Super-octazethrene: An Open-shell Graphene-Like Molecule Possessing Large Diradical Character but Still with Reasonable Stability

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1. Experimental Section

1.1 General

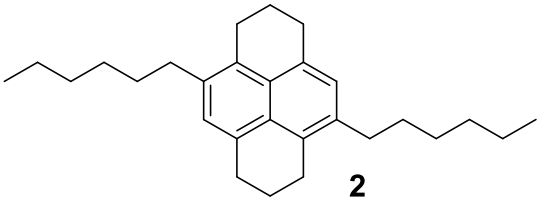
All reagents and starting materials were obtained from commercial suppliers and used without further purification. Anhydrous diethyl ether and dichloromethane (DCM) were distilled under a nitrogen atmosphere over sodium and calcium hydride, respectively. Compound 4,9-dibromo-1,2,3,6,7,8-hexahydropyrene **1**,[1] 2-formylphenylboronic acid,[2] and (4-*tert*-butyl-2,6-bis(methoxymethyl)phenyl)magnesium bromide[3] were prepared according to the literatures. Column chromatography was performed on silica gel 60 (Merck 40-60 nm, 230-400 mesh). All NMR spectra were recorded on the Bruker AMX500 spectrometer. All chemical shifts are quoted in ppm, relative to tetramethylsilane, using the residual solvent peak as a reference standard. Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI MS) measurements were performed on a Finnigan TSQ 7000 triple stage quadrupole mass spectrometer. UV-vis-NIR absorption spectra was recorded on a Shimadzu UV-1700/UV-3600 spectrophotometer. Cyclic voltammetry (CV) measurements were performed in dry THF on a CHI 620C electrochemical analyzer with a three-electrode cell, using 0.1 M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, gold disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV/s. The potential was externally calibrated against the ferrocene/ferrocenium couple. Continuous wave X-band ESR spectra were obtained with a JEOL (FA200) spectrometer using a variable temperature liquid nitrogen cryostat.

A Quantum Design 7 Tesla SQUID-VSM system was available for the magnetic measurement of **SOZ-Cl** in this work. Microcrystalline powder sample with a weight of 5-10 mg was sealed in a plastic capsule. Magnetic moment was measured in the temperature range of 2 to 380 K. The empty plastic capsule exhibited diamagnetic and its magnetic moment was measured for correction. After correction of diamagnetic contributions from the sample, sample holder and paramagnetic contamination, the magnetic data were fitted with Bleaney-Bowers equation:

$$\chi_M T = \frac{2N\beta^2 g^2}{k_B[3 + exp(-2J/k_B T)]}$$

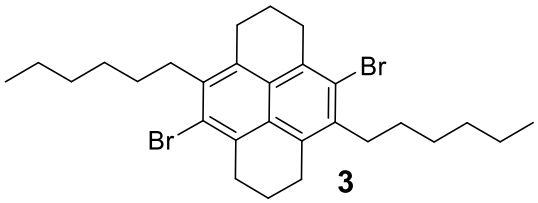
where, -2*J* is correlated to the excitation energy from the singlet ground state to the triplet excited state.

1.2 Synthetic procedures and characterization data



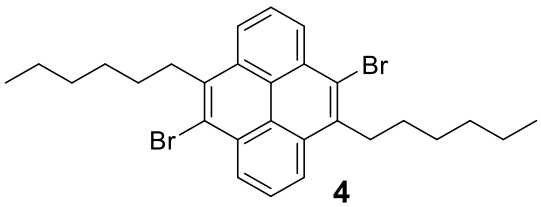
2

4,9-Dibromo-1,2,3,6,7,8-hexahydropyrene (**1**, 10.00 g, 27.40 mmol) and [1,2-bis(diphenylphosphino)ethane]dichloronickel(II) (159.0 mg, 2.74 mmol) were dissolved in 600 mL dry diethyl ether under nitrogen. Hexylmagnesium bromide solution 2.0 M in diethyl ether (55 mL) was added slowly at room temperature and then the mixture was refluxed for 24 h. After cooling to room temperature, water was added and the reaction mixture was extracted with diethyl ether. The organic layer was dried over sodium sulfate and then evaporated to dryness. The crude mixture was subjected to silica gel column chromatography (hexane) to afford the title product as white solid (7.23 g, 70% yield).^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 7.01 (s, 2H), 3.02 (m, 8H), 2.71 (m, 4H), 2.05 (m, 2H), 1.61-1.57 (m, 4H), 1.41-1.30 (m, 12H), 0.90 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ ppm 134.73, 133.34, 130.16, 129.06, 126.22, 33.26, 31.86, 31.46, 30.81, 29.52, 27.44, 23.40, 22.57, 14.13. HR-MS (APCI): *m*/*z* = 377.3200, calcd. for $C_{28}H_{41}$ (M + 1): *m*/*z* = 377.3203, error = 0.9 ppm.



3

To the solution of compounds **2** (5.00 g, 13.29 mmol) in $CHCl_3$ (300 mL) was added *N*-bromosuccinimide (NBS) (2.28 g, 29.26 mmol), and the mixture was stirred at room temperature for 2 h. The reaction mixture was then poured into water (20 mL) and the organic phase was washed with brine (200 mL). The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography (silica gel, hexane) to afford the title products **3** (4.60 g, 65% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 3.16 (t, *J* = 6.25 Hz, 4H), 3.03 (t, *J* = 6.15 Hz, 4H), 2.98 (m, 4H), 2.02 (m, 4H), 1.47 (m, 4H), 1.37-1.25 (m, 12H), 0.93-0.88 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ ppm 135.34, 133.16, 132.12, 129.49, 126.30, 33.96, 33.09, 31.66, 29.73, 29.07, 28.60, 23.05, 22.71, 14.12. HR-MS (APCI): *m*/*z* = 532.1331, calcd. for $C_{28}H_{38}Br_2$: *m*/*z* = 532.1335, error = 0.7 ppm.



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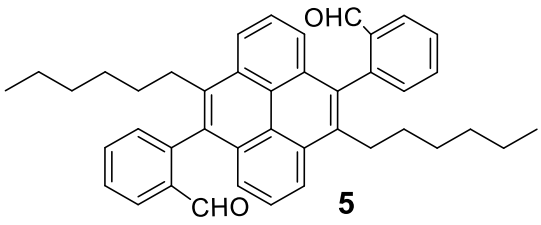
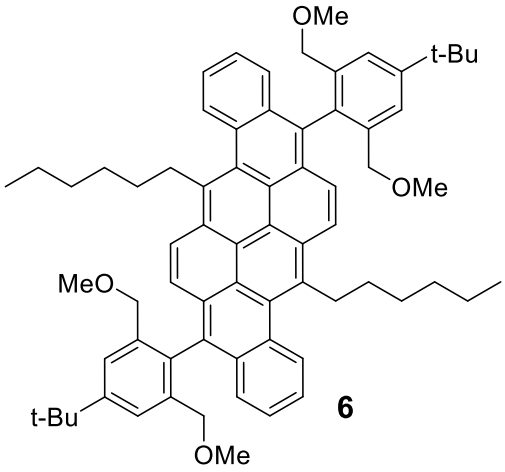
Compound **3** (4.00 g, 7.51 mmol) was dissolved in 150 mL of toluene under argon, DDQ (5.14 g, 22.55 mmol) was added and the mixture was stirred and refluxed for 4 h. The color of the solution tuned from red to yellow. The solvent was removed by vacuum and the residue was purified by column chromatography (silica gel, hexane/DCM = 5/1) to give pure compound **4** (3.17 g, 80% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 8.72 (d, *J* = 8.00 Hz, 2H), 8.31 (d, *J* = 8.00 Hz, 2H), 8.02 (d, *J* = 7.85 Hz, 2H), 3.49 (d, *J* = 8.25 Hz, 2H), 1.83-1.76 (m, 4H), 1.65-1.59 (m, 4H), 1.49-1.37 (m, 8H), 0.94 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ ppm 138.05, 130.36, 130.18, 126.68, 126.29, 124.69, 123.79, 122.78, 34.36, 31.73, 29.83, 29.36, 22.75, 14.16. HR-MS (APCI): *m*/*z* = 526.0848, calcd. for $C_{28}H_{32}Br_2$: *m*/*z* = 526.0865, error = 3.3 ppm.



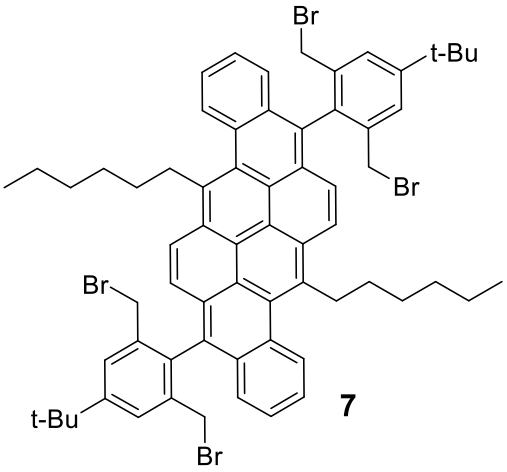
5

A two-necked round bottom flask was charged with 4,9-dibromo-5,10-dihexylpyrene **4** (3.00 g, 5.70 mmol), 2-formylphenylboronic acid (3.42 g, 22.8 mmol), 2M aq. Na_2CO_3 (22.8 mL), ethanol (22.8 mL), toluene (400 mL) and purged with argon for 1 h. $Pd_2(dba)_3$ (261.0 mg, 5 mol%), and SPhos (468.0 mg, 20 mol%) were added subsequently under argon. The resultant mixture was then heated at 110 °C for 24 h. After cooling to room temperature, water was added and the reaction mixture was extracted with chloroform. The organic layer was dried over sodium sulfate and then evaporated to dryness. The crude mixture was subjected to column chromatography (silica gel, hexane/DCM = 3/1) to afford the title product (2.97 g, 90% yield). This compound has two atropisomers due to restricted rotation and thus the NMR peaks are split. ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 9.66 (s, 2H), 8.42 (d, *J* = 7.8 Hz, 2H), 8.26 (d, *J* = 7.7 Hz, 2H), 7.94 (t, *J* = 7.85 Hz, 2H), 7.84 (t, *J* = 7.3 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.52 (m, 4H), 3.08 (m, 4H), 2.90 (m, 4H), 1.69 (m, 4H), 1.33-1.16 (m, 12H), 0.83 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ ppm 192.11, 192.06, 143.34, 137.18, 135.13, 135.07, 134.33, 134.24, 132.81, 132.34, 131.93, 130.51, 129.68, 128.99, 128.45, 127.43, 126.36, 125.47, 127.97, 126.68, 122.21, 31.25, 31.08, 30.41, 29.85, 22.47, 14.01. HR-MS (APCI): *m*/*z* = 578.3180, calcd. for $C_{42}H_{42}O_2$: *m*/*z* = 578.3176, error = -0.1 ppm.



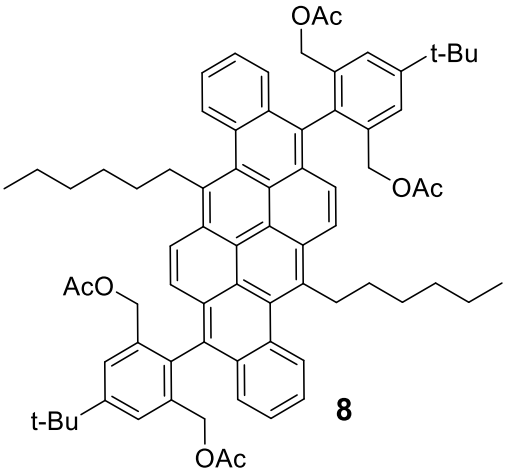
6

Compound **5** (2.00 g, 3.46 mmol) was dissolved in 20 mL of dry THF under argon, (4-*tert*-butyl-2,6-bis(methoxymethyl)phenyl)magnesium bromide (10.38 mmol, 0.5 M in THF) was added and the solution was stirred for 12 h at room temperature. The mixture was then poured into ice water with vigorous stirring, extracted by DCM (200 mL). The organic layer was washed by water, then dried over Na_2SO_4. The solvent was removed under vacuum, and the crude product (diol) was washed by hexane to afford a yellow solid which was used for the next step directly (crude product, 3.80 g). Boron trifluoride diethyl etherate (20 mL) was added to a solution of the as-prepared red solid (3.80 g) in DCM (50 mL) at room temperature under argon and the mixture turned brown immediately. After stirring for 15 min, DDQ (710.0 mg, 3.11 mmol, dissolved in 5 mL toluene) was added slowly and the mixture was stirred for 30 min at room temperature. The mixture was then poured into ice water with vigorous stirring, extracted by DCM (200 mL). The organic layer was washed by water, and then dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/DCM = 2/1) to afford the desired product **6** in 75 % yield for three steps (2.55 g). ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 8.96 (d, *J* = 8.15 Hz, 1.5H), 8.75 (d, *J* = 9.95 Hz, 1 H), 8.32 (d, *J* = 6.85 Hz, 0.5 H), 8.19 (d, *J* = 8.20 Hz, 1H) , 7.78-7.68 (m, 4H), 7.66-7.56 (m, 4H), 7.52-7.49 (m, 2H), 7.42 (d, *J* = 7.60 Hz, 1H), 4.40-3.99 (m, 8H), 3.99-3.92 (m, 4H), 3.12-3.04 (br, 6H), 3.02-2.94 (br, 6H), 1.52 (m, 18H), 1.50 (m, 8H), 1.27-1.25 (m, 8H), 0.96-0.86 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ ppm 151.34, 151.04, 137.83, 136.95, 135.49, 134.65, 134.03, 133.61, 133.19, 132.66, 132.36, 131.59, 130.22, 129.87, 128.96, 128.71, 128.61, 128.46, 128.16, 127.58, 126.29, 126.28, 126.19, 125.87, 125.80, 125.57, 125.10, 124.07, 123.81, 123.38, 123.35, 122.88, 122.57, 122.22, 72.75, 72.58, 72.43, 58.50, 58.35, 35.06, 34.95, 34.09, 33.19, 32.37, 31.64, 30.75, 29.70, 28.32, 26.98, 22.80, 22.68, 14.16, 14.07; HR-MS (APCI): *m*/*z* = 984.6069, calcd. for $C_{70}H_{80}O_4$: *m*/*z* = 984.6051, error = -1.9 ppm.



7

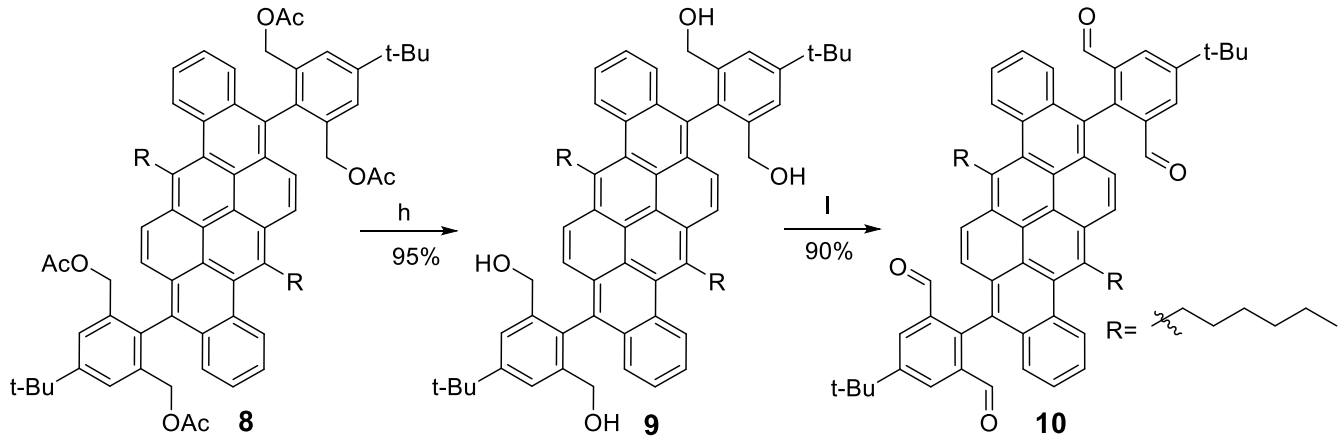
Compound **6** (2.21 g, 2.24 mmol) was dissolved in dry DCM (300 mL). 450 mL of 33% solution of HBr in glacial acetic acid was added and the mixture was stirred at room temperature overnight. The reaction was quenched with water, and the organic layer was washed with saturated Na_2CO_3 solution and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/DCM = 5/1) to afford the desired product **7** (2.58 g, 98%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 9.01 (d, *J* = 8.45 Hz, 2H), 8.41 (d, *J* = 9.90 Hz, 2H), 7.83 (s, 4H), 7.81-7.69 (m, 6H), 7.66 (d, *J* = 9.90 Hz, 2H), 4.20-4.18 (m, 4H), 4.14-4.11 (m, 8H), 2.36 (m, 4H), 1.70-1.67 (m, 4H), 1.54 (m, 18H), 1.54-1.41 (m, 8H), 0.95 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ ppm 152.48, 137.75, 135.36, 135.02, 131.62, 129.64, 129.51, 128.89, 128.86, 128.69, 128.51, 128.39, 127.02, 126.61, 126.26, 125.33, 124.12, 122.87, 122.20, 67.80, 63.47, 41.88, 38.95, 35.03, 33.55, 32.62, 32.16, 31.61, 31.42, 29.78, 22.81, 14.16. HR-MS (APCI): *m*/*z* = 1177.2098, calcd. for $C_{66}H_{69}Br_4$ (M+1): *m*/*z* = 1177.2127, error = 2.5 ppm.



8

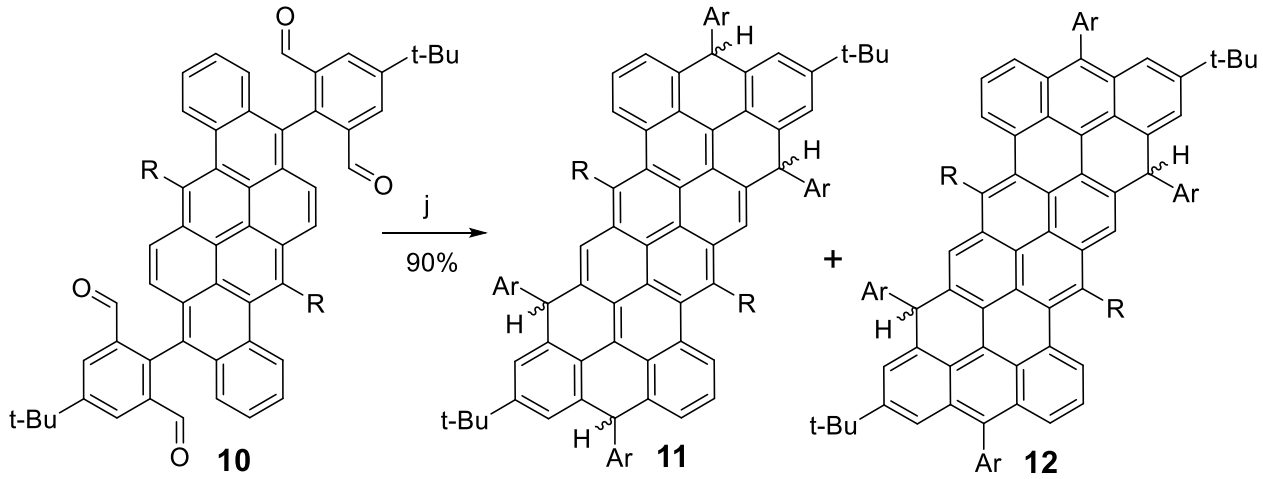
Compound **7** (2.00 g, 1.70 mmol), KOAc (8.33 g, 85.00 mmol) and tetra-*n*-butylammonium bromide (2.72 g, 8.50 mmol) were dissolved in a mixture of 200 mL of THF and 200 mL of CH_3CN under argon atmosphere. The mixture was reflux for 2 days and poured into 200 mL of ice water after cooling down to room temperature. The layers were separated, and the organic layer was washed with

water for several times and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/DCM = 2/1) to afford the desired product **8** (1.68 g, 90% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 8.94 (d, *J* = 8.20 Hz, 2H), 8.33 (d, *J* = 9.90 Hz, 2H), 7.71 (m, 6H), 7.69 (m, 6H), 7.66-7.63 (m, 2H), 7.61 (m, 2H), 4.53-4.66 (m, 8H), 4.06 (br, 4H), 2.30 (br, 4H), 1.67(m, 4H), 1.55 (br, 32 H), 1.50-1.38 (m,12H), 0.97 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ ppm 170.27, 151.62, 135.93, 135.79, 134.77, 131.72, 129.70, 129.30, 128.68, 128.38, 128.34, 128.26, 126.28, 126.65, 126.34, 126.08, 125.14, 123.85, 122.90, 122.13, 65.14, 41.71, 34.96, 33.61, 32.66, 31.67, 31.54, 29.90, 25.31, 22.83, 20.39, 14.16, 13.96. HR-MS (APCI): *m*/*z* = 1097.5916, calcd. for $C_{74}H_{81}O_8$ (M+1): *m*/*z* = 1097.5926, error = 0.9 ppm.

