Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Cu/Fe-Mediated *N*(sp^2)-arylation/alkenylation of pyridines with aryl-/alkenylboronic acids to yield versatile cationic materials

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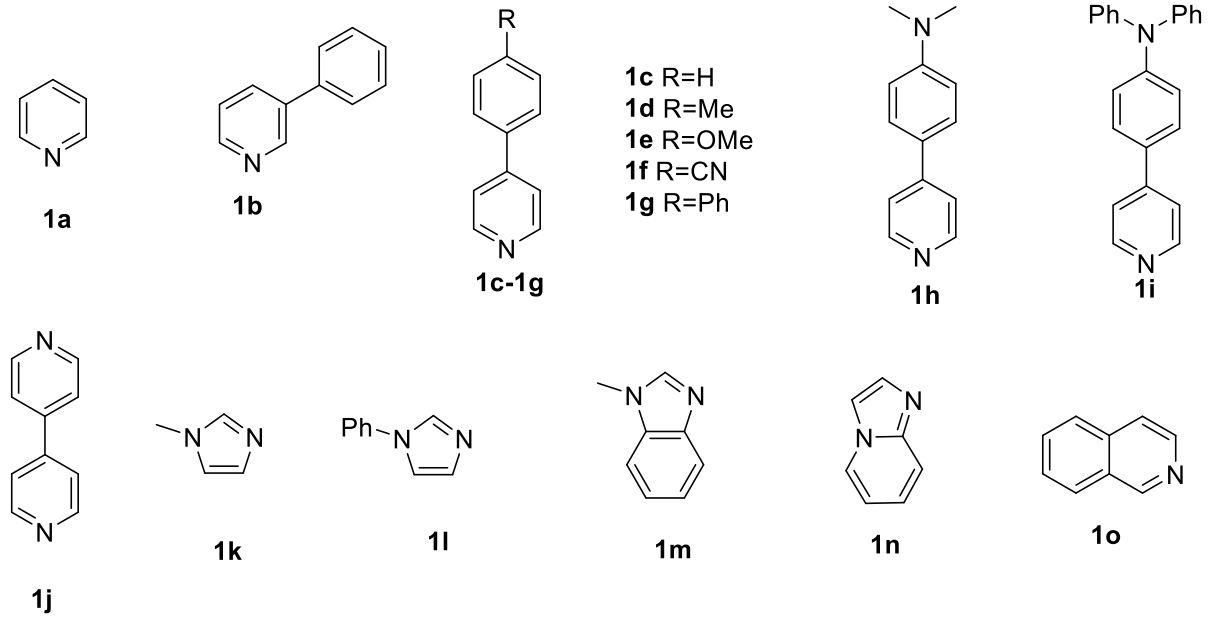
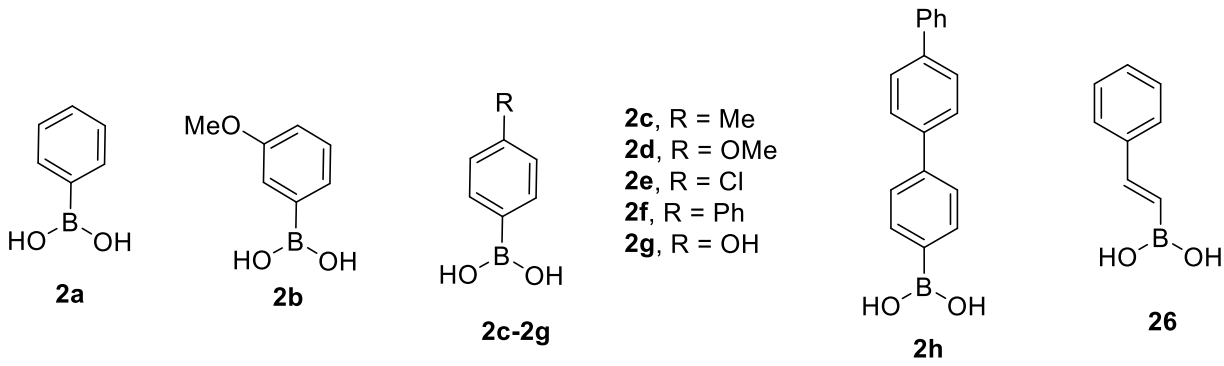
I. General remarks

NMR spectra were obtained on a BRUKER Ascend500. Samples were recorded in $CDCl_3$, CD_3OD, or DMSO-d_6 at room temperature. The ^1H NMR (500 MHz) chemical shifts were measured relative to $CDCl_3$, CD_3OD, or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; CD_3OD: δ = 3.31 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (126 MHz) chemical shifts were given using $CDCl_3$, CD_3OD, or DMSO-d_6 the internal standard ($CDCl_3$: δ = 77.16 ppm; CD_3OD: δ = 49.00 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HR-MS) were obtained with a BRUKER solanX 70 FT-MS (ESI^+). UV-vis spectra were recorded by a Perkin Elmer LAMBDA 365. Fluorescence emission spectra were obtained using a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer. Melting points were determined with SGW® X-4 and are uncorrected.

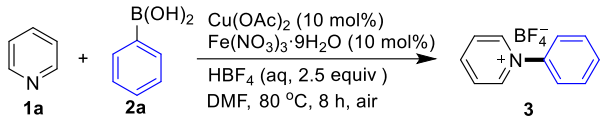
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Pyridines **1a-c** and **1j**, imidazoles **1k-n**, isoquinoline **1o**, arylboronic acids **2**, copper salts, $Fe(NO_3)_3{\cdot}9H_2O$, HBF_4 (50% aqueous) and DMF were purchased from Beijing Innochem Chemical Engineering Reagent (China) Co., Ltd. Pyridines (**1d-1f),**[1] **1g,**[2] **1h**[3] **and 1i**[4] were prepared according to the literature.





II. Optimization data

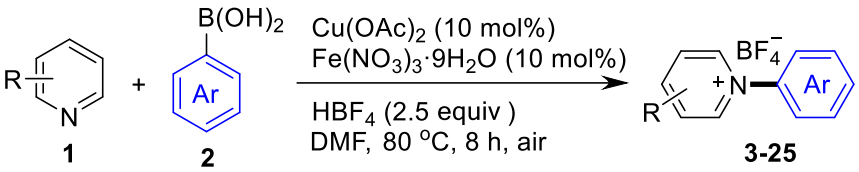
Table S1. *Optimization of the N-arylation reaction conditions*[a]



Entry	Variation of standard conditions	Yield (%)[b]
1	none	88
2	without $Cu(OAc)_2$	0
3	without $Fe(NO_3)_3·9H_2O$	50
4	$Cu(OAc)_2·H_2O$ instead of $Cu(OAc)_2$	82
5	Cu_2O instead of $Cu(OAc)_2$	51
6	CuI instead of $Cu(OAc)_2$	48
7	other metal salts instead of $Cu(OAc)_2$	0[c]
8	$FeCl_3$ instead of $Fe(NO_3)_3·9H_2O$	25
9	Fe_2O_3 instead of $Fe(NO_3)_3·9H_2O$	67
10	$BF_3·Et_2O$ instead of HBF_4	45
11	$NaBF_4$ instead of HBF_4	0
12	EtOH, DCE, and DCB as solvent	0
13	at 100 °C	74
14	at 120 °C	68

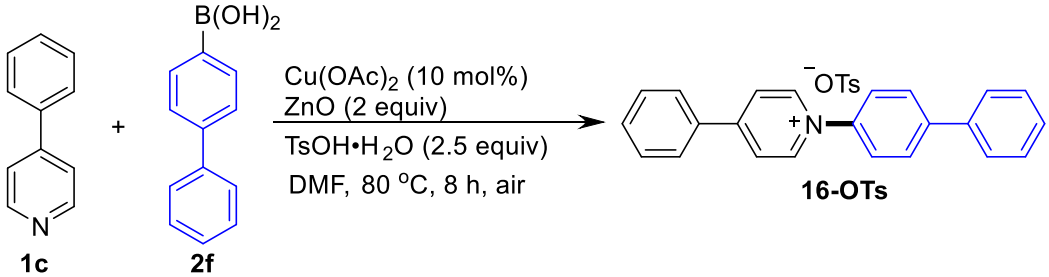
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $Cu(OAc)_2$ (10 mol%), $Fe(NO_3)_3·9H_2O$ (10 mol%) and HBF_4 (50% aqueous, 2.5 equiv) were stirred in DMF (1 mL) at 80 °C for 8 h under air. [b] Isolated yields. [c] Other metal salts = $Pd(OAc)_2$, $Zn(OAc)_2$, and $Co(OAc)_2$. DCE = 1,2-dichloroethane, DCB = *o*-dichlorobenzene.

III. General procedure of N-arylation of pyridines



To a dry Schlenk tube with a magnetic stir bar was added pyridines **1** (0.2 mmol), arylboronic acids **2** (0.3 mmol, 1.5 equiv), $Cu(OAc)_2$ (4 mg, 10 mol%), $Fe(NO_3)_3·9H_2O$ (8 mg, 10 mol%), HBF_4 (50% aq, 2.5 equiv) and DMF (1 mL). The mixture was stirred at 80 °C for 8 h under air. After the reaction was completed, DMF was removed under reduced pressure and the residue was passed through a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 50/1~20/1, v/v) to afford pyridinium products **3-25**.

Synthesis of 16-OTs:



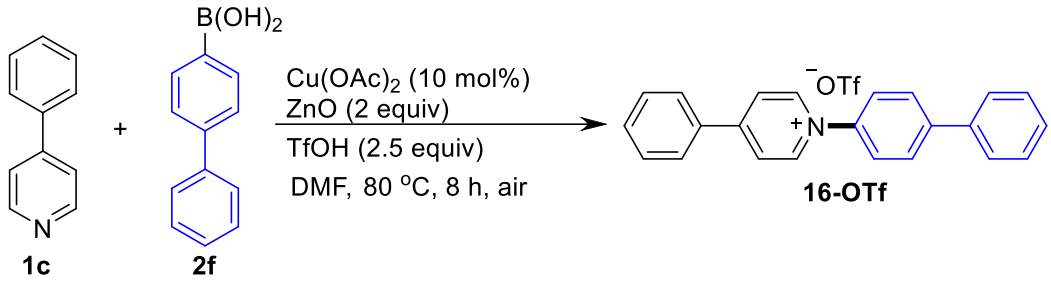
The mixture of 4-phenylpyridine **1c** (0.2 mmol, 31.1mg, 1equiv), 4-phenylboronic acid **2f** (0.3 mmol, 59.4 mg, 1.5 equiv), $Cu(OAc)_2$ (3.6 mg, 10 mol%), ZnO (0.4 mmol, 32.6 mg, 2 equiv), $TsOH·H_2O$

(95.1 mg, 2.5 equiv) and DMF (1 mL) was stirred at 80 °C for 8 h under air. After the reaction was completed, DMF was removed under reduced pressure and the residue was passed through a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 50/1~20/1, v/v) to afford **16-OTs** as a white solid (42 mg, 44% yield).

1-([1,1'-biphenyl]-4-yl)-4-phenylpyridin-1-ium tosylate (16-OTs)

A white solid (42 mg, 44% yield). M.p.: > 240 ºC. **^{1}H NMR (500 MHz, CD_3OD):** δ = 9.21 (d, J = 6.0 Hz, 2H), 8.55 (d, J = 6.0 Hz, 2H), 8.10 (d, J = 6.5 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H), 7.92 (d, J =8.5 Hz, 2H), 7.74–7.68 (m, 7H), 7.52 (t, J =7.5 Hz, 2H), 7.44 (t, J =6.8 Hz, 1H), 7.20 (d, J =7.5 Hz, 2H), 2.33 (s, 3H) ppm. **^{13}C NMR (125 MHz, CD_3OD):** δ = 158.64, 145.69, 145.53, 143.37, 142.92, 141.78, 140.08, 135.05, 133.86, 131.07, 130.27, 130.03, 129.84, 129.69, 129.43, 128.28, 126.96, 126.07, 125.74, 21.29 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{30}H_{25}NO_3S^+$ ([M−OTs^-]$^+$) 308.1434, found 308.1436.

Synthesis of 16-OTf:

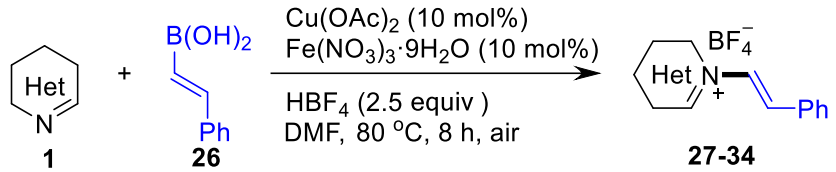


The mixture of 4-phenylpyridine **1c** (0.2 mmol, 31.1mg, 1equiv), 4-phenylboronic acid **2f** (0.3 mmol, 59.4 mg, 1.5 equiv), $Cu(OAc)_2$ (3.6 mg, 10 mol%), ZnO (0.4 mmol, 32.6 mg, 2 equiv), TfOH (44 μL, 2.5 equiv) and DMF (1 mL) was stirred at 80 °C for 8 h under air. After the reaction was completed, DMF was removed under reduced pressure and the residue was passed through a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 50/1~20/1, v/v) to afford **16-OTf** as a white solid (61 mg, 67% yield).

1-([1,1'-biphenyl]-4-yl)-4-phenylpyridin-1-ium triflate (16-OTf)

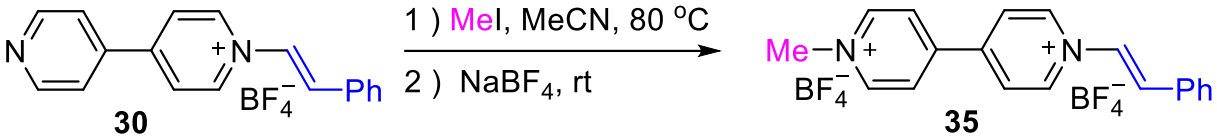
A white solid (61 mg, 67% yield). M.p.: > 240 ºC. **^{1}H NMR (500 MHz, DMSO-d_6):** δ = 9.41 (d, J = 6.5 Hz, 2H), 8.69 (d, J = 6.5 Hz, 2H), 8.22 (d, J = 7.0 Hz, 2H), 8.06 (d, J = 8.5 Hz, 2H), 8.02 (d, J =8.0 Hz, 2H), 7.82 (d, J =7.5 Hz, 2H), 7.71 (d, J =7.0 Hz, 3H), 7.56 (t, J =7.3 Hz, 2H), 7.48 (t, J =7.3 Hz, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-d_6):** δ = 155.59, 144.70, 142.76, 141.41, 138.24, 133.30, 132.61, 129.86, 129.24, 128.56, 128.45, 128.23, 127.09, 125.22, 124.37 ppm. **^{9}F NMR (471 MHz, DMSO-d_6):** δ = -77.84 (s) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{24}H_{18}F_3NO_3S^+$ ([M−OTf^-]$^+$) 308.1434, found 308.1433.

IV. General procedure of N-alkenylation of pyridines



A mixture of nitrogen heterocycle **1** (0.2 mmol, 1 equiv), (*E*)-styrylboronic acid **26** (0.3 mmol, 44.4 mg, 1,5 equiv), $Cu(OAc)_2$ (3.6 mg, 10 mol%), $Fe(NO_3)_3·9H_2O$ (8.1 mg, 10 mol%), HBF_4 (50% aq, 2.5 equiv) and DMF (1 mL) was stirred at 80 °C for 8 h under air. After the reaction was completed, the mixture was passed through a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 50/1~20/1, v/v) to afford products **27-34**.

V. Synthesis of methyl-styryl viologen (35) and its electrochromism



The mixture of **30** (0.2 mmol, 51.9 mg, 1 equiv), CH_3I (0.3 mmol, 1.5 equiv) and MeCN (1 mL) was stirred at 80 °C for 8 h under air. After cooling down to room temperature, $NaBF_4$ (2 equiv) was added to stir at room temperature for 8 h. The mixture was purified by filtration with sequential washing with MeCN (1 mL), H_2O (2 mL) and EtOH (1 mL) to afford **35** as a reddish brown solid (72 mg, 80% yield).

(*E*)-1-methyl-1'-styryl-[4,4'-bipyridine]-1,1'-diium ditetrafluoroborate (35)

M.p.: > 240 ºC. **^{1}H NMR (500 MHz, DMSO-d_6):** δ = 9.61 (d, J = 6.5 Hz, 2H), 9.31 (d, J = 6.5 Hz, 2H), 8.91 (d, J = 6.5 Hz, 2H), 8.84 (d, J = 6.5 Hz, 2H), 8.41 (d, J = 14.5 Hz, 1H), 7.97 (d, J = 14.5 Hz, 1H), 7.74 (d, J = 7.5 Hz, 2H), 7.57–7.50 (m, 3H), 4.45 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-d_6):** δ = 148.56, 147.74, 146.66, 142.48, 132.49, 130.54, 130.47, 129.94, 129.37, 127.92, 126.37, 126.04, 48.07 ppm. **^{19}F NMR (471 MHz, DMSO-d_6):** δ = -148.19 (s), -148.25 (s) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{18}N_2^+$ ($[M-2BF_4^-]^+$) 274.1459, found 274.1455.\

Electrochromism of 35: An electrochromic device is fabricated by using two pieces of FTO coated glasses spaced with two slices of parafilm. The DMF solution of **35** were injected into the space of the device by a syringe. The adding voltage was output from an alkaline battery and was measured by a multimeter.

VI. Photophysical characterization

Table S1. *Photophysical properties* [a]

Compd.	λ_{max}(absorption)	λ_{ex} (excitation)	λ_{max}(emission)
3	266 nm	266 nm	404nm
6	319 nm	319 nm	490nm
7	321 nm	321 nm	406nm

16	335 nm	335 nm	507nm
18	364 nm	364 nm	485nm
19	274 nm, 334 nm	334 nm	565nm
20	375 nm	375 nm	493nm
21	283 nm, 321 nm, 355 nm	355 nm	574nm
22	280 nm, 356 nm	356 nm	579nm

[a] The data were measured in CH_2Cl_2 (10 μM).

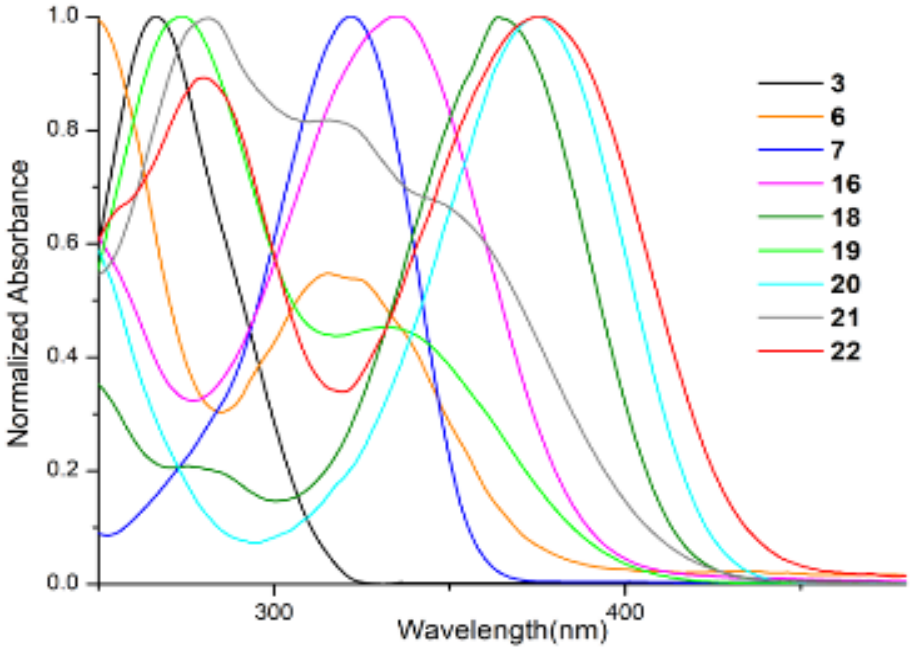


Figure S1. *UV−vis absorption spectra of* ***3***, ***6***, ***7***, ***16***, *and* ***18-20*** *in* CH_2Cl_2 *(10 μM)*

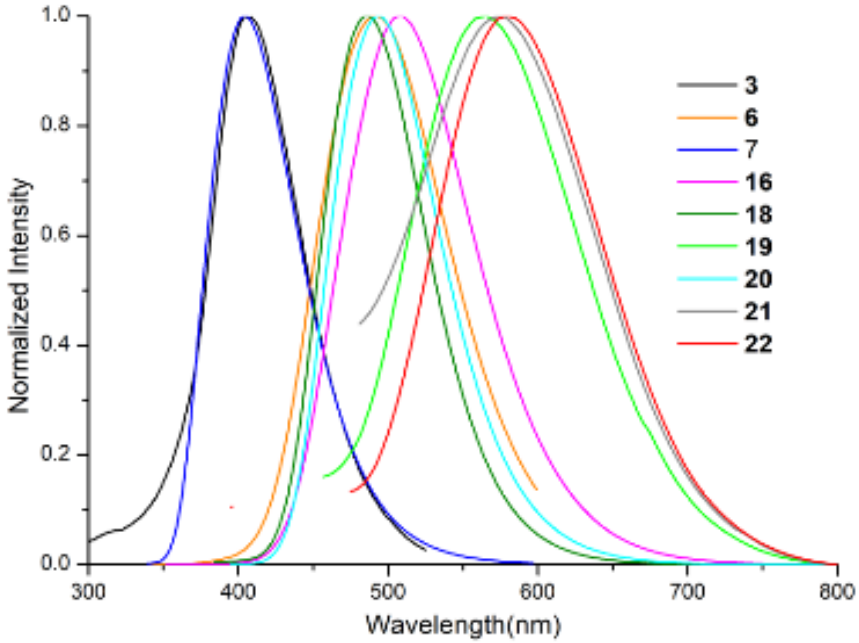


Figure S2. *Fluorescence emission spectra of* ***3***, ***6***, ***7***, ***16***, *and* ***18-20*** *in* CH_2Cl_2 *(10 μM)*

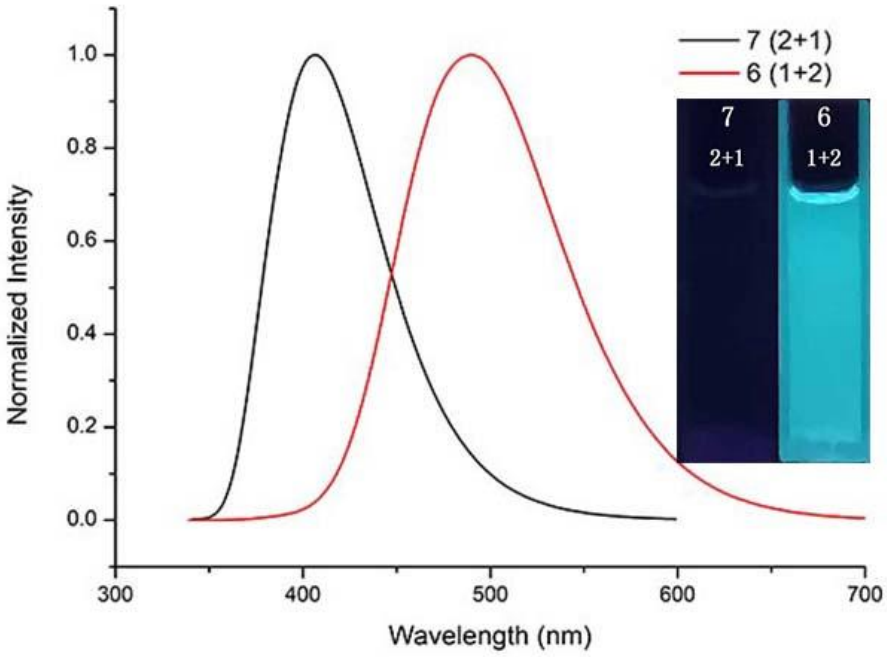


Figure S3. *Fluorescence emission spectra of* ***6*** *and* ***7*** *in* CH_2Cl_2 *(10 μM)*

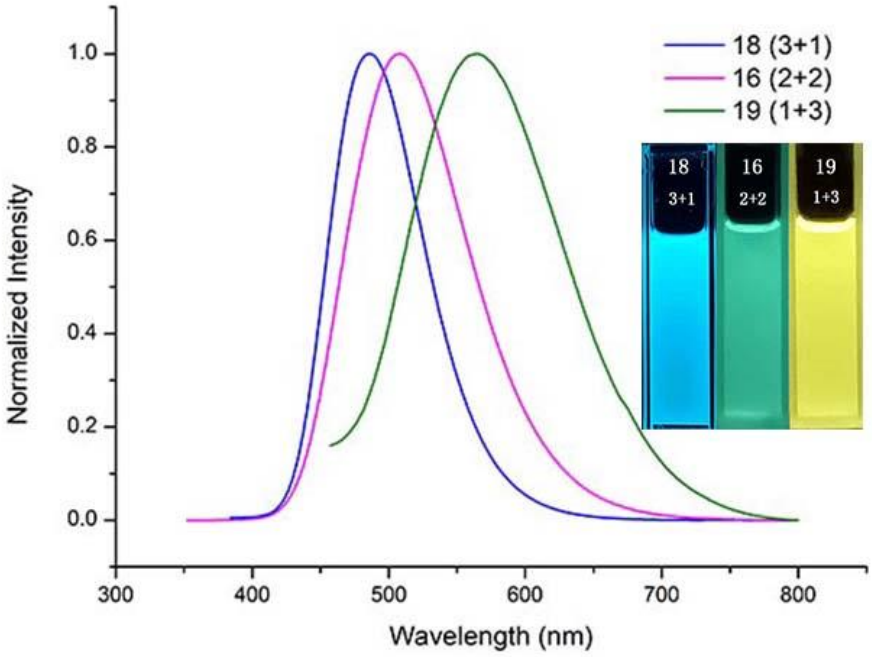


Figure S4. *Fluorescence emission spectra of* ***16***, ***18*** *and* ***19*** *in* CH_2Cl_2 *(10 μM)*

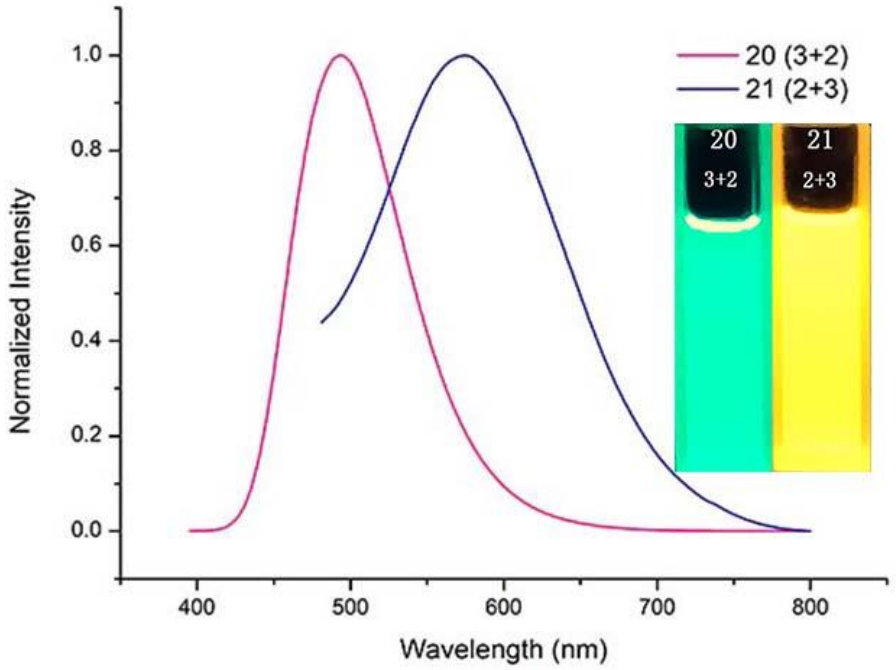


Figure S5. *Fluorescence emission spectra of* ***20*** *and* ***21*** *in CH_2Cl_2 (10 μM)*

VII. AIE characterization

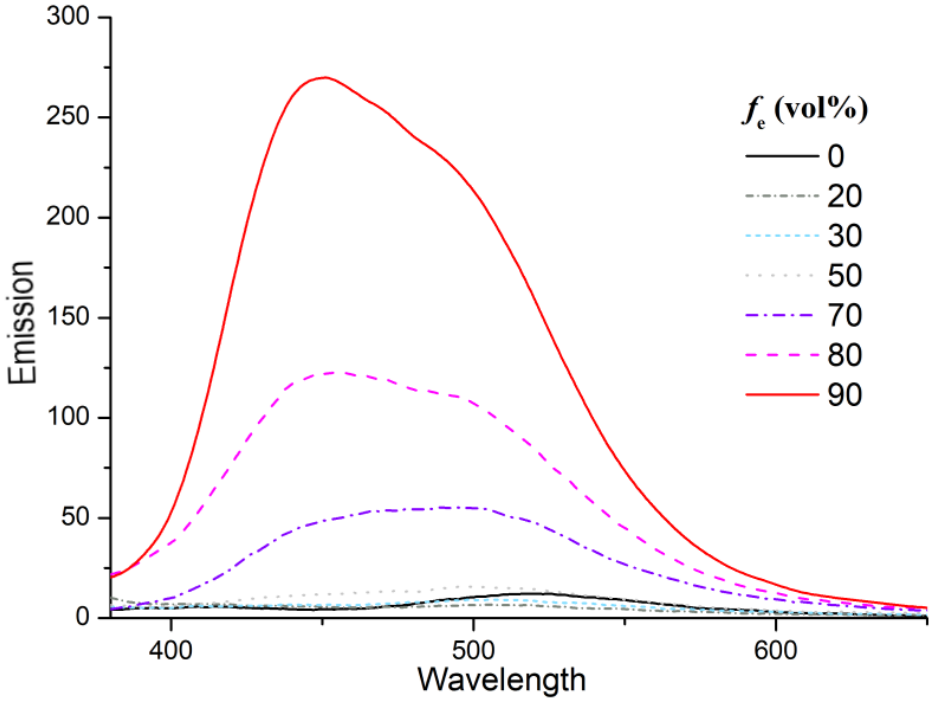


Figure S6. *Fluorescence spectrum of* ***15*** *in MeOH/Et_2O mixture with different Et_2O fractions (10 μM)*

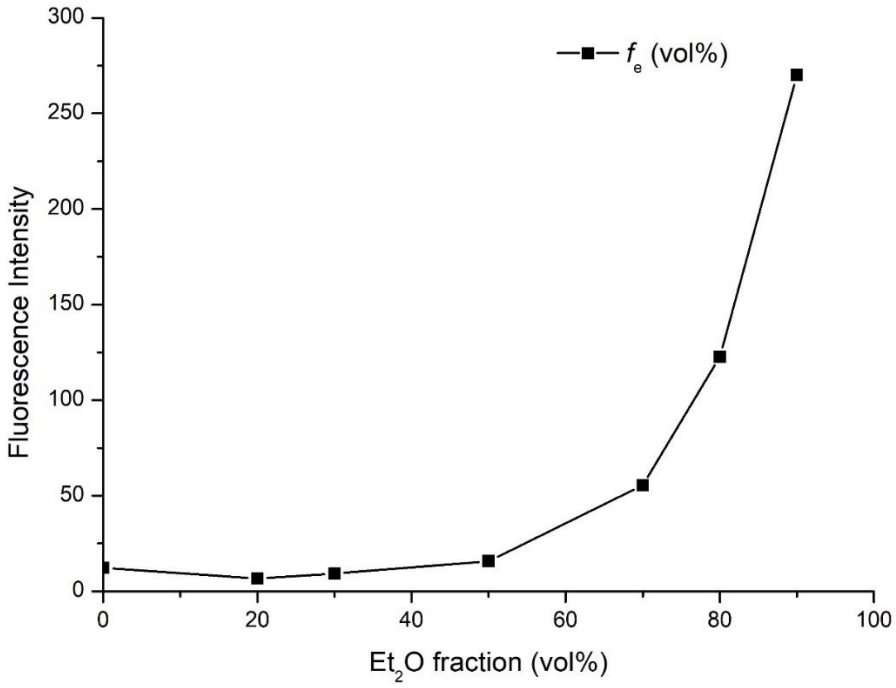


Figure S7. *Plot of the emission intensity of* ***15*** *versus the Et_2O fraction in MeOH/Et_2O mixture (10 μM)*

VIII. pH responsiveness

pH response of 13:

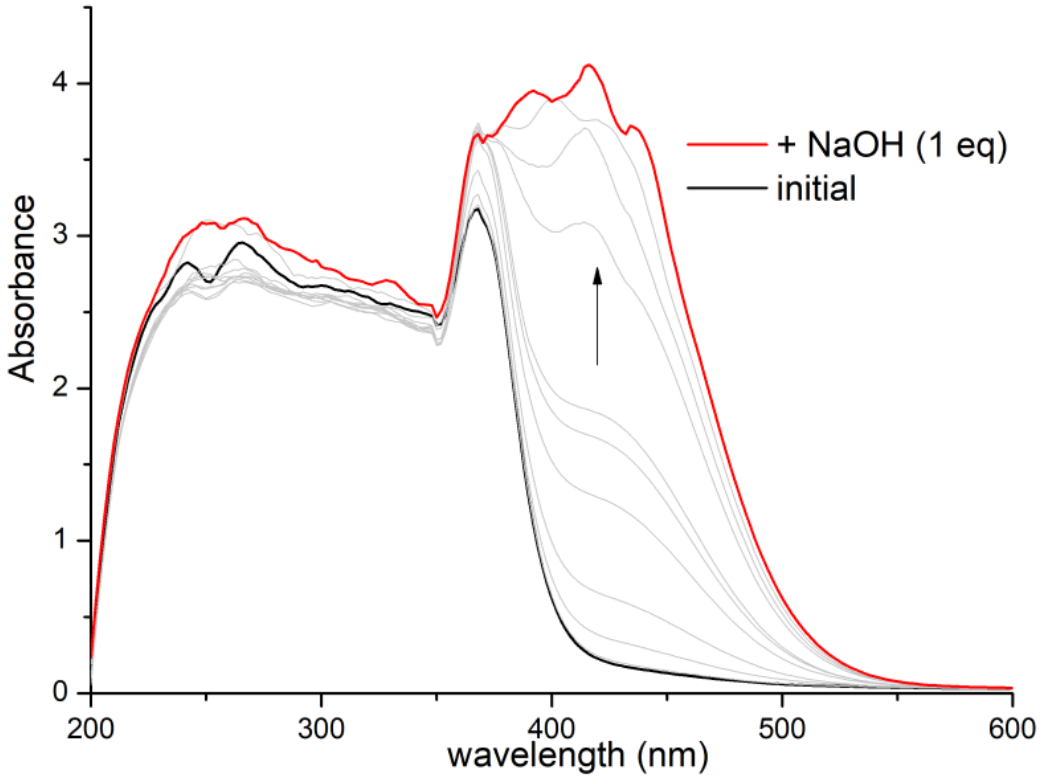


Figure S8. *UV−vis absorption spectroscopic titration of* ***13*** *in MeOH (10 μM, interval: 0.1 eq)*

pH response of 30:

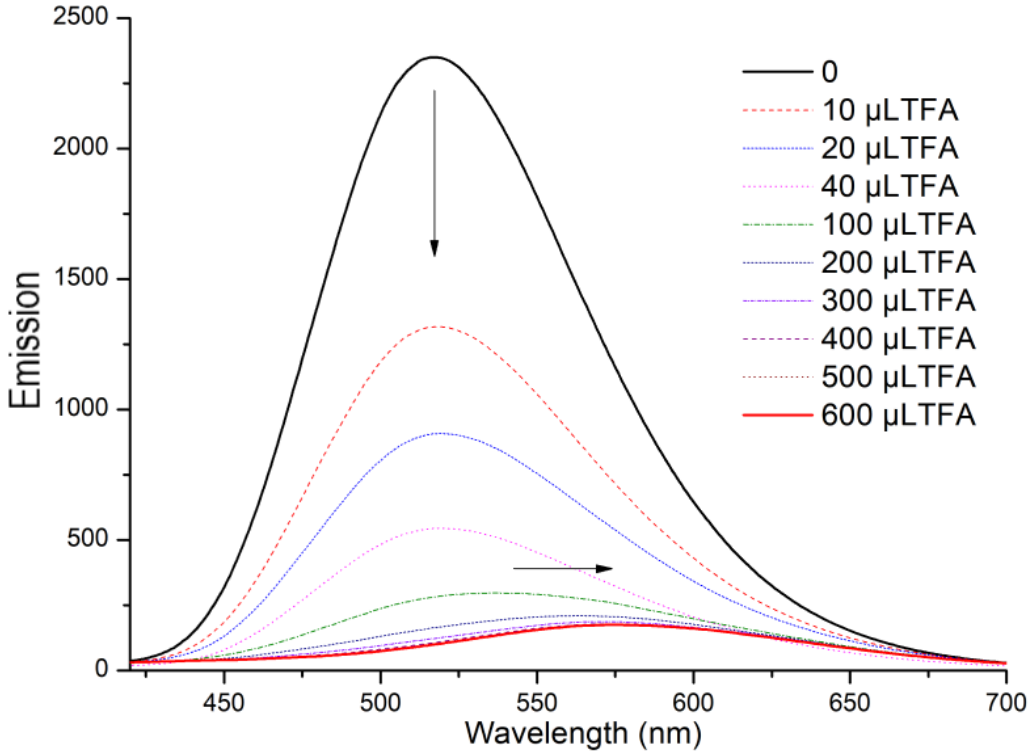


Figure S9. *Fluorescence spectroscopic titration of* ***30*** *(10 μM) in MeOH via adding TFA*

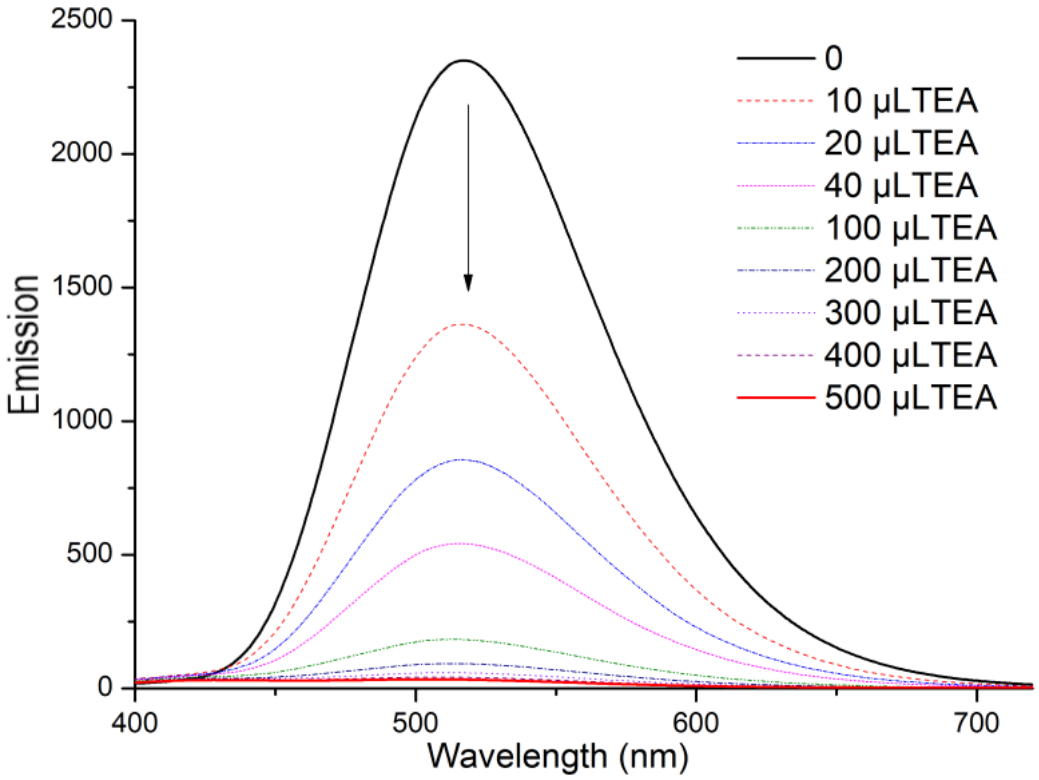
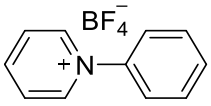


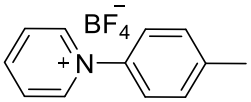
Figure S10. *Fluorescence spectroscopic titration of* ***30*** *(10 μM) in MeOH via adding TEA*

IX. Experimental data for the described substances



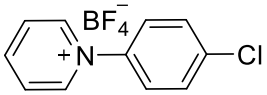
1-phenylpyridin-1-ium tetrafluoroborate (3)[5]

A white solid, (43 mg, 88% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 50/1→20/1, v/v). M.p.: 132–134 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.35 (d, *J* = 5.5 Hz, 2H), 8.79 (t, *J* = 7.8 Hz, 1H), 8.32 (t, *J* = 6.5 Hz, 2H), 7.89 (d, *J* = 3.0 Hz, 2H), 7.76 (br s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 146.63, 144.99, 142.85, 131.26, 130.23, 128.14, 124.78 ppm. **^{19}F NMR (471 MHz, DMSO-*d*$_6$):** δ = -148.23 (s), -148.28 (s) ppm. The data are consistent with the literature.[5]



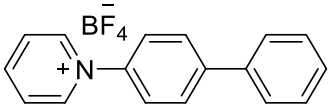
1-(p-tolyl)pyridin-1-ium tetrafluoroborate (4)[6]

A black solid (36 mg, 70% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→30/1, v/v). M.p.: 171–173 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.30 (d, *J* = 6.0 Hz, 2H), 8.76 (t, *J* = 7.8 Hz, 1H), 8.29 (t, *J* = 7.0 Hz, 2H), 7.77 (d, *J* =8.5 Hz, 2H), 7.55 (d, *J* =8.5 Hz, 2H), 2.45 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 146.35, 144.78, 141.36, 140.54, 130.52, 128.10, 124.40, 20.64 ppm. The data are consistent with the literature.[6]



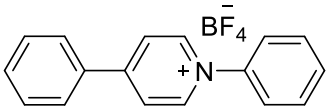
1-(4-chlorophenyl)pyridin-1-ium tetrafluoroborate (5)

A white solid (26 mg, 47% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→20/1, v/v). M.p.: 136–138 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$)**: δ = 9.33 (d, *J* = 6.5 Hz, 2H), 8.79 (t, *J* = 7.8 Hz, 1H), 8.31(t, *J* = 7.3 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.87–7.85 (m, 2H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$)**: δ = 146.83, 144.98, 141.56, 136.11, 130.11, 128.10, 126.86 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{11}H_9ClN^+$ ([M−BF_4^-]$^+$) 190.0418, found 190.0419.



