Electronic Supplementary Information

Dinaphtho[8,1,2-*cde*:2',1',8'-*uva*]pentacene derivative and its analogues: synthesis, structures, photophysical and electrochemical properties

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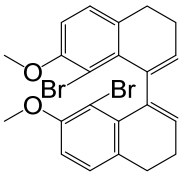
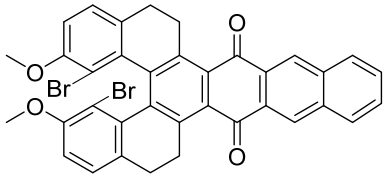
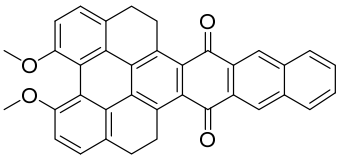
S1. Experimental procedures



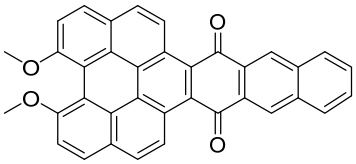
Synthesis of compound 3. To a solution of 1-tetralone (14.5 g, 57 mmol) and Zn power (7.4 g, 114 mmol) in THF at -78℃ was added trimethylsillylcholoride (21 mL, 171 mmol) and conc. HCl (42 mL) over 10 min with vigorous stirring. After the temperature was warmed to room temperature, the mixture was stirred overnight. The white precipitate **3** was filtered (9.4 g, 70%). Mp: 206-207 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 2H), 6.10 (t, *J* = 5.2 Hz, 2H), 3.84 (s, 6H), 2.82–2.69 (m, 4H), 2.26–2.09 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.3, 138.8, 136.2, 133.8, 130.4, 126.6, 111.6, 109.5, 56.5, 29.0, 23.2. HR MS (ESI): *m/z* calcd for $[M + H]^+$ $C_{22}H_{21}Br_2O_2$: 474.9908, found 474.9903.



Synthesis of compound 4a. The mixture of **3** (4 g, 8.48 mmol) and 1, 4-anthraquinone (5.28 g, 25.44 mmol) in AcOH was refluxed for 48 h. After cooling, the solvents were evaporated under reduced pressure. The residue was then subjected to flash column chromatography with CH_2Cl_2: petroleum ether (2:1, v/v) as eluent to afford yellow solids **4a** (3.2 g, 56%). Mp: > 300 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 2H), 8.08 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.67 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.27 (s, 2H), 6.84 (d, *J* = 8.1 Hz, 2H), 4.29 (d, *J* = 14.4 Hz, 2H), 3.76 (s, 6H), 3.01-2.94 (m, 2H), 2.82-2.76 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 185.8, 155.1, 143.9, 140.2, 137.3, 136.7, 135.1, 132.1, 131.3, 129.9, 129.0, 128.5, 126.1, 112.3, 112.2, 56.7, 30.2, 28.2. HR MS (ESI): *m/z* calcd for $[M + H]^+$ $C_{36}H_{25}Br_2O_4$:679.0119, found 679.0079.



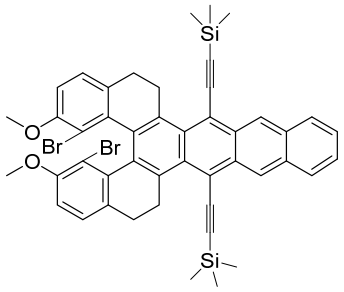
Synthesis of compound 4b. $NiCl_2 \cdot 6H_2O$ (225 mg, 0.95 mmol), Ph_3P (987 mg, 3.76 mmol), and Zn powder (158 mg, 2.44 mmol) were placed in a 100 mL two-necked flask, which was evacuated and refilled three times with argon. Then, anhydrous DMF was added, and the mixture was stirring at 50 ℃ for 1 h. To the mixture was added a solution of **4a** (250 mg, 0.36 mmol) in DMF, and the mixture was continued to be stirred for 5 h at 80℃. After the solvents were evaporated under reduced pressure, CH_2Cl_2 and water were added. The organic phase was dried by anhydrous $MgSO_4$. Then the solvent was removed, and the crude product was purified by flash column chromatography with CH_2Cl_2 : petroleum ether (2:1, v/v) as eluent to afford yellow solids **4b** (136 mg, 73%). Mp: > 300 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 2H), 8.09 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.66 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 4.02 (s, 6H), 3.89 (s, 4H), 3.16 (t, *J* = 7.5 Hz, 4H). ^{13}C NMR(101 MHz, $CDCl_3$): δ 186.5, 156.1, 137.6, 135.2, 131.7, 131.5, 131.3, 129.9, 129.0, 128.6, 128.4, 127.3, 126.4, 118.6, 111.3, 56.0, 27.8, 26.0. HR MS (ESI): *m/z* calcd for $[M + H]^+$ $C_{36}H_{25}O_4$: 521.1752, found 521.1746.



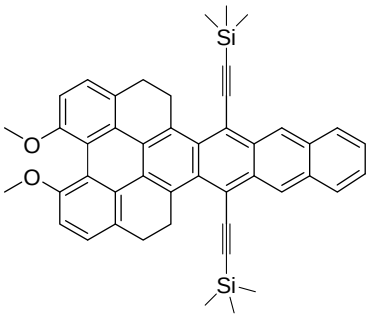
Synthesis of compound 4c. The mixture of **4a** (250 mg, 0.36 mmol), Cu powder (800 mg) and naphthalene was heated at 200℃ for 4 h. After cooling, the reaction mixture was treated with ethanol, and then performed by filtration. The crude product was purified by flash column chromatography with CH_2Cl_2 as eluent to afford black powder **4c** (71 mg, 55%). Mp: > 300 ℃. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.67 (d, *J* = 9.3 Hz, 2H), 8.86 (s, 2H), 8.29 (dd, *J* = 16.8, 9.0 Hz, 4H), 8.16 (dd, *J* = 6.1, 3.2 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.72 (dd, *J* = 6.3, 3.2 Hz, 2H), 4.28 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 187.7, 156.2, 135.2, 131.7, 130.6, 130.0, 129.2, 129.1, 128.9, 128.3, 128.2, 127.2, 126.9, 125.6, 123.4, 115.8, 113.7, 56.4. HR MS (ESI): *m/z* calcd for $[M + H]^+$ $C_{36}H_{21}O_4$: 517.1439, found 517.1429.

General procedure for synthesis of 5a-5c.

To an oven-dried 25 mL two-necked flask at 0℃ under argon atmosphere was added THF (10 mL), then trimethylsilylacetylene (6 eq), *n*-BuLi (5 eq, 2.4 M in cyclohexane) was added dropwise. The mixture was stirred for 4 h at room temperature, and then was transferred to a THF solution of **4** (1.0 eq) at 0℃. After stirring overnight, the reaction was quenched with water, and added DCM. The organic layer was separated, dried over MgSO4, and then concentrated. The residue was dissolved in acetone, and $SnCl_2 \cdot 2H_2O$ in 10% HCl was added. After the reaction proceeded for 12 h and wrapped in foil to block ambient light, the reaction mixture was filtered, and washed with water. The crude product was purified by flash column chromatography with CH_2Cl_2 : petroleum ether (1:2, v/v) as eluent to afford **5**.

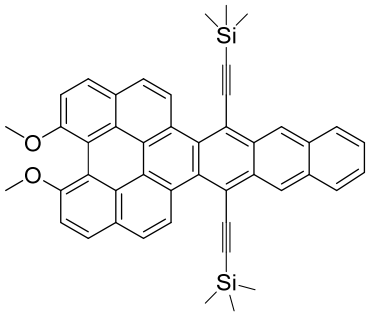


5a. Purple powder, 65% yield. Mp: 173-174 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (s, 2H), 8.04 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.47 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.23 (s, 2H), 6.80 (d, *J* = 8.1 Hz, 2H), 4.35 (d, *J* = 15.4 Hz, 2H), 3.77 (s, 6H), 3.27-3.20 (m, 2H), 2.94-2.90 (m, 2H), 2.77-2.70 (m, 2H), 0.41 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.9, 139.1, 138.9, 136.1, 134.3, 133.0, 132.6, 131.1, 128.8, 126.3, 126.1, 125.3, 117.1, 114.2, 112.2, 110.9, 105.5, 56.8, 32.4, 31.0, 0.0. HR MS (ESI): *m/z* calcd for $[M + H]^+$ $C_{46}H_{43}Br_2O_2Si_2$: 841.1168, found: 841.1128.



