Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information of

Synthesis of Pyrrolo[3`,2`:4,5][1,3]diazepino[2,1,7-*cd*]pyrrolizine Derivative from Dicyanovinylene-bis(*meso*-aryl)dipyrrin

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Content

1. NMR spectra of 2 and 3

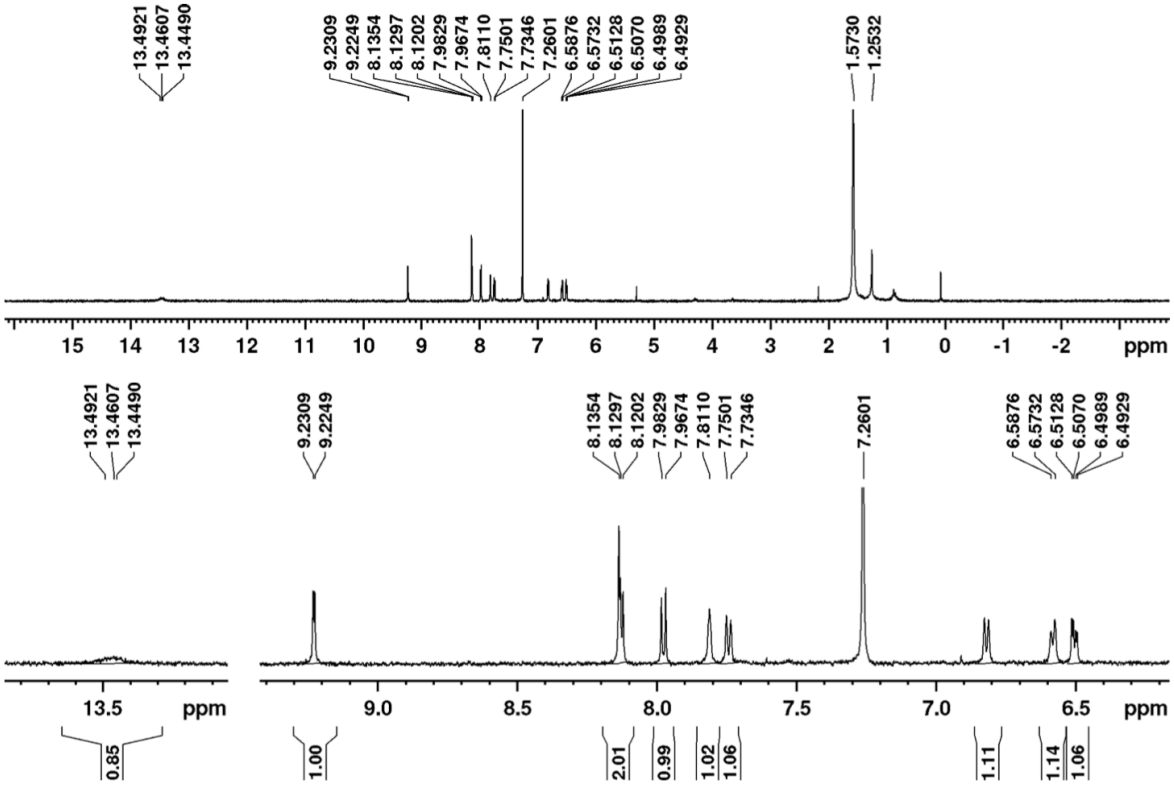

Figure S1. ^{1}H NMR (300 MHz) spectrum of **3** in $CDCl_3$.

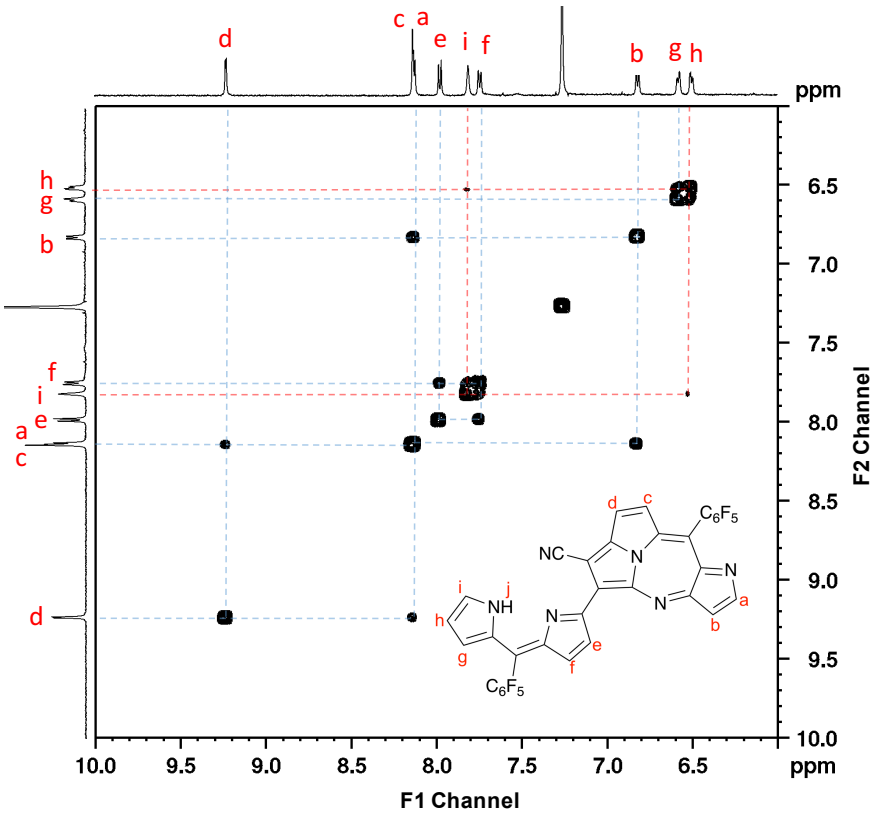

Figure S2. HH COSY (F1 = F2 = 300 MHz) NMR spectrum of **3** in $CDCl_3$.

