Electronic supplementary information for

Synthesis of second-order nonlinear optical chromophores with conjugated steric hindrances for electro-optics @850 nm

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Contents

1. Experiments

1.1 Materials and methods

All reagents and solvents were purchased from commercial sources and used without further purification. Acceptor TCF and triphenylphosphine salt were synthesis according to the literatures.[1, 2] NMR spectra were determined by Advance Bruker (400 MHz) NMR spectrometer. UV–Vis spectra were obtained using a Hitachi U2001 spectrophotometer.

1.2 Synthesis

Synthesis of D1. To a solution of 4-(N, N-dibutylanilne)benzyl aldehyde (1 mmol) in 20 mL THF was added 1.1 equivalent (eqv) triphenylphosphine salt and then 10 eqv NaH was slowly added into the mixture. The solution was refluxed for 4 hours. After cooling to the room temperature, the reaction mixture was poured into 100 ml DI water. The precipitates were extracted by ethyl acetate, dried overnight by $MgSO_4$, and condensed by rotary evaporation. The crude product was purified by silica chromatography with the fluent solvent of ethyl acetate and hexane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.30 (m, 3H), 7.20 (d, *J* = 8.5 Hz, 1H), 6.95 (t, *J* = 12.0 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.54 (d, *J* = 8.6 Hz, 1H), 6.40 (q, *J* = 12.1 Hz, 1H), 3.86 (d, *J* = 3.7 Hz, 3H), 3.69 – 3.10 (m, 4H), 1.75 – 1.54 (m, 4H), 1.39 (dt, *J* = 22.5, 7.5 Hz, 4H), 1.01 (dd, *J* = 13.2, 6.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.26, 147.20, 130.98, 130.07, 130.02, 129.18, 127.51, 127.10, 125.81, 124.13, 114.10, 113.60, 111.75, 111.05, 55.23, 50.87, 50.77, 29.54, 20.42, 14.10. LC-MS: 337.0 g/mol.

Synthesis of D2. The procedure for D1 was followed to synthesize D2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 1H), 6.89 (s, 1H), 6.69 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 8.6 Hz, 1H), 6.34 (s, 1H), 3.33 (dd, *J* = 15.2, 7.7 Hz, 6H), 2.23 (s, 1H), 1.77 – 1.54 (m, 6H), 1.54 – 1.32 (m, 6H), 1.11 – 0.93 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.26, 127.26, 112.04, 50.85, 29.57, 20.41, 13.98. LC-MS: 434.7 g/mol.

Synthesis of DA1. $POCl_3$ (1 mmol) was added to 10 ml DMF in ice bath and the solution was stirred for 1 hour. Then D1 (1 eqv, 1 mmol, in 5 mL DMF) was dropwise added to the solution. The mixture was stirred at 90 °C for 1h. After cooling to the room temperature, the reaction mixture was poured into 100 ml saturate sodium carbonate solution. The precipitates were extracted by ethyl acetate, dried overnight by $MgSO_4$, and condensed by rotary evaporation. The crude product was purified by silica chromatography with the fluent solvent of ethyl acetate and hexane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.67 (d, *J* = 11.6 Hz, 1H), 7.27 – 7.10 (m, 5H), 7.07 – 6.97 (m, 2H), 6.47 (d, *J* = 9.1 Hz, 2H), 3.87 (d, *J* = 9.0 Hz, 3H), 3.31 (dd, *J* = 22.7, 15.3 Hz, 4H), 1.75 – 1.48 (m, 4H), 1.36 (td, *J* = 14.6, 7.3 Hz, 4H), 0.99 (dt, *J* = 11.9, 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.09, 159.16, 151.58, 149.72, 136.45, 133.18, 130.80, 127.02, 121.05, 114.44, 110.92, 55.29, 50.71, 29.39, 20.29, 13.99. LC-MS: 365.2 g/mol.

Synthesis of DA2. The procedure for DA1 was followed to synthesize DA2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.22 (d, *J* = 9.0 Hz, 2H), 7.14 (s, 1H), 7.07 (d, *J* = 8.8 Hz, 2H),

6.75 – 6.65 (m, 2H), 6.46 (d, J = 9.0 Hz, 2H), 3.46 – 3.06 (m, 8H), 1.72 – 1.47 (m, 8H), 1.47 – 1.15 (m, 8H), 1.07 – 0.77 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.37, 163.20, 153.18, 129.25, 113.33, 103.43, 92.26, 67.21, 61.91, 43.98, 31.97, 30.91, 30.76, 28.31, 25.02, 24.72, 21.80, 13.22, 11.78. LC-MS: 460.8 g/mol.

