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Electronic Supplementary Information

Hydrogen Evolution Enabled Rhodaelectro-Catalyzed [4+2] Annulations of Purines and 7-Deazapurines with Alkynes

Chao Xu, Zhensheng Zhang, Tao Liu, Wangqin Zhang, Weihui Zhong and Fei Ling*

College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, P. R. China.

Table of Contents

1. General information

All reagents and solvents were obtained from commercial suppliers and used without further purification. All reagents were weighed and handled in air at room temperature. 6-Aryl-7-deazapurines were synthesized according to previously reported methods. The other alkynes used here are known compounds and synthesized according to the reported methods. Other reagents were commercially available and used as purchased. NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ on 400 MHz or 600 MHz spectrometers. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane (TMS). Flash column chromatography was carried out using silica gel eluting with ethyl acetate, petroleum ether, dichloromethane, methanol. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light (254 and 365 nm). Cyclic voltammetry experiments were carried out in an equipment of CHI761E. CV curves were recorded using a three-electrode scheme. The working electrode was a glassy carbon electrode, A platinum electrode served as counter electrode. Ag/AgCl (KCl sat.) was used as the reference electrode. The working electrode was polished before recording each CV curve. DC power supply DP3005B was used for all experiments.

2. Preparation of starting materials 1 and 2

2.1 Structures of 1 and 2 used in this manuscript

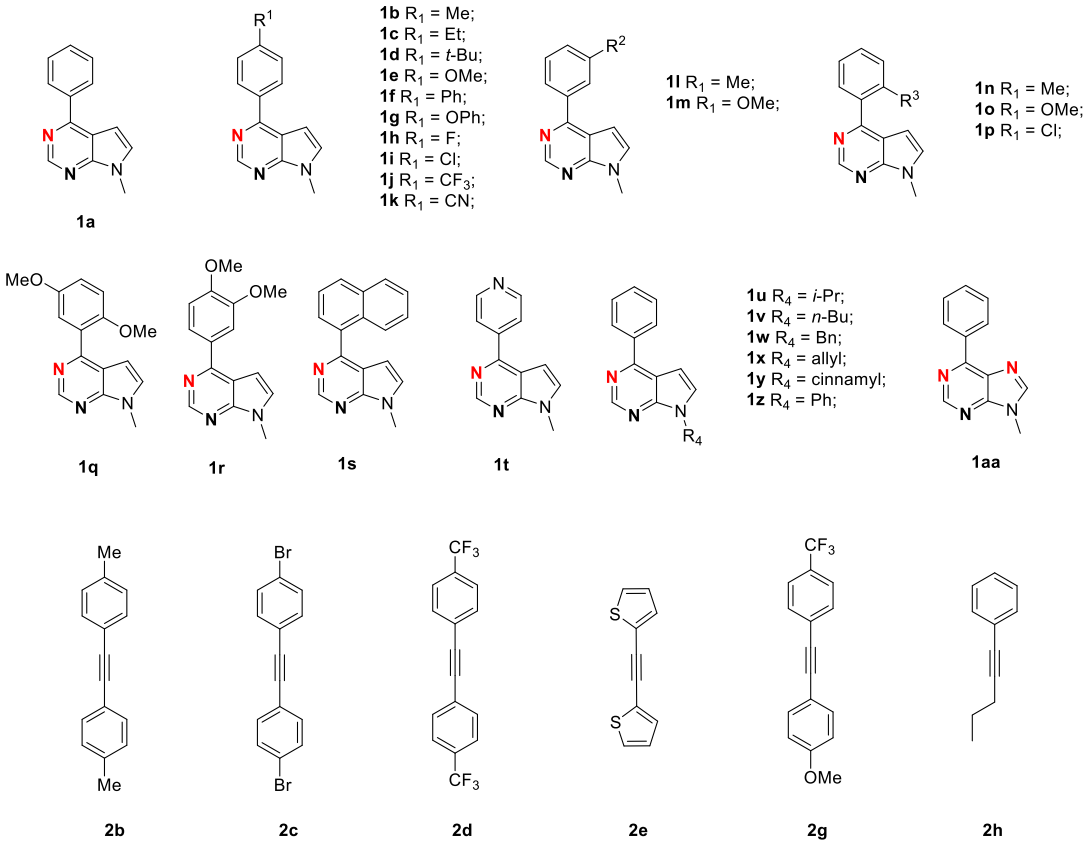
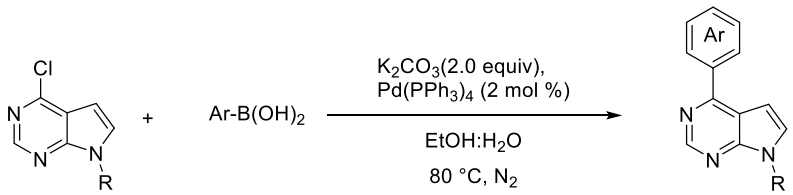


Figure S1 6-Aryl-7-deazapurines derivatives and alkynes used in this manuscript

2.2 General procedure for the synthesis of 7-deazapurines 1

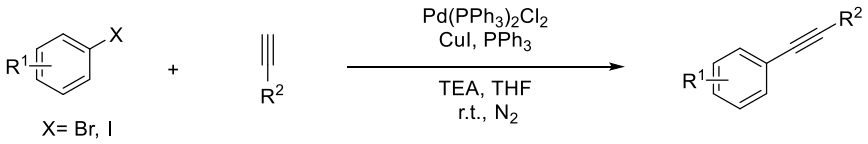
The following starting materials **1** were synthesized according to previously described methods.[1]



To a solution of 6-chloro-7-deazapurines (1.5 mmol) in EtOH (8 mL) was added $Pd(PPh_3)_4$ (0.25 mmol), K_2CO_3 (10 mmol), H_2O (25 mL), ethanol (8 mL) and arylboronic acid (1.8 mmol, 1.2 equiv.) at 80 ºC under an atmosphere of nitrogen. After stirred for 4-8 hours, the oil bath was removed. Then the resulting mixture was quenched with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4.

The solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel (eluent: PE/EA = 10:1-1:1) to afford the desired **1**.

2.3 General procedure for the synthesis of alkynes 2[2]

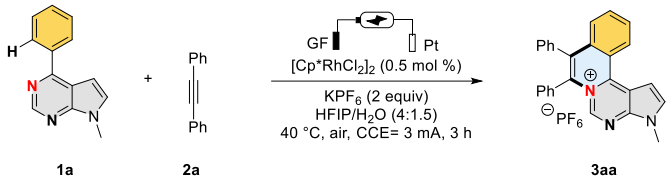


The corresponding aryl halide (5 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol %), CuI (3 mol %), PPh_3 (3 mol %) and corresponding alkynes (7.5 mmol) were added to a 50 mL two-necked flask with a stir bar under an atmosphere of nitrogen. Then tetrahydrofuran (20 mL) and triethylamine (20 mL) were added sequentially. The reaction mixture was then stirred at room temperature overnight. Afterwards 10 mL of water were added and the reaction mixture was extracted with EA. The combined organic fractions were washed with brine and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using PE and EA as the eluent.

3 General procedure for for the synthesis of 3

3.1 Optimization of reaction conditions

Table S1 Optimization of reaction conditions[a]

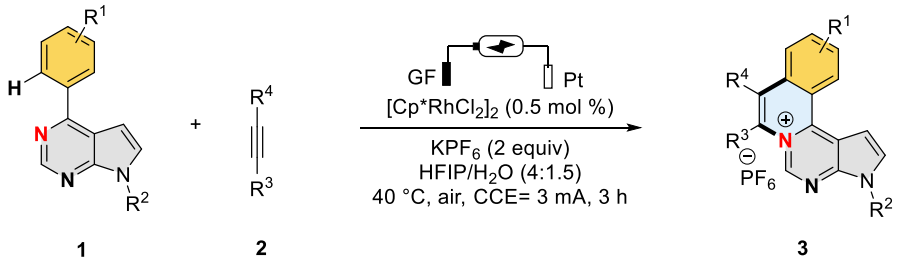


Entry	Deviation from standard conditions	Yield (%)[b]
1	None	90
2	Graphite rod as the anode	11
3	Graphite rod as the cathode	15
4	CH_3CN instead of HFIP	23
5	MeOH instead of HFIP	51
6	2 mA 12 h	40[c]
7	5 mA 2 h	75
8	Room temperature	N.R.

9	50 ℃ 2 h	85
10	$RhCl_3$ instead of $[Cp^*RhCl_2]_2$	25
11	Without $[Cp^*RhCl_2]_2$	N.R.
12	Without electricity	Trace
13	N_2 instead of air	90

[a]Reaction conditions: undivided cell, graphite felt anode, platinum electrode cathode, constant current electrolysis (CCE) = 3 mA, **1a** (0.25 mmol), **2a** (0.50 mmol), $[Cp^*RhCl_2]_2$ (0.5 mol%), KPF_6 (0.5 mmol, 2.0 equiv.), air, 40 ℃, HFIP/H_2O (4 : 1.5, 5.5 mL), 3 h. [b]Isolated yield. N.R. = no reaction. [c]The conversion of **1a** was incompleted.

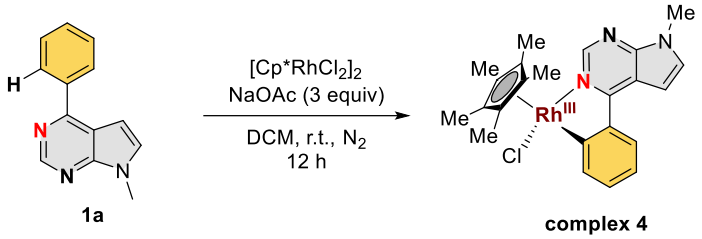
3.2 General procedure for for the synthesis of 3



The electrocatalysis was carried out in an undivided cell under air, with a graphite felt (GF) anode (10 mm x 20 mm x 5 mm) and a platinum cathode (10 mm x 20 mm x 0.25 mm). To a 10-mL schlenk flask, 6-aryl-7-deazapurines **1** (0.25 mmol), alkynes **2** (0.50 mmol), $[Cp^*RhCl_2]_2$ (0.5 mol %) and KPF_6 (0.50 mmol, 2.0 equiv) were dissolved in solvent mixture HFIP/H_2O (4.0:1.5 mL). Electrocatalysis was performed at 40 ºC with a constant current of 3.0 mA maintained for 3.0 h. When the reaction was completed, the mixture was diluted with DCM (10 mL). The GF anode was washed with DCM (3 x 5 mL) in an ultrasonic bath, and all the solvent was transferred to a round bottom flask. The solvent was removed under reduced pressure at 50 ºC. The mixture was concentrated and purified by silica gel column chromatography using PE/EA (1:2) to DCM/MeOH (50:1) as eluent to give the desired product **3**.

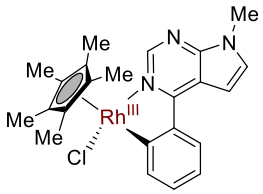
4. Mechanistic studies[3]

4.1 Synthesis of Rh(III) complex 4



$[Cp^*RhCl_2]_2$ (100.0 mg, 0.15 mmol), **1a** (0.35 mmol), sodium acetate (3.0 equiv.), and DCM (3 mL) were charged into a Schleck tube under N_2 atmosphere. Then, the mixture was stirred at room temperature overnight. The resultant mixture was filtered through celite and evaporated to dryness. The complex **4** was purified via silica gel chromatography (eluent: DCM/MeOH = 20:1).

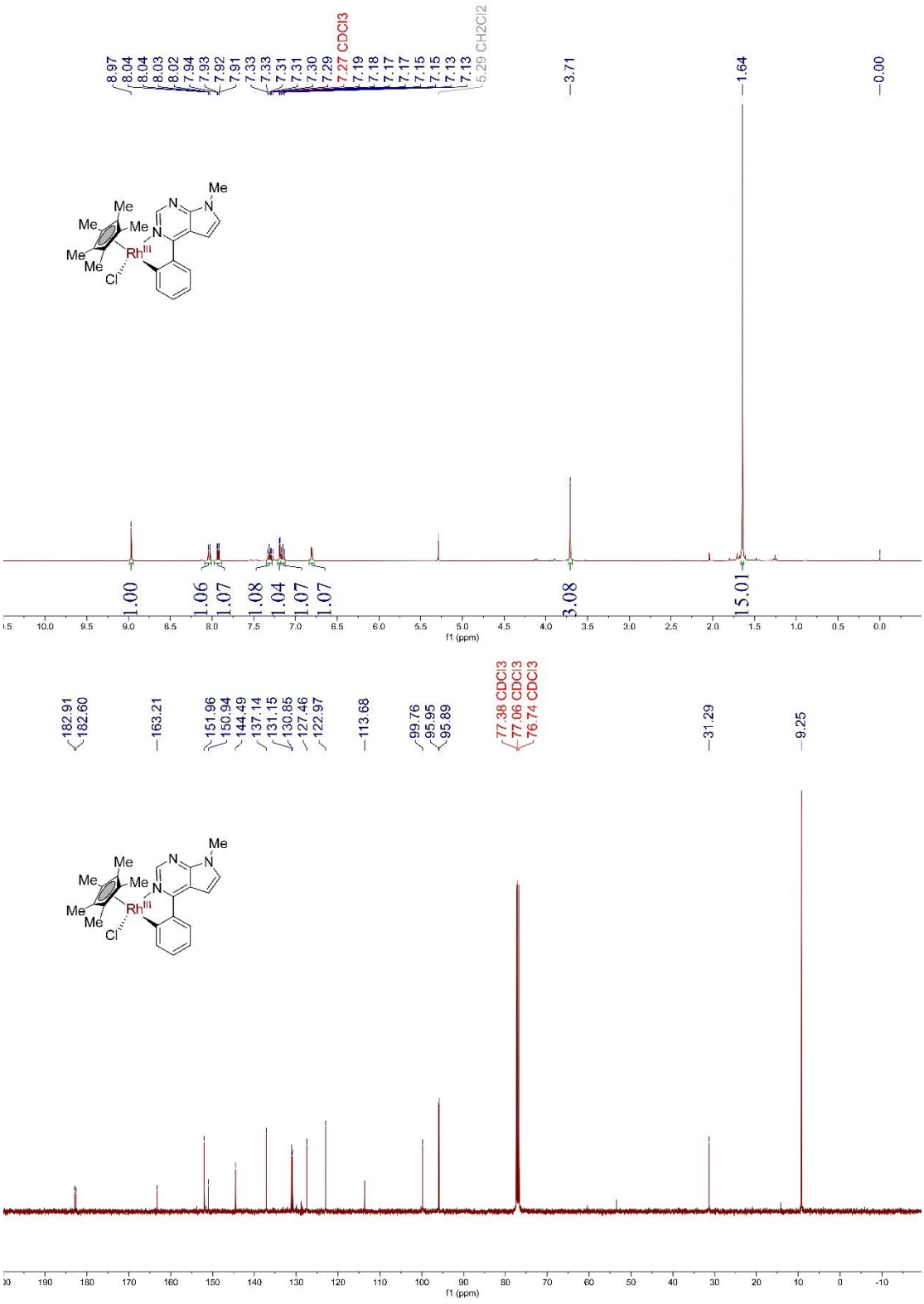
Rh(III) complex 4



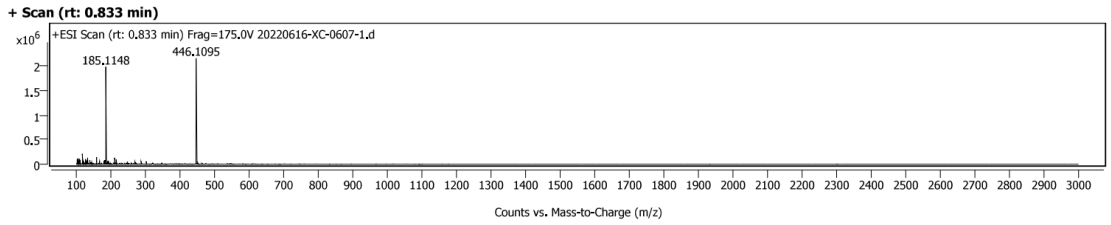
Orange solid, quantitative yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.03 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.92 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.31 (td, *J* = 7.4, 1.4 Hz, 1H), 7.19 (d, *J* = 3.6 Hz, 1H), 7.15 (td, *J* = 7.5, 1.2 Hz, 1H), 3.71 (s, 4H), 1.64 (s, 18H).

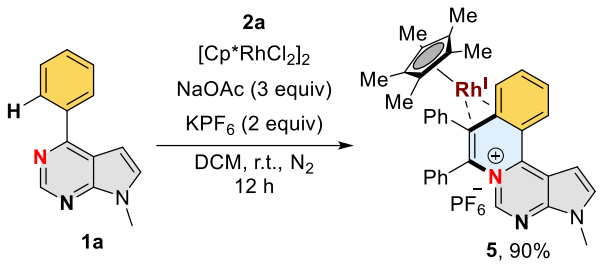
^{13}C NMR (100 MHz, $CDCl_3$): δ 182.9, 182.6, 163.2, 152.0, 150.9, 144.5, 137.1, 131.2, 130.9, 127.5, 123.0, 113.7, 99.8, 95.9, 95.9, 31.3, 9.3.



HRMS (ESI-TOF) m/z $[M\text{-}Cl]^+$ calcd for $C_{23}H_{25}N_3Rh$: 446.1098, found 446.1095.

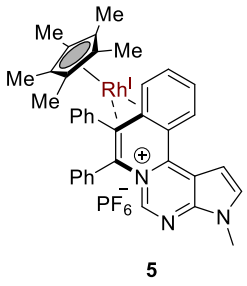


4.2 Synthesis of Rh(I) complex 5



$[Cp^*RhCl_2]_2$ (100.0 mg, 0.15 mmol), **1a** (0.3 mmol), **2a** (0.3 mmol), sodium acetate (0.45 mmol 3.0 equiv.), KPF_6 (0.3 mmol, 2.0 equiv.) and methanol (MeOH, 3 mL) were charged into a Schleck tube under N_2 atmosphere. Then, the mixture was stirred at room temperature for 1 h, and then the corresponding solution was concentrated under vacuum to remove the solvent. The complex **5** was purified via silica gel chromatography (eluent: DCM/MeOH = 20:1).

Rh(I) Complex 5

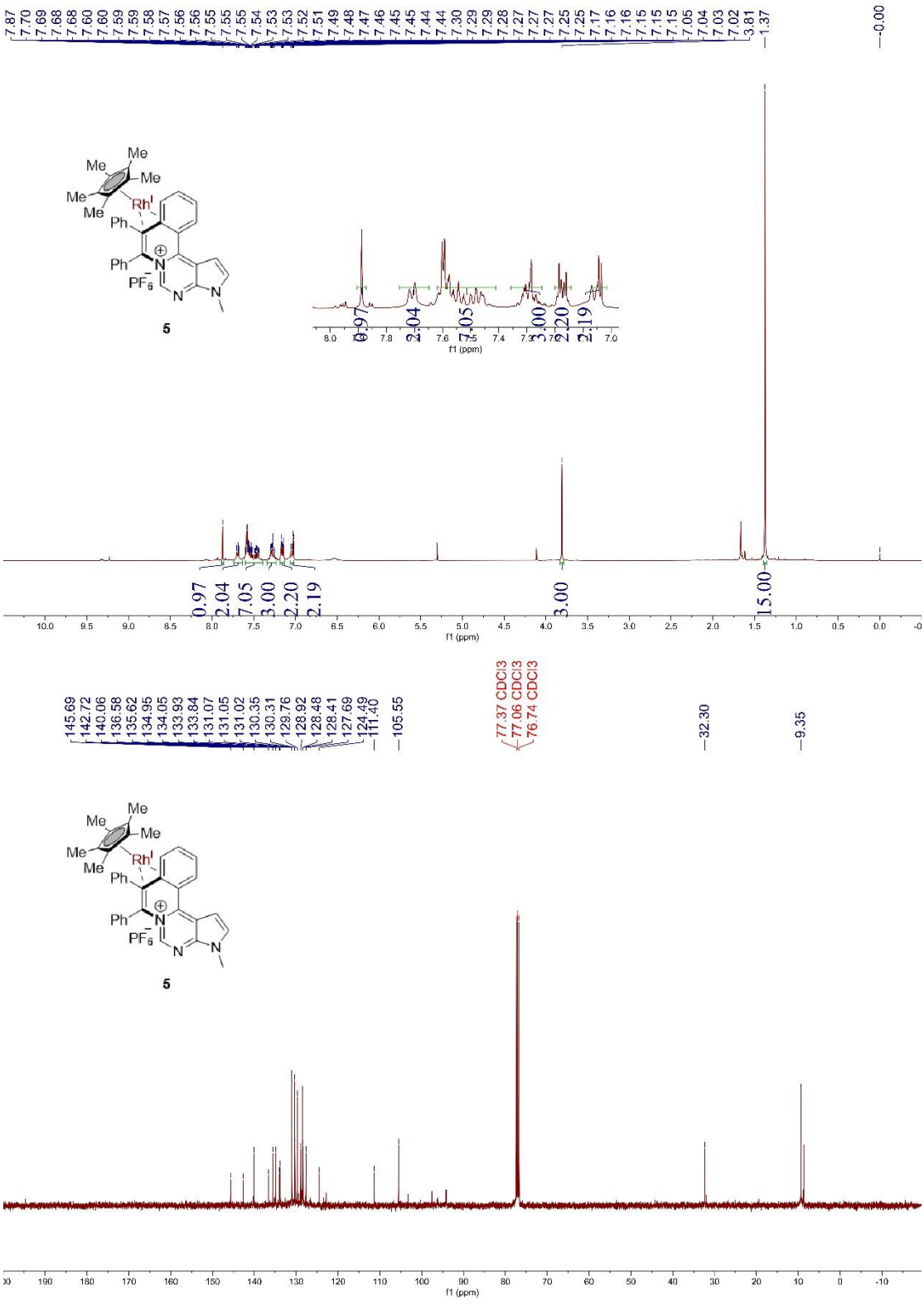


5

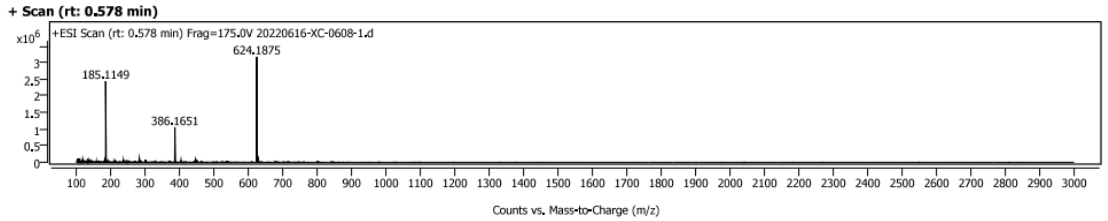
Black solid, yield 90%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.78 – 7.65 (m, 2H), 7.62 – 7.41 (m, 7H), 7.40 – 7.21 (m, 3H), 7.19 – 7.12 (m, 2H), 7.08 – 6.99 (m, 3H), 3.81 (s, 4H), 1.37 (s, 22H).

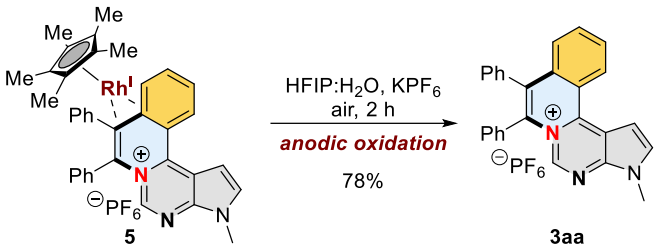
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 142.7, 140.1, 136.6, 135.6, 134.9, 134.1, 133.9, 133.8, 131.1, 131.1, 131.0, 130.4, 130.3, 129.8, 128.9, 128.5, 128.4, 127.7, 124.5, 111.4, 105.6, 32.3, 9.4.



HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ calcd for $C_{37}H_{35}N_3Rh$: 624.1881, found 624.1875.

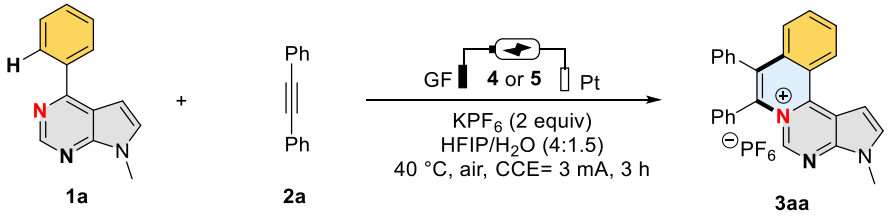


4.3 Electrolysis of complex 5



To a 10-mL Schlenk tube, complex **5** (0.1 mmol), KPF_6 (0.2 mmol, 2.0 equiv.) were dissolved in solvent mixture HFIP/H_2O (4:1, 5 mL). Electrocatalysis was performed at 40 ºC with a constant current of 3.0 mA maintained for 1.5 h. When the reaction was completed, the mixture was diluted with DCM (10 mL). The GF anode was washed with DCM (3 x 5 mL) in an ultrasonic bath, and all the solvent was transferred to a round bottom flask. The solvent was removed under reduced pressure. The mixture was concentrated and purified by silica gel column chromatography using PE/EA (1:2) to DCM/MeOH (50:1) as eluent to give the desired product **3aa** was isolated in 78% yield.

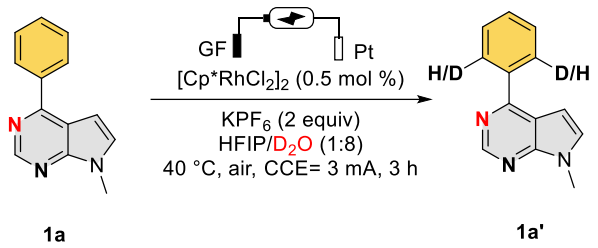
4.4 Rhodium based intermediates 4 and 5 used as catalysts in the [4+2] annulation of 1a with 2a



To a 10-mL Schlenk flask, **1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 equiv.), complex **4** or **5** (1.0 mol %) and KPF_6 (0.2 mmol, 2.0 equiv.) were dissolved in solvent mixture HFIP/H_2O (4:1.5, 5.5 mL). Electrocatalysis was performed at 40 ºC with a constant current of 3.0 mA maintained for 1.5 h. When the reaction was completed, the mixture was diluted with DCM (10 mL). The GF anode was washed with DCM (3 x 5 mL) in

an ultrasonic bath, and all the solvent was transferred to a round bottom flask. The solvent was removed under reduced pressure. The mixture was concentrated and purified by silica gel column chromatography using PE/EA (1:2) to DCM/MeOH (50:1) as eluent to give the desired product **3aa** was isolated in 92% or 90% yield respectively.

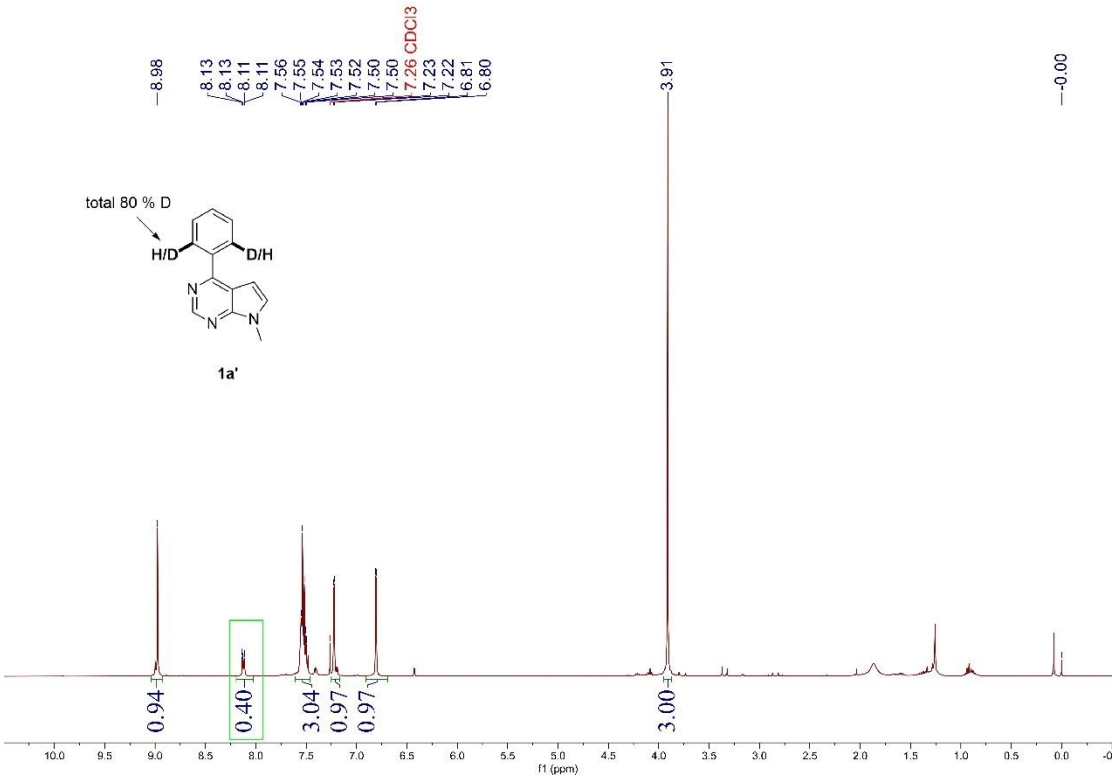
4.5 D/H exchange of 1a with D_2O under eletrochemical conditions.



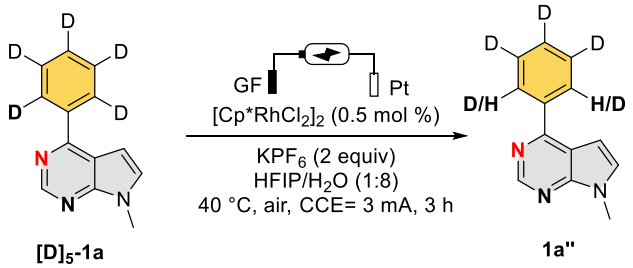
1a **1a'**

To a 10-mL Schlenk flask, **1a** (0.25 mmol), $[Cp^*RhCl_2]_2$ (0.5 mol %) and KPF_6 (0.5 mmol, 2.0 equiv.) were dissolved in solvent mixture HFIP/D_2O (1:8, 5 mL). Electrocatalysis was performed at 40 °C with a constant current of 3.0 mA maintained for 3 h. When the reaction was completed, the mixture was diluted with DCM (10 mL). The GF anode was washed with DCM (3 x 5 mL) in an ultrasonic bath, and all the solvent was transferred to a round bottom flask. The solvent was removed under reduced pressure. The mixture was concentrated and purified by silica gel column chromatography using PE/EA (5:1) as eluent to give the desired product **1a'**. The D/H-incorporation in **1a'** was determined by ^{1}H-NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **1a'**.

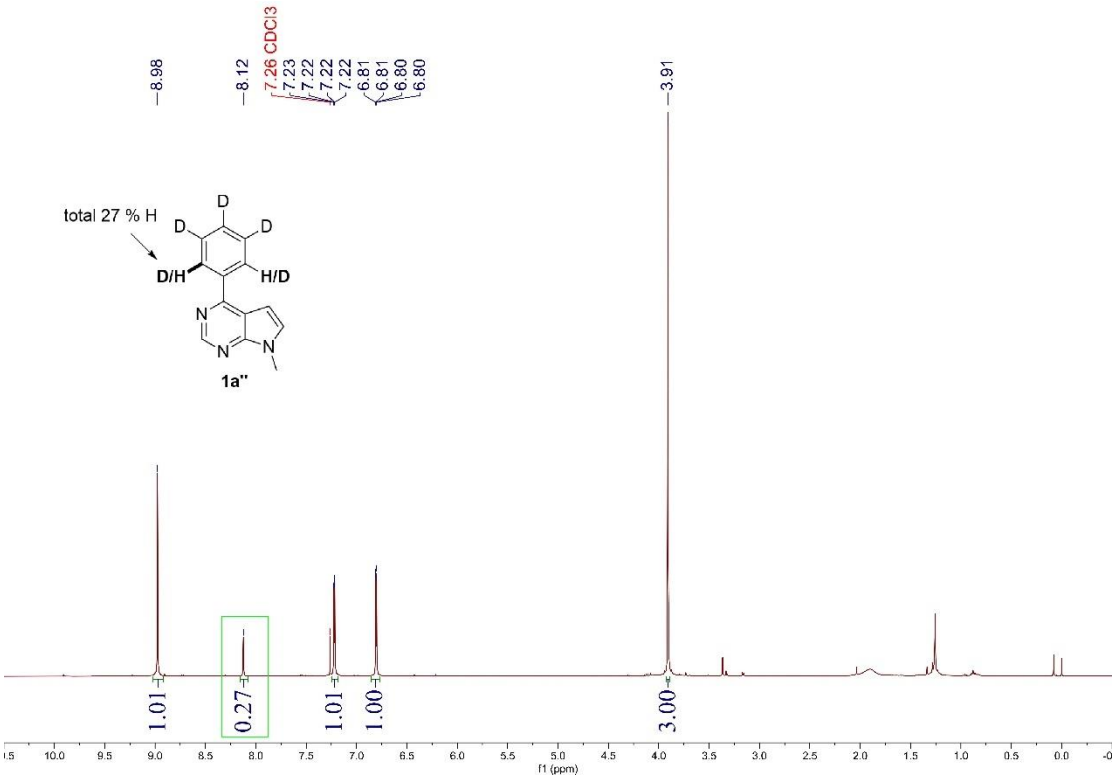


4.6 D/H exchange of [D] $_5$-1a with H_2O under eletrochemical conditions.

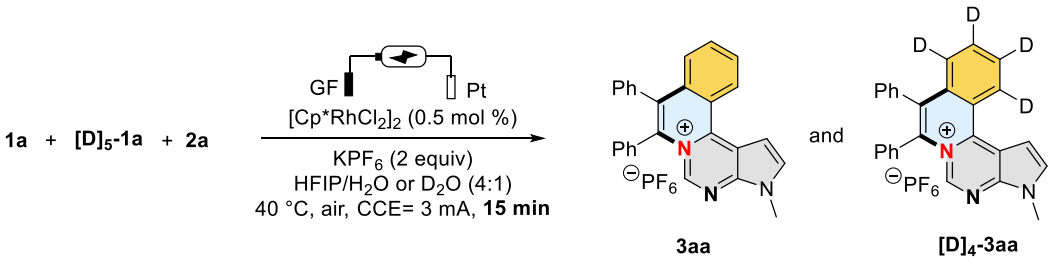


To a 10-mL Schlenk flask, **[D]$_5$-1a** (0.25 mmol), $[Cp^*RhCl_2]_2$ (0.5 mol %) and KPF_6 (0.5 mmol, 2.0 equiv.) were dissolved in solvent mixture HFIP/H_2O (1:8, 5 mL). Electrocatalysis was performed at 40 °C with a constant current of 3.0 mA maintained for 3 h. When the reaction was completed, the mixture was diluted with DCM (10 mL). The GF anode was washed with DCM (3 x 5 mL) in an ultrasonic bath, and all the solvent was transferred to a round bottom flask. The solvent was removed under reduced pressure. The mixture was concentrated and purified by silica gel column chromatography using PE/EA (5:1) as eluent to give the desired product **1a"**. The D/H-incorporation in **1a"** was determined by ^{1}H-NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **1a"**.



