Supporting Information

Effect of number and position of methoxy substituents on triphenylamine-based chalcone visible-light-absorbing photoinitiators

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1. Synthesis

*4-Acetylphenyl)diphenylamine (**CYA**)*

TPA (17.19 g, 0.07 mol), anhydrous zinc chloride (10.19 g, 0.075 mol), and acetyl chloride (4.5 mL, 0.064 mol) were dissolved in dichloromethane (DCM) (40 mL). The solution was stirred at room temperature for 10 min and then heated to 60 °C for 24 h. Once the reaction was complete, a cooled solution comprising $HCl_{(aq)}$ (2 M) was added to terminate the reaction, and the solution was then extracted using DCM. The organic extract was collected and dried over anhydrous $MgSO_4$. Finally, the crude residue was purified through silica gel chromatography (using a DCM/n-hexane = 1/1 eluent) to afford a light yellow powder of mass 8.93 g (yield = 44%). ^{1}H nuclear magnetic resonance (NMR; 400 MHz, $CDCl_3$, δ, ppm): 7.81–7.78 (d, 2H, J = 9.2 Hz, Ar–H), 7.32–7.28 (4H, Ar–H), 7.16–7.08 (6H, Ar–H), 7.05–6.97 (2H, Ar–H), 2.53 (3H, C=O–H).

*1-(4-(bis(4-methoxyphenyl)amino)phenyl)ethenone (**CYB**)*

CYB (yield = 60%) was synthesized using a similar procedure to that used to obtain **CYA** and was obtained as a yellow compound. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.76–7.74 (d, 2H, J = 9.2 Hz, Ar–H), 7.13–7.09 (4H, Ar–H), 6.90–6.86 (4H, Ar–H), 6.83–6.79 (2H, Ar–H), 3.81 (6H, OCH_3), 2.53 (3H, C=O–H).

***CY1–CY5** photoinitiators*

Taking **CY1** as an example. **CYA** (0.5g, 1.74 mmol), **CYC** (0.5g, 1.83 mmol), and NaOH (0.0836g, 2.09 mmol) were dissolved in mixing solvent comprising EtOH (20 mL) and H_2O (10 mL). The solution was stirred at room temperature for 10 min and then heated to a reflux temperature of 90 °C for 5 h. Once the reaction was complete, the mixture was extracted using DCM, and the organic extract was collected and dried over anhydrous $MgSO_4$. The crude product was purified through silica gel chromatography (using a DCM/n-hexane = 1/2 eluent) to afford the orange powder of interest in mass 0.34 g (yield = 34%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.90–7.88 (d, 2H, J = 9.2 Hz, Ar–H), 7.78–7.74 (1H, C=C–Ar), 7.49–7.47 (2H, J = 8.8 Hz, Ar–H), 7.41–7.38 (1H, Ar–C=O–H), 7.34–7.27 (8H, Ar–H), 7.18–7.07 (12H, Ar–H), 7.04–7.01 (4H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 188.2, 151.8, 149.9, 146.9, 146.5, 143.4, 131.1, 130.0, 129.6, 129.5, 129.4, 128.2, 125.9, 125.3, 124.5, 124.0, 121.7, 120.0, 119.3. FT-Mass (m/z) calcd. 543.24309; found 543.24306.

CY2 (yield = 22%, orange powder), **CY3** (yield = 27%, orange powder), **CY4** (yield = 48%, orange powder), and **CY5** (yield = 12%, orange powder) were synthesized using a similar procedure to that for **CY1**. **CY2**: ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.90–7.88 (d, 2H, *J* = 8.8 Hz, Ar–H), 7.77–7.73 (s, 1H, C=C–Ar), 7.46–7.44 (1H, Ar–C=O–H), 7.46–7.25 (8H, Ar–H),, 7.17–6.95 (15H, Ar–H), 6.88–6.86 (2H, Ar–H), 3.82 (3H, -OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 188.3, 156.8, 151.8, 150.2, 147.0, 146.6, 143.5, 139.6, 131.2, 129.9, 129.5, 129.3, 127.9, 127.4, 125.8, 124.6, 124.5, 123.5, 120.4, 120.0, 118.8, 114.9, 55.5. FT-Mass (m/z) calcd. 573.25365; found 573.25373.

CY3: ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.90–7.87 (d, 2H, *J* = 8.8 Hz, Ar–H), 7.76–7.73 (s, 1H, C=C–Ar), 7.44–7.42 (1H, Ar–C=O–H), 7.37–7.26 (6H, Ar–H), 7.17–7.02 (12H, Ar–H), 6.88–6.85 (6H, Ar–H), 3.81 (6H, -OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 188.3, 156.6, 151.7, 150.7, 146.6, 143.8, 139.7, 131.3, 129.9, 129.6, 129.5, 127.4, 126.4, 125.8, 124.4, 120.0, 118.7, 118.2, 114.8, 55.5. FT-Mass (m/z) calcd. 603.26422; found 603.26451.

CY4: ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.87–7.85 (2H, Ar–H), 7.76–7.72 (2H, C=C–Ar, Ar–C=O–H), 7.48–7.37 (2H, Ar–H), 7.31–7.26 (6H, Ar–H), 7.14–7.10 (6H, Ar–H), 7.10–7.01 (4H, Ar–H), 6.89–6.85 (4H, Ar–H), 6.82–6.80 (2H, Ar–H), 3.81 (6H, -OCH_3). ^{13}C NMR (100 MHz, CDCl3, δ, ppm): 188.0, 157.0, 156.9, 152.9, 152.6, 149.7, 147.7, 146.9, 143.0, 139.3, 139.2, 130.1, 129.9, 129.5, 129.4, 129.3, 129.2, 128.4, 128.2, 128.1, 127.8, 127.7, 125.3, 125.0, 124.1, 124.0, 123.9, 123.6, 122.7, 121.8, 119.4, 117.1, 116.8, 114.9, 114.8, 55.4. FT-Mass (m/z) calcd. 603.26422; found 603.26396.

CY5: ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.86–7.84 (d, 2H, *J* = 8.8 Hz, Ar–H), 7.74–7.71 (1H, C=C–Ar), 7.43–7.40 (2H, Ar–H), 7.37–7.33 (1H, Ar–C=O–H), 7.13–7.07 (8H, Ar–H), 6.89–6.85 (12H, Ar–H), 3.81–3.80 (12H, -OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 188.1, 156.9, 156.6, 152.5, 150.6, 143.3, 139.8, 139.4, 130.0, 129.6, 129.5, 127.7, 127.3, 126.6, 118.8, 118.4, 117.2, 114.9, 114.8, 55.5. FT-Mass (m/z) calcd. 663.28535; found 663.28558.

2. Measurement

The nuclear magnetic resonance (NMR) spectra of the samples were dissolved in deuterated chloroform and analyzed under room temperature by using an Agilent Unity plus-400 spectrometer. Fourier-transform mass spectrometry was performed using a JEOL AccuTOF GCx-plus instrument. The light absorption of the samples in dichloromethane (DCM) (concentration = 1×10^{-5} M) was measured using a PerkinElmer Lambda 35 UV–visible (UV-Vis) spectrometer. The photoluminescence (PL) spectra of samples in DCM (concentration = 1×10^{-5} M) were recorded using a Hitachi F-4500 spectrometer at an excitation wavelength of 420 nm. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the photoinitiators were optimized using the UB3LYP/6-31G* level of theory. In addition, the geometries were frequency checked using Gaussian 09 software.[1] Cyclic voltammetry (CV) was performed using a BioLogic SP-150 model at a scan rate of 100 mV s^{-1} in the range of 0 to −2 V. All measurements were conducted at room temperature in DCM solution (concentration = 1×10^{-3} M) with a conventional three-electrode configuration, in which the three electrodes were a platinum working electrode, a platinum wire auxiliary electrode, and a Ag/Ag^+ reference electrode. A Perkin Elmer DSC 6000A was used to determine the melting point (T_m) under nitrogen atmosphere with a scan rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 Simultaneous DTA-TGA device under nitrogen atmosphere at a heating rate of 15 °C min^{-1}; the samples analyzed had a mass of 3–5 mg. The thermal degradation temperature (T_d) was taken as the temperature at which 5% weight loss had occurred.

3. Photolysis experiment

Photolysis was performed with the selected photoinitiation packages, including **CY**s (1 wt%) and TEOA (4 wt%) in DCM as the solvent (concentration = 1×10^{-5} M). The absorption intensity of the solution was determined with various durations of exposure under a Philips 16 W lamp (type Actinic BL; λ = 365 nm). The results were recorded using a PerkinElmer Lambda 35 UV-Vis spectrometer.

4. Electron spinning resonance (ESR) measurement

ESR experiments were conducted using a Bruker EMX Plus X-Band spectrometer. Ultra-high-pressure mercury (MUV-250U-L, λ = 250–450 nm, intensity = 5 mW) was selected as the radiation source used to generate radicals at room temperature under nitrogen atmosphere. The radicals were trapped by N-tert-Butyl-α-phenylnitrone (PBN), and *tert*-butylbenzene as a solvent in accordance with a procedure described in the literature.[2] The concentration of PBN and **CYs** was 1×10^{-2} and 1×10^{-3} M, respectively. In addition, the ratios between **CY** and TEOA or EDB was 1:4 wt%.

5. Photo-differential scanning photocalorimetry (Photo-DSC) experiment

The photopolymerization efficiency of the formulations was tested through photo-DSC analysis, performed using a Perkin Elmer DSC 6000 at 30 °C under nitrogen atmosphere (flow rate = 20 mL min^{-1}). A UV lamp (intensity = 180 mW cm^{-2}; λ = 250–450 nm) or LED@405 nm (intensity = 180 mW cm^{-2}) was used as the radiation source. **CY** (the hydrogen acceptor), TEOA (the hydrogen donor), and TMPTA were mixed without additional solvent to obtain a photoinitiation system. Approximately 15 mg of a sample mixture (containing the hydrogen acceptor, hydrogen donor, and TMPTA under a certain weight ratio) was placed in an aluminum DSC pan, which was used to ensure the different formulations had similar thickness. Heat flow versus time curves were recorded to analyze the reaction of unsaturated moieties in the system during light irradiation. By integrating the area under the exothermic peak, the double bond conversion efficiency (DC; %) could calculated using the following equation:[3]

$DC = (\Delta Ht/\Delta Ho^{theor}) \times 100\%$,

where ΔHt is the total reaction heat enthalpy within the exposure time, and ΔHo^{theor} is the theoretical reaction heat enthalpy of one acrylate for complete conversion. ΔHo^{theor} was 86 kJ mol^{-1}.[4]

Furthermore, the rate of polymerization (Rp) is directly related to the heat flow (dH/dt) by the equation Rp = dC/dt.[5]

1. Æ. F. James B. Foresman. *Exploring Chemistry with Electronic Structure Methods*, Gaussian Inc., Pittsburgh, PA, 1996.
2. T. L. Huang, Y. H. Li and Y. C. Chen, *Journal of Polymer Science*, 2020, **58**, 2914-2925.
3. X. S. Jiang and J. Yin, *Macromolecules*, 2004, **37**, 7850-7853.
4. E. Andrzejewska and M. Andrzejewski, *Journal of Polymer Science Part a-Polymer Chemistry*, 1998, **36**, 665-673.
5. S. X. Chen, C. Qin, M. Jin, H. Y. Pan and D. C. Wan, *Journal of Polymer Science*, 2021, **59**, 578-593.

