

Electronic Supplementary Information

Effect of Structural Manipulation in Hetero-tri-aryl Amine Donor Based D-A'- π -A sensitizers in Dye Sensitized Solar Cells

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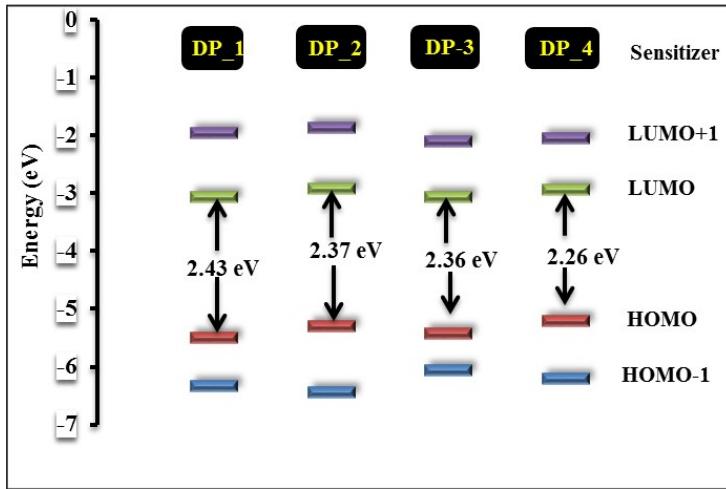


Figure S1. HOMO LUMO energy representation of the all sensitizer, parameters obtained at the B3LYP/6-31G(d) level in vacuum.

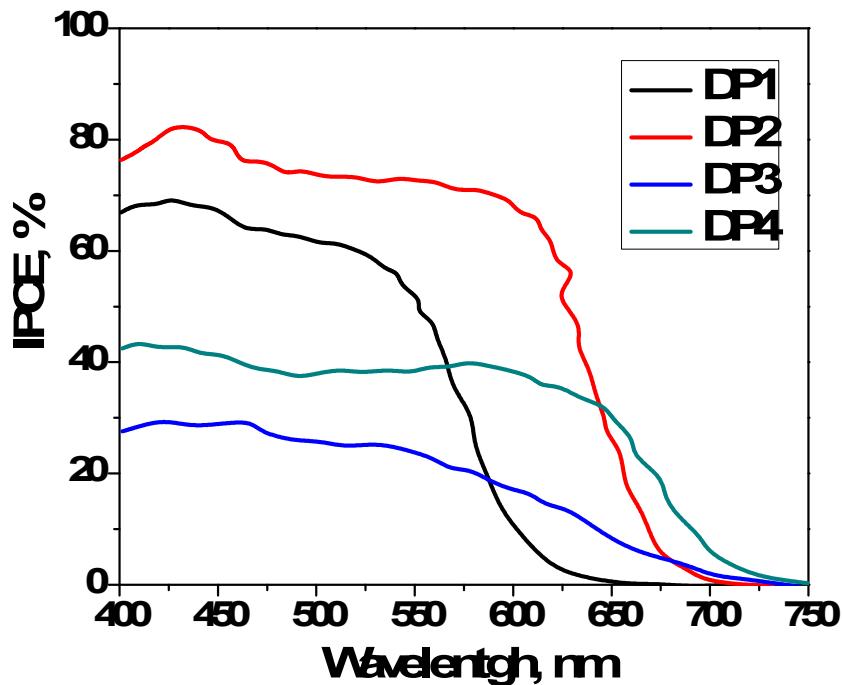


Figure S2. IPCE characteristics of DP devices

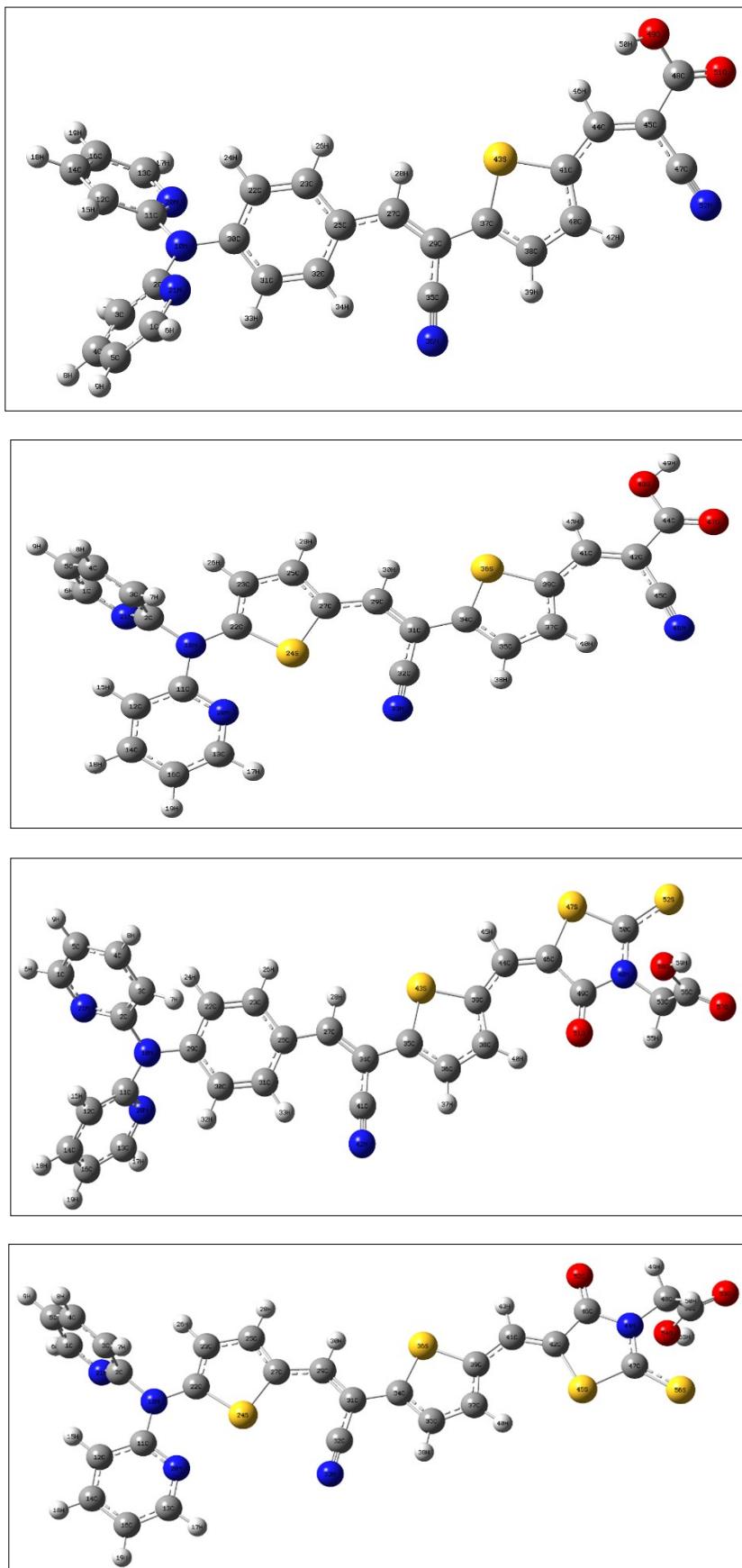


Figure S3. The optimized geometries of the DP1, DP2, DP3 and DP4 sensitizers, obtained at the B3LYP/6-31G(d) level in vacuum.

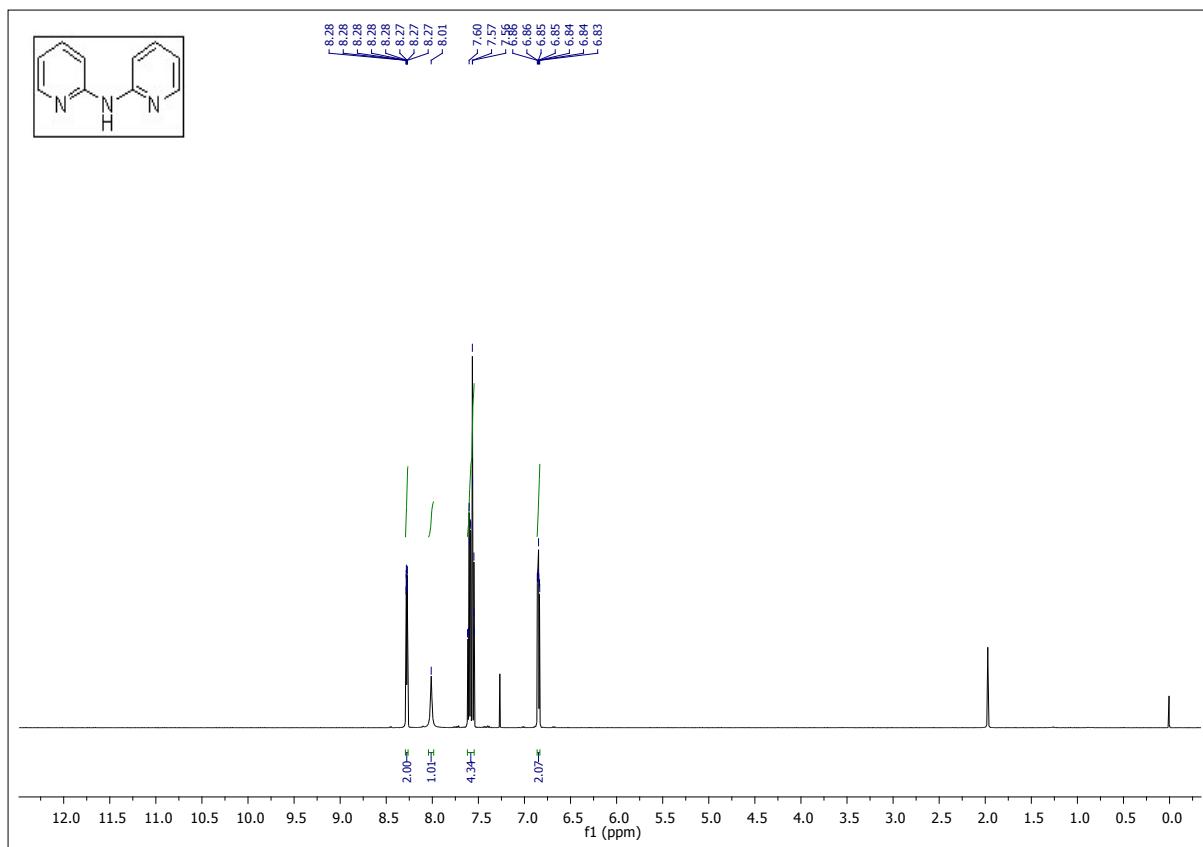


Figure S4: ¹H NMR spectrum of compound 1

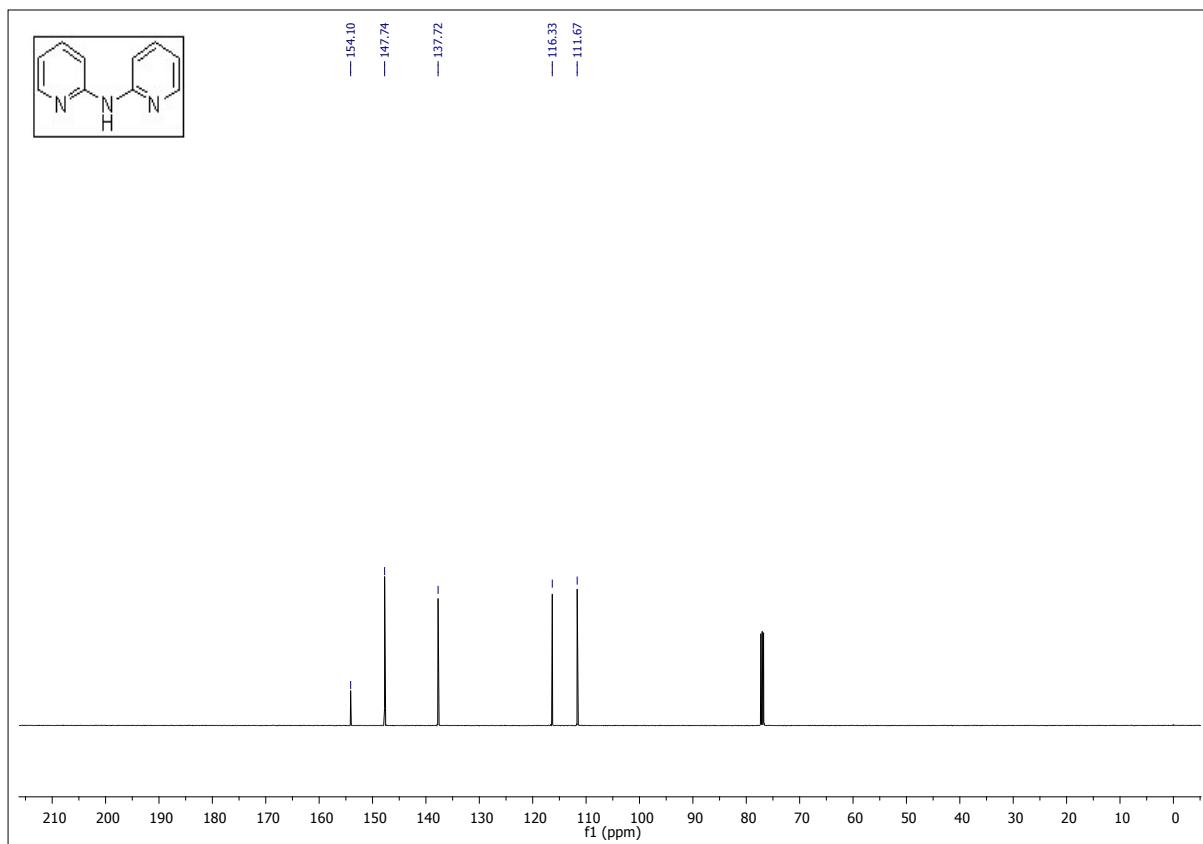


Figure S5: ¹³C NMR spectrum of compound 1

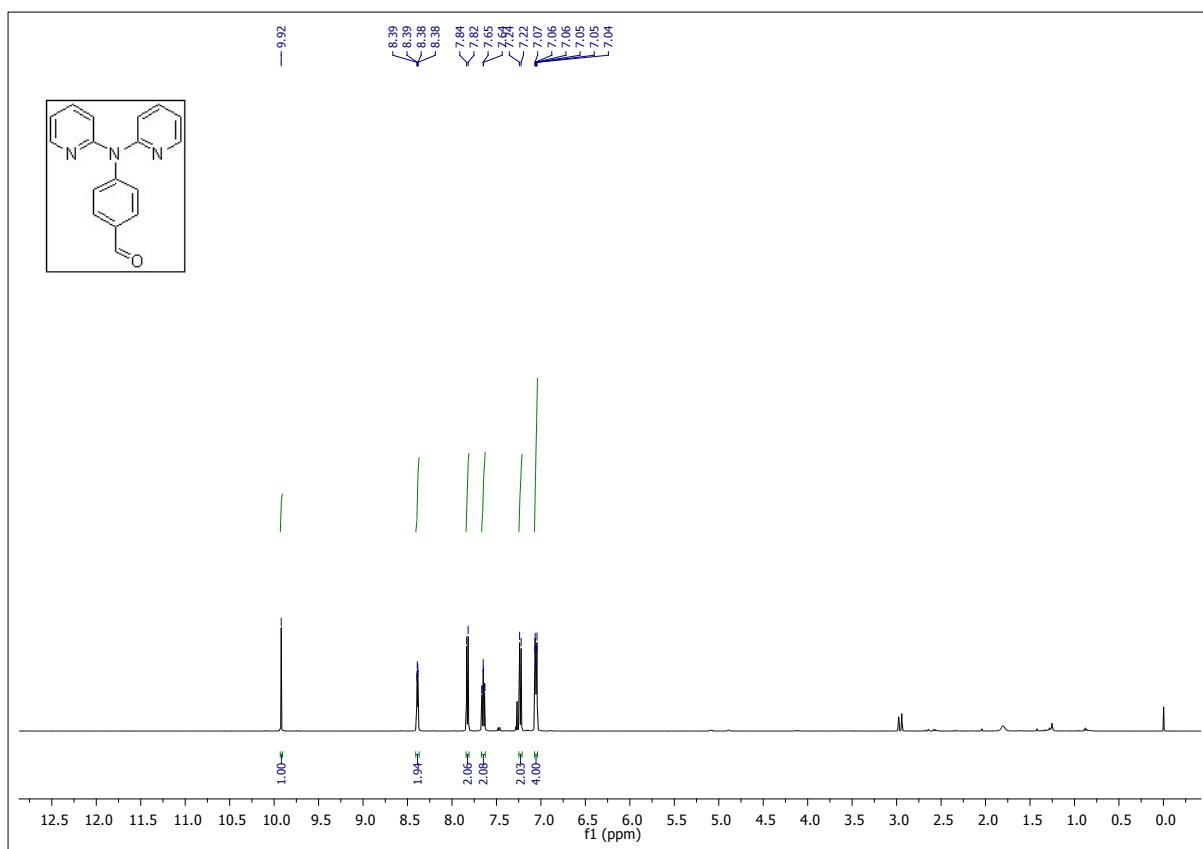


Figure S6: ¹H NMR spectrum of compound 2a

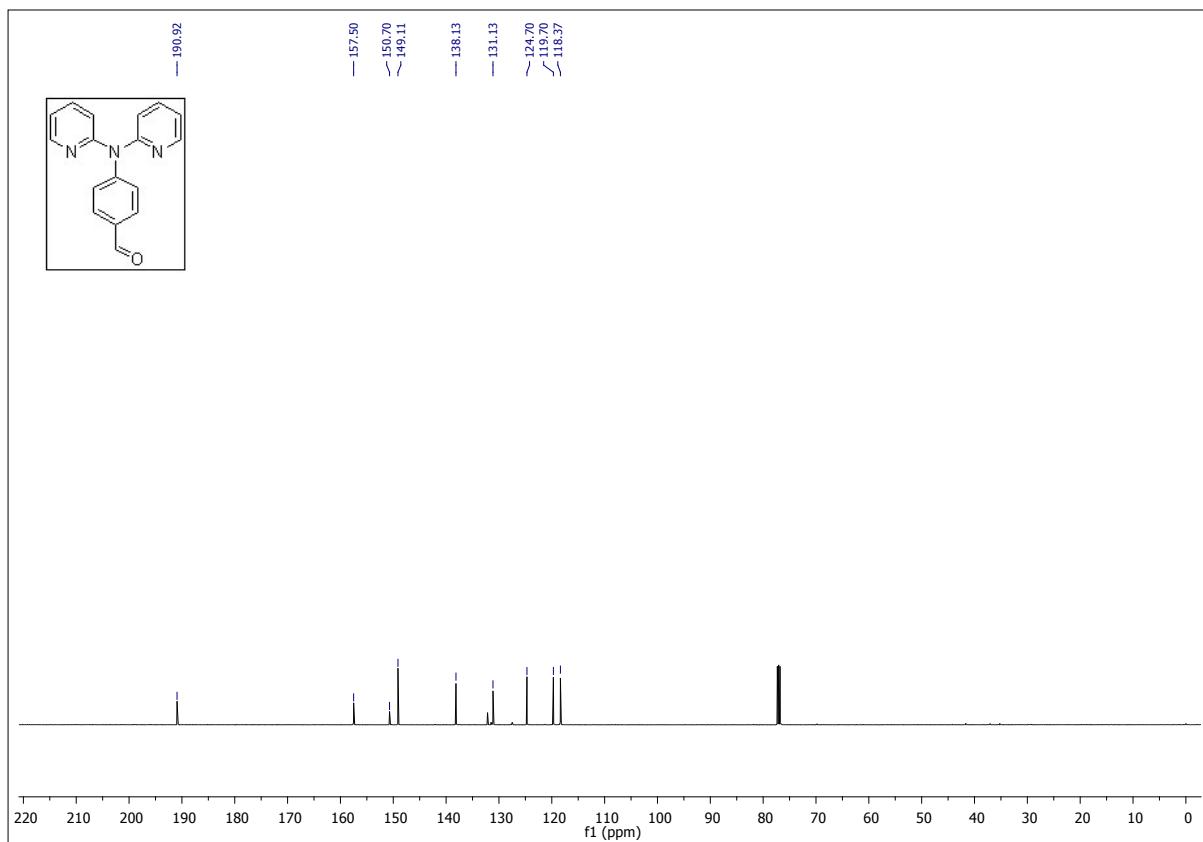


Figure S7: ¹³C NMR spectrum of compound 2a

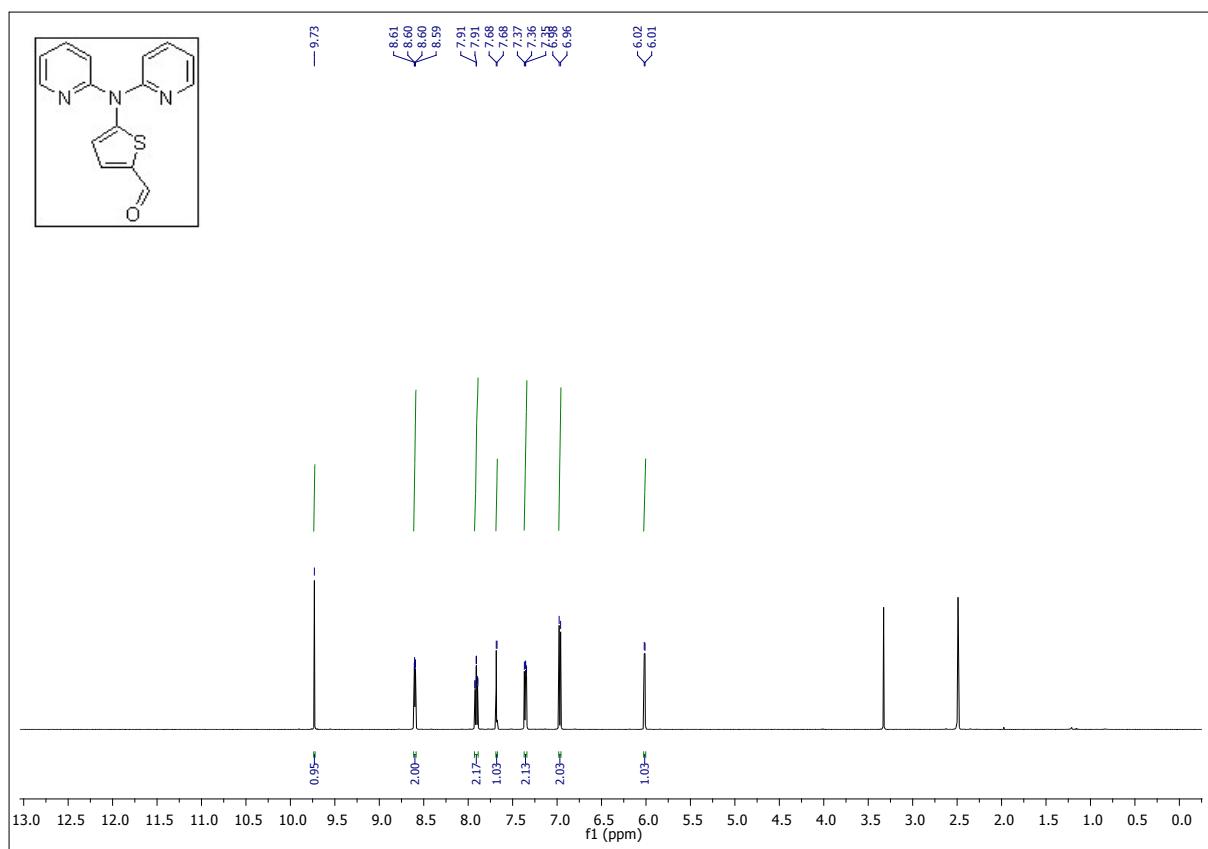


Figure S8: ¹H NMR spectrum of compound 2b

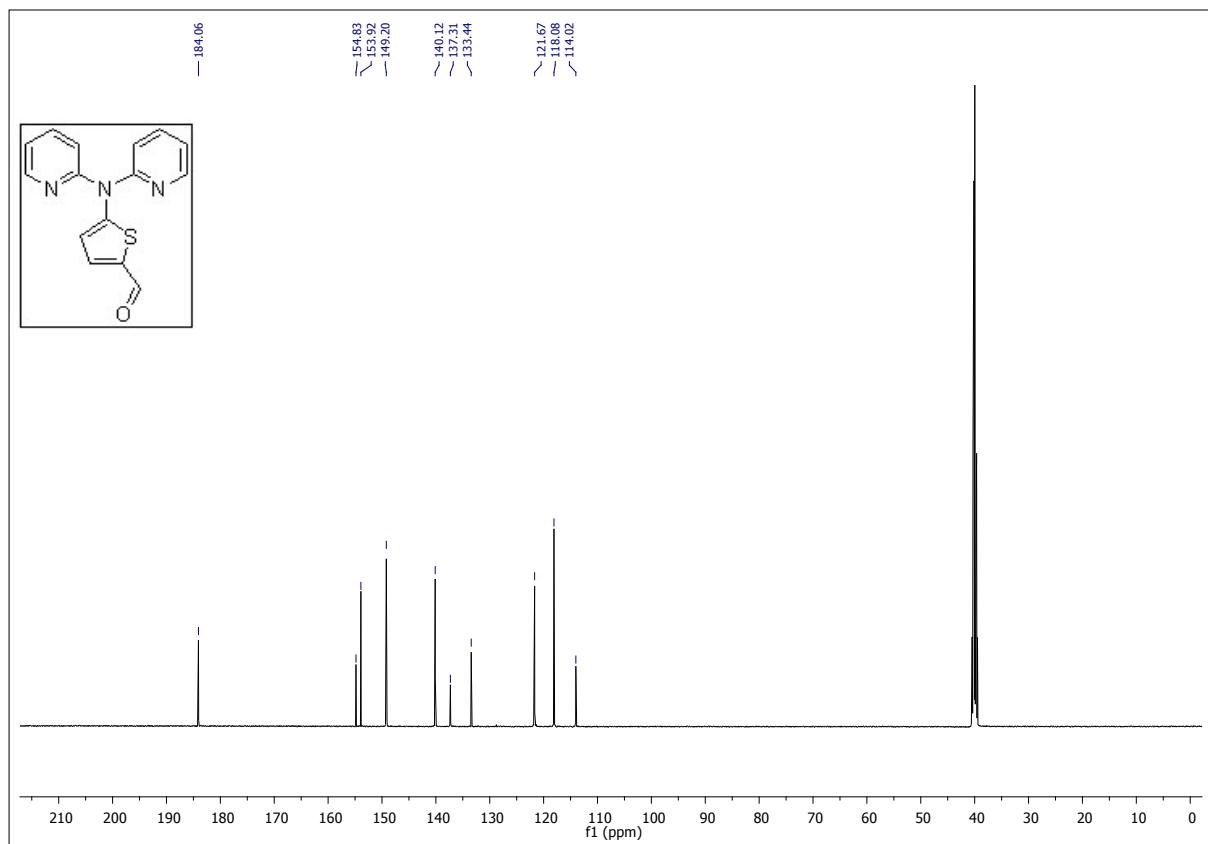


Figure S9: ¹³C NMR spectrum of compound 2b

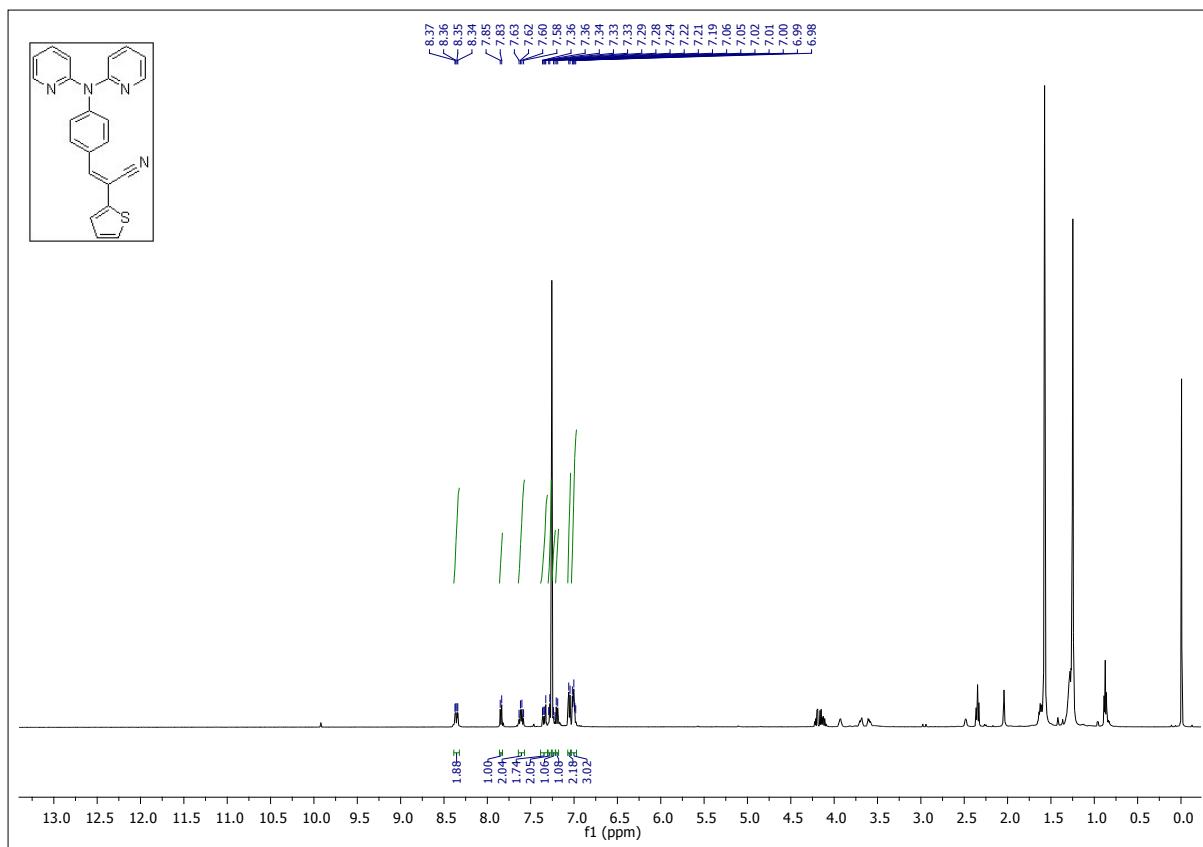


Figure S10: ¹H NMR spectrum of compound 3a

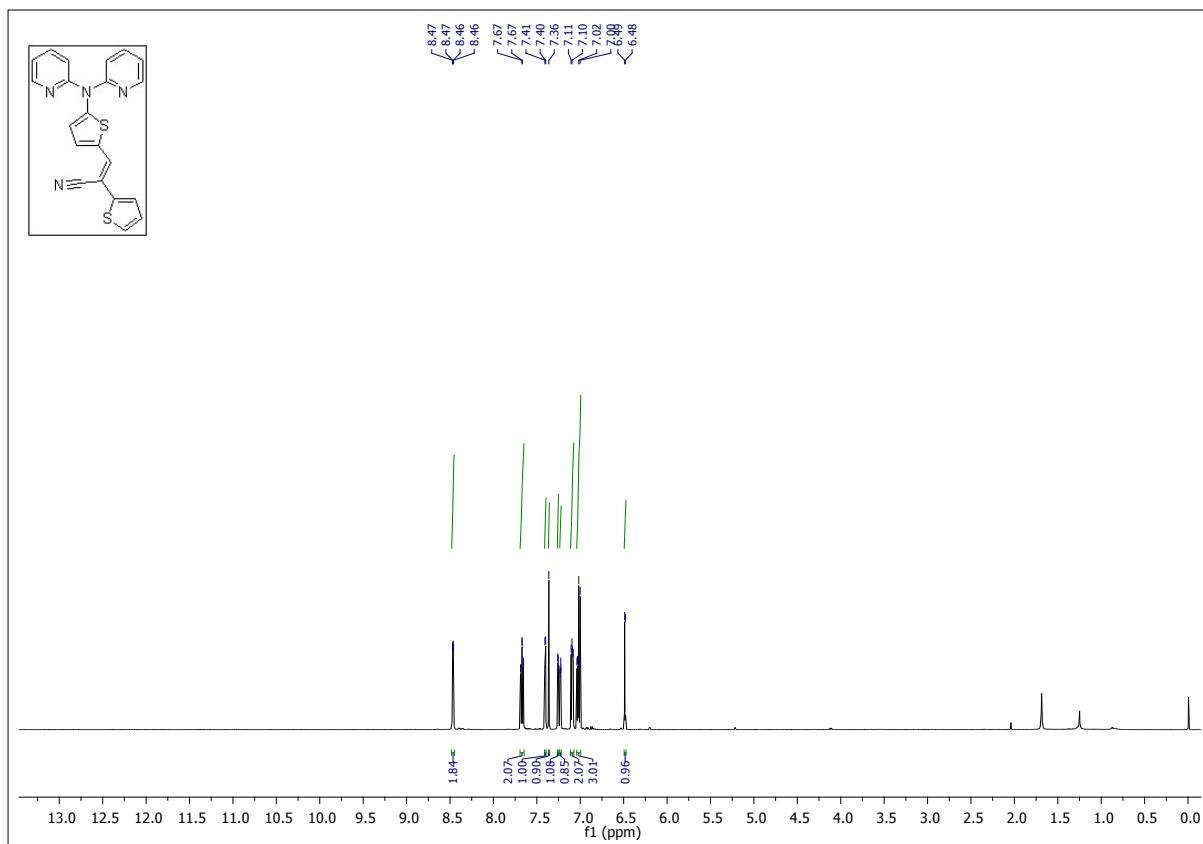


Figure S11: ¹H NMR spectrum of compound 3b

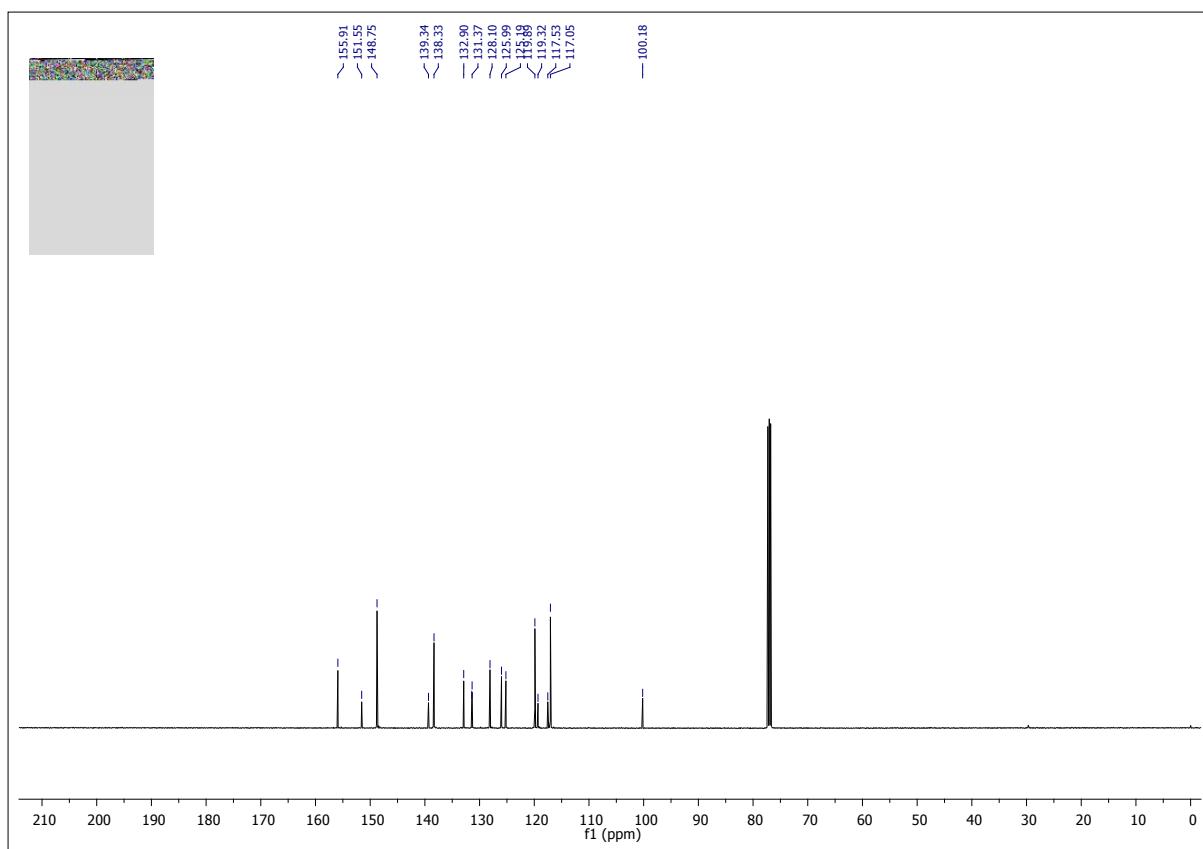


Figure S12: ^{13}C NMR spectrum of compound 3b

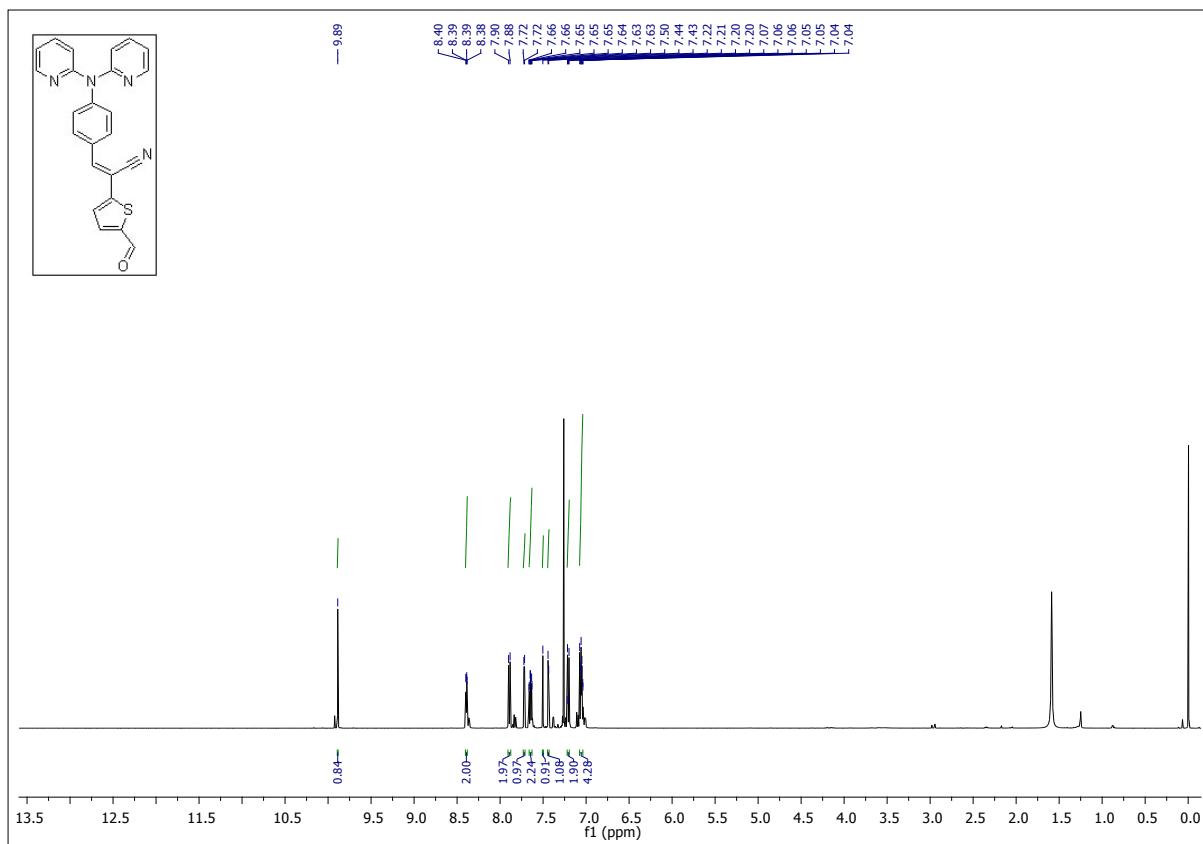


Figure S13: ^1H NMR spectrum of compound 4a

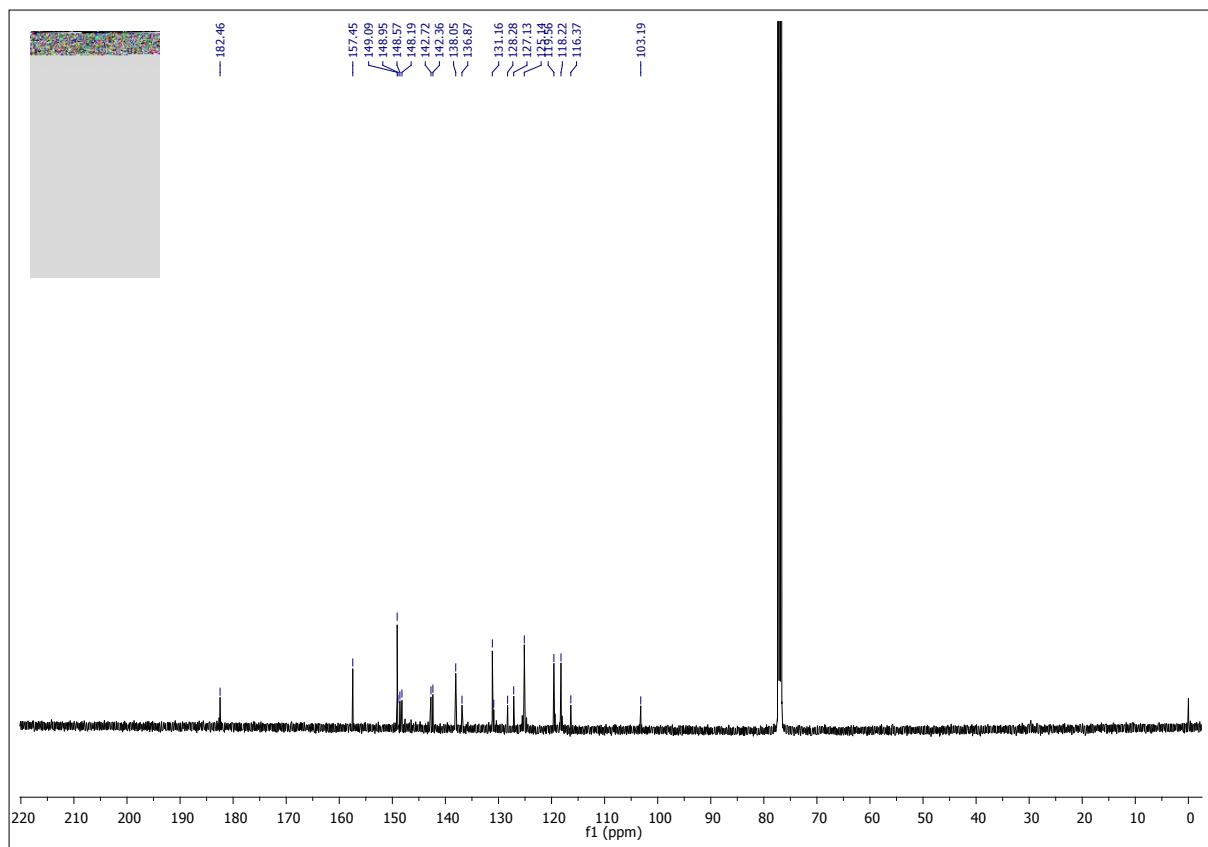


Figure S14: ^{13}C NMR spectrum of compound 4a

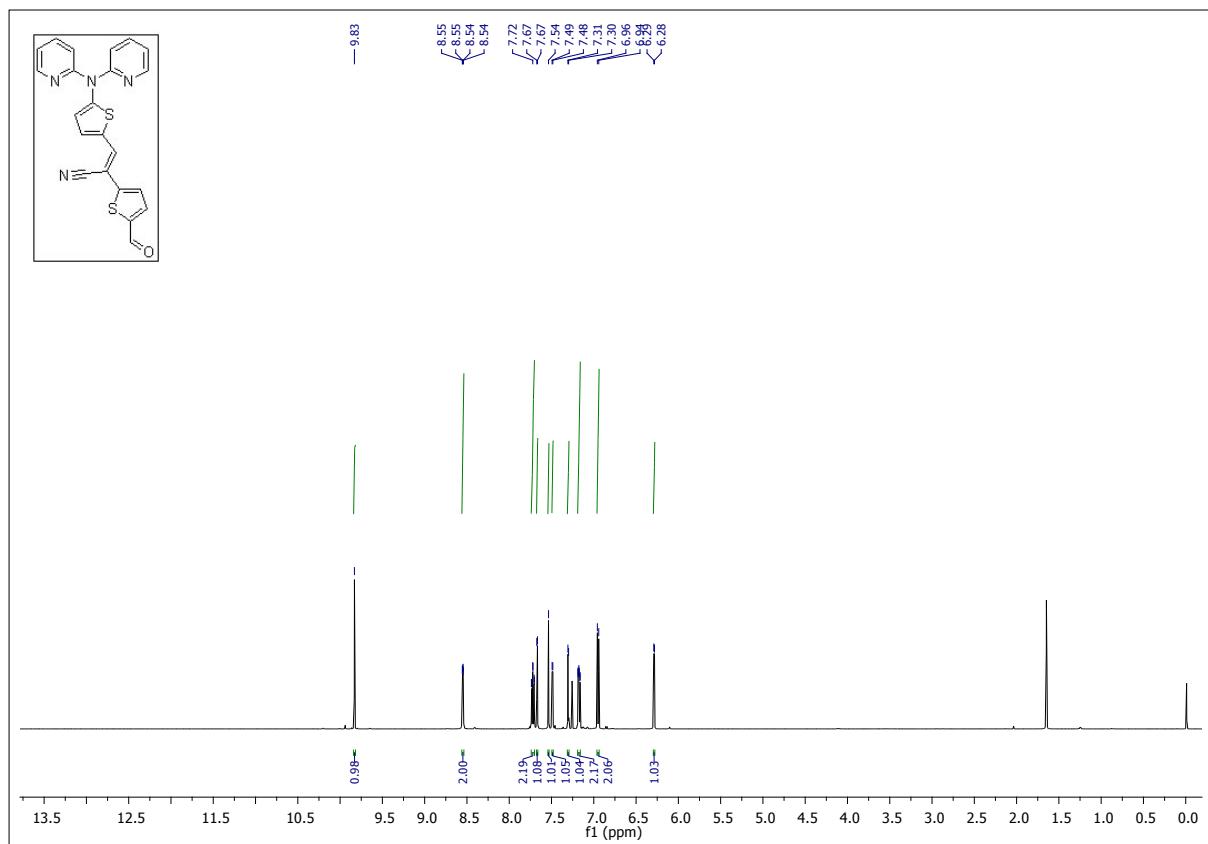


Figure S15: ^1H NMR spectrum of compound 4b

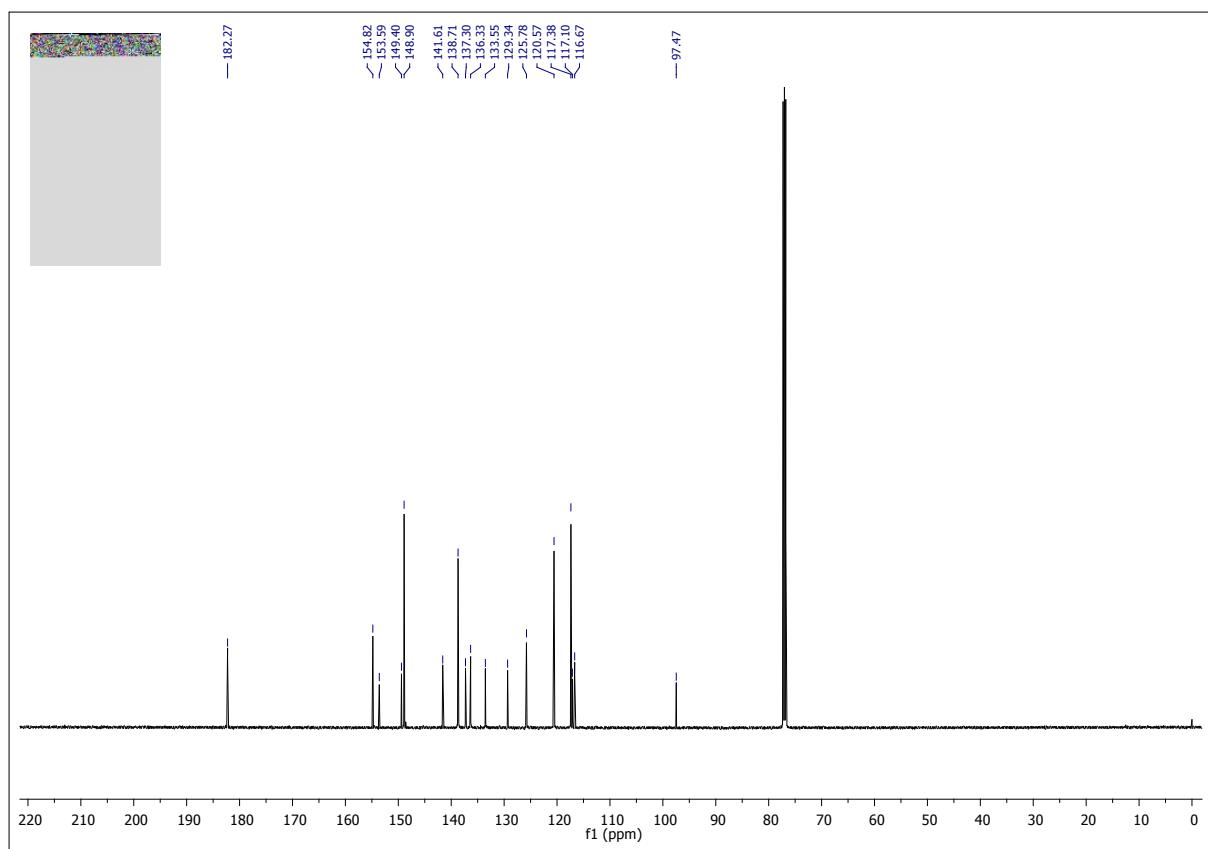


Figure S16: ^{13}C NMR spectrum of compound 4b

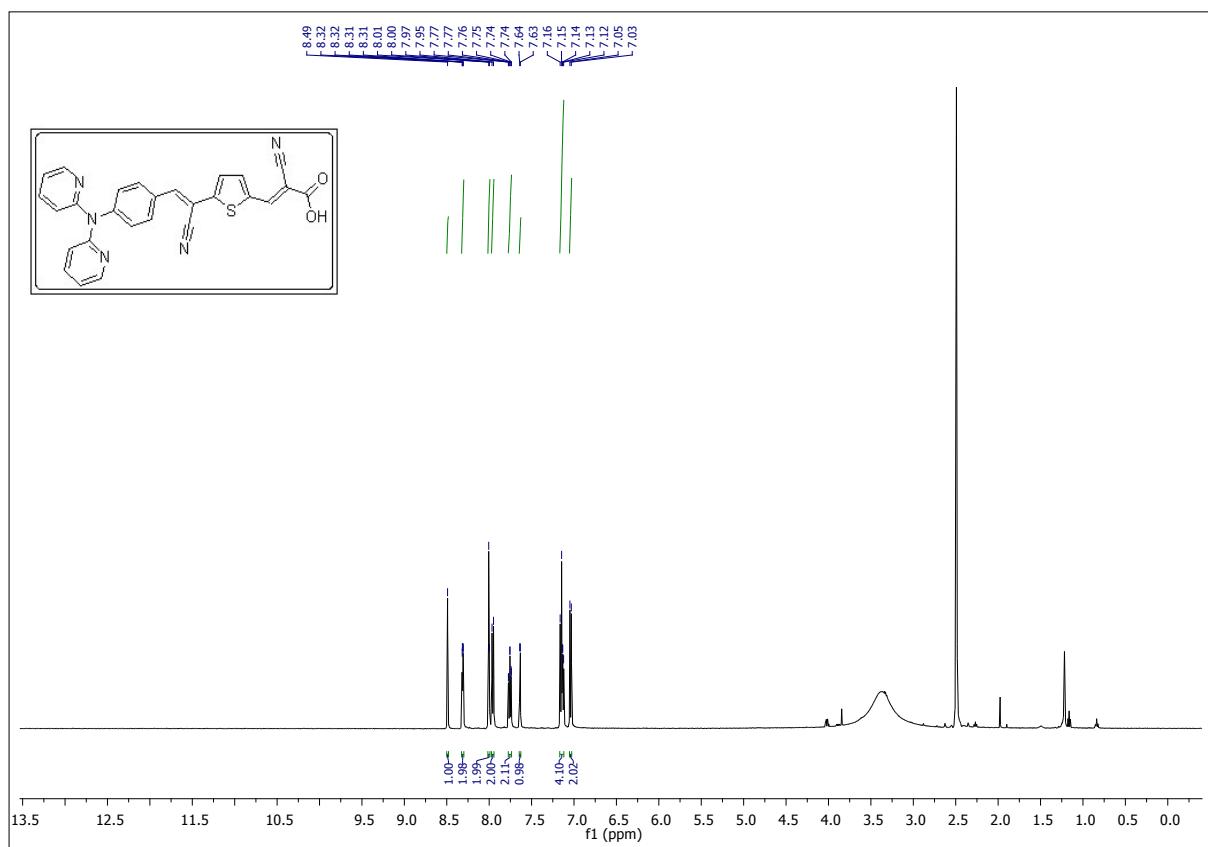


Figure S17: ^1H NMR spectrum of sensitizer DP1

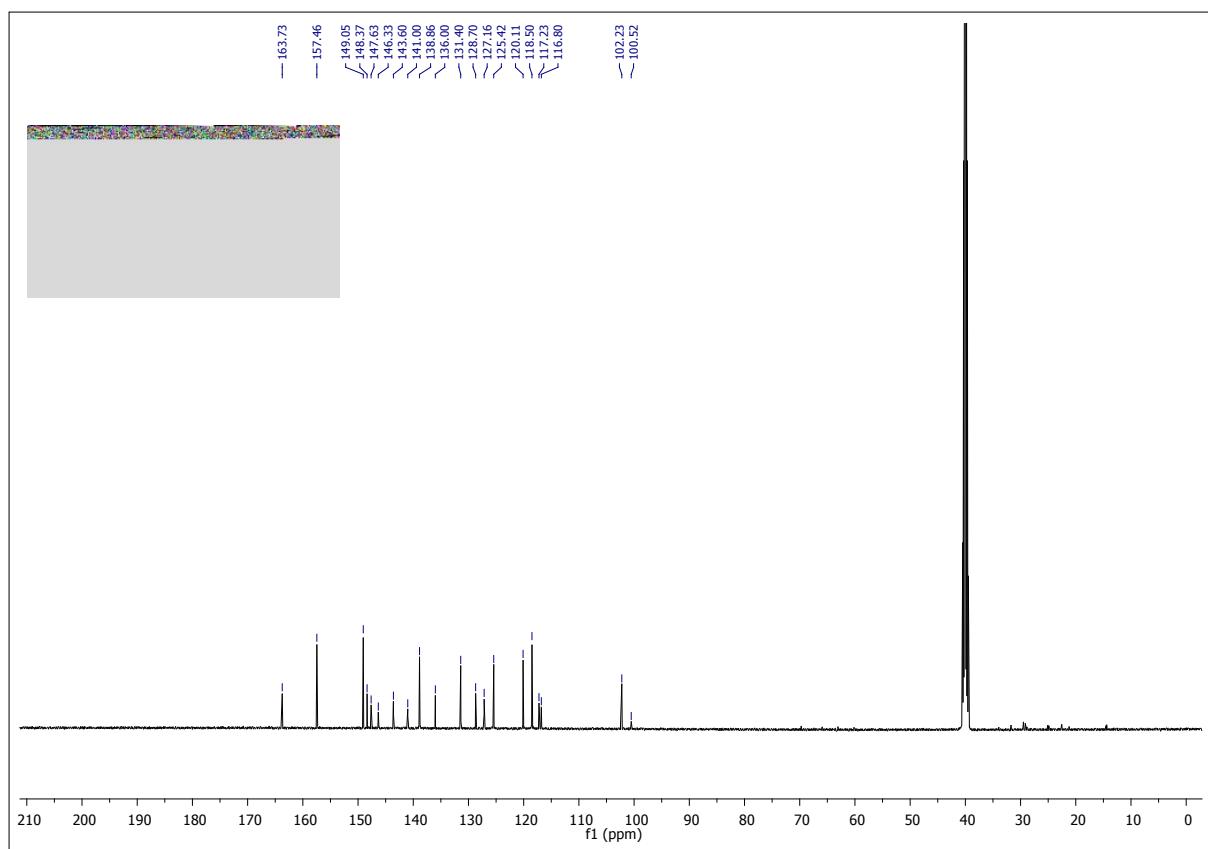


Figure S18: ^{13}C NMR spectrum of sensitizer DP1

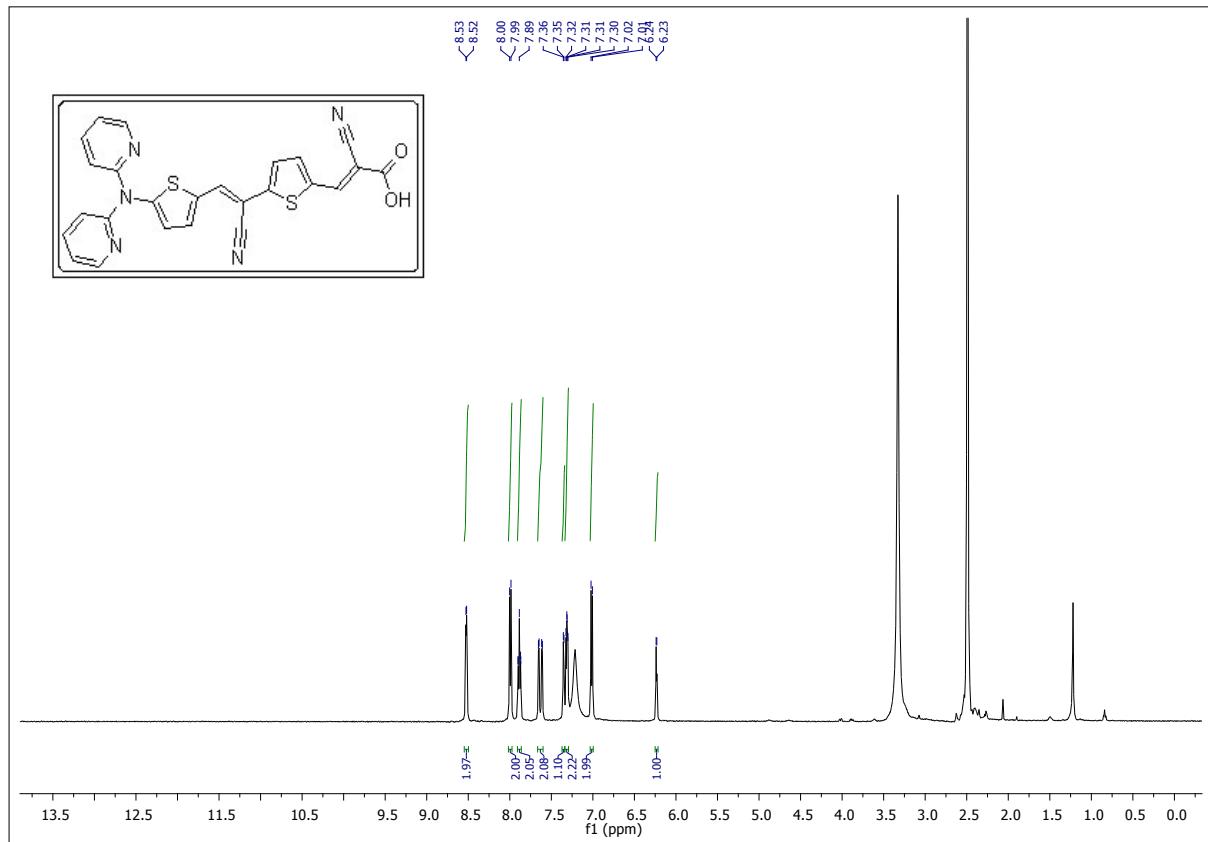


Figure S19: ^1H NMR spectrum of sensitizer DP2

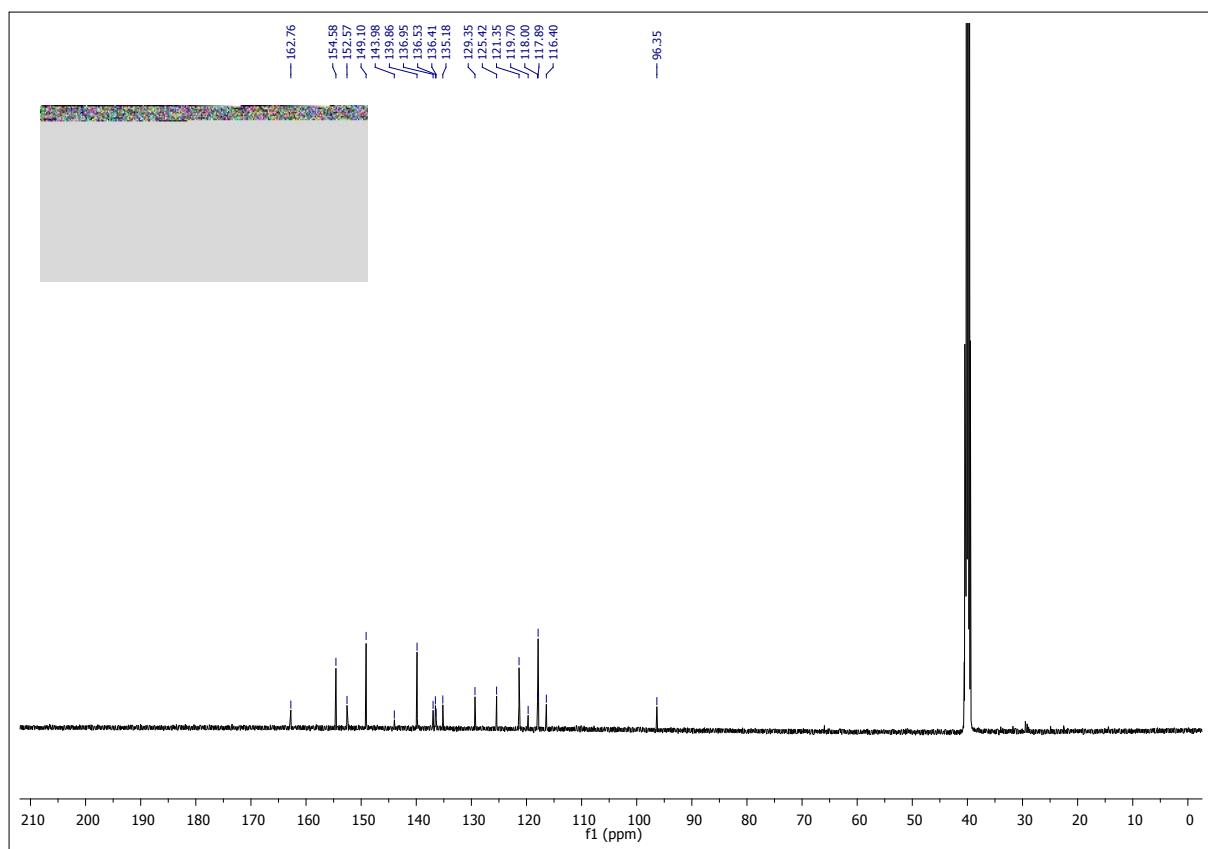


Figure S20: ¹³C NMR spectrum of sensitizer DP2

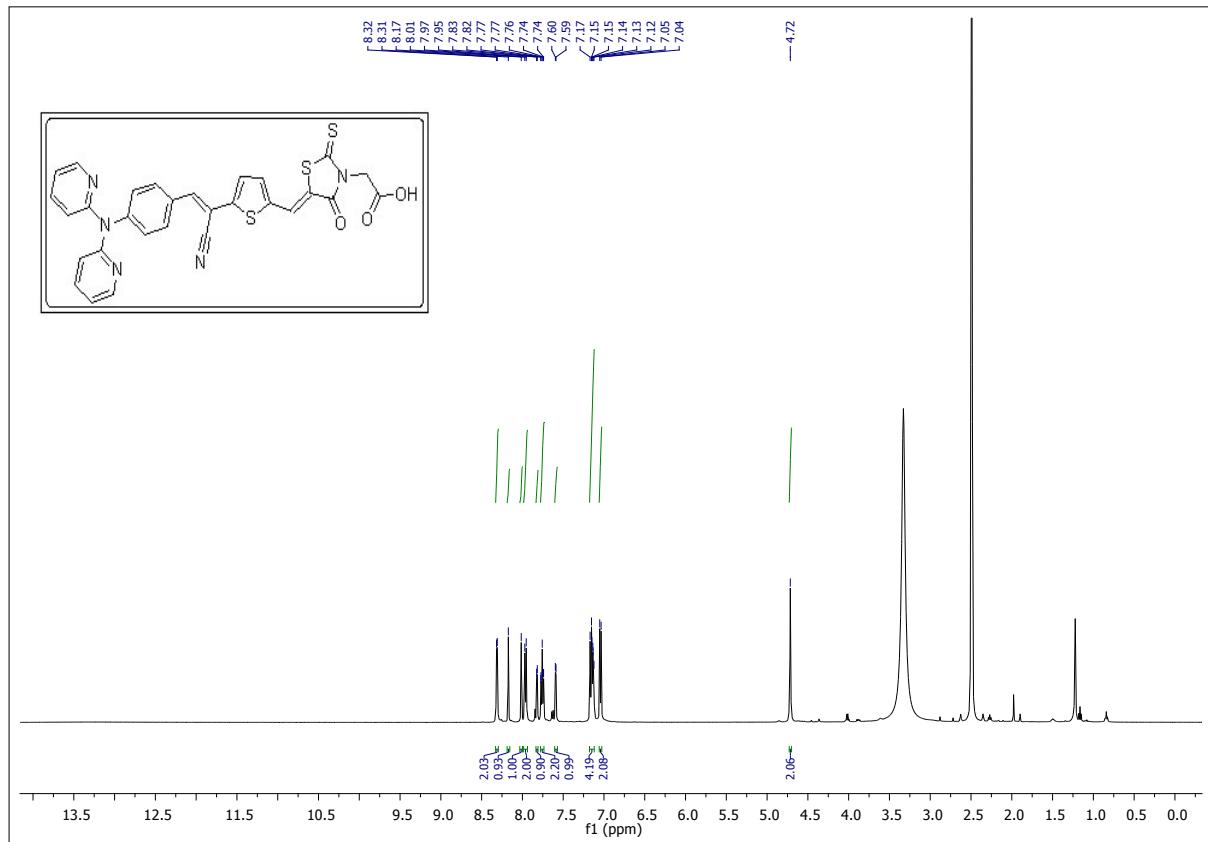


Figure S21: ¹H NMR spectrum of sensitizer DP3

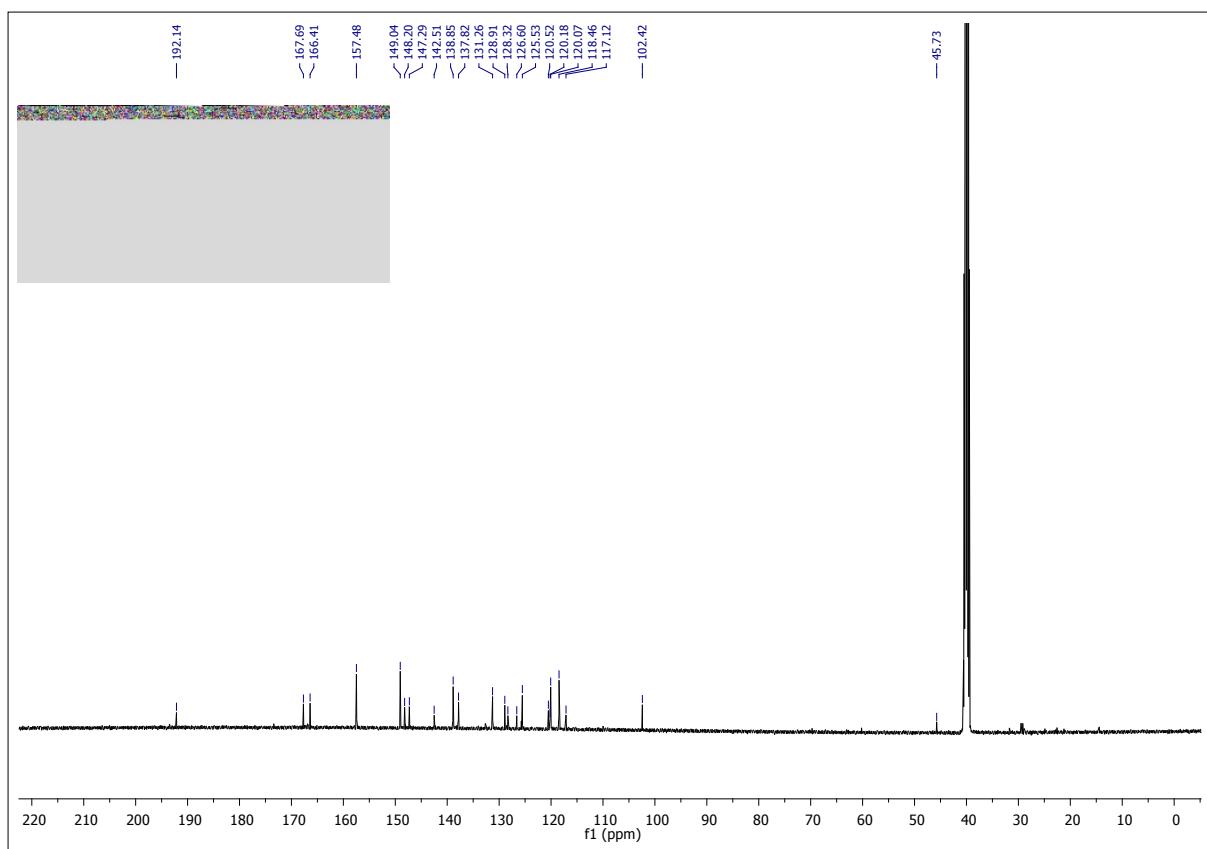


Figure S22: ¹³C NMR spectrum of sensitizer DP3

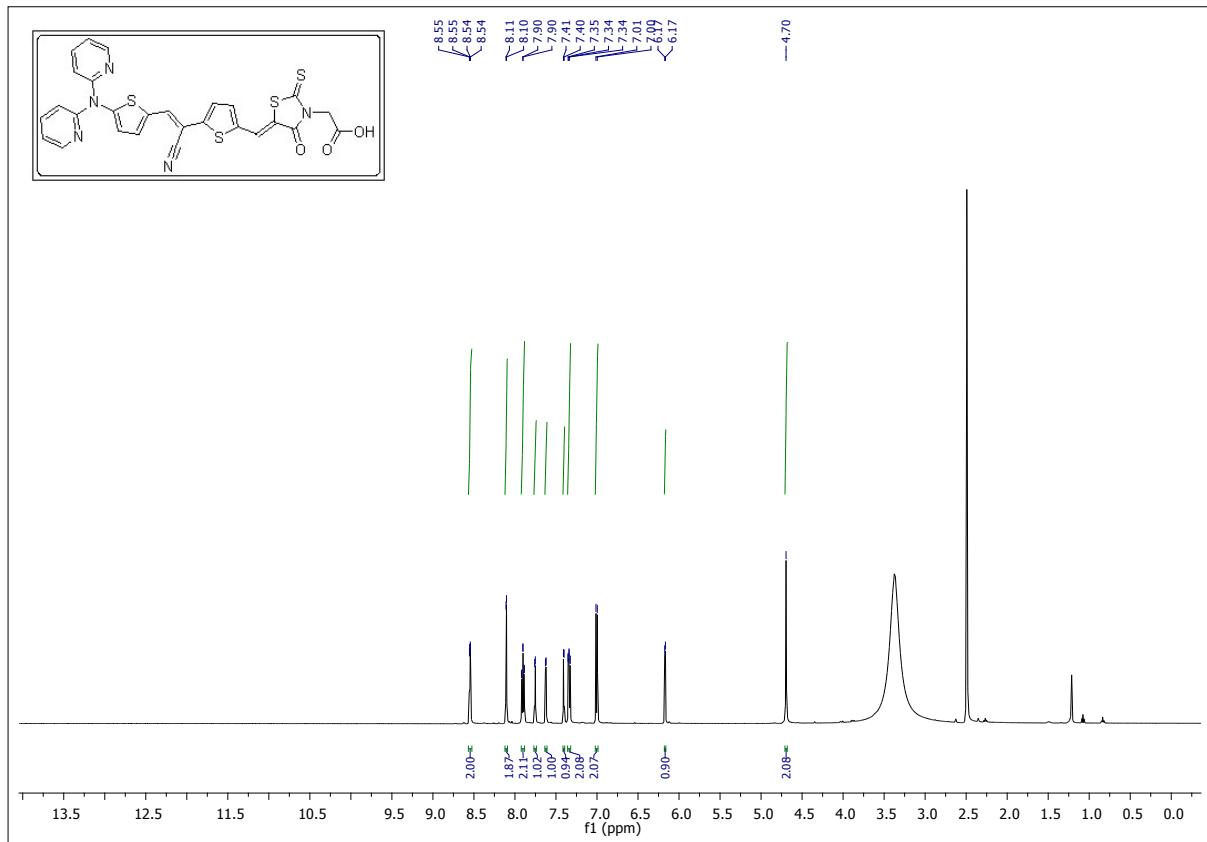


Figure S23: ¹H NMR spectrum of sensitizer DP4

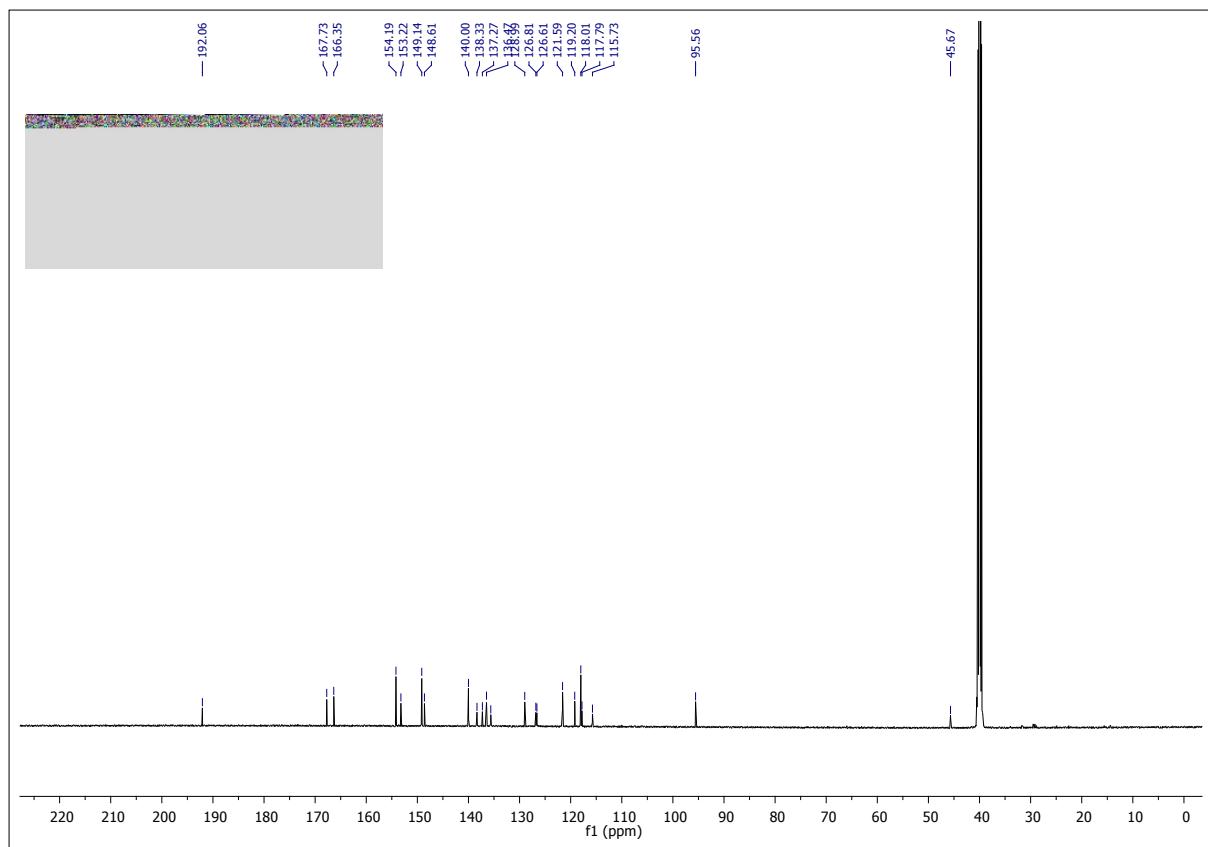


Figure S24: ¹³C NMR spectrum of sensitizer DP4

Table S1. Electrochemical characterization of DP sensitizers by DFT calculations.

| Sensitizer | HOMO (eV) | LUMO (eV) | LUMO+1 (eV) | HL-gap | HL+1-gap |
|------------|--------------|--------------|----------------|--------|----------|
| DP1 | -5.498 | -3.0626 | -1.958 | 2.435 | 3.539 |
| DP2 | -5.297 | -2.9211 | -1.866 | 2.372 | 3.426 |
| DP3 | -5.425 | -3.058 | -2.096 | 2.367 | 3.328 |
| DP4 | -5.211 | -2.945 | -2.053 | 2.266 | 3.158 |

Table S2 Electronic transition data obtained by TD-B3LYP/6-311++G(d,p) level for each molecule in the DMF solution.

| Sensi tizer | State s | λ_{max} (nm) | f | LHE | Excite d energ y (eV) | Transition character |
|----------------|----------------|--------------------------------|-------|--------|--------------------------------|---|
| DP1 | S ₁ | 573 | 1.323 | 0.9525 | 2.16 | H → L (99.56%) |
| | S ₂ | 412 | 0.503 | 0.6859 | 3.01 | H-1 → L (84.53%), H → L+1 (15.13%) |
| | S ₃ | 383 | 0.073 | 0.1547 | 3.24 | H-1 → L (14.66%), H → L+1 (80.46%). |
| DP2 | S ₁ | 594 | 1.644 | 0.9773 | 2.08 | H → L (99.34%) |
| | S ₂ | 452 | 0.441 | 0.6377 | 2.74 | H-1 → L (91.32%), H → L (8.06%) |
| | S ₃ | 431 | 0.001 | 0.0023 | 2.87 | H-2 → L (89.48%), H-2 → L+1 (7.54%), H-2 → L+2 (2.79%). |
| DP3 | S ₁ | 575 | 1.658 | 0.9780 | 2.15 | H → L (99.97%) |
| | S ₂ | 406 | 0.156 | 0.3017 | 3.05 | H-1 → L (26.79%), H → L+1 (71.62%) |
| | S ₃ | 366 | 0.016 | 0.0362 | 3.38 | H-1 → L (71.49%), H → L+1 (24.72%). |
| DP4 | S ₁ | 610 | 1.808 | 0.9844 | 2.03 | H → L (99.79%) |
| | S ₂ | 441 | 0.312 | 0.5124 | 2.81 | H-1 → L (28.27%), H → L+1 (70.47%) |
| | S ₃ | 422 | 0.001 | 0.0023 | 2.93 | H-2 → L (87.51%), H-2 → L+1 (9.31%). |