

Supplementary data

Synthesis of Novel Isophorone-based Dyes for Dye-sensitized Solar Cells

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1. Experimental

Ethyl (*E,Z*)-2-cyano-2-(3,5,5-trimethylcyclohex-2-en-1-ylidene)acetate (B). Isophorone **A** (2.0 g, 14.47 mmol), ethyl cyanoacetate (1.54 mL, 14.47 mmol), ammonium acetate (579 mg, 7.06 mmol), acetic acid (1.2 mL), and benzene (20 mL) were mixed in a three-necked flask under N₂ and heated to reflux by using the Dean–Stark apparatus. After 12 h, the mixture was extracted using ethyl acetate. The organic layer was dried over anhydrous MgSO₄ and evaporated under vacuum, and the crude product was purified through vacuum distillation. An 80% yield of a yellow liquid **B** (*Z*-:*E*- = 1:1) (2.69 g, 11.57 mmol) was obtained. δ_{H} (300 MHz, CDCl₃) 7.41 (s, 0.5H), 6.43 (s, 0.5H), 4.01–4.08 (m, 2H), 2.69 (s, 1H), 2.33 (s, 1H), 1.95 (s, 1H), 1.93 (s, 1H), 1.80 (s, 1.5H), 1.78 (s, 1.5H), 1.14 (t, 3H, *J* = 7.08 Hz), 0.80 (s, 3H), 0.78 (s, 3H). δ_{C} (75 MHz, CDCl₃) 166.3, 165.0, 162.1, 161.5, 156.4, 155.9, 121.9, 119.7, 116.0, 115.3, 98.1, 97.4, 60.5, 44.8, 44.4, 43.6, 39.4, 31.4, 31.0, 27.4, 27.2, 24.8, 24.6, 13.5. MS (FAB, 70 eV): *m/z* (relative intensity) 233 (M⁺, 100); HRMS calcd for C₁₄H₁₉NO₂: 233.1416, found 233.1420.

10-(4-(Hexyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde (D-1). A solution of n-BuLi (6.2 mL, 9.93 mmol, 1.6 M in hexane) was added dropwise to a solution of **C-1** (3.0 g, 6.62 mmol) in THF at –78 °C. The mixture was stirred for 1 h, and dimethyl formamide (DMF; 0.76 mL, 9.93 mmol) was then added to it. Furthermore, the mixture was stirred with a magnetic bar for 6 h, the reaction was quenched by adding water, and the product was extracted using ethyl acetate. The organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure to yield the crude product. The product was purified using a silica gel column chromatograph eluted with dichloromethane/hexane (1/1). A light yellow solid (**D-1**) was obtained in a 77% yield (2.06 g, 5.10 mmol). δ_{H} (400 MHz, CDCl₃) 9.69 (s, 1H), 7.45 (d, 1H, *J* = 1.6 Hz), 7.28 (dd, 1H, *J* = 8.2, 2.0 Hz), 7.27 (d, 2H, *J* = 8.8 Hz), 7.13 (d, 2H, *J* = 8.8 Hz), 6.96 (dd, 1H, *J* = 5.6, 3.6 Hz), 6.84 (dd, 2H, *J* = 5.8, 3.6 Hz), 6.22 (d, 1H, *J* = 8.8 Hz), 6.17–6.19 (m, 1H), 4.05 (t, 2H, *J* = 6.4 Hz), 1.84–1.88 (m, 2H), 1.51–1.55 (m, 2H), 1.38–1.42 (m, 4H), 0.93–0.97 (m, 3H). δ_{C} (100 MHz, CDCl₃) 189.6, 159.2, 149.5, 142.8, 132.0, 131.6, 130.9, 129.9, 127.3, 127.1, 126.6, 123.5, 120.0, 118.9, 116.7, 116.4, 115.0, 68.4, 31.5, 29.2, 25.7, 22.6, 14.0. MS (FAB, 70 eV): *m/z* (relative intensity) 404 ((M+H)⁺, 100). HRMS calcd for C₂₅H₂₅NO₂S: 404.1684, found 404.1694.

4-(Diphenylamino)benzaldehyde (D-2). Compound **D-2** was synthesised using a method similar to that of **D-1**, producing a yellow solid in an 85% yield. δ_{H} (400 MHz, CDCl₃) 9.80 (s, 1H), 7.66 (d, 2H, *J* = 8.6 Hz), 7.31–7.35 (m, 4H), 7.14–7.18 (m, 6H), 7.01 (d, 2H, *J* = 8.6 Hz). δ_{C} (100 MHz, CDCl₃) 190.3, 153.3, 146.1, 131.2, 129.6, 129.0, 126.2, 125.0, 119.2. MS (FAB, 70 eV): *m/z* (relative intensity) 273 ((M+H)⁺, 100); HRMS calcd for C₁₉H₁₅NO: 273.1154, found 273.1160.

4-(N-(naphthalen-1-yl)-N-phenylamino)benzaldehyde (D-3). Compound **D-3** was synthesised using a method similar to that of **D-1**, producing a yellow solid in a 70% yield. δ_{H} (500 MHz, CDCl_3) 9.76 (s, 1H), 7.90 (d, 1H, $J = 8.6$ Hz), 7.89 (d, 1H, $J = 8.9$ Hz), 7.83 (d, 1H, $J = 8.2$ Hz), 7.63 (d, 2H, $J = 8.8$ Hz), 7.46–7.50 (m, 2H), 7.37–7.40 (m, 2H), 7.23–7.30 (m, 4H), 7.10 (t, 2H, $J = 6.7$ Hz), 6.89 (d, 2H, $J = 8.8$ Hz). δ_{C} (125 MHz, CDCl_3) 190.3, 153.7, 146.2, 141.8, 135.2, 131.4, 129.6, 128.6, 124.8, 124.7, 123.6, 117.7. MS (FAB, 70 eV): m/z (relative intensity) 323 ($(\text{M}+\text{H})^+$, 100); HRMS calcd for $\text{C}_{23}\text{H}_{17}\text{NO}$: 323.1310, found 323.1313.

4-(Bis(4-(hexyloxy)phenyl)amino)benzaldehyde (D-4). Compound **D-4** was synthesised using a method similar to that of **D-1**, producing an orange solid in a 58% yield. δ_{H} (300 MHz, CDCl_3) 9.74 (s, 1H), 7.61 (d, 2H, $J = 8.88$ Hz), 7.11 (d, 4H, $J = 8.88$ Hz), 6.82–6.89 (m, 6H), 3.94 (t, 4H, $J = 6.48$ Hz), 1.73–1.80 (m, 4H), 1.41–1.48 (m, 4H), 1.31–1.36 (m, 8H), 0.91 (t, 6H, $J = 7.17$ Hz). δ_{C} (75 MHz, CDCl_3) 190.2, 156.8, 154.0, 138.5, 131.3, 127.9, 127.5, 116.6, 115.5, 68.2, 31.5, 29.2, 25.7, 22.5, 14.0. MS (FAB, 70 eV): m/z (relative intensity) 473 (M^+ , 100); HRMS calcd for $\text{C}_{31}\text{H}_{39}\text{NO}_3$: 473.2924, found 473.2921.

Ethyl (E,Z)-2-cyano-2-(3-((E)-2-(10-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)vinyl)-5,5-dimethyl-cyclohex-2-en-1-ylidene)acetate (E-1). Compounds **D-1** (5 g, 12.4 mmol) and **B** (3g, 9.3 mmol) were mixed in a three-necked flask under a nitrogen atmosphere and stirred in dry ACN for a while. Furthermore, piperidine (1.1 mL, 10.2 mmol) was added, and the mixture was heated at 90 °C overnight. The product was extracted using dichloromethane (DCM), and the organic layer was dried over anhydrous MgSO_4 and evaporated under vacuum. The product was purified using a silica gel column chromatograph, with ethyl acetate/hexane (1/15) as the eluent. A dark red solid (**E-1**) was obtained in a 67% yield. δ_{H} (400 MHz, CDCl_3) 7.89 (s, 1H), 7.27–7.30 (m, 2H), 7.12–7.14 (m, 3H), 6.74–7.00 (m, 6H), 6.13–6.19 (m, 2H), 4.26–4.34 (m, 2H), 6.13–6.19 (m, 2H), 4.06 (t, 2H, $J = 6.52$ Hz), 2.98 (s, 1H), 2.63 (s, 1H), 2.38 (s, 1H), 2.37 (s, 1H), 1.85–1.88 (m, 2H), 1.52–1.55 (m, 2H), 1.35–1.42 (m, 6H), 1.07 (s, 3H), 1.04 (s, 3H), 0.95 (t, 3H, $J = 7.04$ Hz). δ_{C} (100 MHz, CDCl_3) 166.5, 164.9, 163.2, 162.8, 159.0, 152.3, 151.9, 145.3, 145.2, 143.7, 133.6, 132.5, 131.9, 130.4, 130.3, 128.5, 127.8, 126.9, 126.5, 126.4, 126.3, 125.9, 125.1, 124.9, 123.8, 122.6, 120.0, 119.0, 117.4, 116.6, 116.5, 115.9, 115.6, 99.0, 98.3, 68.3, 61.4, 61.3, 44.7, 40.8, 39.2, 38.8, 31.8, 31.5, 31.3, 29.2, 28.3, 28.1, 25.7, 22.6, 14.1, 14.0. MS (FAB, 70 eV): m/z (relative intensity) 618 (M^+ , 100); HRMS calcd for $\text{C}_{39}\text{H}_{42}\text{N}_2\text{O}_3\text{S}$: 618.2911, found 618.2897.

