

Supporting Information

Exploiting the Narrow Gap of Rearrangement between the Substituent
in the Vicinal Disubstitution Reactions of Diaryliodonium Salts with
Pyridine *N*-sulfonamides

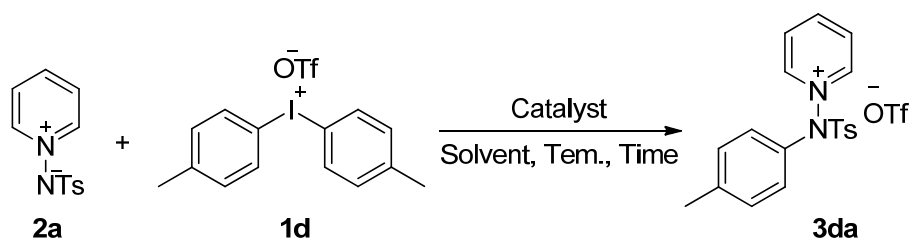
Yong Wang, Ming Li, Lirong Wen, Peng Jing, Xiang Su, Chao Chen**

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Condition Optimization of Product 3^a

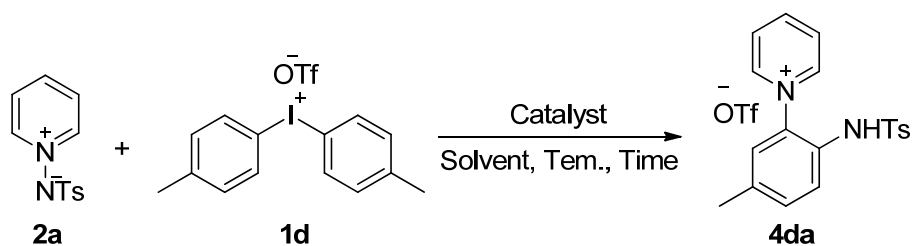


entry	Catalyst (%)	Solvent	Temp. (°C)	Time (h)	Yield (%) ^b
1	No	DCE	120	48	15
2	No	DCE	130	48	30
3	Cu(OTf) ₂ (10)	DCE	100	48	50
4	Cu(OTf) ₂ (10)	DCE	80	48	80
5	Cu(OTf) ₂ (10)	DCE	60	48	Trace
6	Cu(OTf) ₂ (10)	DCE	75	48	87
7	Cu(OTf) ₂ (10)	DCE	75	12	92 (90) ^c
8	Cu(OTf) ₂ (10)	DCE	75	10	88

^a The reaction was performed with 0.2 mmol **1a** and 0.2 mmol **1d**. ^b NMR yield. ^c

Isolated yield.

Condition Optimization of Product 4^a



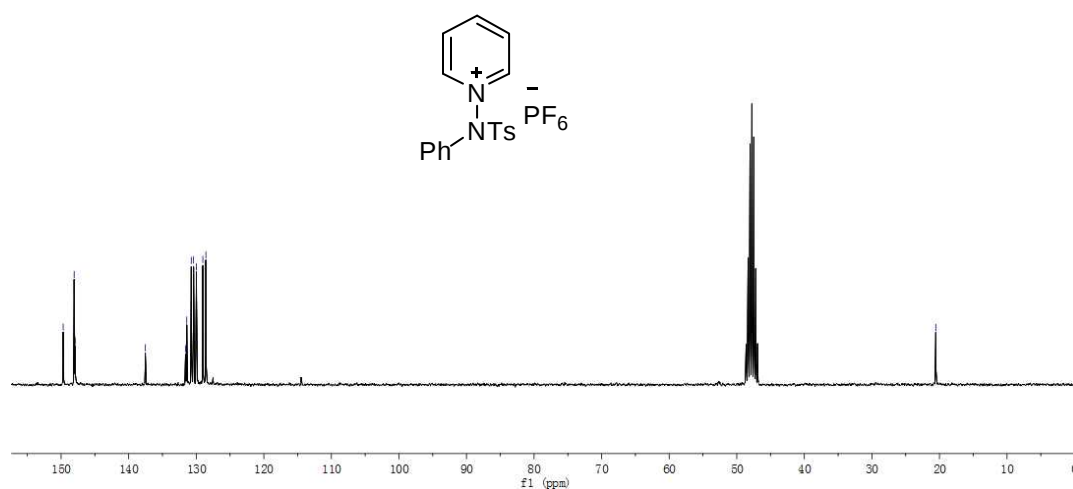
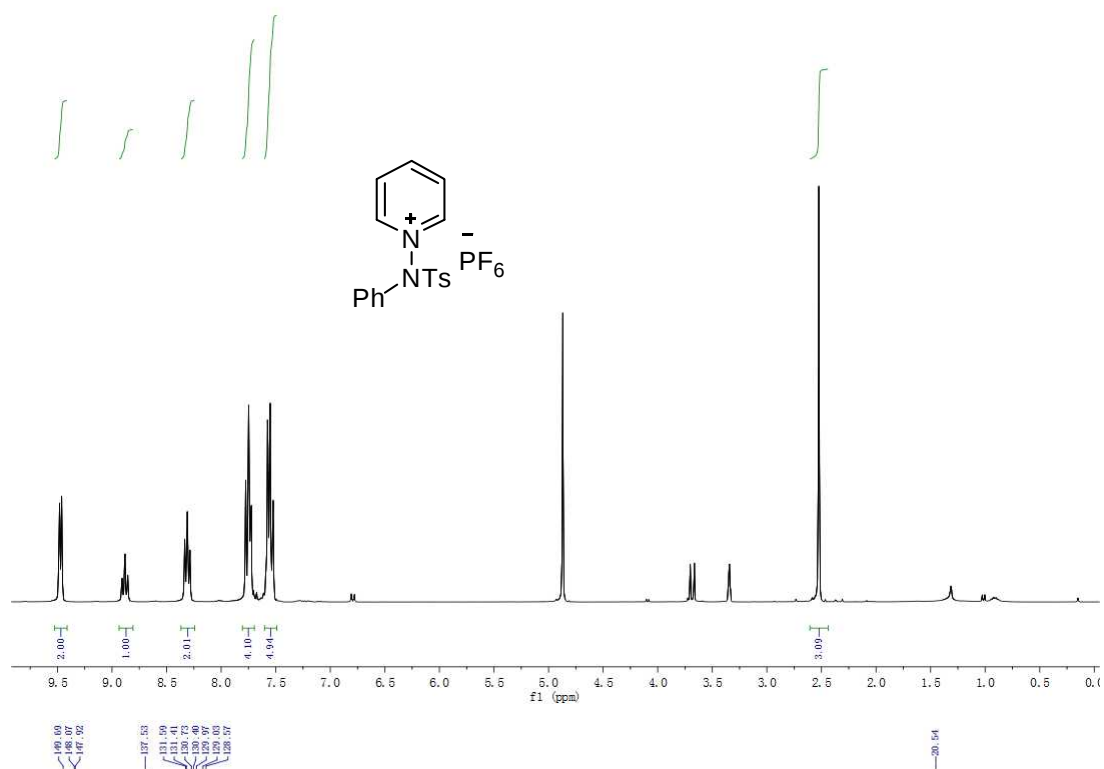
entry	Catalyst (%)	Solvent	Temp. (°C)	Time (h)	Yield (%) ^b
1	No	DCE	120	24	35
2	No	DCE	120	48	45
3	No	DCE	100	48	35
4	No	DCE	130	48	50
5	Cu(OTf) ₂ (5)	DCE	130	48	65
6	Cu(OTf) ₂ (10)	DCE	130	48	80 (77) ^c
7	Cu(OTf) ₂ (15)	DCE	130	48	82
8	CuCl (10)	DCE	130	48	65
9	CuBr (10)	DCE	130	48	62
10	Cu(OAc) ₂ (10)	DCE	130	48	63
11	Pd(OAc) ₂ (10)	DCE	130	48	42
12	Zn(OTf) ₂ (10)	DCE	130	48	22
14	Cu(OTf) ₂ (10)	DCM	130	48	70
15	Cu(OTf) ₂ (10)	Toluene	130	48	60
16	Cu(OTf) ₂ (10)	EA	130	48	65
17	Cu(OTf) ₂ (10)	DCE (1 eq. K ₂ CO ₃)	130	48	Messy
18	Cu(OTf) ₂ (10)	DCE (1 eq. EtN ⁱ Pr ₂)	130	48	Messy

^a The reaction was performed with 0.2 mmol **1a** and 0.2 mmol **1d**. ^b NMR yield. ^c

Isolated yield.

^1H NMR, ^{13}C NMR Spectra of all Compounds

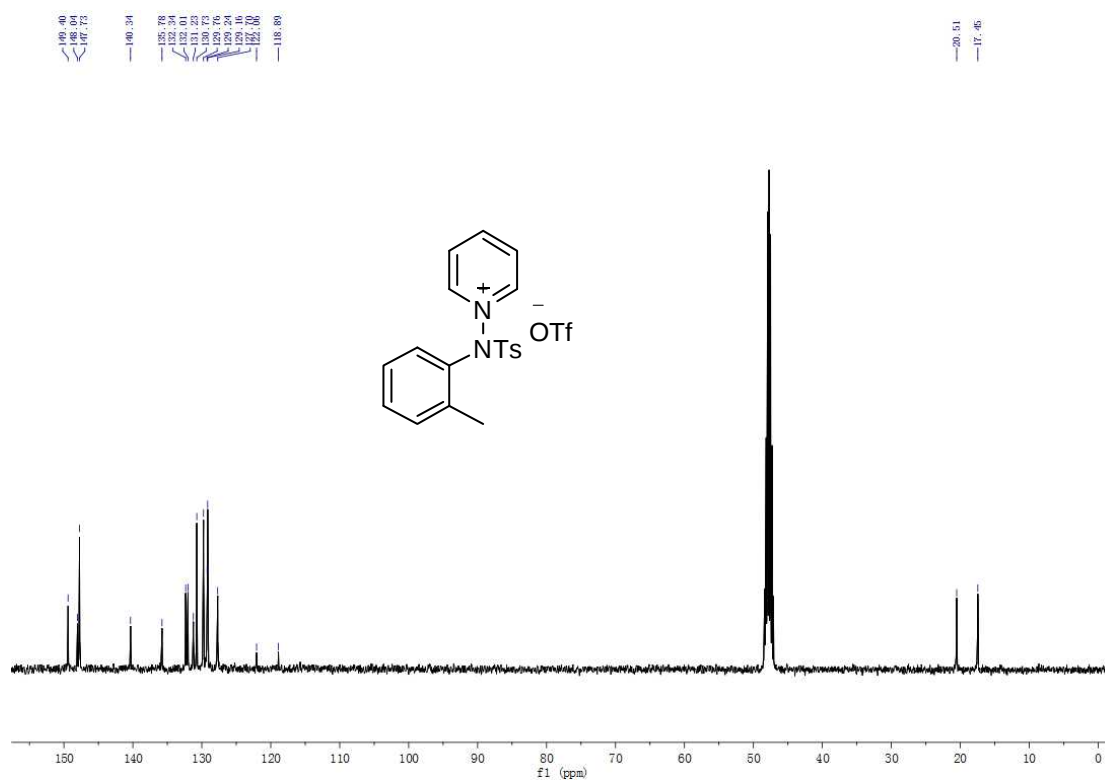
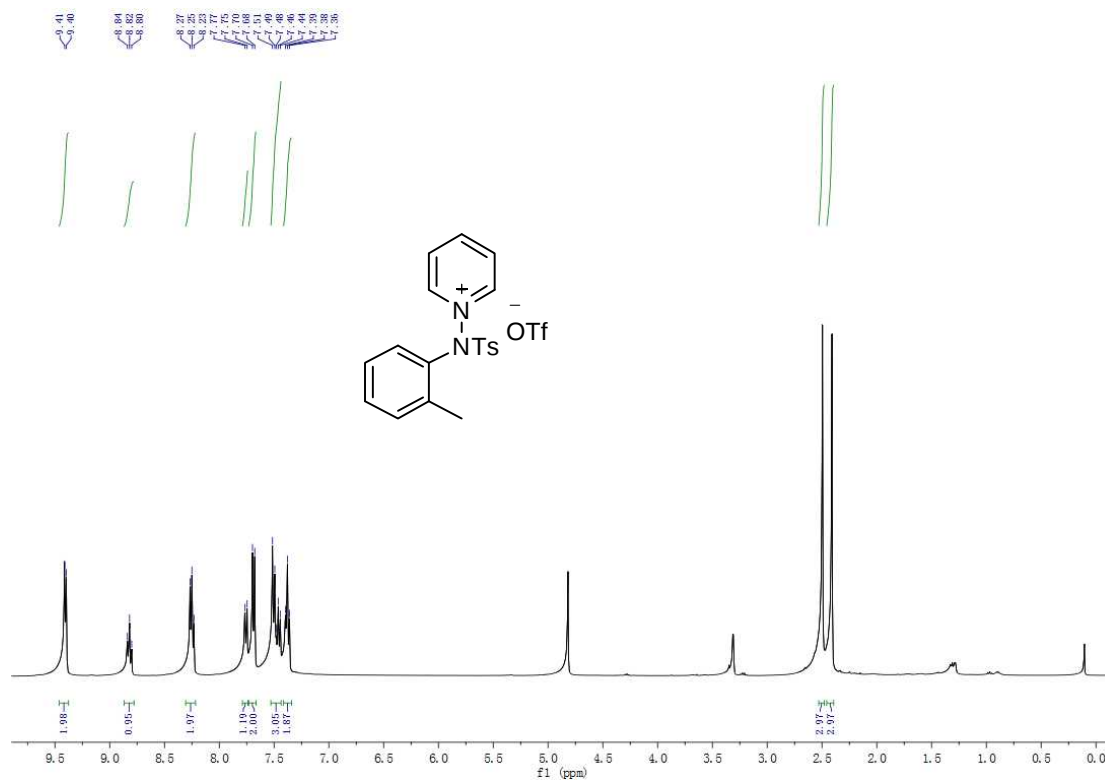
**1-(4-methyl-N-phenylphenylsulfonamido)pyridin-1-ium hexafluorophosphate(V)
(3aa)**



^1H NMR (301 MHz, METHANOL- D_4) (up) and

^{13}C NMR (76 MHz, METHANOL- D_4) (down)

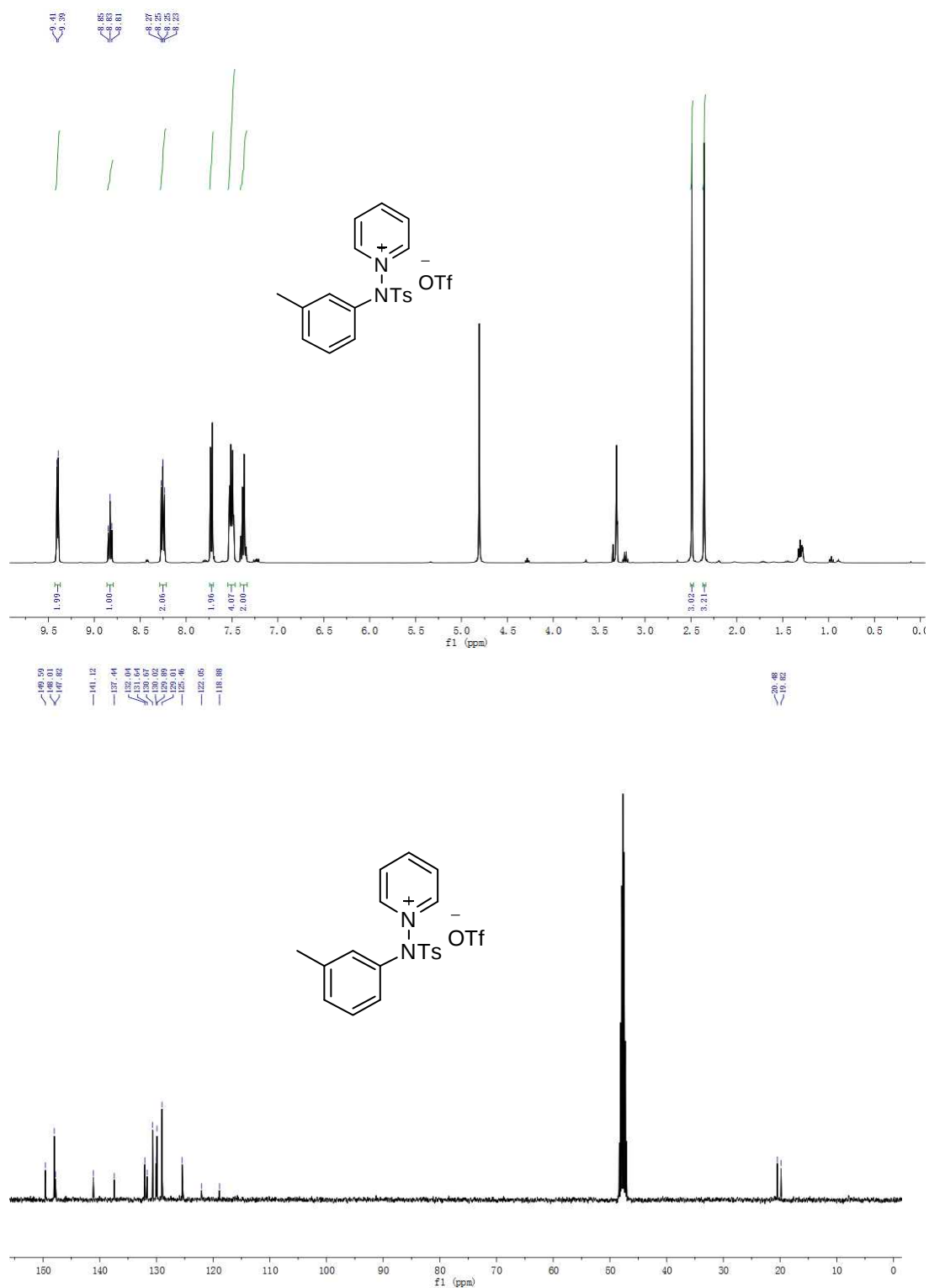
**1-(4-methyl-N-(o-tolyl)phenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3ba)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

¹³C NMR (101 MHz, METHANOL-D₄) (down)

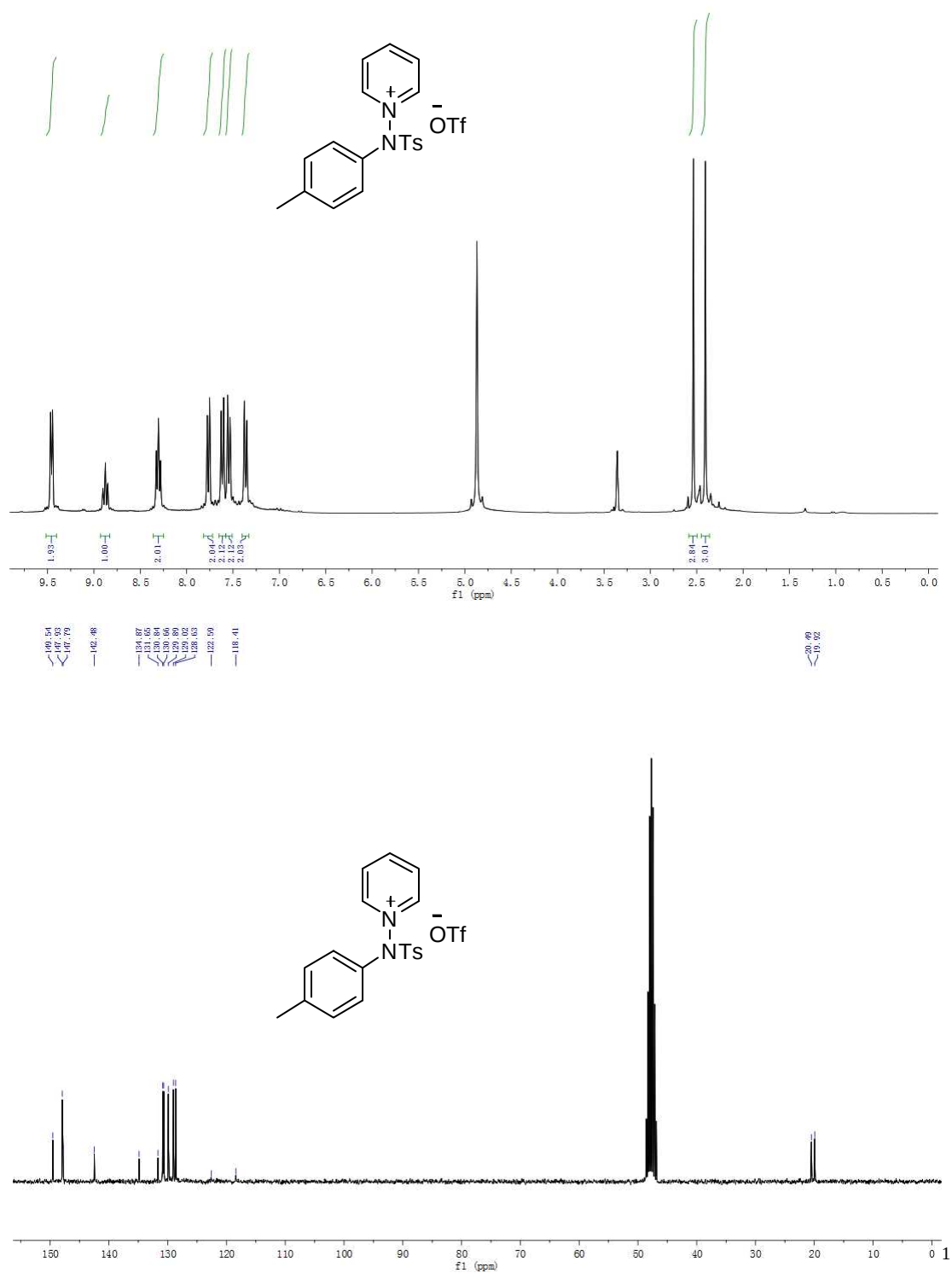
**1-(4-methyl-N-(m-tolyl)phenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3ca)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

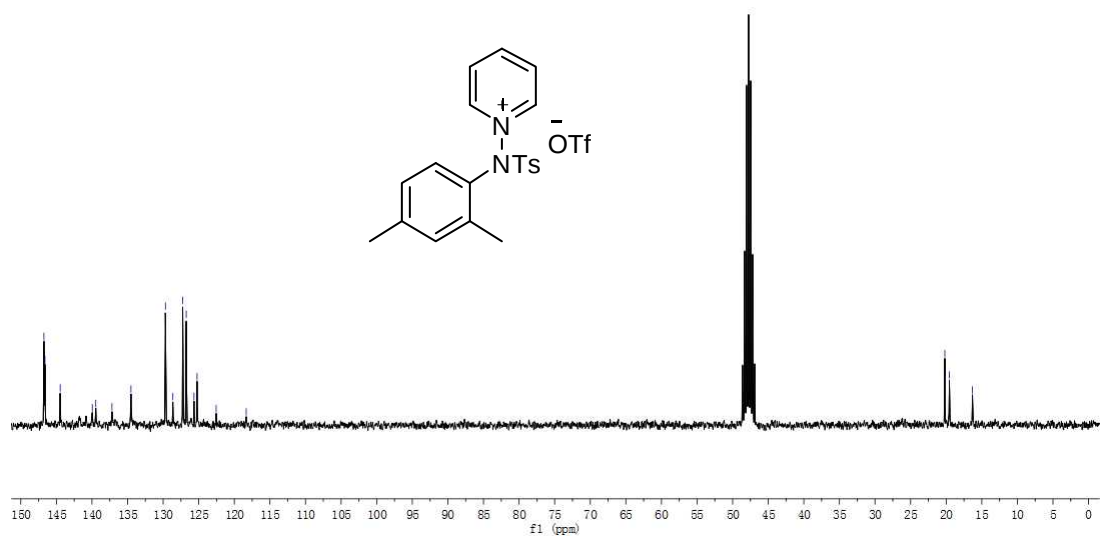
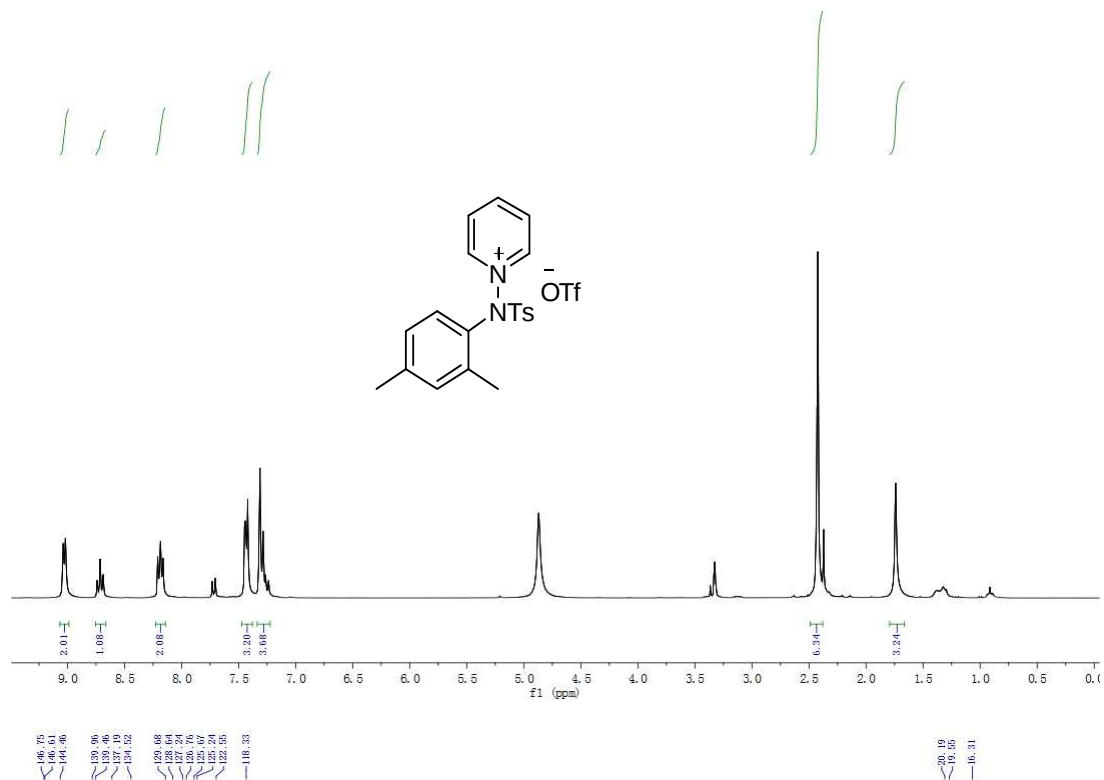
¹³C NMR (101 MHz, METHANOL-D₄) (down)

**1-(4-methyl-N-(p-tolyl)phenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3da):**



¹H NMR (301 MHz, METHANOL-D₄) (up) and
¹³C NMR (76 MHz, METHANOL-D₄) (down)

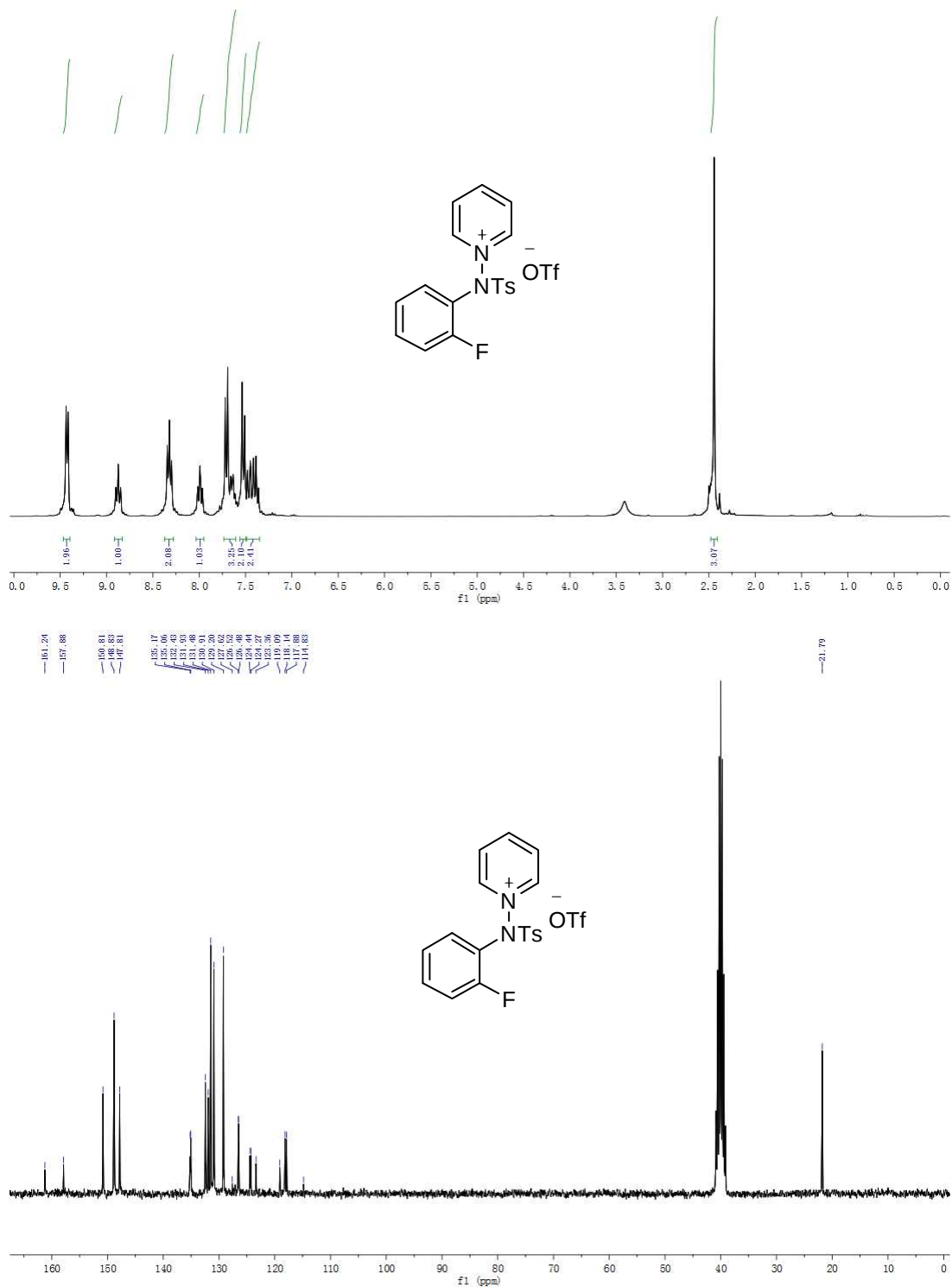
**1-(N-(2,4-dimethylphenyl)-4-methylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3ea)**



