Journal of Materials Chemistry C

Supporting information: Exploration of high-performance light conversion agent based on cyanostilbene and phenanthrenecarbonitrile backbone: E/Z and position isomerism, high-contrast Michael addition reaction activity and intramolecular photocyclization

Yongtao Wang, *[a] Zhean Qian,[a] Xueming Li [a], Anjun Qin,[b] Yanjun Guo[a] and Benzhong Tang[b]

[a] Guangxi Key Laboratory of Electrochemical and Magneto-chemical Function Materia, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, China.

[b] School of Materials Science and Engineering, South China University of Technology, Guangzhou, 510641, PR China

E-mail: wyt_shzu@163.com; msqinaj@scut.edu.cn; tangbenz@ust.hk.

Keywords: Light conversion agent; AIE; Photochemistry; E/Z isomers; Cyanostilbene derivatives.

1. Experimental

1.1. Measurement and characterization. ^{1}H NMR spectra and ^{13}C NMR spectra were obtained with a Varian inova instrument at 500 MHz and 100 MHz using tetramethylsilane (TMS) as the internal standard, and $CDCl_3$ or DMSO as the solvent in all cases. The melting points of the purified samples were tested on LSD128. UV-vis absorption spectra were obtained on a MaPada UV-3200PCS spectrophotometer. The absolute fluorescence quantum yields were determined by a calibrated integrating sphere on Perkin-Elmer LS-55. Fluorescent emission spectra were obtained on a Hitachi F-2500 fluorescence spectrophotometer. MALDI/HRMS was recorded on an UltrafleXtreme MALDI-TOF/TOF mass spectrometer (Bruker, Germany). Powder X-ray diffraction (XRD) was performed on a Bruker D8 Focus Powder X-ray diffraction instrument. Single-crystal X-ray diffraction data were collected by Oxford Diffraction Xcalibur Eos diffractometer equipped with an Eos detector and operating graphite monochromated MoKα radiation (λ = 0.71073Å).

1.2. Materials and Synthesis. THF was dried according to standardized procedures previously described. All the other chemicals and reagents used in this study were of analytical grade without further purification. In general, all the intermediates and final compounds were purified by column chromatography on silica gel (200–300 mesh), and crystallization from analytical grade solvents. Reactions were monitored using thin layer chromatography

(TLC).

1.2.1. Preparation of (Z)-2-(2 (9H-carbazol-9-yl) phenyl)-2-phenylacrylonitrile (Z-oCz).

Carbazole (0.5g, 2.98mmol), 2-fluorobenzaldehyde (0.37g, 2.98mmol), potassium carbonate (0.62g, 4.5mmol), copper iodide (0.066g, 0.35mmol) and 18-crown-6 (0.055g, 0.22mmol) were dissolved into DMF (3-5ml). Then the solution was heated and refluxed for 12h. Next, the mixture was poured into water and extracted with dichloromethane (20×3 mL). Then the organic phase was combined and dried over anhydrous Na_2SO_4. Removing the solvent under reduced pressure and a yellow residue solid was collected. Then, the solid was dried under vacuum followed by dissolving in C_2H_5OH (5ml). Subsequently, phenylacetonitrile (0.35 mL, 3mmol) and aqueous 40% NaOH were added to the above solution, then stirred overnight at room temperature. The crude product was directly filtered and washed three times, then purified by chromatography (silica gel, CH_2Cl_2/petroleum ether, v/v = 1:10). A white solid was obtained. Yield: 92%; mp 132.1-133.3℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm= 8.53-8.51 (m, 1H), 8.20 (d, *J*=5.0, 2H), 7.74-7.68 (m, 2H), 7.60-7.55 (m, 1H), 7.44-7.40 (m, 2H), 7.35-7.31(m, 2H), 7.26-7.15 (m, 5H), 7.11-7.07 (m, 2H), 6.97(s,1H) (Fig. S3); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm= 141.50, 137.89, 137.24, 133.93, 132.57, 131.65, 139.26, 128.98, 128.84, 126.33, 126.05, 123.44, 120.45, 120.37, 117.66, 114.20, 110.06 (Fig. S4); HRMS (MALDI-TOF): m/z 371.1539 [[M +H] $^+$, calculated 371. 1548] (Fig. S5).

1.2.2. Synthesis of (E)-2-(2(9H-carbazol-9-yl) phenyl)-2-phenylacrylonitrile (E-oCz).

1 mM solution of starting material (**Z-oCz**) in THF (10 mL) in a 50 mL screw bottle was irradiated for 3h at a distance of 10 cm from a 150 W high-pressure mercury lamp in the presence of I_2. After filtration of reaction mixture, the solvent was evaporated under reduced pressure. The crude product was purified by chromatography (silica gel, CH_2Cl_2/petroleum ether, v/v = 1:10). A white solid was obtained. Yield: 42%; mp 265.0–266.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm= 8.21 (d, *J*=10.0, 2H), 7.57-7.53 (m, 1H), 7.49-7.31 (m, 12H), 7.13 (d, *J*=5.0, 2H), 6.85(s,1H) (Fig. S6); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm= 141.24, 139.34, 137.27, 129.73, 129.55, 129.10, 128.65, 128.14, 126.26, 123.58, 120.64, 120.40, 119.47, 116.16, 109.56, 117.66, 114.20, 110.06 (Fig. S7); HRMS (MALDI-TOF): m/z 371.1547 [[M +H] $^+$, calculated 371. 1548] (Fig. S8).

1.2.3. 3-(2-(9H-carbazol-9-yl) phenyl)-2,4-diphenylpentanedinitrile (DCN).

Compound **DCN** was prepared by following the synthetic procedure for compound **Z-oCz**, but the difference is that the amount of phenylacetonitrile added is 0. 53 mL (4.5mmol). The crude product was purified by column chromatography (silica gel, CH_2Cl_2–petroleum ether, v/v = 1:10). A white solid was obtained. Yield: 75%. mp 161-162℃. ^{1}H NMR (500 MHz, DMSO) δ/ppm= 8.35-8.21 (m, *3*H), 7.88 (t, *J*=7.5, 1H), 7.72 (t, *J*=7.5, 1H), 7.44 (d, *J*=10.0, 1H), 7.36-7.28(m, *4*H), 7.09(d, *J*=10.0, 2H), 6.98 (t, *J*=7.5, 2H), 6.88 (t, *J*=7.5, 4H), 6.52(d, *J*=5.0, 4H), 4.68(d, *J*=5.0,

2H), 3.60(t, *J*=10.0, 1H) (Fig. S9); ^{13}C NMR (100 MHz, DMSO) δ/ppm= 141.33, 137.34, 130.34, 129.12, 126.27, 123.18, 119.88, 118.79, 110.37, 47.17, 41.35 (Fig. S10); HRMS (MALDI-TOF): m/z 487. 2053 [[M] $^+$, calculated 487. 2048] (Fig. S11).

1.2.4. (Z)-3-(4-(9H-carbazol-9-yl) phenyl)-2-phenylacrylonitrile (Z-pCa).