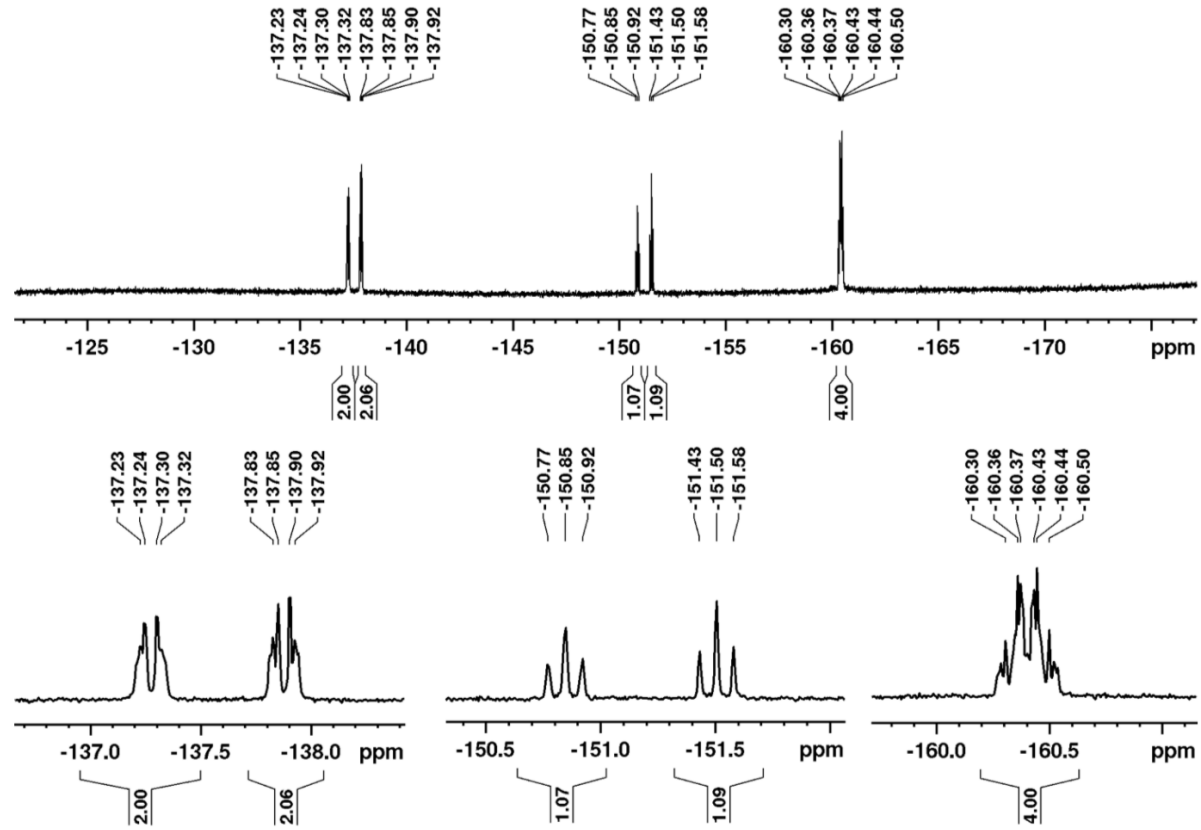

Figure S3. ^{19}F NMR (282.38 MHz) spectrum of **3** in $CDCl_3$.

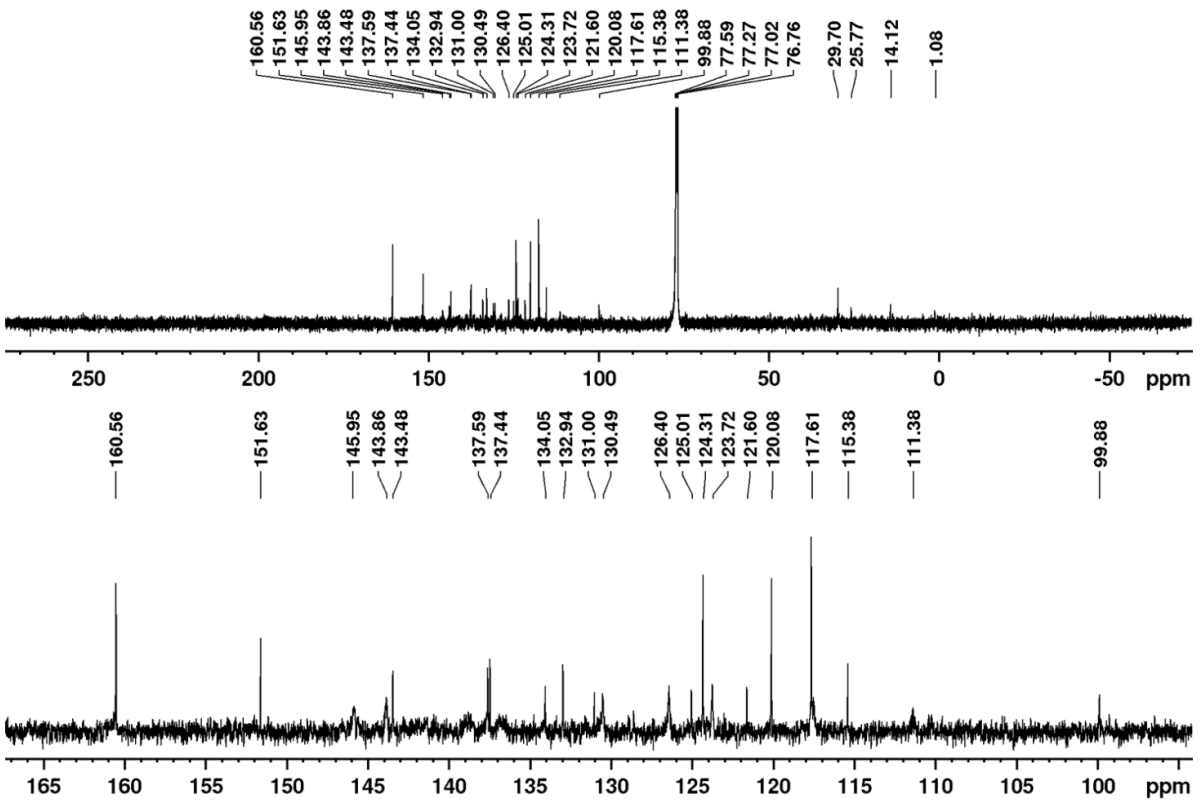

Figure S4. ^{13}C NMR (125.77 MHz) spectrum of **3** in $CDCl_3$.