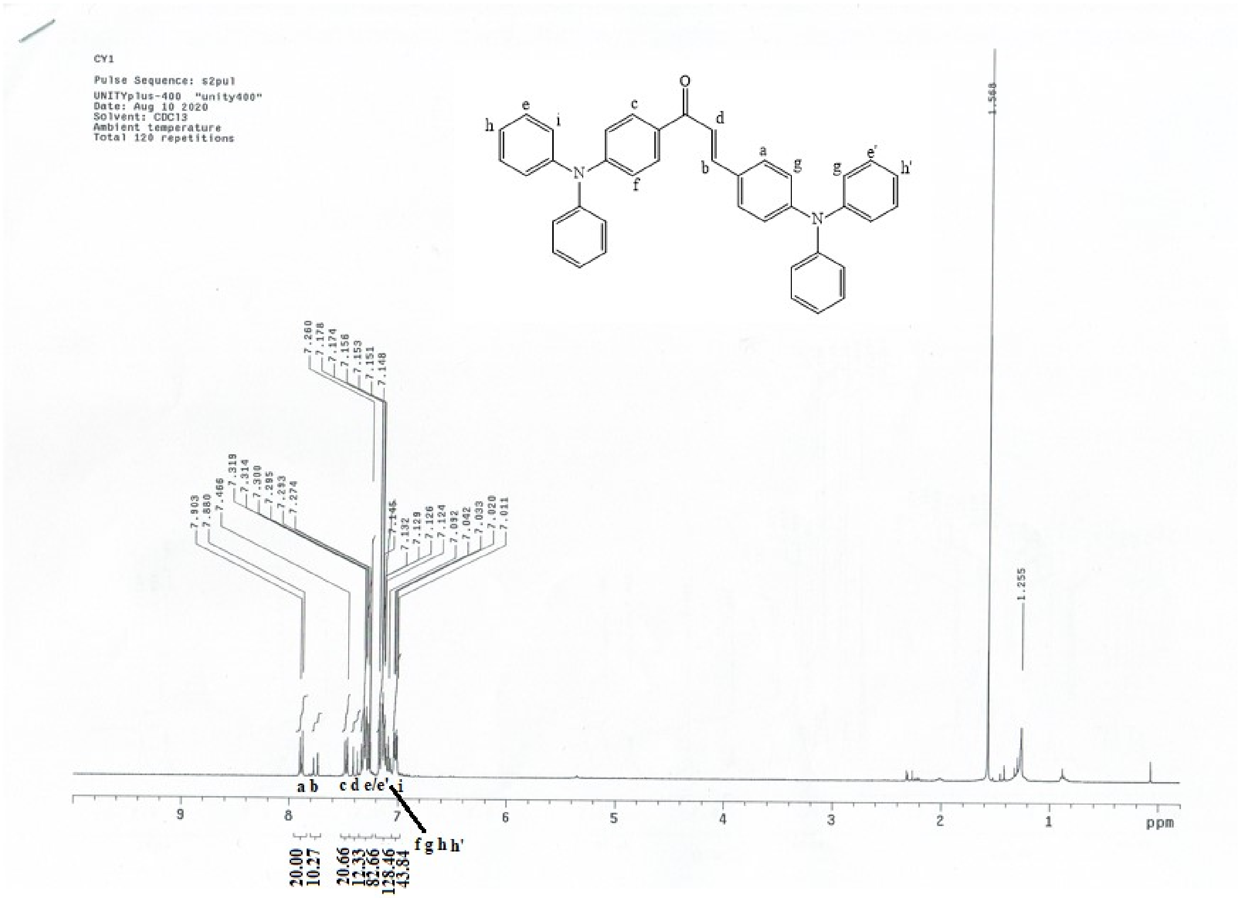


Fig. S1 ^{1}H NMR of the **CY-1**.

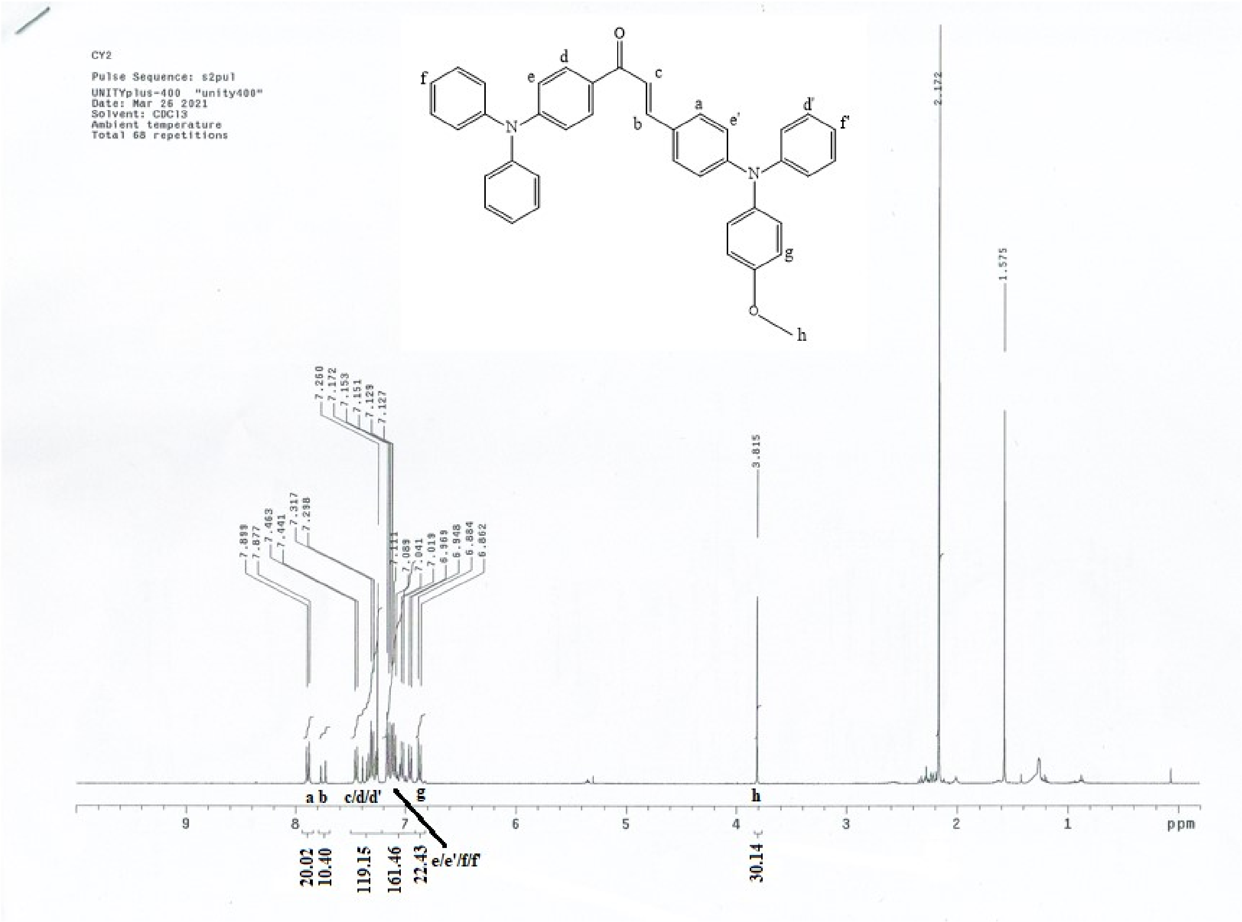


Fig. S2 ^{1}H NMR of the **CY-2**.

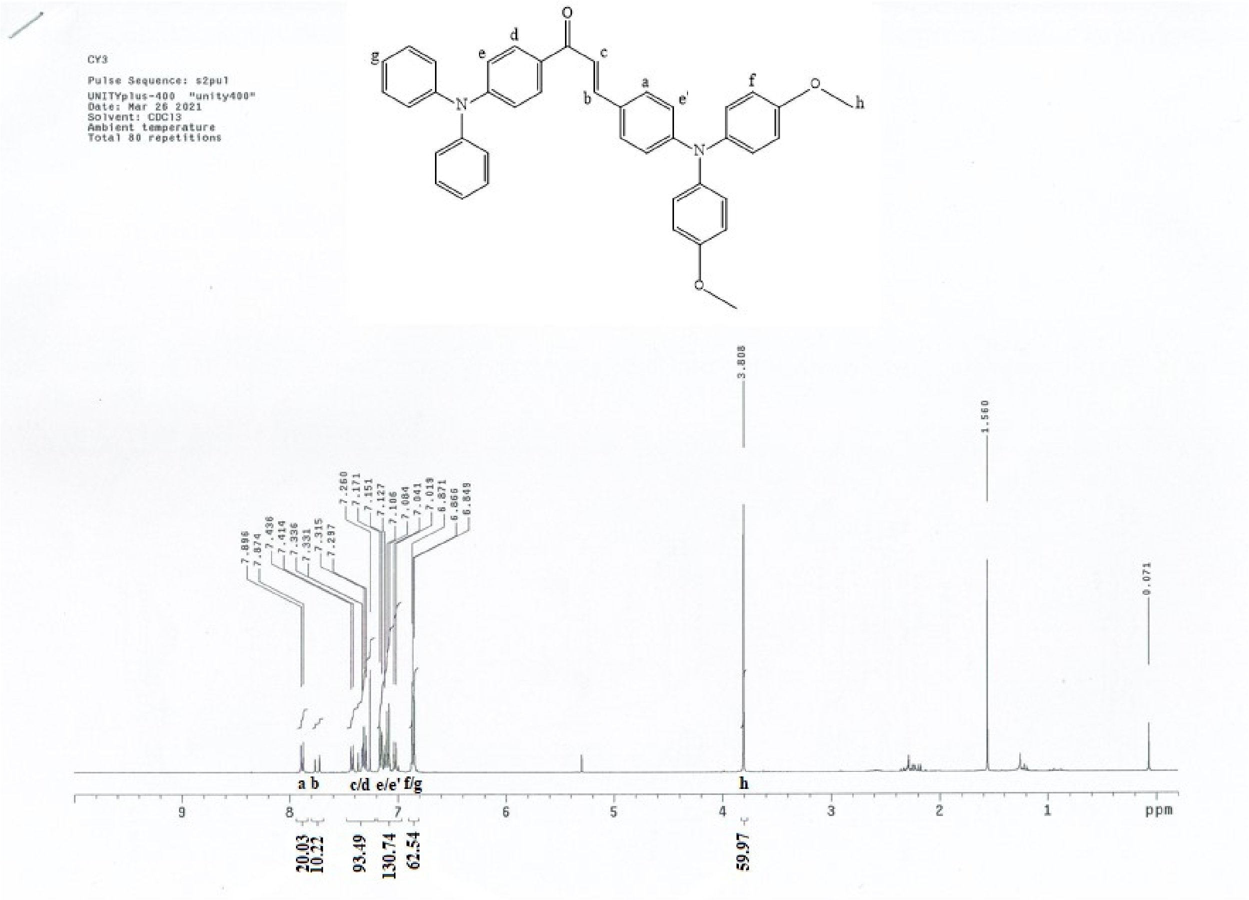


Fig. S3 ^{1}H NMR of the **CY-3**.

