The Roles of Molecular Structure and Effective Optical Symmetry in Evolving Dipolar Chromophoric Building Blocks to Potent Octopolar NLO Chromophores

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Design and Synthesis.

A. Porphyrin Precursors. The syntheses and characterization of starting materials (5-bromo--10,20-bis(2,6-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato)zinc(II) (**S1**), (5-(triisopropylethynyl)-10,20-bis(2,6-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato)zinc(II) (**S2**), and (5-ethynyl-10,20-bis(2,6-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato)zinc(II) (**S3**) have been reported in an earlier work. (**Scheme S1**)[1]

B. Terpyridine Ligands. 2,2';6',2"-Terpyridine was purchased from Aldrich. 4'-bromo-2,2';6',2"-terpyridine (**S4**) was synthesized from the starting material 2,6-bis(2-pyridyl)-4(1*H*)-pyridone,[2,3] phosphorous pentabromide (PBr_5) and phosphorous oxybromide ($POBr_3$) using a previously reported method.[1]

(a) 4-Bromo-2,2';6',2"-terpyridine (**S5**) was synthesized from a literature method (**Scheme S2**).[7]

2,2'-Bipyridine-*N*-oxide (S7).[4] To the solution of 2,2'-bipyridyl (10.008 g, 64.1 mmol) in glacial acetic acid (50 mL), 20% hydroperoxide (aq) (8 mL) was added and the reaction mixture was stirred at 70°C for 18 h. After cooled down to r.t., the solvent was evaporated under vacuo. To the yellow residue, aqueous potassium carbonate (100 mL) was added and extracted with chloroform (500 mL x 3 times). The solvent of the collected organic phase was evaporated and the residue was purified with column chromatography on silica gel eluted with 5% methanol-chloroform. A pale yellow solid of **S7** (6.790 g, 39.4 mmol) was obtained in 61% yield. The obtained compound was used for next reactions without the characterization.

6-Cyano-2,2'-bipyridine (S8).[5] To the solution of **S7** (1.684 g, 9.78 mmol) in dry dichloromethane (20 mL) was added trimethylsilyl cyanide (1.4 mL, 10.5 mmol) and the reaction mixture was stirred for 30 min at r.t. To the solution, dimethylcabamyl-chloride (0.9 mL, 9.77 mmol) was added and stirred for 12 h at r.t. Aqueous potassium carbonate (3.08 g in 25 mL) was added and stirred for 15 min. The mixture was extracted with dichloromethane (25 mL x 3 times) and the combined organic phase was dried over magnesium sulfate. The column purification of the obtained mixture on silica gel eluted with ethyl acetate-hexane 1:5 mixed solvent afforded a white solid of **S8** (1.082 g, 5.97 mmol) in 61% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.7-8.66 (m, 2H), 8.47 (dt, J = 7.8 Hz, 1H, 4'-Py*H*), 7.95 (t, J = 7.8 Hz, 1H, 4-Py*H*), 7.86 (td, J = 7.8, 1.7 Hz, 1H, 5'-Py*H*), 7.70 (dd, J = 7.6, 1.0 Hz, 1H, 5-Py*H*), 7.38 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H, 3'-Py*H*).

2-(2,2'-Bipyridin-6-yl)-carabaimidazone (S9).[6] To the suspension of **S8** (4.526 g, 25.0 ml) in ethanol (25 mL), hydrazine monohydrate (16 mL, 0.33 mol) was added and the reaction mixture was stirred at r.t. for 3 h. Water (250 mL) was added and the resulting white precipitate was filtered and dried under vacuum. The white solid was recrystallized from benzene, giving pale yellow crystals of **S9** (2.925 g, 13.7 mmol) in 55% yield. ^{1}H NMR (300 MHz, $CDCl_3$):

δ8.69 (d, J = 4.1 Hz, 1H, 6'-Py*H*), 8.42 (t, J = 7.1 Hz, 1H, 4-Py*H*), 8.05 (d, J = 7.9 Hz, 1H, 3-Py*H*), 7.84 (t, J = 7.8 Hz, 1H, 4'-Py*H*), 7.33 (td, J = 7.9, 2.9 Hz, 1H, 5'-Py*H*).

3-(2,2'-Bipyridin-6-yl)-1,2,4-triazine (**S10**).[7] To the solution of **S9** (2.90 g, 13.6 mmol) in methanol (150 mL) was added the solution of 2,3-dihydroxy-1,4-dioxane (2.45 g, 20.4 mmol) in methanol (50 mL) with a cannula and the reaction mixture was stirred for 5 min at r.t., and then refluxed for 3 h. The reaction mixture was cooled to r.t. and the solvent was removed under vacuo. The resulting yellow solid was purified with sublimation at 150 °C under reduced pressure (*ca*. 0.15 mmHg) and the yellow solid of **S10** (2.88 g, 12.2 mmol) was obtained in 90% yield. The obtained compound was used for next reactions without the characterization.

4-Tributylstannyl-2,2';6',2"-terpyridine (S11).[7] To the solution of **S10** (1.001 g, 4.26 mmol) in 1,2-dichlorobenzene (10 mL), ethynyltributylstannane (2.25 ml, 7.8 mmol) was added and the reaction mixture was stirred at 180 °C for 20 h, and then cooled to r.t. The solvent was evaporated under vacuo and the residue was purified with column chromatography on silica gel eluted with petroleum ether and ethyl acetate 9:1 mixed solvent. A colorless oil of **S11** (952.1 mg, 1.82 mmol) was obtained in 43% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.81 (s, 1H, 3-Py*H*), 8.70 (d, J = 4.7 Hz, 1H, 6-Py*H*), 8.63-8.56 (m, 2H), 8.45 (t, J = 6.7 Hz, 2H, 4'-Py*H*), 7.95 (t, J = 7.8 Hz, 1H, 4"-Py*H*), 7.83 (td, J = 7.7, 1.8 Hz, 1H, 3"-Py*H*), 7.42 (d, J = 4.6 Hz, 1H, 5-Py*H*), 7.32 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H, 5"-Py*H*), 1.65-1.60 (m, 6H, -SnCH_2-), 1.42-1.35 (m, 6H, -CH_2CH_2-), 1.21-1.15 (m, 6H, -CH_2CH_2-), 0.92 (t, J = 7.3 Hz, 9H, -CH_3).

4-Bromo-2,2';6',2"-terpyridine (S5).[7] To the solution of **S11** (997 mg, 1.91 mmol) in dry chloroform (25 mL), the solution of bromine (0.2 ml, 3.9 mmol) in dry chloroform (25 mL) was added at -50 °C, and then, the ice bath was removed and the reaction mixture was allowed to warm to r.t. The reaction mixture was poured into aqueous solution of sodium thiosulfate and extracted with chloroform (200 mL x 3 times). The combined organic phase was washed with

water and dried over magnesium sulfate. The volatiles were removed under vacuo and the residue was purified with column chromatography on silica gel eluted with petroleum ether and ethyl acetate 95:5 mixed solvent. A white solid of **S5** (542.8 mg, 1.74 mmol) was obtained in 91% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.78 (s, 1H, 3-Py*H*), 8.70 (d, J = 7.9 Hz, 1H, 6-Py*H*), 8.65-8.40 (m, 4H), 7.96 (t, J = 7.8 Hz, 1H, 4”-Py*H*), 7.88 (t, J = 7.6 Hz, 1H, 3”-Py*H*), 7.49 (d, J = 5.0 Hz, 1H, 5-Py*H*), 7.34 (t, J = 6.0 Hz, 1H, 5”-Py*H*).

(b) 4,4”-Dibromo-2,2’;6’,2”-terpyridine (**S6**) was synthesized from a literature method (**Scheme S2**).[7]

2,6-Pyridinedicarboxamide dihydrazone (S12).[8] Pyridine-2,6-dicarbonitrile (1.502 g, 11.6 mmol) was dissolved in hydrazine monohydrate (10 mL, 0.21 mol) and the solution was stirred for 16 h. The resulting white precipitate was filtered and the obtained white solid was recrystallized from water. White crystals of S12 (1.563 g, 8.09 mmol) were obtained in 70% yield. ^{1}H NMR (300 MHz, CD_3CN): δ 7.91 (d, J = 7.7 Hz, 2H, *m*-Py*H*), 7.69 (t, J = 7.4 Hz, 1H, *p*-Py*H*), 5.40 (bs, 4H), 4.62 (bs, 4H).

2,6-Bis(1,2,4-triazin-3-yl)-pyridine (S13).[7] To the solution of **S12** (924.0 mg, 4.78 mmol) in methanol (50 mL), the solution of 2,3-dihydroxy-1,4-dioxane (2.276 g, 18.9 mmol) in methanol (25 mL) was added and the reaction mixture was stirred at r.t. for 3h and then refluxed for 2h. The reaction mixture was allowed to cool to r.t. and the resulting yellow precipitate was filtered. The obtained yellow solid was extracted with dichloromethane by a Soxhlet extractor for 12 h. The solvent was evaporated and a yellow powder of S13 (640.8 mg, 2.70 mmol) was obtained in 57% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.34 (d, J = 2.4 Hz, 2H, 6-Tr*H*), 8.91 (d, J = 2.4 Hz, 2H, 5-Tr*H*), 8.87 (d, J = 7.9 Hz, 2H, *m*-Py*H*), 8.21 (t, J = 7.9 Hz, 1H, *p*-Py*H*).

4,4”-Bis(tributylstannyl)-2,2’;6’,2”-terpyridine (S14).[7] To the solution of **S13** (186.8 mg, 0.787 mmol) in 1,2-dichlorobenzene (2.6 mL), ethynyltributylstannane (0.93 mL, 3.2 mmol)

was added and the reaction mixture was heated to 180 °C and stirred for 18 h. Then, the reaction mixture was allowed to cool to r.t. and the solvent was removed under vacuo. The residue was purified with column chromatography on silica gel eluted with petroleum ether and ethyl acetate 95:5 mixed solvent. The yellow oil of **S14** (336.7 mg, 0.415 mmol) was obtained in 53% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (s, 2H, 3&3'-Py*H*), 8.59 (dd, *J* = 4.5, 1.0 Hz, 2H, 5&5'-Py*H*), 8.43 (d, *J* = 7.8 Hz, 2H, 6&6'-Py*H*), 7.94 (t, *J* = 7.9 Hz, 1H, 4'-Py*H*), 7.43 (dd, *J* = 7.5, 0.6 Hz, 2H, 3'&5'-Py*H*).

4,4"-Dibromo-2,2';6',2"-terpyridine (S6).[7] To the solution of **S14** (536.7 mg, 0.661 mmol) in chloroform (13 mL), the solution of bromine (0.12 mL, 2.3 mmol) in chloroform (13 mL) was added dropwise at -50 °C and then allowed to warm up to r.t. The reaction mixture was poured into aqueous sodium thiosulfate solution (50 mL) and extracted with chloroform (200 mL x 2 times). The combined organic phase was washed with water and dried over magnesium sulfate. The solvent was evaporated under vacuum and the residue was chromatographed on silica gel eluted with petroleum ether and ethyl acetate 9:1 mixed solvent. A white powder of **S6** (260 mg, 0.66 mmol) was obtained quantitatively. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.76 (s, 2H, 5-Py*H*), 8.51 (d, *J* = 5.1 Hz, 2H, 6&6'-Py*H*), 8.47 (d, *J* = 7.8 Hz, 2H, 3'&5'-Py*H*), 7.97 (t, *J* = 7.9 Hz, 1H, 4'-Py*H*), 7.52 (d, *J* = 5.1 Hz, 2H, 5&5'-Py*H*).

C. Ruthenium bis(terpyridine) Complexes. As illustrated in **Scheme S3**, one terpyridine ligand was added to the commercially available ruthenium ($RuCl_3$) starting materials first, followed by addition of the other terpyridine ligands second.

Ruthenium(III) (4'-bromo-2,2';6',2"-terpyridine) trichloride (**S16**). Ruthenium trichloride hydrate (950 mg, 4.2 mmol) and 4-bromo-2,2';6',2"-terpyridine (**S4**) (1.38 g, 4.42 mmol) were brought together in a 1 L round bottom flask with condenser and stirbar and refluxed in ethanol (250 mL) under air for 3 h. The mixture was cooled in an ice bath and

filtered. The brown solid was washed with ethanol and ether, leaving a brown powder that was used without further purification (1.6 g, 73%). Due to the paramagnetic nature of this product and its poor solubility in most common organic solvents, this compound was not further characterized.