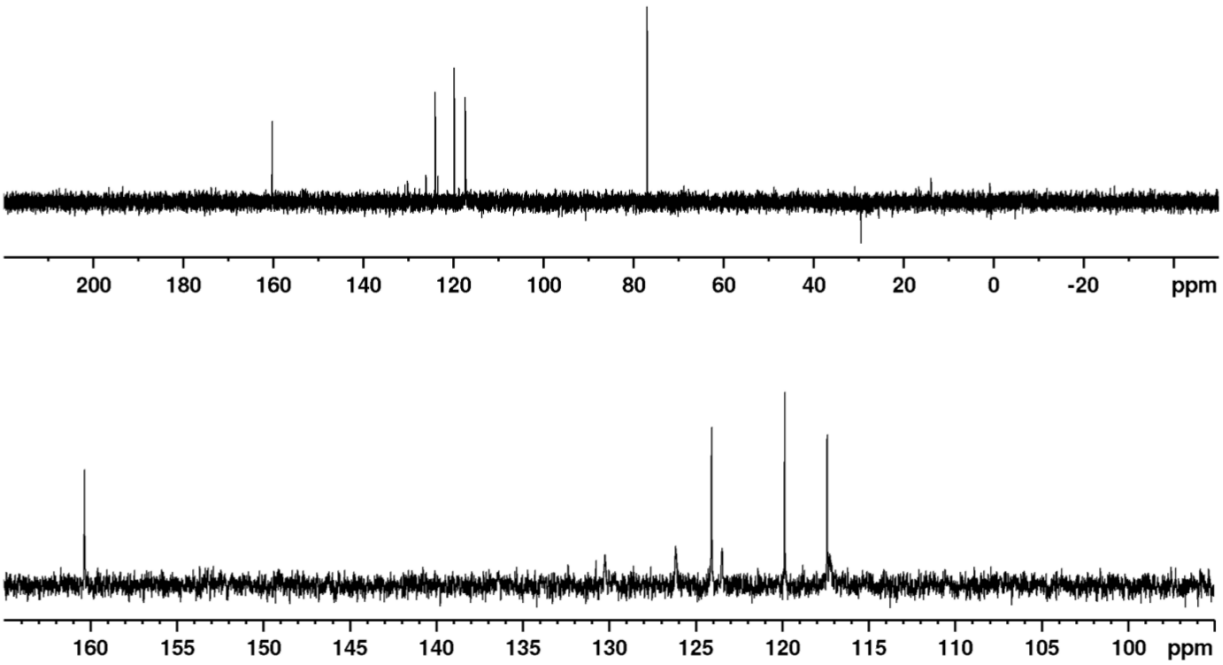

Figure S5. DEPT-135deg NMR (125.77 MHz) spectrum of **3** in $CDCl_3$.

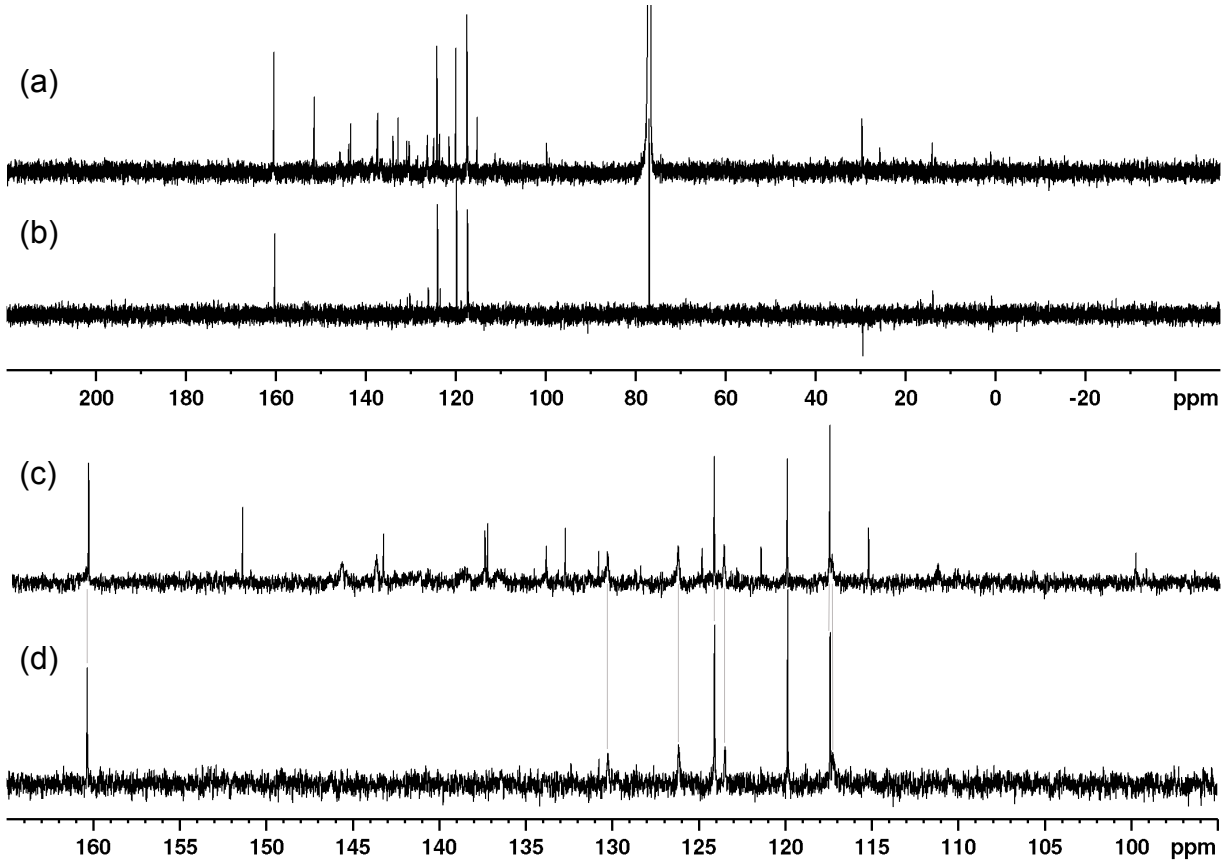

Figure S6. Comparison of carbon peaks between ^{13}C (a and c) and DEPT (b and d) NMR (125.77 MHz) spectra of **3** in $CDCl_3$.

