Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplementary Information

Aggregation-responsive ON–OFF–ON fluorescence switching behavior of twisted tetrakis(benzo[*b*]furyl)ethene made by hafnium-mediated McMurry coupling

Hiroyoshi Hamada,[a] Hayato Tsuji*[b] and Eiichi Nakamura*[a]

[a.] *Department of Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.*

[b.] *Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka 259-1293, Japan.*

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1. General consideration for synthesis and characterization

All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen or argon. Air- and moisture-sensitive liquids and solutions were transferred via syringe or Teflon cannula. Analytical thin-layer chromatography (TLC) 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). 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).

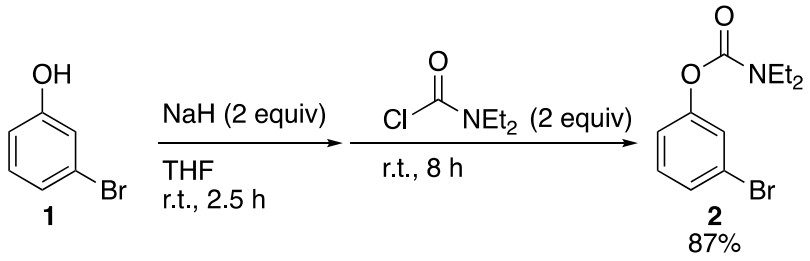
Unless otherwise noted, commercial reagents were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and used as purchased. Anhydrous solvents were purchased from Kanto, and purified by a solvent purification system (GlassContour) equipped with columns of activated alumina and copper catalyst prior to use. Zinc (powder) was purchased from Wako Co., and was washed with 1M HCl aq., methanol, and diethyl ether and dried over before use.

NMR spectra were recorded using a JEOL ECA-500 (^{1}H NMR, 500 MHz; ^{13}C NMR, 125 MHz), JEOL ECZ-500 (^{1}H NMR, 500 MHz), and JEOL ECX-400 (^{1}H NMR, 400 MHz; ^{13}C NMR; 100 Hz) NMR spectrometer. Chemical data for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the residual protons in the NMR solvent ($CDCl_3$: δ 7.26). 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 are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances, br = broad), coupling constant in Hertz (Hz), and integration. Melting points of solid materials were determined on a Mel-Temp II capillary melting-point apparatus and are uncorrected. Mass spectra were obtained on Bruker micrOTOF II (APCI) mass spectrometer. High-resolution mass spectra were obtained with a calibration standard of polyethylene glycol.

2. Synthetic procedures for all compounds

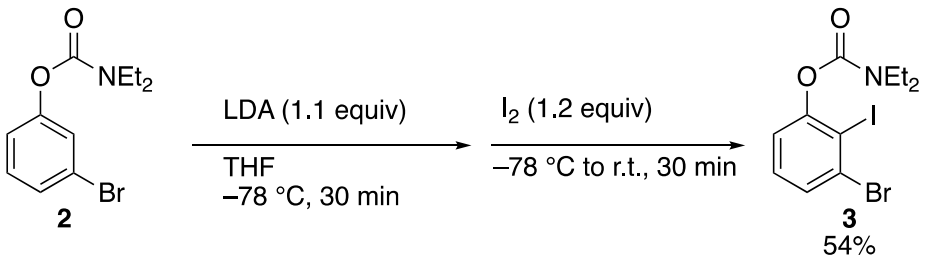
3-Bromophenyl *N*,*N*-diethylcarbamate (2)



The procedure previously reported by Sanz *et al*. was followed.[2]

To a solution of 3-bromophenol (**1**) (5.26 g, 30 mmol) in 7.5 mL THF, a solution of sodium hydride (2.36 g, 65 wt%, 64 mmol) in 20 mL THF was dropwise added at ambient temperature. After stirring for 2.5 h, the resulting brownish mixture was added *N*,*N*-diethylcarbamoyl chloride (7.61 g, 60 mmol) and stirred for 8 h. The reaction mixture was added water and organic layer was three times extracted with ethyl acetate, washed with brine, and dried over anhydrous Na_2SO_4. After the solvent was removed *in vacuo*, the crude material was purified by flash silica-gel column chromatography (eluent: ethyl acetate/hexane, 1/10) to afford the title compound (7.09 g, 87%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (td, J = 7.1, 14.2 Hz, 6H, CH_2CH_3), 3.33–3.46 (m, 4H, CH_2CH_3), 7.06–7.13 (m, 1H, Ar*H*), 7.19–7.25 (m, 1H, Ar*H*), 7.30–7.37 (m, 2H, Ar*H*), which is in agreement with the literature.[2]

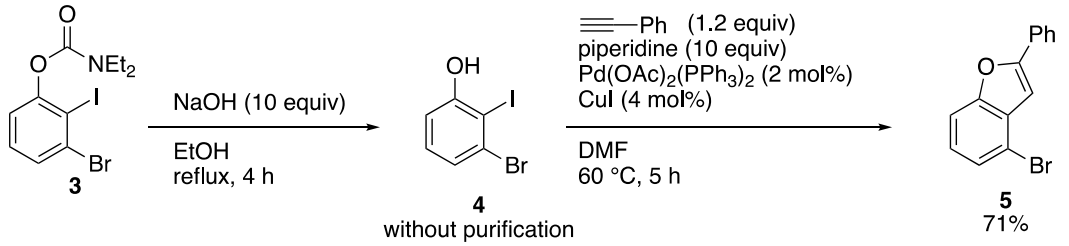
3-Bromo-2-iodophenyl *N*,*N*-diethylcarbamate (3)



The procedure previously reported by Sanz *et al*. was followed.[2]

To a solution of diisopropylamine (3.08 g, 22 mmol) in 60 mL THF, butyllithium in hexane (13.8 mL, 1.60 mol/L, 22 mmol) was dropwise added at 0 °C. After stirring for 30 min at 0 °C, the solution was cooled down to –78 °C, and 3-bromophenyl *N*,*N*-diethylcarbamate (**2**) (5.44 g, 20 mmol) was added to the solution of LDA. The reaction mixture was stirred for 30 min and iodine (6.12 g, 24 mmol) was added at low temperature. After stirring for 30 min at –78 °C, the reaction mixture was allowed to warm to ambient temperature, and $Na_2S_2O_3$ aq. was added to the mixture. Organic layer was twice extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. The crude material was purified by flash silica-gel column chromatography (eluent: ethyl acetate/hexane, 1/10) to afford the title compound (4.26 g, 54%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, J = 7.2 Hz, 3H, CH_2CH_3), 1.32 (t, J = 7.2 Hz, 3H, CH_2CH_3), 3.40 (q, J = 7.2 Hz, 2H, CH_2CH_3), 3.53 (q, J = 7.2 Hz, 2H, CH_2CH_3), 7.09 (dd, J = 1.2, 8.3 Hz, 1H, Ar*H*), 7.23 (t, J = 8.0 Hz, 1H, Ar*H*), 7,48 (dd, J = 1.2, 8.0 Hz, 1H, Ar*H*), which is in agreement with the literature.[2]

4-Bromo-2-phenylbenzo[*b*]furan (5)



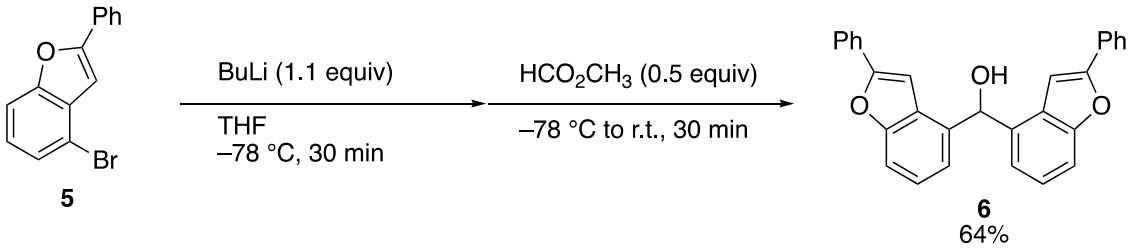
The procedure previously reported by Sanz *et al*. was followed.[2]

3-Bromo-2-iodophenyl *N*,*N*-diethylcarbamate (**3**) (2.00 g, 5.0 mmol) and sodium hydroxide (2.00 g, 50 mmol) was dissolved into 40 mL ethanol and refluxed for 4 h. After cooling down to ambient temperature, the solvent was removed *in vacuo*. The resulting mixture was dissolved into diethyl ether and neutralized by 1M HCl aq. Organic layer was twice extracted with diethyl ether, dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude material was used for the next step without further purification.

The crude material was dissolved in 20 mL DMF. Ethynylbenzene (620 mg, 6.0 mmol), piperidine (4.96 g 58 mmol), $Pd(OAc)_2(PPh_3)_2$ (74.4 mg, 2.0 mol%) and CuI (38.0 mg, 4.0 mol%) were added to the solution and stirred for 5 h at 60 °C. The resulting brown-red mixture was allowed to cool down to ambient temperature and then water was added. The organic layer was extracted three times with ethyl acetate, dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. The crude material was purified by flash silica-gel column chromatography (eluent: hexane) to afford the title compound (976 mg, 71% over 2 steps) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 1H, Ar*H*), 7.15 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.35–7.42 (m, 2H, Ar*H*), 7.43–7.51(m, 3H, Ar*H*),

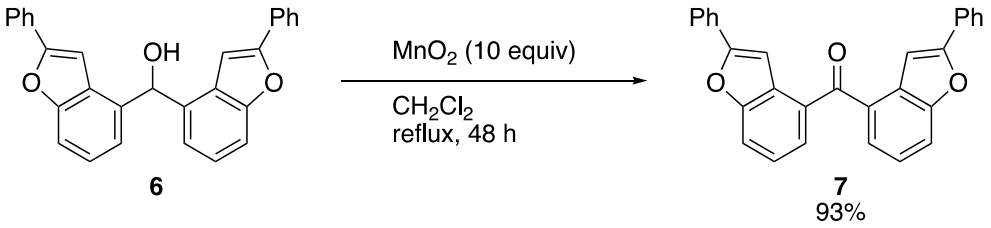
7.85–7.91 (m, 2H, Ar*H*), which is in agreement with the literature.[2]

Bis(2-phenyl-4-benzo[*b*]furyl)methanol (6)



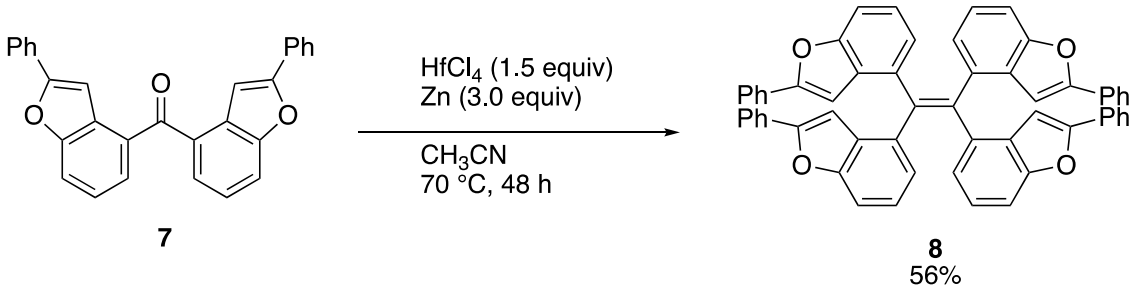
A solution of buthyllithium in hexane (5.16 mL, 1.60 mol/L, 8.3 mmol) was added to a solution of 4-bromo-2-phenylbenzo[*b*]furan (**5**) (2.04 g, 7.5 mmol) in 40 mL THF at –78 °C and stirred for 30 min. After methyl formate (586 mg, 3.8 mmol) was added, the resulting pale yellow solution was allowed to warm to ambient temperature and stirred for 30 min. After addition of water, organic layer was extracted three times with ethyl acetate, washed with brine, and then dried over anhydrous Na_2SO_4. After removing the solvent *in vacuo*, the crude material was purified by flash silica-gel column chromatography (eluent: ethyl acetate/hexane, 1/3) to afford the title compound (991 mg, 64%) as a pale yellow solid. Mp: 84–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (δ, *J* = 3.4 Hz, 1H, C*H*OH), 6.51 (d, *J* = 3.4 Hz, 1H, CHO*H*), 7.08 (s, 2H, Ar*H*), 7.27–7.37 (m, 6H, Ar*H*), 7.42 (t, *J* = 7.7 Hz, 4H, Ar*H*), 7.49 (dd, *J* = 1.7, 6.3 Hz, 2H, Ar*H*), 7.80–7.84 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 74.0 (>*C*HOH), 100.5, 111.0, 121.1, 124.3, 125.1, 127.5, 128.7, 128.9, 130.3, 135.4, 155.4, 156.0; HRMS (APCI+) calcd for $C_{29}H_{20}O_3$ (M): 416.1407; found: 416.1408.

