Synthesis of new quinolizinium-based fluorescent compounds and studies on their applications in photocatalysis

Wai-Ming Yip, ‡ab Qiong Yu, ‡a Ajcharapan Tantipanjaporn, ‡b Wing-Cheung Chan,[b]
Jie-Ren Deng,[ab] Ben Chi-bun Ko*[b] and Man-Kin Wong*[ab]

[a] The Hong Kong Polytechnic University, Shenzhen Research Institute, Shenzhen, 518057, People's Republic of China

[b] State Key Laboratory of Chemical Biology and Drug Discovery, Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hum, Hong Kong

SUPPORTING INFORMATION

General procedure

All of the photochemical experiments were performed in a custom made “light box” with 4 reaction vessels surrounded by 16 Blue LEDs. The temperature was maintained by a fan attached to the “light box”. A voltage transformer was connected with the Blue LEDs and employed to monitor the power of the light source ($P = U \times I = 14.3\ V \times 2.3\ A = 32.9\ W$). 4 reactions were performed in the “light box” every time for measurement of the reaction yields. The emission spectra of the Blue LEDs revealed a maximum emission wavelength of the light source at λ_{max} = 468 nm. The emission spectra of the light source was shown below.

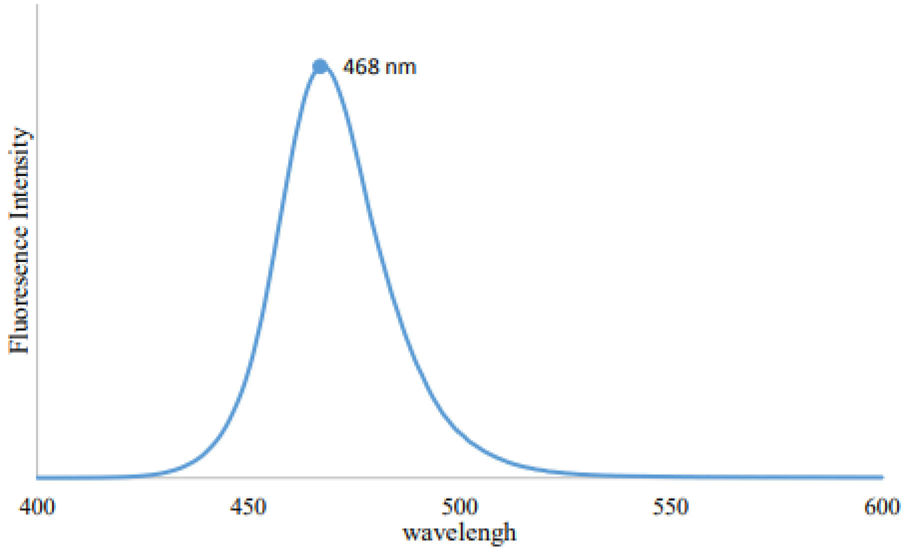
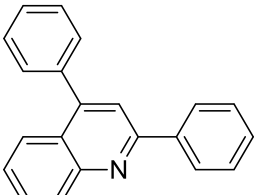
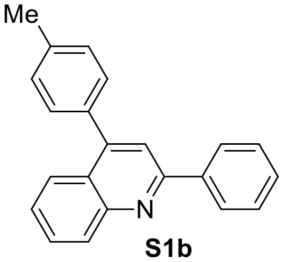
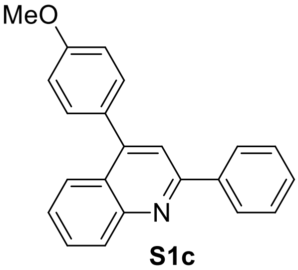
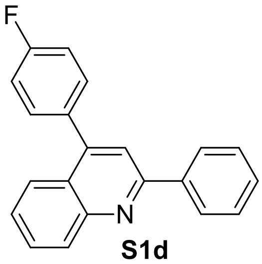
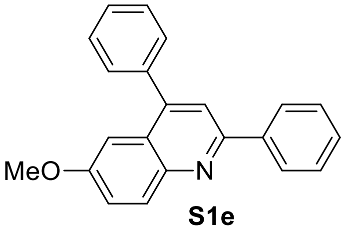
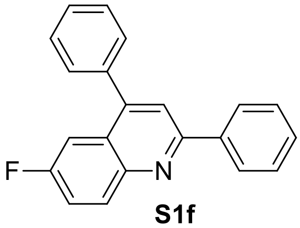
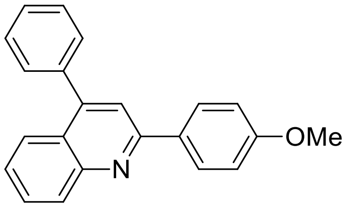
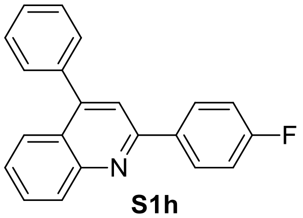
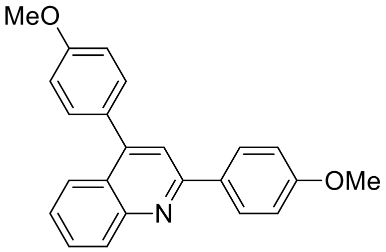
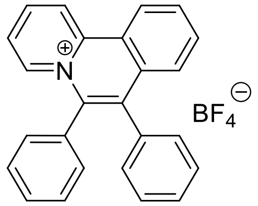
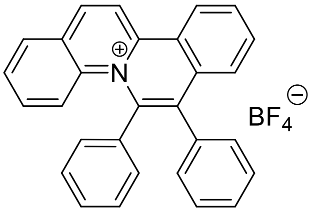
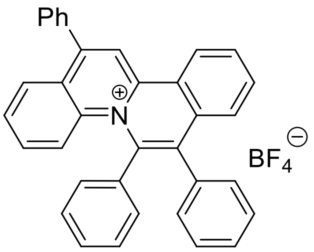
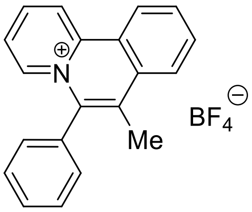


Figure S1 Emission spectrum of the Blue LEDs light source.

Literature references:

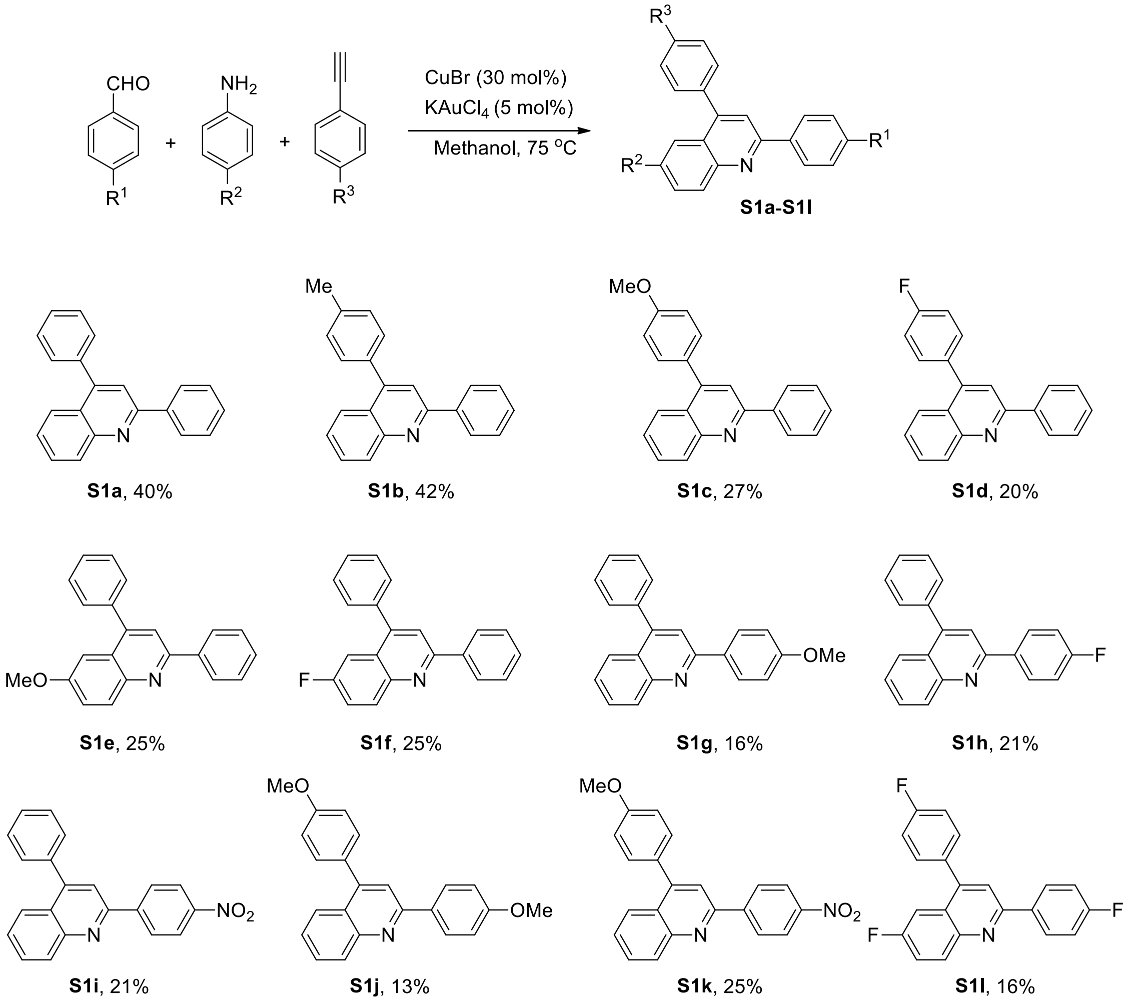
 **S1a**	Y.-Y. Liu, Y. Wei, Z. –H. Huang, Y. Liu, *Org. Biomol. Chem.* 2021, **19**, 659-666.
 **S1b**	A. Purkait, S. Saha, S. Ghosh, C. K. Jana, *Chem. Commun.* 2020, **56**, 15032-15035.
 **S1c**	Y. Zhang, L. Chen, Y. Shao, F. Zhang, Z. Chen, N. Lv, J. Chen, R. Li, *Org. Chem. Front.* 2021, 8, 254-259.
 **S1d**	Y. Zhang, L. Chen, Y. Shao, F. Zhang, Z. Chen, N. Lv, J. Chen, R. Li, *Org. Chem. Front.* 2021, 8, 254-259.
 **S1e**	Y. Zhang, L. Chen, Y. Shao, F. Zhang, Z. Chen, N. Lv, J. Chen, R. Li, *Org. Chem. Front.* 2021, 8, 254-259.
 **S1f**	Y. Zhang, L. Chen, Y. Shao, F. Zhang, Z. Chen, N. Lv, J. Chen, R. Li, *Org. Chem. Front.* 2021, 8, 254-259.

 **S1g**	Y. Zhang, L. Chen, Y. Shao, F. Zhang, Z. Chen, N. Lv, J. Chen, R. Li, *Org. Chem. Front.* 2021, 8, 254-259.
 **S1h**	Y. Zhang, L. Chen, Y. Shao, F. Zhang, Z. Chen, N. Lv, J. Chen, R. Li, *Org. Chem. Front.* 2021, 8, 254-259.
 **S1j**	J. Zhang, J. Chen, Zhang, X. X. Lei, *J. Org. Chem.* 2014, **79**, 10682-10688.
 **1a**	C.-Z. Luo, P. Gandeepan, J. Jayakumar, K. Parthasarathy, Y.-W. Chang and C.-H. Cheng, *Chem. Eur. J.*, 2013, **19,** 14181-14186.
 **1b**	J.-R. Deng, W.-C. Chan, N. Chun-Him Lai, B. Yang, C.-S. Tsang, B. Chi-Bun Ko, S. Lai-Fung Chan and M. -K. Wong, *Chem. Sci.*, 2017, **8**, 7537-7544.
 **1c**	C.-Z. Luo, P. Gandeepan, J. Jayakumar, K. Parthasarathy, Y.-W. Chang and C.-H. Cheng, *Chem. Eur. J.*, 2013, **19,** 14181-14186

 **1t**	C.-Z. Luo, P. Gandeepan, J. Jayakumar, K. Parthasarathy, Y.-W. Chang and C.-H. Cheng, *Chem. Eur. J.*, 2013, **19,** 14181-14186

General procedure for synthesis of quinolines by three-component coupling reaction of aldehydes, amines and alkynes

A mixture of aldehyde (10 mmol, 1equiv.), aniline (12 mmol, 1.2equiv.), aryl alkyne (12 mmol, 1.2 equiv), $KAuCl_4$ (5 mol%), CuBr (30 mol%) and 20 mL of methanol was heated in 50 mL round bottom flask at 40°C under N_2 overnight. The solvent was removed by evaporation under reduced pressure, and the residue was purified by flash column chromatography using DCM/hexane as eluent to give the quinoline products.



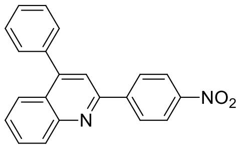
S1a-S1l

S1a, 40% **S1b**, 42% **S1c**, 27% **S1d**, 20%

S1e, 25% **S1f**, 25% **S1g**, 16% **S1h**, 21%

S1i, 21% **S1j**, 13% **S1k**, 25% **S1l**, 16%

Scheme S1 Synthetic routes of Quinoline substrates **S1a-S1l**

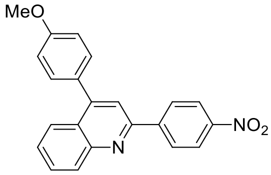


S1i

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (q, *J* = 9.0 Hz, 4H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.81 (s, 1H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.59 – 7.47 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.76, 149.67, 148.62, 148.10, 145.14, 137.74, 130.21, 129.92, 129.39, 128.61, 128.15, 127.99, 127.19, 125.99, 125.62, 123.72, 118.87.

HRMS (ESI) calcd for $C_{21}H_{15}N_2O_2^+$ $(M + H)^+$ 327.1128, found 327.1165.

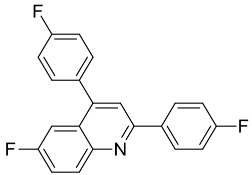


S1k

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.36 (m, 4H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.86 (s, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.56 (dd, *J* = 15.1, 8.2 Hz, 3H), 7.13 (d, *J* = 8.6 Hz, 2H), 3.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.11, 154.13, 149.63, 148.91, 148.34, 145.61, 130.83, 130.35, 130.20, 130.00, 128.35, 127.21, 125.86, 124.04, 119.07, 114.23, 55.48.

HRMS (ESI) calcd for $C_{22}H_{17}N_2O_3^+$ $(M + H)^+$ 357.1234, found 327.1277.



S1l

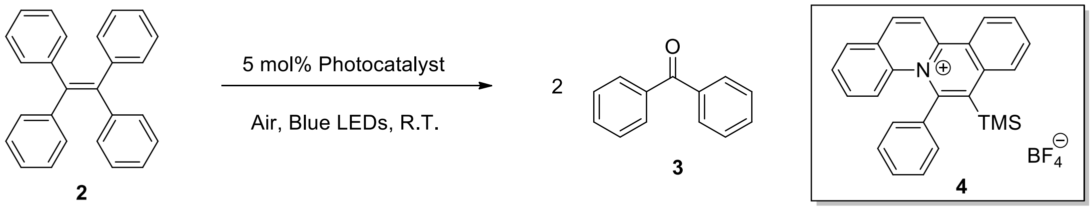
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.12 (m, 3H), 7.78 (s, 1H), 7.60 – 7.39 (m, 4H), 7.33 – 7.21 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.13, 164.30, 162.65, 161.91, 161.83, 159.45, 155.15, 147.80, 147.74, 145.89, 135.34, 133.81, 132.62, 132.53, 131.13, 131.05, 129.35, 129.26, 126.44, 126.34, 120.05, 119.79, 119.53, 116.05, 115.97, 115.83, 115.75, 108.97, 108.74.

^{19}F NMR (377 MHz, $CDCl_3$) δ -112.03, -112.51, -112.64.

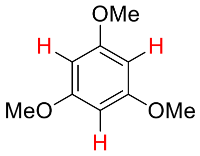
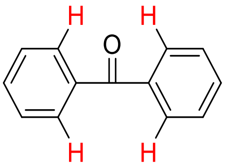
HRMS (ESI) calcd for $C_{21}H_{13}F_3N^+$ $(M + H)^+$ 336.0995, found 336.1007.

General Procedure for Photooxidative of Aromatic Alkene with Quinolizinium Photocatalysts



A mixture of tetraphenylethylene **2** (0.2mmol), photocatalysts (5 mol%) in 5 mL of DCE or 5 mL of chloroform was added to a 20 mL test tube. The test tube was irradiated with Blue LEDs for 4 h. After 4 h, the reaction mixture was concentrated under reduced pressure. To determinate the NMR yield, internal standard 1,3,5-trimethoxybenzene (0.2 mmol, 1equiv.) and 2 mL of $CDCl_3$ were mixed with the residue for ^1H NMR analysis. For product isolation, the resulting residue was purified by flash chromatography on silica gel using EtOAc/hexane as eluent to give the desired product.

Table S1 Chemical shifts of compounds in $CDCl_3$

Compound	**Chemical shift of H in ^1H NMR**
	6.12
	7.84-7.82

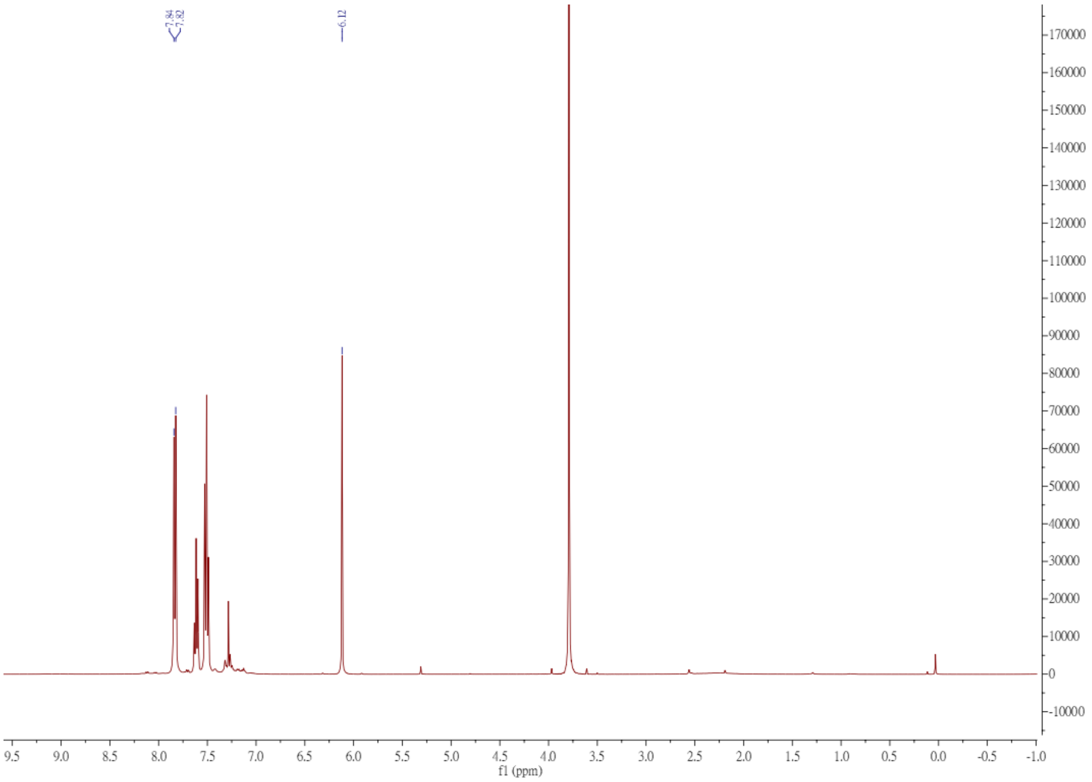
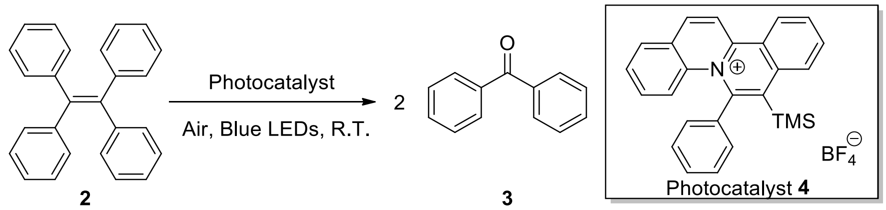


Figure S2 Determination of the NMR yield of **3** when quinolizinium compounds were employed as photocatalyst and 1,3,5-trimethoxybenzene was used as internal standard.

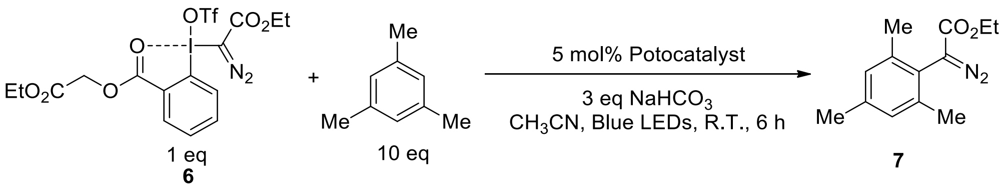
Table S2 Photooxidative cleavage of tetraphenylethylene 2 using photocatalyst 4 [a]



Entry	**4** (mol%)	Solvent	Yield(%)[b]
1	5	Hexane	n.d.
2	5	Toluene	50
3	5	1,4 Dioxane	34
4	5	THF	6
5	5	CCl_4	n.d.
6	5	Chloroform	60
7	5	DCM	37
8	5	DCE	62
9	5	Acetone	29
10	5	DMF	n.d.
11	5	DMSO	n.d.
12	5	CH_3CN	40
13	5	Ethanol	47
14	5	Methanol	51
15	5	H_2O	n.d.
16	5	CH_3CN/H_2O	n.d.
17	10	DCE	60
18	2.5	DCE	57
19	1	DCE	53
20	0	DCE	n.d.
21[c]	5	DCE	n.d.
22[d]	5	DCE	n.d.
23[e]	5	DCE	82

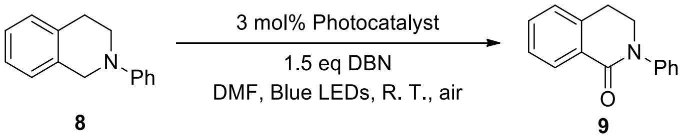
[a] Reaction conditions: treatment of tetraphenylethylene **2** (0.2 mmol), photocatalyst **4** (5 mol%) in 5 mL of solvent under air and blue LEDs light for 4 h at room temperature. [b] Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. [c] The reaction was conducted without light. [d] The reaction was conducted under N_2. [e] The reaction was conducted under 1 atm O_2.

General Procedure for photocatalysts for C-H bond functionalization



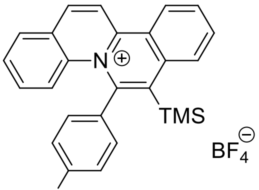
To a 10 mL oven-dried tube equipped with a stirring bar was added photocatalyst (0.01 mmol, 5 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv), the 1,3,5-trimethoxybenzene (2 mmol, 10.0 equiv), hypervalent iodine reagent **6** (0.2 mmol, 1.0 equiv) and MeCN (2.0 mL). The tube was sealed with a septum and degassed by three freeze-pump-thaw cycles under nitrogen. Then the reaction tube was placed in a photoreactor equipped with Blue LEDs. A mini-fan was kept on top to maintain room temperature. After the reaction completed after 6 hours, the reaction mixture was passed through a short pad of silica gel and washed with dichloromethane. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel to give the corresponding diazo compound **7**.

Table S3 Evaluation of photocatalysts for oxygenation of tertiary amine to amide [a]



Entry	Catalyst	Time (h)	Recovery of **8** (%)[b]	Yield of **9** (%)[b]
1	**1n**	17	76	24
2	**1n**	48	39	56
3	**4b**	17	23	67
4	**4b**[c]	24	16	76
5	**4b**	48	0	87[d]
6	**4**	30	0	88[d]

[a] Reaction conditions: treatment of amine 8 (0.15 mmol), photocatalyst (3 mol%) in 0.5 mL of DMF and blue LEDs light at room temperature. [b] Yield was determined by ^{1}H NMR using CH_2Br_2 as internal standard. [c] 5 mol% photocatalyst was used. [d] Isolated yield.



4b

Experimental procedure for light-induced oxygenation of tertiary amine to amide

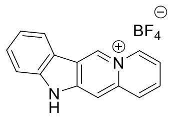
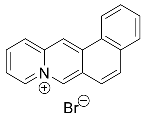
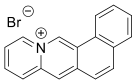
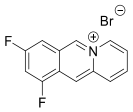
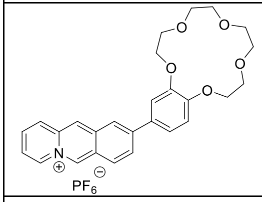
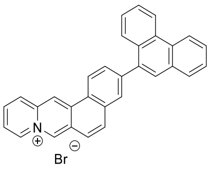
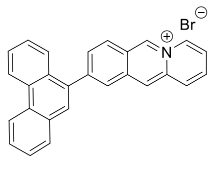
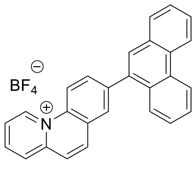
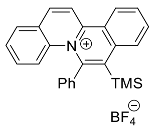
To a mixture of amine **8** (31 mg, 0.15 mmol, 1.0 equiv.) and photocatalyst (0.0045 mmol, 3mol%) in DMF (0.5 mL) was added DBN (28 mg, 0.225 mmol, 1.5 equiv.) in a 10 mL test tube. The solution was stirred at room temperature under Blue LEDs irradiation in open to air (without bubbling air). The mixture was concentrated in vacuo to yield the crude product, which was purified by flash chromatography on silica gel (eluent: Petroleum/EtOAc = 10/1 ~ 5/1) to yield the desired amide **9** as a white solid.

Photophysical measurements of quinolizinium compounds

The absorption and emission spectra were measured by Cary 8454 UV-Vis Diode Array System and Cary Eclipse Fluorescence Spectrophotometer, respectively, and a final concentration of each quinolizinium compound in CH_2Cl_2 was diluted to 1×10^{-5} M. The excitation slit and emission slit for emission measurement were set at 5 nm with scan rate at 120 nm/min and medium PMT voltage. Fluorescent quantum yield of each compound was determined by a comparative method employing fluorescein ($\Phi = 0.95$ in 0.1 N NaOH solution) as standard and calculated with the following equation.

$$\Phi_{sample} = \Phi_{standard} \times \frac{F_{sample}}{F_{standard}} \times \left(\frac{n_{sample}}{n_{standard}}\right)^2 \times \frac{Abs_{sample}}{Abs_{standard}}$$

Table S4 Photophysical properties of published quinolizinium dyes

Quinolizinium	Solvent	λ_{ex} (nm) (ε; $M^{-1}cm^{-1}$)	λ_{em} (nm)	Φ_F	τ_F (ns)	Application (Reference)
	MeCN	350 (-)	457	0.17	10.5	DNA Detection (A. Barbafina, M. Amelia, L. Latterini, G. G. Aloisi and F. Elisei, *J. Phys. Chem.*, 2009, **113**, 14514-14520.)
	MeCN	400 (-)	420	0.15	8.7	
	MeCN	390 (-)	425	0.34	5.6	
	Water	407 (7400)	420	0.30	-	Bromide or iodide sensor (R. B. Jagt, M. S. Kheibari and M. Nitz, *Dyes Pigm.*, 2009, **81**, 161-165.)
	DCM	430 (16596)	559	0.079	-	Magnesium detection (M. Tian, H. Ihmels and S. Ye, *Org. Biomol. Chem.*, 2012, **10**, 3010-3018.)
	DCM	411 (10965)	538	0.17	-	Fluorosolvatochromism (M. Pithan, D. Decker, M. S. Sardo, G. Viola and H. Ihmels, *Beilstein J. Org. Chem.*, 2016, **12**, 854-862.)
	Water	397 (4168)	532	0.056	-	Fluorosolvatochromism (P. M. Pithan, K. Schwan and H. Ihmels, *Arkivoc* , 2020, 1-11.)
	Water	368 (12022)	544	0.012	-	
 Our previous version	DCM	423 (14500)	491	0.44		Photocatalyst, Cell imaging (J. -R. Deng, W. -C. Chan, N. C. -H. Lai, B. Yang, C. -S. Tsang, B. C. -B. Ko, S. L. -F. Chan and M. -K. Wong, *Chem. Sci.*, 2017, **8**, 7537-7544.)