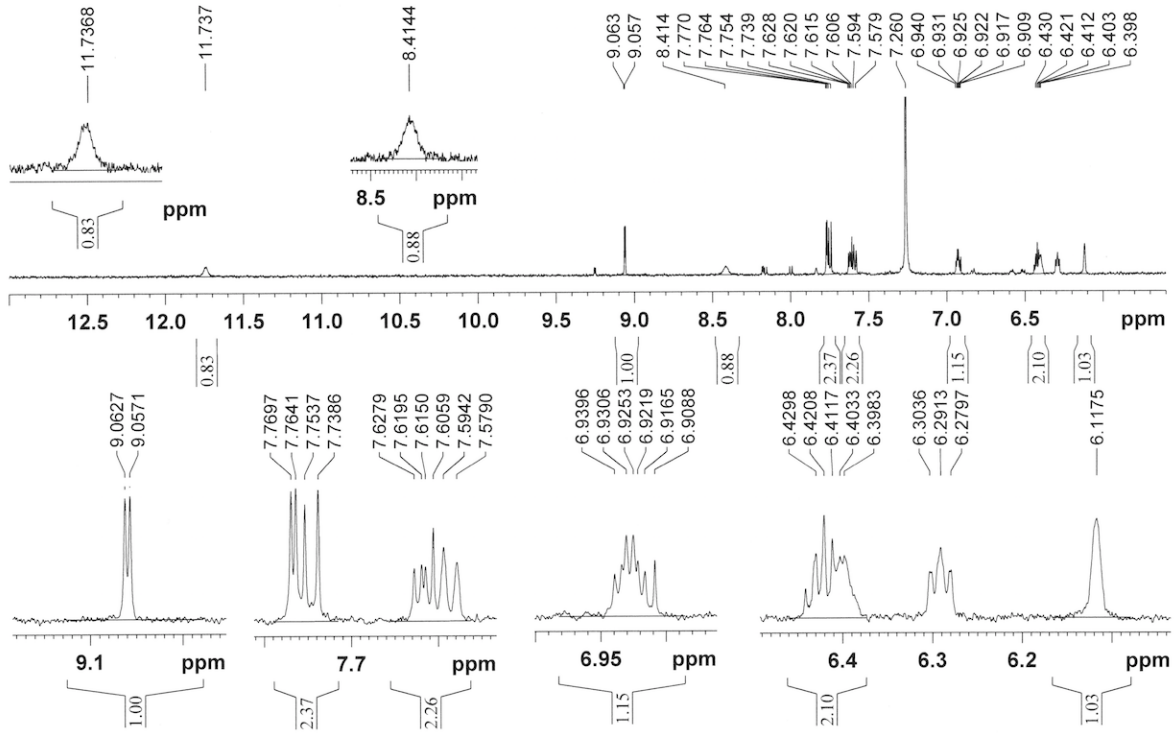

Figure S7. ^{1}H NMR (300 MHz) spectrum of **2** in $CDCl_3$.

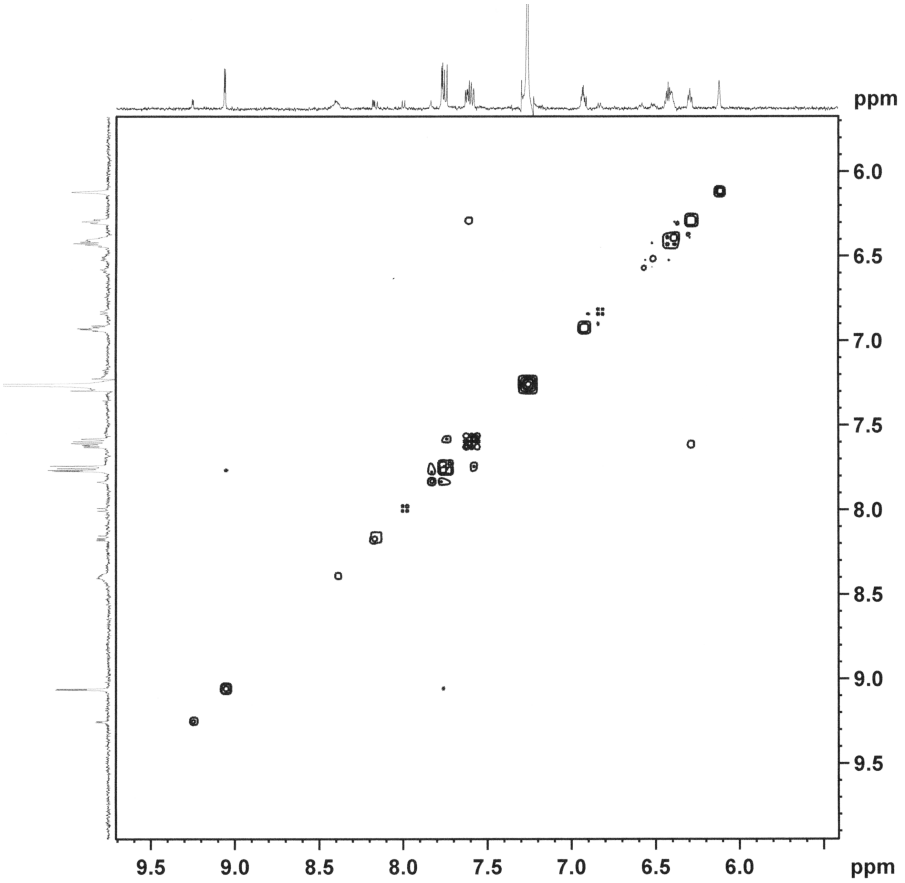

Figure S8. HH COSY (F1 = F2 = 300 MHz) NMR spectrum of **2** in $CDCl_3$.

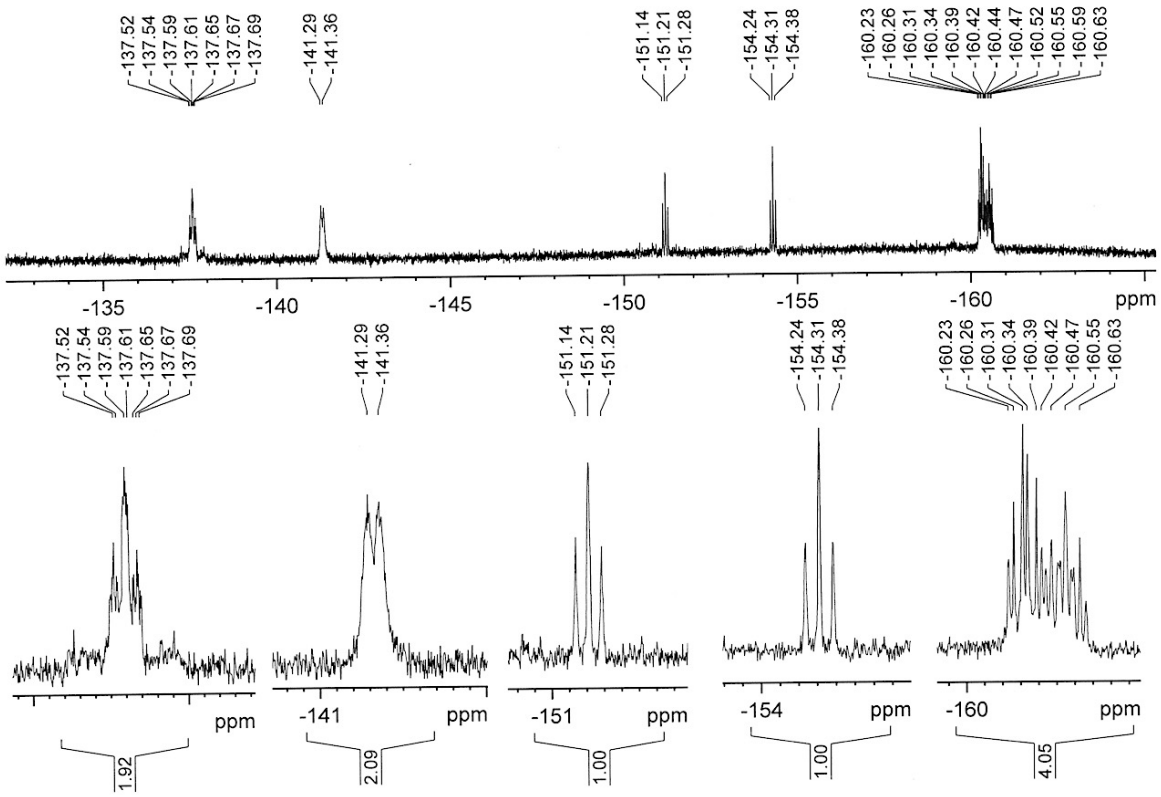

Figure S9. ^{19}F NMR (282.38 MHz) spectrum of **2** in $CDCl_3$.