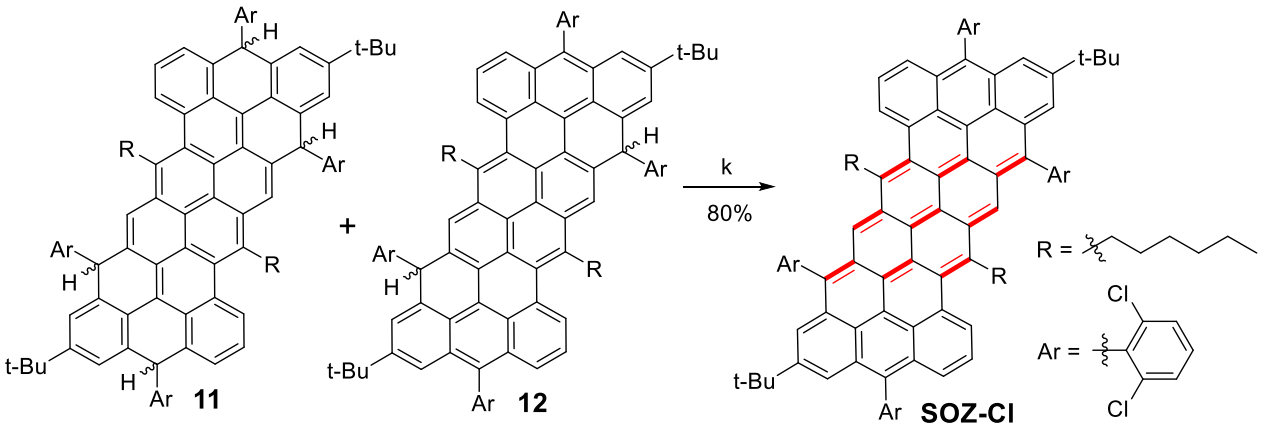


To a solution of tetraester **8** (1.61 g, 1.47 mmol) in dioxane (250 mL) and THF (50 mL) were added $LiOH{\cdot}H_2O$ (54.65 g, 147 mmol) and water (150 mL). The mixture was refluxed for 2 days. After cooling down to room temperature, ethyl acetate (300 mL) and 300 mL of ice water was added. The layers were separated and the organic layer was dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, ethyl acetate) to afford the desired product **9** (1.30 g) in 95% yield. HR-MS (APCI): *m*/*z* = 929.5485, calcd. for $C_{66}H_{73}O_4$(M+1) : *m*/*z* = 929.5503, error = 1.9 ppm. The compoud was used directly for next step. A solution of oxalyl chloride (5.57 mL, 65 mmol) in 150 mL of freshly distilled CH_2Cl_2 was cooled to -78 ^{o}C, and DMSO (9.06 mL, 127.86 mmol) was carefully added under nitrogen atmosphere. After stirring for 15 min, a solution of compound **9** (1.21, 1.30 mmol) in CH_2Cl_2 (100 mL) and THF (100 mL) was added and the mixture was stirred at -78 °C for 2 h. Et_3N (18.10 mL) was added successively and the solution was stirred at -78 ^{o}C for 1 h. Then the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature and stirred for 30 min. The solvent was removed under vacuum and the residue was extracted with ethyl acetate. The extract was washed with saturated aqueous Na_2CO_3 solution, brine, and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, hexane/DCM = 2/1) to afford compound **10** in 90% yield (1.08 g). ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 9.50 (s, 4H), 8.98 (d, *J* = 8.45

Hz, 2H), 8.59 (s, 4H), 8.40 (d, *J* = 9.90 Hz, 2H), 7.77 (t, *J* = 7.05 Hz, 2H), 7.77 (t, *J* = 8.05 Hz, 2H), 7.65 (d, *J* = 7.95 Hz, 2H), 7.55 (br, 2H), 4.09 (br, 4H), 2.28 (br, 4H), 1.67-1.64 (m, 4H), 1.60 (s, 18H). 1.59-1.56 (m, 4H), 1.51-1.37 (m, 8H), 0.93 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ ppm 191.20, 152.98, 143.52, 136.52, 135.86, 133.08, 130.18, 129.53, 129.11, 128.93, 127.94, 127.31, 126.75, 125.97, 124.80, 124.67, 122.45, 122.02, 67.99, 35.48, 33.54, 32.82, 31.54, 31.29, 29.83, 25.63, 22.81, 14.12. HR-MS (APCI): *m*/*z* = 921.4879, calcd. for $C_{66}H_{65}O_4$(M+1) : *m*/*z* = 921.4877, error = -0.2 ppm.



Compound **10** (230.0 mg, 0.25 mmol) was dissolved in THF (8 mL) under argon, and (2,6-dichlorophenyl)magnesium bromide LiCl complex (10 mL, 5 mmol, 0.5 M in THF) was added. The solution was stirred at room temperature for 24 h and then poured into ice water with vigorous stirring. The solution was stirred at room temperature for 3 h and then poured into ice water with vigorous stirring. The mixture was extracted by DCM (50 mL) and the organic layer was washed by water, dried over Na_2SO_4. The solvent was removed under vacuum and the crude product was washed by DCM/MeOH (1/100) to afforded the tetraol intermediate as a red solid (370.0 mg, nearly quantitative yield), which was used for the next step directly. Boron trifluoride diethyl etherate (excess, 2.5 mL) was added to a solution of the tetraol (370.0 mg) in DCM (20 mL) and the yellow solution turned green immediately. After 10 min, methanol (10 mL) and water (20 mL) were added to quench the reaction. The organic layer was separated and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/DCM = 4/1) to afford a mixture of product **11** and **12** in total 90% yield. Some pure compound **12** can be isolated: HR-MS (APCI): *m*/*z* = 1431.3020, calcd. for $C_{90}H_{71}Cl_8$ (M+1): *m*/*z* = 1431.3059, error = 2.7 ppm.



In a nitrogen-filled glove box, a mixture of **11** and **12** (50 mg, 0.035 mmol), potassium *tert*-butoxide (23.5 mg, 0.21 mmol, 6 eq) and anhydrous THF (10 mL) were sequentially added to a 20 mL glass vial equipped with a stir bar. The reaction mixture was stirred at room temperature and monitored by UV-spectroscopy. After 5 min, all the starting materials disappeared to afford a deep green solution of dianion. Then, air was injection to the glass vial, and the solution turned in to purple color immediately. After 1 min, water (20 mL) and DCM (30 mL) were added to quench the reaction. The organic layer was separated and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/DCM = 4/1) to afford the desired product **SOZ-Cl** in 80% yield (39 mg). ^{1}H NMR ($CDCl_3$, 500 MHz, 173 K): δ ppm 8.41-7.75 (br, 8H), 7.25 (d, *J* = 7.50 Hz, 6H), 7.18 (d, *J* = 7.30 Hz, 4H), 7.14 (m, 2H), 7.06 (br, 2H), 6.65 (br, 2H), 3.98 (br, 4H), 3.13 (br,4H), 3.09 (br, 4H), 2.33 (br, 8H), 1.62-1.52 (br, 36H), 1.12 (br, 6H). HR-MS (APCI): *m*/*z* = 1428.2824, calcd. for $C_{90}H_{68}Cl_8$ (M): *m*/*z* = 1428.2789, error = 2.4 ppm.

2. Additional spectra

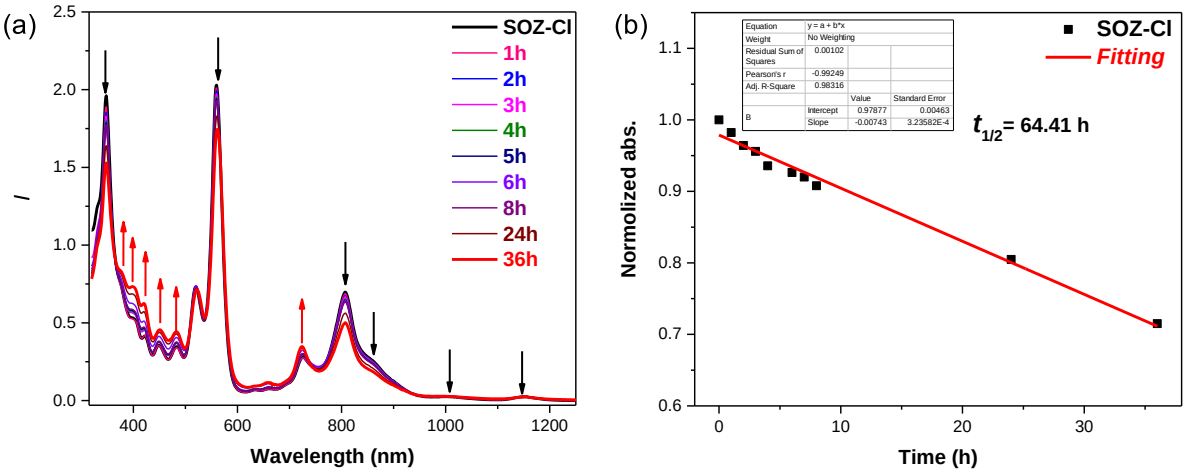


Figure S1. (a) Absorption spectra of **SOZ-Cl** in DCM recorded at different time when exposure to ambient air and light conditions; (b) plot of the absorbance at 807 nm with time and the half-life time was estimated to be 64.41 h.

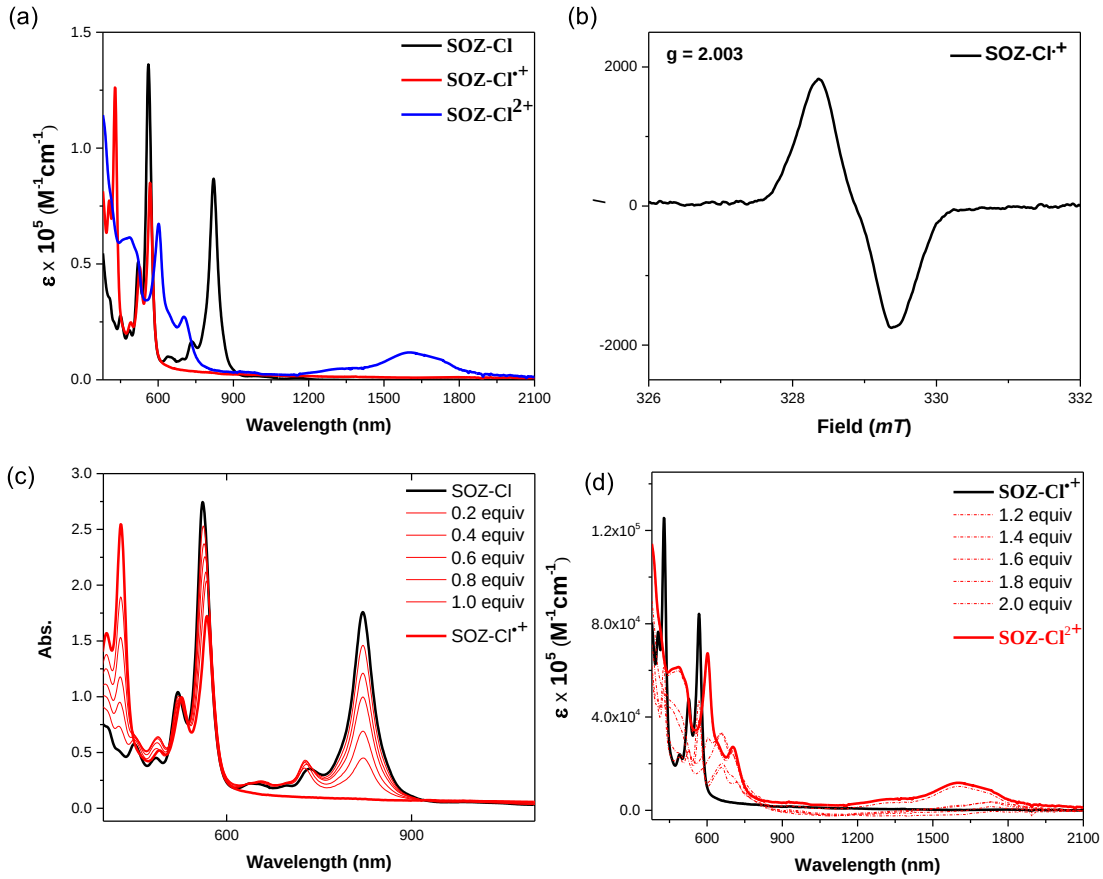


Figure S2. (a) UV-vis-NIR absorption spectra of **SOZ-Cl**, **SOZ-Cl**$^{\bullet+}$ and **SOZ-Cl**$^{2+}$ upon titration with NO•SbF_6 in dry CCl_4; (b) ESR spectrum of **SOZ-Cl**$^{\bullet+}$ in CCl_4; (c) change of the absorption spectrum from neutral to radical cation; (d) change of the absorption spectrum from radical cation to dication.

Table S1. A comparison of the photophysical and electrochemical data of **SOZ-Cl** with **OZ-TIPS**.

	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	$E_{1/2}^{ox}$ (V)	$E_{1/2}^{red}$ (V)	HOMO (eV)	LUMO (eV)	E_g^{EC} (eV)	E_g^{Opt} (eV)
OZ-TIPS[a]	613 667 720 794	83300	0.02 0.22 0.61	-1.30 -1.56 -1.82	-4.73	-3.60	1.13	1.50
SOZ-Cl	564 732 820 990 1152	137000 17000 86800 1640 1000	-0.21 0.14	-1.38 -1.58	-4.48	-3.47	1.01	0.99

ε_{max}: molar extinction coefficient at the absorption maximum. $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ are half-wave potentials of the oxidative and reductive waves, respectively, with potentials *versus* Fc/Fc^+ couple. HOMO and LUMO energy levels were calculated according to equations: HOMO = - (4.8 + E_{ox}^{onset}) eV and LUMO = - (4.8 +E_{red}^{onset}) eV, where E_{ox}^{onset} and E_{red}^{onset} are the onset potentials of the first oxidative and reductive redox wave, respectively. E_g^{EC}: electrochemical energy gap derived from LUMO-HOMO. E_g^{Opt}: optical energy gap derived from lowest energy absorption onset in the absorption spectra. [a] Y. Li *et.al.*, *J. Am. Chem. Soc.* **2012**, *134*, 14913.

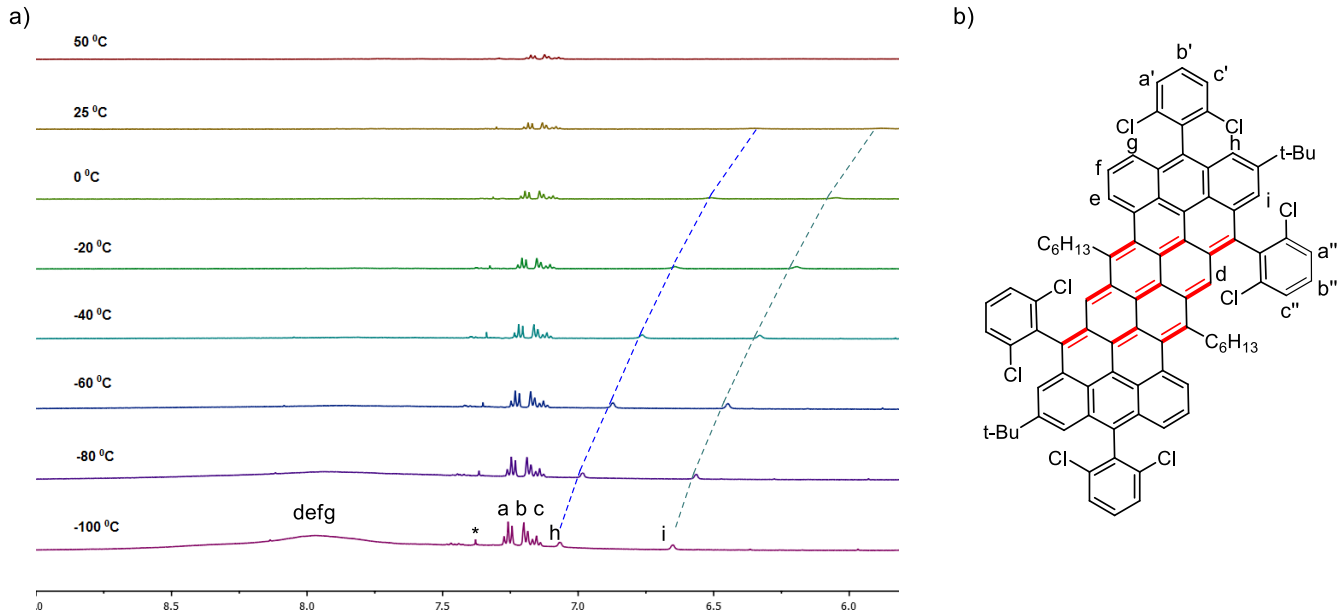
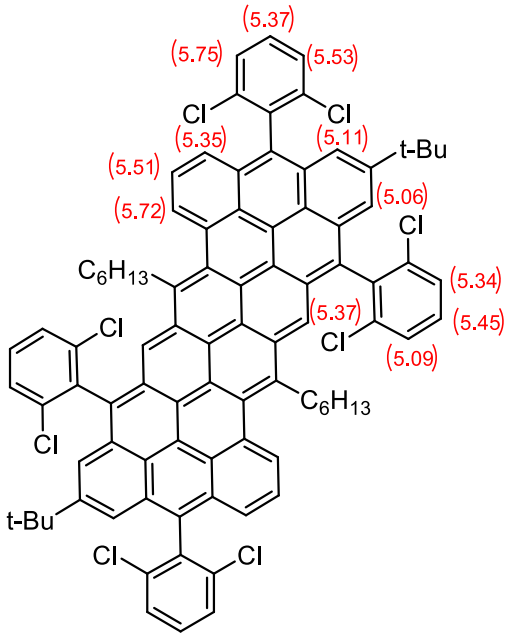


Figure S3. VT ^{1}H NMR spectra of compound **SOZ-Cl** in d_8-THF (500 MHz, *residue chloroform)

Due to the restricted rotation of the 2,6-dichlorolphenyl substituents in **SOZ-Cl** and the broadening induced by the thermally populated paramagnetic species, the ^{1}H NMR signals are quite weak and complicated. The COSY-^{1}H NMR measurements gave limited information due to the low solubility of the sample at low temperature. For the same reason, the NOESY and ROSEY measurements were not successful (showing very weak signal). Herein we only gave rough assignment of some protons in the aromatic region based on the DFT (GIAO-B3LYP/6-31G(d,p)) calculations of the ^{1}H NMR spectrum:



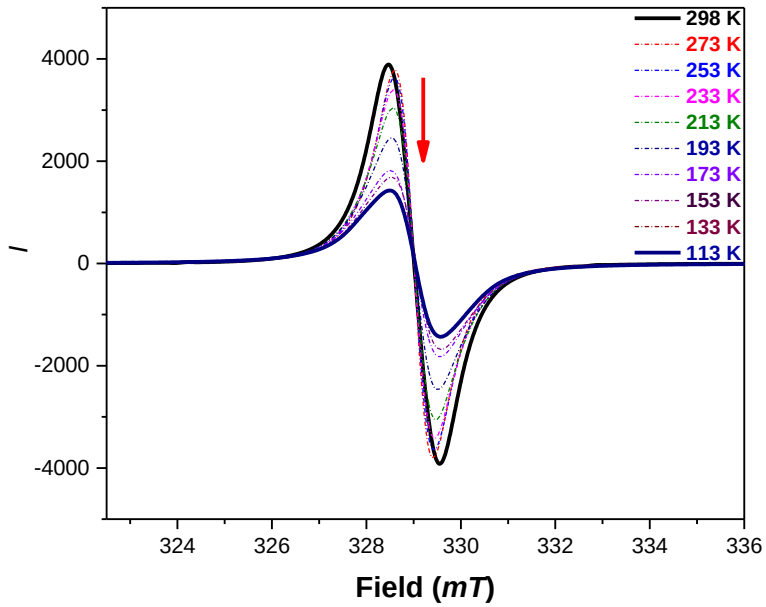


Figure S4. VT ESR spectra of **SOZ-Cl** recorded in powder.

3. DFT calculations

Theoretical calculations were performed with the Gaussian09 program suite.[4] All calculations were carried out using the density functional theory (DFT) method with unrestricted Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional (UB3LYP) employing the 6-31G(d,p) basis set for all atoms.[5] Natural orbital occupation number (NOON)) calculations were done by spin unrestricted UCAM-B3LYP/6-31G(d,p) method and the diradical character (y_0) was calculated according to Yamaguchi's scheme: $y_0 = 1 - (2T/(1 + T^2))$, and $T = (n_{HOMO} - n_{LUMO})/2$ (n_{HOMO} is the occupation number of the HOMO, n_{LUMO} is the occupation number of the LUMO).[6] Time-dependent DFT (TD-DFT) calculations were performed at the UB3LYP/6-31G(d,p) level of theory. ACID plot was calculated by using the method developed by Herges.[7] NICS values were calculated using the standard GIAO (GIAO=NMR)[8] at the level of UB3LYP/6-31G(d,p). The iso-chemical shielding surface (ICSS)[9] calculations were carried out to analyze two-dimensional nucleus induced chemical shifts (2D-NICS) along the XY plane.