Bis(2-phenyl-4-benzo[*b*]furyl)ketone (7)



Bis(2-phenyl-4-benzo[*b*]furyl)methanol (**6**) (832 mg, 2.0 mmol) was added to a suspension of manganese(IV) oxide (1.74 g, 20 mmol) in 20 mL dichloromethane. After refluxing for 48 h, water was added to the reaction mixture. The organic layer was extracted three times with ethyl acetate, and dried over anhydrous Na_2SO_4. After removing the solvent *in vacuo*, the crude material was purified by flash silica-gel column chromatography (eluent: ethyl acetate/hexane, 1/3) and reprecipitation (dichloromethane/methanol) to afford the titled compound (774 mg, 93%) as a pale yellowish white solid. Mp: 205–206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.43 (m, 4H, Ar*H*), 7.47 (t, *J* = 7.6 Hz, 4H, Ar*H*), 7.53 (s, 2H, Ar*H*), 7.64 (d, *J* = 7.9 Hz, 2H, Ar*H*), 7.76 (d, *J* = 7.9 Hz, 2H, Ar*H*), 7.92 (d, *J* = 8.2 Hz, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 102.2, 115.2, 123.3, 125.4, 126.9, 129.0, 129.2, 129.9, 130.1, 130.6, 155.5, 158.2, 196.0 (>*C*=O); HRMS (APCI+) calcd for $C_{29}H_{18}O_3$ (M): 414.1250; found: 414.1257.

Tetrakis(2-phenyl-4-benzo[*b*]furyl)ethene (TBFE, 8)



Hafnium(IV) chloride (23 mg, 0.072 mmol) and pre-washed zinc powder (9.4 mg, 0.144 mmol) were suspended in 0.33 mL acetonitrile and stirred for 5 min at ambient temperature. After addition of bis(2-phenyl-4-benzo[*b*]furyl)ketone (**7**) (20 mg, 0.048 mmol) to the suspension, the reaction mixture was heated to 70 °C. The resulting brownish red mixture was stirred for 48 h, cooled down to ambient temperature, and added water. Organic layer was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. After removing the solvent *in vacuo*, the crude material was purified by flash silica-gel column chromatography (eluent: toluene/hexane, 3/10) to afford the title compound (10.7 mg, 56%) as a yellow solid. Mp: 103–105 °C; ^{1}H NMR (500 MHz, THF-d_8) δ 6.75 (s, 4H, Ar*H*), 7.03 (t, *J* = 7.5 Hz, 4H, Ar*H*), 7.13 (d, *J* = 7.5 Hz 4H, Ar*H*), 7.20–7.29 (m, 16H, Ar*H*), 7.57 (d, *J* = 6.3 Hz, 4H, Ar*H*); ^{13}C NMR (125 MHz, THF-d_8) δ 102.2, 110.7, 124.7, 125.5, 126.8, 129.2, 129.4, 130.3, 131.1, 137.3, 140.7, 155.9, 156.4; HRMS (APCI+) calcd for $C_{58}H_{37}O_4$ (M+H): 797.2686; found: 797.2672.

3. Computational Study

The geometry of each **TBFE** conformers and 2-phenylbenzofuran were optimized with Density Functional Theory (DFT) calculation at the B3LYP/6-31G* level on Gaussian09 packages.[3]

Geometry optimization of TBFE.

Conformation 1 (**TBFE-c1**):

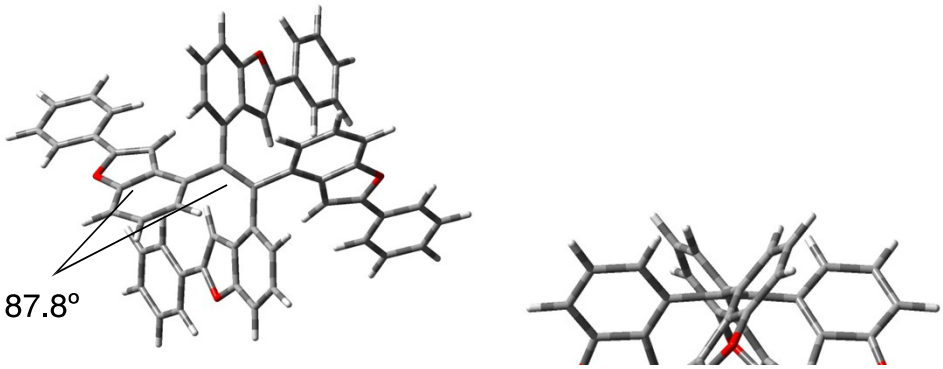


***Figure* S1.** Optimized structure of **TBFE-c1** and a dihedral angle between the BF unit and the central alkene structure.

***Table* S1.** Theoretically optimized coordinates of **TBFE-c1** (calculated at the B3LYP/6-31G* level of theory).

Total energy: *E*(RB3LYP/6-31G*) = –2532.76502081 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0	0	-0.684465
2	6	0	0	0	0.684465
3	6	0	-1.253149	0.159253	1.478439
4	6	0	-1.580424	-0.700728	2.554399

5	6	0	-2.141525	1.214102	1.222935
6	6	0	-2.763283	-0.470873	3.284856
7	6	0	-3.306866	1.418002	1.978317
8	6	0	-3.645639	0.569783	3.032974
9	1	0	-3.955727	2.254591	1.735456
10	1	0	-4.54252	0.709092	3.627159
11	6	0	-1.253149	-0.159253	-1.478439
12	6	0	-2.141525	-1.214102	-1.222935
13	6	0	-3.306866	-1.418002	-1.978317
14	6	0	-3.645639	-0.569783	-3.032974
15	1	0	-3.955727	-2.254591	-1.735456
16	1	0	-4.54252	-0.709092	-3.627159
17	6	0	1.253149	0.159253	-1.478439
18	6	0	2.141525	1.214102	-1.222935
19	6	0	3.306866	1.418002	-1.978317
20	6	0	3.645639	0.569783	-3.032974
21	1	0	3.955727	2.254591	-1.735456
22	1	0	4.54252	0.709092	-3.627159
23	6	0	1.253149	-0.159253	1.478439
24	6	0	1.580424	0.700728	2.554399
25	6	0	2.141525	-1.214102	1.222935
26	6	0	2.763283	0.470873	3.284856
27	6	0	3.306866	-1.418002	1.978317
28	6	0	3.645639	-0.569783	3.032974
29	1	0	3.955727	-2.254591	1.735456
30	1	0	4.54252	-0.709092	3.627159
31	6	0	2.763283	-0.470873	-3.284856
32	6	0	1.580424	-0.700728	-2.554399
33	6	0	0.994865	-1.873153	-3.14548
34	1	0	0.06848	-2.347038	-2.857842
35	6	0	1.821735	-2.264891	-4.161446
36	8	0	2.909919	-1.417328	-4.25958

37	6	0	-2.763283	0.470873	-3.284856
38	6	0	-1.580424	0.700728	-2.554399
39	6	0	-0.994865	1.873153	-3.14548
40	1	0	-0.06848	2.347038	-2.857842
41	6	0	-1.821735	2.264891	-4.161446
42	8	0	-2.909919	1.417328	-4.25958
43	6	0	1.765361	-3.363713	-5.117962
44	6	0	2.765437	-3.522189	-6.093444
45	6	0	0.704454	-4.287296	-5.081559
46	6	0	2.702657	-4.574443	-7.004456
47	1	0	3.587202	-2.815512	-6.130797
48	6	0	0.647551	-5.335936	-5.993895
49	1	0	-0.078008	-4.181404	-4.335885
50	6	0	1.646105	-5.485647	-6.960413
51	1	0	3.483704	-4.68183	-7.75246
52	1	0	-0.179571	-6.039481	-5.951182
53	1	0	1.599532	-6.305275	-7.672135
54	6	0	-1.765361	3.363713	-5.117962
55	6	0	-2.765437	3.522189	-6.093444
56	6	0	-0.704454	4.287296	-5.081559
57	6	0	-2.702657	4.574443	-7.004456
58	1	0	-3.587202	2.815512	-6.130797
59	6	0	-0.647551	5.335936	-5.993895
60	1	0	0.078008	4.181404	-4.335885
61	6	0	-1.646105	5.485647	-6.960413
62	1	0	-3.483704	4.68183	-7.75246
63	1	0	0.179571	6.039481	-5.951182
64	1	0	-1.599532	6.305275	-7.672135
65	6	0	0.994865	1.873153	3.14548
66	1	0	0.06848	2.347038	2.857842
67	6	0	1.821735	2.264891	4.161446
68	6	0	-0.994865	-1.873153	3.14548

69	1	0	-0.06848	-2.347038	2.857842
70	6	0	-1.821735	-2.264891	4.161446
71	8	0	-2.909919	-1.417328	4.25958
72	8	0	2.909919	1.417328	4.25958
73	6	0	-1.765361	-3.363713	5.117962
74	6	0	-2.765437	-3.522189	6.093444
75	6	0	-0.704454	-4.287296	5.081559
76	6	0	-2.702657	-4.574443	7.004456
77	1	0	-3.587202	-2.815512	6.130797
78	6	0	-0.647551	-5.335936	5.993895
79	1	0	0.078008	-4.181404	4.335885
80	6	0	-1.646105	-5.485647	6.960413
81	1	0	-3.483704	-4.68183	7.75246
82	1	0	0.179571	-6.039481	5.951182
83	1	0	-1.599532	-6.305275	7.672135
84	6	0	1.765361	3.363713	5.117962
85	6	0	2.765437	3.522189	6.093444
86	6	0	0.704454	4.287296	5.081559
87	6	0	2.702657	4.574443	7.004456
88	1	0	3.587202	2.815512	6.130797
89	6	0	0.647551	5.335936	5.993895
90	1	0	-0.078008	4.181404	4.335885
91	6	0	1.646105	5.485647	6.960413
92	1	0	3.483704	4.68183	7.75246
93	1	0	-0.179571	6.039481	5.951182
94	1	0	1.599532	6.305275	7.672135
95	1	0	-1.914041	-1.89806	-0.411264
96	1	0	-1.914041	1.89806	0.411264
97	1	0	1.914041	1.89806	-0.411264
98	1	0	1.914041	-1.89806	0.411264

Conformation 2 (**TBFE-c2**):

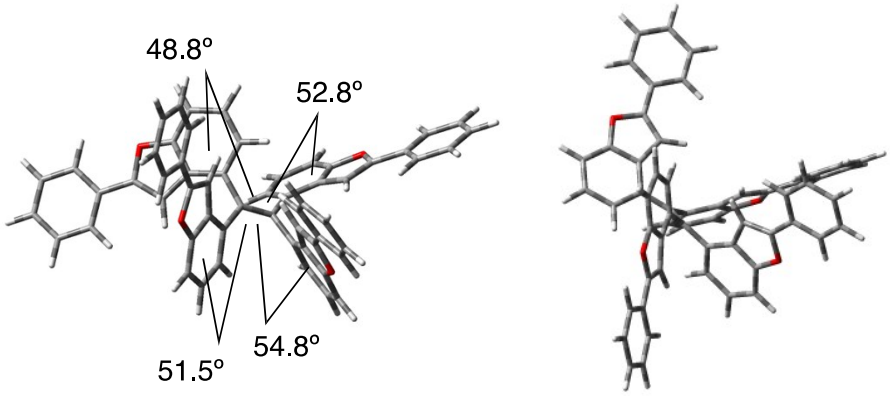


***Figure* S2.** Optimized structure of **TBFE-c2** and dihedral angles between the BF unit and central alkene structure.

