Supplementary Materials: Propeller-Shaped Aluminum Complexes with Azaperylene Core in the Ligands

Masahiro Tsukao, Yoshifumi Hashikawa, Nana Toyama, Masahiro Muraoka, Michihisa Murata, Takahiro Sasamori, Atsushi Wakamiya, and Yasujiro Murata
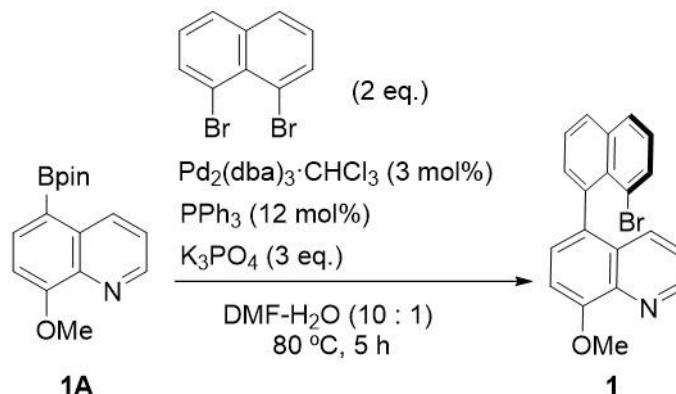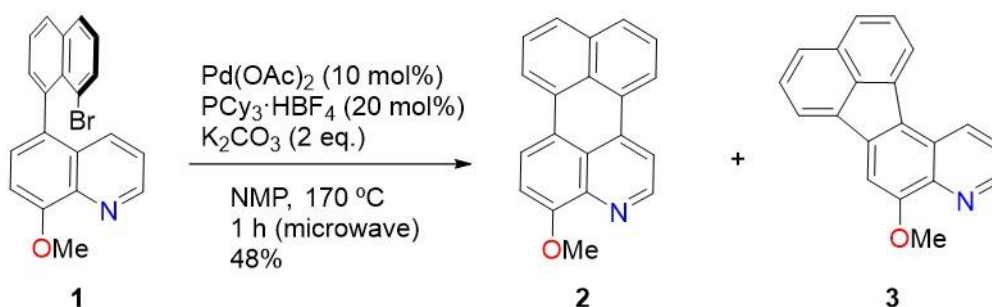

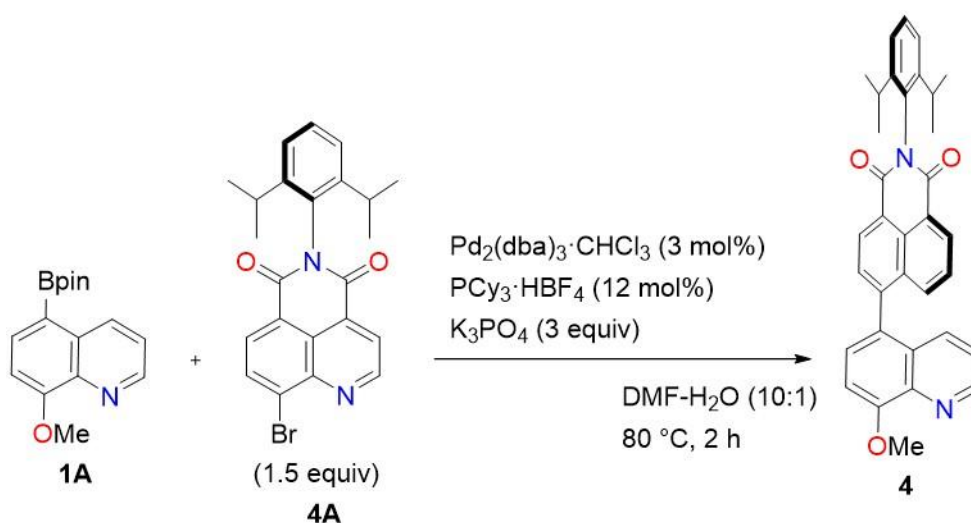**Figure S1.** Synthesis of compound **1**.

Figure S2. Synthesis of compound **2**.

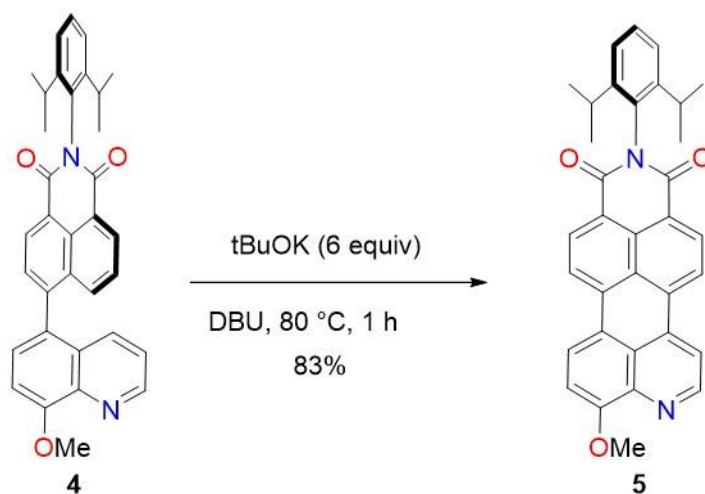**Figure S3.** Synthesis of compound **4**.

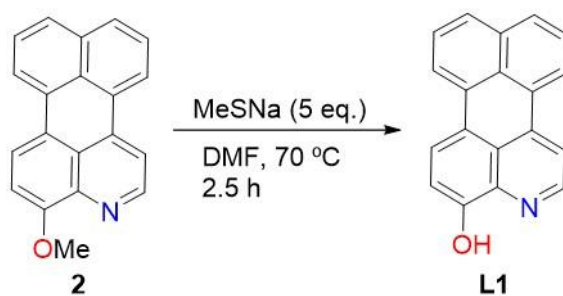**Figure S4.** Synthesis of compound **5**.

Figure S5. Synthesis of compound **L1**.

Figure S6. Synthesis of compound **L2**.
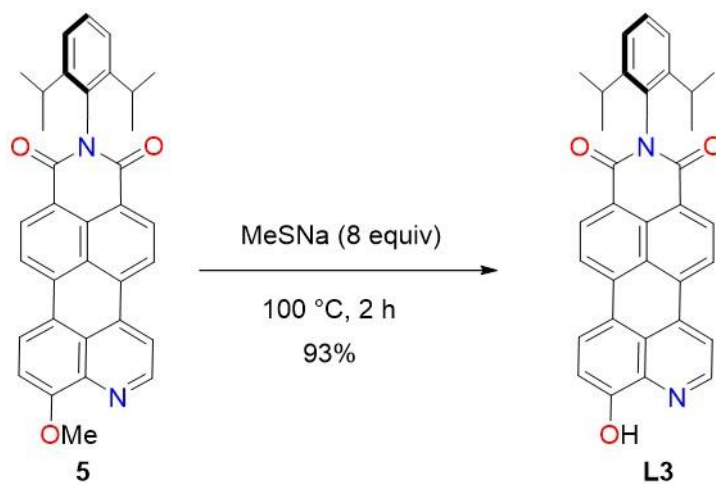
Figure S7. Synthesis of compound **L3**.
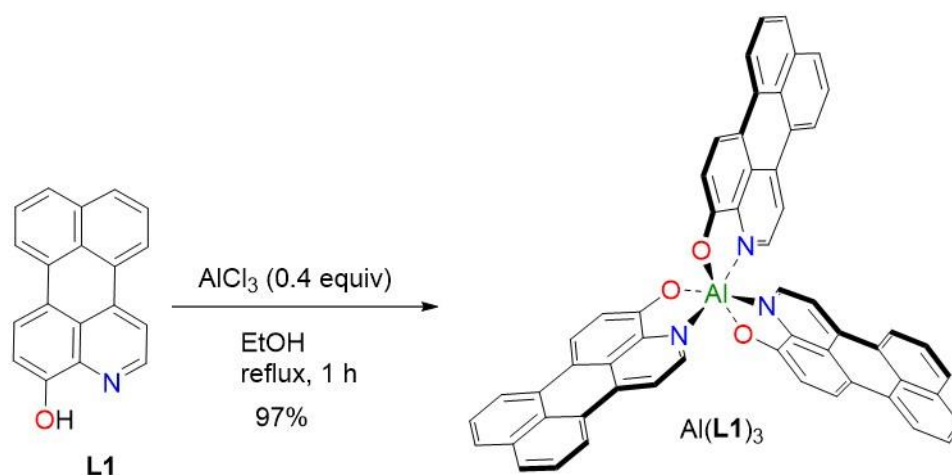
Figure S8. Synthesis of compound Al(**L1**)$_3$.

