Photophysical Properties of Near-Infrared Phosphorescent π-Extended Platinum Porphyrins.

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Supporting Information

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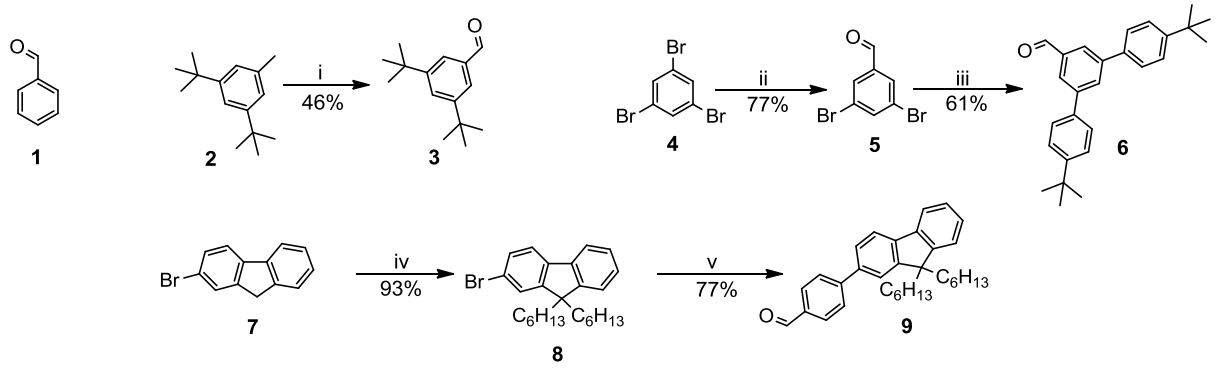
Experimental

Materials and General Procedures. All chemicals used for synthesis were of reagent grade and used without further purification unless noted otherwise. Reactions were carried out under inert atmospheres of argon or nitrogen. Dry solvents were obtained from a solvent purification system or from standard distillation methods unless otherwise noted. All glassware was flame or oven dried prior to use unless otherwise noted. NMR spectra were recorded on a Varian Gemini 300, VXR 300, Mercury 300 or Varian Inova 500 spectrometer and chemical shifts are reported in ppm relative to $CDCl_3$ unless otherwise noted. Ethyl isocyanoacetate was purchased from Sigma Aldrich and vacuum distilled each time prior to use. Solutions of PhSCl were prepared according to literature methods from *N*-chlorosuccinimide and thiophenol.[1] Platinum acetate was prepared from a previously reported method.[2] Purification by column chromatography was performed on SiliaFlash silica-gel (mesh 230-400).



Scheme S-1. Synthetic scheme for aryl-aldehydes.

3,5-Di-*tert*-butylbenzaldehyde (**3**). The title compound was prepared following a modified literature procedure.[3] A solution of **2** (10.00 g, 48.9 mmol) and NBS (18.00 g, 101 mmol) in CCl_4 (160 mL) with benzoyl peroxide (80 mg, 0.33 mmol) was refluxed overnight. The formed precipitated was removed by filtration through celite and the solvent removed to yield an

oil. The crude material was dissolved in mixture of water (15 mL) and EtOH (15 mL) with hexamethylenetetramine (19.90 g, 142 mmol) and then heated to reflux for 4 hours. The reaction was diluted with a toluene/ether (1:1, 200 mL) mixture and then washed with brine (100 ml x 3). The organic layer was dried over $MgSO_4$ and the solvent removed. The crude material was recrystallized twice from MeOH to give 4.94 g of the title compound (46%). The material gave identical spectral data to that previously reported in the literature.[3] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 10.01 (s, 1H), 7.73 (m, 3H), 1.36 (t, 18H).

3,5-Dibromo-benzaldehyde (**5**). The title compound was prepared following a modified literature method.[4] Compound **4** (3.01 g, 9.6 mmol) in diethyl ether (80 mL) was cooled to -78°C followed by the addition of one equivalent of *n*-BuLi dropwise (2.5 M, 3.8 mL). The reaction was stirred for 30 minutes then DMF (740 μL, 9.6 mmol) was added dropwise to the reaction and stirred at -78°C for one hour. The vessel was then placed in an ice bath and stirred for 30 minutes. A 10% HCl solution (100 mL) was added to quench the reaction followed by $CHCl_3$ (150 mL). The organic layer was collected and the aqueous layer washed with $CHCl_3$ (80 mL). The organic layers where combined and dried over $MgSO_4$ and the solvent removed. The crude product was purified by column chromatography eluting with 10% EtOAc in hexanes to give 1.93 g of the title compound (77%). Spectral data for the title compound was not reported in the literature reference.[4] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.90 (s, 1H), 7.92 (d, 2H), 7.60 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 189.3, 139.7, 139.0, 131.37, 124.1; GC-MS $[M+H]^+$ 262.8709, calcd 262.8707.

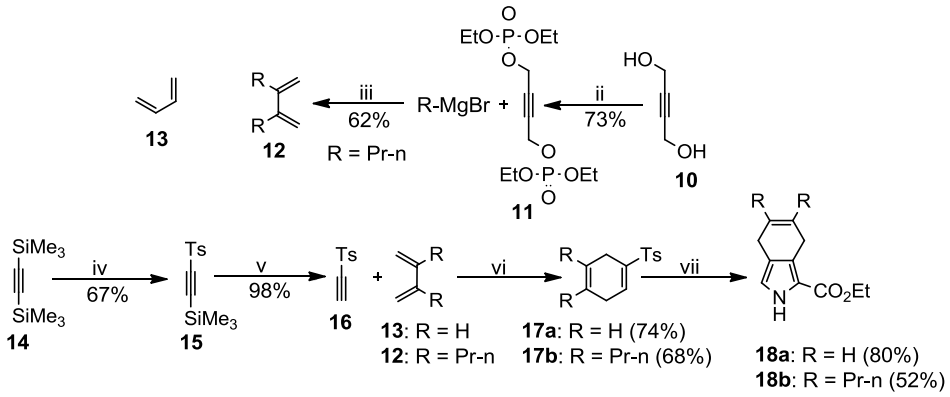
3,5-Di(4-*tert*-butylphenyl)benzaldehyde (**6**). The title compound was prepared following a modified literature method.[5] Compound **5** (1.02 g, 3.9 mmol) and 4-*tert*-butylphenyl boronic acid (1.47 g, 8.3 mmol) were dissolved in toluene (75 mL) and THF (60 mL) with Na_2CO_3 (1.12

g) and water (9 mL). The solution was purged with argon for 15 minutes followed by the addition of $Pd(PPh_3)_4$ (200 mg, 0.2 mmol). The reaction was stirred and purged with argon for 20 minutes and then heated at 100°C for 120 hours. The solvent was removed and the crude material loaded on silica eluting with a hexane/DCM mixture (70/30). The fractions were combined and the solvent removed. The material was dissolved in minimum of DCM and diluted with MeOH precipitating 865 mg of the title compound (61%). The title compound is reported in the literature with no experimental or spectral data.[6] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 10.14 (s, 1H), 8.05 (m, 3H), 7.63 (d, 4H), 7.53 (d, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 192.7, 151.4, 142.7, 137.6, 137.1, 131.7, 127.1, 127.0, 126.2, 34.8, 31.5; DART-MS $[M+H]^+$ 371.2369, calcd 371.2369.

2-Bromo-9,9-dihexylfluorene (**8**). The title compound was prepared following a modified literature method.[7] A mixture of **7** (2.00 g, 8.2 mmol) and bromohexane (10 mL, 70.8 mmol) with NaOH (2.8 g, 70 mmol) and Bu_4NCl in DMSO (20 mL) and water (3 mL) was stirred. The reaction was heated at 80°C overnight and then poured into excess ethyl acetate (200 mL). The precipitated NaOH was filtered off and the organic layer washed with 2N HCl solution (100 mL) and brine (100 mL). The organic layer was collected and dried over $MgSO_4$. The solvent was removed and the crude product purified by column chromatography eluting with hexane to yield 3.14 g of the title compound (93%). The material gave identical spectral data to that previously reported in the literature.[7] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.68-7.64 (m, 1H), 7.57-7.54 (m, 1H), 7.46-7.43 (m, 2H), 7.33-7.31 (m, 3H), 1.97-1.90 (m, 4H), 1.15-1.03 (m, 12H), 0.79 (t, 6H), 0.62-0.58 (m, 4H).

4-(9,9-dihexyl-fluorenyl)-benzaldehyde (**9**). The title compound was prepared following a modified literature method.[8] A solution of **8** (1.10 g, 2.7 mmol) and 4-formylbenzene

boronic acid (438 mg, 2.9 mmol) with Na_2CO_3 (2.96 g) in THF (20 mL) and water (15 mL) mixture was purged with argon for 30 minutes. Then $Pd(PPh_3)_4$ (15 mg, 12.9 μmol) was added and the solution stirred and purged with argon for 15 minutes prior to heating at 80°C overnight. The reaction was cooled to room temperature and then diluted with DCM (100 mL). The organic layer was washed with saturated aqueous NH_4Cl solution (100 mL) and then dried over $MgSO_4$. The solvent was removed and the crude material purified by column chromatography eluting with 45% hexane in DCM to give 900 mg of the title compound (77%). The material gave identical spectral data to that previously reported in the literature.[8] ^1H NMR ($CDCl_3$, 300 MHz): δ = 10.1 (s, 1H), 7.98 (d, 2H), 7.84 (d, 2H), 7.80-7.77 (m, 1H), 7.57-7.72 (m, 1H), 7.64-7.61 (m, 1H), 7.59 (m, 1H), 7.35 (m, 3H), 2.01 (m, 4H), 1.05 (m, 12H), 0.75 (t, 6H), 0.68-0.62 (m, 4H).



Scheme S-2. Synthetic scheme for ester protected benzoporphyrin pyrroles.

2-Butyne-1,4-diyl tetraethyl ester phosphoric acid (11). The title compound was prepared following a modified literature method.[9] In dry pyridine (25 mL) compound **10** (5.76 g, 66.9 mmol) under an argon atmosphere was cooled to 0°C followed by the dropwise addition of diethyl chlorophosphate (25 g, 144.9 mmol). The reaction was stirred for 2 hours at 0°C and then diluted with water (125 mL). The mixture was washed with ether (3 x 70 mL) and the combined

organic layers dried over Na_2SO_4. The solvent was removed to give 16.0 g of the title compound (73%). The material was pure enough for the subsequent Grignard reaction and gave identical spectral data to that previously reported in the literature.[9] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.71 (d, 4H), 4.13 (dq, 8H), 1.34 (t, 12H).

2,3-Dipropyl-1,3-butadiene (12). The title compound was prepared following a modified literature method.[9] The Grignard reagent was prepared from 1-bromopropane (5.15 g, 41.8 mmol) and Mg (1.12 g, 41.8 mmol) turnings in dry THF (60 mL) in a conventional manner. The solution was cooled to 0°C followed by the dropwise addition of **11** (5.00 g, 13.9 mmol) in dry THF (30 mL). The reaction was warmed to room temperature and stirred overnight. Water (300 mL) was added to quench the reaction. The formed precipitate was filtered off and then washed with pentane (150 mL). The aqueous and organic layers were collected and separated. The aqueous layer was washed with pentane (4 x 80 mL). The organic layers combined and dried over Na_2SO_4 and the solvent removed under reduced pressure yielding 1.27 g of the title compound (62%). The material gave identical spectral data to that previously reported in the literature.[9] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.06 (s, 2H), 4.90 (s, 2H), 2.21 (t, 4H), 1.48 (sex, 4H), 0.91 (t, 6H).

p-Tolyl-[2-(trimethylsilyl)ethynyl]-sulfone (15). The title compound was prepared following a modified literature method.[10] A solution of $AlCl_3$ (9.4 g, 70.5 mmol) in dry DCM (40 mL) was cannula transferred to TsCl (13.43 g, 70.4 mmol) in DCM (30 mL) and stirred under N_2 atmosphere turning orange in color. A separate solution of **14** in DCM (40 mL) was cooled to 0°C in an ice bath. The mixture of $AlCl_3$/TsCl was transferred to the alkyne solution over a period of 10 minutes in small portions. The ice bath was removed and the reaction stirred overnight at room temperature. The mixture was poured into ice water (400 g) and the organic

layer separated and collected. The aqueous layer was washed with DCM (3 x 50 mL). The combined organic layers were dried over $MgSO_4$ and the solvent removed. The crude material was extracted with hot hexanes and upon cooling yielded 10.01 g of the title compound (67%). The material gave identical spectral data to that previously reported in the literature.[11] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.90-7.89 (m, 2H), 7.38-7.35 (m, 2H), 2.46 (s, 3H), 0.21 (s, 9H).

Ethynyl p-tolyl sulfone (16). The title compound was prepared following a modified literature method.[12] A solution of **15** (8.01 g, 31.7 mmol) purged with argon in MeOH (65 mL) was cooled to 0°C. The cooled solution was treated dropwise with NaF (2.08 g, 49.5 mmol) in water (35 mL). The reaction was stirred for 90 minutes at 0°C and then diluted with water (100 mL). The organic layer was separated and collected. The aqueous layer was extracted with ether (3 x 100 mL). The combined organic layers were washed with water (2 x 100 mL), 10% aqueous $NaHCO_3$ (1 x 100 mL), and brine (1 x 100 mL). The organic layer was dried over $MgSO_4$ and the solvent removed. The crude material was recrystallized from hexanes to yield 5.70 g of the title compound (98%). The material gave identical spectral data to that previously reported in the literature.[12] ^{1}H NMR ($CDCl_3$, 75 MHz): δ = 7.91-7.88 (d, 2H), 7.40-7.37 (d, 2H), 3.45 (s, 1H), 2.47 (s, 3H).

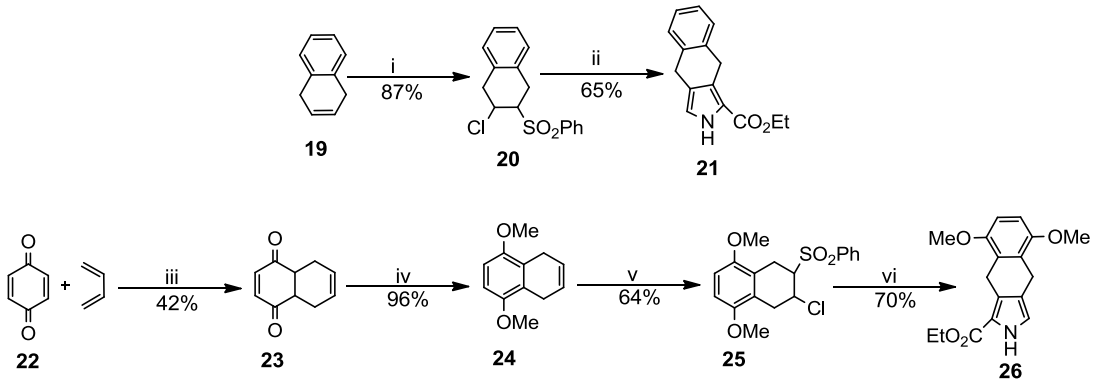
1-Tosyl-1,4-cyclohexadiene (17a). The title compound was prepared following a modified literature method.[13] A thick walled 100 mL vessel with **16** (5.01 g, 27.8 mmol) was cooled to -78°C. Then an excess of **13** (20 mL) was added and the vessel sealed. The reaction was warmed to room temperature and stirred for 48 hours. After removal of excess 1,3-butadiene (**13**) a white oily solid was collected and recrystallized from diethyl ether to give 4.82 g of the title compound (74%). The material gave identical spectral data to that previously reported in the

literature.[13] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.75-7.72 (d, 2H), 7.33-7.30 (d, 2H), 7.01 (m, 1H), 5.66-5.63 (m, 2H), 2.93-290 (m, 2H), 2.82-2.79 (m, 2H), 2.42 (s, 3H).

1-Tosyl-4,5-dipropyl-1,4-cyclohexadiene (17b). The title compound was prepared following a modified literature method.[14] In a thick walled flask with Teflon cap dry toluene (10 mL) and compound **16** (1.31 g, 7.3 mmol) with **12** (1.01 g, 7.3 mmol) under an argon atmosphere was heated at 130°C for 48 hours. The reaction was cooled to room temperature and the solvent removed under reduced pressure. The crude material was purified by column chromatography eluting with $CHCl_3$ to give a 1.58 g of a yellow oil (68%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.76 (d, 2H), 7.33 (d, 2H), 6.96 (m, 1H), 2.86 (m, 2H), 2.74 (m, 2H), 2.42 (s, 3H), 1.96 (m, 4H), 1.32 (m, 2H), 1.30 (m, 2H), 0.87 (t, 3H), 0.86 (t, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ= 144.3, 137.9, 136.4, 135.3, 129.9, 128.3, 127.0, 126.4, 34.7, 34.3, 32.0, 28.2, 21.8, 21.4, 14.3; DART-MS $[M+H]^+$ 319.1737, calcd 319.1726.

