Synthesis of Tetrarylmethanes by TfOH-Promoted Formal Cross Dehydrogenative Coupling of Triarylmethanes with Arenes

Masakazu Nambo,*1 Jacky C.-H. Yim,1 Kevin, G. Fowler,1 and Cathleen M. Crudden*1,2

1Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Nagoya, Aichi, Japan,
2Queen’s University, Department of Chemistry, Chernoff Hall, Kingston, Ontario, Canada

E-mail: mnambo@itbm.nagoya-u.ac.jp, cruddenc@chem.queensu.ca

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1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Anisole was dried over CaH$_2$ under argon and distilled before use. Benzofuran was distilled before use. 1-Tosyindole was prepared according to procedures reported in the literature.$^1$ (4-Methoxyphenyl)diphenylmethane 1c, (4-fluorophenyl)diphenylmethane 1d, Tris(4-methoxyphenyl)methane,$^2$ and (4-bromophenyl)diphenylmethane 1e$^3$ were prepared according to procedures reported in the literature.

Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of argon in flame-dried glassware with standard Schlenk-line techniques. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 pre-coated plates. The developed chromatograms were analyzed by UV (254 nm) and ethanolic phosphomolybdic acid. Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (~ 0.75 mm) prepared in our laboratory. Gas chromatographic (GC) analysis was conducted on a Shimadzu GC-2010 instrument equipped with a HP-5 column (30 m. 0.25 mm, Hewlett-Packard). GCMS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with a HP-5 column (30 m. 0.25 mm, Hewlett-Packard). High-resolution mass spectra (HRMS) were obtained from a Thermo Scientific Exactive orbitrap mass spectrometer (ESI) and a JMS-T100TD instrument (DART). Nuclear magnetic resonance (NMR) spectra were recorded on either a JEOL ECA-400 ($^1$H 400 MHz, $^{13}$C 100 MHz, $^{19}$F 376 MHz) or JEOL ECA-600 ($^1$H 600 MHz, $^{13}$C 150 MHz) spectrometer. Chemical shifts for $^1$H NMR are expressed in parts per million (ppm) relative to tetramethylsilane ($\delta$ 0.00 ppm) or residual solvent (CD$_2$Cl$_2$: $\delta$ 5.32 ppm). Chemical shifts for $^{13}$C NMR are expressed in ppm relative to the residual solvent (CDCl$_3$: $\delta$ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, dm = doublet of multiplet, dt = doublet of triplet, t = triplet, tm = doublet of multiplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.
2. Preparation of Triarylmethanes 1

A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added $[\text{PdCl(allyl)}]_2$ (0.9 mg, 2.5 μmol), SIPr-HCl (2.1 mg, 5 μmol), NaOH (12 mg, 0.3 mmol), dry dioxane (0.25 mL), and degassed water (0.3 mL) at room temperature under a stream of argon. After stirring the mixture at this temperature for 30 min, diarylmethyl phenyl sulfone (0.1 mmol), arylboronic acid (0.2 mmol), and dry dioxane (0.25 mL) were added, and then the vessel was sealed. The mixture was stirred at 120 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washings with EtOAc (~20 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC to afford corresponding triarylmethanes 1.

Compound Data for Triarylmethanes 1

(4-tert-Butylphenyl)diphenylmethane (1b)

Following the typical procedure, diphenylmethyl phenyl sulfone (30.8 mg, 0.1 mmol) and 4-tert-butyphenylboronic acid (35.6 mg, 0.2 mmol) were reacted. Purification by PTLC (hexane). 27.0 mg, 90% isolated yield; a white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.29 (s, 9H), 5.50 (s, 1H), 7.03 (dm, $J = 8.0$ Hz, 2H), 7.11-7.13 (m, 4H), 7.16-7.20 (m, 2H), 7.24-7.30 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 31.4, 34.4, 56.4, 125.1, 126.2, 128.2, 129.0, 129.4, 140.7, 144.2, 149.0. HRMS (DART) $m/z$ calc. for C$_{23}$H$_{23}$ [M-H]$^+$: 299.1800; found 299.1798.