¹H NMR (301 MHz, METHANOL-D₄) (up) and

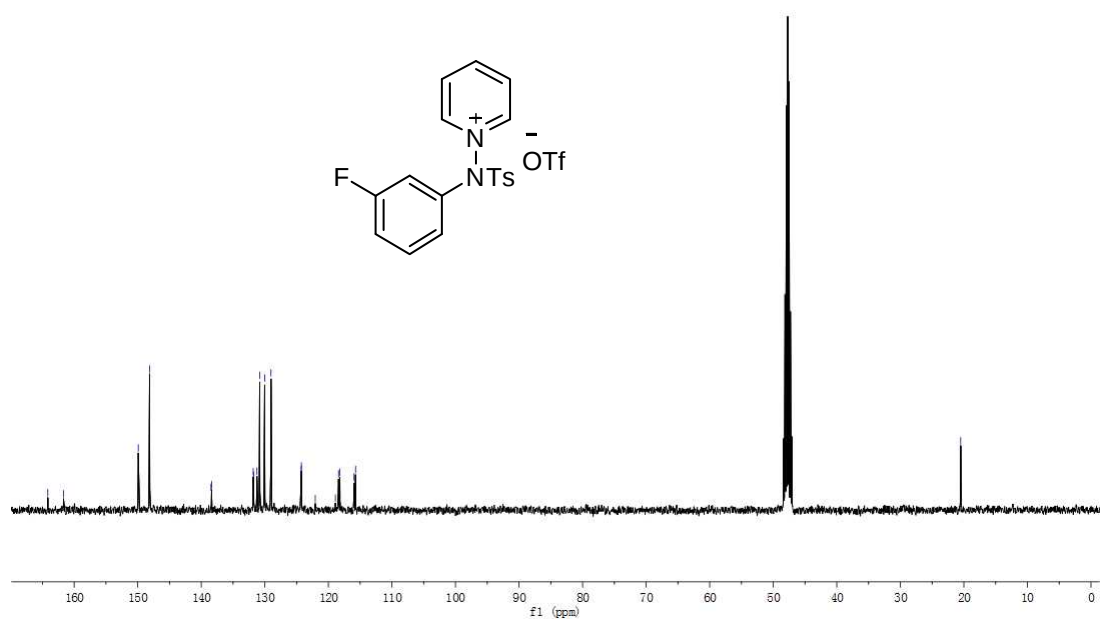
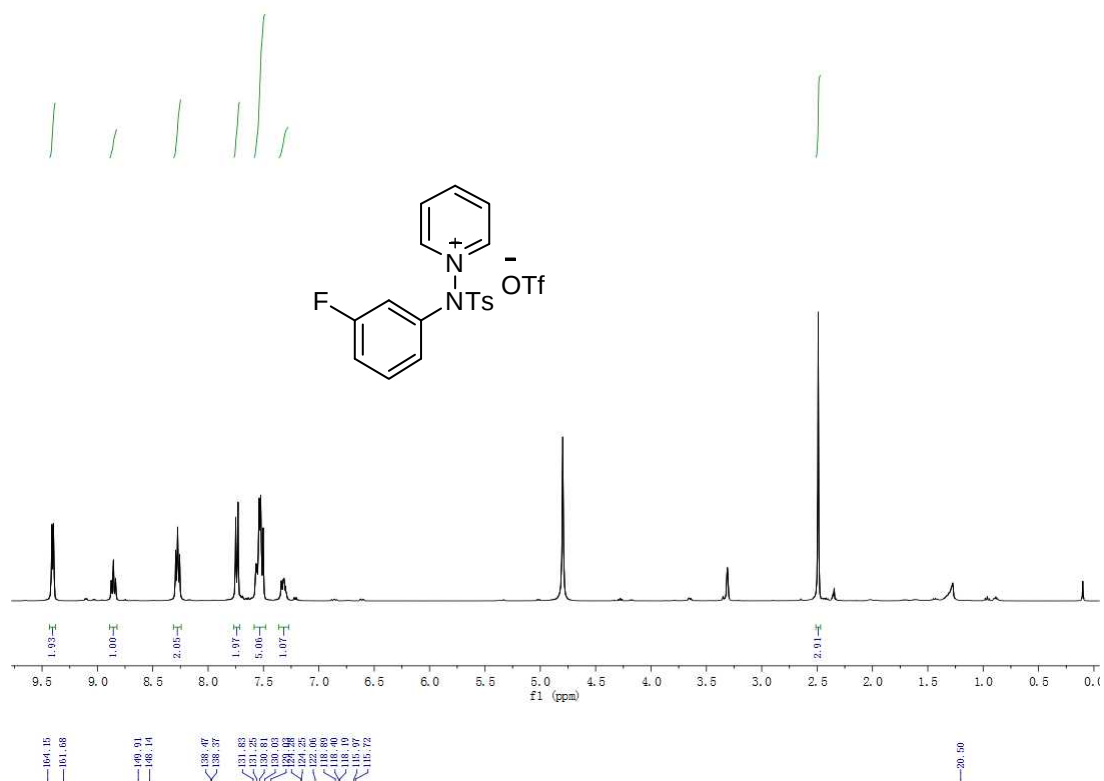
¹³C NMR (76 MHz, METHANOL-D₄) (down)

**1-(N-(2-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3fa)**



¹H NMR (301 MHz, DMSO-D6) (up) and ¹³C NMR (76 MHz, DMSO-D6) (down)

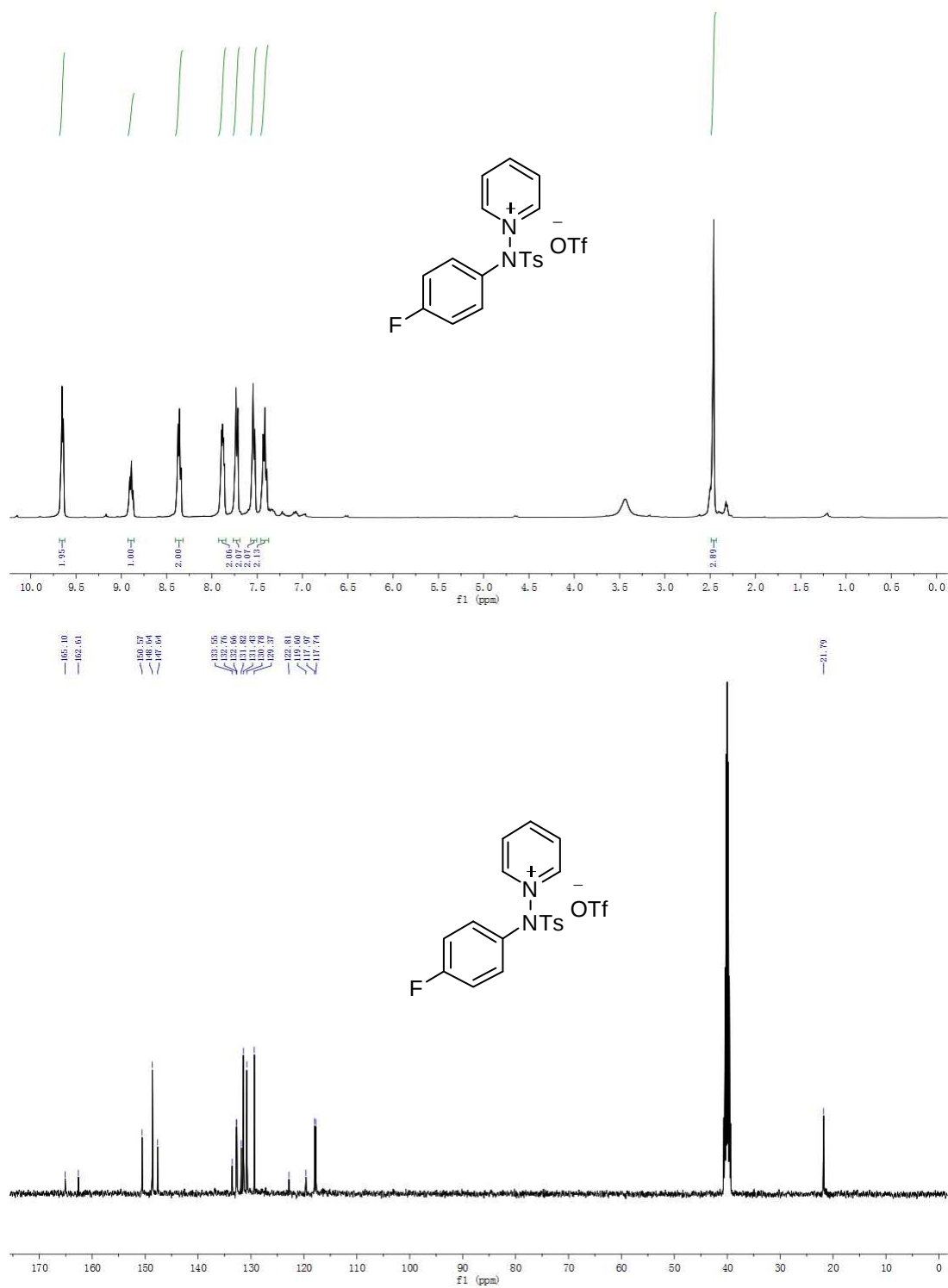
**1-(N-(3-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3ga)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

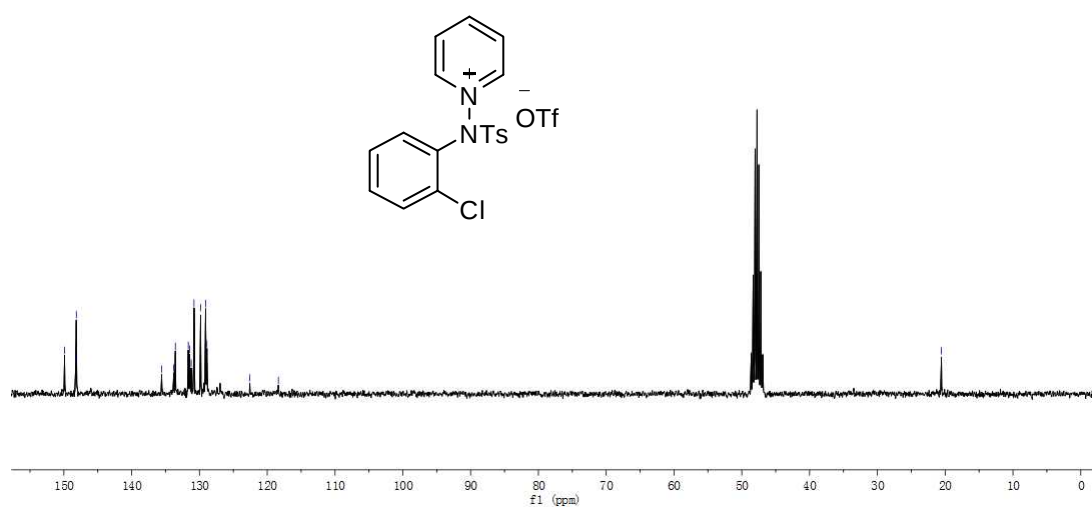
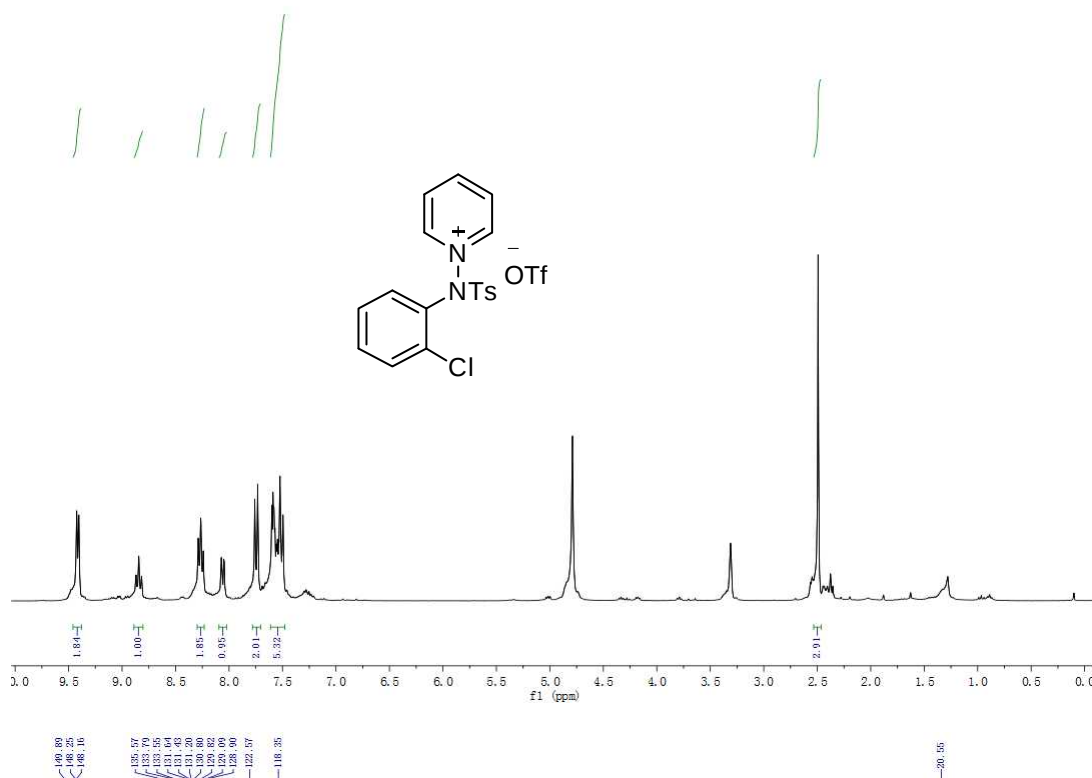
¹³C NMR (101 MHz, METHANOL-D₄) (down)

**1-(N-(4-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3ha)**



¹H NMR (400 MHz, DMSO-D6) (up) and ¹³C NMR (101 MHz, DMSO-D6) (down)

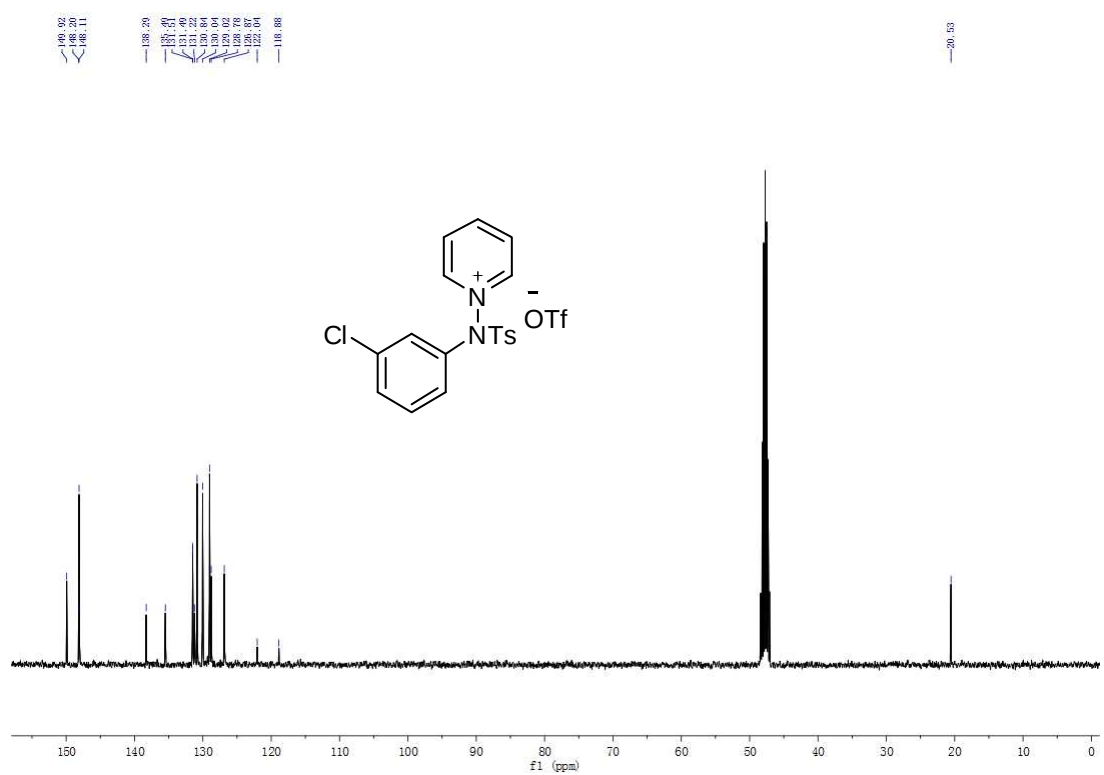
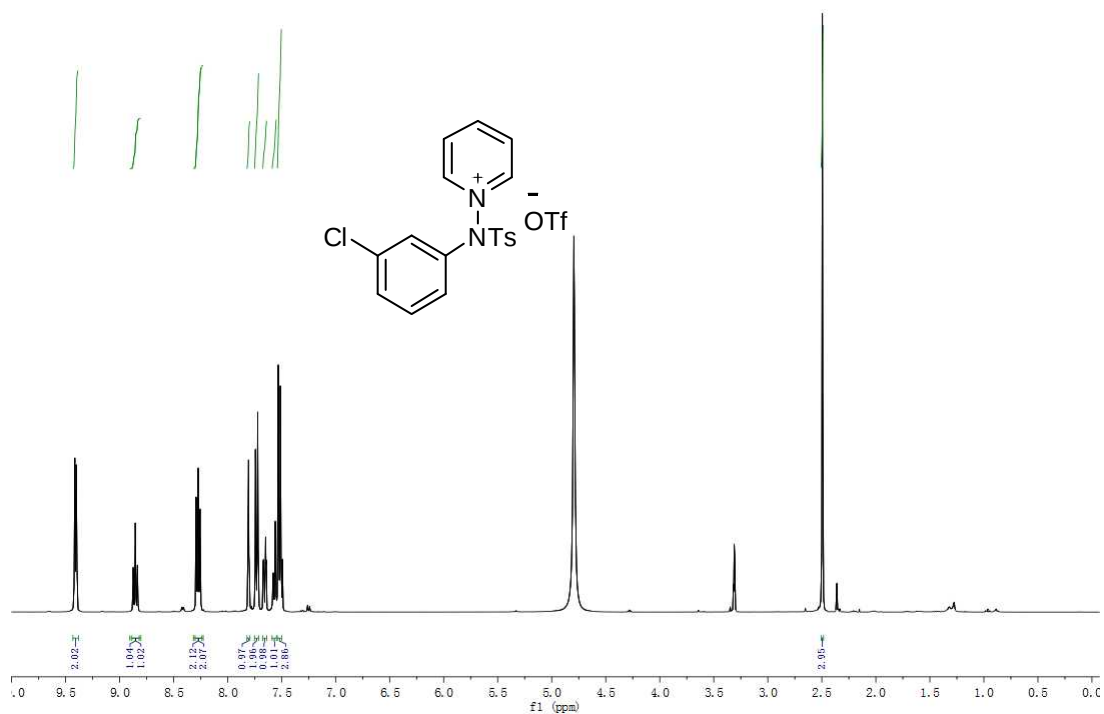
**1-(N-(2-chlorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3ia)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

¹³C NMR (101 MHz, METHANOL-D₄) (down)

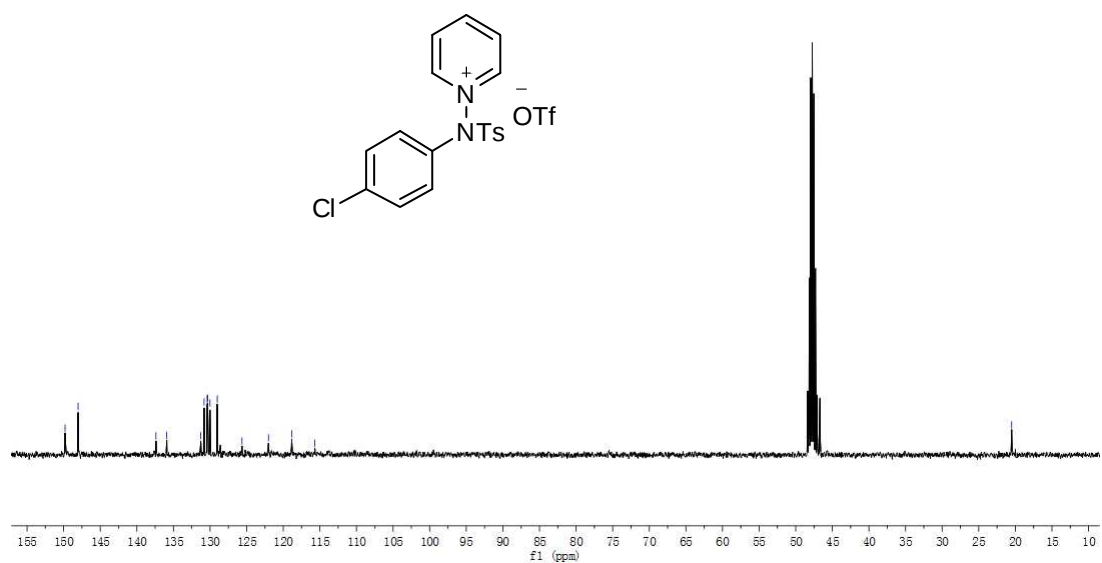
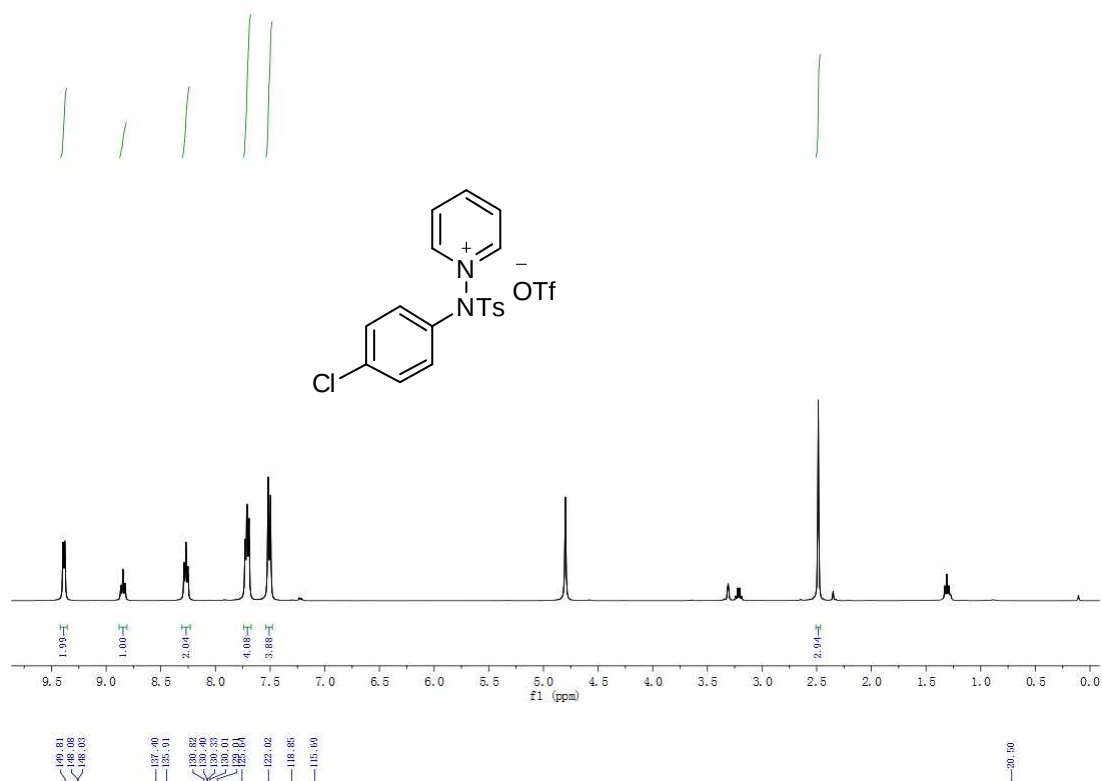
**1-(N-(3-chlorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3ja)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

¹³C NMR (101 MHz, METHANOL-D₄) (down)

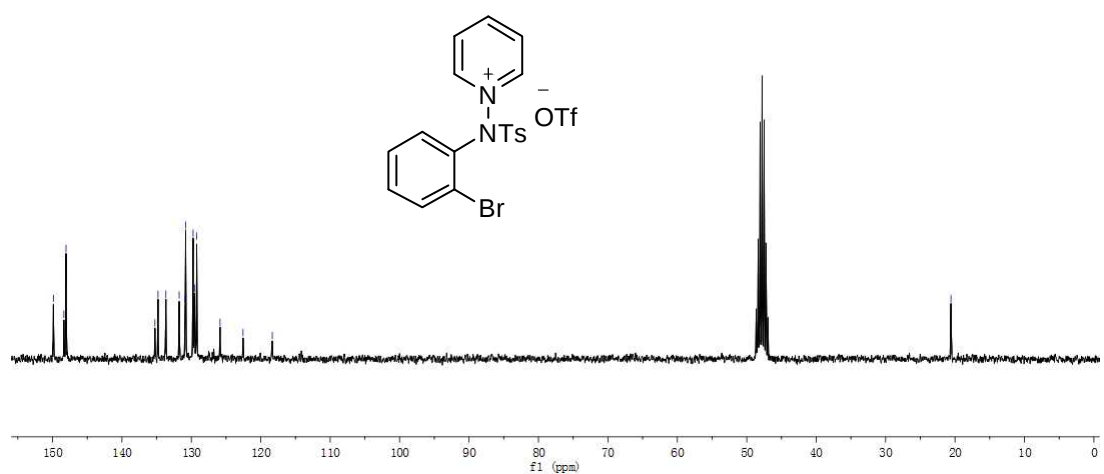
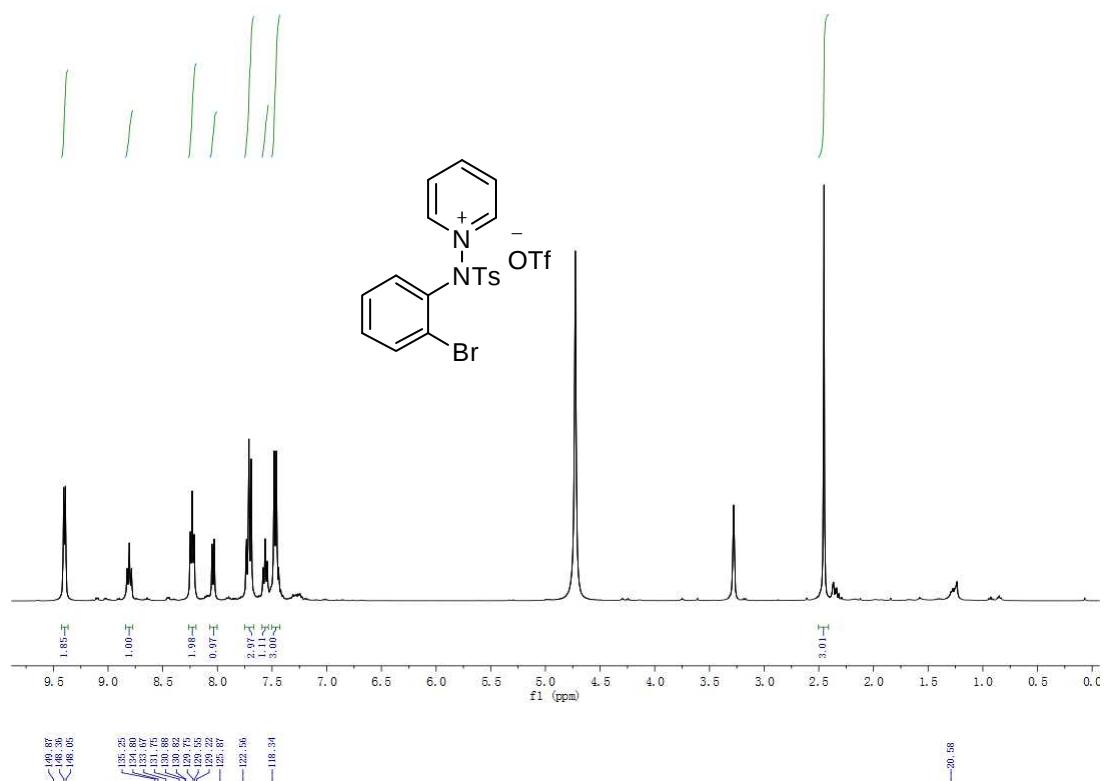
**1-(N-(4-chlorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3ka)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

¹³C NMR (101 MHz, METHANOL-D₄) (down)

