Supplementary Information for

Fluorenes as new molecular scaffolds for carbon–carbon σ-bond cleavage reaction: acylfluorenylation of arynes

Hiroto Yoshida,* Takeshi Kishida, Masahiko Watanabe, and Joji Ohshita

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan.

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General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (1H, 270 MHz; 13C, 67.8 MHz) spectrometer or a JEOL Lambda-400 (1H, 400 MHz; 13C, 99.5 MHz) spectrometer using residual chloroform (H, δ = 7.26) or CDCl₃ (13C, δ = 77.0) as an internal standard. ¹H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a JEOL JMS-SX102A spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. The preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (benzene or chloroform as an eluent). Column chromatography was carried out using Merck Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. 18-Crown-6 was recrystallized from distilled MeCN. KF (spray-dried) was vacuum dried at 100 °C for 12 h. THF was distilled from sodium/benzophenone ketyl. MeCN was distilled from phosphorus pentoxide.

Aryne Precursors. 2-(Trimethylsilyl)phenyl triflate (1a),¹ 3-(trimethylsilyl)-2-naphthyl triflate (1b),² 6-(trimethylsilyl)-5-indanyl triflate (1c),³ 3-(trimethylsilyl)-5,6,7,8-tetrahydro-2-naphthyl triflate (1d),² 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (1e),³ 1-(trimethylsilyl)-2-naphthyl triflate (1f),⁴ 3-methoxy-2-(trimethylsilyl)phenyl triflate (1g)⁵ and 4-methyl-2-(trimethylsilyl)phenyl triflate (1h)⁶ were prepared according to literature procedures.

Fluorenes. Benzoyl fluorene (2b) was prepared according to a literature method.⁷ Other fluorenyl ketones, except for 2g, were synthesized in a similar manner as the preparation of 2b. Ethyl (2i) or isopropyl (2j) fluorene-9-carboxylate was prepared by standard esterification of fluorene-9-carboxylic acid. Ethyl esters of substituted fluorencarboxylic acids (2k–2m) were prepared from the respective substituted fluorenes according to a literature method.⁸ 2,7-Bis(phenylethynyl)fluorene was synthesized by the Sonogashira coupling of 2,7-dibromofluorene and phenylacetylene.⁹

Preparation of 2g. To a THF solution (10 mL) of fluorene (1.66 g, 10.0 mol) was added dropwise n-BuLi (1.57 M in hexane, 7.00 mL, 11.0 mmol) at 0 °C, and the resulting solution was stirred at 0 °C for 1 h before addition of anhydrous MgCl₂ (1.05 g, 11.0 mmol) at 0 °C. After the mixture was stirred at 0 °C for 0.5 h, methyl o-toluate (4.05 g, 27.0 mmol) was added at 0 °C, and stirring was continued for 2 h at room temperature. The mixture was quenched with saturated aqueous NH₄Cl solution, and extracted with ethyl acetate. The
combined organic layer was dried over MgSO₄, and concentrated. Silica gel column chromatography (hexane/dichloromethane as an eluent) followed by recrystallization (hexane/dichloromethane) gave 2g as a yellow solid.

A General Procedure for Acylfluorenylation of Arynes.
A Schlenk tube equipped with a magnetic stirring bar was charged with KF (0.60 mmol) and 18-crown-6 (0.60 mmol). The tube was evacuated at room temperature for 1 h with stirring before addition of a fluorenes (0.20 mmol), THF (10 mL) and an aryne precursosr (0.30 mmol). The resulting mixture was stirred at room temperature for the period as specified in Table 1 or Scheme 2. The mixture was diluted with ethyl acetate, filtered through a Celite plug, washed three times with brine and dried over MgSO₄. Evaporation of the solvent followed by silica gel column chromatography (hexane/dichloromethane as an eluent) or gel permeation chromatography gave the corresponding product.

2-(9H-Fluoren-9-yl)phenyl isopropyl ketone (3aa).