Ru(4-Br-tpy)(tpy)(PF_6)$_2$ (10). 4-Bromo-2,2';6',2"-terpyridine (52.7 mg, 0.169 mmol) and $RuCl_3$(tpy) (73.8 mg, 0.167 mmol) were suspended in MeOH (20 mL). N-ethyl-morpholine (0.020 mL) was added into the suspension and the reaction mixture was refluxed for 2h. The reaction mixture was cooled to r.t. and the solvent was removed under reduced pressure. The residual black solid was chromatographed on silica gel eluted with a mixed solvent of CH_3CN:H_2O:KNO_3 (aq) = 90:9:1. The second orange fraction was collected and the solvent evaporated. The residual red solid was dissolved in CH_3CN and excess ammonium hexafluorophosphate and H_2O were added. Orange crystals of **10** (48.0 mg, 0.0513 mmol) were collected by filtration in 31% yield. ^{1}H NMR (CD_3CN): δ8.74 (m, 5H), 8.47 (d, J = 7.8 Hz, 2H, 6&6"-Py*H* for tpy), 8.41 (m, 3H), 7.92 (m, 3H), 7.32 (m, 3H), 7.16 (m 5H). MS (MALDI-TOF) *m/z*: 646 (calcd for $C_{30}H_{21}BrN_6Ru$ $(M\text{-}2PF_6)^+$ 646) and 792 (calcd for $C_{30}H_{21}F_6BrN_6PRu$ $(M\text{-}PF_6)^+$ 791).

Ru(4'-Br-tpy)$_2$(PF_6)$_2$ (11). 4'-Bromo-2,2';6',2"-terpyridine (80.6 mg, 0.258 mmol) and $RuCl_3$(4'-Br-tpy) (130 mg, 0.250 mmol) were suspended in MeOH (33 mL). N-ethyl-morpholine (0.033 mL) was added into the suspension and the reaction mixture was refluxed for 2h. The reaction mixture was cooled to r.t. and the solvent was removed under reduced pressure. The residual black solid was chromatographed on silica gel eluted with a mixed solvent of CH_3CN:H_2O:KNO_3 (aq) = 90:9:1. The orange fraction was collected and the solvent of the collected fraction was evaporated. To the solution of the residual red solid in CH_3CN were added excess ammonium hexafluorophosphate and H_2O were added. Orange crystals of **11**

(115.4 mg, 0.114 mmol, 46% yield) were collected by filtration. ^{1}H NMR (CD_3CN): δ 8.98 (s, 4H, 3'&5'-Py*H*), 8.47 (ddd, *J* = 8.1, 1.2, 0.9 Hz, 4H, 4&4"-Py*H*), 7.93 (td, *J* = 7.8, 1.5 Hz, 4H, 6&6"-Py*H*), 7.38 (ddd, *J* = 7.7, 1.3, 0.6 Hz, 4H, 5&5"-Py*H*), 7.18 (td, *J* = 7.8, 1.5 Hz, 4H, 3&3"-Py*H*). MS (MALDI-TOF) *m/z*: 724 (calcd for $C_{30}H_{20}Br_2N_6Ru$ $(M\text{-}2PF_6)^+$ 724) and 870 (calcd for $C_{30}H_{20}Br_2F_6N_6PRu$ $(M\text{-}PF_6)^+$ 869).

Ru(4'-Br-tpy)(4-Br-tpy)$(PF_6)_2$ (12). 4-Bromo-2,2';6',2"-terpyridine (47.6 mg, 0.152 mmol) and $RuCl_3$(4'-Br-tpy) (77.5 mg, 0.149 mmol) were suspended in MeOH (19 mL). N-ethyl-morpholine (0.019 mL) was added into the suspension and the reaction mixture was refluxed for 2h. After cooling to r.t., the solvent was removed under reduced pressure and the residual black solid was chromatographed on silica gel eluted with a mixed solvent of CH_3CN:H_2O:KNO_3 (aq) = 90:9:1. The second orange fraction was collected and the solvent was evaporated. To the solution of the residual red solid in CH_3CN were added excess ammonium hexafluorophosphate and H_2O. Orange crystals of **12** (35.3 mg, 0.0348 mmol) were collected by filtration in 23% yield. ^{1}H NMR (CD_3CN): δ 8.97 (s, 2H), 8.74 (m, 4H), 8.44 (m, 4H), 7.93 (m, 2H), 7.34 (m, 4H), 7.18 (m, 4H). MS (MALDI-TOF) *m/z*: 726 (calcd for $C_{30}H_{20}Br_2N_6Ru$ $(M\text{-}2PF_6)^+$ 724) and 870 (calcd for $C_{30}H_{20}Br_2F_6N_6PRu$ $(M\text{-}PF_6)^+$ 869).

Ru(4-Br-tpy)$_2$$(PF_6)_2$ (13). 4-Bromo-2,2';6',2"-terpyridine (51.4 mg, 0.165 mmol) and $RuCl_3$(4-Br-tpy) (80.3 mg, 0.155 mmol) were suspended in MeOH (20 mL). N-ethyl-morpholine (0.020 mL) was added into the suspension and the reaction mixture was refluxed for 2h. After cooling to r.t., the solvent was removed under reduced pressure and the residual black solid was chromatographed on silica gel eluted with a mixed solvent of CH_3CN:H_2O:KNO_3 (aq) = 90:9:1. The orange fraction was collected and the solvent was evaporated. To the solution of the residual red solid in CH_3CN were added excess ammonium hexafluorophosphate and H_2O. Orange crystals of **13** (66.0 mg, 0.065 mmol) were collected by filtration in 42% yield. ^{1}H NMR

(CD_3CN): δ8.73 (m, 6H), 8.47 (dt, J = 7.5, 1.0 Hz, 2H, 4”-Py*H*), 8.41 (d, J = 8.0 Hz, 2H, 5’-Py*H*), 7.92 (td, J = 7.5, 1.5 Hz, 2H, 5”-Py*H*), 7.35 (dd, J = 6.0, 2.0 Hz, 2H, 3’-Py*H*), 7.29 (dt, J = 5.5, 1.0 Hz, 2H, 5-Py*H*), 7.16 (m, 4H). MS (MALDI-TOF) *m/z*: 723 (calcd for $C_{30}H_{20}Br_2N_6Ru$ $(M\text{-}2PF_6)^+$ 724) and 870 (calcd for $C_{30}H_{20}Br_2F_6N_6PRu$ $(M\text{-}PF_6)^+$ 869).

Ru(tpy)(4,4”-Br_2-tpy)(PF_6)$_2$ (14). 4,4”-Dibromo-2,2’;6’,2”-terpyridine (52.1 mg, 0.133 mmol) and $RuCl_3$(tpy) (58.9 mg, 0.134 mmol) were suspended in MeOH (15 mL). N-ethyl-morpholine (0.020 mL) was added into the suspension and the reaction mixture was refluxed for 2h. After cooling to r.t., the solvent was removed under reduced pressure and the residual black solid was chromatographed on silica gel eluted with a mixed solvent of CH_3CN:H_2O:KNO_3 (aq) = 90:9:1. The first and second orange fractions were collected and the solvent was evaporated. To the solution of the residual red solids in CH_3CN were added excess ammonium hexafluorophosphate and H_2O. The first fraction afforded a red crystal of Ru(4,4’’-Br_2-tpy)$_2$(PF_6)$_2$ (**17**) (15.0 mg, 0.0128 mmol) in 19% yield. The resulting orange crystal of **14** from the second fraction (53.2 mg, 0.0524 mmol) was collected by filtration in 39% yield. ^{1}H NMR (CD_3CN) of **14**: δ 8.74 (m, 6H), 8.43 (m, 4H), 7.92 (td, J = 7.8, 1.5 Hz, 2H, 4&4”-Py*H* for tpy), 7.35 (dd, J = 6.0, 2.1 Hz, 2H, 3&3”-Py*H* for tpy), 7.28 (dt, J = 5.7, 0.9 Hz, 2H, 5&5”-Py*H* for tpy), 7.16 (m, 4H). MS of **14** (MALDI-TOF) *m/z*: 726 (calcd for $C_{30}H_{20}Br_2N_6Ru$ $(M\text{-}2PF_6)^+$ 724) and 870 (calcd for $C_{30}H_{20}Br_2F_6N_6F_6PRu$ $(M\text{-}PF_6)^+$ 869). ^{1}H NMR (CD_3CN) of **17**: δ 8.74 (d, J = 8.1 Hz, 4H, 6&6”-Py*H*), 8.71 (d, J = 2.1 Hz, 4H, 3&3”-Py*H*), 8.43 (t, J = 8.4 Hz, 2H, 4’-Py*H*), 7.37 (dd, J = 6.0, 2.0 Hz, 4H, 5&5”-Py*H*), 7.11 (d, J = 6.0 Hz, 4H, 3’&5’-Py*H*). MS of **17** (MALDI-TOF) *m/z*: 881 (calcd for $C_{30}H_{18}Br_4N_6Ru$ $(M\text{-}2PF_6)^+$ 880) and 1026 (calcd for $C_{30}H_{18}Br_4F_6N_6PRu$ $(M\text{-}PF_6)^+$ 1025).

Ru(4'-Br-tpy)(4,4"-Br$_2$-tpy)(PF$_6$)$_2$ (15). 4,4"-Dibromo-2,2';6',2"-terpyridine (51.2 mg, 0.131 mmol) and $RuCl_3$(4'-Br-tpy) (69.3 mg, 0.133 mmol) were suspended in MeOH (15 mL). N-ethylmorpholine (0.020 mL) was added into the suspension and the reaction mixture was refluxed for 2h. After cooling to r.t., the solvent was removed under reduced pressure and the residual black solid was chromatographed on silica gel eluted with a mixed solvent of CH_3CN:H_2O:KNO_3 (aq) = 90:9:1. The second orange fraction was collected and the solvent was evaporated. To the solution of the residual red solids in CH_3CN were added excess ammonium hexafluorophosphate and H_2O. Orange crystals of **15** from the second fraction (39.2 mg, 0.0358 mmol) were collected by filtration in 27% yield. ^{1}H NMR (CD_3CN): δ8.97 (s, 2H, 3'&5'-Py*H* for 4'-Br-tpy), 8.76 (d, *J* = 8.1 Hz, 2H, 6&6"-Py*H* for 4,4"-Br$_2$-tpy), 8.72 (d, *J* = 1.8 Hz, 2H, 3&3"-Py*H* for 4,4"-Br$_2$-tpy), 8.44 (m, 3H), 7.94 (td, *J* = 8.1, 1.2 Hz, 2H, 4&4"-Py*H* for 4'-Br-tpy), 7.36 (dd, *J* = 6.0, 2.1 Hz, 2H, 5&5"-Py*H* for 4,4"-Br$_2$-tpy), 7.30 (d, *J* = 5.7 Hz, 2H, 3'&5'-Py*H* for 4,4"-Br$_2$-tpy), 7.19 (m, 4H). MS (MALDI-TOF) *m/z*: 802 (calcd for $C_{30}H_{19}Br_3N_6Ru$ $(M-2PF_6)^+$ 802) and 947 (calcd for $C_{30}H_{19}Br_3F_6N_6PRu$ $(M-PF_6)^+$ 947).

Ru(4-Br-tpy)(4,4"-Br$_2$-tpy)(PF$_6$)$_2$ (16). 4,4"-Dibromo-2,2';6',2"-terpyridine (34.8 mg, 0.0898 mmol) and $RuCl_3$(4-Br-tpy) (43.1 mg, 0.0830 mmol) were suspended in MeOH (10 mL). N-ethylmorpholine (0.020 mL) was added into the suspension and the reaction mixture was refluxed for 2h. After cooling to r.t, the solvent was removed under reduced pressure and the residual black solid was chromatographed on silica gel eluted with a mixed solvent of CH_3CN:H_2O:KNO_3 (aq) = 90:9:1. The second orange fraction was collected and the solvent was evaporated. To the solution of the residual red solids in CH_3CN were added excess ammonium hexafluorophosphate and H_2O. Orange crystals of **16** from the second fraction (18.5 mg, 0.0169 mmol) were collected by filtration in 20% yield. ^{1}H NMR (CD_3CN): δ 8.73(m, 7H), 8.44 (m, 3H), 7.93 (td, *J* = 8.1, 1.5 Hz, 1H, 4"-Py*H* for 4-Br-tpy), 7.36 (m, 3H), 7.27 (d, *J* = 5.7 Hz, 1H,

5'-Py*H* for 4-Br-tpy), 7.12 (m, 4H). MS (MALDI-TOF) *m/z*: 802 (calcd for $C_{30}H_{19}Br_3N_6Ru$ (M-2PF$_6$)$^+$ 802) and 947 (calcd for $C_{30}H_{19}Br_3F_6N_6PRu$ (M-PF$_6$)$^+$ 947).