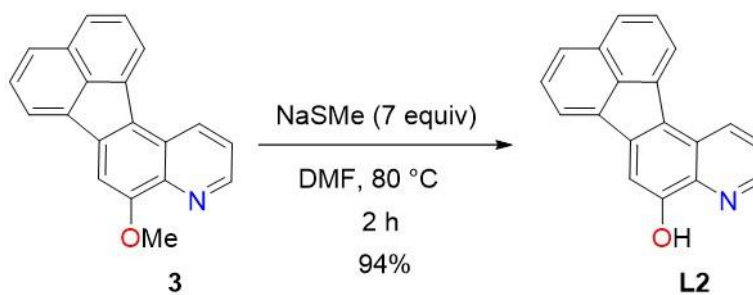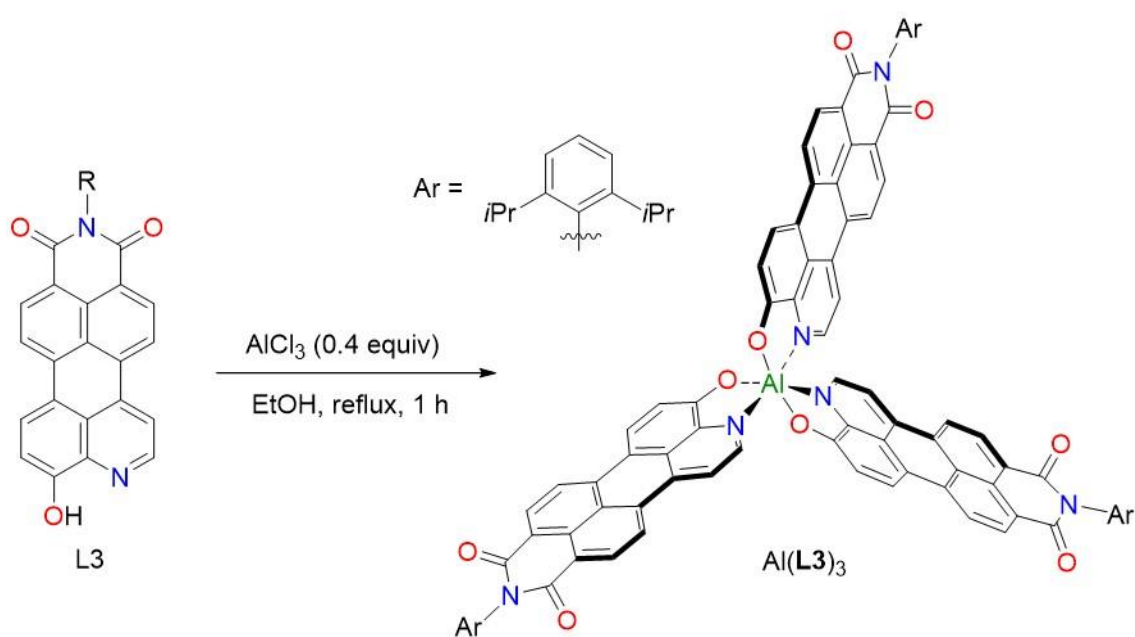**Figure S9.** Synthesis of compound Al(**L3**)$_3$.
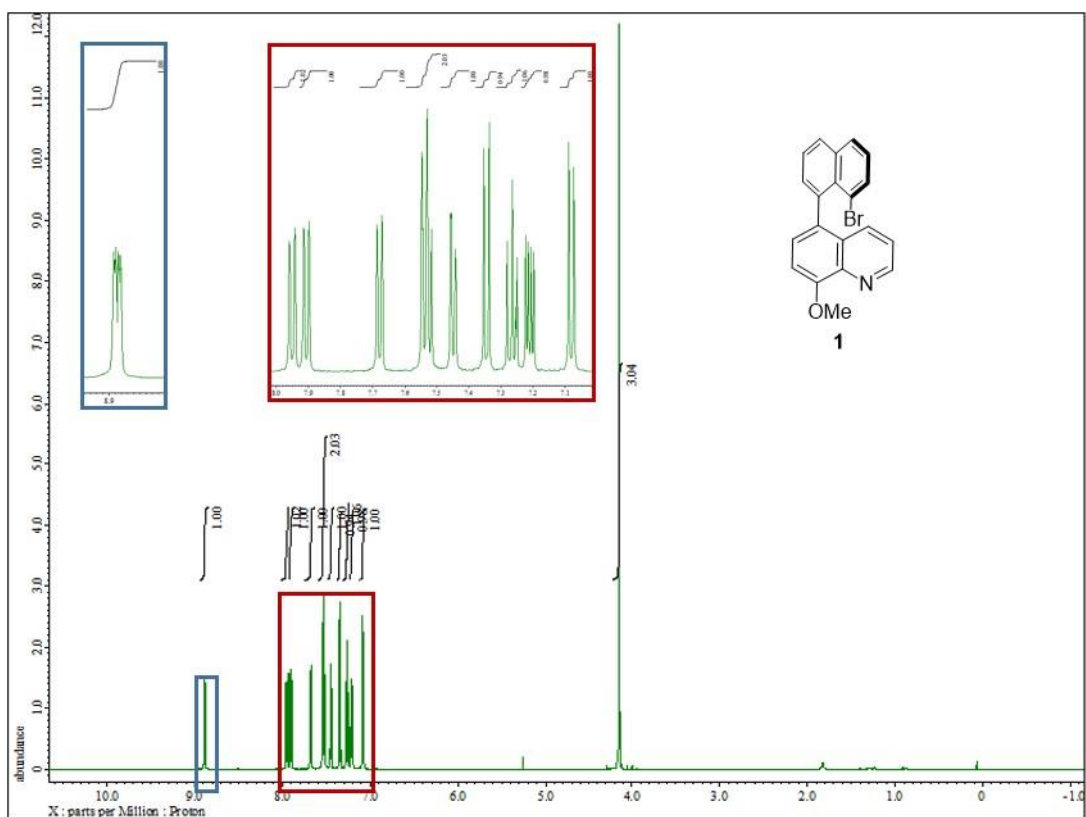
Figure S10. ^{1}H NMR of **1** (500 MHz, CDCl$_3$).
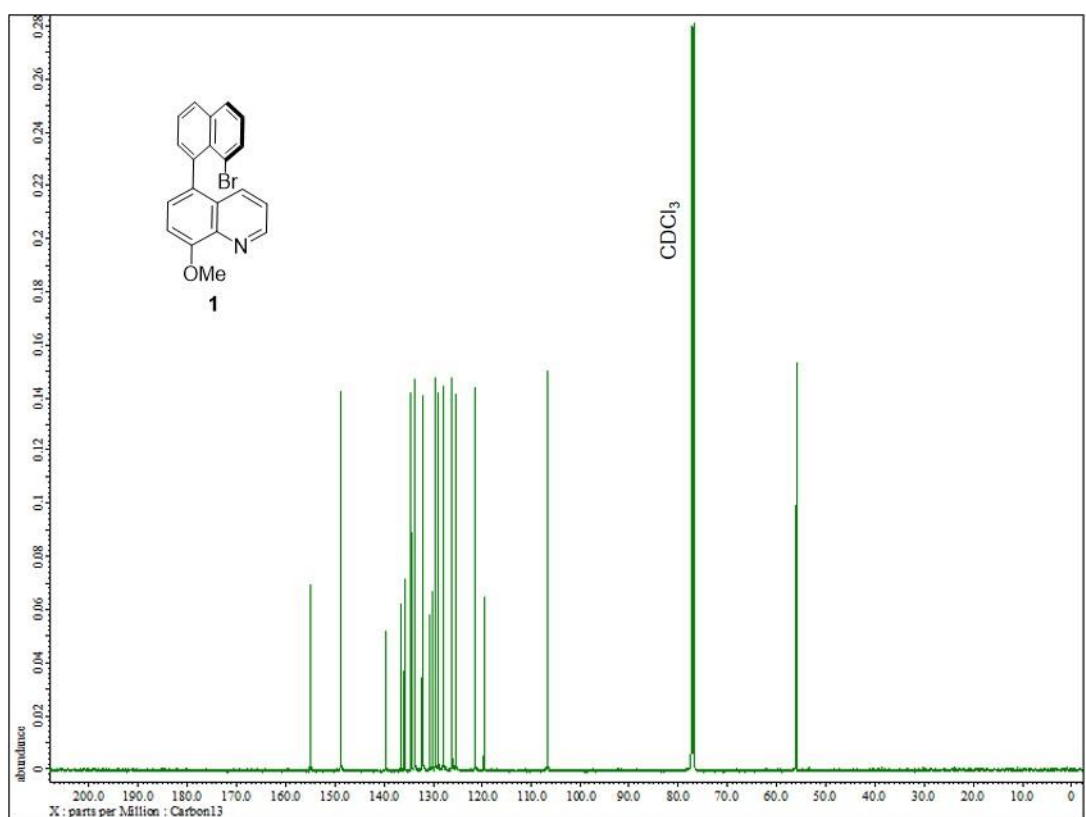
Figure S11. ^{13}C NMR of **1** (126 MHz, CDCl$_3$).
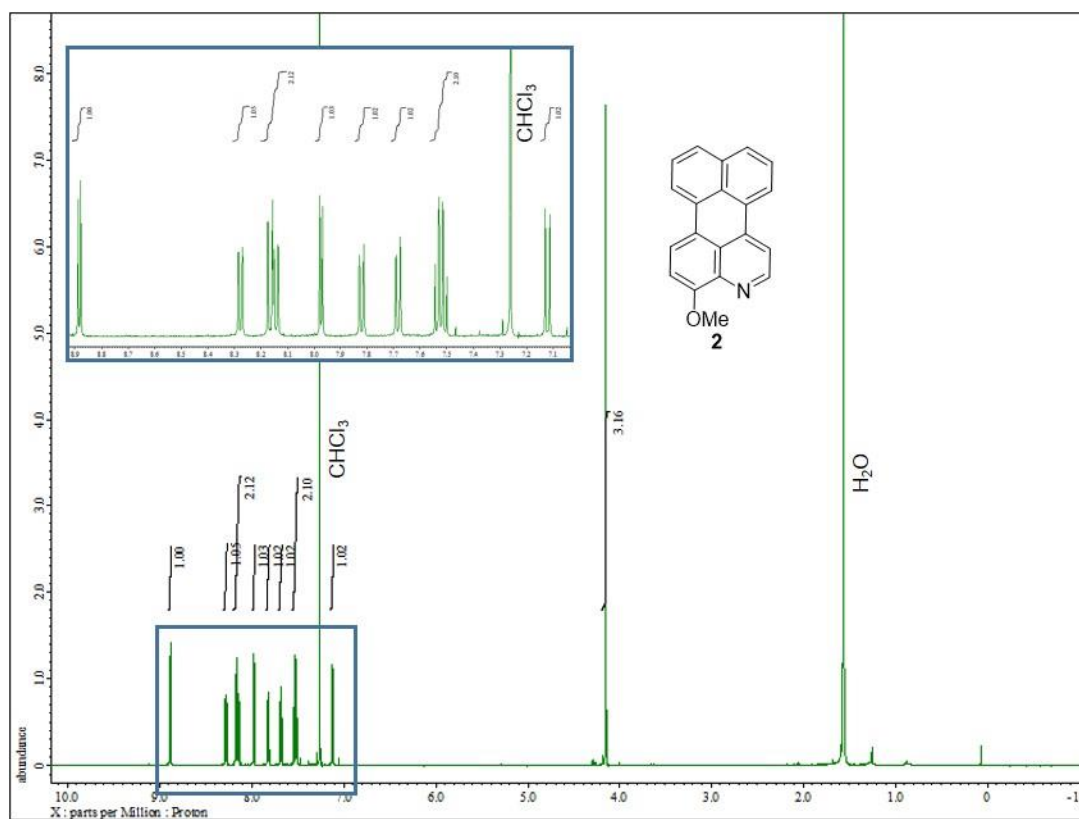
Figure S12. ^{1}H NMR of **2** (500 MHz, CDCl$_3$).
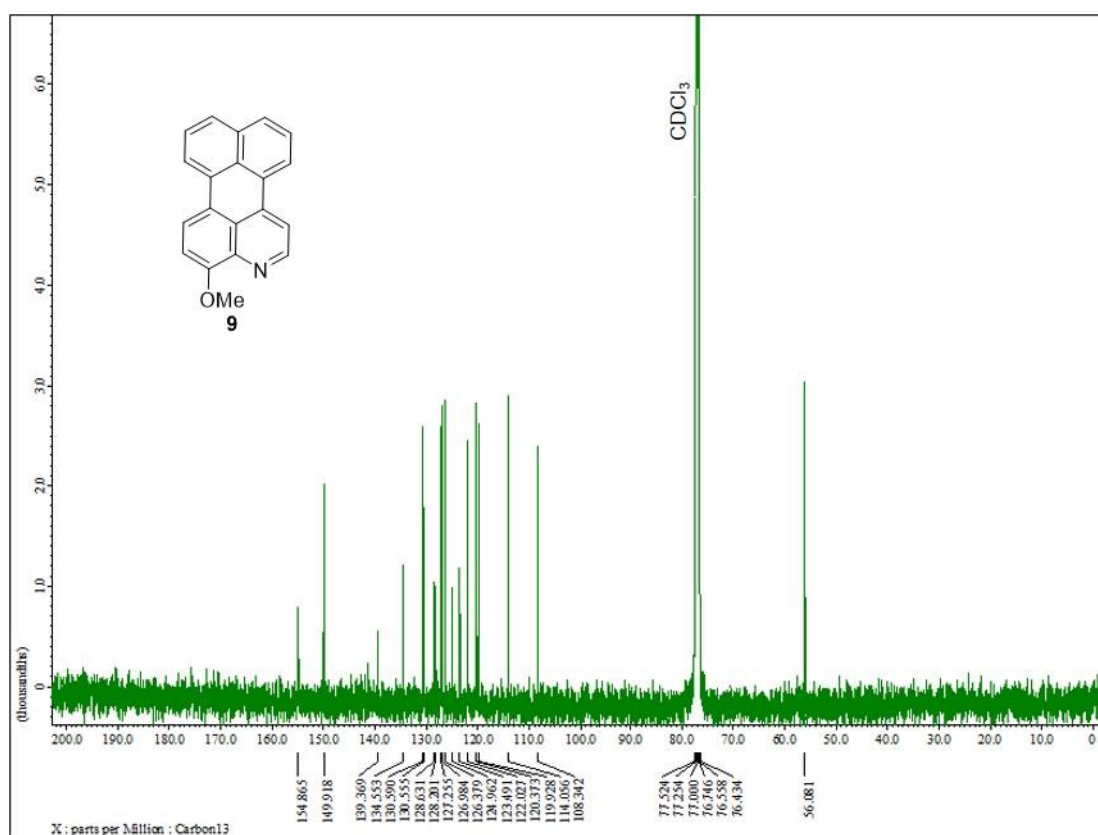
Figure S13. ^{13}C NMR of **2** (126 MHz, CDCl$_3$).