Ethyl (E,Z)-2-cyano-2-(3-((E)-4-(diphenylamino)styryl)-5,5-dimethylcyclohex-2-en-1-ylidene)acetate (E-2). Compound **E-2** was synthesised using a method similar to that of **E-1**, producing a red solid in a 95% yield. δ_{H} (500 MHz, CDCl_3) 7.85 (s, 1H), 7.30 (d, 1H, $J = 8.20$ Hz),

7.28 (d, 1H, $J = 8.35$ Hz), 7.21–7.25 (m, 4H), 7.07 (d, 4H, $J = 7.45$ Hz), 7.03 (t, 2H, $J = 7.35$ Hz), 6.97 (d, 1H, $J = 8.15$ Hz), 6.96 (d, 1H, $J = 8.35$ Hz), 6.84–6.85 (m, 2H), 4.20–4.26 (m, 2H), 2.93 (s, 1H), 2.58 (s, 1H), 2.36 (s, 1H), 2.34 (s, 1H), 1.29–1.33 (m, 3H), 1.01 (s, 3H), 0.99 (s, 3H). δ_C (125 MHz, $CDCl_3$) 166.7, 165.0, 163.3, 162.8, 152.6, 152.2, 148.9, 148.8, 147.0, 134.7, 134.6, 129.5, 129.4, 129.2, 128.4, 128.3, 127.8, 125.7, 125.1, 123.7, 123.6, 122.2, 117.5, 116.7, 98.8, 98.1, 61.4, 61.3, 44.7, 40.9, 39.2, 38.8, 31.8, 31.4, 28.3, 28.1, 14.1. MS (FAB, 70 eV): m/z (relative intensity) 488 (M^+ , 100); HRMS calcd for $C_{33}H_{32}N_2O_2$: 488.2464, found 488.2466.

(Ethyl (*E,Z*)-2-cyano-2-(5,5-dimethyl-3-((*E*)-4-(naphthalen-1-yl(phenyl)amino)styryl)cyclohex-2-en-1-ylidene)acetate (E-3). Compound **E-3** was synthesised using a method similar to that of **E-1**, producing a red solid in a 95% yield. δ_H (500 MHz, $CDCl_3$) 7.90 (s, 1H), 7.88 (d, 2H, $J = 7.40$ Hz), 7.80 (d, 1H, $J = 8.25$ Hz), 7.49 (d, 1H, $J = 8.0$ Hz), 7.46 (d, 1H, $J = 8.50$ Hz), 7.33–7.38 (m, 2H), 7.22–7.30 (m, 4H), 7.12 (d, 2H, $J = 6.35$ Hz), 7.01 (t, 1H, $J = 7.30$ Hz), 4.25–4.28 (m, 2H), 2.96 (s, 1H), 2.61 (s, 1H), 2.38 (s, 1H), 2.37 (s, 1H), 1.33–1.36 (m, 3H), 1.04 (s, 3H), 1.02 (s, 3H). δ_C (125 MHz, $CDCl_3$) 166.9, 165.2, 163.5, 163.0, 152.9, 152.5, 149.7, 149.6, 147.5, 142.8, 135.4, 135.0, 134.9, 131.2, 129.4, 129.3, 128.4, 128.8, 128.7, 128.6, 128.5, 128.2, 127.6, 127.5, 127.1, 126.8, 126.5, 126.4, 125.7, 124.1, 123.6, 123.4, 123.2, 120.4, 117.7, 117.0, 98.8, 98.1, 61.5, 61.4, 44.9, 41.0, 39.4, 39.0, 31.9, 31.5, 28.5, 28.3, 14.3. MS (FAB, 70 eV): m/z (relative intensity) 538 (M^+ , 100); HRMS calcd for $C_{37}H_{34}N_2O_2$: 538.2620, found 538.2621.

Ethyl(*E,Z*)-2-(3-((*E*)-4-(bis(4-(hexyloxy)phenyl)amino)styryl)-5,5-dimethylcyclohex-2-en-1-ylidene)-2-cyanoacetate (E-4). Compound **E-4** was synthesised using a method similar to that of **E-1**, producing an orange solid in an 82% yield. δ_H (400 MHz, $CDCl_3$) 7.91 (s, 0.5H), 7.30 (t, 2H, $J = 4.38$ Hz), 7.06–7.09 (m, 4H), 6.85–6.90 (m, 8.5H), 4.27–4.31 (m, 2H), 3.94–3.97 (m, 4H), 2.99 (s, 1H), 2.64 (s, 1H), 2.42 (s, 1H), 2.40 (s, 1H), 1.76–1.81 (m, 4H), 1.46–1.49 (m, 4H), 1.36–1.39 (m, 11H), 1.05 (s, 3H), 1.07 (s, 3H), 0.91–0.95 (m, 6H). δ_C (100 MHz, $CDCl_3$) 166.8, 165.1, 163.4, 163.0, 156.1, 153.1, 152.7, 149.9, 149.9, 139.7, 135.2, 135.1, 128.4, 128.3, 127.6, 127.5, 127.4, 127.2, 126.7, 125.2, 132.2, 119.1, 115.4, 98.2, 97.5, 68.2, 61.3, 61.2, 44.7, 40.9, 39.3, 38.9, 31.8, 31.6, 31.4, 29.3, 28.3, 28.1, 25.7, 22.6, 14.2, 14.0. MS (FAB, 70 eV): m/z (relative intensity) 688 (M^+ , 100); HRMS calcd for $C_{45}H_{56}N_2O_4$: 688.4233, found 688.4233.

2. ^1H and ^{13}C NMR spectra

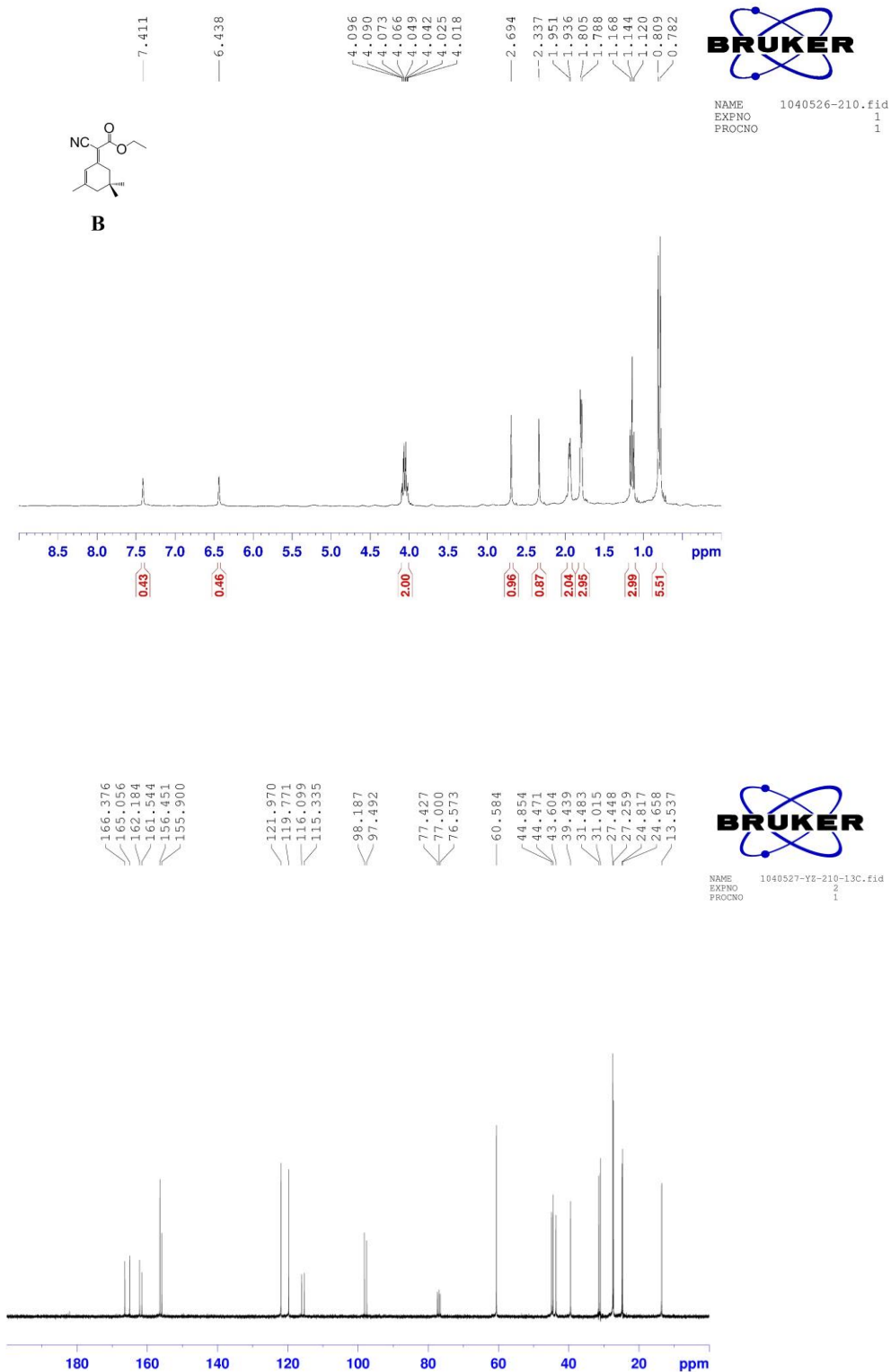


Fig. S1. ^1H NMR (upper) and ^{13}C NMR (lower) spectra of **B** in CDCl₃.