Synthesis of C1. The solution of 0.2 mmol DA1 and TCF (2 eqv) in 10 mL anhydrous ethanol was stirred at 70 °C. The reaction time was according to the TLC. After reaction, the solvent was removed by rotary evaporation and then the precipitate was purified by silica chromatography. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, J = 15.1 Hz, 1H), 7.21 – 7.00 (m, 5H), 6.92 (t, J = 9.8 Hz, 2H), 6.41 (t, J = 12.7 Hz, 2H), 5.72 (d, J = 15.2 Hz, 1H), 3.94 (s, 3H), 3.31 (dd, J = 17.2, 9.8 Hz, 4H), 1.66 – 1.48 (m, 10H), 1.34 (tt, J = 10.7, 5.4 Hz, 4H), 0.96 (t, J = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.59, 173.55, 159.50, 154.99, 150.17, 148.91, 135.63, 134.20, 130.44, 128.19, 122.58, 115.28, 112.86, 111.97, 111.46, 96.81, 55.35, 50.83, 29.46, 26.40, 20.27, 13.95. HR-MS: 547.5052 g/mol.

Synthesis of C2. The procedure for C1 was followed to synthesize C2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J = 15.1 Hz, 1H), 7.03 (d, J = 7.2 Hz, 1H), 6.91 – 6.82 (m, 4H), 6.66 (d, J = 8.7 Hz, 2H), 6.33 (t, J = 11.8 Hz, 2H), 5.80 (d, J = 15.1 Hz, 1H), 3.43 – 3.07 (m, 8H), 1.69 – 1.39 (m, 14H), 1.39 – 1.10 (m, 8H), 1.01 – 0.72 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.98, 173.03, 155.08, 149.25, 148.36, 147.40, 136.01, 133.44, 129.19, 122.23, 120.93, 112.27, 111.85, 111.38, 111.10, 110.58, 96.04, 49.99, 28.69, 28.62, 25.67, 19.63, 19.47, 13.30, 13.16. HR-MS: 643.5248 g/mol.