5b. Dark blue powder, 77% yield. Mp: 254-255 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.24 (s, 2H), 8.06 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.46 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.22 (d, *J* =

8.2 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 3.98 (s, 6H), 2.92 (s, 4H), 2.21 (dd, *J* = 36.8, 15.7 Hz, 3H), 0.40 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.3, 133.1, 132.5, 130.8, 130.4, 128.8, 128.5, 127.7, 126.6, 126.4, 125.9, 125.6, 118.3, 116.6, 113.1, 111.8, 105.3, 56.1, 28.3, 27.4, 0.0. HR MS (ESI): *m/z* calcd for $[M + H]^+$ $C_{46}H_{43}O_2Si_2$: 683.2801, found: 683.2788.



5c. Dark green powder, 82% yield. Mp: 264-265 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (d, *J* = 9.0 Hz, 2H), 9.35 (s, 2H), 8.11 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.86 (dd, *J* = 20.0, 8.9 Hz, 4H), 7.55–7.46 (m, 4H), 4.05 (s, 6H), 0.40 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.7, 132.5, 131.6, 130.2, 129.4, 128.7, 127.6, 127.2, 126.7, 126.2, 126.0, 125.5, 125.1, 124.8, 115.9, 115.4, 115.0, 108.5, 105.8, 56.5, 0.0. HR MS (ESI): *m/z* calcd for $[M + H]^+$ $C_{46}H_{39}O_2Si_2$: 679.2488, found: 679.2472.

S2. ^{1}H NMR and ^{13}C NMR spectra of new compounds

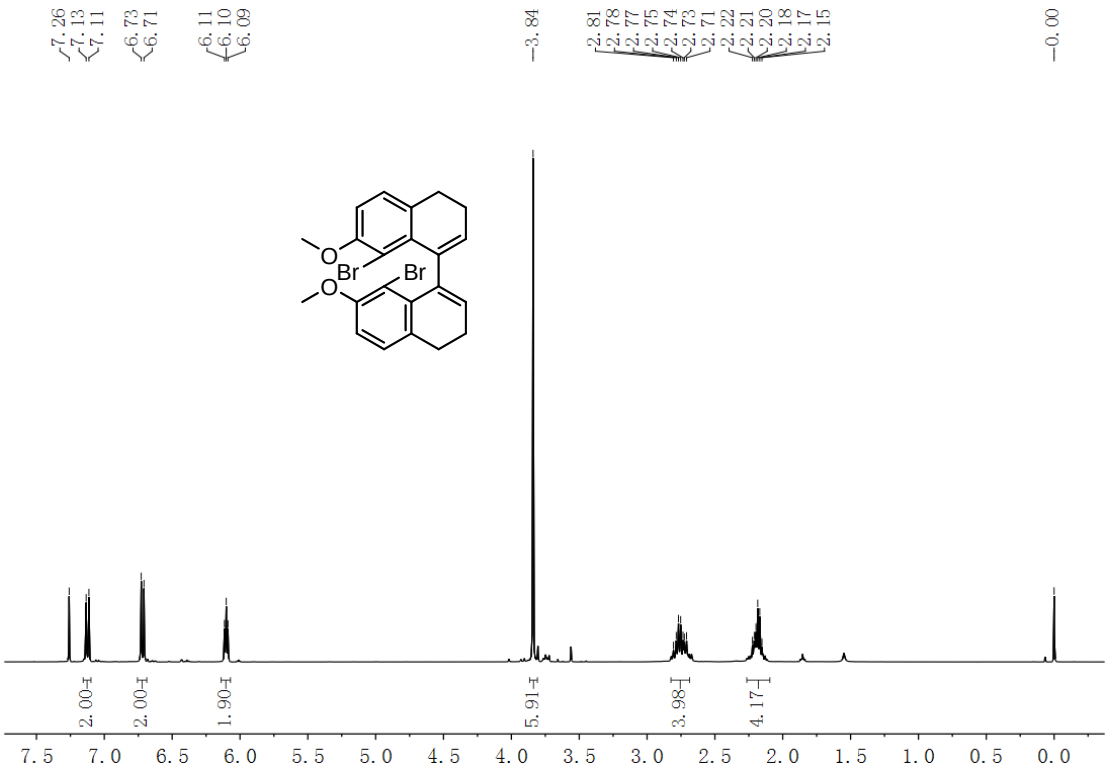


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**.

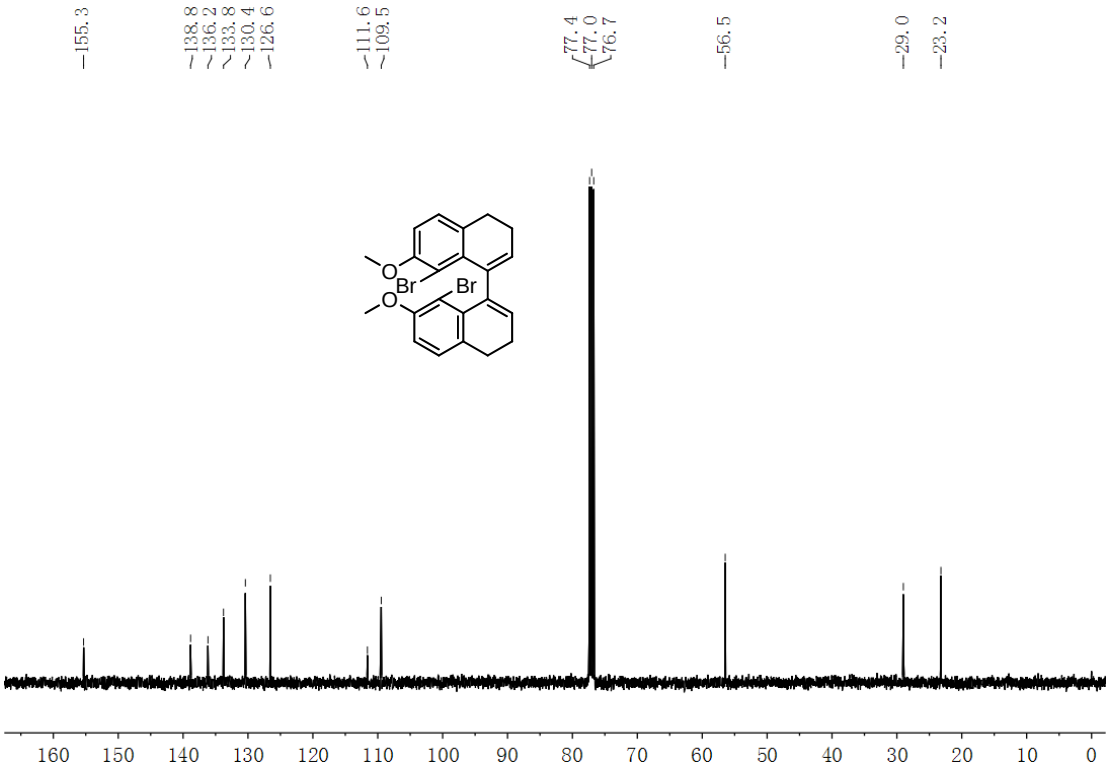


Fig. S2 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3**.

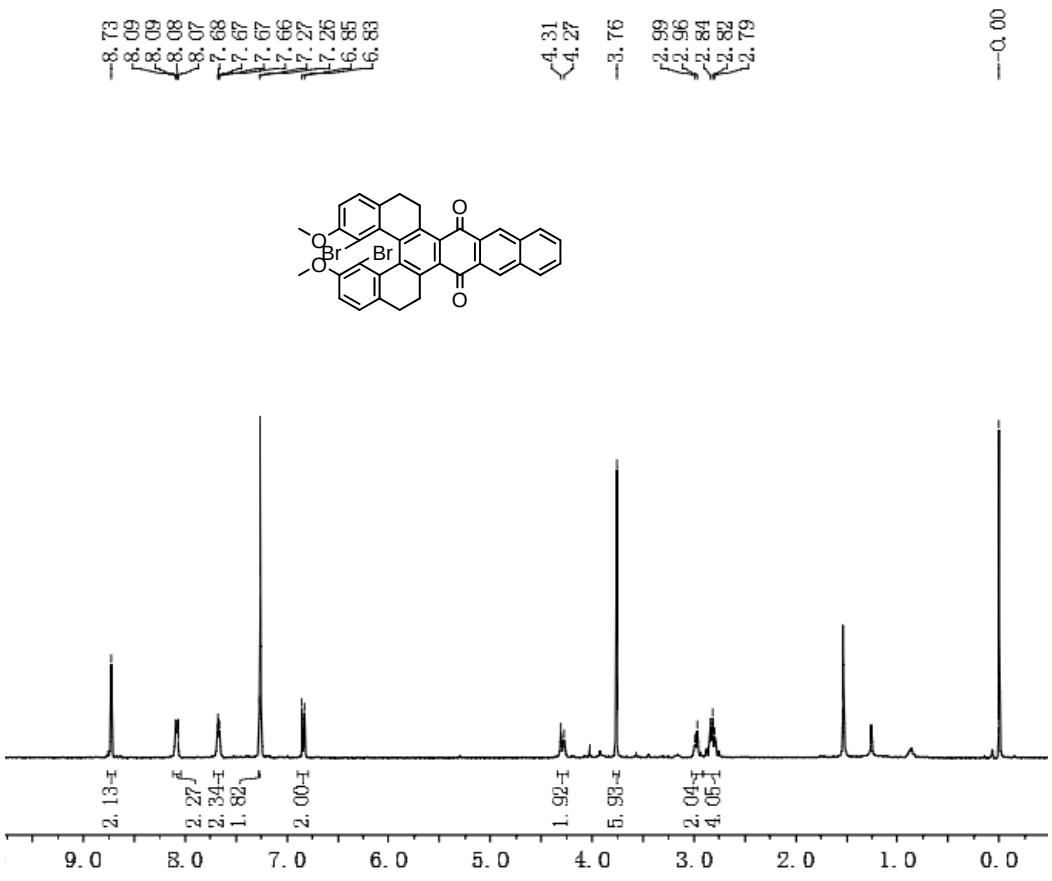


Fig. S3 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4a**.

