Supporting Information

Efficient Approach To Construct Unsymmetrical Biaryls through Oxidative Coupling Reactions of Aromatic Primary Alcohols and Arylboronic Acids with a Rhodium Catalyst

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General Information. The starting materials were synthesized and purified according to the literature procedures.[1-4] Other chemicals and reagents were obtained from commercial sources. All reactions were monitored by analytical thin layer chromatography on 0.20 mm Yantai Huagong silica gel plates and spots were detected by UV-absorption. Silica gel (200-300 mesh) (from Yantai Huagong Chem. Company, Ltd.) was used for flash chromatography.

NMR spectra were obtained on 400 MHz spectrometer with $CDCl_3$ as solvent. The chemical shifts are reported in ppm relative to $CDCl_3$ (δ = 7.26) for ^1H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0) for ^{13}C NMR. For ^{19}F NMR, the (trifluoromethyl)benzene was used as an external standard. Coupling constants (J) are quoted in Hz for ^1H. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Conversions were obtained by ^1H NMR analysis of the sample. NMR data of known compounds is in agreement with literature values. Infrared spectra were recorded on FT-IR spectrophotometer. Elemental analyses were performed by the Elemental Analysis Section of Tianjin University.

IR spectra for the reaction mixture

To an oven-dried screwed vial were added benzo[h]quinoline-10-ylmethanol (0.3 mmol), $Rh(PPh_3)_3Cl$ (19.5 mg) and xylene 3 mL under air atmosphere. The mixture was vigorously stirred at 130 ^oC for 5 h. Organic solvents were removed in vacuo, and then the residue was detected by IR (Figure S1) and an absorption peak of Rh-CO was found at 1976 cm^{-1}.[5]

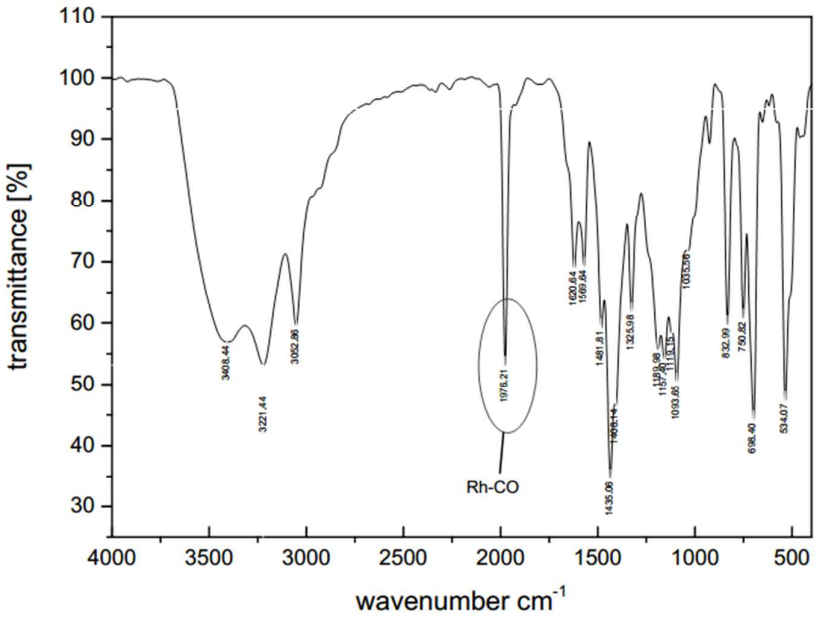

Figure S1. **IR for the reaction mixture**

REFERENCES

[1] Hamada, Y.; Takeuchi, I. *J. Org. Chem.* **1977**, 42, 4209–4213.

[2] Kochi, T.; Urano, S.; Seki, H.; Mizushima, E.; Sato, M.; Kakiuchi, F. *J. Am. Chem. Soc.* **2009**, 131, 2792–2793.

[3] Blanck, S.; Cruchter, T.; Vultur, A.; Riedel, R.; Harms, K.; Herlyn, M.; Meggers, E. *Organometallics* **2011**, 30, 4598–4606.

[4] Liu, C.; Yang, W. *Chem. Comm.* **2009**, 6267–6269.

[5] Ginsberg, A. P.; Edward Lindsell, W.; McCullough, K. J.; Sprinkle, C. R.; Welch, A. J. *J. Am. Chem. Soc.* **1986,** 108, 403-416.