Isolated in 97% yield as a white solid: m.p. 140–142 °C; ¹H NMR (CDCl₃) δ 1.35 (d, J = 6.5 Hz, 6H), 3.57 (sept, J = 6.5 Hz, 1H), 5.44 (s, 1H), 6.49 (d, J = 7.6 Hz, 1H), 7.15 (t, J = 7.3 Hz, 1H), 7.22-7.33 (m, 3H), 7.34-7.46 (m, 4H), 7.60 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 7.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 18.6, 39.4, 50.1, 119.7, 125.5, 126.3, 127.2, 127.3, 129.4, 130.8, 140.2, 140.9, 141.1, 148.9, 209.5; HRMS Calcd for C₂₃H₂₀O: M⁺, 312.1514. Found: m/z 312.1518.

2-(9H-Fluoren-9-yl)benzophenone (3ab).

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Isolated in 90% yield as a white solid: m.p. 170–172 °C; $^1$H NMR (CDCl$_3$) δ 5.18 (s, 1H), 6.45 (brs, 1H), 6.95-7.17 (m, 4H), 7.17-7.56 (m, 8H), 7.63 (d, $J = 7.3$ Hz, 2H), 7.88 (brs, 2H); $^{13}$C NMR (CDCl$_3$) δ 50.3, 119.7, 120.1, 125.5, 125.9, 127.3, 128.2, 128.5, 128.9, 130.3, 130.6, 133.5, 137.8, 139.6, 140.8, 141.0, 148.3, 198.4; HRMS Calcd for C$_{26}$H$_{18}$O: M$^+$, 346.1358. Found: m/z 346.1360.

2-(9H-Fluoren-9-yl)-4'-methoxybenzophenone (3ac).

Isolated in 74% yield as a white solid: m.p. 155–159 °C; $^1$H NMR (CDCl$_3$) δ 3.90 (s, 3H), 5.29 (s, 1H), 6.58 (brs, 1H), 7.00 (d, $J = 8.1$ Hz, 2H), 7.17-7.43 (m, 9H), 7.77 (d, $J = 8.1$ Hz, 2H), 8.00 (brs, 2H); $^{13}$C NMR (CDCl$_3$) δ 50.5, 55.5, 113.7, 119.8, 125.5, 126.0, 127.2, 127.3, 127.8, 128.8, 130.2, 130.8, 132.7, 140.1, 140.5, 141.1, 148.3, 164.0, 197.1; HRMS Calcd for C$_{27}$H$_{20}$O$_2$: M$^+$, 376.1463. Found: m/z 376.1468.

2-(9H-Fluoren-9-yl)phenyl cyclopropyl ketone (3ad).

Isolated in 71% yield as a white solid: m.p. 139–142 °C; $^1$H NMR (CDCl$_3$) δ 1.19 (brs, 2H), 1.41 (brs, 2H), 2.70 (brs, 1H), 5.75 (s, 1H), 6.52 (brs, 1H), 7.10-7.48 (m, 8H), 7.76-7.94 (m, 3H); $^{13}$C NMR (CDCl$_3$) δ 12.5, 21.4, 49.8, 119.8, 125.5, 126.4, 127.1, 127.3, 127.9, 129.0, 131.1, 140.3, 141.0, 141.1, 148.6, 205.4; HRMS Calcd for C$_{23}$H$_{18}$O: M$^+$, 310.1358. Found: m/z 310.1360.

2-(9H-Fluoren-9-yl)phenyl cyclobutyl ketone (3ae).
Isolated in 69% yield as a white solid: m.p. 116–119 °C; \( ^1\)H NMR (CDCl\(_3\)) \( \delta \) 1.80-2.22 (m, 2H), 2.22-2.66 (m, 4H), 4.02-4.30 (m, 1H), 5.85 (s, 1H), 6.52 (d, \( J = 7.2 \) Hz, 1H), 7.08-7.52 (m, 8H), 7.62 (d, \( J = 7.6 \) Hz, 1H), 7.83 (d, \( J = 7.6 \) Hz, 2H); \( ^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 17.8, 25.3, 44.8, 49.8, 119.8, 125.5, 126.3, 127.1, 127.3, 127.7, 129.5, 131.3, 138.3, 141.1, 141.5, 148.8, 205.8; HRMS Calcd for C\(_{24}\)H\(_{20}\)O: M\(^+\), 324.1514. Found: \( m/z \) 324.1528.

2-(9\(H\)-Fluoren-9-yl)phenyl 2-thienyl ketone (3af).

