Increasing and Dispersing Strain in Pyrene-Fused Azaacenes

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Supporting Information

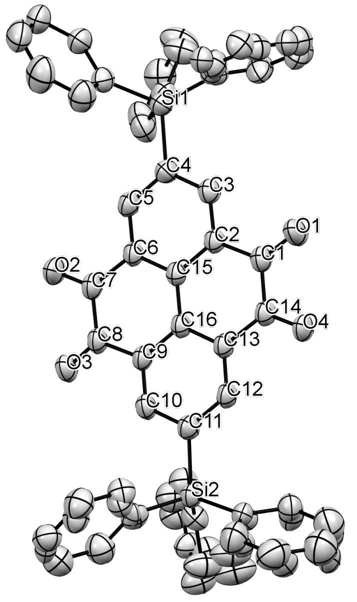
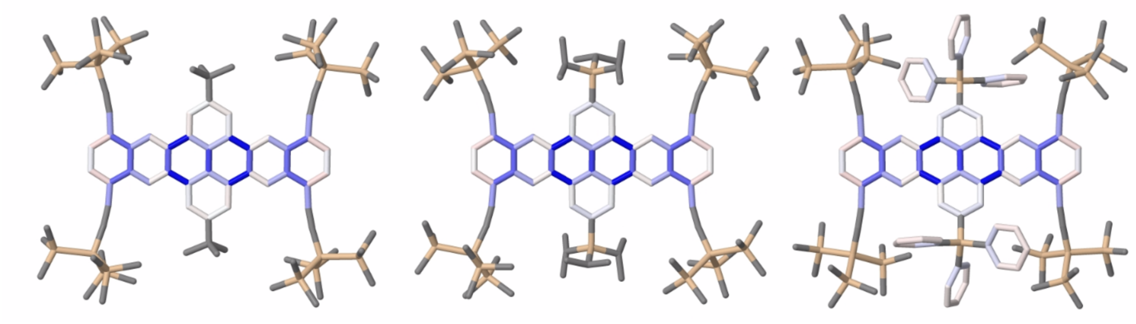


Figure S1. X-ray standard ORTEP plot for compound **7**.



12 **13** **14**

Figure S2. C_{sp2}-C_{sp2} bond alternation for the lowest energy structures at the B3LYP-6-31G(d,p) is rendered in a colour continuum ranging from red (1.33 Å) to white (1.40 Å) to blue (1.47 Å).

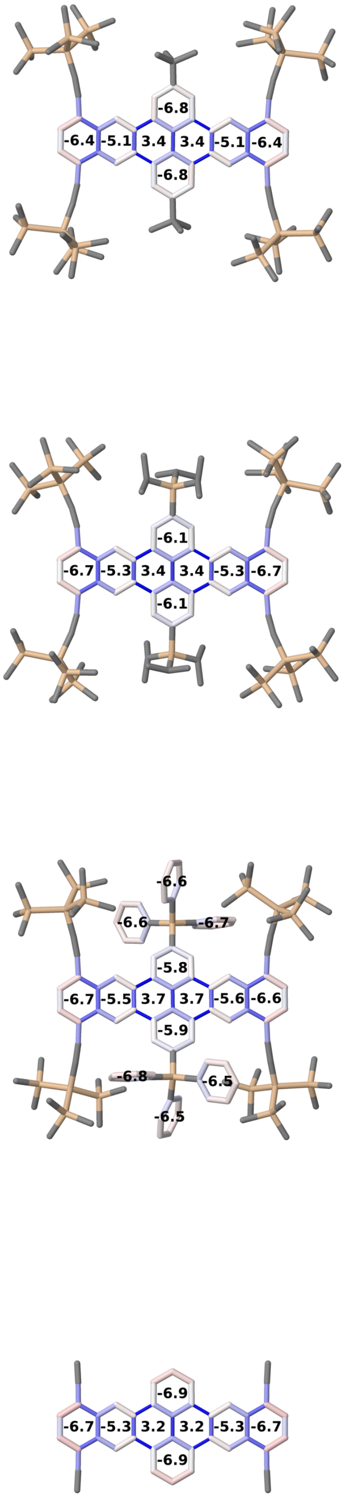


Figure S3. NICS(0) values of compounds **12**, **13** and **14** (respectively 1st to 3rd from top to bottom) compared with those of the unsubstituted core (4th row) at the B3LYP-6-311+G(2d,p) level.

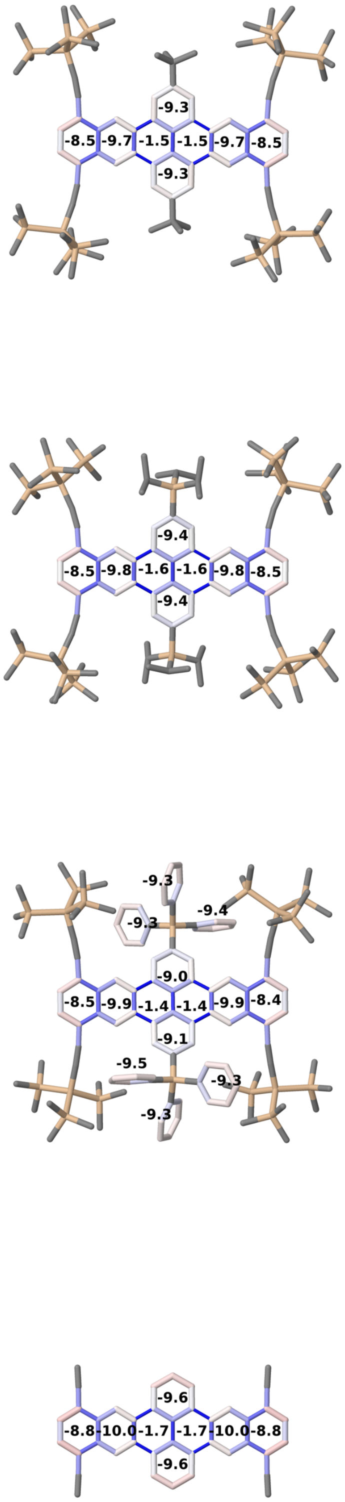


Figure S4. NICS(1) values of compounds **12**, **13** and **14** (respectively 1st to 3rd from top to bottom) compared with those of the unsubstituted core (4th row) at the B3LYP-6-311+G(2d,p) level.

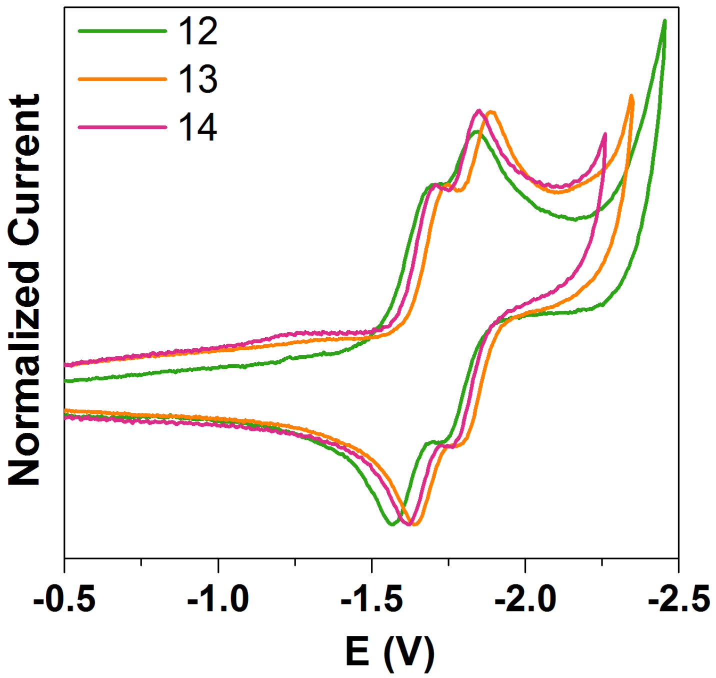


Figure S5. Normalized cyclic voltammograms of **12**, **13** and **14** in 0.1 M *n*Bu_4NPF_6 in CH_2Cl_2 (scan rate = 100 mV/s) internally referenced to ferrocene (0.16 M)

The HOMO–1 and HOMO orbitals show density on both quinoxaline residues of **12** and **13**, but in the case of **14**, the electronic densities are localized in opposite quinoxaline residues in the HOMO–1 and HOMO, respectively. Also, while in the case of **12** and **13**, the LUMO and LUMO+1 densities are almost identical, but in the case of **14** LUMO and the LUMO+1 are exchanged.

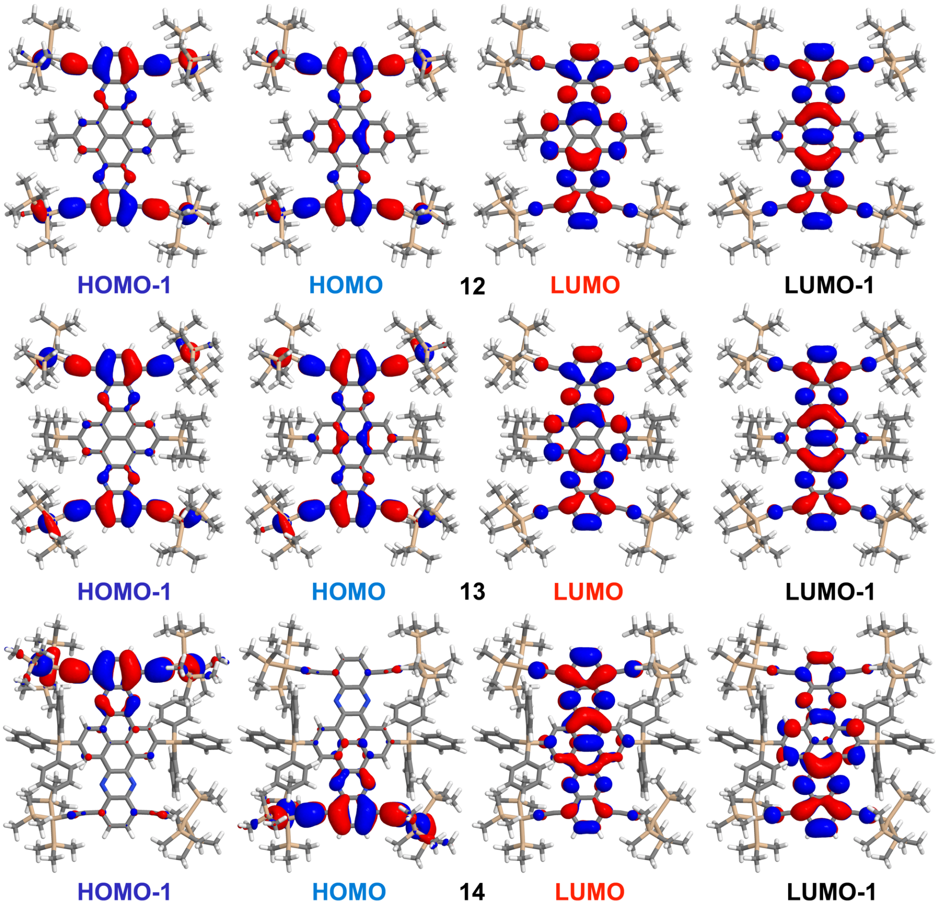


Figure S6. Frontier orbitals of **12**, **13** and **14**.

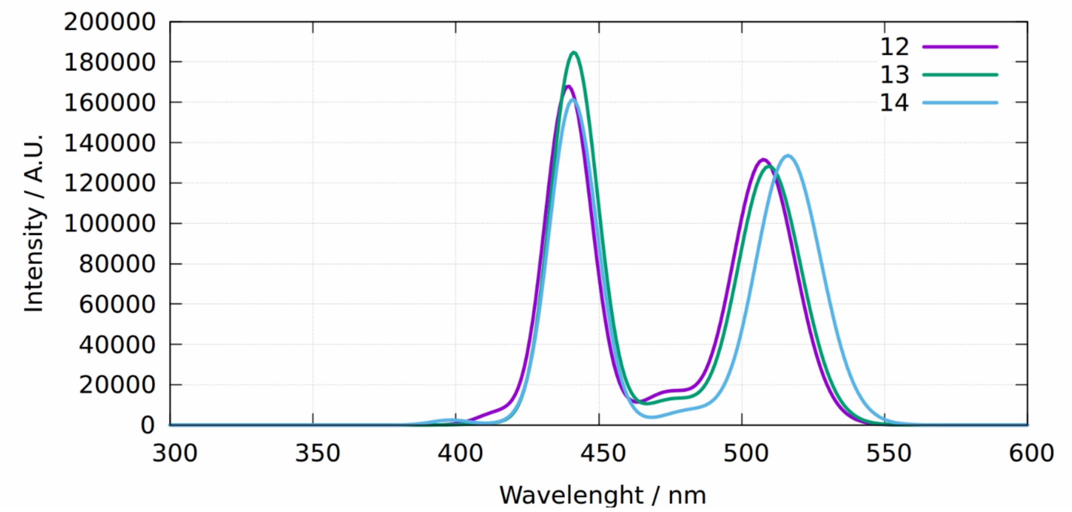


***Figure S7*.** Simulated absorption spectra computed at the TD-B3LYP-CH_2Cl_2-6-311+G(2d,p) /B3LYP-6-31G(d,p) level.

At twist angles >30°, the LUMO density corresponds to the LUMO+1 density of the flat system, exactly as we observed for **14** with respect to **12** and **13** (Figure S6).

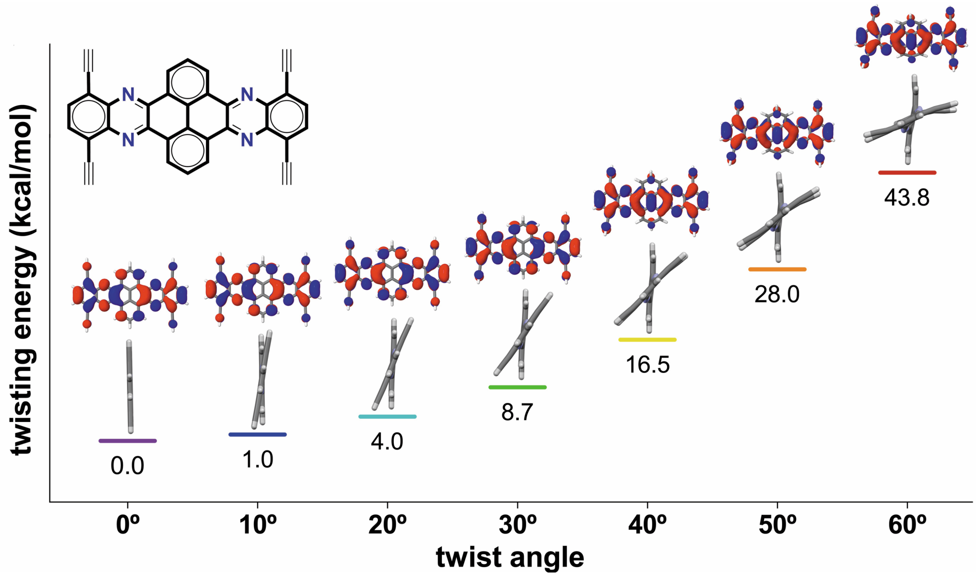


Figure S8. a) Twisting energy as a function of the angle from 0° flat, D_{2h} symmetry, to 60° computed by partial optimizations at the B3LYP-6-31G(d,p) level. Front views (with LUMO density) and side views are shown for each selected angle.

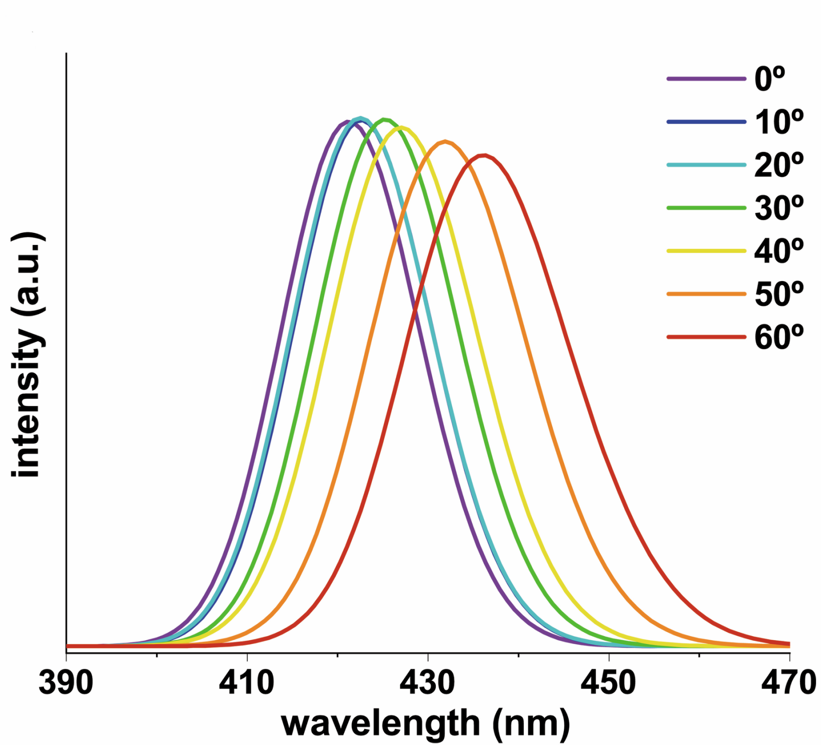


Figure S9. Absorption spectra for different twist angles computed with four excited states at the TD-B3LYP-CH_2Cl_2-6-31G(d,p)/B3LYP-6-31G(d,p) level.

