Supporting Information for

Iron (III) Bromide Catalyzed Bromination of 2-*tert*-Butylpyrene and Corresponding Positions-Dependent Aryl-Functionalized Pyrene Derivatives

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[e] Department of Chemistry, The University of Hull, Cottingham Road, Hull, Yorkshire, HU6 7RX, UK.
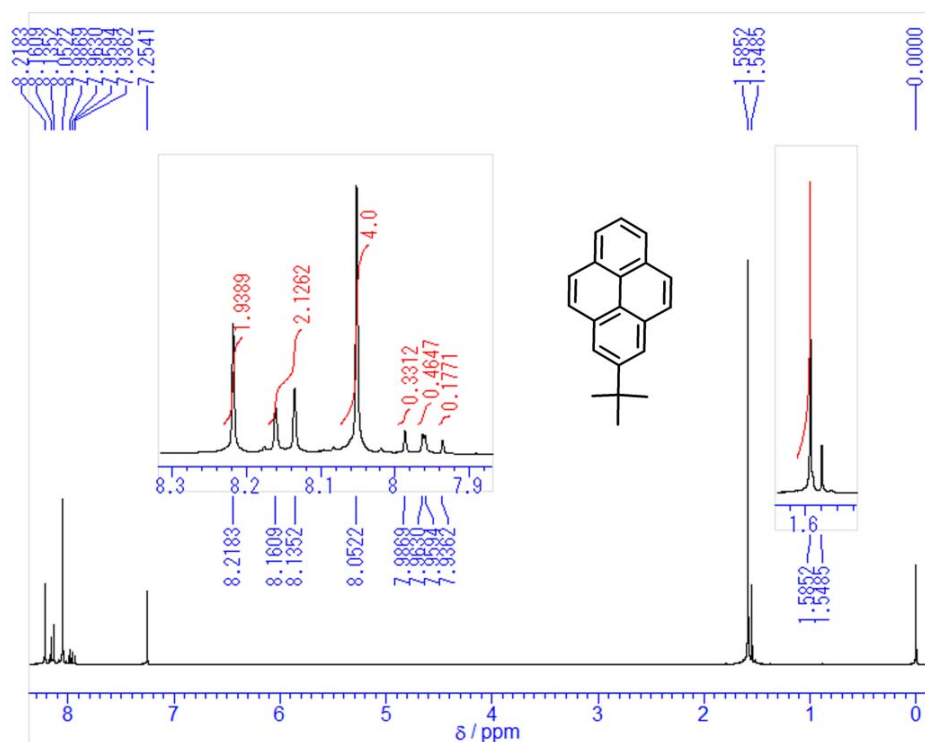[f] Chemistry Department, Loughborough University, Loughborough, LE113TU, UK.
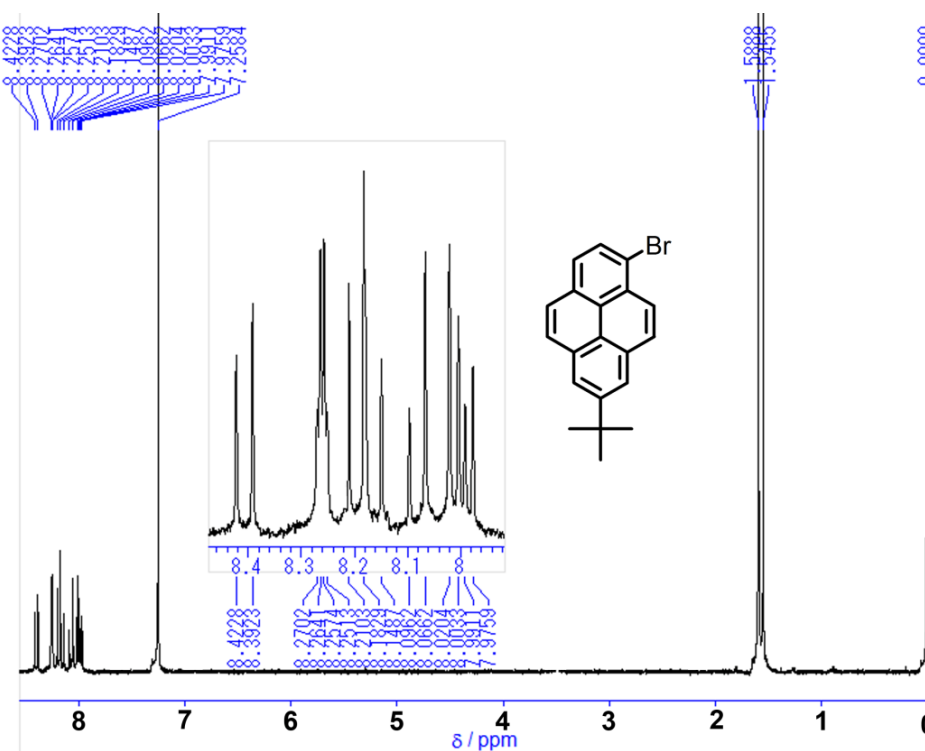[g] ALS, Berkeley Lab, 1 Cyclotron Road, MS2-400, Berkeley, CA 94720,USA.
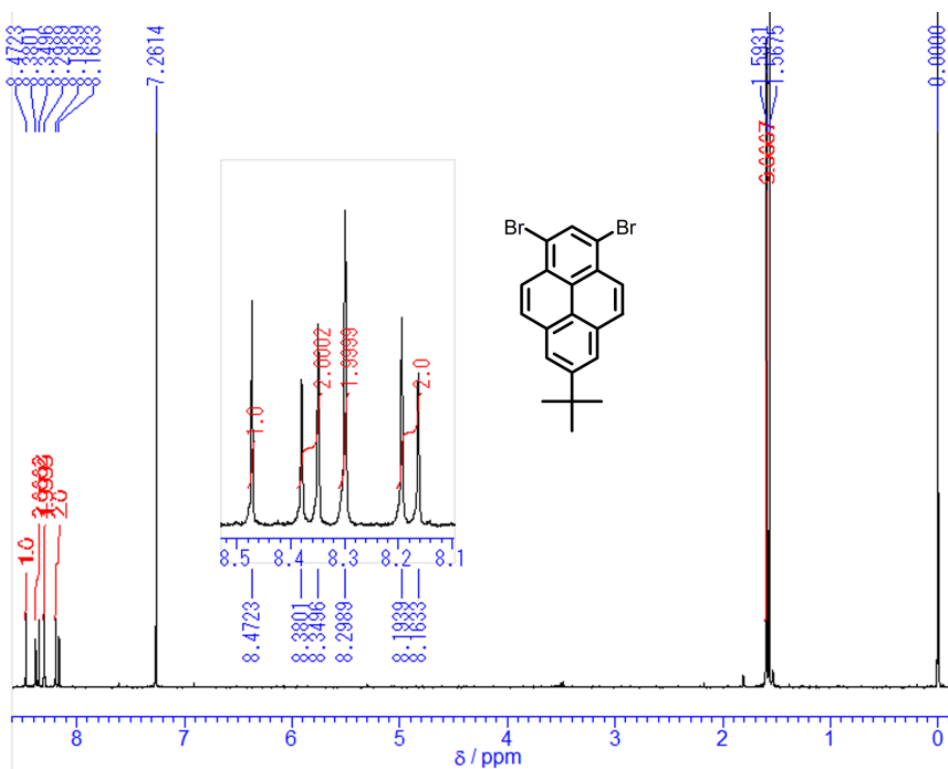
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Copy of NMR Spectra