^{1}H NMR and ^{13}C NMR Spectra of 1aa

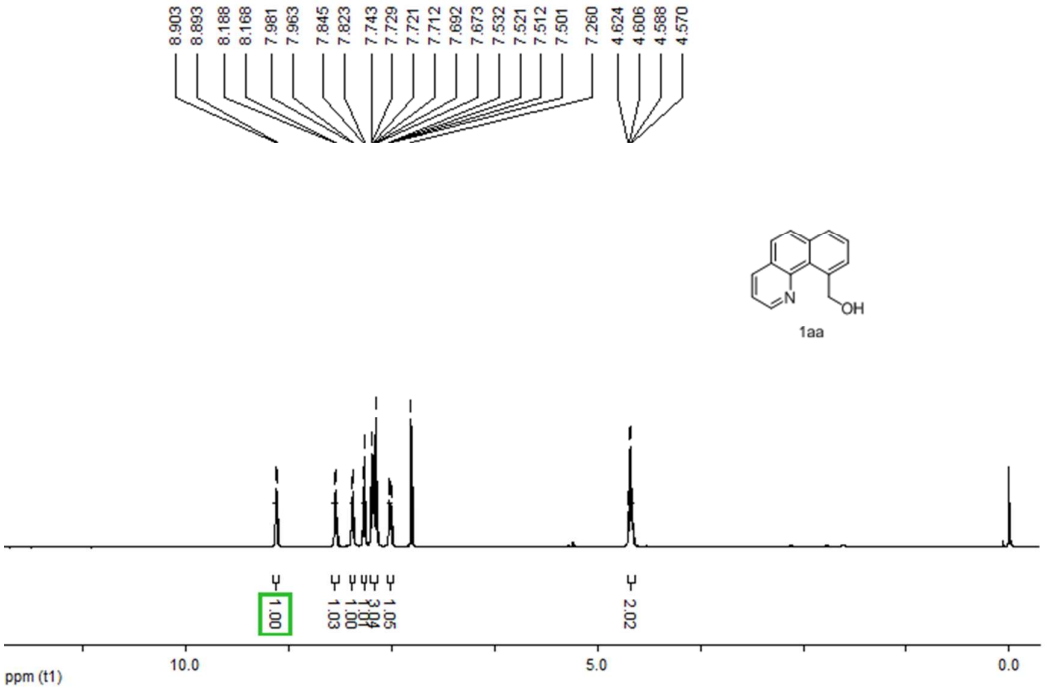

Figure S2. ^{1}H NMR for compound 1aa

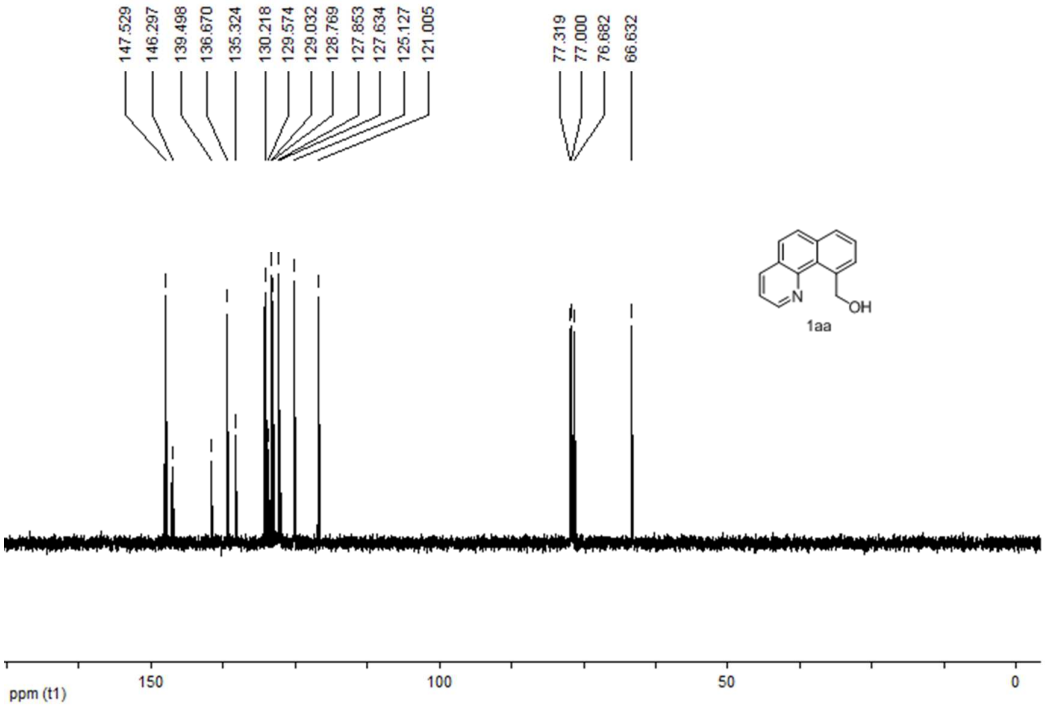

Figure S3. ^{13}C NMR for compound 1aa

^{1}H NMR and ^{13}C NMR Spectra of 1ba

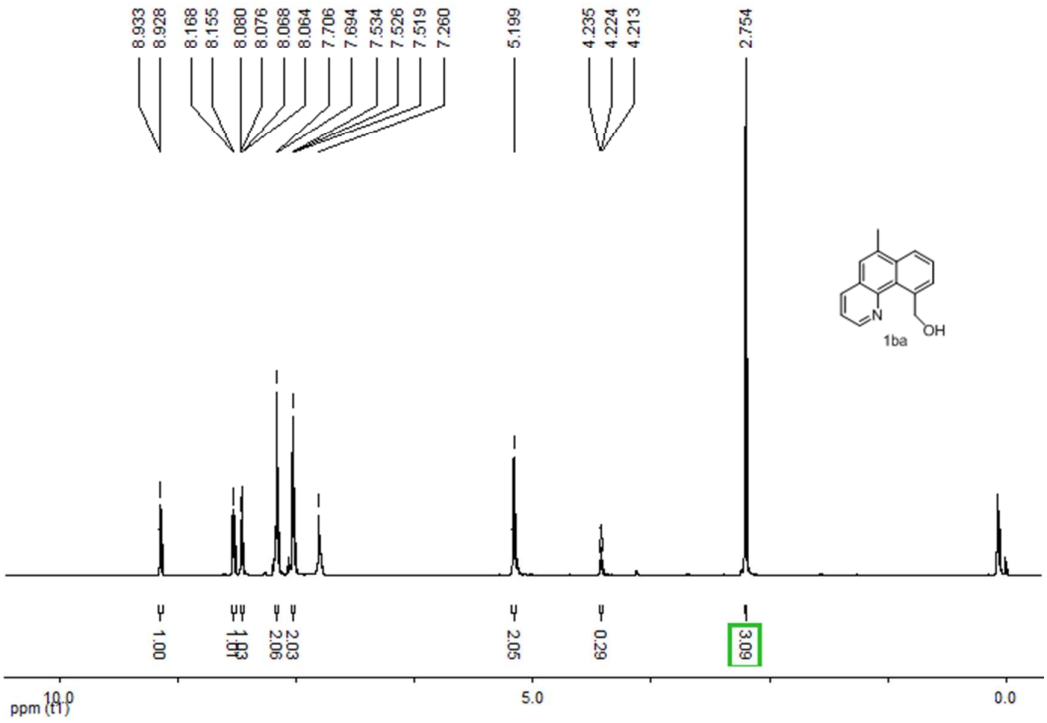

Figure S4. ^{1}H NMR for compound 1ba

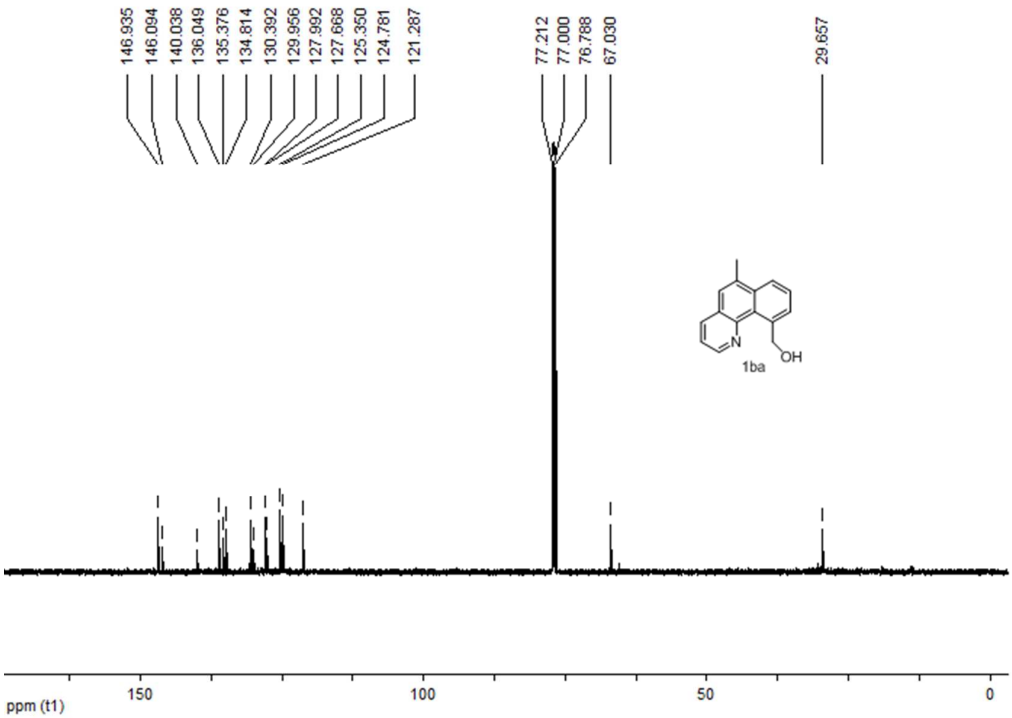

Figure S5. ^{13}C NMR for compound 1ba

^{1}H NMR and ^{13}C NMR Spectra of 1bb

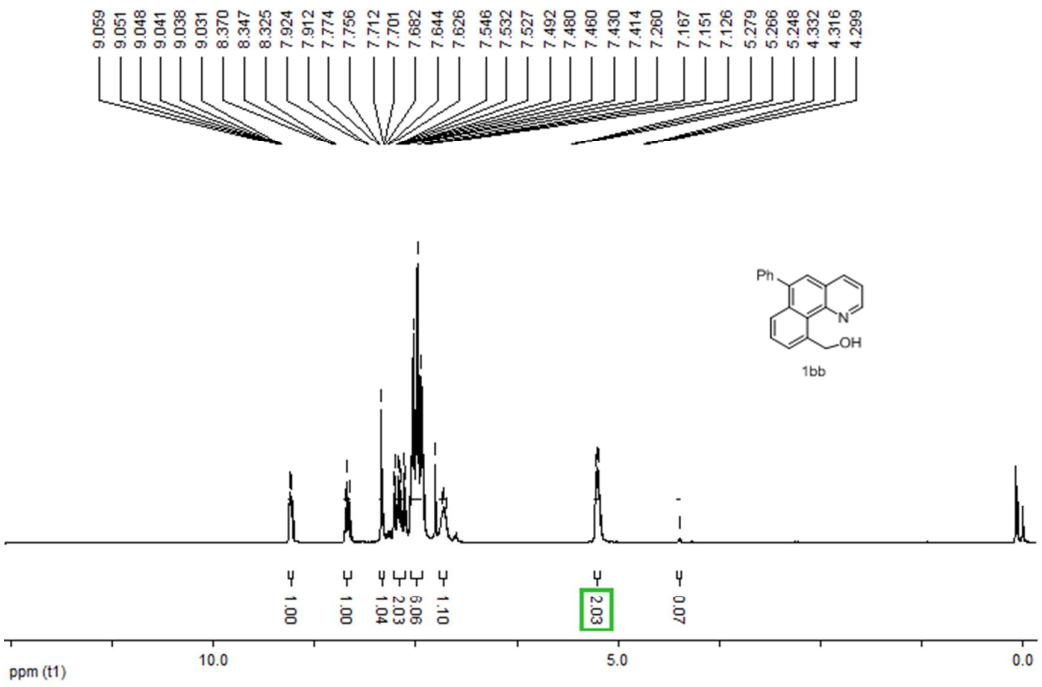

Figure S6. ^{1}H NMR for compound 1bb

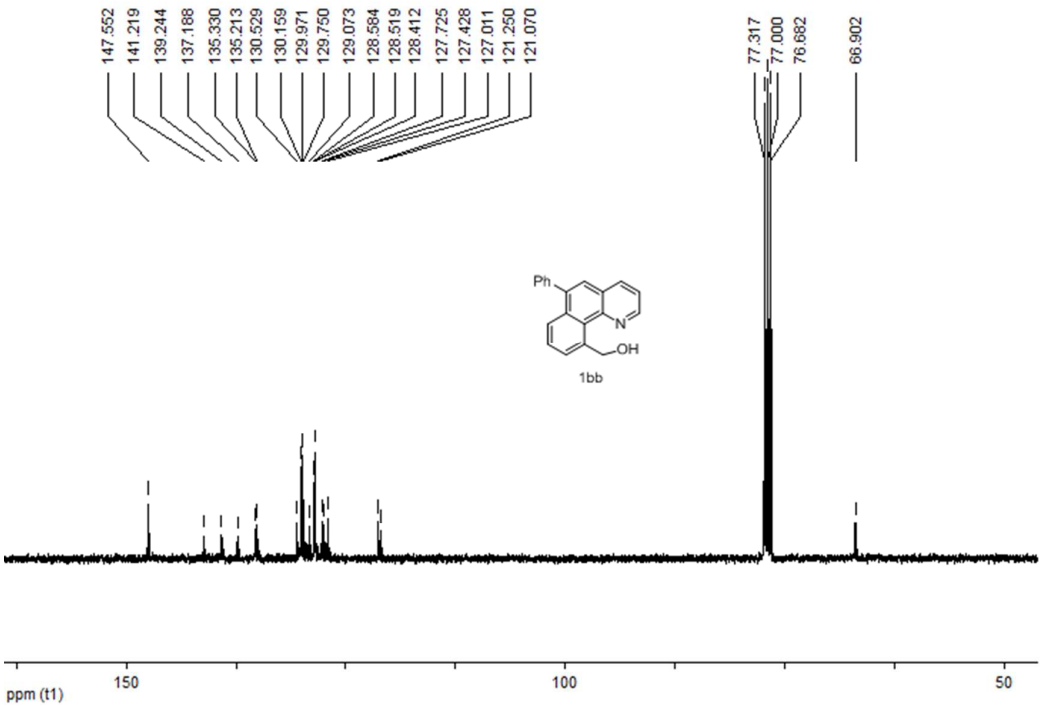

Figure S7. ^{13}C NMR for compound 1bb

^{1}H NMR and ^{13}C NMR Spectra of 1bc

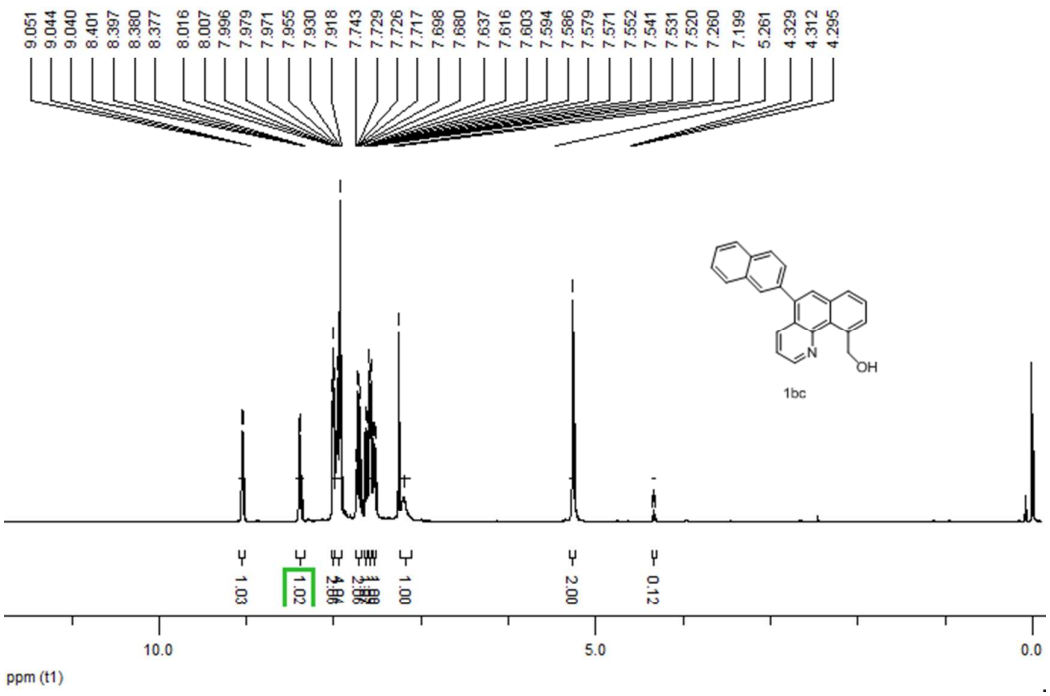

Figure S8. ^{1}H NMR for compound 1bc

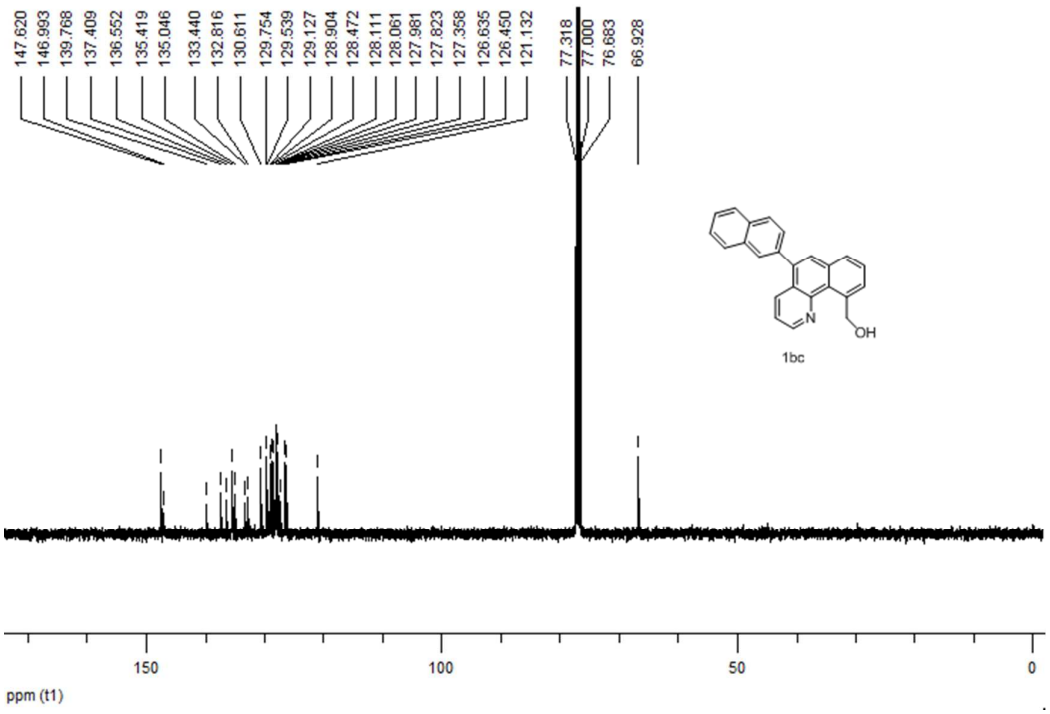

Figure S9. ^{13}C NMR for compound 1bc

^{1}H NMR and ^{13}C NMR Spectra of 1bd

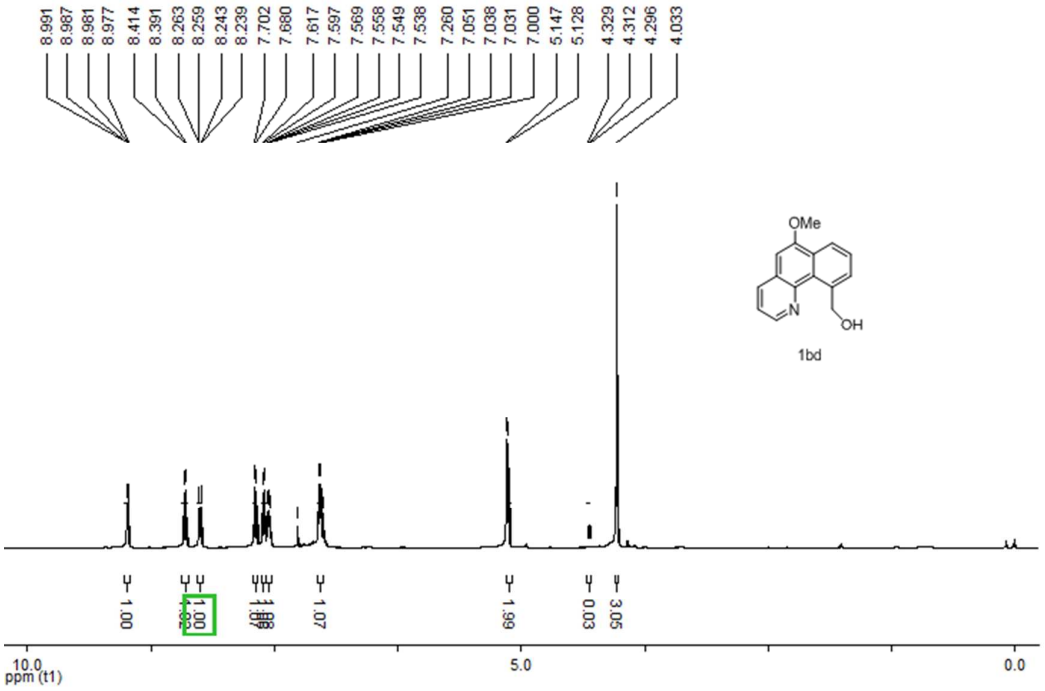

Figure S10. ^{1}H NMR for compound 1bd

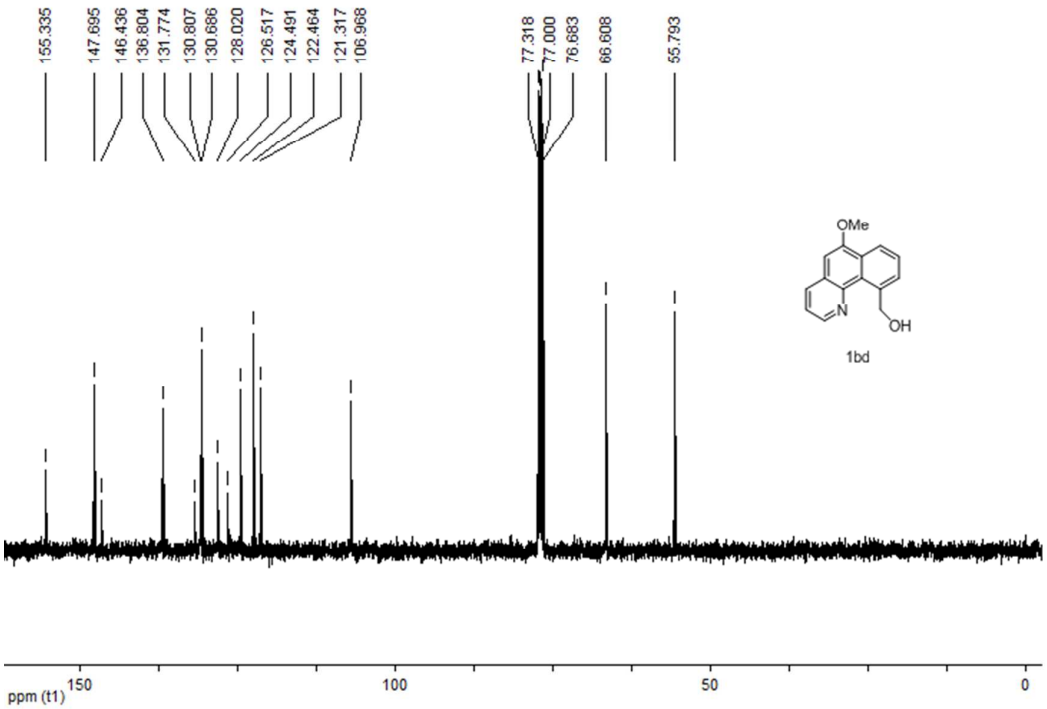

Figure S11. ^{13}C NMR for compound 1bd

^{1}H NMR and ^{13}C NMR Spectra of 1be

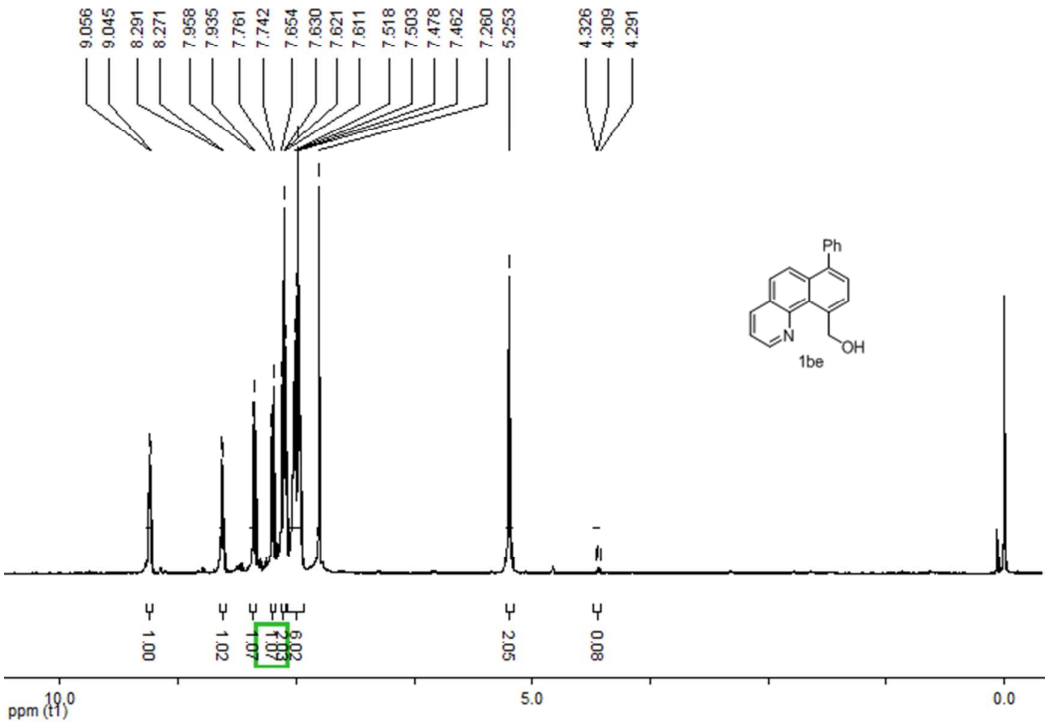

Figure S12. ^{1}H NMR for compound 1be

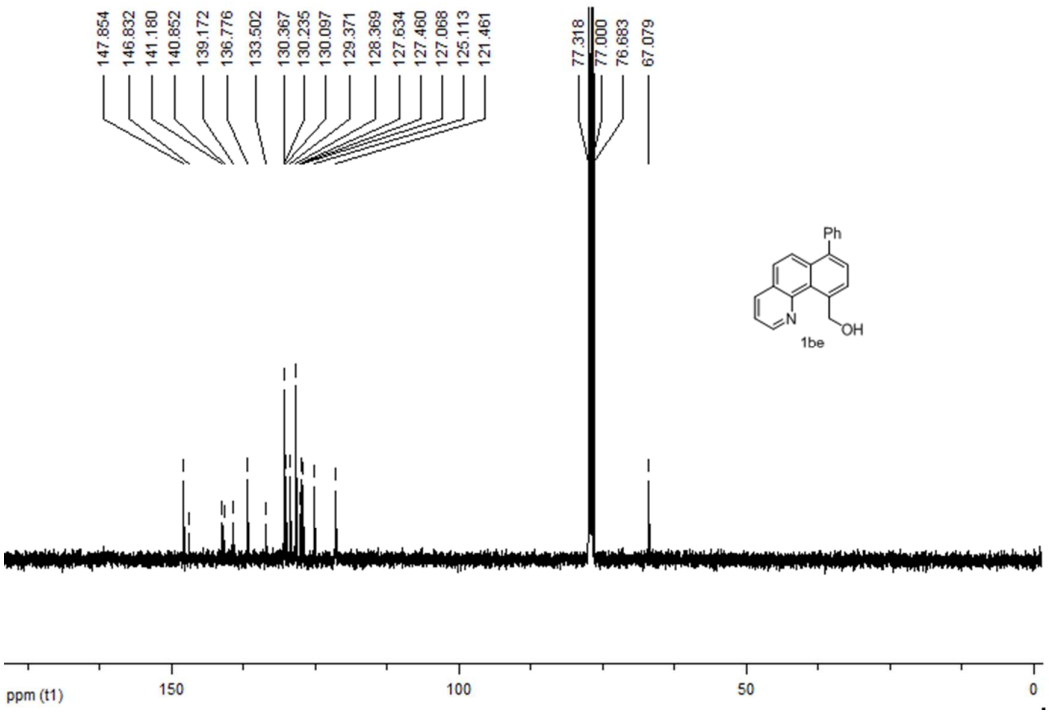

Figure S13. ^{13}C NMR for compound 1be

^{1}H NMR and ^{13}C NMR Spectra of 1bf

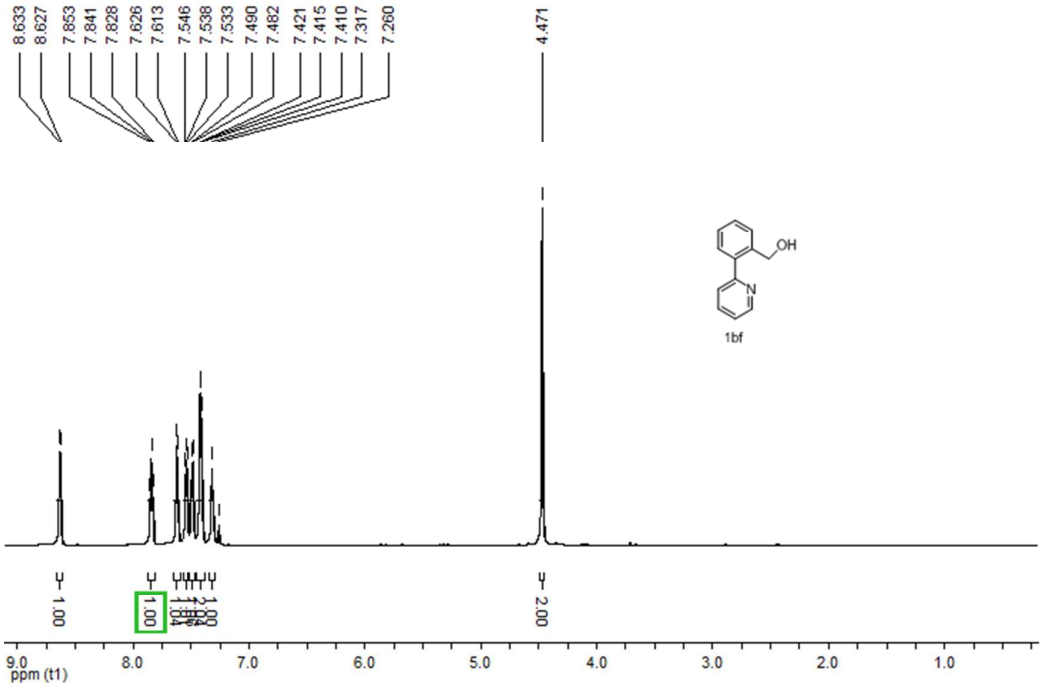

Figure S14. ^{1}H NMR for compound 1bf

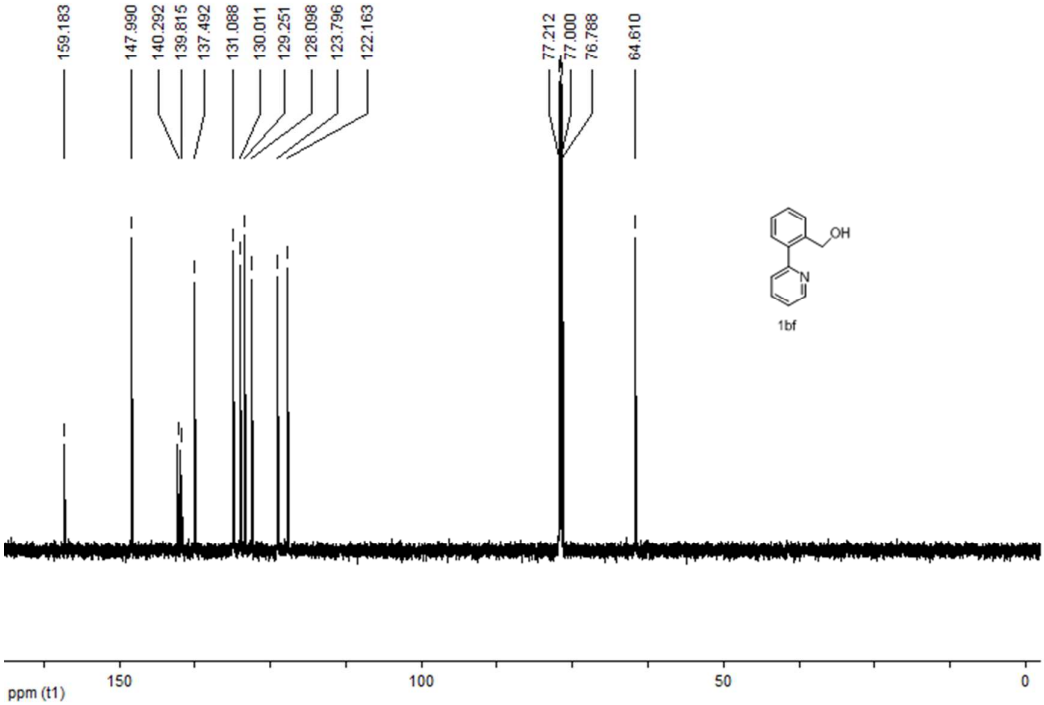

Figure S15. ^{13}C NMR for compound 1bf

^{1}H NMR and ^{13}C NMR Spectra of 1c

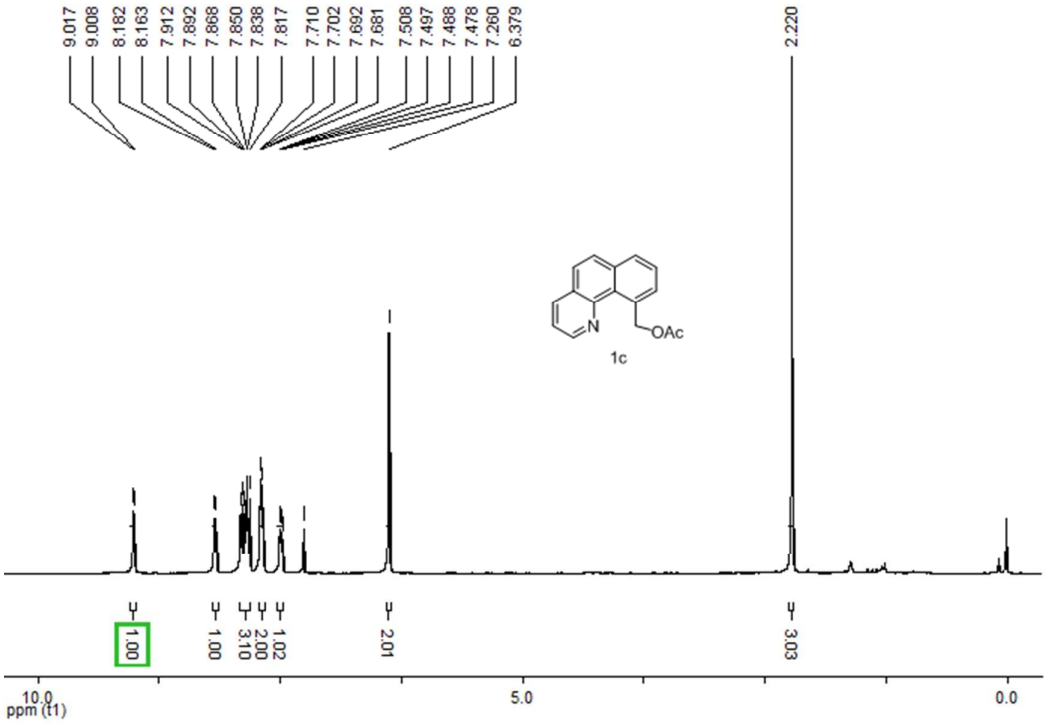

Figure S16. ^{1}H NMR for compound 1c

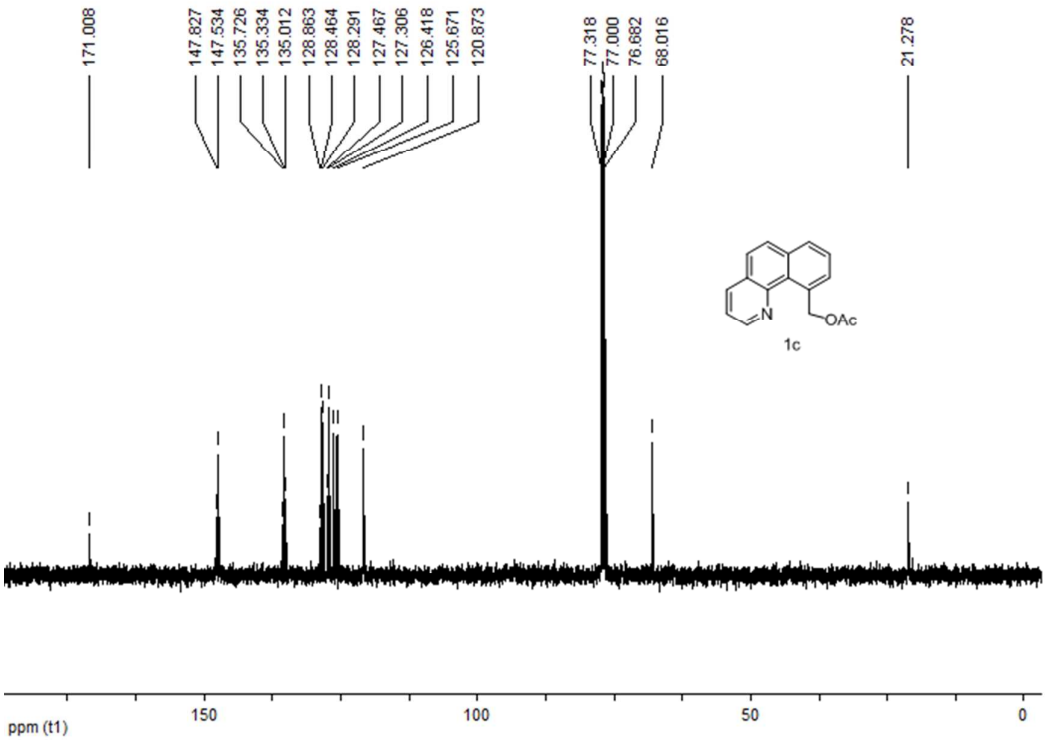

Figure S17. ^{13}C NMR for compound 1c

^{1}H NMR and ^{13}C NMR Spectra of 1d

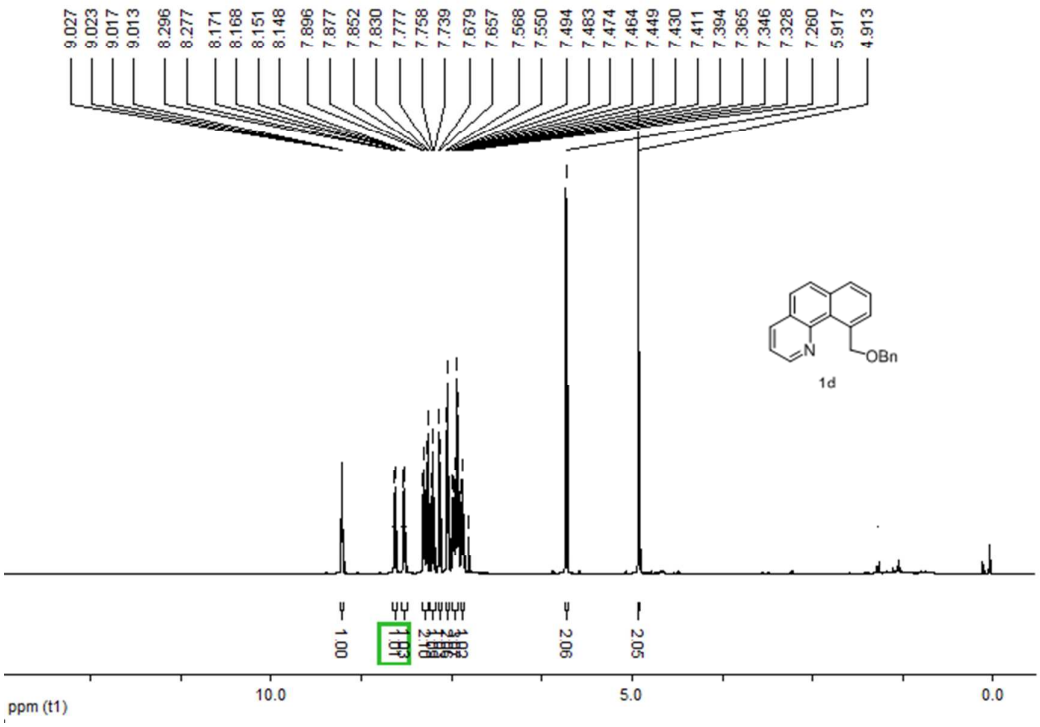

Figure S18. ^{1}H NMR for compound 1d

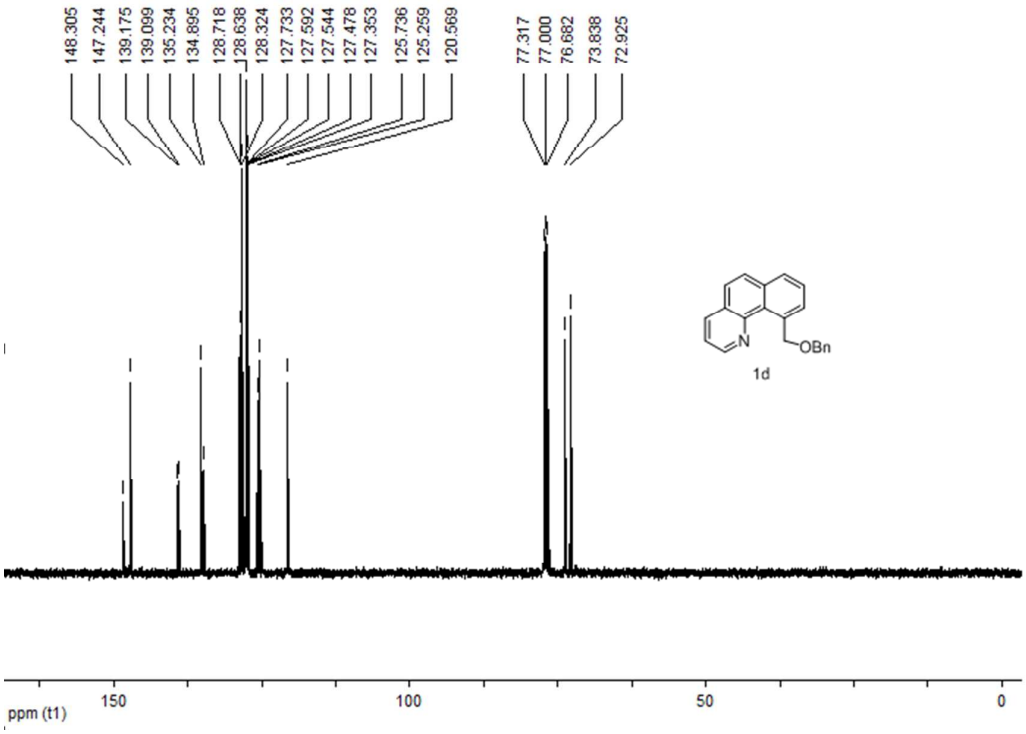

Figure S19. ^{13}C NMR for compound 1d

^{1}H NMR and ^{13}C NMR Spectra of 1aa`

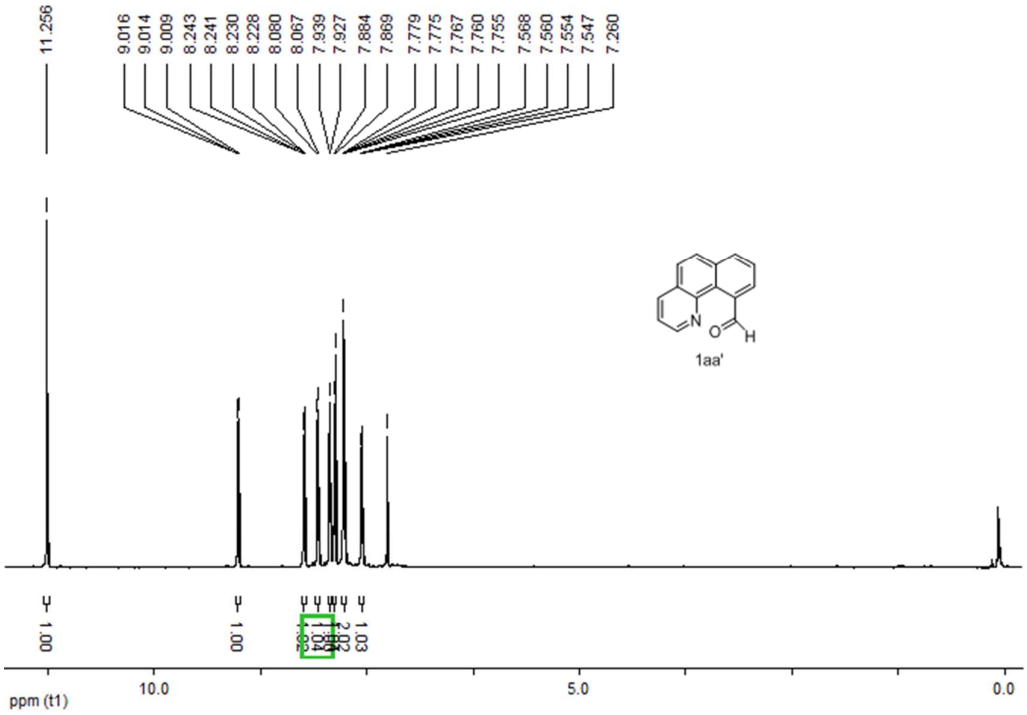

Figure S20. ^{1}H NMR for compound 1aa'

