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 AscendTM 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.**

To an oven-dried screw-cap vial was added (in the following order) 1-bromo-2-[(trimethylsilyl)ethynyl]benzene $\textbf{S1}$ (1.3 g, 5.0 mmol), (4-nitrophenyl)boronic acid $\textbf{S2}$ (1.3 g, 7.5 mmol), Pd(PPh$_3$)$_4$ (577.8 mg, 0.5 mmol), K$_2$CO$_3$ (6.9 g, 50.0 mmol), toluene (50.0 mL, 0.1 M in $\textbf{S1}$), EtOH (12.5 mL, 0.4 M in $\textbf{S1}$), and H$_2$O (12.5 mL, 0.4 M in $\textbf{S1}$) under a nitrogen atmosphere. Then the vial was sealed and heated to 90°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$_2$SO$_4$. The mixture was filtered and the solvent was concentrated under the reduced pressure, then the residue was purified by flash silica gel column chromatography [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$_2$CO$_3$ (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$_2$SO$_4$. The mixture was filtered and the solvent was concentrated under the reduced pressure, then the residue was purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford o-ethynylbiaryl $\textbf{1i}$ (223.2 mg, 0.99 mmol, 99% yield).
$R_f = 0.36 \, [20:1 \text{ petroleum ether/EtOAc}]; \text{ yellow solid; } mp = 79–80 \, ^\circ\text{C}; \, ^1\text{H NMR (400 MHz, CDCl}_3) \, \delta \, 3.08 \, (s, \, 1H), \, 7.37-7.41 \, (m, \, 2H), \, 7.44-7.48 \, (m, \, 1H), \, 7.65-7.67 \, (m, \, 1H), \, 7.73-7.77 \, (m, \, 2H), \, 8.27-8.30 \, (m, \, 2H); \, ^{13}\text{C NMR (100 MHz, CDCl}_3) \, \delta \, 81.4, \, 82.4, \, 120.7, \, 123.5, \, 128.5, \, 129.4, \, 129.5, \, 130.4, \, 134.3, \, 142.2, \, 147.0, \, 147.4; \, \text{IR (neat) (cm}^{-1}) \, 3441\text{w}, \, 3288\text{m}, \, 1599\text{m}, \, 1516\text{s}, \, 1348\text{s}, \, 1111\text{w}; \, \text{HRMS (ESI): } m/z \, \text{calcd for C}_{14}H_{10}NO_2Na [M+Na]^+: \, 246.0525; \, \text{found 246.0535.}$

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

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$_3$N (4.0 mL, 0.25 $M$ in S3) was added PdCl$_2$(PPh$_3$)$_2$ (14.0 mg, 0.02 mmol) and CuI (2.0 mg, 0.01 mmol) 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 chromatography [gradient eluent: 40:1~20:1 petroleum ether/DCM] to afford biarylalkyne **5e** (237.1 mg, 0.80 mmol, 80% yield).

**5e:** $R_f = 0.58 \, [20:1 \text{ petroleum ether/EtOAc}]; \text{ colorless oil; } ^1\text{H NMR (400 MHz, CDCl}_3) \, \delta \, 1.72-1.80 \, (m, \, 2H), \, 2.29 \, (t, \, 2H, \, J = 6.8 \, Hz), \, 2.59 \, (t, \, 2H, \, J = 7.6 \, Hz), \, 7.09 \, (d, \, 2H, \, J = 7.3 \, Hz), \, 7.14-7.19 \, (m, \, 1H), \, 7.23-7.41 \, (m, \, 8H), \, 7.52 \, (d, \, 1H, \, J = 7.7 \, Hz), \, 7.59-7.61 \, (m, \, 2H); \, ^{13}\text{C NMR (100 MHz, CDCl}_3) \, \delta \, 19.0, \, 30.2, \, 34.8, \, 80.9, \, 93.0, \, 122.5, \, 126.0, \, 127.1, \, 127.4, \, 127.9, \, 128.0, \, 128.4, \, 128.7, \, 129.4, \, 129.6, \, 133.2, \, 141.0, \, 141.8, \, 143.9; \, \text{IR (neat) (cm}^{-1}) \, 2938\text{w}, \, 1602\text{w}, \, 1476\text{m}, \, 1330\text{w}, \, 1009\text{w}, \, 699\text{s}; \, \text{HRMS (ESI): } m/z \, \text{calcd for C}_{23}H_{20}Na [M+Na]^+: \, 319.1457; \, \text{found 319.1453.}$

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-butyn (0.17 mL, 1.20 mmol) in 85% yield after stirring at 55 °C for 3.0 h.