	λ_{ONSET} (nm)[a]	λ_{MAX} (nm)[a]	λ_{EM} (nm)[a]	E_G (eV)[a,b]	$E_{I, 1/2}$ (V)[a]	$E_{II, 1/2}$ (V)[a]	E_{LUMO} (eV)[a,c]	E_{HOMO} (eV)[d]
12	491	464	520	2.53	−1.61	−1.72	−3.26	−5.79
13	492	464	524	2.52	−1.67	−1.78	−3.17	−5.69
14	501	472	538	2.48	−1.64	−1.75	−3.21	−5.69

***Table S1*. Photophysical and electrochemical experimental properties.** [a] Measured in dichloromethane. [b] Estimated from absorption onset according to $E_G = 1240/\lambda_{ONSET}$. [c] Estimated from CV $E_{RED,ONSET}$ according to $E_{LUMO} = -4.8 - e\,(E_{RED,\,ONSET} - E_{1/2}^{Fc})$ where $E_{1/2}^{Fc}$ was measured in situ according to $E_{1/2}^{Fc} = -(E_{ONSET}^{red} - E_{ONSET}^{ox})$ (eV). [d] $E_{HOMO} = E_{LUMO}-E_G$.

	LUMO+2	LUMO+1	LUMO	HOMO	HOMO-1	HOMO-2	E_G	*EA*	*IP*
12	−1.84	−2.77	−2.85	−5.71	−5.72	−6.12	-2.86	−2.92	−5.65
13	−1.84	−2.79	−2.85	−5.7	−5.71	−6.13	-2.85	−2.92	−5.65
14	−1.9	−2.82	−2.86	−5.69	−5.7	−6.17	-2.83	−2.92	−5.64

Table S2. Orbital energies, Electron Affinity (EA) and Ionization Potential (IP) computed at the B3LYP-CH_2Cl_2-6-311+G(2d,p)/B3LYP-6-31G(d,p) level.

	eV	nm	Osc. Strength	Contributions			
12	2.43	511	0.00	H-1->L+1	18%	HOMO->LUMO	81%
12	2.44	507	0.61	H-1->LUMO	68%	HOMO->L+1	31%
13	2.43	511	0.00	H-1->L+1	27%	HOMO->LUMO	72%
13	2.43	509	0.59	H-1->LUMO	64%	HOMO->L+1	35%
14	2.39	518	0.15	HOMO->LUMO	60%	HOMO->L+1	31%
14	2.41	515	0.47	H-1->LUMO	63%	H-1->L+1	25%

Table S3. First transition (dark for **12** and **13** in italics) and second transition (active for all) computed at the TD-B3LYP-CH_2Cl_2-6-311+G(2d,p)/B3LYP-6-31G(d,p) level.

S1. General Experimental Methods

All reagents and solvents were purchased from Fisher Scientific, ABCR, Alfa Aesar, Sigma Aldrich or VWR, and were used without further purification unless specified otherwise. Preparation of air moisture sensitive materials was carried out in flamed-dried flasks under nitrogen atmosphere employing standard Schlenk techniques. Anhydrous THF was dried using an Innovative Pure Solve solvent purification system. Commercial chlorotriisopropylsilane was dried by distillation under reduced pressure and stored with molecular sieves under argon atmosphere in a freezer until its use.

Column chromatography was performed on Silica gel 60 (40-60 µm) from Scharlab, employing petroleum ether and dichloromethane as eluents. Analytical thin layer chromatography (TLC) was carried out using aluminum sheets (20x20 cm) pre-coated with silica gel RP-18W 60 F254 from Merck). UV-active compounds were detected using a UV-lamp from CAMAG at wavelength λ = 254 or 366 nm. NMR spectra in solution were recorded on a Bruker Avance 400 MHz or 500 MHz spectrometer at 298K using partially deuterated solvents as internal standards.

High Resolution Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) Mass Spectrometry experiments were recorded in CICbiomaGUNE in a Ultraflex III (Bruker Daltonics) MALDI-ToF (frequency-tripled (355 nm) Nd:YAG laser) by Dr. Javier Calvo. Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) Mass Spectrometry MALDI- ToF experiments were recorded in POLYMAT Fundazioa in a Bruker REF LEX spectrometer by Dr. Estibaliz San Román.

X-ray data collections were performed in an Agilent Supernova diffractometer equipped with an Atlas CCD area detector, and a CuKα micro-focus source with multilayer optics (λ = 1.54184Å, 250µm FWHM beam size) by Dr. Leire Sanfelices (SGiker, University of the Basque Country). The quality of the crystals was checked under a polarizing microscope, and a suitable crystal or fragment was mounted on a Mitegen Micromount^{TM} using Paratone-N inert oil and transferred to the diffractometer. Samples were kept at 150(10)K with an Oxford Cryosystems Cryostream 700 cooler.

Absorption spectra were recorded on a Perkin-Elmer Lambda 950 spectrometer.

Fluorescence spectra were recorded on a LS55 Perkin-Elmer Fluorescence spectrometer.

Electrochemical measurements were carried out on a Princeton Applied Research Parstat 2273 in a 3-electrode single compartment cell with glassy-carbon disc working electrode (ϕ = 3mm), a platinum wire counter electrode (ϕ = 0.5mm) and a silver wire pseudoreference electrode. The cell and the electrodes were custom made. All the potential values are reported versus the redox potential of the ferrocene/ferrocenium couple.

Preparation of starting materials.

Some compounds were synthesized according literature:

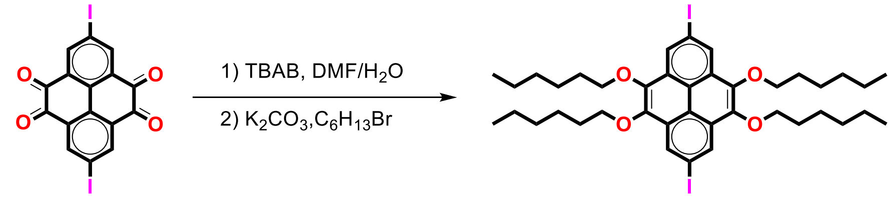
1: 2,7-ditertbutyl-pyrene-4,5,9,10-tetraone.[1]

2: 2,7-diiodo-pyrene-4,5,9,10-tetraone.[1b, 2]

9: 4,7-dibromo-2,1,3-benzothiadiazole.[3]

S2. Synthesis and Analytical Data

3: 2,7-diiodo-4,5,9,10-tetrahexyloxypyrene.



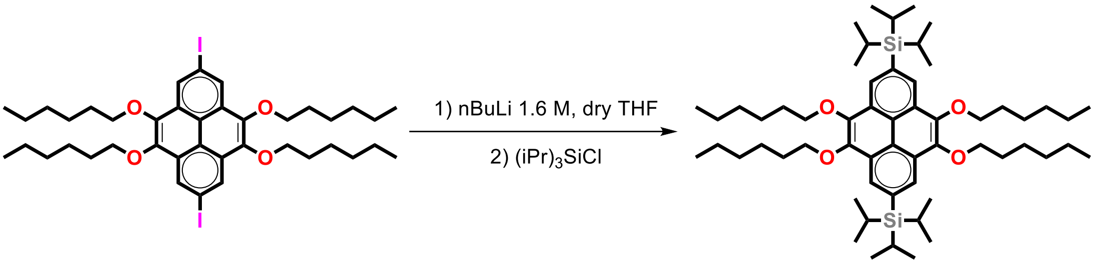
In a flame dried Schlenk flask 2.11 g of **2** (4.11 mmol) was suspended in 48 mL of a mixture DMF/H_2O 3:2, the suspension was purged with N_2 for 15 minutes, then 924 mg of tetrabutylammonium bromide 98% (TBAB, 2.87 mmol, 0.7 eq.) and 4287 mg of sodium dithionite ($Na_2S_2O_4$, 24.63 mmol, 6 eq.) were added under nitrogen stream. Once the solution turns black, 5671 mg of potassium carbonate 99% (41.05 mmol, 10 eq.) and 5.76 mL of 1-bromohexane 98% (41.05 mmol, 1.176 g/mL, 10 eq.) were added under inert atmosphere. Reaction was refluxed for 4 hours under nitrogen. The reaction was cooled to room temperature, water was added. The product was extracted with diethyl ether (3x50 mL), washed with brine and dried over sodium sulfate. Solvent was removed by rotary evaporation. Resulting solids were loaded onto a chromatography column with hexane as eluent. Desired product is precipitated on methanol, affording 1560 mg (2.59 mmol) of white solid **3** in 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$-d^1): δ = 8.51 (4H, s), 4.29 (8H, J = 6.6 Hz, t), 1.95 (8H, J = 7.5 Hz, m), 1.61 (8H, m), 1.41 (16H, m) and 0.94 (12H, J = 6.7 Hz, t).

^{13}C NMR (400 MHz, $CDCl_3$-d^1): δ = 143.36, 130.37, 127.94, 119.39, 93.07, 74.06, 31.84, 30.55, 26.07, 22.88, 14.26.

MS: MS (MALDI-ToF) (*m/z*) $[M+H]^+$ calcd. for $C_{40}H_{56}I_2O_4$: 854.227; found: 854.190.

4: 2,7-bis(triisopropylsilyl)-4,5,9,10-tetrahexyloxypyrene.



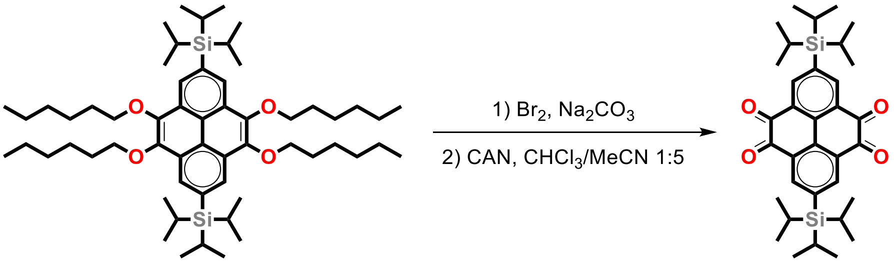
In a flame dried Schlenk flask 800 mg (0.94 mmol) of **3** was dissolved in 10 mL of dry THF, the resultant solution is freeze-pump-thawed three times, then cooled to −94 °C and 5 mL of *n*-BuLi 1.6M in hexanes (7.94 mmol, 8eq.) was added. After three hours 1.6 mL of chlorotriisopropylsilane (7.94 mmol, 0.91 g/mL, 8 eq.) previously dried was added dropwise under inert atmosphere. The reaction was allowed to reach room temperature and reacted overnight. Ammonium chloride is added at 0°C, then extracted with diethyl ether (3x50mL). Resultant organic phase was washed with brine, dried over sodium sulfate and filtered. Solvent was removed by rotary evaporation. Resulting solids were purified by flash chromatography (eluent mixture hexanes/dichloromethane 95:5). Product **4** was precipitated on methanol affording 601 mg (0.66 mmol) of white solid in 70 % yield.

^{1}H NMR (500 MHz, $CDCl_3$-*d*^{1}): δ = 8.58 (4H, s), 4.32 (8H, *J* = 6.6 Hz, t), 1.95 (8H, m), 1.65 (8H, m), 1.41 (22H, m), 1.19 (36H, *J* = 7.5 Hz, d) and 0.94 (12H, *J* = 7.0 Hz, t).

^{13}C NMR (500 MHz, $CDCl_3$-*d*^{1}): δ = 144.20, 132.47, 127.67, 125.55, 121.21, 74.23, 32.08, 30.94, 26.41, 22.88, 18.93, 14.25, 11.30.

HRMS (MALDI-ToF) (*m/z*) $[M+H]^+$ calcd. for $C_{58}H_{98}O_4Si_2$: 914.7001; found: 914.7006.

5: 2,7-bis(triisopropylsilyl)-pyrene-4,5,9,10-tetraone.



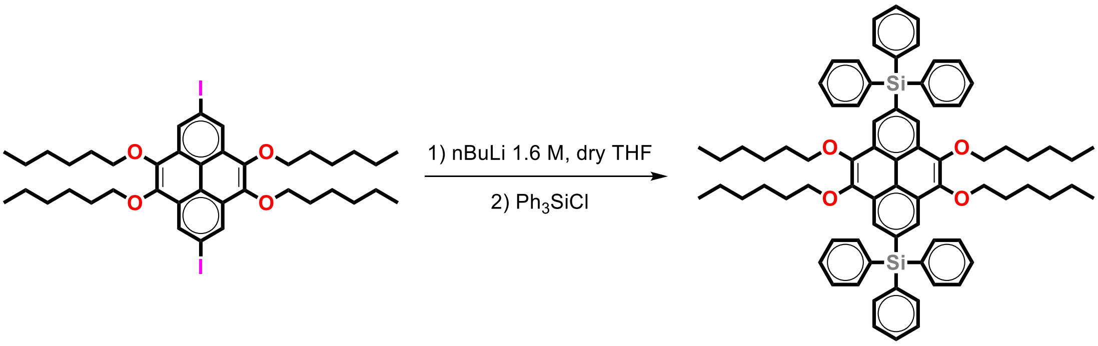
In a round bottom flask 360 mg (0.404 mmol) of **4** and 257 mg of sodium carbonate (2.43 mmol, 6 eq.) were suspended on 10 mL of chloroform and cooled below 0°C, then 1 mL of a solution 1.62M of bromide (3.1 g/mL, 4 eq.) in chloroform was slowly added. After 15 minutes the reaction was stopped. More solvent was added, and the organic phase was treated with a 10% aqueous solution of sodium thiosulfate, then washed with water and brine, dried over sodium sulfate and filtered. Solvent was removed by rotary evaporation. Resulting crude was dissolved in 6 mL of a mixture 1:5 chloroform/acetonitrile and 442 mg of cerium-ammonium-nitrate 99% (CAN, 0.808 mmol, 2 eq.) was added. Reaction was heated up to 70 °C overnight. When reaction was completed dichloromethane was added, the organic phase was washed with water and brine, dried over sodium sulfate and filtered. Solvent was removed by rotary evaporation. Resulting crude was purified by flash chromatography (eluent mixture hexanes/DCM 9:1) affording 106 mg (0.189 mmol) of red solid **5** in 47% yield over two steps.

^{1}H NMR (400 MHz, $CDCl_3$-*d*^{1}): δ = 8.55 (4H, s), 1.59 (6H, *J* = 15.2, 7.4 Hz, hept), 1.15 (36H, *J* = 6.7 Hz, d).

^{13}C NMR (400 MHz, $CDCl_3$-*d*^{1}): δ = 178.71, 143.17, 141.43, 134.7, 129.86, 18.54, and 10.75.

MS (MALDI-ToF) (*m/z*) $[M+Na]^+$ calcd. for $C_{34}H_{46}NaO_4Si_2$: 597.283; found: 597.184.

6: 2,7-bis(triphenylsilyl)-4,5,9,10-tetrahexyloxypyrene.



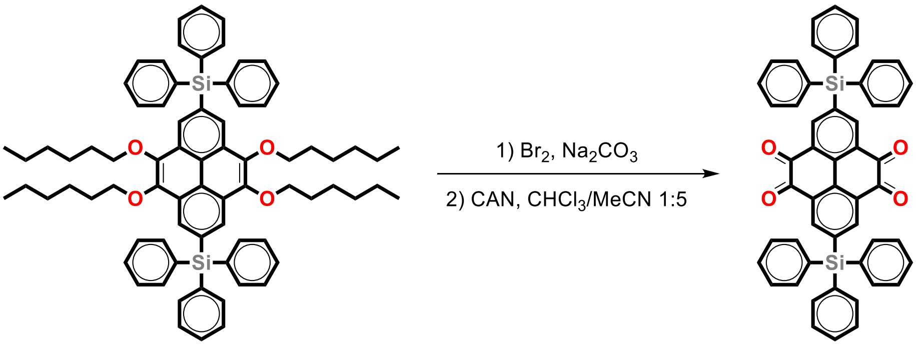
In a flame dried Schlenk flask 714 mg (0.84 mmol) of **3** was dissolved in dry THF, the resultant solution is freeze-pump-thawed three times, then cooled to −94°C and 3.66 mL of *n*-BuLi 1.6M in hexanes (5.86 mmol, 7 eq.) was added. After three hours 1.8 g of chlorotriphenylsilane 96% (5.86 mmol, 7 eq.) previously dissolved in dry THF was added dropwise under inert atmosphere. The reaction was allowed to reach room temperature and reacting overnight. Ammonium chloride was added at 0°C, then extracted with diethyl ether (3 x 50 mL). The organic phase was washed with brine, dried over sodium sulfate and filtered. Solvent was removed by rotary evaporation. Resulting solids were loaded onto a chromatography column (eluent mixture hexanes/dichloromethane 7:3). The desired product is precipitated on methanol, affording 544 mg (0.487 mmol) of white solid **6** in 58% yield

^{1}H NMR (500 MHz, $CDCl_3$-d^1): δ = 8.66 (4H, s), 7.72 (12H, *J* = 8.0 Hz, d), 7.50 (6H, *J* = 7.4 Hz, t), 7.44 (12H, *J* = 7.2 Hz, t) 4.16 (8H, *J* = 6.8 Hz, t), 2.06 (8H, m), 1.71 (8H, *J* = 14.6, 6.9 Hz, p), 1.29 (16H, m) and 0.89 (12H, *J* = 6.9 Hz, t).

