

Supporting Information

Isomeric quinoxalinedicarbonitrile as color managing acceptors of thermally activated delayed fluorescent emitters

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Experimental

General Information

4,4'-dibromobenzil and anhydrous o-xylene were acquired from Sigma Aldrich Chemical Co. 4,7-dibromobenzo[c][1,2,5]thiadiazole (BTD), 3,6-di-tert-butyl-9H-carbazole, 9,9-dimethyl-9,10-dihydroacridine, 4,5-diaminophthalonitrile, tris-tert-butylphosphine, and Tris(dibenzylideneacetone)dipalladium ($\text{Pd}_2(\text{dba})_3$) were purchased from P&H tech. p-toluenesulfonic acid (PTSA) and copper cyanide (CuCN) were purchased from Alfa Aesar Co. Sodium borohydride (NaBH_4) was purchased from Tokyo Chemical Industry Co., Ltd. Caesium carbonate (Cs_2CO_3), anhydrous ethanol, *N,N* dimethyl formamide (DMF), and acetic acid were obtained from Duksan Sci. Co. All these chemicals were used without further purification. Column chromatography (Silica Gel 60, 230–400 mesh, Merck) purified all four TADF emitters were further purified by sublimation (10^{-3} Torr at 300 °C) before applying for OLED devices.

The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in deuterated chloroform (CDCl_3) solution on an Avans 500 MHz spectrometer. Chemical shifts of the ^1H and ^{13}C NMR signals were quoted relative to tetramethylsilane ($\delta = 0.00$). All coupling constants are reported in Hertz. The ultraviolet–visible (UV–vis) spectra were obtained using a UV–vis spectrophotometer (JASCO, Easton, MD; V-730), and the photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (PerkinElmer, Waltham, MA; LS55). CV measurement was carried out in dichloromethane solution with scan rate at 100 mV/s. The glassy carbon, platinum wire and Ag/AgCl were used as working, counter and reference electrode respectively. Internal standard was ferrocenium/ferrocene couple and supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAClO_4). The mass spectra were recorded using a Advion, Expression LCMS spectrometer in APCI mode. Absolute photoluminescence quantum yields (PLQYs) of 1 wt % doped polystyrene film solid film were measured with a Hamamatsu Quantaurus-QY C11347-11 spectrometer under nitrogen atmosphere condition. The transient photoluminescence decay characteristics of solid film samples were recorded using a Quantaurus-Tau fluorescence lifetime measurement system (C11367-31, Hamamatsu Photonics).

Materials and Synthesis

3,6-Dibromobenzene-1,2-diamine (7) was prepared according to the literature procedure¹.

Synthesis of *1,2-bis(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)ethane-1,2-dione (5)*

4,4'-Dibromobenzil (5 g, 13.58 mmol) was reacted with 3,6-di-tert-butyl-9H-carbazole (8.3 g, 29.88 mmol), Cs₂CO₃ (17.71 g, 54.34 mmol), Pd₂(dba)₃ (1.24 g, 1.35 mmol) and tri-tert-butylphosphine (0.32 mL, 1.35 mmol) in anhydrous o-xylene (50 mL). The resulting mixture was stirred at 130 °C for 12 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane. Organic layer was dried over anhydrous MgSO₄ and was concentrated on rotary evaporator. The crude product obtained was purified by column chromatography (1:1 dichloromethane: n-hexane) to afford yellow solid (6.4 g, 62 %). ¹H NMR (500 MHz, CDCl₃): δ 8.29 (d, *J* = 9.0 Hz, 4H), 8.14 (m, 4H), 7.81 (d, *J* = 8.5 Hz, 4H), 7.48-7.52 (m, 8H), 1.47 (s, 36 H). ¹³C NMR (125 MHz, CDCl₃): δ 32.2, 35.1, 109.6, 116.7, 124.2, 124.4, 126.2, 130.6, 132.1, 138.4, 144.3, 144.8, 193.2. MS (FAB) *m/z* 765 [(M + H)⁺].

Synthesis of *1,2-bis(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)ethane-1,2-dione (6)*

Compound 6 was synthesized according to the similar procedure as described for the synthesis of compound 5, except that 9,9-dimethyl-9,10-dihydroacridine was used as the reactant instead of 3,6-di-tert-butyl-9H-carbazole, yielding bright yellow solid (4 g, 59 %). ¹H NMR (500 MHz, CDCl₃): δ 8.25 (d, *J* = 8.5 Hz, 4H), 7.54 (d, *J* = 8.5 Hz, 4H), 7.48-7.50 (dd, *J* = 7.5 and 1.5 Hz, 4H), 7.00-7.06 (m, 8H), 6.49 (d, *J* = 8 Hz, 4H), 1.67 (s, 12 H). ¹³C NMR (125 MHz, CDCl₃): δ 30.7, 36.6, 116.2, 122.2, 125.5, 126.6, 129.1, 131.2, 132.8, 140.4, 148.5, 193.1. MS (FAB) *m/z* 625 [(M + H)⁺].

Synthesis of *6,7-DCQx-Ca (1)*

Intermediate 5 (0.5 g, 0.65 mmol) and 4,5-diaminophthalonitrile (0.1 g, 0.65 mmol) were dissolved in anhydrous ethanol (10 mL). Catalytic amount of p-toluenesulphonic acid was added and the resulting mixture was refluxed for 12 hrs. After cooling to room temperature, the solid precipitated out in the reaction mixture was filtered, dried well and purified on column chromatography (1:1 DCM-hexane mixture) to get the desired product as yellow solid (0.51 g,

89 %). ¹H NMR (500 MHz, CDCl₃): δ 8.67 (s, 2H), 8.14 (d, *J* = 1.0 Hz, 4H), 7.91-7.92 (d, *J* = 6.5 Hz, 4H), 7.72-7.73 (d, *J* = 6 Hz, 4H), 7.46-7.50 (m, 8H), 1.47 (s, 36 H). ¹³C NMR (125 MHz, CDCl₃). δ 31.9, 34.8, 109.2, 114.4, 115.1, 116.5, 123.9, 126.2, 131.6, 135.1, 136.8, 138.5, 140.7, 141.7, 143.8, 156.5. MS (FAB) *m/z* 887 [(M + H)⁺]. Element analysis Calcd. for C₆₂H₅₈N₆ C(83.94 %), H(6.59 %), N(9.47 %); found C(84.60 %), H(6.19 %), N(9.22 %).

Synthesis of 6,7-DCQx-Ac (2)

Compound 2 was synthesized according to the similar procedure as described for the synthesis of compound 1, except that intermediate 6 was used as the reactant instead of intermediate 5, yielding red solid (0.49 g, 82 %). ¹H NMR (500 MHz, CDCl₃): δ 8.70 (s, 2H), 7.89 (d, *J* = 6.0 Hz, 4H), 7.45-7.47 (m, 8H), 6.85-6.93 (m, 8H), 6.32-6.34 (dd, *J* = 6 and 1 Hz, 4H), 1.68 (s, 12 H). ¹³C NMR (125 MHz, CDCl₃). δ 30.8, 36.1, 114.2, 114.6, 114.9, 121.2, 125.2, 126.5, 130.8, 131.3, 132.5, 136.7, 136.9, 140.5, 141.7, 143.7, 156.9. MS (FAB) *m/z* 747 [(M + H)⁺]. Element analysis Calcd. for C₅₂H₃₈N₆ C(83.62 %), H(5.13 %), N(11.25 %); found C(83.56 %), H(5.31 %), N(11.05 %).

Synthesis of 9,9'-((5,8-dibromoquinoxaline-2,3-diyl)bis(4,1-phenylene))bis(3,6-di-tert-butyl-9H-carbazole) (8)

3,6-Dibromobenzene-1,2-diamine (0.15 g, 0.56 mmol) and intermediate 5 (0.43 g, 0.56 mmol) were dissolved in acetic acid (20 mL) and the resulting mixture was stirred at 110 °C for 12 h. After cooling to room temperature, the yellow solid precipitated out in the reaction mixture was filtered, washed with acetic acid and n-hexane and dried well as a yellow solid (0.5 g, 89 %). ¹H NMR (500 MHz, CDCl₃): δ 8.15 (m, 4H), 8.01 (s, 2H), 7.99 (m, 4H), 7.69 (d, *J* = 8 Hz, 4H), 7.47-7.51 (m, 8H), 1.47 (s, 36 H). ¹³C NMR (125 MHz, CDCl₃). δ 32.2, 34.9, 109.5, 116.5, 123.9, 124.1, 126.3, 132.0, 133.6, 136.0, 138.9, 139.7, 140.0, 143.6, 153.5. MS (FAB) *m/z* 993 [(M + H)⁺].

Synthesis of 10,10'-((5,8-dibromoquinoxaline-2,3-diyl)bis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine) (9)

Compound 9 was synthesized according to the similar procedure as described for the synthesis of compound 8, except that intermediate 6 was used as the reactant instead of intermediate 5,

yielding yellow solid as pure product (0.4 g, 78 %). ^1H NMR (500 MHz, CDCl_3): δ 8.01 (s, 2H), 7.96-7.98 (d, J = 8.5 Hz, 4H), 7.41-7.46 (m, 8H), 6.86-6.92 (m, 8H), 6.36-6.38 (dd, J = 7 and 2 Hz, 4H), 1.68 (s, 12 H). ^{13}C NMR (125 MHz, CDCl_3): δ 31.0, 36.2, 114.3, 121.1, 124.0, 125.3, 126.7, 130.5, 131.5, 133.0, 133.9, 137.7, 139.8, 140.7, 142.9, 153.8. MS (FAB) m/z 853 $[(M + H)^+]$.

Synthesis of 5,8-DCQx-Ca (3)

Intermediate 8 (0.5 g, 0.50 mmol) was dissolved in DMF (20 mL), copper cyanide (0.22 g, 2.51 mmol) was added and the resulting mixture was stirred at 140 °C for 12 hrs. After cooling to room temperature water was added in the reaction mixture and extracted with dichloromethane. The organic layer was dried over MgSO_4 , concentrated on rotavapour and purified by column chromatography (1:1 dichloromethane-hexane mixture) to afford an orange solid (0.24 g, 69 %). ^1H NMR (500 MHz, CDCl_3): δ 8.17 (s, 2H), 8.13 (d, J = 1.0 Hz, 4H), 8.00-8.01 (d, J = 6 Hz, 4H), 7.71-7.72 (d, J = 6 Hz, 4H), 7.47-7.51 (m, 8H), 1.47 (s, 36 H). ^{13}C NMR (125 MHz, CDCl_3): δ 32.0, 34.8, 109.4, 114.9, 116.4, 117.1, 123.8, 123.9, 126.1, 131.8, 134.2, 134.8, 138.5, 140.3, 140.7, 143.7, 155.5. MS (FAB) m/z 887 $[(M+H)^+]$. Element analysis Calcd. for $\text{C}_{62}\text{H}_{58}\text{N}_6$ C(83.94 %), H(6.59 %), N(9.47 %); found C(83.86 %), H(6.74 %), N(9.27 %).