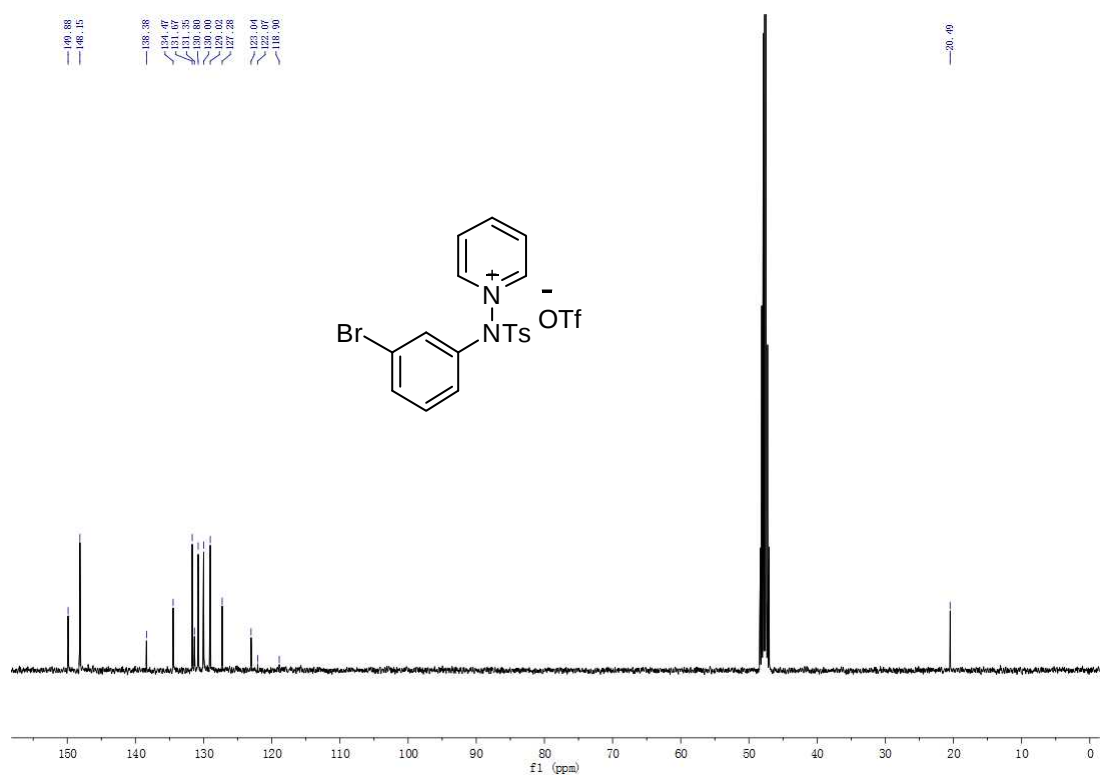
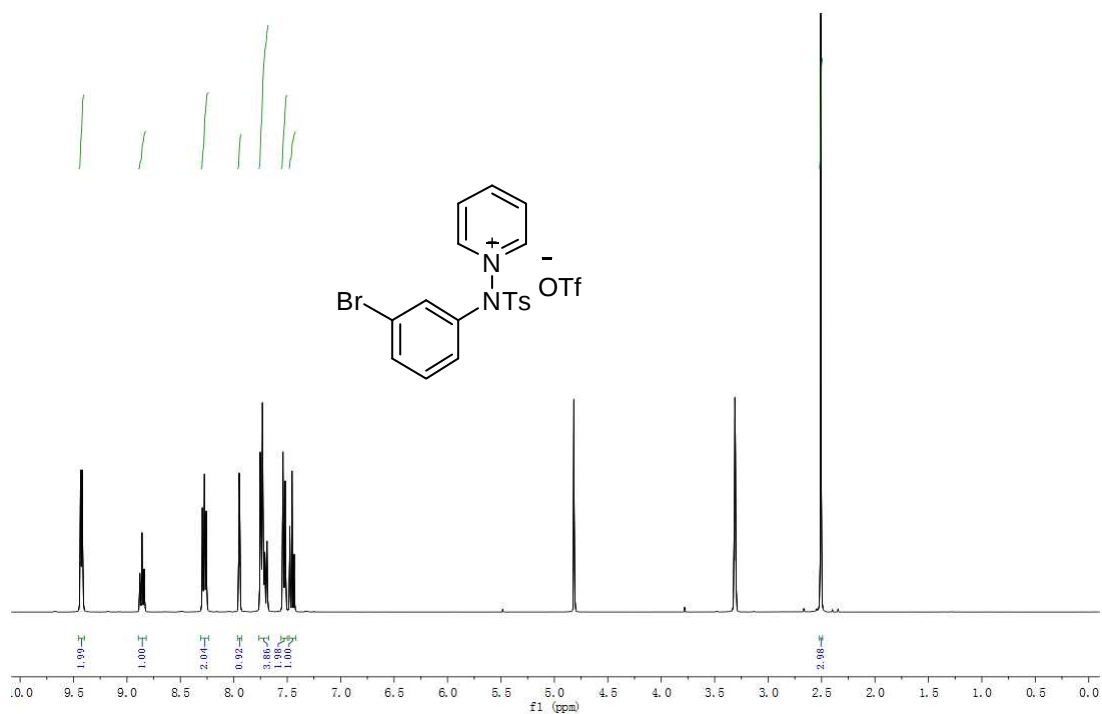
**1-(N-(2-bromophenyl)-4-methylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3la)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

¹³C NMR (101 MHz, METHANOL-D₄) (down)

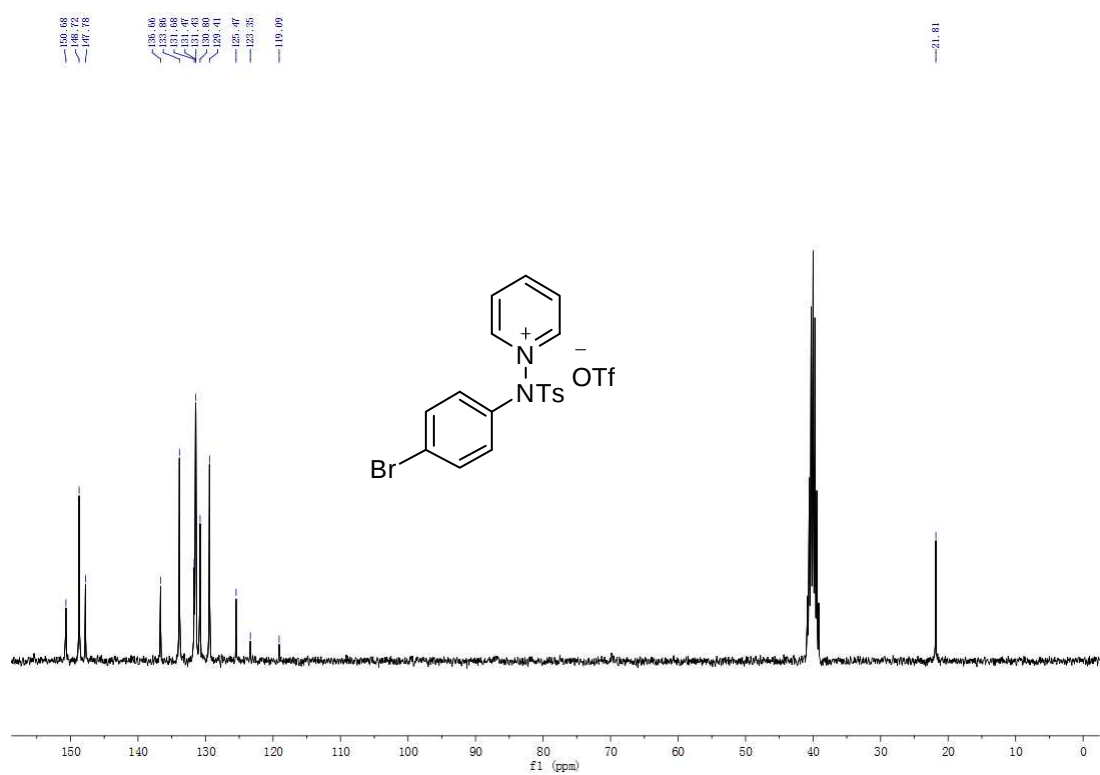
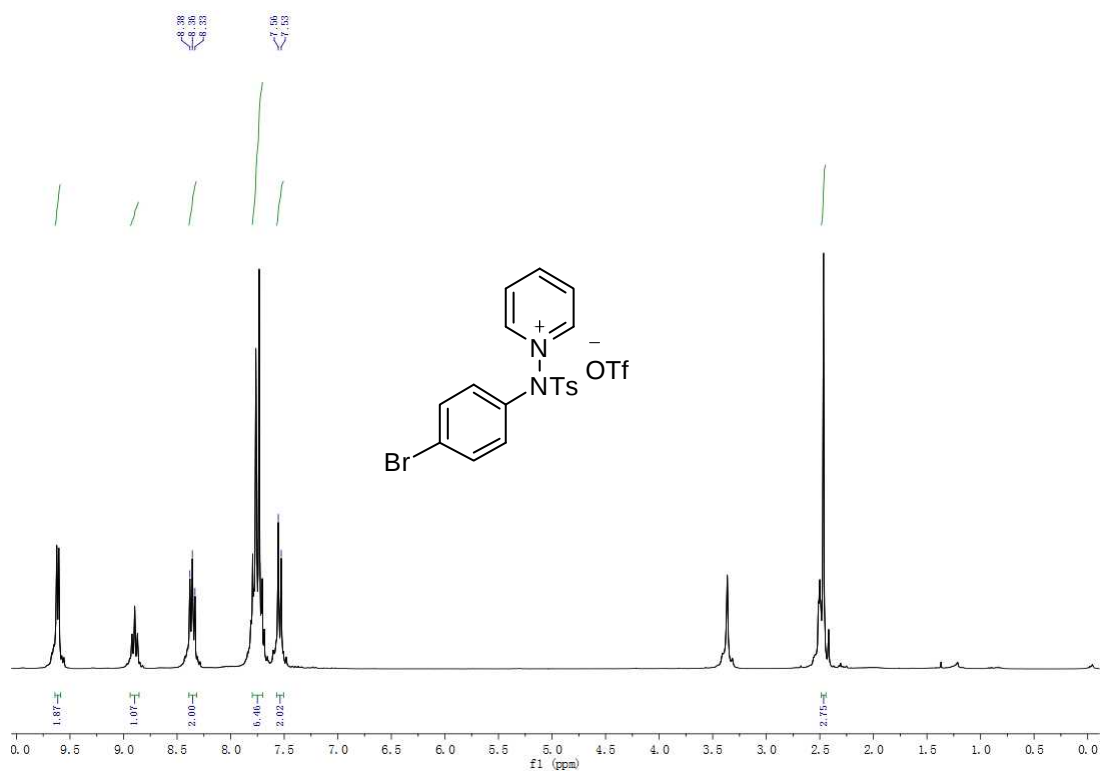
**1-(N-(3-bromophenyl)-4-methylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3ma)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

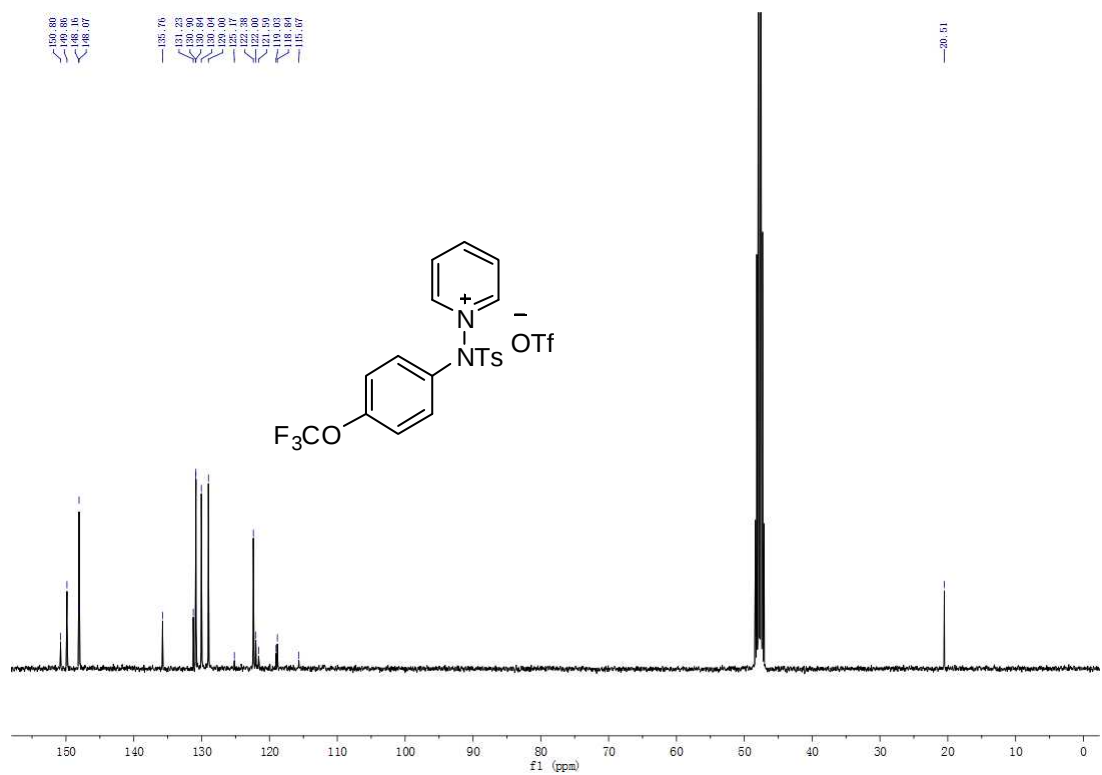
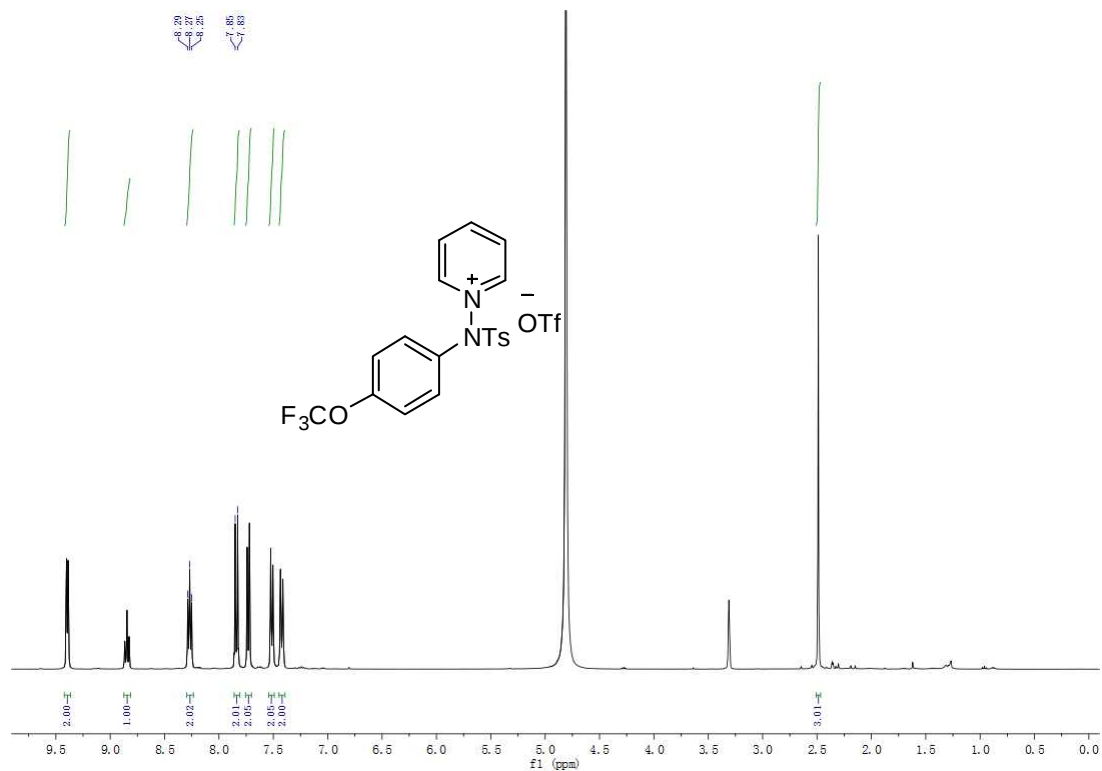
¹³C NMR (101 MHz, METHANOL-D₄) (down)

**1-(N-(4-bromophenyl)-4-methylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3na)**



¹H NMR (301 MHz, DMSO-D₆) (up) and ¹³C NMR (76 MHz, DMSO-D₆) (down)

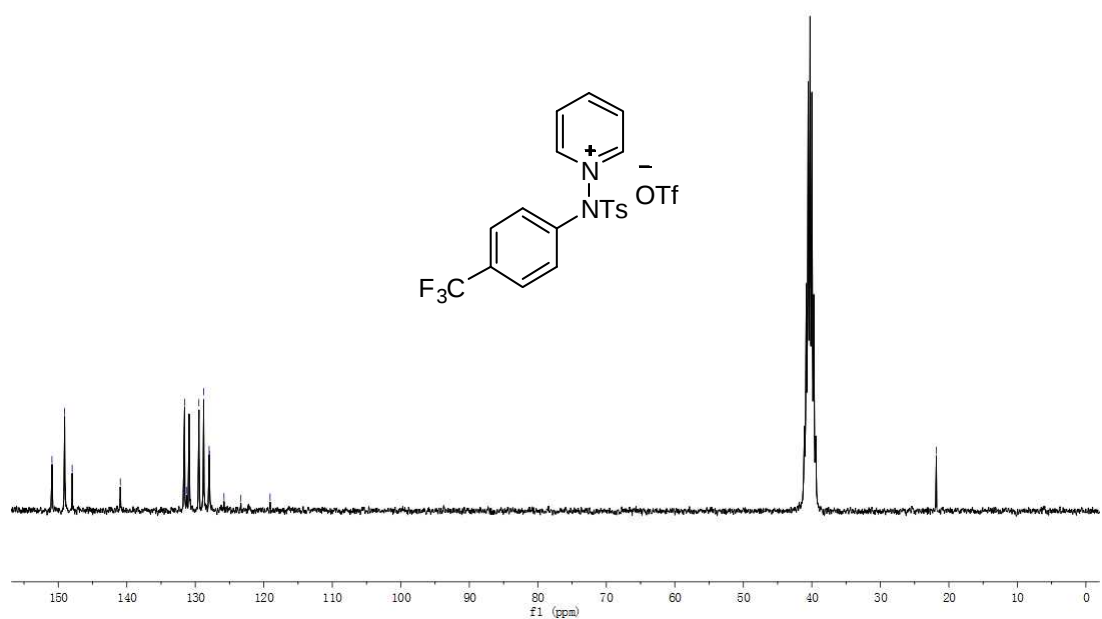
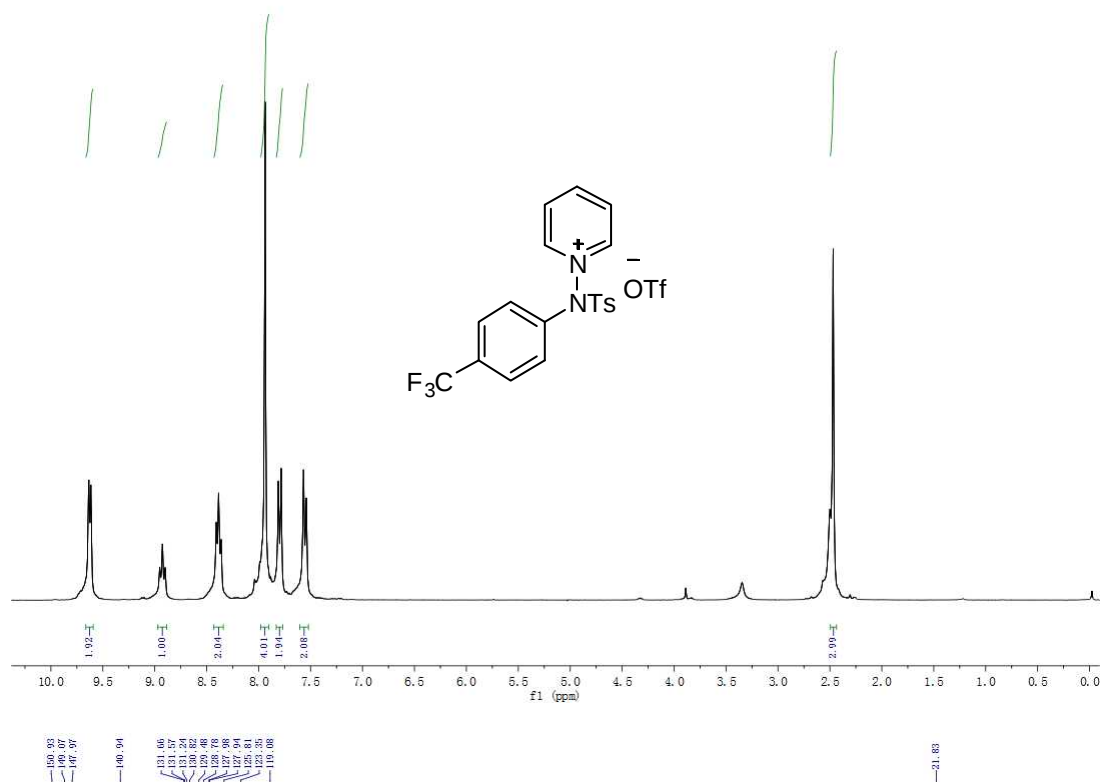
**1-(4-methyl-N-(4-(trifluoromethoxy)phenyl)phenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (30a)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

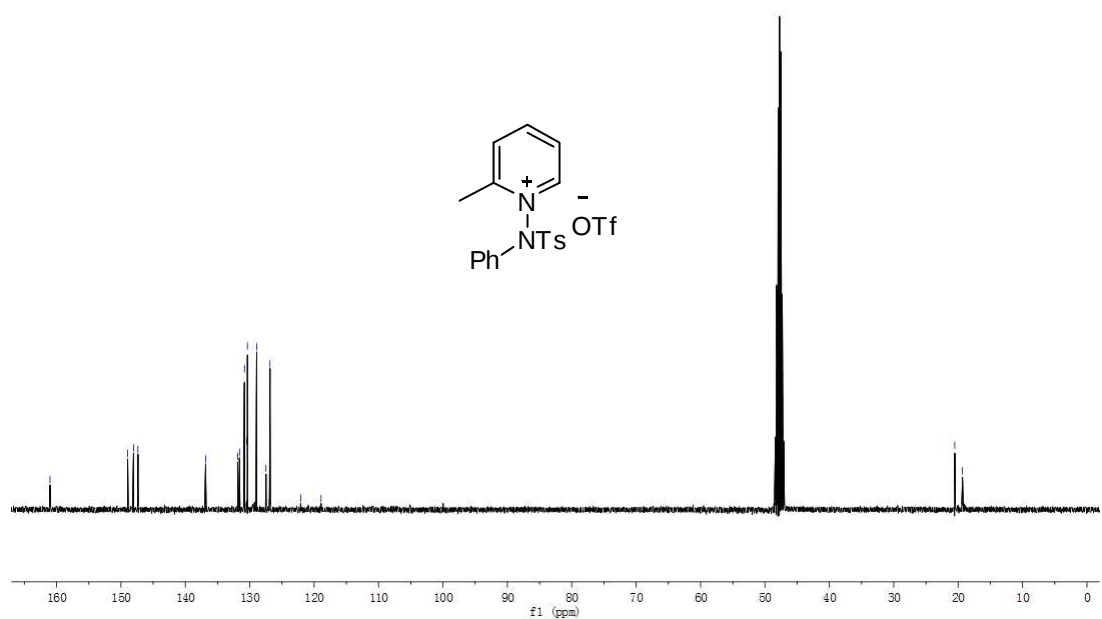
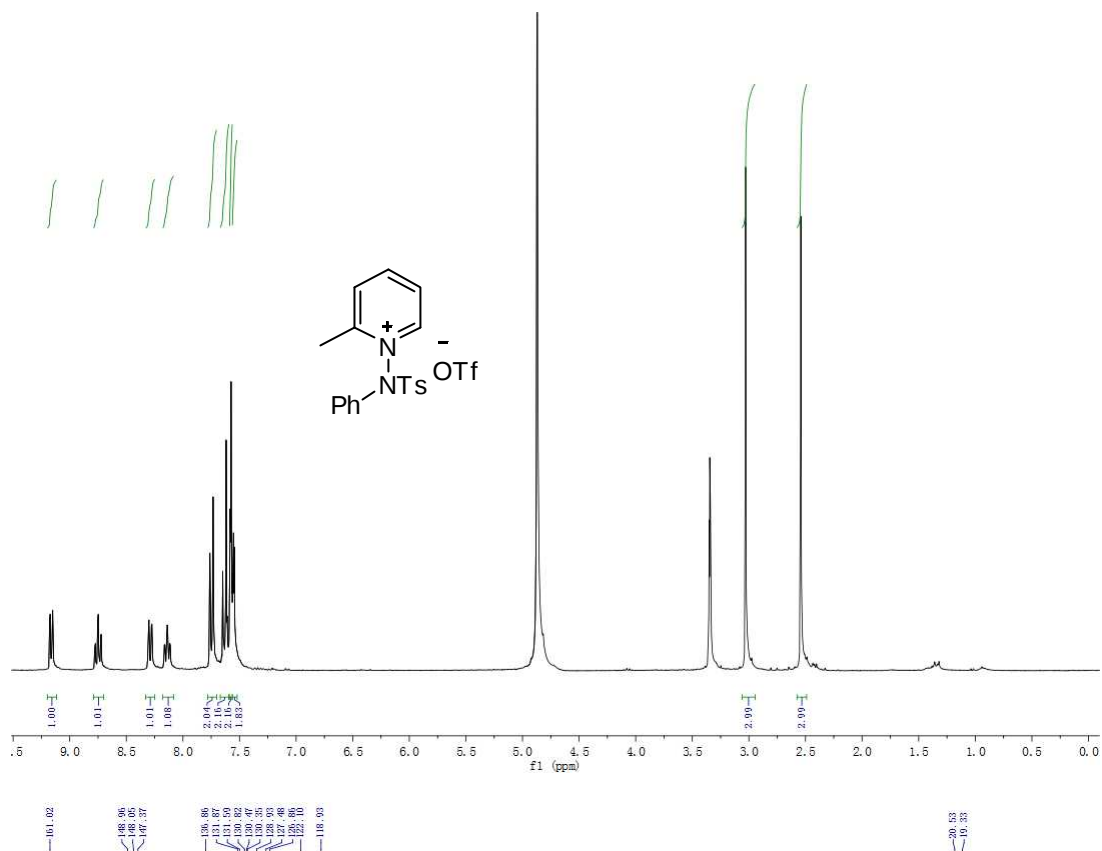
¹³C NMR (101 MHz, METHANOL-D₄) (down)

**1-(4-methyl-N-(4-(trifluoromethyl)phenyl)phenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3pa)**



¹H NMR (301 MHz, DMSO-D₆) (up) and ¹³C NMR (76 MHz, DMSO-D₆) (down)

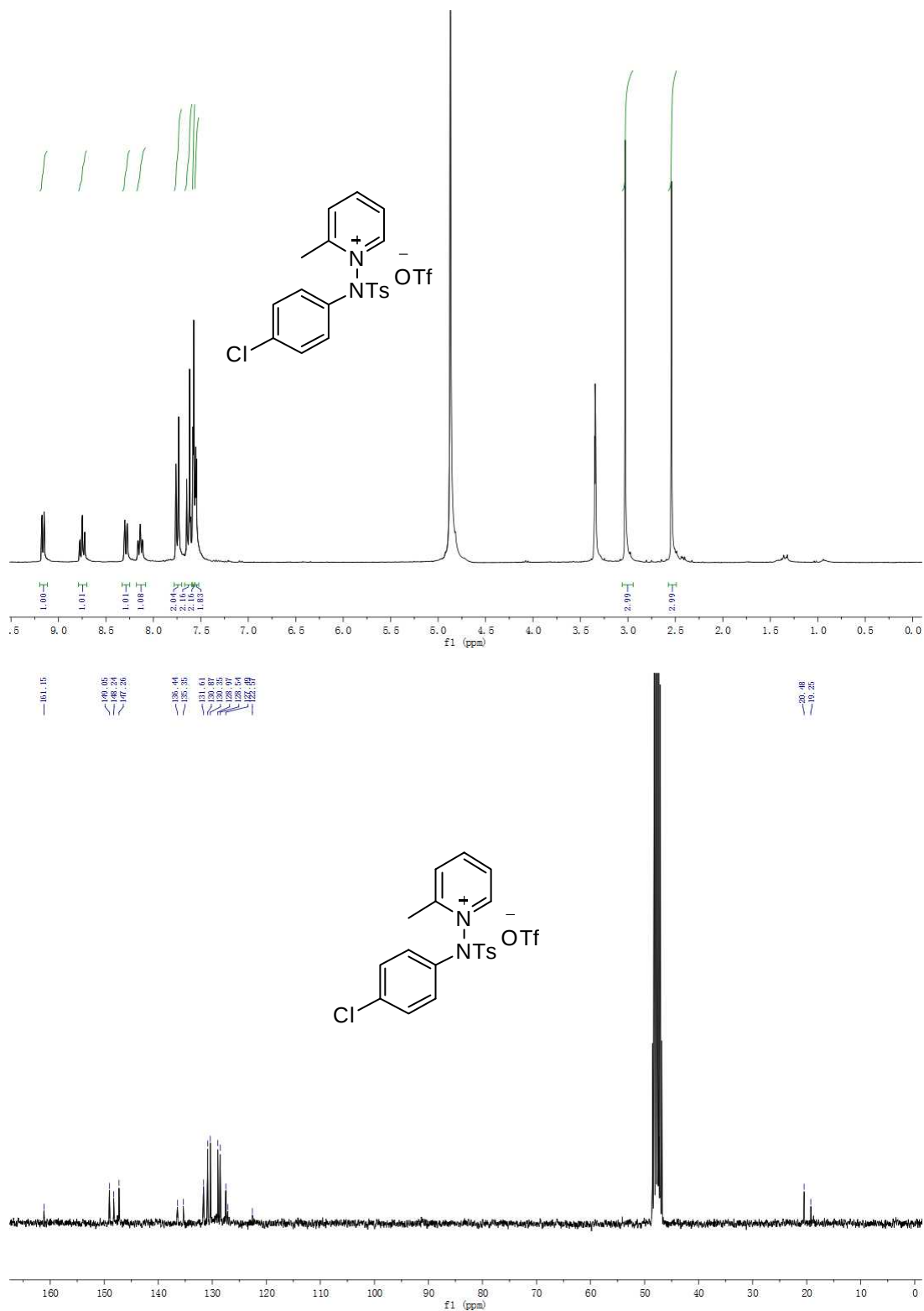
**2-methyl-1-(4-methyl-N-phenylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3ab)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

¹³C NMR (101 MHz, METHANOL-D₄) (down)

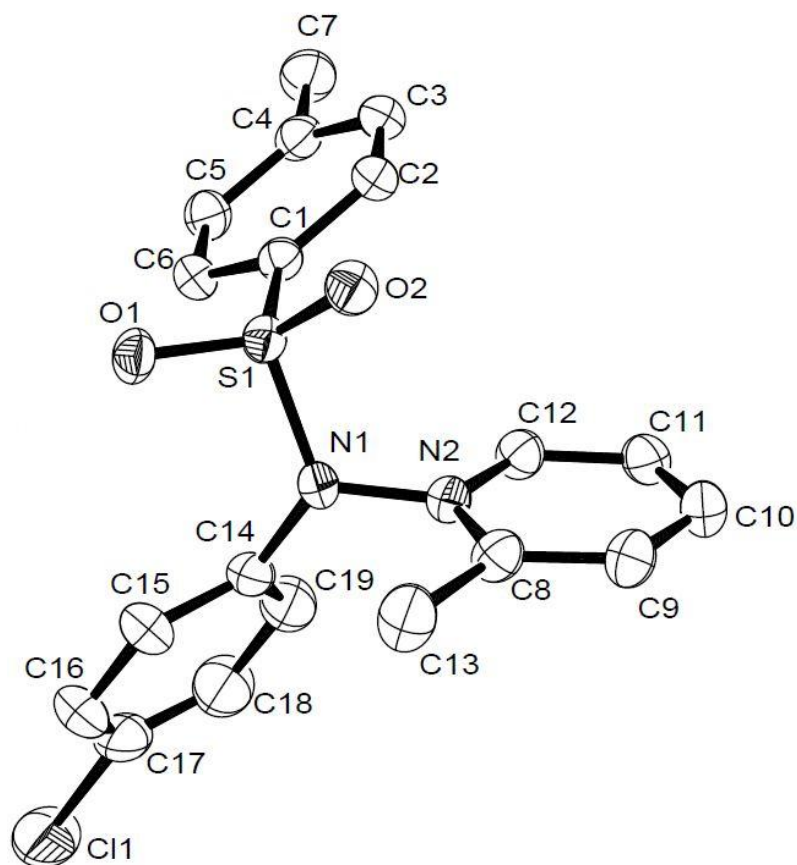
**1-(N-(4-chlorophenyl)-4-methylphenylsulfonamido)-2-methylpyridin-1-ium
trifluoromethanesulfonate (3kb)**