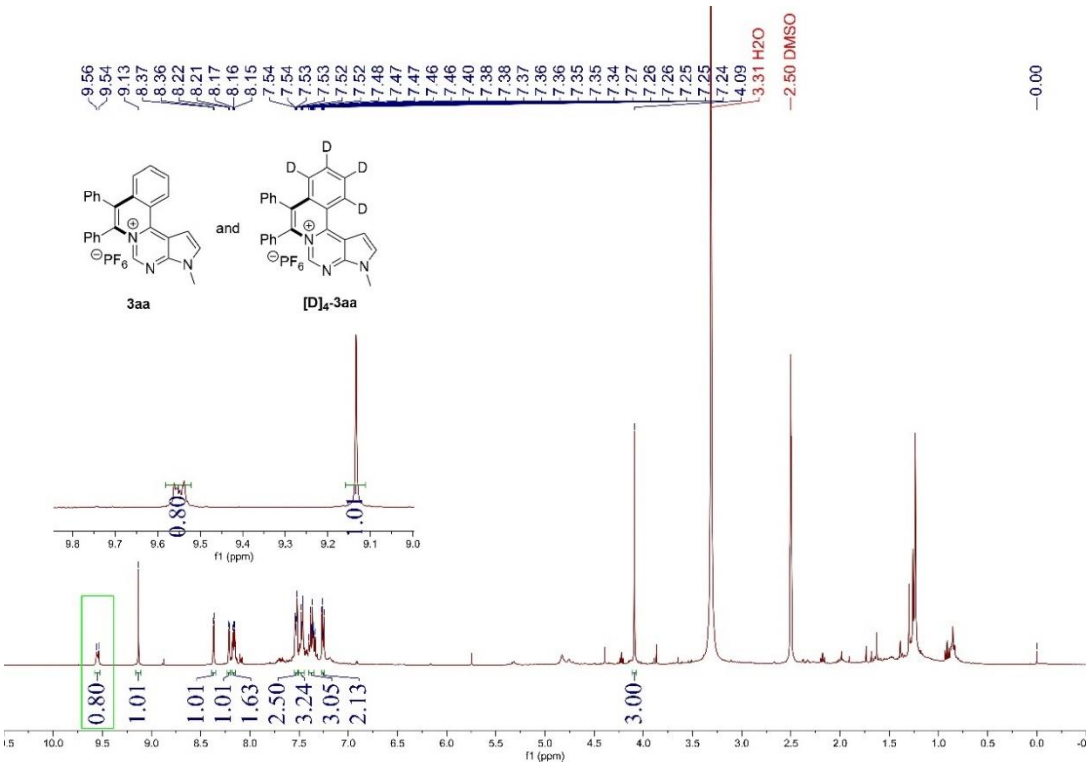
4.7 KIE experiments.



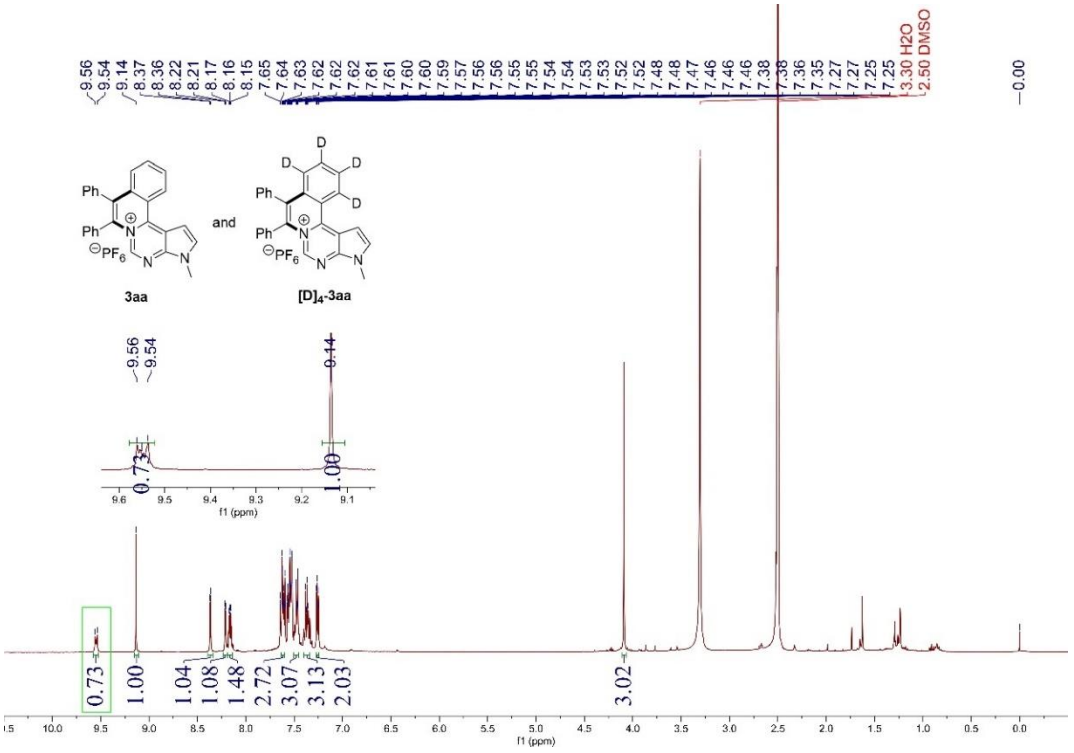
To a 10-mL three-necked flask, **[D]$_5$-1a** (0.20 mmol), **1a** (0.20 mmol), diphenylacetylene **2a** (0.22 mmol), $[Cp^*RhCl_2]_2$ (0.5 mol %) and KPF_6 (0.4 mmol, 2.0 equiv.) were dissolved in solvent mixture HFIP/H_2O (or D_2O) (4:1, 5 mL). Electrocatalysis was performed at 35 ºC with a constant current of 3.0 mA maintained for 15 min. When the reaction was completed, the mixture was diluted with DCM (10 mL). The GF anode was washed with DCM (3 x 5 mL) in an ultrasonic bath, and all the solvent was transferred to a round bottom flask. The solvent was removed under reduced pressure. The mixture was concentrated and purified by silica gel column chromatography using PE/EA (30:60) to DCM/MeOH (50:1) as eluent to give the

desired product **[D]$_4$-3aa**. The D/H-incorporation in **3aa**/**[D]$_4$-3aa** was determined by ^{1}H-NMR spectroscopy. The kinetic isotopic effect of this reaction was determined to be $k_H/k_D \approx 4.0$ in H_2O and $k_H/k_D \approx 2.7$ in D_2O.

^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **3aa**/**[D]$_4$-3aa** in H_2O.



^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **3aa**/**[D]$_4$-3aa** in D_2O.



5. Cyclic Voltammetry Studies

The voltammograms were recorded at room temperature in MeCN at a substrate concentration of 5 mmol/L and with 0.1 mol/L *n*-Bu_4NPF_6 as supporting electrolyte. Using glassy carbon electrode working electrode, Pt wire, and Ag/AgCl as counter and reference electrodes at 100 mV/s scan rate.

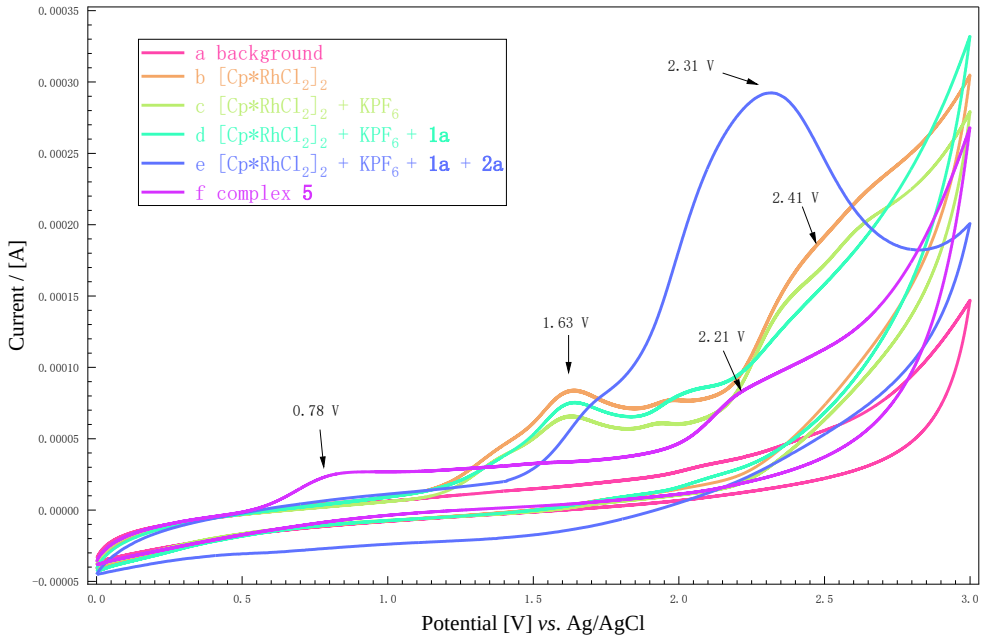


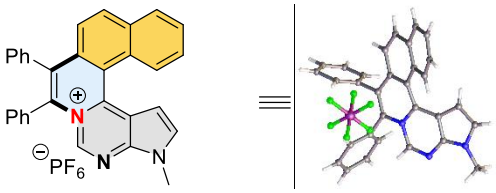
Figure S2. (a): *n*-Bu_4NPF_6 (0.1 M). (b): *n*-Bu_4NPF_6 (0.1 M) and $[Cp^*RhCl_2]_2$ (2.0 mM). (c): *n*-Bu_4NPF_6 (0.1 M), $[Cp^*RhCl_2]_2$ (2.0 mM) and KPF_6 (4.0 mM). (d): *n*-Bu_4NPF_6 (0.1 M), $[Cp^*RhCl_2]_2$ (2.0 mM), KPF_6 (4.0 mM), and **1a** (4.0 mM). (e): *n*-Bu_4NPF_6 (0.1 M), $[Cp^*RhCl_2]_2$ (2.0 mM), KPF_6 (4.0 mM), **1a** (4.0 mM), and **2a** (4.0 mM). (f): *n*-Bu_4NPF_6 (0.1 M) and complex **5** (2.0 mM).

6. X-Ray Crystallographic Data

General procedure for crystal preparation:

Compound **3sa** (around 20 mg) were dissolved in MeOH to make a saturated solution, filtration with microporous membrane, a few drops of cyclohexane were added. The single crystals were grown by slow evaporation of solvents at room temperature. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition number:

CCDC 2180414 for compound **3sa**.

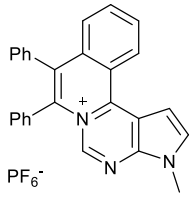


Empirical formula	$C_{31}H_{22}F_6N_3P$
Formula weight	581.48
Temperature/K	193.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.087(2)
b/Å	11.905(3)
c/Å	28.081(7)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2703.4(13)
Z	4
ρcalcg/cm^3	1.429
μ/mm-1	0.170
F (000)	1192.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.716 to 52.858
Index ranges	$-6 \le h \le 10$, $-14 \le k \le 14$, $-35 \le l \le 35$
Reflections collected	15835
Independent reflections	5447 [Rint = 0.0732, Rsigma = 0.0812]
Data/restraints/parameters	5447/0/372
Goodness-of-fit on F^2	1.171

Final R indexes [I>=2σ (I)]	R_1 = 0.1275, wR_2 = 0.3305
Final R indexes [all data]	R_1 = 0.1526, wR_2 = 0.3474
Largest diff. peak/hole / e Å^{-3}	0.61/-0.56
Flack parameter	0.4(6)

8. Characterization data of compounds 3

3-Methyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3aa)



3aa

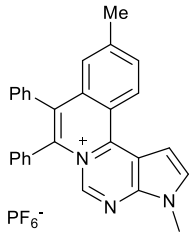
Follow the general procedure, product **3aa** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 119 mg, 90% yield as a yellow solid. **M. p.**: 270 – 271 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.53 (d, *J* = 7.2 Hz, 1H), 9.16 (s, 1H), 8.37 (d, *J* = 3.6 Hz, 1H), 8.21 (d, *J* = 3.6 Hz, 1H), 8.18 – 8.12 (m, 2H), 7.58 – 7.46 (m, 6H), 7.42 – 7.33 (m, 3H), 7.30 – 7.28 (m, 2H), 4.09 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 145.1, 142.2, 140.6, 136.9, 136.1, 135.2, 134.1, 133.5, 132.3, 131.4, 131.0, 130.0, 130.2, 130.0, 129.2, 129.0, 128.4, 128.2, 126.9, 123.8, 110.6, 104.9, 32.0.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{27}H_{20}N_3$ 386.1652, found 386.1647.

3,10-Dimethyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ba)



3ba

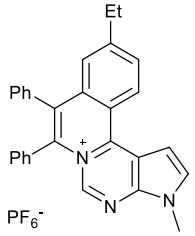
Follow the general procedure, product **3ba** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 124 mg, 91% yield as a yellow solid. **M. p.**: 188 – 190 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.45 (d, *J* = 8.8 Hz, 1H), 9.09 (s, 1H), 8.34 (d, *J* = 3.6 Hz, 1H), 8.19 (d, *J* = 4.0 Hz, 1H), 8.00 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.55 – 7.44 (m, 5H), 7.41 – 7.34 (m, 3H), 7.31 – 7.23 (m, 3H), 4.08 (s, 3H), 2.55 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 146.5, 144.9, 142.1, 140.6, 137.1, 135.8, 134.1, 133.7, 132.5, 132.0, 131.5, 131.0, 130.2, 130.0, 129.2, 129.0, 128.4, 128.2, 126.3, 121.7, 110.2, 104.9, 32.0, 21.8.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{28}H_{22}N_3$ 386.1809, found 386.1805.

10-Ethyl-3-methyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ca)



3ca

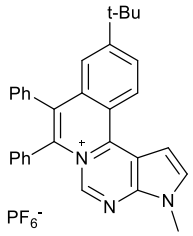
Follow the general procedure, product **3ba** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 118 mg, 85% yield as a yellow solid. **M. p.**: 185 – 188 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.47 (d, *J* = 8.4 Hz, 1H), 9.09 (s, 1H), 8.34 (d, *J* = 3.6 Hz, 1H), 8.18 (d, *J* = 4.0 Hz, 1H), 8.04 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.50 – 7.44 (m, 3H), 7.41 – 7.34 (m, 3H), 7.30 (d, *J* = 1.6 Hz, 1H), 7.28 – 7.23 (m, 2H), 4.08 (s, 3H), 2.83 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 152.2, 144.9, 142.1, 140.6, 137.1, 135.8, 134.1, 133.9, 132.1, 131.5, 131.4, 131.0, 130.2, 130.0, 129.2, 129.2, 128.4, 128.2, 125.1, 121.9, 110.2, 104.9, 32.0, 28.6, 14.9.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{29}H_{24}N_3$ 414.1965, found 414.1963.

10-(tert-butyl)-3-methyl-7,8-diphenyl-3H-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3da)



3da

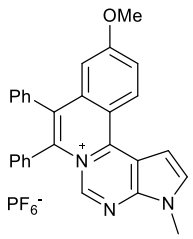
Follow the general procedure, product **3da** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 118 mg, 92% yield as a yellow solid. **M. p.**: 278 – 282 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.49 (d, *J* = 8.8 Hz, 1H), 9.12 (s, 1H), 8.36 (d, *J* = 3.6 Hz, 1H), 8.25 (d, *J* = 9.2 Hz, 1H), 8.18 (d, *J* = 3.6 Hz, 1H), 7.56 – 7.47 (m, 6H), 7.43 – 7.36 (m, 3H), 7.29 (d, *J* = 7.2 Hz, 2H), 4.09 (s, 4H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 158.4, 144.9, 141.9, 140.5, 137.0, 135.9, 134.1, 133.7, 132.4, 131.4, 131.0, 130.2, 130.0, 129.2, 129.0, 128.3, 128.2, 122.4, 121.7, 110.3, 104.8, 35.4, 32.0, 30.3.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{31}H_{28}N_3$ 442.2278, found 442.2276.

10-Methoxy-3-methyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ea)



3ea

Follow the general procedure, product **3ea** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 127 mg, 91% yield as a yellow solid. **M. p.**: 208 – 209 °C.

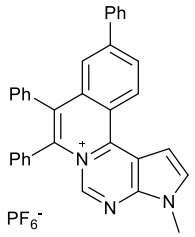
^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 9.48 (d, *J* = 9.0 Hz, 1H), 9.01 (s, 1H), 8.27 (d, *J* = 4.2 Hz, 1H), 8.09 (d, *J* = 3.6 Hz, 1H), 7.74 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.64 – 7.60 (m,

1H), 7.53 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.48 – 7.45 (m, 2H), 7.40 – 7.32 (m, 3H), 7.28 – 7.24 (m, 2H), 6.80 (d, *J* = 3.0 Hz, 1H), 4.06 (s, 3H), 3.84 (s, 3H).

^{13}C NMR (150 MHz, DMSO-d$_6$) δ 164.1, 144.5, 141.9, 140.5, 137.5, 136.4, 135.3, 134.1, 131.7, 131.6, 131.5, 131.5, 131.4, 131.0, 130.1, 130.1, 129.2, 128.8, 128.7, 128.5, 128.3, 119.7, 117.5, 109.5, 108.8, 104.8, 56.0, 32.0.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{28}H_{22}N_3O$ 416.1758, found 416.1751.

3-Methyl-7,8,10-triphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3fa)



3fa

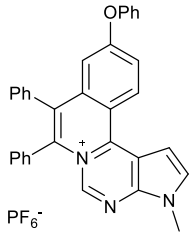
Follow the general procedure, product **3fa** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 127 mg, 91% yield as a yellow solid. **M. p.**: 225 – 226 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.62 (d, *J* = 8.8 Hz, 1H), 9.14 (s, 1H), 8.43 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.39 (d, *J* = 3.6 Hz, 1H), 8.23 (d, *J* = 3.6 Hz, 1H), 7.67 – 7.65 (m, 3H), 7.57 – 7.47 (m, 8H), 7.42 – 7.30 (m, 5H), 4.10 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 146.0, 145.1, 141.9, 140.7, 137.7, 137.4, 136.2, 134.2, 133.9, 132.2, 131.4, 131.0, 130.3, 130.1, 129.9, 129.6, 129.4, 129.3, 128.4, 128.4, 127.2, 123.9, 122.8, 110.5, 104.8, 32.1.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{33}H_{24}N_3$ 462.1965, found 462.1963.

3-Methyl-10-phenoxy-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ga)



3ga

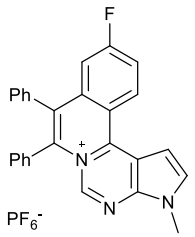
Follow the general procedure, product **3ga** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 134 mg, 86% yield as a yellow solid. **M. p.**: 110 – 115 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.52 (d, *J* = 9.2 Hz, 1H), 9.07 (s, 1H), 8.31 (d, *J* = 3.6 Hz, 1H), 8.08 (d, *J* = 3.6 Hz, 1H), 7.67 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.50 – 7.47 (m, 5H), 7.35 – 7.26 (m, 4H), 7.24 – 7.17 (m, 4H), 6.86 (d, *J* = 2.8 Hz, 1H), 4.07 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 170.3, 162.5, 153.6, 144.8, 141.8, 140.5, 137.6, 136.3, 135.6, 133.8, 132.2, 131.6, 131.3, 130.9, 130.5, 130.1, 130.0, 129.2, 128.3, 128.1, 125.8, 120.6, 120.4, 118.7, 112.2, 109.8, 104.7, 31.8.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{33}H_{24}N_3O$ 478.1914, found 478.1911.

10-Fluoro-3-methyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ha)



3ha

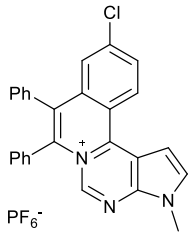
Follow the general procedure, product **3ha** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 107 mg, 78% yield as a yellow solid. **M. p.**: 105 – 106 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.62 (t, *J* = 8.0 Hz, 1H), 9.12 (s, 1H), 8.35 (s, 1H), 8.16 (s, 1H), 8.09 – 7.91 (m, 1H), 7.57 – 7.09 (m, 11H), 4.08 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 165.2 (d, *J* = 257.7 Hz), 145.2, 141.8, 140.7, 138.07, 136.5 (d, *J* = 10.0 Hz), 133.6, 133.1 (d, *J* = 10.2 Hz), 131.5, 131.1, 130.9, 130.2 (d, *J* = 5.4 Hz), 129.3, 128.5 (d, *J* = 8.4 Hz), 120.8, 119.8 (d, *J* = 23.5 Hz), 112.0 (d, *J* = 23.5 Hz), 110.3, 104.8, 32.1.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{27}H_{19}FN_3$ 404.1558, found 404.1550.

10-Chloro-3-methyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate(3ia)



3ia

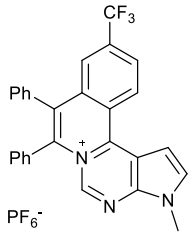
Follow the general procedure, product **3ia** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 99 mg, 70% yield as a yellow solid. **M. p.**: 253 – 256 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.55 (d, J = 9.2 Hz, 1H), 9.15 (s, 1H), 8.40 (d, J = 4.0 Hz, 1H), 8.21 – 8.12 (m, 2H), 7.61 – 7.46 (m, 6H), 7.41 – 7.46 (m, 5H), 7.30 – 7.19 (m, 2H), 4.09 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 145.4, 141.7, 140.8, 140.2, 138.3, 136.6, 135.0, 133.5, 131.3, 131.1, 131.1, 131.0, 130.9, 130.2, 129.3, 128.6, 128.5, 125.7, 122.5, 110.6, 104.7, 32.1.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{27}H_{19}ClN_3$ 420.1263, found 420.1259.

3-Methyl-7,8-diphenyl-10-(trifluoromethyl)-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ja)



3ja

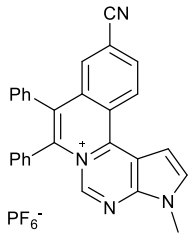
Follow the general procedure, product **3ja** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 101 mg, 68% yield as a yellow solid. **M. p.**: 145 – 148 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.76 (d, *J* = 9.2 Hz, 1H), 9.24 (s, 1H), 8.48 (d, *J* = 3.6 Hz, 1H), 8.39 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.25 (d, *J* = 3.6 Hz, 1H), 7.68 (s, 1H), 7.53 – 7.47 (m, 5H), 7.42 – 7.40 (m, 3H), 7.32 – 7.28 (m, 2H), 4.12 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 145.9, 141.4, 141.0, 138.4, 137.4, 133.7, 133.3, 133.3, 131.7, 130.9, 130.9, 130.3, 130.2, 129.3, 128.6, 128.6, 126.4, 126.3 (q, *J* = 3.0 Hz), 124.39, 123.1 (d, *J* = 4.6 Hz), 121.7, 111.3, 104.7, 32.2.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{28}H_{19}F_3N_3$ 454.1526, found 454.1521.

10-Cyano-3-methyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ka)



3ka

Follow the general procedure, product **3ka** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 92 mg, 66% yield as a yellow solid. **M. p.**: 259 – 260 °C.

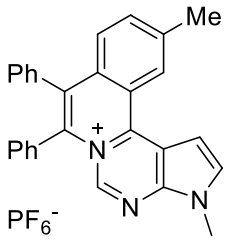
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.67 (d, *J* = 8.8 Hz, 1H), 9.23 (s, 1H), 8.57 – 8.41

(m, 2H), 8.26 (d, *J* = 4.0 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.50 (m, 5H), 7.43 – 7.36 (m, 3H), 7.27 (dd, *J* = 8.0, 2.0 Hz, 2H), 4.11 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 145.9, 141.3, 141.0, 138.5, 137.5, 133.3, 133.1, 132.4, 131.3, 131.0, 130.9, 130.9, 130.3, 130.3, 130.2, 129.3, 128.6, 126.4, 117.4, 116.7, 111.4, 104.8, 32.2.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{28}H_{19}N_4$ 411.1605, found 411.1601.

3,11-Dimethyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3la)



3la

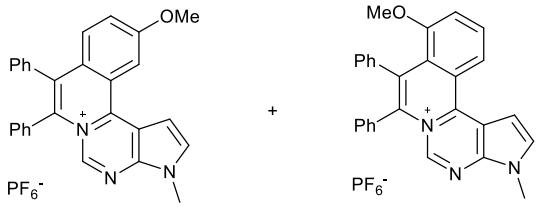
Follow the general procedure, product **3la** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 124 mg, 91% yield as a yellow solid. **M. p.**: 190 – 191 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.23 (s, 1H), 9.13 (s, 1H), 8.37 (d, *J* = 3.6 Hz, 1H), 8.30 (d, *J* = 3.8 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.46 (dt, *J* = 12.9, 7.0 Hz, 4H), 7.36 (dt, *J* = 12.0, 6.7 Hz, 3H), 7.29 – 7.22 (m, 2H), 4.09 (s, 3H), 2.78 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 145.0, 141.9, 141.7, 140.6, 136.9, 136.2, 135.9, 134.2, 132.2, 131.5, 131.4, 131.1, 130.2, 123.0, 129.2, 128.3, 128.1, 127.8, 126.8, 123.9, 110.5, 105.2, 32.0, 21.3.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{28}H_{22}N_3$ 400.1809, found 400.1803.

11-Methoxy-3-methyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ma)



3ma

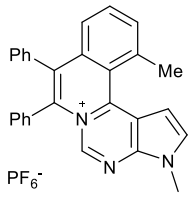
Follow the general procedure, product **3ma** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 119 mg, 85% yield as a yellow solid. **M. p.**: 147 – 149 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.13 (s, 1H), 9.08 (d, *J* = 8.4 Hz, 1H), 9.00 (s, 1H), 8.64 (s, 1H), 8.34 (t, *J* = 3.6 Hz, 2H), 8.15 – 8.05 (m, 3H), 7.82 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.32 (m, 15H), 7.28 – 7.21 (m, 2H), 7.20 – 7.09 (m, 4H), 4.18 (s, 3H), 4.09 (s, 3H), 4.07 (s, 3H), 3.39 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 160.7, 156.5, 145.1, 144.9, 142.2, 141.2, 140.6, 140.4, 138.5, 136.9, 136.1, 136.0, 135.0, 134.3, 132.1, 131.7, 131.5, 131.3, 131.2, 130.5, 130.2, 130.0, 129.7, 129.3, 129.1, 129.0, 128.8, 128.4, 128.2, 127.9, 126.9, 126.4, 125.5, 125.4, 125.0, 123.1, 121.0, 117.5, 110.6, 110.6, 109.4, 105.1, 104.7, 56.4, 56.3, 32.1, 32.0.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{28}H_{22}N_3O$ 416.1758, found 416.1757.

3,12-Dimethyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3na)



3na

Follow the general procedure, product **3na** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 106 mg, 78% yield

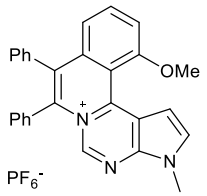
as a white solid. **M. p.**: 150 – 151 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.06 (s, 1H), 8.21 (d, *J* = 3.6 Hz, 1H), 8.05 – 7.96 (m, 2H), 7.53 – 7.52 (m, 2H), , 7.48 – 7.44 (m, 3H), 7.38 – 7.32 (m, 4H) , 7.26 – 7.21 (m, 3H), 4.06 (s, 3H), 2.81 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 158.4, 144.9, 141.9, 140.5, 137.0, 135.9, 134.1, 133.7, 132.4, 131.4, 131.0, 130.2, 130.0, 129.2, 129.0, 128.3, 128.2, 122.4, 121.7, 110.3, 104.8, 35.4, 32.0, 30.3.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{28}H_{22}N_3$ 400.1809, found 400.1806.

12-Methoxy-3-methyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3oa)



3oa

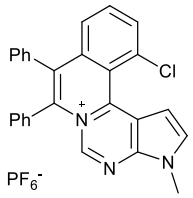
Follow the general procedure, product **3oa** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 112 mg, 80% yield as a yellow solid. **M. p.**: 181 – 183 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.02 (s, 1H), 8.13 – 8.00 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.47 – 7.42 (m, 4H), 7.40 – 7.29 (m, 4H), 7.25 – 7.18 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.17 (s, 3H), 4.03 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 158.7, 145.0, 141.6, 140.2, 136.5, 136.4, 135.4, 134.4, 132.9, 131.5, 131.2, 131.1, 130.2, 130.0, 129.2, 128.8, 128.3, 128.1, 117.8, 113.1, 112.7, 111.9, 108.0, 55.9, 31.8.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{28}H_{22}N_3O$ 416.1758, found 416.1756.

12-chloro-3-methyl-7,8-diphenyl-3H-pyrrolo[2',3':4,5]pyrimido[6,1-a]isoquinolin-6-ium hexafluorophosphate (3pa)



3pa

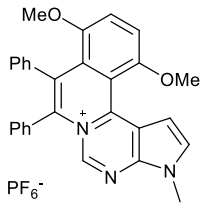
Follow the general procedure, product **3pa** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 96 mg, 68% yield as a yellow solid. **M. p.**: 128 – 129 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.12 (s, 1H), 8.30 – 8.21 (m, 2H), 8.09 (t, *J* = 8.0 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.50 – 7.46 (m, 4H), 7.43 – 7.32 (m, 4H), 7.26 – 7.21 (m, 2H), 4.07 (s, 4H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 145.1, 140.8, 140.1, 136.5, 136.4, 135.2, 134.8, 133.6, 133.2, 132.9, 131.0, 130.7, 130.4, 130.3, 130.2, 129.2, 128.4, 128.3, 125.0, 121.0, 112.9, 108.2, 32.0.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{27}H_{19}ClN_3$ 420.1263, found 420.1259.

9,12-Dimethoxy-3-methyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3qa)



3qa

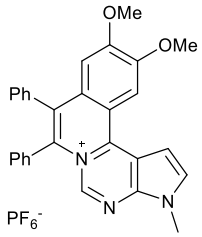
Follow the general procedure, product **3qa** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 100 mg, 68% yield as a yellow solid. **M. p.**: 158 – 162 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.90 (s, 1H), 8.08 (d, *J* = 4.6 Hz, 1H), 7.86 – 7.63 (m, 2H), 7.56 – 7.32 (m, 5H), 7.25 (d, *J* = 3.6 Hz, 1H), 7.21 – 7.04 (m, 5H), 4.10 (s, 3H), 4.02 (s, 3H), 3.28 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 152.3, 149.4, 144.7, 141.0, 139.7, 138.0, 1356.0, 133.0, 131.3, 131.3, 129.8, 129.6, 129.2, 128.9, 126.8, 126.4, 124.4, 120.6, 113.3, 113.0, 112.9, 107.7, 57.2, 55.7, 31.8.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{29}H_{24}N_3O_2$ 446.1864, found 446.1859.

10,11-Dimethoxy-3-methyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ra)



3ra

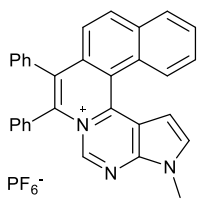
Follow the general procedure, product **3ra** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 100 mg, 68% yield as a yellow solid. **M. p.**: 176– 178 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.06 (s, 1H), 8.51 (s, 1H), 8.26 (d, *J* = 3.6 Hz, 1H), 7.96 (d, *J* = 3.6 Hz, 1H), 7.58 – 7.27 (m, 10H), 6.86 (s, 1H), 4.23 (s, 3H), 4.07 (s, 3H), 3.74 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 155.3, 151.7, 143.8, 140.4, 140.2, 135.9, 134.8, 134.2, 131.6, 131.2, 130.6, 130.2, 130.0, 129.2, 128.4, 128.3, 118.3, 109.3, 107.8, 106.6, 104.7, 56.6, 55.9, 31.9.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{29}H_{24}N_3O_2$ 446.1864, found 446.1861.

14-Methyl-4,5-diphenyl-14*H*-benzo[h]pyrrolo[2',3':4,5]pyrimido[6,1-*a*] isoquinolin-3-ium hexafluorophosphate (3sa)



3sa

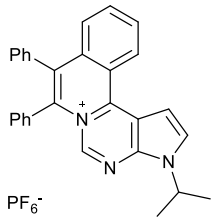
Follow the general procedure, product **3sa** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 135 mg, 93% yield as a yellow solid. **M. p.**: 270– 271 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.19 (s, 1H), 8.97 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 9.2 Hz, 1H), 8.31 (dd, *J* = 8.6, 1.2 Hz, 1H), 8.05 (d, *J* = 3.6 Hz, 1H), 7.96 – 7.92 (m, 1H), 7.86 – 7.82 (m, 1H), 7.57 (d, *J* = 6.4 Hz, 2H), 7.49 (d, *J* = 2.4 Hz, 3H), 7.44 – 7.31 (m, 5H), 7.22 (s, 1H), 7.06 (d, *J* = 3.6 Hz, 1H), 4.07 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 144.1, 141.2, 139.8, 138.0, 136.5, 135.1, 133.8, 133.3, 133.2, 131.9, 130.8, 130.2, 129.5, 129.2, 128.9, 128.4, 128.3, 128.3, 127.6, 127.1, 122.1, 120.6, 112.8, 105.0, 31.9.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{31}H_{22}N_3$ 436.1809, found 436.1808.