Synthesis of 5,8-DCQx-Ac (4)

Compound 4 was synthesized according to the similar procedure as described for the synthesis of compound 3, except that intermediate 9 was used as the reactant instead of intermediate 8, yielding red solid as pure product (0.22 g, 63 %). ^1H NMR (500 MHz, CDCl_3): δ 8.26 (s, 2H), 7.98 (d, J = 6.0 Hz, 4H), 7.44-7.47 (m, 8H), 6.89-6.93 (m, 8H), 6.36-6.38 (dd, J = 6 and 1 Hz, 4H), 1.68 (s, 12 H). ^{13}C NMR (125 MHz, CDCl_3): δ 30.8, 36.1, 114.3, 114.8, 117.5, 121.1, 125.2, 126.5, 130.8, 131.2, 132.8, 134.5, 136.5, 140.5, 143.7, 156.1. MS (FAB) m/z 747 $[(M + H)^+]$. Element analysis Calcd. for $\text{C}_{52}\text{H}_{38}\text{N}_6$ C(83.62 %), H(5.13 %), N(11.25 %); found C(83.98 %), H(4.96 %), N(11.00 %).

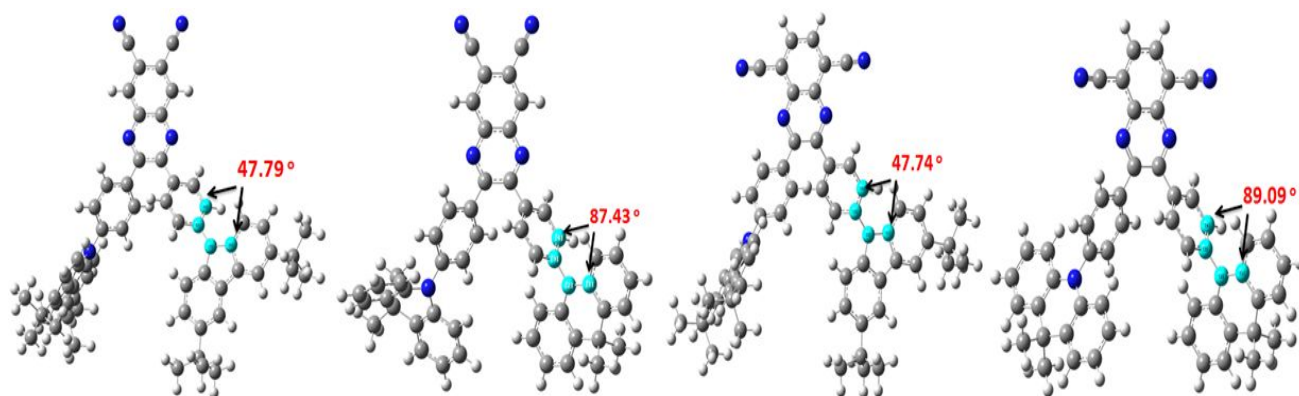


Figure S1. Optimized structures of emitters1-4 with respective dihedral angles between donor and acceptor unit.

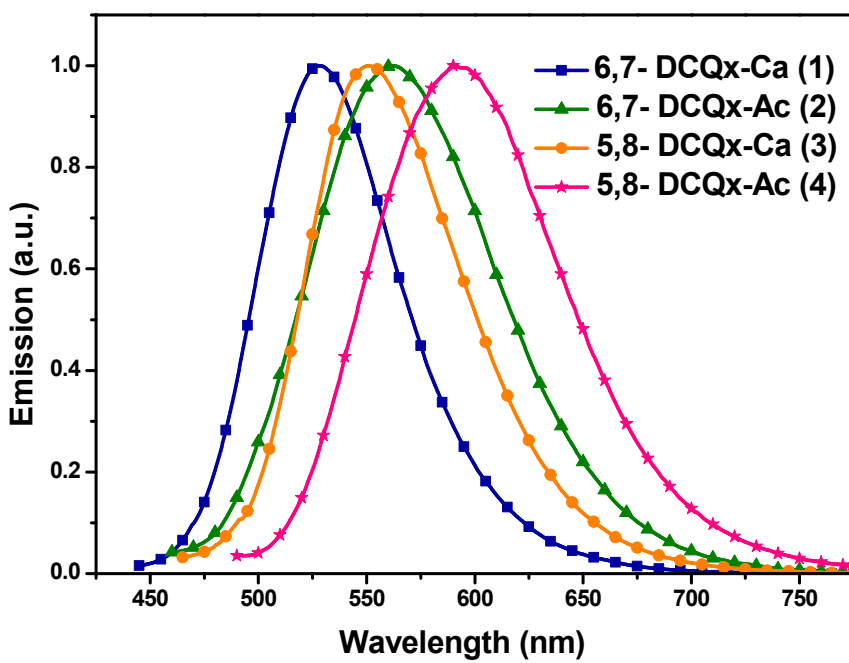


Figure. S2. Solid state (1 % in polystyrene film) PL spectra of TADF emitters 1-4.

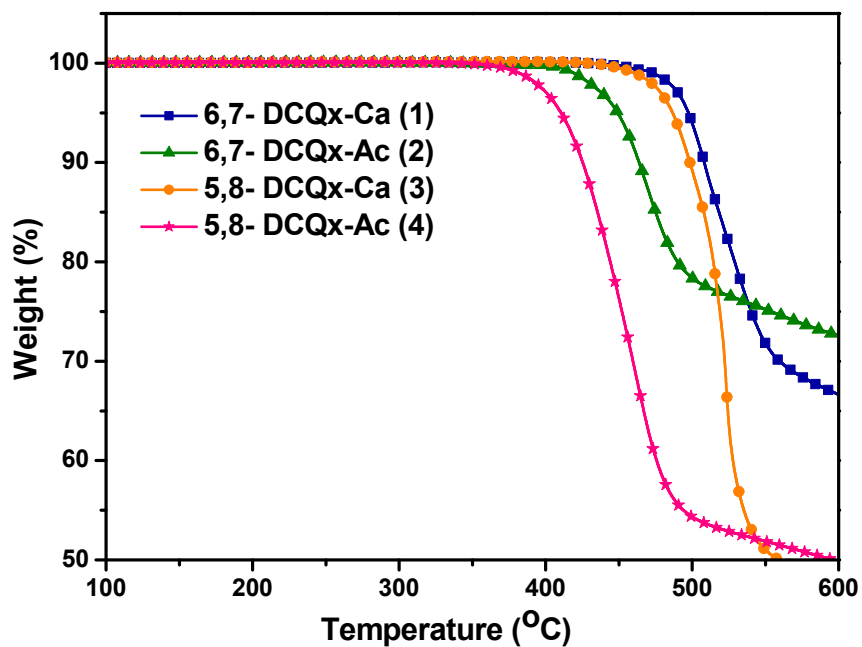


Figure S3. TGA curves of emitters 1-4 at a heating rate of 10 °C min⁻¹ under nitrogen.

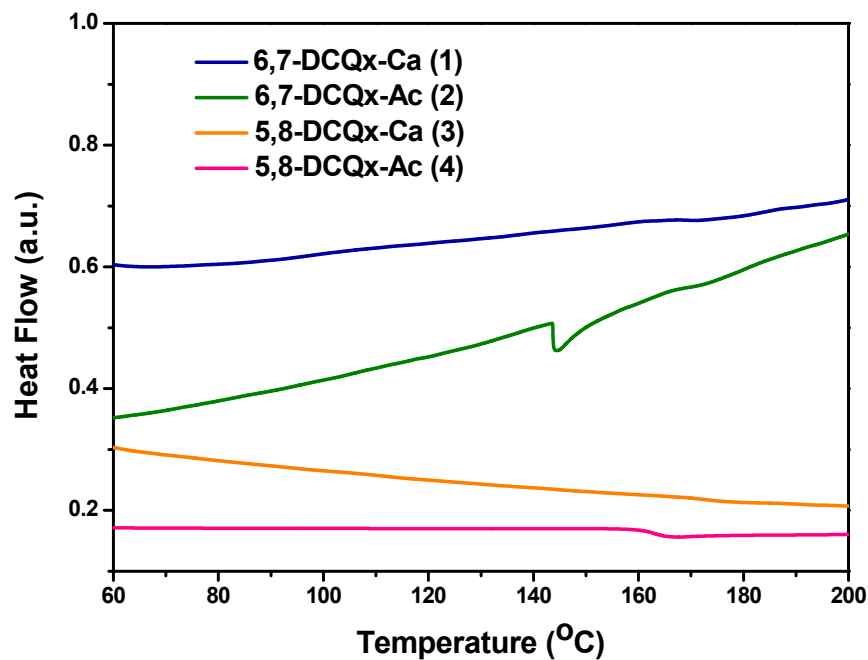


Figure S4. DSC thermograms of four emitters (1-4).

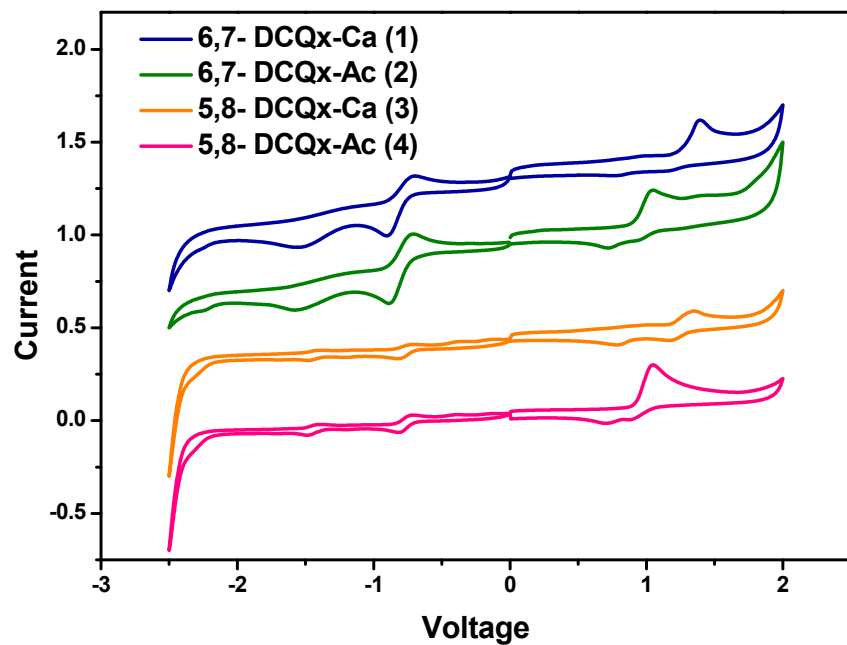


Figure S5. Cyclic voltammograms of TADF emitters 1-4.