Compound **Z-pCa** was prepared by following the synthetic procedure for compound **Z-oCz**. The crude product was purified by column chromatography (silica gel, CH_2Cl_2–petroleum ether, v/v = 1:10). A white solid was obtained. Yield: 95%. mp 170-171.5℃. ^{1}H NMR (500 MHz, DMSO) δ/ppm= 8.28 (t, *J*=7.5, 4H), 8.21 (s, 1H), 7.85 (t, *J*=7.5, 4H), 7.59-7.48 (m, 7H), 7.34(t, *J*=7.5, 4H), 7.09(d, *J*=10.0, 2H), 6.98 (t, *J*=7.5, 2H), 6.88 (t, *J*=7.5, 4H), 6.52(d, *J*=5.0, 4H), 4.68(d, *J*=5.0, 2H), 3.60(t, *J*=10.0, 1H) (Fig. S12); ^{13}C NMR (100 MHz, DMSO) δ/ppm= 142.38, 140.18, 139.12, 129.74, 126.92, 126.38, 123.53, 121.09, 120.98, 118.42, 110.96, 110.32 (Fig. S13); HRMS (MALDI-TOF): m/z 371.1547 [[M +H] $^+$, calculated 371. 1548] (Fig. S14).

1.2.5.3-(9H-carbazol-9-yl) phenanthrene-9-carbonitrile (C-Ca).

Compound **C-Ca** was prepared by following the synthetic procedure for compound **E-oCz**. The crude product was purified by column chromatography (silica gel, CH_2Cl_2–petroleum ether, v/v = 1:10). A white solid was obtained. Yield: 6%. mp 265.0–266.0 °C. ^{1}H NMR (500 MHz, DMSO) δ/ppm= 8.94 (s, 1H), 8.68 (d, *J*=5.0, 1H), 8.42-8.40 (m, 2H), 8.24-8.22 (m, 3H), 7.96(dd, J_1=2.5, J_2=2.5, 1H), 7.85-7.79(m, 2H), 7.57 (d, *J*=5.0, 2H), 7.48 (t, *J*=7.5, 2H), 7.39(t, *J*=7.5, 2H) (Fig. S15); ^{13}C NMR (100 MHz, DMSO) δ/ppm= 140.71, 139.19, 131.35, 129.23, 128.60, 126.36, 123.84, 120.82, 120.60, 109.91, 109.59 (Fig. S16); HRMS (MALDI-TOF): m/z 369.1392 [[M +H] $^+$, calculated 369. 1392] (Fig. S17).

Preparation of light conversion films and blank films. In an oven-dried flask equipped with a mechanical stirrer, polyvinyl chloride/(PABT) (4.95 g) and light conversion agent (0.05 g) were dissolved into 30 mL THF/(CH_2Cl_2). The mixture was stirred for 12 h at room temperature. After that, the flask was placed into an ultrasonic oscillator for 30 min to remove the bubbles in the mixture. Then the mixture was poured onto a prepared glass plate/(adhesive tape) and paved rapidly with a glass rod. Finally, the film was put into a ventilated cabinet until the THF/(CH_2Cl_2) was volatilized completely, and light conversion films of 1% (mass fraction) were obtained. The blank films are prepared by following the procedure for light conversion films, but without the addition of light conversion agent.

Table S1 Absorption and emission maxima of **Z-oCa**, **E-oCa**, **Z-pCa** and **C-Ca** in various solvents.

	Z-oCa		E-oCa		Z-PCa		C-Ca	
	λ_{abs}	λ_{em} (Φ%)	λ_{abs}	λ_{em} (Φ%)	λ_{abs}	λ_{em} (Φ%)	λ_{abs}	λ_{em} (Φ%)
n-Hexane	314	422 (0.19)	316	423 (0.85)	364	400 (0.23)	362	395 (0.98)
Toluene	315	466 (8.60)	318	467 (14.53)	366	433 (6.92)	364	405 (20.66)
CH_2Cl_2	316	506 (14.75)	319	504 (4.44)	359	454 (14.50)	356	451 (19.96)
THF	316	494 (19.57)	320	506 (17.50)	355	482 (15.61)	353	438 (18.62)
DMSO	314	536 (1.92)	321	538 (8.54)	361	517 (5.90)	353	462 (7.70)

λ_{abs} represents absorption maxima, λ_{em} represents emission maxima, Φ represents fluorescence quantum yield.

Table S2 Emission maxima of **Z-oCa**, **E-oCa**, **Z-pCa** and **C-Ca** in different solid-states and PVC doped films.

	Z-oCa	E-oCa	Z-pCa	C-Ca
λ_c	456	450	475	433
λ_g	448	446	469	
λ_f	452	451	467	
λ_h	455	445	461	
λ_m	454	455	457	449
$\Delta\lambda_1$	-8	-4	-6	
$\Delta\lambda_2$	-4	-1	-8	
$\Delta\lambda_3$	-1	-5	-14	
$\Delta\lambda_4$	-2	5	-18	

λ represents emission maxima; c, g, f, h and m represent crystal, ground, fuming, annealed and film in turn.

$\Delta\lambda_1 = \lambda_c-\lambda_g$; $\Delta\lambda_2 = \lambda_c-\lambda_f$; $\Delta\lambda_3 = \lambda_c-\lambda_h$; $\Delta\lambda_4 = \lambda_c-\lambda_m$.

Table S3 The photosynthetic photon flux density (PFD) of the bank and C-Ca film in different wavelength bands

Wavelength band	Blank film PFD (umol/(m^2.s))	**C-Ca** film PFD (umol/(m^2.s))
（380~400nm）	31.70	18.52
（400~500nm）	424.42	637.20
（500~600nm）	588.90	796.00
（600~700nm）	637.76	858.00
（700~780nm）	457.08	615.73

Table S4 Percentages of different wavelength bands among the whole waveband for the bank and C-Ca film.

Wavelength band	Blank film Percentage	**C-Ca** film Percentage
(380~400nm)	2.19%	0.93%
(400~500nm)	25.31%	27.76%
(500~600nm)	29.05%	28.60%
(600~700nm)	26.67%	26.07%
(700~780nm)	16.78%	16.46%

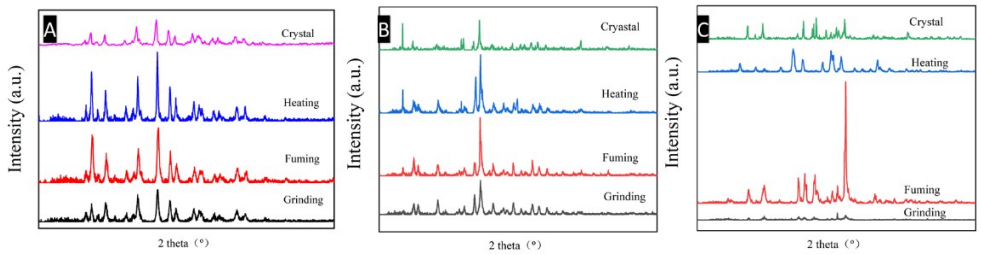


Fig S1 XRD spectra of **Z-oCa**, **E-oCa** and **Z-pCa** in different solid states.

