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Supporting Information

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3-Zinciobenzofuran and Indole: Versatile Tools for Construction of Conjugated Structures Containing Multiple Benzoheterole Units**

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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 stainless steel 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. Anhydrous tetrahydrofuran (THF) and diethylether were purchased from Kanto Chemical Co. and distilled from sodium / benzophenone ketyl at 760 Torr under an argon atmosphere immediately before use. TMEDA and toluene were distilled from calcium hydride at 760 Torr under an argon atmosphere immediately before use. Triethylamine was distilled from calcium hydride at 760 Torr under an argon atmosphere and was 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,[2] 2-(1-hexynyl)phenol,[2]

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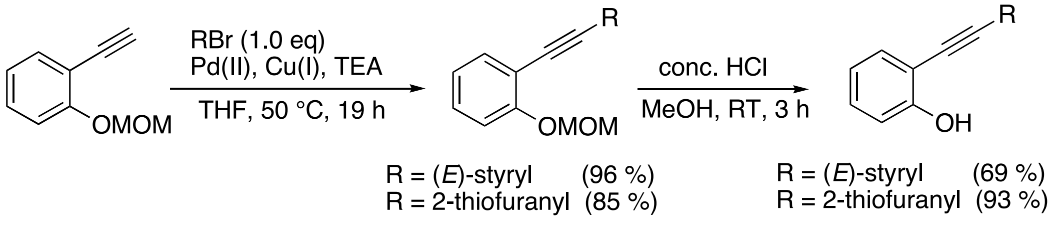
[1] W. C. Still, M. Klahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2924.

[2] E. Yoneda, T. Sugioka, K. Hirao, S. W. Zhang, S. Takahashi, *J. Chem. Soc., Perk. Trans. 1* **1998**, *3,* 477–485..

2-(3,3-dimethyl-1-butynyl)phenol,[2] 2-iodophenoxytrimethylsilane,[3] ethynyl-2-methoxymethoxybenzene,[4] 2-phenylethynylaniline,[5] 2-bromo-5-iodothiophene.[6]

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{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, δ scale) downfield from tetramethylsilane and are referenced to residual proton in the NMR solvent ($CDCl_3$: δ 7.26). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 125 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent ($CDCl_3$: δ = 77.0). The data is presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = 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 × 0.25 mm i.d., 0.25 μm 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.

1. Preparation of Starting Materials.



2-((*E*)-4-Phenylbut-3-en-1-ynyl)phenol: To a mixture of

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[3] F. D. King, D. R. M. Walton, *Synthesis* **1976**, 40–42.

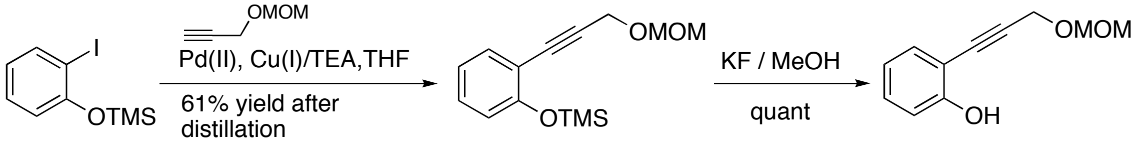
[4] K. Y. Tsang, M. A. Brimble, J. B. Bremner, *Org. Lett.* **2003**, *5*, 4425–4427.

[5] P. D. Woodgate, H. S. Sutherland, *J. Organomet. Chem.* **2001**, *629*, 131–144.

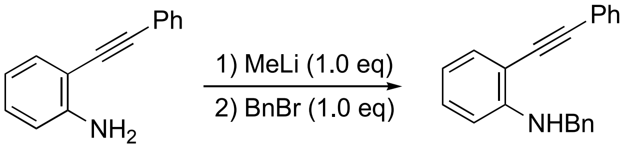
[6] B. T. Holmes, W. T. Pennington, T. W. Hanks, *Molecules* **2002**, *7*, 447–455.

ethynyl-2-methoxymethoxybenzene (1.128 g, 6.95 mmol), $Pd(PPh_3)_2Cl_2$ (98 mg, 0.14 mmol), CuI (53 mg, 0.28 mmol) and Et_3N (1.45 mL, 10.42 mmol) in THF (10.0 mL) was slowly added (*E*)-styryl bromide (0.75 mL, 6.95 mmol) and the dark solution was stirred at 50 °C for 19 h. After cooling to room temperature, the crude mixture was passed over a Celite pad with ether. The volatile material was removed *in vacuo* and the resulted dark brown oil was chromatographed over silica gel (hexane–ethyl acetate) to afford 1.76 g (96%) of 1-methoxymethoxy-2-(*E*)-4-phenylbut-3-en-1-ynyl)benzene as a pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 3.54 (s, 3H), 5.28 (s, 2H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 16.0 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.24–7.29 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.42–7.46 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.3, 88.1, 92.8, 95.0, 108.4, 114.0, 115.2, 121.9, 126.3 (2C), 128.5, 128.7 (2C), 129.6, 133.4, 136.4, 141.0, 157.6. This MOM ether (0.89 g, 3.37 mmol) was dissolved in methanol (7.0 mL), and then hydrochloric acid (36%, 0.70 mL) was slowly added. The resulted mixture was stirred at room temperature for 2 hours. The acid was neutralized with saturated $NaHCO_3$, and the organic material was extracted with diethyl ether (three times). The collected organic layers were washed (brine) and dried (Na_2SO_4). After removal of volatile material *in vacuo*, the crude oil was chromatographed on silica gel (hexanes–ethyl acetate) to obtain 0.51 g (69%) of the title compound, as yellow needles. ^1H NMR (500 MHz, $CDCl_3$): δ 5.79 (s, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 16.0 Hz, 1H), 7.25–7.38 (m, 5H), 7.44 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 85.2, 95.8, 107.2, 109.8, 114.7, 120.4, 126.4 (2C), 128.8 (2C), 128.9, 130.4, 131.6, 135.9, 141.9, 156.4. FTIR (neat) cm^{-1} : 3296 (br), 3057 (w), 3038 (w), 2964 (w), 1258 (m), 946 (s), 803 (m), 741 (s), 687 (s).