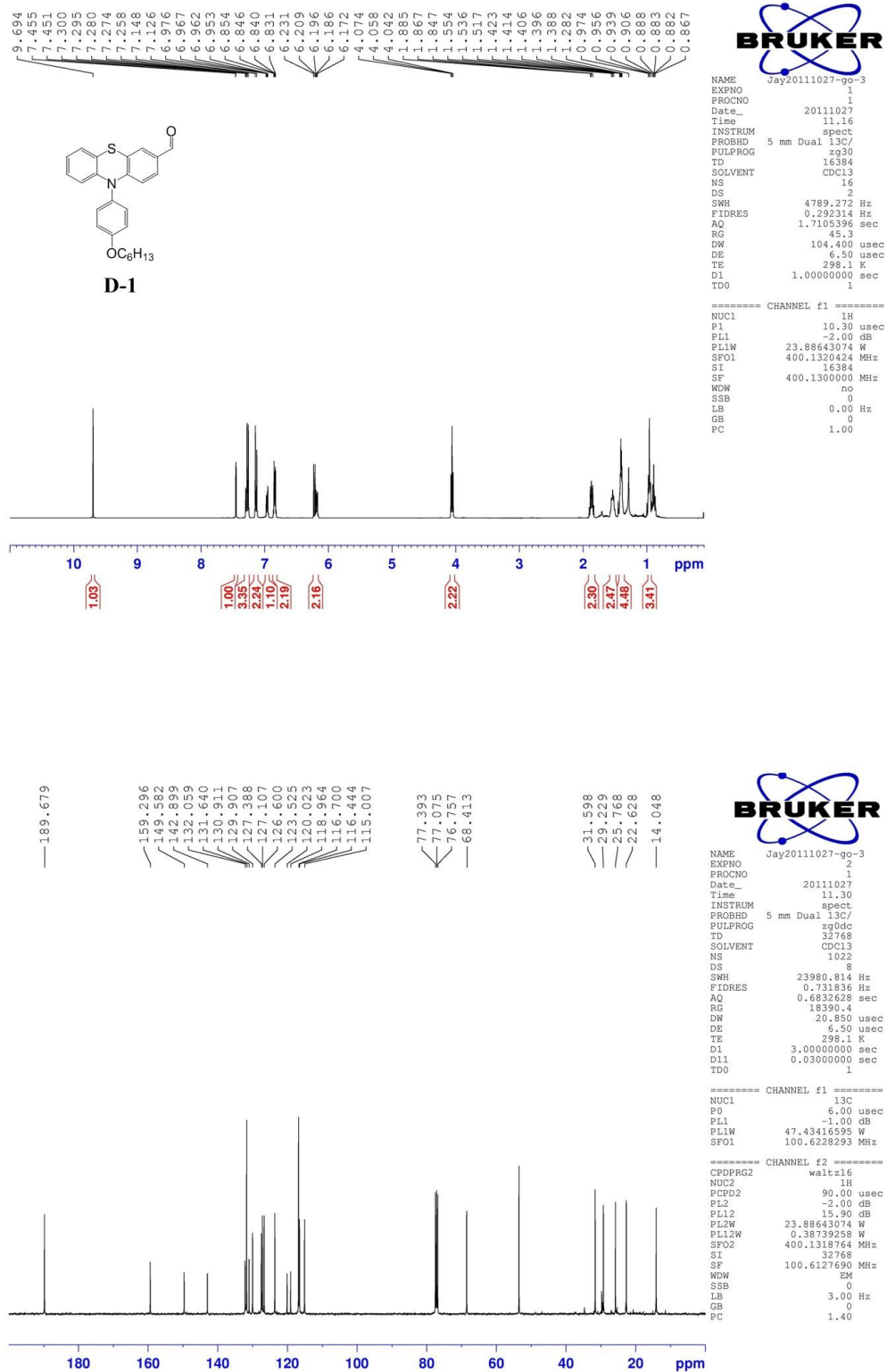


Fig. S2. ¹H NMR (upper) and ¹³C NMR (lower) spectra of **D-1** in CDCl₃.

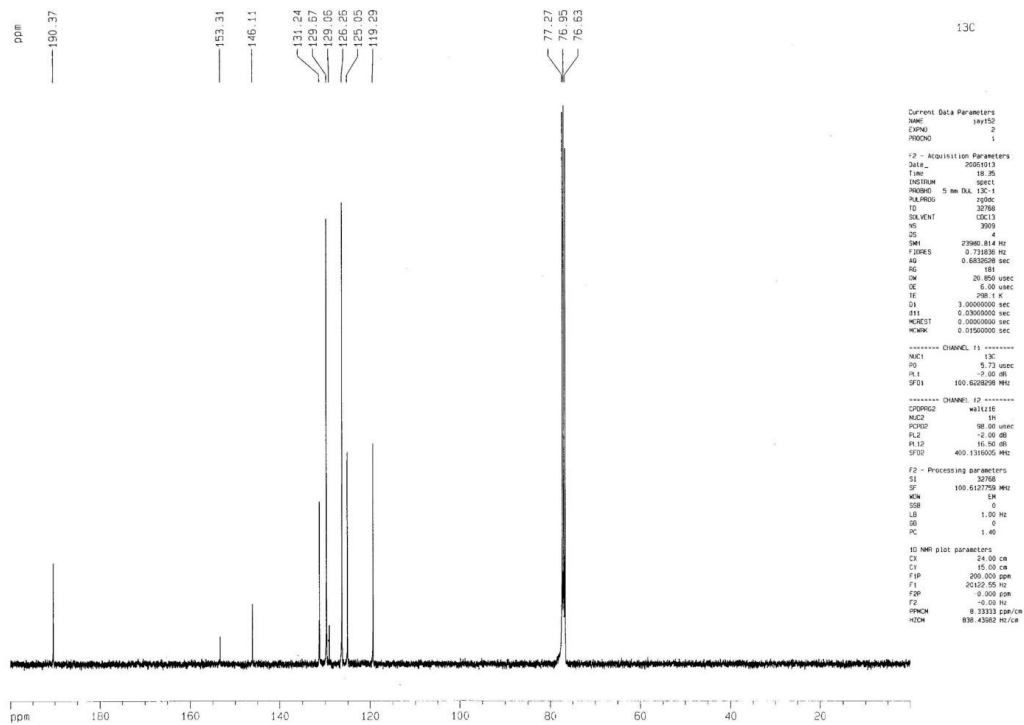
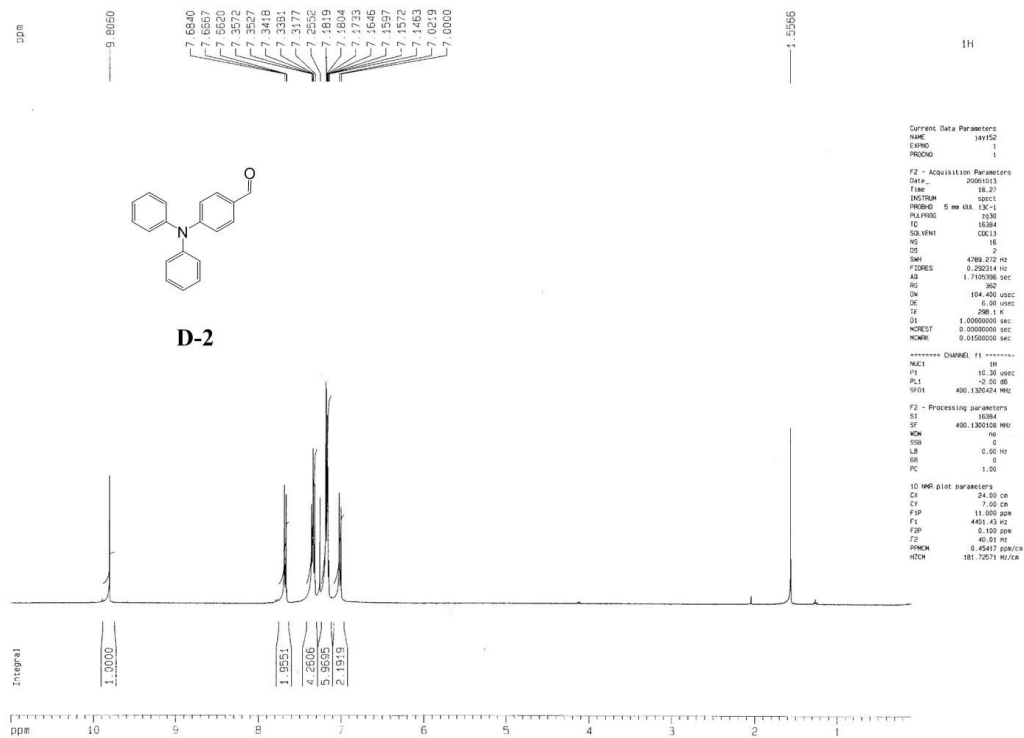


Fig. S3. ¹H NMR (upper) and ¹³C NMR (lower) spectra of D-2 in CDCl₃.