2. NMR spectra

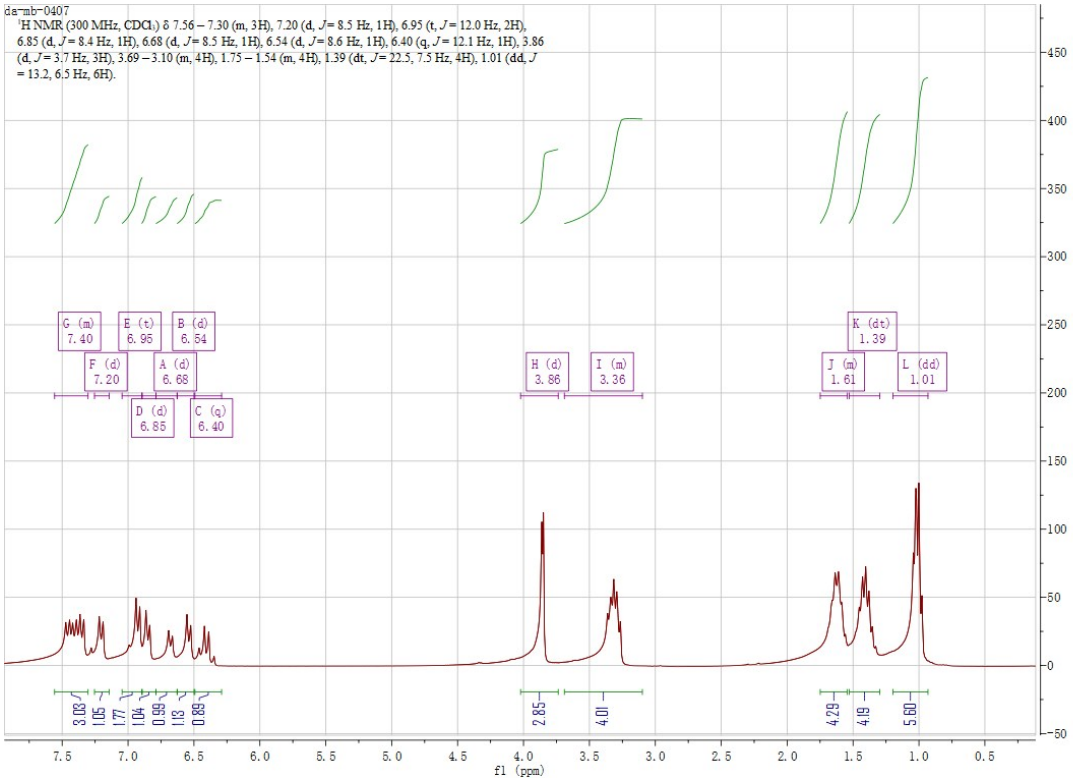

Figure S1. [1]HNMR of D1

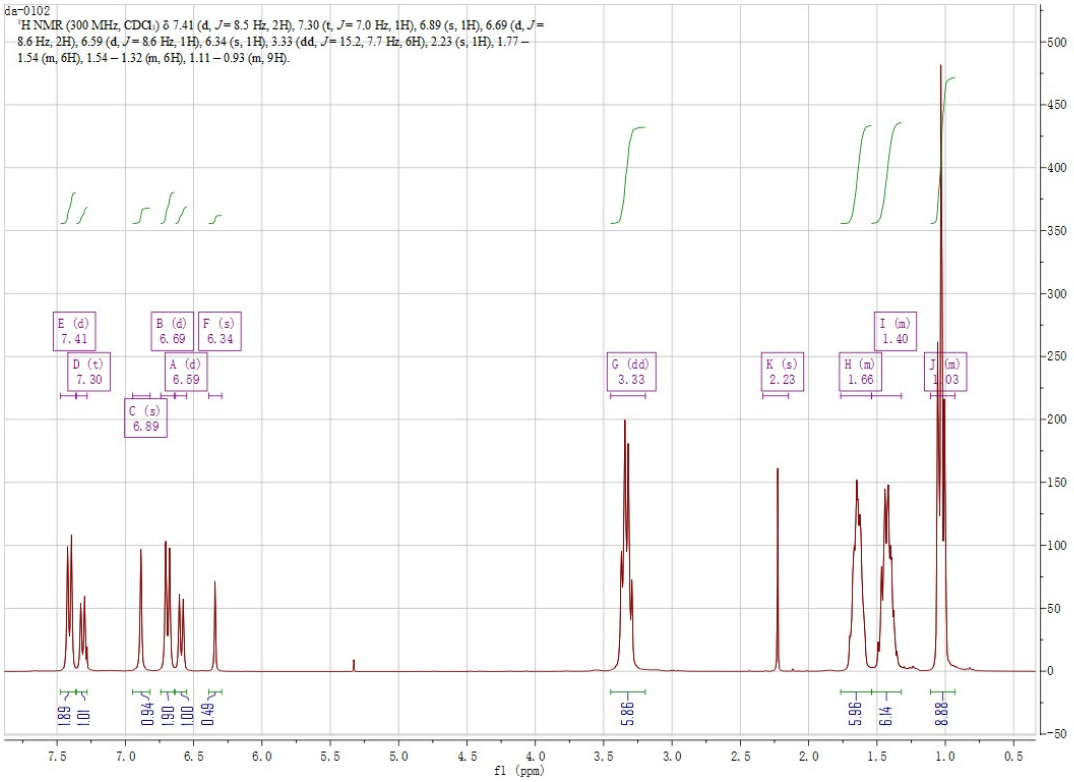

Figure S2. [1]HNMR of D2

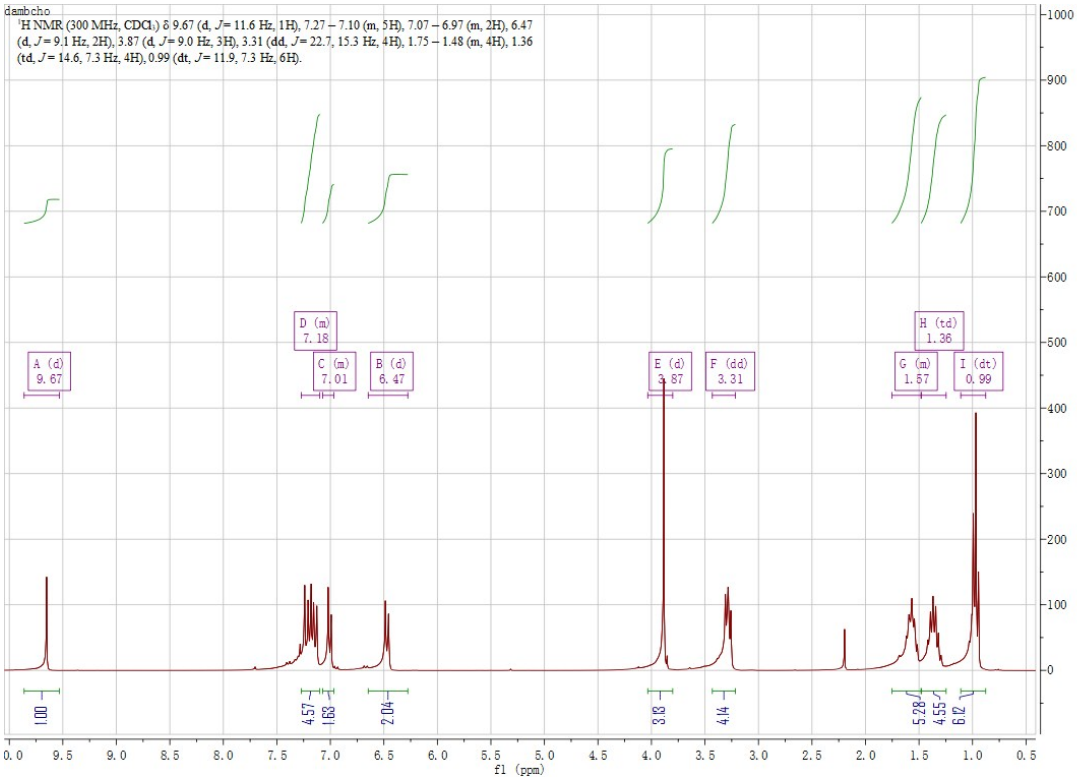

