Electronic Supplementary Material (ESI) for ChemComm.

Metal-free cycloisomerizations of *o*-alkynylbiaryls

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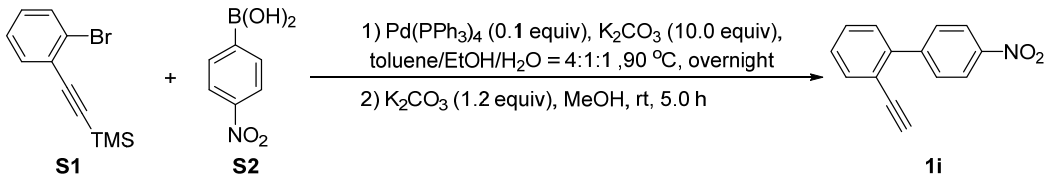
Supporting Information Part 1

General Experimental Information

GENERAL EXPERIMENTAL INFORMATION

All reactions were performed in oven-dried glassware under nitrogen atmosphere. Solvents were distilled prior to use. Chromatographic separations were performed using 200~300 mesh silica gel. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker's Ascend^{TM} 400 NMR spectrometer using $CDCl_3$ as solvent with TMS or residual solvent as standard unless otherwise noted. ^{13}C NMR (100 MHz) spectra were reported in ppm with the internal chloroform signal at 77.2 ppm as a standard. Infrared spectra were obtained on a PerkinElmer FT/IR spectrophotometer and relative intensities are expressed qualitatively as s (strong), m (medium), and w (weak). TLC analysis was performed using 254 nm polyester-backed plates and visualized using UV and $KMnO_4$ stain. High-resolution mass spectra (HRMS) were performed on a Bruker MicrOTOF-Q II mass spectrometer. All spectral data obtained for new compounds are reported here.

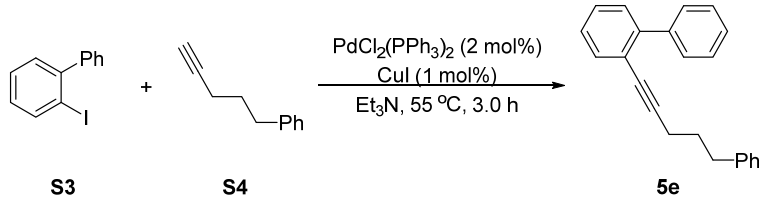
General Procedure for Synthesis of *o*-Ethynylbiaryl 1i.[1]



To an oven-dried screw-cap vial was added (in the following order) 1-bromo-2-[(trimethylsilyl)ethynyl]benzene **S1** (1.3 g, 5.0 mmol), (4-nitrophenyl)boronic acid **S2** (1.3 g, 7.5 mmol), $Pd(PPh_3)_4$ (577.8 mg, 0.5 mmol), K_2CO_3 (6.9 g, 50.0 mmol), toluene (50.0 mL, 0.1 *M* in **S1**), EtOH (12.5 mL, 0.4 *M* in **S1**), and H_2O (12.5 mL, 0.4 *M* in **S1**) under a nitrogen atmosphere. Then the vial was sealed and heated to 90 ^{o}C. When the reaction was judged to be complete by TLC, the mixture was cooled to rt and added water to quench the reaction. The resulting mixture was extracted with EtOAc and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was concentrated under the reduced pressure, then the residue was purified by flash silica gel column chromatrography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford the terminally TMS substituted biarylalkyne (590.8 mg, 2.00 mmol, 40% yield). To a stirred solution of the corresponding biarylalkyne (295.4 mg, 1.0 mmol) in methanol (5.0 mL, 0.2 *M*) was added K_2CO_3 (165.8 mg, 1.2 mmol) under a nitrogen atmosphere at rt. When the reaction was judged to be complete by TLC after 5.0 hours, the reaction mixture was added water, brine and extracted with EtOAc, dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was concentrated under the reduced pressure, then the residue was purified by flash silica gel column chromatrography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *o*-ethynylbiaryl **1i** (223.2 mg, 0.99 mmol, 99% yield).

1i: R_f = 0.36 [20:1 petroleum ether/EtOAc]; yellow solid; mp = 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.08 (s, 1H), 7.37-7.41 (m, 2H), 7.44-7.48 (m, 1H), 7.65-7.67 (m, 1H), 7.73-7.77 (m, 2H), 8.27-8.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.4, 82.4, 120.7, 123.5, 128.5, 129.4, 129.5, 130.4, 134.3, 142.2, 147.0, 147.4; IR (neat) (cm^{-1}) 3441w, 3288m, 1599m, 1516s, 1348s, 1111w; HRMS (ESI): m/z calcd for $C_{14}H_9NO_2Na$ $[M+Na]^+$: 246.0525; found 246.0535.

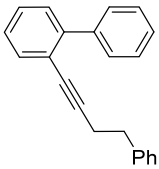
General Procedure for Synthesis of Terminally Substituted *o*-Alkynylbiaryls.[2]



S3 **S4** **5e**

To a solution of 2-iodo-biphenyl **S3** (280.1 mg, 1.0 mmol) and 5-phenyl-1-pentyne **S4** (0.18 mL, 1.2 mmol) in Et_3N (4.0 mL, 0.25 *M* in **S3**) was added $PdCl_2(PPh_3)_2$ (14.0 mg, 0.02mmol) and CuI (2.0 mg, 0.01mmol) under a nitrogen atmosphere. Then the vial was sealed and heated to 55 °C. When the reaction was judged to be complete by TLC after 3.0 hours, the mixture was allowed to cool to rt and the ammonium salt was removed by filtration. The solvent was concentrated under reduced pressure and the residue was purified by flash silica gel column chromatrography [gradient eluent: 40:1~20:1 petroleum ether/DCM] to afford biarylalkyne **5e** (237.1 mg, 0.80 mmol, 80% yield).

5e: R_f = 0.58 [20:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72-1.80 (m, 2H), 2.29 (t, 2H, *J* = 6.8 Hz), 2.59 (t, 2H, *J* = 7.6 Hz), 7.09 (d, 2H, *J* = 7.3 Hz), 7.14-7.19 (m, 1H), 7.23-7.41 (m, 8H), 7.52 (d, 1H, *J* = 7.7 Hz), 7.59-7.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 30.2, 34.8, 80.9, 93.0, 122.5, 126.0 , 127.1, 127.4, 127.9, 128.0, 128.4, 128.7, 129.4, 129.6, 133.2, 141.0, 141.8, 143.9; IR (neat) (cm^{-1}) 2938w, 1602w, 1476m, 1330w, 1009w, 699s; HRMS (ESI): m/z calcd for $C_{23}H_{20}Na$ $[M+Na]^+$: 319.1457; found 319.1453.

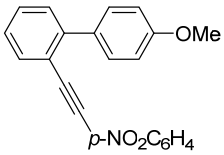


5f

Biarylalkyne **5f** (240.0 mg, 0.85 mmol) was prepared from 2-iodo-biphenyl **S3** (280.1 mg, 1.00 mmol) and 4-phenyl-1-butyne (0.17 mL, 1.20 mmol) in 85% yield after stirring at 55 °C for 3.0 h.

5f: R_f = 0.52 [20:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (t, 2H, *J* = 7.4 Hz), 2.78 (t, 2H, *J* = 7.4 Hz), 7.12-7.27 (m, 6H), 7.30-7.40 (m, 5H), 7.48 (d, 1H, *J* = 7.5 Hz), 7.55-7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 35.0, 81.0, 92.6, 122.3, 126.4, 127.1, 127.4, 128.00, 128.02, 128.5, 128.6, 129.5, 129.6, 133.3, 140.89, 140.91, 143.8; IR (neat) (cm^{-1}) 2938w,

1602w, 1476m, 1330w, 1009w; HRMS (ESI): m/z calcd for $C_{22}H_{18}Na$ $[M+Na]^+$: 305.1301; found 305.1298.

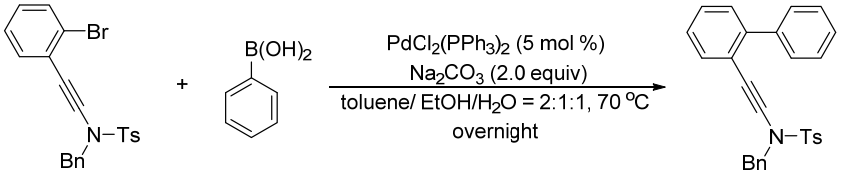


5j

Biarylalkyne **5j** (230.6 mg, 0.70 mmol) was prepared from *o*-ethynylbiaryl **1c**[3] (208.3 mg, 1.00 mmol) and 1-iodo-4-nitrobenzene (298.8 mg, 1.20 mmol) in 70% yield after stirring at 55 ^oC for 3.0 h.

5j: R_f = 0.31 [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 130–131 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H), 6.84-7.02 (m, 2H), 7.34-7.66 (m, 8H), 8.16 (d, 2H, J = 5.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 90.4, 95.4, 113.6, 120.4, 123.8, 127.0, 129.7, 129.8, 130.7, 132.1, 132.8, 133.4, 144.3, 146.9, 159.5, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2213m, 1509s, 1343s, 1306m, 1152w, 1047w; HRMS (ESI): m/z calcd for $C_{21}H_{15}NO_3Na$ $[M+Na]^+$: 352.0944; found 352.0949.

General Procedure for the Synthesis of Biarylynamides.[4]

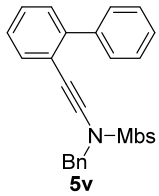


S5 **S6** **5u**

To an oven-dried screw-cap vial was added (in the following order) ynamide **S5**[5] (660.5 mg, 1.5 mmol), phenylboronic acid **S6** (219.5 mg, 1.8 mmol), $PdCl_2(PPh_3)_2$ (52.6 mg, 0.075mmol), Na_2CO_3 (318.0 mg, 3.0 mmol), toluene (7.5 mL, 0.2 *M* in **S5**), EtOH (3.75 mL, 0.4 *M* in **S5**), and H_2O (2.5 mL, 0.4 *M* in **S5**) under a nitrogen atmosphere. Then the vial was sealed and heated to 70 ^oC. When the reaction was judged to be complete by TLC, the mixture was cooled to rt and water was added to quench the reaction. The resulting mixture was extracted with EtOAc and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was concentrated under the reduced pressure, then the residue was purified by flash silica gel column chromatrography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc + 3% NEt_3] to afford biarylynamide **5u** (511.9 mg, 1.17 mmol, 78% yield).

5u: R_f = 0.47 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 150–151 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 4.42 (s, 2H), 7.12-7.15 (m, 4H), 7.18-7.38 (m, 10H), 7.42-7.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 55.8, 71.3, 85.4, 121.4, 127.1, 127.5, 127.7, 127.8, 128.2, 128.4, 128.6, 129.0, 129.3, 129.5, 129.7, 132.4, 134.5, 134.6, 140.8, 142.9, 144.5; IR (neat) (cm^{-1}) 3032w,

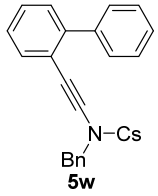
2265w, 1530s, 1170s, 1042m; HRMS (ESI): m/z calcd for $C_{28}H_{23}NO_2SNa$ $[M+Na]^+$: 460.1342; found 460.1339.



5v

Biarylynamide **5v** (673.5 mg, 1.49 mmol) was prepared from the corresponding ynamide (684.5 mg, 1.50 mmol) and phenylboronic acid **S6** (219.5 mg, 1.80 mmol) in 99% yield after stirring at 70 ^oC for 24.0 h.

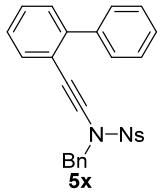
5v: R_f = 0.48 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 100–101 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 4.43 (s, 2H), 6.77-6.81 (m, 2H), 7.14-7.16 (m, 2H), 7.21-7.40 (m, 10H) 7.45-7.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.76, 55.78, 71.3, 85.6, 114.2, 121.5, 127.1, 127.5, 127.8, 128.3, 128.4, 128.6, 129.0, 129.3, 129.4, 129.6, 130.0, 132.4, 134.6, 140.9, 142.9, 163.6; IR (Neat) (cm^{-1}) 2914w, 2229w, 1593m, 1358s, 1264s; HRMS (ESI): m/z calcd for $C_{28}H_{23}NO_3SNa$ $[M+Na]^+$: 476.1291; found 476.1288.



5w

Biarylynamide **5w** (583.9 mg, 1.28 mmol) was prepared from the corresponding ynamide (691.2 mg, 1.50 mmol) and phenylboronic acid **S6** (219.5 mg, 1.80 mmol) in 85% yield after stirring at 70 ^oC for 24.0 h.

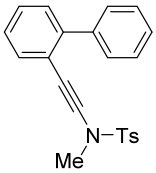
5w: R_f = 0.65 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 97–98 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 4.46 (s, 2H), 7.14-7.16 (m, 2H), 7.21-7.41 (m, 14H), 7.47-7.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.0, 71.4, 84.9, 121.1, 127.1, 127.6, 128.0, 128.3, 128.5, 128.7, 128.96, 129.01, 129.3, 129.4, 129.6, 132.4, 134.2, 135.9, 140.0, 140.8, 143.0; IR (neat) (cm^{-1}) 3064w, 2228w, 1585w, 1366s, 1174m, 1092w; HRMS (ESI): m/z calcd for $C_{27}H_{20}ClNO_2SNa$ $[M+Na]^+$: 480.0795; found 480.0796.



5x

Biarylynamide **5x** (548.2 mg, 1.17 mmol) was prepared from the corresponding ynamide (707.0 mg, 1.50 mmol) and phenylboronic acid **S6** (219.5 mg, 1.80 mmol) in 78% yield after stirring at 70 ^oC for 24.0 h.

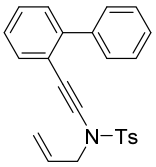
5x: R_f = 0.42 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (s, 2H), 7.16-7.18 (m, 2H), 7.23-7.25 (m, 2H), 7.27-7.44 (m, 8H), 7.48-7.52 (m, 4H), 8.01-8.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.5, 71.8, 84.2, 120.8, 124.1, 127.3, 127.7, 128.4 ,128.81, 128.82, 128.9, 129.1, 129.5, 129.8, 132.5, 133.9, 140.9, 142.9, 143.2, 150.3, one carbon missing due to overlap; IR (neat) (cm^{-1}) 3113w, 2238w, 1531s, 1345m, 1176s, 1088m; HRMS (ESI): m/z calcd for $C_{27}H_{20}N_2O_4SNa$ $[M+Na]^+$: 491.1036; found 491.1035.