(2-Methoxyphenyl)diphenylmethane (1f)

Following the typical procedure, diphenylmethyl phenyl sulfone (30.8 mg, 0.1 mmol) and 2-methoxyphenylboronic acid (30.4 mg, 0.2 mmol) were reacted. Purification by PTLC (hexane:EtOAc = 50:1). 23.8 mg, 87% isolated yield; a white solid.
\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta 3.68 (s, 3H), 5.93 (s, 1H), 6.84-6.86 (m, 3H), 7.08 (d, } J = 7.2, 4H), 7.15-7.26 (m, 7H). \]
\[ ^13C \text{NMR (100 MHz, CDCl}_3 \delta 49.5, 55.5, 110.6, 120.2, 126.0, 127.5, 128.1, 129.4, 130.3, 132.6, 143.9, 157.1. HRMS (DART) } m/z \text{calc. for C}_{20}H_{17}O [\text{M-H}^+] \text{: 273.1279; found 273.1279.} \]

**Bis(4-methoxyphenyl)phenylmethane (1g)**

Following the typical procedure, bis(4-methoxyphenyl)methyl phenyl sulfone (36.8 mg, 0.1 mmol) and phenylboronic acid (24.4 mg, 0.2 mmol) were reacted. Purification by PTLC (hexane:EtOAc = 20:1). 23.2 mg, 76% isolated yield; a white solid.

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta 3.76 (s, 6H), 5.44 (s, 1H), 6.81 (dm, } J = 8.8 \text{ Hz, 4H), 7.01 (dm, } J = 8.8, 4H), 7.09 (d, } J = 7.2 \text{ Hz, 2H), 7.18 (t, } J = 7.2 \text{ Hz, 1H), 7.26 (t, } J = 7.2 \text{ Hz, 2H). } ^13C \text{NMR (100 } \text{MHz, CDCl}_3 \delta 55.1, 55.2, 113.6, 126.1, 128.2, 129.3, 130.2, 136.4, 144.6, 157.9. HRMS (DART) } m/z \text{calc. for C}_{21}H_{19}O_2 [\text{M-H}^+] \text{: 303.1385; found 303.1385.} \]

**((4-tert-Butyl)phenyl)(4-methoxyphenyl)phenylmethane (1h)**

Following the typical procedure, (4-methoxyphenyl)(phenyl)methyl phenyl sulfone (33.8 mg, 0.1 mmol) and 4-tert-butylphenylboronic acid (35.6 mg, 0.2 mmol) were reacted. Purification by PTLC (hexane:EtOAc = 70:1). 25.8 mg, 78% isolated yield; a colorless oil.

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta 1.30 (s, 9H), 3.78 (s, 3H), 5.46 (s, 1H), 6.82 (dm, } J = 9.2 \text{ Hz, 2H), 7.01-7.05 (m, 4H), 7.11-7.13 (m, 2H), 7.19 (tm, } J = 8.4 \text{ Hz, 1H), 7.26-7.29 (m, 4H). } ^13C \text{NMR (150 } \text{MHz, CDCl}_3 \delta 31.4, 34.4, 55.2, 55.6, 113.6, 125.1, 126.1, 128.2, 128.9, 129.4, 130.3, 136.4, 141.1, 144.5, 148.9, 158.0. HRMS (DART) } m/z \text{calc. for C}_{24}H_{25}O [\text{M-H}^+] \text{: 329.1905; found 329.1912.} \]

3. Preparation of 9-phenyl-9H-fluorene 5a\(^4\)
To a stirred solution of 9-fluorenone (540 mg, 3 mmol) in THF (1.5 mL), PhLi in n-Bu₂O (2 mL, 1.8 M, 3.6 mmol) was added dropwise at 0 °C. The reaction mixture was warmed to room temperature and stirred over 16 h. The reaction mixture was then cooled to 0 °C, diluted with Et₂O (~3 mL) before being quenched with NH₄Claq (~3 mL). The product was extracted with Et₂O (3 x ~5 mL). The combined organic layer was sequentially washed with H₂O (~5 mL), then brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residual was passed through a short silica plug (hexanes:EtOAc = 20:1) to afford the 9-phenyl-9-fluorenol in quantitative yield as a white solid. To a stirred solution of 9-phenyl-9-fluorenol (258 mg, 1 mmol) in DCM (5 mL) cooled to 0 °C, trifluoroacetic acid (0.3 mL, 4 mmol) and then Et₃SiH (0.4 mL, 2.5 mmol) were added dropwise. The reaction mixture was stirred at 0 °C for 10 min. before being quenched with Na₂CO₃aq (~4 mL). The product was extracted with DCM (3 x ~10 mL). The combined organic layer was washed with brine, dried over Na₂SO₄, and passed through a silica plug (hexanes:EtOAc = 20:1) to afford the titled compound 5a in 82% yield (197 mg) as a white solid. ¹H NMR (600 MHz, CDCl₃) δ 5.05 (s, 1H), 7.09 (dm, J = 7.2 Hz, 2H), 7.22-7.28 (m, 5H), 7.31 (d, J = 6.6 Hz, 2H), 7.38 (t, J = 7.8 Hz, 2H), 7.80 (d, J = 7.8 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 54.3, 119.9, 125.3, 126.8, 127.3, 128.3, 128.7, 141.0, 141.6, 147.9. (1 aryl carbon signal is obscured) HRMS (DART) m/z calc. for C₁₉H₁₃ [M-H]⁺: 241.1017; found 241.1012.

