Electronic Supplementary Information (ESI)

Stereoselective synthesis of folded luminogens with arene-arene stacking interactions and aggregation-enhanced emission

Experimental

General

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Chemicals and reagents were purchased from Aldrich and used as received without further purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 400 or 500 spectrometer in deuterated chloroform using tetramethylsilane (TMS; $\delta = 0$) as internal reference. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in a MALDT-TOF mode. Single crystal X-ray diffraction intensity data were collected on a Bruker–Nonices Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10). Photoluminescence spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. The UV-vis spectra were recorded on a Perkin-Elmer Lambda 750.

Synthesis

(*Z*)-1,2-Di(biphenyl-2-yl)-1,2-diphenylethene ((*Z*)-*o*-BPTPE): To a solution of 2-phenylbenzophenone (1.3 g, 5 mmol), zinc dust (0.78 g, 12 mmol) in 80 mL dry THF was added dropwise titanium(IV) chloride (1.15 g, 6 mmol) under nitrogen at –78 ^{o}C. After stirring for 20 min, the reaction mixture was warmed to room temperature and then heated to reflux for 12 h. The reaction mixture was cooled to room temperature and poured into water. The organic layer was extracted with dichloromethane and the combined organic layers were washed with saturated brine solution and water, and dried over anhydrous

magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. White solid of (*Z*)-*o*-BPTPE was obtained in 50% yield. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.24–7.16 (m, 10H), 7.09–7.03 (br, 14H), 6.72–6.69 (m, 2H), 5.71 (d, 2H, J = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 144.8, 141.6, 141.2, 141.1, 138.8, 132.5, 131.4, 129.5, 129.0, 127.7, 127.5, 126.9, 126.7, 126.3, 126.2. HRMS (MALDT-TOF): *m*/*z* 484.2187 (M^+, calcd 484.2191). Anal. Calcd for $C_{38}H_{28}$: C, 94.18; H, 5.82. Found: C, 94.10; H, 5.63.

(*Z*)-1,2-Bis(4'-phenylbiphenyl-2-yl)-1,2-diphenylethene ((*Z*)-*o*-BBPTPE): The procedure was analogous to that described for (*Z*)-*o*-BPTPE. White solid, yield 56%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.60 (d, 4H, J = 7.5 Hz), 7.48–7.43 (m, 8H), 7.36–7.33 (m, 2H), 7.27 (d, 4H, J = 8.0 Hz), 7.11 (d, 4H, J = 4.5 Hz), 7.07 (br, 10H), 6.74–6.71 (m, 2H), 5.83 (d, 2H, J = 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 144.9, 141.1, 141.0, 140.7, 140.6, 139.1, 138.8, 132.5, 131.4, 129.5, 129.2, 128.8, 127.6, 127.2, 127.1, 127.0, 126.7, 126.5, 126.3. HRMS (MALDT-TOF): *m*/*z* 636.2819 (M^+, calcd 636.2817). Anal. Calcd for $C_{50}H_{36}$: C, 94.30; H, 5.70. Found: C, 94.27; H, 5.73.

(*Z*)-1,2-Di(2-(naphthalen-2-yl)phenyl)-1,2-diphenylethene ((*Z*)-*o*-BNTPE): The procedure was analogous to that described for (*Z*)-*o*-BPTPE. White solid, yield 46%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.79 (d, 2H, J = 7.5 Hz), 7.74 (d, 2H, J = 8.5 Hz), 7.70 (d, 2H, J = 7.5 Hz), 7.56 (dd, 2H, J_1 = 8.5 Hz, J_2 = 1.5 Hz), 7.46–7.41 (m, 4H), 7.39 (s, 2H), 7.18–7.13 (m, 6H), 7.10–7.05 (m, 8H), 6.29–6.26 (m, 2H), 5.34 (d, 2H, J = 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 145.0, 141.0, 140.9, 139.4, 139.1, 133.7, 132.6, 132.2, 131.5, 129.9, 128.2, 127.7, 127.6, 127.5, 126.8, 126.7, 126.4, 125.6, 125.4. HRMS (MALDT-TOF): *m*/*z* 584.2513 (M^+, calcd 584.2504). Anal. Calcd for $C_{46}H_{32}$: C, 94.48; H, 5.52. Found: C, 94.39; H, 5.43.

(*Z*)-1,2-Bis(4'-methylbiphenyl-2-yl)-1,2-diphenylethene (7a): The procedure was analogous to that described for (*Z*)-*o*-BPTPE. White solid, yield 53%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.10–7.02 (m, 22H), 6.71–6.68 (m, 2H), 5.75 (d, 2H, J = 8.4 Hz), 2.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 144.9, 141.1, 141.0, 138.7, 135.9, 132.4, 131.4, 129.4, 128.8, 128.4, 127.5, 126.6, 126.2,

21.1. HRMS (MALDT-TOF): *m*/*z* 512.2506 (M^+, calcd 512.2504). Anal. Calcd for $C_{40}H_{32}$: C, 93.71; H, 6.29. Found: C, 93.64; H, 6.22.

(*Z*)-1,2-Bis(3'-methylbiphenyl-2-yl)-1,2-diphenylethene (7b): The procedure was analogous to that described for (*Z*)-*o*-BPTPE. White solid, yield 46%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.14–6.98 (m, 18H), 6.98 (d, 2H, J = 7.0 Hz), 6.85 (s, 2H), 6.70–6.67 (m, 2H), 5.66 (d, 2H, J = 7.5 Hz), 2.29 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 145.1, 141.5, 141.3, 141.0, 138.7, 137.1, 132.7, 131.5, 129.8, 129.5, 127.5, 127.0, 126.5, 126.4, 126.2, 126.0, 21.6. HRMS (MALDT-TOF): *m*/*z* 512.2514 (M^+, calcd 512.2504). Anal. Calcd for $C_{40}H_{32}$: C, 93.71; H, 6.29. Found: C, 93.55; H, 6.23.

(*Z*)-1,2-Bis(4'-methoxybiphenyl-2-yl)-1,2-diphenylethene (8a): The procedure was analogous to that described for (*Z*)-*o*-BPTPE. White solid, yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.14 (d, 4H, J = 8.4 Hz), 7.07–7.00 (m, 14H), 6.79 (d, 4H, J = 8.4 Hz), 6.75–6.71 (m, 2H), 5.79 (d, 2H, J = 7.6 Hz), 3.80 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 158.5, 144.7, 141.0, 140.8, 138.8, 134.3, 132.5, 131.4, 130.0, 129.4, 127.5, 126.6, 126.4, 126.3, 113.2, 55.3. HRMS (MALDT-TOF): *m*/*z* 544.2409 (M^+, calcd 544.2402). Anal. Calcd for $C_{40}H_{32}O_2$: C, 88.20; H, 5.92; O, 5.87. Found: C, 88.16; H, 5.89; O, 5.67.