Figure S14. ^{1}H NMR of **3** (500 MHz, CDCl$_3$).

Figure S15. ^{13}C NMR of **3** (126 MHz, CDCl$_3$).
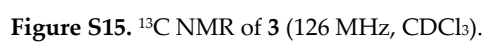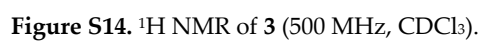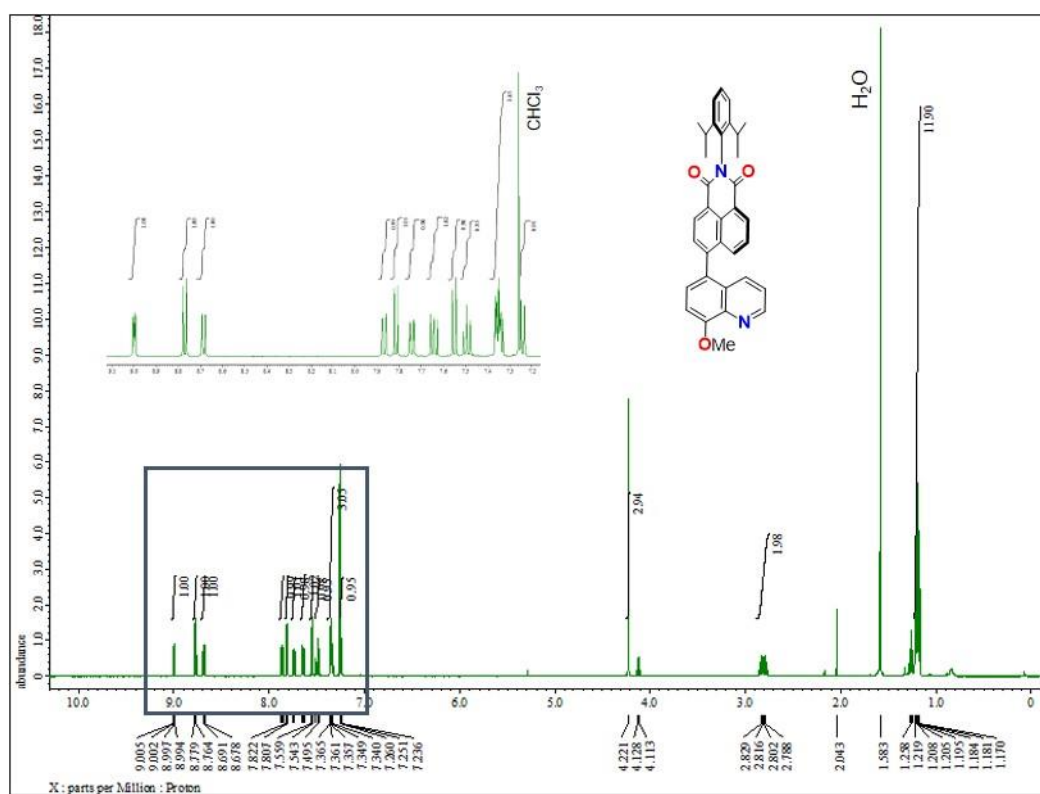
Figure S16. ^{1}H NMR of **4** (500 MHz, CDCl₃).
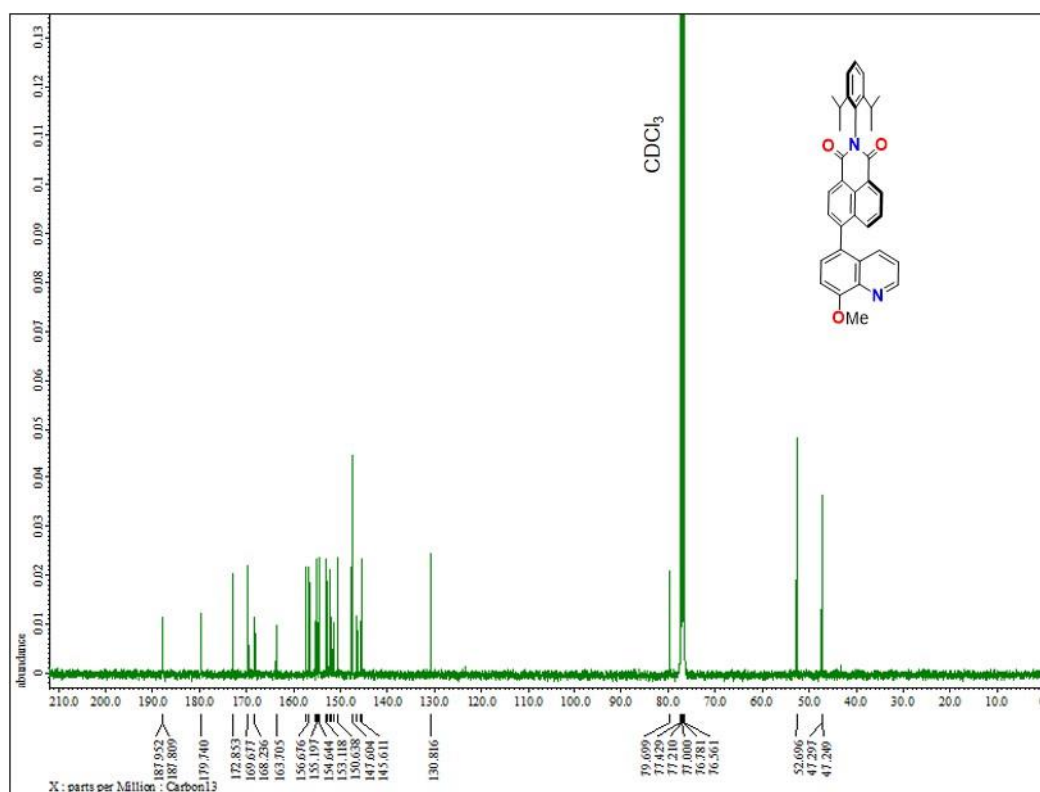
Figure S17. ^{13}C NMR of **4** (126 MHz, CDCl₃).
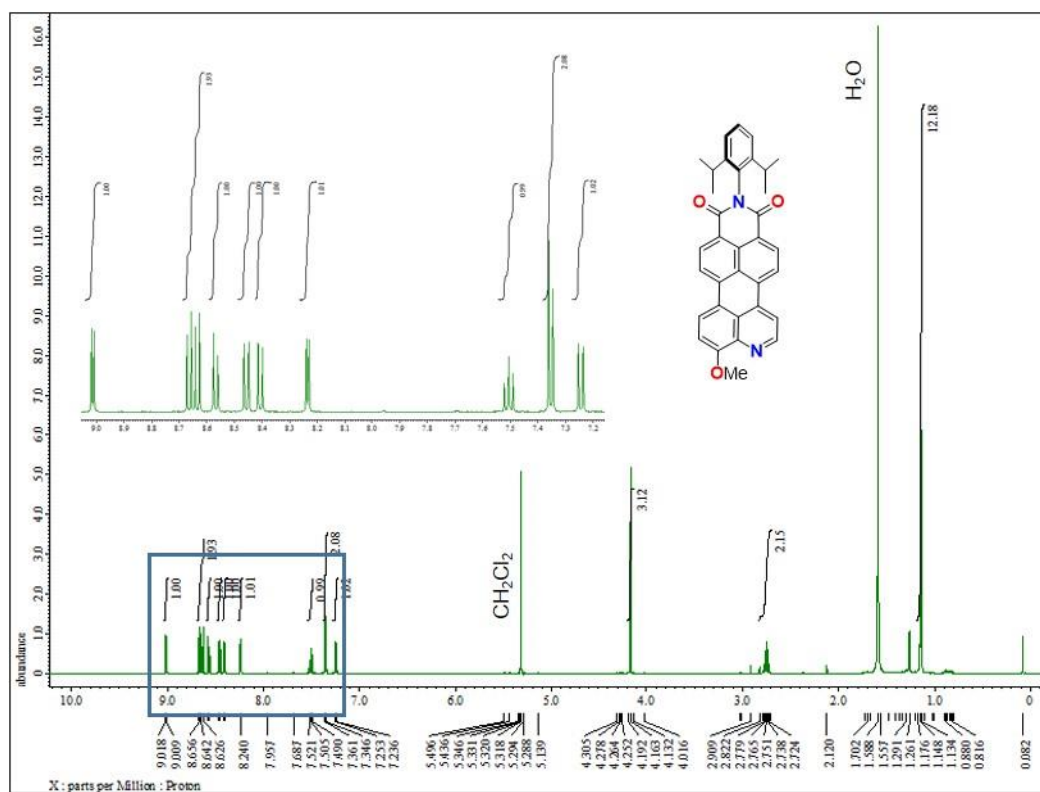