Figure S3. [1]HNMR of DA1

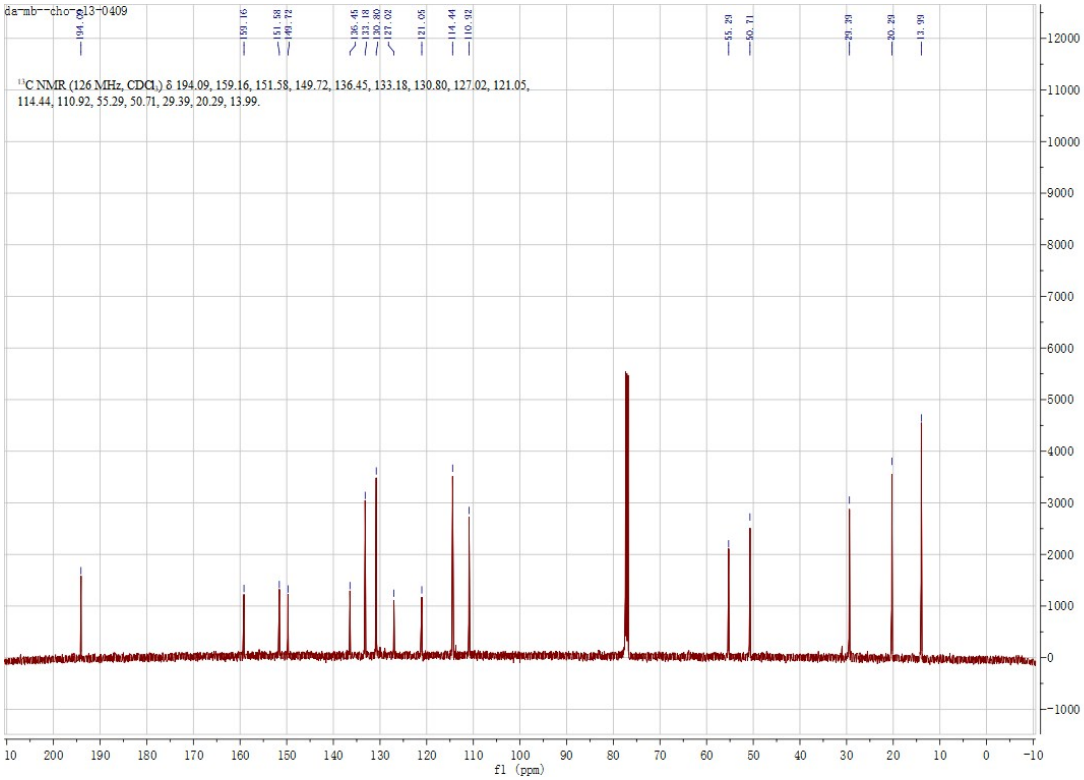

Figure S4. ^{13}CNMR of DA1

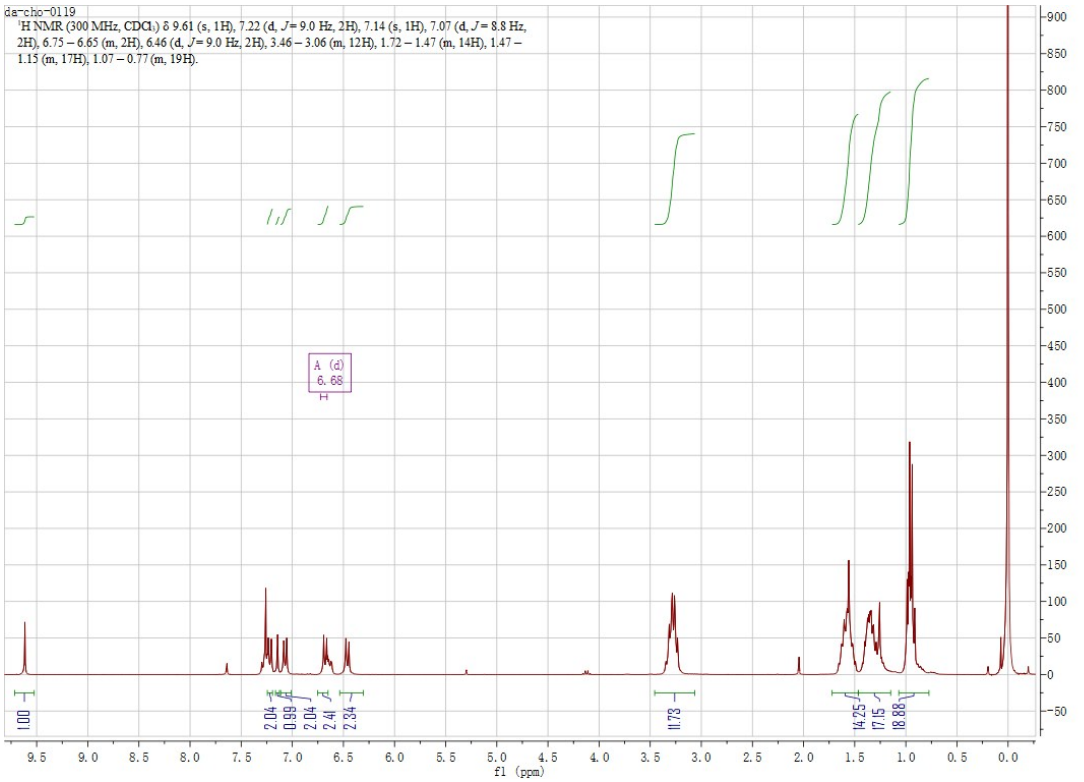

Figure S5. ^{1}HNMR of DA2