(*Z*)-1,2-Bis(3'-methoxybiphenyl-2-yl)-1,2-diphenylethene (8b): The procedure was analogous to that described for (*Z*)-*o*-BPTPE. White solid, yield 40%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.19–7.16 (m, 2H), 7.12–7.05 (m, 14H), 6.98 (d, 2H, J = 7.5 Hz), 6.79–6.74 (m, 4H), 6.51 (s, 2H), 5.90 (d, 2H, J = 7.5 Hz), 3.76 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 159.3, 144.9, 143.0, 141.1, 138.9, 132.7, 131.4, 129.6, 128.4, 127.5, 126.7, 126.6, 126.2, 121.4, 114.5, 112.1, 55.0. HRMS (MALDT-TOF): *m*/*z* 544.2404 (M^+, calcd 544.2402). Anal. Calcd for $C_{40}H_{32}O_2$: C, 88.20; H, 5.92; O, 5.87. Found: C, 88.13; H, 5.72; O, 5.65.

1,2-Bis(4'-phenylbiphenyl-4-yl)-1,2-diphenylethene (BBPTPE): The procedure was analogous to that described for (*Z*)-*o*-BPTPE. White solid, yield 62%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.64–7.62 (m, 12H), 7.44–7.33 (m, 10H), 7.17–7.11 (m, 14H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 143.8, 142.9, 140.8, 140.0,139.5, 138.4, 131.9, 131.5, 129.0, 128.8, 128.2, 127.7, 127.4, 127.3, 127.2,

127.0, 126.5, 126.2. HRMS (MALDT-TOF): *m*/*z* 636.2827 (M^+, calcd 636.2817). Anal. Calcd for $C_{50}H_{36}$: C, 94.30; H, 5.70. Found: C, 94.19; H, 5.53.

(*E*)-1,2-Di(biphenyl-2-yl)-1,2-dimethylethene (10): The procedure was analogous to that described for (*Z*)-*o*-BPTPE. White solid, yield 57%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.42–7.41 (m, 8H), 7.37–7.34 (m, 4H), 7.30–7.27 (m, 4H), 6.93–6.92 (m, 2H), 1.45 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 142.5, 141.8, 140.5, 133.2, 129.8, 128.9, 128.6, 127.8, 127.2, 126.9, 126.7, 22.3. HRMS (MALDT-TOF): *m*/*z* 360.1881 (M^+, calcd 360.1878).

2-Phenylbenzophenone (1): A mixture of 2-bromobenzophenone (1.3 g, 5 mmol), phenylboronic acid (0.73 g, 6 mmol), $Pd(PPh_3)_4$ (0.55 g, 0.5 mmol), and potassium carbonate (3.5 g, 25 mmol) in 100 mL of toluene/ethanol/water (8/1/1 v/v/v) was heated to reflux for 12 h under nitrogen. The reaction mixture was cooled to room temperature and poured into water. The organic layer was extracted with dichloromethane and the combined organic layers were washed with saturated brine solution and water and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. White solid of **1** was obtained in 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.64 (d, 2H, J = 7.6 Hz), 7.59–7.56 (m, 1H), 7.53–7.38 (m, 4H), 7.28–7.24 (m, 4H), 7.21–7.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 198.8, 141.2, 140.2, 139.0, 137.4, 132.8, 130.4, 130.0, 129.9, 129.0, 128.8, 128.3, 128.1, 127.4, 127.1. MS (EI): *m*/*z* 258 (M^+, calcd 258).

2-Biphenyl-4-ylbenzophenone (2): The procedure was analogous to that described for **1**. White solid, yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.68 (d, 2H, J = 8.4 Hz), 7.61–7.57 (m, 1H), 7.54–7.38 (m, 10H), 7.34–7.25 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 198.8, 140.8, 140.5, 140.0, 139.1, 138.9, 137.4, 132.9, 130.4, 130.1, 129.9, 129.4, 128.8, 128.7, 128.1, 127.3, 127.1, 127.0. MS (EI): *m*/*z* 334 (M^+, calcd 334).

2-(Naphthalen-2-yl)benzophenone (3): The procedure was analogous to that described for **1**. White solid, yield 94%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.76–7.72 (m, 3H), 7.69–7.68 (m, 3H), 7.65–7.60 (m, 3H), 7.52–7.49 (m, 1H), 7.45–7.40 (m, 3H), 7.35–7.32 (m, 1H), 7.24–7.21 (m, 2H). ^{13}C

NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 198.8, 141.1, 139.2, 137.7, 137.5, 133.1, 132.8, 132.4, 130.4, 129.8, 128.9, 128.2, 128.1, 128.0, 127.6, 127.2, 127.0, 126.2, 126.0. HRMS (MALDT-TOF): *m*/*z* 308.1201 (M^+, calcd 308.1201).

4-Biphenyl-4-ylbenzophenone (4): The procedure was analogous to that described for **1**. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.92 (d, 2H, J = 8.5 Hz), 7.86 (d, 2H, J = 7.0 Hz) 7.77–7.71 (m, 6H), 7.67–7.66 (m, 2H), 7.63–7.60 (m, 1H), 7.53–7.47 (m, 4H), 7.40–7.37 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 196.3, 144.7, 141.1, 140.4, 138.8, 137.8, 136.3, 132.4, 130.8, 130.0, 128.9, 128.3, 127.7, 127.6, 127.1, 126.8. MS (EI): *m*/*z* 334 (M^+, calcd 334).

2-(4'-Methylphenyl)benzophenone (5a): The procedure was analogous to that described for **1**. White solid, yield 98%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.66 (d, 2H, J = 7.6 Hz), 7.55–7.52 (m, 1H), 7.48–7.38 (m, 4H), 7.28–7.25 (m, 2H), 7.15 (d, 2H, J = 7.6 Hz), 7.00 (d, 2H, J = 8.0 Hz), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 198.9, 141.2, 138.9, 137.4, 137.3, 137.1, 132.8, 130.3, 130.1, 130.0, 129.0, 128.9, 128.7, 128.1, 126.8, 21.1. MS (EI): *m*/*z* 272 (M^+, calcd 272).

2-(3'-Methylphenyl)benzophenone (5b): The procedure was analogous to that described for **1**. White solid, yield 95%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.63 (d, 2H, J = 8.0 Hz), 7.57–7.39 (m, 5H), 7.28–7.24 (m, 2H), 7.08–7.02 (m, 3H), 6.94 (d, 1H, J = 7.2 Hz), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 198.9, 141.3, 140.1, 138.9, 137.8, 137.5, 132.8, 130.4, 130.0, 129.8, 128.8, 128.2, 128.1, 128.0, 127.0, 126.1, 21.3. MS (EI): *m*/*z* 272 (M^+, calcd 272).