Figure S18. ^{1}H NMR of **5** (500 MHz, CD$_2$Cl$_2$).
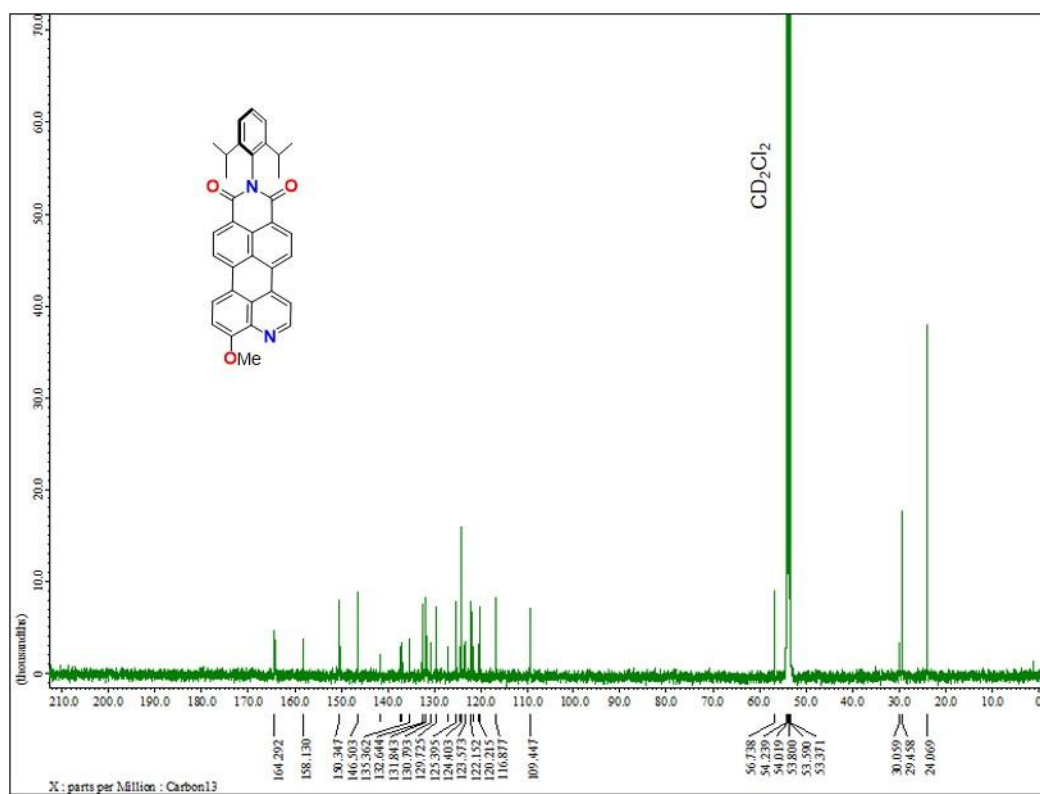
Figure S19. ^{13}C NMR of **5** (126 MHz, CD$_2$Cl$_2$).
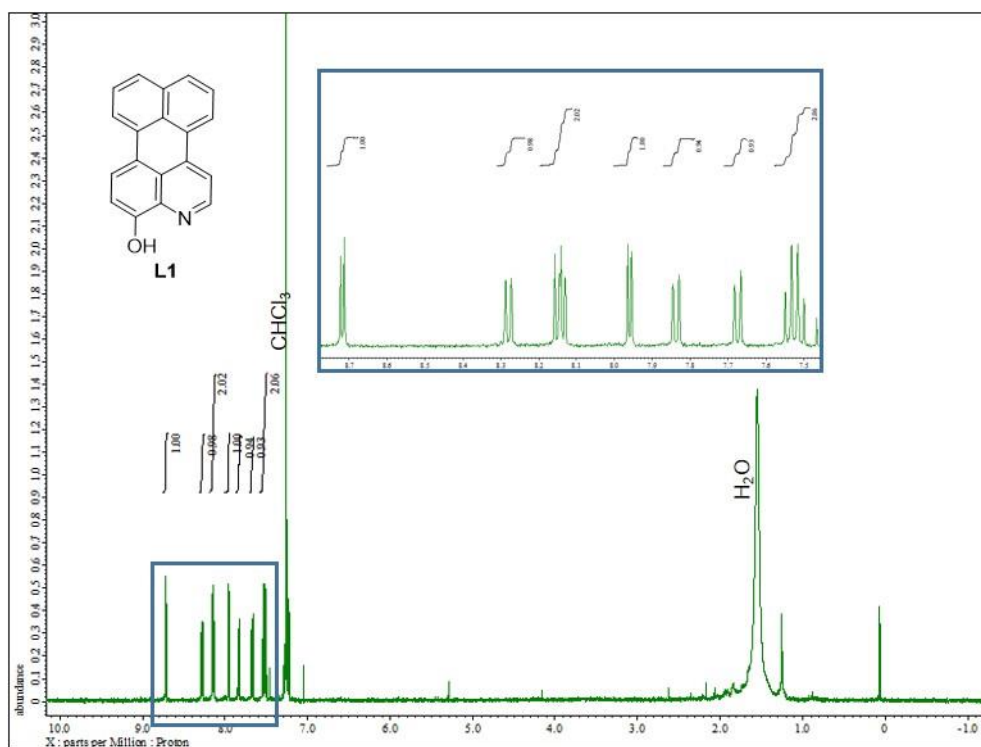
Figure S20. ^{1}H NMR of **L1** (500 MHz, CDCl3).
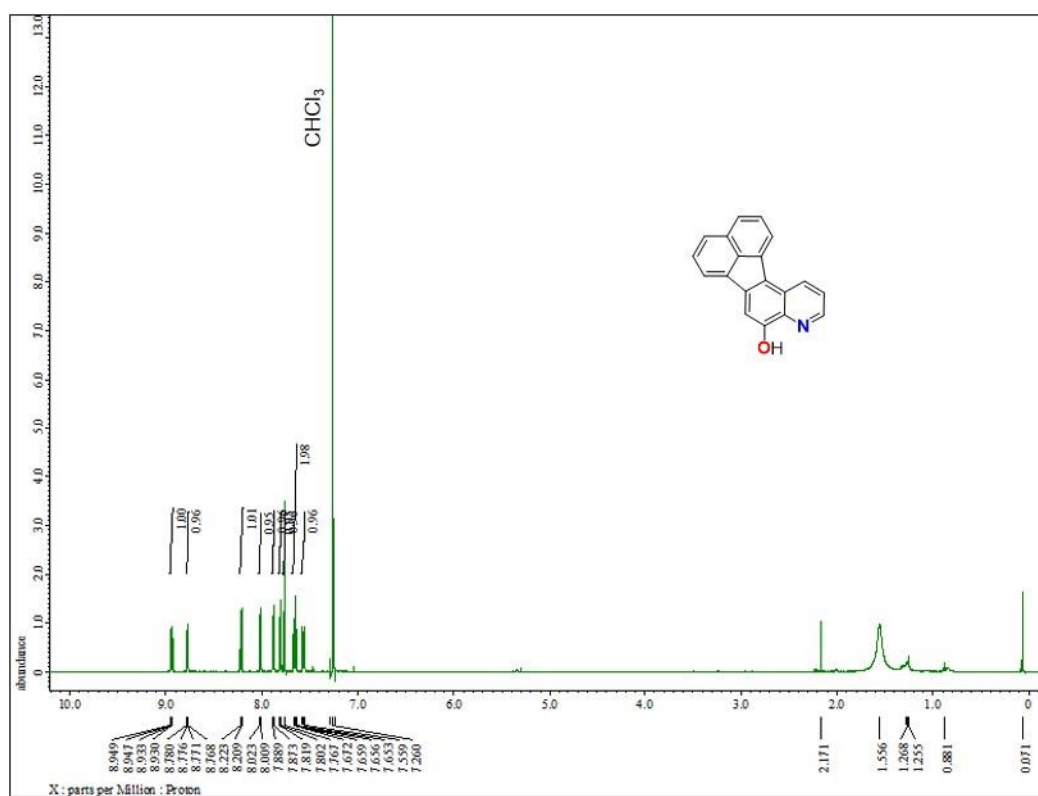
Figure S21. NMR of **L2** (500 MHz, CDCl3).
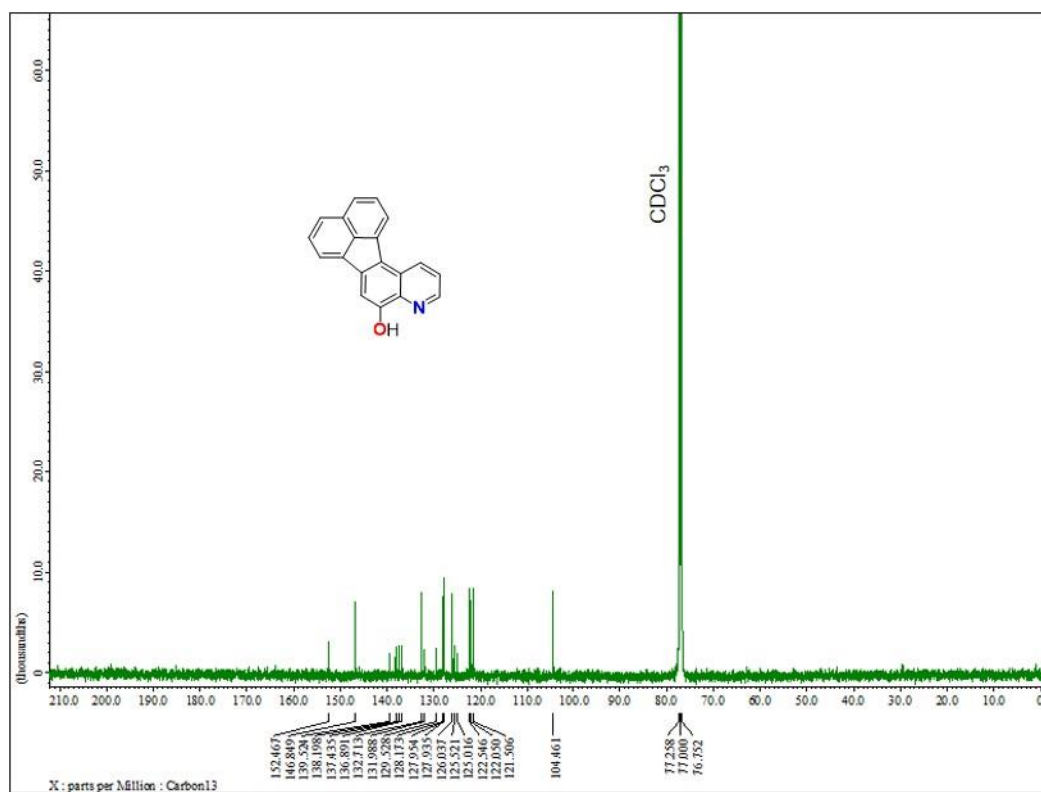