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Figure S1-2 ^{1}H-NMR spectrum (300 MHz, 293K, * CDCl₃) for **2a** including an expansion of the aromatic region.
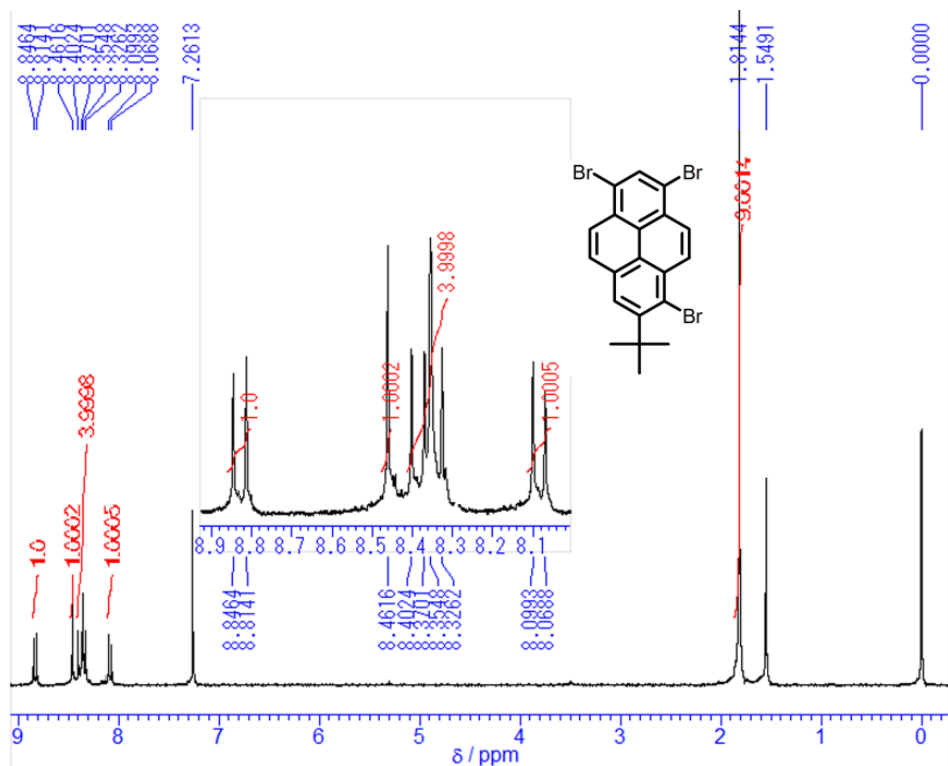
Figure S1-3 ^{1}H-NMR spectrum (300 MHz, 293K, * CDCl$_3$) for **2b** including an expansion of the aromatic region.

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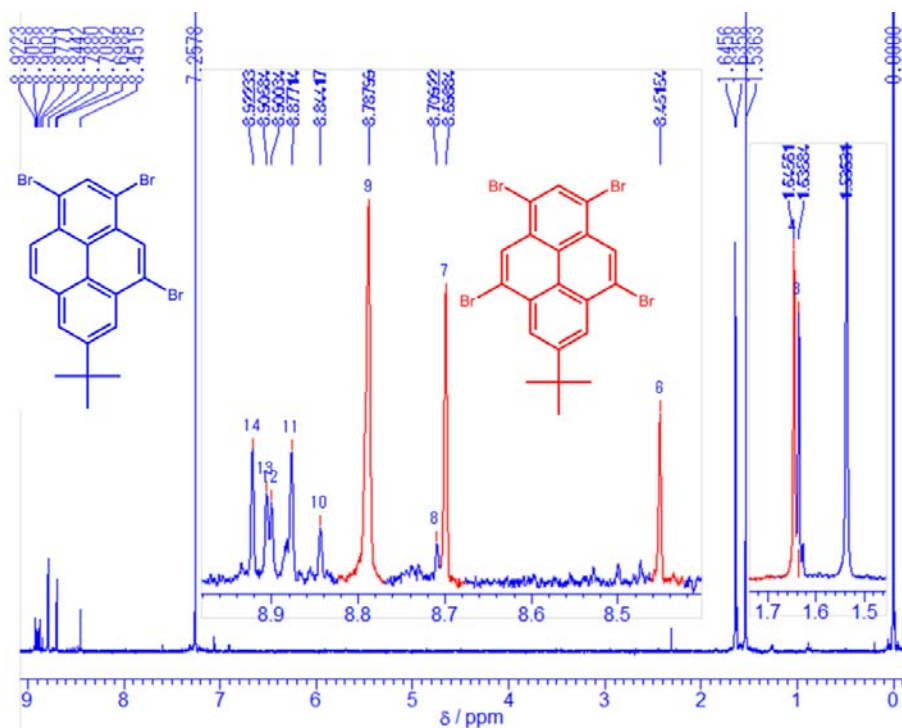**Figure S1-6** ^{1}H-NMR spectrum (300 MHz, 293K, * CDCl$_3$) for **2e** including an expansion of the aromatic region.
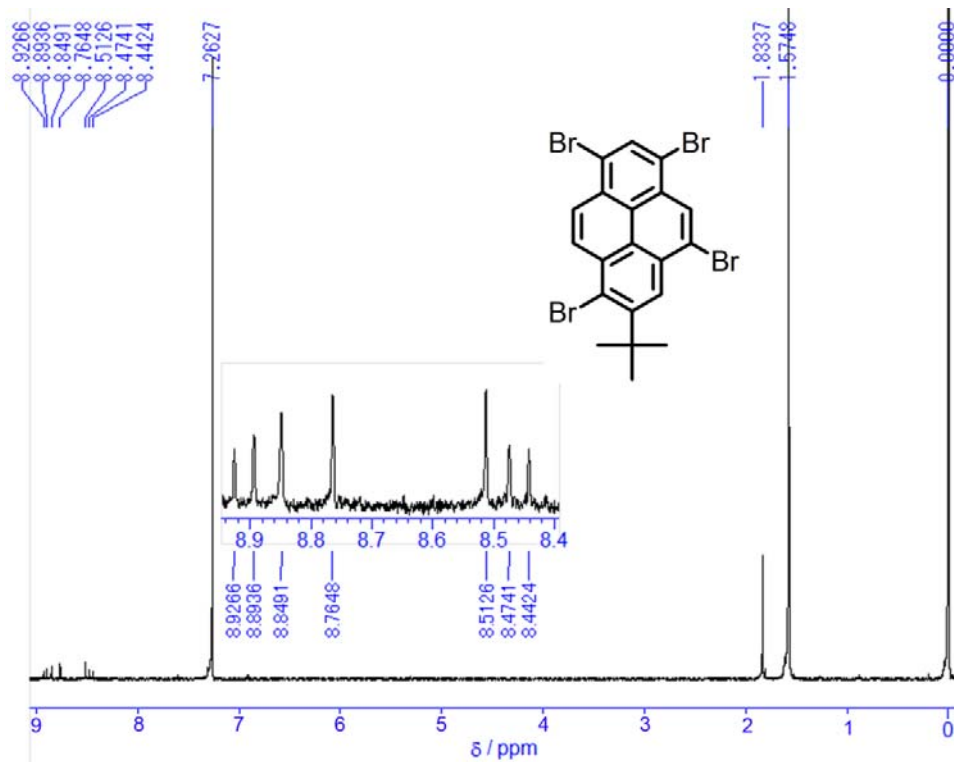
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Figure S1-9 ^{1}H-NMR spectrum (300 MHz, 293K, * CDCl₃) for **3b** including an expansion of the aromatic region.