**5f:** $R_f = 0.52 \, [20:1 \text{ petroleum ether/EtOAc}]; \text{ colorless oil; } ^1\text{H NMR (400 MHz, CDCl}_3) \, \delta \, 2.58 \, (t, \, 2H, \, J = 7.4 \, Hz), \, 2.78 \, (t, \, 2H, \, J = 7.4 \, Hz), \, 7.12-7.27 \, (m, \, 6H), \, 7.30-7.40 \, (m, \, 5H), \, 7.48 \, (d, \, 1H, \, J = 7.5 \, Hz), \, 7.55-7.57 \, (m, \, 2H); \, ^{13}\text{C NMR (100 MHz, CDCl}_3) \, \delta \, 21.9, \, 35.0, \, 81.0, \, 92.6, \, 122.3, \, 126.4, \, 127.1, \, 127.4, \, 128.00, \, 128.02, \, 128.5, \, 128.6, \, 129.5, \, 129.6, \, 133.3, \, 140.89, \, 140.91, \, 143.8; \, \text{IR (neat) (cm}^{-1}) \, 2938\text{w}, \, 1602\text{w}, \, 1476\text{m}, \, 1330\text{w}, \, 1009\text{w}, \, 699\text{s}; \, \text{HRMS (ESI): } m/z \, \text{calcd for C}_{23}H_{20}Na [M+Na]^+: \, 319.1457; \, \text{found 319.1453.}$
Biarylalkyne 5j (230.6 mg, 0.70 mmol) was prepared from o-ethynylbiaryl 1c (208.3 mg, 1.00 mmol) and 1-iodo-4-nitrobenzene (298.8 mg, 1.20 mmol) in 70% yield after stirring at 55 °C for 3.0 h.

5j: 
- Rf = 0.31 [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 130–131 °C; 
- 1H NMR (400 MHz, CDCl₃) 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); 
- 13C NMR (100 MHz, CDCl₃) 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; 

**General Procedure for the Synthesis of Biarylnamides.**

To an oven-dried screw-cap vial was added (in the following order) ynamide 55 (660.5 mg, 1.5 mmol), phenylboronic acid 6 (219.5 mg, 1.8 mmol), PdCl₂(PPh₃)₂ (52.6 mg, 0.075 mmol), Na₂CO₃ (318.0 mg, 3.0 mmol), toluene (7.5 mL, 0.2 M in 55), EtOH (3.75 mL, 0.4 M in 55), and H₂O (2.5 mL, 0.4 M in 55) under a nitrogen atmosphere. Then the vial was sealed and heated to 70 °C. 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 Na₂SO₄. The mixture was filtered and the solvent was concentrated under the reduced pressure, then the residue was purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc + 3% NEt₃] to afford biarylnamide 5u (511.9 mg, 1.17 mmol, 78% yield).

5u: 
- Rf = 0.47 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 150–151 °C; 
- 1H NMR (400 MHz, CDCl₃) 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); 
- 13C NMR (100 MHz, CDCl₃) 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,
Biarylnamide 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 °C for 24.0 h.

5v: \( R_f = 0.48 \) [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 100–101 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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 calcld for C\(_{28}\)H\(_{23}\)NO\(_2\)SNa [M+Na\(^+\)]: 476.1291; found 476.1288.

Biarylnamide 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 °C for 24.0 h.

5w: \( R_f = 0.65 \) [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 97–98 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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 calcld for C\(_{27}\)H\(_{20}\)ClNO\(_2\)SNa [M+Na\(^+\)]: 480.0795; found 480.0796.

Biarylnamide 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 °C 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_2$O$_4$SNa [M+Na]$^+$: 491.1036; found 491.1035.