2-Ethoxycarbonyl-4,7-dihydro-2H-isoindole (18a). The title compound was prepared following a modified literature method.[13] A solution of **17a** (2.5 g , 10.7 mmol) in dry THF (25 mL) was added dropwise at 0°C to one equivalent of ^{t}BuOK (1.44 g , 12.8 mmol) and ethyl isocyanoacetate (1.31 g, 11.6 mmol). The reaction was stirred at room temperature for 4 hours. The solvent was removed and the crude material redissolved in DCM (140 mL). The organic layer was washed with water (2 x 80 mL), and brine (1 x 80 mL) and then dried over Na_2SO_4. The solvent removed and the crude material recrystallized from hexanes yielding 1.64 g of light yellow crystals (80%). The material gave identical spectral data to that previously reported in the literature.[13] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.97 (broad s, 1H), 6.72 (m, 1H), 5.94-5.82 (m, 2H), 4.31 (q, 2H), 3.46-3.43 (m, 2H), 3.24-3.21 (m, 2H), 1.35 (t, 3H).

2-Ethoxycarbonyl-4,7-dihydro-5,6-dipropyl-2H-isoindole (18b). The title compound was prepared according to the procedure for **18a**. A solution of ^{t}BuOK (930 mg, 8.3 mmol) in dry THF (30 mL) was cooled to 0°C followed by the addition of ethyl isocyanoacetate (0.9 mL, 8.2 mmol). The solution was stirred for 10 minutes then a solution of **17b** (2.4 g, 7.5 mmol) in dry THF (30 mL) was added dropwise. The reaction was warmed to room temperature and stirred for 4 hours. The solvent removed and the crude redissolved in DCM (120 mL). The organic layer was washed with water (2 x 80 mL) and brine (1 x 80 mL) then dried over Na_2SO_4. The solvent was removed producing an oil that was purified by column chromatography eluting with $CHCl_3$. The combined fractions were recrystallized from EtOH to give 1.09 g of the title compound as light yellow crystals (52%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.89 (br s, 1H), 6.69 (d, 1H), 4.33 (q, 2H), 3.40 (m, 2H), 3.16 (m, 2H), 2.15 (q, 4H), 1.48 (m, 2H), 1.47 (m, 2H), 1.36 (t, 3H), 0.95 (t, 3H), 0.94 (t, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ= 161.7, 128.4, 127.7, 126.6, 120.5, 117.9, 117.2, 60.0, 35.7, 28.5, 26.9, 22.0, 14.8, 14.5; DART-MS 276.1968, calcd 276.1958.



Scheme S-3. Synthetic scheme for ester protected naphthoporphyrin pyrroles.

2-Chloro-1,2,3,4-tetrahydro-3-(phenylsulfonyl)-naphthalene (20). The title compound was prepared following a modified literature method.[15] A solution of PhSCl (18.6 mmol) in dry DCM (40 mL) was added dropwise to **19** (2.0 g, 11.5 mmol) in DCM (30 mL) at 0°C. After the addition, the reaction was stirred at room temperature for two hours. The mixture was stored in a freezer over night and the precipitated removed by filtration. The filtrate was cooled to 0°C and diluted with DCM (50 mL). In one portion 77% *m*-CPBA (9.2 g, 41 mmol) was added and then stirred at room temperature for one hour. A chilled 10% aqueous Na_2SO_3 (80 mL) was added and the mixture stirred at room temperature for one hour. The organic layer was washed with 10% aqueous Na_2CO_3 (30 mL), 10% aqueous Na_2SO_3 (80 mL), and 10% aqueous Na_2CO_3 (80 mL). The organic layer collected and dried over K_2CO_3 and the solvent removed. The crude product recrystallized from EtOH to give 3.08 g of the title compound (87%). The material gave identical spectral data to that previously reported in the literature.[15] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.96-7.57 (m, 5H), 7.22-7.19 (m, 2H), 7.14-7.09 (m, 2H), 4.84 (m, 1H), 3.75-3.70 (m, 1H), 3.51-3.44 (dd, 1H), 3.51-3.27 (dd, 1H), 3.20-3.11 (dd, 1H), 3.07-3.06 (dd, 1H).

4,9-Dihydro-2H-benzo[f]isoindole-1-carboxylic acid ethyl ester (21). The title compound was prepared following a modified literature method.[15] Compound **20** (3.06 g, 10 mmol) in dry THF (10 mL) was added dropwise to a solution of ^{t}BuOK (3.1 g, 27.6 mmol) with ethyl isocyanoacetate (1.13 g, 10 mmol) in dry THF (40 mL) at 0°C. The reaction was warmed to room temperature and then refluxed for one hour under an argon atmosphere. The solvent was removed and the crude material dissolved in DCM (120 mL). The organic layer was washed with water (2 x 100 mL) and brine (1 x 100 mL) collected and dried over K_2CO_3. The crude material was recrystallized from EtOH and hexanes to yield 1.53 g (65%). The material gave identical

spectral data to that previously reported in the literature.[15] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.04 (broad s, 1H), 7.33 (m, 1H), 7.24-7.17 (m, 2H), 6.81 (d, 1H), 4.37 (q, 2H), 4.17 (s, 2H), 3.89 (s, 2H), 1.40 (t, 3H).

4a,5,8,8a-tetrahydronaphthoquione-1,4-dione (23). The title compound was prepared following a modified literature method.[16] Compound **22** (6.0 g, 55.5 mmol) in AcOH (70 mL) was stirred at room temperature with **13** (12 g, 221.8 mmol) for 24 hours. The mixture was poured into ice water (200 mL) and rapidly stirred. The precipitate was collected and redissolved in warm ether and filtered to remove insoluble material. The solvent was removed to give 3.75 g of the title compound (42%). The material gave identical spectral data to that previously reported in the literature.[17] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.67 (s, 2H), 5.70 (m, 2H), 3.27-3.23 (m, 2H), 2.52-2.16 (m, 4H).

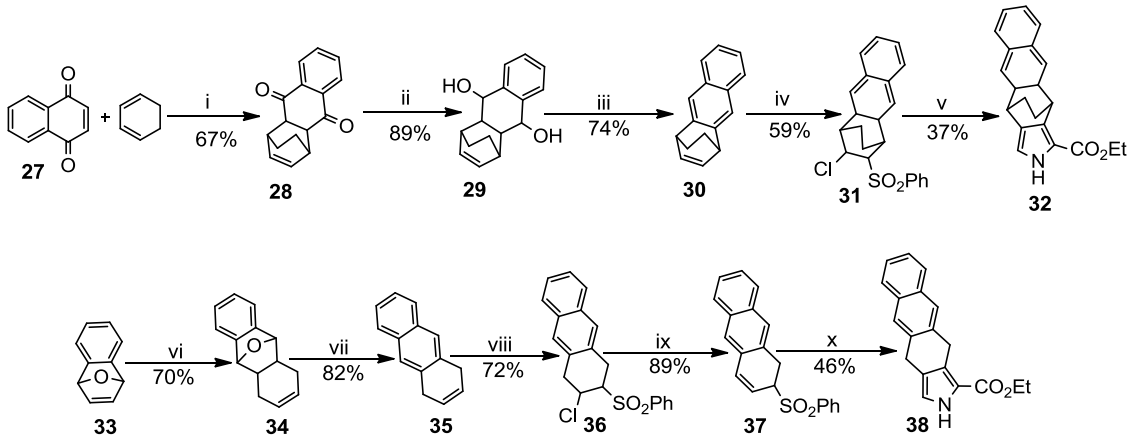
5,8-Dimethoxy-1,4-dihyronaphthalene (24). The title compound was prepared following a modified literature method.[16] In acetone (85 mL) **23** (5.4 g, 33.3 mmol) with an excess of K_2CO_3 (17.0 g) and dimethyl sulfate (20.0 g, 158.5 mmol) under N_2 atmosphere was refluxed for 40 hours. The mixture cooled to room temperature followed by the addition of water (25 mL). The mixture was concentrated and then poured into ice cold water (500 mL) with vigorous stirring. The formed precipitate was collected and washed thoroughly with water to remove any residual K_2CO_3. The crude product was recrystallized from MeOH to give 6.05 g of the title compound (96%). The material gave identical spectral data to that previously reported in the literature.[17] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.65 (s, 2H), 5.89 (s, 2H), 6.70 (s, 6H), 3.28 (s, 4H).

2-Chloro-1,2,3,4-tetrahydro-5,8-dimethoxy-3-(phenylsulfonyl)-naphthalene (25). The title compound was prepared following a modified literature method.[15] In dry DCM (50 mL)

cooled to 0°C with **24** (3.5 g, 18.4 mmol) was treated dropwise with PhSCl (23.0 mmol) in DCM (40 mL). After the addition the reaction was stirred at room temperature for 2 hours. The mixture was stored in a freezer overnight and the formed precipitate removed by filtration. The solution was diluted with DCM (50 mL) and cooled to 0°C followed by the addition of 77% *m*-CPBA (7.95 g, 46.0 mmol) in one portion. The reaction was warmed to room temperature and stirred for one hour. A solution of chilled 10% aqueous Na_2SO_3 (100 mL) was added and the mixture stirred for one hour at room temperature. The organic layer was washed with 10% aqueous Na_2CO_3 (35 mL), 10% aqueous Na_2SO_3 (100 mL), and 10% aqueous Na_2CO_3 (100 mL). The organic layer was dried over K_2CO_3 and the solvent removed. The crude product was recrystallized from an EtOH and hexane mixture to give 4.30 g of the title compound (64%). The material gave identical spectral data to that previously reported in the literature.[15] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.94-7.90 (m, 2H), 7.67-7.54 (m, 3H), 6.66 (s, 2H), 4.85-4.80 (m, 1H), 3.77-3.67 (overlapping s+s+m, 3H+3H+1H), 3.40-3.33 (dd, 1H), 3.24-3.16 (m, 3H).

5,8-Dimethoxy-4,9-dihydro-2H-benzo[f]isoindole-1-carboxylic acid ethyl ester (26). The title compound was prepared following a modified literature method.[15] A solution of ^{t}BuOK (1.83 g, 16.3 mmol) in dry THF (60 mL) was cooled to 0°C followed by the addition of ethyl isocyanoacetate (2.21 g, 19.6 mmol). To this solution, **25** (3.0 g, 8.1 mmol) in THF (30 mL) was added dropwise. The reaction was warmed to room temperature and then refluxed for one hour. The solvent was removed and the material dissolved in DCM (120 mL).The organic layer was washed with water (2 x 100 mL) and brine (1 x 100 mL) then dried over K_2CO_3. The solvent was removed yielding a red oil that precipitated yellow crystals upon the addition of EtOH. The precipitate was filtered and washed with hexanes to give 1.73 g of the title compound (70%). The material gave identical spectral data to that previously reported in the literature.[15] ^{1}H NMR

($CDCl_3$, 300 MHz): δ = 9.03 (br s, 1H), 6.82 (d, 1H), 6.71 (s, 2H), 4.39 (q, 2H), 4.08 (m, 2H), 4.06-3.82 (overlapping s+d, 6H+2H), 1.41 (t, 3H).



Scheme S-4. Synthetic scheme for ester protected anthroporphyrin pyrroles.

1,4,4a,9a-Tetrahydro-1,4-ethanoanthracene-9,10-dione (28). The title compound was prepared following a modified literature method.[18] A mixture of 1,3-cyclohexadiene (7.0 g, 87.3 mmol) and **27** (13.8 g, 87.3 mmol) in EtOH (90 mL) was refluxed for 3 hours. The reaction was cooled overnight in a freezer. The precipitated crystals were collected and then recrystallized from boiling EtOH to give 14.05 g of the title compound (67%). The material gave identical spectral data to that previously reported in the literature.[18] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.99-7.96 (m, 2H), 7.67-7.63 (m, 2H), 6.11 (dd, 2H), 3.32-3.30 (m, 2H), 3.18-3.17 (m, 2H), 1.77-1.73 (m, 2H), 1.39-1.34 (m, 2H).

1,2,3,4,4a,9,9a,10-Octahydro-1,4-ethanoanthracene-9,10-diol (29). The title compound was prepared following a modified literature method.[19] A solution of **28** (5.7 g, 23.9 mmol) in anhydrous MeOH (150 mL) was cooled to 0°C under N_2 atmosphere. In one portion $NaBH_4$ (2.5 g, 66.0 mmol) was added and the reaction stirred at 0°C for two hours. The solvent was removed and the crude material purified by column chromatography eluting with a

hexane:THF (5:2) solvent mixture removing the first light yellow band. The solvent polarity was then increased to pure THF. The combined fractions afforded 5.15 g of the title compound (89%). The material gave identical spectral data to that previously reported in the literature.[19] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.30 (s, 4H), 6.35 (broad s, 2H), 4.70-4.67 (m, 2H), 3.03-3.01 (m, 2H), 2.76 (broad s, 2H), 2.21 (broad s, 2H), 1.60-1.57 (m, 2H), 1.37-1.34 (m, 2H).

1,4-Dihydro-1,4-ethanoanthracene (30). The title compound was prepared following a modified literature method.[20] A mixture of TsCl (12.15 g, 63.7 mmol) and **29** (5.15 g, 21.3 mmol) in dry pyridine (40 mL) under N_2 atmosphere was stirred for 48 hours at room temperature. The reaction was poured over ice (300 g) and stirred. The precipitated material was collected and dried over $MgSO_4$. The crude product was purified by column chromatography eluting with hexanes yielding 3.25 g of the title compound (74%). The material gave identical spectral data to that previously reported in the literature.[21] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.80-7.77 (AA'BB', 2H), 7.59 (s, 2H), 7.43-7.39 (AA'BB', 2H), 6.60-6.57 (m, 2H), 4.06 (m, 2.12), 1.69-1.56 (m, 4H).

2-Chloro-1,2,3,4-tetrahydro-3-phenylsulfonyl-1,4-ethanoanthracene (31). The title compound was prepared following a modified literature method.[22] A solution of **30** (3.25 g, 15.8 mmol) in dry DCM (150 mL) was cooled to 0°C in an ice bath. The solution was then treated dropwise with PhSCl (18.9 mmol) in dry DCM (60 mL). The reaction was stirred at room temperature for one hour. The organic layer was washed with 10% aqueous $NaHCO_3$ (80 mL), water (80 mL), and brine (80 mL). The organic layer was collected and dried over Na_2SO_4.The solvent removed yielding a yellow oil that was diluted with hexanes and EtOH precipitating 4.3 g of white powder that was collected and dried. The crude material was dissolved in DCM (100 mL) and cooled to 0°C followed by the addition of 77% *m*-CPBA (6.8 g, 39.4 mmol) in one

portion. The reaction was warmed to room temperature and stirred overnight. The precipitate was filtered off and the solvent removed. The material was recrystallized from hexanes/EtOH to give 3.53 g of the title compound (59%). The material gave identical spectral data to that previously reported in the literature.[22] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.81-7.78 (m, 4H), 7.68 (s, 1H), 7.62-7.56 (m, 2H), 7.51-7.43 (m, 4H), 4.35-4.32 (m, 1H), 3.85-3.83 (m, 1H), 3.63-3.60 (m, 1H), 3.41-3.38 (m, 1H), 2.43-2.33 (m, 1H), 2.08-1.98 (m, 1H), 1.67-1.43 (m, 2H).

4,11-Dihydro-4,11-ethano-2H-napth[2,3f]isoindole-1-carboxylic acid ethyl ester (32). The title compound was prepared following a modified literature method.[22] A solution of dry THF (40 mL) and **31** (2.63 g, 6.9 mmol) was added dropwise at 0°C to ^{t}BuOK (1.85 g, 16.5 mmol) and ethyl isocyanoacetate (93 mg, 8.2 mmol). After the addition the reaction was warmed to room temperature and stirred overnight. The organic layer was washed with water (2 x 100 mL) and brine (1 x 100 mL) collected and dried over Na_2SO_4. The solvent was removed yielding an oil. The addition of hexane and EtOH precipitated the title compound as a white powder to give 805 mg (37%). The material gave identical spectral data to that previously reported in the literature.[22] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.45 (broad s, 1H), 7.74 (m, 2H), 7.68 (s, 1H), 7.61 (s, 1H), 7.38 (m, 2H), 6.07 (s, 1H), 4.90 (s, 1H), 4.39-4.34 (m, 3H), 1.81 (m, 4H), 1.44-1.40 (m, 3H).