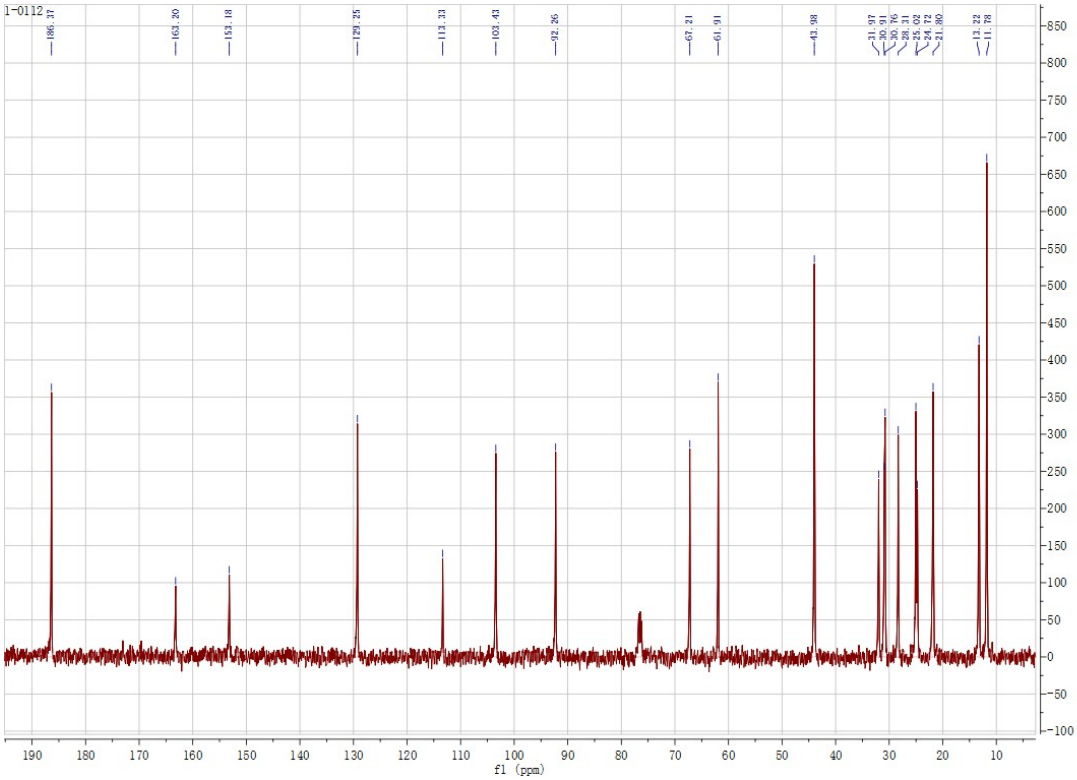

Figure S6. ^{13}CNMR of DA2

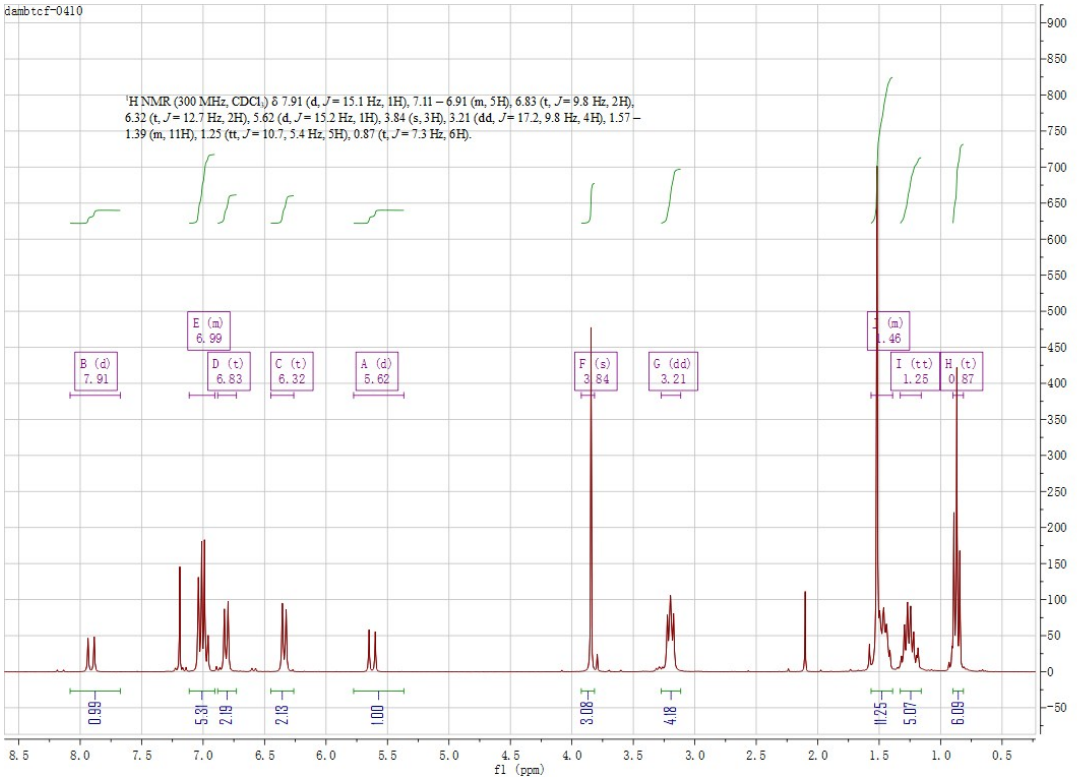

Figure S7. ^{1}HNMR of C1

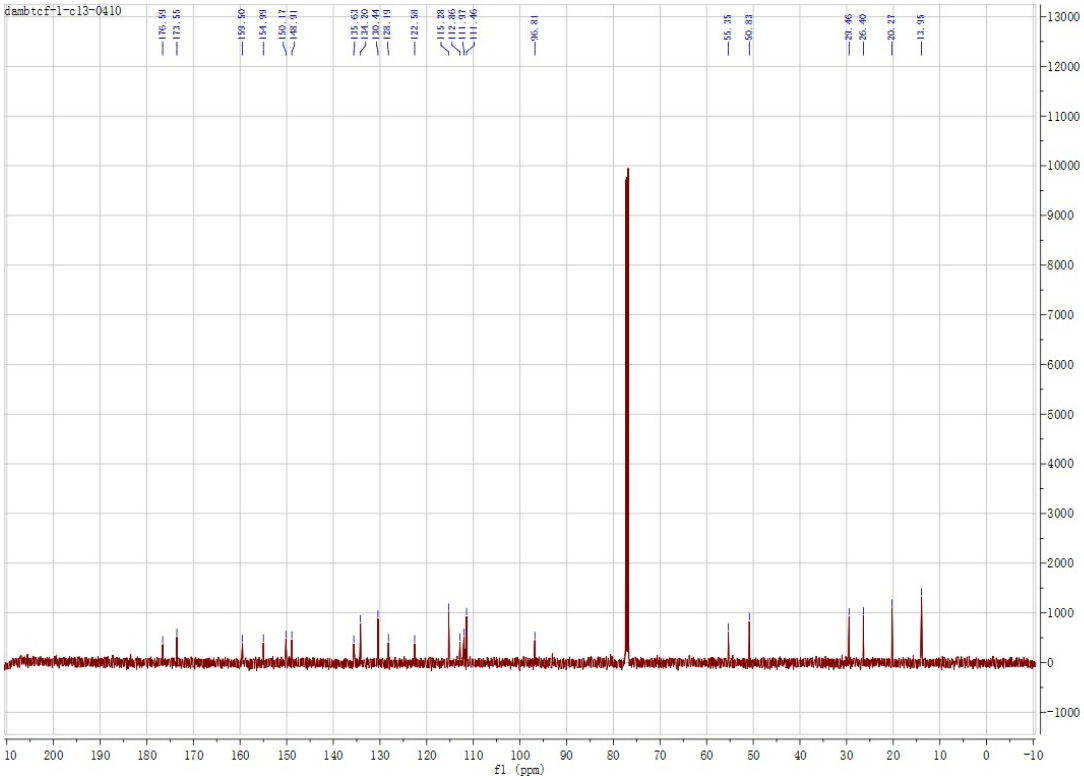