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 °C for 24.0 h.

5y: $R_f = 0.39$ [4:1 petroleum ether/EtOAc]; pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_2$SNa [M+Na]$^+$: 384.1029; found 384.1029.

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 °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$_3$) $\delta$ 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$_3$) $\delta$ 21.8, 54.5, 70.9, 85.1, 120.1, 121.5, 127.1, 127.5, 127.8, 128.7, 128.2, 129.4, 129.6, 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$_2$SNa [M+Na]$^+$: 410.1185; found 410.1182.
Biarylnamid 5bb (304.8 mg, 0.68 mmol) was prepared from ynamide 5s (660.6 mg, 1.50 mmol) and p-tolylboronic acid (244.7 mg, 1.80 mmol) in 45% yield after stirring at 70 °C for 24.0 h.

5bb: \( R_f = 0.56 \) [4:1 petroleum ether/EtOAc]; pale yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 2.37 \) (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\(_3\)) \( \delta 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\(_2\)SNa [M+Na\(^+\)]: 474.1498; found 474.1494.

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Biarylnamid 5cc (460.9 mg, 0.93 mmol) was prepared from ynamide 5s (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 °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\(_3\)) \( \delta 2.40 \) (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\(_3\)) \( \delta 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\(_4\)SNa [M+Na\(^+\)]: 518.1397; found 518.1393.

\[
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\]

Biarylnamid 5dd (388.5 mg, 0.81 mmol) was prepared from ynamide 5s (660.6 mg, 1.50 mmol) and (4-acetylphenyl)boronic acid (295.1 mg, 1.80 mmol) in 54% yield after stirring at 70 °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\(_3\)) \( \delta 2.40 \) (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\(_3\)) \( \delta 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\(_3\)SNa [M+Na\(^+\)]: 502.1447; found 502.1444.
Biarylnamide 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 °C for 24.0 h.

5ee: \( R_f = 0.55 \) [4:1 petroleum ether/EtOAc]; pale yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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\(_2\)Na [M+Na]\(^+\): 510.1498; found 510.1497.

**Condition Optimization of the Cyclization Reaction (Table 1).**

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<tr>
<th>Entry(^a)</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Yield(^b) (%)</th>
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<td>6(^e)</td>
<td>toluene</td>
<td>100</td>
<td>0(^f)</td>
</tr>
</tbody>
</table>

\(^a\) 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% yield 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.
Condition Optimization of the Cyclization Reaction (Table 2).

**General Procedure:** To an oven-dried sealed tube was added o-ethynylbiaryl 1a (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 Et₃N (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 = 1.5:1); Rf = 0.53 [20:1 petroleum ether/DCM]; white solid; mp = 43–44 °C; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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)
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 °C for 2.5 h.  
3ab: $R_f = 0.50$ [20:1 petroleum ether/DCM]; white solid; mp = 69–70 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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 $[\text{M+Na}]^+$: 279.1144; found 279.1150.

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 °C for 2.0 h.  
3ac: $R_f = 0.56$ [20:1 petroleum ether/DCM]; white solid; mp = 97–98 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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 $[\text{M+Na}]^+$: 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).

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 °C for 2.0 h.  
3ad: $R_f = 0.55$ [20:1 petroleum ether/DCM]; white solid; mp = 99–100 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 25.2, 54.4, 120.3, 120.5, 124.1, 127.6, 128.0, 128.5, 131.5, 139.9, 144.4,
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 °C for 2.0 h.

3ae: $R_f = 0.55$ [20:1 petroleum ether/DCM]; white solid; mp = 98–99 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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.

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 °C for 1.0 h.

3af: $R_f = 0.20$ [20:1 petroleum ether/DCM]; white solid; mp = 127–128 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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.

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 °C 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 °C 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 °C 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$_2$COCD$_3$) $\delta$ 6.22 (s, 2H), 7.37 (dt, 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$_2$COCD$_3$) $\delta$ 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.**

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$_3$N (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 = 5.0/1); $R_f = 0.50$ [20:1 petroleum ether/EtOAc]; white solid; mp = 58–59 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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.