1,4-Epoxy-1,4-dihydronaphthalene (33). The title compound was prepared following a modified literature method.[23] In dry THF (120 mL) anthranilic acid (9.5 g, 69.3 mmol) was cooled to 0°C followed by the addition of isoamyl nitrite (20 mL) dropwise. The mixture was then warmed to room temperature and stirred for one hour. The yellow precipitate was collected by filtration (Caution: explosion hazard do not allow precipitate to dry or come in contact with metal) and transferred to a flask with dry THF (120 mL), furan (4.40 g, 64.6 mmol), and

propylene oxide (6 mL). The mixture was slowly warmed to 70°C under a N_2 atmosphere until the precipitate disappeared with adequate venting. The solution was then heated to reflux for 20 minutes. The solvent was removed under reduced pressure and the crude product purified by column chromatography eluting with 10% ethyl acetate in hexanes. The material from the combined fractions was recrystallized from hexanes to give 4.60 g of the title compound (49%). The material gave identical spectral data to that previously reported in the literature.[24] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.23 (dd, 2H), 7.01 (s, 2H), 6.95 (dd, 2H), 5.70 (s, 2H).

9,10-Epoxy-1,4,4a,9,9a,10-hexahydroanthracene (34). The title compound was prepared following a modified literature method.[25] A 60 mL thick walled flask with Teflon screw cap with **33** (5.05 g, 35.0 mmol) and $NaHCO_3$ (2.5 g, 29.75 mmol) dissolved in pyridine (20 mL) freshly distilled over NaOH. To this solution 3-sulfolene (4.55 g, 38.5 mmol) was added in seven equal portions. The reaction was heated at 120°C for 10 hours after each addition of 3-sulfolene. The reaction was carefully vented prior to each new addition and heating cycle. The mixture was filtered through celite and the solvent removed. The crude material was dissolved in DCM and passed through a short (4") column of silica-gel. The solvent was removed to give yellow oil that precipitated crystals upon addition of MeOH. The product was collected and dried to give 4.89 g of the title compound (70%). The material gave identical spectral data to that previously reported in the literature.[25] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.23 (AA'BB', 2H), 7.13 (AA'BB', 2H), 5.95 (m, 2H), 5.00 (s, 2H), 2.52-2.46 (m, 2H), 2.09-2.01 (m, 2H), 1.95-1.89 (m, 2H).

1,4-Dihydroanthracene (35). The title compound was prepared following a modified literature method.[25] Compound **34** (4.89 g, 24.7 mmol) dissolved in a mixture of EtOH (100 mL) and HCl (10 mL) heated to reflux for 24 hours under an argon atmosphere. After cooling in an ice bath a crystalline precipitate formed and was collected. The material was recrystallized from

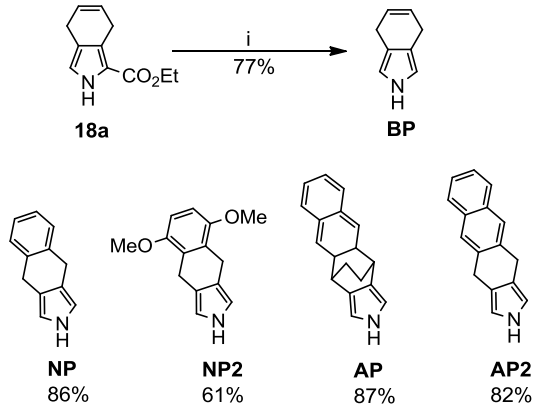
MeOH and dried to give 3.64 g of the title compound (82%). The material gave identical spectral data to that previously reported in the literature.[25] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.77 (AA'BB', 2H), 7.64 (s, 2H), 7.42 (AA'BB', 2H), 6.06 (m, 2H), 3.60 (s, 4H).

2-Chloro-3-(phenylsulfonyl)-1,2,3,4-tetrahydroanthracene (36). The title compound was prepared following a modified literature method.[25] In dry DCM (80 mL) **35** (2.5 g, 13.9 mmol) was cooled to -78°C and treated dropwise with a solution of PhSCl (16.5 mmol) in dry DCM (80 mL). After the addition the reaction mixture was stirred for 4 hours at room temperature and then placed in a freezer for 2 hours. The precipitated was removed. The reaction mixture was then cooled to 0°C followed by the addition of 77% *m*-CPBA (7.18 g, 41.6 mmol). The reaction was warmed to room temperature and stirred under a N_2 atmosphere for 48 hours. The reaction was diluted with aqueous 10% Na_2SO_3 (50 mL) and stirred for 30 minutes. The organic layer was washed with aqueous 10% Na_2CO_3 (80 mL), aqueous10% Na_2SO_3 (80 mL), and aqueous 10% Na_2CO_3 (80 mL) then dried over K_2CO_3. The solvent was removed under reduced pressure and the crude material recrystallized from MeOH yielding 3.55 g of the title compound (72%). The material gave identical spectral data to that previously reported in the literature.[25] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.99 (m, 2H), 7.77 (m, 2H), 7.70 (m, 1H), 7.64 (s, 1H), 7.61 (m, 2H), 7.46 (m, 2H), 4.97 (m, 1H), 3.79 (m, 1H), 3.58 (dd, 1H), 3.45 (dd, 1H), 3.34 (dd, 1H), 3.28 (dd, 1H).

2-(Phenylsulfonyl)-1,2-dihydroanthracene (37). The title compound was prepared following a modified literature method.[25] In dry DCM (30 mL) compound **36** (3.54 g, 9.91 mmol) was treated dropwise with one equivalent of DBU (1.51 g, 9.91 mmol). After the addition the reaction mixture was stirred at room temperature for one hour then diluted with water (30 mL). The layers were separated and the aqueous layer was washed with DCM (3 x 50 mL). The

organic layers combined and dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude material was recrystallized from MeOH yielding 2.80 g of the title compound (89%). The material gave identical spectral data to that previously reported in the literature.[25] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.75 (m, 2H), 7.66 (m, 2H), 7.43-7.37 (m, 3H), 7.34 (m, 1H), 7.29-7.20 (m, overlap with solvent, 3H), 6.80 (d, 1H), 6.13 (dd, 1H), 4.13 (m, 1H), 3.61 (dd, 1H), 3.40 (dd, 1H).

Ethyl-4,11-dihydro-2H-naphtho[2,3-*f*]isoindole-1-carboxylate (38). The title compound was prepared following a modified literature method.[25] In dry THF (30 mL) ^{t}BuOK (1.4 g, 12.5 mmol) was stirred at 0°C followed by the addition of ethyl isocyanoacetate (988 mg, 8.73 mmol) and stirred at room temperature. Compound **37** (2.80 g, 8.73 mmol) in dry THF (30 mL) was added dropwise at 0°C. The mixture was warmed to room temperature and stirred overnight. The solvent was removed and the crude material redissolved in DCM (120 mL). The organic layer was washed with water (2 x 100 mL) and brine (1 x 100 mL) and dried over K_2CO_3. The solvent removed under reduced pressure and the crude material purified by column chromatography eluting with DCM/Hexanes (80:20). The combined fractions recrystallized from MeOH yielding 1.163 g of the title compound (46%). The material gave identical spectral data to that previously reported in the literature.[25] ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.96 (br s, 1H), 7.80 (s overlapped, 1H), 7.76 (m, 2H), 7.74 (s overlapped, 1H), 7.44 (m, 2H), 6.86 (d, 1H), 4.43 (q overlapped, 2H), 4.39 (s, 2H), 4.06 (s, 2H), 1.44 (t, 3H).



Scheme S-5. Synthetic scheme for the deprotection of the ester protected pyrroles.

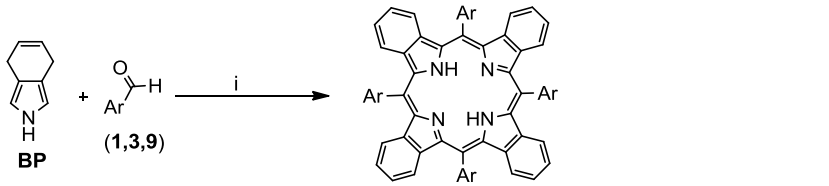
4,7-dihydro-2H-isoindole (BP). A suspension of **18a** (600 mg, 3.1 mmol) in ethylene glycol (20 mL) with KOH (880 mg, 15.7 mmol) was thoroughly purged with argon. The mixture was heated to 170°C for 1 hour. The reaction was immediately cooled in an ice bath and diluted with DCM (100 mL). The organic layer was washed with water (2 x50 mL) and brine (1 x 50 mL) collected and dried over Na_2SO_4. The solvent was removed producing a dark amber colored oil that was vacuum dried to a consistent weight to give 287 mg of the title compound (77%). TLC analysis verified that no starting material was present. The title compound was immediately used in a porphyrin synthesis without further purification due its instability. ESI-TOF [M+H]+ and [2M+H]+ 120.0813, 239.1545, calcd 120.0808, 239.1543.

4,9-Dihydro-2H-benzo[f]isoindole (NP). The title compound was prepared from **21** following the procedure used for **BP** (86 %). APCI-MS $[M+H]^+$ 170.0961, calcd 170.0964.

5,8-Dimethoxy-4,9-dihydro-2H-benzo[f]isoindole (NP2). The title compound was prepared from **26** following the procedure used for **BP** (61%). ESI-TOF $[M+H]^+$ and $[M+Na]^+$ 230.1176, 252.0990, calcd 230.1176, 252.0990.

4,11-Dihydro-4,11-ethano-2H-napth[2,3f]isoindole (AP). The title compound was prepared from **32** following the procedure used for **BP** (87%). ESI-TOF m/z 246.1275, calcd 246.1277.

4,11-Dihydro-2H-naphtho[2,3-f]isoindole (AP2). The title compound was prepared from **38** following the procedure used for **BP** (82%). CI-MS $[M]^+$ and $[M+H]^+$ 219.1054, 220.1132 calcd 219.1048, 220.1126.



39a: Ar = phenyl (29%)
39b: Ar = 3,5-di-*tert*-butylphenyl (20%)
39c: Ar = 4-(9,9-dihexyl-fluorenyl)-phenyl (17%)

Scheme S-6. General synthetic scheme for the synthesis of tetraaryltetrabenzoporphyrins.

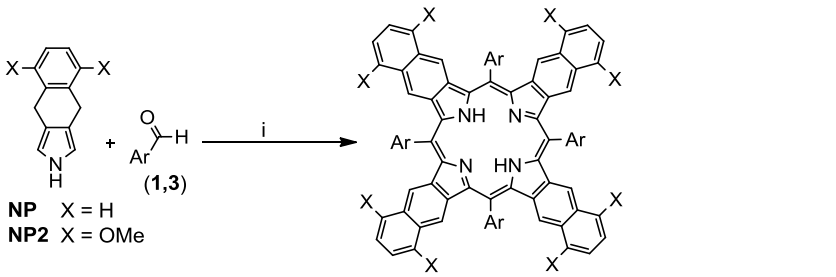
Tetraphenyltetrabenzoporphyrin (39a). The title compound was prepared following a modified literature method.[13] A solution of **BP** (287 mg, 2.4 mmol) and **1** (255 mg, 2.4 mmol) in dry DCM (250 mL) was stirred under an argon atmosphere protected from light. After the addition $BF_3{\cdot}O(Et)_2$ (60 mg, 0.4 mmol) the reaction was stirred for 3 hours at room temperature. In one portion DDQ (603 mg, 2.7 mmol) was added and the reaction stirred for one hour. The solvent was removed and the material redissolved in toluene (80 mL) with DDQ (655 mg, 2.9 mmol) heated to reflux under argon for one hour. The solvent was removed and the crude material dissolved in DCM (120 mL). The organic layer was washed with aqueous 10% Na_2SO_3 (2 x 100 mL), water (2 x 100 mL) and brine (1 x 100 mL) collected and dried over Na_2SO_4. The crude material was loaded on silica and purified by column chromatography eluting with 2% MeOH in DCM. The first bright green band was collected and the solvent removed. The material

was dissolved in a minimal amount of boiling $CHCl_3$ vigorously stirred and diluted with MeOH (10x volume) precipitating small green crystalline flakes. The precipitate was collected and repeatedly washed with MeOH yielding 140 mg of the title compound (29%). The NMR spectra were recorded on a Varian Inova 500 MHz, operating at 500 MHz for ^1H, 125 MHz for ^{13}C, and 50 MHz for ^{15}N. The probe was an indirect detection triple resonance probe, with z-axis gradients. The proton spectrum at 25°C displayed a broad signal for the protons of the orthophenylene moiety, due to the exchange of the NH protons.[26] This broad signal was resolved at -50°C into two AA'BB' patterns, while the NH protons displayed a sharp signal at -1.34 ppm, as the exchange became slower. Because of the limited solubility of H_2TPTBP in the NMR solvent, ^{13}C chemical shifts were measured by indirect detection, in a gHMBC spectrum. The material gave identical spectral data to that previously reported in the literature.[26] ^1H NMR ($CDCl_3$, 500 MHz): δ = 8.40 (m, 8H), 7.96 (m, 4H), 7.88 (m, 8H), 7.43 (AA'BB', 4H), 7.34 (AA'BB', 4H), 7.18 (AA'BB', 4H), 6.98 (AA'BB', 4H), -1.34 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 115.9, 124.2, 124.9, 126.1, 126.7, 129.5, 131.6, 133.7, 134.7, 140.1, 141.9; ESI-TOF $[M+H]^+$ 815.3169, calcd 815.3169.

Tetra(3,5-di-*tert*-butylphenyl)tetrabenzoporphyrin (39b). The title compound (H_2Ar_4TBP) was prepared from a solution of **BP** (296 mg, 2.5 mmol) and **3** (542 mg, 2.5 mmol) in dry DCM (250 mL) according to the procedure for **39a**. The crude product was purified by column chromatography eluting with DCM collecting the second large green band. The solvent was removed and the material dissolved in boiling methanol after cooling 158 mg of the title compound was collected by filtration (20%). ^1H NMR (pyridine-d_5, 500 MHz): δ = 8.48 (s, 8H), 8.25 (s, 4H), 7.66 (d, 8H), 7.47 (m, 8H), 1.59 (s, 72H); ^{13}C NMR (pyridine-d_5, 125 MHz) δ =

152.6, 138.4, 130.2, 126.4, 125.5, 122.7, 118.0, 35.7, 32.0; MALDI-MS $[M]^+$ and $[M+H]^+$ 1262.8042, 1263.8179, calcd 1262.8099, 1263.8177.

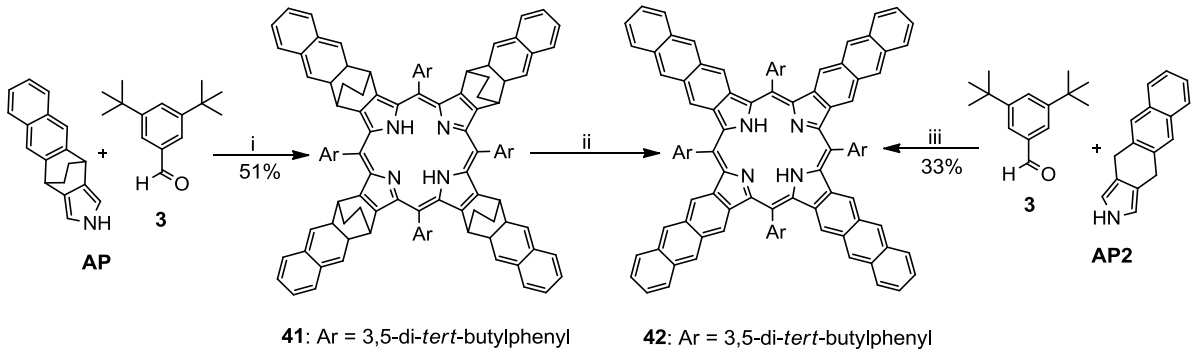
Tetra(4-(9,9-dihexyl-fluorenyl)-phenyl)tetrabenzoporphyrin (39c). The title compound (H_2ArF_4TBP) was prepared from a solution of **BP** (143 mg, 1.2 mmol) and **9** (520 mg, 1.2 mmol) in dry DCM (150 mL) according to the procedure for **39a**. The crude product was purified by column chromatography eluting with 20% EtOAc in hexane collecting the first large green band. The solvent was removed and the material precipitated from DCM and MeOH to give 110 mg of the title compound (17%).^{1}H NMR (pyridine-d_5, 500 MHz): δ = 8.67 (d, 8H), 8.50 (d, 8H), 8.24 (d, 4H), 8.19(d, 4H), 8.05 (d, 4H), 7.85 (d, 8H), 7.70 (d, 4H), 7.55 (m, 8H), 7.42 (m, 8H), 2.44 (dd, 8H), 2.35 (dd, 8H), 1.28 (m, 16H), 1.23 (m, 32H), 1.13 (m, 16H), 0.88 (t, 24H); ^{13}C NMR (pyridine-d_5, 125 MHz) δ = 153.0, 152.3, 143.2, 142.2, 141.9, 141.8, 140.5, 138.0, 136.2, 128.4,128.2, 128.0, 127.5, 127.0, 125.4, 124.1, 122.8, 121.2, 120.9, 116.8, 56.5, 41.1, 32.1, 30.4, 24.9, 23.1, 14.4; MALDI-MS $[M]^+$ and $[M+H]^+$ 2143.3074, 2144.3104, calcd 2143.3107, 2144.3185.