***Table* S2.** Theoretically optimized coordinates of **TBFE-c2** (calculated at the B3LYP/6-31G* level of theory).

Total energy: *E*(RB3LYP/6-31G*) = –2532.76497285 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.472662	-0.954036	0.568073
2	6	0	0.734704	-1.451061	0.97805
3	6	0	1.280968	-2.735017	0.44651
4	6	0	2.585721	-2.828306	-0.093517
5	6	0	0.538919	-3.921412	0.512578
6	6	0	3.054881	-4.074481	-0.55091
7	6	0	1.043847	-5.150433	0.057534
8	6	0	2.321706	-5.251659	-0.491754
9	1	0	0.424555	-6.039158	0.137739
10	1	0	2.727566	-6.191201	-0.851596
11	6	0	-1.175424	-1.489495	-0.635443
12	6	0	-0.518073	-1.605378	-1.86874

13	6	0	-1.162286	-2.070974	-3.025865
14	6	0	-2.505038	-2.449123	-3.006526
15	1	0	-0.601328	-2.136906	-3.953686
16	1	0	-3.020067	-2.814029	-3.888834
17	6	0	-1.174582	0.142747	1.294303
18	6	0	-1.352714	0.096965	2.684403
19	6	0	-2.037045	1.098818	3.390839
20	6	0	-2.578752	2.206181	2.73842
21	1	0	-2.145523	1.006827	4.467691
22	1	0	-3.106026	2.993332	3.266743
23	6	0	1.58654	-0.792651	2.01295
24	6	0	1.970542	0.568098	1.939376
25	6	0	2.107726	-1.536316	3.081493
26	6	0	2.816271	1.1003	2.933087
27	6	0	2.936992	-0.96894	4.061352
28	6	0	3.311463	0.373808	4.006293
29	1	0	3.298523	-1.59136	4.874822
30	1	0	3.95969	0.828232	4.748044
31	6	0	-2.405402	2.246185	1.36258
32	6	0	-1.736694	1.254179	0.619079
33	6	0	-1.788093	1.708526	-0.74476
34	1	0	-1.393421	1.198918	-1.610832
35	6	0	-2.462906	2.898761	-0.745199
36	8	0	-2.84648	3.242176	0.53662
37	6	0	-3.153137	-2.330254	-1.785635
38	6	0	-2.542272	-1.857594	-0.607159
39	6	0	-3.569562	-1.912066	0.397128
40	1	0	-3.476443	-1.618183	1.431598
41	6	0	-4.697466	-2.39101	-0.209202
42	8	0	-4.459025	-2.653248	-1.545879
43	6	0	-2.835793	3.826575	-1.806642
44	6	0	-3.507963	5.025626	-1.510861

45	6	0	-2.528514	3.536729	-3.148875
46	6	0	-3.859894	5.907312	-2.530568
47	1	0	-3.75061	5.257944	-0.479721
48	6	0	-2.881955	4.421807	-4.162414
49	1	0	-2.016003	2.612108	-3.397837
50	6	0	-3.549391	5.611894	-3.859106
51	1	0	-4.379648	6.829535	-2.284857
52	1	0	-2.638178	4.181	-5.193655
53	1	0	-3.825767	6.30095	-4.6524
54	6	0	-6.04516	-2.665406	0.27478
55	6	0	-7.023048	-3.197056	-0.584311
56	6	0	-6.391679	-2.403038	1.613025
57	6	0	-8.308377	-3.458837	-0.115122
58	1	0	-6.766558	-3.401874	-1.617925
59	6	0	-7.676868	-2.667197	2.075612
60	1	0	-5.651526	-1.98779	2.290744
61	6	0	-8.642341	-3.196643	1.214656
62	1	0	-9.052048	-3.86986	-0.792682
63	1	0	-7.927081	-2.45775	3.11218
64	1	0	-9.645496	-3.4015	1.578296
65	6	0	1.740755	1.650108	1.022472
66	1	0	1.141095	1.623332	0.125912
67	6	0	2.418671	2.735126	1.504041
68	6	0	3.653316	-1.902511	-0.355847
69	1	0	3.661794	-0.845521	-0.134703
70	6	0	4.669051	-2.616018	-0.929535
71	8	0	4.318457	-3.947815	-1.056982
72	8	0	3.085035	2.415316	2.672688
73	6	0	5.994919	-2.244504	-1.40905
74	6	0	6.848484	-3.204578	-1.980573
75	6	0	6.444968	-0.915169	-1.307229
76	6	0	8.114145	-2.842101	-2.436245

77	1	0	6.511565	-4.232095	-2.063047
78	6	0	7.709786	-0.559515	-1.764619
79	1	0	5.801615	-0.159569	-0.866044
80	6	0	8.551517	-1.520593	-2.331639
81	1	0	8.761366	-3.596821	-2.875148
82	1	0	8.040638	0.471885	-1.677266
83	1	0	9.539121	-1.240578	-2.687687
84	6	0	2.559015	4.105336	1.026288
85	6	0	3.458428	4.994216	1.640802
86	6	0	1.79256	4.561435	-0.062096
87	6	0	3.590356	6.299816	1.172806
88	1	0	4.050127	4.652769	2.483249
89	6	0	1.930933	5.865834	-0.52598
90	1	0	1.075218	3.896493	-0.534188
91	6	0	2.831064	6.741504	0.087746
92	1	0	4.290449	6.974511	1.658417
93	1	0	1.32822	6.202328	-1.365157
94	1	0	2.935539	7.760433	-0.274871
95	1	0	0.528303	-1.322467	-1.927726
96	1	0	-0.461615	-3.885478	0.932316
97	1	0	-0.946297	-0.747223	3.231716
98	1	0	1.853413	-2.589739	3.153686

Conformation 3 (TBFE-c3):

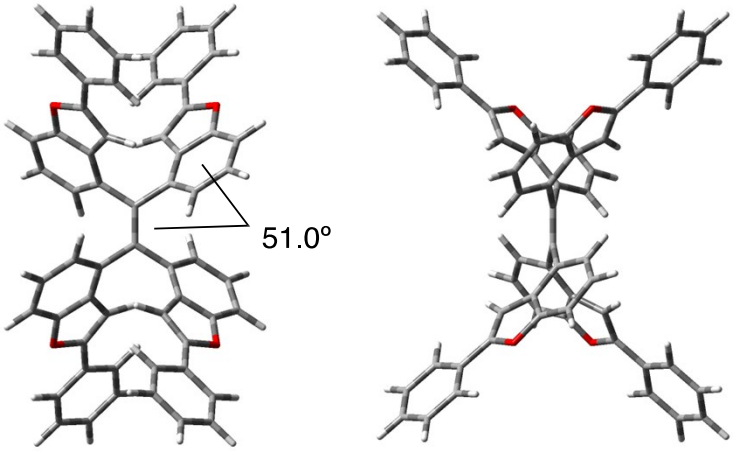


***Figure* S3.** Optimized structure of **TBFE-c3** and a dihedral angle between the BF unit and central alkene structure.

***Table* S3.** Theoretically optimized coordinates of **TBFE-c3** (calculated at the B3LYP/6-31G* level of theory).

Total energy: *E*(RB3LYP/6-31G*) = –2532.76478938 Hartree

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0	0	-0.684465
2	6	0	0	0	0.684465
3	6	0	-1.253149	0.159253	1.478439
4	6	0	-1.580424	-0.700728	2.554399
5	6	0	-2.141525	1.214102	1.222935
6	6	0	-2.763283	-0.470873	3.284856
7	6	0	-3.306866	1.418002	1.978317
8	6	0	-3.645639	0.569783	3.032974
9	1	0	-3.955727	2.254591	1.735456
10	1	0	-4.54252	0.709092	3.627159
11	6	0	-1.253149	-0.159253	-1.478439
12	6	0	-2.141525	-1.214102	-1.222935

13	6	0	-3.306866	-1.418002	-1.978317
14	6	0	-3.645639	-0.569783	-3.032974
15	1	0	-3.955727	-2.254591	-1.735456
16	1	0	-4.54252	-0.709092	-3.627159
17	6	0	1.253149	0.159253	-1.478439
18	6	0	2.141525	1.214102	-1.222935
19	6	0	3.306866	1.418002	-1.978317
20	6	0	3.645639	0.569783	-3.032974
21	1	0	3.955727	2.254591	-1.735456
22	1	0	4.54252	0.709092	-3.627159
23	6	0	1.253149	-0.159253	1.478439
24	6	0	1.580424	0.700728	2.554399
25	6	0	2.141525	-1.214102	1.222935
26	6	0	2.763283	0.470873	3.284856
27	6	0	3.306866	-1.418002	1.978317
28	6	0	3.645639	-0.569783	3.032974
29	1	0	3.955727	-2.254591	1.735456
30	1	0	4.54252	-0.709092	3.627159
31	6	0	2.763283	-0.470873	-3.284856
32	6	0	1.580424	-0.700728	-2.554399
33	6	0	0.994865	-1.873153	-3.14548
34	1	0	0.06848	-2.347038	-2.857842
35	6	0	1.821735	-2.264891	-4.161446
36	8	0	2.909919	-1.417328	-4.25958
37	6	0	-2.763283	0.470873	-3.284856
38	6	0	-1.580424	0.700728	-2.554399
39	6	0	-0.994865	1.873153	-3.14548
40	1	0	-0.06848	2.347038	-2.857842
41	6	0	-1.821735	2.264891	-4.161446
42	8	0	-2.909919	1.417328	-4.25958
43	6	0	1.765361	-3.363713	-5.117962
44	6	0	2.765437	-3.522189	-6.093444

45	6	0	0.704454	-4.287296	-5.081559
46	6	0	2.702657	-4.574443	-7.004456
47	1	0	3.587202	-2.815512	-6.130797
48	6	0	0.647551	-5.335936	-5.993895
49	1	0	-0.078008	-4.181404	-4.335885
50	6	0	1.646105	-5.485647	-6.960413
51	1	0	3.483704	-4.68183	-7.75246
52	1	0	-0.179571	-6.039481	-5.951182
53	1	0	1.599532	-6.305275	-7.672135
54	6	0	-1.765361	3.363713	-5.117962
55	6	0	-2.765437	3.522189	-6.093444
56	6	0	-0.704454	4.287296	-5.081559
57	6	0	-2.702657	4.574443	-7.004456
58	1	0	-3.587202	2.815512	-6.130797
59	6	0	-0.647551	5.335936	-5.993895
60	1	0	0.078008	4.181404	-4.335885
61	6	0	-1.646105	5.485647	-6.960413
62	1	0	-3.483704	4.68183	-7.75246
63	1	0	0.179571	6.039481	-5.951182
64	1	0	-1.599532	6.305275	-7.672135
65	6	0	0.994865	1.873153	3.14548
66	1	0	0.06848	2.347038	2.857842
67	6	0	1.821735	2.264891	4.161446
68	6	0	-0.994865	-1.873153	3.14548
69	1	0	-0.06848	-2.347038	2.857842
70	6	0	-1.821735	-2.264891	4.161446
71	8	0	-2.909919	-1.417328	4.25958
72	8	0	2.909919	1.417328	4.25958
73	6	0	-1.765361	-3.363713	5.117962
74	6	0	-2.765437	-3.522189	6.093444
75	6	0	-0.704454	-4.287296	5.081559
76	6	0	-2.702657	-4.574443	7.004456

77	1	0	-3.587202	-2.815512	6.130797
78	6	0	-0.647551	-5.335936	5.993895
79	1	0	0.078008	-4.181404	4.335885
80	6	0	-1.646105	-5.485647	6.960413
81	1	0	-3.483704	-4.68183	7.75246
82	1	0	0.179571	-6.039481	5.951182
83	1	0	-1.599532	-6.305275	7.672135
84	6	0	1.765361	3.363713	5.117962
85	6	0	2.765437	3.522189	6.093444
86	6	0	0.704454	4.287296	5.081559
87	6	0	2.702657	4.574443	7.004456
88	1	0	3.587202	2.815512	6.130797
89	6	0	0.647551	5.335936	5.993895
90	1	0	-0.078008	4.181404	4.335885
91	6	0	1.646105	5.485647	6.960413
92	1	0	3.483704	4.68183	7.75246
93	1	0	-0.179571	6.039481	5.951182
94	1	0	1.599532	6.305275	7.672135
95	1	0	-1.914041	-1.89806	-0.411264
96	1	0	-1.914041	1.89806	0.411264
97	1	0	1.914041	1.89806	-0.411264
98	1	0	1.914041	-1.89806	0.411264

Conformation 4 (**TBFE-c4**):

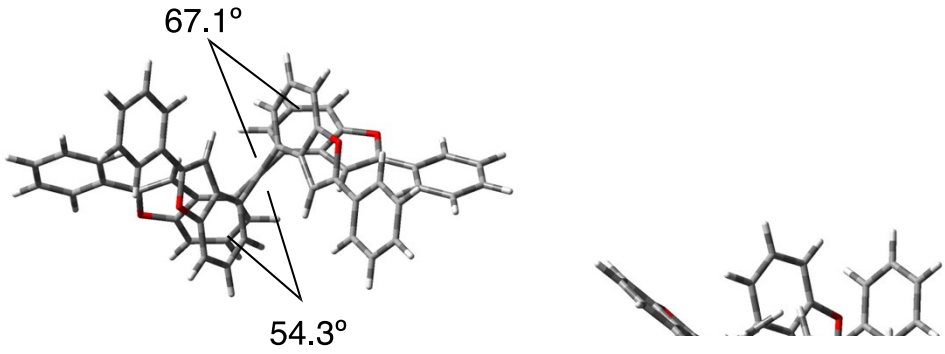


***Figure* S4.** Optimized structure of **TBFE-c4** and dihedral angles between the BF unit and central alkene structure.