2-Thiophenylethynylphenol. 2-(2-Methoxymethoxyphenylethynyl)thiophene was obtained upon a similar Sonogashira cross-coupling protocol as a yellow oil in 85% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 3.55 (s, 3H), 5.28 (s, 2H), 6.99–7.01 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.27–7.29 (m, 3H), 7.48 (dd, J_1 = 7.5 Hz, J_2 = 1.75 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.3, 86.3, 89.4, 95.1, 113.6, 115.4, 121.9, 123.6, 127.0, 127.1, 129.8, 131.7, 133.3, 157.6. Removal of MOM group with HCl / MeOH afforded the title compound as a white solid in 93% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 5.77 (s, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 4.5 Hz, 1H), 7.26–7.34 (m, 3H), 7.41 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 86.6, 89.3, 109.3, 114.8, 120.5, 122.2, 127.2, 128.0, 130.7, 131.7, 132.5, 156.5. FTIR (neat) cm^{-1}: 3381 (br), 3103 (w), 3073 (w), 1571 (m), 1482 (s), 1204 (s), 857 (m), 760 (s), 699 (s).



2-(3-Methoxymethoxyprop-1-ynyl)phenol. To a mixture of 2-iodophenoxytrimethylsilane (6.14 g, 21.0 mmol), $PdCl_2(PPh_3)_2$ (0.295 g, 0.42 mmol), CuI (0.160 g, 0.84 mmol) and Et_3N (4.40 mL, 31.5 mmol) in THF (30 mL) was slowly added 3-methoxymethoxyprop-1-yne (2.73 g, 27.3 mmol). The dark mixture was stirred at ambient temperature for 24 hours. Standard aqueous work-up gave a dark brown oil, which was purified by bulb to bulb distillation to yield 3.38 g (61%) of 2-(3-methoxymethoxyprop-1-ynyl)phenoxytrimethylsilane as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.29 (s, 9H), 3.41 (s, 3H), 4.47 (s, 2H), 4.79 (s, 2H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H). This oil (2.37 g, 8.9 mmol) was dissolved in methanol (200 mL), then KF (2.60 g, 44.7 mmol) was added and the mixture was stirred at ambient temperature for 5 hours. Standard aqueous work-up gave a yellow oil, which was purified by flash column chromatography on silica gel (hexane-ethyl acetate) to yield the title compound (1.75 g, quant.) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.45 (s, 3H), 4.51 (s, 2H), 4.82 (s, 2H), 6.26 (s, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.7, 55.8, 80.6, 92.0, 95.7, 108.7, 114.9, 120.1, 130.6, 131.6, 157.4. FTIR (neat) cm^{-1}: 3370 (br), 2949 (w), 2891 (w), 2223 (w), 1150 (s), 1100 (s), 1034 (s), 988 (s), 915 (s), 830 (m), 753 (s).



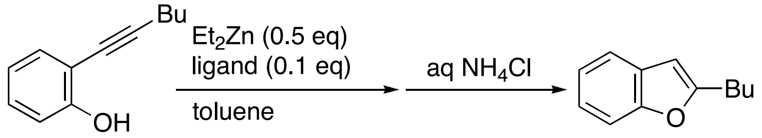
***N*-Benzyl-2-phenylethynylaniline.** A solution of 2-phenylethynylaniline (3.00 g, 15.5

mmol) in THF (30 mL) was cooled to 0 °C and a solution of methyllithium in diethylether (17.10 mL, 0.92 mol / L, 15.5 mmol) was slowly added at that temperature and the resulted red mixture was stirred at ambient temperature for one hour. A solution of benzylbromide (1.84 mL, 15.5 mmol) in THF (30 mL) was then slowly added, and the resulting mixture was stirred for 30 min at ambient temperature. Volatile material was removed *in vacuo* and the resulting brown oil was extracted with diethyl ether, washed (water, brine) and dried (magnesium sulfate). The crude material was purified by flash column chromatography on silica gel (hexane–ethyl acetate) to yield the title compound (3.17 g, 72 %) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.46 (s, 2H), 5.14 (br, 1H), 6.58 (d, J = 8.0 Hz, 1H), 6.67 (t, J = 7.5 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.32–7.40 (m, 8H), 7.47–7.49 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 47.7, 85.9, 95.2, 107.5, 109.9, 116.6, 123.2, 127.0 (2C), 127.2, 128.2, 128.3 (2C), 128.7 (2C), 130.0, 131.4 (2C), 132.1, 139.1, 148.7. FTIR (neat) cm^{-1}: 3406 (m), 3016 (w), 1570 (m), 1324 (s), 1506 (s), 1262 (s), 747 (s), 691 (s).

2. Studies on the Effect of Additives on the Product Yield for the Cyclization Reaction.

Typical Procedure for the Cyclization Reaction in *Table S1*: To a mixture of 2-(1-hexynyl)phenol (65.5 mg, 0.38 mmol) and an additive (0.04 mmol) was slowly added a solution of diethylzinc in toluene (0.19 mL, 1.0 mol/L, 0.19 mmol) at 0 °C. After ethane evolution ceased, toluene (0.60 mL) was added and the clear yellow solution was heated to 30 ~ 120 °C and stirred at that temperature for 1 ~ 10 hours. After cooling to room temperature, saturated ammonium chloride (2.0 mL) was added. After the standard work-up, consumption of the starting material and the yield of 2-butylbenzofuran were determined by GC analysis using *n*-hexadecane as an internal standard (23.0 μL, 0.10 mmol).