Scheme S-7. General scheme for the synthesis of tetraaryltetranaphthoporpyrins.

Tetraphenyltetranaphthoporphyrin (40a). The title compound was prepared following a modified literature method.[15] In dry DCM (250 mL), **NP** (430 mg, 2.54 mmol) and **1** (270 mg, 2.54 mmol) was stirred under argon atmosphere and protected from light. After the addition of $BF_3 \cdot O(Et)_2$ (72 mg, 0.5 mmol) the reaction was stirred at room temperature for 90 minutes. In one portion DDQ (2.88 g, 12.7 mmol) was added and the reaction brought to reflux for one hour. The organic layer was washed with 10% aqueous Na_2SO_3 (2 x 100 mL), and water (2 x 100 mL) and dried over K_2CO_3. The solvent removed and the crude material loaded on neutral silica eluting with DCM collecting the first major green band. The material was redissolved in boiling $CHCl_3$ and diluted with excess MeOH precipitating fine green crystals to give 116 mg of the title compound (20%). The material gave identical spectral data to that previously reported in the literature.[15] ^{1}H NMR ($CDCl_3$-TFA, 300 MHz): δ = 8.63-8.60 (m, 8H), 8.08-7.97 (m, 20H), 7.75-7.72 (m, 8H), 7.53-7.50 (m, 8H), 2.49 (s, 4H).

1,4,10,13,19,22,28,31-Octamethoxy-7,16,25,34-tetrakis(3,5-di-tertbutylphenyl)-tetranaphthoporphyrin (40b). The title compound ($H_2Ar_4TNP(OMe)_8$) (**40b**) was prepared according to the procedure for **40a** from a solution of **NP2** (242 mg, 1.0 mmol) and **3** (230 mg, 1.0 mmol) in dry DCM (180 mL). The solvent was removed and the crude material purified by chromatography eluting with DCM followed by multiple precipitations from DCM and MeOH to give 72 mg of the title compound (16%). ^{1}H NMR (pyridine-d_5, 500 MHz): δ = 8.66 (s, 8H), 8.49 (s, 8H), 8.37 (s, 4H), 6.86 (d, 8H), 4.03 (s, 24H), 1.60 (s, 72H); ^{13}C NMR (pyridine-d_5, 125 MHz) δ = 152.9, 151.1, 142.8, 136.1, 128.5, 125.3, 122.6, 120.2, 119.5, 116.8, 103.5, 55.7, 35.4, 31.8; MALDI-TOF MS $[M]^+$ 1703.9685, calcd 1703.9603.



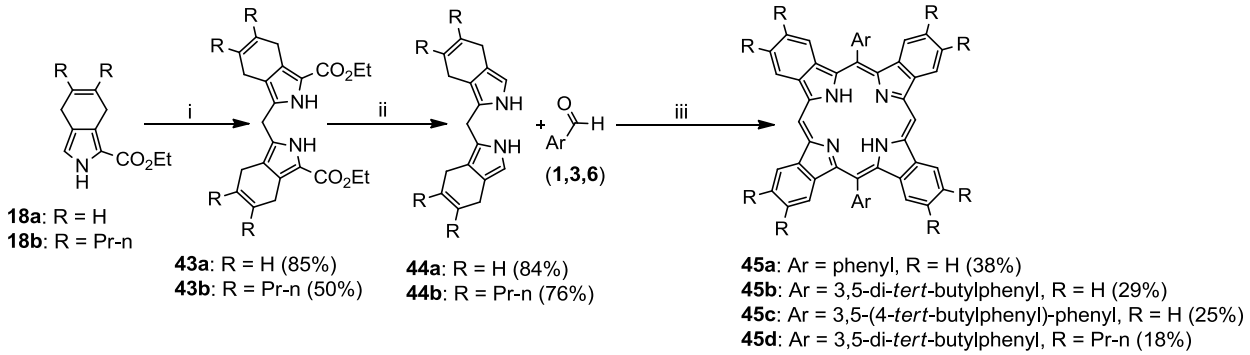
Scheme S-8. Synthetic scheme for tetraarylanthroporphyrins from the retro-Diels-Alder method and the dihydroisoindole method.

8,19,30,41-tetrakis(3,5-di-butylphenyl)-6,10,17,22,27,32,39,43-octahydro-6,43:10,17:21,28:32,39-tetraethano-45H,47H-tetraanthraporphyrin (41). The title compound was prepared following a modified literature method.[22] A mixture of **3** (200 mg, 0.9 mmol) with **AP** (225 mg, 0.9 mmol) in dry DCM (170 mL) was stirred protected from light under an argon atmosphere. After the addition of $BF_3{\cdot}O(Et)_2$ (58 mg, 0.4 mmol) the reaction was stirred at room temperature for 18 hours. In one portion DDQ (1.08 g, 4.75 mmol) was added and the mixture stirred for 90 minutes. The organic layer was washed with 10% aqueous Na_2SO_3 (2 x 100 mL), water (1 x 100 mL), and brine (1 x 100 mL) collected and dried over Na_2SO_4. The solvent removed and the crude material passed through a silica column eluting with DCM. The combined fractions dissolved in warm THF (25 mL) and diluted with MeOH (250 mL). The solution became turbid and was placed in the refrigerator overnight. The formed precipitate was filtered and washed repeatedly with MeOH. The precipitate was collected and dried to give 209 mg of the title compound (51%). The material gave identical spectral data to that previously reported in the literature.[22] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.41-7.26 (mixture of isomers, overlap with solvent, 36H), 3.95 (m, 8H), 1.83-1.63 (m, bridge + t-Bu, 88H).

Conversion of **41** to **42** was accomplished by dissolving **41** in a minimum amount of toluene followed by slow evaporation in a flat bottom sublimation flask to form a uniform film.

(Note: attempts with a sand bath and round bottom flask where the film was created by a rotovap failed to give quantitative conversion to **42** due to the temperature ranges of the sand bath even at reaction times > 7 hrs). The flask was heated directly on top of a hot plate for 3 hrs at 300°C under vacuum protected from light with foil. This gave **42** quantitatively which was then stored in a glove box due to its light and oxygen sensitivity.

Tetra(3,5-di-*tert*-butylphenyl)tetraanthroporphyrin (42). The title compound was prepared following a modified literature method.[25] The solvents used in this procedure were thoroughly purged with argon or subjected to freeze pump thaw cycles due to the oxygen sensitivity of **42**. A mixture of **AP2** (150 mg, 0.67 mmol) and **3** (149 mg, 0.68 mmol) in dry DCM (100 mL) was stirred under an argon atmosphere protected from light. The reaction was stirred for one hour after the addition of $BF_3{\cdot}OEt_2$ (20 μL). A solution of DDQ (232 mg, 1.0 mmol) in toluene (4 mL) was subjected to freeze pump thaw cycles in a schlenk flask prior to addition. After the addition the reaction was stirred for one hour at room temperature and then quenched by the addition of aqueous 10% Na_2SO_3 (100 mL). The organic layer was separated and washed with aqueous 10% Na_2SO_3 (100 mL), aqueous 10% Na_2CO_3 (100 mL), and brine (100 mL). The organic layer was dried over Na_2SO_4 and the solvent removed under reduced pressure. The material was purified by column chromatography eluting with DCM. The combined fractions were concentrated and the material precipitated by the addition of excess MeOH. The precipitate was collected to give 95 mg of the title compound (33%). ^{1}H NMR (pyridine-d_5, 500 MHz): δ = 8.67 (s, 8H), 8.65 (s, 8H), 8.58 (s, 4H), 8.37 (s, 8H), 8.15 (s, 8H), 7.52 (t, 8H), 1.67 (s, 72H); ^{13}C NMR (pyridine-d_5, 125 MHz) δ = 32.2, 35.9, 116.3, 123.2, 125.7, 126.1, 128.2, 129.1, 129.6, 130.8, 132.8, 136.7; MALDI-TOF MS $[M]^+$ 1663.9403, calcd 1663.9384.



Scheme S-9. General synthetic scheme for the synthesis of 5,15-diaryltetrabenzoporphyrins.

Bis(3-ethoxycarbonyl-4,7-dihydro-2H-isoindolyl)methane (43a). The title compound was prepared following a modified literature method.[27] A solution of **18a** (1.606 g, 8.4 mmol) and dimethoxy methane (319 mg, 4.2 mmol) in AcOH (130 mL) and TsOH (165 mg, 0.9 mmol) under N_2 atmosphere was stirred for 24 hours. The reaction was poured into ice water (200 mL) and vigorously stirred. The precipitated material was collected and washed with water (1x 100 mL) and cold MeOH (2 x 50 mL). The title compound was dried under vacuum to give 1.38 g (85%). The material gave identical spectral data to that previously reported in the literature.[27] ^{1}H NMR ($CDCl_3$-d_6-DMSO, 300 MHz): δ = 11.19 (br s, 2H), 5.77 (m, 4H), 4.17 (q, 4H), 3.71 (s, 2H), 3.24 (m, 4H overlap with solvent), 3.02 (m, 4H), 1.27 (t, 6H).

Bis(3-ethoxycarbonyl-4,7-dihydro-5,6-dipropyl-2H-isoindolyl)methane (43b). The title compound was prepared from a solution of **18b** (920 mg, 3.3 mmol), dimethoxy methane (127 mg, 1.7 mmol), TsOH (75 mg, 0.4 mmol) in 75 mL of AcOH following the procedure for **43a**. The crude material was reprecipitated from boiling $CHCl_3$ and excess MeOH to give 470 mg of the title compound (50%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.43 (s, 2H), 4.26 (q, 3H), 3.88 (s, 2H), 3.37 (m, 4H), 3.51 (m, 4H), 2.16 (m, 8H), 1.46 (m, 8H), 1.30 (t, 6H), 0.95 (t, 3H),

0.94 (t, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ= 162.2, 128.7, 128.4, 127.3, 117.5, 116.0, 60.0, 35.7, 28.9, 26.6, 23.3, 22.0, 14.7, 14.6; ESI- MS $[M+H]^+$ 563.3851, calcd 563.3843.

Bis(4,7-dihydro-2H-isoindolyl)methane (44a). The title compound was prepared according to the procedure used for **BP**. A suspension of **43a** (650 mg, 1.65 mmol) in ethylene glycol (40 mL) with KOH (925 mg, 16.5 mmol) was thoroughly purged with argon and heated to 170°C for 1 hour. The isolated material was dried under vacuum to a consistent weight to give 351 mg of the title compound (84%). Due to instability **44a** was used immediately and not subjected to further purification. DART-MS $[M+H]^+$ 251.1563, calcd 251.1543.

Bis(4,7-dihydro-5,6-dipropyl-2H-isoindolyl)methane (44b). The title compound was prepared according to the procedure used for **44a** from **43b** (450 mg, 0.8 mmol) to give 255 mg of the title compound (76%)**.** ESI-MS $[M+H]^+$ 419.3429, calcd 419.3421.

5,15-Diphenyltetrabenzoporphyrin (45a). The title compound was prepared following a modified literature method.[27] In dry DCM (200 mL) **44a** (352 mg, 1.4 mmol) and **1** (149 mg, 1.4 mmol) were stirred protected from light under an argon atmosphere. After the addition of TFA (30 mg, 0.3 mmol) the reaction was stirred for 18 hours at room temperature. DDQ (478 mg, 2.1 mmol) was added in one portion and the reaction stirred for one hour. The solvent was removed under reduced pressure. The material was redissolved in toluene (120 mL) with DDQ (634 mg, 2.8 mmol) and refluxed for 30 minutes. The solvent was removed and the crude material dissolved in DCM (120 mL). The organic layer was washed with aqueous 10% Na_2SO_3 (2 x 100 mL), water (2 x 100 mL), and brine (1 x 100 mL). The organic layer was collected and dried over Na_2SO_4. The material loaded on silica and purified by column chromatography eluting with DCM. The combined fractions were dissolved in a minimal amount of boiling $CHCl_3$ and precipitated by the slow addition of MeOH (excess) under vigorous stirring. The precipitate was

collected and repeatedly washed with MeOH to give 178 mg of the title compound (38%). The material gave identical spectral data to that previously reported in the literature.[27] ^{1}H NMR ($CDCl_3$-TFA, 300 MHz): δ = 10.98 (s, 2H), 9.38 (d, 4H), 8.44 (m, 4H), 8.17 (ddd, 4H), 8.12 (m, 2H), 8.04 (m, 4H), 7.83 (ddd, 4H), 7.58 (d, 4H), 3.51 (br s, 4H).

5,15-Di(3,5-di-*tert*-butylphenyl)tetrabenzoporphyrin (45b). The title compound was prepared following a modified literature method.[27] Following the procedure for **45a** the title compound was prepared from a solution of **44a** (309 mg, 1.2 mmol) and **3** (269 mg, 1.2 mmol) in dry DCM (180 mL). The crude material was purified by column chromatography eluting with DCM. Then precipitated by dissolving in a minimum amount of boiling $CHCl_3$ diluting with MeOH to give 158 mg of the title compound after filtration and repeated washing with MeOH (29%). The material gave identical spectral data to that previously reported in the literature.[27] ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 11.15 (s, 2H), 9.73 (d, 4H), 8.17 (m, 4H), 8.12 (m + d overlapped, 6H), 7.77 (m, 4H), 7.53 (m, 4H), 1.56 (s, 36H), -1.25 (br s, 2H).

5,15-Di((3,5-di-*tert*-butylphenyl)-phenyl)tetrabenzoporphyrin (45c). The title compound was prepared from a solution of **44a** (369 mg, 1.5 mmol) and **6** (546 mg, 1.5 mmol) in dry DCM (180 mL) following the procedure used for **45a**. The material was purified by column chromatography on silica-gel eluting with DCM. The fractions were concentrated and the title compound precipitated from the addition of excess MeOH to give 220 mg (25%). ^{1}H NMR (pyridine-d_5, 500 MHz): δ = 1.44 (s, 36H), 7.67 (d, 8H), 7.94 (t, 4H), 8.14 (d, 8H), 8.21 (t, 4H), 8.29 (d, 4H), 8.90 (s, 2H), 8.92 (s, 4H), 10.00 (d, 4H), 11.56 (s, 2H); ^{13}C NMR (pyridine-d_5, 125 MHz) δ =31.8, 35.0, 94.3, 117.7, 122.4, 125.9, 126.8, 128.0, 128.3, 130.8, 138.0, 138.5, 140.3, 143.5, 150.5,151.9; DART-MS $[M+H]^+$ 1191.6296, calcd 1191.6299.

5,15-Di(3,5-di-*tert*-butylphenyl)octapropyltetrabenzoporphyrin (45d). The title compound was from a solution of **44b** (255 mg, 0.6 mmol) and **3** (133 mg, 0.6 mmol) in dry DCM (110 mL). The material was purified by column chromatography on silica-gel eluting with 2% MeOH in DCM to give 68 mg of the title compound following the procedure for **45a** (18%). ^{1}H NMR (pyridine-d_5, 500 MHz): δ = 11.66 (s, 2H), 9.90 (s, 4H), 8.45 (s, 4H), 8.42 (s, 2H), 7.75 (s, 4H), 3.26 (t, 8H), 3.08 (t, 8H), 2.07 (sex, 8H), 1.93 (sex, 8H), 1.72 (s, 36H), 1.25 (t, 12H), 1.24 (t, 12H); ^{13}C NMR (pyridine-d_5, 125 MHz) δ = 152.8, 141.0, 140.7, 140.2, 138.6, 136.6, 128.0, 126.2, 123.2, 122.1, 117.9, 93.6, 36.6, 36.4, 35.8, 32.2, 25.5, 25.2, 14.8, 14.7; DART-MS $[M+H]^+$ 1223.8763, calcd 1223.8803.