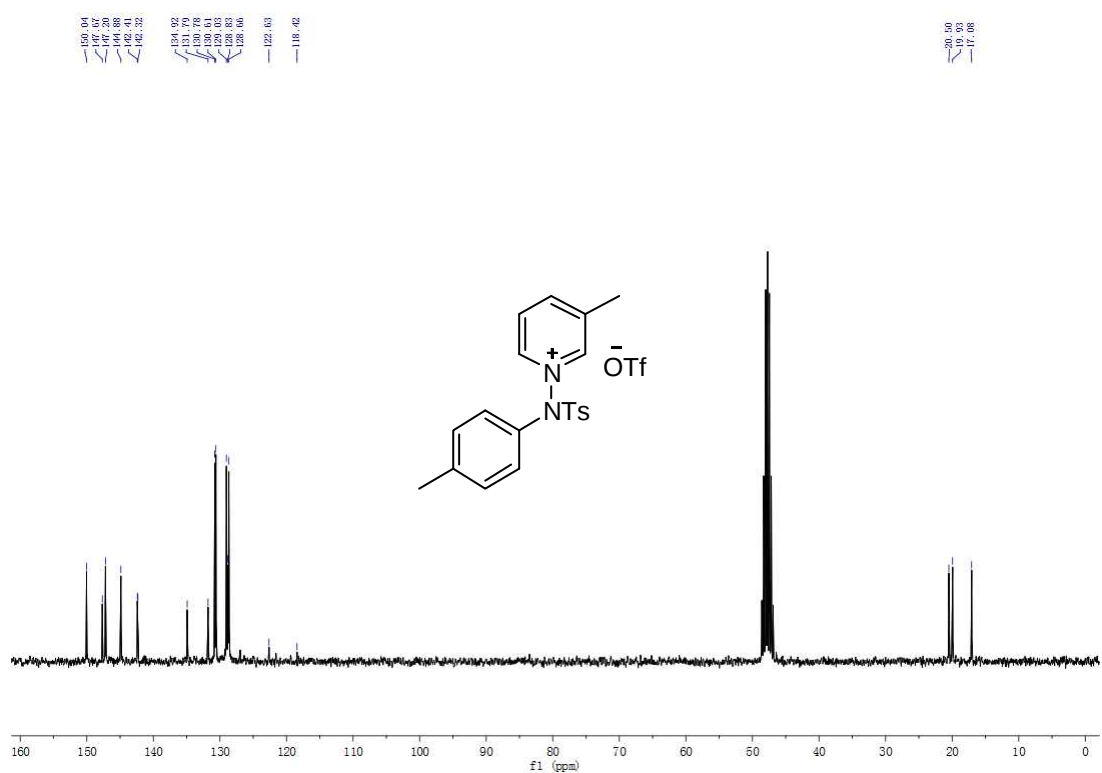
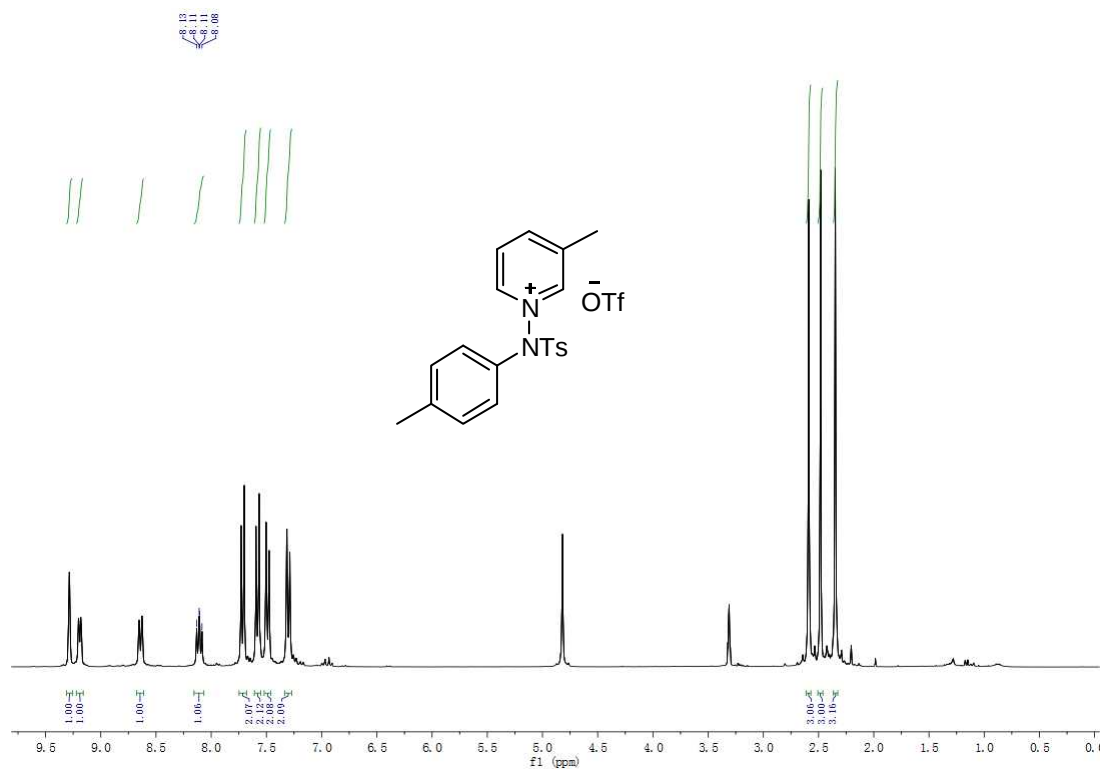
¹H NMR (301 MHz, METHANOL-D₄) (up) and

¹³C NMR (76 MHz, METHANOL-D₄) (down)

X-ray crystal structure analysis of compound 3kb: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in CH₃OH. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC** 1008472. Formula: C₂₀H₁₈ClF₃N₂O₅S₂, *M* = 522.95, colourless crystal, 0.20 x 0.14 x 0.13 mm, *a* = 8.6089(17), *b* = 8.8898(18), *c* = 15.632(3) Å, α = 98.35(3), β = 96.13(3), γ = 104.16(3), *V* = 1135.0(4) Å³, ρ_{calc} = 1.530 gcm⁻³, μ = 0.412 mm⁻¹, *Z* = 2, Triclinic, space group *P*-1, λ = 0.71073 Å, *T* = 173(2) K. Data completeness = 0.987, Theta (max) = 27.46, *R* (reflections) = 0.0884, *wR*₂ (reflections) = 0.2084 (5129).



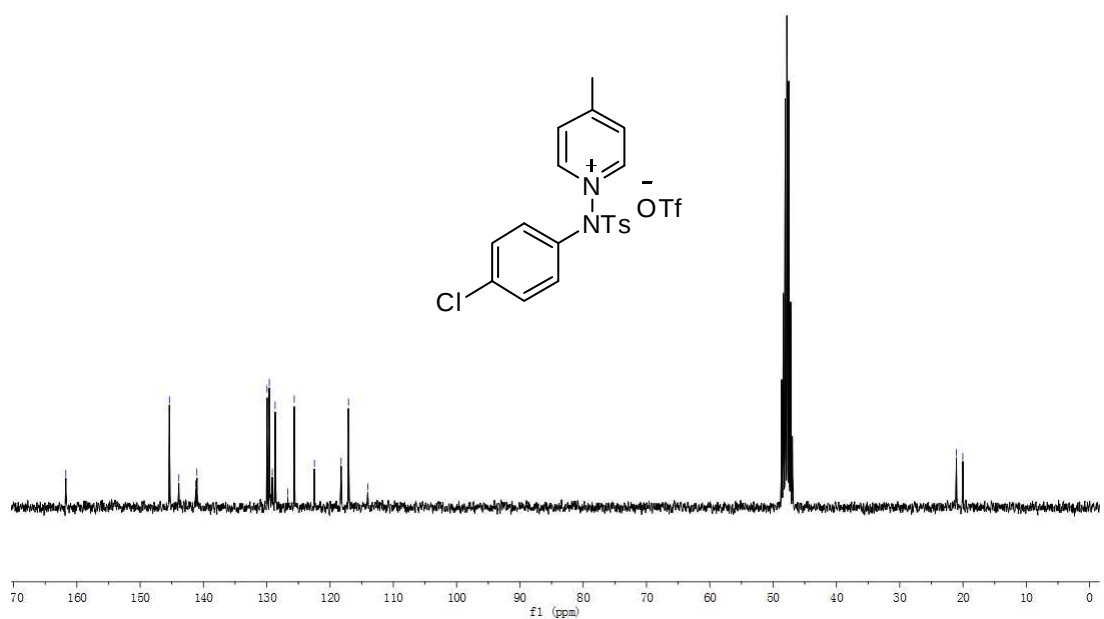
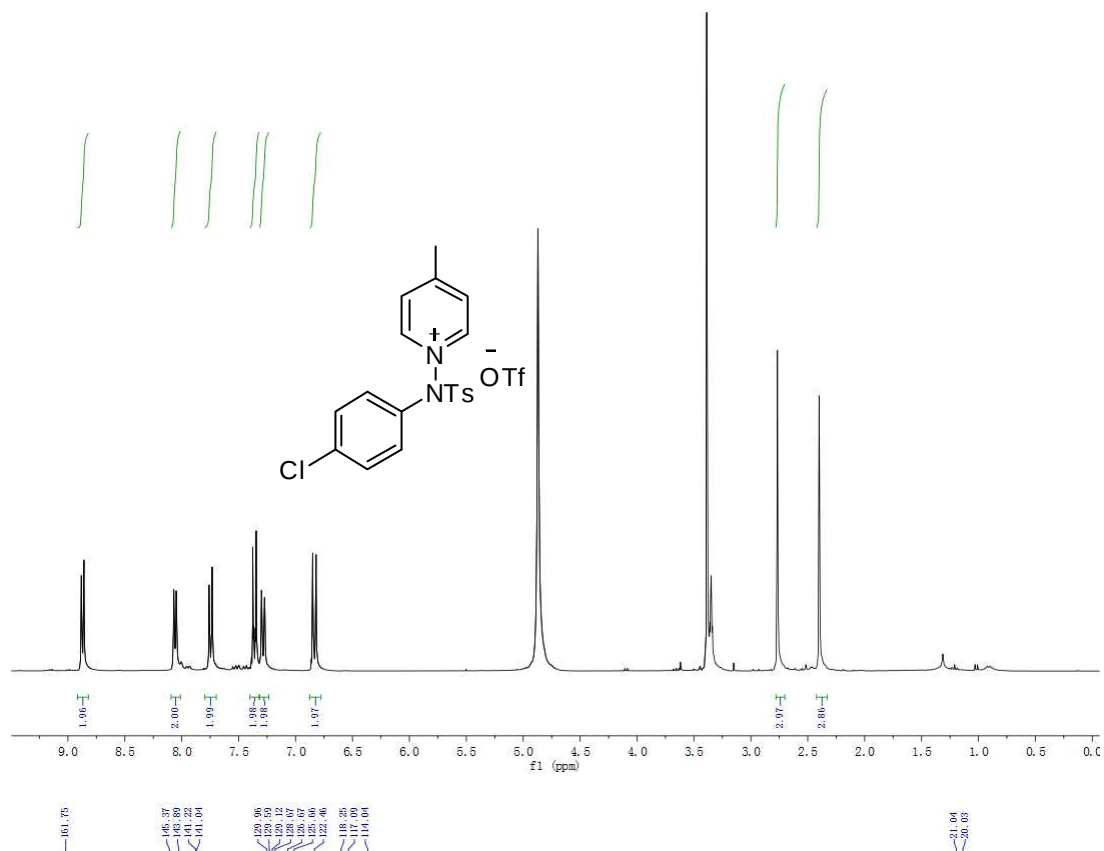
**3-methyl-1-(4-methyl-N-(p-tolyl)phenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3dc)**



¹H NMR (301 MHz, METHANOL-D₄) (up) and

¹³C NMR (76 MHz, METHANOL-D₄) (down)

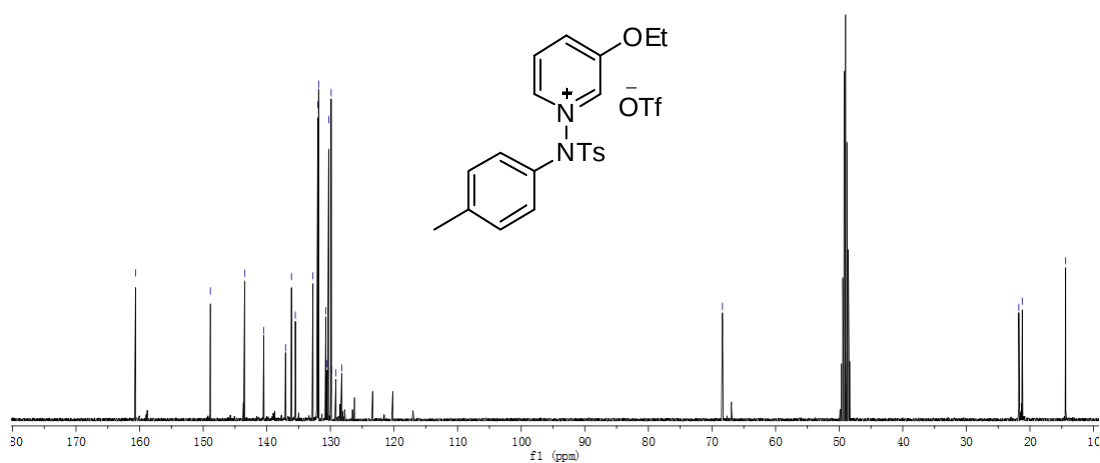
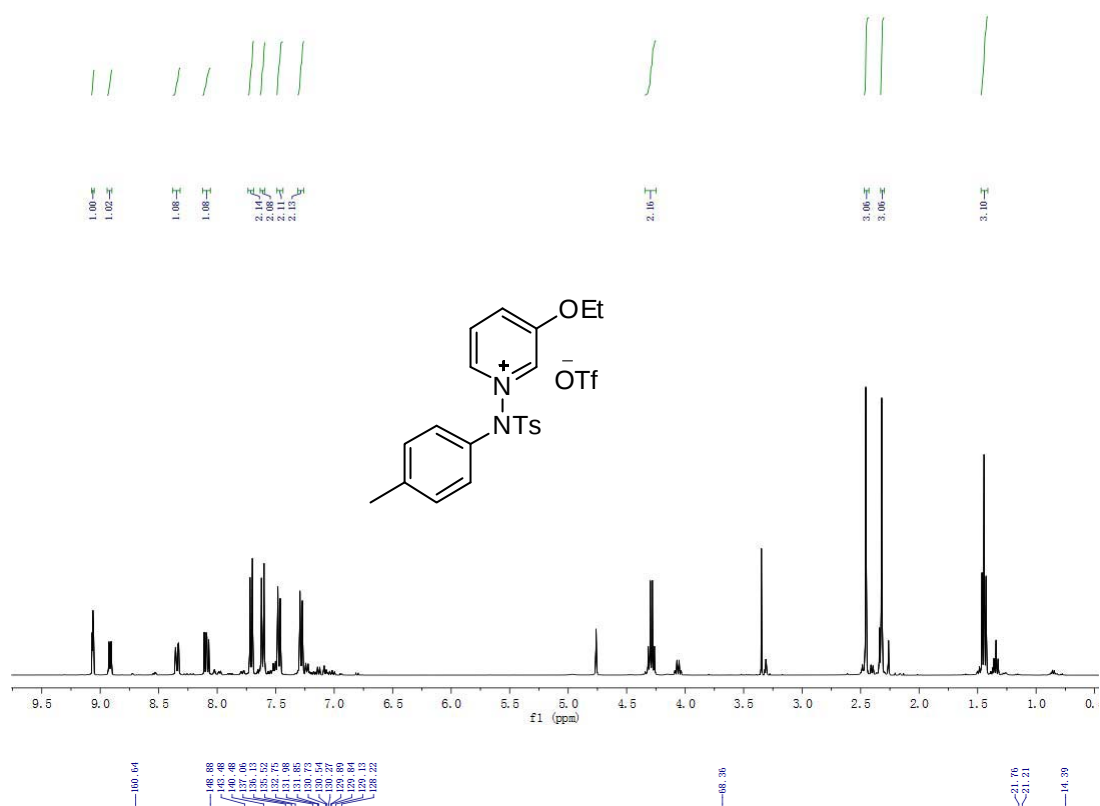
**1-(N-(4-chlorophenyl)-4-methylphenylsulfonamido)-4-methylpyridin-1-ium
trifluoromethanesulfonate (3kd)**



¹H NMR (301 MHz, METHANOL-D₄) (up) and

¹³C NMR (76 MHz, METHANOL-D₄) (down)

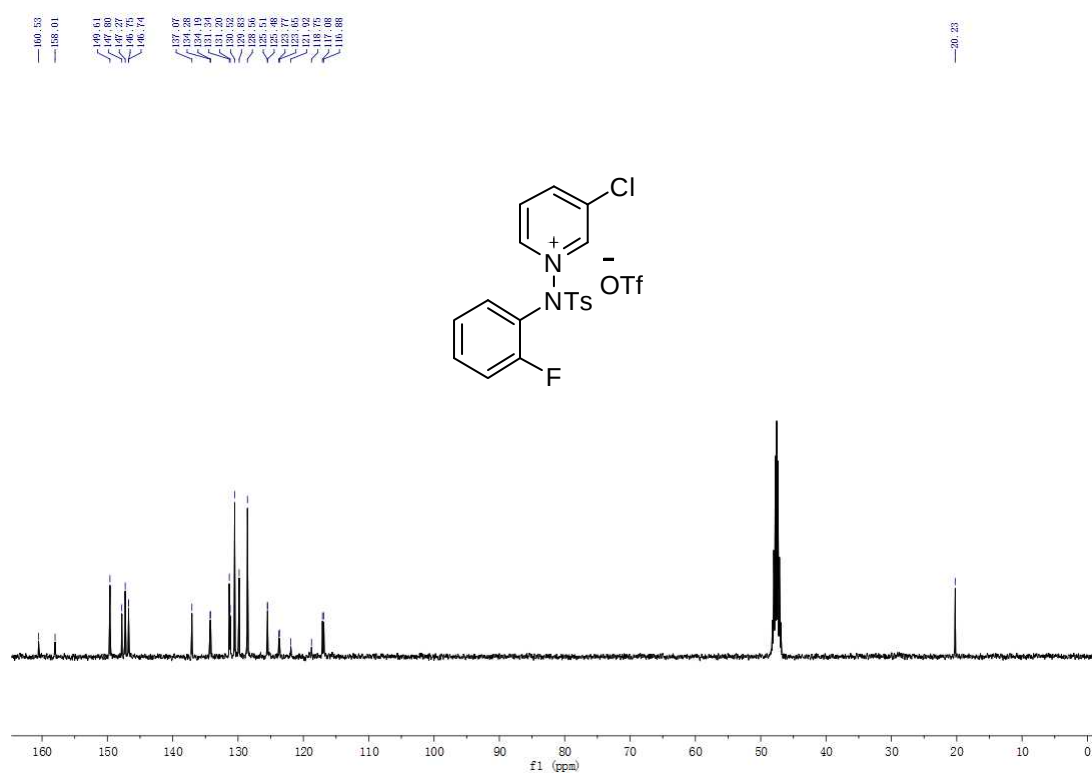
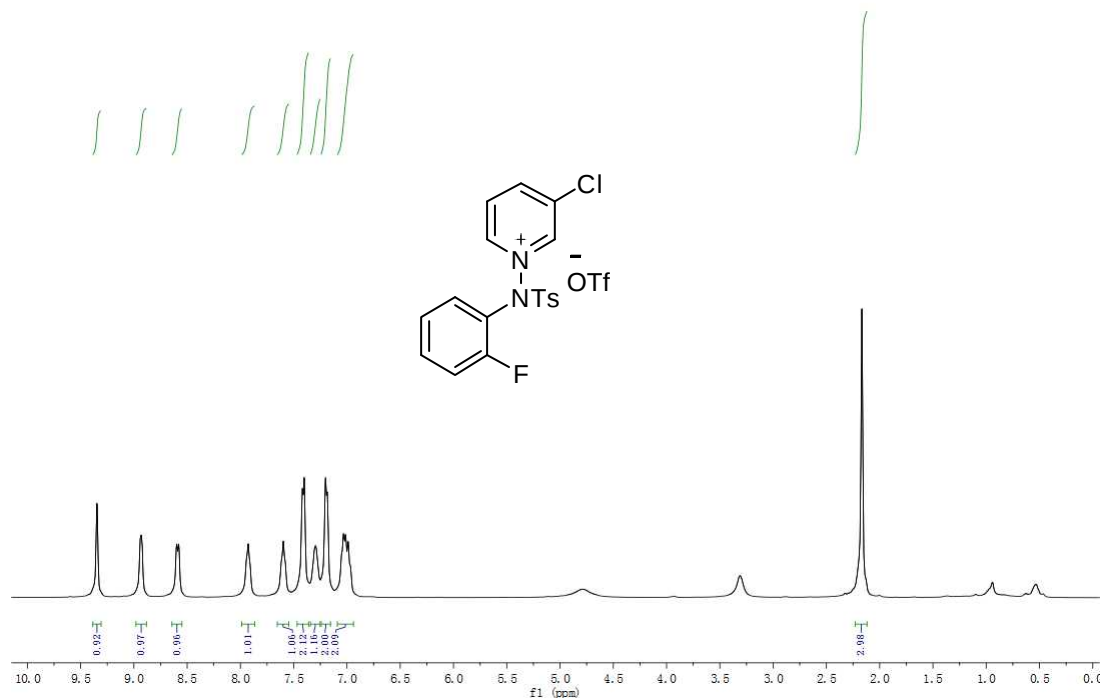
**3-ethoxy-1-(4-methyl-N-(p-tolyl)phenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3de)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

¹³C NMR (101 MHz, METHANOL-D₄) (down)

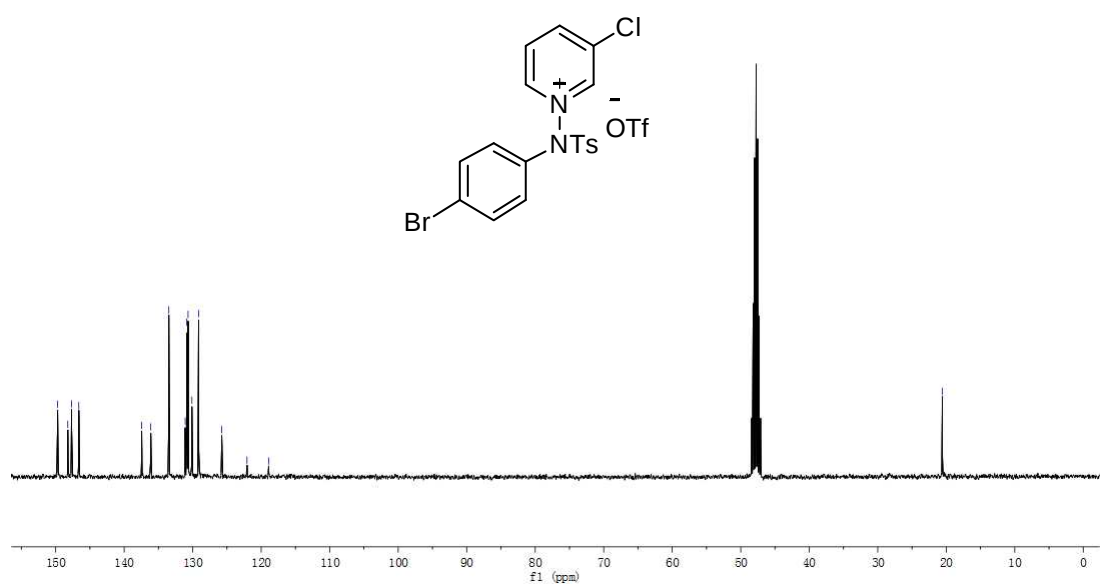
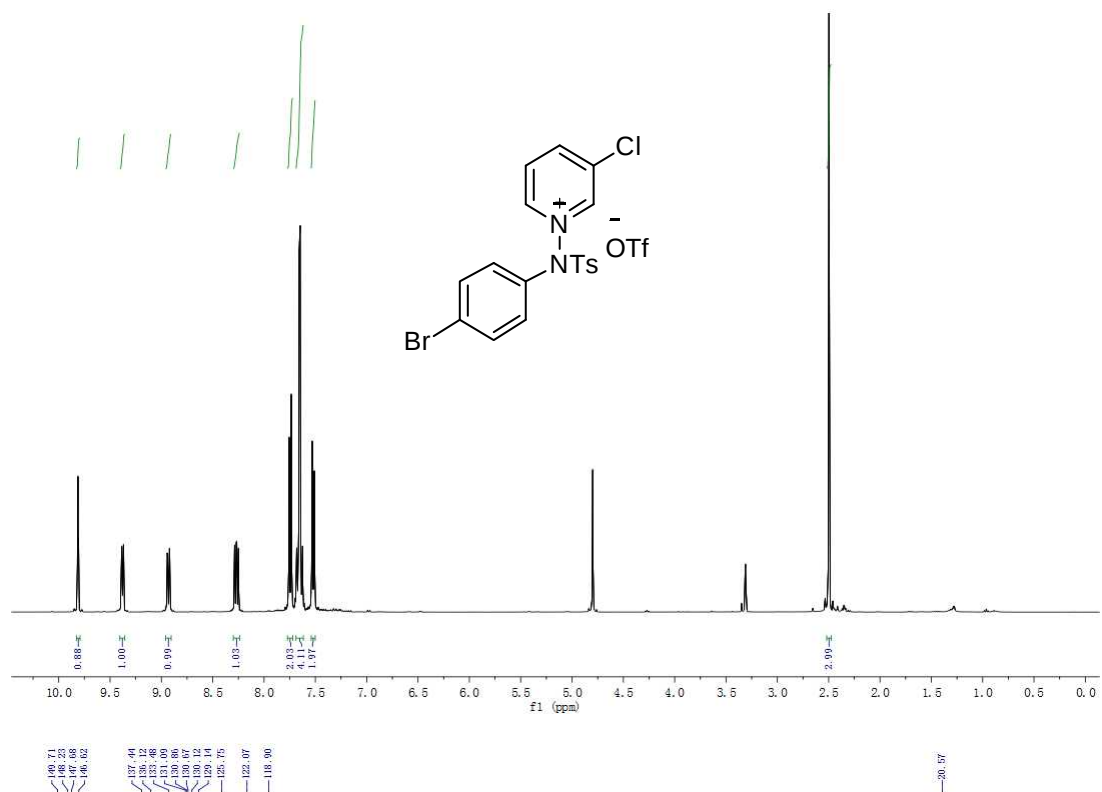
**3-chloro-1-(N-(2-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3ff)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

¹³C NMR (101 MHz, METHANOL-D₄) (down)

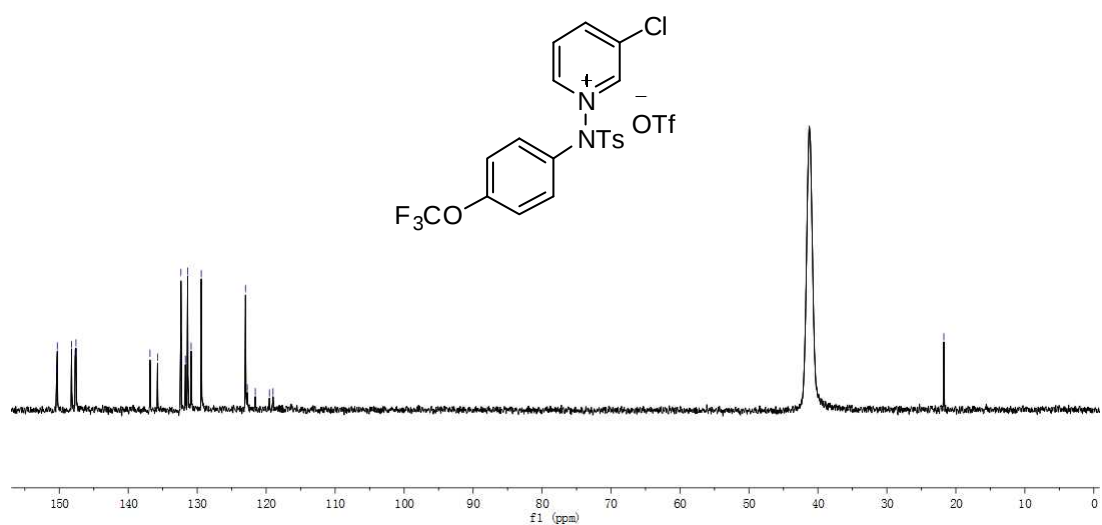
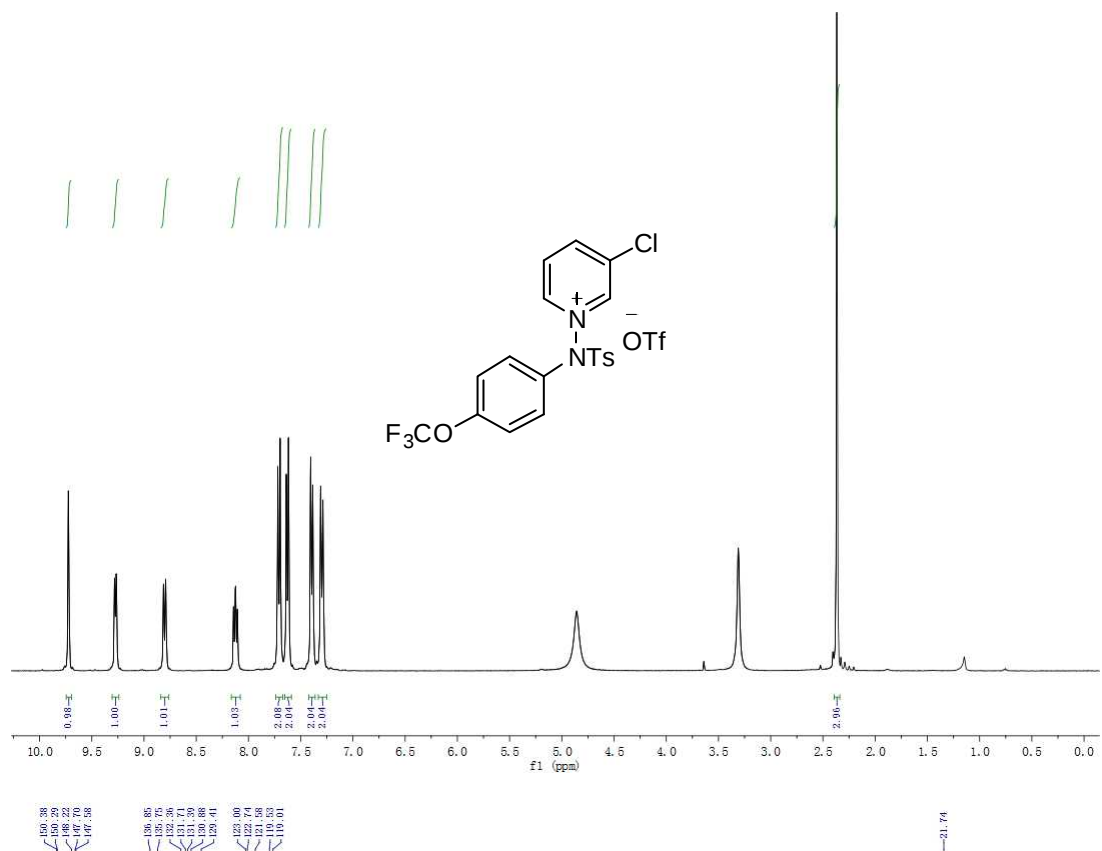
**1-(N-(4-bromophenyl)-4-methylphenylsulfonamido)-3-chloropyridin-1-ium
trifluoromethanesulfonate (3nf)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