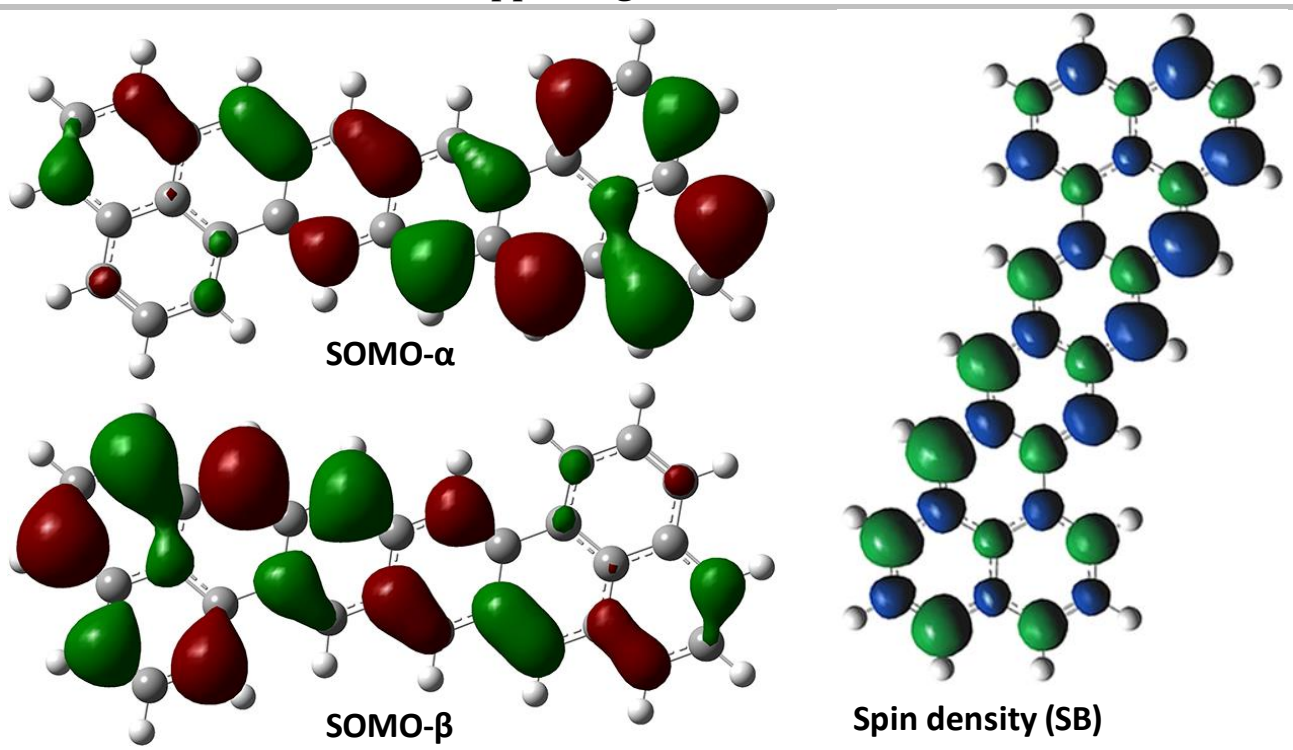


Figure S5. Calculated (UB3LYP/6-31G(d,p)) molecular orbital profiles of α and β spins, and the spin density distribution of the singlet biradical (SB) state of **OZ**.

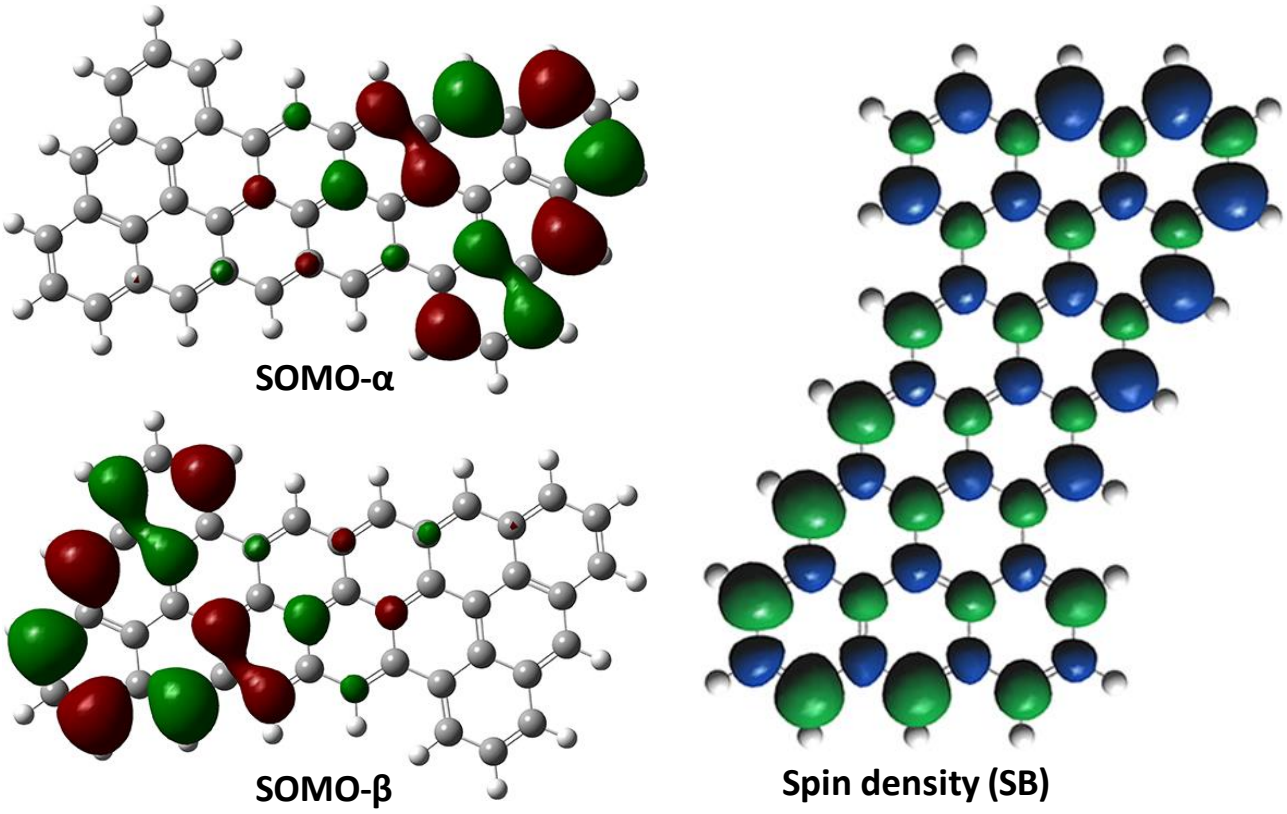


Figure S6. Calculated (UB3LYP/6-31G(d,p)) molecular orbital profiles of α and β spins, and the spin density distribution of the singlet biradical (SB) state of **SOZ**.

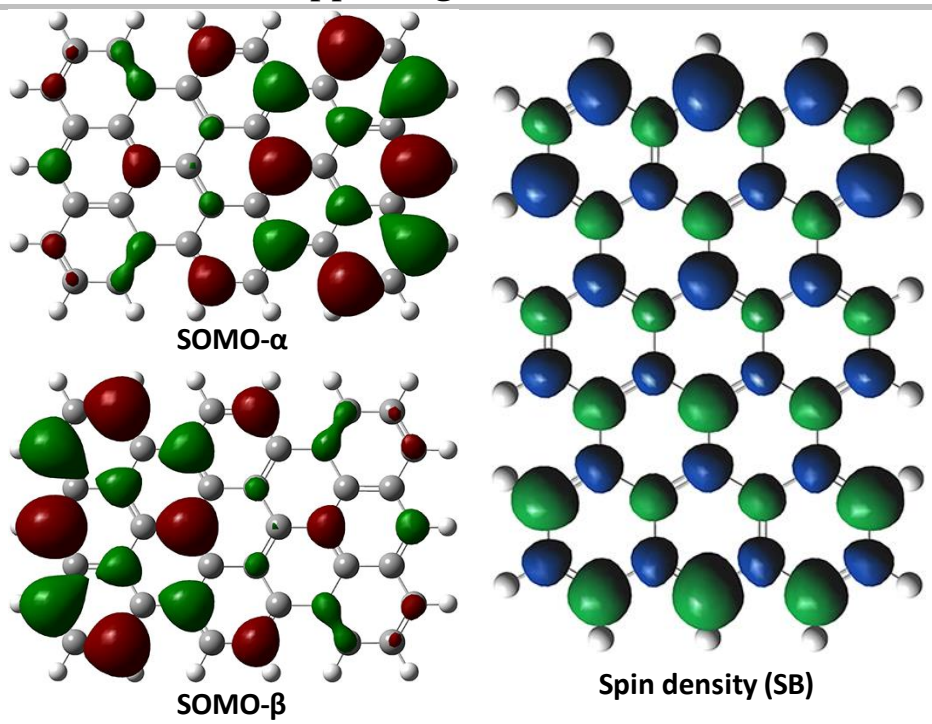


Figure S7. Calculated (UB3LYP/6-31G(d,p)) molecular orbital profiles of α and β spins, and the spin density distribution of the singlet biradical (SB) state of **TAn**.

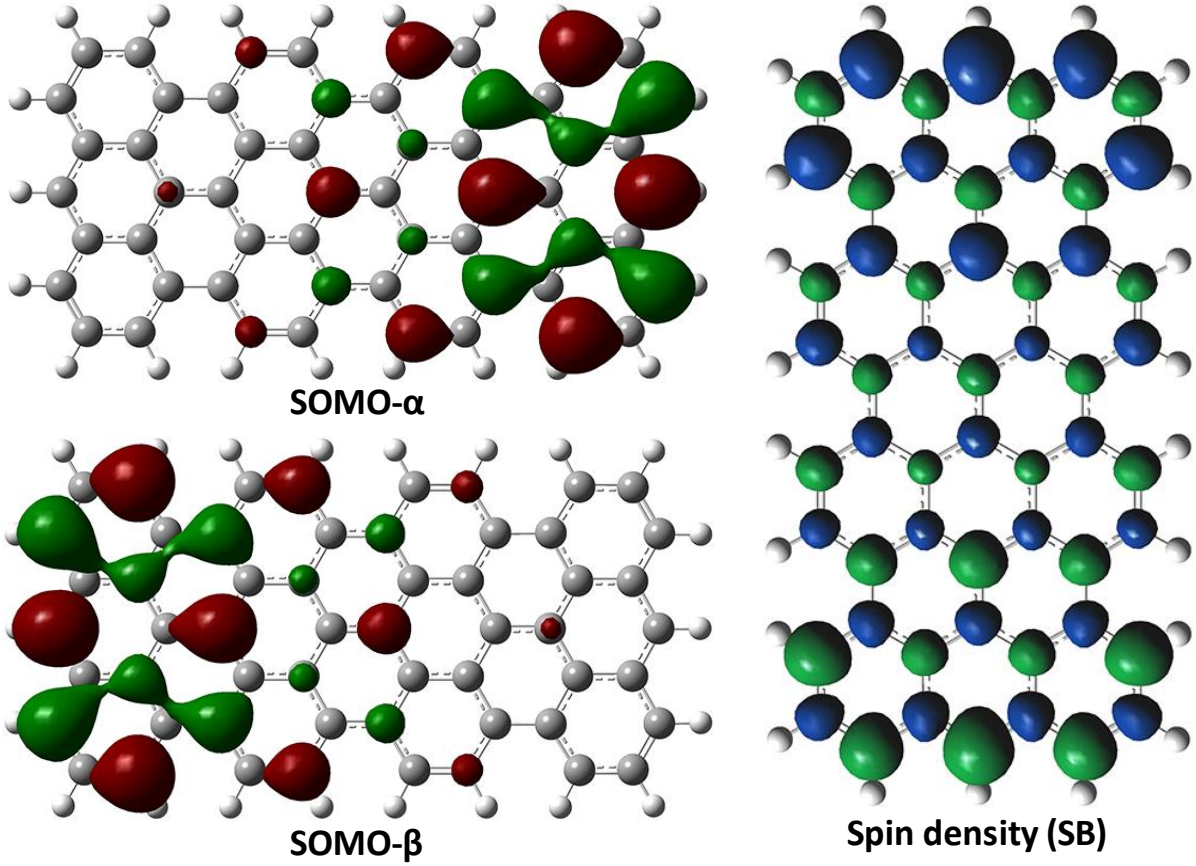


Figure S8. Calculated (UB3LYP/6-31G(d,p)) molecular orbital profiles of α and β spins, and the spin density distribution of the singlet biradical (SB) state of **QAn**.

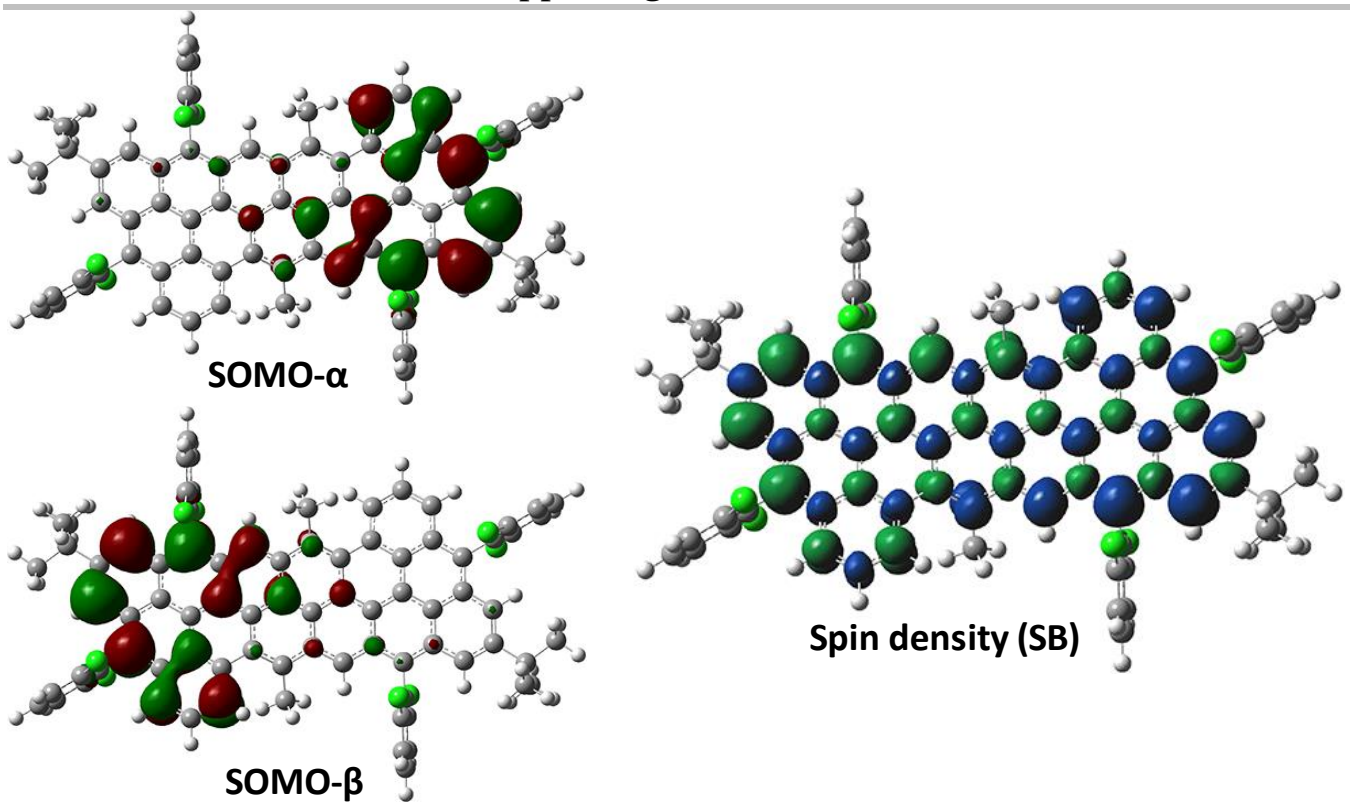


Figure S9. Calculated (UB3LYP/6-31G(d,p)) molecular orbital profiles of α and β spins, and the spin density distribution of the singlet biradical (SB) state of **SOZ-Cl**.

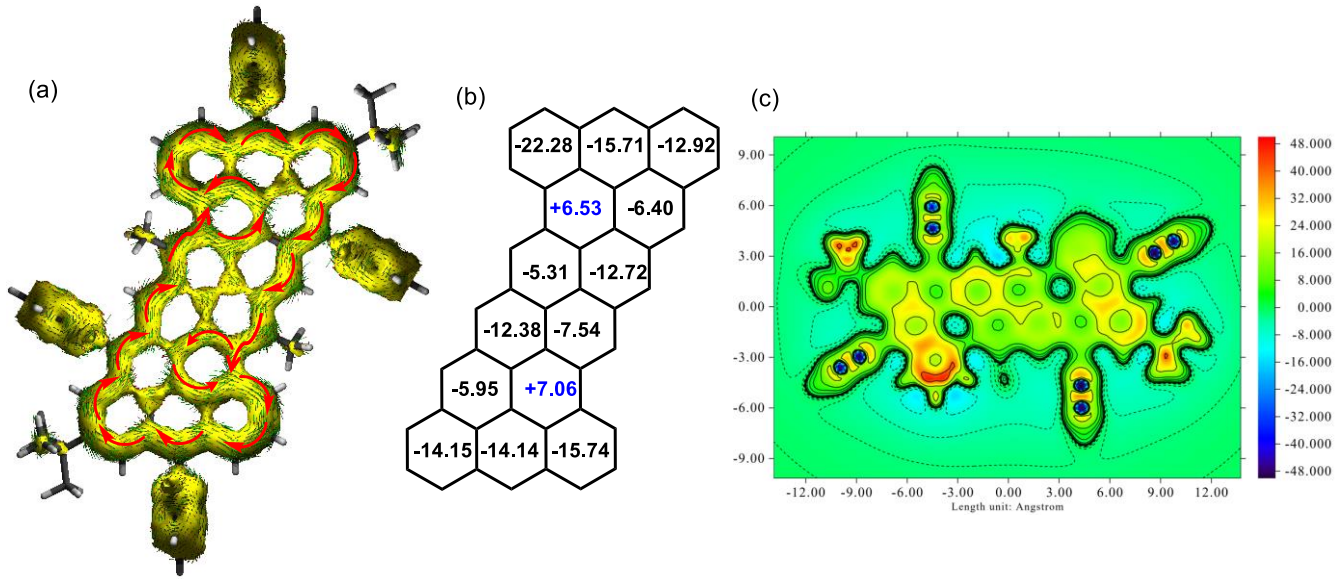


Figure S10. (a) Calculated (RB3LYP/6-31G(d,p)) ACID plot of **SOZ-Cl** (isovalue: 0.03). The magnetic field is perpendicular to the XY plane and points out through the paper. The red arrows indicate the clockwise diatropic ring current flow. (b) Calculated (GIAO-RB3LYP/6-31G(d,p)) NCIS(1)zz values on the backbone of **SOZ-Cl**. (c) Calculated (RB3LYP/6-31G(d,p)) 2D-ICSS maps of **SOZ-Cl**. The image was mapped at XY plane.

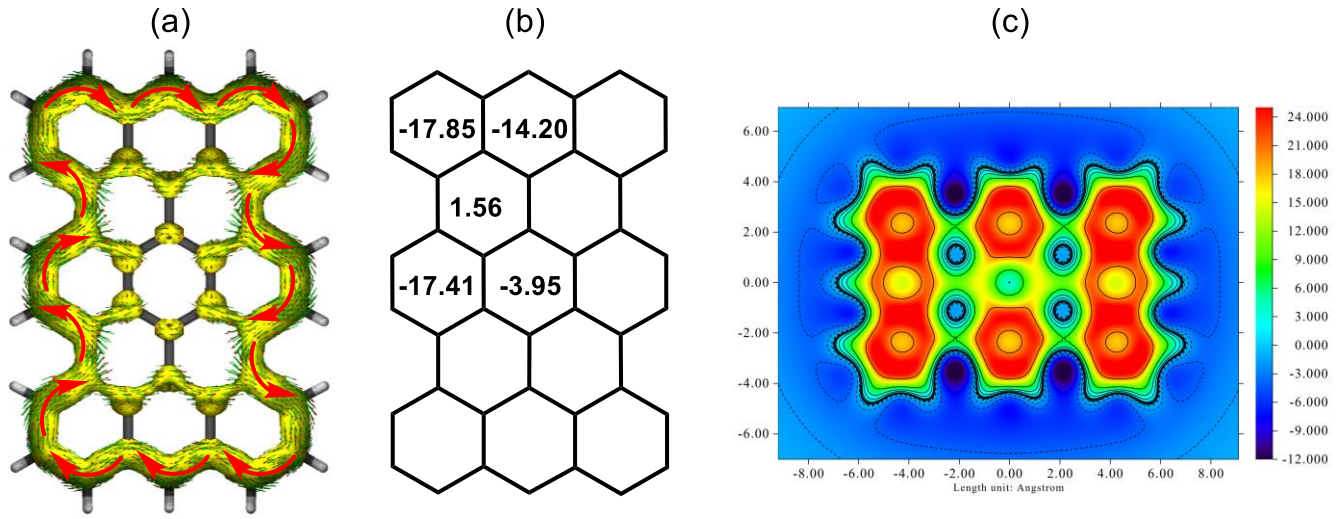


Figure S11. (a) Calculated (RB3LYP/6-31G(d,p)) ACID plot of **TAn** (isovalue: 0.03). The magnetic field is perpendicular to the XY plane and points out through the paper. The red arrows indicate the clockwise diatropic ring current flow. (b) Calculated (GIAO-RB3LYP/6-31G(d,p)) NCIS(1)zz values on the backbone of **SOZ-Cl**. (c) Calculated (RB3LYP/6-31G(d,p)) 2D-ICSS maps of **TAn**. The image was mapped at XY plane.