UV/Vis Absorption Spectrum of Quinolizinium Compounds

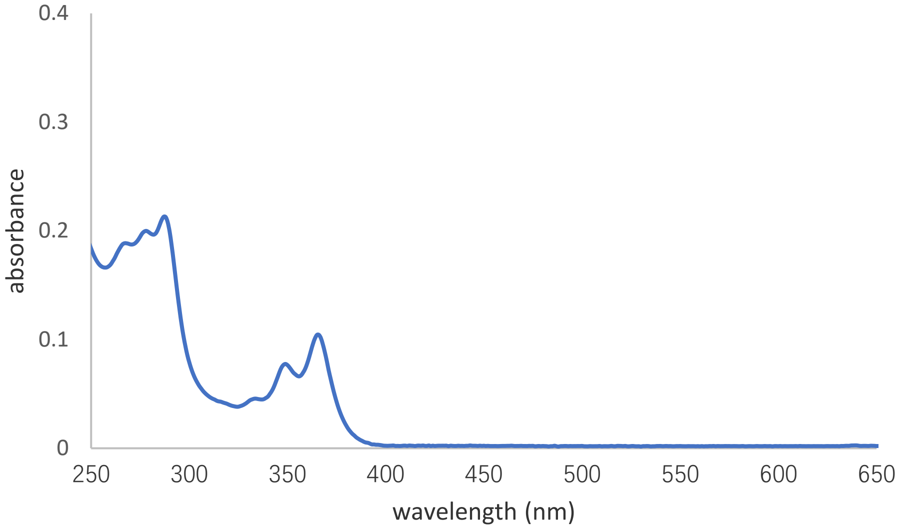


Figure S3 Absorption spectrum of compound **1a**

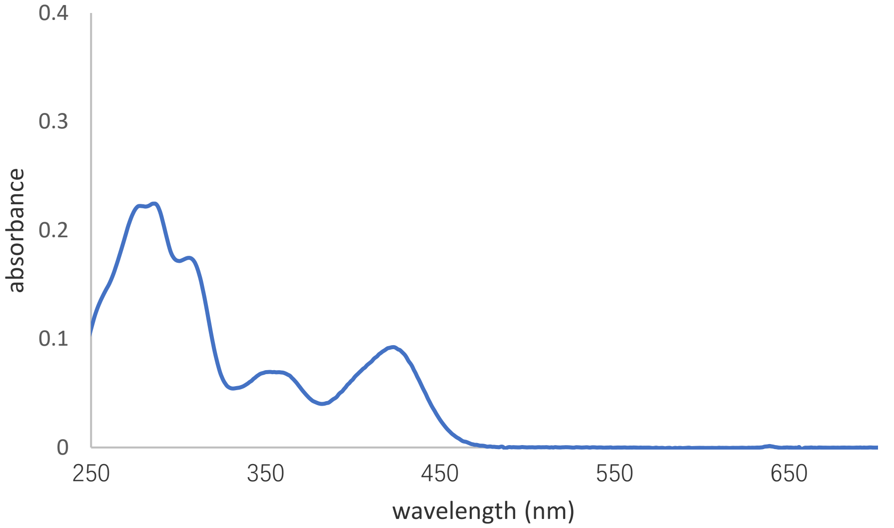


Figure S4 Absorption spectrum of compound **1b**

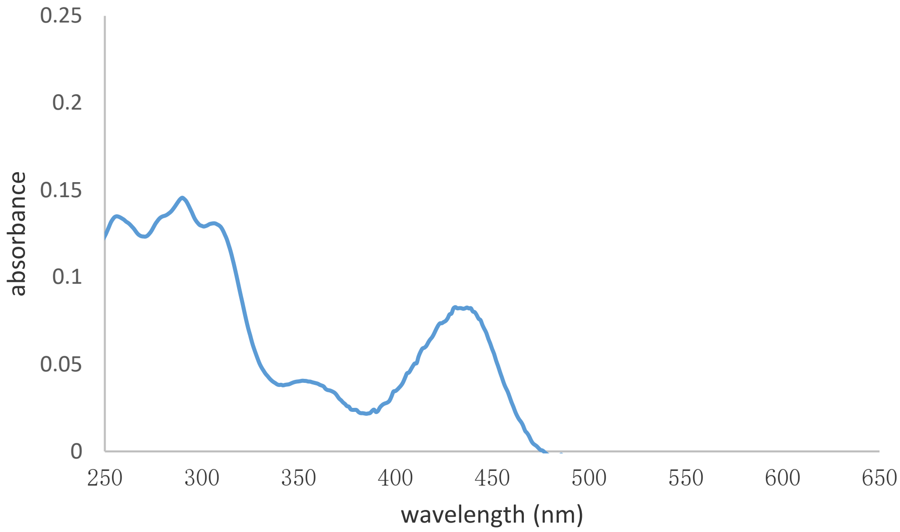


Figure S5 Absorption spectrum of compound **1c**

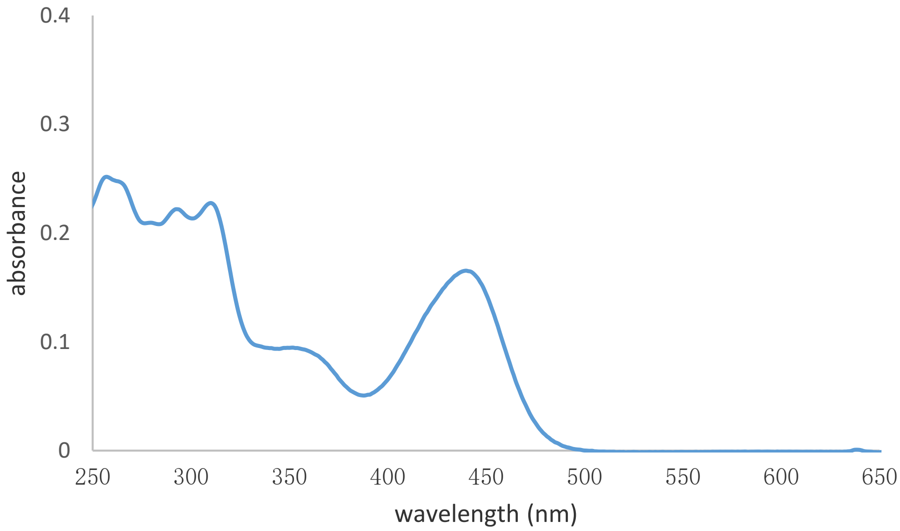


Figure S6 Absorption spectrum of compound **1d**

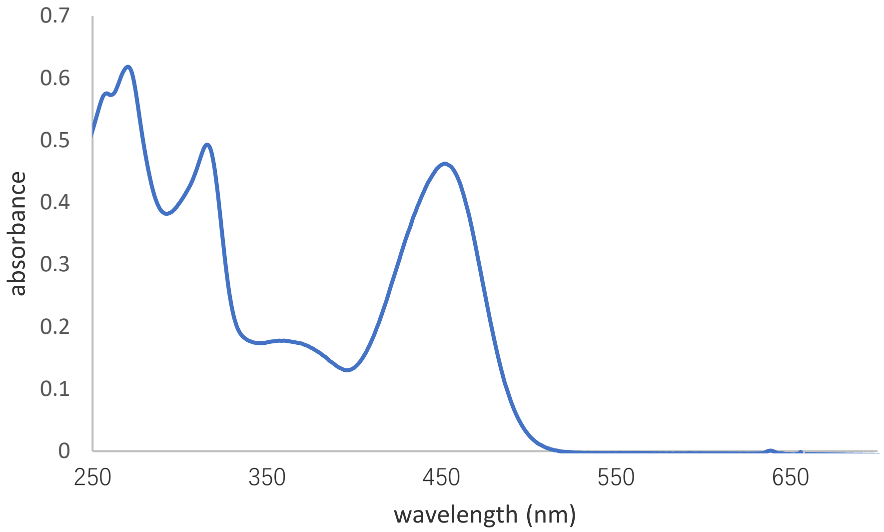


Figure S7 Absorption spectrum of compound **1e**

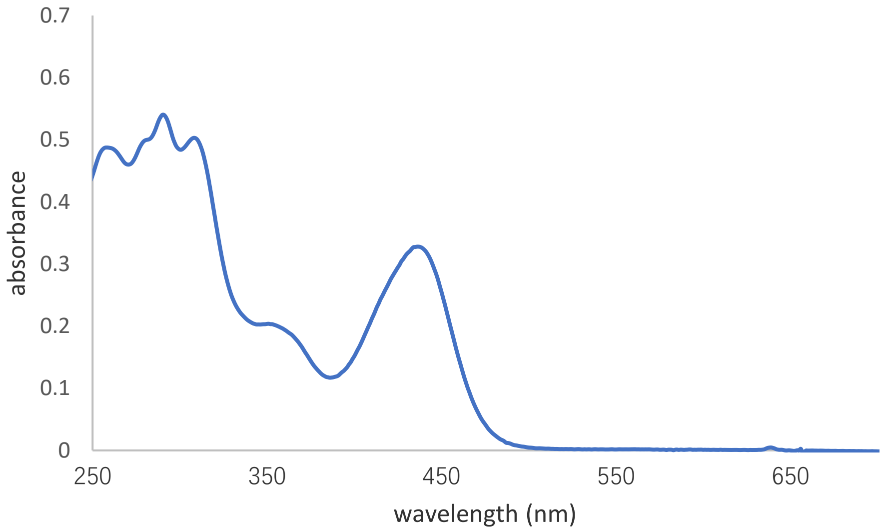


Figure S8 Absorption spectrum of compound **1f**

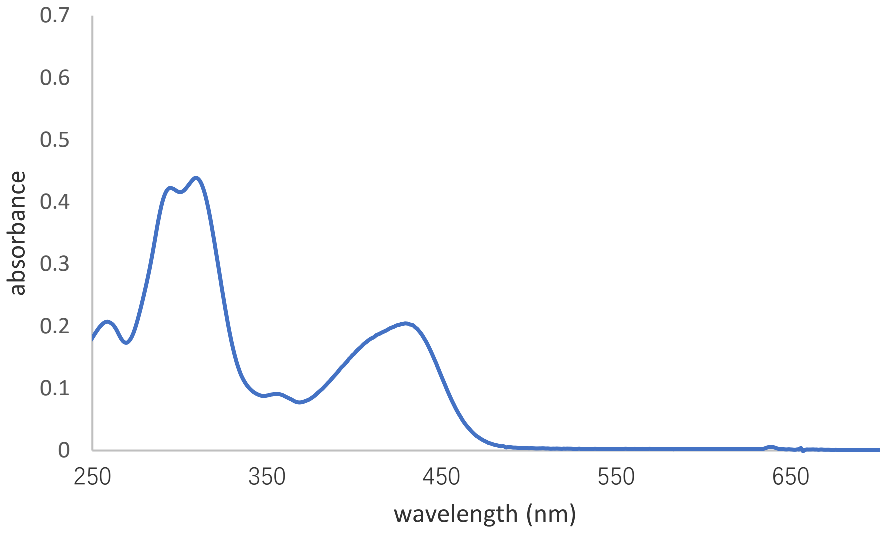


Figure S9 Absorption spectrum of compound **1g**

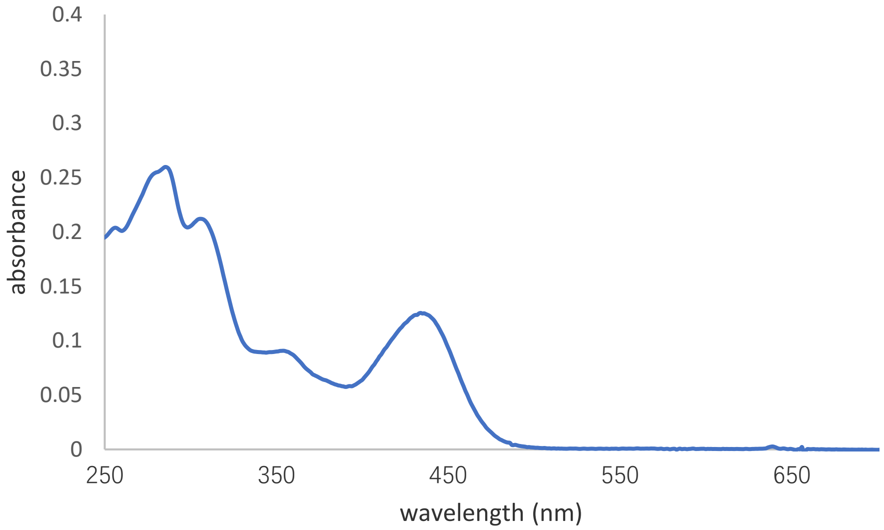


Figure S10 Absorption spectrum of compound **1h**

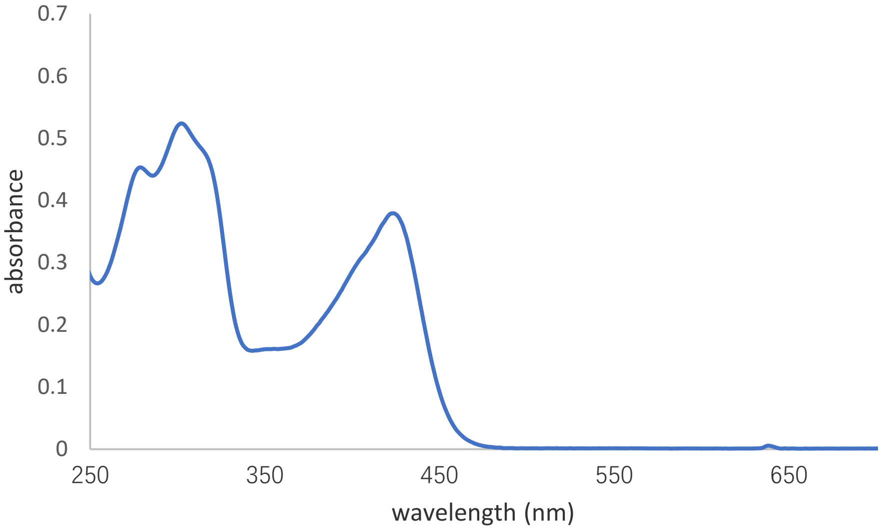


Figure S11 Absorption spectrum of compound **1i**

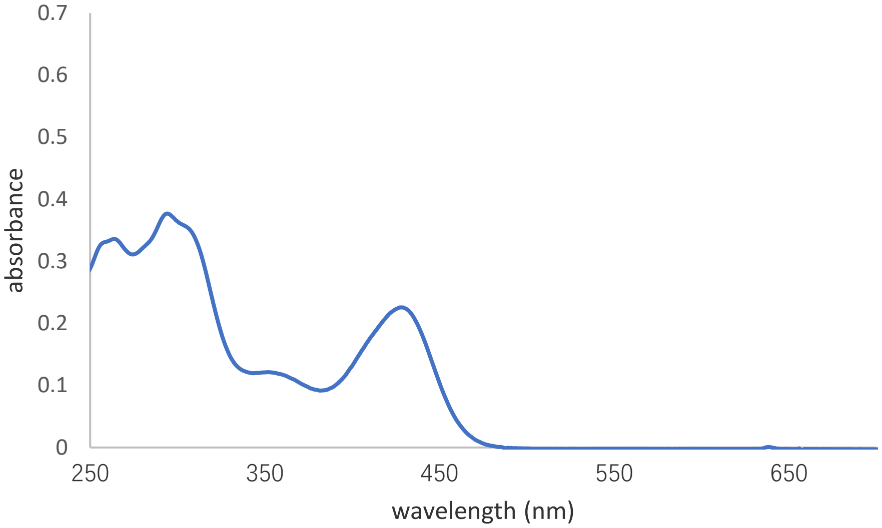


Figure S12 Absorption spectrum of compound **1j**

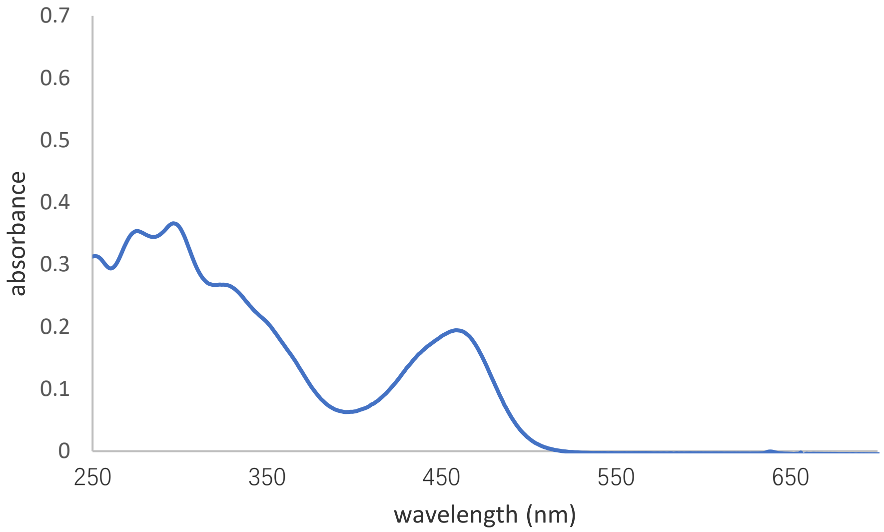


Figure S13 Absorption spectrum of compound **1k**

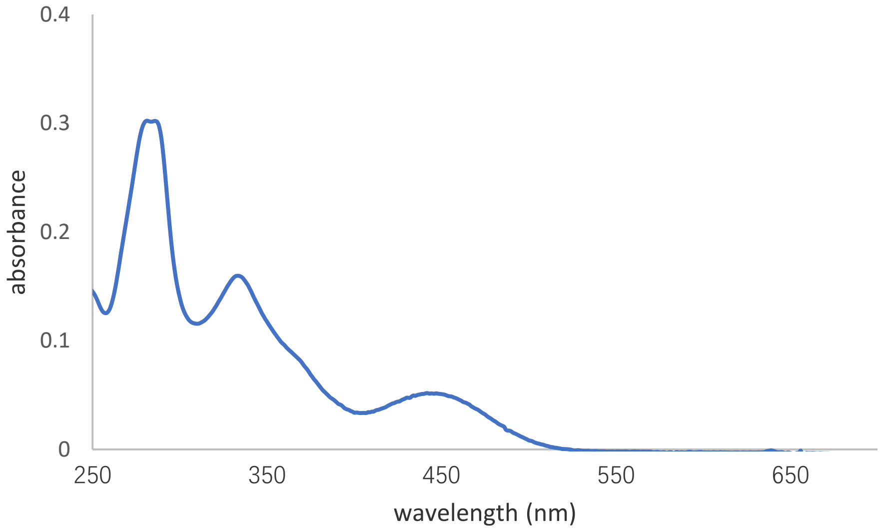


Figure S14 Absorption spectrum of compound **1l**

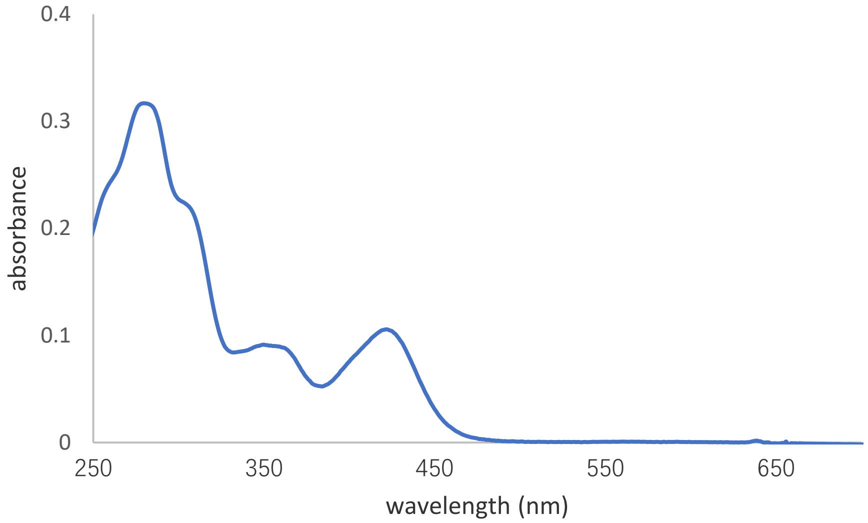


Figure S15 Absorption spectrum of compound **1m**

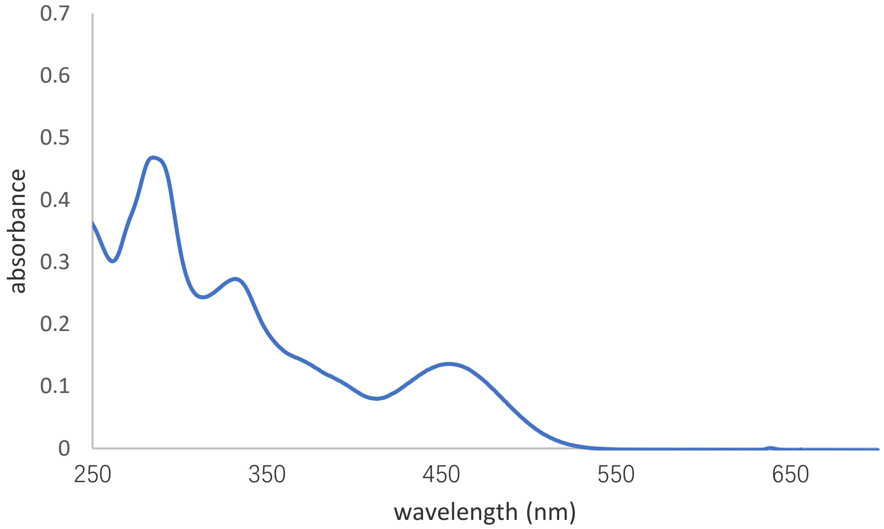


Figure S16 Absorption spectrum of compound **1n**

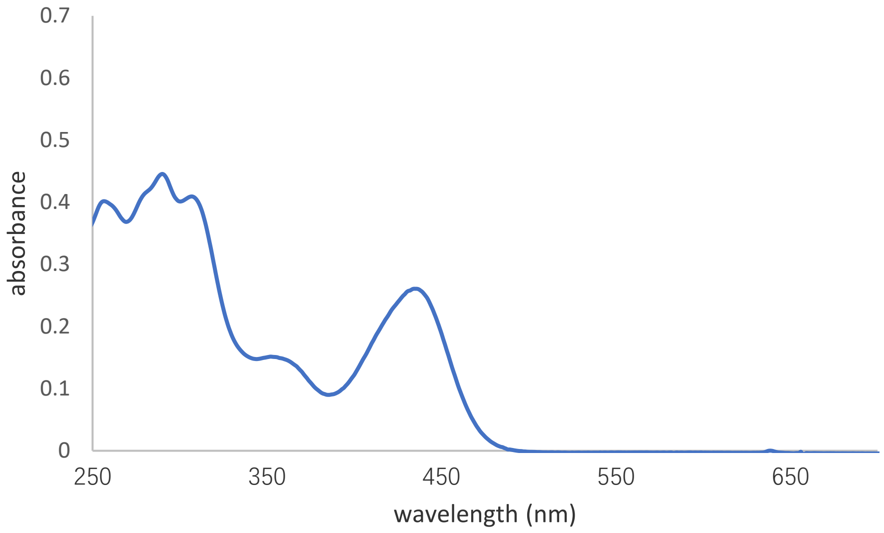


Figure S17 Absorption spectrum of compound **1o**

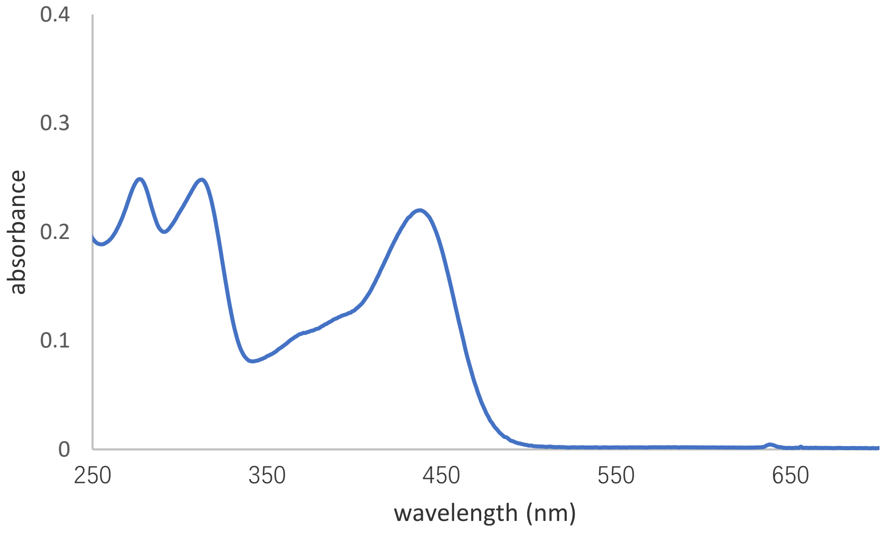


Figure S18 Absorption spectrum of compound **1p**

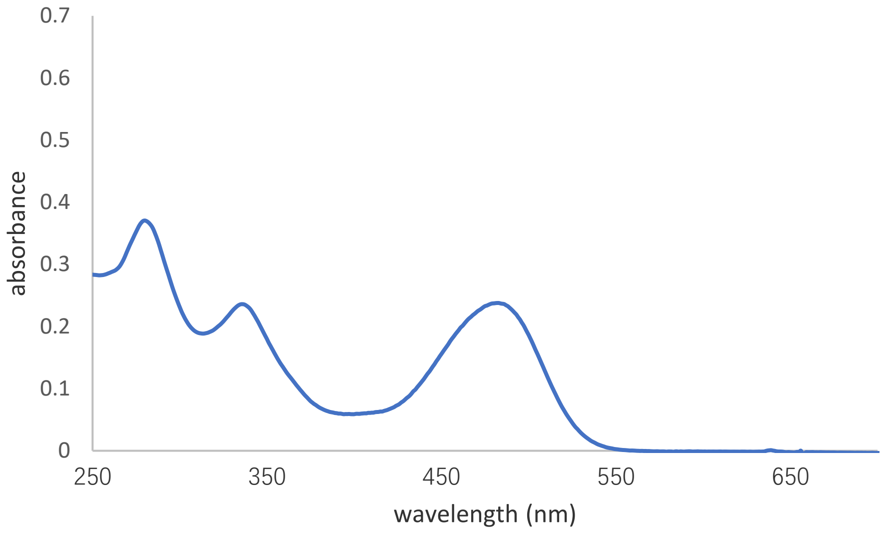


Figure S19 Absorption spectrum of compound **1q**

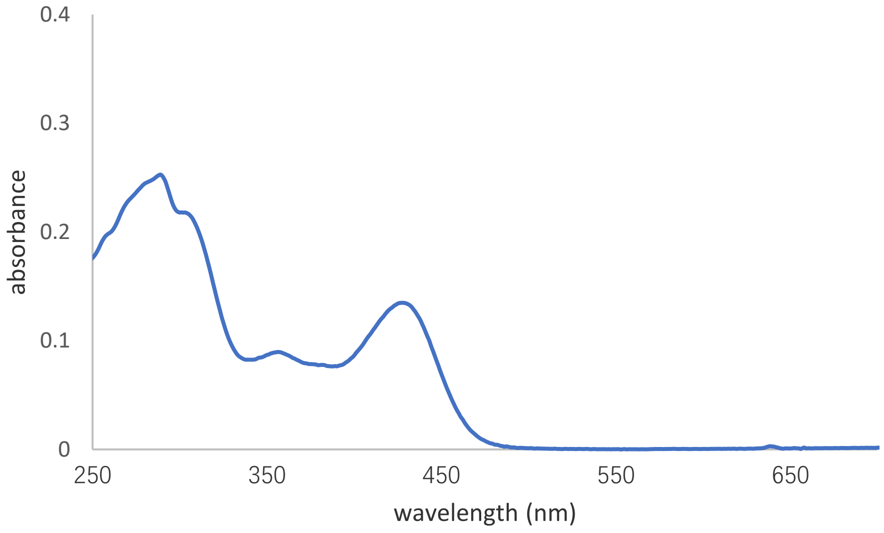


Figure S20 Absorption spectrum of compound **1r**

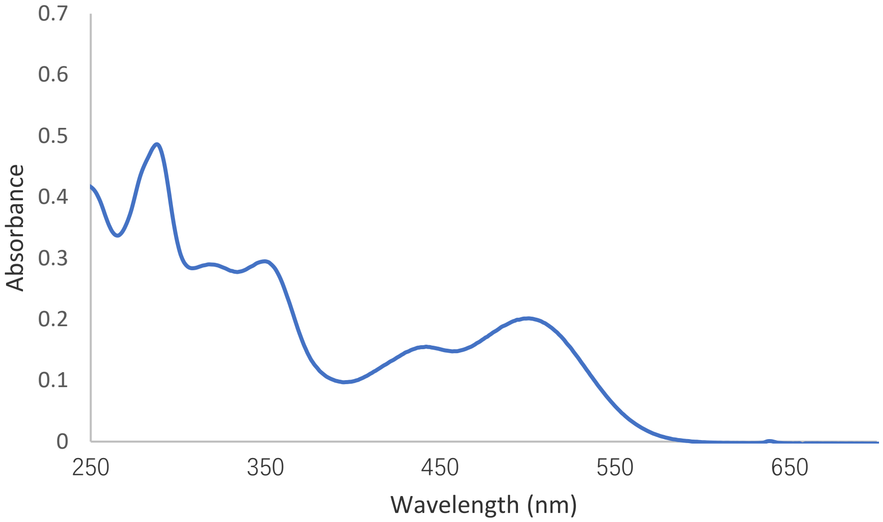


Figure S21 Absorption spectrum of compound **1s**

Emission Spectrum of Quinolizinium Compounds

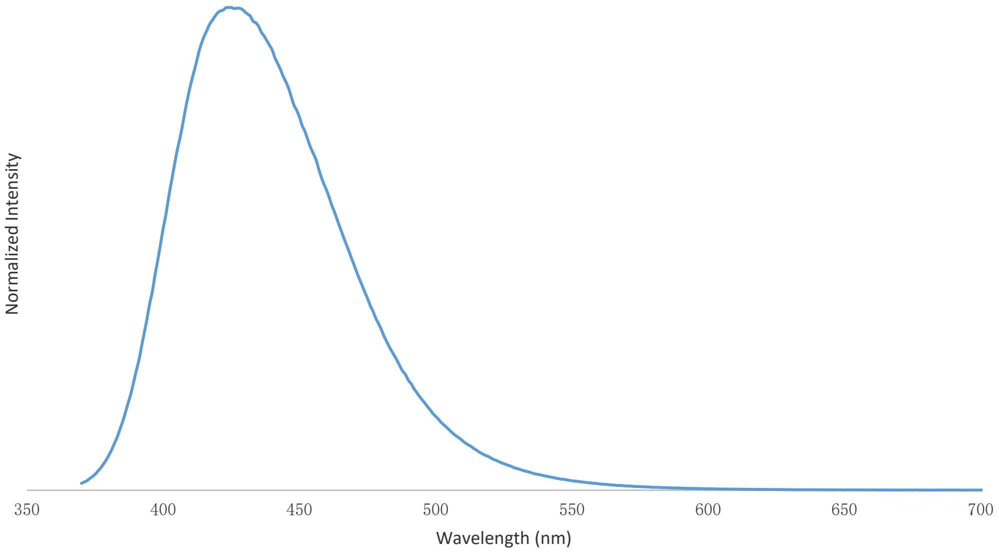


Figure S22 Emission spectrum of compound **1a**.

