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An Investigation of Palladium-Catalyzed Stille-Type Cross-Coupling of Nitroarenes in Perylenediimide Series

Aline Makhloutah[1], Danylo Hatych[1], Thomas Chartier[1], Lou Rocard[1], Antoine Goujon[1], François-Xavier Felpin[2], and Piétrick Hudhomme[1]*

1. *Univ Angers, CNRS, MOLTECH-Anjou, SFR MATRIX, F- 49000 Angers, France*
2. *CNRS UMR 6230, CEISAM, Université de Nantes, F-44000 Nantes, France*

pietrick.hudhomme@univ-angers.fr

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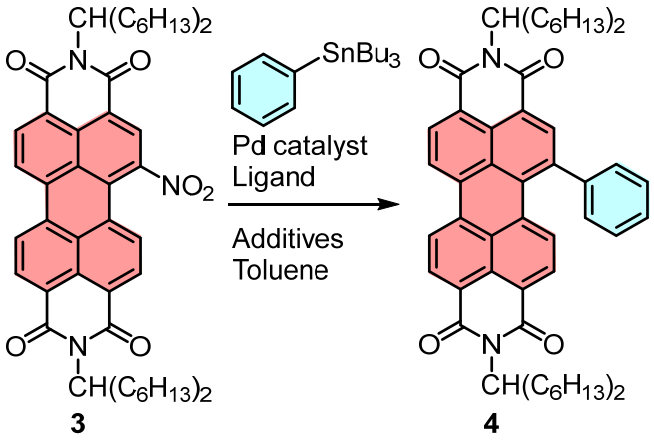
1. Materials and Methods

Materials and General Methods. Thin Layer Chromatography (TLC) was conducted on pre-coated aluminum sheets with 0.20 mm MerckAlugram SIL G/UV254 with fluorescent indicator UV254. Column chromatography was carried out using Sigma-Aldrich silica gel 60 (particle size 63-200 μm). Nuclear magnetic resonance (NMR) ^{1}H, ^{19}F and ^{13}C spectra were obtained on a Bruker 300 MHz Avance III spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) or 500 MHz Advance III HD spectrometer (500 MHz for ^{1}H, 470 MHz for ^{19}F, 125 MHz for ^{13}C). Chemical shifts were reported in ppm using the solvent residual signal as an internal reference ($CDCl_3$: δ H= 7.26 ppm, δ C= 77.2 ppm). Coupling constants (*J*) were given in Hz. Resonance multiplicity was described as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet) and br (broad signal). Carbon spectra were acquired with a complete decoupling for the proton. High resolution mass spectrometry (HRMS) was performed with a JEOL JMS-700 B/E. Chemicals were purchased from Sigma Aldrich, Acros Organics, Fisher Scientific, Alfa Aesar, Fluorochem, and were used as received. Solvents were purchased from Sigma Aldrich, Fluorochem, or Fischer Scientific while deuterated solvents from Sigma Aldrich. Toluene was refluxed over sodium with benzophenone indicator as the standard drying method.

Tributyl(naphthalen-2-yl)stannane[1], NitroPDI[2] and DiNitroPDI[3] were prepared by methods adapted from the literature.

Abbreviations NMR : nuclear magnetic resonance; PDI : perylenediimide; TFP: tri(2-furyl)phosphine; dba: Dibenzylideneacetone ; dppf: 1,1′-Ferrocenediyl-bis(diphenylphosphine) ; P(*o*-tolyl)$_3$: Tris(*o*-tolyl)phosphine; Xantphos: 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene; SPhos: 2-Dicyclohexylphosphino-2′,6′-dimethoxybiphenyl; en: ethylenediamine.

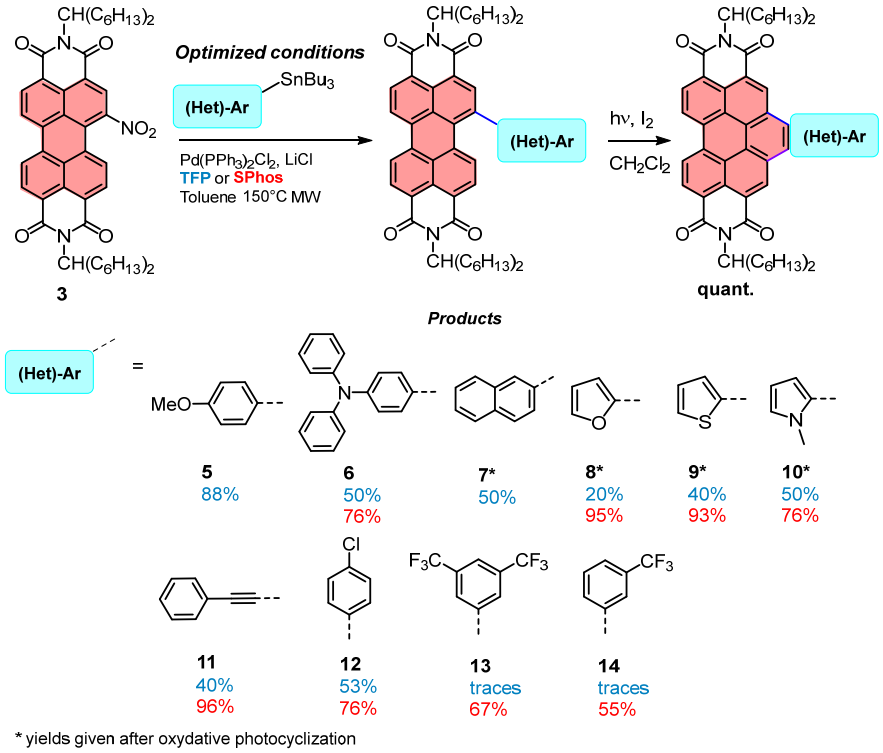
2. Synthesis

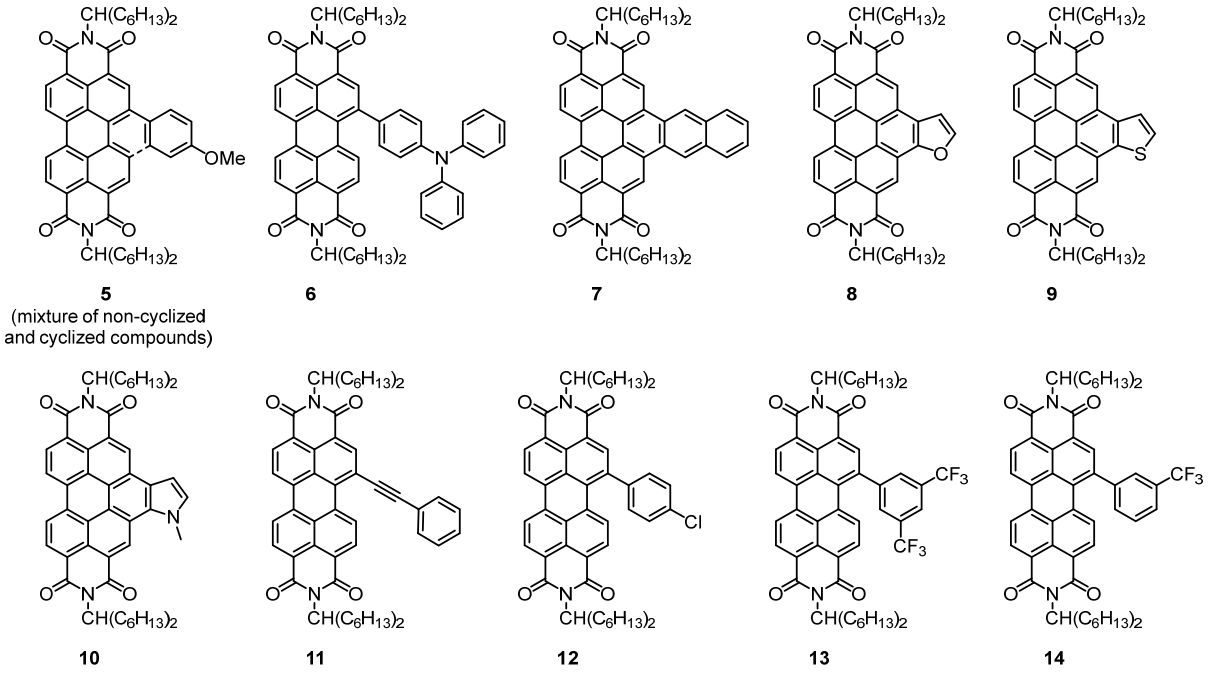


Scheme S1. General scheme for Stille reaction on NitroPDI.

Entry	[Pd] catalyst (%)	$ArSnR_3$ (equiv.)	Additive (equiv.)	Ligand (%)	Yield (%)
1*	$Pd(PPh_3)_4$ (10%)	Bu (2)	-	-	-
2*	$Pd(PPh_3)_4$ (10%)	Bu (2)	LiCl (2)	-	25
3*	$PdCl_2(PPh_3)_2$ (10%)	Bu (2)	LiCl (2)	-	70
4*	$PdCl_2(PPh_3)_2$ (10%)	Bu (2)	-	TFP (20%)	69
5* *or* **5****	$PdCl_2(PPh_3)_2$ (10%)	Bu (2)	LiCl (2)	TFP (20%)	98
6*	$PdCl_2(PPh_3)_2$ (10%)	Bu (2)	LiF (2)	TFP (20%)	57
7**	$PdCl_2(PPh_3)_2$ (10%)	Bu (1.2)	LiCl (2)	TFP (20%)	50
8**	$PdCl_2(PPh_3)_2$ (10%)	Me (1.2)	LiCl (2)	TFP (20%)	40
9**	$PdCl_2(PPh_3)_2$ (10%)	Bu (1.2)	LiCl (2)	$AsPh_3$ (20%)	53
10**	$PdCl_2(PPh_3)_2$ (10%)	Bu (1.2)	LiCl (2)	P(*o*-tolyl)$_3$ (20%)	Traces
11**	$PdCl_2(PPh_3)_2$ (10%)	Bu (1.2)	LiCl (2)	SPhos (20%)	75
12**	$PdCl_2(CH_3CN)_2$ (10%)	Bu (2)	LiCl (2)	TFP (20%)	4
13**	$PdCl_2(CH_3CN)_2$ (10%)	Bu (2)	LiCl (2)	SPhos (20%)	21
14**	$Pd(en)(NO_3)_2$ (10%)	Bu (2)	LiCl (2)	SPhos (20%)	-
15**	$PddppfCl_2$ (10%)	Bu (1.2)	LiCl (2)	-	60
16**	Pd_2dba_3 (5%)	Bu (1.2)	-	P(*o*-tolyl)$_3$ (10%)	40
17*	*$PdCl_2(PPh_3)_2$ (10%)*	*Me (1.2)*	*LiCl (2)*	*Xantphos (10%)*	*39*
18*	*$PdCl_2(PPh_3)_2$ (10%)*	*Bu (1.2)*	*LiCl (0.5)*	*TFP (20%)*	*37*
19*	*$PdCl_2(PPh_3)_2$ (10%)*	*Me (1.2)*	*LiCl (0.5)*	*TFP (20%)*	*42*
20*	*$PdCl_2(PPh_3)_2$ (10%)*	*Bu (1.2)*	*LiCl (2)*	*TFP (40%)*	*42*
21*	*$PdCl_2(PPh_3)_2$ (7%)*	*Bu (1.2)*	*LiCl (2)*	*TFP (14%)*	*45*
22*	*$PdCl_2(PPh_3)_2$ (1%)*	*Bu (1.2)*	*LiCl (2)*	*TFP (2%)*	*6*
23*	*$PdCl_2(PPh_3)_2$ (10%)*	*Bu (1.5)*	*LiCl (2)*	*TFP (20%)*	*47*
24*	*$PdCl_2(PPh_3)_2$ (10%)*	*Bu (1.7)*	*LiCl (2)*	*TFP (20%)*	*45*
25*	*$PdCl_2(CH_3CN)_2$ (10%)*	*Bu (2)*	*LiCl (2)*	-	-
26*	*$Pd(en)(NO_3)_2$ (10%)*	*Bu (2)*	*LiCl (2)*	-	-
27*	*$Pd(en)(NO_3)_2$ (10%)*	*Bu (2)*	*LiCl (2)*	*TFP (20%)*	-
28*	*$PddppfCl_2$ (10%)*	*Bu (1.2)*	*LiCl (2)*	-	*17*
29*	*$PddppfCl_2$ (10%)*	*Me (1.2)*	*LiCl (2)*	-	*60*

Table 1 Optimization of the reaction conditions (* Schlenk tube, [3] = 16.7 mM, Toluene, 120°C, overnight; ** Microwaves, [3] = 25 mM, Toluene, 150°C, 2h) TFP: tri(2-furyl)phosphine; dba: dibenzylideneacetone ; dppf: 1,1′-Ferrocenediyl-bis(diphenylphosphine) ; P(*o*-tolyl)$_3$: Tris(*o*-tolyl)phosphine; SPhos: 2-Dicyclohexylphosphino-2′,6′-dimethoxybiphenyl; xantphos: 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene; en: ethylenediamine





Scheme S2. Reaction scope for Stille reaction on NitroPDI.

General Procedure: Stille coupling

Conditions A = TFP

Conditions B = SPhos

In a 10 mL microwave reactor, PDI-NO_2 (100 mg, 0.125 mmol, 1 equiv.), LiCl (10.6 mg, 0.25 mmol, 2 equiv.), tributylphenylstannane (92 mg, 0.25 mmol, 2 equiv.), and a phosphine derivative, TFP (5.8 mg, 25 mmol, 0.2 equiv.) or SPhos (10.3 mg, 0.025 mmol, 0.2 equiv.), were suspended in dry toluene (5 mL). The solution was degassed under argon during ultrasonication for 15 minutes. Then $PdCl_2(PPh_3)_2$ (8.8 mg, 0.012 mmol, 0.1 equiv.) was added. The reaction was stirred at 150 °C for 2 h under MW irradiation. The reaction was cooled down and the solvent evaporated under reduced pressure. The crude product was purified through silica gel column chromatography (n-pentane/diethyl ether, 4:1 to diethyl ether) and precipitated in CH_2Cl_2/MeOH to afford the final product.

During the work-up, some of the final products were prone to photocyclisation. In order to obtain clear characterisation of the product, the mixture of photocyclised and non-photocyclised products was isolated together using column chromatography (n-pentane/diethyl ether, 4:1 to diethyl ether). The mixture was then diluted in 10 mL of CH_2Cl_2 and 2 equiv. of iodine were added, then placed in a photoreactor. The final photocyclised product was then washed with a solution of $Na_2S_2O_3$, extracted in CH_2Cl_2 and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to afford the final product.

NMR and mass spectrometry were then performed on the final product.

Compound 4. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 – 8.50 (m, 5H), 8.16 – 8.04 (m, 1H), 7.87 – 7.80 (d, *J* = 7.8 Hz, 1H), 7.43 – 7,58 (m, 5H), 5.25 – 5.07 (m, 2H), 2.33 – 2.11 (m, 4H), 1.92 – 1.73 (m, 4H), 1.41 – 1.11 (m, 32H), 0.92 – 0.75 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 163.7, 142.6, 141.7, 136.5, 135.8, 134.8, 134.4, 132.4, 131.5, 130.6, 130.3, 130.0, 129.1, 128.6, 128.5, 128.4, 128.0, 127.8, 127.5, 123.5, 122.6, 122.1, 54.8, 54.6, 32.3, 31.7, 31.4, 30.2, 29.2, 26.9, 22.6, 14.1. HRMS (MALDI-TOF) m/z: calcd for $C_{56}H_{66}N_2O_4$ ($[M]^-$): 830.5023; found: 830.5033 (0.65 ppm error).

Compound 5. (General conditions A, 95 mg, 88%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 – 8.46 (m, 5H), 8.21 – 8.07 (m, 1H), 7.89 and 7.79 (2d, *J* = 8.3 Hz, 1H)*, 7.43 – 7.36 (m, 2H), 7.41 (d, *J* = 9.5 Hz, 1H), 7,04 (d, *J* = 10 Hz, 1H), 5.18 (s, 2H), 3.91 (m, 3H), 2.30 – 2.16 (m, 4H), 1.82 (m, 4H), 1.24 (m, 32H), 0.90 – 0.77 (m, 12H). * The two doublets at 7.89 and 7.79 ppm are attributed to the mixture of non-cyclised and cyclised compounds in a ratio 80/20. ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 163.2, 159.6, 141.2, 134.3, 129.4, 129.2, 128.8, 128.6, 128.4, 128.0, 127.8, 127.7, 127.2, 124.9, 123.1, 122.1, 121.6, 115.4, 65.3, 55.0, 54.3, 54.2, 32.0, 31.40, 31.3, 29.3, 28.8, 26.5, 22.2, 21.1, 13.6. HRMS (MALDI-TOF) *m/z*: calcd for $C_{57}H_{68}N_2O_5$ ($[M]^-$):860.5128; found: 860.5135 (0.20 ppm error).

Compound 6. (General conditions A, 62 mg, 50%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 – 8.53 (m, 5H), 8.31 – 8.20 (m, 1H), 8.16 (d, *J* = 8 Hz, 1H), 7.35 (t, *J* = 8 Hz, 6H), 7.20 (t, *J* = 8 Hz, 6H), 7.10 (t, *J* = 7.3 Hz, 2H), 5.28 – 5.08 (m, 2H), 2.35 – 2.13 (m, 4H), 1.94 – 1.78 (m, 4H), 1.46 – 1.07 (m, 32H), 0.82 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8, 163.7, 148.4, 147.2, 141.6, 136.6, 136.0, 135.6, 135.1, 134.7, 129.5, 129.4, 129.2, 128.4, 128.1, 127.6, 125.0, 124.3, 124.1, 123.6, 123.5, 122.5, 54.7, 54.6, 32.3, 31.9, 31.7, 31.7, 29.3, 29.2, 27.0, 26.9, 26,9, 22.6, 14.0. HRMS (MALDI-TOF) *m*/*z*: calcd for $C_{68}H_{75}N_3O_4$ ($[M]^-$): 997.5758; found: 997.5752 (1.11 ppm error).

Compound 7. (General conditions A, 55 mg, 50%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.20 (s, 1H), 9.96 (s, 1H), 9.15 (s, 2H), 9.09 – 8.79 (m, 4H), 8.27 (dd, *J* = 9,2; 4,6 Hz, 2H), 7.95 – 7.75 (m, 2H), 5.25 – 5.45 (m, 2H), 2.37 (m, 4H), 2.08 – 1.90 (m, 4H), 1.58 – 1.12 (m, 32H), 0.84 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 164.0, 133.5, 133.1, 129.9, 129.4, 128.2, 128.6, 128.3, 127.6, 127.2, 126.8, 126.6, 124.4, 123.7, 122.7, 120.5, 55.0, 53.4, 32.5, 31.8, 29.3, 27.1, 22.6, 14.0. HRMS (MALDI-TOF) *m*/*z*: calcd for $C_{60}H_{66}N_2O_4$ ($[M]^-$): 878.5023; found: 878.5020 (0.96 ppm error).