5y

Biarylynamide **5y** (406.6 mg, 1.13 mmol) was prepared from the corresponding ynamide (546.4 mg, 1.50 mmol) and phenylboronic acid **S6** (219.5 mg, 1.80 mmol) in 75% yield after stirring at 70 ^{o}C for 24.0 h.

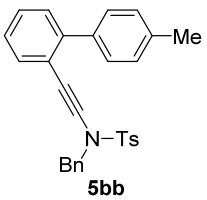
5y: R_f = 0.39 [4:1 petroleum ether/EtOAc]; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.99 (s, 3H), 7.21 (d, 2H, J = 8.1 Hz), 7.26-7.37 (m, 4H), 7.40-7.56 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 39.3, 69.1, 86.7, 121.4, 127.2, 127.5, 127.88, 127.91, 128.2, 129.4, 129.6, 129.8, 132.3, 133.3, 140.8, 143.1, 144.7; IR (neat) (cm^{-1}) 3025w, 2232w, 1449w, 1364s, 1167s; HRMS (ESI): m/z calcd for $C_{22}H_{19}NO_2SNa$ $[M+Na]^+$: 384.1029; found 384.1029.



5aa

Biarylynamide **5aa** (342.9 mg, 0.89 mmol) was prepared from the corresponding ynamide (585.4 mg, 1.50 mmol) and phenylboronic acid **S6** (219.5 mg, 1.80 mmol) in 59% yield after stirring at 70 ^{o}C for 24.0 h.

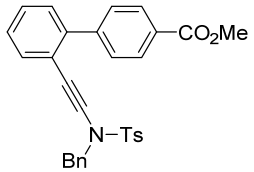
5aa: R_f = 0.58 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 45–46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.90 (dt, 2H, J = 6.4, 1.3 Hz), 5.07-5.12 (m, 2H), 5.55-5.65 (m, 1H), 7.20 (d, 2H, J = 8.2 Hz), 7.24-7.46 (m, 7H), 7.51-7.54 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 54.5, 70.9, 85.1, 120.1, 121.5, 127.1, 127.5, 127.8, 127.9, 128.2, 129.4, 129.6, 129.8, 131.0, 132.5, 134.8, 140.9, 143.1, 144.6; IR (Neat) (cm^{-1}) 3023w, 2231w, 1596w, 1363s, 1169s; HRMS (ESI): m/z calcd for $C_{24}H_{21}NO_2SNa$ $[M+Na]^+$: 410.1185; found 410.1182.



5bb

Biarylynamide **5bb** (304.8 mg, 0.68 mmol) was prepared from ynamide **S5** (660.6 mg, 1.50 mmol) and *p*-tolylboronic acid (244.7 mg, 1.80 mmol) in 45% yield after stirring at 70 ^{o}C for 24.0 h.

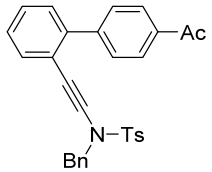
5bb: R_f = 0.56 [4:1 petroleum ether/EtOAc]; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.40 (s, 3H), 4.44 (s, 2H), 7.14-7.26 (m, 10H), 7.27-7.32 (m, 3H), 7.37-7.39 (m, 2H), 7.46-7.48 (m, 2H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 21.4, 21.8, 55.8, 71.3, 85.3, 121.4, 126.9, 127.80, 127.83, 128.4, 128.6, 128.9, 129.0, 129.2, 129.5, 129.7, 132.5, 134.6, 134.8, 137.1, 137.9, 142.9, 144.5; IR (Neat) (cm^{-1}) 3030w, 2231w, 1597w, 1363s, 1167s, 1089m; HRMS (ESI): m/z calcd for $C_{29}H_{25}NO_2SNa$ $[M+Na]^+$: 474.1498; found 474.1494.



5cc

Biarylynamide **5cc** (460.9 mg, 0.93 mmol) was prepared from ynamide **S5** (660.6 mg, 1.50 mmol) and (4-(methoxycarbonyl)phenyl)boronic acid (323.9 mg, 1.80 mmol) in 62% yield after stirring at 70 ^{o}C for 24.0 h.

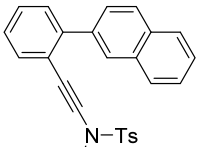
5cc: R_f = 0.43 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.94 (s, 3H), 4.45 (s, 2H), 7.13-7.18 (m, 4H), 7.22-7.24 (m, 2H), 7.27-7.34 (m, 5H), 7.49-7.52 (m, 4H), 7.98-8.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 52.3, 55.7, 70.8, 85.8, 121.4, 127.7, 127.8, 128.1, 128.4, 128.7, 128.8, 129.0, 129.36, 129.44, 129.5, 129.8, 133.0, 134.5, 134.8, 141.9, 144.7, 145.4, 167.2; IR (neat) (cm^{-1}) 2993w, 2228w, 1720s, 1275s, 1172s; HRMS (ESI): m/z calcd for $C_{30}H_{25}NO_4SNa$ $[M+Na]^+$: 518.1397; found 518.1393.



5dd

Biarylynamide **5dd** (388.5 mg, 0.81 mmol) was prepared from ynamide **S5** (660.6 mg, 1.50 mmol) and (4-acetylphenyl)boronic acid (295.1 mg, 1.80 mmol) in 54% yield after stirring at 70 ^{o}C for 24.0 h.

5dd: R_f = 0.37 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 119–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.60 (s, 3H), 4.45 (s, 2H), 7.14-7.17 (m, 4H), 7.22-7.24 (m, 2H), 7.28-7.33 (m, 5H), 7.45-7.47 (m, 2H), 7.55-7.58 (m, 2H), 7.90-7.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 26.9, 55.7, 70.9, 85.9, 121.5, 127.7, 127.9, 128.1, 128.3, 128.4, 128.7, 128.8, 129.4, 129.6, 129.8, 132.8, 134.5, 134.8, 136.0, 141.7, 144.8, 145.5, 198.1; IR (neat) (cm^{-1}) 3006w, 2230w, 1686m, 1356s, 1266s, 1172s; HRMS (ESI): m/z calcd for $C_{30}H_{25}NO_3SNa$ $[M+Na]^+$: 502.1447; found 502.1444.

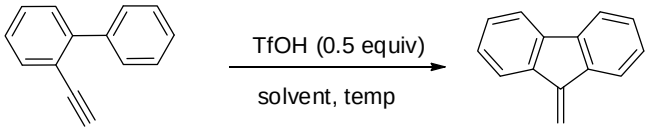


5ee

Biarylynamide **5ee** (651.0 mg, 1.34 mmol) was prepared from ynamide **S5** (660.6 mg, 1.50 mmol) and naphthalen-2-ylboronic acid (309.6 mg, 1.80 mmol) in 89% yield after stirring at 70 ^{o}C for 24.0 h.

5ee: R_f = 0.55 [4:1 petroleum ether/EtOAc]; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 4.37 (s, 2H), 6.88 (d, 2H, J = 8.2 Hz), 7.03-7.06 (m, 2H), 7.11 (t, 2H, J = 7.5 Hz), 7.17-7.24 (m, 2H), 7.31-7.34 (m, 4H), 7.39-7.42 (m, 1H), 7.47-7.51 (m, 2H), 7.60 (dd, 1H, J = 8.4, 1.7 Hz), 7.78-7.86 (m, 3H), 7.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 55.7, 71.1, 85.5, 121.7, 126.22, 126.24, 127.2, 127.56, 127.61, 127.76, 127.79, 128.0, 128.1, 128.3, 128.5, 128.8, 129.5, 129.8, 132.8, 133.4, 134.4, 134.6, 138.4, 143.0, 144.4, two carbons missing due to overlap ; IR (neat) (cm^{-1}) 3055w, 2230w, 1734w, 1362s, 1167s; HRMS (ESI): m/z calcd for $C_{32}H_{25}NO_2SNa$ $[M+Na]^+$: 510.1498; found 510.1497.

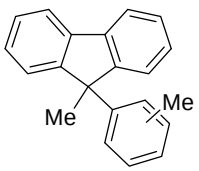
Condition Optimization of the Cyclization Reaction (Table 1).



1a **4**

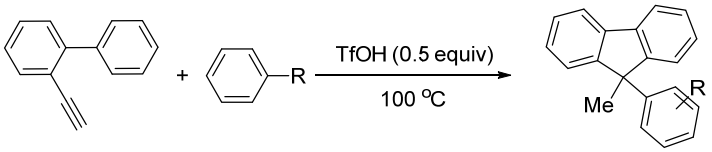
Entry[a]	Solvent	Temp. (^{o}C)	Yield[b] (%)
1	DCE	80	trace
2	THF	80	21
3	MeCN	80	14
4	toluene	80	0[c]
5	toluene	100	0[d]
6[e]	toluene	100	0[f]

[a] Reactions were carried out using **1a** (0.20 mmol) in solvent (0.5 mL) with TfOH (0.10 mmol). [b] Isolated yields. [c] **3aa** was obtained in 79% yield with 0.9:1 rr. [d] **3aa** was obtained in 95% yiled with 1.5:1 rr. [e] Blank reaction: reaction was carried out in the absence of TfOH for 10.0 h. [f] 97% of **1a** was recovered.

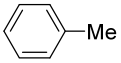
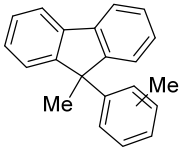
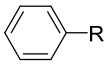
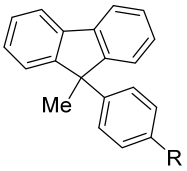
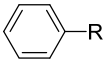
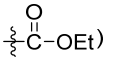
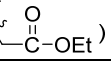
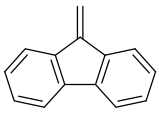


3aa-p/o

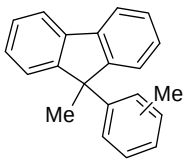
Condition Optimization of the Cyclization Reaction (Table 2).



1a **2** **3**

entry	arene	product
1	 **2a**	 **3aa:** 95% (*p*-Me:*o*-Me = 1.5:1)
2	 **2b** (R = H) **2c** (R = Cl) **2d** (R = Br) **2e** (R = I) **2f** (R = OMe)	 **3ab:** 67% **3ac:** 13% **3ad:** 14% **3ae:** 8% **3af:** 99%
3	 **2g** (R = CN) **2h** (R = ) **2i** (R = )	 **4:** 28% **4:** 19% **4:** 8%

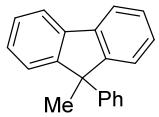
General Procedure: To an oven-dried sealed tube was added *o*-ethynylbiaryl **1a**[3] (35.6 mg, 0.20 mmol), toluene **2a** (0.5 mL, *o*-ethynylbiaryl *concn* = 0.4 *M*) and TfOH (8.9 μL, 0.10 mmol) at rt. When the reaction was judged to be complete by TLC after stirred at 100 °C for 1.5 h, the mixture was quenched by Et_3N (13.9 μL, 0.10 mmol) and purified using silica gel flash column chromatography [eluent: petroleum ether] to afford fluorene **3aa** (51.4 mg, 0.19 mmol) in 95% yield.



3aa-*p*/*o*

3aa: (***p*/*o*** = 1.5/1); R_f = 0.53 [20:1 petroleum ether/DCM]; white solid; mp = 43–44 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85 (s, 7.5H), 2.22 (s, 3.0H), 2.25 (s, 4.5H), 6.95-7.11 (m, 10.0H), 7.18-7.25 (m, 10.0H), 7.28-7.35 (m, 5.0H), 7.73-7.76 (m, 5.0H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.8, 25.4, 25.5, 54.5, 54.8, 120.2, 123.8, 124.2, 124.3, 126.5, 127.26, 127.32, 127.8, 128.3, 129.2, 136.0, 137.9, 139.85, 139.87, 142.2, 145.0, 154.1, 154.2, four carbons missing due to overlap; IR (neat)

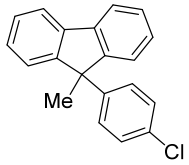
(cm^{-1}) 2920w, 1906w, 1590w, 1445w, 1153w, 1025w; HRMS (ESI): m/z calcd for $C_{21}H_{18}Na$ $[M+Na]^+$: 293.1301; found 293.1301.



3ab

Fluorene **3ab** (34.4 mg, 0.13 mmol) was prepared from *o*-ethynylbiaryl **1a** (35.6 mg, 0.20 mmol) and benzene **2b** (0.5 mL) in 67% yield after stirring at 100 ^oC for 2.5 h.

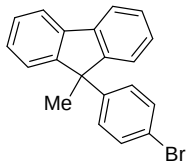
3ab: R_f = 0.50 [20:1 petroleum ether/DCM]; white solid; mp = 69–70 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.87 (s, 3H), 7.13-7.26 (m, 9H), 7.31-7.35 (m, 2H), 7.76 (dt, 2H, J = 7.6, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 54.8, 120.2, 124.3, 126.5, 126.7, 127.3, 127.8, 128.5, 139.9, 145.2, 154.1; IR (neat) (cm^{-1}) 2922w, 1596w, 1496w, 1442w, 1261w, 1027w; HRMS (ESI): m/z calcd for $C_{20}H_{16}Na$ $[M+Na]^+$: 279.1144; found 279.1150.



3ac

Fluorene **3ac** (7.6 mg, 0.03 mmol) was prepared from *o*-ethynylbiaryl **1a** (35.6 mg, 0.20 mmol) and chlorobenzene **2c** (0.5 mL) in 13% yield after stirring at 100 ^oC for 2.0 h.