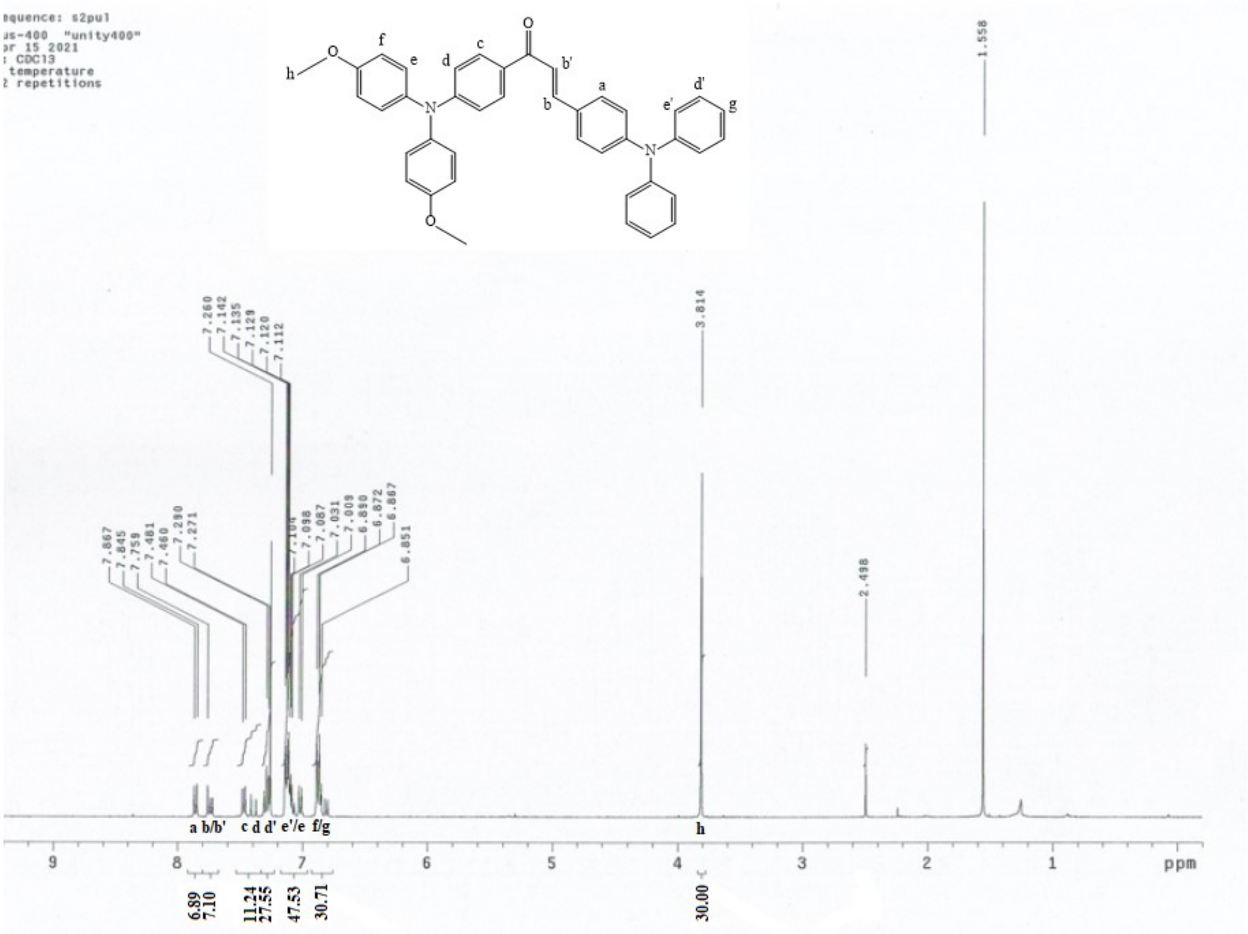


Fig. S4 ^{1}H NMR of the **CY-4**.


CY5

Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Mar 26 2021
Solvent: CDCl3
Ambient temperature
Total 64 repetitions

Fig. S5 ^{1}H NMR of the **CY-5**.

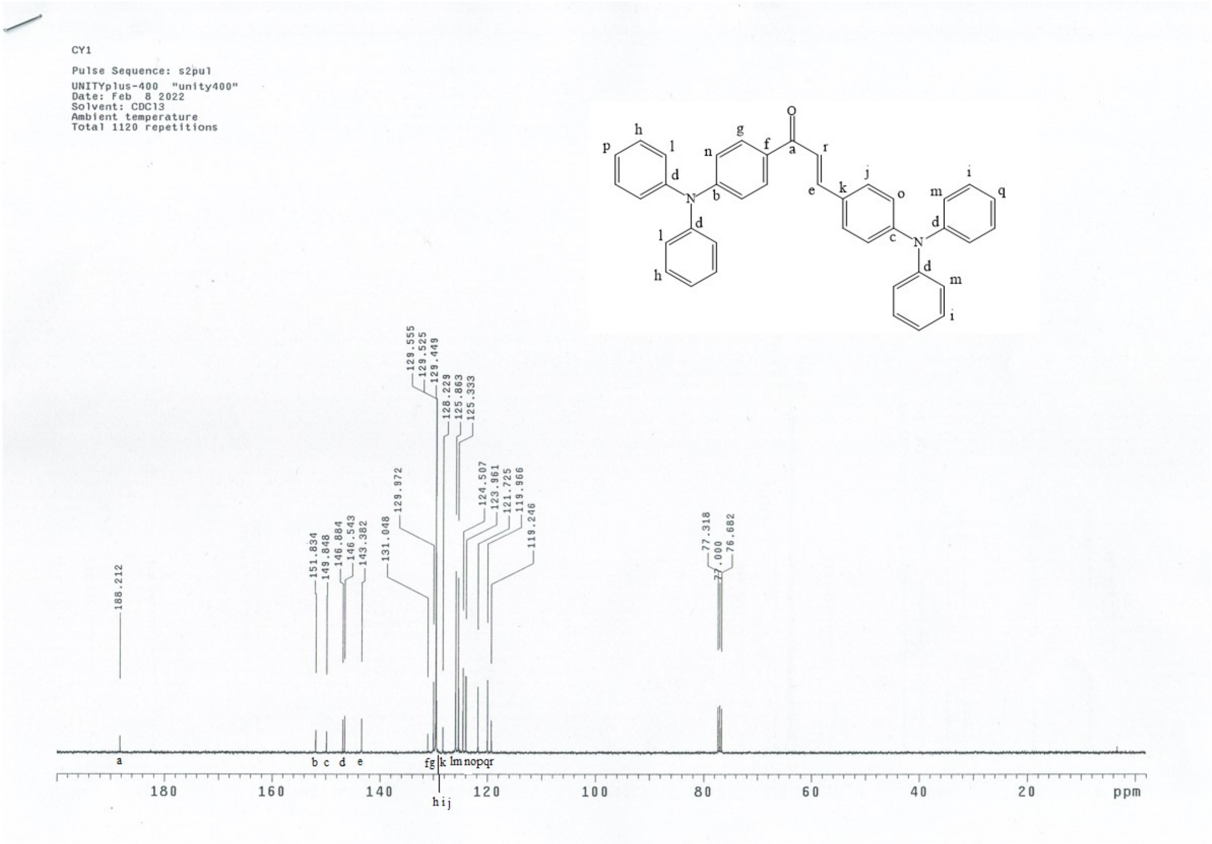


Fig. S6 ^{13}C NMR of the **CY1**.

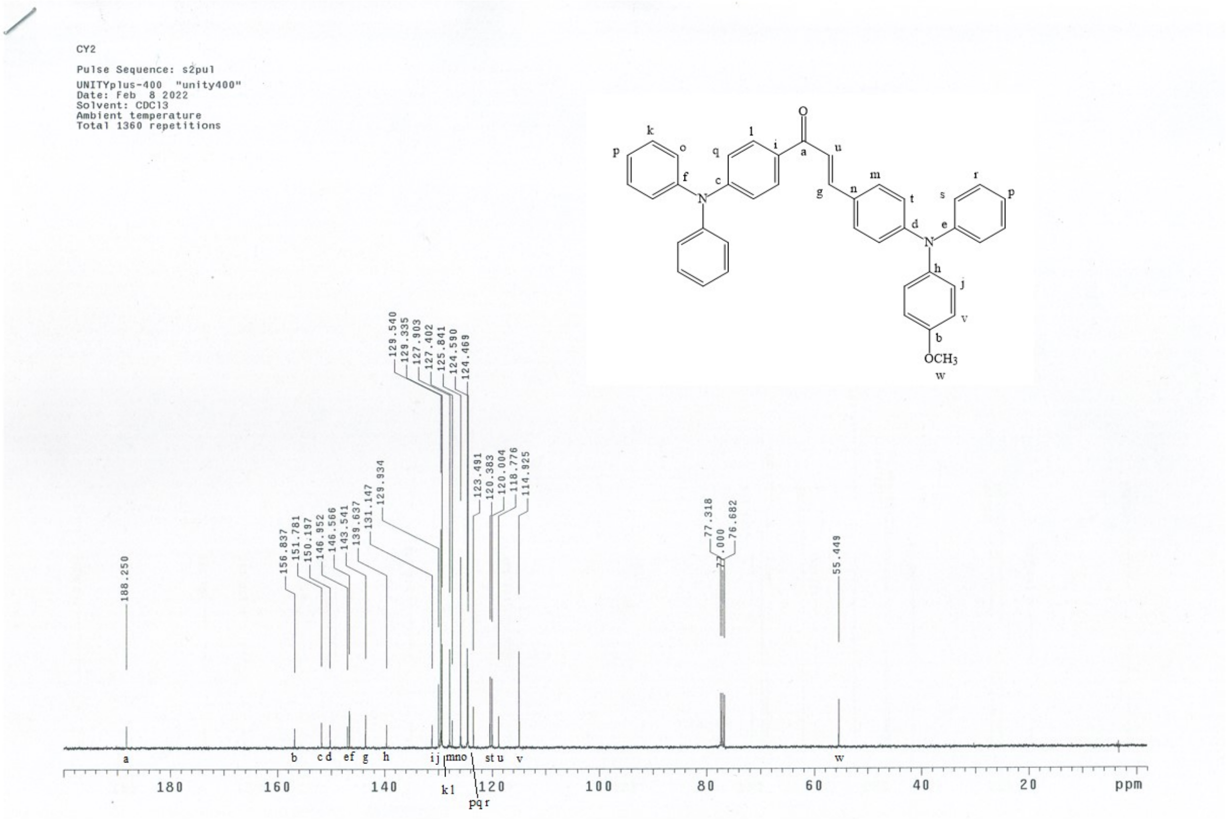


Fig. S7 ^{13}C NMR of the **CY2**.

