Supporting Information

2,3-Disubstituted Benzofuran and Indole by Copper-Mediated C-C Bond Extension Reaction of 3-Zinciobenzoheterole

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Table of Contents

1. General .................................................. S3

2. Preparation of Starting Materials .......... S5

3. Typical Procedure for Cyclization of 2-Alkynylphenols and Anilines in the Presence of Butyllithium and Zinc Chloride .......... S7

4. Typical Procedure for Cu(I)-Mediated Coupling of Benzofuranylzinc and Indolylzinc with Electrophiles .......... S11

5. NMR Charts ............................................. S12
1. General. All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under a positive pressure of argon or nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via syringe or teflon cannula. Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25-mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light (UV) and/or by immersion in an acidic staining solution of p-anisaldehyde followed by heating on a hot plate. Organic solutions were concentrated by rotary evaporation at ca. 15 Torr (evacuated with a diaphragm pump). Flash column chromatography was performed as described by Still et al.,\(^1\) employing Kanto Silica gel 60 (spherical, neutral, 140–325 mesh).

Materials. Commercial reagents were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used either distilled or recrystallized before use. Zinc chloride (anhydrous, beads, -10 mesh, 99.99 %) was purchased from Aldrich and was flame-dried just before use. Butyllithium solution in hexane was purchased from Aldrich, passed over a pad of Celite under nitrogen to remove insoluble materials and the concentration was determined by titration with menthol in the presence of 2,2'-bipyridyl. Lithium chloride was dried at 120 °C, ~ 0.5 Torr for at least 2 h before use. Anhydrous tetrahydrofuran (THF), diethyl ether and toluene were purchased from Kanto Chemical Co. and purified by successive passing over a molecular sieves column, then over an alumina column. Triethylamine and chlorotrimethylsilane were distilled from calcium hydride at 760 Torr under an argon atmosphere and were subsequently stored over 4-Å molecular sieves in a storage flask. The water content of the solvent was confirmed with a Karl-Fischer moisture titrator to be less than 20 ppm. The following starting materials were prepared as described in the literature: 2-phenylethynylphenol 1a,\(^2\) 2-(1-hexynyl)phenol 1b,\(^2\) 2-(3,3-dimethyl-1-butynyl)phenol 1c,\(^2\) 2-ethynylphenol, 1d\(^2\) 2-((E)-4-phenylbut-3-en-1-ynyl)phenol 1e,\(^4\) 2-thiophenylethynylphenol 1f,\(^4\) 2-(3-methoxymethoxyprop-1-ynyl)phenol 1g,\(^4\) N-benzyl-2-phenylethynylaniline 1h,\(^4\) N-

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benzyl-2-iodoaniline,\textsuperscript{5} \textit{N}-benzyl-2-ethynylaniline \textbf{1k},\textsuperscript{6} (\textit{E})-2-(4-phenylbut-3-en-1-ynyl)aniline,\textsuperscript{7} 3-iodo-2-cyclohexen-1-one.\textsuperscript{8}

**Instrumentation.** Melting points are uncorrected. Proton nuclear magnetic resonance (\textsuperscript{1}H NMR) and carbon nuclear magnetic resonance (\textsuperscript{13}C NMR) spectra were recorded with JEOL ECA-500 (500 MHz) NMR spectrometer. Chemical data for protons are reported in parts per million (ppm, \(\delta\) scale) downfield from tetramethylsilane and are referenced to residual proton in the NMR solvent (CDCl\(_3\); \(\delta\) 7.26). Carbon nuclear magnetic resonance spectra (\textsuperscript{13}C NMR) were recorded at 125 MHz: chemical data for carbons are reported in parts per million (ppm, \(\delta\) scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent (CDCl\(_3\); \(\delta = 77.0\)). The data is presented as follows: chemical shift, multiplicity (\(s =\) singlet, \(d =\) doublet, \(t =\) triplet, \(q =\) quartet, \(q =\) quintet, \(s =\) sextet, \(m =\) multiplet and/or multiplet resonances, \(br =\) broad), coupling constant in Hertz (Hz), and integration. Gas chromatographic (GC) analyses were performed on Shimadzu GC-14B instruments equipped with an FID detector and a capillary column, HR-1 (25 m \times 0.25 mm i.d., 0.25 \(\mu\)m film). IR spectra recorded on a React IR 1000 Reaction Analysis System equipped with DuraSample IR (ASI Applied System) are reported in cm\(^{-1}\). High resolution mass spectra (HRMS) are taken at JEOL Accu TOF JMS-T100LC.