2-(4'-Methoxyphenyl)benzophenone (6a): The procedure was analogous to that described for **1**. White solid, yield 98%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.64 (d, 2H, J = 8.0 Hz), 7.56–7.53 (m, 1H), 7.49–7.39 (m, 4H), 7.29–7.25 (m, 2H), 7.18 (d, 2H, J = 8.8 Hz), 6.73 (d, 2H, J = 8.4 Hz), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 199.0, 158.9, 140.7, 138.8, 137.4, 132.9, 132.7, 130.3, 130.1, 130.0, 129.9, 128.7, 128.1, 126.6, 113.8, 55.2. MS (EI): *m*/*z* 288 (M^+, calcd 288).

2-(3'-Methoxyphenyl)benzophenone (6b): The procedure was analogous to that described for **1**. White solid, yield 95%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.66 (d, 2H, J = 7.6 Hz), 7.59–7.55 (m,

1H), 7.52–7.40 (m, 4H), 7.30–7.26 (m, 2H), 7.12–7.08 (m, 1H), 6.86–6.80 (m, 2H), 6.69 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.6 Hz), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 198.8, 159.3, 141.5, 140.9, 139.0, 137.4, 132.9, 130.3, 129.9, 129.8, 129.3, 128.7, 128.1, 127.2, 121.6, 114.4, 113.3, 55.1. MS (EI): *m*/*z* 288 (M^+, calcd 288).

X-Ray crystallography

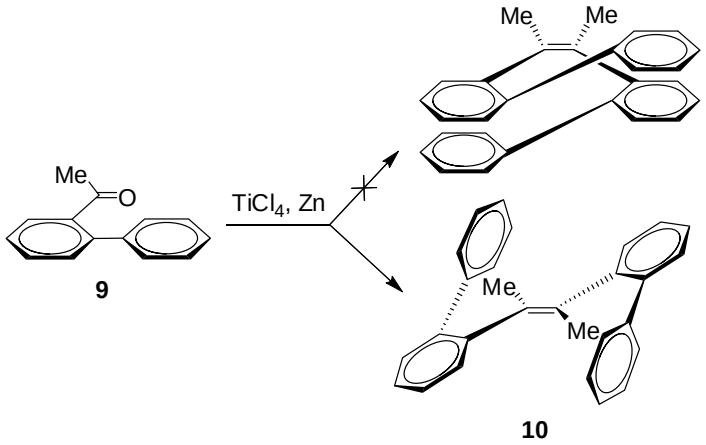
Crystal data for (*Z*)-*o*-BPTPE (CCDC 955718): $C_{38}H_{28}$, M = 484.60, monoclinic, P21/n, a = 12.3653(9), b = 22.7961(12), c = 19.7772(14) Å, β = 98.854(7)°, V = 5508.4(6) Å^3, Z = 8, Dc = 1.169 g cm^{-3}, μ = 0.066 mm^{-1} (MoKα, λ = 0.71073), F(000) = 2048, T = 293(2) K, 22956 measured reflections, 10046 independent reflections (R_{int} = 0.0853), GOF on F^2 = 0.953, R_1 = 0.1892, wR_2 = 0.1601 (all data), Δe 0.283 and –0.168 eÅ^{-3}.

Crystal data for 7a (CCDC 955719): $C_{40}H_{32}$, M = 512.66, monoclinic, P21/c, a = 9.6300(5), b = 9.2473(5), c = 33.2387(17) Å, β = 97.115(5)°, V = 2937.2(3) Å^3, Z = 4, Dc = 1.159 g cm^{-3}, μ = 0.065 mm^{-1} (MoKα, λ = 0.71073), F(000) = 1088, T = 293(2) K, 14439 measured reflections, 5358 independent reflections (R_{int} = 0.0417), GOF on F^2 = 1.079, R_1 = 0.0951, wR_2 = 0.1532 (all data), Δe 0.185 and –0.154 eÅ^{-3}.

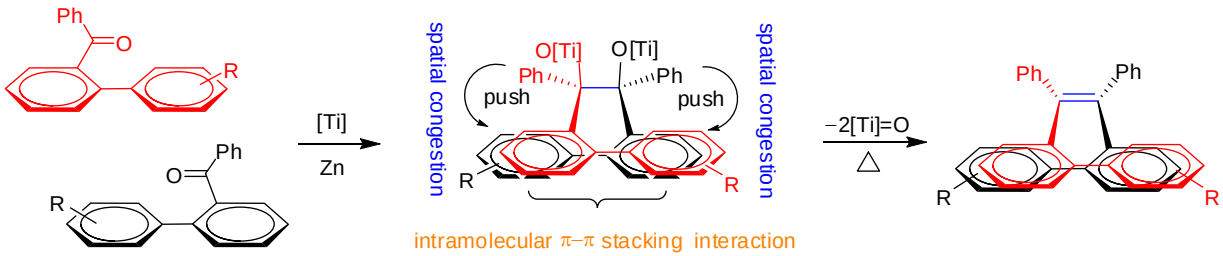
Crystal data for 8a (CCDC 955720): $C_{40}H_{32}O_2$, M = 544.66, monoclinic, P21/c, a = 9.3819(3), b = 9.2363(5), c = 34.2924(15) Å, β = 90.577(4)°, V = 2971.4(2) Å^3, Z = 4, Dc = 1.217 g cm^{-3}, μ = 0.073 mm^{-1} (MoKα, λ = 0.71073), F(000) = 1152, T = 293(2) K, 11990 measured reflections, 5418 independent reflections (R_{int} = 0.0333), GOF on F^2 = 1.025, R_1 = 0.0805, wR_2 = 0.1278 (all data), Δe 0.172 and –0.196 eÅ^{-3}.

Crystal data for 10 (CCDC 955721): $C_{28}H_{24}$, M = 360.47, monoclinic, P21/c, a = 7.3760(5), b = 16.8413(9), c = 8.6153(5) Å, β = 105.155(6)°, V = 1032.98(10) Å^3, Z = 2, Dc = 1.159 g cm^{-3}, μ = 0.065 mm^{-1} (MoKα, λ = 0.71073), F(000) = 384, T = 298(2) K, 4201 measured reflections, 1890 independent

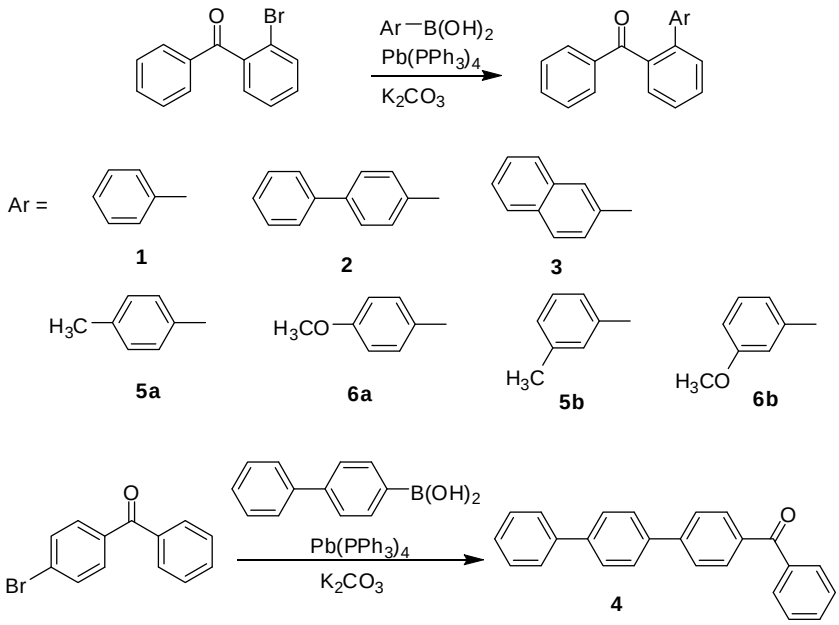
reflections (R_{int} = 0.0291), GOF on F^2 = 1.056, R_1 = 0.0993, wR_2 = 0.1968 (all data), Δe 0.286 and –0.266 eÅ^{-3}.