4. Typical Procedure for Cross Dehydrogenative Coupling of Triarylmethane 1 with Arene 2

A 10-mL sealable reaction tube equipped with a magnetic stirring bar and a septum was evacuated, flame-dried under vacuum, cooled to room temperature and backfilled with argon. The reaction tube was charged with triarylmethane 1 (0.1 mmol) and DDQ (45.4 mg, 0.2 mmol, 2 equiv) under a constant stream of argon. The mixture was evacuated under vacuum for 5 min and refilled with argon. This cycle was repeated two more times. DCE (0.3 mL), TfOH (0.9 μL, 0.01 mmol, 10 mol %), and arene 2 (0.5 mmol, 5 equiv) were added, and the vessel was sealed. The mixture was stirred at 100 °C for 6 h. After cooling to room temperature, EtOAc (~5 mL) was added and the solution was passed through a pad of Celite
with copious washings with EtOAc. The solvent was evaporated under reduced pressure. The crude product was purified by PTLC to afford the corresponding tetraarylmethane 3.

Table S1. Optimization of the cross dehydrogenative coupling.

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<th>Entry</th>
<th>Catalyst</th>
<th>Modification</th>
<th>Yield of 3aa (%)</th>
<th>Yield of 4a (%)</th>
<th>Yield of 6 (%)</th>
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* GC yield was determined using dodecane as an internal standard.

**Compound Data for Tetraarylmethanes 3 and 4a**

(4-Methoxyphenyl)triphenylmethane (3aa)

Following the typical procedure, triphenylmethane 1a (24.4 mg, 0.1 mmol) and anisole 2a (51 μL, 0.5 mmol) were reacted. Purification by PTLC (hexane:EtOAc = 50:1). 25.9 mg, 74% isolated yield; a white solid.

\[\text{H}^1\text{NMR} (400 \text{ MHz}, \text{CDCl}_3) \delta 3.78 (s, 3\text{H}), 6.80 (d, J = 9.2 \text{ Hz}, 2\text{H}), 6.80 (d, J = 9.2 \text{ Hz}, 2\text{H}), 7.16-7.26 (m, 15\text{H}).\]

\[\text{C}^13\text{NMR} (150 \text{ MHz}, \text{CDCl}_3) \delta 55.2, 64.3, 112.7, 125.8, 127.4, 131.1, 132.2, 139.0, 147.0, 157.5.\]

HRMS (DART) \textit{m/z} calc. for C\textsubscript{26}H\textsubscript{22}O \([\text{M}]^+: 350.1671;\] found 350.1663.

(3,4-Dimethoxyphenyl)triphenylmethane (3ab)

Following the typical procedure, triphenylmethane 1a (24.4 mg, 0.1 mmol) and 1,2-dimethoxybenzene 2b (65.5 μL, 0.5 mmol) were reacted. Purification by PTLC (hexane). 36.0 mg, 95% isolated; a white solid.
1H NMR (400 MHz, CDCl3) δ 3.61 (s, 3H), 3.85 (s, 3H), 6.68 (d, J = 2.0 Hz, 1H), 6.73-6.77 (m, 2H), 7.16-7.27 (m, 15H). 13C NMR (150 MHz, CDCl3) δ 55.7 (overlapped), 64.6, 109.8, 115.4, 123.1, 125.9, 127.4, 131.1, 139.4, 146.9, 147.07, 147.10. HRMS (DART) m/z calc. for C27H24O2 [M]+: 380.1776; found 380.1774.