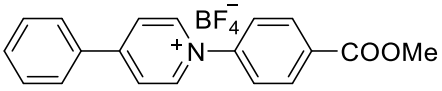
1-([1,1'-biphenyl]-4-yl)pyridin-1-ium tetrafluoroborate (6)

A white solid (40 mg, 62% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 50/1→30/1, v/v). M.p.: 234–236 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.39 (d, *J* = 5.5 Hz, 2H), 8.79 (t, *J* = 7.8 Hz, 1H), 8.33 (t, *J* = 7.3 Hz, 2H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* =8.5 Hz, 2H), 7.81 (d, *J* =7.5 Hz, 2H), 7.55 (t, *J* =7.5 Hz, 2H), 7.47 (t, *J* =7.3 Hz, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 146.61, 144.90, 142.89, 141.96, 138.19, 129.26, 128.60, 128.26, 128.15, 127.12, 125.35 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{17}H_{15}BF_4N$ (M+H) 320.1234, found 320.1235. **HRMS (ESI) *m/z*:** calcd for $C_{17}H_{14}N^+$ ([M−BF_4^-]$^+$) 232.1121, found 232.1124.



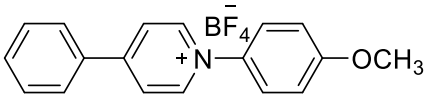
1,4-diphenylpyridin-1-ium tetrafluoroborate (7)

A light yellow solid (30 mg, 47% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→20/1, v/v). M.p.: 201–203 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.37 (d, *J* = 6.5 Hz, 2H), 8.67 (d, *J* = 7.0 Hz, 2H), 8.21 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.78–7.75 (m, 3H), 7.72–7.69 (m, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 155.61, 144.81, 142.30, 133.27, 132.59, 131.12, 130.19, 129.85, 128.45, 124.67, 124.35 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{17}H_{15}BF_4N$ (M+H) 320.1234, found 320.1235. **HRMS (ESI) *m/z*:** calcd for $C_{17}H_{14}N^+$ ([M−BF_4^-]$^+$) 232.1121, found 232.1123.



1-(4-(methoxycarbonyl)phenyl)-4-phenylpyridin-1-ium tetrafluoroborate (8)

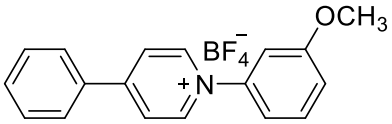
A yellow solid (33 mg, 44% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→30/1, v/v). M.p.: 188–190 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.41 (d, *J* = 7.0 Hz, 2H), 8.71 (d, *J* = 7.0 Hz, 2H), 8.29 (d, *J* = 9.0 Hz, 2H), 8.23–8.21 (m, 2H), 8.08 (d, *J* = 9.0 Hz, 2H), 7.73–8.68 (m, 3H), 3.95 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 165.16, 156.14, 145.33, 144.79, 133.18, 132.76, 131.85, 130.87, 129.87, 128.53, 125.43, 124.33, 52.77 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{16}NO_2^+$ ([M−BF_4^-]$^+$) 290.1176, found 290.1175.



1-(4-methoxyphenyl)-4-phenylpyridin-1-ium tetrafluoroborate (9)

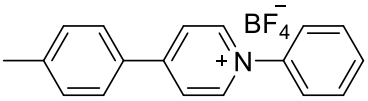
A yellow solid (43 mg, 61% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→20/1, v/v). M.p.: 141–143 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 9.31 (d, *J* =

6.5 Hz, 2H), 8.63 (d, *J* = 7.0 Hz, 2H), 8.19–8.18 (m, 2H), 7.86 (d, *J* = 9.0 Hz, 2H), 7.71–7.67 (m, 3H), 7.28 (d, *J* = 9.0 Hz, 2H), 3.89 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 161.05, 155.02, 144.64, 135.36, 133.32, 132.45, 129.81, 128.35, 125.96, 124.29, 115.17, 55.93 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{18}H_{16}NO^+$ ($[M-BF_4^-]^+$) 262.1226, found 262.1225.



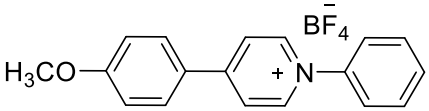
1-(3-methoxyphenyl)-4-phenylpyridin-1-ium tetrafluoroborate (10)

A white solid (41 mg, 58% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→20/1, v/v). M.p.: 177–179 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.92 (s, 2H), 8.36 (s, 2H), 7.85 (br s, 3H), 7.57–7.45 (m, 5H), 7.10 (d, *J* = 7.0 Hz, 1H), 3.87 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 161.41, 157.69, 143.85, 143.15, 133.40, 132.96, 131.65, 130.12, 128.43, 125.68, 118.39, 115.62, 109.19, 56.35 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{18}H_{16}NO^+$ ($[M-BF_4^-]^+$) 262.1226, found 262.1228.



1-phenyl-4-(*p*-tolyl)pyridin-1-ium tetrafluoroborate (11)

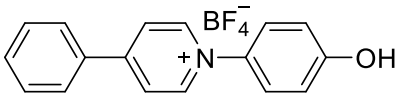
A yellow oil (36 mg, 53% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→20/1, v/v). M.p.: 138–140 ºC. **^{1}H NMR (500 MHz, DMSO-d_6):** δ = 9.32 (d, *J* = 6.8 Hz, 2H), 8.64 (d, *J* = 6.8 Hz, 2H), 8.14 (d, *J* = 8.0 Hz, 2H), 7.93–7.90 (m, 2H), 7.80–7.72 (m, 3H), 7.50 (d, *J* = 8.4 Hz, 2H), 2.45 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 155.39, 144.58, 143.28, 142.24, 131.01, 130.44, 130.27, 130.14, 128.34, 124.57, 123.73, 21.02 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{18}H_{16}N^+$ ($[M-BF_4^-]^+$) 246.1277, found 246.1279.



4-(4-methoxyphenyl)-1-phenylpyridin-1-ium tetrafluoroborate (12)

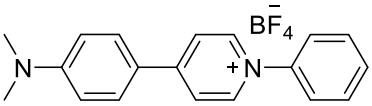
A yellow solid (41 mg, 59% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→20/1, v/v). M.p.: 188–190 ºC. **^{1}H NMR (500 MHz, DMSO-d_6):** δ = 9.26 (d, *J* = 6.5 Hz, 2H), 8.61 (d, *J* = 7.0 Hz, 2H), 8.26 (d, *J* = 9.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.77–7.73 (m, 3H), 7.23 (d, *J* =9.0 Hz, 2H), 3.91 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-d_6):** δ = 163.20, 154.87, 144.32, 142.23, 130.94, 130.50, 130.17, 125.03, 124.56, 122.93, 115.37, 55.78 ppm. **HRMS**

(ESI) *m/z*: calcd for $C_{18}H_{16}NO^+$ ([M−BF_4^-]$^+$) 262.1226, found 262.1225.



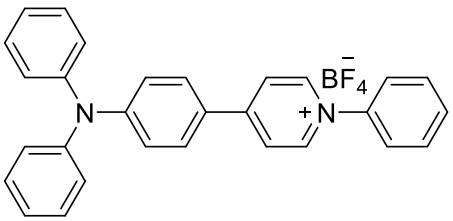
1-(4-hydroxyphenyl)-4-phenylpyridin-1-ium tetrafluoroborate (13)

A white solid (52 mg, 78% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→20/1, v/v). M.p.: 226–228 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 10.41 (s, 1H), 9.27 (d, *J* = 6.5 Hz, 2H), 8.61 (d, *J* = 7.0 Hz, 2H), 8.18–8.17 (m, 2H), 7.73–7.67 (m, 5H), 7.06 (d, *J* = 9.0 Hz, 2H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 159.74, 154.78, 144.48, 134.06, 133.35, 132.41, 129.81, 128.33, 125.91, 124.31, 116.35 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{17}H_{14}NO^+$ ([M−BF_4^-]$^+$) 248.1070, found 248.1073.



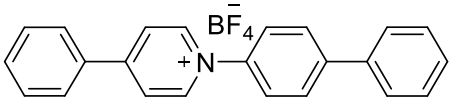
4-(4-(dimethylamino)phenyl)-1-phenylpyridin-1-ium tetrafluoroborate (14)

An orange solid (48 mg, 66% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→20/1, v/v). M.p.: 164–166 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.01 (d, *J* = 7.0 Hz, 2H), 8.43 (d, *J* = 7.0 Hz, 2H), 8.15 (d, *J* = 9.5 Hz, 2H), 7.86 (d, *J* = 7.0 Hz, 2H), 7.75–7.69 (m, 3H), 6.90 (d, *J* = 9.5 Hz, 2H), 3.11 (s, 6H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 154.51, 153.44, 143.15, 142.17, 130.54, 130.14, 130.12, 124.25, 120.53, 118.25, 112.35, 39.78 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{19}N_2^+$ ([M−BF_4^-]$^+$) 275.1543, found 275.1545.



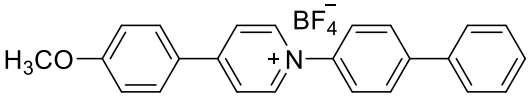
4-(4-(diphenylamino)phenyl)-1-phenylpyridin-1-ium tetrafluoroborate (15)

A black solid (57 mg, 59% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 100/1→80/1, v/v). M.p.: 156–158 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.77 (d, *J* = 4.5 Hz, 2H), 8.28 (d, *J* = 4.5 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 6.0 Hz, 2H), 7.61 (d, *J* = 3.5 Hz, 3H), 7.37 (t, *J* = 7.8 Hz, 4H), 7.23–7.17 (m, 6H), 7.05 (d, *J* = 8.0 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 156.14, 152.93, 145.71, 143.45, 131.52, 131.17, 130.21, 130.05, 129.98, 126.61, 125.81, 124.31, 123.66, 123.53, 120.19 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{29}H_{23}N_2^+$ ([M−BF_4^-]$^+$) 399.1856, found 399.1858.



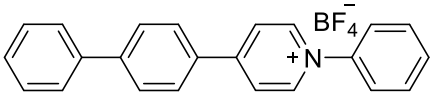
1-([1,1'-biphenyl]-4-yl)-4-phenylpyridin-1-ium tetrafluoroborate (16)

A white solid (38 mg, 48% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→30/1, v/v). M.p.: > 240 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.42 (d, *J* = 6.5 Hz, 2H), 8.70 (d, *J* = 7.0 Hz, 2H), 8.22 (d, *J* = 6.5 Hz, 2H), 8.07 (d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* =8.5 Hz, 2H), 7.82 (d, *J* =7.0 Hz, 2H), 7.73–7.70 (m, 3H), 7.56 (t, *J* =7.5 Hz, 2H), 7.48 (t, *J* =7.3 Hz, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 155.58, 144.72, 142.75, 141.42, 138.25, 133.30, 132.62, 129.87, 129.25, 128.57, 128.47, 128.23, 127.10, 125.24, 124.36 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{23}H_{18}N^+$ ([M−BF_4^-]$^+$) 308.1434, found 308.1438.



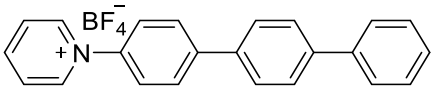
1-([1,1'-biphenyl]-4-yl)-4-(4-methoxyphenyl)pyridin-1-ium tetrafluoroborate (17)

A white solid (56 mg, 66% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→20/1, v/v). M.p.: 164–166 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.30 (d, *J* = 6.5 Hz, 2H), 8.62 (d, *J* = 6.5 Hz, 2H), 8.27 (d, *J* = 9.0 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 7.0 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 2H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 163.24, 154.87, 144.19, 142.60, 141.35, 138.27, 130.50, 129.24, 128.52, 128.21, 127.07, 125.10, 122.94, 115.40, 55.79 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{23}H_{18}N^+$ ([M−BF_4^-]$^+$) 308.1434, found 308.1438.



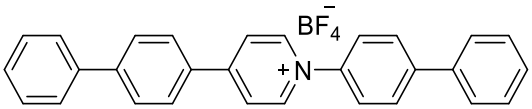
4-([1,1'-biphenyl]-4-yl)-1-phenylpyridin-1-ium tetrafluoroborate (18)

A white solid (38 mg, 48% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→20/1, v/v). M.p.: 223–225 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.36 (d, *J* = 7.0 Hz, 2H), 8.73 (d, *J* = 6.5 Hz, 2H), 8.33 (d, *J* = 8.5 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.94–7.92 (m, 2H), 7.84 (d, *J* = 7.5 Hz, 2H), 7.79–7.76 (d, *J* = 7.0 Hz, 3H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 154.97, 144.71, 144.05, 142.30, 138.51, 132.03, 131.11, 130.21, 129.21, 129.14, 128.64, 127.91, 127.01, 124.64, 124.06 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{23}H_{18}N^+$ ([M−BF_4^-]$^+$) 308.1434, found 308.1436.



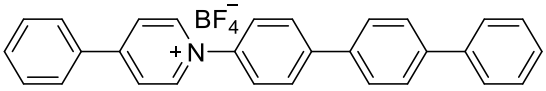
1-([1,1':4',1''-terphenyl]-4-yl)pyridin-1-ium tetrafluoroborate (19)

A white solid (35 mg, 44% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→20/1, v/v). M.p.: 161–163 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.39 (d, *J* = 6.0 Hz, 2H), 8.80 (t, *J* = 8.0 Hz, 1H), 8.33 (t, *J* = 7.0 Hz, 2H), 8.12 (d, *J* = 9.0 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 146.62, 144.86, 142.31, 141.99, 140.30, 139.37, 137.10, 129.11, 128.18, 128.13, 127.85, 127.67, 127.48, 126.73, 125.39 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{23}H_{18}N^+$ ([M−BF_4^-]$^+$) 308.1434, found 308.1435.



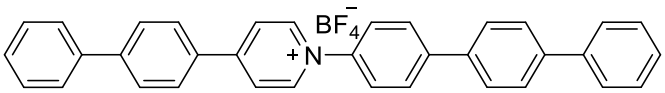
1,4-di([1,1'-biphenyl]-4-yl)pyridin-1-ium tetrafluoroborate (20)

A white solid (36 mg, 38% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→20/1, v/v). M.p.: > 240 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ =9.41 (d, *J* = 7.0 Hz, 2H), 8.76 (d, *J* = 7.0 Hz, 2H), 8.35 (d, *J* = 8.5 Hz, 2H), 8.07 (d, *J* = 8.5 Hz, 2H), 8.04–8.01 (m, 4H), 7.86–7.82 (m, 4H), 7.58–7.54 (m, 4H), 7.50–7.46 (m, 2H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 154.92, 144.62, 144.08, 142.73, 141.41, 138.51, 138.24, 132.04, 129.25, 129.22, 129.15, 128.66, 128.56, 128.22, 127.92, 127.09, 127.02, 125.21, 124.05 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{29}H_{22}N^+$ ([M−BF_4^-]$^+$) 384.1747, found 384.1749.



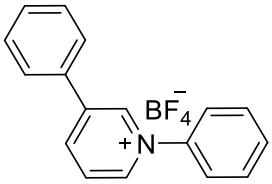
1-([1,1':4',1''-terphenyl]-4-yl)-4-phenylpyridin-1-ium tetrafluoroborate (21)

A yellow solid (34 mg, 36% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→30/1, v/v). M.p.: > 240 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ =9.43 (d, *J* = 7.0 Hz, 2H), 8.70 (d, *J* = 7.0 Hz, 2H), 8.23 (d, *J* = 6.5 Hz, 2H), 8.14 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.73–7.69 (m, 3H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 155.56, 144.69, 142.14, 141.42, 140.25, 139.34, 137.11, 133.29, 132.60, 129.85, 129.07, 128.45, 128.06, 127.82, 127.61, 127.45, 126.69, 125.27, 124.34 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{29}H_{22}N^+$ ([M−BF_4^-]$^+$) 384.1747, found 384.1749.



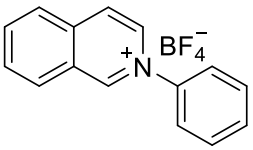
4-([1,1'-biphenyl]-4-yl)-1-([1,1':4',1''-terphenyl]-4-yl)pyridin-1-ium tetrafluoroborate (22)

A yellow solid (52 mg, 48% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→20/1, v/v). M.p.: > 240 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.42 (d, *J* = 6.5 Hz, 2H), 8.76 (d, *J* = 6.5 Hz, 2H), 8.35 (d, *J* = 8.5 Hz, 2H), 8.14 (d, *J* = 8.5 Hz, 2H), 8.05–8.01 (m, 4H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.87–7.84 (m, 4H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.57–7.48 (m, 5H), 7.42 (t, *J* = 7.3 Hz, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 154.94, 144.60, 144.09, 142.15, 141.44, 140.27, 139.36, 138.52, 137.14, 132.06, 129.23, 129.16, 129.10, 128.67, 128.09, 127.93, 127.63, 127.48, 127.02, 126.71, 125.26, 124.07 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{35}H_{26}N^+$ ([M−BF_4^-]$^+$) 460.2060, found 460.2062.



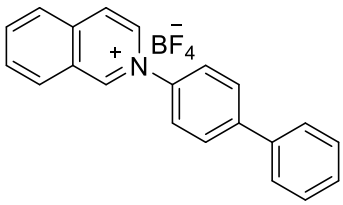
1,3-diphenylpyridin-1-ium tetrafluoroborate (23)

A white solid (44 mg, 69% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→20/1, v/v). M.p.: 153–155 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.61 (s, 1H), 9.30 (d, *J* = 6.0 Hz, 1H), 9.09 (d, *J* = 8.0 Hz, 1H), 8.39–8.36 (m, 1H), 8.03–8.00 (m, 4H), 7.77–7.76 (m, 3H), 7.65–7.58 (m, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 143.74, 143.26, 142.97, 142.85, 139.88, 133.12, 131.25, 130.25, 130.09, 129.44, 128.05, 127.92, 125.05 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{17}H_{14}N^+$ ([M−BF_4^-]$^+$) 232.1121, found 232.1123.



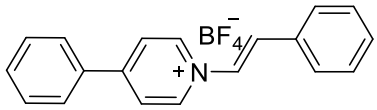
2-phenylisoquinolin-2-ium tetrafluoroborate (24)[7]

A white solid (25 mg, 43% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→30/1, v/v). M.p.: 130–132 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 10.40 (s, 1H), 9.07 (d, *J* = 7.0 Hz, 1H), 8.74 (d, *J* = 7.0 Hz, 1H), 8.62(d, *J* = 8.5 Hz, 1H), 8.46 (d, *J* = 8.5 Hz, 1H), 8.36 (t, *J* =7.8 Hz, 1H), 8.16 (t, *J* =7.5 Hz, 1H) , 8.00 (d, *J* =7.5 Hz, 2H), 7.82–7.76 (m, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ =150.56, 143.03, 137.71, 137.28, 135.00, 131.50, 131.26, 131.12, 130.27, 127.38, 127.31, 125.74, 124.99 ppm. The data are consistent with the literature.[7]



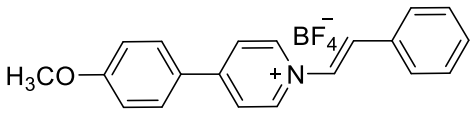
2-([1,1'-biphenyl]-4-yl)isoquinolin-2-ium tetrafluoroborate (25)

A yellow solid (41 mg, 56% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→20/1, v/v). M.p.: 187–189 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 10.43 (s, 1H), 9.12–9.10 (m, 1H), 8.75 (d, *J* = 7.0 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.36 (t, *J* = 7.5 Hz, 1H), 8.16 (t, *J* = 8.0 Hz, 1H), 8.12–8.08 (m, 4H), 7.84 (d, *J* = 7.0 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 150.38, 142.74, 142.09, 138.23, 137.70, 137.26, 134.87, 131.50, 131.26, 129.24, 128.57, 128.29, 127.39, 127.31, 127.13, 125.74, 125.49 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{16}N^+$ ($[M-BF_4^-]^+$) 282.1277, found 282.1277.



(*E*)-4-phenyl-1-styrylpyridin-1-ium tetrafluoroborate (27)

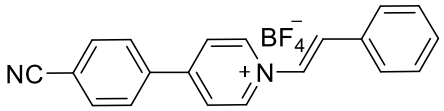
A yellow solid (33 mg, 48% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→20/1, v/v). M.p.: > 240 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.34 (d, *J* = 7.0 Hz, 2H), 8.65 (d, *J* = 7.0 Hz, 2H), 8.29 (d, *J* = 14.5 Hz, 1H), 8.19–8.17 (m, 2H), 7.84 (d, *J* = 14.5 Hz, 1H), 7.70–7.67 (m, 5H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 155.12, 141.57, 133.30, 132.75, 132.58, 130.05, 129.80, 129.78, 129.25, 128.68, 128.33, 127.65, 124.28 ppm. **^{19}F NMR (471 MHz, DMSO-*d*$_6$):** δ = -148.22 (s), -148.27 (s) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{16}N^+$ ($[M-BF_4^-]^+$) 258.1277, found 258.1279.



(*E*)-4-(4-methoxyphenyl)-1-styrylpyridin-1-ium tetrafluoroborate (28)

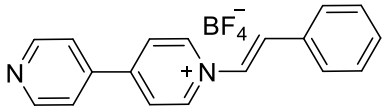
A yellow solid (32 mg, 42% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→20/1, v/v). M.p.: > 240 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.28 (d, *J* = 7.0 Hz, 2H), 8.59 (d, *J* = 7.0 Hz, 2H), 8.31 (d, *J* = 14.5 Hz, 1H), 8.22 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 14.0 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 163.23, 154.45, 141.14, 132.92, 130.42, 129.90, 129.75, 129.23, 127.84, 127.59, 125.18, 122.86, 115.34, 55.80 ppm. **HRMS (ESI) *m/z*:**

calcd for $C_{20}H_{18}NO^+$ ([M−BF_4^-]$^+$) 288.1383, found 288.1386.



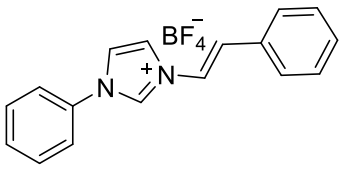
(*E*)-4-(4-cyanophenyl)-1-styrylpyridin-1-ium tetrafluoroborate (29)

A yellow solid (24 mg, 32% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→20/1, v/v). M.p.: 139–141 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.42 (d, *J* = 7.5 Hz, 2H), 8.72 (d, *J* = 7.0 Hz, 2H), 8.35–8.31 (m, 3H), 8.17 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 14.5 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ =153.22, 141.89, 137.65, 133.45, 132.67, 130.23, 129.85, 129.33, 129.30, 129.17, 127.76, 125.19, 118.17, 114.42 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{15}N_2^+$ ([M−BF_4^-]$^+$) 283.1230, found 283.1233.



(*E*)-1-styryl-[4,4'-bipyridin]-1-ium tetrafluoroborate (30)

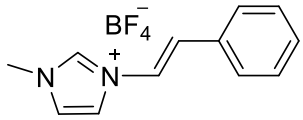
A yellow solid (37 mg, 54% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→20/1, v/v). M.p.: 183–185 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.58 (d, *J* = 6.5 Hz, 2H), 8.89 (d, *J* = 6.0 Hz, 2H), 8.78 (d, *J* = 6.5 Hz, 2H), 8.51 (d, *J* = 14.5 Hz, 1H), 8.14–8.13 (m, 2H), 7.97 (d, *J* = 14.0 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 152.53, 151.08, 142.11, 140.55, 132.72, 130.19, 129.94, 129.39, 129.26, 127.83, 125.21, 121.91 ppm. **HRMS (ESI) *m/z*: HRMS (ESI) *m/z*:** calcd for $C_{18}H_{15}N_2^+$ ([M−BF_4^-]$^+$) 259.1230, found 259.1231.



(*E*)-1-phenyl-3-styryl-1H-imidazol-3-ium tetrafluoroborate (31)

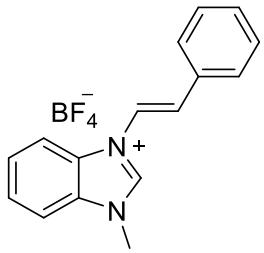
A white solid (60 mg, 90% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→30/1, v/v). M.p.: 171–173 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 10.10 (s, 1H), 8.48 (s, 1H), 8.41 (s, 1H), 7.92 (d, *J* = 14.5 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 2H), 7.71 (t, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 15.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 134.53, 134.02, 132.84, 130.17, 129.99, 129.24, 129.15, 126.87, 124.99, 121.90, 121.86, 121.83, 120.72 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{17}H_{15}N_2^+$

([M−BF_4^-]$^+$) 247.1230, found 247.1231.



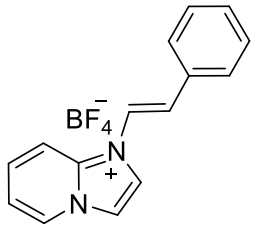
(*E*)-1-methyl-3-styryl-1H-imidazol-3-ium tetrafluoroborate (32)

A yellow solid (25 mg, 46% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→30/1, v/v). M.p.: 161–163 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.39 (s, 1H), 8.20 (s, 1H), 7.93 (d, *J* = 14.5 Hz, 1H), 7.86 (s, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.41–7.38 (m, 2H), 3.92 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 135.75, 133.11, 129.11, 129.07, 126.87, 124.53, 123.85, 122.13, 119.32, 36.13 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{12}H_{13}N_2^+$ ([M−BF_4^-]$^+$) 185.1073, found 185.1075.



(*E*)-1-methyl-3-styryl-1H-benzo[d]imidazol-3-ium tetrafluoroborate (33)

A white solid (31 mg, 47% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→20/1, v/v). M.p.: 198–200 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 10.22 (s, 1H), 8.37–8.35 (m, 1H), 8.22 (d, *J* = 14.5 Hz, 1H), 8.10–8.08 (m, 1H), 7.80–7.77 (m, 2H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.51–7.41 (m, 4H), 4.15 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 140.82, 133.24, 131.72, 130.12, 129.20, 129.05, 127.22, 127.13, 126.97, 126.43, 126.00, 120.04, 113.80, 33.58 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{16}H_{15}N_2^+$ ([M−BF_4^-]$^+$) 235.1230, found 235.1232.



(*E*)-1-styrylimidazo[1,2-*a*]pyridin-1-ium tetrafluoroborate (34)

A white solid (30 mg, 48% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→20/1, v/v). M.p.: 231–233 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.03 (d, *J* = 7.0 Hz, 1H), 8.91 (d, *J* = 2.5 Hz, 1H), 8.71 (d, *J* = 9.5 Hz, 1H), 8.65 (d, *J* = 2.0 Hz, 1H), 8.35 (d, *J* = 14.5 Hz, 1H), 8.19–8.15 (m, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 6.8 Hz, 1H), 7.52 (d, *J* = 14.5 Hz, 1H), 7.46 (t,

J = 7.8 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 138.24, 134.91, 133.82, 130.24, 128.90, 128.65, 127.03, 122.64, 121.23, 120.34, 118.16, 116.95, 111.85 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{15}H_{13}N_2^+$ ([M−BF_4^-]$^+$) 221.1073, found 221.1075.

X. References

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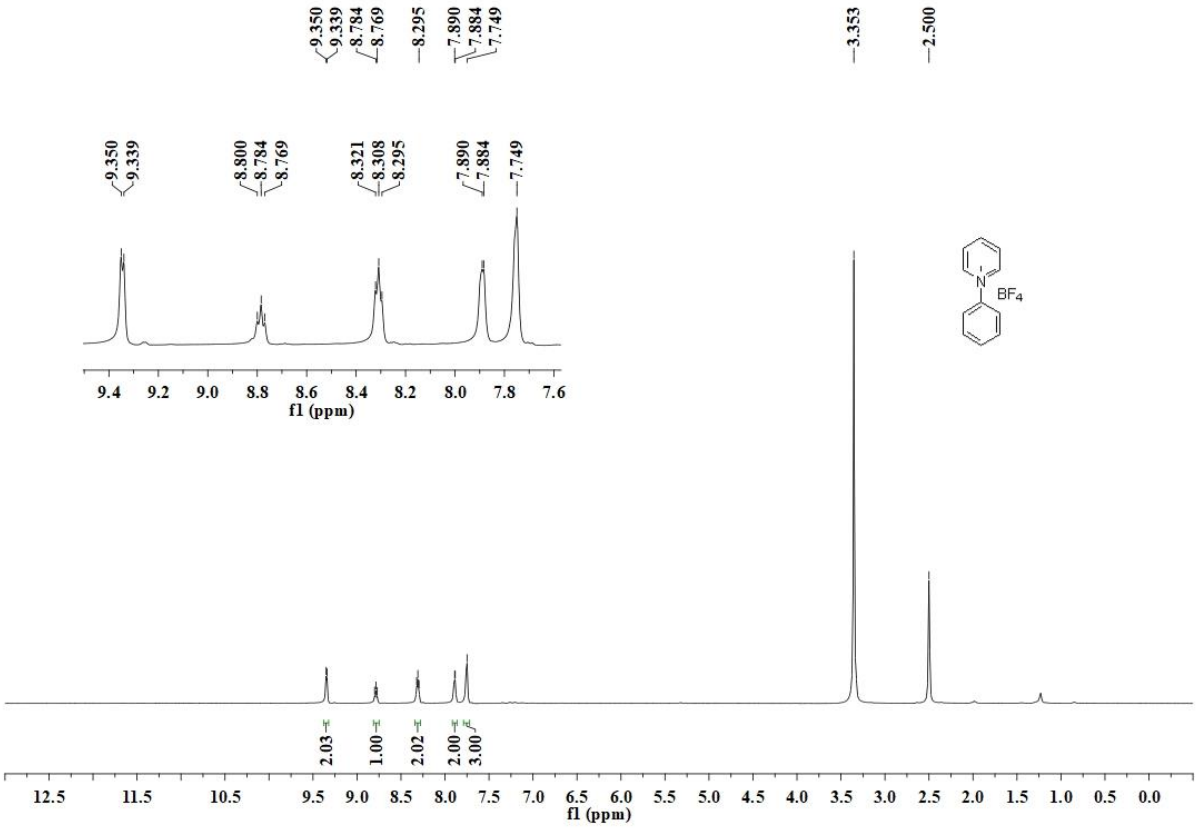
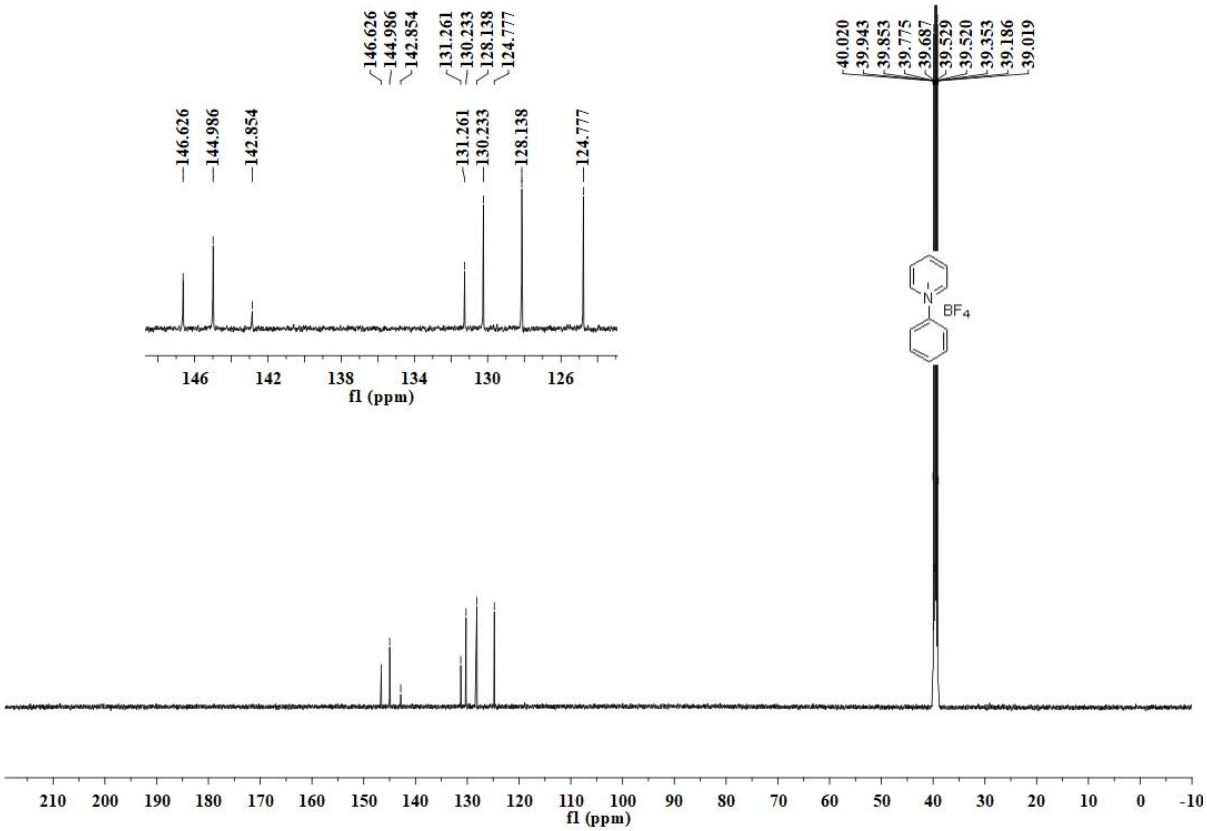
XI. Copies of ^{1}H, ^{13}C and ^{19}FNMR spectra