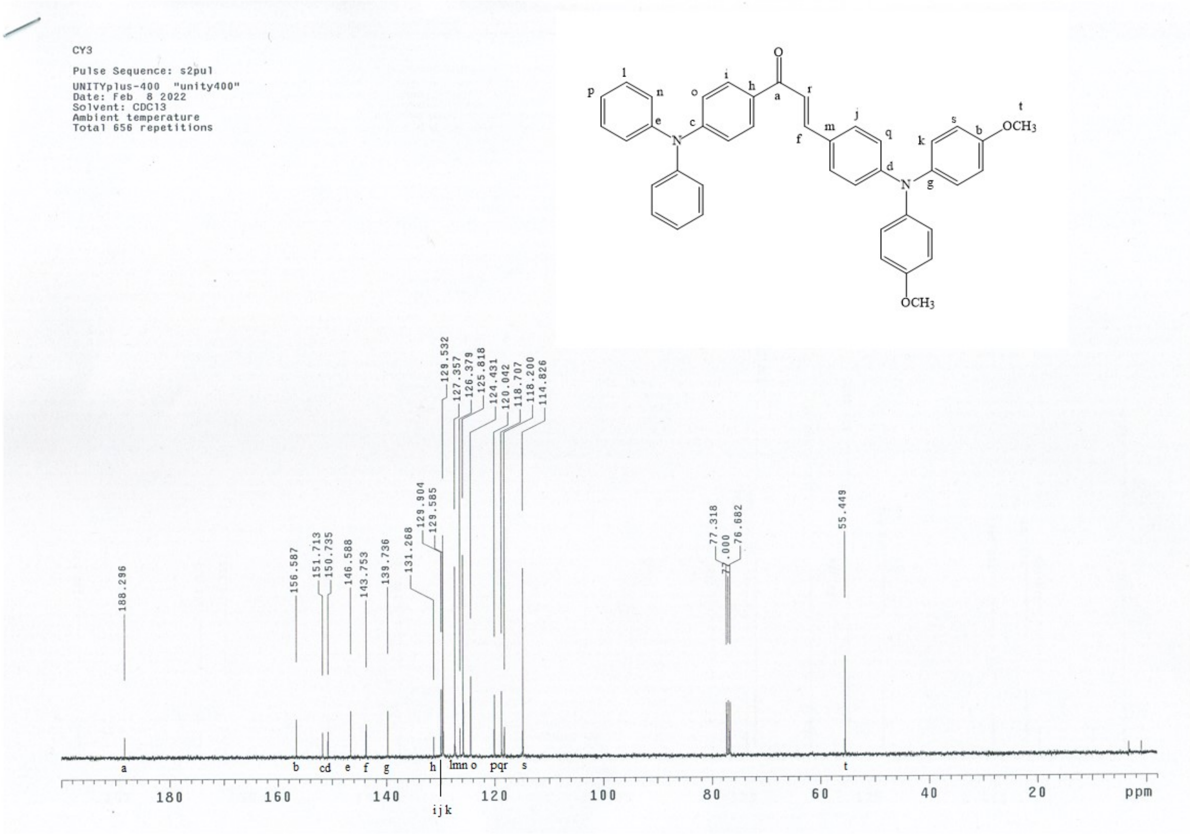


Fig. S8 ^{13}C NMR of the **CY3**.

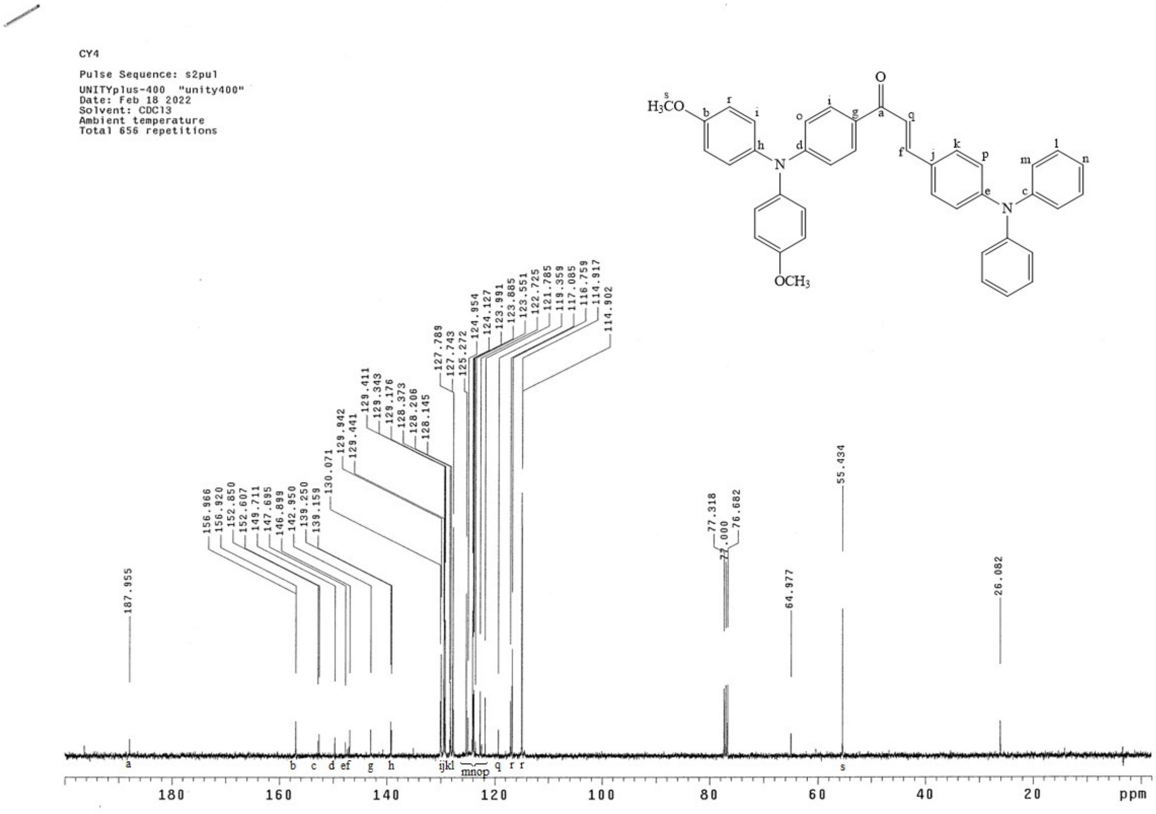


Fig. S9 ^{13}C NMR of the **CY4**.

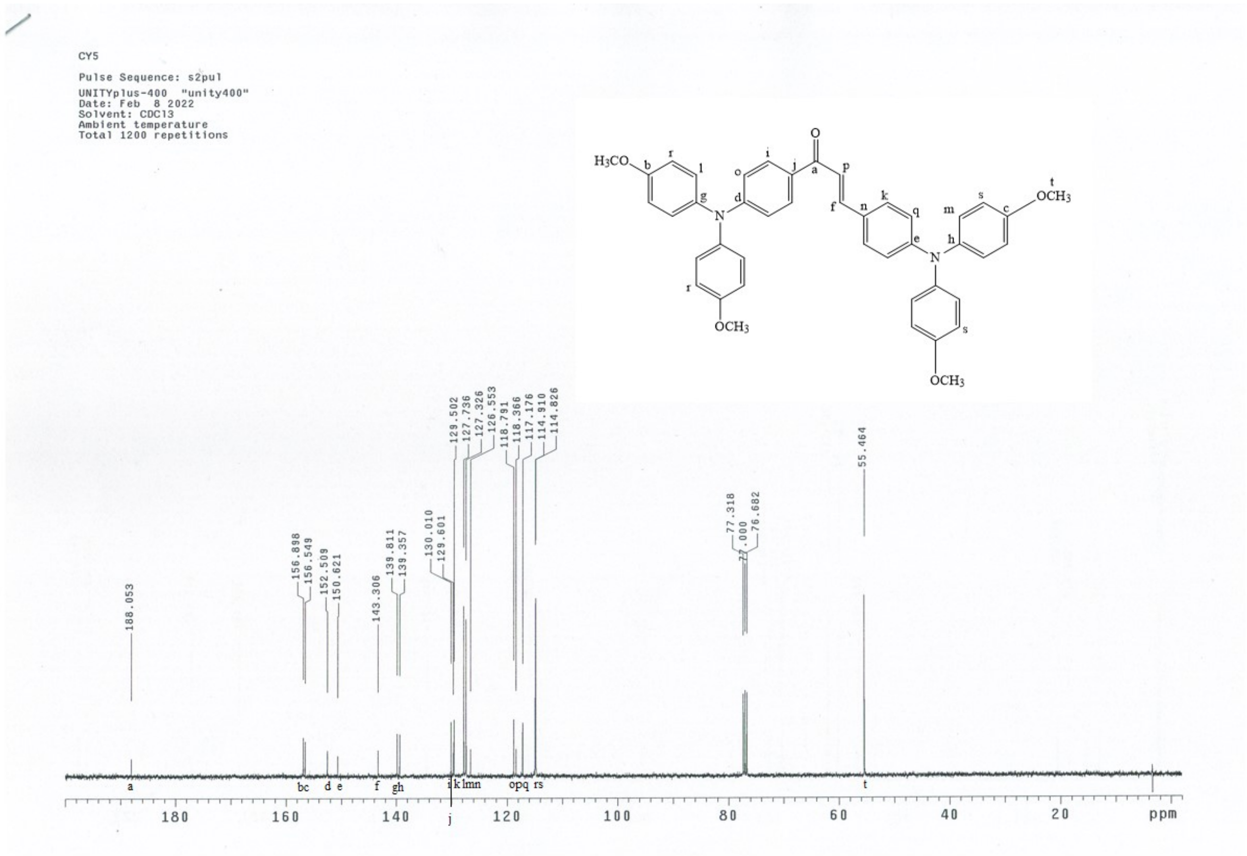
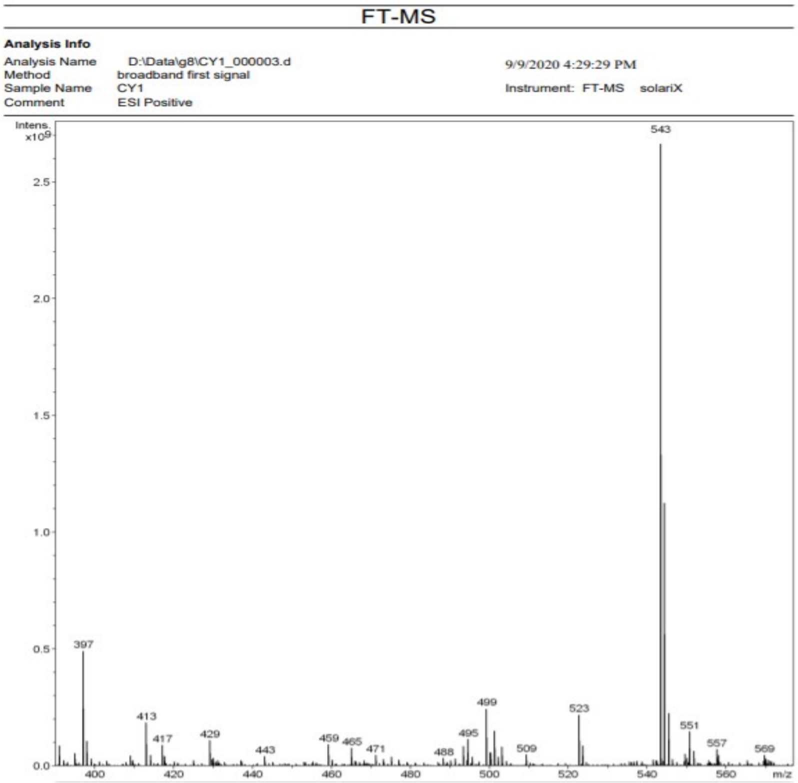


Fig. S10 ^{13}C NMR of the **CY5**.