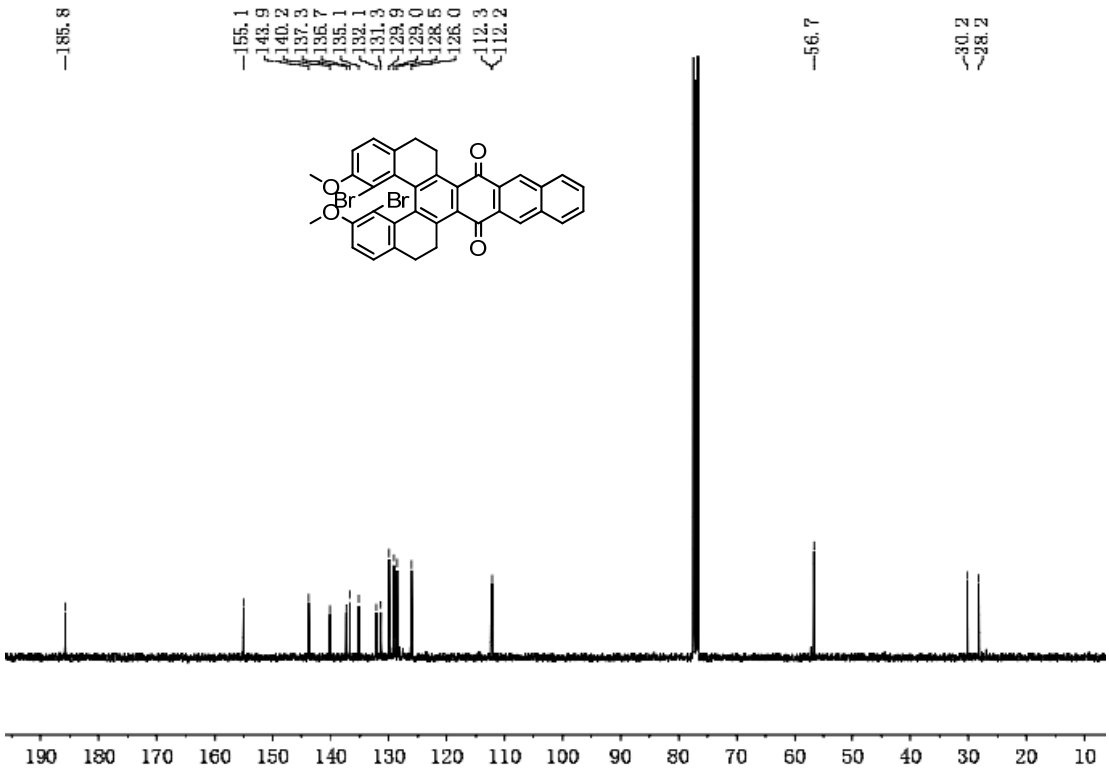


Fig. S4 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4a**

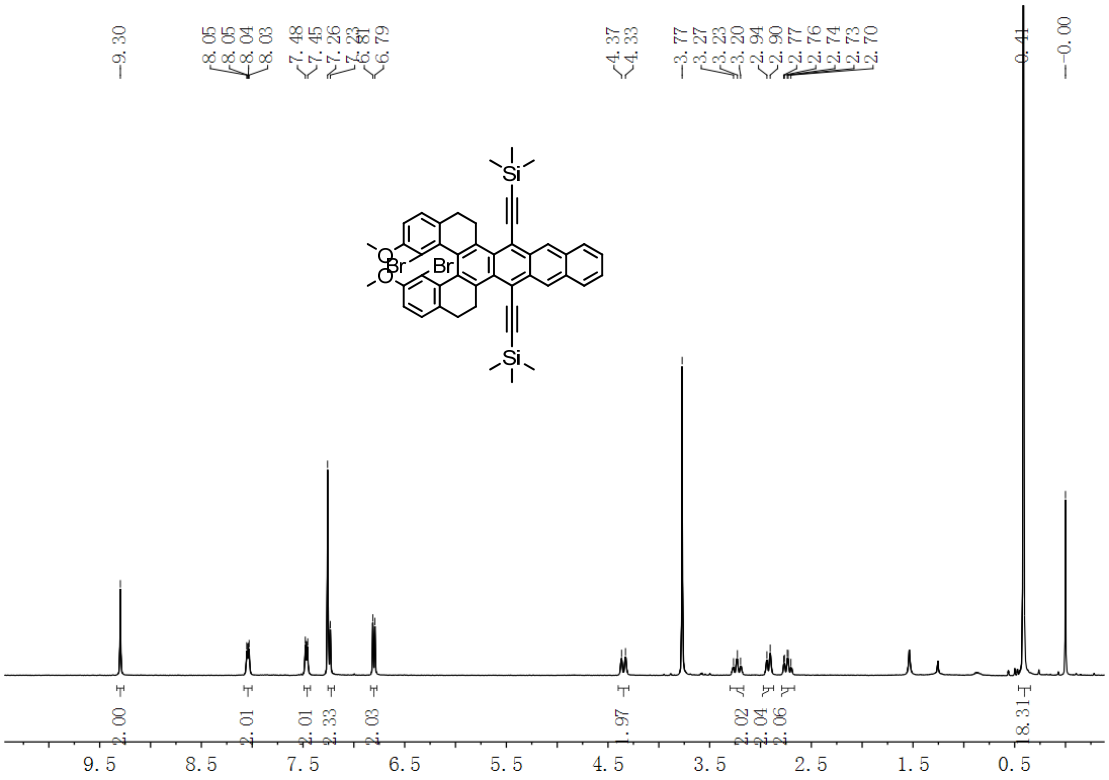


Fig. S5 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5a**.

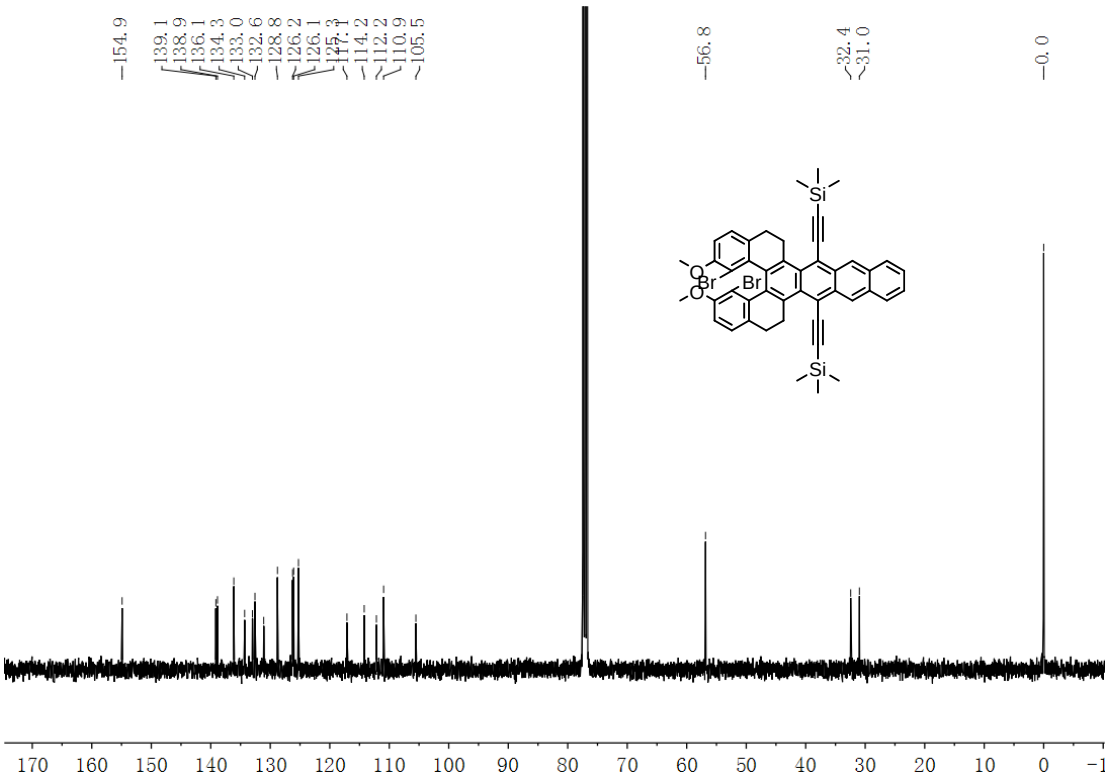


Fig. S6 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5a**.