3ac: R_f = 0.56 [20:1 petroleum ether/DCM]; white solid; mp = 97–98 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.85 (s, 3H), 7.05-7.09 (m, 2H), 7.15-7.27 (m, 6H), 7.35 (td, 2H, J = 7.4, 1.2 Hz), 7.76 (dt, 2H, J = 7.6, 0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.3, 54.4, 120.3, 124.1, 127.6, 128.0, 128.1, 128.6, 132.4, 139.8, 143.8, 153.6; IR (neat) (cm^{-1}) 2920w, 1645w, 1489m, 1439w, 1115w, 1091m; MS (ESI): m/z calcd for $C_{20}H_{15}ClNa$ $[M+Na]^+$: 313; found 313. The data are consistent with that reported in the literature (H. Takano, K. S. Kanyiva and T. Shibata, *Org. Lett.*, 2016, **18**, 1860).

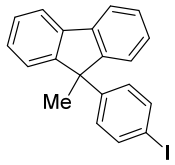


3ad

Fluorene **3ad** (9.4 mg, 0.03 mmol) was prepared from *o*-ethynylbiaryl **1a** (35.6 mg, 0.20 mmol) and bromobenzene **2d** (0.5 mL) in 14% yield after stirring at 100 ^oC for 2.0 h.

3ad: R_f = 0.55 [20:1 petroleum ether/DCM]; white solid; mp = 99–100 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.85 (s, 3H), 7.00-7.03 (m, 2H), 7.18-7.37 (m, 8H), 7.76 (dt, 2H, J = 7.5, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 54.4, 120.3, 120.5, 124.1, 127.6, 128.0, 128.5, 131.5, 139.9, 144.4,

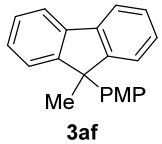
153.5; IR (neat) (cm^{-1}) 2920w, 1907w, 1645w, 1485m, 1261w, 1005s; HRMS (ESI): m/z calcd for $C_{20}H_{15}BrNa$ $[M+Na]^+$: 357.0249; found 357.0249.



3ae

Fluorene **3ae** (6.1 mg, 0.02 mmol) was prepared from *o*-ethynylbiaryl **1a** (35.6 mg, 0.20 mmol) and iodobenzene **2e** (0.5 mL) in 8% yield after stirring at 100 ^oC for 2.0 h.

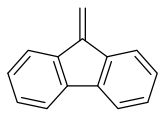
3ae: R_f = 0.55 [20:1 petroleum ether/DCM]; white solid; mp = 98–99 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.84 (s, 3H), 6.87-6.91 (m, 2H), 7.18-7.27 (m, 4H), 7.35 (td, 2H, J = 7.4, 1.2 Hz), 7.50-7.53 (m, 2H), 7.76 (dt, 2H, J = 7.6, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1, 54.5, 92.0, 120.3, 124.1, 127.6, 128.0, 128.9, 137.5, 139.9, 145.1, 153.5; IR (neat) (cm^{-1}) 2921s, 2851m, 1645w, 1482w, 1445m, 1001m; HRMS (ESI): m/z calcd for $C_{20}H_{15}INa$ $[M+Na]^+$: 405.0111; found 405.0113.



3af

Fluorene **3af** (56.7 mg, 0.20 mmol) was prepared from *o*-ethynylbiaryl **1a** (35.6 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 99% yield after stirring at 100 ^oC for 1.0 h.

3af: R_f = 0.20 [20:1 petroleum ether/DCM]; white solid; mp = 127–128 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.84 (s, 3H), 3.72 (s, 3H), 6.72-6.75 (m, 2H), 7.05-7.09 (m, 2H), 7.20-7.24 (m, 4H), 7.30-7.34 (m, 2H), 7.75 (dt, 2H, J = 7.6, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 54.2, 55.3, 113.8, 120.2, 124.2, 127.3, 127.7, 127.8, 137.2, 139.8, 154.2, 158.2; IR (neat) (cm^{-1}) 2927w, 1508s, 1439m, 1247s, 1122w, 1030s; HRMS (ESI): m/z calcd for $C_{21}H_{18}ONa$ $[M+Na]^+$: 309.1250; found 309.1250.



4

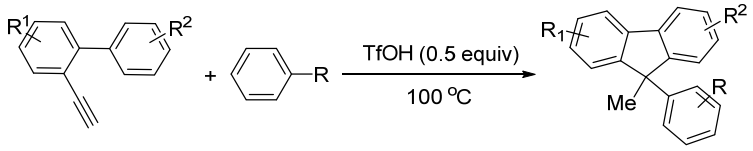
Fluorene **4** (10.0 mg, 0.06 mmol) was prepared from *o*-ethynylbiaryl **1a** (35.6 mg, 0.20 mmol) and benzonitrile **2g** (0.5 mL) in 28% yield after stirring at 100 ^oC for 3.0 h.

Fluorene **4** (6.8 mg, 0.04 mmol) was prepared from *o*-ethynylbiaryl **1a** (35.6 mg, 0.20 mmol) and ethyl benzoate **2h** (0.5 mL) in 19% yield after stirring at 100 ^oC for 2.0 h.

Fluorene **4** (2.9 mg, 0.02 mmol) was prepared from *o*-ethynylbiaryl **1a** (35.6 mg, 0.20 mmol) and ethyl 2-phenylacetate **2i** (0.5 mL) in 8% yield after stirring at 100 ^oC for 2.0 h.

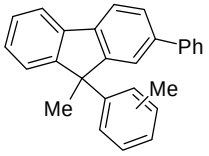
4: R_f = 0.66 [20:1 petroleum ether/DCM]; white solid; mp = 46–47 °C; ^{1}H NMR (400 MHz, CD_3COCD_3) δ 6.22 (s, 2H), 7.37 (dtd, 4H, J = 29.6, 7.4, 0.9 Hz), 7.84 (ddt, 4H, J = 21.2, 7.5, 1.0 Hz); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 108.8, 120.6, 122.0, 128.1, 129.7, 138.8, 140.9, 144.3; IR (neat) (cm^{-1}) 2922w, 1653w, 1485w, 1030s, 899s; HRMS (ESI): m/z calcd for $C_{14}H_{11}$ $[M+H]^+$: 179.0855; found 179.0843.

General Procedure for the Cycloisomerization of *o*-Ethynylbiaryls.



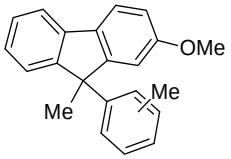
1 **2** **3**

To an oven-dried sealed tube was added *o*-ethynylbiaryl **1b**[3] (50.9 mg, 0.20 mmol), toluene **2a** (0.5 mL, *o*-ethynylbiaryl *concn* = 0.40 *M*) and TfOH (8.9 μL, 0.10 mmol) at rt. When the reaction was judged to be complete by TLC after stirred at 100 °C for 3.0 h, the mixture was quenched by Et_3N (13.9 μL, 0.10 mmol) and purified using silica gel flash column chromatography [eluent: petroleum ether] to afford fluorene **3ba** (61.7 mg, 0.18 mmol) in 89% yield.



3ba-*p*/*o*

3ba: (***p*/*o*** = 5.0/1); R_f = 0.50 [20:1 petroleum ether/EtOAc]; white solid; mp = 58–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.89 (s, 18.0H), 2.23 (s, 3.0H), 2.25 (s, 15.0H), 7.00-7.10 (m, 24.0H), 7.22-7.39 (m, 36.0H), 7.44-7.45 (m, 6.0H), 7.55-7.59 (m, 18.0H), 7.75-7.81 (m, 12.0H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.8, 25.6, 25.7, 54.6, 54.9, 120.3, 120.5, 123.0, 123.8, 124.2, 124.3, 126.5, 126.6, 127.31, 127.35, 127.8, 128.4, 128.8, 129.2, 136.1, 138.0, 139.1, 139.5, 140.9, 141.5, 142.0, 144.9, 154.5, 154.8, eighteen carbons missing due to overlap; IR (neat) (cm^{-1}) 2921w, 1467w, 1452m, 1260w, 1061w, 1019m; HRMS (ESI): m/z calcd for $C_{27}H_{22}Na$ $[M+Na]^+$: 369.1614; found 369.1621.

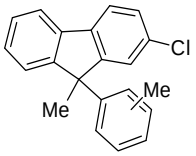


3ca-*p*/*o*

Fluorene **3ca** (57.1 mg, 0.19 mmol) was prepared from *o*-ethynylbiaryl **1c** (41.7 mg, 0.20 mmol) and toluene **2a** (0.5 mL) in 95% yield after stirring at 100 °C for 1.5 h.

3ca: (***p*/*o*** = 7.7/1); R_f = 0.23 [20:1 petroleum ether/DCM]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (s, 26.1H), 2.23 (s, 3.0H), 2.26 (s, 23.1H), 3.72 (s, 3.0H), 3.75 (s, 23.1H), 6.75-6.76 (m, 8.7H),

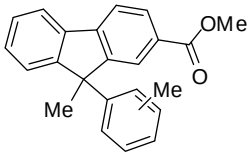
6.86-6.89 (m, 8.7H), 7.00-7.06 (m, 34.8H), 7.13-7.19 (m, 17.4H), 7.26-7.31 (m, 8.7H), 7.63-7.65 (m, 17.4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.8, 25.5, 25.6, 54.5, 55.6, 109.8, 109.9, 113.0, 113.2, 119.4, 119.5, 121.0, 121.2, 123.7, 124.0, 124.1, 126.5, 126.7, 127.2, 127.3, 128.3, 129.2, 132.0, 132.8, 136.0, 137.9, 139.8, 142.2, 145.1, 153.8, 156.0, 160.0, nine carbons missing due to overlap; IR (neat) (cm^{-1}) 2923w, 1610m, 1457s, 1425m, 1263s, 1035s; HRMS (ESI): m/z calcd for $C_{22}H_{20}ONa$ $[M+Na]^+$: 323.1406; found 323.1402.



3da-*p*/*o*

Fluorene **3da** (57.3 mg, 0.19 mmol) was prepared from *o*-ethynylbiaryl **1d**[3] (42.5 mg, 0.20 mmol) and toluene **2a** (0.5 mL) in 94% yield after stirring at 100 ^{o}C for 1.5 h.

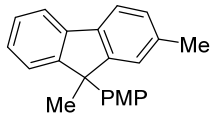
3da: (***p*/*o*** = 4.3/1); R_f = 0.56 [20:1 petroleum ether/DCM]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (s, 15.9H), 2.24 (s, 3.0H), 2.27 (s, 12.9H), 7.02 (s, 15.9H), 7.18-7.35 (m, 31.8H), 7.64-7.73 (m, 10.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.8, 25.3, 25.4, 54.7, 54.9, 120.2, 121.2, 123.7, 124.27, 124.32, 124.67, 124.71, 126.5, 127.3, 127.5, 127.6, 128.1, 128.5, 129.3, 133.4, 136.4, 138.1, 138.4, 138.8, 141.3, 144.2, 154.0, 155.87, 155.91, ten carbons missing due to overlap; IR (neat) (cm^{-1}) 2964w, 1511w, 1466w, 1443s, 1261w, 1079m; HRMS (ESI): m/z calcd for $C_{21}H_{17}ClNa$ $[M+Na]^+$: 327.0911; found 327.0911.



3ea-*p*/*o*

Fluorene **3ea** (47.9 mg, 0.15 mmol) was prepared from *o*-ethynylbiaryl **1e**[3] (47.3 mg, 0.20 mmol) and toluene **2a** (0.5 mL) in 73% yield after stirring at 100 ^{o}C for 70 h.

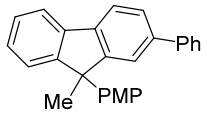
3ea: (***p*/*o*** = 3.7/1); R_f = 0.28 [20:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (s, 3.0H), 1.88 (s, 11.1H), 2.23 (s, 3.0H), 2.26 (s, 11.1H), 3.84 (s, 3.0H), 3.86 (s, 11.1H), 6.89-7.10 (m, 18.8H), 7.16-7.23 (m, 4.7H), 7.28-7.38 (m, 9.4H), 7.76-7.83 (m, 9.4H), 7.89-7.91 (m, 4.7H), 8.04-8.09 (m, 4.7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 21.1, 21.7, 25.2, 52.1, 54.6, 54.8, 55.2, 119.9, 120.1, 121.0, 121.2, 123.6, 123.7, 124.39, 124.44, 124.7, 125.49, 125.55, 125.9, 126.5, 127.3, 127.4, 127.5, 127.8, 129.0, 129.27, 129.29, 129.33, 132.1, 136.3, 137.7, 138.6, 138.9, 140.6, 141.2, 144.5, 144.6, 153.3, 154.2, 155.2, 167.31, 167.34; IR (neat) (cm^{-1}) 2949w, 1714s, 1611w, 1434m, 1285s, 1191m; HRMS (ESI): m/z calcd for $C_{23}H_{20}O_2Na$ $[M+Na]^+$: 351.1356; found 351.1359.



3ff

Fluorene **3ff** (54.1 mg, 0.18 mmol) was prepared from *o*-ethynylbiaryl **1f**[3] (38.5 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 90% yield after stirring at 100 °C for 1.0 h.

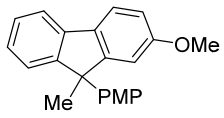
3ff: R_f = 0.15 [20:1 petroleum ether/DCM]; white solid; mp = 144–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 2.42 (s, 3H), 3.71 (s, 3H), 6.71-6.74 (m, 2H), 7.04-7.12 (m, 4H), 7.19-7.22 (m, 2H), 7.29-7.33 (m, 1H), 7.566-7.573 (m, 1H), 7.71-7.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 25.6, 53.8, 55.3, 113.7, 120.1, 120.8, 123.8, 124.1, 127.2, 127.6, 127.7, 128.7, 136.9, 137.4, 139.8, 139.9, 151.5, 154.6, 158.1; IR (neat) (cm^{-1}) 2965w, 1507s, 1250s, 1182s, 1030s; HRMS (ESI): m/z calcd for $C_{22}H_{20}ONa$ $[M+Na]^+$: 323.1406; found 323.1401.



3bf

Fluorene **3bf** (70.3 mg, 0.19 mmol) was prepared from *o*-ethynylbiaryl **1b** (50.9 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 97% yield after stirring at 100 °C for 1.0 h.