***Table* S4.** Theoretically optimized coordinates of **TBFE-c4** (calculated at the B3LYP/6-31G* level of theory).

Total energy: *E*(RB3LYP/6-31G*) = –2532.76440056 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.000067	-2.165376	0.00005
2	6	0	-0.000043	-0.796416	0.000024
3	6	0	-0.717644	-0.003	1.039935
4	6	0	-1.560476	1.085209	0.70547
5	6	0	-0.553146	-0.272624	2.406115
6	6	0	-2.198507	1.805191	1.734368
7	6	0	-1.194501	0.476525	3.405463
8	6	0	-2.041421	1.537927	3.086601
9	1	0	-1.026568	0.221289	4.44782
10	1	0	-2.551095	2.12426	3.843692
11	6	0	-0.909744	-2.98	0.861411
12	6	0	-0.39626	-4.011452	1.661231
13	6	0	-1.214679	-4.8236	2.460708
14	6	0	-2.600926	-4.663566	2.476637
15	1	0	-0.758745	-5.596036	3.073367
16	1	0	-3.252015	-5.288337	3.078883

17	6	0	0.909591	-2.980067	-0.861284
18	6	0	0.396086	-4.011558	-1.661031
19	6	0	1.214482	-4.82379	-2.460449
20	6	0	2.600731	-4.663794	-2.476387
21	1	0	0.758521	-5.59626	-3.073045
22	1	0	3.251812	-5.288632	-3.078572
23	6	0	0.717614	-0.003063	-1.039898
24	6	0	1.560533	1.085082	-0.705438
25	6	0	0.553105	-0.272696	-2.406077
26	6	0	2.198641	1.804981	-1.734347
27	6	0	1.194535	0.476376	-3.40543
28	6	0	2.041548	1.537709	-3.086575
29	1	0	1.026592	0.221139	-4.447784
30	1	0	2.55129	2.123984	-3.843665
31	6	0	3.107548	-3.661443	-1.662623
32	6	0	2.314884	-2.815214	-0.860989
33	6	0	3.247382	-1.962456	-0.178187
34	1	0	3.014719	-1.185784	0.533733
35	6	0	4.498181	-2.317377	-0.599049
36	8	0	4.431492	-3.358938	-1.506704
37	6	0	-3.107724	-3.661275	1.662789
38	6	0	-2.315031	-2.815124	0.861096
39	6	0	-3.247508	-1.962419	0.178201
40	1	0	-3.014846	-1.185897	-0.533884
41	6	0	-4.498313	-2.317259	0.5991
42	8	0	-4.431661	-3.358753	1.50684
43	6	0	5.829489	-1.82014	-0.273574
44	6	0	6.979032	-2.503401	-0.707589
45	6	0	5.985348	-0.644437	0.483571
46	6	0	8.247409	-2.026409	-0.384239
47	1	0	6.868376	-3.408297	-1.295269
48	6	0	7.255033	-0.174847	0.805245

49	1	0	5.109099	-0.088894	0.804893
50	6	0	8.392517	-0.863595	0.374532
51	1	0	9.126074	-2.566963	-0.726192
52	1	0	7.356934	0.737005	1.387415
53	1	0	9.382915	-0.493413	0.625034
54	6	0	-5.829596	-1.82004	0.273496
55	6	0	-6.979174	-2.503824	0.70659
56	6	0	-5.985368	-0.643838	-0.48289
57	6	0	-8.247513	-2.02686	0.383048
58	1	0	-6.86857	-3.409099	1.293699
59	6	0	-7.255017	-0.174289	-0.804779
60	1	0	-5.109083	-0.087887	-0.803406
61	6	0	-8.392536	-0.863564	-0.375003
62	1	0	-9.126214	-2.567818	0.724271
63	1	0	-7.356865	0.737949	-1.386352
64	1	0	-9.382905	-0.49341	-0.625659
65	6	0	2.015944	1.692554	0.516309
66	1	0	1.729372	1.41791	1.520342
67	6	0	2.865339	2.706557	0.166969
68	6	0	-2.015886	1.692668	-0.516286
69	1	0	-1.729405	1.417936	-1.520323
70	6	0	-2.865187	2.706751	-0.166962
71	8	0	-2.988288	2.788263	1.20664
72	8	0	2.988494	2.788008	-1.206623
73	6	0	-3.631417	3.671988	-0.946717
74	6	0	-4.515027	4.565567	-0.316114
75	6	0	-3.501496	3.724087	-2.346844
76	6	0	-5.248195	5.481384	-1.067558
77	1	0	-4.621538	4.533886	0.762642
78	6	0	-4.237523	4.640232	-3.09164
79	1	0	-2.815891	3.049189	-2.850942
80	6	0	-5.114976	5.523626	-2.456505

81	1	0	-5.92707	6.164777	-0.564463
82	1	0	-4.123409	4.667784	-4.171964
83	1	0	-5.687338	6.239332	-3.040165
84	6	0	3.631602	3.671766	0.946726
85	6	0	4.51498	4.565554	0.31609
86	6	0	3.501939	3.723641	2.346883
87	6	0	5.248165	5.481358	1.067531
88	1	0	4.621298	4.534042	-0.76269
89	6	0	4.237973	4.639784	3.091677
90	1	0	2.816548	3.048554	2.851019
91	6	0	5.115189	5.523388	2.456509
92	1	0	5.92686	6.164911	0.56441
93	1	0	4.12406	4.667158	4.172026
94	1	0	5.687562	6.239087	3.040167
95	1	0	0.676511	-4.181667	1.664221
96	1	0	0.094432	-1.092616	2.69888
97	1	0	-0.676691	-4.181742	-1.664027
98	1	0	-0.094539	-1.092641	-2.698822

Conformation 5 (**TBFE-c5**):

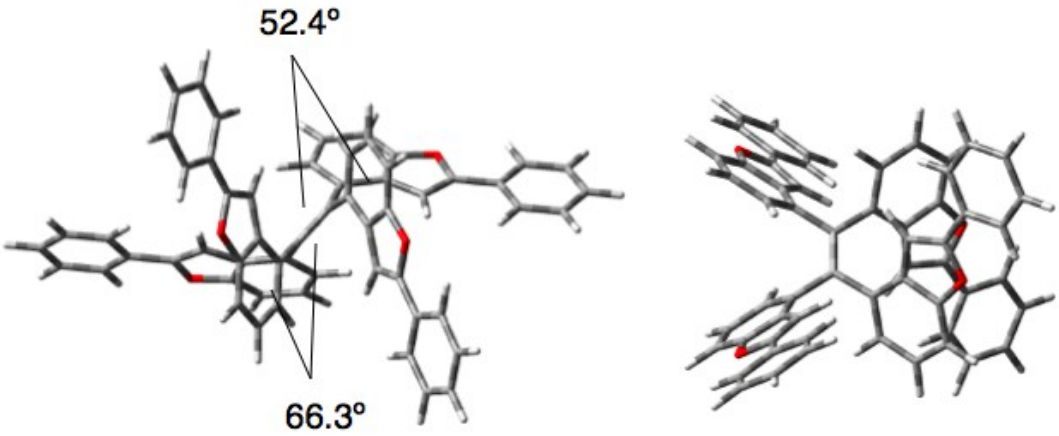


***Figure* S5.** Optimized structure of **TBFE-c5** and dihedral angles between the BF unit and central alkene structure.

***Table* S5.** Theoretically optimized coordinates of **TBFE-c5** (calculated at the B3LYP/6-31G* level of theory).

Total energy: *E*(RB3LYP/6-31G*) = –2532.76338993 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.460103	-0.678823	-0.505498
2	6	0	-0.460195	-0.678822	0.505858
3	6	0	-1.10091	0.557382	1.043793
4	6	0	-1.746145	1.514012	0.223514
5	6	0	-1.15447	0.779702	2.427851
6	6	0	-2.366013	2.628965	0.824112
7	6	0	-1.768086	1.909303	2.989818
8	6	0	-2.39152	2.867178	2.190173
9	1	0	-1.763944	2.034332	4.068735
10	1	0	-2.883052	3.741094	2.604184
11	6	0	1.100794	0.557407	-1.043418
12	6	0	1.154259	0.779759	-2.427476
13	6	0	1.767883	1.909345	-2.989471

14	6	0	2.391418	2.867178	-2.18986
15	1	0	1.763678	2.034384	-4.068387
16	1	0	2.882958	3.741078	-2.603897
17	6	0	0.877707	-1.942154	-1.184845
18	6	0	-0.062546	-2.801647	-1.767327
19	6	0	0.309129	-3.974697	-2.444705
20	6	0	1.647034	-4.347868	-2.570191
21	1	0	-0.46371	-4.601517	-2.880137
22	1	0	1.95301	-5.25152	-3.08664
23	6	0	-0.877877	-1.942184	1.185094
24	6	0	-2.239708	-2.30336	1.317677
25	6	0	0.062277	-2.801762	1.767613
26	6	0	-2.575537	-3.491804	1.993714
27	6	0	-0.309525	-3.974846	2.444851
28	6	0	-1.647464	-4.347979	2.570155
29	1	0	0.463233	-4.601745	2.880313
30	1	0	-1.95352	-5.251673	3.086485
31	6	0	2.575209	-3.491769	-1.993791
32	6	0	2.239512	-2.30336	-1.317627
33	6	0	3.491629	-1.750787	-0.879089
34	1	0	3.635784	-0.834584	-0.325922
35	6	0	4.474395	-2.601757	-1.30316
36	8	0	3.930187	-3.673126	-1.987777
37	6	0	2.366026	2.628927	-0.8238
38	6	0	1.746165	1.513984	-0.223179
39	6	0	2.016779	1.647426	1.181966
40	1	0	1.702334	0.976975	1.966129
41	6	0	2.738569	2.796962	1.345328
42	8	0	2.959482	3.411443	0.126895
43	6	0	5.92608	-2.586341	-1.16818
44	6	0	6.709362	-3.62807	-1.695678
45	6	0	6.570134	-1.525998	-0.504268

46	6	0	8.095812	-3.607095	-1.560256
47	1	0	6.222865	-4.449921	-2.209508
48	6	0	7.954937	-1.511192	-0.371908
49	1	0	5.982937	-0.710399	-0.092602
50	6	0	8.725624	-2.551427	-0.898835
51	1	0	8.686246	-4.420365	-1.973896
52	1	0	8.435091	-0.683886	0.143753
53	1	0	9.80705	-2.537522	-0.794565
54	6	0	3.29761	3.458898	2.517871
55	6	0	4.077342	4.621265	2.384365
56	6	0	3.06894	2.94277	3.806656
57	6	0	4.614149	5.244254	3.508948
58	1	0	4.257589	5.028613	1.395574
59	6	0	3.609221	3.568489	4.925597
60	1	0	2.460039	2.052076	3.930444
61	6	0	4.385216	4.722279	4.783206
62	1	0	5.214611	6.14196	3.388008
63	1	0	3.42199	3.156045	5.913413
64	1	0	4.805213	5.209967	5.658569
65	6	0	-3.491742	-1.750692	0.879024
66	1	0	-3.63579	-0.834307	0.326129
67	6	0	-4.474588	-2.60172	1.302791
68	6	0	-2.016616	1.647505	-1.181652
69	1	0	-1.702457	0.976877	-1.965782
70	6	0	-2.738252	2.797132	-1.345054
71	8	0	-2.959308	3.411559	-0.126628
72	8	0	-3.930524	-3.673137	1.987442
73	6	0	-3.297128	3.459111	-2.517651
74	6	0	-4.080069	4.619293	-2.383909
75	6	0	-3.065075	2.945209	-3.806717
76	6	0	-4.616798	5.242253	-3.508542
77	1	0	-4.262867	5.024966	-1.394896

78	6	0	-3.605375	3.570832	-4.925706
79	1	0	-2.453328	2.05649	-3.930671
80	6	0	-4.384623	4.722398	-4.783081
81	1	0	-5.219774	6.138249	-3.387423
82	1	0	-3.415496	3.160143	-5.913748
83	1	0	-4.804577	5.210053	-5.658485
84	6	0	-5.926255	-2.586207	1.167624
85	6	0	-6.709902	-3.626443	1.697518
86	6	0	-6.56993	-1.527244	0.501143
87	6	0	-8.096342	-3.605322	1.562001
88	1	0	-6.223696	-4.447248	2.213292
89	6	0	-7.954728	-1.512254	0.368756
90	1	0	-5.982432	-0.712944	0.08734
91	6	0	-8.725783	-2.550977	0.898118
92	1	0	-8.68706	-4.417424	1.977524
93	1	0	-8.434581	-0.686033	-0.148922
94	1	0	-9.807201	-2.536952	0.793785
95	1	0	0.700766	0.045647	-3.087576
96	1	0	-0.701047	0.045563	3.087965
97	1	0	-1.115593	-2.548973	-1.690312
98	1	0	1.115343	-2.549125	1.690711

Geometry optimization of 2-phenylbenzofuran.