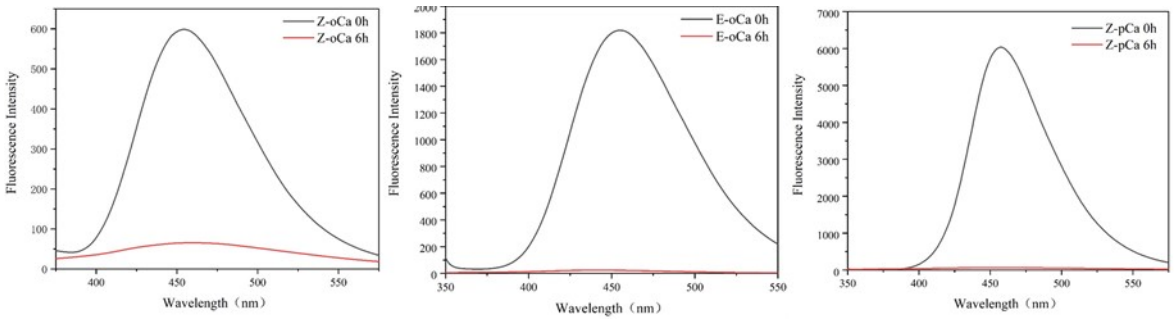
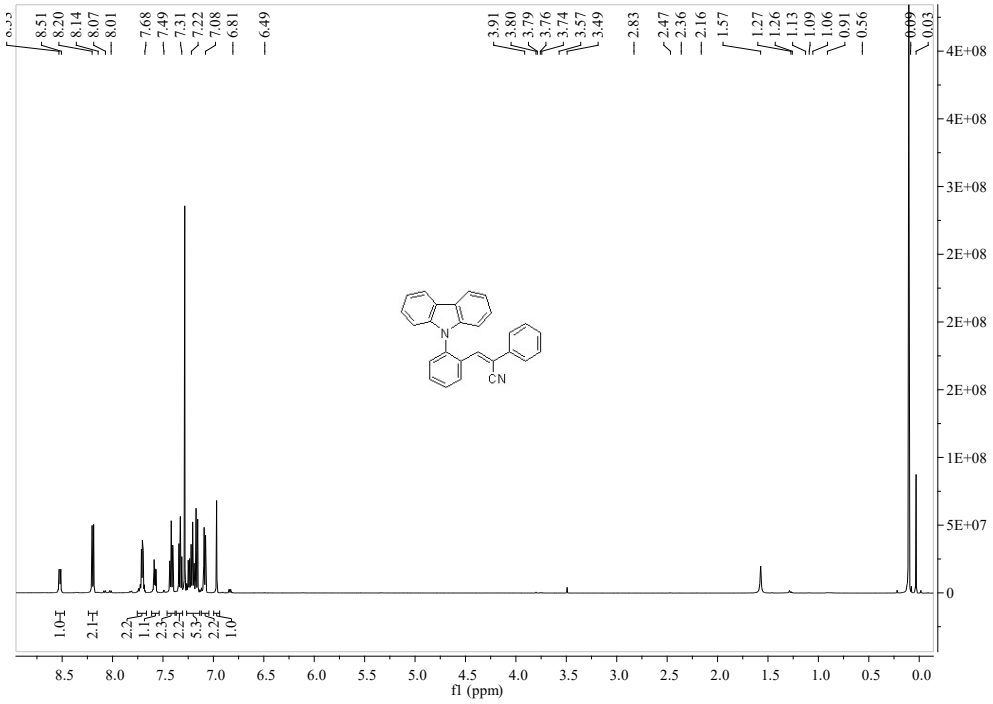


Fig S2 The fluorescence spectra of **Z-oCa**, **E-oCa** and **Z-pCa** in PVC films by 150 W high-pressure mercury lamp emitting a near-UV radiation of 365 nm wavelength for 6h.

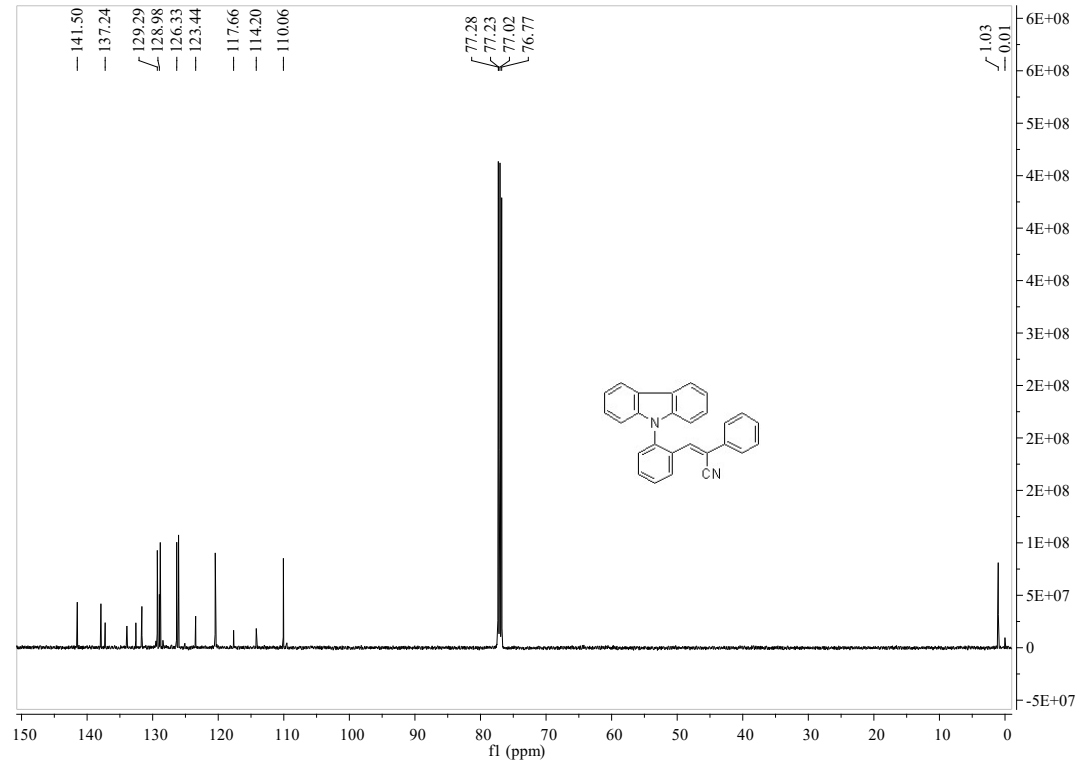


116

117 **Fig S3.** ^{1}H NMR (500 MHz) spectrum of **Z-oCa** in $CDCl_3$.

