

Supporting Information

Synthesis of N-Fused Dithia and Dibenzi Homoporphyrins

Rima Sengupta, Prosenjit Isar and Mangalampalli Ravikanth*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076,
India, E-mail: ravikanth@chem.iitb.ac.in

Sr. no	Details	Page no.
1	Experimental Section	S2-S7
2	Figures S1-S20. Characterization (HRMS and NMR) data for all new compounds	S8-S27
3	Figure S21. Absorption spectra for compounds 3-7 with and without TFA	S28
4	Tables S2-S4. X-ray crystal data for the compound 6	S29-S32
5	Figure S22. DFT optimized structure of 6	S33
6	Tables S5-S6. Cartesian coordinates of the optimized (S0) geometries of the compounds 3 and 6 .	S34-S36
7	Table S7. Absorption data of compounds 3-7	S37
8	References	S37-S38

Experimental Section

General Experimental: The chemicals such as $\text{BF}_3 \cdot \text{OEt}_2$, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were obtained from Aldrich. All other chemicals used for the synthesis were reagent grade unless and otherwise specified. Column chromatography was performed on silica gel and basic alumina. The ^1H , and ^{13}C NMR spectra were recorded in CDCl_3 on Bruker 400 and 500 MHz instruments. The frequencies for ^{13}C nucleus are 100.06 and 125.77 MHz for 400 MHz and 500 MHz instruments respectively. Tetramethylsilane [$\text{Si}(\text{CH}_3)_4$] was used as an internal standard for ^1H and ^{13}C NMR. Absorption spectra were obtained with Shimadzu UV-Vis-NIR Spectrophotometer. X-ray Crystal Structure Analysis. Single-crystal X-ray structure analysis was performed on a Bruker D8 Quest that was equipped with a low-temperature attachment. Data were collected at 293 K using graphite-monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) by ω -scan technique. The data were reduced by using CrysAlisPro 1.171.38.43 software. The structures were solved by direct methods and refined by least-squares against F^2 utilizing the software packages SHELXL-2018/3 in Olex2 1.2. All non-hydrogen atoms were refined anisotropically. An empirical absorption correction by multiscans was applied, and all of the non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were placed in ideal positions and fixed with relative isotropic displacement parameters. The solvent molecules that could not be identified or modeled were found and eventually squeezed using the function squeeze in Olex2. The corresponding loop of the residual electron-voids (from Olex2) was appended in the corresponding cif file. CCDC No. 2078340 (for compound **6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. IR spectra were recorded with a Nicolet Impact-400 FTIR

spectrometer with KBr plates and analyzed.

Computational Information. A Gaussian 09 program package was used for performing all the calculations. The optimized structures of compound **3** and **6** in ground (S₀) states were generated using the density functional theory (DFT)¹ technique, hybrid functional B3LYP with basis set 6-31G(d,p).² Identical basis and functional hybrid set were used to obtain the oscillator strengths, and vertical excitation energies were obtained for S₀→S_n transitions by the help of TD-DFT techniques.³⁻⁷ By making use of the self-consistent reaction field (SCRF), several computations were performed in toluene under the polarizable continuum model (PCM).^{8,9}

General procedure for synthesis of N-fused dibenzi homoporphyrins 3-7:

The dithienyl diol **8**, *p*-phenylene diol **9** and N-confused dipyrromethane **10** were synthesized by the reported methods. Samples of appropriate diol **8/9** (0.60 mmol, 1 eqv) and appropriate N-confused dipyrromethane **10** (0.60 mmol, 1 eqv) were dissolved in 200 mL CH₂Cl₂ and purged N₂ gas for 15 mins. BF₃.OEt₂ (0.18 mmol, 0.3 eqv) was added to initiate the reaction and stirred the reaction mixture under nitrogen for 30 mins. DDQ (1.5 mmol, 2.5 eqv) was added to the solution and continued stirring in open air for another 30 mins. The reaction mixture was concentrated on a rotary evaporator under reduced pressure and the crude compound was purified by neutral alumina column chromatography using petroleum ether/dichloromethane as eluent and afforded the desired N-fused homoporphyrins **3-7** in 3-10 % yields as dark red/green solids.

Table S1. Reaction conditions used for the synthesis of N-fused homoporphyrin 6.

Acid (Equivalent)	Solvent	Oxidant (Equivalent)	Yield (%)
BF ₃ .OEt ₂ (0.1)	200 mL	DDQ (1.5)	0.5
BF ₃ .OEt ₂ (0.1)	200 mL	DDQ (2.5)	1
BF ₃ .OEt ₂ (0.3)	200 mL	DDQ (1.5)	1
BF ₃ .OEt ₂ (0.3)	200 mL	DDQ (2.5)	3
BF ₃ .OEt ₂ (0.3)	50 mL	DDQ (2.5)	2
BF ₃ .OEt ₂ (1)	200 mL	DDQ (1.5)	0.6
BF ₃ .OEt ₂ (1)	200 mL	DDQ (2.5)	1.2
BF ₃ .OEt ₂ (1)	50 mL	DDQ (2.5)	1.2
BF ₃ .OEt ₂ (0.3)	200 mL	<i>p</i> -Chloranil (2.5)	1
BF ₃ .OEt ₂ (0.3)	200 mL	<i>p</i> -Chloranil (3.5)	1
TFA (0.5)	200 mL	DDQ (2.5)	X
TFA (1)	200 mL	DDQ (2.5)	X
TFA (0.5)	50 mL	DDQ (2.5)	X

Synthesis of compound 3a:

Purified by basic alumina column chromatography using petroleum ether/CH₂Cl₂ (80:20), 10% yield (41.22 mg); red colored crystalline solid; R_f = 0.7; mp. >300° C; ¹H NMR (500 MHz, CDCl₃), δ 7.38 (d, J = 8.4 Hz, 2H, Ar), 7.34 (d, J = 7.9 Hz, 2H, Ar), 7.22 (d, J = 3.1 Hz, 3H, Ar, Thiophene-H), 7.14 (d, J = 7.8 Hz, 2H, Ar), 7.05 (d, J = 3.3 Hz, 1H, Thiophene-H), 6.95 (d, J = 8.4 Hz, 2H, Ar), 6.86 (d, J = 8.5 Hz, 2H, Ar), 6.79 (d, J = 3.9 Hz, 1H, Pyrrole-H), 6.65 (dd, J = 10.1, 4.8 Hz, 2H, Pyrrole-H, Thiophene-H), 6.51 (d, J = 5.7 Hz, 1H, Thiophene-H), 6.34 (s, 1H, Pyrrole-H), 3.88 (s, 3H, OCH₃), 3.84 (s, 3H, OCH₃), 2.34 (s, 3H, Tolylyl-CH₃), 2.16 (s, 6H, Ethene-CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 164.1, 160.2, 159.6, 156.5, 154.4, 154.0, 150.5, 146.4, 143.1, 141.3, 140.7, 136.4, 136.0, 135.7, 134.3, 132.9, 132.4, 130.9, 130.8, 130.2, 130.1, 129.4, 127.7, 127.5, 127.1, 125.7, 123.9, 120.7, 119.4, 119.1, 113.3, 109.4, 55.3, 55.2, 23.0, 21.2, 17.9. IR (KBr) 3434, 2923, 2852, 1601, 1507, 1461, 1401, 1364, 1247, 1174, 1123, 1031, 835, 732, 689 cm⁻¹. HRMS (ESI-TOF) calcd. for C₄₄H₃₅N₂O₂S₂ (M+H)⁺ 687.2134; found 687.2133.

Synthesis of compound 3b:

Purified by basic alumina column chromatography using petroleum ether/CH₂Cl₂ (80:20), 10% yield (40.38 mg); red colored crystalline solid; R_f = 0.7; mp. >300° C; ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, J = 7.5 Hz, 2H, Ar), 7.39 (d, J = 8.6 Hz, 2H, Ar), 7.33 (t, J = 7.7 Hz, 2H, Ar), 7.25 – 7.15 (m, 4H, Ar, Thiophene-H), 7.06 (d, J = 3.5 Hz, 1H, Thiophene-H), 6.95 (d, J = 8.6 Hz, 2H, Ar), 6.86 (d, J = 8.8 Hz, 2H, Ar), 6.79 (d, J = 4.0 Hz, 1H, Pyrrole-H), 6.68 (d, J = 5.7 Hz, 1H, Thiophene-H), 6.64 (d, J = 4.0 Hz, 1H, Pyrrole-H), 6.53 (d, J = 5.7 Hz, 1H, Thiophene-H), 6.36 (s, 1H, Pyrrole-H), 3.88 (s, 3H, Anisyl-CH₃), 3.84 (s, 3H, Anisyl-CH₃), 2.16 (s, 6H, Ethene-CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 164.3, 160.5, 159.9, 156.7, 155.1, 154.3, 150.9, 146.6, 143.4, 141.8, 140.8, 137.0, 136.0, 134.5, 134.0, 133.2, 132.7, 131.22, 130.64, 130.3, 129.0, 128.0, 127.8, 127.4, 126.3, 126.1, 124.2, 120.9, 119.9, 119.7, 181.8 – 6.3, 113.7, 113.6, 109.6, 55.6, 55.5, 30.0, 23.3. IR (KBr) 3434, 2930, 2850, 1601, 1503, 1465, 1401, 1362, 1247, 1172, 1123, 1031, 835, 732, 689 cm⁻¹. HRMS (ESI-TOF) calcd. for C₄₃H₃₃N₂O₂S₂ (M+H)⁺ 673.1978; found 673.1977.

Synthesis of compound 4:

Purified by neutral alumina column chromatography using petroleum ether/CH₂Cl₂ (80:20), 4% yield (15.40 mg); green colored crystalline solid; R_f = 0.5; mp. >300° C; ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, J = 7.8 Hz, 2H, Ar), 7.38 (d, J = 7.8 Hz, 2H, Ar), 7.23 (d, J = 7.8 Hz, 2H, Ar), 7.17 (d, J = 4.3 Hz, 4H, Ar), 7.13 – 7.08 (m, 4H, Ar), 7.04 (d, J = 7.8 Hz, 2H, Ar), 6.97 (d, J = 7.8 Hz, 2H, Ar), 6.73 (s, 1H, Pyrrole), 6.65 (d, J = 8.0 Hz, 2H, Ar), 6.58 (d, J = 5.7 Hz, 1H, Pyrrole), 6.41 (d, J = 5.8 Hz, 1H, Pyrrole), 2.42 (s, 3H, Toly-CH₃), 2.36 (d, J = 3.2 Hz, 6H, Toly-CH₃), 2.24 (s, 3H, Ethene-CH₃), 2.08 (s, 3H, Ethene-CH₃). ¹³C{¹H} NMR (126 MHz,

CDCl₃) δ 167.2, 159.7, 156.7, 149.0, 145.2, 144.8, 142.5, 141.7, 139.9, 139.6, 139.3, 137.4, 136.7, 136.5, 136.3, 135.4, 134.5, 133.7, 132.7, 132.0, 131.5, 131.1, 129.8, 129.1, 128.9, 127.9, 127.7, 126.2, 124.6, 119.4, 118.0, 107.5, 23.0, 21.6, 21.5, 20.1, 18.9. IR (KBr) 3474, 3393, 2954, 2924, 2853, 1602, 1508, 1456, 1408, 1361, 1249, 1176, 1159, 1016, 829, 815, 798, 573 cm⁻¹. HRMS (ESI-TOF) calcd. for C₄₈H₃₈N₂ (M+H)⁺ 643.3108; found 643.3107.

Synthesis of compound 5:

Purified by neutral alumina column chromatography using petroleum ether/CH₂Cl₂ (80:20), 6% yield (22.60 mg); green colored crystalline solid; R_f = 0.5; mp. >300° C; ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 7.1 Hz, 2H, Ar), 7.43 (d, J = 7.3 Hz, 2H, Ar), 7.39 – 7.33 (m, 2H, Ar), 7.17-7.23 (m, 5H, Ar), 7.15 – 7.09 (m, 4H, Ar), 7.04 (d, J = 7.2 Hz, 2H, Ar), 6.97 (d, J = 7.3 Hz, 2H, Ar), 6.76 (s, 1H, Pyrrole-H), 6.66 (d, J = 7.7 Hz, 2H, Ar), 6.61 (d, J = 5.6 Hz, 1H, Pyrrole-H), 6.44 (d, J = 5.3 Hz, 1H, Pyrrole-H), 2.43 (s, 3H, Tolylyl-CH₃), 2.37 (s, 3H, Tolylyl-CH₃), 2.24 (s, 3H, Ethene-CH₃), 2.08 (s, 3H, Ethene-CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 145.3, 144.9, 142.3, 142.0, 139.9, 139.9, 139.3, 137.8, 137.0, 136.5, 135.4, 134.7, 134.1, 133.7, 132.7, 132.0, 131.6, 129.1, 129.2, 128.9, 127.9, 127.8, 126.5, 126.2, 119.4, 118.0, 107.4, 30.0, 21.7, 20.1, 18.9. IR (KBr) 3440, 2925, 2849, 1607, 1510, 1465, 1400, 1359, 1245, 1165, 1119, 1026, 842, 755, 602 cm⁻¹. HRMS (ESI-TOF) calcd. for C₄₇H₃₆N₂ (M+H)⁺ 629.2951; found 629.2958.

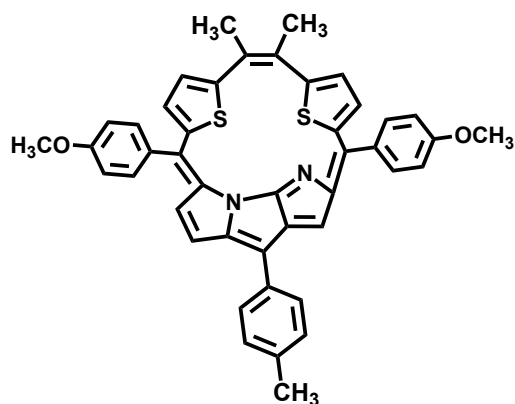
Synthesis of compound 6:

Purified by neutral alumina column chromatography using petroleum ether/CH₂Cl₂ (60:40), 3% yield (12.13 mg); green colored crystalline solid; R_f = 0.8; mp. >300° C; ¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, J = 7.5 Hz, 2H, Ar), 7.39 (d, J = 7.3 Hz, 2H, Ar), 7.18 (d, J = 5.4 Hz, 4H, Ar),

7.12 (d, $J = 7.1$ Hz, 2H, Ar), 7.06 (d, $J = 7.5$ Hz, 2H, Ar), 7.01 – 6.92 (m, 4H, Ar), 6.83 (d, $J = 7.3$ Hz, 2H, Ar), 6.73 (s, 1H, Pyrrole-H), 6.66 (d, $J = 7.2$ Hz, 2H, Ar), 6.59 (d, $J = 4.7$ Hz, 1H, Pyrrole-H), 6.41 (d, $J = 4.7$ Hz, 1H, Pyrrole-H), 3.87 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃), 2.36 (s, 3H, Toly-CH₃), 2.24 (s, 3H, Ethene-CH₃), 2.08 (s, 3H, Ethene-CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 160.3, 158.8, 156.1, 141.8, 139.3, 136.5, 136.1, 135.8, 134.9, 134.0, 133.8, 133.2, 133.0, 132.7, 132.4, 131.6, 131.2, 130.7, 129.4, 129.3, 129.2, 127.9, 127.5, 126.7, 125.7, 123.9, 113.5, 113.4, 113.1, 112.1, 106.8, 63.2, 53.4, 52.8, 52.2, 45.8. IR (KBr) 3432, 2930, 2848, 1605, 1505, 1455, 1395, 1352, 1234, 1162, 1123, 1023, 830, 762, 633 cm⁻¹. HRMS (ESI-TOF) calcd. for C₄₈H₃₈N₂O₂ (M+H)⁺ 675.3006; found 675.3001.

Synthesis of compound 7:

Purified by neutral alumina column chromatography using petroleum ether/CH₂Cl₂ (60:40), 5% yield (19.80 mg); green colored crystalline solid; $R_f = 0.8$; mp. >300° C; ¹H NMR (400 MHz, CDCl₃) δ 7.49 (t, $J = 8.6$ Hz, 4H, Ar), 7.37 (t, $J = 7.7$ Hz, 2H, Ar), 7.19 (d, $J = 8.0$ Hz, 3H, Ar), 7.13 (d, $J = 8.2$ Hz, 2H, Ar), 7.07 (d, $J = 8.6$ Hz, 2H, Ar), 6.97 (t, $J = 8.8$ Hz, 4H, Ar), 6.83 (d, $J = 8.6$ Hz, 2H, Ar), 6.76 (s, 1H, Pyrrole-H), 6.66 (d, $J = 8.2$ Hz, 2H, Ar), 6.61 (d, $J = 5.9$ Hz, 1H, Pyrrole-H), 6.43 (d, $J = 5.8$ Hz, 1H, Pyrrole-H), 3.88 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃), 2.24 (s, 3H, Ethene-CH₃), 2.09 (s, 3H, Ethene-CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 166.6, 160.4, 159.0, 158.8, 156.6, 148.7, 144.9, 144.6, 142.1, 139.8, 137.0, 136.5, 135.4, 134.5, 134.3, 134.1, 133.7, 133.3, 132.8, 132.1, 131.6, 129.1, 127.9, 127.8, 126.3, 126.2, 124.8, 119.3, 117.7, 113.9, 113.2, 106.9, 55.4, 55.2, 22.7, 19.8, 18.6. IR (KBr) 3485, 3390, 2952, 2930, 2850, 1615, 1505, 1454, 1420, 1357, 1245, 1165, 1154, 1009, 825, 795, 571 cm⁻¹. HRMS (ESI-TOF) calcd. for C₄₇H₃₆N₂O₂ (M+H)⁺ 661.2850; found 661.2848.



Compound 3a

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

Analysis Info

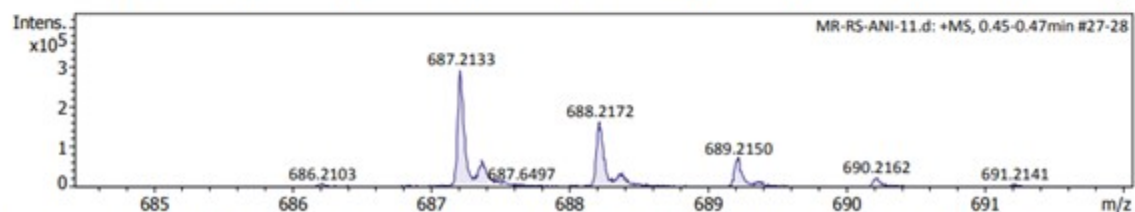
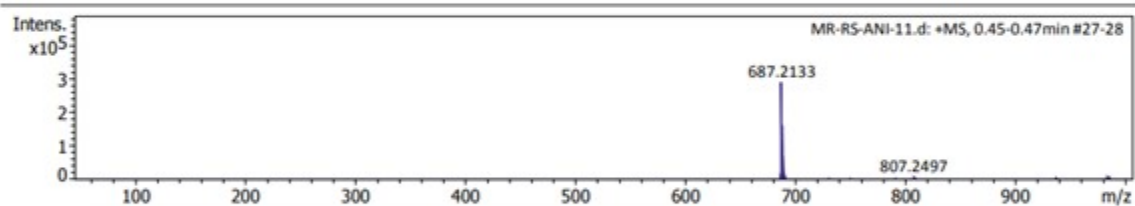
Analysis Name D:\Data\AUG 2021\MR-RS-ANI-11.d
 Method NaICSI_pos_1000.m
 Sample Name MR-RS-ANI-11
 Comment C44H34N2O2S2

Acquisition Date 8/12/2021 6:36:43 PM

Operator MSB-OUT
 Instrument maXis impact 282001.00081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3800 V	Set Dry Heater	180 °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 Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
687.2133	1	C44H35N2O2S2	687.2134	0.3	28.3	1	100.00	33.0	even	ok

Figure S1. HR mass spectrum of the compound 3a.

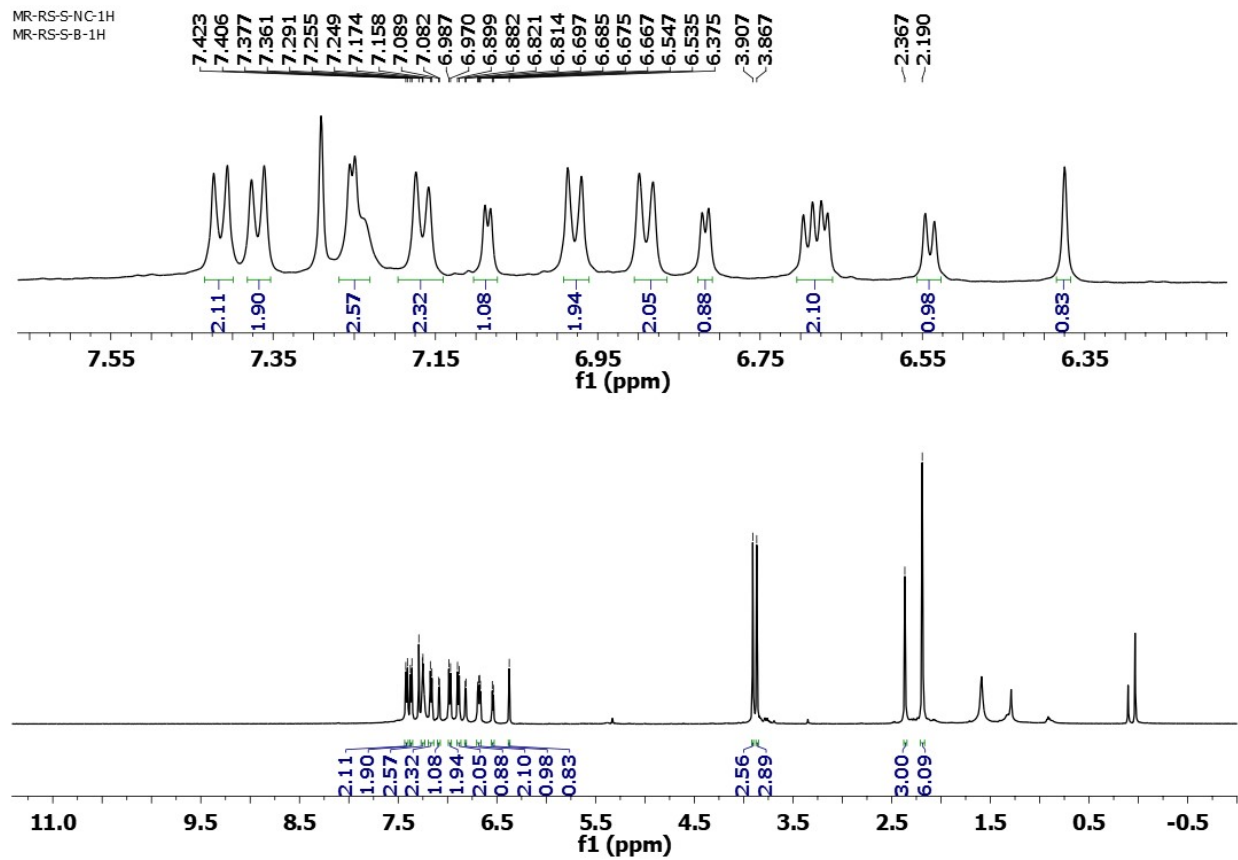


Figure S2. ^1H NMR spectrum of the compound **3a** recorded in CDCl_3 in 500 MHz.

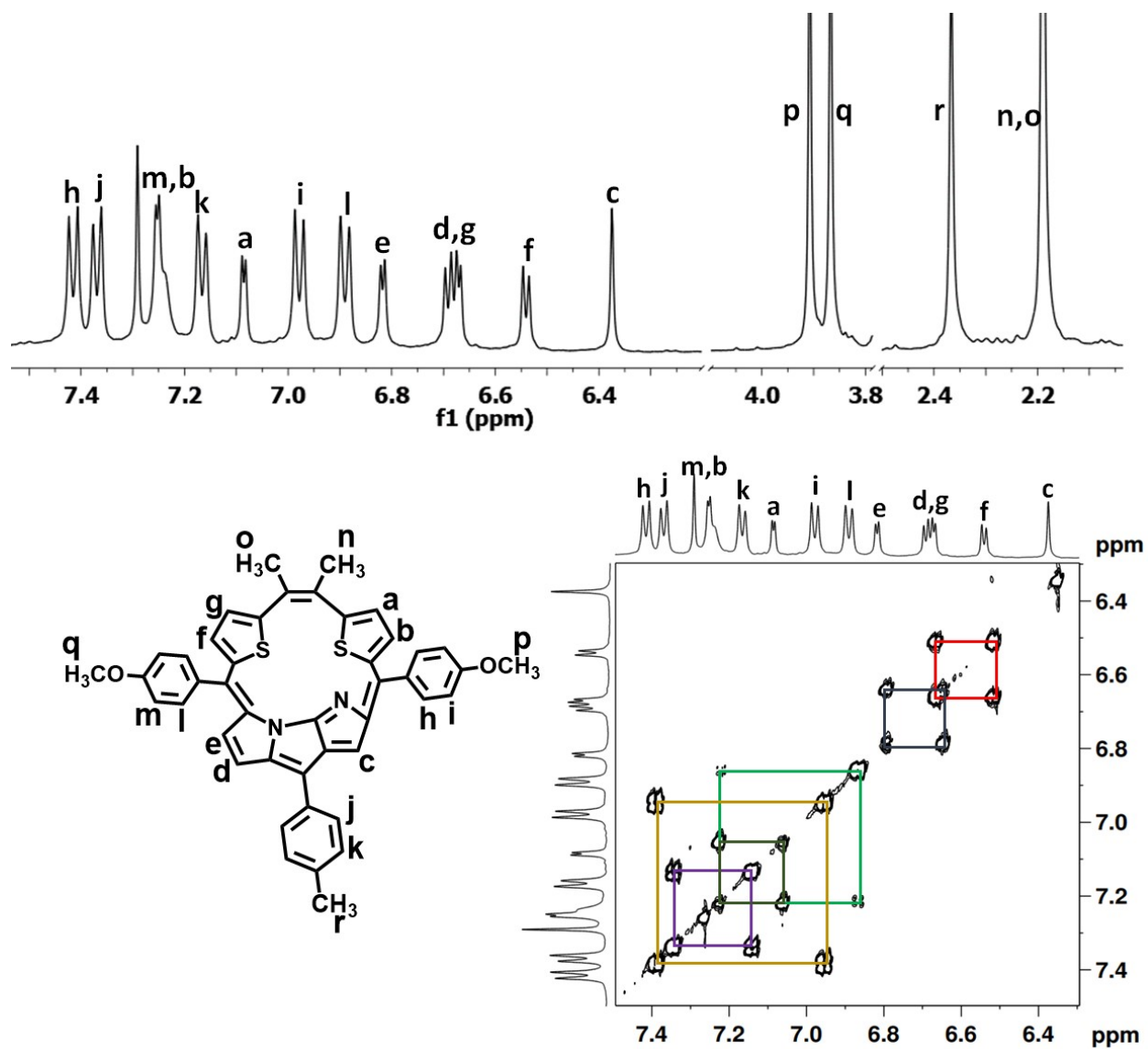


Figure S3. ^1H - ^1H COSY spectrum of the compound **3a** recorded in CDCl_3 in 500 MHz.

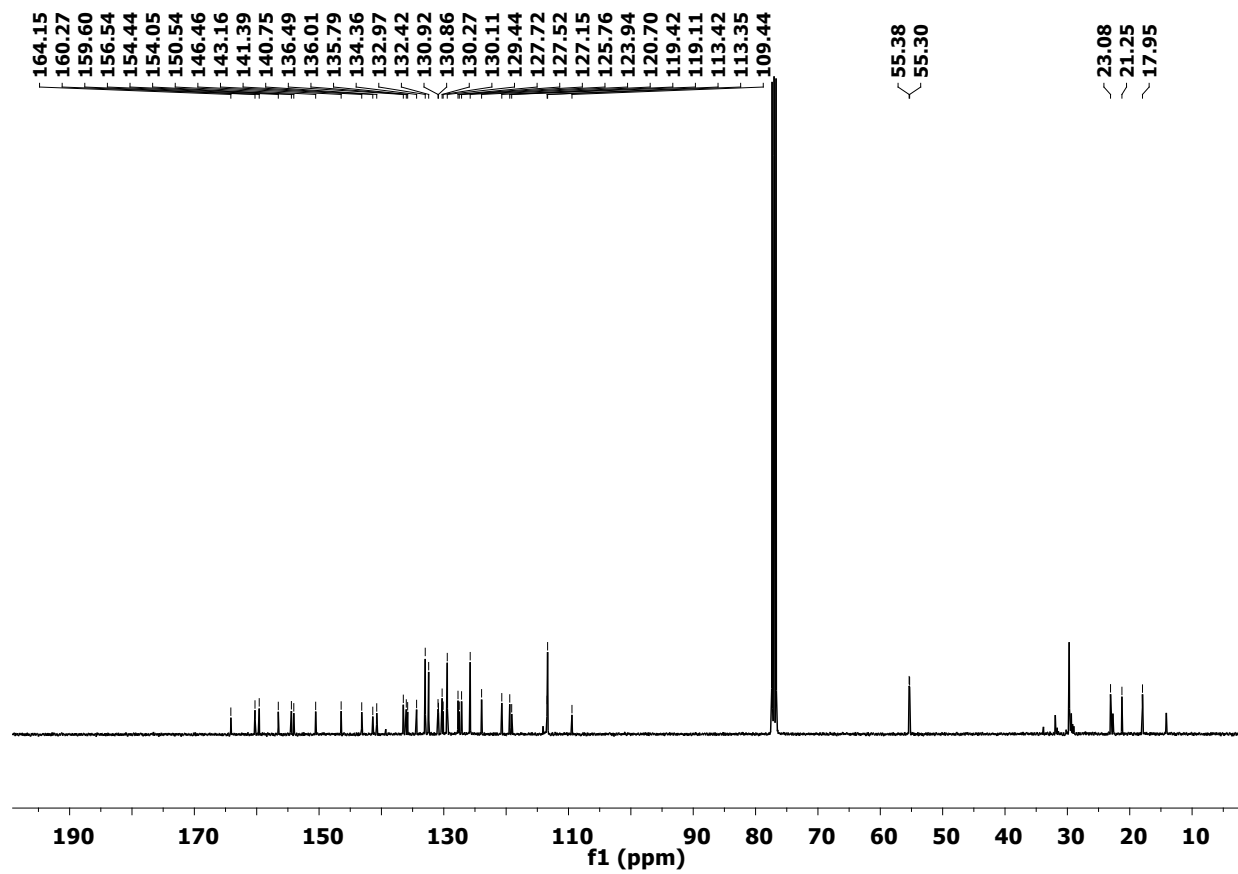
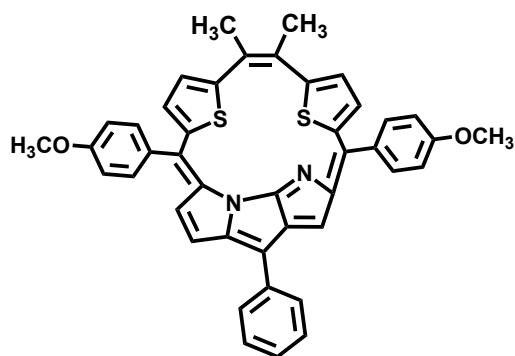


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the compound **3a** recorded in CDCl_3 in 101 MHz.

Compound **3b**

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

Analysis Info

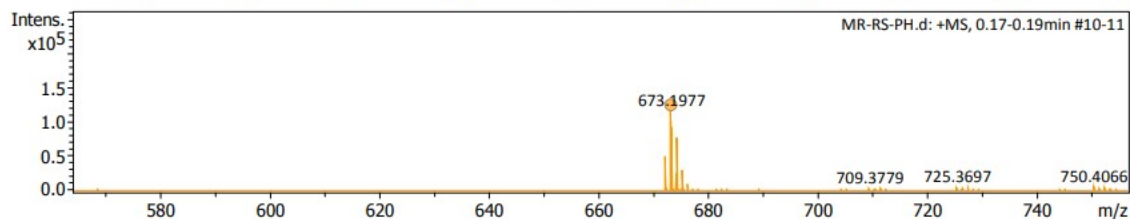
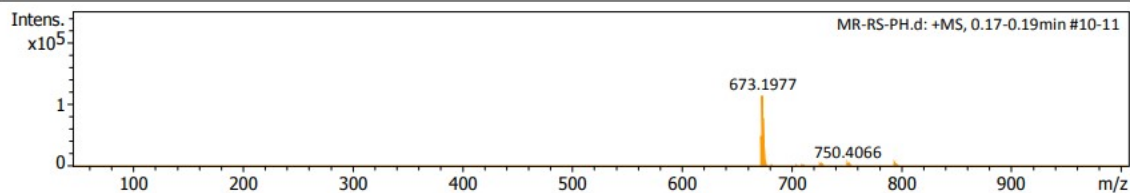
Analysis Name D:\Data\JAN-2022\MR-RS-PH.d
 Method NaICSI_pos_1000-a.m
 Sample Name MR-RS-PH
 Comment C43H32N2O2S2

Acquisition Date 1/21/2022 3:43:21 PM

Operator SJG-IN
 Instrument maXis impact 282001.00081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3700 V	Set Dry Heater	180 °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 Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
673.1977	1	C43H33N2O2S2	673.1978	0.1	85.1	1	100.00	33.0	even	ok

Figure S5. HR mass spectrum of the compound **3b**.

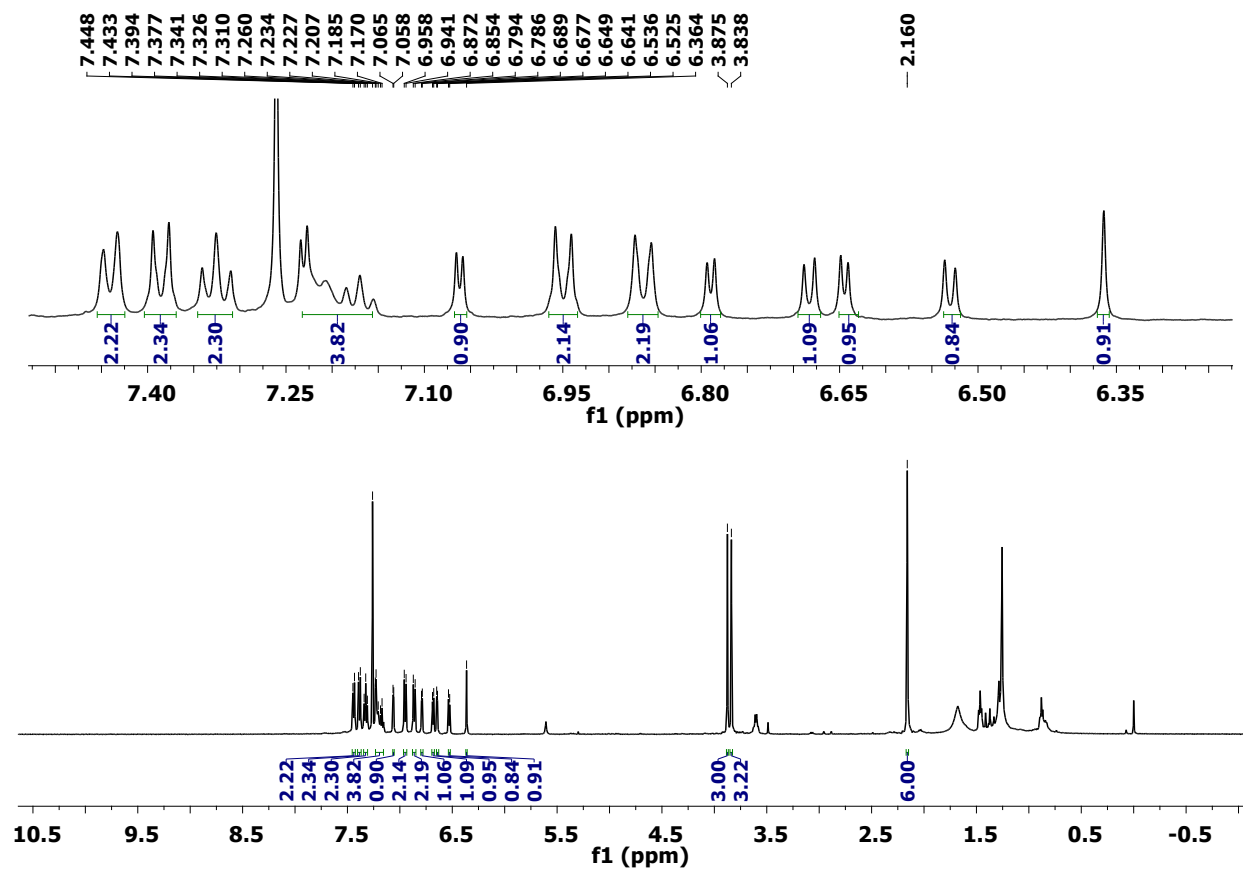


Figure S6. ^1H NMR spectrum of the compound **3b** recorded in CDCl_3 in 500 MHz.

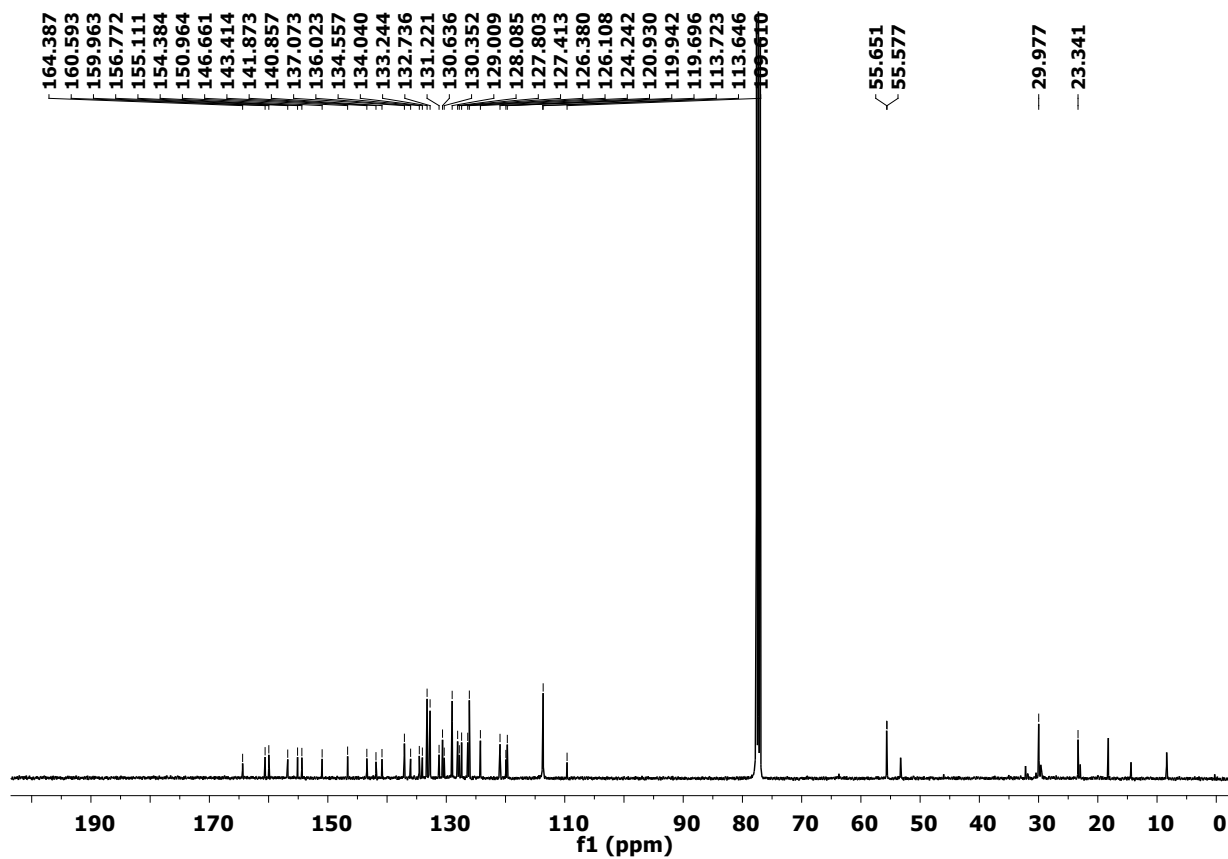
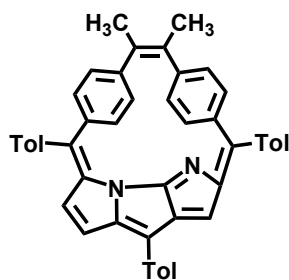


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the compound **3b** recorded in CDCl_3 in 101 MHz.



Compound 4

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

Analysis Info

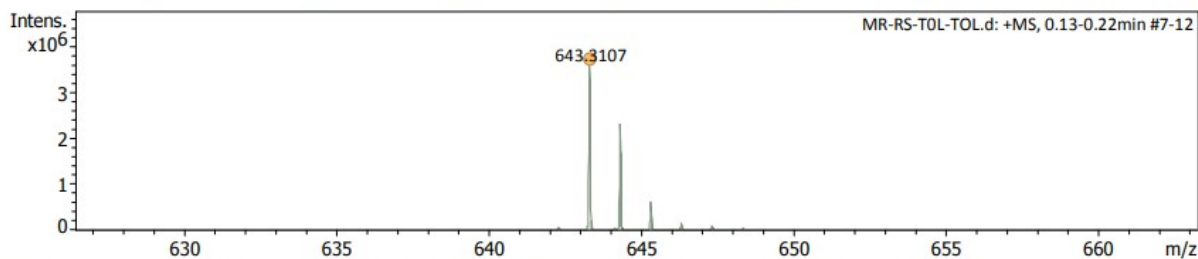
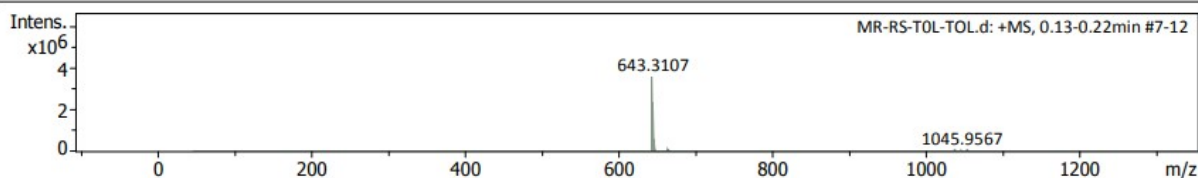
Analysis Name D:\Data\MAR-21\MR-RS-T0L-TOL.d
 Method NaICSI_pos_1500.m
 Sample Name MR-RS-T0L-TOL
 Comment C48H38N2

Acquisition Date 3/9/2021 2:19:00 PM

Operator srk in
 Instrument maXis impact 282001.00081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
643.3107	1	C48H39N2	643.3108	0.1	62.4	1	100.00	31.0	even	ok

Figure S8. HR mass spectrum of the compound 4.

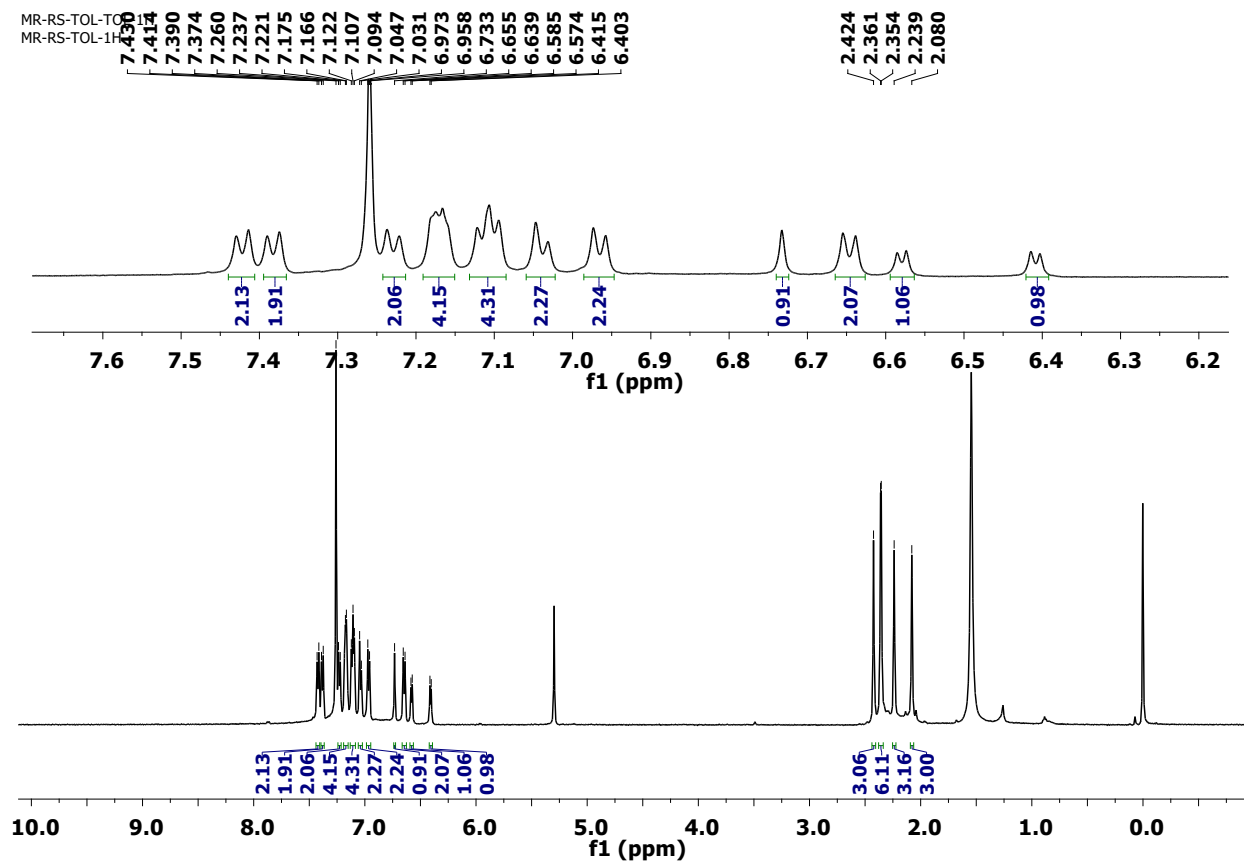


Figure S9. ^1H NMR spectrum of the compound **4** recorded in CDCl_3 in 500 MHz.

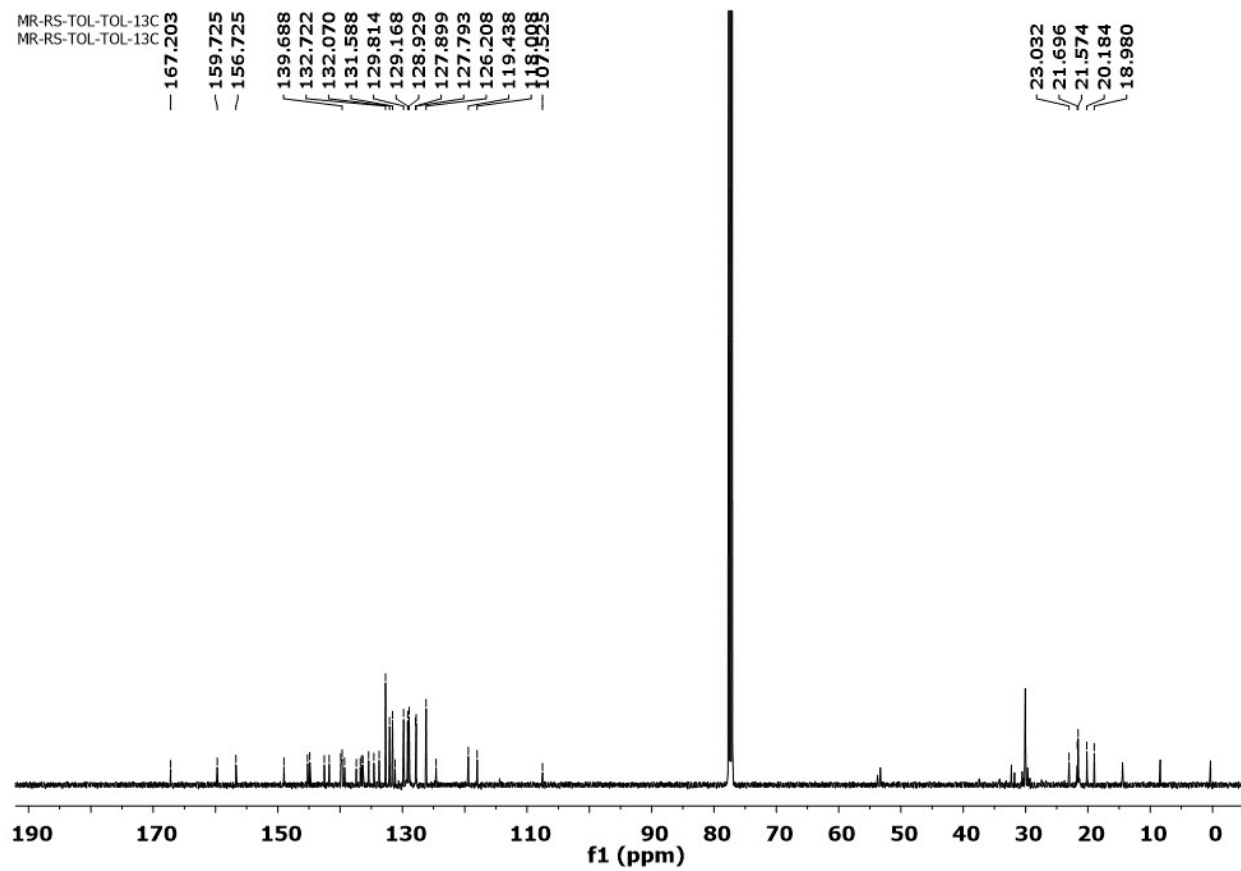
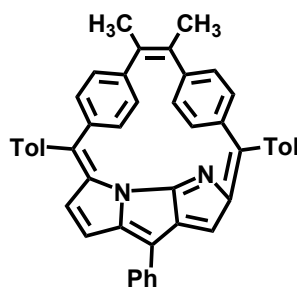


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the compound **4** recorded in CDCl_3 , in 126 MHz.



Compound 5

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

Analysis Info

Analysis Name D:\Data\APR 21\MR-RS-TOL-PH.d
 Method Tune_pos_NAICSI-1000a.m
 Sample Name MR-RS-TOL-PH
 Comment C47H36N2

Acquisition Date 4/12/2021 9:01:11 AM

Operator gkl-in
 Instrument maXis impact 282001.00081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

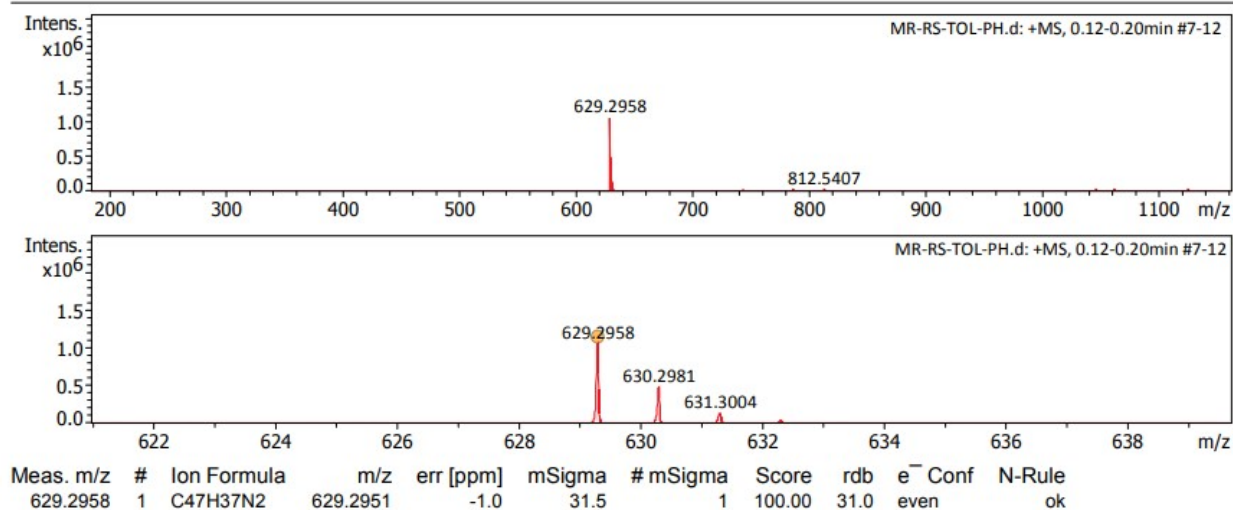


Figure S11. HR mass spectrum of the compound 5.

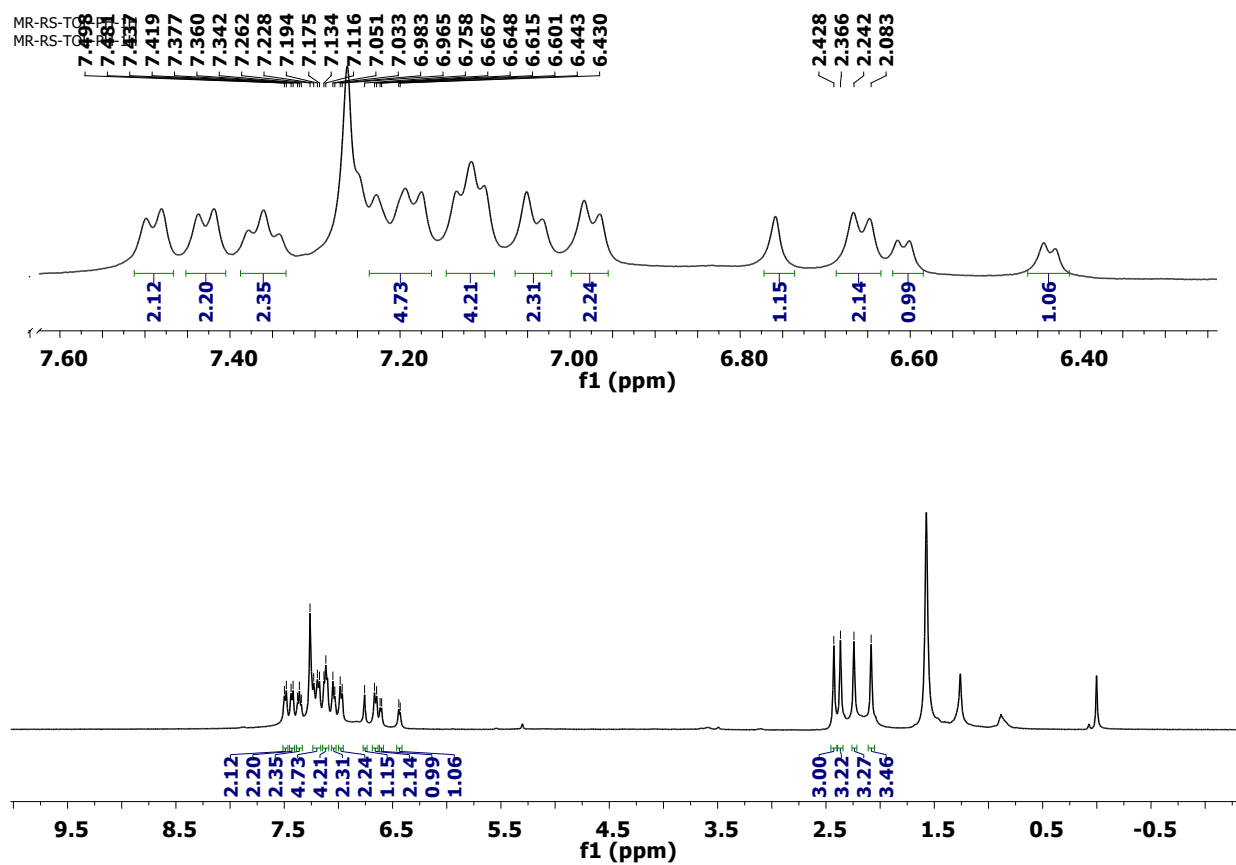


Figure S12. ^1H NMR spectrum of the compound **5** recorded in CDCl_3 in 400 MHz.

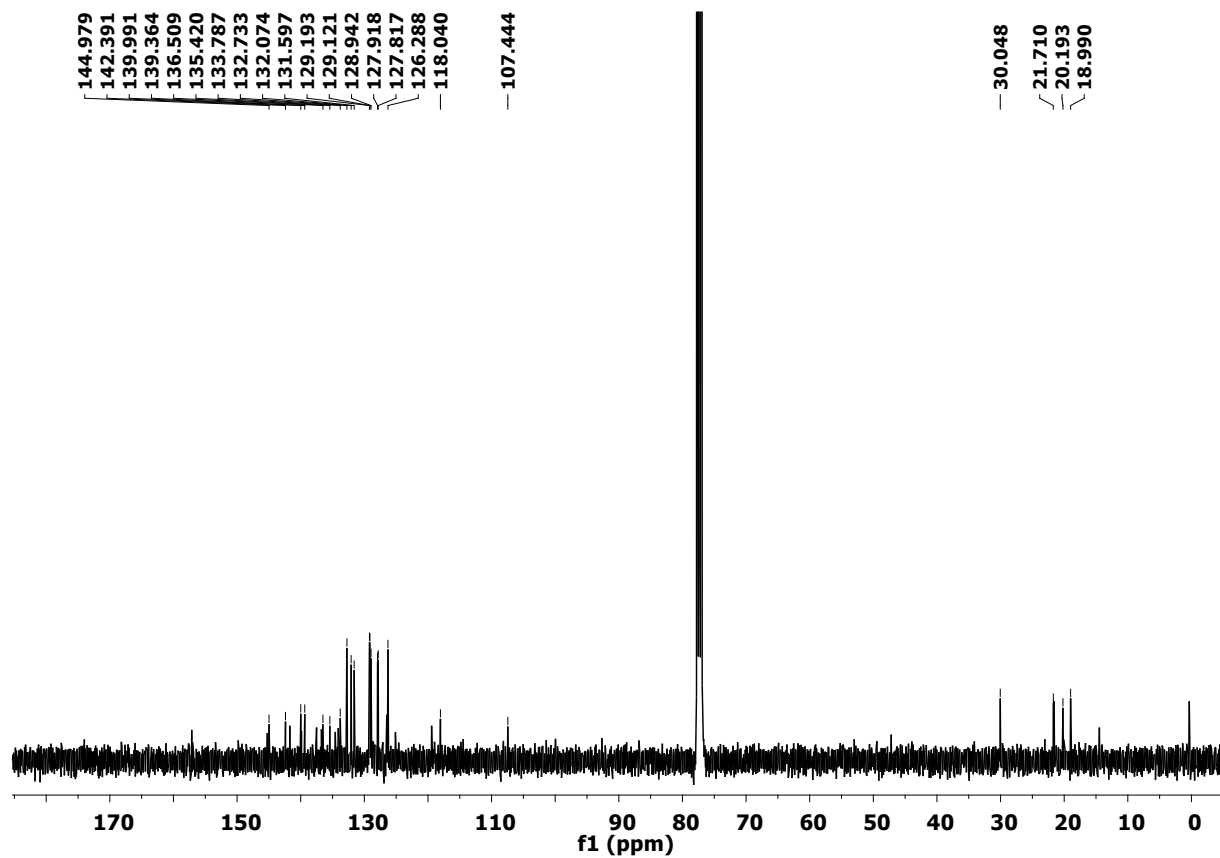
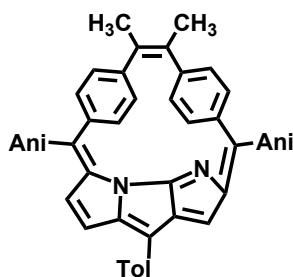


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the compound **5** recorded in CDCl_3 in 101 MHz.



Compound 6

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

Analysis Info

Analysis Name D:\Data\MAR-21\MR-RS-ANI-TOL1.d
 Method NaICsl_pos_1500.m
 Sample Name MR-RS-ANI-TOL1
 Comment C48H38N2O2

Acquisition Date 3/11/2021 12:52:50 PM

Operator PG SRD out
 Instrument maXis impact 282001.00081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

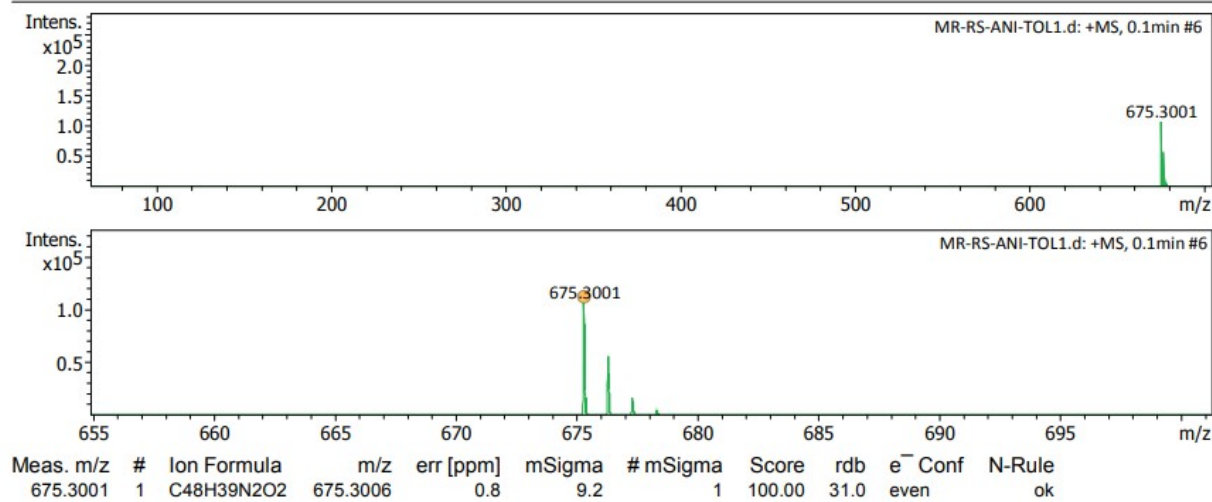


Figure S14. HR mass spectrum of the compound 6.

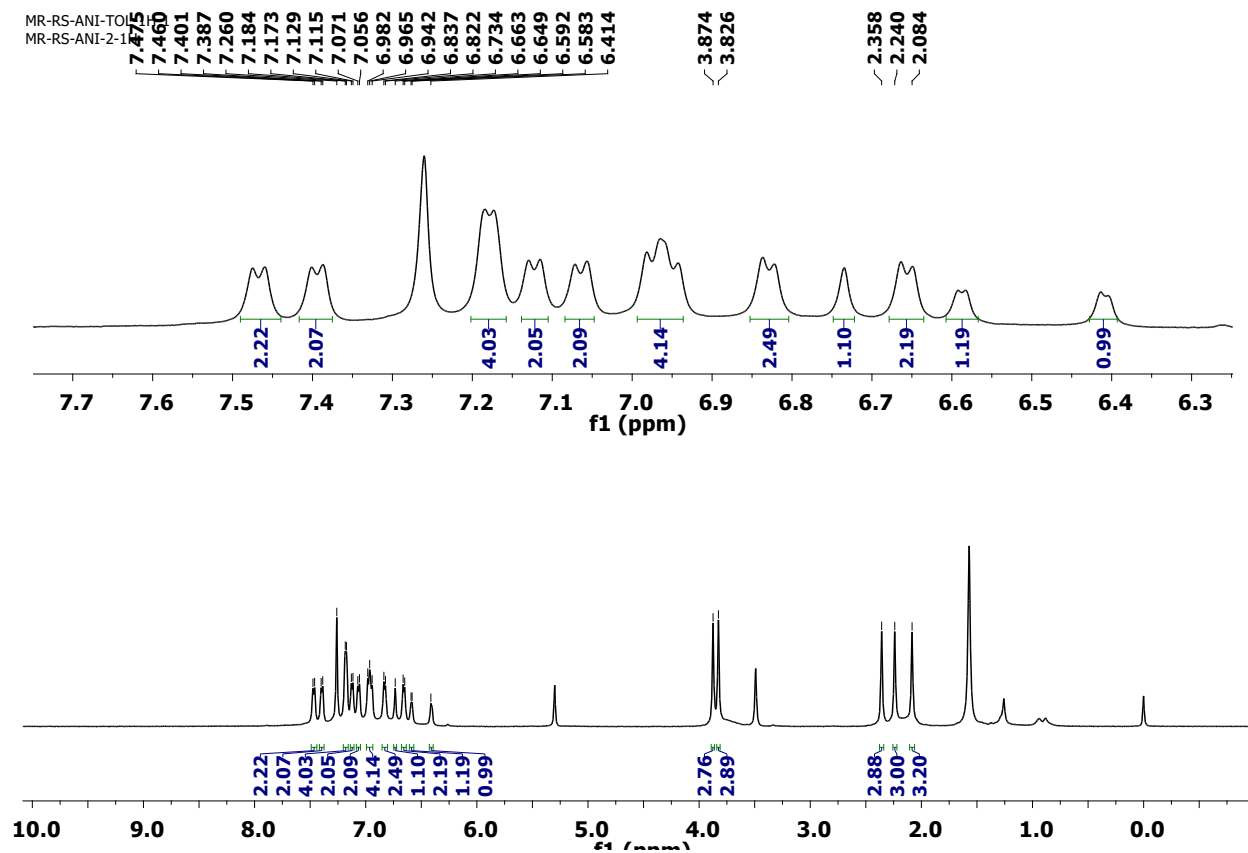


Figure S15. ^1H NMR spectrum of the compound **6** recorded in CDCl_3 in 500 MHz.

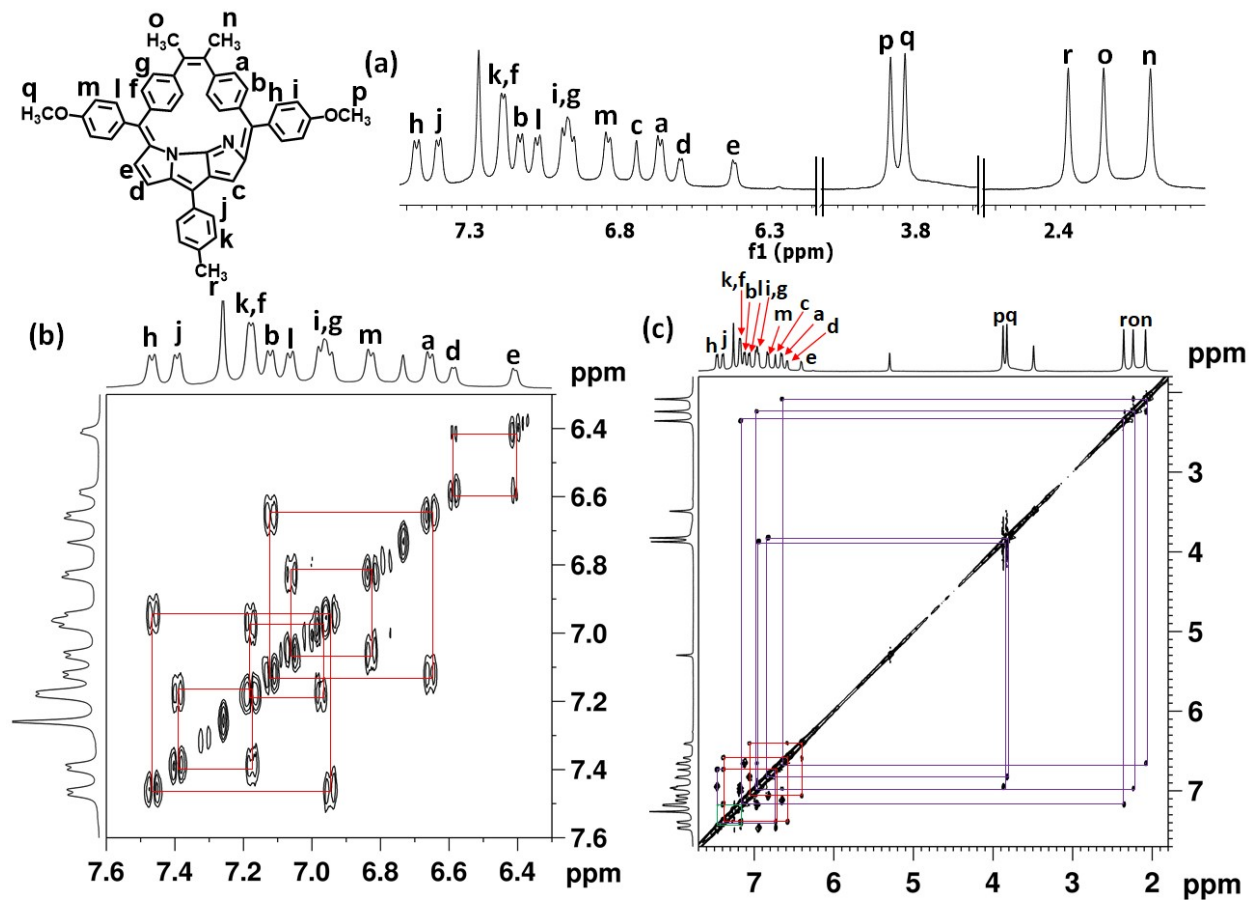


Figure S16. ^1H - ^1H COSY and ^1H - ^1H NOESY spectra of the compound **6** recorded in CDCl_3 in 500 MHz.

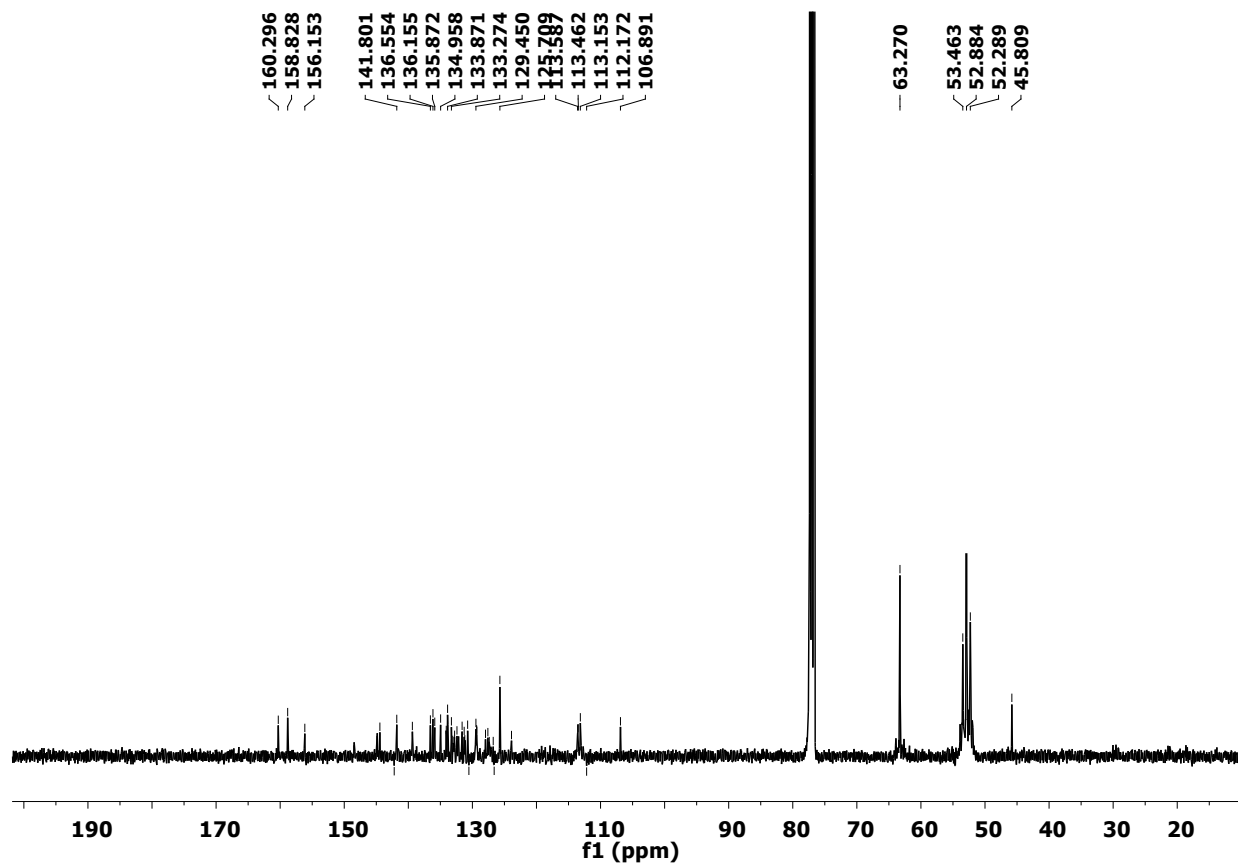
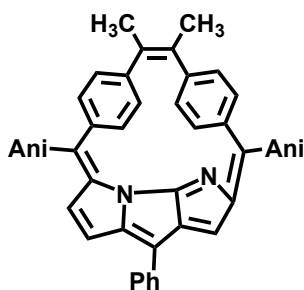


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the compound 6 recorded in CDCl_3 in 101 MHz.



Compound 7

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

Analysis Info

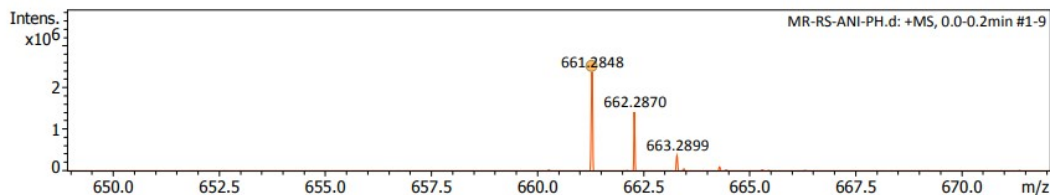
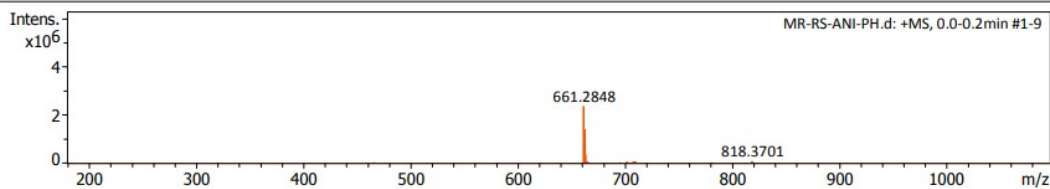
Analysis Name D:\Data\MR-RS-ANI-PH.d
 Method NaICsI_pos_1500.m
 Sample Name MR-RS-ANI-PH
 Comment C47H36N2O2

Acquisition Date 3/16/2021 2:37:15 PM

Operator AK IN
 Instrument maXis impact 282001.00081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
661.2848	1	C47H37N2O2	661.2850	0.2	39.7	1	100.00	31.0	even	ok

Figure S18. HR mass spectrum of the compound 7.

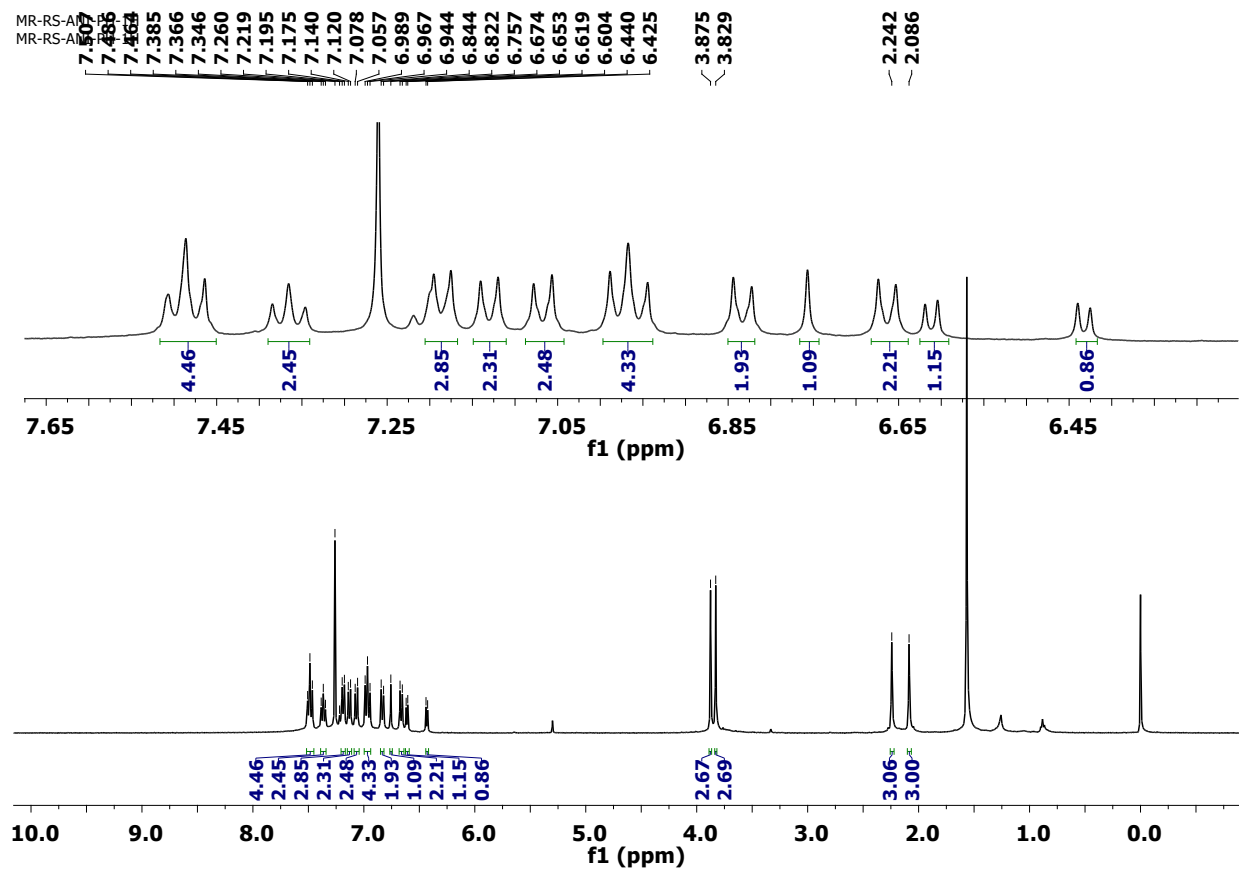


Figure S19. ^1H NMR spectrum of the compound **7** recorded in CDCl_3 in 400 MHz.

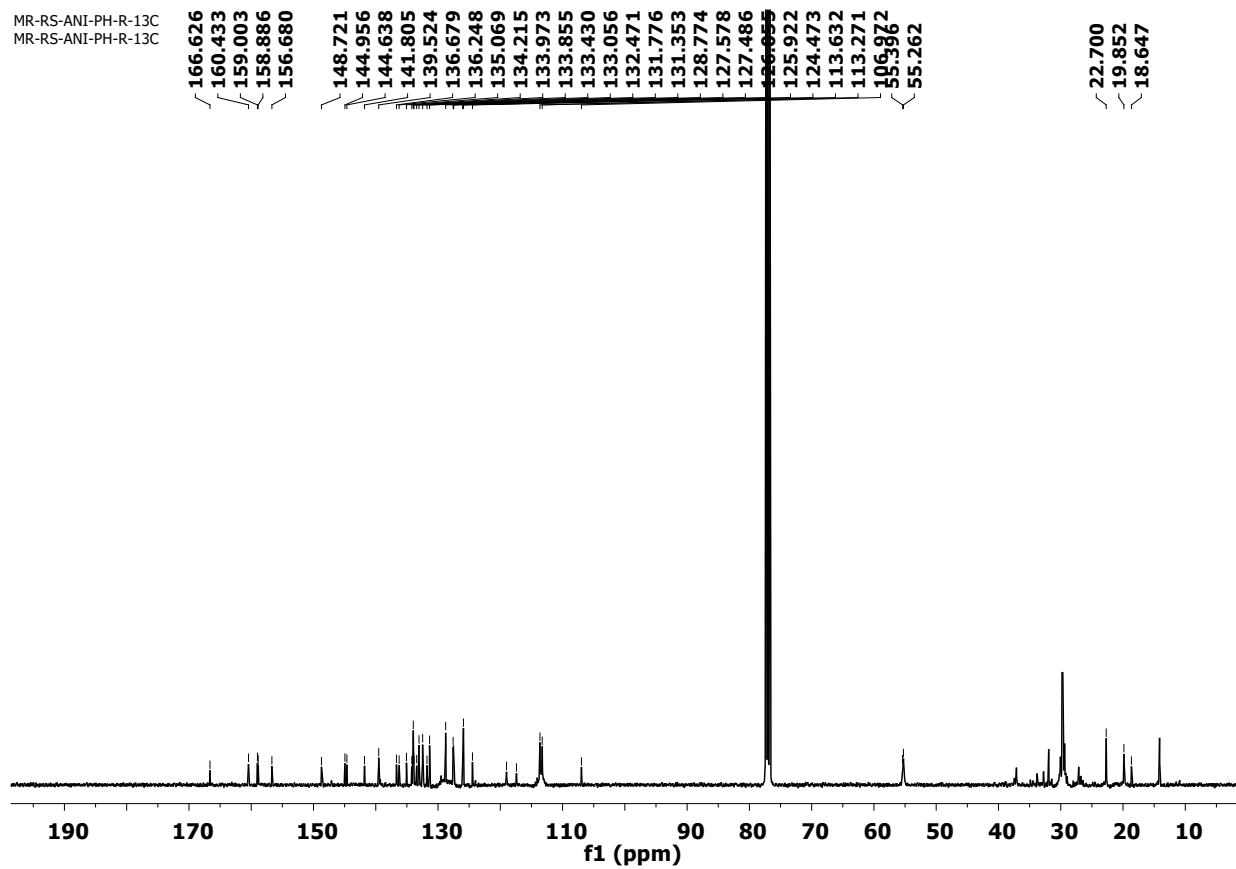


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the compound **7** recorded in CDCl_3 in 101 MHz.

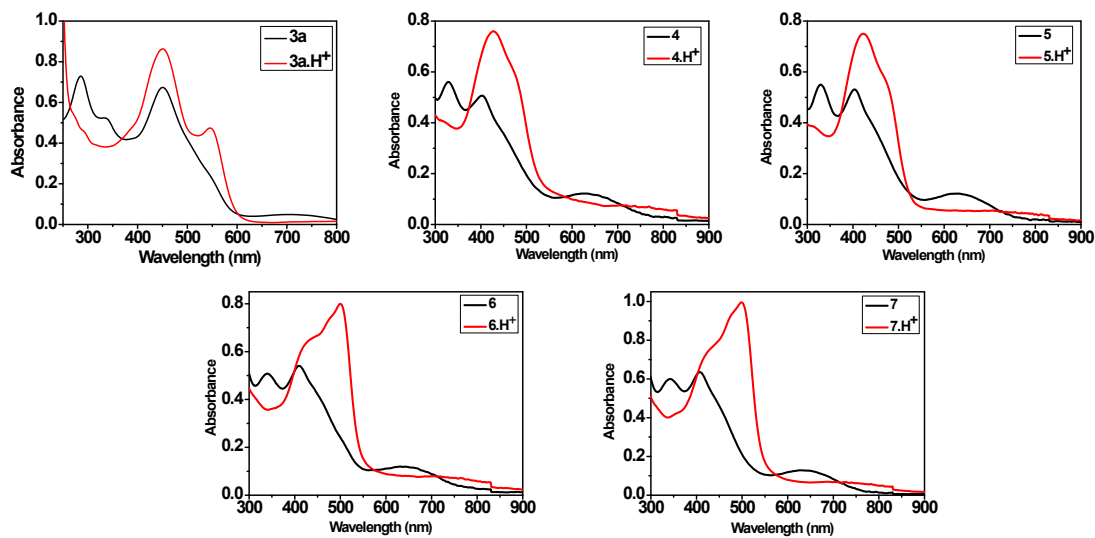


Figure S21. Comparison of absorption spectra of the compounds **3-7** (25 μ M) free base and in presence of TFA (100 eq.) recorded in chloroform at room temperature.

Table S2. Crystal data and data correction parameters for compound **6**.

CCDC	2078340
Identification code	MR_RS_Confuse_autored
Empirical formula	C ₁₀₂ H ₈₂ Cl ₁₈ N ₃ O ₄
Formula weight	2051.80
Temperature/K	150.00(10)
Crystal system	Triclinic
Space group	P1
a/Å	12.5432(7)
b/Å	14.2515(8)
c/Å	14.5415(8)
α/°	110.146(5)
β/°	93.841(4)
γ/°	100.900(5)
Volume/Å ³	2371.6(2)
Z	1
ρ _{calc} /g/cm ³	1.437
μ/mm ⁻¹	0.574
F(000)	1053.0
Crystal size/mm ³	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.014 to 50
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	106960
Independent reflections	16654 [R _{int} = 0.1001, R _{sigma} = 0.0681]
Data/restraints/parameters	16654/3/1148
Goodness-of-fit on F ²	1.044

Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0807$, $wR_2 = 0.2123$
Final R indexes [all data]	$R_1 = 0.1212$, $wR_2 = 0.2521$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.52/-0.92
Flack parameter	0.46(6)

Table S3. Selected bond lengths (\AA) for compound **6**.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
O2	C45	1.392(19)	C17	C18	1.438(19)
O2	C48	1.36(2)	C35	C40	1.42(2)
C3	C2	1.461(19)	C37	C38	1.38(2)
C3	C6	1.404(19)	C19	C20	1.464(18)
C3	C4	1.41(2)	C19	C42	1.51(2)
O1	C31	1.372(17)	C19	C18	1.398(19)
O1	C34	1.397(18)	C40	C39	1.41(2)
N1	C10	1.454(18)	C20	C23	1.415(18)
N1	C13	1.304(18)	C25	C22	1.38(2)
C14	C15	1.36(2)	C25	C1	1.520(19)
C14	C12	1.488(18)	C25	C24	1.387(19)
C14	C35	1.452(19)	C33	C32	1.40(2)
C21	C20	1.424(19)	C33	C28	1.432(19)
C21	C22	1.35(2)	C42	C47	1.37(2)
C16	C15	1.43(2)	C31	C30	1.36(2)
C16	C17	1.38(2)	C31	C32	1.41(2)
C15	N2	1.442(18)	C38	C39	1.41(3)
C10	C11	1.479(19)	C38	C41	1.52(2)
C10	C9	1.35(2)	C9	C28	1.46(2)
C36	C35	1.36(2)	C7	C6	1.406(19)
C36	C37	1.43(2)	N2	C13	1.395(18)
C8	C9	1.536(19)	N2	C18	1.414(18)
C8	C7	1.40(2)	C30	C29	1.37(2)
C8	C5	1.330(19)	C29	C28	1.36(2)
C27	C2	1.52(2)	C47	C46	1.41(2)
C43	C42	1.437(19)	C23	C24	1.366(19)
C43	C44	1.37(2)	C46	C45	1.39(2)
C12	C11	1.37(2)	C1	C26	1.51(2)
C12	C13	1.428(19)	C4	C5	1.40(2)
C2	C1	1.30(2)	C45	C44	1.37(2)

Table S4. Selected bond angles [°] for compounds 6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C48	O2	C45	118.0(13)	C43	C42	C19	119.5(13)
C6	C3	C2	122.4(13)	C47	C42	C43	118.7(13)
C4	C3	C2	120.2(13)	C47	C42	C19	121.8(11)
C4	C3	C6	116.7(13)	O1	C31	C32	114.1(12)
C31	O1	C34	118.2(12)	C30	C31	O1	125.9(13)
C13	N1	C10	101.4(11)	C30	C31	C32	120.0(13)
C15	C14	C12	104.1(12)	C37	C38	C39	119.3(15)
C15	C14	C35	129.7(13)	C37	C38	C41	120.5(16)
C35	C14	C12	126.2(13)	C39	C38	C41	120.2(15)
C22	C21	C20	122.5(13)	C21	C22	C25	122.7(14)
C17	C16	C15	109.1(12)	C38	C39	C40	120.4(15)
C14	C15	C16	141.8(14)	C10	C9	C8	117.9(13)
C14	C15	N2	113.2(12)	C10	C9	C28	124.4(13)
C16	C15	N2	104.9(12)	C28	C9	C8	117.3(13)
N1	C10	C11	110.4(12)	C8	C7	C6	118.6(13)
C9	C10	N1	122.8(12)	C13	N2	C15	105.8(11)
C9	C10	C11	126.3(14)	C13	N2	C18	143.1(12)
C35	C36	C37	122.6(15)	C18	N2	C15	110.8(11)
C7	C8	C9	118.0(12)	C31	C30	C29	120.5(14)
C5	C8	C9	121.1(13)	C3	C6	C7	121.5(13)
C5	C8	C7	120.2(13)	C28	C29	C30	123.6(14)
C44	C43	C42	120.7(14)	C42	C47	C46	119.6(13)
C11	C12	C14	146.1(13)	C24	C23	C20	121.9(13)
C11	C12	C13	105.8(12)	N1	C13	C12	117.6(13)
C13	C12	C14	108.1(12)	N1	C13	N2	133.7(13)
C3	C2	C27	112.9(13)	N2	C13	C12	108.7(12)
C1	C2	C3	121.9(12)	C45	C46	C47	120.7(15)
C1	C2	C27	125.1(13)	C2	C1	C25	121.9(13)
C16	C17	C18	110.6(12)	C2	C1	C26	124.6(13)
C12	C11	C10	104.9(13)	C26	C1	C25	113.5(12)
C36	C35	C14	121.3(14)	C33	C32	C31	118.1(13)
C36	C35	C40	118.1(14)	C3	C4	C5	119.9(14)
C40	C35	C14	120.6(13)	C23	C24	C25	122.5(12)
C38	C37	C36	119.2(16)	C8	C5	C4	121.9(14)
C20	C19	C42	114.1(11)	C46	C45	O2	123.4(16)
C18	C19	C20	128.8(13)	C44	C45	O2	116.3(14)
C18	C19	C42	117.1(12)	C44	C45	C46	120.3(15)

C39	C40	C35	120.3(15)	C45	C44	C43	119.9(14)
C21	C20	C19	119.9(11)	C17	C18	N2	104.6(12)
C21	C20	C23	114.2(12)	C19	C18	C17	123.9(13)
C23	C20	C19	125.6(12)	C19	C18	N2	131.5(12)
C22	C25	C1	121.1(12)	C9	C28	C33	121.5(13)
C24	C25	C22	116.0(13)	C29	C28	C33	116.2(13)
C24	C25	C1	122.9(13)	C29	C28	C9	122.1(13)
C32	C33	C28	121.5(13)				

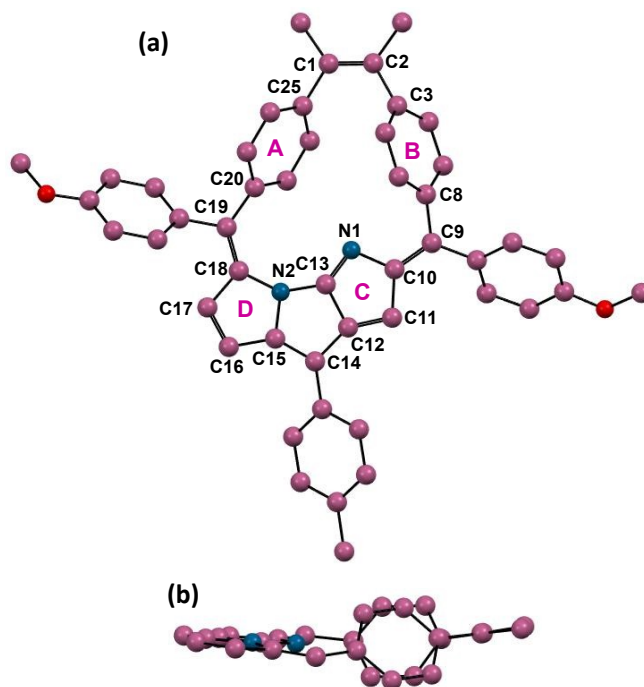


Figure S22. Ground state optimized structures of compound **6** ((A) top view (B) side view).

Table S5. S₀ optimized geometry of the compound **6** at B3LYP/6-31g (d,p) level of theory

Sum of imaginary frequencies= 0

Total Energy (hartree) = -2111.92842359

Atom	X	Y	Z	Atom	X	Y	Z
O	8.61687	1.73208	0.84275	C	-2.2642	-3.5872	-0.5946
C	-0.2397	-4.7476	0.08008	H	-3.0811	-3.4653	-1.2994
O	-8.4212	-1.4493	-0.1321	N	0.85603	1.79829	-0.1785
N	-0.6199	-0.1899	0.16573	C	-6.3802	-2.3302	0.89354
C	-0.9077	3.34293	-0.1276	H	-6.9118	-3.0405	1.51527
C	3.47334	-1.7436	0.63779	C	-1.3637	-4.6372	-0.7532
H	4.16569	-1.3693	1.38448	H	-1.4866	-5.3189	-1.5905
C	1.66114	3.93656	-0.3826	C	-4.9901	-2.2698	0.96181
H	1.70551	5.01089	-0.4839	H	-4.4658	-2.9379	1.63784
C	0.46325	3.16756	-0.2594	C	5.55052	0.35058	-0.6944
C	-2.0414	-0.1556	0.26921	H	5.24495	-0.2895	-1.5162
C	-2.876	4.71728	0.53483	C	1.90927	-1.3553	-1.1472
H	-3.2411	3.87545	1.11463	H	1.38414	-0.6867	-1.82
C	-2.0499	-2.6078	0.39025	C	-0.3054	1.06377	0.03612
C	0.55276	-7.1198	-0.3771	C	6.90837	0.60302	-0.5029
H	0.25885	-7.5176	0.60245	H	7.63043	0.16218	-1.1798
H	1.36799	-7.7337	-0.7611	C	2.12627	-5.1201	-0.4842
H	-0.31	-7.2661	-1.0376	C	-6.3448	-0.5771	-0.7772
C	5.00721	1.71753	1.20455	H	-6.8906	0.05455	-1.4703
H	4.27392	2.1373	1.88618	C	-0.1478	-3.882	1.18079
C	-1.4269	2.00819	0.06632	H	0.68046	-3.9908	1.8726
C	0.89656	-5.6516	-0.2714	C	1.71529	-2.7303	-1.2621
C	2.71732	3.07856	-0.3422	H	1.02219	-3.1058	-2.0078
H	3.75803	3.34786	-0.4352	C	-1.0228	-2.8151	1.32304
C	-2.537	1.22585	0.23218	H	-0.8739	-2.0939	2.1182
H	-3.5679	1.52592	0.33932	C	7.31892	1.42138	0.5575
C	-1.6584	4.59661	-0.1609	C	6.35611	1.97313	1.41395
C	-3.6022	5.90425	0.51402	H	6.69031	2.58888	2.24253
H	-4.5377	5.96439	1.06546	C	2.27004	1.69465	-0.1934
C	3.11991	0.61356	-0.0878	C	-4.2473	-1.3536	0.19688
C	-1.2158	5.71667	-0.8907	C	3.36161	-5.9304	-0.8125
H	-0.3112	5.64352	-1.4859	H	4.16892	-5.7071	-0.105
C	2.79048	-0.8251	-0.1881	H	3.74317	-5.6627	-1.8057
C	2.36939	-3.6392	-0.4154	H	3.19428	-7.0077	-0.7909
C	-4.9624	-0.5207	-0.6908	C	-9.2061	-2.3436	0.64329
H	-4.4164	0.154	-1.3406	H	-8.9643	-3.3906	0.42149

C	4.56765	0.90897	0.13749	H	-10.243	-2.1486	0.36795
C	-7.0681	-1.4752	0.02232	H	-9.0781	-2.1654	1.71829
C	-3.1513	7.02331	-0.1981	C	-3.9252	8.31963	-0.1934
C	3.26935	-3.1123	0.52599	H	-4.9946	8.14755	-0.0385
H	3.79278	-3.7815	1.20386	H	-3.8032	8.86253	-1.1359
C	-1.9455	6.90105	-0.9023	H	-3.5841	8.98567	0.60965
H	-1.58	7.74429	-1.4839	C	9.63477	1.19291	0.01388
C	-2.7773	-1.3197	0.31767	H	9.53138	1.52881	-1.0258
				H	9.63768	0.09567	0.03674
				H	10.5786	1.5623	0.41742

Table S6. S_0 optimized geometry of the compound **3a** at B3LYP/6-31g (d,p) level of theory

Sum of imaginary frequencies= 0

Total Energy (hartree) = -2753.44351623

Atom	X	Y	Z	Atom	X	Y	Z
C	-2.37195	-4.58135	-1.00894	C	4.065486	5.468932	-1.09757
C	-1.2167	-5.19623	-0.61659	C	3.243809	4.348322	-1.02944
C	-3.67397	-5.29583	-1.30223	C	4.516781	7.9394	-0.73797
C	-1.11645	-6.7006	-0.44329	O	-8.38142	1.443752	1.522359
C	-3.05465	0.733524	-0.29371	C	-8.68799	2.245973	2.652245
C	-4.43453	0.941065	0.205171	O	8.071734	-1.7241	1.606844
C	2.566048	-1.52763	0.286462	C	8.960057	-2.64216	0.986747
C	4.006985	-1.60412	0.618136	H	-3.64078	-6.37359	-1.14357
C	-5.53718	0.324412	-0.42642	H	-3.98499	-5.11046	-2.33796
C	-6.8306	0.514289	0.02979	H	-4.47057	-4.88807	-0.66757
C	-7.07452	1.324107	1.151052	H	-1.95388	-7.23737	-0.88513
C	-5.99858	1.932748	1.806751	H	-0.19914	-7.07637	-0.90682
C	-4.70038	1.731921	1.335494	H	-1.07372	-6.96952	0.619276
C	4.580541	-0.75261	1.58555	H	-5.36469	-0.29874	-1.29799
C	5.931061	-0.81736	1.891857	H	-7.67637	0.049205	-0.46595
C	6.760618	-1.74036	1.236868	H	-6.15355	2.541766	2.689437
C	6.212106	-2.60189	0.278167	H	-3.87078	2.180088	1.872721
C	4.850595	-2.5314	-0.01394	H	3.944705	-0.05072	2.114198
C	-2.48489	-3.10408	-1.1737	H	6.36879	-0.1713	2.645536
C	-2.22848	-2.34853	-2.29329	H	6.830365	-3.32086	-0.24574
C	-2.33893	-0.94659	-2.07856	H	4.436698	-3.19617	-0.7649
C	-2.72176	-0.60588	-0.79958	H	-1.91118	-2.78861	-3.23236
S	-2.96438	-2.06327	0.155184	H	-2.16338	-0.20257	-2.8472
C	0.026719	-4.48698	-0.26956	H	1.127692	-5.98154	0.889051
C	1.091102	-4.97538	0.48908	H	2.972568	-4.21398	1.344113

C	2.094668	-4.01772	0.740198	H	-3.60809	3.54287	-0.40712
C	1.818699	-2.76811	0.187935	H	-1.4784	5.087777	-0.69195
S	0.30907	-2.8253	-0.67803	H	3.613456	1.2266	-0.05311
C	-2.19176	1.813404	-0.34881	H	0.471694	5.816861	0.267781
C	-2.57772	3.219144	-0.40318	H	1.917203	7.791962	0.109306
C	-1.47888	4.015592	-0.55892	H	5.079052	5.362439	-1.47718
C	-0.31548	3.181962	-0.54218	H	3.615522	3.388133	-1.3731
N	-0.78781	1.84248	-0.45448	H	5.241104	7.868176	-1.55527
C	1.075658	3.251493	-0.50264	H	3.946182	8.863535	-0.87149
C	1.510097	1.878673	-0.33521	H	5.08893	8.043374	0.192999
C	0.322535	1.03422	-0.27872	H	-9.77252	2.20803	2.763217
C	2.55501	1.016989	-0.08917	H	-8.37633	3.288007	2.505605
C	1.942851	-0.30083	0.087382	H	-8.21827	1.856879	3.564536
N	0.535955	-0.22193	-0.02865	H	9.017558	-2.48047	-0.097
C	1.920637	4.442468	-0.55704	H	9.9397	-2.45738	1.429323
C	1.469373	5.711038	-0.14525	H	8.667212	-3.68191	1.179628
C	2.29643	6.827276	-0.21991				
C	3.611463	6.732003	-0.69501				

Table S7. Absorption and electrochemical data of the compounds **3-7**.

Compound	Absorption data		
	λ (nm)		
3a	283	449	704
	(4.46)	(4.43)	(3.29)
3a.H⁺	449	545	-
	(4.53)	(4.27)	
3b	282	446	704
	(4.42)	(4.41)	(3.31)
3b.H⁺	450	545	-
	(4.55)	(4.25)	
4	328	403	631
	(4.34)	(4.32)	(3.68)
4.H⁺	-	427	-
		(4.47)	
5	328	403	630
	(4.35)	(4.30)	(3.69)
5.H⁺	-	422	-
		(4.48)	
6	339	409	640
	(4.37)	(4.40)	(3.70)
6.H⁺	-	499	-
		(4.60)	
7	340	407	637
	(4.31)	(4.33)	(3.67)
7.H⁺	-	499	-
		(4.50)	

References:

- 1 O. Treutler and R. Ahlrichs, Efficient molecular numerical integration schemes, *J. Chem. Phys.*, 1995, **102**, 346–354.
- 2 A. D. Becke, A New Mixing of Hartree–Fock and Local Density-Functional Theories, *J. Chem. Phys.* 1993, **98**, 1372–1377.
- 3 W. J. Hehre, Ab Initio Molecular Orbital Theory, *Acc. Chem.Res.*, 1976, **9**, 399–406.
- 4 R. Bauernschmitt and R. Ahlrichs, Treatment of Electronic Excitations within the Adiabatic Approximation of Time Dependent Density Functional Theory, *Chem. Phys. Lett.*, 1996, **256**,

454–464.

5 Y. Gabe, T. Ueno, Y. Urano, H. Kojima and T. Nagano, Tunable Design Strategy for Fluorescence Probes Based on 4-SubstitutedBODIPY Chromophore: Improvement of Highly Sensitive Fluorescence Probe for Nitric Oxide, *Anal. Bioanal. Chem.*, 2006, **386**, 621–626.

6 F. Furche and R. Ahlrichs, Adiabatic Time-Dependent Density Functional Methods for Excited State Properties, *J. Chem. Phys.*, 2002, **117**, 7433–7447.

7 G. Scalmani, M. J. Frisch, B. Mennucci, J. Tomasi, R. Cammi and V. Barone, Geometries and Properties of Excited States in the GasPhase and in Solution: Theory and Application of a Time-Dependent Density Functional Theory Polarizable Continuum Model, *J. Chem.Phys.*, 2006, **124**, 94107–94115

8 M. Cossi, V. Barone, R. Cammi and J. Tomasi, Ab Initio Study of Solvated Molecules: A New Implementation of the Polarizable Continuum Model, *Chem. Phys. Lett.*, 1996, **255**, 327–335.

9 J. Tomasi, B. Mennucci and R. Cammi, Quantum Mechanical Continuum Solvation Models, *Chem. Rev.*, 2005, **105**, 2999–3094.