3-Isopropyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ua)



3ua

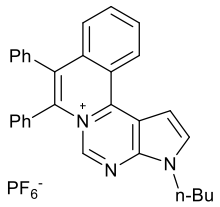
Follow the general procedure, product **3ua** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 102 mg, 73% yield as a yellow solid. **M. p.**: 171– 173 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.62 – 9.51 (m, 1H), 9.13 (s, 1H), 8.61 (d, *J* = 3.6 Hz, 1H), 8.29 (d, *J* = 4.0 Hz, 1H), 8.22 – 8.11 (m, 2H), 7.57 – 7.53 (m, 3H), 7.50 – 7.43 (m, 3H), 7.41 – 7.34 (m, 3H), 7.31 – 7.22 (m, 2H), 5.33 – 5.23 (m, 1H), 1.63 (s, 3H), 1.61 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 144.2, 142.3, 140.4, 136.9, 135.2, 134.1, 133.4, 132.3, 132.2, 131.3, 131.1, 131.0, 130.2, 130.0, 129.2, 129.2, 128.4, 128.2, 126.8, 123.8, 110.8, 105.5, 47.8, 22.1.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{29}H_{24}N_3$ 414.1965, found 414.1960.

3-Butyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3va)



3va

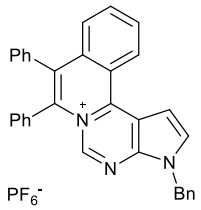
Follow the general procedure, product **3va** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 104 mg, 73% yield as a yellow solid. **M. p.**: 185 – 186 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.57 (d, *J* = 8.0 Hz, 1H), 9.14 (s, 1H), 8.47 (d, *J* = 3.6 Hz, 1H), 8.26 (d, *J* = 3.6 Hz, 1H), 8.22 – 8.12 (m, 2H), 7.61 – 7.44 (m, 6H), 7.41 – 7.33 (m, 3H), 7.27 (d, *J* = 6.8 Hz, 2H), 4.53 (t, *J* = 6.8 Hz, 2H), 1.95 – 1.88 (m, 2H), 1.34 – 1.27 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 145.0, 142.2, 140.6, 137.0, 135.2, 135.1, 134.1, 133.5, 132.2, 131.3, 131.1, 131.0, 130.2, 130.0, 129.2, 129.1, 128.4, 128.2, 126.9, 123.8, 110.6, 105.1, 44.5, 31.5, 19.2, 13.3.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{30}H_{26}N_3$ 428.2122, found 428.2121.

3-Benzyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3wa)



3wa

Follow the general procedure, product **3wa** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 120 mg, 79% yield as a yellow solid. **M. p.**: 298– 299 °C.

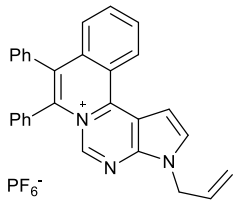
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.57 (d, *J* = 8.8 Hz, 1H), 9.18 (s, 1H), 8.54 (d, *J* = 3.6 Hz, 1H), 8.29 (d, *J* = 4.0 Hz, 1H), 8.21 – 8.10 (m, 2H), 7.60 – 7.47 (m, 6H), 7.44 –

7.32 (m, 8H), 7.31 – 7.24 (m, 2H), 5.76 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 144.9, 142.4, 140.9, 137.0, 136.2, 135.3, 135.1, 134.1, 133.5, 132.4, 131.3, 131.1, 131.1, 131.0, 130.2, 130.0, 129.2, 129.1, 128.8, 128.4, 128.2, 128.1, 127.7, 126.9, 123.8, 110.8, 105.5, 48.5.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{33}H_{24}N_3$ 462.1965, found 462.1965.

3-Allyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3xa)



3xa

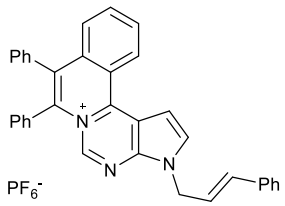
Follow the general procedure, product **3va** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 110 mg, 79% yield as a yellow solid. **M. p.**: 132– 135°C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.57 (d, *J* = 9.2 Hz, 1H), 9.14 (s, 1H), 8.39 (d, *J* = 3.6 Hz, 1H), 8.27 (d, *J* = 3.6 Hz, 1H), 8.20 – 8.14 (m, 2H), 7.58 – 7.24 (m, 11H), 6.20 – 6.10 (m, 1H), 5.28 (dd, *J* = 10.0, 1.2 Hz, 1H), 5.17 (d, *J* = 5.6 Hz, 2H), 5.09 (dd, *J* = 17.2, 1.6 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 144.9, 142.42 140.8, 137.0, 135.3, 135.1, 134.1, 133.6, 132.7, 132.4, 131.4, 131.1, 131.1, 130.2, 130.1, 129.3, 129.1, 128.4, 128.2, 126.9, 123.8, 118.3, 110.7, 105.4, 47.2.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{29}H_{22}N_3$ 412.1809, found 412.1808.

3-Cinnamyl-7,8-diphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ya)



3ya

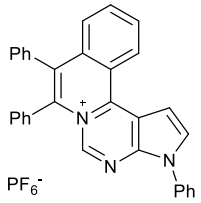
Follow the general procedure, product **3ya** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 120 mg, 76% yield as a yellow solid. **M. p.**: 169– 172 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.58 (d, *J* = 8.8 Hz, 1H), 9.18 (s, 1H), 8.48 (d, *J* = 3.6 Hz, 1H), 8.30 (d, *J* = 3.6 Hz, 1H), 8.21 – 8.14 (m, 2H), 7.74 – 7.24 (m, 20H), 6.63 (d, *J* = 4.0 Hz, 3H), 5.34 (d, *J* = 4.8 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 144.8, 142.4, 140.8, 137.0, 135.6, 135.3, 135.0, 134.1, 133.5, 133.4, 132.4, 131.3, 131.1, 130.2, 130.1, 129.2, 129.1, 128.6, 128.4, 128.2, 128.1, 126.9, 126.5, 123.8, 123.6, 110.9, 105.4, 46.9.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{35}H_{26}N_3$ 488.2122, found 488.2119.

3,7,8-Triphenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3za)



3za

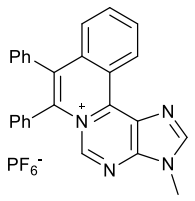
Follow the general procedure, product **3za** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 119 mg, 80% yield as a yellow solid. **M. p.**: 223– 224 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.64 (d, *J* = 8.4 Hz, 1H), 9.18 (s, 1H), 8.75 (d, *J* = 3.6 Hz, 1H), 8.46 (d, *J* = 4.0 Hz, 1H), 8.30 – 8.13 (m, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 8.0 Hz, 2H), 7.59 – 7.53 (m, 4H), 7.49 – 7.44 (m, 3H), 7.41 – 7.35 (m, 3H), 7.30 – 7.28 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 144.6, 142.7, 141.3, 137.1, 135.5, 135.4, 134.8, 134.0, 133.6, 132.8, 131.2, 131.2, 131.0, 130.2, 130.1, 129.7, 129.2, 128.8, 128.4, 128.3, 127.0, 124.8, 123.8, 111.9, 106.4.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{32}H_{22}N_3$ 448.1809, found 448.1808.

3-Methyl-7,8-diphenyl-3*H*-purino[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3aaa)



3aaa

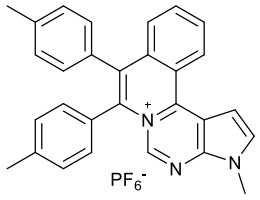
Follow the general procedure, product **3aaa** was purified through flash short column chromatography on silica gel (PE/EA: 3/1 –1/1) in 101 mg, 76% yield as a yellow solid. **M. p.**: 192 – 195 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.53 (s, 1H), 8.67 – 8.59 (m, 1H), 8.67 – 8.59 (t, *J* = 18.0 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.72 (m, 10H), 3.73 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 161.3, 148.7, 140.1, 136.6, 136.2, 135.3, 130.9, 130.1, 128.4, 127.4, 127.3, 126.3, 125.3, 124.8, 32.2.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{26}H_{19}N_4$ 387.1605, found 387.1603.

3-Methyl-7,8-di-*p*-tolyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ab)



3ab

Follow the general procedure, product **3ab** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 119 mg, 85% yield as a yellow solid. **M. p.**: 243– 244 °C.

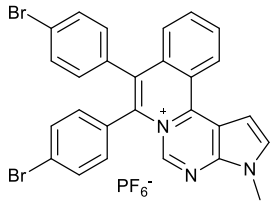
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.51 (d, *J* = 9.2 Hz, 1H), 9.08 (s, 1H), 8.33 (d, *J* = 4.0 Hz, 1H), 8.17 (d, *J* = 3.6 Hz, 1H), 8.15 – 8.09 (m, 2H), 7.64 – 7.40 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 4.07 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 145.2, 142.3, 140.7, 139.7, 137.5, 137.1, 136.1,

135.2, 133.8, 132.3, 132.1, 132.1, 131.6, 131.5, 131.3, 130.9, 130.14 130.0, 129.1, 128.9, 128.8, 128.7, 127.0, 110.6, 105.0, 32.1, 21.0, 20.8.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{29}H_{24}N_3$ 414.1965, found 414.1965.

7,8-Bis(4-bromophenyl)-3-methyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*] isoquinolin-6-ium hexafluorophosphate (3ac)



3ac

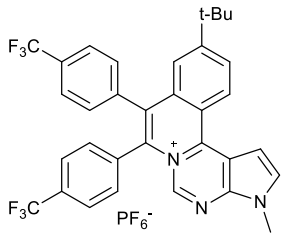
Follow the general procedure, product **3ac** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 99 mg, 58% yield as a yellow solid. **M. p.**: 259– 260 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.60 – 9.50 (m, 1H), 9.25 (s, 1H), 8.39 (d, *J* = 4.0 Hz, 1H), 8.23 (d, *J* = 4.0 Hz, 1H), 8.20 – 8.15 (m, 2H), 7.77 – 7.71 (m, 2H), 7.66 – 7.62 (m, 2H), 7.55 – 7.46 (m, 3H), 7.26 – 7.18 (m, 2H), 4.10 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 145.3, 142.2, 141.1, 136.3, 136.0, 135.4, 133.3, 133.1, 133.0, 132.5, 132.3, 131.6, 131.3, 131.2, 130.5, 129.1, 126.9, 123.9, 123.8, 121.9, 110.5, 104.9, 32.1.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{27}H_{18}Br_2N_3$ 543.9842, found 543.9838.

10-(tert-butyl)-3-Methyl-7,8-bis(4-(trifluoromethyl)phenyl)-3*H*-pyrrolo[2',3':4,5] pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ad)



3ad

Follow the general procedure, product **3ad** was purified through flash short column

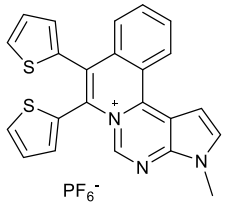
chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 110 mg, 61% yield as a yellow solid. **M. p.**: 274– 278 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.52 (d, *J* = 8.8 Hz, 1H), 9.24 (s, 1H), 8.39 (d, *J* = 3.6 Hz, 1H), 8.28 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.20 (d, *J* = 4.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 4H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 2.0 Hz, 1H), 4.10 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 158.7, 145.1, 142.0, 141.2, 138.2, 136.2, 135.8, 135.3, 132.9, 132.2, 131.3, 129.4, 129.3, 128.7, 126.2, 126.2, 125.3, 125.3, 122.1, 121.9, 110.3, 104.8, 35.4, 32.1, 30.2.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{33}H_{26}F_6N_3$ 578.2026, found 578.2025.

3-Methyl-7,8-di(thiophen-2-yl)-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate(3ae)



3ae

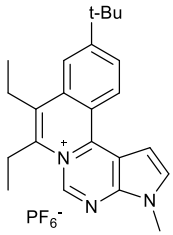
Follow the general procedure, product **3ae** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 64 mg, 47% yield as a yellow solid. **M. p.**: 255– 258 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.51 (d, *J* = 10.0 Hz, 1H), 9.33 (s, 1H), 8.36 (d, *J* = 3.6 Hz, 1H), 8.24 – 8.12 (m, 3H), 7.93 (dd, *J* = 5.2, 1.2 Hz, 2H), 7.80 – 7.69 (m, 2H), 7.45 (dd, *J* = 3.6, 1.2 Hz, 2H), 7.23 (dd, *J* = 5.2, 3.6 Hz, 2H), 7.18 – 7.06 (m, 2H), 4.10 (s, 5H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 146.01, 143.21, 141.33, 136.84, 135.89, 134.51, 133.83, 133.79, 132.86, 132.62, 132.11, 131.54, 130.69, 129.60, 129.43, 128.84, 128.33, 127.69, 127.44, 124.45, 111.00, 105.50, 32.57.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{23}H_{16}N_3S_2$ 398.0781, found 398.0780.

10-(tert-butyl)-7,8-Diethyl-3-methyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*] isoquinolin-6-ium hexafluorophosphate (3af)



3af

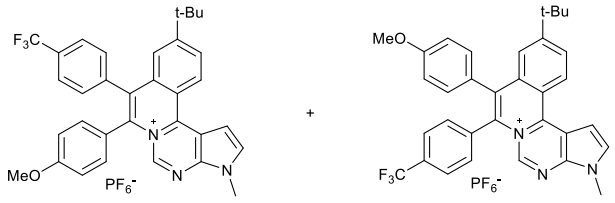
Follow the general procedure, product **3ac** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 90 mg, 73% yield as a yellow solid. **M. p.**: 143– 144 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.00 (s, 1H), 9.27 (d, *J* = 8.8 Hz, 1H), 8.23 – 8.20 (m, 2H), 8.12 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.95 (d, *J* = 3.6 Hz, 1H), 4.10 (s, 3H), 3.59 (q, *J* = 7.6 Hz, 2H), 3.31 (q, *J* = 7.6 Hz, 2H), 1.49 (s, 9H), 1.40 (t, *J* = 7.6 Hz, 3H), 1.36 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 158.3, 144.7, 141.6, 140.1, 138.3, 135.1, 132.3, 130.1, 129.3, 128.0, 121.2, 120.3, 110.3, 104.6, 35.6, 31.9, 30.6, 21.9, 21.3, 14.1, 12.1.

HRMS (ESI-TOF) m/z $[M\text{-}PF_6]^+$ Calcd for $C_{23}H_{28}N_3$ 346.2278, found 346.2272.

10-(tert-butyl)-7-(4-methoxyphenyl)-3-Methyl-8-(4-(trifluoromethyl)phenyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*]isoquinolin-6-ium hexafluorophosphate (3ag)



3ag

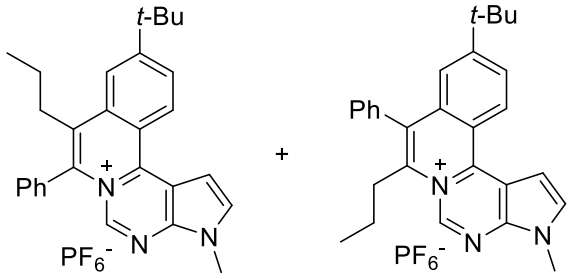
Follow the general procedure, product **3ag** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 108 mg, 63% yield as a yellow solid. **M. p.**: 184– 188 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.60 – 9.50 (m, 1H), 9.25 (s, 1H), 8.39 (d, *J* = 3.6 Hz, 1H), 8.26 – 8.13 (m, 3H), 7.77 – 7.71 (m, 2H), 7.66 – 7.62 (m, 2H), 7.55 – 7.46 (m, 3H), 7.26 – 7.18 (m, 2H), 4.10 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 160.3, 158.9, 158.5, 158.5, 145.1, 145.0, 142.1, 141.9, 141.0, 140.7, 138.9, 137.3, 135.9, 135.8, 134.0, 133.2, 132.5, 132.5, 132.2, 131.5, 131.3, 130.6, 130.2, 129.9, 129.2, 129.1, 126.2, 126.2, 125.6, 122.9, 122.6, 122.0, 121.9, 121.7, 114.9, 113.9, 110.3, 104.8, 55.3, 55.1, 35.4, 32.0, 30.3, 30.2.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{33}H_{29}F_3N_3O$ 540.2258, found 540.2255.

10-(tert-butyl)-3-Methyl-7-phenyl-8-propyl-3*H*-pyrrolo[2',3':4,5]pyrimido[6,1-*a*] isoquinolin-6-ium hexafluorophosphate(3ah)



3ah

Follow the general procedure, product **3ah** was purified through flash short column chromatography on silica gel (PE/EA: 1/2 – DCM/MeOH: 50/1) in 80 mg, 58% yield as a yellow solid. **M. p.**: 166– 169 °C.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.42 (d, *J* = 8.8 Hz, 1H), 8.94 (s, 1H), 8.32 – 8.19 (m, 3H), 8.07 (d, *J* = 4.0 Hz, 1H), 7.87 – 7.74 (m, 3H), 7.67 – 7.65 (m, 2H), 4.05 (s, 3H), 2.83 – 2.79 (m, 2H), 1.64 – 1.58 (m, 2H), 1.52 (s, 9H), 0.86 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 158.5, 144.6, 141.5, 140.5, 136.2, 135.5, 132.3, 131.8, 130.7, 130.4, 130.4, 130.1, 129.5, 129.4, 129.2, 128.6, 121.8, 121.0, 110.1, 104.6, 35.6, 35.3, 31.9, 30.7, 30.5, 30.2, 22.9, 14.1, 13.5.

HRMS (ESI-TOF) m/z $[M-PF_6]^+$ Calcd for $C_{28}H_{30}N_3$ 408.2435, found 408.2433.

9. References

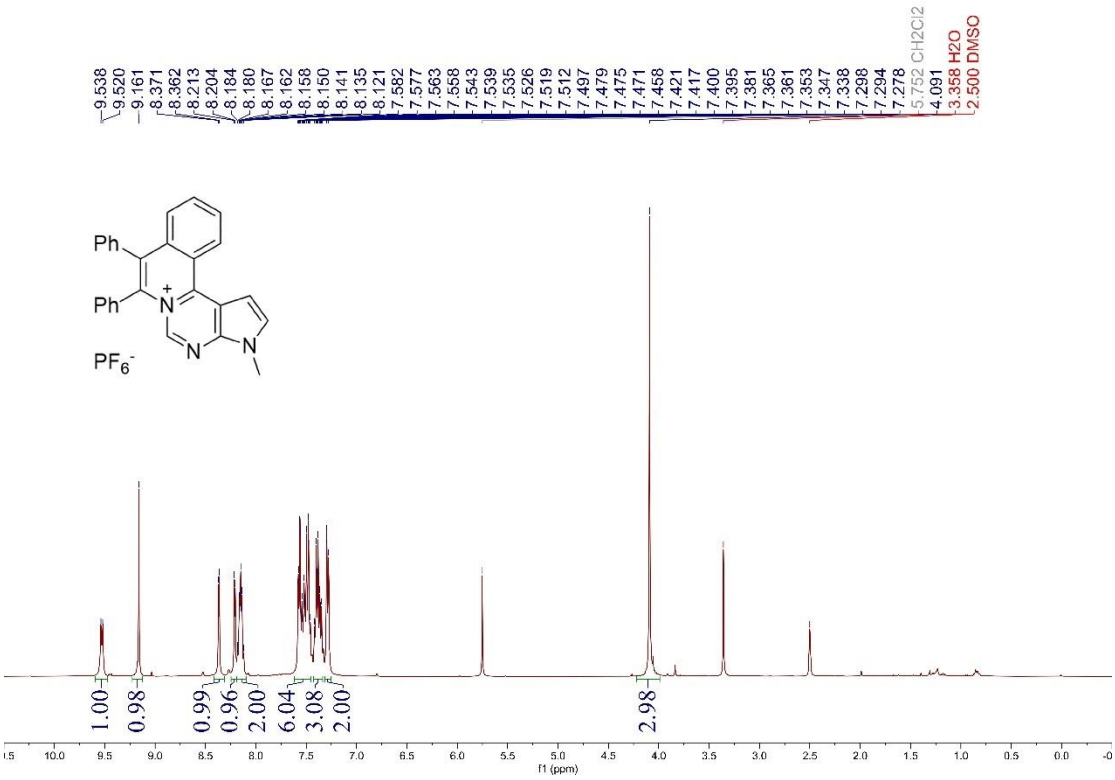
[1] Q. Gou, W.-X. Li, Q.-S. Zhao, J. Xie, P. Luo, G. Cao, S.-Y. Chen and Jun Qin, *Eur. J. Org. Chem.*, 2018, **30**, 4089–409.

[2] (a) P. Chuentragool, K. Vongnam, P. Rashatasakhon, M. Sukwattanasinitt and Sumrit Wacharasindhu. *Tetrahedron*, **2011**, *67*, 8177-8182. (b) C. He, J. Ke, H. Xu and A. -W. Lei. *Angew. Chem. Int. Ed.*, **2013**, *52*, 1527 –1530.

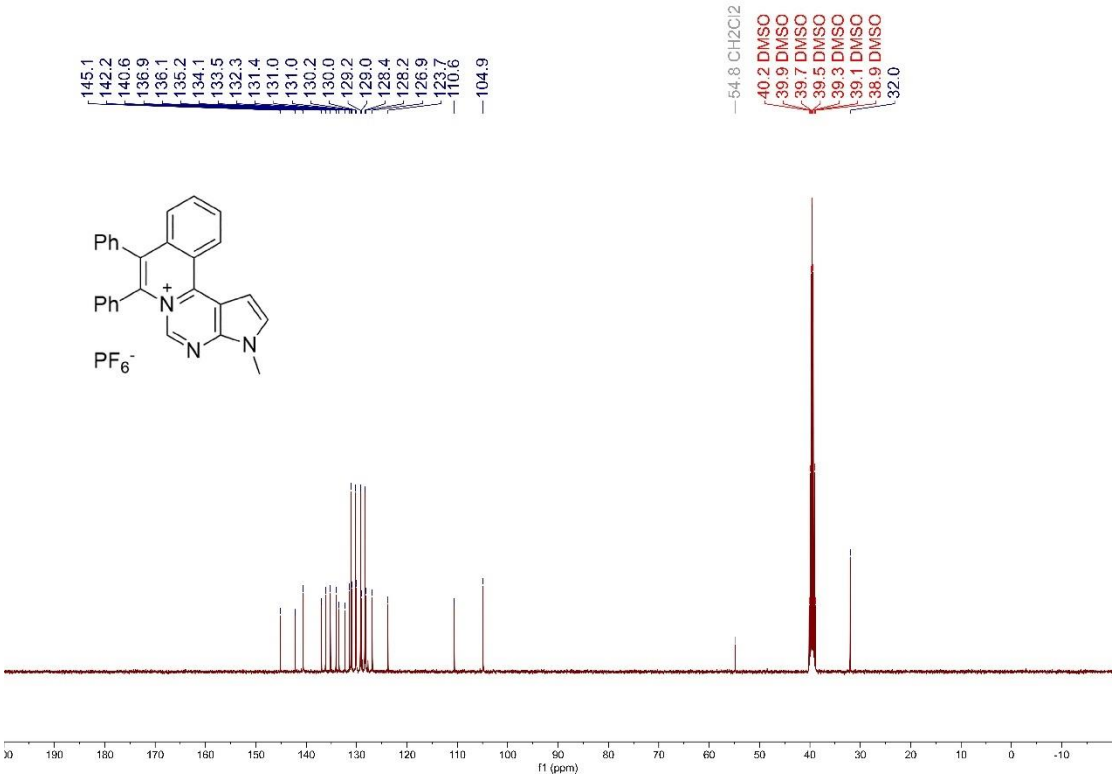
[3] Z.-C. Wang, R.-T. Li, Q. Ma, J.-Y. Chen, S.-F. Ni, M. Li, L.-R. Wen and L.-B. Zhang. *Green Chem.*, **2021**, *23*, 9515–9522.

10. NMR Spectra

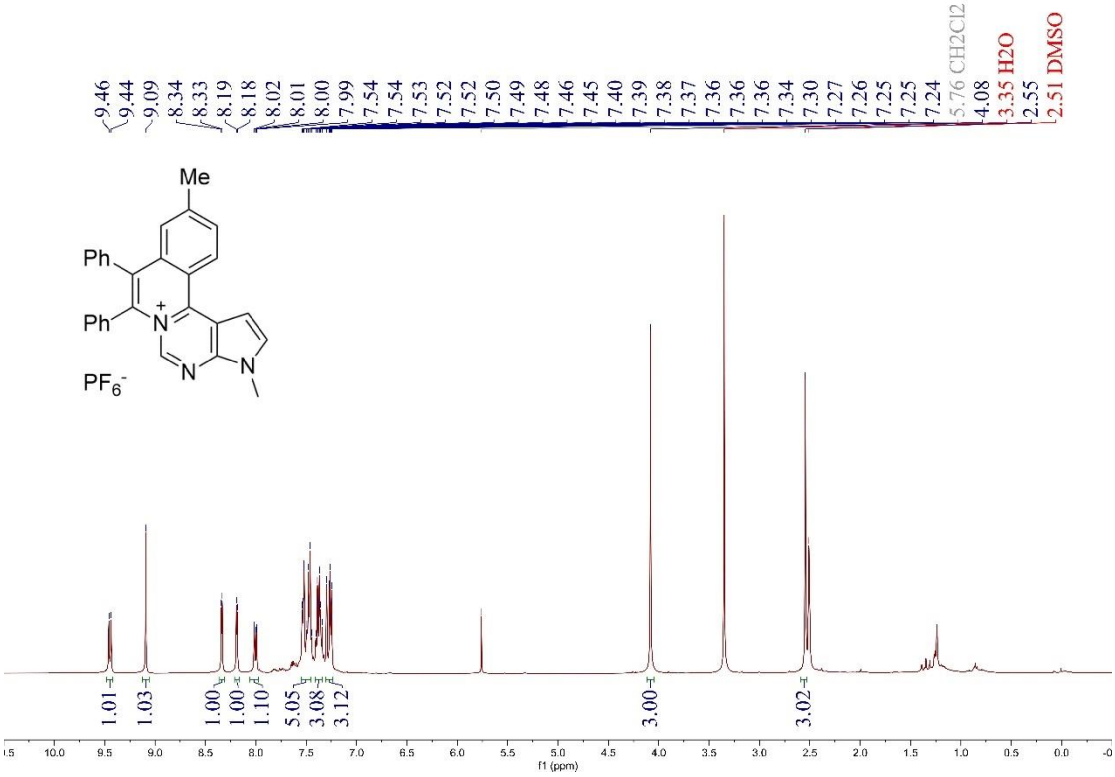
^{1}H NMR Spectrum of 3aa at 25 °C (DMSO-d_6, 400 MHz)



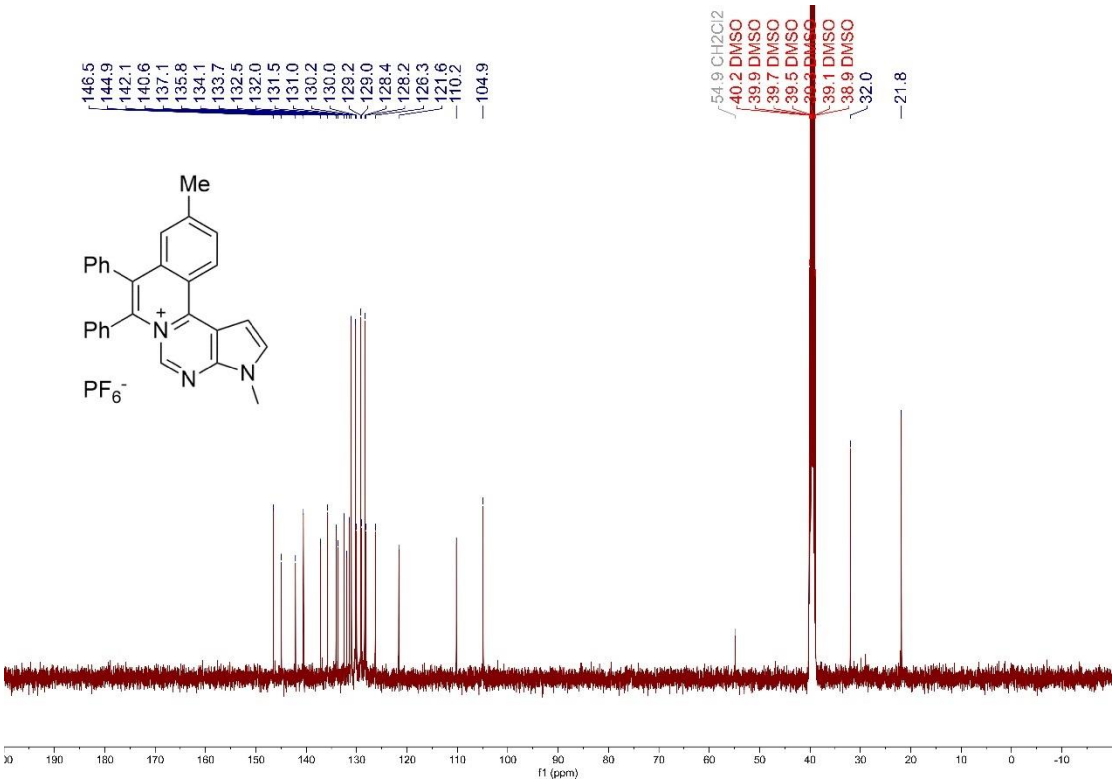
^{13}C NMR Spectrum of 3aa at 25 °C (DMSO-d_6, 100 MHz)



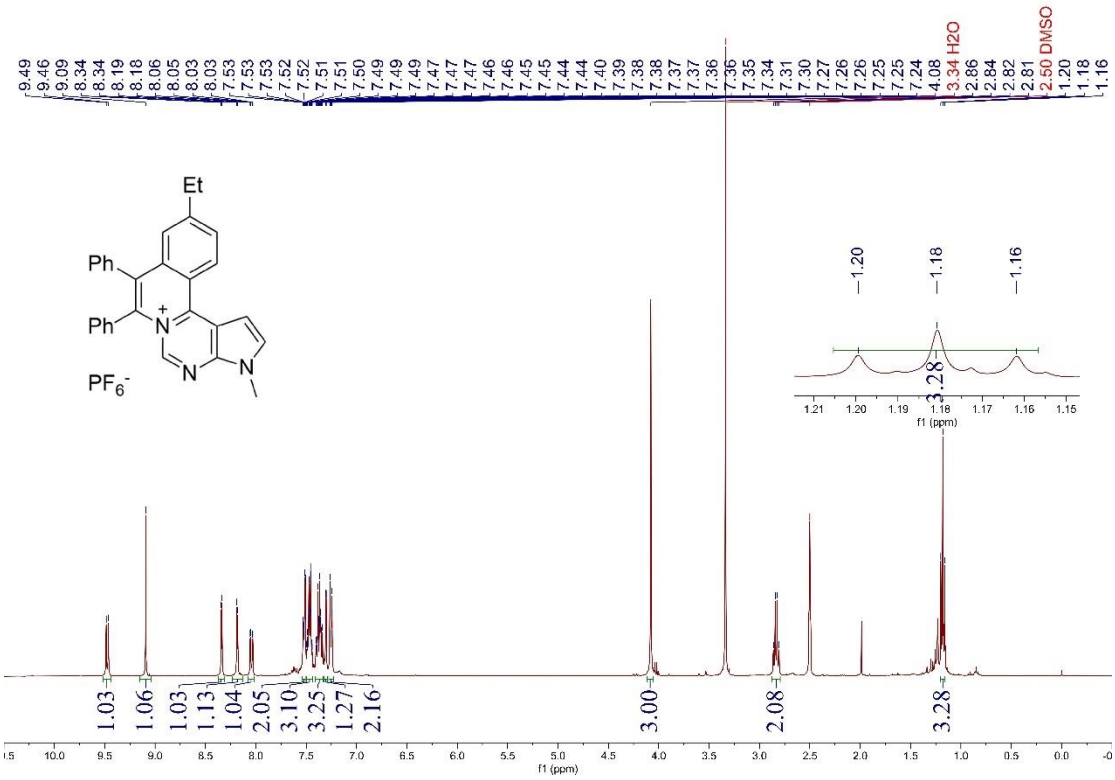
^{1}H NMR Spectrum of 3ba at 25 ^{o}C (DMSO-d_6, 400 MHz)