^{13}C NMR (500 MHz, $CDCl_3$-d^1): δ = 144.40, 136.72, 134.56, 132.34, 129.75, 128.23, 128.03, 126.88, 121.53, 74.26, 31.84, 30.48, 25.87, 22.71, 14.23.

HRMS (MALDI-ToF) (*m/z*) $[M+H]^+$ calcd. for $C_{76}H_{86}O_4Si_2$: 1118.6062; found: 1118.6211

7: 2,7-bis(triphenylsilyl)-pyrene-4,5,9,10-tetraone.



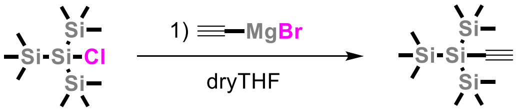
In a round bottom flask 210 mg (0.188 mmol) of **6** and 120 mg of sodium carbonate (1.13 mmol, 6 eq.) were suspended on chloroform and cooled below 0°C, then 1 mL of a 0.75M solution of bromide (3.1 g/mol, 4 eq.) in chloroform was slowly added. After 15 minutes the reaction was stopped. More solvent was added, and the organic phase was treated with a 10% aqueous solution of sodium thiosulfate, then washed with water and brine, dried over sodium sulfate and filtered. Solvent was removed by rotary evaporation. Resulting crude was dissolved in 6 mL of 1:5 mixture chloroform/acetonitrile and 206 mg of cerium-ammonium-nitrate 99% (0.376 mmol, 2 eq.) was added. Reaction was heated up to 70 °C overnight. When reaction was completed dichloromethane is added, the organic phase was washed with water and brine, dried over sodium sulfate and filtered. Solvent was removed by rotary evaporation. Resulting crude was purified by flash chromatography (eluent mixture hexanes/DCM 3:2) affording 60mg (0.0771 µmol) of red solid **7** in 45% yield over two steps. Crystals for **7** were obtained by chloroform evaporation.

^{1}H NMR (400 MHz, $CDCl_3$-d^{1}): δ = 8.67 (4H, s), 7.55 (12H, *J* = 8.0 Hz, s), 7.48 (6H, *J* = 7.4 Hz, t), 7.42 (12H, *J* = 7.2 Hz, t).

^{13}C NMR (500 MHz, $CDCl_3$-d^{1}): δ = 178.32, 146.34, 144.09, 141.19, 136.39, 135.07, 131.80, 130.66, 130.26 and 128.59.

MS (MALDI-ToF) (*m/z*) $[M+Na]^+$ calcd. for $C_{52}H_{34}NaO_4Si_2$: 801.189; found: 801.408.

8: (tris(trimethylsilyl)silyl)acetylene.

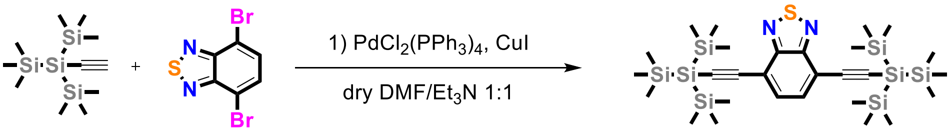


In a Shlenk flask 4 g of chlorotris(trimethylsilyl)silane 97% (14.15 mmol) were dissolved in 20 mL of dry THF and freeze-pump-thawed twice. In a 250 mL round bottom flask 85ml of ethynyl magnesium bromide in hexane (42.4 mmol) was placed under nitrogen and cooled below 0°C. Then the silane solution was added dropwise over the previous solution, allow to react overnight at RT under nitrogen. The solution was cooled to 0°C and quenched with ammonium chloride. The product was extracted with dichloromethane (3x100 mL), washed with brine, dried over sodium sulfate. Rotary evaporation afforded 3.66g (13.43 mmol) of yellow oil **8** that solidifies with time, in 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$-d^{1}): δ = 2.30 (1H, s) and 0.21 (27H, s).

All analytical data agrees with literature.[4]

10: 4,7-bis((tris(trimethylsilyl)silyl)ethynyl)benzo*[c]*[1,2,5]thiadiazole.



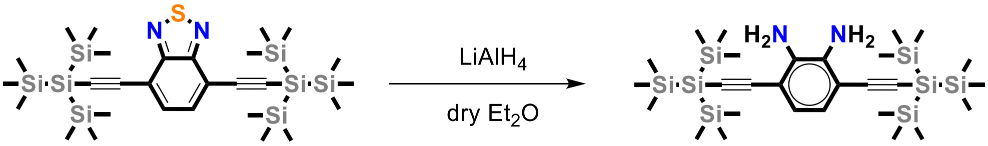
In a flame dried Schlenk 1176 mg (4 mmol) of **8**, 140 mg (0.2 mmol, 0.05 eq.) of catalyst $PdCl_2(PPh_3)_2$, 15.24 mg (0.08 mmol, 0.02 eq) of CuI were dissolved in 30 mL of THF/Et_3N 1:1 and freeze-pump-thawed twice. Then 3.272g (12 mmol, 3 eq.) of **9** was added under nitrogen atmosphere. Solution was heated at room temperature overnight. Resulting solution was cooled to room temperature and filtered through Celite pad. Solvents were rotary evaporated, crude was redissolved in hexanes and washed with brine, dried over sodium sulfate and the organic phase was removed by rotary evaporation. Resulting solid was purified by flash chromatography (eluent hexane/dichloromethane 95:5) and desired product was triturated on methanol. Recrystallization by dichloromethane evaporation afforded 2.02 g (2.95 mmol) of **10** as bright yellow crystals in 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$-*d^1*): δ = 7.53 (2H, s) and 0.28 (27H, s).

^{13}C NMR (400 MHz, $CDCl_3$-*d^1*): δ = 154.36, 131.80, 117.52, 103.96, 98.74, 0.29.

HRMS (MALDI-ToF) (*m/z*) $[M+Ag]^+$ calcd. for $C_{28}H_{56}AgN_2SSi_8$: 789.1361; found: 783.1369.

11: 3,6-bis((tris(trimethylsilyl)silyl)ethynyl)benzene-1,2-diamine.



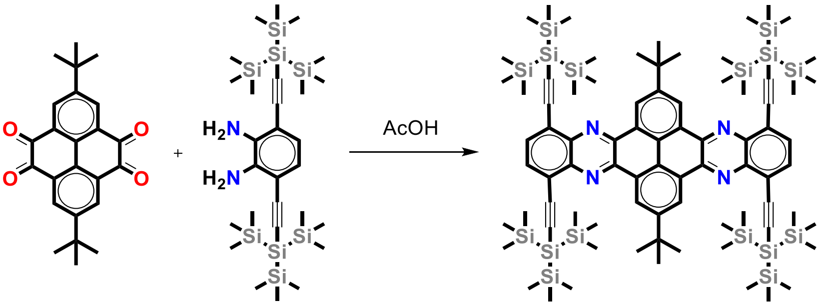
In a two-neck 250 mL round bottom flask 500 mg (0.747 mmol) of **10** was dissolved in 35 mL of dry diethyl ether and cooled to −15°C, then under nitrogen atmosphere 300 mg (7.47 mmol, 10 eq.) of $LiAlH_4$ was slowly added. Reaction was allowed to reach room temperature, after two hours was quenched with ammonium chloride and extracted with hexane. Organic phase was washed with water and brine, dried over sodium sulfate and solvent was removed by rotary evaporation. Trituration on methanol afforded 176 mg (0.26 mmol) of pale yellow solid **11** in 35% yield.

^{1}H NMR (400 MHz, $CDCl_3$-*d^1*): δ = 7.26 (2H, s) and 0.24 (27H, s).

^{13}C NMR (400 MHz, $CDCl_3$-*d^1*): δ = 136.23, 122.10, 105.10, 94.99, 0.53.

HRMS (MALDI-ToF): (*m/z*) $[M+Ag]^+$ m/z calcd. for $C_{28}H_{60}AgN_2Si_8$: 648.2911, found 648.3079.

12: TTMS-TBU-TTMS-dibenzotetrazahexacene.



In a Schlenk flask 13 mg of tetraketone **1** (36 µmol, 1 eq.) and 52 mg of diamine **11** (80 µmol, 2.2 eq.) were dissolved in little amount chloroform and 1.5 mL of acetic acid was added. Mixture was heated up to 40°C for three hours under nitrogen atmosphere. Reaction was cooled to room temperature. Chloroform was removed, methanol was added, and the suspension was filtered.

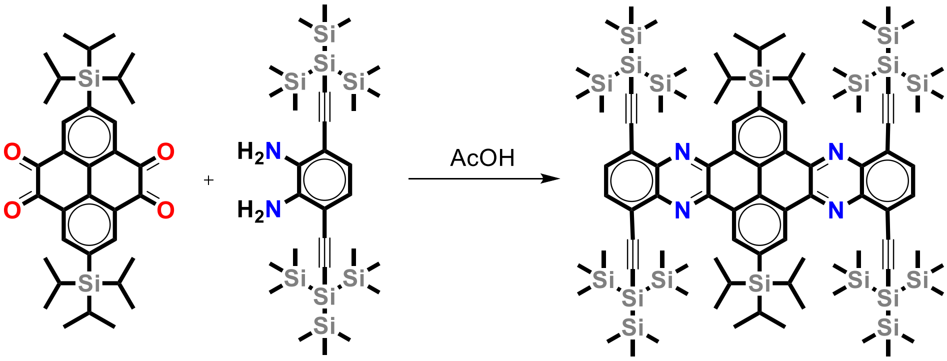
Resulting solids were purified by flash chromatography (eluent mixture hexane/DCM 7:3). Desired product was isolated by precipitation on methanol affording 49.4 mg (30 µmol) of yellow solid **12** in 83% yield. Crystals were obtained by low vapor diffusion of ethanol over a toluene solution of **12.**

^{1}H NMR (400 MHz, $CDCl_3$-*d*^{1}): δ = 9.88 (4H, s), 7.96 (4H, s), 1.72 (18H, s) and 0.36 (108H, s).

^{13}C NMR (400 MHz, $CDCl_3$-*d*^{1}): δ = 150.88, 143.18, 141.72, 135.66, 129.43, 126.39, 125.57, 124.72, 106.592, 98.53, 35.94, 32.52 and 0.92.

HRMS (MALDI-ToF): (*m/z*) [M]+H^{+} calcd. for $C_{80}H_{135}N_4Si_{16}$: 1599.6991; found: 1599.6955.

13: TTMS-TIPS-TTMS-dibenzotetrazahexacene.



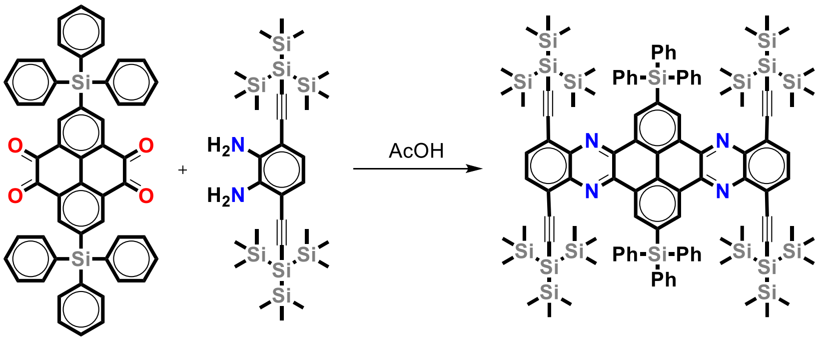
In a Schlenk flask 20 mg of tetraketone **5** (34 µmol, 1 eq.) and 65 mg of diamine **11** (104 µmol, 3 eq.) were suspended in 1.5 mL of acetic acid. Mixture is heated up 40° for three hours under nitrogen atmosphere. Reaction was cooled to room temperature, methanol was added, and the suspension was filtered. Resulting solids were purified by flash chromatography (eluent mixture hexane/DCM 4:1). Desired product was isolated by precipitation on methanol affording 23.8 mg (14 µmol) of yellow solid **13** in 40% yield. Crystals were obtained by low vapor diffusion of ethanol over a toluene solution of **13.**

^{1}H NMR (400 MHz, $CDCl_3$-*d*^{1}): δ = 9.83 (4H, s), 7.95 (4H, s), 1.78 (6H, *J* = 7.4 Hz, p), 1.23 (36H, *J* = 7.5 Hz, d) and 0.35 (108H, s).

^{13}C NMR (400 MHz, $CDCl_3$-*d*^{1}): δ = 142.93, 141.52, 136.37, 135.94, 135.11, 128.68, 128.55, 124.87, 107.68, 99.04, 31.75, 29.87, 22.82, 19.41, 11.54 and 0.91.

HRMS (MALDI-ToF): (*m/z*) [M]+H^{+} calcd. for $C_{90}H_{159}N_4Si_{18}$: 1799.8412; found: 1799.8580.

14: TTMS-TPS-TTMS-dibenzotetrazahexacene.



In a Schlenk flask 20 mg of tetraketone **7** (26 µmol, 1 eq.) and 50 mg of diamine **11** (77 µmol, 3 eq.) were suspended in 3 mL of acetic acid. Mixture was heated at 40 °C for three hours under nitrogen atmosphere. Reaction was cooled to room temperature, methanol was added, and the suspension was filtered. Resulting solids were purified by flash chromatography (eluent mixture hexane/DCM 4:1). Desired product was isolated by precipitation on methanol affording 23.8 mg (12 µmol) of yellow solid **14** in 47% yield. Crystals were obtained by low vapor diffusion of ethanol over a toluene solution of **14.**

^{1}H NMR (400 MHz, $CDCl_3$-*d*^{1}): δ = 9.90 (4H, s), 7.87 (4H, s), 7.72 (12H, *J* = 1.68, 5.8 Hz, dd), 7.42 (24H, m) and 0.13 (108H, s).

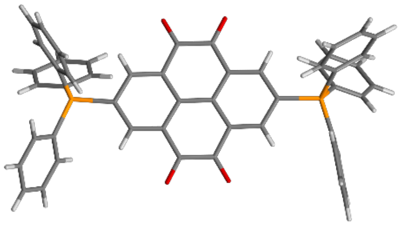
^{13}C NMR (400 MHz, $CDCl_3$-*d*^{1}): δ = 142.28, 141.58, 136.92, 135.07, 134.33, 134.01, 129.75, 129.28, 128.80, 128.21, 106.99, 99.26, and 0.68.

HRMS (MALDI-ToF): (*m/z*) [M]+H$^+$ calcd. for $C_{108}H_{147}N_4Si_{18}$: 2003,7473; found: 2003.7451.

S3. Crystal structures and X-Ray Diffraction data for compounds 7, 12, 13 and 14

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 1997927 (**7**), 1998202(**12**), 1998195 (**13**) and 1998197(**14**). The crystallographic data is shown below.