Compound 8. (General conditions A, 92 mg, 95%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.37 (s, 1H), 9.21 (s, 1H), 8.95 – 8.79 (m, 4H), 8.20 – 8.13 (m, 1H), 7.59 (s, 1H), 5.36 (m, 2H), 2.49 – 2.32 (m, 4H), 2.11 – 1.90 (m, 4H), 1.57 – 1.19 (m, 32H), 0.85 (t, *J* = 6.8 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 164.7, 150.0, 147.9, 132.9, 132.6, 130.0, 129.5, 128.9, 126.7, 124.5, 124.1, 123.2, 122.4, 122.0, 121.5, 117.9, 106.9, 55.7, 54.1, 33.2, 32.6, 31.6, 27.9, 24.2, 23.4, 14.8. HRMS (MALDI-TOF) *m*/*z*: calcd for $C_{54}H_{62}N_2O_5$ ($[M]^-$): 818.4559; found: 818.4645 (2.35 ppm error).

Compound 9. (General conditions A, 97 mg, 93%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 – 8.85 (br, 1H), 8.77 – 8.66 (m, 3H), 8.64 – 8.52 (m, 2H), 8.02 – 7.94 (m, 1H), 7,90 – 7.85 (m, 1H), 5.39 – 5.25 (m, 2H), 2.47 – 2.34 (m, 4H), 2.13-2.01 (s, 4H), 1.71 – 1.17 (m, 32H), 0.94 – 0.82 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 162.4, 136.6, 134.5, 130.4, 128.1, 127.7, 127.0, 126.6, 124.6, 124.5, 123.2, 121.3, 120.9, 120.7, 119.8, 119.1, 54.1, 31.7, 31.1, 28.6, 26.6, 21.9, 13.3. HRMS (MALDI-TOF) *m*/*z*: calcd for $C_{54}H_{62}N_2O_4S$ ($[M]^-$): 834.4430; found: 834.4444 (1.00 ppm error).

Compound 10. (General conditions B, 80 mg, 76%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.67 – 9.56 (br, 1H), 9.36 – 9.20 (br, 1H), 8.97 – 8.76 (m, 4H), 7.48 – 7.44 (m, 1H), 7.32 – 7.26 (br, 1H), 5.39 – 5.22 (m, 2H), 4.53 (s, 3H), 2.49 – 2.24 (m, 4H), 2.16 – 1.95 (m, 4H), 1.61 – 1.17 (m, 32H), 0.90 – 0.74 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 164.1, 133.9, 132.7, 132.0, 131.3, 128.9, 128.4, 127.7, 127.0, 125.9, 125.5, 124.9, 124.4, 123.5, 123.2, 121.6, 120.6, 118.7, 100.7, 54.9, 39.1, 32.6, 31.9, 29.4, 29.3, 27.3, 22.7, 14.1. HRMS (MALDI-TOF) *m*/*z*: calcd for $C_{55}H_{65}N_3O_4$ ($[M]^-$):831.4975; found: 831.4985 (0.49 ppm in error).

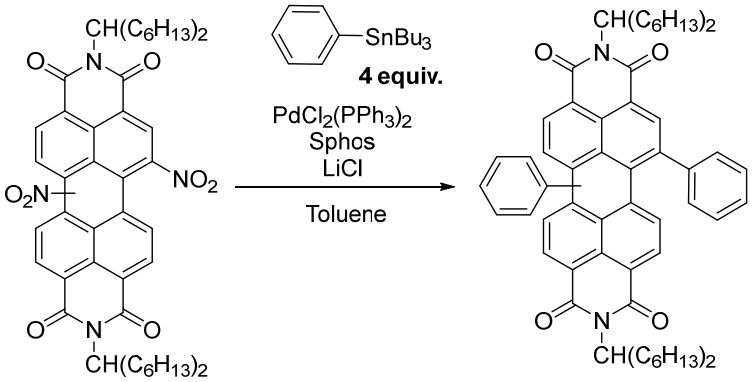
Compound 11. (General conditions B, 101 mg, 96%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.30 (d, *J* = 8.3 Hz, 1H), 8.91 – 8,83 (br, 1H), 8.79 – 8.59 (m, 5H), 7.79 – 7.63 (m, 2H), 7.55 – 7.42 (m, 3H),

5.26 – 5.11 (m, 2H), 2.34 – 2.18 (m, 4H), 1.94 – 1.78 (m, 4H), 1.42 – 1.14 (m, 32H), 0.83 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 163.7, 138.9, 138.2, 134.6, 134.3, 134.1, 131.9, 131.6, 130.9, 129.9, 129.3, 129.0, 128.7, 127.5, 127.1, 126.9, 123.7, 123.1, 122.4, 120.4, 99.6, 91.2, 55.0, 54.9, 32.5, 32.4, 31.9, 29.3, 27.1, 27.0, 22.7, 14.2. HRMS (MALDI-TOF) *m*/*z*: calcd for $C_{58}H_{66}N_2O_4$ ($[M]^-$): 854.5023; found: 855.5036 (0.98 ppm error).

Compound 12. (General conditions B, 78 mg, 76%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 – 8.53 (m, 5H), 8.50 – 8.42 (m, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 5.16 – 5.02 (m, 2H), 2.24 – 2.08 (m, 4H), 1.82 – 1.70 (m, 4H), 1.30 – 1.05 (m, 32H), 0.83 – 0.70 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 163.3, 140.9, 134.7, 134.2, 132.5, 131.4, 130.8, 130.7, 130.5, 130.0, 129.9, 129.8, 129.0, 128.5, 127.9, 127.4, 126.6, 126.5, 123.4, 123.0, 122.7, 54.7, 54.6, 32.2, 31.6, 29.1, 26.8, 22.4, 13.9. HRMS (MALDI-TOF) *m*/*z*: calcd for $C_{56}H_{65}ClN_2O_4$ ($[M]^-$): 864.4633; found: 864.4624 (1.68 ppm error).

Compound 13. (General conditions B, 80 mg, 67%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 – 8.60 (m, 5H), 8.54 – 8.43 (m, 1H), 8.21– 8.10 (m, 1H), 8.04 (s, 1H), 8.00 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 5.24 – 5. (m, 2H), 2.28 – 2.11 (m, 4H), 1.93 – 1.74 (m, 4H), 1.43 – 1.07 (m, 32H), 0.96 – 0.73 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 163.4, 144.9, 137.6, 134.0, 133.9, 133.6, 133.4, 132.9, 130.3, 129.8, 129.5, 129.3, 129.2, 129.0, 128.0, 127.4, 123.9, 123.2, 123.0, 122.3, 121.8, 54.9, 54.8, 53.4, 31.7, 31.7, 30.9, 29.1, 29.1, 22.5, 22.5, 14.04, 14.01.^{19}F NMR (470 MHz, $CDCl_3$)δ -62.82. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.82. HRMS (MALDI-TOF) *m*/*z*: calcd for $C_{58}H_{64}F_6N_2O_4$ ($[M]^-$): 966.4770; found: 966.4788 (1.29 ppm error).

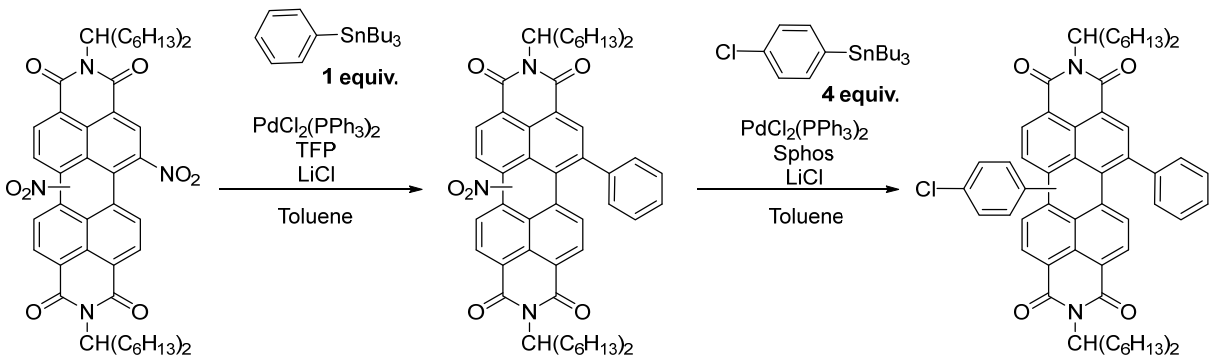
Compound 14. (General conditions B, 62 mg, 55%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 – 8.60 (m, 4H), 8.54 – 8.45 (br, 1H), 8.2 – 8,09 (br, 1H), 7.83 (s, 1H), 7.80 – 7.71 (m, 2H), 7.71 – 7.63 (m 2H), 5.23 – 5.07 (m, 2H), 2.36 – 2.07 (m, 4H), 1.94 – 1.72 (m, 4H), 1.37 – 1.09 (m, 32H), 0.93 – 0.73 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 163.4, 143.4, 139.5, 136.0, 135.5, 135.3, 134.8, 134.1, 133.9, 133.3, 132.9, 132.6, 132.3, 132.0, 131.6, 130.8, 130.7, 129.8, 129.1, 128.6, 127.9, 127.3, 126.7, 125.4, 125.2, 124.6, 123.6, 123.1, 122.8, 122.5, 54.7, 54.6, 36.8, 32.2, 31.6, 31.6, 29.1, 29.0, 26.7, 22.4, 13.9. ^{19}F NMR (470 MHz, $CDCl_3$)δ -62.64. HRMS (MALDI-TOF) *m*/*z*: calcd for $C_{57}H_{65}F_3N_2O_4$ ($[M]^-$): 898.4896; found: 898.4902 (0.05 ppm error).



Scheme S3. Synthesis of Ph-PDI-Ph.

The general procedure was followed starting from a regioisomeric mixture of 1,6 and 1,7 PDI-$(NO_2)_2$ (100 mg, 0.118 mmol, 1 equiv.), LiCl (10 mg, 0.24 mmol, 2 equiv.) and tributyl(phenyl)stannane (217 mg, 0.6 mmol, 5 equiv.), with Sphos (19.5 mg, 0.043 mmol, 0.4 equiv.) dissolved in toluene (5 mL). The solution was degassed under argon during ultrasonication for 15 minutes. Then $PdCl_2(PPh_3)_2$ (8.7 mg, 0.023 mmol, 0.2 equiv.) was added. The reaction was stirred at 150 °C for 2 h under MW irradiation. The reaction was cooled down and the solvent evaporated under reduced pressure. The crude product was purified through silica gel column chromatography (n-pentane/diethyl ether, 4:1 to diethyl ether). The reaction afforded inseparable **16-*(1,6)*** and **16-*(1,7)*** regioisomers. Recrystallization from CH_2Cl_2/MeOH gave after filtration a mixture of inseparable **16-*(1,6)*** and **16-*(1,7)*** regioisomers (78 mg; 76 % yield). **16-(*1,6*)** and **16-(*1,7*)** were characterized as a regioisomeric mixture.

Compound 16. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 – 8,54 (m, 2H), 8.17 – 8,03 (m, 2H), 7.82 (d, *J* = 7,8 Hz, 1H), 7.77 (d, *J* = 7,6 Hz, 1H), 7.61 – 7.40 (m, 10H), 5.25 – 5.05 (m, 2H), 2.34 – 2.10 (m, 4H), 1.93 – 1.71 (m, 4H), 1.42 – 1.08 (m, 32H), 0.92 – 0.71 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 163.6, 142.6, 142.2, 142.0, 141.1, 135.8, 135.1, 134.8, 134.2, 132.8, 132.5, 130.3, 130.2, 129.7, 129.4, 129.2, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 127.9, 127.3, 122.6, 122.1, 54.8, 54.7, 54.6, 32.3, 31.8, 31.7, 31.6, 29.2, 26.93, 26.8, 22.6, 14.0. HRMS (MALDI-TOF) *m*/*z*: calcd for $C_{62}H_{70}N_2O_4$ ($[M]^-$): 906.5336; found: 906.5355 (1.55 ppm error).



Scheme S4. Synthesis of dissymmetrical PDI via two successive Stille couplings.

The general procedure was followed starting from a regioisomeric mixture of 1,6 and 1,7 PDI-$(NO_2)_2$ (100 mg, 0.118 mmol, 1 equiv.), LiCl (10 mg, 0.24 mmol, 2 equiv.) and tributyl(phenyl)stannane (43,5 mg, 0.12 mmol, 1 equiv.), with tri(2-furyl)phosphine (4.5 mg, 0.024 mmol, 0.2 equiv.) dissolved in toluene (5 mL). Then $PdCl_2(PPh_3)_2$ (8.3 mg, 0.012 mmol, 0.1 equiv.) was added. The reaction afforded inseparable **15-*(1,6)*** and **15-*(1,7)*** regioisomers. Purification was carried out by silica gel column chromatography using n-pentane/diethyl ether, 4:1 to diethyl ether. Recrystallization from CH_2Cl_2/MeOH gave after filtration a mixture of inseparable **17-*(1,6)*** and **17-*(1,7)*** regioisomers (78 mg; 76% yield). **17-(*1,6*)** and **17-(*1,7*)** were characterized as a regioisomeric mixture.

In a 10 mL microwave reactor, Ph-PDI-NO_2 (40 mg, 0.045 mmol, 1 equiv.), LiCl (3.9 mg, 0.091 mmol, 2 equiv.), and tributyl(4-chlorophenyl)stannane (73.4 mg, 0.18 mmol, 4 equiv.) and Sphos (3.8 mg, 0.009 mmol, 0.2 equiv.) were suspended in dry toluene. The solution was degassed under argon during ultrasonication for 15 minutes. Then $PdCl_2(PPh_3)_2$ (3.2 mg, 0.005 mmol, 0.1 equiv.) was added. The reaction was stirred at 150 °C for 2 h under MW irradiation. The reaction was cooled down and the solvent evaporated under reduced pressure. The crude product was purified through silica gel column chromatography (n-pentane/diethyl ether, 4:1 to diethyl ether). Recrystallization from gave after filtration a mixture of inseparable **18-*(1,6)*** and **18-*(1,7)*** regioisomers (35 mg; 81% yield). **18-(*1,6*)** and **18-(*1,7*)** were characterized as a regioisomeric mixture.

Compound 17. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 – 8.52 (m, 3H), 8,34 – 8.31 (m, 1H), 8.25 – 8.06 (m, 1H), 7.88 (t, *J* = 8.0 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.48 – 7.42 (m, 2H), 5.26 – 7.04 (m, 2H), 2.33 – 2.10 (m, 4H), 1.92 – 1.72 (m, 4H), 1.41 – 1.05 (m, 32H), 0.91 – 0.74 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 163.1, 148.7, 148.3, 147.6, 143.3, 142.8, 141.8, 141.8, 141.6, 135.5, 133.1, 132.8, 130.9, 130.7, 130.5, 130.4, 130.3, 130.16, 129.5, 129.2, 129.2, 129.1, 129.0, 128.9, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.4, 128.0, 127.9, 127.6, 127.5, 127.5, 54.8, 53.4, 32.4, 32.3, 32.2, 32.1, 31.8, 31.7, 31.7, 29.2, 29.1, 29.1, 26.8, 26.8, 22.5, 14.0. HRMS (MALDI-TOF) *m*/*z*: calcd for $C_{56}H_{65}N_3O_6$ ($[M]^-$): 875.4873; found: 875.4885 (0.65 ppm error).

Compound 18. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 – 8.51 (m, 2H), 8.34 – 8.05 (m, 2H), 7.82 (d, *J* = 9 Hz, 1H), 7.80 – 7.74 (d, *J* = 8 Hz, 1H), 7.60 – 7.42 (m, 5H), 7.42 – 7.37 (m, 1H), 7.36 – 7.31 (m, 1H), 7.22 – 7.18 (m, 1H), 7.17 – 7.07 (m, 1H), 5.29 – 5.09 (m, 2H), 2.38 – 2.14 (m, 4H), 1.85 (m, 4H), 1.45 – 1.11 (m, 32H), 0.91 – 0.71 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 162.8, 146.4, 141.7, 141.3, 140.2, 139.7, 138.7, 135.0, 133.9, 131.8, 129.6, 129.6, 129.4, 129.3, 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.9, 127.8, 127.7, 127.6, 127.1, 126.5, 124.1, 123.2, 122.8, 121.9, 121.2, 76.2, 53.9, 53.8, 31.5, 30.9, 28.4, 26.0, 21.7, 13.2. HRMS (MALDI-TOF) *m*/*z*: calcd for $C_{62}H_{69}N_2O_4$ ($[M]^-$): 940.4946; found: 940.4944 (0.76 ppm error).

3. NMR

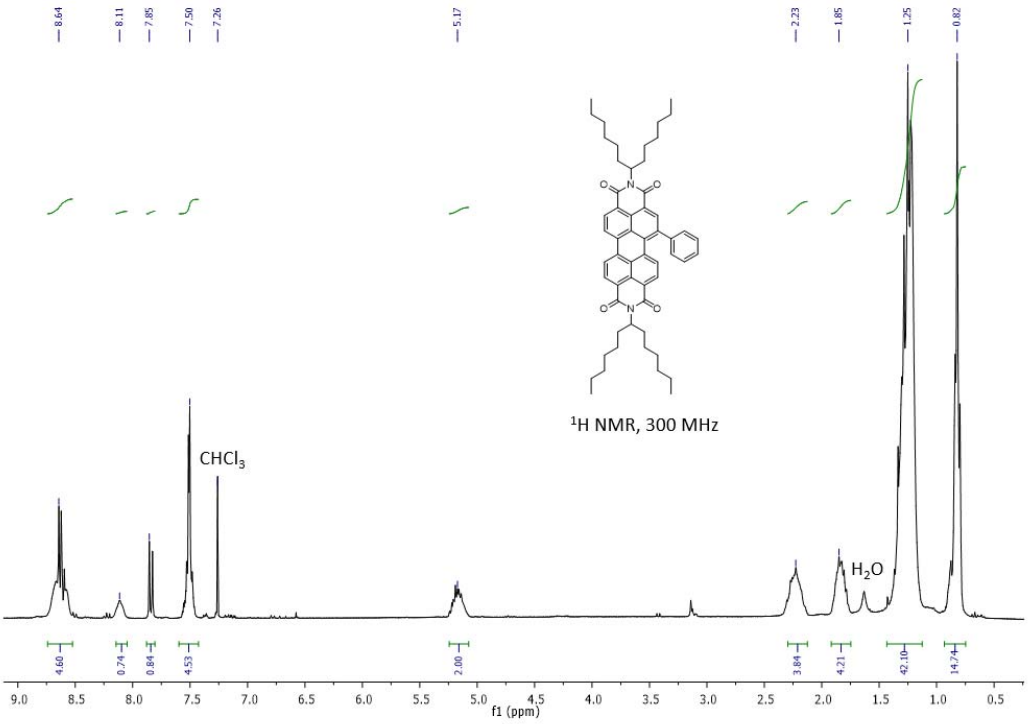


Figure S1. ^{1}H NMR (300 MHz) spectrum of compound **4** in $CDCl_3$.