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$_3$) $\delta$ 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\(_3\)) \(\delta\) 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.

Fluorene \(3\)da (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 \(^\circ\)C for 1.5 h.

\(3\)da: (\(p/o = 4.3/1\)); \(R_f = 0.56 [20:1 \text{ petroleum ether/DCM}]; \) colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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.

Fluorene \(3\)ea (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 \(^\circ\)C for 70 h.

\(3\)ea: (\(p/o = 3.7/1\)); \(R_f = 0.28 [20:1 \text{ petroleum ether/EtOAc}]; \) colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_2\)Na [M+Na]\(^+\): 351.1356; found 351.1359.
Fluorene 3ff (54.1 mg, 0.18 mmol) was prepared from o-ethynylbiaryl 1f (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: Rf = 0.15 [20:1 petroleum ether/DCM]; white solid; mp = 144–145 °C; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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 C22H20ONa [M+Na]⁺: 323.1406; found 323.1401.

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: Rf = 0.46 [20:1 petroleum ether/EtOAc]; white solid; mp = 113–114 °C; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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, 1507s, 1451m, 1249m, 1029m; HRMS (ESI): m/z calcd for C27H22ONa [M+Na]⁺: 385.1563; found 385.1572.

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: Rf = 0.48 [20:1 petroleum ether/EtOAc]; white solid; mp = 70–71 °C; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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, 1507s, 1451m, 1248s, 1029s; HRMS (ESI): m/z calcd for C22H20O2Na [M+Na]⁺: 339.1356; found 339.1352.
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 °C for 2.0 h.

3df: Rf = 0.25 [20:1 petroleum ether/DCM]; white solid; mp = 96–97 °C; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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 C21H17ClONa [M+Na]+: 343.0860; found 343.0854.

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

3gf: Rf = 0.18 [20:1 petroleum ether/DCM]; white solid; mp = 103–104 °C; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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, 1030m; HRMS (ESI): m/z calcd for C21H17FONa [M+Na]+: 327.1156; found 327.1148.

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 °C for 17.0 h.

3ef: Rf = 0.25 [20:1 petroleum ether/EtOAc]; white solid; mp = 52–53 °C; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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
Fluorene 3hf (19.7 mg, 0.06 mmol) and fluorene 3(hf)' (51.6 mg, 0.10 mmol) were prepared from o-ethynylbiaryl 1h (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: Rf = 0.51 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 49–50 °C; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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 C23H20O2Na [M+Na]⁺: 351.1356; found 351.1354.

3(hf)’: Rf = 0.14 [10:1 petroleum ether/EtOAc]; white solid; mp = 39–40 °C; 1H NMR (400 MHz, CDCl3) 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), 7.10 (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); 13C NMR (100 MHz, CDCl3) 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 C37H34O3Na [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 (44.6 mg, 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: Rf = 0.36 [20:1 petroleum ether/EtOAc]; yellow solid; mp = 123–124 °C; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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, 147.2, 155.5, 155.9, 157.6; IR (neat) (cm⁻¹) 2920w, 1593w, 1516m, 1458m, 1331s, 1249s; HRMS (ESI): m/z calcd for C₂₁H₁₇NO₃Na [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, CDCl₃) \( \delta \) 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, CDCl₃) \( \delta \) 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 C₂₁H₁₇NO₃Na [M+Na]⁺: 354.1101; found 354.1100.

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 °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, CDCl₃) \( \delta \) 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, CDCl₃) \( \delta \) 18.6, 21.7, 22.8, 25.6, 53.9, 54.6, 55.27, 55.30, 113.76, 113.80, 117.7, 120.0, 120.8, 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, 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 C₂₂H₂₀ONa [M+Na]⁺: 323.1406; found 323.1402.

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 °C for 1.0 h.

3kf: \( R_f = 0.30 \) [20:1 petroleum ether/EtOAc]; colourless oil; \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 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, CDCl₃) \( \delta \) 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.

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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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.

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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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.

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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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.

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\(_3\)) \(\delta 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\(_3\)) \(\delta 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.

