Supporting Information

Innovative molecular design of bridged biphenyl for calamitic nematic liquid crystals with extensive π -conjugated mesogens

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Measurements

¹H NMR and ¹³C NMR spectra were recorded on BRUKER Ascend 500 (125 MHz) spectrometers and JEOL 400 (100 MHz) spectrometers, respectively, for CDCl₃ solution using tetramethylsilane (TMS) as an internal standard. Date for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constants (Hz). ¹³C NMR spectra were reported as chemical shifts in ppm and multiplicity where appropriate. High-resolution (HR) EI and FAB spectra were recorded on a double-focusing mass spectrometer JEOL JMS-70. Fourier-transform infrared (FT-IR) spectra were recorded on a JASCO FT-IR 469 plus spectrometer. The phase transition behaviors were investigated by polarizing optical microscopy (POM) (Olympus BX51 optical microscope) with a METTLER TOREDO FP82HT Hot stage controlled with the METTLER TOREDO Central Processor of the FP900 System at a rate of 10°C min⁻¹, and differential scanning calorimetry (DSC) (Perkin-ElmerDSC 8500) at a scanning rate of 10°C min⁻¹ under a flow of dry nitrogen. The lowest temperatures of the DSC measurements were as follows; 5CB: 0 °C, B5CB[6]: 0 °C, B5CB[7]: -30 °C, B8CB[7]: -20 °C, B7OCB[7]: -20 °C, 5CT: 90 °C, DMc5CT: -20 °C, Bc5CT[6]: 25 °C, Bc5CT[7]: 0 °C, B5CT[7]: 0 °C, B5T[7]: -50 °C, B5(50)T[7]: 0 °C, B5Q[7]: 40 °C, B5OQ[7]: 110 °C, B5PhT[7]: -20 °C, B5(50)PhT[7]: 0 °C, BC5PhT[7]: 0 °C, and B5CPhT[7]: 0 °C. Measurement of birefringence were performed within a uniaxially aligned nematic cell, which contained an indium tin oxide layer purchased from E.H.C. Co. Ltd. Cell gaps ($d = 2-3 \mu m$), and were measured by the interferometric method. The transmittance of light under crossed nicol conditions was observed as a function of wavelength by a coupled spectroscopy/microscopy method, using a Nikon LV100 Pol optical microscope equipped with a UEB4000 (Ocean photonics) spectrometer. UV-Vis spectra were recorded on a JASCO V-670 UV-vis spectrophotometer, and fluorescence spectra were recorded on a JASCO FP-6500 spectrofluorometer. All photophysical measurements were performed using dilute solutions with optical densities (ODs) around 0.1 at the maximum absorption wavelength in 1 cm path length quartz cells at room temperature (298 K). In addition, all sample solutions were deaerated by bubbling with argon gas for 15 min prior to the quantum yield and fluorescence lifetime. Fluorescence lifetimes were also measured by FS5 spectrofluorometer. The excitation light sources were LED pulse Lamps (EPLED, 340 nm, EDINBURGH INSTRUMENTS). In all samples, the time-to-amplitude converter ranges was 100 ns, and the counts amounts were 10,000.

Materials

All solvents and chemicals were commercially available and used without further purification unless otherwise noted. Column chromatography was performed on silica

gel (Silica Gel 60N, 63-210 µm, Kanto Chemical Co., Inc.). 2'-Bromoacetophenone, tritert-butylphosphonium tetrafluoride, tris(dibenzylideneacetone)dipalladium(0), ptoluenesulfonic acid monohydrate, triethylsilane, bromide, ammonia solution, iodide, 4-pentylphenylboronic acid, potassium phosphate, 1-pentene, 4-cyanophenylboronic acid. 4-bromophenol, potassium carbonate. 1-bromo-4-pentylbenzene, 4,4'-diiodo-2,2'-dimethyl-1,1'trimethylsilylacetylene, 4-bromo-4'-pentylbiphenyl, cyclohexane, 9,10-dibromophenanthrene, biphenyl, *n*-butyllithium 2.3 Μ hydroxylamine hydrochloride, 1-octene, triisopropyl borate, *m*-chloroperoxybenzoic acid (contains ca. 30% water), 4-(pentyloxy)phenylboronic acid, and 4bromobenzonitrile were purchased from TCI (Tokyo, Japan). 2-Formylphenylboronic acid, potassium fluoride dihydrate, trifluoroacetic acid, dimethylformamide, ammonium chloride, tetrakis(triphenylphosphine)palladium(0), 1-bromopentane, triphenylphosphine, *n*-butyllithium 2.6 M hexane, anhydrate *N*-methyl-2-pyroridine, hydrochloric acid, 1-bromoheptane, celite® No.503, tetrahydrofuran, anhydrate tetrahydrofuran, diethyl ether, ethanol, chloroform, toluene, and chloroform- d_1 99.8 atom% D with TMS were purchased from Kanto Chem (Tokyo, Japan). Sodium hydride, iron powder, sodium thiosulfate, 2-butanone, and copper(I) chloride, triethylamine were purchased from Fujifilm Wako Pure Chem (Tokyo, Japan). Anhydrate magnesium sulfate, n-butyllithium 2.0 M cyclohexane, and 9-borabicyclo[3.3.1]nonane 0.5 M tetrahydrofuran were purchased from Sigma-Aldrich Japan (Tokyo, Japan). Sodium hydrogen carbonate was purchased from Nacalai Tesque (Kyoto, Japan). Hexane, ethyl acetate, and methanol were purchased from GODO (Tokyo, Japan). Dichloromethane was purchased from AGC Chemicals (Tokyo, Japan).

DSC thermograms and POM images









Fig. S3 POM images of B5CB[6] at room temperature, left for (a) 50 minutes, (b) 51 minutes, and (c) 52 minutes.



Fig. S5 DSC thermogram of B8CB[7] at a rate of 10 °C min⁻¹.



Fig. S6 A POM image of B8CB[7] at room temperature left for a few days.



Fig. S7 DSC thermogram of B7OCB[7] at a rate of 10 °C min⁻¹.



Fig. S8 A POM image of B70CB[7] at room temperature left for a few days.



Fig. S10 DSC thermogram of Bc5CT[6] at a rate of 10 °C min⁻¹.





Fig. S11 POM images of **Bc5CT[6]** at (a) 140 °C during heating, (b) 100 °C during cooling, and (c) 40 °C.



Fig. S12 DSC thermogram of B5CT[7] at a rate of 10 °C min⁻¹.





Fig. S13 POM images of **B5CT[7]** at room temperature left for (a) 10 minutes, (b) 2 days, and (c) more a few days.



Fig. S14 DSC thermogram of B5T[7] at a rate of 10 °C min⁻¹.



Fig. S15 A POM image of B5T[7] at 0 °C.



Fig. S16 DSC thermogram of B5(50)T[7] at a rate of 10°C min⁻¹.



Fig. S17 POM images of **B5(50)T[7]** at (a) room temperature, (b) 55°C during heating, and (c) 40°C during cooling.



Fig. S18 DSC thermogram of B5Q[7] at a rate of 10°C min⁻¹.



Fig. S19 POM images of B5Q[7] at (a) room temperature and (b) 160°C during heating.



Fig. S20 DSC thermogram of B5OQ[7] at a rate of 10°C min⁻¹.



Fig. S21 POM images of B5OQ[7] at (a) room temperature, (b) 180°C during heating, and (c) 145°C during cooling.



Fig. S23 DSC thermogram of B5(50)PhT[7] at a rate of 10°C min⁻¹.





Fig. S24 POM images of **B5(50)PhT[7]** at (a) 60°C during heating, (b) 85°C during heating, and (c) room temperature during cooling.



Fig. S25 DSC thermogram of BC5PhT[7] at a rate of 10°C min⁻¹.



Fig. S26 POM images of BC5PhT[7] at (a) room temperature and (b) 120°C during cooling.



Fig. S27 DSC thermogram of B5CPhT[7] at a rate of 10°C min⁻¹.



Fig. S28 POM images of B5CPhT[7] at room temperature (a) during cooling and (b) left for a few .minutes



Fig. S29 POM images of **B5BPhEB[7]** at (a) room temperature and (b) 200°C during heating.



Fig. S30 POM images of B5OBPhEB[7] at (a) room temperature, (b) 200°C during heating, and (c) 140°C during cooling.

Birefringence measurements



Fig. S31 Above: the representative transmittance spectrum (blue dot) and fitting curve (brown solid line) of a uniaxial specimen of **5CT** at 221 °C. Below: wavelength dependence of Δn of **5CT** measured at 221 °C.



Fig. S32 Above: the representative transmittance spectrum (blue dot) and fitting curve (brown solid line) of a uniaxial specimen of B5Q[7] at 161 °C. Below: wavelength dependence of Δn of B5Q[7] measured at 161 °C.



Fig. S33 Above: the representative transmittance spectrum (blue dot) and fitting curve (brown solid line) of a uniaxial specimen of B5OQ[7] at 212 °C. Below: wavelength dependence of Δn of B5OQ[7] measured at 212 °C.



Fig. S34 Above: the representative transmittance spectrum (blue dot) and fitting curve (brown solid line) of a uniaxial specimen of **B5BPhEB[7]** at 222 °C. Below: wavelength dependence of Δn of **B5BPhEB[7]** measured at 222 °C.



Fig. S35 Above: the representative transmittance spectrum (blue dot) and fitting curve (brown solid line) of a uniaxial specimen of **B5OBPhEB[7]** at 239 °C. Below: wavelength dependence of Δn of **B5OBPhEB[7]** measured at 239 °C.

Photophysical measurements



Fig. S36 Absorption (dashed line) and fluorescence (solid line) spectra of B5PhT[7] in 1 wt% doped PMMA cast film.



Fig. S37 Time resolved fluorescence decay of B5PhT[7] in the THF solution, the solid state, and the nematic phase on excitation at 340 nm.

Table S1 Fluorescence lifetime (T) of **B5PhT[7]** in THF, in the solid state, and in the nematic phase, excited at 340 nm.

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State	ז₁ [ns] (Contribution)	τ ₂ [ns] (Contribution)	χ²	
THF ^a	-	-	-	
Solid	1.4 (0.71)	6.8 (0.29)	1.30	
Nematic phase	1.7 (0.81)	12.8 (0.19)	1.19	

a) The life time was too short to obtain the values.

Structural analysis



Fig. S38 The crystal structure of 5CT.^[1]



Fig. S39 Optimized structure of biphenyl.



Fig. S40 The E_{bar} of the dihedral angle for 40 to -140°.



Fig. S41 The molecular structures of **BT[7]** at $\varphi_1 = -50^\circ$ (left) and 45° (right)



Fig. S42 The molecular structures of **BT**[7] at $\varphi_2 = -70^\circ$ (left) and 70° (right).



Fig. S43 The E_{bar} of φ_1 for 25 to 35°.



Fig. S45 The E_{bar} (blue dots) and φ_1 (red dots) of **BT**[7] relative to the each φ_2 .

Table S2	Atom coordinates	and absolute	energies	of BT[7]	(Opt-BT[7]	-1) in the g	as
	р	hase in theore	etical calcu	ulation.			