Figure S8. ^{13}CNMR of C1

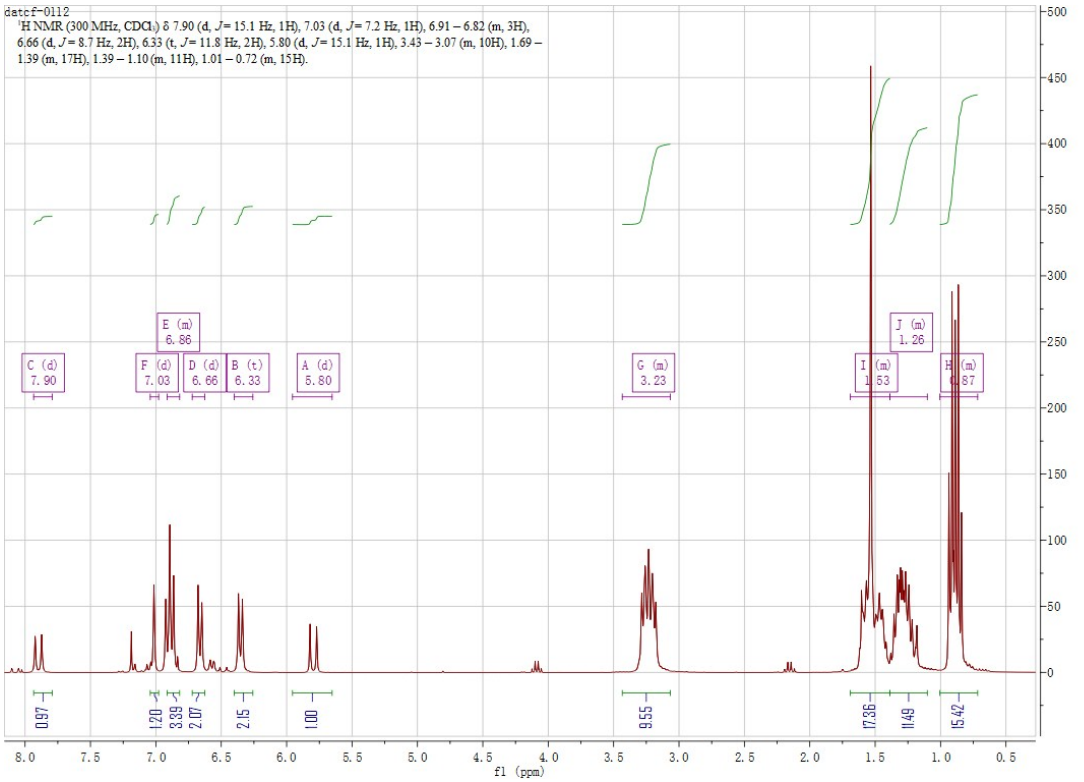

Figure S9. ^{1}HNMR of C2

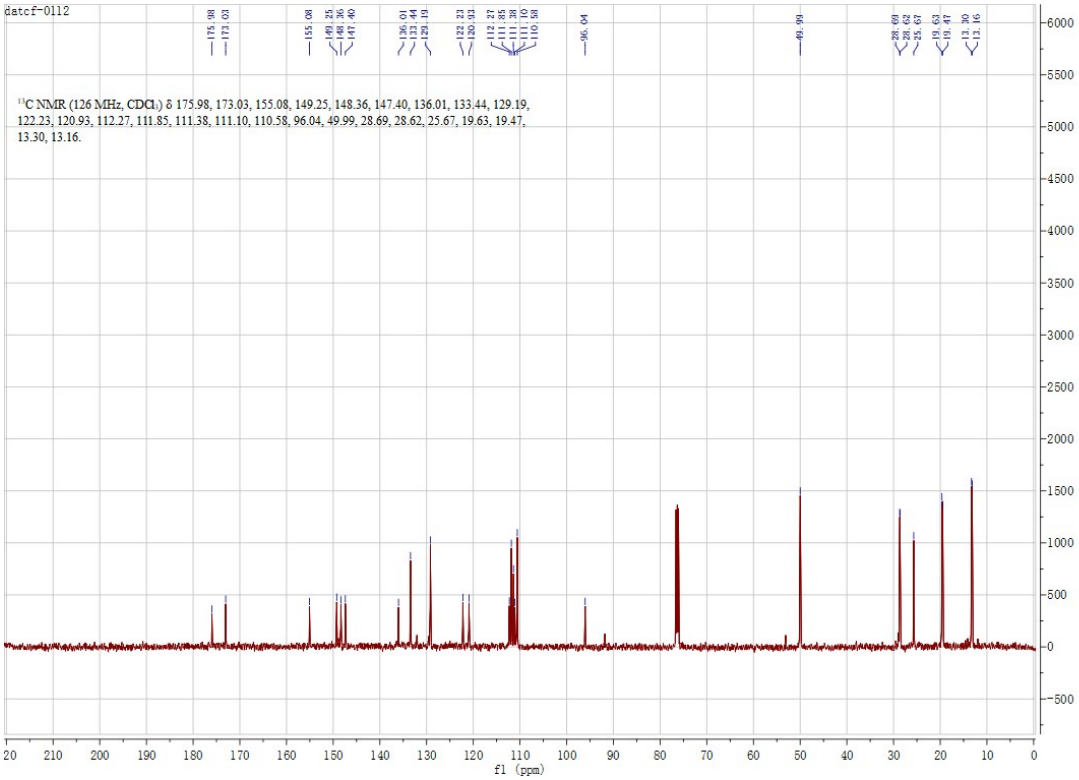

Figure S10. ^{13}CNMR of C2

3. DFT calculations