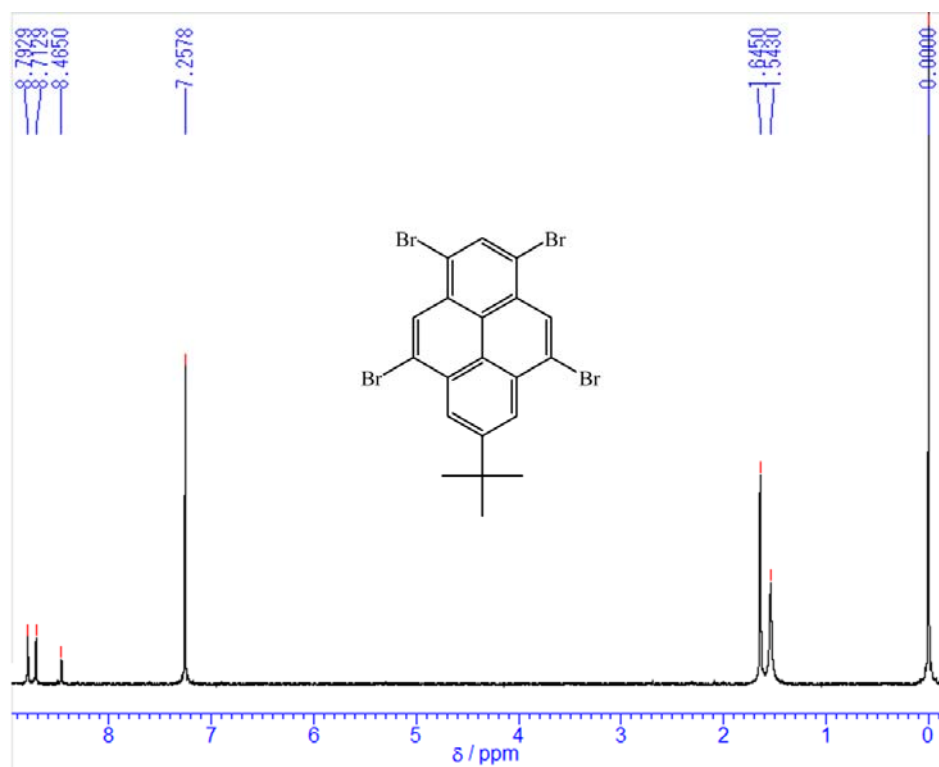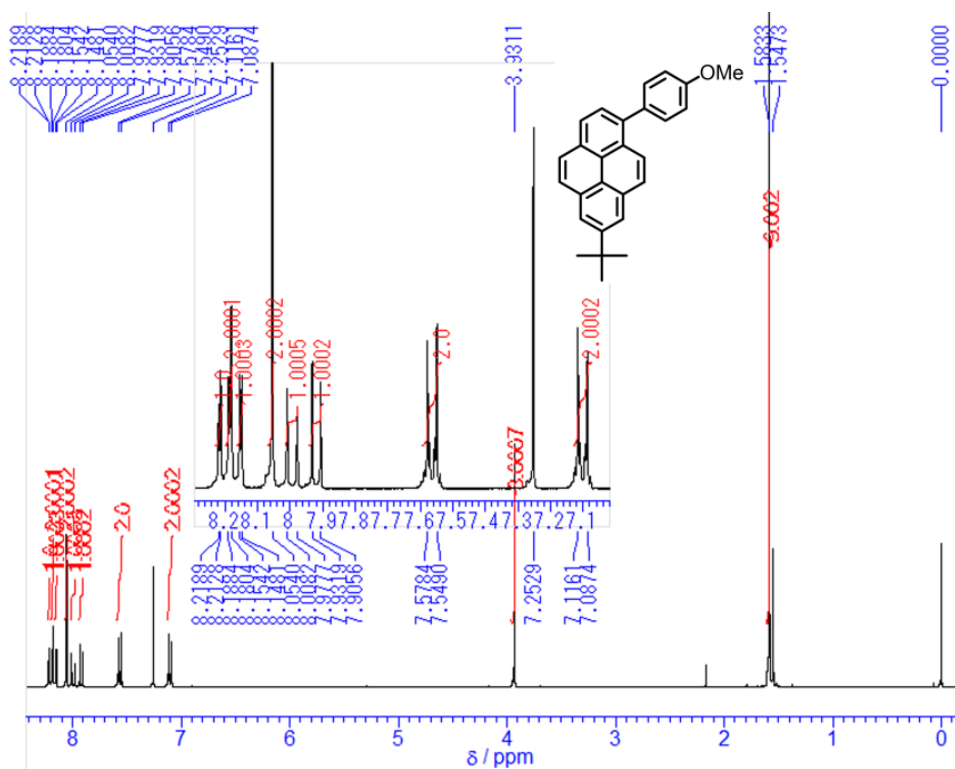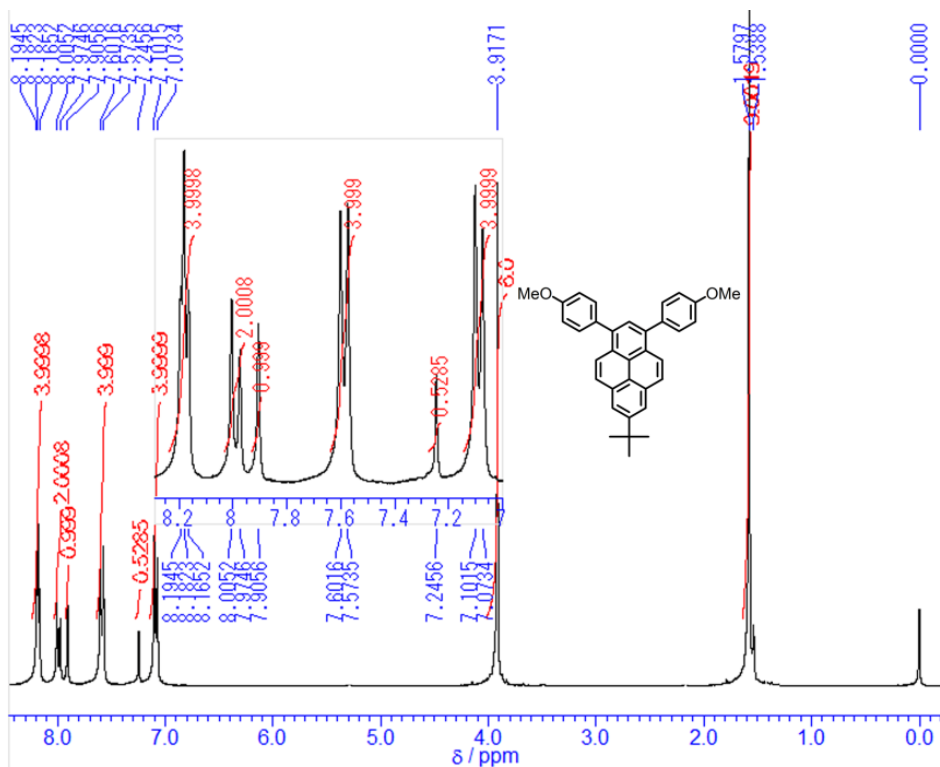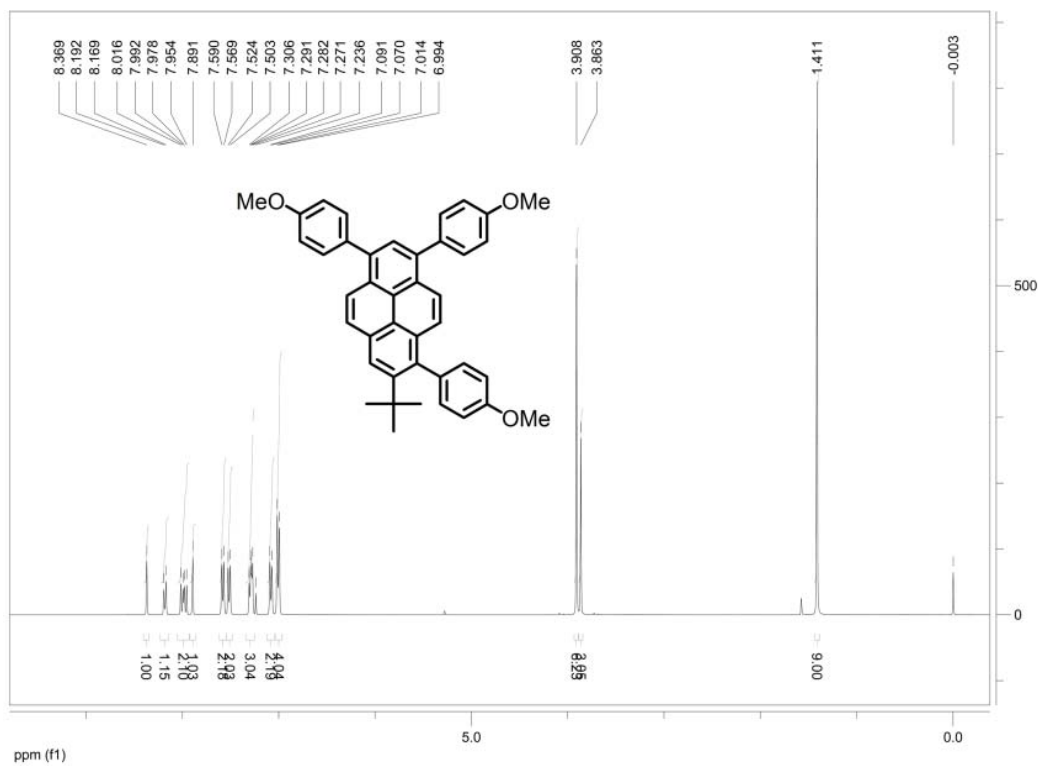**Figure S1-10** ^{1}H-NMR spectrum (400 MHz, 293K, * CDCl₃) for **3c**.