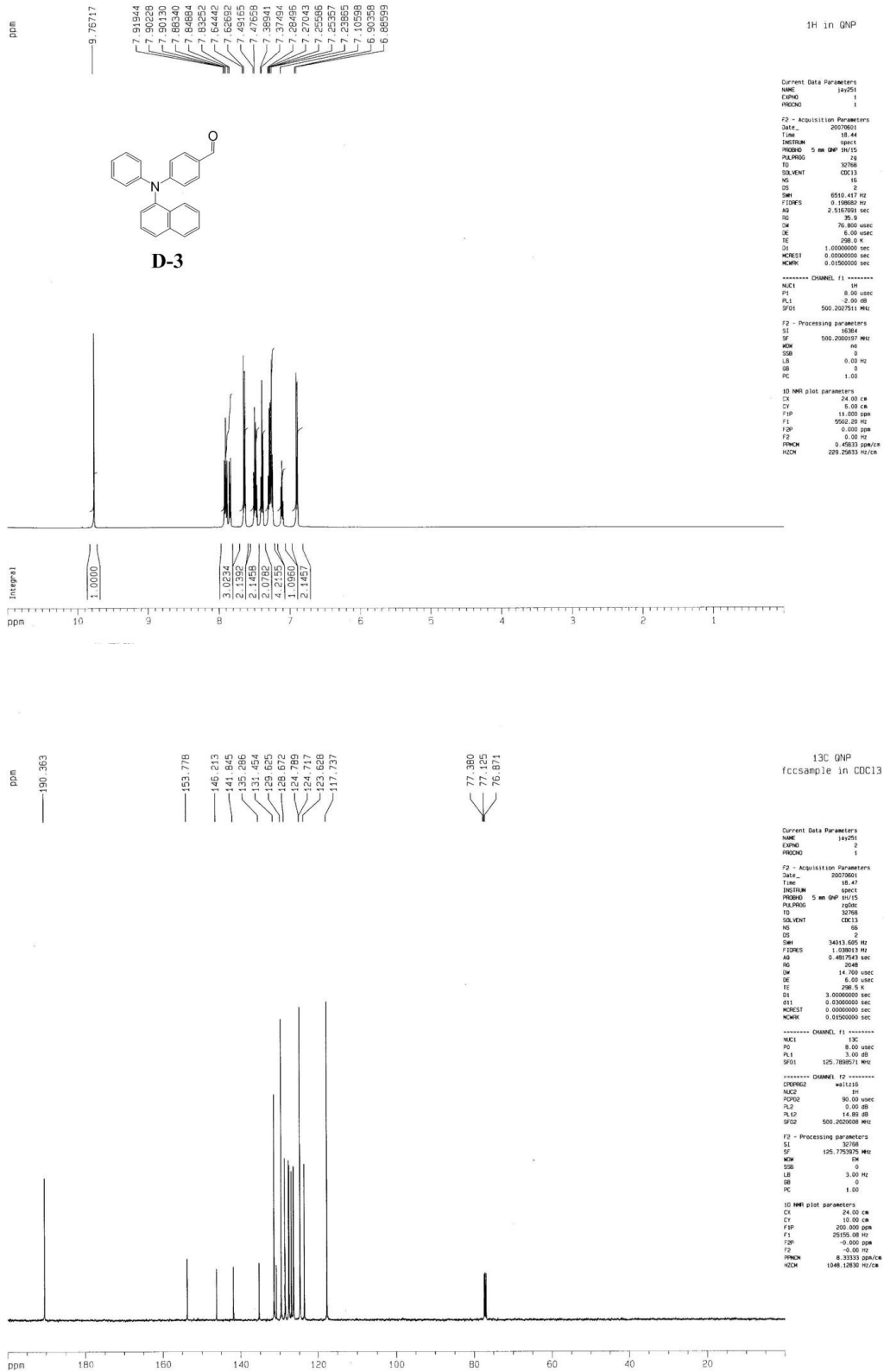


Fig. S4. ¹H NMR (upper) and ¹³C NMR (lower) spectra of **D-3** in CDCl₃.

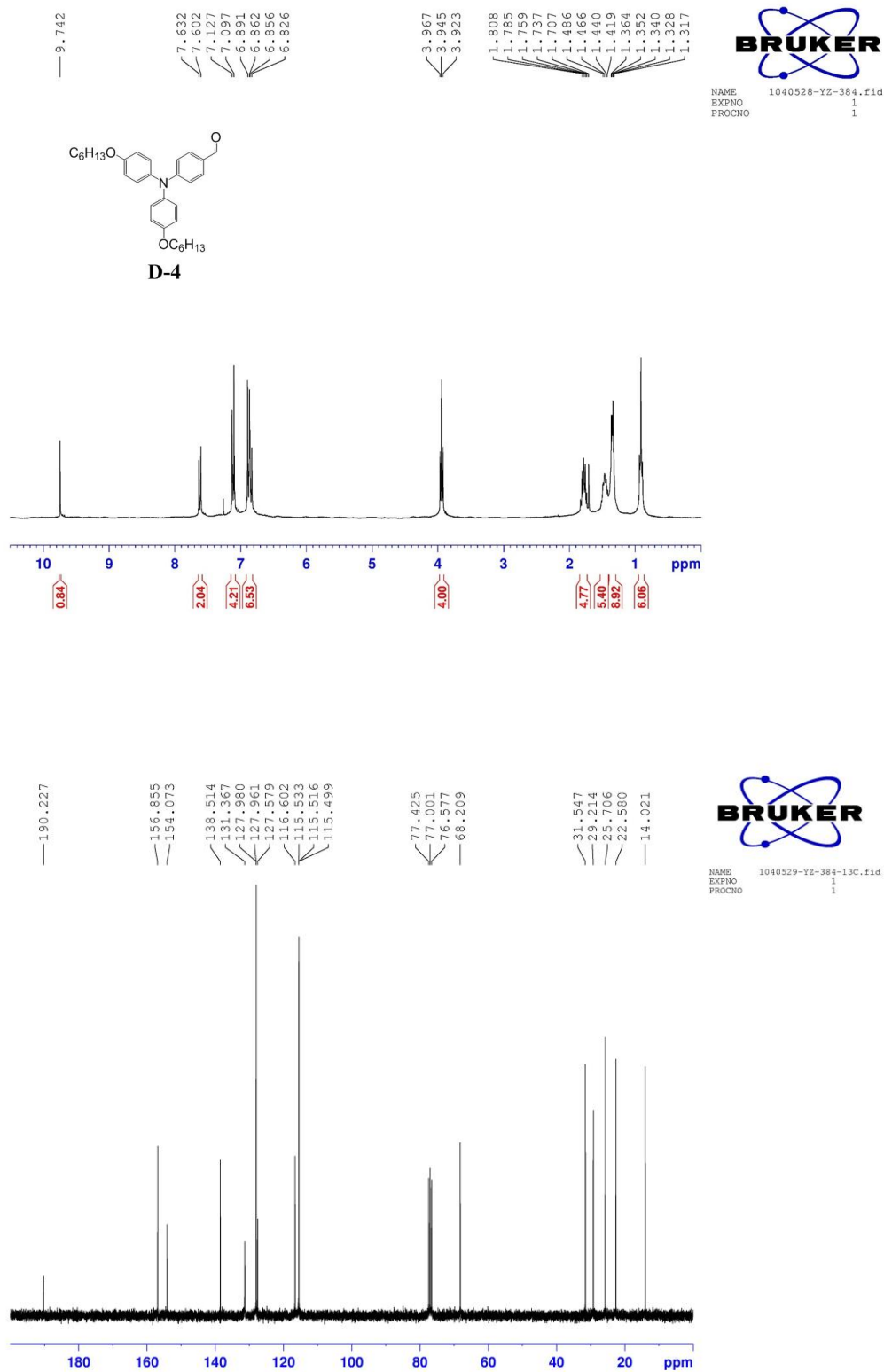


Fig. S5. ¹H NMR (upper) and ¹³C NMR (lower) spectra of **D-4** in CDCl₃.

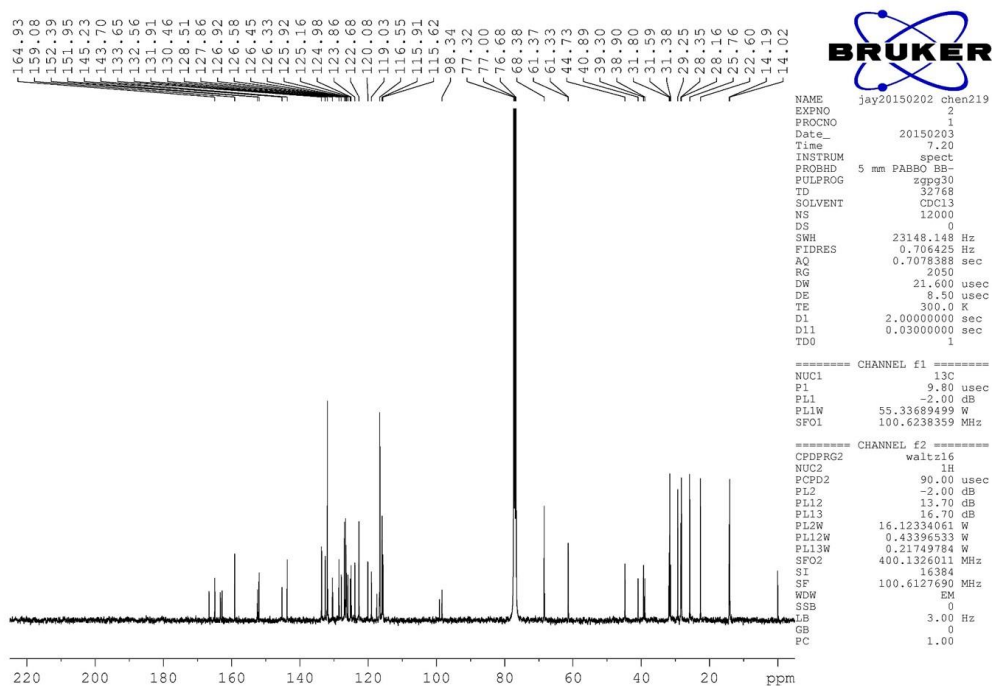
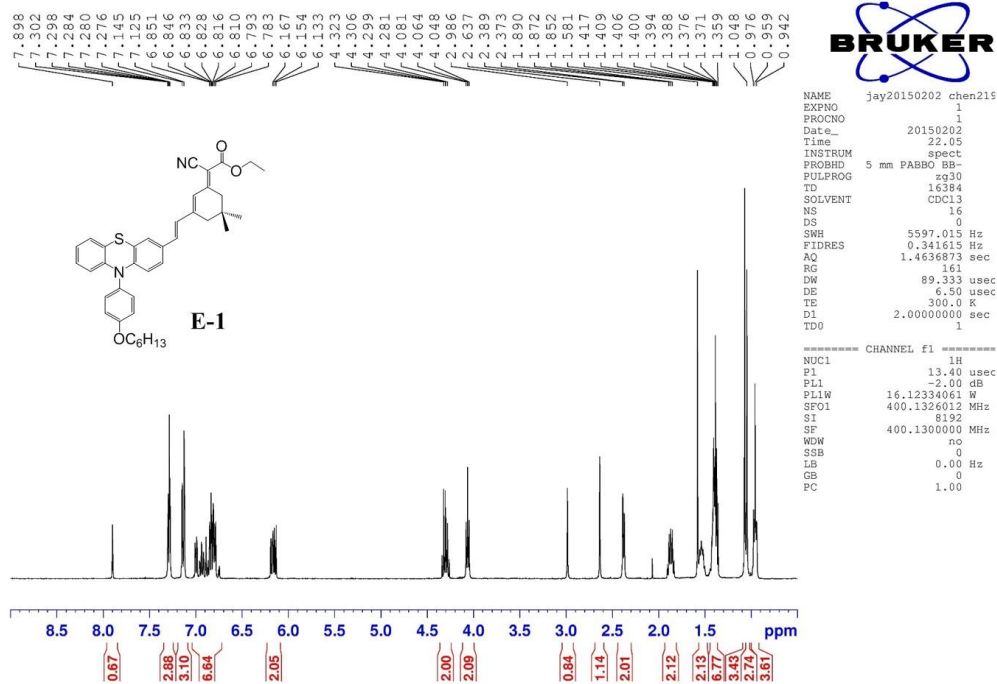


Fig. S6. ¹H NMR (upper) and ¹³C NMR (lower) spectra of E-1 in CDCl₃.