Ru[4'-(Zn-porphyrin)ethynyl-tpy]$_2$(PF$_6$)$_2$ (3). The synthesis of **3** was accomplished using methods similar to that described for **2**. Zinc(II) 5-ethynyl-10,20-bis[2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl]porphyrinate (96.1 mg, 0.101 mmol) and **11** (Scheme 1, 52.2 mg, 0.0514 mmol) were placed into a 25 mL Schlenk tube with a stir bar. Bis(triphenylphosphine)palladium dichloride (30 mg, 0.043 mmol) and CuI (10 mg, 0.053 mmol) were added, followed by dry THF (10 mL), CH_3CN (10 mL) and iPr_2NH (4 mL); this mixture was completely degassed by repeated freeze-pump-thaw cycles. The Schlenk tube was refilled with Ar gas and the reaction mixture was stirred at 70 °C for 24 h. The reaction mixture was cooled to r.t. and the solvent evaporated. The residue was purified by column chromatography on silica gel eluted with a mixed solvent system [CH_3CN:H_2O:KNO_3 (aq) = 90:9:1]. The second green-brown fraction was collected and the solvent evaporated. The residual dark brown solid was dissolved in CH_3CN, and excess ammonium hexafluorophosphate and H_2O were added. Dark brown crystals of **3** (50.7 mg, 0.0184 mmol, 36% yield) were collected by filtration. ^{1}H NMR (CD_3CN): δ 10.17 (s, 2H, *meso*-H), 10.03 (d, J = 4.5 Hz, 4H, β-H), 9.42 (s, 4H), 9.30 (d, J = 4.5 Hz, 4H, β-H), 9.03 (d, J = 4.5 Hz, 4H, β-H), 8.83 (m, 8H), 8.08 (td, J = 6.3, 2.0 Hz, 4H), 7.83 (t, J = 8.5 Hz, 4H, -*p*-Ph), 7.65 (d, J = 6.3 Hz, 4H), 7.31 (t, J = 6.5 Hz, 4H), 7.19 (d, J = 8.5 Hz, 8H, -*m*-Ph), 4.01 (t, J = 7.0 Hz, 16H, -OCH_2-), 0.81 (t, J = 7.0 Hz, 16H, -CH$_2$CH_2-), 0.19 (s, 72 H, -CH_3). ^{19}F NMR (CD3CN): δ -71.67 (d, J = 752 Hz). UV-vis (CH_3CN): λ_{max} [nm] (ε [x 10^{-5} $M^{-1}cm^{-1}$]) 313 (0.75), 426 (1.95), 521 (0.89), 565 (0.32), 648 (1.13). MS (MALDI-TOF) *m/z*: 2462 (calcd for $C_{146}H_{154}N_{14}O_8RuZn_2$ (M-2PF$_6$)$^+$ 2461) and 2609 (calcd for $C_{146}H_{154}N_{14}O_8F_6PRuZn_2$ (M-PF$_6$)$^+$ 2606).

Ru[4-(Zn-porphyrin)ethynyl-tpy][4'-(Zn-porphyrin)ethynyl-tpy](PF$_6$)$_2$ (4). The synthesis of **4** was accomplished using methods similar to that described for **2**. Zinc(II) 5-ethynyl-10,20-bis[2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl]porphyrinate (28.1 mg, 0.0296 mmol) and **12** (Scheme 1, 12.1 mg, 0.0119 mmol) were placed into a 25 mL Schlenk tube with a stir bar. Trisdibenzylideneacetone dipalladium(0) (4.3 mg, 4.7 μmol) and triphenylarsine (24 mg, 0.078 mmol) were added, followed by dry THF (3.75 mL), CH_3CN (7.5 mL) and iPr_2NH; this mixture was completely degassed by repeated freeze-pump-thaw cycles. The Schlenk tube was refilled with Ar gas and the reaction mixture was stirred at 70 °C for 24 h. The reaction mixture was cooled to r.t. and the solvent evaporated. The residue was purified by column chromatography on silica gel eluted with a mixed solvent of CH_3CN:H_2O:KNO_3 (aq) = 95:4.5:0.5. The second green-brown fraction was collected and the solvent evaporated. The residual dark brown solid was dissolved in CH_3CN, and excess ammonium hexafluorophosphate and H_2O were added. Dark brown crystals of **4** (25.4 mg, 9.22 μmol, 77% yield) were collected by filtration. ^{1}H NMR (CD_3CN): δ 10.16 (s, 2H, *meso*-H), 10.04 (m, 4H, β-H), 9.42 (s, 4H), 9.30 (d, J = 3.6 Hz, 4H, β-H), 9.04 (d, J = 4.5 Hz, 4H, β-H), 8.83 (m, 5H), 8.59 (m, 4H), 8.02 (m, 3H), 7.80 (m, 4H, -*p*-Ph), 7.51 (m, 4H), 7.27 (m, 4H), 7.16 (m, 8H, -*m*-Ph), 4.01 (t, J = 7.0 Hz, 8H, -OCH_2-), 3.93 (m, 8H, -OCH_2-), 0.83 (t, J = 7.0 Hz, 8H, -CH_2CH_2-), 0.73 (m, 8H, -CH_2CH_2-), 0.10 (s 36H, -CH_3), 0.07 (s, 36H, -CH_3). ^{19}F NMR (CD3CN): δ -71.67 (d, J = 752 Hz). UV-vis (CH_3CN): λ_{max} [nm] (ε [x 10^{-5} $M^{-1}cm^{-1}$]) 316 (0.79), 445 (2.44), 509 (0.65), 567 (0.32), 642 (0.95). MS (MALDI-TOF) *m/z*: 2466 (calcd for $C_{146}H_{154}N_{14}O_8RuZn_2$ $(M\text{-}2PF_6)^+$ 2461) and 2609 (calcd for $C_{146}H_{154}N_{14}O_8F_6PRuZn_2$ $(M\text{-}PF_6)^+$ 2606).

Ru[4-(Zn-porphyrin)ethynyl-tpy]$_2$(PF$_6$)$_2$ (5). The synthesis of **5** was accomplished using methods similar to that described for **2**. Zinc(II) 5-ethynyl-10,20-bis[2',6'-bis(3,3-

dimethyl-1-butyloxy)phenyl]porphyrinate (29.0 mg, 0.0305 mmol) and **13** (Scheme 1, 15.1 mg, 0.0149 mmol) were placed into a 25 mL Schlenk tube with a stir bar. Trisdibenzylideneacetone dipalladium(0) (5.0 mg, 5.5 μmol) and triphenylarsine (10 mg, 0.033 mmol) were added, followed by dry THF (3.75 mL), CH_3CN (7.5 mL), and iPr_2NH (1.25 mL); this mixture was completely degassed by repeated freeze-pump-thaw cycles. The Schlenk tube was refilled with Ar gas and the reaction mixture was stirred at 70 °C for 24 h. The reaction mixture was cooled to r.t. and the solvent evaporated. The residue was purified by column chromatography on silica gel eluted using a mixed solvent system [CH_3CN:H_2O:KNO_3 (aq) = 95:4.5:0.5]. The second green-brown fraction was collected and the solvent evaporated. The residual dark brown solid was dissolved in CH_3CN, and excess ammonium hexafluorophosphate and H_2O were added. Dark brown crystals of **5** (33.1 mg, 12.0 μmol, 81% yield) were collected by filtration. ^{1}H NMR (CD_3CN): δ 10.00 (s, 2H, *meso*-H), 9.19 (d, J = 4.5 Hz, 4H, β-H), 9.04 (m, 2H), 8.89 (d, J = 8.5 Hz, 4H, 6-Py*H*), 8.83 (d, J = 4.5 Hz, 4H, β-H), 8.75 (d, J = 4.5 Hz, 8H, β-H), 8.60 (m, 4H), 8.00 (t, J = 8.5 Hz, 2H, 4'-Py*H*), 7.76 (t, J = 8.5 Hz, 4H, -*p*-Ph), 7.49 (m, 4H), 7.28 (m, 2H), 7.11 (m, 10H), 3.91 (m 16H, -OCH_2-), 0.72 (m, 16H, -CH_2CH_2-), 0.10 (m, 72H, -CH_3). ^{19}F NMR (CD3CN): δ -71.67 (d, J = 752 Hz). UV-vis (CH_3CN): λ_{max} [nm] (ε [x 10^{-5} $M^{-1}cm^{-1}$]) 317 (0.66), 446 (2.23), 566 (0.27), 639 (0.75). MS (MALDI-TOF) *m/z*: 2464 (calcd for $C_{146}H_{154}N_{14}O_8RuZn_2$ $(M-2PF_6)^+$ 2461) and 2609 (calcd for $C_{146}H_{154}N_{14}O_8F_6PRuZn_2$ $(M-PF_6)^+$ 2606).

Ru(tpy)[4,4''-bis(Zn-porphyrin)ethynyl-tpy]$(PF_6)_2$ (6). The synthesis of **6** was accomplished using methods similar to that described for **2**. Zinc(II) 5-ethynyl-10,20-bis[2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl]porphyrinate (20.0 mg, 0.0210 mmol) and **14** (Scheme 1, 11.4 mg, 0.0112 mmol) were placed into a 25 mL Schlenk tube with a stir bar.

Trisdibenzylidebeacetone dipalladium(0) (5.8 mg, 6.3 μmol) and triphenylarsine (4.3 mg, 0.014 mmol) were added, followed by dry THF (1.8 mL), CH_3CN (3.75 mL), and iPr_2NH (0.6 mL); this mixture was completely degassed by repeated freeze-pump-thaw cycles. The Schlenk tube was refilled with Ar gas and the reaction mixture was stirred at 70 °C for 24 h. The reaction mixture was cooled to r.t. and the solvent evaporated. The residue was purified by column chromatography on silica gel eluted with a mixed solvent system [CH_3CN:H_2O:KNO_3 (aq) = 95:4.5:0.5]. The second green-brown fraction was collected and the solvent evaporated. The residual dark brown solid was dissolved in CH_3CN, and excess ammonium hexafluorophosphate and H_2O were added. Dark brown crystals of **6** (16.1 mg, 5.8 μmol, 56% yield) were collected by filtration. ^{1}H NMR (CD_3CN): δ 10.10 (s, 2H, *meso*-H), 9.68 (m, 4H, β-H), 9.24 (d, J = 8.4 Hz, 2H, 6,6”-Py*H* for 4,4-PZn_2-tpy), 9.12 (m, 4H), 8.88 (m, 8H), 8.78 (d, J = 4.5 Hz, 4H, β-H), 8.60 (m, 4H), 8.78 (d, J = 4.5 Hz, 4H, β-H), 8.60 (m, 6H), 8.01 (t, J = 8.4 Hz, 2H, 4,4”-Py*H* for tpy), 7.76 (m, 6H), 7.53 (m, 2H), 7.45 (m, 2H), 7.29 (t, J = 6.3 Hz, 2H, 5,5”-Py*H* for tpy), 7.15 (d, J = 8.4 Hz, 8H, -*m*-Ph), 3.95 (t, J = 6.9 Hz, 16H, -OCH_2-), 0.74 (t, J = 6.9 Hz, 16H, -CH_2CH_2-), 0.14 (s, 72H, -CH_3). ^{19}F NMR (CD3CN): δ -71.67 (d, J = 752 Hz). UV-vis (CH_3CN): λ_{max} [nm] (ε [x 10^{-5} $M^{-1}cm^{-1}$]) 313 (0.79), 447 (2.17), 564 (0.30), 644 (0.87). MS (MALDI-TOF) *m/z*: 2610 (calcd for $C_{146}H_{154}N_{14}O_8F_6PRuZn_2$ $(M\text{-}PF_6)^+$ 2606).