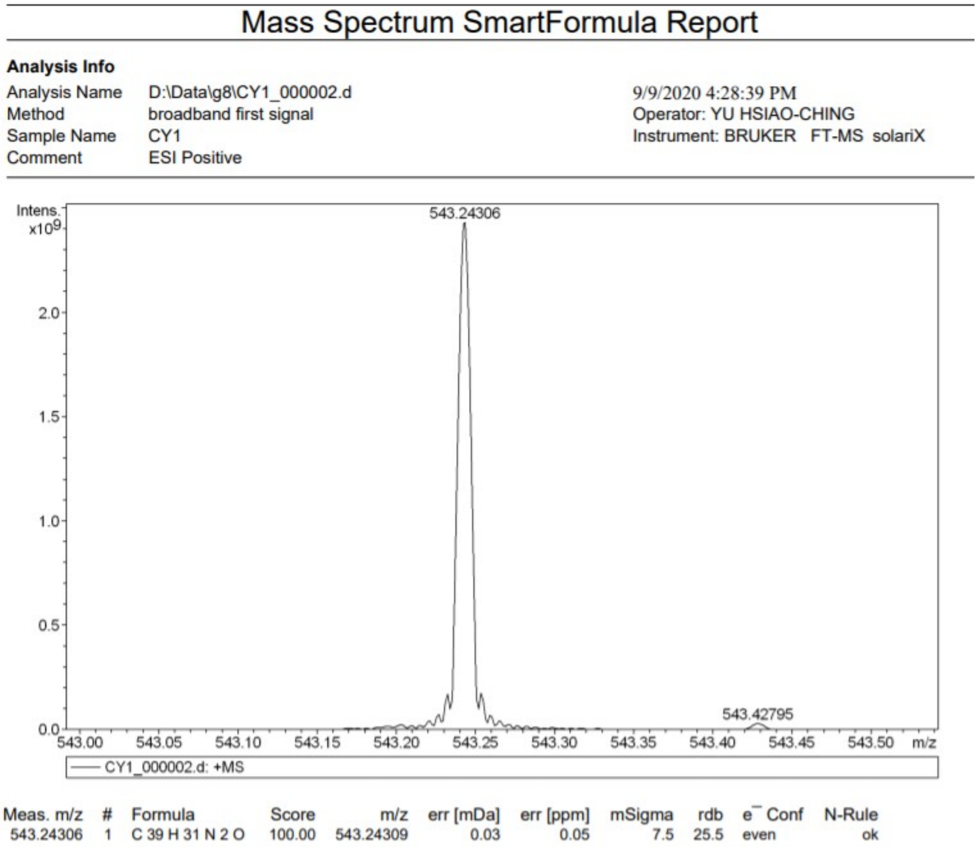


FT-MS

Analysis Info

Analysis Name D:\Data\g8\CY1_000003.d
Method broadband first signal
Sample Name CY1
Comment ESI Positive

9/9/2020 4:29:29 PM
Instrument: FT-MS solariX



Mass Spectrum SmartFormula Report

Analysis Info

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Method broadband first signal
Sample Name CY1
Comment ESI Positive

9/9/2020 4:28:39 PM
Operator: YU HSIAO-CHING
Instrument: BRUKER FT-MS solariX

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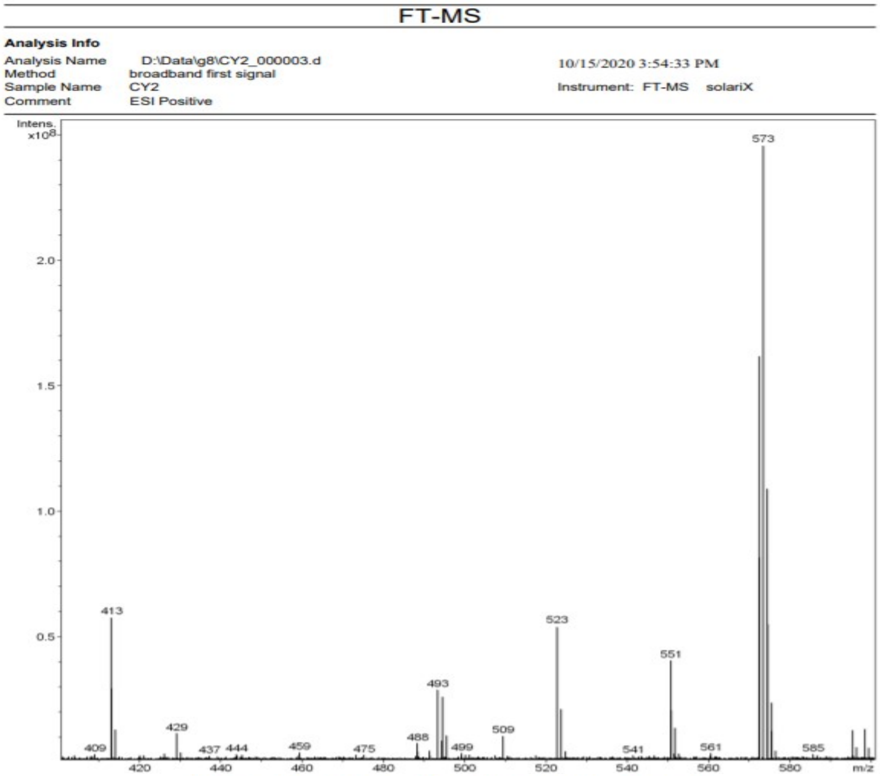
543.24306	1	C 39 H 31 N 2 O	100.00	543.24309	0.03	0.05	7.5	25.5	even	ok

Fig. S11 HR-MS of the **CY-1**



FT-MS

Analysis Info

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Sample Name CY2
Comment ESI Positive

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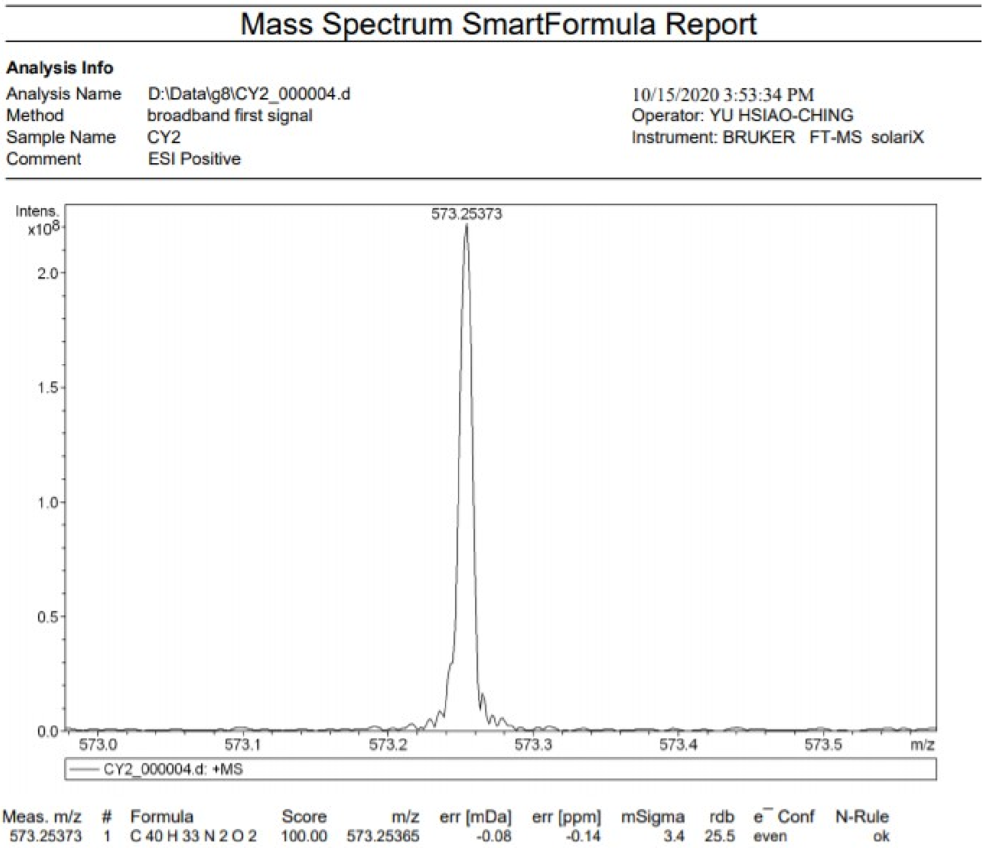

Mass Spectrum SmartFormula Report

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Sample Name CY2
Comment ESI Positive