Figure S22. NMR of **L2** (126 MHz, CDCl₃).
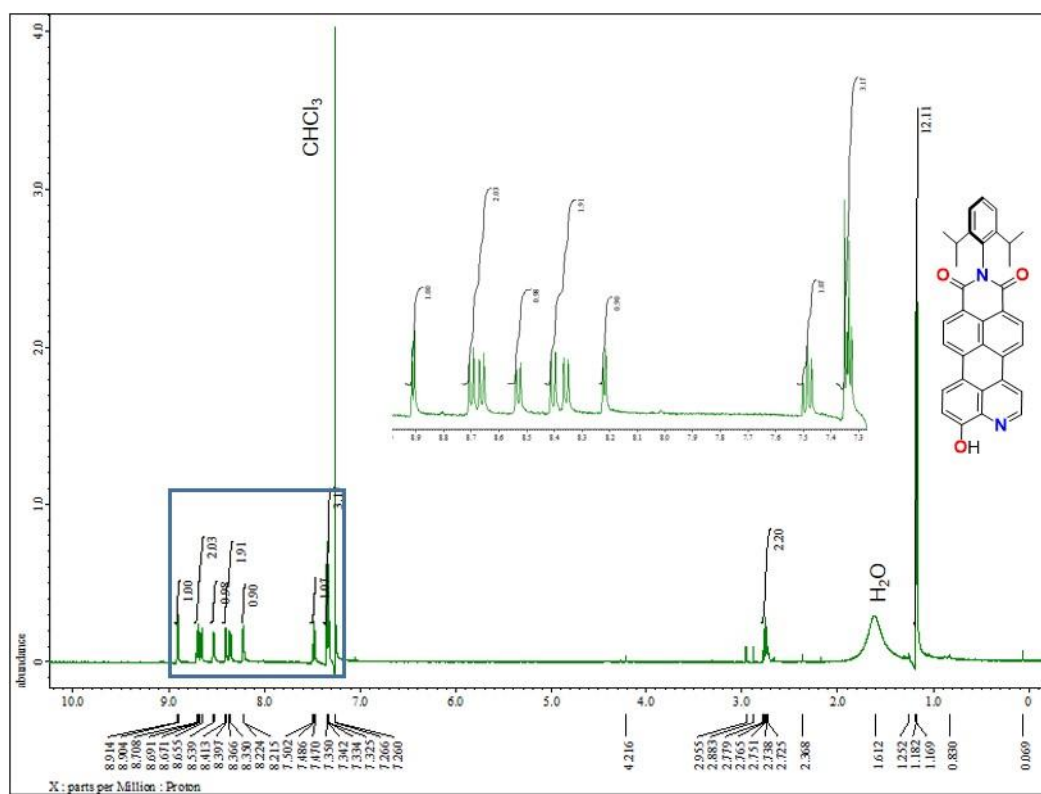
Figure S23. NMR of **L3** (500 MHz, CDCl₃).
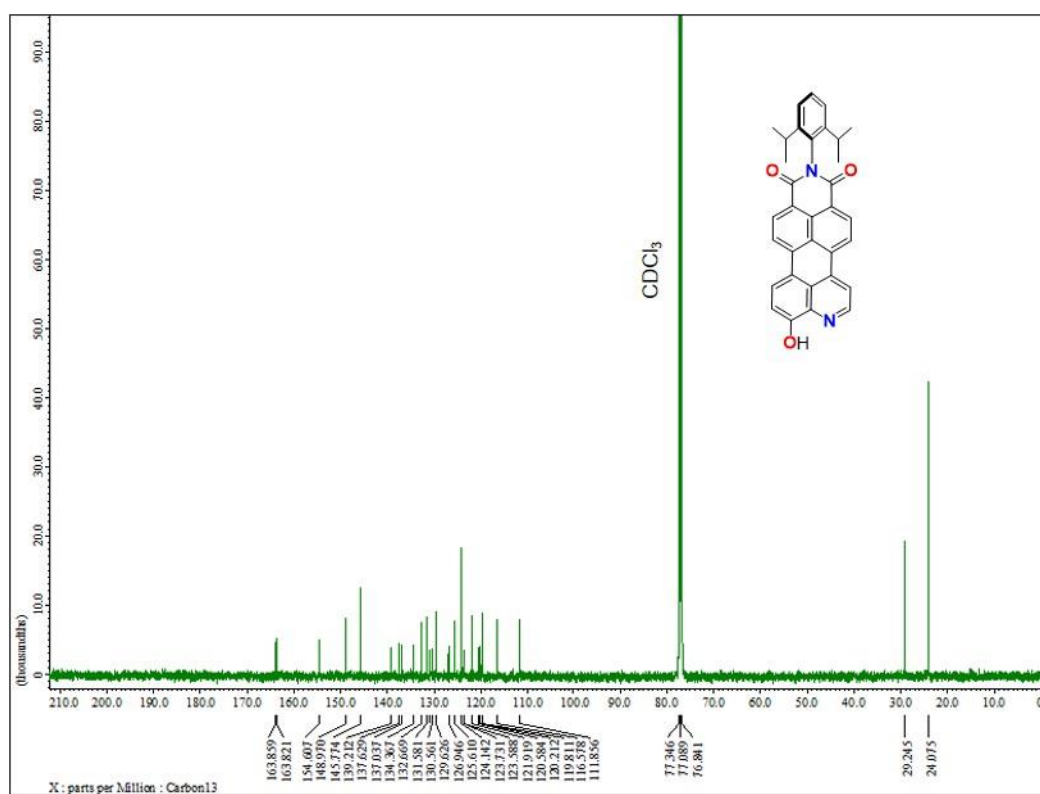
Figure S24. NMR of **L3** (126 MHz, CDCl$_3$).
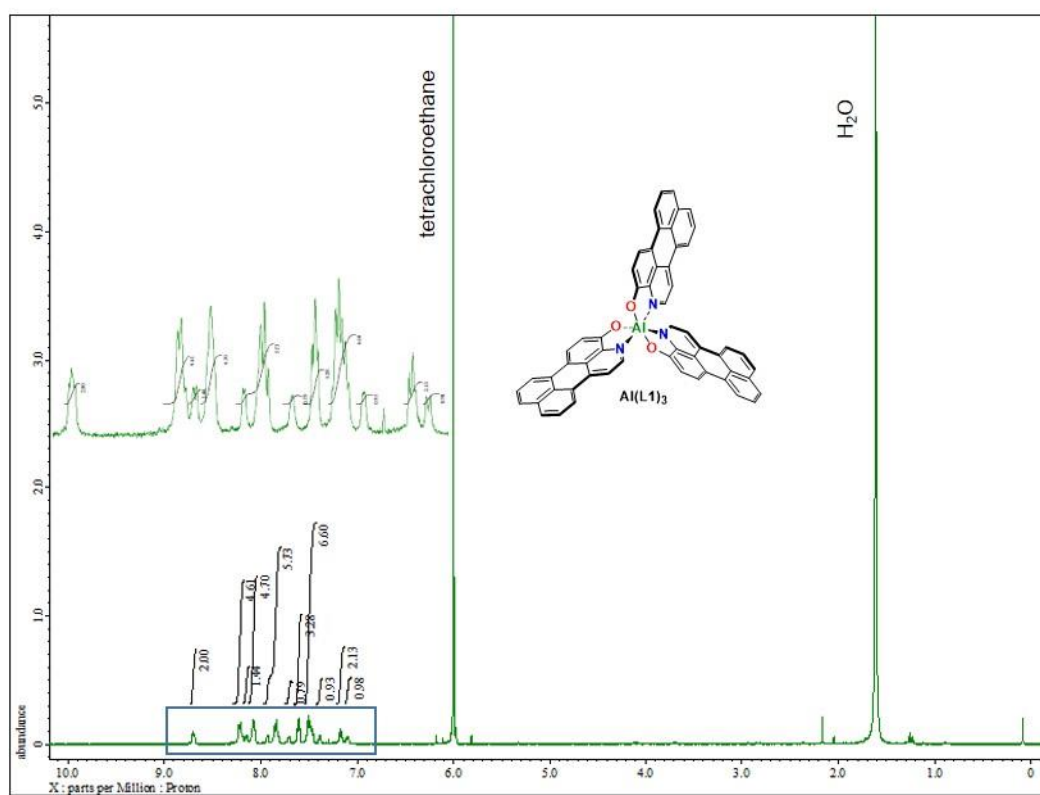
Figure S25. NMR of Al(**L1**)$_3$ (500 MHz, tetrachloroethane-*d$_2$*).
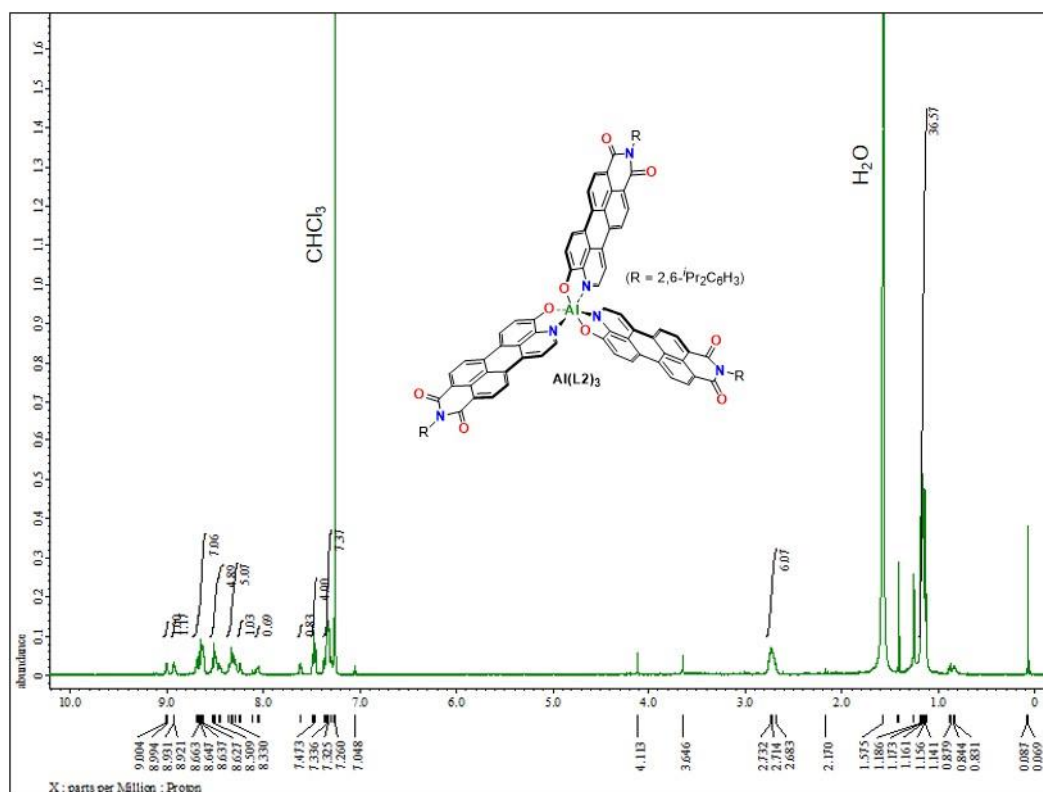
Figure S26. NMR of Al(**L2**)₃ (500 MHz, CDCl₃).