Ru[4’-(Zn-porphyrin)ethynyl-tpy][4,4’’-bis(Zn-porphyrin)ethynyl-tpy]$(PF_6)_2$ (7). The synthesis of **7** was accomplished using methods similar to that described for **2**. Zinc(II) 5-ethynyl-10,20-bis[2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl]porphyrinate (20.8 mg, 0.0219 mmol) and **15** (Scheme 1, 5.0 mg, 4.6 μmol) were placed into a 25 mL Schlenk tube with a stir bar. Trisdibenzylidebeacetone dipalladium(0) (6.1 mg, 6.7 μmol) and triphenylarsine (11.0 mg, 0.036 mmol) were added, followed by dry THF (1.8 mL), CH_3CN (3.75 mL), and iPr_2NH (0.6

mL); this mixture was completely degassed by repeated freeze-pump-thaw cycles. The Schlenk tube was refilled with Ar gas and the reaction mixture was stirred at 70 °C for 48 h. The reaction mixture was cooled to r.t. and the solvent evaporated. The residue was purified by column chromatography on silica gel eluted with a mixed solvent system [CH_3CN:H_2O:KNO_3 (aq) = 95:4.5:0.5]. The second green-brown fraction was collected and the solvent evaporated. The residual dark brown solid was dissolved in CH_3CN, and excess ammonium hexafluorophosphate and H_2O were added. Dark brown crystals of **7** (11.8 mg, 3.2 μmol, 70% yield) were collected by filtration. ^{1}H NMR (CD_3CN): δ 10.19 (s, 1H, *meso*-H), 10.08 (m, 2H, *meso*-H), 9.67 (bs, 3H), 9.50 (s, 2H, 3',5'-PyH for 4'-PZn-tpy), 9.32 (d, J = 4.5 Hz, 2H, β-H), 9.23 (d, J = 4.5 Hz, 2H, β-H), 9.16 (d, J = 6.9 Hz, 2H, 6,6"-PyH for 4,4-PZn$_2$-tpy), 9.07 (d, J = 4.5 Hz, 2H, β-H), 8.89 (m, 6H), 8.77 (t, J = 4.5 Hz, 4H, β-H), 8.71 (m, 12H,), 8.11 (t, J = 8.1 Hz, 2H, 4,4"-PyH for 4'-PZn-tpy), 7.81 (m, 6H), 7.55 (d, J = 5.4 Hz, 2H, 5,5"-PyH for 4,4-PZn$_2$-tpy), 7.36 (t, J = 7.8 Hz, 2H, 5,5"-PyH for 4'-PZn-tpy), 7.21 (d, J = 8.4 Hz, 2H, 3,3"-PyH for 4'-PZn-tpy), 7.13 (d, J = 8.4 Hz, 12H, -*m*-Ph), 4.03 (t, J = 7.2 Hz, 8H, -OC*H*$_2$-), 3.94 (t, J = 6.9 Hz, 16H, -OC*H*$_2$-), 0.84 (t, J = 6.9 Hz, 8H, -CH$_2$C*H*$_2$-), 0.74 (t, J = 7.2 Hz, 16H, -CH$_2$C*H*$_2$-), 0.12 (bs, 108H, -C*H*$_3$). ^{19}F NMR (CD3CN): δ -71.67 (d, J = 752 Hz). UV-vis (CH_3CN): λ_{max} [nm] (ε [x 10^{-5} $M^{-1}cm^{-1}$]) 317 (0.79), 445 (2.89), 517 (0.80), 565 (0.42), 646 (1.43). MS (MALDI-TOF) *m/z*: 3414 (calcd for $C_{204}H_{220}N_{18}O_{12}Zn_3Ru$ $(M-2PF_6)^+$ 3413) and 3556 (calcd for $C_{204}H_{220}N_{18}O_{12}F_6PZn_3Ru$ $(M-PF_6)^+$ 3552).

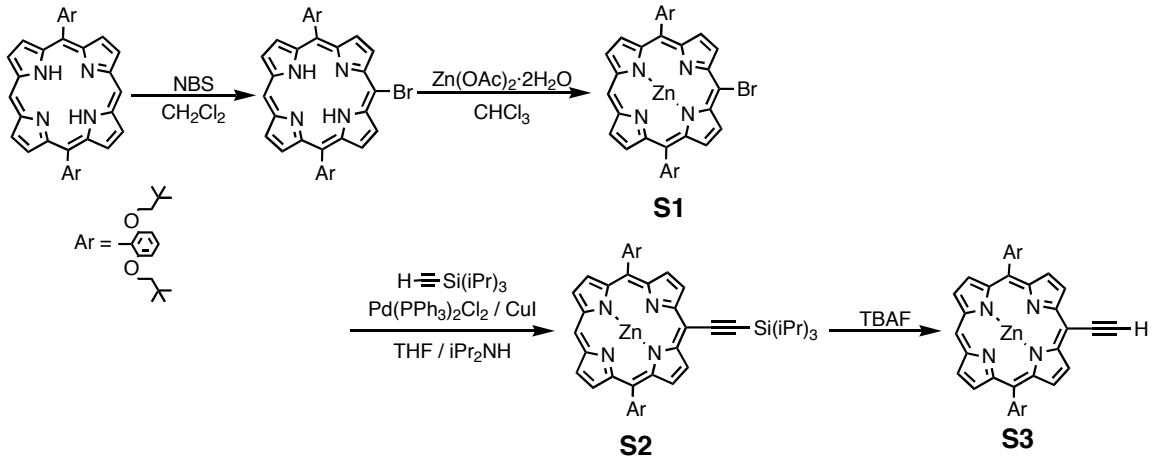
Ru[4-(Zn-porphyrin)ethynyl-tpy][4,4''-bis(Zn-porphyrin)ethynyl-tpy](PF$_6$)$_2$ (8). The synthesis of **8** was accomplished using methods similar to that described for **2**. Zinc(II) 5-ethynyl-10,20-bis[2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl]porphyrinate (20.7 mg, 0.0218 mmol) and **16** (7.8 mg, 7.1 μmol) were placed into a 25 mL Schlenk tube with a stir bar.

Trisdibenzylideneacetone dipalladium(0) (3.6 mg, 3.9 μmol) and triphenylarsine (8.8 mg, 0.029 mmol) were added, followed by dry THF (1.8 mL), CH_3CN (3.75 mL), and iPr_2NH (0.6 mL); this mixture was completely degassed by repeated freeze-pump-thaw cycles. The Schlenk tube was refilled with Ar gas and the reaction mixture was stirred at 70 °C for 48 h. The reaction mixture was cooled to r.t. and the solvent evaporated. The residue was purified by column chromatography on silica gel eluted with a mixed solvent system [CH_3CN:H_2O:KNO_3 (aq) = 95:4.5:0.5]. The second green-brown fraction was collected and the solvent evaporated. The residual dark brown solid was dissolved in CH_3CN, and excess ammonium hexafluorophosphate and H_2O were added. Dark brown crystals of **8** (14.2 mg, 3.8 μmol, 54% yield) were collected by filtration. ^{1}H NMR (CD_3CN): δ 10.03 (s, 2H, *meso*-H), 9.97 (s, 1H, *meso*-H), 9.57 (bs, 4H), 9.45 (bs, 2H), 9.20 (bs, 4H), 9.14 (bs, 2H), 9.05 (bs, 8H), 8.85 (d, J = 4.2 Hz, 4H, β-H), 8.75 (m, 8H), 8.63 (bs, 3H), 8.03 (bs, 1H), 7.77 (m, 12H), 7.58 (bs, 1H), 7.50 (bs, 1H), 7.34 (bs, 1H), 7.11 (m, 12H), 3.94 (m, 24H, -OCH_2-), 0.72 (m, 24H, -CH_2CH_2-), 0.08 (m, 108H, -CH_3). ^{19}F NMR (CD3CN): δ -71.67 (d, J = 752 Hz). UV-vis (CH_3CN): λ_{max} [nm] (ε [x 10^{-5} $M^{-1}cm^{-1}$]) 324 (0.75), 446 (2.96), 565 (0.39), 644 (1.16). MS (MALDI-TOF) *m/z*: 3410 (calcd for $C_{204}H_{220}N_{18}O_{12}Zn_3Ru$ $(M\text{-}2PF_6)^+$ 3413) and 3553 (calcd for $C_{204}H_{220}N_{18}O_{12}F_6PZn_3Ru$ $(M\text{-}PF_6)^+$ 3552).

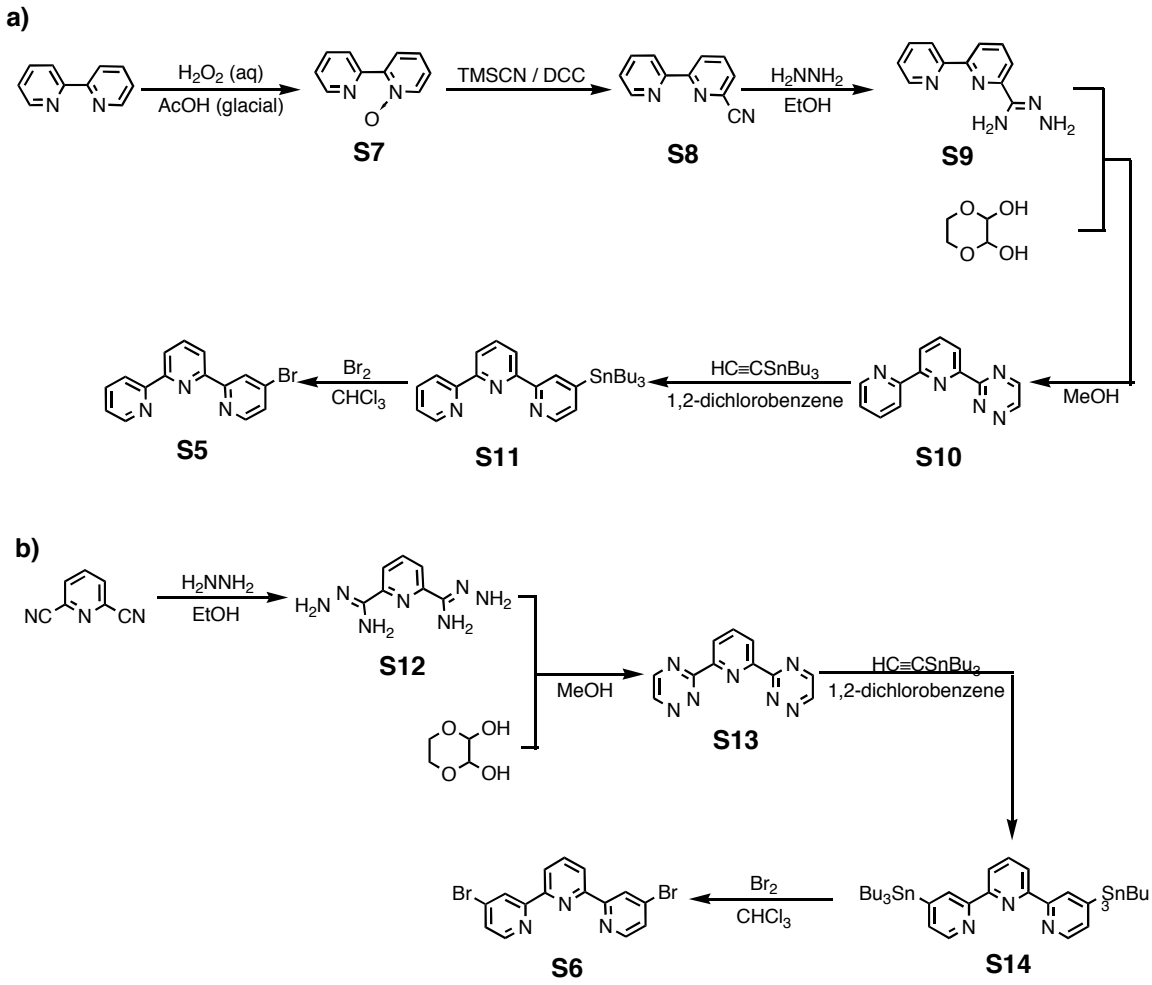
Ru[4,4''-bis(Zn-porphyrin)ethynyl-tpy]$_2$(PF_6)$_2$ (9). The synthesis of **9** was accomplished using methods similar to that described for **2**. Zinc(II) 5-ethynyl-10,20-bis[2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl]porphyrinate (30.6 mg, 0.0322 mmol) and **17** (Scheme 1, 11.6 mg, 10.6 μmol) were placed into a 25 mL Schlenk tube with a stir bar. Trisdibenzylidebeacetone dipalladium(0) (7.3 mg, 8.0 μmol) and triphenylarsine (14.3 mg, 0.047 mmol) were added, followed by dry THF (1.8 mL), CH_3CN (3.75 mL) and iPr_2NH (0.6 mL); this

mixture was completely degassed by repeated freeze-pump-thaw cycles. The Schlenk tube was refilled with Ar gas and the reaction mixture was stirred at 70 °C for 48 h. The reaction mixture was cooled to r.t. and the solvent evaporated. The residue was purified by column chromatography on silica gel eluted with a mixed solvent system [CH_3CN:H_2O:KNO_3 (aq) = 95:4.5:0.5]. The second green-brown fraction was collected and the solvent evaporated. The residual dark brown solid was dissolved in CH_3CN, and excess ammonium hexafluorophosphate and H_2O were added. Dark brown crystals of **9** (28.7 mg, 6.2 μmol, 63% yield) were collected by filtration. ^{1}H NMR (CD_3CN): δ 10.04 (s, 4H, *meso*-H), 9.58 (bs, 8H), 9.20 (d, J = 4.2 Hz, 8H, β-H), 9.13 (bs, 8H), 8.80 (m, 18H), 7.75 (t, J = 8.1 Hz, 8H, -*p*-Ph*H*), 7.53 (bs, 8H), 7.10 (d, J = 8.4 Hz, 16H, -*m*-Ph*H*), 3.89 (t, J = 6.9 Hz, 32H, -OCH_2-), 0.70 (t, J = 6.6 Hz, 32H, -CH_2CH_2-), 0.07 (s, 144H, -CH_3). ^{19}F NMR (CD3CN): δ -71.67 (d, J = 752 Hz). UV-vis (CH_3CN): λ_{max} [nm] (ε [x 10^{-5} $M^{-1}cm^{-1}$]) 322 (0.80), 446 (3.54), 566 (0.49), 647 (1.48). MS (MALDI-TOF) *m/z*: 4363 (calcd for $C_{262}H_{286}N_{22}O_{16}Zn_4Ru$ $(M\text{-}2PF_6)^+$ 4354) and 4509 (calcd for $C_{262}H_{286}N_{22}O_{16}F_6PZn_4Ru$ $(M\text{-}PF_6)^+$ 4499).