4. X-ray crystallographic data

4.1 Crystallographic data for compound 6

Single crystal of compound **6** (CCDC No. 1856684) was obtained through slow diffusion of acetonitrile to the DCM solution.

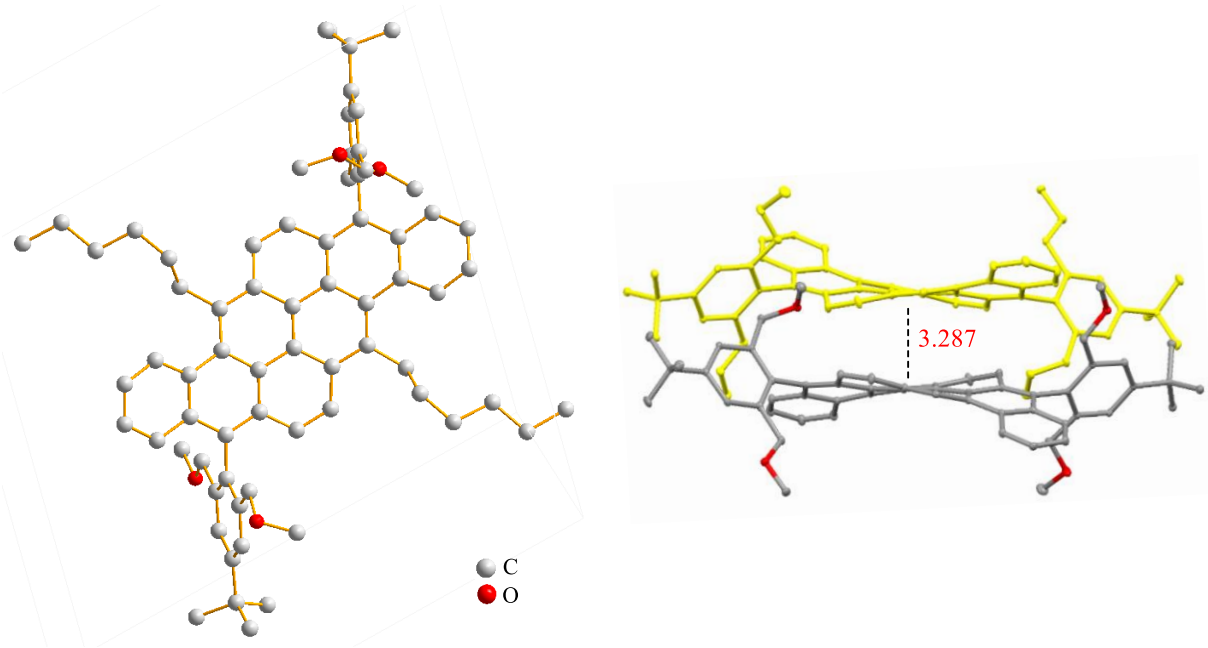


Figure S12. X-ray crystallographic structure of compound **6** showing dimerization via π-π interaction. Hydrogen atoms, solvent molecules and any disorders are omitted for clarity.

Table S2. Crystallographic data for compound **6**.

Identification code	i105	
Empirical formula	C_{70} H_{80} O_4	
Formula weight	985.34	
Temperature	152(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 17.612(2) Å	□= 103.889(6)°.
	b = 17.855(2) Å	□= 97.137(6)°.
	c = 18.518(2) Å	□ = 91.927(6)°.
Volume	5597.1(11) $Å^3$	
Z	4	
Density (calculated)	1.169 Mg/m^3	
Absorption coefficient	0.540 mm^{-1}	
F(000)	2128	
Crystal size	0.334 x 0.259 x 0.142 mm^3	
Theta range for data collection	3.296 to 66.595°.	
Index ranges	-20<=h<=20, -21<=k<=21, -22<=l<=22	
Reflections collected	67574	
Independent reflections	19394 [R(int) = 0.0704]	
Completeness to theta = 66.595°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.5938	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19394 / 160 / 1427	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.1534, wR2 = 0.3955	
R indices (all data)	R1 = 0.1699, wR2 = 0.4034	
Extinction coefficient	0.00071(10)	
Largest diff. peak and hole	0.820 and -0.485 e.$Å^{-3}$	

4.2 Crystallographic data for compound SOZ-Cl

Single crystal of compound **SOZ-Cl** (CCDC No. 1856685) was obtained through slow diffusion of acetonitrile to the toluene solution.

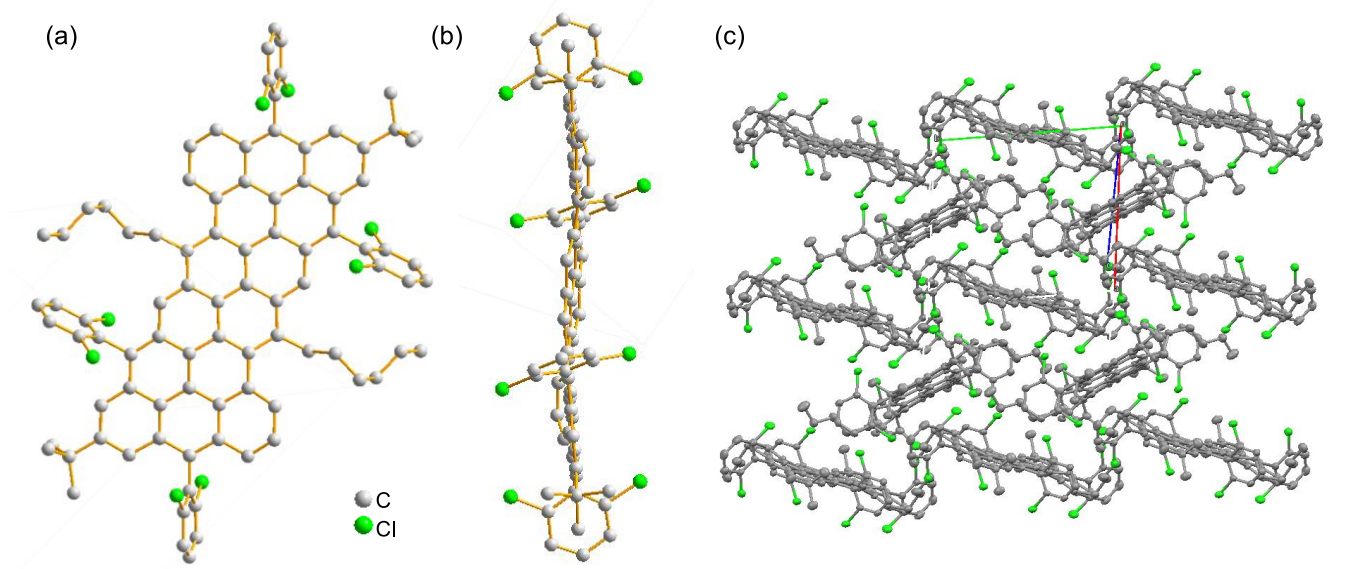


Figure S13. (a) Top view of X-ray crystallographic structure of compound **SOZ-Cl**. (b) side view of X-ray crystallographic structure of compound **SOZ-Cl**; Hydrogen atoms, solvent molecules and any disorders are omitted for clarity. (c) 3D packing structure of **SOZ-Cl**. There is no close π-π stacking between the SOZ backbones, and thus intermolecular spin-spin interaction can be ignored during the SQUID data analysis.

Table S3. Crystallographic data for compound **SOZ-Cl**.

Identification code	180606wu	
Empirical formula	C_{99} H_{67} Cl_8 N	
Formula weight	1554.13	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.0759(9) Å	□= 74.875(6)°.
	b = 13.5700(11) Å	□= 89.235(6)°.
	c = 22.5690(16) Å	□ = 89.210(6)°.
Volume	3865.4(5) $Å^3$	
Z	2	
Density (calculated)	1.335 Mg/m^3	
Absorption coefficient	3.055 mm^{-1}	
F(000)	1608	
Crystal size	0.170 x 0.130 x 0.020 mm^3	
Theta range for data collection	2.028 to 62.488°.	
Index ranges	-14<=h<=15, -15<=k<=15, -25<=l<=25	
Reflections collected	45562	
Independent reflections	11976 [R(int) = 0.1798]	
Completeness to theta = 62.488°	97.3 %	

Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11976 / 314 / 957
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.1169, wR2 = 0.2877
R indices (all data)	R1 = 0.2775, wR2 = 0.4086
Extinction coefficient	n/a
Largest diff. peak and hole	0.624 and -0.605 e.Å^{-3}

5. NMR spectra and HR-Mass spectra

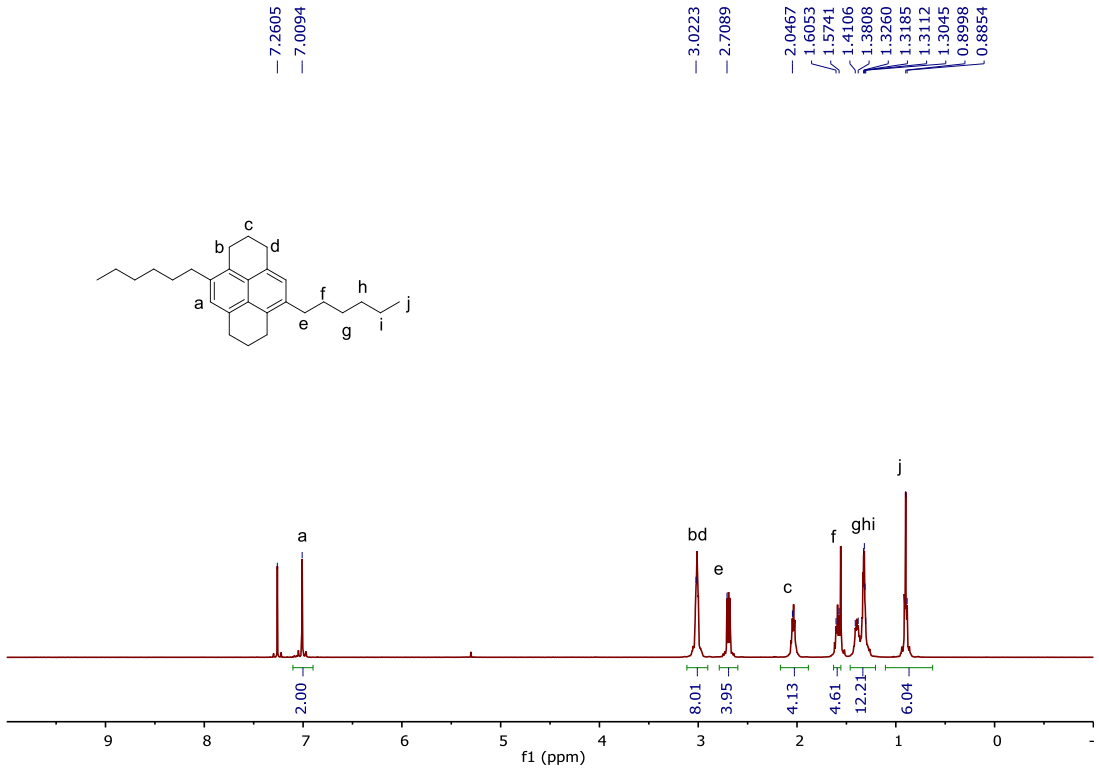


Figure S14. ^{1}H NMR spectrum of compound **2** (500 MHz, $CDCl_3$, rt).

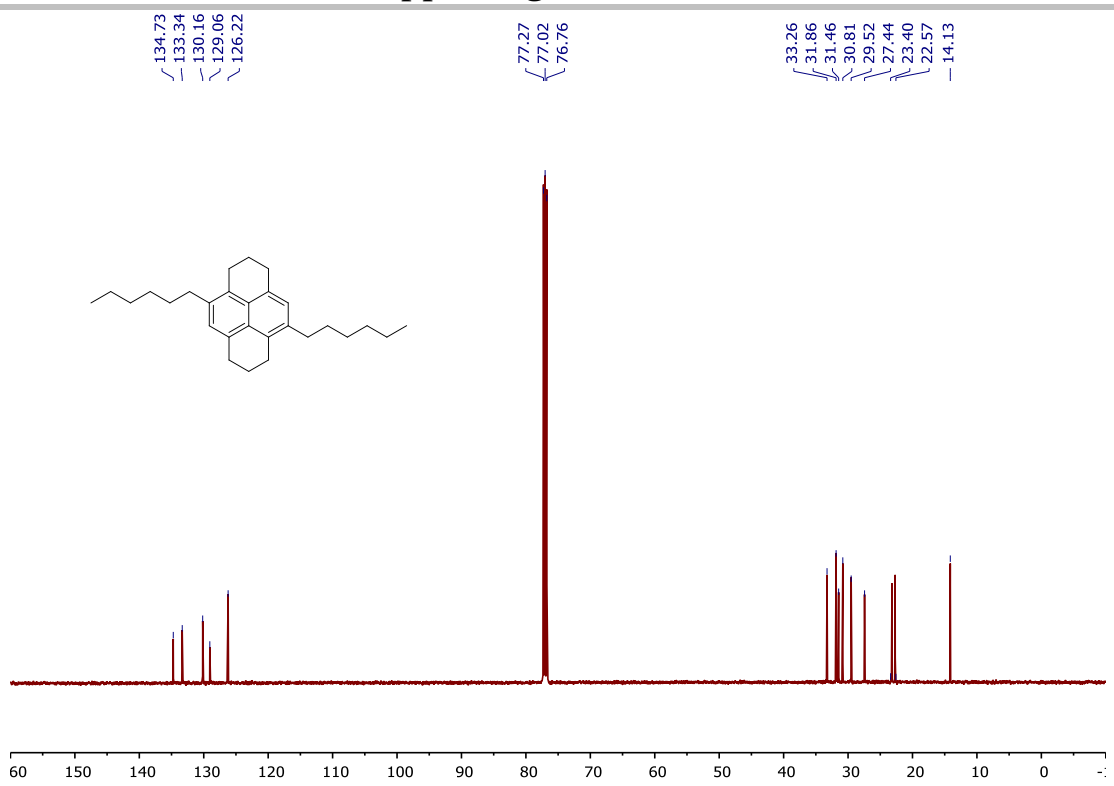


Figure S15. ^{13}C NMR spectrum of compound **2** (500 MHz, $CDCl_3$, rt)

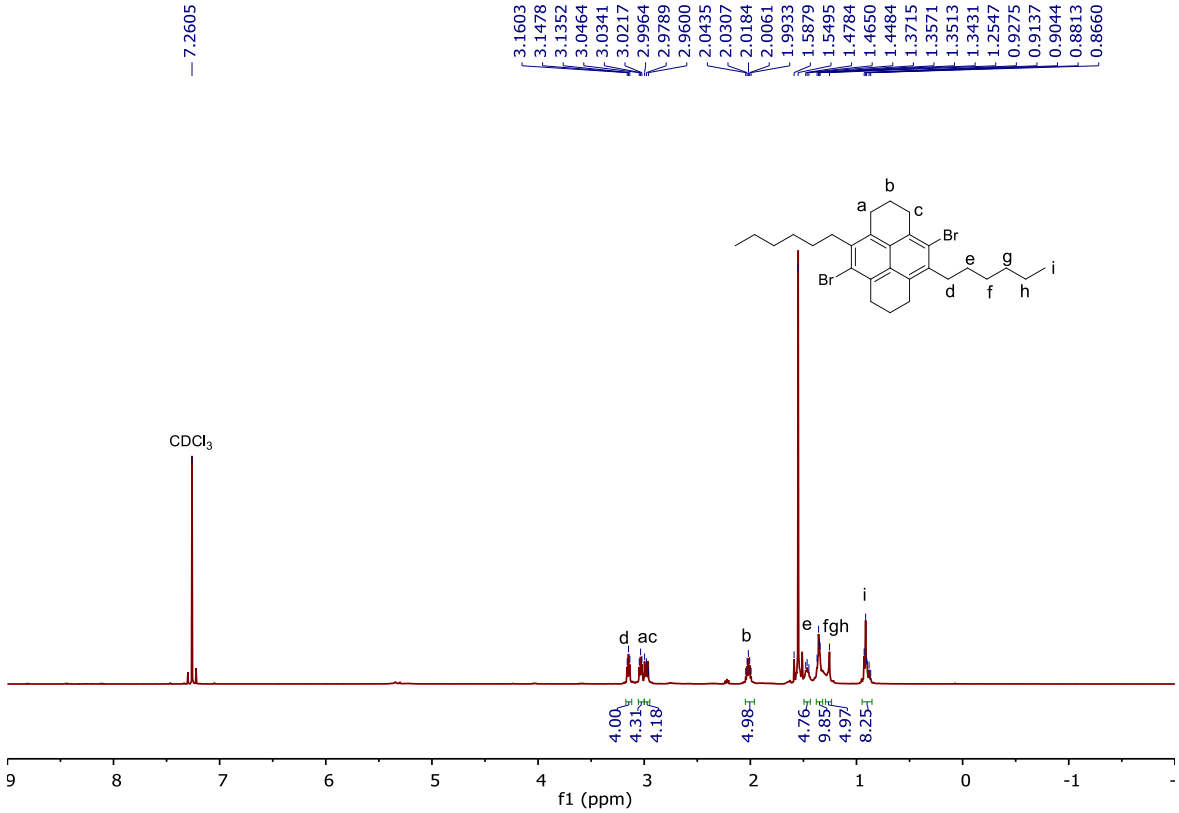


Figure S16. ^{1}H NMR spectrum of compound **3** (500 MHz, $CDCl_3$, rt).