BT[7] (Opt-BT[7]-1) (Ground): <i>E</i> (B3LYP/6-311G(g)) = -463.400337					
		Hartree			
Center	Atom numbor	Atom number Coordinates (Angstroms)			
number	Atom number	Х	Y	Z	
1	6	-5.03867	0.849149	0.731147	
2	6	-3.64372	0.891926	0.778918	
3	6	-2.90374	0.019585	-0.05045	
4	6	-3.59086	-0.86839	-0.88868	
5	6	-4.98174	-0.89854	-0.92306	
6	6	-5.7102	-0.03405	-0.11104	
7	1	-5.60855	1.513403	1.375158	
8	1	-3.02278	-1.52766	-1.5375	

9	1	-5.49234	-1.58973	-1.5861
10	1	-6.79541	-0.0475	-0.12998
11	6	-1.41605	0.031964	-0.03106
12	6	-0.69689	-1.16648	0.054682
13	6	-0.69781	1.245456	-0.10799
14	6	0.692189	-1.17951	0.074453
15	1	-1.23917	-2.1045	0.120794
16	6	0.695837	1.213149	-0.08853
17	6	1.418564	0.015839	0.004549
18	1	1.217388	-2.12777	0.122524
19	1	1.237992	2.153423	-0.13109
20	6	2.902786	0.016261	0.025471
21	6	3.637621	0.874642	-0.80607
22	6	3.611978	-0.84337	0.877761
23	6	5.029233	0.873542	-0.78656
24	1	3.112588	1.529322	-1.49403
25	6	5.003578	-0.84474	0.898184
26	1	3.066063	-1.49762	1.549711
27	6	5.719023	0.013826	0.065939
28	1	5.57627	1.540446	-1.44569
29	1	5.530302	-1.51287	1.572453
30	1	6.804166	0.012857	0.081485
31	6	-2.9267	1.824371	1.72942
32	1	-2.19448	1.243736	2.3007
33	1	-3.6352	2.227205	2.458796
34	6	-2.19034	2.989244	1.03534
35	1	-2.90308	3.777012	0.767331
36	1	-1.48931	3.43202	1.751475
37	6	-1.43875	2.557205	-0.24091
38	1	-0.74406	3.348089	-0.53779
39	1	-2.16509	2.464052	-1.055 <u></u> 39

 Table S3 Atom coordinates and absolute energies of BT[7] (Opt-BT[7]-2) in the gas phase in theoretical calculation.

BT[7] (Opt-BT[7]-2) (Ground): <i>E</i> (B3LYP/6-311G(g)) = -811.265992					
 Hartree					
 Center	A t a a a a a a a	Coordinates (Angstroms)			
number	Atom number	Х	Y	Z	
С	6	-4.82695	-0.90321	1.400472	
С	6	-3.4813	-0.56015	1.299489	
С	6	-2.69189	-1.04314	0.24679	
С	6	-3.29261	-1.88479	-0.69954	
С	6	-4.63963	-2.22594	-0.60213	
С	6	-5.41207	-1.73589	0.448423	
Н	1	-5.41799	-0.5236	2.228113	
Н	1	-2.69787	-2.26287	-1.52514	
Н	1	-5.08597	-2.87409	-1.34988	
Н	1	-6.46136	-2.00197	0.526161	
С	6	-1.23838	-0.71951	0.149671	
С	6	-0.32196	-1.7791	0.182033	

С	6	-0.74543	0.598301	0.024782
С	6	1.047471	-1.56392	0.113396
Н	1	-0.69905	-2.79291	0.272781
С	6	0.634635	0.793041	-0.04576
С	6	1.55258	-0.26353	0.003089
Н	1	1.724819	-2.4115	0.121683
Н	1	1.008997	1.805775	-0.13463
С	6	3.013743	-0.00946	-0.06929
С	6	3.537077	0.965092	-0.93221
С	6	3.911867	-0.73943	0.723594
С	6	4.9071	1.200276	-1.00022
Н	1	2.865149	1.525907	-1.5735
С	6	5.282039	-0.50445	0.656434
Н	1	3.529524	-1.47967	1.418941
С	6	5.786361	0.466586	-0.20625
Н	1	5.289413	1.953789	-1.6818
Н	1	5.956713	-1.07608	1.286165
Н	1	6.854703	0.650101	-0.25913
С	6	-0.50733	3.983781	-0.42146
Н	1	-0.236	4.085154	0.626462
Н	1	-0.17739	4.777084	-1.08444
С	6	-1.23386	2.960583	-0.86313
Н	1	-1.46637	2.90475	-1.92585
Н	1	-1.86911	2.146547	0.998245
С	6	-1.69936	1.794944	-0.02756
Н	1	-3.0308	0.074143	2.055975
Н	1	-2.6733	1.457924	-0.38787

 Table S4 Atom coordinates and absolute energies of BT[7] (TS) in the gas phase in theoretical calculation.

BT[7] (TS) (Ground): <i>E</i> (B3LYP/6-311G(g)) = -811.244925 Hartree						
Center	Atom number	Coordinates (Angstroms)				
number	Atom number	Х	Y	Z		
С	6	-4.92659	-0.03512	-0.91039		
С	6	-3.57438	0.34803	-0.91478		
С	6	-2.58468	-0.56202	-0.44369		
С	6	-3.0857	-1.81009	0.004665		
С	6	-4.42307	-2.16872	-0.0051		
С	6	-5.37101	-1.27007	-0.47368		
Н	1	-5.65606	0.683411	-1.2721		
Н	1	-2.41523	-2.56169	0.386411		
Н	1	-4.71367	-3.14946	0.357846		
Н	1	-6.42724	-1.51813	-0.49226		
С	6	-1.07795	-0.34897	-0.37296		
С	6	-0.29139	-1.41105	0.138096		
С	6	-0.33279	0.799709	-0.76487		
С	6	1.0854	-1.38656	0.256845		
Н	1	-0.75561	-2.32748	0.462054		
С	6	1.064324	0.801454	-0.63358		
С	6	1.812979	-0.26236	-0.13821		

Н	1	1.595745	-2.26587	0.636181
Н	1	1.589655	1.708652	-0.91502
С	6	3.289367	-0.19855	-0.02836
С	6	4.063671	0.418063	-1.02285
С	6	3.953984	-0.75662	1.074228
С	6	5.450138	0.476053	-0.91811
Н	1	3.575602	0.83096	-1.89961
С	6	5.340338	-0.69845	1.179779
Н	1	3.375736	-1.21622	1.869159
С	6	6.095202	-0.08164	0.184
Н	1	6.028942	0.950687	-1.70433
Н	1	5.831749	-1.12939	2.046513
Н	1	7.176427	-0.03663	0.265788
С	6	-3.35564	1.741575	-1.47141
Н	1	-4.29575	2.288151	-1.3582
Н	1	-3.19124	1.672612	-2.5559
С	6	-2.23029	2.564077	-0.86668
Н	1	-2.36245	3.609329	-1.16684
Н	1	-2.28039	2.545505	0.227713
С	6	-0.87031	2.091388	-1.35159
Н	1	-0.13121	2.871956	-1.15273
Н	1	-0.90537	1.999041	-2.44612

 Table S5 Atom coordinates and absolute energies of biphenyl in the gas phase in theoretical calculation.

Biphenyl (Ground): <i>E</i> (B3LYP/6-311G(g)) = -811.244925 Hartree				
Center	Atom number Coordinates (Angstroms)			
number	Atom number	Х	Y	Z
С	6	-8.00675	-1.35793	3.881821
С	6	-6.61492	-1.35775	3.882258
С	6	-5.89315	-0.23209	3.458754
С	6	-6.61417	0.893747	3.034432
С	6	-8.00598	0.894262	3.033266
С	6	-8.70882	-0.23176	3.457141
Н	1	-8.54407	-2.23758	4.222292
Н	1	-6.07935	-2.23098	4.240442
Н	1	-6.07796	1.766851	2.676889
Н	1	-8.54272	1.774036	2.692191
Н	1	-9.79408	-0.23162	3.456513
С	6	-4.40792	-0.23225	3.459611
С	6	-3.68664	0.893682	3.883196
С	6	-3.68641	-1.35838	3.03687
С	6	-2.29482	0.893865	3.884365
Н	1	-4.22263	1.767153	4.240181
С	6	-2.2946	-1.35889	3.037309
Н	1	-4.22221	-2.23172	2.67929
С	6	-1.59225	-0.23259	3.461244
Н	1	-1.75789	1.773743	4.224868
Н	1	-1.75747	-2.23889	2.697439
<u> </u>	1	-0.507	-0.23273	3.461867

Synthesis and characterization

General procedure (GP)-A: Formylation of bromide

A solution of aryl halide (1.0 eq) in dry THF was cooled to -78 °C under argon atmosphere, then *n*-butyllithium (1.1 eq) was dropped to the mixture. The reaction mixture was stirred at -78°C for 30 minutes, then DMF (1.1 eq) was added to the mixture and stirred at -78°C for 10 minutes and then at room temperature for 3 hours. Saturated NH₄Claq was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed over silica gel to give the target compound.

GP-B: Cyanation of aldehyde²

Aryl aldehyde (1.0 eq) was dissolved in 1/5 (v/v) THF/30% NH₃aq and stirred at room temperature. Iodide (1.1 eq) was added to the mixture, then the reaction mixture was stirred at room temperature for 13 hours in dark. Saturated Na₂S₂O₃aq was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed over silica gel (and recrystallised) to give the target compound.

GP-C: Suzuki-Miyaura cross-coupling³

Aryl bromide (1.0 eq), arylboronic acid (1.1-1.2 eq), K_3PO_4 (3.0 eq), and $Pd(PPh_3)_4$ (3.0 mol%) were dissolved in 5/2/1 (v/v) toluene/water/methanol, and the reaction mixture was refluxed at 100 °C for more than 2 hours. Water was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed over silica gel (and recrystallised) to give the target compound.

GP-D: B-alkyl Suzuki-Miyaura cross-coupling⁴

1-Alkene (1.5 eq) was added to 0.5 M 9-BBN in THF (1.5 eq) at 0 °C under argon atmosphere, and stirred at room temperature for 4 hours. Aryl bromide (1.0 eq), 3M NaOHaq (3.0 eq), and Pd(PPh₃)₄ (3.0 mol%) were added the mixture, then the reaction mixture was refluxed at 70 °C overnight. Water was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed over silica gel to give the target compound.

GP-E: Sonogashira cross-coupling⁵

Aryl bromide (1.0 eq), aryl/trimethylsilyl acetylene (1.5 eq), $Pd(PPh_3)_4$ (5.0 mol%), Cul (5.0 mol%), and PPh₃ (5.0 mol%) were dissolved in 1/1 (v/v) triethylamine/THF under argon atmosphere. The reaction mixture was stirred at 50 °C for more than 8 hours. 2 M HCl was added, and the mixture was extracted with diethyl ether. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed over silica gel (and recrystallised) to give the target compound.

GP-F: Deprotection of trimethylsilyl group

Trimethylsilyl protected aryl acetylene (1.0 eq) and K_2CO_3 (3.0-5.0 eq) were dissolved in 1/1 (v/v) THF/MeOH, and the reaction mixture was stirred at room temperature for more than 2 hours. Water was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed over silica gel to give the target compound.

2'-acetyl-[1,1'-biphenyl]-2-carbaldehyde (3)⁶

2'-Bromoacetophenone (**1**, 1.36 mL, 10.0 mmol), 2-formylphenylboronic acid (**2**, 1.65 g, 11.0 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.030 g, 0.12 mmol), potassium fluoride dihydrate (3.11 g, 33.0 mmol), Pd₂(dba)₃ (0.05 g, 0.05 mmol) were dissolved in dry THF (20 mL) under argon atmosphere. The mixture was refluxed at 50 °C overnight, then filtrated through celite by diethyl ether. The filtrate was evaporated under reduced pressure. The residue was chromatographed over silica gel eluting with 6/1 (v/v) hexane/ethyl acetate to give crude **3** as yellow oil. Yield: 90%; ¹H-NMR (500 MHz, CDCl₃) δ 9.83 (s, 1H), 8.01 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.79 (dd, *J* = 7.5, 1.4 Hz, 1H, ArH), 7.61 (td, *J* = 7.5, 1.4 Hz, 1H, ArH), 7.57-7.51 (m, 3H, ArH), 7.28 (dd, *J* = 7.3, 1.2 Hz, 1H, ArH), 7.25 (dd, *J* = 7.6, 0.6 Hz, 1H, ArH), 2.24 (s, 3H, CH₃) ppm (Fig. S46).