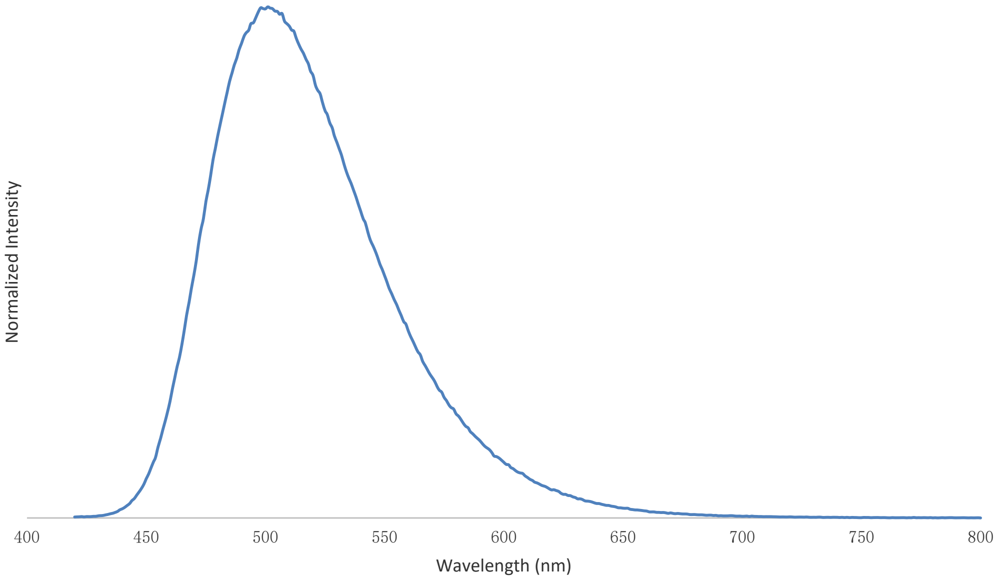


Figure S23 Emission spectrum of compound **1b**.

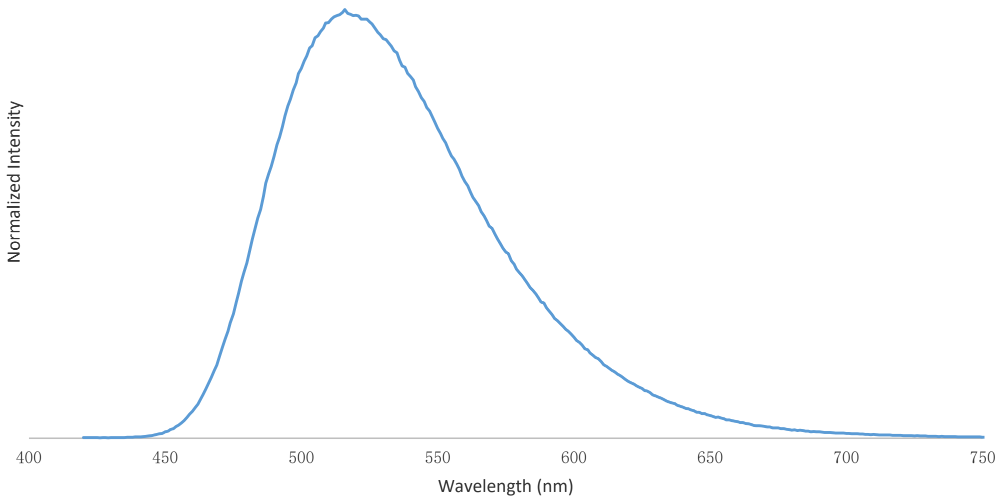


Figure S24 Emission spectrum of compound **1c**

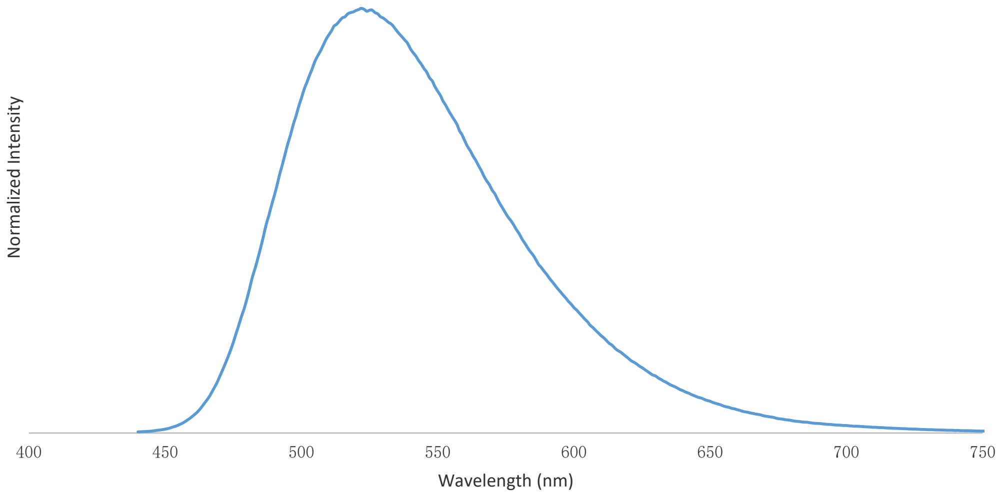


Figure S25 Emission spectrum of compound **1d**

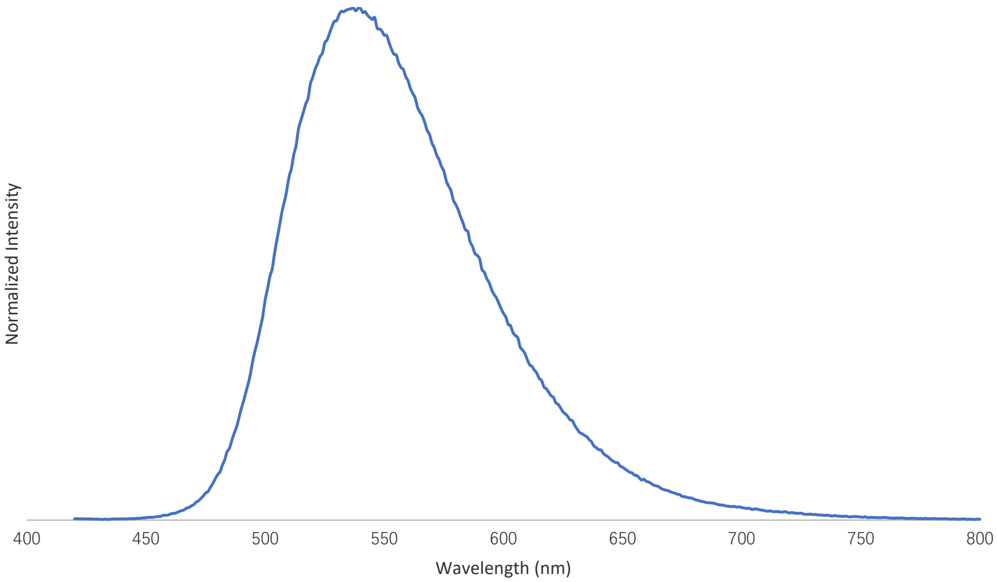


Figure S26 Emission spectrum of compound **1e**

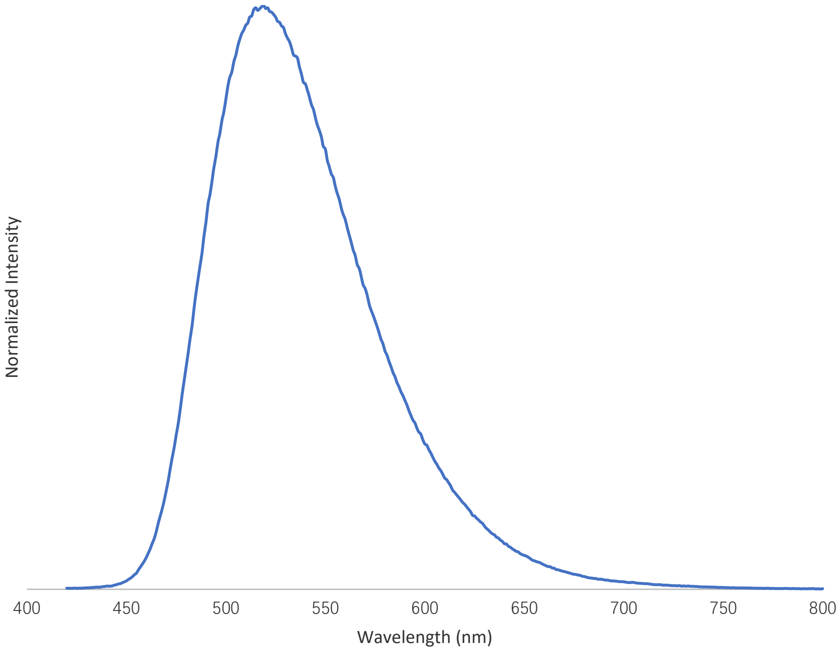


Figure S27 Emission spectrum of compound **1f**

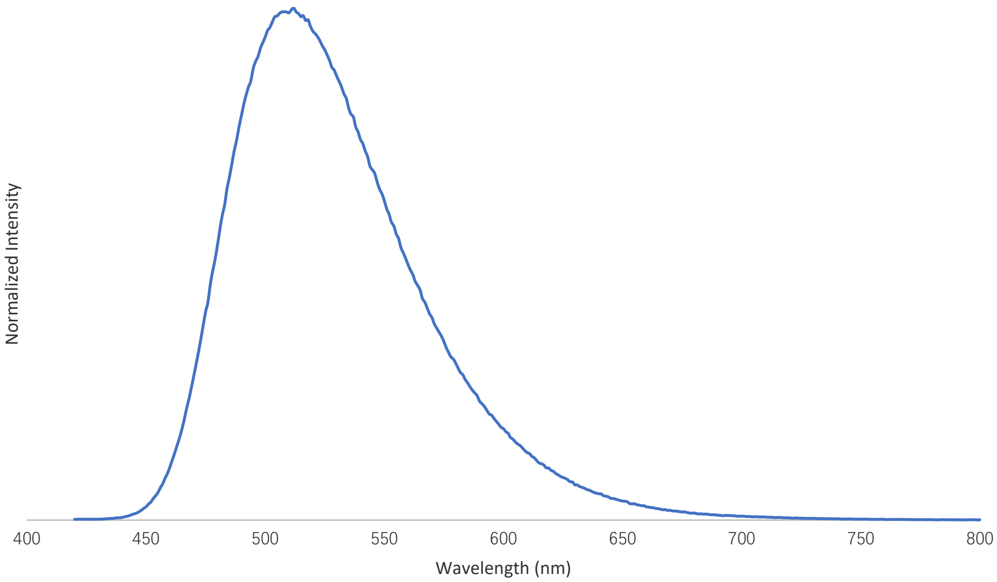


Figure S28 Emission spectrum of compound **1g**

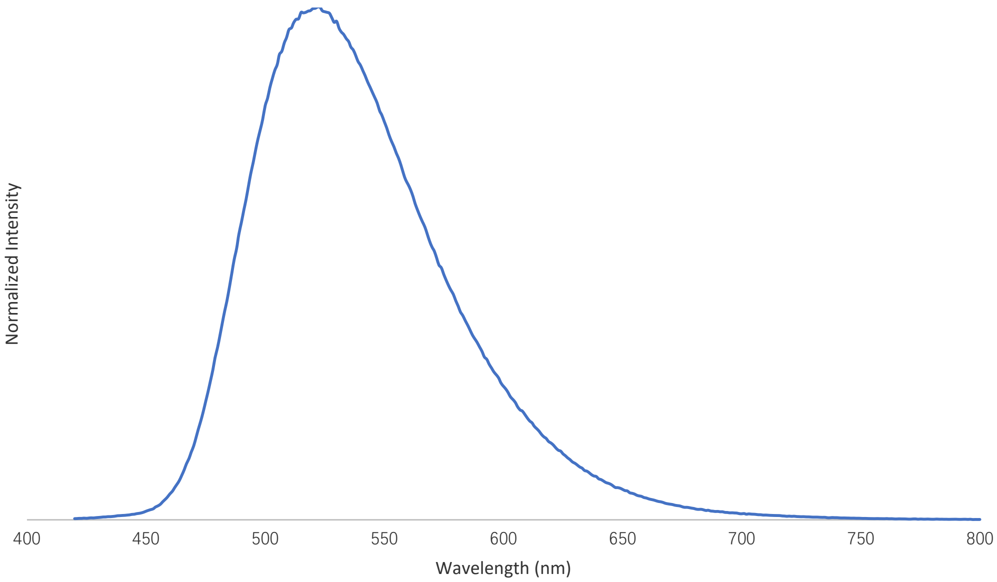


Figure S29 Emission spectrum of compound **1h**

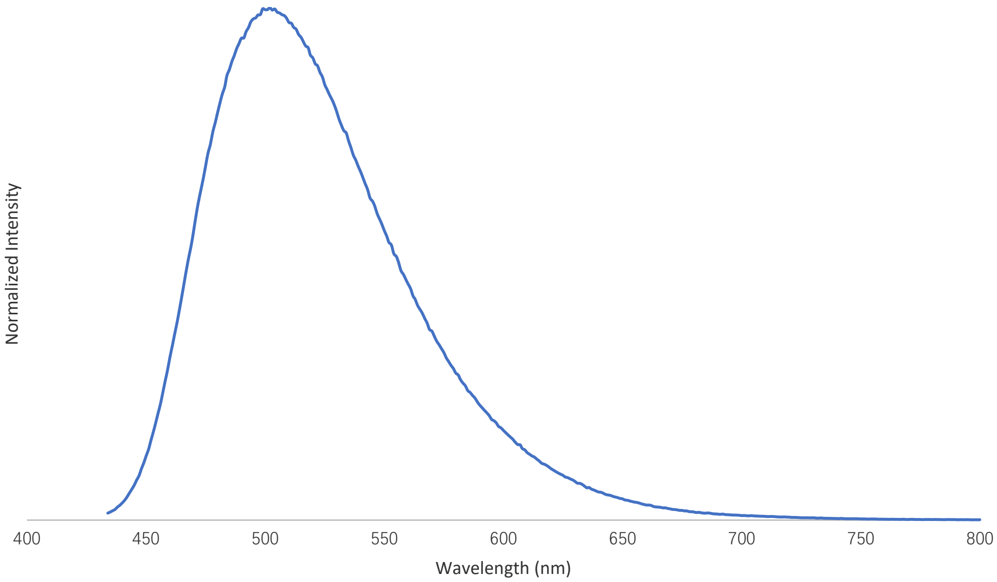


Figure S30 Emission spectrum of compound **1i**

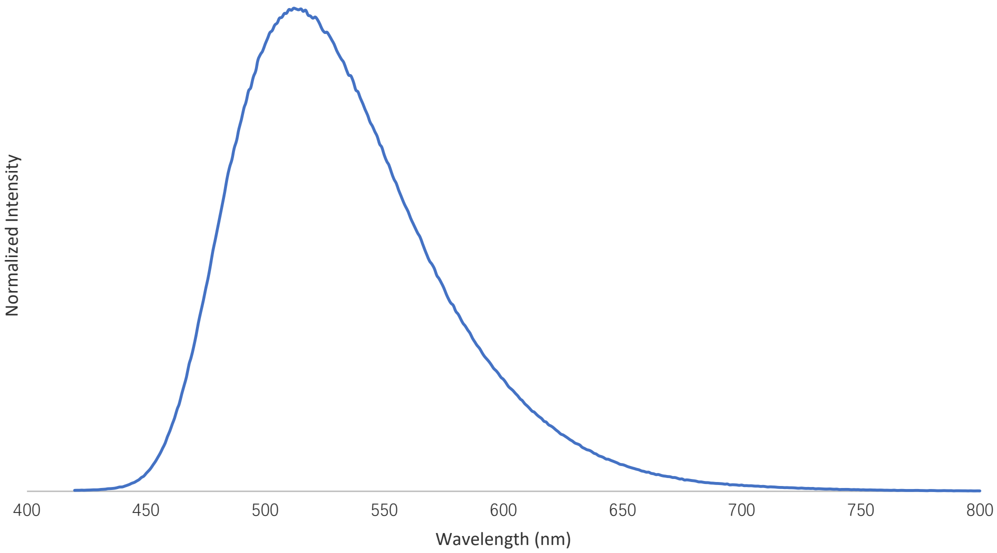


Figure S31 Emission spectrum of compound **1j**

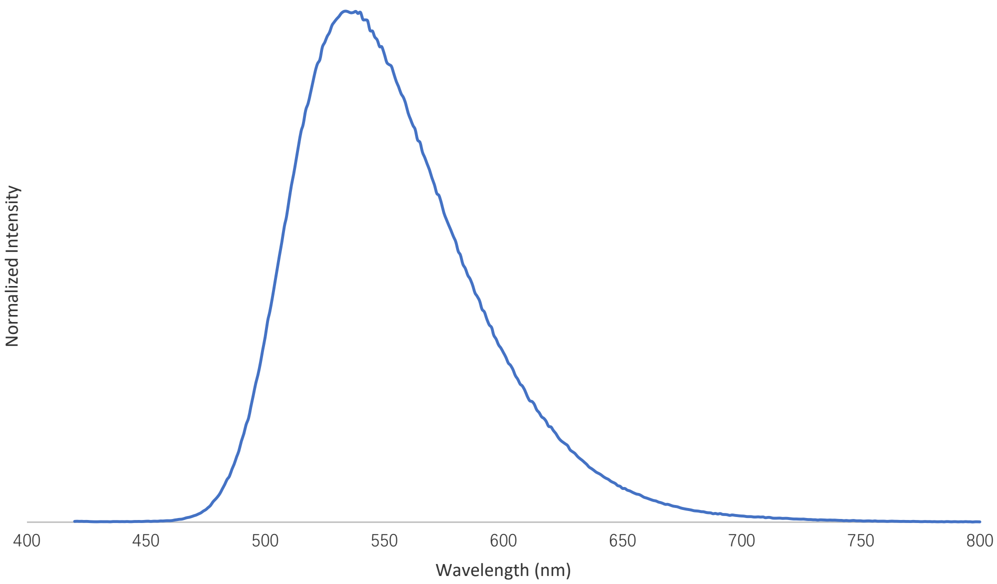


Figure S32 Emission spectrum of compound **1k**

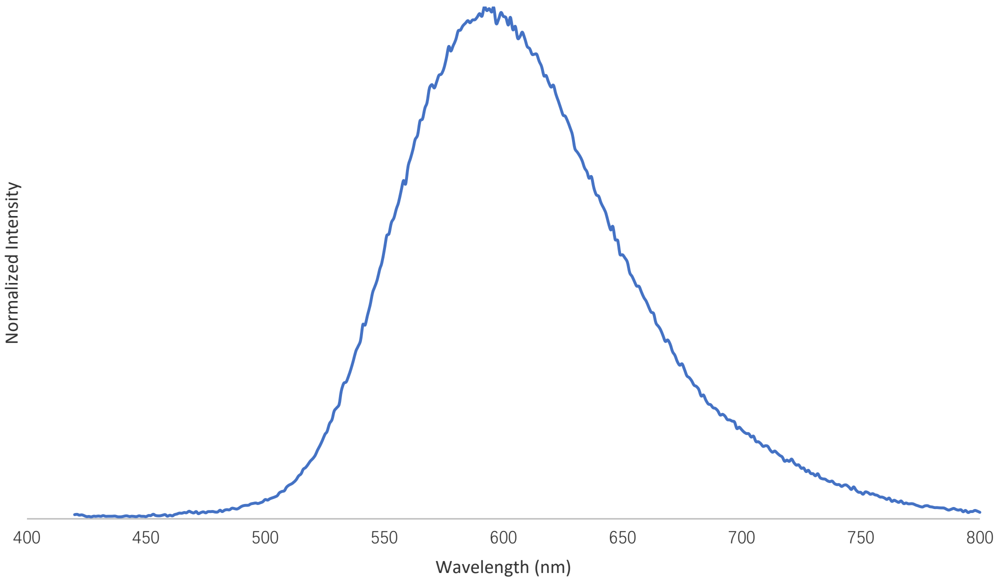


Figure S33 Emission spectrum of compound **1l**

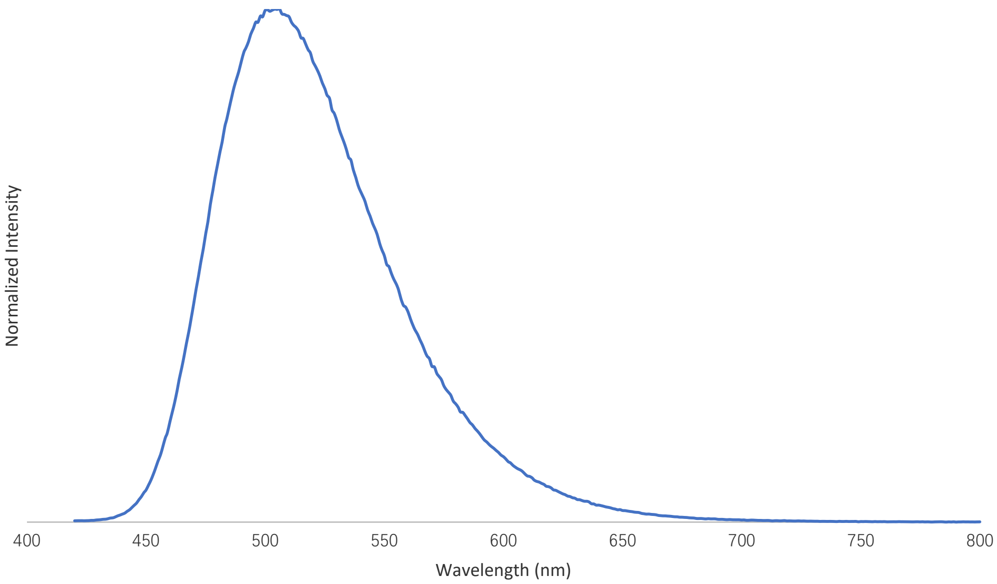


Figure S34 Emission spectrum of compound **1m**

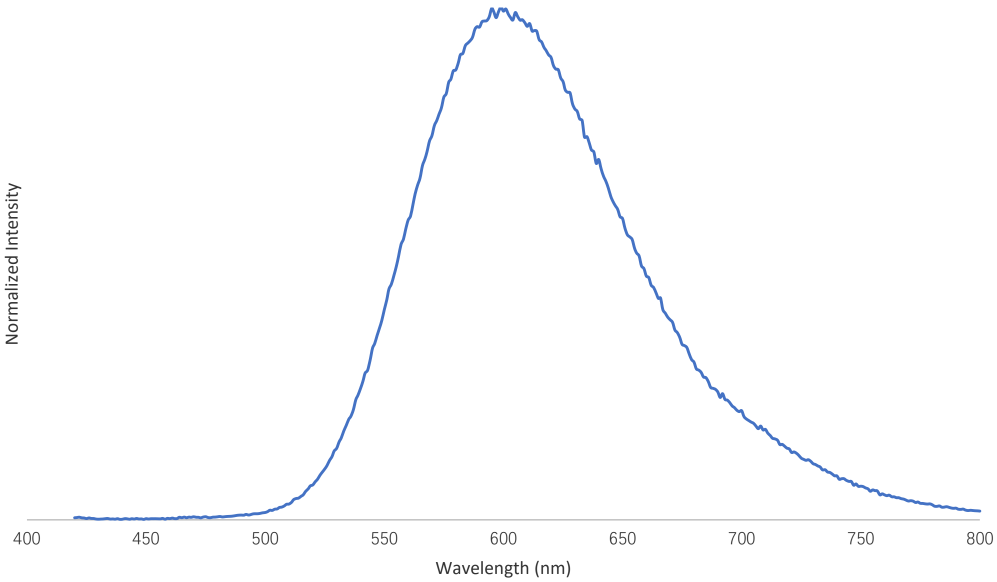


Figure S35 Emission spectrum of compound **1n**

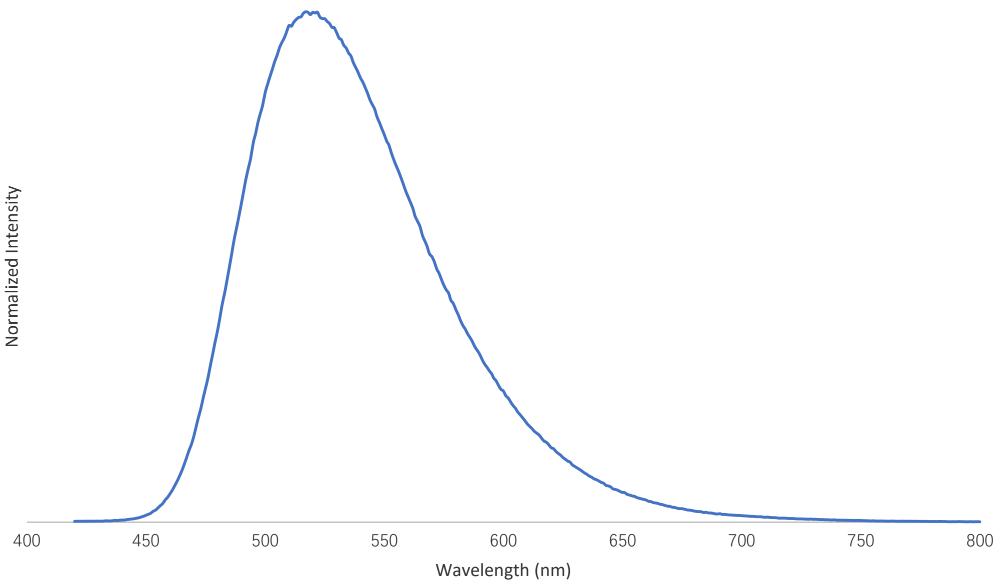


Figure S36 Emission spectrum of compound **1o**

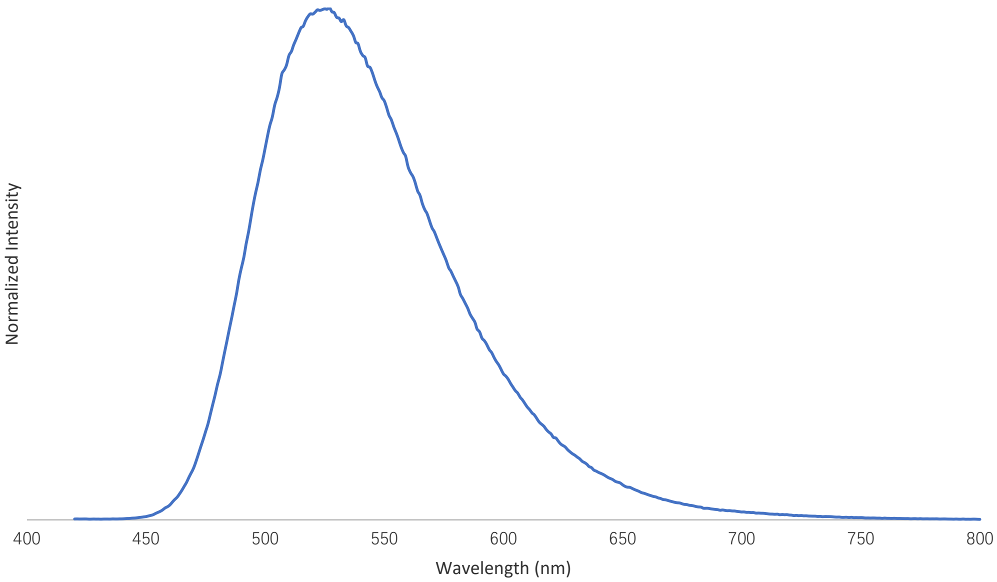


Figure S37 Emission spectrum of compound **1p**

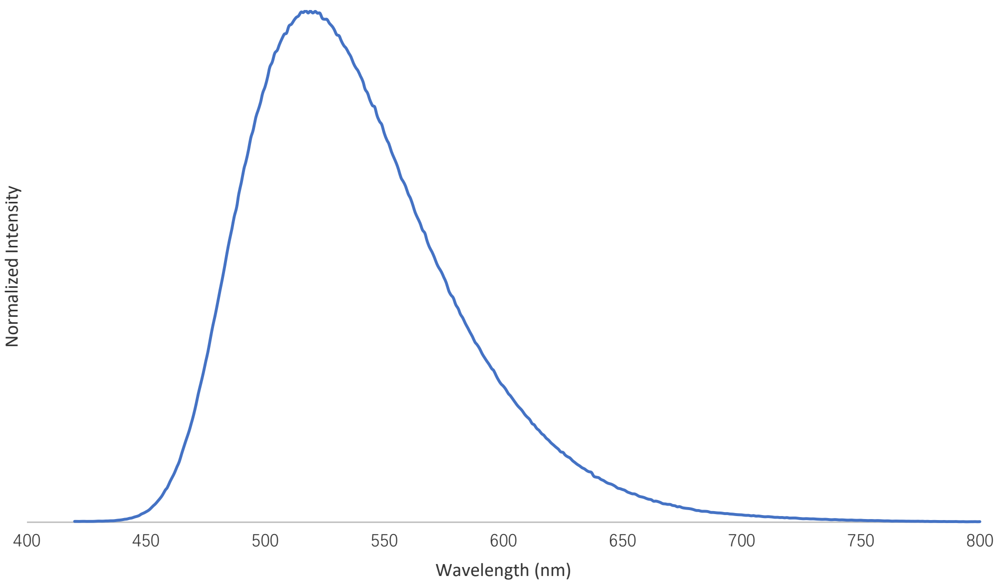


Figure S38 Emission spectrum of compound **1q**

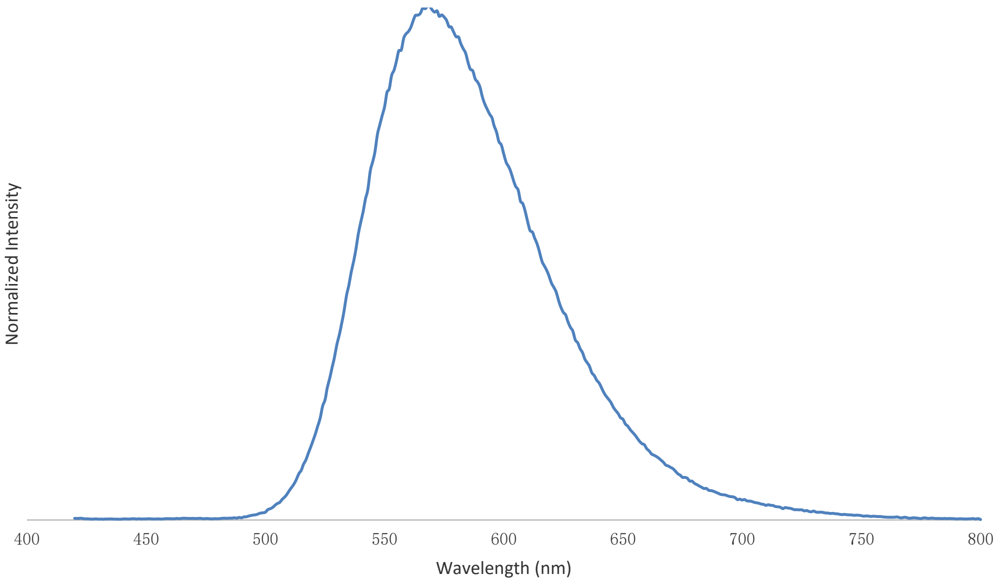


Figure S39 Emission spectrum of compound **1r**

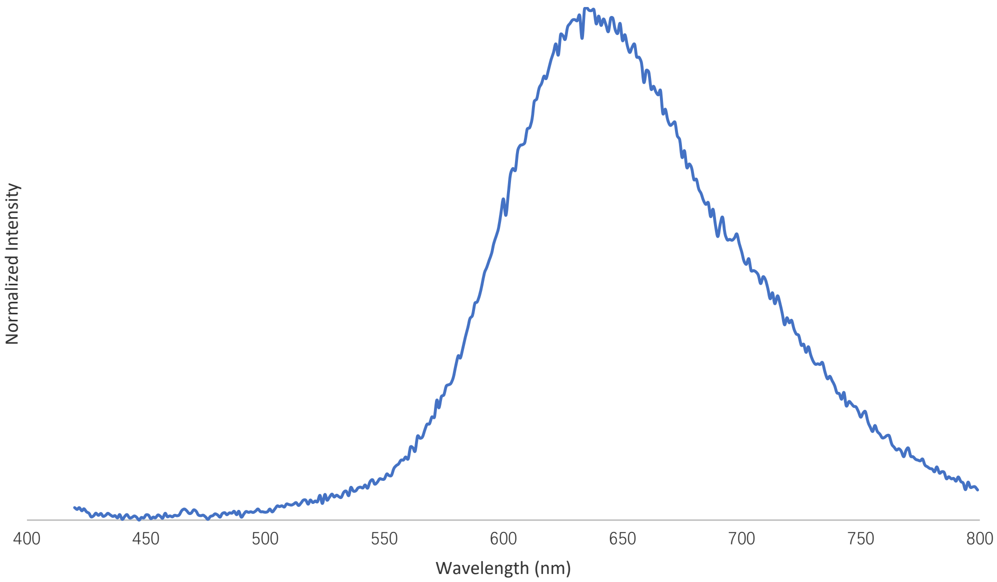


Figure S40 Emission spectrum of compound **1s**

DFT Calculations

All calculations were performed using Gaussian 16/A.03.[1] The counter ion was omitted for all calculations. DFT geometry optimizations were performed using B3LYP/Def2SVPP functional/basis set.[2-3] Frequency calculations were performed for the optimized structures. No imaginary vibrational frequency was encountered confirming the optimized stationary point to be local minimum. TD-DFT calculations were conducted for the first 32 excited states and the CH_2Cl_2 PCM solvent model was used.[4] Natural transition orbitals (NTOs) were calculated for the excited state S_1 for compounds **1b** and **1c**.[5]

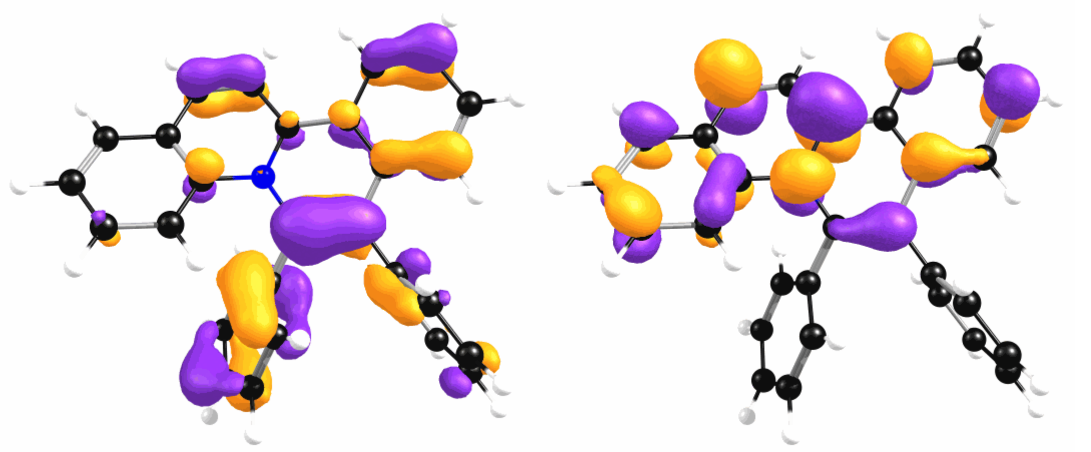


Figure S41 (left) HOMO of compound **1b**; (right) LUMO of compound **1b** (isovalue = 0.04).