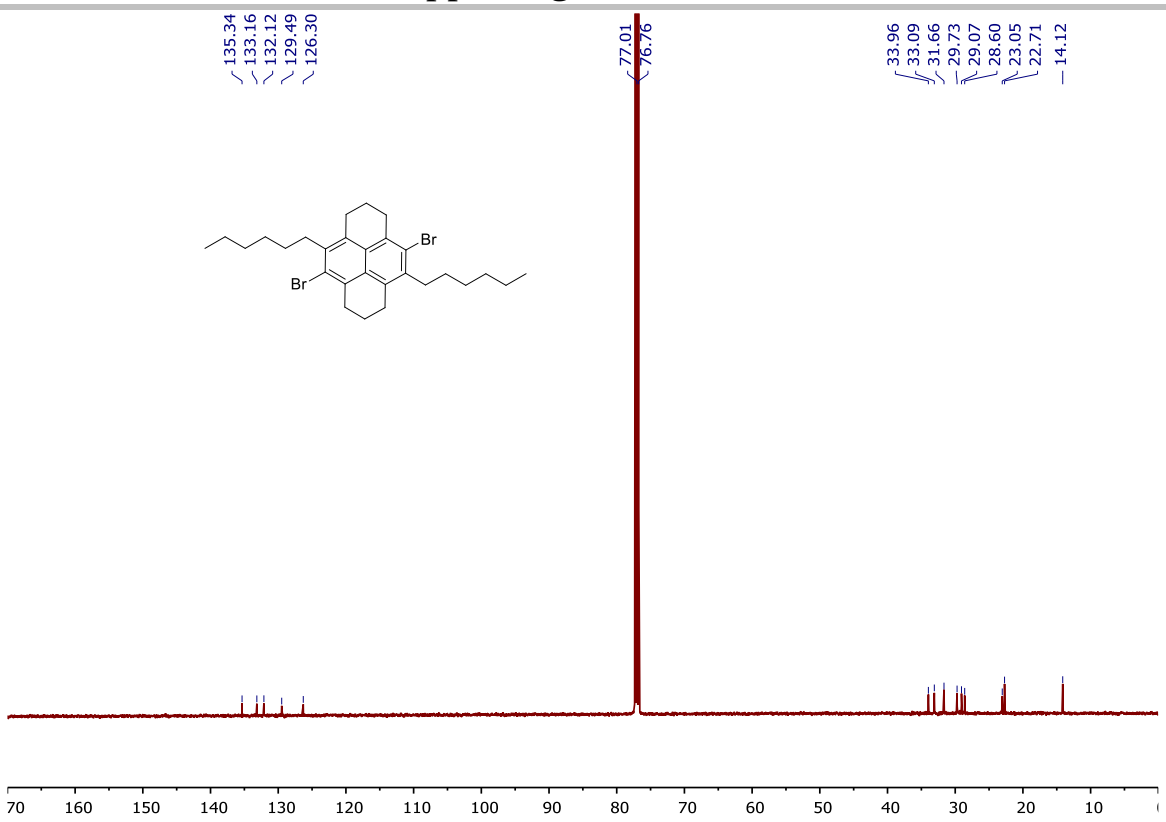


Figure S17. ^{13}C NMR spectrum of compound **3** (500 MHz, $CDCl_3$, rt)

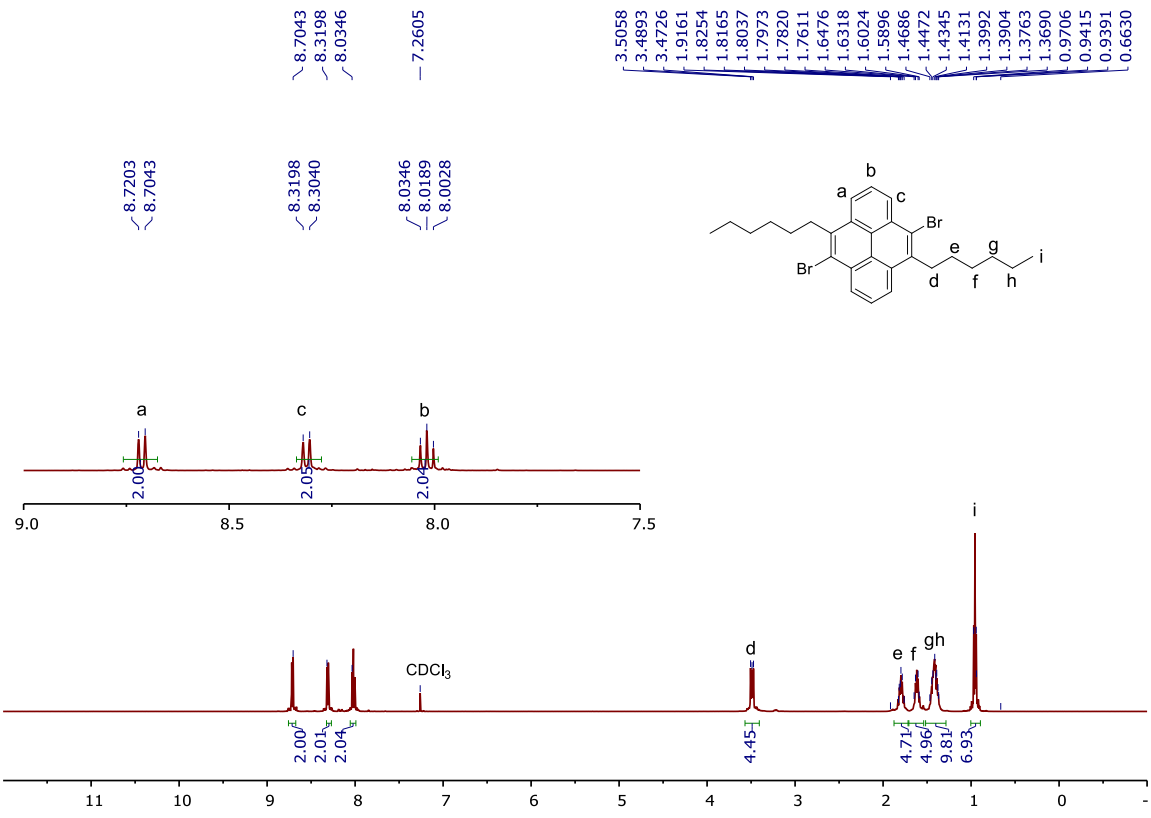


Figure S18. ^{1}H NMR spectrum of compound **4** (500 MHz, $CDCl_3$, rt).

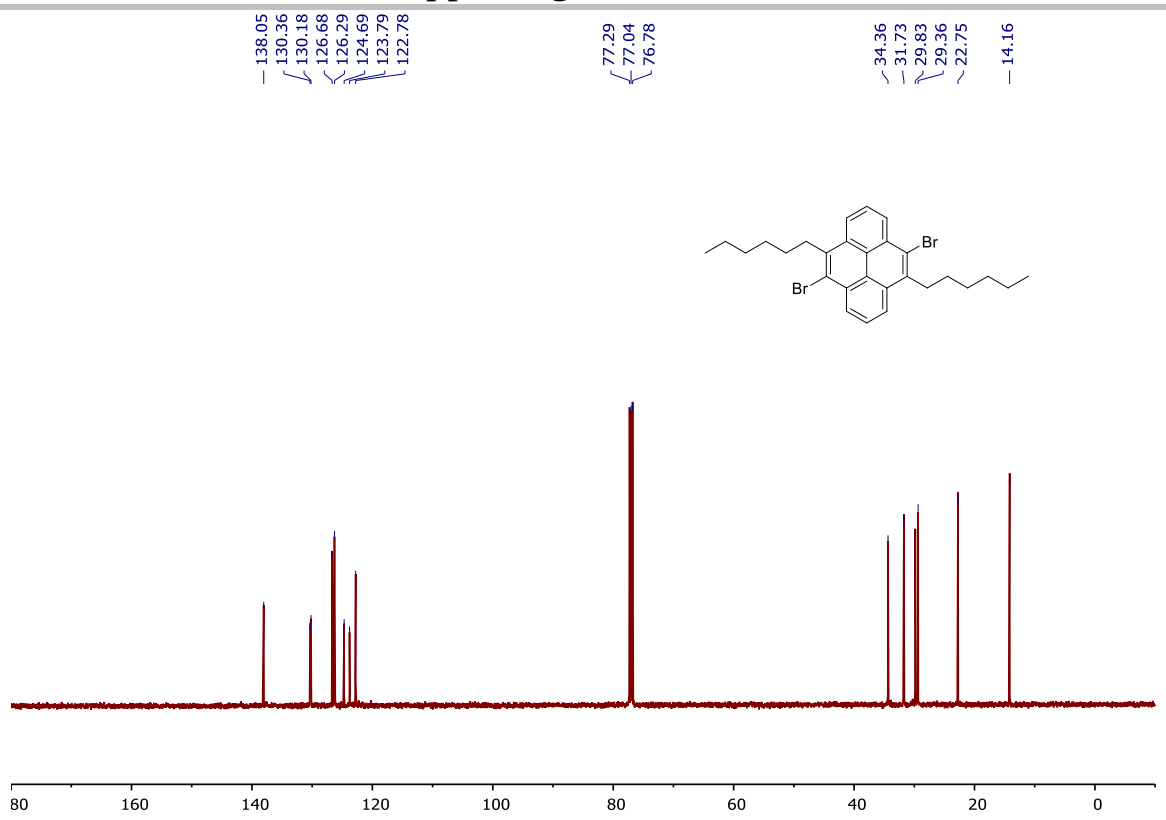


Figure S19. ^{13}C NMR spectrum of compound **4** (500 MHz, $CDCl_3$, rt)

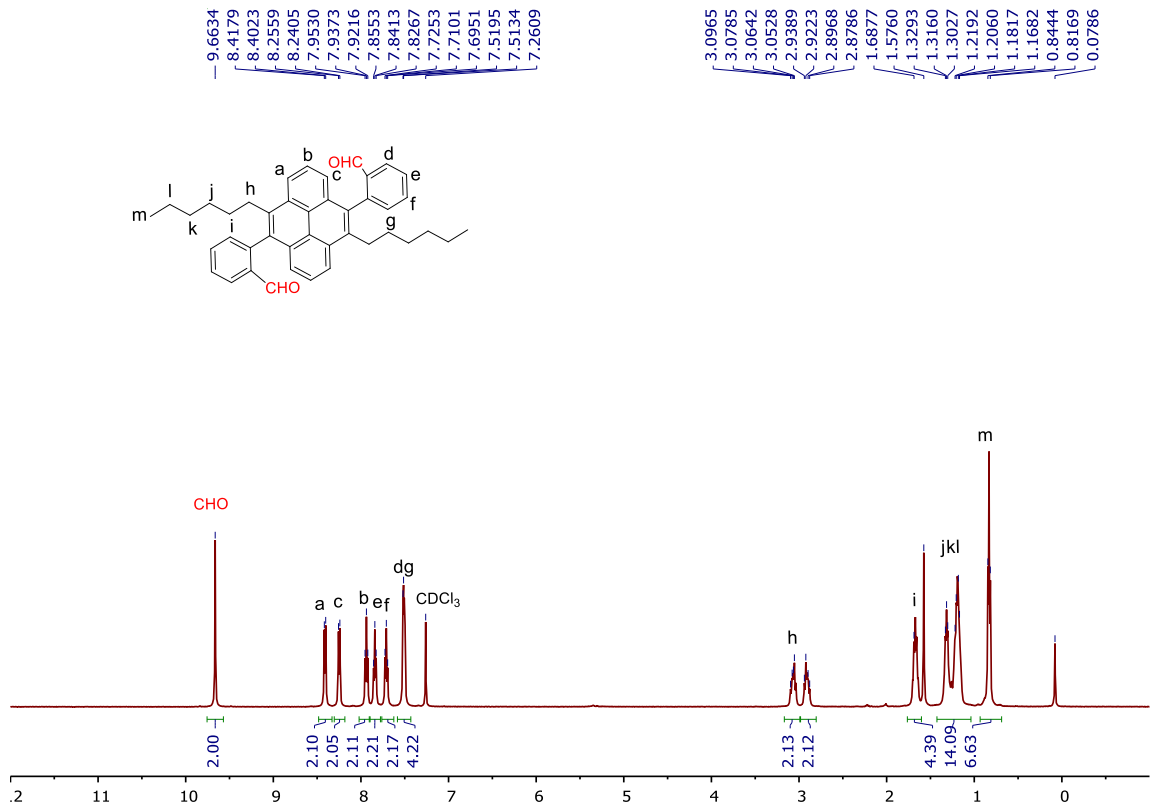


Figure S20. ^{1}H NMR spectrum of compound **5** (500 MHz, $CDCl_3$, rt).

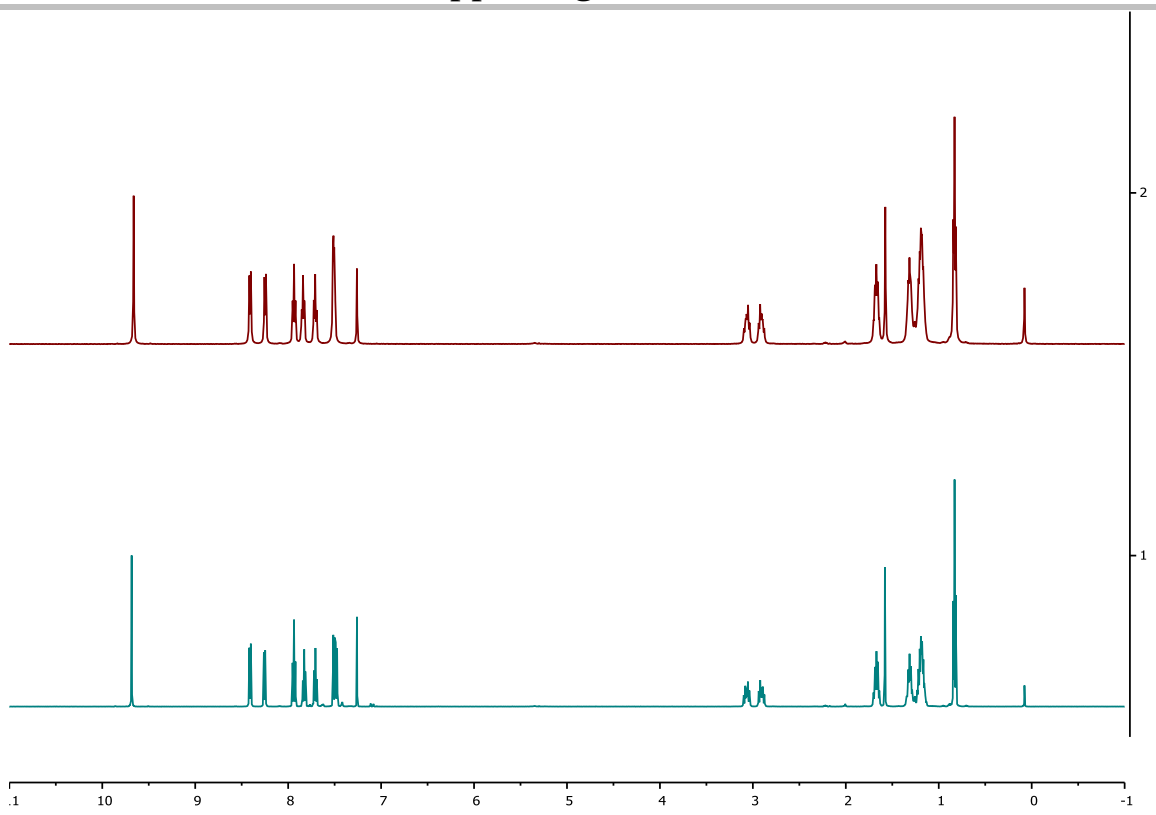


Figure S21. ^{1}H NMR spectrum of two isomers of compound **5** (500 MHz, $CDCl_3$, rt).

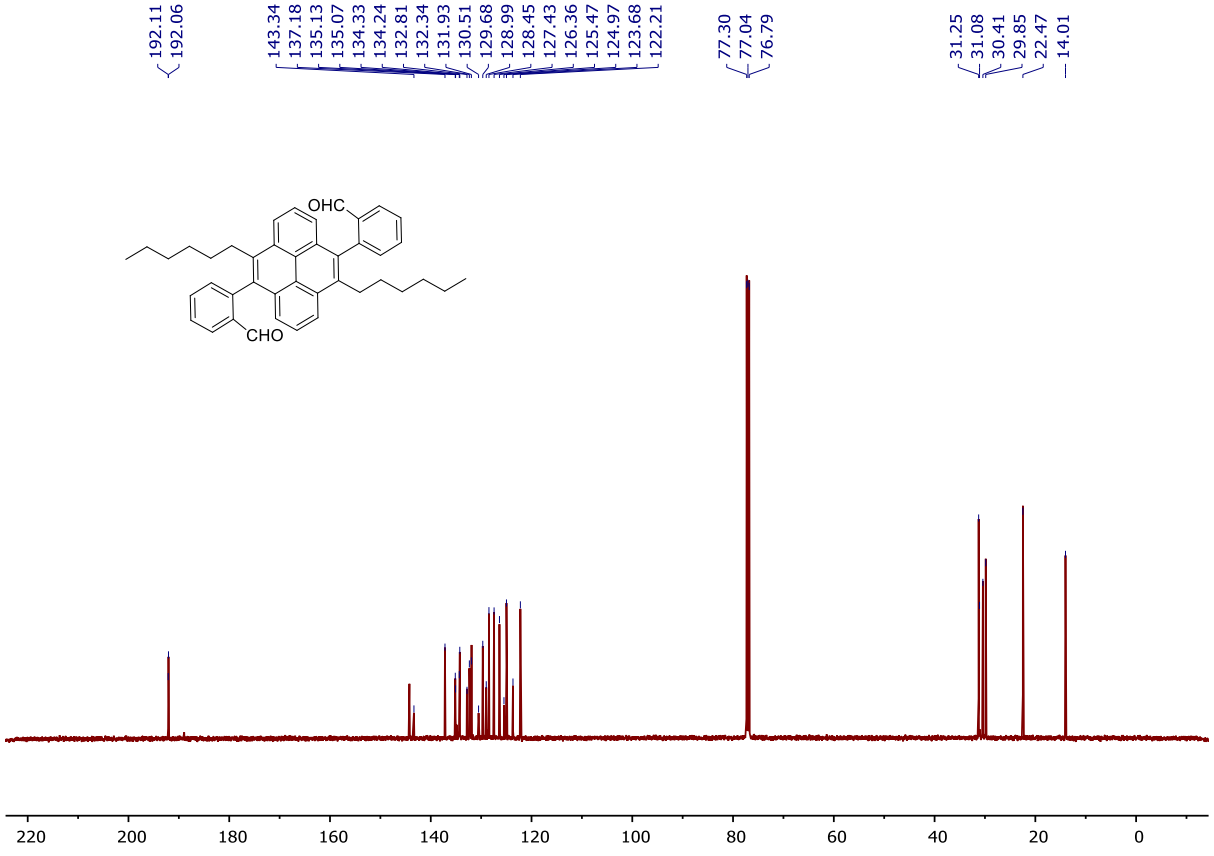


Figure S22. ^{13}C NMR spectrum of compound **5** (500 MHz, $CDCl_3$, rt).

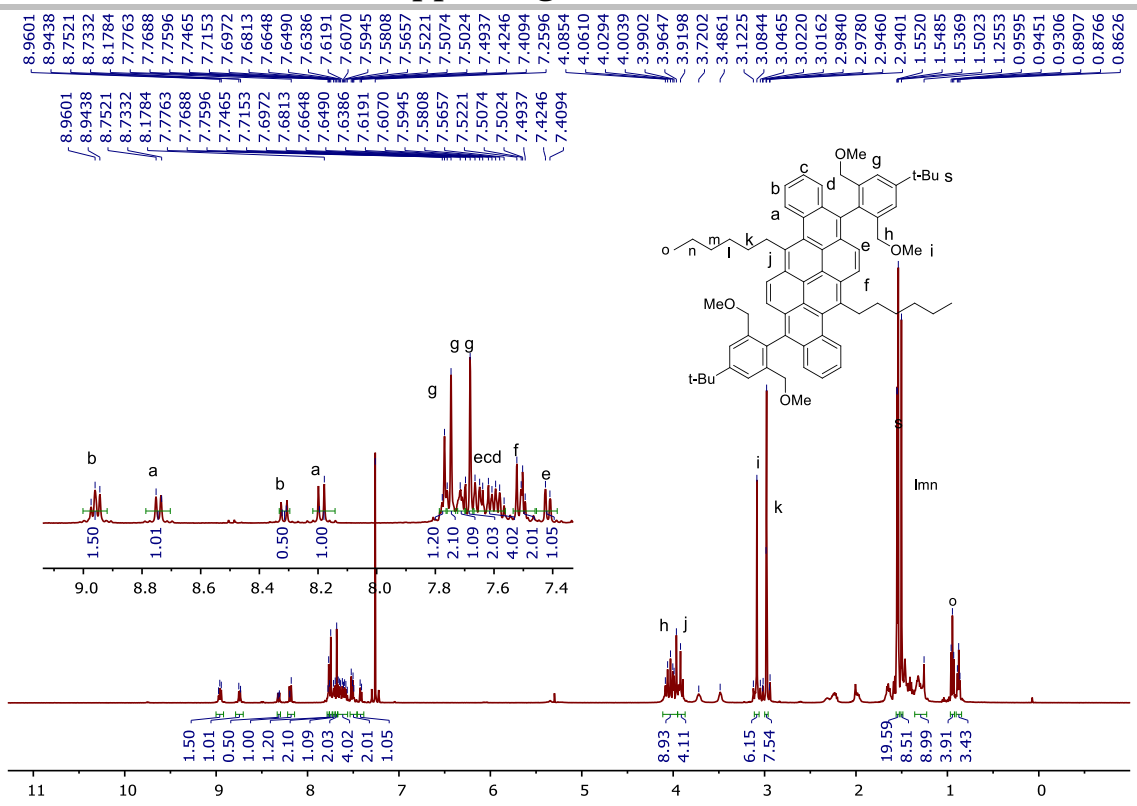


Figure S23. ^{1}H NMR spectrum of compound **6** (500 MHz, $CDCl_3$, rt).