(2,4-Dimethoxyphenyl)triphenylmethane (3ac)

Following the typical procedure, triphenylmethane 1a (24.4 mg, 0.1 mmol) and 1,3-dimethoxybenzene 2c (66 μL, 0.5 mmol) were reacted. Purification by PTLC (hexane:EtOAc = 40:1). 28.0 mg, 74% isolated yield; a white solid.

1H NMR (600 MHz, CDCl3) δ 3.13 (s, 3H), 3.79 (s, 3H), 6.39-6.41 (m, 2H), 7.04 (d, J = 9.0 Hz, 1H), 7.12-7.15 (m, 9H), 7.19-7.21 (m, 6H). 13C NMR (100 MHz, CDCl3) δ 55.0, 55.2, 62.8, 100.8, 103.4, 125.3, 126.9, 129.1, 131.0, 146.3, 159.2, 160.0. (1 carbon signal was obscured) HRMS (ESI) m/z calc. for C27H25O2 [M+H]+: 381.1850; found 381.1849.

2-Chloro-5-tritylthiophene (3ad)

Following the typical procedure, triphenylmethane 1a (24.4 mg, 0.1 mmol) and 2-chlorothiophene 2d (46 μL, 0.5 mmol) were reacted. Purification by PTLC (hexane). 34 mg, 94% isolated yield; a pale yellow solid.

1H NMR (400 MHz, CDCl3) δ 6.52 (d, J = 4.0 Hz, 1H), 6.77 (d, J = 4.0 Hz, 1H), 7.17-7.22 (m, 6H), 7.23-7.31 (m, 9H). 13C NMR (100 MHz, CDCl3) δ 65.5, 125.2, 126.8, 127.6, 128.5, 129.1, 130.5, 146.1, 151.5. HRMS (DART) m/z calc. for C23H17ClS [M]+: 360.0740; found 360.0743.

2-Bromo-5-tritylthiophene (3ae)

Following the typical procedure, triphenylmethane 1a (24.4 mg, 0.1 mmol) and 2-bromothiophene 2e (80.5 mg, 0.5 mmol) were reacted. Purification by PTLC (hexane). 29.0 mg, 72% isolated yield; a white solid.

1H NMR (400 MHz, CDCl3) δ 6.50 (d, J = 3.9 Hz, 1H), 6.91 (d, J = 3.9 Hz, 1H), 7.18-7.20 (m, 6H), 7.24-7.29 (m, 9H). 13C NMR (150 MHz, CDCl3) δ 62.6, 111.5, 126.8, 127.6, 129.0, 129.5, 130.4, 146.1, 154.4. HRMS (DART) m/z calc. for C23H17SBr [M]+: 404.0234; found 404.0230.

2-Phenyl-5-tritylthiophene (3af)

Following the typical procedure, triphenylmethane 1a (24.4 mg, 0.1
mmol) and 2-phenylthiophene 2f (80.0 mg, 0.5 mmol) were reacted. Purification by PTLC (hexane). 35.0 mg, 87% isolated yield; a white solid.

\[ \text{1H NMR (600 MHz, CDCl}_3] \delta 6.72 (d, J = 3.6 Hz, 1H), 7.17 (d, J = 3.6 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.24-7.32 (m, 17H), 7.51 (d, J = 7.8 Hz, 2H). \]

\[ \text{13C NMR (150 MHz, CDCl}_3] \delta 62.4, 122.0, 125.5, 126.6, 127.2, 127.5, 128.7, 130.3, 130.6, 134.3, 143.3, 146.6, 152.3. \]

HRMS (DART) \( m/z \) calc. for C\(_{29}\)H\(_{22}\)S [M]+: 402.1442; found 402.1431.

2-Tritylbenzofuran (3ag)

Following the typical procedure, triphenylmethane 1a (24.4 mg, 0.1 mmol) and benzofuran 2g (55 \( \mu \)L, 0.5 mmol) were reacted. Purification by PTLC (hexane:EtOAc = 50:1). 35.0 mg, 98% isolated yield; a white solid.

\[ \text{1H NMR (600 MHz, CDCl}_3] \delta 6.74 (s, 1H), 7.18-7.21 (m, 7H), 7.23-7.29 (m, 10H), 7.44 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H). \]

\[ \text{13C NMR (150 MHz, CDCl}_3] \delta 61.3, 108.4, 111.4, 120.9, 122.7, 123.9, 126.8, 127.8, 128.0, 130.4, 144.6, 155.1, 162.3. \]

HRMS (DART) \( m/z \) calc. for C\(_{27}\)H\(_{21}\)O [M+H]+: 361.1592; found 361.1601.