### 2. Preparation of Starting Materials

![Reaction Scheme](image)

\textit{N}-\textit{Benzyl}-2-(1-hexynyl)aniline \textit{li}: To a mixture of \textit{N}-benzyl-2-iodoaniline (2.98 g, 9.6 mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (133 mg, 0.19 mmol), CuI (72 mg, 0.38 mmol) and Et\(_3\)N (2.00 mL, 14.4 mmol) in THF (13.0 mL) was slowly added phenylacetylene (1.30 mL, 14.4 mmol). The dark brown mixture was stirred at ambient temperature for 12 hours. Standard aqueous work-up gave a dark brown oil, which we purified by flash column


chromatography on silica gel (hexane–ethyl acetate) to yield the title compound (2.51 g, 100%) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.89 (t, $J = 7.5$ Hz, 3H), 1.43 (sext, $J = 7.5$ Hz, 2H), 1.55 (quint, $J = 7.5$ Hz, 2H), 2.45 (t, $J = 7.5$ Hz, 2H), 4.41 (d, $J = 5.0$ Hz, 2H), 5.00 (br, 1H), 6.54 (d, $J = 8.0$ Hz, 1H), 6.61 (dt, $J_1 = 7.5$ Hz, $J_2 = 1.0$ Hz, 1H), 7.10 (dt, $J_1 = 8.0$ Hz, $J_2 = 1.0$ Hz, 1H), 7.26–7.38 (m, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 13.6, 19.3, 22.0, 30.9, 47.8, 96.3, 108.6, 109.6, 116.4, 120.7, 127.1, 127.2 (2C), 128.6 (2C), 129.0, 131.9, 139.2, 148.6. FTIR (neat) cm$^{-1}$: 3402 (w), 3031 (w), 2956 (m), 2929 (m), 2860 (m), 1600 (m), 1574 (m), 1507 (s), 1453 (s), 1322 (s), 743 (s), 729 (s), 695 (s). HRMS (APCI+) Calcd. for $^{12}$C$_{19}$H$_{21}$N (M+1): 264.1644; Found: 264.1732.

$N$-Benzyl-2-(3,3-dimethylbut-1-ynyl)aniline $I$: The title compound was obtained in 98% yield as a yellow solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.28 (s, 9H), 4.40 (d, $J = 5.5$ Hz, 2H), 4.95 (br, 1H). 6.55 (d, $J = 8.0$ Hz, 1H), 6.61 (dt, $J_1 = 7.5$ Hz, $J_2 = 1.0$ Hz, 1H), 7.11 (dt, $J_1 = 8.0$ Hz, $J_2 = 1.0$ Hz, 1H), 7.24–7.39 (m, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 28.3, 31.2, 47.8, 75.4, 104.8, 108.4, 109.6, 116.4, 127.1 (2C), 127.2, 128.6 (2C), 129.0, 131.6, 139.2, 148.5. FTIR (neat) cm$^{-1}$: 3415 (m), 2968 (m), 1600 (m), 1574 (m), 1511 (s), 1449 (m), 1434 (m), 1362 (m), 1326 (s), 1285 (s), 1266 (s), 745 (s), 697 (s). HRMS (APCI+) Calcd. for $^{12}$C$_{19}$H$_{21}$N (M): 263.1674; Found: 263.1733.

(E)-$N$-Benzyl-2-(4-phenylbut-3-en-1-ynyl)aniline $II$: A solution of (E)-2-(4-phenylbut-3-en-1-ynyl)aniline (1.58 g, 7.2 mmol) in THF (25 mL) was cooled to 0 °C and a solution of butyllithium in hexane (4.7 mL, 1.55 mol/L, 7.2 mmol) was added slowly. The deep red solution was warmed to room temperature, stirred for 1 h, then benzyl bromide (0.86 mL, 7.2 mmol) was slowly added. The resulted mixture was stirred at ambient room temperature for 17 h. After quenching with methanol, standard aqueous work-up gave a dark brown oil, which we purified by flash column chromatography on silica gel (hexane–ethyl acetate) to yield the title compound (1.92 g, 86%) as a yellow viscous oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.46 (d, $J = 5.5$ Hz, 2H), 5.10 (br, 1H), 6.42 (d, $J = 16.0$ Hz, 1H), 6.56 (d, $J = 8.0$ Hz, 1H), 6.65 (t, $J = 7.5$ Hz,
1H), 6.97 (d, J = 16.0 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.26–7.41 (m, 11H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 47.6, 88.4, 94.8, 107.8, 108.1, 109.9, 116.6, 126.2 (4C), 127.1, 127.2, 128.5, 128.6 (2C), 128.7 (2C), 129.9, 132.1, 136.3, 139.1, 140.6, 148.6. FTIR (neat) cm$^{-1}$: 3415 (w), 3018 (w), 1501 (m), 1324 (m), 1160 (w), 945 (m), 737 (s), 687 (s). HRMS (APCI+) Calcd. for $^{13}$C$_{23}$H$_{19}$N (M): 309.1517; Found: 309.1457.