X-Ray Crystallographic Analysis

Crystallographic data were deposited at the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1943910 (**2**), CCDC-1943911 (Al(**L1**)₃), and CCDC-1943912 (**L3**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

X-Ray Crystal Structure Analysis of 2

Single crystals of **2** were obtained by recrystallization from a CH₂Cl₂/hexane solution. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 5888 reflections were measured at the maximum 2θ angle of 50.0°, of which 2318 were independent reflections (R_{int} = 0.0158). The structure was solved by direct methods (*SHELXT*-2014[3]) and refined by the full-matrix least-square on F^2 (*SHELXL*-2014[4]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C₂₀H₁₃NO; FW = 283.31, crystal size 0.15 × 0.08 × 0.07 mm³, Orthorhombic, *Pna*2₁, *a* = 6.9224(7) Å, *b* = 8.8551(9) Å, *c* = 21.377(2) Å, *V* = 1310.4(2) Å³, Z = 4, D_c = 1.436 Mg/m³. The refinement converged to R_1 = 0.0268, wR_2 = 0.0709 ($I > 2\sigma(I)$), GOF = 1.059.
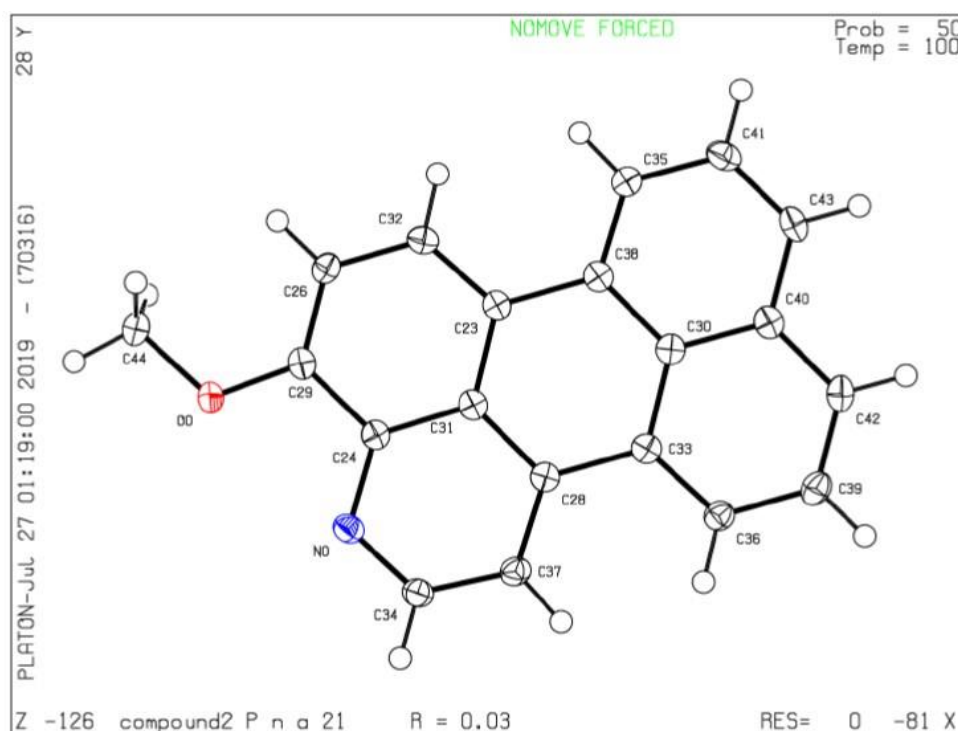
Figure S27. ORTEP drawing of **2** (50% probability for thermal ellipsoids).

X-Ray Analysis of Compound Al(L1)₃

Single crystals of Al(**L1**)₃ were obtained by recrystallization from an ODCB/CH₃CN solution of crude products, which might be contaminated with CH₂Cl₂. Intensity data were collected at 83 K using a diffractometer equipped with an Rigaku Saturn 724 CCD system (RIGAKU, Tokyo, Japan) with synchrotron radiation at a wavelength 0.78224 Å at the SPring-8 beamline BL40XU. A total of 68178 reflections were measured at the maximum 2θ angle of 55.0°, of which 6965 were independent reflections (R_{int} = 0.0681). The structure was solved by direct methods (*SHELXT*-2014[3]) and refined by the full-matrix least-square on F^2 (*SHELXL*-2014[4]). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{57}H_{30}AlN_3O_3·CH_3CN·0.15(CH_2Cl_2)$; FW = 885.61, Trigonal, *R*-3, *a* = 34.0652(3) Å, *c* = 18.1656(2) Å, *V* = 18255.9(4) Å³, Z = 18, D_c = 1.459 mg/m³. The refinement converged to R_1 = 0.0791, wR_2 = 0.2134 ($I > 2\sigma(I)$), GOF = 1.124.

Figure S28. ORTEP drawing of Al(**L1**)$_3$ (50% probability for thermal ellipsoids).
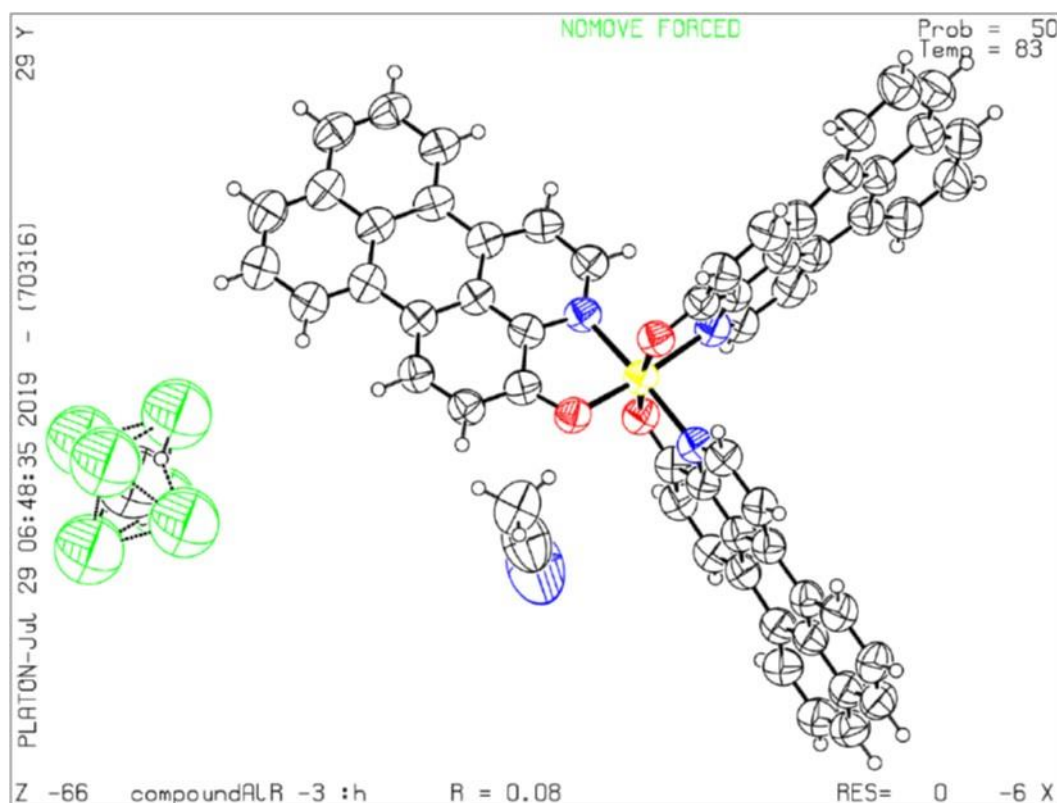
X-Ray Crystal Structure Analysis of L3