2. Mass spectra of 2 and 3

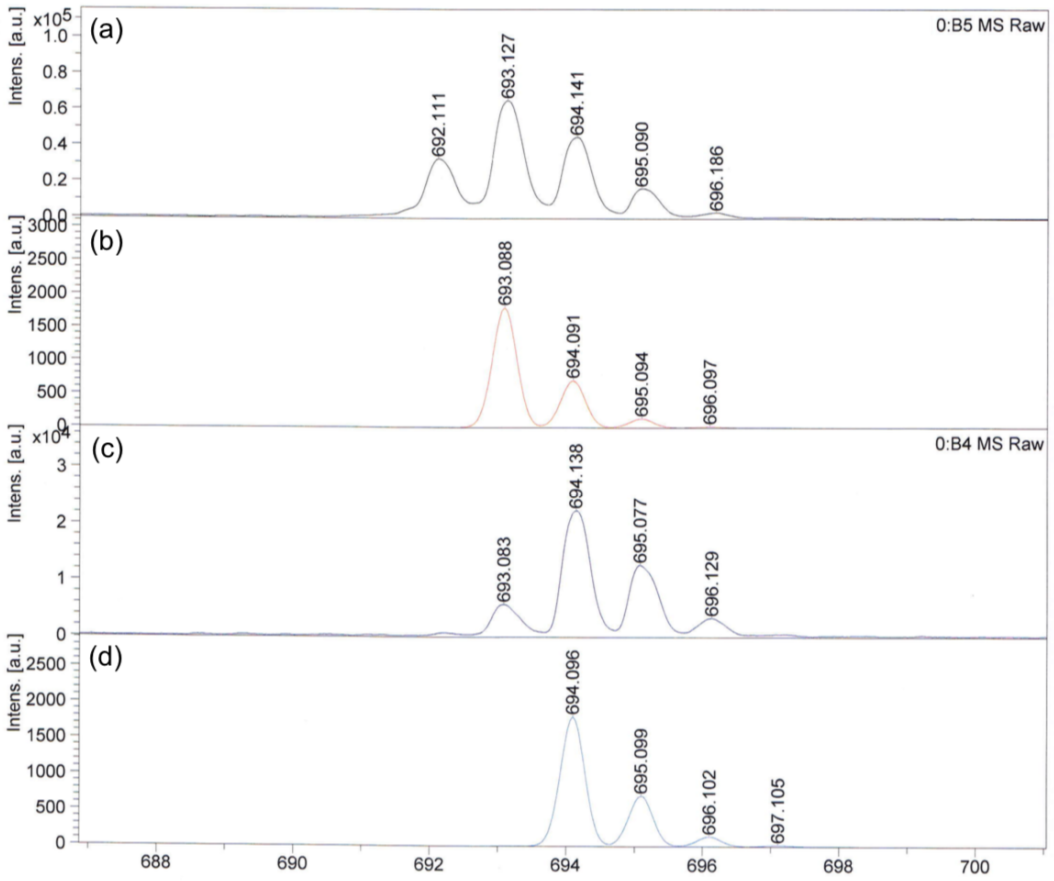

Figure S10. MALDI-TOF mass spectra of **3** (a and b) and **2** (c and d): measured (a and c) and calculated (b and d) masses. (b) and (d) are for $[\mathbf{3} + H]^+$ and $[\mathbf{2}]^+$.

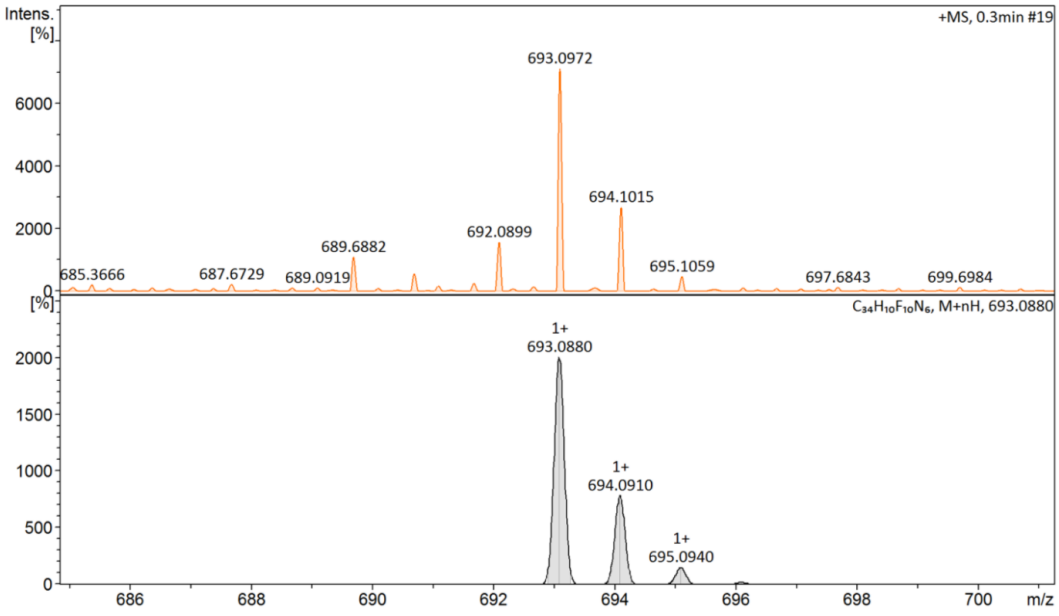

Figure S11. High resolution APCI mass spectrum of **3**.