![Diagram of reaction](image)

2-Phenylbenzofuran 4a. To a solution of 2-phenylethylnaphthalen 1a (195.0 mg, 1.0 mmol) in diethylether (0.5 mL) was added a solution of butyllithium in hexane (0.67 mL, 1.57 mol/L, 1.0 mmol) at 0 °C. The resulted yellow solution was allowed to warm to ambient temperature and stirred for 30 min. A solution of zinc chloride in THF (1.0 mL, 1.0 mol/L, 1.0 mmol) was then added, the volatiles were removed in vacuo, and toluene (2.0 mL) was added. The yellow solution was heated to 120 °C and stirred for 1 h at that temperature. After cooling to ambient temperature, the reaction mixture was quenched with aqueous ammonium chloride. After standard aqueous work-up, the crude material was purified by flash column chromatography on silica gel (100% hexanes) to afford the title compound as white shiny crystals (194.5 mg, 100%). Analytical data were in good accordance with those reported in the literature.$^9$

![Diagram of reaction](image)

2-Butylbenzofuran 4b: The title compound was obtained in 98% yield as a colorless oil. Analytical data were in good accordance with those reported in the literature.$^{10}$

![Diagram of reaction](image)

2-(1,1-Dimethylpropyl)benzofuran 4c: The title compound was obtained in 98% yield

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as a colorless oil. Analytical data were in good accordance with those reported in the literature.\textsuperscript{10}

![Image of 2-(E)-Styrylbenzofuran](image)

**2-(E)-Styrylbenzofuran 4e:** The title compound was obtained in 100% yield as white flakes. Analytical data were in good accordance with those reported in the literature.\textsuperscript{11}

![Image of 2-(2-Thienyl)benzofuran](image)

**2-(2-Thienyl)benzofuran 4f:** The title compound was obtained in 96% yield as white needles. Analytical data were in good accordance with those reported in the literature.\textsuperscript{9}

![Image of 2-Hydroxymethylbenzofuran, methoxymethyl ether](image)

**2-Hydroxymethylbenzofuran, methoxymethyl ether 4g:** The title compound was obtained in 86% yield as a pale yellow oil. Analytical data were in good accordance with those reported in the literature.\textsuperscript{4}

![Image of 1-Benzyl-2-phenylindole](image)

**1-Benzyl-2-phenylindole 4h:** The title compound was obtained in 100% yield as a pale yellow solid. Analytical data were in good accordance with those reported in the literature.\textsuperscript{12}

![Image of 1-Benzyl-2-butylindole](image)

**1-Benzyl-2-butylindole 4i:** The title compound was obtained in 97% yield as a colorless oil. \textsuperscript{13}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 0.90 (t, \(J = 7.5\) Hz, 3H), 1.40 (sext, \(J = 7.5\) Hz, 2H), 1.67 (quint, \(J = 7.5\) Hz, 2H), 2.66 (t, \(J = 7.5\) Hz, 2H), 5.32 (s, 2H), 6.34 (s, 1H), 6.95 (d, \(J = 8.0\) Hz, 2H), 7.06–7.09 (m, 2H), 7.17–7.27 (m, 4H), 7.56–7.58 (m, 2H), 7.61–7.64 (m, 2H).