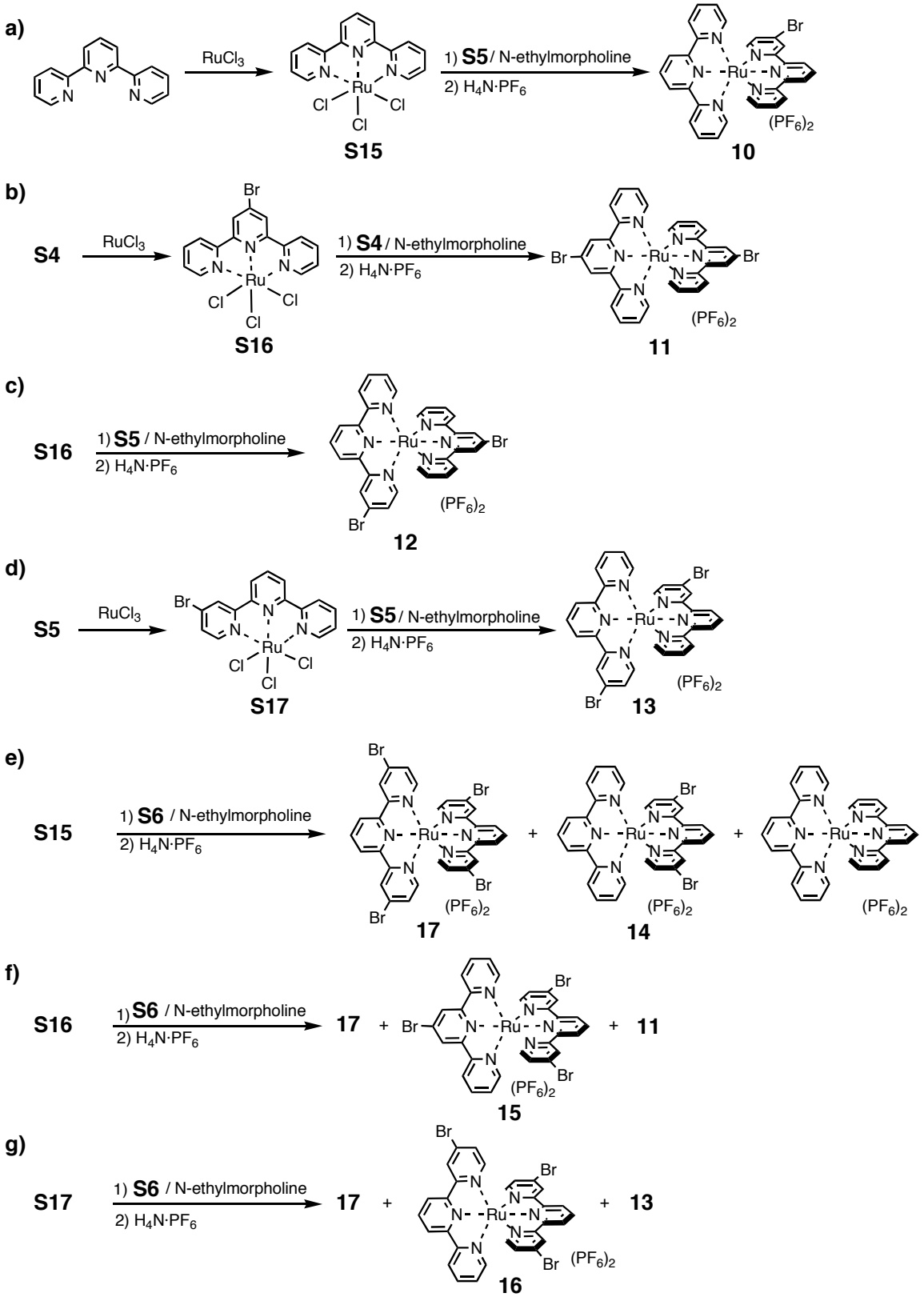
Supplemental Schemes and Figures.



Scheme S1.



Scheme S2


a)
RuCl3
1) S5 / N-ethylmorpholine
2) H4N·PF6
S15
10
b)
S4
RuCl3
1) S4 / N-ethylmorpholine
2) H4N·PF6
S16
11
c)
S16
1) S5 / N-ethylmorpholine
2) H4N·PF6
12
d)
S5
RuCl3
1) S5 / N-ethylmorpholine
2) H4N·PF6
S17
13
e)
S15
1) S6 / N-ethylmorpholine
2) H4N·PF6
17
14
f)
S16
1) S6 / N-ethylmorpholine
2) H4N·PF6
17
11
15
g)
S17
1) S6 / N-ethylmorpholine
2) H4N·PF6
17
13
16

Scheme S3.

Additional Spectroscopic Data:

Table S1. Time constants from fs-ns transient dynamical experiments.

	τ_1	τ_2	τ_3
PZn-(4Ru) (**2**)		1.7	18.9
PZn-(4'Ru4')-PZn (**3**)		3.6	
PZn-(4Ru4')-PZn (**4**)		4.3	
PZn-(4Ru4)-PZn (**5**)		1.3	12.3
PZn_2-(4,4''Ru) (**6**)	0.5	4.4	
PZn-(4'Ru4,4'')-PZn_2 (**7**)		1.6	14
PZn-(4Ru4,4'')-PZn_2 (**8**)	0.3	2.3	
PZn_2-(4,4''Ru4,4'')-PZn_2 (**9**)		1.3	

Compounds 2 and 7

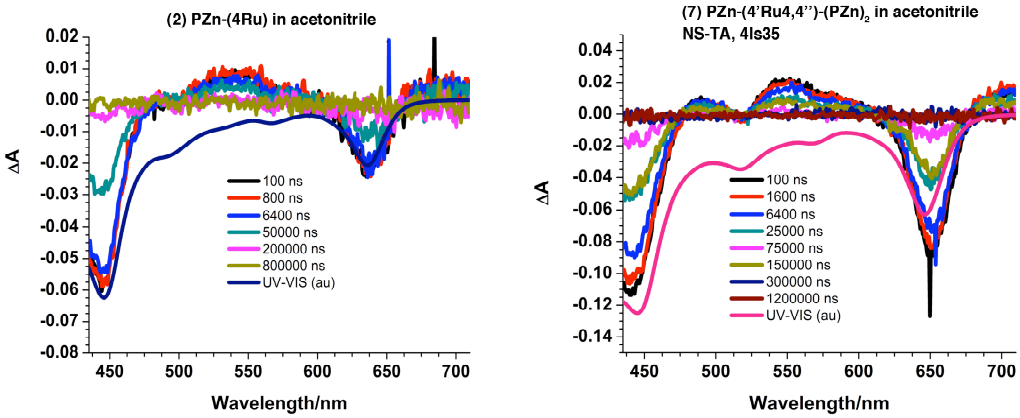


Figure S1. Transient absorption spectra (ns-μs time domain) of **2** (left) and **7** (right) at multiple time delays after photoexcitation. Experimental conditions: solvent = aceonitrile, λ_{exc} = 532 nm, ambient temperature, degassed. See main text for fs-ns spectra of these compounds.

PZn-(4'Ru4')-PZn (3)

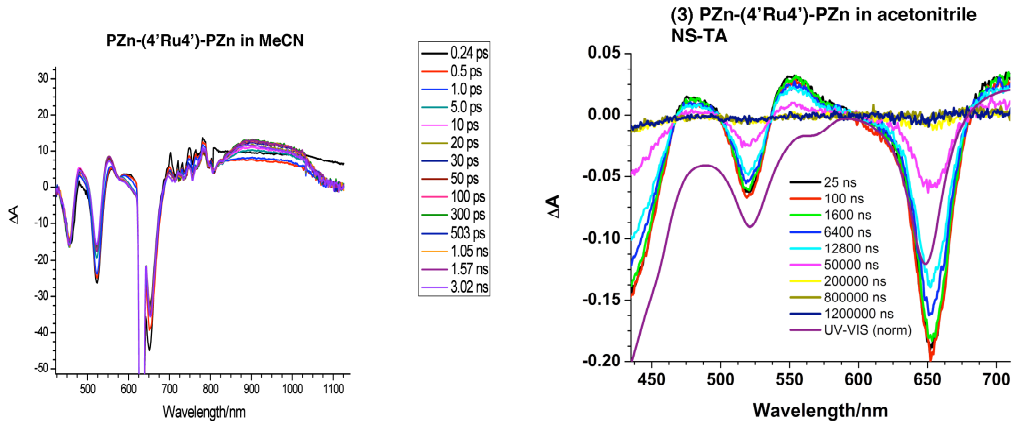


Figure S2. Transient absorption spectra of **3** in (degassed) acetonitrile at multiple time delays after photoexcitation, λ_{exc} = 630 nm. Left: magic angle femtosecond transient absorption spectra. Right: ns-µs timescale transient absorption, λ_{exc} = 532 nm.

PZn-(4Ru4')-PZn (4)

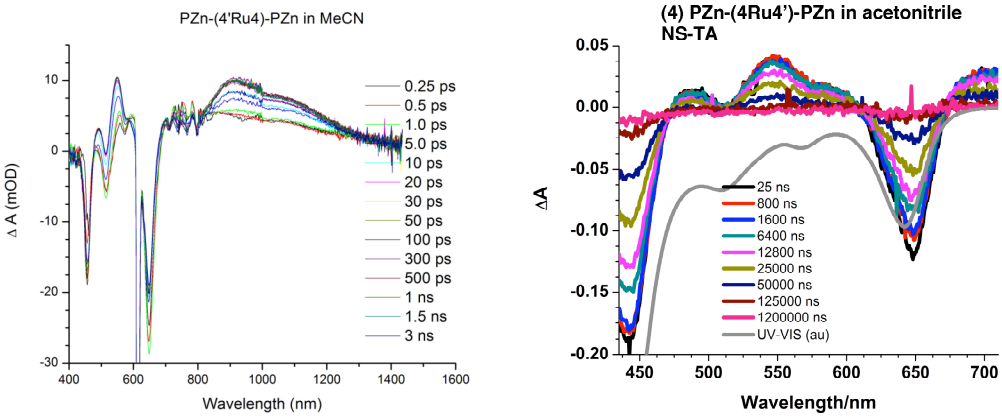


Figure S3. Transient spectra of **4** in (degassed) acetonitrile at multiple time delays after photoexcitation, λ_{exc} = 620 nm. Left: magic angle femtosecond transient absorption spectra. Right: ns-µs timescale transient absorption, λ_{exc} = 532 nm.

PZn-(4Ru4)-PZn (5)

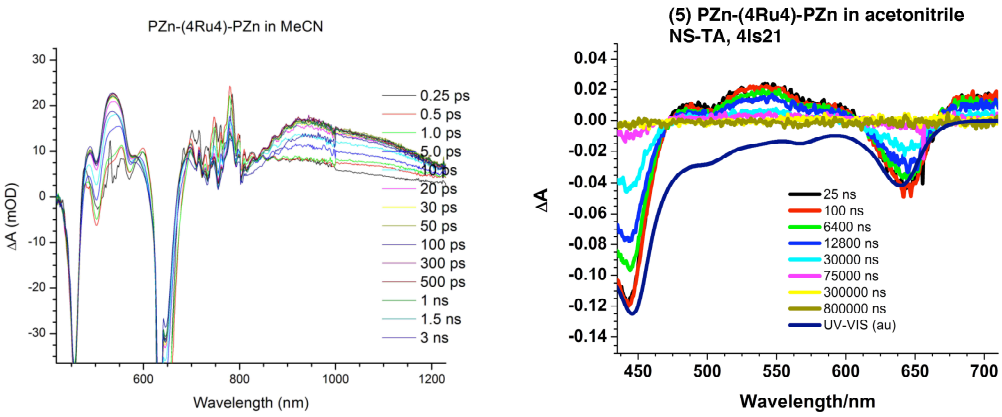


Figure S4. Transient spectra of **5** in (degassed) acetonitrile at multiple time delays after photoexcitation, λ_{exc} = 630 nm. Left: magic angle femtosecond transient absorption spectra. Right: ns-μs timescale transient absorption, λ_{exc} = 532 nm.