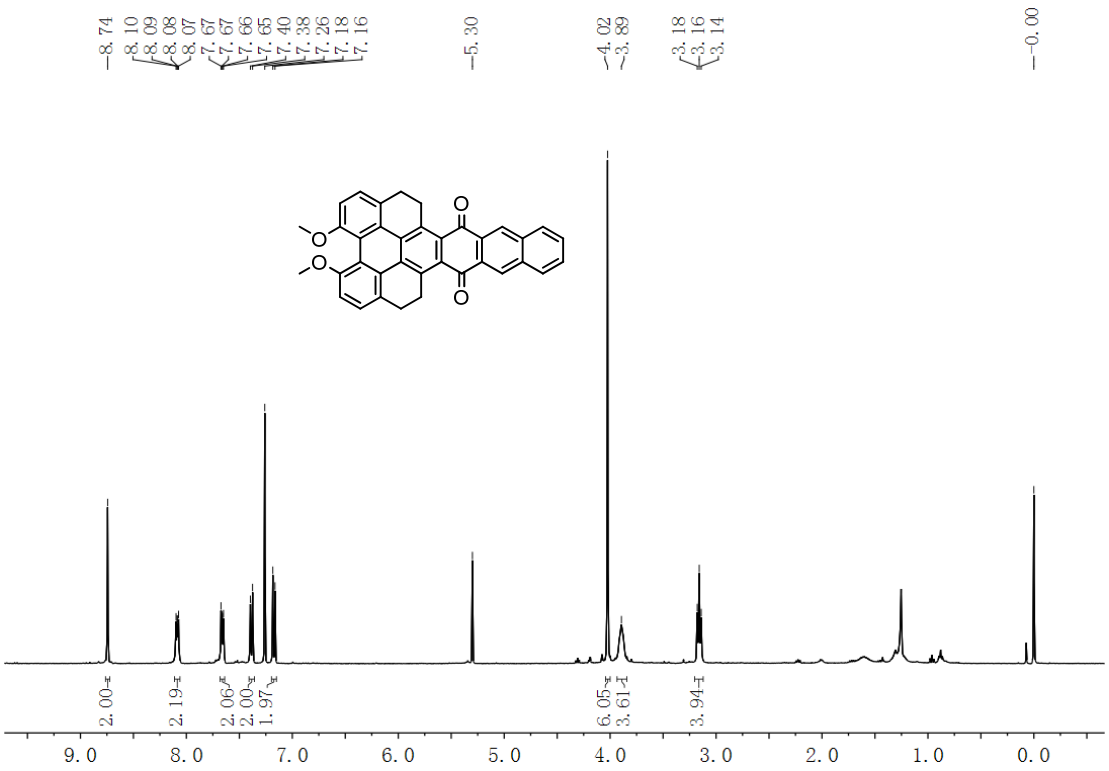


Fig. S7 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4b**.

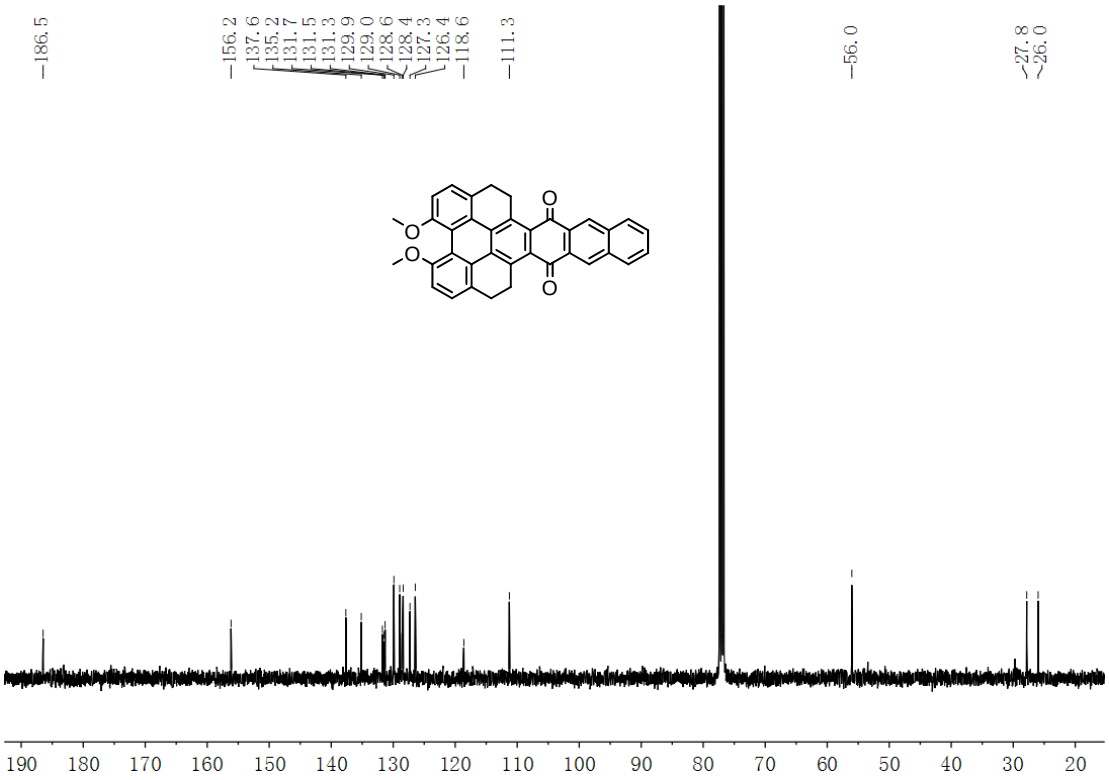
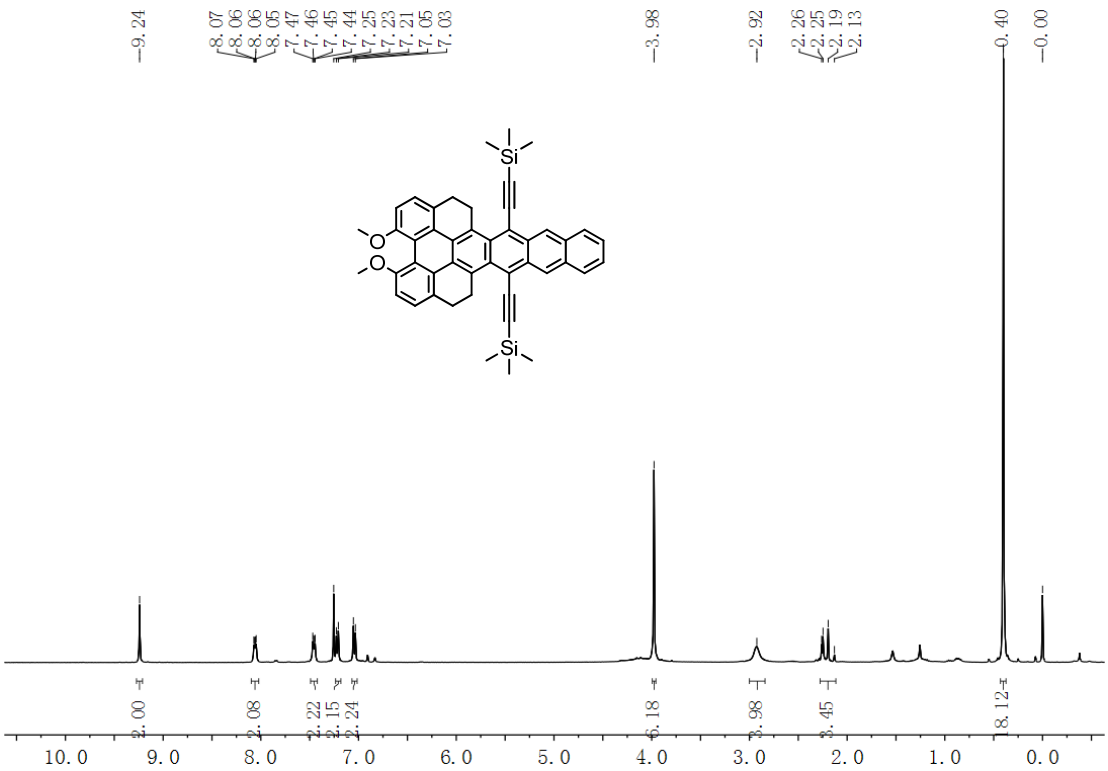


Fig. S8 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4b**.