Scheme S1. Synthesis of (*E*)-2,2'-(but-2-ene-2,3-diyl)dibiphenyl (**10**).



Scheme S2. Proposed mechanism for the formation of folded TPE derivatives.



Scheme S3. Synthetic routes to benzophenone derivatives.

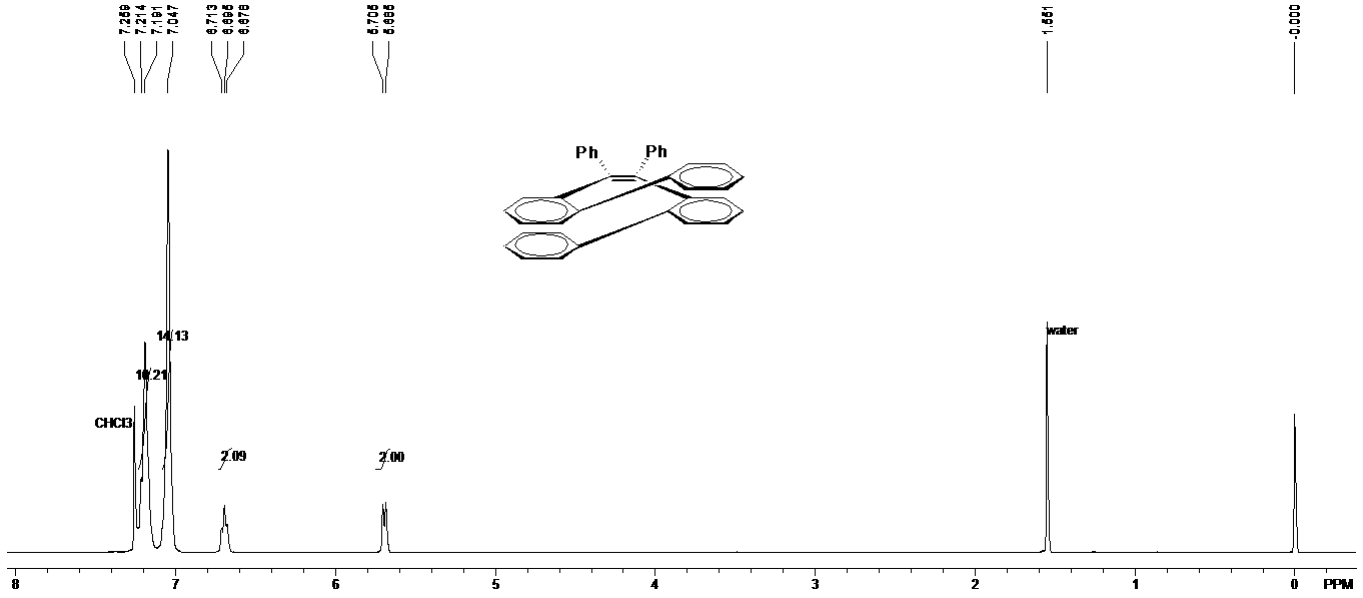


Figure S1. ^{1}H spectrum of (*Z*)-*o*-BPTPE.

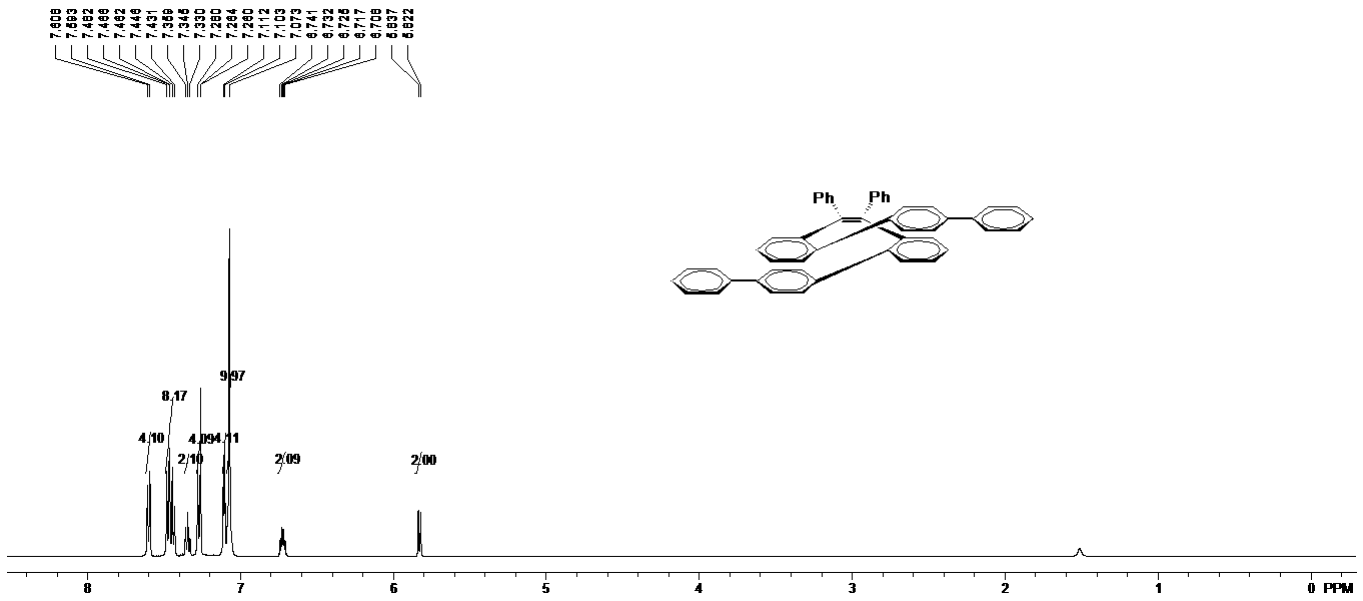


Figure S2. ^{1}H spectrum of (*Z*)-*o*-BBPTPE.