PZn_2-(4,4''Ru) (6)

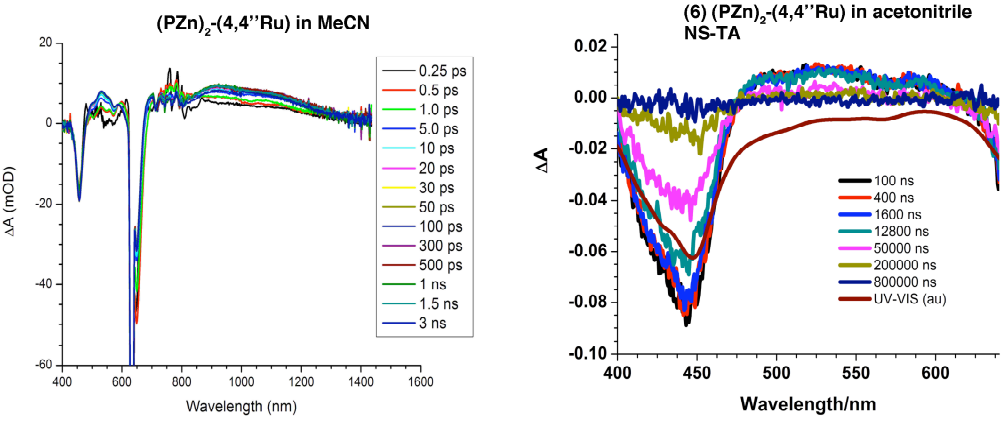


Figure S5. Transient spectra of **6** in (degassed) acetonitrile at multiple time delays after photoexcitation, λ_{exc} = 630 nm. Left: magic angle femtosecond transient absorption spectra. Right: ns-μs timescale transient absorption, λ_{exc} = 532 nm.

PZn-(4Ru4,4'')-PZn$_2$ (8)

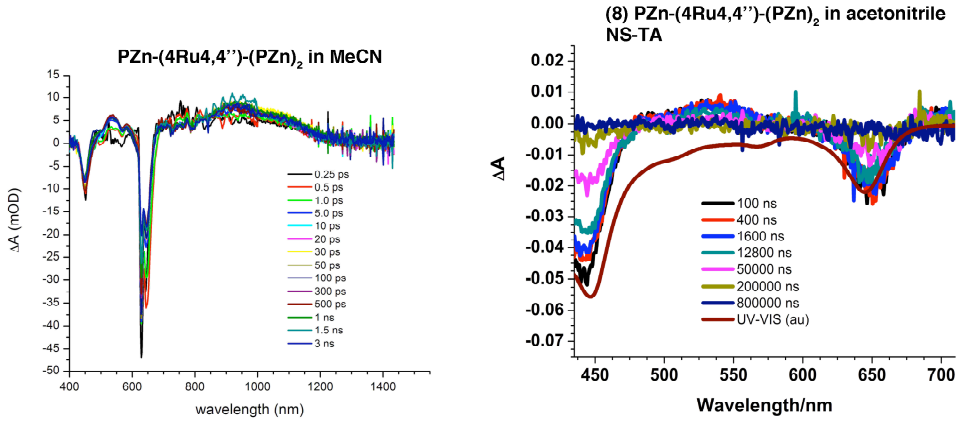


Figure S6. Transient spectra of **8** in (degassed) acetonitrile at multiple time delays after photoexcitation, λ_{exc} = 630 nm. Left: magic angle femtosecond transient absorption spectra. Right: ns-µs timescale transient absorption, λ_{exc} = 532 nm.

PZn$_2$-(4,4''Ru4,4'')-PZn$_2$ (9)

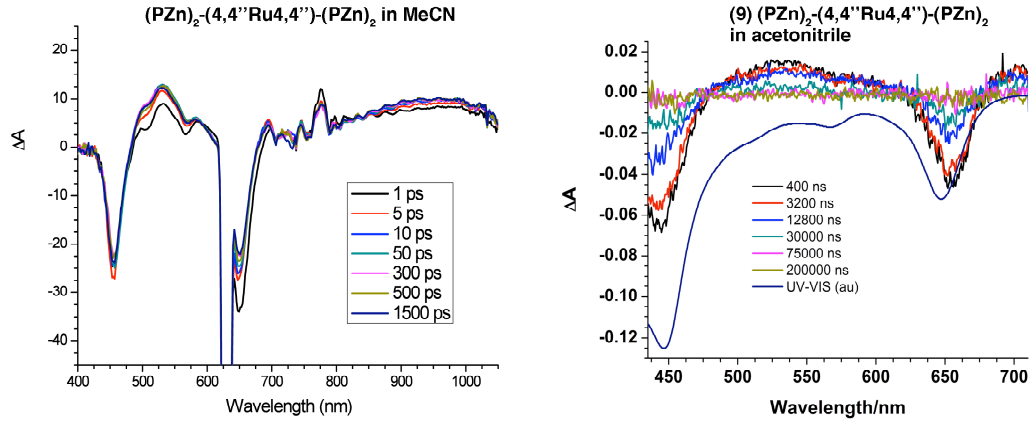


Figure S7. Transient spectra of **9** in (degassed) acetonitrile at multiple time delays after photoexcitation, λ_{exc} = 630 nm. Left: magic angle femtosecond transient absorption spectra. Right: ns-µs timescale transient absorption, λ_{exc} = 532 nm.

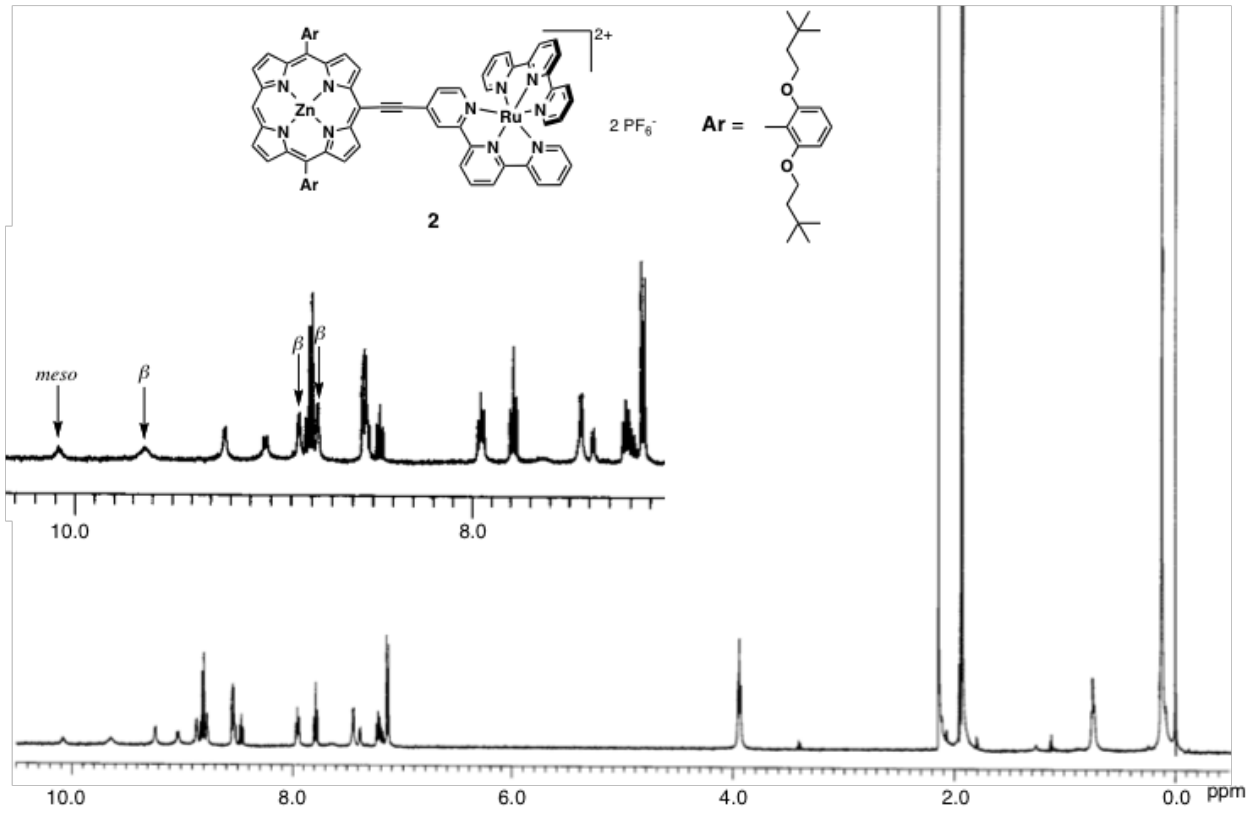


Figure S8. ^{1}H NMR Spectra of **2** in CD_3CN at r.t.

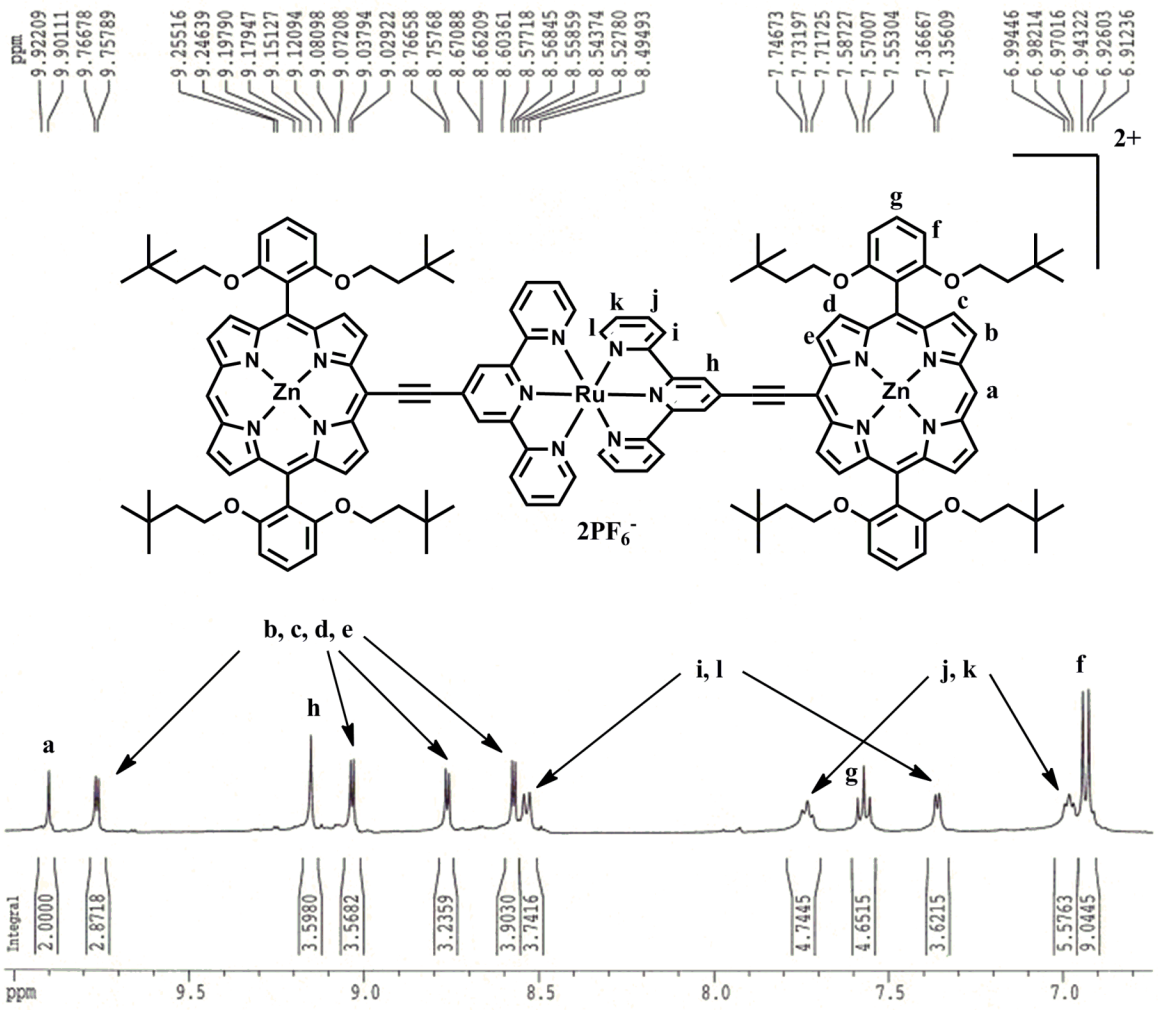


Figure S9. Aromatic region of the ^{1}H NMR spectrum of **3** demonstrating assignments of all peaks corresponding to the protons present in the compound.