5H-dibenzo[a,c][7]annulen-5-one (4)

3 (2.01 g, 9.0 mmol) and *p*-toluenesulfonic acid monohydrate (0.34 g, 1.8 mmol) were dissolved in 1/1 (v/v) ethanol/water (40 mL). The mixture was stirred for 1 minute, then 10 % NaOHaq (1.4 mL) was added to the mixture and stirred at 70°C for 10 minutes. Water was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with water and saturated NaClaq three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed over silica gel, eluting with 5/1 (v/v) hexane/ethyl acetate to give crude **4** as a yellowish solid. Yield: 79%; ¹H-NMR (500 MHz, CDCl₃) δ 7.96 (dd, *J* = 7.8, 1.4 Hz, 1H, Ar**H**), 7.92-7.90

(m, 2H, Ar**H**), 7.70-7.67 (m, 1H, Ar**H**), 7.60-7.48 (m, 4H, Ar**H**), 7.37 (d, *J* = 12.2 Hz, 1H, Ar**H**), 6.68 (d, *J* = 12.2 Hz, 1H, Ar**H**) ppm (Fig. S47).

6,7-dihydro-5H-dibenzo[a,c][7]annulene (5)

4 (1.44 g, 7.0 mmol) was dissolved in 3/1 (v/v) trifluoroacetic acid/triethylsilane (40 mL). The reaction mixture was stirred at room temperature for 0.5 hours. Water was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed over silica gel, eluting with hexane to give crude **5** as colourless oil. Yield: 83 %; ¹H-NMR (500 MHz, CDCl₃) δ 7.40 (dd, *J* = 7.3, 1.2 Hz, 2H, ArH), 7.35 (td, *J* = 7.4, 1.3 Hz, 2H, ArH), 7.30 (td, *J* = 7.2, 1.4 Hz, 2H, ArH), 7.26 (d, *J* = 10.1 Hz, 2H, ArH), 2.52 (t, *J* = 7.0 Hz, 4H, CH₂), 2.23-2.18 (m, 2H, CH₂) ppm (Fig. S48).

3,9-dibromo-6,7-dihydro-5H-dibenzo[a,c]cycloheptene (6)

5 (1.06 g, 5.4 mmol) and Fe powder (0.030 g, 0.54 mmol) were dissolved in chloroform (15 mL). Br₂ (11 mmol, 0.58 mL) dissolved in chloroform (4.0 mL) was dropped in the mixture over 10 min at 0°C. The reaction mixture was stirred for 4 hours at room temperature. Saturated Na₂S₂O₃aq was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed over silica gel, eluting with hexane and recrystallization from hexane to give **6** as a colourless solid. Yield: 68 %; ¹H-NMR (500 MHz, CDCl₃) δ 7.46 (dd, *J* = 8.1, 2.0 Hz, 2H, ArH), 7.39 (d, *J* = 1.8 Hz, 2H, ArH), 7.19 (d, *J* = 8.2 Hz, 2H, ArH), 2.45 (t, *J* = 7.0 Hz, 4H, CH₂), 2.21-2.15 (m, 2H, CH₂) ppm (Fig. S49).

9-bromo-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene-3-carbaldehyde (7)

7 was synthesized from **6** (2.11 g, 6.0 mmol), 2.0 M *n*-butyllithium in cyclohexane (3.3 ml, 6.0 mmol), DMF (0.51 ml, 6.6 mmol), and dry THF (15 ml) by using GP-A. Eluting with 12/1 (v/v) hexane/ethyl acetate on silica gel chromatography. Colourless oil. Yield: 63%; ¹H-NMR (500 MHz, CDCl₃) δ 10.05 (s, 1H, CHO), 7.85 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.77 (d, *J* = 1.5 Hz, 1H, ArH), 7.50 (dd, *J* = 7.9, 2.1 Hz, 1H, ArH), 7.52 (d, *J* = 7.6 Hz, 1H, ArH), 7.43 (d, *J* = 2.1 Hz, 1H, ArH), 7.27 (d, *J* = 8.2 Hz, 1H, ArH), 2.58 (s, 2H, CH₂), 2.47 (t, *J* = 6.6 Hz, 2H, CH₂), 2.25-2.20 (m, 2H, CH₂) ppm (Fig. S50).

9-bromo-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene-3-carbonitrile (8)

8 was synthesized from **7** (1.14 g, 3.8 mmol), iodine (1.06 g, 4.2 mmol), and 1/5 (v/v) THF/30% NH₃aq (30 ml) by using GP-B. Eluting with 2/1 (v/v) hexane/dichloromethane on silica gel chromatography. A colourless solid. Yield: 93%; ¹H-NMR (500 MHz,

CDCl₃) δ 7.63 (dd, J = 7.8, 1.7 Hz, 1H, Ar**H**), 7.53 (d, J = 1.2 Hz, 1H, Ar**H**), 7.50 (dd, J = 8.1, 2.0 Hz, 1H, Ar**H**), 7.43 (s, 1H, Ar**H**), 7.42 (d, J = 6.1 Hz, 1H, Ar**H**), 7.22 (d, J = 8.2 Hz, 1H, Ar**H**), 2.52 (t, J = 6.6 Hz, 2H, C**H**₂), 2.46 (t, J = 6.3 Hz, 2H, C**H**₂), 2.24-2.18 (m, 2H, C**H**₂) ppm (Fig. S51).

Synthesis of 9-(4-pentylphenyl)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene-3-carbonitrile (**Bc5CT[7]**)

Bc5CT[7] was synthesized from **8** (0.15 g, 0.5 mmol), 4-amylphenylboronic acid (0.12 g, 0.6 mmol), Pd(PPh₃)₄ (0.02 g, 0.02 mmol), K₃PO₄ (0.32 g, 1.5 mmol), and 5/2/1 (v/v/v) toluene/water/methanol (10 ml) by using GP-C. Eluting with 3/2 (v/v) hexane/dichloromethane on silica gel chromatography, and recrystallized from the mixture of methanol and hexane. A colourless solid. Yield: 48%; ¹H-NMR (500 MHz, CDCl₃) δ 7.64 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.59 (dd, J = 7.9, 1.8 Hz, 1H, ArH), 7.57 (dd, J = 6.4, 1.8 Hz, 2H, ArH), 7.55 (d, J = 1.5 Hz, 1H, ArH), 7.51-7.49 (m, 2H, ArH), 7.41 (d, J = 7.9 Hz, 1H, ArH), 7.28 (d, J = 8.2 Hz, 2H, ArH), 2.66 (t, J = 7.8 Hz, 2H, CH₂), 2.58-2.54 (m, 4H, CH₂), 2.28-2.22 (m, 2H, CH₂), 1.69-1.64 (m, 2H, CH₂), 1.37-1.33 (m, 4H, CH₂), 0.91 (t, J = 7.0 Hz, 3H, CH₃) ppm (Fig. S52); ¹³C-NMR (100 MHz, CDCl₃) δ 146.0, 142.6, 141.7, 141.0, 140.0, 138.0, 138.0, 132.1, 130.6, 129.1, 129.0, 128.8, 127.5, 127.1, 125.5, 119.4, 110.9, 35.7, 33.2, 31.7, 31.4, 31.4, 31.3, 22.7, 14.2 ppm (Fig. S53); FT-IR (KBr) 2224 cm⁻¹ (Fig. S106); HRMS(EI) Calcd for C₂₇H₂₇N: 365.2144, Found 365.2147 (Fig. S116).

Synthesis of 3-bromo-9-pentyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene (9)

The mixture of 1/2 (mol/mol) **6/9** was synthesized from 1-pentene (0.55 ml, 5.0 mmol), 0.5M 9-BBN in THF (10 ml), **6** (3.52 g, 10.0 mmol), 3M NaOHaq (5.0 ml), and Pd(PPh₃)₄ (0.14 g, 0.1 mmol) by using GP-D. Eluting with hexane on silica gel chromatography, recrystallized from hexane, filtered, and evaporated. Total amount: 2.38 g; Yield 91%; ¹H-NMR (500 MHz, CDCl₃): δ 7.50-7.46 (m, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.31-7.28 (m, 1H), 7.26-7.21 (m, 1H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.08 (s, 1H), 2.66 (t, *J* = 7.8 Hz, 2H), 2.49 (s, 4H), 2.23-2.17 (m, 2H), 1.69 (t, *J* = 6.1 Hz, 2H), 1.39 (s, 4H), 0.94 (t, *J* = 6.0 Hz, 3H) ppm (Fig. S54).

Synthesis of 4-(9-pentyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-3-yl)benzonitrile (**B5CT[7]**).

Bc5CT[7] was synthesized from the mixture of 1/2 (mol/mol) **6/9** (0.32 g, 0.3 mmol/0.6 mmol), 4-cyanophenylboronic acid (0.15 g, 1.0 mmol), K₃PO₄ (0.38 g, 1.8 mmol), Pd(PPh₃)₄ (0.03 g, 0.03 mmol), and 5/2/1 (v/v) toluene/water/methanol (10 ml) by using GP-C. Eluting with 3/2 hexane/dichloromethane on silica gel chromatography. A colourless solid. Yield: 26%; ¹H-NMR (500 MHz, CDCl₃): δ 7.77 (t, *J* = 9.5 Hz, 4H),

7.58 (d, J = 7.9 Hz, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 7.6 Hz, 1H), 7.21 (d, J = 7.9 Hz, 1H), 7.11 (s, 1H), 2.67 (t, J = 7.6 Hz, 2H), 2.61 (t, J = 8.6 Hz, 2H), 2.54 (t, J = 6.9 Hz, 2H), 2.28-2.32 (m, 2H), 1.72-1.68 (m, 2H), 1.40 (s, 4H), 0.95 (t, J = 5.6Hz, 3H) ppm (Fig. S55); ¹³C-NMR (100 MHz, CDCl₃) δ 145.7, 142.9, 141.9, 140.6, 139.6, 137.9, 137.6, 132.7, 129.1, 128.9, 128.2, 127.7, 127.4, 126.8, 125.5, 119.2, 110.8, 35.9, 33.4, 31.8, 31.5, 31.4, 22.7, 14.2 ppm (Fig. S56); FT-IR (KBr) 2224 cm⁻¹ (Fig. S107); HRMS(EI) Calcd for C₂₇H₂₇N: 365.2144, Found 365.2145 (Fig. S117).

Scheme S1 Synthesis of aryl acetylene

1-Bromo-4-(pentyloxy)benzene (S2b)

4-bromophenol (**S1**) (1.74 g, 10.0 mmol), 1-bromopentane (1.86 ml, 15.0 mmol), and K₂CO₃ (3.45 g, 25.0 mol) were dissolved in 2-butanone (15.0 ml). The mixture was refluxed for 6 hours. Water was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed over silica gel, eluting with 6/1 (v/v) hexane/dichloromethane to give crude **S2b** as a colourless oil. Yield: 1.66 g, 82%; ¹H-NMR (500 MHz, CDCl₃) δ 7.36 (d, *J* = 7.3 Hz, 2H, Ar**H**), 6.77 (d, *J* = 7.6 Hz, 2H, Ar**H**), 3.91 (t, *J* = 6.6 Hz, 2H, OCH₂), 1.80-1.74 (m, 2H, CH₂), 1.46-1.34 (m, 4H, CH₄), 0.93 (t, *J* = 6.7 Hz, 3H, CH₃) ppm (Fig. S57).

Trimethyl((4-pentylphenyl)ethynyl)silane (S3a)

S3a was synthesised from 1-bromo-4-pentylbenzene (**S2a**) (0.93 ml, 6.0 mmol), trimethylsilylacetylene (1.23 ml, 9.0 mmol), Pd(PPh₃)₄ (0.35 g, 0.3 mmol), Cul (0.06 g, 0.3 mmol), triphenylphosphine (0.08 g, 0.3 mmol), and 1/1 (v/v) triethylamine/THF (20.0 ml) by using GP-E. Eluting with 3/1 (v/v) hexane/dichloromethane on silica gel chromatography. Colourless oil. Yield: 1.52 g, >99%. **S3a** was used for the next reaction without ¹H-NMR measurement.