. **Fig. S9** ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5b**.

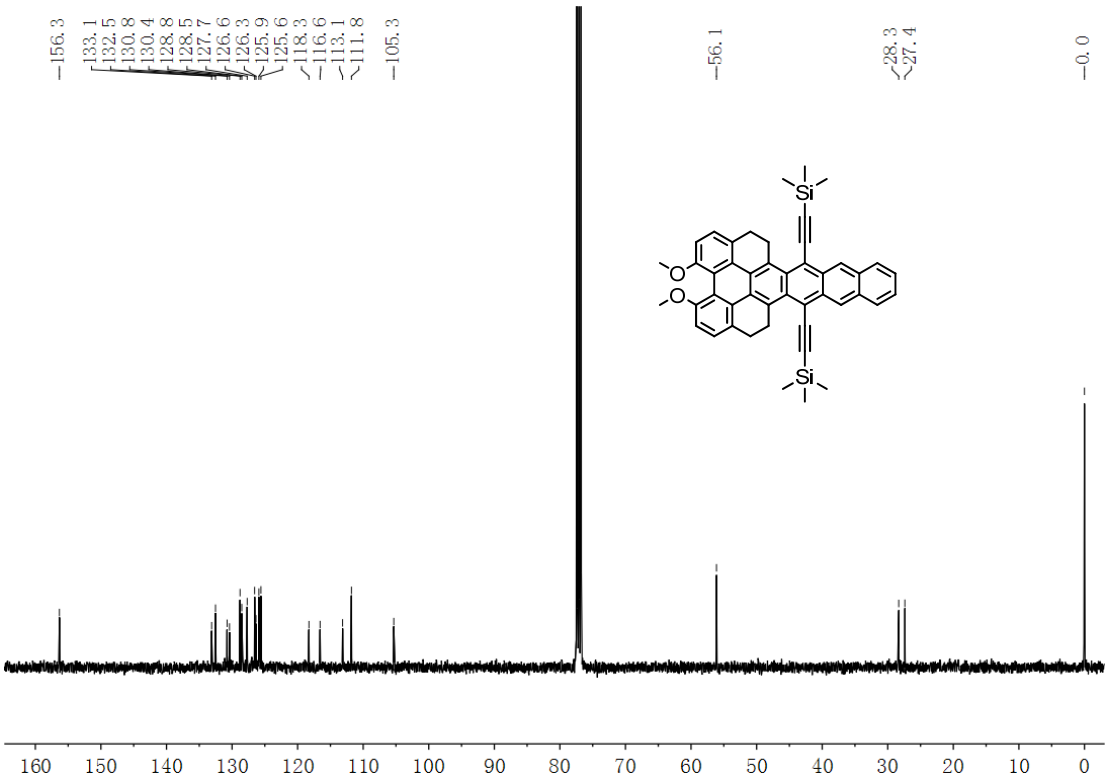


Fig. S10 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5b**.

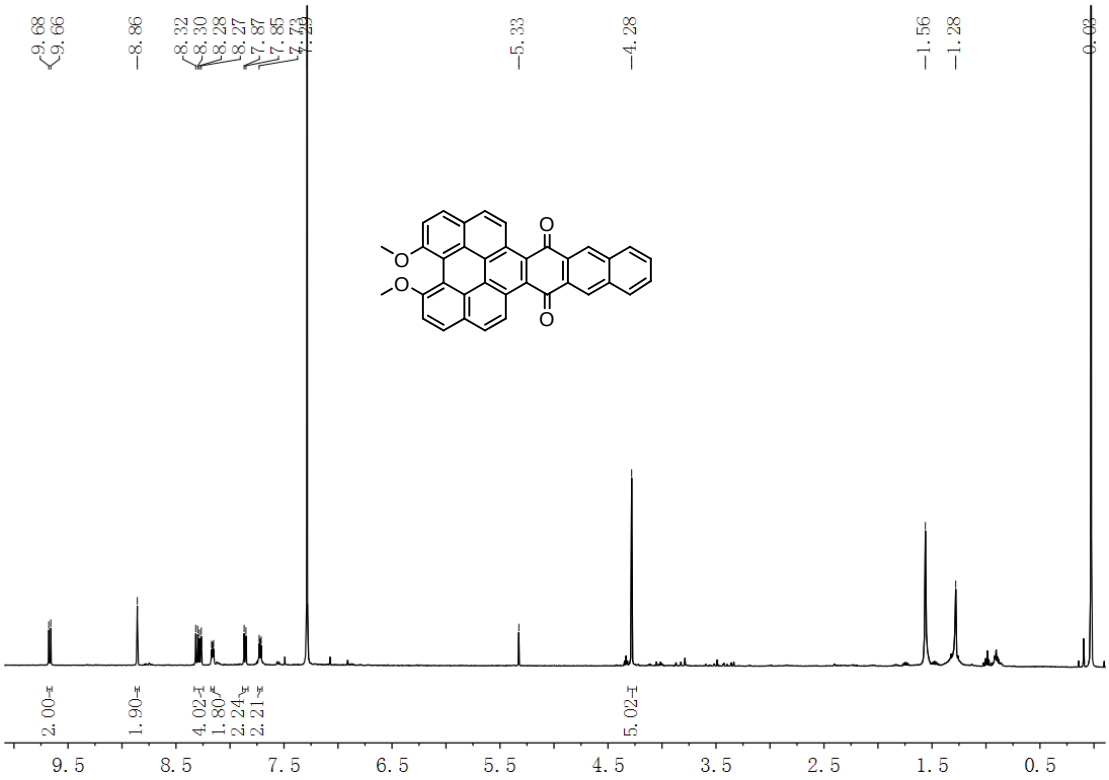


Fig. S11 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4c**.