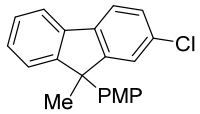
3bf: R_f = 0.46 [20:1 petroleum ether/EtOAc]; white solid; mp = 113–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (s, 3H), 3.70 (s, 3H), 6.72-6.75 (m, 2H), 7.09-7.13 (m, 2H), 7.22-7.39 (m, 6H), 7.435-7.439 (m, 1H), 7.55-7.58 (m, 3H), 7.75-7.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8, 54.3, 55.3, 113.8, 120.3, 120.5, 122.9, 124.2, 126.5, 127.29, 127.34, 127.7, 127.8, 128.9, 137.0, 139.0, 139.4, 140.9, 141.5, 154.5, 154.9, 158.2, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2928w, 1608w, 1508m, 1451m, 1249m, 1029m; HRMS (ESI): m/z calcd for $C_{27}H_{22}ONa$ $[M+Na]^+$: 385.1563; found 385.1572.



3cf

Fluorene **3cf** (59.5 mg, 0.19 mmol) was prepared from *o*-ethynylbiaryl **1c** (41.7 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 94% yield after stirring at 100 °C for 1.0 h.

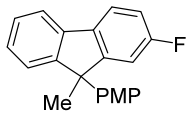
3cf: R_f = 0.48 [20:1 petroleum ether/EtOAc]; white solid; mp = 70–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 3.71 (s, 3H), 3.75 (s, 3H), 6.72-6.75 (m, 3H), 6.87 (dd, 1H, J = 8.4, 2.4 Hz), 7.05-7.08 (m, 2H), 7.15-7.19 (m, 2H), 7.26-7.30 (m, 1H), 7.63-7.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 54.2, 55.3, 55.6, 109.7, 113.2, 113.8, 119.4, 121.0, 124.0, 126.6, 127.2, 127.7, 132.7, 137.2, 139.7, 153.9, 156.1, 158.2, 160.0; IR (neat) (cm^{-1}) 2932w, 1604w, 1507m, 1248s, 1029s; HRMS (ESI): m/z calcd for $C_{22}H_{20}O_2Na$ $[M+Na]^+$: 339.1356; found 339.1352.



3df

Fluorene **3df** (62.2 mg, 0.19 mmol) was prepared from *o*-ethynylbiaryl **1d** (42.5 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 97% yield after stirring at 100 ^{o}C for 2.0 h.

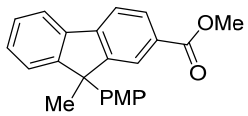
3df: R_f = 0.25 [20:1 petroleum ether/DCM]; white solid; mp = 96–97 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 3.73 (s, 3H), 6.73-6.77 (m, 2H), 7.03-7.06 (m, 2H), 7.18-7.35 (m, 5H), 7.65 (d, 1H, J = 8.1 Hz), 7.71 (d, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 54.4, 55.3, 113.9, 120.2, 121.2, 124.2, 124.6, 127.5, 127.6, 127.7, 128.1, 133.4, 136.2, 138.3, 138.7, 154.1, 156.0, 158.4; IR (neat) (cm^{-1}) 2928w, 1608w, 1509s, 1442s, 1249s, 1030m; HRMS (ESI): m/z calcd for $C_{21}H_{17}ClONa$ $[M+Na]^+$: 343.0860; found 343.0854.



3gf

Fluorene **3gf** (49.3 mg, 0.16 mmol) was prepared from *o*-ethynylbiaryl **1g**[3] (39.2 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 81% yield after stirring at 100 ^{o}C for 1.0 h.

3gf: R_f = 0.18 [20:1 petroleum ether/DCM]; white solid; mp = 103–104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 3.73 (s, 3H), 6.73-6.77 (m, 2H), 6.90 (dd, 1H, J = 8.8, 2.4 Hz), 6.99-7.07 (m, 3H), 7.18-7.24 (m, 2H), 7.30-7.34 (m, 1H), 7.65-7.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 54.4 (d, J = 2.1 Hz), 55.3, 111.5 (d, J = 22.6 Hz), 113.9, 114.5 (d, J = 22.9 Hz), 119.9, 121.2 (d, J = 8.7 Hz), 124.2, 127.4, 127., 127.7, 135.7 (d, J = 2.2 Hz), 136.5, 138.9, 154.1 (d, J = 1.9 Hz), 156.5 (d, J = 7.5 Hz), 158.4, 163.0 (d, J = 244.3 Hz); IR (neat) (cm^{-1}) 2963w, 1508s, 1451s, 1244s, 1184s, 1023s; HRMS (ESI): m/z calcd for $C_{21}H_{17}FONa$ $[M+Na]^+$: 327.1156; found 327.1148.

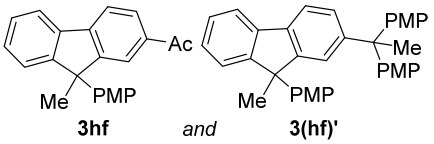


3ef

Fluorene **3ef** (64.1 mg, 0.19 mmol) was prepared from *o*-ethynylbiaryl **1e** (47.3 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 93% yield after stirring at 100 ^{o}C for 17.0 h.

3ef: R_f = 0.25 [20:1 petroleum ether/EtOAc]; white solid; mp = 52–53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.87 (s, 3H), 3.72 (s, 3H), 3.86 (s, 3H), 6.73-6.76 (m, 2H), 7.04-7.08 (m, 2H), 7.226-7.232 (m, 1H), 7.33 (dtd, 2H, J = 23.7, 7.3, 1.4 Hz), 7.78-7.80 (m, 2H), 7.90 (d, 1H, J = 1.0 Hz), 8.05 (dd, 1H, J = 8.0, 1.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 52.2, 54.3, 55.3, 113.9, 120.0, 121.0, 124.4, 125.5, 127.5, 127.7, 129.0, 129.28, 129.31, 136.2, 138.5, 144.4, 154.3, 155.3, 158.3, 167.3; IR

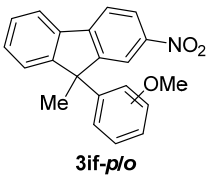
(neat) (cm^{-1}) 2921w, 1713s, 1509s, 1434m, 1248s; HRMS (ESI): m/z calcd for $C_{23}H_{20}O_3Na$ $[M+Na]^+$: 367.1305; found 367.1303.



Fluorene **3hf** (19.7 mg, 0.06 mmol) and fluorene **3(hf)'** (51.6 mg, 0.10 mmol) were prepared from *o*-ethynylbiaryl **1h**[3] (44.1 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 30% yield and 49% yield, respectively, after stirring at 100 °C for 6.0 h.

3hf: R_f = 0.51 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 49–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (s, 3H), 2.58 (s, 3H), 3.74 (s, 3H), 6.75 (d, 2H, J = 8.7 Hz), 7.06 (d, 2H, J = 8.7 Hz), 7.35 (dt, 3H, J = 23.1, 7.2 Hz), 7.80-7.82 (m, 3H), 7.97 (dd, 1H, J = 7.8, 1.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 27.0, 54.4, 55.4, 114.0, 120.1, 121.2, 124.1, 124.4, 127.6, 127.7, 128.4, 129.2, 136.2, 136.7, 138.5, 144.7, 154.6, 155.5, 158.4, 198.0; IR (neat) (cm^{-1}) 2926w, 1674s, 1605m, 1509s, 1248s, 1029m; HRMS (ESI): m/z calcd for $C_{23}H_{20}O_2Na$ $[M+Na]^+$: 351.1356; found 351.1354.

3(hf)': R_f = 0.14 [10:1 petroleum ether/EtOAc]; white solid; mp = 39–40 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (s, 3H), 2.09 (s, 3H), 3.73 (s, 3H), 3.766 (s, 3H), 3.773 (s, 3H), 6.69-6.79 (m, 6H), 6.95-7.01 (m, 5H), 7.02-7.06 (m, 2H), 7.10 (d, 1H, J = 1.5 Hz), 7.20-7.23 (m, 2H), 7.27-7.31 (m, 1H), 7.59 (d, 1H, J = 8.0 Hz), 7.69 (dt, 1H, J = 7.6, 0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 31.0, 51.7, 54.2, 55.32, 55.35, 113.17, 113.20, 113.6, 119.3, 120.1, 124.1, 124.5, 127.2, 127.5, 127.6, 128.0, 129.8, 137.4, 137.7, 139.4, 141.8, 141.9, 149.5, 153.7, 154.3, 157.67, 157.69, 158.1, two carbons missing due to overlap; IR (neat) (cm^{-1}) 2932w, 1607w, 1508s, 1463m, 1295m, 1179s; HRMS (ESI): m/z calcd for $C_{37}H_{34}O_3Na$ $[M+Na]^+$: 526.2508; found 526.2512.

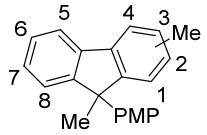


Fluorene **3if-*o*** (7.3 mg, 0.02 mmol) and fluorene **3if-*p*** (53.7 mg, 0.16 mmol) were prepared from *o*-ethynylbiaryl **1i** (44.6mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 11% yield and 81% yield, respectively, after stirring at 100 °C for 5.0 h.

3if-*o*: R_f = 0.36 [20:1 petroleum ether/EtOAc]; yellow solid; mp = 123–124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, 3H), 3.01 (s, 3H), 6.67 (dd, 1H, J = 8.1, 0.9 Hz), 7.07 (td, 1H, J = 7.6, 1.2 Hz), 7.15 (dt, 1H, J = 7.5, 0.9 Hz), 7.27-7.33 (m, 2H), 7.38 (td, 1H, J = 7.4, 1.1 Hz), 7.74 (dd, 1H, J = 7.7, 1.6 Hz), 7.84-7.87 (m, 2H), 7.98 (d, 1H, J = 2.1 Hz), 8.24 (dd, 1H, J = 8.4, 2.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0, 53.3, 55.4, 112.9, 118.2, 119.8, 120.9, 121.3, 123.09, 123.12, 127.2, 128.2,

129.0, 129.4, 131.5, 137.9, 146.9, 147.2, 155.5, 155.9, 157.6; IR (neat) (cm^{-1}) 2920w, 1593w, 1516m, 1458m, 1331s, 1249s; HRMS (ESI): m/z calcd for $C_{21}H_{17}NO_3Na$ $[M+Na]^+$: 354.1101; found 354.1103.

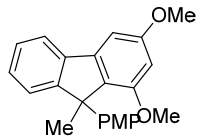
3if-*p*: R_f = 0.17 [20:1 petroleum ether/EtOAc]; yellow solid; mp = 35–36 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90 (s, 3H), 3.75 (s, 3H), 6.75-6.79 (m, 2H), 7.04-7.08 (m, 2H), 7.27-7.29 (m, 1H), 7.35-7.44 (m, 2H), 7.83-7.86 (m, 2H), 8.07 (d, 1H, J = 2.1 Hz), 8.25 (dd, 1H, J = 8.4, 2.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.3, 54.6, 55.4, 114.1, 119.8, 120.4, 121.6, 123.6, 124.6, 127.6, 127.9, 130.0, 135.1, 137.4, 146.2, 155.4, 155.7, 158.6, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2931w, 1609w, 1509s, 1444m, 1337s, 1250s; HRMS (ESI): m/z calcd for $C_{21}H_{17}NO_3Na$ $[M+Na]^+$: 354.1101; found 354.1100.



3jf

Fluorene **3jf** (55.9 mg, 0.19 mmol) was prepared from *o*-ethynylbiaryl **1j**[3] (38.5 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 93% yield after stirring at 100 ^{o}C for 1.0 h.

3jf: (3-Me:1-Me = 1.0:1); R_f = 0.16 [20:1 petroleum ether/DCM]; colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3.0H), 1.88 (s, 3.0H), 2.03 (s, 3.0H), 2.42 (s, 3.0H), 3.71 (s, 3.0H), 3.72 (s, 3.0H), 6.71-6.74 (m, 1.4.0), 7.00-7.11 (m, 8.0H), 7.15-7.19 (m, 2.0H), 7.21-7.33 (m, 4.0H), 7.56-7.64 (m, 2.0H), 7.71 (tt, 2.0H, J = 6.7, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 21.7, 22.8, 25.6, 53.9, 54.6, 55.27, 55.30, 113.76, 113.80, 117.7, 120.0, 120.1, 120.8, 123.7, 123.8, 124.1, 127.0, 127.2, 127.57, 127.65, 127.8, 128.7, 130.0, 134.8, 135.9, 136.9, 137.4, 139.2, 139.8, 139.9, 140.6, 151.2, 151.5, 154.6, 155.1, 158.08, 158.14, two carbons missing due to overlap; IR (neat) (cm^{-1}) 2929w, 1610w, 1508s, 1249s, 1180s, 1030s; HRMS (ESI): m/z calcd for $C_{22}H_{20}ONa$ $[M+Na]^+$: 323.1406; found 323.1402.

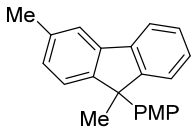


3kf

Fluorene **3kf** (62.4 mg, 0.18 mmol) was prepared from *o*-ethynylbiaryl **1k**[1] (47.7 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 90% yield after stirring at 100 ^{o}C for 1.0 h.

3kf: R_f = 0.30 [20:1 petroleum ether/EtOAc]; colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 3H), 3.63 (s, 3H), 3.70 (s, 3H), 3.87 (s, 3H), 6.36 (d, 1H, J = 2.0 Hz), 6.68-6.72 (m, 2H), 6.92 (d, 1H, J = 2.1 Hz), 7.05-7.08 (m, 2H), 7.15-7.22 (m, 2H), 7.28 (td, 1H, J = 7.3, 1.4 Hz), 7.67 (dt, 1H, J = 7.4, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5, 53.6, 55.2, 55.5, 55.7, 96.5, 98.7, 113.3, 120.0,

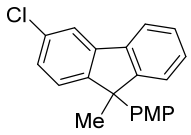
123.8, 126.9, 127.4, 127.9, 132.9, 136.7, 139.5, 142.2, 155.7, 157.1, 157.8, 161.4; IR (neat) (cm^{-1}) 2931w, 1508s, 1248s, 1203s, 1030s; HRMS (ESI): m/z calcd for $C_{23}H_{22}O_3Na$ $[M+Na]^+$: 369.1461; found 369.1451.