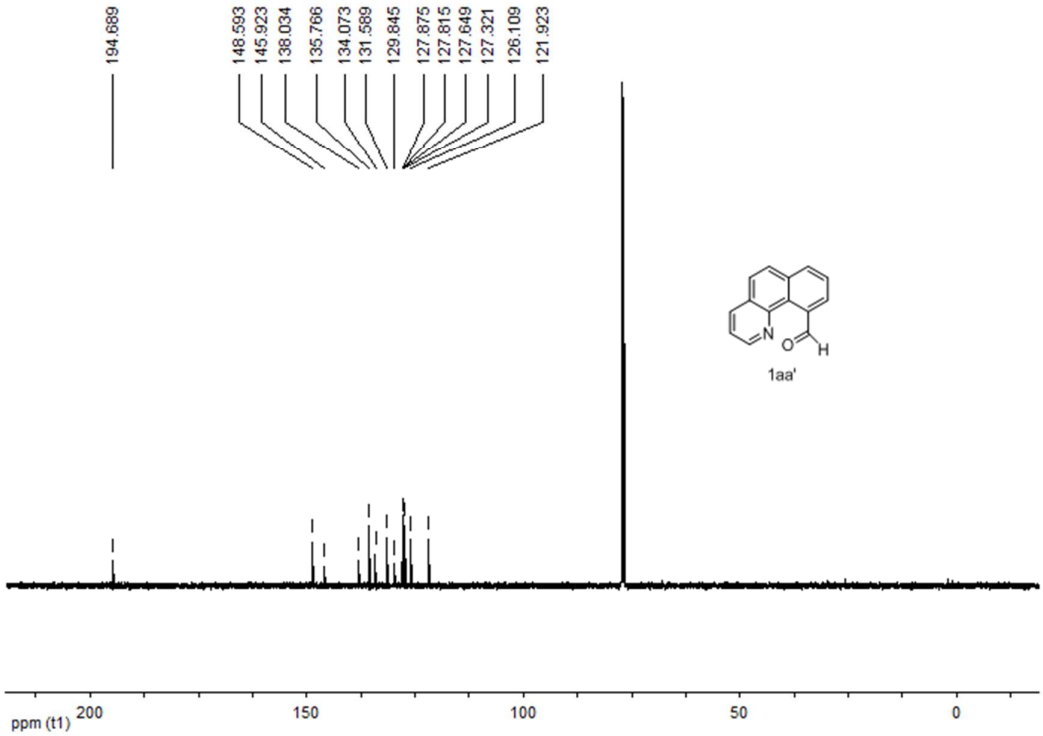

Figure S21. ^{13}C NMR for compound 1aa'

Experimental Procedure for Rhodium-catalyzed Direct Arylation with Organoboron Compounds via Primary alcohols

To an oven-dried screwed vial were added primary alchohol (0.1 mmol), substituted phenylboronic acid (0.2 mmol), copper (I) chloride (9.9 mg, 0.1 mmol), $Rh(PPh_3)_3Cl$ (6.5 mg, 0.007 mmol) and xylene 1 mL under air atmosphere. The mixture was vigorously stirred at 130 ^oC to the end of the reaction. Organic solvents were removed in vacuo, and then the residue was purified by a silica gel column chromatography to give the desired product.