\textsuperscript{12} Lane, B. S.; Sames, D. Org. Lett. 2004, 6, 2897–2900.
\textsuperscript{13} Fujiwara, J.; Fukutani, Y.; Sano, H.; Maruoka, K.; Yamamoto, H. J. Am. Chem. Soc. 1983, 105, 7177–7179. Analytical data were not reported.
1H. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 13.9, 22.4, 26.4, 30.5, 46.3, 99.3, 109.2, 119.4, 119.7, 120.7, 125.9 (2C), 127.2, 128.1, 128.7 (2C), 137.1, 138.0, 141.4. FTIR (neat) cm$^{-1}$: 3051 (w), 2954 (m), 2869 (w), 1546 (s), 1465 (s), 1453 (s), 1403 (m), 1351 (s), 1310 (s), 1246 (m), 1013 (m), 770 (s), 743 (s), 700 (s). HRMS (APCI+) Calcd. for $^{12}$C$_{16}$H$_{21}$N (M+1): 264.1644; Found: 264.1660.

1-Benzyl-2-tert-butylindole 4j: The title compound was obtained in 98% yield as a pale yellow oil. Analytical data were in good accordance with those reported in the literature.$^{14}$

1-Benzylindole 4k: The title compound was obtained in 99% yield as a pale yellow oil. Analytical data were in good accordance with those reported in the literature.$^{15}$

(E)-1-Benzyl-2-styrylindole 4l: The title compound was obtained in 48% yield as a yellow solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.45 (s, 2H), 6.89 (s, 1H), 7.04–7.34 (m, 13H), 7.41 (d, $J = 7.5$ Hz, 2H), 7.63 (t, $J = 7.5$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): 46.8, 99.6, 109.5, 116.9, 120.2, 120.5, 122.0, 126.0 (2C), 126.4 (2C), 127.4, 127.8, 128.2, 128.7 (2C), 128.8 (2C), 131.2, 137.0, 137.8, 137.9, 138.3. FTIR (neat) cm$^{-1}$: 3025 (w), 2925 (w), 1603 (w), 1493 (m), 1453 (s), 1405 (m), 1347 (s), 1320 (m), 955 (m), 787 (m), 751 (s), 725 (s), 691 (s). HRMS (APCI+) Calcd. for $^{12}$C$_{23}$H$_{19}$N (M+1): 310.1488; Found: 310.1499.

4. Typical Procedure for Cu(I)-Mediated Coupling of Benzofuranylzinc and Indolylzinc with Electrophiles.


3-Allyl-2-phenylbenzofuran 5: To a solution of 2-phenylethynylphenol 1a (194.0 mg, 1.0 mmol) in diethylether (0.5 mL) was added a solution of butyllithium in hexane (0.67 mL, 1.57 mol/L, 1.0 mmol) at 0 °C. The resulted yellow solution was heated to ambient temperature and stirred for 30 min. A solution of zinc chloride in THF (1.0 mL, 1.0 mol/L, 1.0 mmol) was then added, the volatiles were removed in vacuo, and toluene (1.0 mL) was added. The yellow solution was heated to 120 °C and stirred for 1 h at that temperature. The yellow mixture was cooled to −78 °C and a THF solution of CuCN·2LiCl (1.0 mol/L, 1.0 mL, 1.0 mmol), then allyl bromide (0.10 mL, 1.2 mmol) were successively added. When required (Table 2), trimethylsilyl chloride (0.30 mL, 2.4 mmol) or BF₃·OEt₂ (0.30 mL, 2.4 mmol) was added prior to the electrophile. The resulting mixture was gradually warmed to 0 °C and stirred for 12 h at that temperature (or to the temperature in Table 2). The resulting mixture was quenched with saturated ammonium chloride, and standard aqueous work-up afforded the crude material, which we purified by flash column chromatography on silica gel (100% pentane) to give 4 as a colorless oil (228.4 mg, 97%). Analytical data were in good accordance with those reported in the literature.₁⁶

3-Allyl-2-butylbenzofuran 6: The title compound was obtained in 81% yield as a colorless oil.¹ H NMR (500 MHz, CDCl₃): δ 0.93 (t, J = 7.5 Hz, 3H), 1.37 (sext, J = 7.5 Hz, 2H), 1.69 (qvint, J = 7.5 Hz, 2H), 2.72 (t, J = 7.5 Hz, 2H), 3.37 (d, J = 6.0 Hz, 2H), 5.04–5.12 (m, 2H), 5.91–6.00 (m, 1H), 7.15–7.21 (m, 2H), 7.37–7.44 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): 13.8, 22.3, 26.0, 27.9, 30.4, 110.6, 111.6, 115.5, 119.1, 121.9, 123.0, 129.6, 135.9, 153.9, 155.1. FTIR (neat) cm⁻¹: 3081 (w), 2958 (m), 2931 (m), 2873 (w), 1640 (w), 1455 (s), 1254 (m), 1171 (m), 915 (m), 741 (s). Anal. Calcd. for

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C_{14}H_{16}O: C, 83.96; H, 8.05. Found: C, 83.81; H, 8.30.