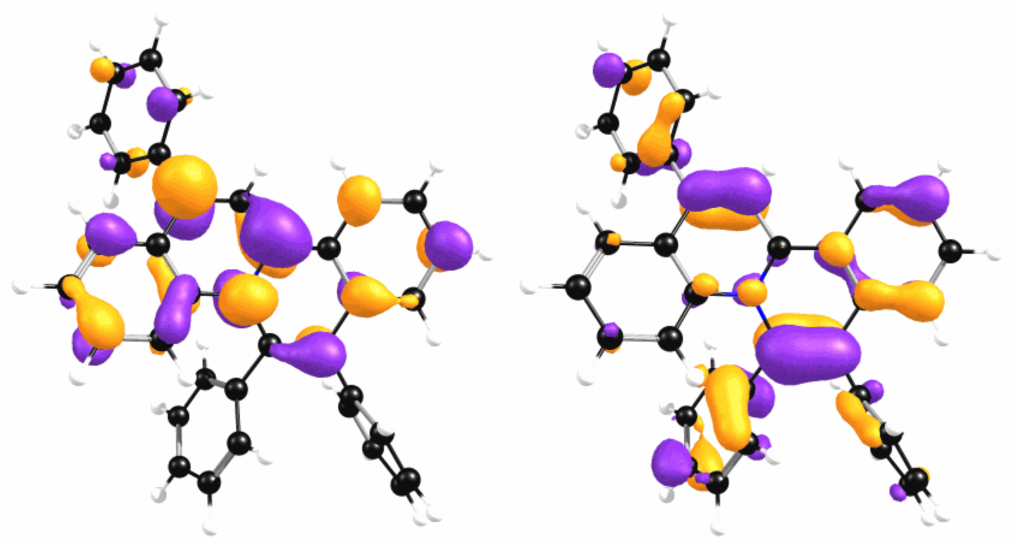


Figure S42 (left) HOMO of compound **1c**; (right) LUMO of compound **1c** (isovalue = 0.04).

Table S5 TD-DFT excitation energies and oscillator strengths (*f*) of **1b** and **1c**.

Compound **1b**				Compound **1c**			
excited state	nm	eV	*f*	excited state	nm	eV	*f*
1	428.67	2.8923	0.1351	1	443.03	2.7986	0.3421
2	382.05	3.2452	0.0595	2	390.47	3.1753	0.1216
3	372	3.3329	0.0102	3	374.55	3.3102	0.009
4	357.48	3.4683	0.0487	4	364.73	3.3993	0.0638
5	354.19	3.5005	0.0755	5	357.44	3.4686	0.0131
6	343.57	3.6087	0.0009	6	352.1	3.5213	0.0101
7	318.89	3.888	0.2744	7	345.37	3.5899	0.0067
8	308.56	4.0182	0.0116	8	340.35	3.6428	0.0585
9	296.8	4.1774	0.1841	9	321.15	3.8606	0.3571
10	292.23	4.2427	0.1816	10	309.58	4.0049	0.0303
11	284.61	4.3563	0.1787	11	300.27	4.1291	0.2699
12	284.12	4.3638	0.1385	12	293.67	4.2219	0.0685
13	277.86	4.462	0.0533	13	290.38	4.2697	0.0077
14	275.59	4.4989	0.2415	14	286.96	4.3206	0.0493
15	261.88	4.7345	0.1826	15	279.06	4.4429	0.2024
16	255.19	4.8585	0.1118	16	276.28	4.4876	0.0691
17	251.09	4.9378	0.0254	17	270.88	4.577	0.0102
18	249.71	4.9651	0.0485	18	266.26	4.6566	0.1342
19	246.95	5.0207	0.0853	19	263.03	4.7137	0.1896
20	245	5.0606	0.0704	20	256.3	4.8375	0.085
21	242.89	5.1046	0.023	21	253.38	4.8932	0.0792
22	240.46	5.1562	0.0048	22	251.52	4.9294	0.0263
23	238.31	5.2025	0.02	23	250.82	4.9431	0.1487
24	236.34	5.246	0.0348	24	247.32	5.0131	0.0204
25	233.86	5.3015	0.0049	25	246.06	5.0387	0.0335
26	229.92	5.3925	0.0194	26	244.38	5.0734	0.0373
27	226.4	5.4764	0.0222	27	241.42	5.1357	0.0102
28	224.34	5.5266	0.0404	28	239.04	5.1868	0.0858
29	222.72	5.5668	0.0074	29	238.78	5.1925	0.0124
30	221.01	5.6099	0.0052	30	236.23	5.2485	0.0067
31	220.06	5.6341	0.0081	31	234.62	5.2844	0.0055
32	219.74	5.6424	0.0632	32	233.98	5.2989	0.0297

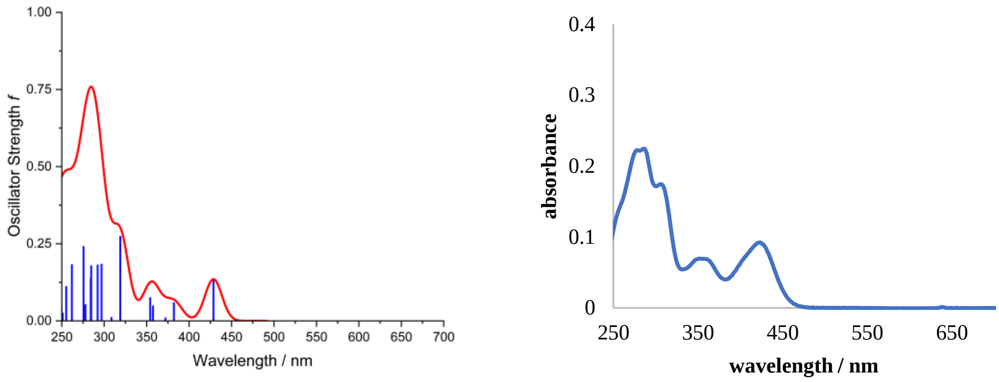


Figure S43 Left: Simulated absorption spectrum of **1b** assuming a Gaussian line-shape for each transition, with width 25 nm. Calculated for the first 64 excited states. Right: Experimental absorption spectrum of **1b**.

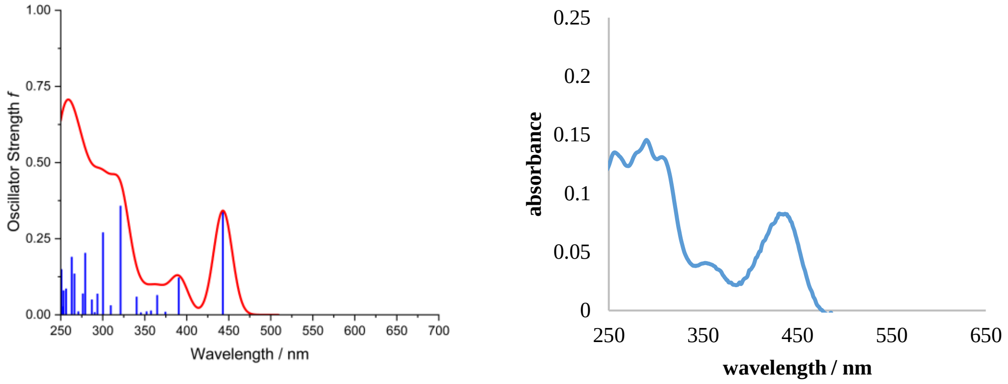


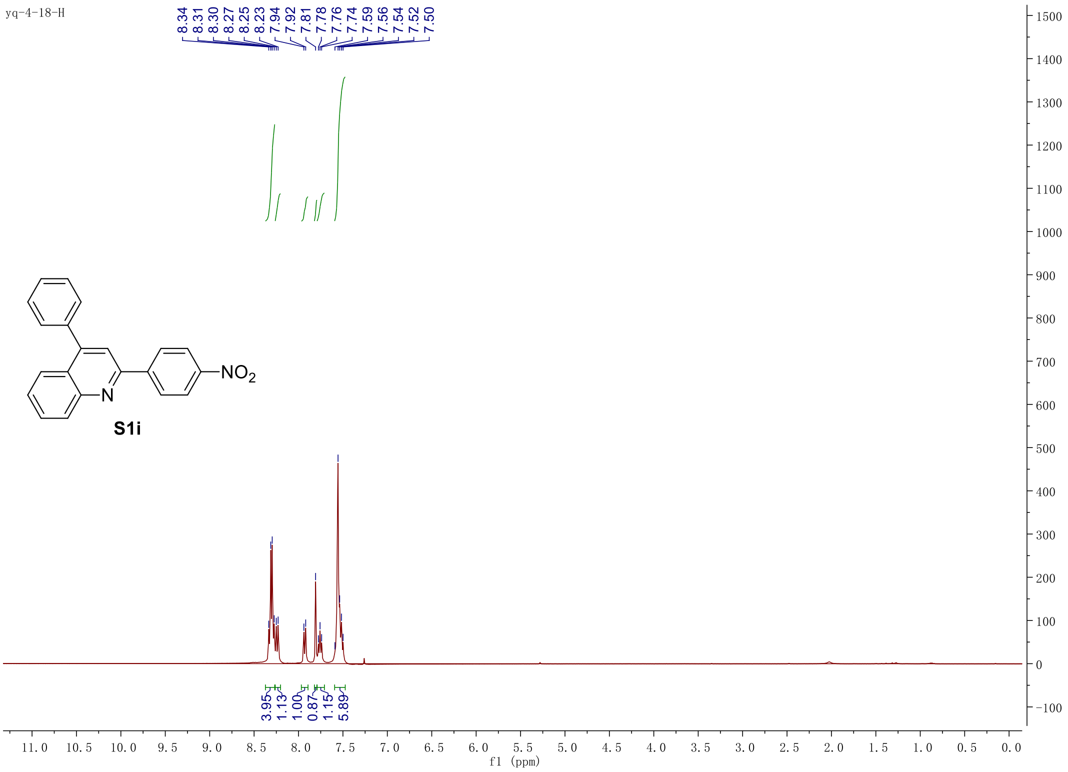
Figure S44 Left: Simulated absorption spectrum of **1c** assuming a Gaussian line-shape for each transition, with width 25 nm. Calculated for the first 64 excited states. Right: Experimental absorption spectrum of **1c**.

1. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari,

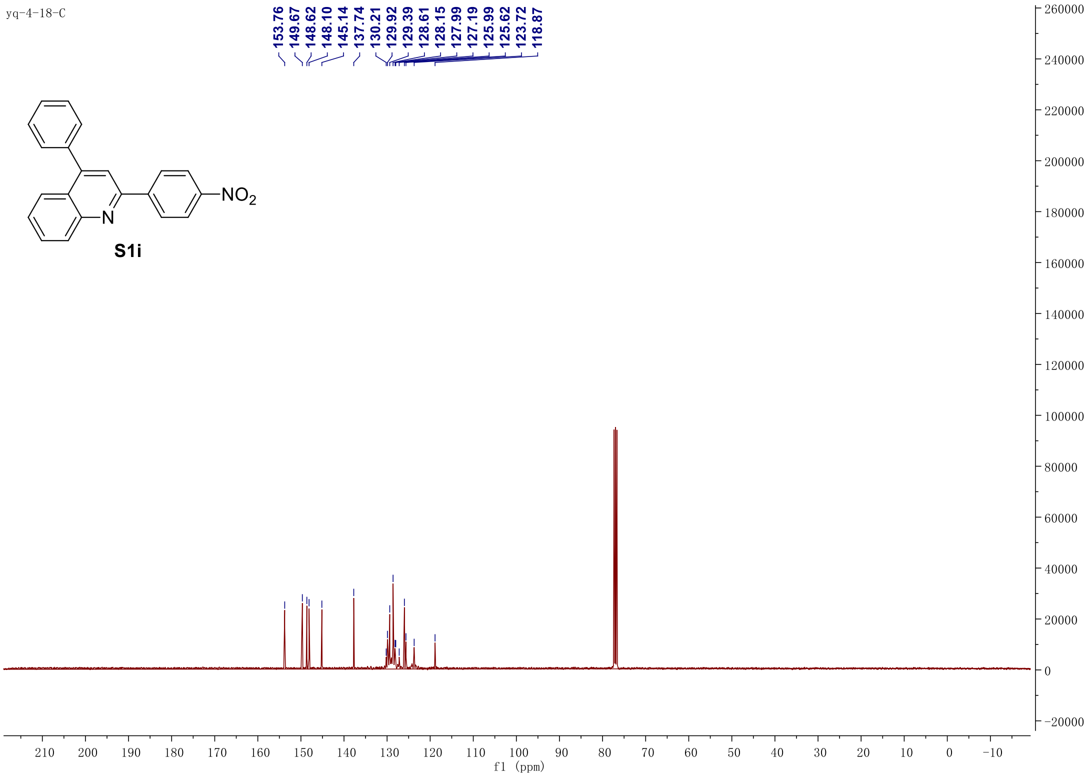
A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

2. J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, **2008**, *10*, 6615.
3. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, **2005**, *7*, 3297.
4. Furche, F.; Ahlrichs, R. Adiabatic Time-Dependent Density Functional Methods for Excited State Properties. *J. Chem. Phys.* **2002**, *117*, 7433.
5. Martin, R. L. Natural Transition Orbitals. *J. Chem. Phys.* **2003**, *118*, 4775.