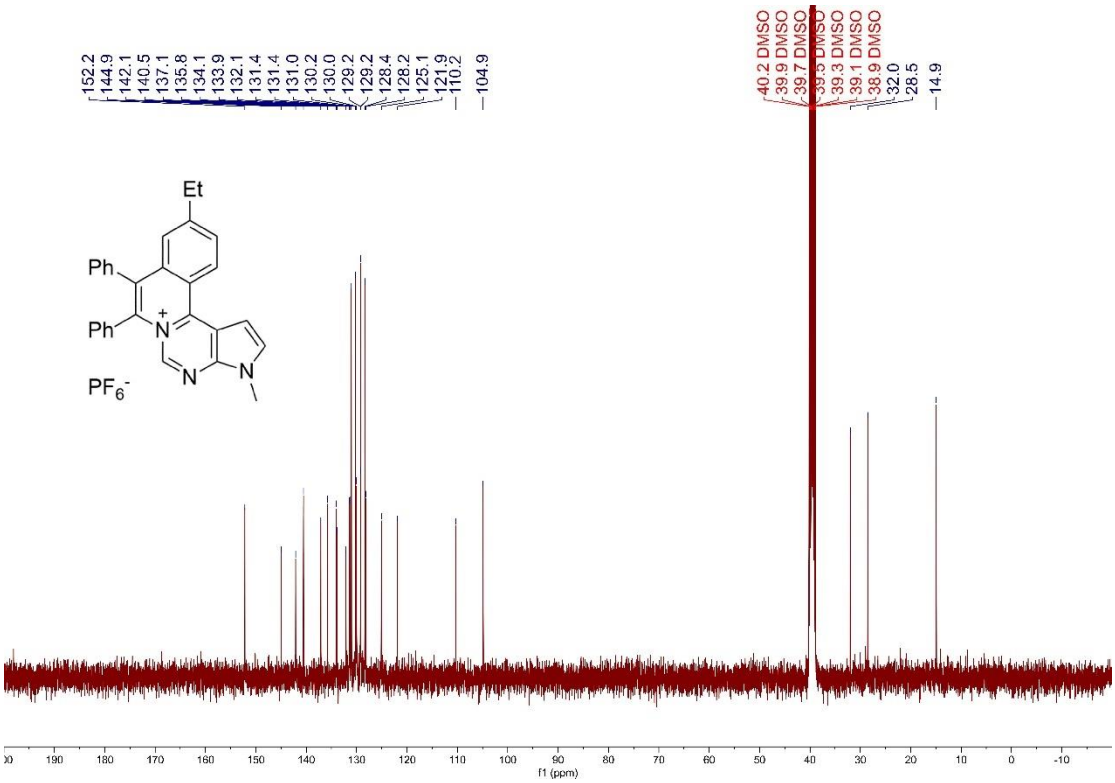
^{13}C NMR Spectrum of 3ba at 25 ^{o}C (DMSO-d_6, 100 MHz)



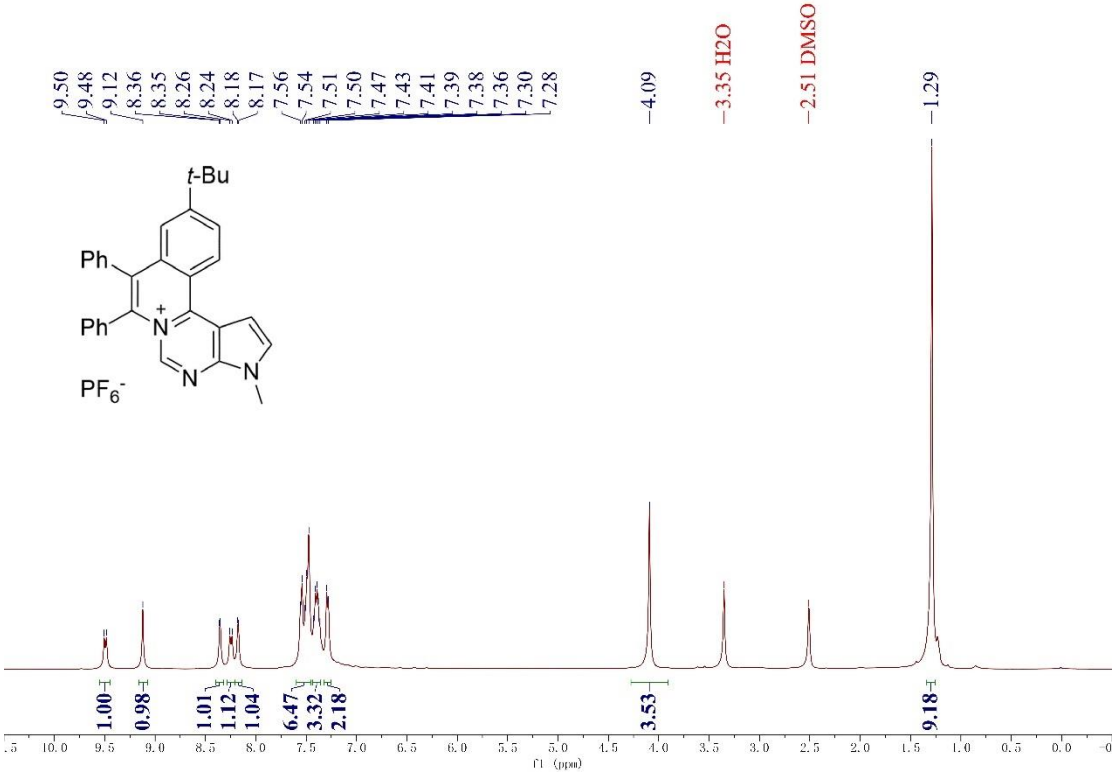
^{1}H NMR Spectrum of 3ca at 25 ^{o}C (DMSO-d_6, 400 MHz)



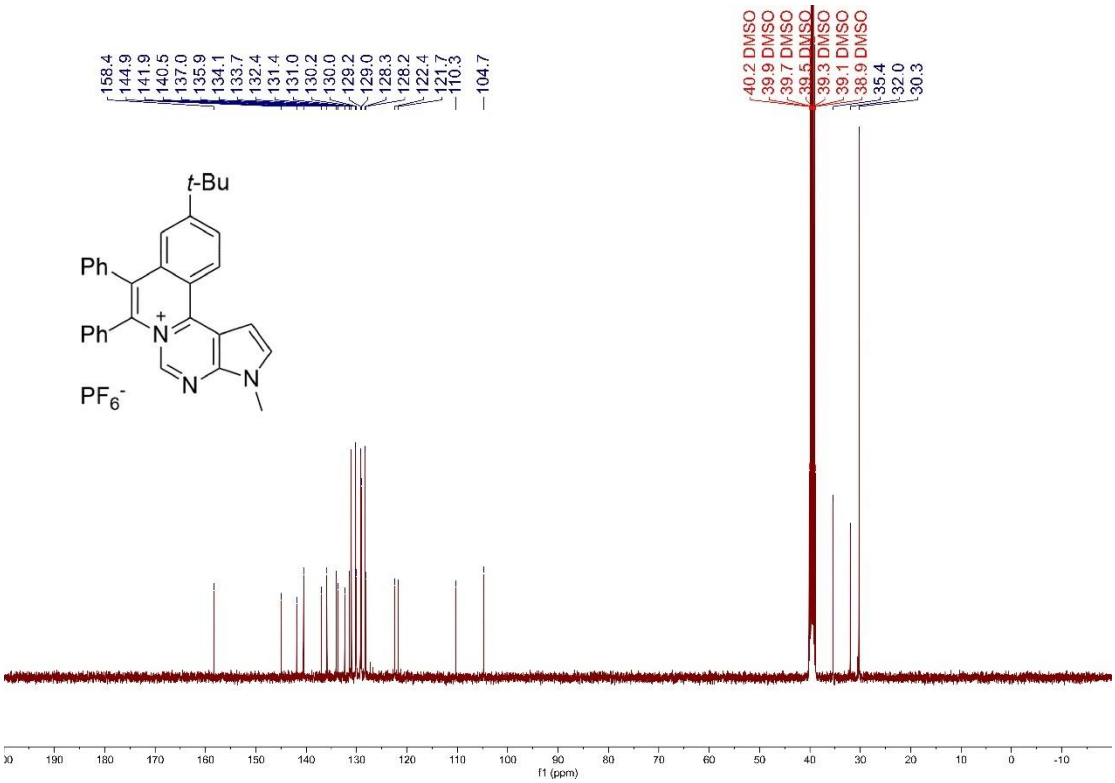
^{13}C NMR Spectrum of 3ca at 25 ^{o}C (DMSO-d_6, 100 MHz)



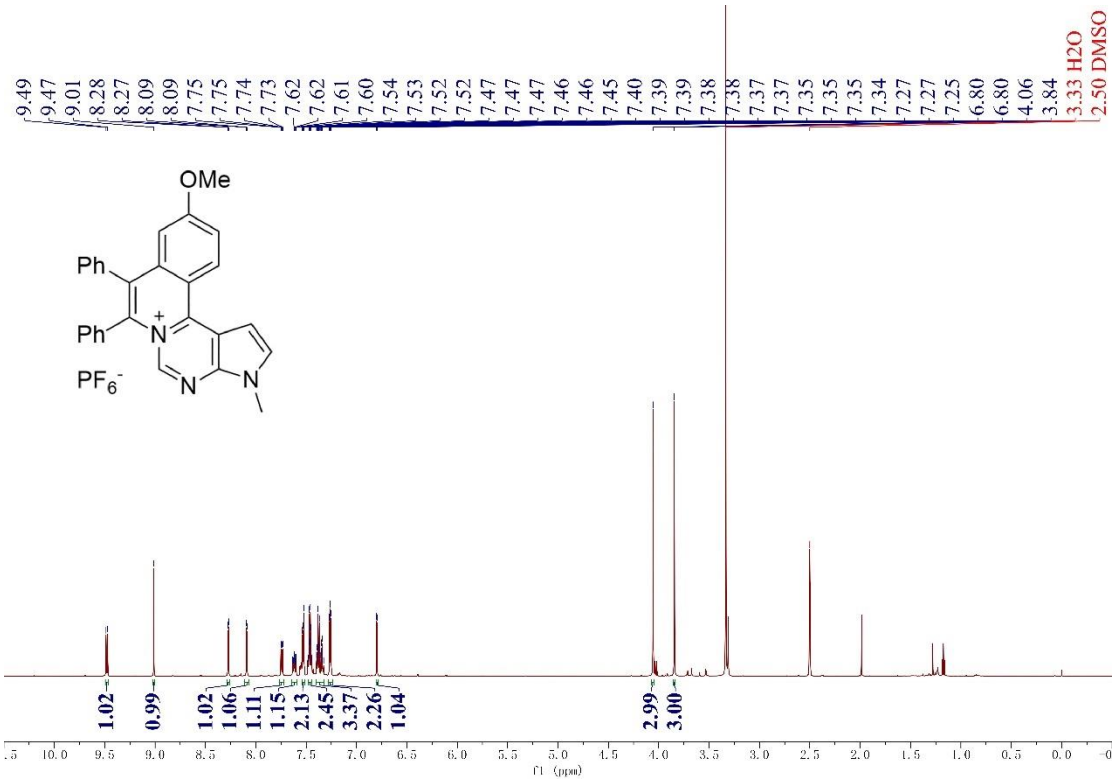
^{1}H NMR Spectrum of 3da at 25 ^{o}C (DMSO-d_6, 400 MHz)



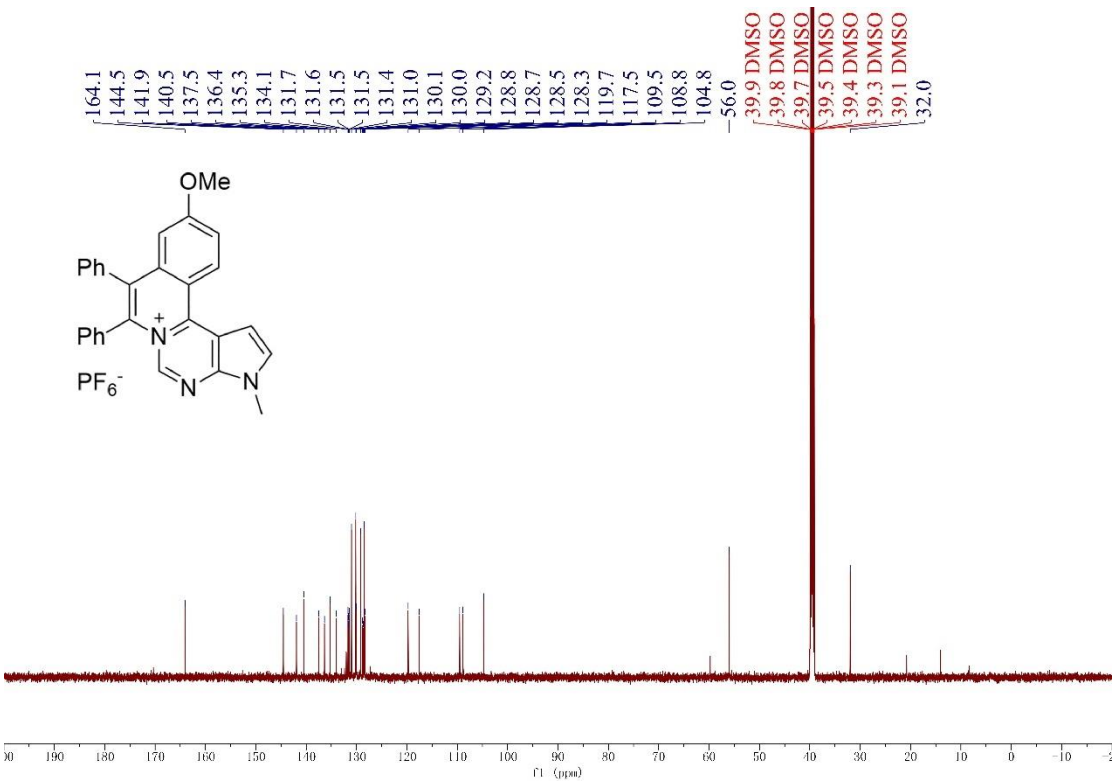
^{13}C NMR Spectrum of 3da at 25 ^{o}C (DMSO-d_6, 100 MHz)



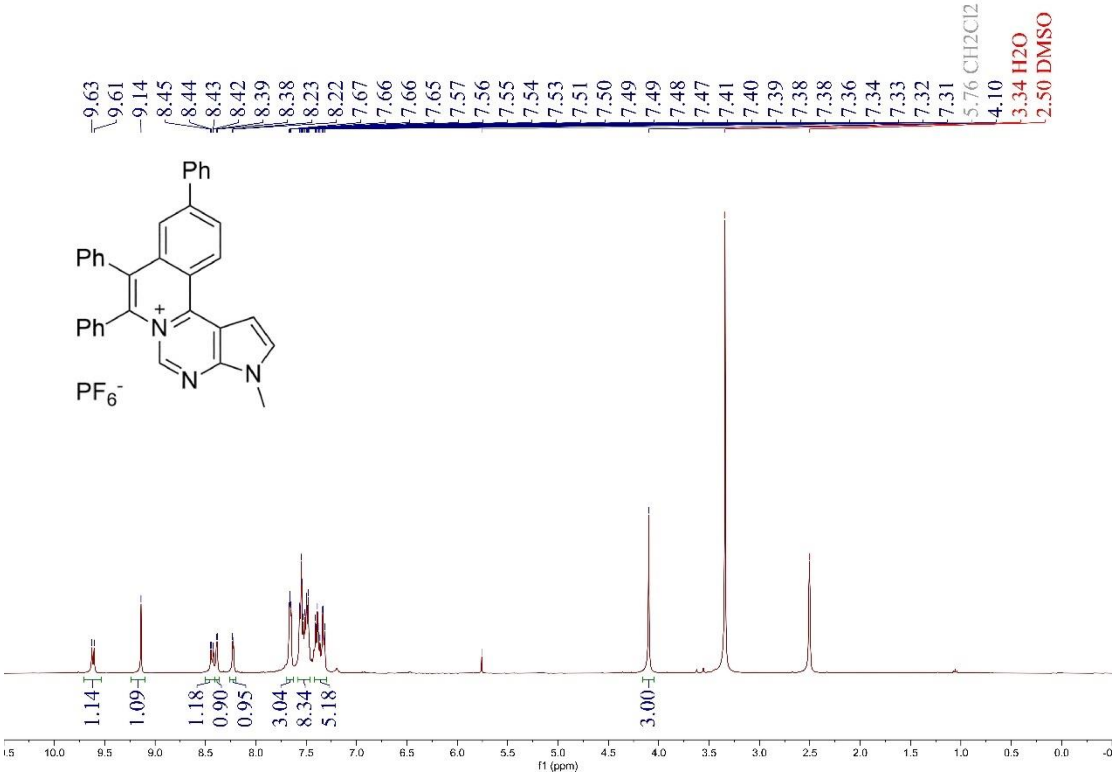
^{1}H NMR Spectrum of 3ea at 25 ^{o}C (DMSO-d_6, 600 MHz)



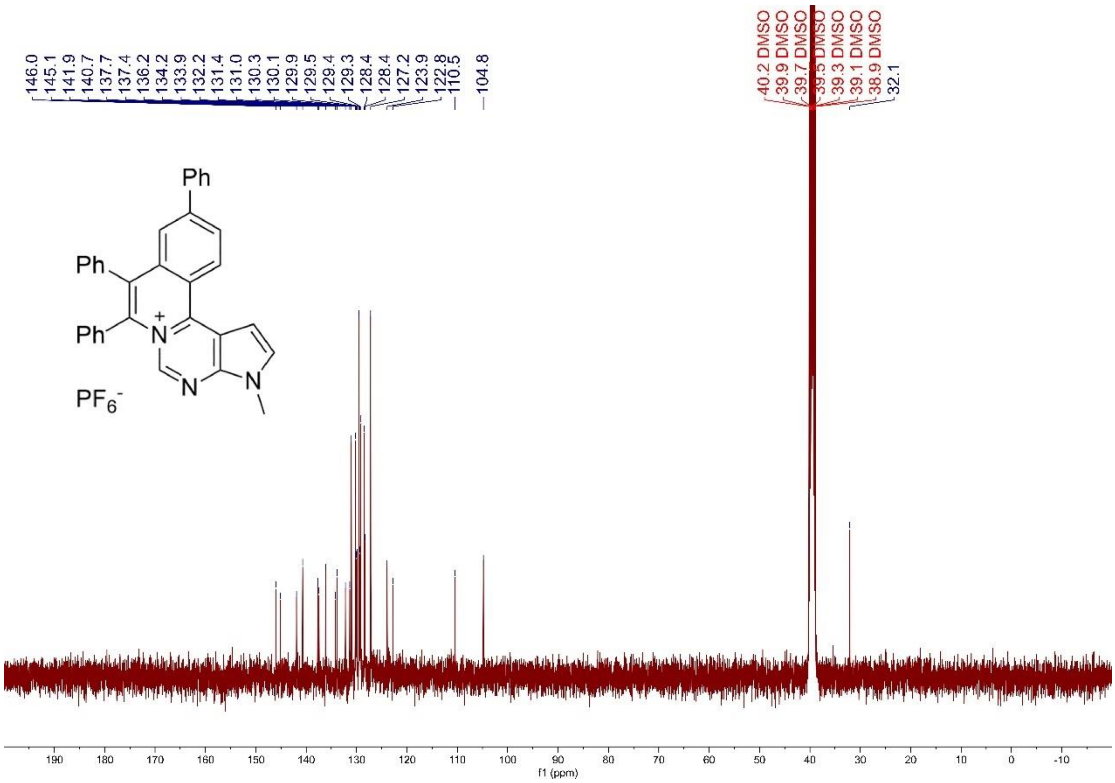
^{13}C NMR Spectrum of 3ea at 25 ^{o}C (DMSO-d_6, 150 MHz)



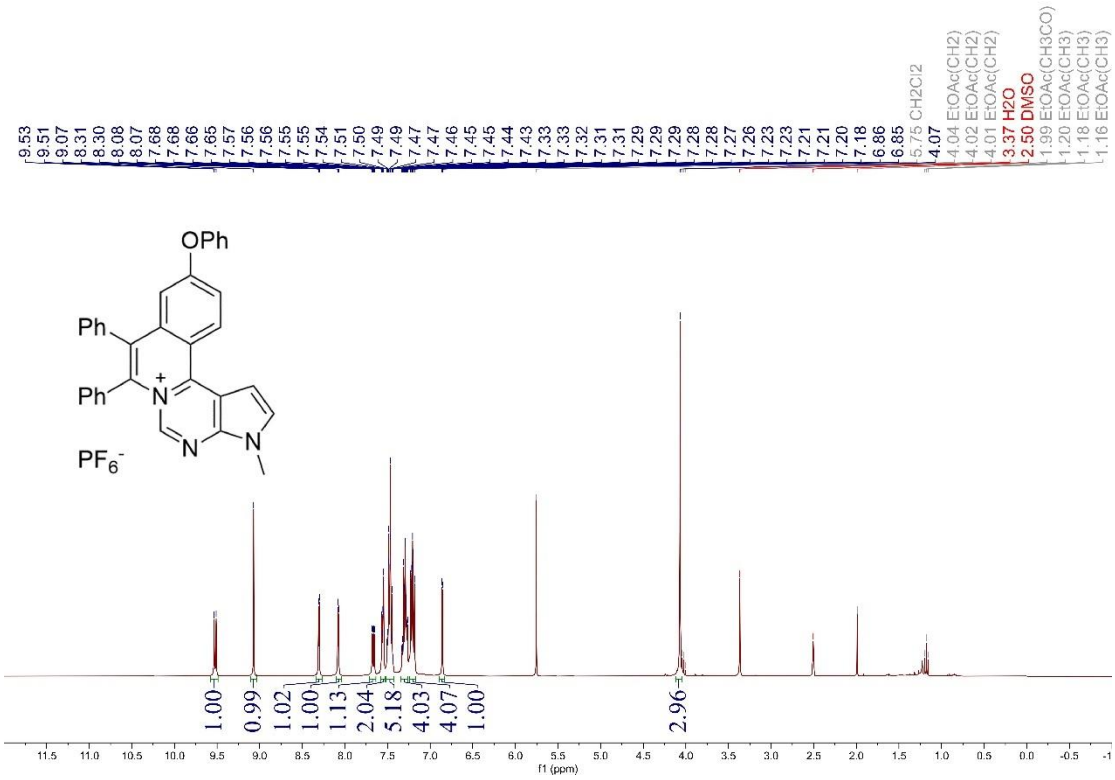
^{1}H NMR Spectrum of 3fa at 25 ^{o}C (DMSO-d_6, 400 MHz)



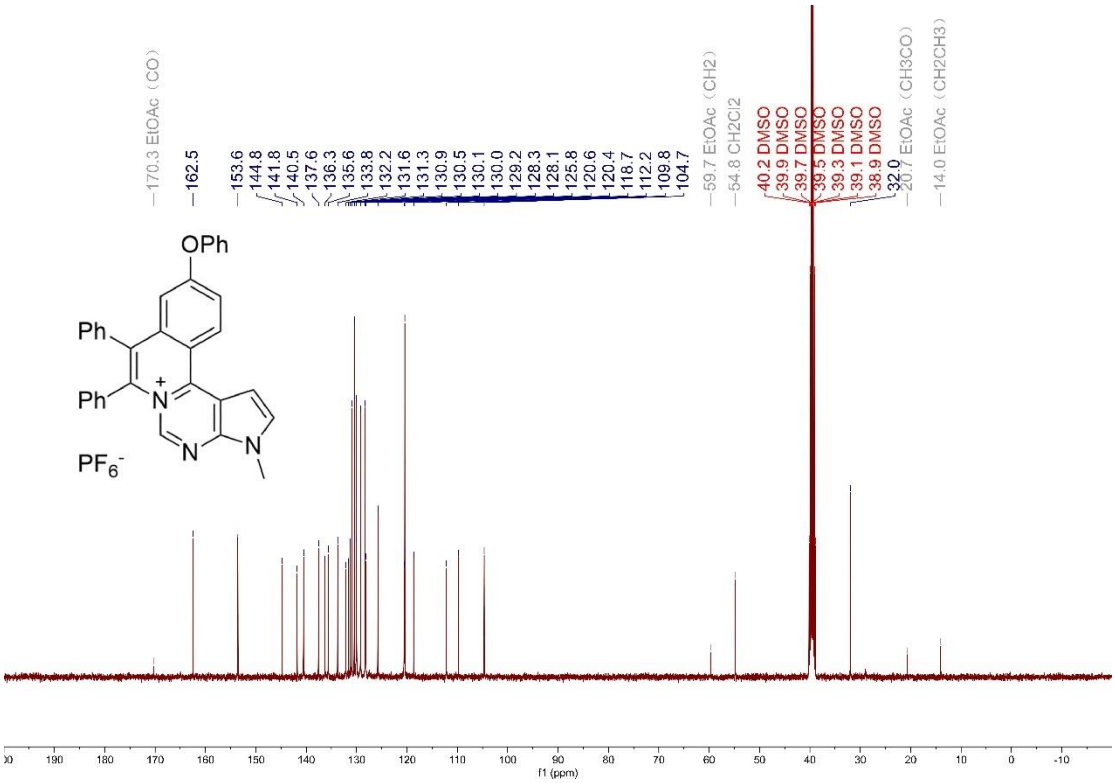
^{13}C NMR Spectrum of 3fa at 25 ^{o}C (DMSO-d_6, 100 MHz)



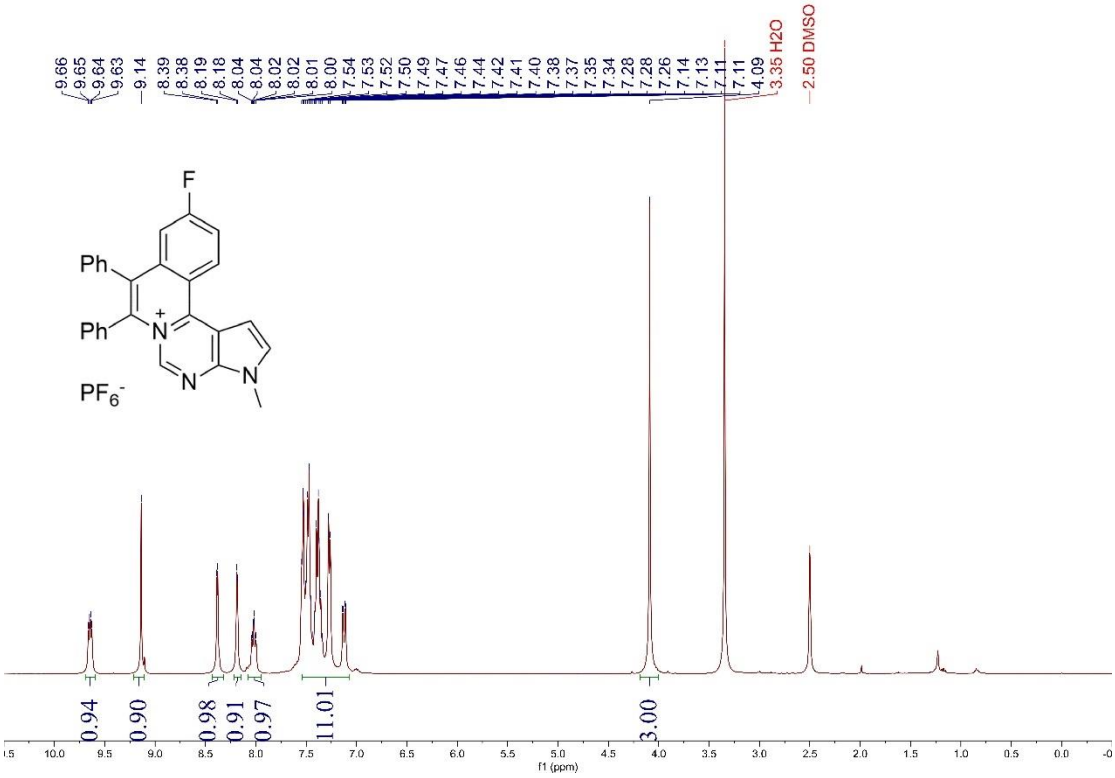
^{1}H NMR Spectrum of 3ga at 25 °C (DMSO-d_6, 400 MHz)



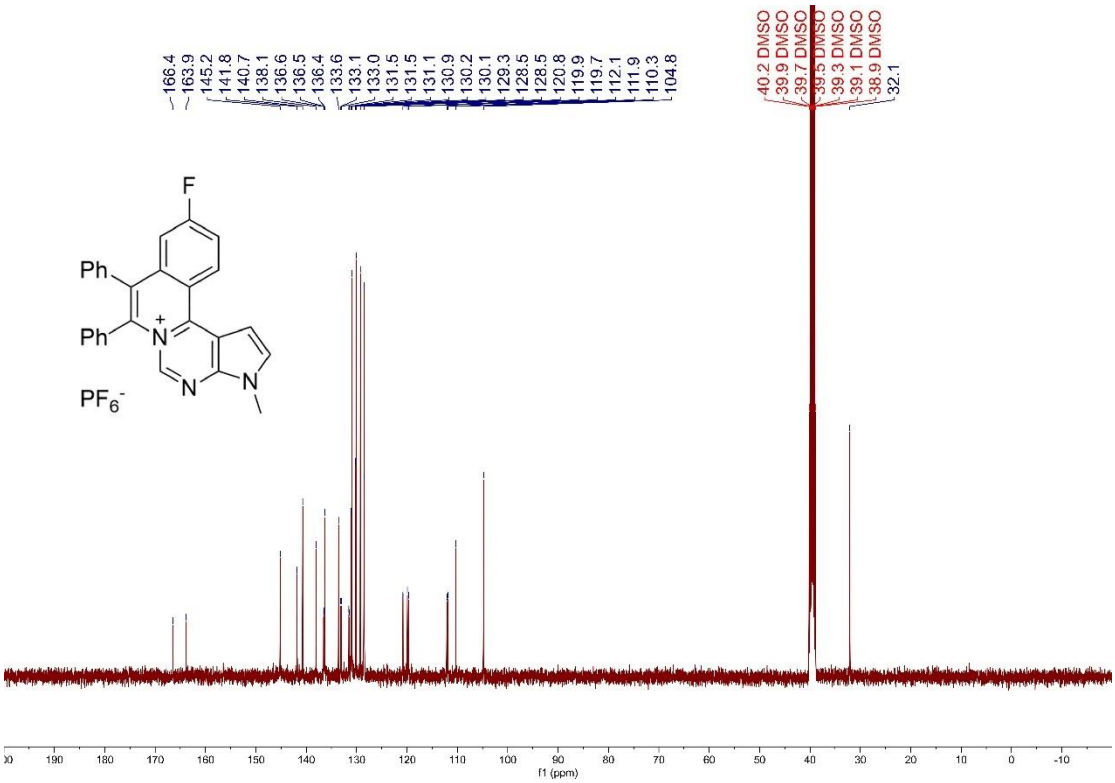
^{13}C NMR Spectrum of 3ga at 25 °C (DMSO-d_6, 100 MHz)



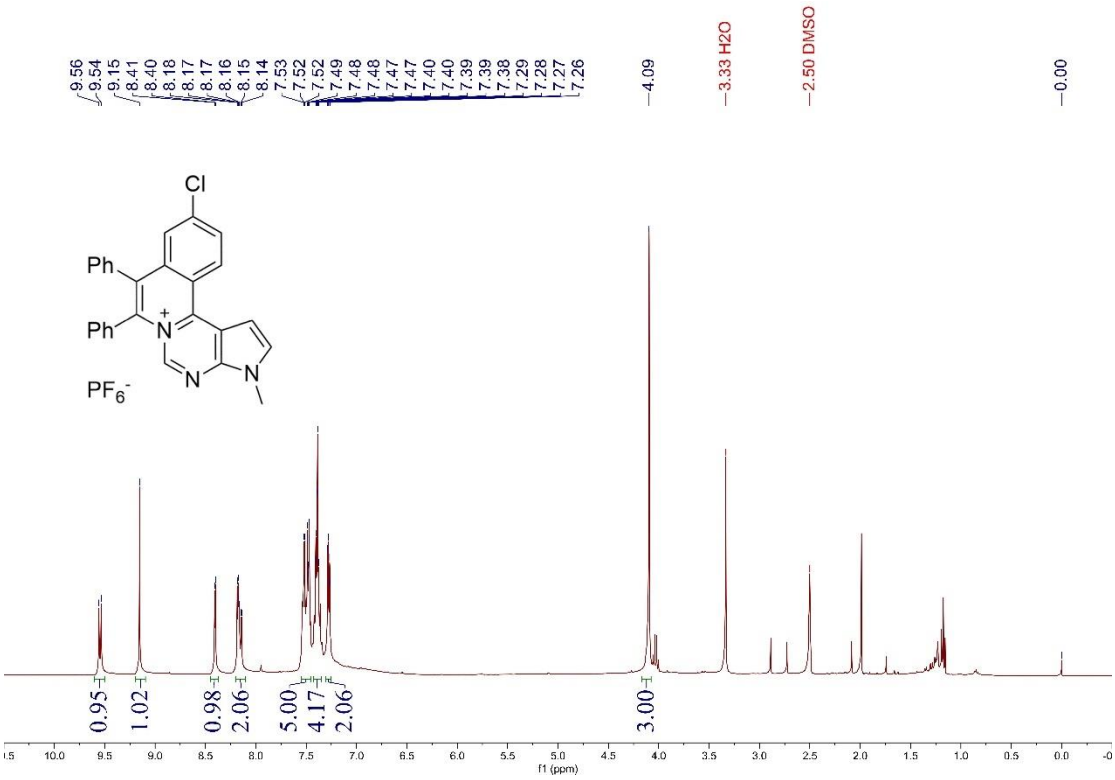
^{1}H NMR Spectrum of 3ha at 25 ^{o}C (DMSO-d_6, 400 MHz)



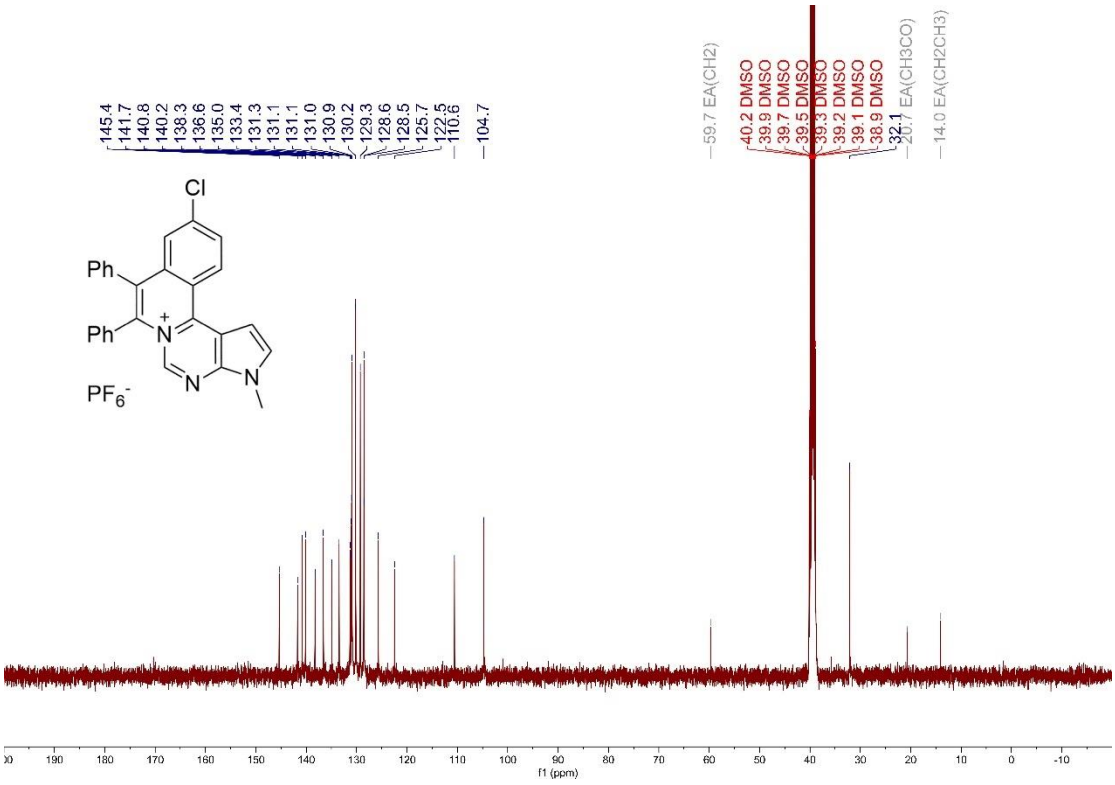
^{13}C NMR Spectrum of 3ha at 25 ^{o}C (DMSO-d_6, 100 MHz)



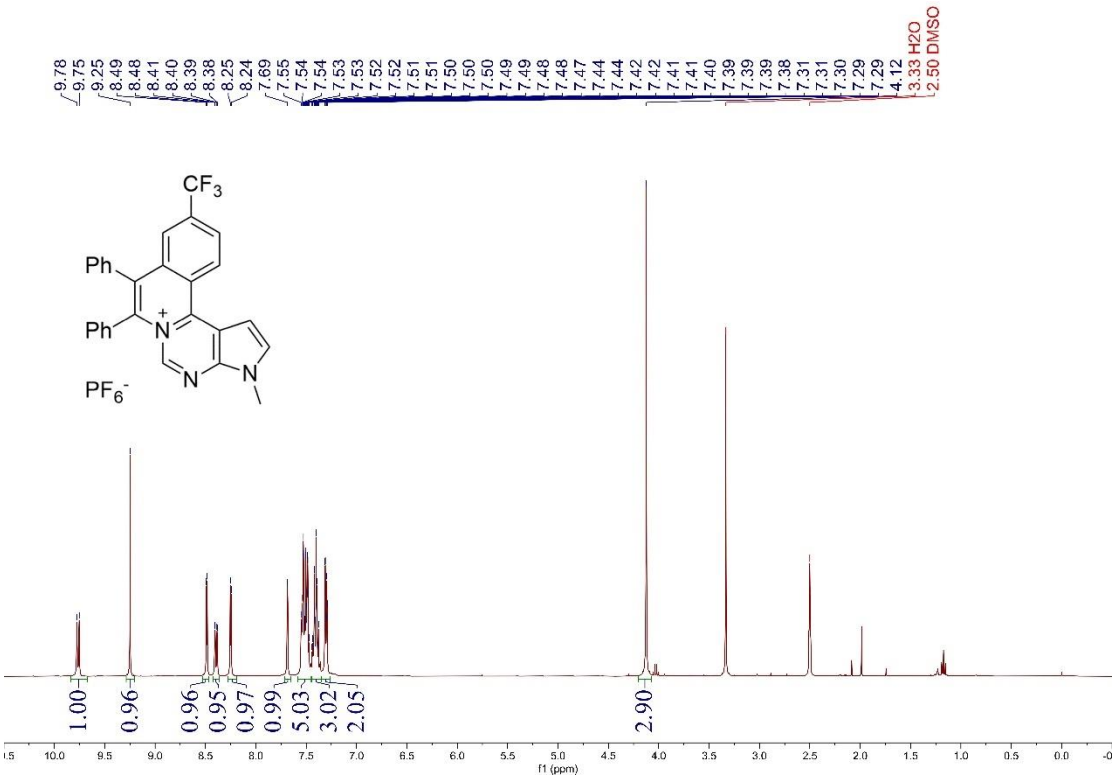
^{1}H NMR Spectrum of 3ia at 25 ^{o}C (DMSO-d_6, 400 MHz)



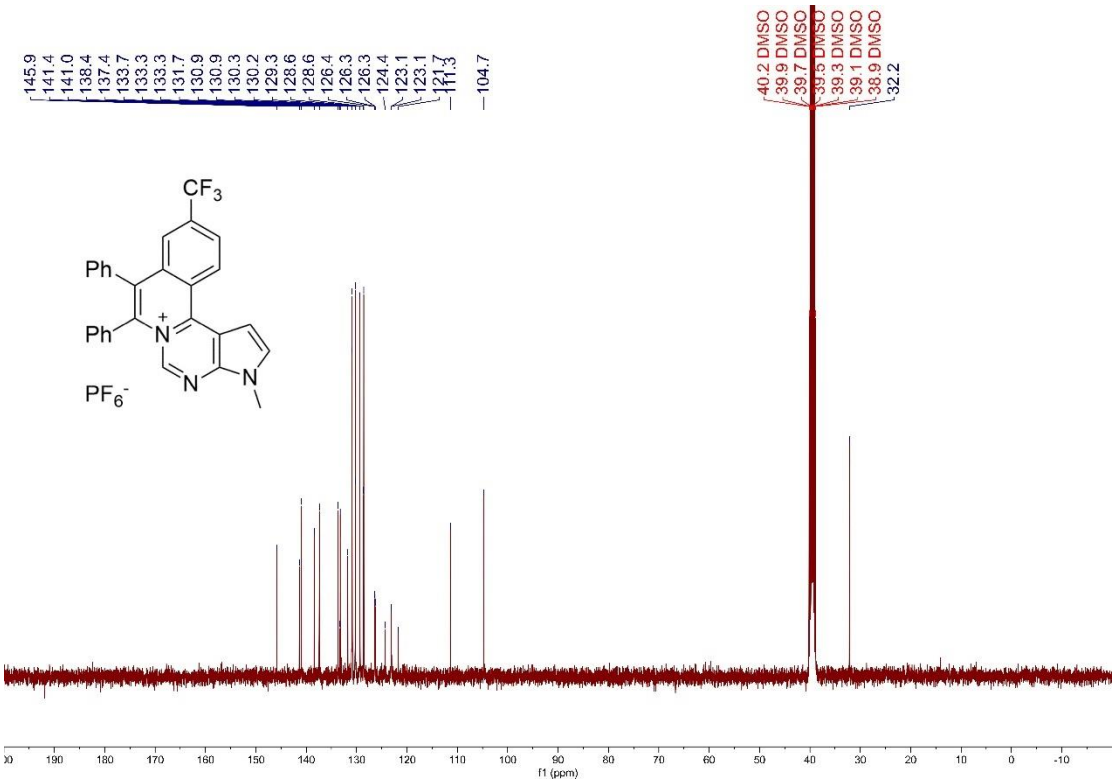
^{13}C NMR Spectrum of 3ia at 25 ^{o}C (DMSO-d_6, 100 MHz)



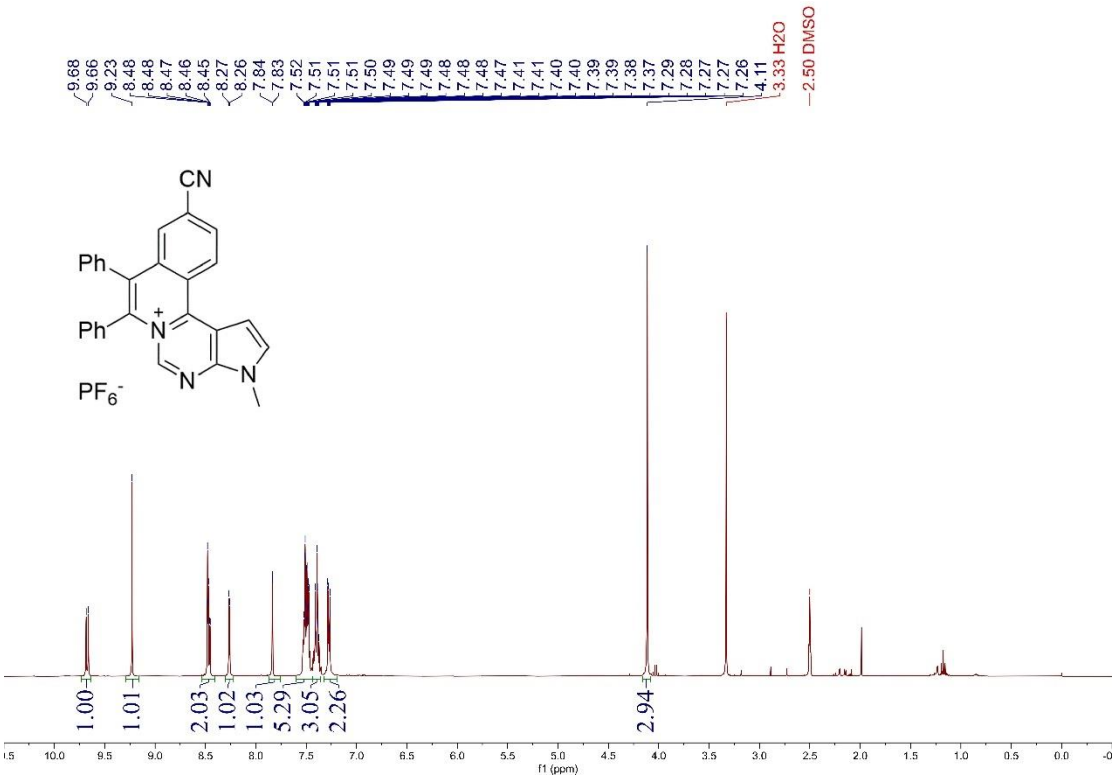
^{1}H NMR Spectrum of 3ja at 25 ^{o}C (DMSO-d_6, 400 MHz)



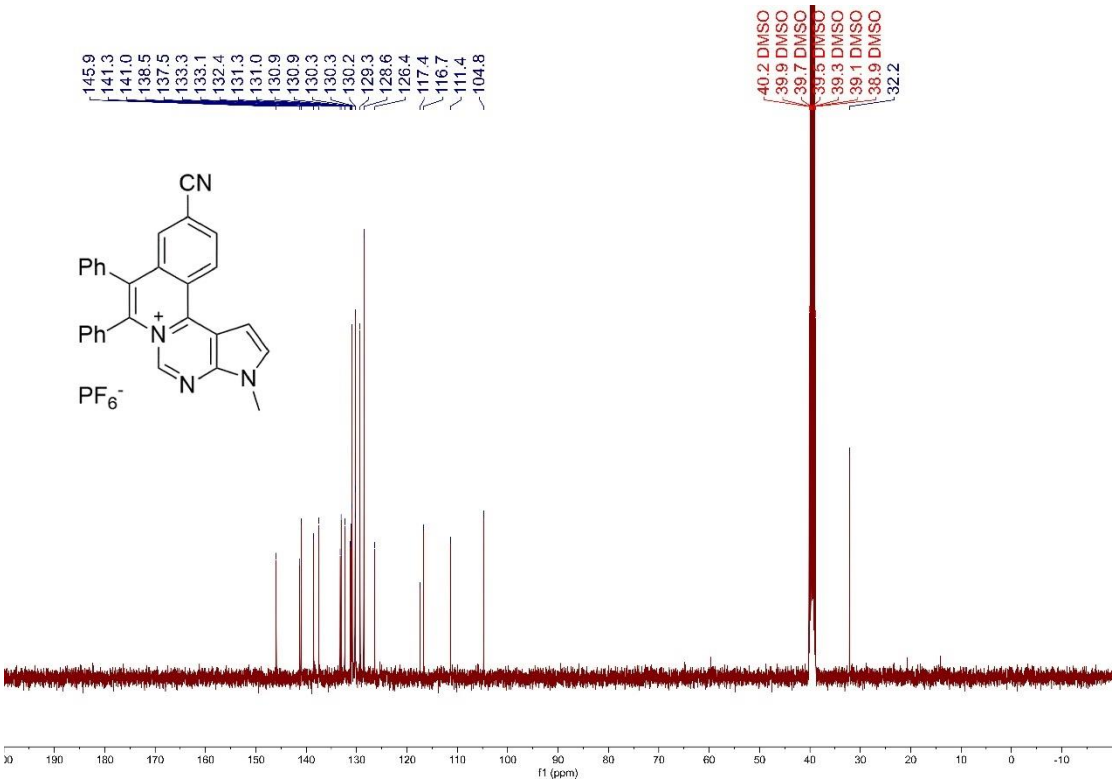
^{13}C NMR Spectrum of 3ja at 25 ^{o}C (DMSO-d_6, 100 MHz)



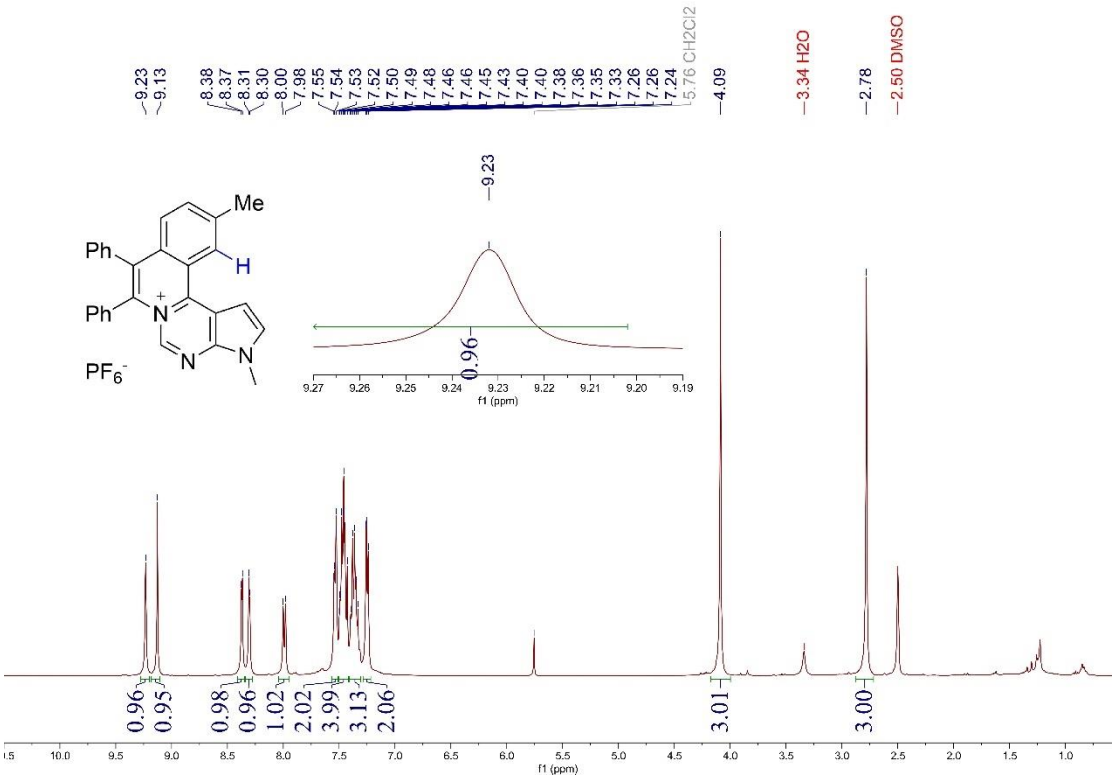
^{1}H NMR Spectrum of 3ka at 25 ^{o}C (DMSO-d_6, 400 MHz)



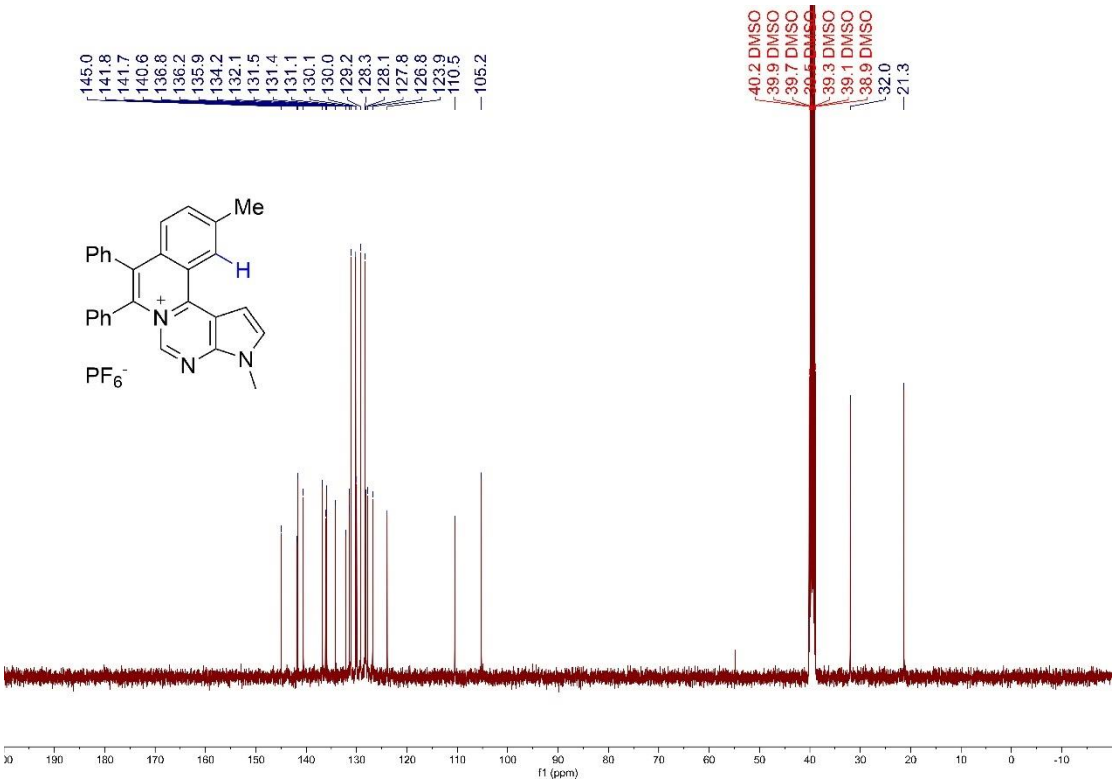
^{13}C NMR Spectrum of 3ka at 25 ^{o}C (DMSO-d_6, 100 MHz)



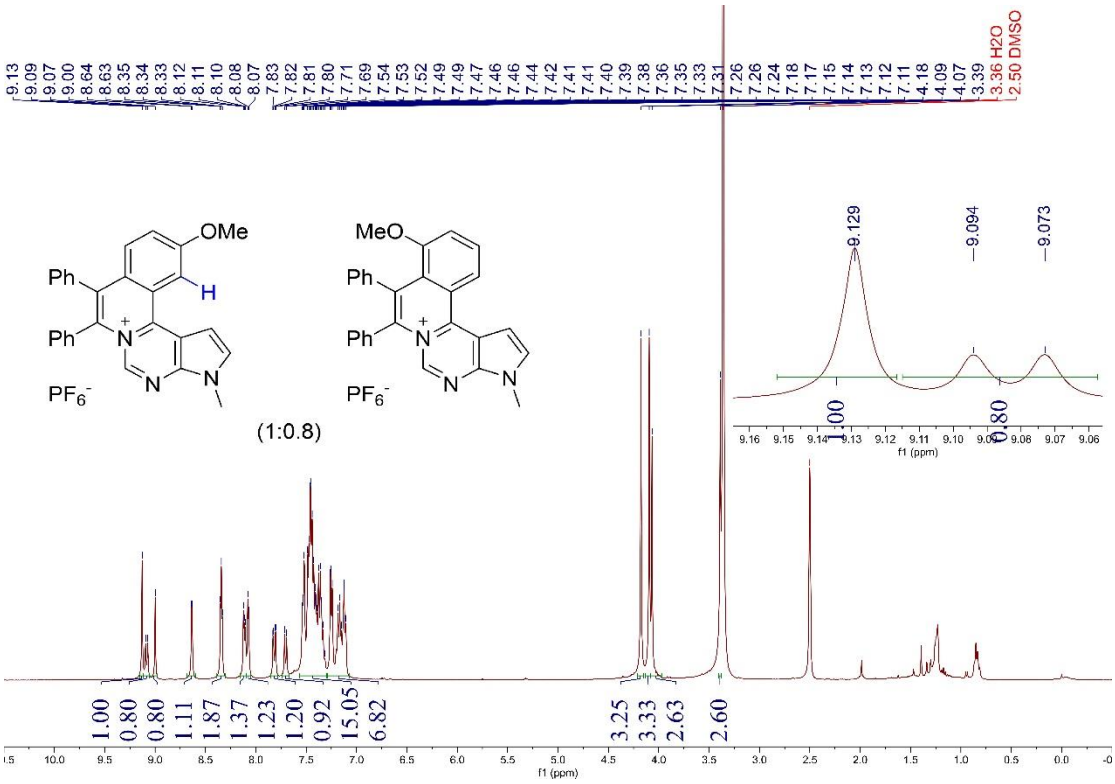
^{1}H NMR Spectrum of 3la at 25 °C (DMSO-d_6, 400 MHz)



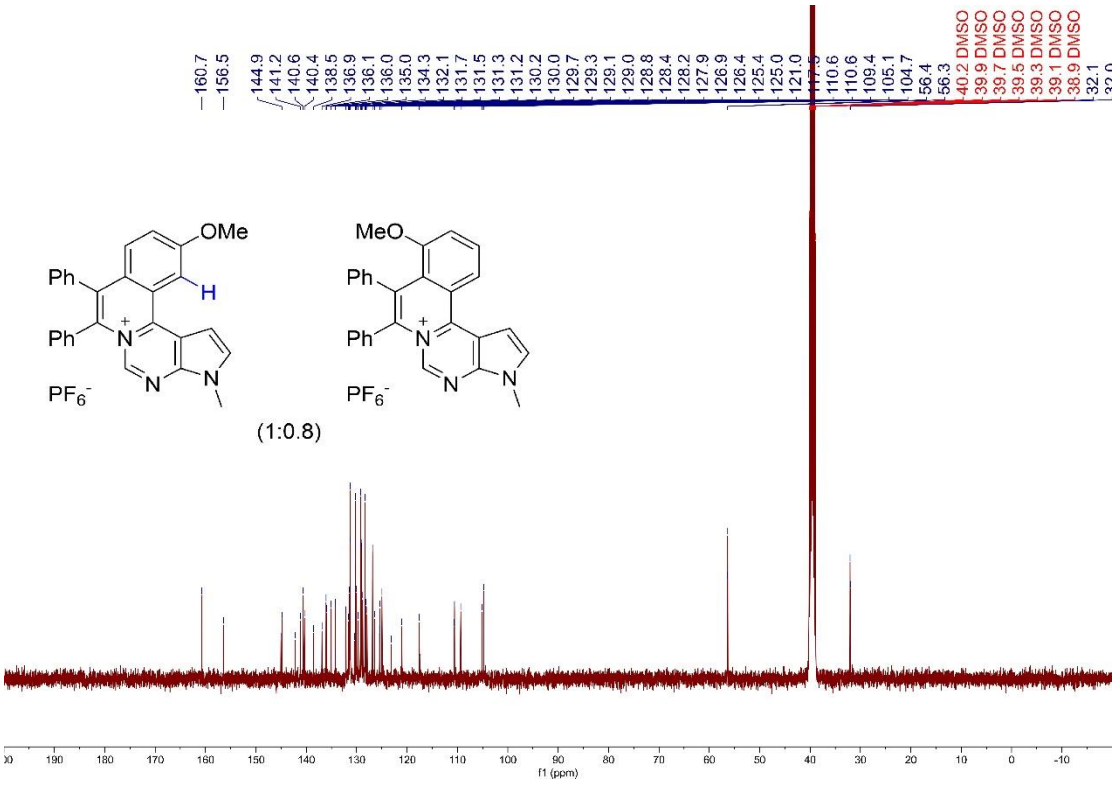
^{13}C NMR Spectrum of 3la at 25 °C (DMSO-d_6, 100 MHz)



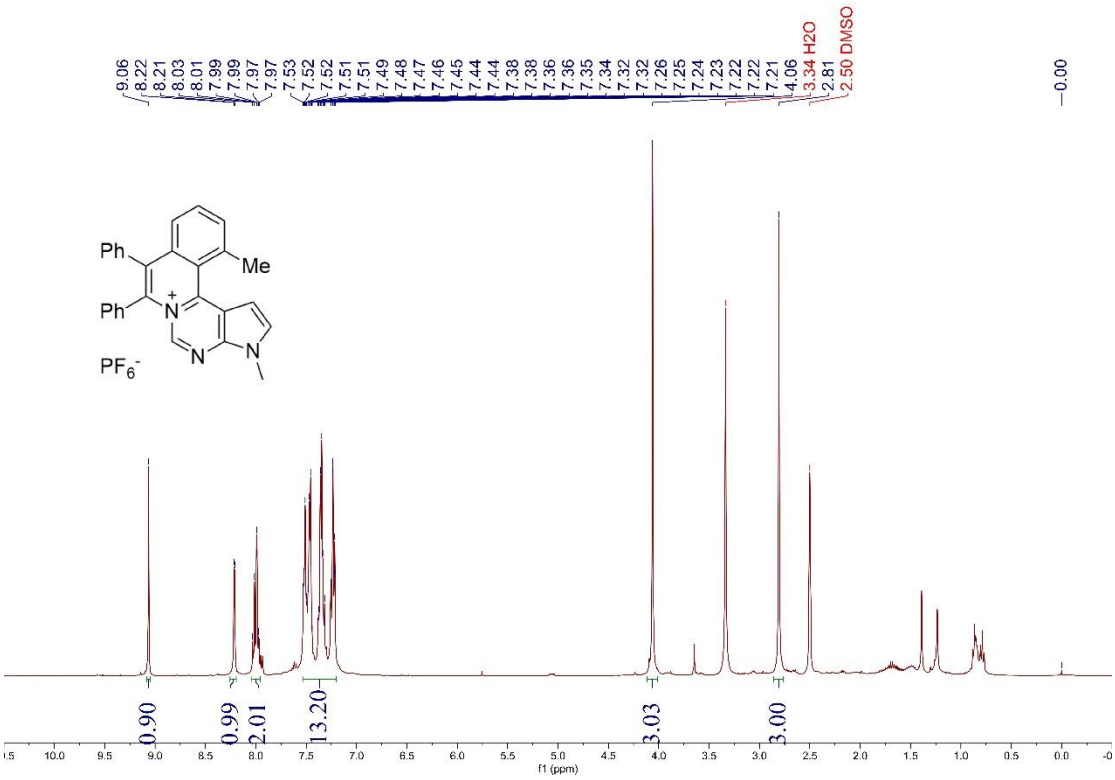
^{1}H NMR Spectrum of 3ma at 25 °C (DMSO-d_6, 400 MHz)



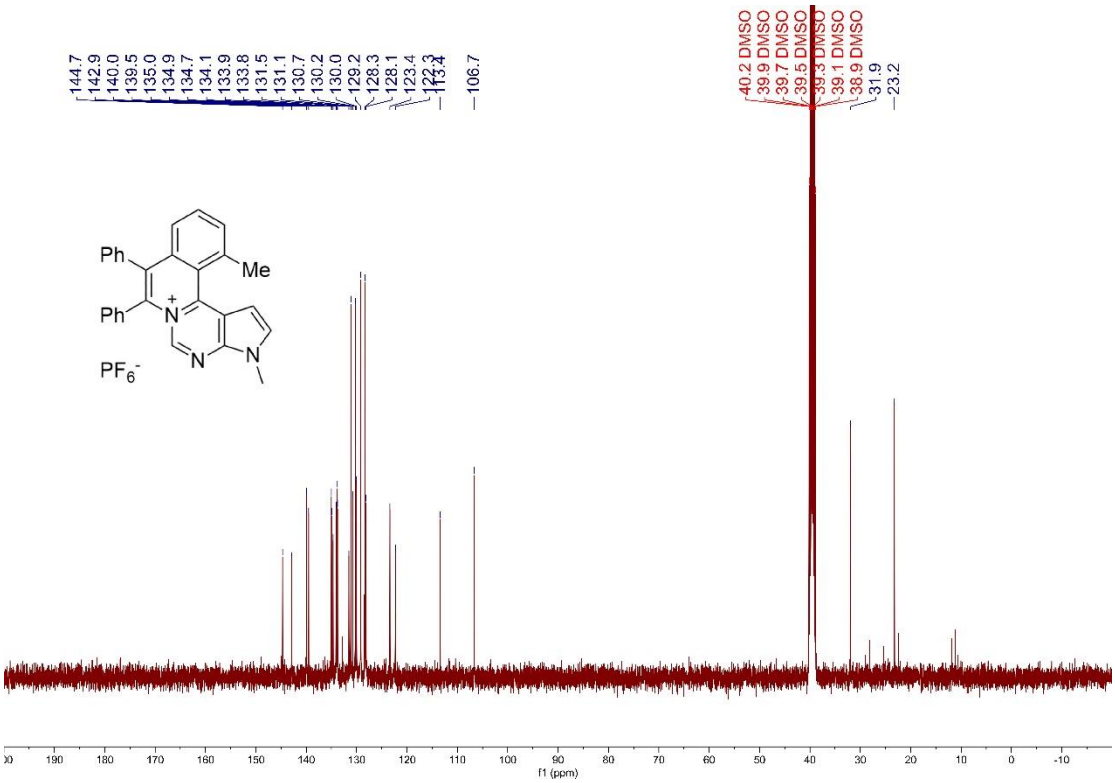
^{13}C NMR Spectrum of 3ma at 25 °C (DMSO-d_6, 100 MHz)



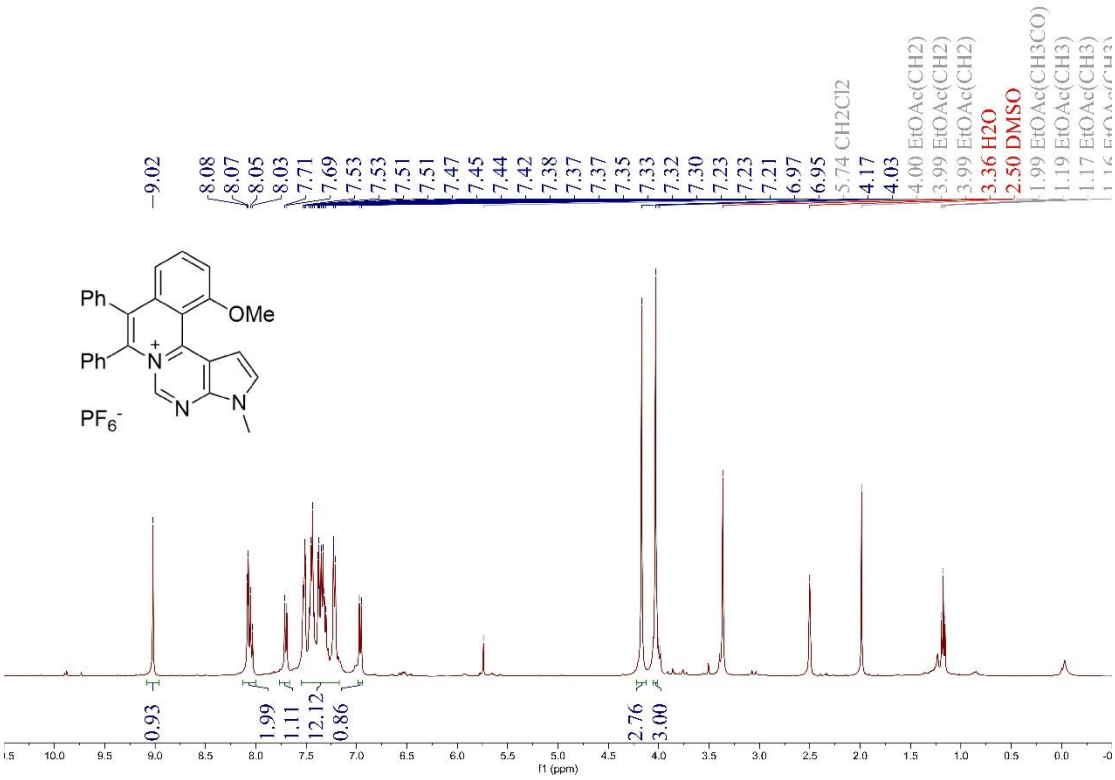
^{1}H NMR Spectrum of 3na at 25 ^{o}C (DMSO-d_6, 400 MHz)



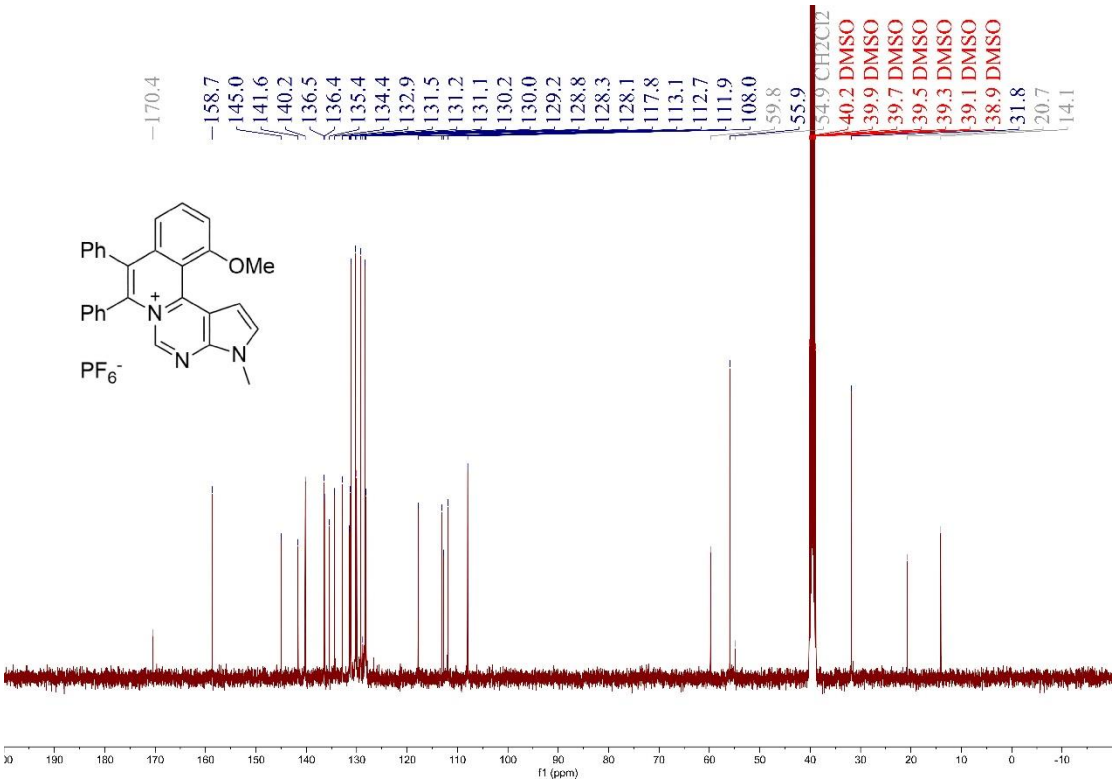
^{13}C NMR Spectrum of 3na at 25 ^{o}C (DMSO-d_6, 100 MHz)



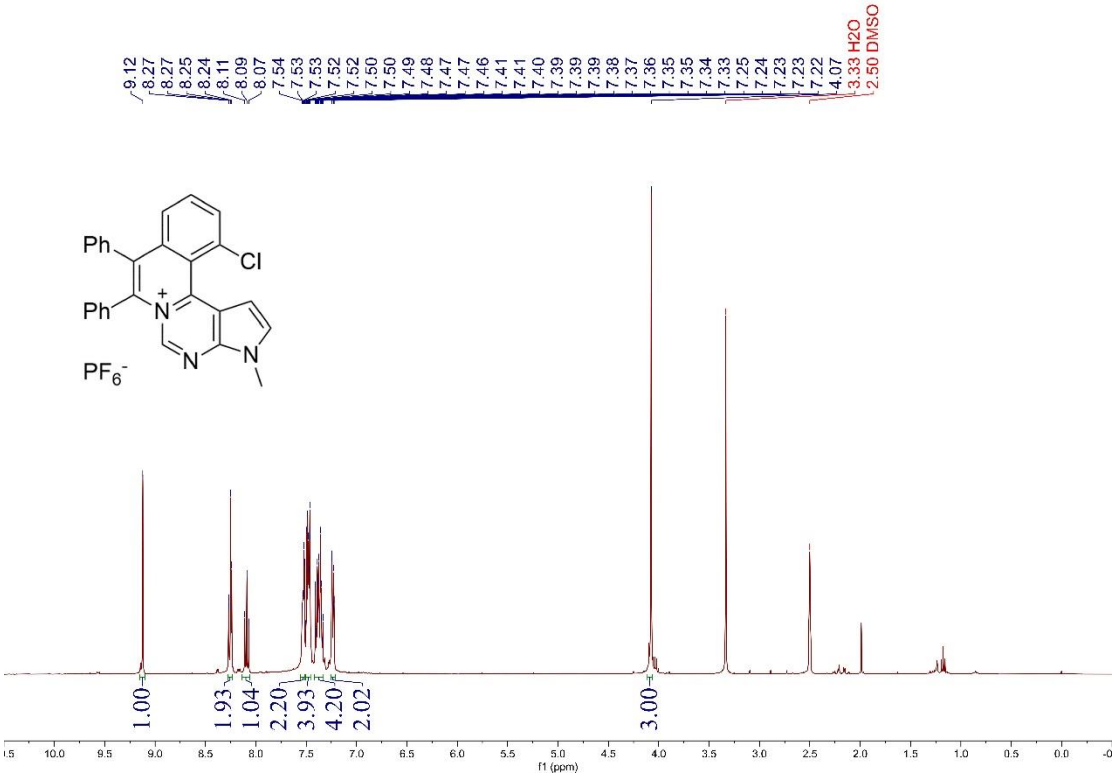
^{1}H NMR Spectrum of 3oa at 25 ^{o}C (DMSO-d_6, 400 MHz)



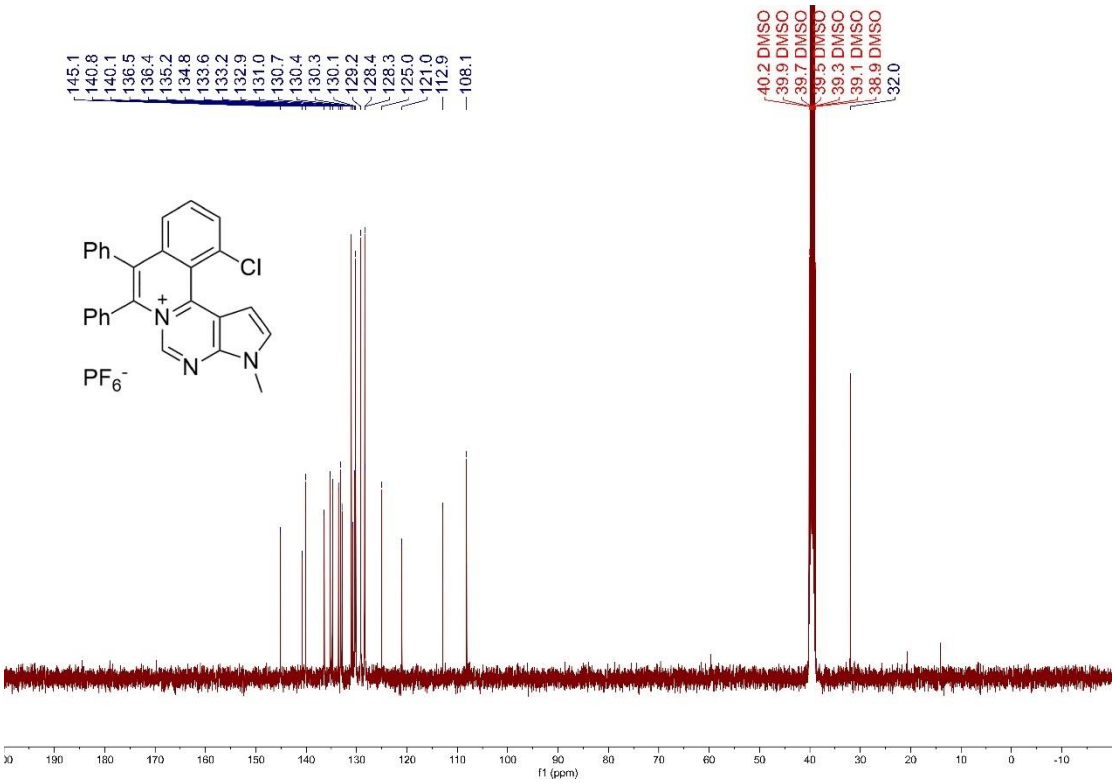
^{13}C NMR Spectrum of 3oa at 25 ^{o}C (DMSO-d_6, 100 MHz)



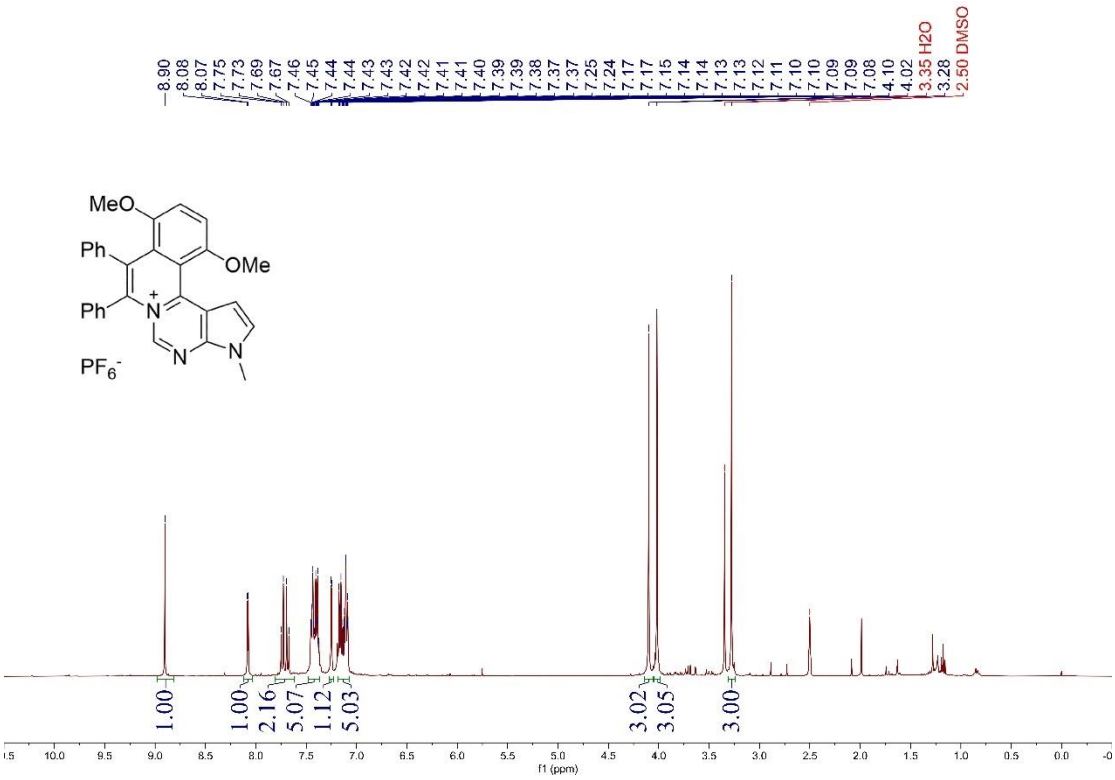
^{1}H NMR Spectrum of 3pa at 25 ^{o}C (DMSO-d_6, 400 MHz)



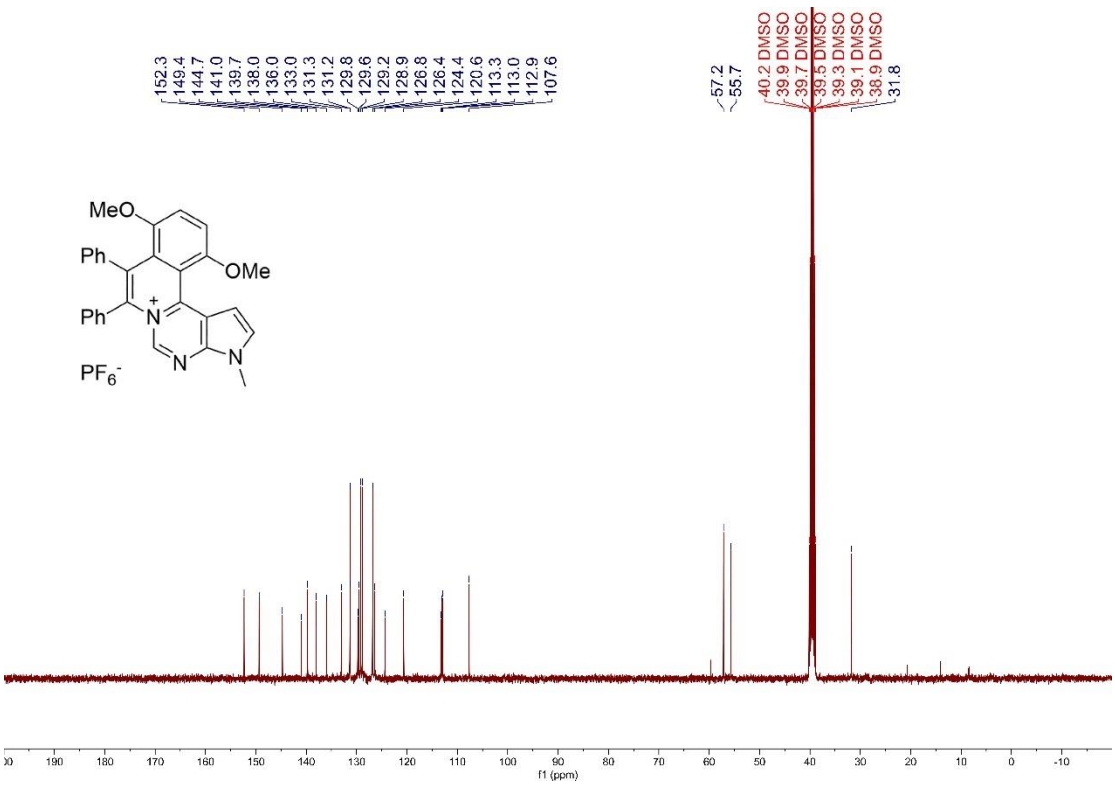
^{13}C NMR Spectrum of 3pa at 25 ^{o}C (DMSO-d_6, 100 MHz)



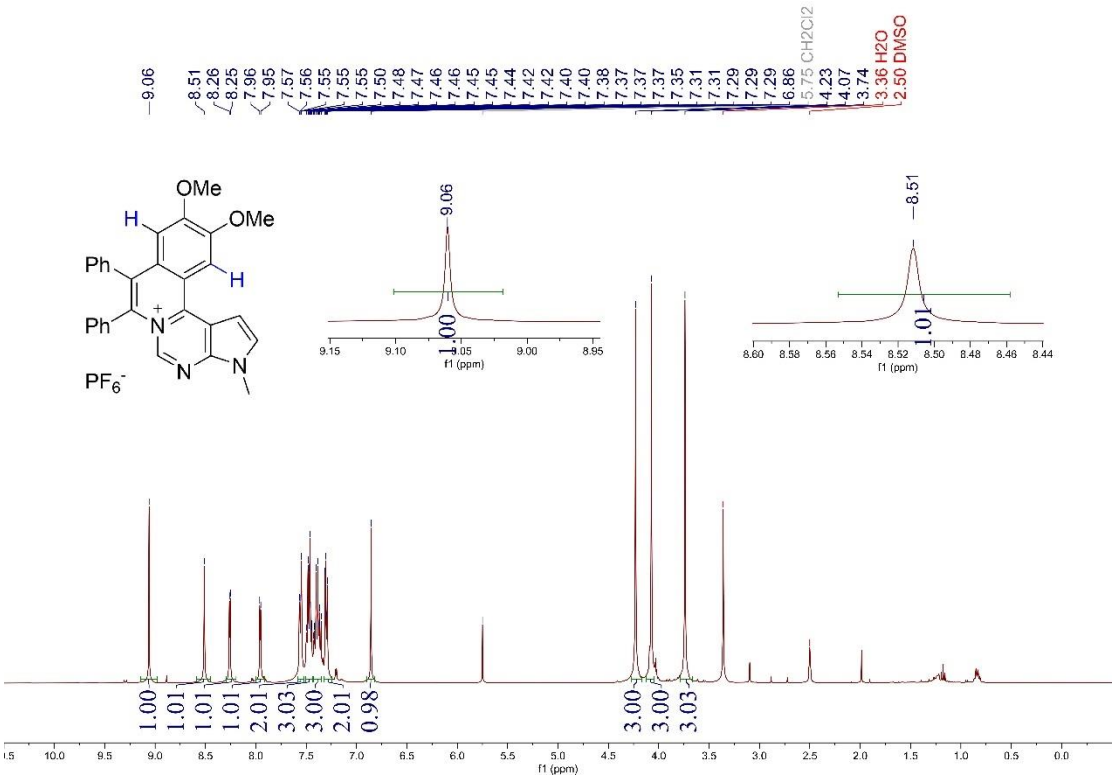
^{1}H NMR Spectrum of 3qa at 25 ^{o}C (DMSO-d_6, 400 MHz)



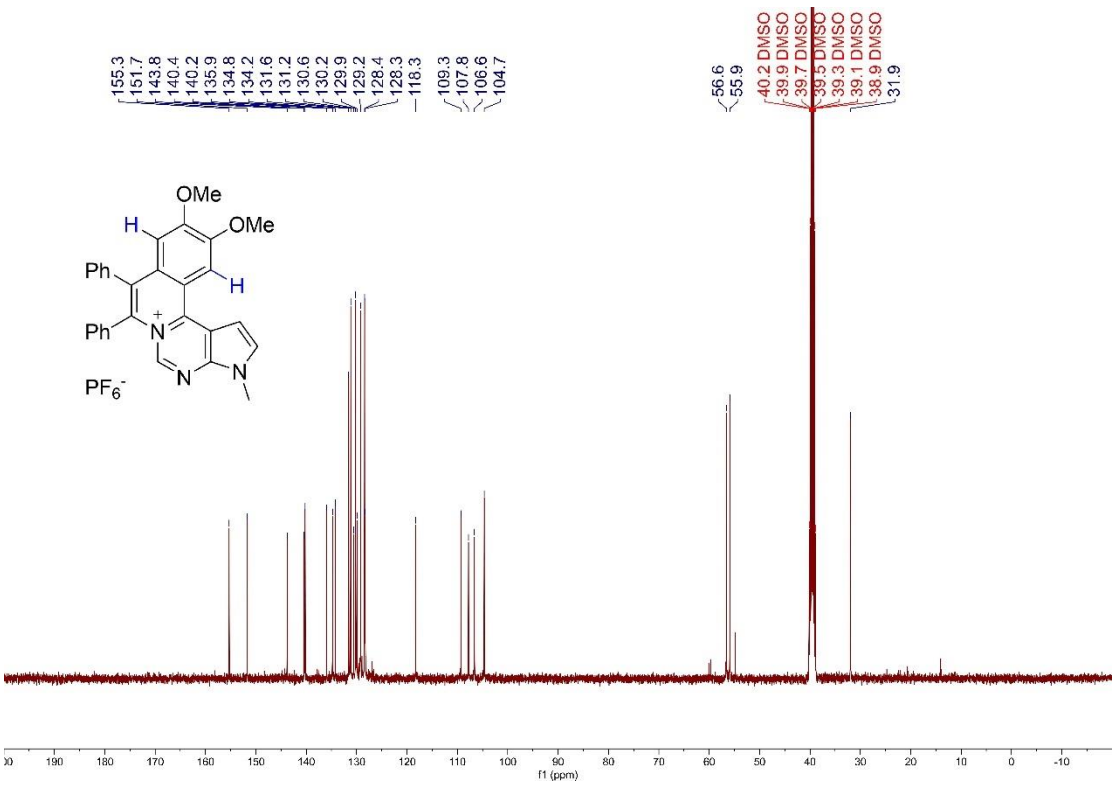
^{13}C NMR Spectrum of 3qa at 25 ^{o}C (DMSO-d_6, 100 MHz)



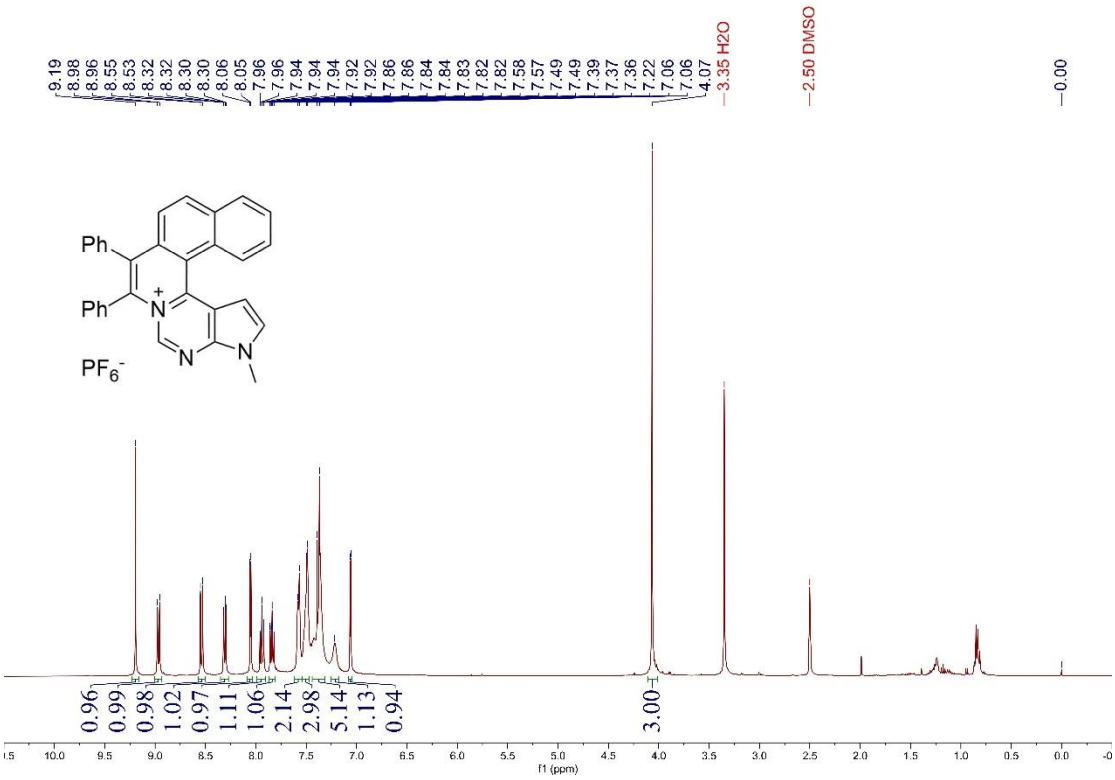
^{1}H NMR Spectrum of 3ra at 25 ^{o}C (DMSO-d_6, 400 MHz)



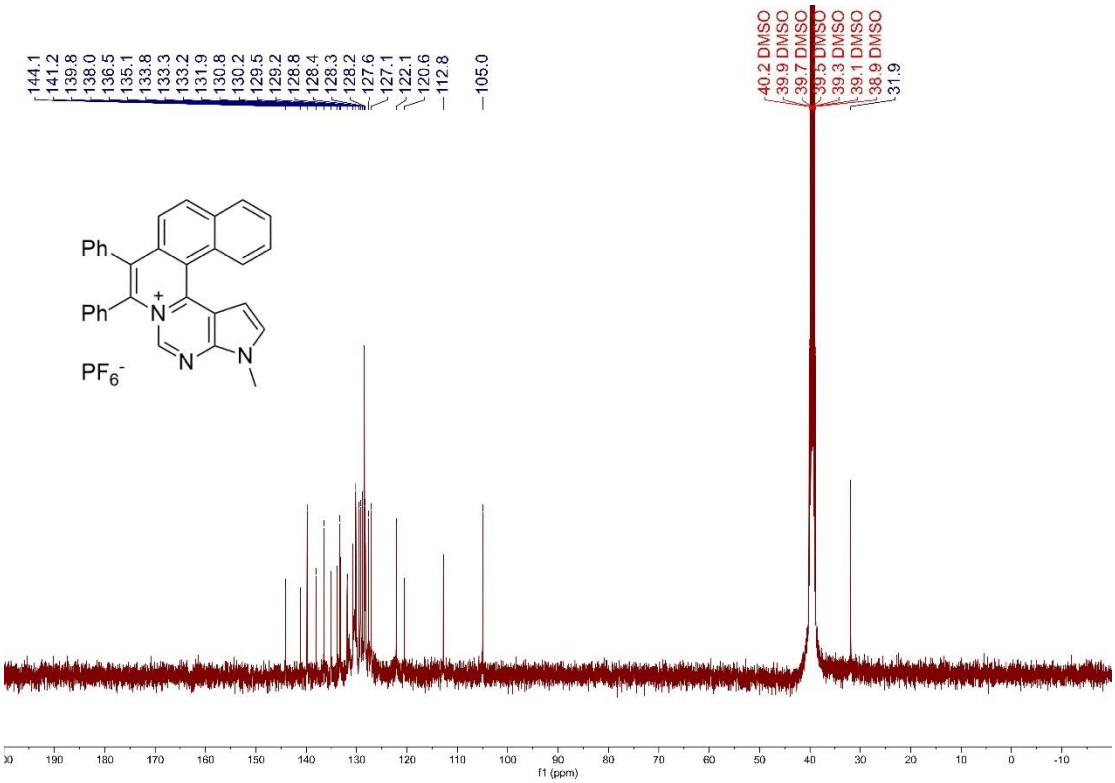
^{13}C NMR Spectrum of 3ra at 25 ^{o}C (DMSO-d_6, 100 MHz)



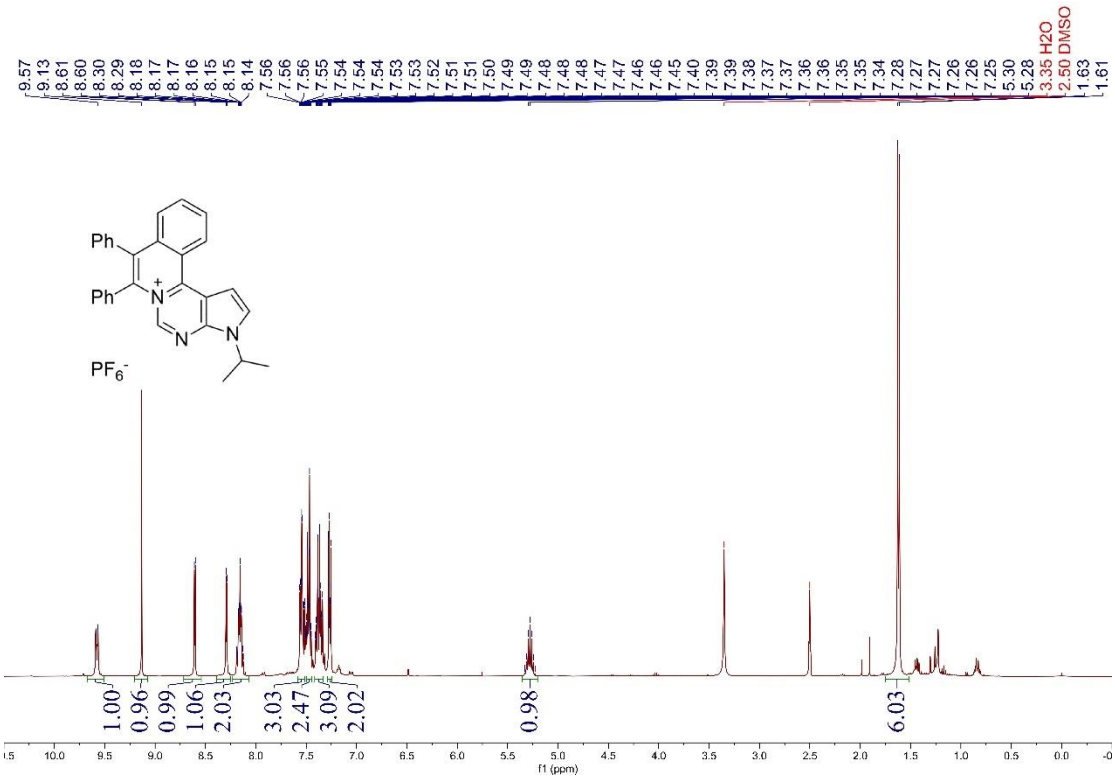
^{1}H NMR Spectrum of 3sa at 25 ^{o}C (DMSO-d_6, 400 MHz)



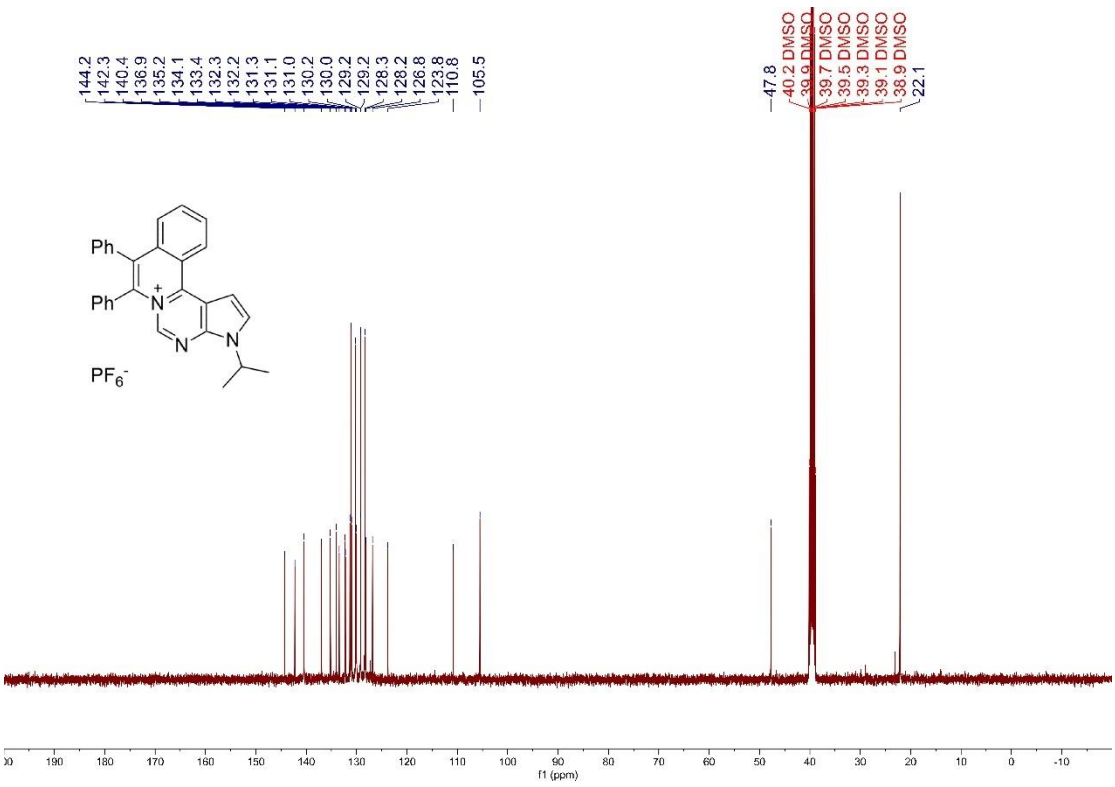
^{13}C NMR Spectrum of 3sa at 25 ^{o}C (DMSO-d_6, 100 MHz)



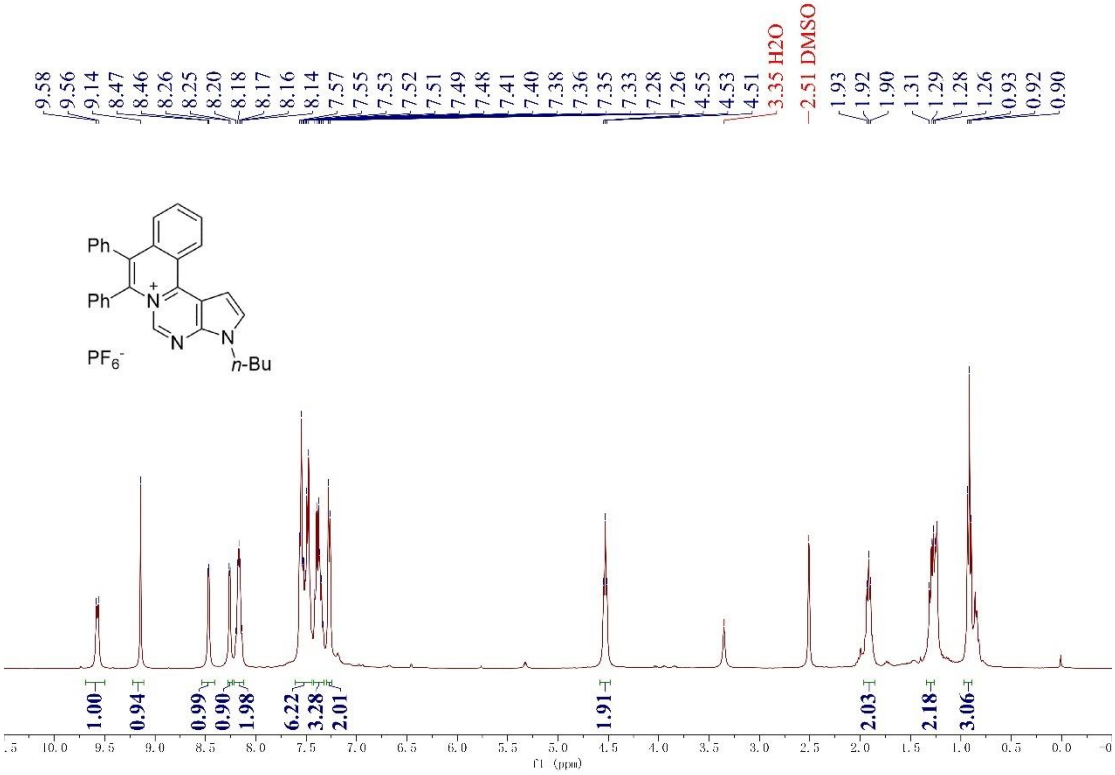
^{1}H NMR Spectrum of 3ua at 25 ^{o}C (DMSO-d_6, 400 MHz)