Single crystals of **L3** were obtained by recrystallization from a PhCN/MeOH solution. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 22947 reflections were measured at the maximum 2θ angle of 50.0°, of which 8093 were independent reflections (R_{int} = 0.0403). The structure was solved by direct methods (*SHELXT*-2014[3]) and refined by the full-matrix least-square on F^2 (*SHELXL*-2014[4]). The azaperylene moiety in each **L3** molecules were disordered. The occupancies of the disordered moieties, (N2A-C17-C16A-O3A-H3A) and (N2B-C17-C16B-O3B-H3B), were refined to be 0.62 and 0.38, respectively. Similarly, another disordered moieties, (N4A, C50, C49A, O6A, H6A) and (N4B, C50, C49B, O6B, H6B), were refined to be 0.61 and 0.39, respectively. All non-hydrogen atoms except for minor parts of disordered hydroxyl groups were refined anisotropically. The C16B, C49B, N2B, and O6B were restrained using DFIX instruction. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{66}H_{52}N_4O_6$; FW = 997.11, crystal size 1.00 × 0.15 × 0.14 mm^3, Orthorhombic, *Pca*2$_1$, *a* = 19.195(3) Å, *b* = 8.5030(13) Å, *c* = 30.611(5) Å, *V* = 4996.2(13) Å^3, Z = 4, D_c = 1.326 Mg/m^3. The refinement converged to R_1 = 0.0455, wR_2 = 0.1057 ($I > 2\sigma(I)$), GOF = 1.013.
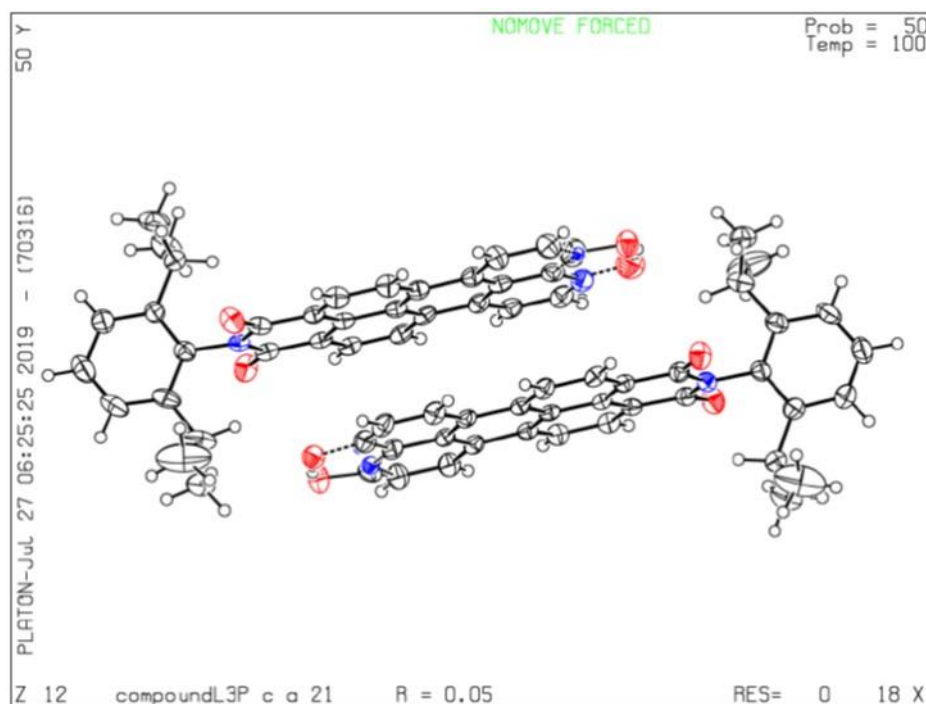
Figure S29. ORTEP drawing of **L3** (50% probability for thermal ellipsoids).

Photophysical Properties
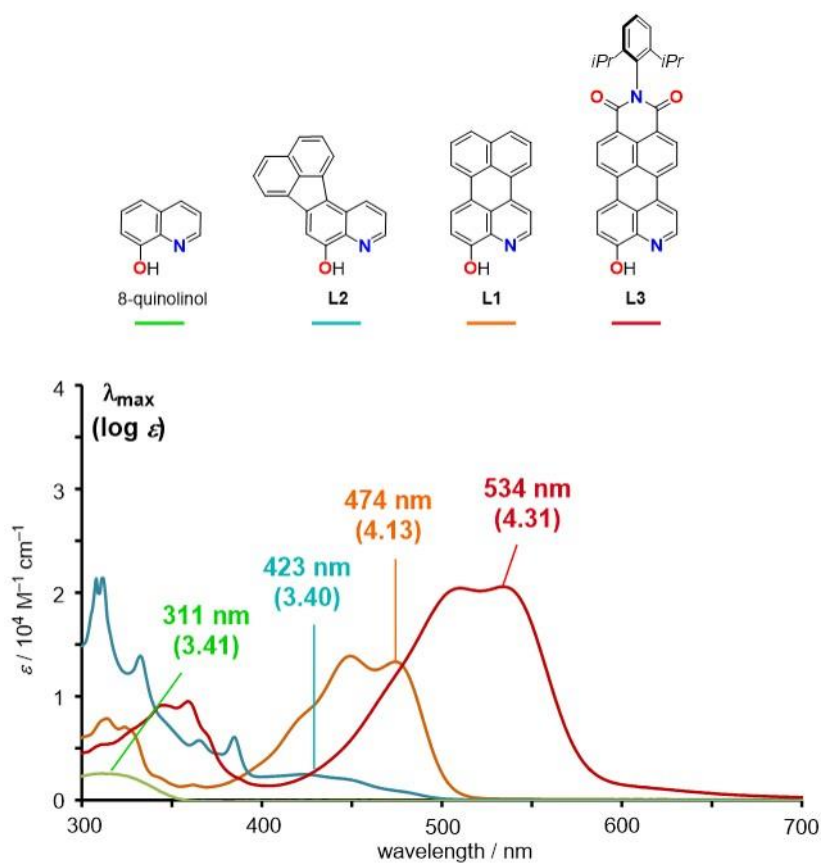
Figure S30. UV-vis absorption spectra of 8-quinolinol and **L1-L3** in CH_2Cl_2.
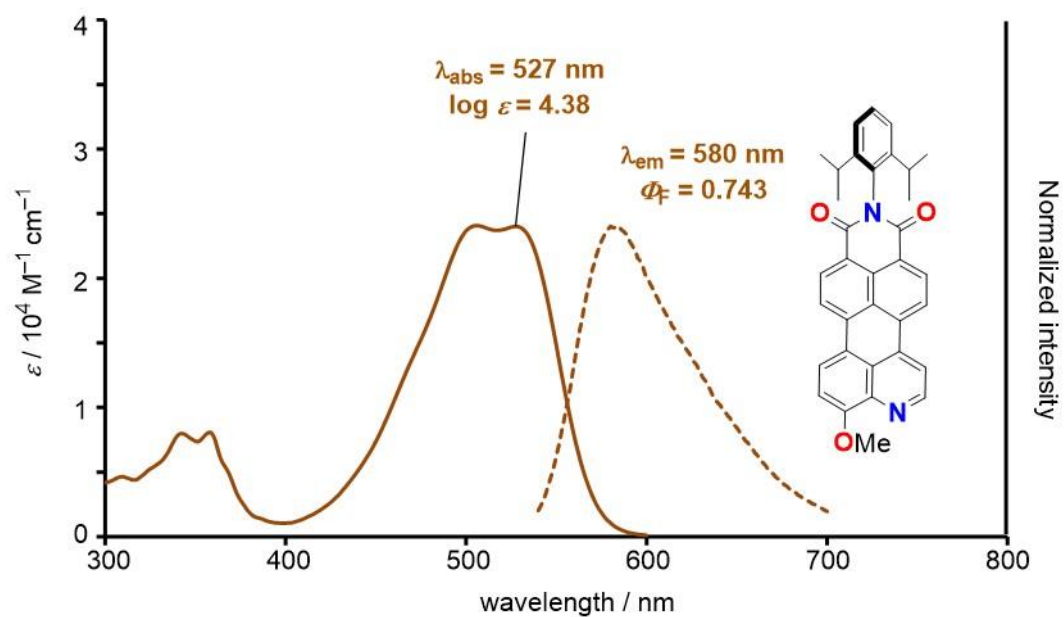
Figure S31. Photochemical properties of **2** in CH₂Cl₂.
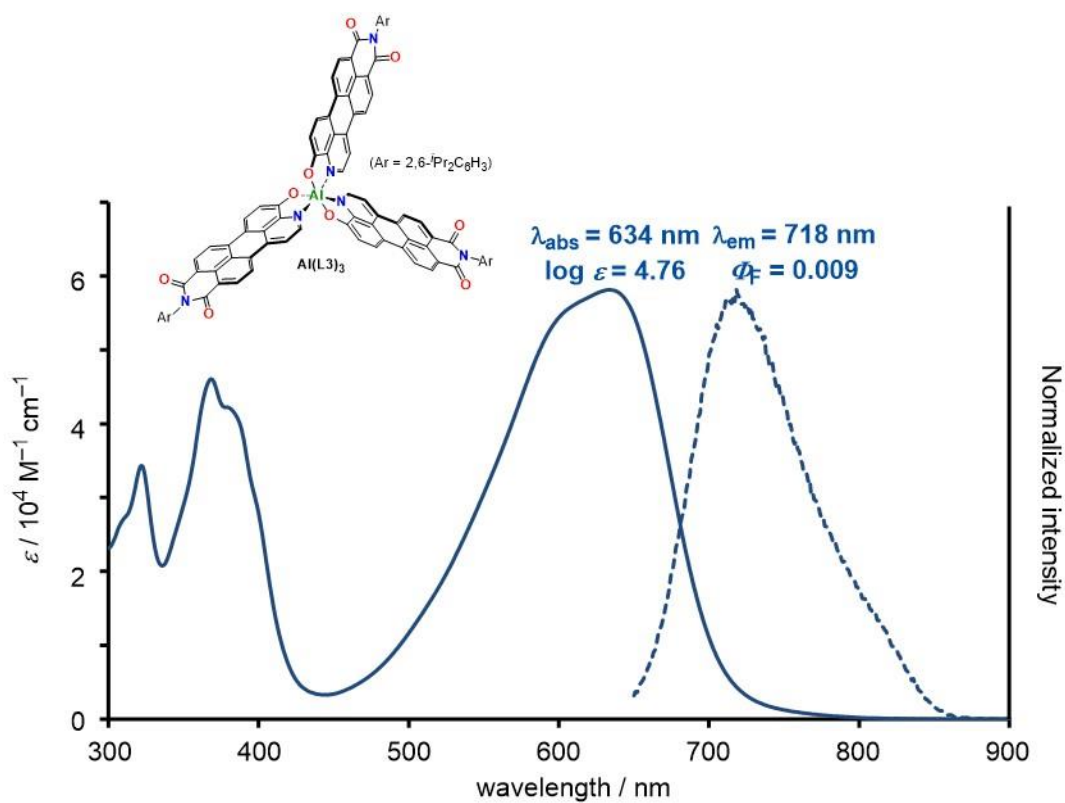
Figure S32. Photochemical properties of Al(**L3**)₃ in CH₂Cl₂.