^{1}H NMR and ^{13}C NMR Spectra of 3aa

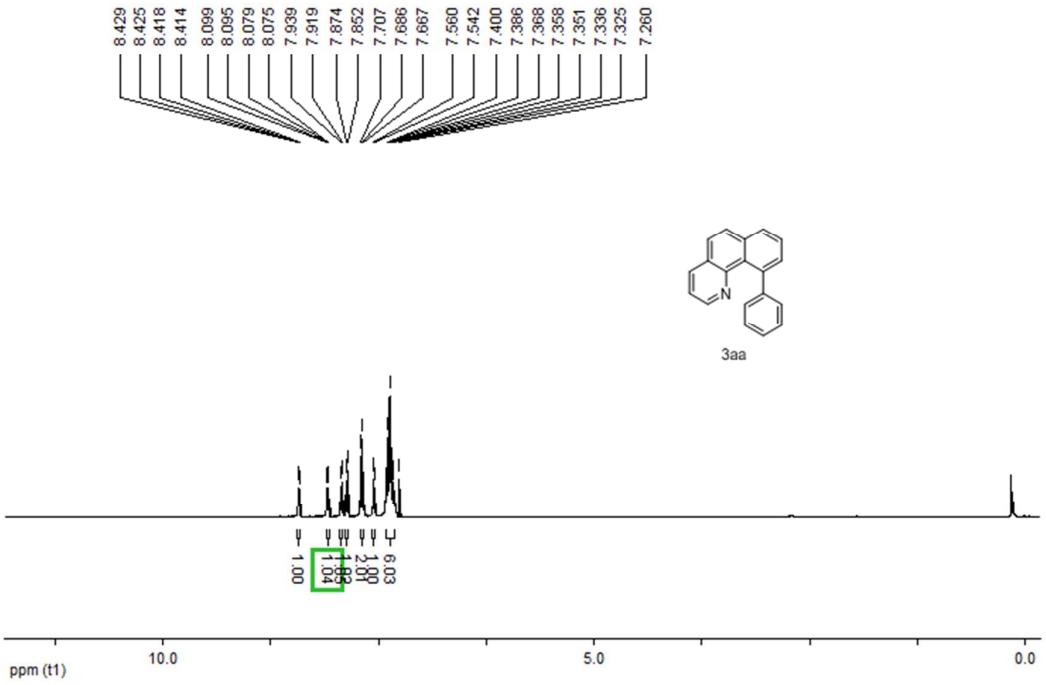

Figure S22. ^{1}H NMR for compound 3aa

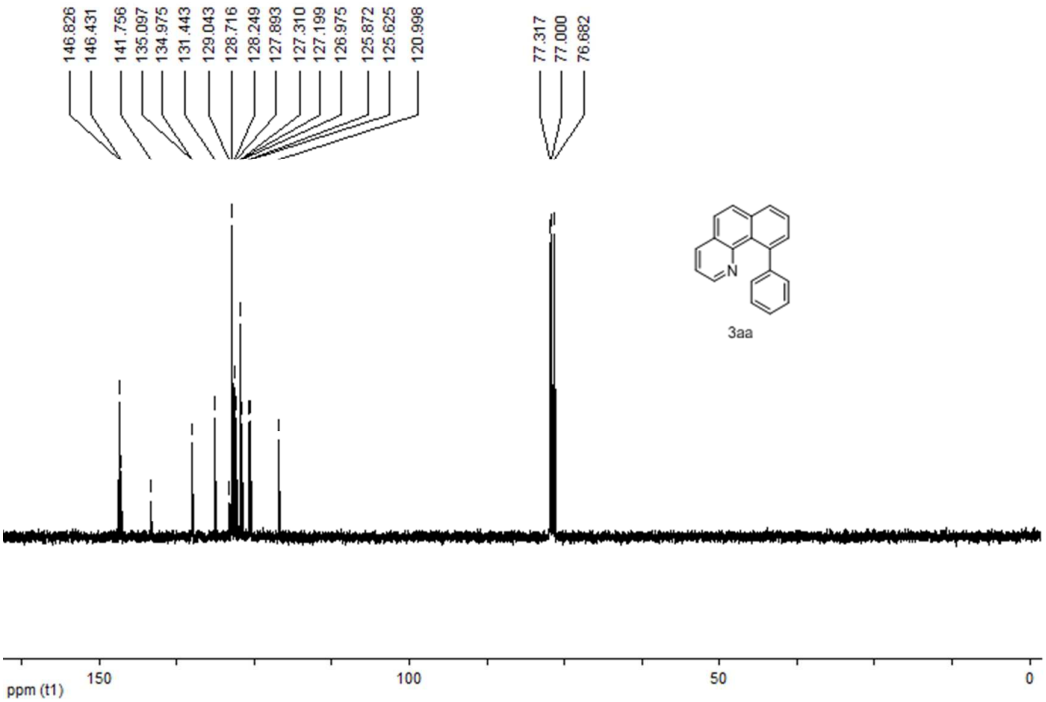

Figure S23. ^{13}C NMR for compound 3aa

^{1}H NMR and ^{13}C NMR Spectra of 3ab

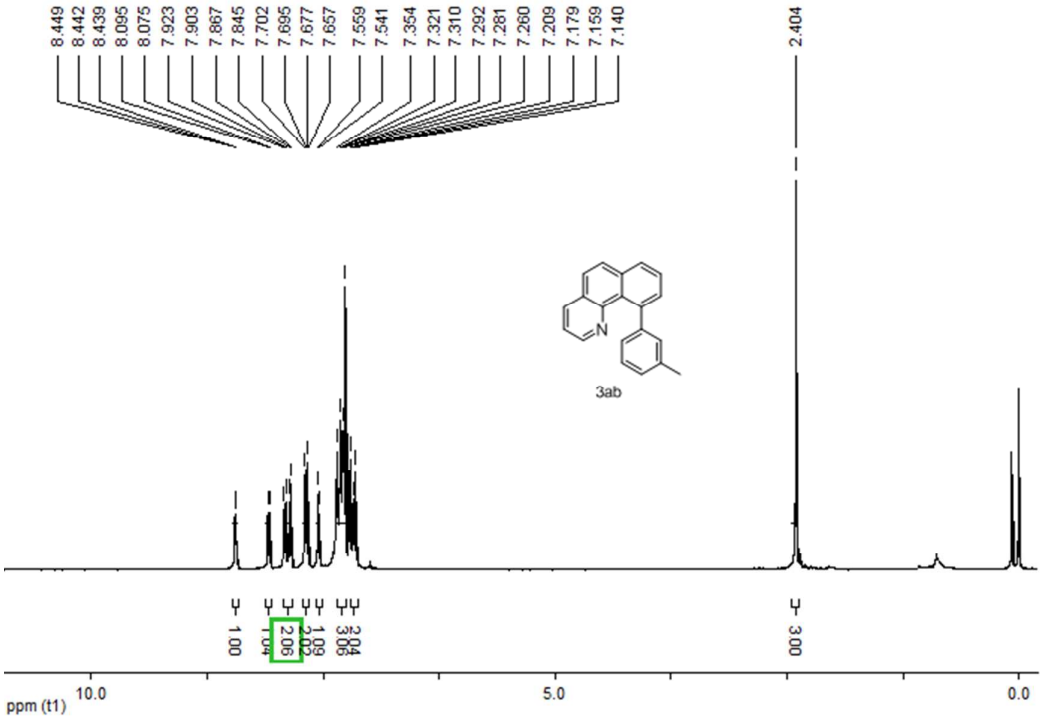

Figure S24. ^{1}H NMR for compound 3ab

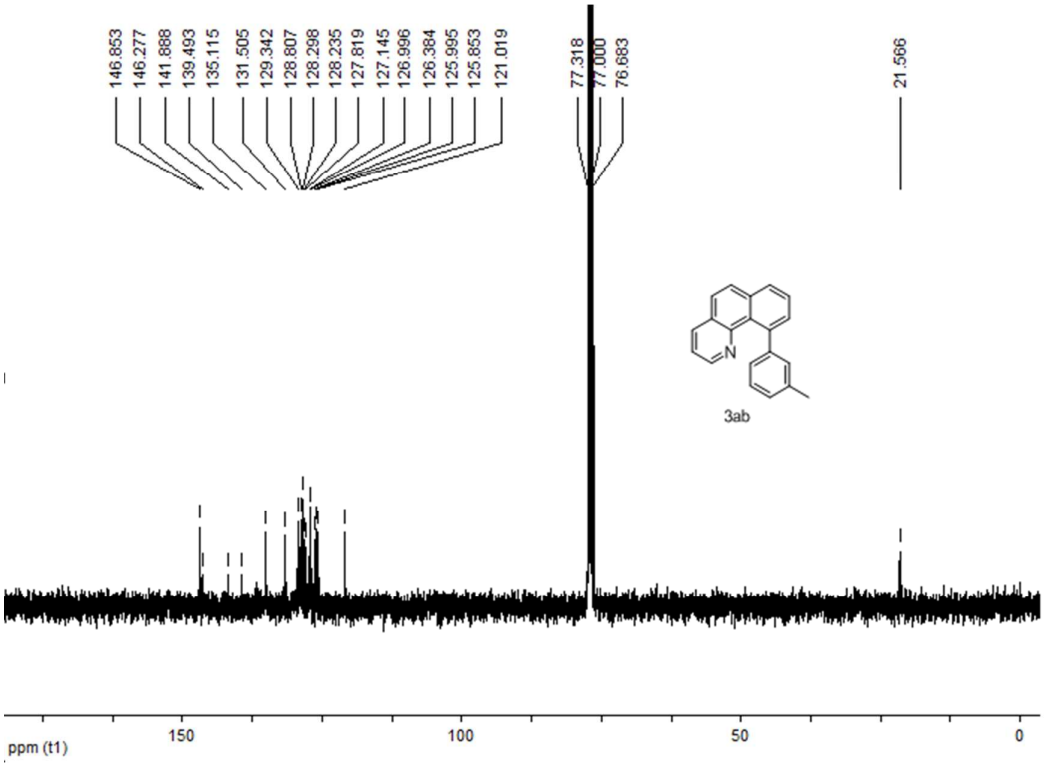

Figure S25. ^{13}C NMR for compound 3ab

^{1}H NMR and ^{13}C NMR Spectra of 3ac

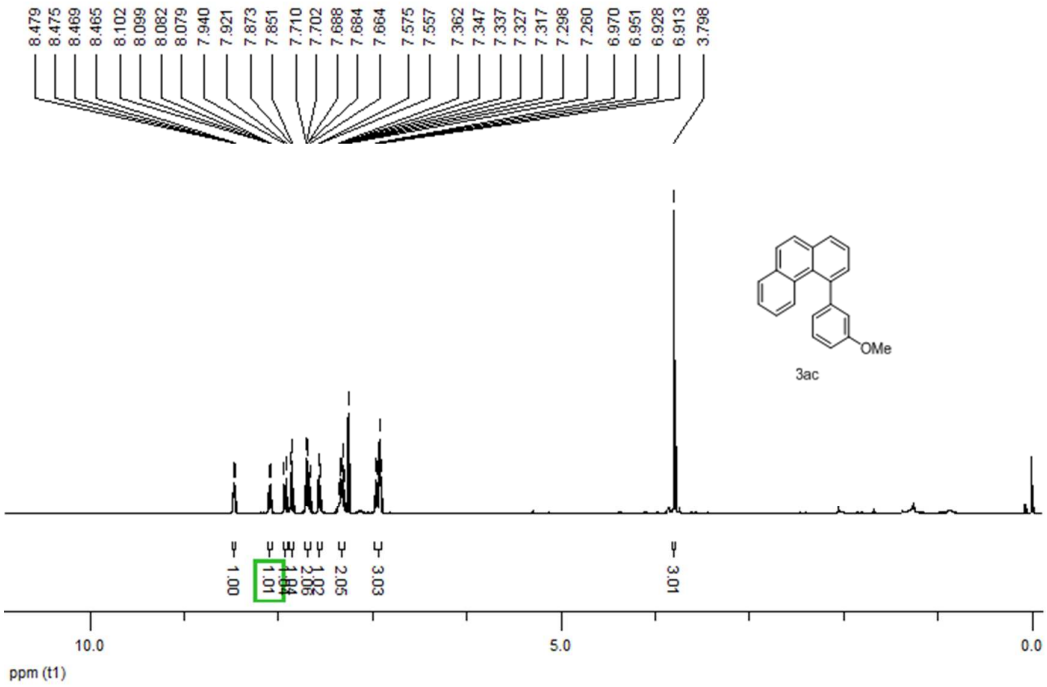

Figure S26. ^{1}H NMR for compound 3ac

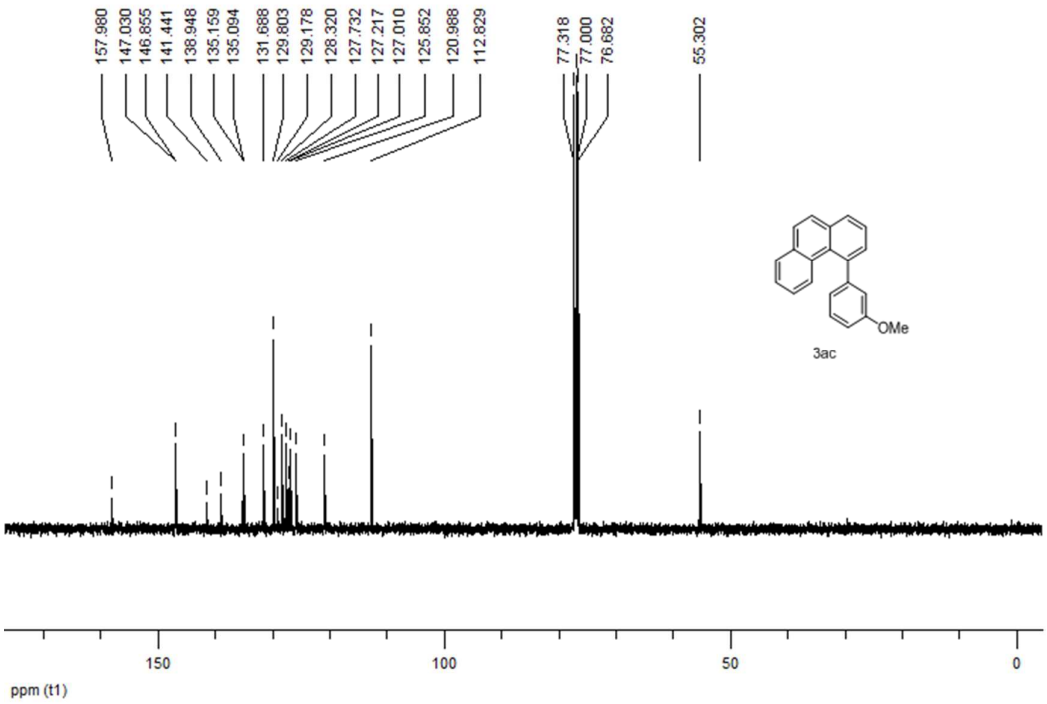

Figure S27. ^{13}C NMR for compound 3ac

^{1}H NMR and ^{13}C NMR Spectra of 3ad

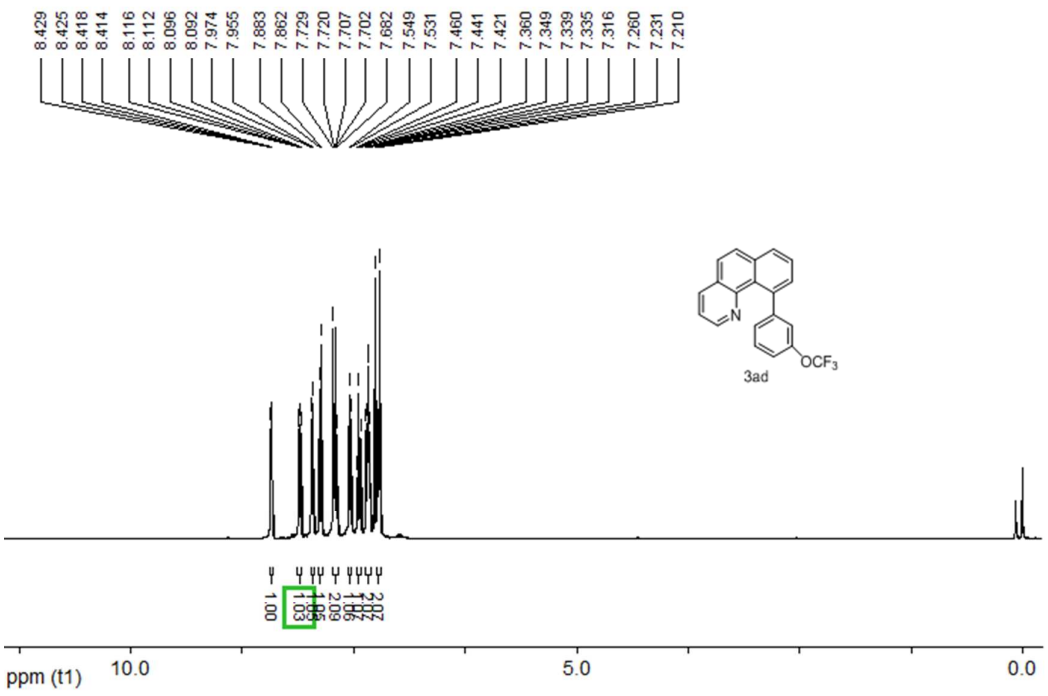

Figure S28. ^{1}H NMR for compound 3ad

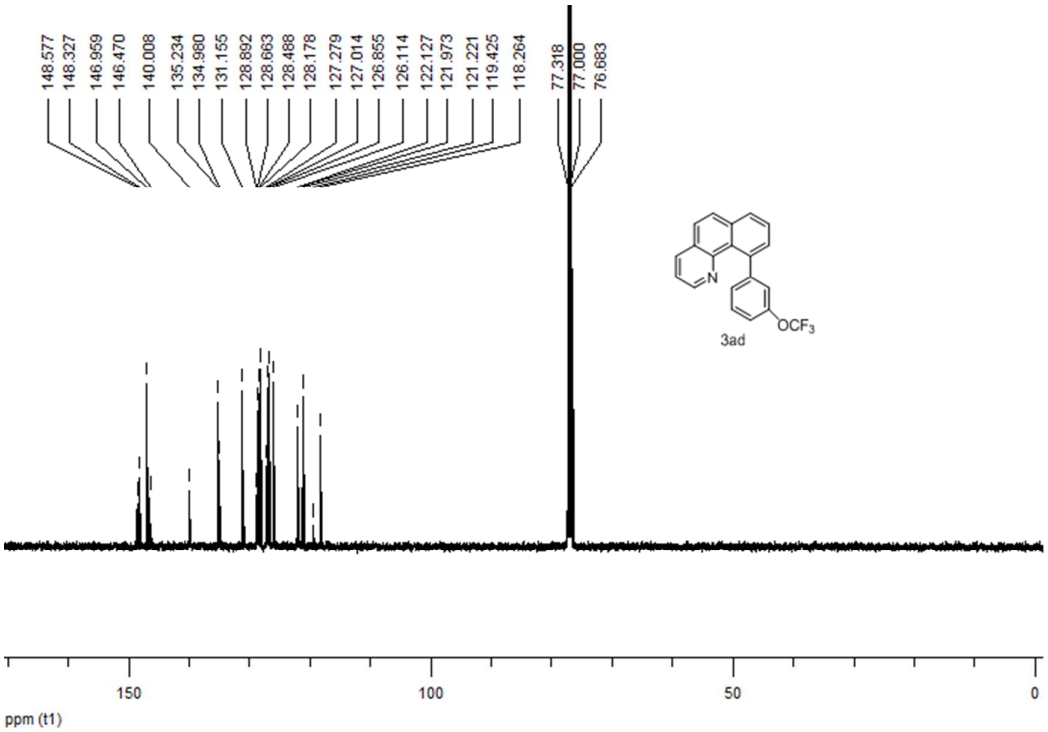

Figure S29. ^{13}C NMR for compound 3ad

^{19}F NMR for compound 3ad

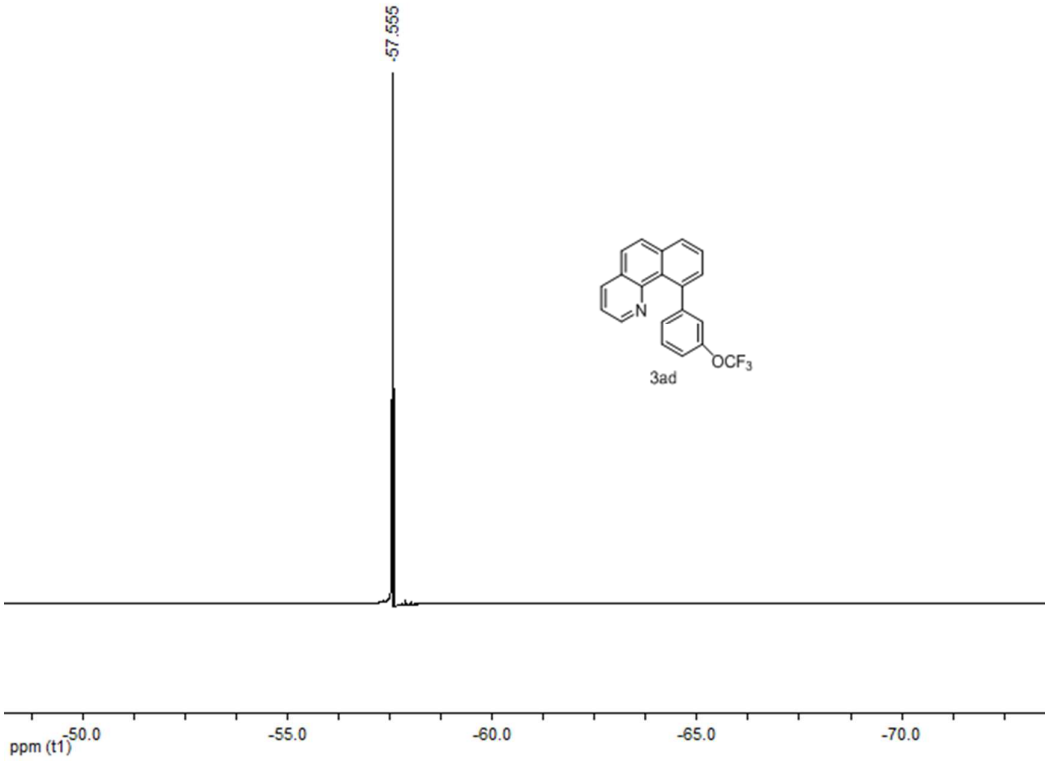

Figure S30. ^{19}F NMR for compound 3ad

^{1}H NMR and ^{13}C NMR Spectra of 3ae

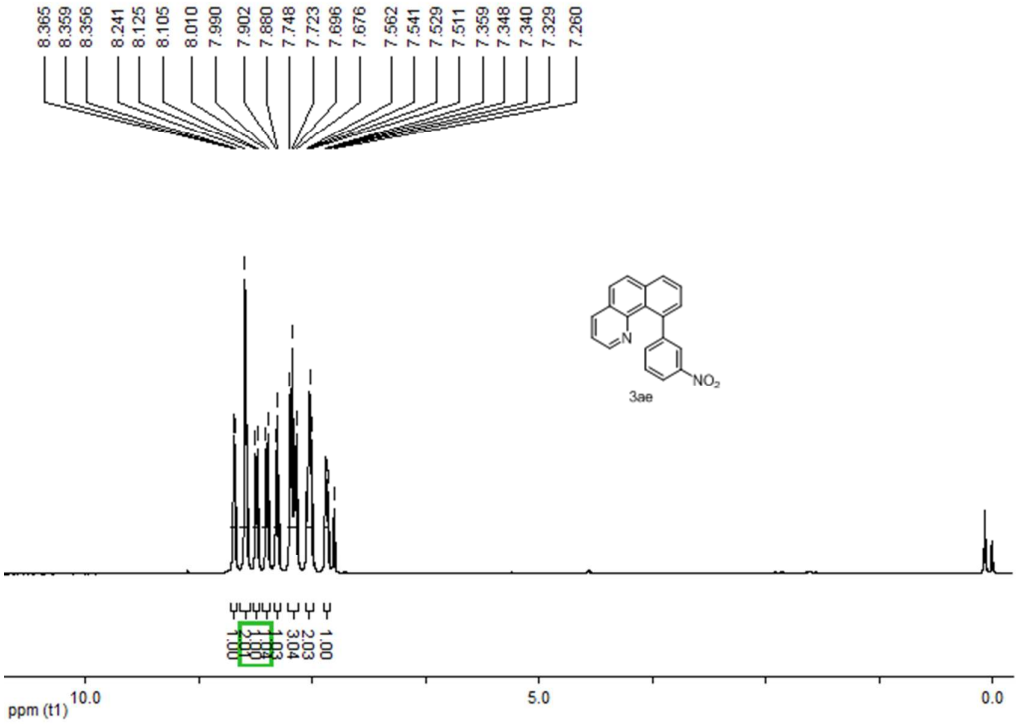

Figure S31. ^{1}H NMR for compound 3ae

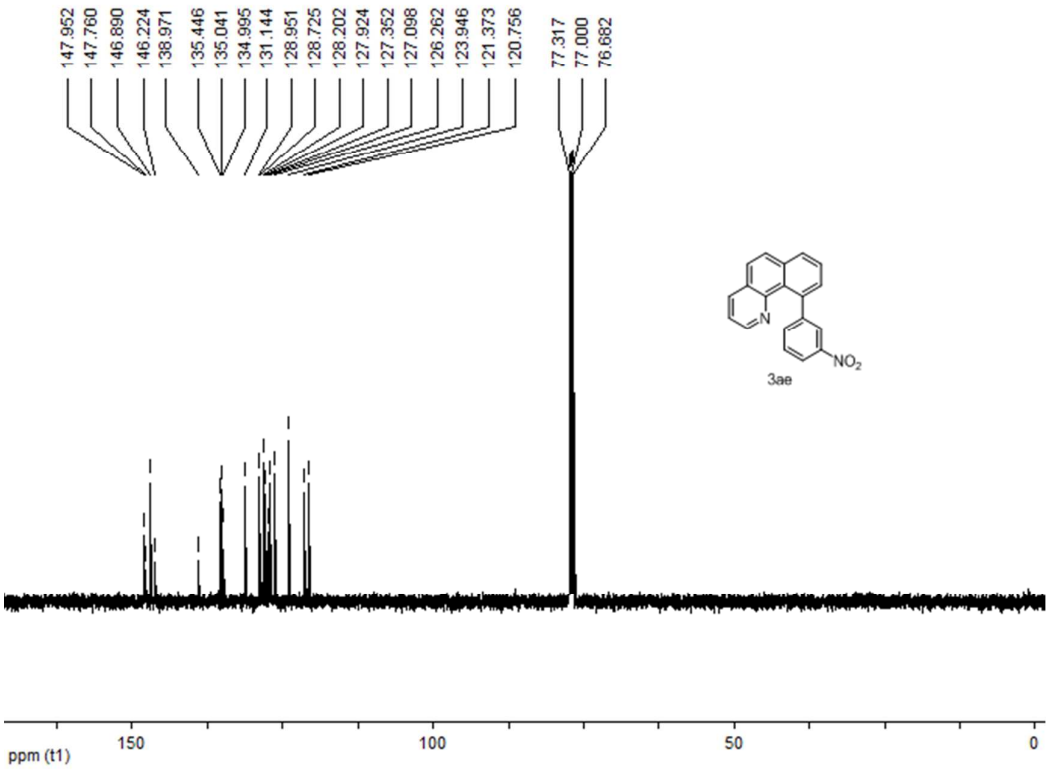

Figure S32. ^{13}C NMR for compound 3ae

^{1}H NMR and ^{13}C NMR Spectra of 3af

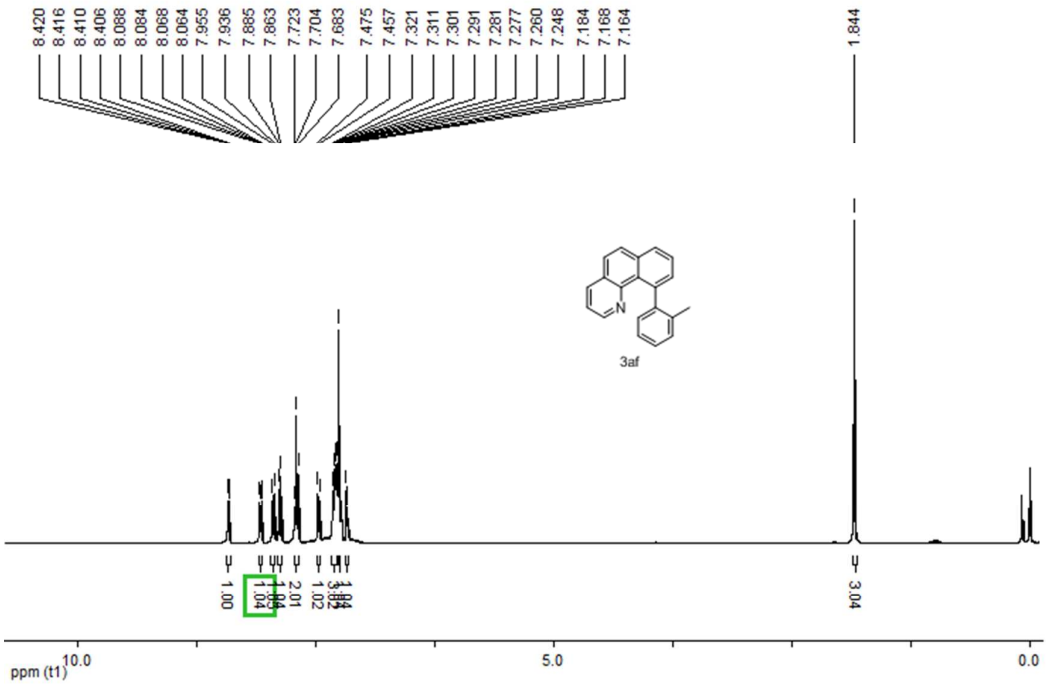