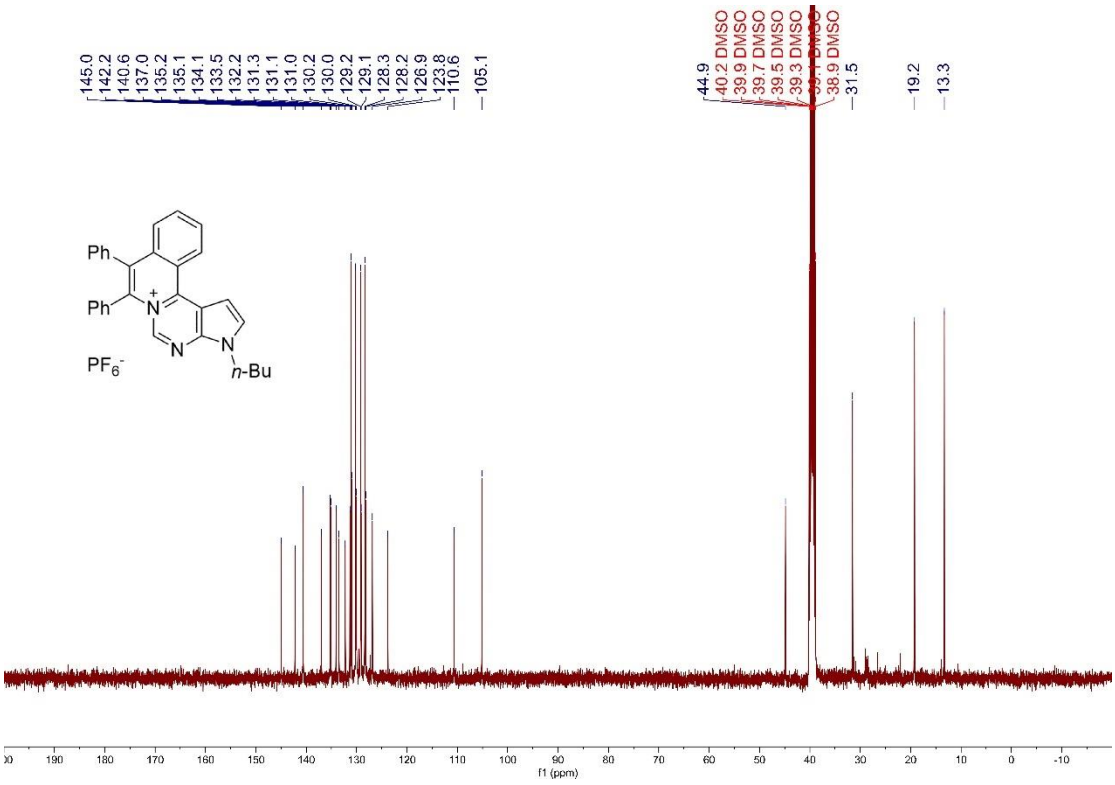
^{13}C NMR Spectrum of 3ua at 25 ^{o}C (DMSO-d_6, 100 MHz)



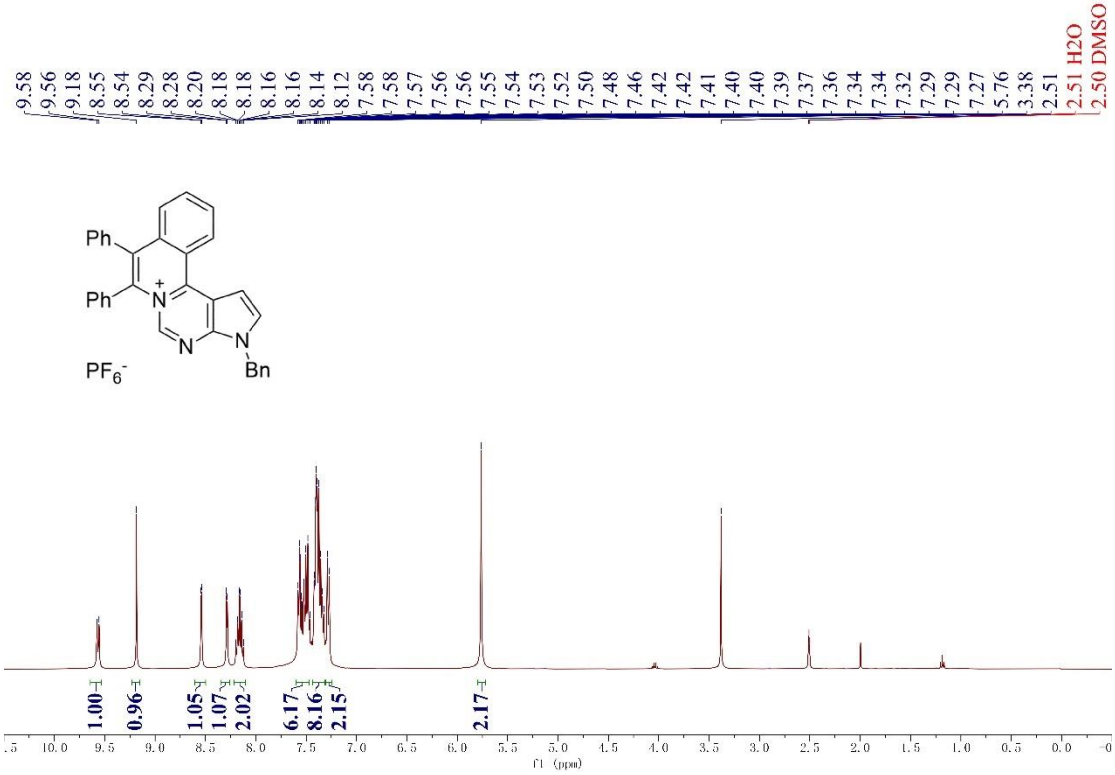
^{1}H NMR Spectrum of 3va at 25 ^{o}C (DMSO-d_6, 400 MHz)



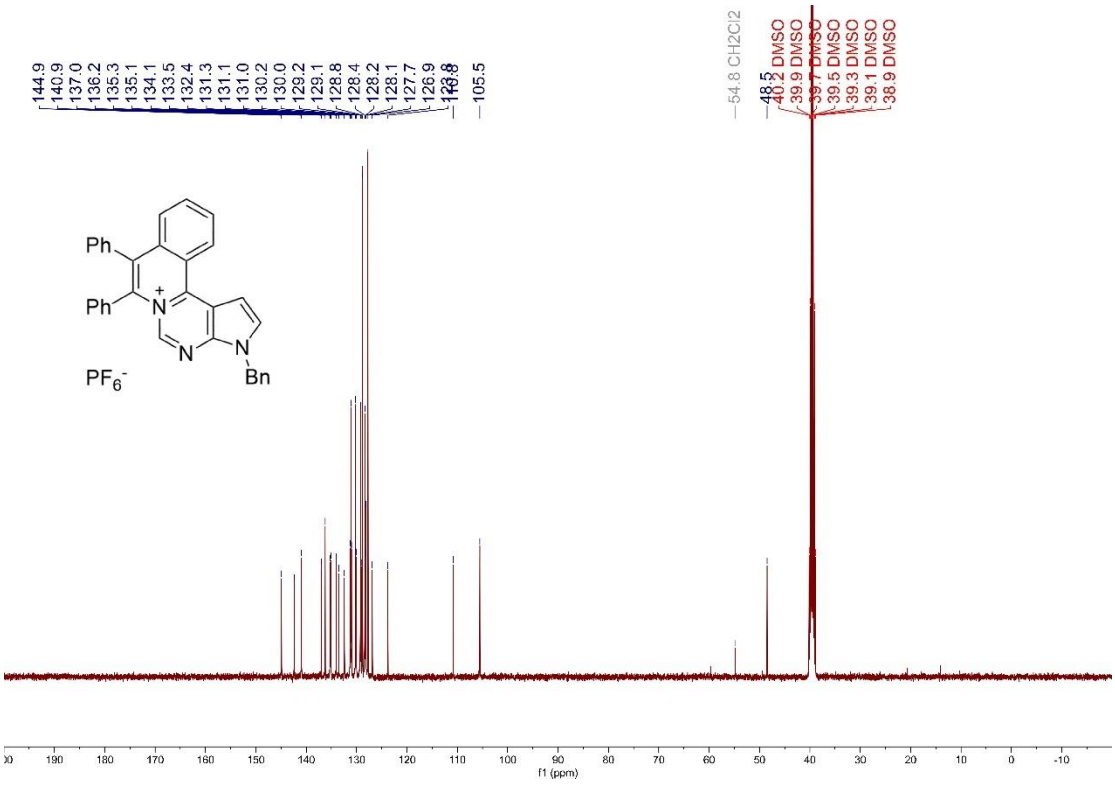
^{13}C NMR Spectrum of 3va at 25 ^{o}C (DMSO-d_6, 100 MHz)



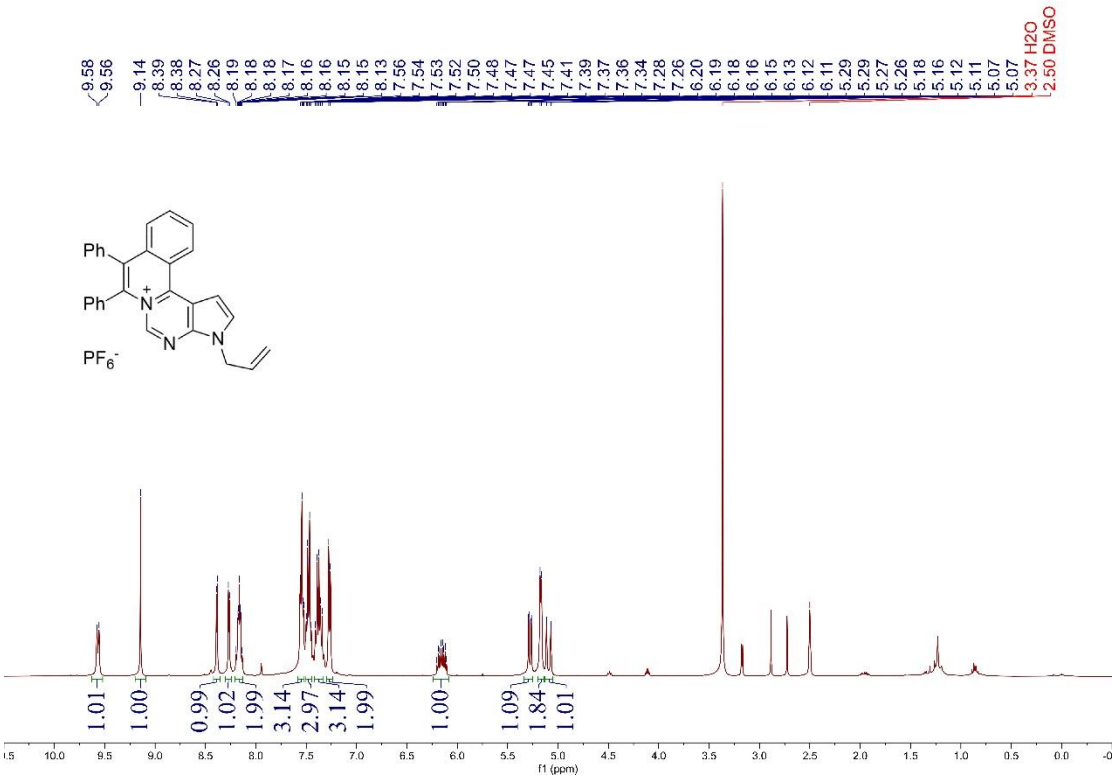
^{1}H NMR Spectrum of 3wa at 25 °C (DMSO-d_6, 400 MHz)



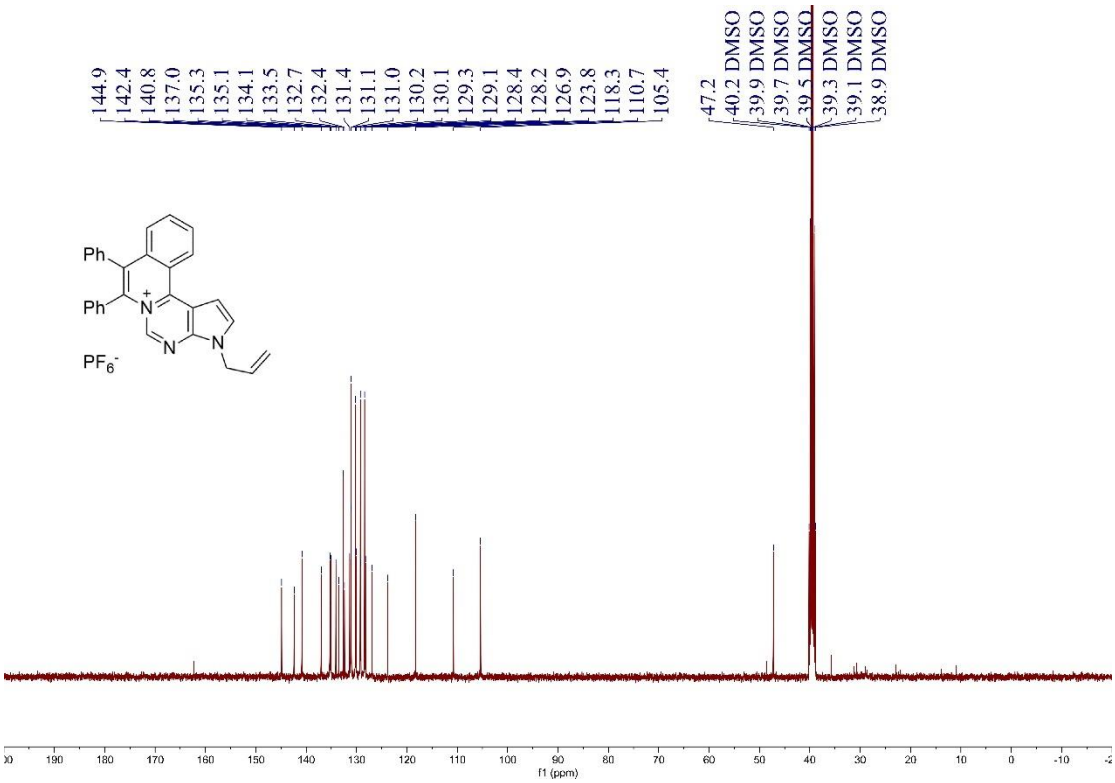
^{13}C NMR Spectrum of 3wa at 25 °C (DMSO-d_6, 100 MHz)



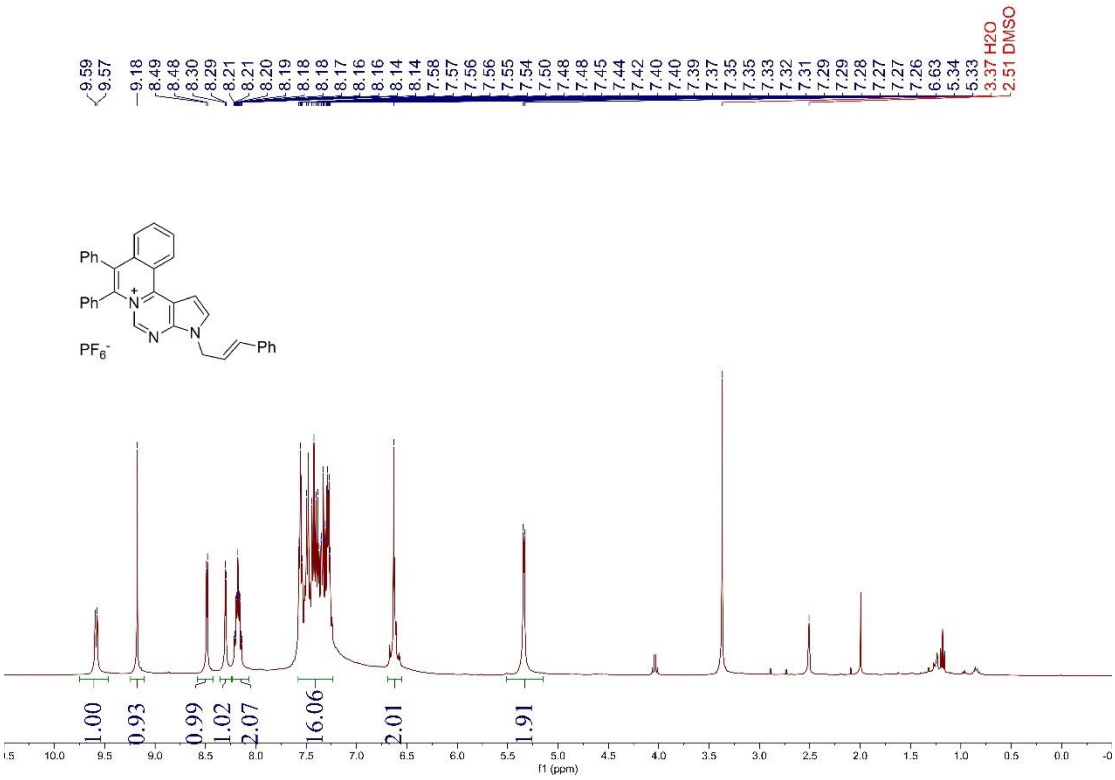
^{1}H NMR Spectrum of 3xa at 25 ^{o}C (DMSO-d_6, 400 MHz)



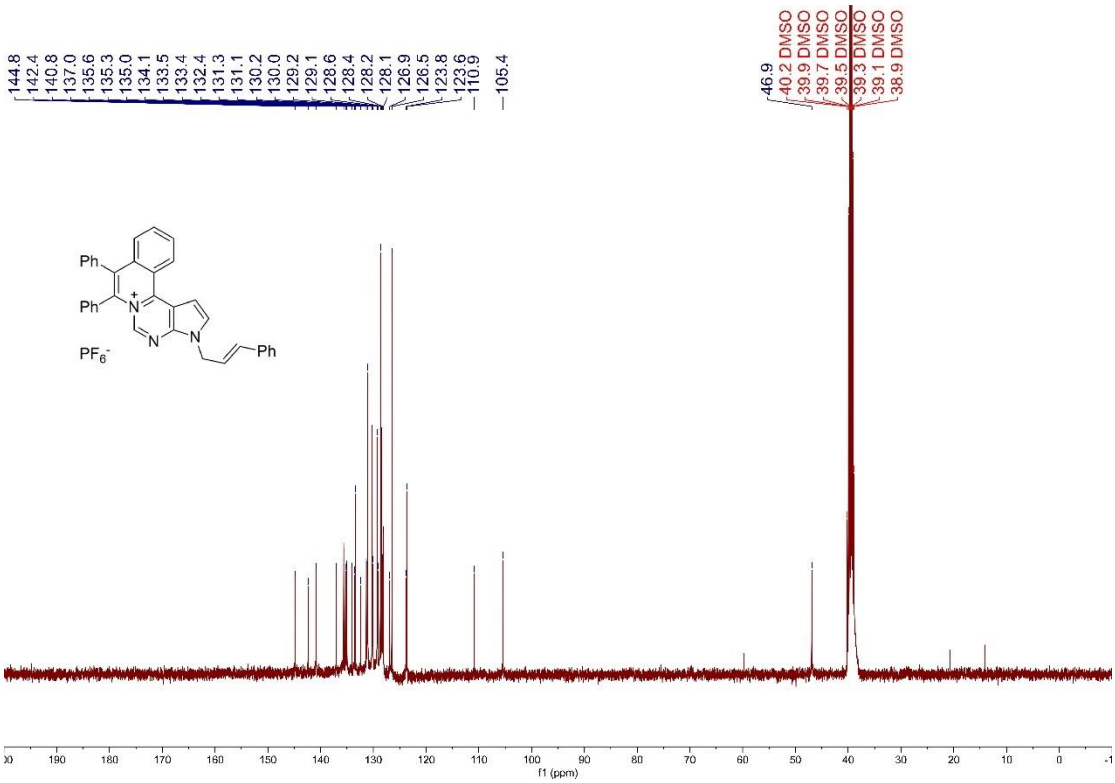
^{13}C NMR Spectrum of 3xa at 25 ^{o}C (DMSO-d_6, 100 MHz)



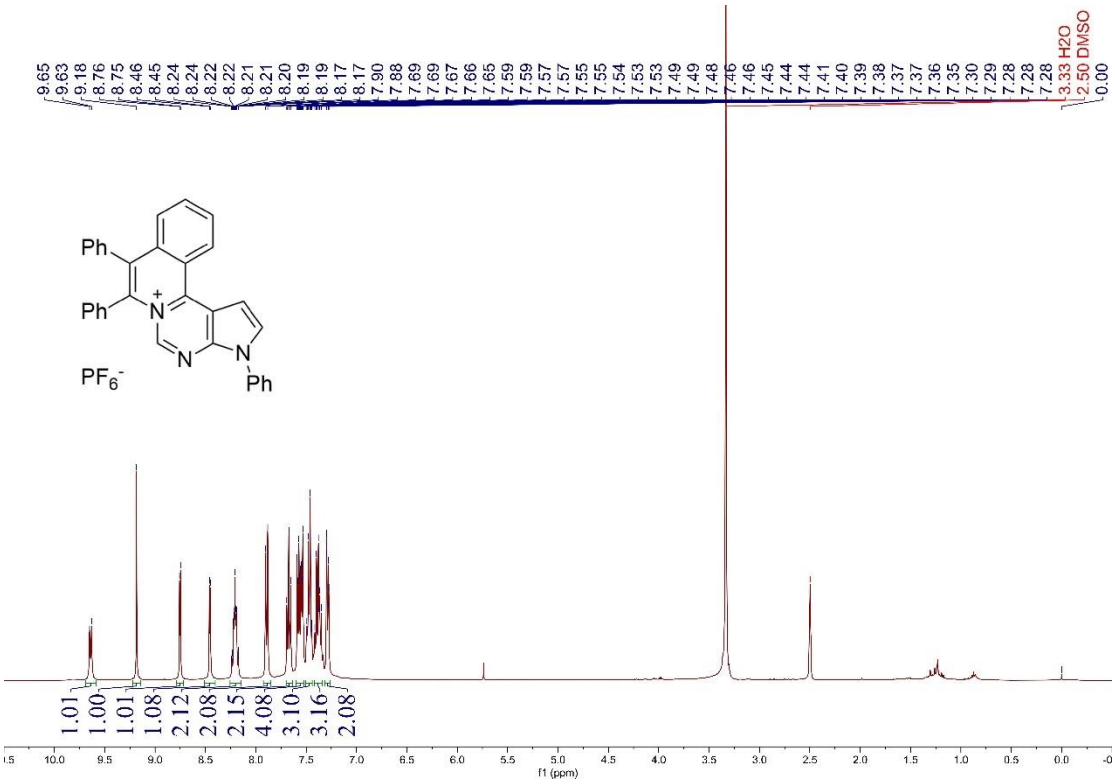
^{1}H NMR Spectrum of 3ya at 25 ^{o}C (DMSO-d_6, 400 MHz)



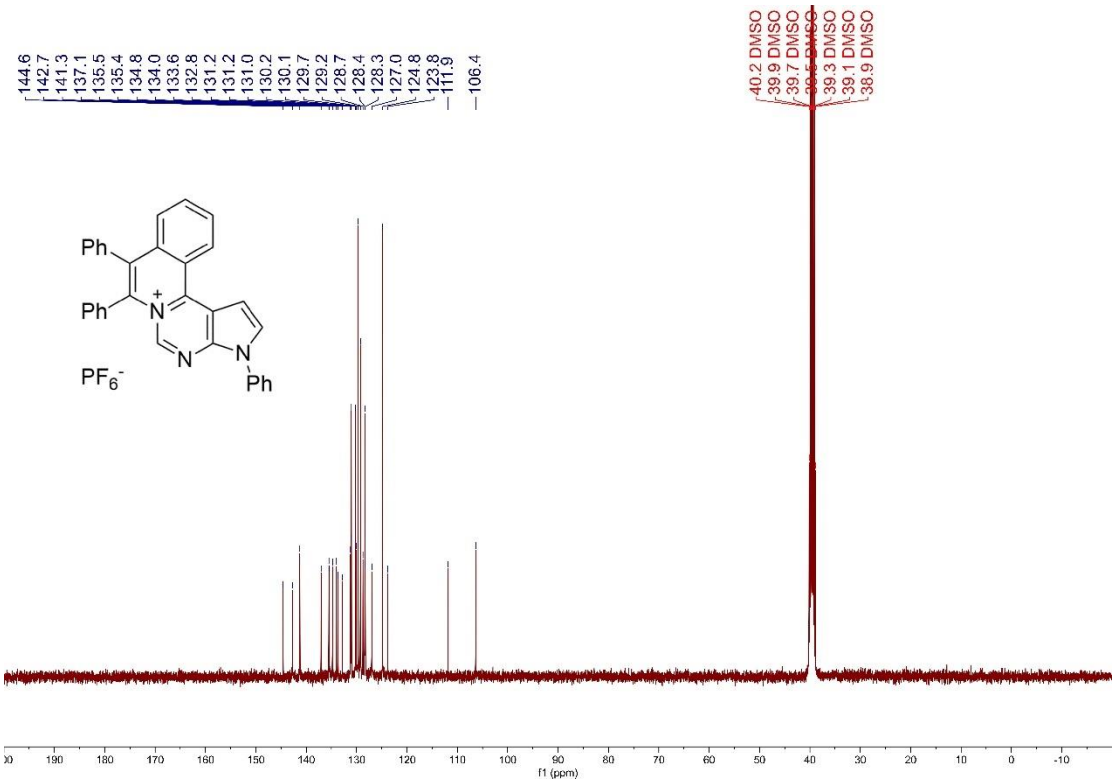
^{13}C NMR Spectrum of 3ya at 25 ^{o}C (DMSO-d_6, 100 MHz)



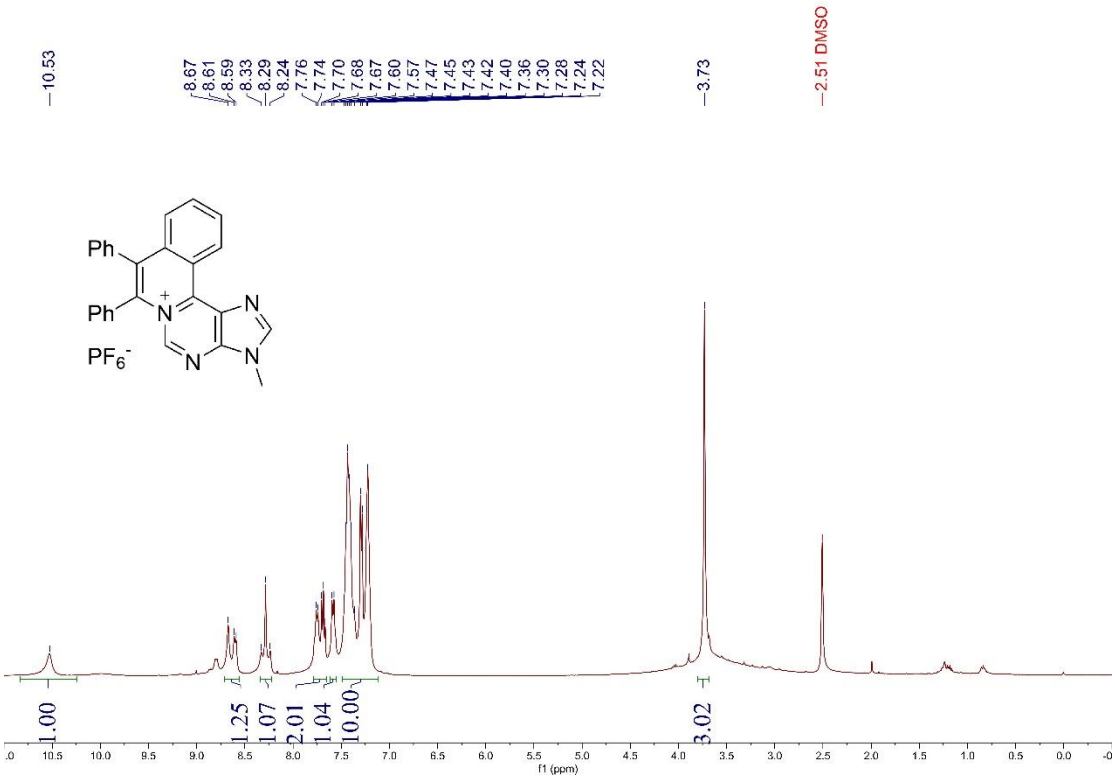
^{1}H NMR Spectrum of 3za at 25 ^{o}C (DMSO-d_6, 400 MHz)



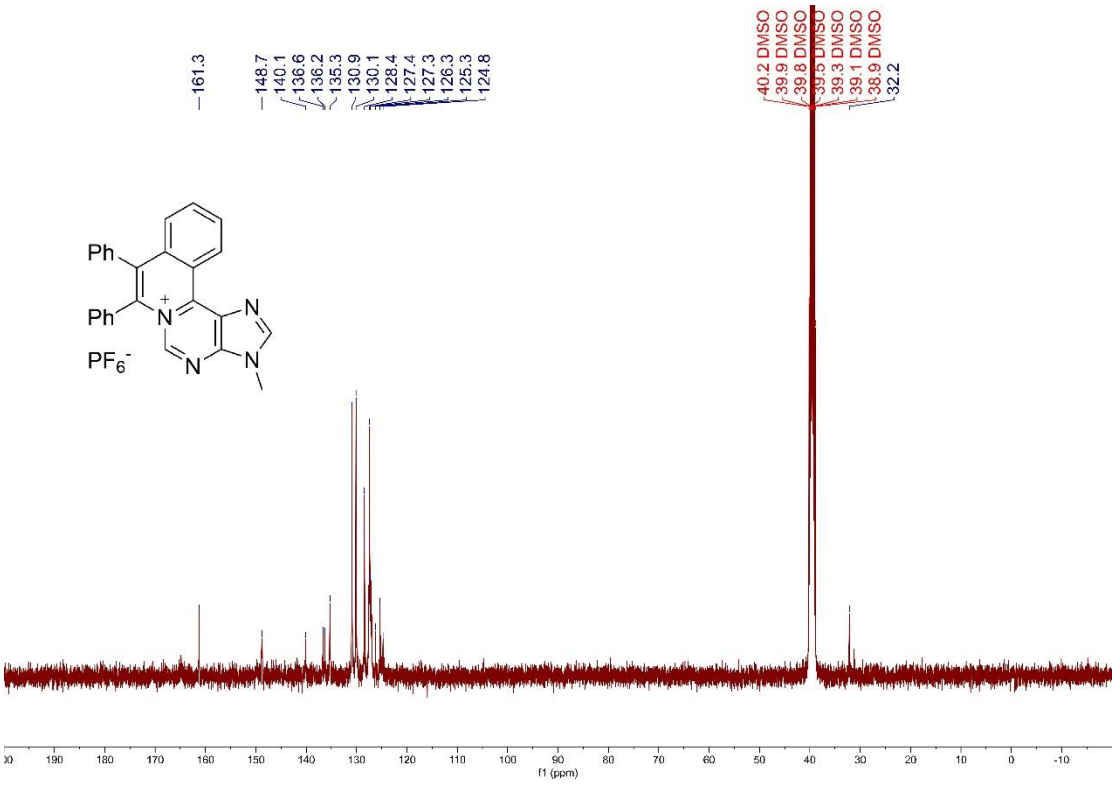
^{13}C NMR Spectrum of 3za at 25 ^{o}C (DMSO-d_6, 100 MHz)



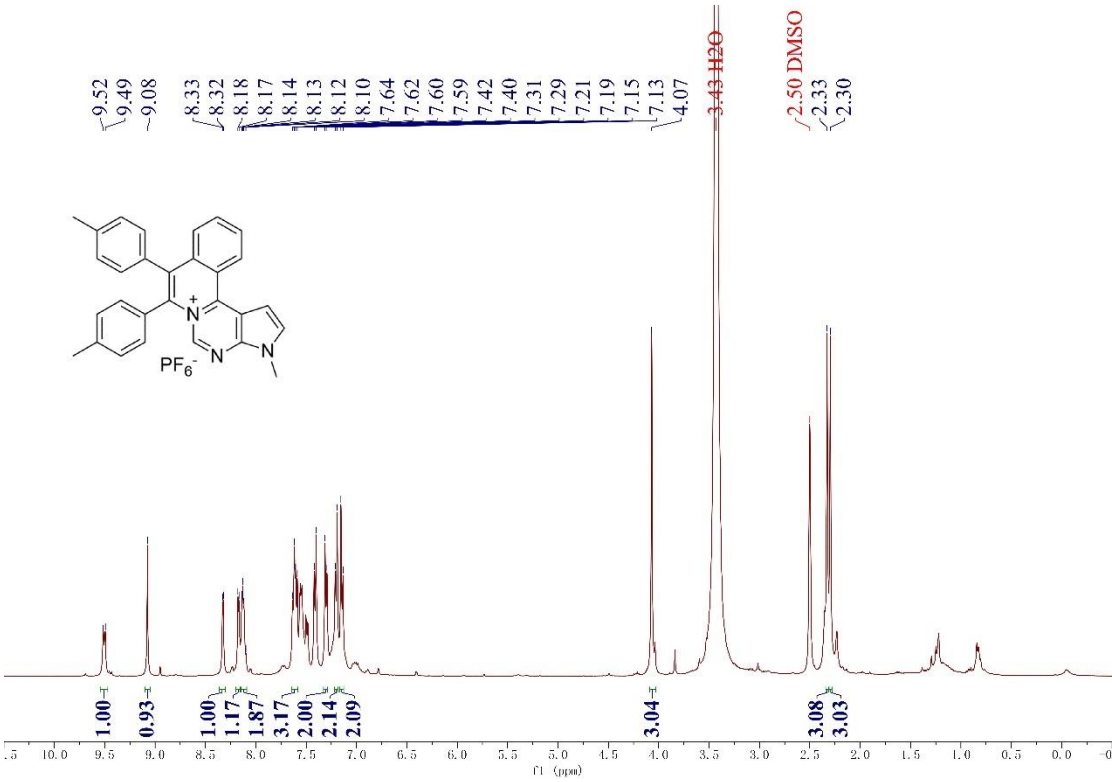
^{1}H NMR Spectrum of 3aaa at 25 ^{o}C (DMSO-d_6, 400 MHz)