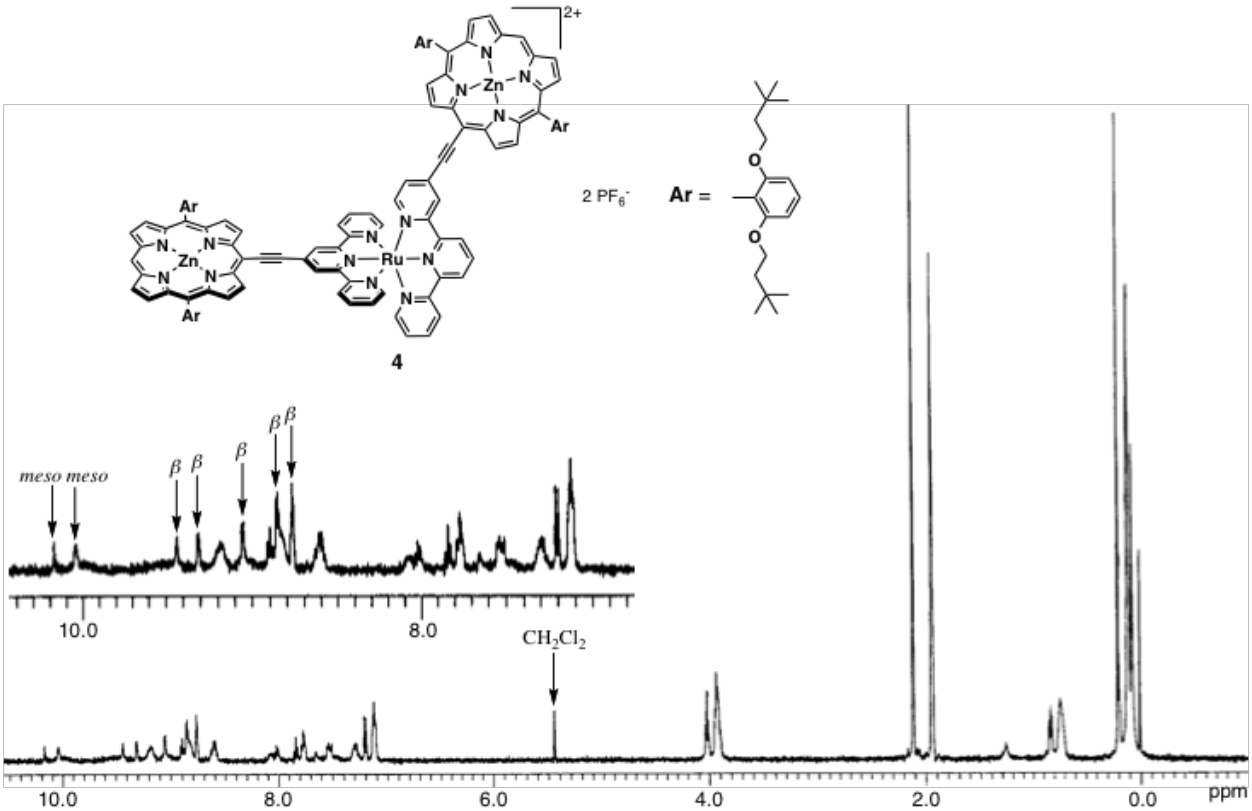


Figure S10. ^{1}H NMR Spectra of **4** in CD_3CN at r.t.

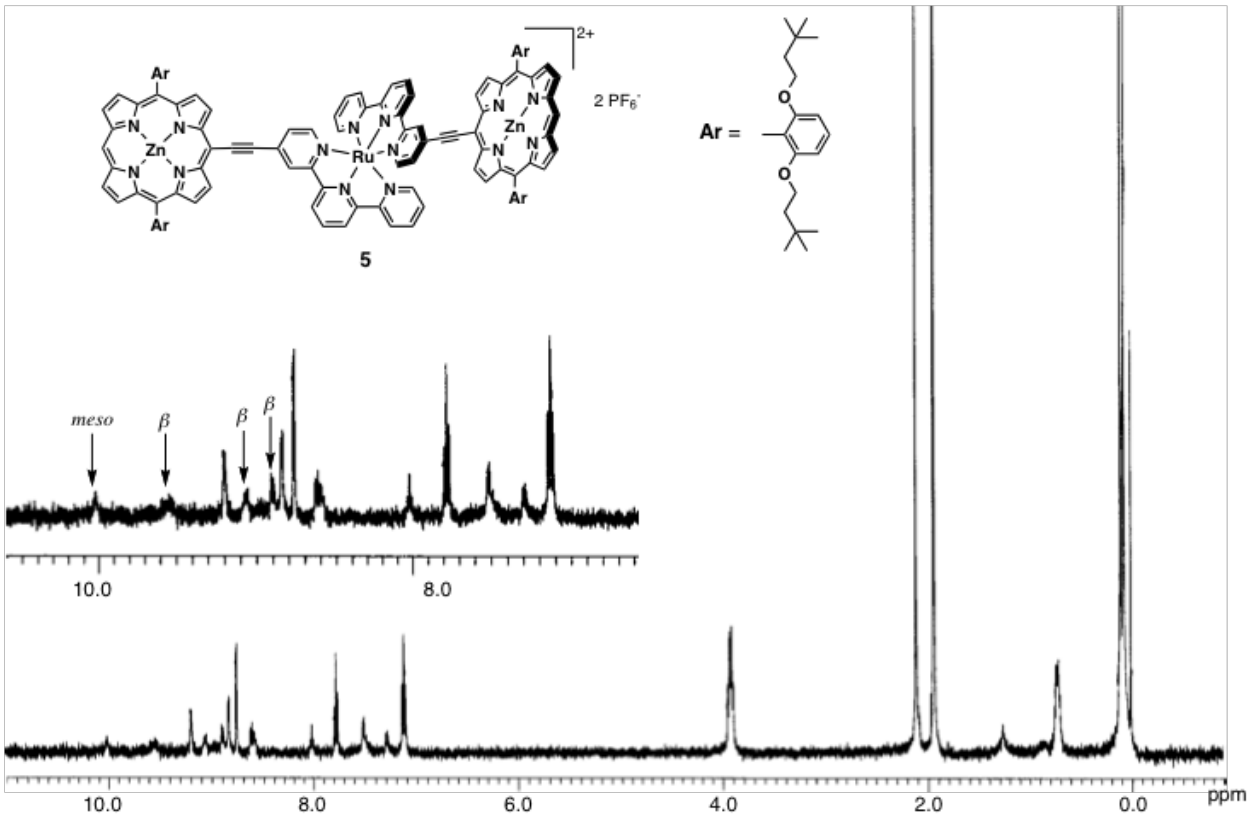


Figure S11. ^{1}H NMR Spectra of **5** in CD_3CN at r.t.

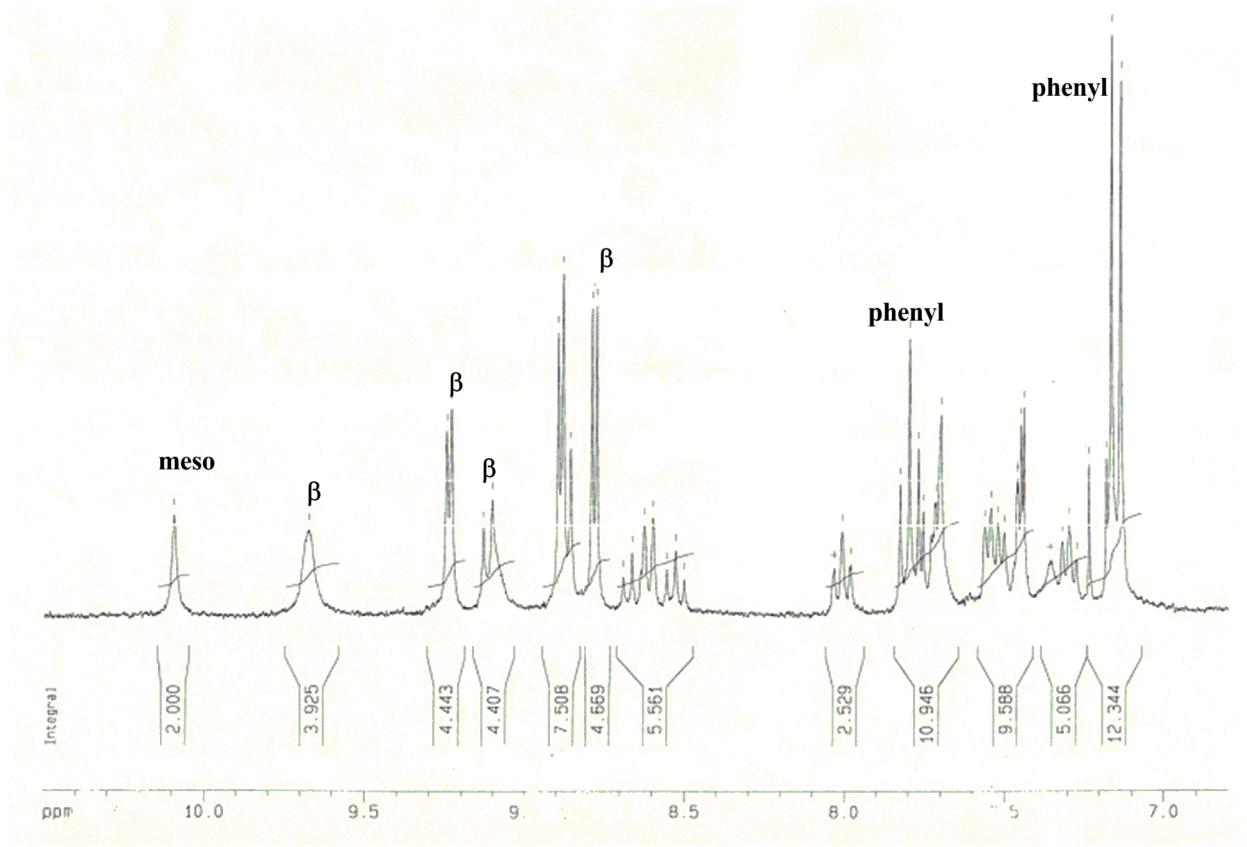


Figure S12. Aromatic region of the ^{1}H NMR spectrum of **6** demonstrating identity and acceptable purity of the desired compound.

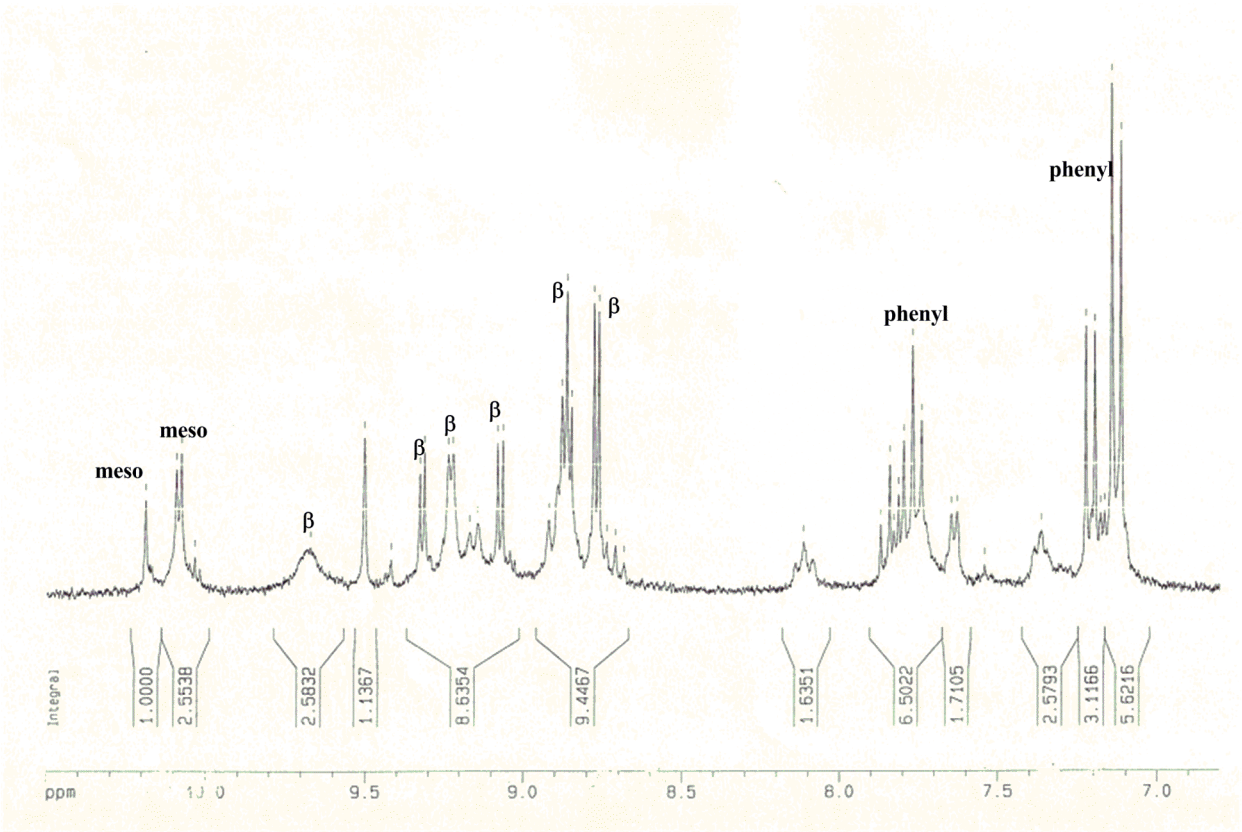


Figure S13. Aromatic region of the ^{1}H NMR spectrum of **7** demonstrating identity and acceptable purity of the desired compound.