Trimethyl((4-(pentyloxy)phenyl)ethynyl)silane (S3b)

S3b was synthesised from **S2b** (1.66 g, 6.8 mmol), trimethylsilylacetylene (1.40 ml, 10.4 mmol), Pd(PPh₃)₄ (0.40 g, 0.3 mmol), Cul (0.06 g, 0.4 mmol), triphenylphosphine (0.09 g, 0.3 mmol), and 1/1 (v/v) triethylamine/THF (20.0 ml) by using GP-E. Eluting with 3/1 (v/v) hexane/dichloromethane on silica gel chromatography. Yellow oil. Yield: >99%. **S3b** was used for the next reaction without ¹H-NMR measurement.

1-Ethynyl-4-pentylbenzene (S4a)

S4a was synthesised from **S3a** (1.54 g, 6.2 mmol), K₂CO₃ (4.31 g, 31.2 mmol), and 1/1 (v/v) THF/methanol (30.0 ml) by using GP-F. Eluting with hexane on silica gel chromatography. Colourless oil. Yield: 0.90 g, 84%; ¹H-NMR (500 MHz, CDCl₃) δ 7.40 (d, J = 7.6 Hz, 2H, ArH), 7.13 (d, J = 7.3 Hz, 2H, ArH), 3.03 (s, 1H, CH), 2.60 (t, J = 7.8 Hz, 2H, CH₂), 1.63-1.57 (m, 2H, CH₂), 1.37-1.27 (m, 4H, CH₂), 0.89 (t, J = 6.7 Hz, 3H, CH₃) ppm (Fig. S58).

1-Ethynyl-4-(pentyloxy)benzene (S4b)

S4b was synthesised from **S3b** (1.81 g, 7.0 mmol), K₂CO₃ (2.89 g, 20.9 mmol), and 1/1 (v/v) THF/methanol (30.0 ml) by using GP-F. Eluting with hexane on silica gel chromatography. Colorless oil. Yield: 43%; ¹H-NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* = 8.2 Hz, 2H, Ar**H**), 6.83 (d, *J* = 8.2 Hz, 2H, Ar**H**), 3.95 (t, *J* = 5.8 Hz, 2H, OC**H**₂), 2.99 (s, 1H, C**H**), 1.82-1.75 (m, 2H, C**H**₂), 1.45-1.38 (m, 4H, C**H**₂), 0.93 (t, *J* = 6.3 Hz, 3H, C**H**₃) ppm 0.56 g, (Fig. S59).

Scheme S2 Synthesis of 5CT.

4"-Pentyl-[1,1':4',1"-terphenyl]-4-carbonitrile (5CT)

5CT was synthesised from 4-bromo-4'-pentylbiphenyl (**S5**) (0.30 g, 1.0 mmol), 4cyanophenylboronic acid (0.18 g, 1.2 mmol), K₃PO₄ (0.64 g, 3.0 mmol), Pd(PPh₃)₄ (0.03 g, 0.03 mmol), and 5/2/1 (v/v) toluene/water/methanol (10.0 ml) by using GP-C. Eluting with 1/1 (v/v) hexane/dichloromethane on silica gel chromatography and recrystallisation from the mixed solvent of hexane and dichloromethane. Colourless solid. Yield: 0.12 g, 37%; ¹H-NMR (500 MHz, CDCl₃) δ 7.74 (s, 4H, ArH), 7.71 (dt, *J* = 8.3, 2.0 Hz, 2H, ArH), 7.66 (dt, *J* = 8.4, 1.9 Hz, 2H, ArH), 7.56 (dt, *J* = 8.4, 2.0 Hz, 2H, ArH), 7.29 (d, *J* = 8.2 Hz, 2H, ArH), 2.66 (t, *J* = 7.8 Hz, 2H, CH₂), 1.70-1.63 (m, 2H, CH₂), 1.39-1.34 (m, 4H, CH₂), 0.93-0.90 (m, 3H, CH₃) ppm (Fig. S60).

Scheme S3 Synthesis of DMc5CT.

4'-lodo-2,2'-dimethyl-[1,1'-biphenyl]-4-carbaldehyde (S7)

S7 was synthesised from 4,4'-diiodo-2,2'-dimethyl-1,1'-biphenyl (**S6**) (0.35 g, 0.8 mmol), 2.3 M *n*-butyllithium in cyclohexane (0.38 ml, 0.9 mmol), DMF (0.07 ml, 0.9 mmol), and dry THF (5.0 ml) by using GP-A. Eluting with 12/1 (v/v) hexane/ethyl acetate on silica gel chromatography. Yellow oil. Yield: 0.07 g, 26%; ¹H-NMR (500 MHz, CDCl₃) δ 10.03 (s, 1H, CHO), 7.79 (s, 1H, ArH), 7.74 (dd, J = 7.6, 1.2 Hz, 1H, ArH), 7.66 (s, 1H, ArH), 7.59 (dd, J = 7.9, 1.5 Hz, 1H, ArH), 7.24 (d, J = 7.6 Hz, 1H, ArH), 6.82 (d, J = 7.9 Hz, 1H, ArH), 2.13 (s, 3H, CH₃), 2.00 (s, 3H, CH₃) ppm (Fig. S61).

4'-lodo-2,2'-dimethyl-[1,1'-biphenyl]-4-carbonitrile (S8)

S8 was synthesised from **S7** (0.07 g, 0.2 mmol), iodide (0.06 g, 0.2 mmol), and 1/6 (v/v) THF/30% NH₃aq (2.5 ml) by using GP-B. Eluting with 2/1 (v/v) hexane/dichloromethane on silica gel chromatography. Colourless solid. Yield: 0.05 g, 72%; ¹H-NMR (500 MHz, CDCl₃) δ 7.66 (d, *J* = 0.6 Hz, 1H, ArH), 7.60-7.58 (m, 1H, ArH), 7.57 (s, 1H, ArH), 7.52 (dd, *J* = 7.8, 1.1 Hz, 1H, ArH), 7.17 (d, *J* = 7.9 Hz, 1H, ArH), 6.78 (d, *J* = 7.9 Hz, 1H, ArH), 2.08 (s, 3H, CH₃), 1.98 (s, 3H, CH₃) ppm (Fig. S62).

2,2'-Dimethyl-4"-pentyl-[1,1':4',1"-terphenyl]-4-carbonitrile (DMc5CT)

DMc5CT was synthesized from **S8** (0.05 g, 0.2 mmol), 4-pentylphenylboronic acid (0.03 g, 0.2 mmol), K₃PO₄ (0.10 g, 0.5 mmol), Pd(PPh₃)₄ (0.01 g, 0.01 mmol), and 5/2/1 (v/v) toluene/water/methanol (5.0 ml) by using GP-C. Eluting with 2/1 (v/v) hexane/dichloromethane on silica gel chromatography. Colourless solid. Yield: 0.04 g, 75%; ¹H-NMR (500 MHz, CDCl₃) δ 7.58 (s, 1H, ArH), 7.56-7.53 (m, 3H, ArH), 7.50 (s, 1H, ArH), 7.47 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.28-7.25 (m, 3H, ArH), 7.10 (d, *J* = 7.6 Hz, 1H, ArH), 2.66 (t, J = 7.8 Hz, 2H, CH₂), 2.14 (s, 3H, CH₃), 2.09 (s, 3H, CH₃), 1.71-1.64 (m, 2H, CH₂), 1.39-1.34 (m, 4H, CH₂), 0.91 (t, *J* = 6.9 Hz, 3H, CH₃) ppm (Fig. S63); ¹³C-NMR (126 MHz, CDCl₃) δ 146.6, 142.5, 141.0, 138.5, 138.1, 137.8, 135.7, 133.5, 130.4, 129.5, 129.2, 129.0, 128.8, 127.0, 124.6, 119.2, 111.3, 35.7, 31.7, 31.3, 22.7, 20.0, 19.9, 14.2 ppm (Fig. S64); FT-IR (KBr) 2227 cm⁻¹ (Fig. S108); HRMS(EI)

Calcd for C₂₆H₂₇N: 353.2144, Found 353.2142 (Fig. S118).

Scheme S4 Synthesis of 6-membered bridged biphenyl derivatives.

2,7-Dibromo-9,10-dihydrophenanthrene (S10)

9,10-Dihydrophenanthrene (**S9**) (1.80 g, 10.0 mmol) and Fe (0.06 g, 1.1 mmol) were dissolved in chloroform (15 mL). Br₂ (1.08 ml, 21.0 mmol) dissolved in chloroform (5.0 mL) was dropped in the mixture over 10 min at 0 °C. The reaction mixture was stirred for 4 hours at room temperature. Saturated Na₂S₂O₃aq was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was recrystallised from dichloromethane to give crude **S10** as a colourless solid. Yield: 2.49 g, 74%; ¹H-NMR (500 MHz, CDCl₃) δ 7.55 (d, *J* = 8.2 Hz, 2H, Ar**H**), 7.42 (dd, *J* = 8.2, 2.1 Hz, 2H, Ar**H**), 7.38 (d, *J* = 2.1 Hz, 2H, Ar**H**), 2.83 (s, 4H, C**H**₂) ppm (Fig. S65).

7-Bromo-9,10-dihydrophenanthrene-2-carbaldehyde (S11)

S11 was synthesised from **S10** (2.37 g, 7.0 mmol), 2.6 M *n*-butyllithium in hexane (2.96 ml, 7.7 mmol), DMF (0.64 ml, 7.7 mmol), and dry THF (50 ml) by using GP-A. Eluting with 1/3 (v/v) hexane/dichloromethane on silica gel chromatography. Yellow solid. Yield: 1.81 g, 90%; ¹H-NMR (500 MHz, CDCl₃) δ 10.01 (s, 1H, CHO), 7.85 (d, *J* = 7.9 Hz, 1H, ArH), 7.81 (d, *J* = 7.9 Hz, 1H, ArH), 7.76 (s, 1H, ArH), 7.66 (d, *J* = 8.5 Hz, 1H, ArH), 7.47 (d, *J* = 8.5 Hz, 1H, ArH), 7.44 (s, 1H, ArH), 2.96-2.88 (m, 4H, CH₂) ppm (Fig. S66).

7-Pentyl-9,10-dihydrophenanthrene-2-carbaldehyde (S12)

S12 was synthesised from **S11** (0.26 g, 0.9 mmol), 1-pentene (0.16 ml, 1.5 mmol), 0.5 M 9-BBN in THF (3.0 ml, 1.5 mmol), 3.0 M NaOHaq (1.0 mml, 3.0 mmol), and $Pd(PPh_3)_4$ (0.03 g, 0.03 mmol) by using GP-D. Eluting with 1/6 (v/v) hexane/dichloromethane on silica gel chromatography. Yellow oil. Yield: 0.19 g, 75%;
¹H-NMR (500 MHz, CDCl₃) δ 9.99 (s, 1H, CHO), 7.86 (d, *J* = 7.9 Hz, 1H, ArH), 7.79 (dd, *J* = 8.1, 1.4 Hz, 1H, ArH), 7.74 (s, 1H, ArH), 7.72 (d, *J* = 7.9 Hz, 1H), ArH, 7.16 (d, *J* = 7.9 Hz, 1H, ArH), 7.09 (s, 1H, ArH), 2.96-2.87 (m, 4H, CH₂), 2.63 (t, *J* = 7.8 Hz, 2H, CH₂), 1.68-1.62 (m, 2H, CH₂), 1.38-1.34 (m, 4H, CH₂), 0.91 (t, *J* = 6.9 Hz, 3H, CH₃) ppm (Fig. S67).