3lf

Fluorene **3lf** (59.5 mg, 0.20 mmol) was prepared from *o*-ethynylbiaryl **1l**[3] (38.5 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 99% yield after stirring at 100 °C for 1.0 h.

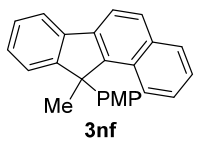
3lf: R_f = 0.15 [20:1 petroleum ether/DCM]; white solid; mp = 144–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 2.42 (s, 3H), 3.71 (s, 3H), 6.71-6.74 (m, 2H), 7.04-7.12 (m, 4H), 7.19-7.22 (m, 2H), 7.29-7.33 (m, 1H), 7.56-7.57 (m, 1H), 7.71-7.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 25.6, 53.8, 55.3, 113.7, 120.1, 120.8, 123.8, 124.1, 127.2, 127.6, 127.7, 128.7, 136.9, 137.4, 139.8, 139.9, 151.5, 154.6, 158.1; IR (neat) (cm^{-1}) 2965w, 1507s, 1250s, 1182s, 1030s; HRMS (ESI): m/z calcd for $C_{22}H_{20}ONa$ $[M+Na]^+$: 323.1406; found 323.1401.



3mf

Fluorene **3mf** (63.5 mg, 0.20 mmol) was prepared from *o*-ethynylbiaryl **1m**[3] (42.5 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 99% yield after stirring at 100 °C for 2.0 h.

3mf: R_f = 0.25 [20:1 petroleum ether/DCM]; white solid; mp = 96–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 3.73 (s, 3H), 6.73-6.77 (m, 2H), 7.03-7.06 (m, 2H), 7.18-7.35 (m, 5H), 7.65 (d, 1H, J = 8.1 Hz), 7.71 (dt, 1H, J = 7.6, 0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 54.4, 55.3, 113.9, 120.2, 121.2, 124.2, 124.6, 127.5, 127.6, 127.7, 128.1, 133.4, 136.2, 138.3, 138.7, 154.1, 156.0, 158.4; IR (neat) (cm^{-1}) 2928w, 1608w, 1509s, 1442s, 1249s, 1030m; HRMS (ESI): m/z calcd for $C_{21}H_{17}ClONa$ $[M+Na]^+$: 343.0860; found 343.0854.

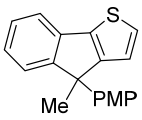


3nf

Fluorene **3nf** (66.6 mg, 0.20 mmol) was prepared from *o*-ethynylbiaryl **1n**[3] (45.7 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 99% yield after stirring at 100 °C for 1.0 h.

3nf: R_f = 0.40 [20:1 petroleum ether/EtOAc]; white solid; mp = 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99 (s, 3H), 3.69 (s, 3H), 6.70-6.74 (m, 2H), 7.06-7.10 (m, 2H), 7.20-7.22 (m, 2H), 7.28-7.39 (m, 3H), 7.58 (d, 1H, J = 8.3 Hz), 7.81 (dt, 1H, J = 7.5, 1.0 Hz), 7.89-7.97 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.9, 55.1, 55.3, 114.1, 118.8, 120.0, 123.5, 124.7, 125.1, 126.3, 127.1,

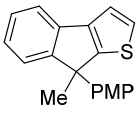
127.5, 127.6, 129.0, 129.4, 129.5, 134.2, 136.3, 137.8, 139.5, 148.2, 156.2, 158.2; IR (neat) (cm^{-1}) 2963w, 1609w, 1508m, 1249s, 1028w; HRMS (ESI): m/z calcd for $C_{25}H_{20}ONa$ $[M+Na]^+$: 359.1406; found 359.1398.



3of

Fluorene **3of** (21.1 mg, 0.07 mmol) was prepared from *o*-ethynylbiaryl **1o**[3] (36.9 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 36% yield after stirring at 100 °C for 1.0 h.

3of: R_f = 0.20 [petroleum ether]; white solid; mp = 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (s, 3H), 3.73 (s, 3H), 6.74-6.78 (m, 2H), 6.89 (d, 1H, J = 4.9 Hz), 7.11-7.15 (m, 3H), 7.19-7.21 (m, 1H), 7.25-7.28 (m, 2H), 7.44 (dt, 1H, J = 7.5, 0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 52.5, 55.4, 113.9, 119.2, 121.7, 124.0, 125.8, 127.3, 127.4, 128.2, 135.9, 136.9, 140.7, 156.8, 158.3, 158.4; IR (neat) (cm^{-1}) 2922w, 1601w, 1508m, 1464w, 1247s, 1030s; HRMS (ESI): m/z calcd for $C_{19}H_{17}OS$ $[M+H]^+$: 293.0995; found 293.0994.

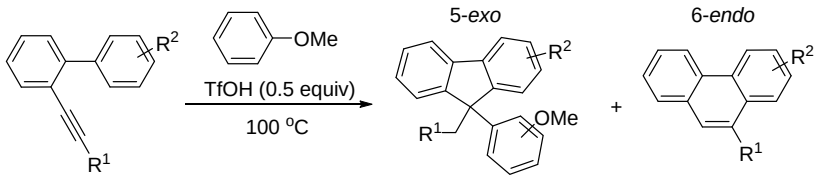


3pf

Fluorene **3pf** (22.8 mg, 0.08 mmol) was prepared from *o*-ethynylbiaryl **1p**[6] (36.9 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 39% yield after stirring at 100 °C for 1.0 h.

3pf: R_f = 0.23 [20:1 petroleum ether/DCM]; white solid; mp = 107–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.89 (s, 3H), 3.74 (s, 3H), 6.75-6.79 (m, 2H), 7.11-7.21 (m, 4H), 7.23-7.24 (m, 1H), 7.27 (dd, 1H, J = 7.4, 1.1 Hz), 7.35 (d, 1H, J = 5.0 Hz), 7.50 (dt, 1H, J = 7.6, 0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 53.4, 55.4, 113.9, 118.8, 119.6, 123.9, 125.4, 127.2, 127.4, 129.2, 136.3, 137.4, 144.2, 156.6, 157.5, 158.5; IR (neat) (cm^{-1}) 2922w, 1508s, 1250s, 1179m, 1028s; HRMS (ESI): m/z calcd for $C_{19}H_{16}OSNa$ $[M+Na]^+$: 315.0814; found 315.0807.

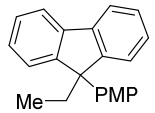
General Procedure for Cycloisomerization of Terminally Substituted Biarylalkynes.



5 **6** **7**

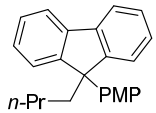
To an oven-dried sealed tube was added biarylalkyne **5a**[7] (38.5 mg, 0.20 mmol), anisole **2f** (0.5 mL, biarylalkyne *concn* = 0.40 *M*) and TfOH (8.9 μL, 0.10 mmol) at rt. When the reaction was judged to be complete by TLC after stirred at 100 °C for 1.0 h, the mixture was quenched by Et_3N

(13.9 μL, 0.10 mmol) and purified using silica gel flash column chromatography [gradient eluent: 50:1~40:1 petroleum ether/EtOAc] to afford fluorene **6a** (59.5 mg, 0.20 mmol) in 99% yield.



6a

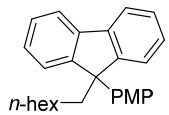
6a: R_f = 0.19 [20:1 petroleum ether/DCM]; white solid; mp = 115–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.40 (t, 3H, J = 7.3 Hz), 2.47 (q, 2H, J = 7.3 Hz), 3.69 (s, 3H), 6.71-6.75 (m, 2H), 7.07-7.11 (m, 2H), 7.18-7.25 (m, 4H), 7.31 (td, 2H, J = 7.3, 1.5 Hz), 7.73 (d, 2H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.7, 30.9, 55.3, 58.8, 113.8, 120.0, 124.4, 127.2, 127.7, 127.9, 137.2, 141.0, 151.9, 158.1; IR (neat) (cm^{-1}) 2964w, 1608w, 1509s, 1446m, 1251s, 1035m; HRMS (ESI): m/z calcd for $C_{22}H_{20}ONa$ $[M+Na]^+$: 323.1406; found 323.1403.



6b

Fluorene **6b** (65.0 mg, 0.20 mmol) was prepared from biarylalkyne **5b**[8] (44.1 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 99% yield after stirring at 100 ^{o}C for 1.0 h.

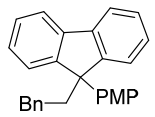
6b: R_f = 0.23 [20:1 petroleum ether/DCM]; white solid; mp = 69–70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.66-0.74 (m, 5H), 1.13-1.22 (m, 2H), 2.39-2.43 (m, 2H), 3.71 (s, 3H), 6.71-6.75 (m, 2H), 7.07-7.11 (m, 2H), 7.19-7.24 (m, 4H), 7.32 (td, 2H, J = 7.3, 1.6 Hz), 7.73 (dt, 2H, J = 7.4, 0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 23.3, 26.3, 38.0, 55.3, 58.3, 113.8, 120.0, 124.4, 127.2, 127.7, 127.8, 137.3, 140.8, 152.3, 158.1; IR (neat) (cm^{-1}) 2956w, 1607w, 1508s, 1246s, 1037m; HRMS (ESI): m/z calcd for $C_{24}H_{24}ONa$ $[M+Na]^+$: 351.1719; found 351.1720.



6c

Fluorene **6c** (69.7 mg, 0.19 mmol) was prepared from biarylalkyne **5c**[9] (52.5 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 94% yield after stirring at 100 ^{o}C for 1.0 h.

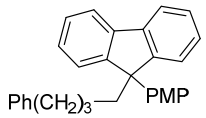
6c: R_f = 0.24 [20:1 petroleum ether/DCM]; colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.68-0.76 (m, 2H), 0.79 (t, 3H, J = 7.2 Hz), 1.07-1.20 (m, 8H), 2.38-2.43 (m, 2H), 3.71 (s, 3H), 6.71-6.75 (m, 2H), 7.07-7.10 (m, 2H), 7.19-7.25 (m, 4H), 7.32 (td, 2H, J = 7.2, 1.6 Hz), 7.73 (dt, 2H, J = 7.6, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 24.1, 29.1, 30.2, 32.0, 38.2, 55.3, 58.3, 113.8, 120.0, 124.4, 127.2, 127.7, 127.8, 137.3, 140.8, 152.3, 158.1; IR (neat) (cm^{-1}) 2927m, 1509s, 1447s, 1248s, 1182s; HRMS (ESI): m/z calcd for $C_{27}H_{30}ONa$ $[M+Na]^+$: 393.2189; found 393.2182.



6d

Fluorene **6d** (74.5 mg, 0.20 mmol) was prepared from biarylalkyne **5d**[10] (53.7 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 99% yield after stirring at 100 ^{o}C for 1.0 h.

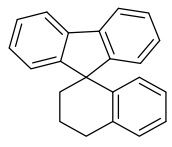
6d: R_f = 0.40 [20:1 petroleum ether/EtOAc]; white solid; mp = 105–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.96-2.02 (m, 2H), 2.72-2.76 (m, 2H), 3.69 (s, 3H), 6.71-6.74 (m, 2H), 6.97-6.99 (m, 2H), 7.07-7.12 (m, 3H), 7.16-7.20 (m, 2H), 7.25-7.29 (m, 4H), 7.32-7.37 (m, 2H), 7.76-7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.6, 40.4, 55.3, 58.3, 113.8, 120.2, 124.3, 125.8, 127.4, 127.8, 127.9, 128.4, 136.9, 140.9, 142.7, 151.8, 158.2, one carbon missing due to overlap; IR (neat) (cm^{-1}) 3005w, 1604w, 1508m, 1275m, 1177w, 1033w; HRMS (ESI): m/z calcd for $C_{28}H_{24}ONa$ $[M+Na]^+$: 399.1719; found 399.1717.



6e

Fluorene **6e** (77.7 mg, 0.19 mmol) was prepared from biarylalkyne **5e** (59.3 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 96% yield after stirring at 100 ^{o}C for 1.0 h.

6e: R_f = 0.42 [20:1 petroleum ether/EtOAc]; white solid; mp = 82–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78-0.85 (m, 2H), 1.42-1.50 (m, 2H), 2.37-2.48 (m, 4H), 3.72 (s, 3H), 6.72-6.75 (m, 2H), 7.01-7.04 (m, 2H), 7.07-7.13 (m, 3H), 7.17-7.26 (m, 6H), 7.33 (tt, 2H, J = 7.3, 1.5 Hz), 7.74 (d, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.0, 32.2, 35.8, 38.0, 55.3, 58.3, 113.8, 120.0, 124.4, 125.7, 127.2, 127.7, 127.8, 128.3, 128.4, 137.2, 140.8, 142.8, 152.2, 158.2; IR (neat) (cm^{-1}) 2934w, 1603w, 1510s, 1448m, 1182m, 1030m; HRMS (ESI): m/z calcd for $C_{30}H_{28}ONa$ $[M+Na]^+$: 427.2032; found 427.2028.

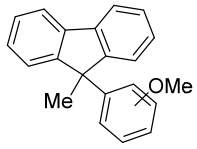


6f'

Fluorene **6f'** (53.4 mg, 0.19 mmol) was prepared from biarylalkyne **5f** (56.5 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 95% yield after stirring at 100 ^{o}C for 1.0 h.

6f': R_f = 0.57 [20:1 petroleum ether/EtOAc]; pale yellow solid; mp = 80–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03-2.06 (m, 2H), 2.16-2.22 (m, 2H), 3.09 (t, 2H, J = 6.3 Hz), 6.25 (dd, 1H, J = 7.8, 1.3 Hz), 6.81 (t, 1H, J = 7.5 Hz), 7.06 (td, 1H, J = 7.4, 1.4 Hz), 7.17-7.24 (m, 5H), 7.32-7.36 (m, 2H), 7.76 (d, 2H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 30.0, 37.1, 54.8, 120.0, 125.0, 126.2,

126.4, 127.2, 127.6, 129.0, 129.3, 137.5, 139.0, 140.0, 155.5; IR (neat) (cm^{-1}) 2931w, 1490w, 1444w, 1275m, 1115w, 1029w; HRMS (ESI): m/z calcd for $C_{22}H_{18}Na$ $[M+Na]^+$: 305.1301; found 305.1297.