S3.1 Compound **7**



Bond precision: C-C = 0.0050 Å Wavelength=1.54184

Cell: a=14.4193(9) b=15.3229(7) c=18.2720(6)
alpha=90 beta=93.967(4) gamma=90

Temperature: 150 K

	Calculated	***Reported***
Volume	4027.4(3)	4027.5(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{52} H_{34} O_4 Si_2$	$C_{52} H_{34} O_4 Si_2$
Sum formula	$C_{52} H_{34} O_4 Si_2$	$C_{52} H_{34} O_4 Si_2$
M_r	778.97	778.97
D_x (g cm^{-3})	1.285	1.285
Z	4	4
Mu (mm^{-1})	1.177	1.178
F000	1624.0	1624.0
F000’	1630.39	
h,k,l_{max}	17,18,22	17,18,22
N_{ref}	7644	7641
T_{min},T_{max}	0.657,0.799	0.674,0.836
$T_{min'}$	0.530	

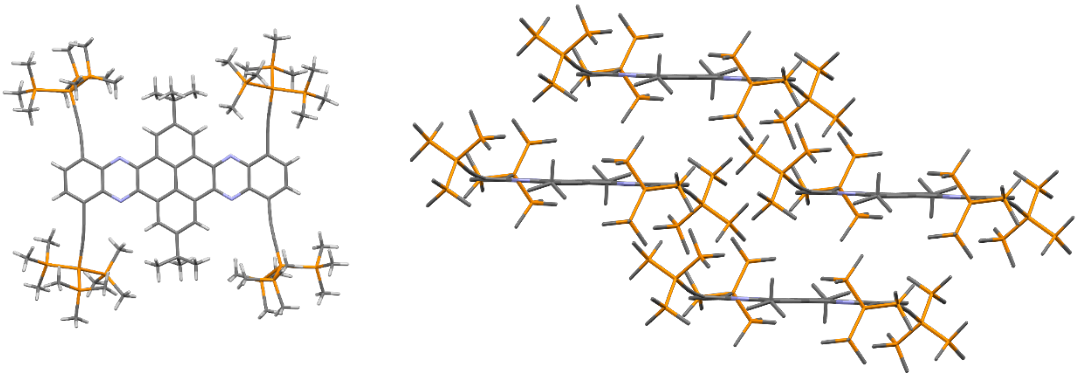
Correction method= #
Reported T Limits: T_{min}=0.674 T_{max}=0.836

AbsCorr = ANALYTICAL

Data completeness= 1.000 Theta(max)= 69.999
R(reflections)= 0.0692 (5190) wR2(reflections)= 0.2211 (7641)

S = 1.033 N_{par}= 650

S3.2 Compound **12**



Bond precision: C-C = 0.0038 Å Wavelength=1.54184

Cell: a=9.8911(2) b=16.0352(4) c=19.2371(5)
alpha=88.170(2) beta=76.903(2) gamma=73.041(2)

Temperature: 150 K

	Calculated	***Reported***
Volume	2840.61(12)	2840.61(12)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{80} H_{134} N_4 Si_{16}$, 2($C_7 H_8$)	$C_{80} H_{134} N_4 Si_{16}$, 2($C_7 H_8$)
Sum formula	$C_{94} H_{150} N_4 Si_{16}$	$C_{94} H_{150} N_4 Si_{16}$
Mr	1785.62	1785.61
D_x (g cm^{-3})	1.044	1.044
Z	1	1
Mu (mm^{-1})	1.998	2.002
F000	966.0	966.0
F000’	971.77	
h,k,l_{max}	11,19,23	11,19,23
N_{ref}	10543	10521
T_{min},T_{max}	0.544,0.812	0.599,0.844
T_{min}’	0.394	

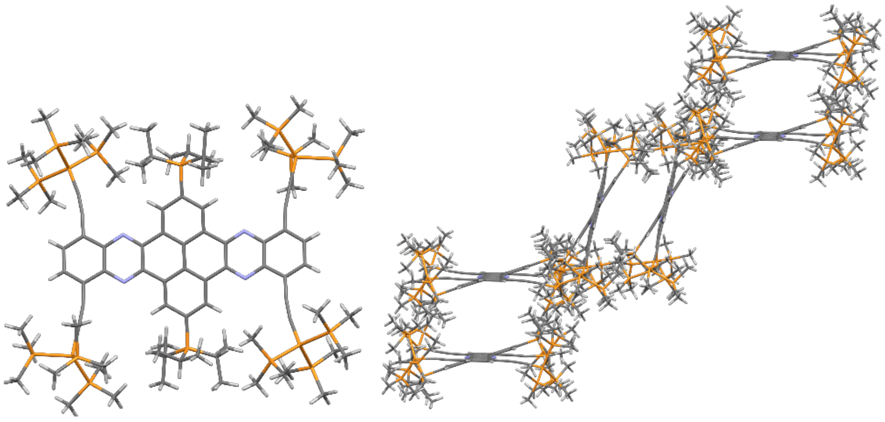
Correction method= #
Reported T Limits: T_{min}=0.599 T_{max}=0.844

AbsCorr = ANALYTICAL

Data completeness= 0.998 Theta(max)= 68.994
R(reflections)= 0.0477 (9007) wR2(reflections)= 0.1419 (10521)

S = 1.035 N_{par}= 576

S3.3 Compound **13**



Bond precision: C-C = 0.0067Å Wavelength=1.54184

Cell: a=43.6057(12) b=8.5663(2) c=33.2570(9)
alpha=90 beta=101.568(3) gamma=90

Temperature: 150 K

	Calculated	***Reported***
Volume	12170.5(6)	12170.5(6)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	$C_{90}H_{158}N_4Si_{18}$ [+solvent]	$C_{90}H_{158}N_4Si_{18}$
Sum formula	$C_{90}H_{158}N_4Si_{18}$ [+solvent]	$C_{90}H_{158}N_4Si_{18}$
M_r	1801.82	1801.81
D_x(g cm^{-3})	0.983	0.983
Z	4	4
Mu (mm^{-1})	2.049	2.049
F000	3912.0	3912.0
F000’	3936.82	
h,k,l_{max}	52,10,40	52,10,40
N_{ref}	11320	11316
T_{min},T_{max}	0.825,0.868	0.552,0.876
$T_{min'}$	0.299	

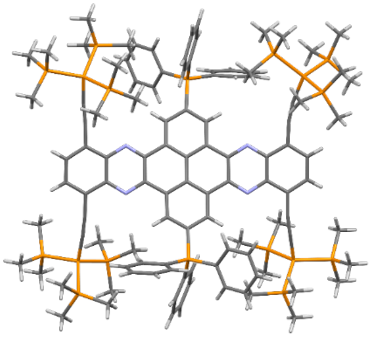
Correction method= #
Reported T Limits: T_{min}=0.552 T_{max}=0.876

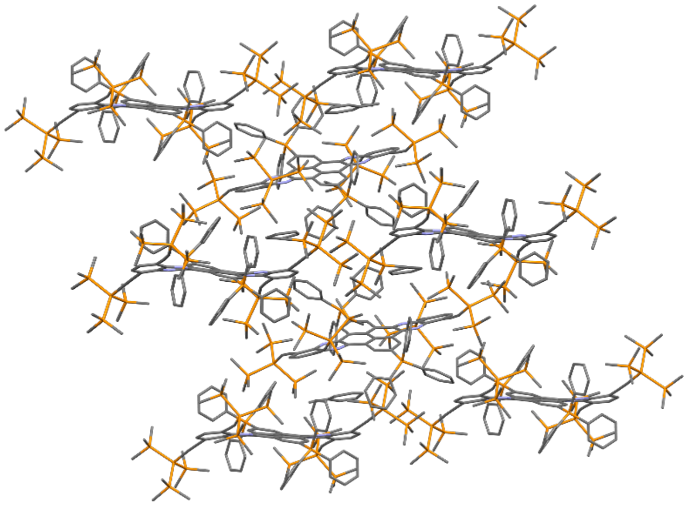
AbsCorr = ANALYTICAL

Data completeness= 1.000 Theta(max)= 68.987
R(reflections)= 0.0933 (8597) wR2(reflections)= 0.2693(11316)

S = 1.023 N_{par}= 643

S3.4 Compound **14**





Bond precision: C-C = 0.0148 Å Wavelength=1.54184

Cell: a=22.1092(12) b=22.3180(13) c=29.0414(13)
alpha=74.547(4) beta=79.773(4) gamma=71.053(5)

Temperature: 150 K

	Calculated	***Reported***
Volume	12998.3(13)	12998.0(10)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{108} H_{146} N_4 Si_{18}$, $C_7 H_8$	2($C_{108} H_{146} N_4 Si_{18}$), 2($C_7 H_8$)
Sum formula	$C_{115} H_{154} N_4 Si_{18}$	$C_{230} H_{308} N_8 Si_{36}$
Mr	2098.05	4196.07
Dx, g cm^{-3}	1.072	1.072
Z	4	2
Mu (mm^{-1})	1.988	1.988
F000	4496.0	4496.0
F000’	4522.55	
h,k,l_{max}	26,27,35	26,27,35
Nref	48333	48242
T_{min},T_{max}	0.658,0.858	0.615,0.896
T_{min}’	0.372	

Correction method= #
Reported T Limits: T_{min}=0.615 T_{max}=0.896

AbsCorr = ANALYTICAL

Data completeness= 0.998 Theta(max)= 69.000
R(reflections)= 0.1286 (21047) wR2(reflections)= 0.4078 (48242)

S = 1.020 N_{par}= 2431

S4. General Methods for Calculations

The geometries from the crystallographic data were first optimized in cartesian space to a very small gradient with the GFN2-xTB method (Geometry, Frequency, Non-covalent, Extended Tight-Binding)[5] and then they were optimized at the B3LYP-6-31G(d,p) level.

S4.1 Strain calculations

The strain energies for the three systems under consideration were estimated with a simplified H-capped molecular analogue where the bulky groups were deleted, the H-capping atoms optimized, and then the molecule allowed to relax.

	H-capped molecules		
	Aromatic core	Polycyclic core	Acetylenes
	Total Strain E. *\/ Kcal/mol*	Total Strain E. *\/ Kcal/mol*	Total Strain E. *\/ Kcal/mol*
12	4.0	3.1	0.9
13	8.2	5.1	3.1
14	11.2	9.8	1.4

	H-capped molecules	**StrainViz**	
	Total Strain E. / *Kcal/mol*	Max. bond strain E. / *Kcal/mol*	Min. bond strain E. / *Kcal/mol*
12	4.0	0.44	0.00
13	8.2	0.62	0.00
14	11.2	0.45	0.01

S5. Fluorescence Quantum Yield of products 12, 13 and 14.

Quantum yields were calculated following the next equation:

$$\Phi_f^i = \Phi_f^s \cdot \frac{F^i\, f_s\, \eta_i^2}{F^s\, f_i\, \eta_s^2}$$

where Φ_f^s stands for the quantum yield of the reference standard, F^i for the measured fluorescence (area) of a solution at known concentration of products **12, 13** and **14** at the selected excitation wavelength, F^S for the measured fluorescence (area) of a solution at known concentration of reference standard at the selected excitation wavelength.

$f_s = 1 - 10^{-A_s(\lambda_{exc})}$ stands for the absorption factor of a solution at known concentration of reference standard at the excitation wavelength, $f_i = 1 - 10^{-A_i(\lambda_{exc})}$ stands for the absorption factor of a solution at known concentration of products **12**, **13** and **14** at the excitation wavelength. Finally, η_i is the refraction index of the solvent of the solution of compounds **12**, **13** and **14**; η_s refers to the refraction index of the solvent of the solution of the reference standard.

The error of was calculated as follows:

$$Error = \frac{\sqrt{\sum_{n=m}^{m}(\Phi_{f,\,i_n} - \bar{\Phi}_{f,i})^2}}{m}$$

To measure quantum yield of **12**, **13** and **14**, 9,10-Diphenylanthracene (DPA) was selected as reference standard (Φ_f^{DPA} = 0.93)[6] at 7.57·10^{-7} M in cyclohexane (η_{cHex} = 1.45). The excitation wavelength was set at 340 nm and three different solutions at different concentration of **12**, **13** and **14** were analyzed.

Quantum yields ($\Phi_f^{\mathbf{12}}$, $\Phi_f^{\mathbf{13}}$and $\Phi_f^{\mathbf{14}}$) are expressed as the average of the three measurements with its associated error.

Entry	**Concentration (mol·L^{-1})**	**Φ_f^{12} (%)**
1	2.70E-07	19.56
2	4.05E-07	17.58
3	5.40E-07	16.76

$\bar{\Phi}_f^{\mathbf{12}}$ = 17.90 $\pm$ 0.68

Entry	**Concentration (mol·L^{-1})**	**Φ_f^{13} (%)**
1	2.50E-07	18.06
2	3.75E-07	15.24
3	5.00E-07	17.57

$\bar{\Phi}_f^{\mathbf{13}}$= 16.91 ± 0.71

Entry	**Concentration (mol·L^{-1})**	**Φ_f^{14} (%)**
1	1.93E-07	20.55
2	2.90E-07	20.19
3	3.86E-07	19.36

$\bar{\Phi}_f^{\mathbf{14}}$ = 20.03 ± 0.29

S6. ^{1}H and ^{13}C NMR Spectra

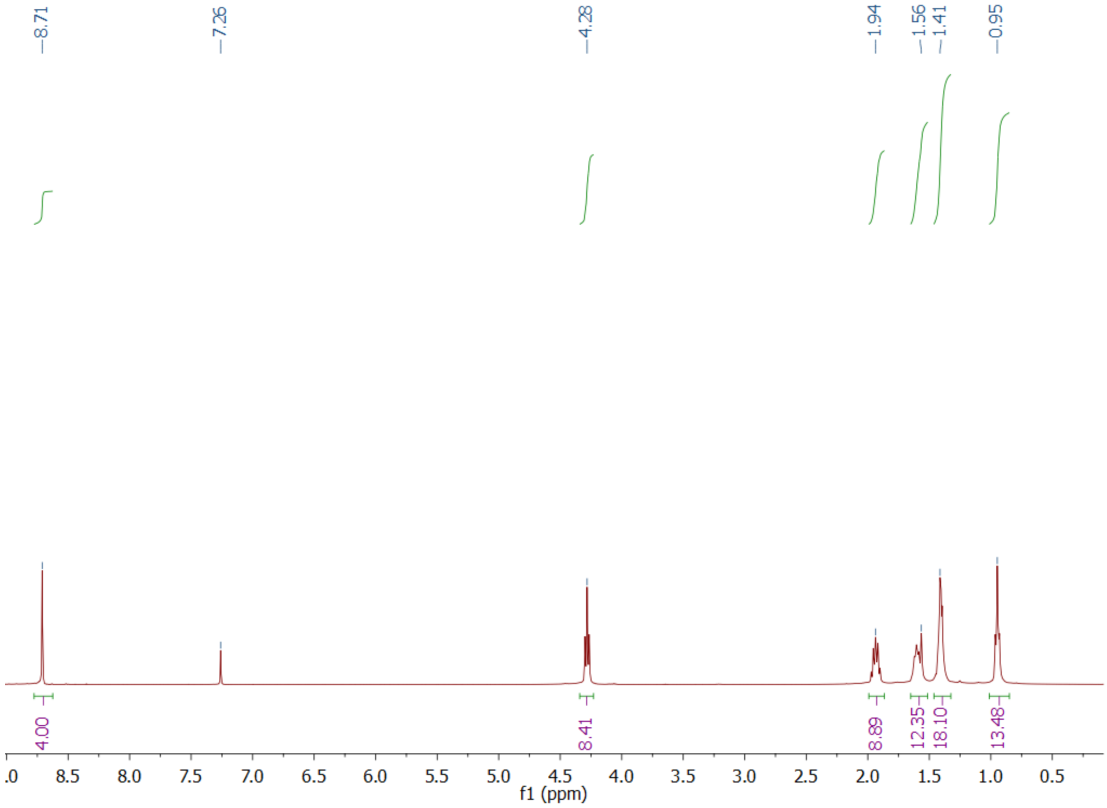


Figure S10. ^{1}H NMR on $CDCl_3$ of compound **3**.

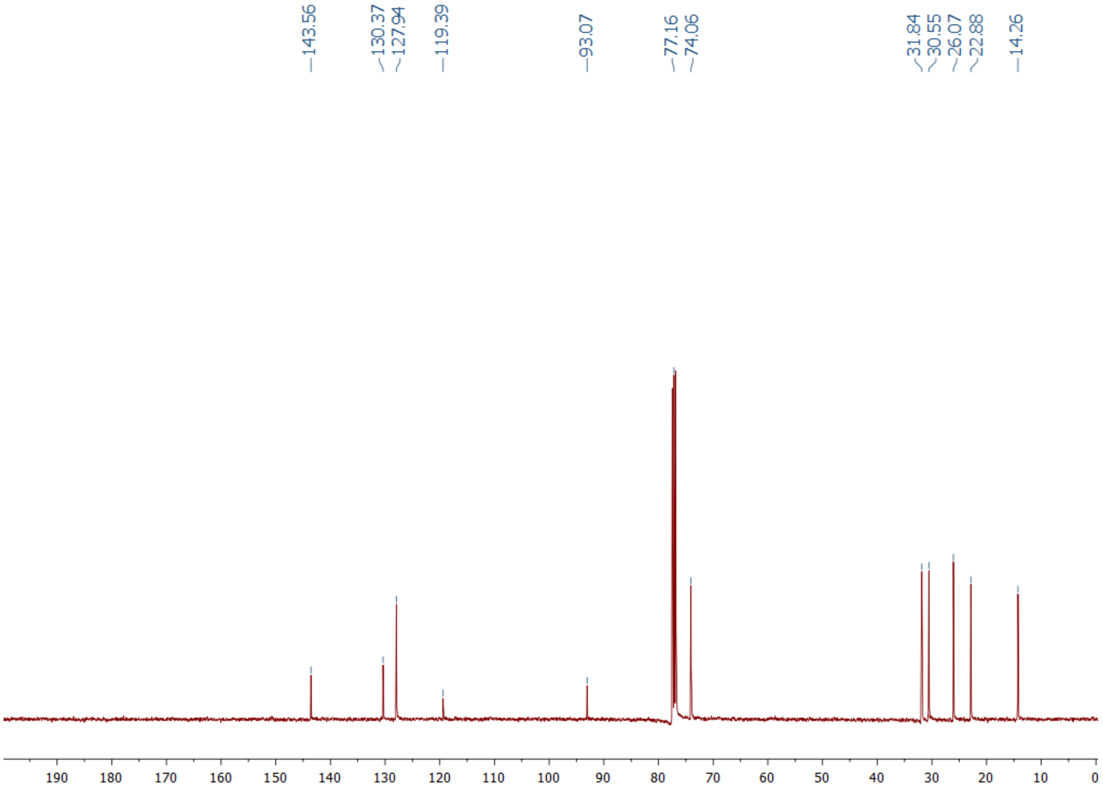


Figure S11. ^{13}C NMR on $CDCl_3$ of compound **3**.