Isolated in 58% yield as a yellow solid: m.p. 186–190 °C; \( ^1\)H NMR (CDCl\(_3\)) \( \delta \) 5.40 (s, 1H), 6.59 (brs, 1H), 7.16-7.50 (m, 9H), 7.59 (d, \( J = 7.3 \) Hz, 1H), 7.64-7.90 (m, 4H); \( ^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 50.3, 119.7, 125.6, 125.9, 127.2, 127.3, 127.9, 128.3, 129.0, 130.7, 135.4, 135.7, 139.5, 140.6, 141.1, 145.3, 148.3, 190.2; HRMS Calcd for C\(_{24}\)H\(_{16}\)OS: M\(^+\), 352.0922. Found: \( m/z \) 352.0912.

2-(9\(H\)-Fluoren-9-yl)-2’-methylbenzophenone (3ag).

Isolated in 63% yield as a white solid: m.p. 124–127 °C; \( ^1\)H NMR (CDCl\(_3\)) \( \delta \) 2.63 (s, 3H), 5.59 (s, 1H), 6.55 (brs, 1H), 7.19-7.62 (m, 13H), 7.79 (d, \( J = 7.6 \) Hz, 2H); \( ^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 21.3, 50.0, 119.8, 125.5, 126.1, 127.2, 127.4, 129.1, 129.4, 129.5, 131.1, 131.4,
131.75, 131.81, 137.6, 138.4, 139.2, 140.5, 141.1, 148.6, 200.7; HRMS Calcd for C_{27}H_{20}O: M^+, 360.1514. Found: m/z 360.1515.

2-(9H-Fluoren-9-yl)phenyl t-butyl ketone (3ah).

\[
\begin{align*}
\text{Isolated in 52% yield as a white solid: m.p. 168–171 °C; } & \quad ^1H \text{ NMR (CDCl}_3\text{) } \delta 1.43 (s, 9H), 4.81 (s, 1H), 6.42 (d, J = 8.1 Hz, 1H), 7.08 (t, J = 6.9 Hz, 1H), 7.15-7.51 (m, 8H), 7.80 (d, J = 7.6 Hz, 2H); \\
& \quad ^13C \text{ NMR (CDCl}_3\text{) } \delta 27.6, 45.3, 51.4, 119.8, 124.5, 125.6, 125.8, 127.4, 127.5, 128.6, 129.2, 138.7, 141.0, 141.7, 148.3, 214.6; \\
& \quad \text{HRMS Calcd for C}_{24}H_{22}O: M^+, 326.1671. \quad \text{Found: m/z 326.1677.}
\end{align*}
\]

Ethyl 2-(9H-fluoren-9-yl)benzoate (3ai).

\[
\begin{align*}
\text{Isolated in 93% yield as a white solid: m.p. 86–89 °C; } & \quad ^1H \text{ NMR (CDCl}_3\text{) } \delta 1.48 (t, J = 7.1 Hz, 3H), 4.52 (q, J = 7.1 Hz, 2H), 6.23 (s, 1H), 6.52 (d, J = 7.5 Hz, 1H), 7.15-7.41 (m, 8H), 7.84 (d, J = 7.5 Hz, 2H), 8.00 (d, J = 7.8 Hz, 1H); \\
& \quad ^13C \text{ NMR (CDCl}_3\text{) } \delta 14.3, 50.0, 61.3, 119.8, 125.5, 126.4, 127.1, 127.3, 129.0, 130.1, 131.1, 132.0, 141.1, 142.8, 148.4, 168.3; \\
& \quad \text{HRMS Calcd for C}_{22}H_{18}O_{2}: M^+, 314.1307. \quad \text{Found: m/z 314.1302.}
\end{align*}
\]

Isopropyl 2-(9H-fluoren-9-yl)benzoate (3aj).