3-Allyl-1-benzyl-2-phenylindole 7: The title compound was obtained in 97% yield as a yellow solid. M.p.: 93–4 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ 3.46 (d, $J = 6.0$ Hz, 2H), 5.00–5.07 (m, 2H), 5.23 (s, 2H), 6.00–6.07 (m, 1H), 6.94 (d, $J = 7.0$ Hz, 2H), 7.11–7.23 (m, 7H), 7.31–7.33 (m, 2H), 7.35–7.39 (m, 2H), 7.65 (d, $J = 6.5$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 29.2, 47.6, 110.3, 111.1, 114.6, 119.3, 119.5, 121.9, 126.0 (2C), 127.0, 128.11 (2C), 128.14, 128.3, 128.5 (2C), 130.4 (2C), 131.7, 136.9, 137.9, 138.3, 138.4. FTIR (neat) cm$^{-1}$: 3060 (w), 2873 (w), 1640 (w), 1605 (w), 1465 (m), 1343 (m), 1194 (w), 915 (s), 745 (s), 729 (s), 700 (s). Anal. Calcd. for C$_{28}$H$_{21}$N: C, 89.12; H, 6.54; N, 4.33; Found: C, 89.01; H, 6.68; N, 4.16.

3-Cinnamyl-2-phenylbenzofuran 8: The title compound was obtained in 98% yield as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 3.83 (d, $J = 3.5$ Hz, 2H), 6.49–6.51 (m, 2H), 7.18–7.59 (m, 12 H), 7.80 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 27.69, 111.07, 113.12, 119.78, 122.54, 124.40, 126.13, 126.96 (2C), 127.12 (2C), 127.18, 128.47 (2C), 128.63 (2C), 128.70, 130.35, 130.86, 131.03, 137.20, 151.67, 154.01. FTIR (neat) cm$^{-1}$: 3058 (w), 3024 (w), 1598 (w), 1455 (m), 1260 (m), 1061 (m), 965 (m), 743 (s), 691 (s). HRMS (APCI+) Calcd. for $^{12}$C$_{25}$H$_{18}$O (M): 310.1357; Found: 310.1376.

3-Benzoyl-2-phenylbenzo[b]furan 9: The title compound was obtained in 91% yield as a white solid. M.p.: 95–6 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.25–7.39 (m, 7H), 7.48 (t,
$J = 7.3$ Hz, 1H), 7.55–7.60 (m, 2H), 7.67–7.69 (m, 2H), 7.84 (d, $J = 7.3$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 111.2, 116.1, 121.5, 123.8, 125.3, 128.4 (6C), 129.4, 129.7, 129.8 (4C), 133.1, 137.7, 153.8, 157.7, 192.3. FTIR (neat) cm$^{-1}$: 1650 (m), 1449 (m), 1356 (m), 1243 (m), 884 (m), 756 (s), 697 (s). Anal. Calcd. for C$_{21}$H$_{14}$O$_2$: C, 84.54; H, 4.73. Found: C, 84.47; H, 4.81.

![Diagram](image)

3-Benzoyl-1-benzyl-2-phenylindole $^{10}$: The title compound was obtained in 72% yield as a white solid. M.p.: 147–8 $^\circ$C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.31 (s, 2H), 6.99 (d, $J = 7.0$ Hz, 2H), 7.11–7.29 (m, 14H), 7.56 (d, $J = 7.5$ Hz, 2H), 8.03–8.05 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 47.9, 110.8, 115.2, 121.9, 122.4, 123.4, 126.0 (2C), 127.5, 127.6 (2C), 127.9, 128.0 (2C), 128.8 (2C), 129.3 (2C), 130.6, 130.8 (2C), 131.0, 136.8, 136.9, 140.0, 146.4, 193.0. FTIR (neat) cm$^{-1}$: 3062 (w), 1623 (s), 1405 (s), 1183 (m), 1044 (m), 884 (s), 749 (s), 737 (s), 697 (s). Anal. Calcd. for C$_{28}$H$_{21}$NO: C, 86.79; H, 5.46; N, 3.47. Found: C, 86.77; H, 5.45; N, 3.47.