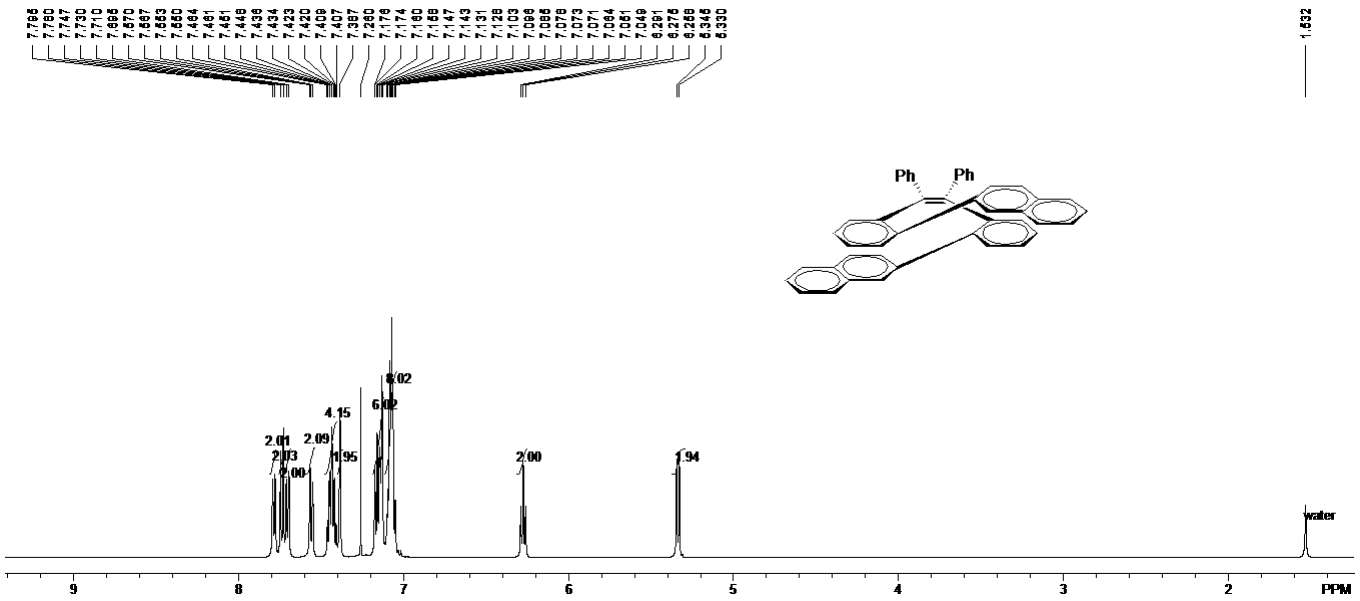


Figure S3. ^{1}H spectrum of (*Z*)-*o*-BNTPE.

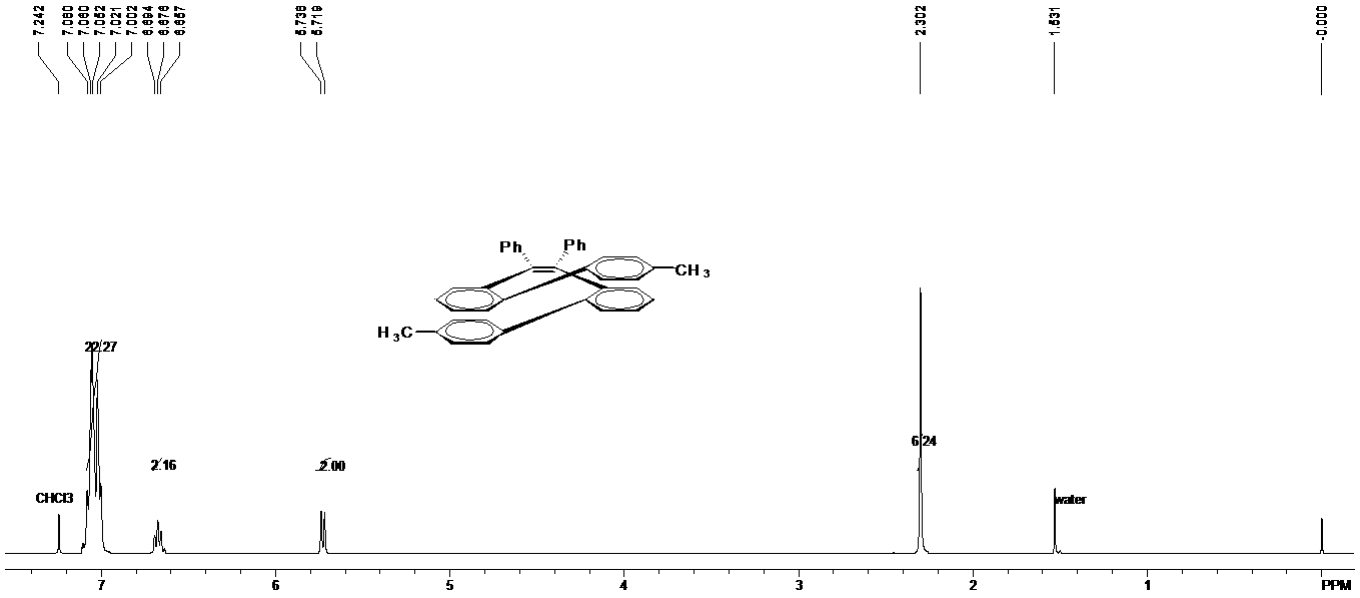


Figure S4. ^{1}H spectrum of **7a**.