10/15/2020 3:53:34 PM
Operator: YU HSIAO-CHING
Instrument: BRUKER FT-MS solariX

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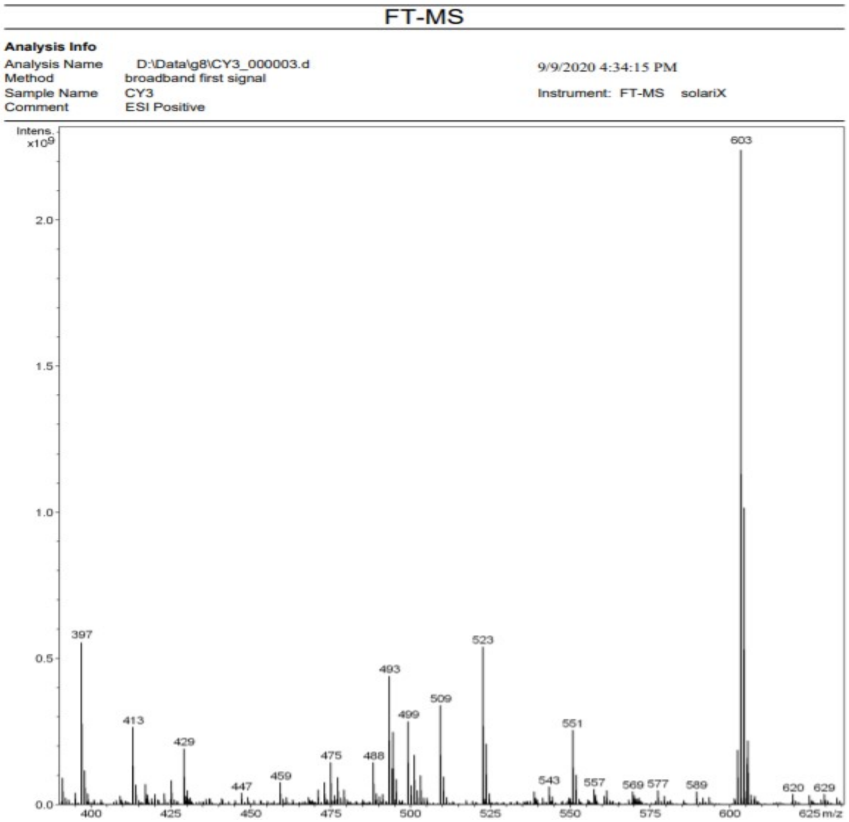
573.25373	1	C 40 H 33 N 2 O 2	100.00	573.25365	-0.08	-0.14	3.4	25.5	even	ok

Fig. S12 HR-MS of the **CY-2**.



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Analysis Info

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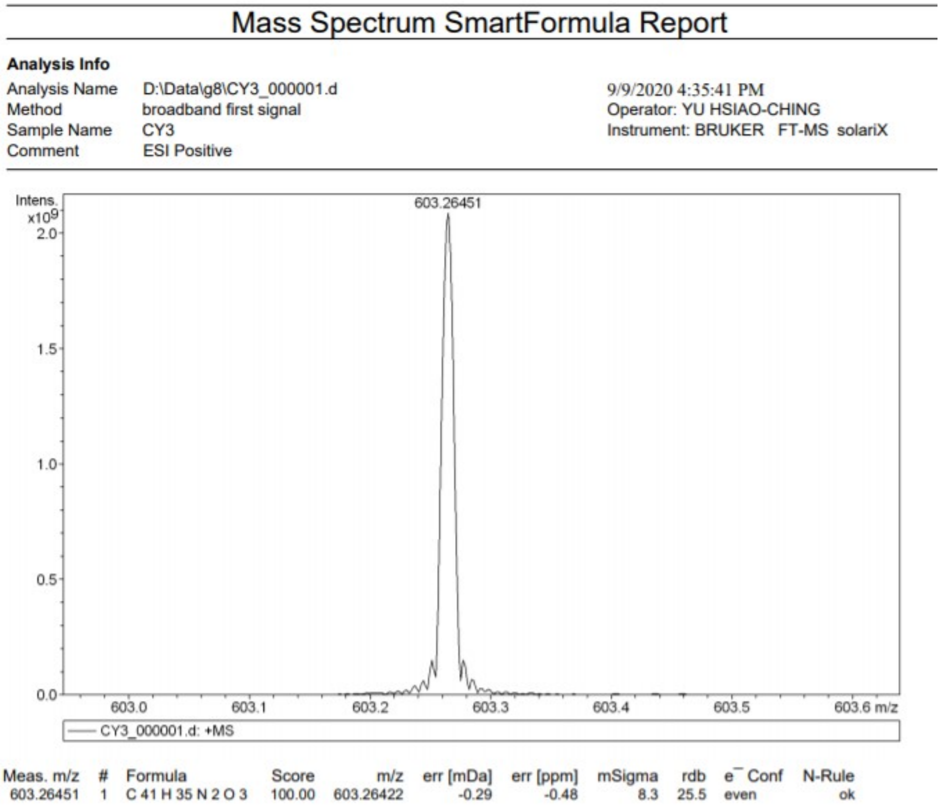
Sample Name	CY3	Instrument: FT-MS solariX
Comment	ESI Positive	



Mass Spectrum SmartFormula Report

Analysis Info

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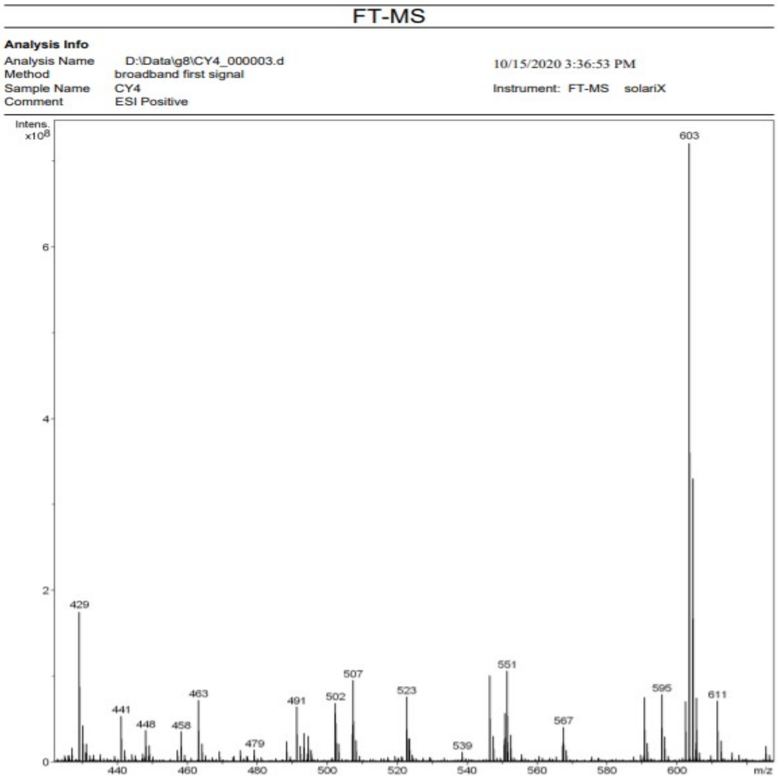
Sample Name	CY3	Instrument: BRUKER FT-MS solariX
Comment	ESI Positive	

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
603.26451	1	C 41 H 35 N 2 O 3	100.00	603.26422	-0.29	-0.48	8.3	25.5	even	ok

Fig. S13 HR-MS of the **CY-3**.



FT-MS

Analysis Info

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Method broadband first signal
Sample Name CY4
Comment ESI Positive

10/15/2020 3:36:53 PM
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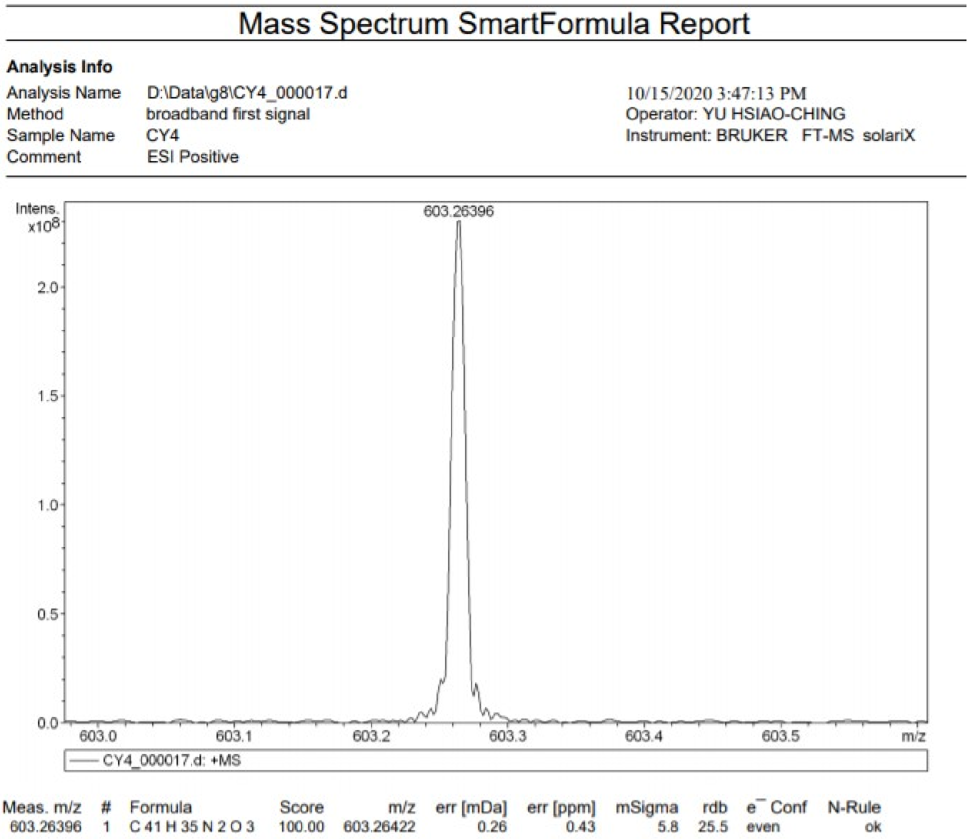

Mass Spectrum SmartFormula Report

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Sample Name CY4
Comment ESI Positive

10/15/2020 3:47:13 PM
Operator: YU HSIAO-CHING
Instrument: BRUKER FT-MS solariX

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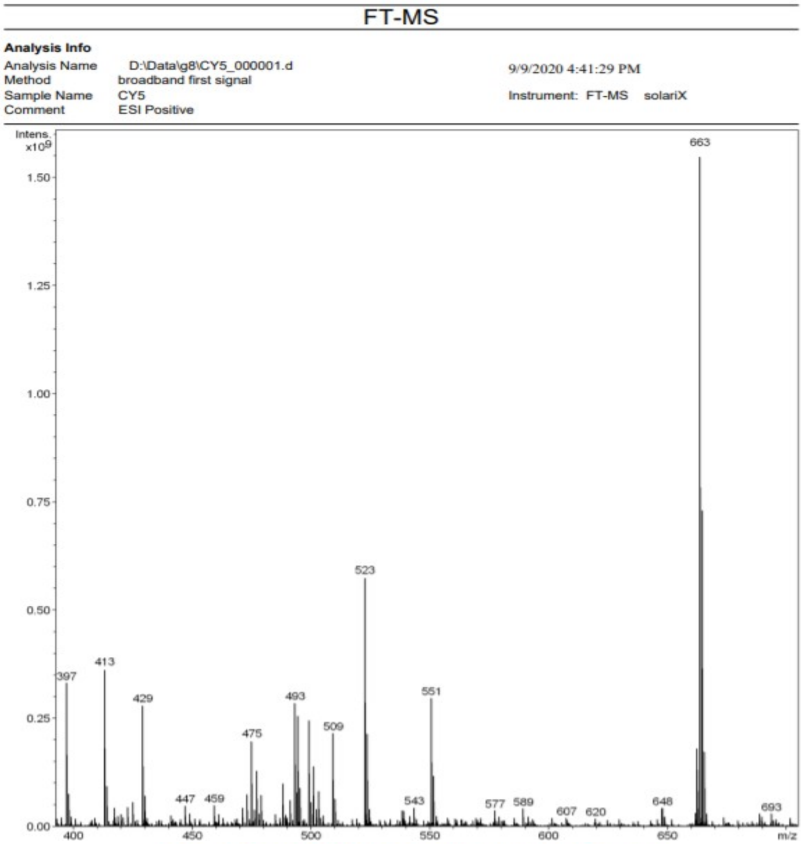
603.26396	1	C 41 H 35 N 2 O 3	100.00	603.26422	0.26	0.43	5.8	25.5	even	ok

Fig. S14 HR-MS of the **CY-4**.