7-Pentyl-9,10-dihydrophenanthrene-2-carbonitrile (B5CB[6])

B5CB[6] was synthesised from **S12** (0.19 g, 0.7 mmol), iodide (0.19 g, 0.7 mmol), and 1/5 (v/v) THF/30% NH₃aq (6.0 ml) by using GP-B. Eluting with 3/2 (v/v) hexane/dichloromethane on silica gel chromatography. Colourless oil. 0.10 g, Yield: 51%; ¹H-NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* = 7.9 Hz, 1H, ArH), 7.66 (d, *J* = 7.9 Hz, 1H, ArH), 7.56 (dd, *J* = 7.9, 1.5 Hz, 1H, ArH), 7.50 (s, 1H, ArH), 7.16 (dd, *J* = 8.1, 1.1 Hz, 1H, ArH), 7.08 (s, 1H, ArH), 2.91-2.84 (m, 4H, CH₂), 2.62 (t, *J* = 7.8 Hz, 2H, CH₂), 1.67-1.61 (m, 2H, CH₂), 1.38-1.33 (m, 4H, CH₂), 0.91 (t, *J* = 6.9 Hz, 3H, CH₃) ppm (Fig. S68); ¹³C-NMR (126 MHz, CDCl₃) δ 144.5, 139.3, 138.1, 137.9, 131.7, 130.9, 130.4, 128.6, 127.6, 124.4, 124.0, 119.4, 110.1, 35.9, 31.7, 31.2, 28.9, 28.6, 22.7, 14.2 ppm (Fig. S69); FT-IR (KBr) 2224 cm⁻¹ (Fig. S109); HRMS (EI) Calcd for C₂₀H₂₁N: 275.1674, Found 275.1669 (Fig. S119).

7-Bromo-9,10-dihydrophenanthrene-2-carbonitrile (S13)

A solution of **S11** (1.81 g, 6.3 mmol) and hydroxylamine hydrochloride (0.44 g, 6.3 mmol) in NMP (30.0 ml) was stirred at 115°C for 6 hours. Water was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The chromatographed over silica gel, eluting with residue was 1/1 (v/v)hexane/dichloromethane to give crude **S13** as a colourless solid. Yield: 0.95 g, 53%; ¹H-NMR (500 MHz, CDCl₃) δ 7.77 (d, J = 8.2 Hz, 1H, Ar**H**), 7.61-7.58 (m, 2H, Ar**H**), 7.52 (s, 1H, ArH), 7.47 (d, J = 8.2 Hz, 1H, ArH), 7.43 (s, 1H, ArH), 2.90-2.85 (m, 4H, CH₂) ppm (Fig. S70).

7-(4-Pentylphenyl)-9,10-dihydrophenanthrene-2-carbonitrile (Bc5CT[6])

Bc5CT[6] was synthesised from **S13** (0.28 g, 1.0 mmol), 4-pentylphenylboronic acid (0.23 g, 1.2 mmol), K₃PO₄ (0.64 g, 3.0 mmol), Pd(PPh₃)₄ (0.03 g, 0.03 mmol), and 5/2/1 (v/v) toluene/water/methanol (15.0 ml) by using GP-C. Eluting with 1/1 (v/v) hexane/dichloromethane on silica gel chromatography and recrystallisation from the mixed solvent of hexane and dichloromethane. Colourless solid. Yield: 0.25 g, 71%; ¹H-NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 7.9 Hz, 1H, ArH), 7.81 (d, *J* = 8.2 Hz, 1H, ArH), 7.60-7.53 (m, 5H, ArH), 7.49 (s, 1H, ArH), 7.28 (d, *J* = 7.9 Hz, 2H, ArH), 2.98-2.92 (m, 4H, CH₂), 2.66 (t, *J* = 7.8 Hz, 2H, CH₂), 1.69-1.63 (m, 2H, CH₂), 1.38-1.34 (m,

4H, CH₂), 0.91 (t, J = 6.6 Hz, 3H, CH₃) ppm (Fig. S71); ¹³C-NMR (126 MHz, CDCl₃) δ 142.8, 142.0, 139.0, 138.3, 138.2, 137.7, 131.7, 131.6, 130.9, 129.1, 127.0, 126.9, 126.0, 125.0, 124.2, 119.4, 110.4, 35.7, 31.7, 31.3, 28.8, 28.8, 22.7, 14.2 ppm (Fig. S72); FT-IR (KBr) 2224 cm⁻¹ (Fig. S110); HRMS (EI) Calcd for C₂₆H₂₅N: 351.1987, Found 351.1993 (Fig. S120).



Scheme S5 Synthesis of 7-membered bridged-biphenyl derivatives.

9-Pentyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene-3-carbaldehyde (S14a)

S14a was synthesised from **7** (0.30 g, 1.0 mmol), 1-pentene (0.23 ml, 1.5 mmol), 0.5 M 9-BBN in THF (3.0 ml, 1.5 mmol), 3.0 M NaOHaq (1.0 ml, 3.0 mmol), and Pd(PPh₃)₄ (0.03 g, 0.03 mmol) by using GP-D. Eluting with 2/1 (v/v) hexane/dichloromethane on silica gel chromatography. Yellow oil. Yield: 0.19 g, 65%; ¹H-NMR (500 MHz, CDCl₃) δ 10.03 (s, 1H, CHO), 7.83 (d, *J* = 7.9 Hz, 1H, ArH), 7.75 (s, 1H, ArH), 7.52 (d, *J* = 7.9 Hz, 1H, ArH), 7.18 (d, *J* = 7.6 Hz, 1H, ArH), 7.08 (s, 1H, ArH), 2.65 (t, *J* = 7.9 Hz, 2H, CH₂), 2.58 (t, *J* = 6.9 Hz, 2H, CH₂), 2.48 (t, *J* = 6.9 Hz, 2H, CH₂), 2.25-2.19 (m, 2H, CH₂), 1.70-1.64 (m, 2H, CH₂), 1.38-1.33 (m, 4H, CH₂), 0.92 (t, *J* = 6.7 Hz, 3H, CH₂) ppm (Fig. S73).

9-Octyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene-3-carbaldehyde (S14b)

S14b was synthesised from **7** (0.65 g, 2.2 mmol), 1-octene (0.50 ml, 3.2 mmol), 0.5 M 9-BBN in THF (6.5 ml, 3.3 mmol), 3.0 M NaOHaq (2.2 ml,6.6 mmol), and Pd(PPh₃)₄ (0.06 g, 0.05 mmol) by using GP-D. Eluting with 2/1 (v/v) hexane/dichloromethane on silica gel chromatography. Yellow oil. Yield: 0.40 g, 55%; ¹H-NMR (500 MHz, CDCl₃) δ 10.03 (s, CHO 1H), 7.83 (dd, *J* = 7.9, 1.8 Hz, 1H, ArH), 7.75 (d, *J* = 1.5 Hz, 1H, ArH), 7.52 (d, *J* = 7.9 Hz, 1H. ArH), 7.31 (d, *J* = 7.6 Hz, 1H, ArH), 7.18 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.08 (d, *J* = 1.2 Hz, 1H, ArH), 2.67-2.63 (m, 2H, CH₂), 2.58 (t, *J* = 7.0 Hz, 2H, CH₂), 2.47 (t, *J* = 7.0 Hz, 2H, CH₂), 2.25-2.19 (m, 2H, CH₂), 1.69-1.63 (m, 2H, CH₂), 1.45-1.26 (m, 10H, CH₂), 0.90-0.87 (m, 3H, CH₃) ppm (Fig. S74).

S14b contained small amounts of 9-butyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene-3-carbaldehyde (octyl group of **S14b** replaced by butyl group), which was synthesised in the synthesis of **7**. We have synthesised **7** several times, and in the synthesis of **S14a** we used different **7** which did not contain this contamination.

9-Pentyl-6,7-dihydro-5H-dibenzo[a,c][7]annulene-3-carbonitrile (B5CB[7])

B5CB[7] was synthesised from **S14a** (0.21 g, 0.7 mmol), iodide (0.20 g, 0.8 mmol), and 1/5 (v/v) THF/30% NH₃aq (12.0 ml) by using GP-B. Eluting with 1/1 (v/v) hexane/dichloromethane on silica gel chromatography. Colourless oil. 0.09 g, Yield: 43%; ¹H-NMR (500 MHz, CDCl₃) δ 7.61 (d, J = 7.9 Hz, 1H, ArH), 7.51 (s, 1H, ArH), 7.44 (d, J = 7.9 Hz, 1H, ArH), 7.26 (d, J = 7.6 Hz, 1H, ArH), 7.18 (d, J = 7.9 Hz, 1H, ArH), 7.08 (s, 1H, ArH), 2.64 (t, J = 7.9 Hz, 2H, CH₂), 2.51 (t, J = 7.0 Hz, 2H, CH₂), 2.46 (t, J = 6.7 Hz, 2H, CH₂), 2.23-2.18 (m, 2H, CH₂), 1.69-1.64 (m, 2H, CH₂), 1.39-1.35 (m, 4H, CH₂), 0.92 (t, J = 6.7 Hz, 3H, CH₃) ppm (Fig. S75); ¹³C-NMR (100 MHz, CDCl₃) δ 146.4, 143.9, 140.9, 139.5, 136.7, 132.0, 130.5, 129.0, 128.9, 128.3, 127.0, 119.4, 110.6, 35.9, 33.2, 31.8, 31.4, 31.3, 31.2, 22.7, 14.2 ppm (Fig. S76); FT-IR (KBr) 2224 cm⁻¹ (Fig. S111); HRMS (EI) Calcd for C₂₁H₂₃N: 289.1830. Found 289.1825 (Fig. S121).

9-Octyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene-3-carbonitrile (B8CB[7])

B8CB[7] was synthesised from **S14b** (0.40 g, 1.2 mmol), iodide (0.33 g, 1.3 mmol), and 1/6 (v/v) THF/30% NH₃aq (14.0 ml) by using GP-B. Eluting with 2/1 (v/v) hexane/dichloromethane on silica gel chromatography. Colourless oil. Yield: 0.31 g, 94%; ¹H-NMR (500 MHz, CDCl₃) δ 7.61 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.51 (d, J = 1.5 Hz, 1H, ArH), 7.44 (d, J = 7.9 Hz, 1H, ArH), 7.26 (d, J = 7.6 Hz, 1H, ArH), 7.18 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.18 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.08 (s, 1H, ArH), 2.67-2.62 (m, 2H, CH₂), 2.51 (t, J = 7.0 Hz, 2H, CH₂), 2.46 (t, J = 6.9 Hz, 2H, CH₂), 2.23-2.17 (m, 2H, CH₂), 1.69-1.62 (m, 2H, CH₂), 1.44-1.26 (m, 10H, CH₂), 0.89 (t, J = 7.0 Hz, 3H, CH₃) ppm (Fig. S77); ¹³C-NMR (126 MHz, CDCl₃) δ 146.2, 143.8, 140.8, 139.3, 136.5, 131.9, 130.4, 128.9, 128.8, 128.2, 126.9, 119.3, 110.5, 35.8, 33.1, 31.9, 31.5, 31.3, 31.1, 29.5, 29.5, 29.3, 22.7, 14.1 ppm (Fig. S78); FT-IR (KBr) 2224 cm⁻¹ (Fig. S112); HRMS (EI) Calcd for C₂₄H₂₉N: 331.2300, Found 331.2305 (Fig. S122).

B8CB[7] contained **B4CB[7]** with a mol ratio of 4:1, calculated from ¹H-NMR spectra. The peaks derived from **B4CB[7]** were observed in ¹H-NMR and ¹³C-NMR. However, the fact that the contaminated **B8CB[7]** did not form a nematic was not the primary focus of this work, so we decided not to resynthesise **B8CB[7]**.

(9-Bromo-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-3-yl)boronic acid (S15)

A solution of **6** (1.06 g, 3.0 mmol) in dry THF (15.0 ml) was cooled to -78 °C. 2.0 M *n*butyllithium in cyclohexane (1.58 ml, 3.2 mmol) was dropped into the mixture under argon atmosphere. The reaction mixture was stirred at -78 °C for 1 hour, then triisopropyl borate (1.43 ml, 6.6 mmol) was added. The reaction mixture was stirred at -78 °C for 30 minutes, then at room temperature for 18.5 hours. 5% HClaq was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was triturated with hexane to give crude **S15** as a colourless solid. Yield: 0.45 g, 47%. **S15** was used for the next step without ¹H-NMR measurement.