118

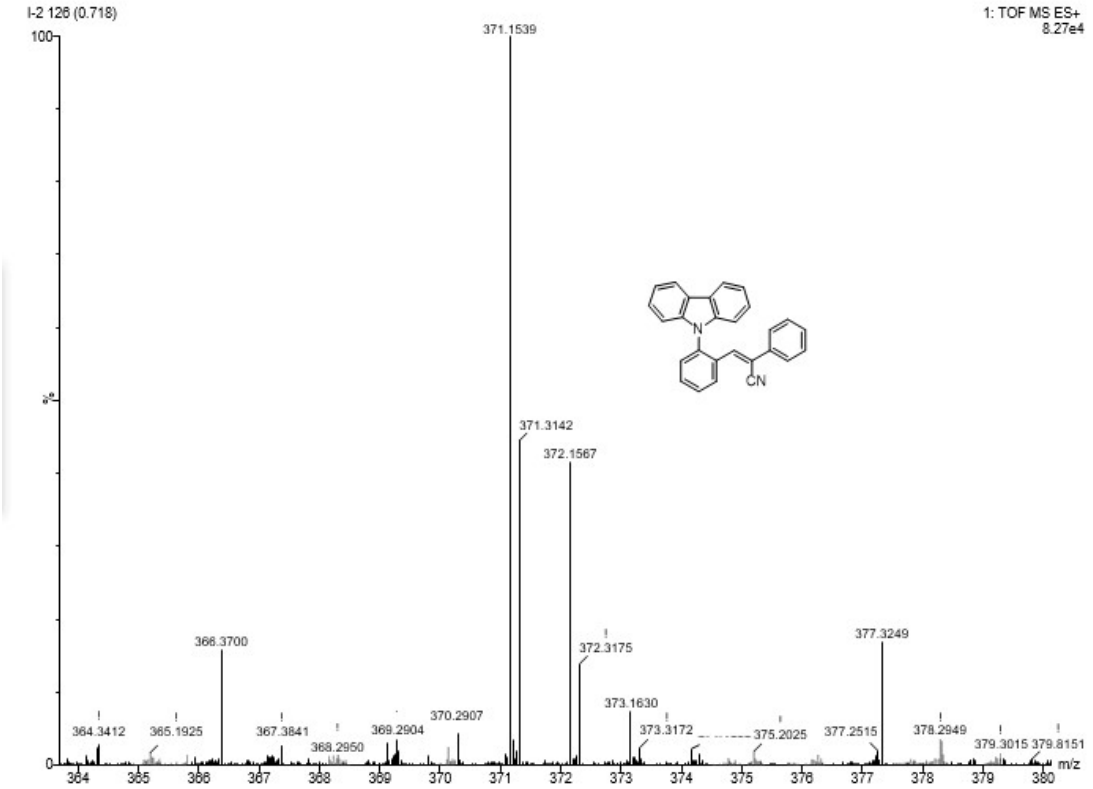
119



120

121 **Fig S4.** ^{13}C NMR (125 MHz) spectrum of **Z-oCa** in $CDCl_3$.

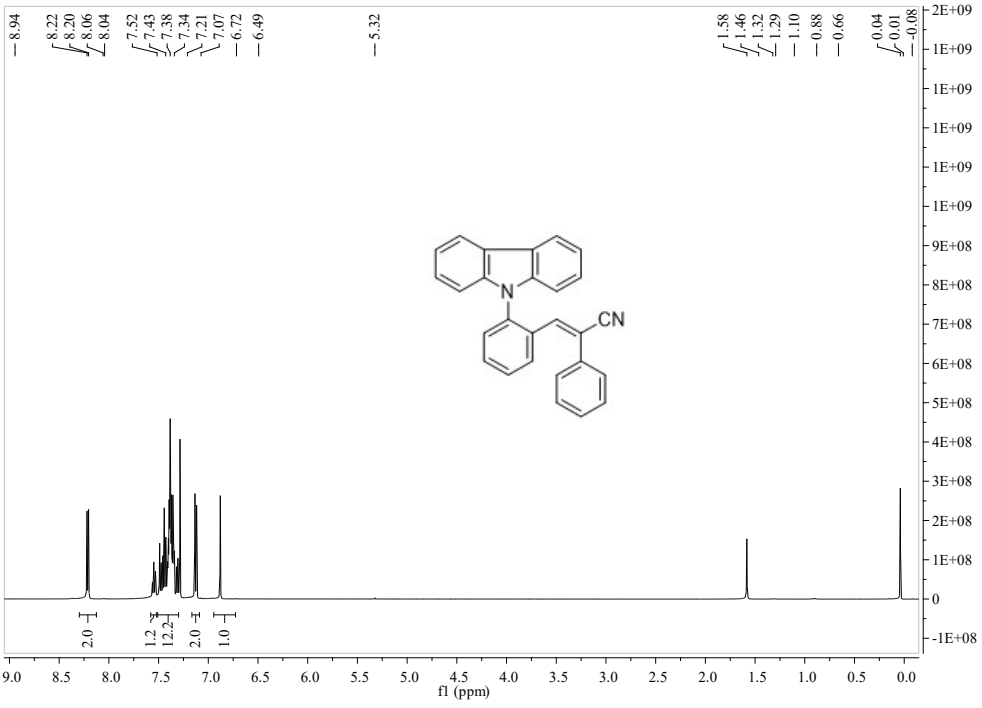
122



123

124 **Fig S5.** MALDI/TOF MS spectrum of compound **Z-oCa**.

125



126

127 **Fig S6.** ^{1}H NMR (500 MHz) spectrum of **E-oCa** in $CDCl_3$.

128

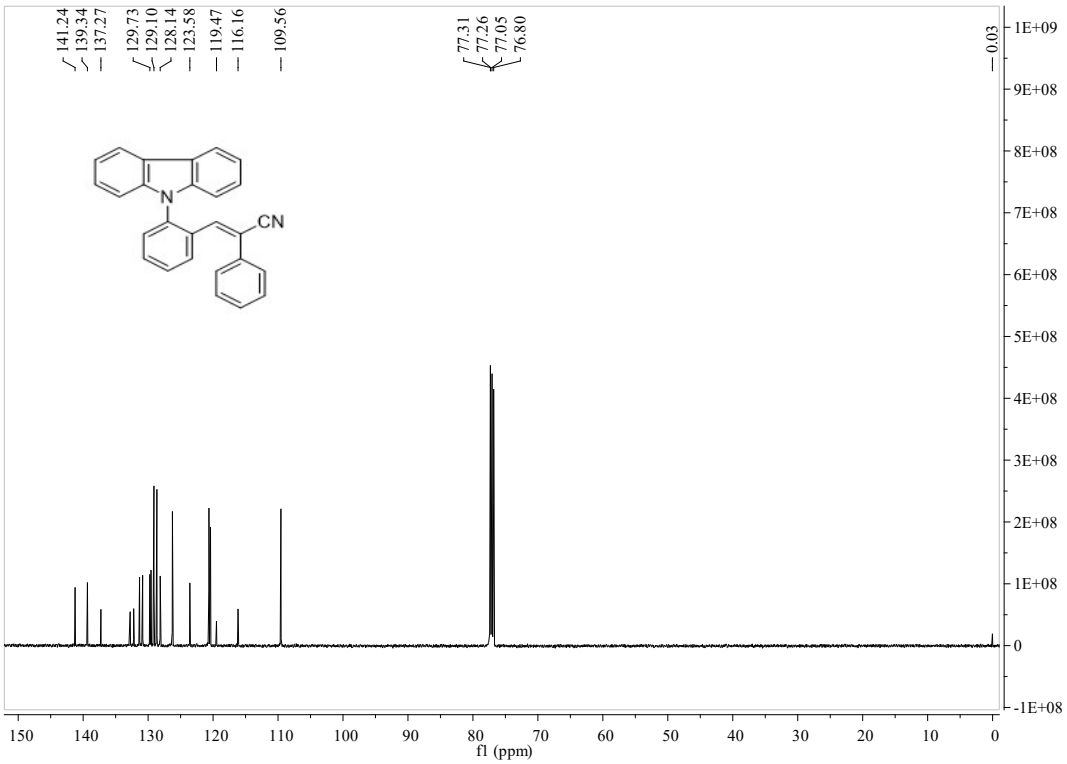
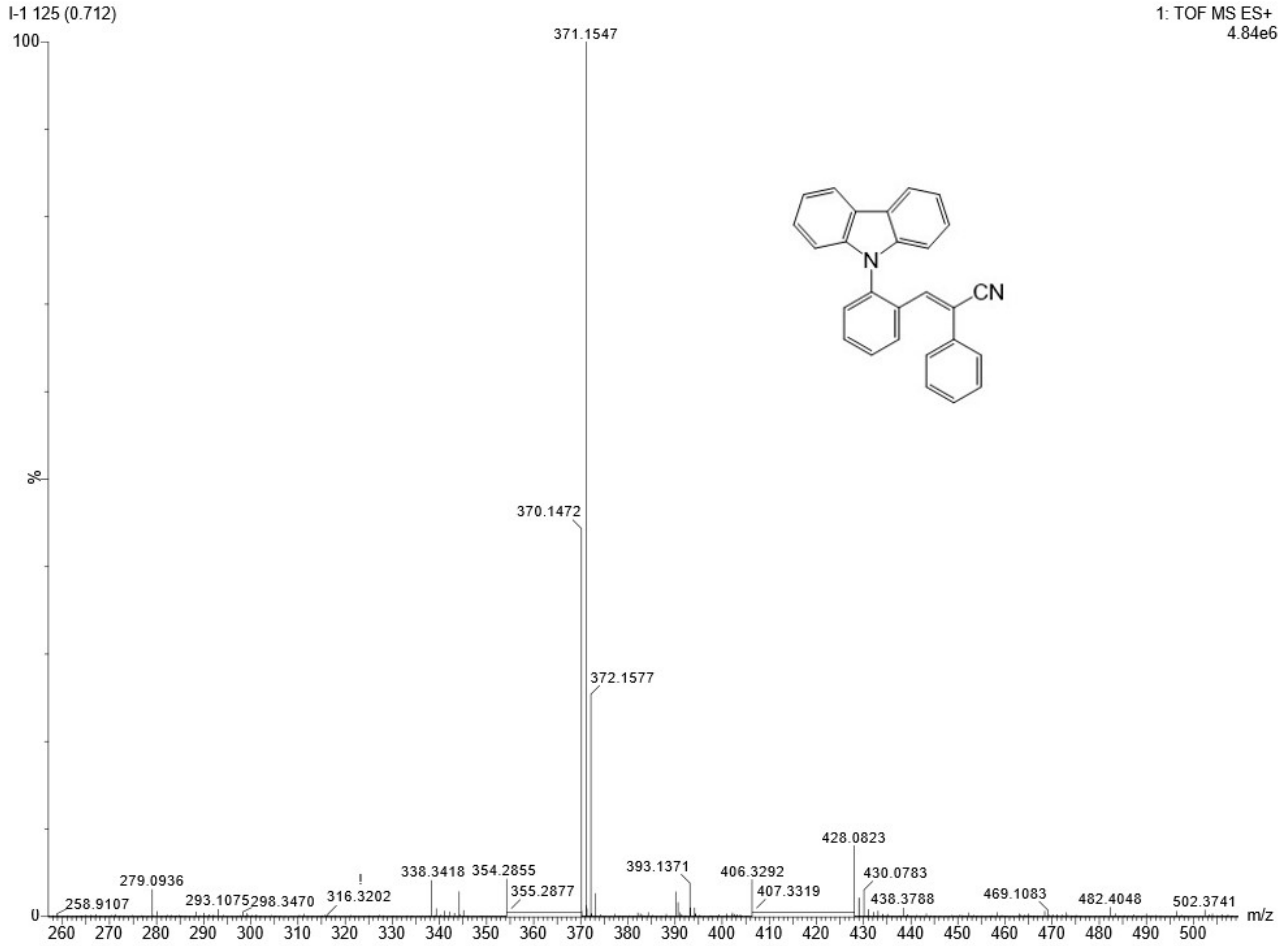