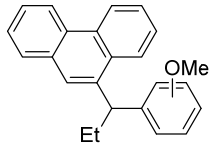


6g-*p*/*o*

Fluorene **6g-*o*** (16.6 mg, 0.06 mmol) and fluorene **6g-*p*** (**3af**) (34.9 mg, 0.12 mmol) were prepared from biarylalkyne **5g**[1] (50.1 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 29% yield and 61% yield, respectively, after stirring at 100 ^oC for 1.0 h.

6g-*o*: R_f = 0.21 [20:1 petroleum ether/DCM]; white solid; mp = 125–126 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.77 (s, 3H), 3.01 (s, 3H), 6.68 (d, 1H, J = 8.0 Hz), 7.02 (td, 1H, J = 7.6, 1.2 Hz), 7.11-7.13 (m, 2H), 7.17-7.22 (m, 3H), 7.31 (td, 2H, J = 7.4, 1.1 Hz), 7.69 (dd, 1H, J = 7.7, 1.4 Hz), 7.77 (d, 2H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3, 53.1, 55.9, 113.6, 119.8, 120.7, 122.7, 126.6, 127.2, 128.2, 128.3, 133.8, 140.3, 154.3, 158.3; IR (neat) (cm^{-1}) 3393w, 2920w, 1645w, 1489w, 1247m; HRMS (ESI): m/z calcd for $C_{21}H_{18}ONa$ $[M+Na]^+$: 309.1250; found 309.1249.

6g-*p* is the same as **3af**, for the data of **6g-*p*** see the data of **3af**.



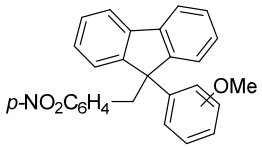
7h-*p*/*o*

Phenanthrene **7h-*o*** (10.4 mg, 0.03 mmol) and phenanthrene **7h-*p*** (51.6 mg, 0.16 mmol) were prepared from biarylalkyne **5h**[11] (43.7 mg, 0.20 mmol) in anisole **2f** (0.5 mL) with 16% yield and 79% yield, respectively, after stirring at 100 ^oC for 1.0 h.

7h-*o*: R_f = 0.29 [20:1 petroleum ether/DCM]; white solid; mp = 57–58 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (t, 3H, J = 7.3 Hz), 2.09-2.29 (m, 2H), 3.93 (s, 3H), 5.13 (t, 1H, J = 7.4 Hz), 6.76 (td, 1H, J = 7.5, 0.9 Hz), 6.90 (dd, 1H, J = 8.2, 1.2 Hz), 7.06-7.15 (m, 2H), 7.50-7.63 (m, 4H), 7.76 (s, 1H), 7.88-7.90 (m, 1H), 8.18 (dd, 1H, J = 8.2, 1.6 Hz), 8.64-8.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 28.8, 39.9, 55.7, 110.6, 120.8, 122.6, 123.1, 124.87, 124.90, 126.1, 126.2, 126.66, 126.70, 127.2, 128.2, 128.6, 129.8, 130.9, 131.9, 132.0, 133.7, 139.2, 156.8; IR (neat) (cm^{-1}) 2920w, 1598w, 1489m, 1237s, 1027m; HRMS (ESI): m/z calcd for $C_{24}H_{22}ONa$ $[M+Na]^+$: 349.1563; found 349.1557.

7h-*p*: R_f = 0.47 [20:1 petroleum ether/EtOAc]; white solid; mp = 94–95 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (t, 3H, J = 7.3 Hz), 2.10-2.35 (m, 2H), 3.71 (s, 3H), 4.51 (t, 1H, J = 7.4 Hz), 6.76-6.80 (m, 2H), 7.21-7.23 (m, 2H), 7.49-7.61 (m, 4H), 7.72 (s, 1H), 7.86-7.88 (m, 1H), 8.13 (dd, 1H, J = 8.2,

1.5 Hz), 8.62-8.64 (m, 1H), 8.69 (dd, 1H, *J* = 8.2, 1.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 29.6, 47.9, 55.3, 113.9, 122.6, 123.3, 124.8, 125.0, 126.1, 126.3, 126.6, 126.8, 128.7, 129.3, 129.8, 131.1, 131.6, 131.9, 137.0, 138.9, 158.0; IR (neat) (cm^{-1}) 2925w, 1606w, 1508s, 1441w, 1246s, 1178s, 1025s; HRMS (ESI): m/z calcd for $C_{24}H_{22}ONa$ $[M+Na]^+$: 349.1563; found 349.1555.

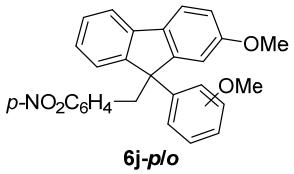


6i-*p*/*o*

Fluorene **6i-*o*** (11.4 mg, 0.03 mmol) and fluorene **6i-*p*** (69.3 mg, 0.17 mmol) were prepared from biarylalkyne **5i**[2] (59.9 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 14% yield and 85% yield, respectively, after stirring at 100 ^{o}C for 1.0 h.

6i-*o*: R_f = 0.27 [20:1 petroleum ether/EtOAc]; yellow solid; mp = 205–206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.16 (s, 3H), 3.87 (s, 2H), 6.36-6.39 (m, 2H), 6.79 (dd, 1H, *J* = 8.1, 1.0 Hz), 7.04 (td, 1H, *J* = 7.6, 1.1 Hz), 7.20-7.25 (m, 4H), 7.28-7.33 (m, 3H), 7.39-7.43 (m, 2H), 7.54-7.58 (m, 2H), 7.66 (dd, 1H, *J* = 7.8, 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.6, 55,8, 57.9, 113.7, 119.7, 120.9, 121.7, 123.6, 127.1, 127.2, 128.0, 128.6, 131.0, 132.8, 141.3, 144.7, 146.1, 150.1, 158.4; IR (neat) (cm^{-1}) 2922w, 1596w, 1516m, 1449w, 1345m, 1257m; HRMS (ESI): m/z calcd for $C_{27}H_{21}NO_3Na$ $[M+Na]^+$: 430.1414; found 430.1415.

6i-*p*: R_f = 0.14 [20:1 petroleum ether/EtOAc]; yellow solid; mp = 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.83 (s, 2H), 6.49-6.52 (m, 2H), 6.79-6.83 (m, 2H), 7.17-7.21 (m, 2H), 7.23-7.26 (m, 3H), 7.27-7.29 (m, 1H), 7.32-7.36 (m, 2H), 7.43-7.46 (m, 2H), 7.58-7.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.2, 55.4, 59.2, 114.0, 120.2, 122.0, 124.8, 127.6, 127.8, 127.9, 130.7, 135.9, 140.7, 144.7, 146.2, 150.1, 158.6; IR (neat) (cm^{-1}) 3006w, 1605w, 1508s, 1448w, 1343s, 1251m; HRMS (ESI): m/z calcd for $C_{27}H_{21}NO_3Na$ $[M+Na]^+$: 430.1414; found 430.1415.



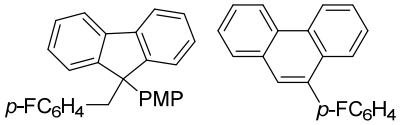
6j-*p*/*o*

Fluorene **6j-*o*** (14.0 mg, 0.03 mmol) and fluorene **6j-*p*** (67.4 mg, 0.15 mmol) were prepared from biarylalkyne **5j** (65.9 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 16% yield and 77% yield, respectively, after stirring at 100 ^{o}C for 1.0 h.

6j-*o*: R_f = 0.17 [20:1 petroleum ether/EtOAc]; yellow solid; mp = 156–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.22 (s, 3H), 3.81 (s, 3H), 3.85 (s, 2H), 6.40-6.44 (m, 2H), 6.77 (dd, 1H, *J* = 8.3, 2.4 Hz), 6.81 (dd, 1H, *J* = 8.2, 1.2 Hz), 6.87 (d, 1H, *J* = 2.3 Hz), 7.03 (td, 1H, *J* = 7.6, 1.3 Hz), 7.13-7.21 (m,

2H), 7.25-7.28 (m, 2H), 7.30-7.32 (m, 2H), 7.57-7.63 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.7, 55.7, 55.8, 58.0, 109.7, 112.5, 113.7, 118.9, 120.5, 120.9, 121.7, 123.5, 126.0, 127.2, 128.0, 128.6, 131.0, 132.7, 134.4, 141.1, 144.7, 146.1, 149.7, 152.0, 158.4, 159.5; IR (neat) (cm^{-1}) 3358w, 2920m, 1605w, 1519s, 1436m, 1031m; HRMS (ESI): m/z calcd for $C_{28}H_{23}NO_4Na$ $[M+Na]^+$: 460.1519; found 460.1507.

6j-*p*: R_f = 0.18 [20:1 petroleum ether/DCM]; yellow solid; mp = 64–65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.81 (s, 2H), 3.82 (s, 3H), 6.53-6.57 (m, 2H), 6.80-6.84 (m, 3H), 6.87 (d, 1H, J = 2.3 Hz), 7.18-7.25 (m, 4H), 7.29-7.31 (m, 1H), 7.35-7.37 (m, 2H), 7.61-7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.4, 55.4, 55.8, 59.3, 110.8, 113.3, 114.1, 119.4, 121.0, 122.1, 124.7, 126.4, 127.8, 127.9, 130.7, 133.8, 136.0, 140.7, 144.7, 146.3, 149.7, 152.0, 158.6, 159.8; IR (neat) (cm^{-1}) 3358w, 2920m, 1606m, 1456m, 1343s, 1182m; HRMS (ESI): m/z calcd for $C_{28}H_{23}NO_4Na$ $[M+Na]^+$: 460.1519; found 460.1523.

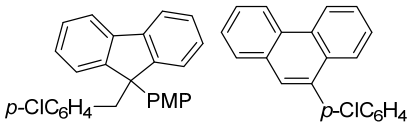


6k *and* **7k**

Fluorene **6k** (16.7 mg, 0.04 mmol) and phenanthrene **7k** (41.9 mg, 0.15 mmol) were prepared from biarylalkyne **5k**[9] (54.5 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 22% yield and 77% yield, respectively, after stirring at 100 ^{o}C for 1.0 h.

6k: R_f = 0.35 [20:1 petroleum ether/EtOAc]; white solid; mp = 160–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 2H), 3.77 (s, 3H), 6.32-6.37 (m, 2H), 6.42-6.48 (m, 2H), 6.78-6.82 (m, 2H), 7.19-7.22 (m, 2H), 7.23-7.27 (m, 4H), 7.29-7.32 (m, 2H), 7.46-7.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.6, 55.4, 59.4, 113.7 (d, J = 21.0 Hz), 113.9, 120.0, 125.0, 127.4 (d, J = 7.8 Hz), 128.1, 131.4 (d, J = 7.8 Hz), 132.3 (d, J = 3.3 Hz), 136.5, 140.9, 150.8, 158.4, 160.1, 162.5; IR (neat) (cm^{-1}) 2920w, 1600m, 1509s, 1449m, 1253m, 1037m; HRMS (ESI): m/z calcd for $C_{27}H_{21}FONa$ $[M+Na]^+$: 403.1469; found 403.1462.

7k: R_f = 0.55 [20:1 petroleum ether/EtOAc]; blue solid; mp = 139–140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.21 (m, 2H), 7.45-7.54 (m, 3H), 7.58-7.67 (m, 4H), 7.83-7.87 (m, 2H), 8.72 (dd, 2H, J = 22.8, 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.4 (d, J = 21.1 Hz) ,122.7, 123.1, 126.7, 126.77, 126.85, 126.9, 127.1, 127.8, 128.8, 130.2, 130.8, 131.3, 131.6, 131.8 (d, J = 7.9 Hz), 136.9 (d, J = 3.4 Hz), 137.8, 162.5 (d, J = 244.7 Hz); IR (neat) (cm^{-1}) 3061w, 1504m, 1449w, 1212m, 1157m, 1093w; HRMS (ESI): m/z calcd for $C_{20}H_{14}F$ $[M+H]^+$: 273.1074; found 273.1082.

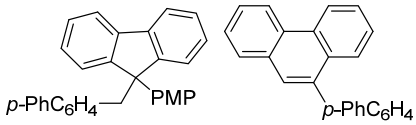


6l *and* **7l**

Fluorene **6l** (29.4 mg, 0.07 mmol) and phenanthrene **7l** (35.8 mg, 0.12 mmol) were prepared from biarylalkyne **5l**[12] (57.8 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 37% yield and 62% yield, respectively, after stirring at 100 ^{o}C for 1.0 h.

6l: R_f = 0.34 [20:1 petroleum ether/EtOAc]; pale yellow solid; mp = 129–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 2H), 3.75 (s, 3H), 6.30-6.34 (m, 2H), 6.71-6.74 (m, 2H), 6.78-6.81 (m, 2H), 7.18-7.21 (m, 2H), 7.23-7.27 (m, 4H), 7.28-7.32 (m, 2H), 7.47-7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.7, 55.4, 59.3, 113.9, 120.1, 125.0, 127.0, 127.3, 127.5, 128.0, 131.4, 131.7, 135.2, 136.4, 140.9, 150.6, 158.4; IR (neat) (cm^{-1}) 2924m, 1607w, 1507s, 1447m, 1246s, 1015m; HRMS (ESI): m/z calcd for $C_{27}H_{21}ClONa$ $[M+Na]^+$: 419.1173; found 419.1175.

7l: R_f = 0.54 [20:1 petroleum ether/EtOAc]; white solid; mp = 115–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.50 (m, 4H), 7.52-7.56 (m, 1H), 7.59-7.69 (m, 4H), 7.84-7.89 (m, 2H), 8.71 (d, 1H, J = 8.2 Hz), 8.77 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.7, 123.2, 126.76, 126.78, 126.81, 127.0, 127.1, 127.8, 128.7, 128.9, 130.2, 130.8, 131.0, 131.5, 133.6, 137.6, 139.4, one carbon missing due to overlap; IR (neat) (cm^{-1}) 3007w, 1486w, 1378w, 1276m, 1136w, 1088w; HRMS (ESI): m/z calcd for $C_{20}H_{14}Cl$ $[M+H]^+$: 289.0779; found 289.0778.