9-Bromo-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-3-ol (S16)

m-Chloroperoxybenzoic acid (contains ca. 30% water) (0.25 g, 1.0 mmol) was added to a solution of **S15** (0.32 g, 1.0 mmol) in 1/2 (v/v) water/ethanol (4.0 ml) and stirred at room temperature for 6 hours. Saturated NaHCO₃aq was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with water three times, dried over MgSO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed over silica gel, eluting with 6/1 (v/v) hexane/ethyl acetate to give crude **S16** as a viscous brown oil. Yield: 0.25 g, 86%; ¹H-NMR (500 MHz, CDCl₃) δ 7.44 (dd, *J* = 8.1, 2.0 Hz, 1H, Ar**H**), 7.37 (d, *J* = 2.1 Hz, 1H, Ar**H**), 7.21 (d, *J* = 8.2 Hz, 1H, Ar**H**), 7.19 (d, *J* = 8.2 Hz, 1H, Ar**H**), 6.80 (dd, *J* = 8.2, 2.7 Hz, 1H, Ar**H**), 6.74 (d, *J* = 2.7 Hz, 1H, Ar**H**), 4.72 (s, 1H, O**H**), 2.48-2.43 (m, 4H, C**H**₂), 2.20-2.14 (m, 2H, C**H**₂) ppm (Fig. S79).

3-Bromo-9-(heptyloxy)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene (S17)

S17 was synthesised from **S16** (0.25 g 0.09 mmol), 1-bromoheptane (0.20 ml, 1.3 mmol), K₂CO₃ (0.30 g, 2.2 mmol), and 2-butanone (5.0 ml) by using the similar procedure for the synthesis of **S2b**. Eluting with 6/1 (v/v) hexane/dichloromethane gave crude **S17** as colourless oil. Yield: 0.27 g, 81%; ¹H-NMR (500 MHz, CDCl₃) δ 7.42 (dd, J = 8.1, 2.0 Hz, 1H, Ar**H**), 7.36 (d, J = 2.1 Hz, 1H, Ar**H**), 7.23 (d, J = 8.2 Hz, 1H, Ar**H**), 7.19 (d, J = 8.2 Hz, 1H, Ar**H**), 6.85 (dd, J = 8.4, 2.6 Hz, 1H, Ar**H**), 6.79 (d, J = 2.4 Hz, 1H, Ar**H**), 3.99 (t, J = 6.6 Hz, 2H, OCH₂), 2.45 (t, J = 7.0 Hz, 4H, CH₂), 2.19-2.13 (m, 2H, CH₂), 1.83-1.77 (m, 2H, CH₂), 1.50-1.43 (m, 2H, CH₂), 1.40-1.26 (m, 6H, CH₂), 0.90 (t, J = 6.9 Hz, 3H, CH₃) ppm (Fig. S80).

9-(Heptyloxy)-6,7-dihydro-5H-dibenzo[a,c][7]annulene-3-carbaldehyde (S18)

S18 was synthesised from **S17** (0.27 g, 0.7 mmol), 2.0 M *n*-butyllithium in cyclohexane (0.38 ml, 0.8 mmol), DMF (0.06 ml, 0.8 mmol), and dry THF (5.0 ml) by using GP-A. Eluting with 12/1 (v/v) hexane/ethyl acetate on silica gel chromatography. Yield: 0.15 g, 64%; ¹H-NMR (500 MHz, CDCl₃) δ 10.02 (s, 1H, CHO), 7.82 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.74 (d, *J* = 1.5 Hz, 1H, ArH), 7.49 (d, *J* = 7.6 Hz, 1H, ArH), 7.32 (d, *J* = 8.5 Hz, 1H, ArH), 6.89 (dd, *J* = 8.4, 2.6 Hz, 1H, ArH), 6.82 (d, *J* = 2.7 Hz, 1H, ArH), 4.01 (t, *J* = 6.6 Hz, 2H, OCH₂), 2.57 (t, *J* = 7.0 Hz, 2H, CH₂), 2.47 (t, *J* = 7.0 Hz, 2H, CH₂), 2.24-2.18 (m, 2H, CH₂), 1.84-1.79 (m, 2H, CH₂), 1.51-1.45 (m, 2H, CH₂), 1.41-1.29 (m, 6H, CH₂), 0.90 (t, *J* = 6.9 Hz, 3H, CH₃) ppm (Fig. S81).

9-(Heptyloxy)-6,7-dihydro-5*H***-dibenzo[***a,c***][7]annulene-3-carbonitrile (B7OCB[7]) B7OCB[7] was synthesised from S18 (0.15 g, 0.5 mmol), iodide (0.12 g, 0.5 mmol), and 1/5 (v/v) THF/30% NH₃aq (6.0 ml) by using CP-B. Eluting with 2/1 (v/v) hexane/dichloromethane on silica gel chromatography. Colourless solid. Yield: 0.12 g, 80%; ¹H-NMR (500 MHz, CDCl₃) δ 7.60 (dd,** *J* **= 7.9, 1.5 Hz, 1H, ArH), 7.50 (d,** *J* **= 1.5 Hz, 1H, ArH), 7.41 (d,** *J* **= 7.9 Hz, 1H, ArH), 7.27 (d,** *J* **= 8.2 Hz, 1H, ArH), 6.88 (dd,** *J* **= 8.2, 2.7 Hz, 1H, ArH), 6.82 (d,** *J* **= 2.4 Hz, 1H, ArH), 4.01 (t,** *J* **= 6.6 Hz, 2H, OCH₂), 2.51 (t,** *J* **= 7.0 Hz, 2H, CH₂), 2.45 (t,** *J* **= 7.0 Hz, 2H, CH₂), 2.23-2.17 (m, 2H, CH₂), 1.84-1.78 (m, 2H, CH₂), 1.51-1.45 (m, 2H, CH₂), 1.41-1.29 (m, 6H, CH₂), 0.90 (t,** *J* **= 7.0 Hz, 3H, CH₃) ppm (Fig. S82); ¹³C-NMR (126 MHz, CDCl₃) δ 159.7, 146.2, 141.1, 140.7, 132.1, 131.6, 130.5, 129.6, 128.8, 119.4, 115.2, 112.6, 110.3, 68.2, 33.0, 31.9, 31.5, 31.4, 29.5, 29.2, 26.2, 22.8, 14.2 ppm (Fig. S83); FT-IR (KBr) 2224 cm⁻¹ (Fig.** S103); HRMS (EI) Calcd for C₂₃H₂₇NO: 333.2093, Found 333.2098 (Fig. S123).

3-Pentyl-9-(4-pentylphenyl)-6,7-dihydro-5H-dibenzo[a,c][7]annulene (B5T[7])

B5T[7] was synthesised from **9** (0.34 g, 1.0 mmol), 4-pentylphenylboronic acid (0.38 g, 2.0 mmol), K₃PO₄ (0.64 g, 3.0 mmol), Pd(PPh₃)₄ (0.06 g, 0.05 mmol), and 5/2/1 (v/v) toluene/water/methanol (15.0 ml) by using GP-C. Eluting with hexane on silica gel chromatography. Colourless oil. Yield: 0.29 g, 70%; ¹H-NMR (399 MHz, CDCl₃) δ 7.58-7.53 (m, 3H, ArH), 7.45 (d, *J* = 1.4 Hz, 1H, ArH), 7.42 (d, *J* = 8.2 Hz, 1H, ArH), 7.33 (d, *J* = 7.8 Hz, 1H, ArH), 7.27-7.25 (m, 2H, ArH), 7.16 (dd, *J* = 7.5, 1.6 Hz, 1H, ArH), 7.07 (s, 1H, ArH), 2.67-2.62 (m, 4H, CH₂), 2.56 (t, *J* = 7.1 Hz, 2H, CH₂), 2.52 (t, *J* = 7.1 Hz, 2H, CH₂), 2.25-2.18 (m, 2H, CH₂), 1.72-1.63 (m, 4H, CH₂), 1.40-1.34 (m, 8H, CH₂), 0.94-0.89 (m, 6H, CH₃) ppm (Fig. S84); ¹³C-NMR (100 MHz, CDCl₃) δ 142.4, 142.1, 140.1, 139.6, 138.5, 138.2, 129.0, 128.8, 128.7, 128.2, 127.2, 127.0, 126.7, 125.2, 35.9, 35.8, 33.5, 31.9, 31.9, 31.7, 31.7, 31.4, 31.3, 22.7, 14.2 ppm (Fig. S85); HRMS (EI) Calcd for C₃₁H₃₈: 410.2974, Found 410.2965 (Fig. S124).

3-Pentyl-9-(4-(pentyloxy)phenyl)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene (B5(5O)T[7])

B5(5O)T[7] was synthesised from **9** (0.38 g, 1.1 mmol), 4-(pentyloxy)phenylboronic acid (0.42 g, 2.0 mmol), K₃PO₄ (0.64 g, 3.0 mmol), Pd(PPh₃)₄ (0.06 g, 0.05 mmol), and 5/2/1 (v/v) toluene/water/methanol (15.0 ml) by using GP-C. Eluting with 9/1 (v/v) hexane/dichloromethane on silica gel chromatography. Colourless oil. Yield: 0.24 g, 51%;; ¹H-NMR (500 MHz, CDCl₃) δ 7.58 (d, J = 7.6 Hz, 2H, ArH), 7.51 (d, J = 7.6 Hz, 1H, ArH), 7.41 (d, J = 9.8 Hz, 2H, ArH), 7.32 (d, J = 7.9 Hz, 1H, ArH), 7.16 (d, J = 7.6 Hz, 1H, ArH), 7.07 (s, 1H, ArH), 6.98 (d, J = 7.6 Hz, 2H, ArH), 4.01 (t, J = 6.4 Hz, 2H, OCH₂), 2.64 (t, J = 7.8 Hz, 2H, CH₂), 2.56 (t, J = 6.7 Hz, 2H, CH₂), 2.52 (t, J = 6.9 Hz, 2H, CH₂), 2.24-2.19 (m, 2H, CH₂), 1.85-1.79 (m, 2H, CH₂), 1.68 (t, J = 6.4 Hz, 2H, CH₂), 1.50-1.38 (m, 8H, CH₂), 0.96-0.91 (m, 6H, CH₃) ppm (Fig. S86); ¹³C-NMR (100 MHz, CDCl₃) δ 158.8, 142.4, 140.1, 139.8, 139.7, 139.6, 138.3, 133.5, 128.8, 128.2, 128.2, 126.9, 126.7, 124.9, 114.9, 68.2, 35.9, 33.5, 31.9, 31.7, 31.4, 29.2, 28.4, 22.7, 22.6, 14.2, 14.2 ppm (Fig. S87); HRMS (EI) Calcd for C₃₁H₃₈O: 426.2923, Found 426.2922 (Fig. S125).

3,9-Bis(4-pentylphenyl)-6,7-dihydro-5H-dibenzo[a,c][7]annulene (B5Q[7])

B5Q[7] was synthesised from **6** (0.14 g, 0.4 mmol), 4-pentylphenylboronic acid (0.18 g, 0.09 mmol), K₃PO₄ (0.51 g, 2.4 mmol), Pd(PPh₃)₄ (0.03 g, 0.03 mmol), and 5/2/1 (v/v) toluene/water/methanol (10.0 ml) by using GP-C. Eluting with 19/1 (v/v) hexane/dichloromethane on silica gel chromatography and recrystallisation from hexane. Colourless solid. Yield: 0.09 g, 45%; ¹H-NMR (500 MHz, CDCl₃) δ 7.59-7.56

(m, 6H, Ar**H**), 7.48 (d, J = 7.9 Hz, 4H, Ar**H**), 7.27 (d, J = 8.2 Hz, 4H, Ar**H**), 2.66 (t, J = 7.8 Hz, 4H, Ar**H**), 2.61 (t, J = 7.0 Hz, 4H, C**H**₂), 2.29-2.23 (m, 2H, C**H**₂), 1.70-1.64 (m, 4H, C**H**₂), 1.41-1.35 (m, 8H, C**H**₂), 0.91 (t, J = 7.0 Hz, 6H, C**H**₃) ppm (Fig. S88); ¹³C-NMR (126 MHz, CDCl₃) δ 142.2, 140.4, 140.2, 139.7, 138.5, 129.0, 128.8, 127.3, 127.1, 125.3, 35.8, 33.5, 31.9, 31.7, 31.3, 22.7, 14.2 ppm (Fig. S99); HRMS (EI) Calcd for C₃₇H₄₂: 486.3287, Found 486.3294 (Fig. S126).