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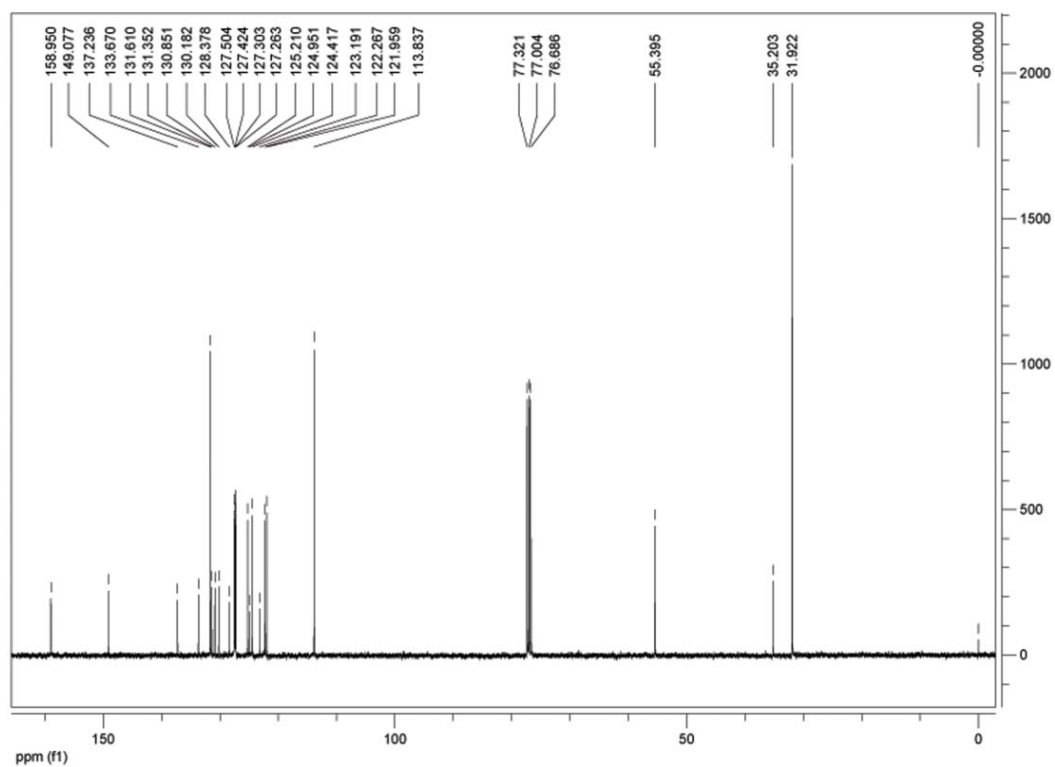
Figure S1-13 ^{13}C-NMR spectrum (100 MHz, 293K, * CDCl$_3$) for **3a**.