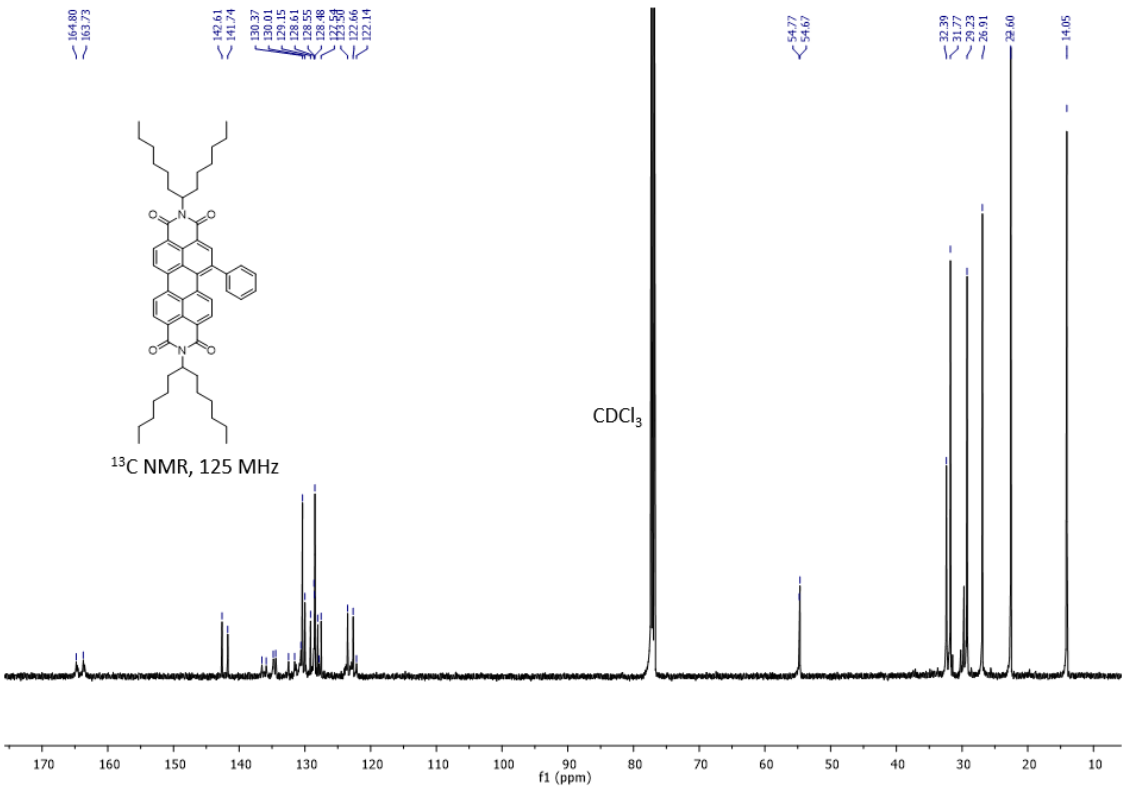


Figure S2. ^{13}C NMR (125 MHz) spectrum of compound **4** in $CDCl_3$.

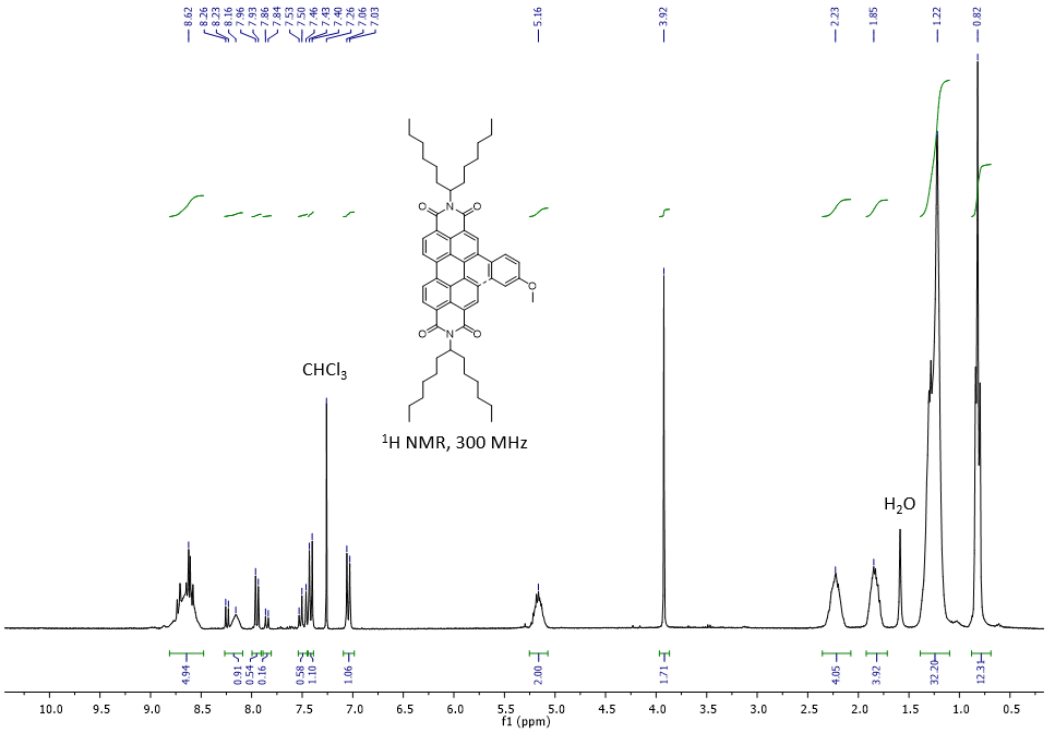


Figure S3. ^{1}H NMR (300 MHz) spectrum of compound **5** in $CDCl_3$.

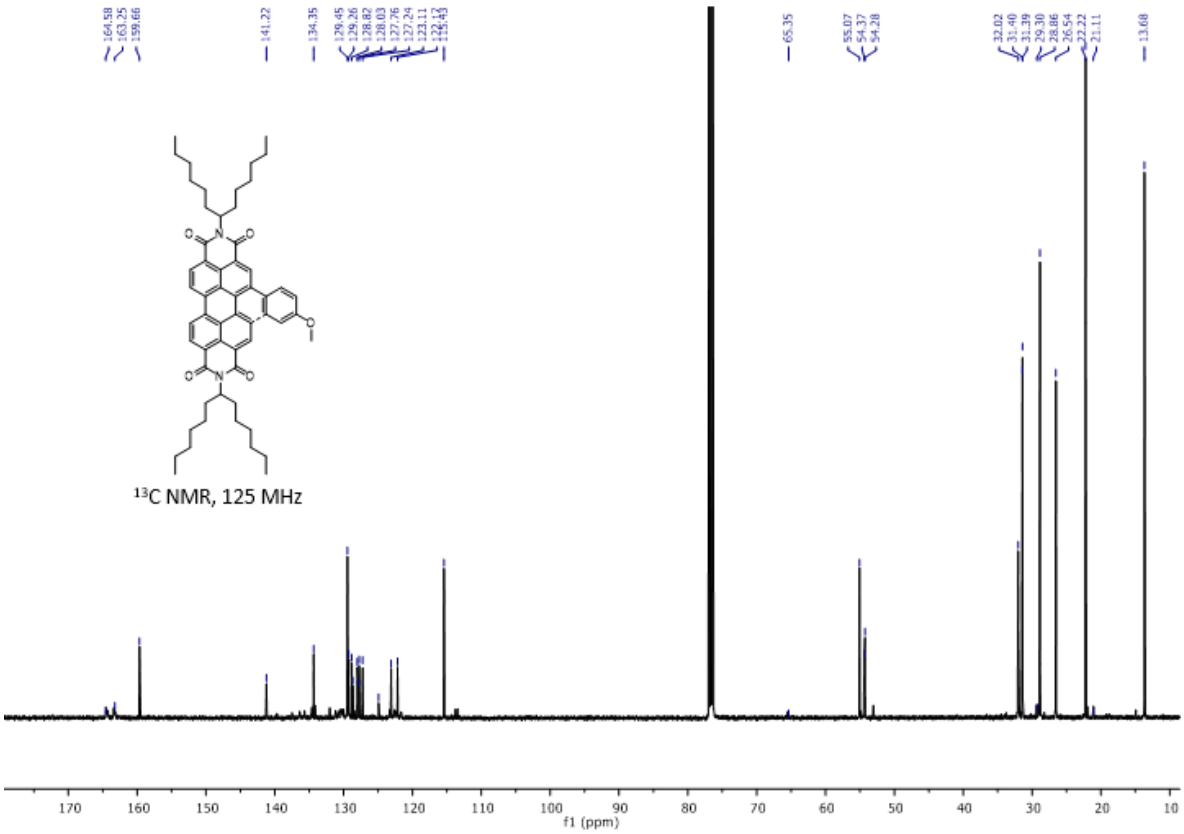


Figure S4. ^{13}C NMR (125 MHz) spectrum of compound **5** in $CDCl_3$.

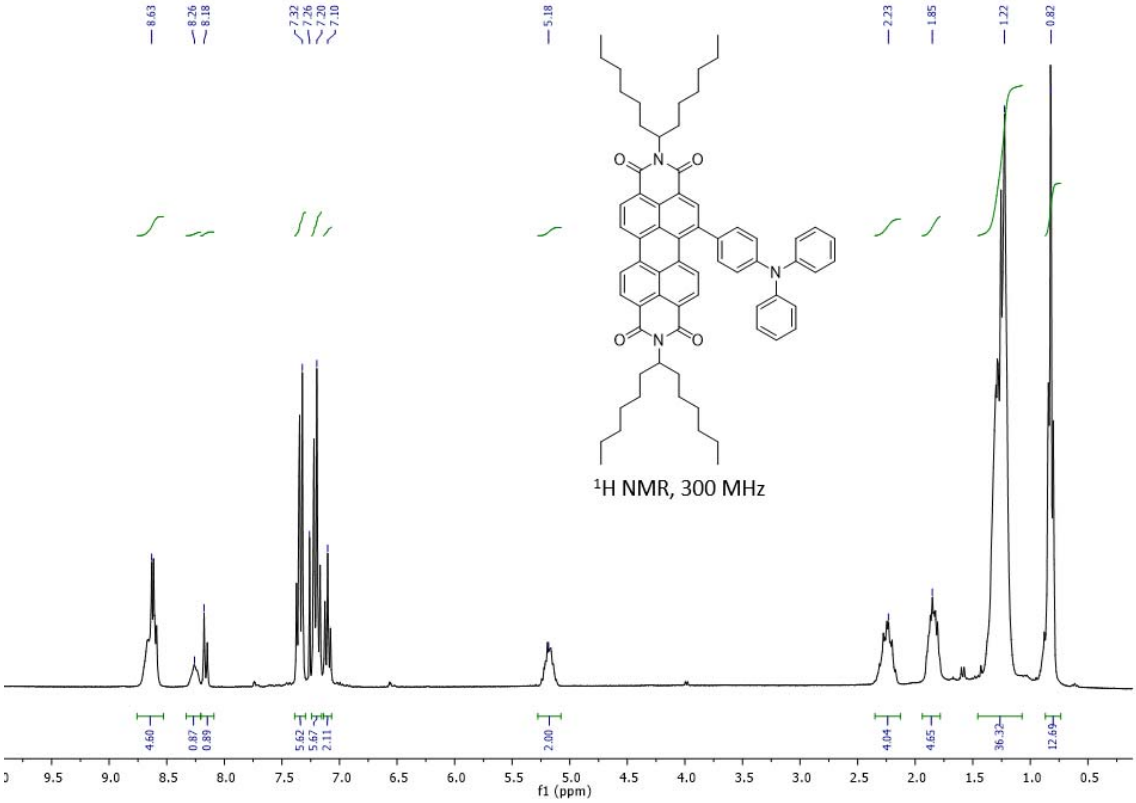


Figure S5. ^{1}H NMR (300 MHz) spectrum of compound **6** in $CDCl_3$.

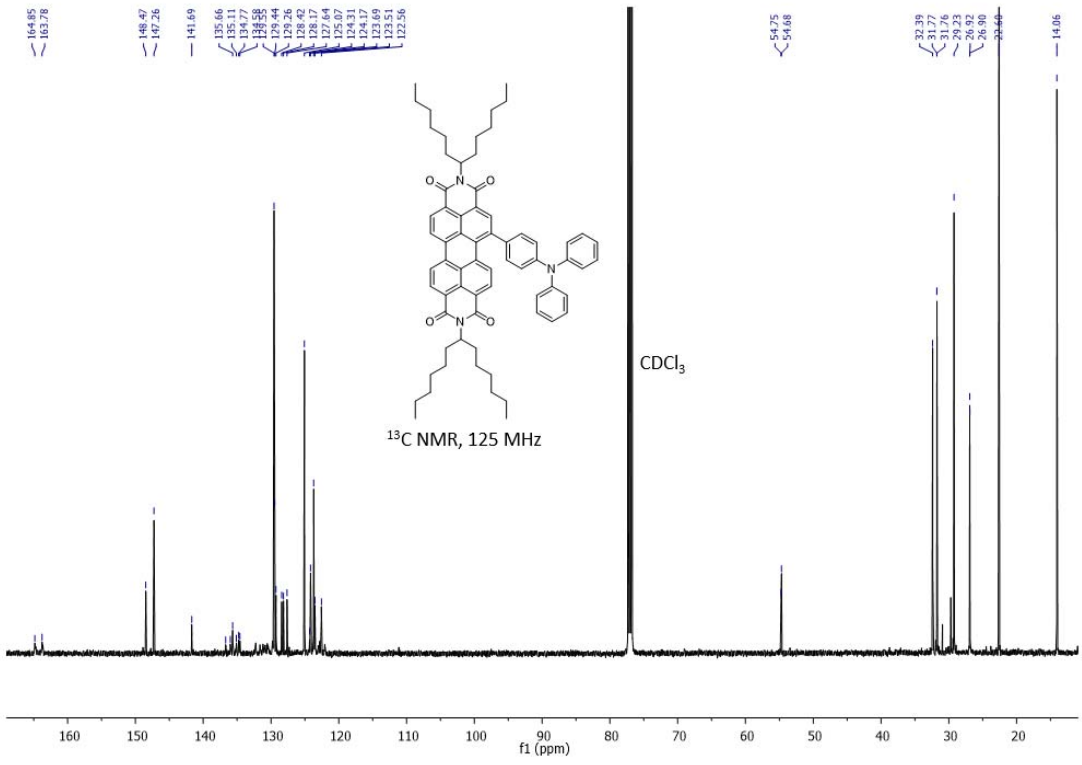


Figure S6. ^{13}C NMR (125 MHz) spectrum of compound **6** in $CDCl_3$.

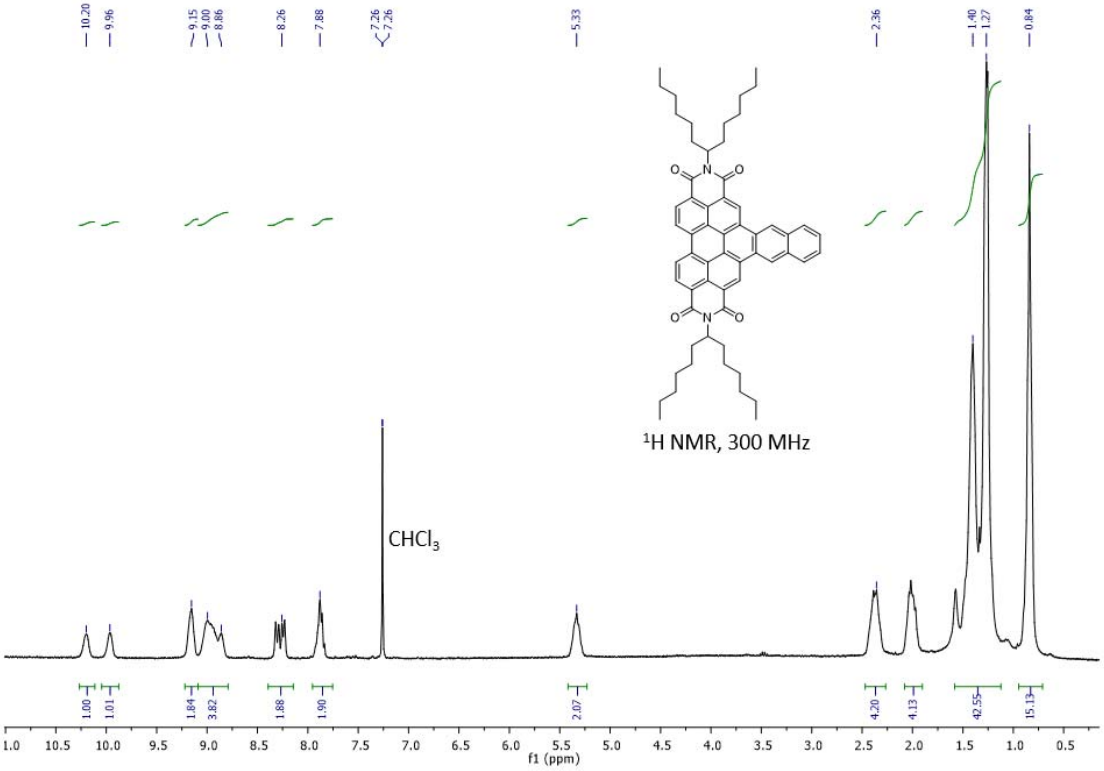


Figure S7. ^{1}H NMR (300 MHz) spectrum of compound **7** in $CDCl_3$.