Table S1. Effect of Additives on the Product Yield.



1 **2**

ligand	temp. (°C)	time (h)	**2** (%)[b]	**1** (%)[b]
none	30	10	32	67
TMEDA[c]	30	10	45	54
none	80	6	48	52
Ph$_3$P	80	6	53	46
dppp[d]	80	6	84	9
Et$_3$N	80	6	42	55
TMEDA	80	6	91	8
TMEDA	120	1	99	<1

[a] The reaction conditions are described above. [b] The yield was determined by GC in the presence of *n*-hexadecane as an internal standard. [c] *N,N,N',N'*-Tetramethylethylenediamine. [d] 1,3-Bis(diphenylphosphino)propane.

3. Preparation of 2-Substituted Benzofurans and Indoles.

Scope and limitations of the cyclization reaction were studied according to the typical procedure described below and the results are summarized in Table S2.

Table S2. Cyclization of 2-Alkynylphenol or Aniline into Benzoheterole **3** (E = H).

Entry	X	R	**1**	time	yield (%) (**3**)[a]
1	O	Ph	**1a**	1 h	94 (**3a**)
2	O	*n*Bu	**1b**	1 h	99 (**3b**)
3	O	*t*Bu	**1c**	3 d	50 (**3c**)[b]
4	O	(*E*)-styryl	**1d**	1 h	99 (**3d**)
5	O	2-thienyl	**1e**	3 h	93 (**3e**)
6	O	CH$_2$OMOM[c]	**1f**	1 h	98 (**3f**)
7	NBn	Ph	**1g**	1 h	99 (**3g**)

[a] Isolated yield. [b] **1c** was recovered in 31% yield. [c] MOM = methoxymethyl.

Typical Procedure for Cyclization of 2-Alkynylphenols in the Presence of Diethylzinc.

2-Phenylbenzofuran. To a mixture of 2-phenylethynylphenol (194.5 mg, 1.0 mmol) and TMEDA (15.0 μL, 0.1 mmol) was slowly added a solution of diethylzinc in toluene (0.50 mL, 1.0 mol/L, 0.5 mmol) at 0 °C. After ethane evolution ceased, toluene (1.5 mL) was added and the clear yellow solution was heated to 120 °C and stirred at that temperature for one hour. After cooling to room temperature, saturated ammonium chloride (3.0 mL) was added. 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 shinny crystals (182.0 mg, 94%). Analytical data were in good accordance with those reported in the literature.[7]

2-Butylbenzofuran: The title compound was obtained in 99% yield as a colorless oil. Analytical data were in good accordance with those reported in the literature.[8]

2-(1,1-Dimethylpropyl)benzofuran: The title compound was obtained in 99% yield as a colorless oil. Analytical data were in good accordance with those reported in the literature.[8]

2-(*E*)-Styrylbenzofuran: The title compound was obtained in 99% yield as white flakes. Analytical data were in good accordance with those reported in the literature.[9]

2-(2-Thienyl)benzofuran: The title compound was obtained in 93% yield as white needles. Analytical data were in good accordance with those reported in the literature.[7]

2-Hydroxymethylbenzofuran, methoxymethyl ether: The title compound was obtained in 98% yield as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.44 (s, 3H), 4.70 (s, 2H), 4.74 (s, 2H), 6.71 (s, 1H), 7.22 (t, J = 8.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 61.3, 95.5, 105.8, 111.3, 121.1, 122.8, 124.4, 128.0, 153.8, 155.2. FTIR (neat) cm^{-1}: 2937 (m), 2887 (m), 2826 (w), 1606 (w), 1455 (s), 1150 (s), 1100 (s), 1034 (s), 807 (m), 741 (s).

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[7] G. W. Kabalka, L. W. Wang, R. M. Pagni, *Tetrahedron* **2001**, *57*, 8017–8028.

[8] T. Kitamura, L. Zheng, H. Taniguchi, *Tetrahedron Lett.* **1993**, *34*, 4055.

[9] A. R. Katritzky, C. N. Fali, J. Li, *J. Org. Chem.* **1997**, *62*, 8205–8209.

Typical Procedure for Cyclization of 2-Alkynylanilines in the Presence of Buthyllithium / Zinc Chloride.

1-Benzyl-2-phenylindole: A solution of *N*-benzyl-2-phenylethynylaniline (283.9 mg, 1.0 mmol) in diethylether (1.0 mL) was cooled to 0 °C and a solution of butyllithium in hexane (0.63 mL, 1.60 mol / L, 1.0 mmol) was slowly added at that temperature. The resulted red solution was warmed to ambient temperature, stirred for 30 min and then a solution of zinc chloride in THF (1.0 mL, 1.00 mol / L, 1.0 mmol) was added. The solvents were removed *in vacuo*, toluene (2.0 mL) was added and the mixture was stirred at 120 °C for one hour. After cooling to room temperature, the reaction mixture was quenched with aqueous ammonium chloride and standard work-up gave the title compound as a pale yellow solid (281.9 mg, 99.5 %). Analytical data were in good accordance with those reported in the literature.[10]

5. Pd(0) Catalyzed Coupling of Zinc Intermediate with Aryl and Vinyl Halides.

Various conjugated compounds containing one or more benzoheterole moieties were prepared according to the procedure described below and the results are summarized in Table S3.