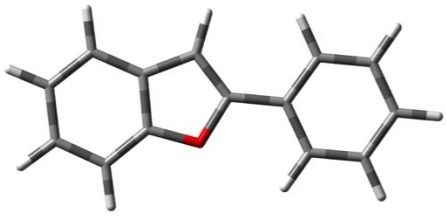


***Figure* S6.** Optimized structure of 2-phenylbenzofuran.

***Table* S6.** Theoretically optimized coordinates of 2-phenylbenzofuran (calculated at the B3LYP/6-31G* level of theory).

Total energy: *E*(RB3LYP/6-31G*) = –614.738458820 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.776875	-0.593294	-0.000026
2	6	0	-1.905217	0.809325	0.000001
3	6	0	-3.193134	1.369082	0.000029
4	6	0	-4.288713	0.510805	0.000034
5	6	0	-4.124567	-0.887477	0.000009
6	6	0	-2.855825	-1.46745	-0.000023
7	6	0	0.273384	0.229305	0.00001
8	6	0	-0.55959	1.31372	-0.000022
9	1	0	-3.331542	2.446715	0.000046
10	1	0	-5.292883	0.925709	0.000055
11	1	0	-5.001895	-1.528	0.00001
12	1	0	-2.711685	-2.542891	-0.000046
13	1	0	-0.256922	2.351277	-0.000027
14	8	0	-0.45584	-0.946463	-0.00006
15	6	0	1.725184	0.091591	0.000012
16	6	0	2.327011	-1.179149	0.000033
17	6	0	2.551721	1.230142	-0.000015
18	6	0	3.714589	-1.303361	0.000033
19	1	0	1.699144	-2.063398	0.00005

20	6	0	3.936781	1.099695	-0.000016
21	1	0	2.106484	2.220848	-0.000038
22	6	0	4.526183	-0.167662	0.000009
23	1	0	4.163043	-2.293279	0.000053
24	1	0	4.559298	1.99043	-0.000035
25	1	0	5.608092	-0.267348	0.000007

***Table* S7.** Oscillator strength f, wavelength λ, and estimated radiative rate constant k_r^o of HOMO -> LUMO excitation calculated for optimized structures of each **TBFE** conformers and 2-phenylbenzofuran. k_r^o was estimated by substituting calculated f and λ into $k_r^o \approx f/\lambda^2$.

	TBFE					BF
	1	2	3	4	5	
f	0.2163	0.3587	0.7282	0.1839	0.3312	0.7782
λ (nm)	451.68	485.01	415.03	483.59	485.15	298.65
k_r^o (10^7 s^{-1})	10.60	15.25	42.28	7.864	14.07	87.25

TD-DFT (B3LYP/6-31G*)

4. UV-Vis Absorption, Fluorescence spectra

UV-Vis absorption spectra were measured with a JASCO V-670 spectrometer. Fluorescence and excitation spectra were measured with a HITACHI F-4500 spectrometer for solution and Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer for solid. Photoluminescence quantum yields were measured on Hamamatsu Photonics C9920–02 Absolute PL Quantum Yield Measurement System, and absolute quantum yields were determined by using a calibrated integrating sphere system. Fluorescence lifetimes were measured on Hamamatsu Photonics C11367-02 Quantaurus-Tau. The absorption maximum wavelengths were used as excitation wavelengths. Spectral grade solvents (cyclohexane, dichloromethane, ethanol), anhydrous solvents purified by a solvent purification system (THF, benzonitrile), Millipore Milli-Q water were used as solvents for UV-Vis absorption and fluorescence measurements.

The radiative and nonradiative rate constants k_r and k_{nr} are calculated by substituting fluorescence quantum yield Φ_{FL} and fluorescence lifetime τ for the following formula:

$$k_r = \Phi_{FL}/\tau \qquad (1)$$

$$k_{nr} = (1-\Phi_{FL})/\tau \qquad (2)$$

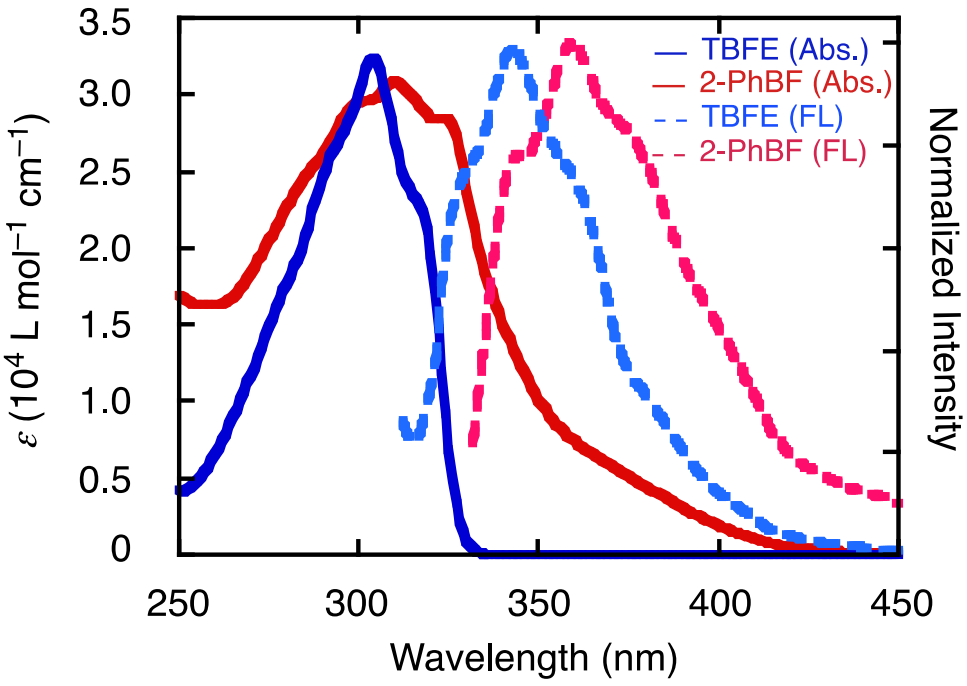


***Figure* S7.** Absorption (1.0×10^{-5} M) and fluorescence (1.0×10^{-6} M, excited at the maximum absorption wavelength) spectra of **TBFE** and 2-phenylbenzofuran in THF.

***Table* S8**. Photoluminescence properties of **TBFE** in THF/H_2O (λ_{ex} = 317 nm).

THF/H_2O (v/v)	λ_{em} (nm)	Φ_{FL}
10/90	503	0.273
20/80	510	0.259
30/70	351/530	0.159
40/60	360	0.035
50/50	360	0.030
60/40	360	0.028
70/30	359	0.033
80/20	360	0.039
90/10	360	0.048
100/0	359	0.094

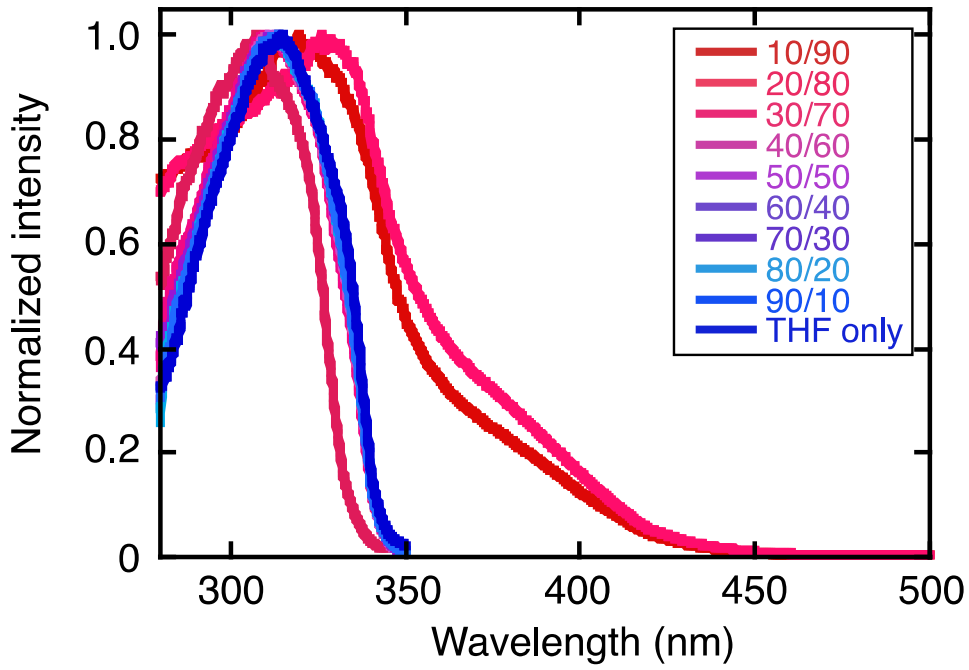


Figure S8. Excitation spectra of TBFE in THF/H2O solvents. Fluorescence wavelength λ_{FL} are 360 nm for THF/H_2O = 100/0-30/70, and 510 nm for THF/H_2O =20/80-10/90).

***Table* S9.** Fluorescence wavelengths of **TBFE** in various solvents and relative permittivity of the solvents (λ_{ex} = 317 nm).