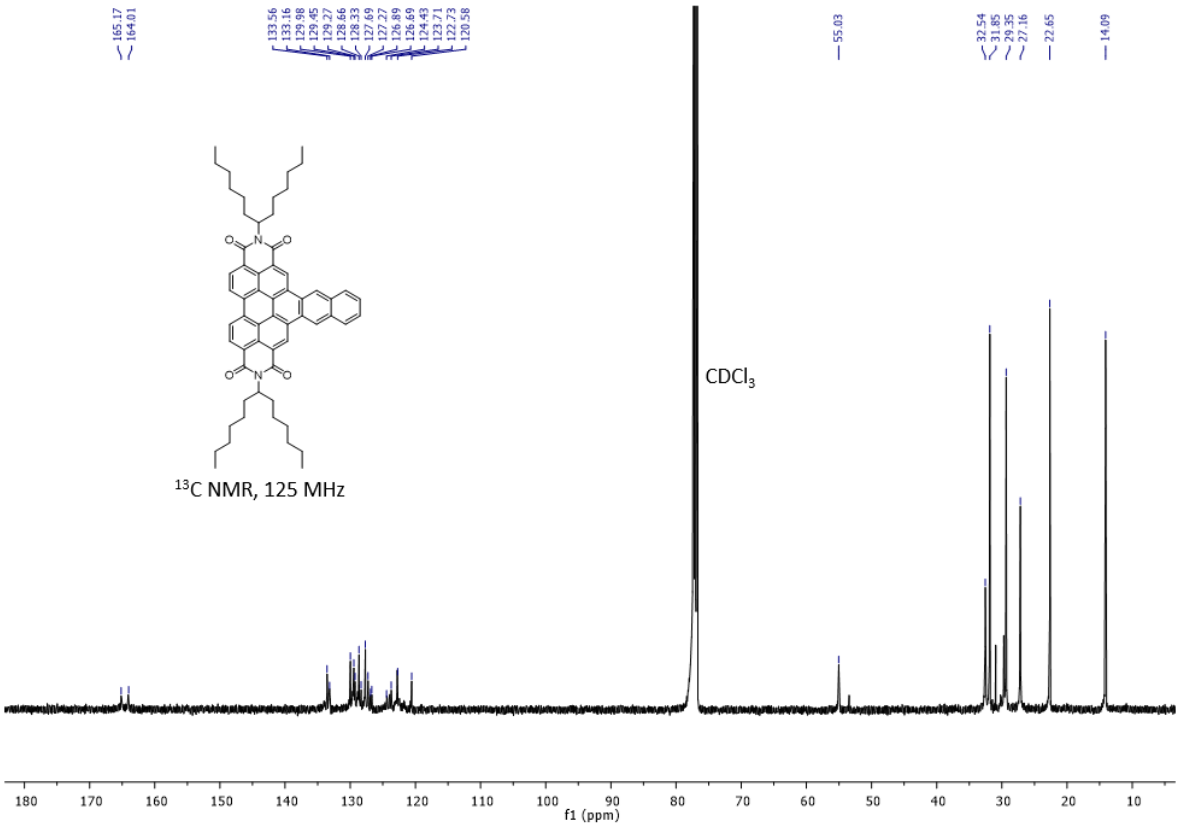


Figure S8. ^{13}C NMR (125 MHz) spectrum of compound **7** in $CDCl_3$.

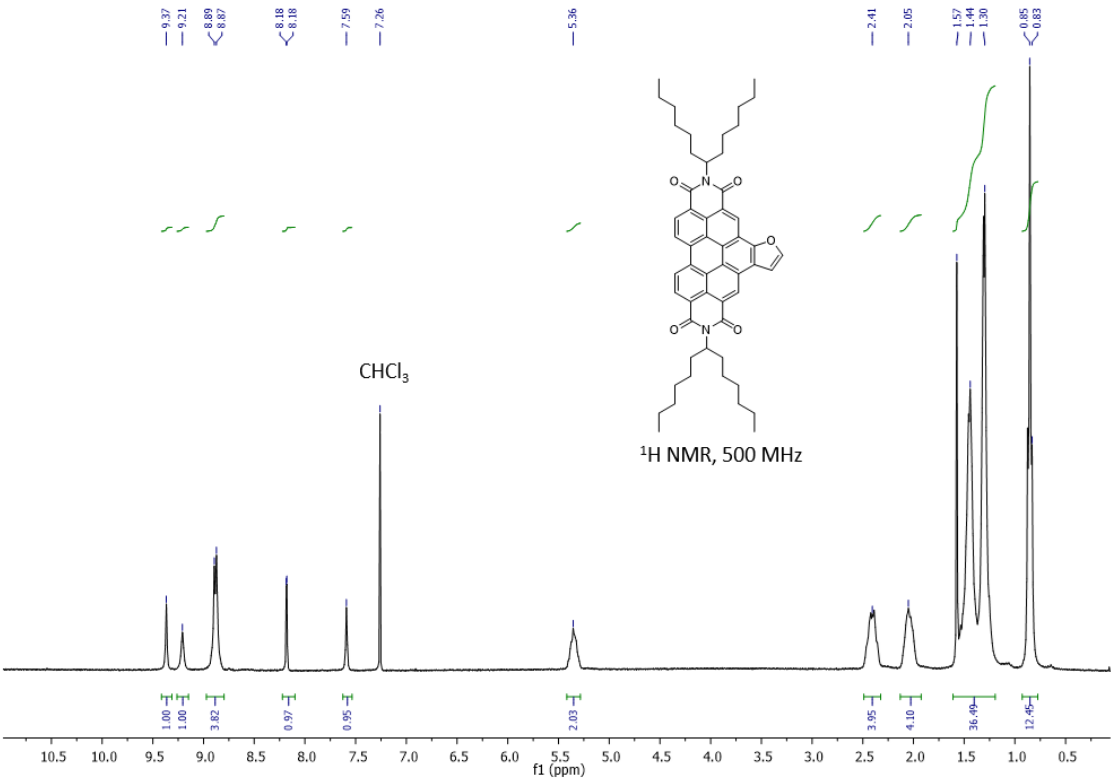


Figure S9. ^{1}H NMR (500 MHz) spectrum of compound **8** in $CDCl_3$.

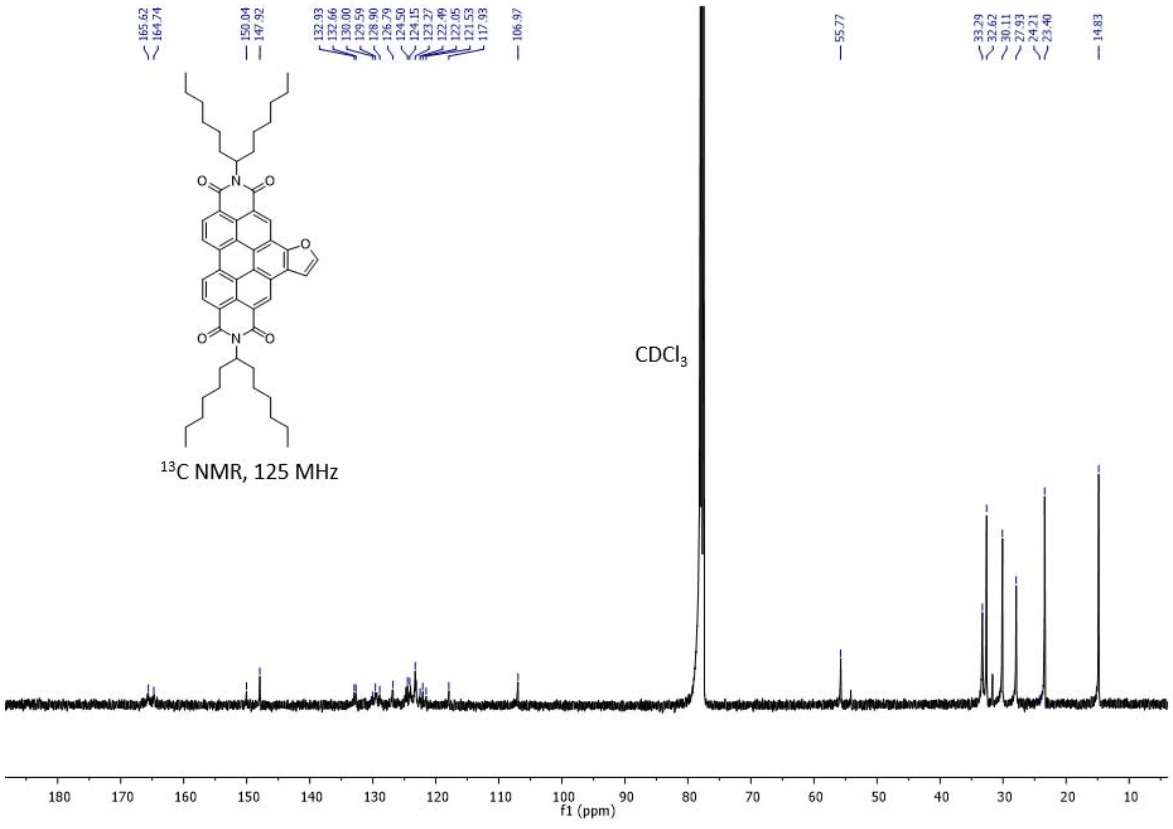


Figure S10. ^{13}C NMR (125 MHz) spectrum of compound **8** in $CDCl_3$.

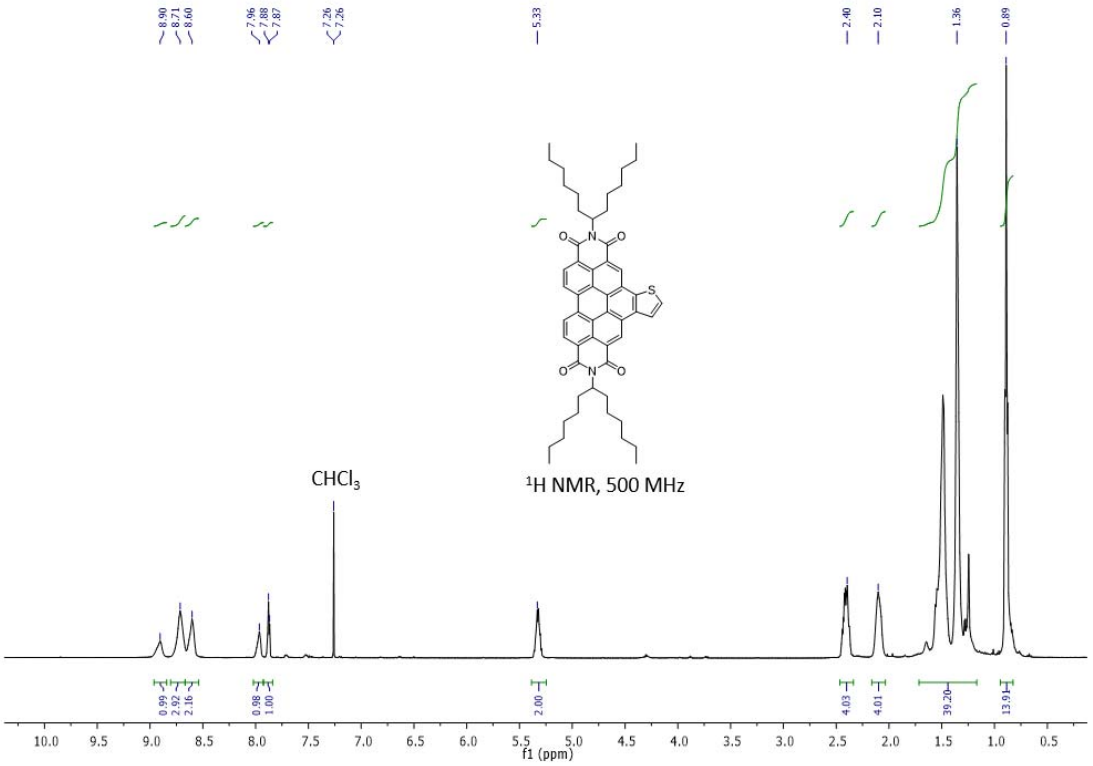


Figure S11. ^{1}H NMR (500 MHz) spectrum of compound **9** in $CDCl_3$.

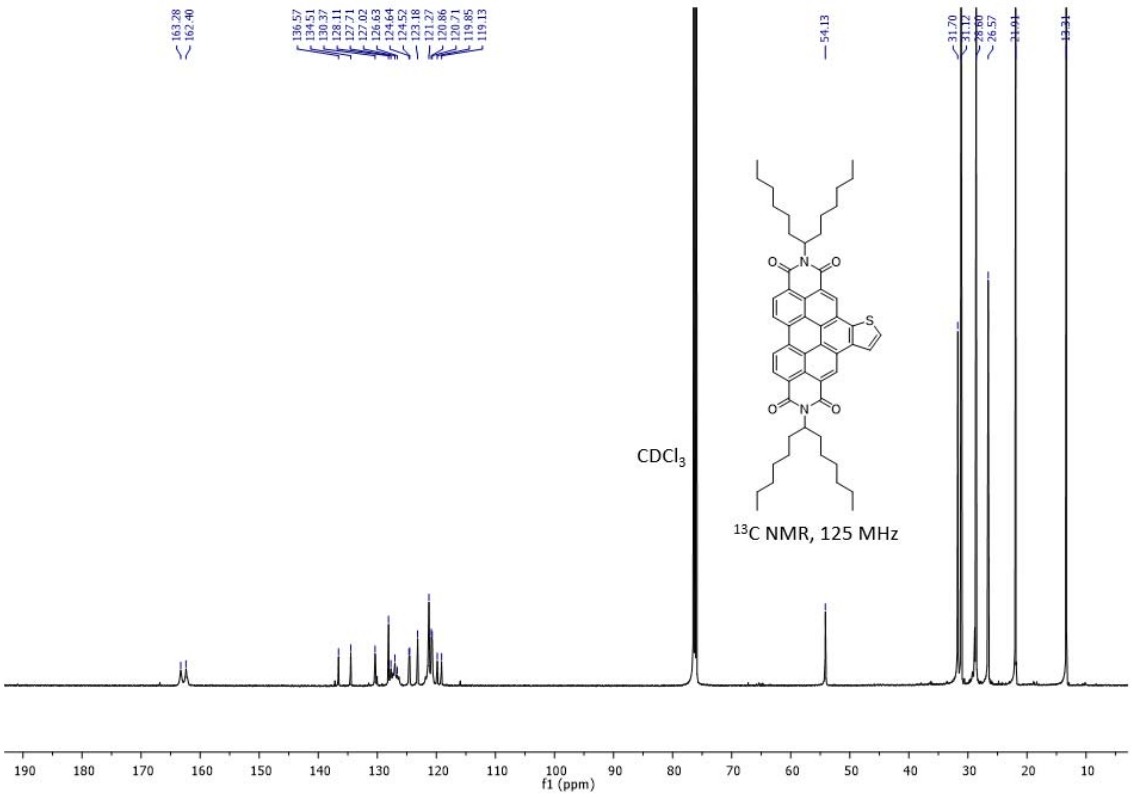


Figure S12. ^{13}C NMR (125 MHz) spectrum of compound **9** in $CDCl_3$.

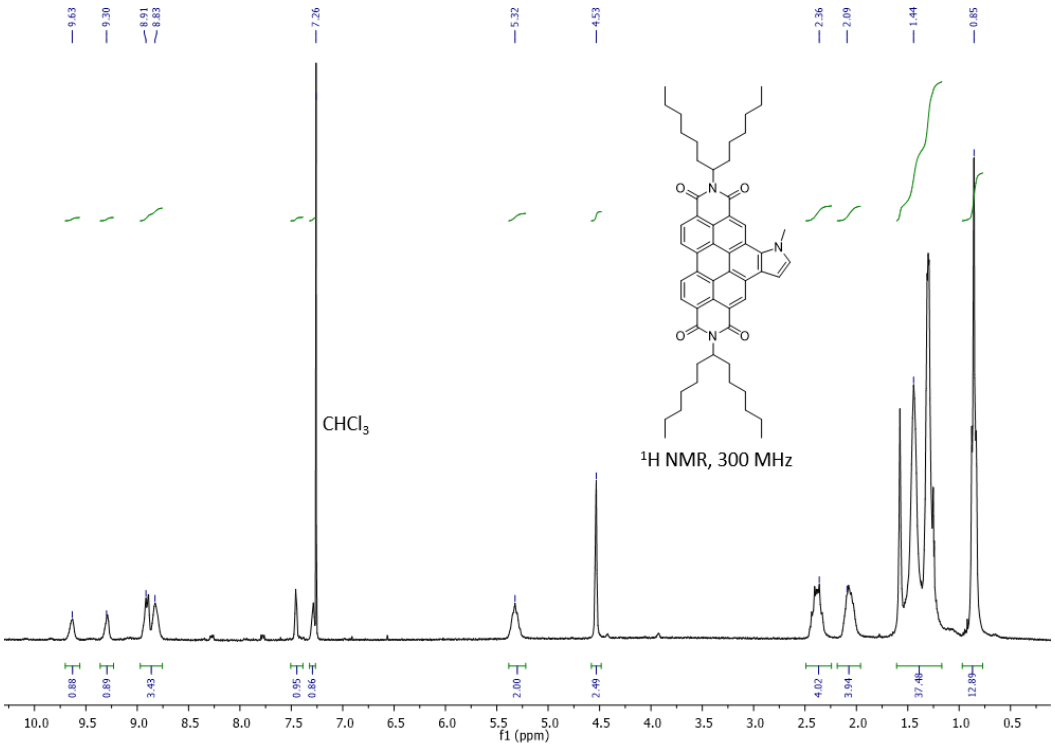


Figure S13. ^{1}H NMR (300 MHz) spectrum of compound **10** in $CDCl_3$.