3. Crystal structures of 4, 2, and 3

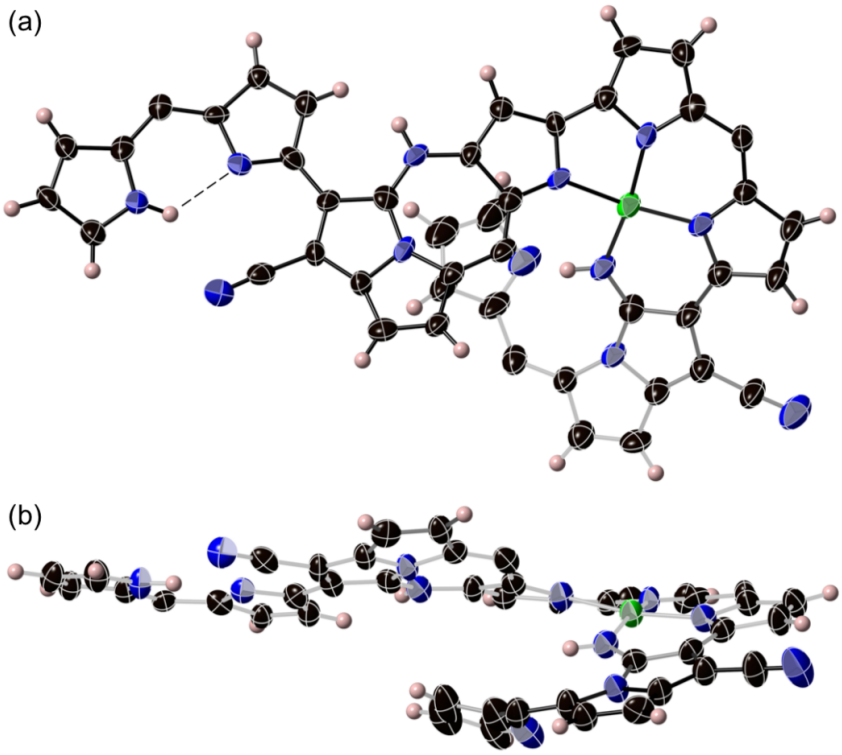

Figure S12. Crystal structure of acyclic Ni^{II} complex **4** (CCDC No. = 1520688): top view (a) and side view (b). *meso*-Pentafluorophenyl groups were omitted for clarity. Thermal ellipsoids are scaled at the 50% probability level. Crystal data of **4**: $(C_{68}H_{20}F_{20}N_{12}Ni_2)_2 \cdot (N_6Ni_{14})$ M_r = 2973.51, T = 93(2) K, Crystal size = 0.04 x 0.03 x 0.03 mm^3, Mo radiation, triclinic, space group P-1 (#2), a = 16.0744(7) Å, b = 16.7126(6) Å, c = 26.6119(10) Å, α = 105.829(3)°, β = 103.161(4)°, γ = 97.511(3)°, V = 6554.0(5) $Å^3$, Z = 2, $P_{calcd.}$ = 1.507 g/cm, $R_1(F)$ = 0.1124 (I > 2(I)), $wR_2(F^2)$ = 0.3732 (all), GoF = 1.023, Data completeness = 0.965.

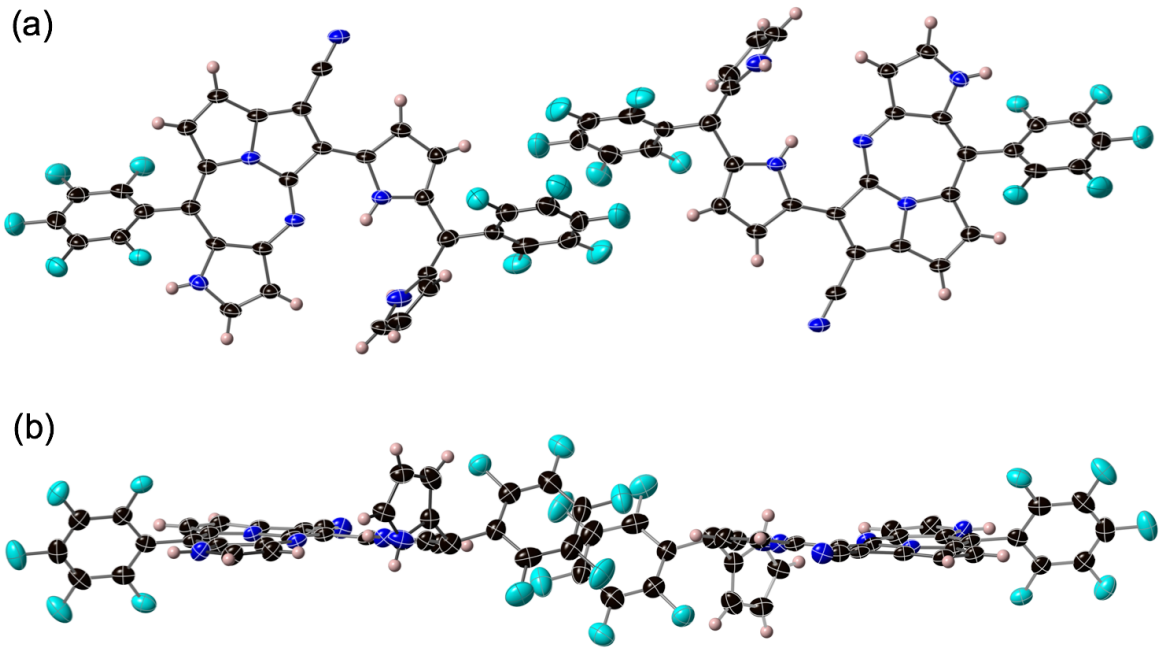

Figure S13. Crystal structure of **2**: top view (a) and side views (b). Thermal ellipsoids are scaled at the 50% probability level.