Figure S33. ^{1}H NMR for compound 3af

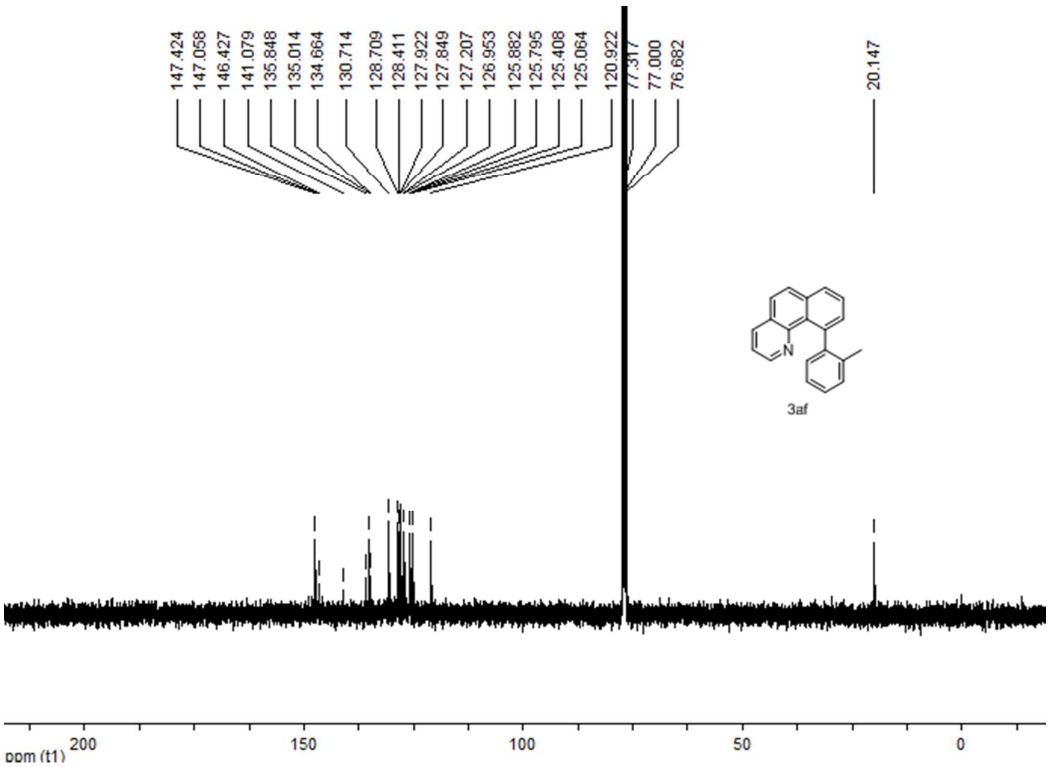

Figure S34. ^{13}C NMR for compound 3af

^{1}H NMR and ^{13}C NMR Spectra of 3ag

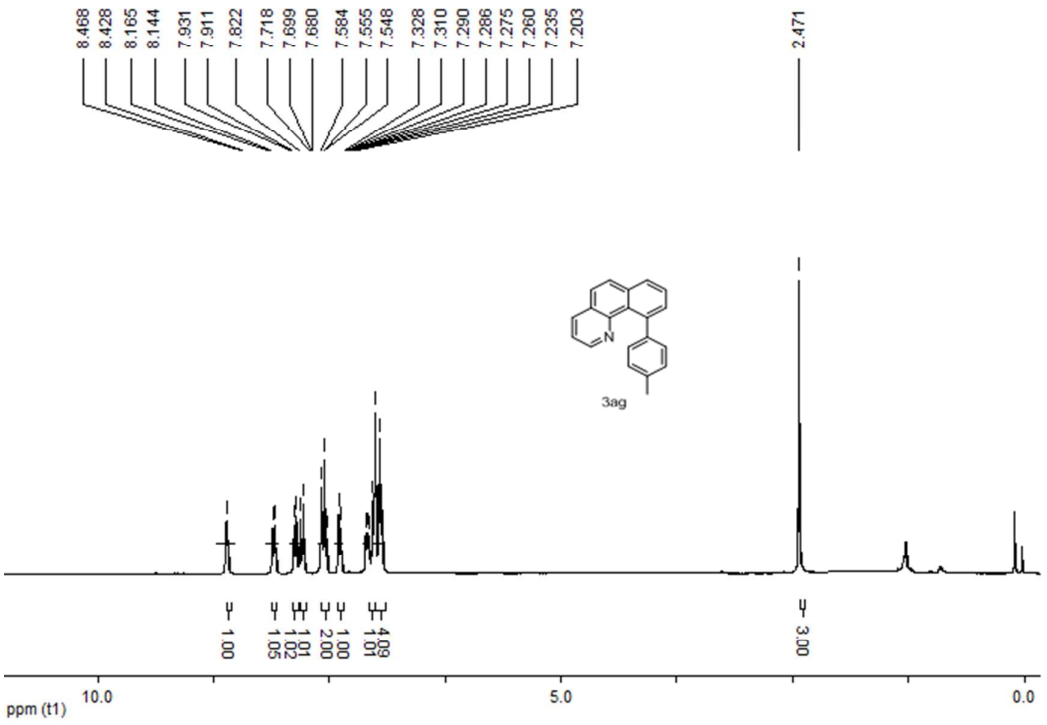

Figure S35. ^{1}H NMR for compound 3ag

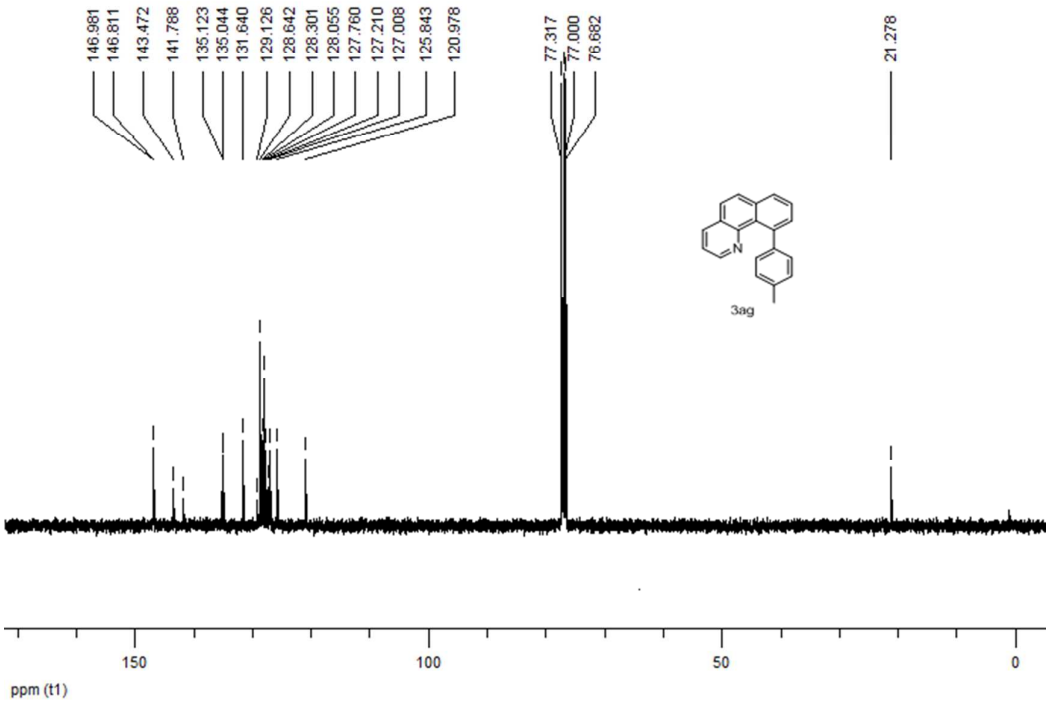

Figure S36. ^{13}C NMR for compound 3ag

^{1}H NMR and ^{13}C NMR Spectra of 3ah

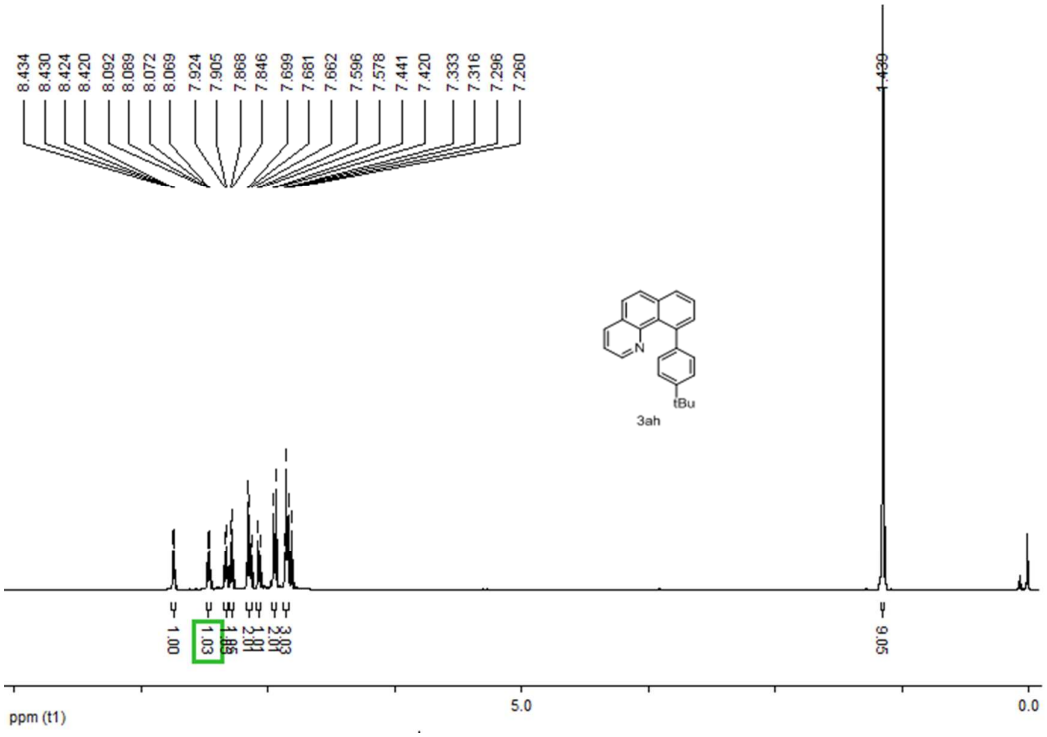

Figure S37. ^{1}H NMR for compound 3ah

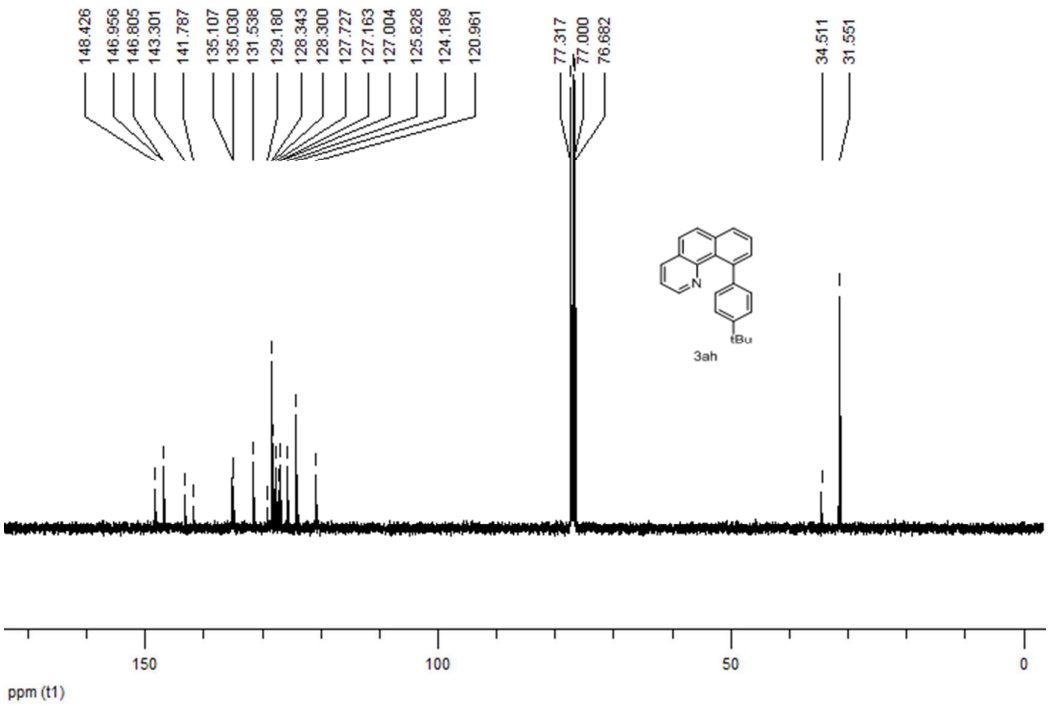

Figure S38. ^{13}C NMR for compound 3ah

^{1}H NMR and ^{13}C NMR Spectra of 3ai

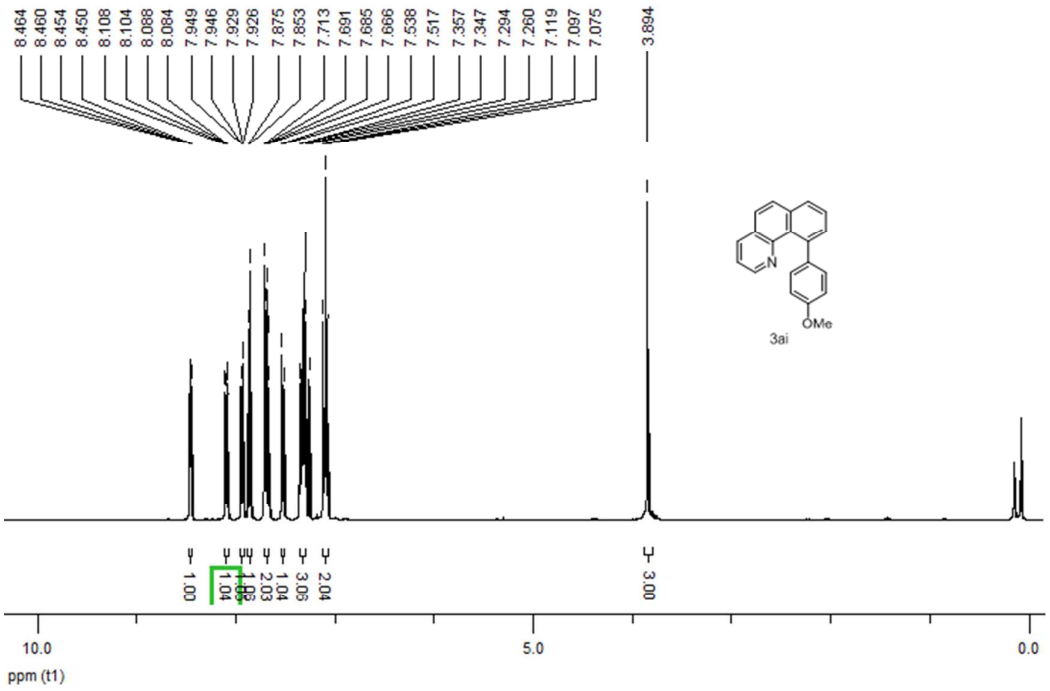

Figure S39. ^{1}H NMR for compound 3ai

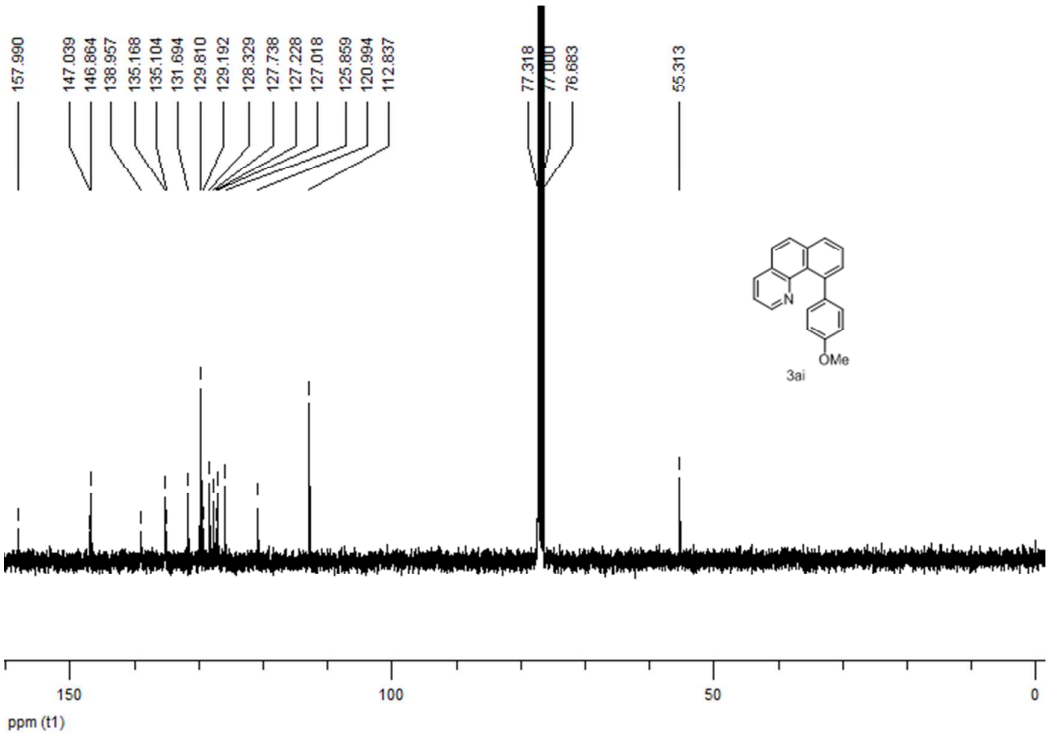

Figure S40. ^{13}C NMR for compound 3ai

^{1}H NMR and ^{13}C NMR Spectra of 3aj

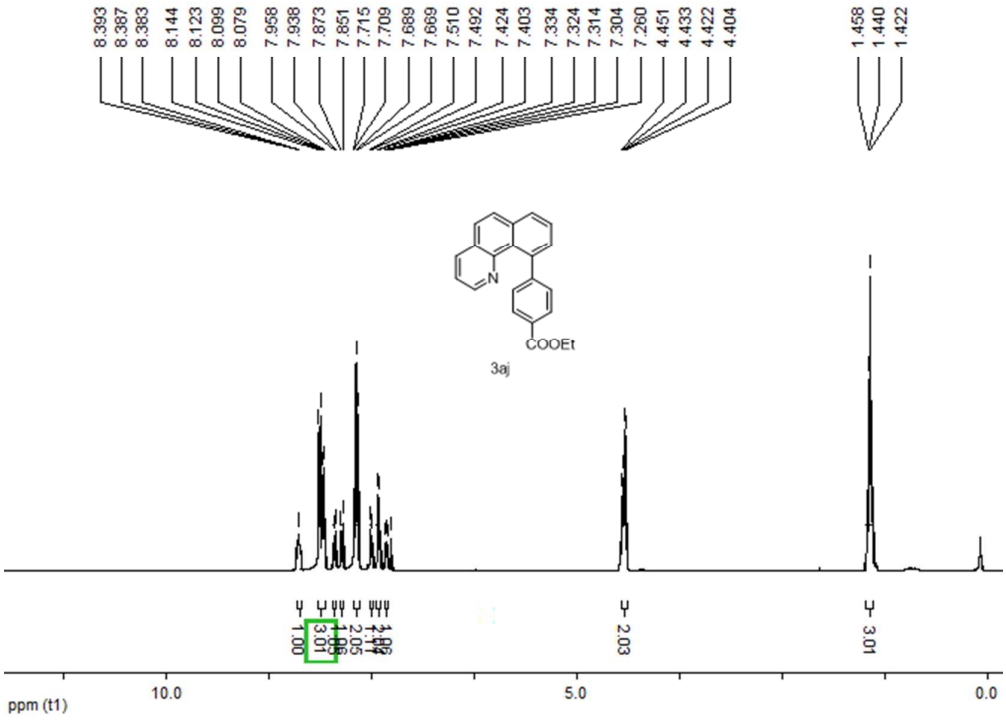

Figure S41. ^{1}H NMR for compound 3aj

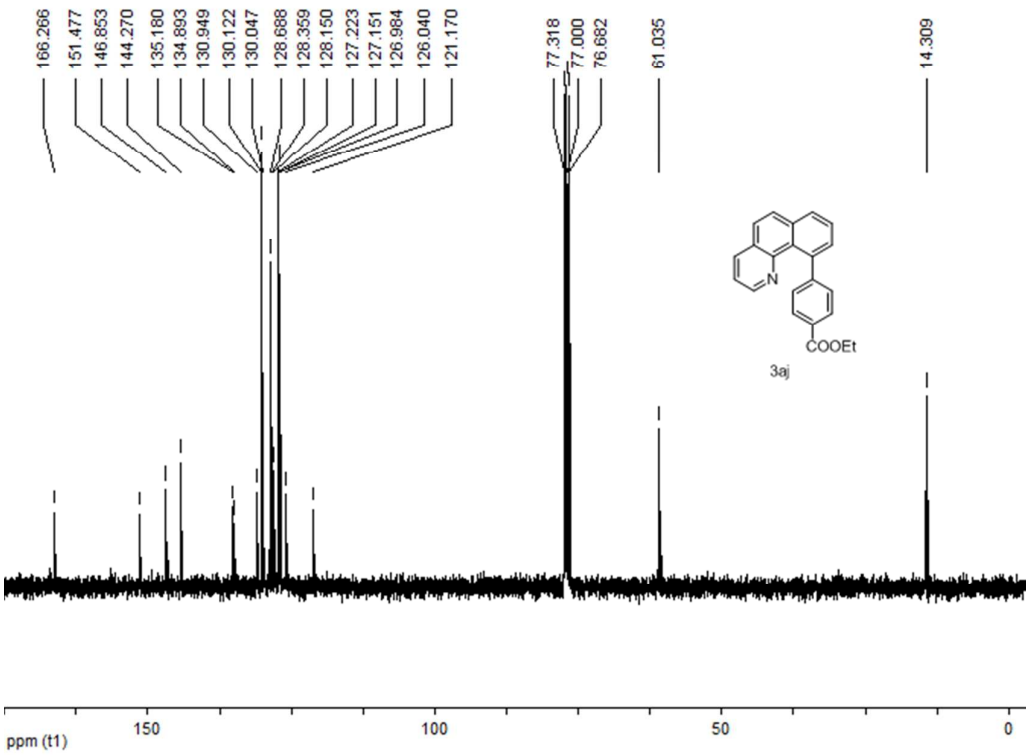

Figure S42. ^{13}C NMR for compound 3aj

^{1}H NMR and ^{13}C NMR Spectra of 3ak

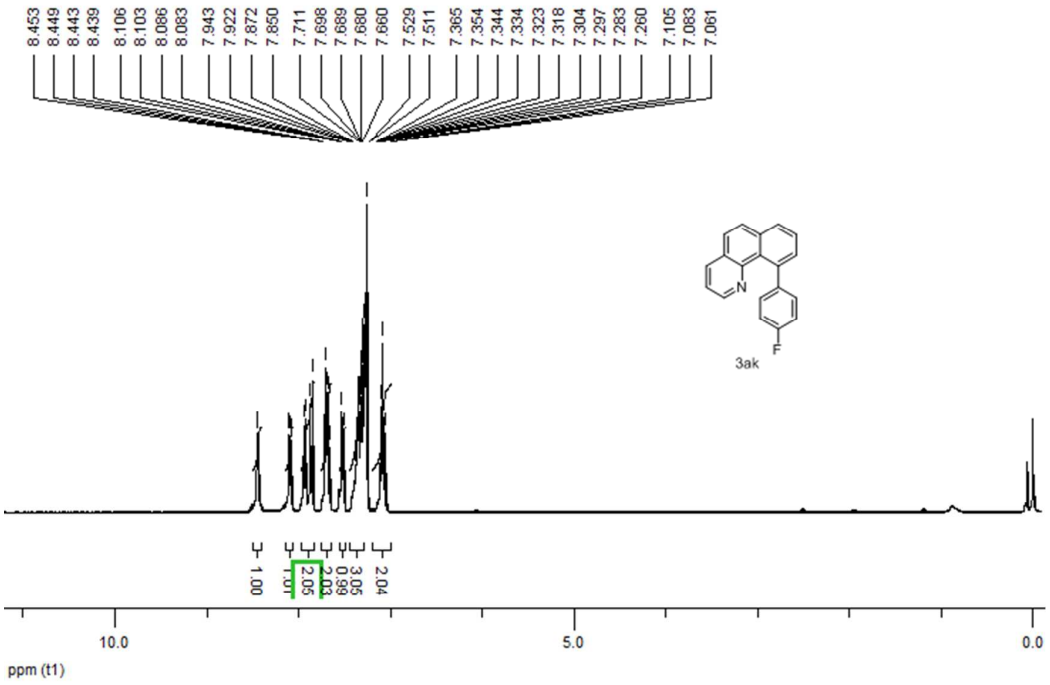

Figure S43. ^{1}H NMR for compound 3ak

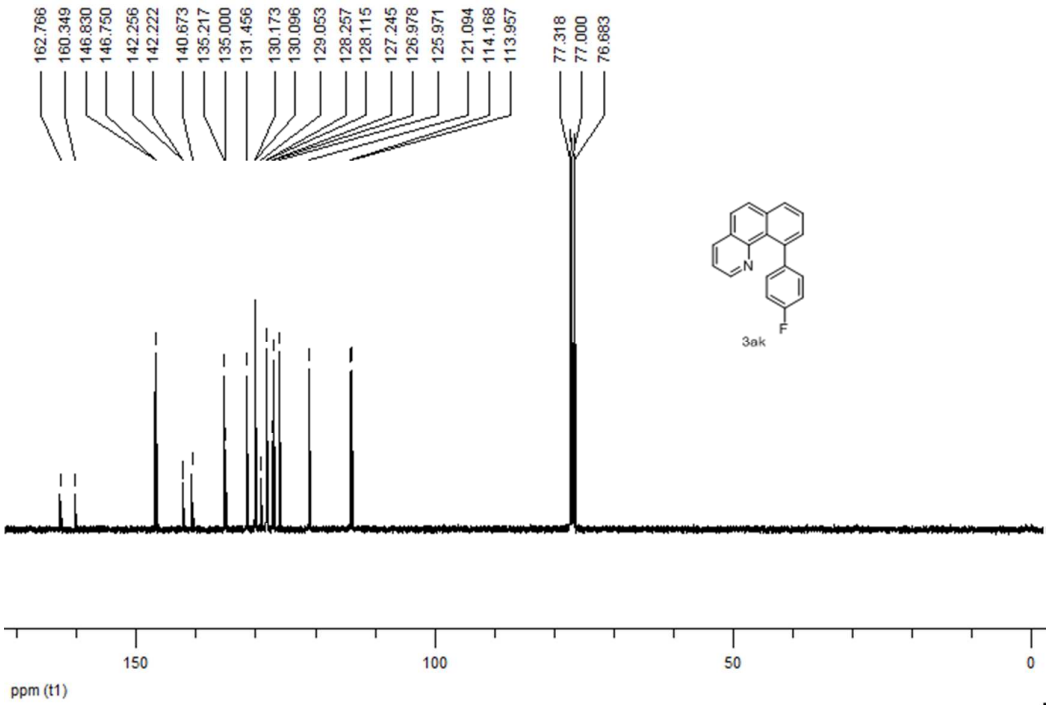

Figure S44. ^{13}C NMR for compound 3ak

^{19}F NMR for compound 3ak