3,9-Bis(4-(pentyloxy)phenyl)-6,7-dihydro-5H-dibenzo[a,c][7]annulene (B5OQ[7])

B5OQ[7] was synthesised from **6** (0.14 g, 0.4 mmol), 4-(pentyloxy)phenylboronic acid (0.20 g, 0.9 mmol), K₃PO₄ (0.51 g, 2.4 mmol), Pd(PPh₃)₄ (0.03 g, 0.03 mmol), and 5/2/1 (v/v) toluene/water/methanol (10.0 ml) by using GP-C. Eluting with 3/1 (v/v) hexane/dichloromethane on silica gel chromatography and recrystallisation from the mixture of hexane and dichloromethane. Colorless solid. Yield: 0.09 g, 42%; ¹H-NMR (500 MHz, CDCl₃) δ 7.59 (dt, *J* = 9.4, 2.5 Hz, 4H, ArH), 7.54 (dd, *J* = 7.9, 1.8 Hz, 2H, ArH), 7.46 (d, J = 6.4 Hz, 2H, ArH), 7.45 (s, 2H, ArH), 6.98 (dt, *J* = 9.4, 2.5 Hz, 4H, ArH), 4.01 (t, *J* = 6.6 Hz, 4H, OCH₂), 2.60 (t, *J* = 7.0 Hz, 4H, ArH), 2.28-2.23 (m, 2H, CH₂), 1.85-1.79 (m, 4H, CH₂), 1.50-1.37 (m, 8H, CH₂), 0.95 (t, *J* = 7.2 Hz, 6H, CH₃) ppm (Fig. S90); ¹³C-NMR (126 MHz, CDCl₃) δ 158.9, 140.2, 140.1, 139.4, 133.5, 128.7, 128.2, 127.0, 125.0, 114.9, 68.2, 33.5, 31.9, 29.2, 28.4, 22.6, 14.2 ppm (Fig. S91); HRMS (EI) Calcd for C₃₇H₄₂O₂: 518.3185, Found 518.3193 (Fig. S127).

3-Pentyl-9-((4-pentylphenyl)ethynyl)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene (B5PhT[7]) and 3,9-bis((4-pentylphenyl)ethynyl)-6,7-dihydro-5*H*dibenzo[*a*,*c*][7]annulene (B5BPhEB[7]).

B5PhT[7] and **B5BPhEB[7]** were synthesised from 1/2 (mol/mol) **6/9** (0.36 g, 0.3 mmol/0.7 mmol), **S4a** (0.26 g, 1.5 mmol), triphenylphosphine (0.02 g, 0.08 mmol), Cul (0.01 g, 0.05 mmol), Ph(PPh₃)₄ (0.06 g, 0.05 mmol), and 1/1 (v/v) THF/triethylamine (10.0 ml) by using GP-E. **B5PhT[7]**: Eluting with 9/1 (v/v) hexane/dichloromethane on silica gel chromatography. Colorless liquid crystal. Yield: 0.22 g, 62%; ¹H-NMR (500 MHz, CDCl₃) δ 7.48 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.46-7.44 (m, 2H, ArH), 7.41 (d, *J* = 1.5 Hz, 1H, ArH), 7.34 (d, *J* = 7.6 Hz, 1H, ArH), 7.29 (d, *J* = 7.9 Hz, 1H, ArH), 7.17-7.15 (m, 3H, ArH), 7.06 (d, *J* = 1.5 Hz, 1H, ArH), 2.63 (dd, *J* = 15.9, 8.9 Hz, 4H, CH₂), 2.49 (q, *J* = 7.3 Hz, 4H, CH₂), 2.21-2.16 (m, 2H, CH₂), 1.70-1.59 (m, 4H, CH₂), 1.38-1.26 (m, 8H, CH₂), 0.93-0.87 (m, 6H, CH₃) ppm (Fig. S92); ¹³C-NMR (100 MHz, CDCl₃) δ 143.4, 142.8, 141.4, 139.8, 139.6, 137.9, 131.6, 129.9, 128.8, 128.6, 128.4, 128.2, 126.8, 122.1, 120.7, 89.7, 89.2, 36.0, 35.9, 33.4, 31.8, 31.6, 31.5, 31.5, 31.4, 31.1, 22.7, 22.7, 14.2, 14.2 ppm (Fig. S93); HRMS (EI) C₃₃H₃₈: 434.2974, Found 434.2982 (Fig. S128). **B5BPhEB[7]**: Eluting with 9/1 (v/v) hexane/dichloromethane on silica gel chromatography and recrystallisation from hexane. Yield: 0.08 g, 31%; ¹H-NMR (500

MHz, CDCl₃) δ 7.50 (dd, J = 7.8, 1.7 Hz, 2H, ArH), 7.46 (dd, J = 6.4, 1.8 Hz, 4H, ArH), 7.43 (d, J = 1.5 Hz, 2H, ArH), 7.36 (d, J = 7.9 Hz, 2H, ArH), 7.17 (d, J = 8.2 Hz, 4H, ArH), 2.62 (t, J = 7.6 Hz, 4H, CH₂), 2.50 (t, J = 7.0 Hz, 4H, CH₂), 2.23-2.18 (m, 2H, CH₂), 1.66-1.60 (m, 4H, CH₂), 1.36-1.32 (m, 8H, CH₂), 0.90 (t, J = 7.2 Hz, 6H, CH₃) ppm (Fig. S94); ¹³C-NMR (100 MHz, CDCl₃) δ 143.6, 140.6, 139.8, 131.7, 131.7, 130.0, 128.6, 128.3, 122.8, 120.6, 90.1, 89.0, 36.0, 33.2, 31.6, 31.3, 31.1, 22.7, 14.2 ppm (Fig. S95); HRMS (EI) Calcd for C₄₁H₄₂: 534.3287, Found 534.3299 (Fig. S129).

3-Pentyl-9-((4-(pentyloxy)phenyl)ethynyl)-6,7-dihydro-5*H*dibenzo[*a*,*c*][7]annulene (B5(5O)PhT[7]) and 3,9-bis((4-(pentyloxy)phenyl)ethynyl)-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene (B5OBPhEB[7])

B5(50)PhT[7] and B50BPhEB[7] were synthesised from 1/2 (mol/mol) 6/9 (0.36 g, 0.3 mmol/0.7 mmol), **S4b** (0.28 g, 1.5 mmol), triphenylphosphine (0.02 g, 0.08 mmol), Cul (0.01 g, 0.05 mmol), Ph(PPh₃)₄ (0.06 g, 0.05 mmol), and 1/1 (v/v) THF/triethylamine (10.0 ml) by using GP-E. **B5(50)PhT[7]**: Eluting with 6/1 (v/v) hexane/dichloromethane on silica gel chromatography. Colourless solid. Yield: 0.10 g, 36%; ¹H-NMR (500 MHz, DCl₃) δ 7.46 (d, J = 7.9 Hz, 3H, Ar**H**), 7.40 (s, 1H, Ar**H**), 7.33 (d, *J* = 7.0 Hz, 1H, Ar**H**), 7.29 (d, *J* = 7.3 Hz, 1H, Ar**H**), 7.15 (d, *J* = 8.5 Hz, 1H, Ar**H**), 7.06 (s, 1H, ArH), 6.87 (d, J = 7.9 Hz, 2H, ArH), 3.99-3.96 (m, 2H, OCH₂), 2.63 (t, J = 6.6 Hz, 2H, CH₂), 2.48 (q, J = 6.7 Hz, 4H, CH₂), 2.21-2.15 (m, 2H, CH₂), 1.83-1.77 (m, 2H, CH₂), 1.70-1.64 (m, 2H, CH₂), 1.48-1.37 (m, 8H, CH₂), 0.95-0.92 (m, 6H, CH₃) ppm (Fig. S96); ¹³C-NMR (100 MHz, CDCl₃) δ 159.3, 142.7, 141.2, 139.8, 139.6, 137.9, 133.1, 131.5, 129.8, 128.8, 128.3, 128.2, 126.8, 122.3, 115.4, 114.7, 89.6, 88.4, 68.2, 35.9, 33.4, 31.8, 31.5, 31.5, 31.4, 29.1, 28.3, 22.7, 22.6, 14.2, 14.2 ppm (Fig. S97); HRMS (EI) Calcd for C₃₃H₃₈O: 450.2923, Found 450.2918 (Fig. S130). **B5OBPhEB**[7]: Eluting with 6/1 (v/v) hexane/dichloromethane on silica gel chromatography and recrystallisation from the mixture of methanol and dichloromethane. Colorless solid. Yield: 0.06 g, 29%; ¹H-NMR (500 MHz, CDCl₃) δ 7.50-7.46 (m, 6H, Ar**H**), 7.41 (d, J = 1.5 Hz, 2H, ArH), 7.35 (d, J = 7.6 Hz, 2H, ArH), 6.88 (dt, J = 9.2, 2.3 Hz, 4H, ArH), 3.98 $(t, J = 6.6 \text{ Hz}, 4\text{H}, \text{OCH}_2), 2.50 (t, J = 6.9 \text{ Hz}, 4\text{H}, \text{CH}_2), 2.23-2.17 (m, 2\text{H}, \text{CH}_2), 1.83-$ 1.77 (m, 4H, CH₂), 1.48-1.36 (m, 8H, CH₂), 0.94 (t, J = 7.2 Hz, 6H, CH₃) ppm (Fig. S98); ¹³C-NMR (100 MHz, CDCl₃) δ 159.4, 140.5, 139.8, 133.2, 131.6, 129.9, 128.3, 122.9, 115.3, 114.7, 90.0, 88.2, 68.2, 33.2, 31.3, 29.0, 28.3, 22.6, 14.2 ppm (Fig. S99); HRMS (EI) Calcd for C₄₁H₄₂O₂: 566.3185, Found 566.3176 (Fig. S131).

Trimethyl((9-pentyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-3-yl)ethynyl)silane (S19a)

S19a was synthesised from 1/2 (mol/mol) 6/9 (0.79 g, 0.7/1.5 mmol),

trimethylsilylacetylene (0.65 ml, 3.6 mmol), Pd(PPh₃)₄ (0.13 g, 0.1 mmol), Cul (0.02 g, 0.1 mmol), triphenylphosphine (0.03 g, 0.1 mmol), and 1/1 (v/v) triethylamine/THF (10.0 ml) by using GP-E. Eluting with 9/1 (v/v) hexane/dichloromethane on silica gel chromatography. Colorless oil. **S19a** contained 3,9-bis((trimethylsilyl)ethynyl)-6,7-dihydro-5H-dibenzo[a,c][7]annulene (**S19b**) with a mol ratio of 4:1. Yield (**S19a**): 0.47 g, 87%; ¹H-NMR (500 MHz, CDCl₃) δ 7.42 (d, *J* = 7.9 Hz, 1H, ArH), 7.35 (s, 1H, ArH), 7.30-7.25 (m, 2H, ArH), 7.14 (d, *J* = 7.6 Hz, 1H, ArH), 7.04 (s, 1H, ArH), 2.62 (t, *J* = 7.8 Hz, 2H, CH₂), 2.46 (t, *J* = 7.3 Hz, 2H, CH₂), 2.44 (t, *J* = 7.3 Hz, 2H, CH₂), 2.18-2.13 (m, 2H, CH₂), 1.69-1.63 (m, 2H, CH₂), 1.37-1.34 (m, 4H, CH₂), 0.91 (t, *J* = 6.6 Hz, 3H, CH₂), 0.26 (s, 9H, SiCH₃) ppm (Fig. S100).