![Diagram](image)

Phenyl(2-phenylbenzofuran-3-yl)methanol $^{11}$: The title compound was obtained in 68% yield as a very viscous, colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.33 (d, $J = 3.5$ Hz, 1H), 7.09 (t, $J = 8.0$ Hz, 1H), 7.23–7.51 (m, 11H), 7.75 (d, $J = 7.5$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 68.6, 111.2, 117.5, 121.8, 122.7, 124.5, 126.3 (2C), 127.5, 127.7, 127.8 (2C), 128.5 (2C), 128.8 (2C), 129.0, 130.2, 141.9, 152.8, 154.4. FTIR (neat) cm$^{-1}$: 3350 (br), 3058 (w), 1588 (w), 1492 (m), 1453 (s), 1254 (w), 1123 (w), 1063 (m), 1007 (m), 897 (m), 743 (s), 693 (s). HRMS (APCI–) Calcd. for $^{12}$C$_{21}$H$_{15}$O$_2$ (M-1): 299.1072; Found: 299.1110.

S11
Phenyl-bis(2-phenylbenzofuran-3-yl)methane 12: 1.0 Equiv. of benzaldehyde was used. The title compound was obtained in 76% yield as a white solid. M.p.: 176–7 °C. 

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 6.17 (s, 1H), 6.88 (d, \(J = 8.0\) Hz, 2H), 6.96 (t, \(J = 8.0\) Hz, 2H), 7.20–7.27 (m, 8H), 7.31–7.33 (m, 5H), 7.50–7.53 (m, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 39.00, 111.18 (2C), 116.88 (2C), 121.93 (2C), 122.55 (2C), 124.13 (2C), 127.03 (2C), 127.43 (4C), 128.46 (4C), 128.73 (2C), 128.95 (2C), 129.49 (2C), 130.43 (2C), 130.44 (2C), 140.32, 141.68, 152.59 (2C), 154.21 (2C). FTIR (neat) cm\(^{-1}\): 1598 (w), 1484 (m), 1252 (w), 1071 (w), 828 (w), 752 (s), 700 (s). Anal. Calcd. for C\(_{35}\)H\(_{24}\)O\(_2\): C, 88.21; H, 5.08. Found: C, 87.98; H, 5.18.

3-(2-Phenylbenzofuran-3-yl)cyclohexanone 13: The title compound was obtained in 77% yield as a colorless solid. M.p.: 116–7 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.75–1.82 (m, 1H), 2.08 (d, \(J = 14.0\) Hz, 1H), 2.20–2.25 (m, 1H), 2.36–2.54 (m, 3H), 2.63 (d, \(J = 14.0\) Hz, 1H), 3.07 (t, \(J = 14.0\) Hz, 1H), 3.48–3.54 (m, 1H), 7.25–7.54 (m, 7H), 7.61 (d, \(J = 8.0\) Hz, 1H), 7.76 (d, \(J = 8.0\) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 25.71, 30.83, 36.47, 41.33, 47.08, 111.74, 117.58, 120.63, 122.35, 124.29, 127.90, 128.00 (2C), 128.77 (2C), 128.83, 130.61, 151.14, 154.49, 210.40. FTIR (neat) cm\(^{-1}\): 2917 (w), 2856 (w), 1704 (s), 1455 (m), 1248 (m), 1061 (m), 766 (m), 743 (s), 695 (s). Anal. Calcd. for C\(_{20}\)H\(_{18}\)O\(_2\): C, 82.73; H, 6.25. Found: C, 82.70; H, 6.38.

3-(2-Butylbenzofuran-3-yl)cyclohexanone 14: The title compound was obtained in
74% yield as a colorless oil. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 0.93 (t, J = 7.5 Hz, 3H), 1.35 (sext, J = 7.5 Hz, 2H), 1.67 (quint, J = 7.5 Hz, 2H), 1.76–1.82 (m, 1H), 1.98 (d, br, J = 14.0 Hz, 1H), 2.18–2.30 (m, 2H), 2.42–2.52 (m, 3H), 2.71 (t, J = 7.5 Hz, 2H), 2.92 (t, J = 14.0 Hz, 3H), 3.10–3.16 (m, 1H), 7.16–7.24 (m, 2H), 7.41 (d, J = 7.0 Hz, 1H), 7.60 (d, J = 7.0 Hz, 1H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ 13.7, 22.2, 25.8, 26.2, 30.6, 30.9, 36.4, 41.2, 46.1, 111.1, 116.1, 119.5, 121.9, 123.0, 127.6, 154.0, 154.1, 210.5.