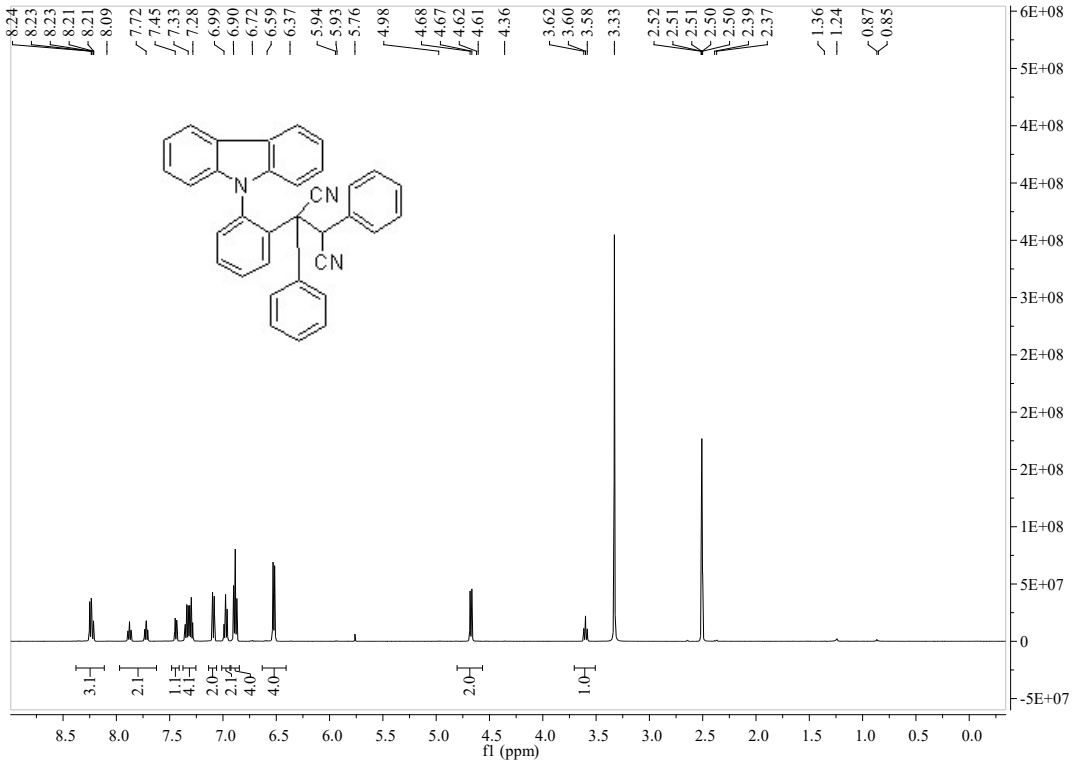
Fig S7. ^{13}C NMR (125 MHz) spectrum of **E-oCa** in $CDCl_3$.



134

135 **Fig S8.** MALDI/TOF MS spectrum of compound **E-oCa**.