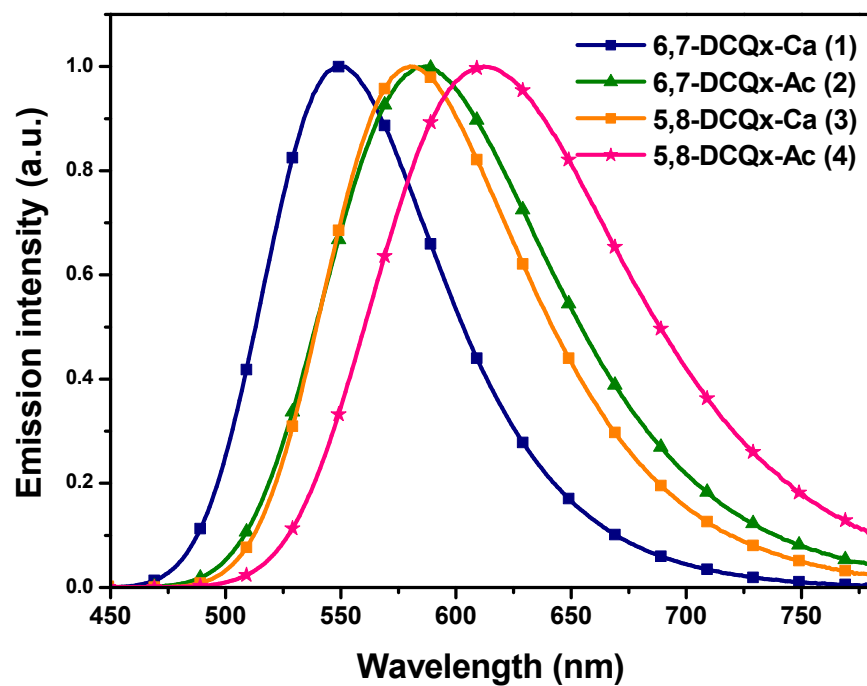


Figure S6. Electroluminescence (EL) spectra of emitters 1-4 (3 % doping concentration)

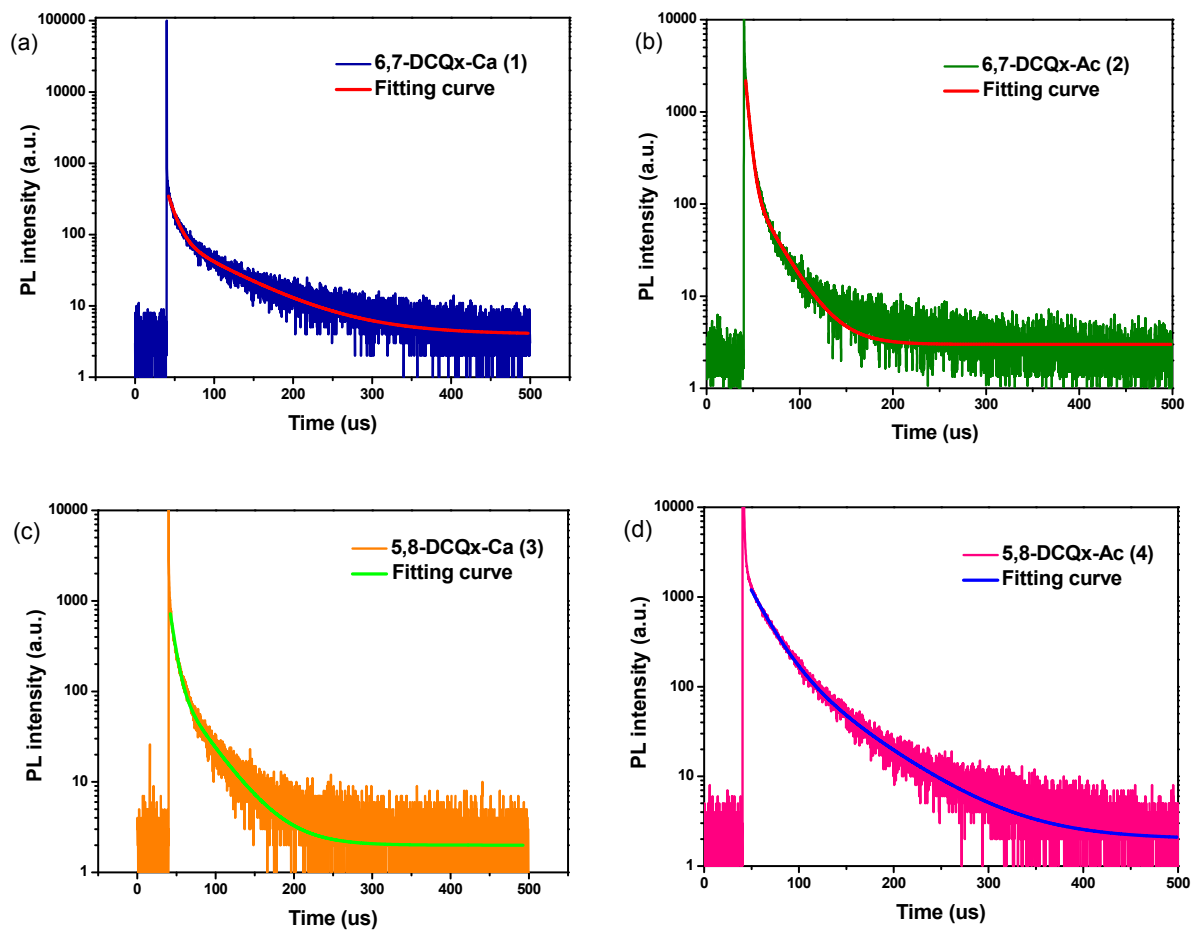


Figure S7. TRPL curves of emitters 1-4 with respective fitting line (a) 6, 7-DCQx-Ca (1); (b) 6,7-DCQx-Ac (2); (c) 5,8-DCQx-Ca (3) and (d) 5,8-DCQx-Ac (4).

Table S1. Electroluminescence (EL) performance of the TADF-OLEDs based on emitters 1–4 (3 % doping concentration).

Emitter	λ_{EL} [nm]	CE_{max} [cd A ⁻¹]	PE_{max} [lm W ⁻¹]	EQE_{max} [%]	CIE (x , y)
1	550	62.7	56.2	18.6	(0.40, 0.56)
2	587	39.9	35.8	17.5	(0.51, 0.48)
3	580	45.9	41.1	17.5	(0.51, 0.48)
4	612	17.2	15.5	10.8	(0.57, 0.43)