Electrochemical Properties
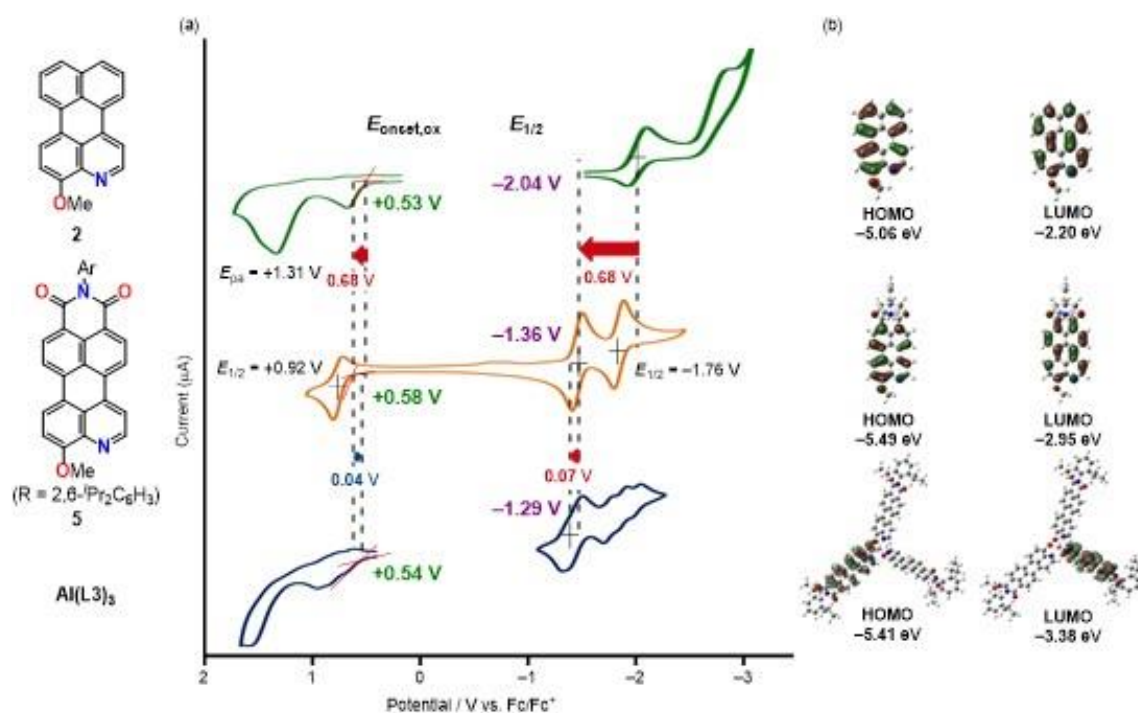
Figure S33. (**a**) Cyclic voltammograms in CH₂Cl₂ with 0.1 M TBAPF₆ and (**b**) the results of DFT calculations (B3LYP/6-31G*).

DFT Calculations
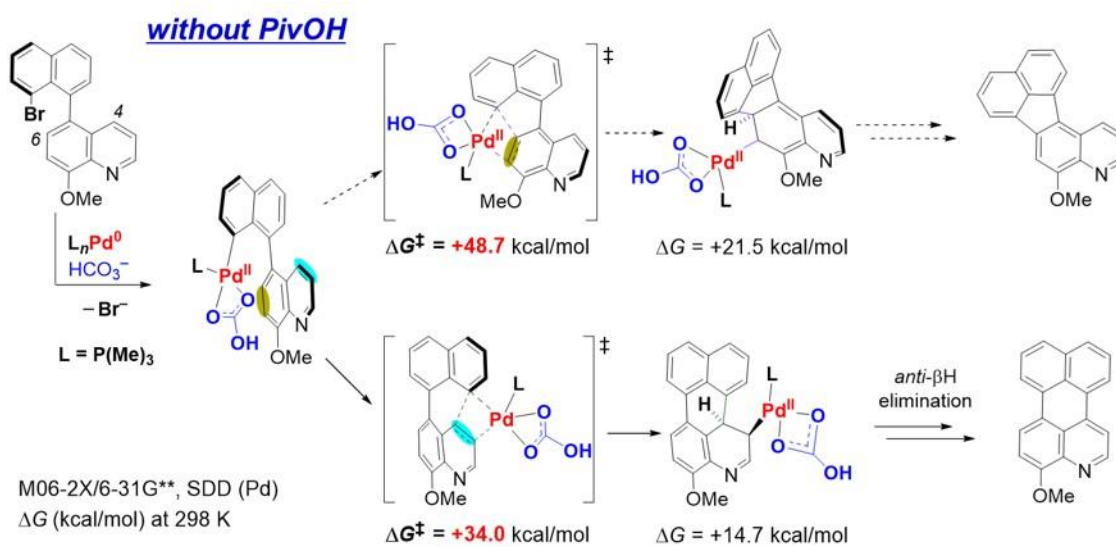
Figure S34. Calculated barriers for the Pd-catalyzed direct C−H arylation by Heck-type mechanism.
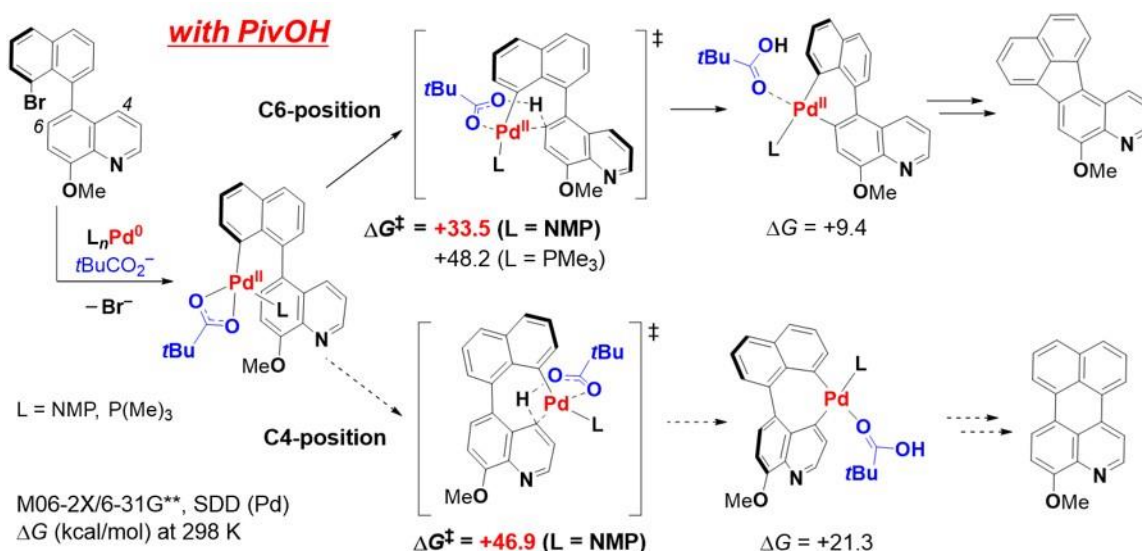
Figure S35. Calculated barriers for the Pd-catalyzed direct C−H arylation by CMD mechanism.

Optimized Geometries

M06-2X/ SDD(for Pd), 6-31G**(for C, N, O, P, H) level of theory

Transition-States I

1 imaginary frequency (−404.1759 cm^{-1})
Charge = 0 Multiplicity = 1
C, 0, −4.0371653967, −2.7897205639, 1.0406341642
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 C, 0, −1.8308145556, −2.0788707553, 0.266955307
 C, 0, −2.4327527556, −0.9220612415, −0.3382552578
 C, 0, −3.8499652104, −0.7651739256, −0.2640357994
 C, 0, −4.6300498828, −1.698642932, 0.4622784689
 C, 0, −1.6884519409, 0.0282585921, −1.1138207582
 C,0,−2.3580867404,0.9680806526,−1.8762797397
 C, 0, −3.7599288876, 1.127847111, −1.7794876484
 C, 0, −4.4836729636, 0.2956894962, −0.968691391
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 C, 0, 0.2728053043, −2.9967163924, 1.258267865
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 C, 0, 2.4546692498, −2.5027250561, 0.3399983393
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 C, 0, 0.4349240972, −1.7240474087, −0.7704519823
 N, 0, 2.6736823202, −1.1036566783, −1.6039666071
 C, 0, 2.1172072495, −0.2879733144, −2.436136118
 C, 0, 0.69204808, −0.0862676472, −2.5796485151
 C, 0, −0.1936617454, −0.9740920183, −1.8842574566
 Pd, 0, 0.1531015778, 1.0636380823, −0.7504285733
 P, 0, −0.5546487249, 1.786963199, 1.3730405603
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 C, 0, −0.4088785798, 0.4450142399, 2.6066547125
 C, 0, −2.3119841666, 2.300050176, 1.4962352249
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 C, 0, 2.7358264676, 1.7693970574, 0.2305395775

O, 0, 3.9807383571, 2.3062667277, 0.1319627847
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Transition-States II

1 imaginary frequency (−571.4092 cm^{-1})
Charge = 0 Multiplicity = 1
C, 0, 3.4949002196, 3.4789036617, 1.1812165184
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C, 0, 2.6384536624, −3.9465409322, 1.675476643
O, 0, 1.4426499146, −1.9166734188, 1.9681128136
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H, 0, 3.7689440709, −2.4873832644, 2.828717805
H, 0, 4.4122450387, −2.7642530678, 1.2017654278
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H, 0, 3.3513798561, −4.5673953449, −0.2808437942
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H, 0, 2.6822361557, −5.3221278099, 3.3500306399
H, 0, 1.0621219495, −5.0839835101, 2.6694638053
H, 0, 1.7932774481, −3.8160816996, 3.6763252085
H, 0, 0.9450340781, −1.0291833482, 1.4881926723

References for Experimental Section

1.   Qin, Y.; Kiburu, I.; Shah, S.; Jäkle, S. *Org. Lett.* **2006**, *8*, 5227–5230.
2.   Kim, H.N.; Puhl, L.; Nolde, F.; Li, C.; Chen, L.; Basché, T.; Müllen, K. *Chem. Eur. J.* **2013**, *19*, 9160–9166.
3.   Sheldrick, G.M. *Acta Cryst.* **2015**, *A71*, 3–8.
4.   Sheldrick, G.M. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.