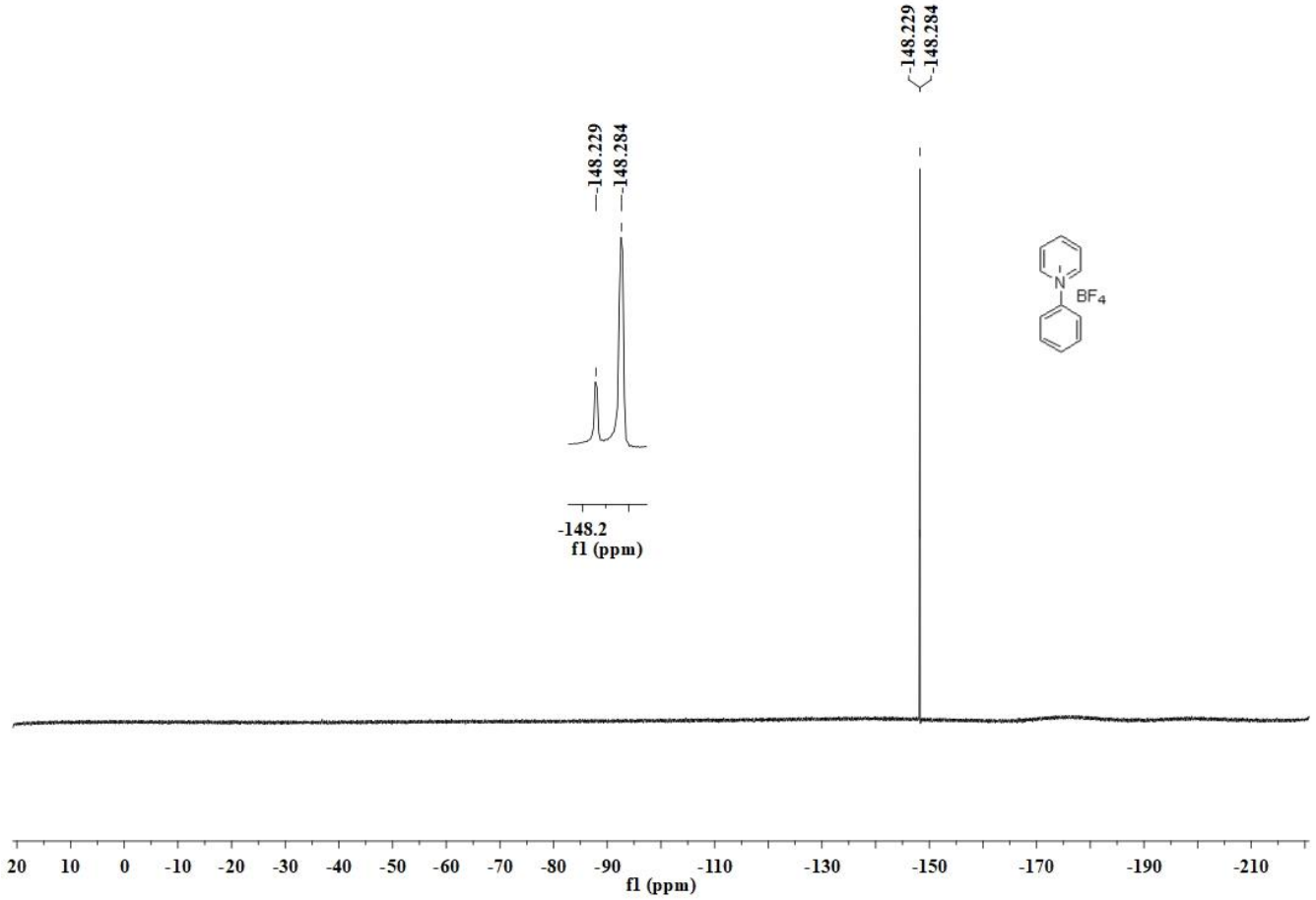
^{1}H NMR (500 MHz, DMSO-d_6) of **3**



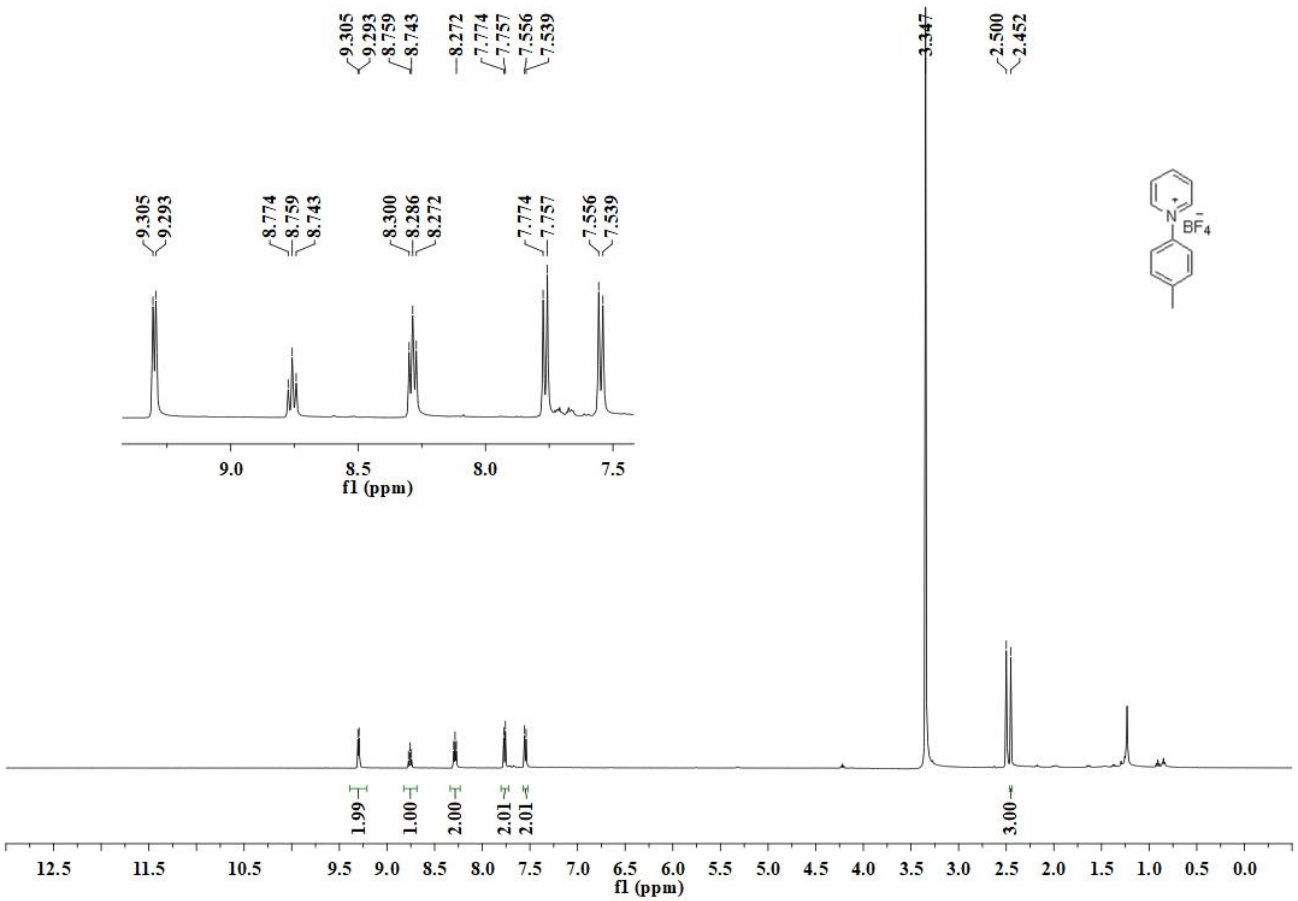
^{13}C NMR (125 MHz, DMSO-d_6) of **3**



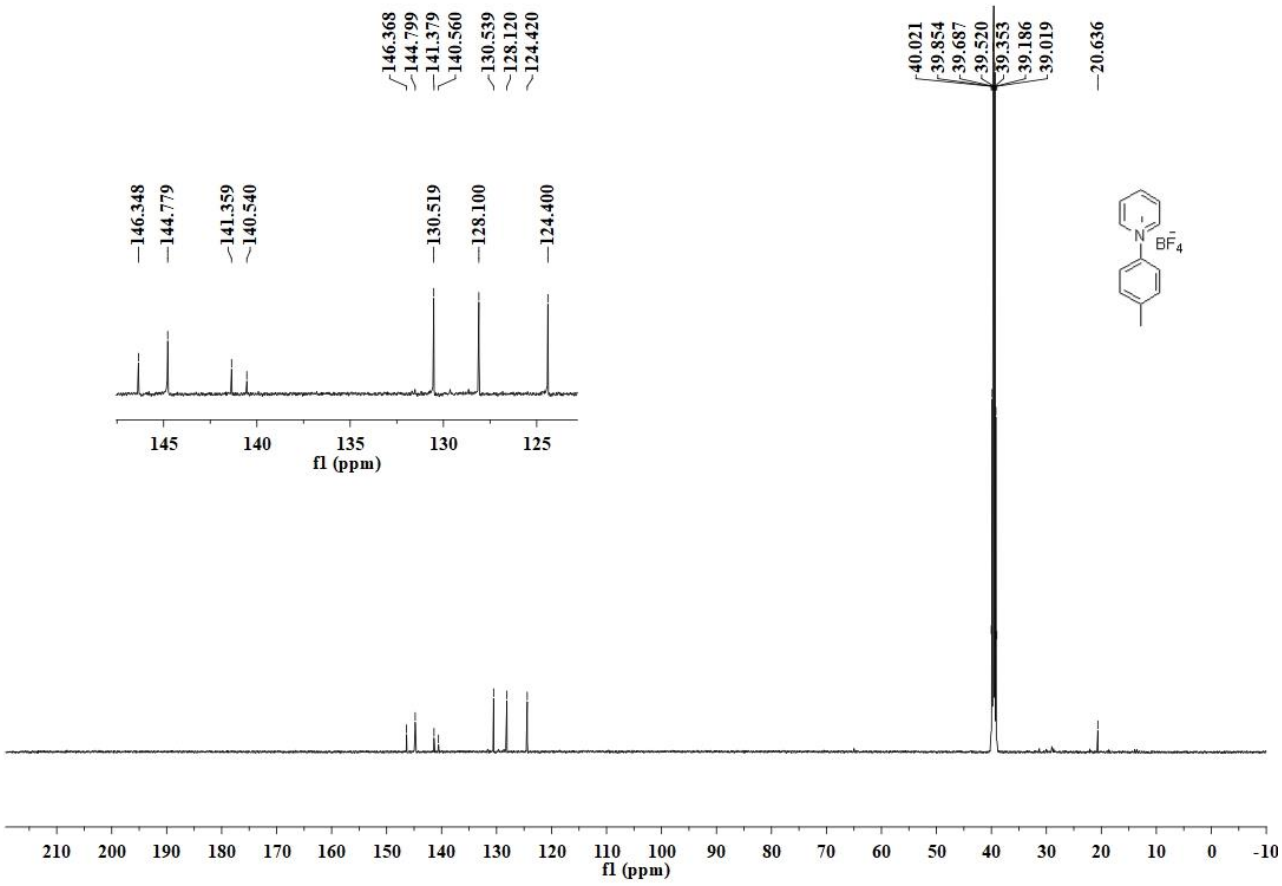
^{19}F NMR (471 MHz, DMSO-d_6) of **3**



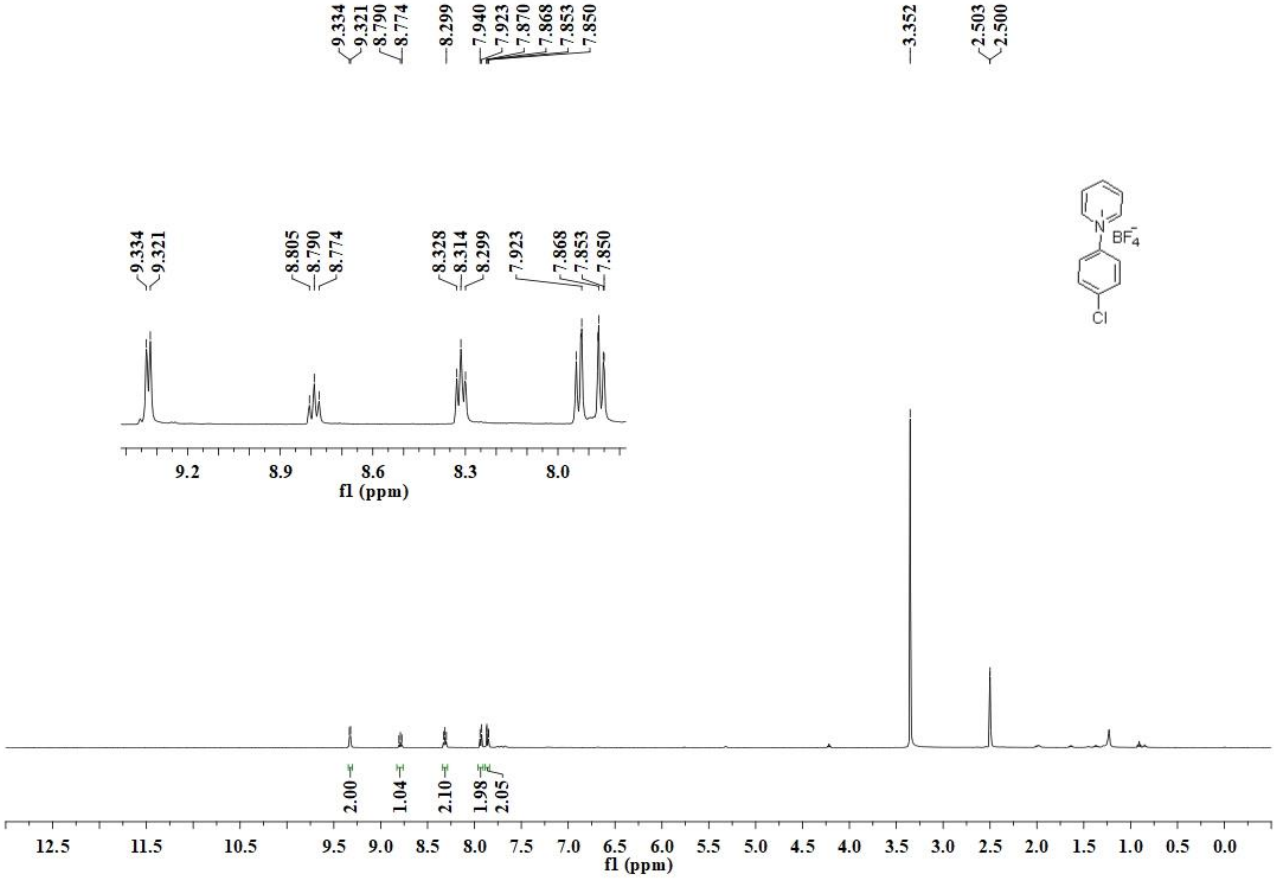
^{1}H NMR (500 MHz, DMSO-d_6) of **4**



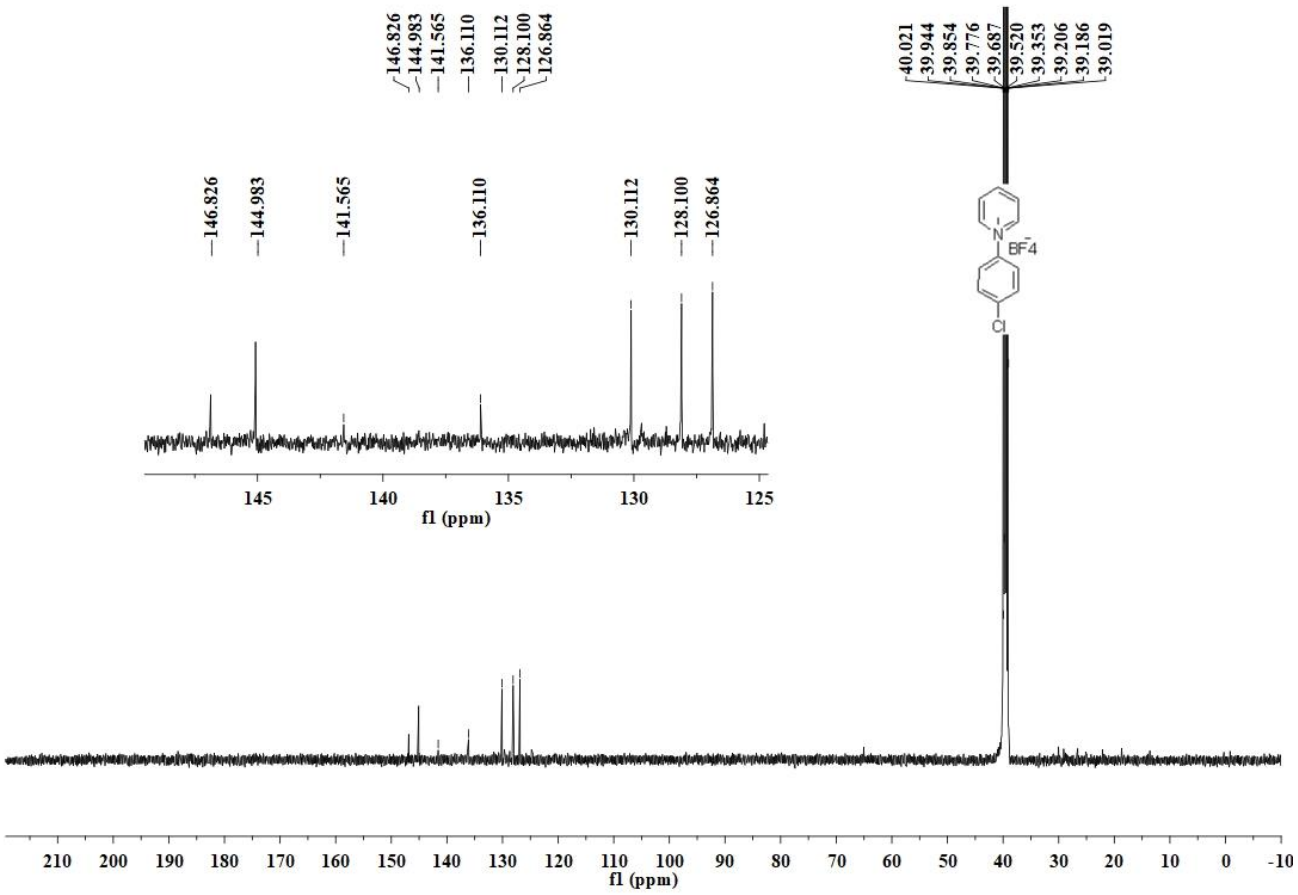
^{13}C NMR (125 MHz, DMSO-d_6) of **4**



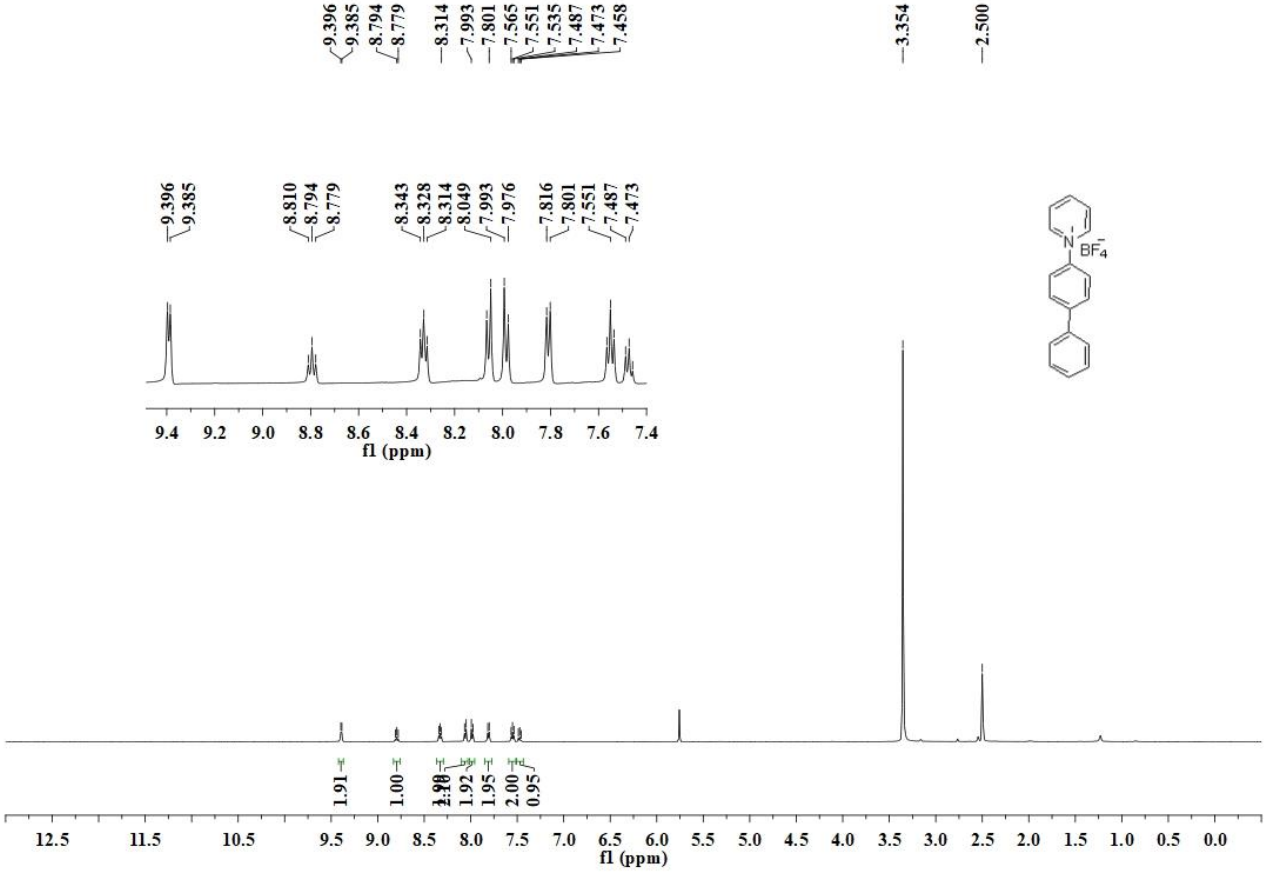
^{1}H NMR (500 MHz, DMSO-d_6) of **5**



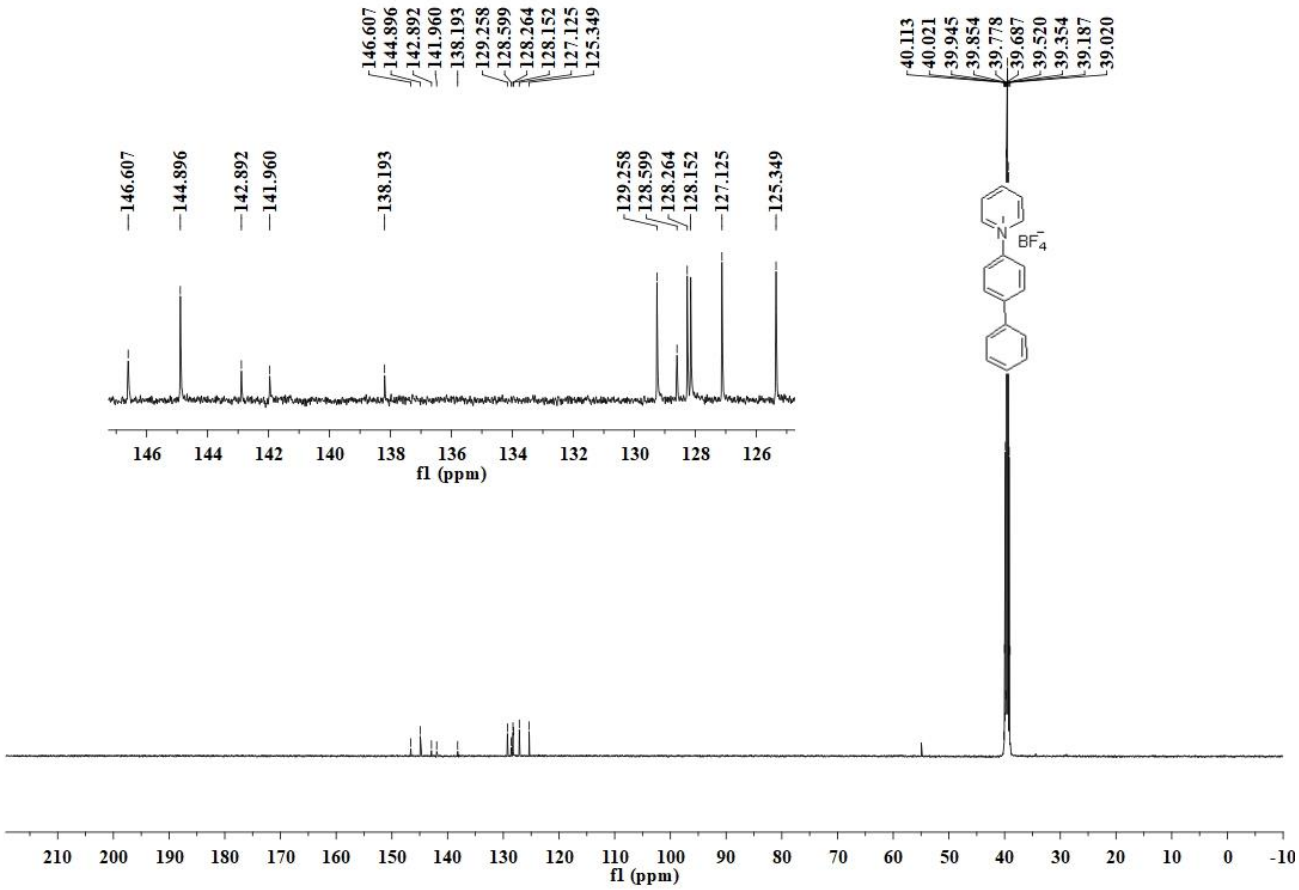
^{13}C NMR (125 MHz, DMSO-d_6) of **5**



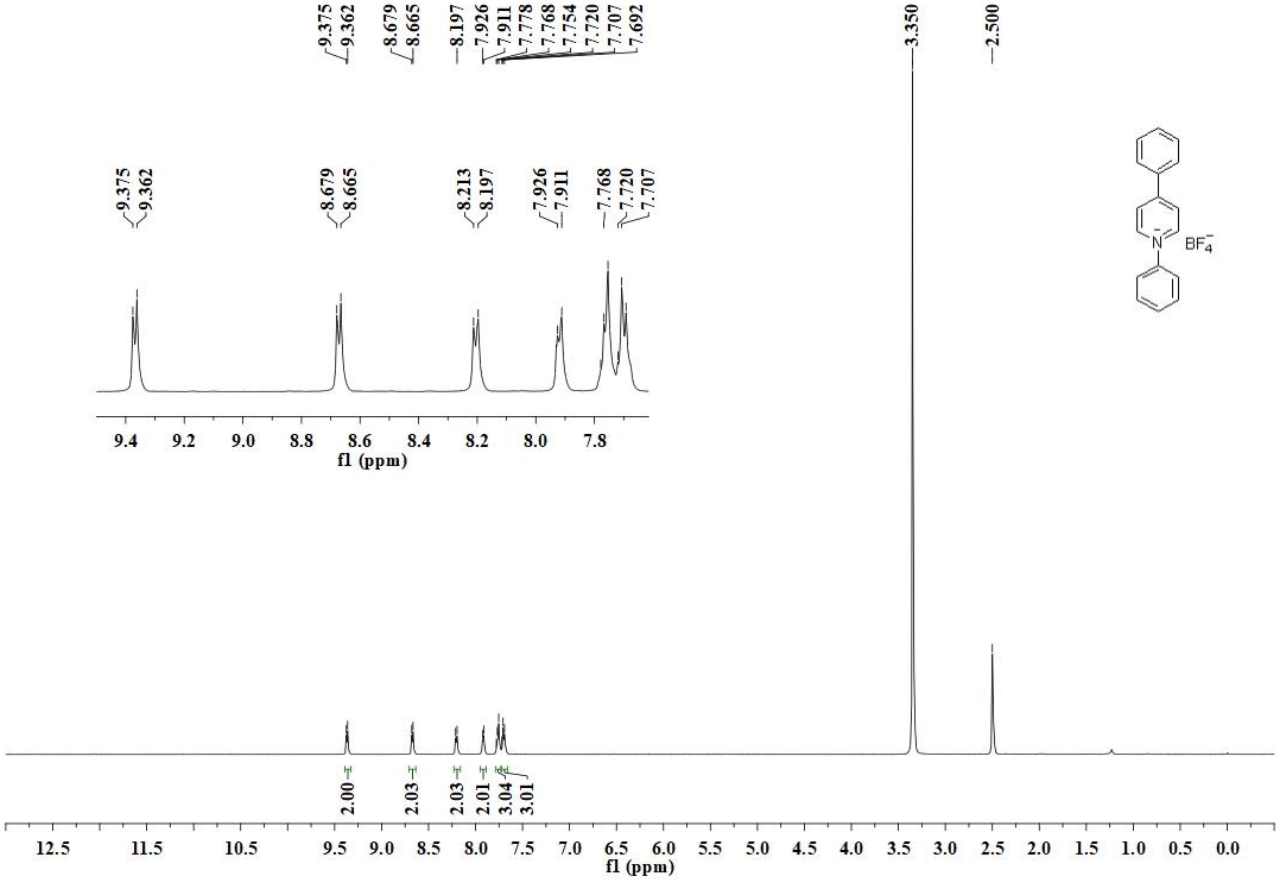
^{1}H NMR (500 MHz, DMSO-d_6) of **6**



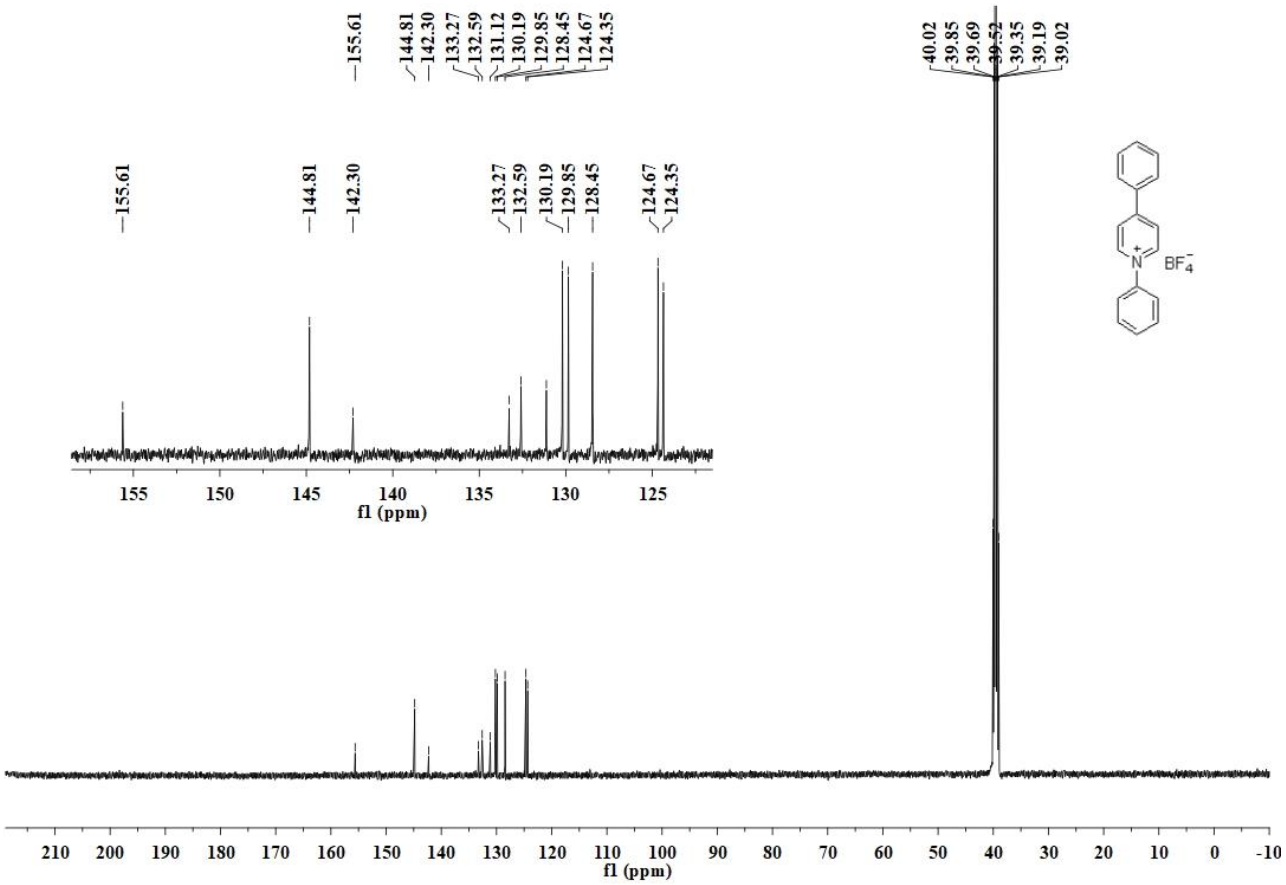
^{13}C NMR (125 MHz, DMSO-d_6) of **6**



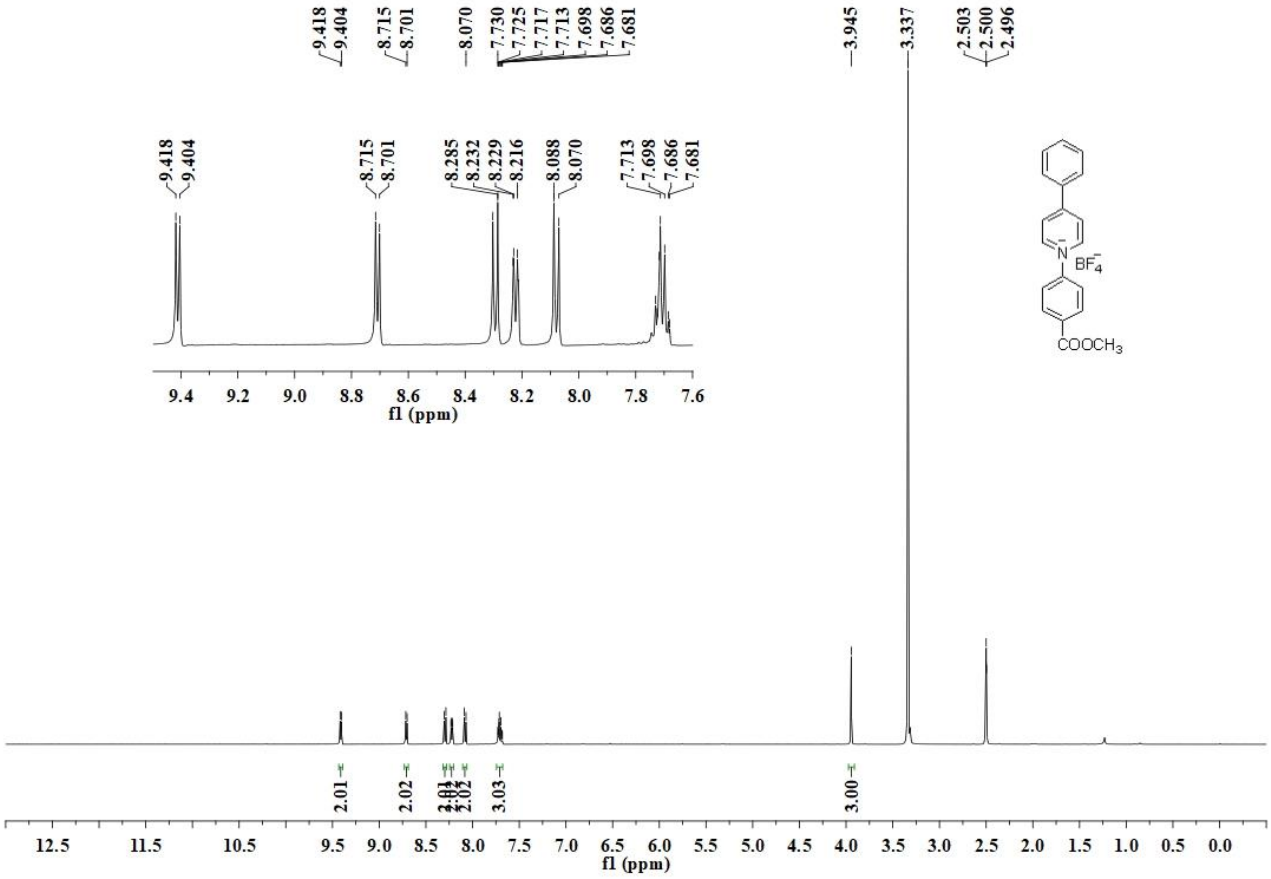
^{1}H NMR (500 MHz, DMSO-d_6) of **7**



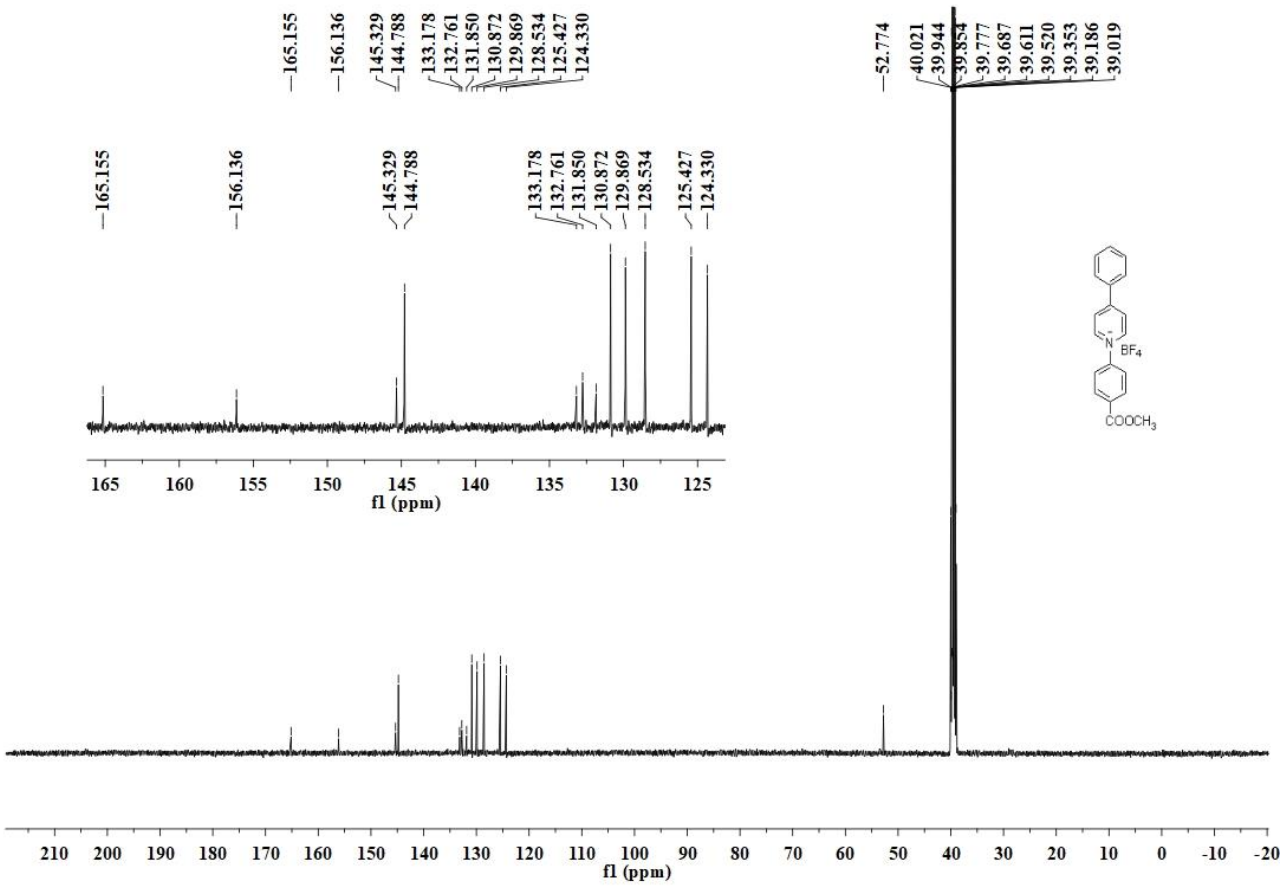
^{13}C NMR (125 MHz, DMSO-d_6) of **7**



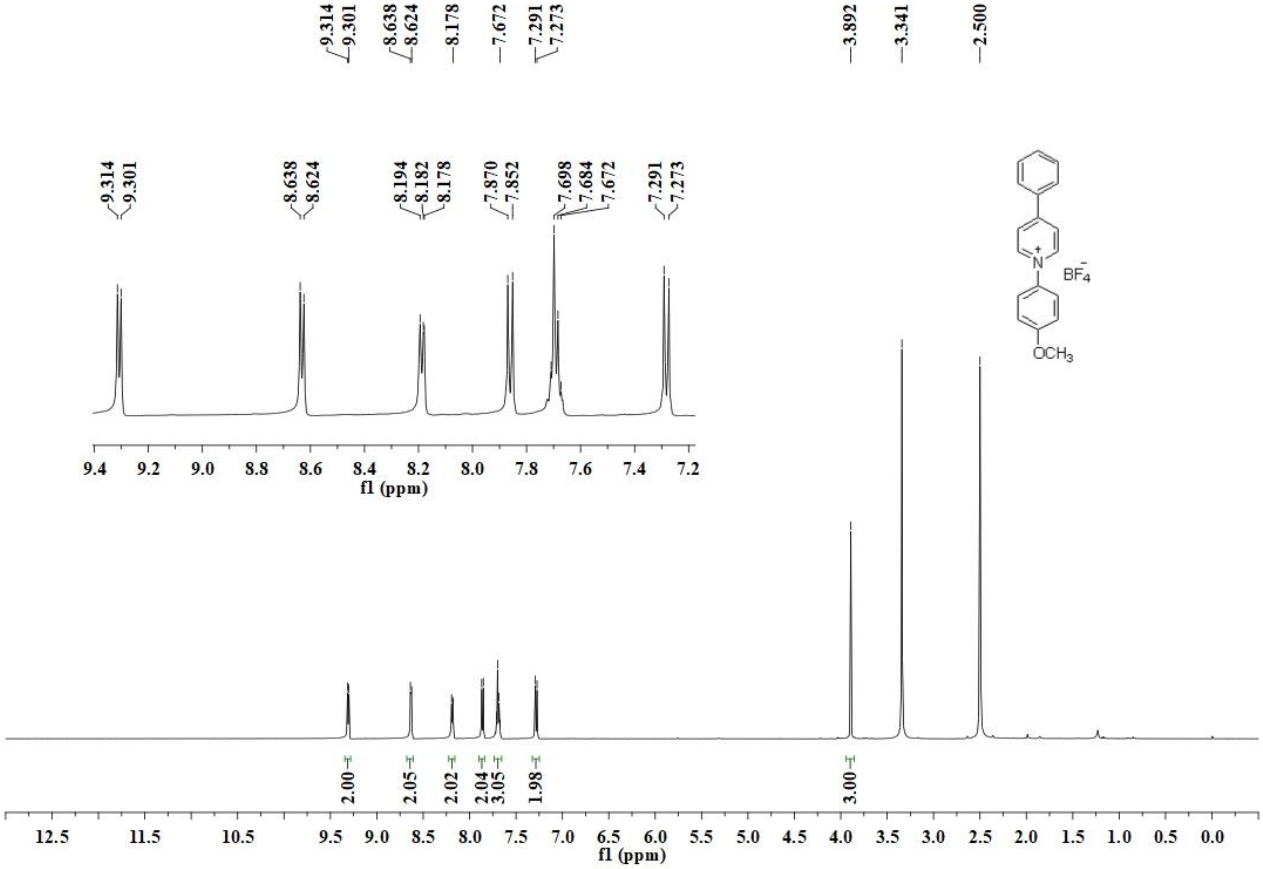
^{1}H NMR (500 MHz, DMSO-d_6) of **8**



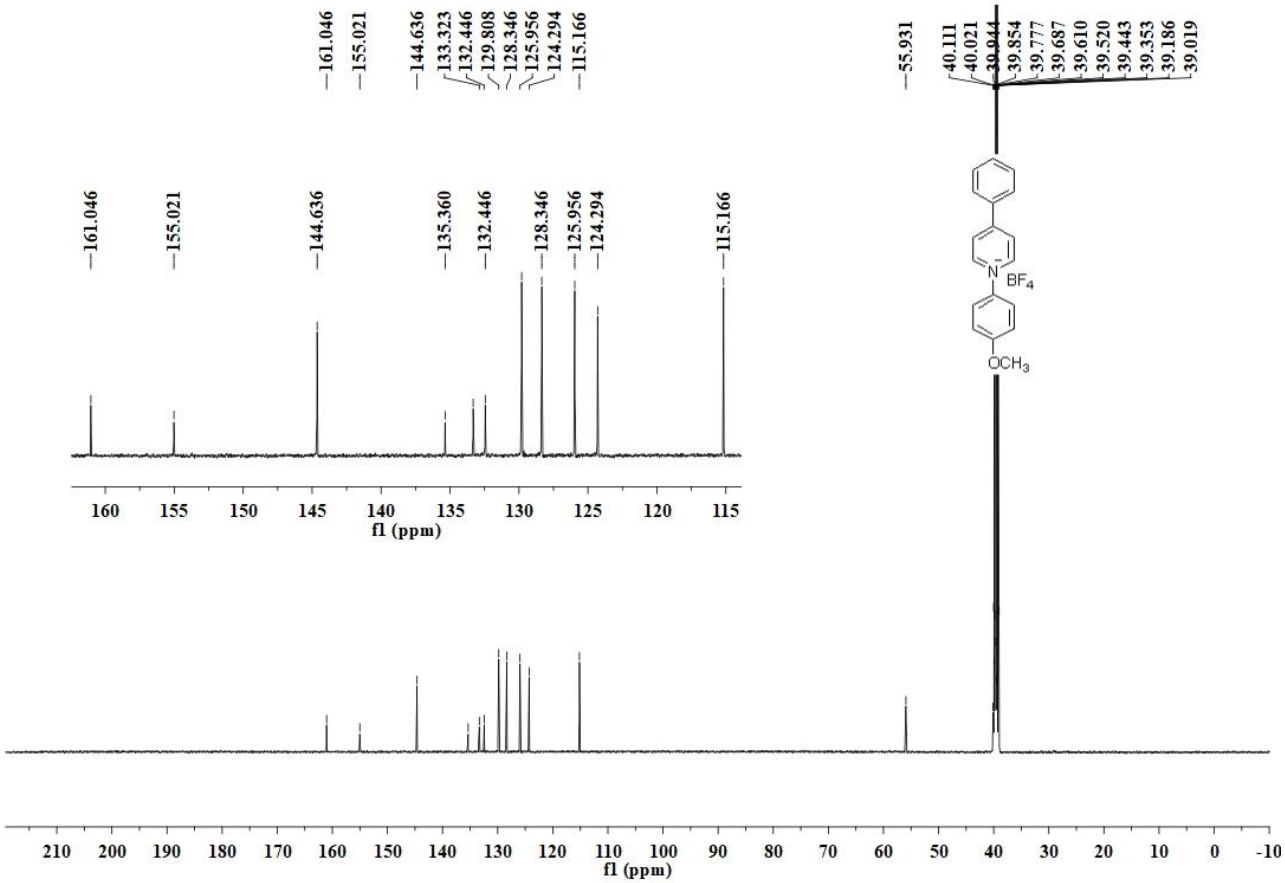