1-Tosyl-3-tritylindole (3ah)

Following the typical procedure, triphenylmethane 1a (24.4 mg, 0.1 mmol) and N-tosylindole 2h (135.5 mg, 0.5 mmol) were reacted. Purification by PTLC (hexane). 51.3 mg, 99% isolated yield; a white solid.

\[ \text{1H NMR (600 MHz, CDCl}_3] \delta 2.37 (s, 3H), 6.57 (d, J = 8.4 Hz, 1H), 6.86 (t, J = 7.8 Hz, 1H), 7.10-7.12 (m, 6H), 7.17 (t, J = 7.8 Hz, 1H), 7.19-7.23 (m, 12H), 7.65 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 8.4 Hz, 1H). \]

\[ \text{13C NMR (150 MHz, CDCl}_3] \delta 21.6, 59.2, 113.8, 122.9, 123.5, 124.3, 126.4, 126.7, 127.1, 127.6, 129.8, 130.5, 130.6, 131.2, 135.1, 136.0, 144.8, 144.9. \]

HRMS (ESI) \( m/z \) calc. for C\(_{34}\)H\(_{27}\)NO\(_2\)S\(_2\)Na [M+Na]+: 536.1655; found 536.1651.

2-[(4-(tert-Butyl)phenyl)diphenylmethyl]benzofuran (3bg)

Following the typical procedure, (4-tert-butylphenyl)diphenylmethane 1b (29.8 mg, 0.1 mmol) and benzofuran 2g (55 \( \mu \)L, 0.5 mmol) were reacted. Purification by PTLC (hexane:EtOAc = 50:1). 36.0 mg, 86% isolated yield; a off-white solid.
1H NMR (400 MHz, CDCl3) δ 1.31 (s, 9H), 6.46 (d, J = 1.2 Hz, 1H), 7.08 (dt, J = 8.4, 2.4 Hz, 2H), 7.17-7.30 (m, 14H), 7.42-7.49 (m, 2H). 13C NMR (100 MHz, CDCl3) δ 31.3, 34.4, 61.0, 108.3, 111.4, 120.8, 122.6, 123.8, 124.6, 126.7, 127.7, 128.1, 129.9, 130.3, 141.3, 144.8, 149.5, 155.1, 162.6. HRMS (DART) m/z calc. for C31H29O [M+H]+: 417.2218; found 417.2214.

2-[(4-Methoxyphenyl)diphenylmethyl]benzofuran (3cg)

Following the typical procedure, (4-methoxyphenyl)-diphenylmethane 1c (27.4 mg, 0.1 mmol) and benzofuran 2g (55 μL, 0.5 mmol) were reacted. Purification by PTLC (hexane:EtOAc = 40:1). 32.9 mg, 84% isolated yield; a while solid.

1H NMR (400 MHz, CDCl3) δ 3.80 (s, 3H), 6.45 (d, J = 0.8 Hz, 1H), 6.81 (dm, J = 9.2 Hz, 2H), 7.08 (dm, J = 9.2 Hz, 2H), 7.16-7.31 (m, 12H), 7.44 (dm, J = 7.6 Hz, 1H), 7.48 (dm, J = 7.6 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 55.2, 60.7, 108.3, 111.4, 113.0, 120.9, 122.7, 123.9, 126.8, 127.7, 128.0, 130.3, 131.4, 136.7, 144.8, 155.1, 158.2, 162.6. HRMS (ESI) m/z calc. for C28H22O2Na [M+Na]+: 413.1517; found 413.1513.

2-[(4-Fluorophenyl)diphenylmethyl]benzofuran (3dg)

Following the typical procedure, (4-fluorophenyl)-diphenylmethane 1d (26.2 mg, 0.1 mmol) and benzofuran 2g (55 μL, 0.5 mmol) were reacted. Purification by PTLC (hexane), 31.7 mg, 87% isolated yield; an off-while solid.