Spectra

Figure S8. ^1H NMR spectrum of Intermediate 5

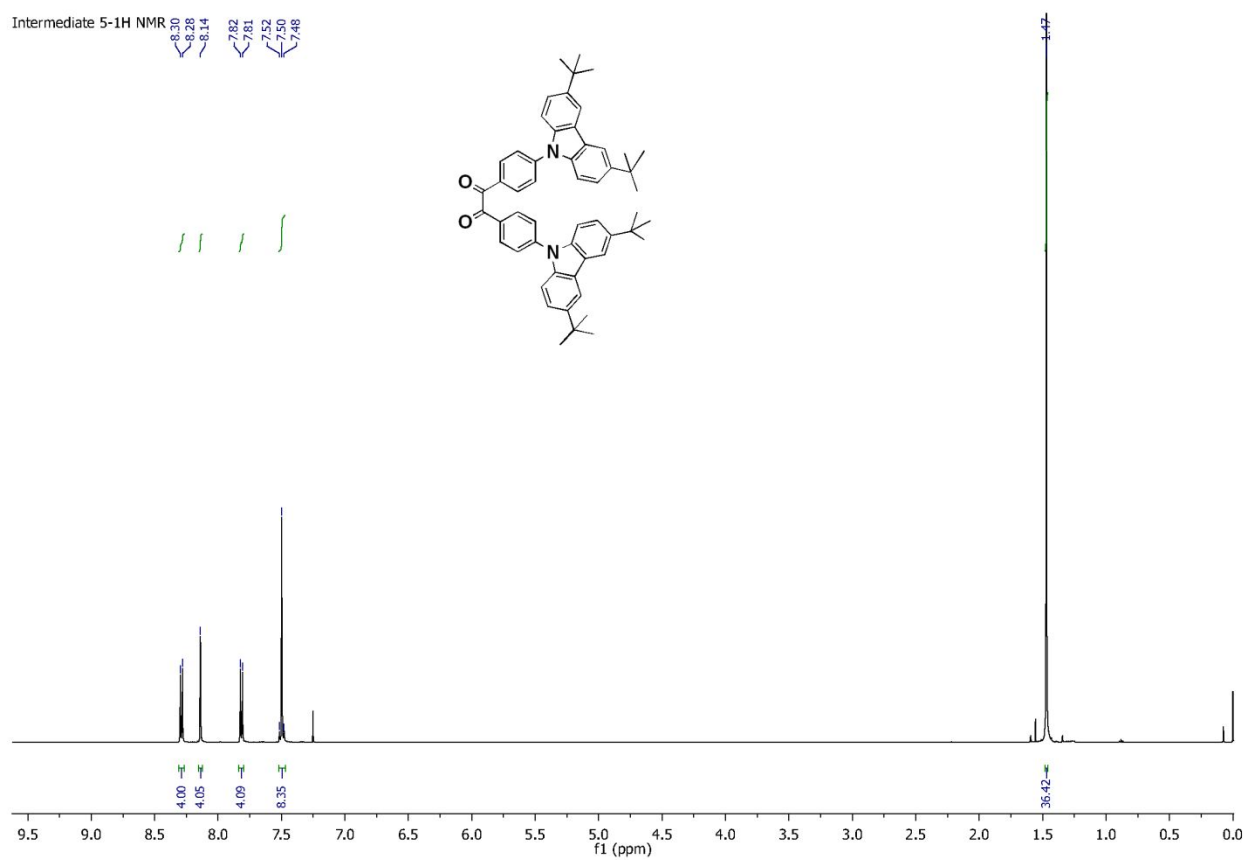


Figure S9. ^{13}C NMR spectrum of Intermediate 5

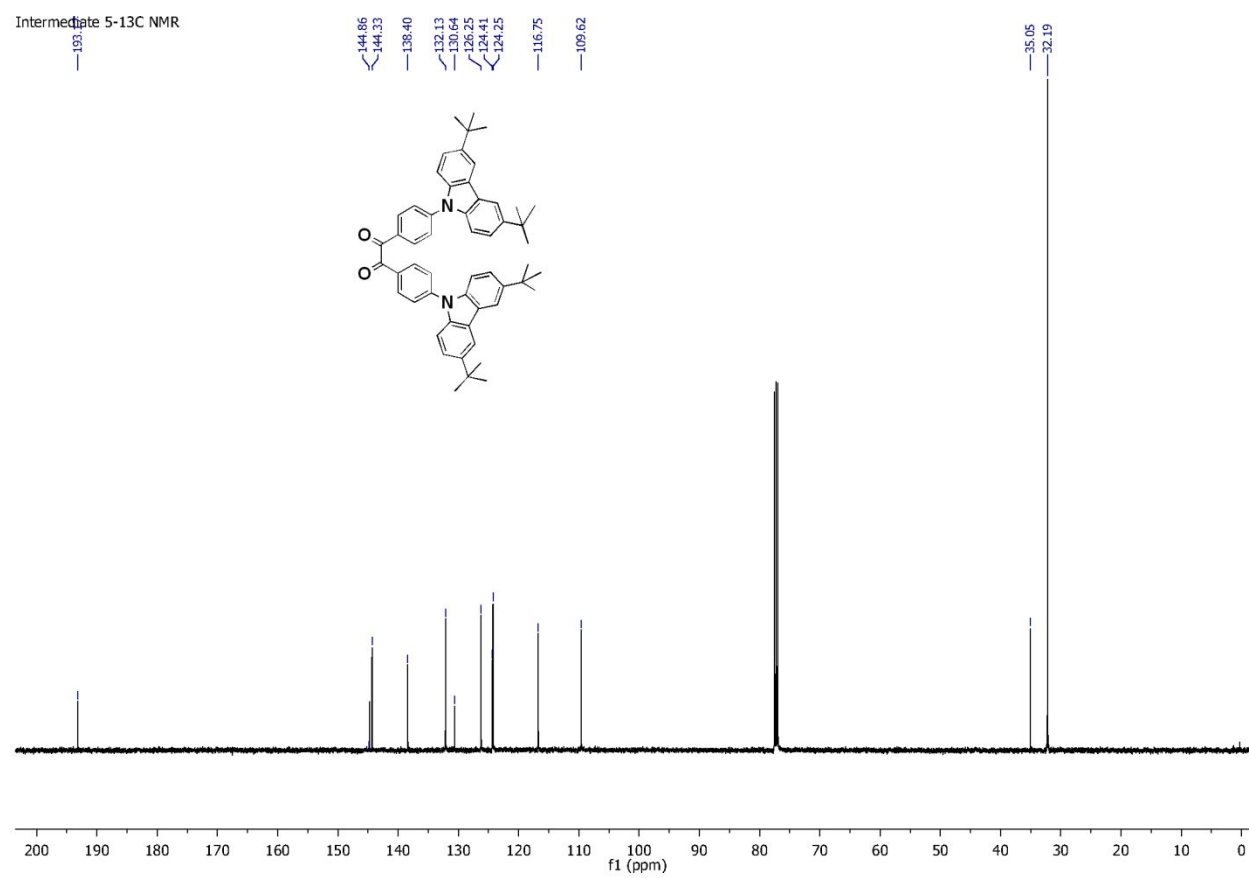


Figure S10. ^1H NMR spectrum of Intermediate 6

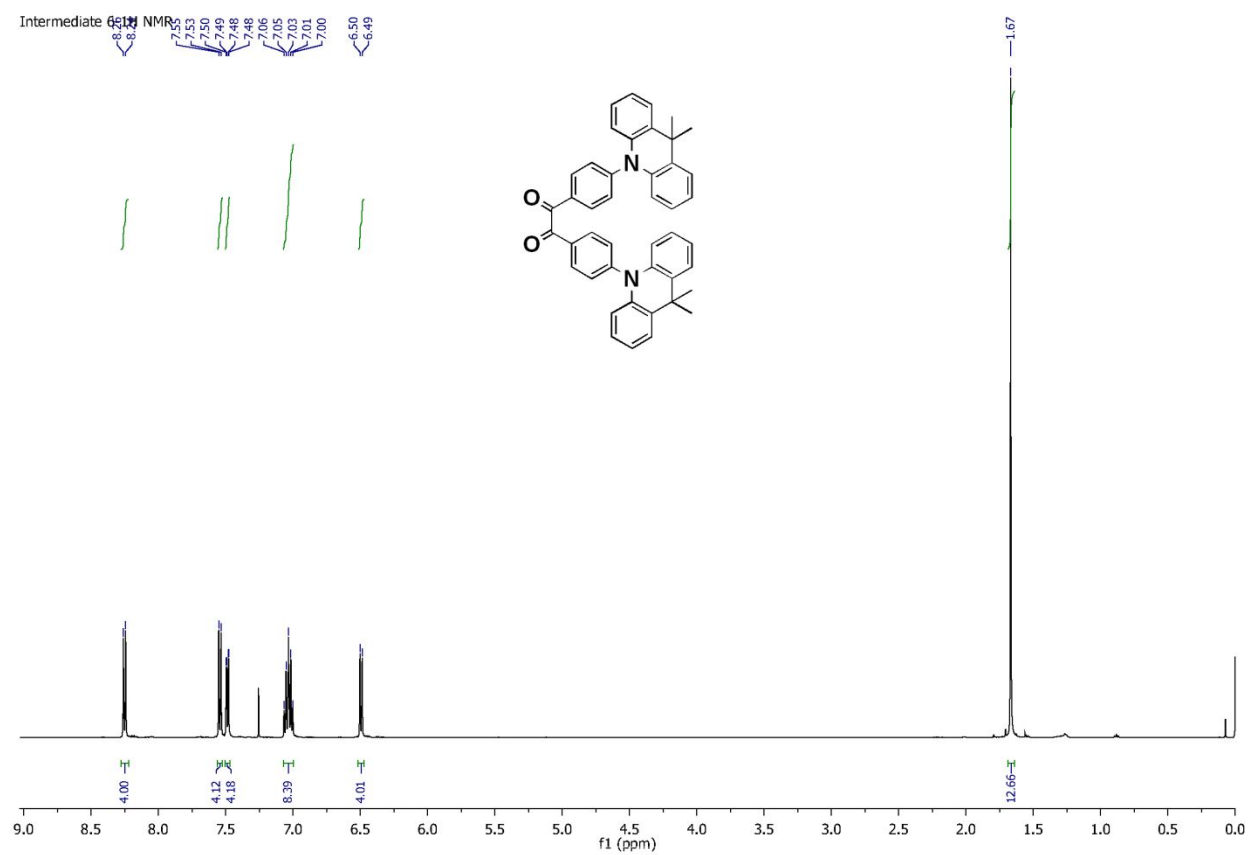


Figure S11. ^{13}C NMR spectrum of Intermediate 6