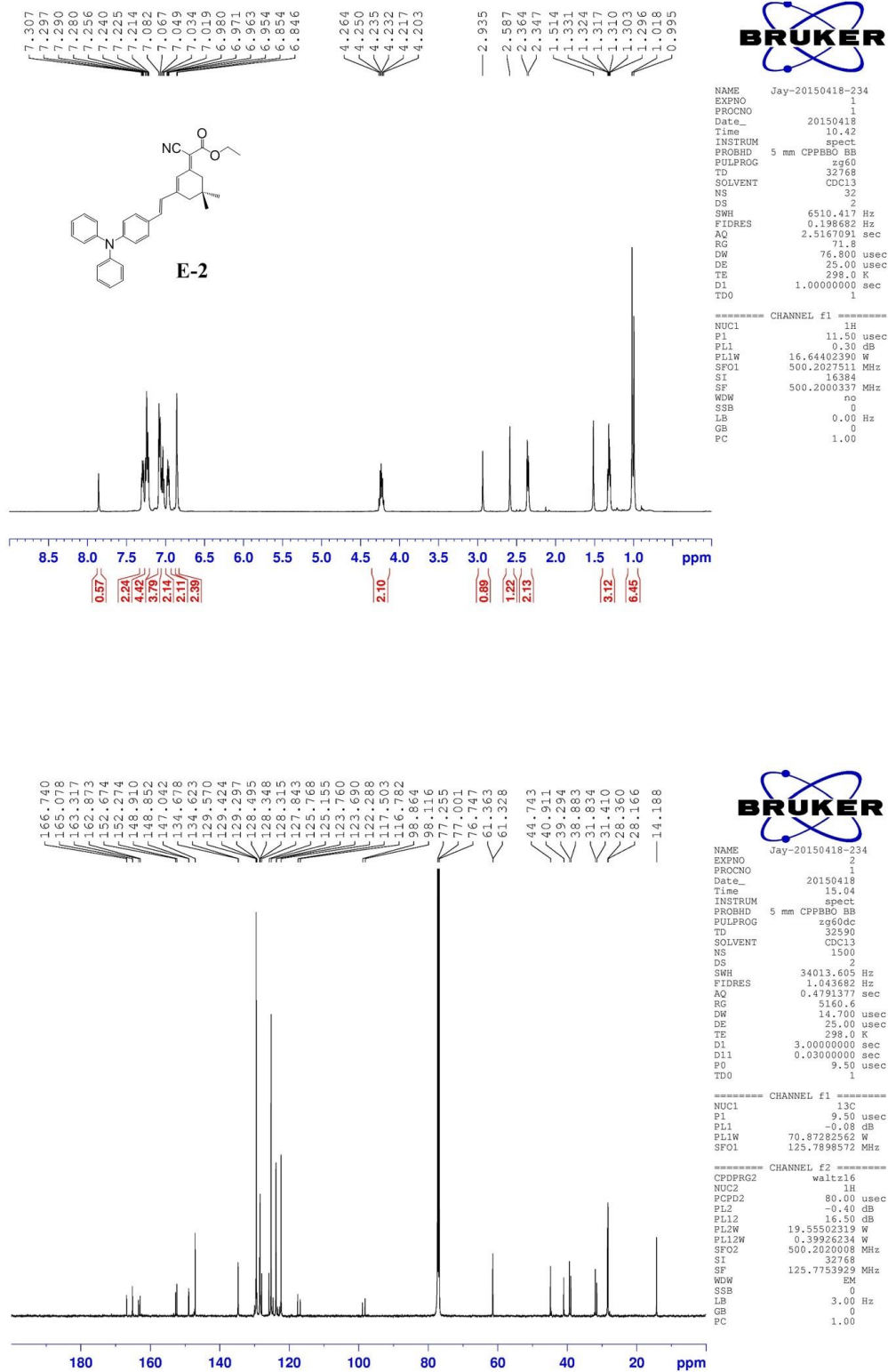


Fig. S7. ¹H NMR (upper) and ¹³C NMR (lower) spectra of **E-2** in CDCl₃.

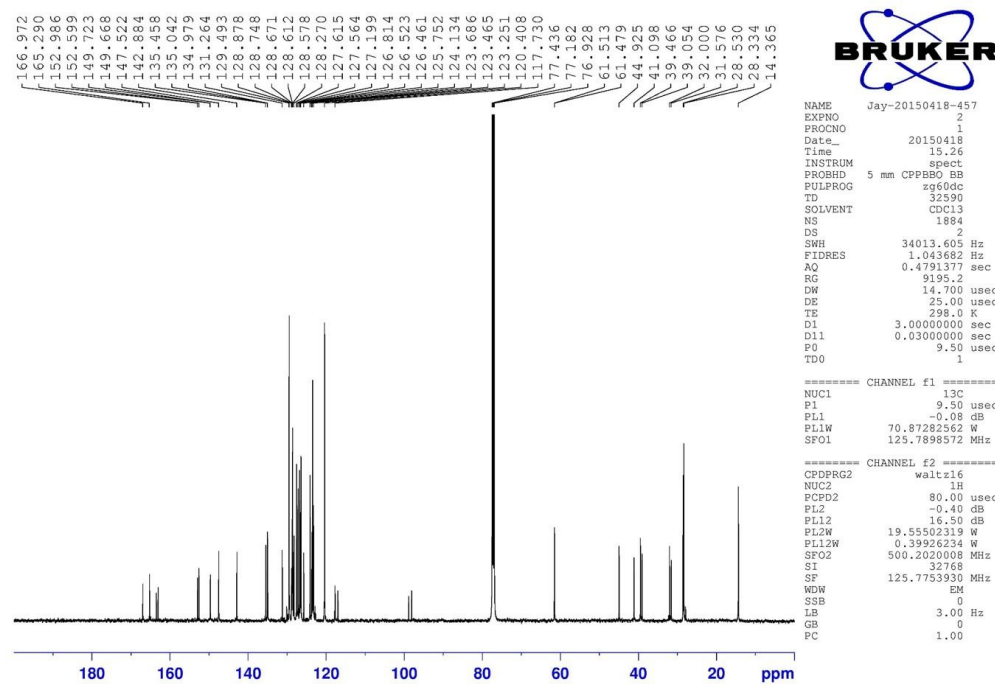
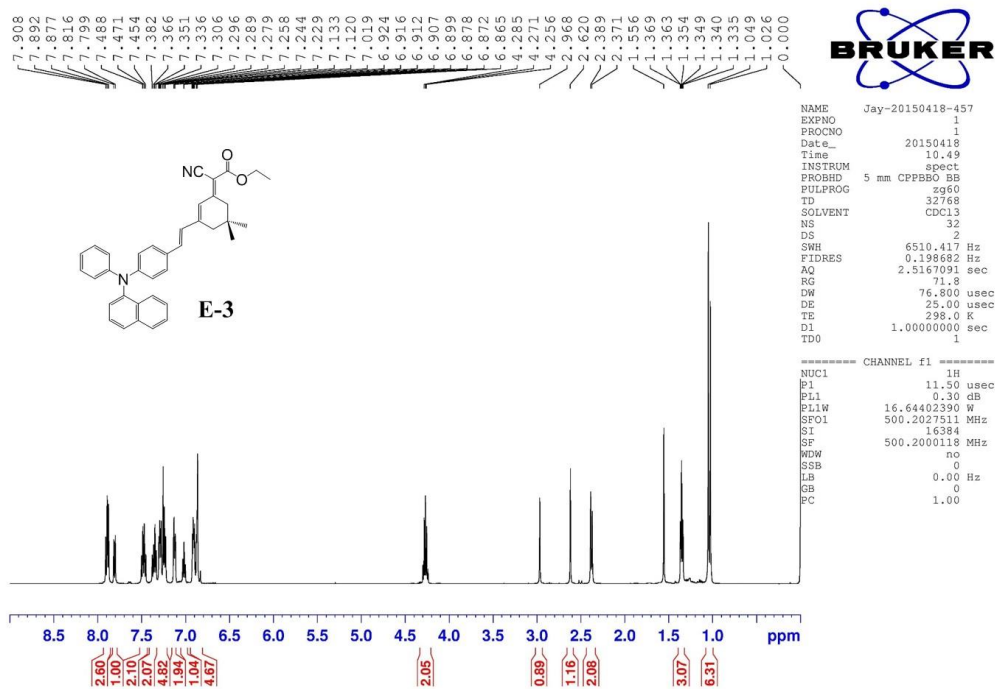


Fig. S8. ¹H NMR (upper) and ¹³C NMR (lower) spectra of E-3 in CDCl₃.