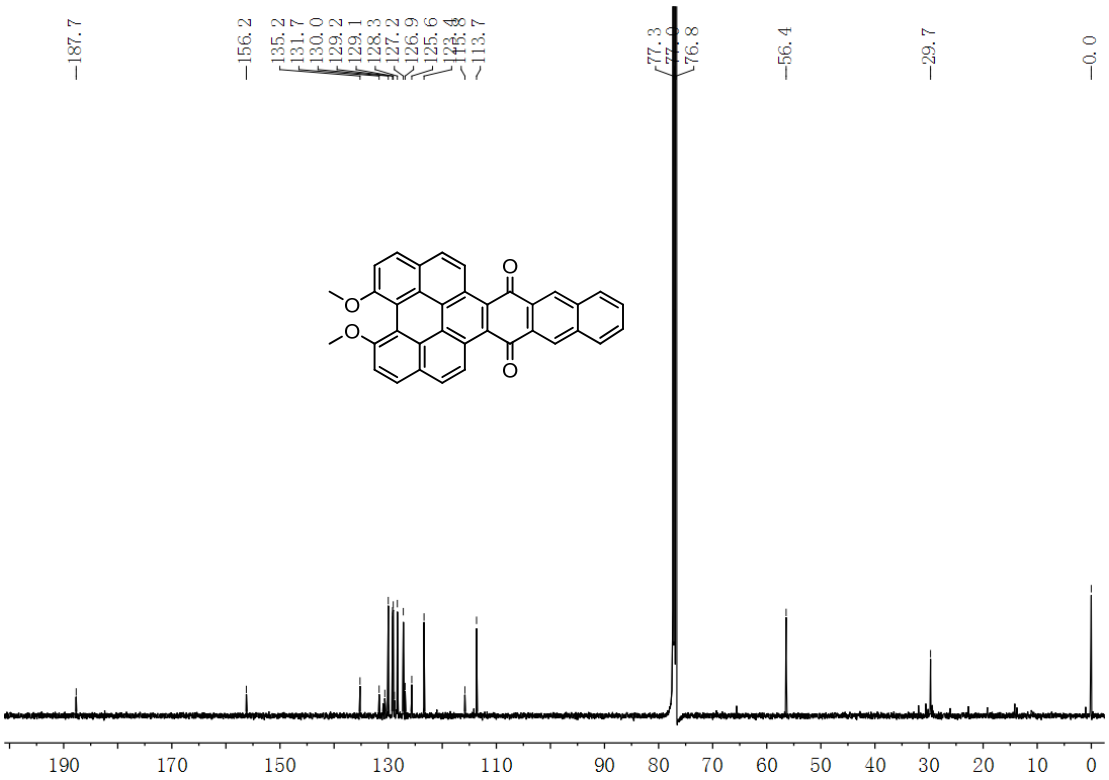
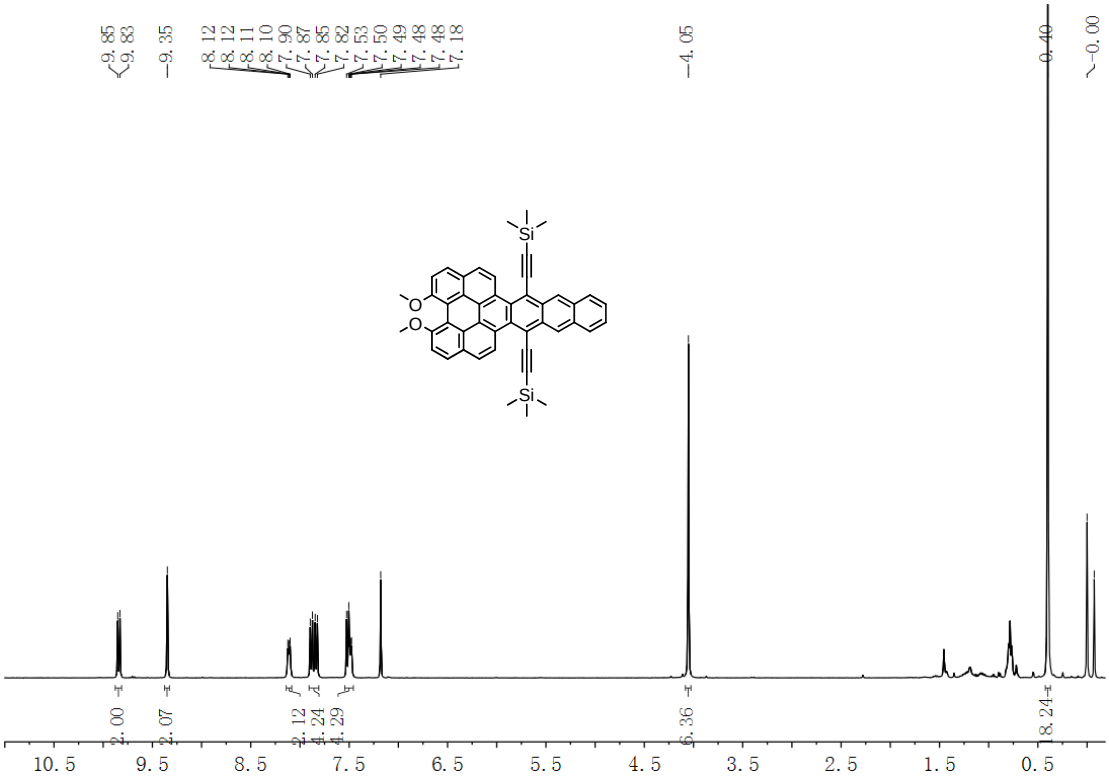


Fig. S12 ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **4c**.



. **Fig. S13** ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5c**.

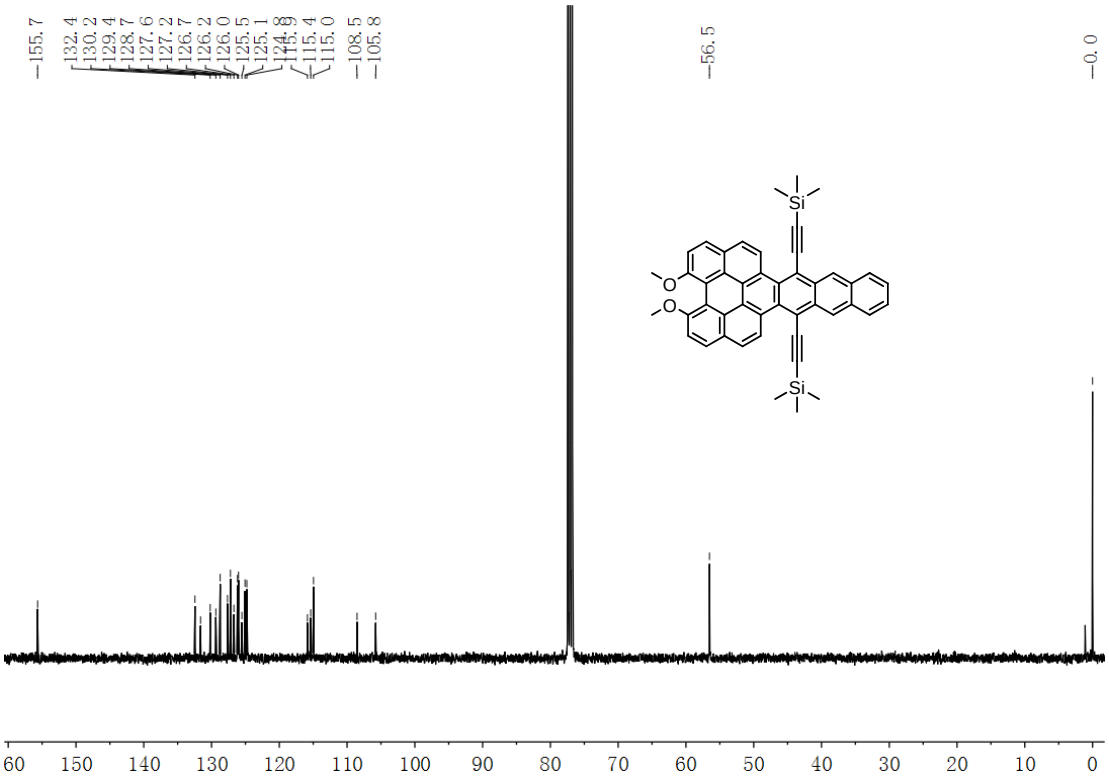


Fig. S14 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5c**.

S3. UV-vis spectra of 5c

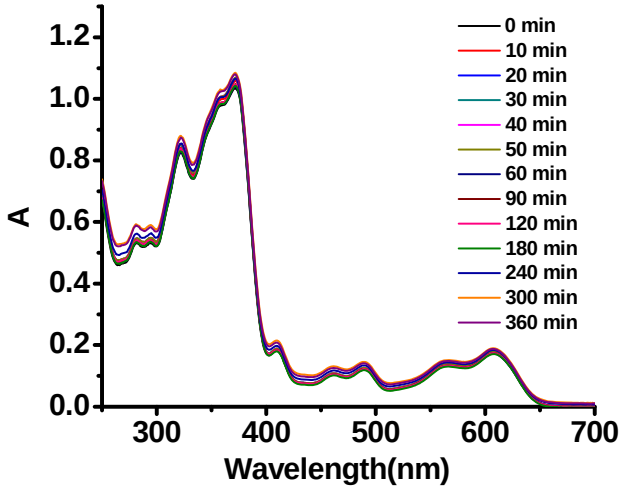


Fig. S15 UV-vis spectra of **5c** in cyclohexane (c =1.0 ×10^{-5} M) in the presence of light and air at different periods of time.

S4. The torsion angle of 5c

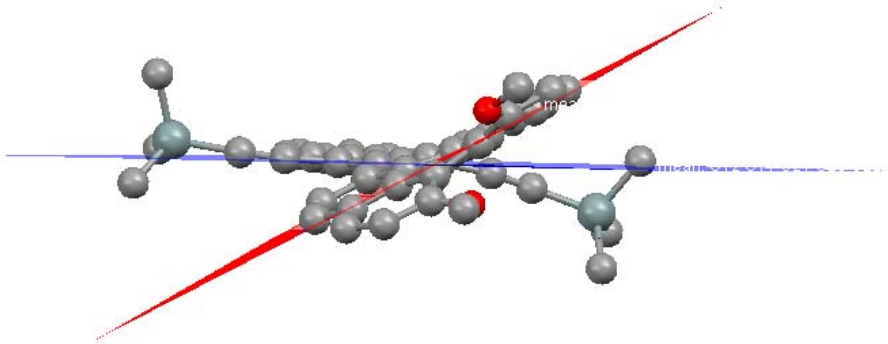


Fig. S16 The torsion angle of **5c**.

S5. Cyclic voltammogram

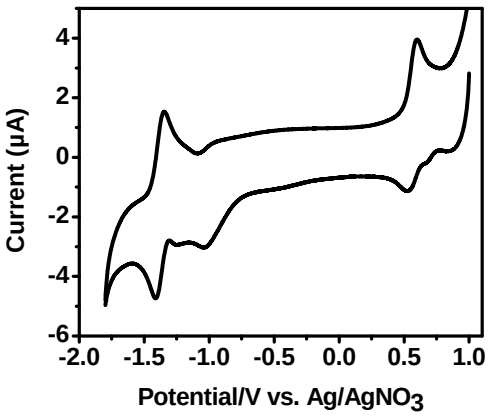


Fig. S17 Cyclic voltammograms of **5a** in 0.1 M *n*-Bu_4NPF_6 of CH_2Cl_2 solution at a scan rate of 100 mV/s, and with ferrocene/ferrocenium couple as standard.