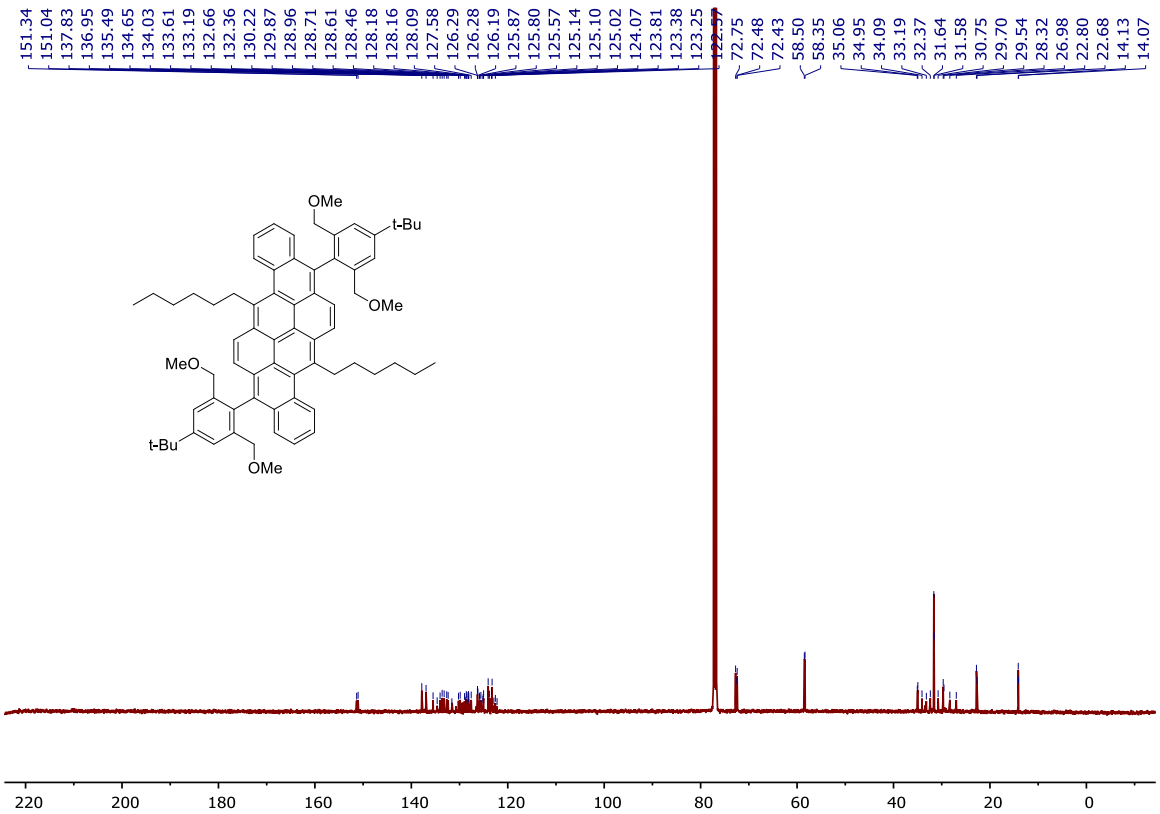


Figure S24. ^{13}C NMR spectrum of compound **6** (500 MHz, $CDCl_3$, rt)

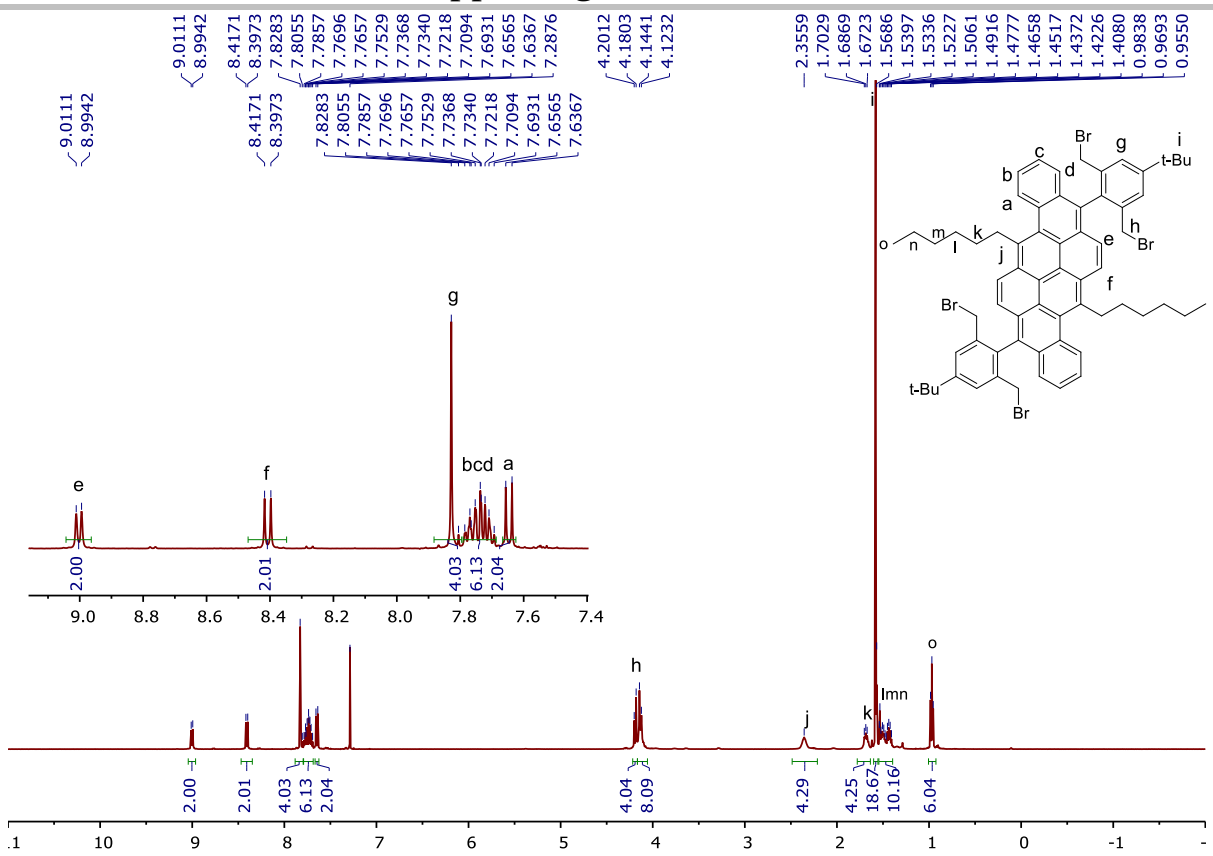


Figure S25. ^{1}H NMR spectrum of compound **7** (500 MHz, $CDCl_3$, rt).

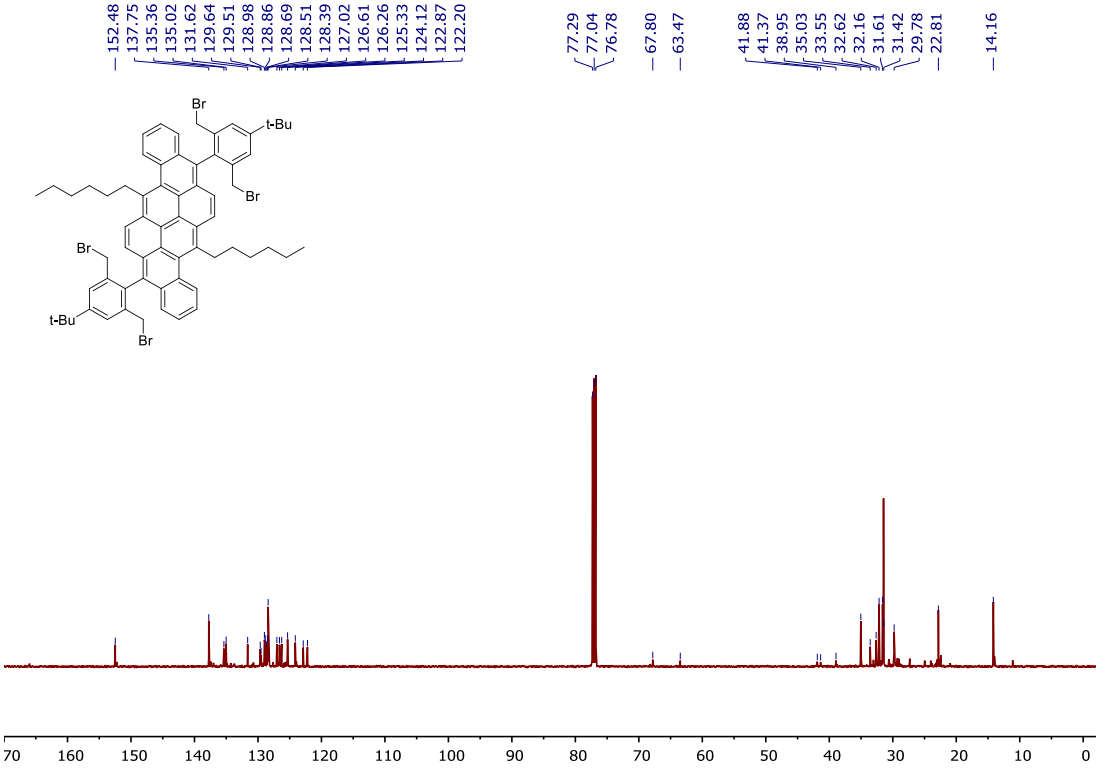


Figure S26. ^{13}C NMR spectrum of compound **7** (500 MHz, $CDCl_3$, rt)

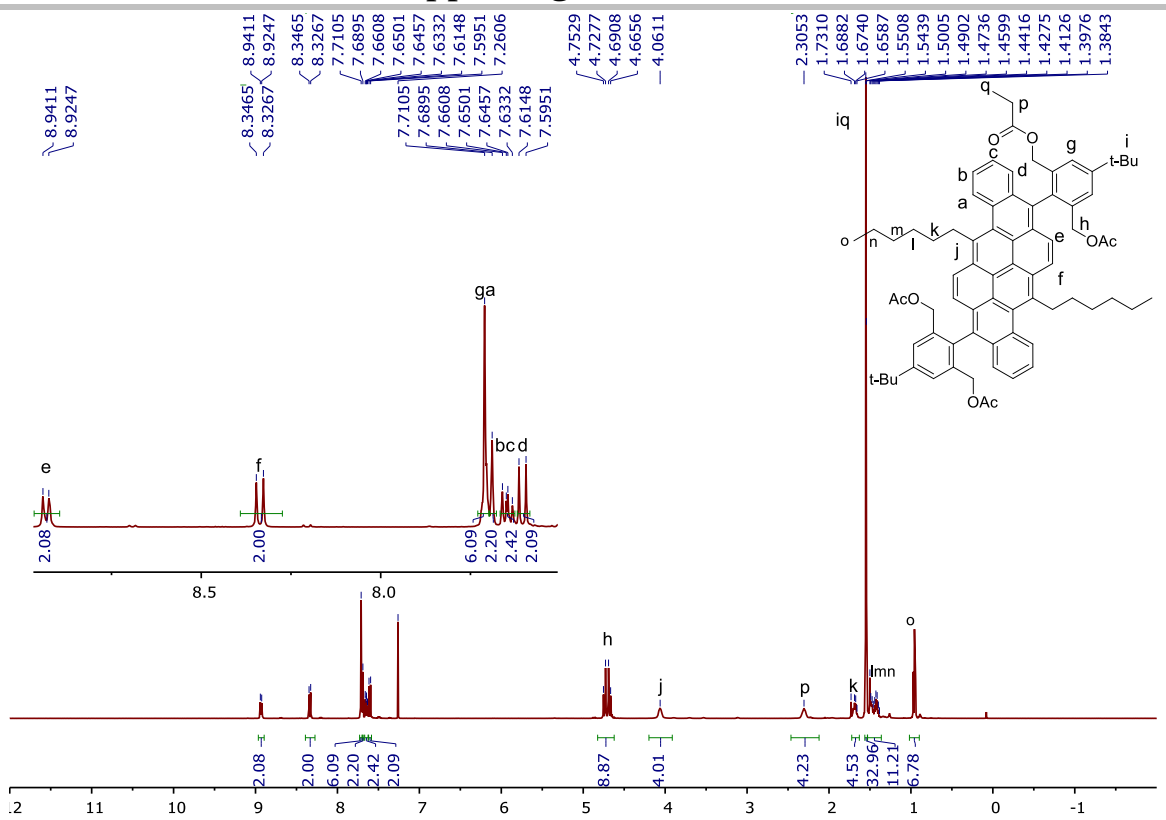


Figure S27. ^{1}H NMR spectrum of compound **8** (500 MHz, $CDCl_3$, rt).

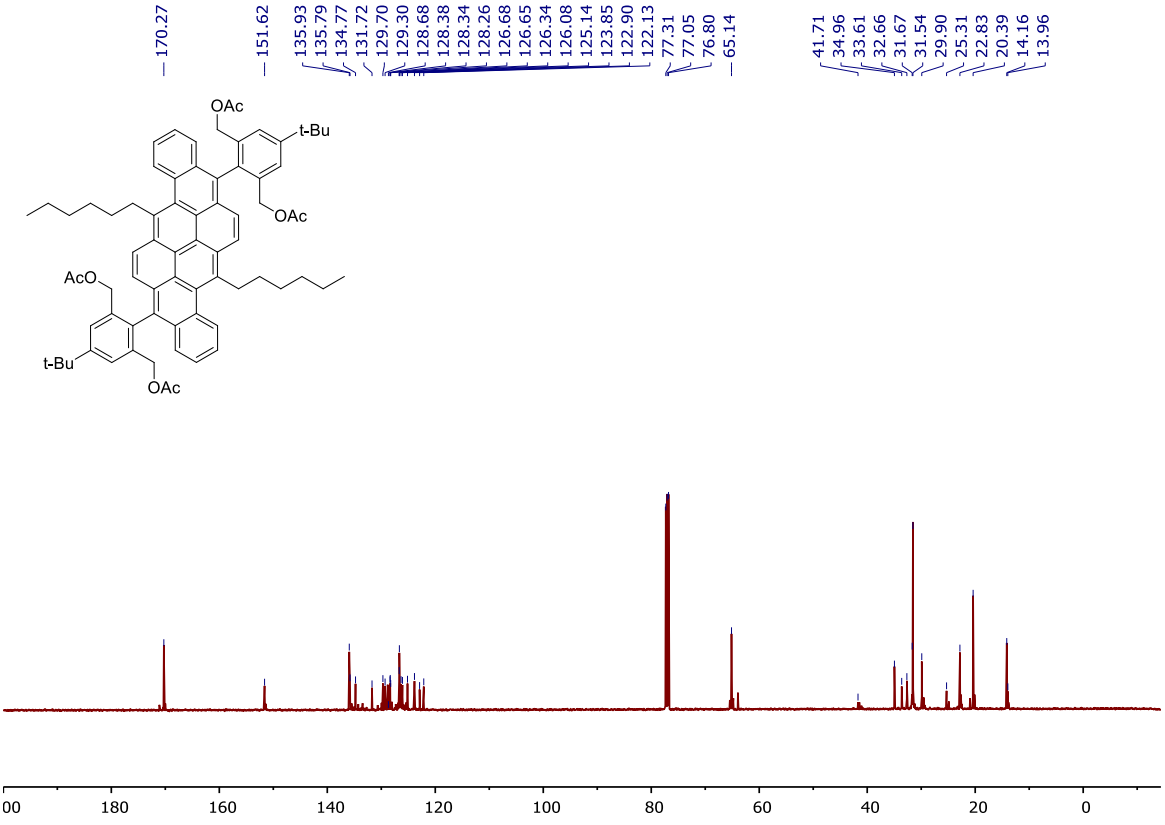


Figure S28. ^{13}C NMR spectrum of compound **8** (500 MHz, $CDCl_3$, rt)

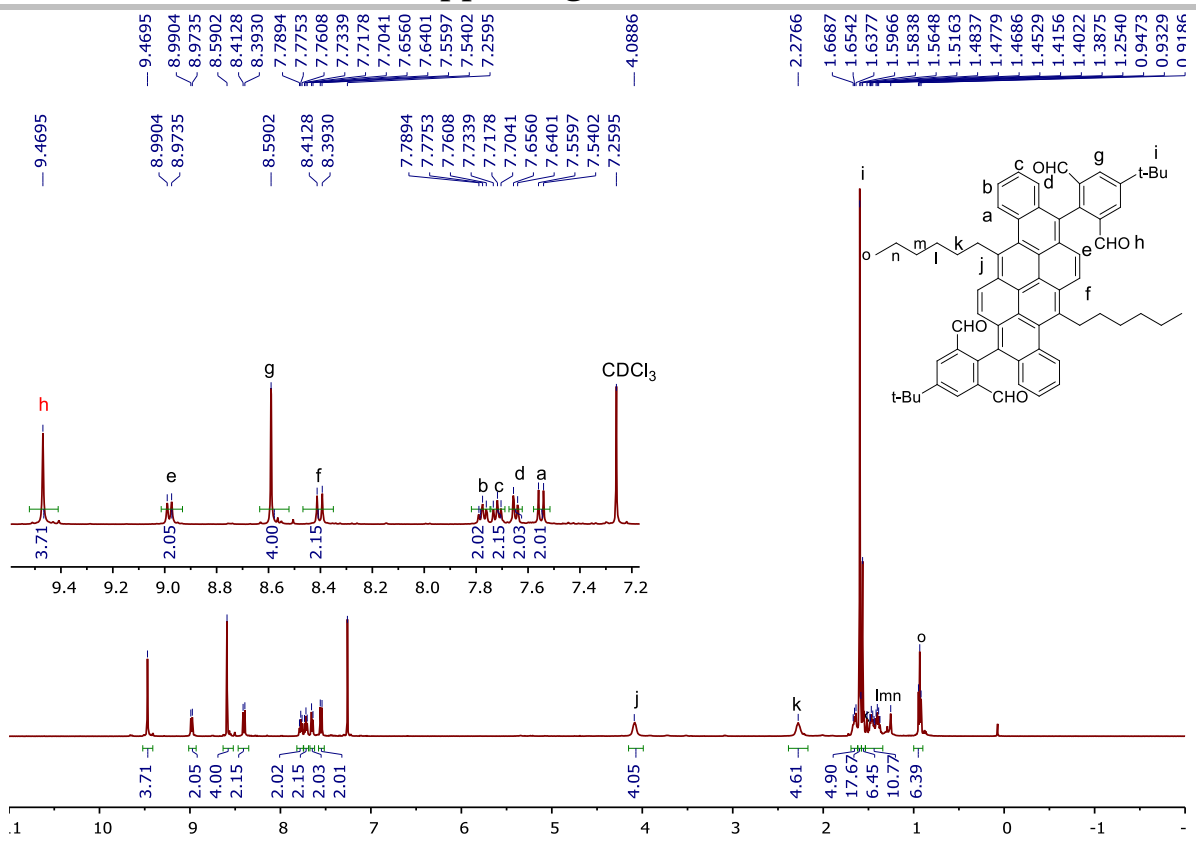


Figure S29. ^{1}H NMR spectrum of compound **8** (500 MHz, $CDCl_3$, rt).