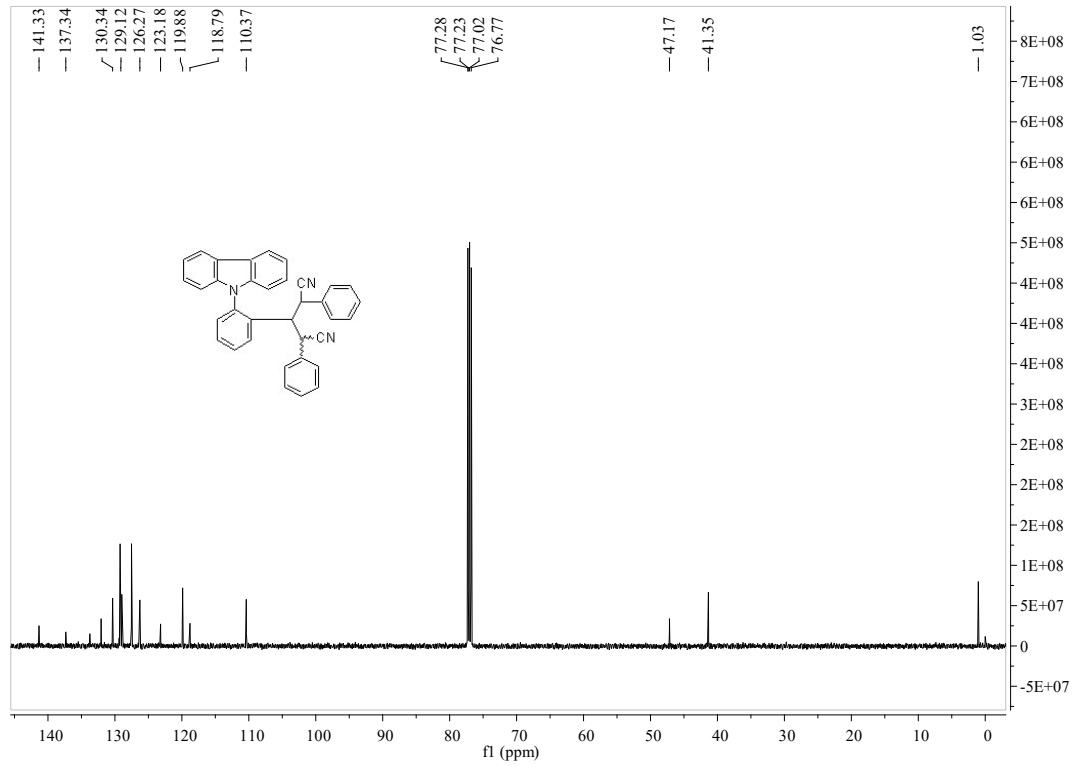
136



137

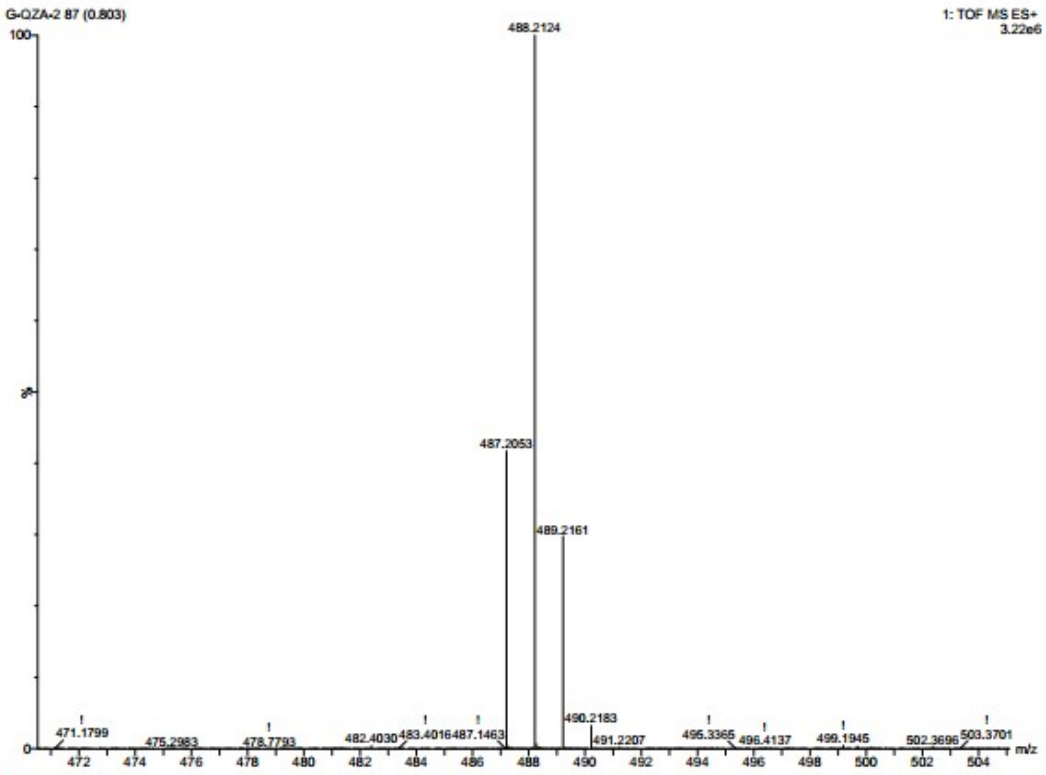
138 **Fig S9.** ^{1}H NMR (500 MHz) spectrum of **DCN** in DMSO.

139



140

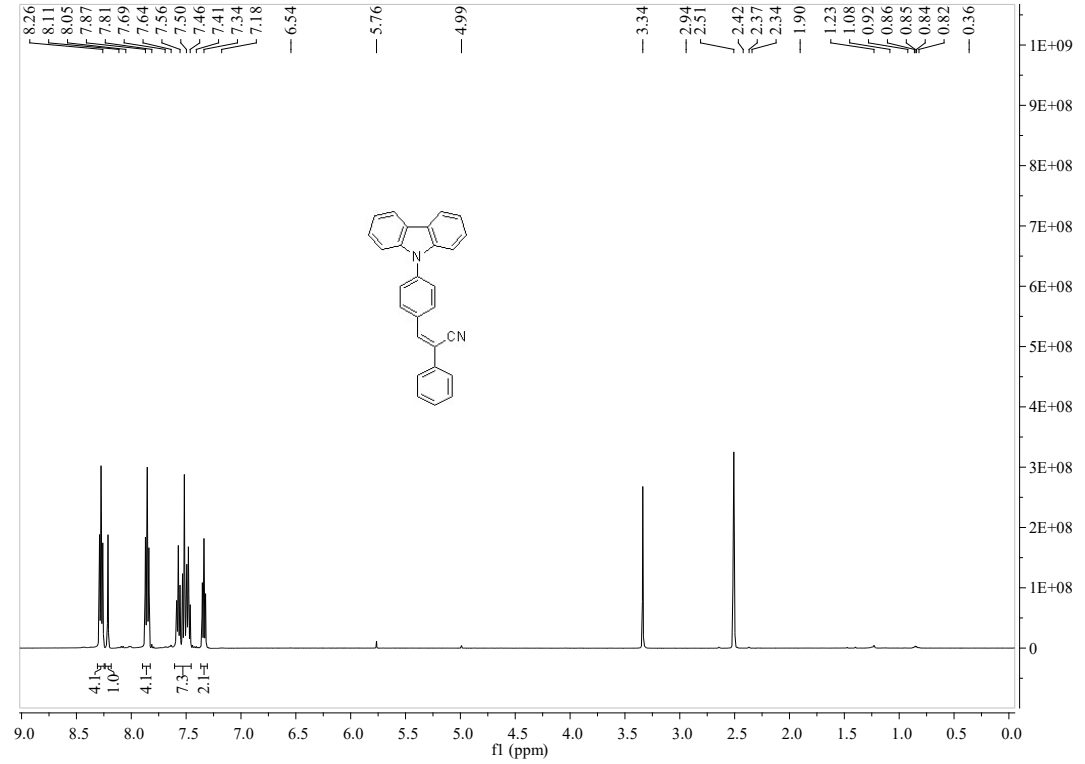
141 **Fig S10.** ^{13}C NMR (125 MHz) spectrum of **DCN** in DMSO.



142

143 **Fig S11.** MALDI/TOF MS spectrum of compound **DCN**.

144



145

146 **Fig S12.** ^{1}H NMR (500 MHz) spectrum of **Z-pCa** in DMSO.