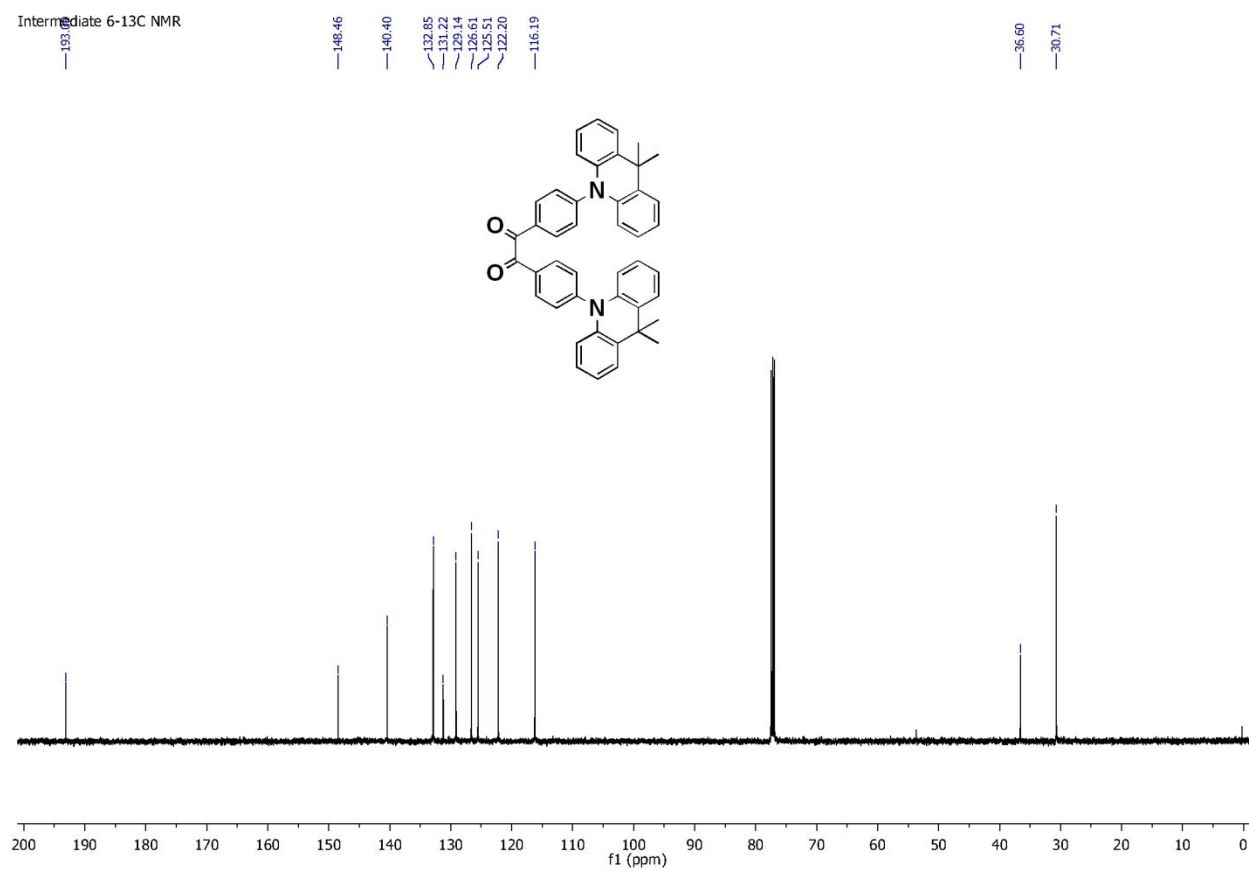


Figure S12. ^1H NMR spectrum of Intermediate 8

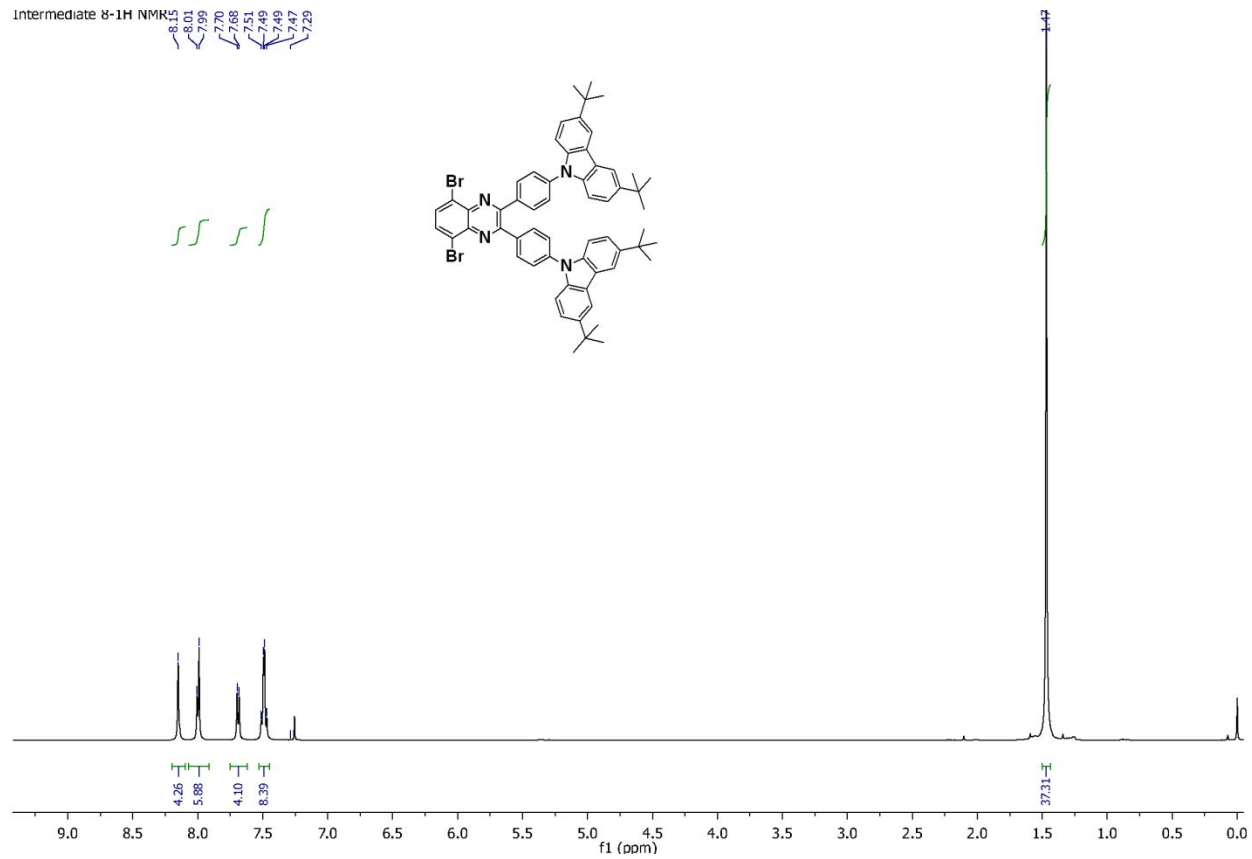


Figure S13. ^{13}C NMR spectrum of Intermediate 8

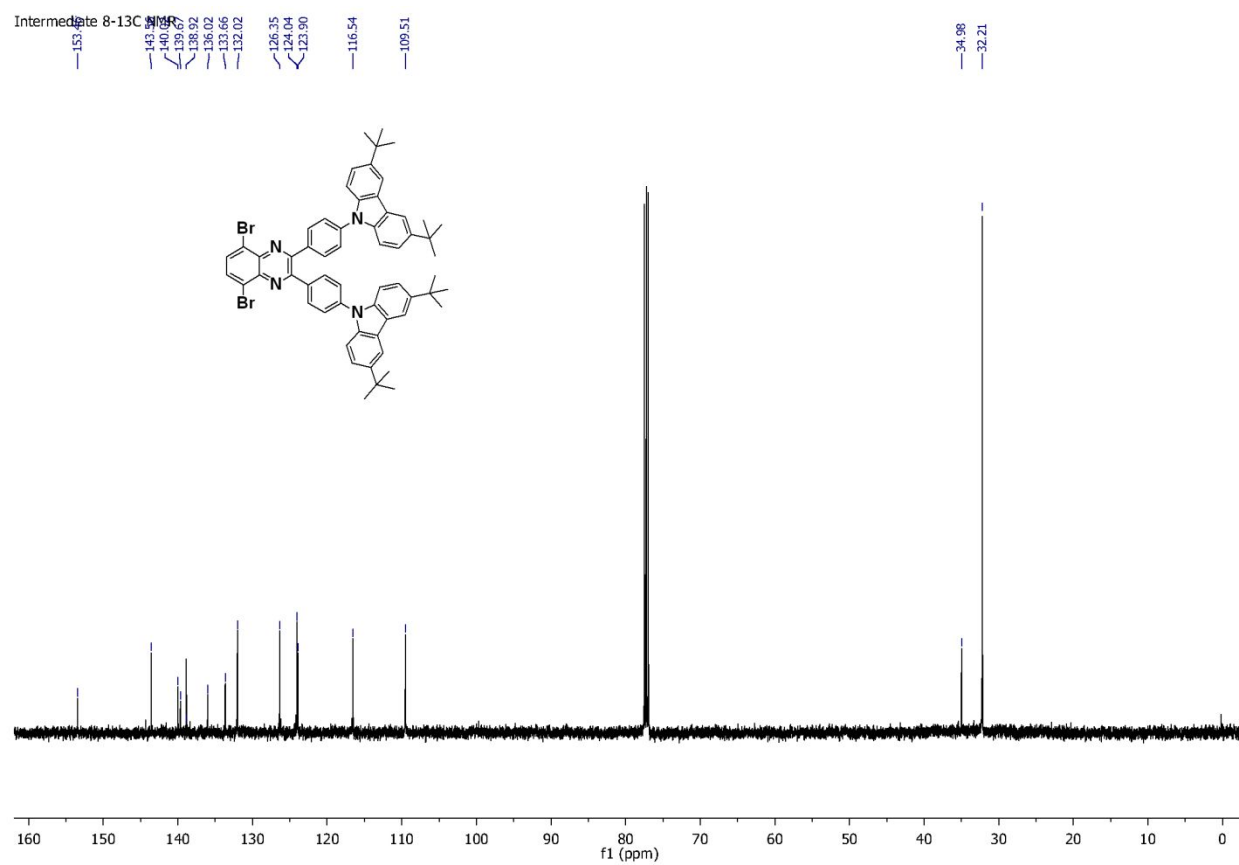


Figure S14. ^1H NMR spectrum of Intermediate 9

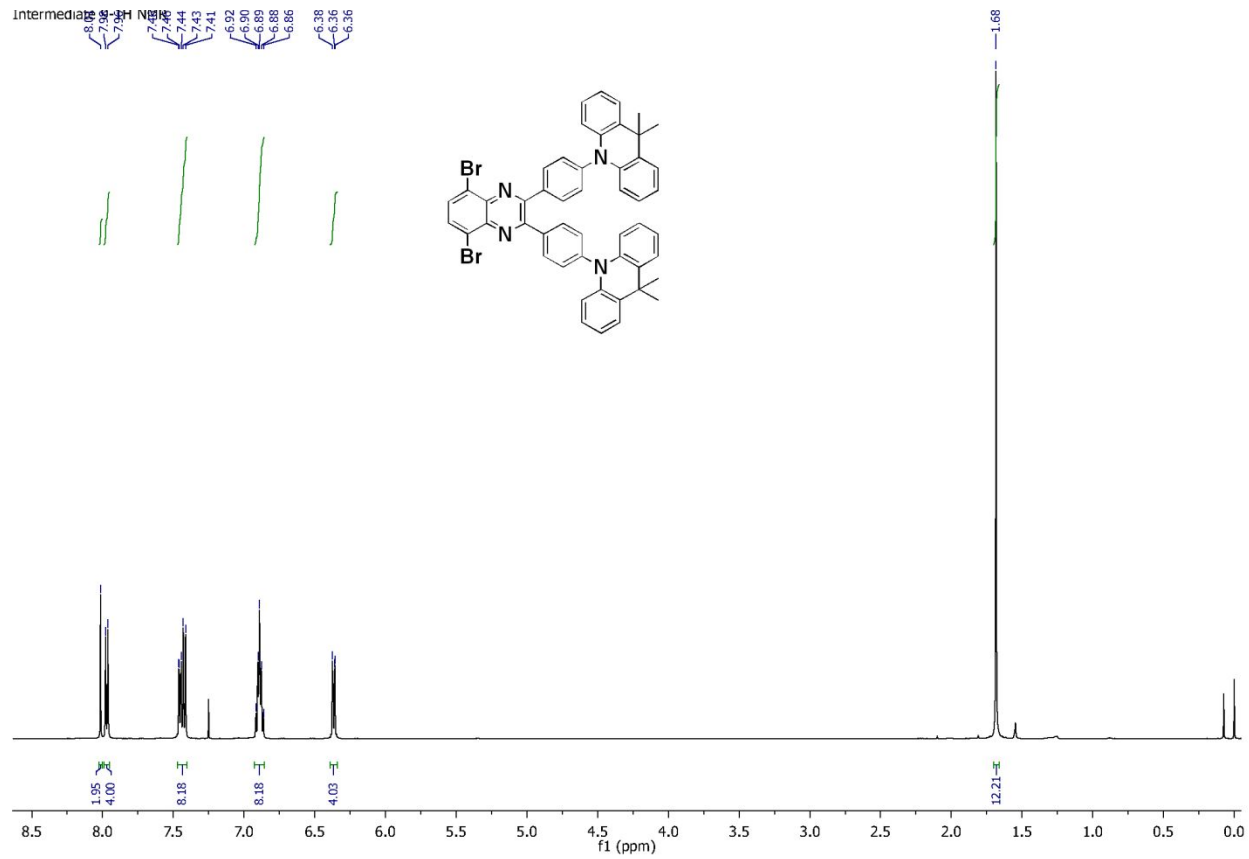