Figure S1-14 ^{13}C-NMR spectrum (75 MHz, 293K, * CDCl$_3$) for **3b**.
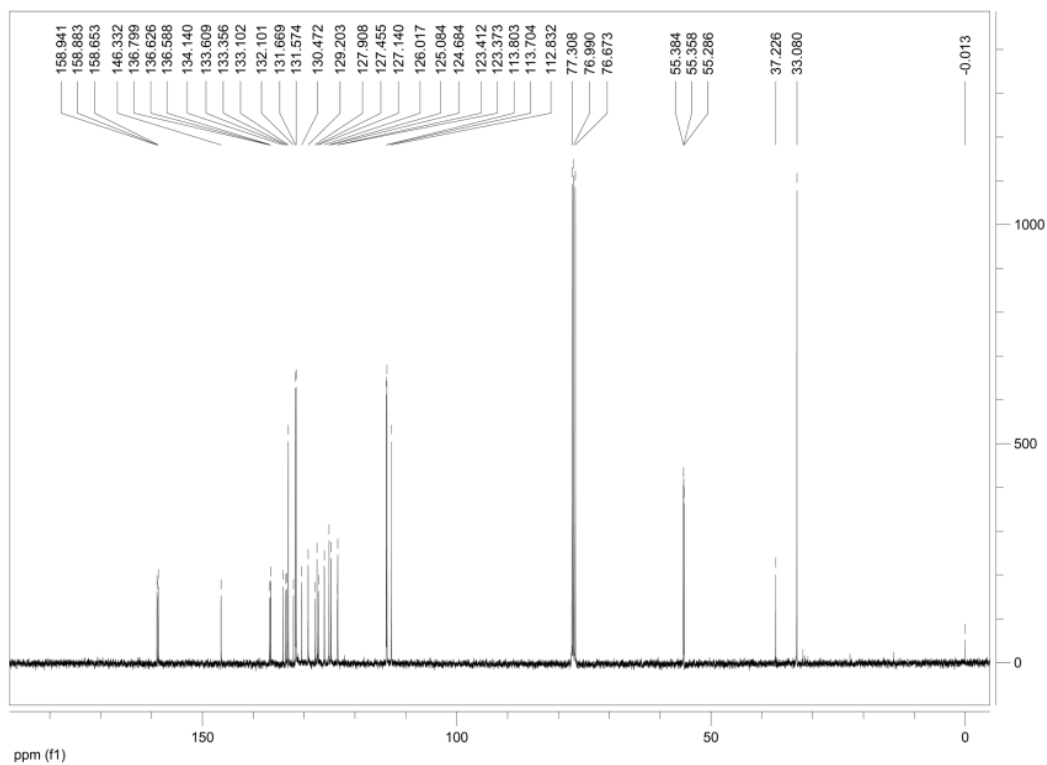
Figure S1-15 ^{13}C-NMR spectrum (100 MHz, 293K, * CDCl$_3$) for **3c**.