1H NMR (600 MHz, CD2Cl2) δ 6.49 (s, 1H), 7.00 (tm, J = 6.6 Hz, 2H), 7.15-7.19 (m, 6H), 7.21 (tm, J = 6.0 Hz, 1H), 7.26 (tm, J = 6.6 Hz, 1H), 7.29-7.32 (m, 6H), 7.43 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H). 13C NMR (150 MHz, CDCl3) δ 60.8, 108.5, 111.4, 114.5 (d, J = 20.1 Hz), 120.9, 122.8, 124.1, 127.0, 127.86, 127.92, 130.2, 132.0 (d, J = 7.2 Hz), 140.3, 144.4, 155.1, 161.6 (d, J = 244 Hz), 162.1. 19F NMR (376 MHz, CDCl3) δ −115.9. HRMS (DART) m/z calc. for C27H20FO [M+H]+: 379.1498; found 379.1499.

2-[(4-Trifluoromethylphenyl)diphenylmethyl]benzofuran (3eg)

2-[(4-Trifluoromethylphenyl)diphenylmethyl]benzofuran
Following the typical procedure, (4-trifluoromethylphenyl)diphenylmethane 1e (31.2 mg, 0.1 mmol) and benzofuran 2g (55 μL, 0.5 mmol) were reacted. Purification by GPC. 30.4 mg, 71% isolated yield; a while solid.

\[ \text{1H NMR (400 MHz, CDCl}_3 \text{)} \delta 6.48 \text{ (s, 1H), 7.12-7.18 (m, 4H), 7.20-7.35 (m, 10H), 7.44 (d, } J = 8.0 \text{ Hz, 1H), 7.50 (dm, } J = 8.0 \text{ Hz, 1H), 7.54 (d, } J = 8.4 \text{ Hz, 2H).} \]

\[ \text{13C NMR (150 MHz, CDCl}_3 \text{)} \delta 61.3, 108.7, 111.4, 121.0, 122.9, 124.1 (q, } J = 270 \text{ Hz), 124.2, 124.7 (m), 127.1, 127.8, 128.0, 129.0 (q, } J = 31.7 \text{ Hz), 130.2, 130.7, 143.8, 148.6, 155.2, 161.4.} \]

\[ \text{19F NMR (376 MHz, CDCl}_3 \text{)} \delta -62.4. \]

\[ \text{HRMS (DART) } m/z \text{ calc. for C}_{28}\text{H}_{20}\text{F}_3\text{O [M+H]}^+: 429.1466; \text{ found 429.1460.} \]

2-[(4-Bromophenyl)diphenylmethyl]benzofuran (3fg)

Following the typical procedure, (4-bromophenyl)diphenylmethane 1f (32.3 mg, 0.1 mmol) and benzofuran 2g (55 μL, 0.5 mmol) were reacted. Purification by PTLC (hexane). 37.1 mg, 85% isolated yield; a while solid.

\[ \text{1H NMR (600 MHz, CDCl}_3 \text{)} \delta 6.46 \text{ (s, 1H), 7.07 (d, } J = 8.4 \text{ Hz, 2H), 7.15 (dm, } J = 8.4 \text{ Hz, 4H), 7.21 (t, } J = 7.8 \text{ Hz, 1H), 7.25-7.30 (m, 7H), 7.40-7.44 (m, 3H), 7.49 (d, } J = 7.8 \text{ Hz, 1H).} \]

\[ \text{13C NMR (150 MHz, CDCl}_3 \text{)} \delta 61.0, 108.6, 111.4, 121.0, 121.0, 122.8, 124.1, 127.0, 127.9, 130.2, 130.9, 132.1, 143.7, 144.0, 155.2, 161.7. \]

(1 aryl carbon signal is obscured) HRMS (DART) \( m/z \) calc. for C\(_{27}\)H\(_{20}\)O\(_{Br}\) [M+H]\(^+\): 439.0698; found 439.0702.

2-[(2-Methoxyphenyl)diphenylmethyl]benzofuran (3gg)

Following the typical procedure, (2-methoxyphenyl)diphenylmethane 1g (27.5 mg, 0.1 mmol) and benzofuran 2g (55 μL, 0.5 mmol) were reacted. Purification by PTLC (hexane:EtOAc = 50:1). 34.0 mg, 87% isolated yield; an off-white solid.