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\(_3\)) \(\delta 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\(_3\)) \(\delta 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.**

To an oven-dried sealed tube was added biarylalkyne 5a\(^7\) (38.5 mg, 0.20 mmol), anisole 2f (0.5 mL, biarylalkyne \(\text{concn} = 0.40\) \(M\)) 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\(_3\)N.
(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: $R_f = 0.19$ [20:1 petroleum ether/DCM]; white solid; mp = 115–116 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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.

Fluorene 6b (65.0 mg, 0.20 mmol) was prepared from biarylalkyne 5b (44.1 mg, 0.20 mmol) and anisole 2f (0.5 mL) in 99% yield after stirring at 100 °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$_3$) $\delta$ 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$_3$) $\delta$ 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.

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

6c: $R_f = 0.24$ [20:1 petroleum ether/DCM]; colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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.
Fluorene 6d (74.5 mg, 0.20 mmol) was prepared from biarylalkyne 5d (53.7 mg, 0.20 mmol) and anisole 2f (0.5 mL) in 99% yield after stirring at 100 °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\(_3\)) \( \delta \) 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, 2H), 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\(_3\)) \( \delta \) 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.

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 °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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 24.0, 32.2, 35.8, 38.0, 55.3, 58.3, 113.8, 120.0, 124.4, 125.7, 127.2, 127.7, 128.8, 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.

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 °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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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.

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 (50.1 mg, 0.20 mmol) and anisole 2f (0.5 mL) in 29% yield and 61% yield, respectively, after stirring at 100 °C for 1.0 h.

6g-o: \(R_f = 0.21\) [20:1 petroleum ether/DCM]; white solid; mp = 125–126 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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), 7.31 (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\(_3\)) \(\delta\) 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.

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 °C for 1.0 h.

7h-o: \(R_f = 0.29\) [20:1 petroleum ether/DCM]; white solid; mp = 57–58 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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), 7.49-7.63 (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\(_3\)) \(\delta\) 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; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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, \(J = 8.2, 1.4\) Hz), 8.64-8.70 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 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.
1.5 Hz), 8.62-8.64 (m, 1H), 8.69 (dd, 1H, J = 8.2, 1.4 Hz); 13C NMR (100 MHz, CDCl3) 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 C24H22ONa [M+Na]⁺: 349.1563; found 349.1555.

Fluorene 6i-o (11.4 mg, 0.03 mmol) and fluorene 6i-p (69.3 mg, 0.17 mmol) were prepared from biarylalkyne 5i² (59.9 mg, 0.20 mmol) and anisole 2f (0.5 mL) in 14% yield and 85% yield, respectively, after stirring at 100 °C for 1.0 h.

6i-o: Rf = 0.27 [20:1 petroleum ether/EtOAc]; yellow solid; mp = 205–206 °C; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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, 1569w, 1516m, 1449w, 1345m, 1257m; HRMS (ESI): m/z calcd for C27H21NO3Na [M+Na]⁺: 430.1414; found 430.1415.

6i-p: Rf = 0.14 [20:1 petroleum ether/EtOAc]; yellow solid; mp = 120–121 °C; 1H NMR (400 MHz, CDCl3) 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, 19H); HRMS (ESI): m/z calcd for C27H21NO3Na [M+Na]⁺: 430.1414; found 430.1415.

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 °C for 1.0 h.

6j-o: Rf = 0.17 [20:1 petroleum ether/EtOAc]; yellow solid; mp = 156–157 °C; 1H NMR (400 MHz, CDCl3) 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, CDCl₃) 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$_4$Na [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, CDCl₃) δ 3.78 (s, 3H), 3.81 (s, 2H), 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, CDCl₃) 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$_4$Na [M+Na]$^+$: 460.1519; found 460.1523.

Fluorene **6k** (16.7 mg, 0.04 mmol) and phenanthrene **7k** (41.9 mg, 0.15 mmol) were prepared from biarylalkyne **5k** (54.5 mg, 0.20 mmol) and anisole **2f** (0.5 mL) in 22% yield and 77% yield, respectively, after stirring at 100 °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, CDCl₃) 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, CDCl₃) 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, 1590s, 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, CDCl₃) 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, CDCl₃) 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, $J = 3.4$ 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.
Fluorene 6l (29.4 mg, 0.07 mmol) and phenanthrene 7l (35.8 mg, 0.12 mmol) were prepared from biarylalkyne 5l (57.8 mg, 0.20 mmol) and anisole 2f (0.5 mL) in 37% yield and 62% yield, respectively, after stirring at 100 °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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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.