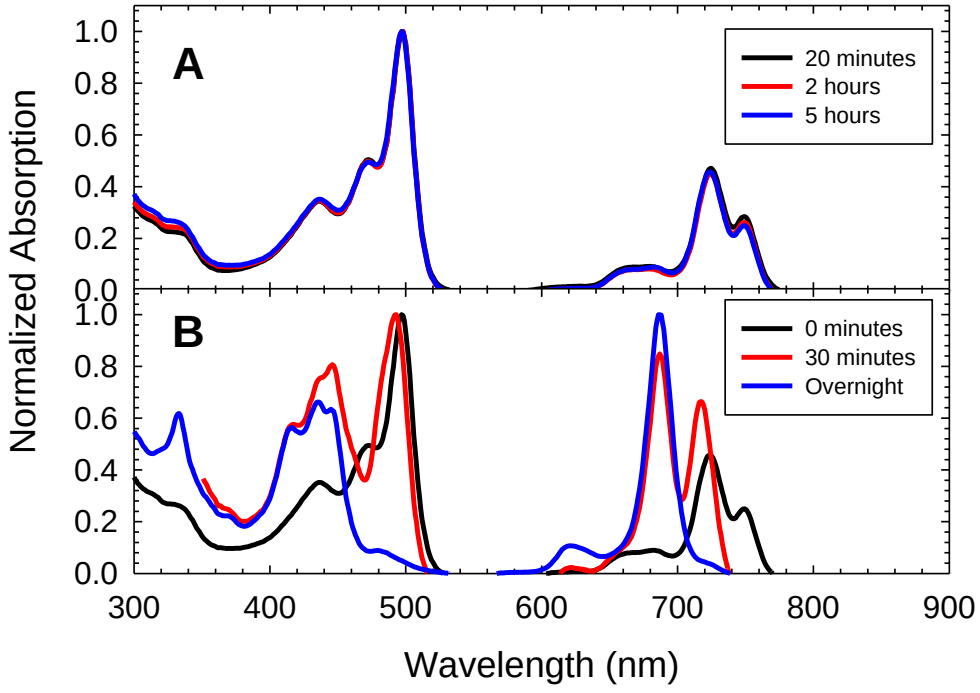


Figure S-1. A) Reaction of H_2TPTNP in benzonitrile with $PtCl_2$ at 200°C. The reaction was followed by UV-Vis spectroscopy over 5 hrs. B) Reaction of H_2TPTNP with $[Pt_4(OAc)_8]\cdot 2HOAc$ in benzonitrile at 180°C. The reaction was followed by UV-Vis spectroscopy.

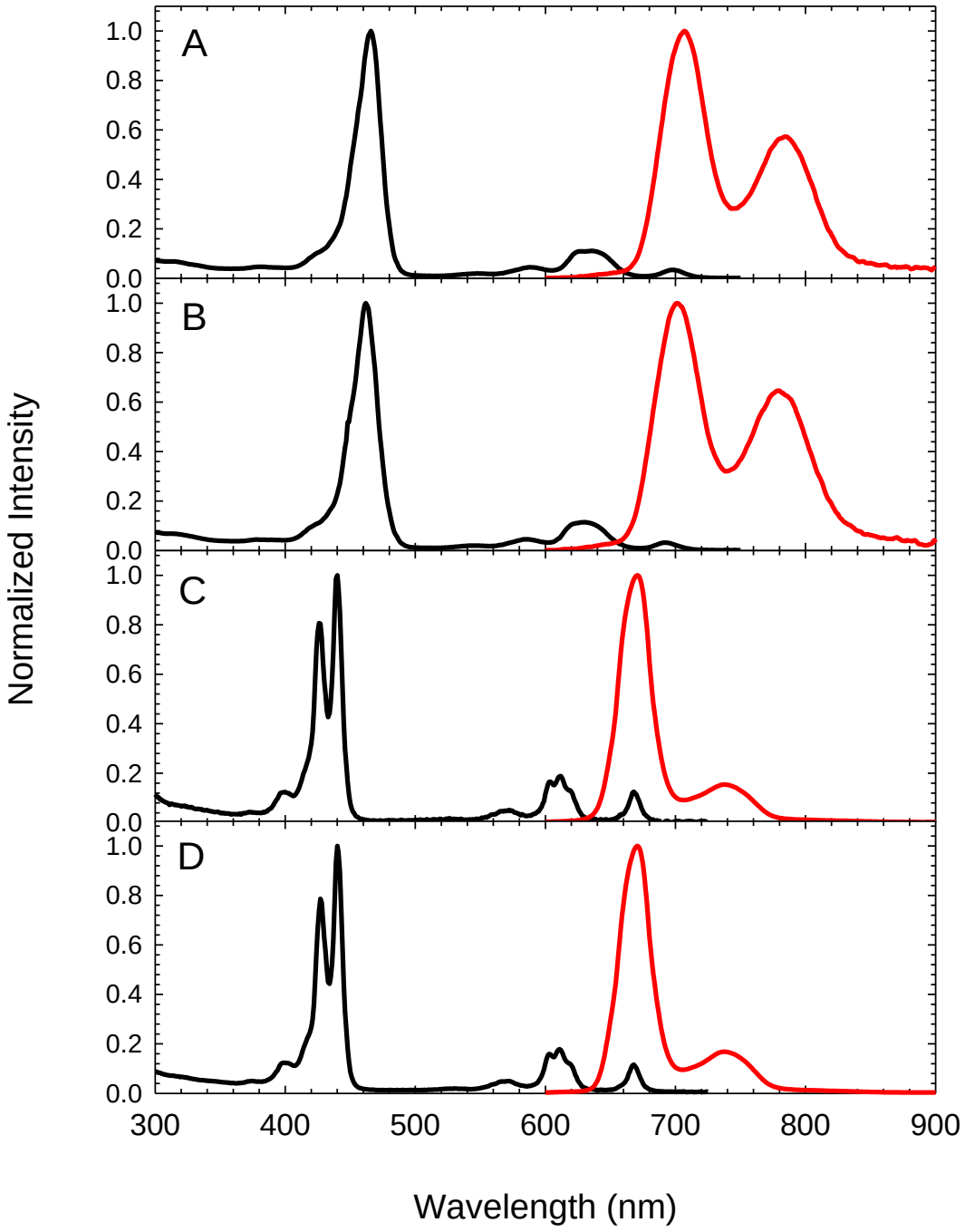


Figure S-2. Normalized absorption (black) and photoluminescence (red) of free-base TBPs in toluene: A) H_2TPTBP, B) H_2Ar_4TBP, C) H_2DPTBP, D) H_2Ar_2TBP.

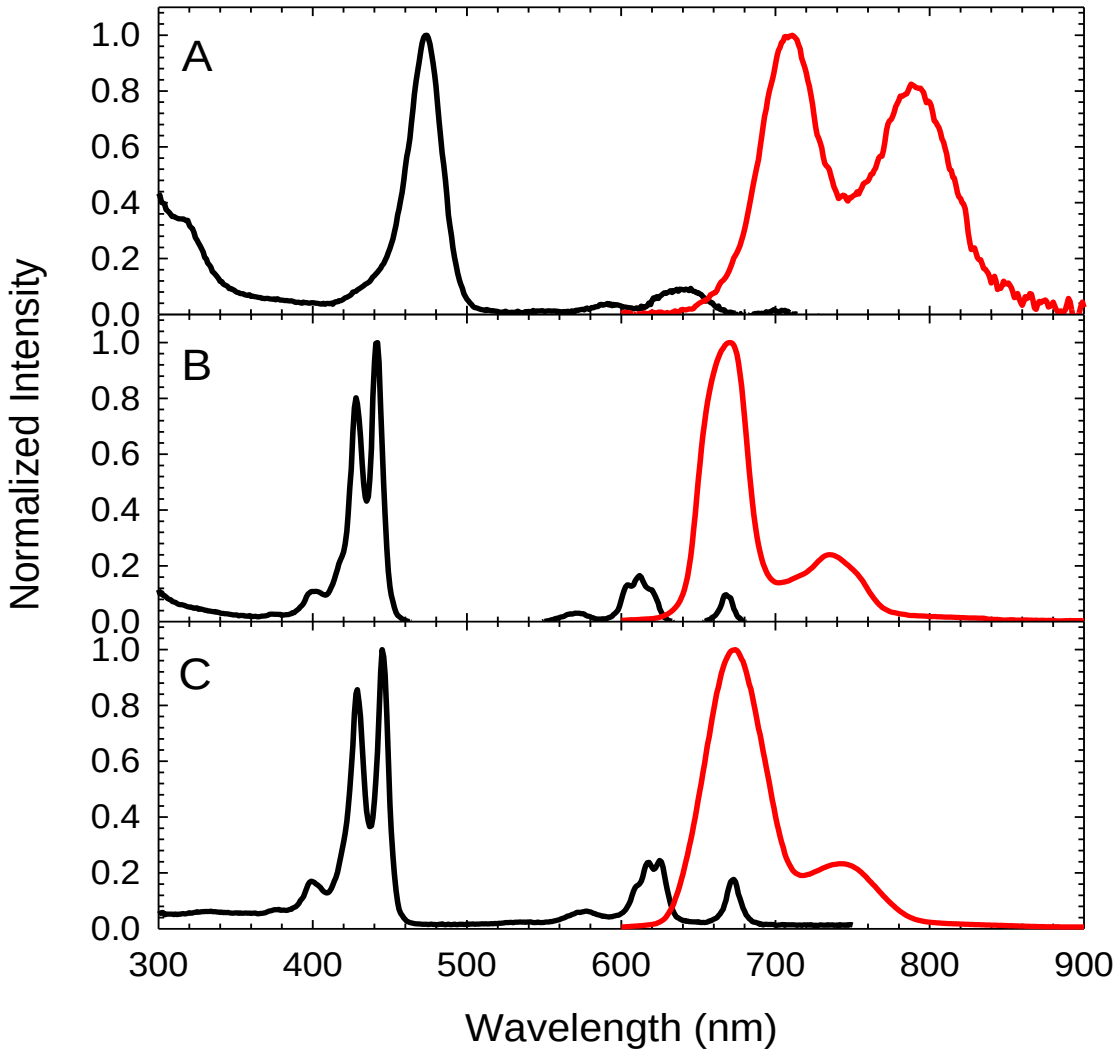


Figure S-3. Normalized absorption (black) and photoluminescence (red) for free-base TBPs in air saturated toluene: A) H_2ArF_4TBP, B) H_2TAr_2TBP, C) $H_2Ar_2OPrTBP$.

Table S-1. Photophysical properties of Series 2 free-base TBPs in air saturated toluene. Fluorescence quantum yields were measured relative to ZnTPP (0.03) with excitation at 420 nm in toluene. The fluorescence quantum yield for H_2TAr_2TBP and $H_2Ar_2OPrTBP$ was measured relative to H_2Ar_2TBP (0.38) with excitation at 420 nm in toluene. The S_1 decays were obtained by single photon counting method.

Free-base TBP's	Absorption λ_{max} (Soret, Q-band) nm (ε_{max} = M^{-1} cm^{-1})	Fluorescence λ_{max} nm	Φ_{fl} (τ_{fl} (ns))	k_r (s^{-1}) k_{nr} (s^{-1})
H_2TPTBP	465 (5.48) 633 (4.52)	704, 785	0.031 ±0.01 (3.1)	9.9×10^6 (3.1×10^8)
H_2Ar_4TBP	462 (5.51) 633 (4.62)	701, 779	0.032 ±0.01 (3.5)	9.2×10^6 (2.8×10^8)
H_2ArF_4TBP	474 (5.48) 642 (4.56)	711, 788	0.045 ±0.04 (2.8)	1.6×10^7 (3.4×10^8)
H_2DPTBP	440 (5.56) 612 (4.83)	671, 738	0.28 ±.04 (10.6)	2.6×10^7 (6.8×10^7)
H_2Ar_2TBP	440 (5.58) 612 (4.83)	671, 738	0.29 ±0.04 (10.3)	2.8×10^7 (6.9×10^7)
H_2TAr_2TBP	442 (5.54) 612 (4.75)	670, 735	0.29 ±0.01 (10.4)	2.8×10^7 (6.8×10^7)
$H_2Ar_2OPrTBP$	445 (5.51) 625 (4.86)	674, 743	0.32 ±3.0 (10.6)	3.0×10^7 (6.4×10^7)

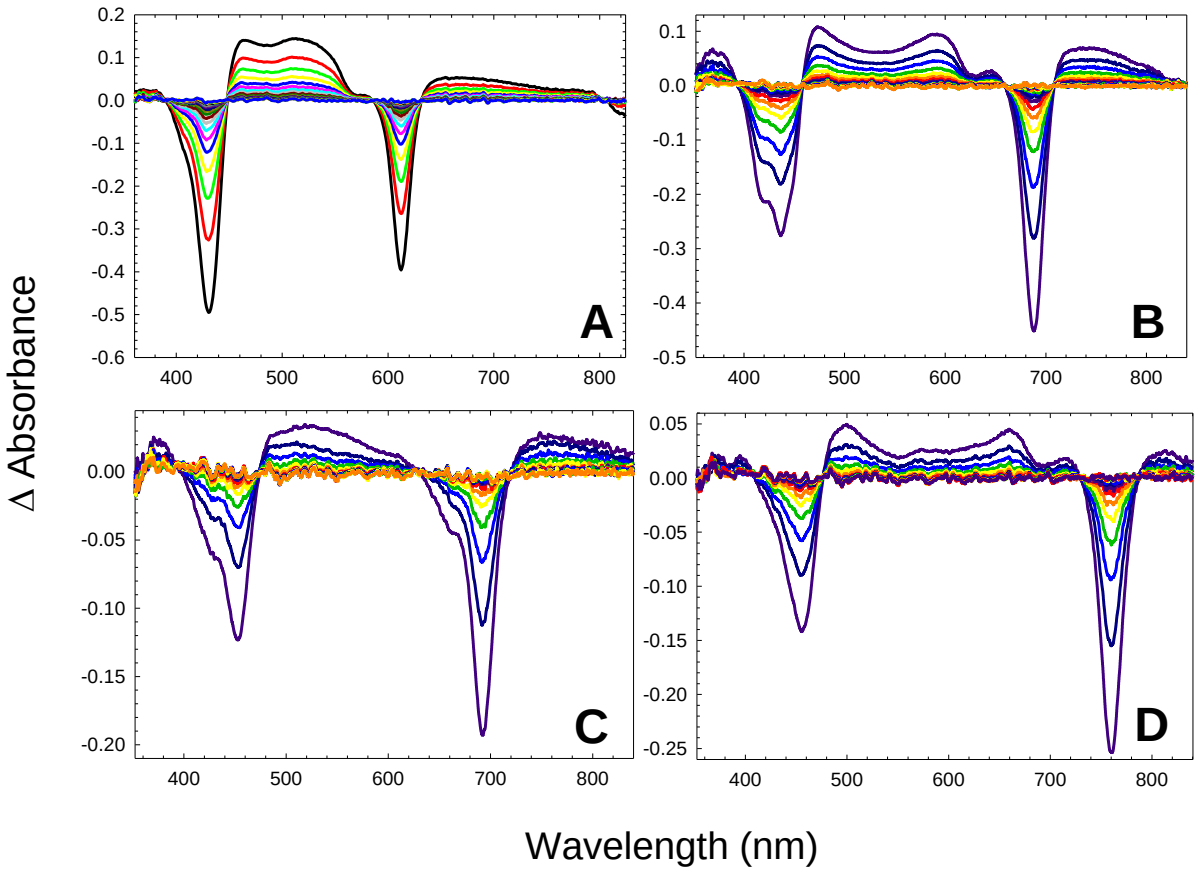


Figure S-4. T_1-T_n absorption data for series 1 π-extended platinum porphyrins in deoxygenated toluene: A) Pt-TPTBP, B) Pt-TPTNP, C) Pt-Ar_4TNP$(OMe)_8$, D) Pt-Ar_4TAP. Excitation with 355 nm, 5 ns pulses, ~5 mj-pulse^{-1} energy.

