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Supporting Information

A Facile Access to Substituted Cationic 12-Azapyrene Salts by Rhodium(III)-Catalyzed C–H Annulation of *N*-Arylpyridinium Salts

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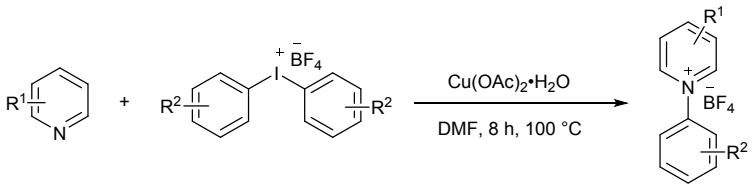
I. General remarks

Unless otherwise noted, all reagents were prepared from commercial suppliers and used without further purification. Alkynes[1] and $[Cp^*RhCl_2]_2$[2] were prepared according to the literature procedure. DCE, MeCN, DMF, DMSO were dried by refluxing over CaH_2 and freshly distilled prior to use. Toluene and 1,4-dioxane were dried by refluxing over sodium and freshly distilled prior to use. NMR spectra were recorded on a Bruker AV II-400 MHz or Agilent 400-MR DD2 spectrometer (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz and ^{19}F at 376 MHz). The ^{1}H NMR (400 MHz) chemical shifts and the ^{13}C NMR (100 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.52 ppm). High resolution mass spectra (HRMS) were recorded on a Waters-Q-TOF-Premier (ESI) or a Shimadzu LCMS-IT-TOF (ESI). UV/vis spectra were measured on a HITACHI U-2910. Fluorescence spectra were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system.

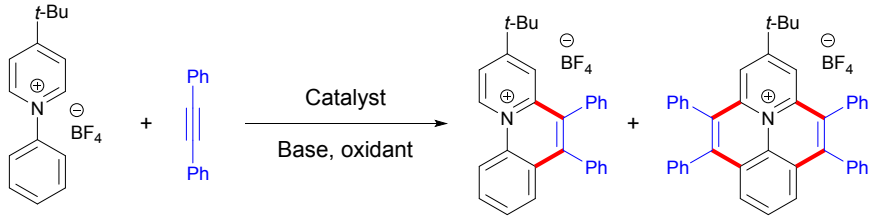
II. General procedure for the synthesis of *N*-arylpyridinium salts



The *N*-arylpyridinium salts were synthesized from a modified procedure of our previous report.[3] To a 25 mL round bottom flask, a substituted pyridine (2 mmol), a diaryliodonium tetrafluoroborate (3 mmol, 1.5 equiv), copper acetate monohydrate (10 mol%, 0.2 mmol) and DMF (8 ml) were added. The reaction mixture was then heated at 100 ºC for 8 hours. After cooled down to room temperature, DMF was removed under vacuum. The mixture was dissolved in methanol and precipitated using ethyl ether to give the pure product suitable for analysis.

III. Optimization of the reaction conditions

Table S1 Optimization of the reaction conditions.[a]

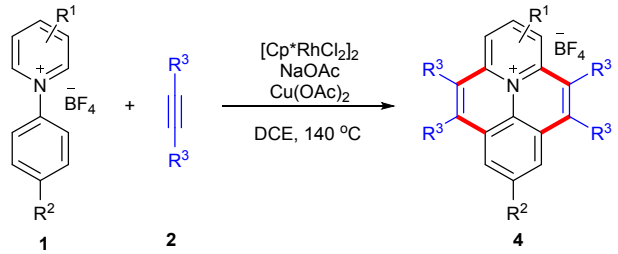


1a **2a** **3a** **4a**

Entry	Catalyst (5 mol %)	Oxidant (equiv)	Base (equiv)	Solvent	Yield [b] of **3a**	Yield [b] of **4a**
1	$[Cp^*RhCl_2]_2$	$AgBF_4$(2)	NaOAc(2)	DCE	Trace	n.d.
2	$[Cp^*Rh(MeCN)_3(SbF_6)_2]$	$Cu(OAc)_2$(4)	NaOAc(4)	DCE	n.d.	88 %
3	$[Cp^*RhCl_2]_2$	$Cu(acac)_2$(4)	NaOAc(4)	DCE	n.d.	n.d.
4	$[Cp^*RhCl_2]_2$	CuO(4)	NaOAc(4)	DCE	n.d.	n.d.
5	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$(4)	–	DCE	n.d.	n.d.
6	$[Cp^*RhCl_2]_2$	–	NaOAc(4)	DCE	n.d.	n.d.
7	–	$Cu(OAc)_2$(4)	NaOAc(4)	DCE	n.d.	n.d.
8	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$(4)	NaOAc(4)	DMF	n.d.	n.d.
9	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$(4)	NaOAc(4)	DMSO	n.d.	n.d.
10	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$(4)	NaOAc(4)	Toluene	28%	21%
11	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$(4)	NaOAc(4)	MeCN	24%	45%
12	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$(4)	NaOAc(4)	Dioxane	42%	Trace
13	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$(4)	KOAc(4)	DCE	20%	36%
14	$[Cp^*IrCl_2]_2$	$Cu(OAc)_2$(4)	NaOAc(4)	DCE	40%	Trace
15	$[Cp^*CoCl_2]_2$	$Cu(OAc)_2$(4)	NaOAc(4)	DCE	n.d.	n.d.

[a] Reaction conditions: **1a**(0.1 mmol, 1 equiv), **2a**(0.4 mmol, 4 equiv), catalyst, base, oxidants in solvent (2 mL) under N_2 at 140 ºC for 16 h. [b] Isolated yields.

IV. General procedure for the synthesis of 12-azapyrene derivatives

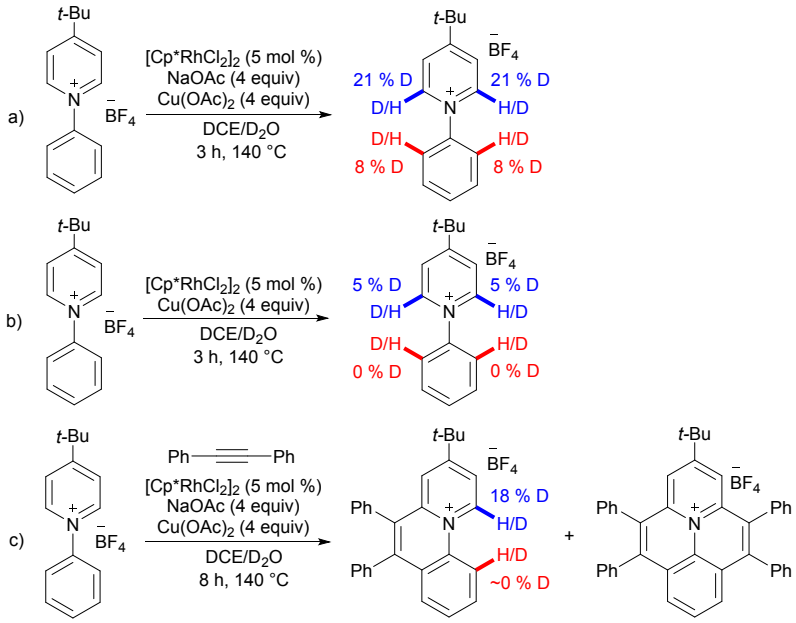


1 **2** **4**

A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with an

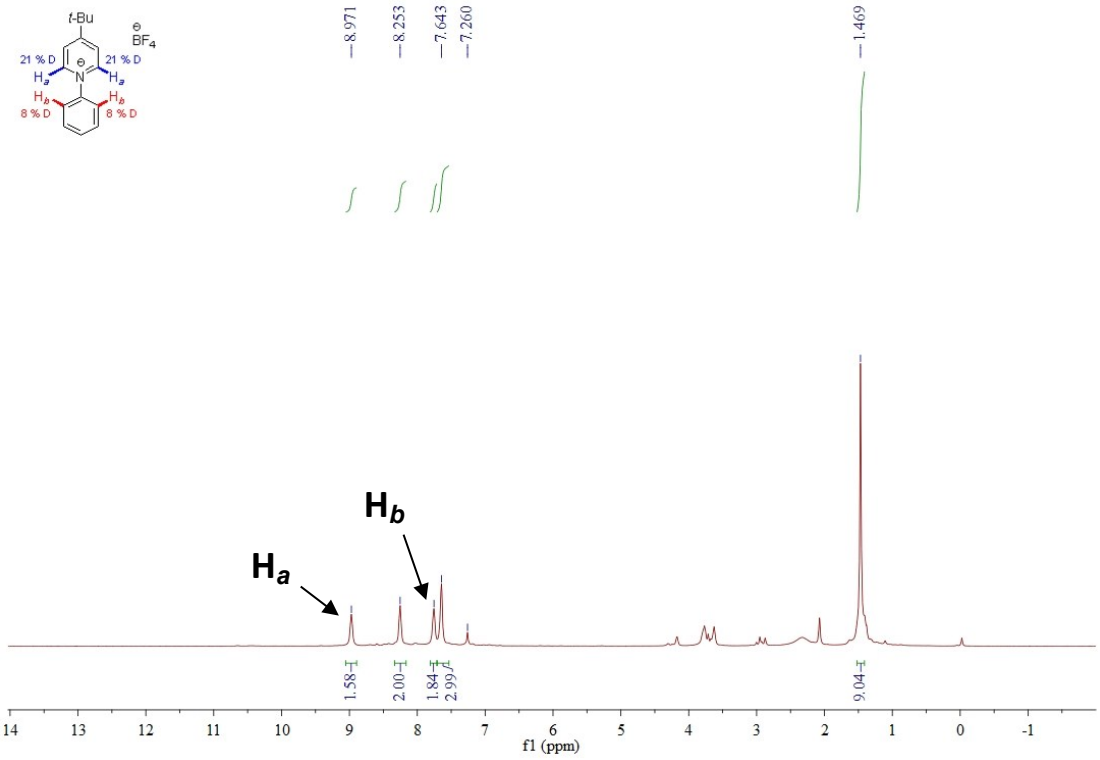
arylpyridinium salt **1** (0.1 mmol), an alkyne **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $Cu(OAc)_2$ (73 mg, 0.4 mmol) and NaOAc (32.8 mg, 0.4 mmol) under N_2. Dry DCE (2.0 mL) was then added and the tube was sealed with a teflon-coated screw cap. The reaction solution was heated at 140 ºC for 16 h. After cooled to ambient temperature, 4.0 mL of saturated $NaBF_4$ (aq.) was added and the mixture was stirred at room temperature for another 0.5 h under air. The organic layer was then separated and the water layer was extracted with CH_2Cl_2 (5.0 mL×3). The combined organic phase was concentrated under vacuum and the residue was purified by column chromatography on Al_2O_3 (neutral, 200-300 mesh) with MeCN/CH_2Cl_2 (1/10 to 1/3) to provide the desired product.

V. H/D Exchange experiments

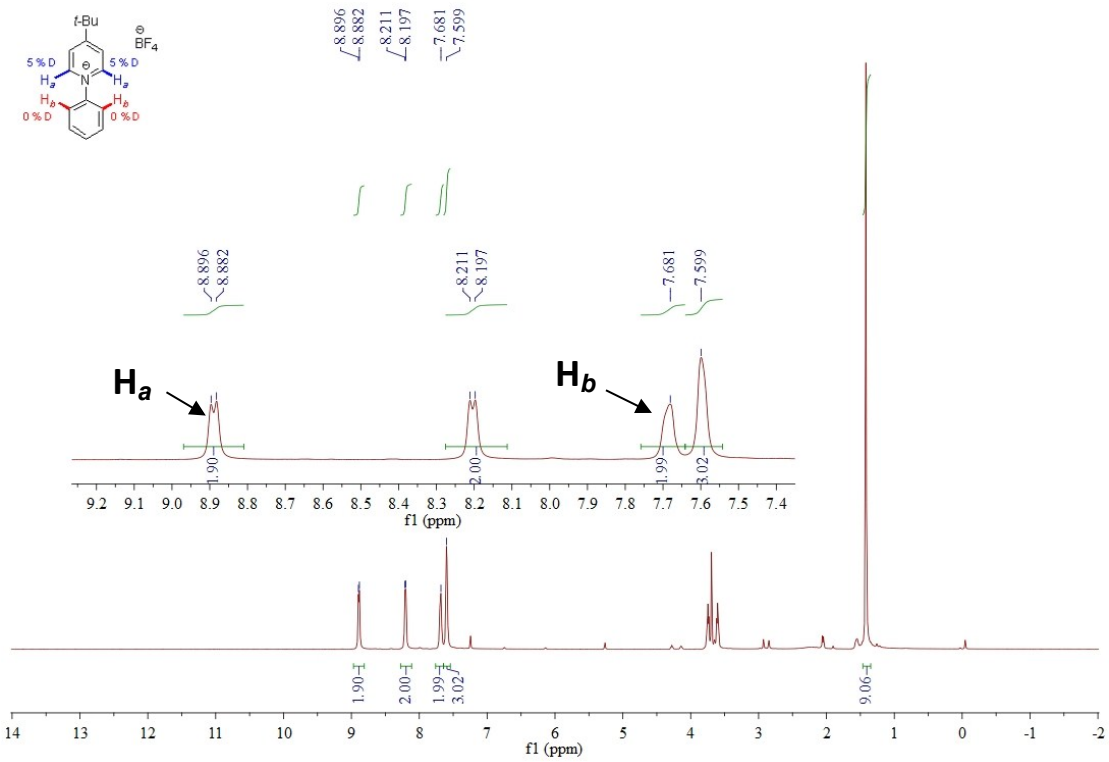


a) A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.1 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $Cu(OAc)_2$ (73 mg, 0.4 mmol) and NaOAc (32.8 mg, 0.4 mmol) under N_2. Dry DCE (2.0 mL) and D_2O (1.0 mL) was then added and the tube was sealed with a teflon-coated screw cap. The reaction solution was heated at 140 ºC for 3 h. After the mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The crude residue was subjected to the ^1H NMR analysis. The ^1H NMR spectum shows the incorporation

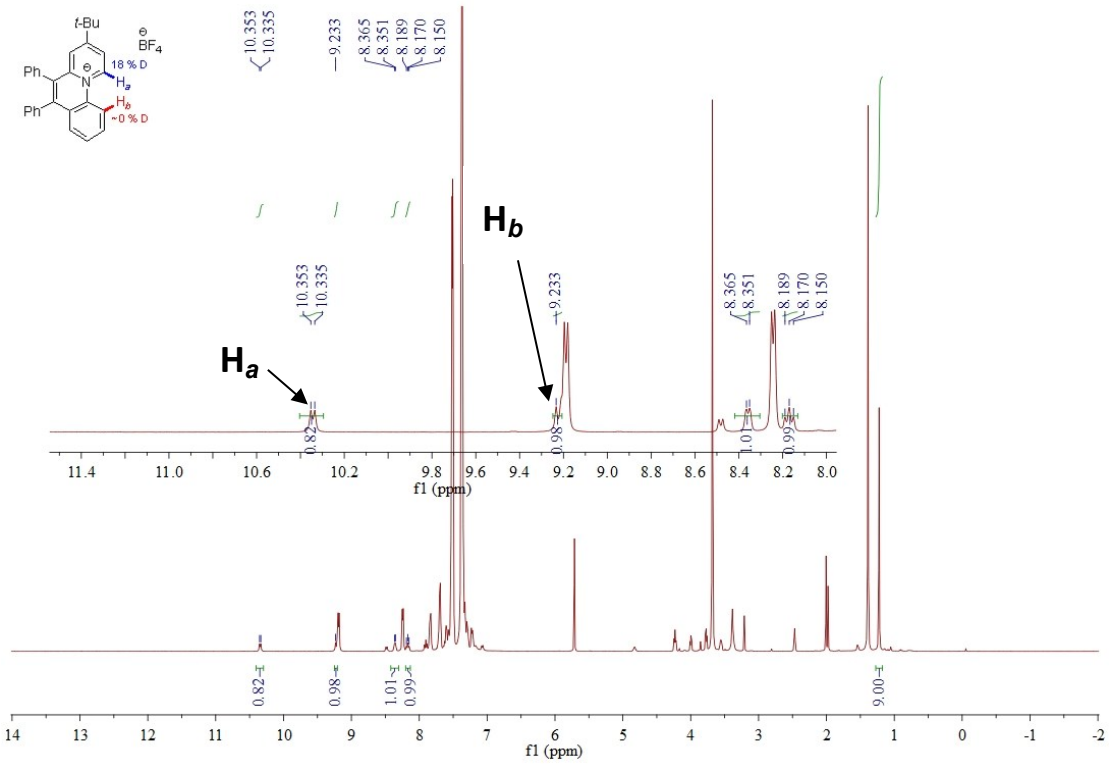
of deuterium into the labeled protons of the substrate **1a**.

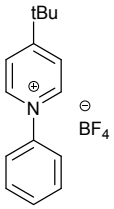


b) A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.1 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) and $Cu(OAc)_2$ (73 mg, 0.4 mmol) under N_2. Dry DCE (2.0 mL) and D_2O (1.0 mL) was then added and the tube was sealed with a teflon-coated screw cap. The reaction solution was heated at 140 ºC for 3 h. After the mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The crude residue was subjected to the ^1H NMR analysis. The ^1H NMR spectum shows the incorporation of deuterium into the labeled protons of the substrate **1a**.



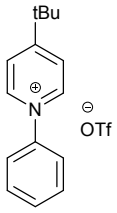
c) A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.1 mmol), diphenylacetylene (0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $Cu(OAc)_2$ (73 mg, 0.4 mmol) and NaOAc (32.8 mg, 0.4 mmol) under N_2. Dry DCE (2.0 mL) and D_2O (1.0 mL) was then added and the tube was sealed with a teflon-coated screw cap. The reaction solution was heated at 140 ºC for 3 h. After the mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The crude residue was subjected to the ^1H NMR analysis. The ^1H NMR spectrum shows the incorporation of deuterium into the labeled protons of the single annulated product **3a**.





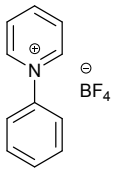
VI. Experimental data for the described substances

4-(*tert*-Butyl)-1-phenylpyridin-1-ium tetrafluoroborate (1a): A white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 9H), 7.61 – 7.68 (m, 5H), 8.21 (d, J = 5.6 Hz, 2H), 8.88 (d, J = 5.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.0, 37.0, 124.0, 126.3, 130.9, 131.7, 142.3, 143.4, 172.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -151.92 (s) ppm. HRMS (ESI) calcd for $[C_{15}H_{18}N]^+$ $[M\text{-}BF_4]^+$ 212.1434, found 212.1431.

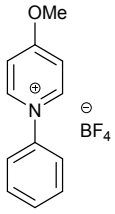


4-(*tert*-butyl)-1-phenylpyridin-1-ium trifluoromethanesulfonate (4a'): A white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 9H), 7.63 – 7.64 (m, 3H), 7.72 – 7.74 (m, 2H), 8.21 (d, J = 6.8 Hz, 2H), 8.93 (dd, J = 6.4 Hz, 1.2 Hz 2H) ppm. ^{13}C NMR (100

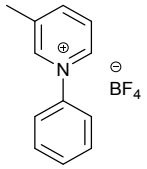
MHz, $CDCl_3$): δ = 30.1, 37.1, 124.1, 126.3, 131.0, 131.8, 142.2, 143.6, 172.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -78.27 (s) ppm. HRMS (ESI) calcd for $[C_{15}H_{18}N]^+$ [M-BF_4]$^+$ 212.1434, found 212.1430.



1-Phenylpyridin-1-ium tetrafluoroborate (1b): An off-white solid. ^1H NMR (400 MHz, DMSO-*d6*): δ = 7.70 – 7.80 (m, 3H), 7.88 – 7.90 (m, 2H), 8.29 – 8.33 (m, 2H), 8.79 (tt, *J* = 8.0 Hz, 1.2 Hz, 1H), 9.34 – 9.35 (m, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-*d6*): δ = 124.8, 128.1, 130.2, 131.2, 142.8, 145.0, 146.6 ppm. ^{19}F NMR (376 MHz, DMSO-*d6*): δ = -148.25 (s) ppm. HRMS (ESI) calcd for $[C_{11}H_{10}N]^+$ [M-BF_4]$^+$ 156.0808, found 156.0808.

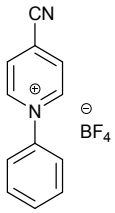


4-Methoxy-1-phenylpyridinium tetrafluoroborate (1c): An off-white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.19 (s, 3H), 7.61 – 7.64 (m, 7H), 8.67 – 8.70 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 58.6, 114.6, 123.9, 131.0, 131.4, 142.0, 145.3, 172.4 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -152.15 (s) ppm. HRMS (ESI) calcd for $[C_{12}H_{12}NO]^+$ [M-BF_4]$^+$ 186.0913, found 186.0913.

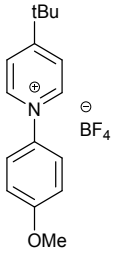


3-Methyl-1-phenylpyridinium tetrafluoroborate (1d): A reddish-brown solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.71 (s, 3H), 7.60 – 7.69 (m, 5H), 8.01 (d, *J* = 6.4 Hz, 2H), 8.77 – 8.79 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.5, 124.07, 124.09, 129.7, 130.97, 130.99, 131.8, 142.4, 143.2, 161.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -151.93 (s) ppm. HRMS (ESI) calcd for $[C_{12}H_{12}N]^+$ [M-BF_4]$^+$ 170.0964, found

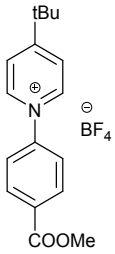
170.0964.



4-Cyano-1-phenylpyridin-1-ium tetrafluoroborate (1e): A light-brown solid. ^{1}H NMR (400 MHz, DMSO-*d6*): δ = 7.77 – 7.79 (m, 3H), 7.87 – 7.91 (m, 2H), 8.90 (d, *J* = 6.0 Hz, 2H), 9.67 (d, *J* = 7.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-*d6*): δ = 114.8, 124.8, 127.6, 130.3, 131.0, 131.9, 142.5, 146.4 ppm. ^{19}F NMR (376 MHz, DMSO-*d6*): δ = -148.26 (s) ppm. HRMS (ESI) calcd for $[C_{12}H_9N]^+$ $[M\text{-}BF_4]^+$ 181.0760, found 181.0758.

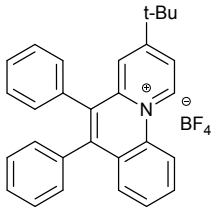


4-(*tert*-Butyl)-1-(4-methoxyphenyl)pyridin-1-ium tetrafluoroborate (1f): A yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 9H), 3.86 (s, 9H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 6.4 Hz, 2H), 8.81 (d, *J* = 6.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.1, 36.9, 56.0, 110.2, 116.0, 125.3, 126.1, 143.2, 161.9, 172.1 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -152.11 (s) ppm. HRMS (ESI) calcd for $[C_{16}H_{20}NO]^+$ $[M\text{-}BF_4]^+$ 242.1539, found 242.1541.

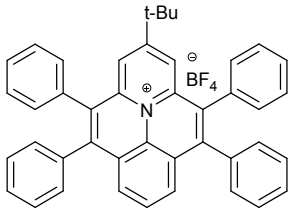


4-*tert*-Butyl-1-(4-(methoxycarbonyl)phenyl)pyridinium tetrafluoroborate (1g): A white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 9H), 3.96 (s, 3H), 7.82 (d, *J* = 8.4 Hz, 2H), 8.20 (d, *J* = 6.8 Hz, 2H), 8.25 (d, *J* = 8.4 Hz, 2H), 8.90 (d, *J* = 6.8 Hz, 2H)

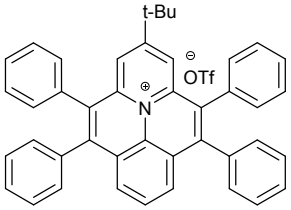
ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.99, 37.2, 52.9, 124.4, 126.4, 132.2, 133.2, 143.3, 145.2, 165.3, 173.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -151.70 (s) ppm. HRMS (ESI) calcd for $[C_{17}H_{20}NO_2]^+$ $[M\text{-}BF_4]^+$ 270.1489, found 270.1487.



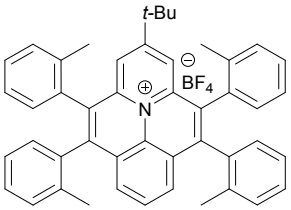
3-(*tert*-Butyl)-5,6-bis(4-chlorophenyl)pyrido[1,2-*a*]quinolin-11-ium tetrafluoroborate (3a): Product **3a** was prepared according to the general procedure as a white solid (39.3 mg, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 9H), 7.16 – 7.20 (m, 4H), 7.32 – 7.37 (m, 6H), 7.74 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 7.2 Hz, 1H), 7.83 (s, 1H), 8.15 (t, J = 8.0 Hz, 1H), 8.38 (d, J = 6.8 Hz, 1H), 9.19 (d, J = 8.8 Hz, 1H), 10.41 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.9, 36.5, 118.5, 122.7, 123.9, 126.9, 128.6, 128.9, 129.09, 129.11, 129.5, 129.8, 130.5, 130.6, 133.1, 133.8, 133.9, 134.0, 134.6, 134.9, 143.3, 147.3, 166.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -152.78 (s) ppm. HRMS (ESI) calcd for $[C_{29}H_{26}N]^+$ $[M\text{-}BF_4]^+$ 388.2060, found 388.2051.



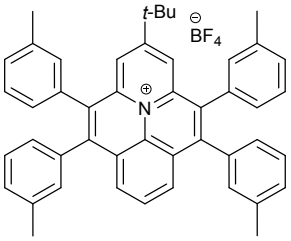
2-(*tert*-Butyl)-4,5,9,10-tetraphenylquinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4a): Product **4a** was prepared according to the general procedure as a yellow-green solid (58.5 mg, 90 %). ^{1}H NMR (400 MHz, DMSO-*d6*): δ = 1.12 (s, 9H), 7.34 – 7.36 (m, 4H), 7.39 – 7.51 (m, 16H), 7.83 (s, 2H), 7.86 (d, J = 8.0 Hz, 2H), 8.19 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d6*): δ = 29.4, 35.5, 120.3, 126.8, 127.4, 128.6, 128.80, 128.83, 128.9, 129.2, 129.8, 130.3, 131.4, 134.5, 134.7, 134.9, 141.9, 144.8, 159.9 ppm. ^{19}F NMR (376 MHz, DMSO-*d6*): δ = -148.34 (s) ppm. HRMS (ESI) calcd for $[C_{43}H_{34}N]^+$ $[M\text{-}BF_4]^+$ 564.2686, found 564.2682.



2-(*tert*-Butyl)-4,5,9,10-tetraphenylquinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4a'): Product **4a'** was prepared according to the general procedure as a yellow solid (48.4 mg, 68 %). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 1.12 (s, 9H), 7.32 – 7.36 (m, 4H), 7.39 – 7.51 (m, 16H), 7.83 (s, 2H), 7.876 (d, *J* = 8.0 Hz, 2H), 8.19 (t, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 29.4, 35.5, 120.3, 126.8, 127.4, 128.6, 128.80, 128.83, 128.9, 129.2, 129.8, 130.3, 131.4, 134.5, 134.7, 134.9, 141.9, 144.8, 159.9 ppm. ^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ = -77.77 (s) ppm. HRMS (ESI) calcd for $[C_{43}H_{34}N]^+$ $[M\text{-}BF_4]^+$ 564.2686, found 564.2684.

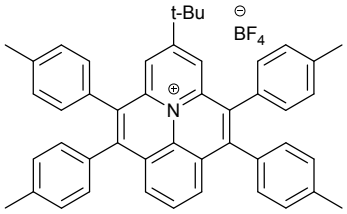


2-(*tert*-Butyl)-4,5,9,10-tetra-*o*-tolylquinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4b): Product **4b** was prepared according to the general procedure as a green solid (58.1 mg, 82 %). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 1.1 – 1.13 (m, 9H), 2.03 – 2.30 (m, 12H), 7.10 – 7.44 (m, 16H), 7.65 – 7.67 (m, 4H), 8.14 – 8.20 (m, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 19.2, 19.3, 29.4, 35.3, 109.6, 112.4, 119.6, 125.8, 126.0, 126.4, 126.5, 127.0, 128.9, 129.2, 129.3, 130.46, 130.47, 130.54, 130.6, 131.9, 133.5, 133.8, 133.9, 134.09, 134.13, 135.5, 135.6, 136.4, 141.36, 141.38, 144.9, 145.0, 160.3, 160.4 ppm. HRMS (ESI) calcd for $[C_{47}H_{42}N]^+$ $[M\text{-}BF_4]^+$ 620.3312, found 620.3307.

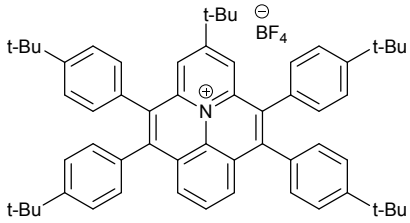


2-*tert*-Butyl-5,6,10,11-tetram-tolylquinolizino[3,4,5,6-*ija*]quinolinium

tetrafluoroborate (4c): Product **4c** was prepared according to the general procedure as a yellow-green solid (60.1 mg, 85 %). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = δ = 1.13 (s, 9H), 2.30 (s, 6H), 2.31 (s, 6H), 7.11-7.26 (m, 12H), 7.32-7.40 (m, 4H), 7.84-7.86 (m, 4H), 8.17 (t, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ =20.9, 20.9, 20.98, 21.01, 29.4, 35.5, 120.3, 126.3, 126.4, 126.8, 127.3, 127.37, 127.39, 128.61, 128.63, 128.7, 129.2, 129.25, 129.34, 129.4, 129.5, 129.7, 130.7, 130.8, 131.2, 134.39, 134.44, 134.66, 134.69, 134.8, 134.85, 137.91, 137.93, 138.1, 141.86, 141.88, 144.66, 144.72, 159.7 ppm. HRMS (ESI) calcd for $[C_{47}H_{42}N]^+$ $[M\text{-}BF_4]^+$ 620.3312, found 620.3311.

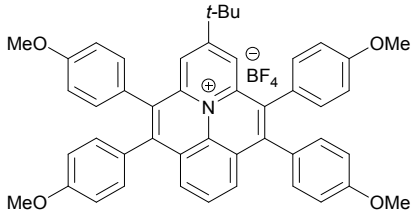


2-(*tert*-Butyl)-4,5,9,10-tetra-*p*-tolylquinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4d): Product **4d** was prepared according to the general procedure as a yellow-green solid (61.4 mg, 87 %). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 1.12 (s, 9H), 2.34 (s, 6H), 2.35 (s, 6H), 7.21 – 7.23 (m, 4H), 7.27 – 7.32 (m, 12H), 7.81 – 7.82 (m, 4H), 8.13 (t, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 20.90, 20.93, 29.5, 35.5, 120.2, 126.7, 127.6, 129.1, 129.4, 129.5, 129.6, 130.2, 131.3, 132.0, 132.1, 134.5, 137.9, 138.0, 142.1, 144.8, 159.7 ppm. HRMS (ESI) calcd for $[C_{47}H_{42}N]^+$ $[M\text{-}BF_4]^+$ 620.3312, found 620.3308.