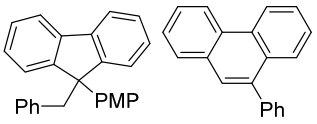
6m *and* **7m**

Fluorene **6m** (20.2 mg, 0.05 mmol) and phenanthrene **7m** (50.2 mg, 0.15 mmol) were prepared from biarylalkyne **5m**[13] (66.1 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 23% yield and 76% yield, respectively, after stirring at 100 ^{o}C for 1.0 h.

6m: R_f = 0.65 [10:1 petroleum ether/EtOAc]; white solid; mp = 183–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.79 (s, 2H), 6.49-6.51 (m, 2H), 6.79-6.83 (m, 2H), 7.03-7.05 (m, 2H), 7.21-7.24 (m, 3H), 7.25-7.27 (m, 4H), 7.30-7.36 (m, 4H), 7.39-7.41 (m, 2H), 7.47-7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.1, 55.4, 59.5, 113.9, 120.0, 125.1, 125.5, 126.9, 127.0, 127.2, 127.3, 128.1, 128.7, 130.6, 136.0, 136.7, 138.3, 140.9, 141.0, 150.9, 158.4; IR (neat) (cm^{-1}) 2922w, 1605w, 1508w, 1440w, 1276s, 1261s; HRMS (ESI): m/z calcd for $C_{33}H_{26}ONa$ $[M+Na]^+$: 461.1876; found 461.1877.

7m: R_f = 0.73 [10:1 petroleum ether/EtOAc]; white solid; mp = 199–200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.42 (m, 1H), 7.50 (t, 2H, J = 7.6 Hz), 7.55-7.59 (m, 1H), 7.61-7.76 (m, 10H), 7.91 (d, 1H, J = 7.6 Hz), 8.01 (d, 1H, J = 8.1 Hz), 8.74 (d, 1H, J = 8.2 Hz), 8.80 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.7, 123.1, 126.69, 126.74, 126.8, 127.07, 127.11, 127.2, 127.3, 127.6, 127.8, 128.9, 129.1, 130.2, 130.7, 130.8, 131.3, 131.8, 138.6, 140.0, 140.4, 141.0; IR (neat) (cm^{-1}) 3006w, 1598w, 1485w, 1276s, 1261s, 1155w; MS (ESI): m/z calcd for $C_{26}H_{19}$ $[M+H]^+$: 331; found

331. The data are consistent with that reported in the literature (J. L. Serrano, J. Pérez, L. García, G. Sánchez, J. García, P. Lozano, V. Zende and A. Kapdi, *Organometallics*, 2015, **34**, 522.).

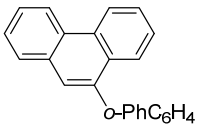


6n *and* **7n**

Fluorene **6n** (23.9 mg, 0.07 mmol) and phenanthrene **7n** (33.6 mg, 0.13 mmol) were prepared from biarylalkyne **5n**[9] (50.9 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 33% yield and 66% yield, respectively, after stirring at 100 ^{o}C for 1.0 h.

6n: R_f = 0.12 [20:1 petroleum ether/DCM]; white solid; mp = 150–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 5H), 6.41-6.43 (m, 2H), 6.75-6.81 (m, 4H), 6.85-6.89 (m, 1H), 7.20-7.24 (m, 6H), 7.30-7.33 (m, 2H), 7.45-7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.4, 55.4, 59.5, 113.9, 119.9, 125.1, 125.8, 126.9, 127.2, 127.3, 128.1, 130.2, 136.7, 140.9, 150.9, 158.4, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2963w, 1509s, 1450s, 1245s, 1183m, 1036w; HRMS (ESI): m/z calcd for $C_{27}H_{22}ONa$ $[M+Na]^+$: 385.1563; found 385.1567.

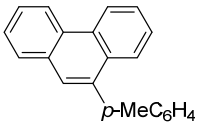
7n: R_f = 0.52 [20:1 petroleum ether/DCM]; white solid; mp = 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.67 (m, 10H), 7.85-7.92 (m, 2H), 8.69 (d, 1H, J = 8.2 Hz), 8.75 (d, 1H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.7, 123.1, 126.6, 126.66, 126.74, 127.0, 127.1, 127.5, 127.7, 128.5, 128.8, 130.1, 130.2, 130.8, 131.3, 131.7, 138.9, 140.9; IR (neat) (cm^{-1}) 3054w, 2852w, 1612w, 1453w, 1243w, 1037w; HRMS (ESI): m/z calcd for $C_{20}H_{15}$ $[M+H]^+$: 255.1168; found 255.1155.



7o

Phenanthrene **7o** (65.4 mg, 0.20 mmol) was prepared from biarylalkyne **5o**[14] (66.1 mg, 0.20 mmol) in anisole **2f** (0.5 mL) with 99% yield after stirring at 100 ^{o}C for 1.0 h.

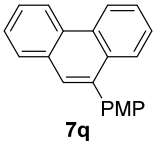
7o: R_f = 0.60 [20:1 petroleum ether/EtOAc]; white solid; mp = 45–46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94-6.98 (m, 3H), 7.12-7.15 (m, 2H), 7.37-7.41 (m, 1H), 7.45-7.46 (m, 2H), 7.50-7.60 (m, 6H), 7.66 (dd, 1H, J = 8.2, 1.3 Hz), 7.73 (dd, 1H, J = 7.9, 1.4 Hz), 8.63 (dd, 2H, J = 8.1, 4.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.6, 122.8, 126.4, 126.46, 126.54, 126.6, 126.7, 127.2, 127.3, 127.8, 128.1, 128.7, 128.9, 129.1, 130.0, 130.4, 130.5, 131.6, 131.7, 131.9, 138.3, 139.1, 141.5, 142.1; IR (neat) (cm^{-1}) 3054w, 1598w, 1478w, 1448w, 1430w, 1139w; HRMS (ESI): m/z calcd for $C_{26}H_{18}Na$ $[M+Na]^+$: 353.1301; found 353.1290.



7p

Phenanthrene **7p** (53.1 mg, 0.20 mmol) was prepared from biarylalkyne **5p**[9] (53.7 mg, 0.20 mmol) in anisole **2f** (0.5 mL) with 99% yield after stirring at 100 ^{o}C for 1.0 h.

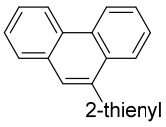
7p: R_f = 0.53 [20:1 petroleum ether/EtOAc]; white solid; mp = 83–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 7.31 (d, 2H, J = 7.8 Hz), 7.42-7.44 (m, 2H), 7.49-7.53 (m, 1H), 7.56-7.66 (m, 4H), 7.86 (dd, 1H, J = 7.8, 1.5 Hz), 7.94 (d, 1H, J = 8.2 Hz), 8.69 (d, 1H, J = 8.1 Hz), 8.75 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 122.7, 123.0, 126.56, 126.61, 126.64, 127.0, 127.1, 127.6, 128.8, 129.2, 130.06, 130.11, 130.8, 131.4, 131.8, 137.2, 138.0, 138.9; IR (neat) (cm^{-1}) 3006w, 1509w, 1450w, 1276m, 1261m, 1041w; HRMS (ESI): m/z calcd for $C_{21}H_{17}$ $[M+H]^+$: 269.1325; found 269.1327.



7q

Phenanthrene **7q** (56.3 mg, 0.20 mmol) was prepared from biarylalkyne **5q**[9] (56.9 mg, 0.20 mmol) in anisole **2f** (0.5 mL) with 99% yield after stirring at 100 ^{o}C for 1.0 h.

7q: R_f = 0.41 [20:1 petroleum ether/EtOAc]; white solid; mp = 143–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 7.01-7.05 (m, 2H), 7.43-7.47 (m, 2H), 7.50-7.54 (m, 1H), 7.56-7.60 (m, 1H), 7.61-7.66 (m, 3H), 7.86 (dd, 1H, J = 7.9, 1.2 Hz), 7.94 (dd, 1H, J = 8.2, 0.8 Hz), 8.69 (d, 1H, J = 8.0 Hz), 8.74 (d, 1H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 113.9, 122.7, 123.1, 126.5, 126.60, 126.61, 127.0, 127.1, 127.6, 128.7, 130.0, 130.8, 131.3, 131.5, 131.8, 133.3, 138.5, 159.2; IR (neat) (cm^{-1}) 2922w, 1607w, 1506m, 1451w, 1276s, 1242s; HRMS (ESI): m/z calcd for $C_{21}H_{16}ONa$ $[M+Na]^+$: 307.1093; found 307.1094.

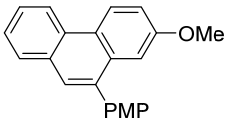


7r

Phenanthrene **7r** (51.0 mg, 0.20 mmol) was prepared from biarylalkyne **5r**[12] (52.1 mg, 0.20 mmol) in anisole **2f** (0.5 mL) with 98% yield after stirring at 100 ^{o}C for 1.0 h.

7r: R_f = 0.50 [20:1 petroleum ether/DCM]; white solid; mp = 67–68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.19 (m, 1H), 7.27 (dd, 1H, J = 3.5, 1.2 Hz), 7.41 (dd, 1H, J = 5.1, 1.2 Hz), 7.54-7.66 (m, 4H), 7.82-7.85 (m, 2H), 8.24 (dd, 1H, J = 8.2, 1.1 Hz), 8.64-8.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.7, 123.1, 125.7, 126.76, 126.85, 126.9, 127.1, 127.2, 127.4, 127.8, 128.9, 129.3, 130.3, 130.8,

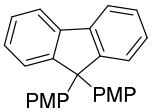
131.1, 131.2, 131.4, 141.9; IR (neat) (cm^{-1}) 2921w, 1949w, 1492w, 1448w, 1238w, 1036w; HRMS (ESI): m/z calcd for $C_{18}H_{13}S$ $[M+H]^+$: 261.0732; found 261.0738.



7s

Phenanthrene **7s** (59.7 mg, 0.19 mmol) was prepared from biarylalkyne **5s**[14] (62.9 mg, 0.20 mmol) in anisole **2f** (0.5 mL) with 95% yield after stirring at 100 ^oC for 0.2 h.

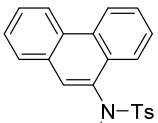
7s: R_f = 0.31 [20:1 petroleum ether/EtOAc]; white solid; mp = 35–36 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.91 (s, 3H), 7.04-7.07 (m, 2H), 7.30 (dd, 1H, J = 9.0, 2.7 Hz), 7.34 (d, 1H, J = 2.6 Hz), 7.47-7.50 (m, 2H), 7.52-7.56 (m, 1H), 7.60-7.65 (m, 2H), 7.85 (dd, 1H, J = 7.9, 1.4 Hz), 8.61 (d, 1H, J = 8.3 Hz), 8.67 (d, 1H, J = 9.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 55.6, 108.0, 114.0, 116.5, 122.2, 124.7, 125.2, 126.0, 126.7, 128.2, 128.7, 130.1, 130.8, 131.1, 133.0, 133.4, 138.0, 158.3, 159.2; IR (neat) (cm^{-1}) 3005w, 1610w, 1462w, 1276s, 1261s, 1032m; HRMS (ESI): m/z calcd for $C_{22}H_{18}O_2Na$ $[M+Na]^+$: 337.1199; found 337.1193.



6t'

Fluorene **6t'** (61.3 mg, 0.16 mmol) was prepared from biarylalkyne **5t**[15] (56.5 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 81% yield after stirring at 100 ^oC for 1.0 h.

6t': R_f = 0.27 [20:1 petroleum ether/EtOAc]; white solid; mp = 43–44 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 6H), 6.72-6.76 (m, 4H), 7.10-7.13 (m, 4H), 7.26 (dd, 2H, J = 7.5, 1.3 Hz), 7.33 (td, 2H, J = 7.4, 1.0 Hz), 7.38 (d, 2H, J = 7.5 Hz), 7.74 (d, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 64.3, 113.7, 120.3, 126.2, 127.5, 127.8, 129.3, 138.3, 140.1, 152.0, 158.4; IR (neat) (cm^{-1}) 2929w, 1606w, 1506s, 1447m, 1245s, 1031s; HRMS (ESI): m/z calcd for $C_{27}H_{22}O_2Na$ $[M+Na]^+$: 401.1512; found 401.1520.

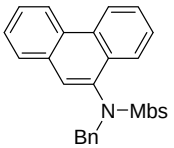


7u

Phenanthrene **7u** (83.0 mg, 0.19 mmol) was prepared from biarylynamide **5u** (87.5 mg, 0.20 mmol) in anisole **2f** (0.5 mL) with 98% yield after stirring at rt for 0.5 h.

7u: R_f = 0.56 [4:1 petroleum ether/EtOAc]; white solid; mp = 150–151 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 4.74 (d, 1H, J = 13.9 Hz), 5.01 (d, 1H, J = 13.9 Hz), 7.07-7.18 (m, 6H), 7.24 (d, 2H, J = 4.6 Hz), 7.44-7.65 (m, 7H), 8.03 (dd, 1H, J = 8.2, 1.3 Hz), 8.59 (t, 2H, J = 8.1 Hz); ^{13}C

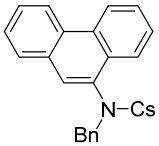
NMR (100 MHz, $CDCl_3$) δ 21.7, 56.5, 122.6, 122.8, 125.1, 126.8, 126.9, 127.1, 127.6, 127.9, 128.2, 128.3, 128.4, 128.8, 129.4, 129.7, 130.5, 131.1, 131.2, 131.4, 134.9, 135.9, 136.1, 143.8; IR (neat) (cm^{-1}) 2921w, 1598w, 1451w, 1344s, 1159s, 1087m; HRMS (ESI): m/z calcd for $C_{28}H_{23}NO_2SNa$ $[M+Na]^+$: 460.1342; found 460.1339.



7v

Aminophenanthrene **7v** (74.4 mg, 0.16 mmol) was prepared from biarylynamide **5v** (90.7 mg, 0.20 mmol) in CH_2Cl_2 (0.5 mL) with 82% yield after stirring at rt for 0.5 h.