FTIR (neat) cm\textsuperscript{-1}: 2950 (m), 2863 (w), 1710 (s), 1455 (s), 1256 (m), 1219 (w), 1178 (w), 970 (w), 909 (m), 730 (s).

HRMS (APCI+) Calcd. for C\textsubscript{12}H\textsubscript{18}O\textsubscript{2} (M): 270.1620; Found: 270.1657.

3-(1-Benzyl-2-phenylnindol-3-yl)cyclohexanone 15: The title compound was obtained in 65% yield as a white solid. M.p.: 185–6 °C. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 1.60–1.68 (m, 1H), 2.03 (br d, J = 13.0 Hz, 1H), 2.10–2.15 (m, 1H), 2.30–2.43 (m, 3H), 2.52–2.55 (m, 1H), 3.01 (t, J = 13.0 Hz, 1H), 3.10–3.16 (m, 1H), 5.14 (s, 2H), 6.90 (d, J = 6.5 Hz, 2H), 7.13–7.24 (m, 8H), 7.36–7.39 (m, 3H), 7.81–7.83 (m, 1H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ 25.8, 32.0, 37.4, 41.3, 47.4, 48.4, 99.9, 110.7, 115.7, 119.4, 119.7, 121.8 (2C), 126.0 (2C), 126.1, 127.1 (2C), 128.4, 128.5 (2C), 130.6, 131.6, 136.9, 137.6, 138.0, 211.5. FTIR (neat) cm\textsuperscript{-1}: 3049 (w), 2944 (w), 1702 (s), 1605 (w), 1465 (w), 1356 (m), 1223 (m), 1027 (m), 749 (s), 735 (s), 700 (s). Anal. Calcd. for C\textsubscript{27}H\textsubscript{25}NO: C, 85.45; H, 6.64; N, 3.69: Found: C, 85.25; H, 6.80; N, 3.48.

2-(1-(2-Phenylbenzofuran-3-yl)ethyl)malonic acid diethyl ester 16: The title compound was obtained in 95% yield as a colorless viscous oil which solidifies upon standing. M.p.: 77–8 °C. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 0.72 (t, J = 7.0 Hz, 3H), 1.31 (t, J = 7.0 Hz, 3H), 1.49 (d, J = 7.0 Hz, 3H), 3.70–3.76 (m, 1H), 3.82–3.89 (m, 1H), 4.09
(d, J = 11.5 Hz, 1H), 4.17–4.29 (m, 3H), 7.23–7.30 (m, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.48–7.52 (m, 3H), 7.69 (d, J = 7.0 Hz, 1H), 7.82 (t, J = 7.5 Hz, 2H). 13C NMR (125 MHz, CDCl3): δ 13.3, 14.1, 19.0, 31.1, 57.1, 61.1, 61.6, 111.4, 116.5, 120.9, 122.3, 124.2, 128.0 (2C), 128.6, 128.7 (2C), 130.8, 151.7, 154.2, 167.9, 168.3. FTIR (neat) cm⁻¹: 2981 (w), 1720 (s), 1455 (m), 1368 (m), 1177 (s), 1025 (s), 858 (m), 745 (s), 690 (s). Anal. Calcd. for C23H24O5: C, 72.61; H, 6.36. Found: C, 72.47; H, 6.46.