	Relative permittivity	λ_{em} (nm)
Cyclohexane	2.02	352
THF	7.58	359
Dichloromethane	8.93	354
Ethanol	24.5	349
Benzonitrile	26.0	359

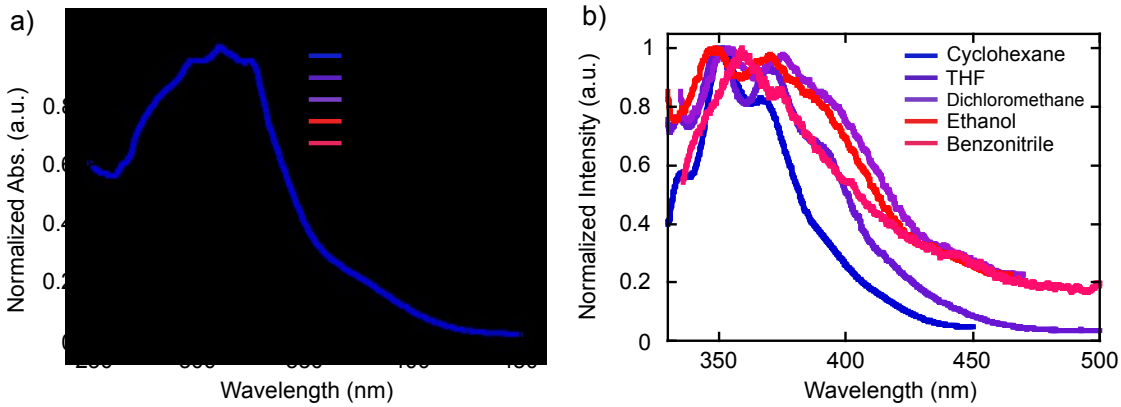


***Figure* S9.** a) Absorption and b) fluorescence spectra of **TBFE** in various solvents.

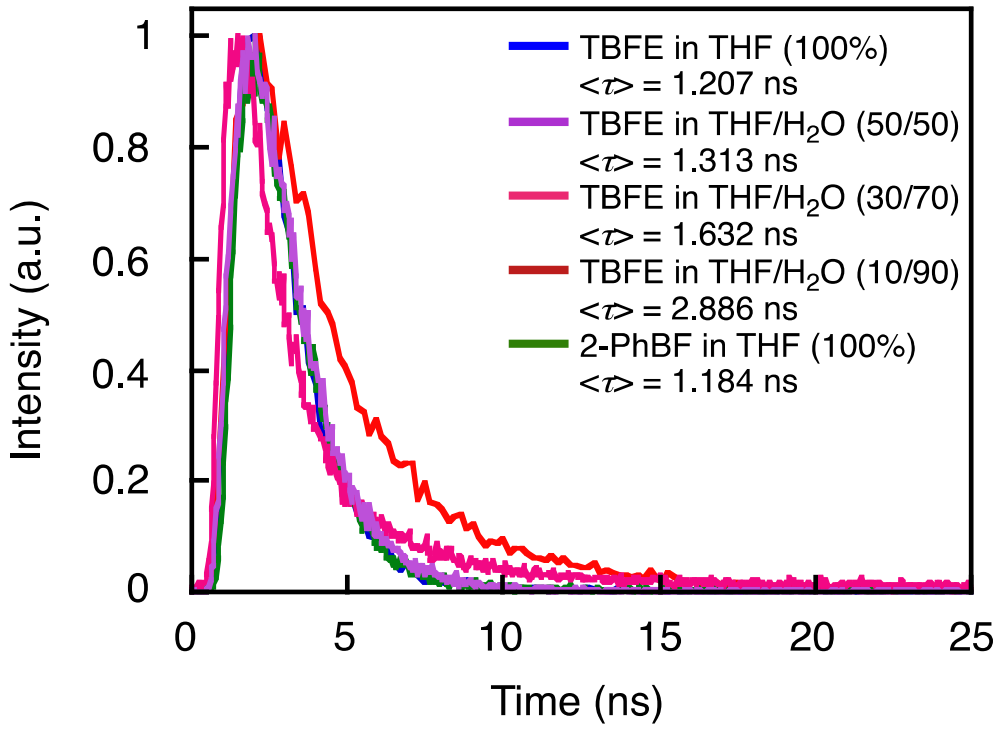


***Figure* S10.** Fluorescence decay curves of **TBFE** in THF, THF/H_2O (50/50, 30/70, 10/90), and 2-phenylbenzofuran in THF.

***Table* S10**. Fluorescence quantum yield Φ_{FL}, fluorescence lifetime τ, radiative rate constant k_r and nonradiative rate constant k_{nr} of **TBFE** and 2-phenylbenzofuran.

	TBFE in THF	**TBFE** in THF/H_2O (50/50)	**TBFE** in THF/H_2O (30/70)		
			Average	Component 1	Component 2
Φ_{FL}	0.094	0.050	0.159	0.132	0.027
Amp.				120.607	24.394
τ (ns)	1.207	1.313	1.632	0.3824	2.556
k_r (10^7 s^{-1})	7.79	3.81	9.74	34.6	1.05
k_{nr} (10^7 s^{-1})	75.1	7.23	5.15	227	3.81

	TBFE in THF/H_2O (10/90)			BF in THF
	Average	Component 1	Component 2	
Φ_{FL}	0.273	0.154	0.119	0.656
Amp.		166.093	128.169	
τ (ns)	2.886	3.579	1.031	1.184
k_r (10^7 s^{-1})	9.46	4.31	11.5	55.4
k_{nr} (10^7 s^{-1})	25.2	23.6	85.4	29.1

5. Dynamic Laser Light Scattering (DLS)

Dynamic laser light scattering (DLS) study on size distribution was carried out on a Malvern Zetasizer Nano ZS machine.

TBFE (31 mg, 38.9 μmol) was dissolved in 10 mL THF. 1 mL of the solution was added in 10 mL measuring flasks and diluted with water and THF to make the sample solutions (0.39 mM, THF/H_2O = 100/0–10/90). After sonication for 10 min, each solution was put in glass cells and the measurement took place at 25 °C. Viscosity and refractive index of the mixed solvents at ambient temperature (*Table* S11) were estimated from their mole fraction of THF by linear interpolations of the values previously reported by Walter *et al*.[4] The estimated values were used for transformation of the resulting correlation function into volume distribution. The correlation functions obtained in the measurements (*Figure* S10) were output as volume distribution through the treatment of a Malvern Zetasizer Nano ZS software.

***Table* S11.** Estimated viscosity and refractive index of THF/H_2O at 25 °C.

THF/H_2O (v/v)	Mole fraction of THF	Viscosity (cps)	Refractive index ($n^{25}D$)
10/90	0.283	1.47	1.384
20/80	0.470	1.02	1.395
30/70	0.604	0.796	1.399
40/60	0.703	0.676	1.401
50/50	0.780	0.604	1.402
60/40	0.842	0.558	1.403
70/30	0.892	0.529	1.403
80/20	0.934	0.506	1.404
90/10	0.970	0.486	1.404
100/0	1.000	0.470	1.405

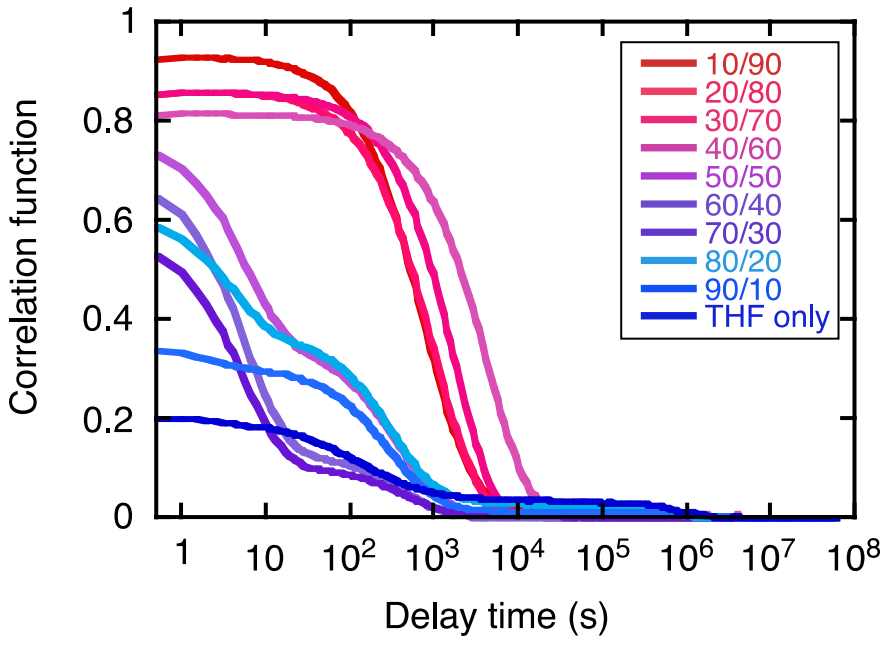


***Figure* S11.** The resulting correlation functions of **TBFE** solutions obtained by DLS measurement.

6. Scanning Electron Microscopy (SEM)

SEM observation was performed on an FEI Magellan 400L instrument scanning electron microscope equipped with AMETEK/EDAZ Genesis APEX4 instrument at a landing voltage of 1 kV under a reduced pressure of 5×10^{-5} Pa.

A solution of **TBFE** (10 μL, 0.4 mM) were deposited on the surface of an ITO / glass substrate treated by UV/ozone and spin coated. The sample was dried under reduced pressure (10^{-2} Pa) at room temperature for 2 h prior to measurement.

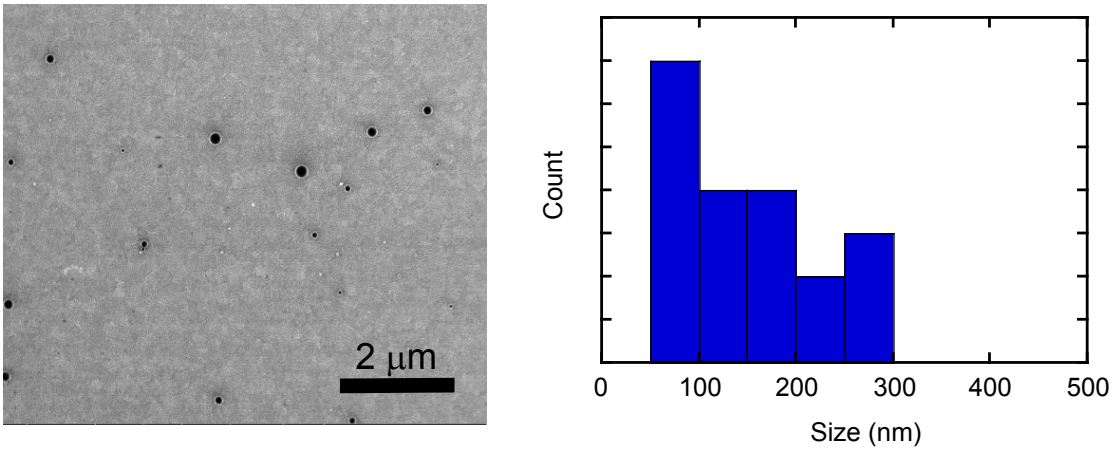


***Figure* S12.** SEM image of aggregations of **TBFE** on in ITO formed by the spin-coating using THF/H_2O = 10/90 (left) and the histogram on diameters of the aggregations (right).

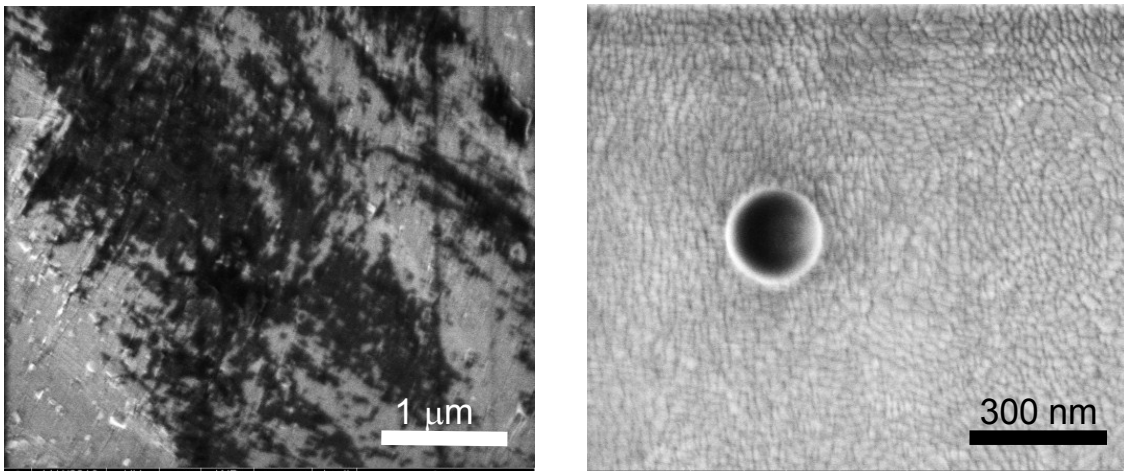


Figure S13. SEM images of TBFE on ITO surface. Left: TBEF from THF solution stuck on ITO surface can be seen as black stains. Right: TBFE from 90% water solution forms spherical aggregation.

7. Powder XRD

Powder XRD experiment was performed on a Rigaku SmartLab X-ray diffractometer equipped with a scintillation counter. The measurement employed Cu Kα (l = 1.5419 Å) radiation at 9 kW (45 kV, 200mA) power.