\[ \text{1H NMR (400 MHz, CDCl}_3 \text{)} \delta 3.22 \text{ (s, 3H), 6.45 (d, } J = 0.8 \text{ Hz, 1H), 6.85-6.91 (m, 3H), 7.15-7.28 (m, 12H), 7.31-7.35 (m, 1H), 7.37-7.39 (m, 1H), 7.46-7.48 (m, 1H).} \]

\[ \text{13C NMR (100 MHz, CDCl}_3 \text{)} \delta 55.3, 59.7, 106.8, 111.3, 112.8, 120.5, 120.7, 122.4, 123.4, 126.3, 127.5, 128.5, 128.9, 130.0, 130.5, 133.8, 144.0, 154.8, 158.1, 162.2. \]

HRMS (ESI) \( m/z \) calc. for C\(_{28}\)H\(_{22}\)O\(_2\)Na [M+Na]\(^+\): 413.1517; found 413.1508.
2-[Bis(4-methoxyphenyl)(phenyl)methyl]benzofuran (3hg)

Following the typical procedure, bis(4-methoxyphenyl)-phenylmethane 1h (30.5 mg, 0.1 mmol) and benzofuran 2g (55 μL, 0.5 mmol) were reacted. Purification by PTLC (hexane:EtOAc = 30:1). 16.6 mg, 40% isolated yield; an off-white solid.

$^1$H NMR (600 MHz, CDCl₃) δ 3.80 (s, 6H), 6.43 (s, 1H), 6.81 (dm, J = 9.0 Hz, 4H), 7.08 (dm, J = 9.0 Hz, 4H), 7.16–7.28 (m, 7H), 7.44 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 7.2 Hz, 1H). $^{13}$C NMR (150 MHz, CDCl₃) δ 55.2, 60.0, 108.1, 111.4, 113.0, 120.8, 122.6, 123.8, 126.7, 127.7, 128.1, 130.2, 131.3, 137.0, 145.1, 155.1, 158.2, 162.9. HRMS (ESI) m/z calc. for C₂₉H₂₄O₃Na [M+Na]+: 443.1623; found 443.1615.

2-[(4-tert-Butyl)phenyl](4-methoxyphenyl)(phenyl)methyl]benzofuran (3jg)

Following the typical procedure, (4-tert-butylphenyl)(4-methoxyphenyl)phenylmethane 1j (33.0 mg, 0.1 mmol) and benzofuran 2g (55 μL, 0.5 mmol) were reacted. Purification by PTLC (hexane:EtOAc = 30:1). 37.3 mg, 83% isolated yield; a while solid.

$^1$H NMR (600 MHz, CDCl₃) δ 1.31 (s, 9H), 3.79 (s, 3H), 6.44 (s, 1H), 6.81 (dm, J = 9.0 Hz, 2H), 7.07–7.10 (m, 4H), 7.17–7.20 (m, 3H), 7.22–7.29 (m, 6H), 7.44 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 7.2 Hz, 1H). $^{13}$C NMR (150 MHz, CDCl₃) δ 31.3, 34.4, 55.2, 60.3, 108.1, 111.4, 113.0, 120.8, 122.6, 123.8, 124.6, 126.7, 127.7, 128.1, 129.8, 130.3, 131.4, 137.0, 141.6, 145.1, 149.5, 155.1, 158.2, 162.8. HRMS (DART) m/z calc. for C₃₂H₃₁O₂ [M+H]+: 447.2324; found 447.2318.

9-(4-Methoxyphenyl)-9-phenylfluorene (4a)

Following the typical procedure, 9-phenyl-9H-fluorene 5a (24.2 mg, 0.1 mmol) and anisole 2a (51 μL, 0.5 mmol) were reacted. Purification by PTLC (hexane:EtOAc = 40:1). 31.1 mg, 86% isolated yield; a while solid.

$^1$H NMR (600 MHz, CDCl₃) δ 3.74 (s, 3H), 6.75 (dm, J = 9.0 Hz, 2H), 7.11 (dm, J = 9.0 Hz, 2H), 7.18–7.20 (m, 5H), 7.26 (tm, J = 7.8 Hz, 2H), 7.34 (tm, J = 7.8 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 7.8 Hz, 2H). $^{13}$C NMR (150 MHz, CDCl₃) δ 55.1, 64.8,
5. X-ray Crystallography

Single crystals of 3ag suitable for X-ray crystal structure analysis were obtained by slow evaporation from CHCl₃. Single crystals of 3ah suitable for X-ray crystal structure analysis were also obtained by slow evaporation from MeCN. Details of the crystal data and a summary of the intensity data collection parameters for 3ag and 3ah are listed in Table S2.