Figure S15. ^{13}C NMR spectrum of Intermediate 9

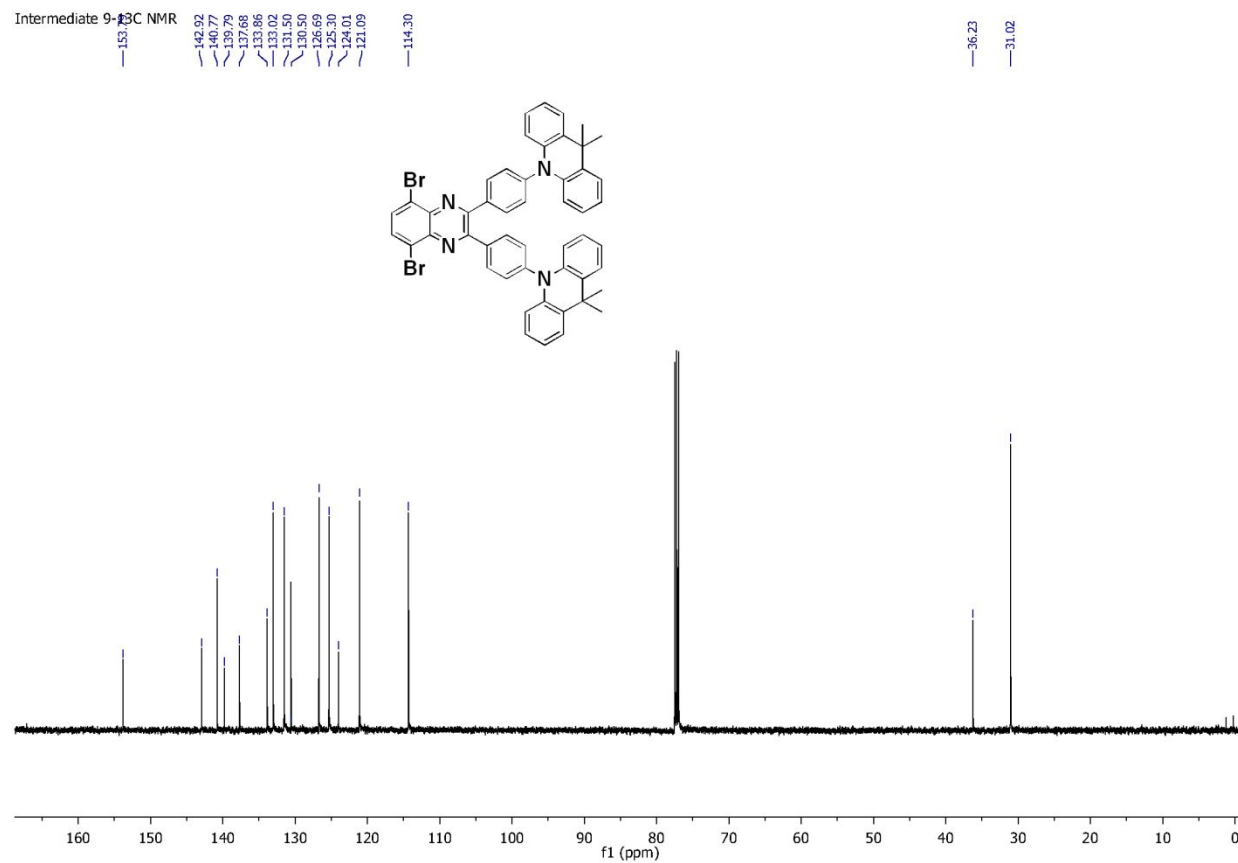


Figure S16. ^1H NMR spectrum of 6,7-DCQx-Ca (1)

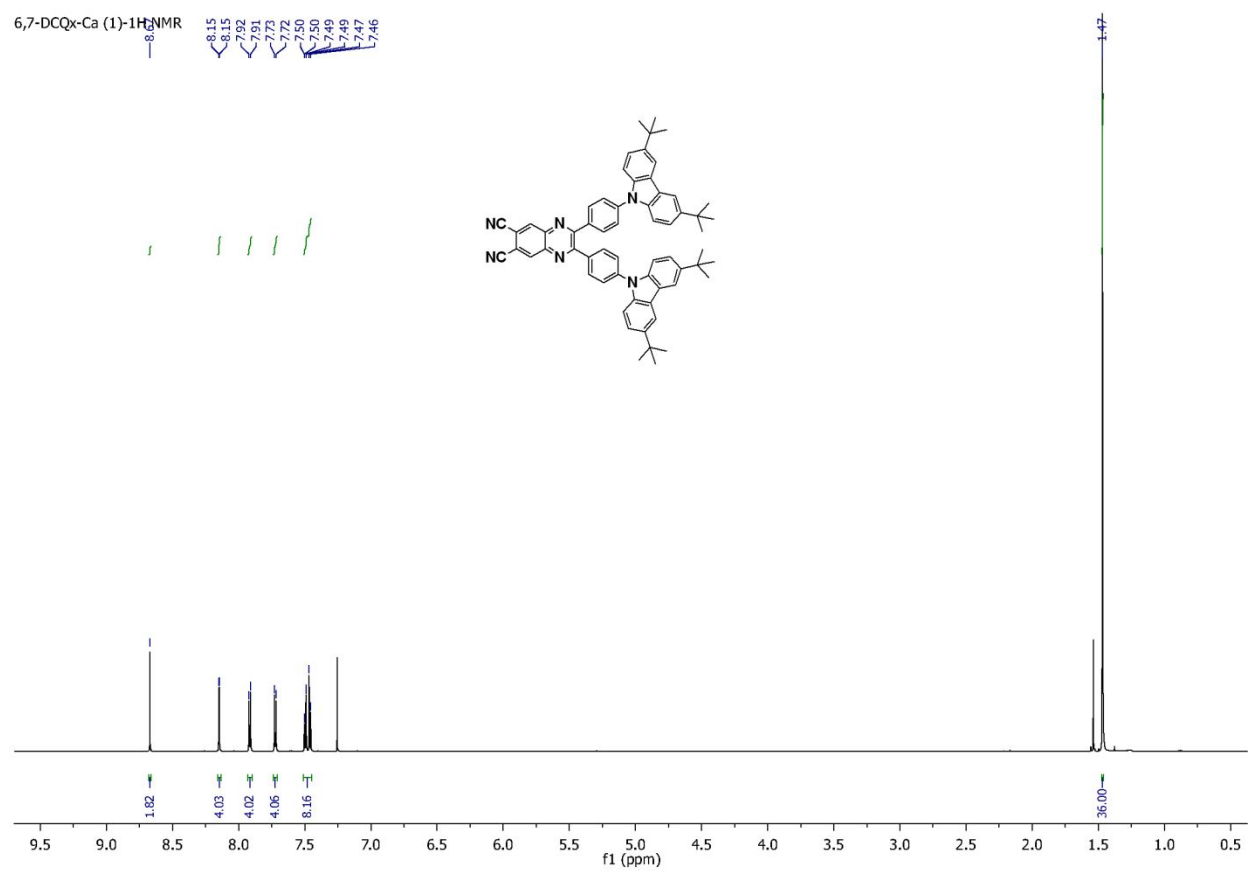


Figure S17. ^{13}C NMR spectrum of 6,7-DCQx-Ca (1)

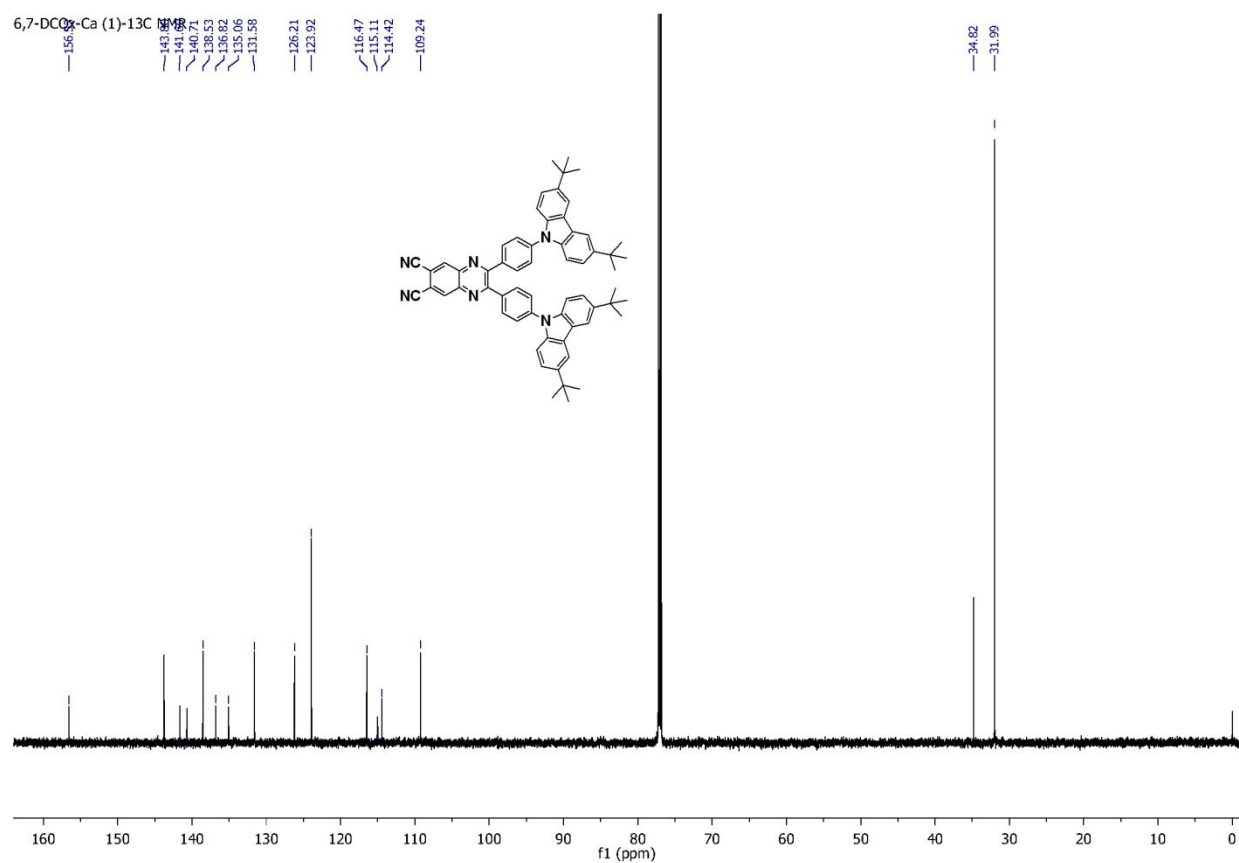


Figure S18. ^1H NMR spectrum of 6,7-DCQx-Ac (2)