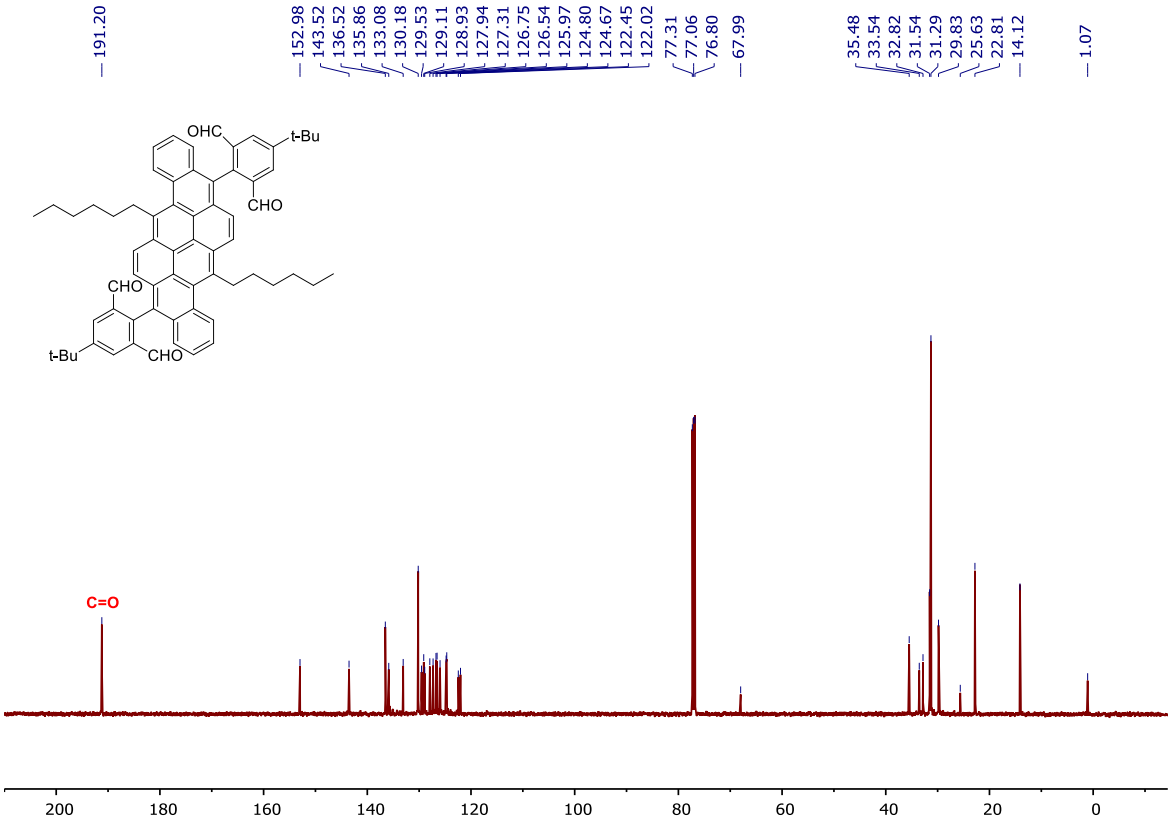


Figure S30. ^{13}C NMR spectrum of compound **9** (125 MHz, $CDCl_3$, rt)

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201806\0612\C-1.d	Acquisition Date	6/12/2018 5:06:41 PM
Method	YCH-150-1800.m	Operator	default user
Sample Name	C-1	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
377.3200	1	C 28 H 41	377.3203	0.9	8.5	even	ok

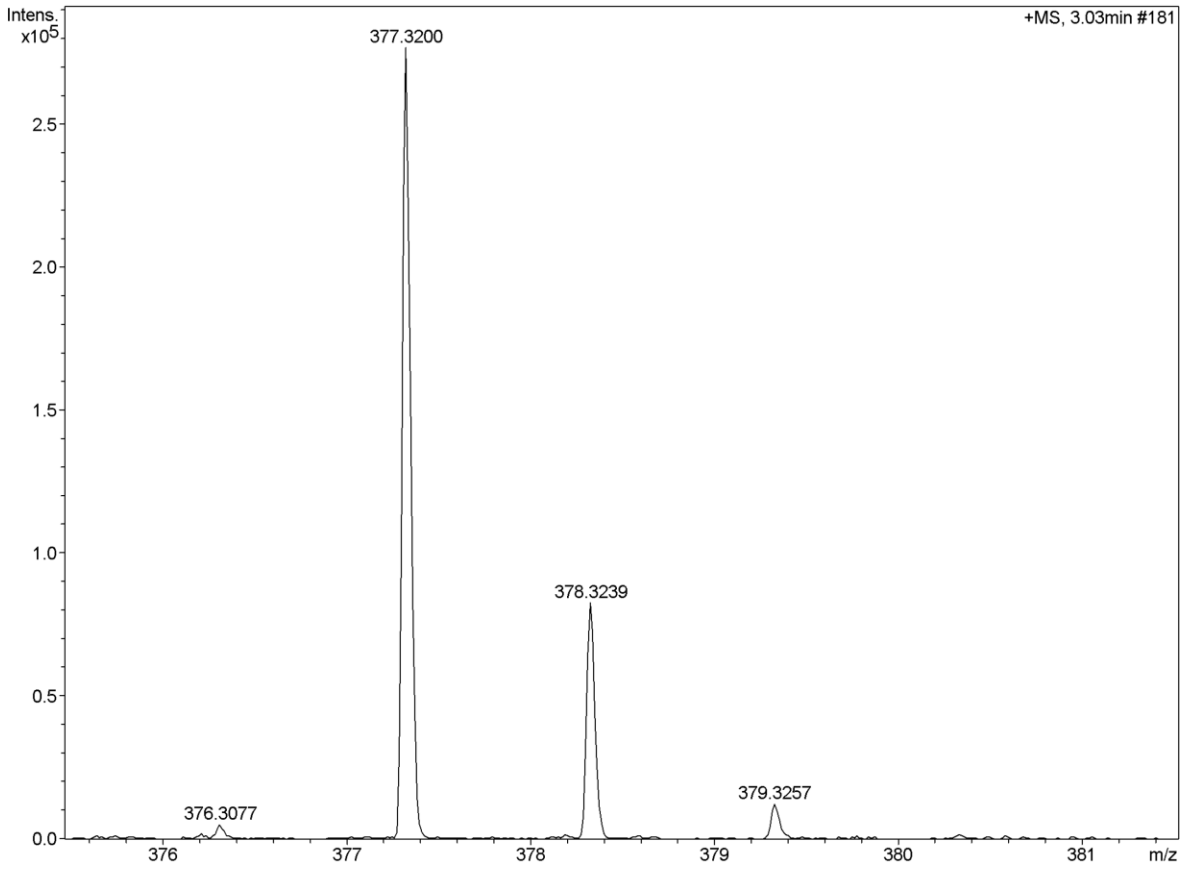

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Figure S31. HR mass spectrum (APCI) of the compound **2**.

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201806\0612\C-2.d	Acquisition Date	6/12/2018 5:14:56 PM
Method	YCH-150-1800.m	Operator	default user
Sample Name	C-2	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
532.1331	1	C 28 H 38 Br 2	532.1335	0.7	9.0	odd	ok

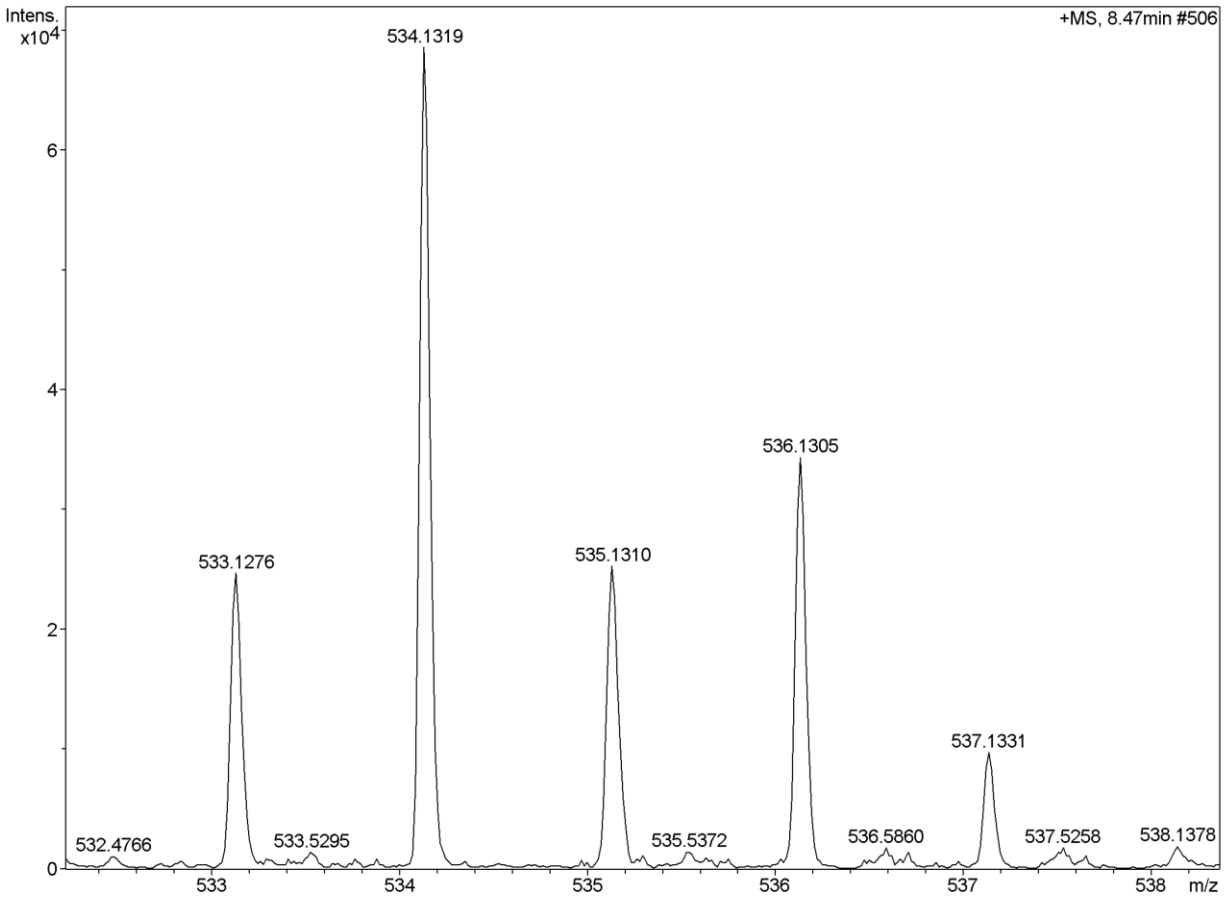

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Figure S32. HR mass spectrum (APCI) of the compound **3**.

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201806\0612\C-3.d	Acquisition Date	6/12/2018 5:32:43 PM
Method	YCH-150-1800.m	Operator	default user
Sample Name	C-3	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
526.0848	1	C 28 H 32 Br 2	526.0865	3.3	12.0	odd	ok

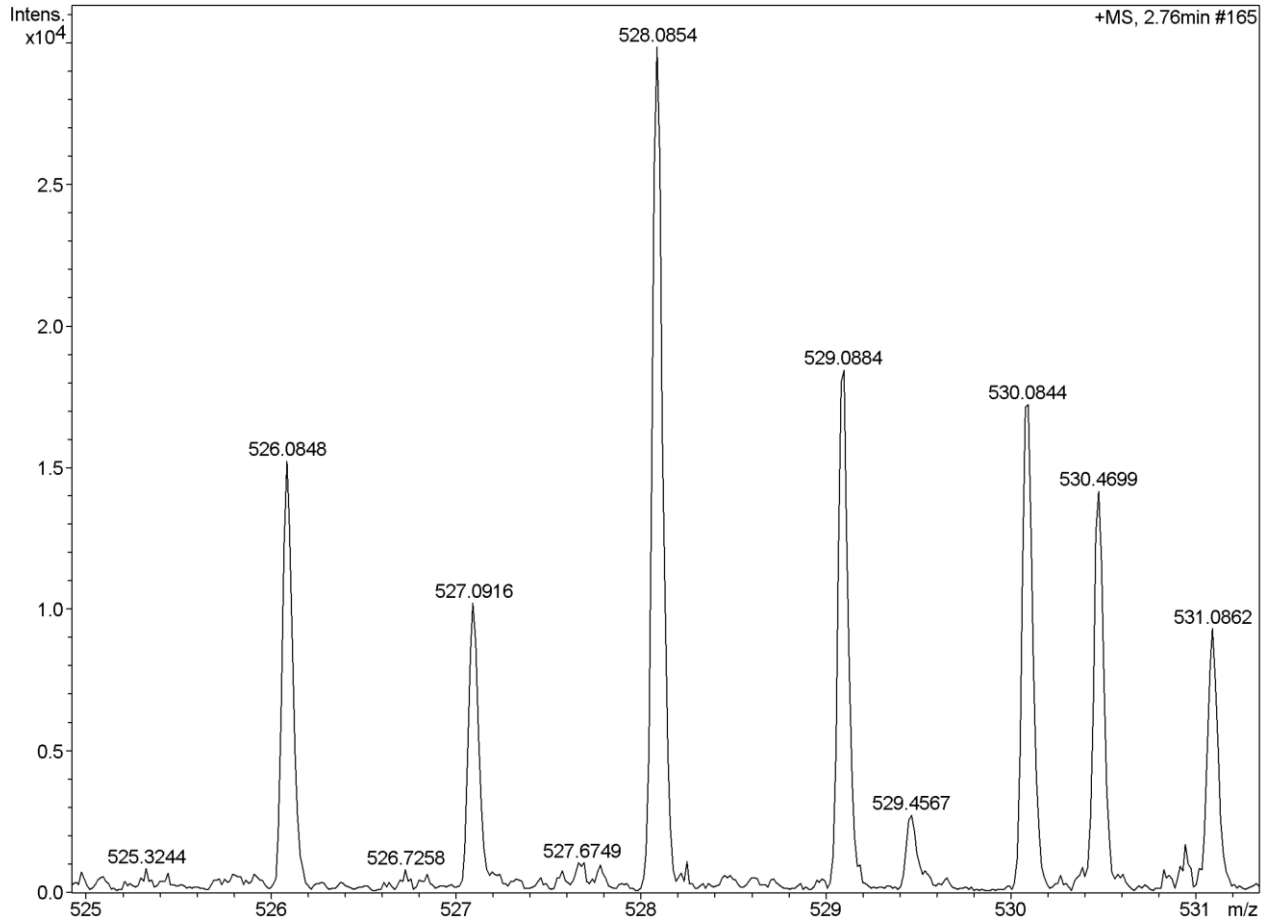

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Figure S33. HR mass spectrum (APCI) of the compound **4**.

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201806\0612\C-4.d	Acquisition Date	6/12/2018 5:44:33 PM
Method	YCH-150-1800.m	Operator	default user
Sample Name	C-4	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
578.3180	1	C 42 H 42 O 2	578.3179	-0.1	22.0	odd	ok

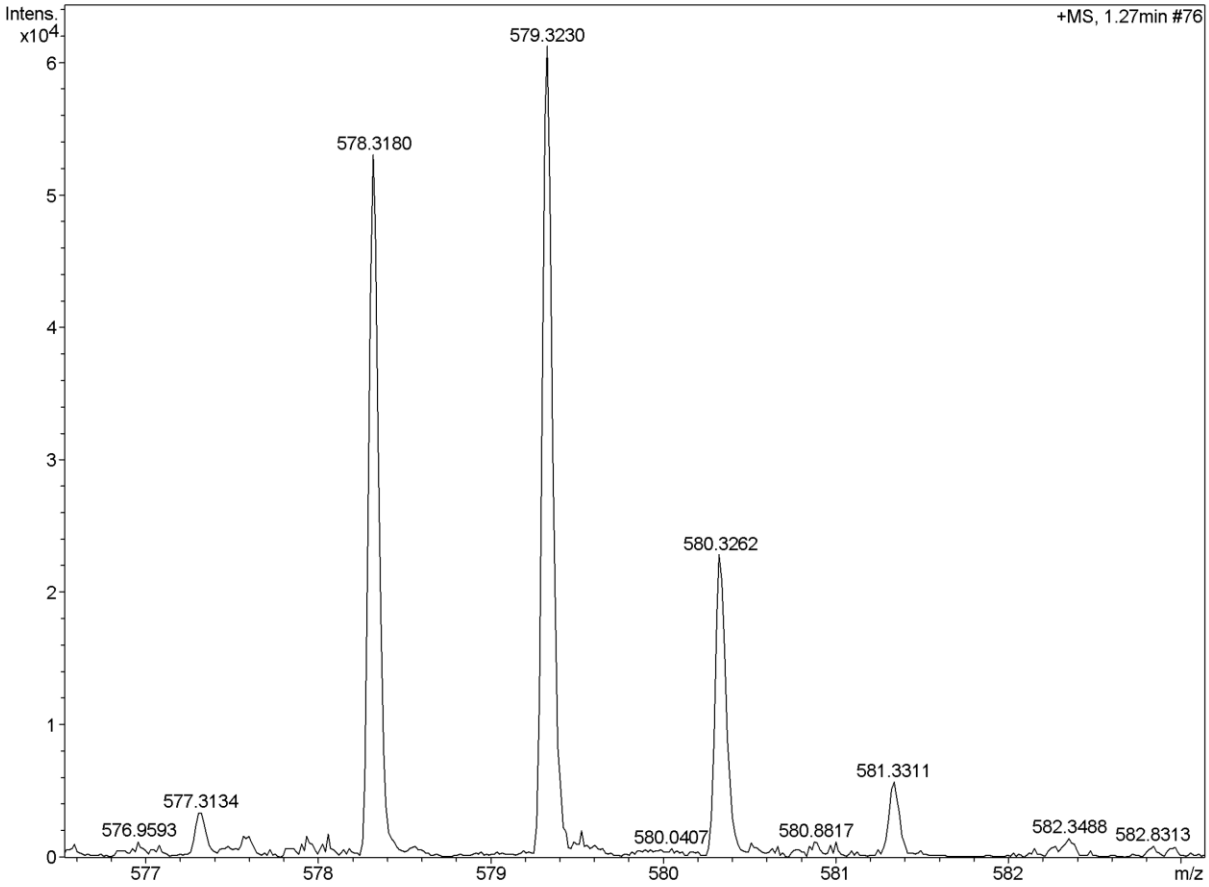

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Figure S34. HR mass spectrum (APCI) of the compound **5**.

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201806\0612\C-5.d	Acquisition Date	6/12/2018 5:52:10 PM
Method	YCH-150-1800.m	Operator	default user
Sample Name	C-5	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
984.6069	1	C 70 H 80 O 4	984.6051	-1.9	31.0	odd	ok

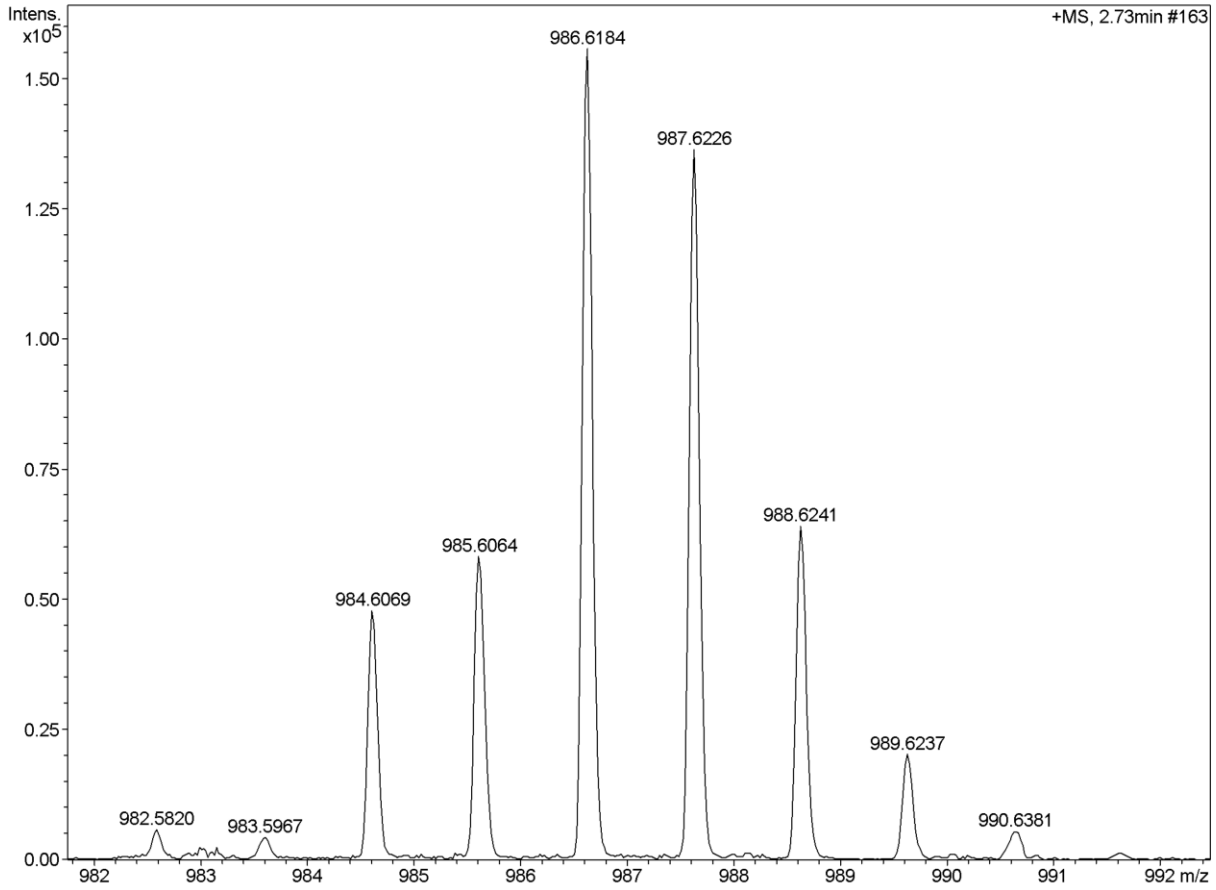

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Figure S35. HR mass spectrum (APCI) of the compound **6**.