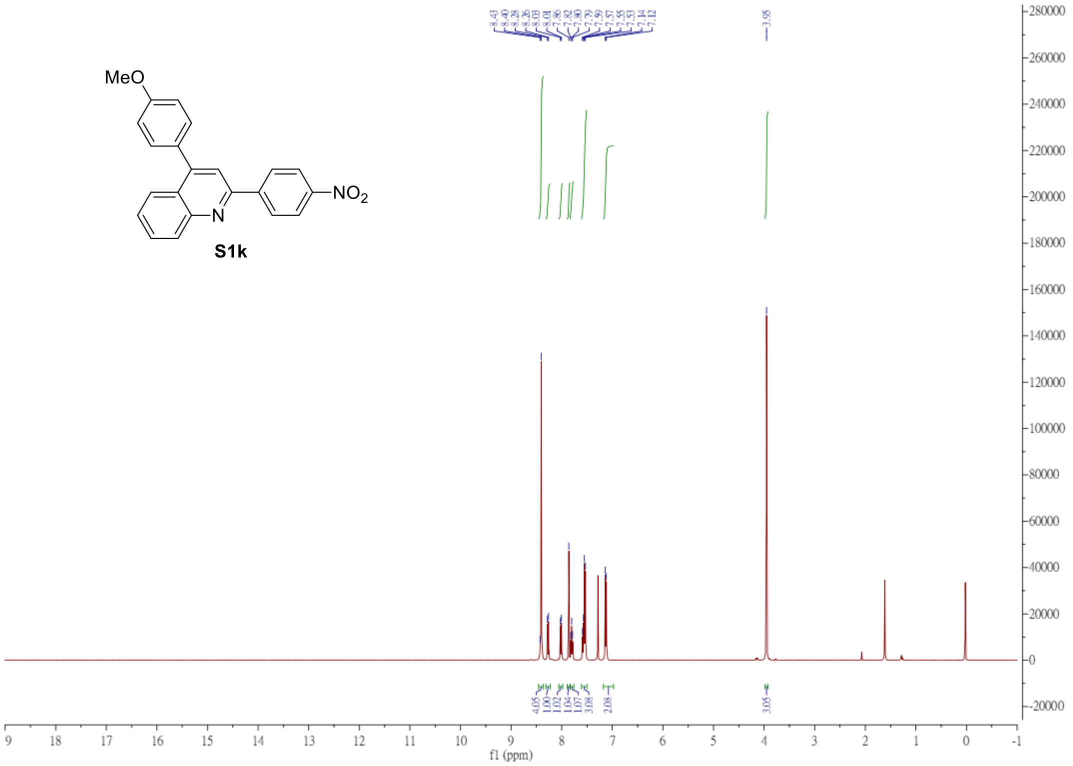
^{1}H NMR S1i



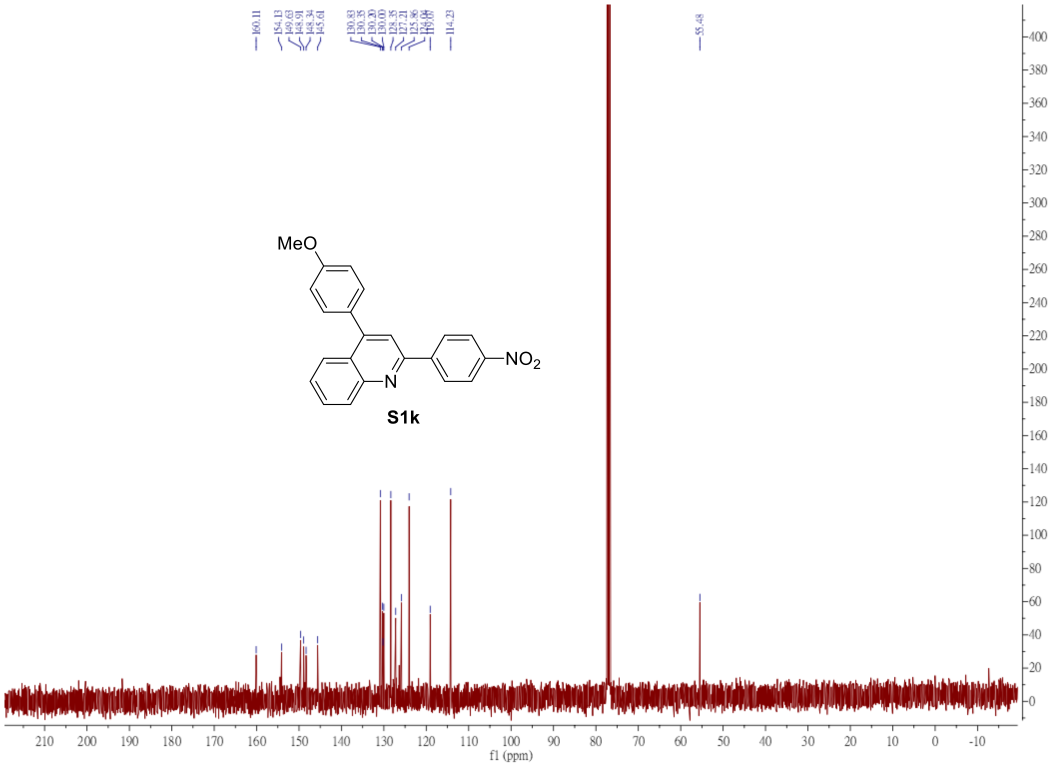
^{13}C NMR



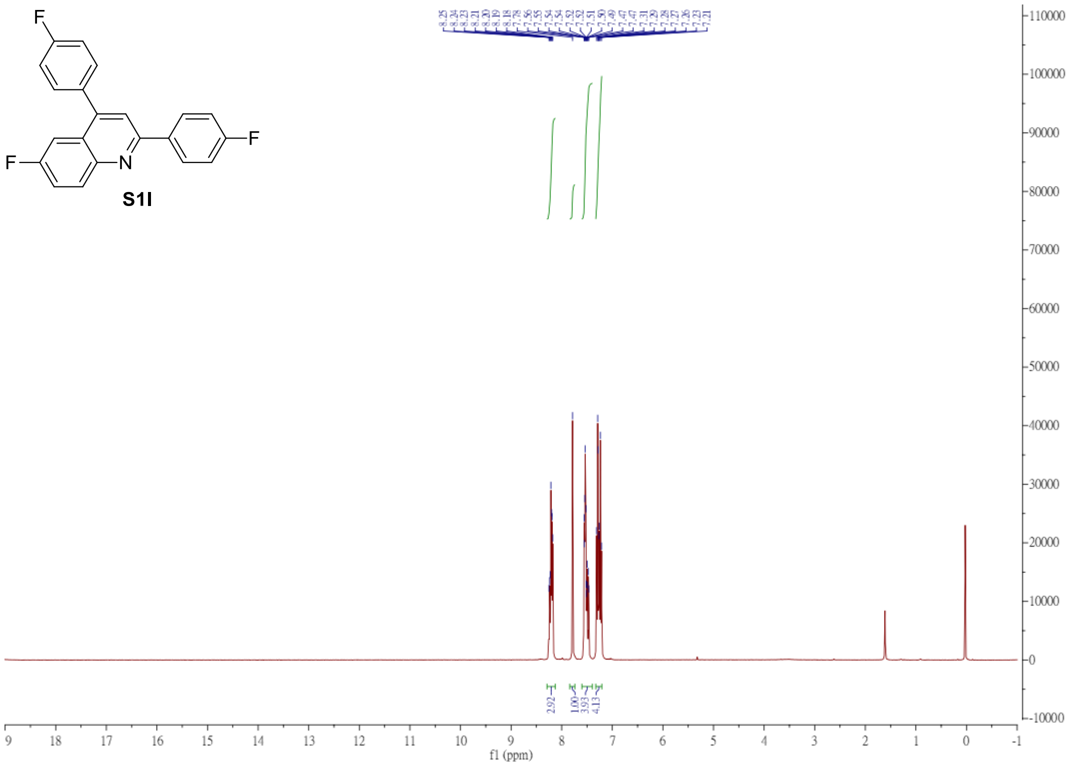
^{1}H NMR S1k



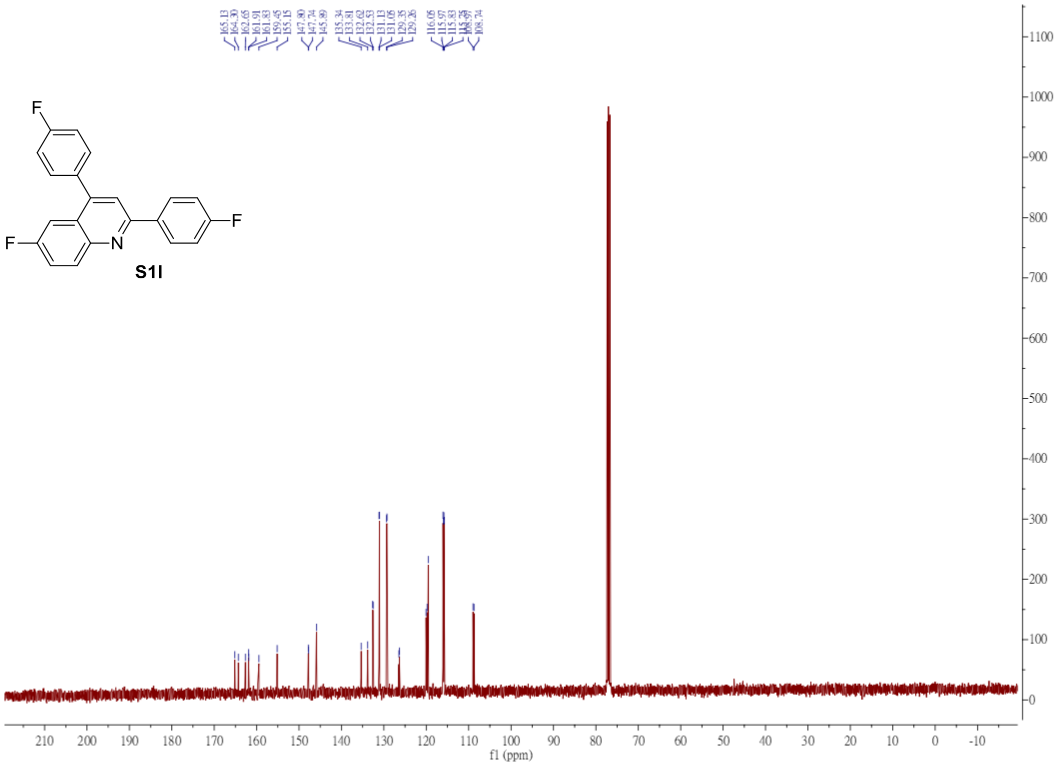
^{13}C NMR



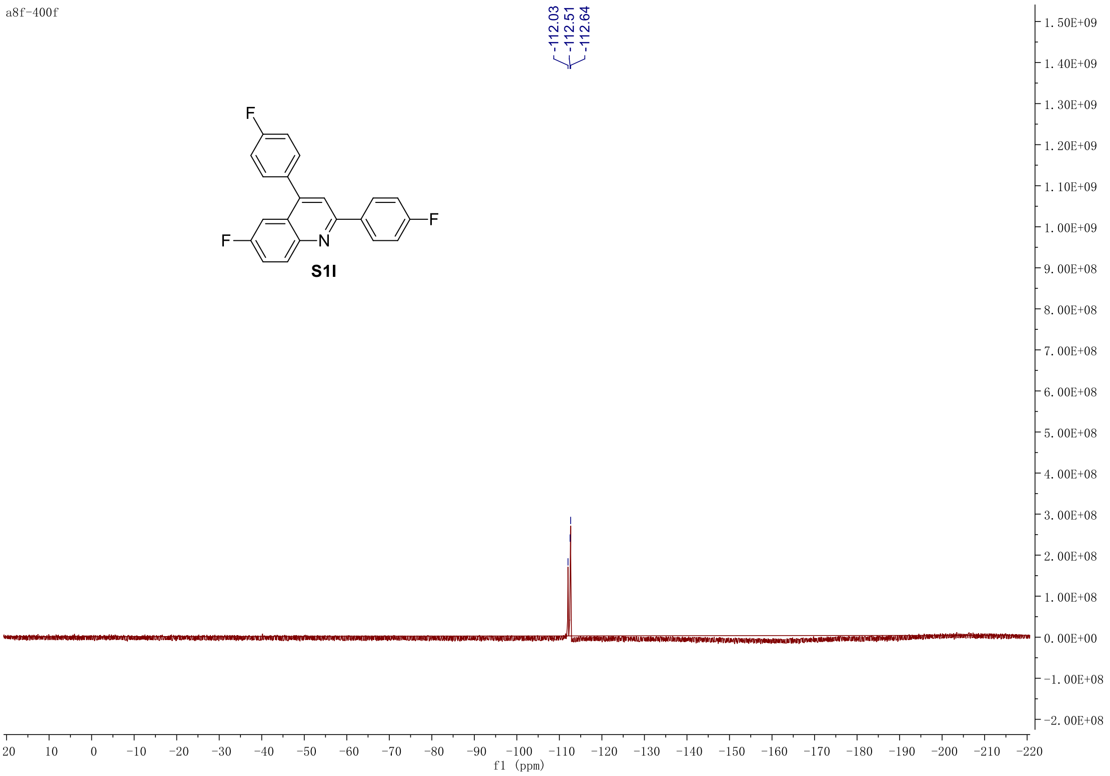
^{1}H NMR S1l



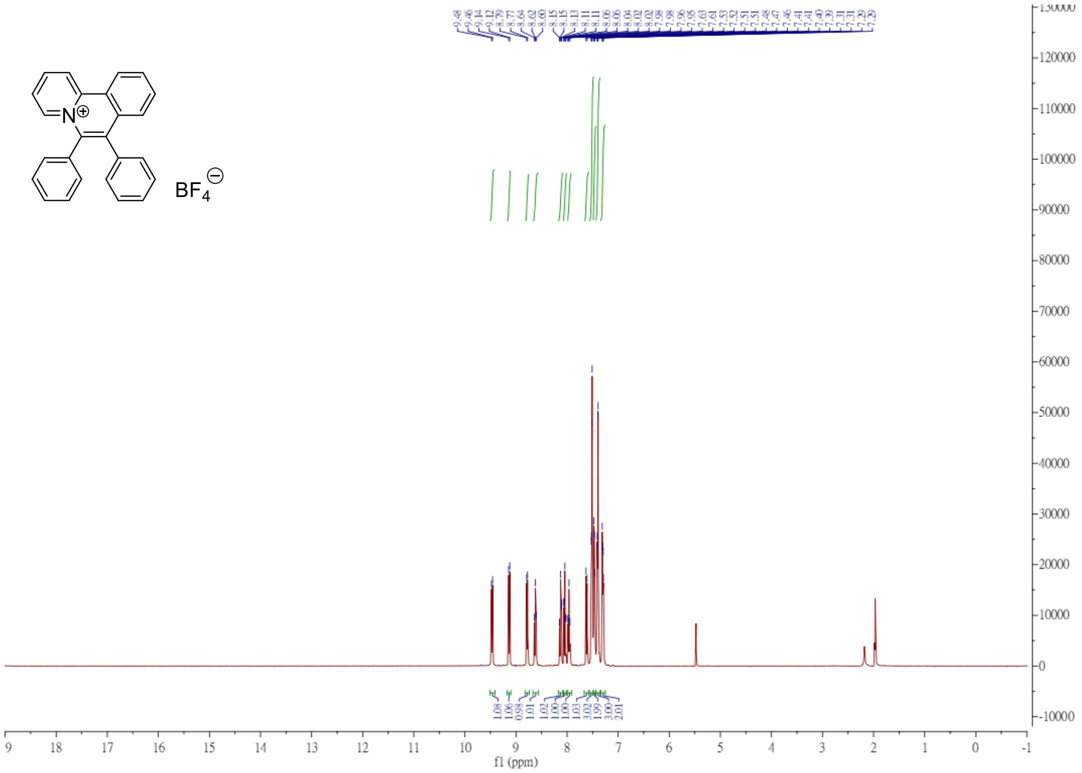
^{13}C NMR



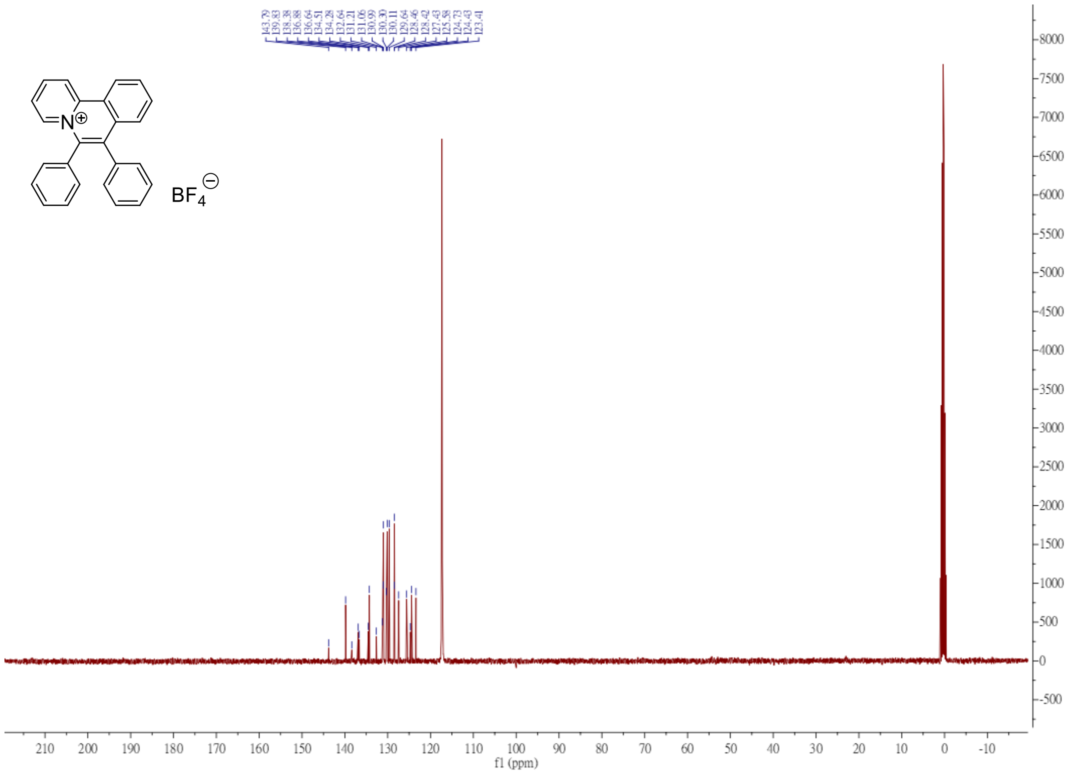
^{19}F NMR


a8f-400f
-112.03
-112.51
-112.64
F
F
F
N
S1l
1.50E+09
1.40E+09
1.30E+09
1.20E+09
1.10E+09
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
−1.00E+08
−2.00E+08
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