Fluorene 6m (20.2 mg, 0.05 mmol) and phenanthrene 7m (50.2 mg, 0.15 mmol) were prepared from biarylalkyne 5m (66.1 mg, 0.20 mmol) and anisole 2f (0.5 mL) in 23% yield and 76% yield, respectively, after stirring at 100 °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$_3$) $\delta$ 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$_3$) $\delta$ 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, 150.6, 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$_3$) $\delta$ 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$_3$) $\delta$ 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
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.).

Fluorene 6n (23.9 mg, 0.07 mmol) and phenanthrene 7n (33.6 mg, 0.13 mmol) were prepared from biarylalkyne 5n (50.9 mg, 0.20 mmol) and anisole 2f (0.5 mL) in 33% yield and 66% yield, respectively, after stirring at 100 °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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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, 1432w, 1037w; HRMS (ESI): m/z calcd for C\(_{20}\)H\(_{15}\) [M+H]^+: 255.1168; found 255.1155.

Phenanthrene 7o (65.4 mg, 0.20 mmol) was prepared from biarylalkyne 5o (66.1 mg, 0.20 mmol) in anisole 2f (0.5 mL) with 99% yield after stirring at 100 °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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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\(_{28}\)H\(_{18}\)Na [M+Na]^+: 353.1301; found 353.1290.
Phenanthrene 7p (53.1 mg, 0.20 mmol) was prepared from biarylalkyne 5p9 (53.7 mg, 0.20 mmol) in anisole 2f (0.5 mL) with 99% yield after stirring at 100 °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, CDCl3) $\delta$ 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, CDCl3) $\delta$ 21.5, 122.7, 123.0, 126.56, 126.61, 126.64, 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; HR MS (ESI): m/z calcd for C$_{21}$H$_{17}$ [M+H]$^+$: 269.1325; found 269.1327.

Phenanthrene 7q (56.3 mg, 0.20 mmol) was prepared from biarylalkyne 5q9 (56.9 mg, 0.20 mmol) in anisole 2f (0.5 mL) with 99% yield after stirring at 100 °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, CDCl3) $\delta$ 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, CDCl3) $\delta$ 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.

Phenanthrene 7r (51.0 mg, 0.20 mmol) was prepared from biarylalkyne 5r12 (52.1 mg, 0.20 mmol) in anisole 2f (0.5 mL) with 98% yield after stirring at 100 °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, CDCl3) $\delta$ 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, CDCl3) $\delta$ 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, 1238w, 1036w; HRMS (ESI): m/z calcd for C$_{18}$H$_{13}$S [M+H]$^+$: 261.0732; found 261.0738.

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 °C for 0.2 h.

7s: $R_f = 0.31$ [20:1 petroleum ether/EtOAc]; white solid; mp = 35–36 °C; $^1$H 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; HRMS (ESI): m/z calcd for C$_{22}$H$_{18}$O$_2$Na [M+Na]$^+$: 337.1199; found 337.1193.

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 °C for 1.0 h.

6t$: R_f = 0.27$ [20:1 petroleum ether/EtOAc]; white solid; mp = 43–44 °C; $^1$H 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$_2$Na [M+Na]$^+$: 401.1512; found 401.1520.

Phenanthrene 7u (83.0 mg, 0.19 mmol) was prepared from biarylamide 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; $^1$H 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
Aminophenanthrene 7v (74.4 mg, 0.16 mmol) was prepared from biaryldynamide 5v (90.7 mg, 0.20 mmol) in CH$_2$Cl$_2$ (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$SNa [M+Na]$^+$: 476.1291; found 476.1288.

Aminophenanthrene 7w (88.8 mg, 0.19 mmol) was prepared from biaryldynamide 5w (91.6 mg, 0.20 mmol) in CH$_2$Cl$_2$ (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_2$SNa [M+H]$^+$: 458.0976; found 458.0964.