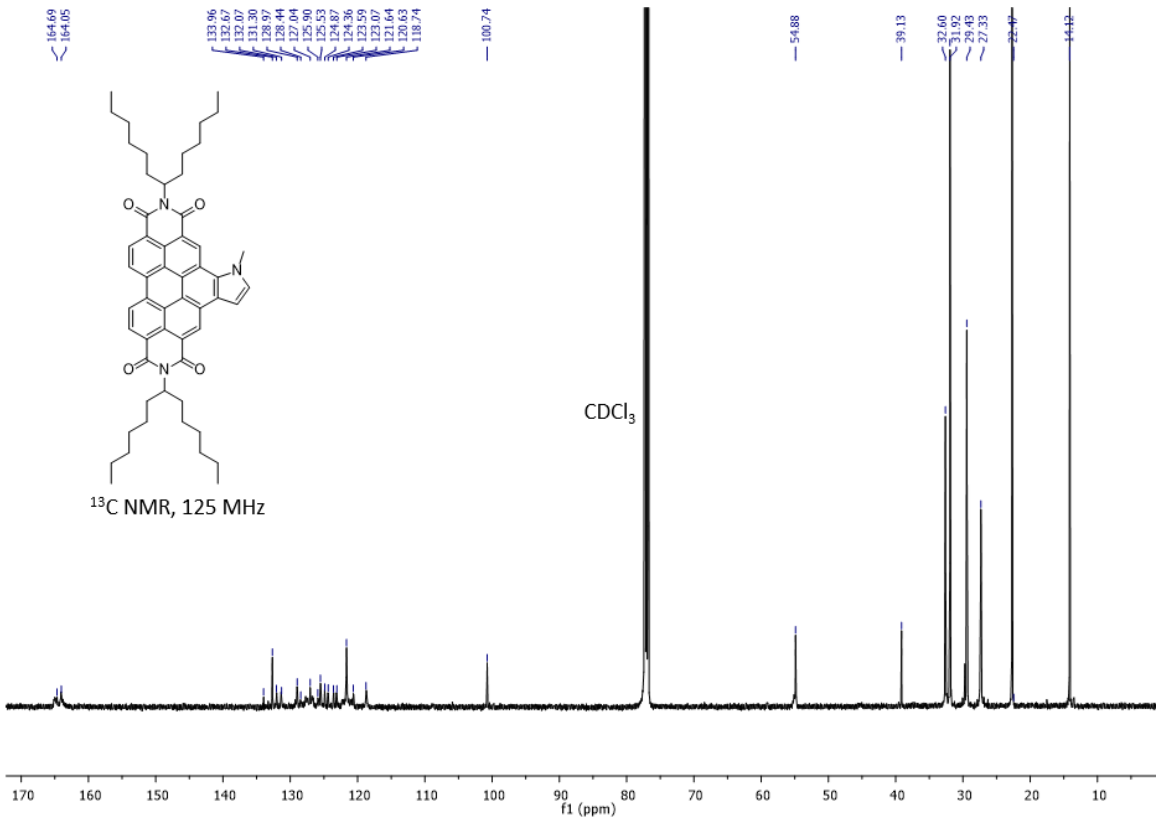


Figure S14. ^{13}C NMR (125 MHz) spectrum of compound **10** in $CDCl_3$.

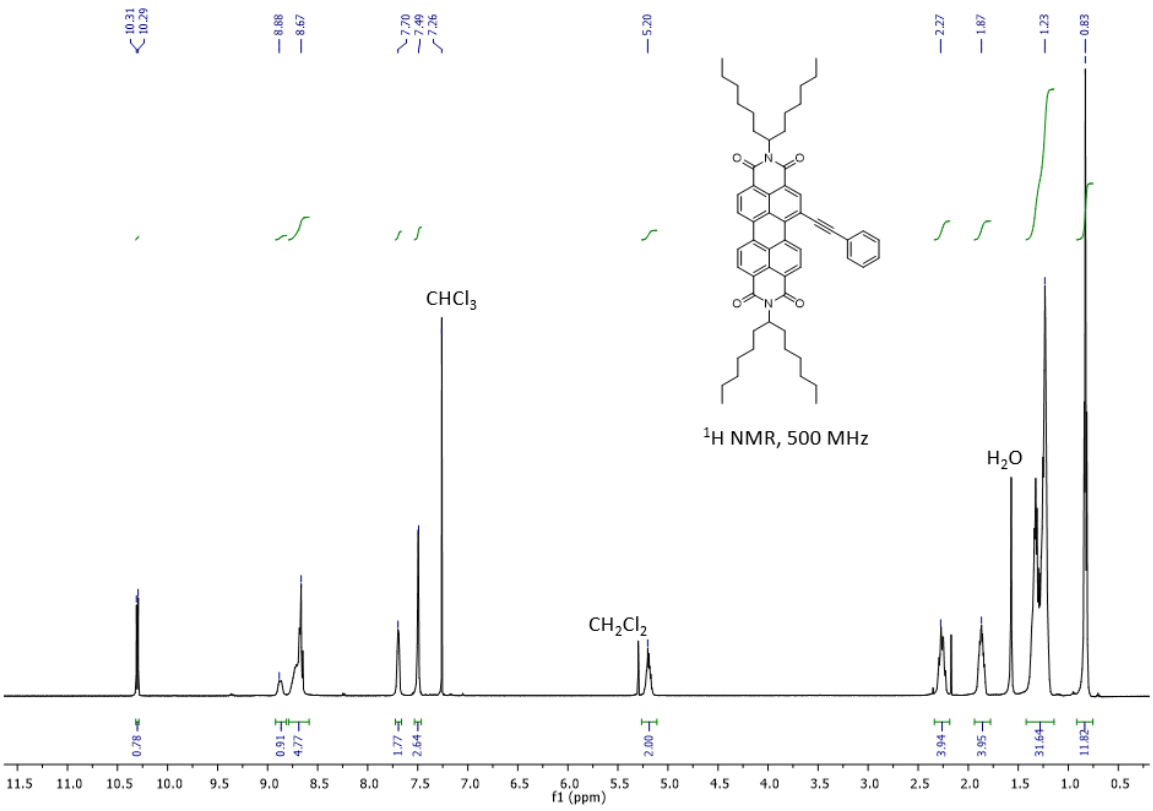


Figure S15. ^{1}H NMR (500 MHz) spectrum of compound **11** in $CDCl_3$.

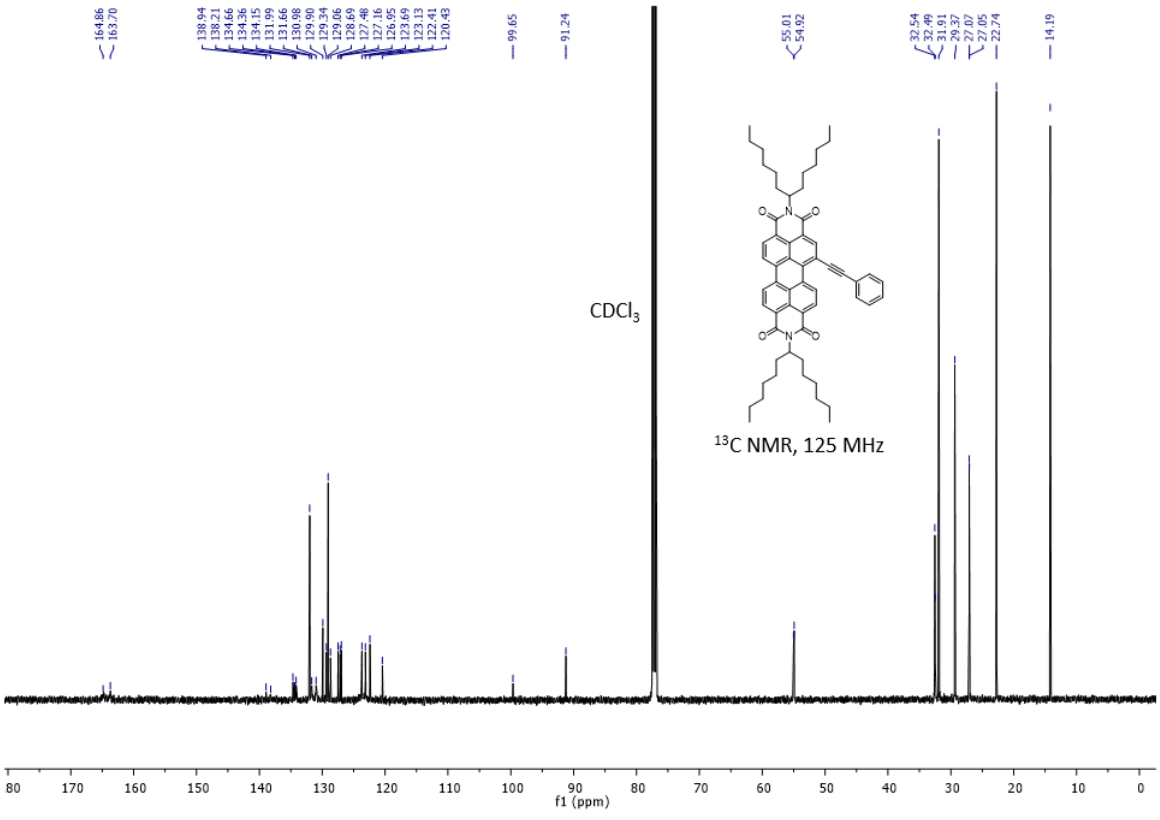


Figure S16. ^{13}C NMR (125 MHz) spectrum of compound **11** in $CDCl_3$.

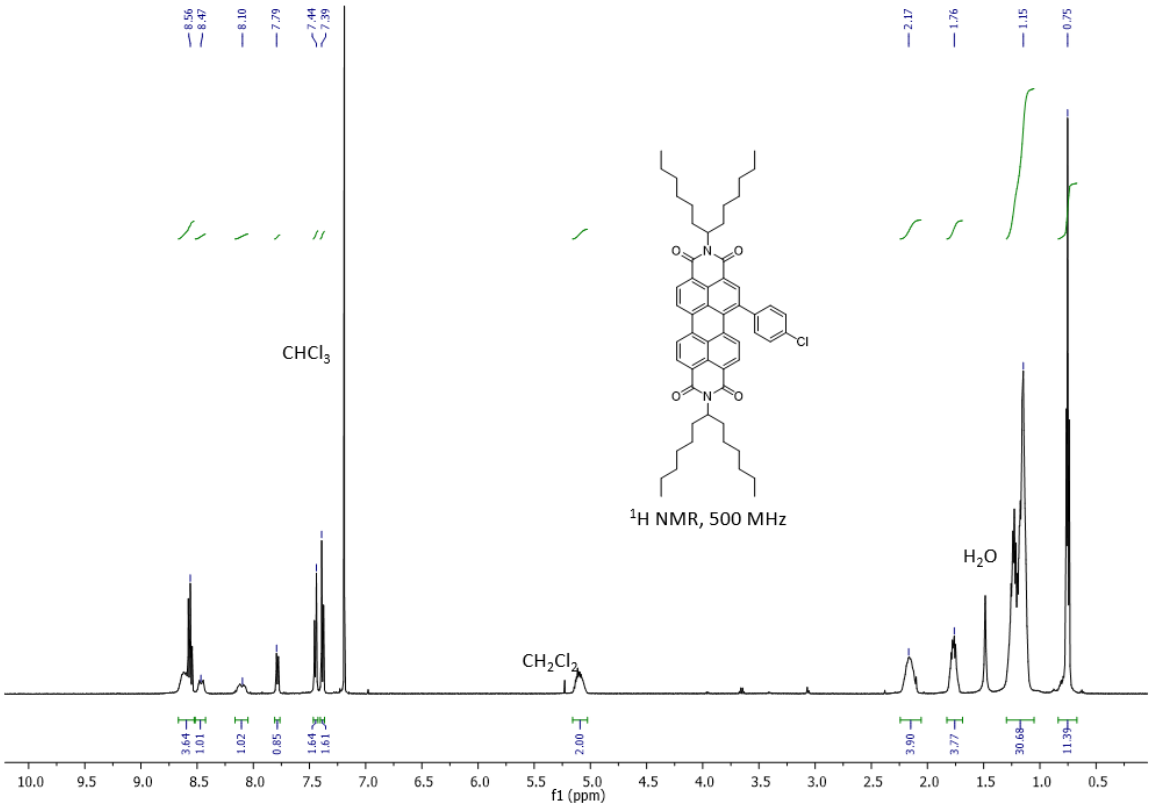


Figure S17. ^{1}H NMR (500 MHz) spectrum of compound **12** in $CDCl_3$.

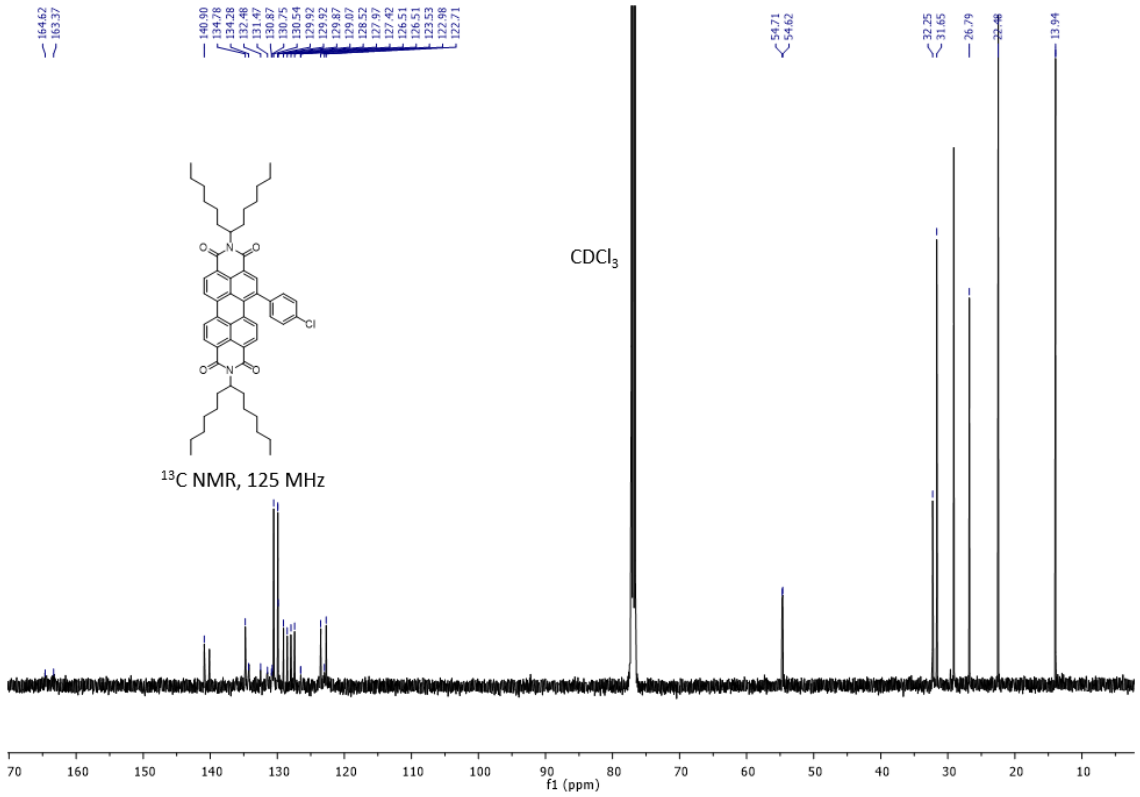


Figure S18. ^{13}C NMR (125 MHz) spectrum of compound **12** in $CDCl_3$.

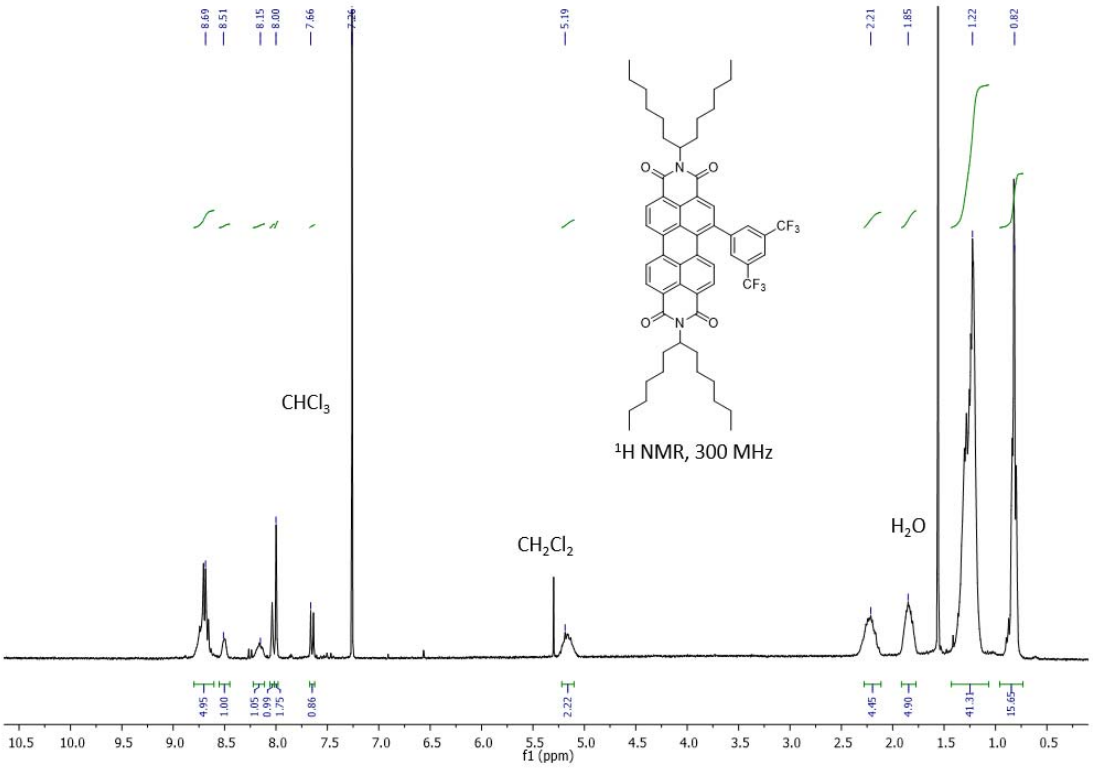


Figure S19. ^{1}H NMR (300 MHz) spectrum of compound **13** in $CDCl_3$.