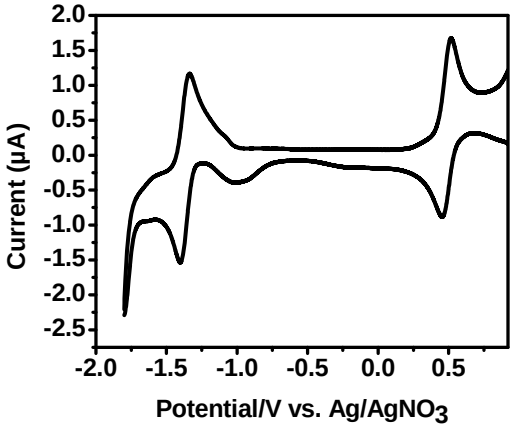


Fig. S18 Cyclic voltammograms of **5b** in 0.1 M *n*-Bu_4NPF_6 of CH_2Cl_2 solution at a scan rate of 100 mV/s, and with ferrocene/ferrocenium couple as standard.

S6. DFT calculations

Calculations were performed with the DFT method at the B3LYP/6-31G(d) level with Gaussian 09 program

Cartesian Coordinates (Å), SCF Energies and Free Energies at 298.15 K and 1 atm for the Optimized

Structure of **5a**.

B3LYP/6-31G* SCF energy: -2533.888793 a.u;

B3LYP/6-31G*free energy: -2533.236367a.u.

Table. S1 Cartesian coordinates (Å) of **5a**

	X	Y	Z
Br	3.211872	0.643026	2.567933
Br	3.213713	-0.667912	-2.568200
Si	-2.899837	-5.864886	0.018993
Si	-2.827300	5.887756	-0.018645
O	5.562179	-2.235120	-1.715757
O	5.571722	2.196883	1.722289
C	-6.135054	0.744422	-0.033768
C	-7.389331	1.435752	-0.065254
H	-7.381361	2.521884	-0.115767
C	-8.570875	0.746156	-0.032141
H	-9.516466	1.281053	-0.055793
C	-8.576285	-0.682320	0.034171
H	-9.525900	-1.209970	0.059288
C	-7.399994	-1.380911	0.065619
H	-7.400017	-2.467052	0.116308
C	-6.140581	-0.699020	0.032337
C	-4.913427	1.414989	-0.071602
H	-4.908703	2.497401	-0.135257
C	-3.682555	0.731922	-0.052217
C	-3.688126	-0.705544	0.047750
C	-4.924217	-1.379149	0.068659
H	-4.928349	-2.461527	0.132662
C	-2.429966	1.423333	-0.172325
C	-1.199562	0.709897	-0.175043
C	-1.204955	-0.703410	0.168653
C	-2.440952	-1.406838	0.166864
C	-2.498627	2.845128	-0.179085
C	-2.656859	4.057588	-0.115892
C	-4.169536	6.308954	1.245622
H	-5.139056	5.886238	0.957763
H	-4.292067	7.395855	1.333555
H	-3.917148	5.918993	2.238183
C	-3.310781	6.548989	-1.724290

H	-2.552477	6.304822	-2.476999
H	-3.420258	7.640582	-1.700662
H	-4.263359	6.124157	-2.060989
C	-1.170959	6.622408	0.522837
H	-0.872185	6.243875	1.506960
H	-1.233267	7.715906	0.588791
H	-0.372034	6.375896	-0.185945
C	-2.522221	-2.827901	0.174527
C	-2.694542	-4.038434	0.112376
C	-4.748258	-6.267075	0.034299
H	-5.227660	-5.903039	0.950419
H	-4.911046	-7.350855	-0.019122
H	-5.263522	-5.810520	-0.818692
C	-2.054863	-6.650658	1.518533
H	-0.985889	-6.410144	1.547010
H	-2.151117	-7.743334	1.490082
H	-2.501688	-6.299544	2.455724
C	-2.108551	-6.488898	-1.580949
H	-2.581970	-6.037135	-2.460016
H	-2.211483	-7.578022	-1.666244
H	-1.039739	-6.249386	-1.618410
C	0.066661	1.351743	-0.442096
C	0.165774	2.686634	-1.167325
H	-0.724497	2.836453	-1.779202
H	0.216077	3.535378	-0.473586
C	1.410359	2.684559	-2.071265
H	1.316986	1.878041	-2.812163
H	1.482756	3.629837	-2.621060
C	2.621309	2.491562	-1.201510
C	3.766623	3.266835	-1.306436
H	3.853501	3.985032	-2.117878
C	4.804492	3.151824	-0.380644
H	5.695950	3.757406	-0.493396
C	4.658149	2.305832	0.721154
C	3.483148	1.534932	0.831304

C	2.496952	1.535784	-0.163301
C	1.258852	0.699351	-0.158911
C	6.747953	2.983913	1.649543
H	6.517392	4.057634	1.644583
H	7.344796	2.738969	0.760860
H	7.320610	2.741672	2.546576
C	1.253598	-0.711183	0.154246
C	2.486085	-1.555902	0.161237
C	3.474994	-1.561095	-0.830660
C	4.645161	-2.338830	-0.717223
C	4.783396	-3.185723	0.384939
H	5.670976	-3.796513	0.500139
C	3.742211	-3.294668	1.307745
H	3.822457	-4.013471	2.119336
C	2.601835	-2.512548	1.199692
C	1.387219	-2.698779	2.065822
H	1.296604	-1.892396	2.807213
H	1.451931	-3.645030	2.614882
C	0.145420	-2.692050	1.158113
H	-0.747515	-2.839628	1.766415
H	0.194192	-3.539315	0.462268
C	0.056355	-1.355182	0.435285
C	6.734321	-3.027856	-1.639078
H	7.311115	-2.788445	-2.534219
H	6.498579	-4.100463	-1.634862
H	7.329374	-2.785755	-0.748418

Cartesian Coordinates (Å), SCF Energies and Free Energies at 298.15 K and 1 atm for the Optimized

Structure of **5b**.

B3LYP/6-31G* SCF energy: -2507.612499 a.u;

B3LYP/6-31G*free energy: -2506.953289a.u.

Table S2. Cartesian coordinates (Å) of **5b**

	X	Y	Z

Si	2.162623	5.844839	0.681629
Si	2.177798	-5.843243	-0.669199
O	-6.453833	0.171710	1.276353
O	-6.454346	-0.181436	-1.277654
C	-7.609892	-0.036932	2.063612
H	-8.065670	-1.016903	1.866709
H	-8.311162	0.749870	1.777874
H	-7.393467	0.047845	3.137459
C	-7.611120	0.025195	-2.064391
H	-7.395095	-0.059447	-3.138324
H	-8.068355	1.004476	-1.867449
H	-8.310995	-0.762665	-1.778146
C	-5.401026	-0.681519	1.414139
C	-5.365828	-1.681799	2.388290
H	-6.238887	-1.889570	2.995240
C	-4.185785	-2.389847	2.624273
H	-4.168082	-3.151571	3.400628
C	-3.019264	-2.081076	1.938108
C	-1.687341	-2.669030	2.328938
H	-1.819945	-3.680924	2.730743
C	-0.696854	-2.700529	1.161164
H	-1.014129	-3.456821	0.428769
C	-0.612264	-1.337403	0.497718
C	0.633165	-0.717960	0.120181
C	1.861877	-1.423974	0.013824
C	3.110073	-0.717471	-0.041602
C	4.343382	-1.391793	-0.108337
H	4.343028	-2.474524	-0.175552
C	5.561899	-0.714880	-0.062819
C	6.819582	-1.398323	-0.116851
H	6.816718	-2.482377	-0.201830
C	7.998139	-0.704645	-0.062563
H	8.946165	-1.234102	-0.105202