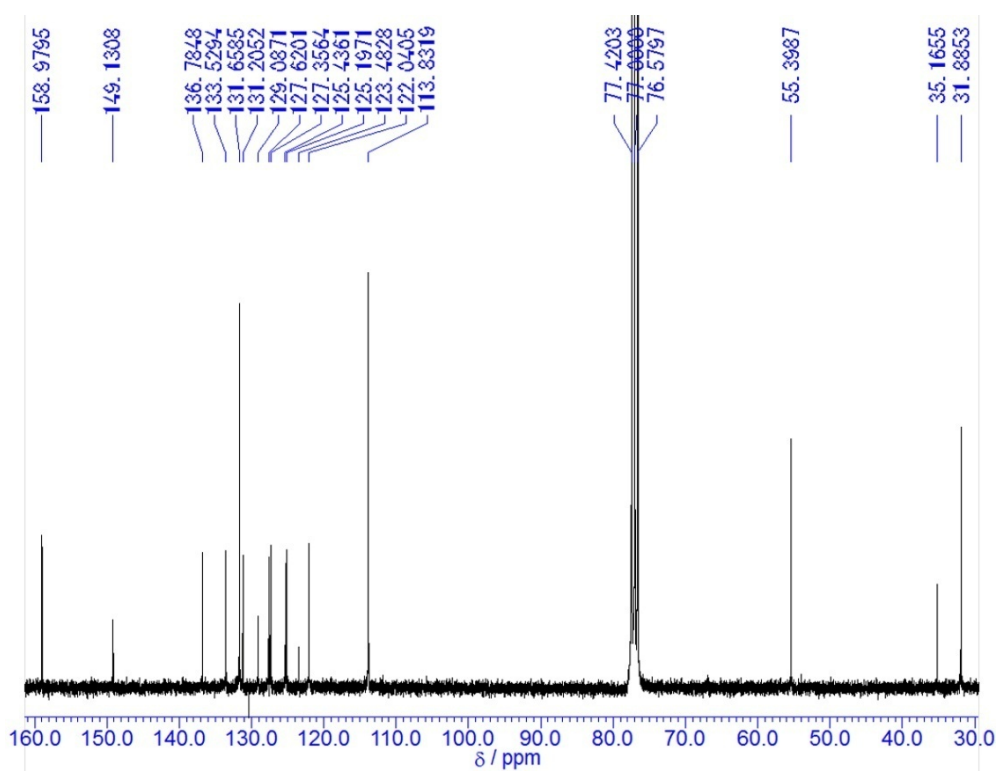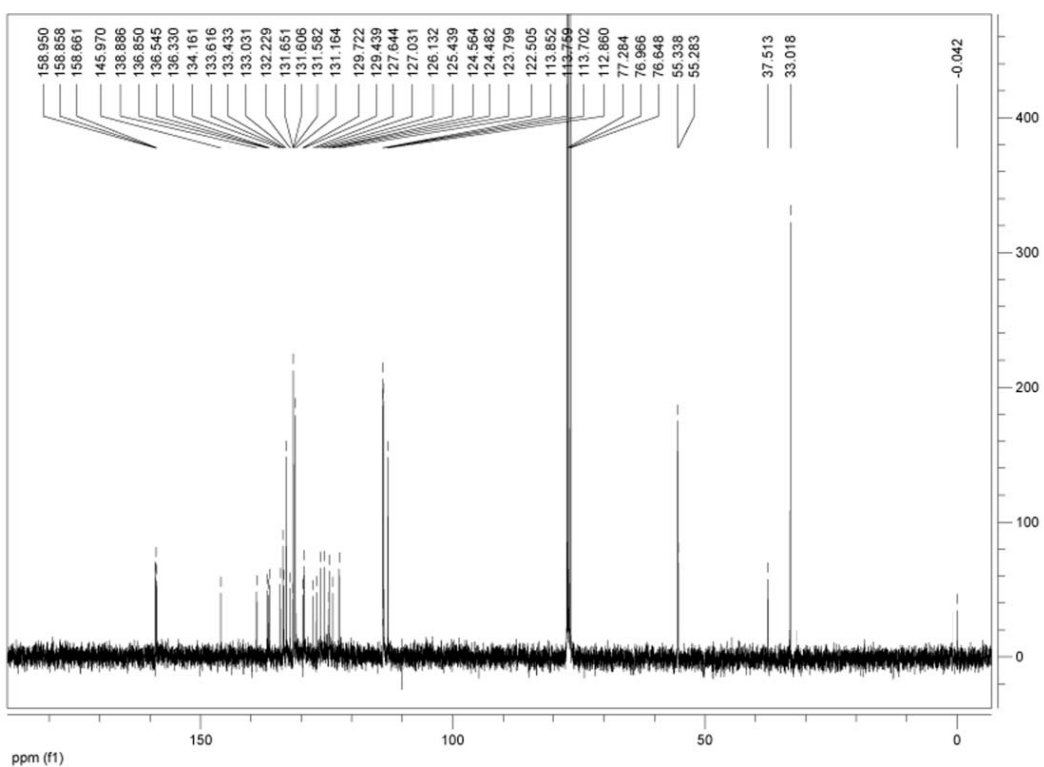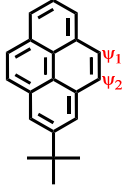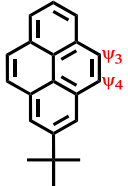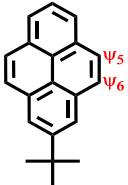**Figure S1-16** ^{13}C-NMR spectrum (100 MHz, 293K, * CDCl$_3$) for **3e**.
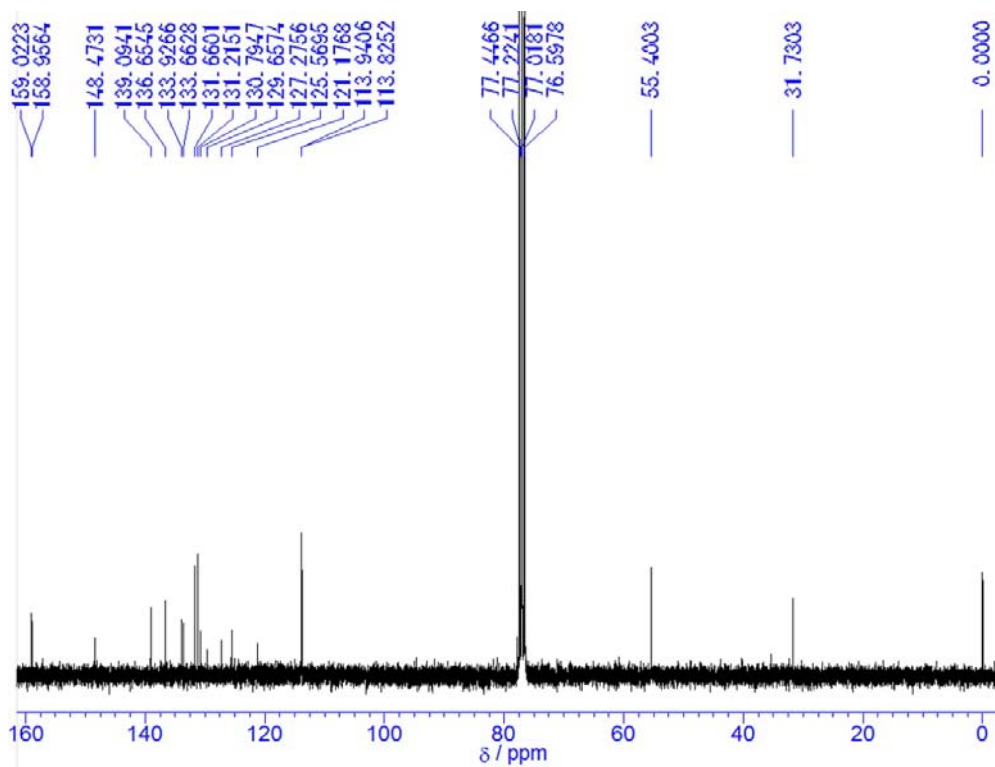
Figure S1-17 ^{13}C-NMR spectrum (75 MHz, 293K, * CDCl$_3$) for **3f**.