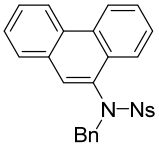
7v: R_f = 0.39 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 148–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 4.74 (d, 1H, J = 13.9 Hz), 5.01 (d, 1H, J = 13.9 Hz), 6.91-6.94 (m, 2H), 7.08-7.19 (m, 6H), 7.46-7.70 (m, 7H), 8.05 (dd, 1H, J = 8.2, 1.3 Hz), 8.60 (t, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 56.4, 114.2, 122.6, 122.8, 125.1, 126.9, 127.2, 127.6, 127.9, 128.3, 128.4, 128.8, 129.4, 130.3, 130.5, 130.8, 131.1, 131.2, 131.5, 135.0, 136.0, 163.2, one carbon missing due to overlap; IR (neat) (cm^{-1}) 3003w, 1495m, 1262s, 1156s, 1021m; HRMS (ESI): m/z calcd for $C_{28}H_{23}NO_3SNa$ $[M+Na]^+$: 476.1291; found 476.1288.



7w

Aminophenanthrene **7w** (88.8 mg, 0.19 mmol) was prepared from biarylynamide **5w** (91.6 mg, 0.20 mmol) in CH_2Cl_2 (0.5 mL) with 97% yield after stirring at rt for 0.5 h.

7w: R_f = 0.64 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 169–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (d, 1H, J = 14.0 Hz), 4.96 (d, 1H, J = 14.0 Hz), 7.11-7.19 (m, 6H), 7.41-7.50 (m, 3H), 7.54-7.69 (m, 6H), 7.95 (dd, 1H, J = 8.2, 0.8 Hz), 8.62 (dd, 2H, J = 8.2, 4.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.5, 122.82, 122.83, 124.8, 127.0, 127.1, 127.3, 127.9, 128.2, 128.5, 128.7, 128.9, 129.3, 129.5, 129.6, 130.5, 130.8, 131.0, 131.6, 134.4, 135.7, 137.8, 139.5; IR (neat) (cm^{-1}) 2921w, 1583w, 1453w, 1344m, 1160s, 1091s; HRMS (ESI): m/z calcd for $C_{27}H_{21}ClNO_2S$ $[M+H]^+$: 458.0976; found 458.0964.

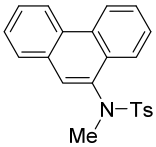


7x

Aminophenanthrene **7x** (90.0 mg, 0.19 mmol) was prepared from biarylynamide **5x** (93.7 mg, 0.20

mmol) in CH_2Cl_2 (0.5 mL) with 96% yield after stirring at rt for 0.5 h.

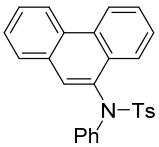
7x: R_f = 0.23 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 224–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (d, 1H, J = 14.0 Hz), 5.00 (d, 1H, J = 14.0 Hz), 7.13-7.18 (m, 6H), 7.46 (t, 1H, J = 7.5 Hz), 7.56-7.71 (m, 4H), 7.82-7.89 (m, 3H), 8.26 (d, 2H, J = 8.6 Hz), 8.64 (d, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.7, 122.9, 123.1, 124.2, 124.3, 127.1, 127.3, 127.5, 128.2, 128.4, 128.7, 129.0, 129.27, 129.32, 129.6, 130.2, 130.6, 130.9, 131.8, 133.7, 135.4, 145.4, 150.2; IR (neat) (cm^{-1}) 3081w, 1530m, 1349m, 1167s, 1087m; HRMS (ESI): m/z calcd for $C_{27}H_{20}N_2O_4SNa$ $[M+Na]^+$: 491.1036; found 491.1032.



7y

Aminophenanthrene **7y** (69.4 mg, 0.19 mmol) was prepared from biarylynamide **5y** (72.3 mg, 0.20 mmol) in CH_2Cl_2 (0.5 mL) with 96% yield after stirring at rt for 0.5 h.

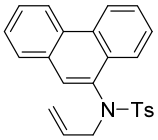
7y: R_f = 0.52 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 152–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H), 3.33 (s, 3H), 7.13 (s, 1H), 7.30-7.33 (m, 2H), 7.53-7.57 (m, 1H), 7.62-7.72 (m, 6H), 8.35-8.38 (m, 1H), 8.65-8.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 39.9, 122.8, 122.9, 124.9, 126.1, 127.0, 127.3, 127.5, 127.7, 128.4, 128.7, 129.7, 130.4, 130.8, 131.2, 131.7, 134.9, 137.5, 143.9; IR (neat) (cm^{-1}) 2920w, 1598w, 1450w, 1344m, 1156s, 1001m; HRMS (ESI): m/z calcd for $C_{22}H_{19}NO_2SNa$ $[M+Na]^+$: 384.1029; found 384.1028.



7z

Aminophenanthrene **7z** (77.1 mg, 0.18 mmol) was prepared from biarylynamide **5z**[16] (84.7 mg, 0.20 mmol) in CH_2Cl_2 (0.5 mL) with 91% yield after stirring at rt for 0.5 h.

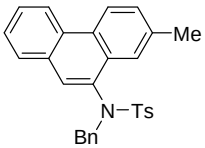
7z: R_f = 0.55 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 193–194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 7.14-7.19 (m, 1H), 7.23-7.28 (m, 4H), 7.52-7.68 (m, 9H), 7.74 (dd, 1H, J = 7.9, 1.4 Hz), 8.40-8.42 (m, 1H), 8.63-8.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 122.8, 123.0, 124.9, 126.8, 126.9, 127.1, 127.4, 127.5, 127.9, 128.3, 128.7, 129.0, 129.2, 129.7, 130.6, 131.0, 131.2, 131.9, 136.0, 137.4, 141.4, 144.0; IR (neat) (cm^{-1}) 2920w, 1593w, 1485w, 1351s, 1155s, 1090m; HRMS (ESI): m/z calcd for $C_{27}H_{21}NO_2SNa$ $[M+Na]^+$: 446.1185; found 446.1177.



7aa

Aminophenanthrene **7aa** (72.9 mg, 0.19 mmol) was prepared from biarylynamide **5aa** (77.5 mg, 0.20 mmol) in CH_2Cl_2 (0.5 mL) with 94% yield after stirring at rt for 0.25 h.

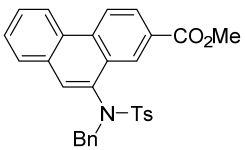
7aa: R_f = 0.58 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 130–131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 4.23 (ddt, 1H, J = 14.3, 7.1, 1.1 Hz), 4.43 (ddt, 1H, J = 14.3, 6.2, 1.4 Hz), 4.89-4.97 (m, 2H), 5.77-5.87 (m, 1H), 7.16 (s, 1H), 7.26 (d, 2H, J = 8.0 Hz), 7.52-7.56 (m, 1H), 7.60-7.68 (m, 6H), 8.25-8.28 (m, 1H), 8.63-8.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 55.3, 119.6, 122.8, 125.0, 127.0, 127.2, 127.3, 127.7, 127.8, 128.2, 128.8, 129.7, 130.5, 131.1, 131.5, 131.6, 132.6, 134.8, 136.0, 143.8, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2922w, 1596w, 1339m, 1159s, 1088m; HRMS (ESI): m/z calcd for $C_{24}H_{21}NO_2SNa$ $[M+Na]^+$: 410.1185; found 410.1186.



7bb

Aminophenanthrene **7bb** (87.6 mg, 0.19 mmol) was prepared from biarylynamide **5bb** (90.3 mg, 0.20 mmol) in CH_2Cl_2 (0.5 mL) with 97% yield after stirring at rt for 5.0 min.

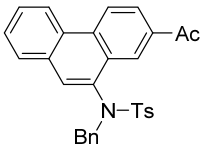
7bb: R_f = 0.59 [4:1 petroleum ether/EtOAc]; white solid; mp = 144–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.44 (s, 3H), 4.82 (d, 1H, J = 14.0 Hz), 4.94 (d, 1H, J = 14.0 Hz), 7.11-7.14 (m, 4H), 7.18-7.20 (m, 2H), 7.24 (s, 2H), 7.37 (dd, 1H, J = 8.4, 1.8 Hz), 7.47-7.51 (m, 1H), 7.58-7.65 (m, 5H), 8.46 (d, 1H, J = 8.4 Hz), 8.55 (d, 1H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.72, 21.74, 56.4, 122.5, 122.6, 124.5, 126.4, 127.6, 127.9, 128.1, 128.3, 128.8, 129.1, 129.4, 129.5, 129.6, 130.5, 130.8, 130.9, 134.3, 136.1, 136.6, 136.7, 143.7, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2919w, 1598w, 1337m, 1158s, 1089m; HRMS (ESI): m/z calcd for $C_{29}H_{25}NO_2SNa$ $[M+Na]^+$: 474.1498; found 474.1498.



7cc

Aminophenanthrene **7cc** (91.2 mg, 0.18 mmol) was prepared from biarylynamide **5cc** (99.1 mg, 0.20 mmol) in CH_2Cl_2 (0.5 mL) with 92% yield after stirring at rt for 0.5 h.

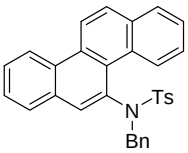
7cc: R_f = 0.52 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 205–206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.97 (s, 3H), 4.80 (d, 1H, J = 13.9 Hz), 5.03 (d, 1H, J = 13.9 Hz), 7.09-7.11 (m, 3H), 7.18-7.21 (m, 2H), 7.27-7.32 (m, 3H), 7.58-7.70 (m, 5H), 8.16 (dd, 1H, J = 8.6, 1.7 Hz), 8.56 (d, 1H, J = 1.4 Hz), 8.61-8.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 52.4, 56.6, 123.1, 123.4, 127.0, 127.2, 128.0, 128.1, 128.17, 128.22, 128.4, 129.0, 129.5, 129.7, 129.81, 129.84, 130.5, 132.1, 134.4, 134.8, 135.7, 136.1, 143.9, 167.0, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2940w, 1717s, 1455w, 1333m, 1165s, 1049m; HRMS (ESI): m/z calcd for $C_{30}H_{25}NO_4SNa$ $[M+Na]^+$: 518.1397; found 518.1381.



7dd

Aminophenanthrene **7dd** (87.3 mg, 0.18 mmol) was prepared from biarylynamide **5dd** (95.9 mg, 0.20 mmol) in CH_2Cl_2 (0.5 mL) with 91% yield after stirring at rt for 0.5 h.

7dd: R_f = 0.45 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 207–208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H), 2.57 (s, 3H), 4.59 (d, 1H, J = 13.7 Hz), 5.22 (d, 1H, J = 13.7 Hz), 7.09-7.12 (m, 3H), 7.18-7.20 (m, 2H), 7.31 (d, 2H, J = 8.1 Hz), 7.61-7.73 (m, 6H), 8.13 (dd, 1H, J = 8.7, 1.8 Hz), 8.47 (d, 1H, J = 1.7 Hz), 8.64 (t, 2H, J = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 26.7, 57.1, 123.2, 123.5, 125.3, 127.1, 128.1, 128.18, 128.25, 128.6, 128.96, 129.03, 129.5, 129.9, 131.0, 132.2, 134.4, 134.9, 135.6, 135.8, 136.0, 144.1, 198.2, two carbons missing due to overlap; IR (neat) (cm^{-1}) 2920w, 1674s, 1349s, 1274m, 1164s; HRMS (ESI): m/z calcd for $C_{30}H_{25}NO_3SNa$ $[M+Na]^+$: 502.1447; found 502.1442.

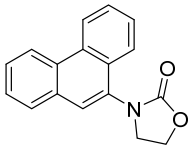


7ee

Aminophenanthrene **7ee** (92.6 mg, 0.19 mmol) was prepared from biarylynamide **5ee** (97.5 mg, 0.20 mmol) in CH_2Cl_2 (0.5 mL) with 95% yield after stirring at rt for 5.0 min.

7ee: R_f = 0.48 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 183–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 4.96 (d, 1H, J = 13.9 Hz), 5.02 (d, 1H, J = 13.9 Hz), 6.96-7.03 (m, 3H), 7.07-7.09 (m, 2H), 7.16 (d, 2H, J = 8.0 Hz), 7.22 (s, 1H), 7.54-7.60 (m, 6H), 7.63-7.67 (m, 1H), 7.84-7.90 (m, 2H), 8.62 (d, 1H, J = 9.2 Hz), 8.66 (d, 1H, J = 8.5 Hz), 9.71-9.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 56.5, 121.1, 123.5, 126.5, 126.6, 126.9, 127.0, 127.6, 127.7, 128.08, 128.10, 128.2, 128.5, 128.7, 128.9, 129.4, 130.0, 130.4, 130.6, 130.8, 131.1, 133.2, 134.7, 135.1,

135.9, 143.9, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2920w, 1595w, 1428w, 1341s, 1156s, 1026m; HRMS (ESI): m/z calcd for $C_{32}H_{25}NO_2SNa$ $[M+Na]^+$: 510.1498; found 510.1494.



7ff

Aminophenanthrene **7ff** (52.1 mg, 0.20 mmol) was prepared from biarylynamide **5ff**[17] (52.7 mg, 0.20 mmol) in CH_2Cl_2 (0.5 mL) with 99% yield after stirring at rt for 0.5 h.

7ff: R_f = 0.45 [1:1 petroleum ether/EtOAc]; pale yellow solid; mp = 126–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03 (t, 2H, J = 7.9 Hz), 4.59 (d, 2H, J = 7.9 Hz), 7.55-7.69 (m, 4H), 7.73 (s, 1H), 7.81 (dd, 1H, J = 7.9, 1.4 Hz), 7.91-7.94 (m, 1H), 8.62 (d, 1H, J = 8.3 Hz), 8.69 (dd, 1H, J = 7.9, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.1, 62.7, 122.7, 123.1, 123.5, 125.9, 127.2, 127.3, 127.4, 127.6, 128.6, 128.8, 130.2, 131.4, 131.6, 132.7, 157.8; IR (neat) (cm^{-1}) 2920w, 1736s, 1409m, 1223m, 1073m; HRMS (ESI): m/z calcd for $C_{17}H_{13}NO_2Na$ $[M+Na]^+$: 286.0838; found 286.0833.

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