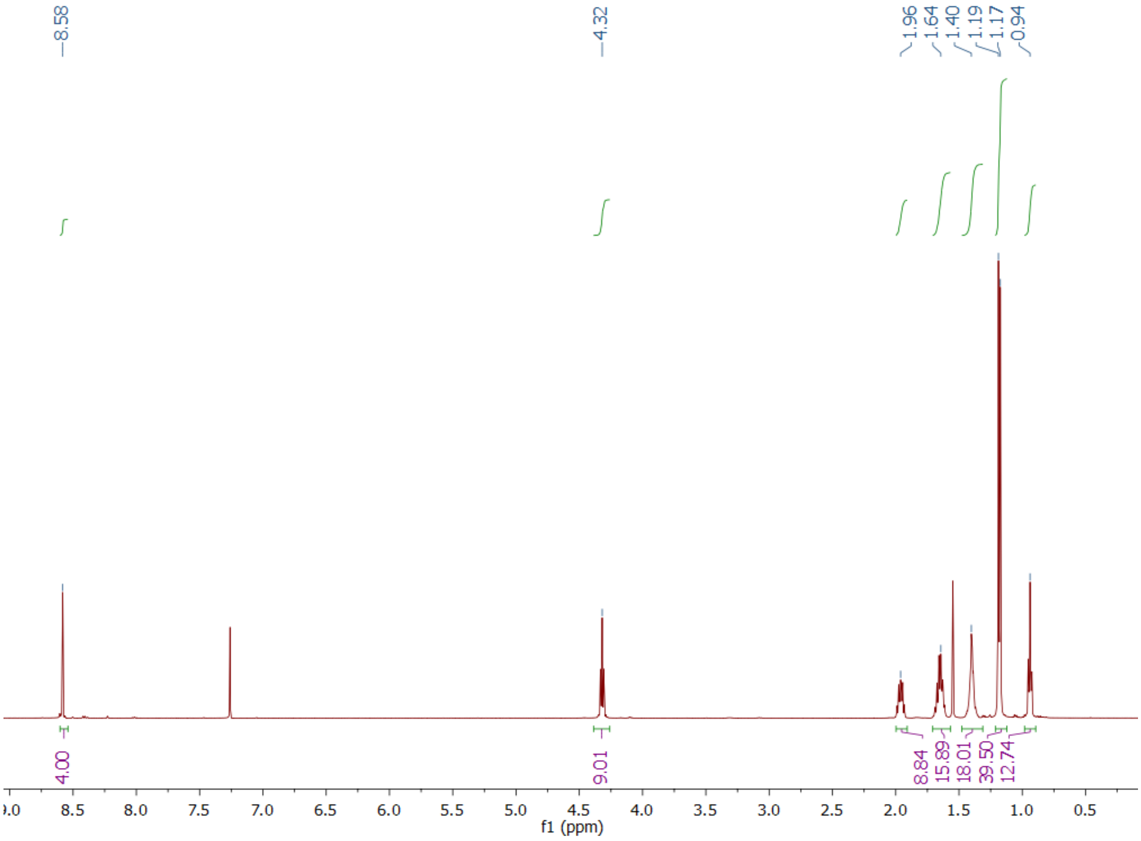


Figure S12. ^{1}H NMR on $CDCl_3$ of compound **4**.

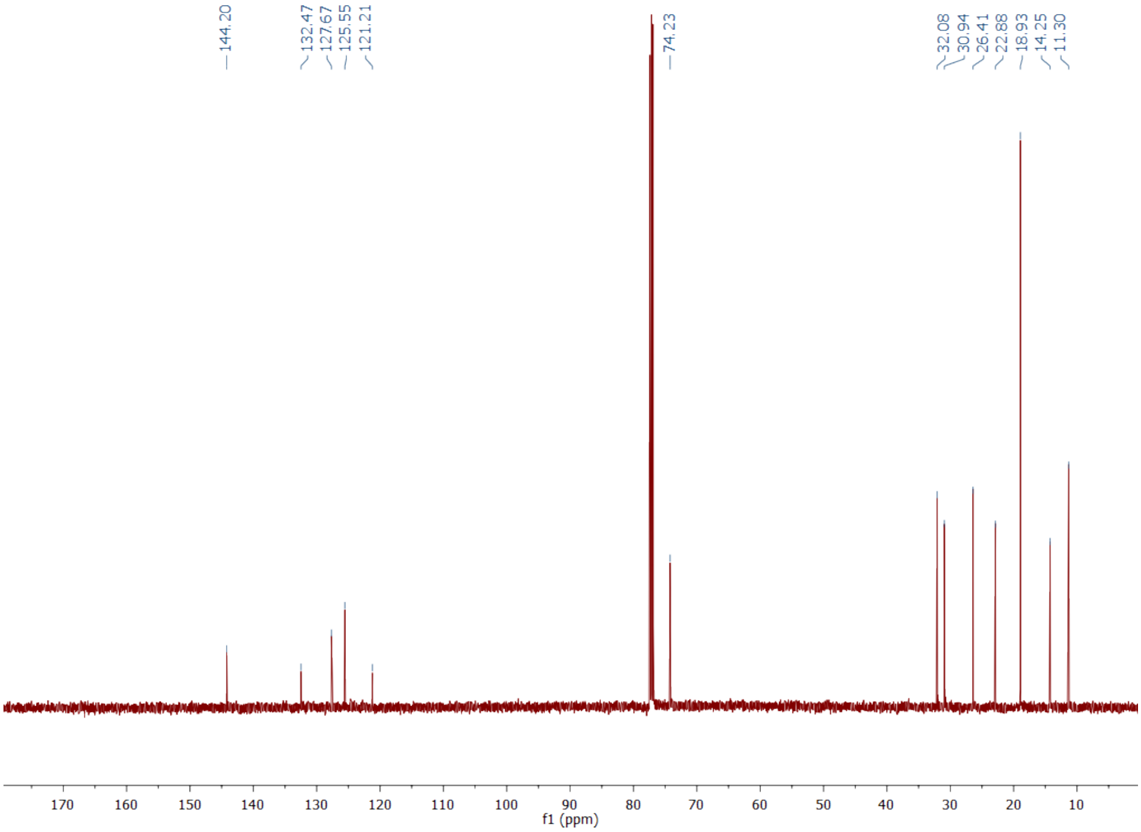


Figure S13. ^{13}C NMR on $CDCl_3$ of compound **4**.

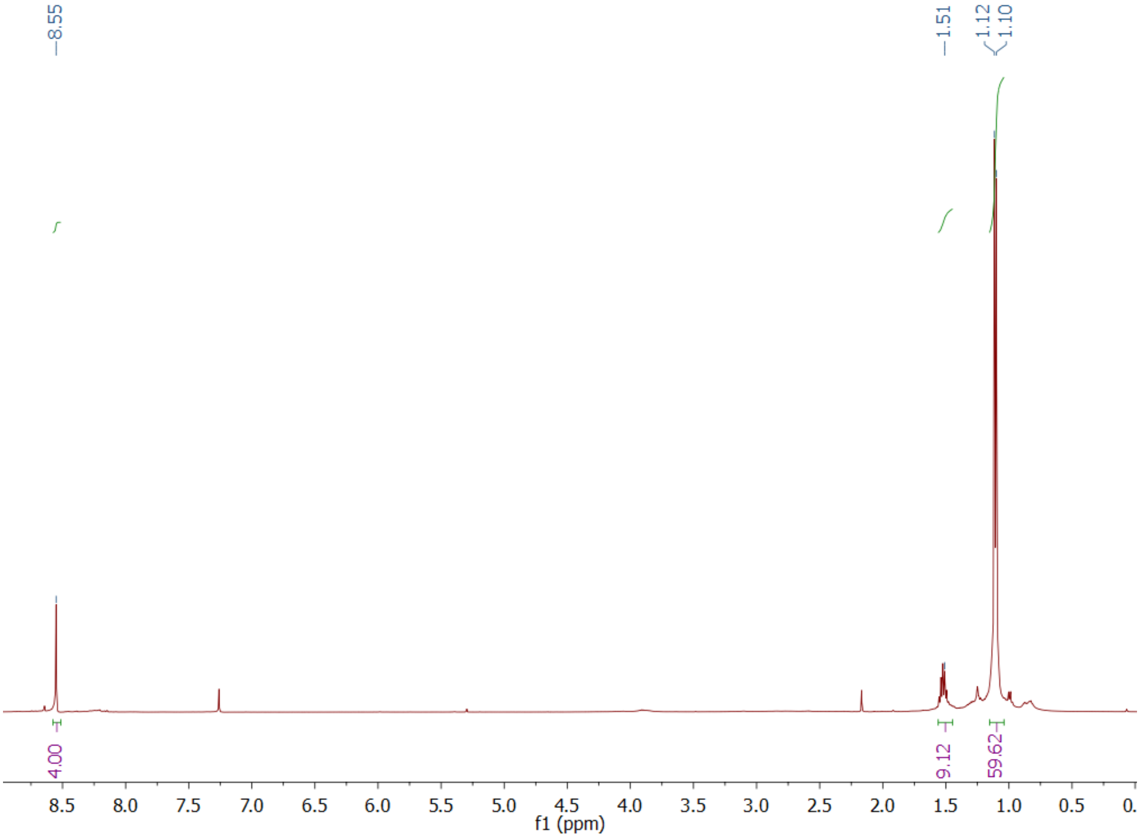


Figure S14. ^{1}H NMR on $CDCl_3$ of compound **5**.

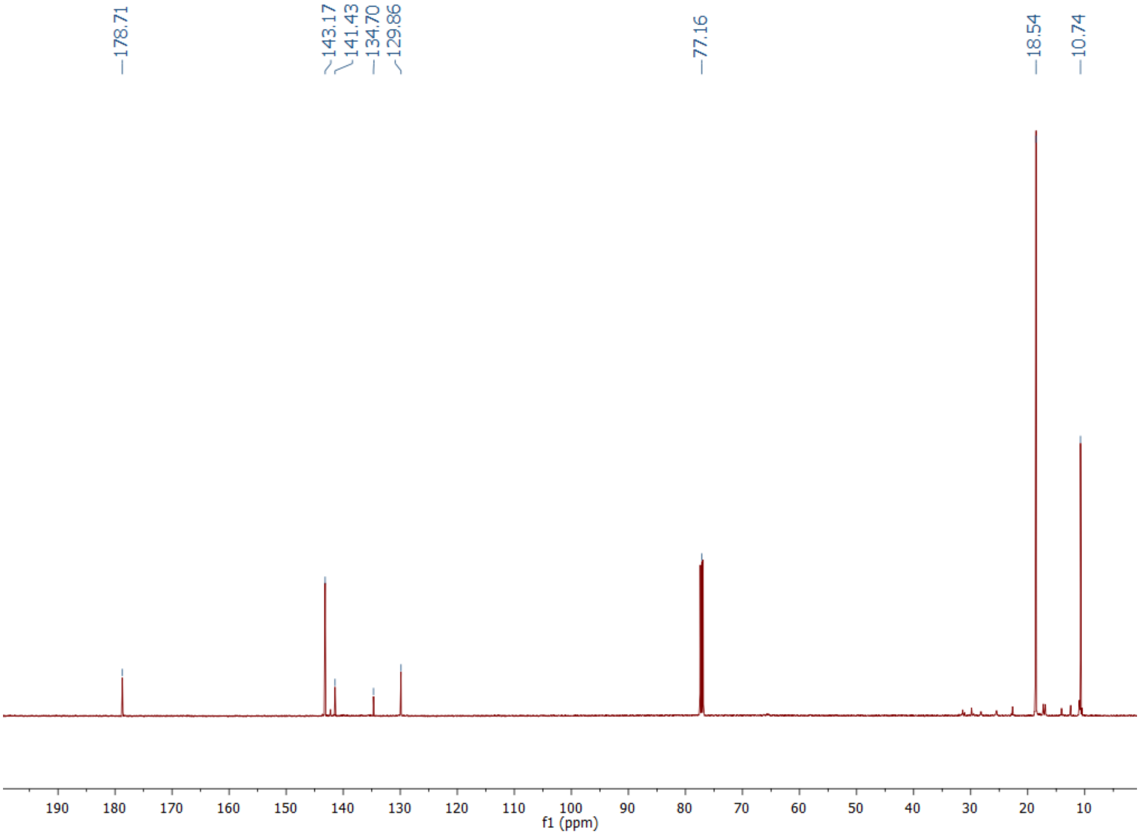


Figure S15. ^{13}C NMR on $CDCl_3$ of compound **5**.

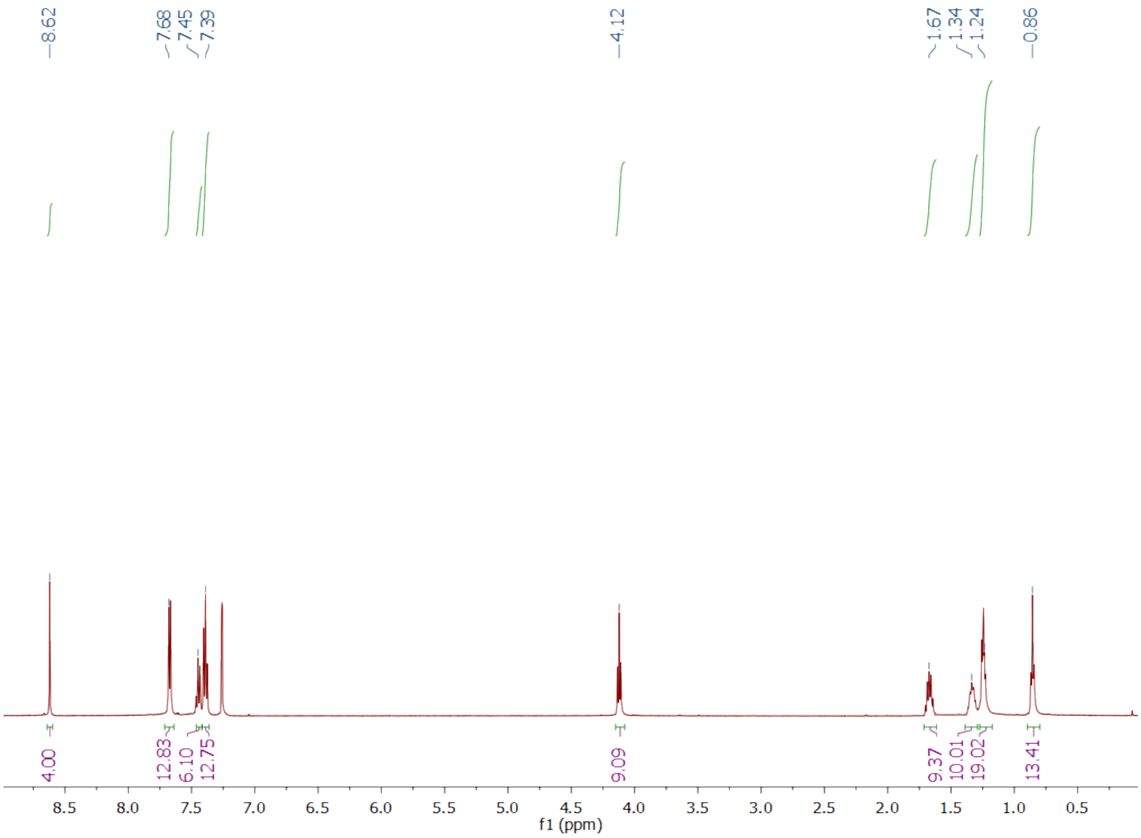


Figure S16 ^{1}H NMR on $CDCl_3$ of compound **6**.