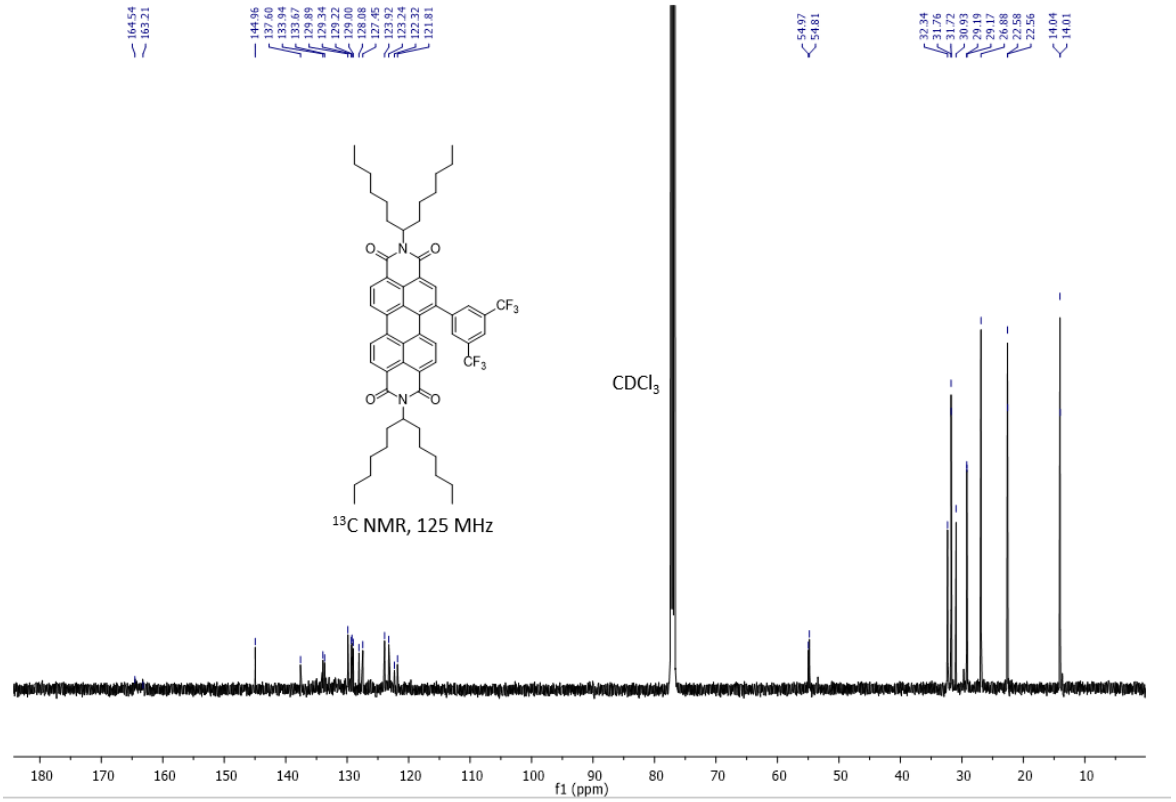


Figure S20. ^{13}C NMR (125 MHz) spectrum of compound **13** in $CDCl_3$.

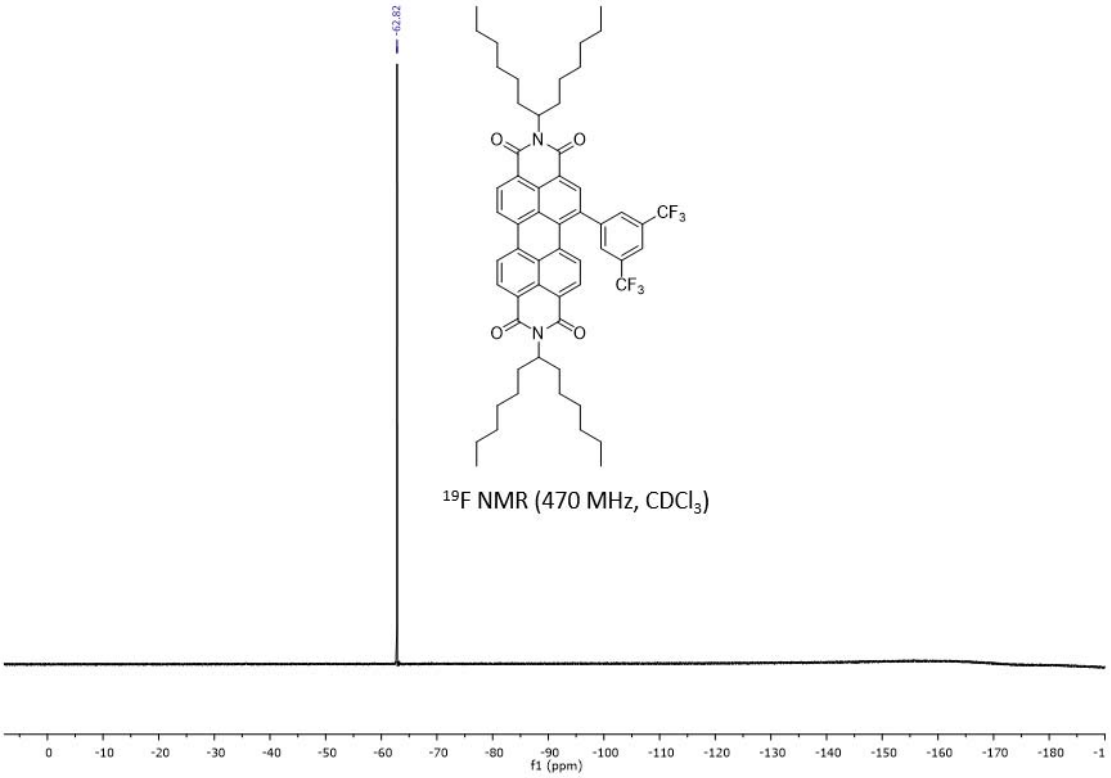


Figure S21. ^{19}F NMR (470 MHz) spectrum of compound **13** in $CDCl_3$.

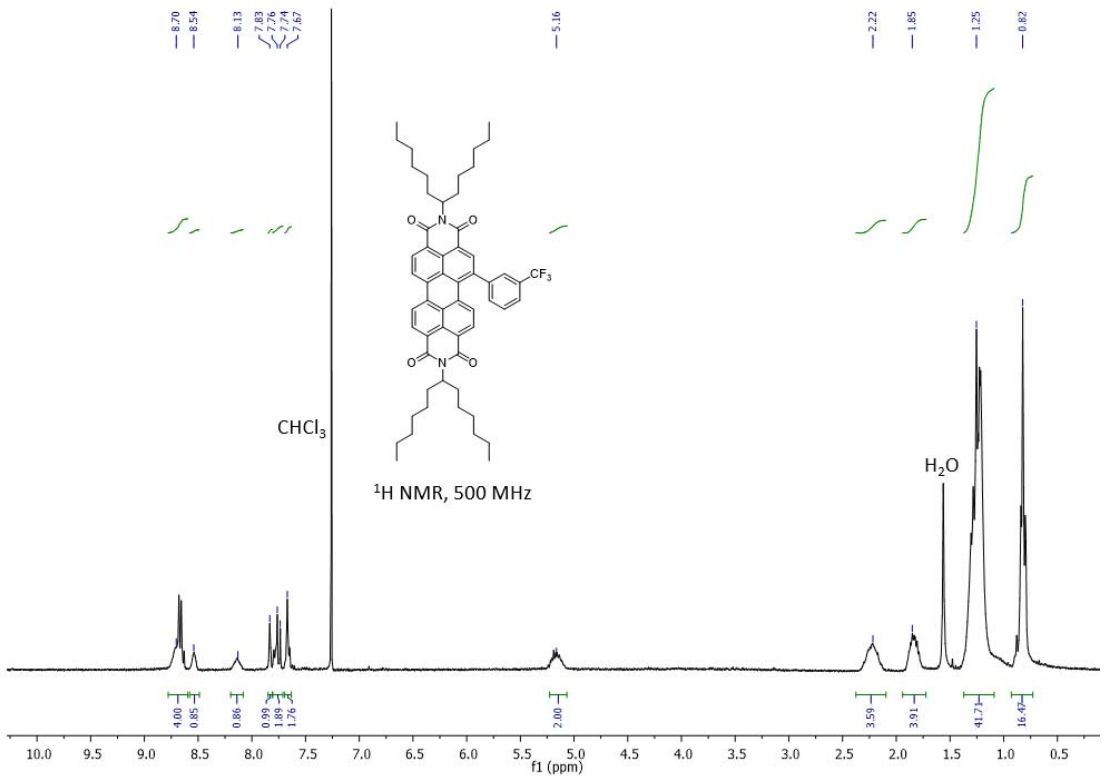


Figure S22. ^{1}H NMR (500 MHz) spectrum of compound **14** in $CDCl_3$.

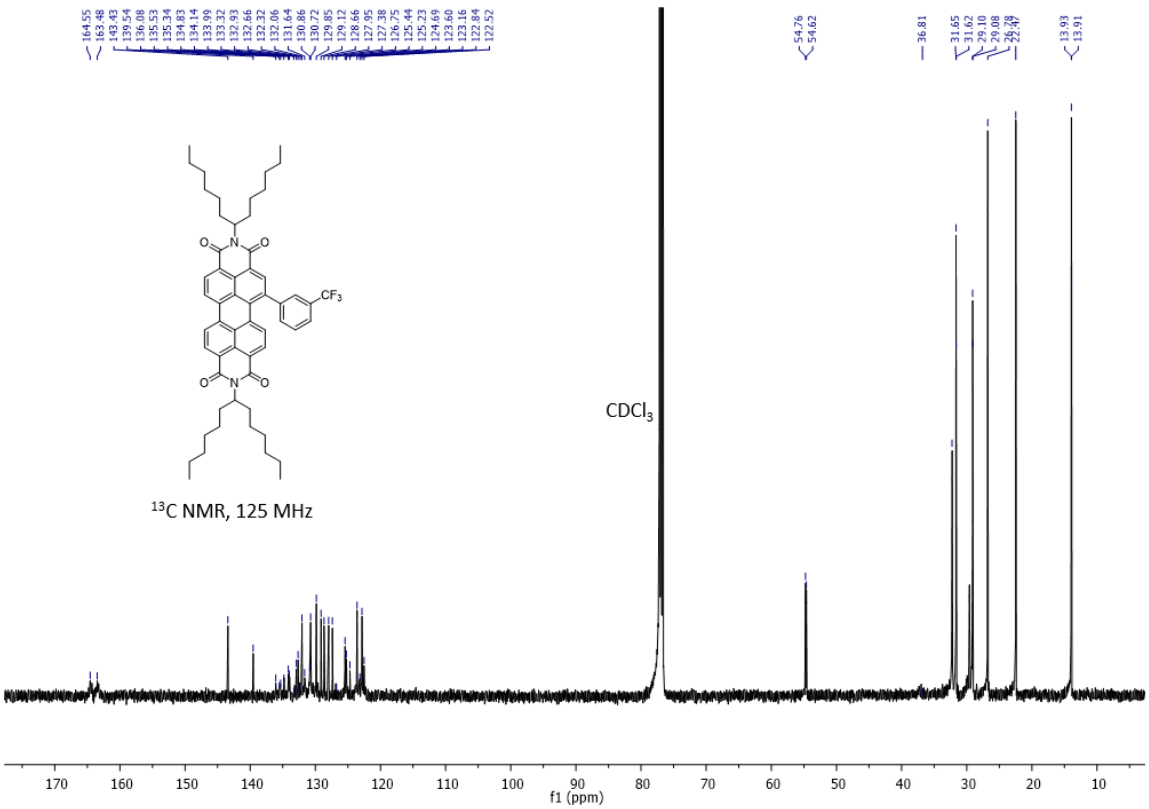


Figure S23. ^{13}C NMR (125 MHz) spectrum of compound **14** in $CDCl_3$.

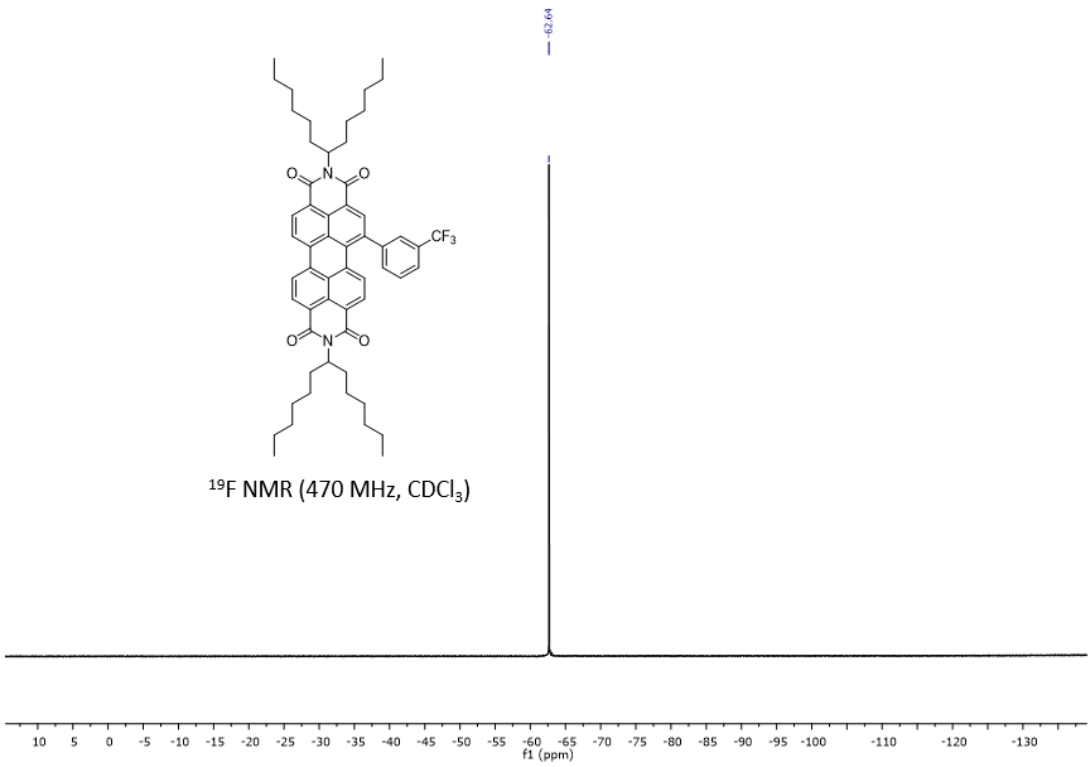


Figure S24. ^{19}F NMR (470 MHz) spectrum of compound **14** in $CDCl_3$.

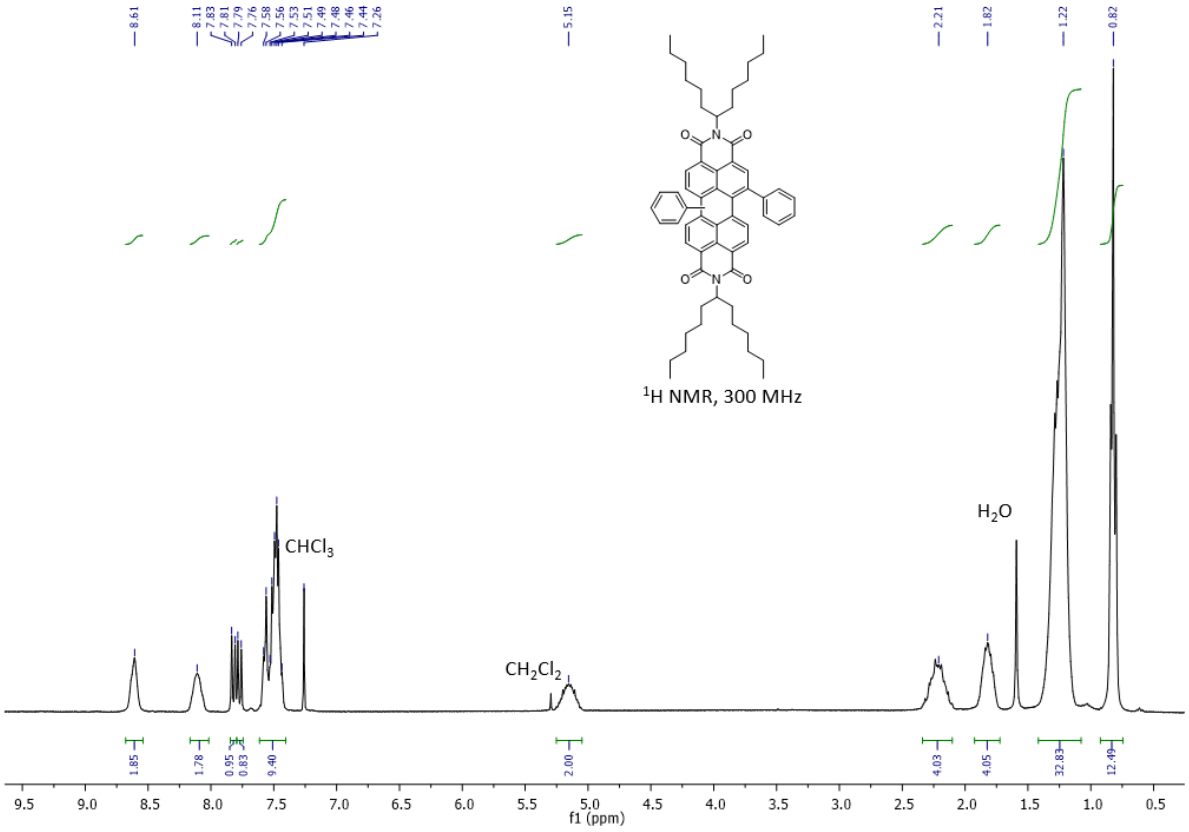


Figure S25. ^{1}H NMR (300 MHz) spectrum of compound **16** in $CDCl_3$.

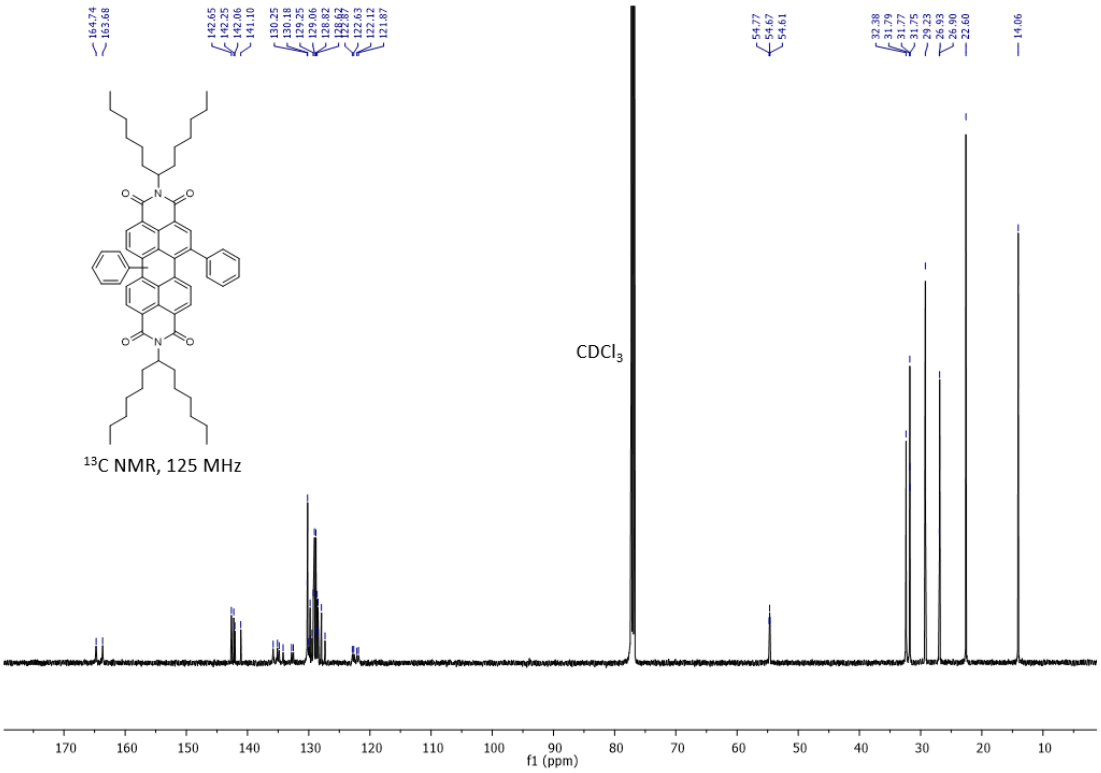


Figure S26. ^{13}C NMR (125 MHz) spectrum of compound **16** in $CDCl_3$.