Mechanism of bromination of 2-*tert*-butyl pyrene

Table S1 the ratio of benzenoid rings and double bonds[1]

Structure	Ratio	Coefficients	Nb	Ne
	$\psi 1 : \psi 2$	1.31	2	2
	$\psi 3 : \psi 4$	1.27	3	2
	$\psi 5 : \psi 6$	1.00	1	1

Nb=number of benzenoid rings ;Ne=number of exposed bonds
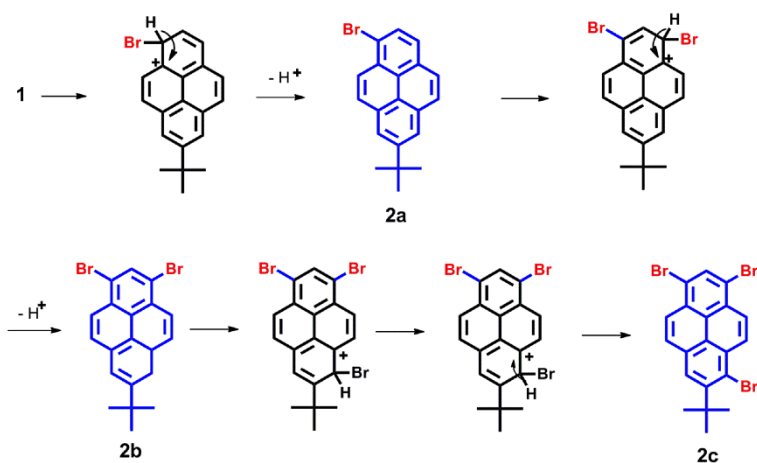
Scheme S1 Possible regioselective bromination mechanism of **1**

[1] Moffitt, W. E.; Coulson, C. A. *Proc. Phys. Soc.*; **1948**, *60*, 309–315.

X-Ray diffraction data

Table S2 Summary of crystal data of pyrene derivatives **3**

| Parameter	3a	3b	3c	3d	3e	3f
Empirical formula	$C_{27}H_{24}O$	$C_{34}H_{30}O_2$	$C_{41}H_{36}O_3$	$C_{41}H_{36}O_3$	$C_{48}H_{42}O_4$	$C_{48}H_{42}O_4$
Formula weight [g mol^{-1}]	364.49	470.61	576.70	576.70	682.81	682.82
Crystal system	orthorhombic	monoclinic	Monoclinic	triclinic	monoclinic	triclinic
Space group	*P b c a*	*P2$_1$/c*	*P2$_1$/c*	*P -1*	*P2$_1$/c*	*P-1*
a [Å]	34.643(4)	18.815(14)	9.136 (2)	10.299(6)	17.5703(6)	12.642(2)
b [Å]	11.0927(16)	15.629(11)	17.638 (4)	12.845(7)	8.8286(3)	12.960(2)
c [Å]	10.1811(13)	8.851(6)	19.524 (4)	13.482(12)	24.0368(9)	13.854(2)
α [°]	-	-		111.174(9)		86.048(2)°
β [°]	-	103.255(9)	98.252 (4)°	103.142(10)	101.190(2)	67.354(2)°
γ [°]	-	-		102.291(7)		60.942(2)°
Volume [Å^3]	3912.4(9)	2533(3)	3113.5 (12)	1531.8(19)	3657.7(2)	1811.4(5)
Z	8	4	4	2	4	2
Density, calcd [gm^{-3}]	1.237	1.234	1.230	1.250	1.240	1.252
Temperature [K]	113	123	150	296(2)	100(2)	150(2)
Unique reflns	3495	5722	7734	5187	73709	10122
Obsdreflns	2925	4734	6709	3075	13376	7260
Parameters	257	330	500	397	637	476
R_{int}	0.0475	0.0640	0.034	0.0535	0.0404	0.0255
R[I>2σ(I)][a]	0.0360	0.1034	0.048	0.0911	0.0441	0.0475
wR[I>2σ(I)][b]	0.1041	0.3036	0.146	0.2649	0.1317	0.1413
GOF on F^2	1.123	1.186	1.06	0.988	1.035	1.047