\[
\begin{align*}
\text{Isolated in 93% yield as a white solid: m.p. 86–89 °C; } & \quad ^1H \text{ NMR (CDCl}_3\text{) } \delta 1.48 (t, J = 7.1 Hz, 3H), 4.52 (q, J = 7.1 Hz, 2H), 6.23 (s, 1H), 6.52 (d, J = 7.5 Hz, 1H), 7.15-7.41 (m, 8H), 7.84 (d, J = 7.5 Hz, 2H), 8.00 (d, J = 7.8 Hz, 1H); \\
& \quad ^13C \text{ NMR (CDCl}_3\text{) } \delta 14.3, 50.0, 61.3, 119.8, 125.5, 126.4, 127.1, 127.3, 129.0, 130.1, 131.1, 132.0, 141.1, 142.8, 148.4, 168.3; \\
& \quad \text{HRMS Calcd for C}_{22}H_{18}O_{2}: M^+, 314.1307. \quad \text{Found: m/z 314.1302.}
\end{align*}
\]
Isolated in 88\% yield as a white solid: m.p. 76–78 °C; $^1$H NMR (CDCl$_3$) $\delta$ 1.47 (d, $J = 6.2$ Hz, 6H), 5.42 (sept, $J = 6.2$ Hz, 1H), 6.20 (s, 1H), 6.51 (d, $J = 7.6$ Hz, 1H), 7.05-7.45 (m, 8H), 7.84 (d, $J = 7.6$ Hz, 2H), 7.97 (d, $J = 7.6$ Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 22.0, 50.1, 68.9, 119.8, 125.5, 126.4, 127.1, 127.3, 128.9, 130.0, 131.7, 131.9, 141.1, 142.6, 148.5, 167.9; HRMS Calcd for C$_{23}$H$_{20}$O$_2$: M$^+$, 328.1463. Found: m/z 328.1465.

3-(9H-Fluoren-9-yl)-2-naphthyl isopropyl ketone (3ba).

Isolated in 83\% yield as a white solid: m.p. 125–128 °C; $^1$H NMR (CDCl$_3$) $\delta$ 1.38 (d, $J = 6.9$ Hz, 6H), 3.75 (sept, $J = 6.9$ Hz, 1H), 5.56 (s, 1H), 6.98 (s, 1H), 7.20-7.25 (m, 2H), 7.35-7.44 (m, 7H), 7.82-7.88 (m, 3H), 8.15 (s, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 18.7, 39.5, 50.1, 119.8, 125.6, 126.3, 127.1, 127.3, 127.4, 127.5, 128.2, 128.5, 129.0, 131.1, 134.3, 137.9, 138.4, 141.0, 149.4, 209.4; HRMS Calcd for C$_{27}$H$_{22}$O: M$^+$, 362.1671. Found: m/z 362.1663.

6-(9H-Fluoren-9-yl)-5-indanyl isopropyl ketone (3ca).

Isolated in 81\% yield as a white solid: m.p. 127–131 °C; $^1$H NMR (CDCl$_3$) $\delta$ 1.34 (d, $J = 6.9$ Hz, 6H), 1.99 (quint, $J = 7.2$ Hz, 2H), 2.63 (t, $J = 7.6$ Hz, 2H), 2.90 (t, $J = 7.3$ Hz, 2H), 3.57 (sept, $J = 6.9$ Hz, 1H), 5.46 (s, 1H), 6.32 (s, 1H), 7.23-7.48 (m, 7H), 7.82 (d, $J = 8.2$Hz, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 18.8, 25.2, 32.4, 32.6, 39.2, 50.1, 119.7, 122.5, 124.9, 125.6, 127.0, 127.3, 128.3, 138.4, 141.1, 142.3, 147.7, 149.3, 209.4; HRMS Calcd for C$_{26}$H$_{24}$O: M$^+$, 352.1827. Found: m/z 352.1835.

3-(9H-Fluoren-9-yl)-5,6,7,8-tetrahydro-2-naphthyl isopropyl ketone (3da).
Isolated in 74% yield as a white solid: m.p. 118–121 °C; ¹H NMR (CDCl₃) δ 1.32 (d, J = 6.9 Hz, 6H), 1.67-1.74 (m, 4H), 2.42 (t, J = 5.9 Hz, 2H), 2.77 (t, J = 5.9 Hz, 2H), 3.57 (sept, J = 6.9 Hz, 1H), 5.46 (s, 1H), 6.17 (s, 1H), 7.22-7.40 (m, 7H), 7.79-7.82 (m, 2H); ¹³C NMR (CDCl₃) δ 18.8, 22.7, 22.9, 29.01, 29.04, 39.0, 49.8, 119.6, 125.6, 127.0, 127.2, 127.6, 129.6, 135.2, 137.4, 137.9, 140.7, 141.0, 149.2, 209.4; HRMS Calcd for C₂₇H₂₆O: M⁺, 366.1984. Found: m/z 366.1991.