2-(1-(2-Butylbenzofuran-3-yl)ethyl)malonic acid diethyl ester 17: The title compound was obtained in 83% yield as a colorless oil. 1H NMR (500 MHz, CDCl3): δ 0.83 (t, J = 7.0 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H), 1.32 (t, J = 7.5 Hz, 3H), 1.38–1.44 (m, 5H), 1.68 (quint, J = 7.5 Hz, 2H), 2.71–2.75 (m, 1H), 2.81–2.86 (m, 1H), 3.69–3.75 (m, 1H), 3.81–3.92 (m, 3H), 4.27 (q, J = 7.5 Hz, 2H), 7.17–7.20 (m, 2H), 7.36–7.38 (m, 1H). 13C NMR (125 MHz, CDCl3): δ 13.5, 13.9, 14.1, 18.6, 22.5, 26.3, 30.4, 31.0, 57.2, 61.0, 61.6, 110.9, 114.8, 119.8, 121.9, 122.9, 127.6, 154.0, 155.4, 168.0, 168.5. FTIR (neat) cm⁻¹: 2962 (m), 2875 (w), 1731 (s), 1455 (m), 1368 (w), 1268 (m), 1177 (s), 1017 (s), 859 (w), 745 (s). HRMS (APCI–) Calcd. for 12C21H28O5 (M): 360.1937; Found: 360.1978.

3-(2-Phenylbenzofuran-3-yl)cyclohex-2-en-1-one 18: The title compound was obtained in 90% yield as a pale yellow solid. M.p.: 120–2 oC. 1H NMR (500 MHz, CDCl3): δ 2.14 (quint, J = 6.9 Hz, 2H), 2.57 (t, J = 6.9 Hz, 4H), 6.44 (s, 1H), 7.30 (t, J = 7.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.43–7.49 (m, 3H), 7.54 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 7.0 Hz, 2H). 13C NMR (125 MHz, CDCl3): δ 23.2, 29.7, 37.5, 111.4, 116.4, 119.9, 123.4, 125.1, 127.7 (2C), 128.0, 128.8 (2C), 129.4, 129.8, 130.3, 152.5, 154.2, 155.0, 199.2. FTIR (neat) cm⁻¹: 2954 (w), 1661 (s), 1613 (m), 1453
(w), 1189 (m), 972 (w), 773 (w), 750 (s), 700 (s). Anal. Calcd. for C$_{20}$H$_{16}$O$_2$: C, 83.31; H, 5.59. Found: C, 83.26; H, 5.72.
Figure S1. $^{13}$C NMR Spectrum of 4a.
Figure S2. $^1$H NMR Spectrum of 4b.
Figure S3. $^{13}$C NMR Spectrum of 4c.
Figure S4. $^{13}$C NMR Spectrum of 4e.
Figure S5. $^{13}$C NMR Spectrum of 4f.
Figure S6. $^{13}$C NMR Spectrum of 4g.
Figure S7. $^{13}$C NMR Spectrum of 4h.
Figure S8. $^1$H NMR Spectrum of 4i.
Figure S9. $^{13}$C NMR Spectrum of 4j.
Figure S10. $^{13}$C NMR Spectrum of 4k.
Figure S11. $^1$H NMR Spectrum of 4l.
Figure S12. $^{13}$C NMR Spectrum of 4l.
Figure S13. $^{13}$C NMR Spectrum of 5.
Figure S14. $^1$H NMR Spectrum of 6.
Figure S15. $^{13}$C NMR Spectrum of 6.
Figure S16. $^1$H NMR Spectrum of 7.
Figure S17. $^{13}$C NMR Spectrum of 7.
Figure S18. $^1$H NMR Spectrum of 8.
Figure S19. $^{13}$C NMR Spectrum of 8.
Figure S20. $^1$H NMR Spectrum of 9.
Figure S21. $^{13}$C NMR Spectrum of 9.
Figure S22. $^1$H NMR Spectrum of 10.
Figure S23. $^{13}$C NMR Spectrum of 10.
Figure S24. $^1$H NMR Spectrum of 11.
Figure S25. $^{13}$C NMR Spectrum of 11.
Figure S26. $^1$H NMR Spectrum of 12.
Figure S27. $^{13}$C NMR Spectrum of 12.
Figure S28. $^1$H NMR Spectrum of 13.
Figure S29. $^{13}$C NMR Spectrum of 13.
Figure S30. $^1$H NMR Spectrum of 14.
**Figure S31.** $^{13}$C NMR Spectrum of 14.
Figure S32. $^1$H NMR Spectrum of 15.
Figure S33. $^{13}$C NMR Spectrum of 15.
Figure S34. $^1$H NMR Spectrum of 16.
Figure S35. $^{13}$C NMR Spectrum of 16.
Figure S36. $^1$H NMR Spectrum of 17.
Figure S37. $^{13}$C NMR Spectrum of 17.
Figure S38. $^1\text{H}$ NMR Spectrum of 18.
Figure S39. $^{13}$C NMR Spectrum of 18.