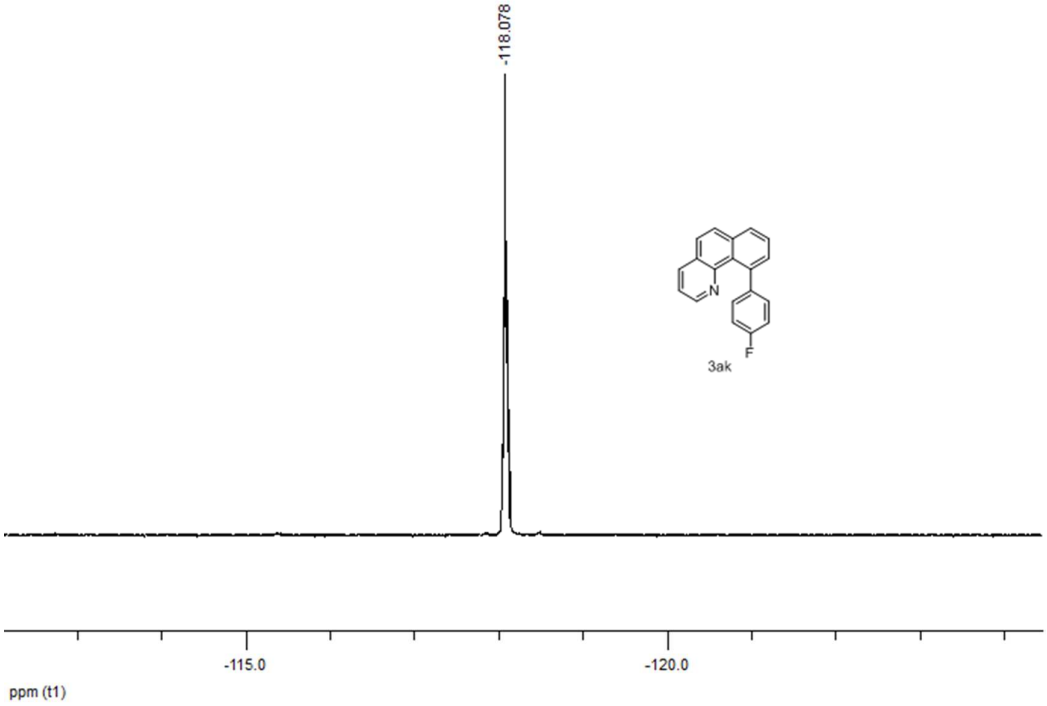

Figure S45. ^{19}F NMR for compound 3ak

^{1}H NMR and ^{13}C NMR Spectra of 3al

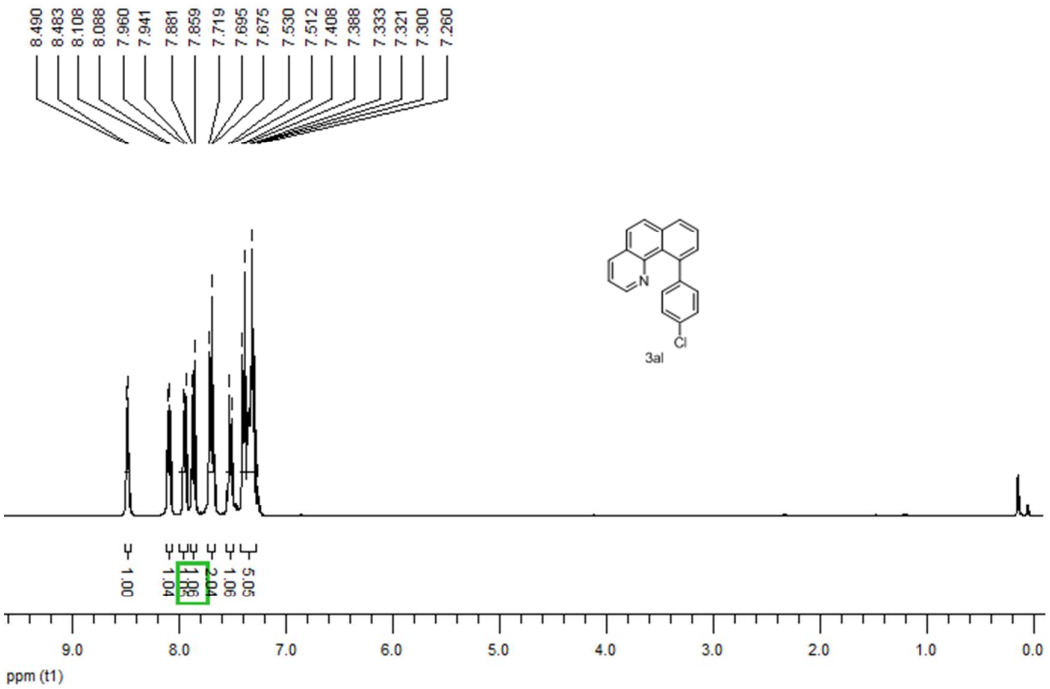

Figure S46. ^{1}H NMR for compound 3al

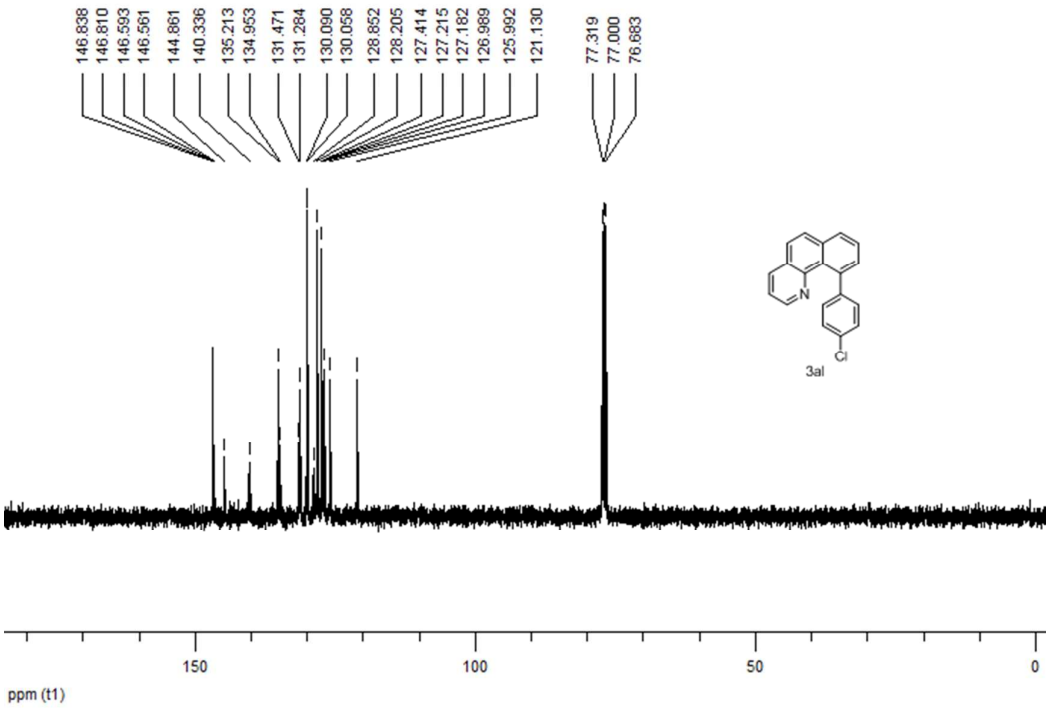

Figure S47. ^{13}C NMR for compound 3al

^{1}H NMR and ^{13}C NMR Spectra of 3am

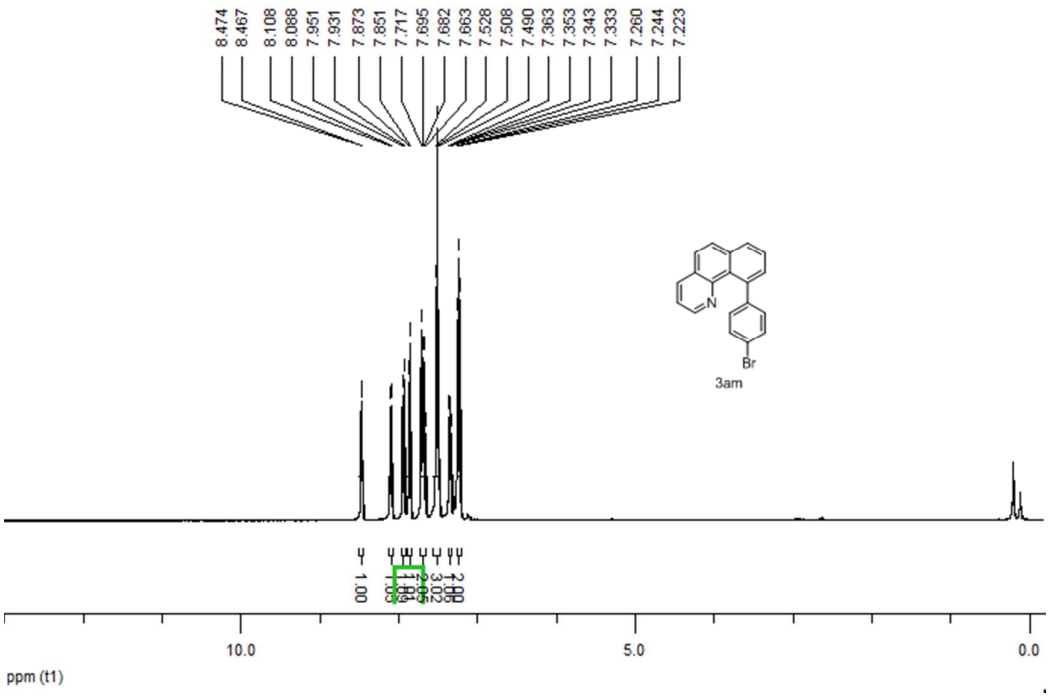

Figure S48. ^{1}H NMR for compound 3am

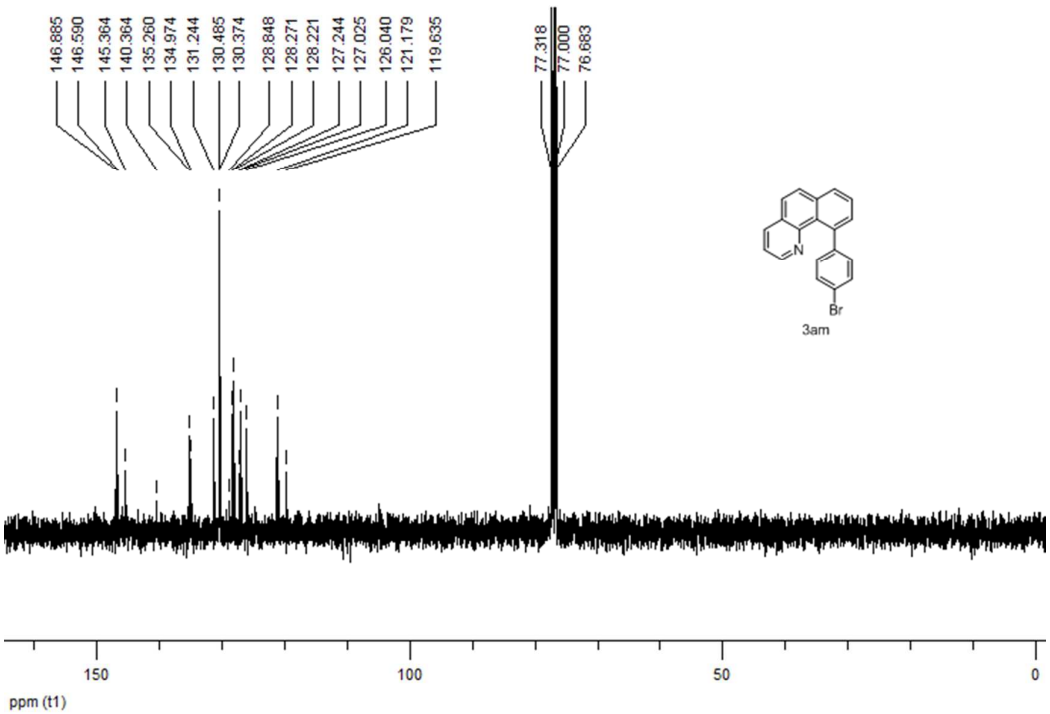

Figure S49. ^{13}C NMR for compound 3am

^{1}H NMR and ^{13}C NMR Spectra of 3an

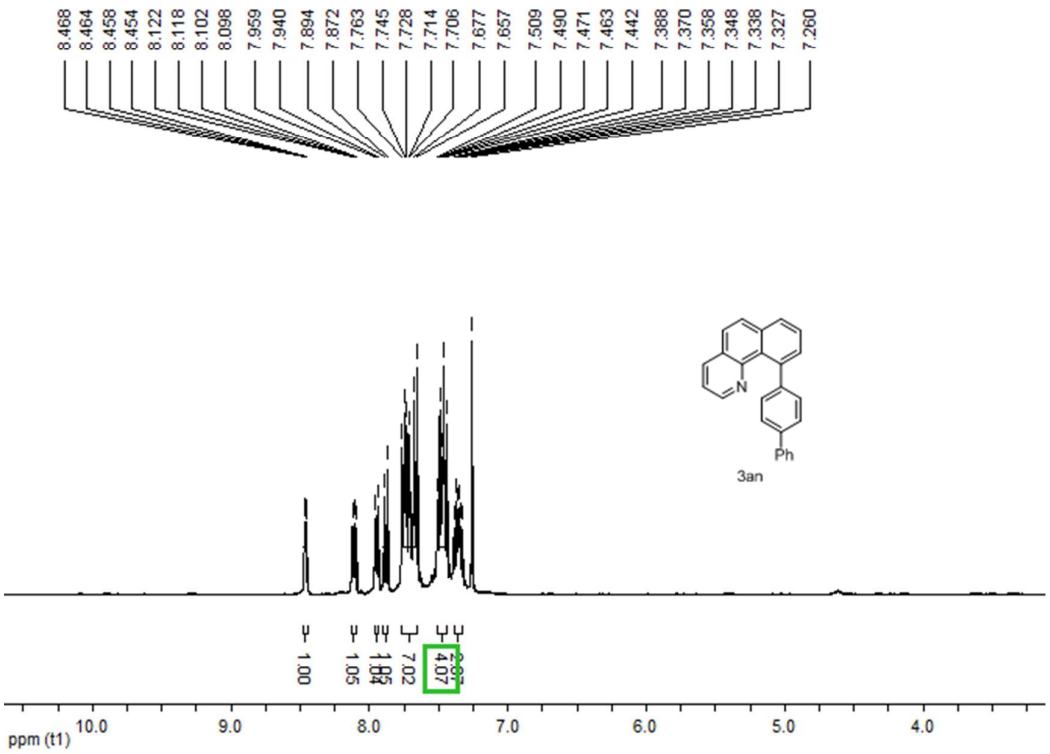

Figure S50. ^{1}H NMR for compound 3an

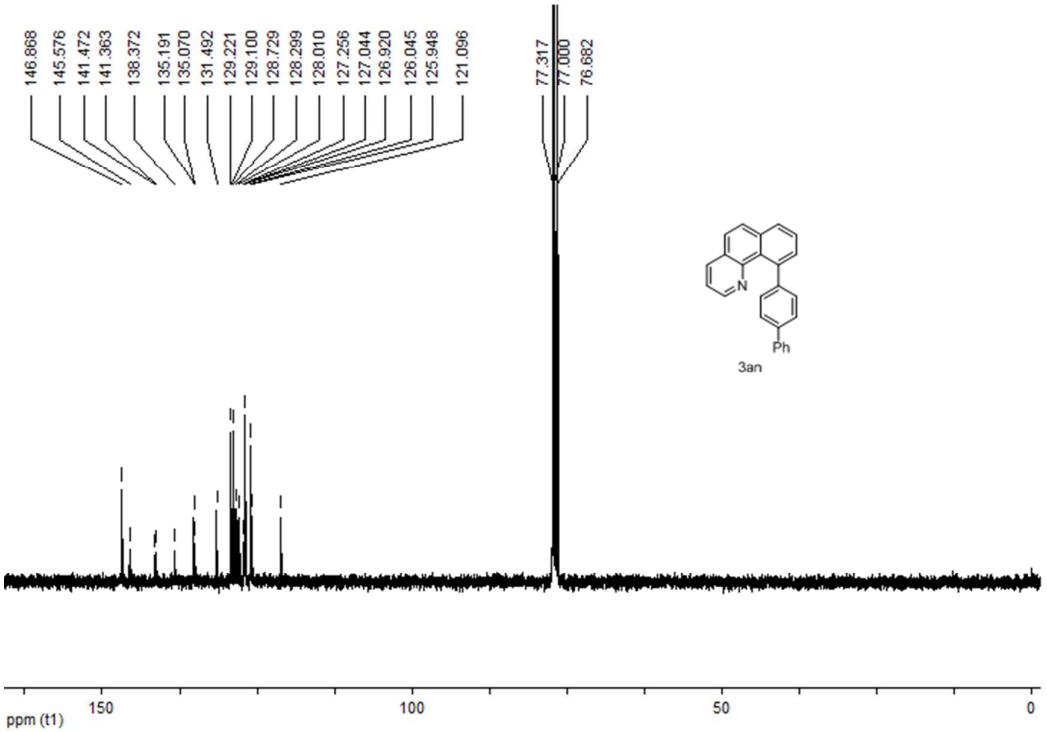

Figure S51.^{13}C NMR for compound 3an

^{1}H NMR and ^{13}C NMR Spectra of 3ao

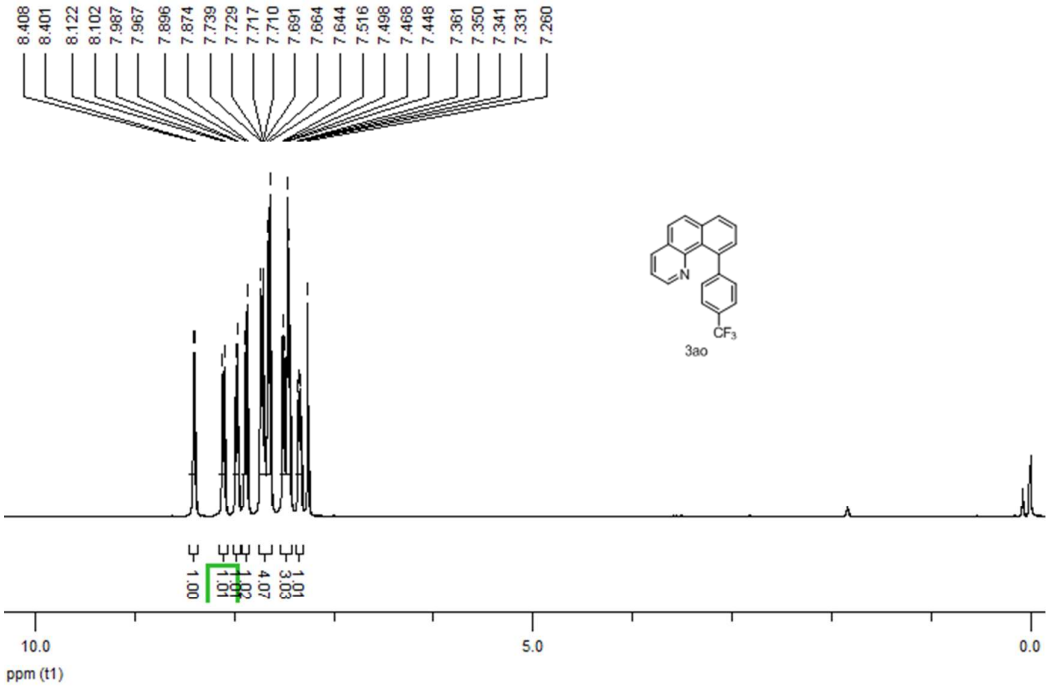

Figure S52. ^{1}H NMR for compound 3ao

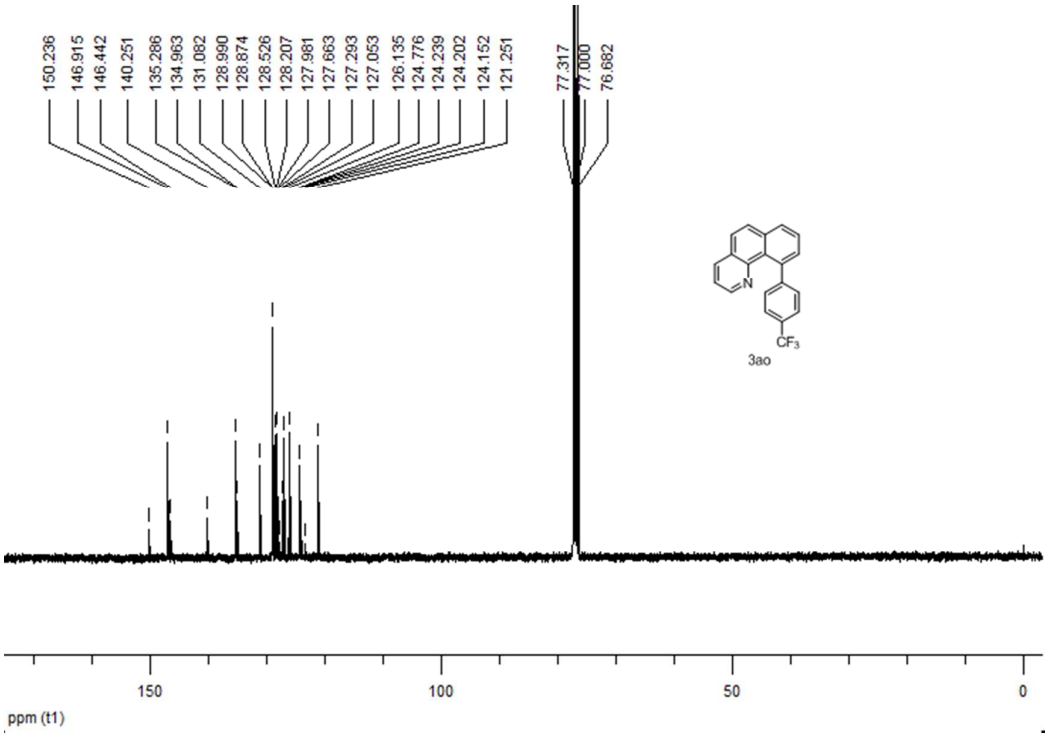

Figure S53. ^{13}C NMR for compound 3ao

^{19}F NMR for compound 3ao

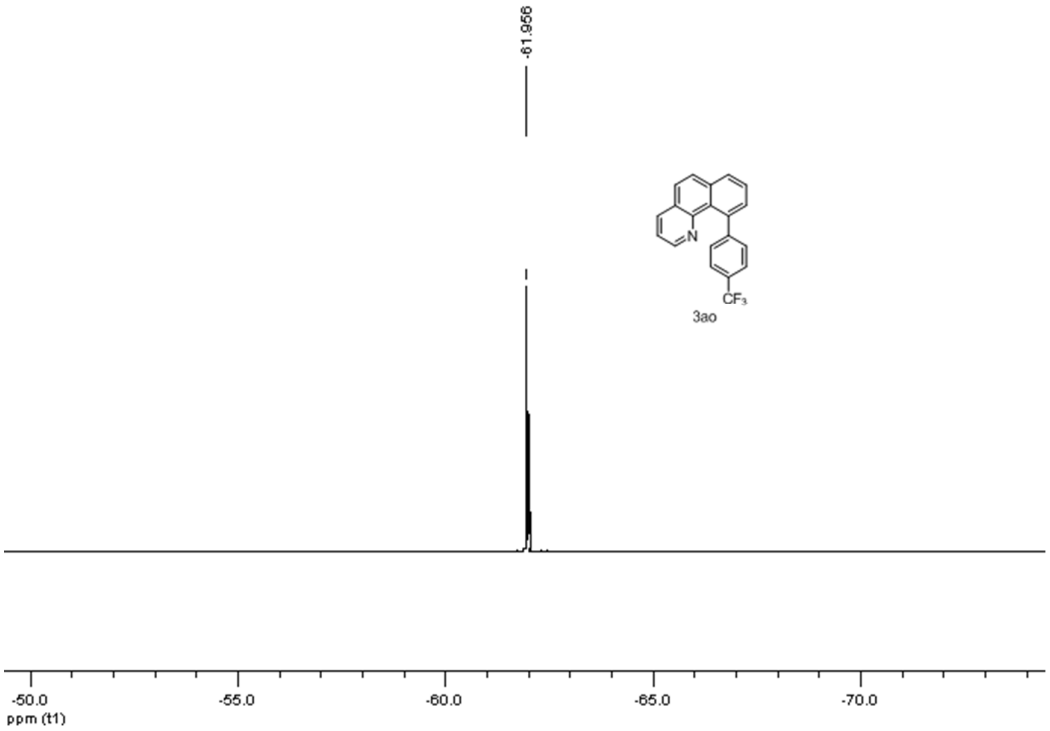

Figure S54. ^{19}F NMR for compound 3ao

^{1}H NMR and ^{13}C NMR Spectra of 3ap

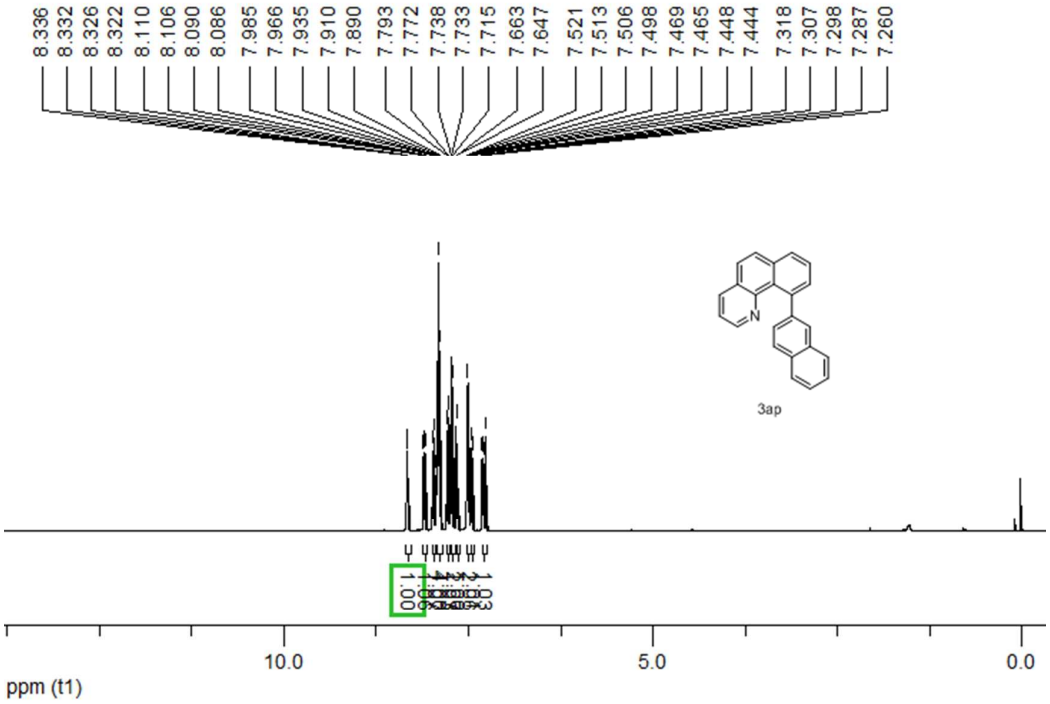

Figure S55. ^{1}H NMR for compound 3ap

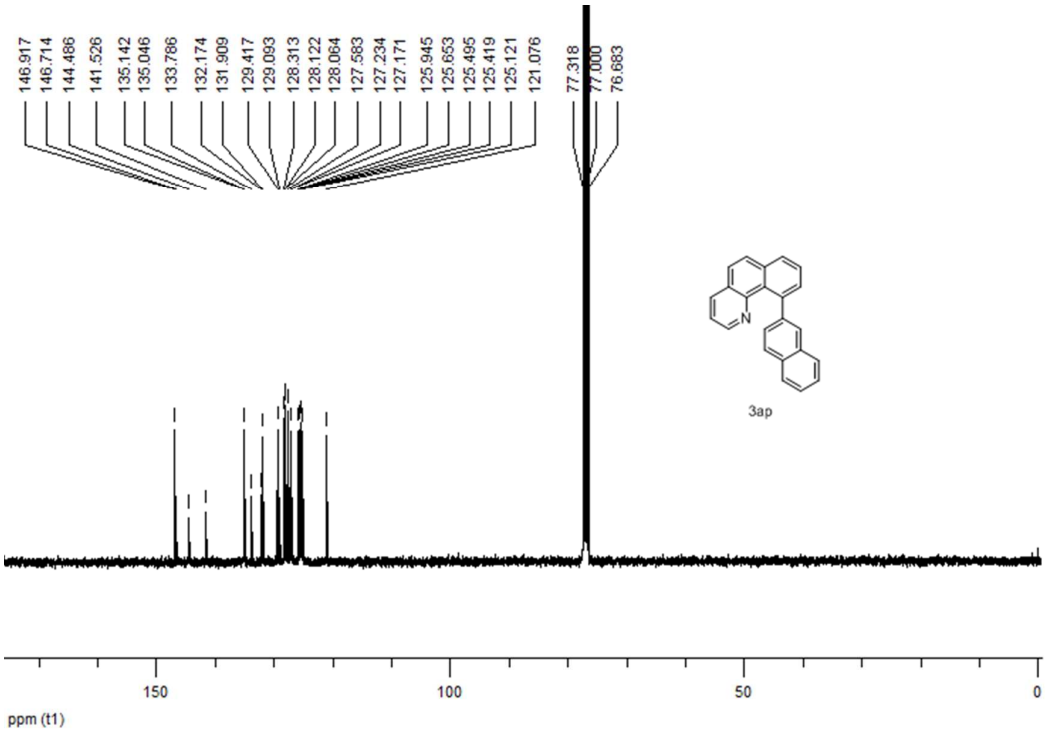

Figure S56. ^{13}C NMR for compound 3ap

^{1}H NMR and ^{13}C NMR Spectra of 3aq

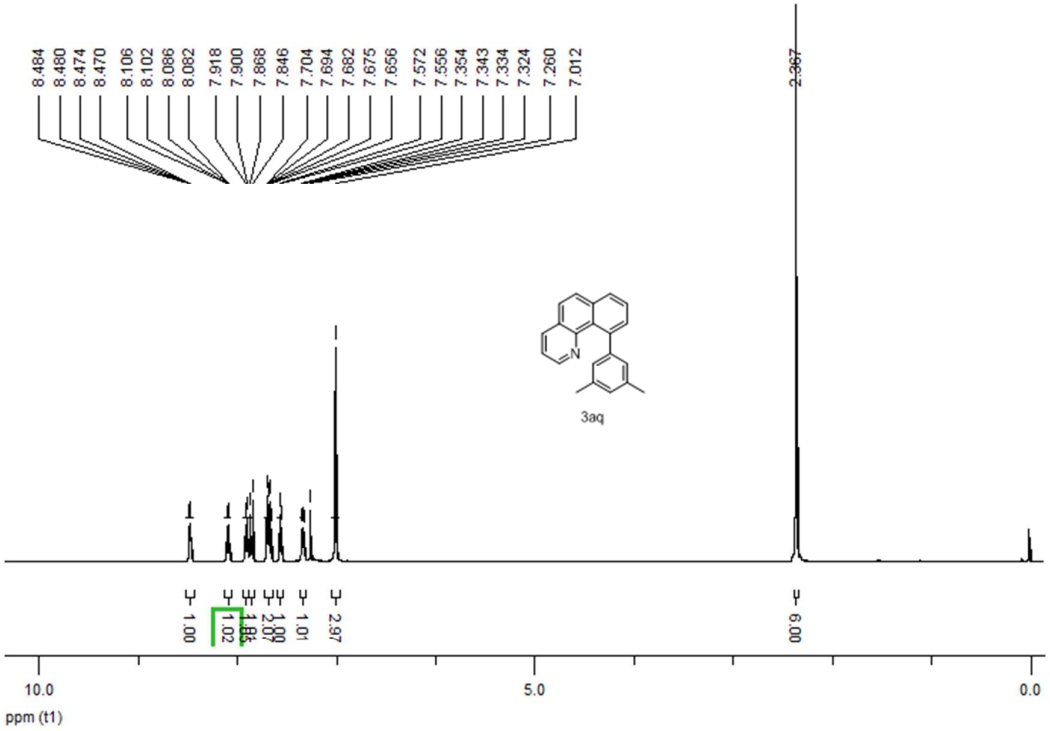

Figure S57. ^{1}H NMR for compound 3aq

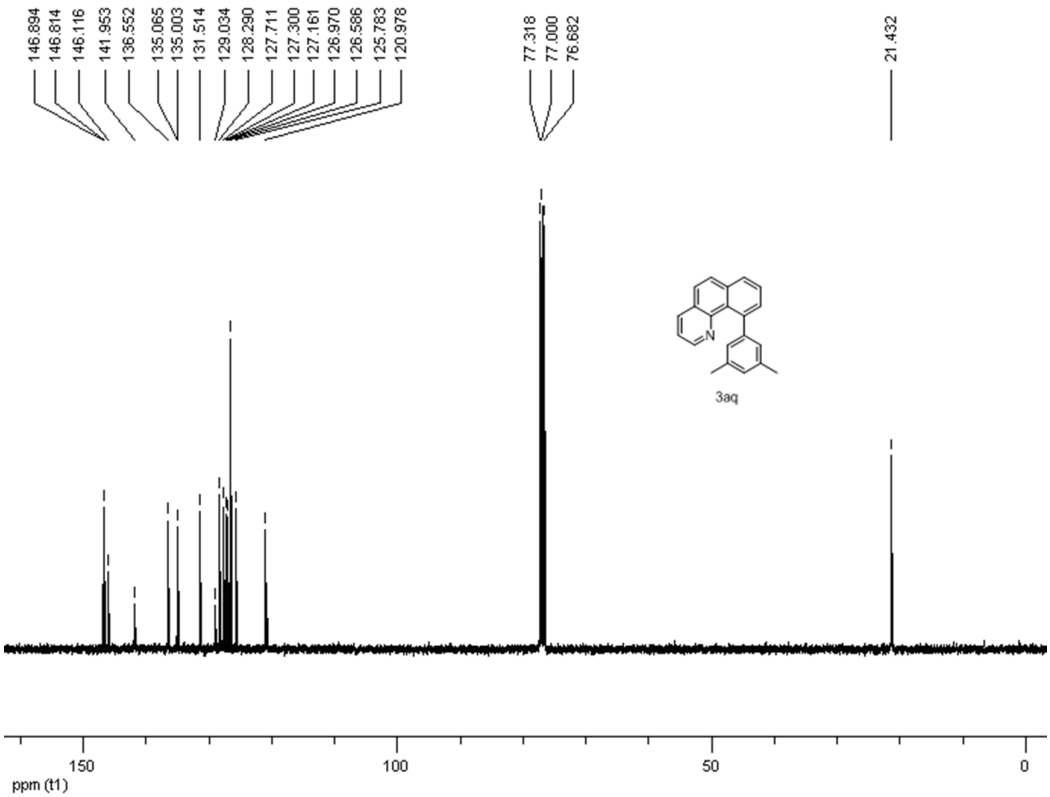

Figure S58. ^{13}C NMR for compound 3aq

^{1}H NMR and ^{13}C NMR Spectra of 3ar

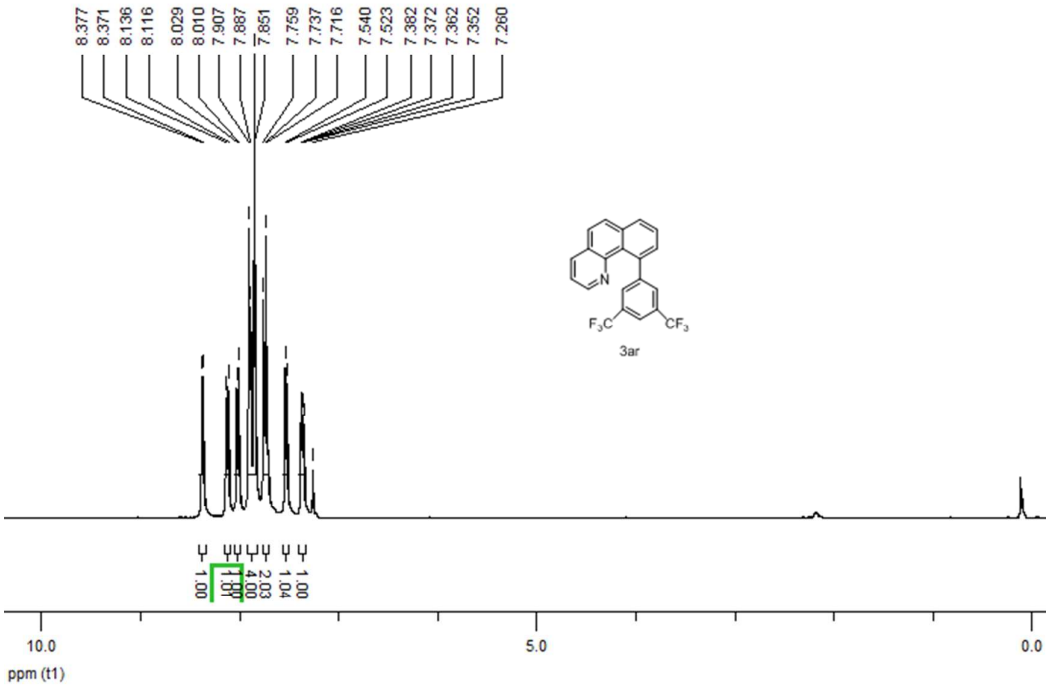

Figure S59. ^{1}H NMR for compound 3ar

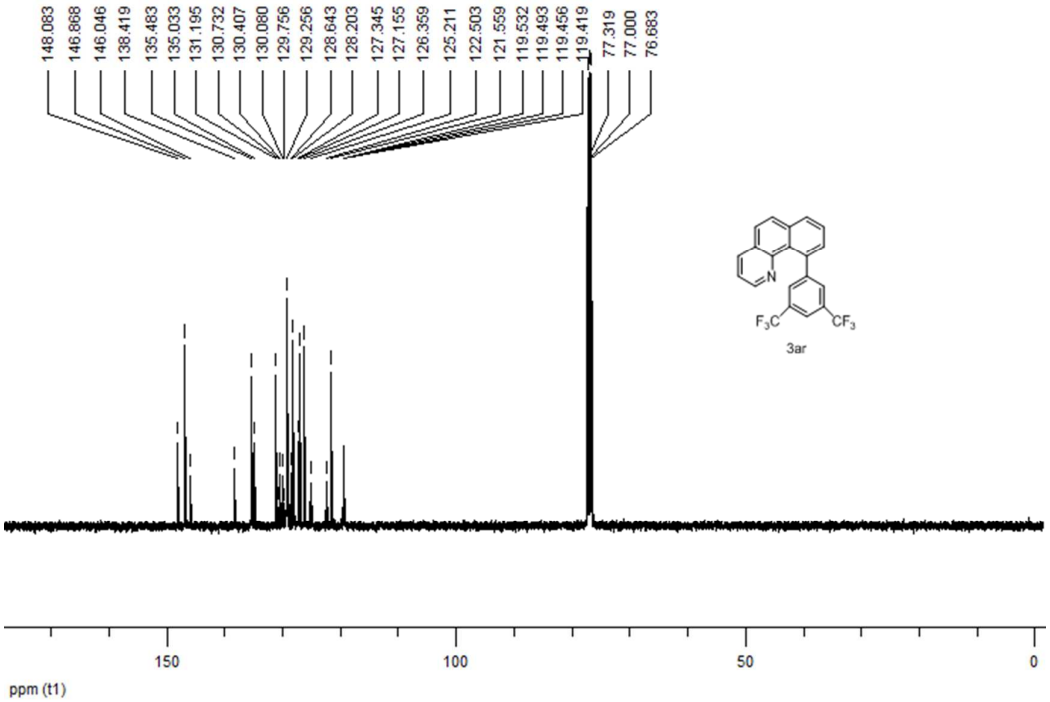

Figure S60. ^{13}C NMR for compound 3ar

^{19}F NMR for compound 3ar

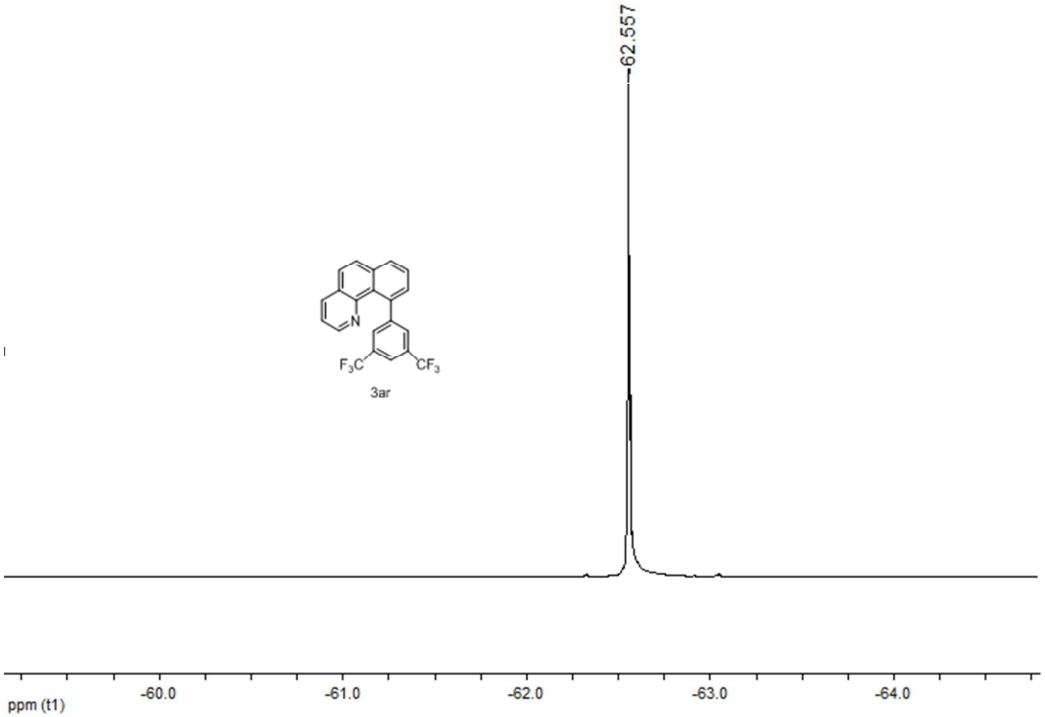

Figure S61. ^{19}F NMR for compound 3ar

^{1}H NMR and ^{13}C NMR Spectra of 3as

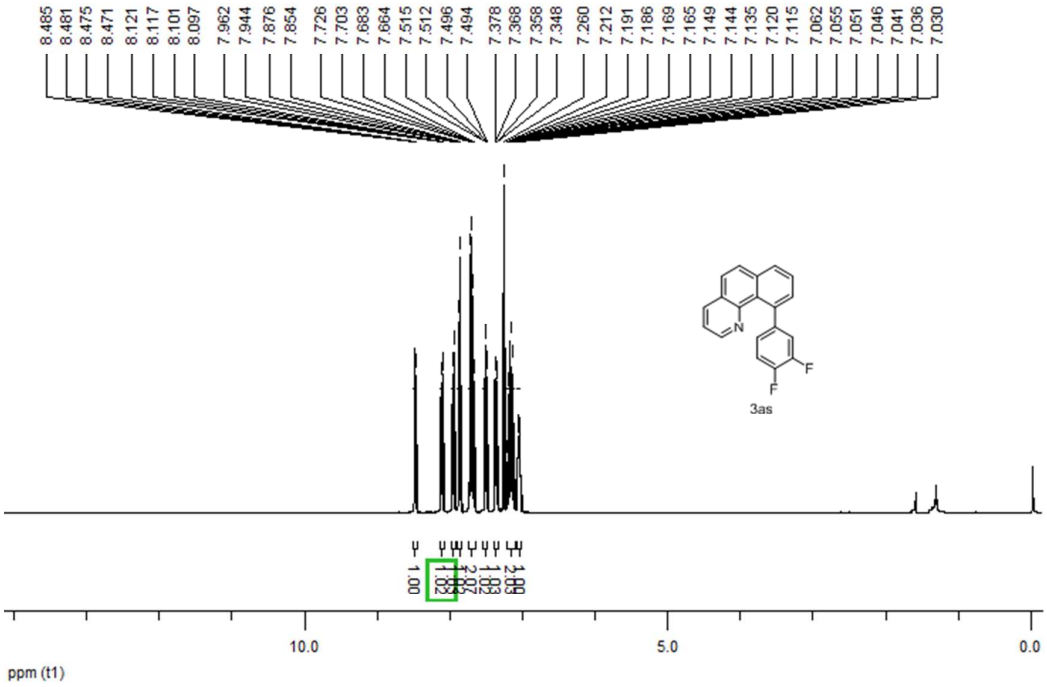

Figure S62. ^{1}H NMR for compound 3as

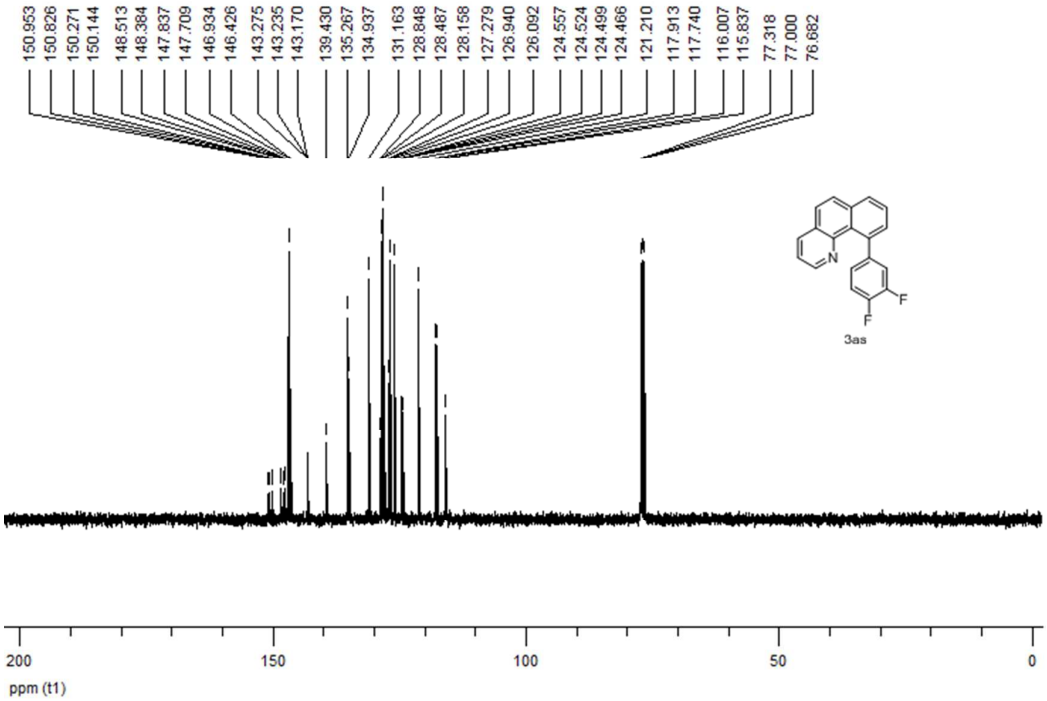

Figure S63. ^{13}C NMR for compound 3as

^{19}F NMR for compound 3as

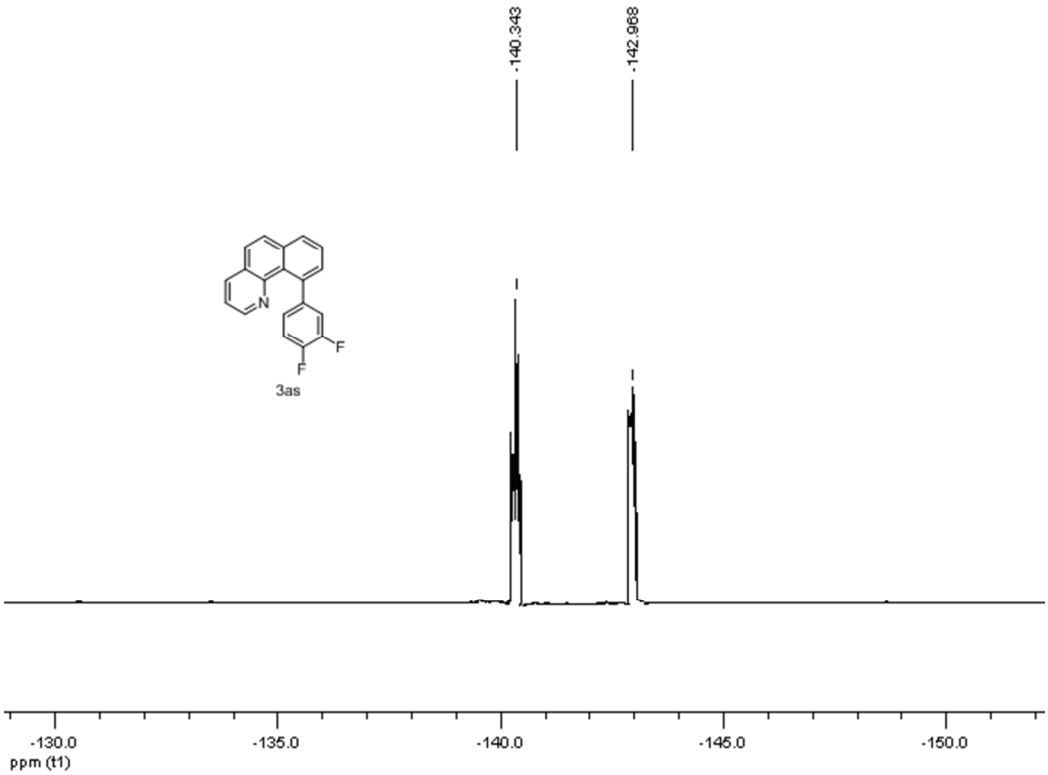

Figure S64. ^{19}F NMR for compound 3as

^{1}H NMR and ^{13}C NMR Spectra of 3at

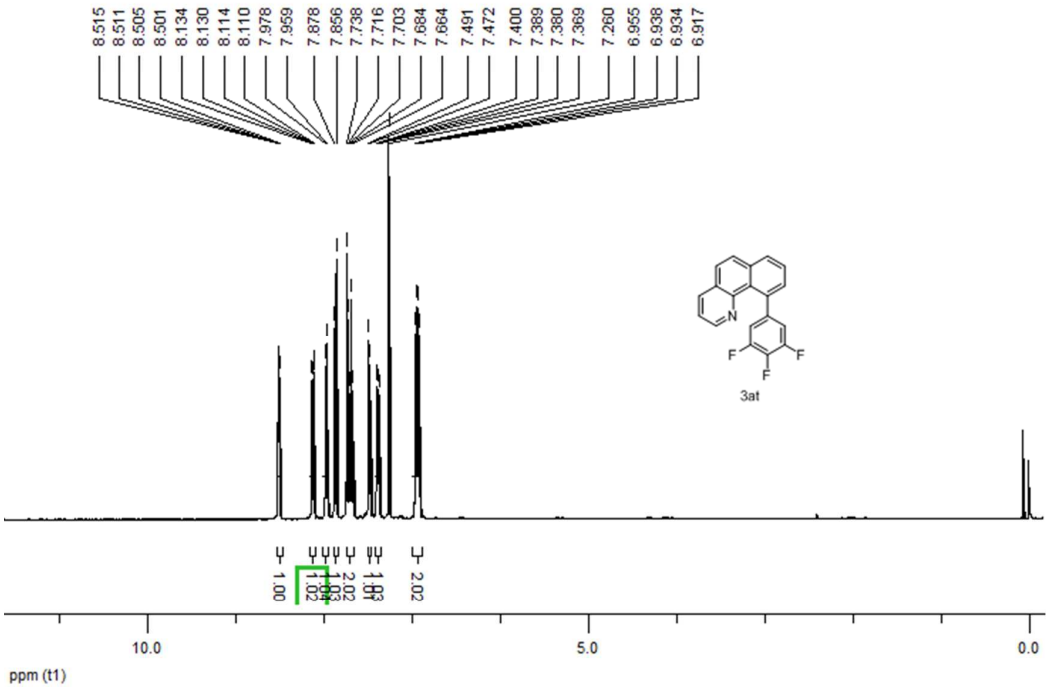

Figure S65. ^{1}H NMR for compound 3at

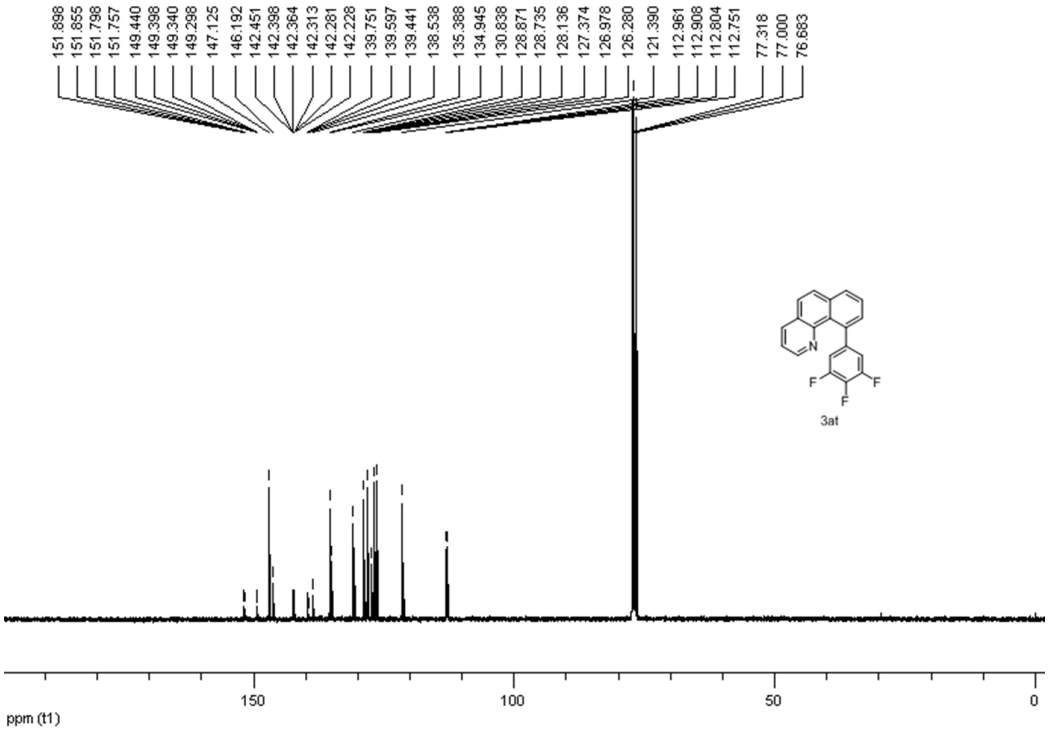

Figure S66. ^{13}C NMR for compound 3at

^{19}F NMR for compound 3at

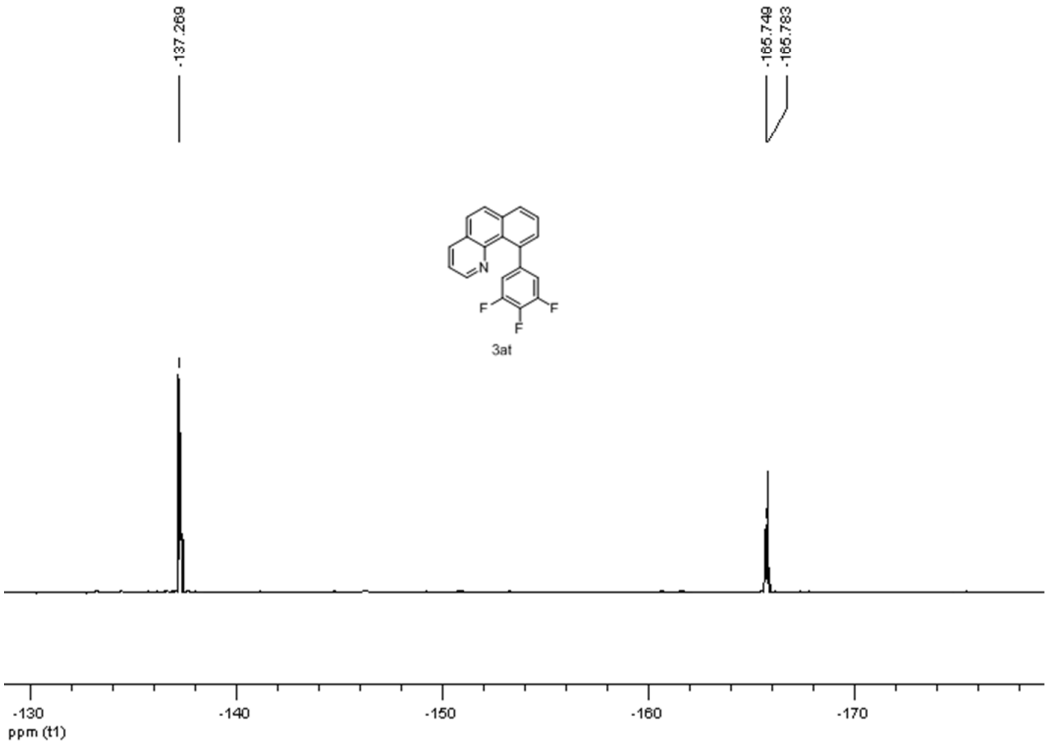

Figure S67. ^{19}F NMR for compound 3at

^{1}H NMR and ^{13}C NMR Spectra of 3ba

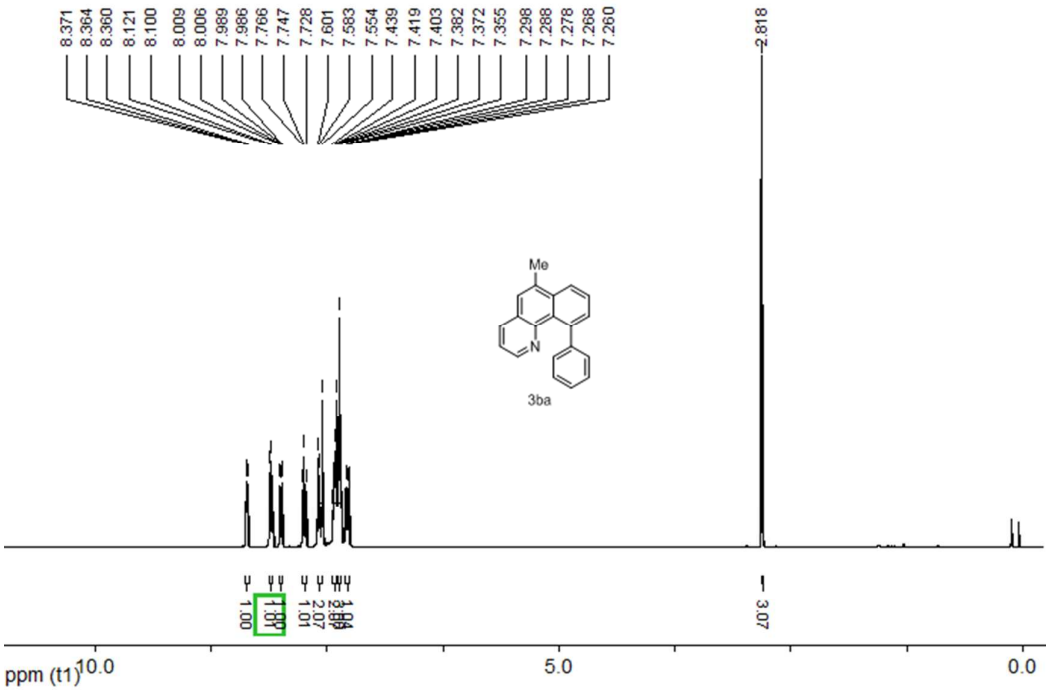

Figure S68. ^{1}H NMR for compound 3ba

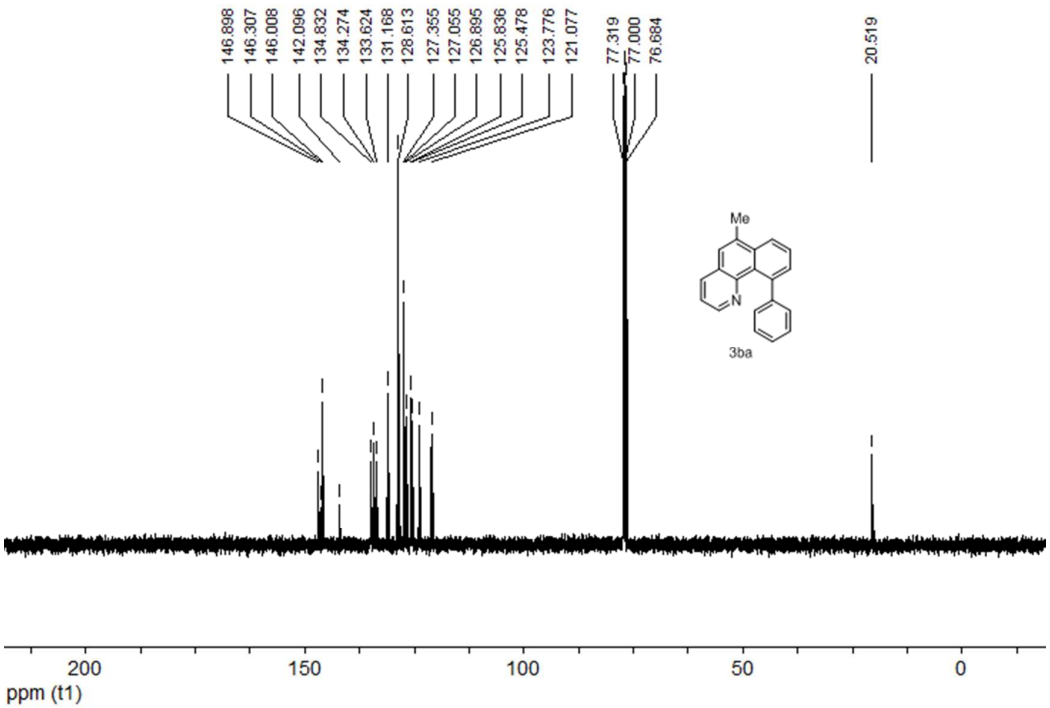

Figure S69. ^{13}C NMR for compound 3ba

^{1}H NMR and ^{13}C NMR Spectra of 3bb

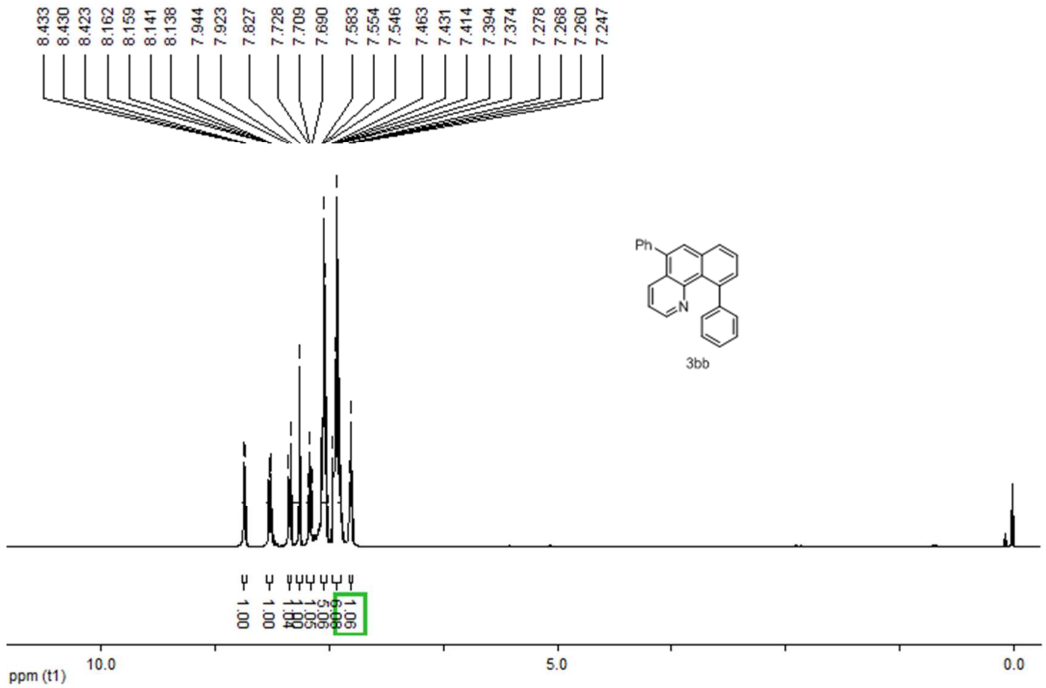

Figure S70. ^{1}H NMR for compound 3bb

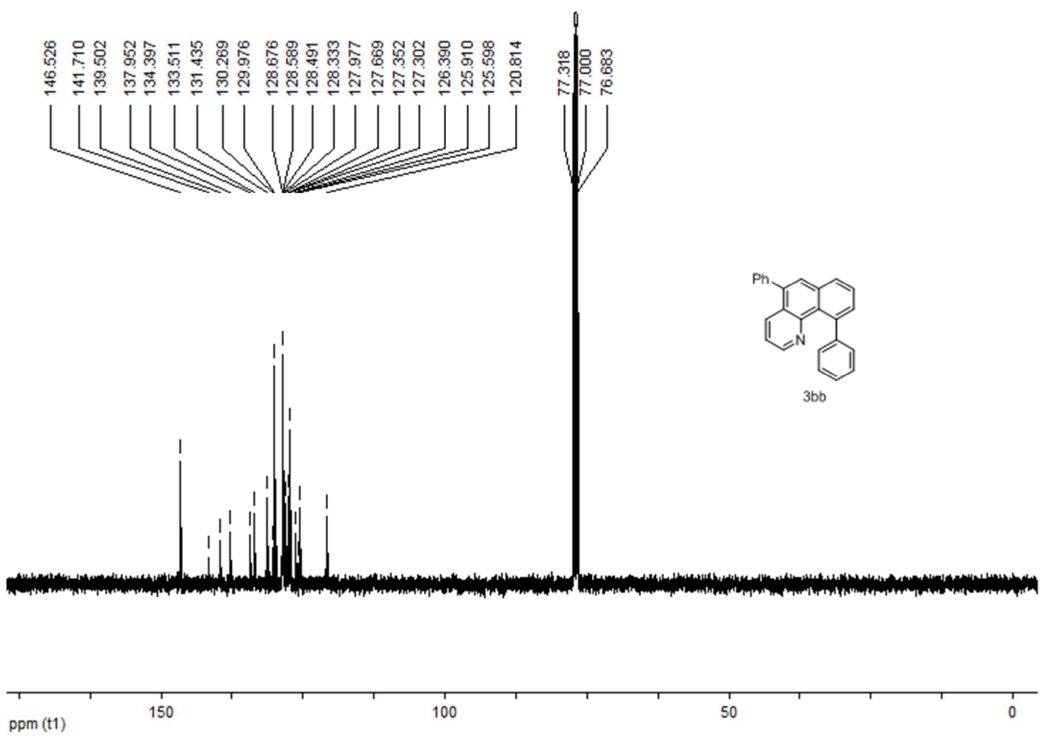

Figure S71. ^{13}C NMR for compound 3bb

^{1}H NMR and ^{13}C NMR Spectra of 3bc

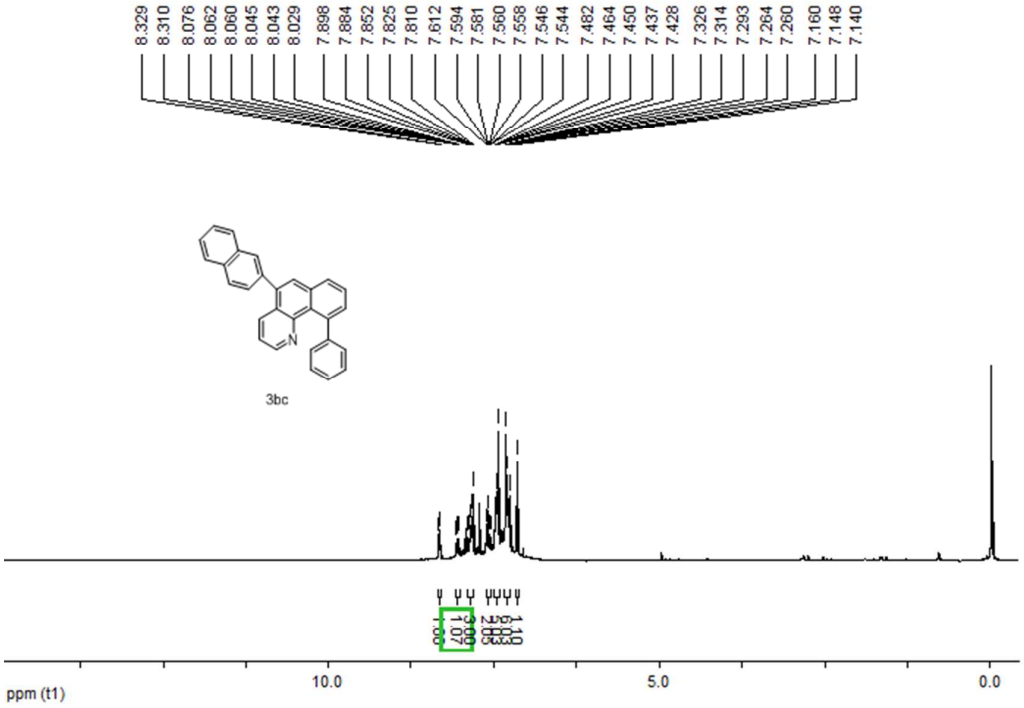

Figure S72. ^{1}H NMR for compound 3bc

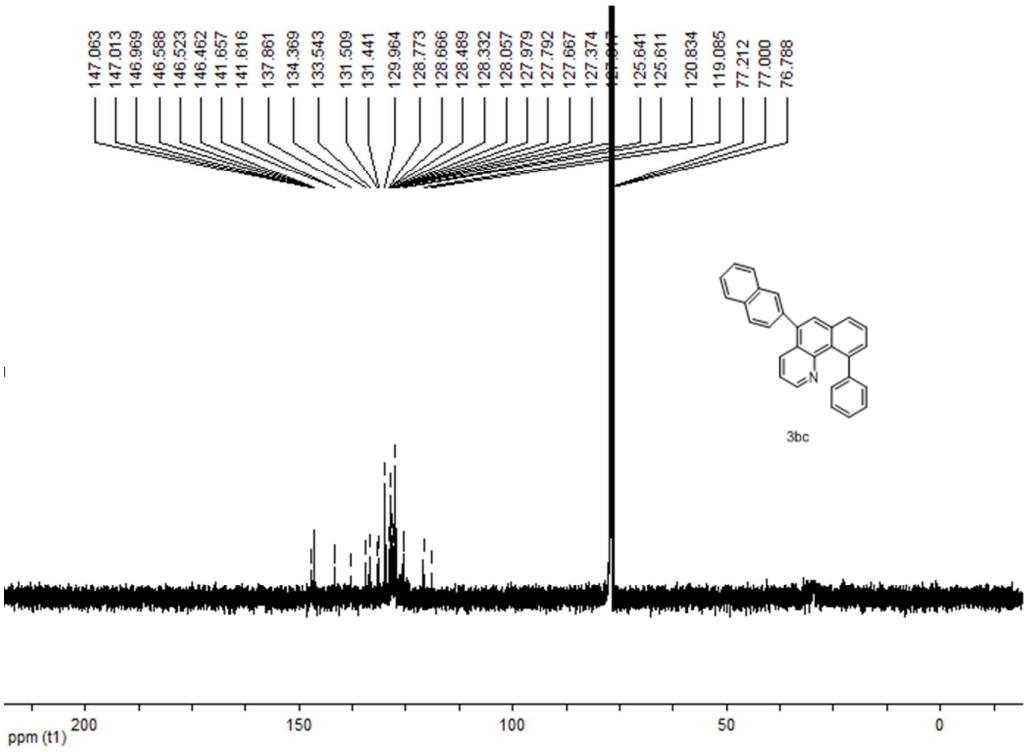

Figure S73. ^{13}C NMR for compound 3bc

^{1}H NMR and ^{13}C NMR Spectra of 3bd

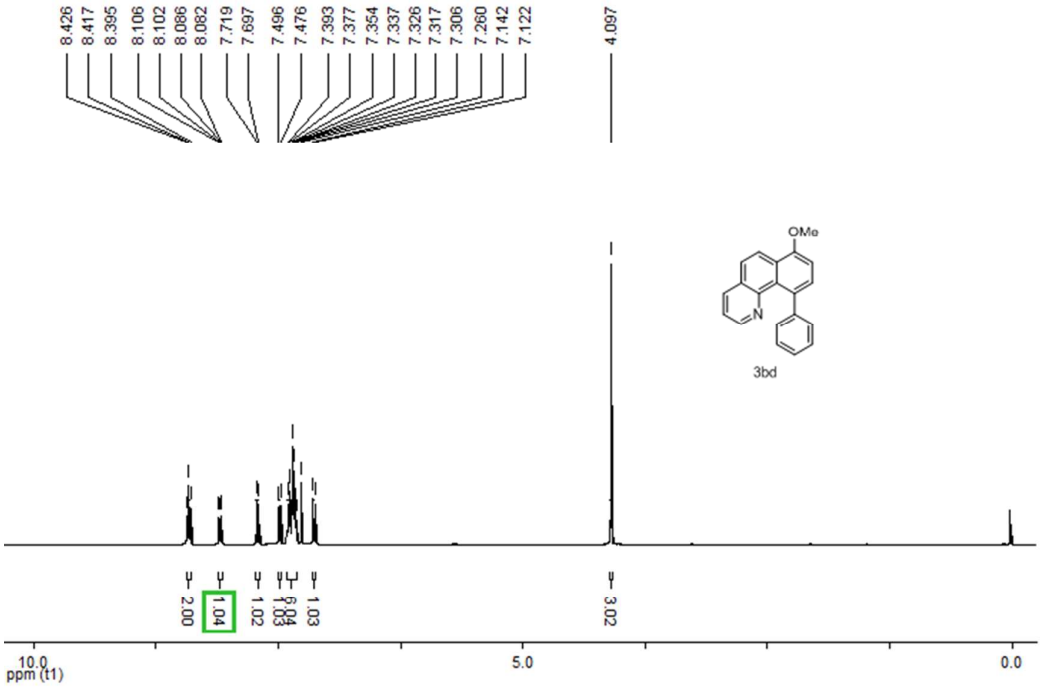

Figure S74. ^{1}H NMR for compound 3bd

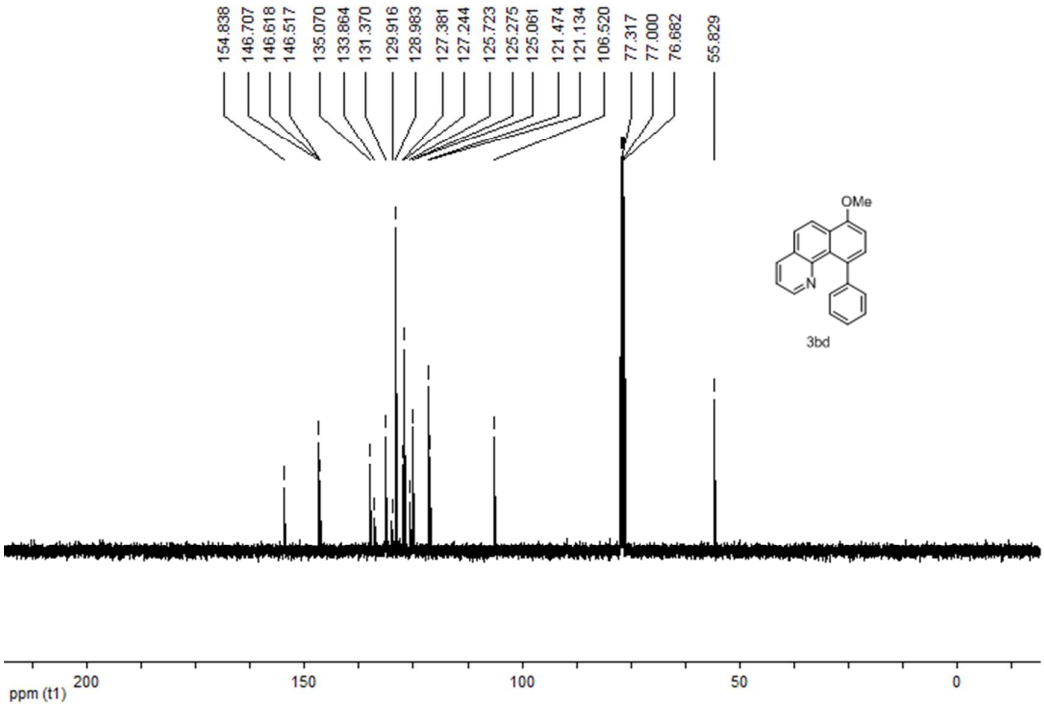

Figure S75. ^{13}C NMR for compound 3bd

^{1}H NMR and ^{13}C NMR Spectra of 3be

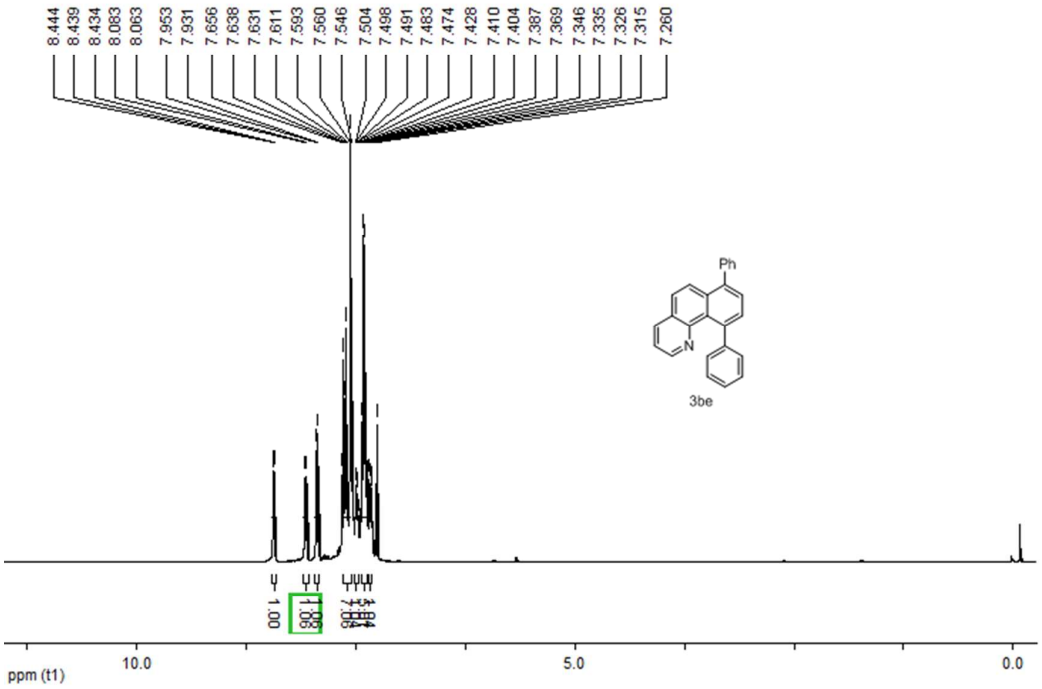

Figure S76. ^{1}H NMR for compound 3be

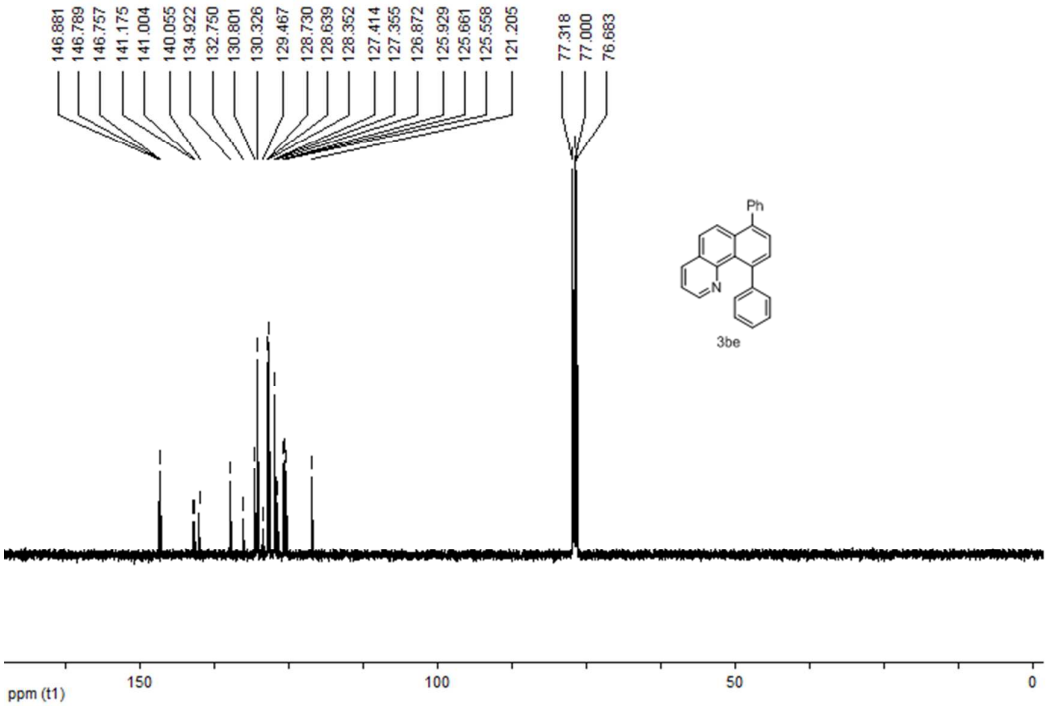

Figure S77. ^{13}C NMR for compound 3be

^{1}H NMR and ^{13}C NMR Spectra of 3bf

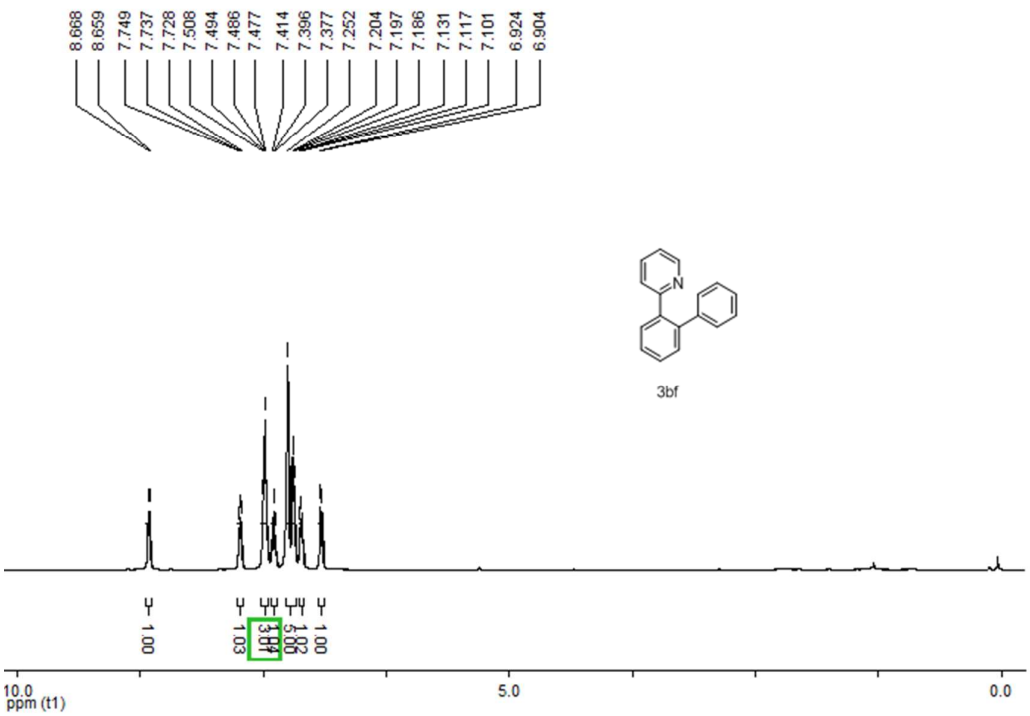

Figure S78. ^{1}H NMR for compound 3bf

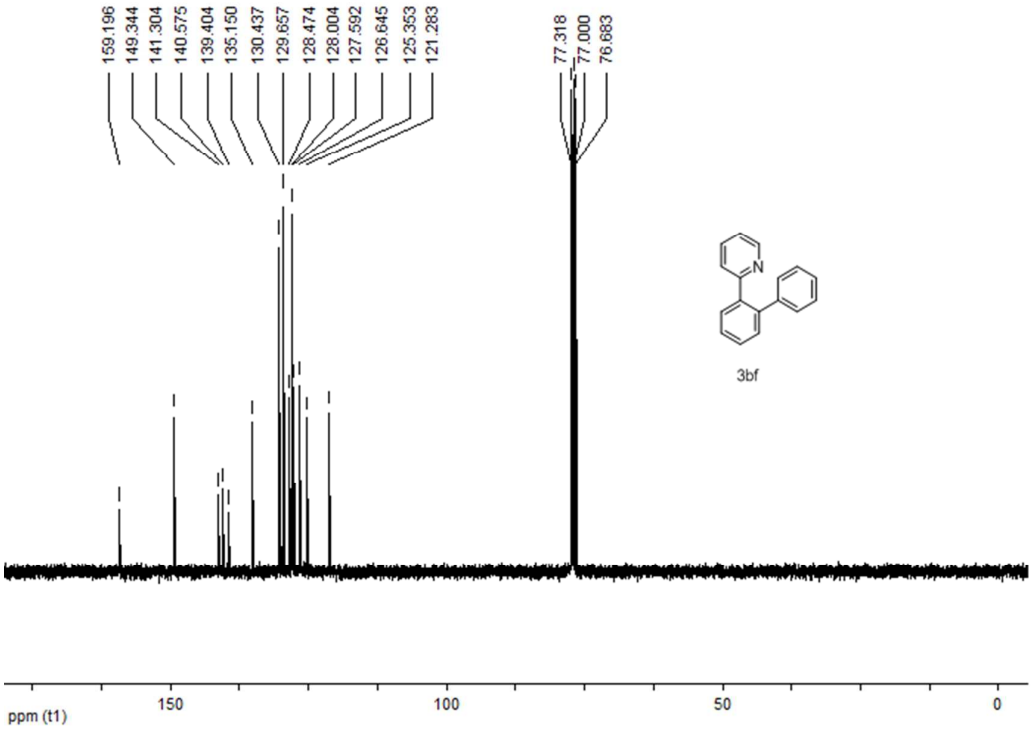

Figure S79. ^{13}C NMR for compound 3bf