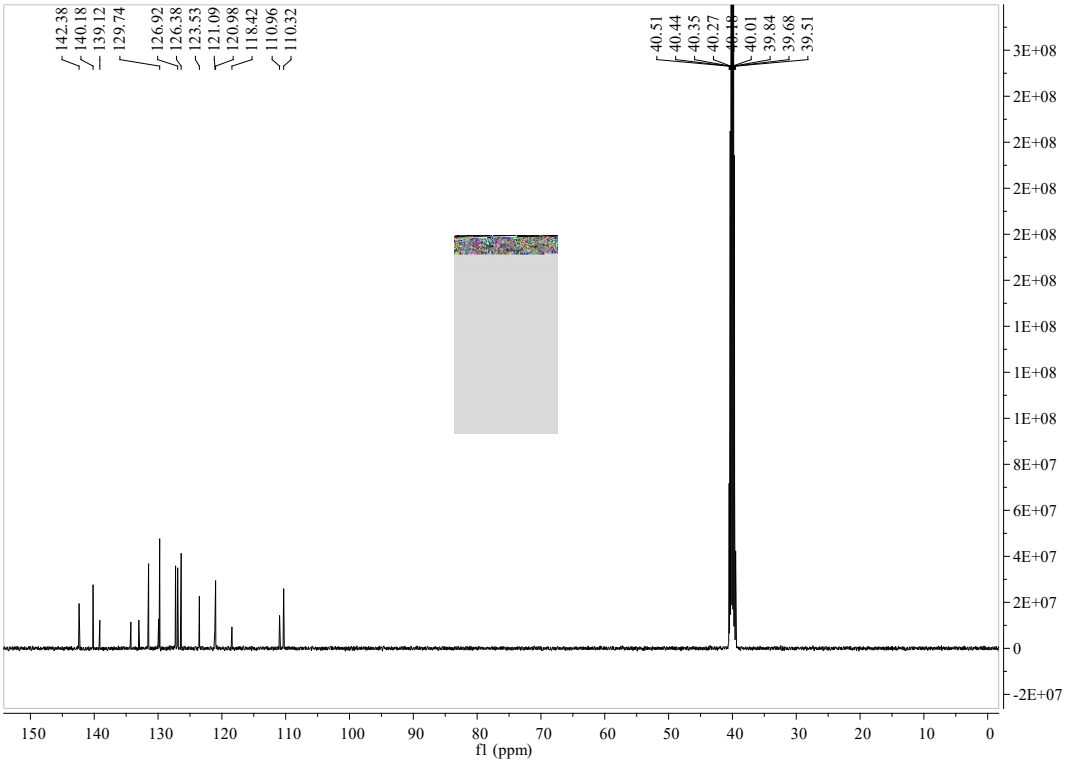


Fig S13. ^{13}C NMR (125 MHz) spectrum of **Z-pCa** in DMSO.

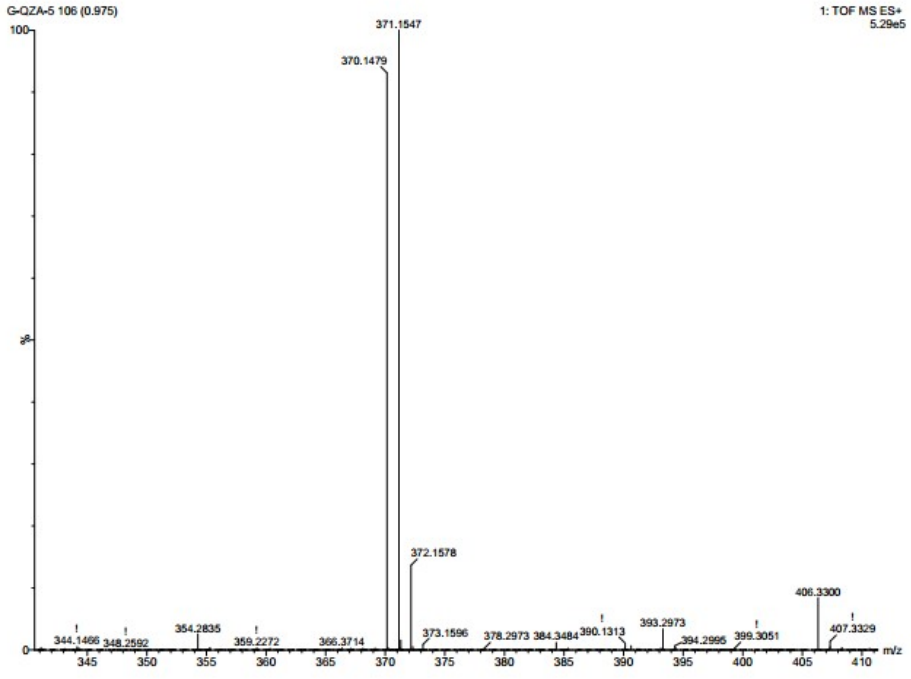
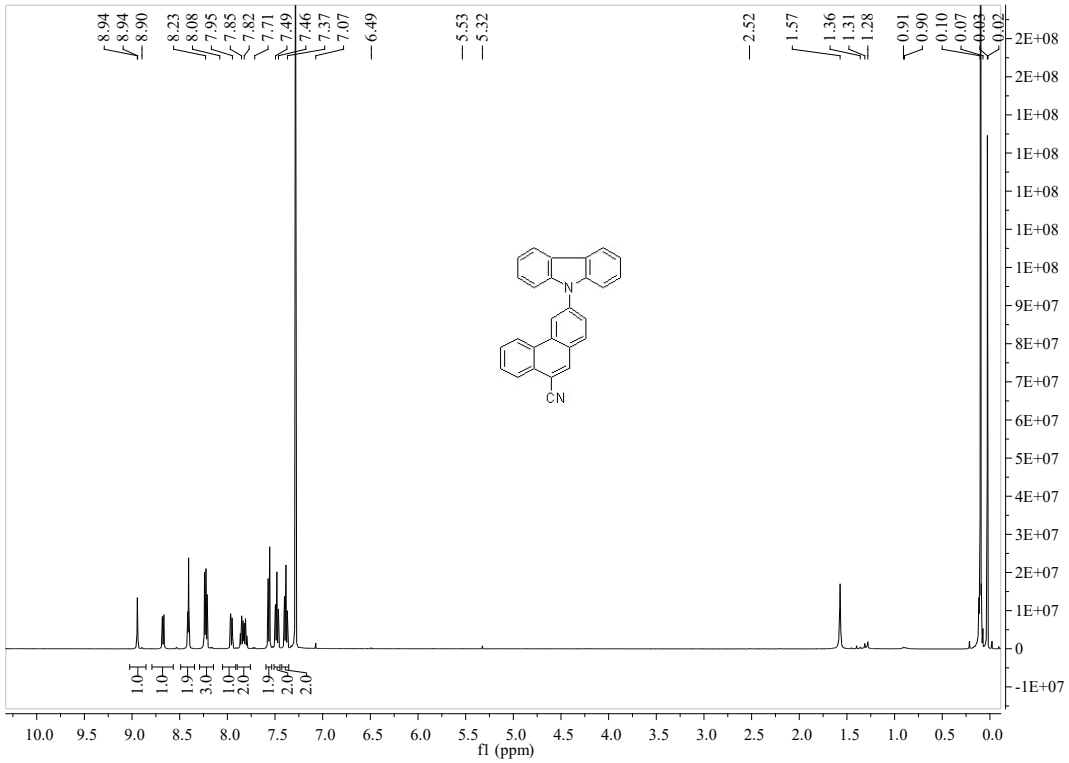