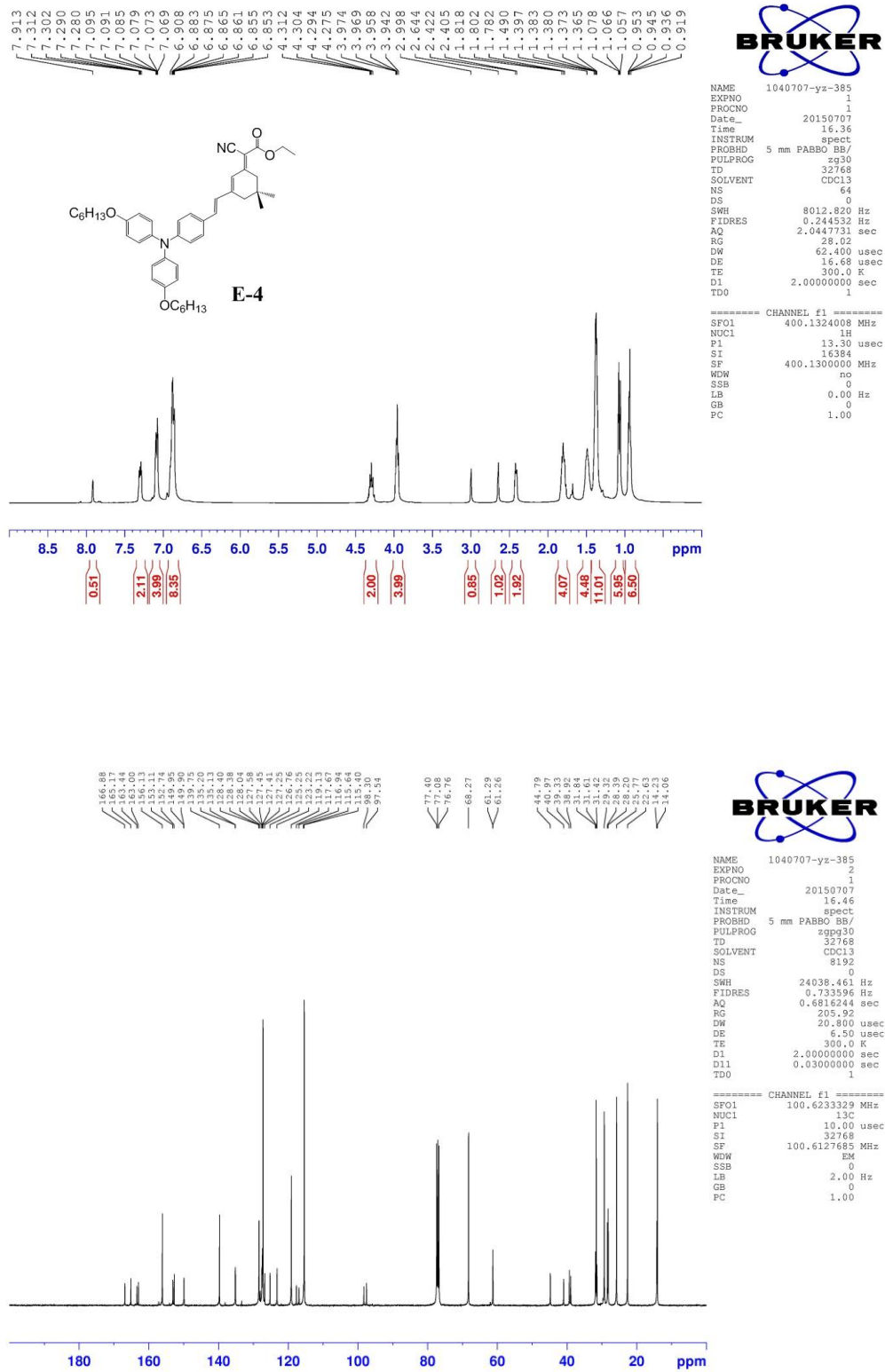


Fig. S9. ¹H NMR (upper) and ¹³C NMR (lower) spectra of **E-4** in CDCl₃.

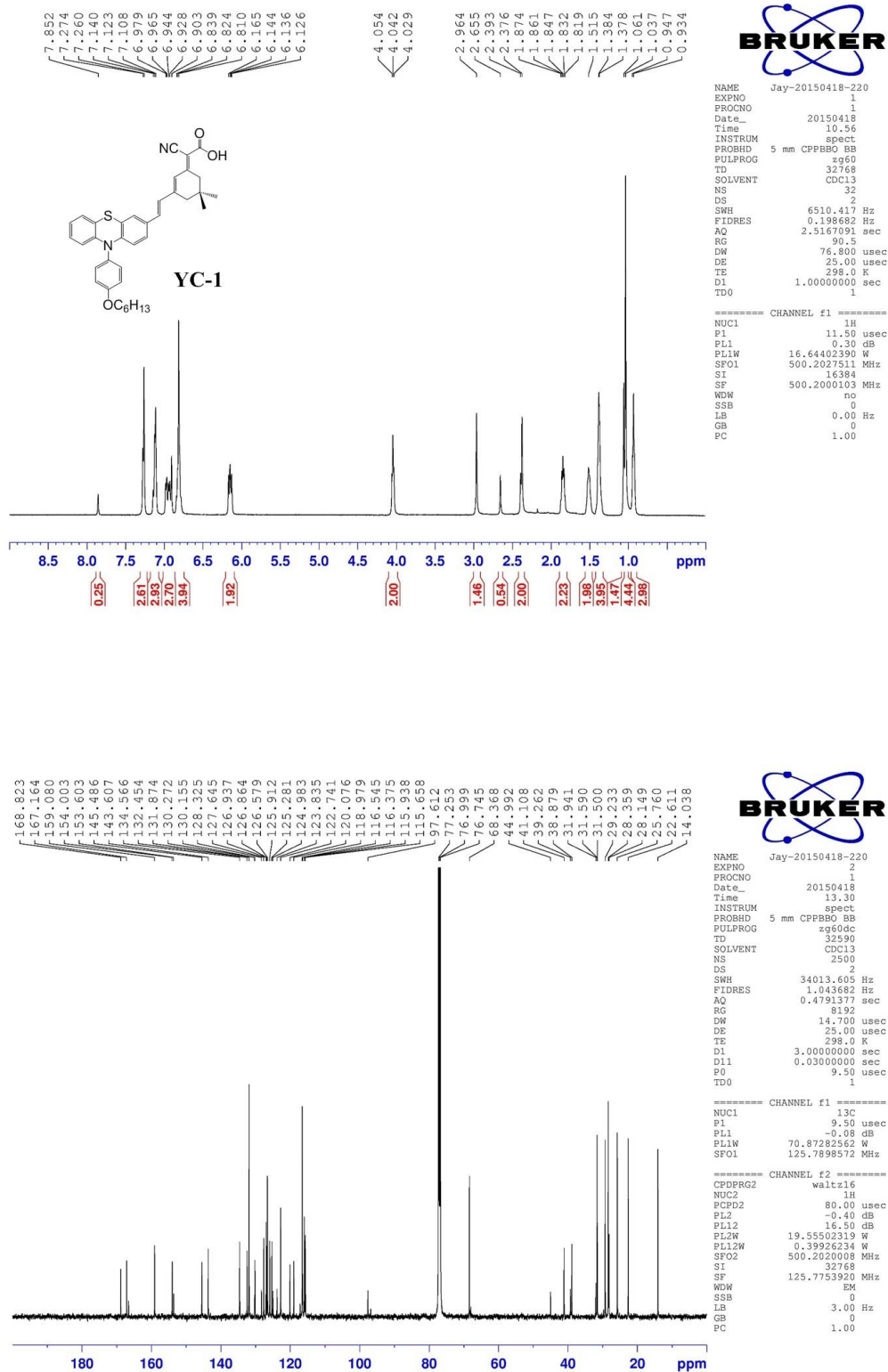


Fig. S10. ¹H NMR (upper) and ¹³C NMR (lower) spectra of YC-1 in CDCl₃.

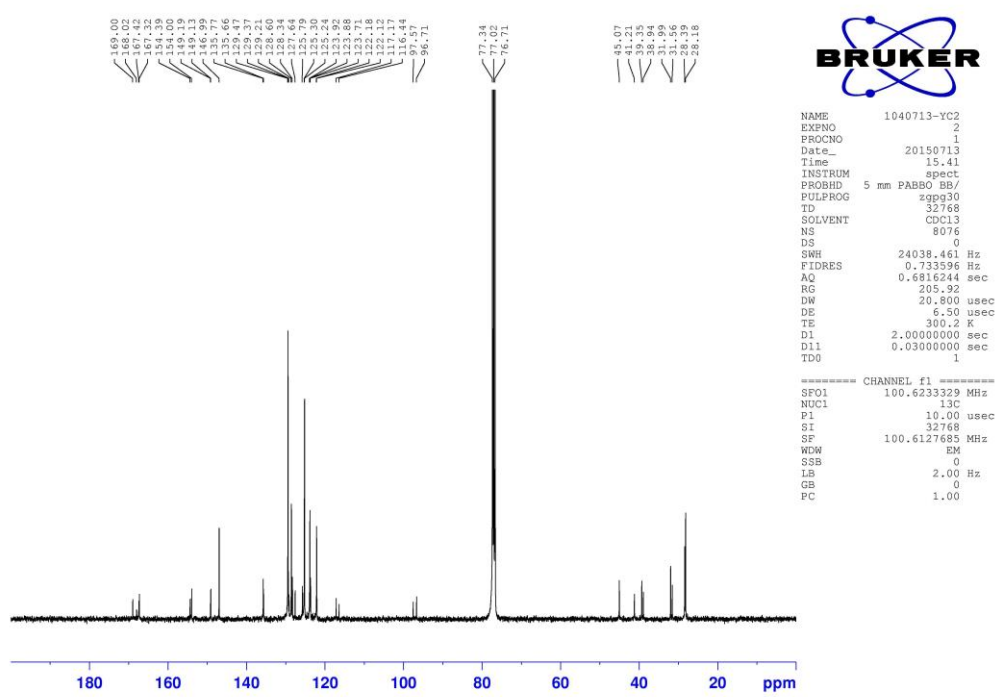
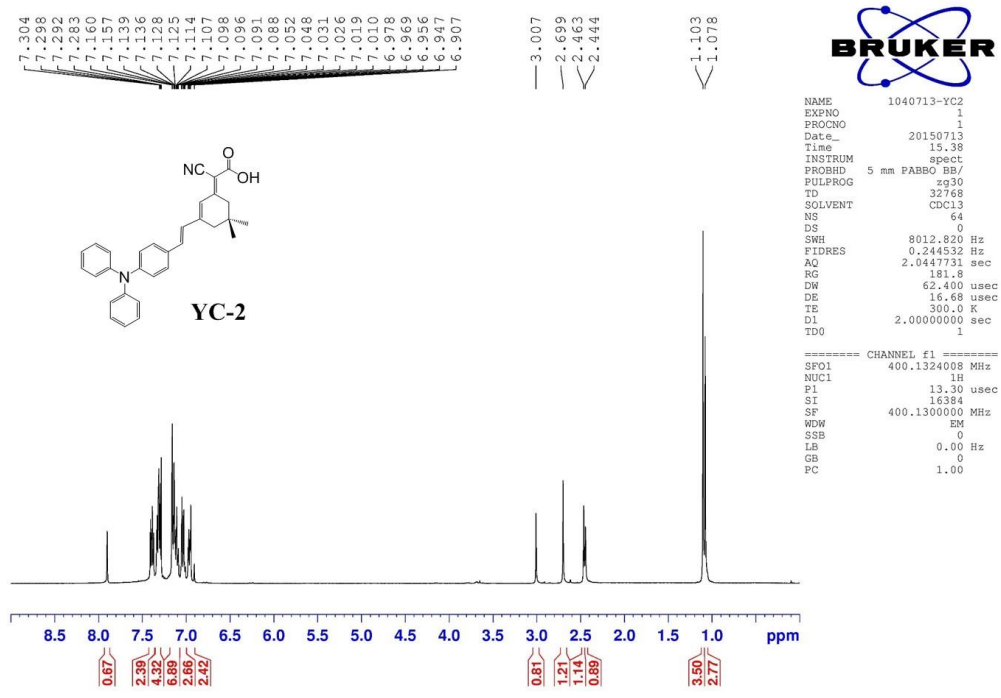