¹³C NMR (101 MHz, METHANOL-D₄) (down)

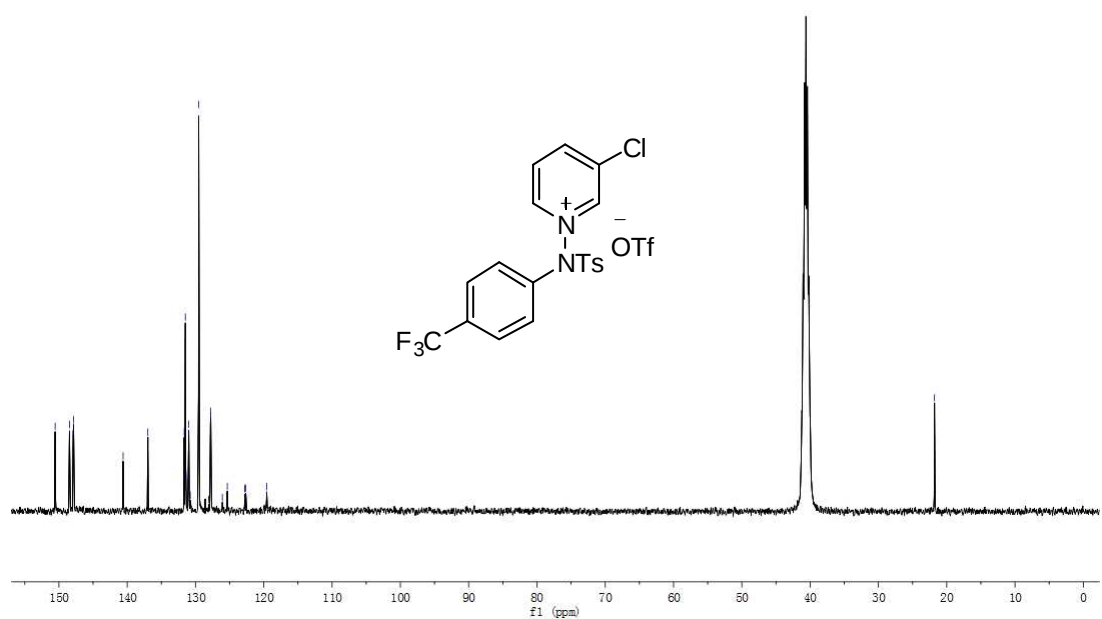
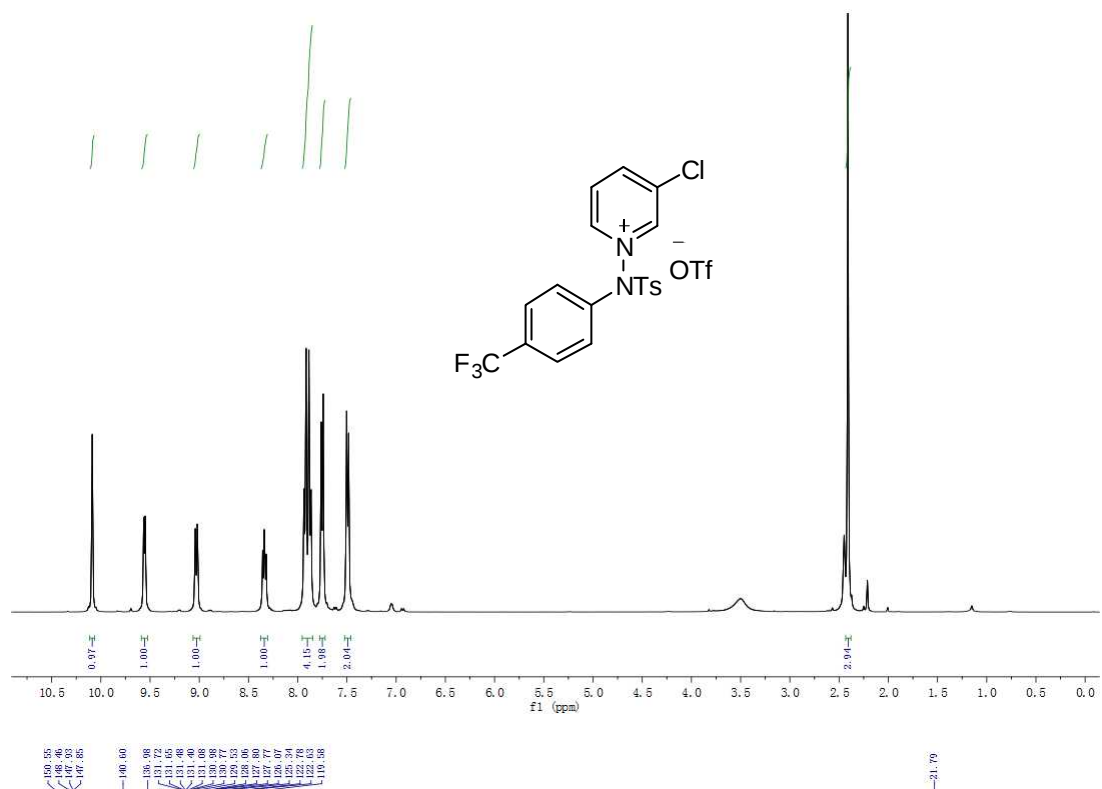
3-chloro-1-(4-methyl-N-(4-(trifluoromethoxy)phenyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3of)



¹H NMR (400 MHz, METHANOL-D₄) (up) and

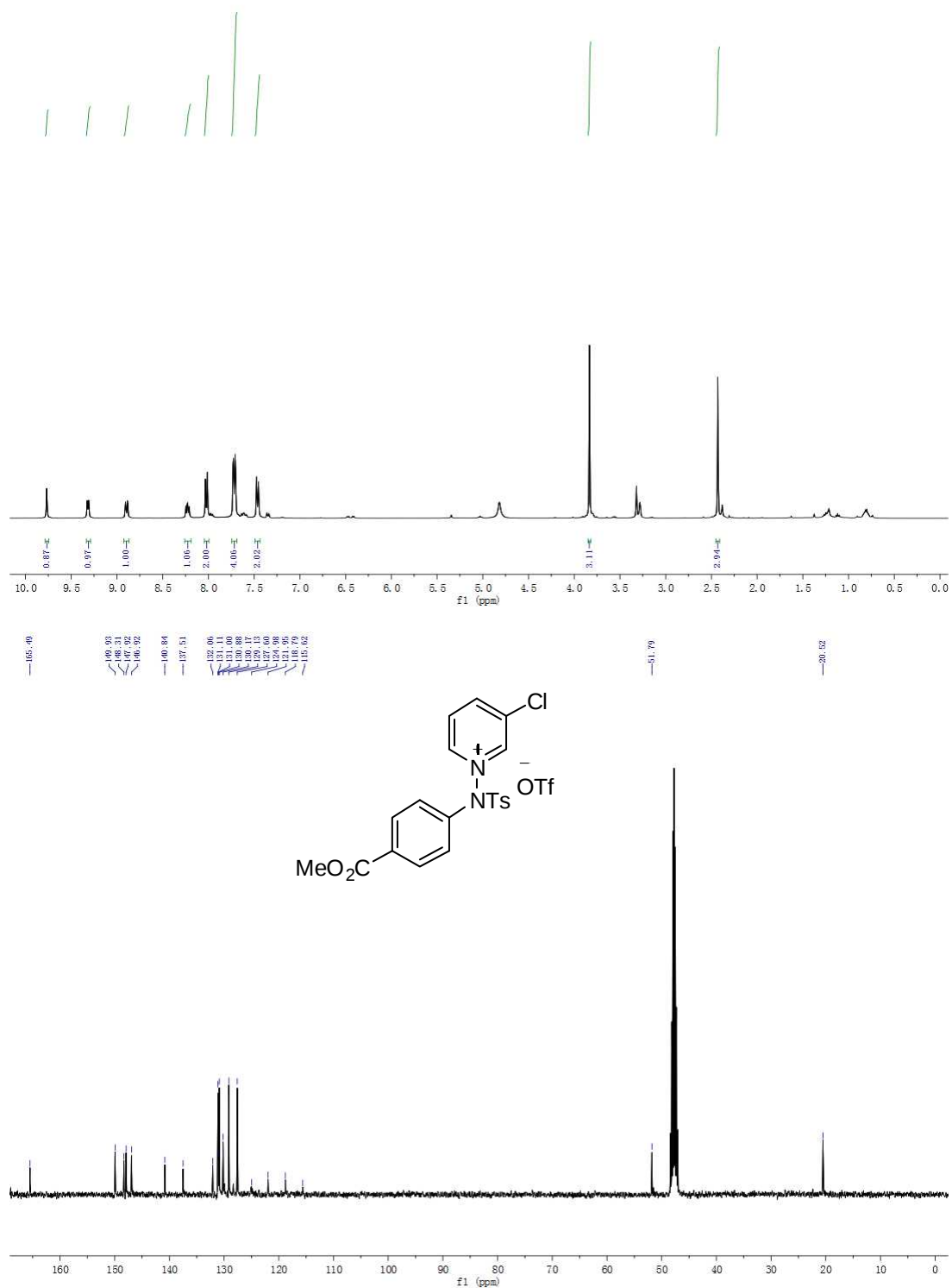
¹³C NMR (101 MHz, DMSO-D₆) (down)

3-chloro-1-(4-methyl-N-(4-(trifluoromethyl)phenyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3pf)



¹H NMR (400 MHz, DMSO-D6) (up) and ¹³C NMR (101 MHz, DMSO-D6) (down)

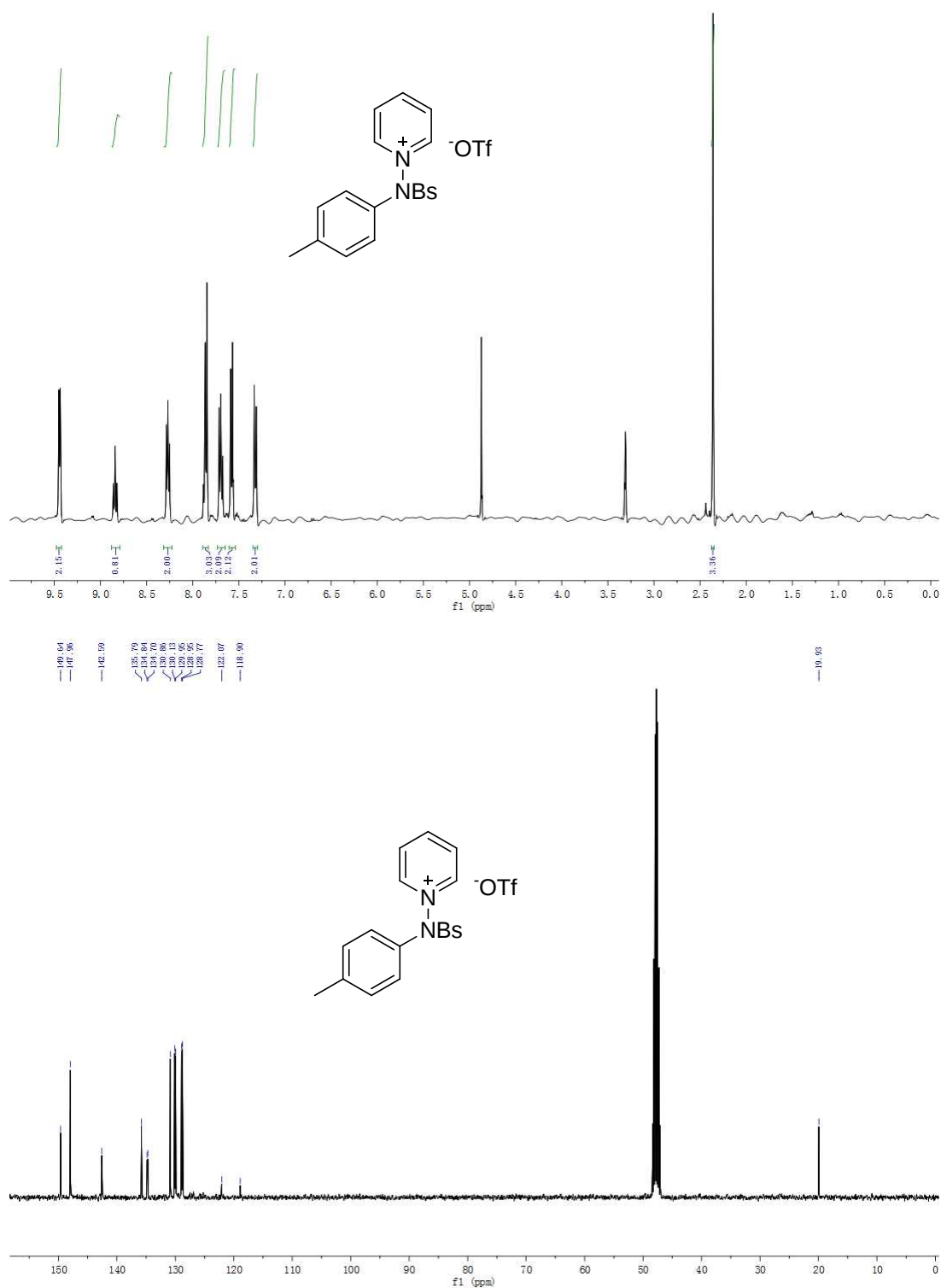
3-chloro-1-(N-(4-(methoxycarbonyl)phenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3qf)



¹H NMR (400 MHz, METHANOL-D₄) (up) and

¹³C NMR (101 MHz, METHANOL-D₄) (down)

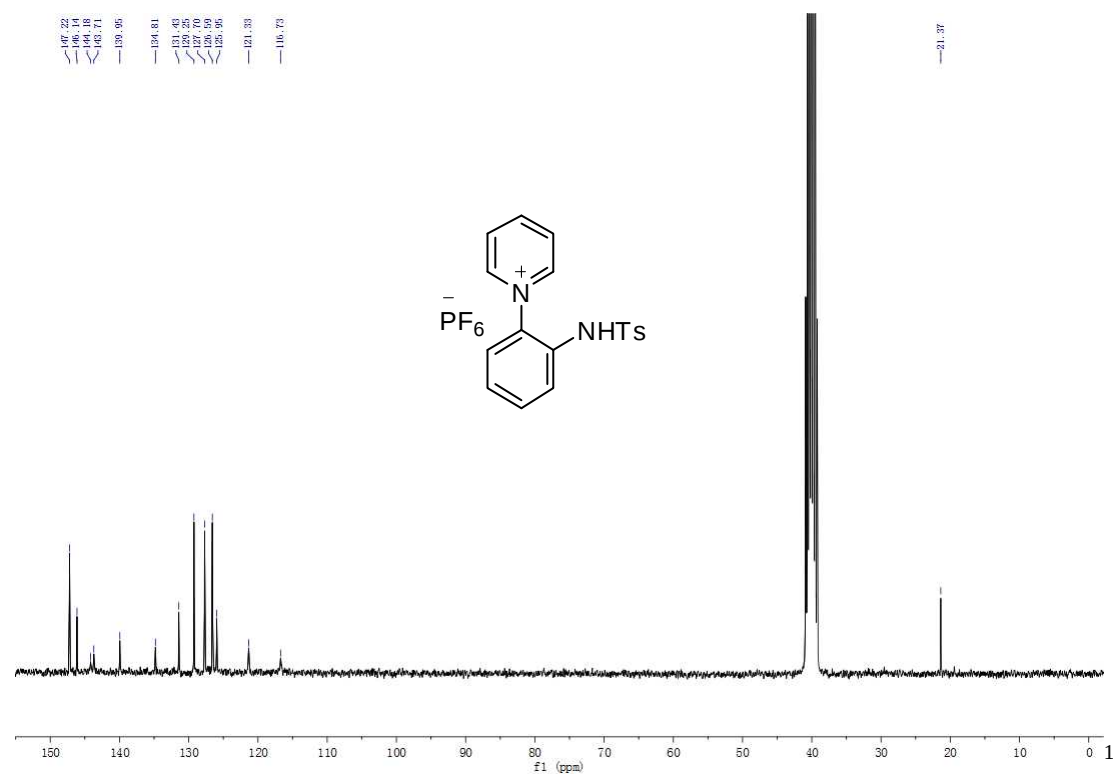
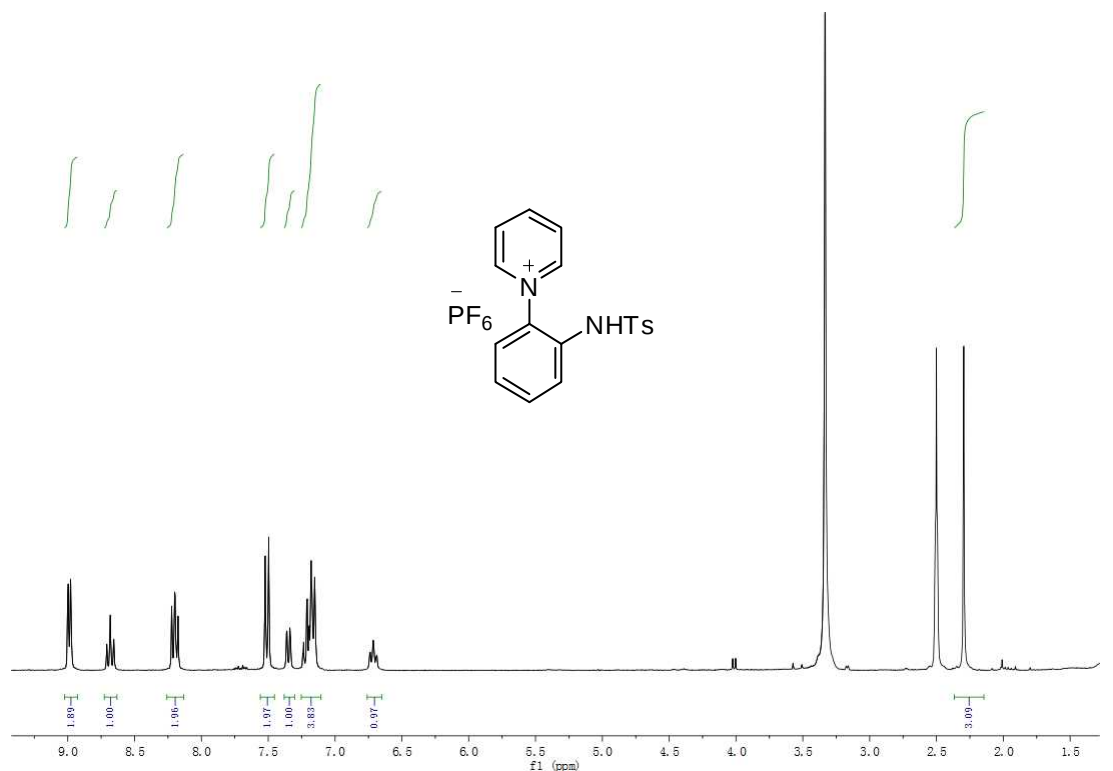
1-(N-(p-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3dg)



¹H NMR (400 MHz, METHANOL-D4) (up) and

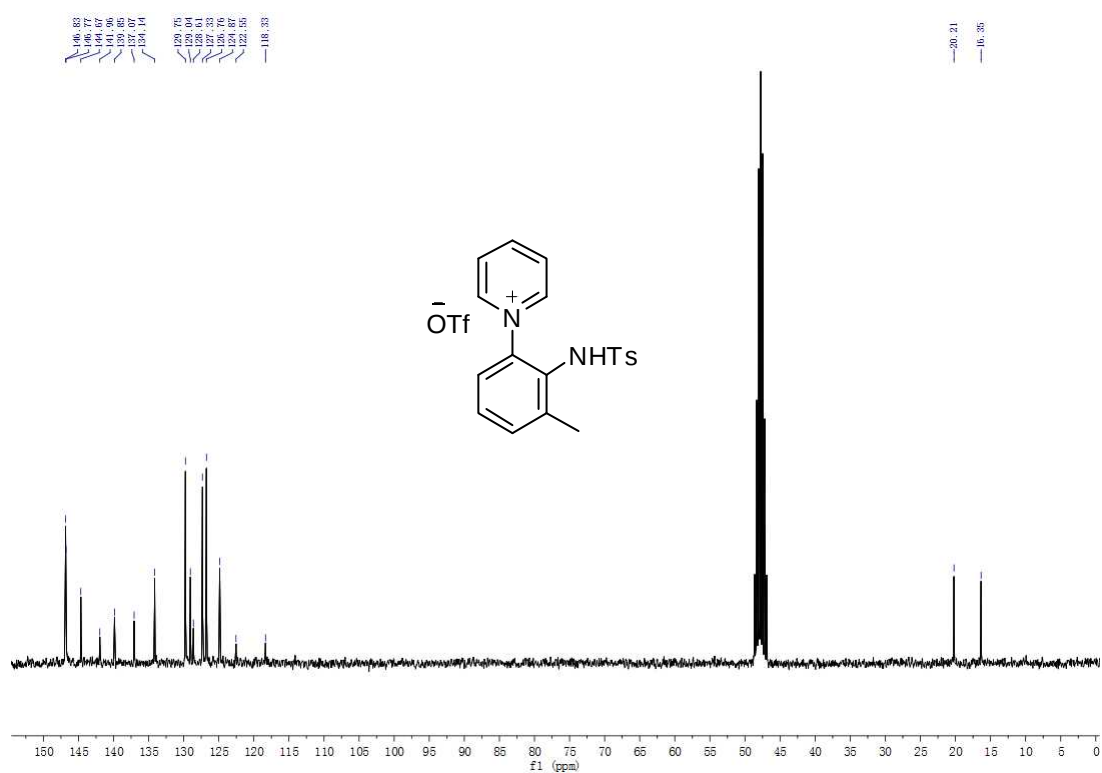
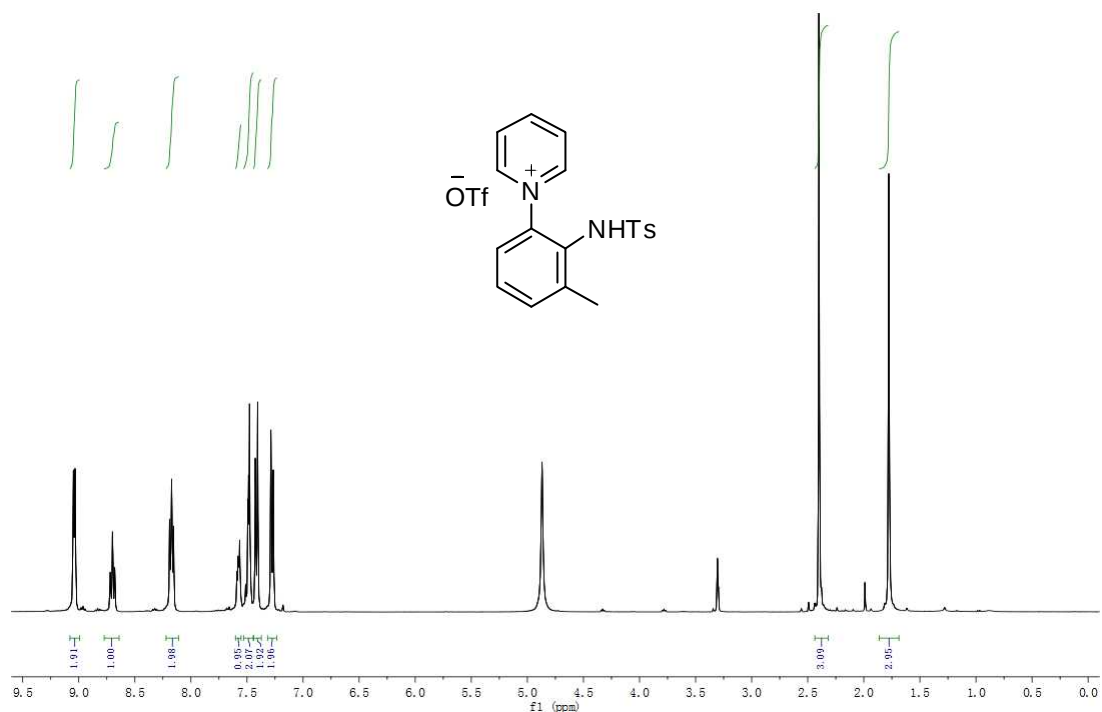
¹³C NMR (101 MHz, METHANOL-D4) (down)

1-(2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium hexafluorophosphate(V)
(4aa)



¹H NMR (301 MHz, DMSO-D₆) (up) and ¹³C NMR (76 MHz, DMSO-D₆) (down)

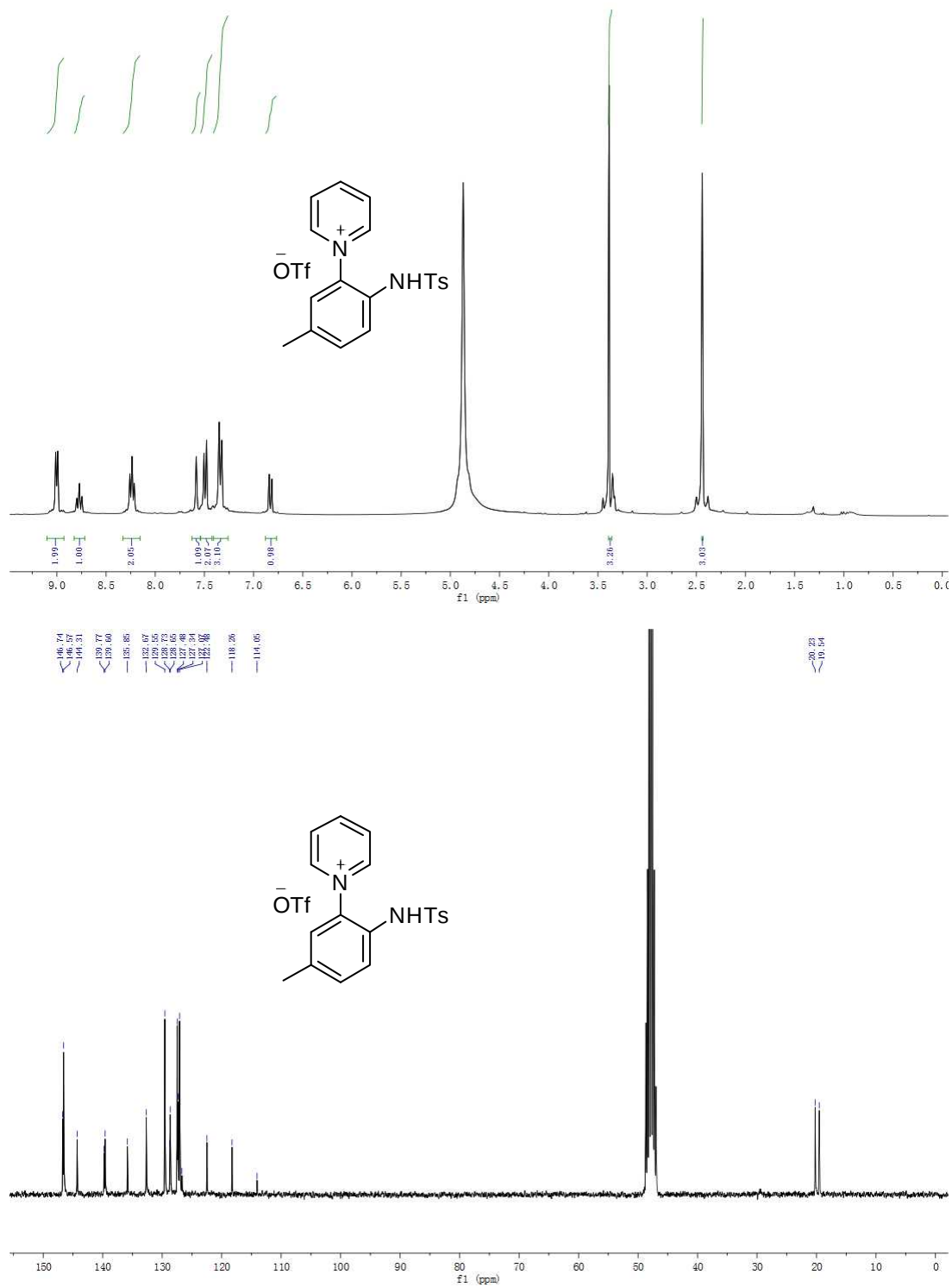
**1-(3-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4ba)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