C	7.996788	0.720720	0.050595
H	8.943807	1.252034	0.092473
C	6.816910	1.412065	0.105968
H	6.811917	2.496087	0.191216
C	5.560555	0.726094	0.052993
C	4.340738	1.400559	0.099647
H	4.338234	2.483279	0.167051
C	3.108760	0.723696	0.033961
C	1.859261	1.427829	-0.019778
C	0.631813	0.719646	-0.125778
C	-0.614817	1.337195	-0.502255
C	-0.702388	2.700390	-1.165303
H	0.269354	3.022697	-1.535606
C	-1.692778	2.666582	-2.333121
H	-1.258991	2.064398	-3.147701
C	-3.023640	2.076554	-1.941733
C	-4.190967	2.383276	-2.627440
H	-4.174847	3.144812	-3.404018
C	-5.369769	1.673438	-2.390639
H	-6.243497	1.879656	-2.997161
C	-5.402902	0.673347	-1.416217
C	-4.278522	0.459755	-0.573077
C	-4.277436	-0.466051	0.570421
C	-3.060828	-1.105420	0.919058
C	-1.796889	-0.635784	0.337705
C	-1.798161	0.633543	-0.341711
C	-3.063149	1.101051	-0.922440
C	1.912977	-2.837433	-0.139118
C	2.035650	-4.037562	-0.350219
C	1.780698	-6.181820	-2.487110
H	0.762680	-5.862015	-2.736997
H	1.860278	-7.253580	-2.708723
H	2.470050	-5.649365	-3.152155

C	0.952288	-6.759023	0.444022
H	1.154931	-6.566057	1.503696
H	1.016239	-7.842543	0.282850
H	-0.079650	-6.451307	0.239405
C	3.945274	-6.390935	-0.273993
H	4.675709	-5.865510	-0.900145
H	4.068702	-7.466946	-0.450061
H	4.198326	-6.192621	0.773853
C	1.907317	2.841046	0.135949
C	2.026582	4.040844	0.350737
C	1.413216	6.215672	2.378217
H	0.357672	5.923515	2.418444
H	1.473713	7.287453	2.606027
H	1.939173	5.673498	3.172221
C	1.223447	6.787584	-0.663642
H	1.643447	6.589573	-1.656448
H	1.275379	7.869414	-0.487544
H	0.165091	6.503264	-0.685584
C	3.991385	6.328279	0.654671
H	4.559366	5.783336	1.417563
H	4.113930	7.400926	0.850301
H	4.445598	6.112666	-0.319335
H	-1.254598	-2.066684	3.143960
H	0.275641	-3.020105	1.531849
H	-1.022038	3.455444	-0.432557
H	-1.827129	3.677935	-2.735740

Cartesian Coordinates (Å), SCF Energies and Free Energies at 298.15 K and 1 atm for the Optimized

Structure of **5c**

B3LYP/6-31G* SCF energy: -2505.222106 a.u;

B3LYP/6-31G*free energy: -2504.60819a.u.

Table S3. Cartesian coordinates (Å) of **5c**

	X	Y	Z
Si	2.125692	5.853401	0.654954
Si	2.125907	-5.853457	-0.653954
O	-6.479669	-0.109567	1.272064
O	-6.479251	0.109030	-1.273210
C	-7.651200	-0.498125	1.965271
H	-8.089423	-1.413609	1.545911
H	-8.355658	0.326820	1.841088
H	-7.460902	-0.647925	3.036440
C	-7.651413	0.498183	-1.964995
H	-7.462210	0.648439	-3.036305
H	-8.088974	1.413575	-1.544752
H	-8.355934	-0.326664	-1.840488
C	-5.413047	-0.952611	1.236948
C	-5.389871	-2.154822	1.978165
H	-6.281928	-2.491127	2.492971
C	-4.234850	-2.901537	2.068075
H	-4.229470	-3.832073	2.629904
C	-3.033358	-2.433320	1.497477
C	-1.793047	-3.091099	1.708210
H	-1.778638	-3.999956	2.305258
C	-0.623113	-2.574276	1.221813
H	0.303919	-3.079180	1.448704
C	-0.595943	-1.342694	0.501842
C	0.669846	-0.715045	0.113585
C	1.885100	-1.423667	0.000795
C	3.141145	-0.718178	-0.050638
C	4.368860	-1.393850	-0.125686
H	4.367011	-2.475581	-0.207870
C	5.591214	-0.718302	-0.069432
C	6.846225	-1.402462	-0.133706

H	6.842156	-2.485033	-0.235695
C	8.026752	-0.710782	-0.068308
H	8.973910	-1.241088	-0.119006
C	8.026776	0.710829	0.066814
H	8.973952	1.241127	0.117285
C	6.846270	1.402520	0.132489
H	6.842240	2.485089	0.234484
C	5.591235	0.718373	0.068517
C	4.368902	1.393936	0.125067
H	4.367077	2.475668	0.207247
C	3.141164	0.718271	0.050299
C	1.885103	1.423767	-0.000864
C	0.669833	0.715147	-0.113593
C	-0.595960	1.342808	-0.501814
C	-0.623141	2.574469	-1.221655
H	0.303883	3.079451	-1.448415
C	-1.793059	3.091275	-1.708104
H	-1.778659	4.000209	-2.305037
C	-3.033347	2.433370	-1.497594
C	-4.234809	2.901530	-2.068318
H	-4.229449	3.832130	-2.630041
C	-5.389760	2.154660	-1.978701
H	-6.281740	2.490862	-2.493705
C	-5.412892	0.952353	-1.237646
C	-4.290778	0.555233	-0.478838
C	-4.290830	-0.555395	0.478342
C	-3.053371	-1.225360	0.736020
C	-1.810734	-0.657599	0.299398
C	-1.810738	0.657639	-0.299515
C	-3.053353	1.225340	-0.736267
C	1.937131	-2.838968	-0.148571
C	2.055107	-4.040698	-0.348688
C	1.391034	-6.212053	-2.358937

H	0.349318	-5.876974	-2.417789
H	1.411340	-7.287783	-2.574996
H	1.950978	-5.700079	-3.149717
C	1.118290	-6.730042	0.686359
H	1.535851	-6.547348	1.683223
H	1.109743	-7.814689	0.520614
H	0.078502	-6.383302	0.689604
C	3.930388	-6.416498	-0.584661
H	4.535975	-5.911453	-1.346063
H	4.007135	-7.496826	-0.760176
H	4.376974	-6.204898	0.393743
C	1.937120	2.839043	0.148731
C	2.054962	4.040735	0.349168
C	1.390366	6.211568	2.359826
H	0.348040	5.878266	2.417768
H	1.412448	7.287059	2.576954
H	1.948980	5.697861	3.150419
C	1.118579	6.730438	-0.685447
H	1.536221	6.547658	-1.682260
H	1.110505	7.815088	-0.519618
H	0.078642	6.384179	-0.688867
C	3.930167	6.416531	0.586434
H	4.535641	5.910939	1.347570
H	4.006798	7.496721	0.762803
H	4.377000	6.205713	-0.392029

S7. Crystal Data

Table S4. Crystal data of **5a** (CCDC: 1058255)

Identification code	mx3431_sq
Empirical formula	C_{46} H_{42} Br_2 O_2 Si_2

Formula weight	842.79	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.917(3) Å	a= 72.399(15)°.
	b = 15.959(4) Å	b= 76.618(15)°.
	c = 25.657(5) Å	g = 71.646(12)°.
Volume	4364.2(17) $Å^3$	
Z	4	
Density (calculated)	1.283 Mg/m^3	
Absorption coefficient	1.947 mm^{-1}	
F(000)	1728	
Crystal size	0.41 x 0.36 x 0.05 mm^3	
Theta range for data collection	1.433 to 27.483°.	
Index ranges	-15<=h<=15, -20<=k<=15, -33<=l<=33	
Reflections collected	50951	
Independent reflections	19925 [R(int) = 0.0768]	
Completeness to theta = 26.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.5226	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19925 / 0 / 953	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0741, wR2 = 0.1773	
R indices (all data)	R1 = 0.0906, wR2 = 0.1898	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.100 and -0.648 $e.Å^{-3}$	

Table S5. Crystal data of **5c** (CCDC 1058256).

Identification code	mx3830	
Empirical formula	C_{49} H_{44} O_3 Si_2	
Formula weight	737.02	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.361(5) Å	= 72.031(18)°.

	b = 12.402(5) Å	= 82.67(2)°.
	c = 15.056(5) Å	= 89.49(3)°.
Volume	2000.4(14) $Å^3$	
Z	2	
Density (calculated)	1.224 Mg/m^3	
Absorption coefficient	0.131 mm^{-1}	
F(000)	780	
Crystal size	0.26 x 0.24 x 0.04 mm^3	
Theta range for data collection	1.808 to 25.198°.	
Index ranges	-13<=h<=13, -14<=k<=14, -18<=l<=18	
Reflections collected	15133	
Independent reflections	7149 [R(int) = 0.0843]	
Completeness to theta = 25.198°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.5001	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7149 / 0 / 497	
Goodness-of-fit on F^2	1.114	
Final R indices [I>2sigma(I)]	R1 = 0.1175, wR2 = 0.3062	
R indices (all data)	R1 = 0.1480, wR2 = 0.3362	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.462 and -0.735 $e.Å^{-3}$	