2-(9H-Fluoren-9-yl)-4,5-dimethylphenyl isopropyl ketone (3ea).

Isolated in 59% yield as a white solid: m.p. 112–117 °C; ¹H NMR (CDCl₃) δ 1.33 (d, J = 6.6 Hz, 6H), 1.98 (s, 3H), 2.25 (s, 1H), 3.57 (sept, J = 6.6 Hz, 1H), 5.47 (s, 1H), 6.23 (s, 1H), 7.22-7.41 (m, 7H), 7.82 (d, J = 7.2 Hz, 2H); ¹³C NMR (CDCl₃) δ 18.8, 19.5, 19.6, 39.1, 49.8, 119.7, 125.5, 127.0, 127.3, 128.0, 130.2, 134.7, 137.7, 138.4, 140.1, 141.1, 149.1, 209.4; HRMS Calcd for C₂₅H₂₄O: M⁺, 340.1827. Found: m/z 340.1821.

2-(9H-Fluoren-9-yl)-1-naphthyl isopropyl ketone (3fa).

Isolated in 80% yield as a white solid: m.p. 143–145 °C; ¹H NMR (CDCl₃) δ 1.47 (d, J = 6.9 Hz, 6H), 3.54 (sept, J = 6.9 Hz, 1H), 5.07 (s, 1H), 6.46 (d, J = 8.9 Hz, 1H), 7.26-7.61 (m, 9H), 7.73-7.89 (m, 4H); ¹³C NMR (CDCl₃) δ 18.3, 43.8, 51.3, 119.9, 124.8, 125.3, 125.4,

2-(9H-Fluoren-9-yl)-6-methoxyphenyl isopropyl ketone (3ga).

Isolated in 55% yield as a white solid: m.p. 159–162 °C; \(^1^H\) NMR (CDCl\(_3\)) \(\delta\) 1.33 (d, \(J = 6.9\) Hz, 6H), 3.38 (sept, \(J = 6.9\) Hz, 1H), 3.87 (s, 3H), 4.83 (s, 1H), 6.01 (d, \(J = 7.9\) Hz, 1H), 6.75 (d, \(J = 8.2\) Hz, 1H), 7.02 (t, \(J = 8.2\) Hz, 1H), 7.26 (t, \(J = 7.3\) Hz, 2H), 7.38 (t, \(J = 7.3\) Hz, 2H), 7.46 (d, \(J = 7.3\) Hz, 2H), 7.79 (d, \(J = 7.3\) Hz, 2H); \(^1^3^C\) NMR (CDCl\(_3\)) \(\delta\) 18.1, 42.1, 50.8, 55.6, 108.6, 119.7, 120.4, 125.6, 127.3, 128.3, 130.2, 132.1, 140.3, 141.0, 148.2, 156.1, 211.8; Anal. Calcd for C\(_{24}\)H\(_{22}\)O\(_2\): C, 84.18; H, 6.48. Found: C, 83.96; H, 6.59.

2-(9H-Fluoren-9-yl)-5-methylphenyl isopropyl ketone (3ha).

Isolated in 38% yield as a white solid: m.p. 98–101 °C; \(^1^H\) NMR (CDCl\(_3\)) \(\delta\) 1.33 (d, \(J = 6.6\) Hz, 6H), 2.34 (s, 3H), 3.56 (sept, \(J = 6.8\) Hz, 1H), 5.37 (s, 1H), 6.37 (d, \(J = 7.9\) Hz, 1H), 6.96 (d, \(J = 7.9\) Hz, 1H), 7.25 (t, \(J = 7.3\) Hz, 2H), 7.34–7.42 (m, 5H), 7.82 (d, \(J = 7.3\) Hz, 2H); \(^1^3^C\) NMR (CDCl\(_3\)) \(\delta\) 18.6, 21.0, 39.4, 49.9, 119.7, 125.5, 127.0, 127.1, 127.3, 129.2, 131.7, 135.9, 137.8, 140.3, 141.1, 149.0, 209.7; HRMS Calcd for C\(_{24}\)H\(_{22}\)O: M\(^+\), 326.1671. Found: m/z 326.1674.