Fig. S11. ¹H NMR (upper) and ¹³C NMR (lower) spectra of YC-2 in CDCl₃.

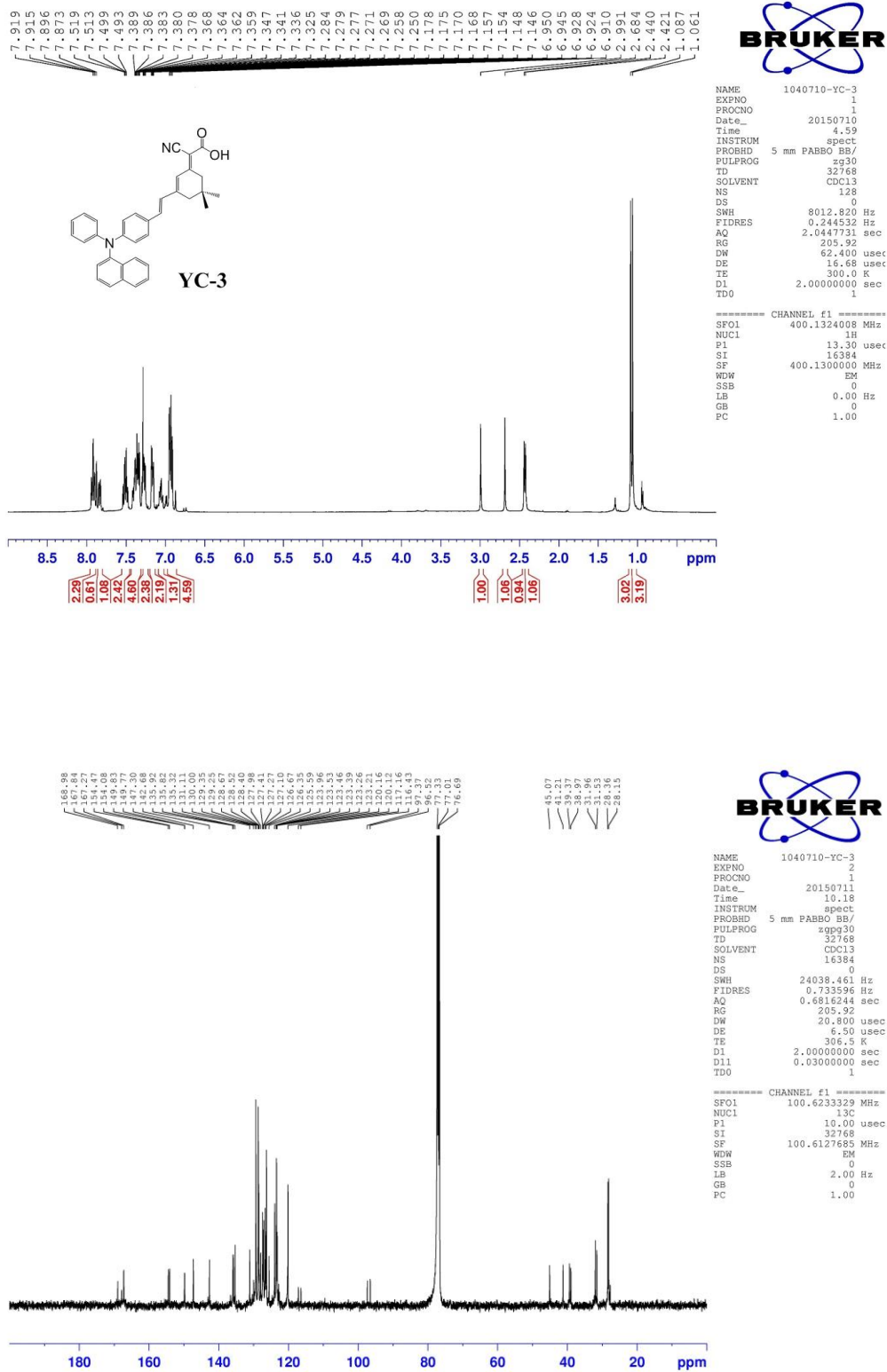
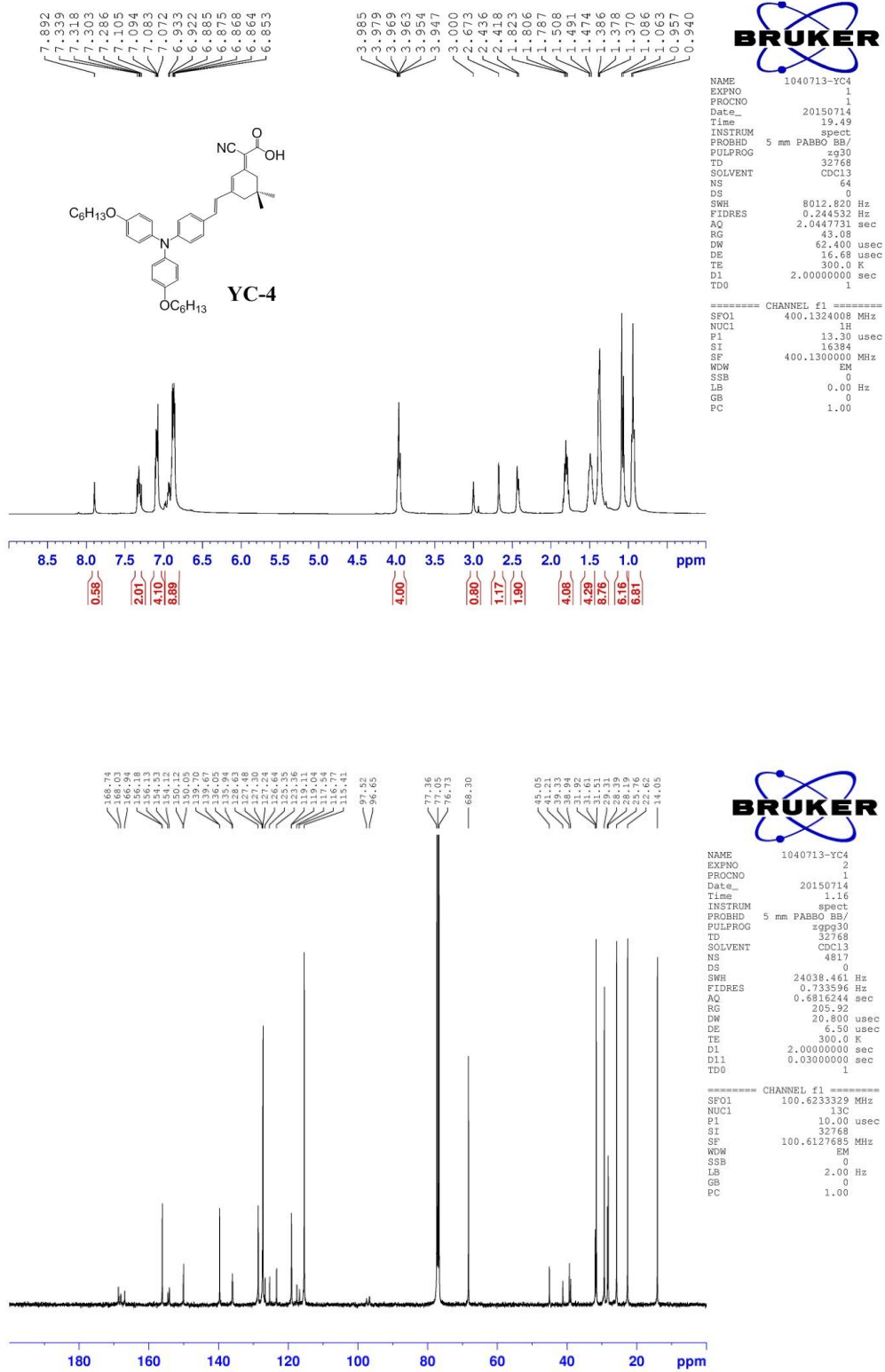


Fig. S12. ¹H NMR (upper) and ¹³C NMR (lower) spectra of YC-3 in CDCl₃.



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180 160 140 120 100 80 60 40 20 ppm

Fig. S13. ^1H NMR (upper) and ^{13}C NMR (lower) spectra of YC-4 in CDCl_3 .