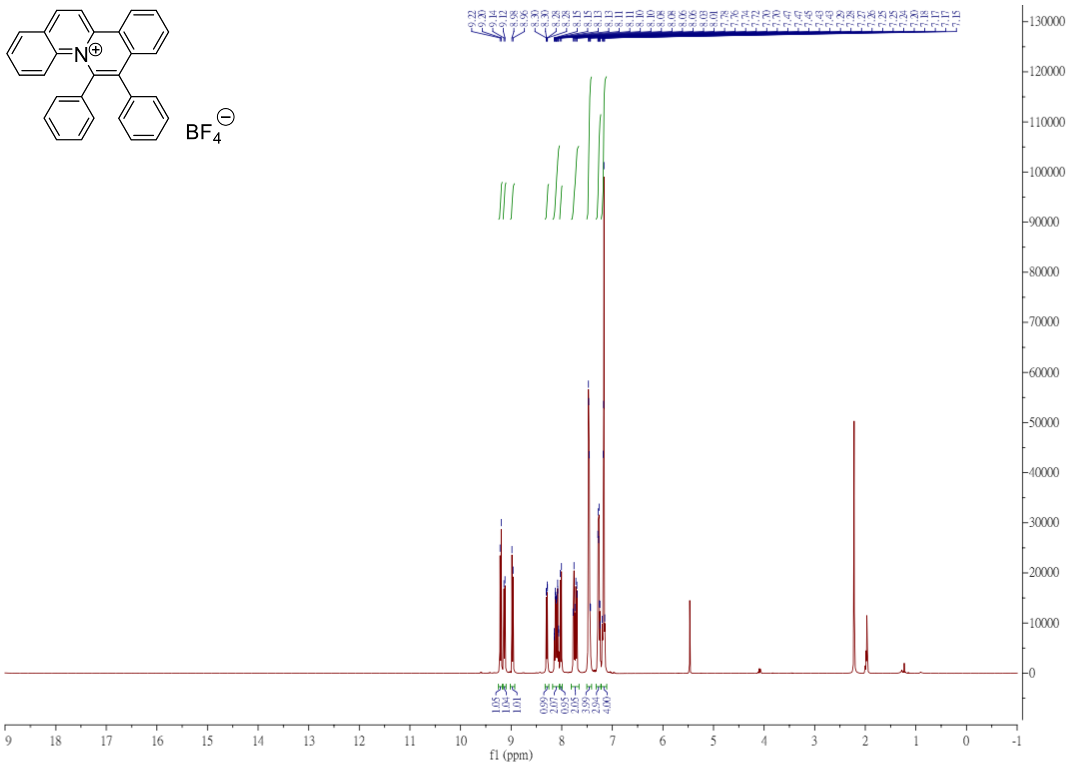
^{1}H NMR 1a



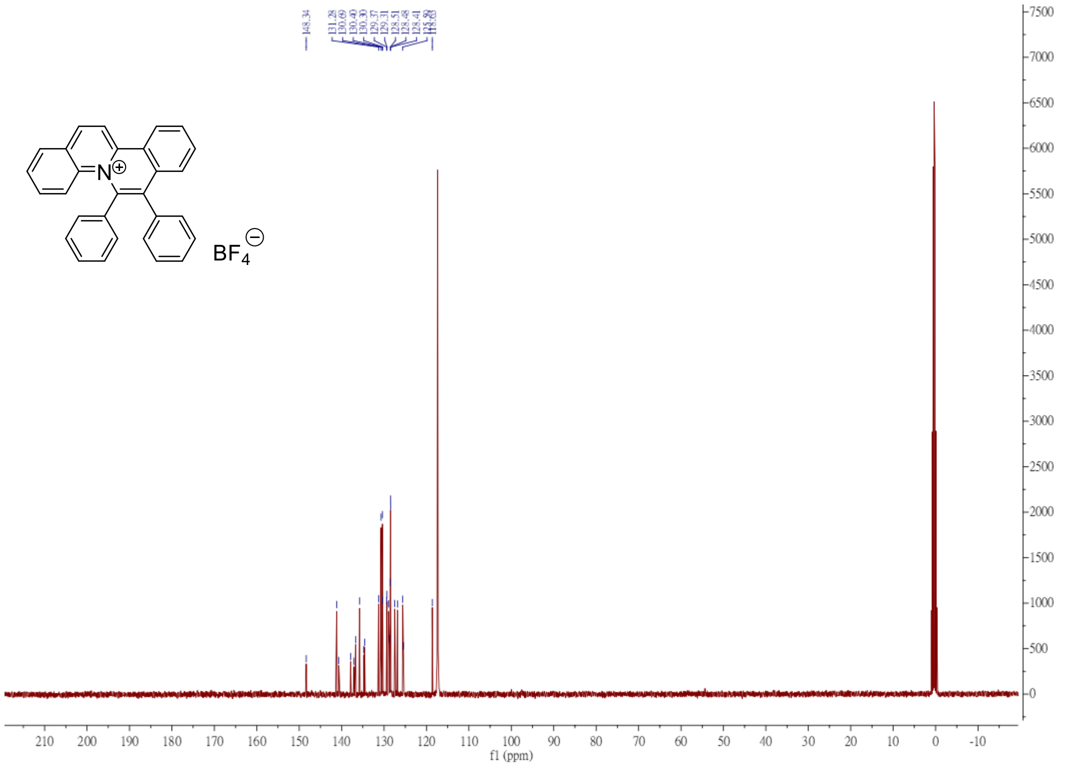
^{13}C NMR



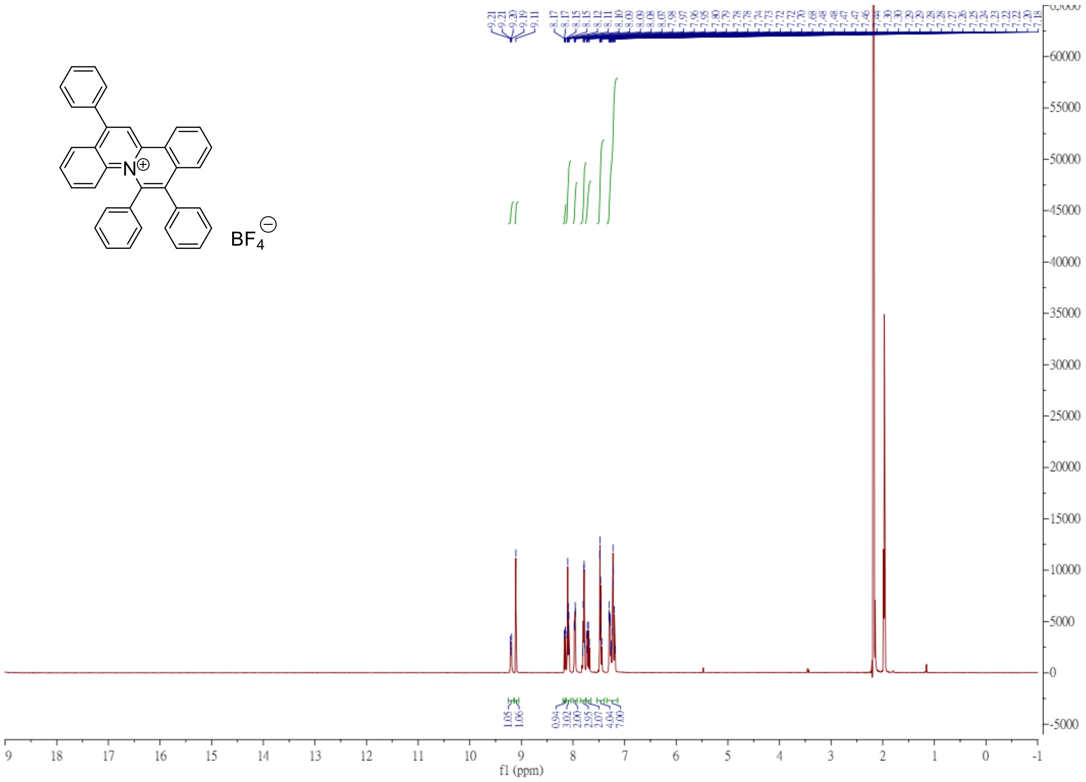
^{1}H NMR 1b



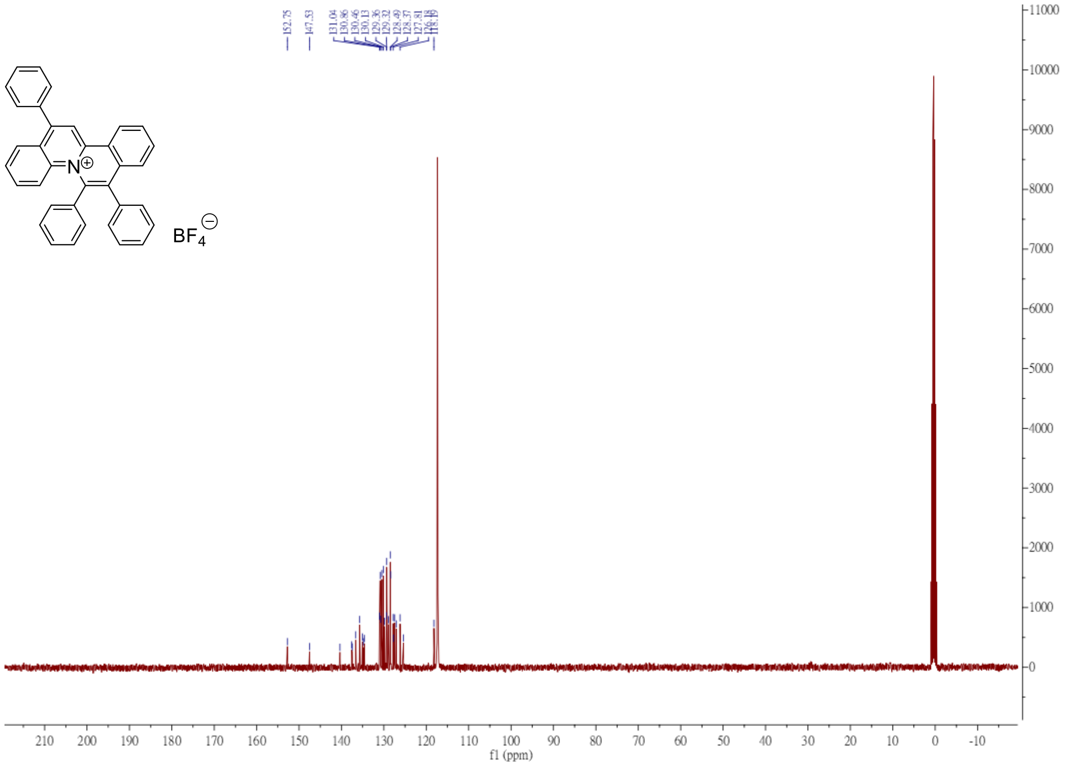
^{13}C NMR



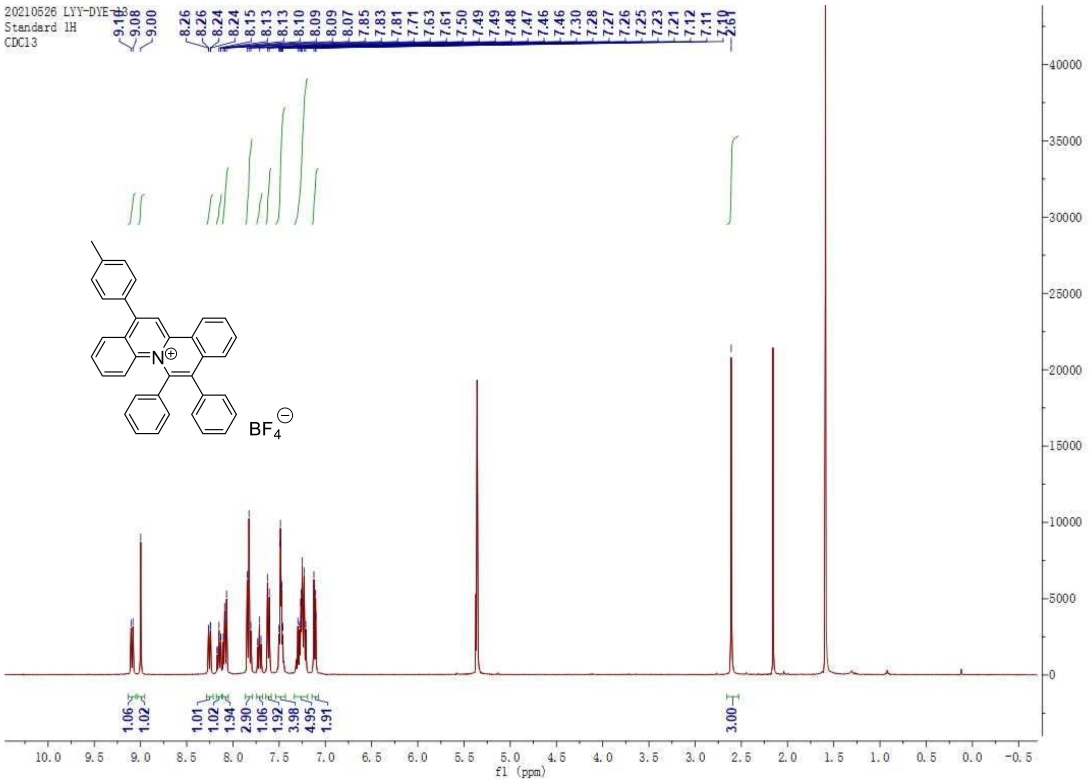
^{1}H NMR 1c



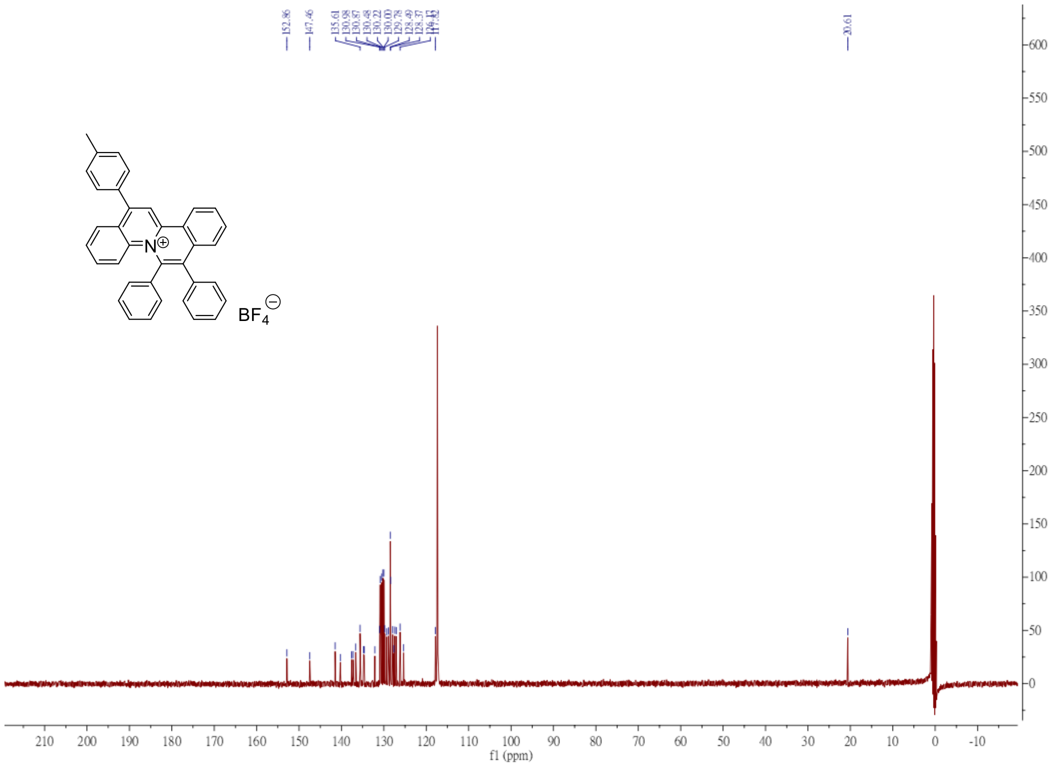
^{13}C NMR



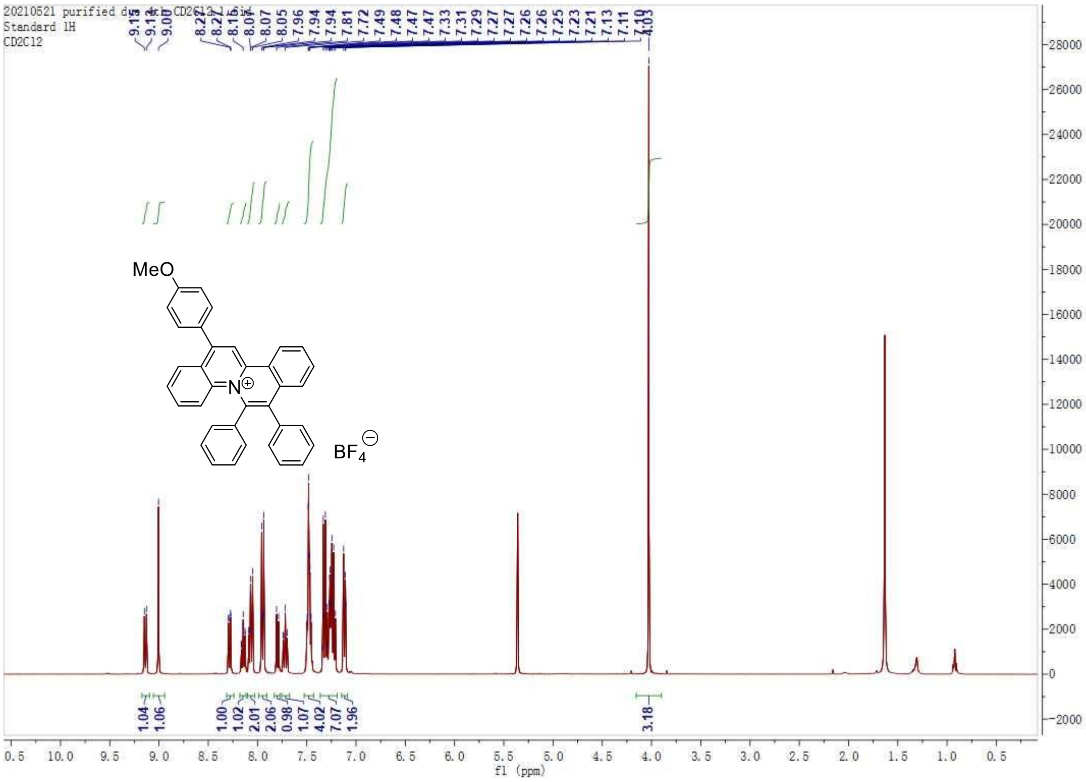
^{1}H NMR 1d



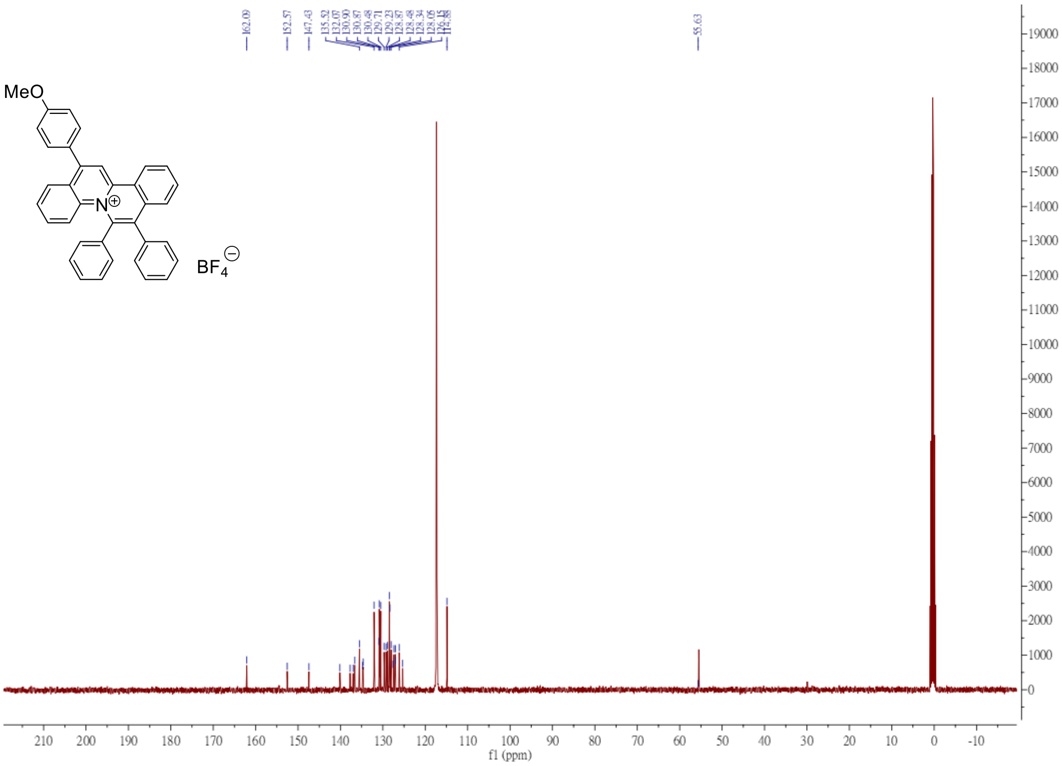
^{13}C NMR



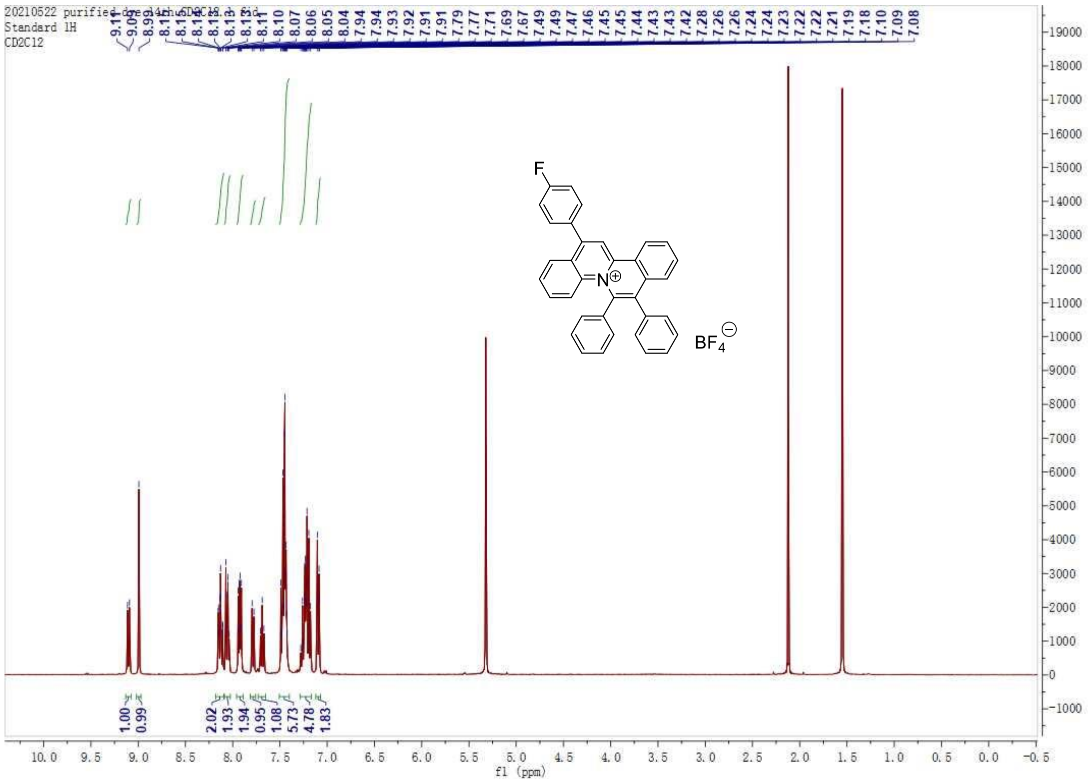
^{1}H NMR 1e



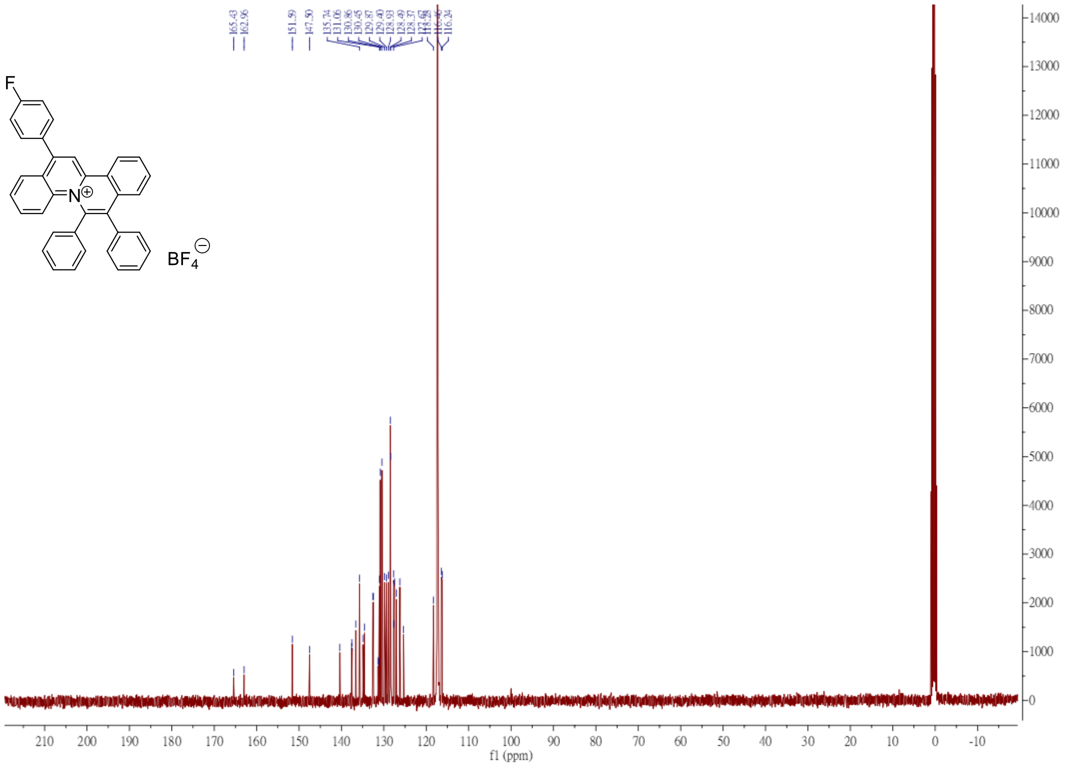
^{13}C NMR



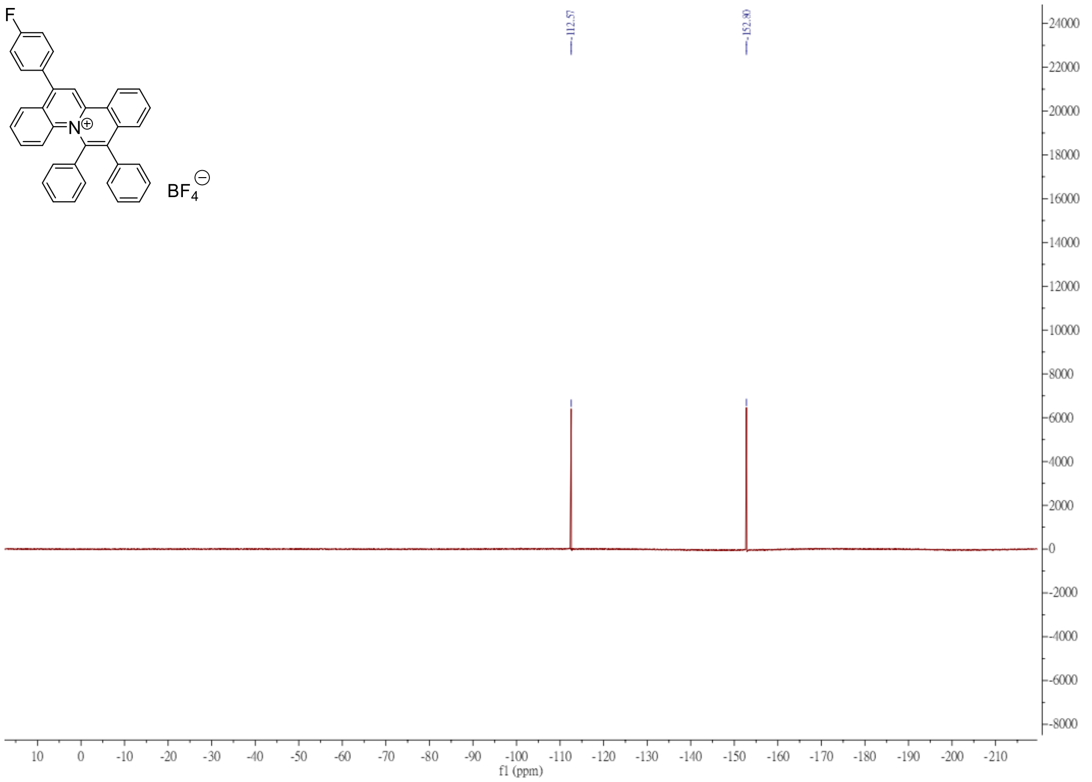
^{1}H NMR 1f



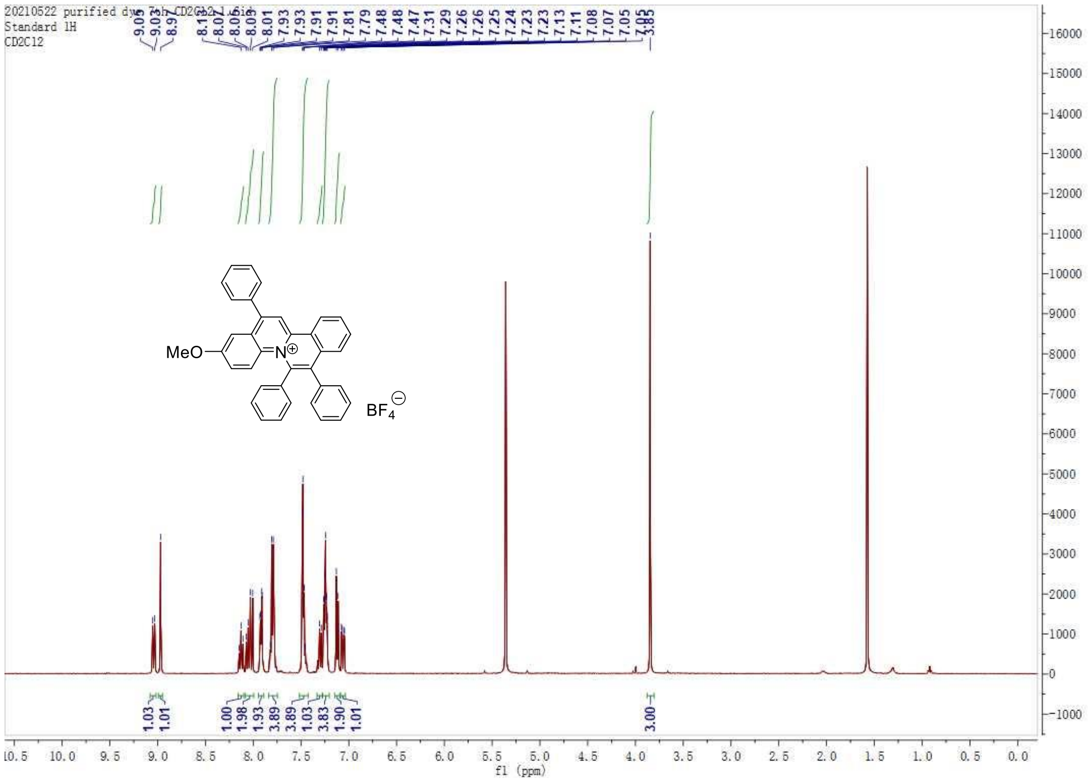
^{13}C NMR



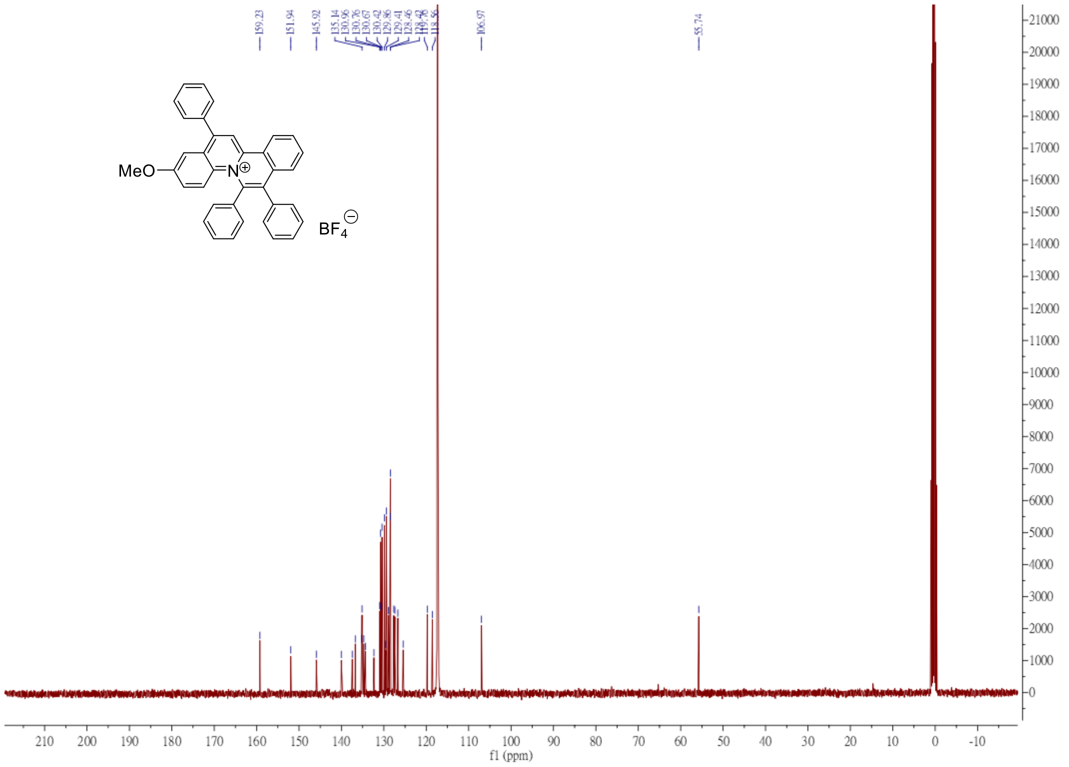
^{19}F NMR


F
N⊕
BF4⊖
-112.57
-152.80
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
-6000
-8000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