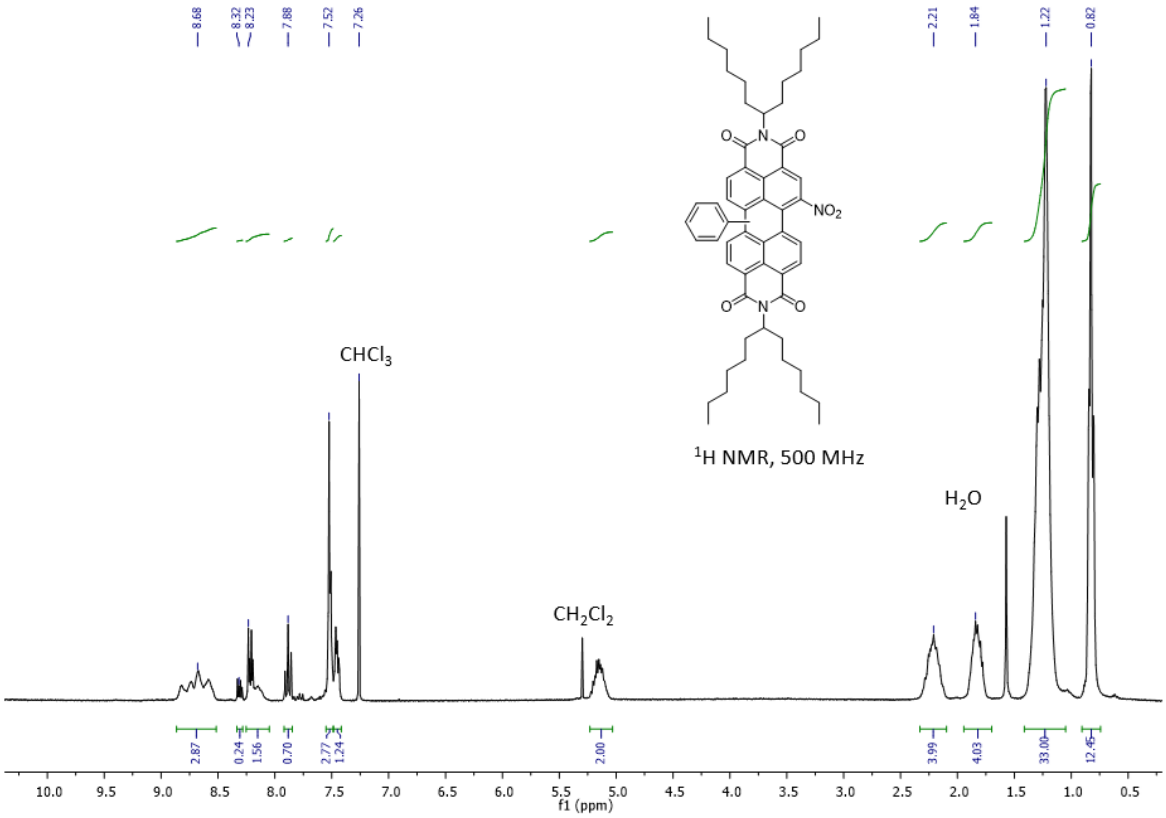


Figure S27. ^{1}H NMR (500 MHz) spectrum of compound **17** in $CDCl_3$.

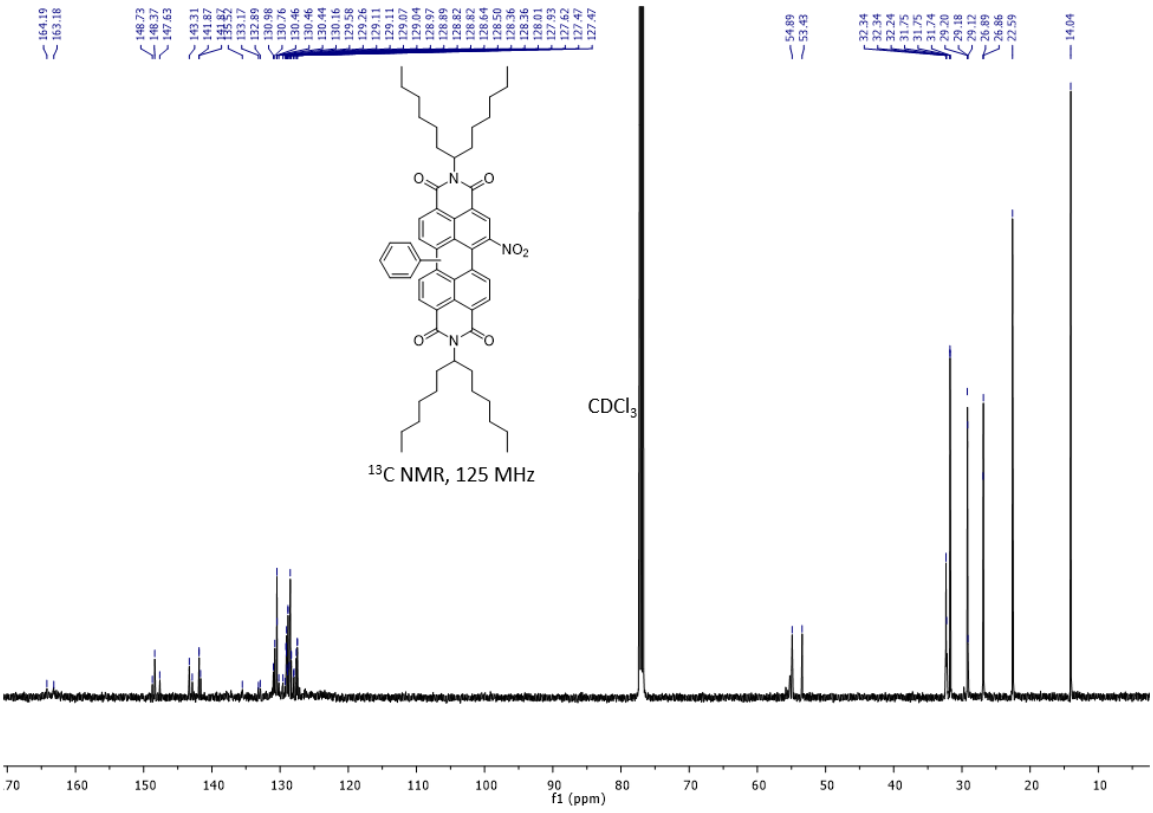


Figure S28. ^{13}C NMR (125 MHz) spectrum of compound **17** in $CDCl_3$.

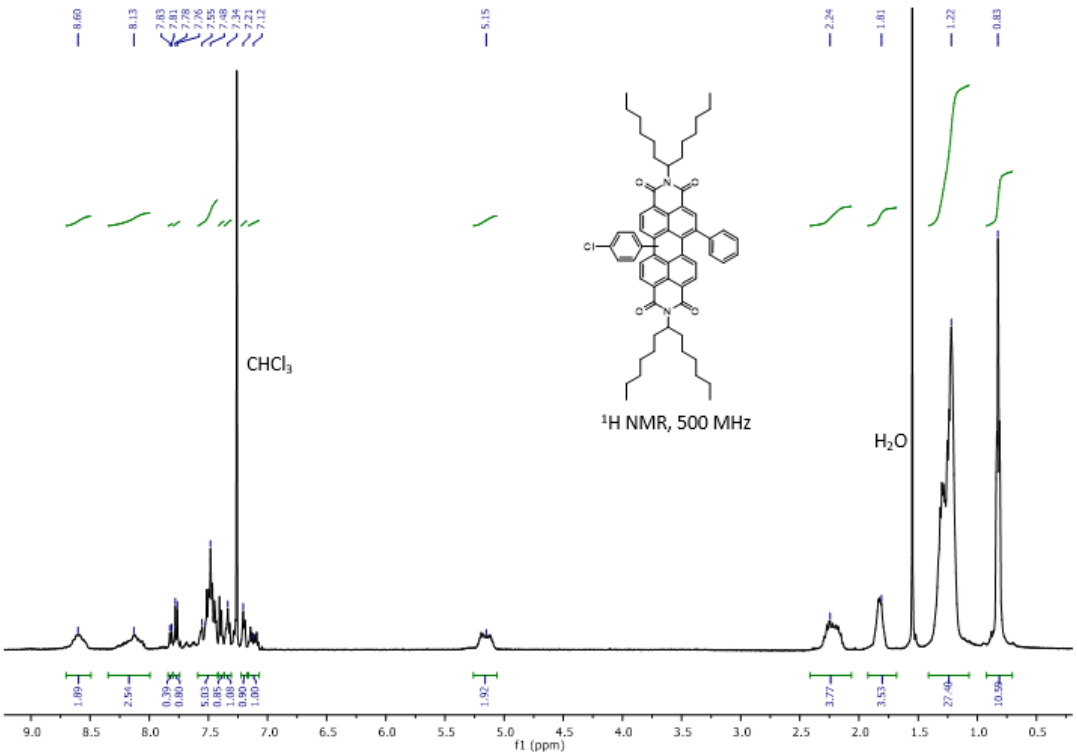


Figure S29. ^{1}H NMR (300 MHz) spectrum of compound **18** in $CDCl_3$.

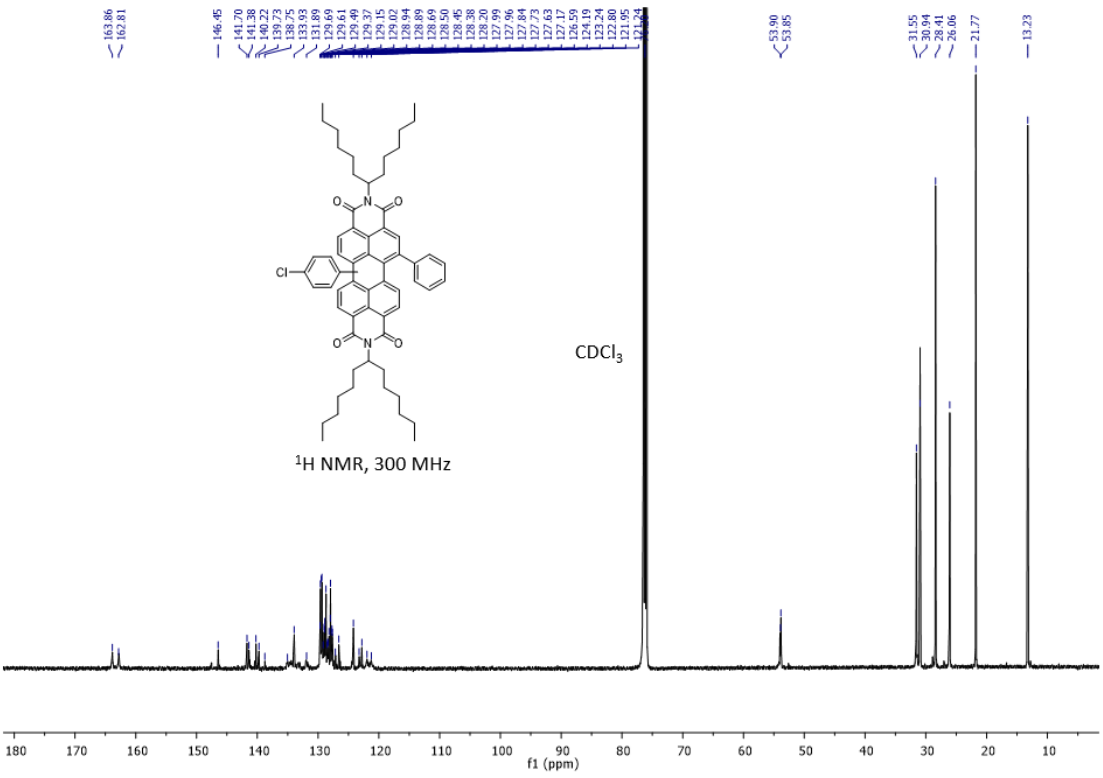


Figure S30. ^{13}C NMR (125 MHz) spectrum of compound **18** in $CDCl_3$.

4. High Resolution Mass Spectrometry

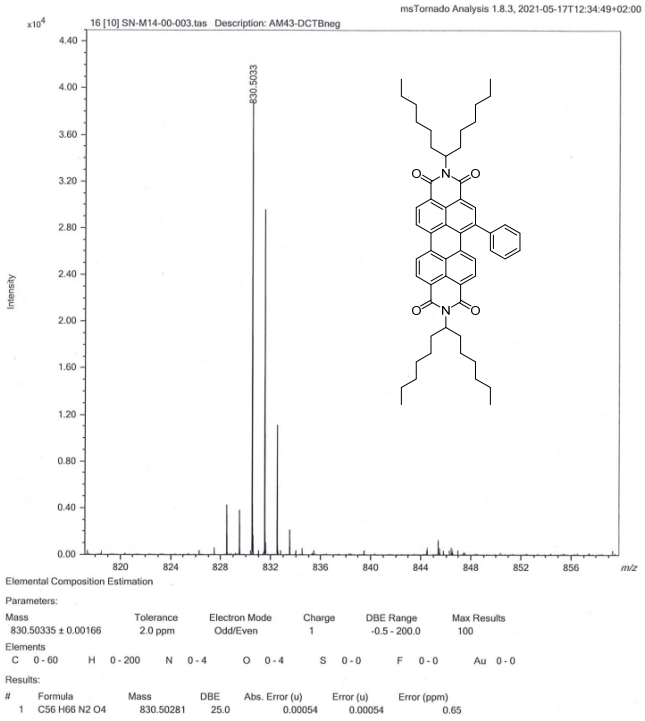


Figure S31. HRMS spectrum of compound **4**.

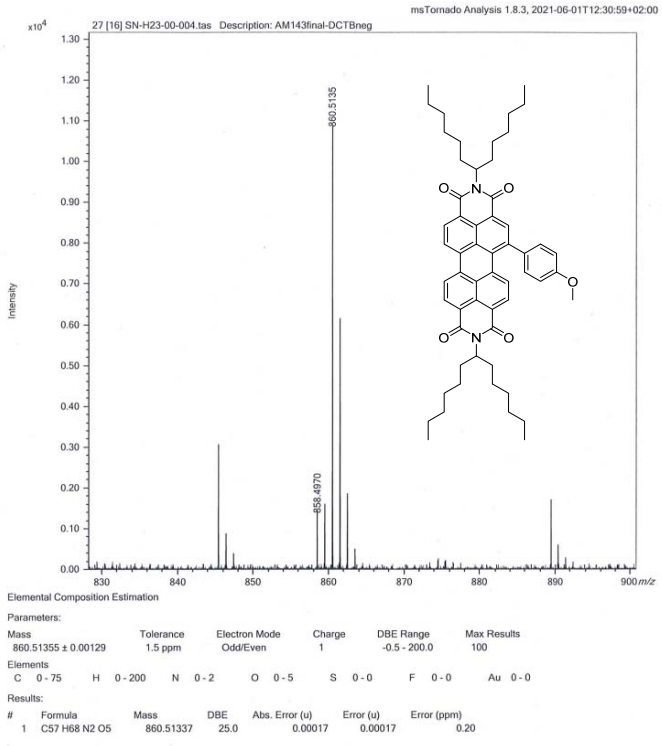


Figure S32. HRMS spectrum of compound **5**.

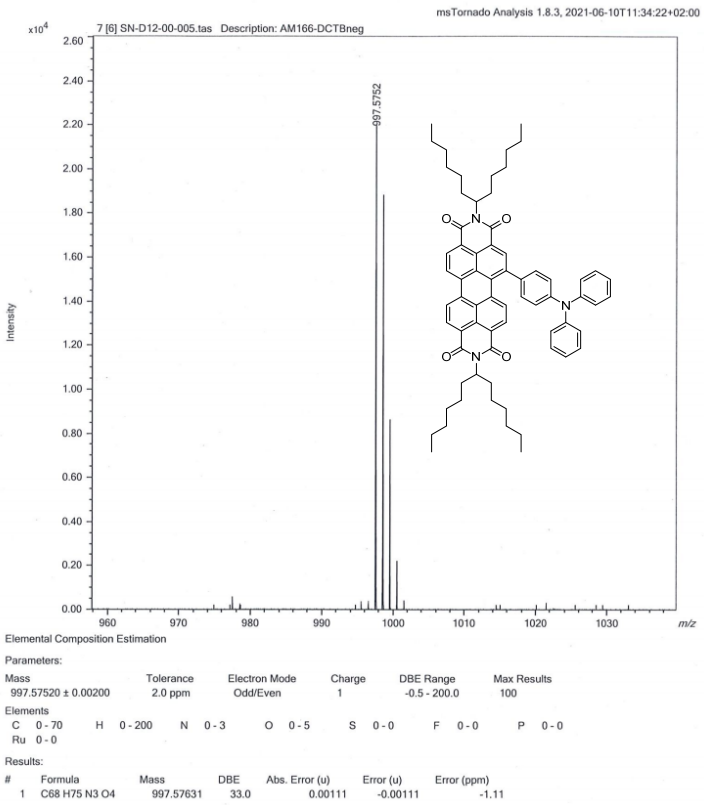


Figure S33. HRMS spectrum of compound **6**.

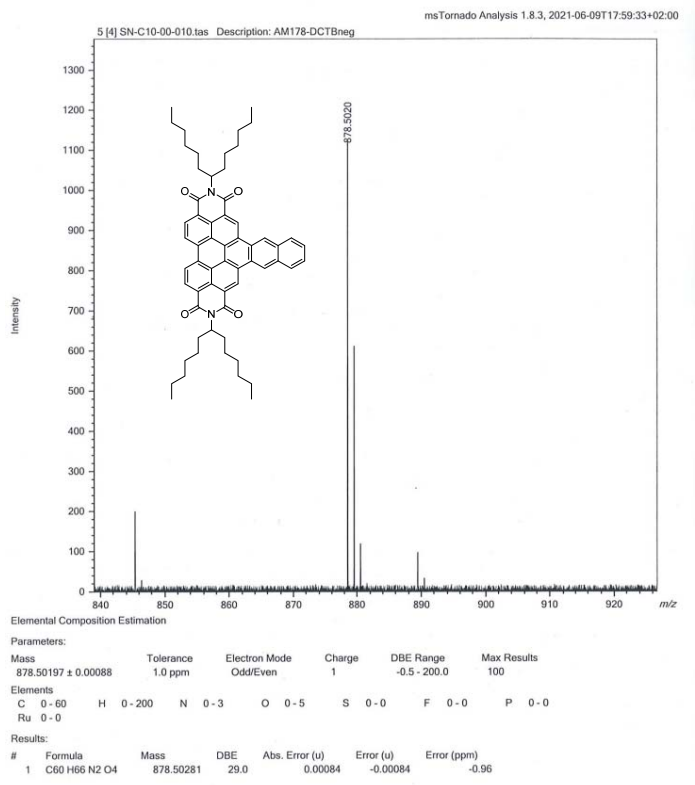


Figure S34. HRMS spectrum of compound **7**.

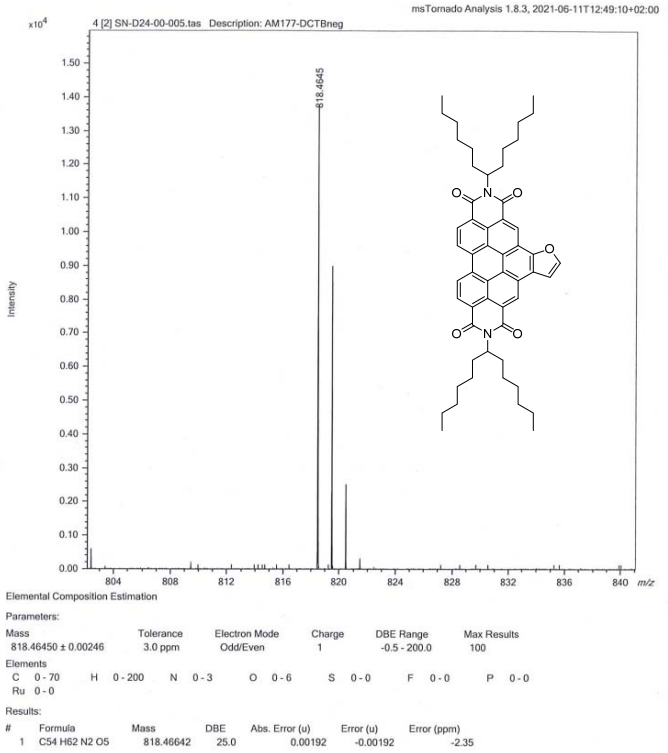


Figure S35. HRMS spectrum of compound **8**.

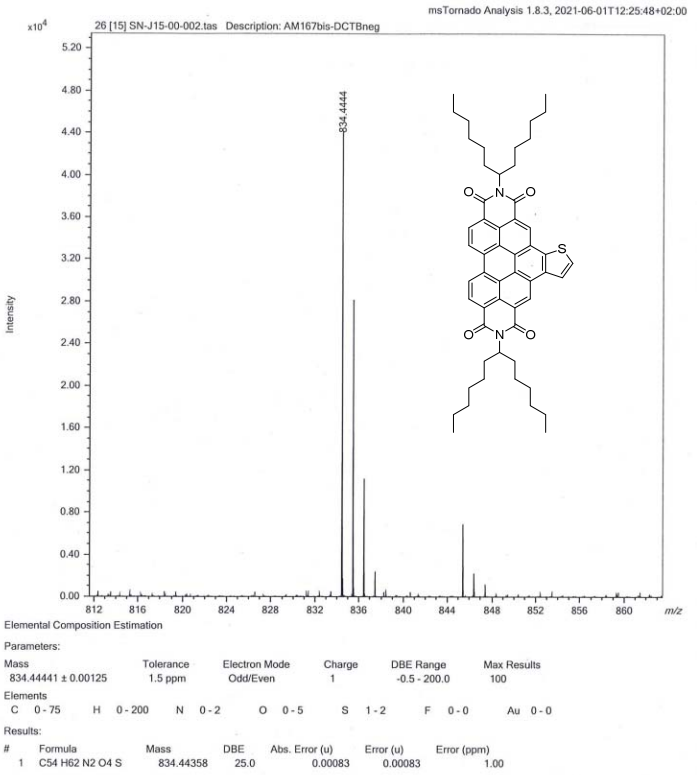


Figure S36. HRMS spectrum of compound **9**.

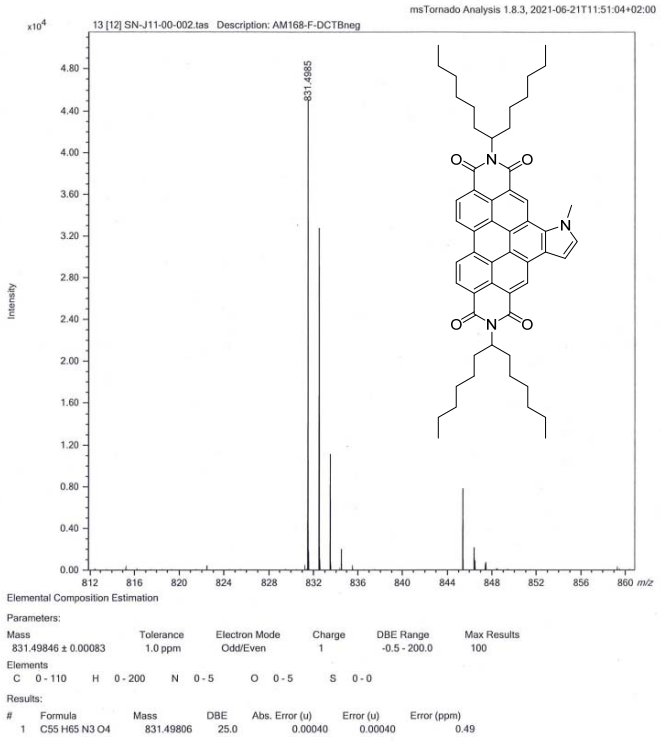


Figure S37. HRMS spectrum of compound **10**.

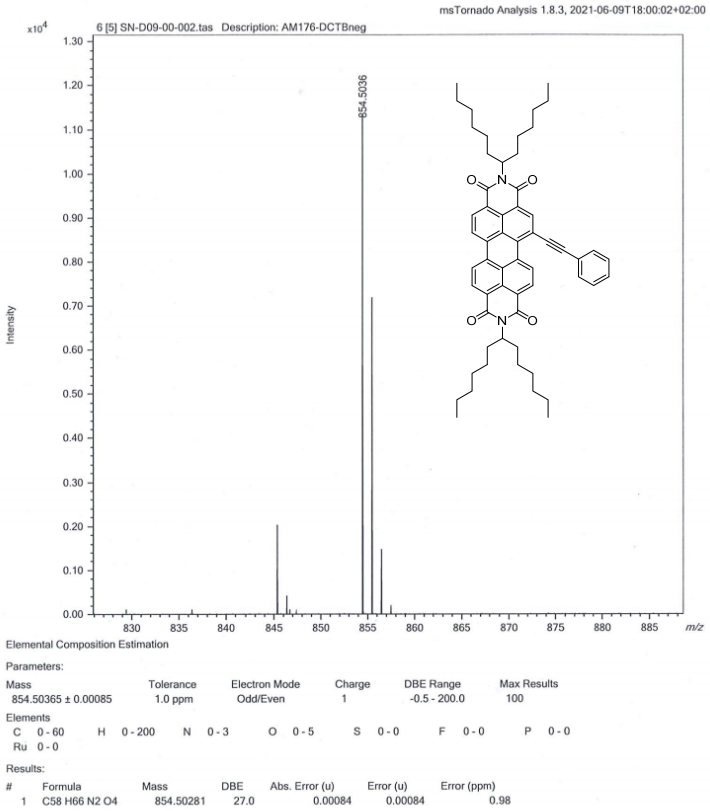


Figure S38. HRMS spectrum of compound **11**.

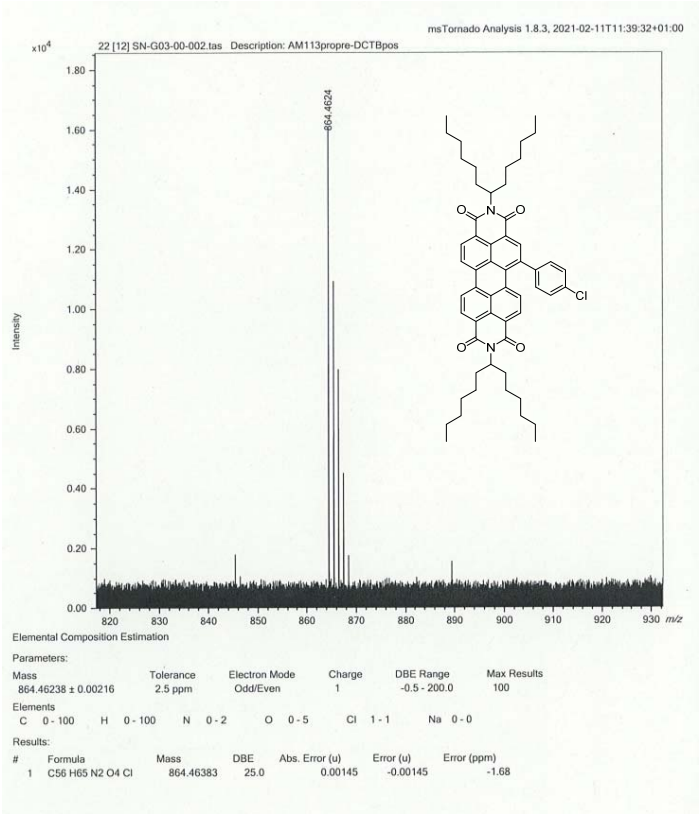


Figure S39. HRMS spectrum of compound **12**.

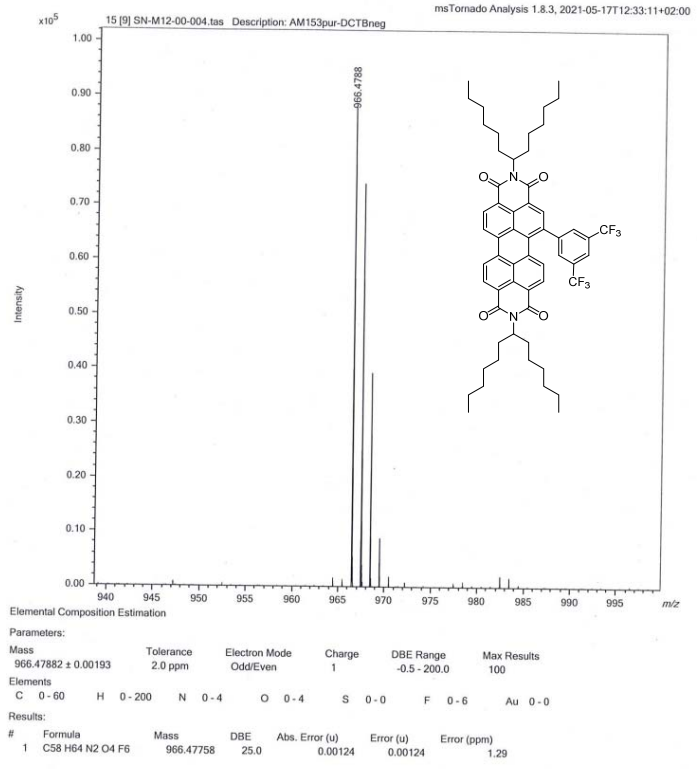


Figure S40. HRMS spectrum of compound **13**.

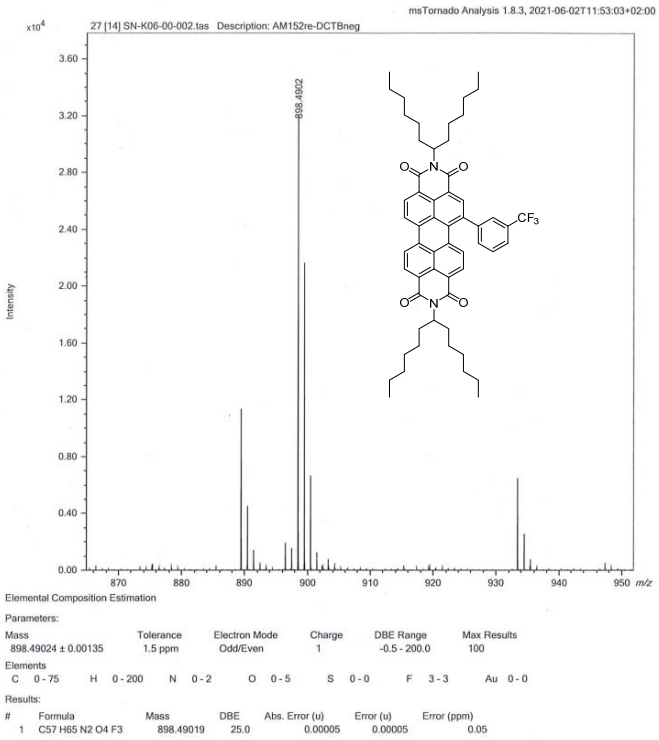


Figure S41. HRMS spectrum of compound **14**.

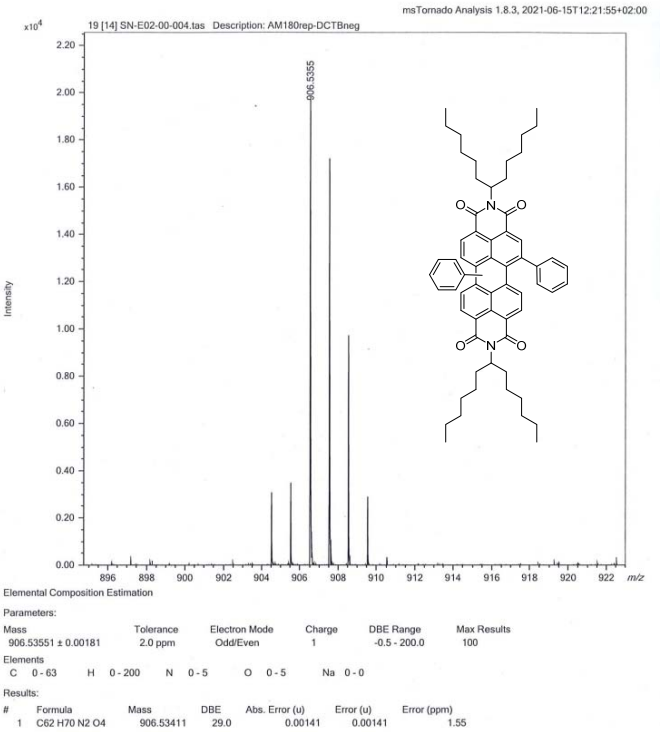


Figure S42. HRMS spectrum of compound **16**.

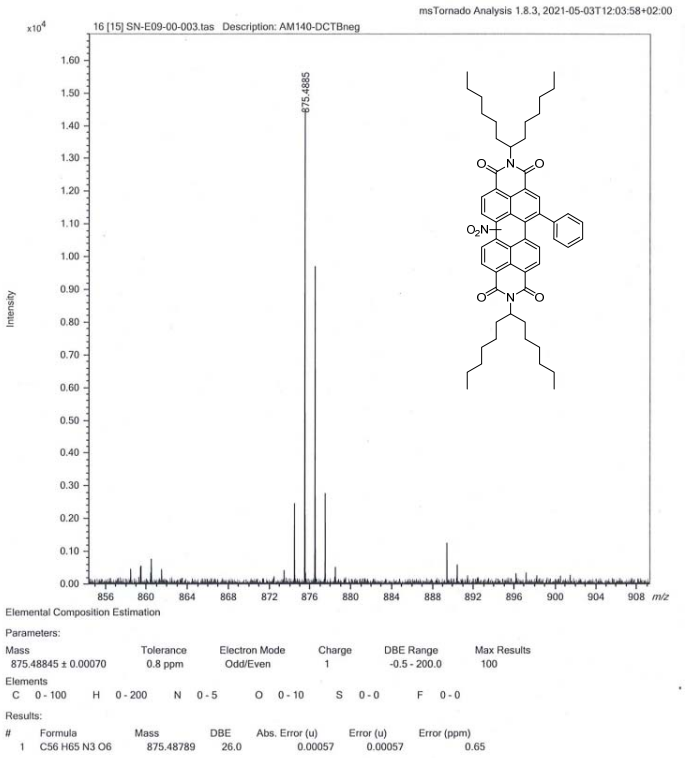


Figure S43. HRMS spectrum of compound **17**.

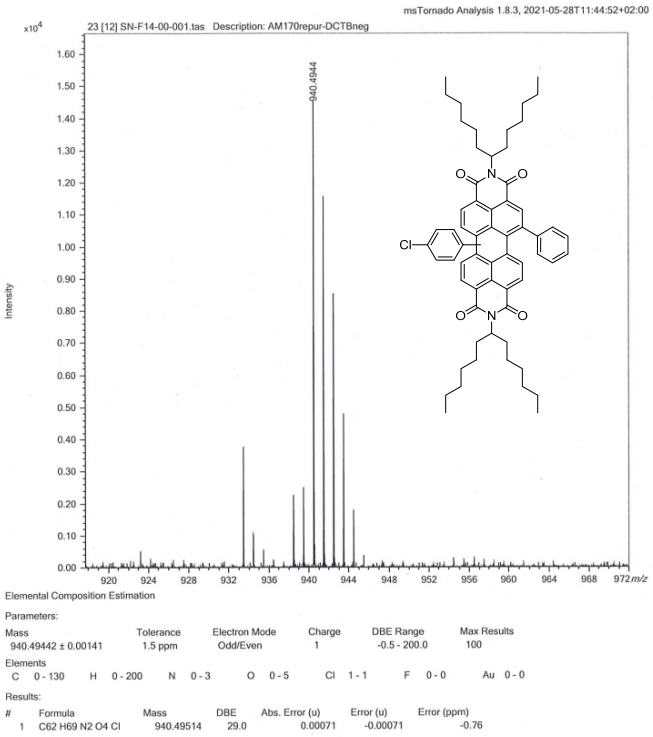


Figure S44. HRMS spectrum of compound **18**.

5. References

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