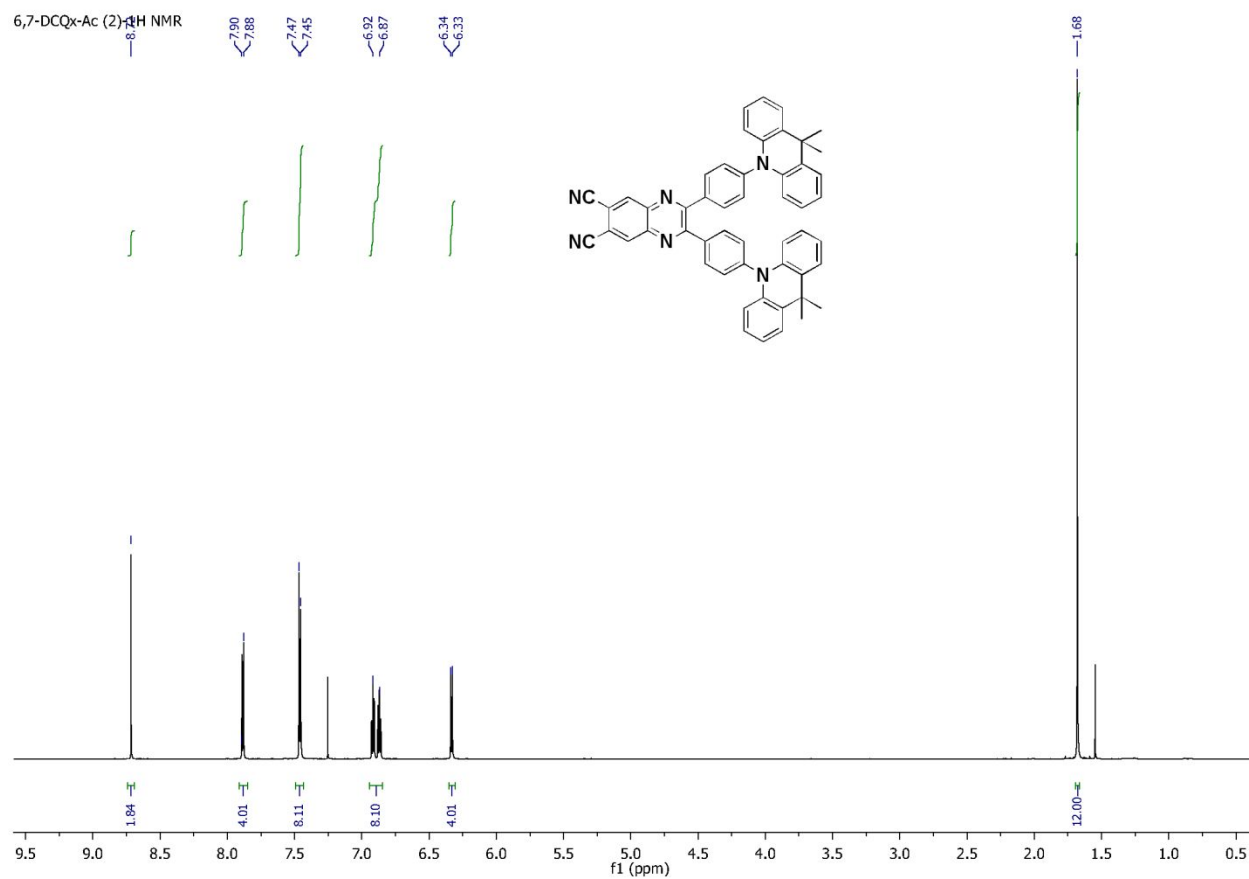


Figure S19. ^{13}C NMR spectrum of 6,7-DCQx-Ac (2)

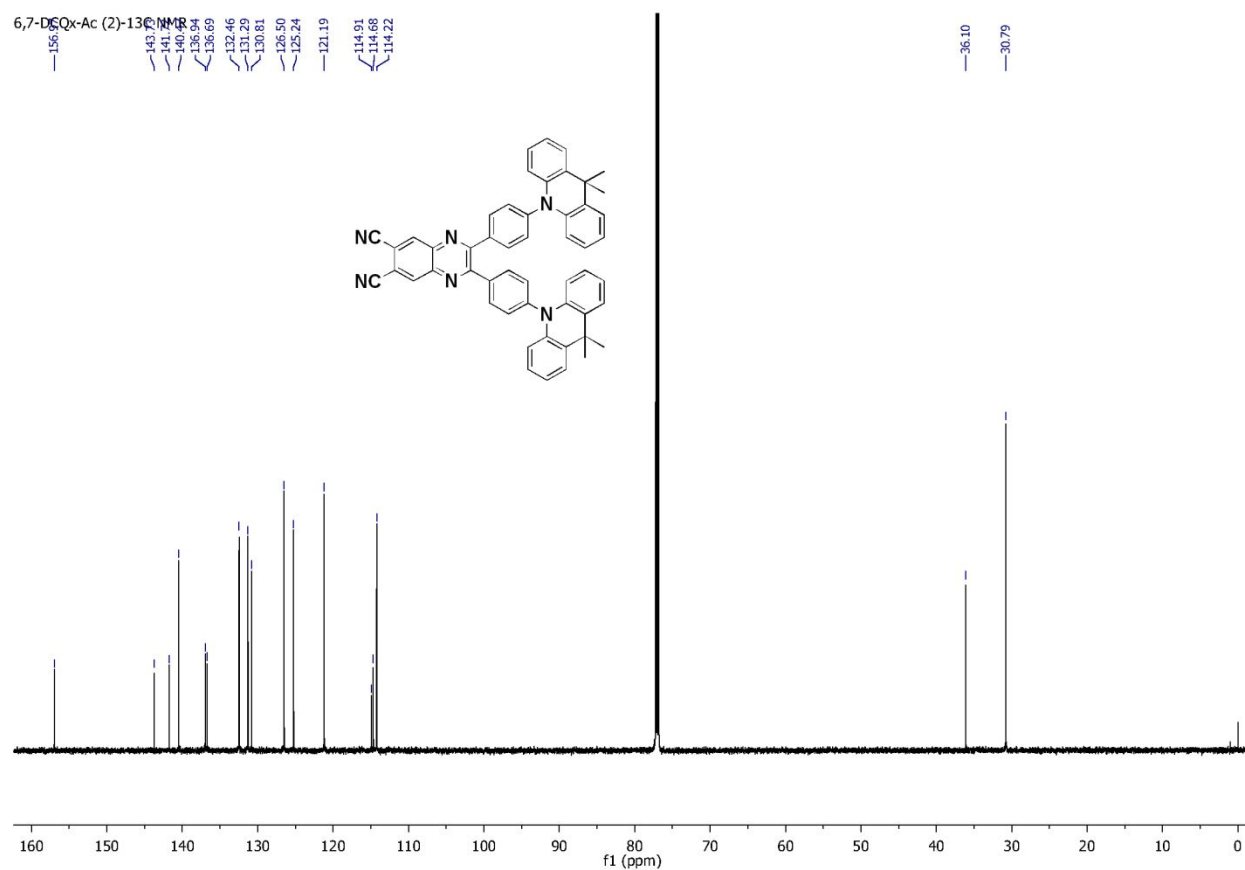


Figure S20. ^1H NMR spectrum of 5,8-DCQx-Ca (3)

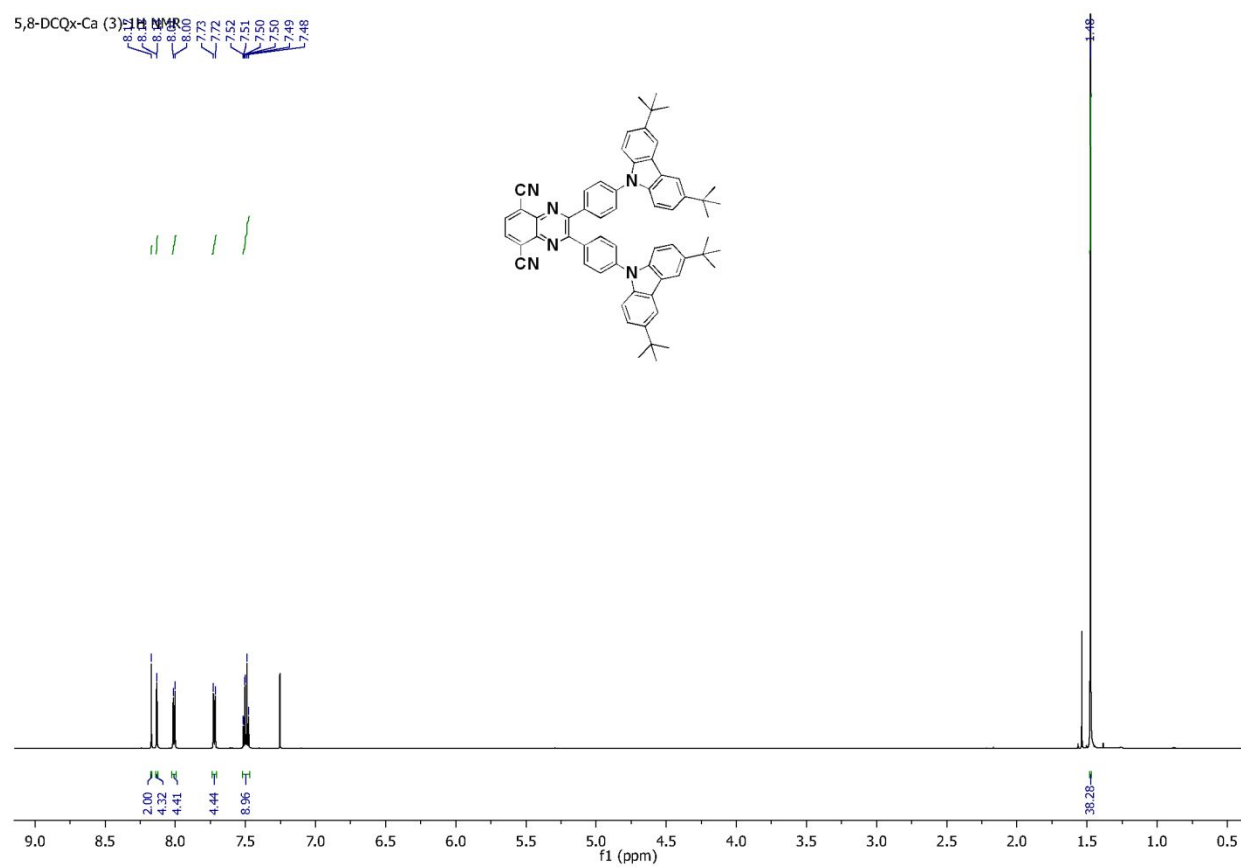


Figure S21. ^{13}C NMR spectrum of 5,8-DCQx-Ca (3)