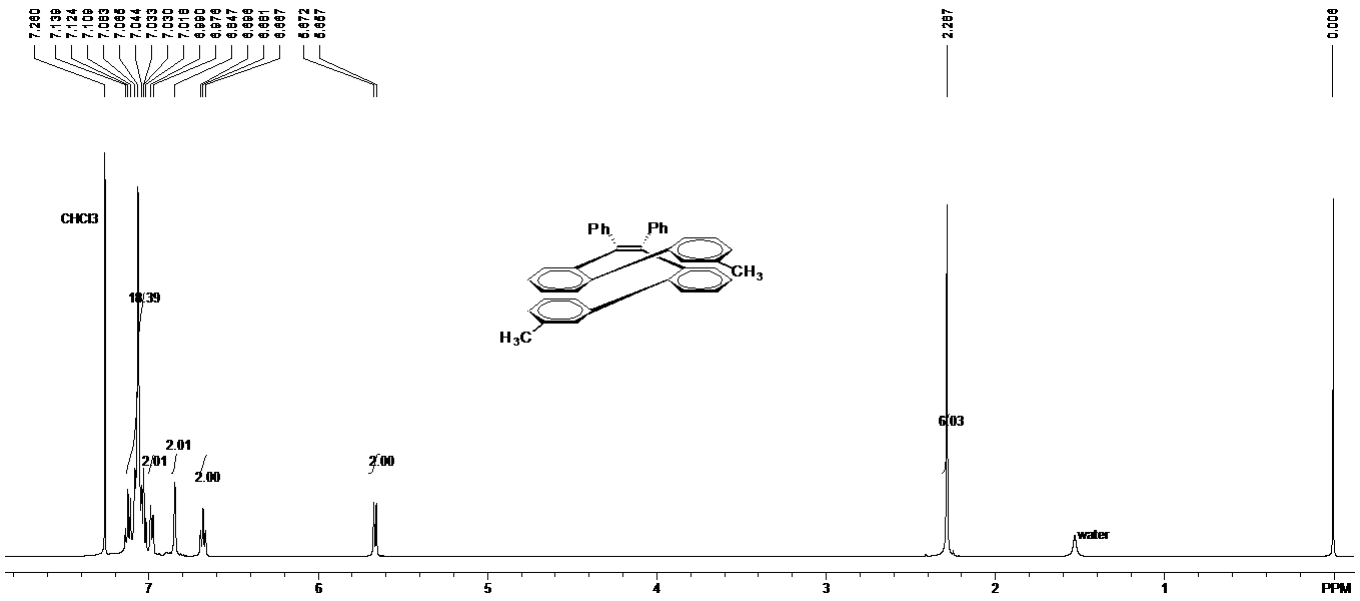


Figure S5. ^{1}H spectrum of **7b**.

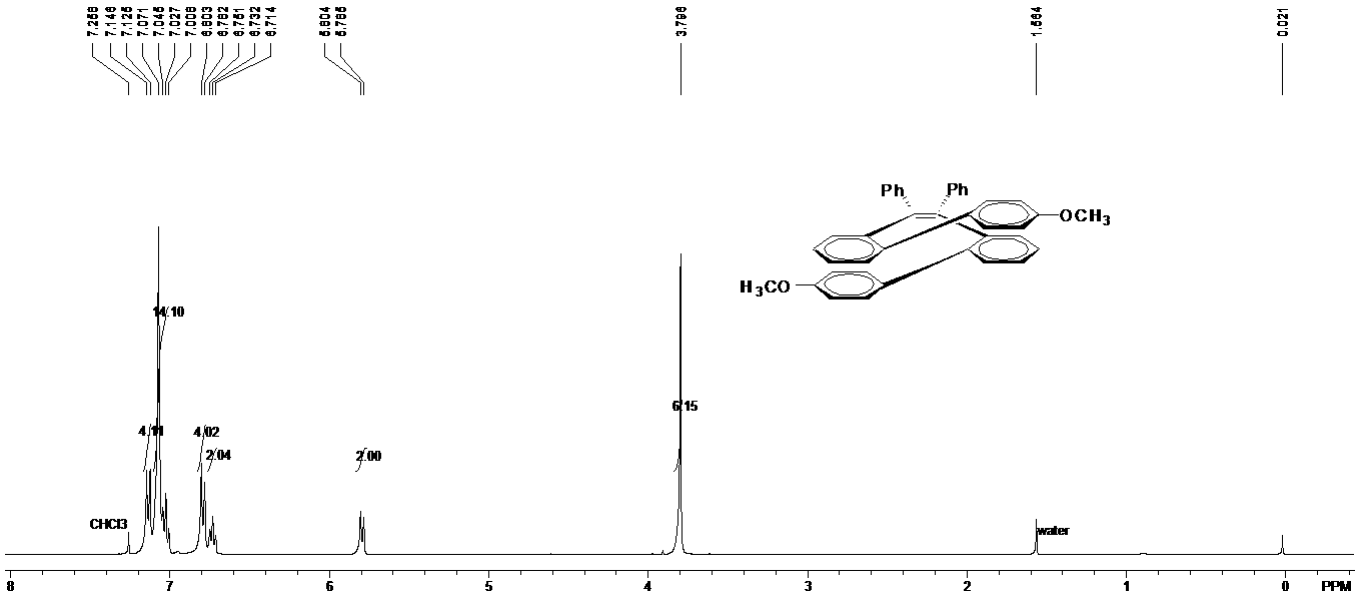


Figure S6. ^{1}H spectrum of **8a**.

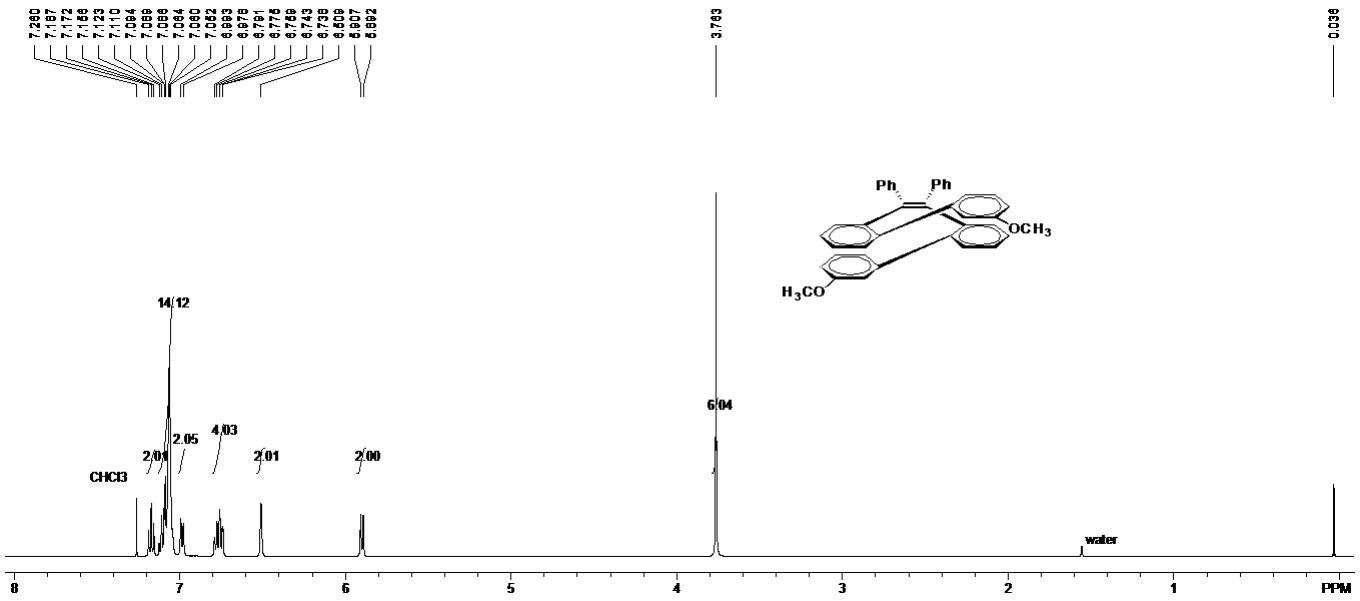


Figure S7. ^{1}H spectrum of **8b**.