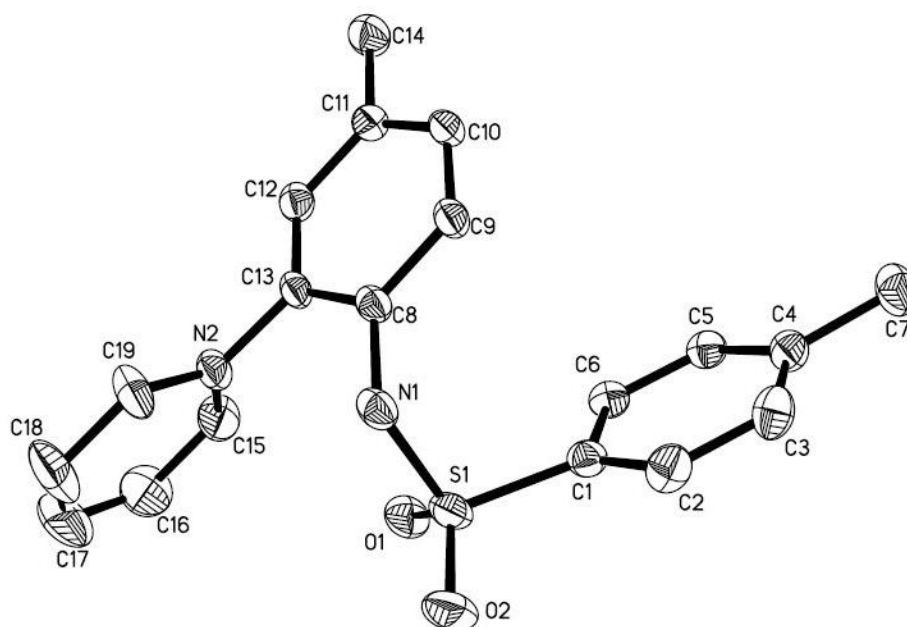
¹³C NMR (76 MHz, METHANOL-D₄) (down)

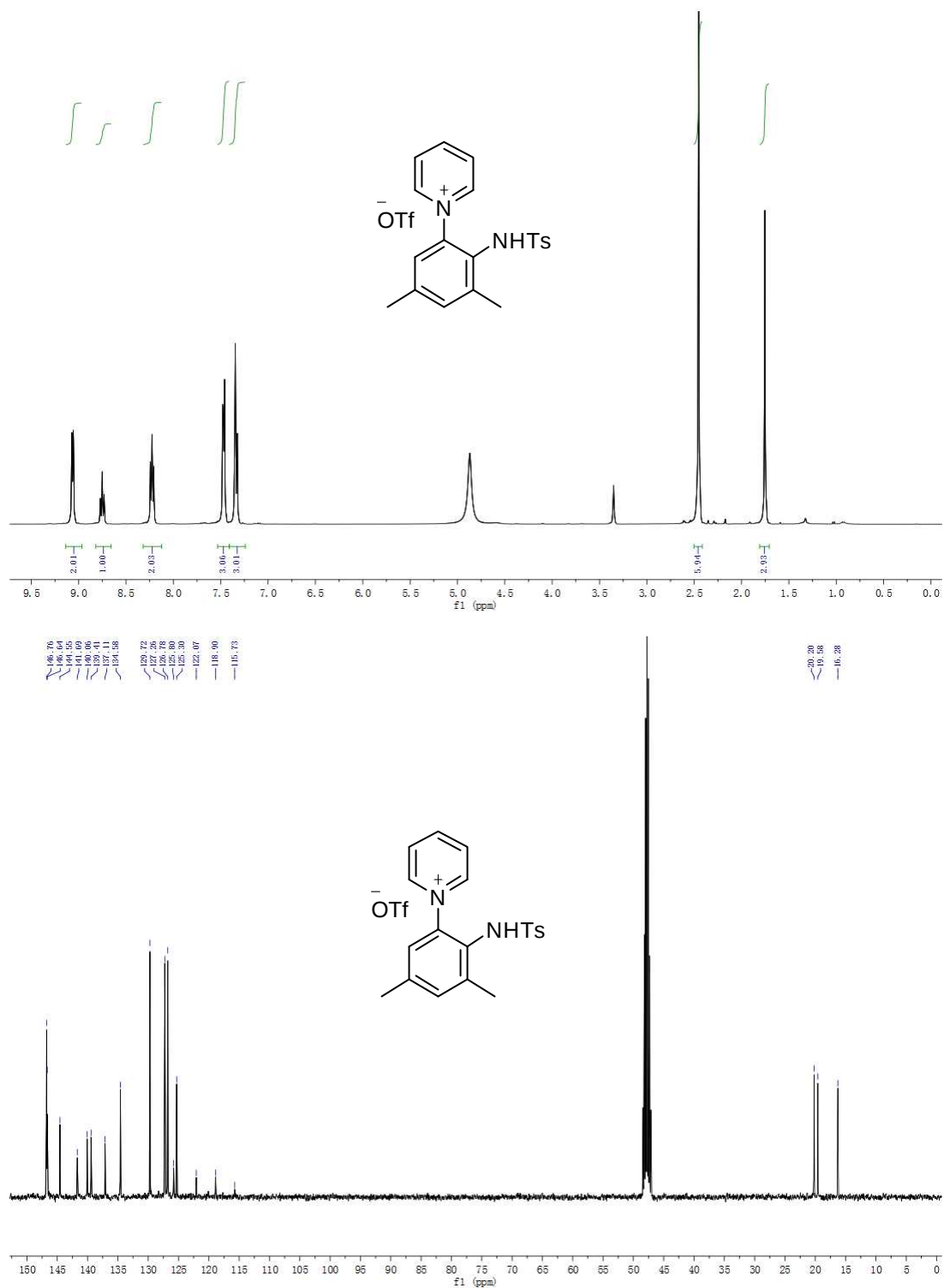
**1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4da)**



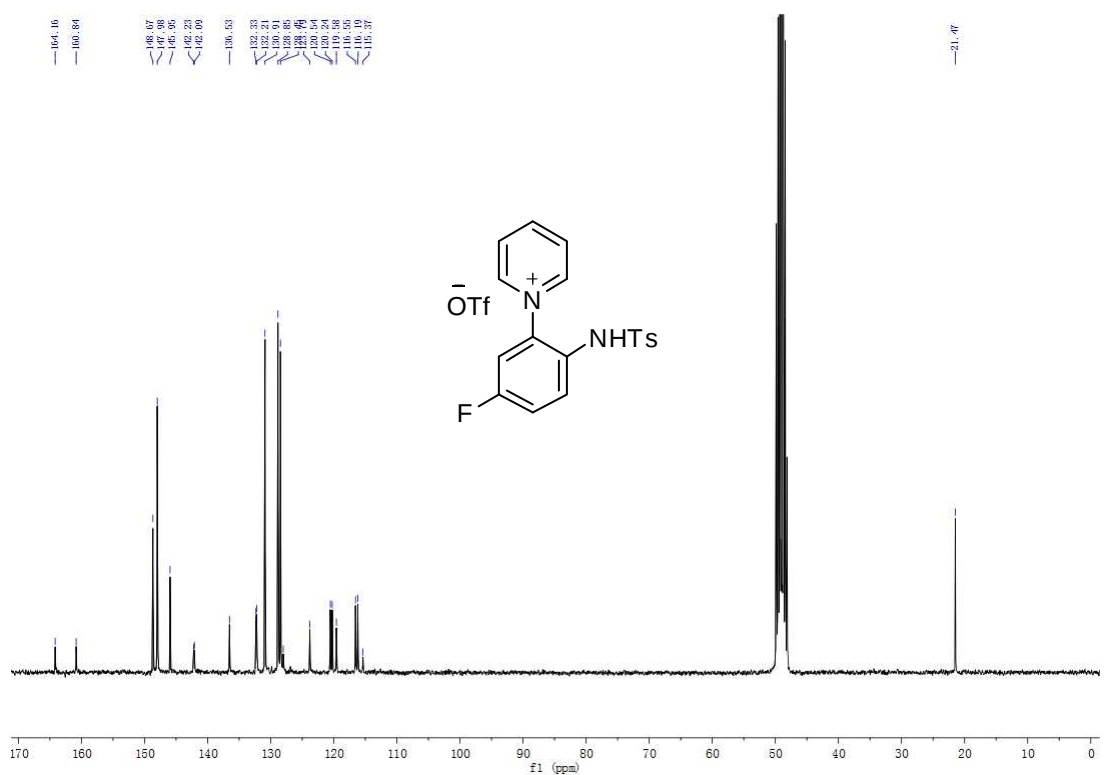
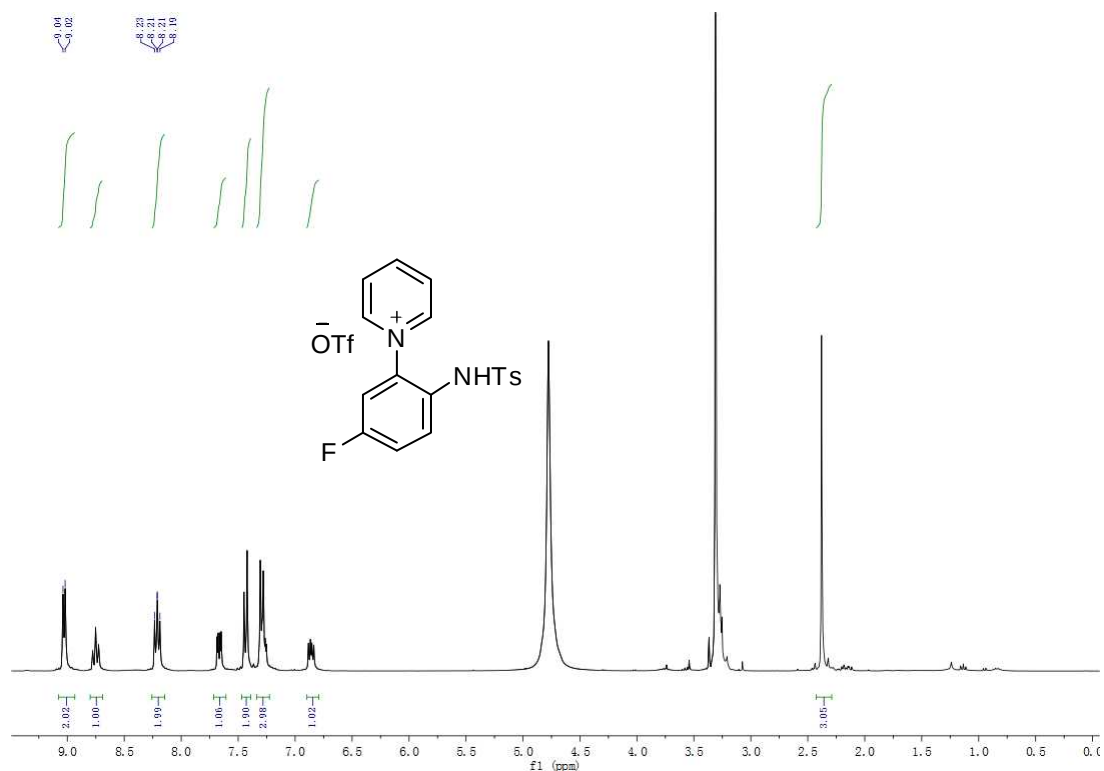
¹H NMR (301 MHz, METHANOL-D₄) (up) and
¹³C NMR (76 MHz, METHANOL-D₄) (down)

X-ray crystal structure analysis of compound 4da: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in CH₃OH. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC** 1008474. Formula: C₁₉H₁₉F₆N₂O₂PS, *M* = 484.40, colourless crystal, 0.48 x 0.43 x 0.26 mm, *a* = 15.338(3), *b* = 10.040(2), *c* = 14.189(3) Å, α = 90, β = 94.34(3), γ = 90, *V* = 2178.7(8) Å³, ρ_{calc} = 1.477 gcm⁻³, μ = 0.291 mm⁻¹, *Z* = 4, Monoclinic, space group *P2(1)c*, λ = 0.71073 Å, *T* = 173(2) K. Data completeness = 0.997, Theta (max) = 27.48, *R* (reflections) = 0.0811, *wR2* (reflections) = 0.2007 (4971).



¹H NMR (400 MHz, METHANOL-D₄) (up) and¹³C NMR (101 MHz, METHANOL-D4) (down)

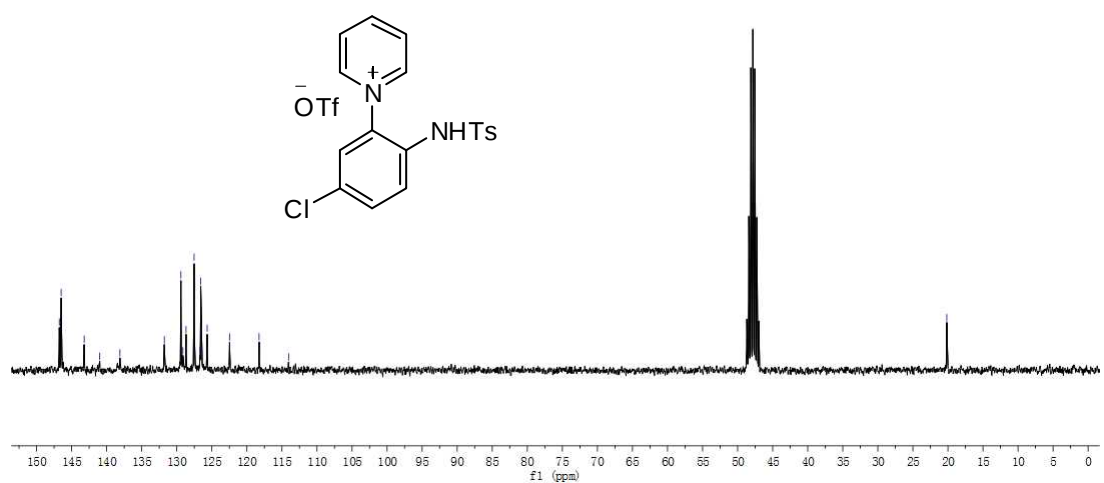
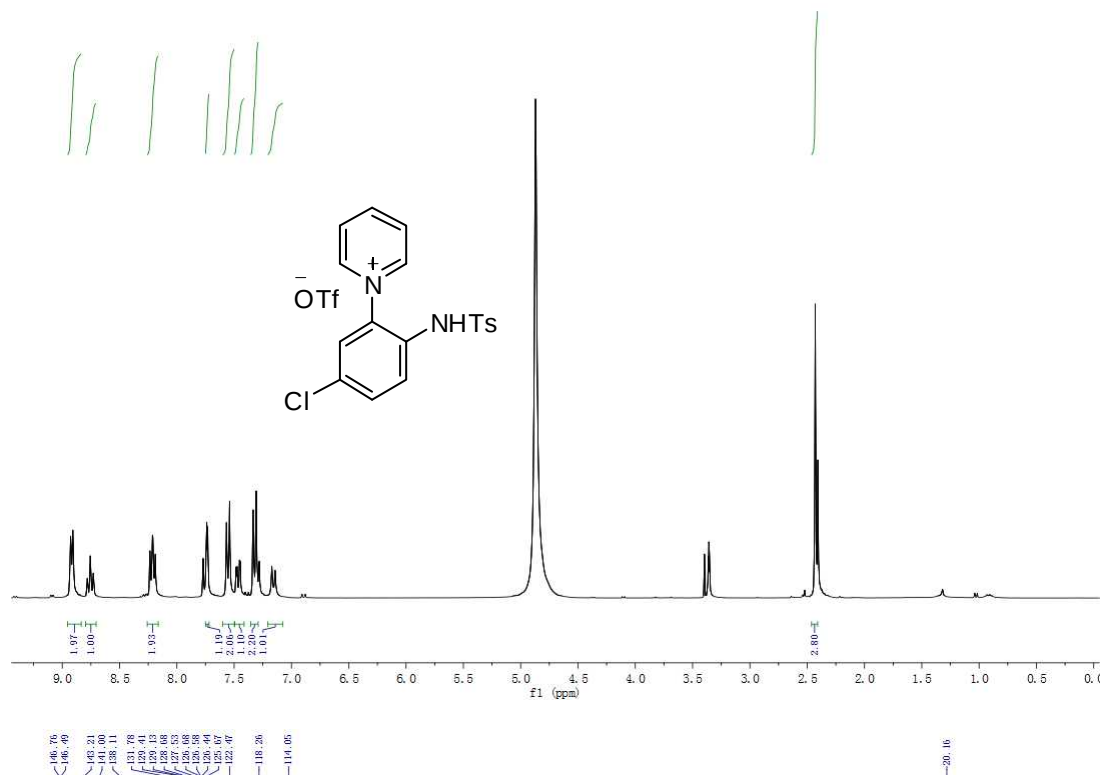
**1-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4ha)**



¹H NMR (301 MHz, METHANOL-D₄) (up) and

¹³C NMR (76 MHz, METHANOL-D₄) (down)

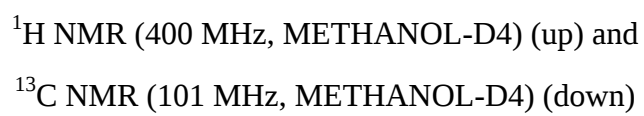
**1-(5-chloro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4ka)**



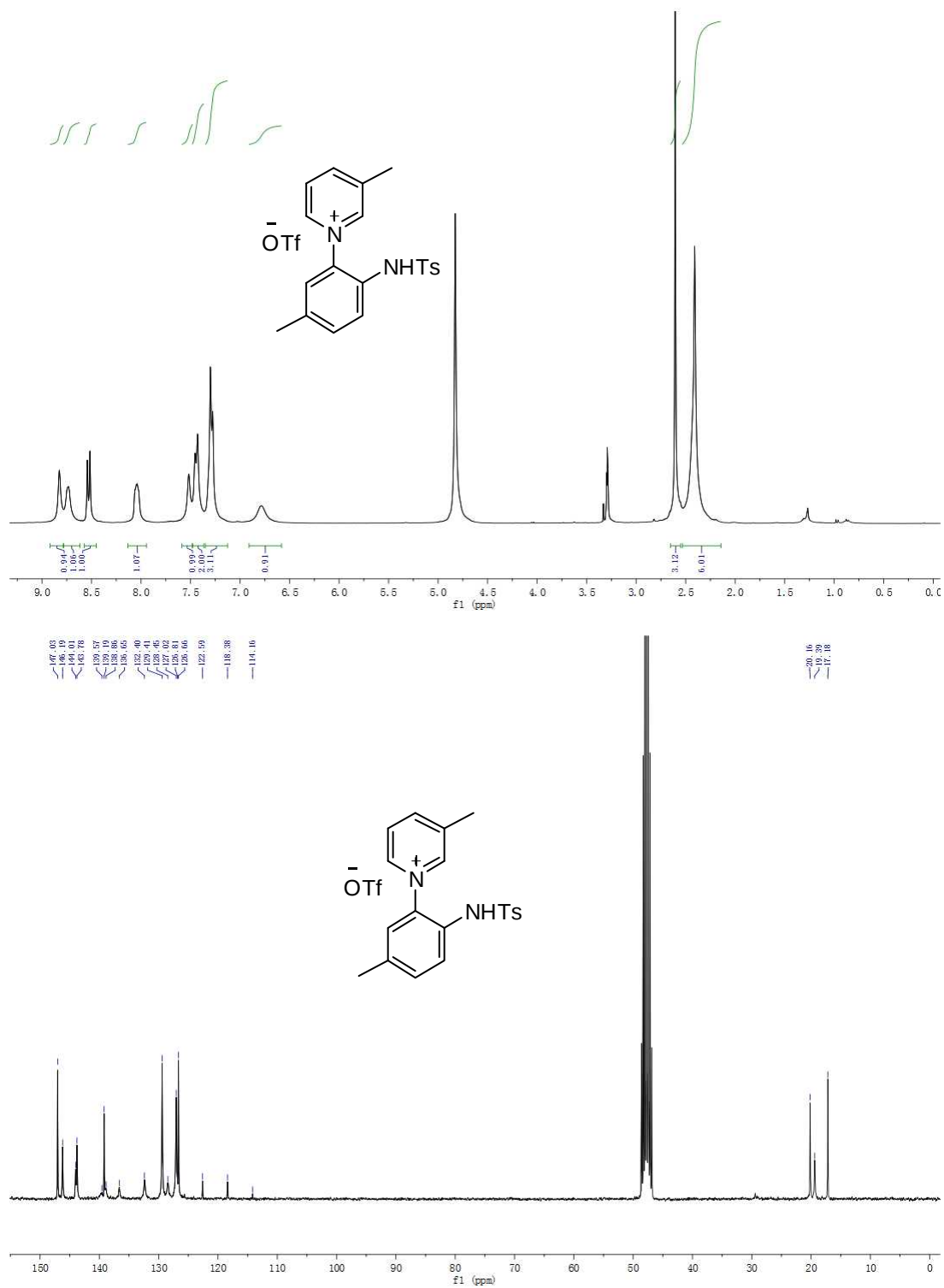
¹H NMR (301 MHz, METHANOL-D₄) (up) and

¹³C NMR (76 MHz, METHANOL-D₄) (down)

Chemical structure of NHTs (2-(4-methylphenyl)-1-methylpyridinium triflate) is shown above the spectrum.



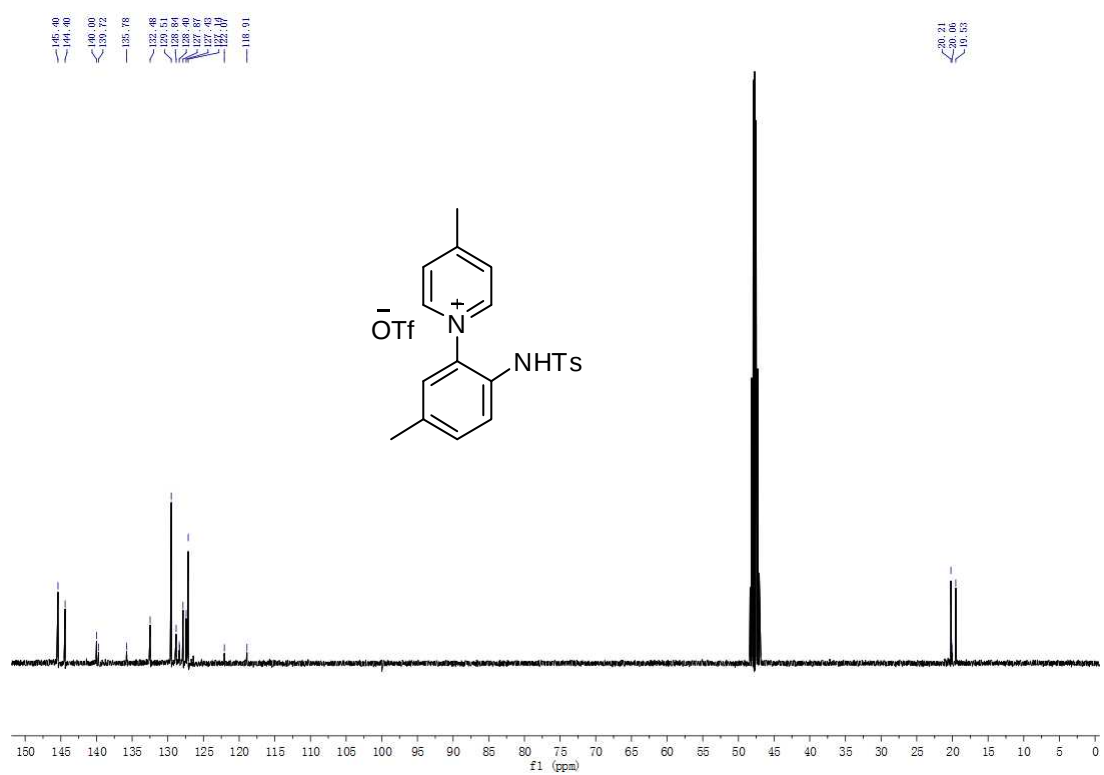
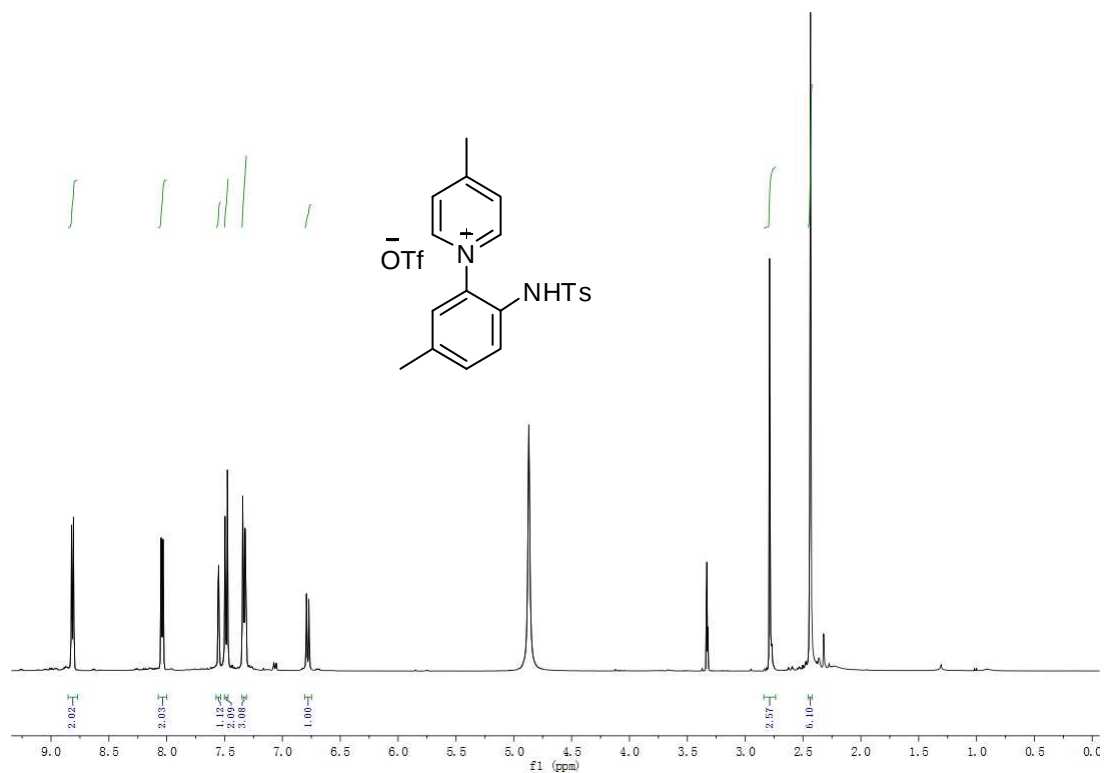
**3-methyl-1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4dc)**



¹H NMR (301 MHz, METHANOL-D4) (up) and

¹³C NMR (76 MHz, METHANOL-D4) (down)

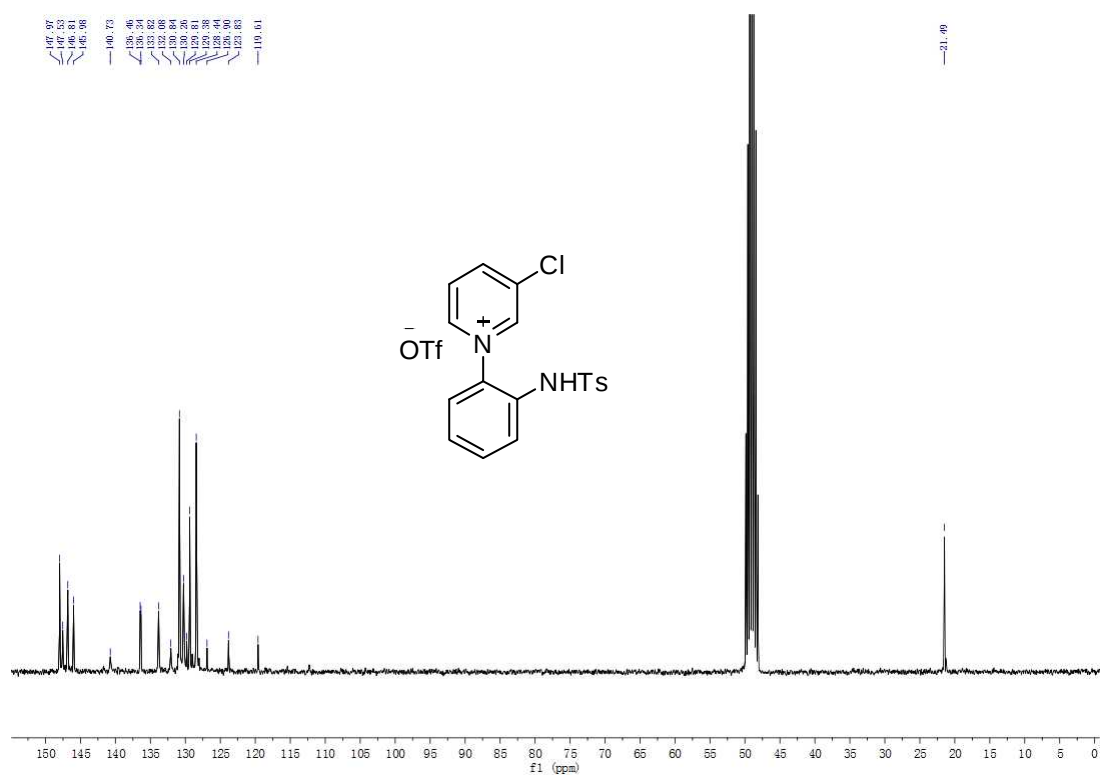
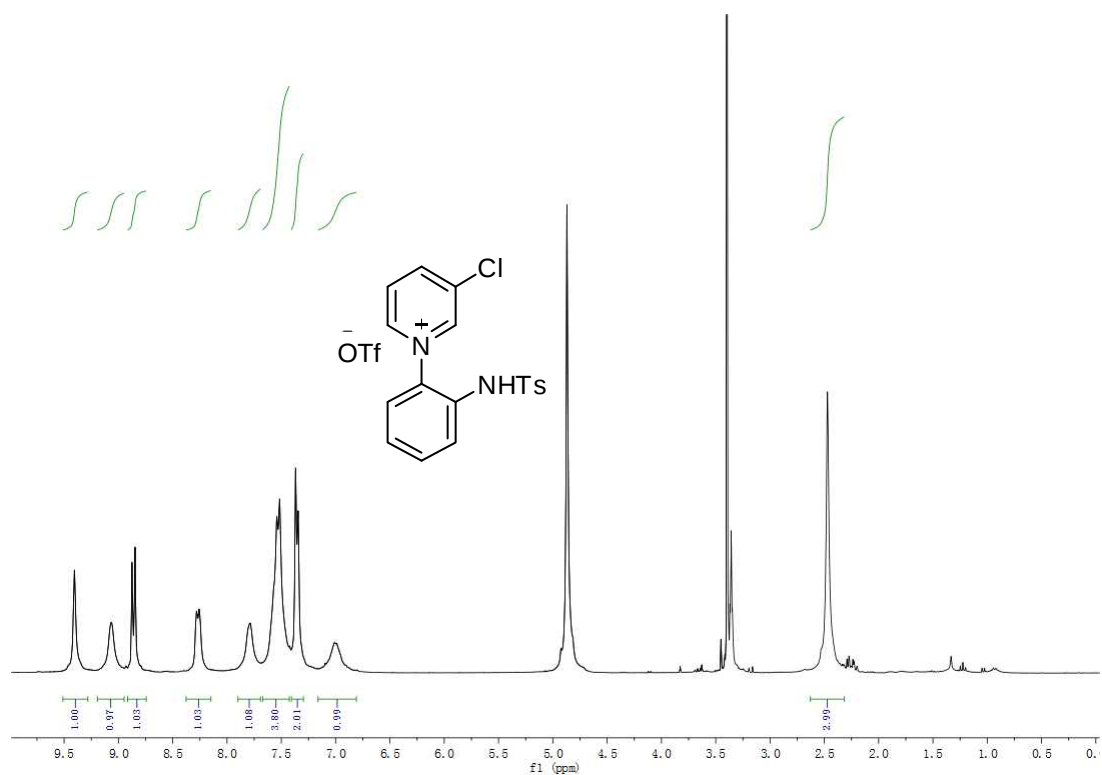
**4-methyl-1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4dd)**