Aminophenanthrene 7x (90.0 mg, 0.19 mmol) was prepared from biaryldynamide 5x (93.7 mg, 0.20
mmol) in CH₂Cl₂ (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, CDCl₃) \( \delta \) 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); \(^1^3^C\) NMR (100 MHz, CDCl₃) \( \delta \) 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\(_2\)O\(_4\)SNa [M+Na]\(^+\): 491.1036; found 491.1032.

![Diagram of 7x](image)

Aminophenanthrene 7y (69.4 mg, 0.19 mmol) was prepared from biaryldiamide 5y (72.3 mg, 0.20 mmol) in CH₂Cl₂ (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, CDCl₃) \( \delta \) 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); \(^1^3^C\) NMR (100 MHz, CDCl₃) \( \delta \) 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\(_2\)SNa [M+Na]\(^+\): 384.1029; found 384.1028.

![Diagram of 7y](image)

Aminophenanthrene 7z (77.1 mg, 0.18 mmol) was prepared from biaryldiamide 5z\(^1^6\) (84.7 mg, 0.20 mmol) in CH₂Cl₂ (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, CDCl₃) \( \delta \) 2.43 (s, 3H), 7.14-7.19 (m, 1H), 7.23-7.28 (m, 4H), 7.52-7.58 (m, 9H), 7.74 (dd, 1H, \( J = 7.9, 1.4 \) Hz), 8.40-8.42 (m, 1H), 8.63-8.66 (m, 2H); \(^1^3^C\) NMR (100 MHz, CDCl₃) \( \delta \) 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\(_2\)SNa [M+Na]\(^+\): 446.1185; found 446.1177.
Aminophenanthrene 7aa (72.9 mg, 0.19 mmol) was prepared from biarylnamide 5aa (77.5 mg, 0.20 mmol) in CH$_2$Cl$_2$ (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_2$SNa [M+Na]$^+$: 410.1185; found 410.1186.

Aminophenanthrene 7bb (87.6 mg, 0.19 mmol) was prepared from biarylnamide 5bb (90.3 mg, 0.20 mmol) in CH$_2$Cl$_2$ (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_2$SNa [M+Na]$^+$: 474.1498; found 474.1498.

Aminophenanthrene 7cc (91.2 mg, 0.18 mmol) was prepared from biarylnamide 5cc (99.1 mg, 0.20 mmol) in CH$_2$Cl$_2$ (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_4$SNa [M+Na]$^+$: 518.1397; found 518.1381.

Aminophenanthrene 7dd (87.3 mg, 0.18 mmol) was prepared from biarylnamide 5dd (95.9 mg, 0.20 mmol) in CH$_2$Cl$_2$ (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$_3$) $\delta$ 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$_3$) $\delta$ 21.8, 26.7, 57.1, 123.2, 123.5, 125.3, 127.1, 128.1, 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, 1717s, 1455w, 1333m, 1165s, 1049m; HRMS (ESI): m/z calcd for C$_{30}$H$_{25}$NO$_3$SNa [M+Na]$^+$: 502.1447; found 502.1442.

Aminophenanthrene 7ee (92.6 mg, 0.19 mmol) was prepared from biarylnamide 5ee (97.5 mg, 0.20 mmol) in CH$_2$Cl$_2$ (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$_3$) $\delta$ 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$_3$) $\delta$ 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\(_2\)SNa [M+Na]\(^+\): 510.1498; found 510.1494.

Aminophenanthrene 7ff (52.1 mg, 0.20 mmol) was prepared from biarylnamide 5ff\(^\dagger\) (52.7 mg, 0.20 mmol) in CH\(_2\)Cl\(_2\) (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\(_3\)) \(\delta\) 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), 7.81-7.94 (m, 1H), 8.62 (d, 1H, \(J = 7.9\) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 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\(_2\)Na [M+Na]\(^+\): 286.0838; found 286.0833.

References

8. G. Zheng, Y. Li, J. Han, T. Xiong and Q. Zhang, Nat. Commun., 2015, 6, 7011.