3. UV/Vis spectra

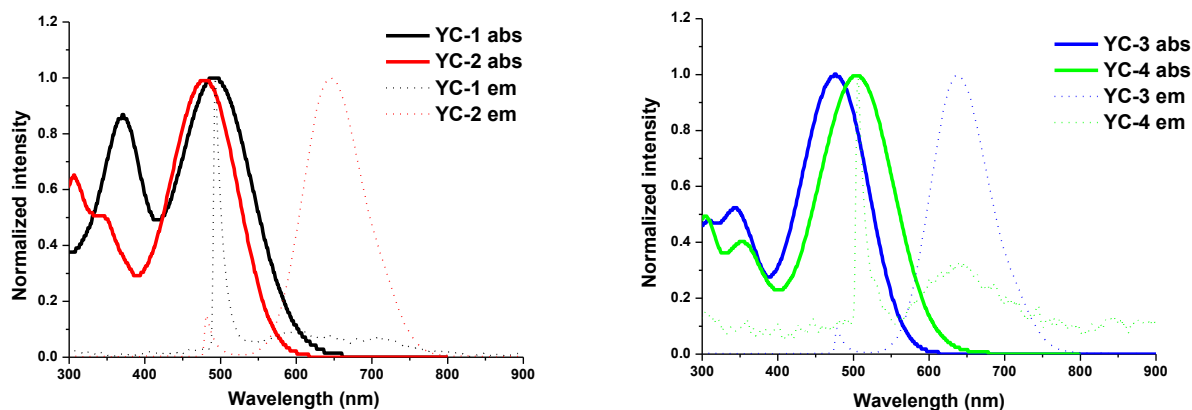


Fig. S14. The absorption and emission spectra of YC-series organic dyes in CH_2Cl_2 .

4. Theoretical calculation

Table S1. Calculated Low-Lying Transition for dyes.

dye	state	excitation ^a	λ_{cal} (eV, nm)	f^b B3LYP/631G*	Dipole moment (D)
YC-1	S1	96.21% H→L	2.30(538)	0.6122	12.8343
	S2	84.82% H-1→L	3.12(397)	0.8568	
	S3	83.44% H-2→L	3.52 (352)	0.1828	
YC-2	S1	98.16% H→L	2.41(512)	1.0267	9.2625
	S2	89.88% H-1→L	3.39(365)	0.7681	
	S3	54.37% H→L+2	3.81(325)	0.0109	
YC-3	S1	97.69% H→L	2.45(505)	1.1211	9.1517
	S2	81.12% H→L+1	3.20(387)	0.0856	
	S3	52.53% H-1→L	3.33(371)	0.3573	
YC-4	S1	98.66% H→L	2.28(542)	1.1391	11.9272
	S2	91.35% H-1→L	3.26(379)	0.8260	
	S3	96.00% H-2→L	3.61(343)	0.0094	

^aH=HOMO, L=LUMO, H+1=HOMO+1, L+1=LUMO+1, and L+2=LUMO+2. ^bOscillator strengths.

Table S2. Difference of Mulliken charges between ground state (S_0) and excited state (S_1), estimated by time dependent DFT/B3LYP model.

dye	state	D	B	A
YC-1	S_1-S_0	0.72242	-0.50128	-0.22114
YC-2	S_1-S_0	0.66009	-0.45257	-0.20752
YC-3	S_1-S_0	0.63324	-0.43408	-0.19916
YC-4	S_1-S_0	0.68887	-0.47468	-0.21419

Difference of Mulliken charge between ground state and excited state.

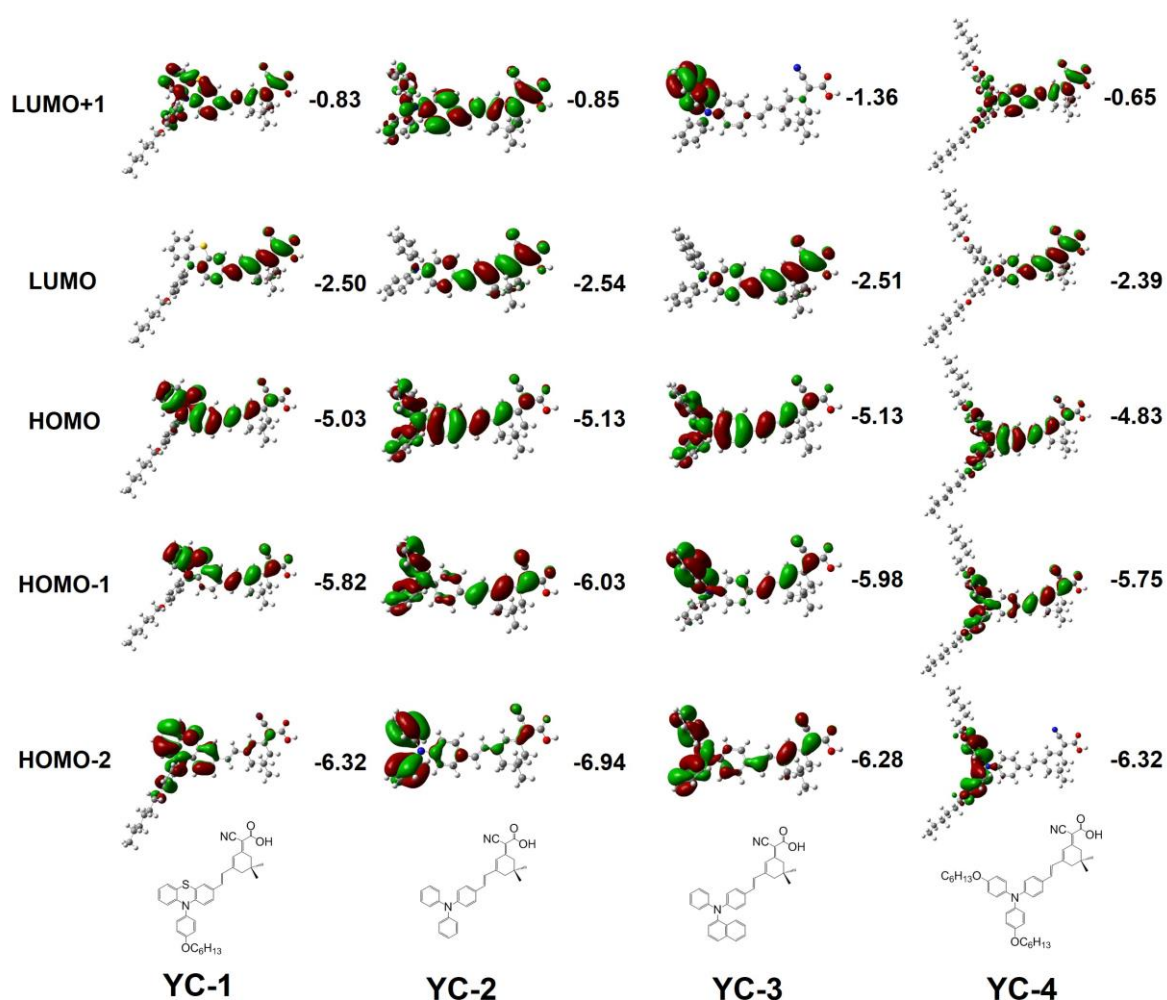


Fig. S15. Computed HOMO and LUMO orbitals of organic dyes.

5. CV spectra and HOMO-LUMO level

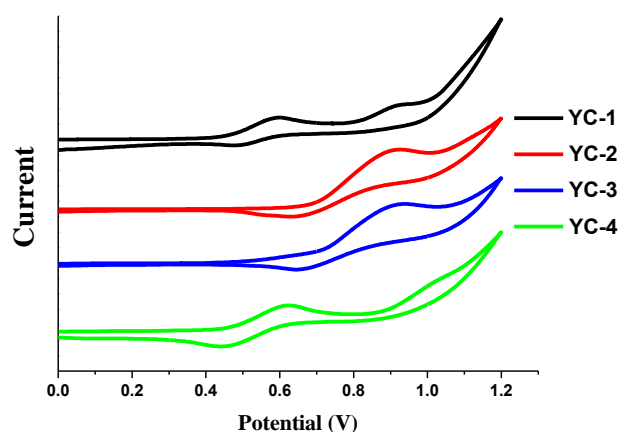


Fig. S16. Oxidative voltammograms of YC-series organic dyes in CH₂Cl₂.

6. Different solvent system in DSSCs performance

Table S3. Photovoltaic parameters of Devices made YC-1, YC-2, YC-3 and YC-4 in THF and CH₂Cl₂.

Solvent system	dye	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF	η^a (%)
THF	YC-1	10.47	0.67	0.54	4.50
	YC-2	9.65	0.63	0.60	3.61
	YC-3	10.63	0.63	0.60	3.99
	YC-4	11.14	0.65	0.55	3.97
CH ₂ Cl ₂	YC-1	14.86	0.67	0.62	6.18
	YC-2	12.18	0.64	0.62	4.92
	YC-3	12.43	0.65	0.63	5.08
	YC-4	13.44	0.66	0.60	5.37
MeCN/ <i>t</i> -BuOH(1/1)	N719	15.94	0.73	0.60	7.02

J_{sc} : short-circuit photocurrent density; V_{oc} : open-circuit photovoltage; FF: fill factor; η : total power conversion efficiency. ^a Performance of DSSC measured in a 0.25 cm² working area on an FTO (7Ω/square) substrate. Electrolyte 1 (E1): LiI (0.5M), I₂ (0.05M), and TBP (0.5M) in MeCN.

7. Dyes loading amount

Table S4 Dyes loading amount on TiO₂ surface using **YC-1-4** with and without deoxycholic acid

dye ^a	DCA (mM)	Loading amount (10 ⁻⁷ mol/cm ²)
YC-1	0	13.4
	10	10.2
YC-2	0	6.3
	10	9.0
YC-3	0	8.3
	10	8.7
YC-4	0	11.8
	10	10.1

^a Concentration of dye is 3 × 10⁻⁴ M in CH₂Cl₂.