^1H NMR (400 MHz, METHANOL-D₄) (up) and

^{13}C NMR (101 MHz, METHANOL-D₄) (down)

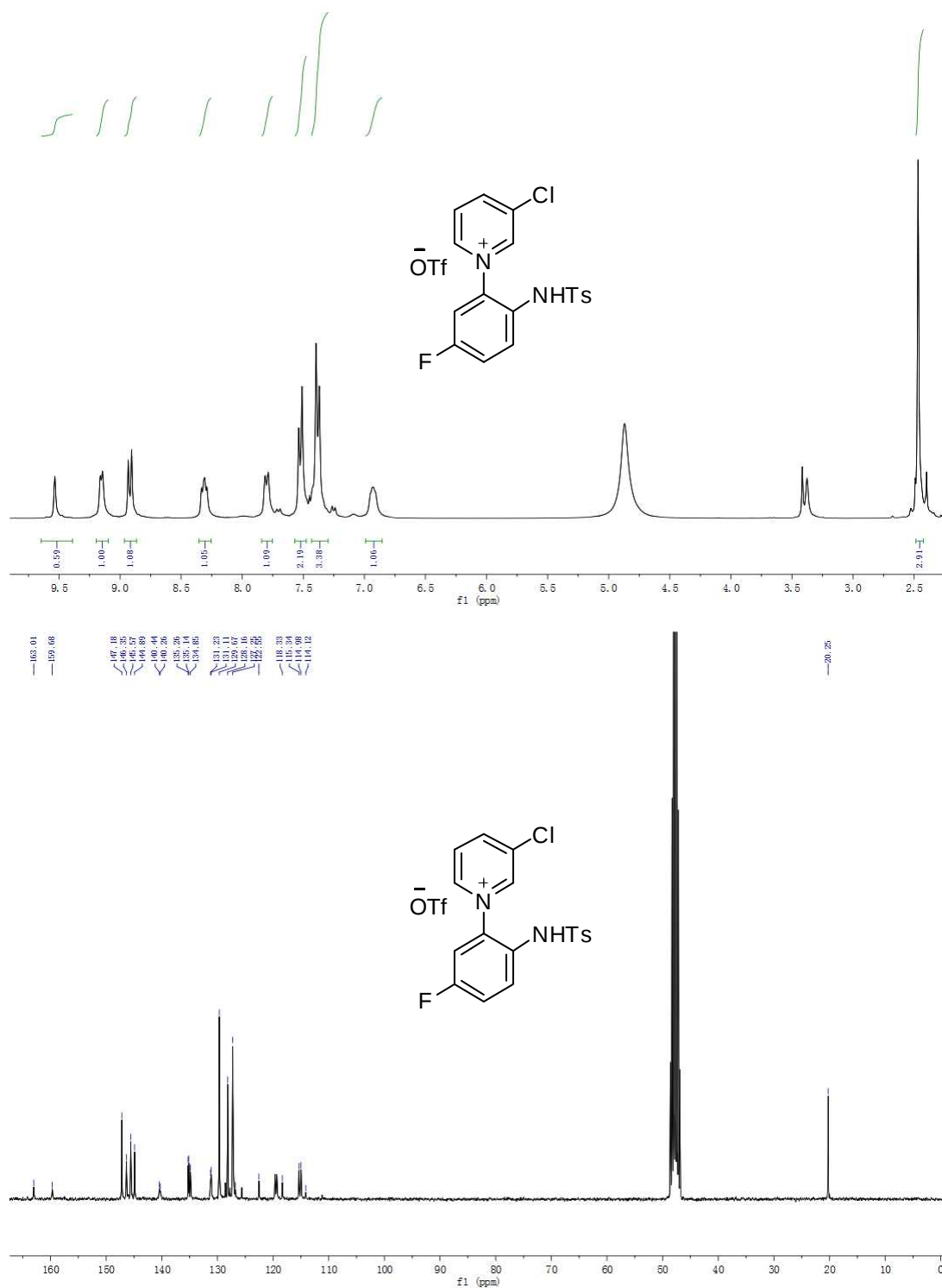
**3-chloro-1-(2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4af)**



¹H NMR (301 MHz, METHANOL-D₄) (up) and

¹³C NMR (76MHz, METHANOL-D₄) (down)

**3-chloro-1-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4hf)**

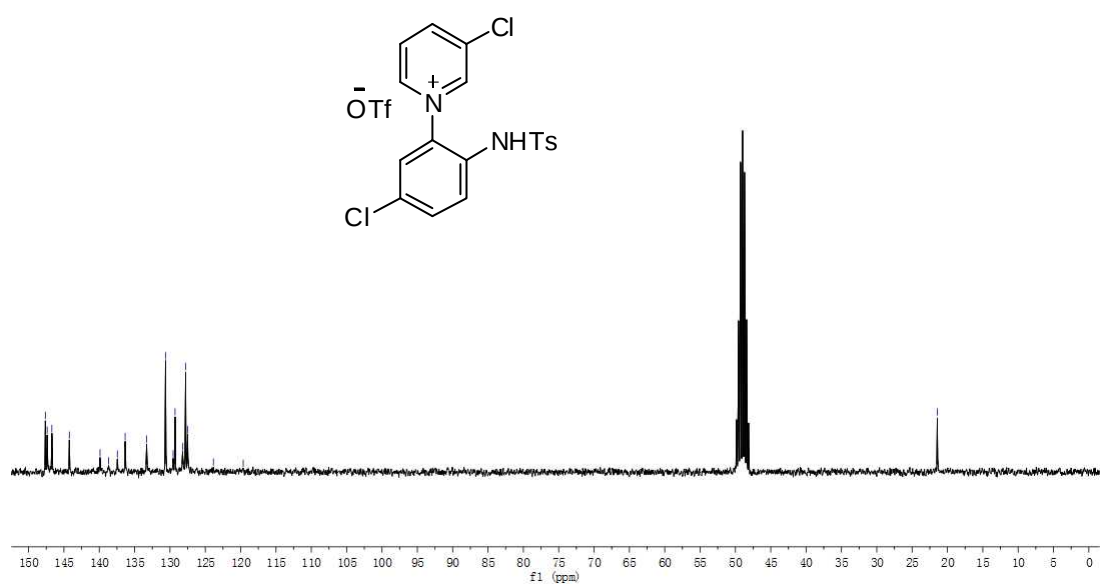


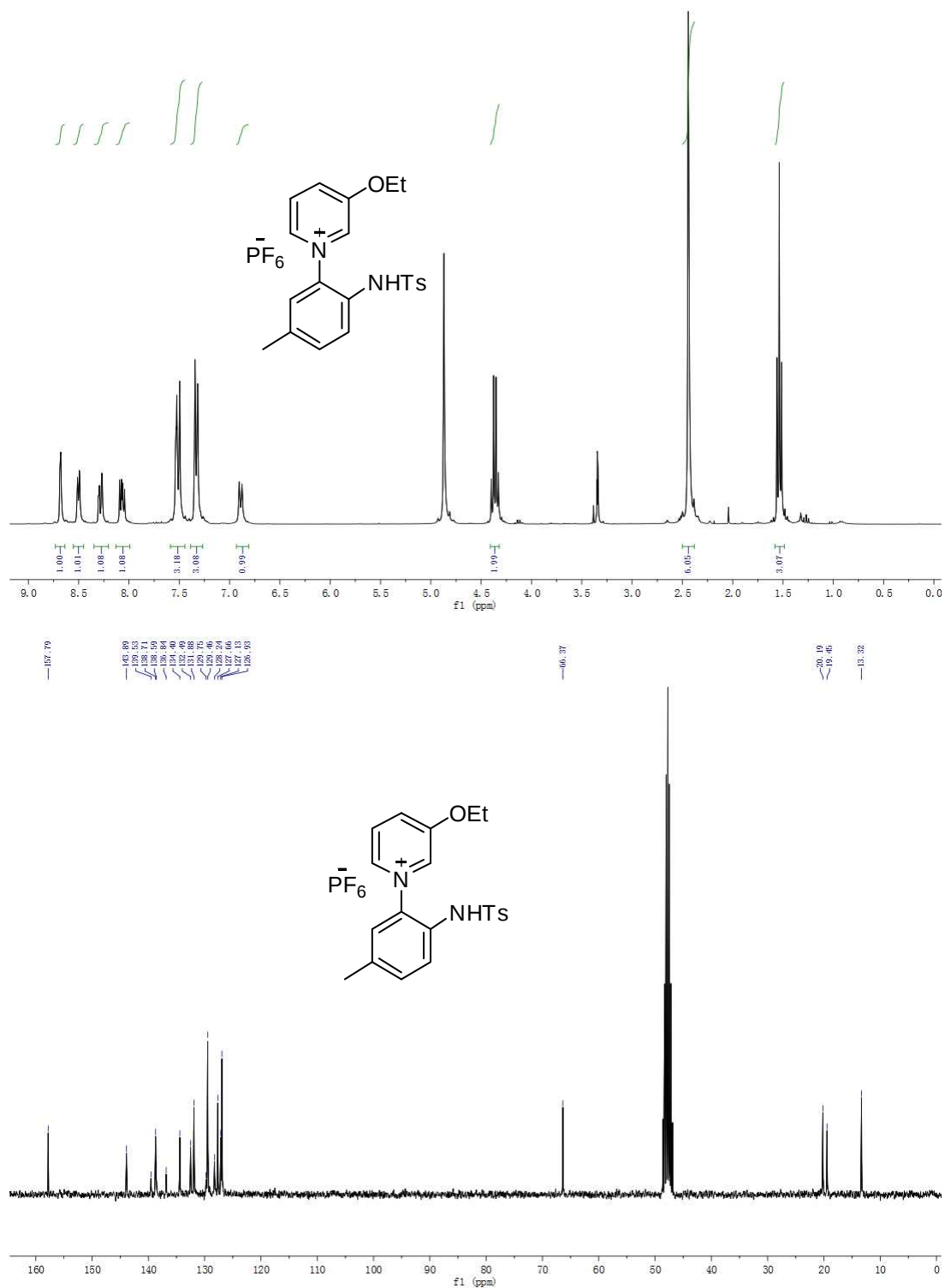
¹H NMR (301 MHz, METHANOL-D4) (up) and

¹³C NMR (76 MHz, METHANOL-D4) (down)

Chemical structure of compound 10: Clc1ccc(NC(=O)c2ccc(Cl)cc2)cc1.[O-]S(=O)(=O)c3ccc(Cl)cc3

¹H NMR spectrum (CDCl₃) of compound 10. The spectrum shows peaks from 0 to 10 ppm. Aromatic protons appear between 7.0 and 9.0 ppm, a singlet for the NHTs group at ~3.2 ppm, a singlet for the CDCl₃ solvent at ~7.26 ppm, and a large singlet for the OTf group at ~2.3 ppm. Integration values are shown below the peaks.

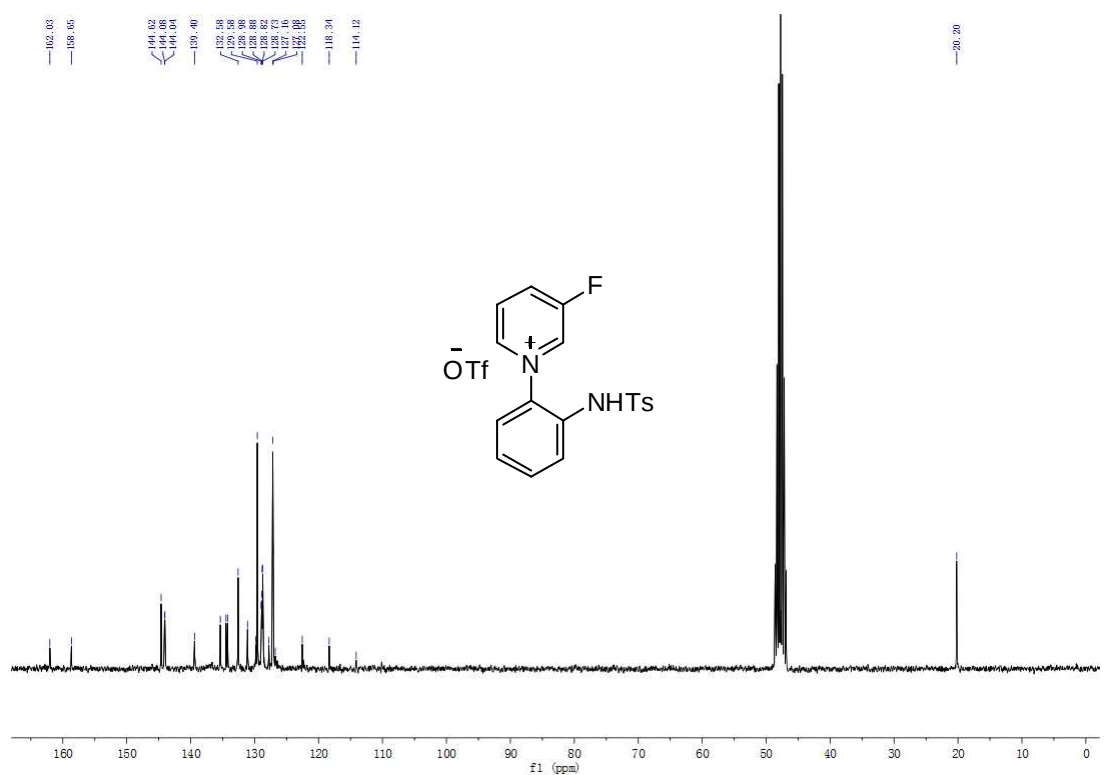
¹³C NMR (76 MHz, METHANOL-D4) (down)

¹H NMR (301 MHz, METHANOL-D₄) (up) and¹³C NMR (76 MHz, METHANOL-D4) (down)

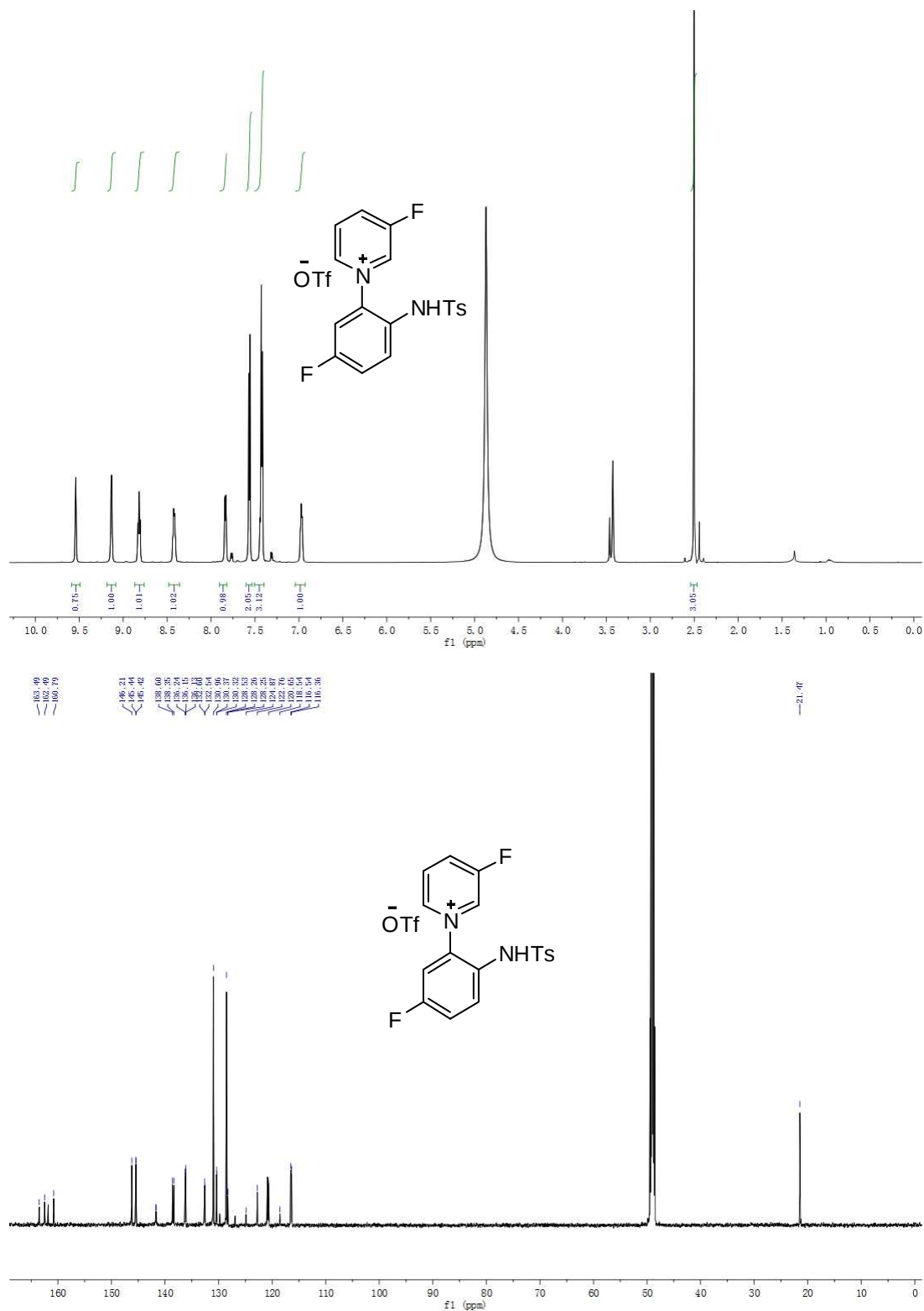
Chemical structure of the NHTs salt is shown above the spectrum:

[Na+].[O-]C(=O)c1ccc(cc1)[n+]2ccc(F)cc2

The structure consists of a pyridinium ring with a fluorine atom at the 4-position, a trifluoromethyl group (OTf) at the 1-position, and a 2-naphthyl group (NHTs) at the 2-position.

¹³C NMR (76 MHz, METHANOL-D4) (down)

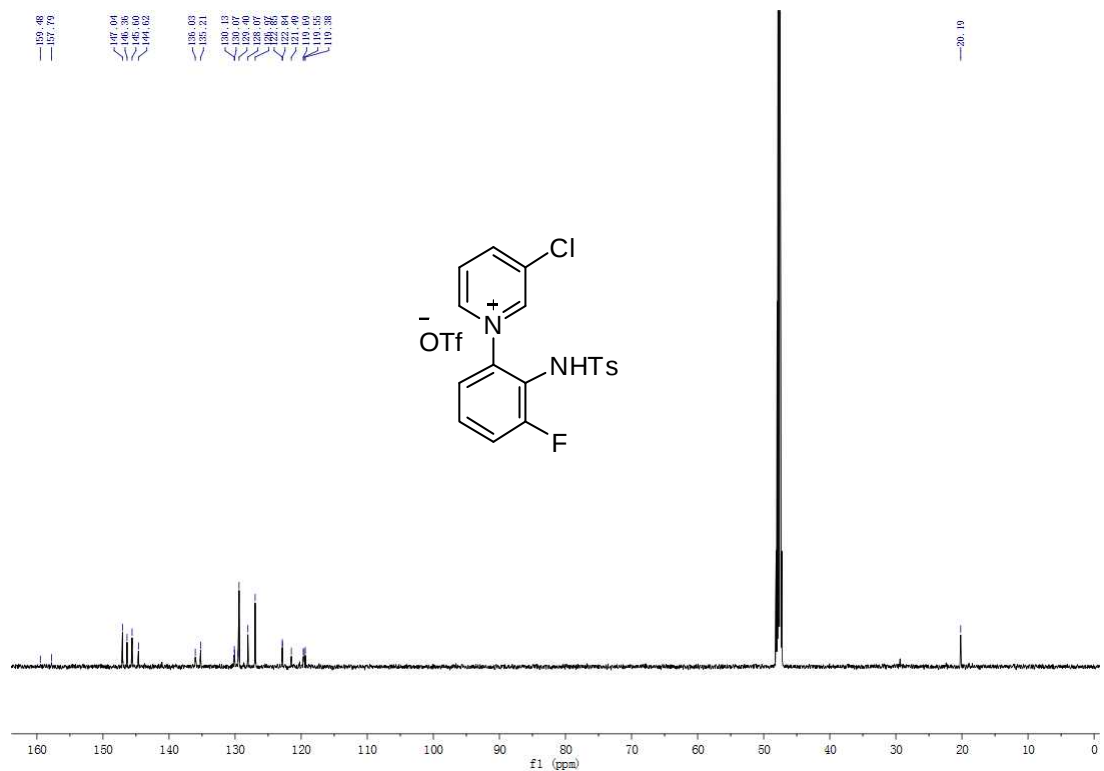
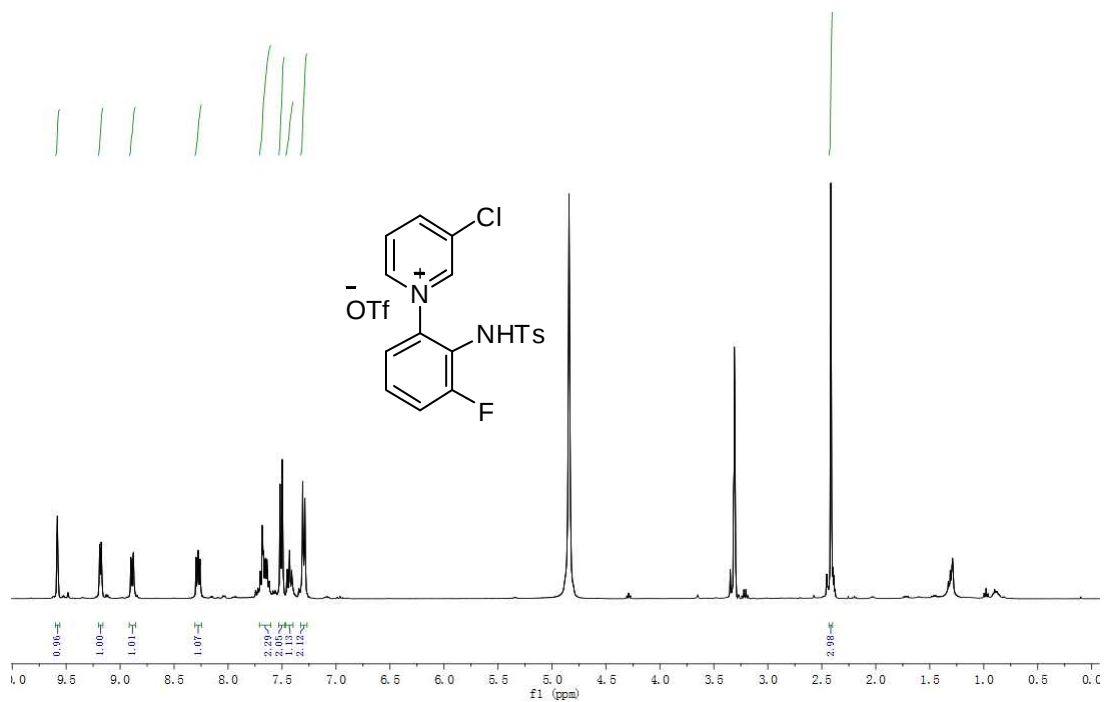
**3-fluoro-1-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4hh)**



¹H NMR (600 MHz, METHANOL-D4) (up) and

¹³C NMR (151 MHz, METHANOL-D4) (down)

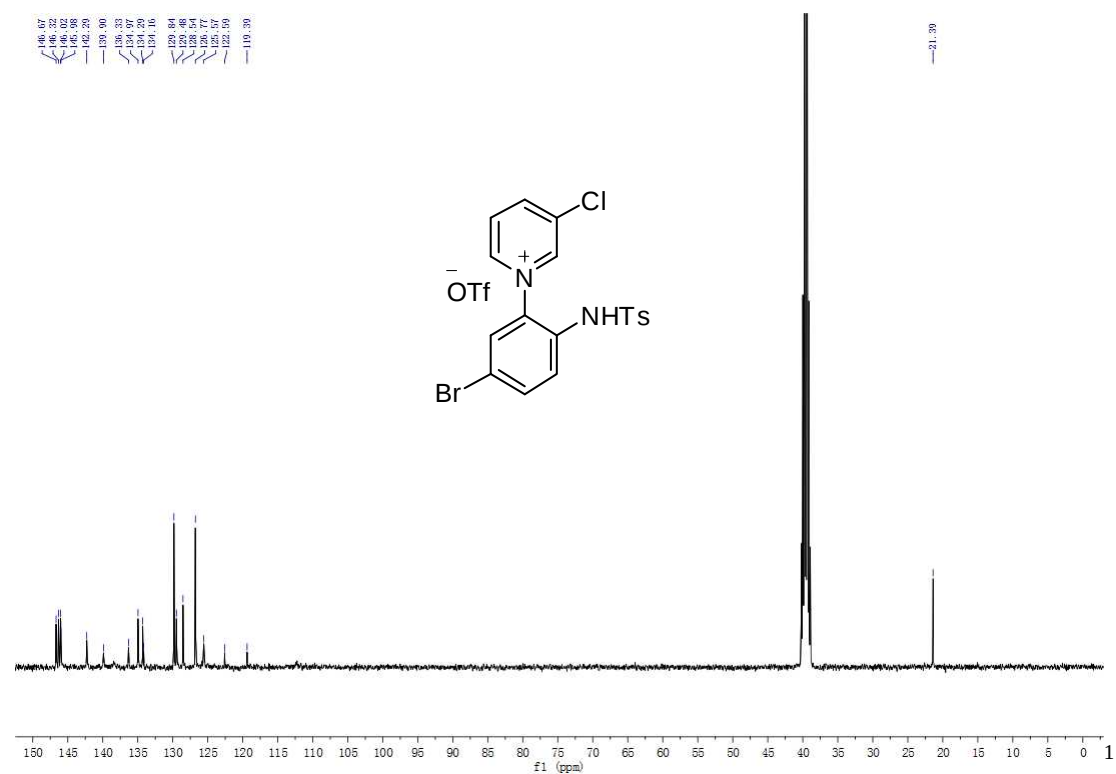
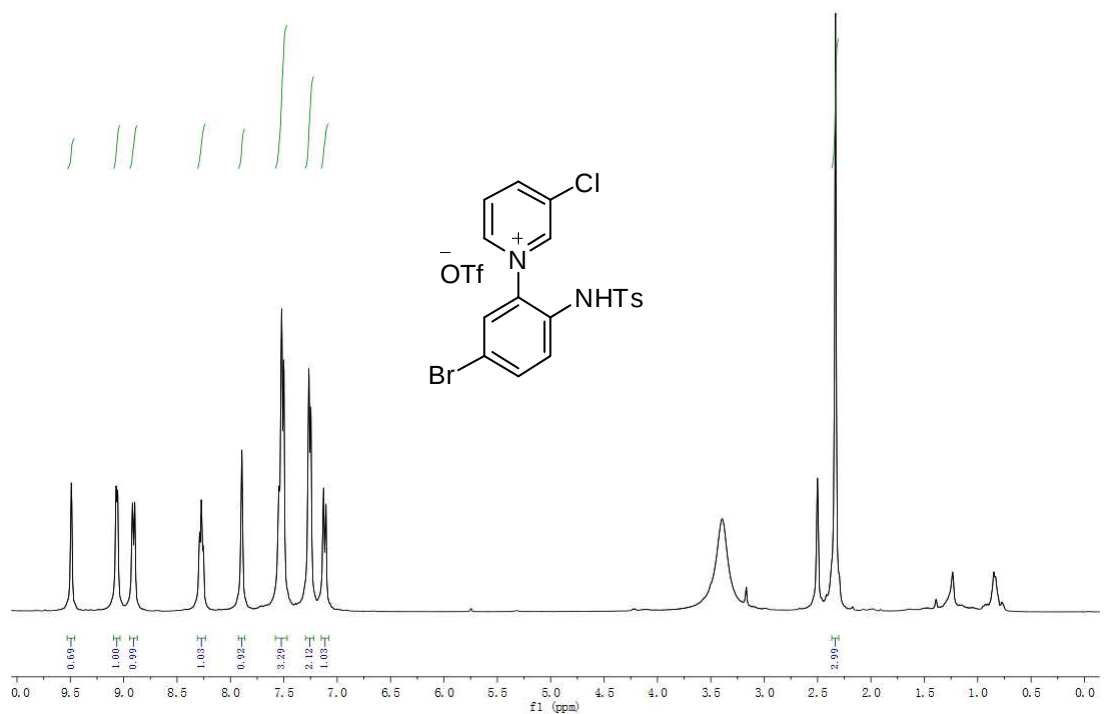
**3-chloro-1-(3-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4ff)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