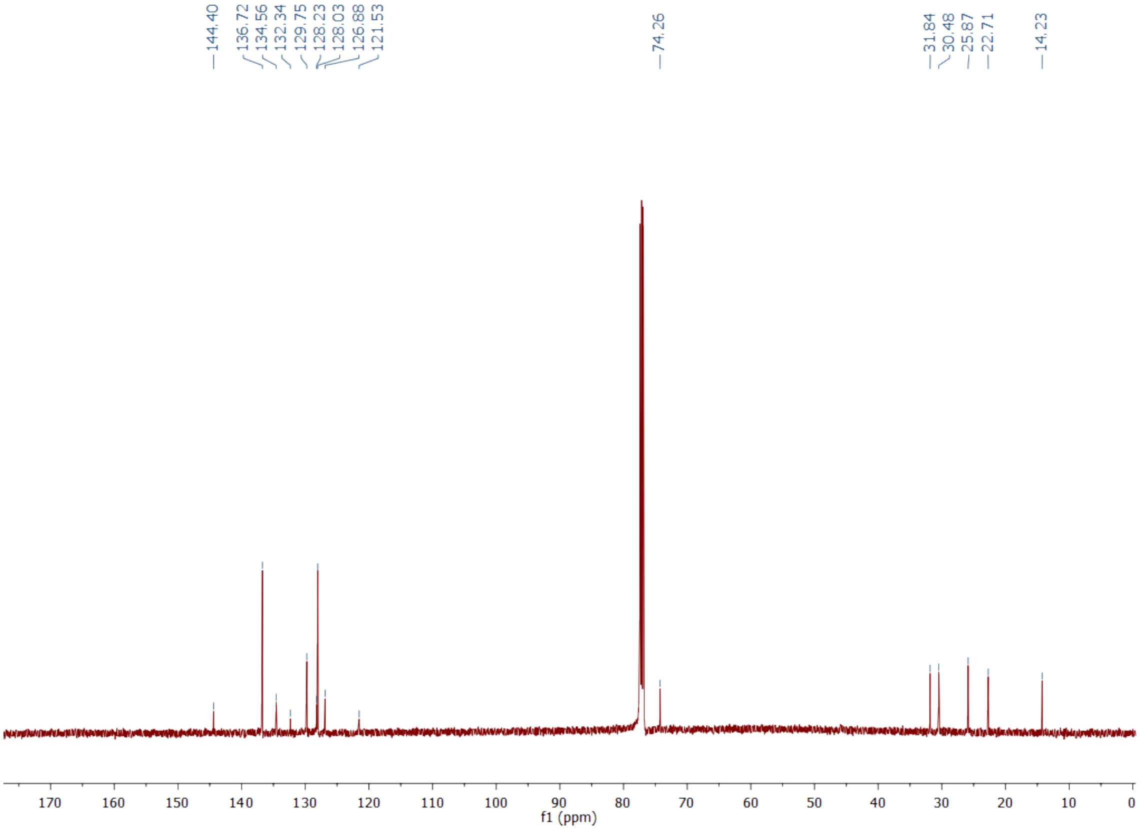


Figure S17 *^{13}C NMR on $CDCl_3$ of compound* ***6.***

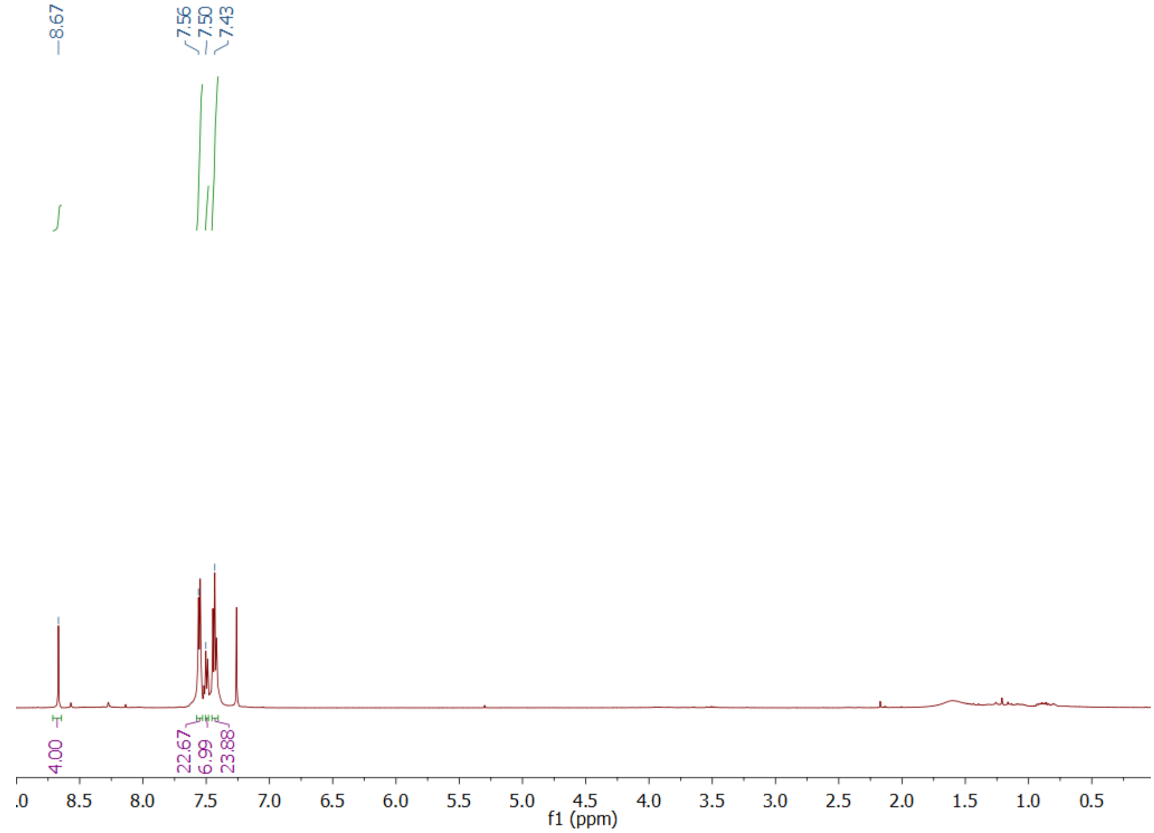


Figure S18 ^{1}H NMR on $CDCl_3$ of compound **7.**

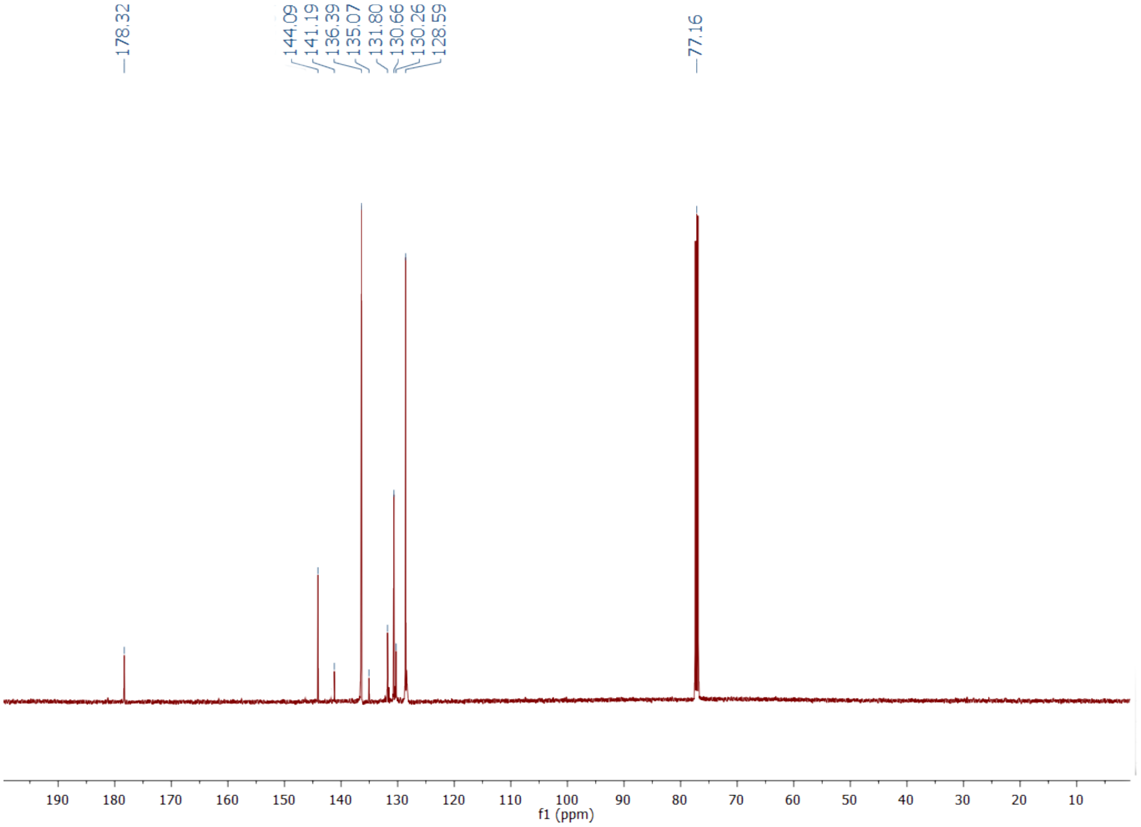


Figure S19. ^{13}C NMR on $CDCl_3$ of compound **7.**

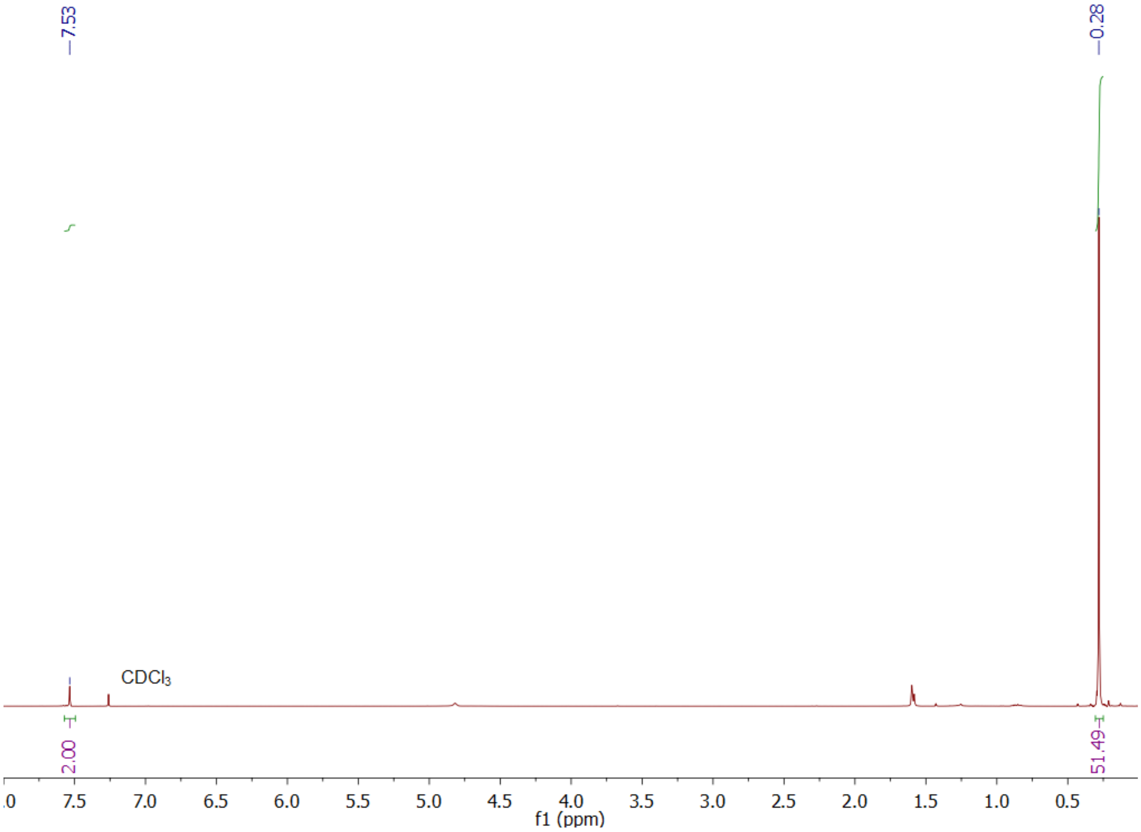


Figure S20 ^{1}H NMR on $CDCl_3$ of compound **10.**

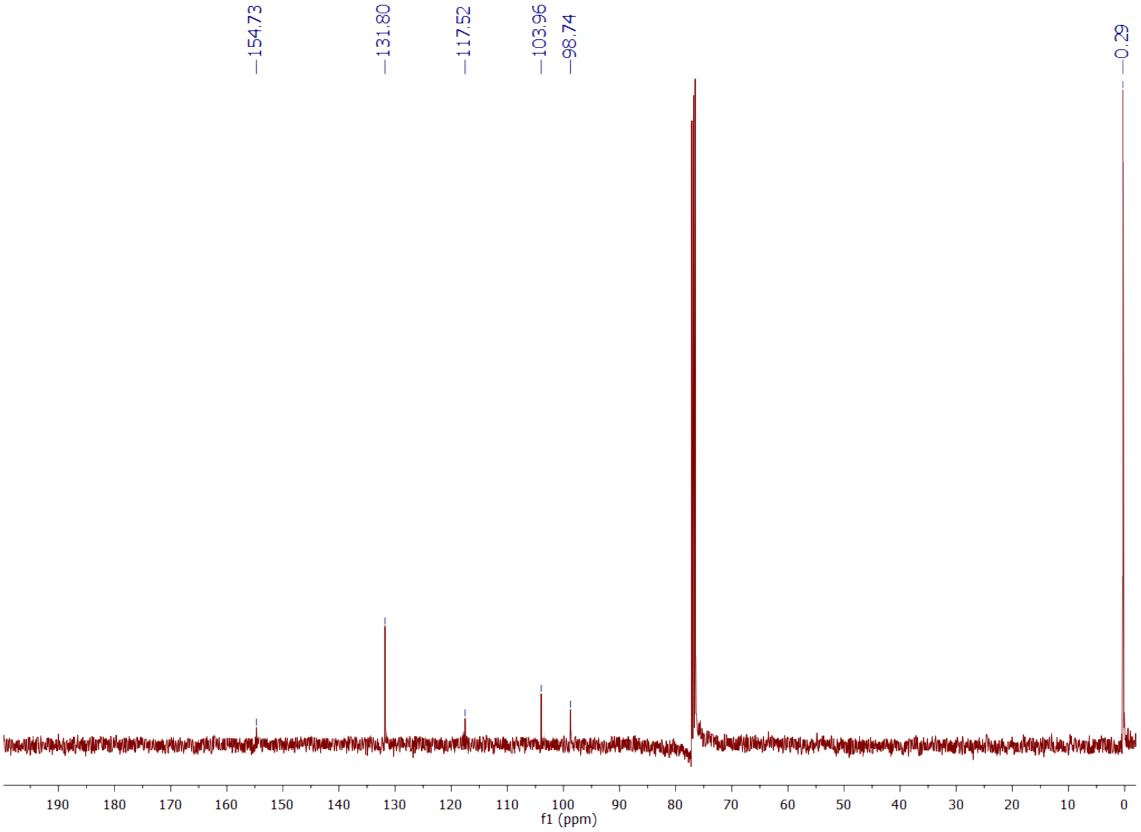


Figure S21 ^{13}C NMR on $CDCl_3$ of compound **10**.