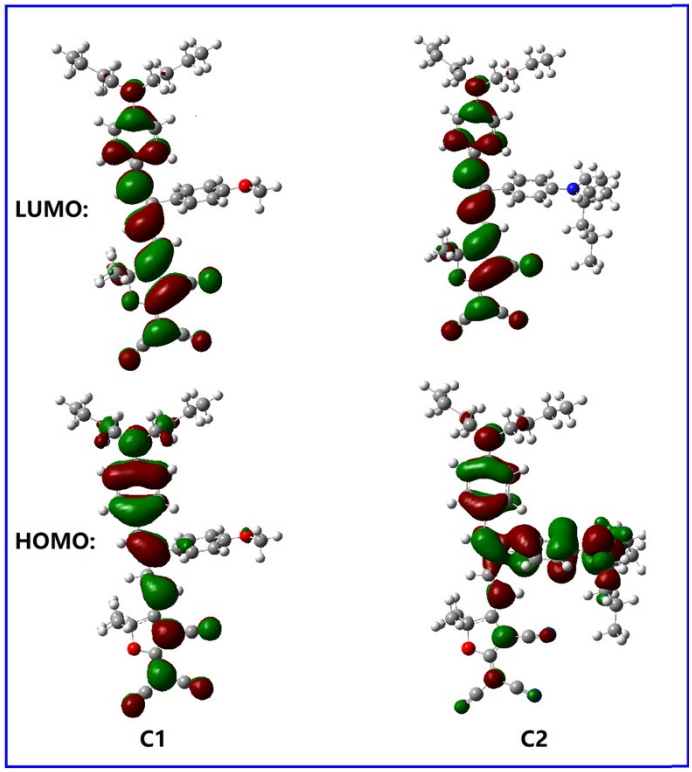

Figure S11. Intramolecular electron distribution of HOMO and LUMO states

4. Reference

1. J. Wu, J. Liu, T. Zhou, S. Bo, L. Qiu, Z. Zhen and X. Liu, *Rsc Adv*, 2012, **2**, 1416.
2. G. W. Deng, H. J. Xu, Z. Q. Zhou, Z. Y. Zhao, J. Y. Wu, X. L. Zhang, K. Sun, Z. H. Li and Z. N. Yonghao, *Dyes Pigments*, 2019, **164**, 97-104.