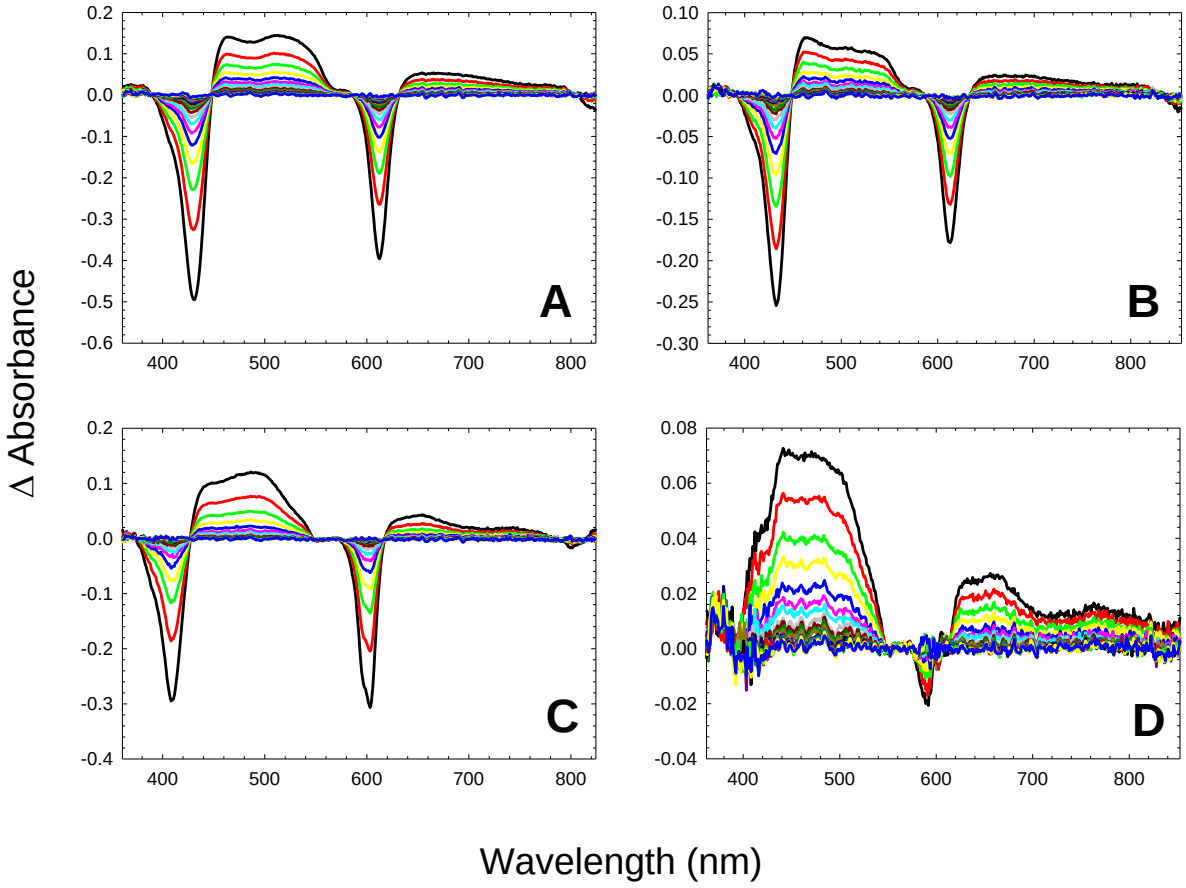


Figure S-5. T_1-T_n absorption data for Series 2 π-extended platinum TBPs in deoxygenated toluene: A) Pt-TPTBP, B) Pt-Ar_4TBP, C) Pt-DPTBP, D) Pt-Ar_2TBP. Excitation with 355 nm, 5 ns pulses, ~5 mj-pulse^{-1} energy.

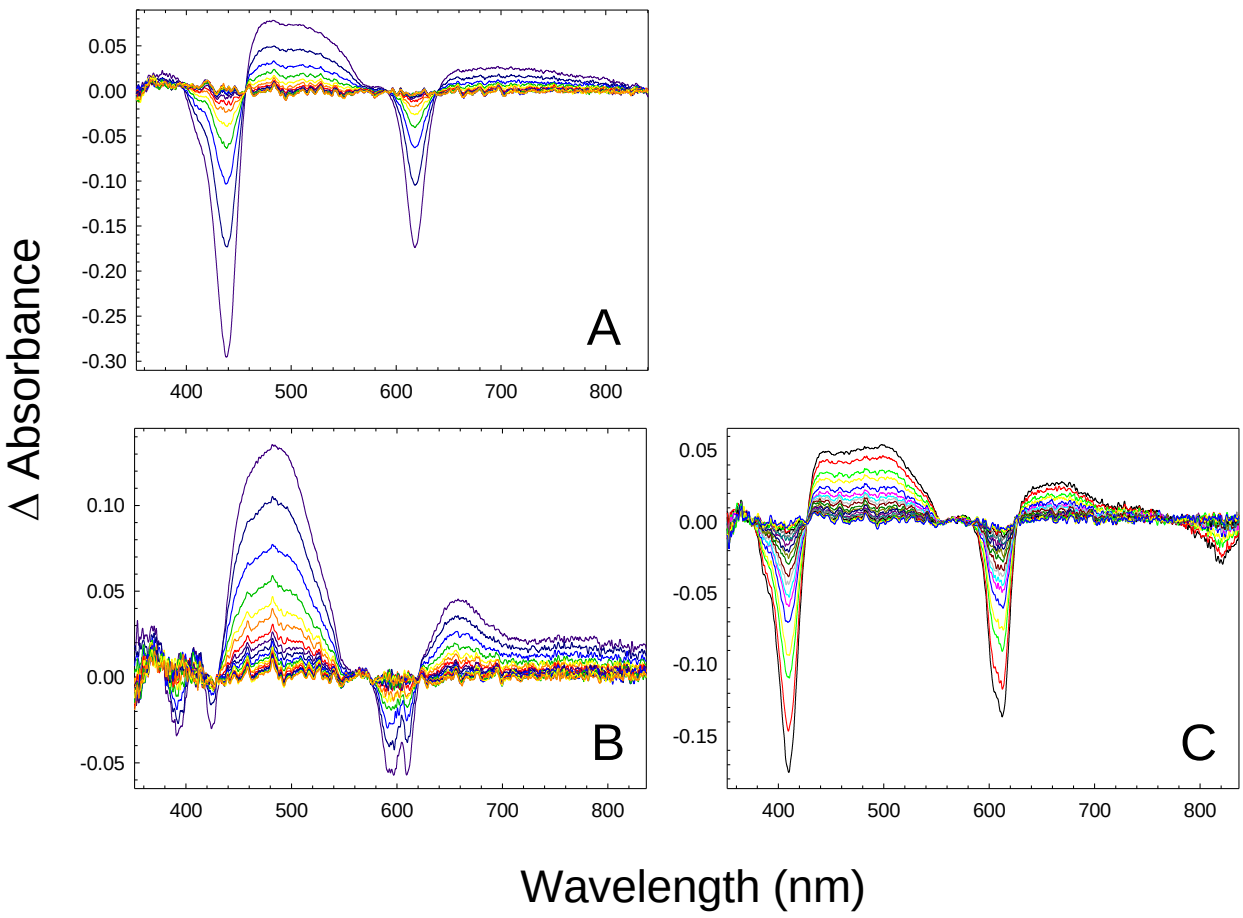


Figure S-6. T_1-T_n absorption data for Series 2 π-extended platinum TBPs in deoxygenated toluene: A) Pt-ArF_4TBP, B) Pt-TAr$_2$TBP, C) Pt-Ar$_2$OPrTBP. Excitation with 355 nm, 5 ns pulses, ~5 mj-pulse^{-1} energy.

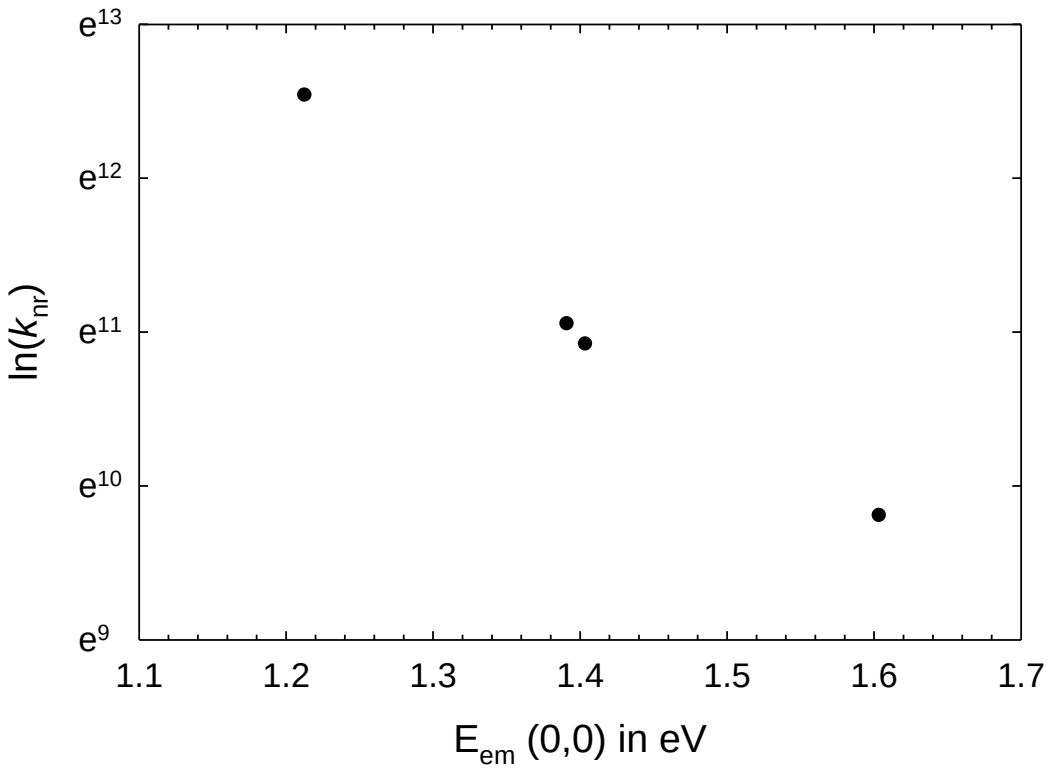


Figure S-7. Plot of the natural log of the non-radiative decay constant (k_{nr}) and the emission maximum in eV (E_{em}) for series 1 π-extended plantium porphyrins.

NMR SPECTRA

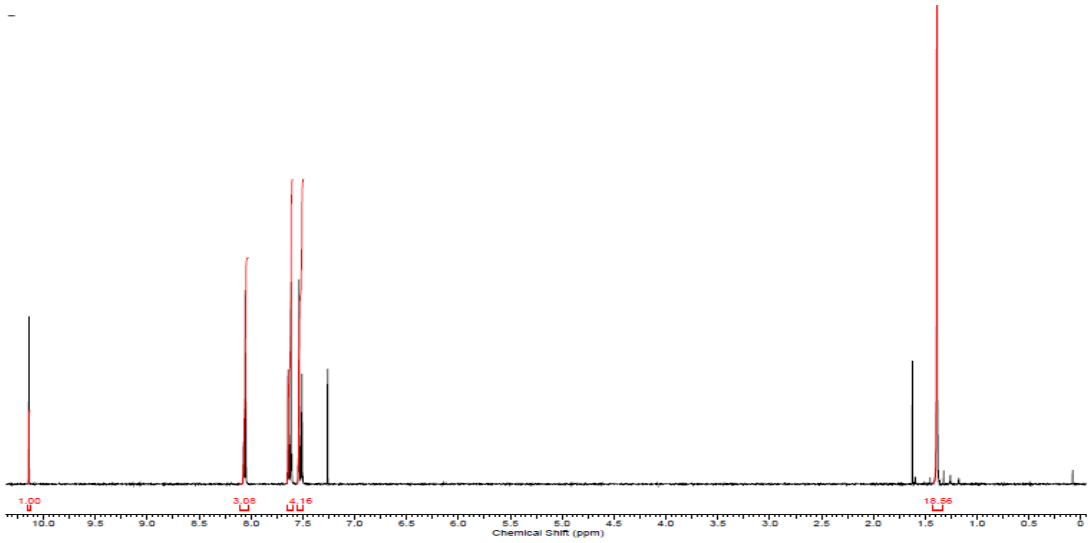


Figure S-8. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **6**.

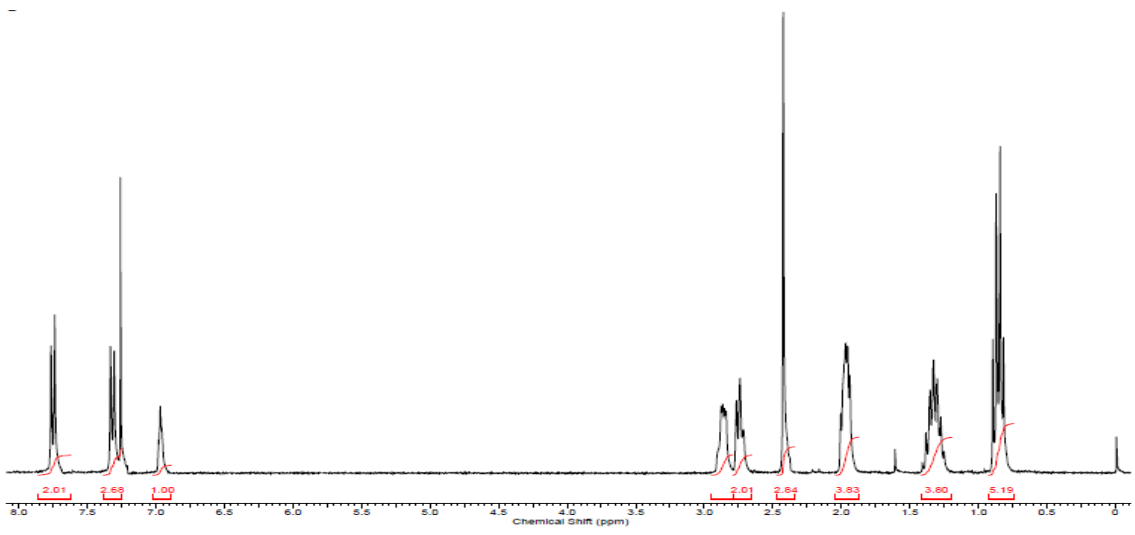


Figure S-9. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **17b**.

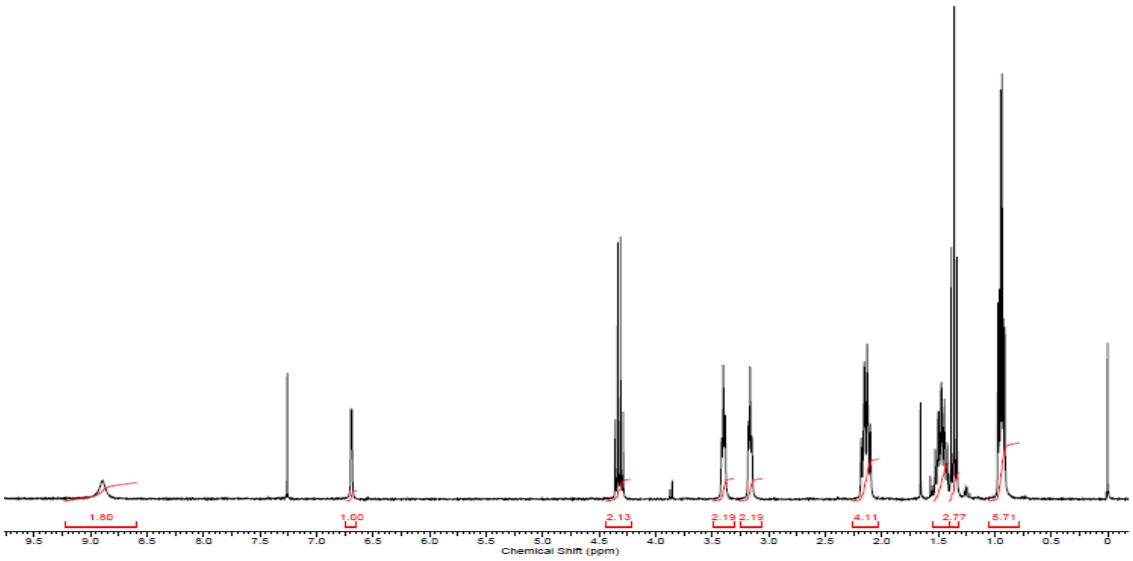


Figure S-10. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **18b**.