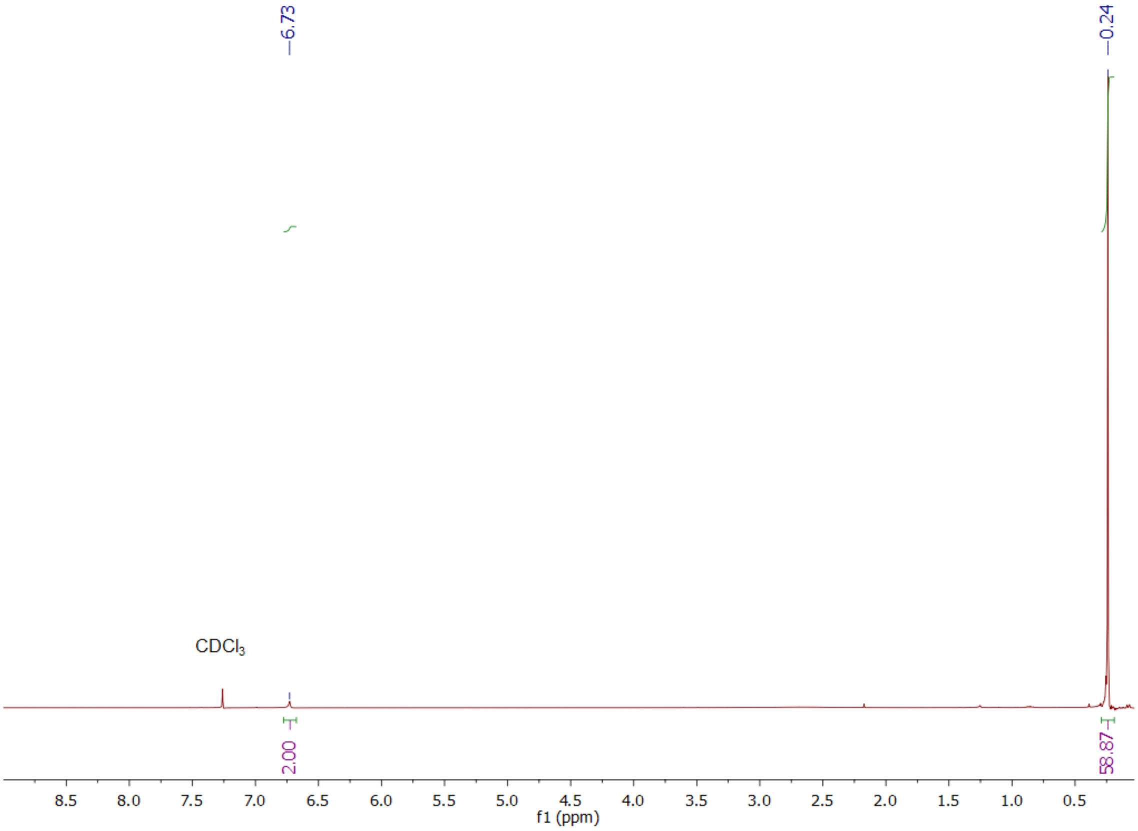


Figure S22 ^{1}H NMR on $CDCl_3$ of compound **11.**

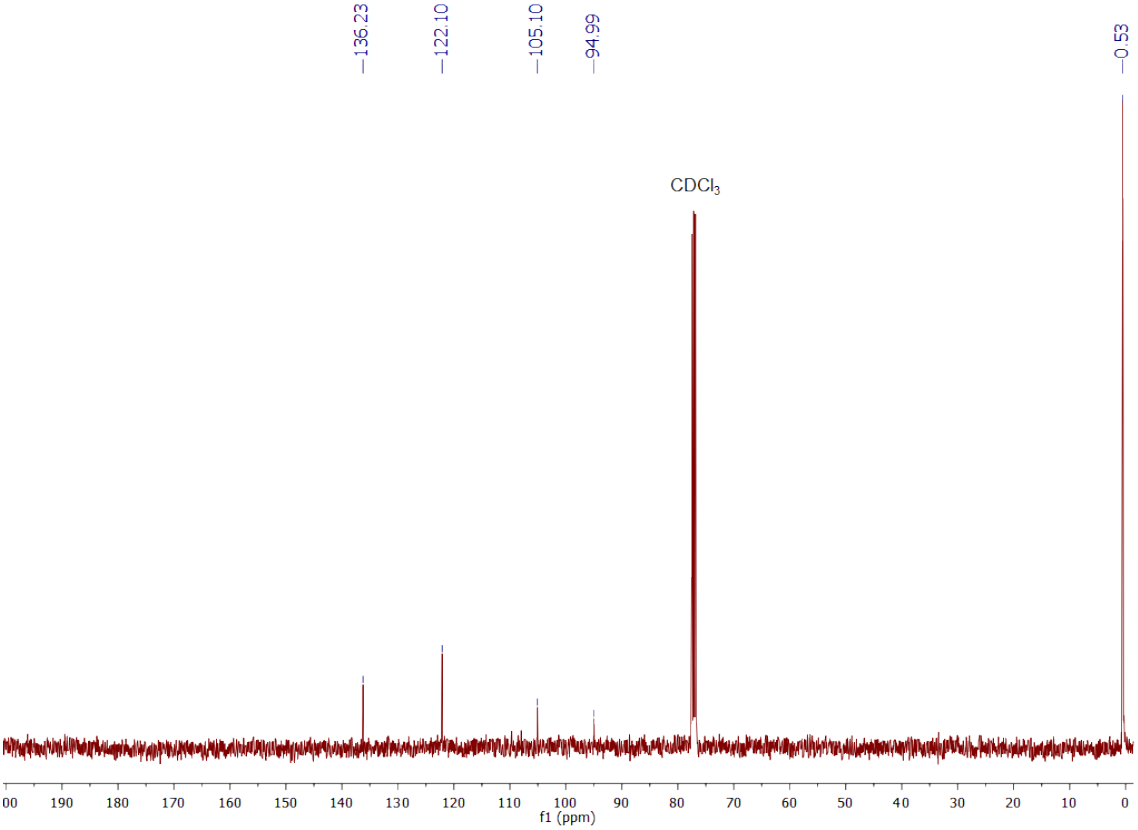


Figure S23 ^{13}C NMR on $CDCl_3$ of compound **11.**

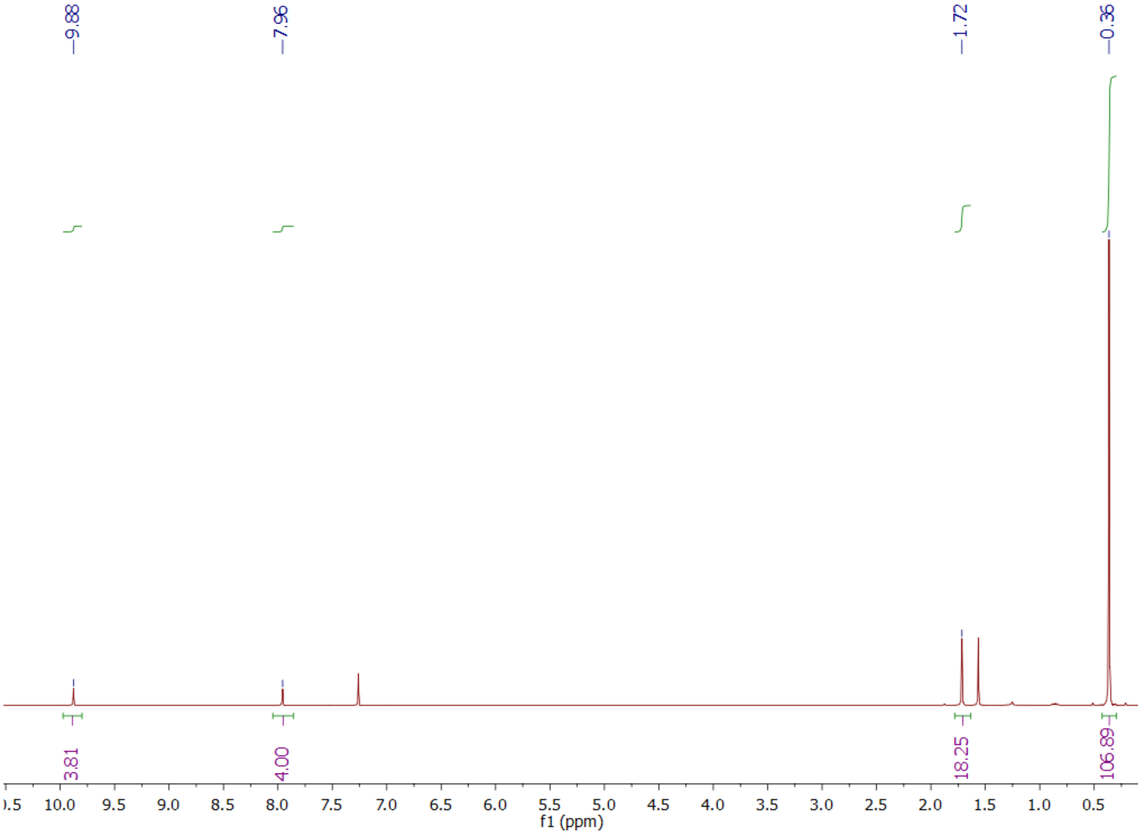


Figure S24. ^{1}H NMR on $CDCl_3$ of compound **12**.

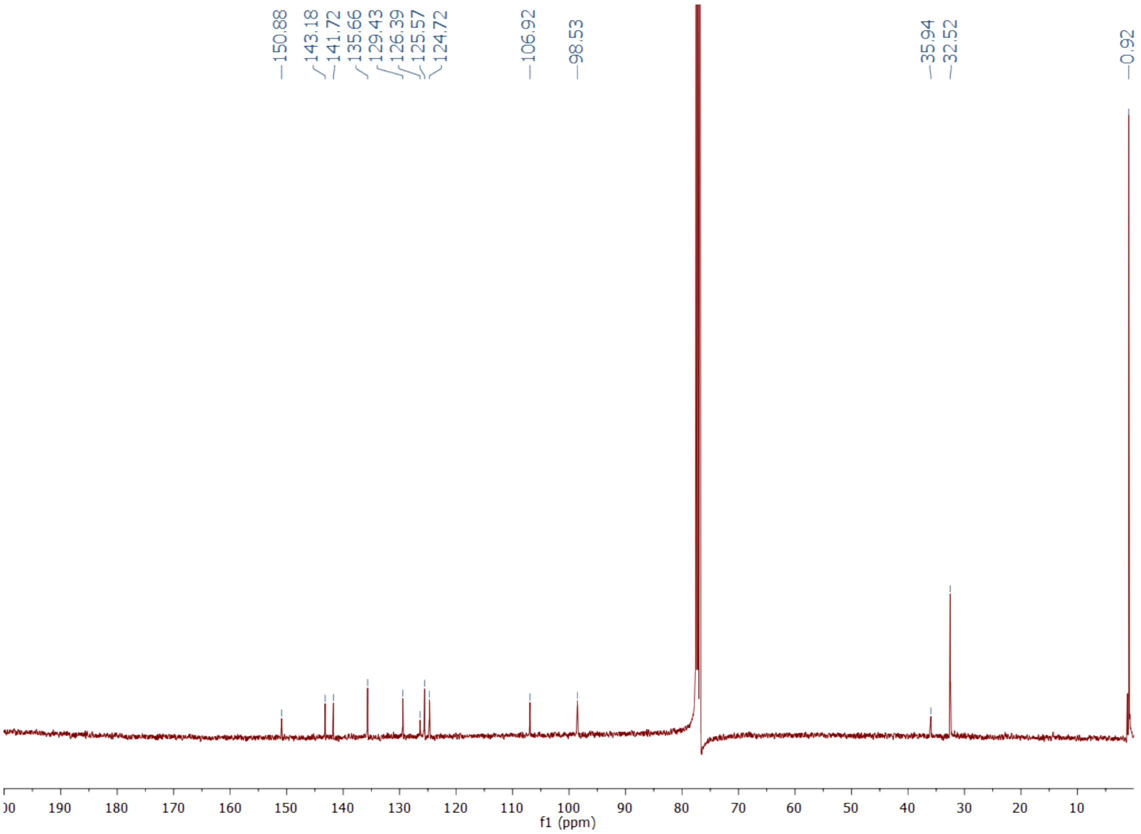


Figure S25. ^{13}C NMR on $CDCl_3$ of compound **12**.

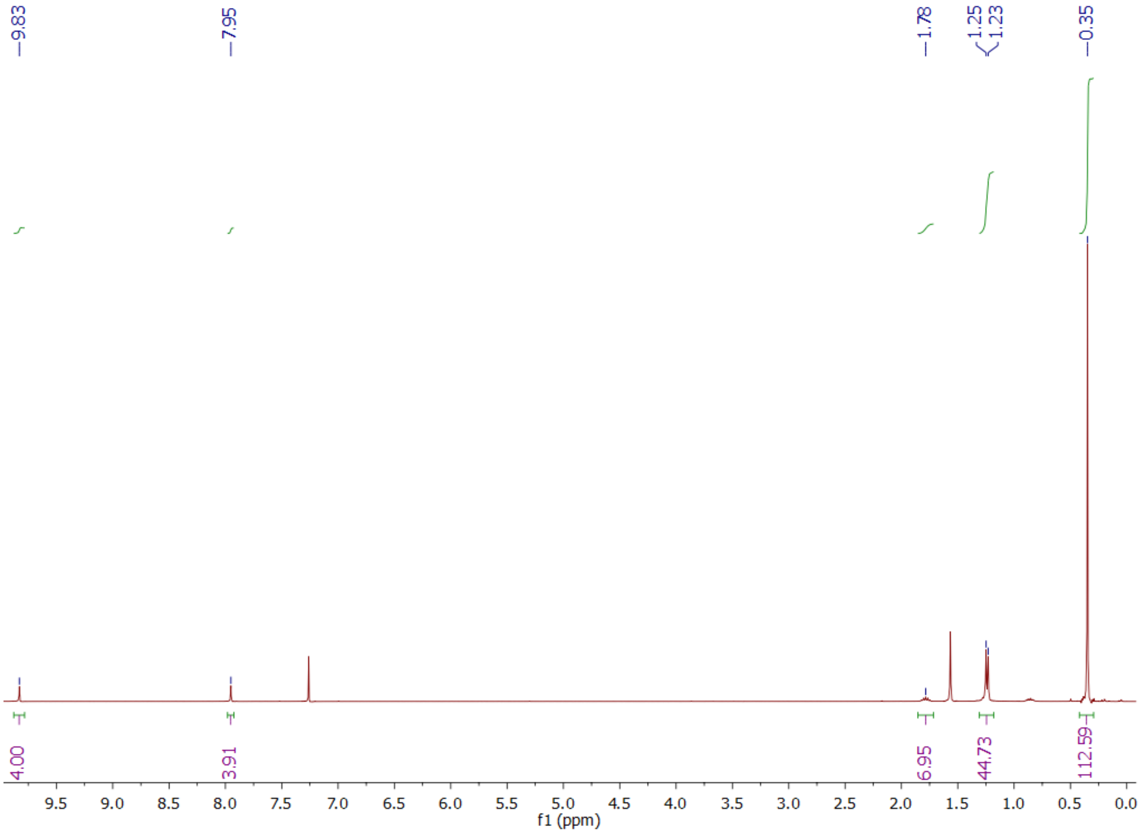


Figure S26. ^{1}H NMR on $CDCl_3$ of compound **13**.

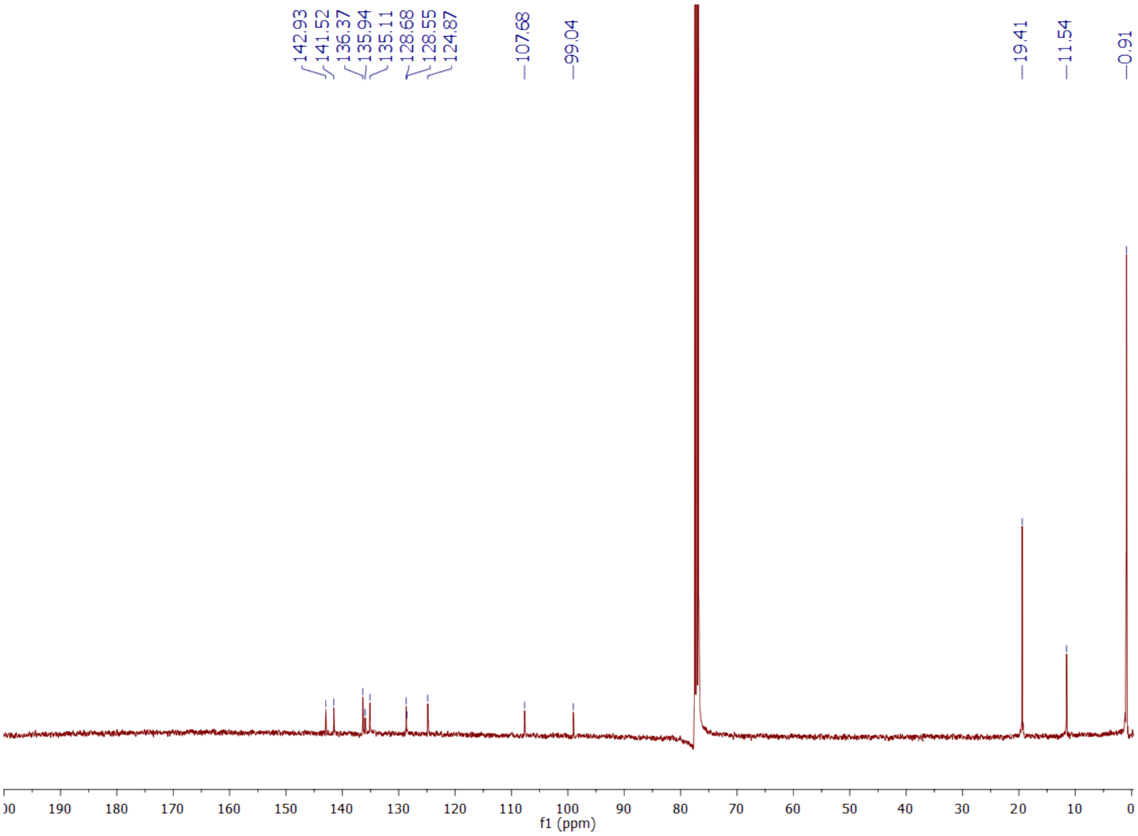


Figure S27. ^{13}C NMR on $CDCl_3$ of compound **13**.