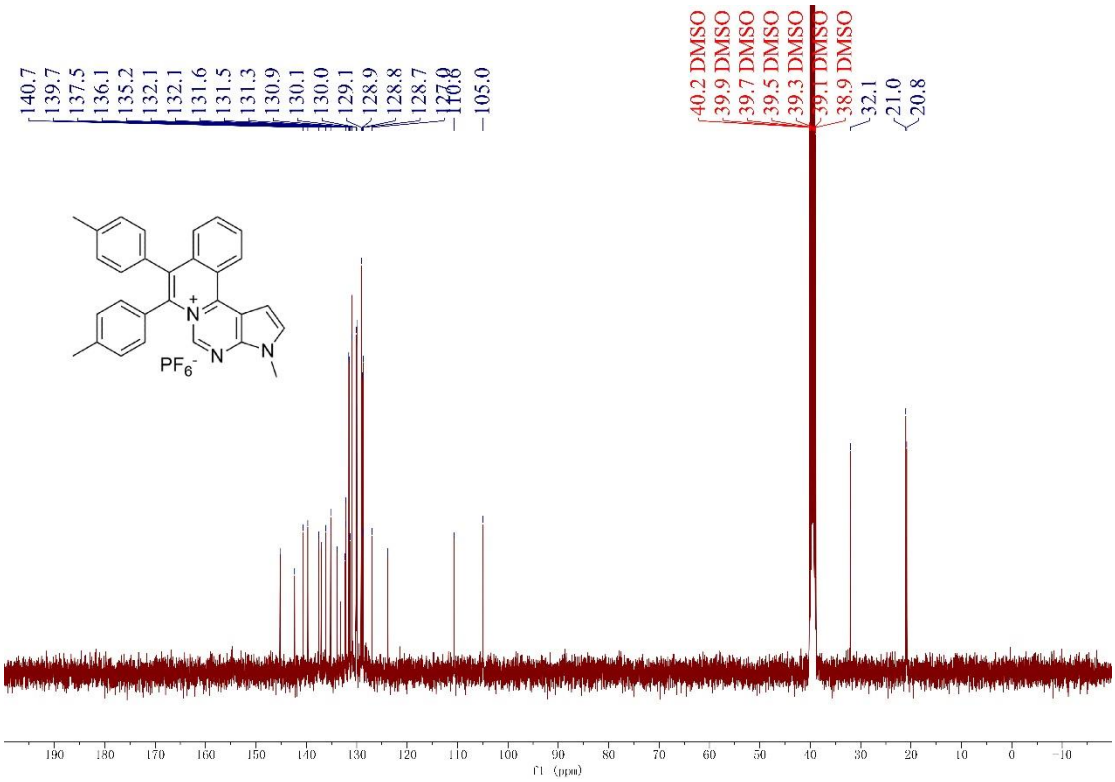
^{13}C NMR Spectrum of 3aaa at 25 ^{o}C (DMSO-d_6, 100 MHz)



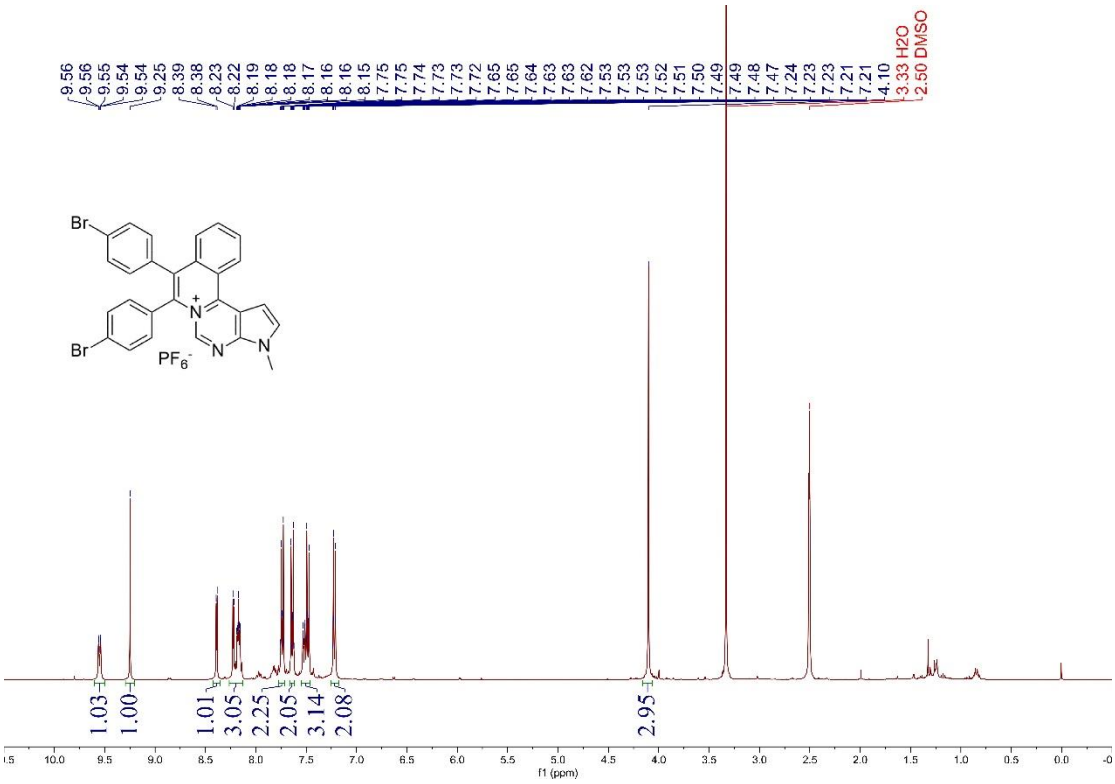
^{1}H NMR Spectrum of 3ab at 25 ^{o}C (DMSO-d_6, 400 MHz)



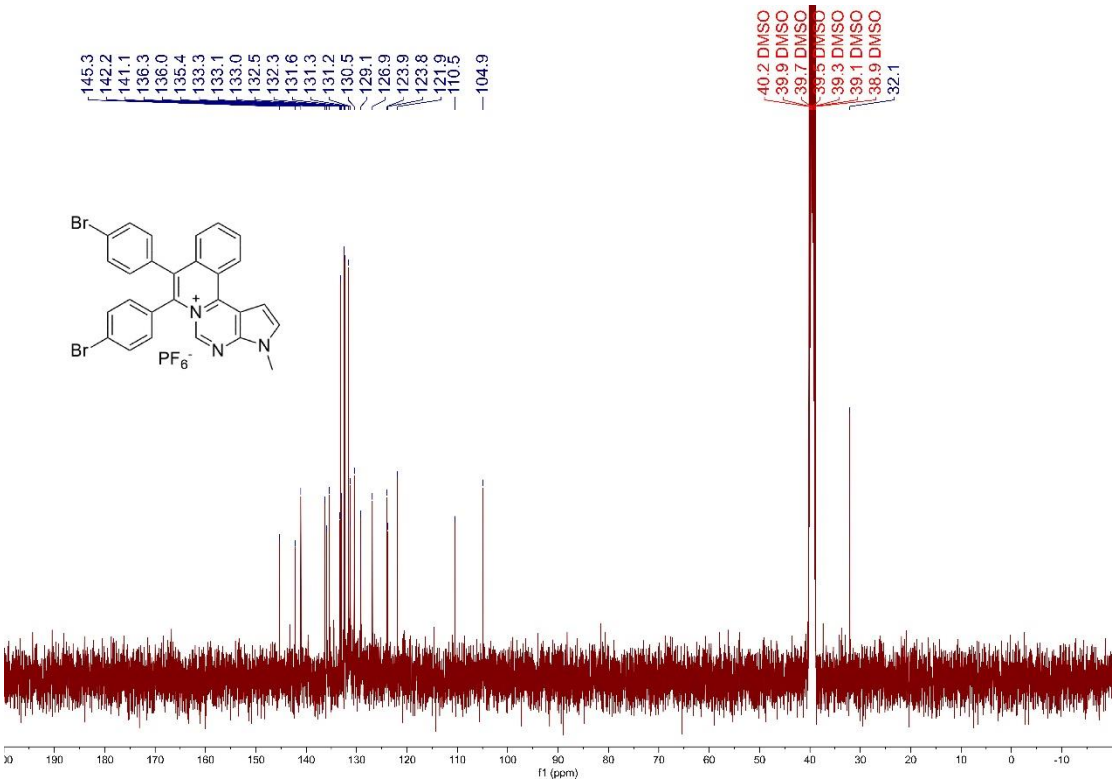
^{13}C NMR Spectrum of 3ab at 25 ^{o}C (DMSO-d_6, 100 MHz)



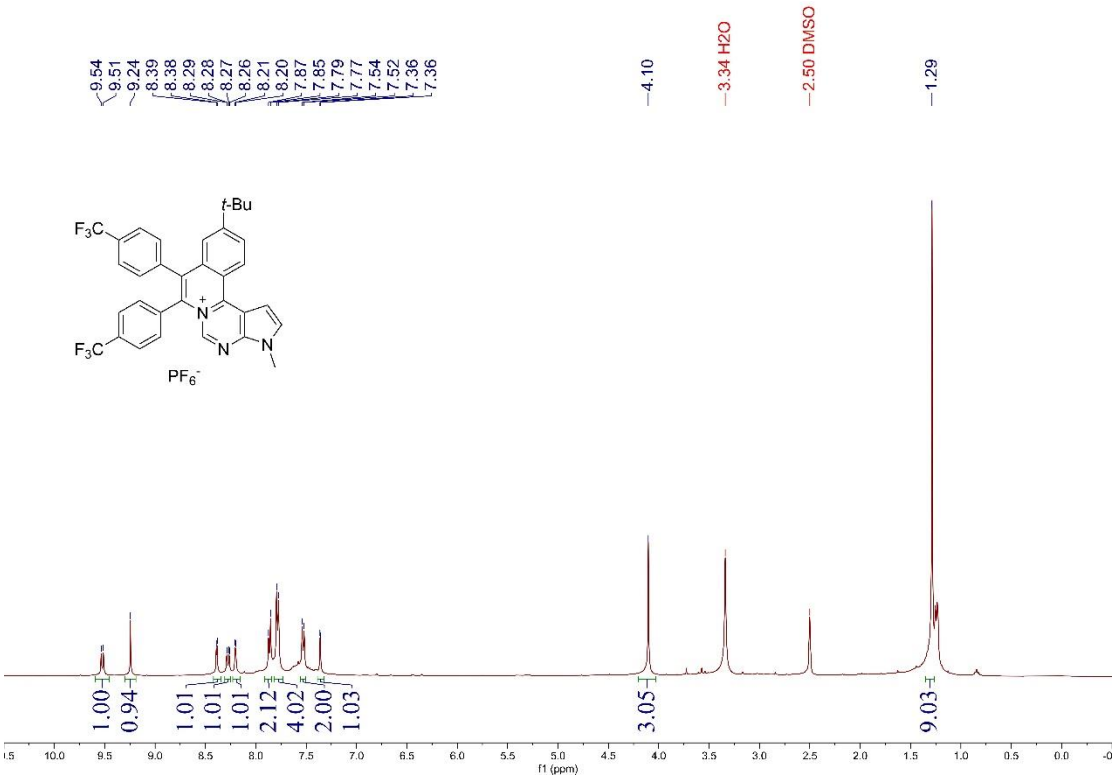
^{1}H NMR Spectrum of 3ac at 25 ^{o}C (DMSO-d_6, 400 MHz)



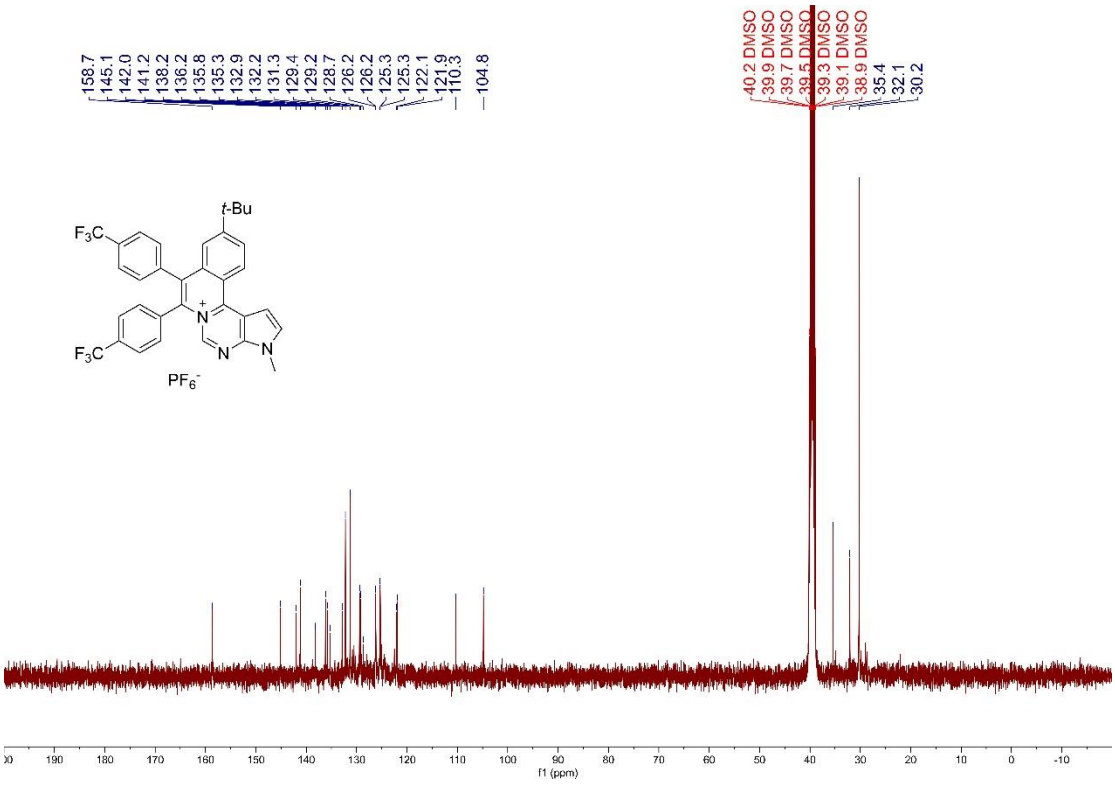
^{13}C NMR Spectrum of 3ac at 25 ^{o}C (DMSO-d_6, 100 MHz)



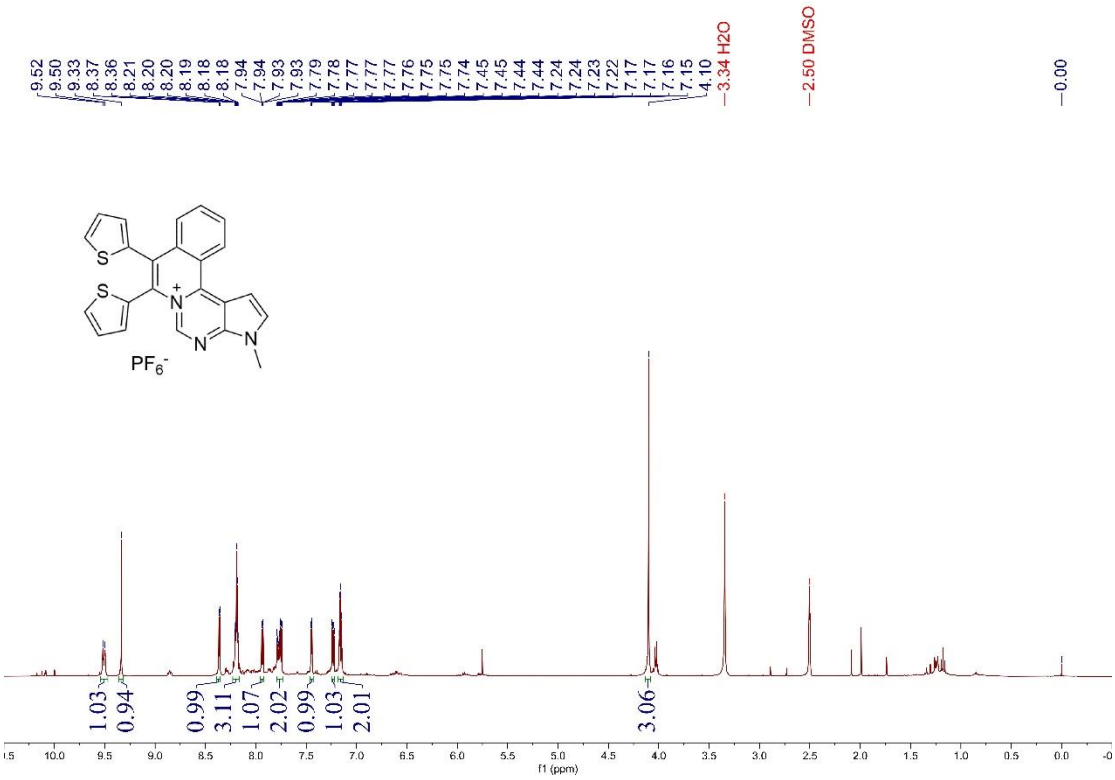
^{1}H NMR Spectrum of 3ad at 25 °C (DMSO-d_6, 400 MHz)



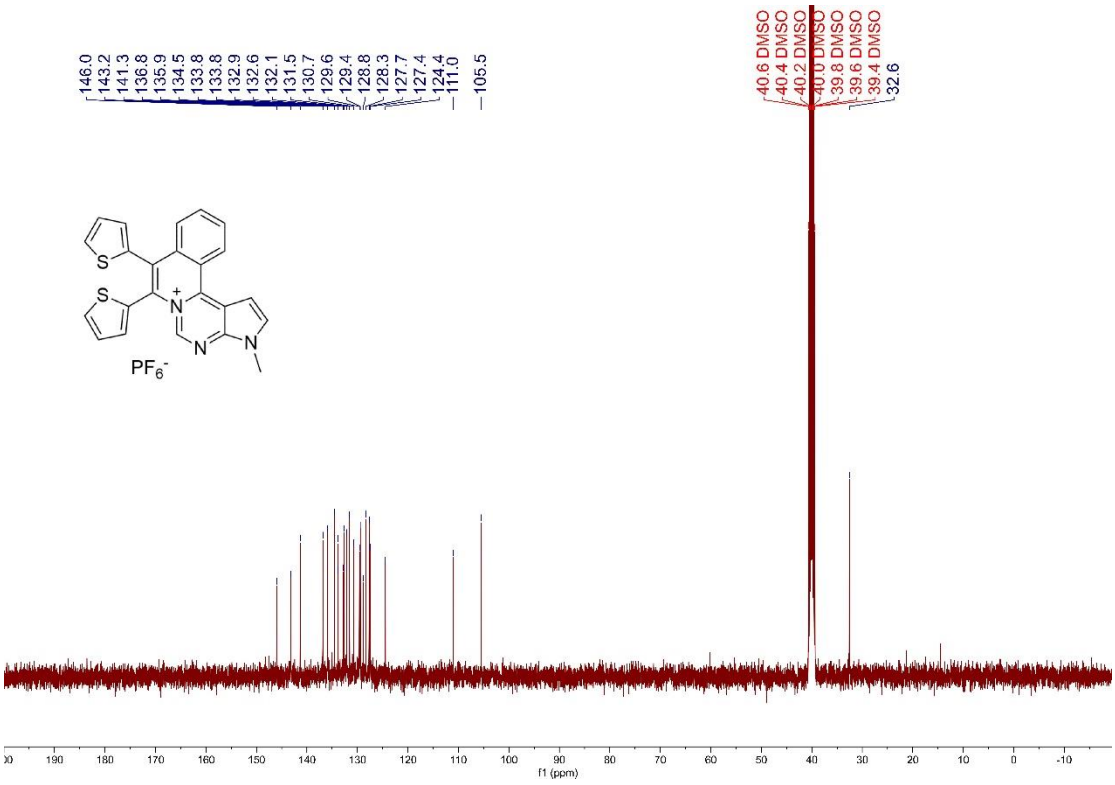
^{13}C NMR Spectrum of 3ad at 25 °C (DMSO-d_6, 100 MHz)



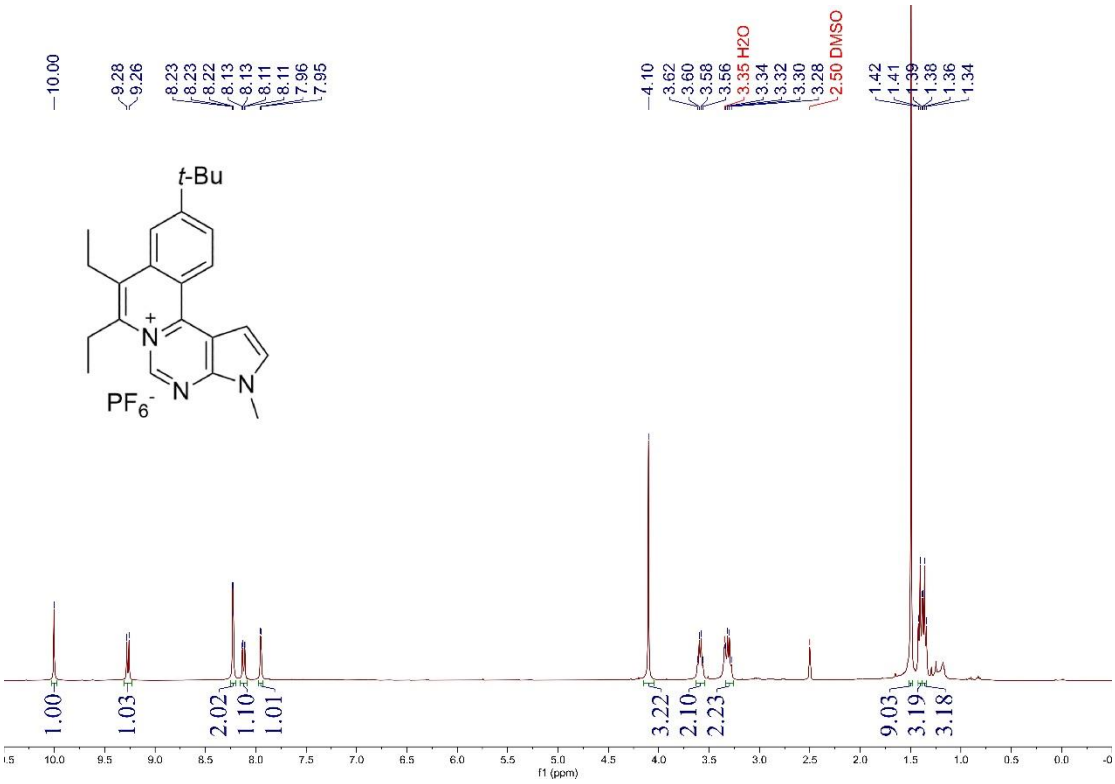
^{1}H NMR Spectrum of 3ae at 25 ^{o}C (DMSO-d_6, 400 MHz)



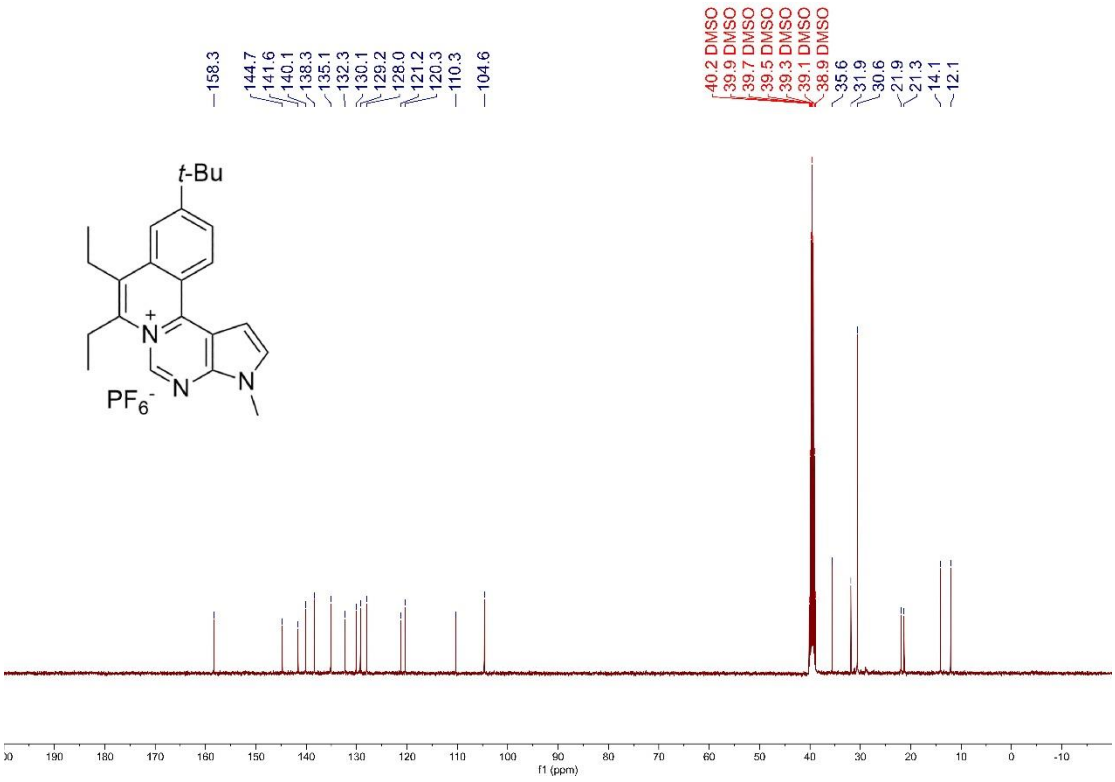
^{13}C NMR Spectrum of 3ae at 25 ^{o}C (DMSO-d_6, 100 MHz)



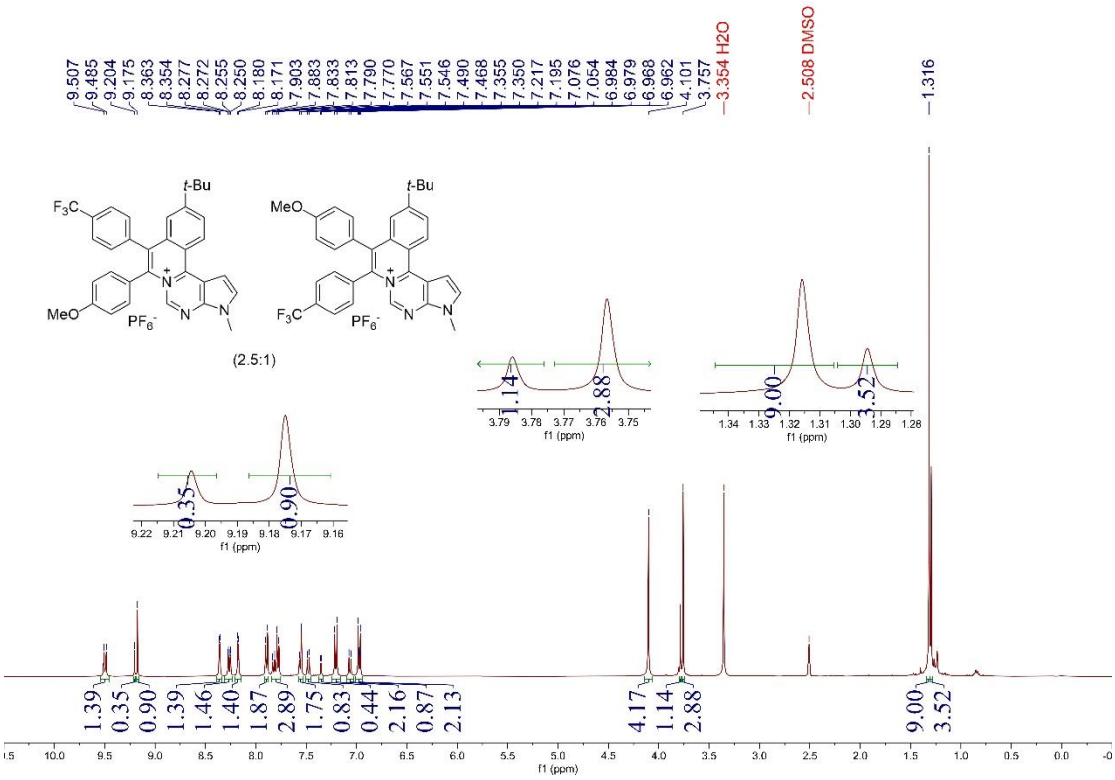
^{1}H NMR Spectrum of 3af at 25 ^{o}C (DMSO-d_6, 400 MHz)



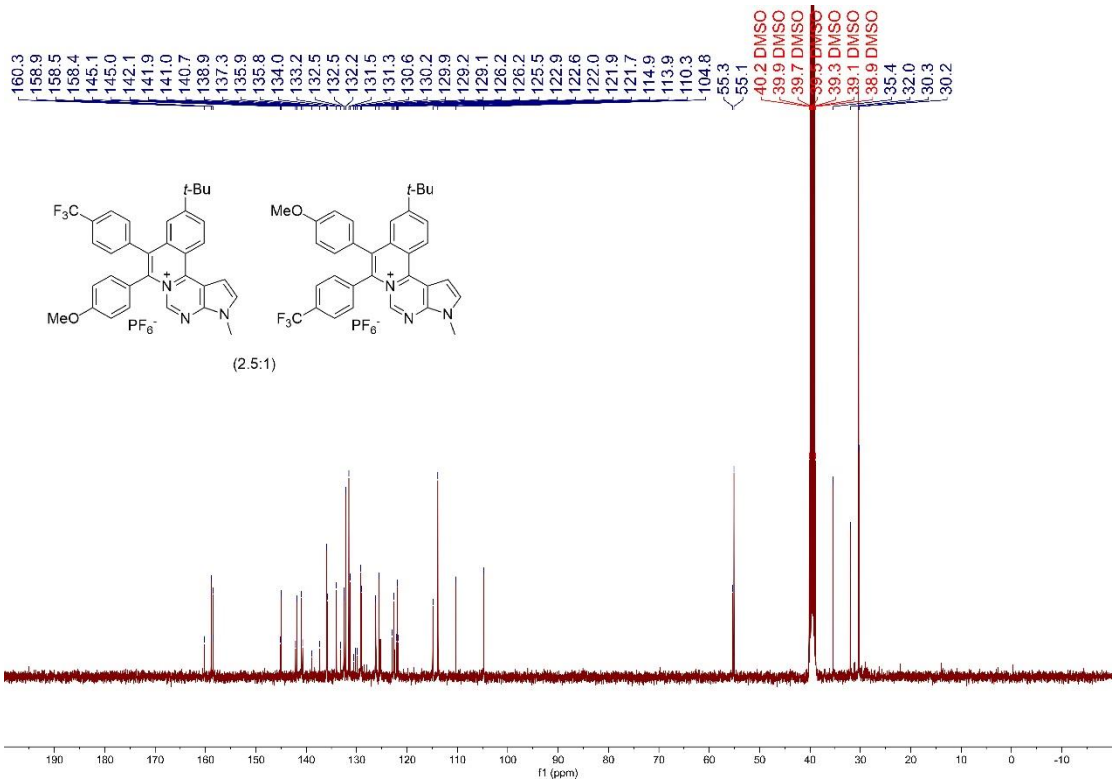
^{13}C NMR Spectrum of 3af at 25 ^{o}C (DMSO-d_6, 100 MHz)



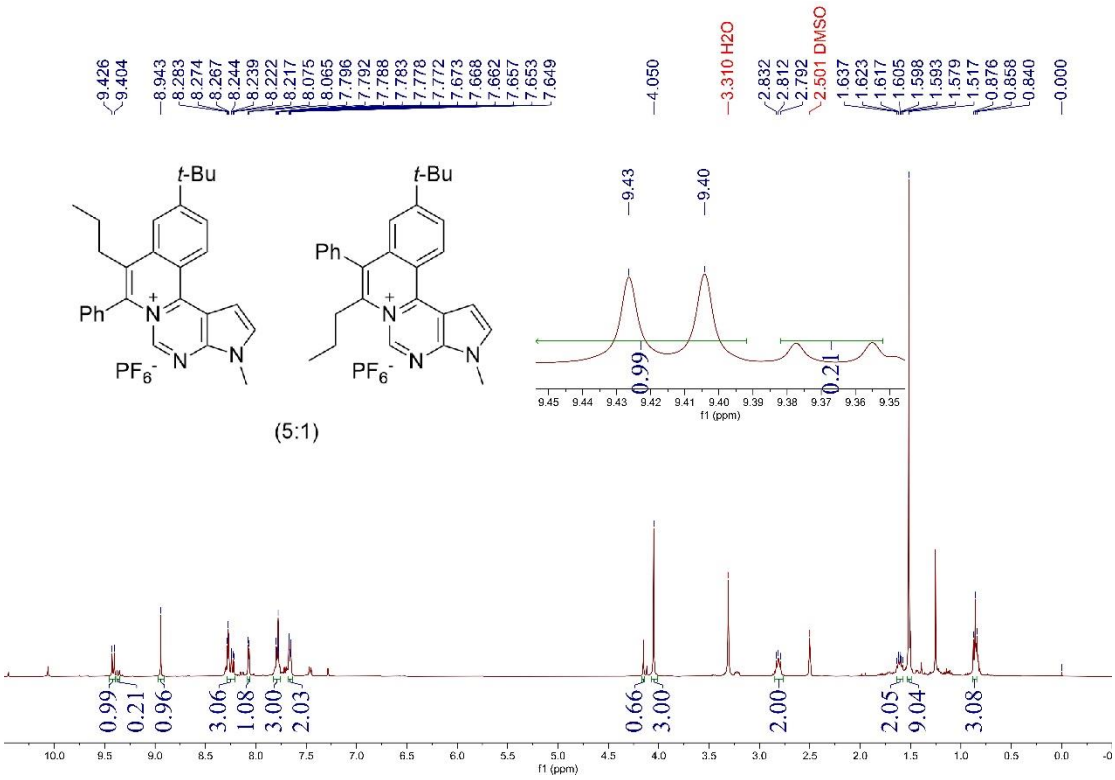
^{1}H NMR Spectrum of 3ag at 25 °C (DMSO-d_6, 400 MHz)



^{13}C NMR Spectrum of 3ag at 25 °C (DMSO-d_6, 100 MHz)



^{1}H NMR Spectrum of 3ah at 25 °C (DMSO-d_6, 400 MHz)



^{13}C NMR Spectrum of 3ah at 25 °C (DMSO-d_6, 100 MHz)