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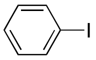
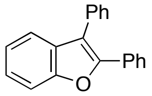
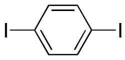
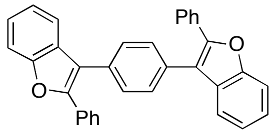
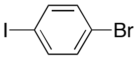
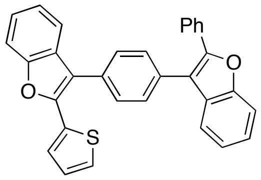
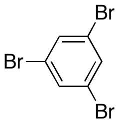
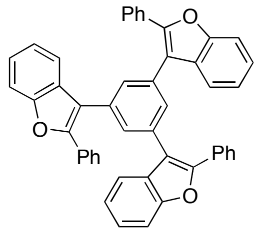
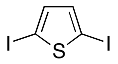
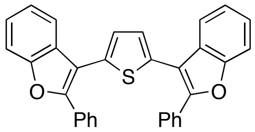
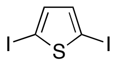
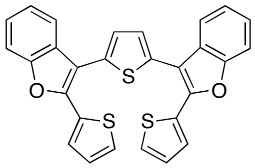
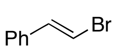
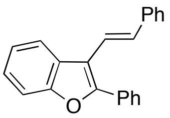
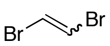
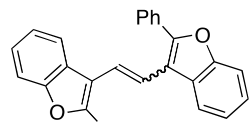
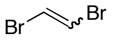
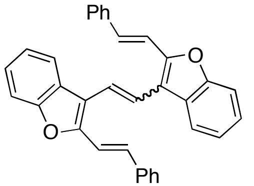
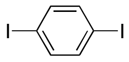
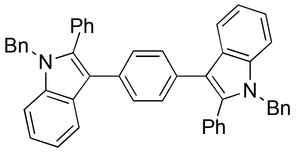
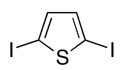
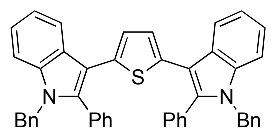
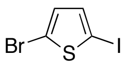
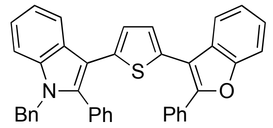
[10] B. S. Lane, D. Sames, *Org. Lett.* **2004**, *6*, 2897–2900.

Table S3: Conjugated compounds obtained via coupling with halides under Pd catalysis

Entry	Phenol	Electrophile	Coupling Product	Yield [%][a]
1	**1a**		 **4**	99
2	**1a**		 **5**	87
3	**1a** **1e**		 **6**	82[b]
4	**1a**[c]		 **7**	74
5	**1a**		 **8**	89
6	**1e**		 **9**	67
7	**1a**		 **10**	94
8	**1a**	 (E:Z = 38:62)[d]	 (E:Z = 36:64)[d] **11**	92

9	**1d**	 (E:Z = 38:62)[d]	 (E:Z = 43:57)[d] **12**	88
10	**1g**		 **13**	93
11	**1g**		 **14**	91
12	**1a** **1g**		 **15**	48

[a] Isolated yield. [b] Symmetric coupling products were obtained in about 15% yield (GC). [c] 10 mol% of palladium and 40 mol% of P(t-Bu)$_3$ were used. [d] Determined by ^{1}H NMR.

Typical Procedure for Pd(0) Catalyzed Cross-Coupling of Benzofuranylzinc with Aryl and Vinyl Halides.

1,3,5-Tris(2-phenylbenzofuran-3-yl)benzene. To a mixture of 2-phenylethynylphenol (350 mg, 1.80 mmol) and TMEDA (26 μL, 0.18 mmol) was added a solution of diethylzinc in toluene (0.93 mL, 0.96 mol/L, 0.90 mmol) at 0 °C. After ethane evolution ceased, toluene (3.0 mL) was added and the clear yellow solution was heated to 120 °C and stirred at that temperature for one hour. After cooling to room temperature, volatile material was removed *in vacuo* (~ 0.5 Torr, 30 min) and the residue was dissolved in THF (1.0 mL). The clear yellow solution was transferred via a cannula to a Schlenck tube containing 1,3,5-tribromobenzene (157.5 mg, 0.50 mmol), $Pd_2dba_3 \cdot CHCl_3$ (26 mg, 0.025 mmol) and P(tBu)$_3$ (0.25 mL, 10% in hexane, 0.10 mmol). The dark mixture was stirred at room temperature for 4 hours, then another portion of $Pd_2dba_3 \cdot CHCl_3$ (26 mg, 0.035 mmol) and P(tBu)$_3$ (0.25 mL, 10% in hexane, 0.10 mmol) was added and the mixture was stirred for another 16 hours at ambient temperature. The dark mixture was quenched (aq. NH_4Cl, aq. $Na_2S_2O_3$), the aqueous layer was extracted with CH_2Cl_2 (3 times), and the combined organic layers were passed through a Florisil column. After removing the solvent *in vacuo*, the crude material was purified by flash column chromatography on silica gel (hexanes–ethyl acetate) to afford the title compound as a white solid (242 mg, 74% based on 1,3,5-tribromobenzene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (t, *J* = 7.5 Hz, 3H), 7.27–7.37 (m, 15H), 7.51 (d, *J* = 8.0 Hz, 3H), 7.67 (s, 3H), 7.48 (d, *J* = 7.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 111.1 (3C), 116.9 (3C), 119.9 (3C), 122.9 (3C), 124.7 (3C), 127.4 (6C), 128.5 (3C), 128.6 (6C), 129.8 (3C), 130.4 (3C), 130.6 (3C), 134.6 (3C), 151.1 (3C), 154.0 (3C). FTIR (neat) cm^{-1} : 3057 (w), 3038 (w), 1602 (w),1258 (m), 1065 (m), 1455 (m), 764 (s), 690 (s). HRMS (APCI+) Calcd. for $^{12}C_{48}{}^1H_{30}{}^{16}O_3$ (M): 654.2195; Found: 654.2196.