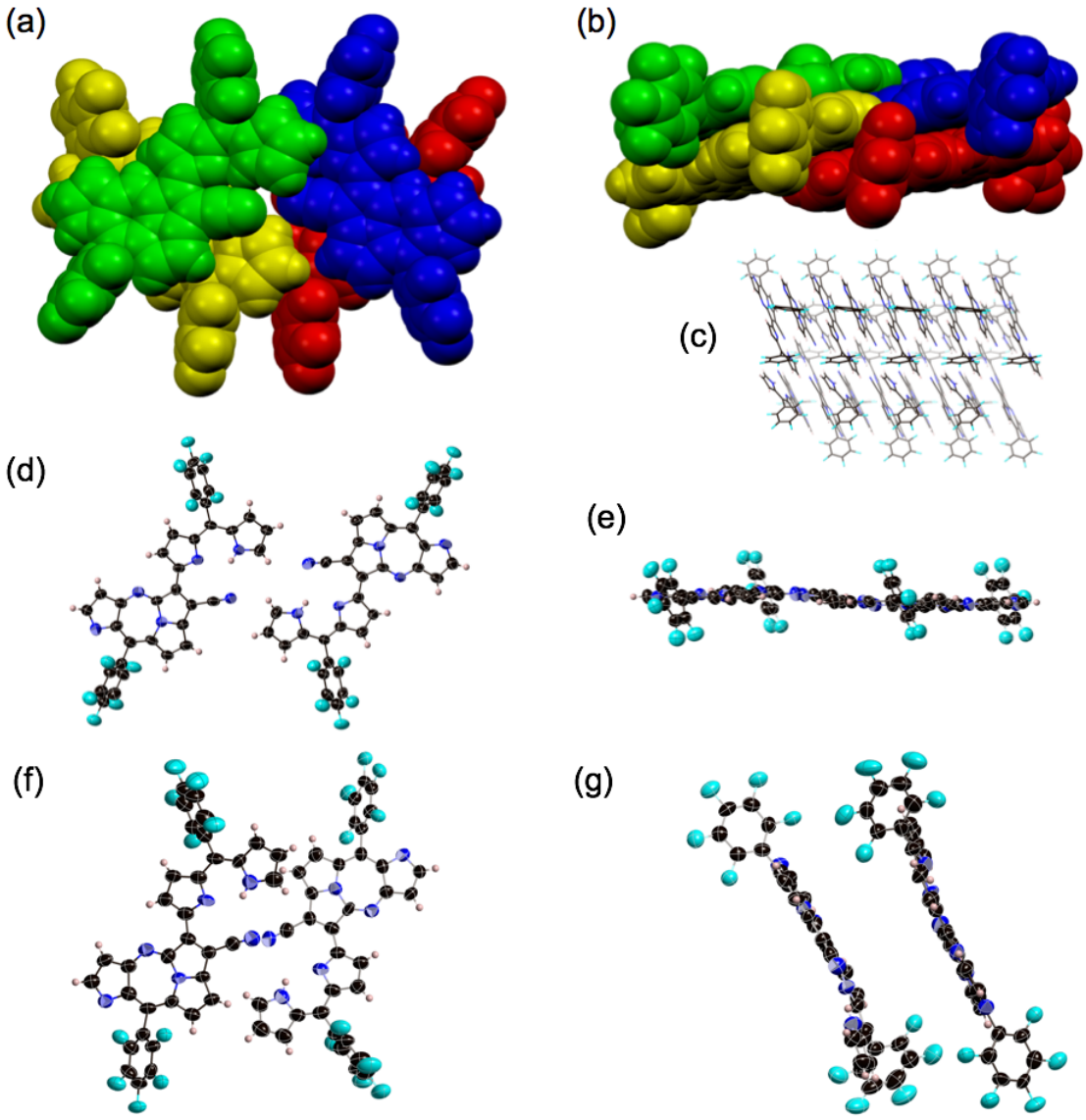

Figure S14. Unit-packing diagrams of **3**: Space-filling structures of top (a) and side (b) views and stick model structure showing a packing pattern. The unit presented a combination of two sets of enantiomers: (d) and (f) are the top view for each of the enantiomers and e and g are their side views, respectively.

4. Absorption spectra of 2, 3_{ox}, and $3_{red.}$

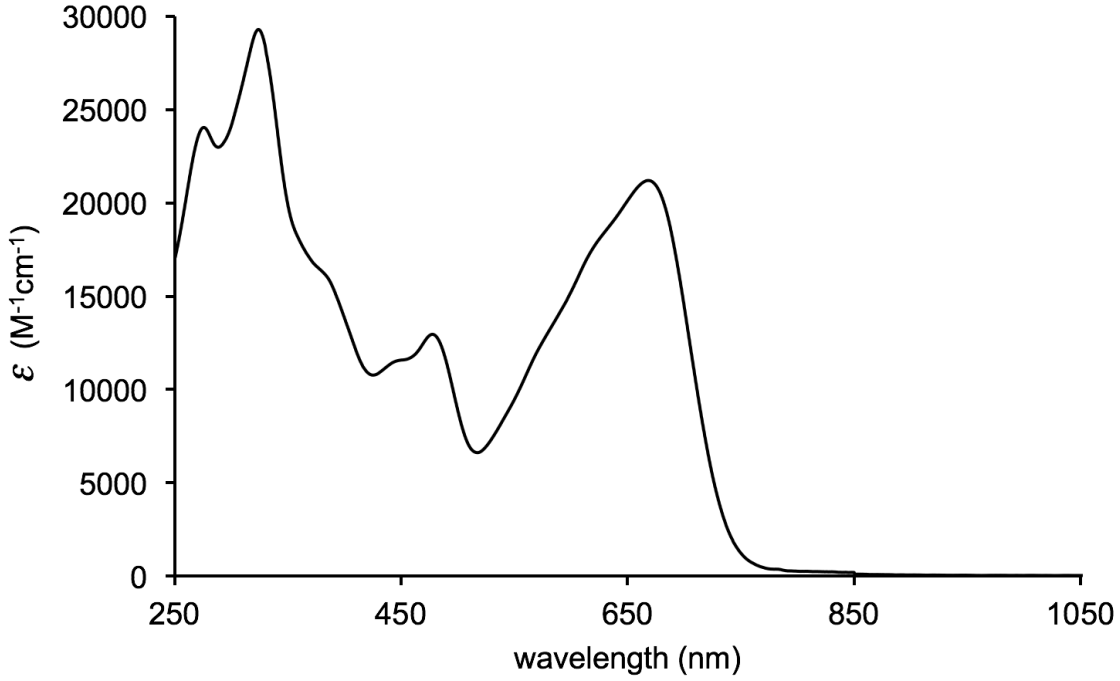

Figure S15. UV Absorption spectrum of **3** in CH_2Cl_2.