3-Ethynyl-9-pentyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulene (S20)

S20 was synthesised from 4/1 (mol/mol) **S19a/S19b** (0.61 g, 1.3/0.4 mmol), K₂CO₃ (0.56 g, 4.1 mmol), and 1/1 (v/v) THF/methanol (6.0 ml) by using GP-F. Eluting with 10/1 (v/v) hexane/dichloromethane on silica gel chromatography. Colourless oil. Yield: 0.3 g, 74%; ¹H-NMR (500 MHz, CDCl₃) δ 7.45 (d, *J* = 7.9 Hz, 1H, Ar**H**), 7.38-7.35 (m, 1H, Ar**H**), 7.34-7.27 (m, 2H, Ar**H**), 7.15 (d, *J* = 7.6 Hz, 1H, Ar**H**), 7.05 (s, 1H, Ar**H**), 3.09 (s, 1H, C**H**), 2.63 (t, *J* = 7.9 Hz, 2H, C**H**₂), 2.49-2.45 (m, 4H, C**H**₂), 2.20-2.14 (m, 2H, C**H**₂), 1.69-1.63 (m, 2H, C**H**₂), 1.38-1.35 (m, 4H, C**H**₂), 0.91 (t, *J* = 6.9 Hz, 3H, C**H**₃) ppm (Fig. S101).

4-((9-Pentyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*][7]annulen-3-yl)ethynyl)benzonitrile (B5CPhT[7])

B5CPhT[7] was synthesised from **S20** (0.29 g, 1.0 mmol), 4-bromobenzonitrile (0.27 g, 1.5 mmol), Pd(PPh₃)₄ (0.06 g, 0.05 mmol), Cul (0.01 g, 0.5 mmol), triphenylphosphine (0.01 g, 0.4 mmol), and 1/1 (v/v) triethylamine/THF (6.0 ml) by using GP-E. Eluting with 9/1 (v/v) hexane/ethyl acetate on silica gel chromatography and recrystallisation from hexane. Colourless solid. Yield: 0.1 g, 24%; ¹H-NMR (500 MHz, CDCl₃) δ 7.64 (d, J = 8.2 Hz, 2H, ArH), 7.61 (d, J = 8.2 Hz, 2H, ArH), 7.50 (d, J = 7.9 Hz, 1H, ArH), 7.43 (s, 1H, ArH), 7.37 (d, J = 7.9 Hz, 1H, ArH), 7.29 (d, J = 7.9 Hz, 1H, ArH), 7.17 (d, J = 7.6 Hz, 1H, ArH), 7.07 (s, 1H, ArH), 2.64 (t, J = 7.9 Hz, 2H, CH₂), 2.52-2.47 (m, 4H, CH₂), 2.22-2.17 (m, 2H, CH₂), 1.70-1.64 (m, 2H, CH₂), 1.38-1.37 (m, 4H, CH₂), 0.92 (t, J = 6.6 Hz, 3H, CH₃) ppm (Fig. S102); ¹³C-NMR (126 MHz, CDCl₃) δ 143.1, 142.6, 140.1, 139.5, 137.6, 132.2, 132.1, 131.8, 130.2, 128.8, 128.6, 128.5, 128.2, 126.8, 120.8, 118.7, 111.4, 94.4, 87.9, 35.9, 33.3, 31.8, 31.5, 31.5, 31.3, 22.7, 14.2 ppm (Fig. S103); FT-IR (KBr) 2207 cm⁻¹, 2225 cm⁻¹ (Fig. S114); HRMS (EI) Calcd for C₂₉H₂₇N: 389.2144, Found 389.2145 (Fig. S132).

9-((4-Pentylphenyl)ethynyl)-6,7-dihydro-5H-dibenzo[a,c][7]annulene-3-

carbonitrile (BC5PhT[7])

BC5PhT[7] was synthesised from **8** (0.59 g, 1.4 mmol), **S4a** (0.37 g, 2.1 mmol), Pd(PPh₃)₄ (0.08 g, 0.07 mmol), Cul (0.01 g, 0.5 mmol), triphenylphosphine (0.02 g, 0.8 mmol), and 1/1 (v/v) triethylamine/THF (6.0 ml) by using GP-E. Eluting with 1/1 (v/v) hexane/dichloromethane on silica gel chromatography and recrystallisation from hexane. Colourless solid. Yield: 0.21 g, 39%; ¹H-NMR (500 MHz, CDCl₃) δ 7.64 (d, *J* = 7.9 Hz, 1H, ArH), 7.53 (d, *J* = 11.3 Hz, 2H, ArH), 7.46 (d, *J* = 7.9 Hz, 3H, ArH), 7.44 (s, 1H, ArH), 7.33 (d, *J* = 7.9 Hz, 1H, ArH), 7.18 (d, *J* = 7.9 Hz, 2H, ArH), 2.62 (t, *J* = 7.6 Hz, 2H, CH₂), 2.54-2.49 (m, 4H, CH₂), 2.25-2.20 (m, 2H, CH₂), 1.66-1.60 (m, 2H, CH₂), 1.37-1.31 (m, 4H, CH₂), 0.90 (t, *J* = 6.7 Hz, 3H, CH₂) ppm (Fig. S104); ¹³C-NMR (126 MHz, CDCl₃) δ 145.5, 143.8, 140.9, 139.7, 139.1, 132.1, 131.9, 131.7, 130.6, 130.2, 128.9, 128.6, 128.4, 123.9, 120.3, 119.2, 111.3, 90.7, 88.6, 36.0, 33.0, 31.6, 31.2, 31.0, 22.7, 14.2 ppm (Fig. S105); FT-IR (KBr) 2228 cm⁻¹ (Fig. S115); HRMS (EI) Calcd C₂₉H₂₇N: 389.2144, Found 389.2141 (Fig. S133).

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NMR chart







Fig. S47 ¹H-NMR spectra of 4 (500 MHz, CDCl₃).







Fig. S49 ¹H-NMR spectra of 6 (500 MHz, CDCl₃).



Fig. S50 ¹H-NMR spectra of 7 (500 MHz, CDCl₃).







Fig. S52 ¹H-NMR spectra of Bc5CT[7] (500 MHz, CDCl₃).



Fig. S53 ¹³C-NMR spectra of Bc5CT[7] (100 MHz, CDCl₃).







Fig. S55 ¹H-NMR spectra of B5CT[7] (500 MHz, CDCl₃).



Fig. S56 ¹³C-NMR spectra of B5CT[7] (100 MHz, CDCl₃).











Fig. S59 ¹H-NMR spectra of S4b (500 MHz, CDCl₃).







Fig. S61 ¹H-NMR spectra of S7 (500 MHz, CDCl₃).







Fig. S63 ¹H-NMR spectra of DMc5CT (500 MHz, CDCl₃).







Fig. S65 ¹H-NMR spectra of S10 (500 MHz, CDCl₃).







Fig. S67 ¹H-NMR spectra of S12 (500 MHz, CDCl₃).



Fig. S68 ¹H-NMR spectra of B5CB[6] (500 MHz, CDCl₃).















Fig. S72 ¹³C-NMR spectra of Bc5CT[6] (126 MHz, CDCl₃).



Fig. S73 ¹H-NMR spectra of S14a (500 MHz, CDCl₃).



Fig. S74 ¹H-NMR spectra of S14b (500 MHz, CDCl₃).











Fig. S77 ¹H-NMR spectra of B8CB[7] (500 MHz, CDCl₃).











Fig. S80 ¹H-NMR spectra of S17 (500 MHz, CDCl₃).







Fig. S82 ¹H-NMR spectra of B7OCB[7] (500 MHz, CDCl₃).



Fig. S83 ¹³C-NMR spectra of B7OCB[7] (126 MHz, CDCl₃).











Fig. S86 ¹H-NMR spectra of B5(50)T[7] (500 MHz, CDCl₃).



Fig. S87 ¹³C-NMR spectra of B5(5O)T[7] (100 MHz, CDCl₃).



Fig. S88 ¹H-NMR spectra of B5Q[7] (500 MHz, CDCl₃).



Fig. S89 ¹³C-NMR spectra of B5Q[7] (126 MHz, CDCl₃).











Fig. S92 ¹H-NMR spectra of B5PhT[7] (500 MHz, CDCl₃).



Fig. S93 ¹³C-NMR spectra of B5PhT[7] (100 MHz, CDCl₃).



Fig. S94 ¹H-NMR spectra of B5BPhEB[7] (500 MHz, CDCl₃).



Fig. S95 ¹³C-NMR spectra of B5BPhEB[7] (100 MHz, CDCl₃).



Fig. S96 ¹H-NMR spectra of B5(50)PhT[7] (500 MHz, CDCl₃).



Fig. S97 ¹³C-NMR spectra of B5(50)PhT[7] (100 MHz, CDCl₃).



Fig. S98 ¹H-NMR spectra of B5OBPhEB[7] (500 MHz, CDCl₃).



Fig. S99 ¹³C-NMR spectra of B5OBPhEB[7] (100 MHz, CDCl₃).



Fig. S100 ¹H-NMR spectra of S19a (500 MHz, CDCl₃).



Fig. S101 ¹H-NMR spectra of S20 (500 MHz, CDCl₃).



Fig. S102 ¹H-NMR spectra of B5CPhT[7] (500 MHz, CDCl₃).







Fig. S104 ¹H-NMR spectra of BC5PhT[7] (500 MHz, CDCl₃).



Fig. S105 ¹³C-NMR spectra of BC5PhT[7] (126 MHz, CDCl₃).









Fig. S107 FT-IR spectra of B5CT[7].



Fig. S108 FT-IR spectra of DMc5CT.



Fig. S109 FT-IR spectra of B5CB[6].



Fig. S110 FT-IR spectra of Bc5CT[6].



Fig. S111 FT-IR spectra of B5CB[7].



Fig. S112 FT-IR spectra of B8CB[5].



Fig. S113 FT-IR spectra of B7OCB[7].






Fig. S115 FT-IR spectra of B5CPhT[7].



High resolution mass spectrometry (HRMS) chart

Fig. S116 HR-MS spectra of Bc5CT[7] (above: calculated data; below: experimental data).



Fig. S117 HR-MS spectra of B5CT[7] (above: calculated data; below: experimental data).



Fig. S118 HR-MS spectra of DMc5CT (above: calculated data; below: experimental



Fig. S119 HR-MS spectra of B5CB[6] (above: calculated data; below: experimental data).





Fig. S120 HR-MS spectra of Bc5CT[6] (above: calculated data; below: experimental data).



Fig. S121 HR-MS spectra of B5CB[7] (above: calculated data; below: experimental



Fig. S122 HR-MS spectra of B8CB[7] (above: calculated data; below: experimental data).

data).



Fig. S123 HR-MS spectra of B7OCB[7] (above: calculated data; below: experimental data).



Fig. S124 HR-MS spectra of B5T[7] (above: calculated data; below: experimental



Fig. S125 HR-MS spectra of B5(50)T[7] (above: calculated data; below: experimental data).

data).



Fig. S126 HR-MS spectra of B5Q[7] (above: calculated data; below: experimental data).



Fig. S127 HR-MS spectra of B5O[7] (above: calculated data; below: experimental



Fig. S128 HR-MS spectra of B5PhT[7] (above: calculated data; below: experimental data).

data).



Fig. S129 HR-MS spectra of **B5BPhEB[7]** (above: calculated data; below: experimental data).



Fig. S130 HR-MS spectra of B5(50)PhT[7] (above: calculated data; below:

experimental data).



Fig. S131 HR-MS spectra of B5OBPhEB[7] (above: calculated data; below: experimental data).



Fig. S132 HR-MS spectra of B5CPhT[7] (above: calculated data; below: experimental data).



Fig. S133 HR-MS spectra of BC5PhT[7] (above: calculated data; below:

experimental data).