FT-MS

Analysis Info

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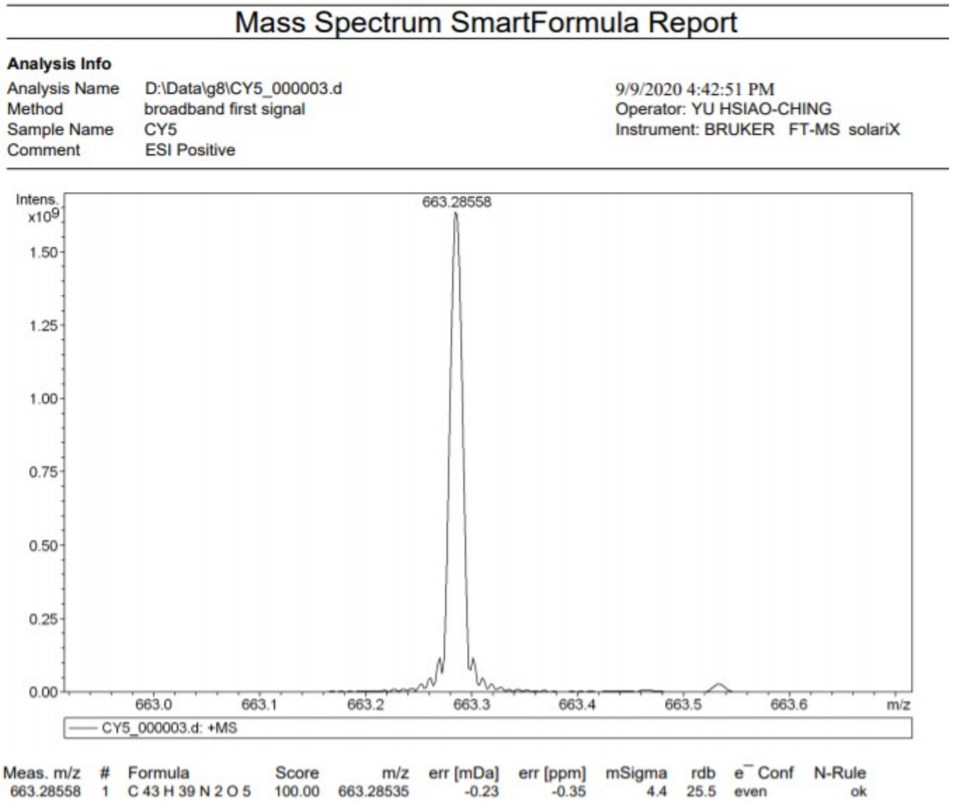
Method broadband first signal
Sample Name CY5
Comment ESI Positive

9/9/2020 4:41:29 PM
Instrument: FT-MS solariX



Mass Spectrum SmartFormula Report

Analysis Info

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Method broadband first signal
Sample Name CY5
Comment ESI Positive

9/9/2020 4:42:51 PM
Operator: YU HSIAO-CHING
Instrument: BRUKER FT-MS solariX

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
663.28558	1	C 43 H 39 N 2 O 5	100.00	663.28535	-0.23	-0.35	4.4	25.5	even	ok

Fig. S15 HR-MS of the **CY-5**.

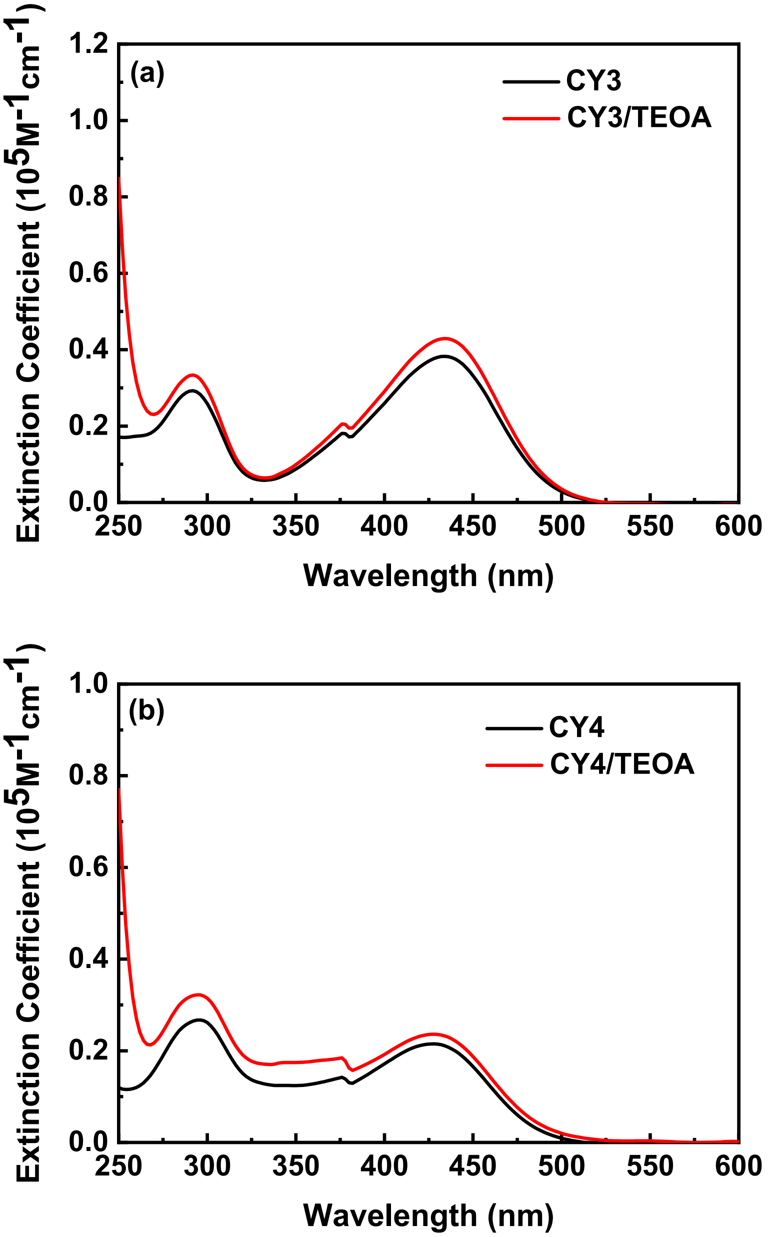

Fig. S16 UV-Vis spectra of (a) **CY3**, **CY3**/TEOA and (b) **CY4**, **CY4**/TEOA in DCM solution

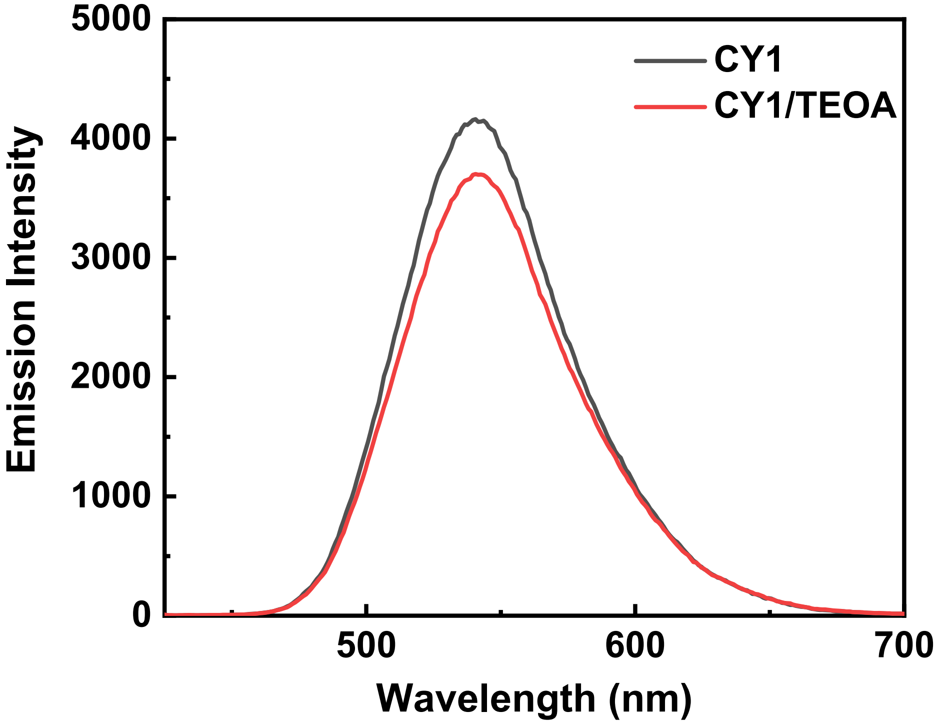

Fig. S17 PL spectra of **CY1** and **CY1**/TEOA (1:4 wt%) in DCM solutions (Conc. = 1*10^{-5} M).