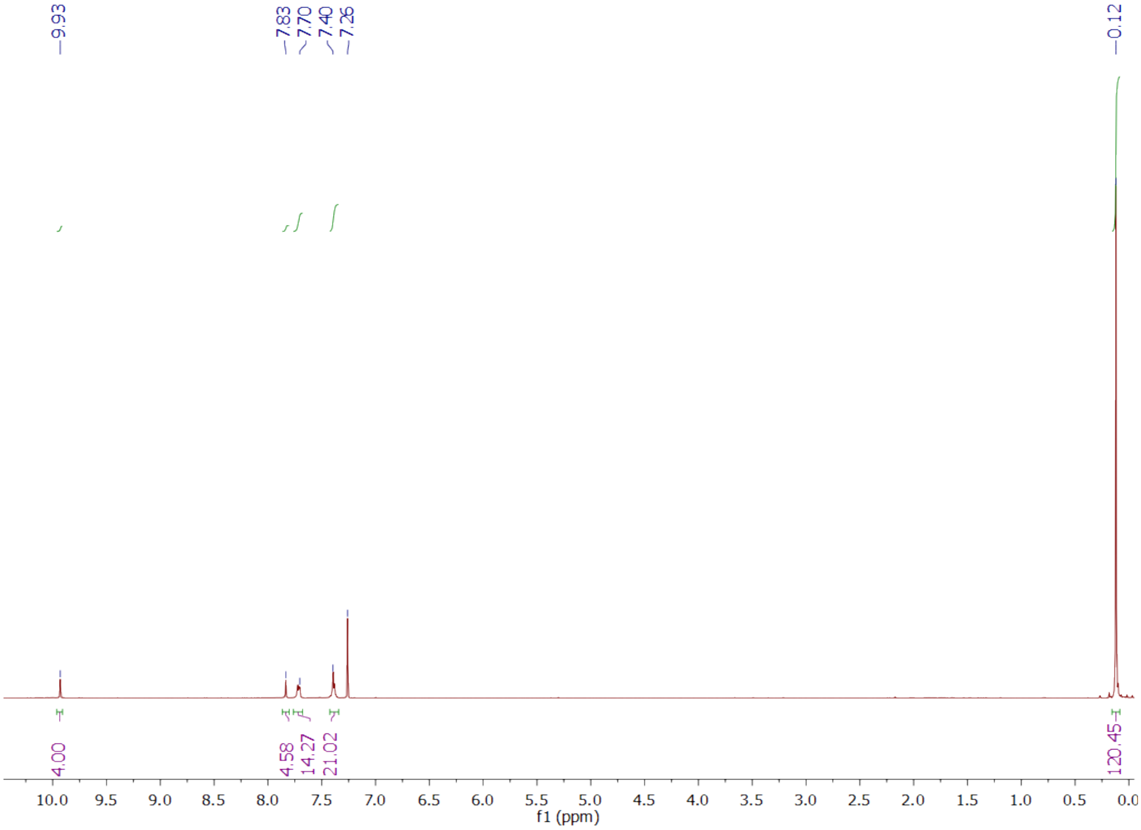


Figure S28. ^{1}H NMR on $CDCl_3$ of compound **14**.

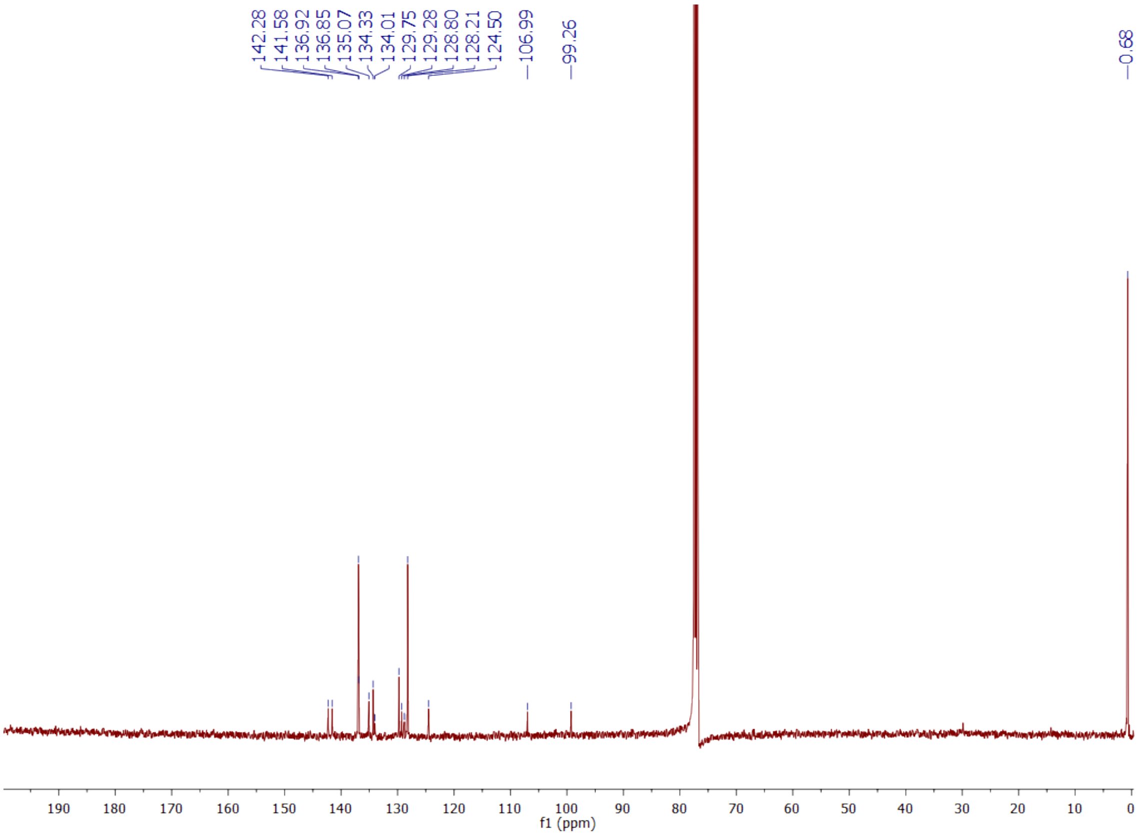


Figure S29. ^{13}C NMR on $CDCl_3$ of compound **14.**

S7. MS spectra

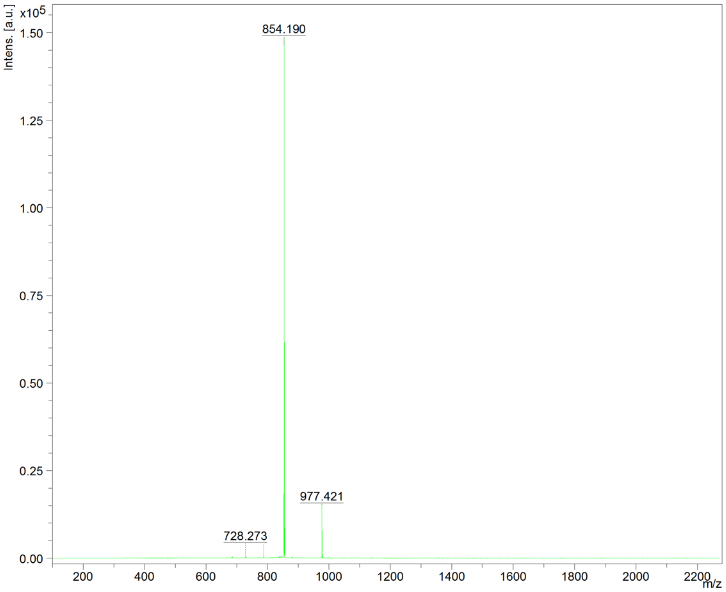


Figure S30. MS spectra of compound **3.**

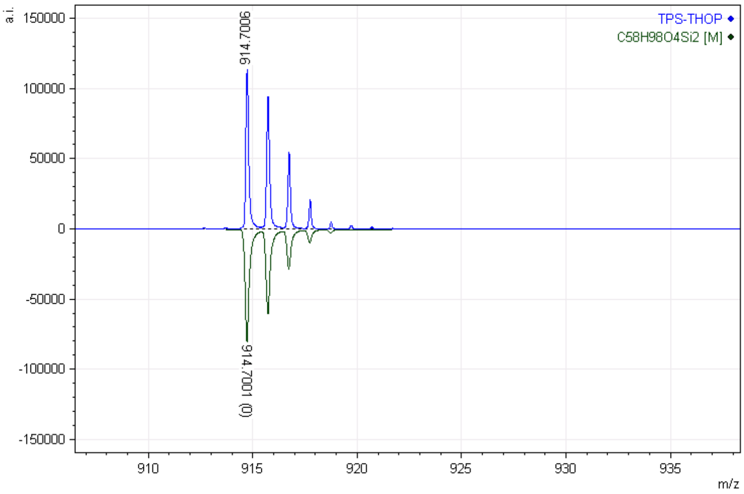


Figure S31. HRMS spectra for compound **4.**

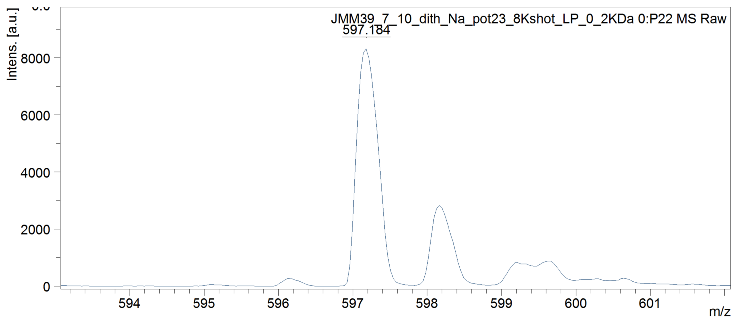


Figure S32. MS spectra for compound **5.**

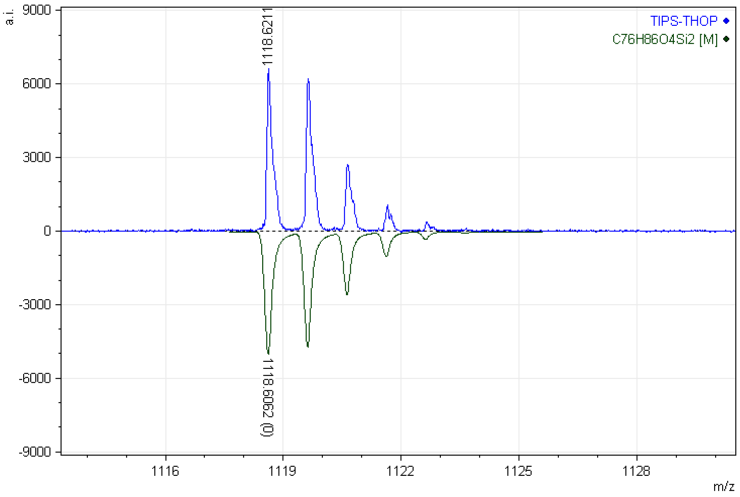


Figure S33. HRMS spectra for compound **6.**

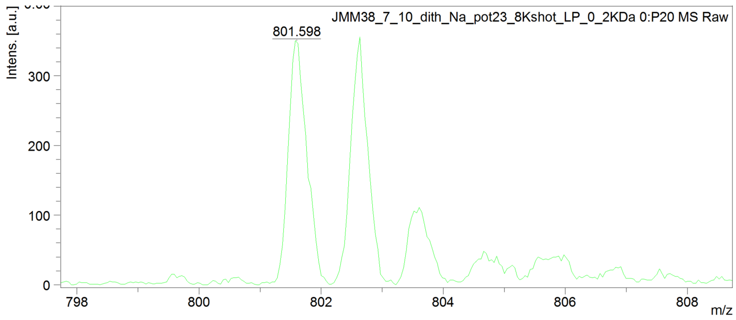


Figure S34. MS spectra for compound **7.**

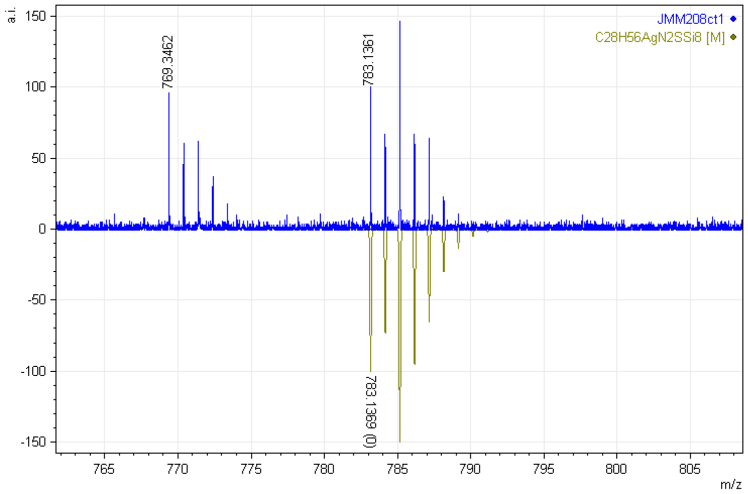


Figure S35. HRMS spectra for compound **10.**

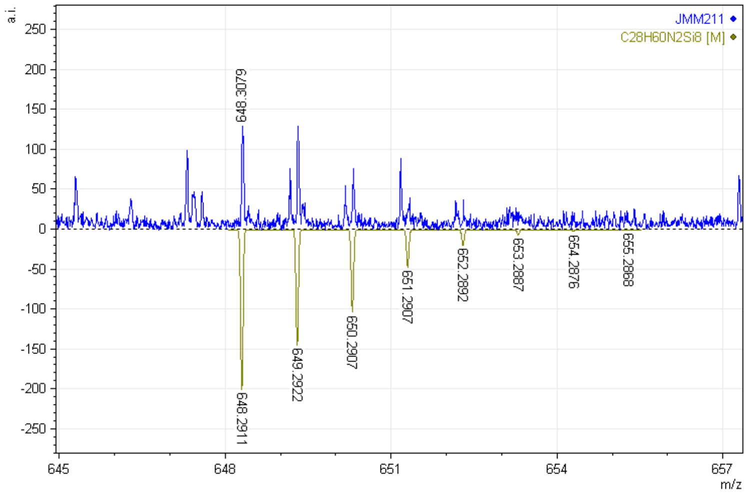


Figure S36. HRMS spectra for compound **11.**

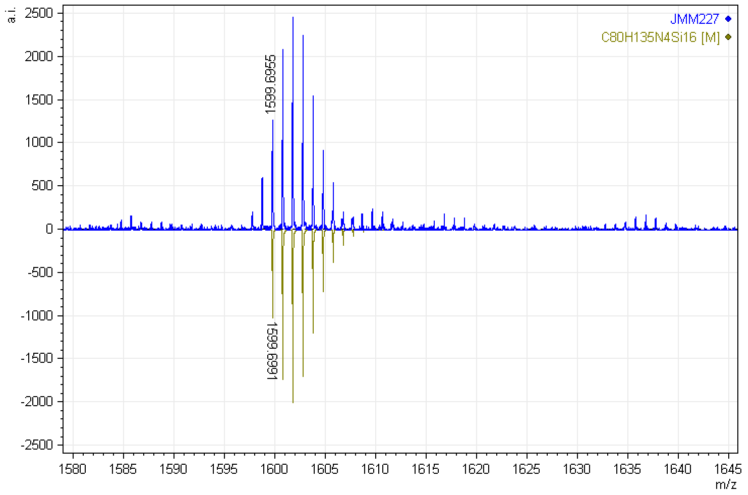


Figure S37. HRMS spectra for compound **12.**

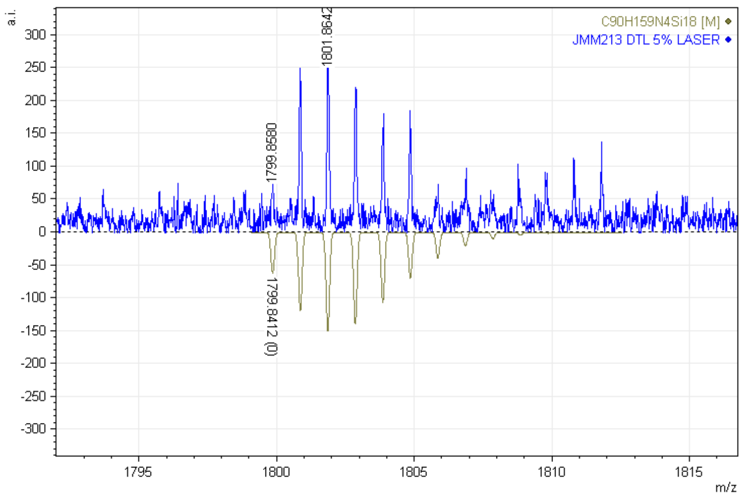


Figure S38. HRMS spectra for compound **13.**

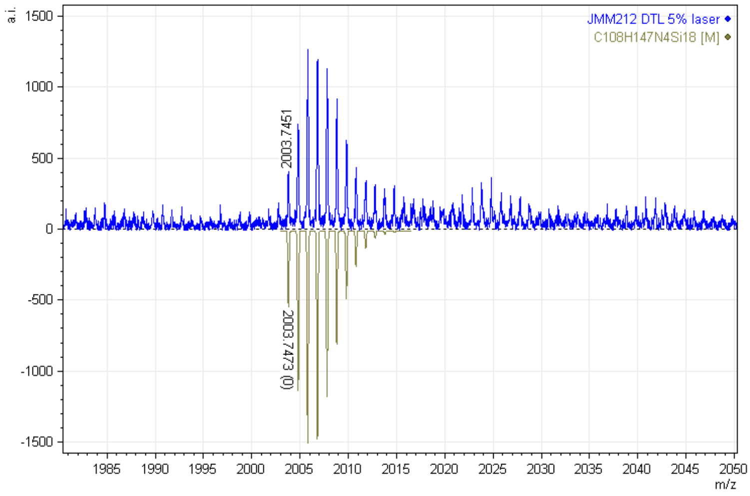


Figure S39. HRMS spectra for compound **14.**

S8. References

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