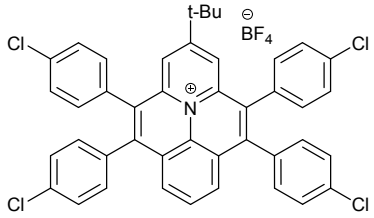


2-(*tert*-Butyl)-4,5,9,10-tetrakis(4-(*tert*-butyl)phenyl)quinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4e): Product **4e** was prepared according to the general procedure as a yellow solid (78.8 mg, 90 %). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 1.13 (s, 9H), 1.27 (s, 36H), 7.22 (d, *J* = 8.0 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 4H), 7.43

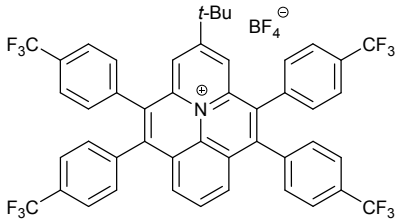
– 7.47 (m, 8H), 7.87 (s, 2H), 7.92 (d, J = 8.0 Hz, 2H), 8.20 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 29.4, 30.92, 30.93, 34.41, 34.44, 35.4, 120.1, 125.3, 125.4, 126.67, 126.68, 127.4, 129.0, 130.1, 131.3, 131.9, 132.1, 134.7, 141.9, 145.0, 150.9, 151.1, 159.7 ppm. HRMS (ESI) calcd for $[C_{59}H_{66}N]^+$ $[M\text{-}BF_4]^+$ 788.5190, found 788.5184.



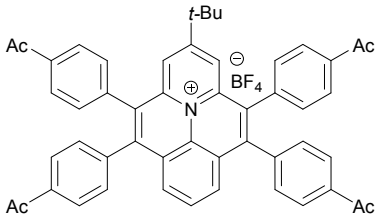
2-(*tert*-Butyl)-4,5,9,10-tetrakis(4-methoxyphenyl)quinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4f): Product **4f** was prepared according to the general procedure as a green solid (71 mg, 92 %). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 1.16 (s, 9H), 3.79 (s, 6H), 3.80 (s, 6H), 7.02 – 7.06 (m, 8H), 7.25 (d, J = 8.8 Hz, 4H), 7.31 (d, J = 8.8 Hz, 4H), 7.87 (s, 3H), 7.89 (s, 1H), 8.15 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 29.5, 35.5, 55.16, 55.18, 114.25, 114.31, 120.1, 126.7, 126.9, 127.1, 127.8, 129.6, 130.7, 131.3, 131.7, 134.5, 142.3, 144.9, 159.0, 159.1, 159.7 ppm. HRMS (ESI) calcd for $[C_{47}H_{42}NO_4]^+$ $[M\text{-}BF_4]^+$ 684.3108, found 684.3099.



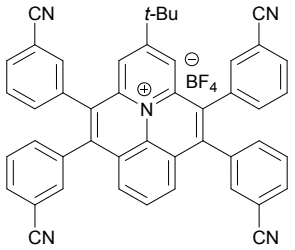
2-(*tert*-Butyl)-4,5,9,10-tetrakis(4-chlorophenyl)quinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4g): Product **4g** was prepared according to the general procedure as a yellow solid (78.8 mg, 90 %). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 1.18 (s, 9H), 7.38 (d, J = 8.0 Hz, 4H), 7.46 (d, J = 8.4 Hz, 4H), 7.59 (t, J = 8.0 Hz, 8H), 7.84 (s, 2H), 7.89 (d, J = 8.0 Hz, 2H), 8.19 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 29.5, 35.7, 120.5, 127.0, 127.2, 129.1, 129.2, 130.1, 131.2, 131.4, 132.3, 133.3, 133.5, 133.59, 133.61, 133.8, 141.6, 144.1, 160.6 ppm. HRMS (ESI) calcd for $[C_{47}H_{30}Cl_4N]^+$ $[M\text{-}BF_4]^+$ 700.1127, found 700.1134.



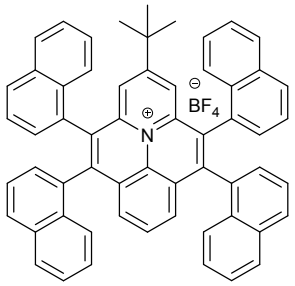
2-*tert*-Butyl-5,6,10,11-tetrakis(4-(trifluoromethyl)phenyl)quinolizino[3,4,5,6-*ija*]quinolinium tetrafluoroborate (4h): Product **4h** was prepared according to the general procedure as a green solid (85.8 mg, 93 %). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 1.16 (s, 9H), 7.62 (d, J = 8.0 Hz, 4H), 7.70 (d, J = 7.6 Hz, 4H), 7.80 (s, 2H), 7.87 – 7.91 (m, 10H), 8.22 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 29.35, 35.71, 120.67, 123.89 (q, $J_{C\text{-}F}$ =272.1 Hz), 123.92 (q, $J_{C\text{-}F}$ = 272.4 Hz), 125.90 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.98 (q, $J_{C\text{-}F}$ = 3.5 Hz), 126.75, 127.43, 129.28 (q, $J_{C\text{-}F}$ = 32.1 Hz), 129.45 (q, $J_{C\text{-}F}$ = 32.1 Hz), 130.40, 131.49, 131.53, 133.44, 138.72, 141.31, 143.90, 160.89 ppm. ^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ = -61.24 (d, J = 4.0 Hz, 4H), -148.34 (s) ppm. HRMS (ESI) calcd for $[C_{47}H_{30}NF_{12}]^+$ $[M\text{-}BF_4]^+$ 836.2181, found 836.2179.



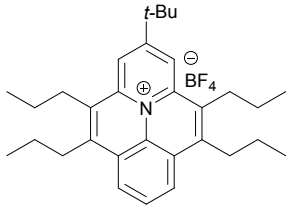
4,5,9,10-Tetrakis(4-acetylphenyl)-2-(*tert*-butyl)quinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4i): Product **4i** was prepared according to the general procedure as a yellow solid (68.8 mg, 84%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 1.13 (s, 9H), 2.60 (s, 6H), 2.61 (s, 6H), 7.55 (d, J = 8.4 Hz, 4H), 7.62 (d, J = 8.4 Hz, 4H), 7.79 (s, 2H), 7.82 (d, J = 8.0 Hz, 2H), 8.05 – 8.08 (m, 8H), 8.18 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 26.85, 26.88, 29.4, 35.7, 120.6, 126.9, 127.2, 128.8, 128.9, 129.8, 130.2, 130.9, 131.4, 133.6, 136.7, 136.8, 139.0, 139.2, 141.4, 144.1, 160.6, 197.5, 197.6 ppm. HRMS (ESI) calcd for $[C_{51}H_{42}NO_4]^+$ $[M\text{-}BF_4]^+$ 732.3108, found 732.3093.



2-(*tert*-Butyl)-4,5,9,10-tetrakis(3-cyanophenyl)quinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4j): Product **4j** was prepared according to the general procedure as a yellow solid (61.6 mg, 82 %). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 1.19 (s, 9H), 7.61 – 7.82 (m, 11H), 7.91 – 8.06 (m, 9H), 8.22 (t, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 29.4, 35.9, 112.06, 112.14, 118.2, 121.0, 126.7, 127.7, 130.4, 130.47, 130.53, 131.5, 132.9, 133.1, 133.2, 133.95, 133.98, 134.2, 135.1, 135.2, 135.3, 135.4, 135.6, 141.2, 143.6 ppm. HRMS (ESI) calcd for $[C_{47}H_{30}N_5]^+$ $[M\text{-}BF_4]^+$ 664.2496, found 664.2499.

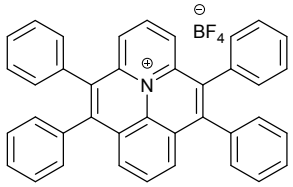


2-(*tert*-Butyl)-4,5,9,10-tetra(naphthalen-1-yl)quinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4k): Product **4k** was prepared according to the general procedure as a yellow solid (63.8 mg, 75 %). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 0.68 (s, 9H), 7.14 – 7.30 (m, 8H), 7.50 – 7.74 (m, 11H), 7.80 – 8.02 (m, 14H) ppm. HRMS (ESI) calcd for $[C_{59}H_{42}N]^+$ $[M\text{-}BF_4]^+$ 764.3312, found 764.3302.

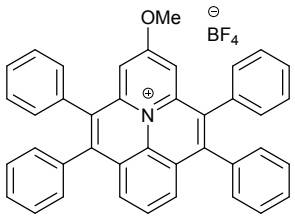


2-(*tert*-butyl)-4,5,9,10-tetrapropylquinolizino[3,4,5,6-*ija*]quinolin-11-ium (4l): Product **4l** was prepared according to the general procedure as a yellow solid (39.6 mg, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.236 – 1.244 (m, 12H), 1.62 (s, 9H), 1.78 –

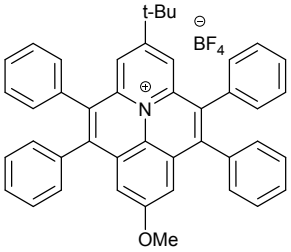
1.84 (m, 8H), 3.23 – 3.29 (m, 8H), 8.31 (t, J = 8.0 Hz, 1H), 8.43 – 8.47 (m, 4H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.7, 14.8, 22.7, 23.0, 30.6, 31.8, 32.0, 36.5, 117.8, 124.3, 126.8, 129.9, 130.4, 132.1, 140.9, 144.6, 160.8 ppm. HRMS (ESI) calcd for $[C_{31}H_{42}N]^+$ $[M\text{-}BF_4]^+$ 428.3312, found 428.3310.



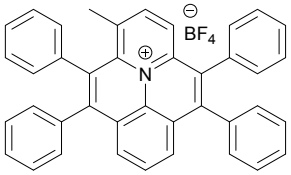
4,5,9,10-Tetraphenylquinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4m): Product **4m** was prepared according to the general procedure as a yellow solid (48.2 mg, 81 %). ^{1}H NMR (400 MHz, DMSO-*d6*): δ = 7.32 – 7.34 (m, 4H), 7.39 – 7.46 (m, 16H), 7.88 (d, J = 8.0 Hz, 2H), 8.02 (d, J = 8.0 Hz, 2H), 8.21 (t, J = 8.0 Hz, 1H), 8.55 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d6*): δ = 124.0, 126.6, 127.7, 128.6, 128.7, 128.8, 128.9, 129.2, 129.9, 130.3, 131.3, 131.8, 134.8, 134.9, 137.7, 141.9, 144.8 ppm. HRMS (ESI) calcd for $[C_{43}H_{34}N]^+$ $[M\text{-}BF_4]^+$ 564.2686, found 564.2682.



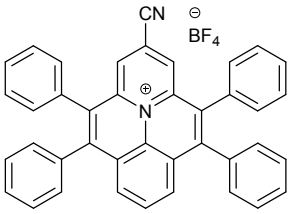
2-Methoxy-4,5,9,10-tetraphenylquinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4n): Product **4n** was prepared according to the general procedure as a grey solid (48.1 mg, 77 %). ^{1}H NMR (400 MHz, DMSO-*d6*): δ = 3.34 – 4.32 (m, 3H), 7.21 – 7.27 (m, 3H), 7.32 – 7.33 (m, 4H), 7.38 – 7.45 (m, 15H), 7.77 (d, J = 8.0 Hz, 2H), 8.09 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d6*): δ = 56.9, 109.0, 126.5, 127.17, 127.18, 128.5, 128.7, 128.8, 128.9, 129.2, 130.3, 131.2, 133.8, 134.6, 134.9, 144.4, 144.5, 163.6 ppm. HRMS (ESI) calcd for $[C_{40}H_{28}NO]^+$ $[M\text{-}BF_4]^+$ 548.2165, found 548.2169.



2-(*tert*-Butyl)-7-methoxy-4,5,9,10-tetraphenylquinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4o): Product **4o** was prepared according to the general procedure as a yellow solid (50.4 mg, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (s, 9 H), 3.70 (s, 3H), 7.28 – 7.37 (m, 22H), 7.93 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.1, 35.9, 55.9, 112.6, 121.7, 128.65, 128.74, 128.9, 129.0, 129.6, 130.0, 130.7, 131.8, 135.2, 135.3, 135.5, 141.3, 144.9, 159.2, 159.5 ppm. HRMS (ESI) calcd for $[C_{44}H_{36}NO]^+$ $[M\text{-}BF_4]^+$ 594.2791, found 594.2794.



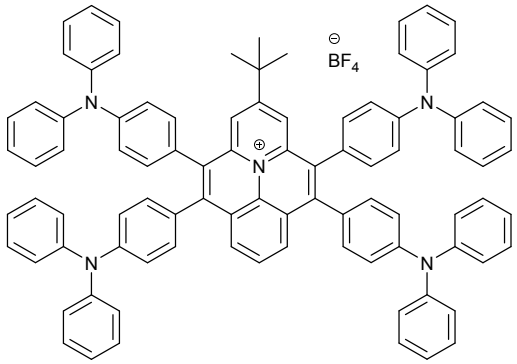
1-Methyl-4,5,9,10-tetraphenylquinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4p): Product **4p** was prepared according to the general procedure as a green solid (36.6 mg, 70 %). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 2.56 (s, 3H), 7.30 – 7.47 (m, 20H), 7.76 (s, 2H), 7.82 (d, J = 8.0 Hz, 2H), 8.16 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 21.6, 124.1, 126.7, 127.3, 128.5, 128.69, 128.72, 128.8, 129.2, 129.6, 130.4, 131.5, 134.3, 134.7, 135.0, 141.5, 144.8, 149.7 ppm. HRMS (ESI) calcd for $[C_{44}H_{36}N]^+$ $[M\text{-}BF_4]^+$ 522.2216, found 522.2208.



2-Cyano-4,5,9,10-tetraphenylquinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4q): Product **4q** was prepared according to the general procedure as a reddish-brown solid (37.9 mg, 61 %). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 7.32 –

7.33 (m, 4H), 7.37 – 7.46 (m, 16H), 8.02 (d, J = 7.6 Hz, 2H), 8.33-8.39 (m, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 115.4, 118.9, 125.5, 127.6, 128.0, 128.8, 128.98, 129.03, 129.1, 130.5, 131.2, 131.84, 133.84, 134.5, 135.0, 142.2, 146.8 ppm. HRMS (ESI) calcd for $[C_{40}H_{25}N_2]^+$ $[M\text{-}BF_4]^+$ 533.2012, found 533.2007.

2-(*tert*-Butyl)-7-(methoxycarbonyl)-4,5,9,10-tetra-*o*-tolylquinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4r): Product **4r** was prepared according to the general procedure as a greenwish solid (49.9 mg, 64 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.13 (s, 9H), 2.03 – 2.31 (m, 12H), 3.79 (s, 3H), 7.26 – 7.43 (m, 16H), 7.72 (s, 2H), 8.13 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 19.2, 19.3, 29.4, 35.5, 53.2, 109.6, 112.4, 120.1, 125.8, 126.0, 126.1, 127.5, 129.2, 129.4, 130.6, 130.7, 131.8, 133.2, 133.4, 135.1, 135.47, 135.51, 136.3, 141.8, 144.9, 164.6, 192.5 ppm. HRMS (ESI) calcd for $[C_{49}H_{44}NO_2]^+$ $[M\text{-}BF_4]^+$ 678.3367, found 678.3360.

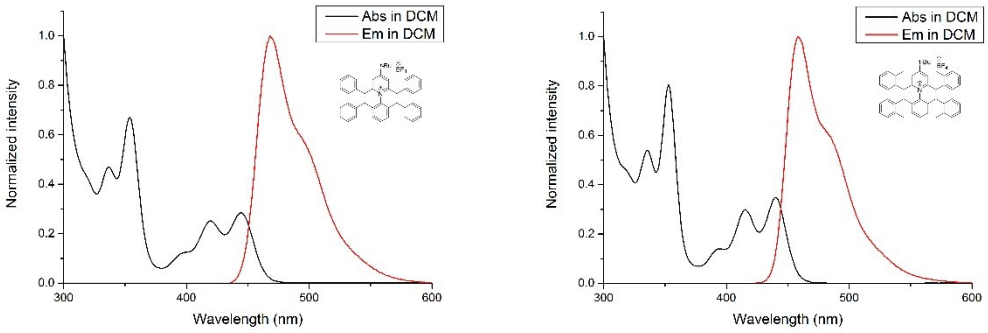


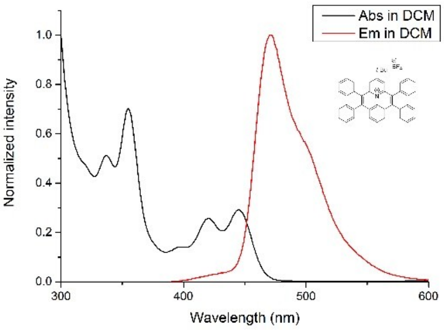
2-(*tert*-Butyl)-4,5,9,10-tetrakis(4-(diphenylamino)phenyl)quinolizino[3,4,5,6-*ija*]quinolin-11-ium tetrafluoroborate (4s): Product **4s** was prepared according to the general procedure as a crimson solid (121.2 mg, 92 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 1.28 (s, 9H), 7.05 – 7.12 (m, 32H), 7.21 – 7.25 (m, 8H), 7.32 – 7.36 (m, 16H), 8.07 (s, 2H), 8.17 (d, J = 8 Hz, 2H), 8.29 (t, J = 8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 29.5, 35.6, 120.16, 122.58, 123.22, 123.23, 123.5, 123.6, 124.0, 124.2, 126.9, 127.3, 128.6, 128.8, 129.69, 129.70, 130.8, 131.5, 131.8, 134.5, 141.9, 144.8, 146.8, 146.9, 147.35, 147.38, 159.85 ppm. HRMS (ESI) calcd for $[C_{91}H_{71}N_5]^+$ $[M\text{-}BF_4\text{+}H]^+$ 1233.5704, found 1233.5708.

VII. Photophysical spectra of 12-azapyrene derivatives in CH_2Cl_2

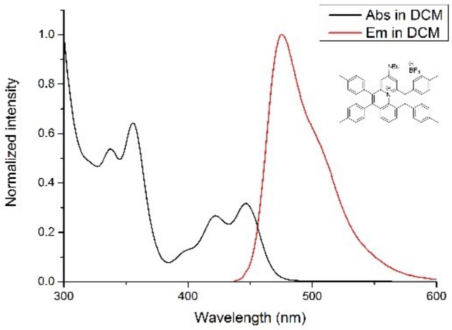
Compound	λ_{max}	λ_{ex}	λ_{em}	Φ_F
4a	354	356	468	0.76
4b	353	354	458	0.79
4c	355	356	472	0.75
4d	356	356	475	0.62
4e	358	359	476	0.91
4f	357	353	489	0.78
4g	354	351	471	0.61
4h	351	352	464	0.28
4i	353	355	469	0.68
4j	351	352	463	0.68
4k	352	353	467	0.59
4l	354	351	451	0.48
4m	355	355	481	0.58
4n	355	355	452	0.66
4o	316	362	460	0.59
4p	355	355	468	0.70
4q	365	360	536	0.36
4r	354	355	460	0.77
4s	438	489	614	0.26

Table S2 Photophysical data of 12-azapyrene derivatives in CH_2Cl_2

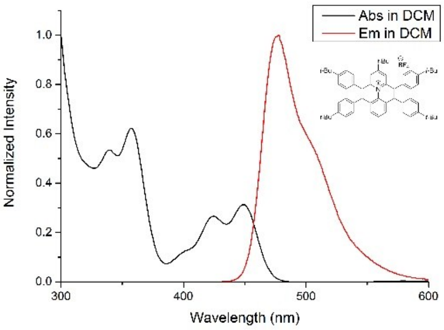




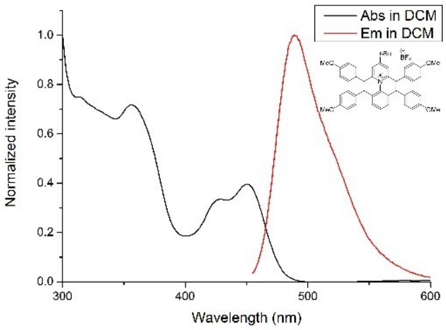
Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)



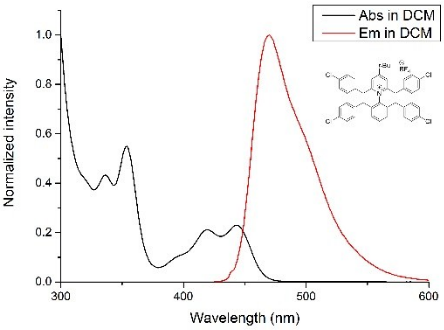
Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)



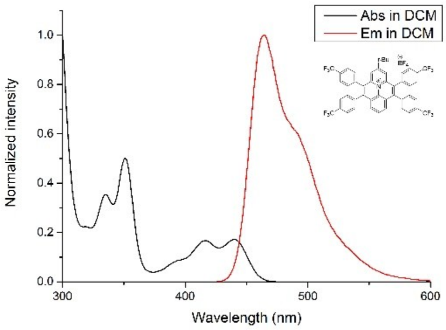
Abs in DCM
Em in DCM
Normalized Intensity
Wavelength (nm)



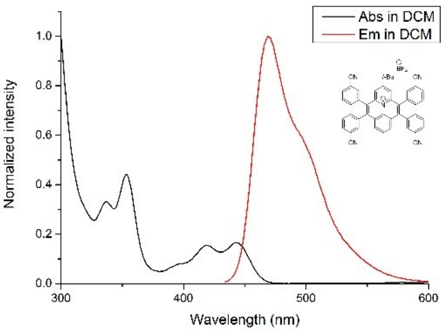
Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)



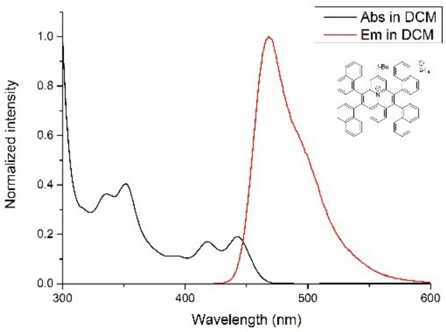
Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)



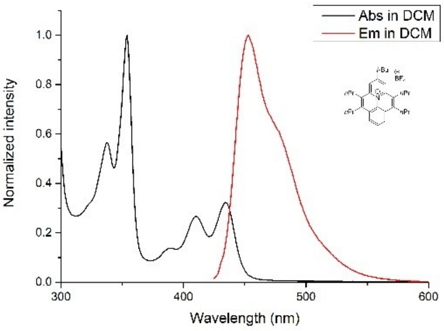
Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)

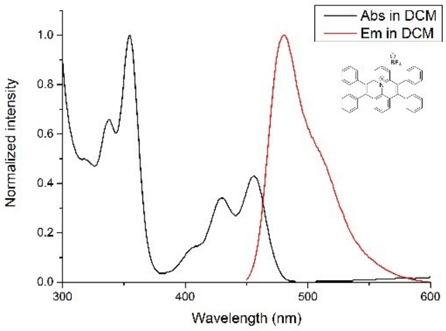


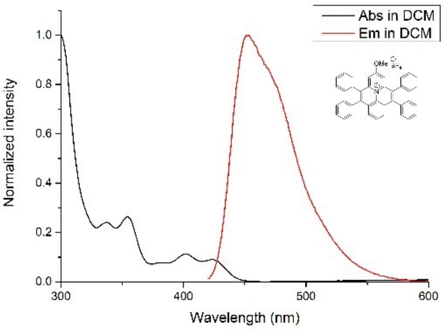
Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)

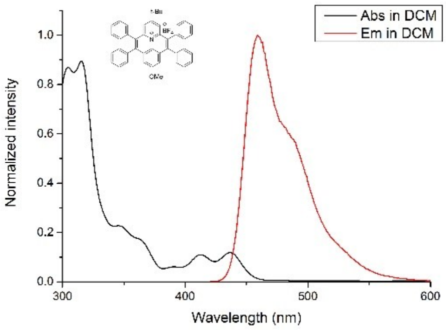


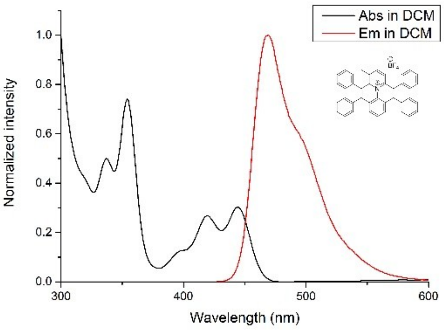
Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)

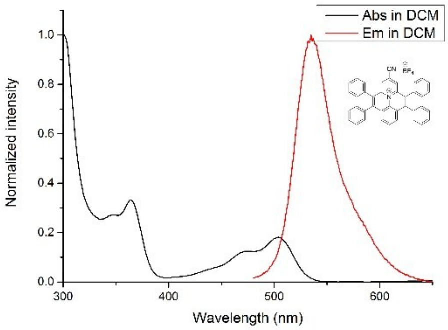

Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)

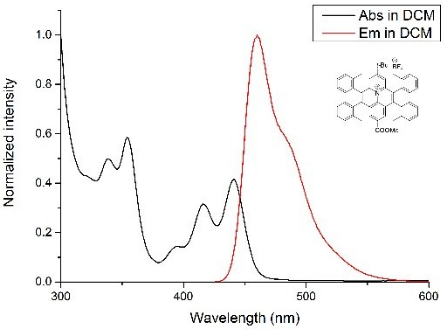

Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)

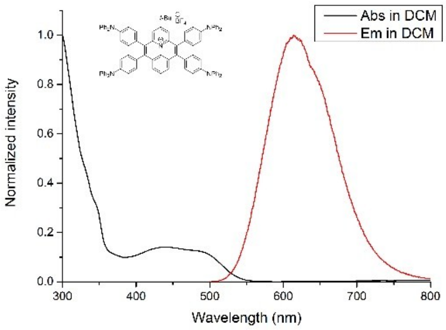

Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)


Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)


Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)


Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)


Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)


Abs in DCM
Em in DCM
Normalized intensity
Wavelength (nm)

VIII. Single crystal X-Ray structure

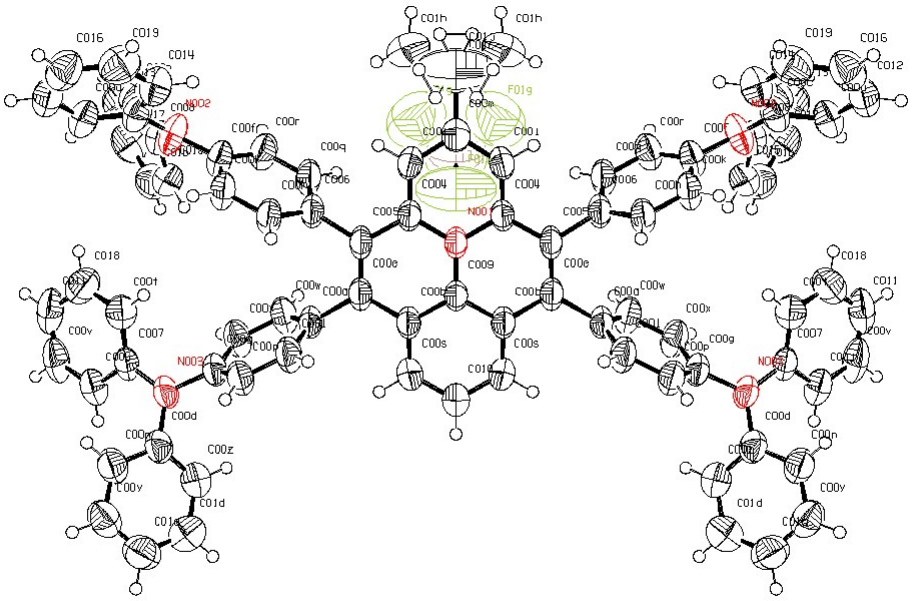


Figure S1 X-Ray single crystal structure of **4s**

XI. References

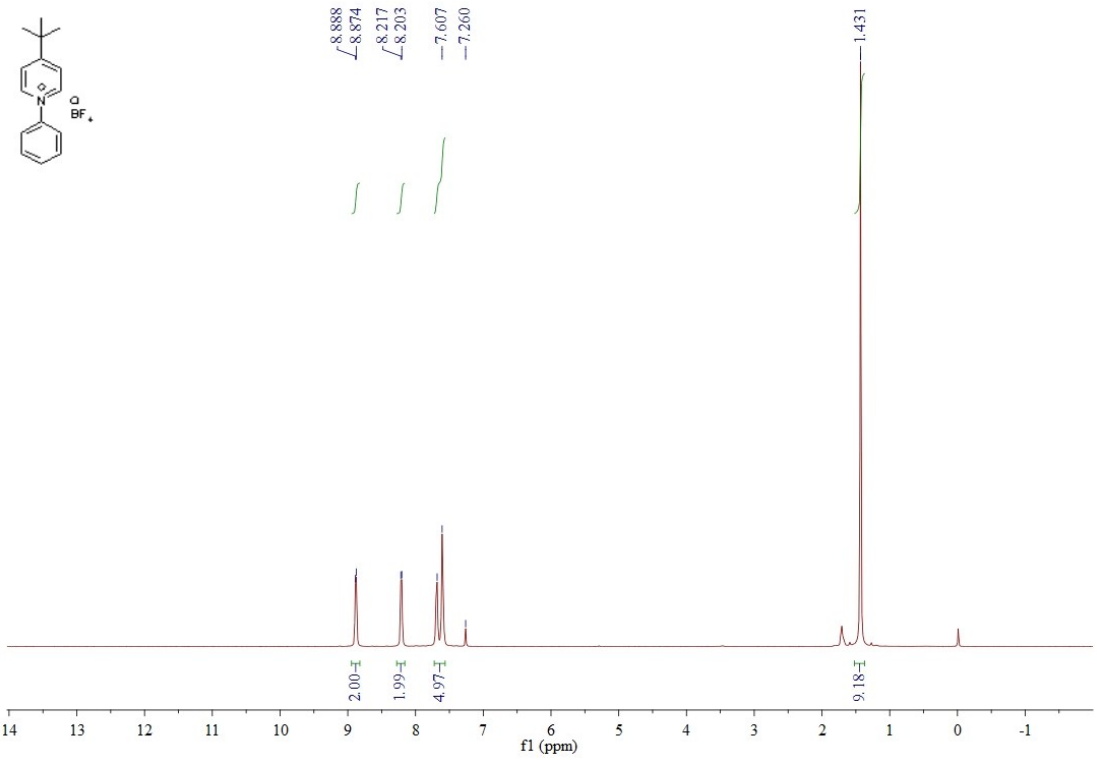
(1) (a) M. J. Mio, L. C. Kople, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth, and P. A. Grieco, *Org. Lett.*, 2002, **4**, 3199; b) K. Park, G. Bae, J. Moon, J. Choe, K. H. Song, and S. Lee, *J. Org. Chem.*, 2010, **75**, 6244.