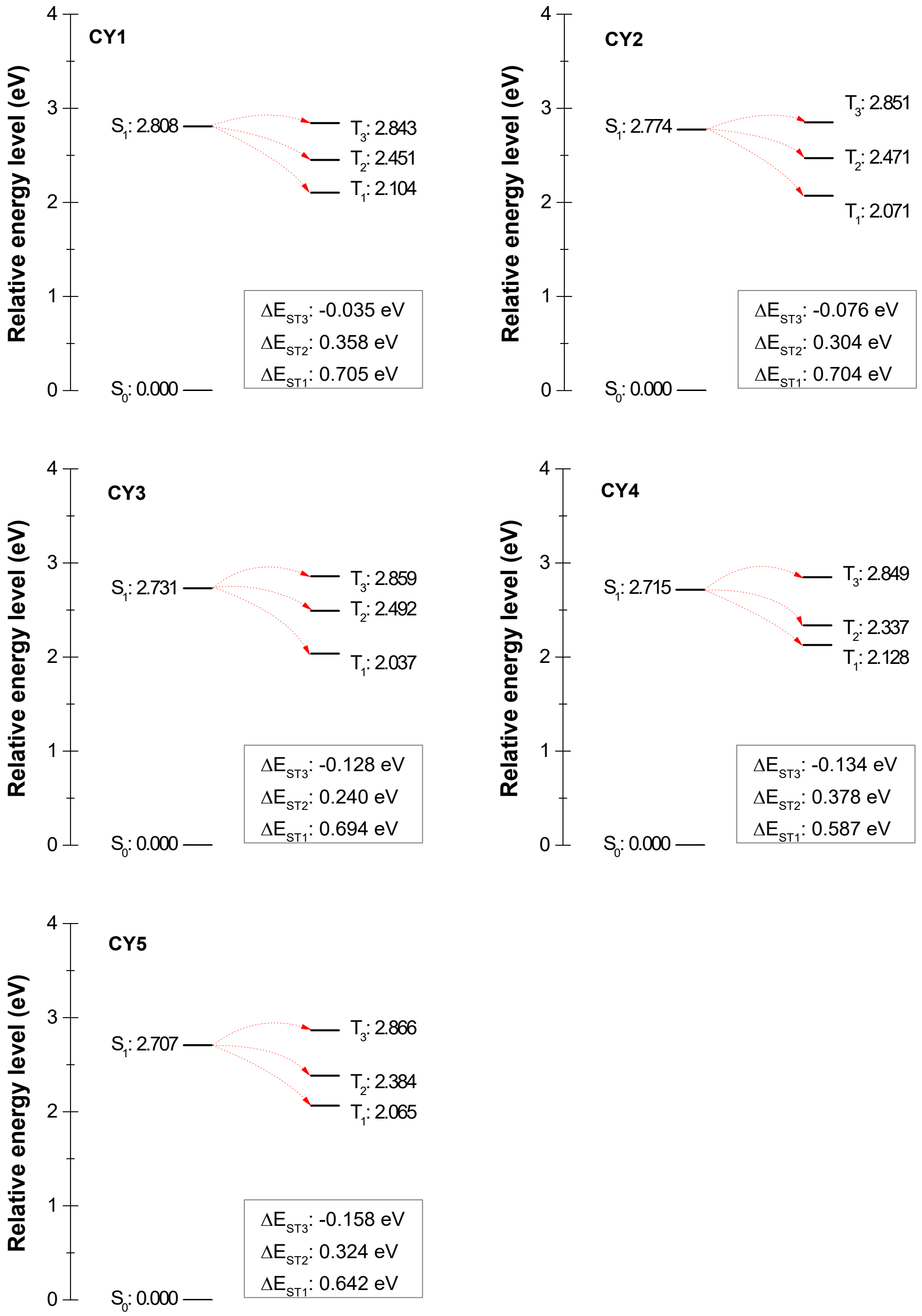

Fig. S18 Energy changes of the **CYs** between singlet and triplet states.

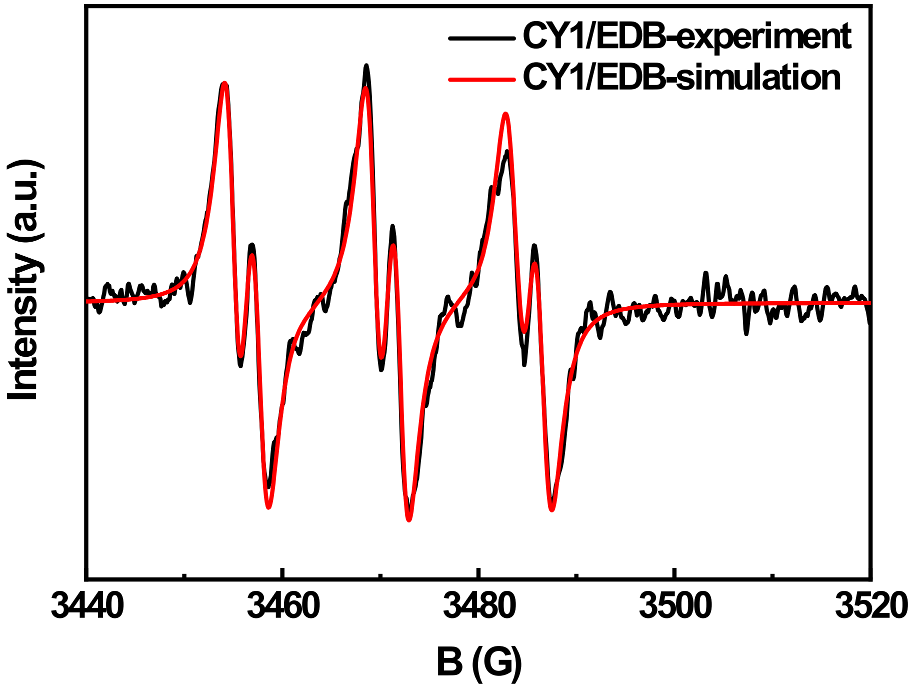

Fig. S19 Experimented and simulated ESR spectra conducted by **CY1**/EDB (1:4 wt%) irradiated with a UV lamp for 2 min and trapped by PBN in *t*-butylbenzene solution.

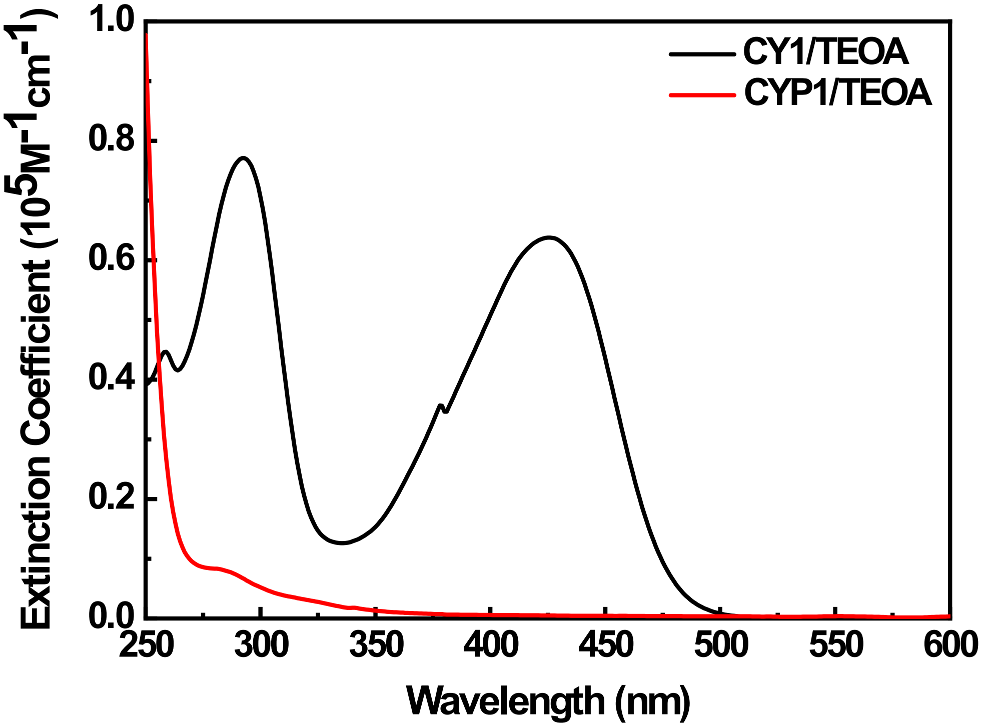

Fig. S20 UV-Vis spectra of **CY1**/TEOA and **CYP1**/TEOA (1:4 wt%) in DCM solution (concentration = 1 × 10^{-5} M).

Table S1 Photo-DSC data derived from **CY1**/hydrogen donor packages[a]

Sample	**Final Conversion (%)**	**ΔHt (kJ mol^{-1})[b]**	***H_{max}* (mW mg^{-1})[c]**	**Rp_{max} (s^{-1})[d]**	***T_{max}* (s)[e]**
CY1/TEA (1:4)	46	120	81	0.67	34
CY1/TEOA (1:2)	41	107	108	0.84	28
CY1/TEOA (1:4)	43	112	133	1.01	26
CY1/TEOA (1:9)	43	112	143	1.10	26

[a] Photo-DSC at various formulations measured with UV light of intensity 180 mW cm^{-2} for 3 min and a total measurement time of 6 min.

[b.] ΔH_t is the total reaction heat enthalpy within 3 min.

[c] H_{max}: maximum heat flow.

[d.] Rp_{max}: maximum rate of polymerization.

[e.] T_{max}: time at maximum heat flow.

Table S2 Photo-DSC data derived from **CY**/TEOA packages under UV light irradiation[a]

PI package	Final Conversion (%)	ΔHt (kJ mol^{-1})[b]	H_{max} (mW mg^{-1})[c]	Rp$_{max}$ (s^{-1})[d]	T_{max} (s)[e]
CY1/TEOA	43	112	133	1.01	26
CY2/TEOA	22	57	60	0.44	25
CY3/TEOA	10	23	27	0.20	28
CY4/TEOA	40	103	101	0.78	27
CY5/TEOA	18	45	42	0.30	28
CYP1/TEOA	38	98	258	1.98	23
CYP1/TPA/TEOA[f]	33	85	167	1.29	24

[a] Photo-DSC of the **CY**/TEOA blend at the ratio of **CY**:TEOA:TMPTA = 1:4:95), measured with UV light of intensity 180 mW cm^{-2} for 3 min and a total measurement time of 6 min.

[b.] ΔH_t is the total reaction heat enthalpy within 3 min.

[c] H_{max}: maximum heat flow.

[d.] Rp_{max}: maximum rate of polymerization.

[e.] T_{max}: time at maximum heat flow.

[f.] The weight ratio of **CYP1**+TPA:TEOA:TMPTA (w/w/w) was 1:4:95). The weight percentage of **CYP1** and TPA depended on their molecular weights.

Table S3 Photo-DSC data derived from different photoinitiation packages under 405-nm LED light irradiation[a]

PI package	**Final Conversion (%)**	**ΔHt (kJ mol^{-1})**[b]	***H_{max}* (mW mg^{-1})**[c]	**Rp_{max} (s^{-1})**[d]	***T_{max}* (s)**[e]
CY1/TEOA	37	96	118	0.90	20
CY2/TEOA	22	58	46	0.35	25
CY3/TEOA	13	33	17	0.13	38
CY4/TEOA	43	112	188	1.38	22
CY5/TEOA	17	45	30	0.21	26
CYP1/TEOA	19	50	68	0.52	28
CYP1/TPA/TEOA	15	40	55	0.43	25

[a] Photo-DSC of the **CY**/TEOA blend at the ratio of **CY**:TEOA:TMPTA of 1:4:95, measured with 405 nm LED light of intensity 180 mW cm^{-2} for 3 min and a total measurement time of 6 min.

[b] ΔH_t: total reaction heat enthalpy within 3 min.

[c] H_{max}: maximum heat flow.

[d] Rp_{max}: maximum rate of polymerization.

[e] T_{max}: time at maximum heat flow.