^{13}C NMR (125 MHz, DMSO-d_6) of **8**



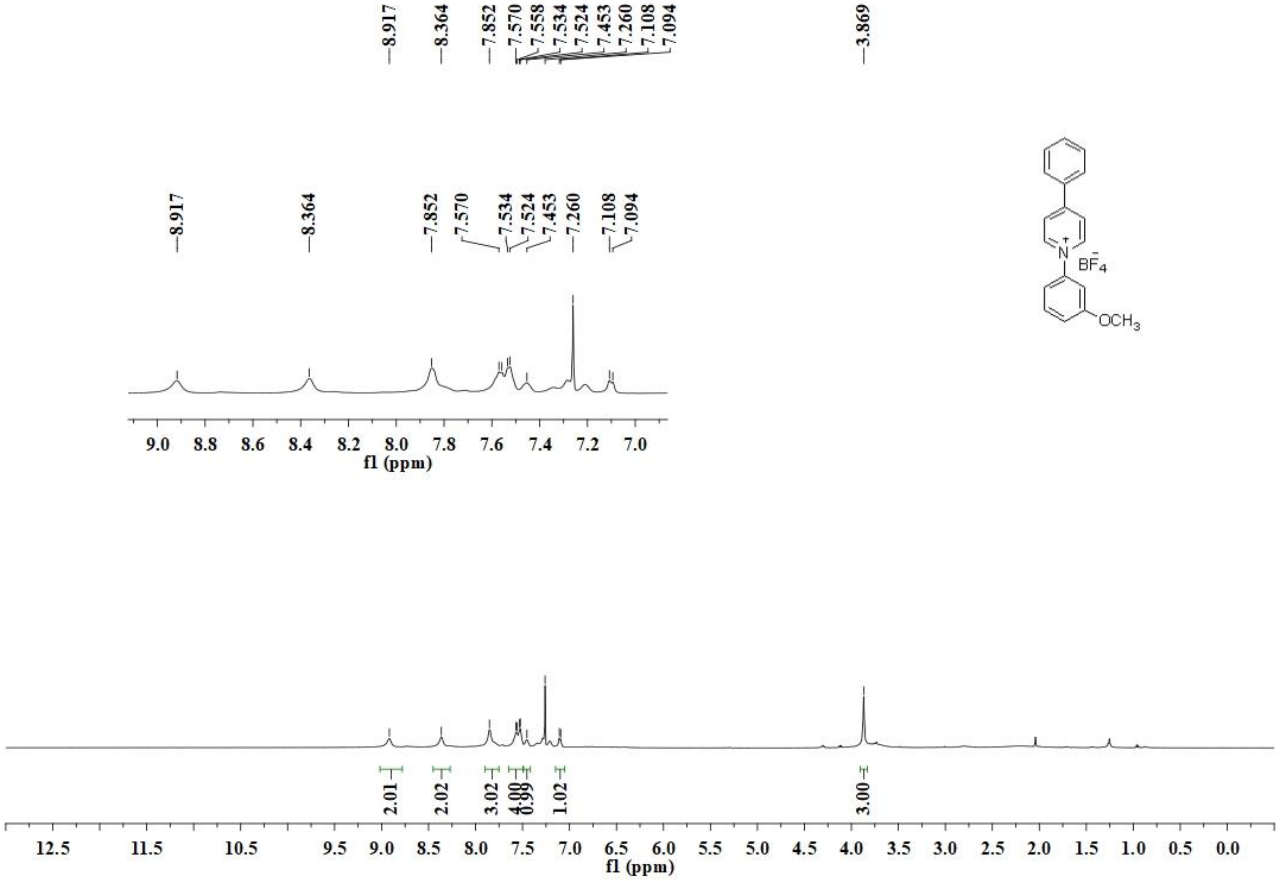
^{1}H NMR (500 MHz, DMSO-d_6) of **9**



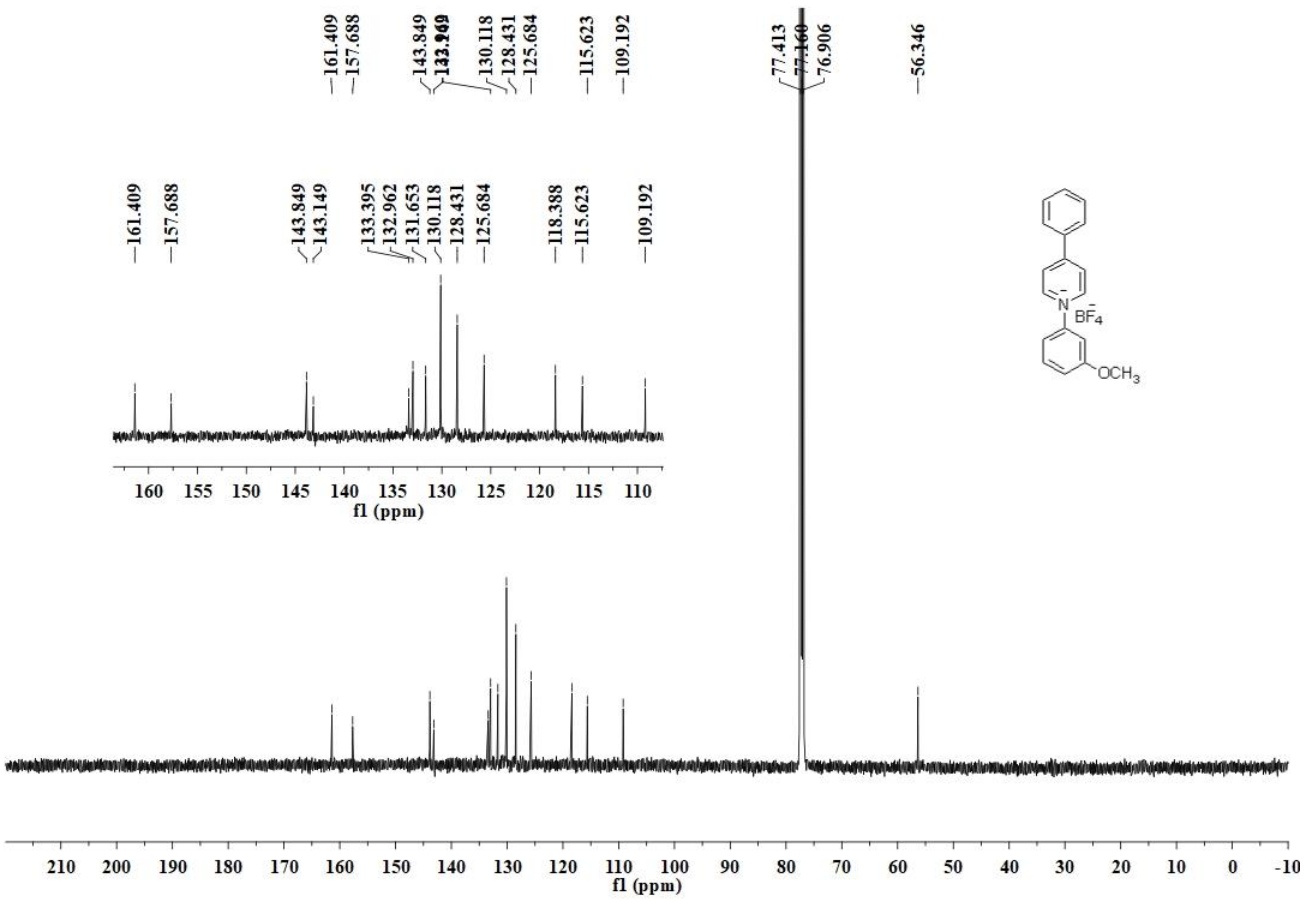
^{13}C NMR (125 MHz, DMSO-d_6) of **9**



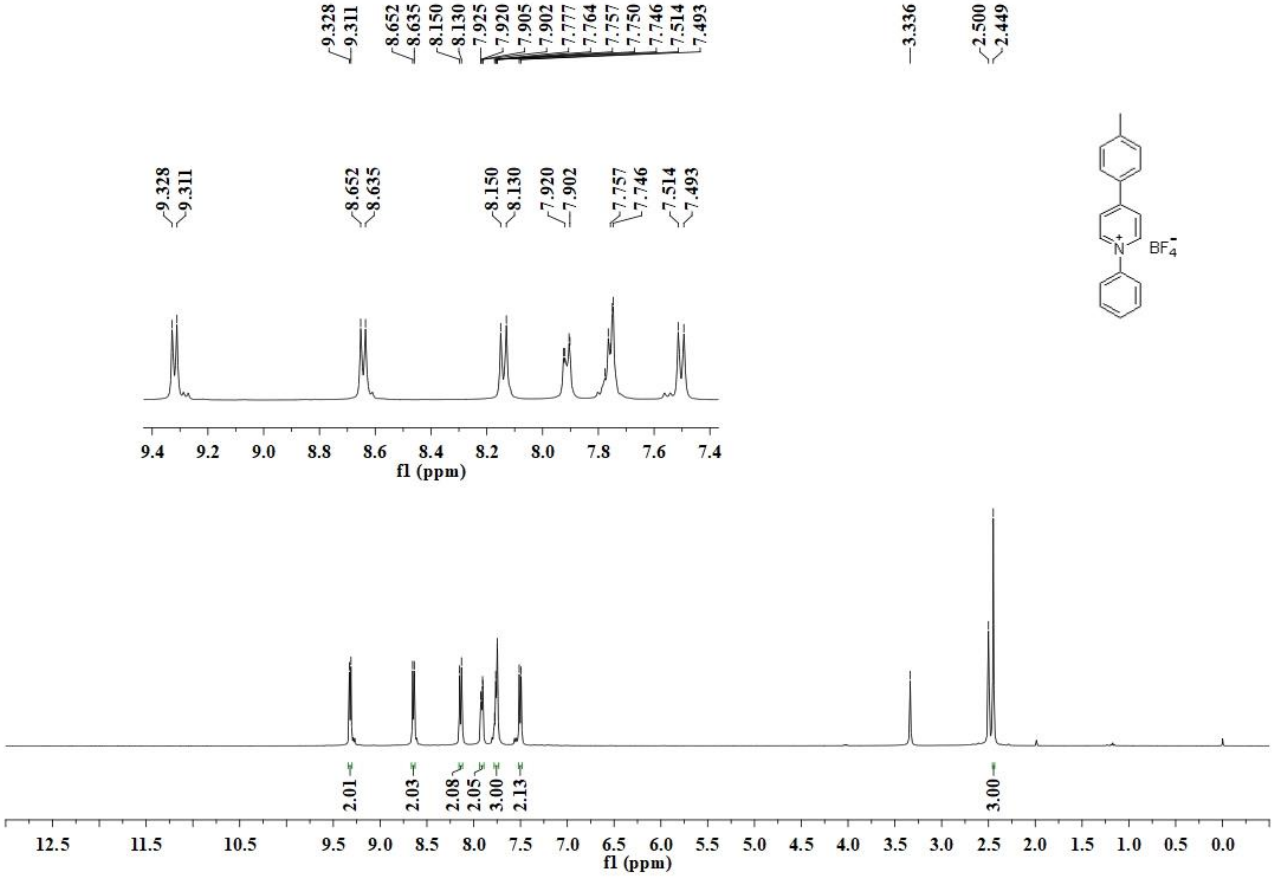
^{1}H NMR (500 MHz, $CDCl_3$) of **10**



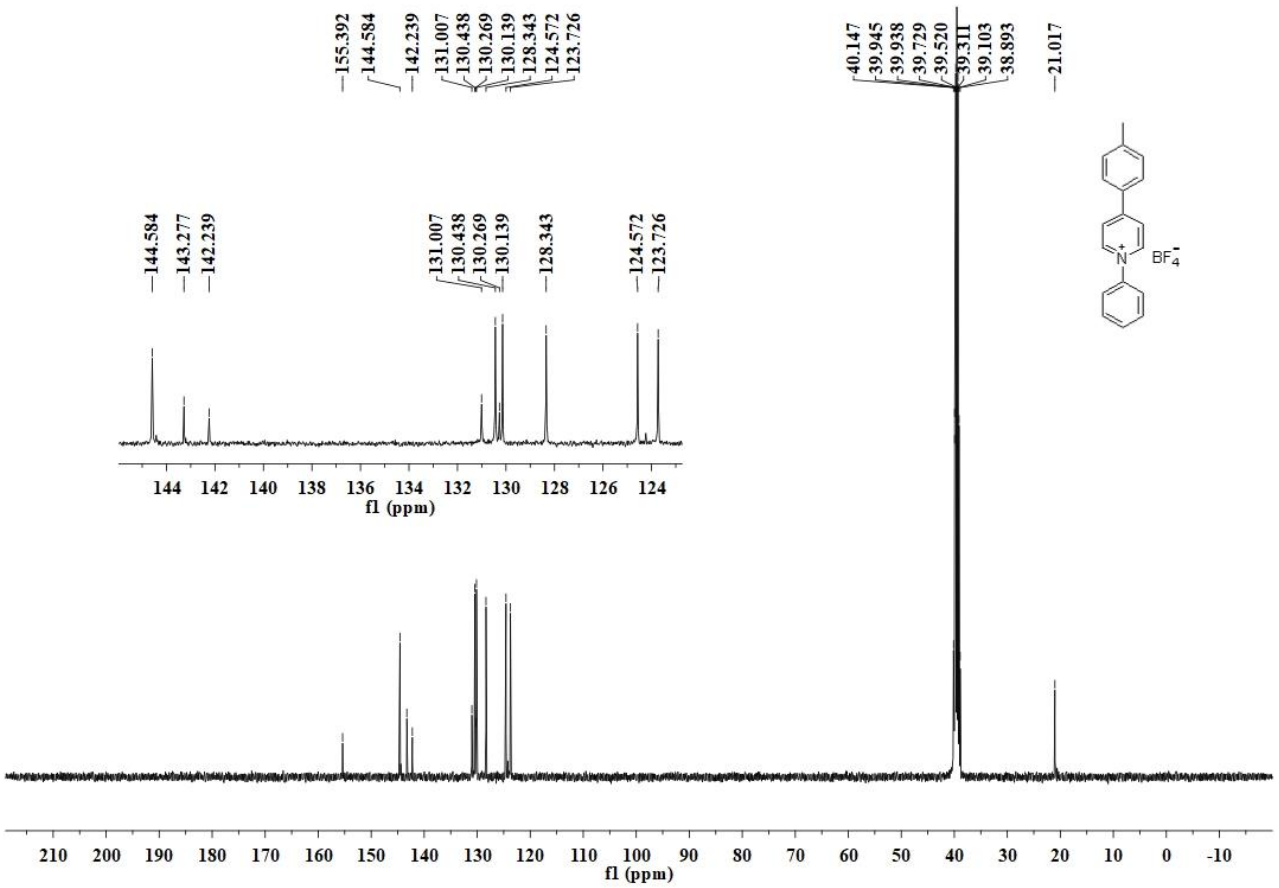
^{13}C NMR (125 MHz, $CDCl_3$) of **10**



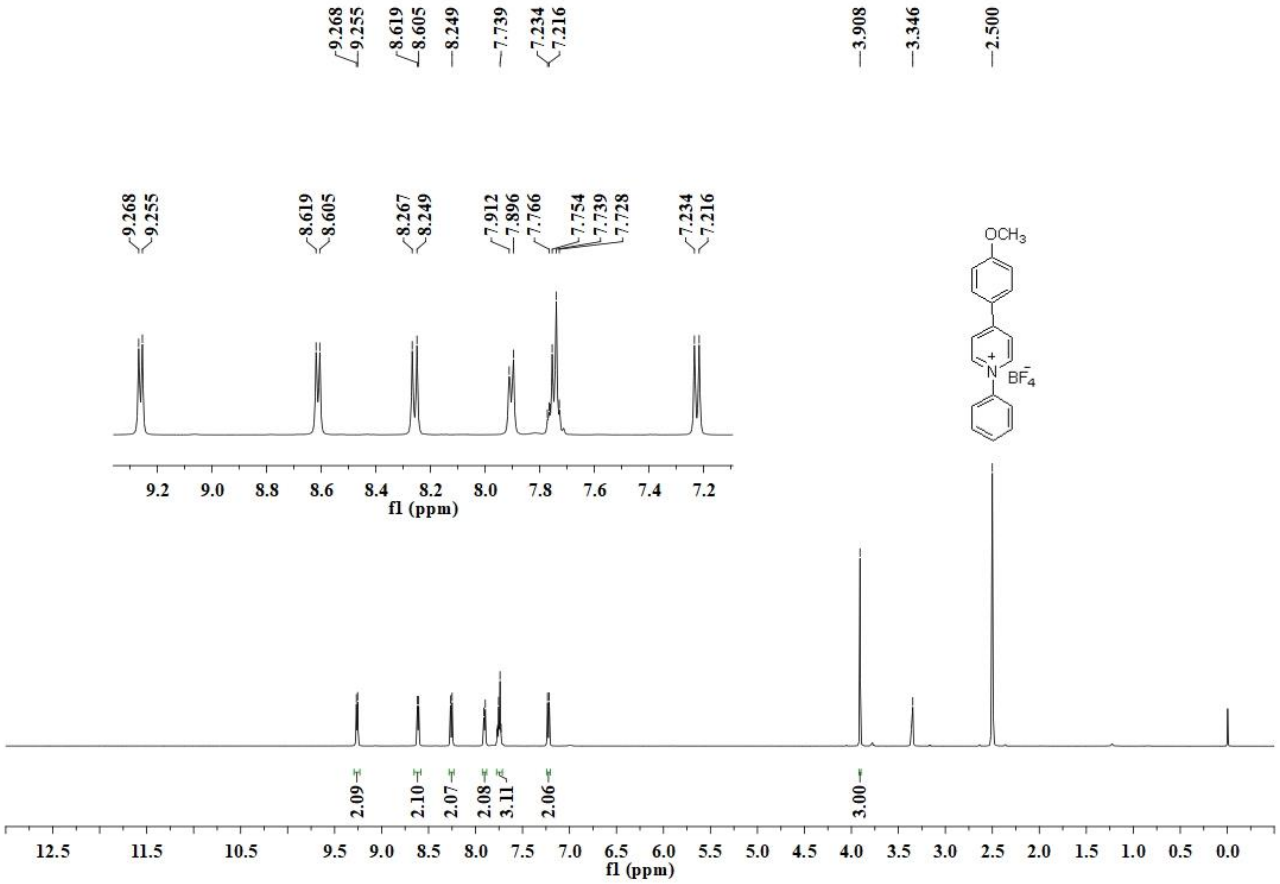
^{1}H NMR (500 MHz, DMSO-d_6) of **11**



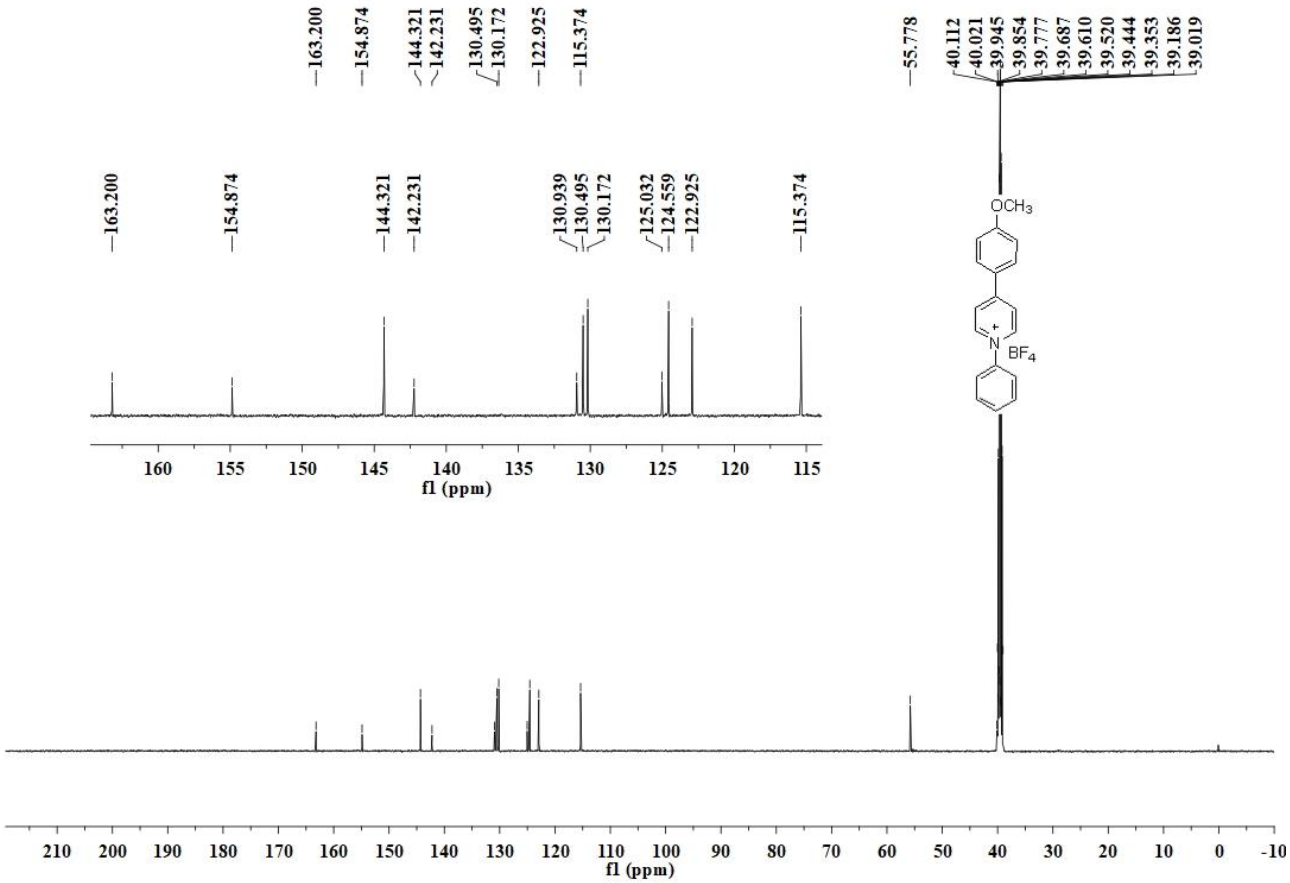
^{13}C NMR (125 MHz, DMSO-d_6) of **11**



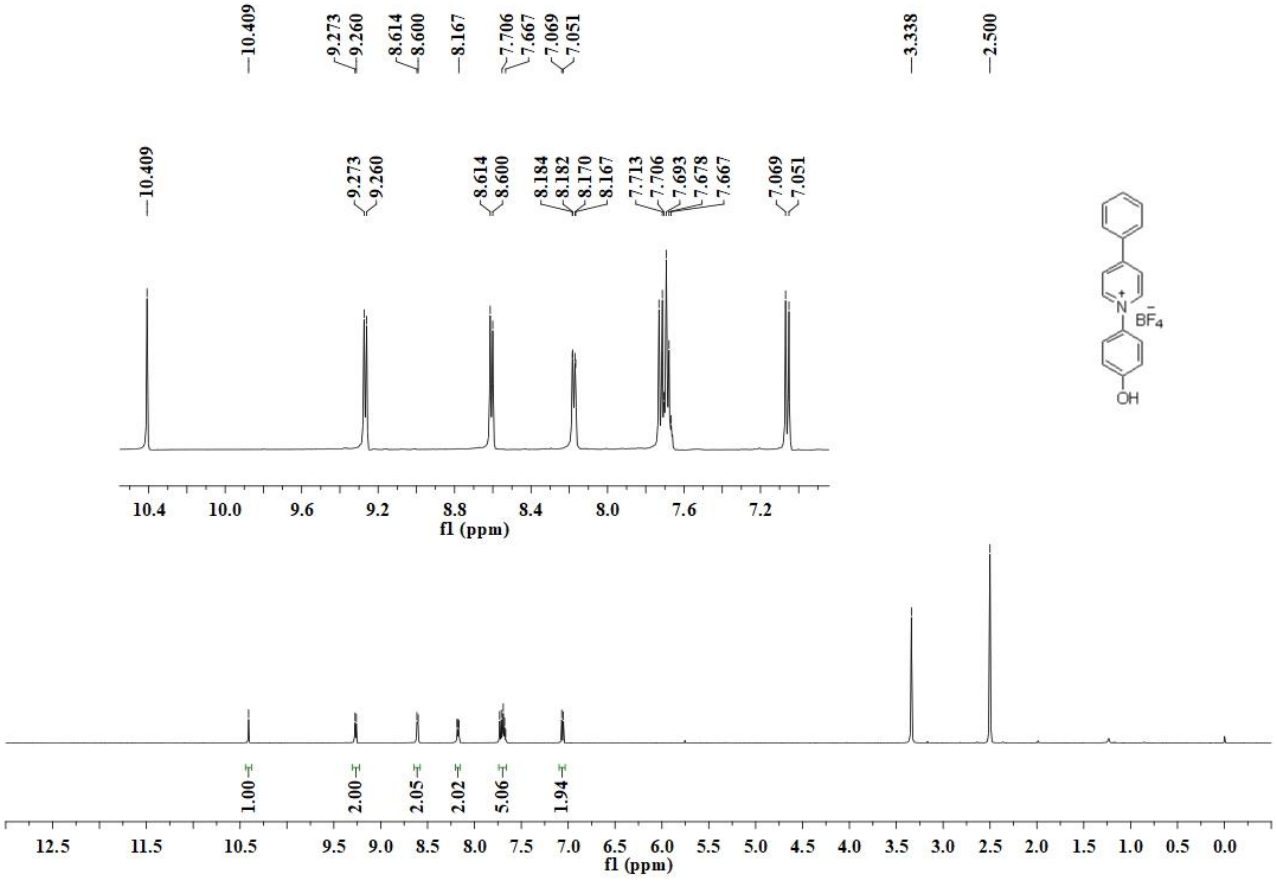
^{1}H NMR (500 MHz, DMSO-d_6) of **12**



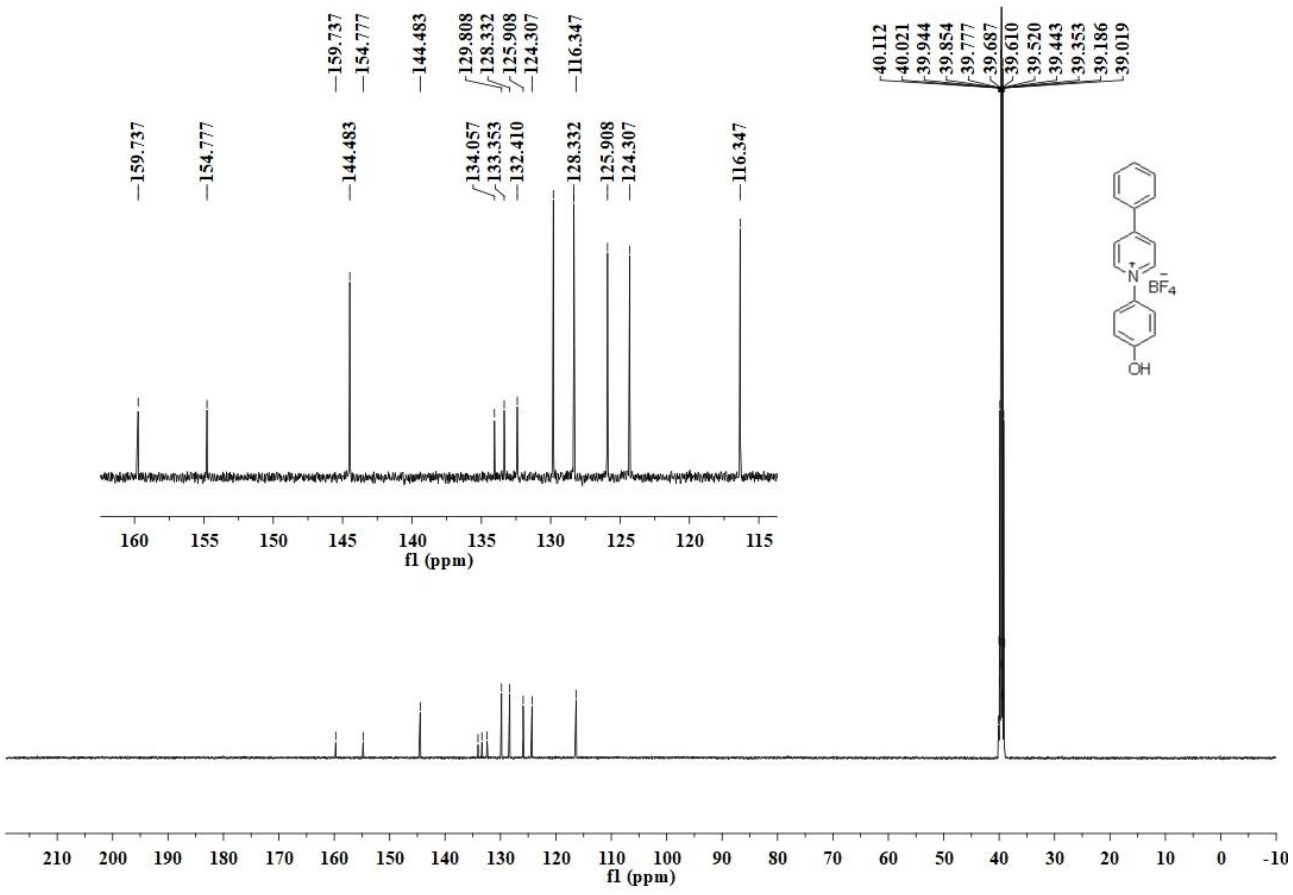
^{13}C NMR (125 MHz, DMSO-d_6) of **12**



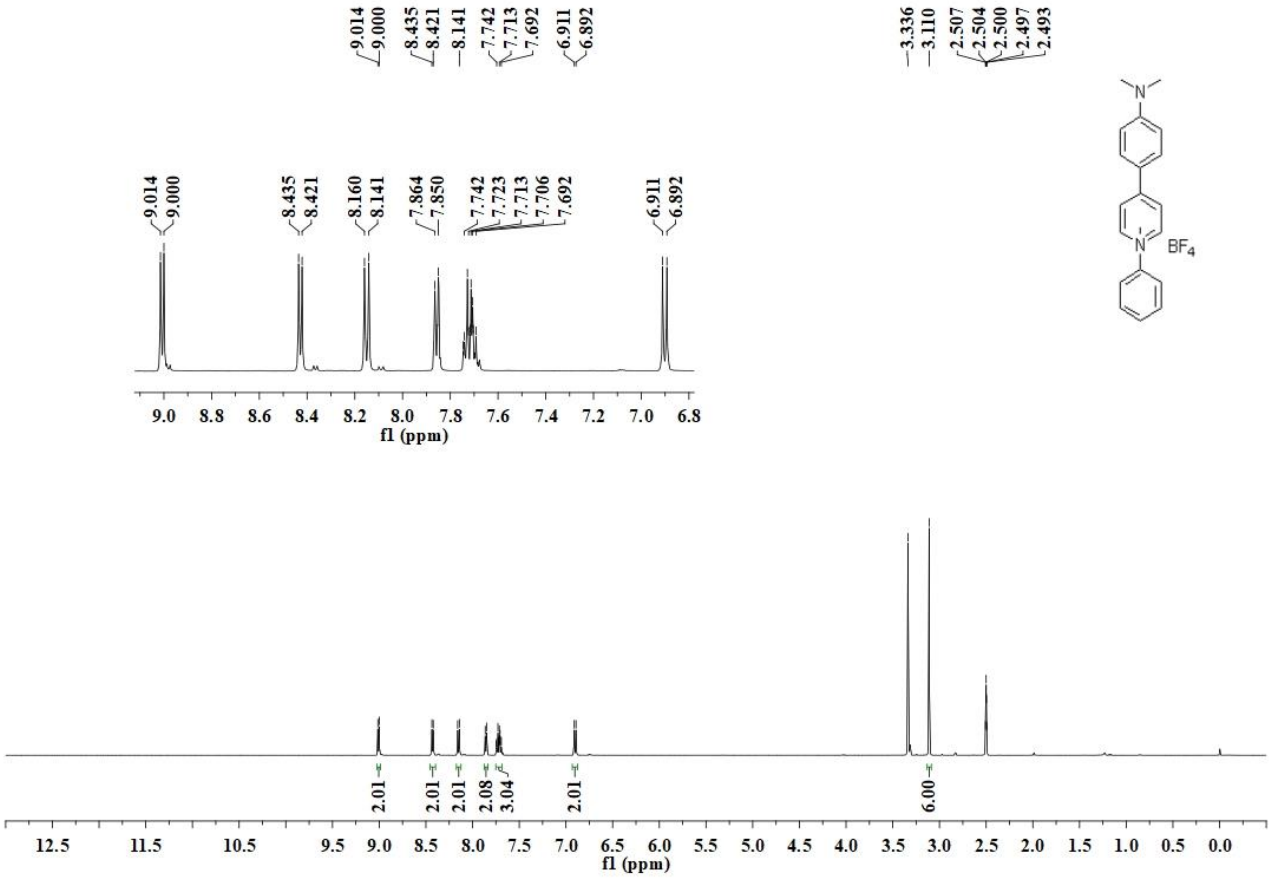
^{1}H NMR (500 MHz, DMSO-d_6) of **13**



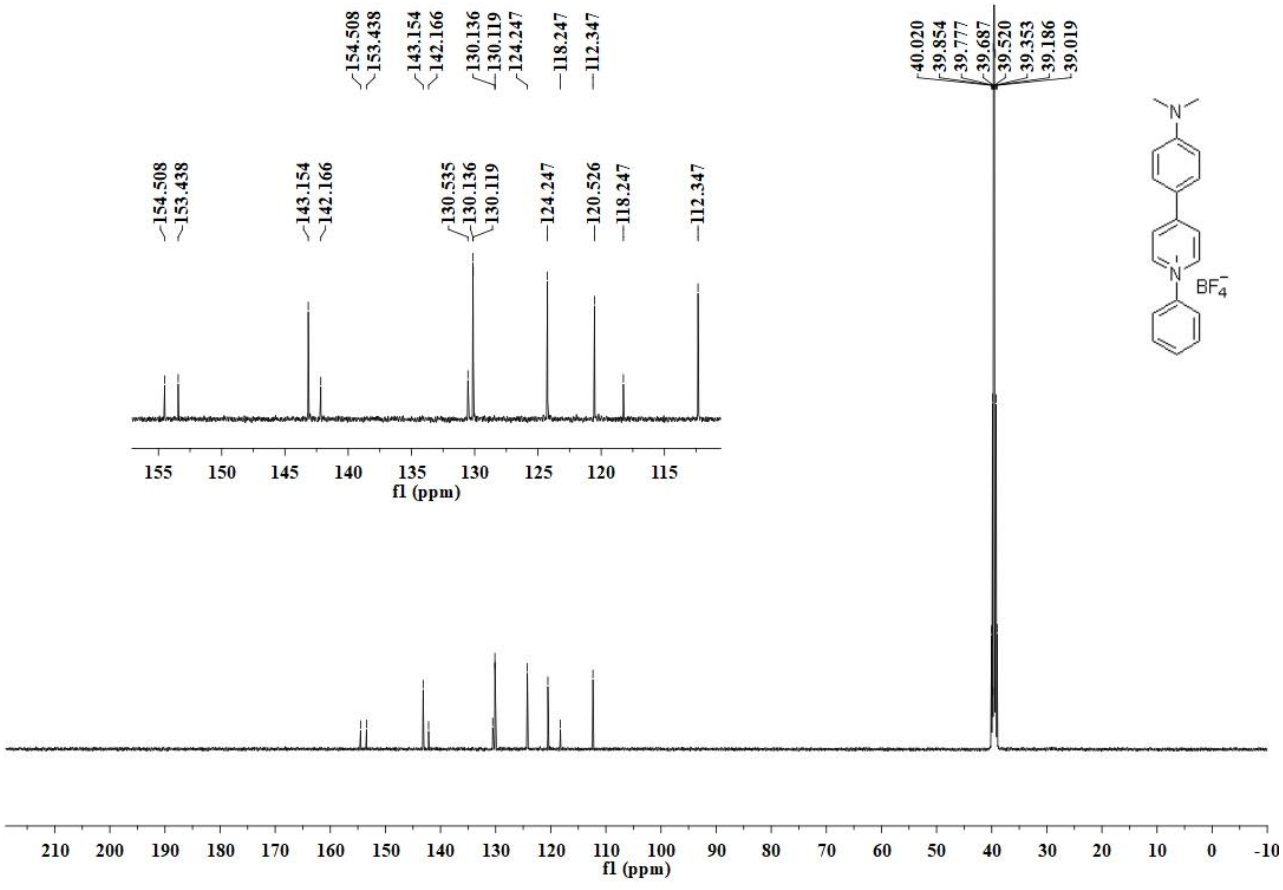
^{13}C NMR (125 MHz, DMSO-d_6) of **13**



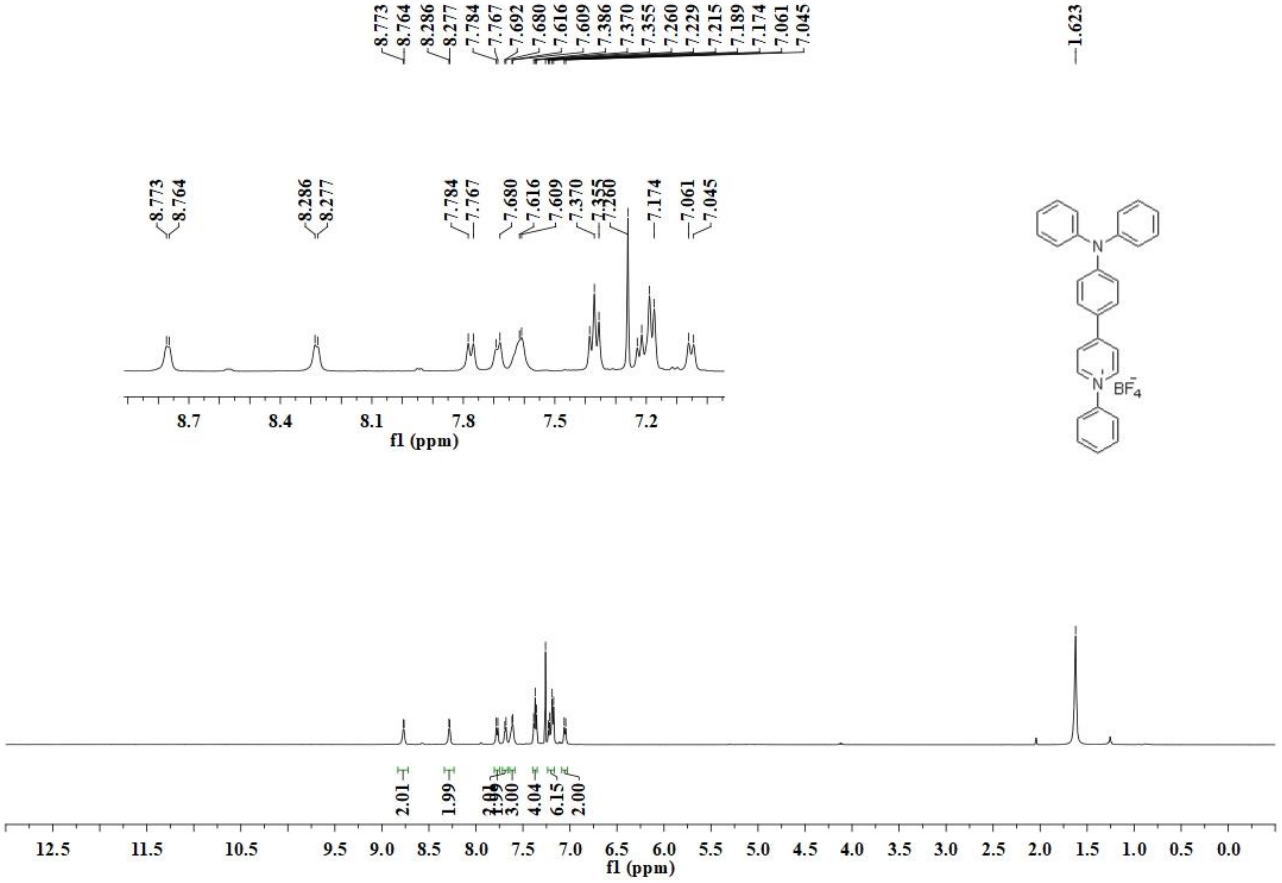
^{1}H NMR (500 MHz, DMSO-d_6) of **14**



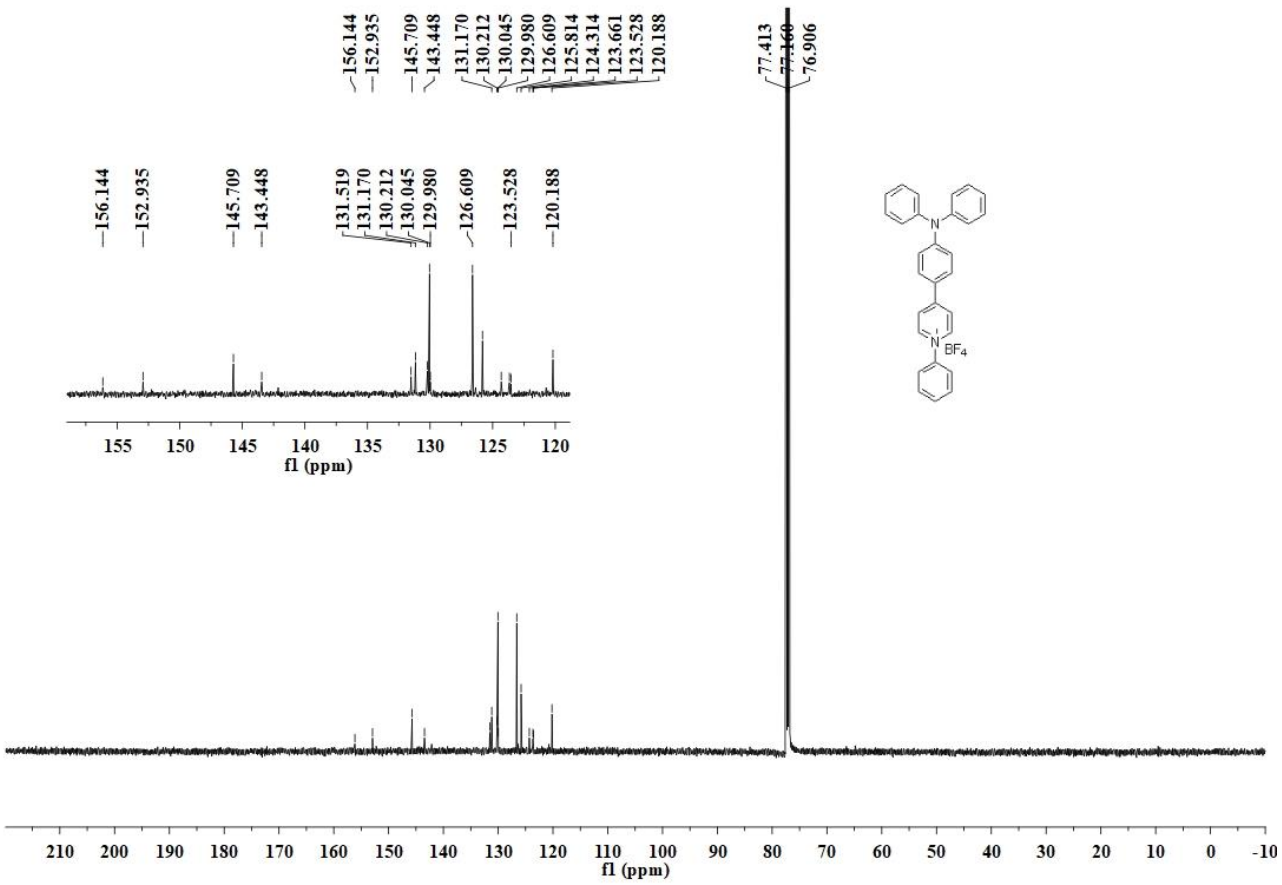
^{13}C NMR (125 MHz, DMSO-d_6) of **14**



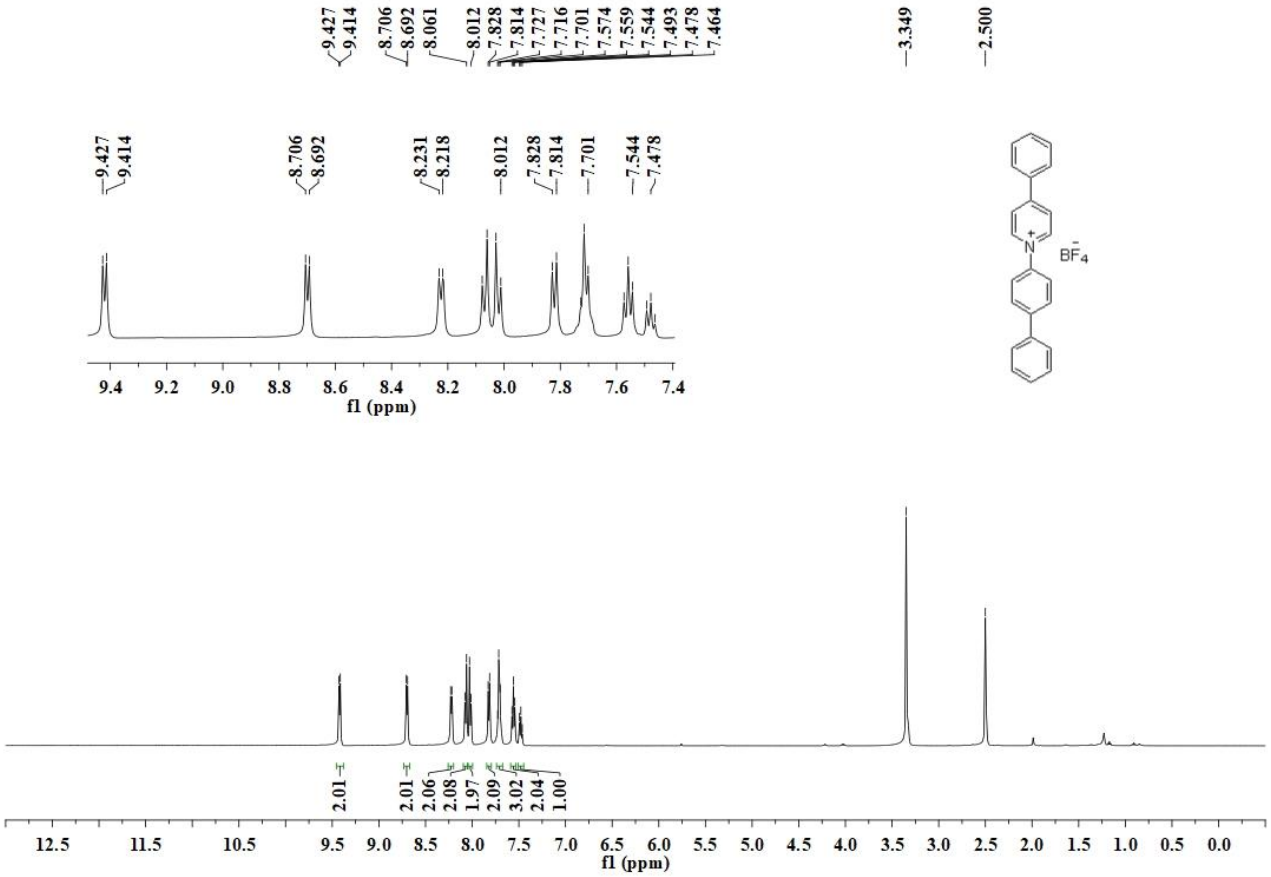
^{1}H NMR (500 MHz, $CDCl_3$) of **15**



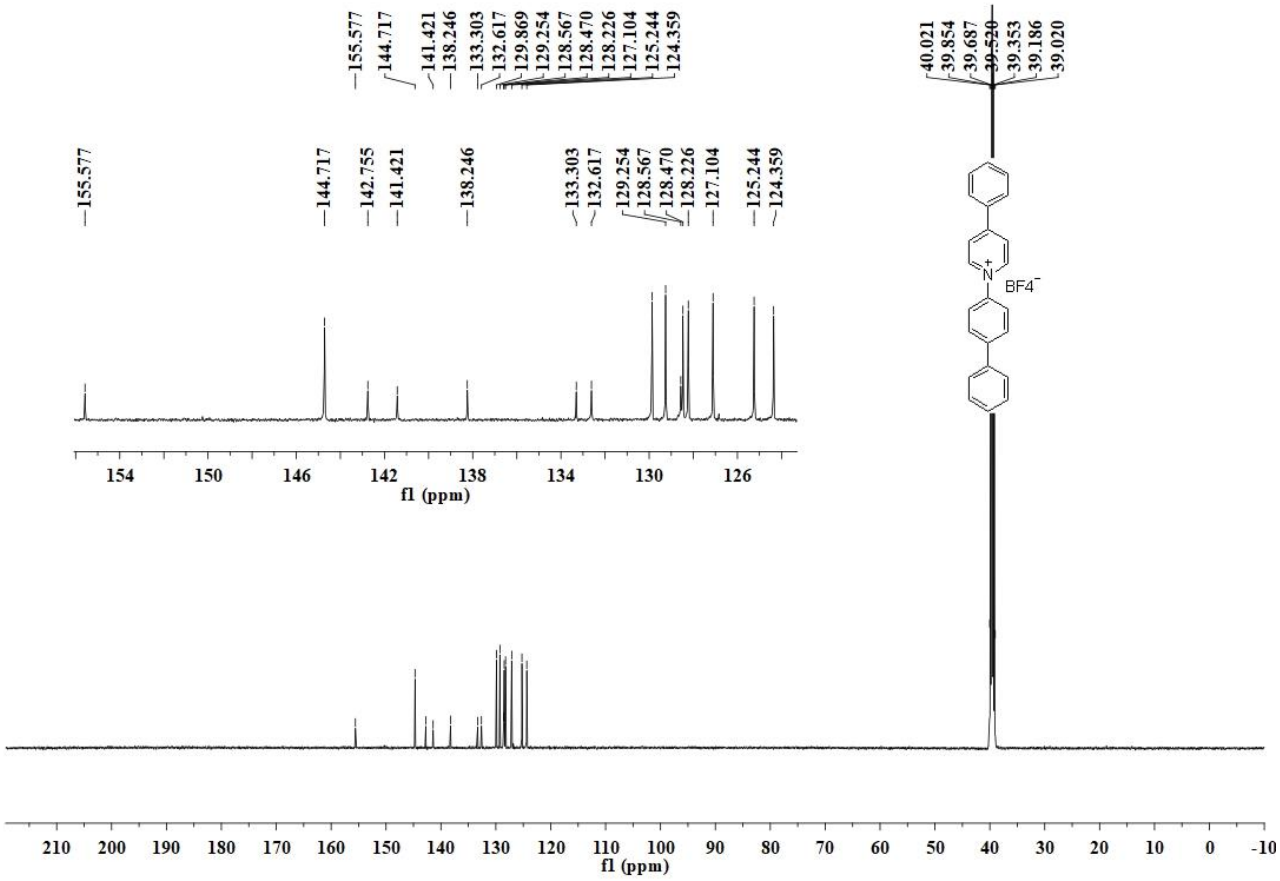
^{13}C NMR (125 MHz, $CDCl_3$) of **15**



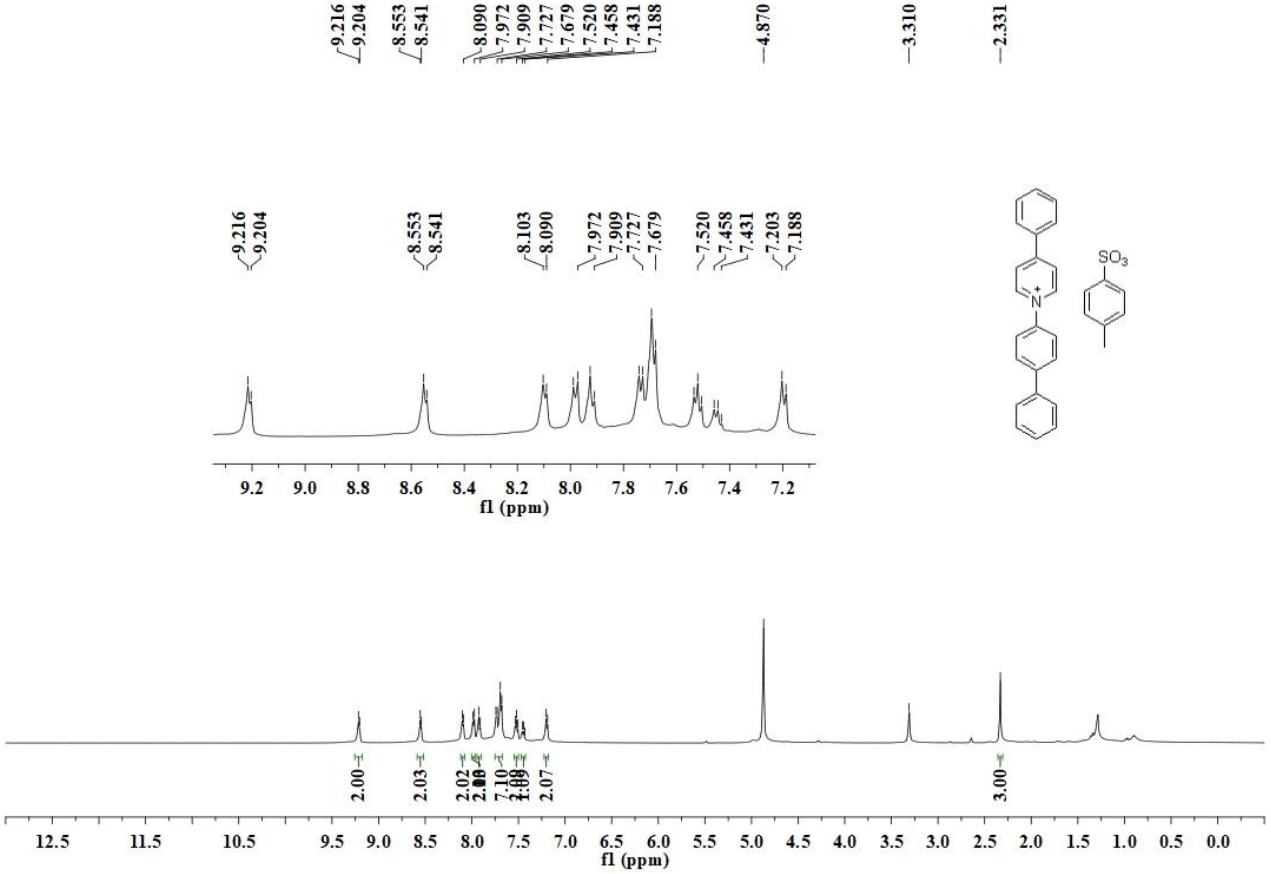
^{1}H NMR (500 MHz, DMSO-d_6) of **16**



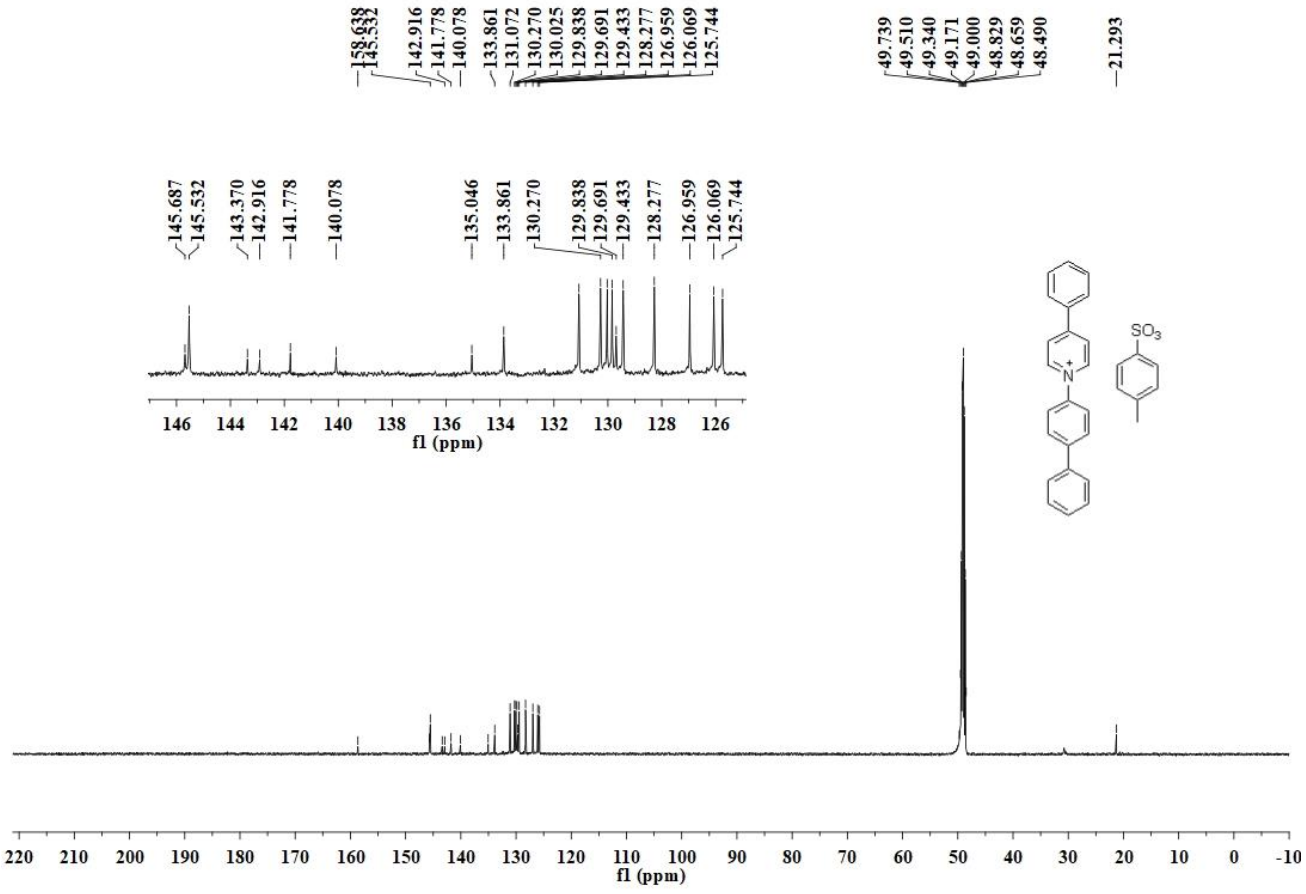
^{13}C NMR (125 MHz, DMSO-d_6) of **16**



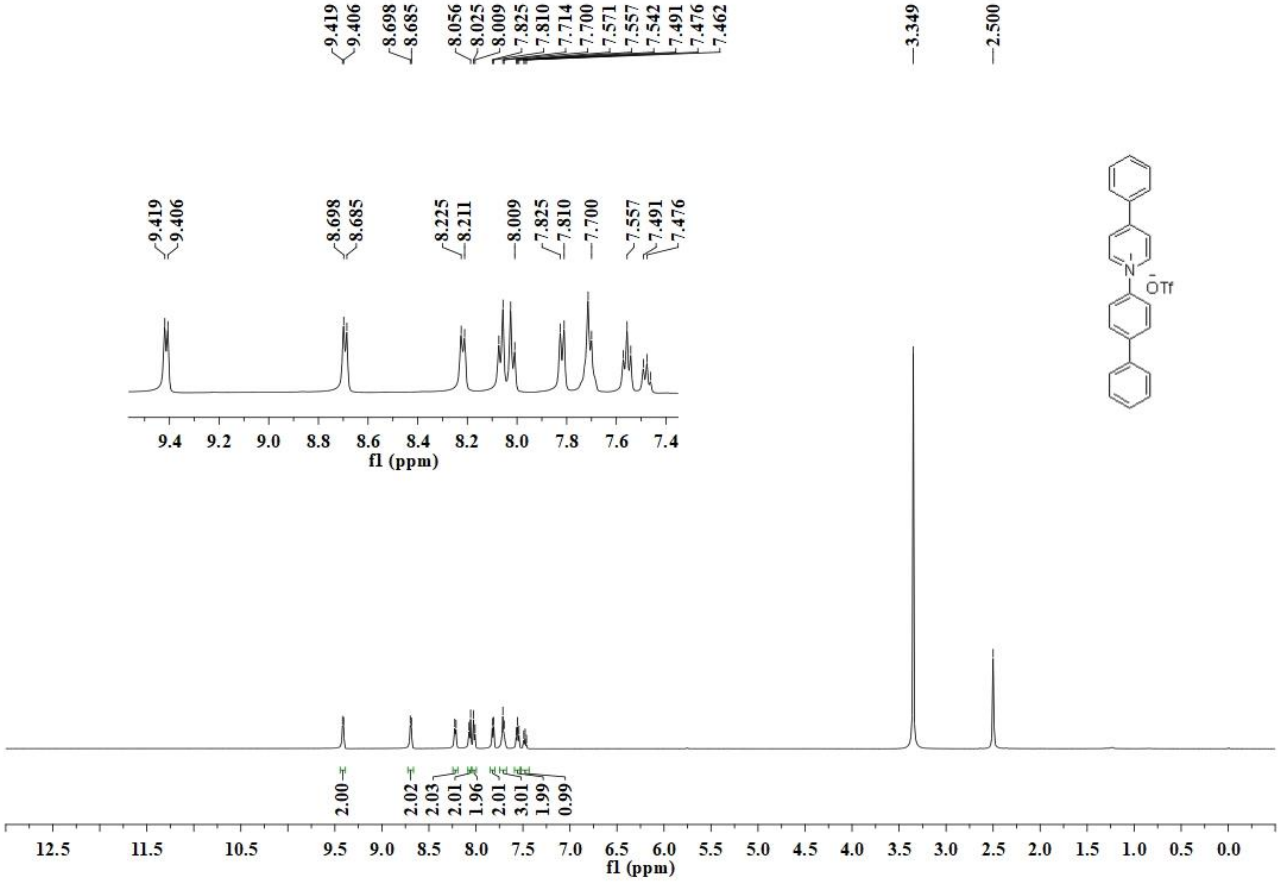
^{1}H NMR (500 MHz, CD_3OD) of **16-OTs**



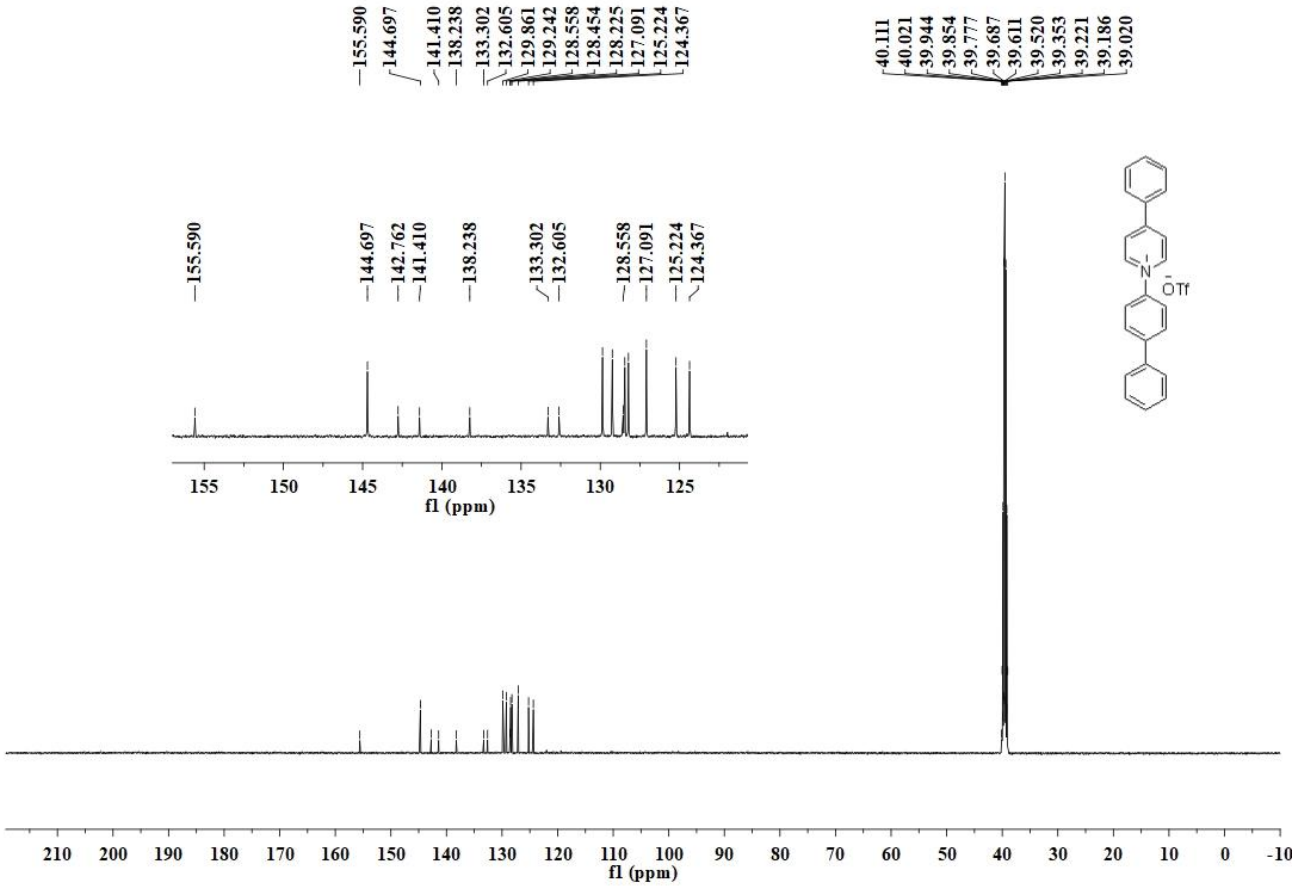
^{13}C NMR (125 MHz, CD_3OD) of **16-OTs**



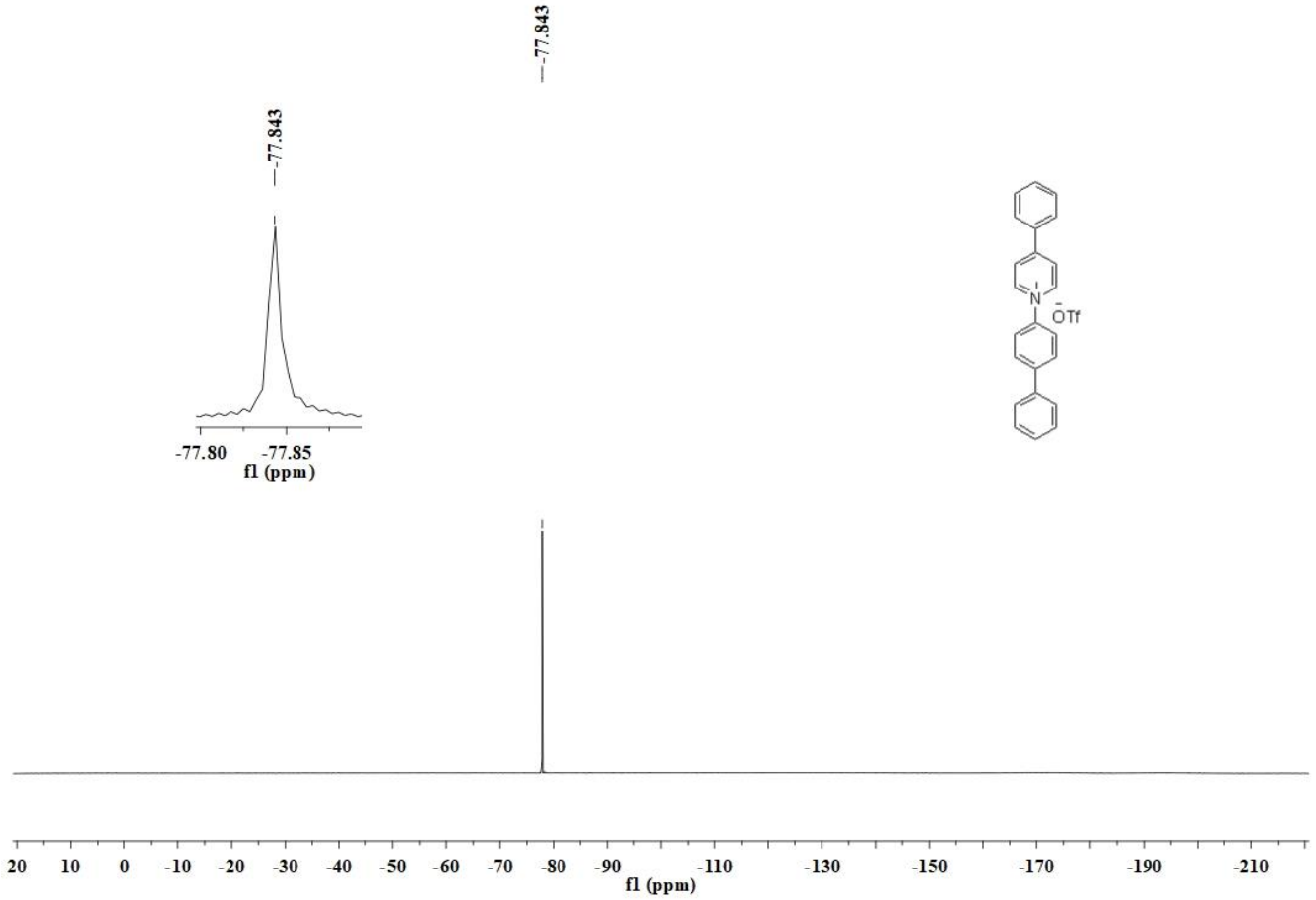
^{1}H NMR (500 MHz, DMSO-d_6) of **16-OTf**



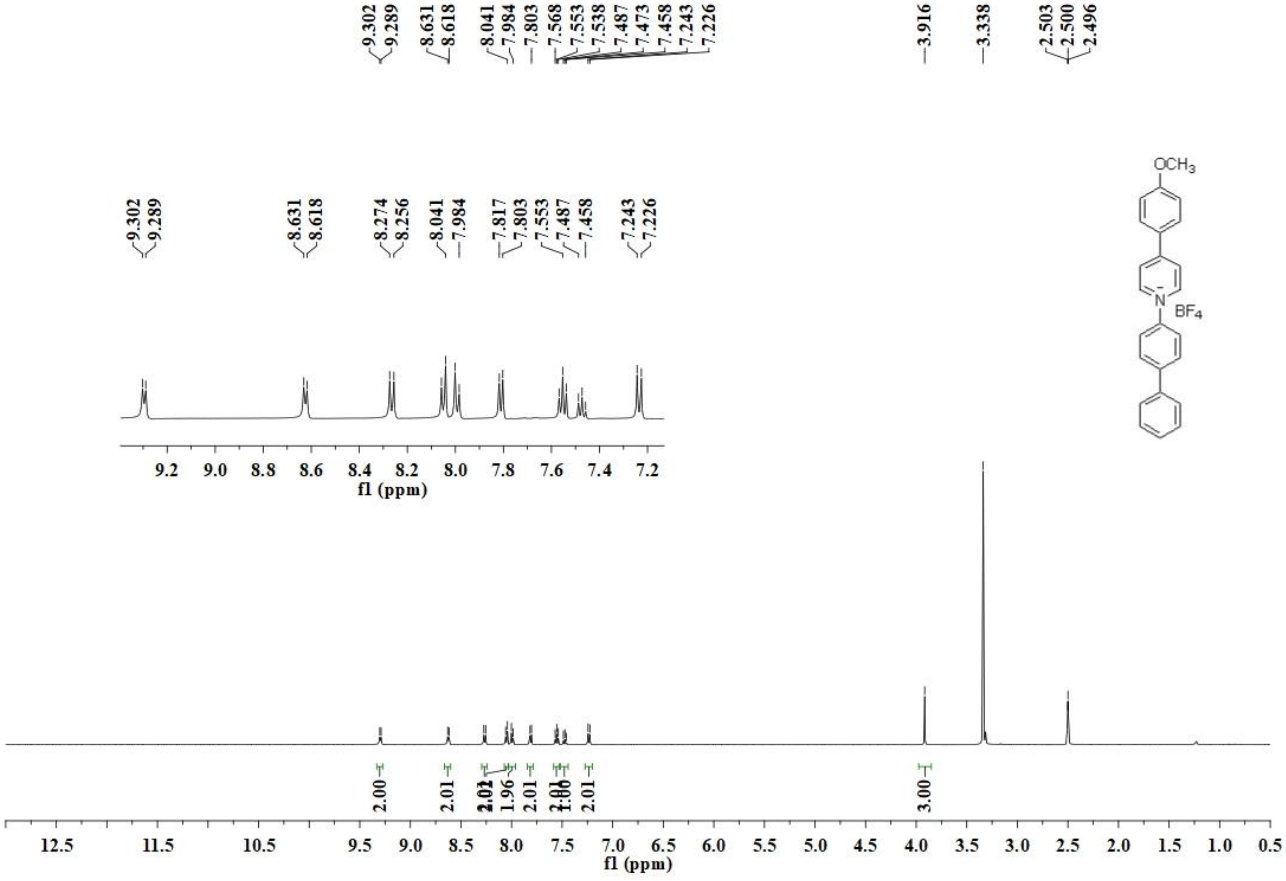
^{13}C NMR (125 MHz, DMSO-d_6) of **16-OTf**



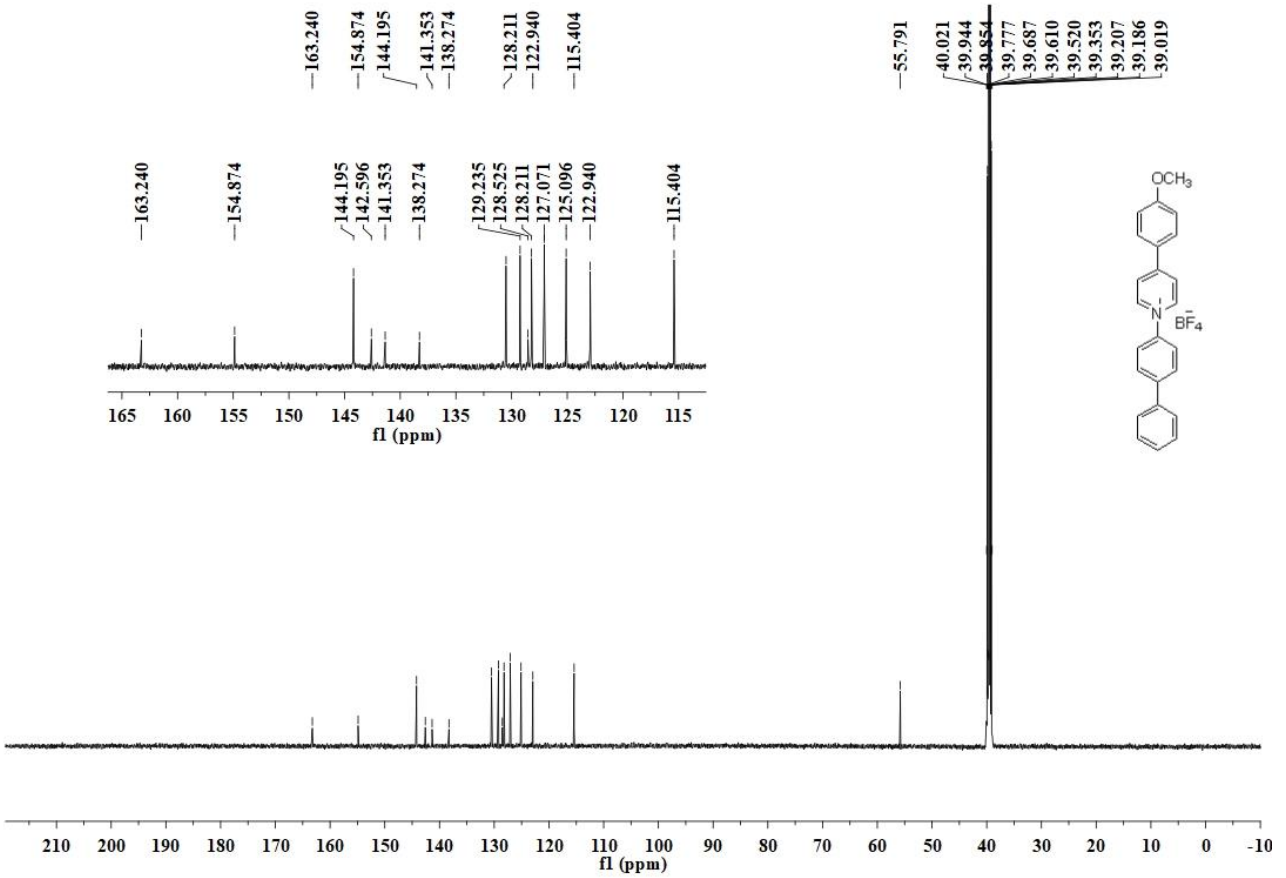
^{19}F NMR (471 MHz, DMSO-d_6) of **16-OTf**



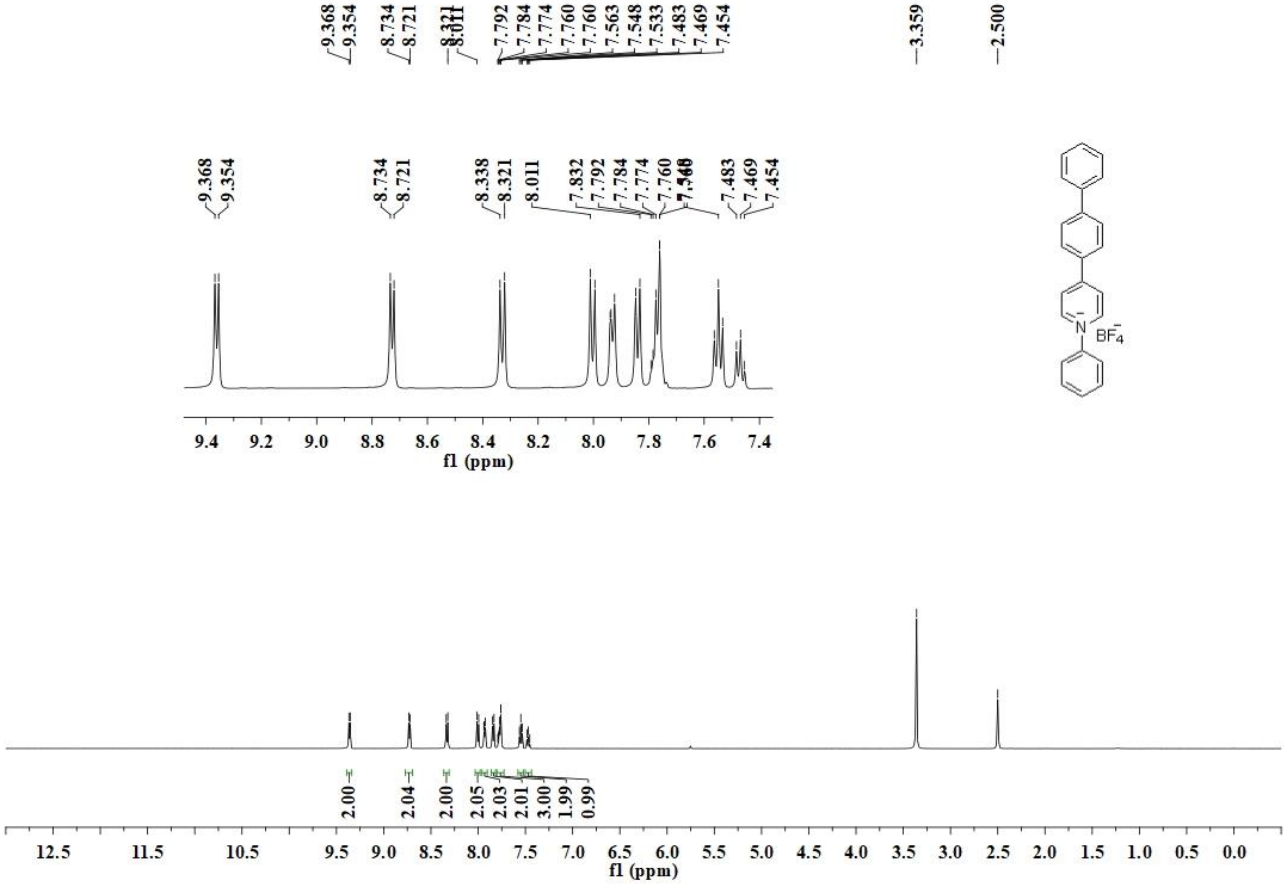
^{1}H NMR (500 MHz, DMSO-d_6) of **17**



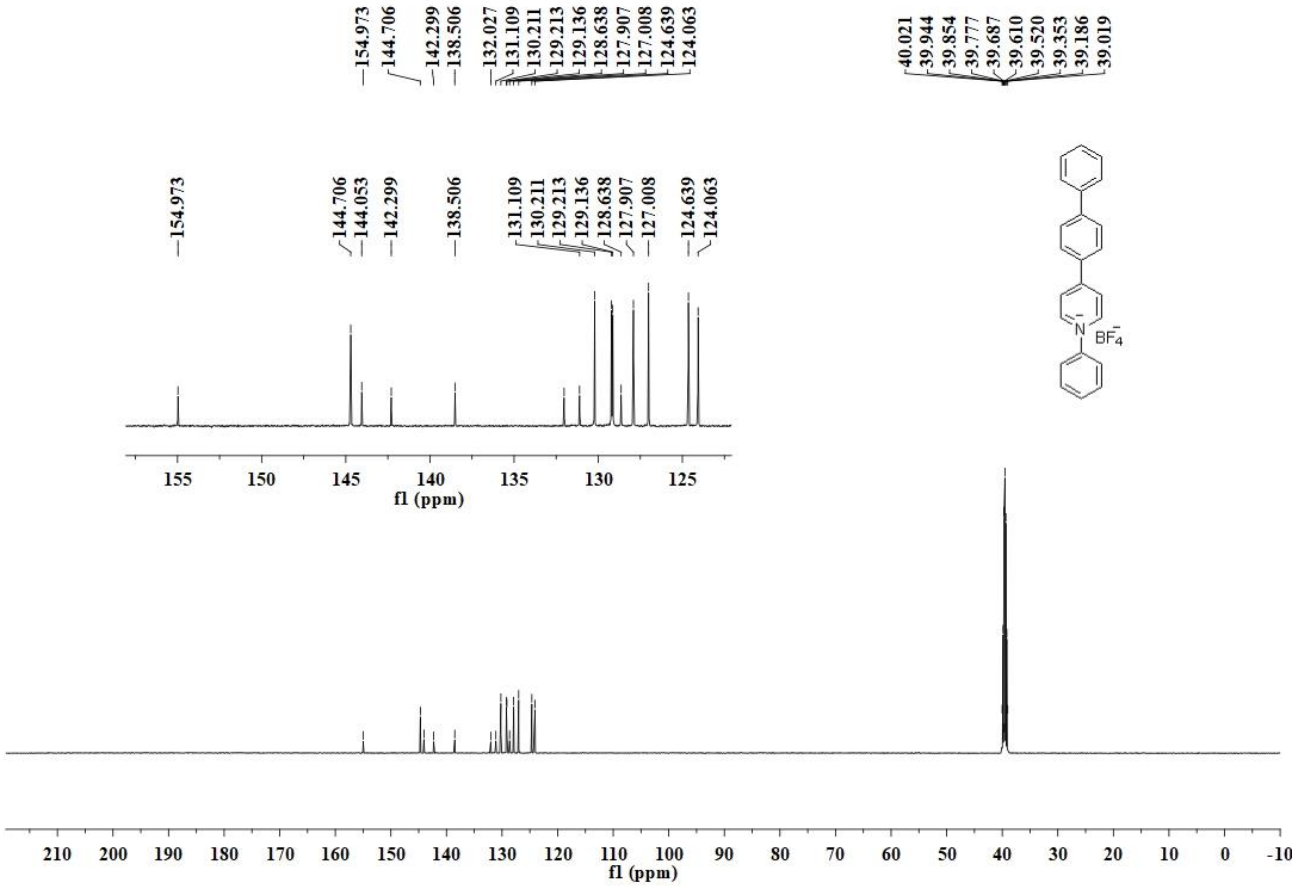
^{13}C NMR (125 MHz, DMSO-d_6) of **17**



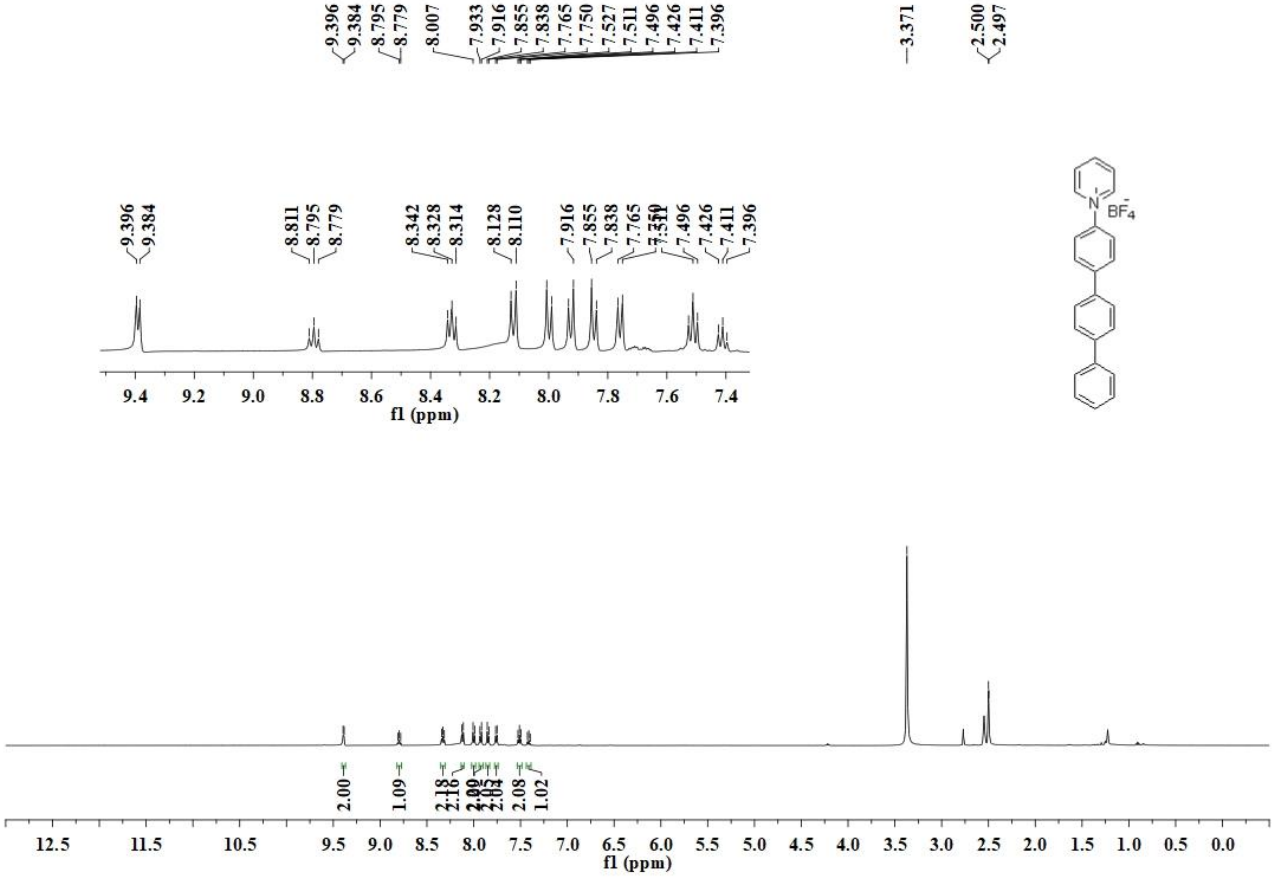
^{1}H NMR (500 MHz, DMSO-d_6) of **18**



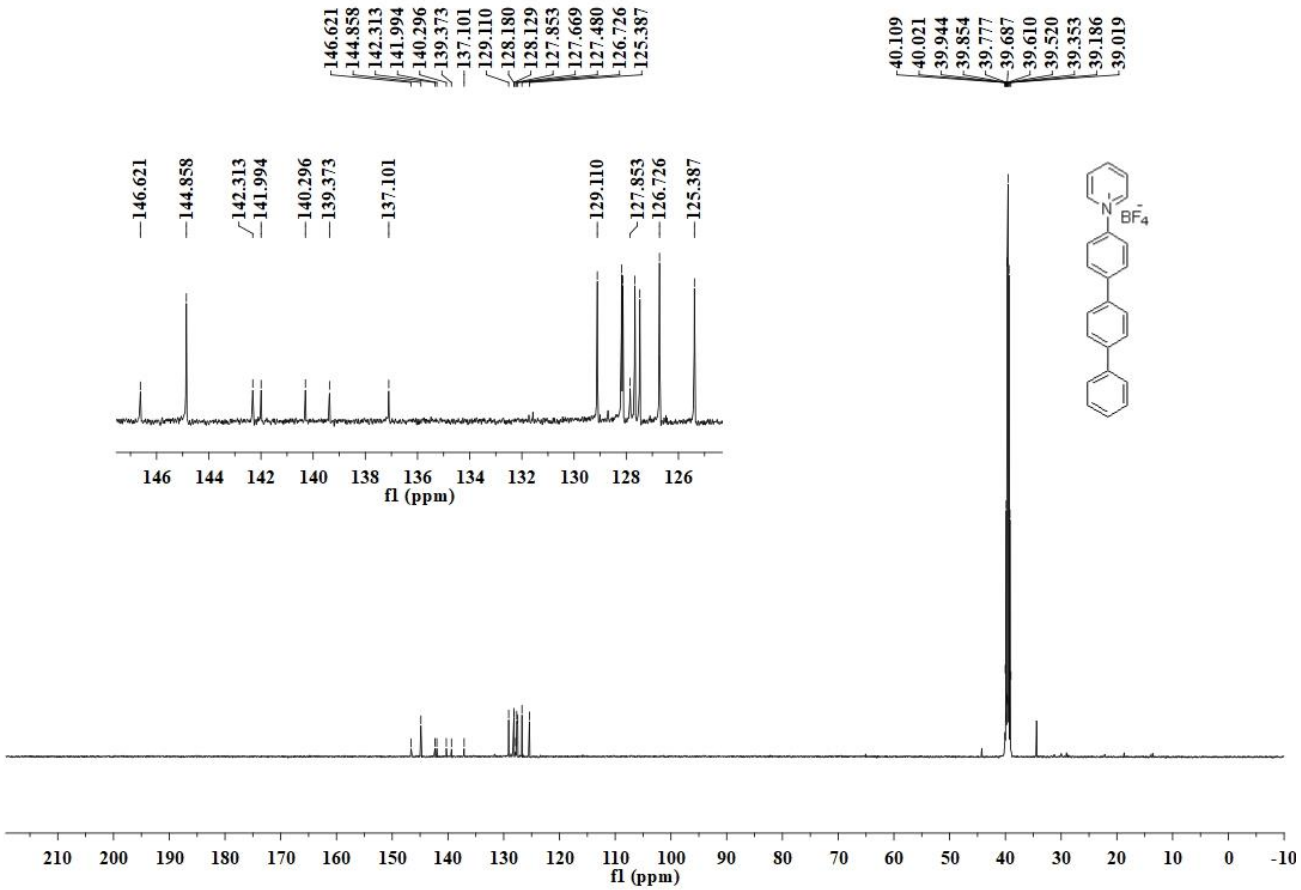
^{13}C NMR (125 MHz, DMSO-d_6) of **18**



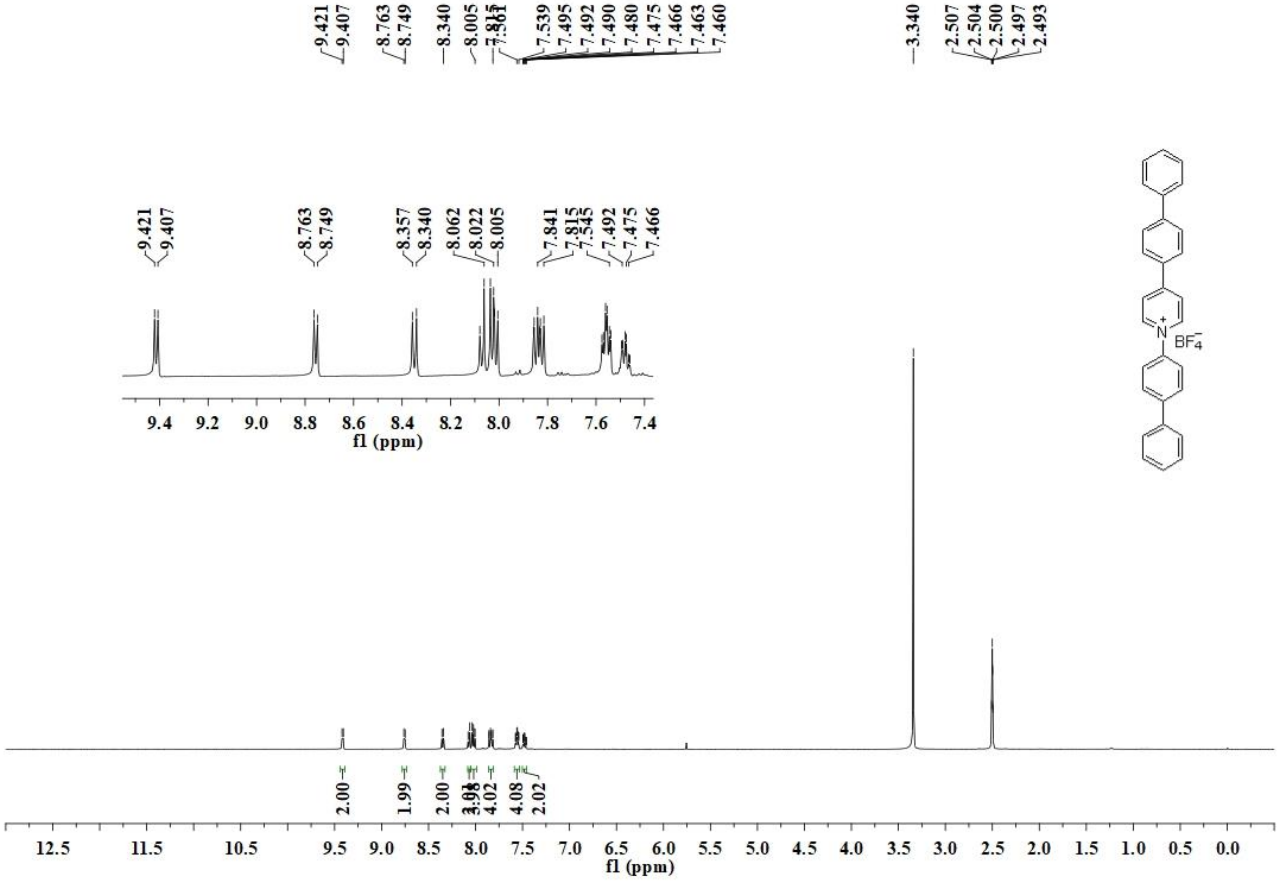
^{1}H NMR (500 MHz, DMSO-d_6) of **19**



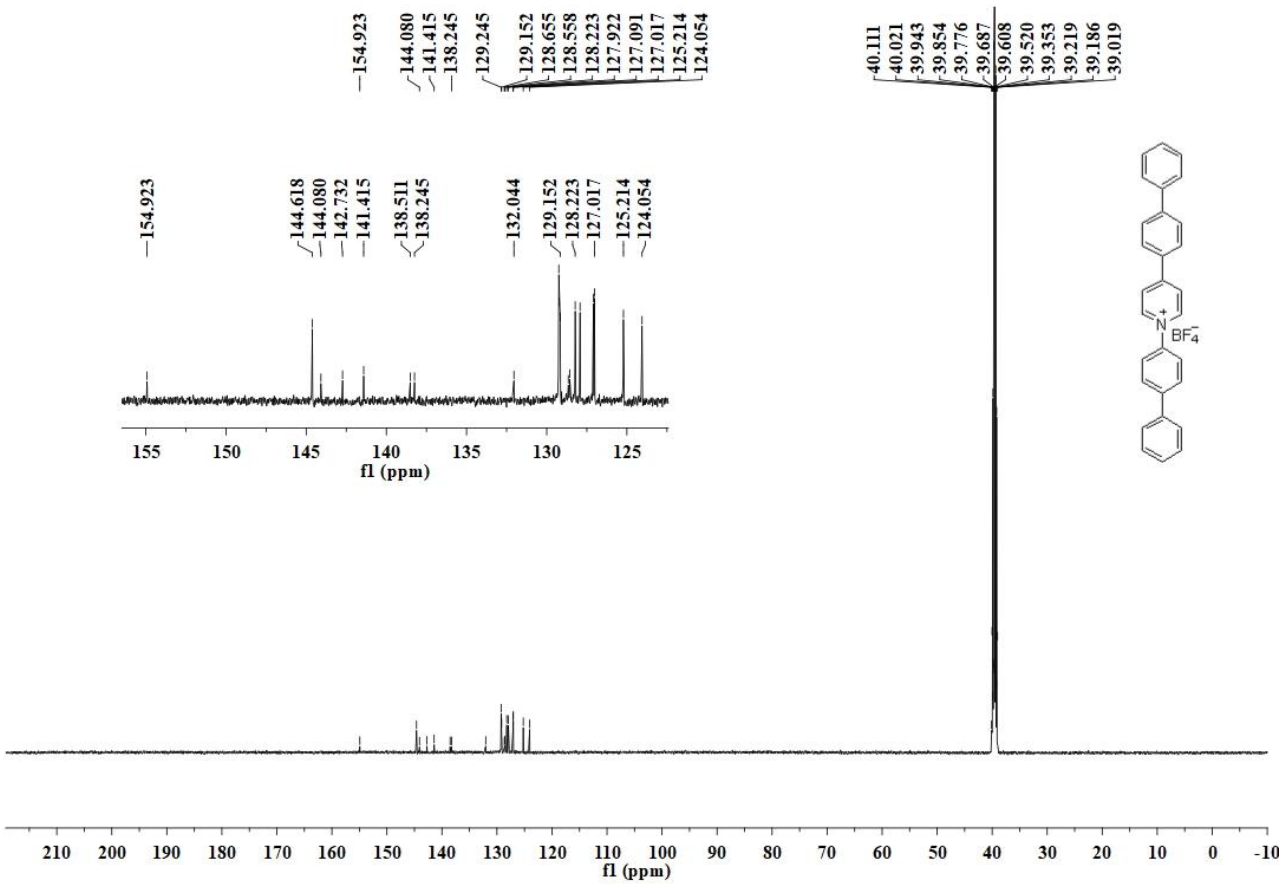
^{13}C NMR (125 MHz, DMSO-d_6) of **19**



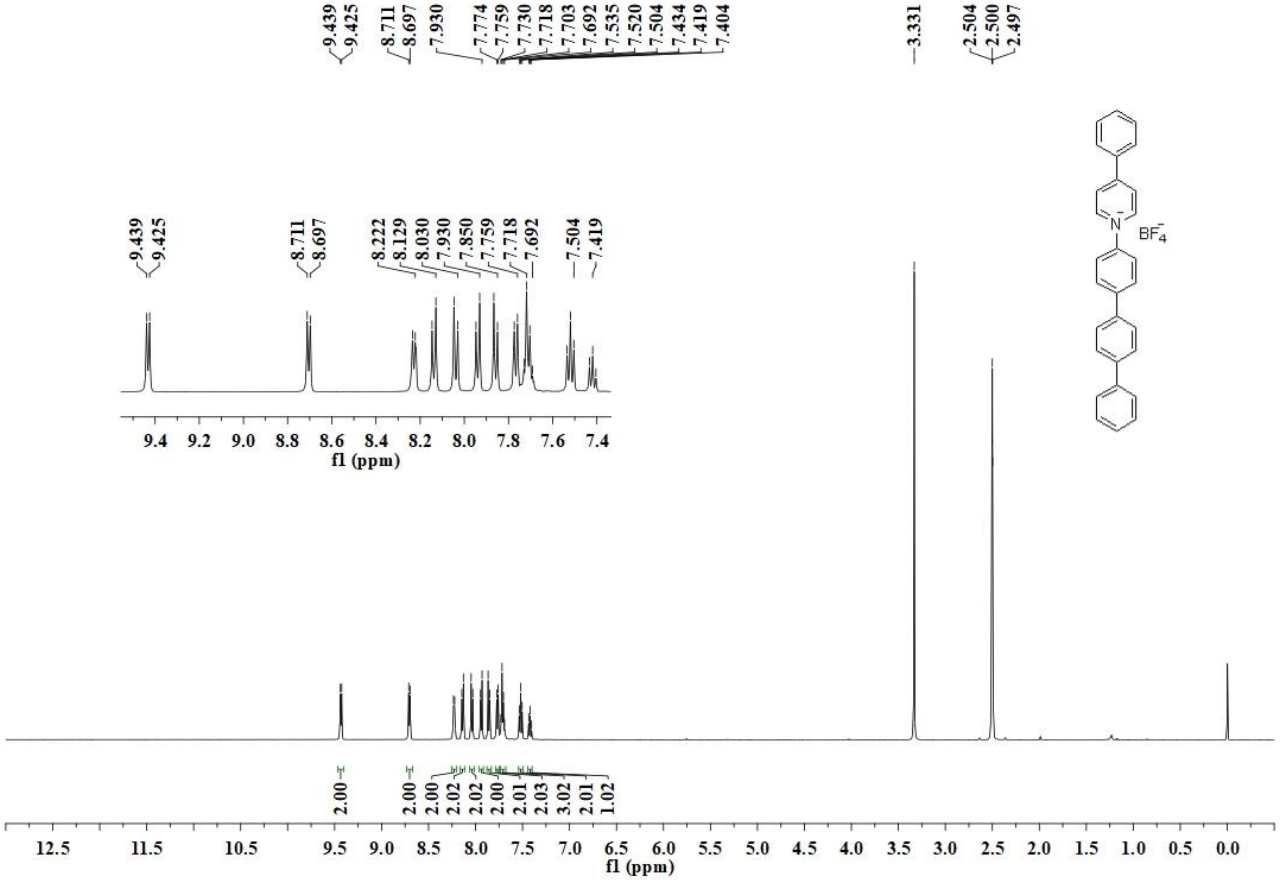
^{1}H NMR (500 MHz, DMSO-d_6) of **20**



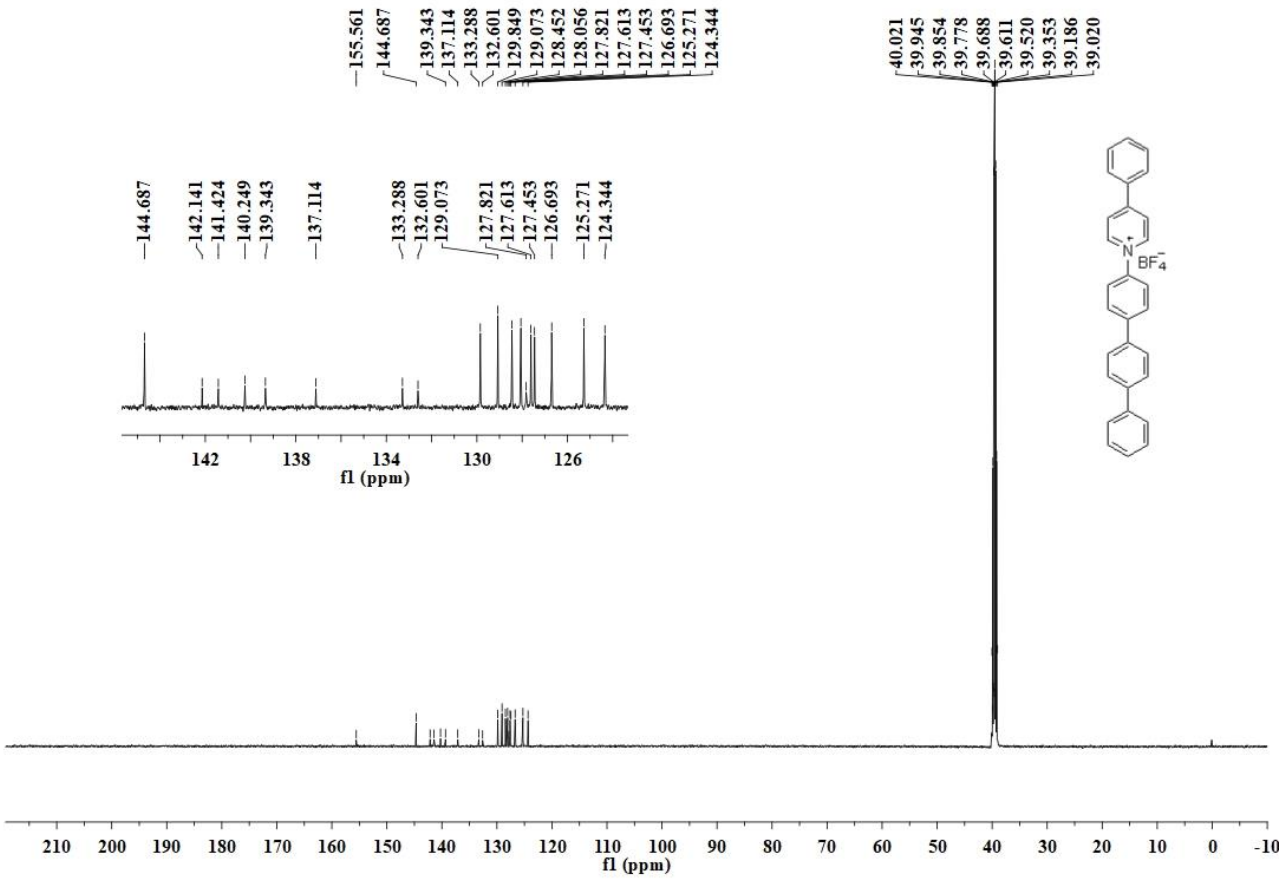
^{13}C NMR (125 MHz, DMSO-d_6) of **20**



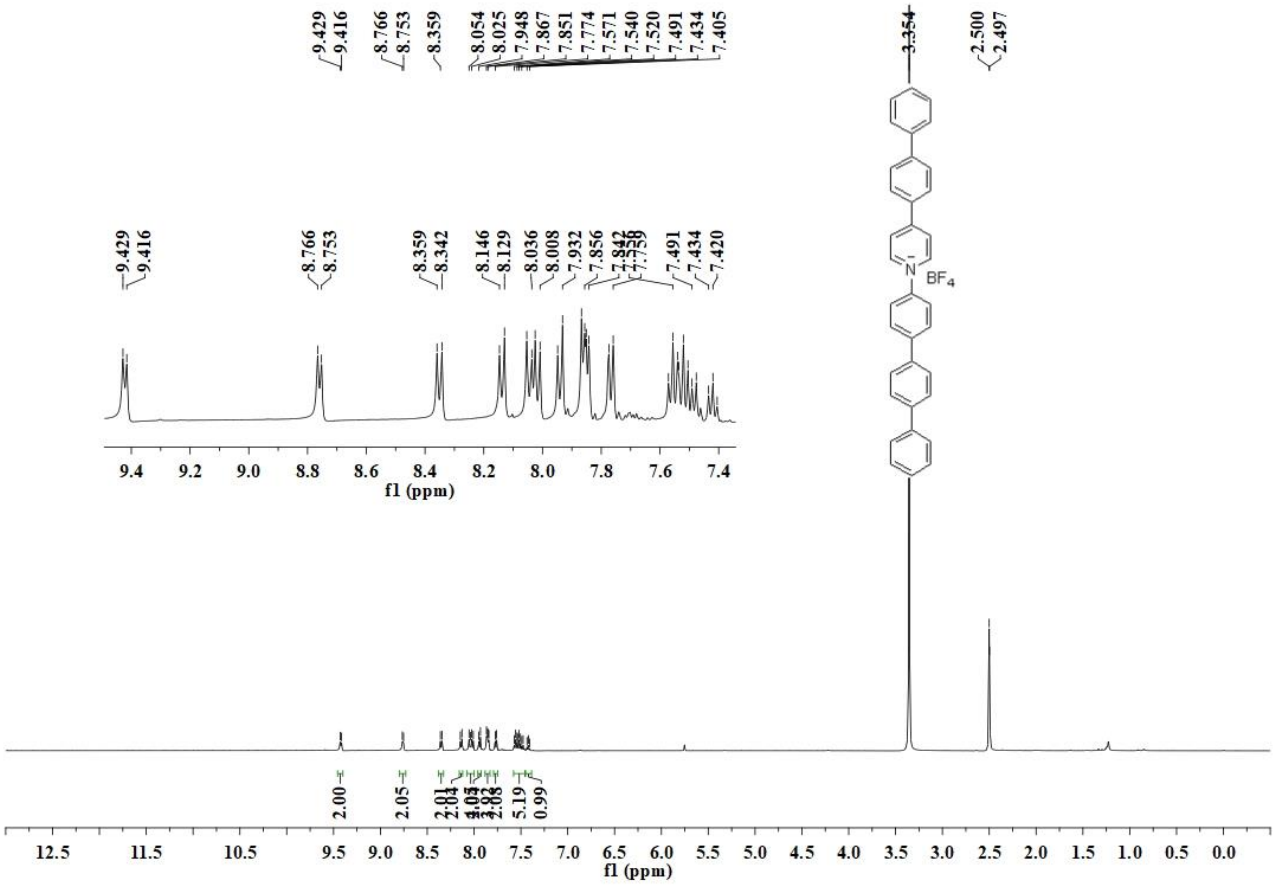
^{1}H NMR (500 MHz, DMSO-d_6) of **21**



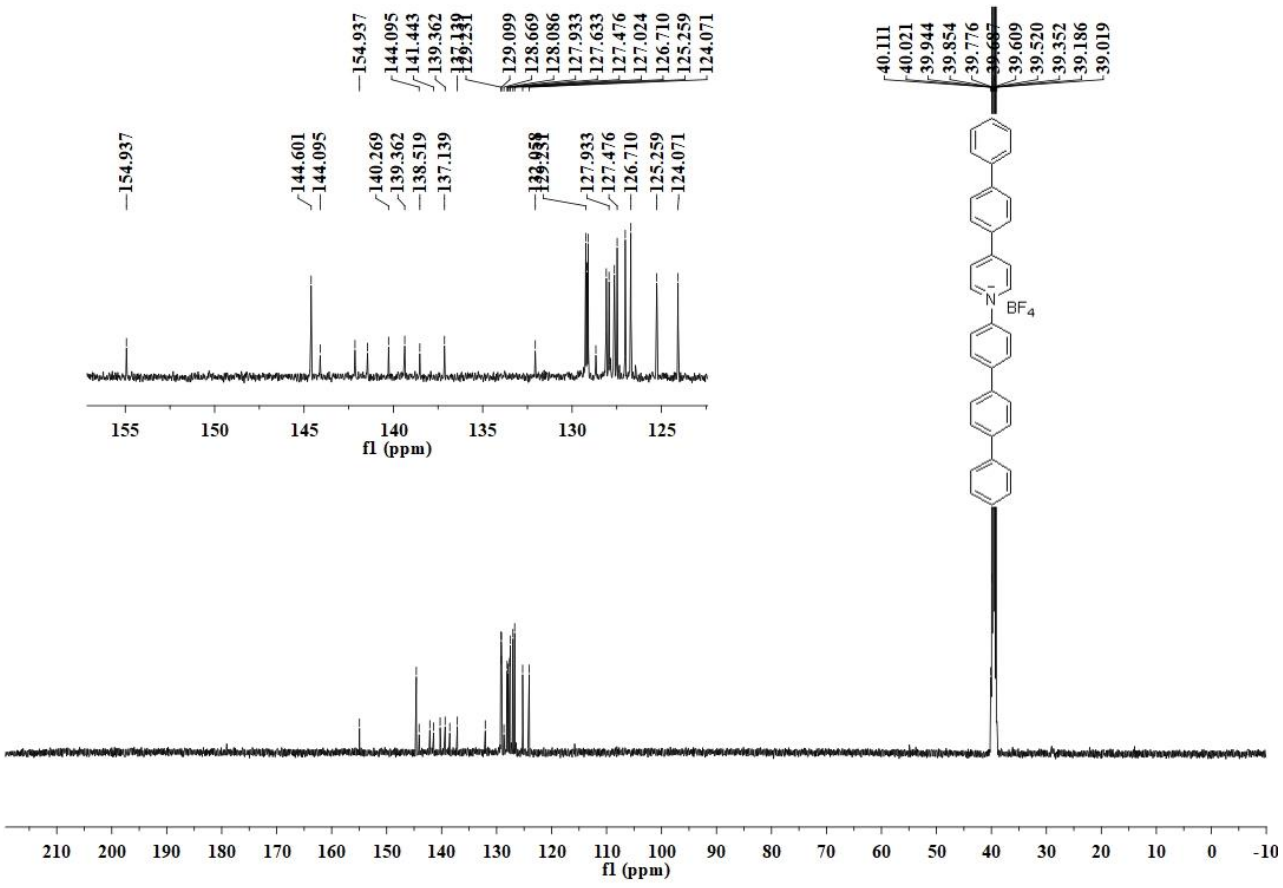
^{13}C NMR (125 MHz, DMSO-d_6) of **21**



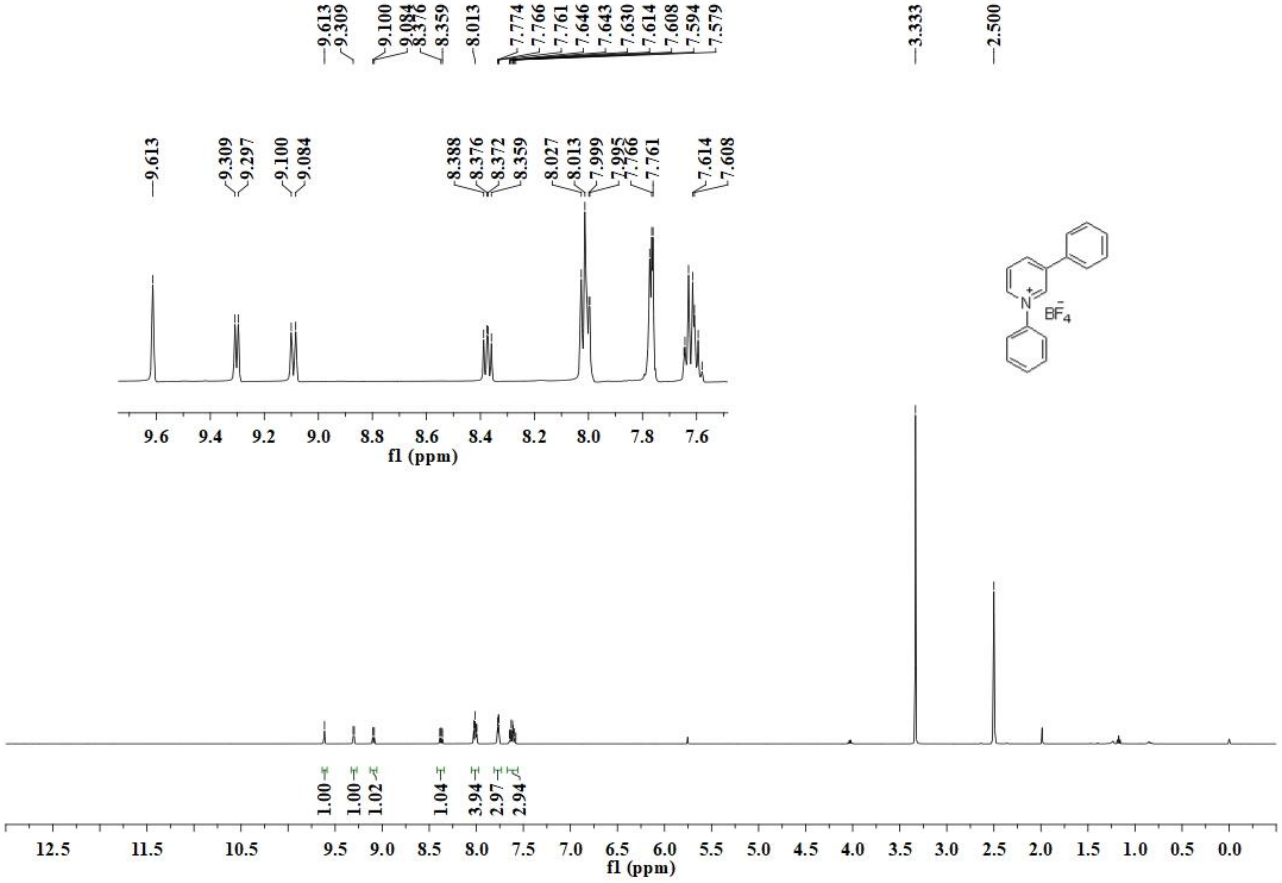
^{1}H NMR (500 MHz, DMSO-d_6) of **22**



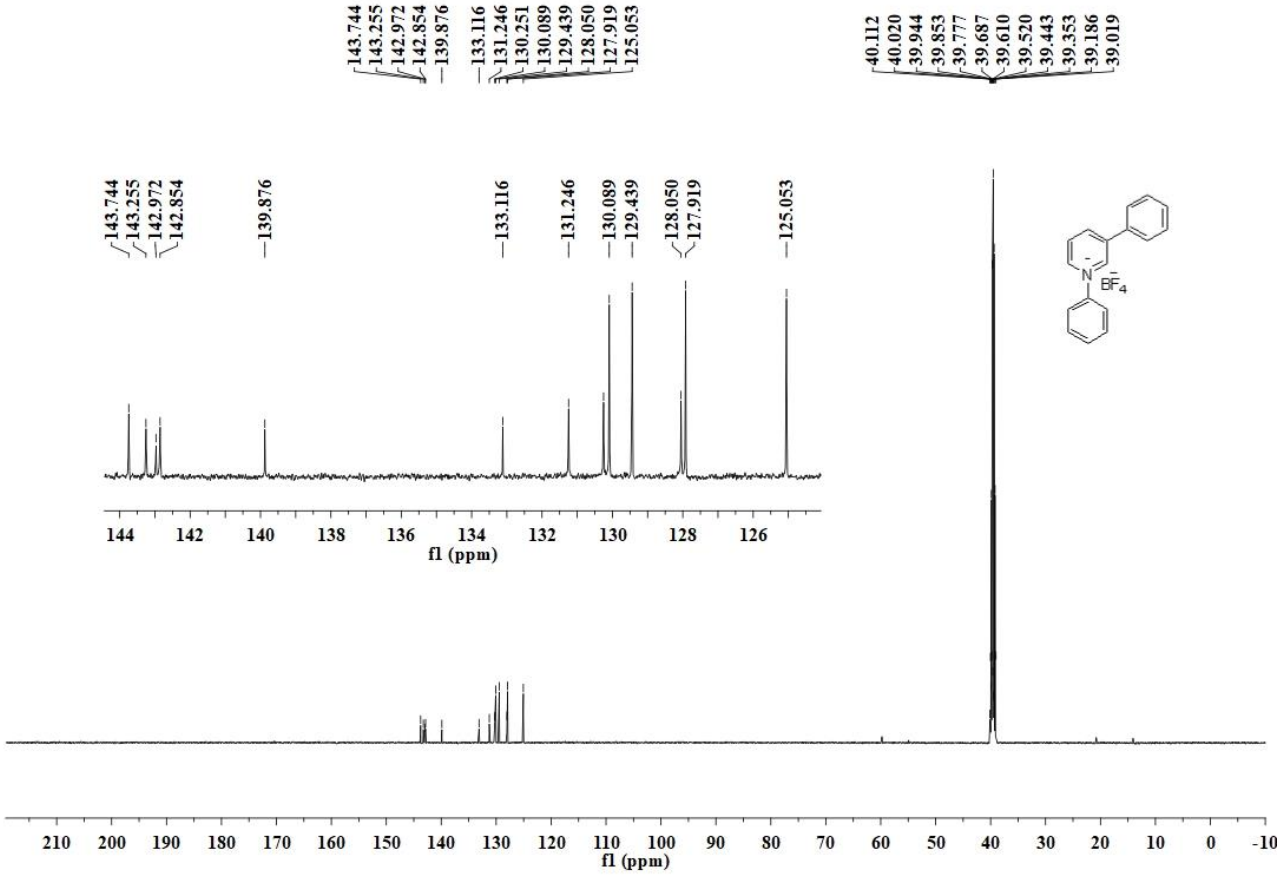
^{13}C NMR (125 MHz, DMSO-d_6) of **22**



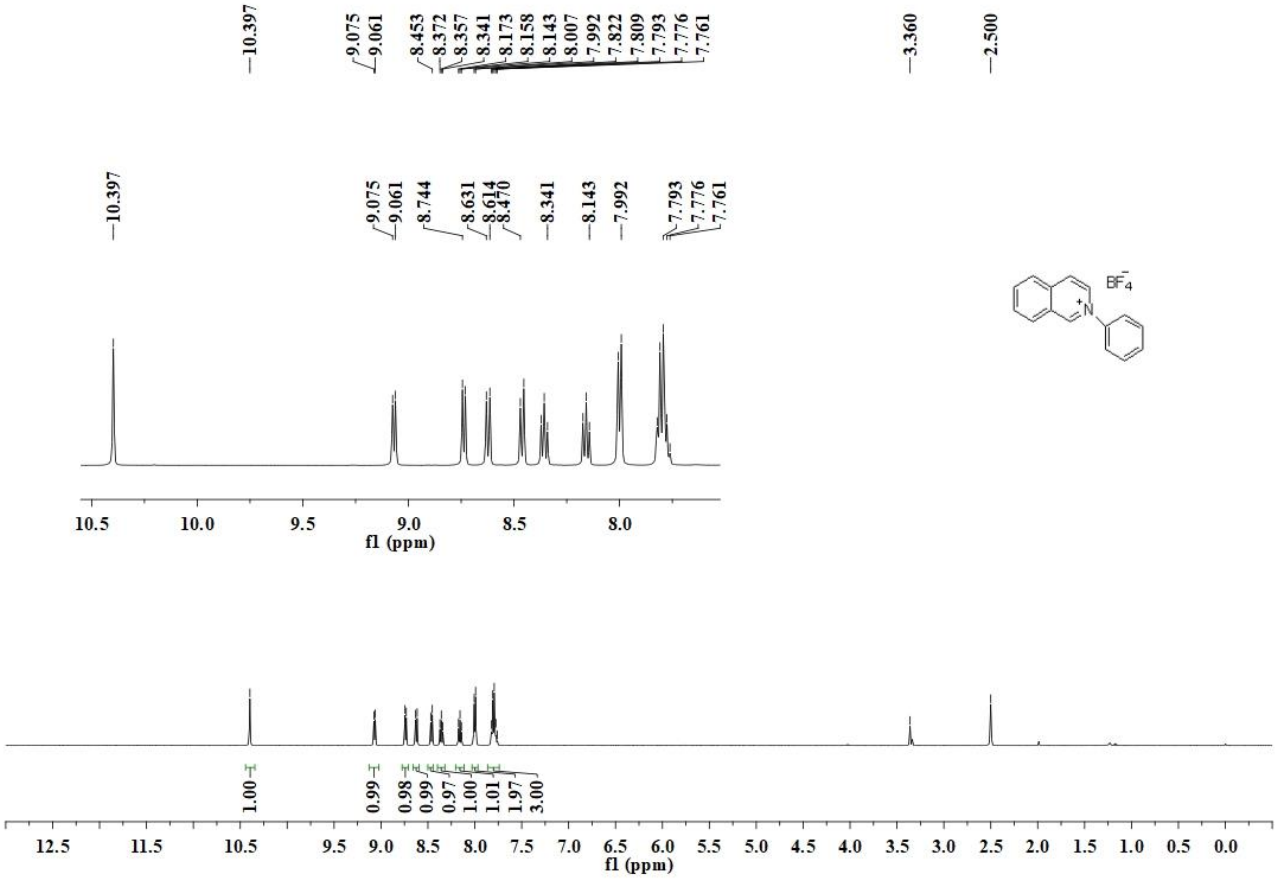
^{1}H NMR (500 MHz, DMSO-d_6) of **23**



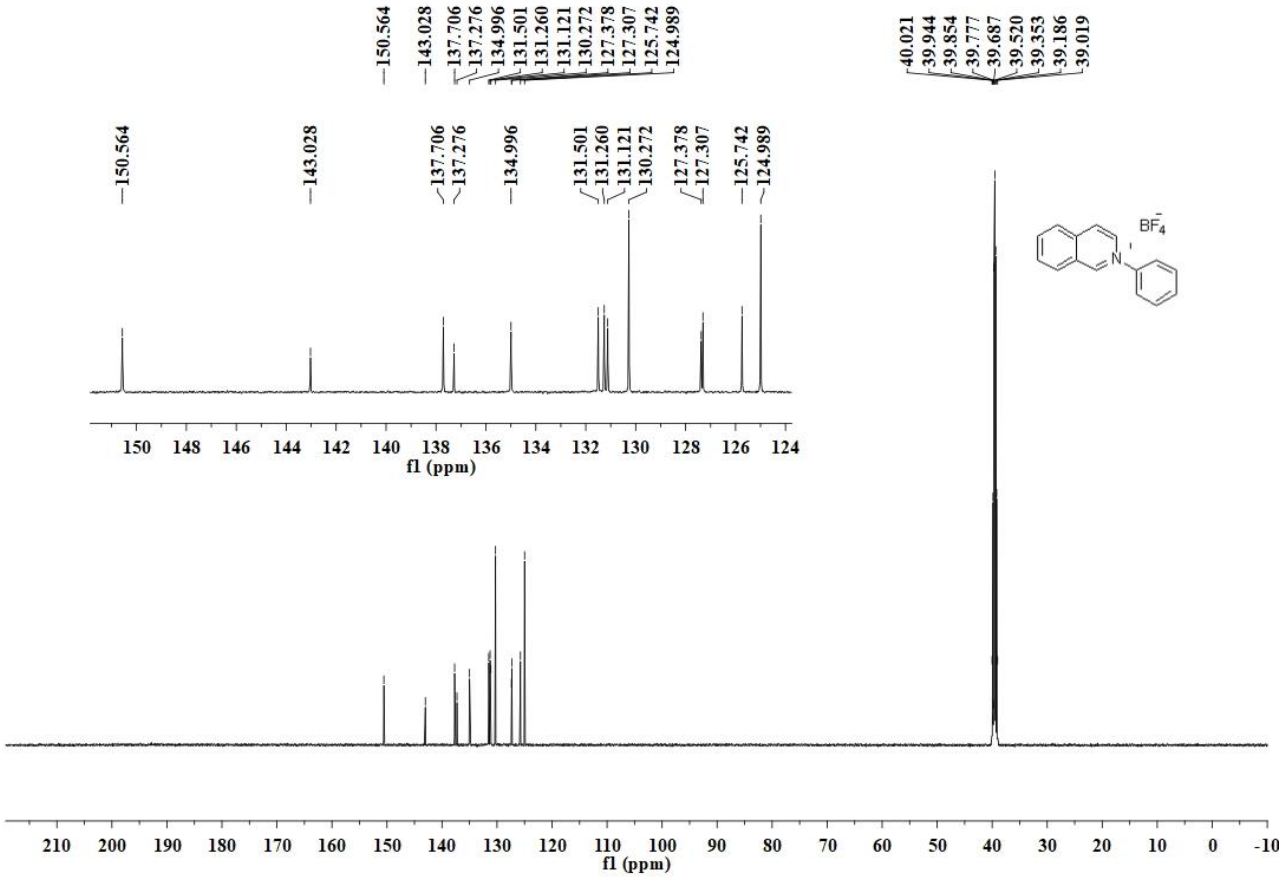
^{13}C NMR (125 MHz, DMSO-d_6) of **23**



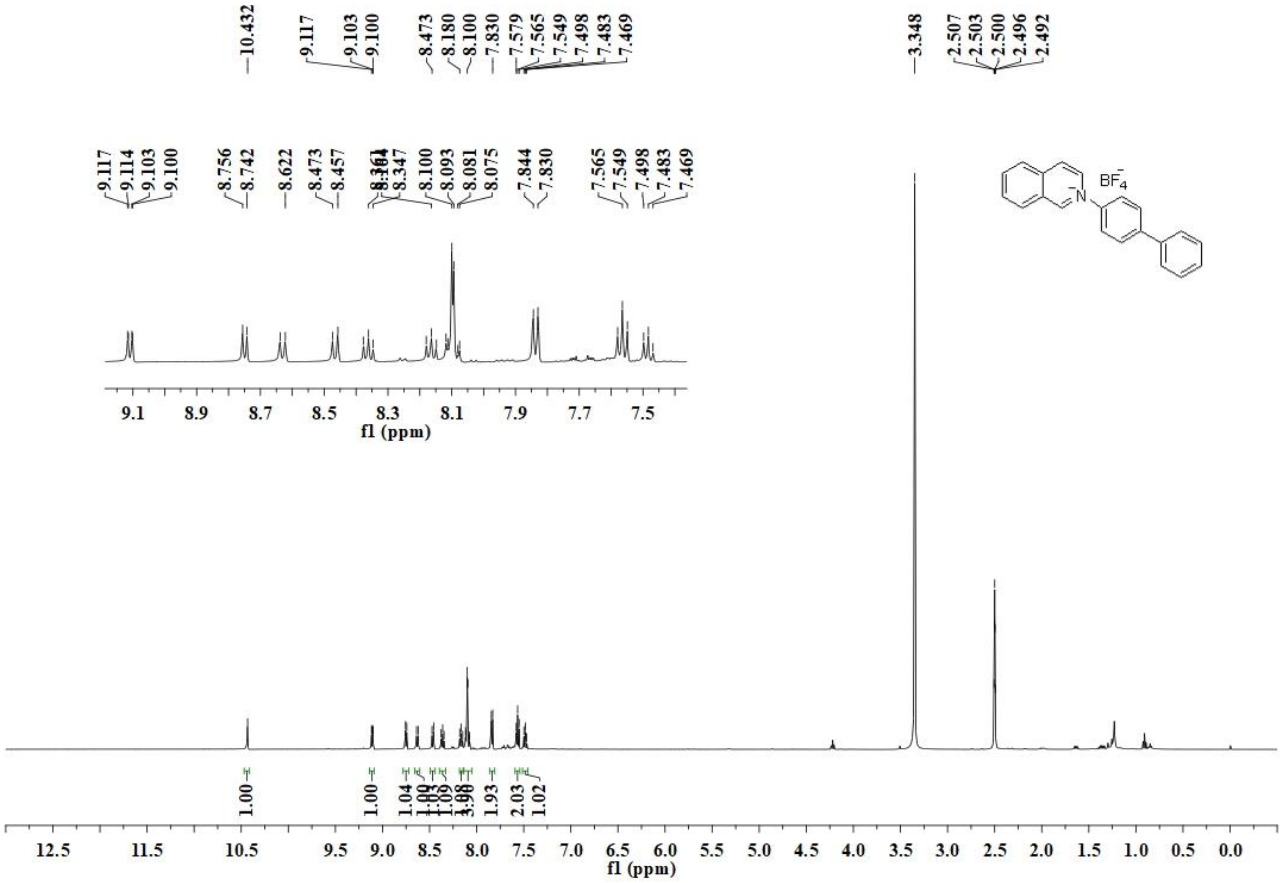
^{1}H NMR (500 MHz, DMSO-d_6) of **24**



^{13}C NMR (125 MHz, DMSO-d_6) of **24**



^{1}H NMR (500 MHz, DMSO-d_6) of **25**



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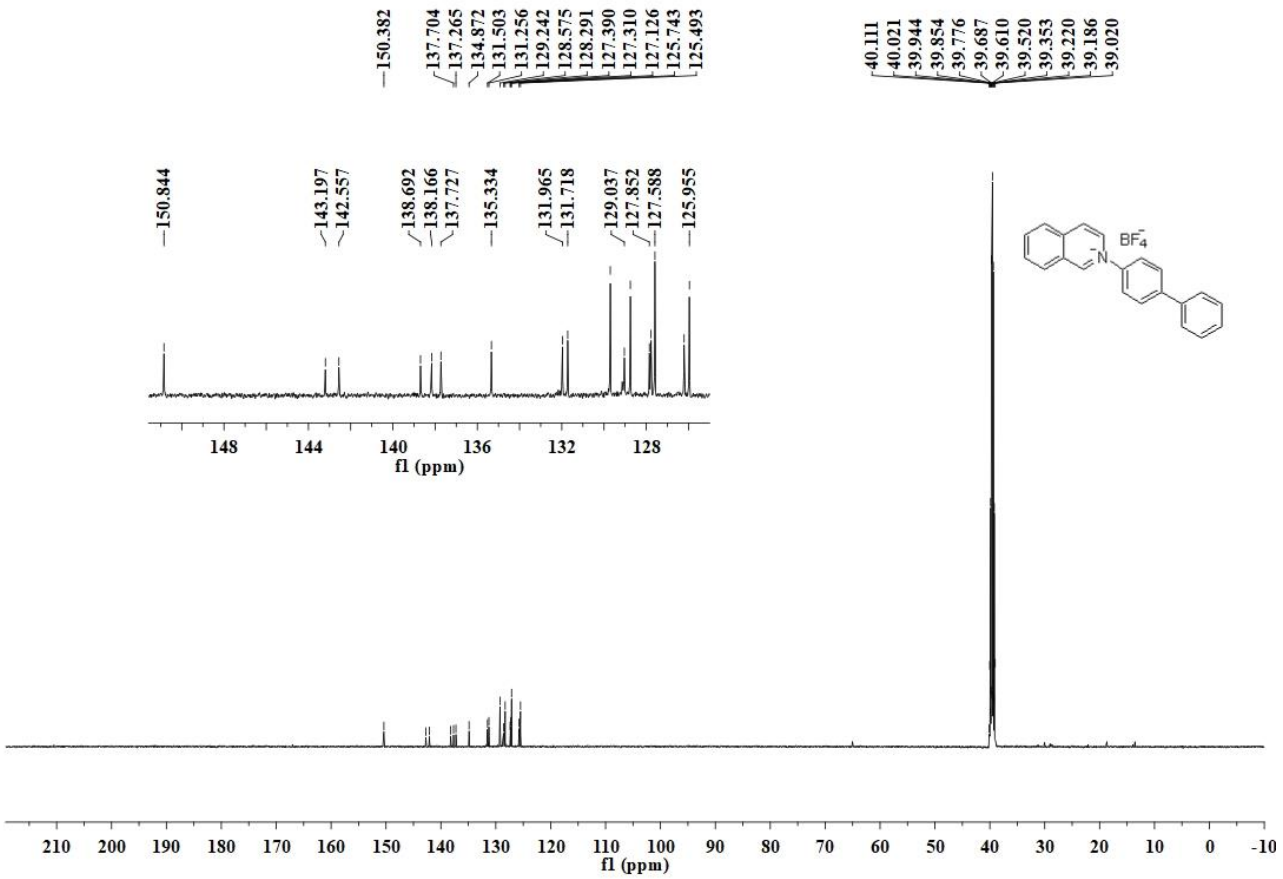
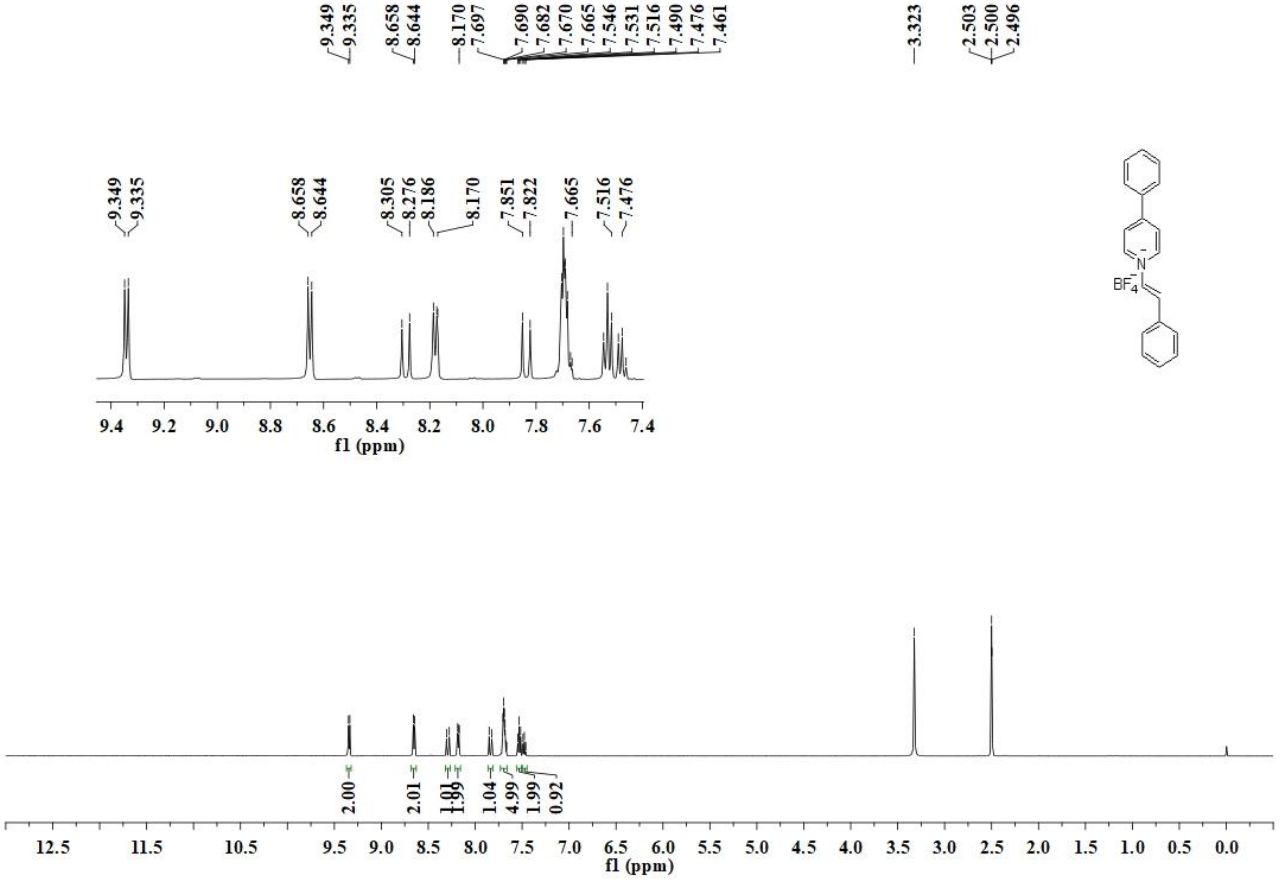
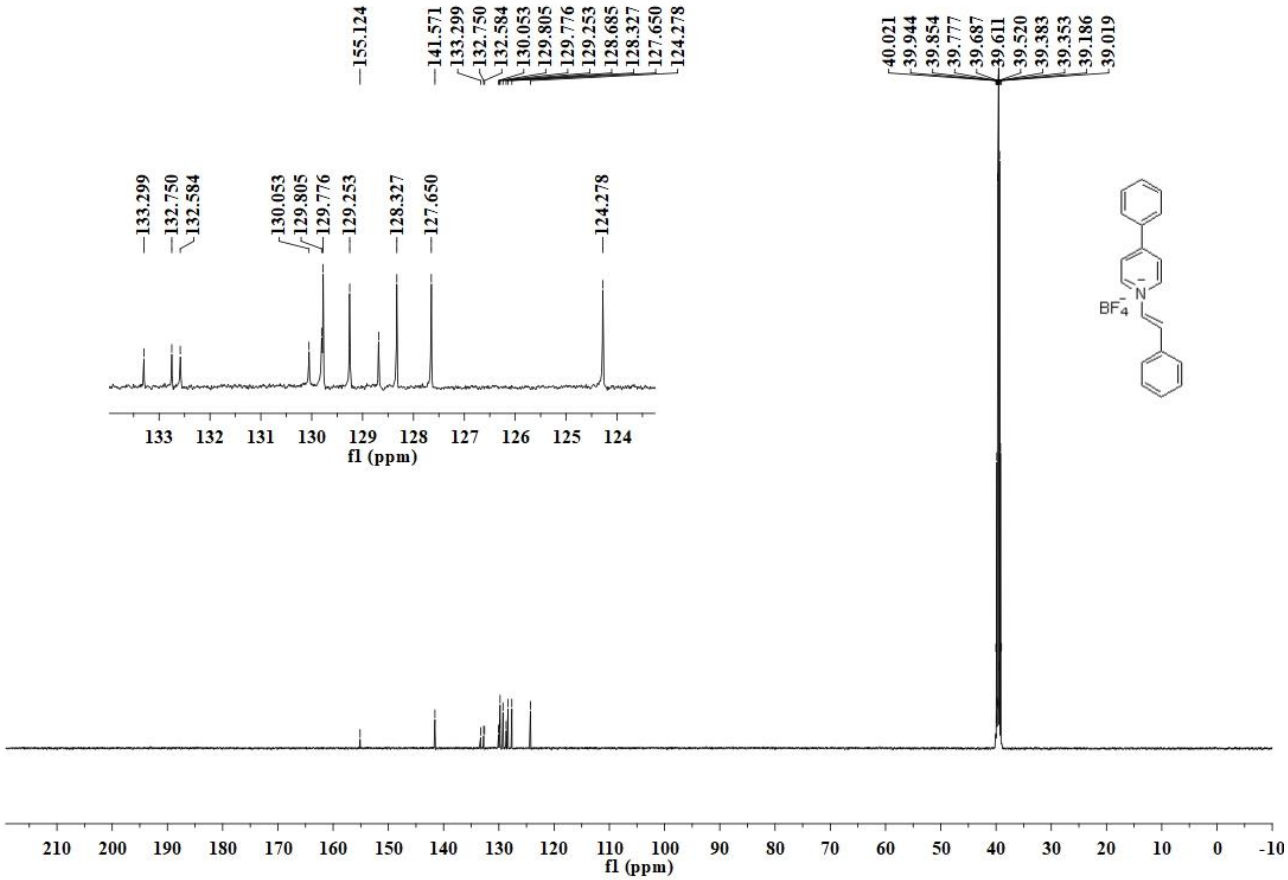


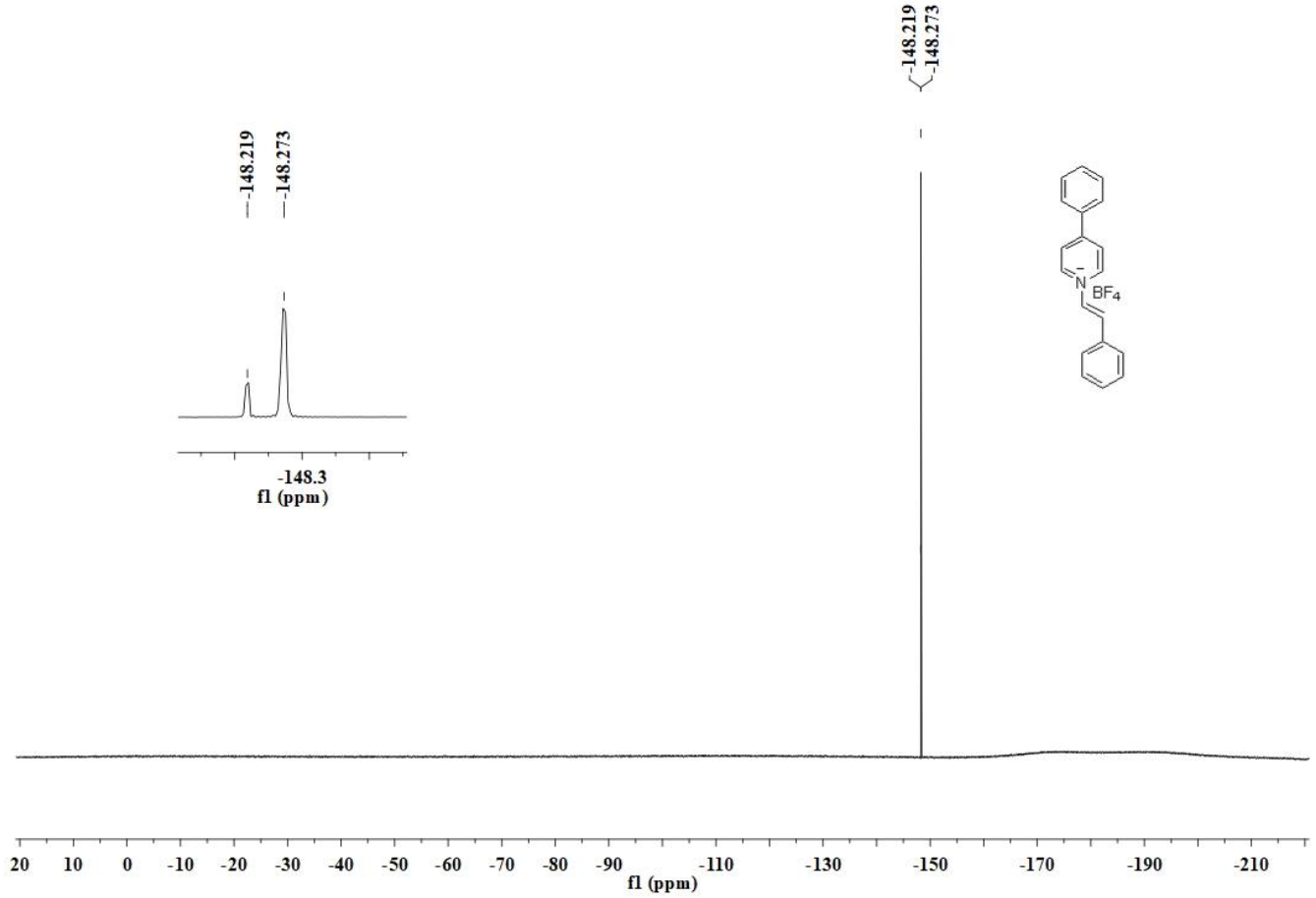
^{1}H NMR (500 MHz, DMSO-d_6) of **27**



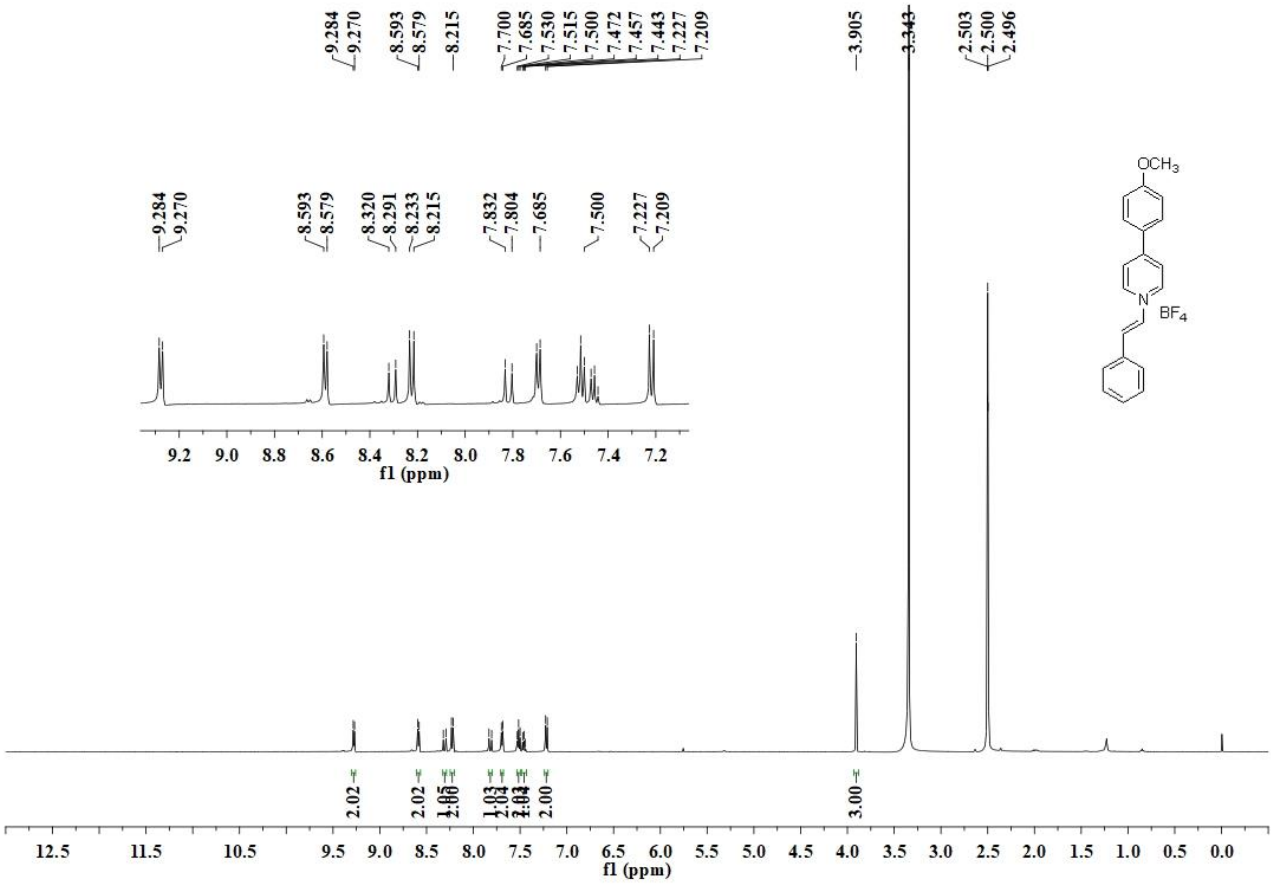
^{13}C NMR (125 MHz, DMSO-d_6) of **27**



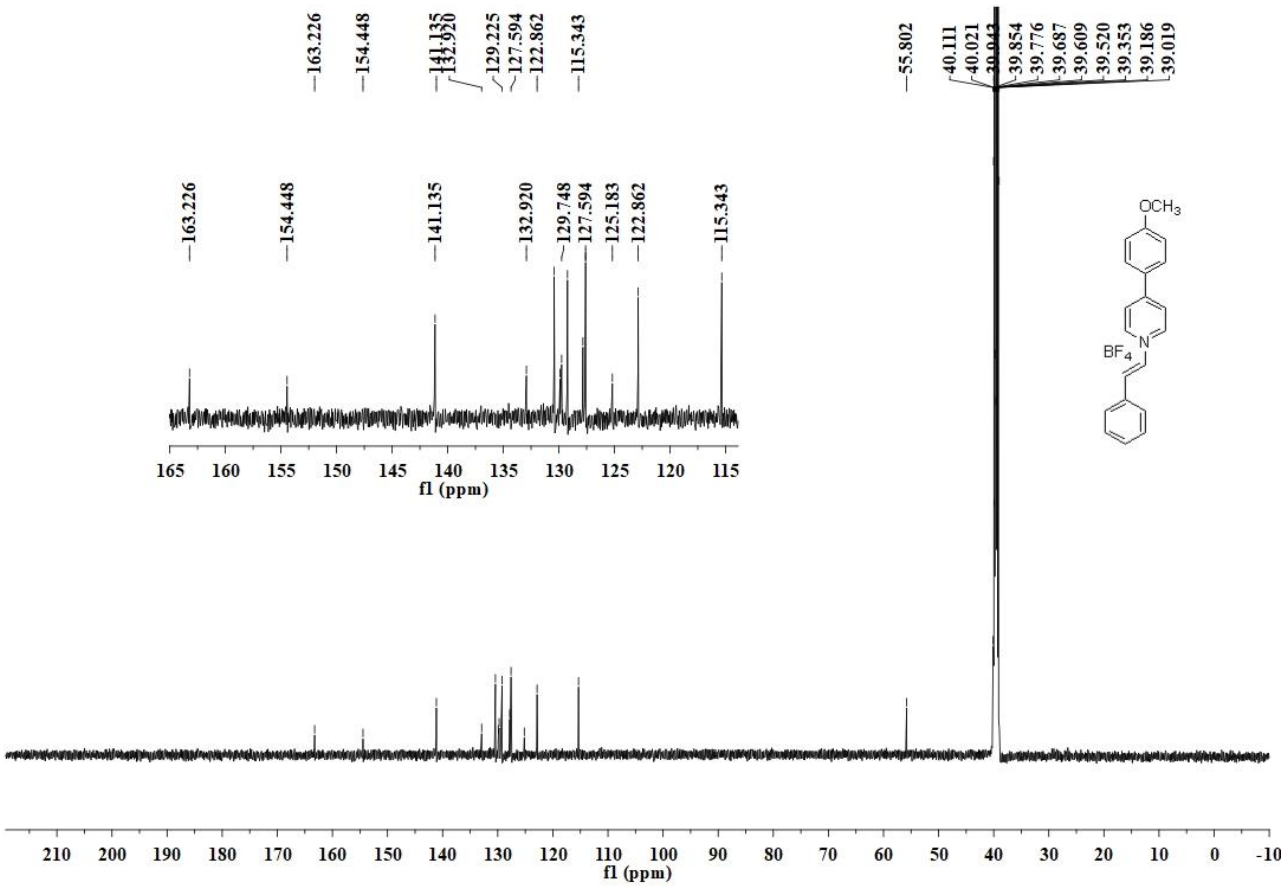
^{19}F NMR (471 MHz, DMSO-d_6) of **27**



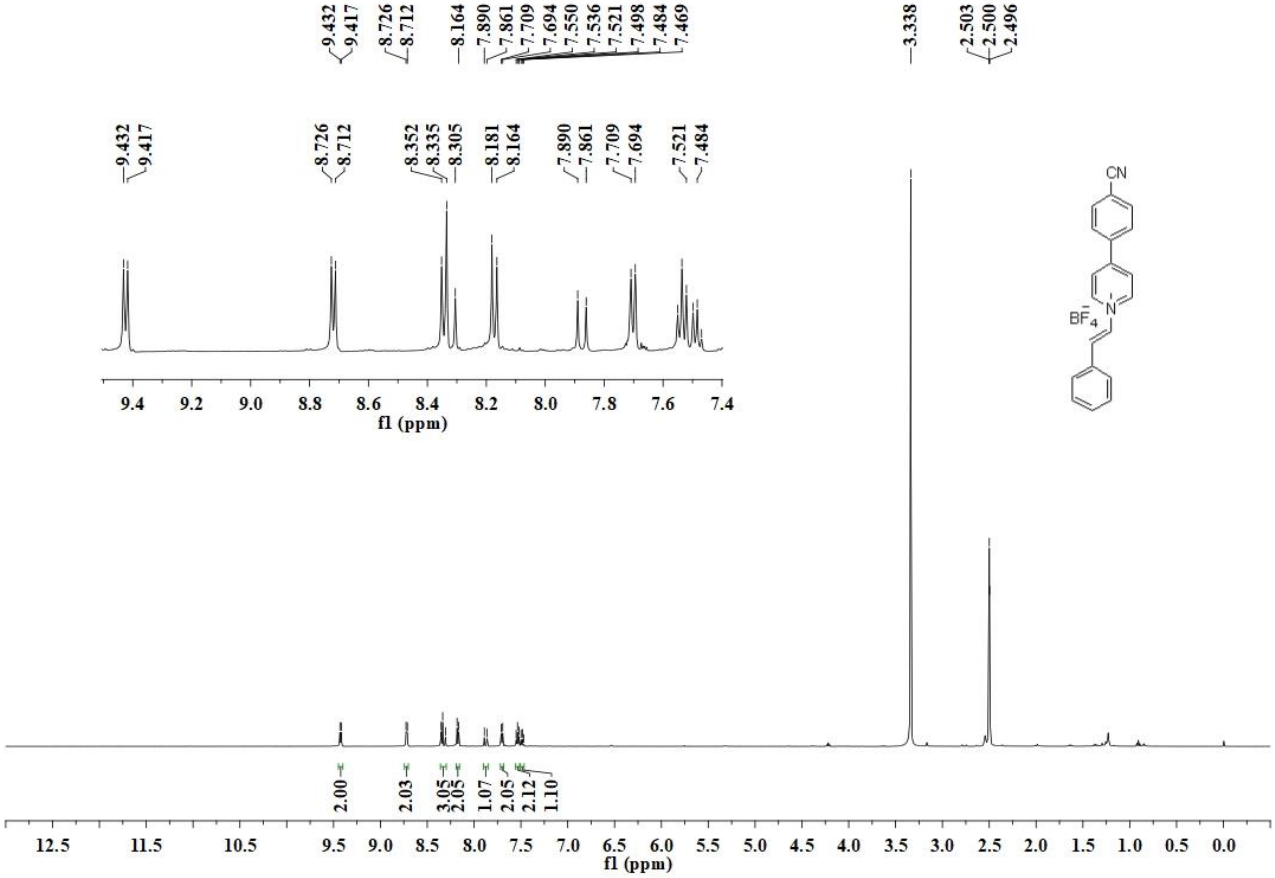
^{1}H NMR (500 MHz, DMSO-d_6) of **28**



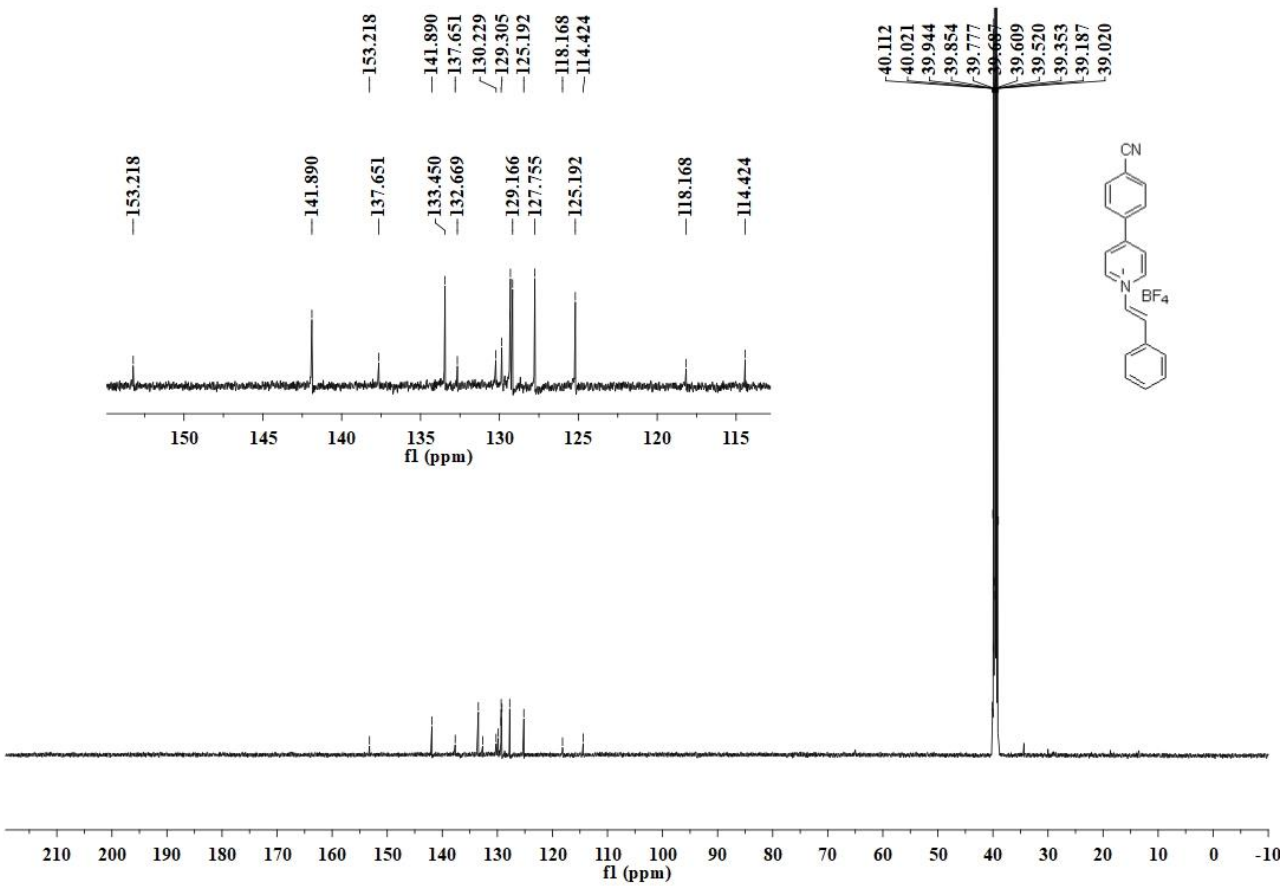
^{13}C NMR (125 MHz, DMSO-d_6) of **28**