[a] Conventional R on F_{hkl}: $\Sigma||F_o| - |F_c||/\sigma|F_o|$. [b] Weighted R on $|F_{hkl}|^2$: $\Sigma[w(F_o^2 - F_c^2)2]/\Sigma[w(F_o^2)^2]^{1/2}$
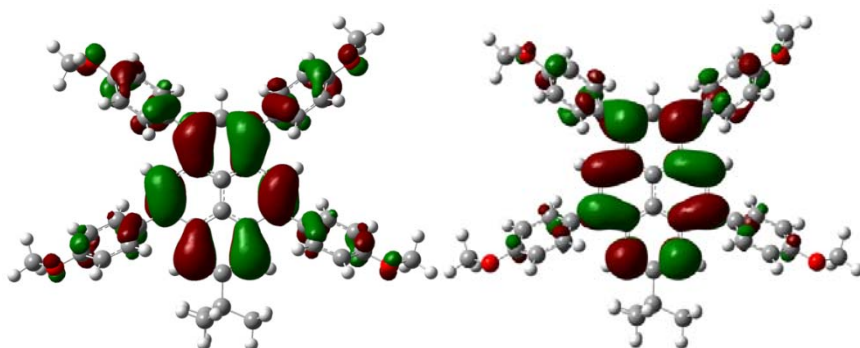
Quantum Chemistry Computation
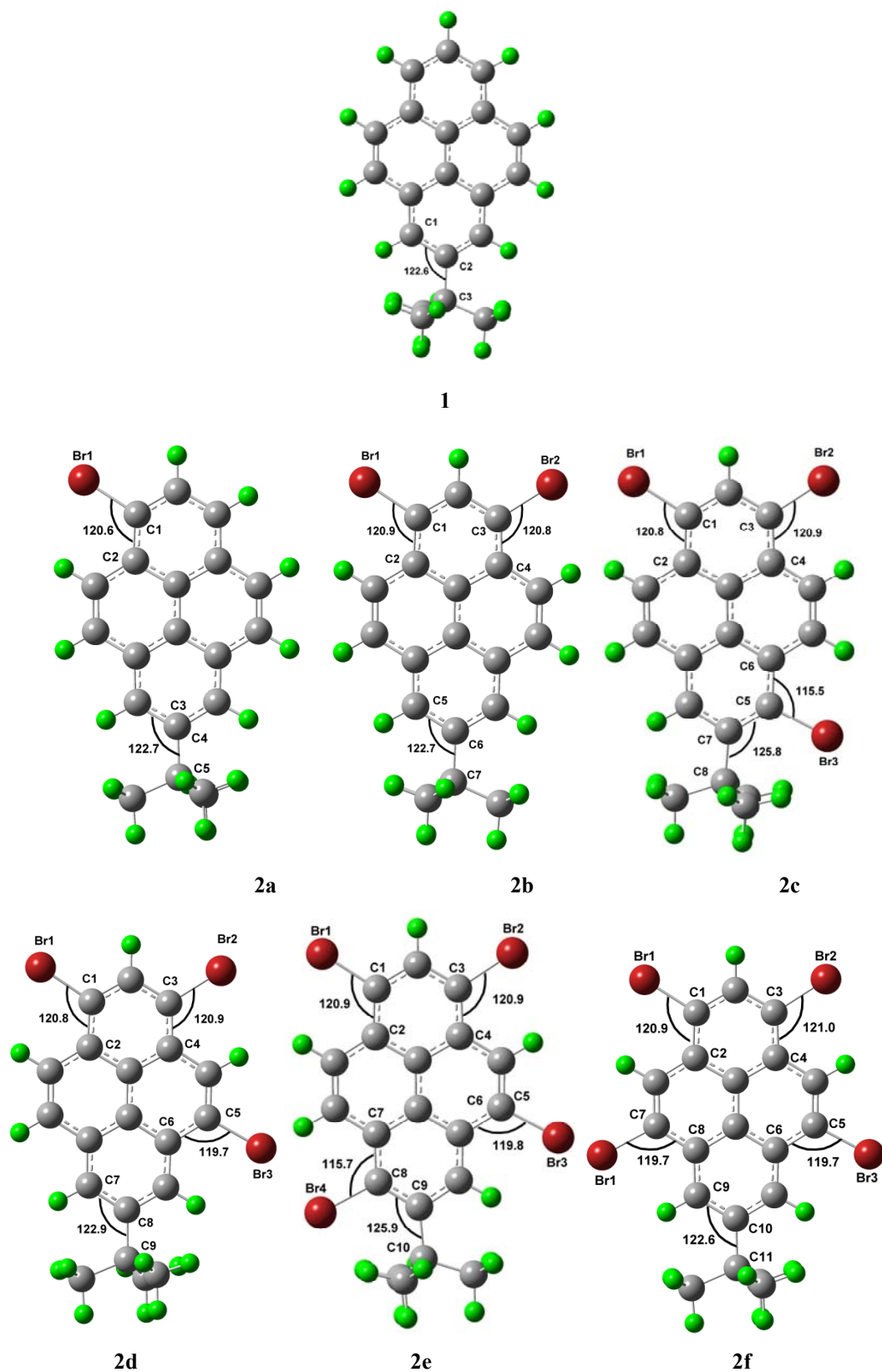
Figure S2-2 Geometric structures of bromo-substituted pyrene **2** in the FeBr₃-catalyzed reactions. The unit of angle is in °.
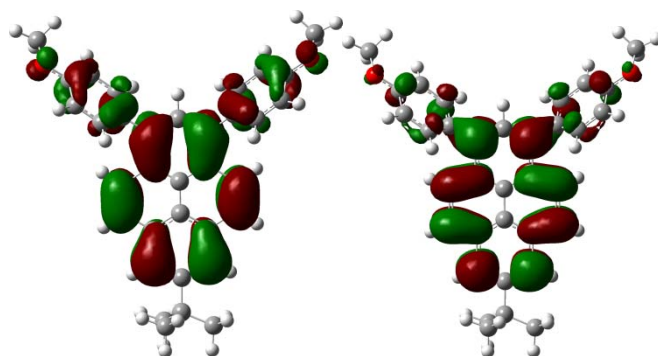
Figure S3-1 Computed molecular orbital plots (B3LYP/6–31G*) for **3b**: The left plots represent the HOMOs, and the right plots represent the LUMOs.

Figure S3-2 Computed molecular orbital plots (B3LYP/6–31G*) for **3f**: The left plots represent the HOMOs, and the right plots represent the LUMOs.
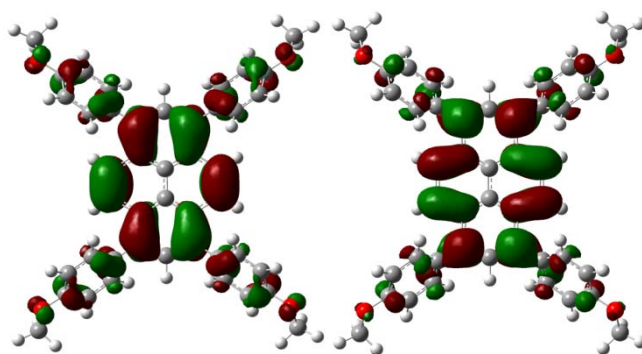
Figure S3-3 Computed molecular orbital plots (B3LYP/6–31G*) for **4**: The left plots represent the HOMOs, and the right plots represent the LUMOs.

Table S3. Physical and electrochemical properties of compounds **3**, **4** and **5**.

Compound	LUMO (eV)[a]	LUMO (eV)[b]	$E_{ox}^{1/2[c]}$ (eV)	$E_{ox}^{onset[d]}$ (eV)	$E_{ox\,(Fc)}^{onset[d]}$ (eV)	HOMO (eV)	HOMO-LUMO ΔE (eV)
3a	-1.41	nd	nd	nd	nd	-5.06[a] / nd	3.65[a] / 3.30 [e]
3b	-1.41	-2.27	1.45	1.36	0.66	-4.93 / -5.44[b]	3.51 / 3.17
3c	-1.39	-2.13	1.51	1.32	0.64	-4.84 / -5.06	3.45 / 3.13
3d	-1.39	nd	nd	nd	nd	-4.82 / nd	3.43 / nd
3e	-1.39	-2.33	1.64	1.59	0.65	-4.76 / -5.36	3.37 / 3.03
3f	-1.36	-2.34	1.67	1.61	0.65	-4.76 / -5.37	3.40 / 3.03
4	-1.47	nd	nd	nd	nd	-4.71 / nd	3.24 / 2.94
5	-1.22	nd	nd	nd	nd	-4.93 / nd	3.70 / 3,31

[a] DFT/B3LYP/6-31G* using Gaussian, [b] HOMO and LUMO energy levels were calculated according to equations: $-(4.8+E_{ox}^{onset})$ and LUMO = HOMO + E_g, [c] $E_{ox}^{1/2}$ is the half-wave potential of the oxidative waves, [d] E_{ox}^{onset} is the onset potential of the first oxidative wave, with potentials *versus* Fc/Fc$^+$ couple. [e] E_g: estimated from UV-vis absorption spectra in solution. nd. No determination.