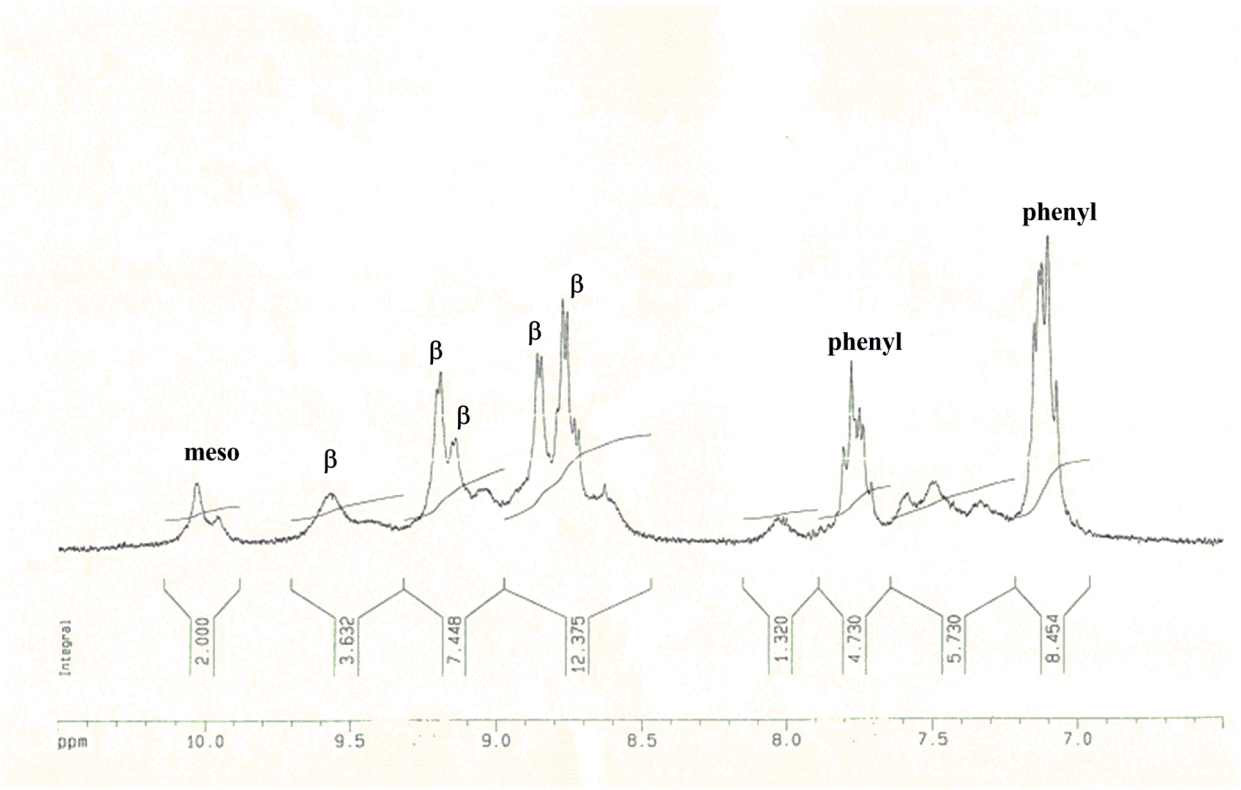


Figure 14. Aromatic region of the ^{1}H NMR spectrum of **8** demonstrating identity and acceptable purity of the desired compound.

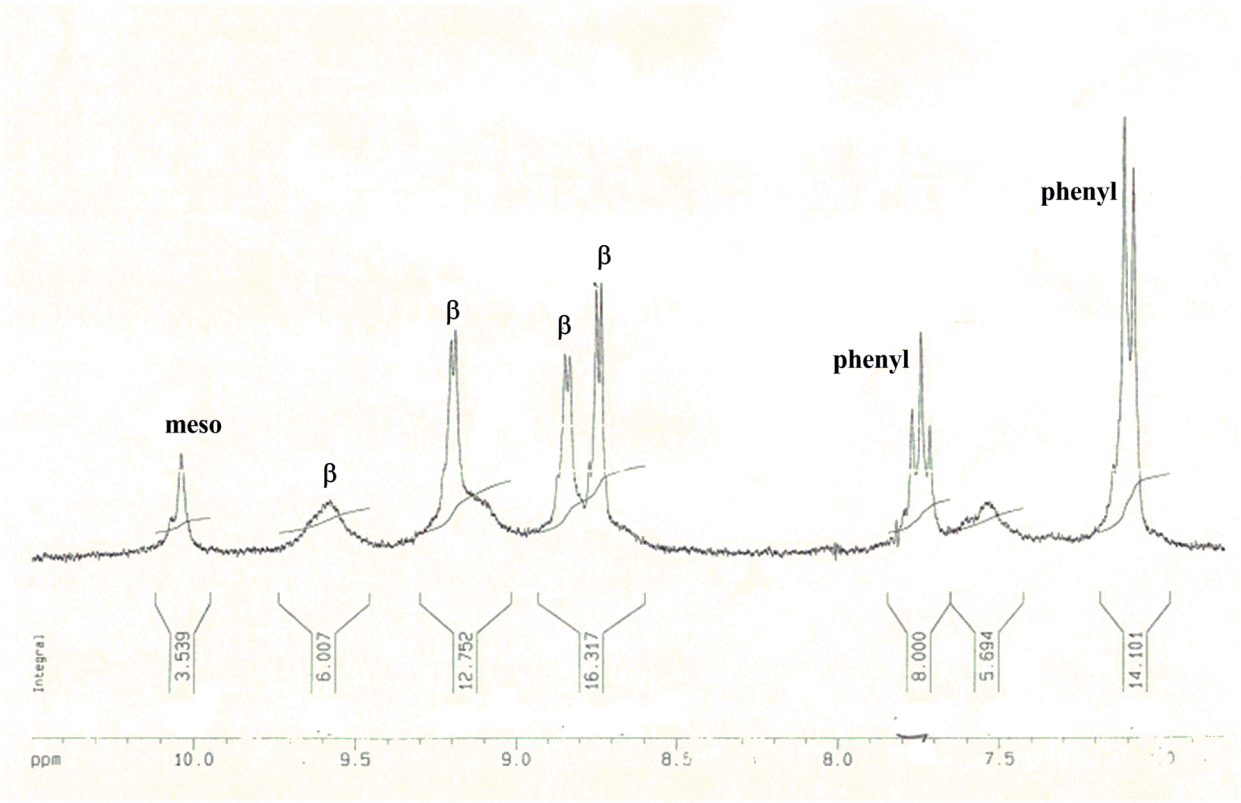


Figure S15. Aromatic region of the ^{1}H NMR spectrum of **9** demonstrating identity and acceptable purity of the desired compound.

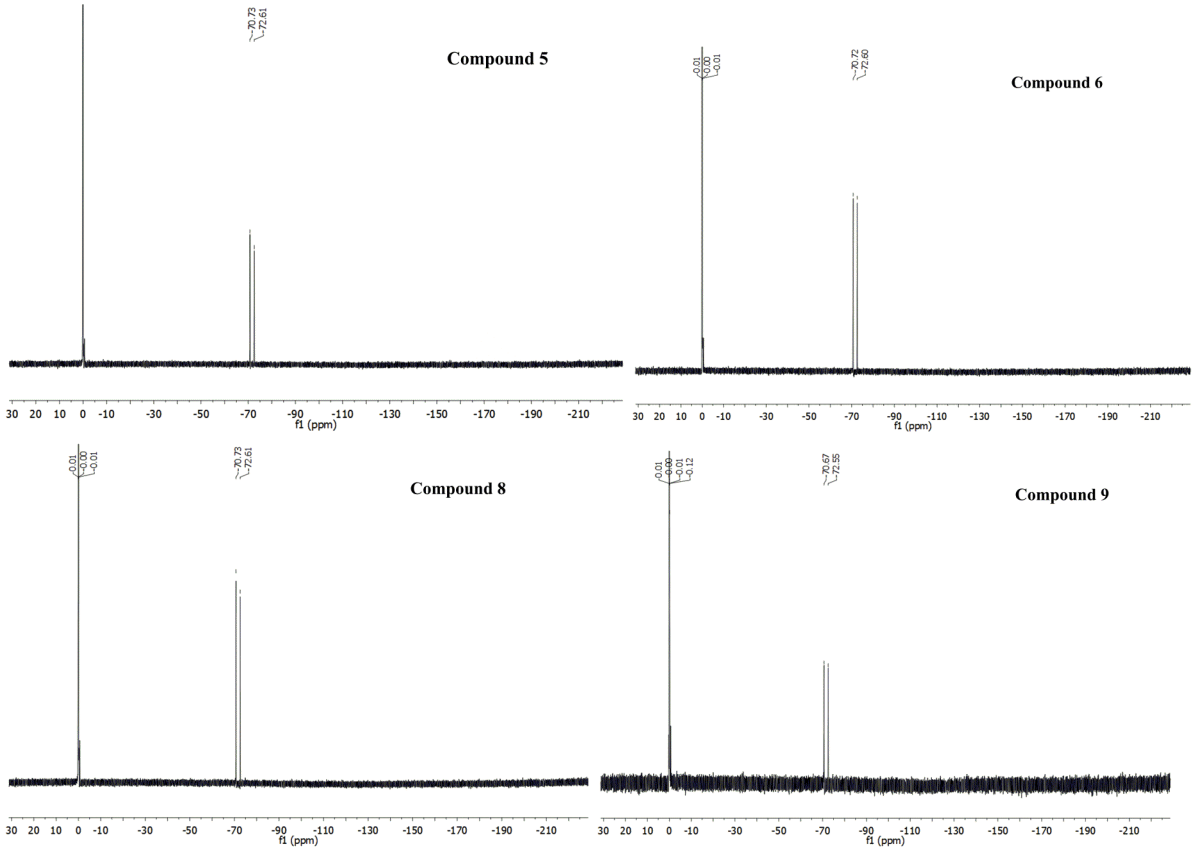


Figure S16. Representative ^{19}F NMR spectra of **5**, **6**, **8** and **9** showing acceptable compound purity.

References:

(1) Uyeda, H. T.; Zhao, Y. X.; Wostyn, K.; Asselberghs, I.; Clays, K.; Persoons, A.; Therien, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 13806-13813.
(2) Holbrey, J. D.; Tiddy, G. J. T.; Bruce, D. W. *J. Chem. Soc., Dalton Trans.* **1995**, 1769-1774.
(3) Potts, K. T.; Konwar, D. *J. Org. Chem.* **1991**, *56*, 4815-4816.
(4) Moran, D. B.; Mortan, G. O.; Albright, J. D. *J. Heterocycl. Chem.* **1986**, *23*, 1071-1077.
(5) Masood, M. A.; Sullivan, B. P.; Hodgson, D. J. *Inorg. Chem.* **1999**, *38*, 5425-5430.
(6) Case, F. H. *J. Org. Chem.* **1966**, *31*, 2398-2400.
(7) Sauer, J.; Heldmann, D. K.; Pabst, G. R. *Eur. J. Org. Chem.* **1999**, 313-321.
(8) Case, F. H. *J. Heterocyclic. Chem.* **1971**, *8*, 1043-1046.

Full author list for manuscript references 58 and 59:

(58) Robinson, B. H.; Dalton, L. R.; Harper, A. W.; Ren, A.; Wang, F.; Zhang, C.; Todorova, G.; Lee, M.; Aniszfeld, R.; Garner, S.; Chen, A.; Steier, W. H.; Houbrecht, S.; Persoons, A.; Ledoux, I.; Zyss, J.; Jen, A. K. Y. *Chem. Phys.* **1999**, *245*, 35-50.
(59) Steier, W. H.; Chen, A.; Lee, S. S.; Garner, S.; Zhang, H.; Chuyanov, V.; Dalton, L. R.; Wang, F.; Ren, A. S.; Zhang, C.; Todorova, G.; Harper, A.; Fetterman, H. R.; Chen, D. T.; Udupa, A.; Bhattacharya, D.; Tsap, B. *Chem. Phys.* **1999**, *245*, 487-506.