A suitable crystal was mounted with mineral oil on a glass fiber and transferred to the goniometer of a Rigaku PILATUS diffractometer. Graphite-monochromated Mo Kα radiation (λ = 0.71075 Å) was used. The structures were solved by direct methods with (SIR-97)⁶ and refined by full-matrix least-squares techniques against F² (SHELXL-2013/4)⁷ with Yadokari-XG program.⁸ The intensities were corrected for Lorentz and polarization effects. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Table S2. Crystallographic data and structure refinement details for 3ag and 3ah.

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<th>3ah</th>
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</table>

**Figure S1.** ORTEP drawing of 3ag and 3ah with thermal ellipsoids shown at 30% probability level. All hydrogen atoms are omitted for clarity.
8. $^1$H, $^{13}$C and $^{19}$F NMR Spectra

$^1$H-NMR (400 MHz, CDCl$_3$) of 1b
$^{13}$C-NMR (100 MHz, CDCl$_3$) of $1b$

$^1$H-NMR (400 MHz, CDCl$_3$) of $1f$
$^{13}$C-NMR (100 MHz, CDCl$_3$) of 1f
$^1$H-NMR (400 MHz, CDCl$_3$) of 1g
$^{13}$C-NMR (100 MHz, CDCl$_3$) of 1g

$^1$H-NMR (400 MHz, CDCl$_3$) of 1h
$^{13}$C-NMR (150 MHz, CDCl$_3$) of 1h
$^1$H-NMR (600 MHz, CDCl$_3$) of 5a
$^{13}$C-NMR (150 MHz, CDCl$_3$) of 5a
$^1$H-NMR (400 MHz, CDCl$_3$) of 3aa
$^{13}$C-NMR (150 MHz, CDCl$_3$) of 3aa
$^{11}$H
NMR
(400 MHz, CDCl$_3$)
of 3ab
$^{13}$C-NMR (150 MHz, CDCl$_3$) of 3ab
$^1$H-NMR (600 MHz, CDCl$_3$) of 3ac
$^{13}$C-NMR (100 MHz, CDCl$_3$) of 3ac
$^1$H-NM R (400 MHz, CDCl$_3$) of 3ad
$^{13}$C-NMR (100 MHz, CDCl$_3$) of 3ad
$^1$H-NMR (600 MHz, CDCl$_3$) of 3ae
$^{13}$C-NMR (150 MHz, CDCl$_3$) of 3ae
$^1$H-NMR (600 MHz, CDCl$_3$) of 3af
$^1$H-NMR (600 MHz, CDCl$_3$) of 3ag
$^{13}$C-NMR (150 MHz, CDCl$_3$) of 3ag
$^1$H-NMR (600 MHz, CDCl$_3$) of 3ah
$^{13}$C-NMR (150 MHz, CDCl₃) of 3ah
$^1$H-NMR (400 MHz, CDCl$_3$) of 3bg
$^{13}$C-NMR (100 MHz, CDCl$_3$) of 3bg
$^1$H-NMR (400 MHz, CDCl₃) of 3cg
$^{13}$C-NMR (100 MHz, CDCl$_3$) of 3cg
$^1$H-NMR (600 MHz, CD$_2$Cl$_2$) of 3dg
$^{13}$C-NMR (150 MHz, CDCl$_3$) of 3dg
$^{19}$F-NMR (376 MHz, CDCl₃) of 3dg
$^1$H-NMR (400 MHz, CDCl$_3$) of 3eg
$^{13}$C-NMR (150 MHz, CDCl$_3$) of 3eg

$^{19}$F-NMR (376 MHz, CDCl$_3$) of 3eg
$^1$H-NMR (600 MHz, CDCl$_3$) of 3fg
$^{13}$C-NMR (150 MHz, CDCl$_3$) of 3fg
$^1$H-NMR (400 MHz, CDCl$_3$) of 3gg
$^{13}$C-NMR (100 MHz, CDCl₃) of 3gg
$^1$H-NMR (600 MHz, CDCl$_3$) of $3_{hg}$
$^{13}$C-NMR (150 MHz, CDCl$_3$) of 3hg
$^1$H-NMR (600 MHz, CDCl₃) of $3_{jg}$
$^{13}$C-NMR (150 MHz, CDCl$_3$) of 3jg
$^1$H-NMR (600 MHz, CDCl$_3$) of 4a

$^{13}$C-NMR (150 MHz, CDCl$_3$) of 4a
9. References