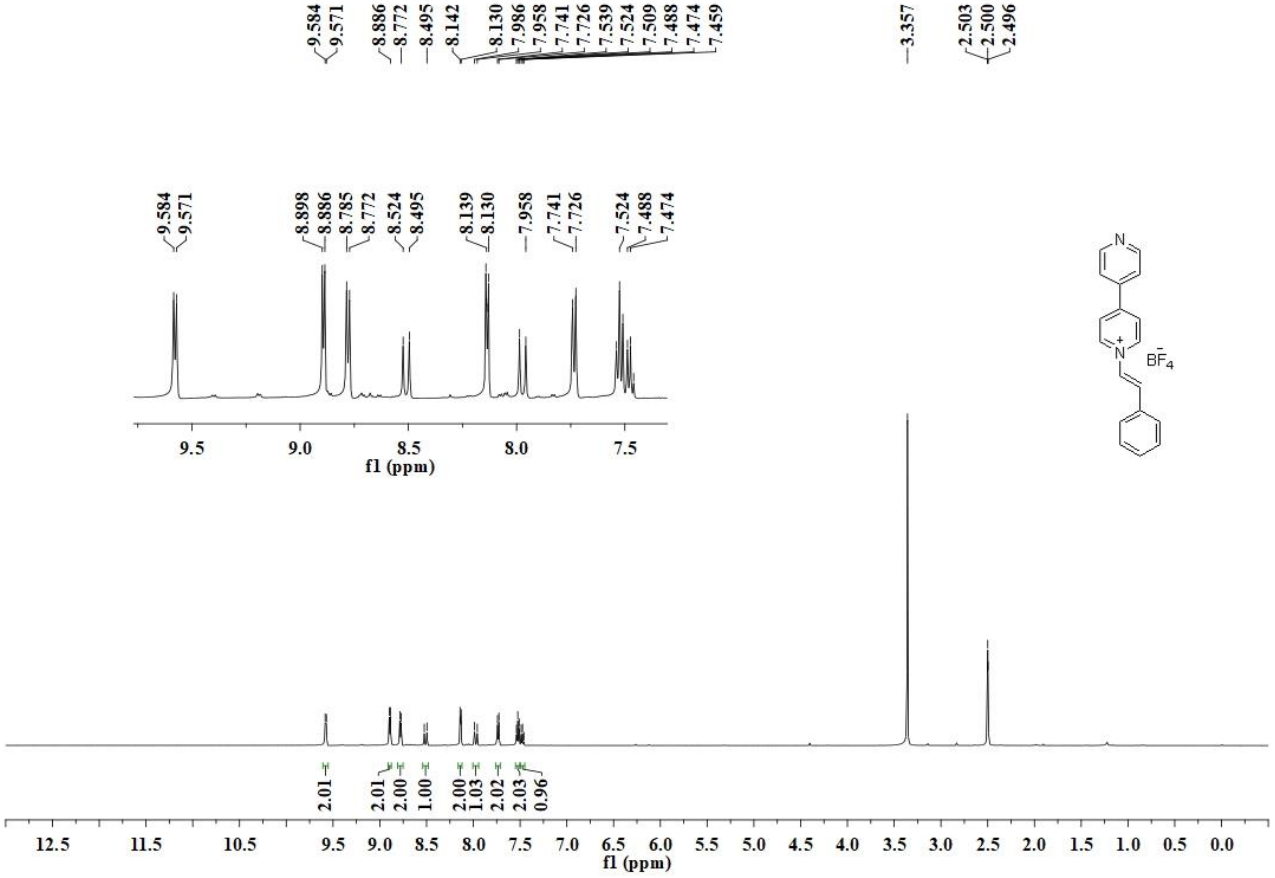
^{1}H NMR (500 MHz, DMSO-d_6) of **29**



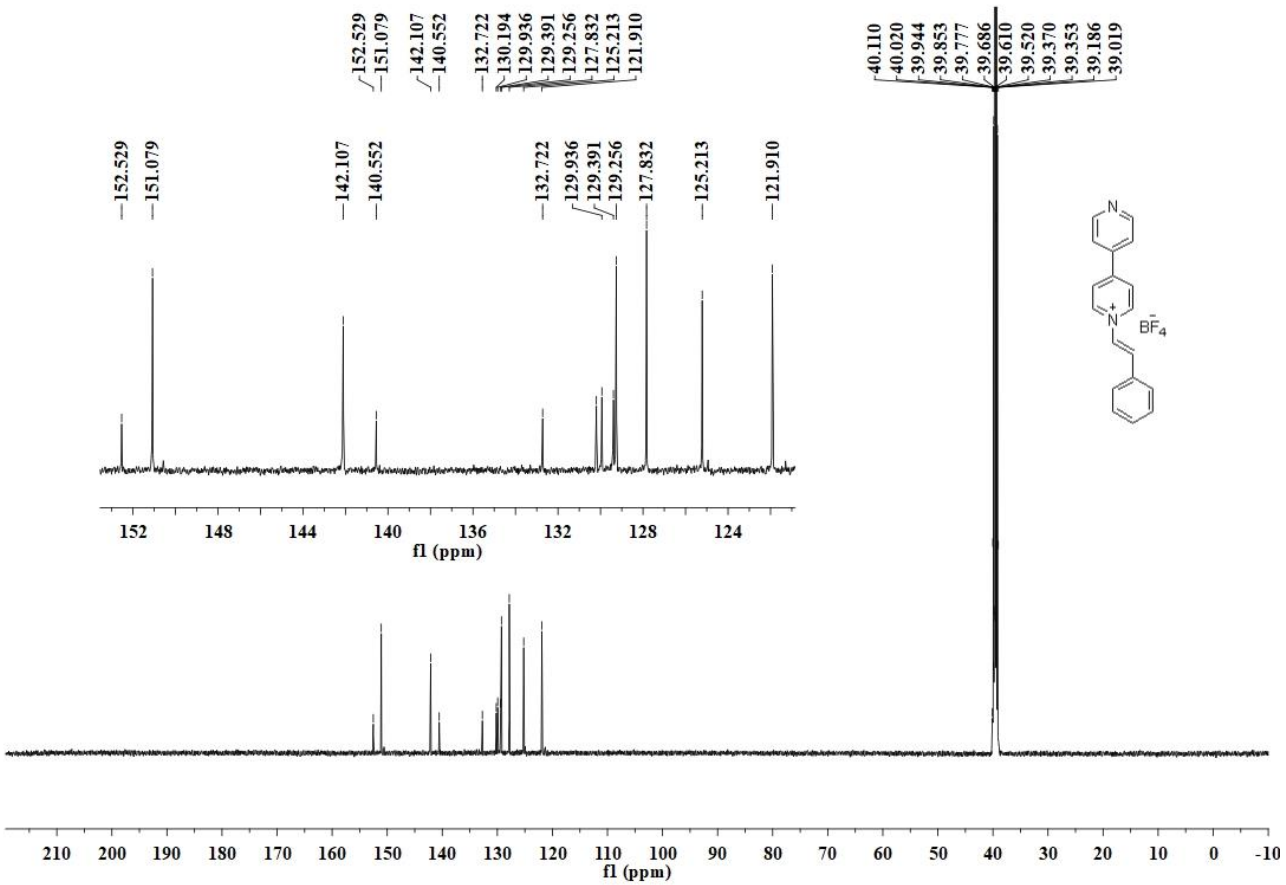
^{13}C NMR (125 MHz, DMSO-d_6) of **29**



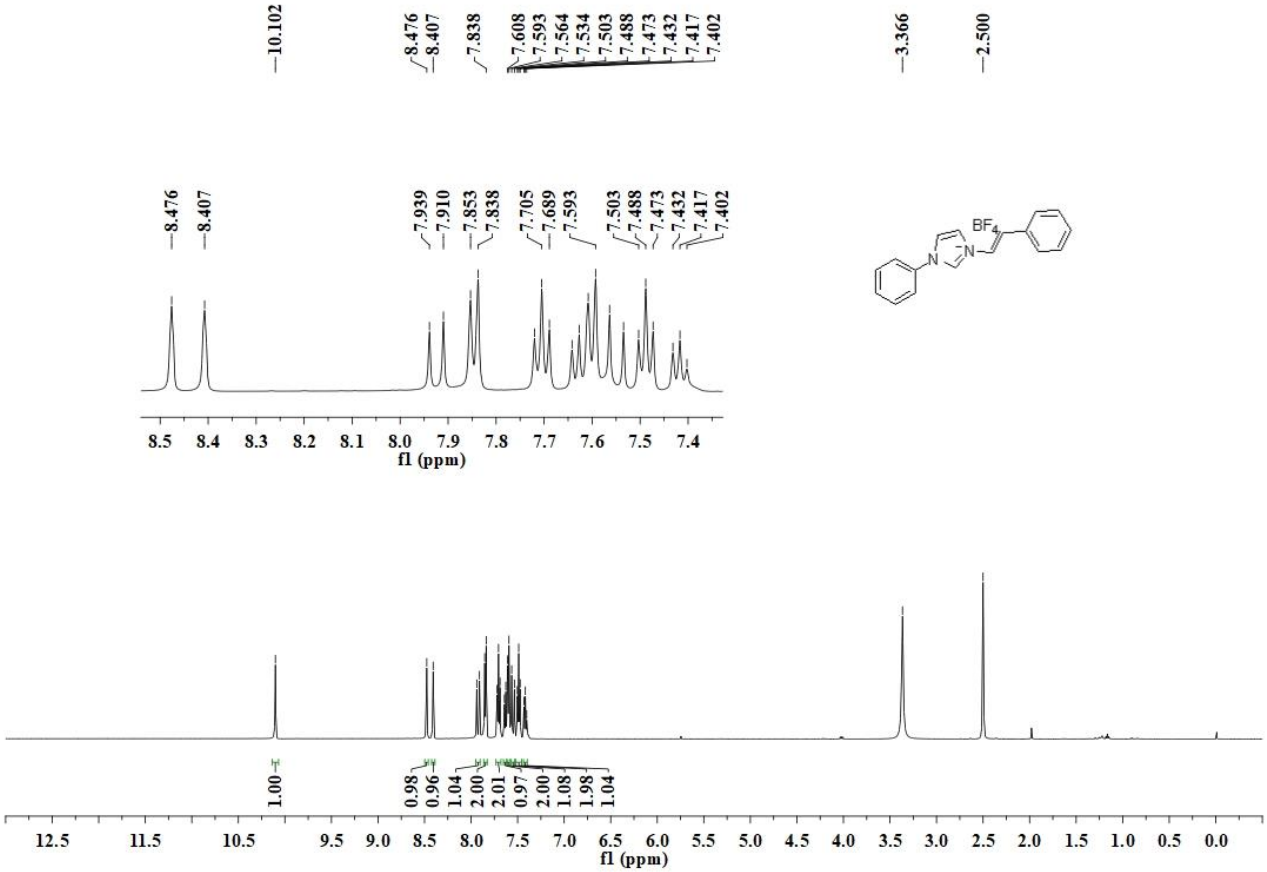
^{1}H NMR (500 MHz, DMSO-d_6) of **30**



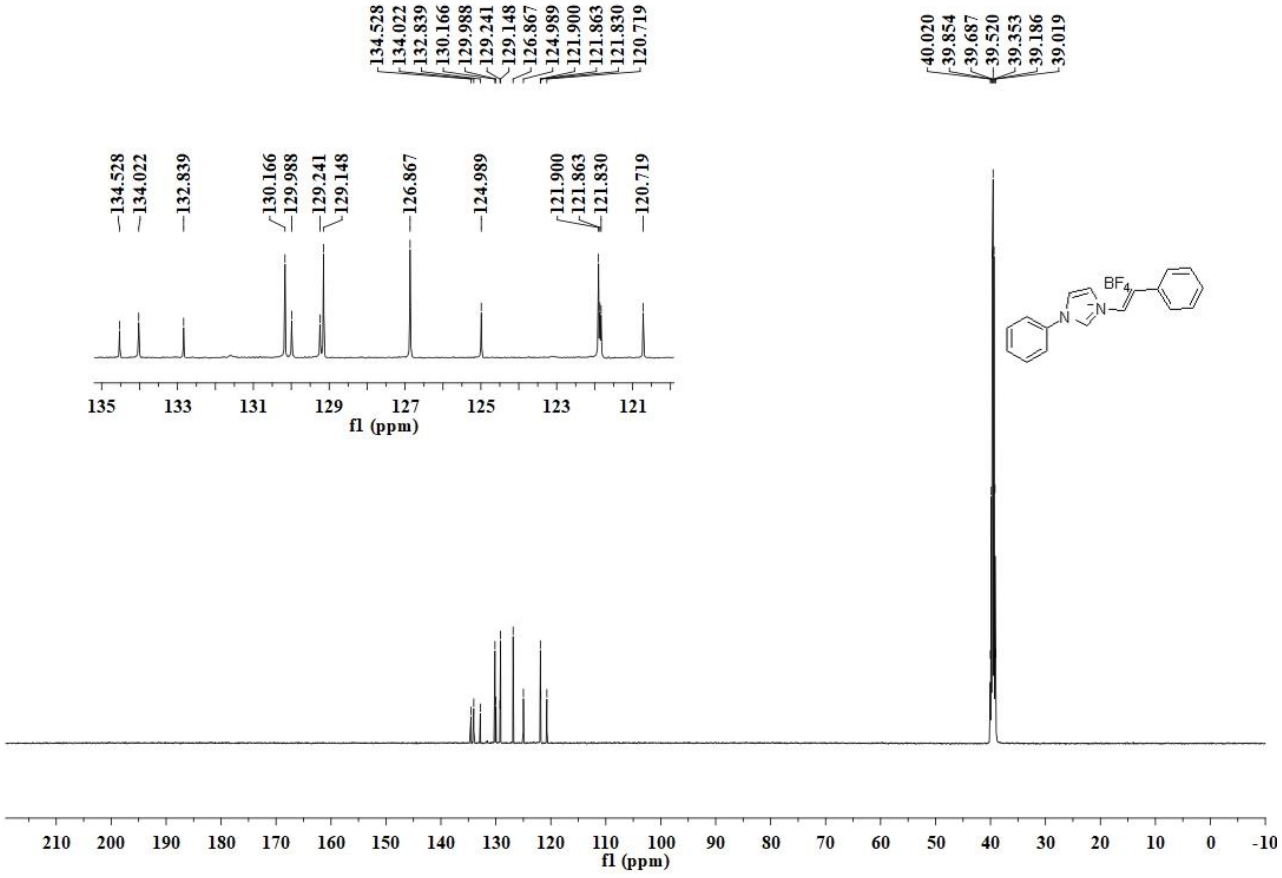
^{13}C NMR (125 MHz, DMSO-d_6) of **30**



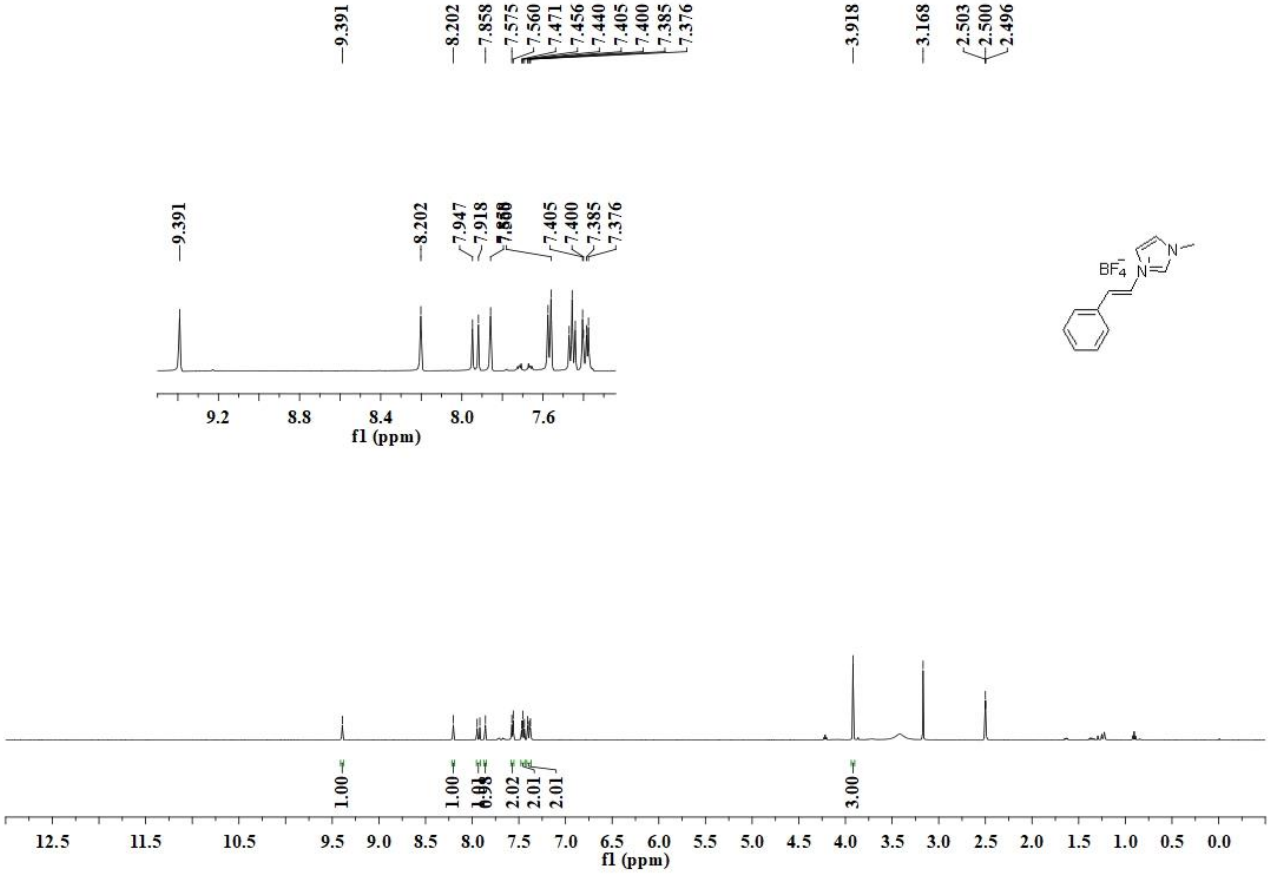
^{1}H NMR (500 MHz, DMSO-d_6) of **31**



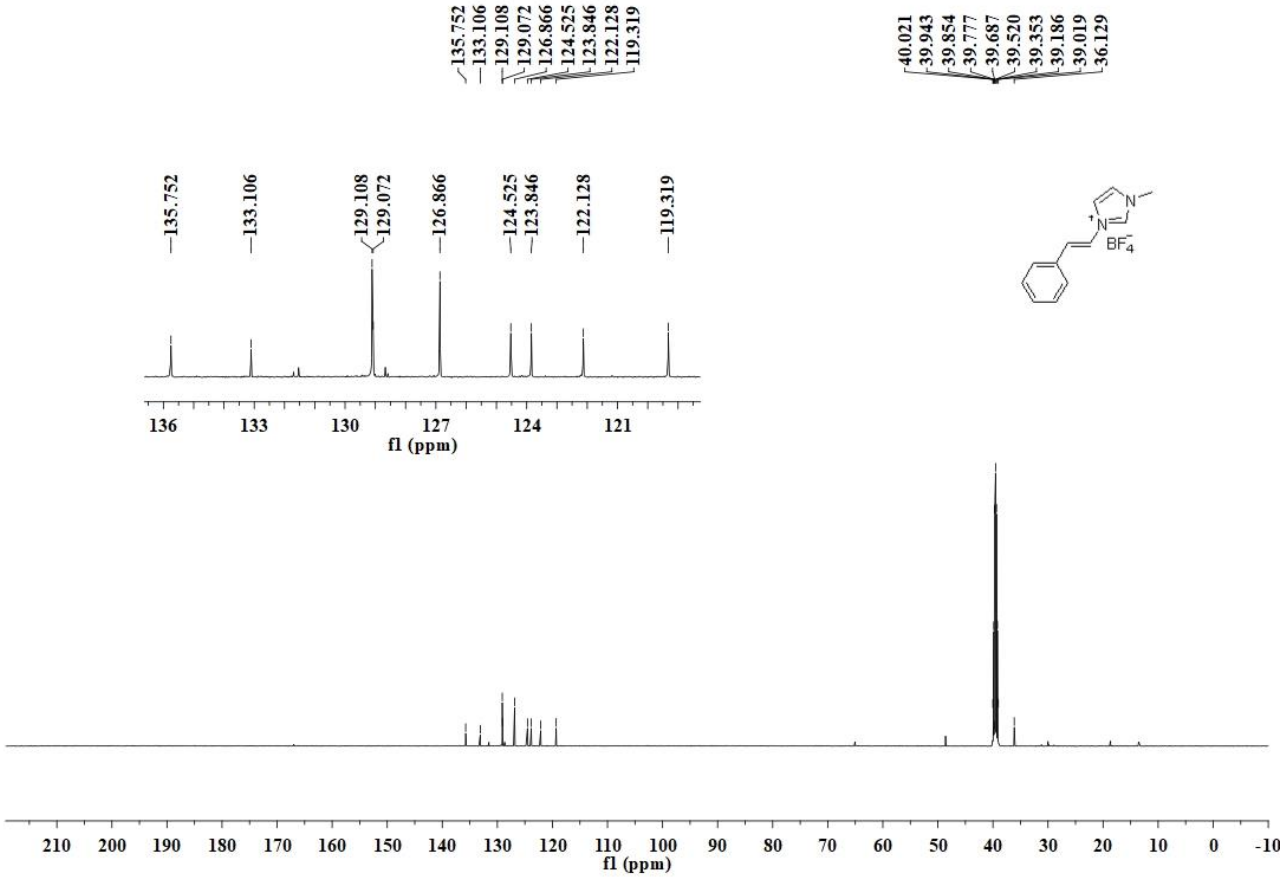
^{13}C NMR (125 MHz, DMSO-d_6) of **31**



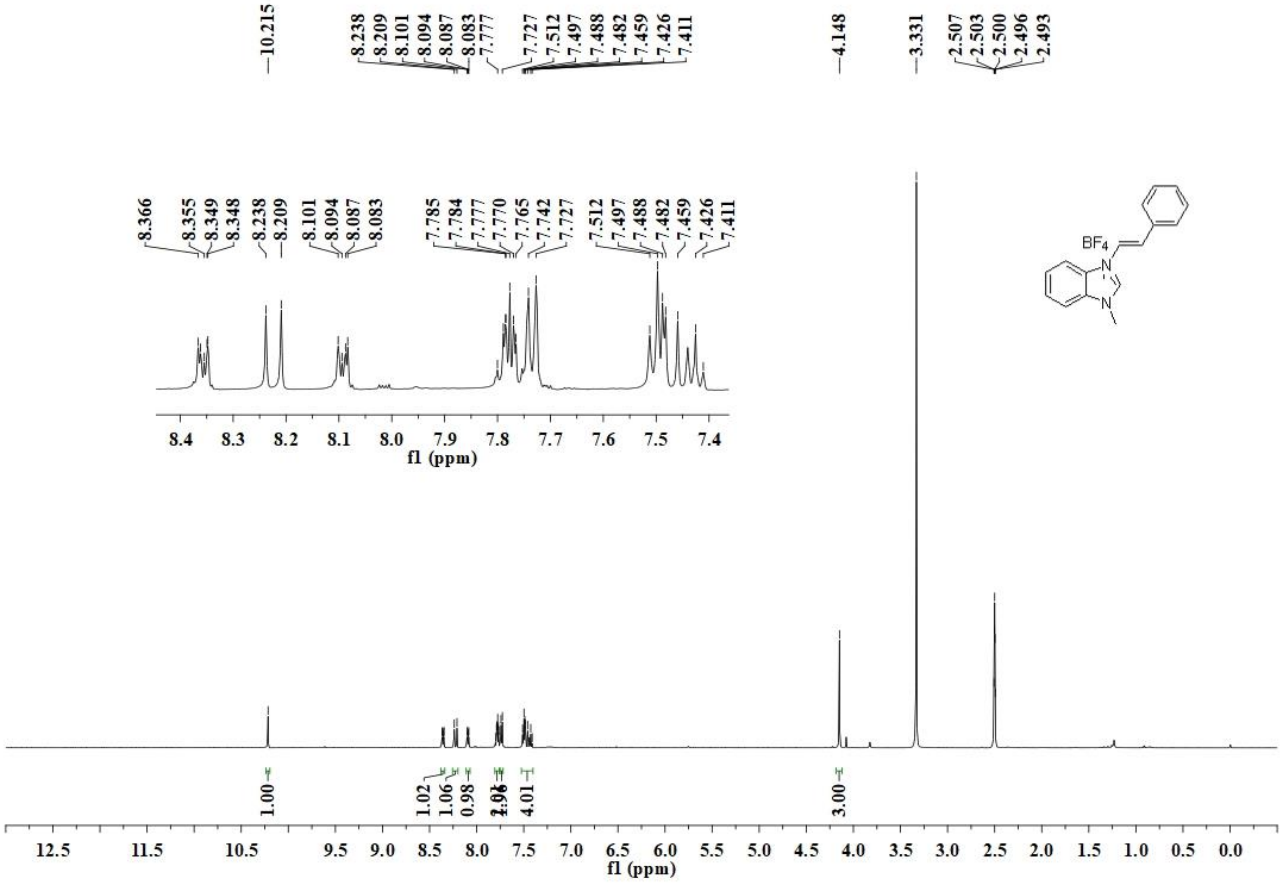
^{1}H NMR (500 MHz, DMSO-d_6) of **32**



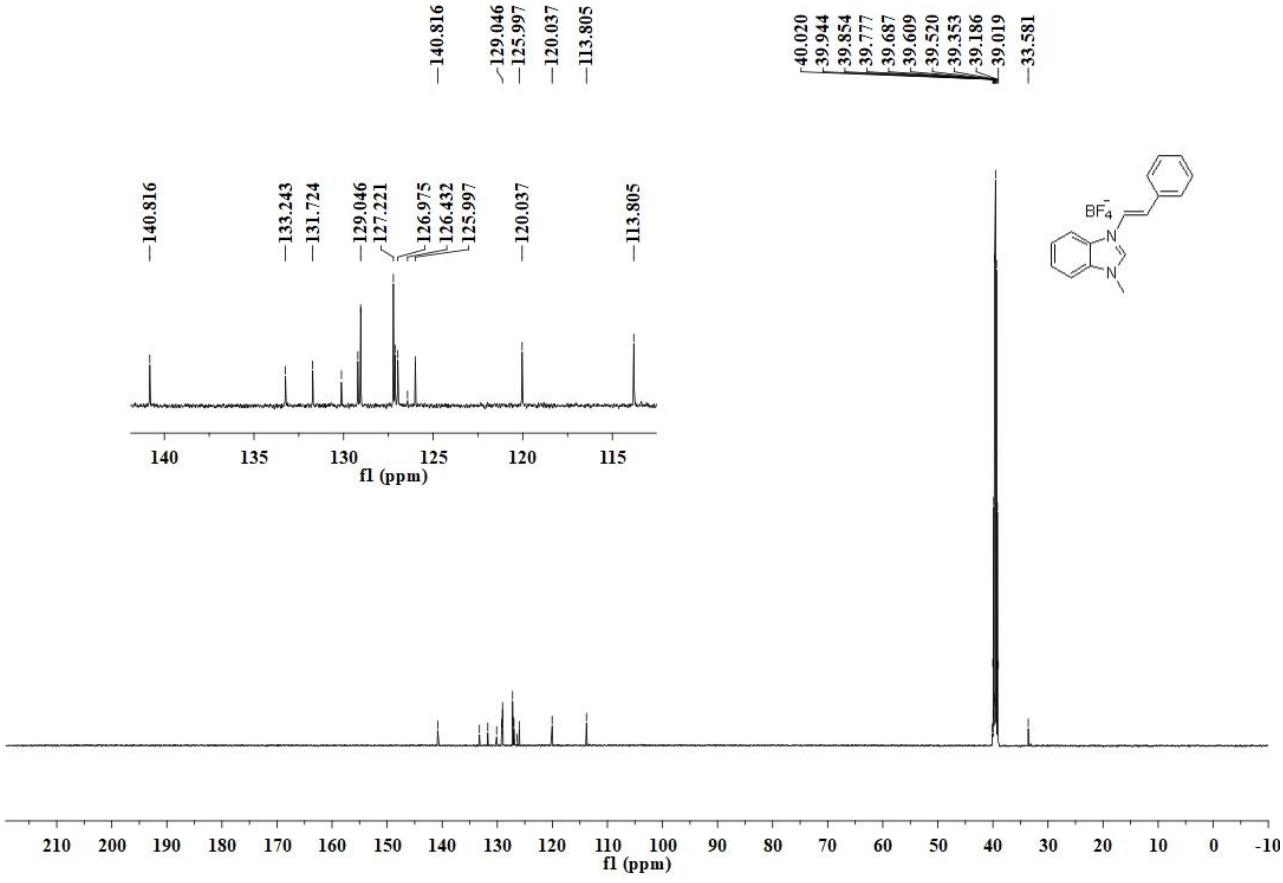
^{13}C NMR (125 MHz, DMSO-d_6) of **32**



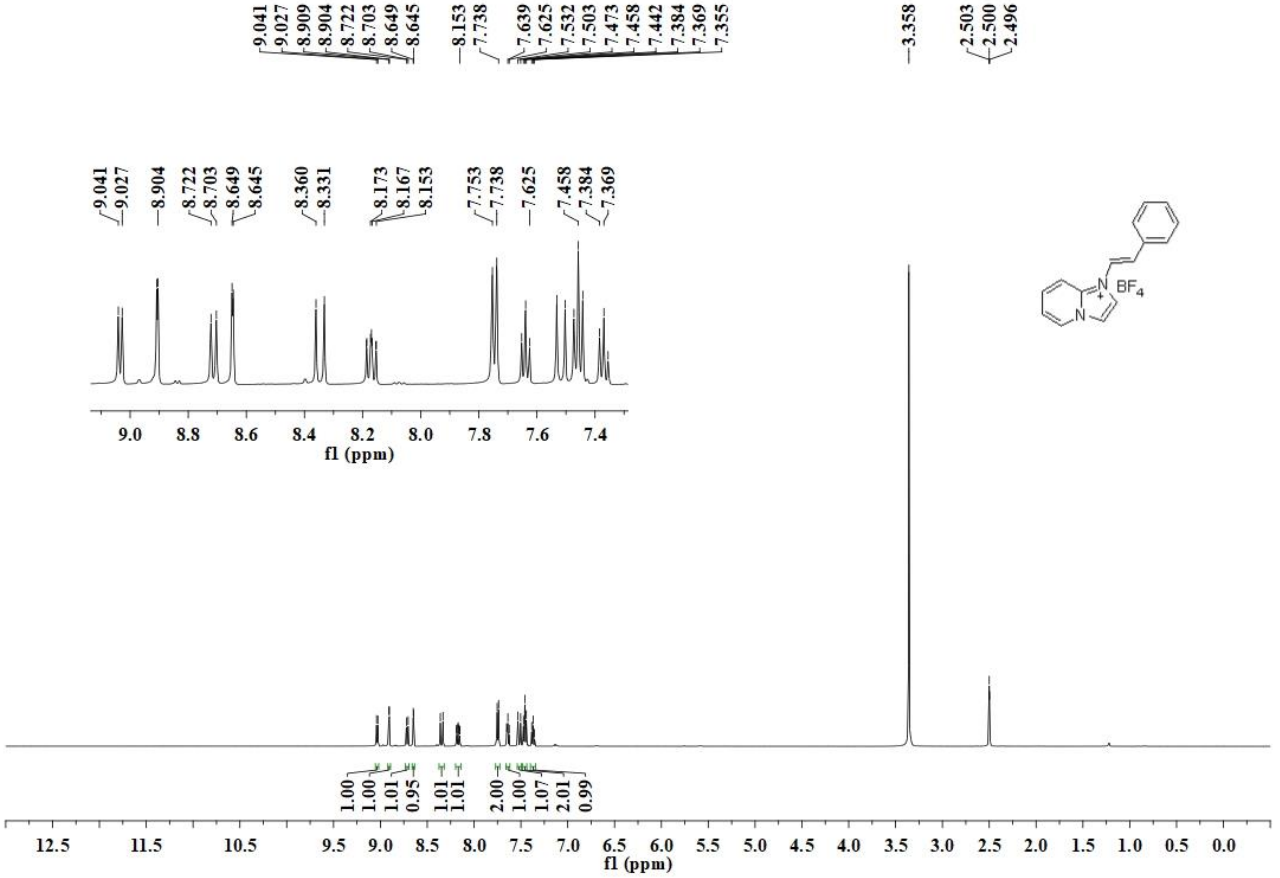
^{1}H NMR (500 MHz, DMSO-d_6) of **33**



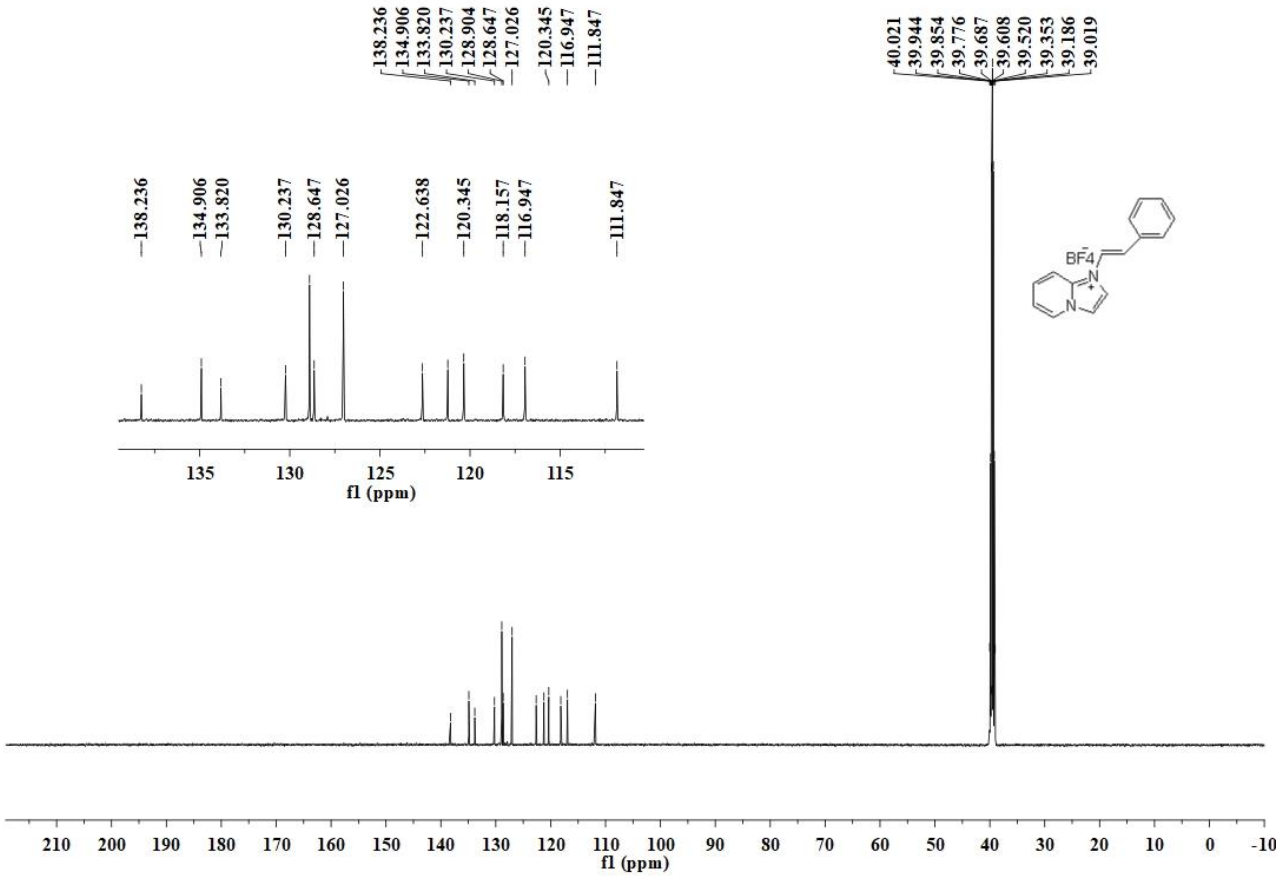
^{13}C NMR (125 MHz, DMSO-d_6) of **33**



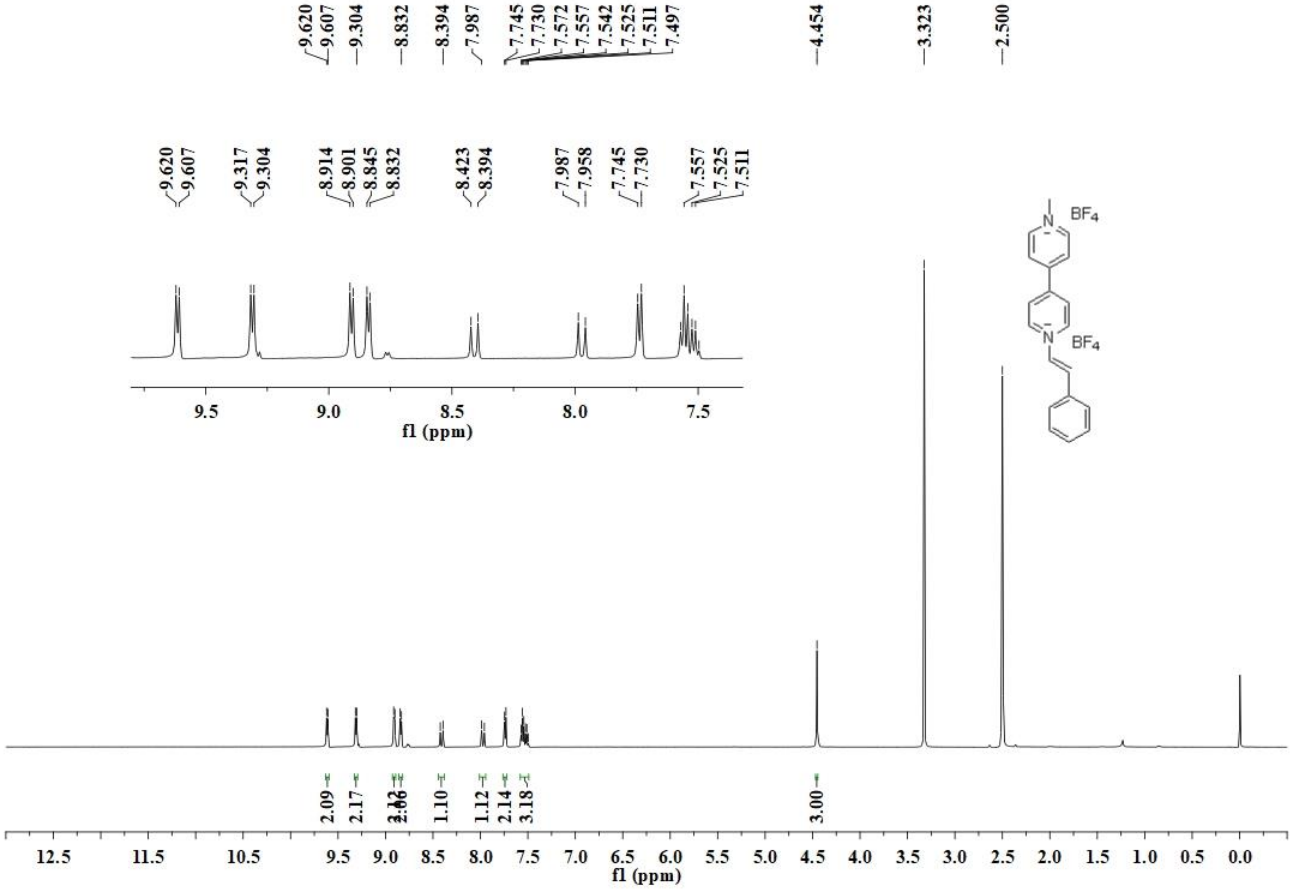
^{1}H NMR (500 MHz, DMSO-d_6) of **34**



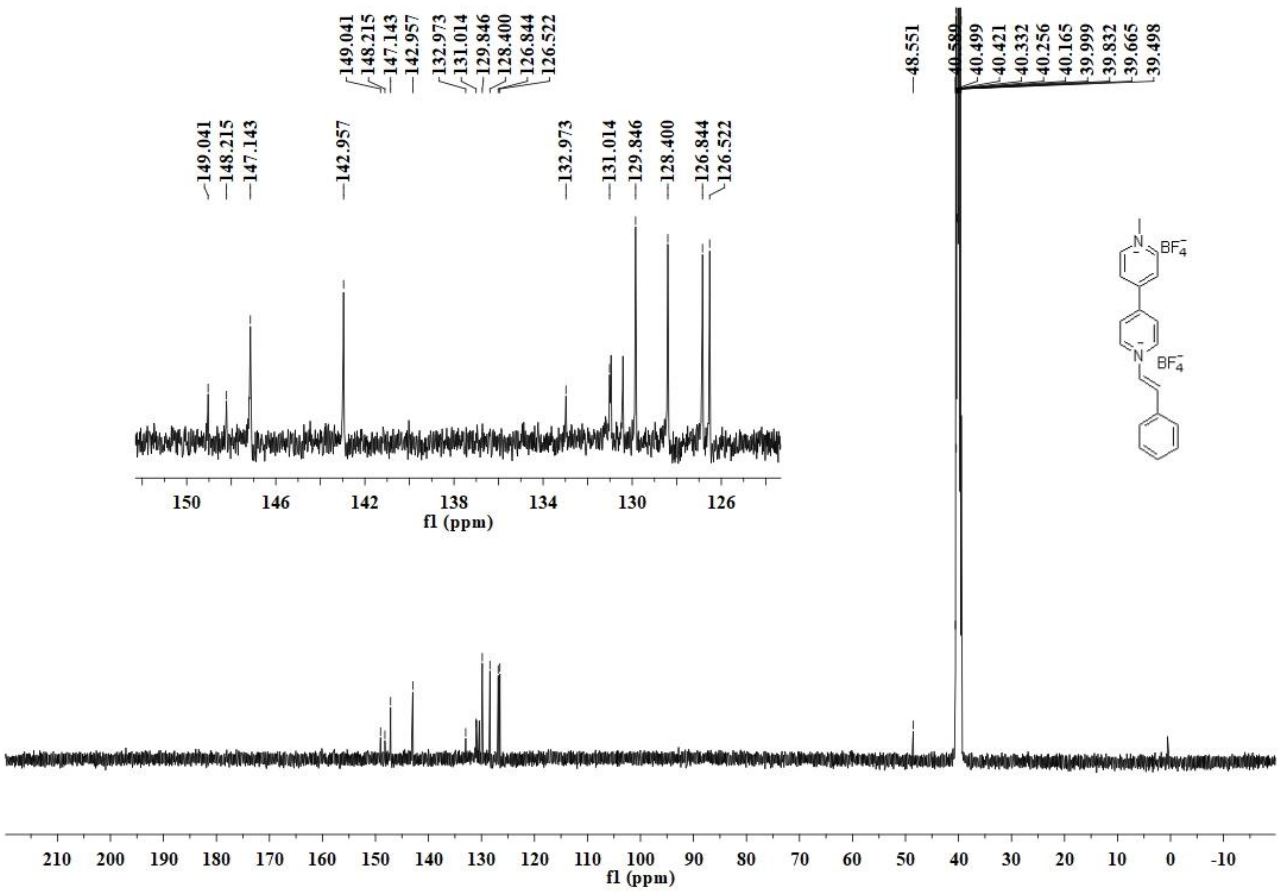
^{13}C NMR (125 MHz, DMSO-d_6) of **34**



^{1}H NMR (500 MHz, DMSO-d_6) of **35**



^{13}C NMR (125 MHz, DMSO-d_6) of **35**



^{19}F NMR (471 MHz, DMSO-d_6) of **35**