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201806\0612\C-6.d	Acquisition Date	6/12/2018 6:02:36 PM
Method	YCH-150-1800.m	Operator	default user
Sample Name	C-6	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
1177.2098	1	C 66 H 69 Br 4	1177.2127	2.5	30.5	even	ok

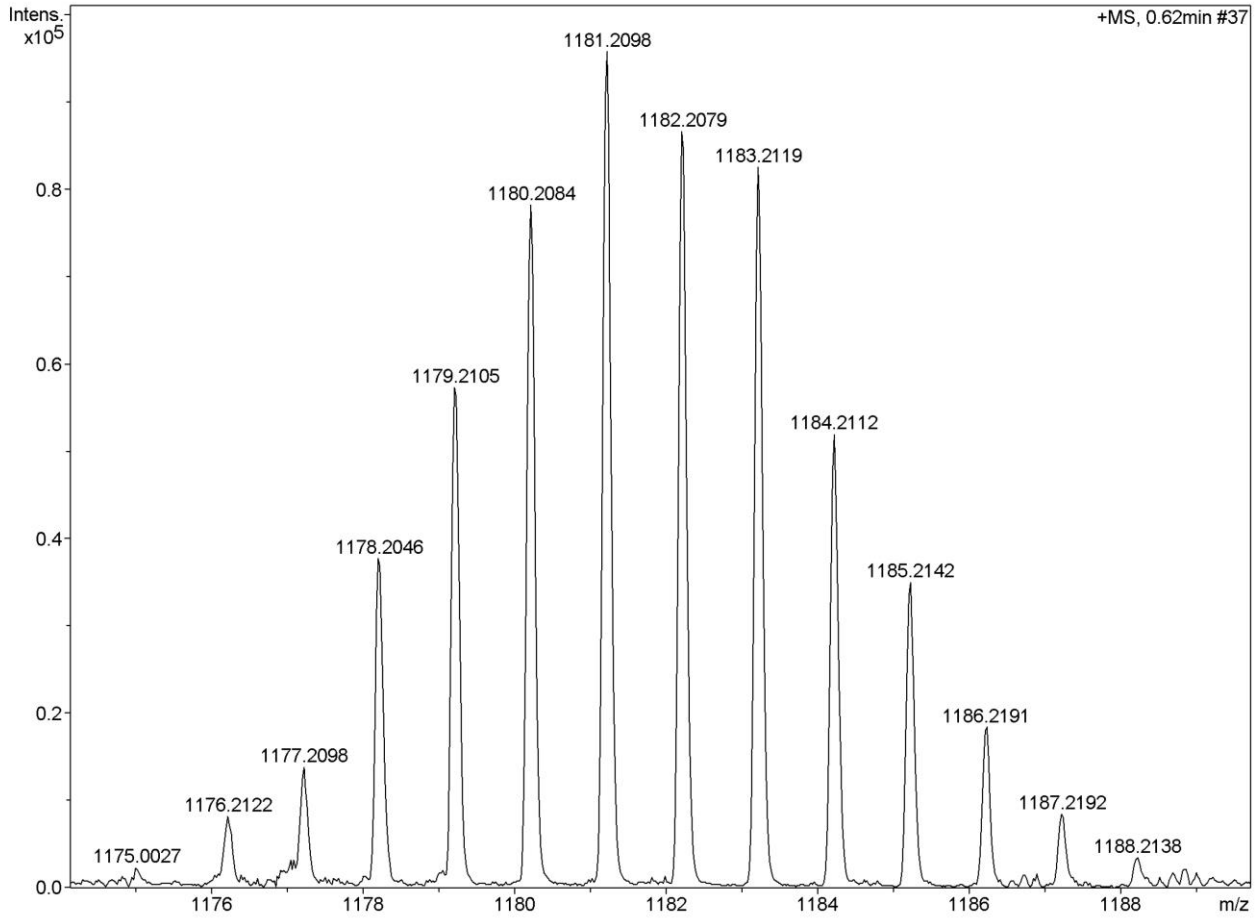

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Figure S36. HR mass spectrum (APCI) of the compound **7**.

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201806\0612\C-7.d	Acquisition Date	6/12/2018 6:10:12 PM
Method	YCH-150-1800.m	Operator	default user
Sample Name	C-7	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
1097.5916	1	C 74 H 81 O 8	1097.5926	0.9	34.5	even	ok

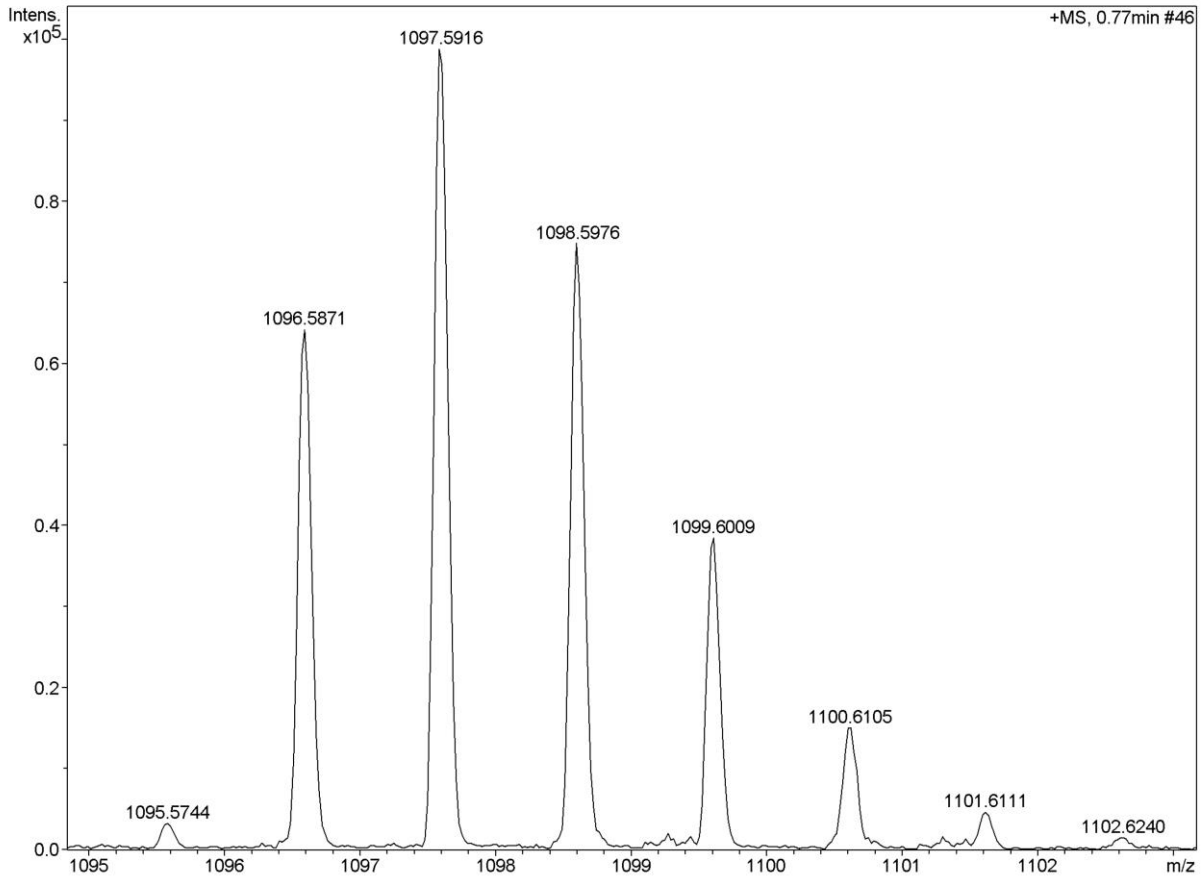

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Figure S37. HR mass spectrum (APCI) of the compound **8**.

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201806\0612\C-8.d	Acquisition Date	6/12/2018 6:16:55 PM
Method	YCH-150-1800.m	Operator	default user
Sample Name	C-8	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
929.5485	1	C 66 H 73 O 4	929.5503	1.9	30.5	even	ok

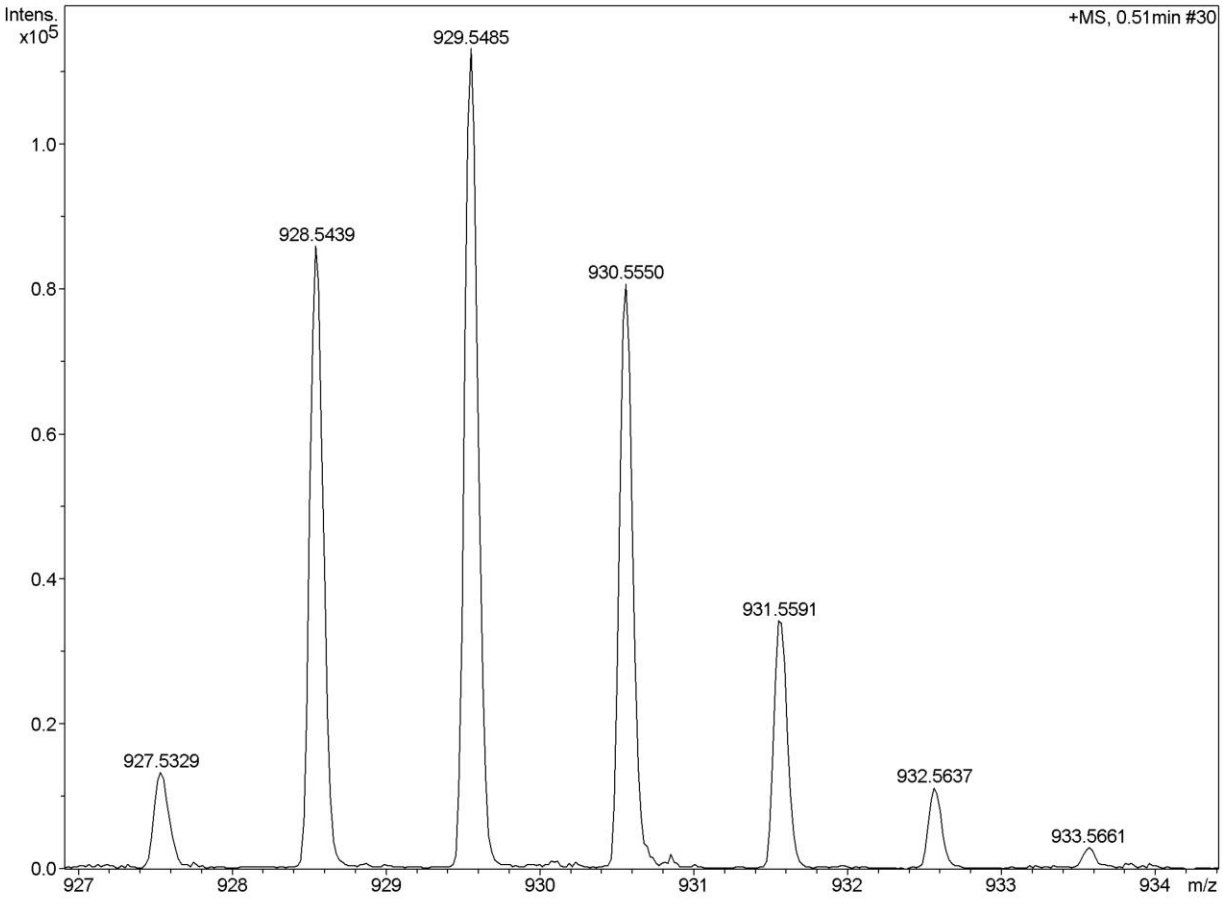

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Figure S38. HR mass spectrum (APCI) of the compound **9**.

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201806\0612\C-9.d	Acquisition Date	6/12/2018 6:21:29 PM
Method	YCH-150-1800.m	Operator	default user
Sample Name	C-9	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
921.4879	1	C 66 H 65 O 4	921.4877	-0.2	34.5	even	ok

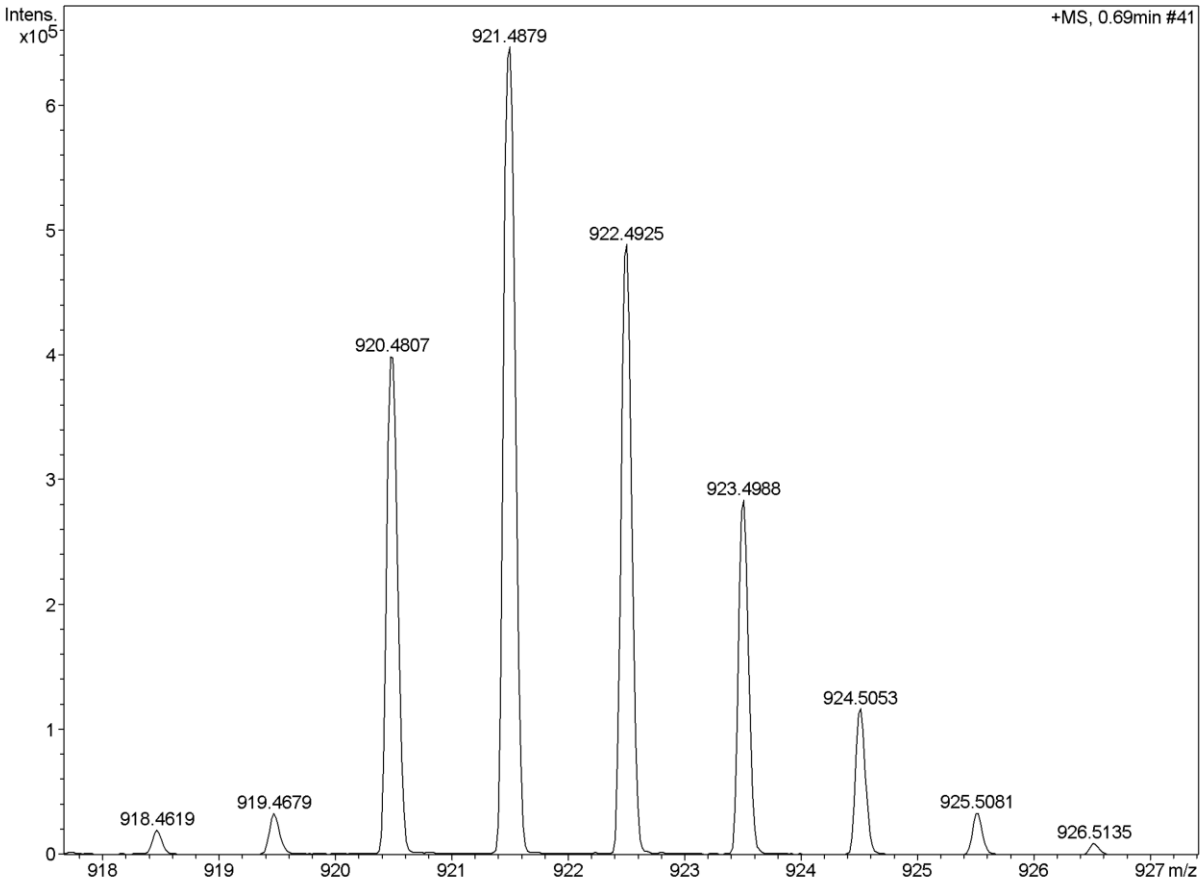

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Figure S39. HR mass spectrum (APCI) of the compound **10**.

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201806\0612\C-10.d	Acquisition Date	6/12/2018 6:25:59 PM
Method	YCH-150-1800.m	Operator	default user
Sample Name	C-10	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
1431.3020	1	C 90 H 71 Cl 8	1431.3059	2.7	51.5	even	ok

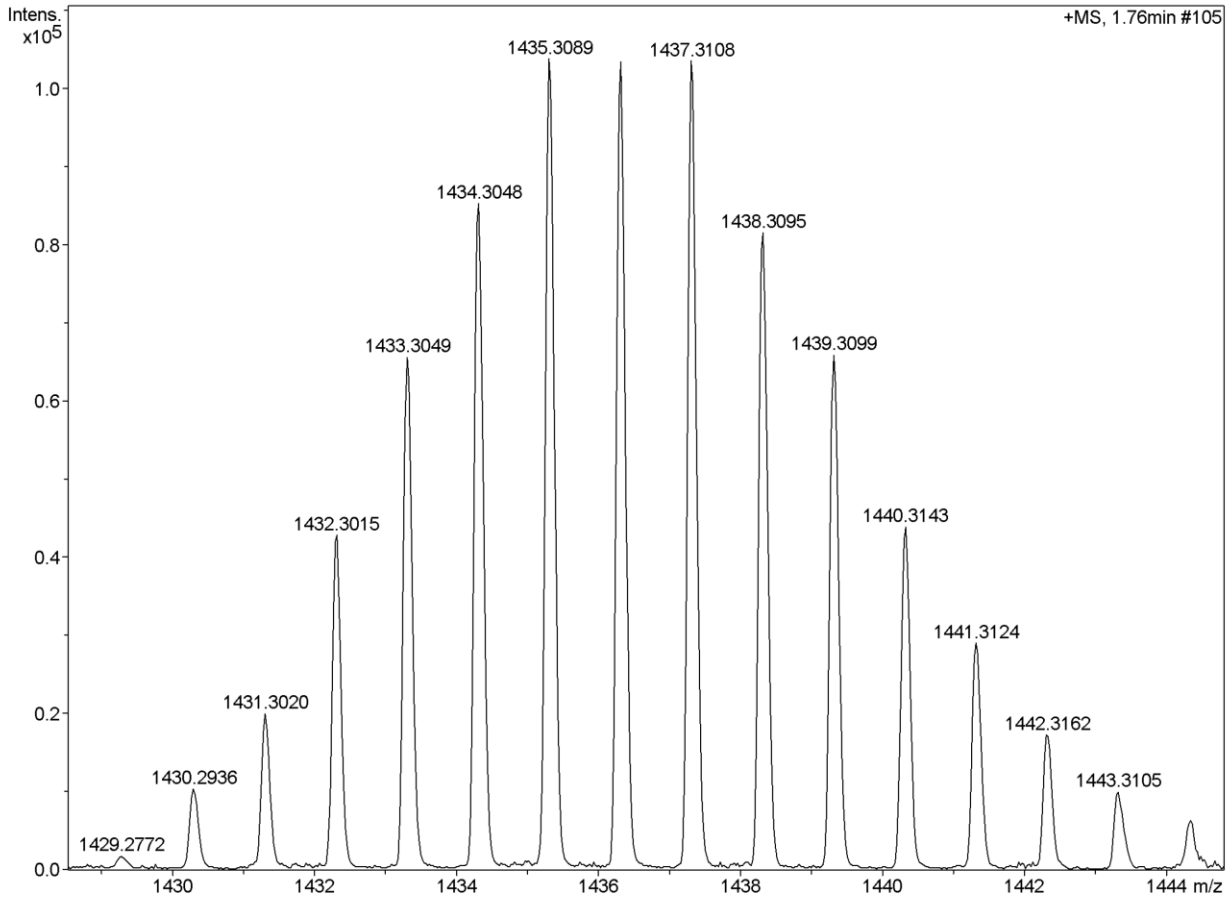

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Figure S40. HR mass spectrum (APCI) of the compound **12.**

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201806\0612\C-11-b.d	Acquisition Date	6/13/2018 2:57:14 PM
Method	YCH-150-1800.m	Operator	default user
Sample Name	C-11	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Ge Shaozhong		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	800.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
1428.2789	1	C 90 H 68 Cl 8	1428.2824	2.4	53.0	odd	ok

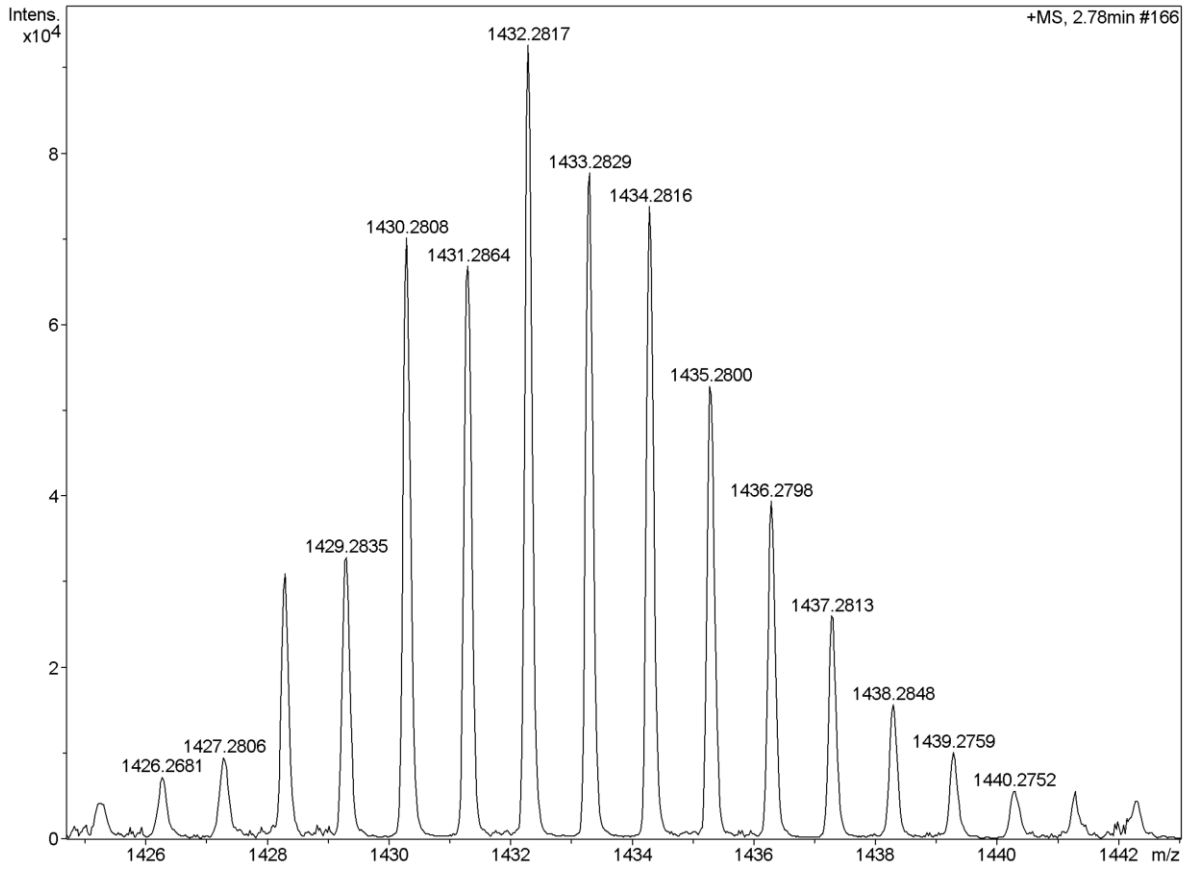

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Figure S41. HR mass spectrum (APCI) of the compound **SOZ-Cl**.

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