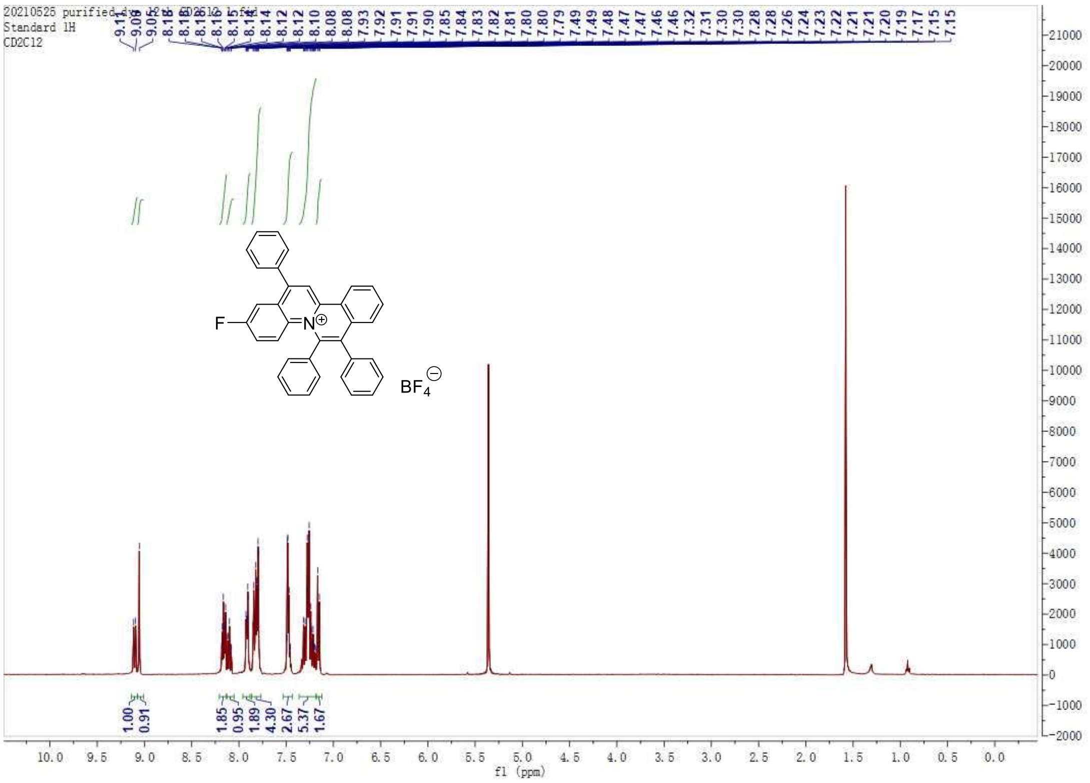
^{1}H NMR 1g



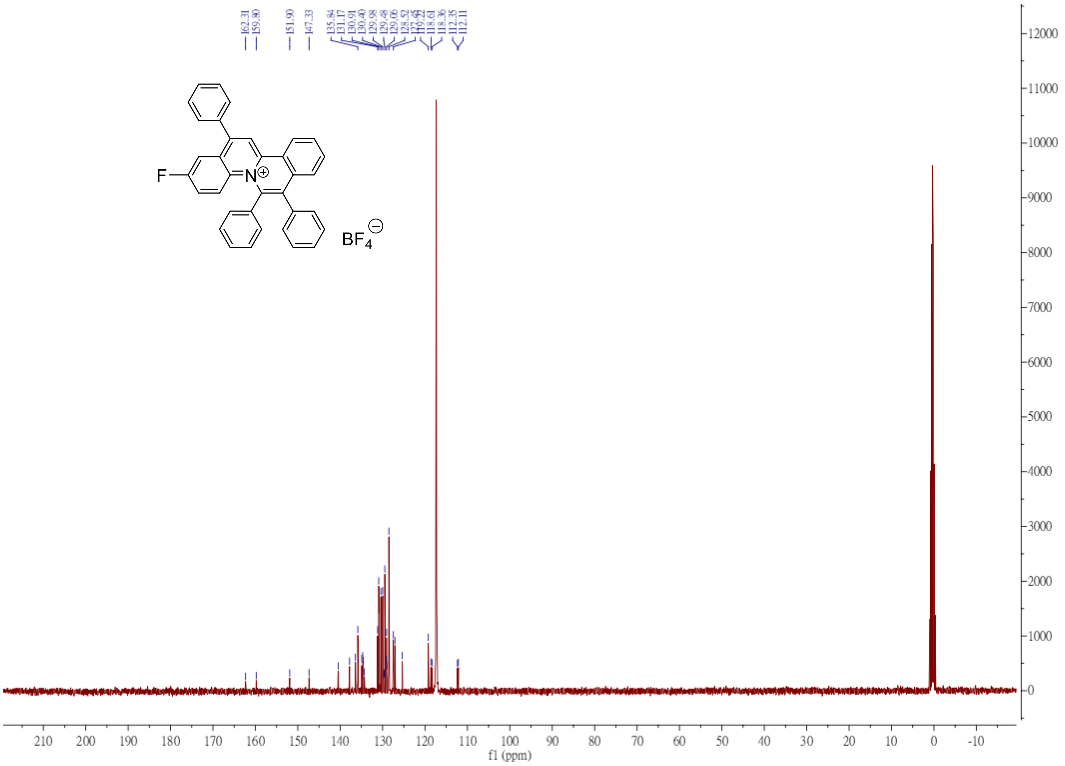
^{13}C NMR



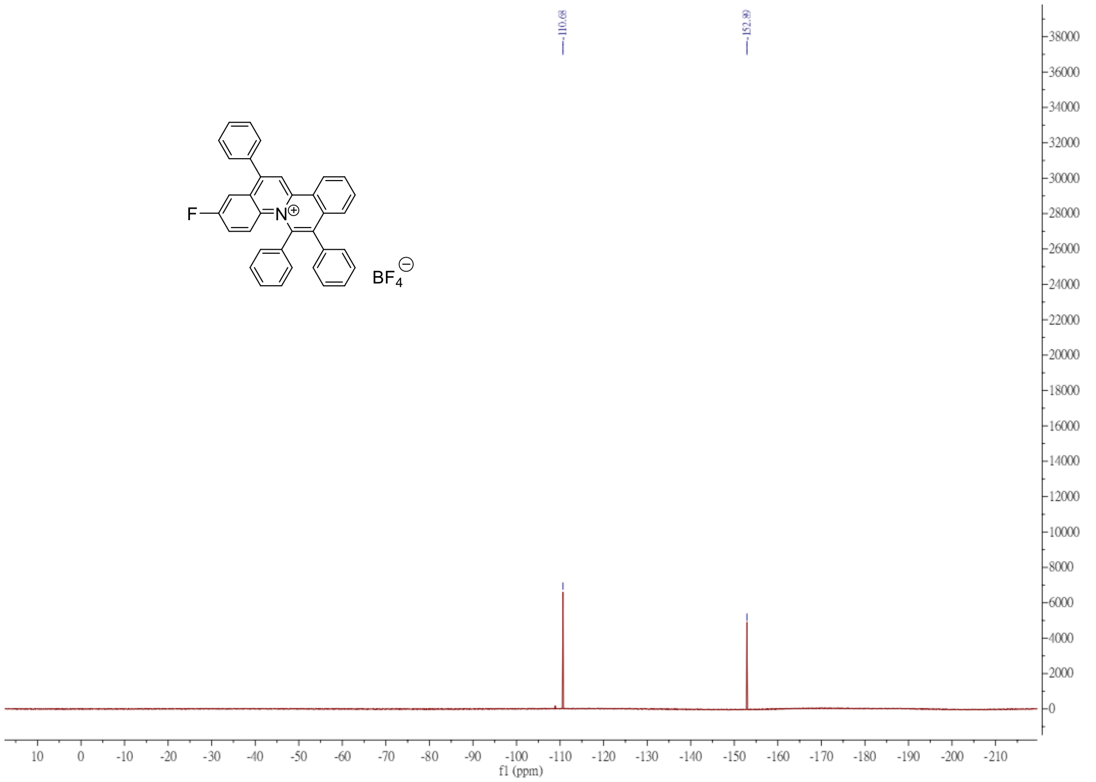
^{1}H NMR 1h



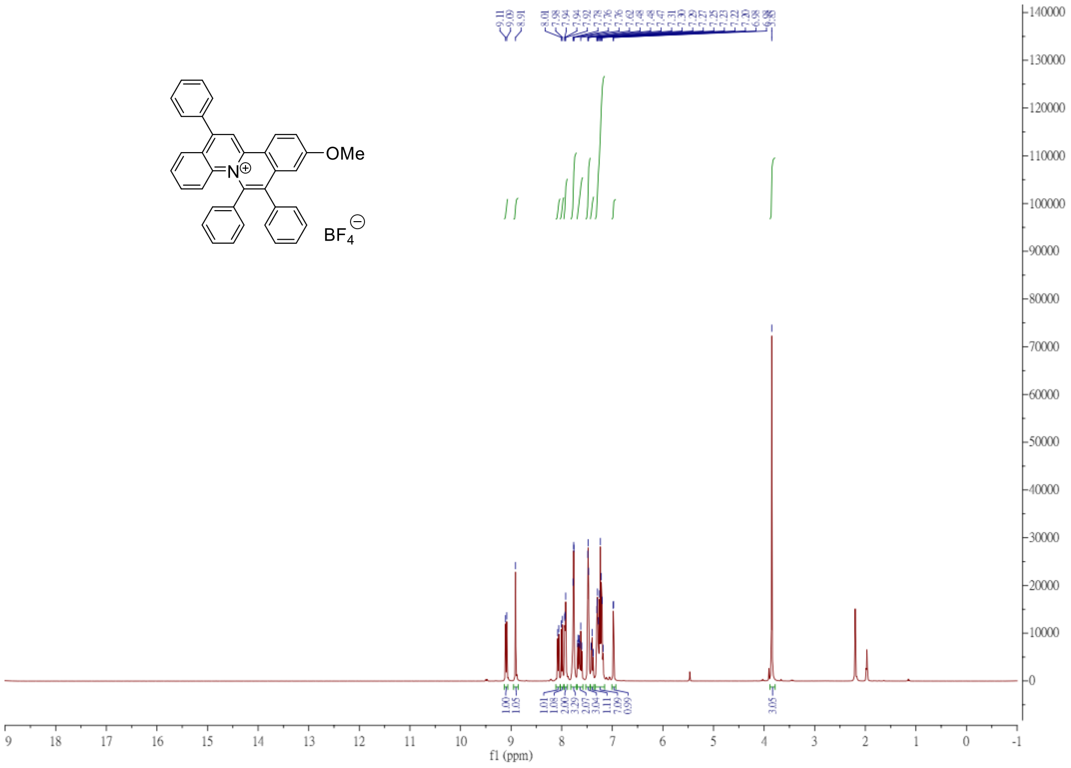
^{13}C NMR



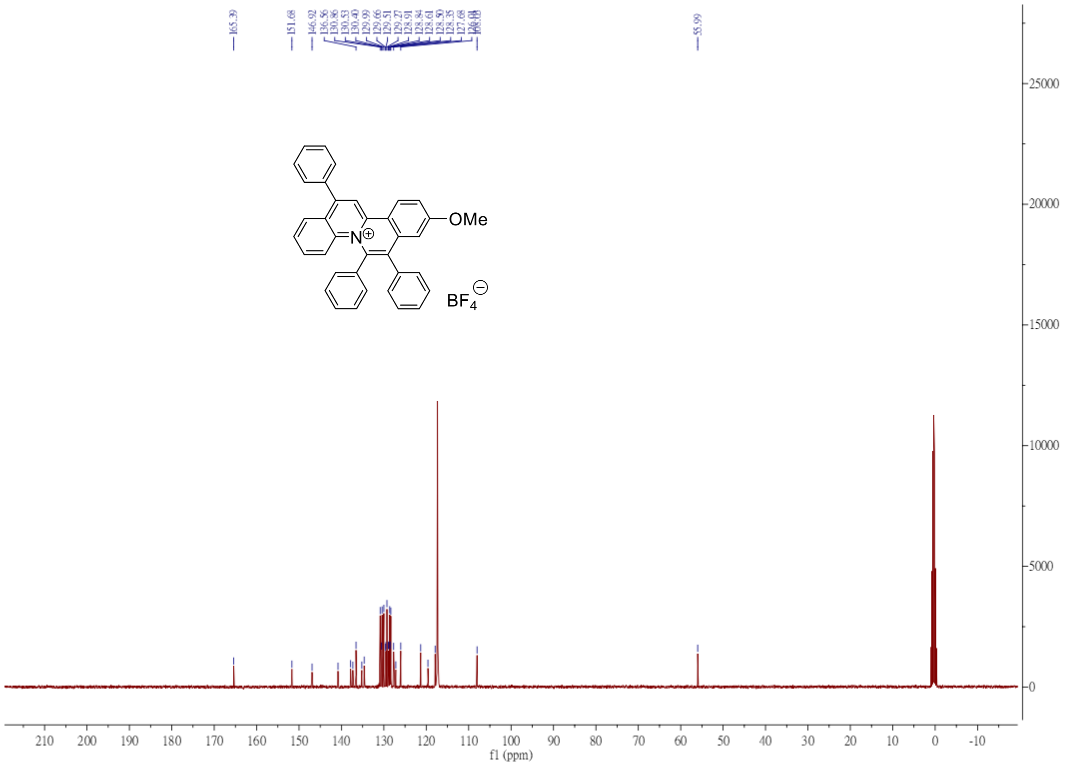
^{19}F NMR


-110.68
-152.89
F
N
BF4
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

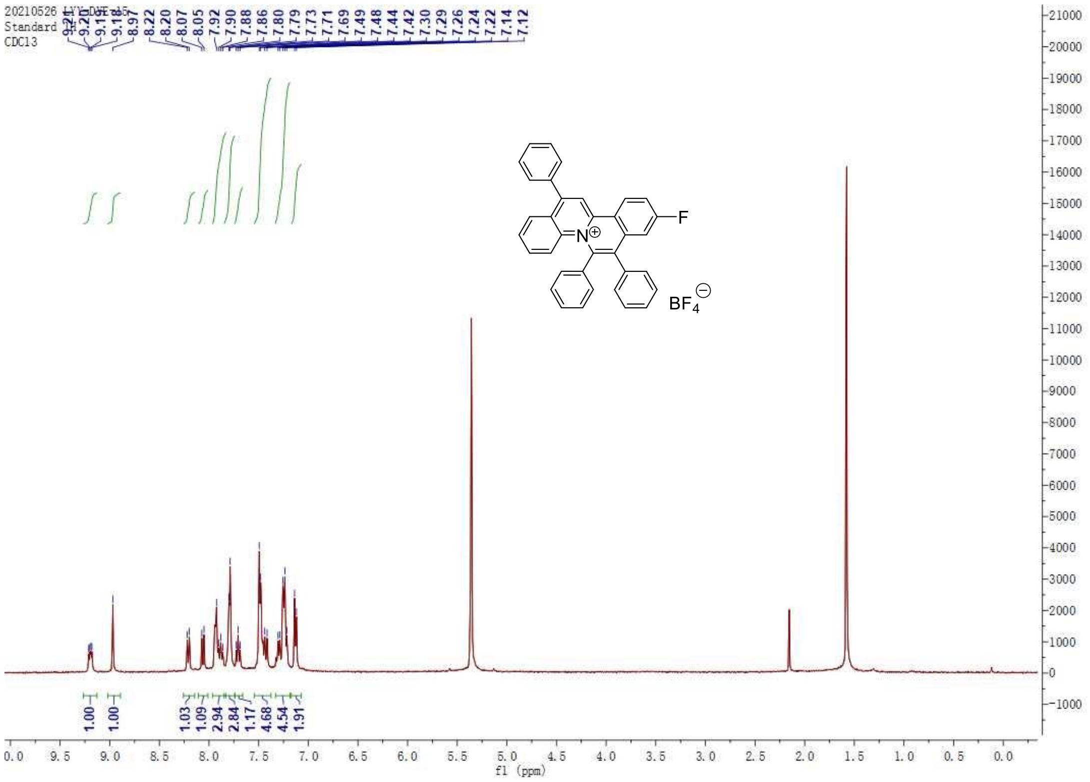
^{1}H NMR 1i



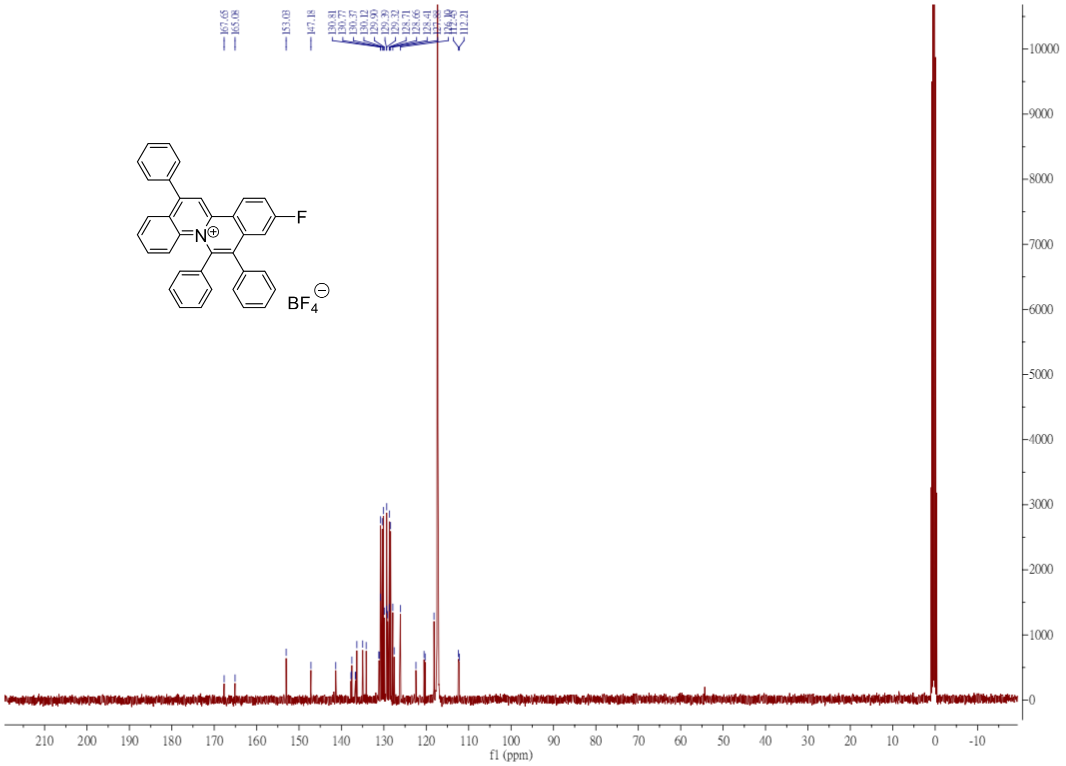
^{13}C NMR



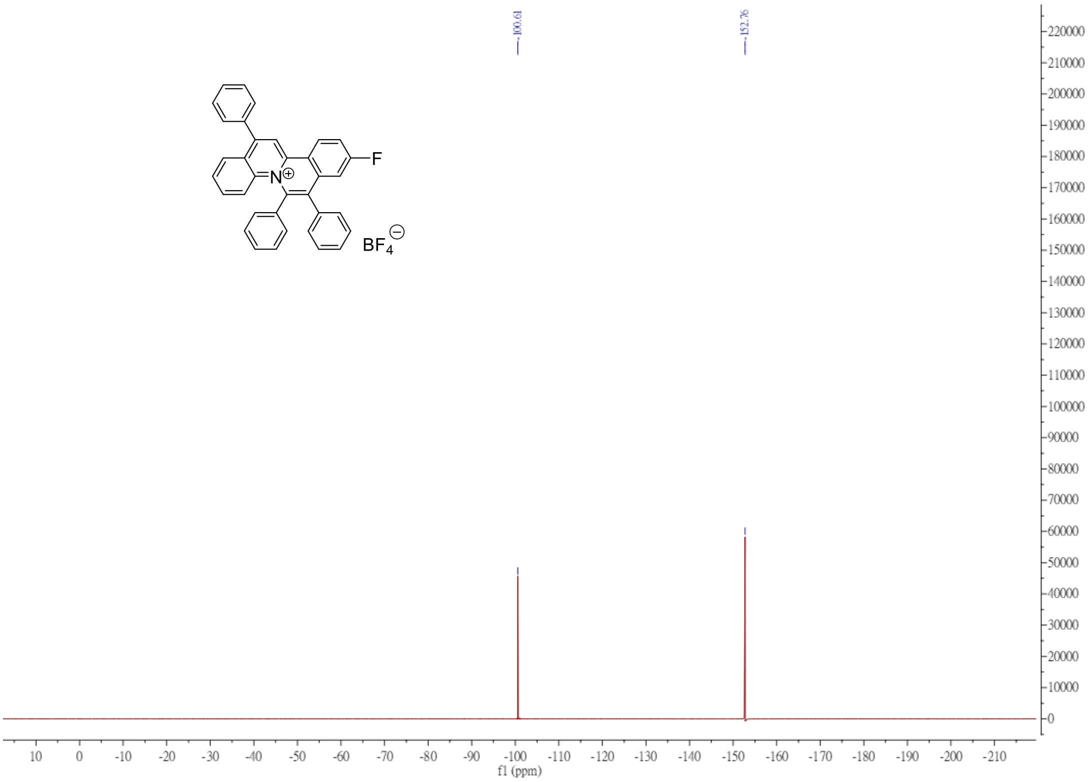
^{1}H NMR 1j



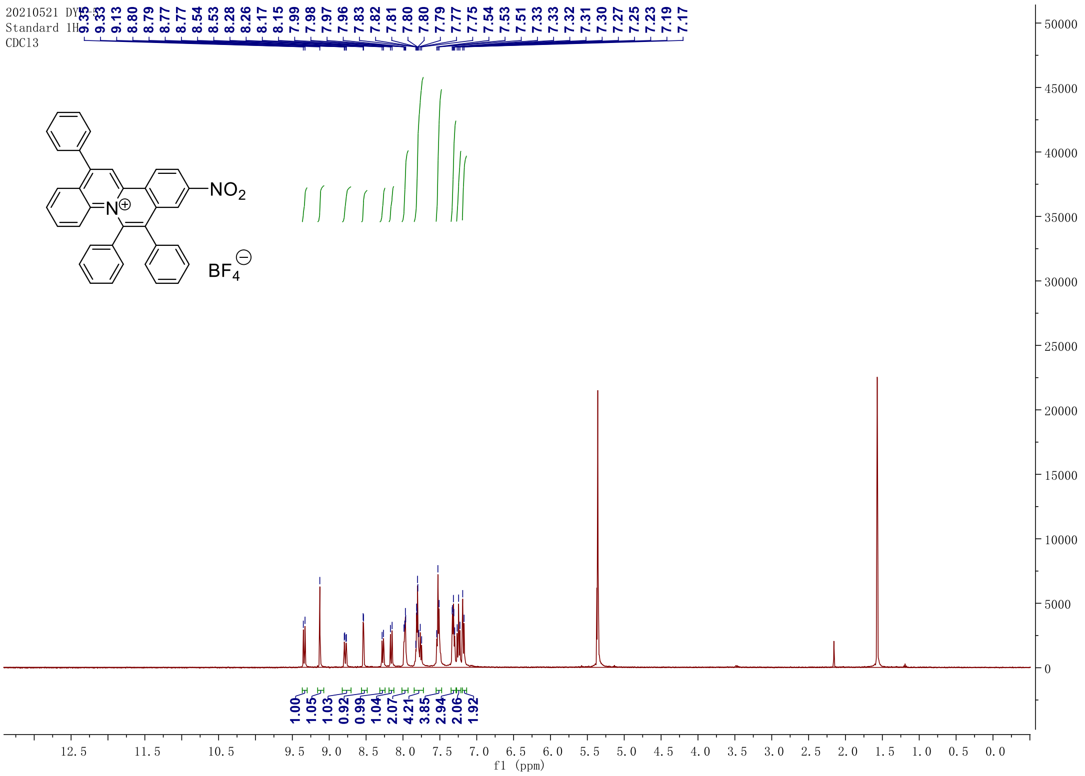
^{13}C NMR



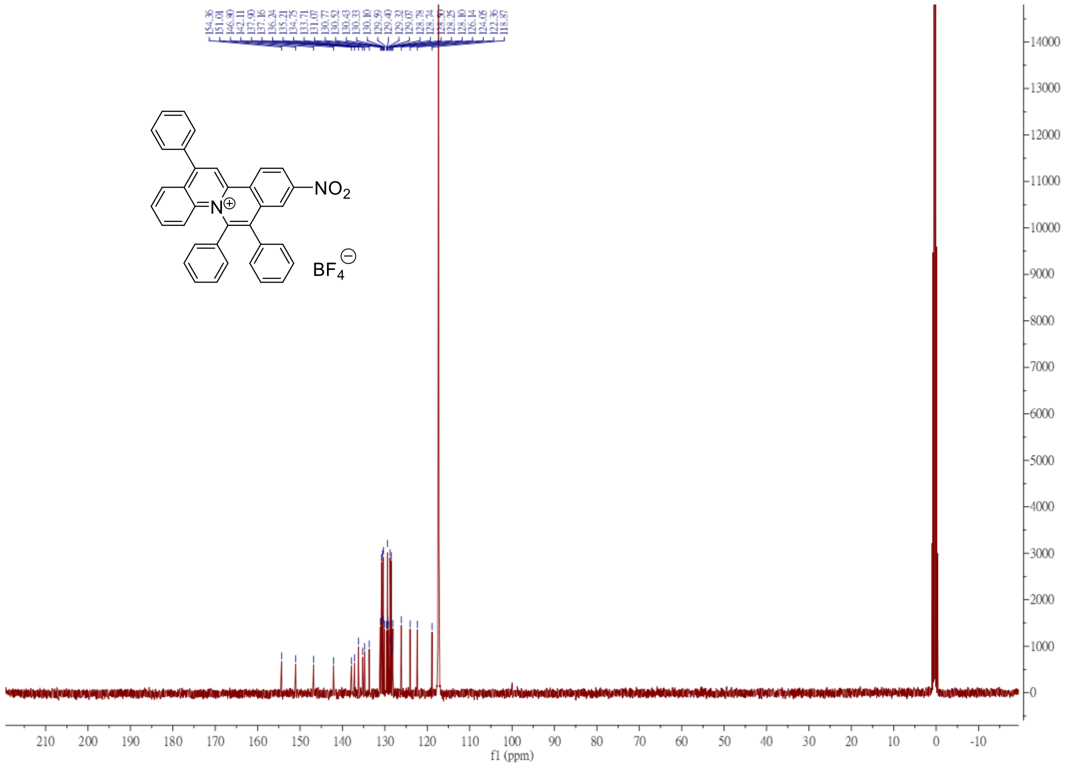
^{19}F NMR


-100.61
-152.76
F
N⊕
BF4⊖
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

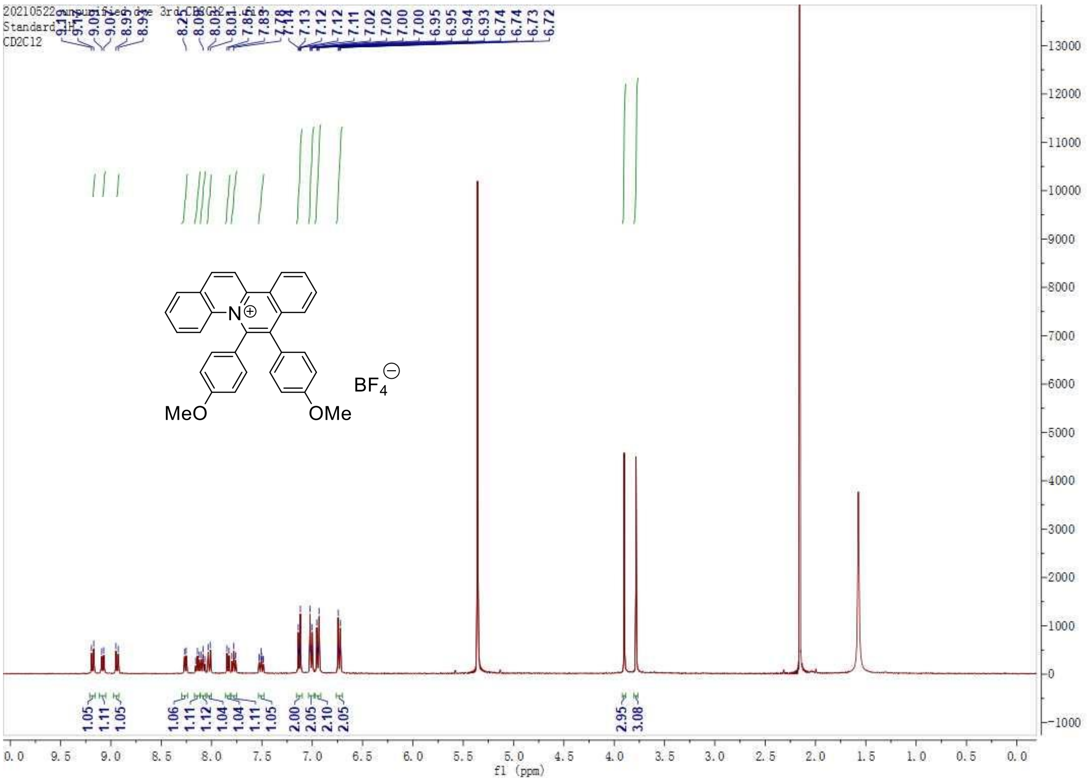
^{1}H NMR 1k



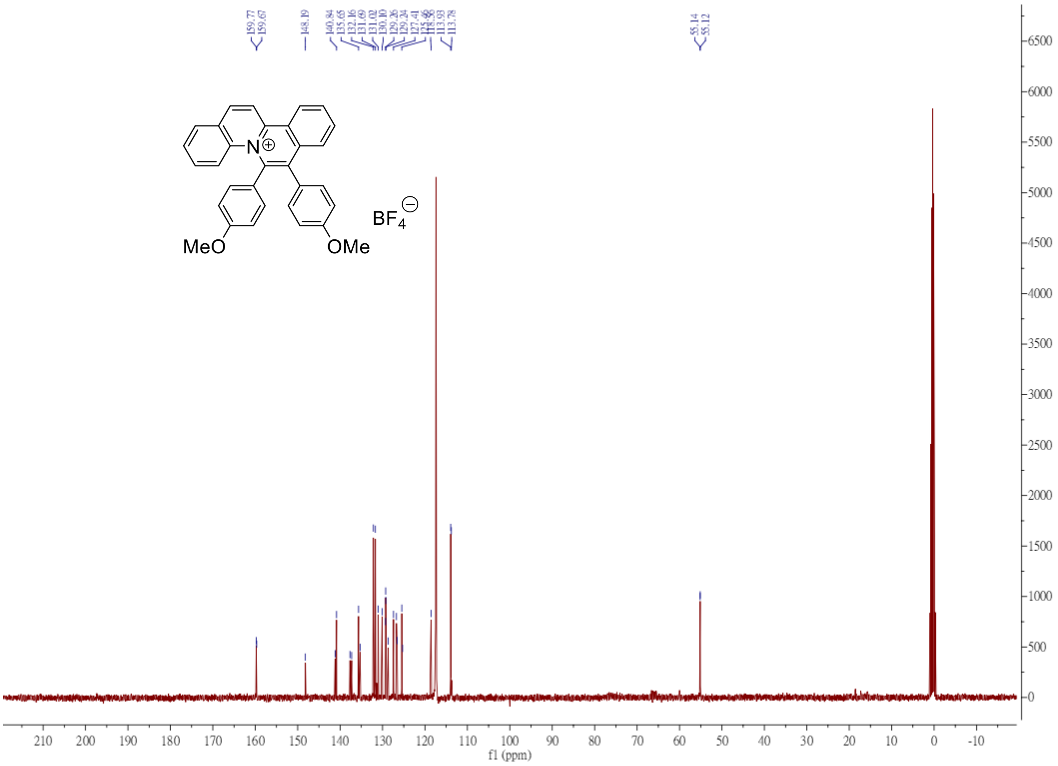
^{13}C NMR



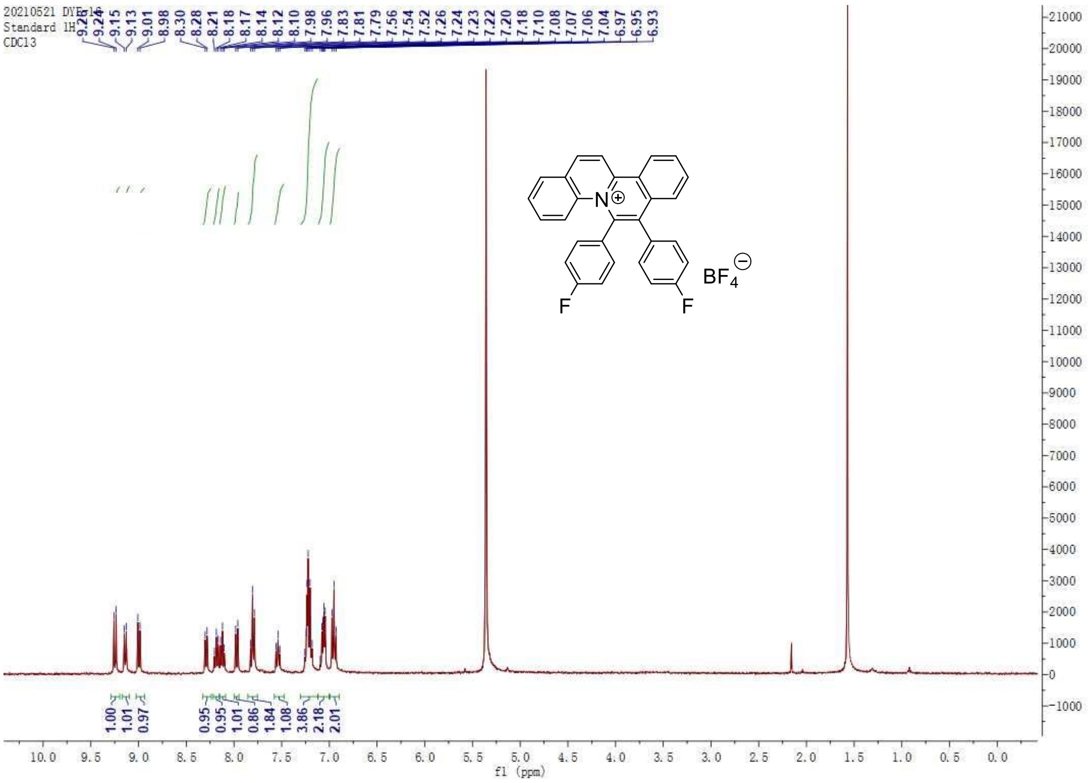
^{1}H NMR 1l



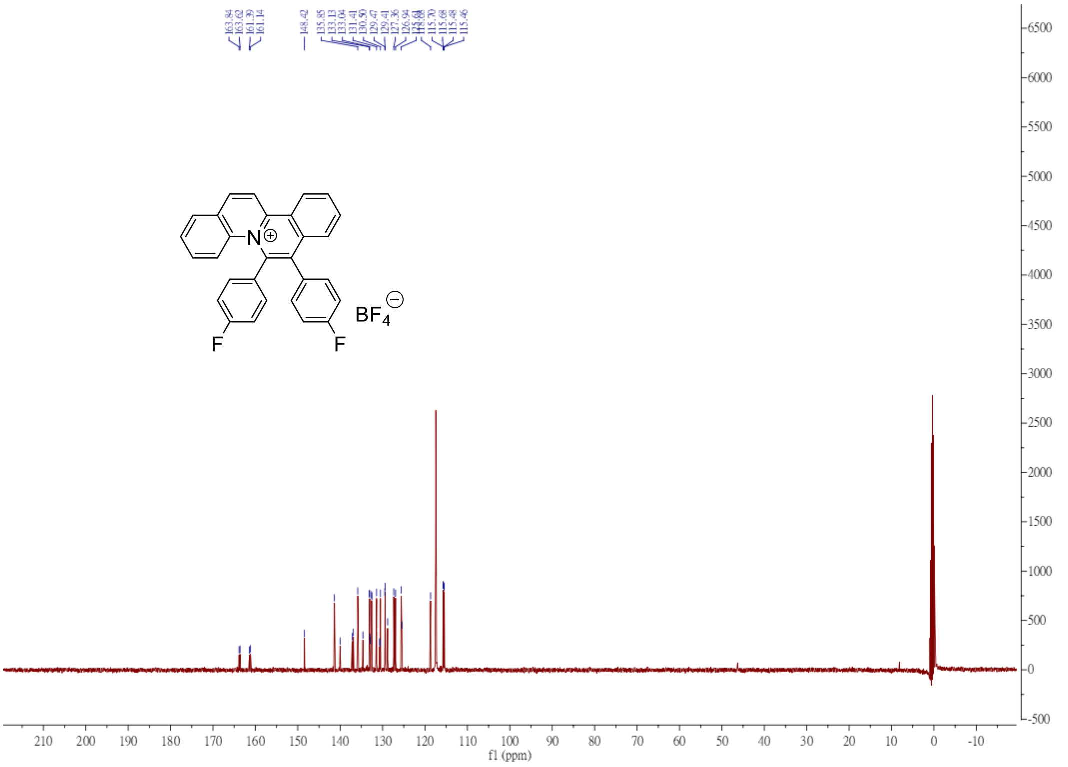
^{13}C NMR



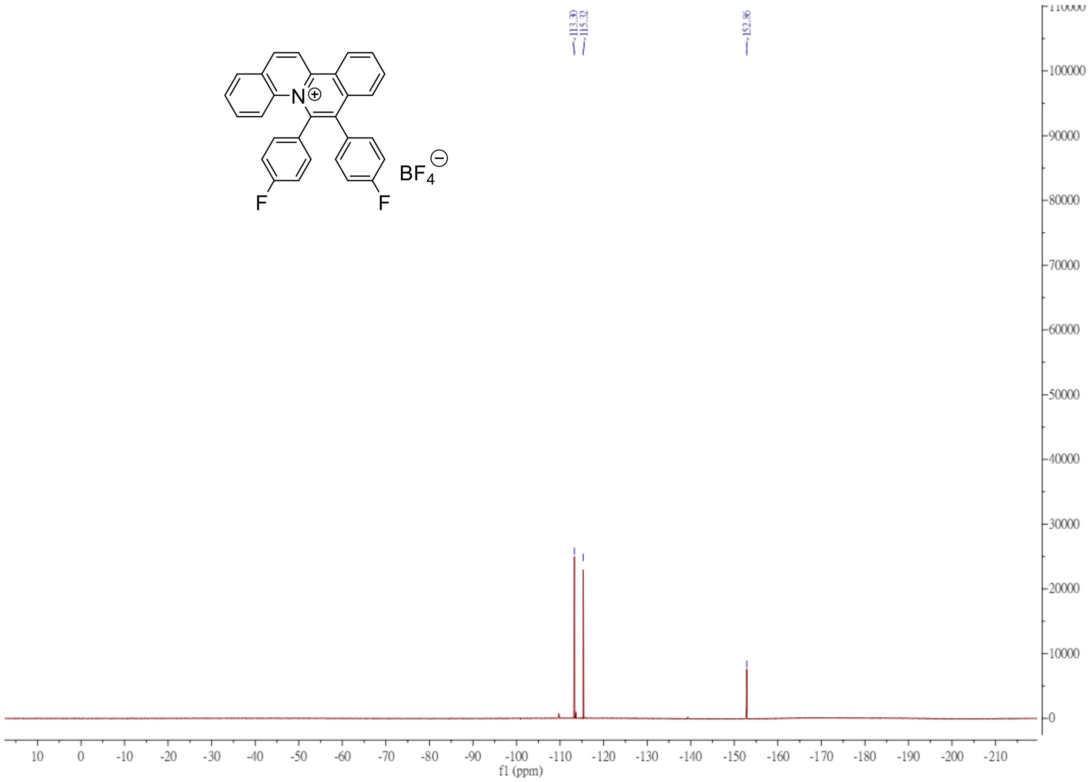
^{1}H NMR 1m



^{13}C NMR

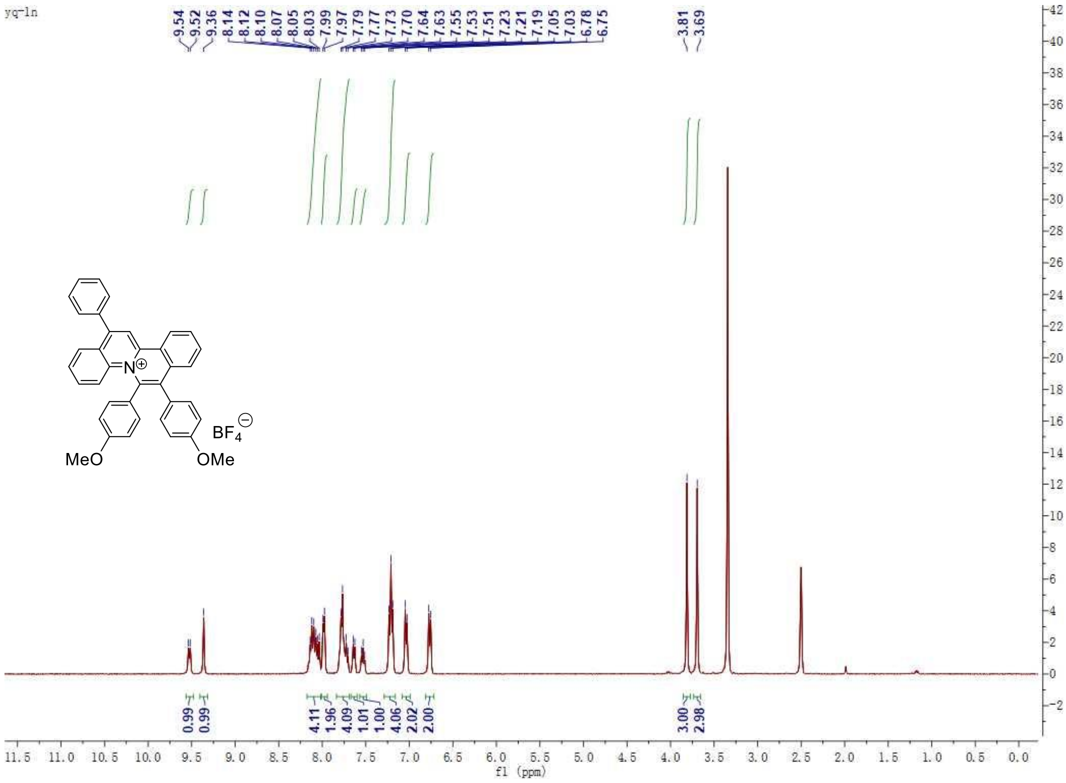


^{19}F NMR

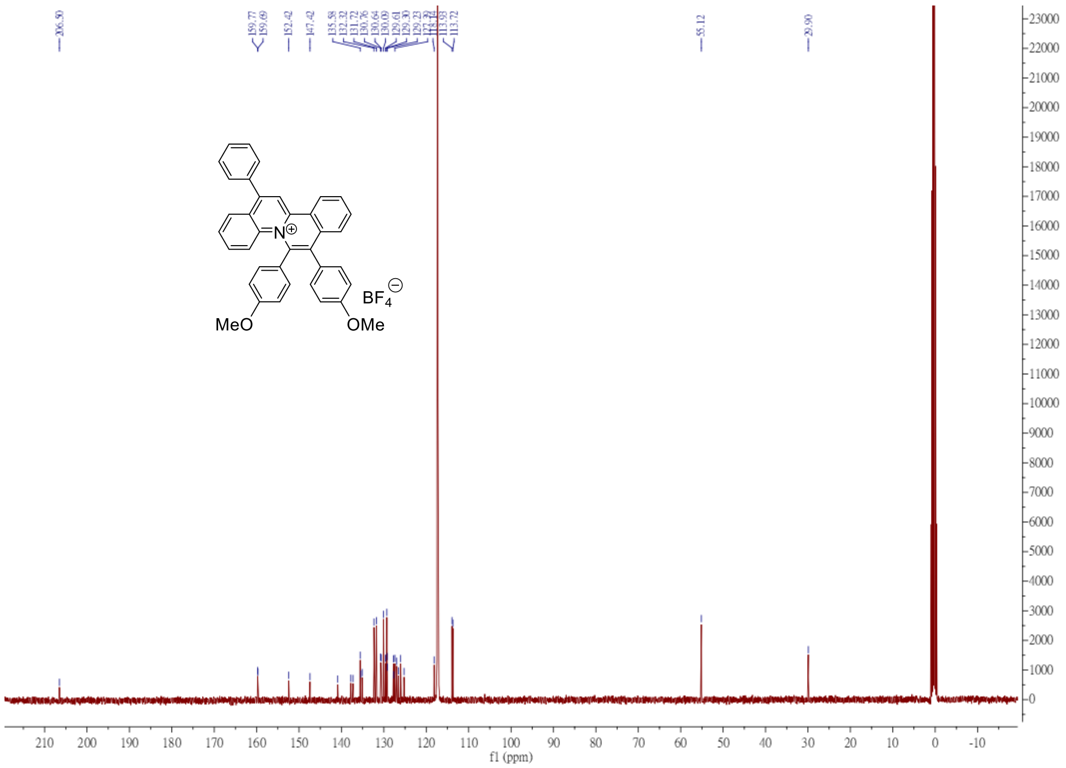


N
BF$_4$
F
F
-113.30
-115.32
-152.86
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