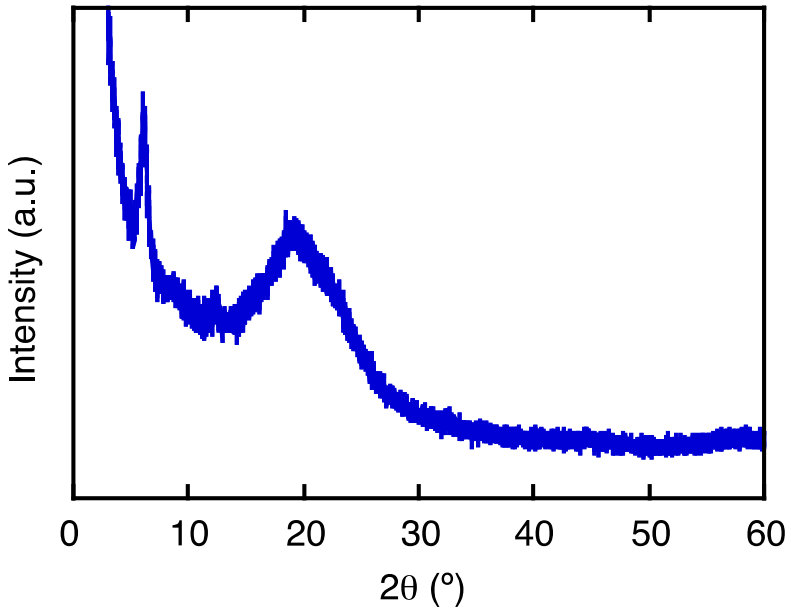
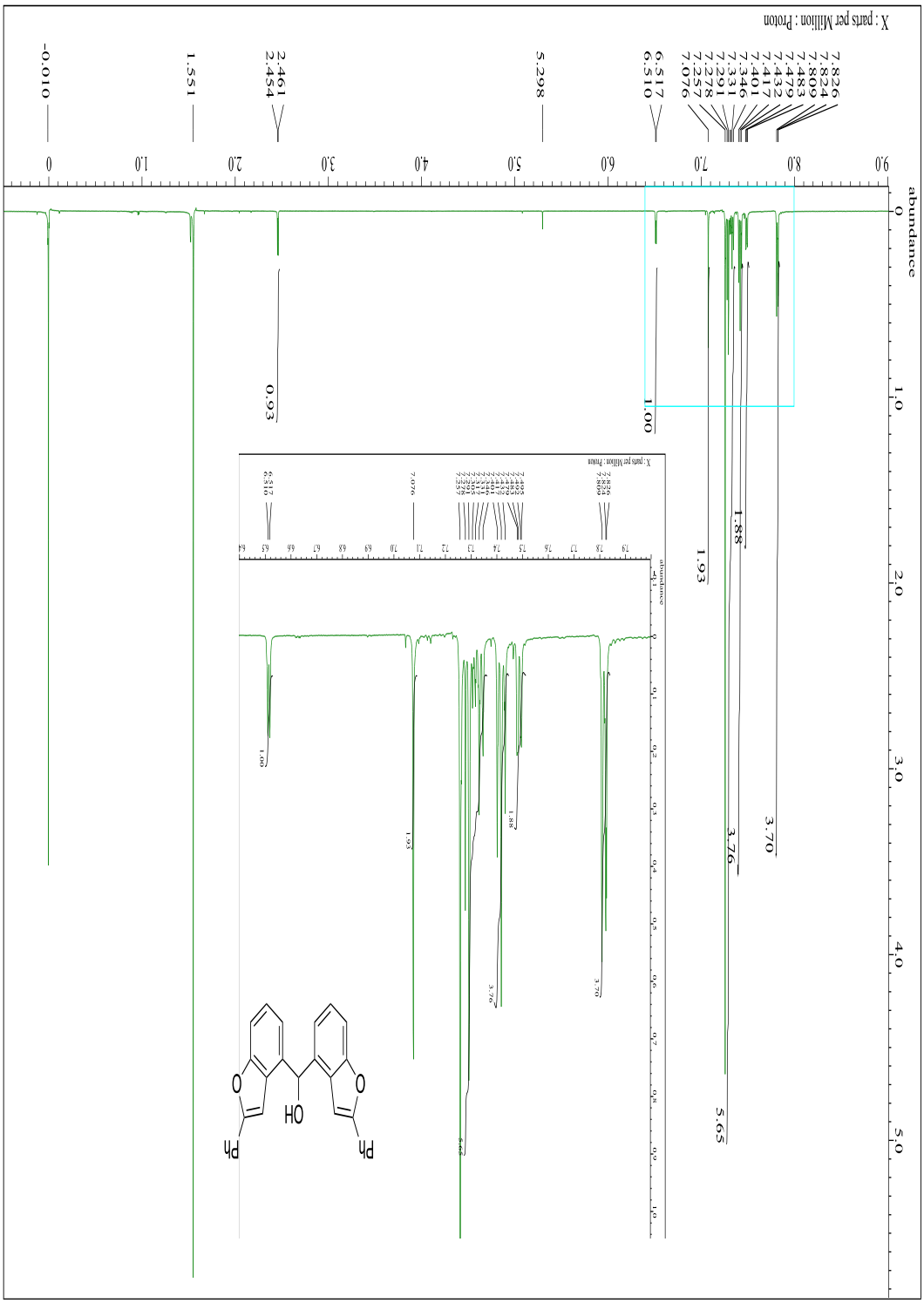


Figure S14. XRD diffraction pattern of TBFE powder obtained from THF/H_2O = 10/90 solution.

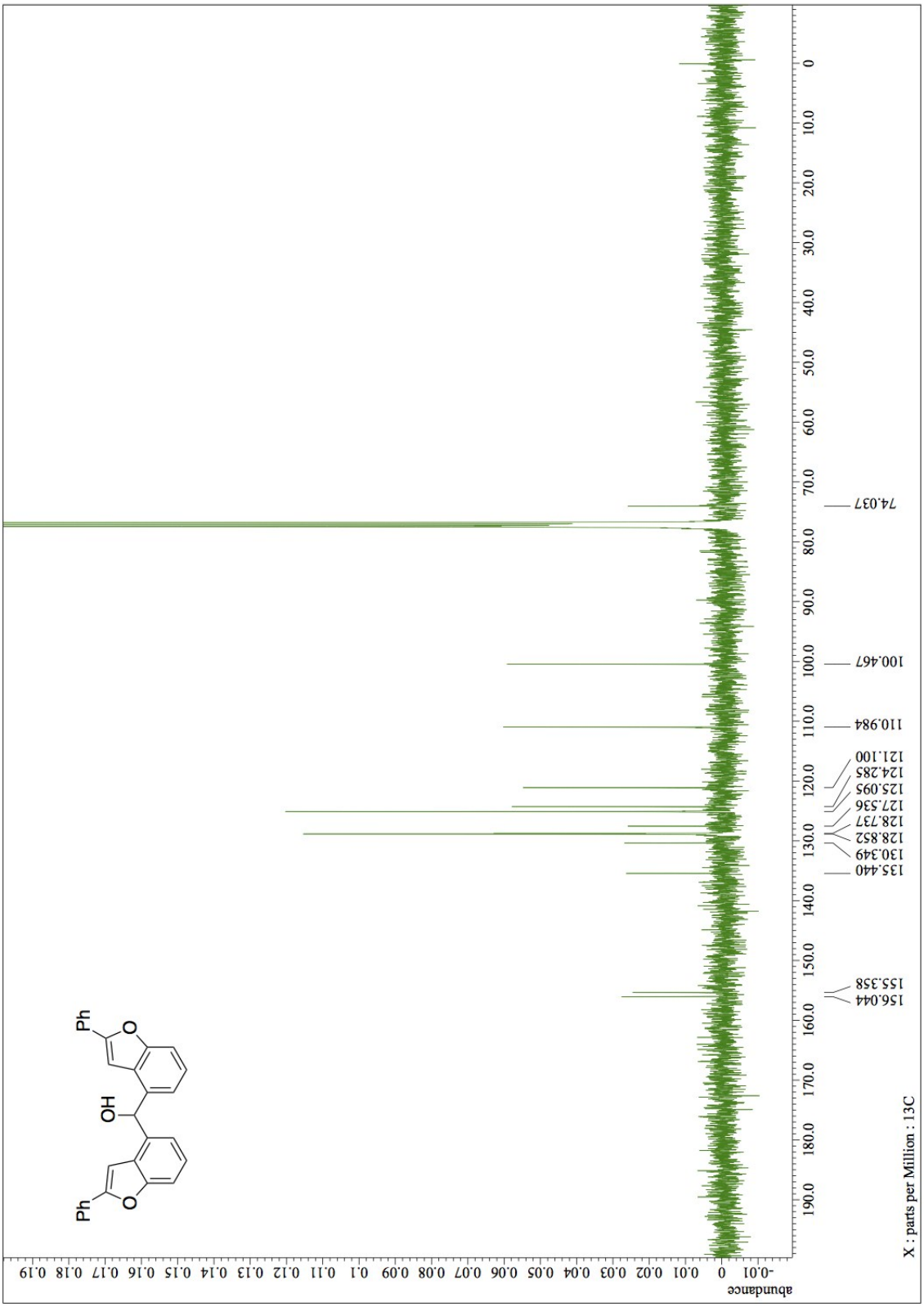
8. NMR charts

^{1}H NMR spectrum of **6** in $CDCl_3$.

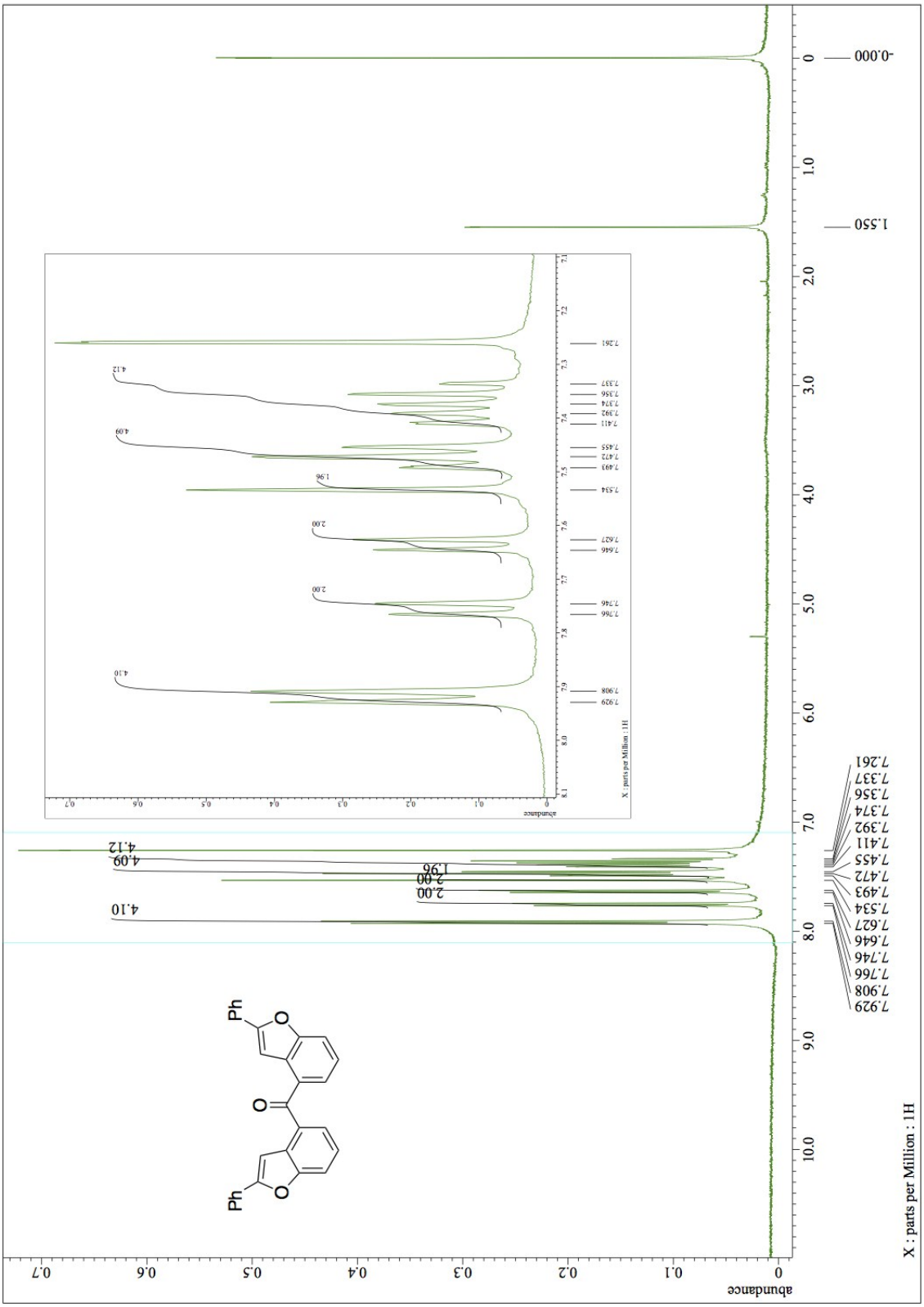
The peak at 5.298 ppm corresponds to dichrolomethane.