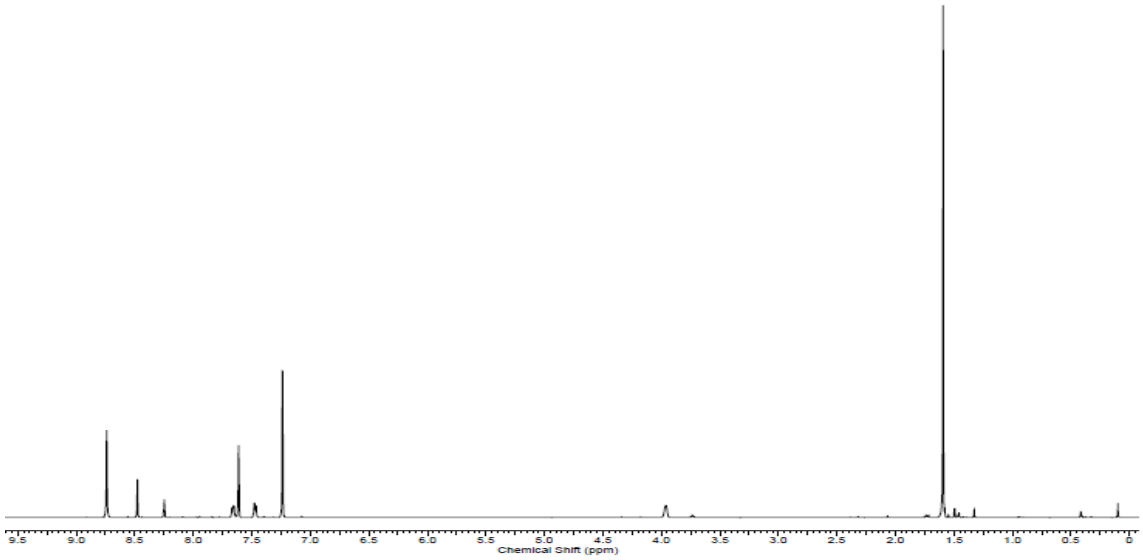


Figure S-11. ^{1}H NMR (300 MHz, pyridine-d_5) spectrum of **39b** (H_2Ar_4TBP).

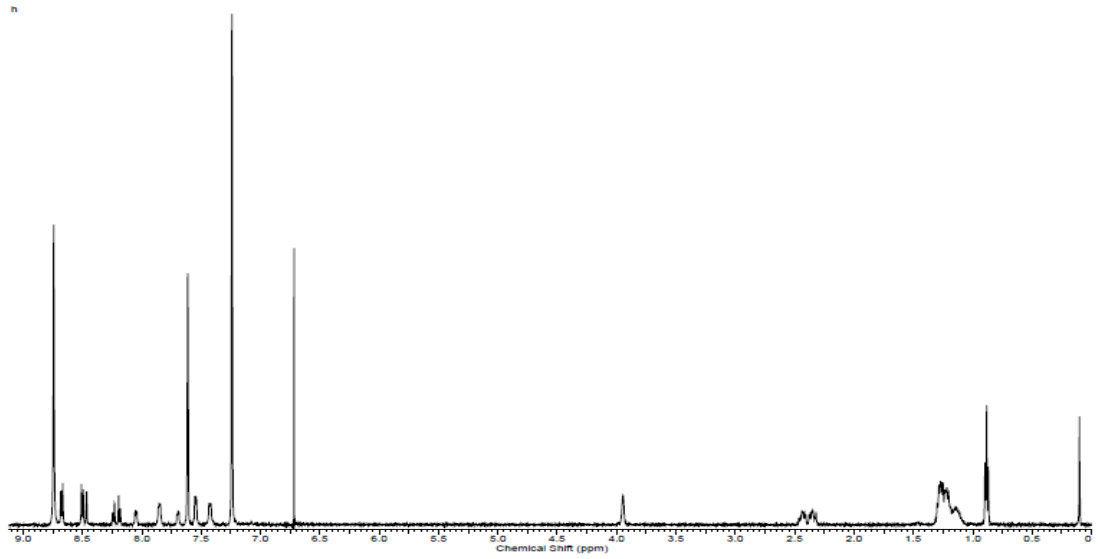


Figure S-12. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **39c** (H_2ArF_4TBP).

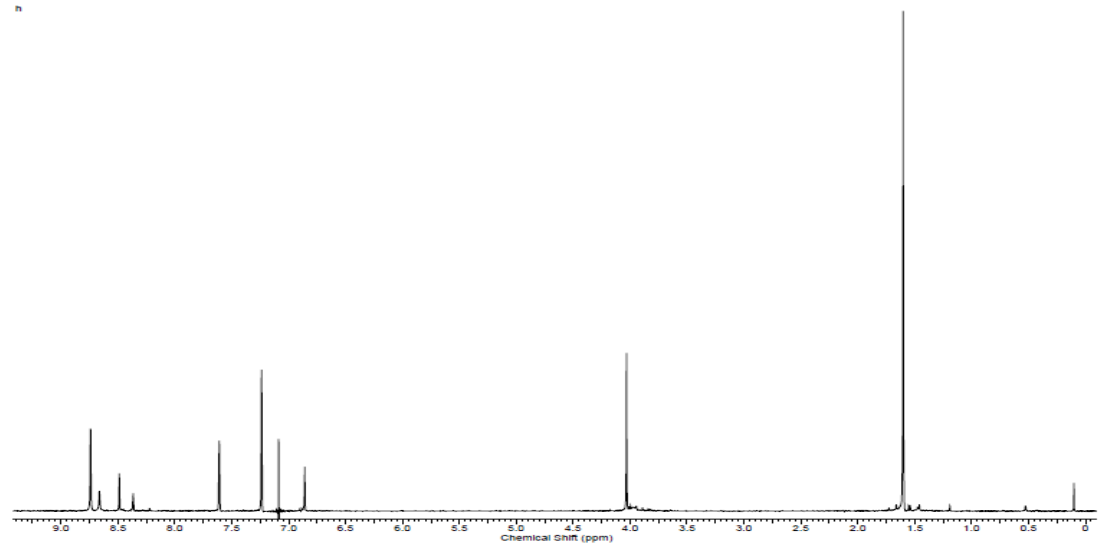


Figure S-13. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **40b** ($H_2Ar_4TNP(OMe)_8$).

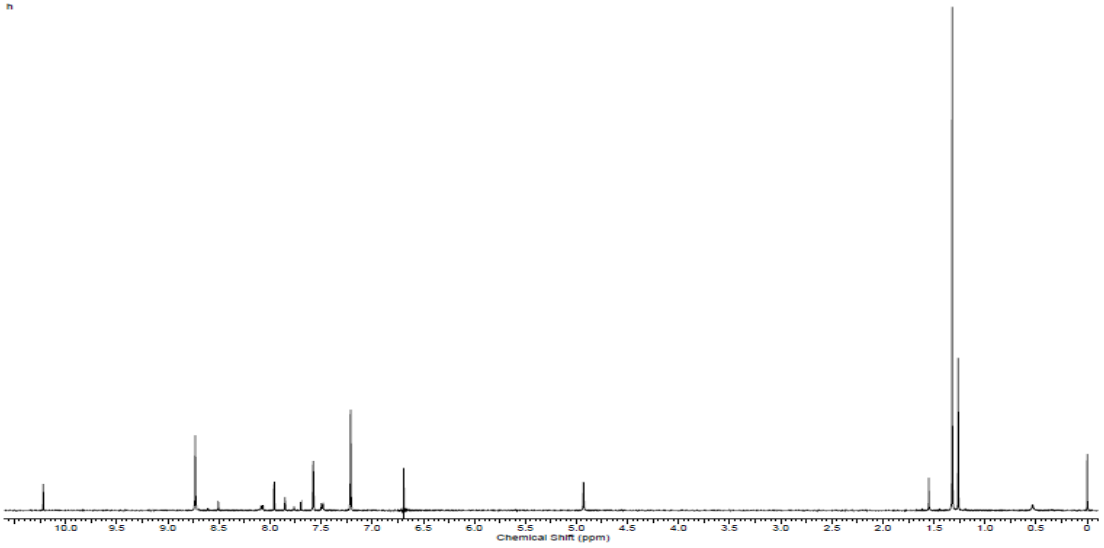


Figure S-14. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **42** (H_2Ar_4TAP).

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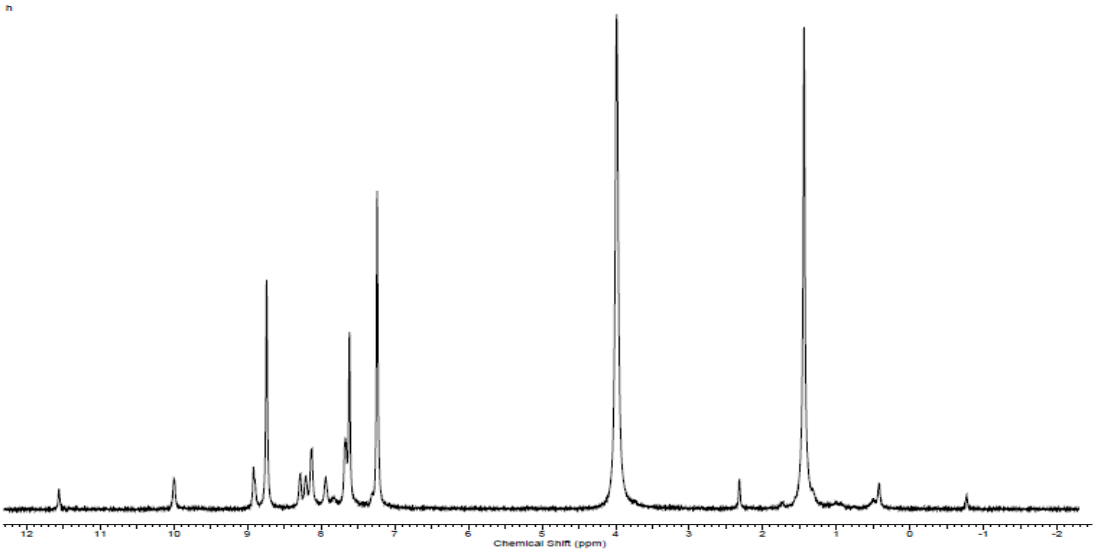

Figure S-15. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **45c** (H_2Ar_2TBP).

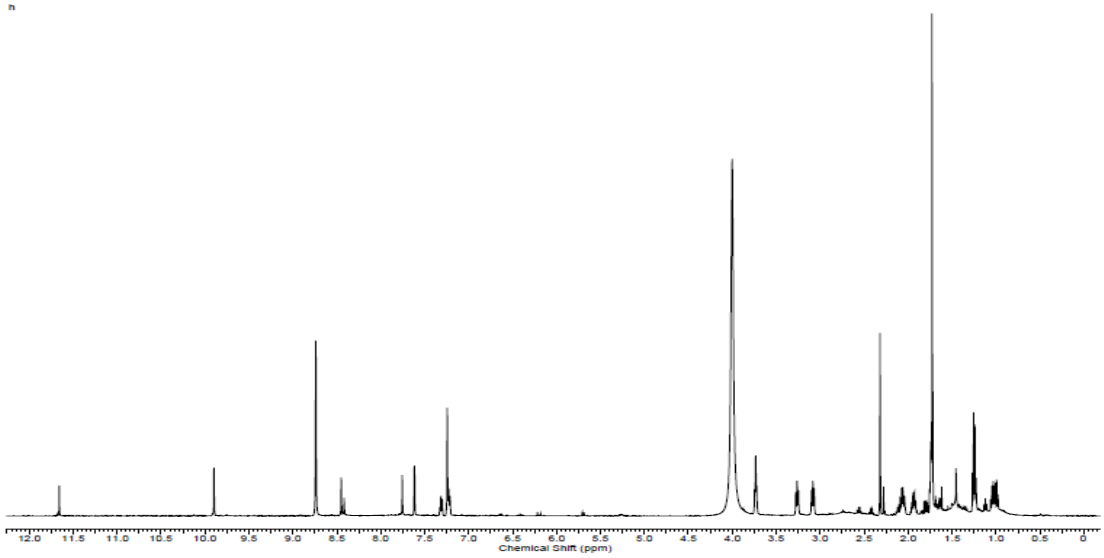

Figure S-16. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **45d** (H_2ArF_4TBP).

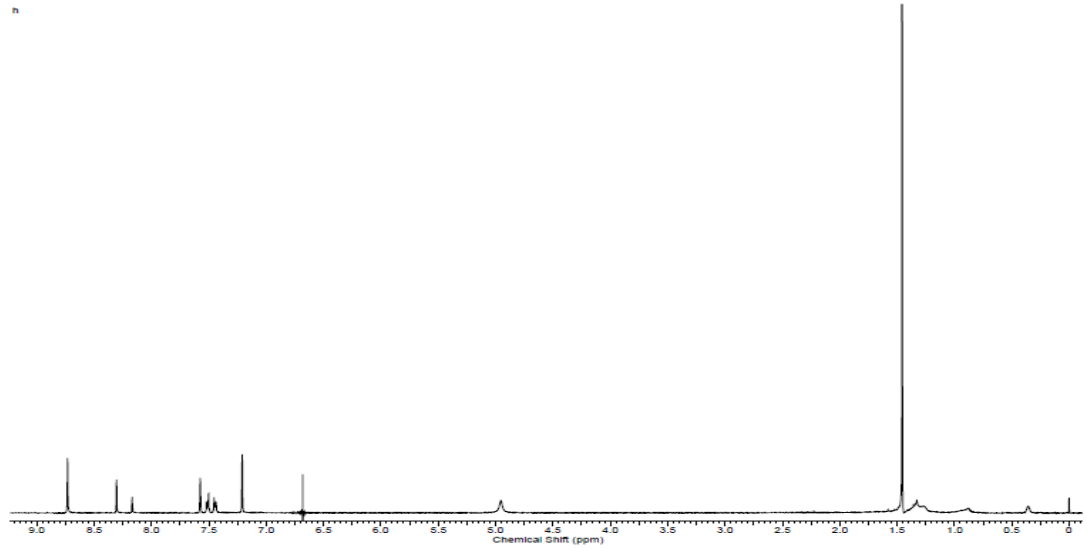

Figure S-17. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **Pt-39b** (Pt-Ar_4TBP).

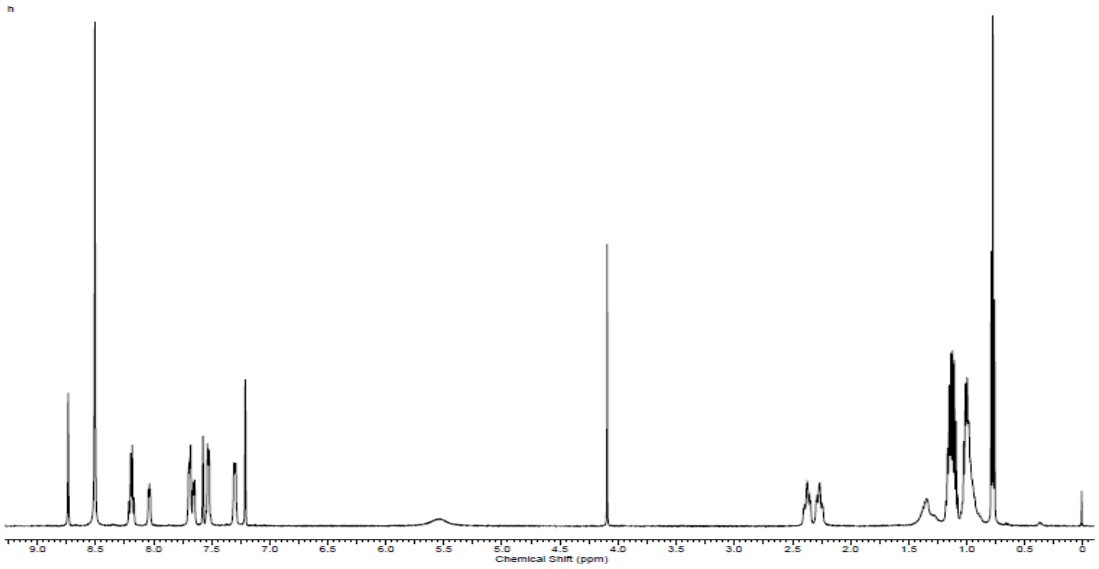

Figure S-18. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **Pt-39c** (Pt-ArF_4TBP).

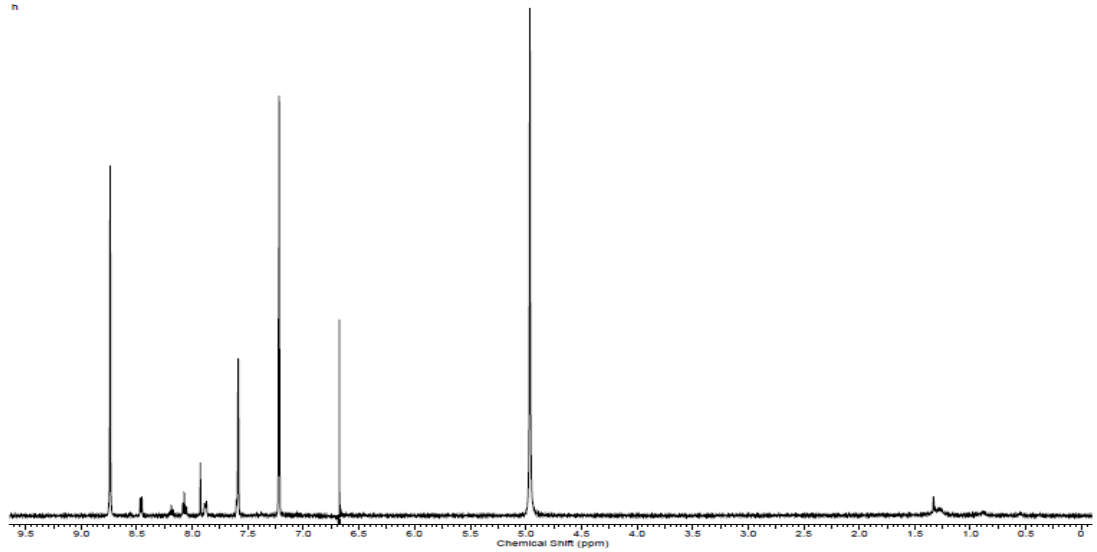

Figure S-19. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **Pt-40a** (Pt-TPTNP).

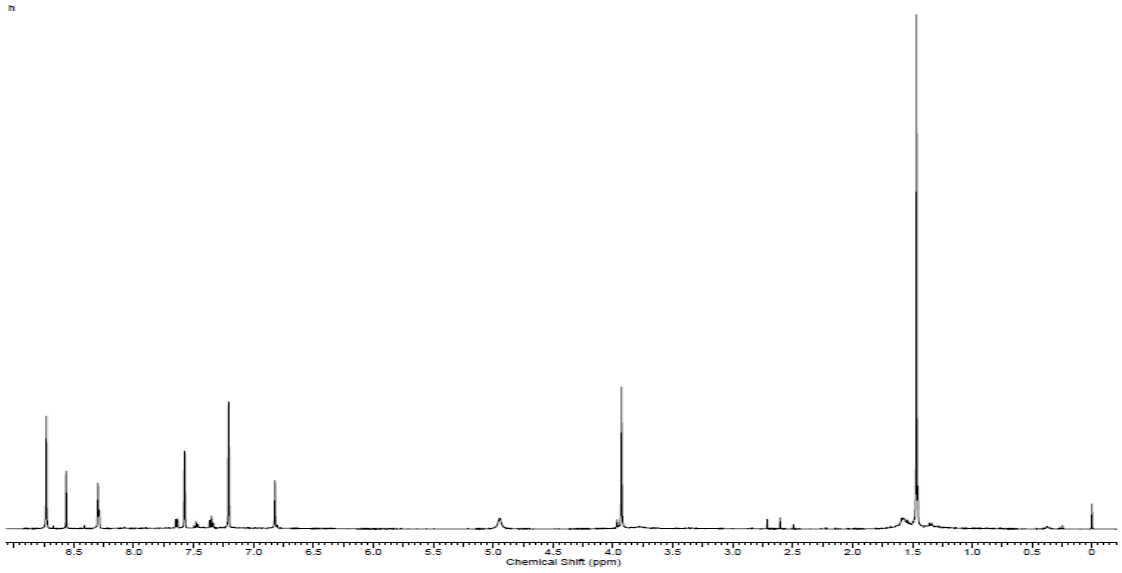

Figure S-20. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **Pt-40b** (Pt-Ar$_4$TNP(OMe)$_8$).

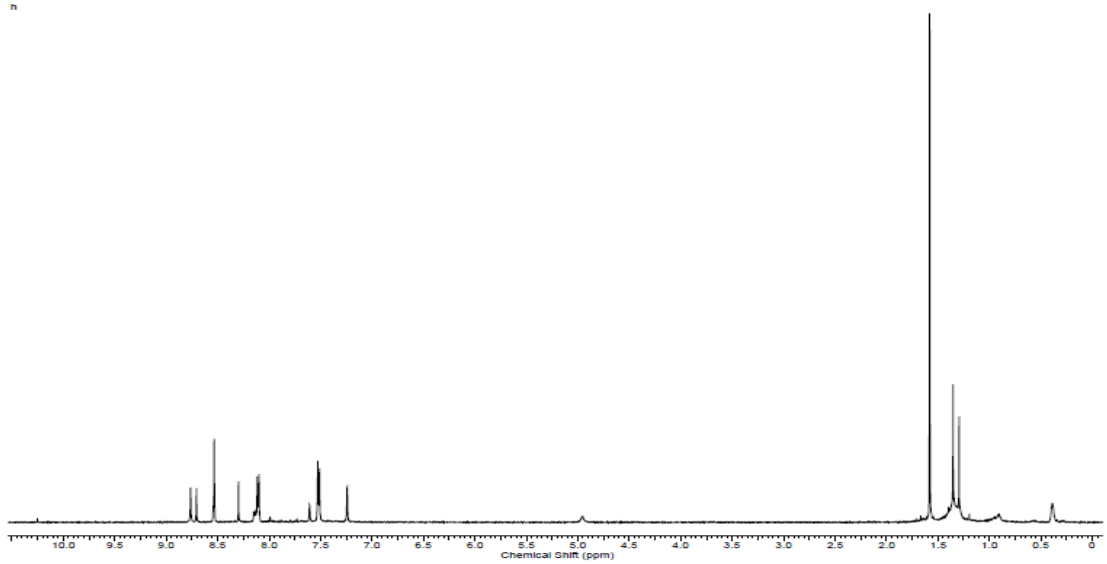

Figure S-21. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **Pt-42** (Pt-Ar$_4$TAP).

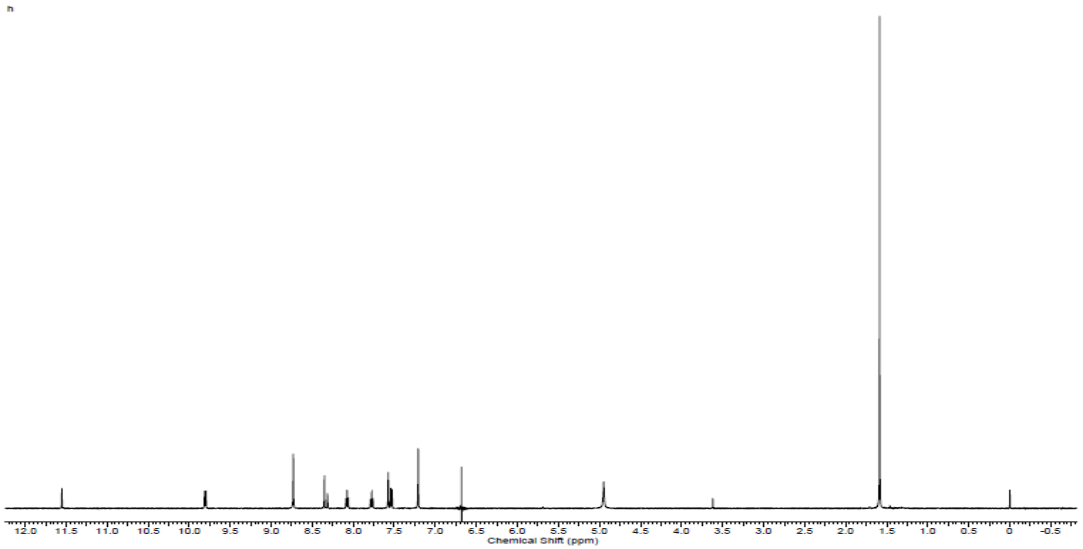

Figure S-22. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **Pt-45b** (Pt-Ar$_2$TBP).

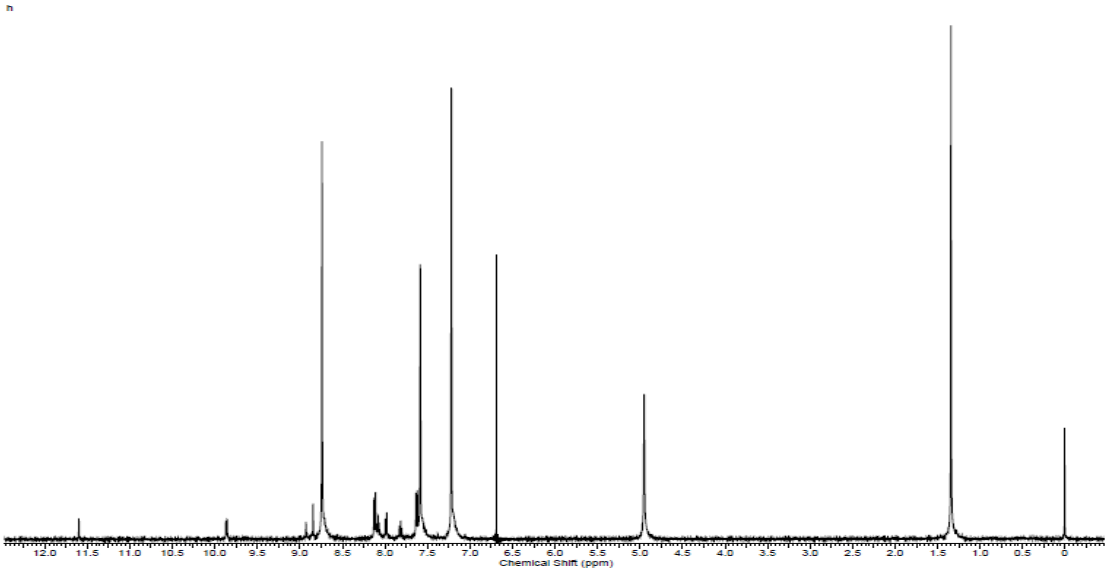

Figure S-23. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **Pt-45c** (Pt-TAr$_2$TBP).

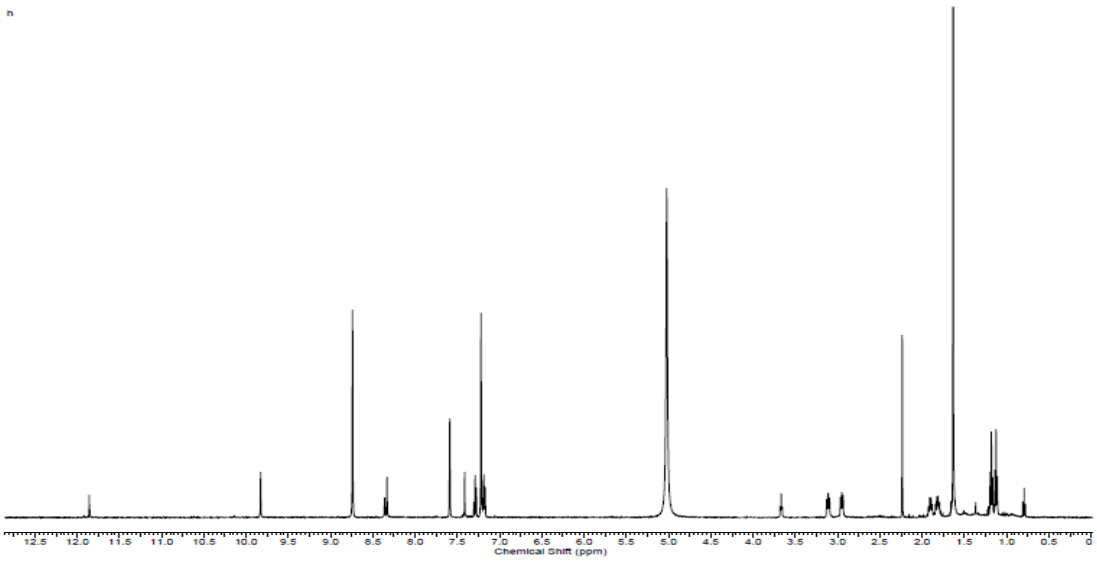

Figure S-24. ^{1}H NMR (500 MHz, pyridine-d_5) spectrum of **Pt-45d** (Pt-Ar_2OPrTBP).

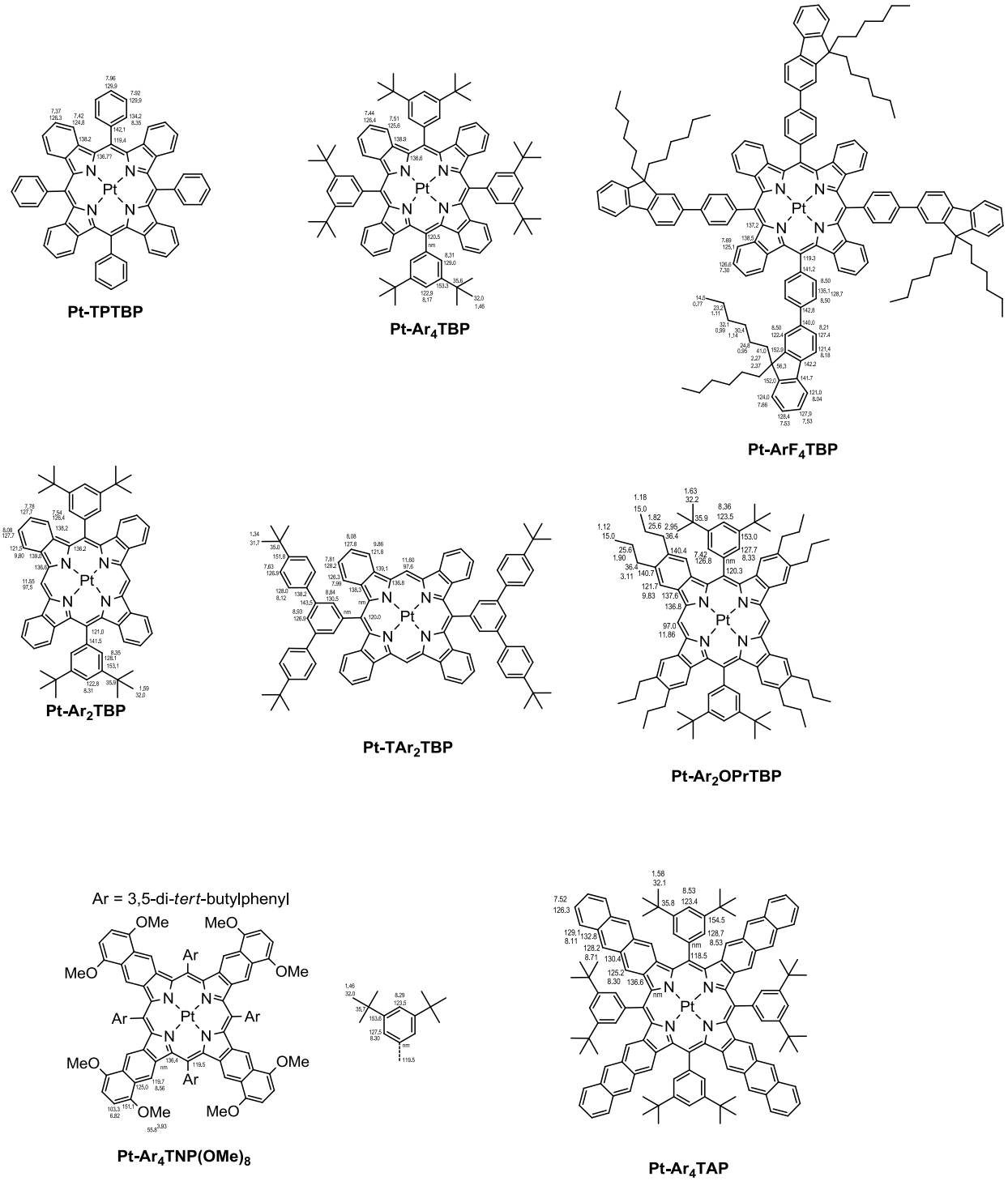

Figure S-25. Structures and peak assignment for ^{1}H and ^{13}C chemical shifts determined by 2D NMR.

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