2-(9H-Fluoren-9-yl)-4-methylphenyl isopropyl ketone (3’ha).
Isolated in 36% yield as a white solid: m.p. 106–111 °C; $^1$H NMR (CDCl$_3$) δ 1.33 (d, $J$ = 6.6 Hz, 6H), 2.08 (s, 3H), 3.56 (sept, $J$ = 6.6 Hz, 1H), 5.53 (s, 1H), 6.28 (s, 1H), 7.06 (d, $J$ = 7.9 Hz, 1H), 7.26 (t, $J$ = 7.2 Hz, 2H), 7.33-7.45 (m, 4H), 7.53 (s, 1H), 7.54 (d, $J$ = 7.9 Hz, 1H), 7.82 (d, $J$ = 7.2 Hz, 2H); $^{13}$C NMR (CDCl$_3$) δ 18.7, 21.2, 39.1, 50.0, 119.7, 125.5, 127.1, 127.2, 127.3, 129.7, 137.3, 141.1, 141.3, 149.0, 209.2; HRMS Calcd for C$_{24}$H$_{22}$O: M$^+$, 326.1671. Found: m/z 326.1670.

Ethyl 2-[2,7-bis(phenylethynyl)-9H-fluoren-9-yl]benzoate (3ak).

Isolated in 64% yield as a yellow solid: m.p. 147–150 °C; $^1$H NMR (CDCl$_3$) δ 1.52 (t, $J$ = 7.3 Hz, 3H), 4.55 (q, $J$ = 7.3 Hz, 2H), 6.33 (s, 1H), 6.57 (d, $J$ = 7.7 Hz, 1H), 7.24-7.40 (m, 9H), 7.52-7.63 (m, 7H), 7.80 (d, $J$ = 7.7 Hz, 2H), 8.05 (d, $J$ = 7.7 Hz, 1H); $^{13}$C NMR (CDCl$_3$) δ 14.3, 49.7, 61.4, 89.9, 90.0, 120.1, 122.3, 123.2, 126.8, 128.1, 128.3, 128.7, 129.1, 130.3, 131.0, 131.5, 132.3, 140.6, 141.9, 148.9, 168.0; HRMS Calcd for C$_{36}$H$_{26}$O$_2$: M$^+$, 514.1933. Found: m/z 514.1939.

Ethyl 2-(2,7-di-t-butyl-9H-fluoren-9-yl)benzoate (3al).
Isolated in 61% yield as a white solid: m.p. 166–171 °C; $^1$H NMR (CDCl$_3$) $\delta$ 1.30 (s, 18H), 1.47 (t, $J = 7.3$ Hz, 3H), 4.52 (q, $J = 7.3$ Hz, 2H), 6.09 (s, 1H), 6.55 (d, $J = 7.9$ Hz, 1H), 7.16-7.42 (m, 6H), 7.70 (d, $J = 7.9$ Hz, 2H), 7.97 (d, $J = 6.3$ Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 14.4, 31.5, 34.8, 50.3, 61.4, 119.0, 122.3, 124.2, 126.3, 129.1, 130.0, 131.3, 132.0, 138.6, 143.2, 148.4, 150.1, 168.7; HRMS Calcd for C$_{30}$H$_{34}$O: M$,^+$, 426.2559. Found: m/z 426.2552.

Ethyl 2-(2,7-dibromo-9H-fluoren-9-yl)benzoate (3am).

Isolated in 32% yield as a white solid: m.p. 135–138 °C; $^1$H NMR (CDCl$_3$) $\delta$ 1.47 (t, $J = 7.3$ Hz, 3H), 4.49 (q, $J = 7.2$ Hz, 2H), 6.23 (s, 1H), 6.47 (d, $J = 7.6$ Hz, 1H), 7.21-7.36 (m, 2H), 7.45-7.52 (m, 4H), 7.63 (d, $J = 8.2$ Hz, 2H), 8.01 (dd, $J = 7.6$, 1.9 Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 14.3, 49.9, 61.5, 121.2, 121.5, 127.1, 128.3, 129.0, 130.5, 130.6, 130.8, 132.4, 139.1, 141.3, 150.1, 167.8; Anal. Calcd for C$_{22}$H$_{16}$Br$_2$O$_2$: C, 55.96; H, 3.42. Found: C, 56.00; H, 3.54.

References
Supplementary Material (ESI) for Chemical Communications
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