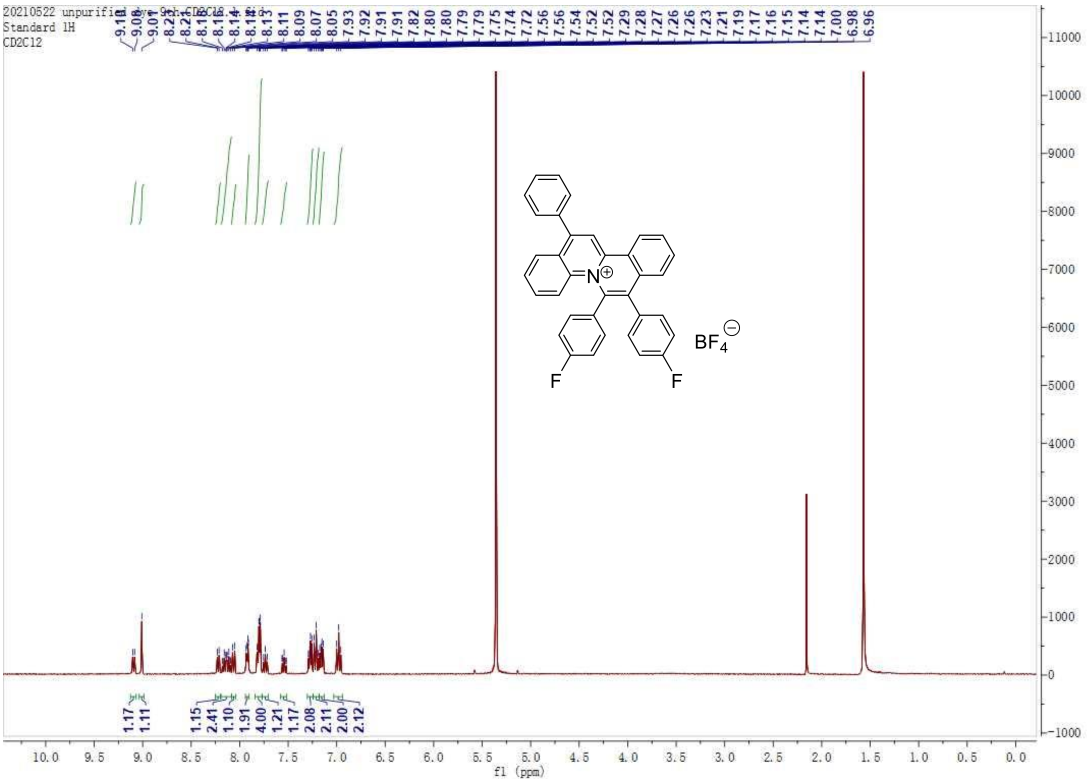
^{1}H NMR 1n



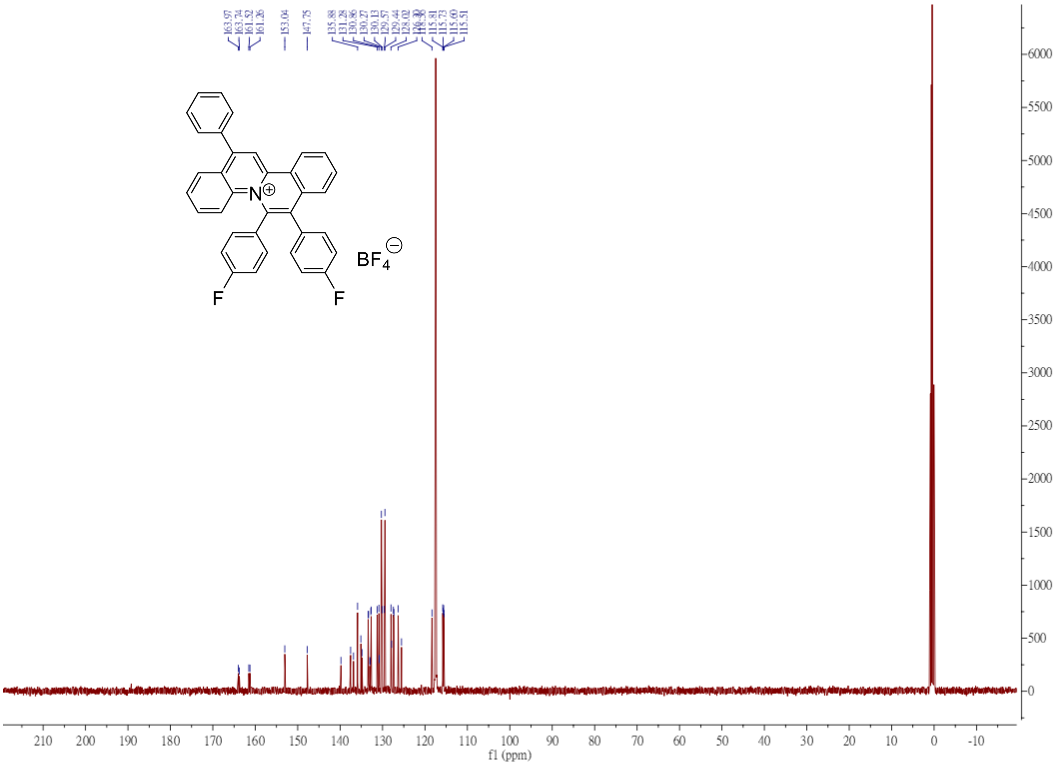
^{13}C NMR



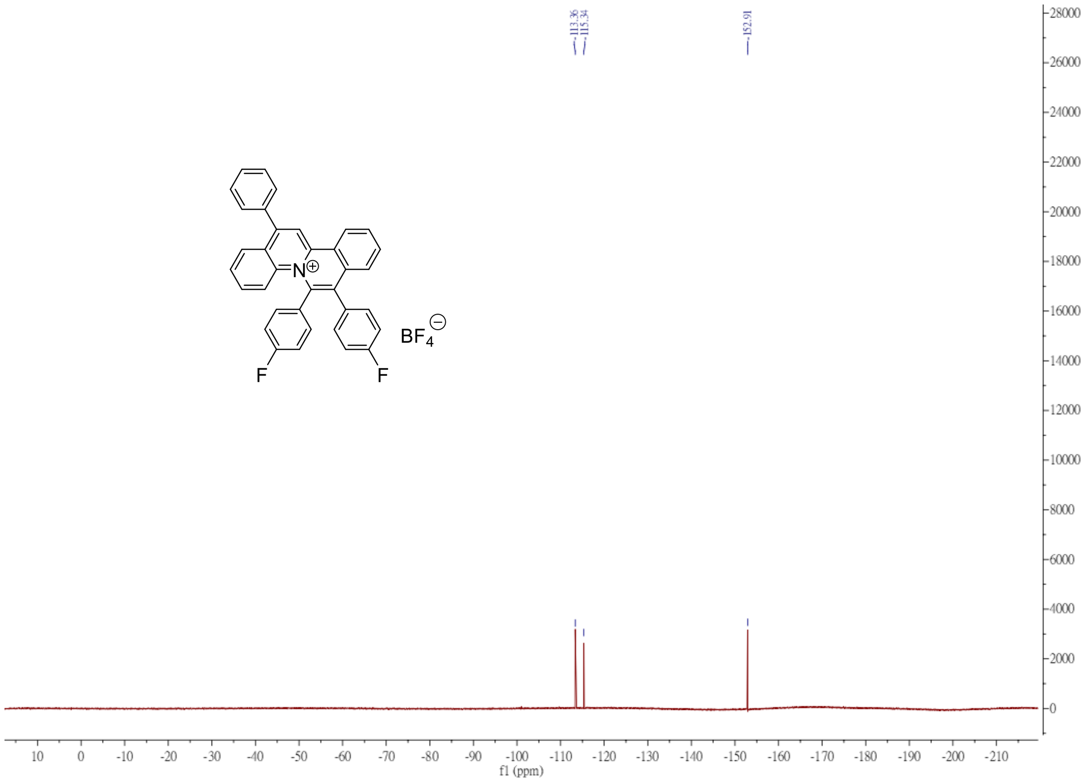
^{1}H NMR 1o



^{13}C NMR

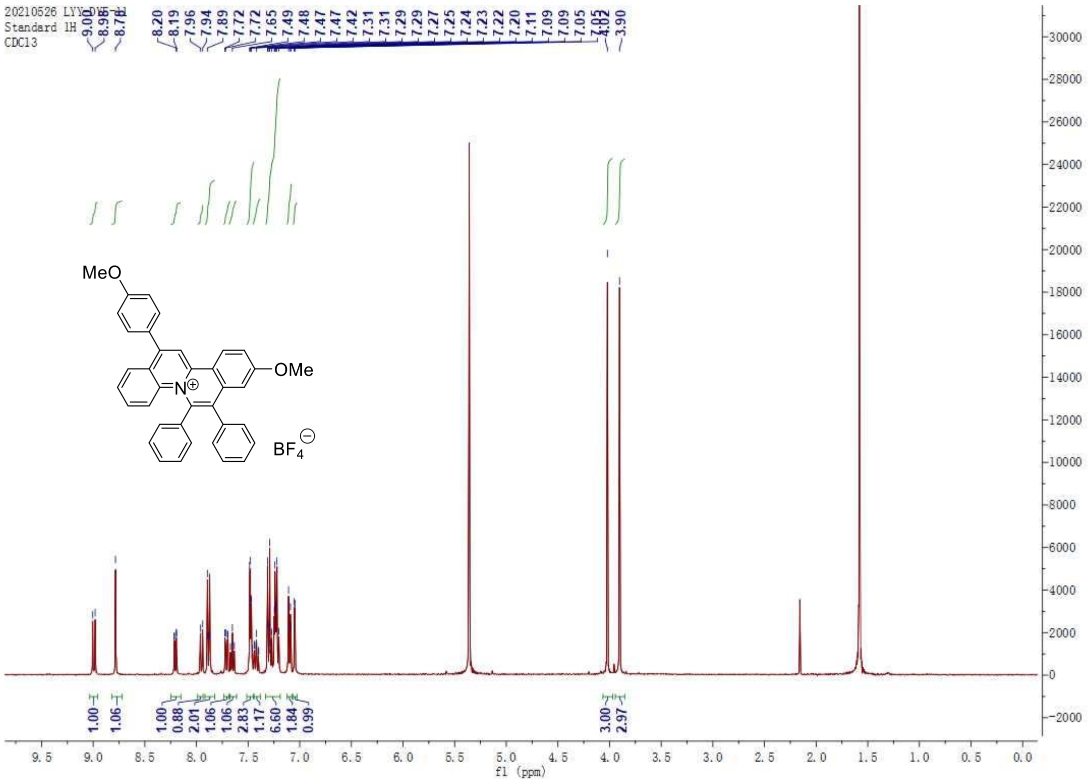


^{19}F NMR

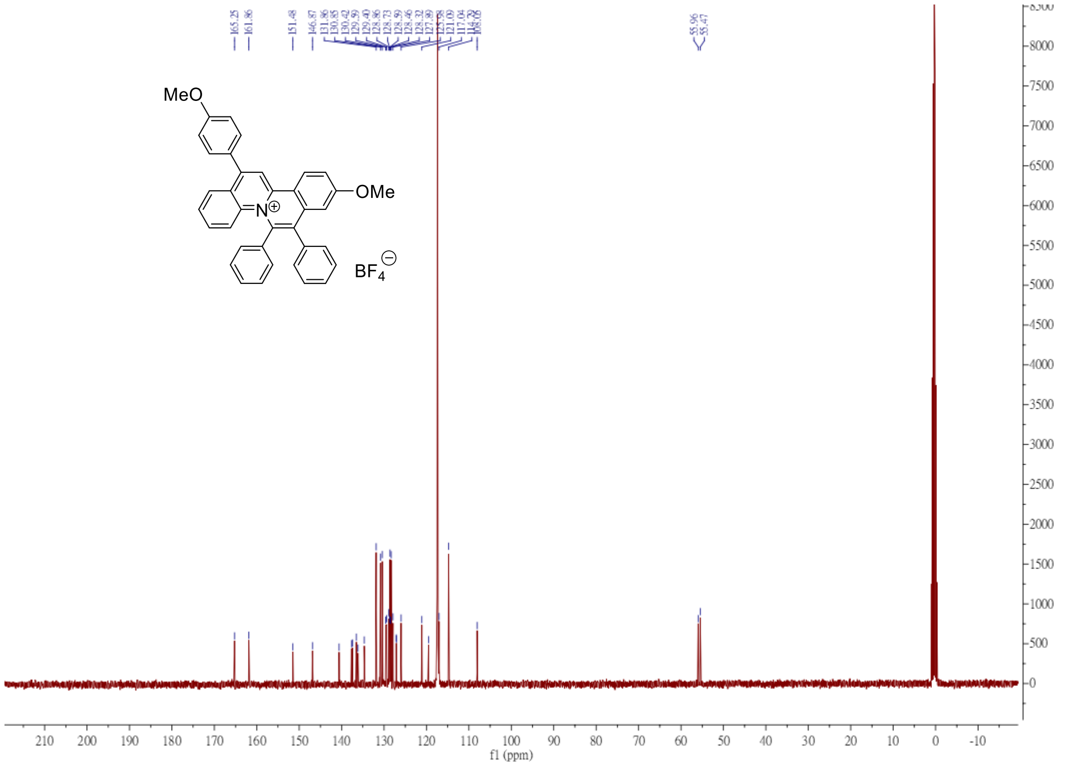


-113.36
-115.34
-152.91
N
BF4
F
F
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

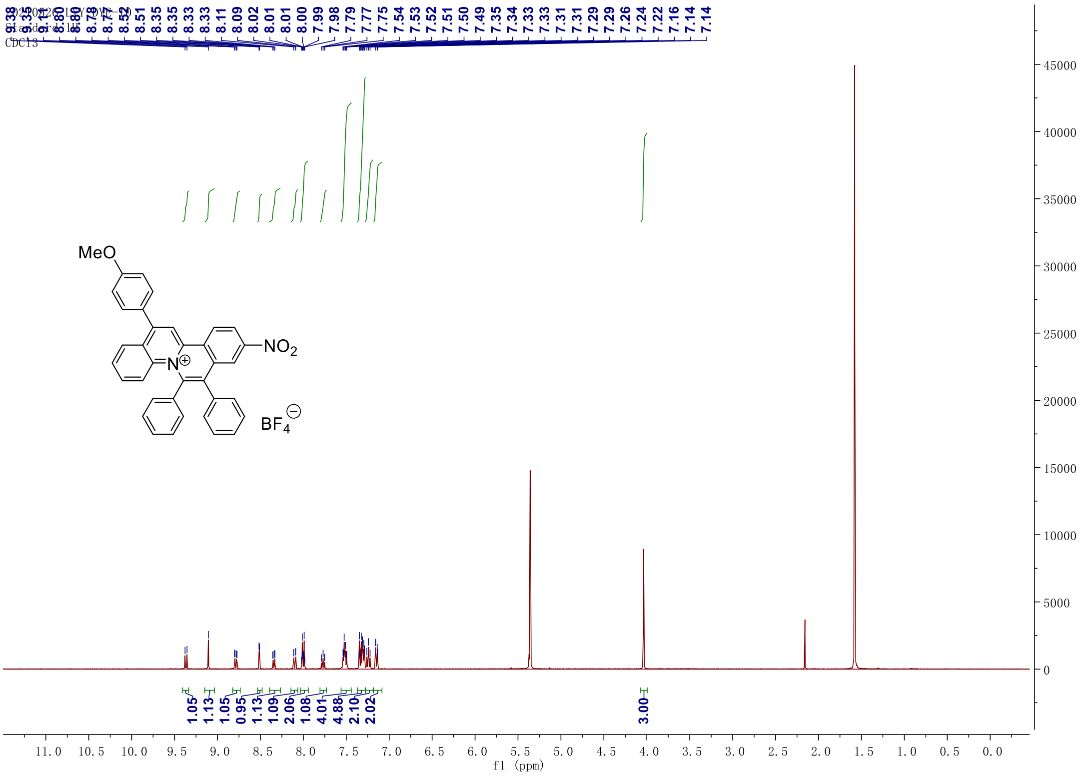
^{1}H NMR 1p



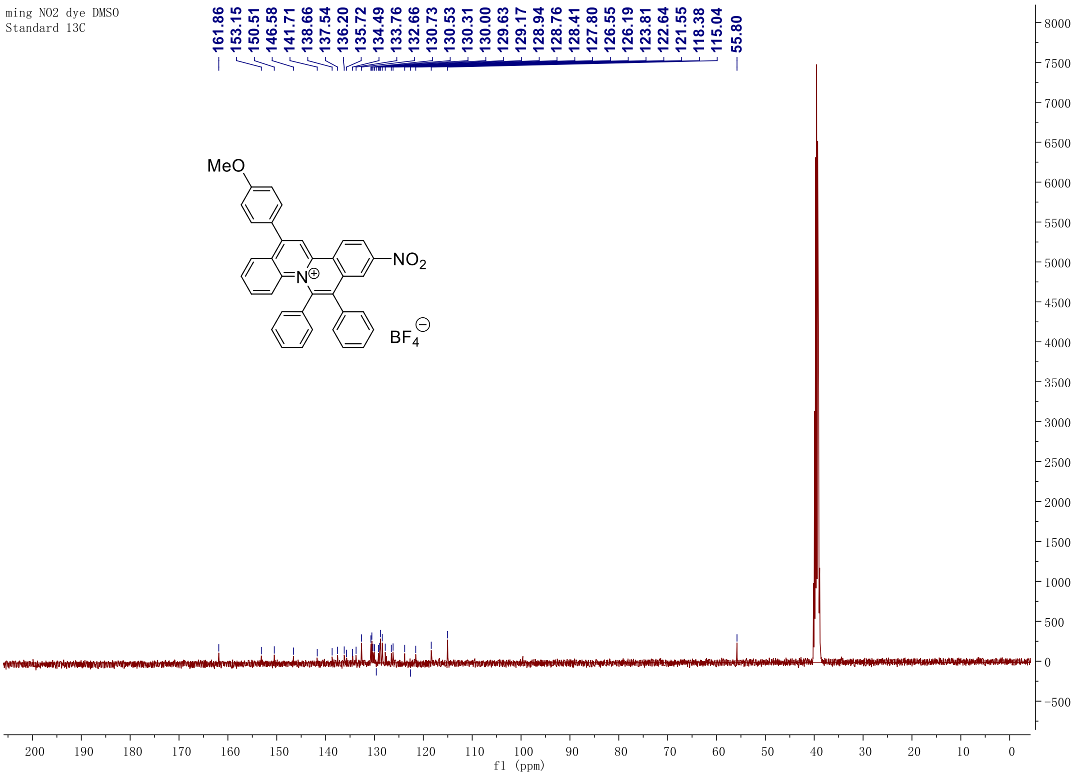
^{13}C NMR



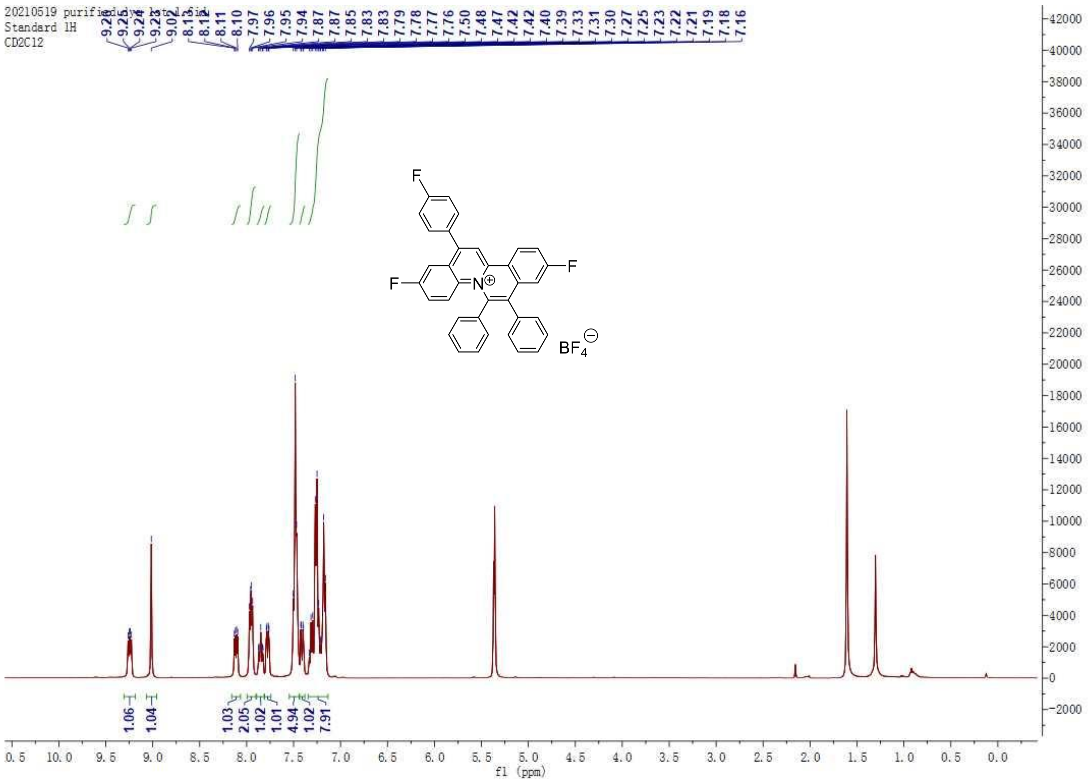
^{1}H NMR 1q



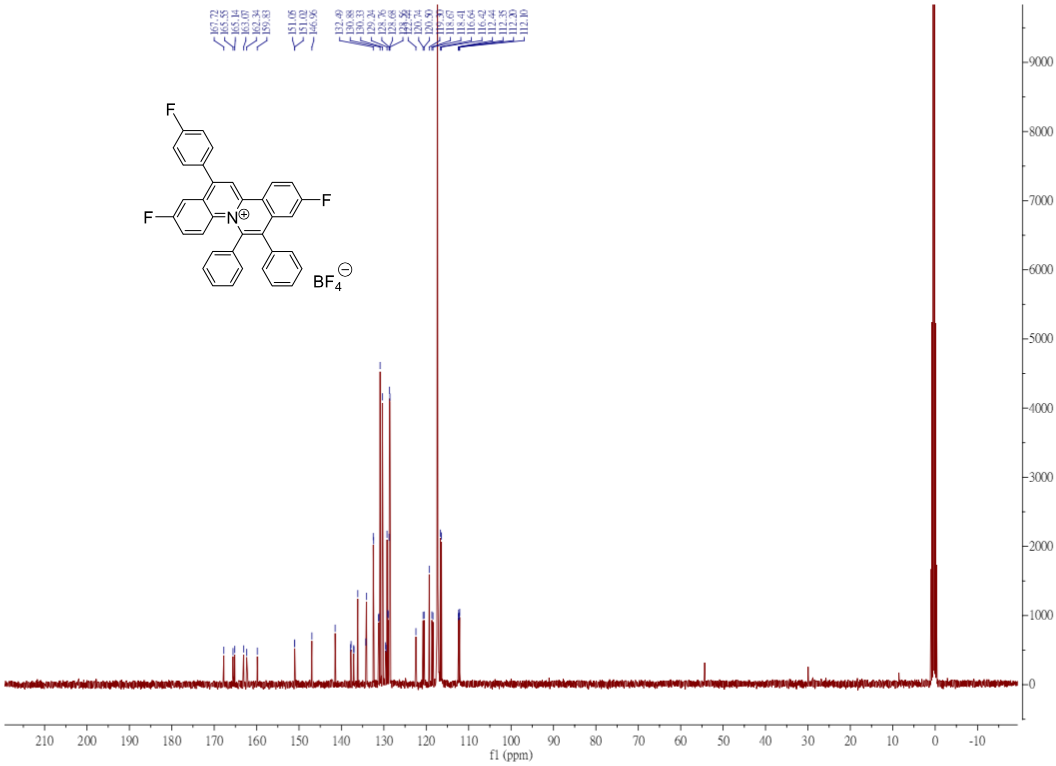
^{13}C NMR



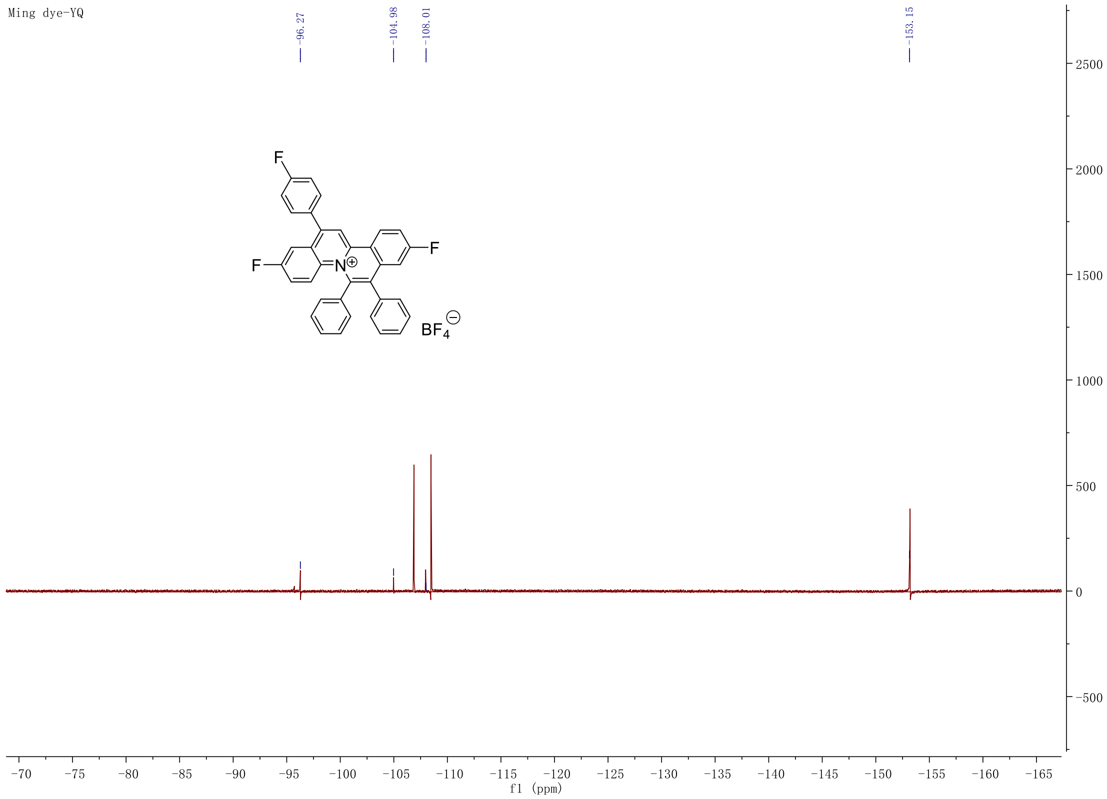
^{1}H NMR 1r



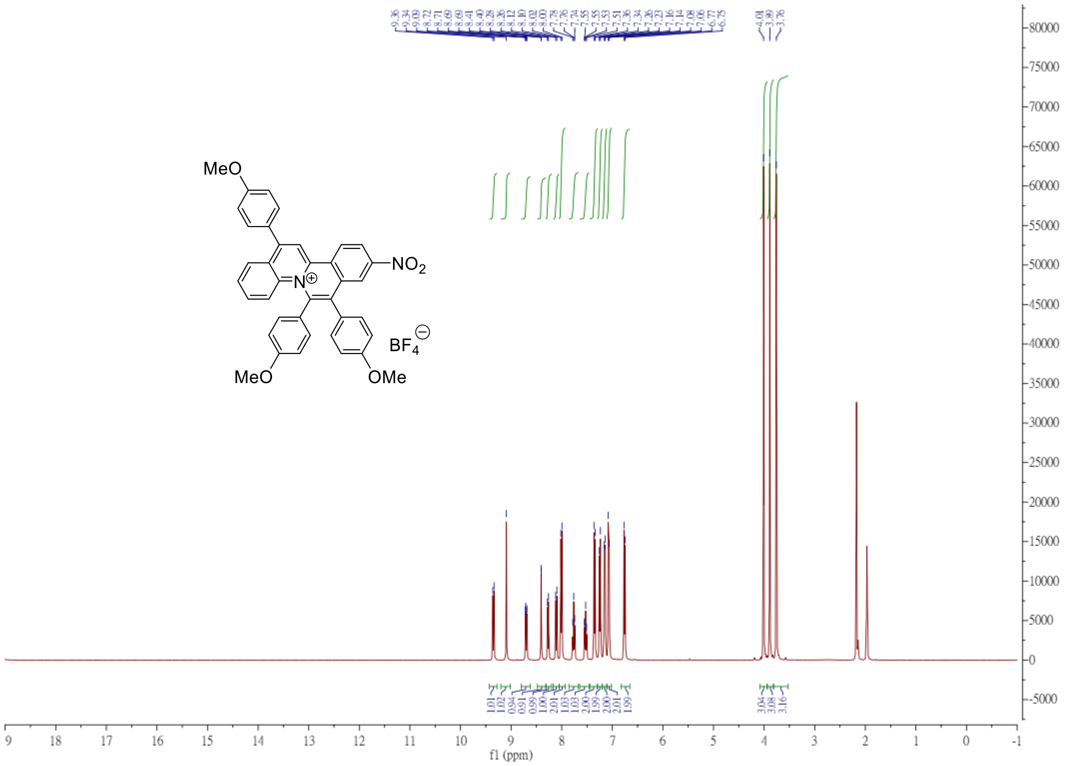
^{13}C NMR



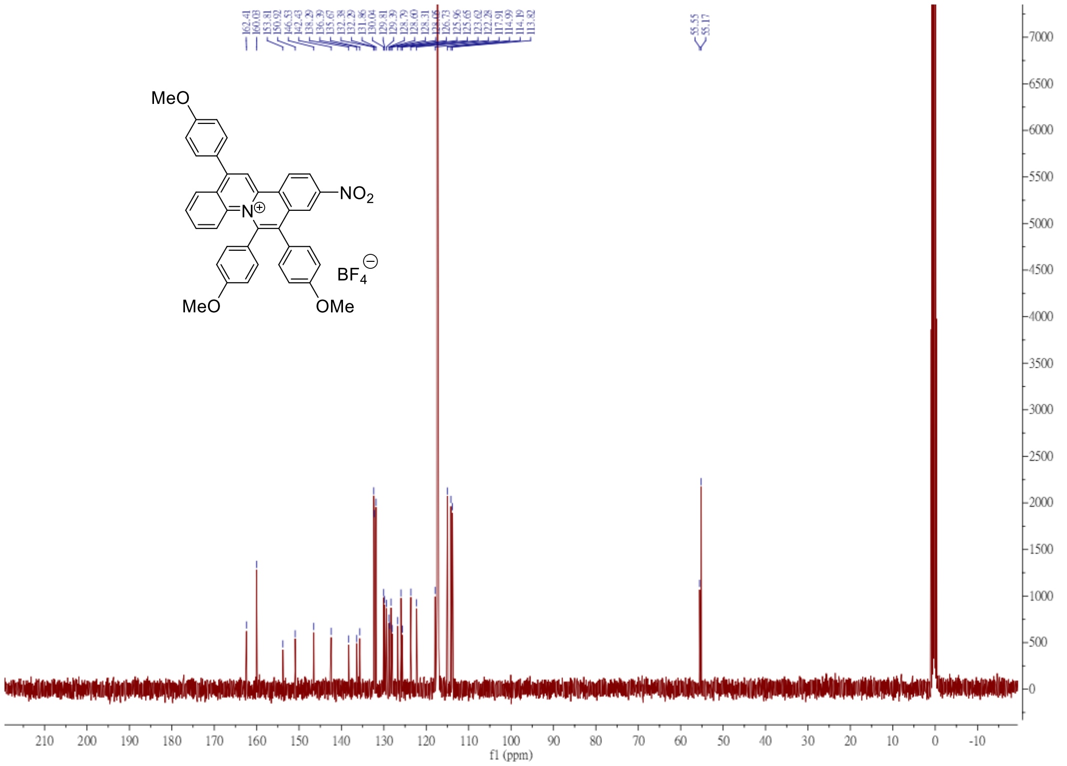
^{19}F NMR


Ming dye-YQ
-96.27
-104.98
-108.01
-153.15
F
F
F
N⊕
BF4⊖
2500
2000
1500
1000
500
0
-500
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165
f1 (ppm)

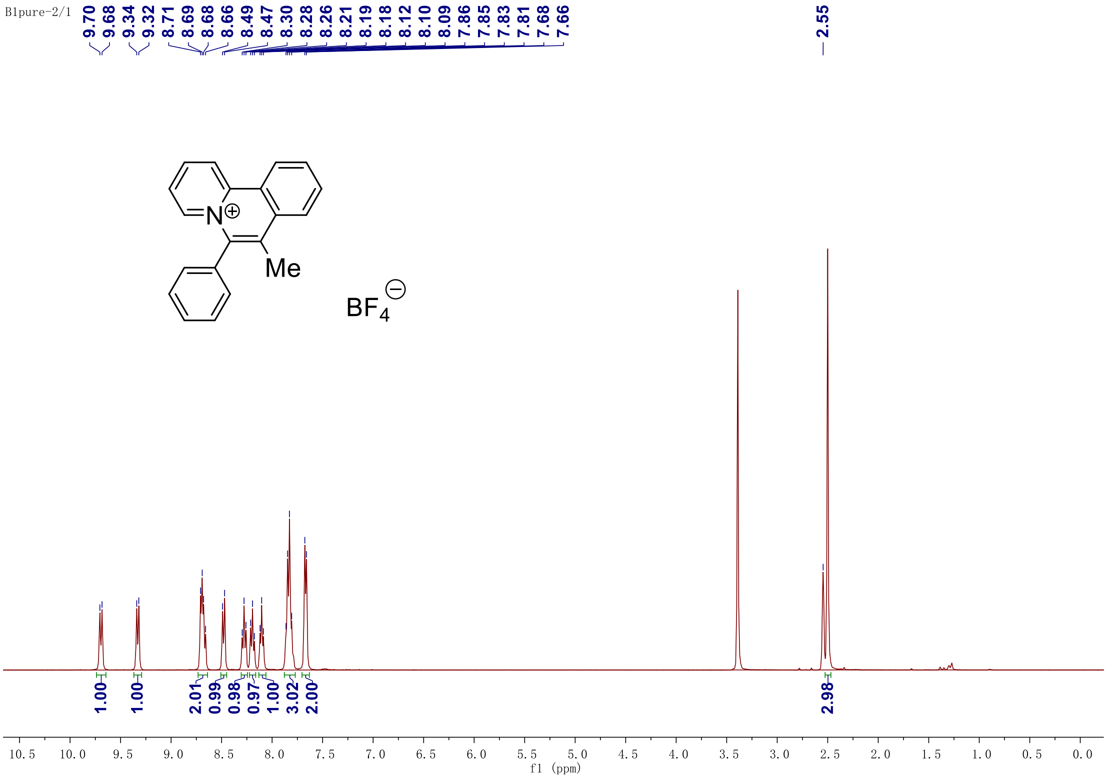
^{1}H NMR 1s



^{13}C NMR



^{1}H NMR 1t


B1pure-2/1
9.70
9.68
9.34
9.32
8.71
8.69
8.68
8.66
8.49
8.47
8.30
8.28
8.26
8.21
8.19
8.18
8.12
8.10
8.09
7.86
7.85
7.83
7.81
7.68
7.66
2.55
N
Me
BF4
1.00
1.00
2.01
0.99
0.98
0.97
1.00
3.02
2.00
2.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)