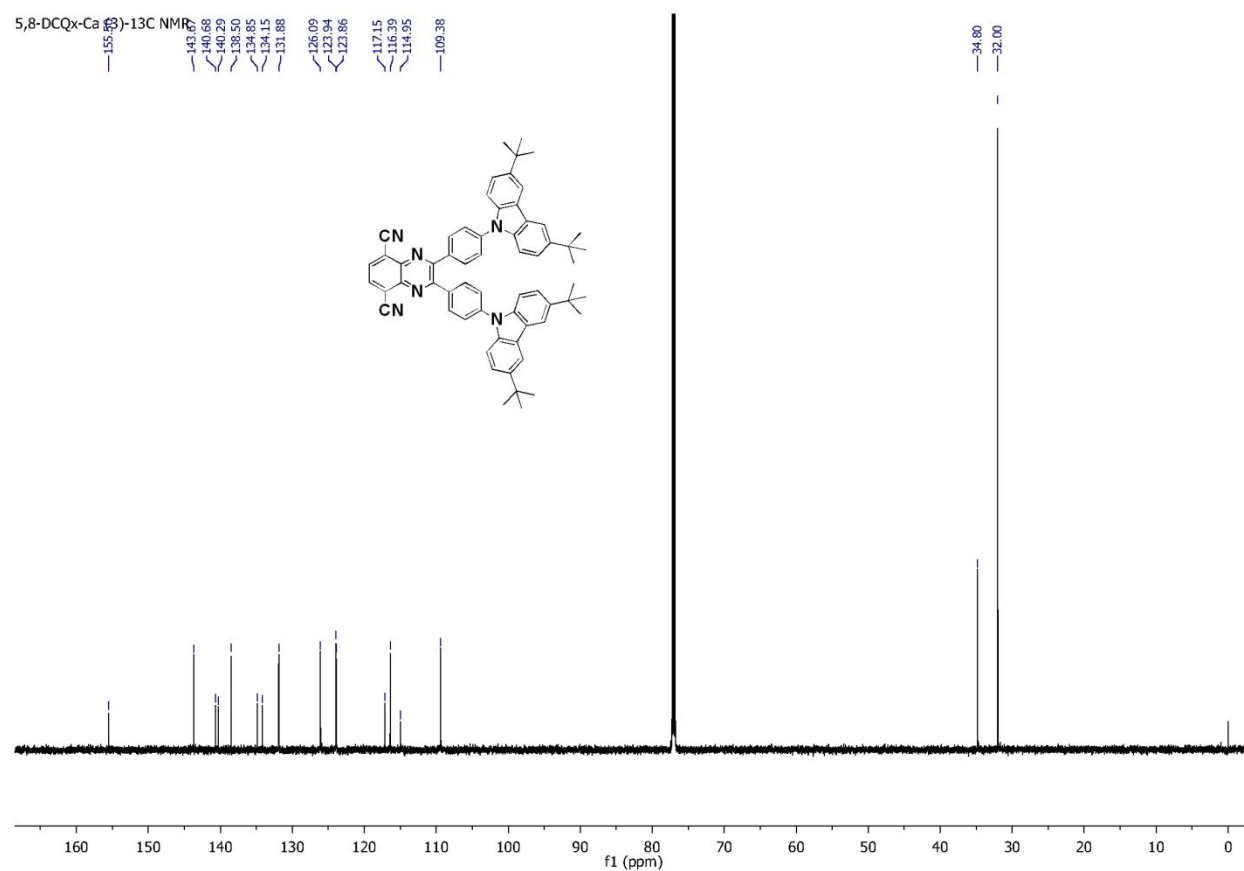


Figure S22. ^1H NMR spectrum of 5,8-DCQx-Ac (4)

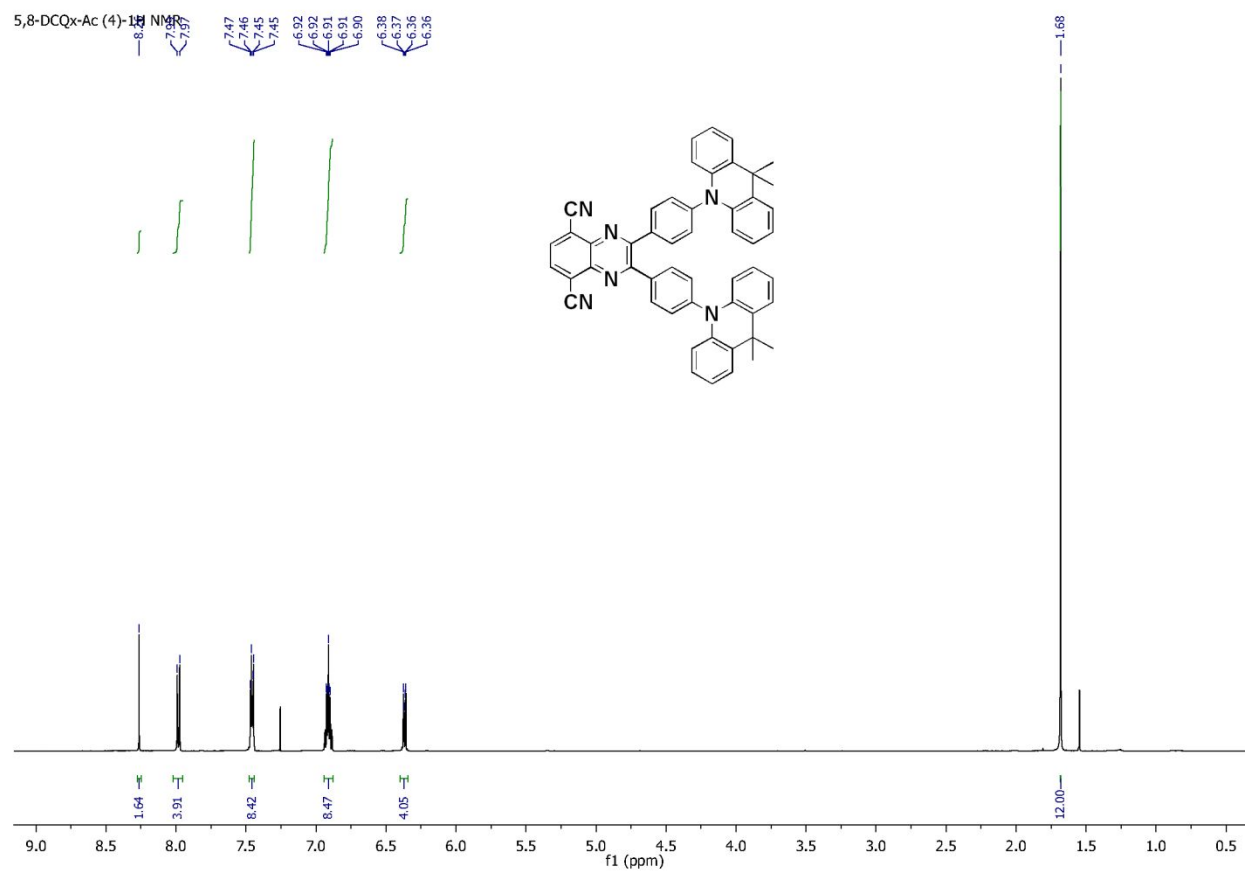
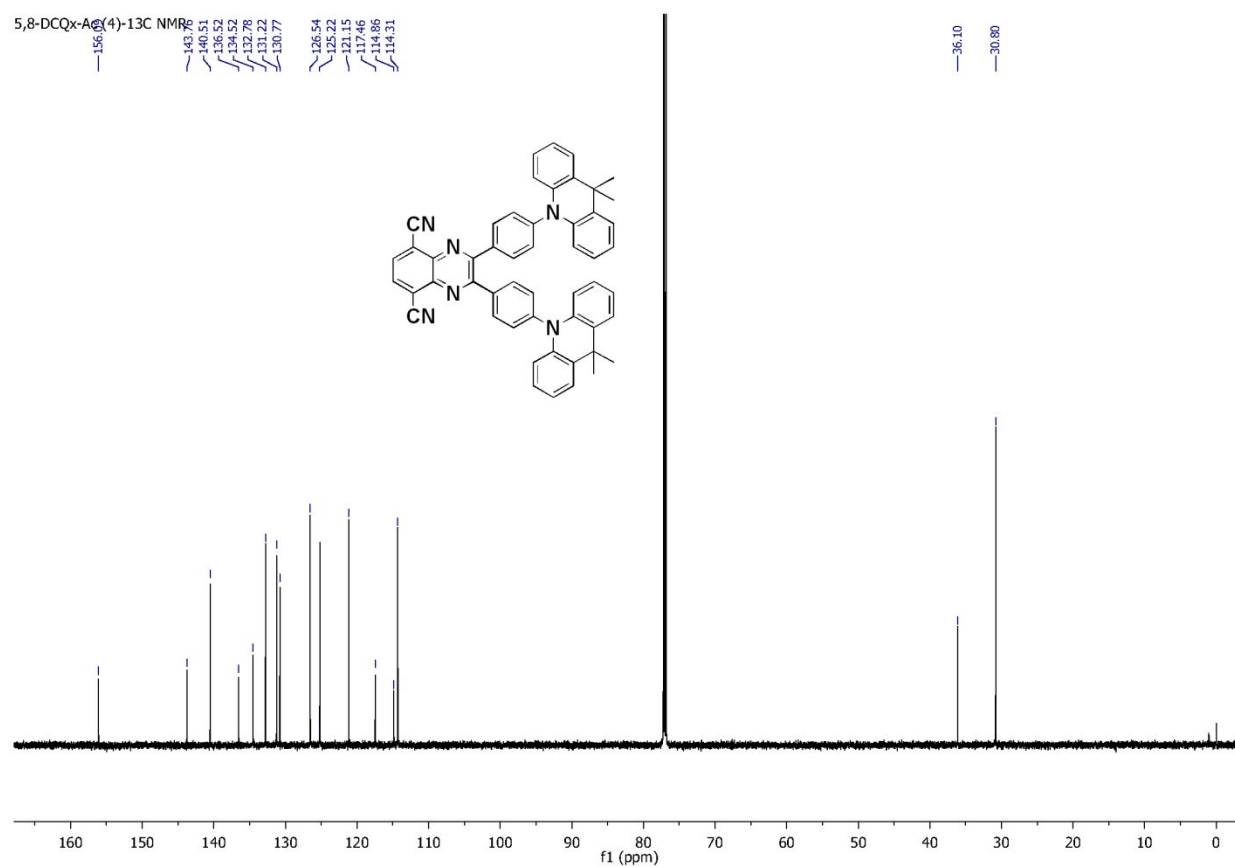


Figure S23. ^{13}C NMR spectrum of 5,8-DCQx-Ac (4)



Equations for the calculation of rate constants

$$\tau_p = 1/k_p \quad (1)$$

$$\tau_d = 1/k_d \quad (2)$$

$$k_{ISC} = (1 - \Phi_F) \times k_p \quad (3)$$

$$k_{RISC} = (k_p k_d / k_{ISC}) \times (\Phi_{TADF} / \Phi_F) \quad (4)$$

$$k_r^S = k_p \Phi_F \quad (5)$$

$$k_{nr}^T = k_d - k_{RISC} \Phi_F \quad (6)$$

$$\Phi_F = \Phi_{O_2} \quad (7)$$

$$\Phi_{TADF} = \Phi_{N_2-O_2} \quad (8)$$

Reference

- (1) Kim, J.; Park, S. H.; Kim, J.; Cho, S.; Jin, Y.; Shim, J. Y.; Shin, H.; Kwon, S.; Kim, I.; Lee, K.; Heeger, A. J.; Suh, H. Syntheses and Characterization of Carbazole Based New Low-Band Gap Copolymers Containing Highly Soluble Benzimidazole Derivatives for Solar Cell Application. *J. Polym. Sci. Part A Polym. Chem.* **2011**, 49 (2), 369–380.