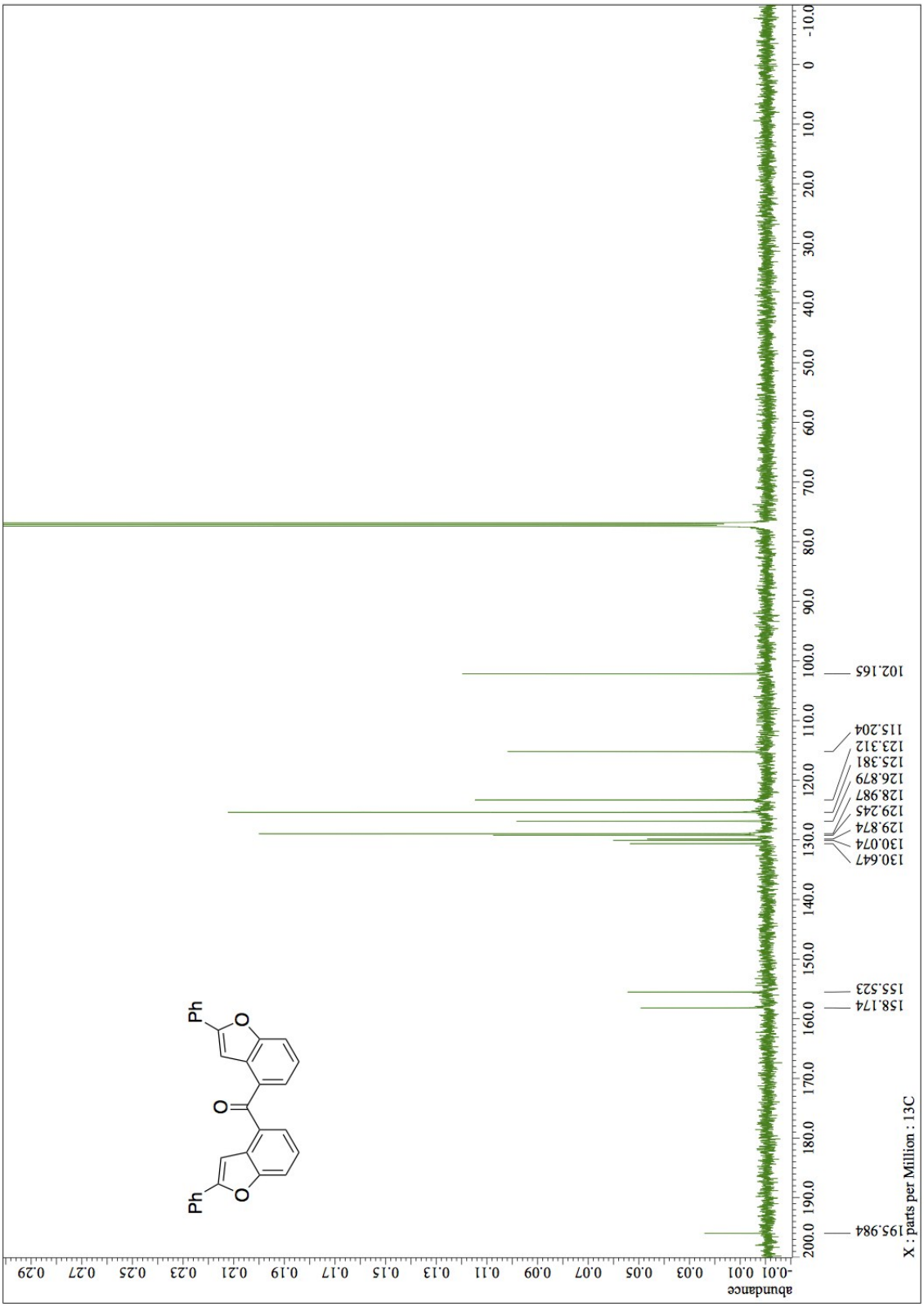
^{13}C NMR spectrum of **6** in $CDCl_3$.



^{1}H NMR spectrum of **7** in $CDCl_3$.

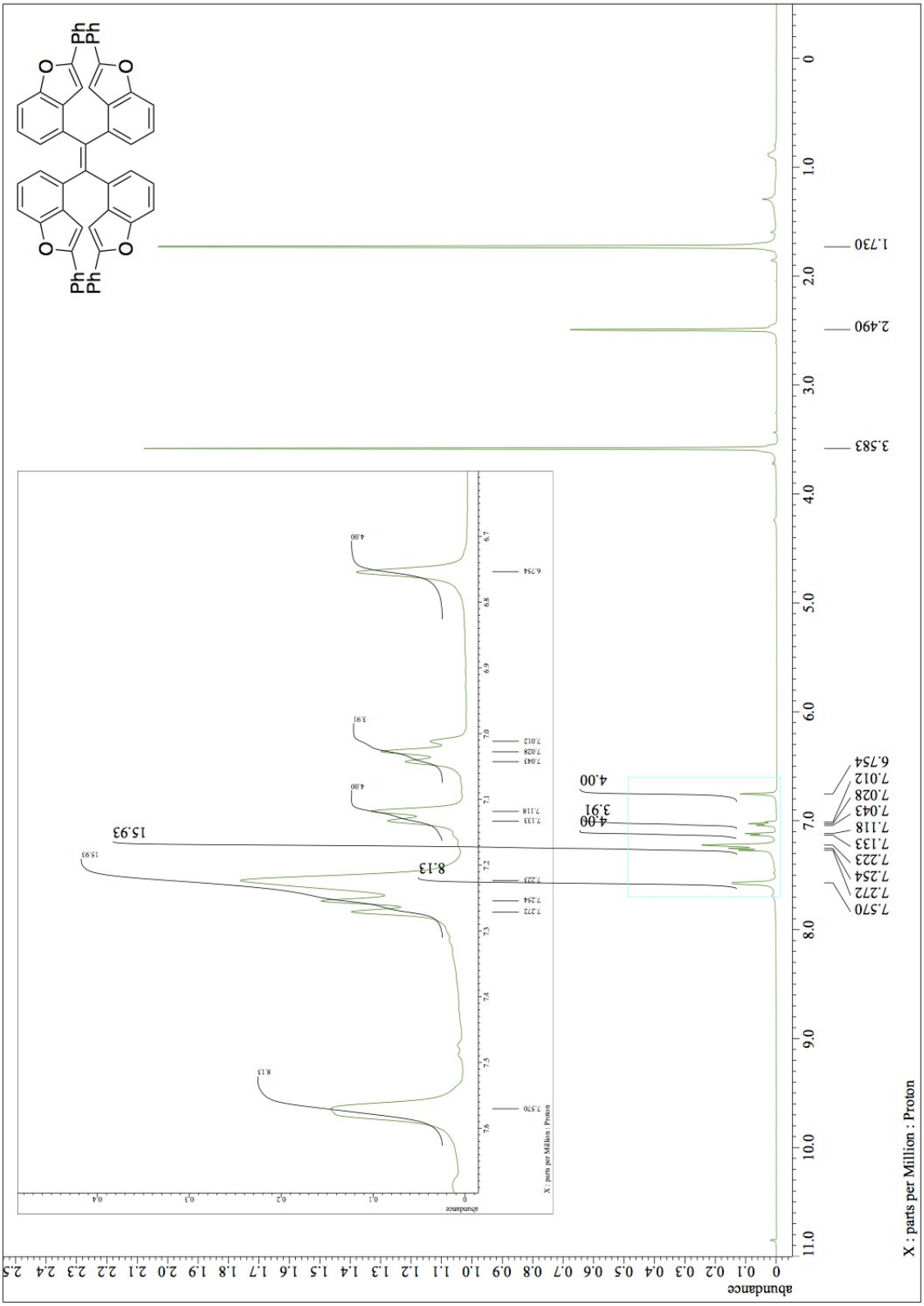


^{13}C NMR spectrum of **7** in $CDCl_3$.



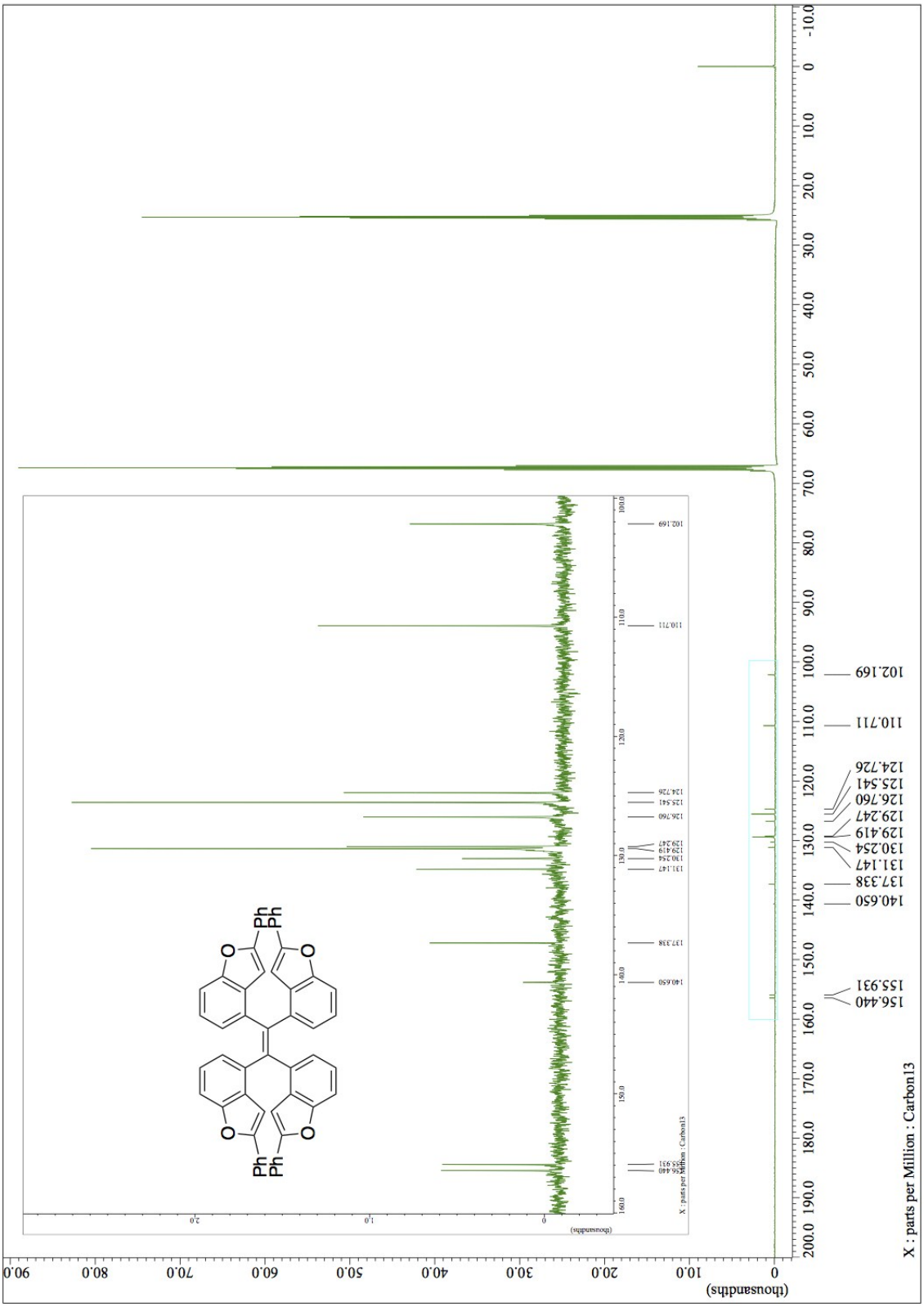
^{1}H NMR spectrum of **8** in THF-d_8.

The peak at 10.8 ppm corresponds to an impurity in the deuterated solvent.



^{13}C NMR spectrum of **8** in THF-d_8.

The peak at 10.8 ppm corresponds to an impurity in the deuterated solvent.



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