2,3-Diphenylbenzofuran: The title compound was obtained in 99% yield as a white solid. Analytical data were in good accordance with those reported in the literature.[11]

1,4-Bis(2-phenylbenzofuran-3-yl)benzene: Obtained in 87% yield as a white solid.[12] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.38 (m, 10H), 7.58–7.64 (m, 8H), 7.74 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 111.2 (2C), 117.2 (2C), 120.0 (2C), 123.0 (2C), 124.8 (2C), 127.1 (4C), 128.4 (4C), 128.5 (2C), 130.0 (2C), 130.3 (4C), 130.6 (2C), 132.2 (2C), 150.8 (2C), 154.1 (2C). FTIR (neat): cm^{-1} : 3065 (w), 3038 (w), 2964 (w), 1590 (w), 1455 (m), 1258 (s), 1065 (s), 849 (s), 745 (s), 695 (s). Anal. Calcd. for $C_{34}H_{22}O_2$: C, 88.29; H, 4.79. Found: C, 88.03; H, 4.99.

1-(2-Phenylbenzofuran-3-yl)-4-(2-(2-thienyl)benzofuran-3-yl)benzene. To a mixture of 1-bromo-4-iodobenzene (96.7 mg, 0.34 mmol), $Pd_2dba_3 \cdot CHCl_3$ (10.5 mg, 0.01 mmol) and P(*t*Bu)$_3$ (0.10 mL, 10 % in hexane, 0.04 mmol) was added a solution of (2-(2-thienyl)benzofuran-3-yl)zinc in THF (0.42 mL, 1.0 mol / L, 0.42 mmol) and the resulted mixture was stirred for 13 hours at ambient temperature. Then, a solution of (2-phenylbenzofuran-3-yl)zinc in THF (0.42 mL, 1.0 mol / L, 0.42 mmol) was added,

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[11] Y. Hu, K. J. Nawoschik, Y. Liao, J. Ma, R. Fathi, Z. Yang, *J. Org. Chem.* **2004**, *69*, 2235–2239.

[12] Preparation of this compound was reported by M. A. Meador, M. Abdulaziz, *Polymeric Materials Science and Engineering,* **1989**, *60*, 117–121. However, no spectral data were reported and supporting information was not available to us.

then another portion of $Pd_2dba_3 \cdot CHCl_3$ (10.5 mg, 0.01 mmol) and $P(tBu)_3$ (0.10 mL, 10 % in hexane, 0.04 mmol) was added and the resulted mixture stirred an additional 20 hours at ambient temperature. Standard aqueous work-up followed by purification by flash column chromatography on silica gel (hexanes – ethyl acetate) gave the title compound as a white solid (130.7 mg, 82 % based on halide). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.04–7.05 (m, 1H), 7.26–7.39 (m, 8H), 7.45 (d, *J* = 3.5Hz, 1H), 7.55–7.68 (m, 8H), 7.73–7.76 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 111.1, 111.2, 116.5, 117.2, 119.9, 120.0, 123.0, 123.2, 124.8, 124.9, 125.8, 126.2, 127.2 (2C), 127.4 (2C), 128.4 (2C), 128.5, 130.0, 130.3, 130.5, 130.55 (2C), 130.6, 131.3, 132.6, 132.7, 146.8, 150.8, 153.8, 154.1. FTIR (neat) cm^{-1} : 3061 (w), 3038 (w), 1594 (w), 1455 (m), 1204 (m), 741 (s), 691 (s). Anal. Calcd. for $C_{32}H_{20}O_2S$: C, 82.03; H, 4.30. Found: C, 82.03; H, 4.49.

2,5-Bis(2-phenylbenzofuran-3-yl)thiophene: Obtained in 89% yield as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29–7.41 (m, 12H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 7.50 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 110.6 (2C), 111.2 (2C), 120.2 (2C), 123.2 (2C), 125.0 (2C), 127.4 (4C), 127.9 (2C), 128.5 (4C), 128.9 (2C), 129.9 (2C), 130.3 (2C), 134.1 (2C), 151.8 (2C), 153.9 (2C). FTIR (neat) cm^{-1} : 2957 (m), 2926 (m), 2860 (w), 1725 (s), 1455 (m), 1258 (s), 741 (s), 687 (s). HRMS (APCI+) Calcd. for $^{12}C_{32}{}^1H_{20}{}^{16}O_2{}^{32}S$ (M): 468.1184; Found: 468.1156.

2,5-Bis(2-(2-thienyl)benzofuran-3-yl)thiophene: Obtained in 67% yield as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (t, *J* = 3.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.34–7.38 (m, 6H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 3.5 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 109.8 (2C), 111.0 (2C), 120.1 (2C), 123.4 (2C), 125.1 (2C), 126.6 (2C), 126.9 (2C), 127.5 (2C), 128.8 (2C), 130.0 (2C), 132.1 (2C),, 133.6 (2C), 147.9 (2C), 153.7 (2C). FTIR (neat) cm^{-1} : 3100 (w), 3061 (w), 1606 (w), 1451 (m), 1197 (m), 745 (s), 695 (s). HRMS (APCI+) Calcd. for $^{12}C_{28}{}^1H_{16}{}^{16}O_2{}^{32}S_3$ (M): 480.0312; Found: 480.0301.

2-Phenyl-3-(2-(*E*)-phenylethenyl)benzofuran: Obtained in 94% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24–7.39 (m, 8H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.49–7.52

(m, 3H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.93 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 111.3, 114.5, 119.8, 121.0, 123.1, 124.8, 126.2, 127.5, 127.7, 127.9 (2C), 128.6 (2C), 128.7 (4C), 130.7, 131.0, 137.7, 153.2, 154.4. FTIR (neat) cm^{-1}: 3057 (w), 3030 (w), 1598 (w), 1451 (m), 1204 (m), 961 (m), 722 (m), 741 (s), 691 (s). HRMS (APCI+) Calcd. for $^{12}C_{22}{}^{1}H_{16}{}^{16}O$ (M): 296.1201; Found: 296.1183.

1,2-(*E*)-Bis(2-phenylbenzofuran-3-yl)ethylene: Obtained as a white solid, less soluble in cold ethyl acetate. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (t, *J* = 7.0 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 4H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.63 (s, 2H), 7.90 (d, *J* = 7.0 Hz, 4H), 7.94 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 111.5 (2C), 114.9 (2C), 120.9 (2C), 122.4 (2C), 123.2 (2C), 124.8 (2C), 127.8 (2C), 127.9 (4C), 128.8 (6C), 130.8 (2C), 153.0 (2C), 154.5 (2C). FTIR (neat) cm^{-1}: 3053 (w), 1586 (w), 1455 (m), 1204 (m), 1065 (m), 733 (s), 695 (s).

1,2-(*Z*)-Bis(2-phenylbenzofuran-3-yl)ethylene: Obtained as a white solid, soluble in cold ethyl acetate. ^{1}H NMR (500 MHz, $CDCl_3$): d 6.88 (d, *J* = 7.5 Hz, 2H), 7.01 (s, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 2H), 7.29–7.7.39 (m, 8H), 7.78 (d, *J* = 7.5 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): d 110.7 (2C), 114.6 (2C), 120.7 (2C), 122.4 (2C), 122.8 (2C), 124.3 (2C), 127.1 (4C), 128.2 (2C), 128.3 (2C), 128.4 (4C), 130.9 (2C), 152.0 (2C), 153.8 (2C).

Anal. (mixture of stereoisomers) Calcd. for $C_{30}H_{20}O_2$: C, 87.36; H, 4.89. Found: C, 87.17; H, 4.89.

1,2-(*E*)-Bis(2-(*E*)-styrylbenzofuran-3-yl)ethylene: Obtained as a yellow solid, less soluble in cold chloroform. ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): d 7.28 (d, *J* = 16.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.32–7.7.39 (m, 8H), 7.44 (d, *J* = 16 Hz, 2H), 7.47 (s, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 4H), 7.94 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, CS_2–$CDCl_3$): d 111.0 (2C), 113.5 (2C), 116.7(2C), 120.1(2C), 120.7(2C), 123.1 (2C), 125.3 (2C), 126.7 (4C), 127.1 (2C), 128.1 (2C), 128.7 (4C), 130.9 (2C), 136.4 (2C), 152.0 (2C), 154.4 (2C). FTIR (neat) cm^{-1}: 3057 (w), 1594 (w), 1451 (m), 1282 (m), 1193 (s), 942 (s), 749 (s), 691 (s).

1,2-(*Z*)-Bis(2-(*E*)-styrylbenzofuran-3-yl)ethylene: Obtained as a yellow solid, soluble in cold chloroform. ^{1}H NMR (500 MHz, CDCl$_3$): d 6.78 (d, J = 16.0 Hz, 2H), 6.96 (s, 2H), 7.05–7.07 (m, 4H), 7.11 (d, J = 16.0 Hz, 2H), 7.15–7.18 (m, 8H), 7.25 (m, 2H), 7.33–7.36 (m, 4H). ^{13}C NMR (125 MHz, CDCl$_3$): d 110.9 (2C), 115.0 (2C), 115.9 (2C), 119.9 (2C), 121.9 (4C), 122.8 (2C), 125.0 (2C), 126.6 (2C), 127.9 (2C), 128.4 (2C), 128.5 (4C), 130.4 (2C), 136.5 (2C), 151.1 (2C), 154.4 (2C). HRMS (APCI+) Calcd. for $^{12}C_{34}{}^{1}H_{24}{}^{16}O_2$ (M): 464.1773; Found: 464.1768.

1,4-Bis(1-Benzyl-2-phenylindol-3-yl)benzene. A solution of *N*-benzyl-2-phenylethynylaniline (311.7 mg, 1.1 mmol) in diethylether (1.1 mL) was cooled to 0 °C and a solution of butyllithium in hexane (0.69 mL, 1.60 mol / L, 1.1 mmol) was slowly added at that temperature. The red solution was warmed to ambient temperature, stirred for 30 min and then a solution of zinc chloride in THF (1.10 mL, 1.00 mol / L, 1.0 mmol) was added. The solvents were removed *in vacuo*, toluene (2.2 mL) was added and the mixture was stirred at 120 °C for one hour. After cooling to room temperature, Pd$_2$dba$_3$·CHCl$_3$ (13.0 mg, 0.012 mmol), P(tBu)$_3$ (25 μL, 2.0 mol / L in hexane, 0.05 mmol) and 1,4-diiodobenzene (165.4 mg, 0.50 mmol) were added, and the mixture was stirred for 3 hours at ambient temperature. Another portion of Pd$_2$dba$_3$·CHCl$_3$ (13.0 mg, 0.012 mmol) and P(tBu)$_3$ (25 μL, 2.0 mol / L in hexane, 0.05 mmol) was then added and the resulted mixture was stirred for 16 hours at ambient temperature. Chloroform was added and the solids were filtered off and washed with hot chloroform. The volatile material was removed *in vacuo* and the crude material was purified by flash column chromatography on silica gel (hexanes–chloroform) to give the title compound as an off-white solid (298.5 mg, 93 % based on diiodobenzene).

^{1}H NMR (500 MHz, CDCl$_3$): δ 5.29 (s, 4H), 6.99 (d, J = 6.8 Hz, 4H), 7.16–7.29 (m, 26H), 7.84 (d, J = 5.7 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 47.3 (2C), 99.6 (2C), 110.2 (2C), 115.5 (2C), 119.8 (2C), 120.4 (2C), 122.2 (2C), 125.9 (4C), 127.0 (2C), 127.2 (2C), 127.8 (2C), 128.1 (4C), 128.5 (4C), 129.4 (4C), 130.9 (4C), 131.7 (2C), 132.0 (2C), 136.8 (2C), 137.9 (2C). FTIR (neat) cm^{-1}: 3026 (w), 2924 (w), 1457 (m), 1351 (m), 1325 (m), 745 (s), 732 (s), 699 (s). HRMS (APCI+) Calcd. for $^{12}C_{48}{}^{1}H_{36}{}^{14}N_2$ (M): 640.2878; Found: 640.2906.

2,5-Bis(1-benzyl-2-phenylindol-3-yl)thiophene: Obtained in 91 % yield as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.21 (s, 4H), 6.77 (s, 2H), 6.96 (d, J = 8.5 Hz, 4H), 7.18–7.25 (m, 12H), 7.30–7.38 (m, 10H), 7.93–7.96 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$–CS_2): d 47.3 (2C), 109.4 (2C), 110.1 (2C), 120.2 (2C), 120.5 (2C), 122.4 (2C), 124.5 (2C), 125.9 (4C), 126.8 (2C), 127.0 (2C), 128.2 (4C), 128.4 (4C), 128.5 (4C), 131.1 (2C), 131.4 (2C), 134.7 (2C), 136.4 (2C), 137.4 (2C), 137.6 (2C). FTIR (neat) cm^{-1}: 3058 (w), 3016 (w), 1569 (w), 1458 (s), 1349 (m), 1325 (m), 1197 (m), 746 (s), 731 (s), 699 (s). HRMS (APCI+) Calcd. for $^{12}C_{46}{}^{1}H_{34}{}^{14}N_2{}^{32}S$ (M): 646.2443; Found: 646.2440.

2-(2-Phenylbenzofuran-3-yl)-5-(1-benzyl-2-phenylindol-3-yl)thiophene. To a mixture of 2-bromo-5-iodothiophene (140.5 mg, 0.47 mmol) and $Pd_2dba_3{\cdot}CHCl_3$ (13.0 mg, 0.012 mmol) was added a solution of (2-phenylbenzofuran-3-yl)zinc in THF (0.55 mL, 1.0 mol / L, 0.55 mmol) and the resulted mixture was stirred at ambient temperature for 24 hours. $Pd_2dba_3{\cdot}CHCl_3$ (13.0 mg, 0.012 mmol), P(*t*Bu)$_3$ (50 mL, 2.0 mol / L in hexane, 0.10 mmol) and then a solution of (1-benzyl-2-phenylindol-3-yl)zinc chloride in THF (0.55 mL, 1.0 mol / L, 0.55 mmol) were added and the resulted mixture was stirred at ambient temperature for 24 hours. Chloroform was added and the solids were filtered off and washed with hot chloroform. The volatile material was removed *in vacuo* and the crude product was purified by flash column chromatography on silica gel (hexanes–chloroform) to give the title compound as a bright-yellow solid (125.8 mg, 48 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.26 (s, 2H), 6.98–7.00 (m, 3H), 7.04 (d, J = 4.0 Hz, 1H), 7.24–7.26 (m, 6H), 7,32–7.39 (m, 10H), 7.51 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 6.8 Hz, 1H), 7.78 (dd, J_1 = 8.0 Hz, J_2 = 1.7 Hz, 2H), 8.03–8.05 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$–CS_2): d 47.5, 109.0, 110.4, 110.9, 111.0, 120.0, 120.4, 120.8, 122.6, 122.9, 124.7, 125.1, 126.0 (2C), 126.7, 127.13, 127.17, 127.19 (2C), 128.3 (2C), 128.42, 128.44 (2C), 128.6 (2C), 128.7 (2C), 130.1, 130.7, 131.1, 131.3, 136.5, 137.6, 138.0, 138.1, 151.2, 153.7. FTIR (neat) cm^{-1}: 3058 (w), 2920 (w), 2860 (w), 1451 (s), 1348 (m), 1210 (m), 1063 (m), 915 (m), 739 (s), 692 (s). HRMS (APCI+) Calcd. for $^{12}C_{39}{}^{1}H_{27}{}^{14}N{}^{16}O{}^{32}S$ (M): 557.1813; Found: 557.1826.

Molecular Modeling Study with Quantum Chemical Calculation.

All calculations were performed with Spartan ’04 package.[13] The molecular structures and harmonic vibrational frequencies were obtained with the hybrid density functional method based on Becke's three–parameter exchange function and the Lee–Yang–Parr non-local correlation functional (B3LYP).[14] Geometry optimization and vibrational analysis were performed by using by using 6–31G* basis set[15] at the same theoretical model. All stationary points were optimized without any symmetry assumptions, and characterized all by normal coordinate analysis at the same level of the geometry optimization.

Equilibrium structure and total electron energy of 1,3,5-Tris(2-phenylbenzofuran-3-yl)benzene:

The structure optimizations have been performed with several starting geometries of possible conformers. By comparison of the total electron energies obtained for those optimized structures, we obtained the C_{3v}-like structure shown below as the most stable conformer.

Energy: -2072.88149 au (B3LYP/6-31G*). Normal coordination analysis showed no imaginary frequency.

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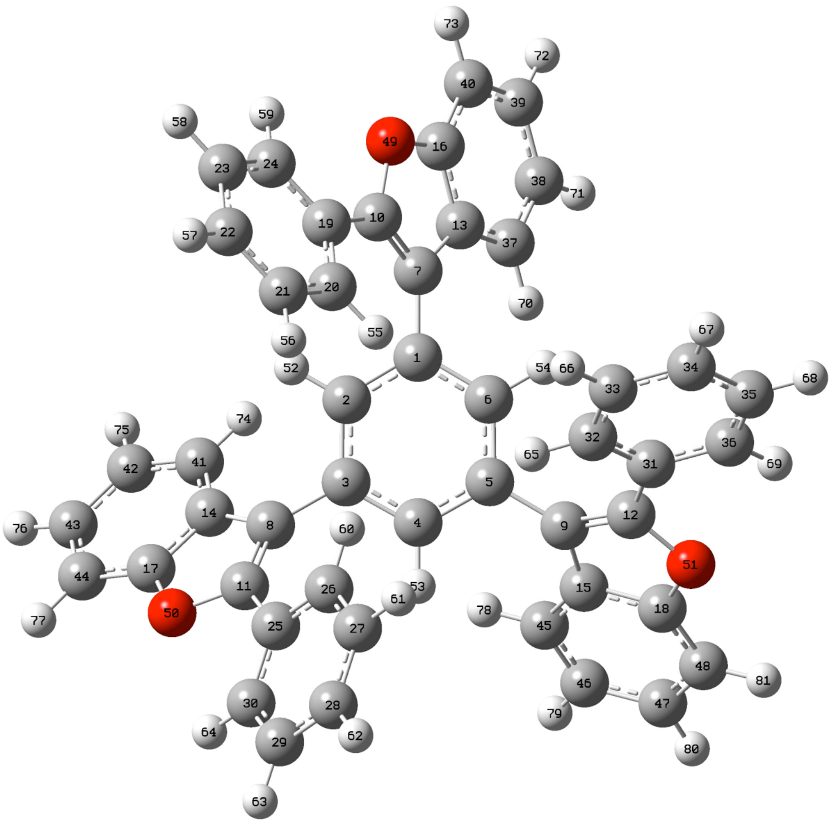

	Coordinates (Angstroms)		
	x	y	z
C	0.45664327	0.17620175	-1.40493275
C	0.50264327	-1.10879825	-0.83893275
C	0.53964327	-1.28779825	0.55006725
C	0.53964327	-0.15479825	1.37906725
C	0.49564327	1.13820175	0.84106725
C	0.46064327	1.28920175	-0.55493275
C	0.46464327	0.36120175	-2.87093275
C	0.63864327	-2.64879825	1.11806725
C	0.54264327	2.31620175	1.73106725
C	-0.33035673	-0.23079825	-3.82493275

C	-0.10135673	-3.22779825	2.12406725
C	-0.24935673	3.44220175	1.71506725
C	1.41164327	1.18520175	-3.59693275
C	1.63364327	-3.63179825	0.73906725
C	1.52564327	2.53620175	2.77306725
C	1.11264327	1.00620175	-4.95693275
C	1.41664327	-4.73979825	1.57306725
C	1.24964327	3.80820175	3.29906725
C	-1.48435673	-1.13079825	-3.77893275
C	-2.33135673	-1.18279825	-2.65793275
C	-3.42735673	-2.04179825	-2.63893275
C	-3.70535673	-2.85579825	-3.73893275
C	-2.87835673	-2.80179825	-4.86193275
C	-1.77835673	-1.94779825	-4.88593275
C	-1.25835673	-2.80879825	2.91506725
C	-2.17235673	-1.85279825	2.43606725
C	-3.26935673	-1.47379825	3.20606725
C	-3.48235673	-2.04679825	4.46206725
C	-2.59035673	-3.00879825	4.94006725
C	-1.48935673	-3.38879825	4.17606725
C	-1.42435673	3.85420175	0.94706725
C	-2.31835673	2.91120175	0.40906725
C	-3.43135673	3.32720175	-0.31693275
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C	-2.80535673	5.63220175	0.03006725
C	-1.68935673	5.22320175	0.75506725
C	2.48564327	2.01720175	-3.24293275
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C	2.86364327	2.45320175	-5.61493275
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C	3.46864327	-4.82679825	-0.24393275
C	3.21764327	-5.92579825	0.59906725

C	2.18064327	-5.89979825	1.53206725
C	2.61664327	1.81520175	3.28706725
C	3.36364327	2.38820175	4.31206725
C	3.05064327	3.66120175	4.82506725
C	1.98164327	4.40020175	4.32006725
O	0.05864327	0.14920175	-5.09793275
O	0.36764327	-4.49779825	2.41206725
O	0.17564327	4.35920175	2.66006725
H	0.50764327	-1.97579825	-1.49193275
H	0.57064327	-0.28579825	2.45606725
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H	-3.08835673	-3.42879825	-5.72493275
H	-1.13835673	-1.90779825	-5.75993275
H	-2.02835673	-1.41879825	1.45206725
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H	-2.75035673	-3.46579825	5.91306725
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H	4.03064327	3.29520175	-4.00693275
H	3.43964327	2.96120175	-6.38393275
H	1.54164327	1.45620175	-7.02793275
H	2.89764327	-2.82879825	-0.83093275
H	4.28964327	-4.88079825	-0.95293275
H	3.84464327	-6.80979825	0.52606725

H	1.97764327	-6.73379825	2.19506725
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H	1.72964327	5.38620175	4.69806725