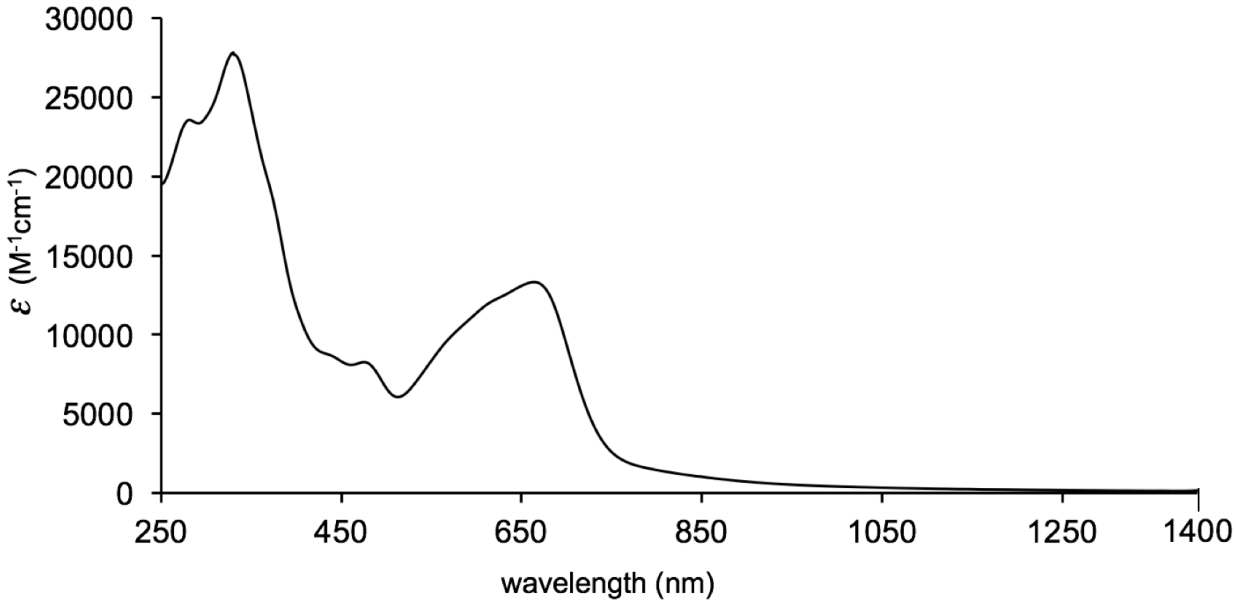

Figure S16. UV Absorption spectrum of **2** in CH_2Cl_2.

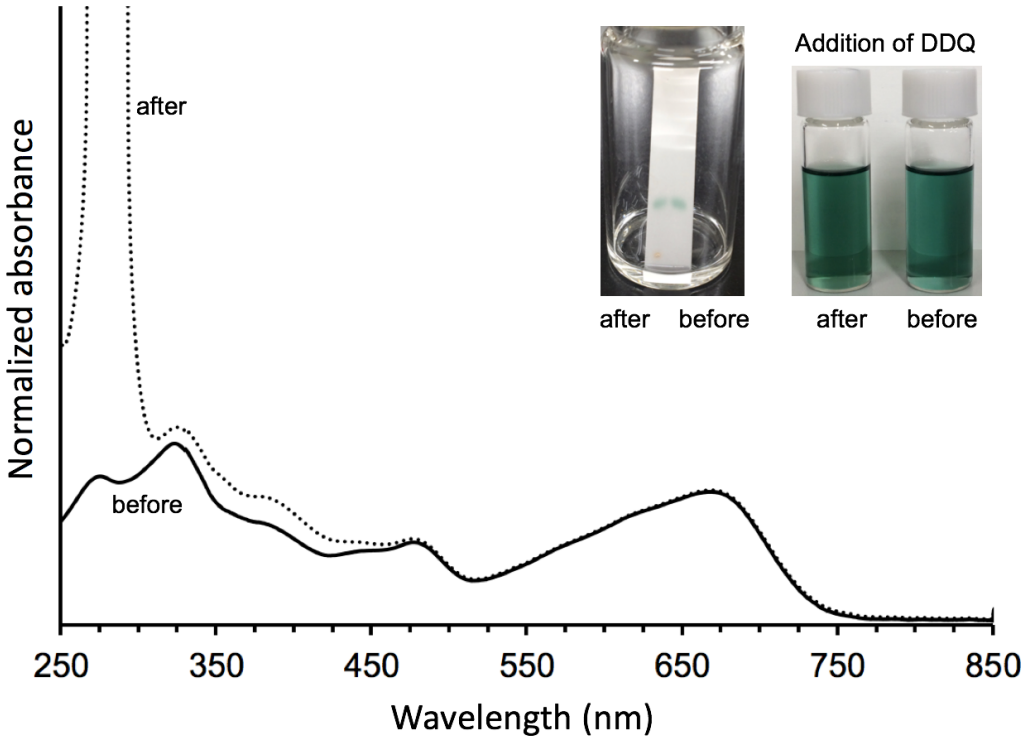

Figure S17. Examine of absorption dependence on a chemical oxidation with DDQ: UV absorption spectra of **3** in CH_2Cl_2, before (——) and after (·····) addition of excess DDQ. Any significant difference between two samples was observed: The solutions exhibited same green in color as well as exactly same retention time on TLC plate (silica gel with neat CH_2Cl_2).

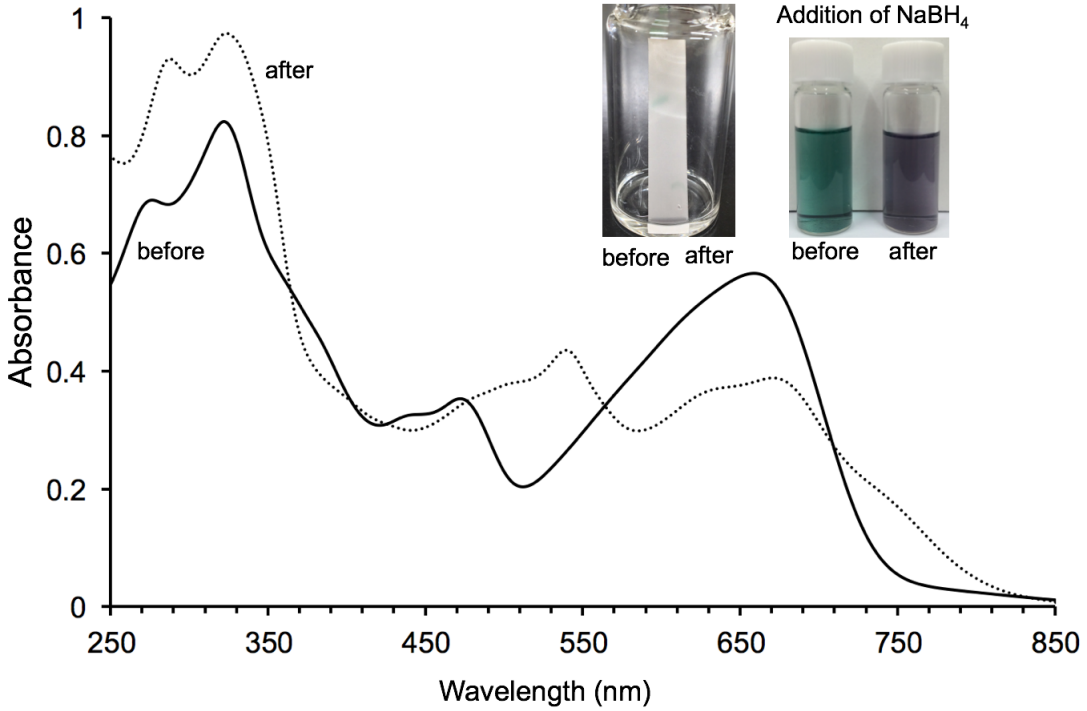

Figure S18. Examine of absorption dependence on a chemical reduction with $NaBH_4$: UV absorption spectra of **3** in CH_3OH, before (——) and after (·····) addition of excess $NaBH_4$. The initial green was changed to violet in color. Retention time on TLC plate increased with the chemical reduction (silica gel with CH_2Cl_2 including tiny amount of CH_3OH).