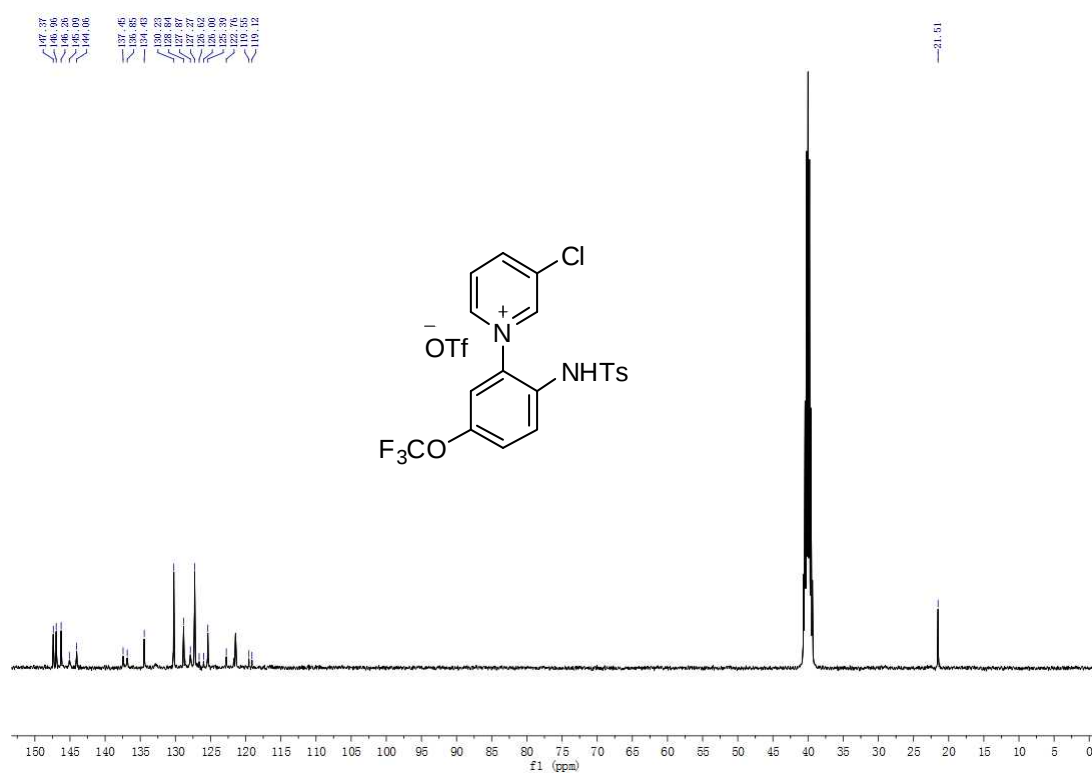
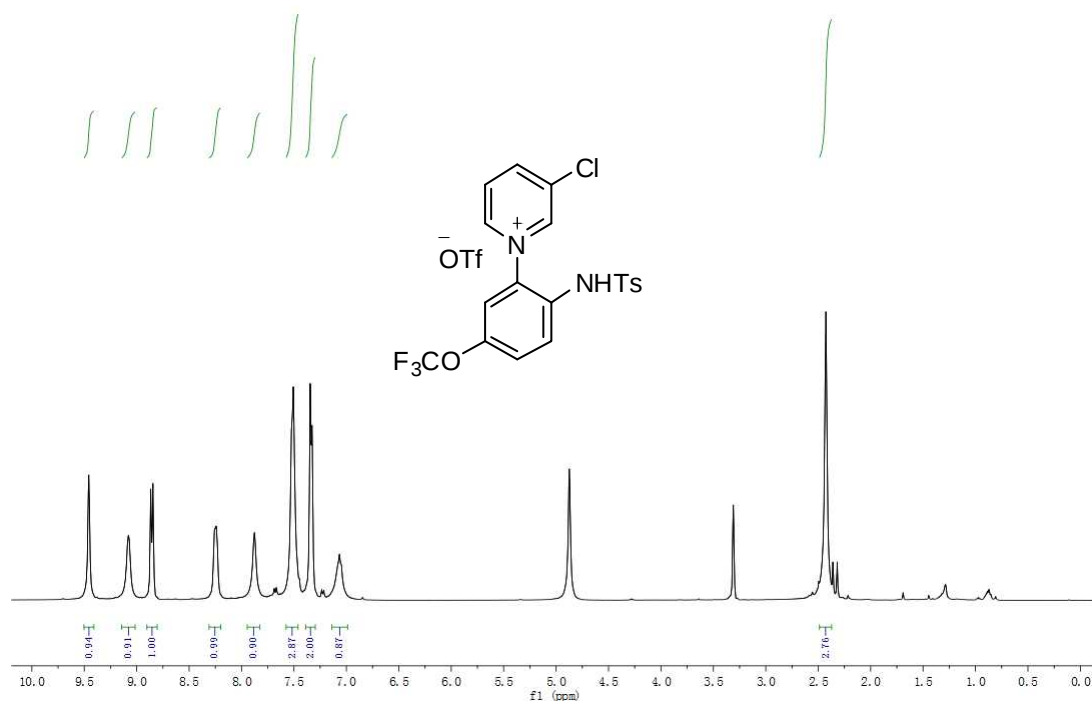
¹³C NMR (151 MHz, METHANOL-D₄) (down)

**1-(5-bromo-2-(4-methylphenylsulfonamido)phenyl)-3-chloropyridin-1-ium
trifluoromethanesulfonate (4nf)**



¹H NMR (400 MHz, DMSO-D₆) (up) and ¹³C NMR (101 MHz, DMSO-D₆) (down)

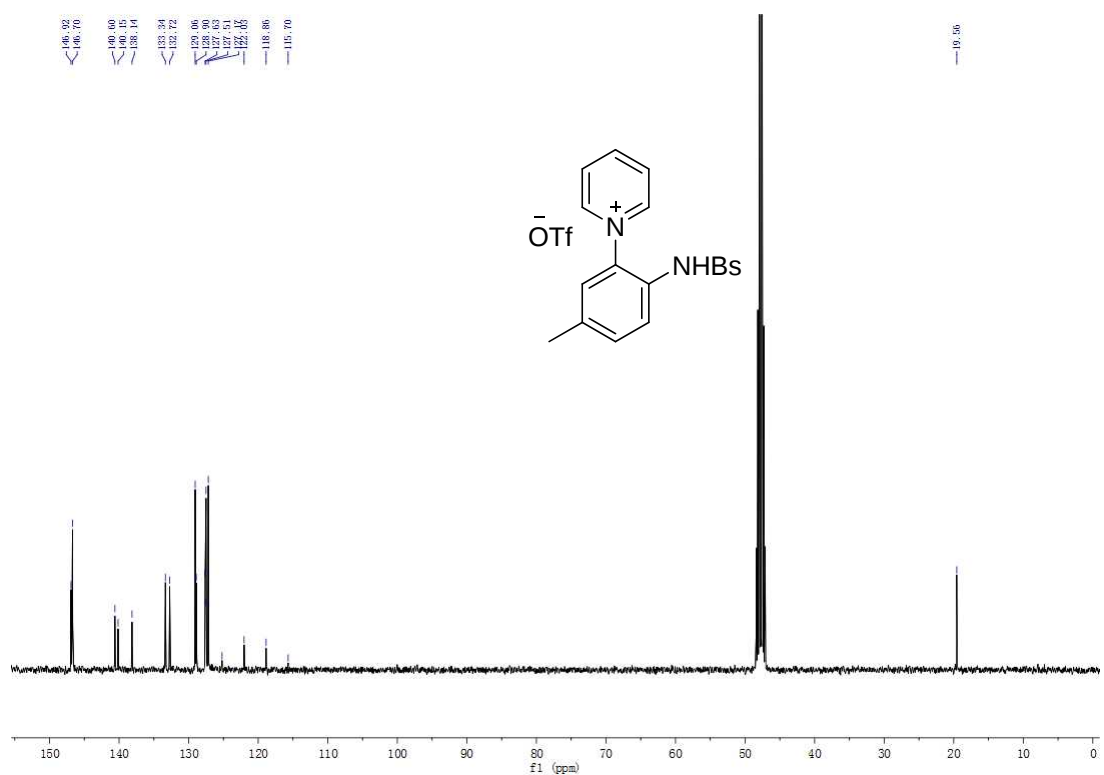
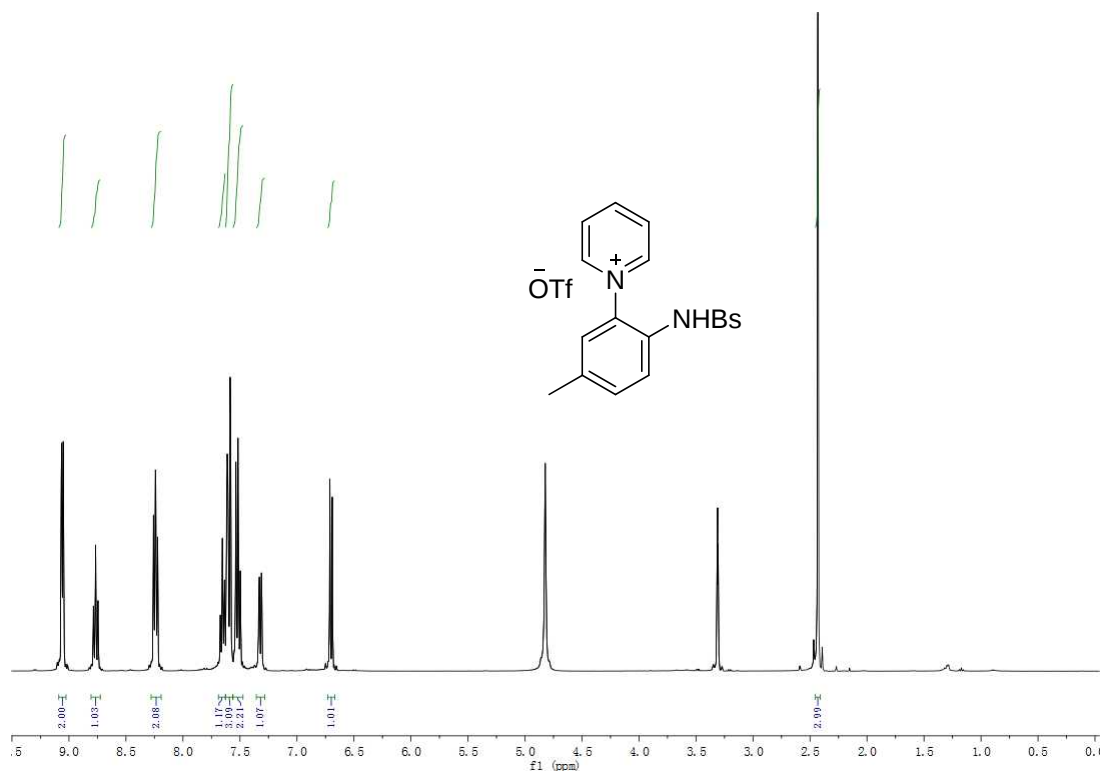
3-chloro-1-(2-(4-methylphenylsulfonamido)-5-(trifluoromethoxy)phenyl)pyridin-1-ium trifluoromethanesulfonate (4of)



¹H NMR (400 MHz, METHANOL-D₄) (up) and

¹³C NMR (101 MHz, DMSO-D₆) (down)

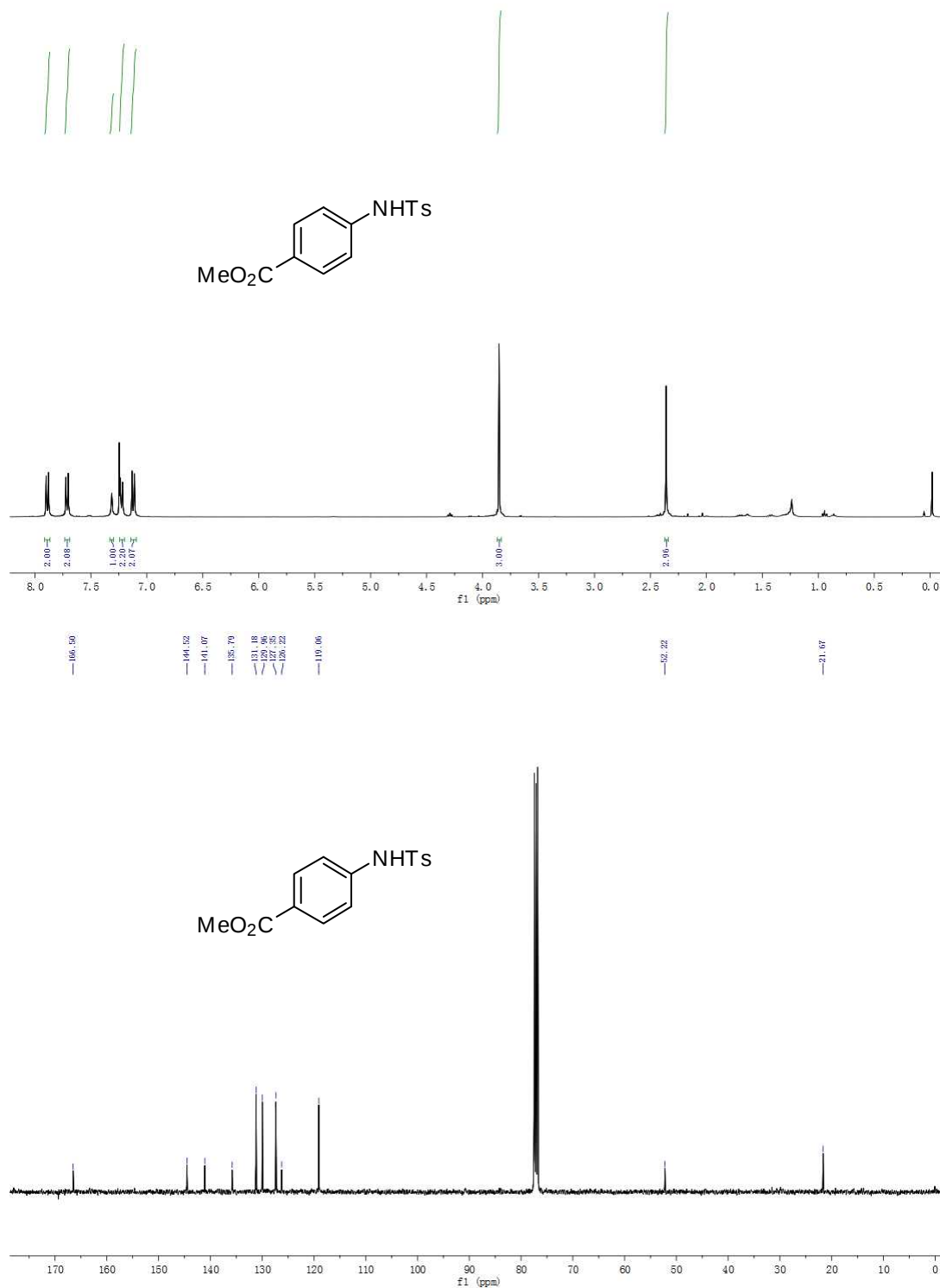
**1-(5-methyl-2-(phenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4dg)**



¹H NMR (400 MHz, METHANOL-D₄) (up) and

¹³C NMR (101 MHz, METHANOL-D₄) (down)

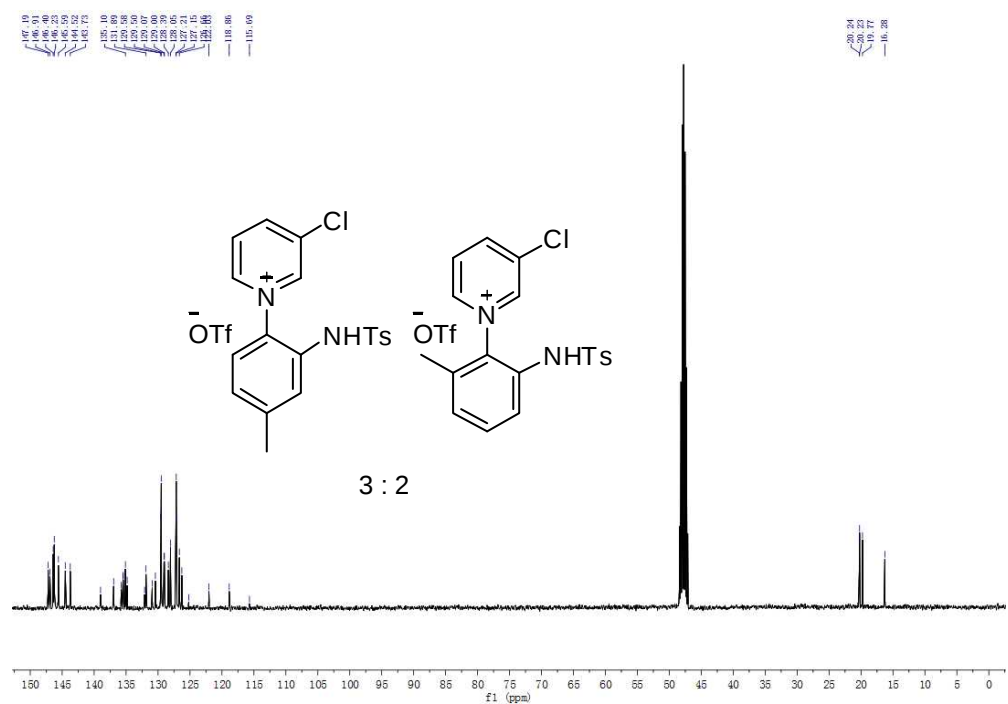
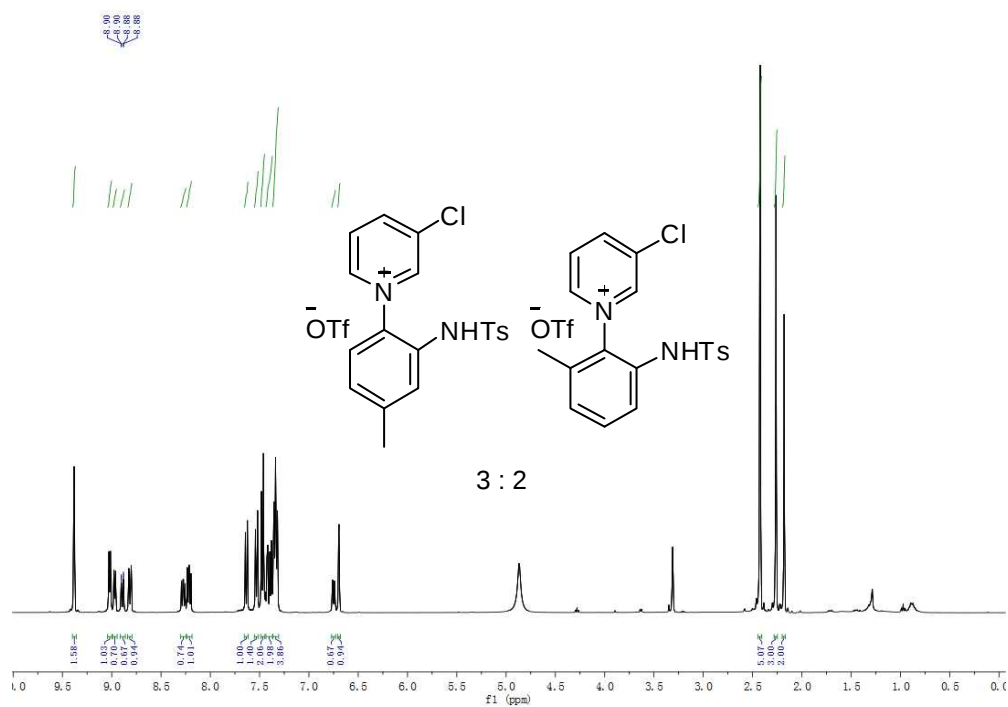
methyl 4-(4-methylphenylsulfonamido)benzoate (7)



¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

**3-chloro-1-(4-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4cf-1)**

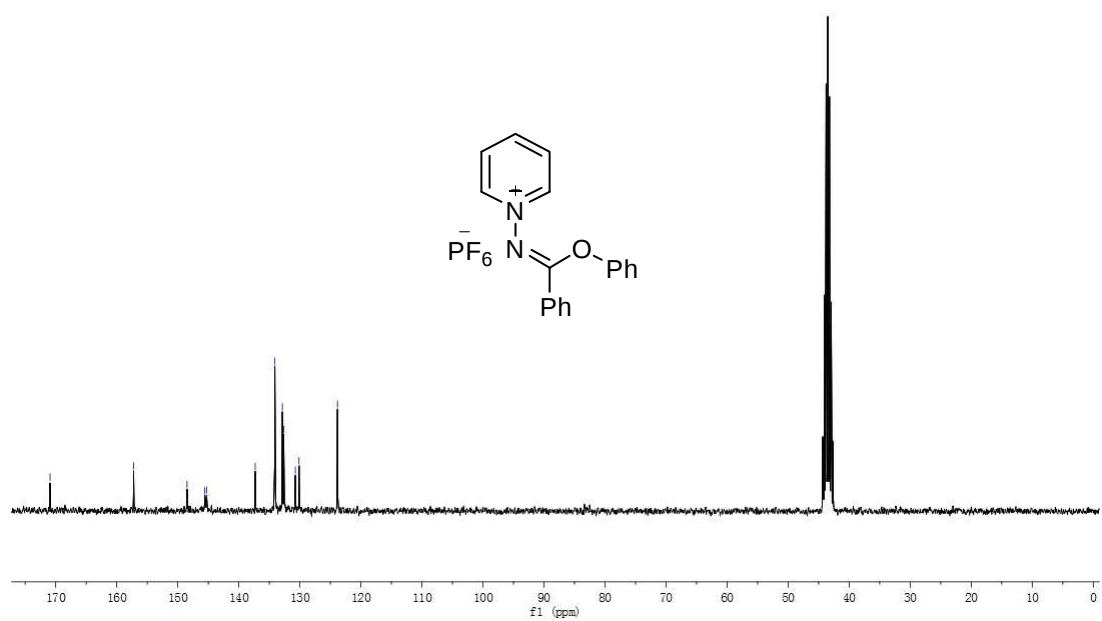
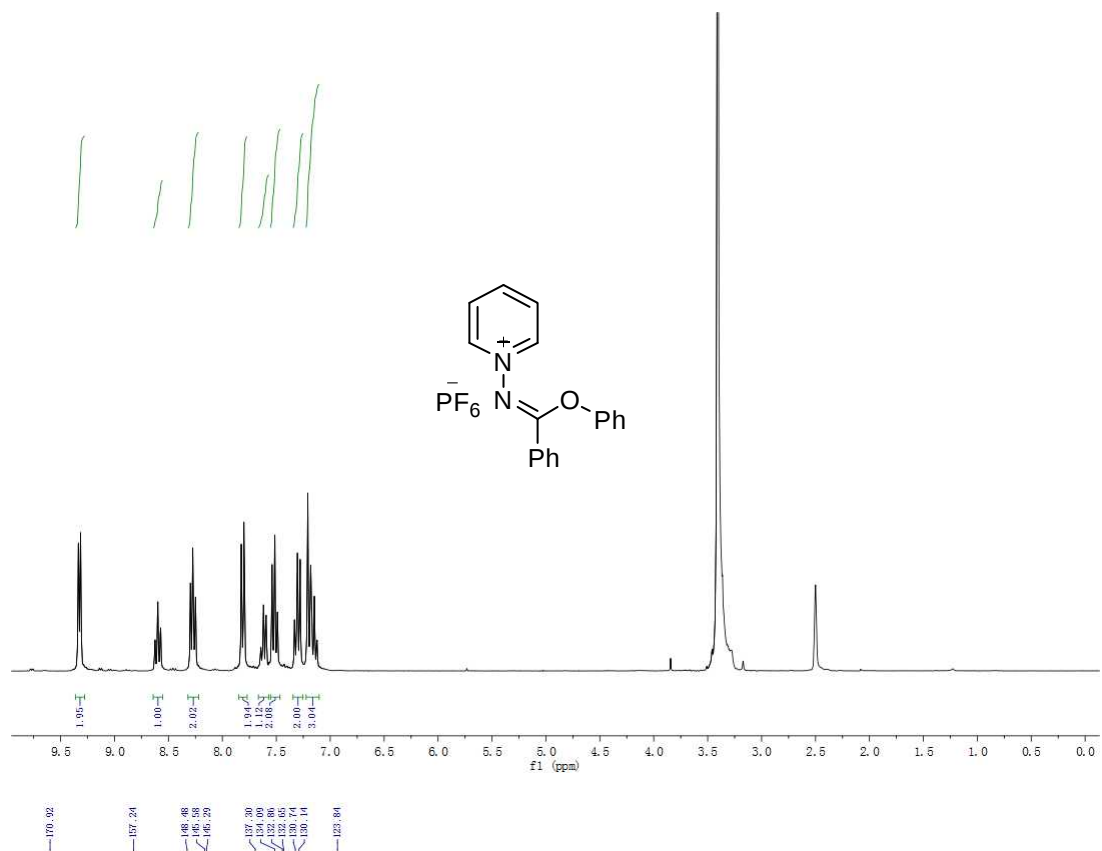
**3-chloro-1-(2-methyl-6-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium
trifluoromethanesulfonate (4cf-2)**



^1H NMR (400 MHz, METHANOL- D_4) (up) and

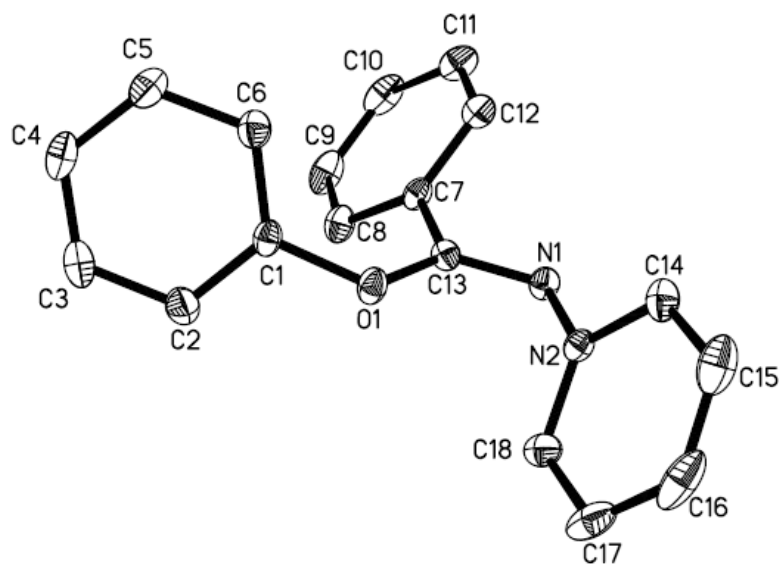
^{13}C NMR (101 MHz, METHANOL- D_4) (down)

(Z)-1-((phenoxy(phenyl)methylene)amino)pyridin-1-ium hexafluorophosphate(V)
(6a)

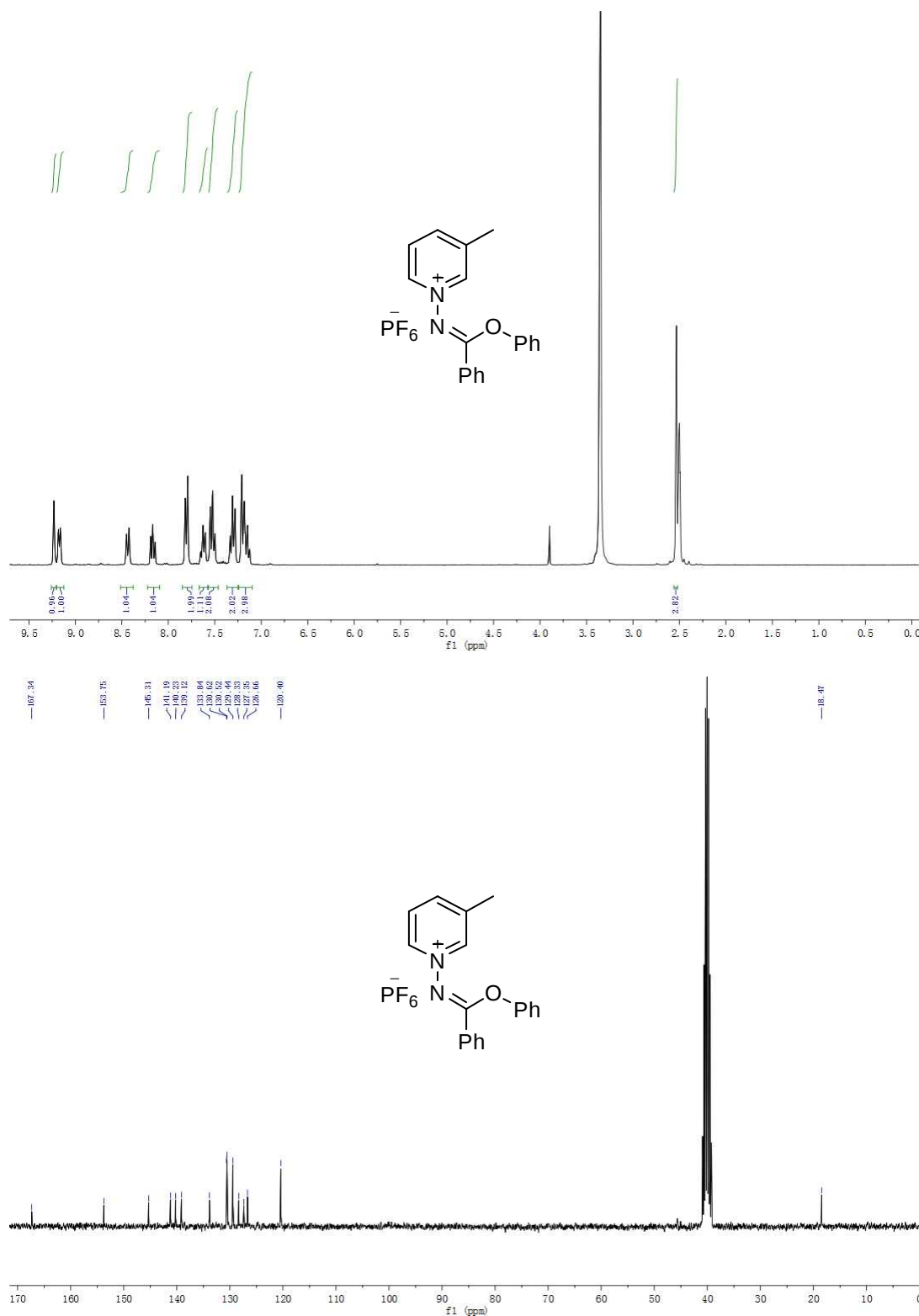


¹H NMR (301 MHz, DMSO-D₆) (up) and ¹³C NMR (76 MHz, DMSO-D₆) (down)

X-ray crystal structure analysis of compound 6a: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in CH₃OH. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC** 1008473. Formula: C₁₈H₁₅F₆N₂OP, *M* = 420.29, colourless crystal, 0.28 x 0.25 x 0.19 mm, *a* = 13.927(3), *b* = 10.771(2), *c* = 24.361(5) Å, α = 90, β = 93.49(3), γ = 90, *V* = 3647.6(13) Å³, ρ_{calc} = 1.531 gcm⁻³, μ = 0.221 mm⁻¹, *Z* = 8, Monoclinic, space group *C2/c*, λ = 0.71073 Å, *T* = 173(2) K. Data completeness = 0.997, Theta (max) = 27.47, *R* (reflections) = 0.0567, *wR2* (reflections) = 0.1107 (4173).



**(Z)-3-methyl-1-((phenoxy(phenyl)methylene)amino)pyridin-1-ium
hexafluorophosphate(V) (6b)**



¹H NMR (301 MHz, DMSO-D6) (up) and ¹³C NMR (76 MHz, DMSO-D6) (down)