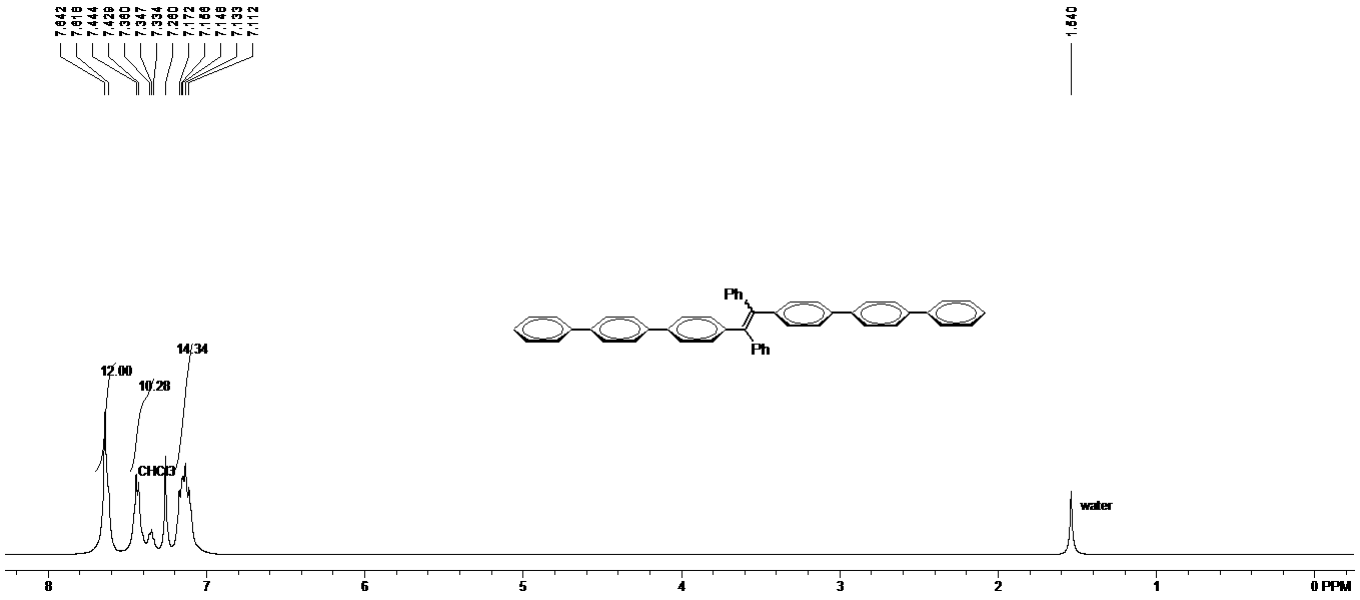


Figure S8. ^{1}H spectrum of BBPTPE.

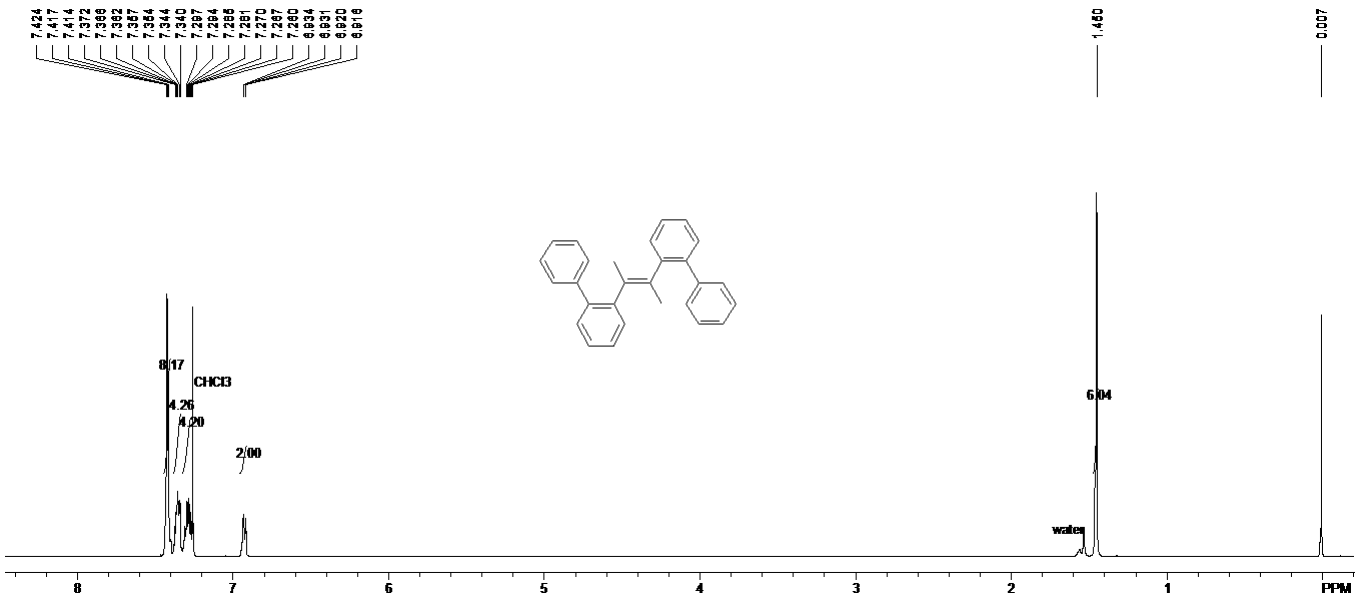


Figure S9. ^{1}H spectrum of **10**.

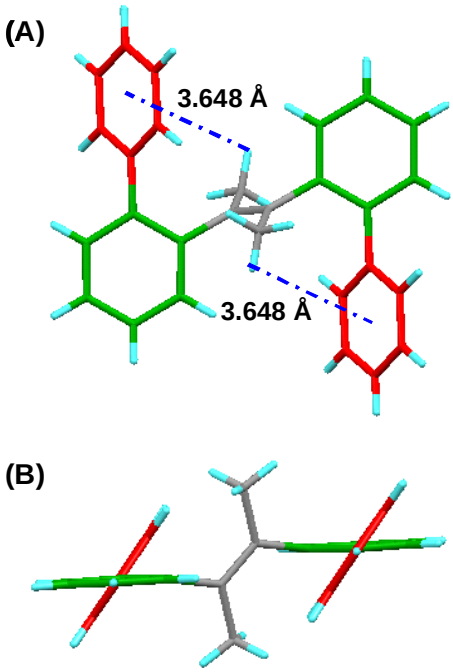


Figure S10. Crystal structure of **10** (CCDC 955721). (A) Top view and (B) side view along Φ_2.

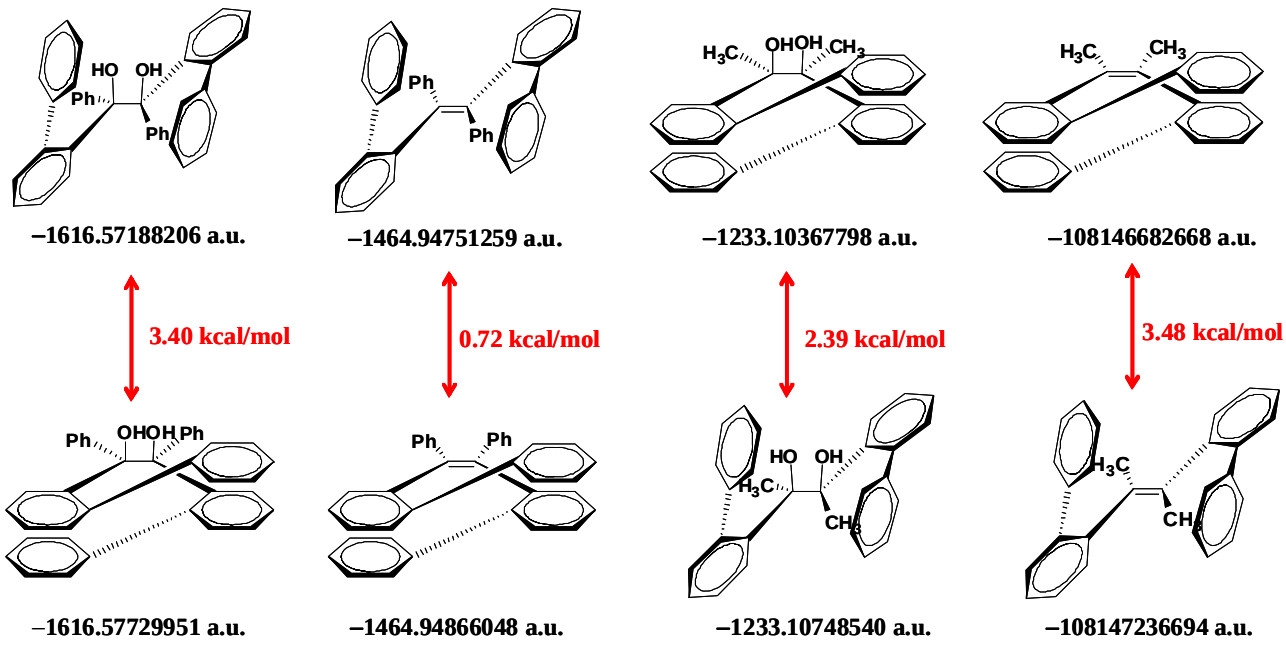


Figure S11. The total electronic energies of *Z*-/*E*-isomers of (*Z*)-*o*-BPTPE and **10** as well as corresponding pinacolates in ground state, calculated at DFT B3LYP/6-31g(d,p) level and performed by Gaussian 09 package program.

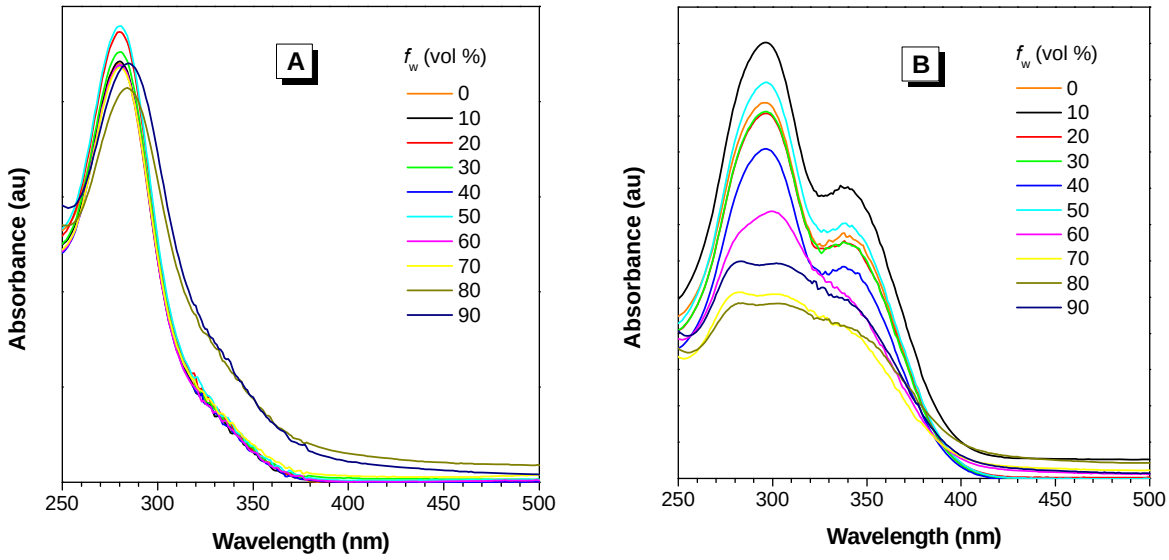


Figure S12. Absorption spectra of (A) (*Z*)-*o*-BBPTPE and (B) BBPTPE in THF/water mixtures with different water fractions (f_w).

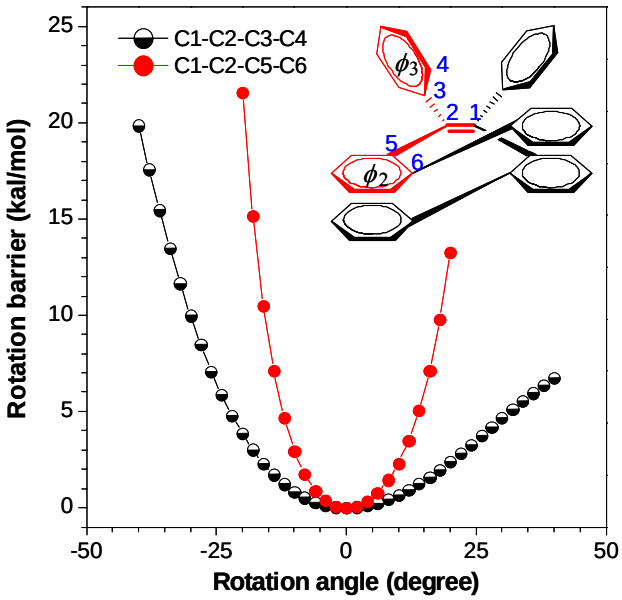


Figure S13. Potential energy curves along the torsion angles (C1−C2−C3−C4 and C1−C2−C5−C6) of the ground state for the isolated (*Z*)-*o*-BPTPE molecule.

Table S1. Optical properties of selected TPE derivatives.

	λ_{abs} (nm)	λ_{em} (nm)		Φ_F (%)	
	Soln[a]	Soln	Film[b]	Soln[c]	Film[d]
(*Z*)-*o*-BPTPE	316	493	476	33	64
(*Z*)-*o*-BBPTPE	-	492	472	45	72
(*Z*)-*o*-BNTPE	326	496	468	28	60
7a	317	497	483	40	53
8a	323	495	477	30	57
BBPTPE	339	-	477	0.62	96

[a] In THF solution (10 μM). [b] Film drop-casted on quartz plate. [c] Determined in THF solutions using 9,10-diphenylanthracene (Φ_F = 90% in cyclohexane) as standard. [d] Determined in amorphous film by integrating sphere.