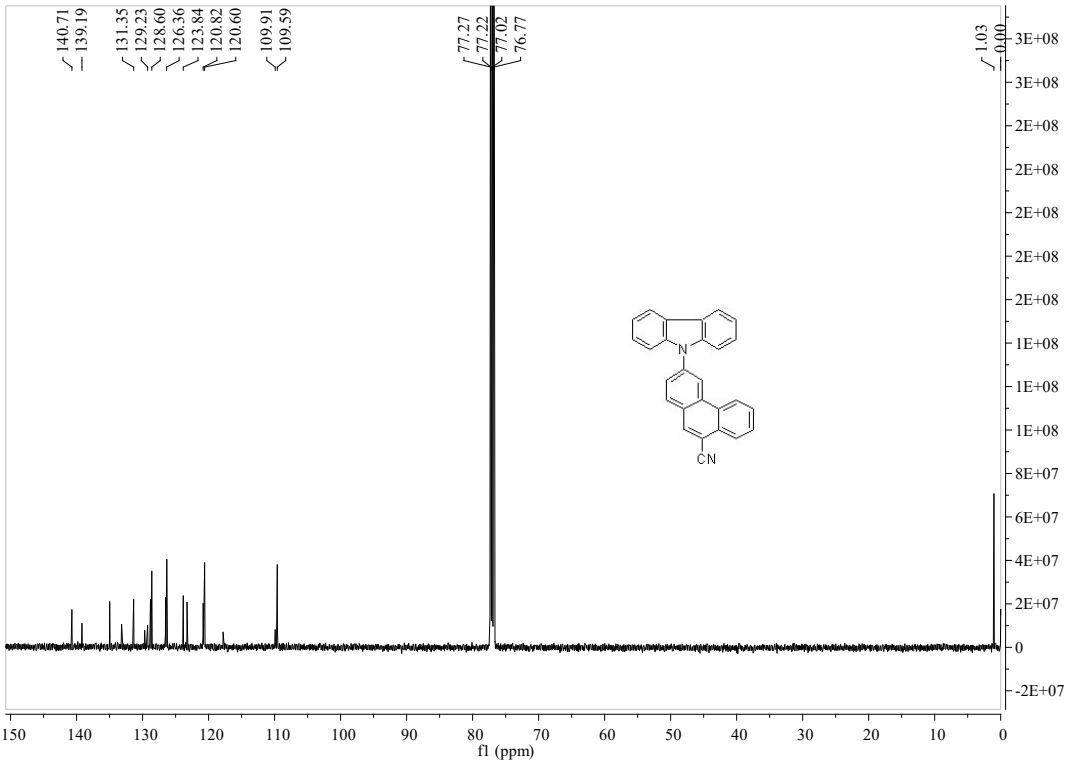
Fig S14. MALDI/TOF MS spectrum of compound **Z-pCa**.



154

155 **Fig S15.** ^{1}H NMR (500 MHz) spectrum of **C-Ca** in $CDCl_3$.

156



157

158 **Fig S16.** ^{13}C NMR (125 MHz) spectrum of **C-Ca** in $CDCl_3$.

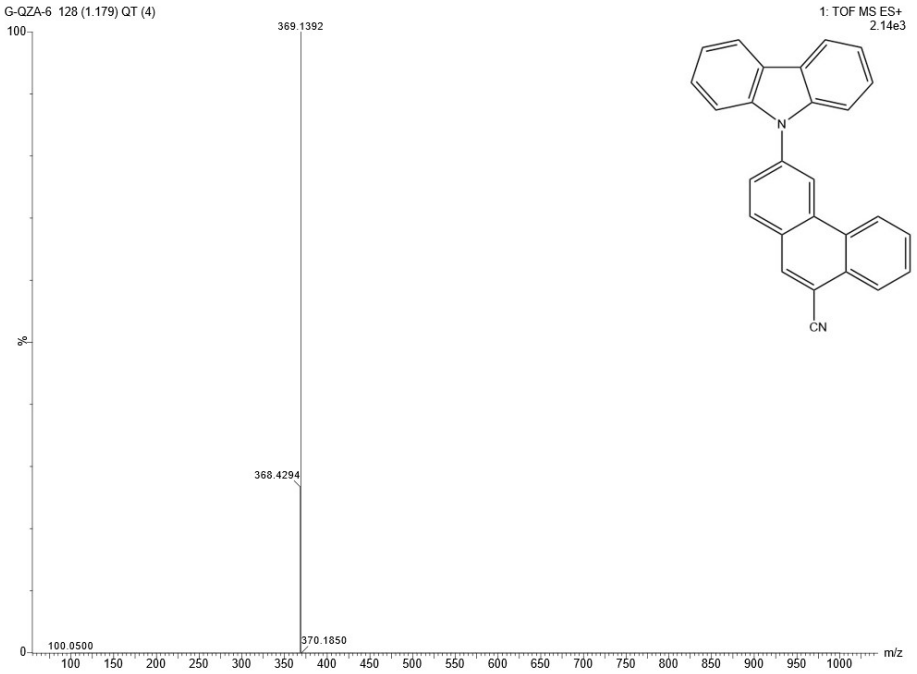


Fig S17. MALDI/TOF MS spectrum of compound **C-Ca**.

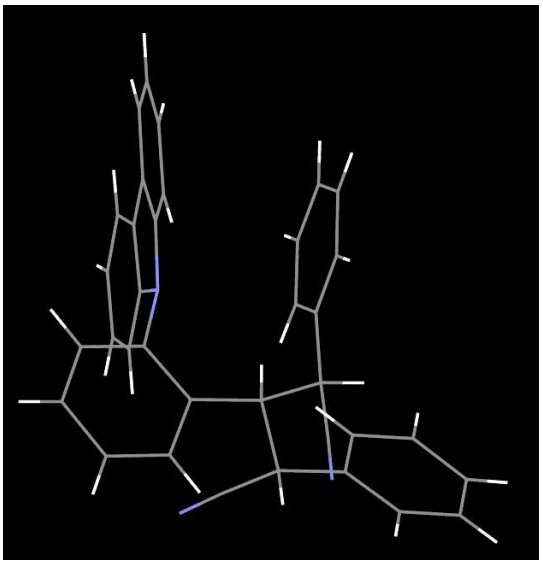


Fig S18. Single crystal structure of compound **DCN**.

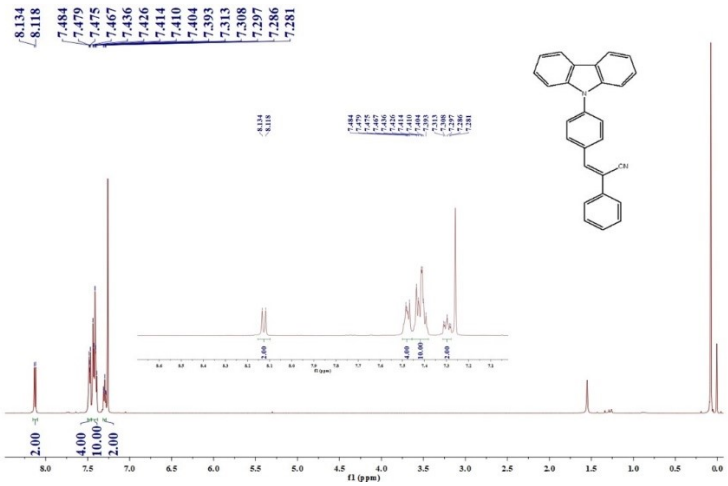


Fig S19. ^{1}H NMR (500 MHz) spectrum of **Z-pCa** and **E-pCa** in $CDCl_3$.