(2) C. White, A. Yates, and P. M. Maitlis, *Inorg. Synth.*, 1992, **29**, 228.

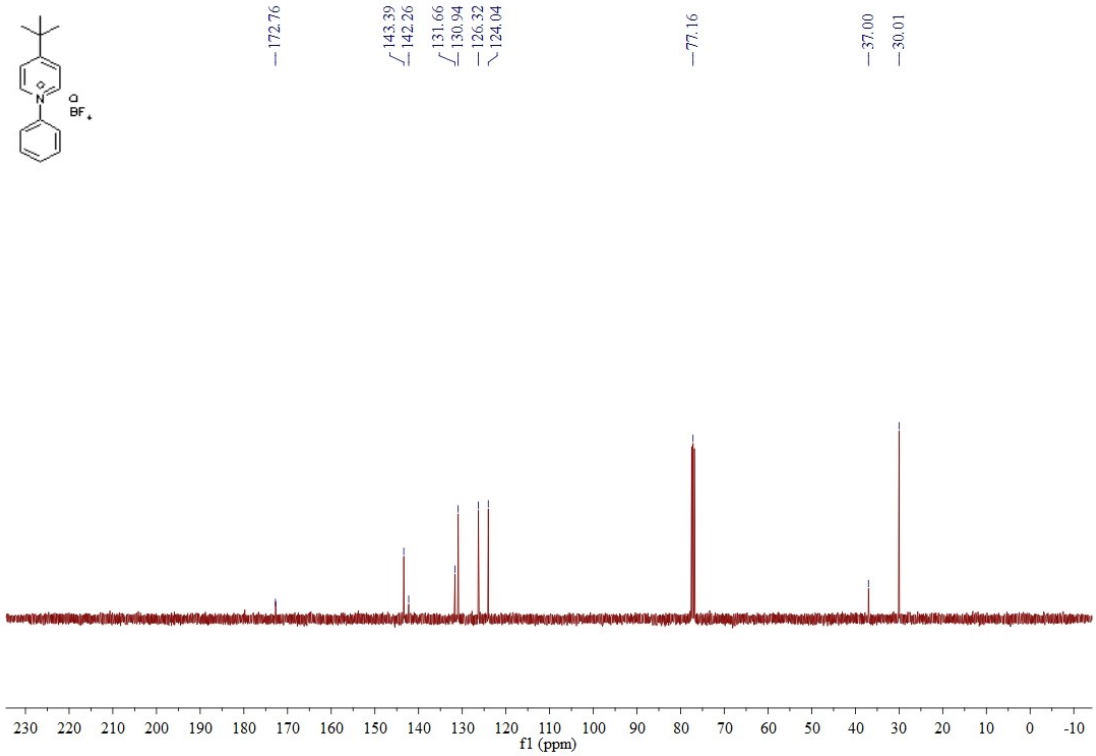
(3) T. Lv, Z. Wang, J. You, J. Lan, and G Gao, *J. Org. Chem.*, 2013, ***78***, 5723

IX. Copies of NMR Spectra for Compounds

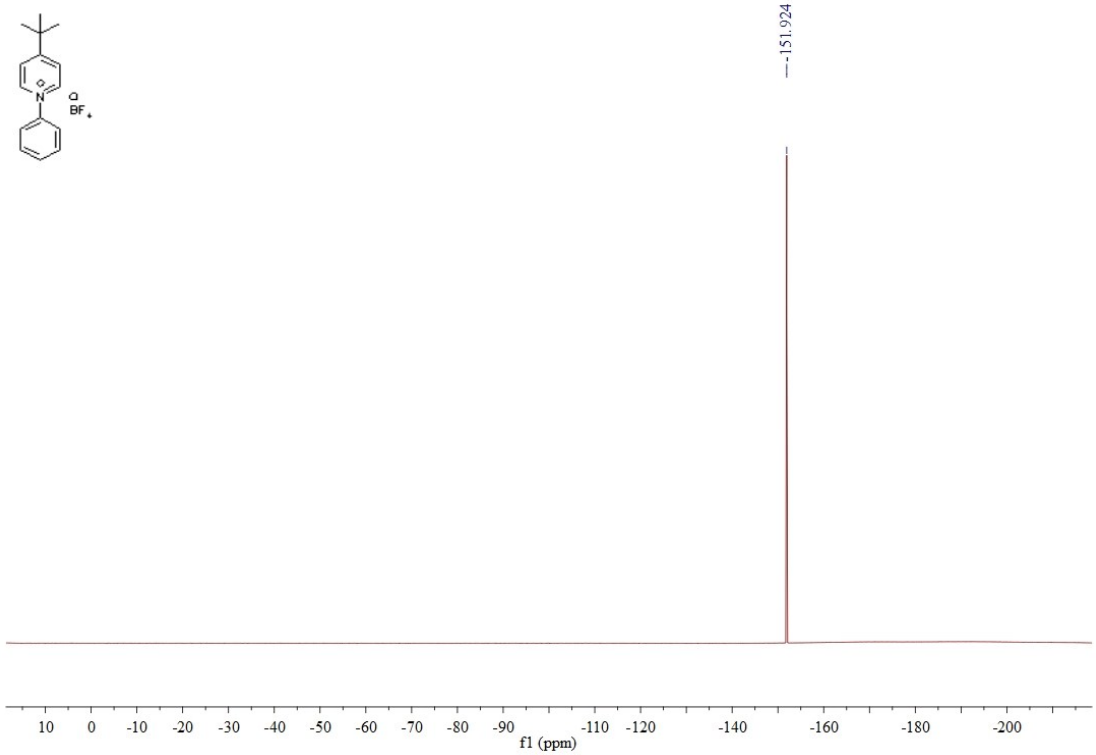
^{1}H NMR spectra of **1a**:



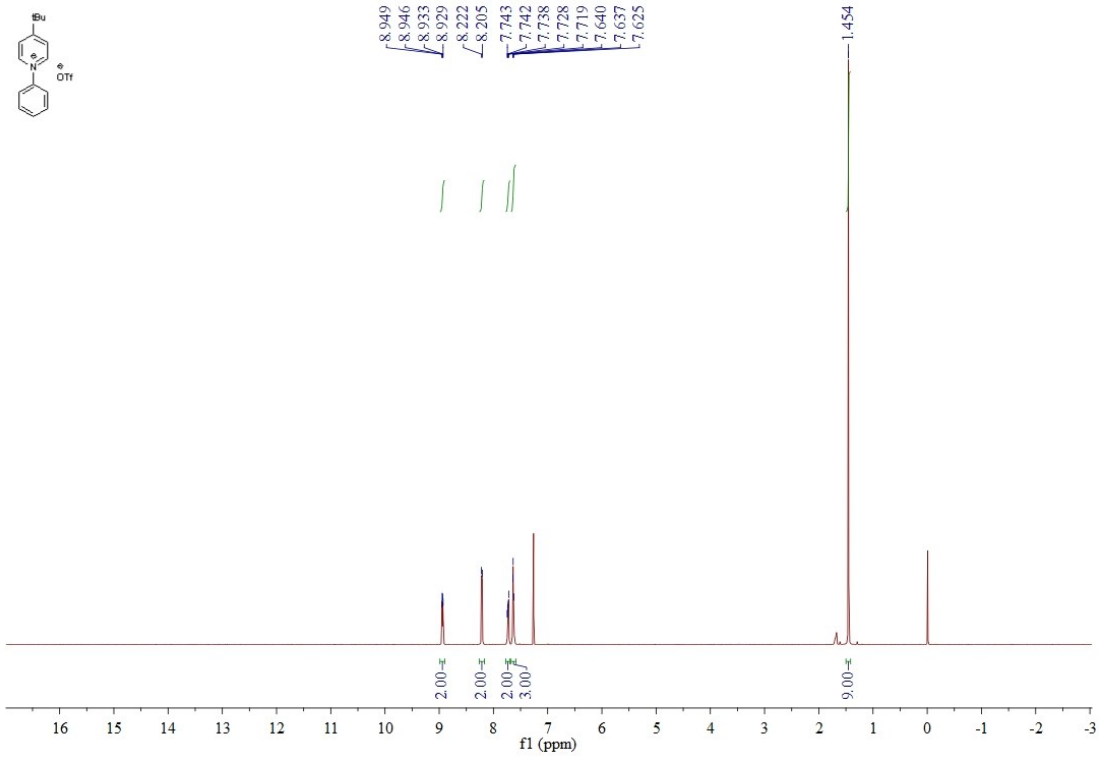
^{13}C NMR spectra of **1a**:



^{19}F NMR spectra of **1a**:



^{1}H NMR spectra of **1a'**:



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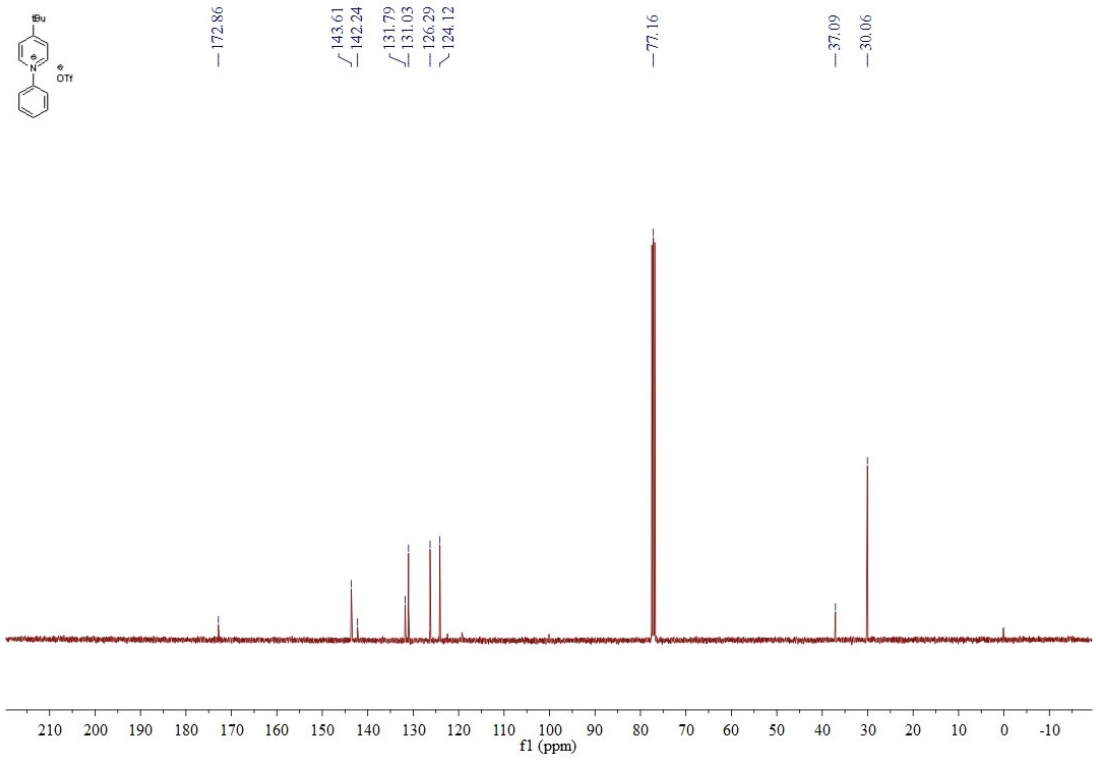
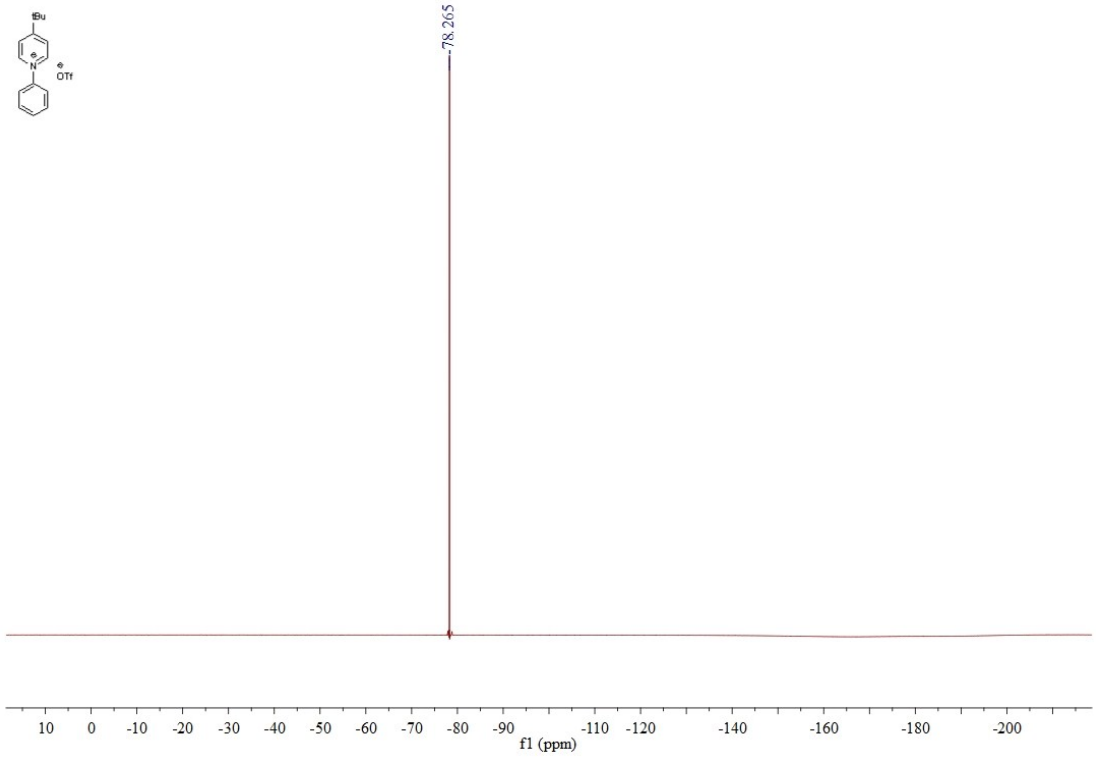
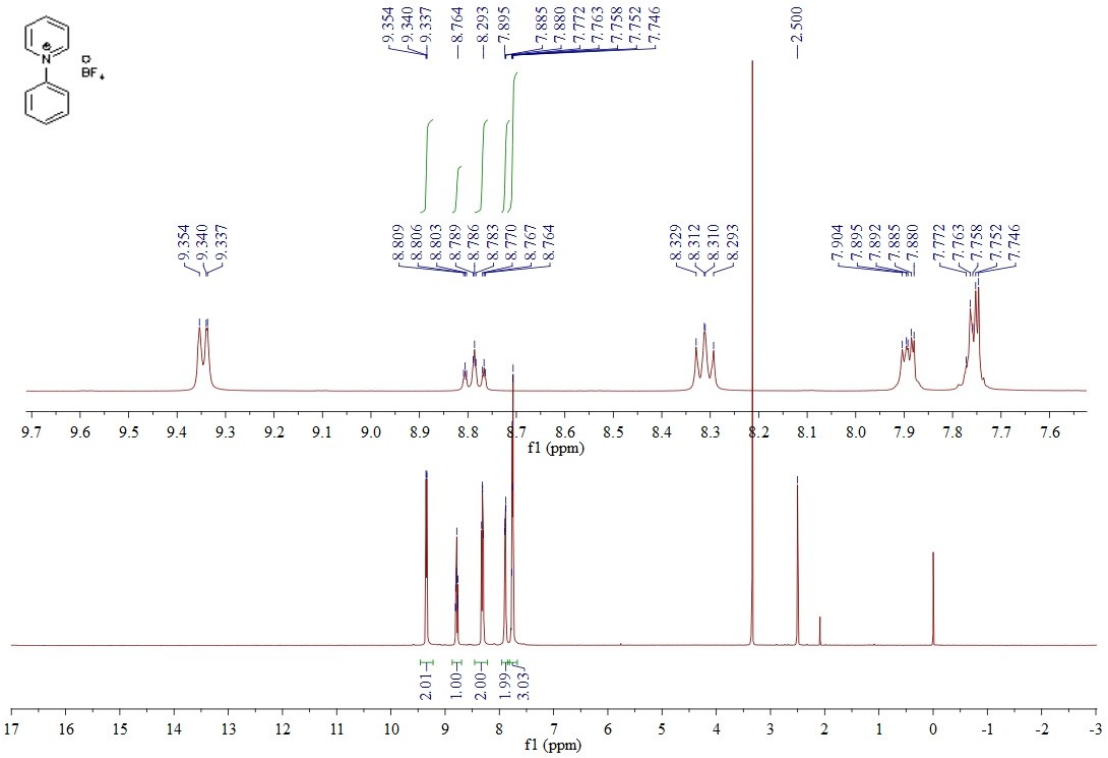


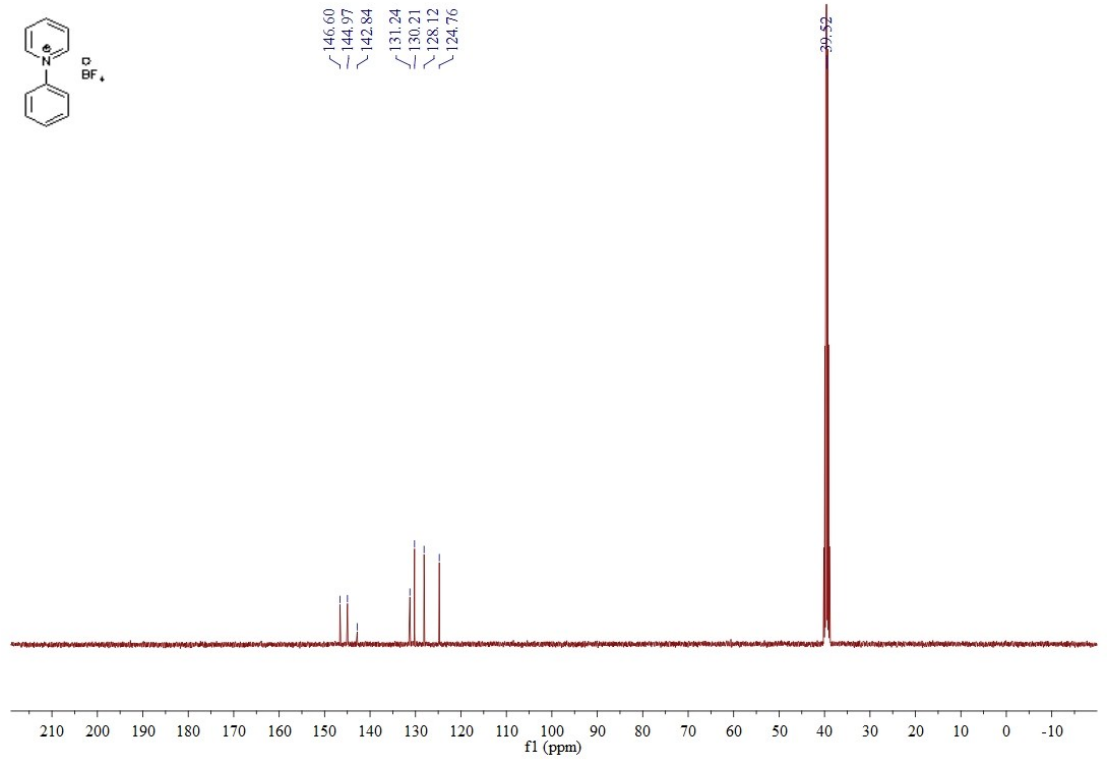
^{19}F NMR spectra of **1a'**:



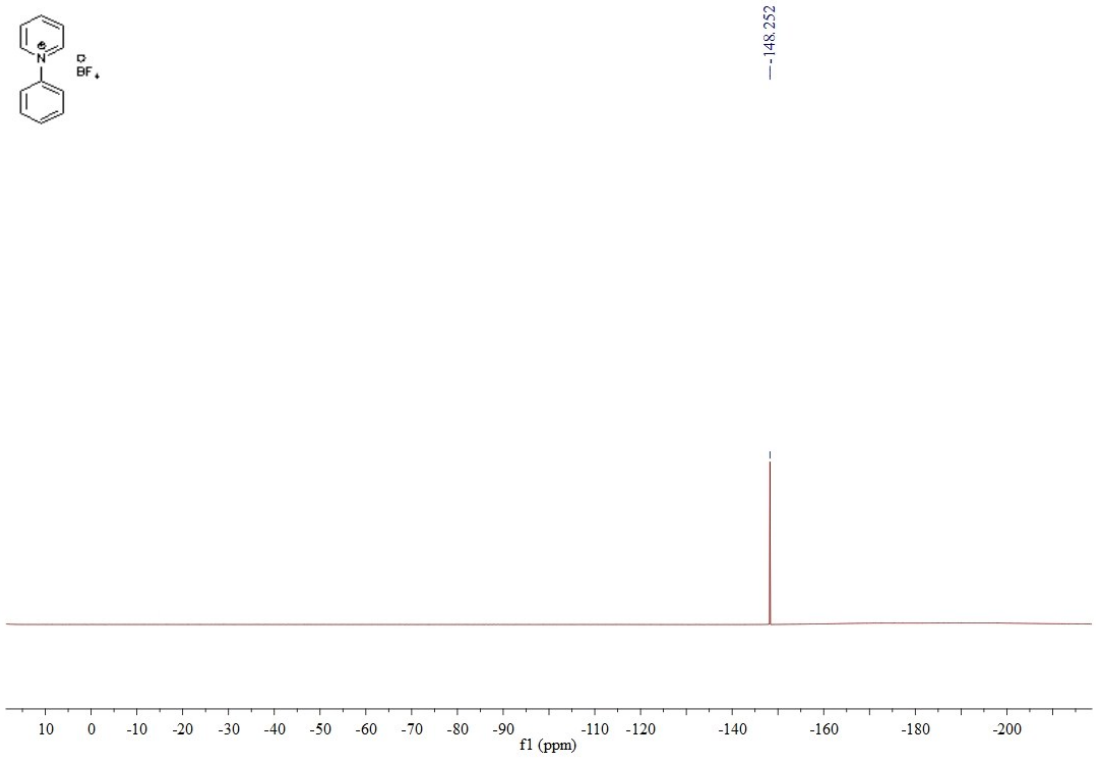
^{1}H NMR spectra of **1b**:



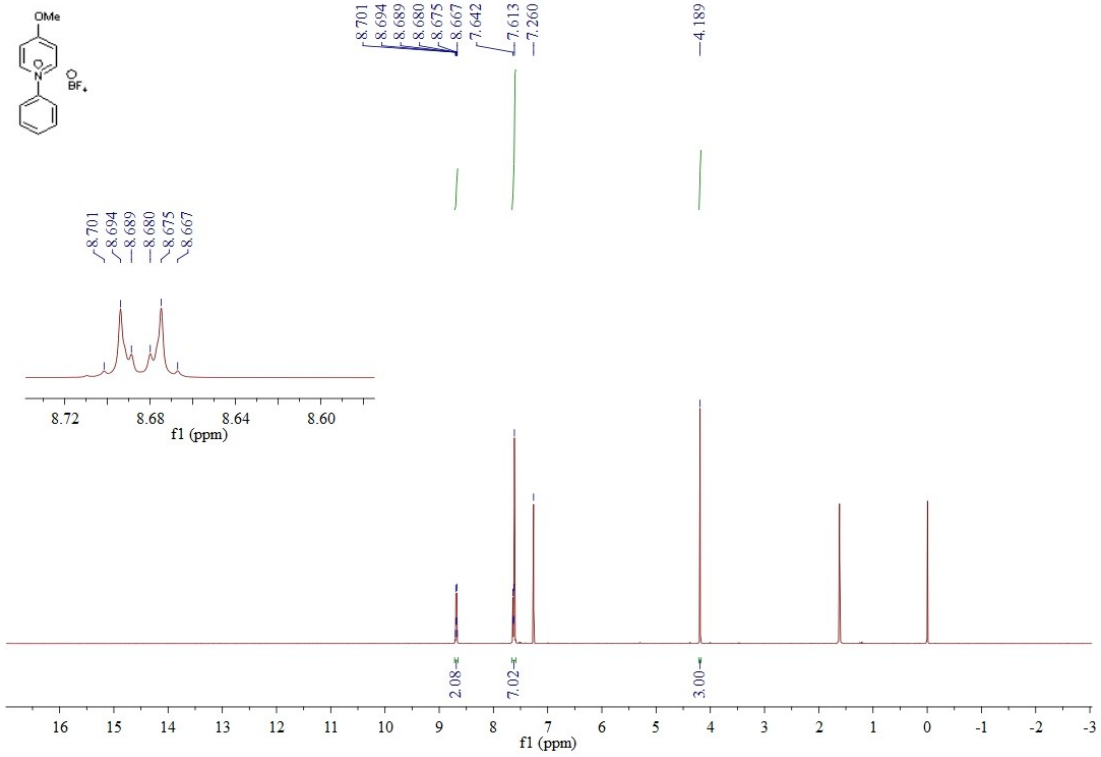
^{13}C NMR spectra of **1b**:



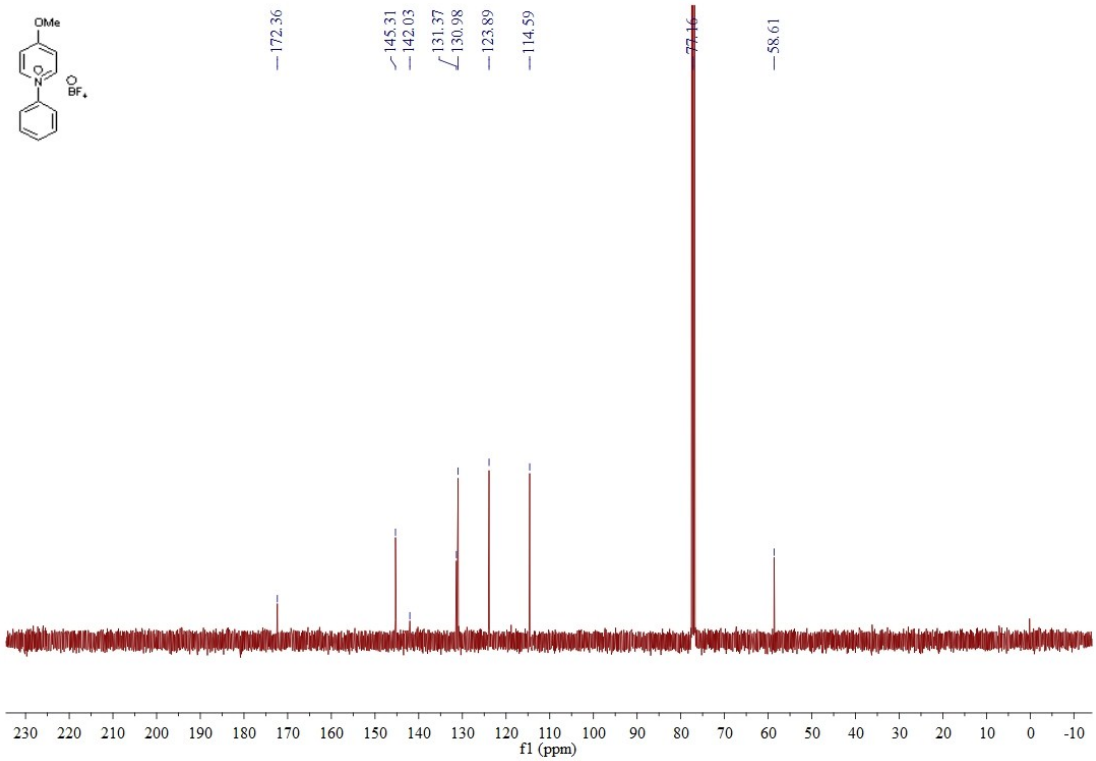
^{19}F NMR spectra of **1b**:



^{1}H NMR spectra of **1c**:



^{13}C NMR spectra of **1c**:



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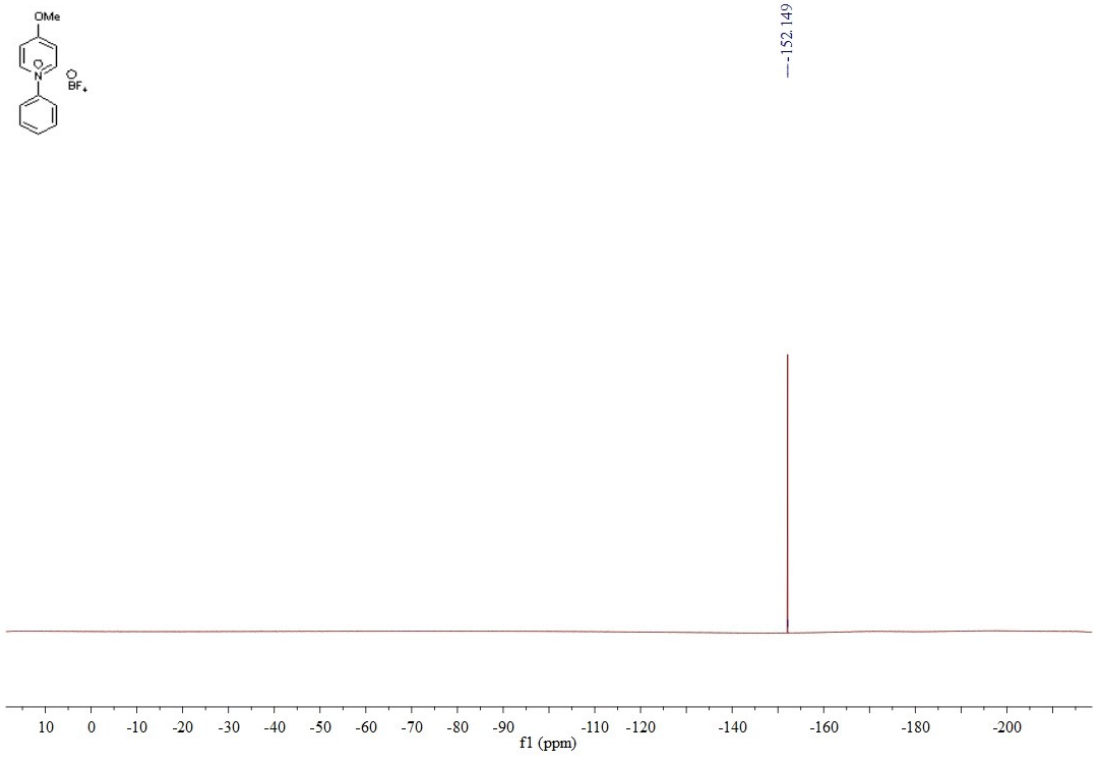
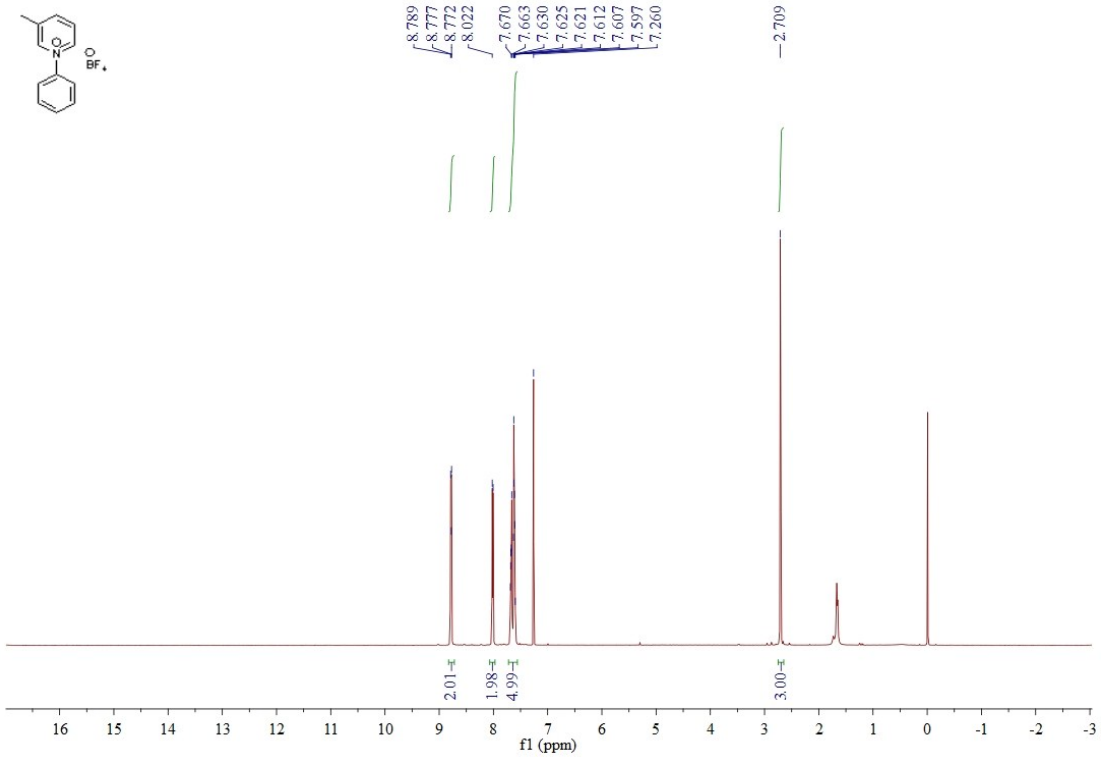
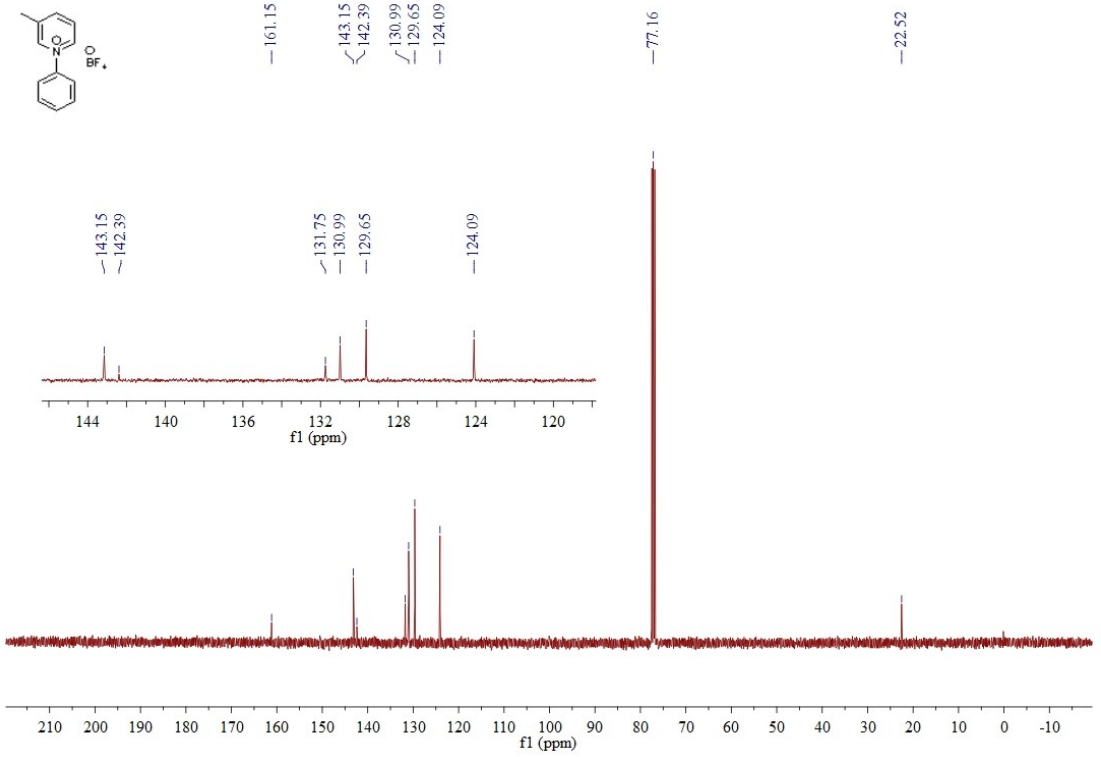


^{1}H NMR spectra of **1d**:



^{13}C NMR spectra of **1d**:



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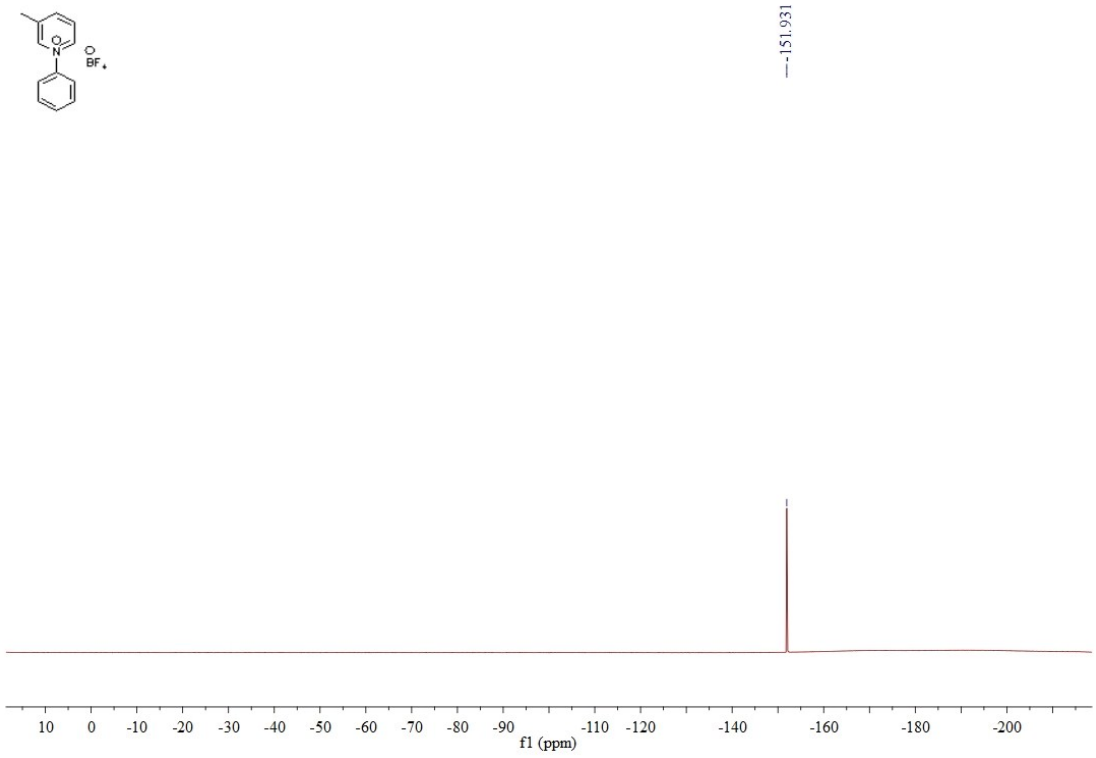

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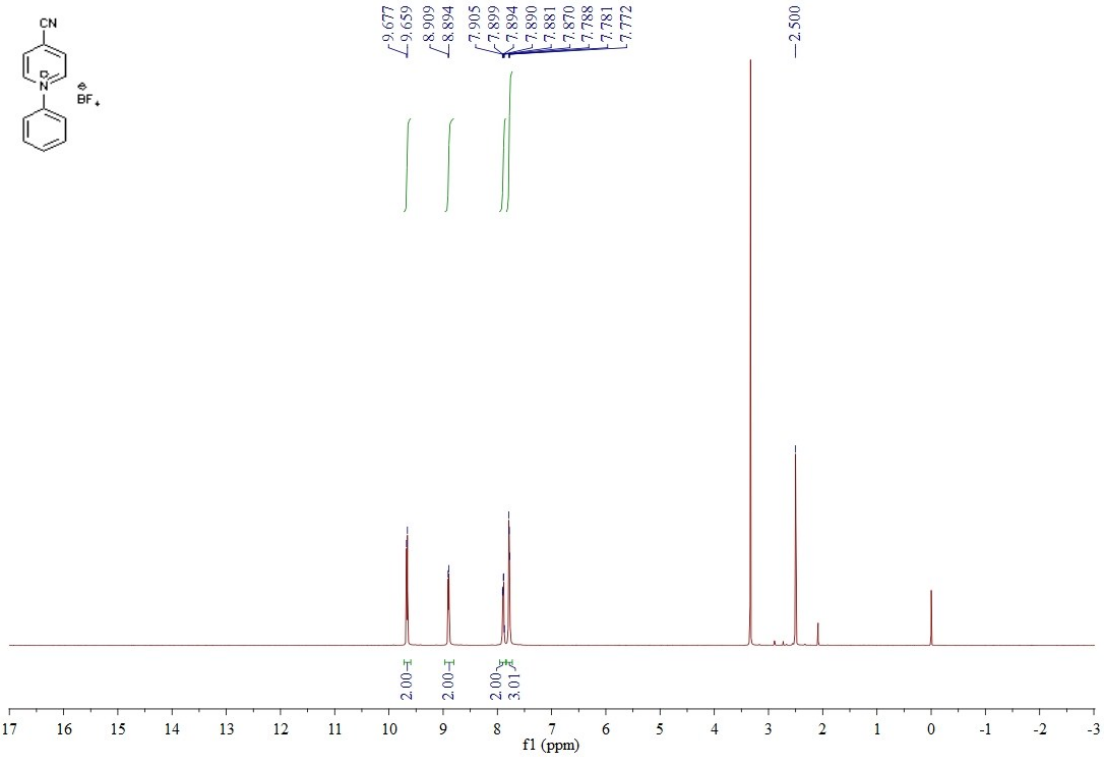

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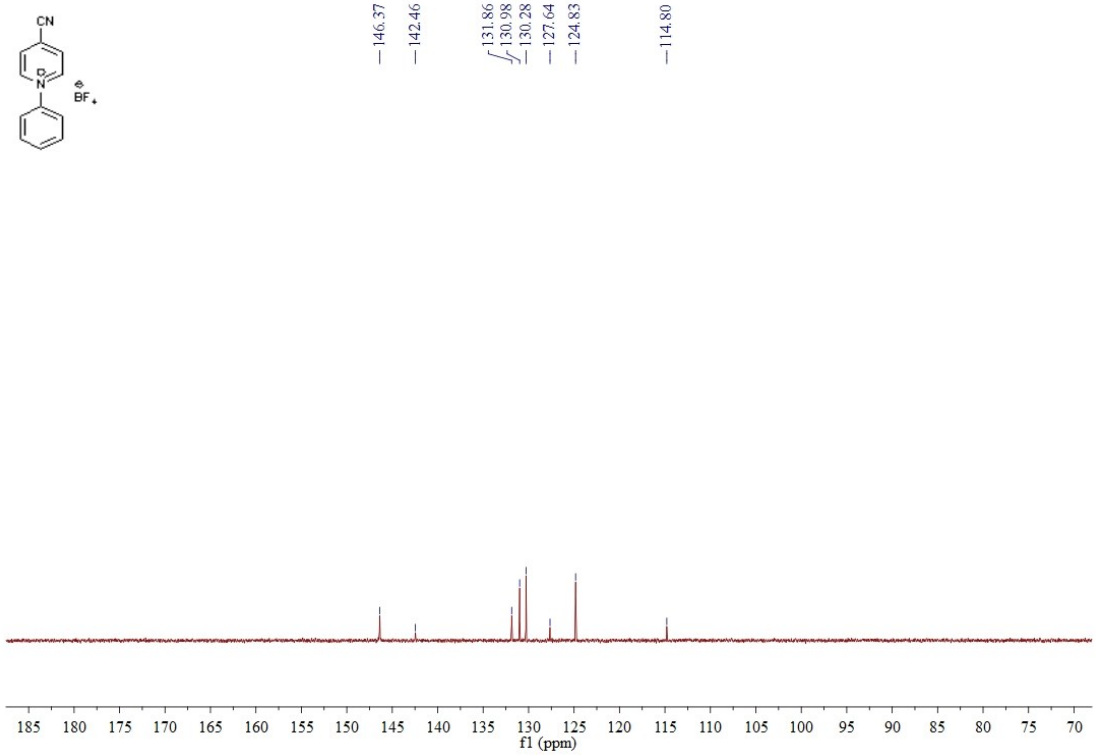
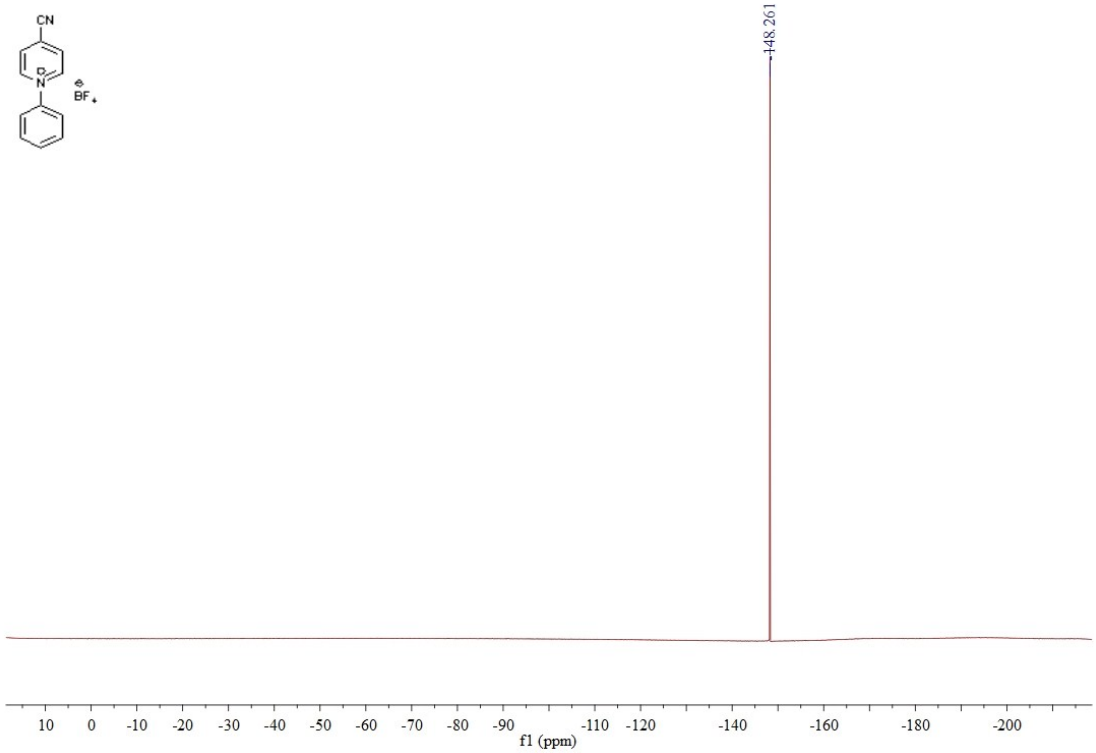
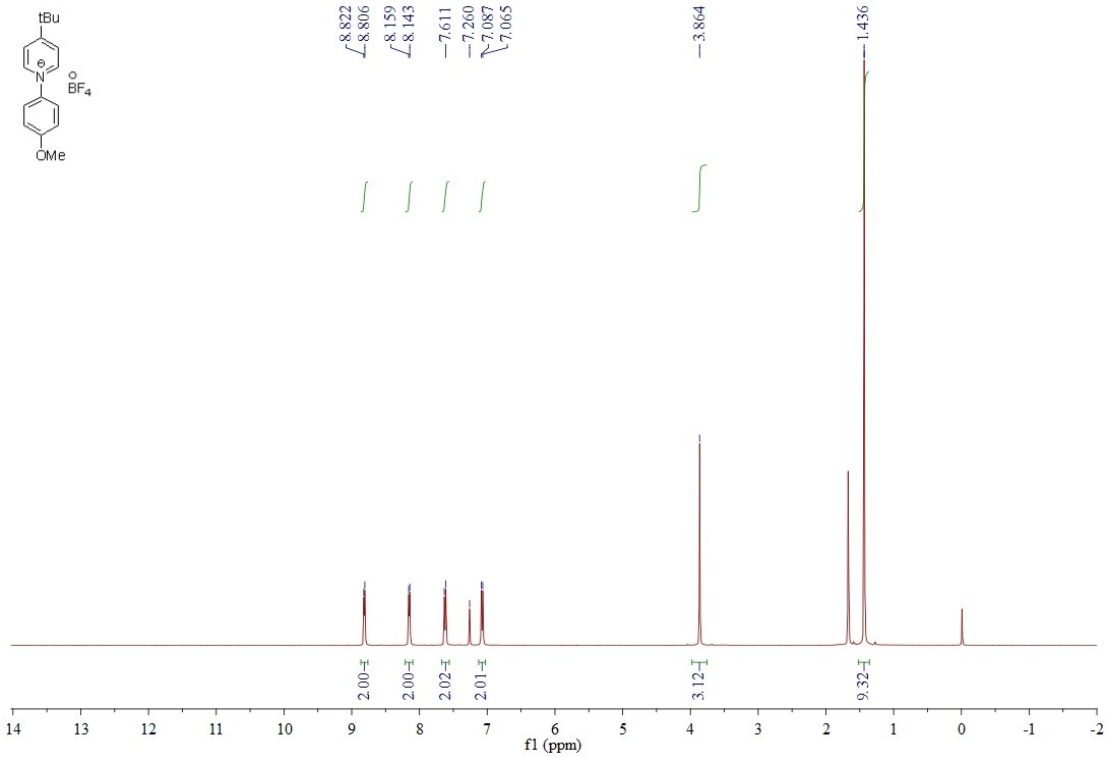


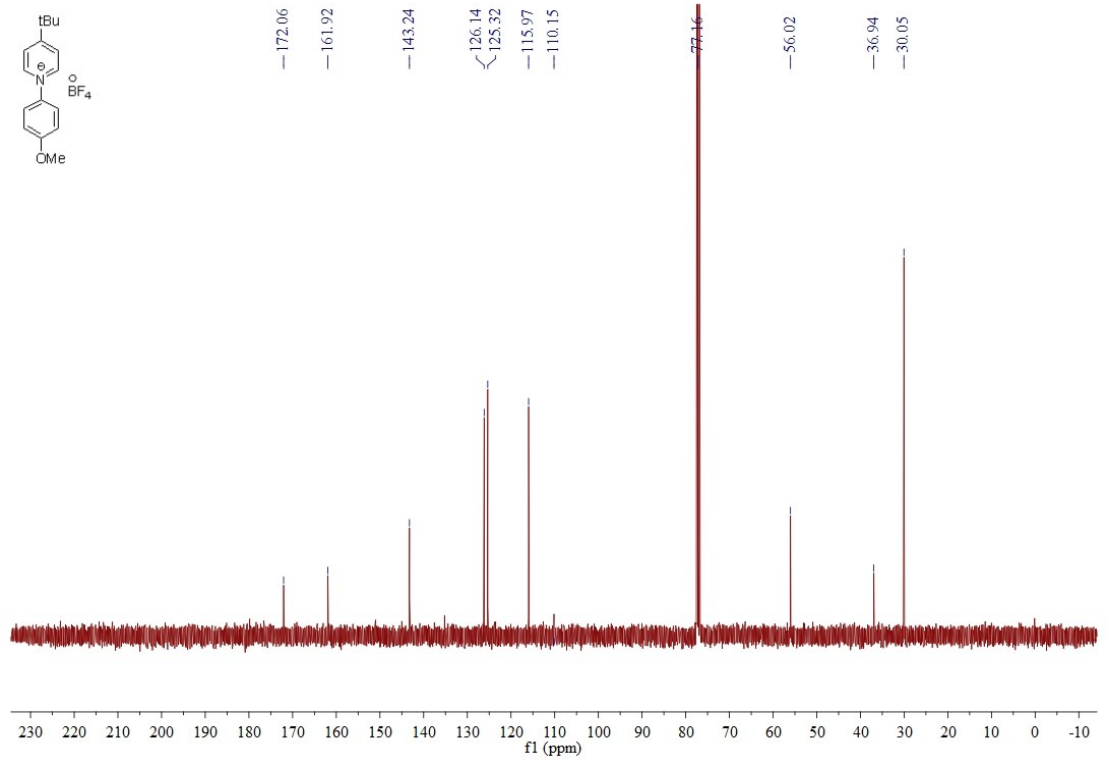
^{19}F NMR spectra of **1e**:



^{1}H NMR spectra of **1f**:



^{13}C NMR spectra of **1f**:



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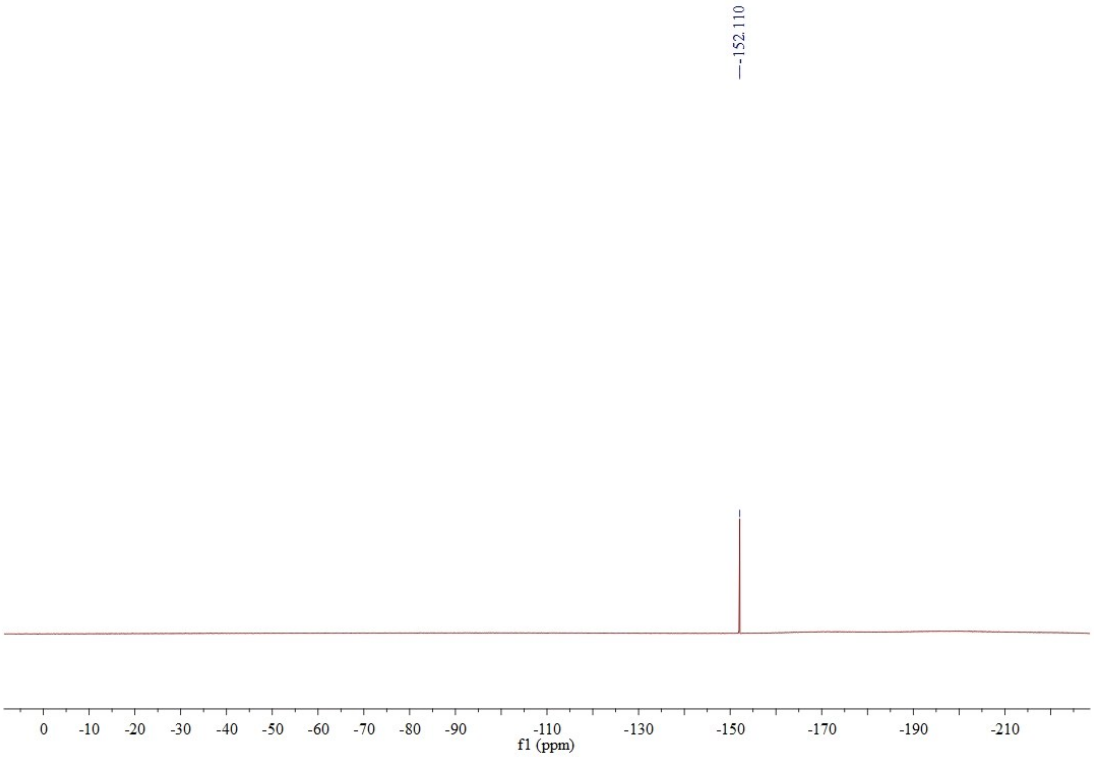
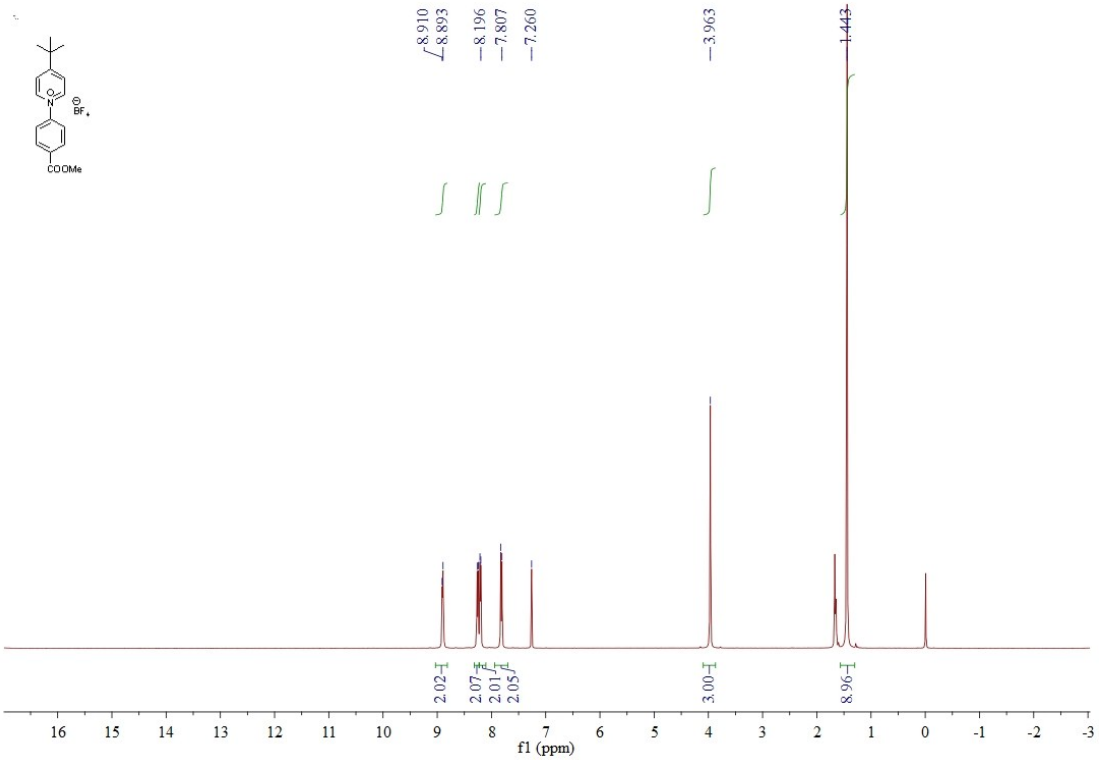
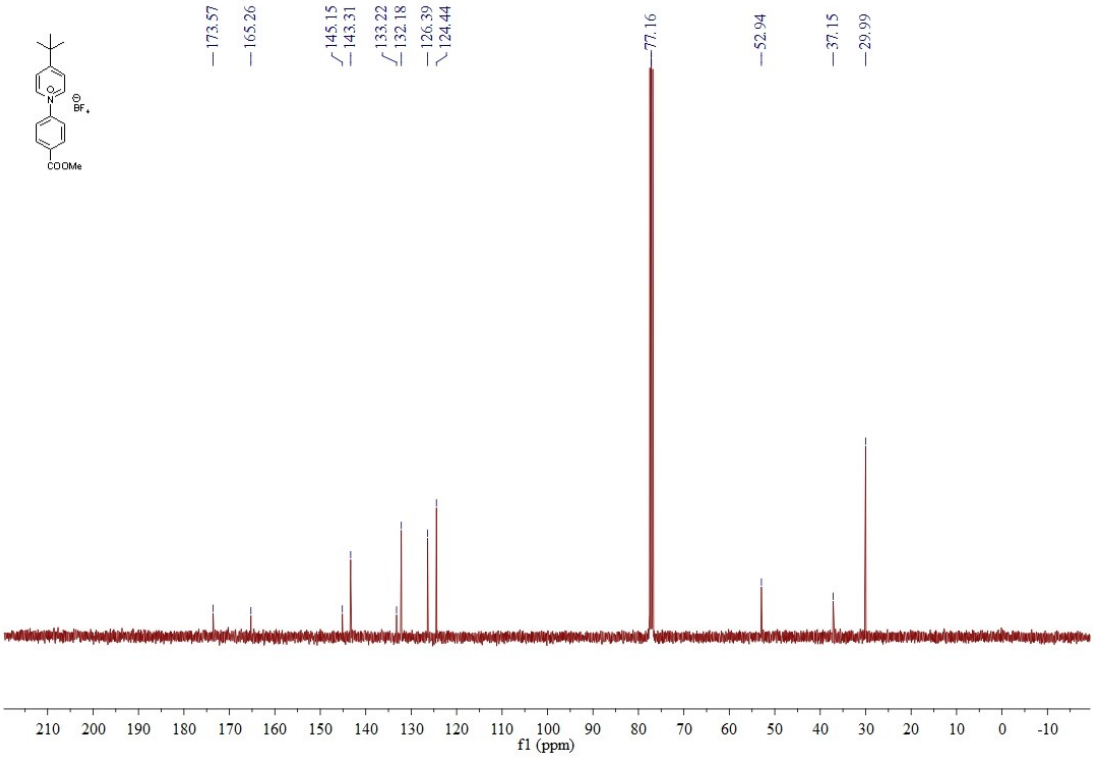


^{1}H NMR spectra of **1g**:



^{13}C NMR spectra of **1g**:



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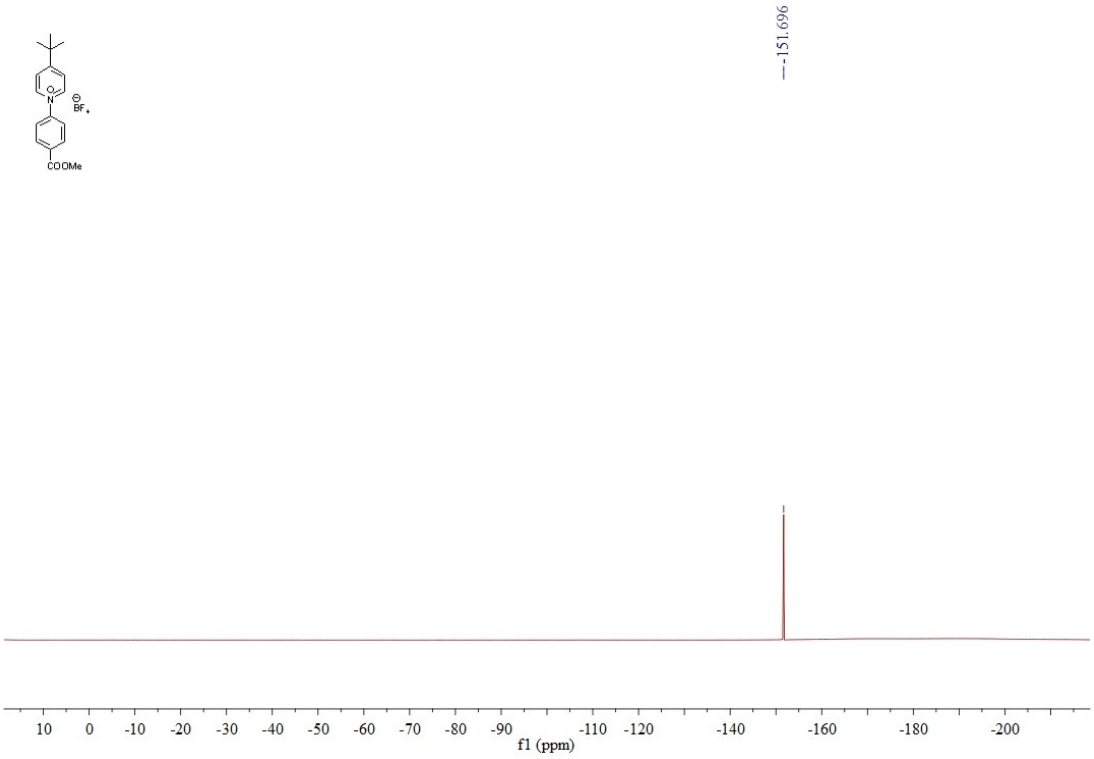
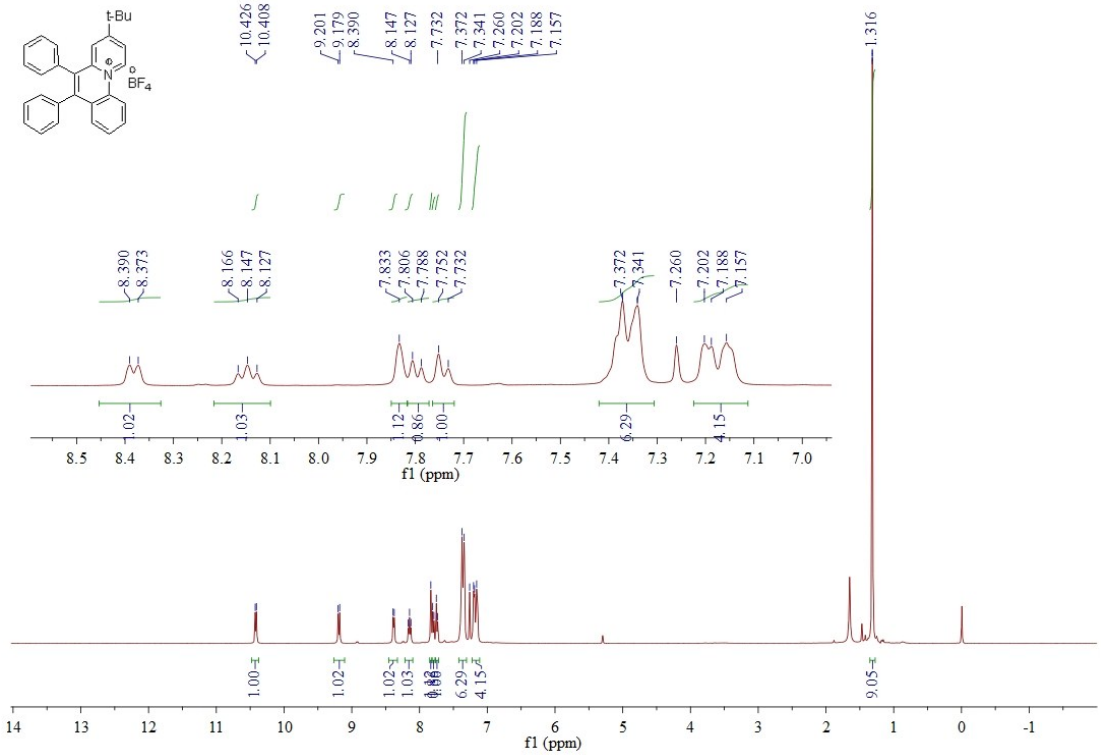


^{1}H NMR spectra of **3a**:



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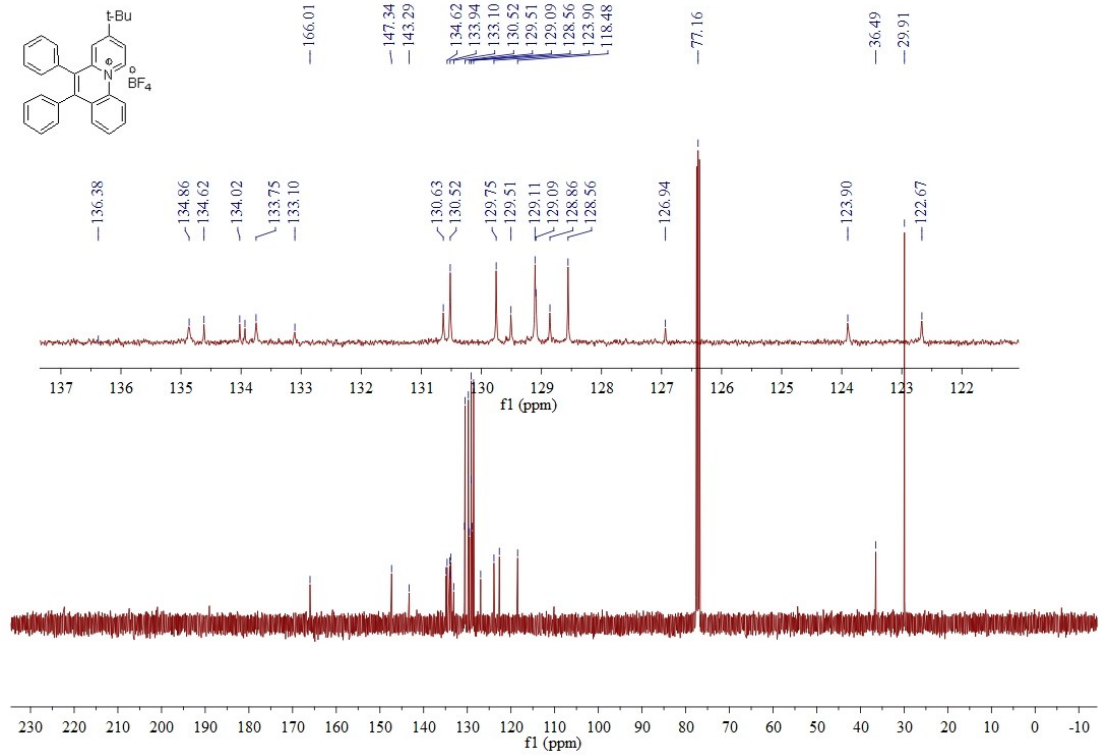
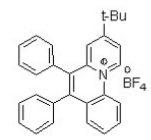
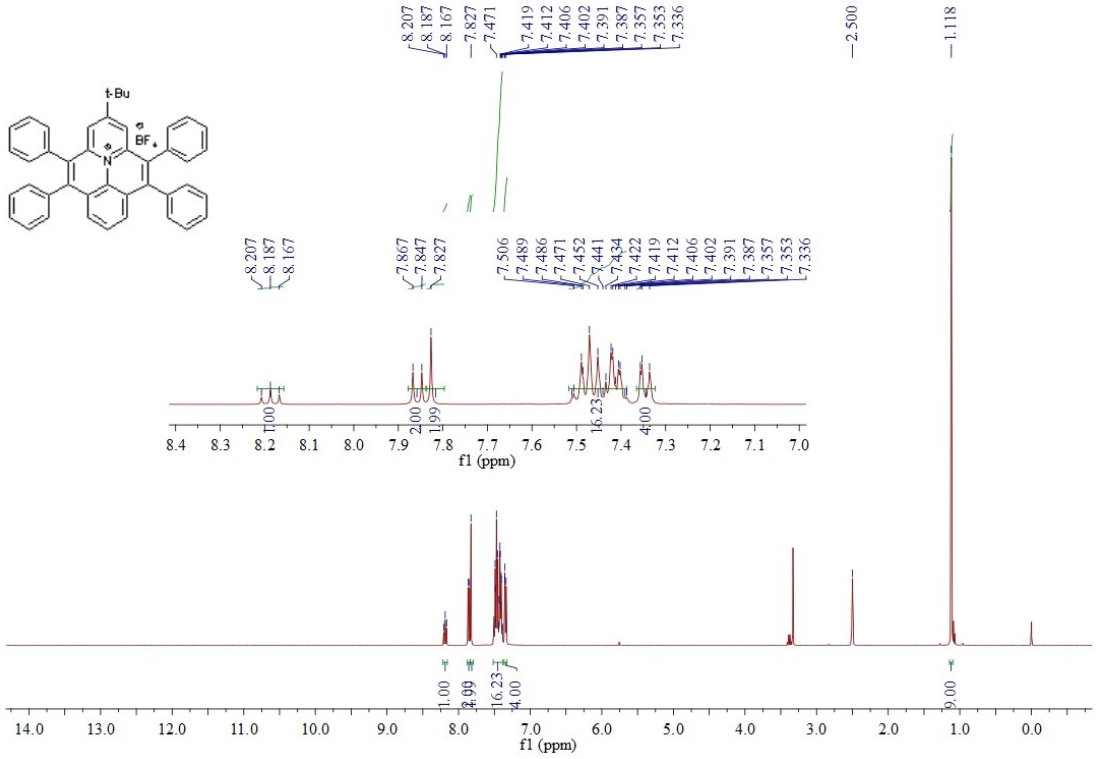


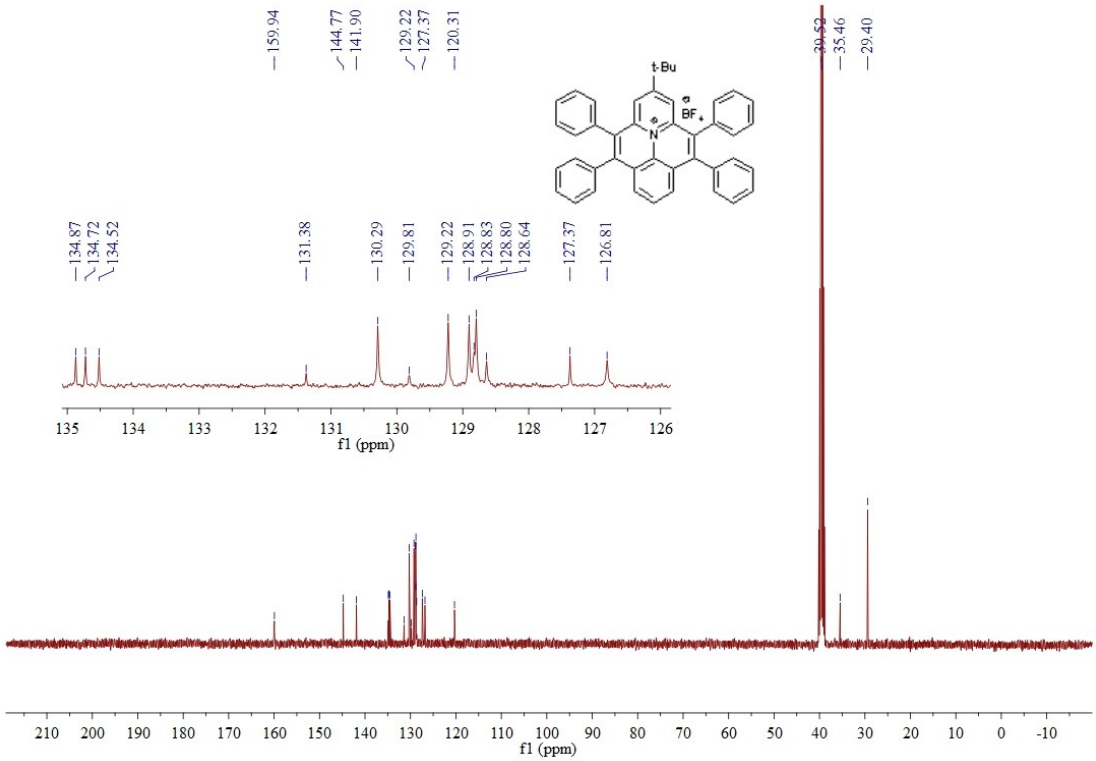
^{19}F NMR spectra of **3a**:



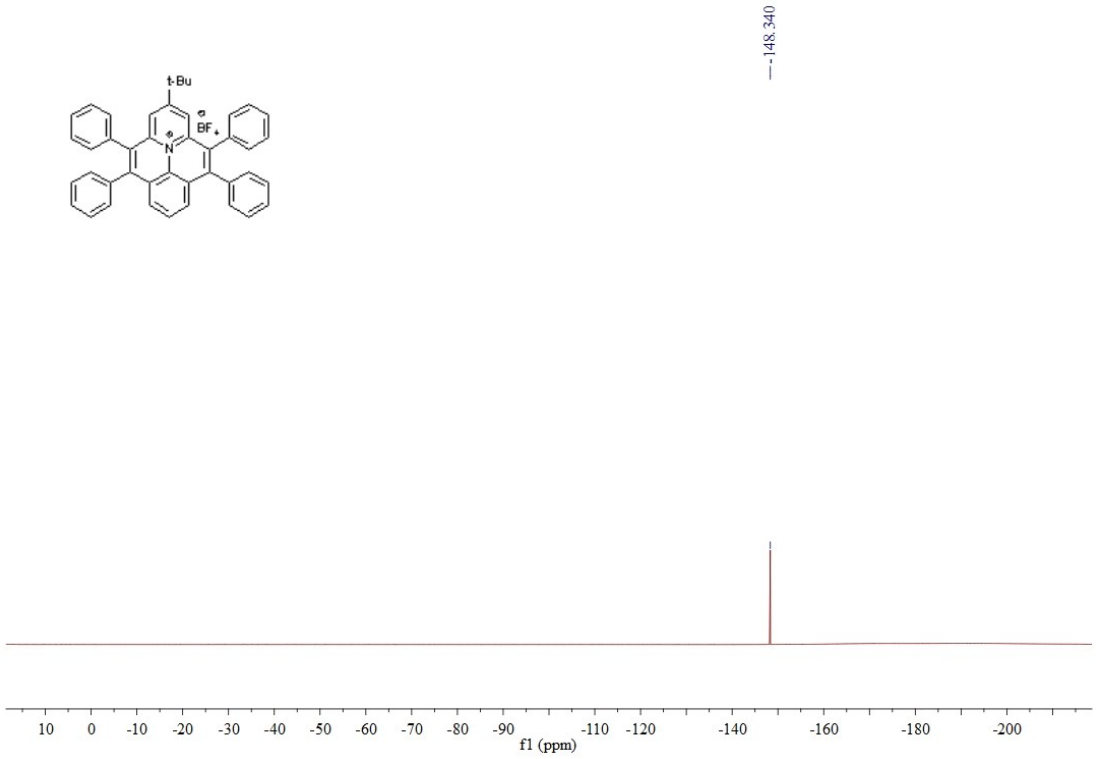
^{1}H NMR spectra of **4a**:



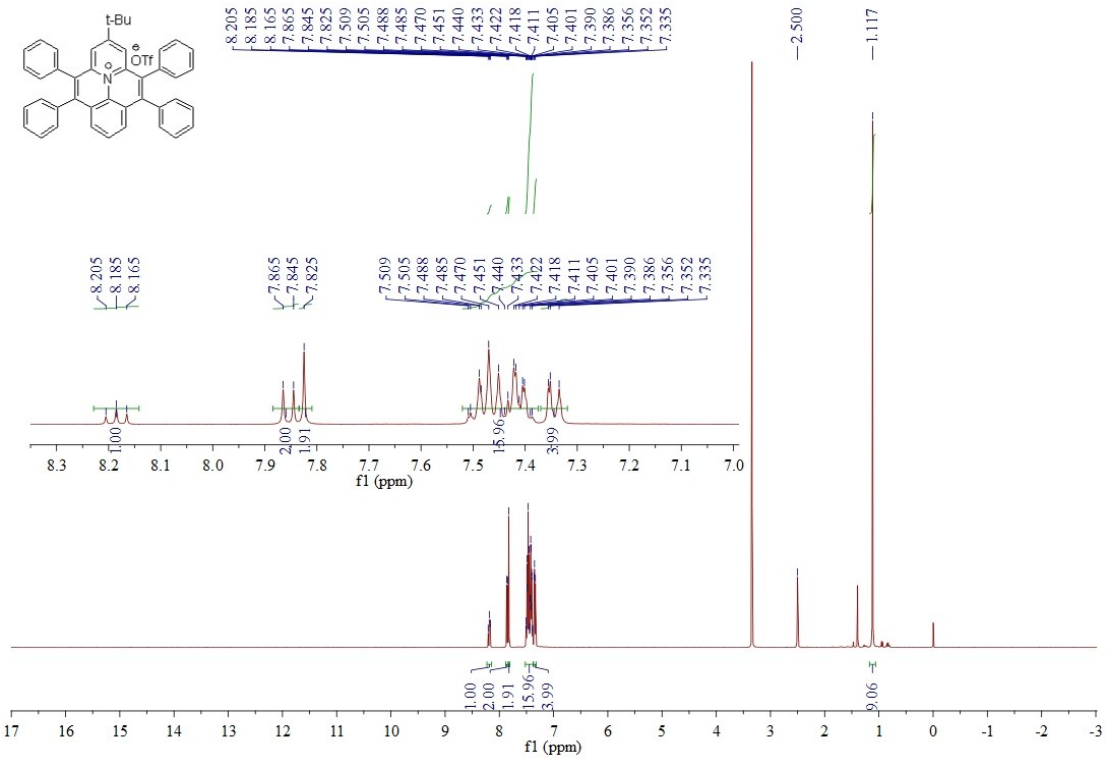
^{13}C NMR spectra of **4a**:



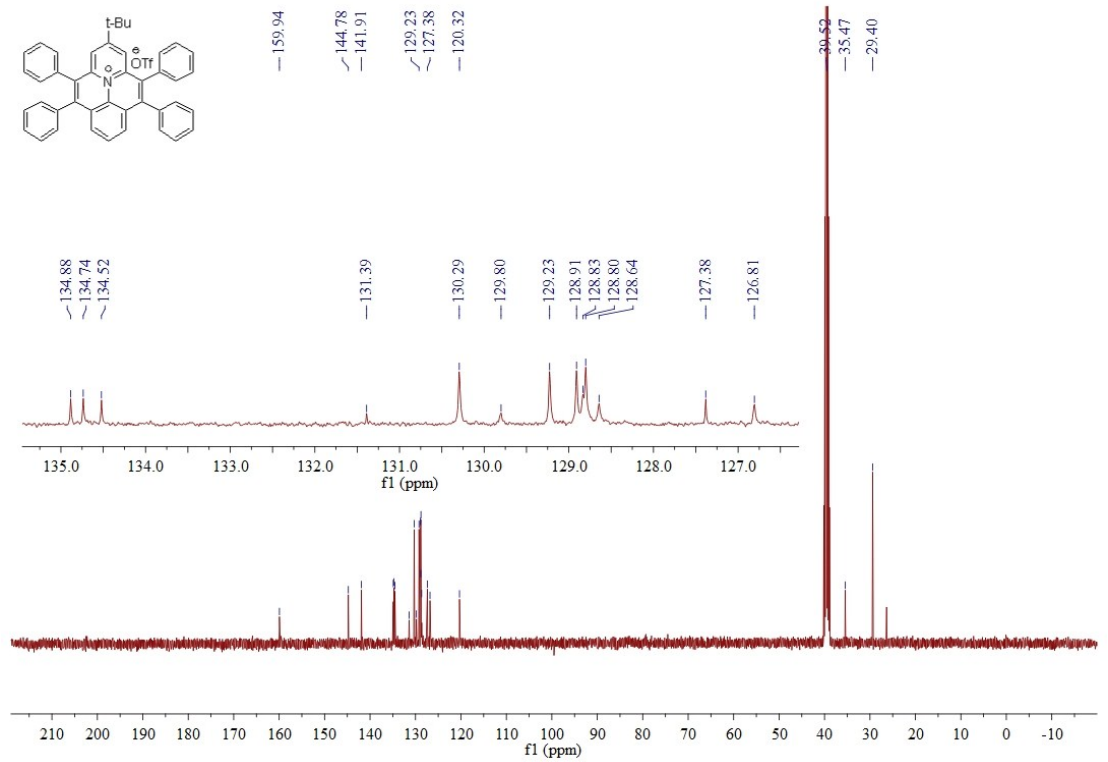
^{19}F NMR spectra of **4a**:



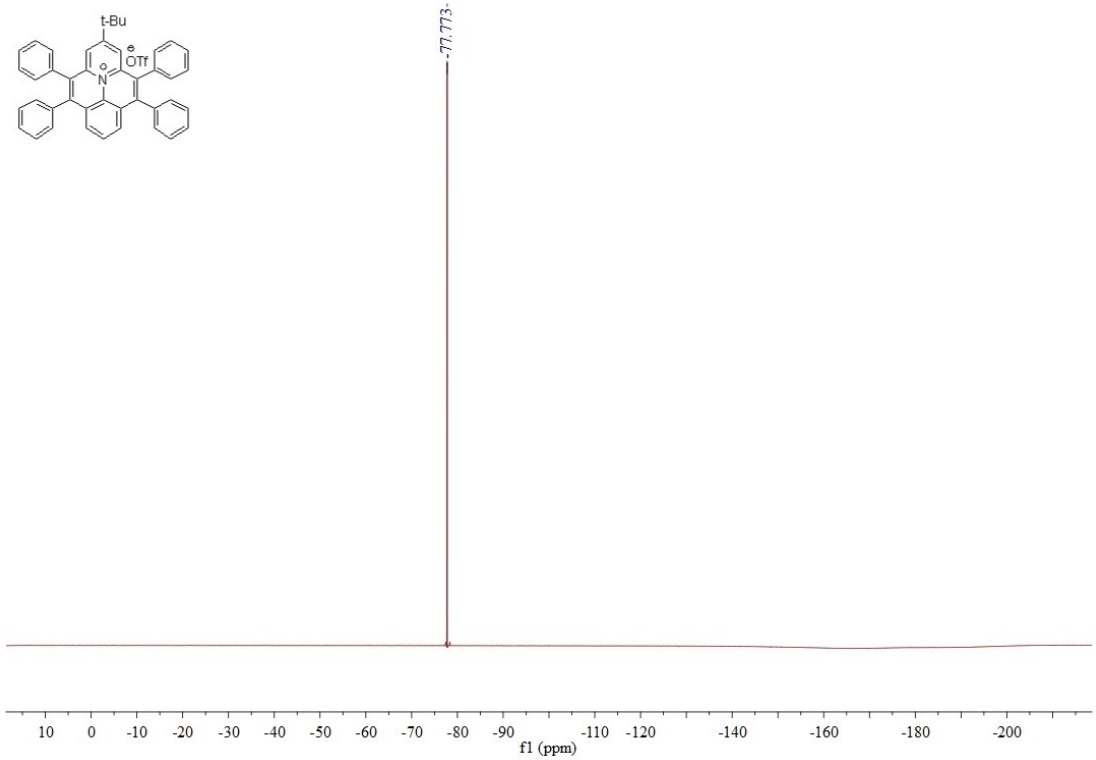
^{1}H NMR spectra of **4a'**:



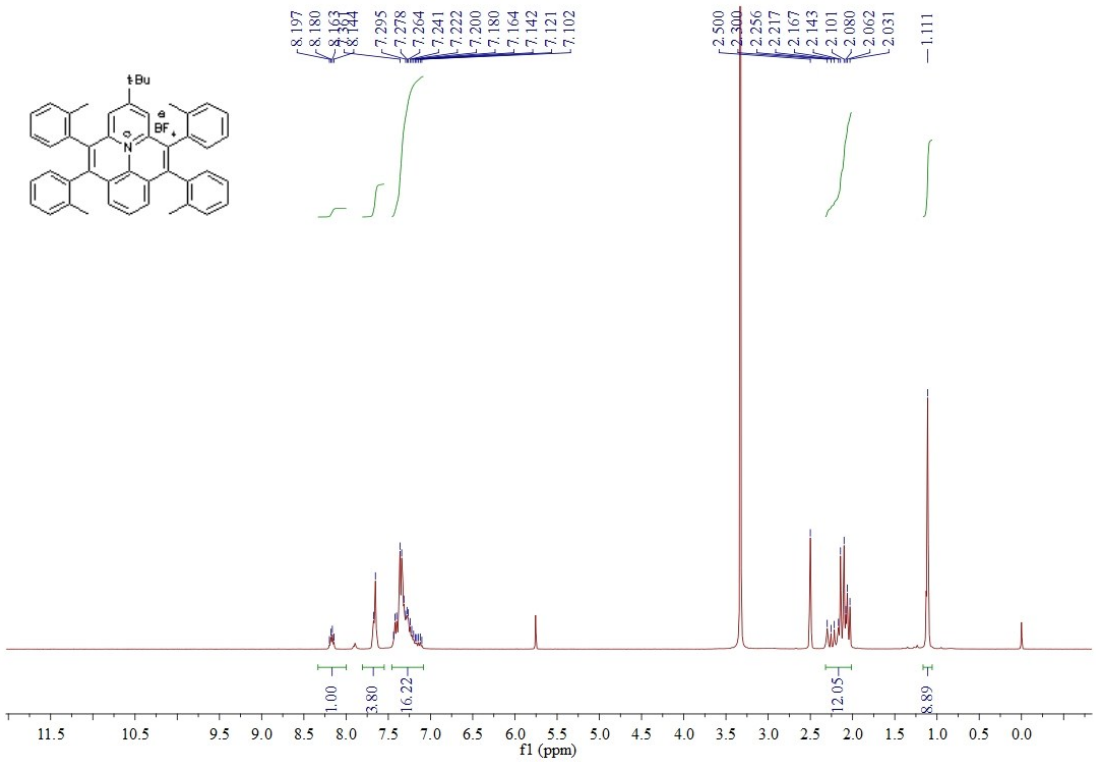
^{13}C NMR spectra of **4a'**:



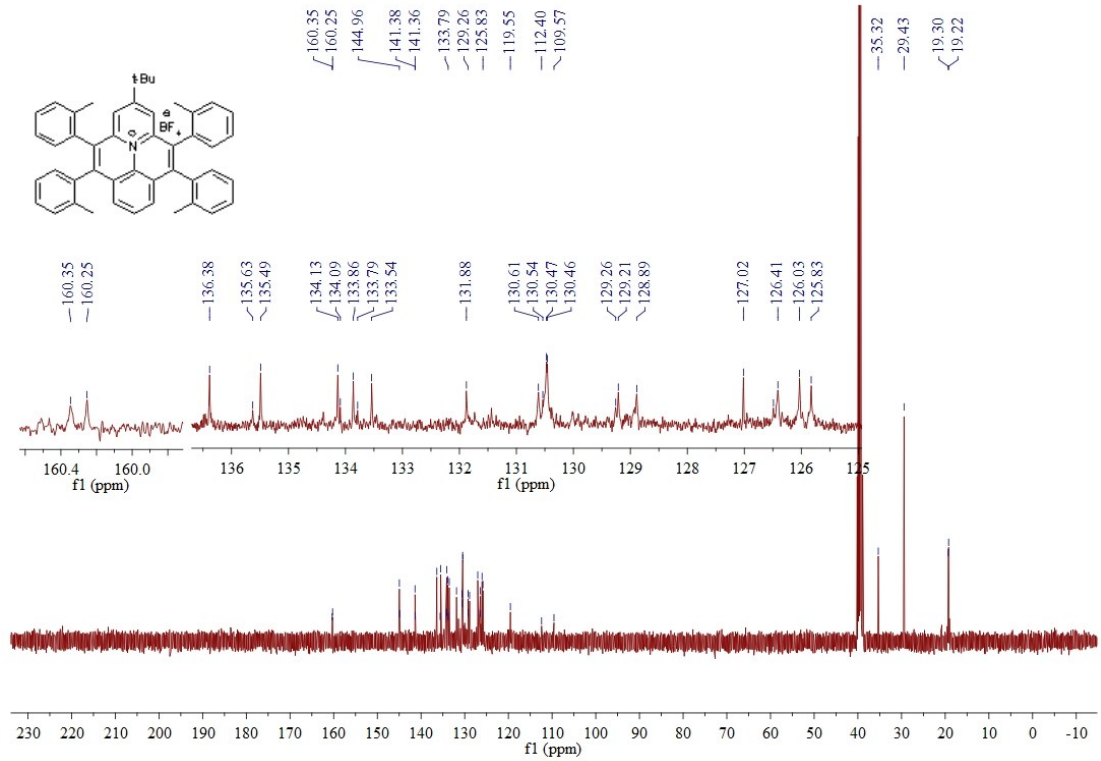
^{19}F NMR spectra of **4a'**:



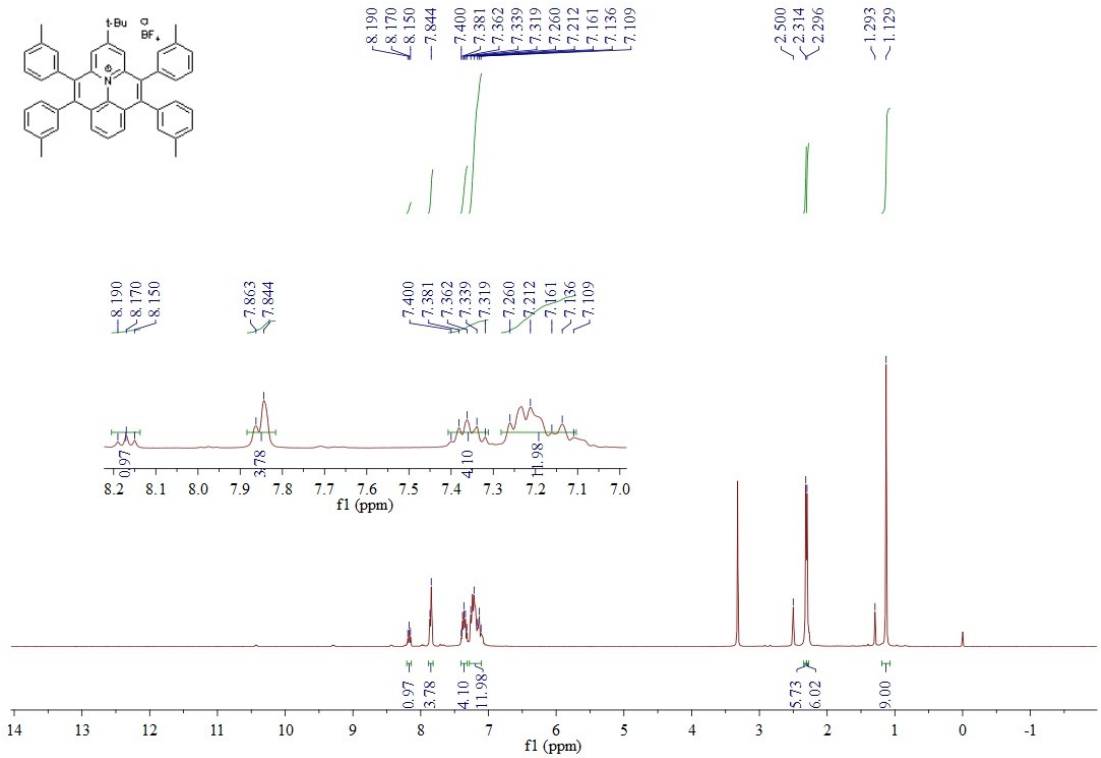
^{1}H NMR spectra of **4b**:



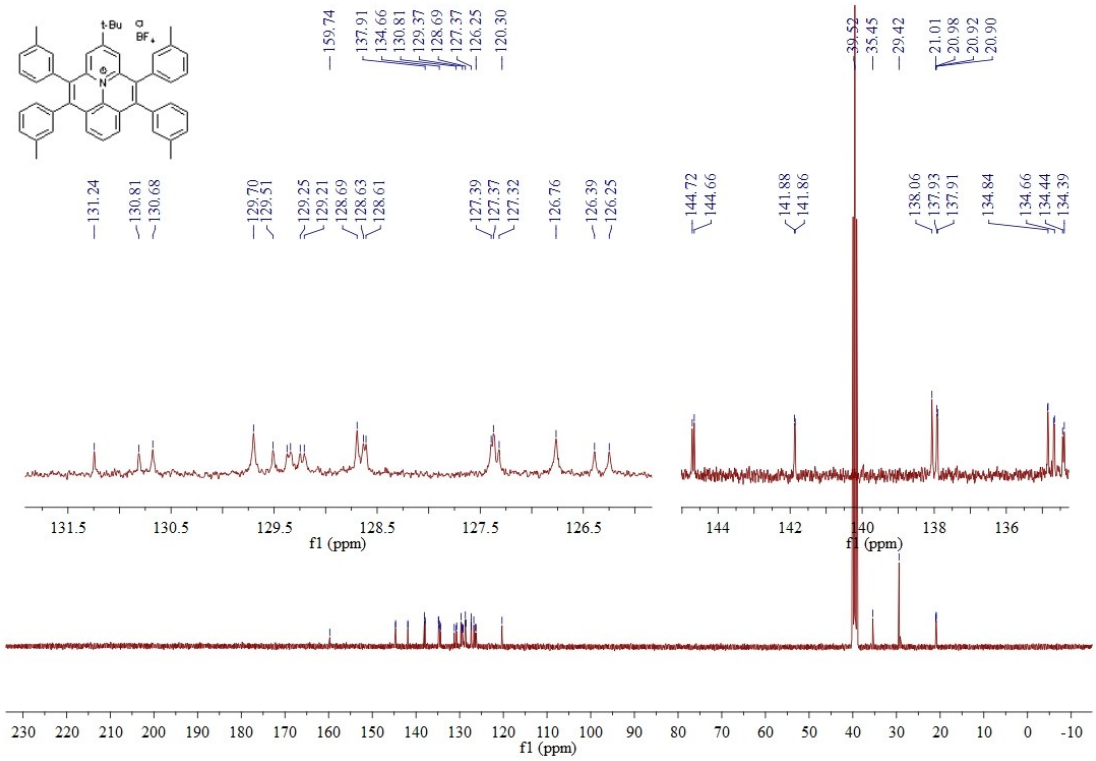
^{13}C NMR spectra of **4b**:



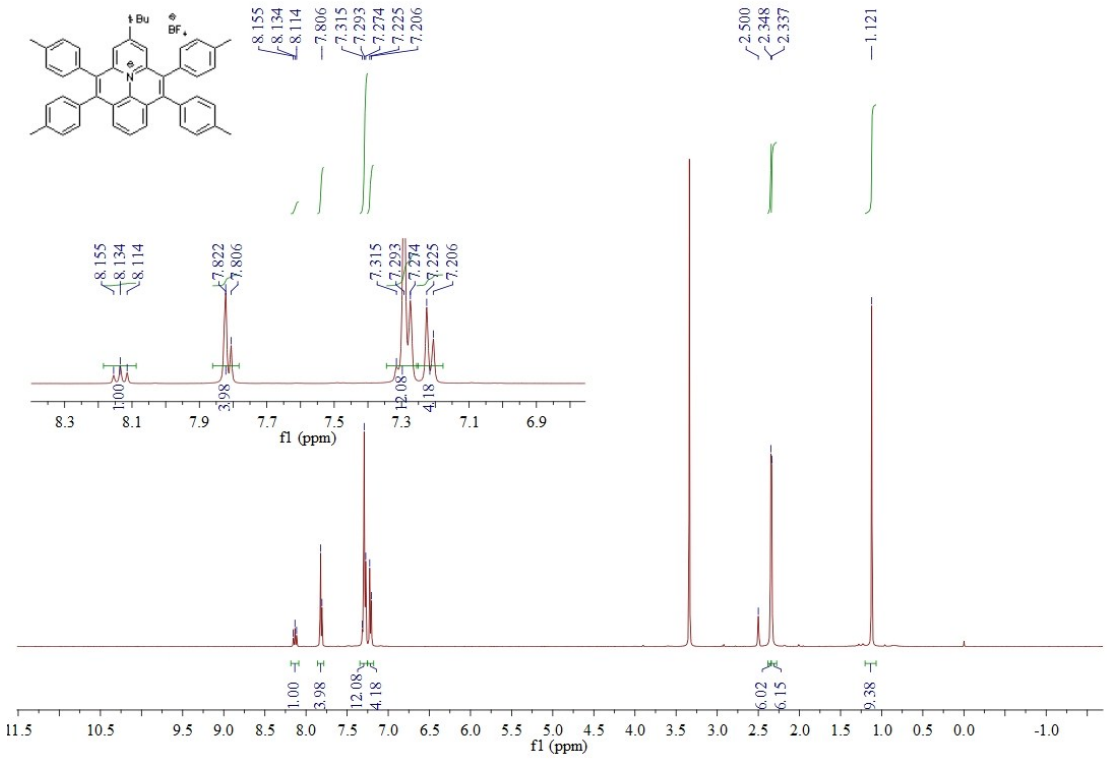
^{1}H NMR spectra of **4c**:



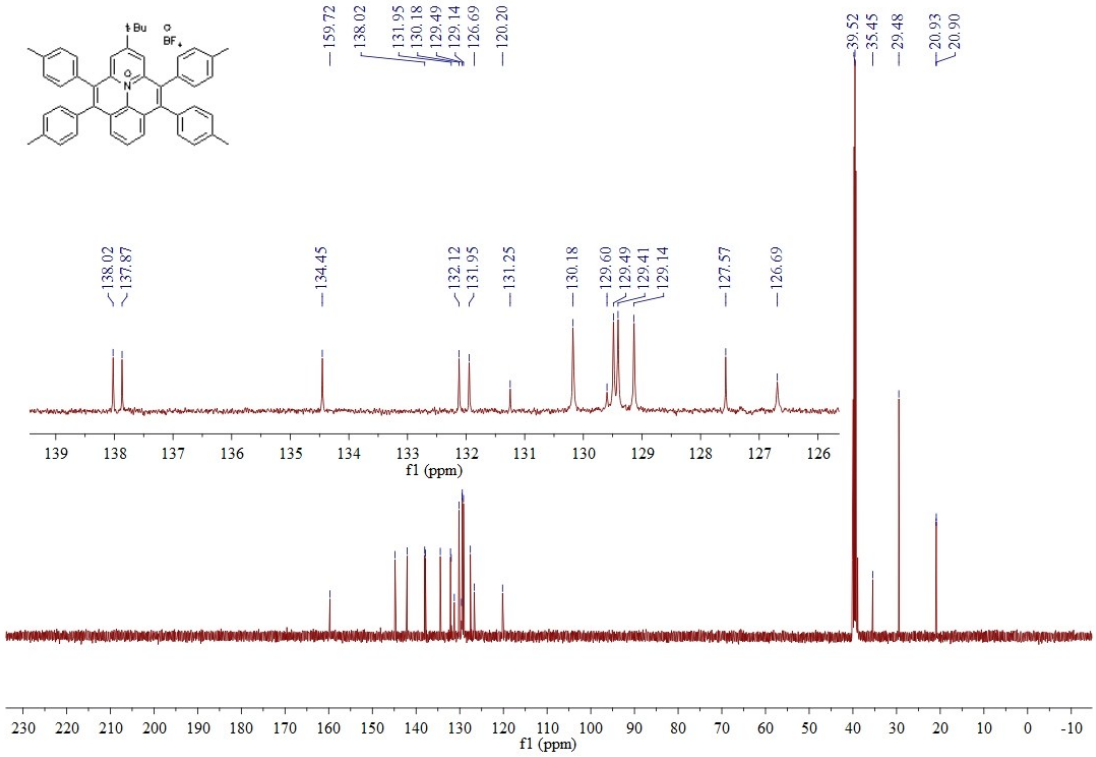
^{13}C NMR spectra of **4c**:



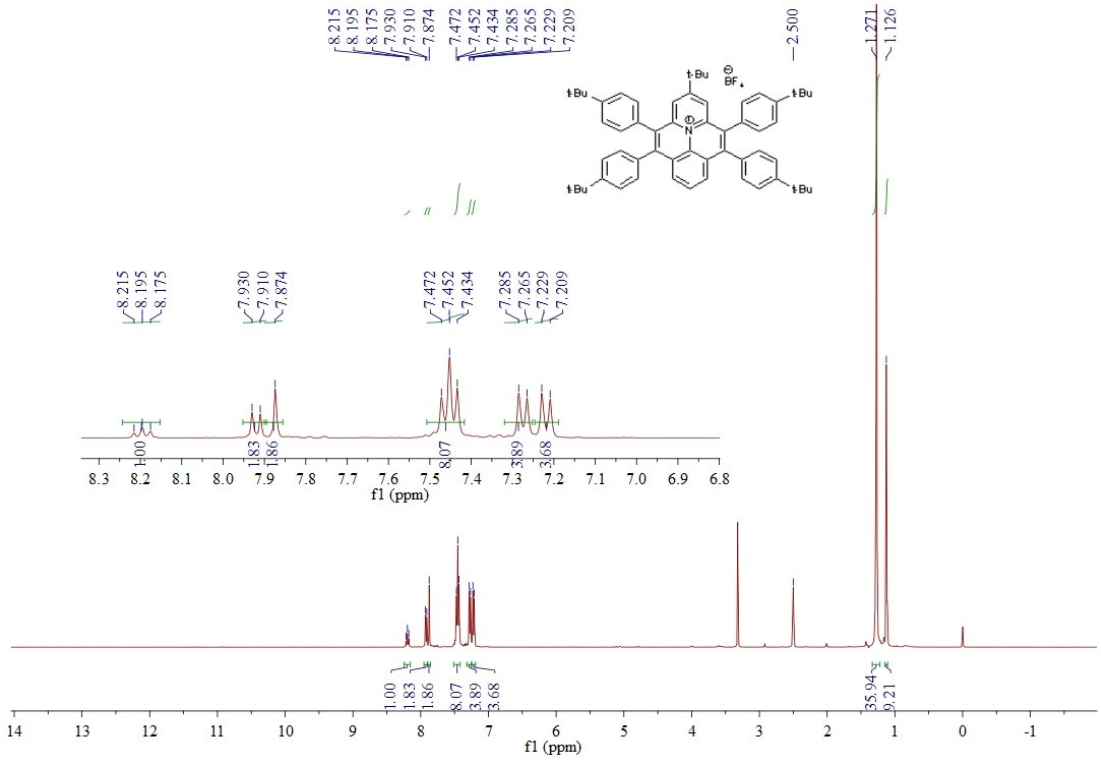
^{1}H NMR spectra of **4d**:



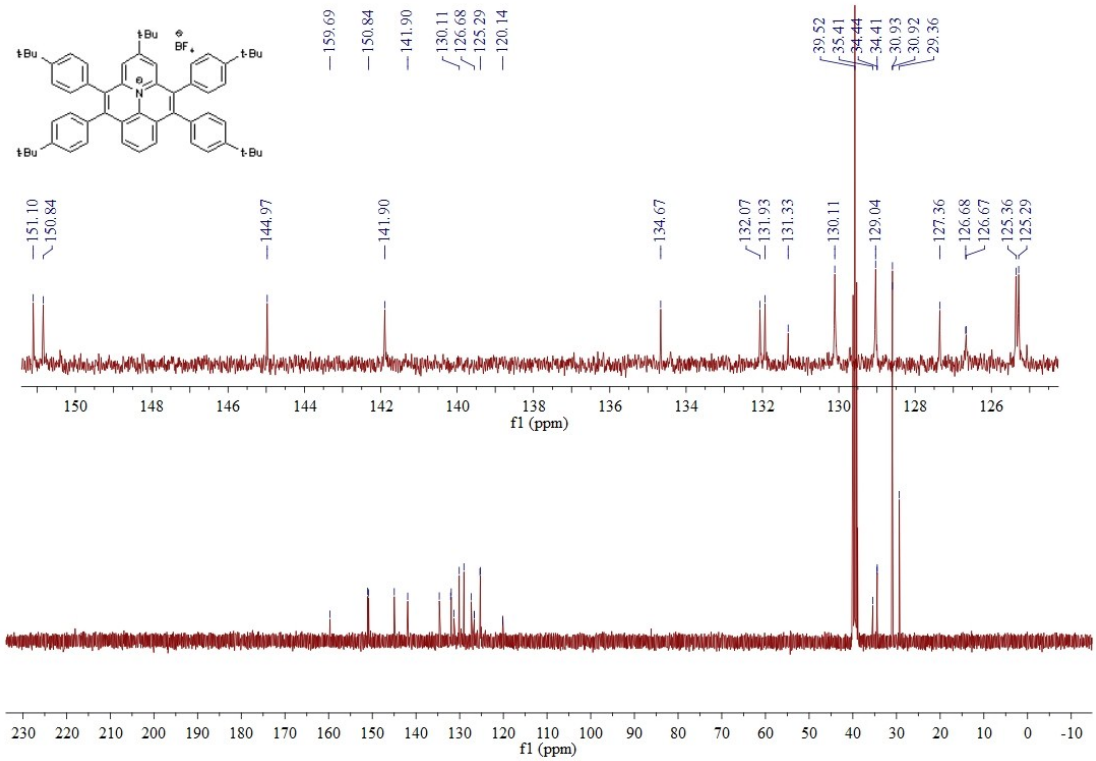
^{13}C NMR spectra of **4d**:



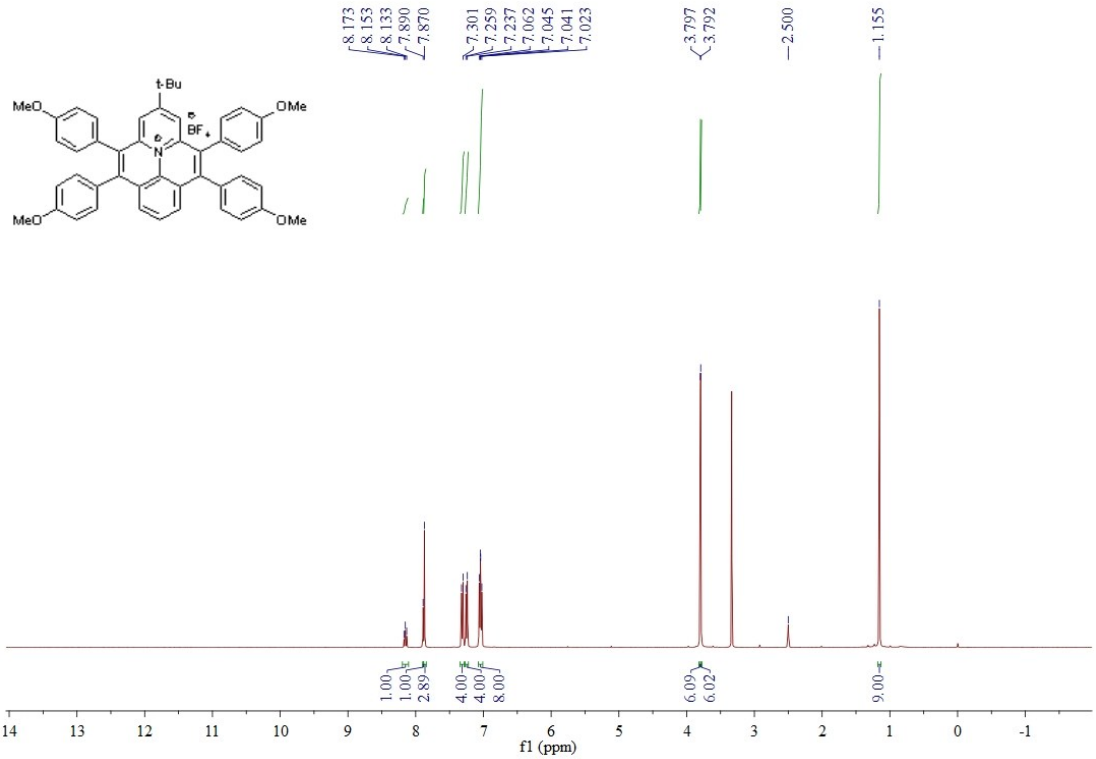
^{1}H NMR spectra of **4e**:



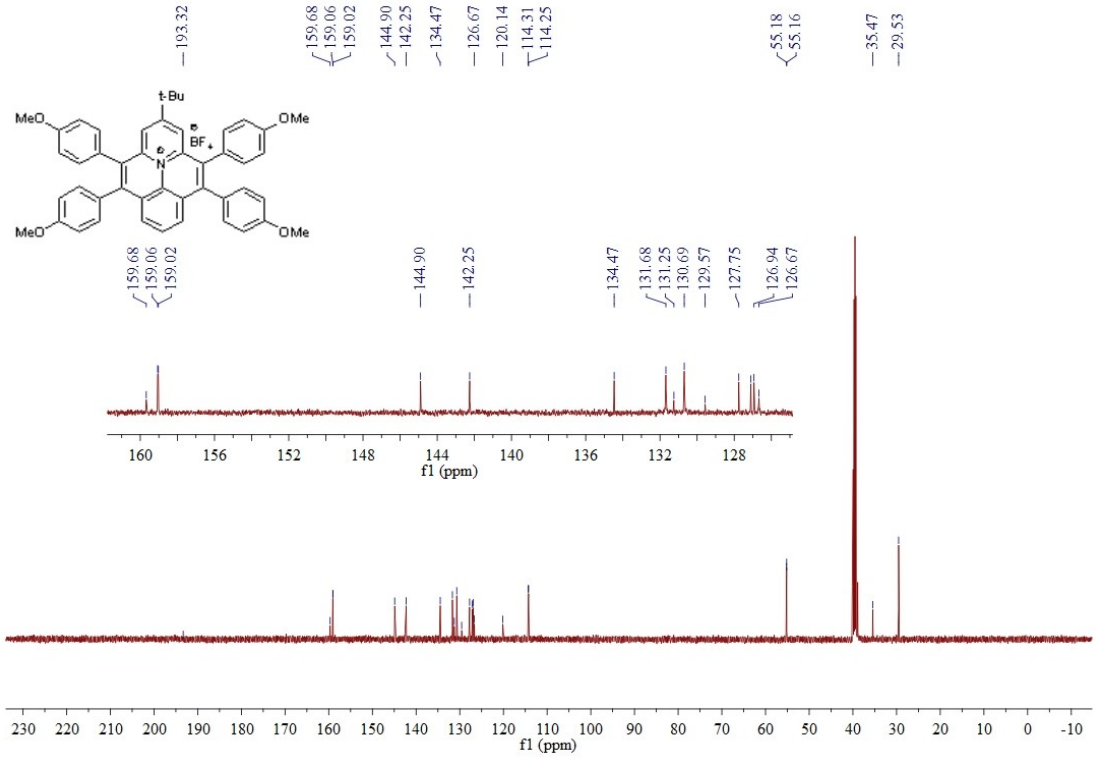
^{13}C NMR spectra of **4e**:



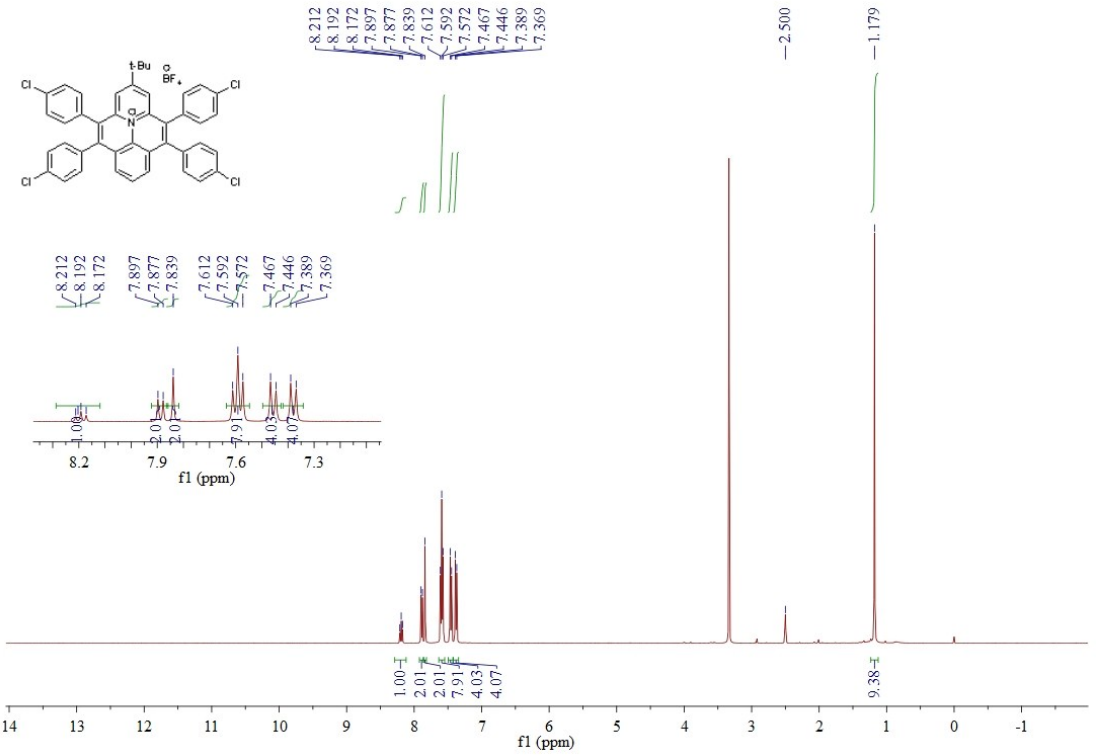
^{1}H NMR spectra of **4f**:



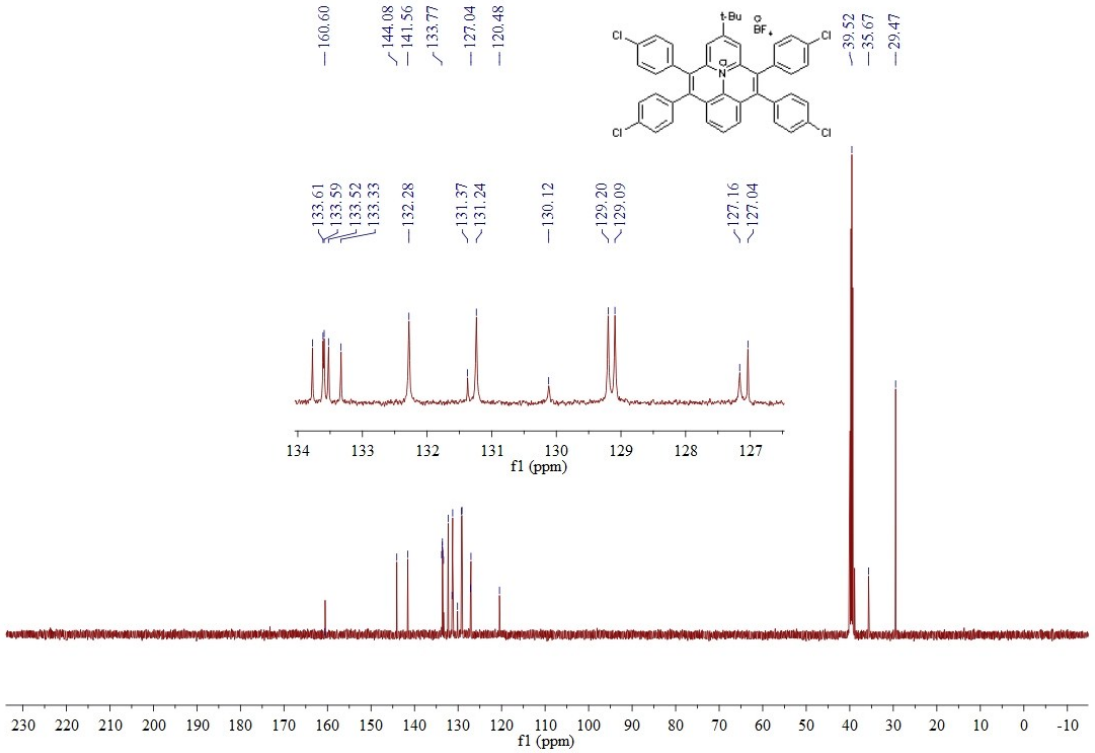
^{13}C NMR spectra of **4f**:



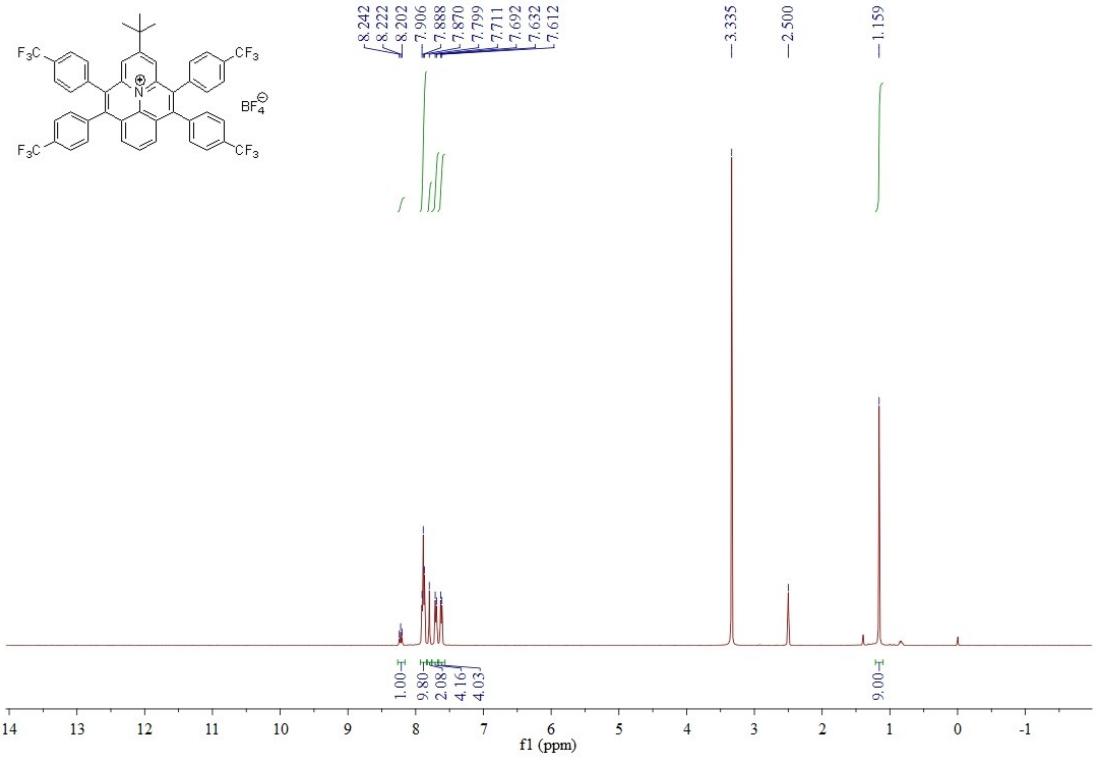
^{1}H NMR spectra of **4g**:



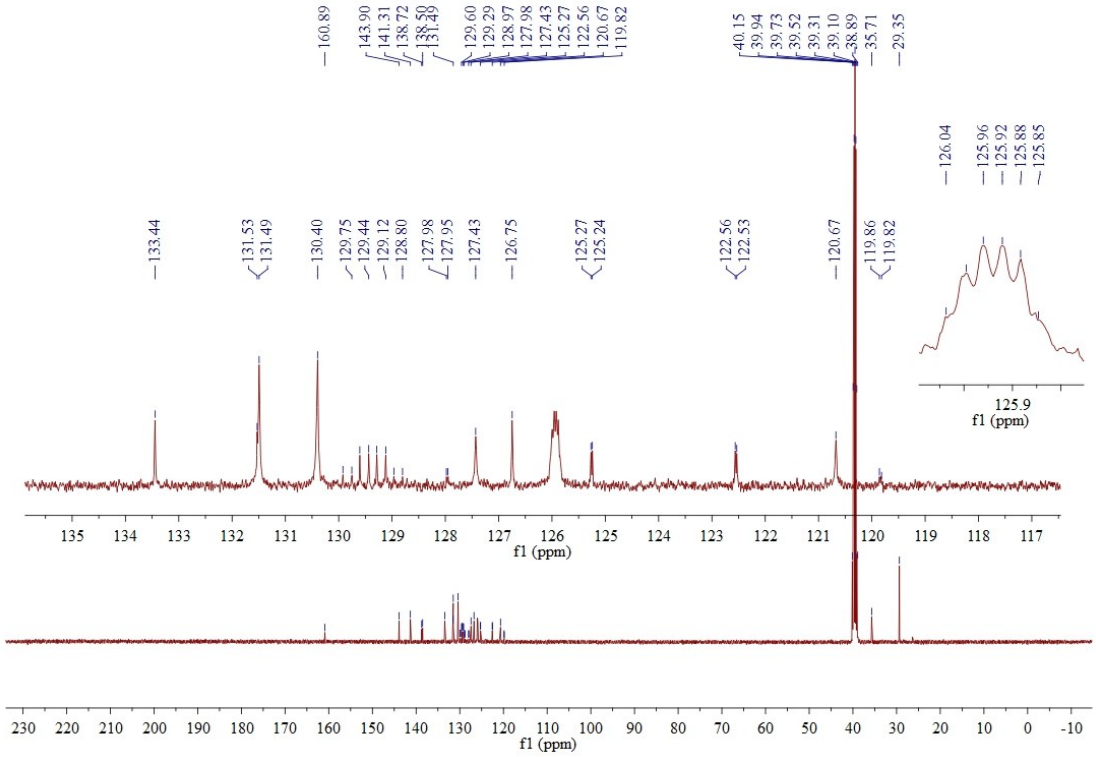
^{13}C NMR spectra of **4g**:



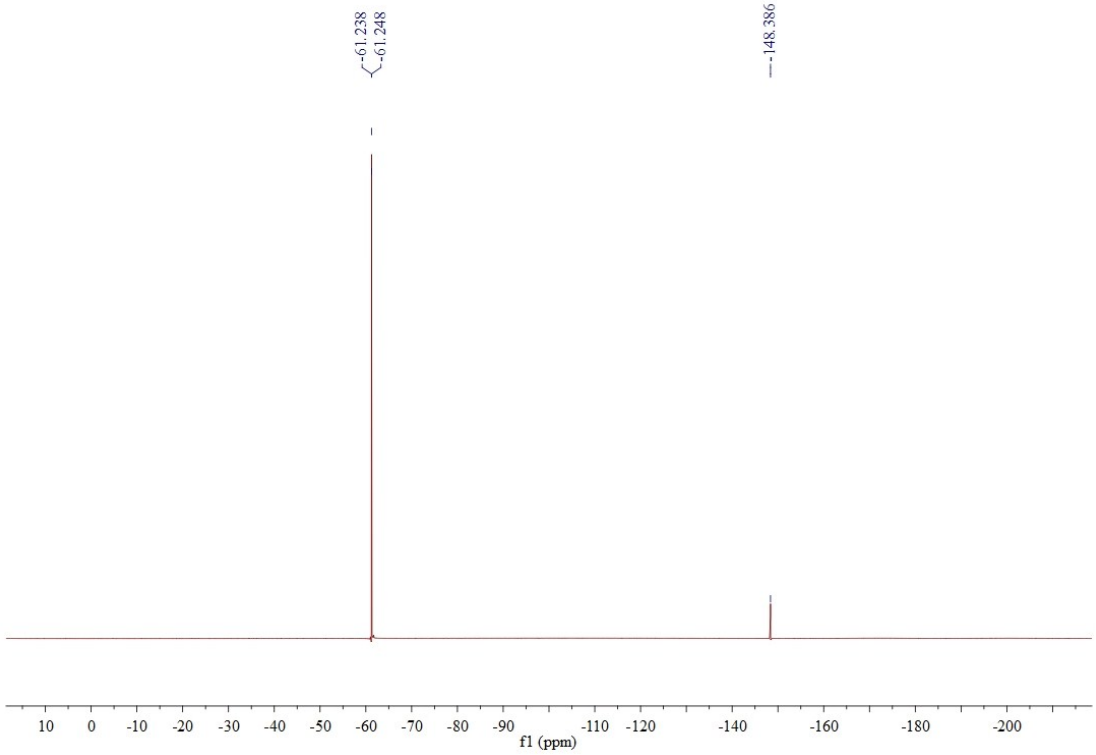
^{1}H NMR spectra of **4h**:



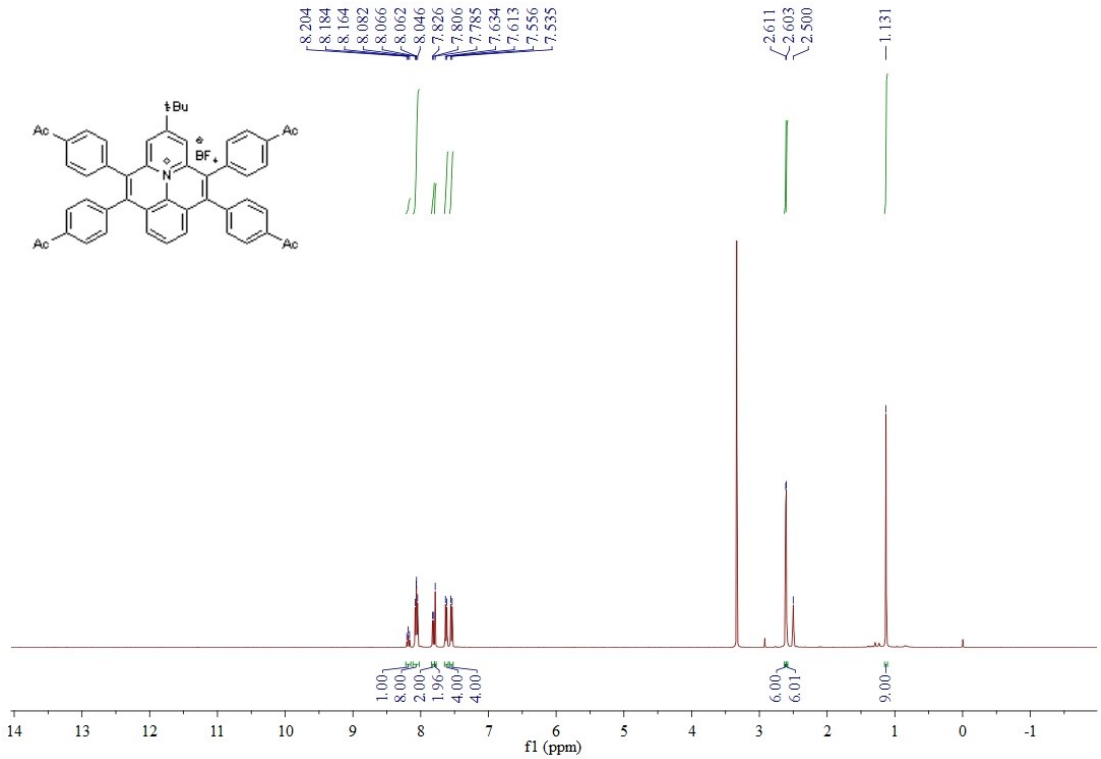
^{13}C NMR spectra of **4h**:



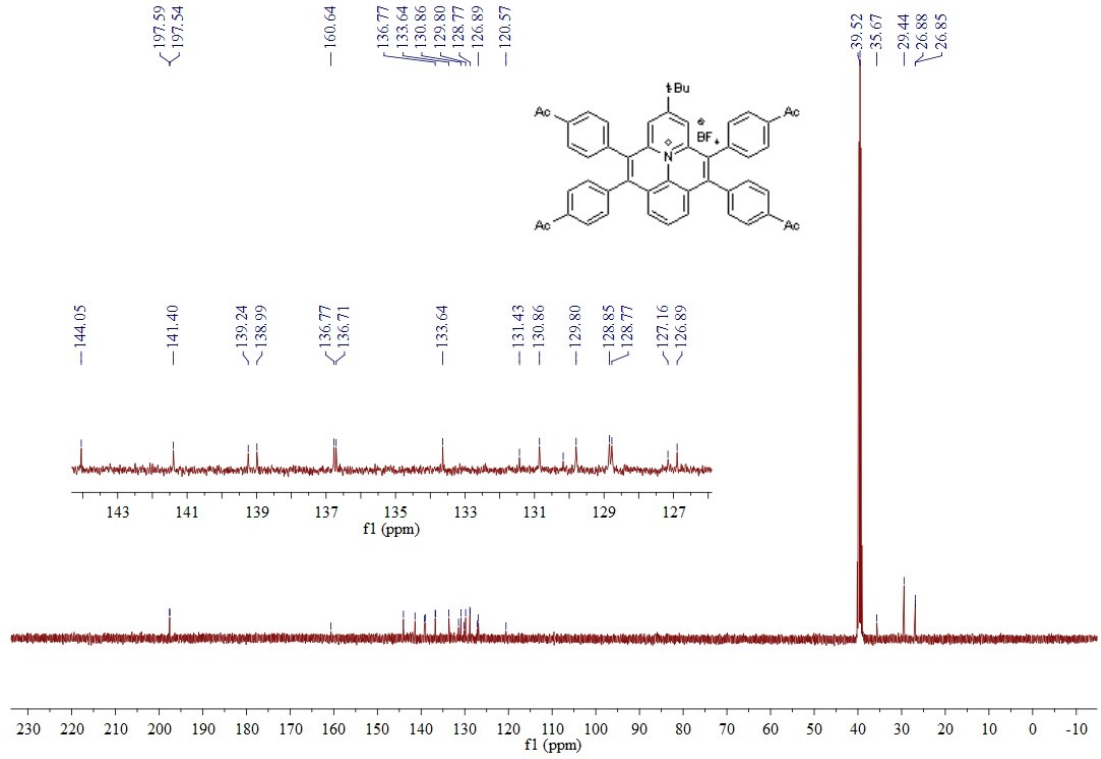
^{19}F NMR spectra of **4h**:



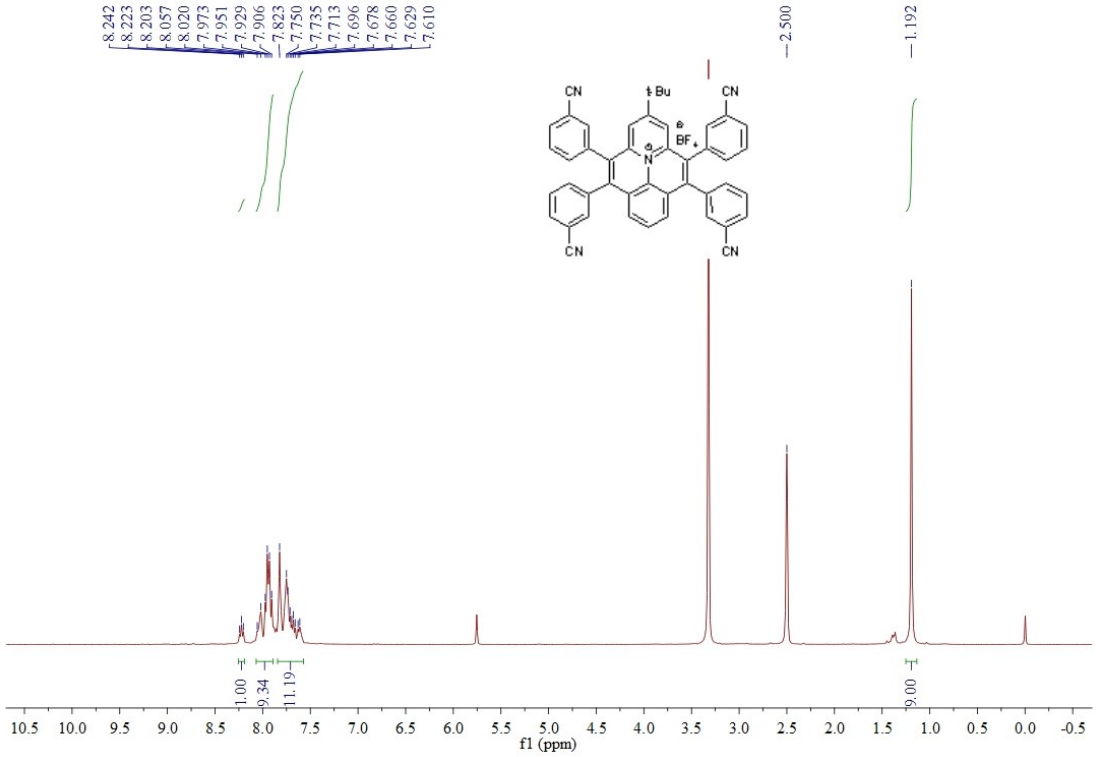
^{1}H NMR spectra of **4i**:



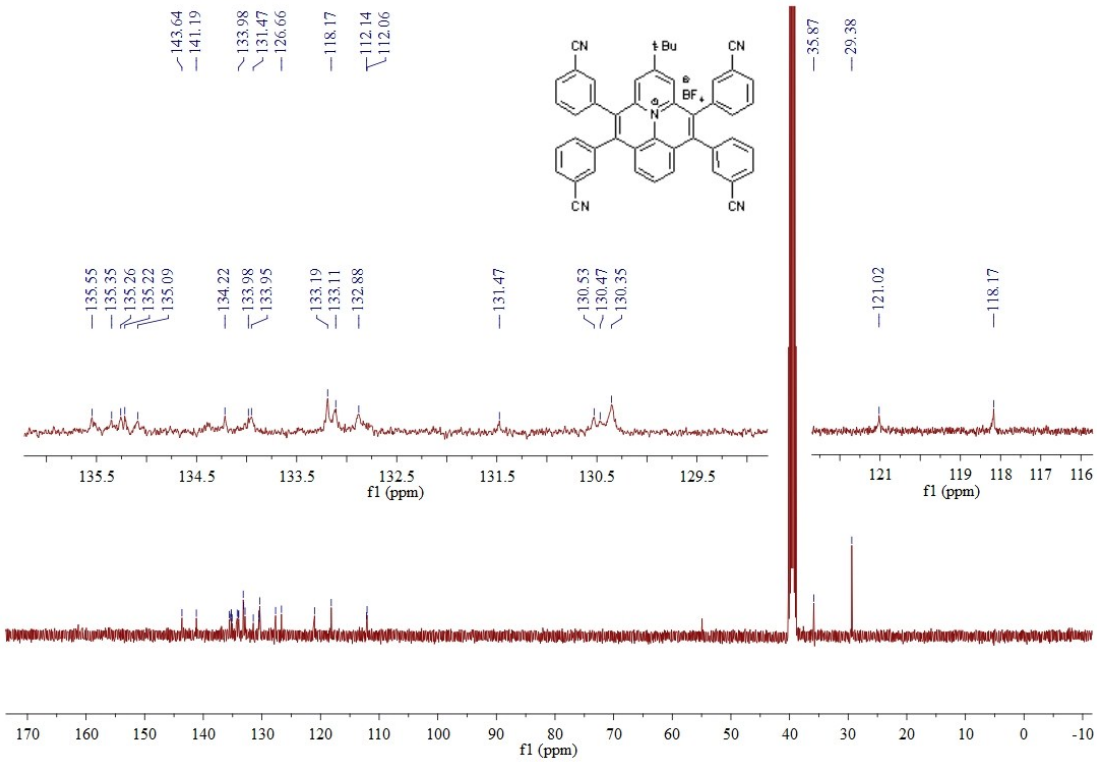
^{13}C NMR spectra of **4i**:



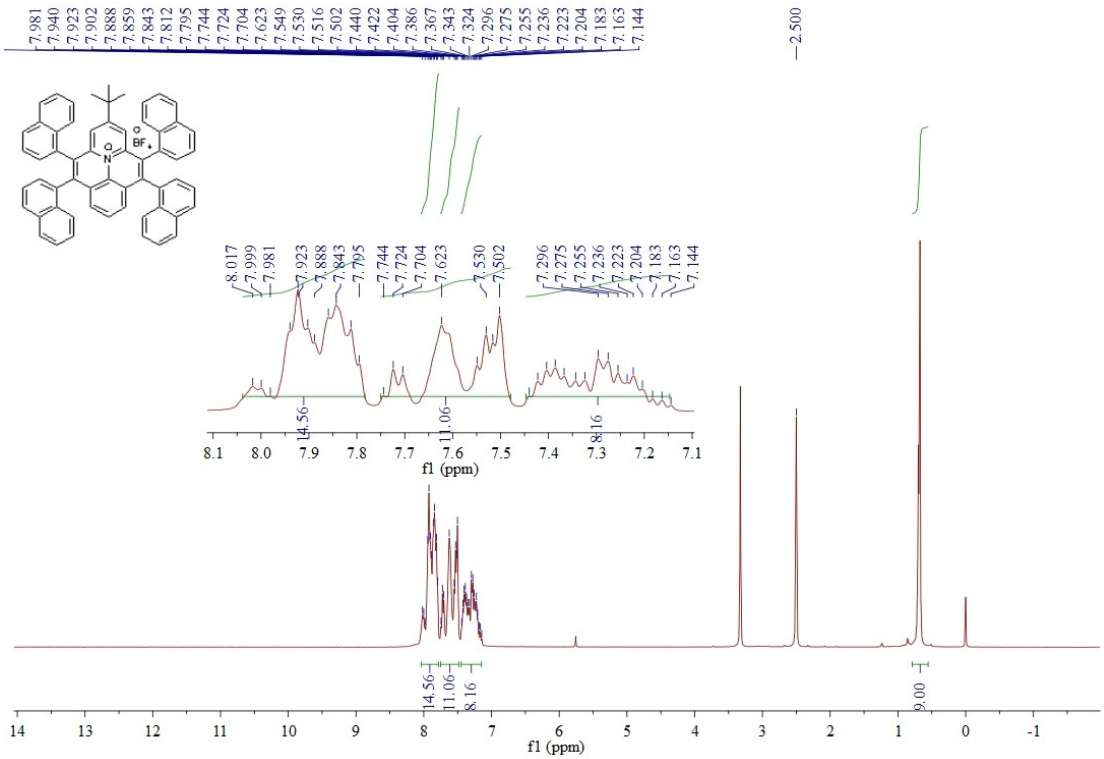
^{1}H NMR spectra of **4j**:



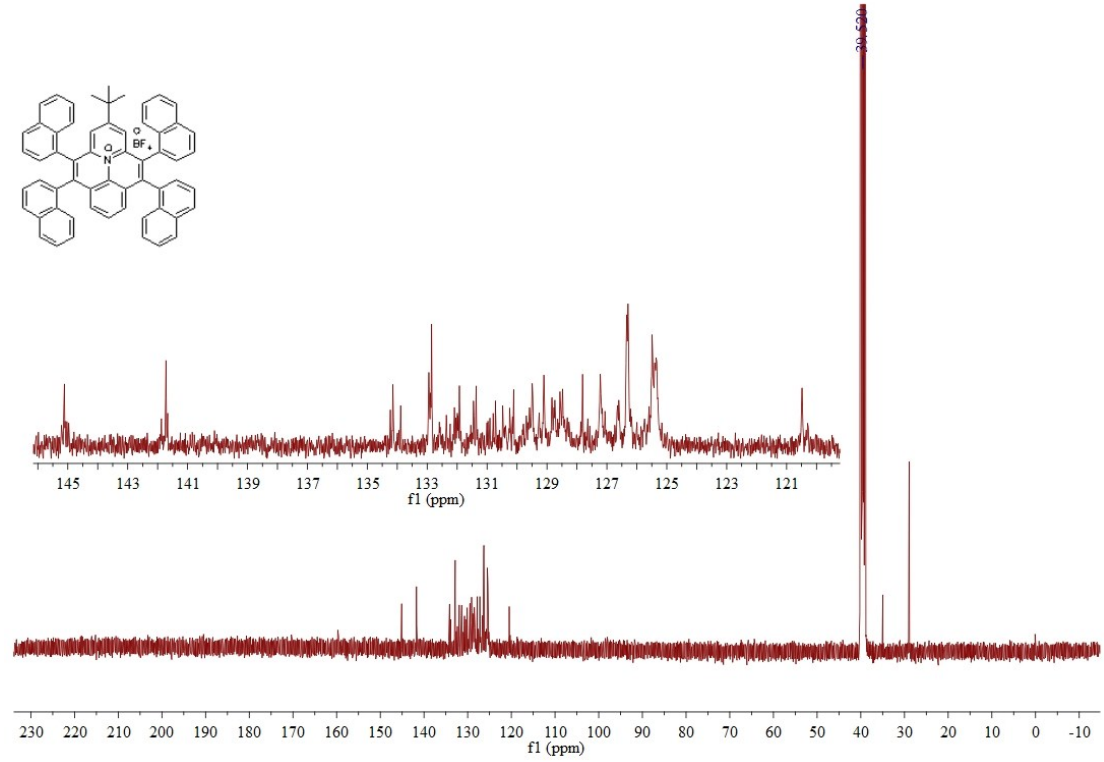
^{13}C NMR spectra of **4j**:



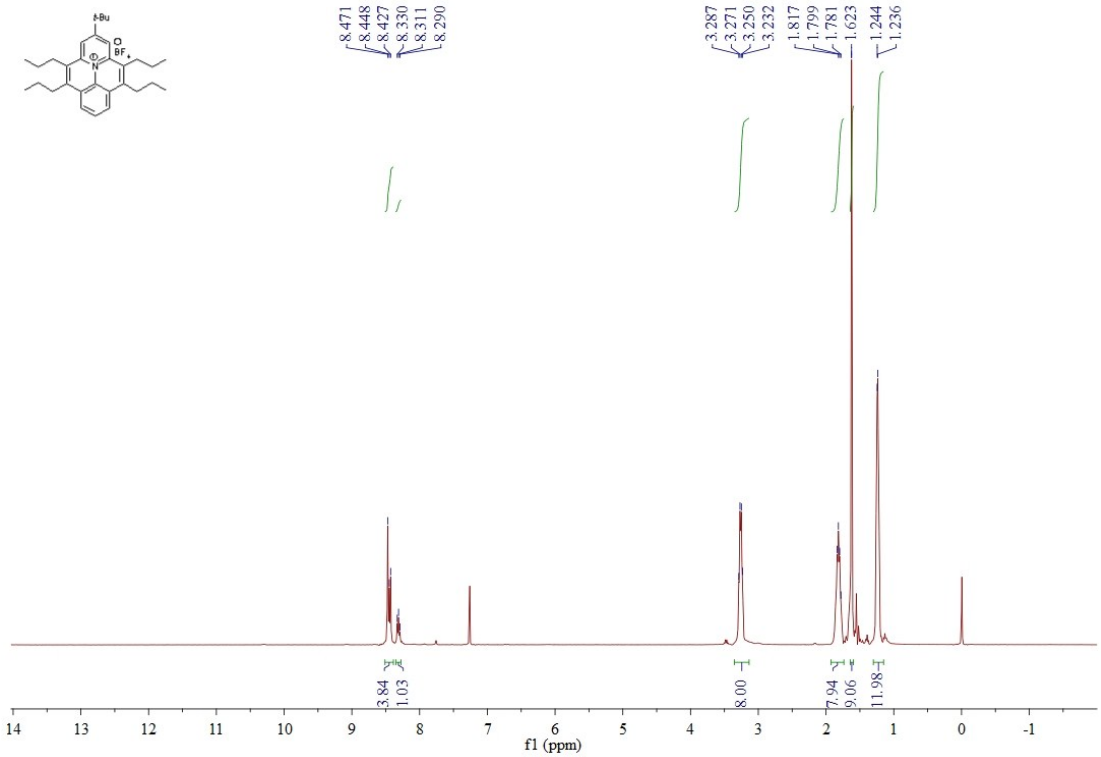
^{1}H NMR spectra of **4k**:



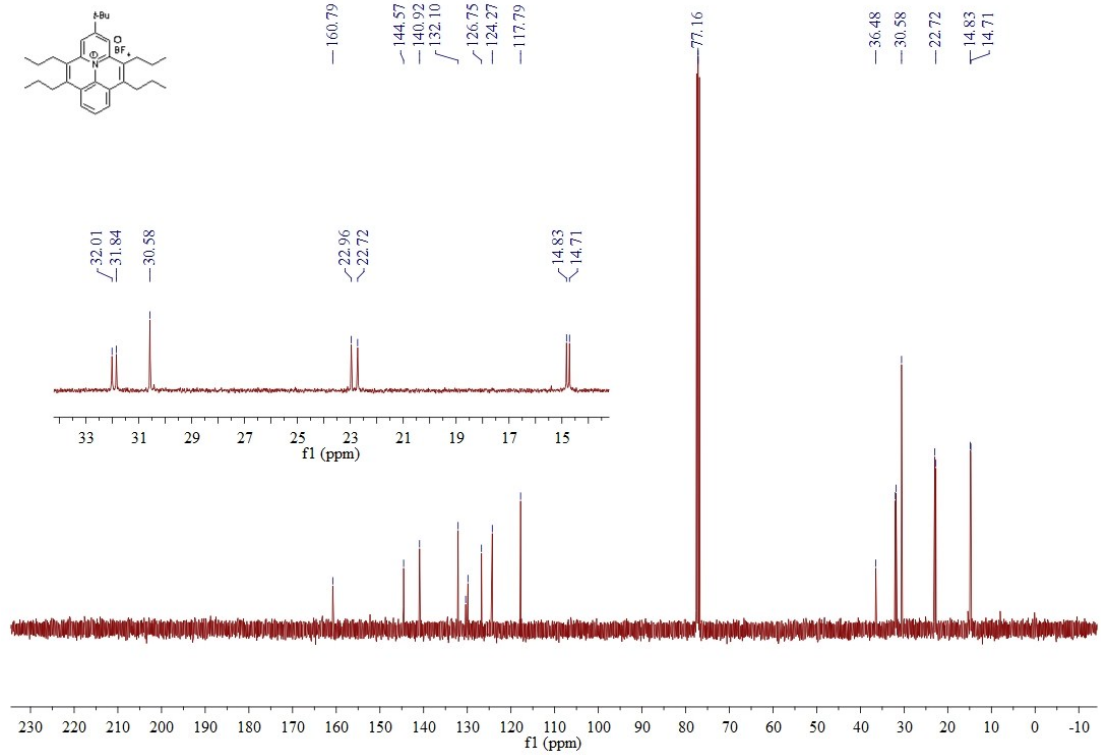
^{13}C NMR spectra of **4k**:



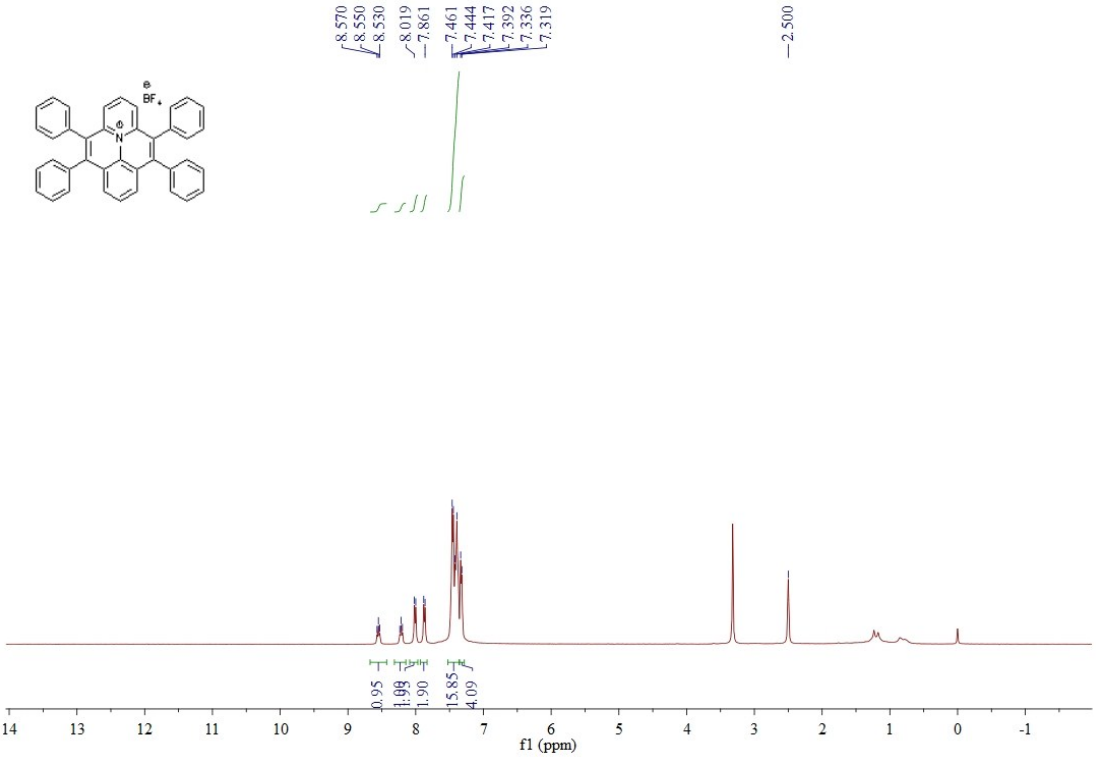
^{1}H NMR spectra of **4l**:



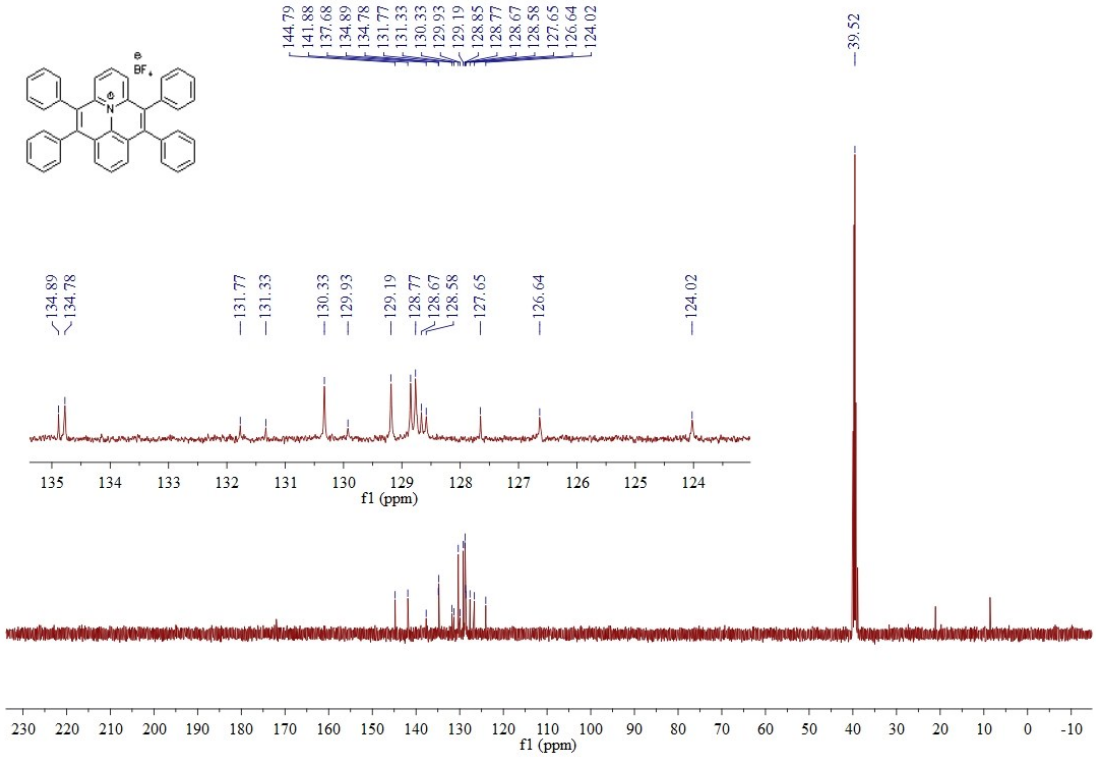
^{13}C NMR spectra of **4l**:



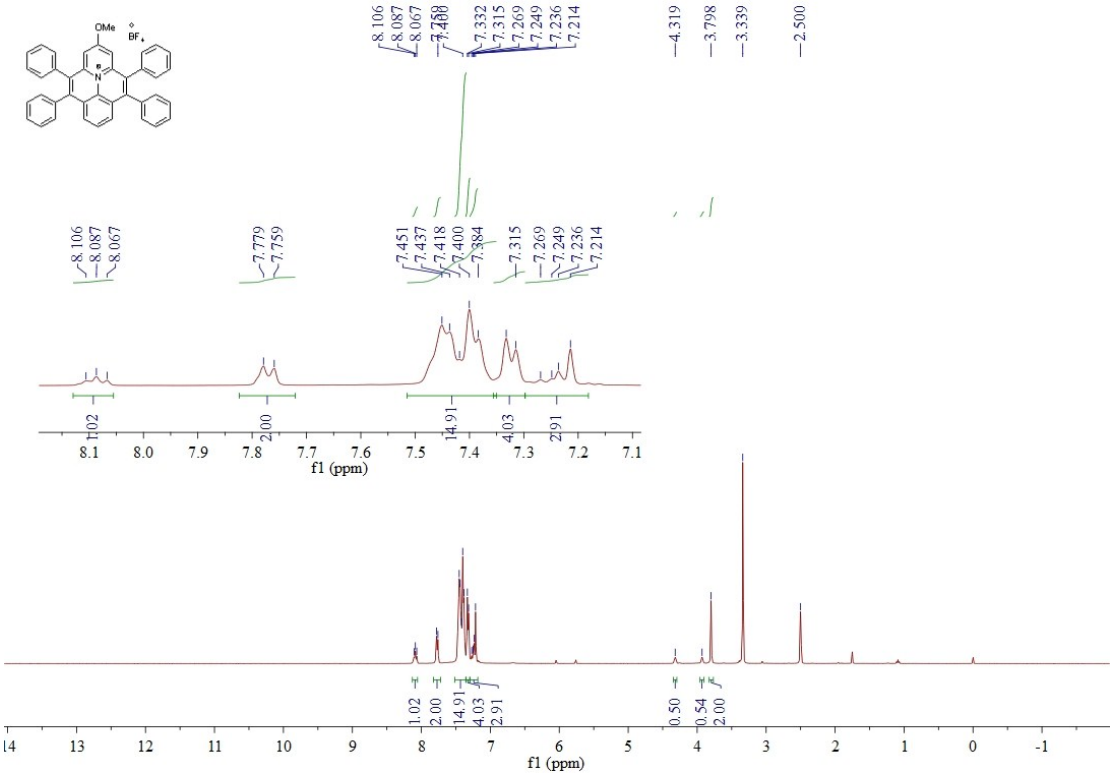
^{1}H NMR spectra of **4m**:



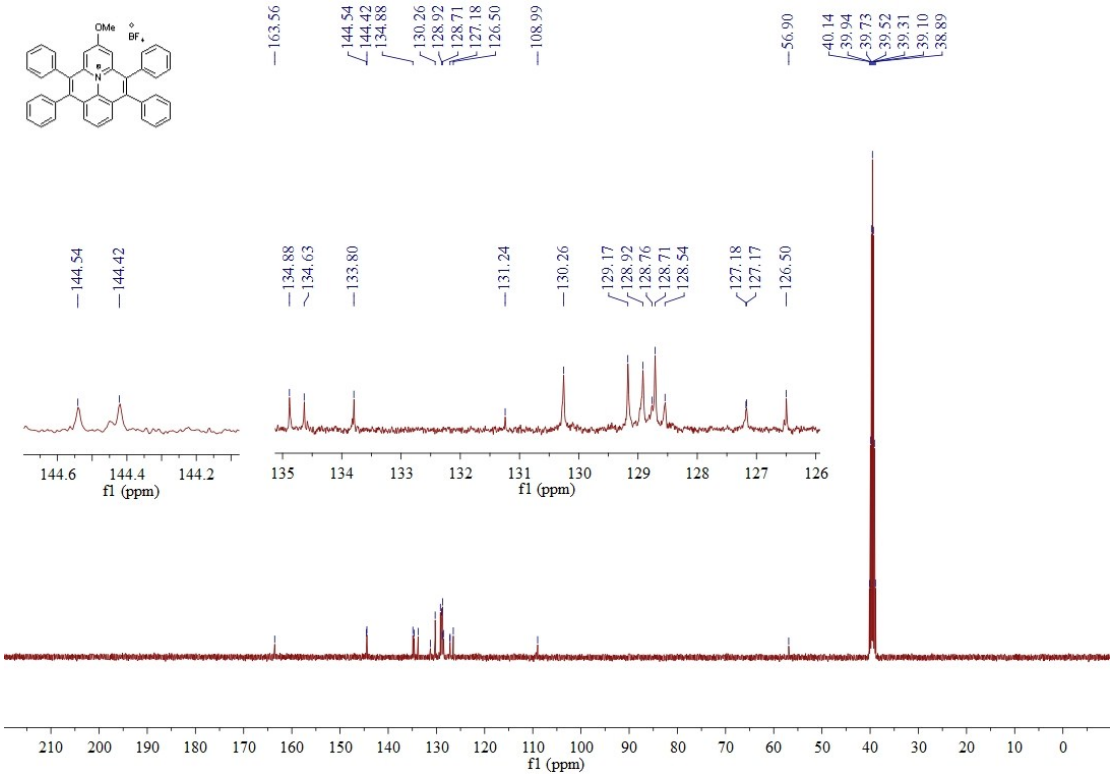
^{13}C NMR spectra of **4m**:



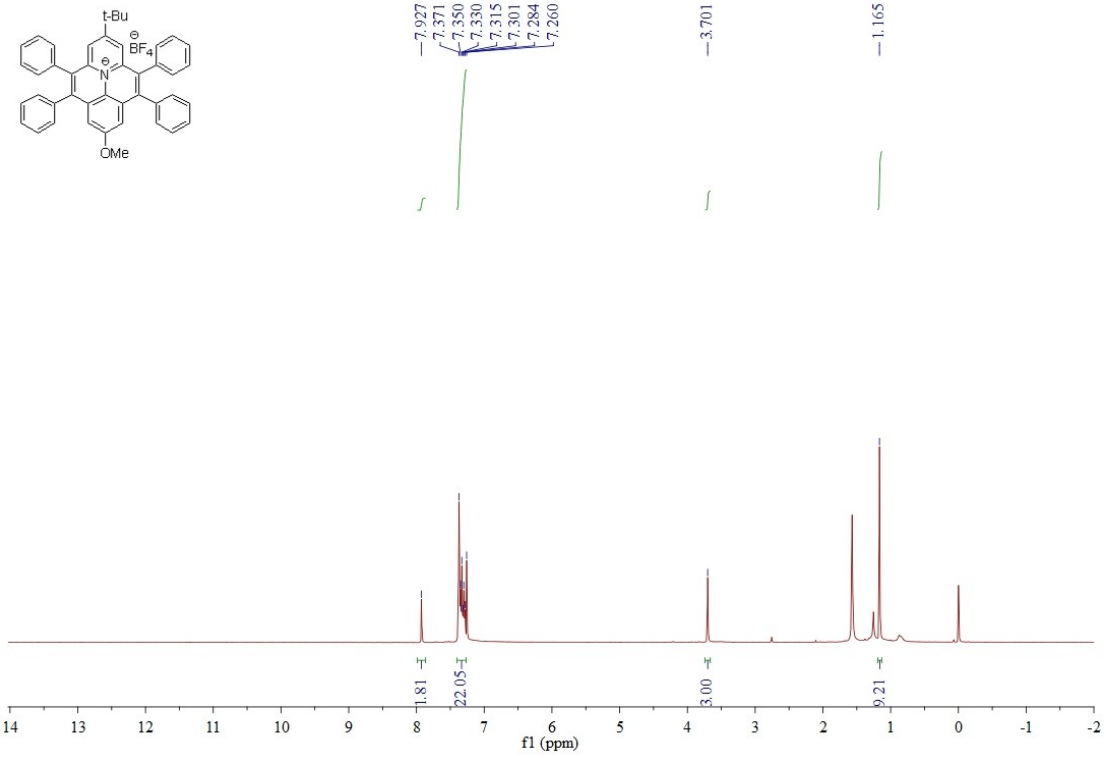
^{1}H NMR spectra of **4n**:



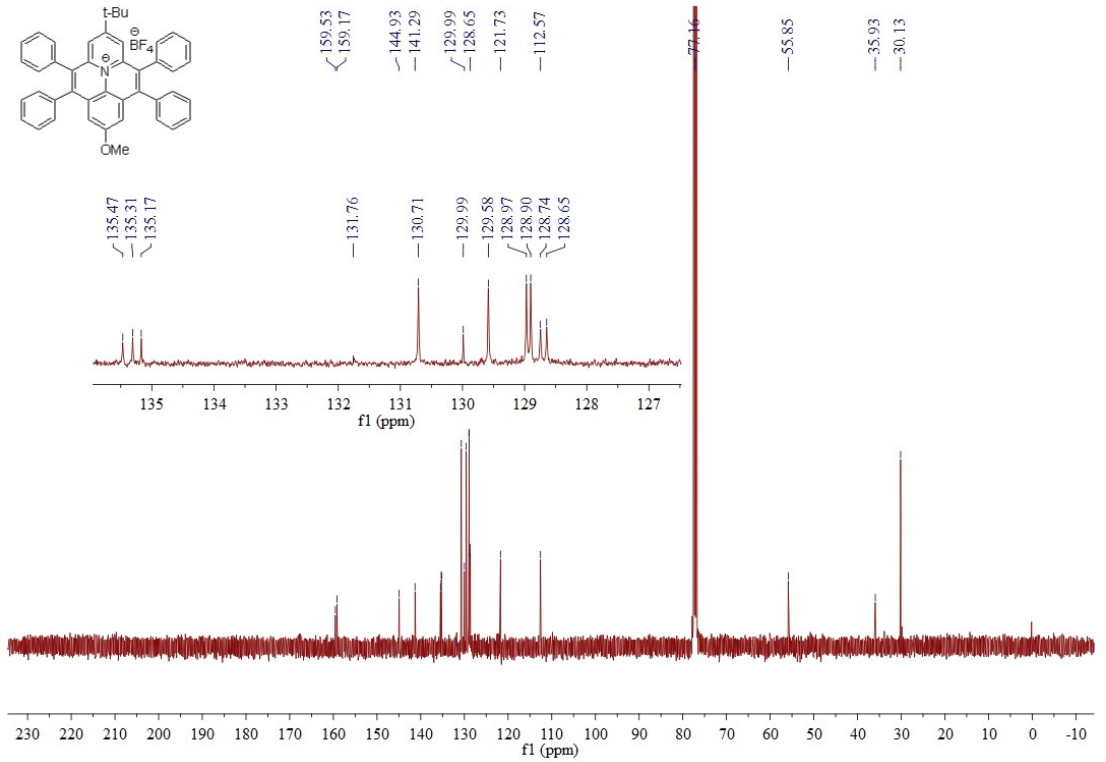
^{13}C NMR spectra of **4n**:



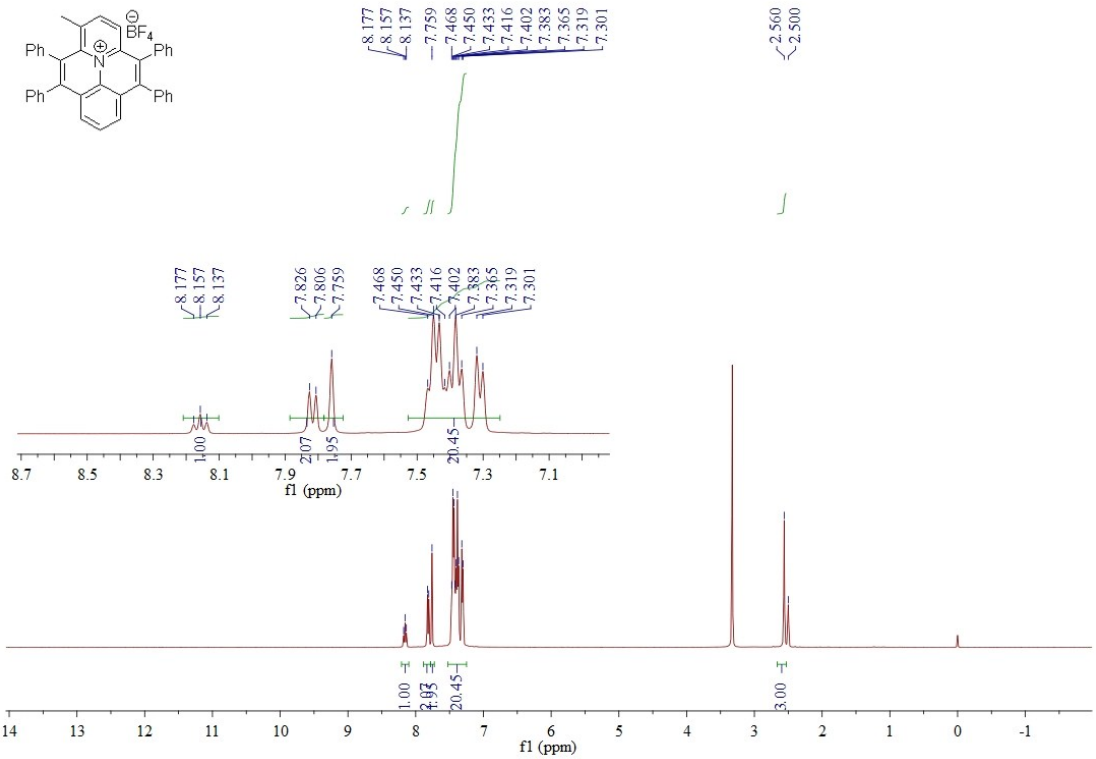
^{1}H NMR spectra of **4o**:



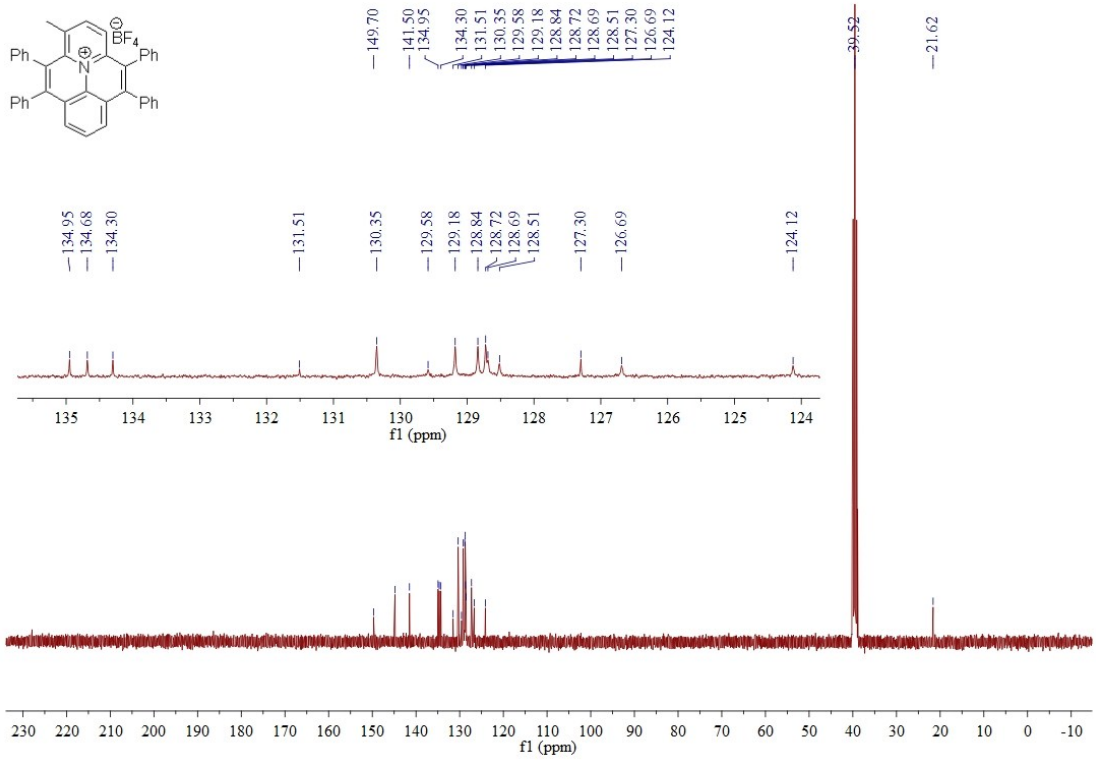
^{13}C NMR spectra of **4o:**



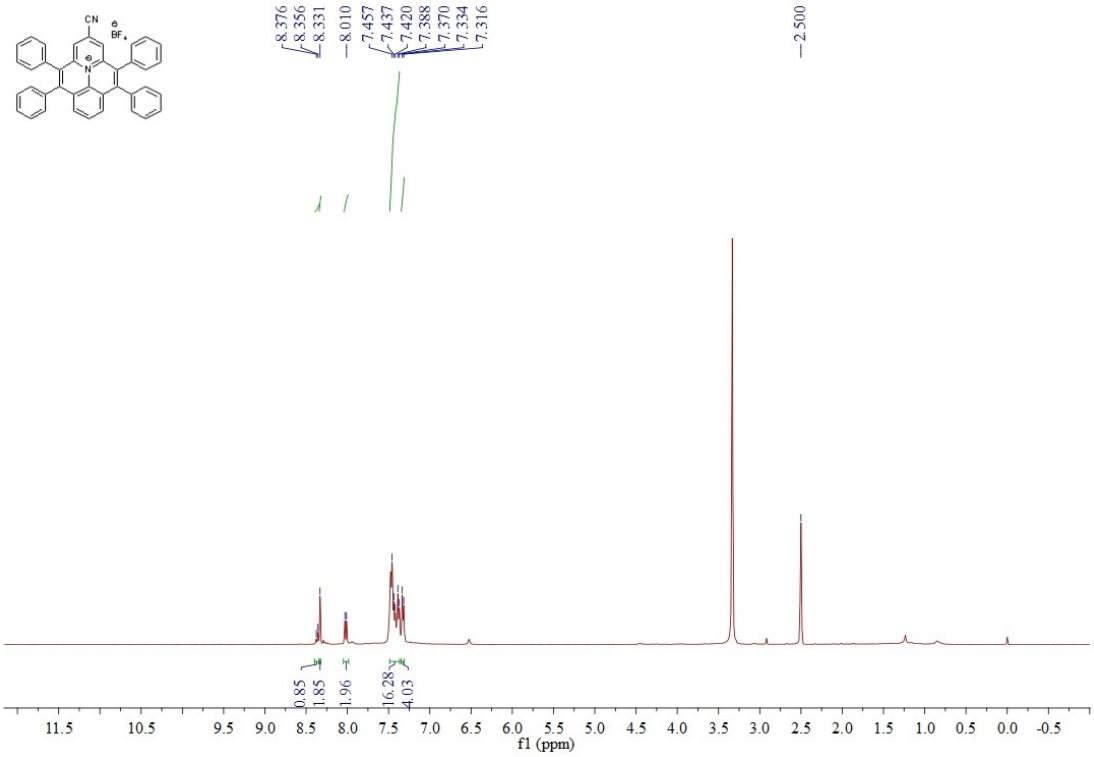
^{1}H NMR spectra of **4p**:



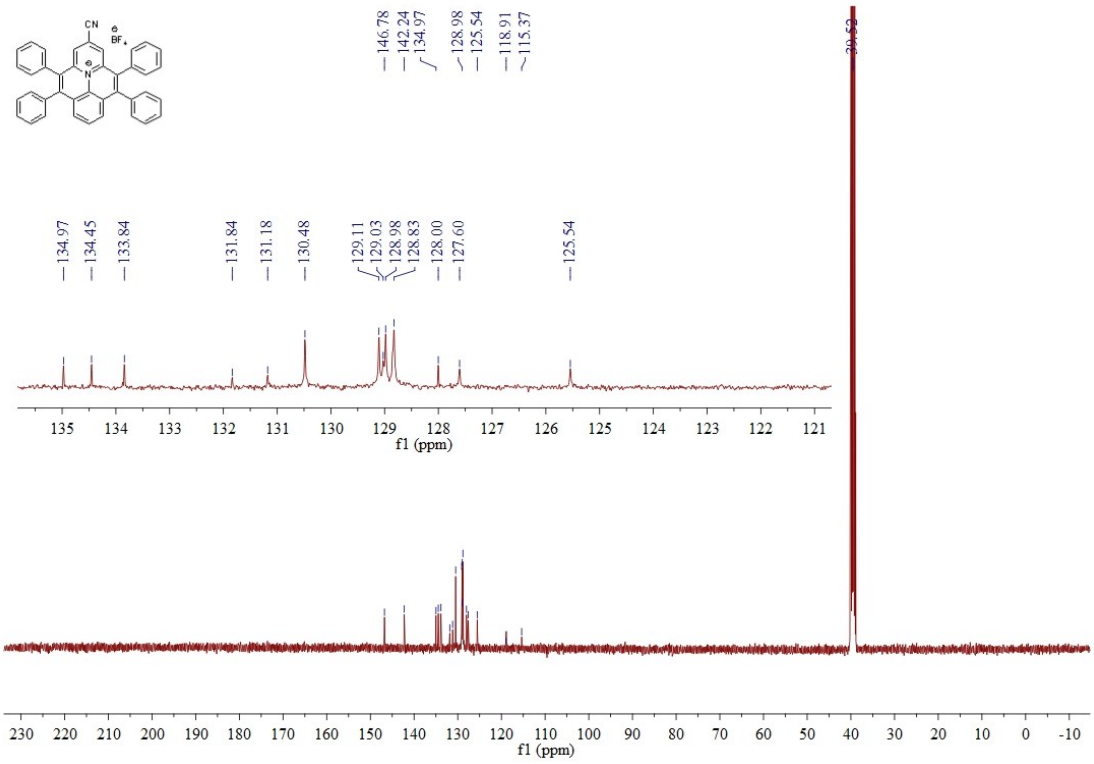
^{13}C NMR spectra of **4p**:



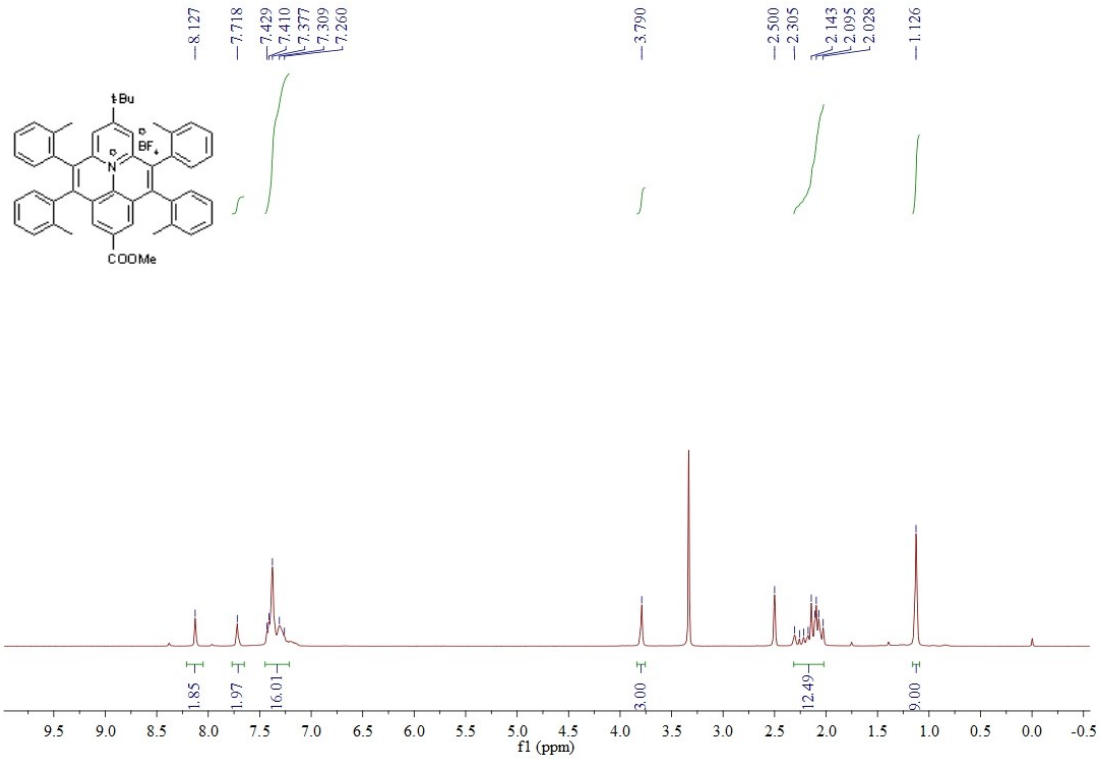
^{1}H NMR spectra of **4q**:



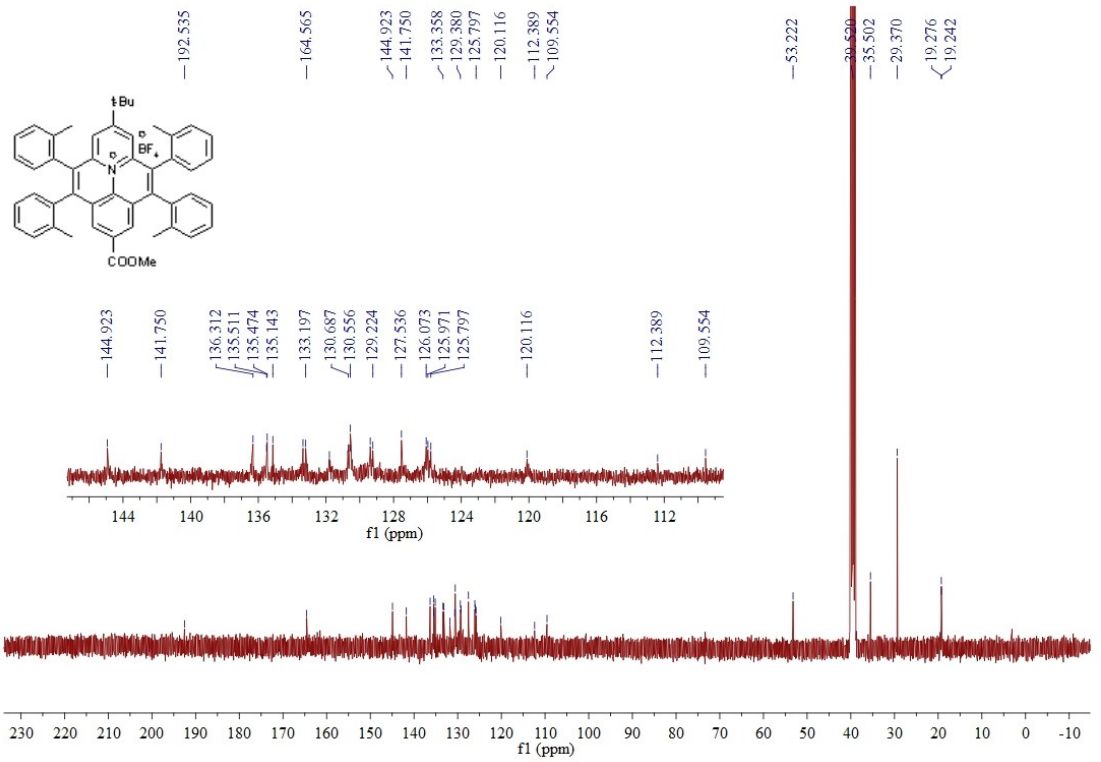
^{13}C NMR spectra of **4q**:



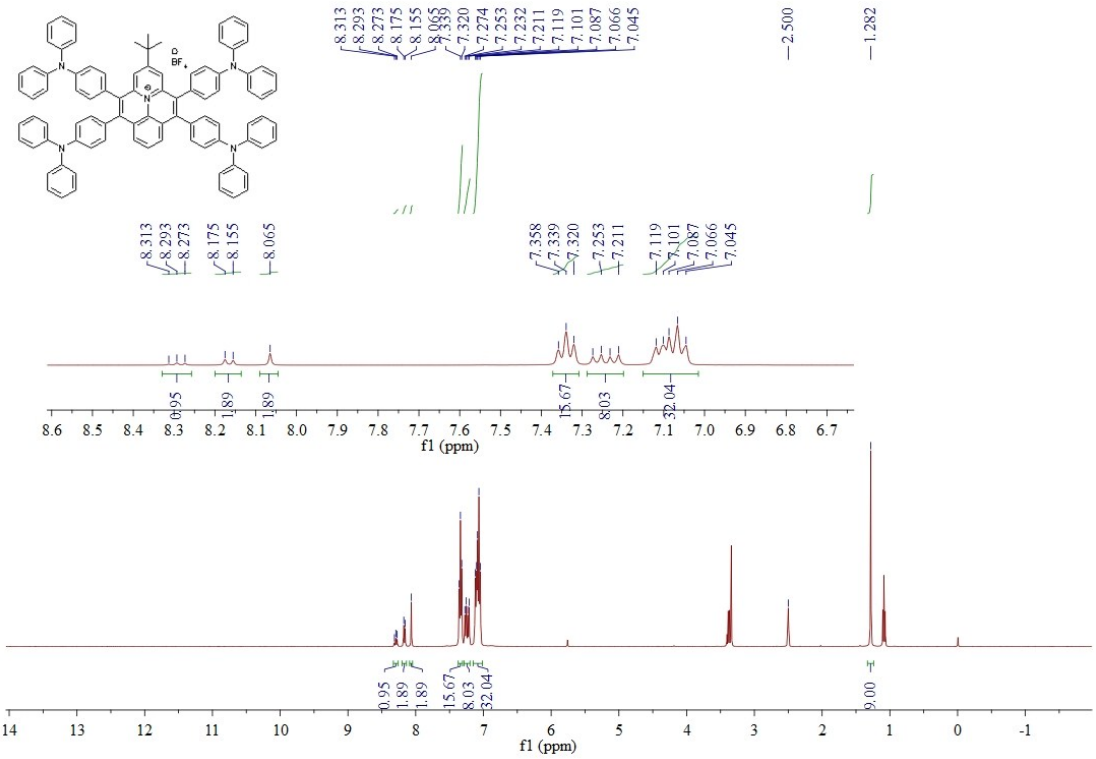
^{1}H NMR spectra of **4r**:



^{13}C NMR spectra of **4r**:



^{1}H NMR spectra of **4s**:



^{13}C NMR spectra of **4s**: