Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

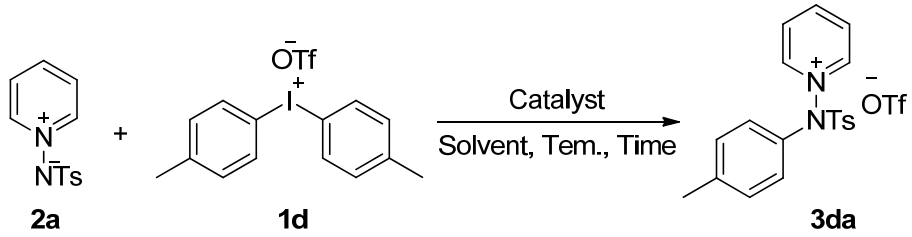
Supporting Information

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

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

Contents

Condition Optimization of Product 3[a]

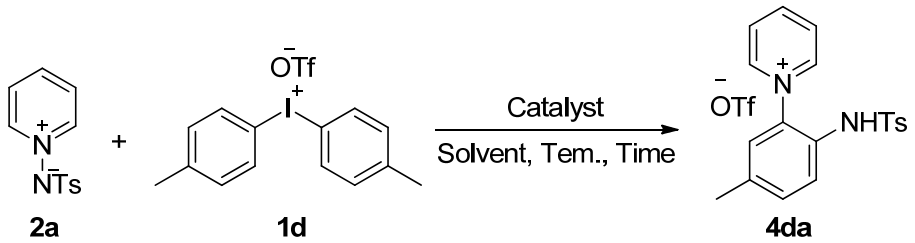


2a **1d** **3da**

entry	Catalyst (%)	Solvent	Temp. (^{o}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]



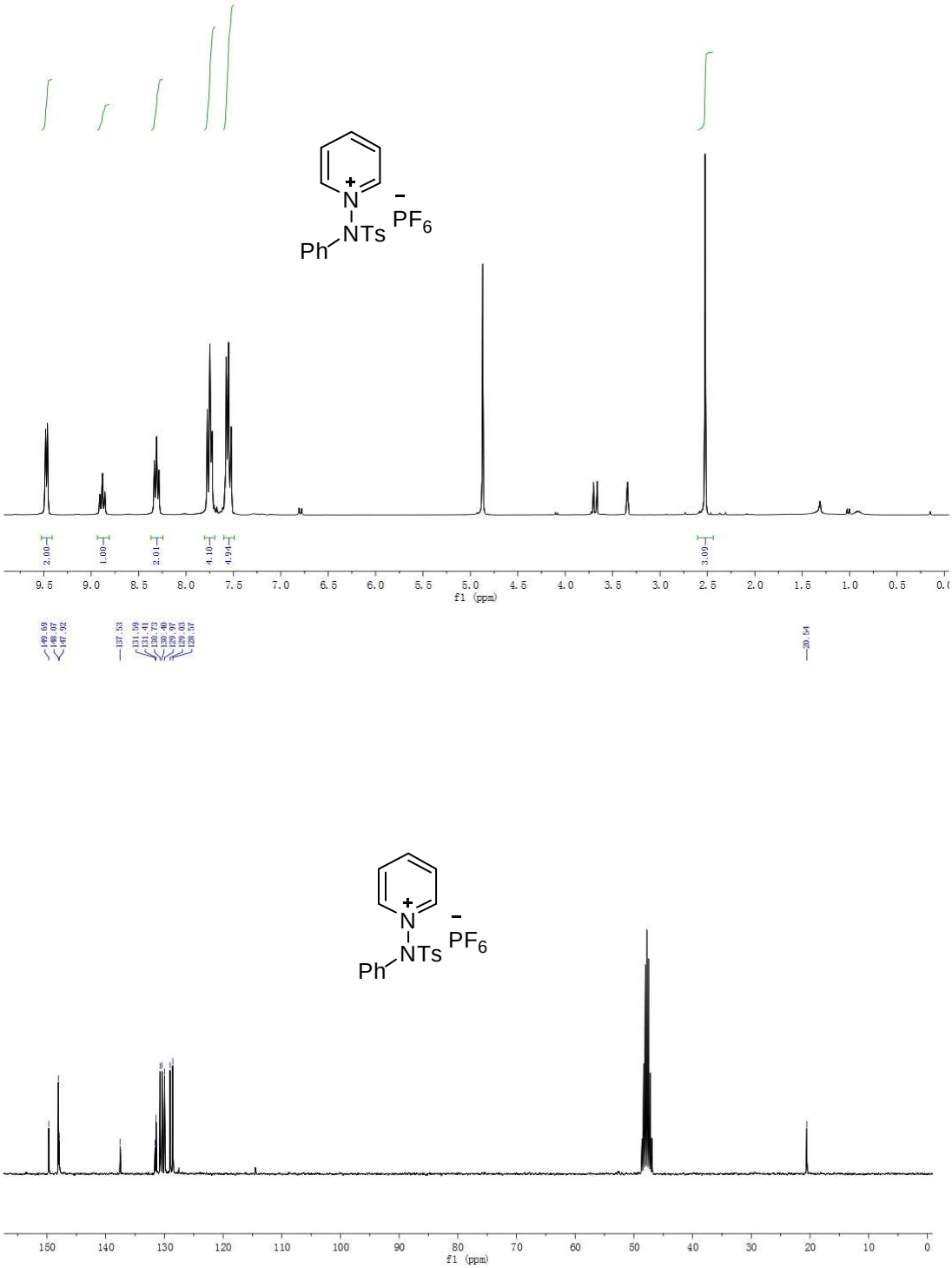
2a **1d** **4da**

entry	Catalyst (%)	Solvent	Temp. (^{o}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_2CO_3)	130	48	Messy
18	$Cu(OTf)_2$ (10)	DCE (1 eq. EtN^iPr_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.

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

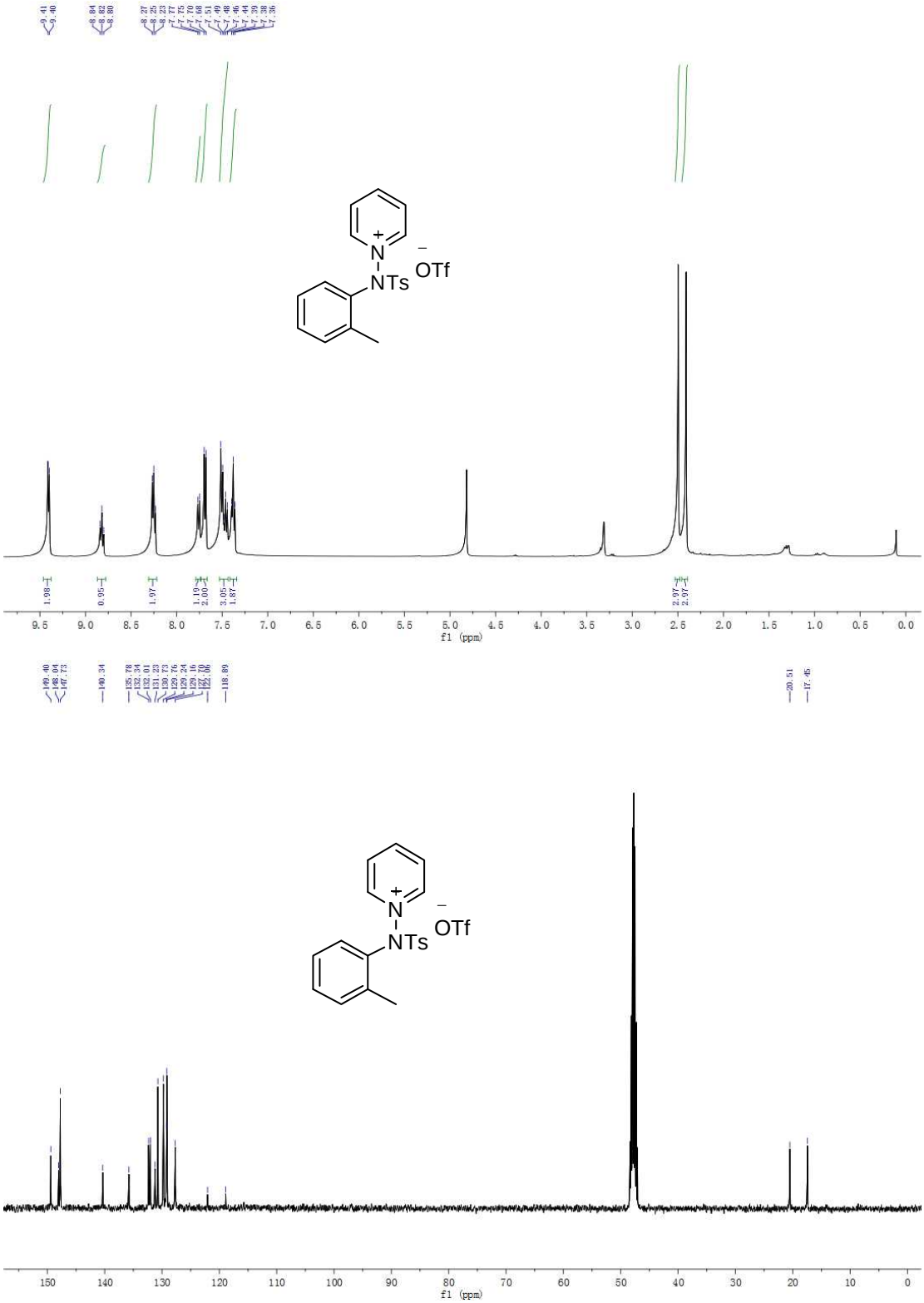
1-(4-methyl-N-phenylphenylsulfonamido)pyridin-1-ium hexafluorophosphate(V) (3aa)



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

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

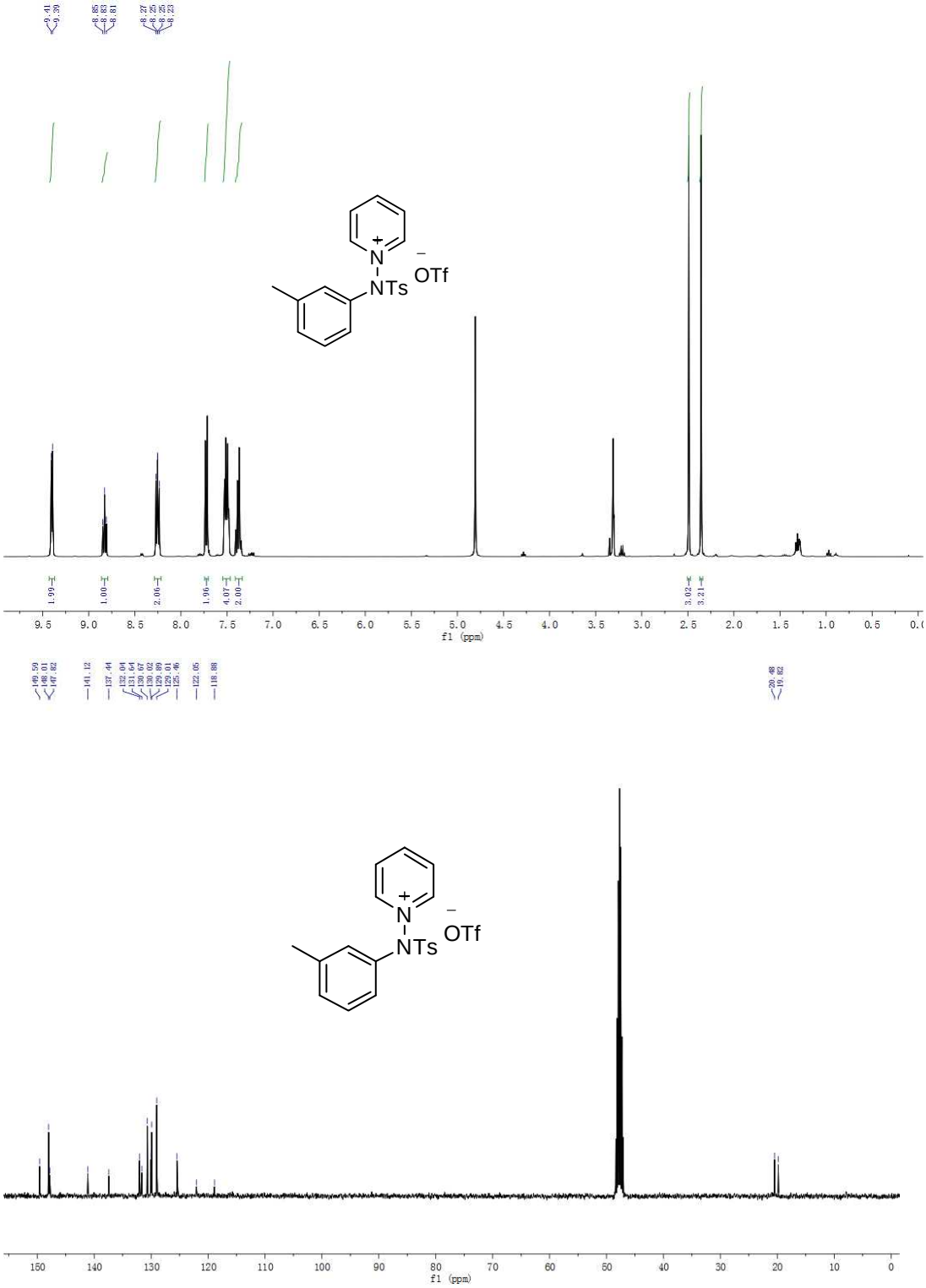
1-(4-methyl-N-(o-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ba)



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

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

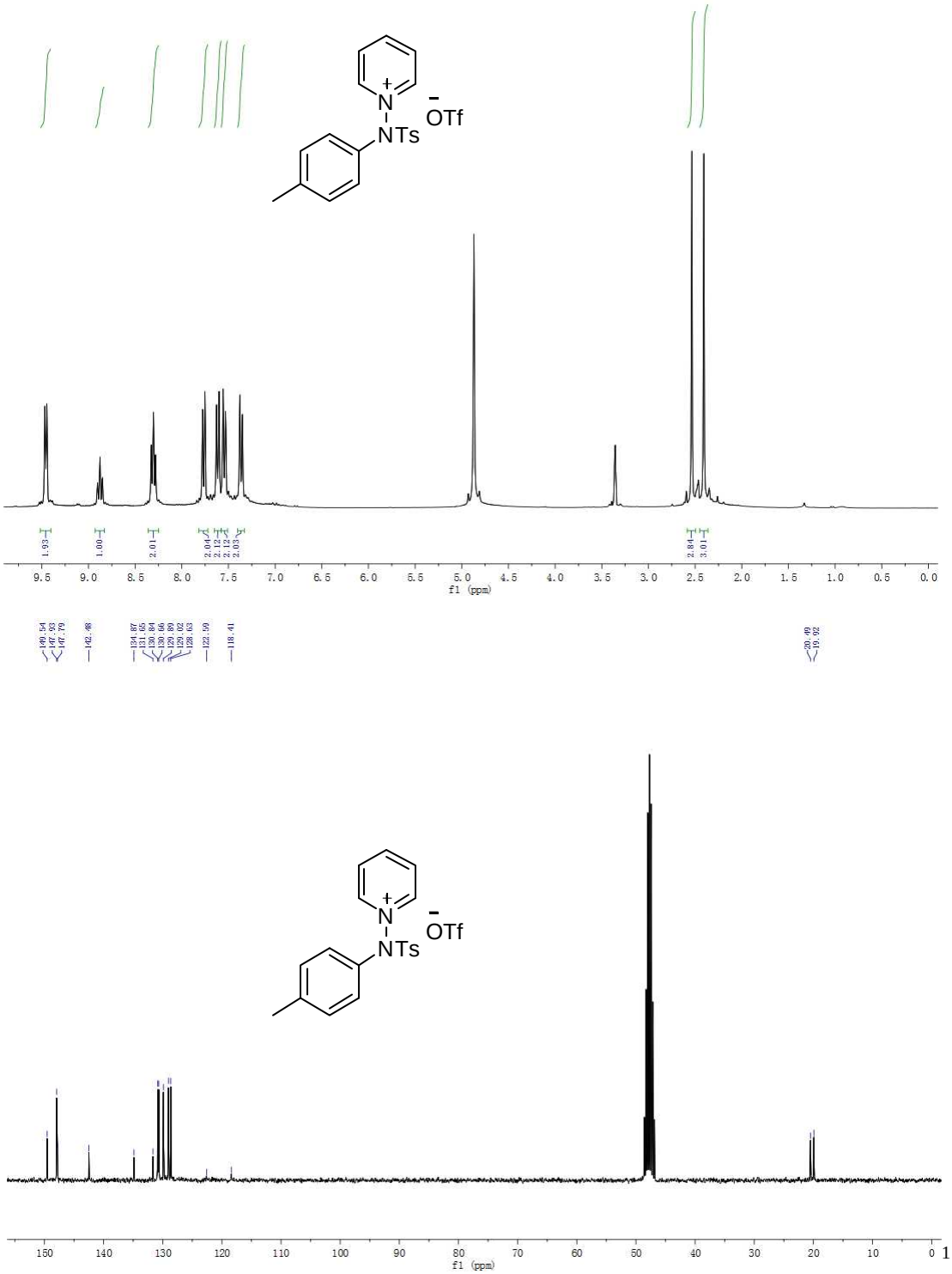
1-(4-methyl-N-(m-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ca)



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

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

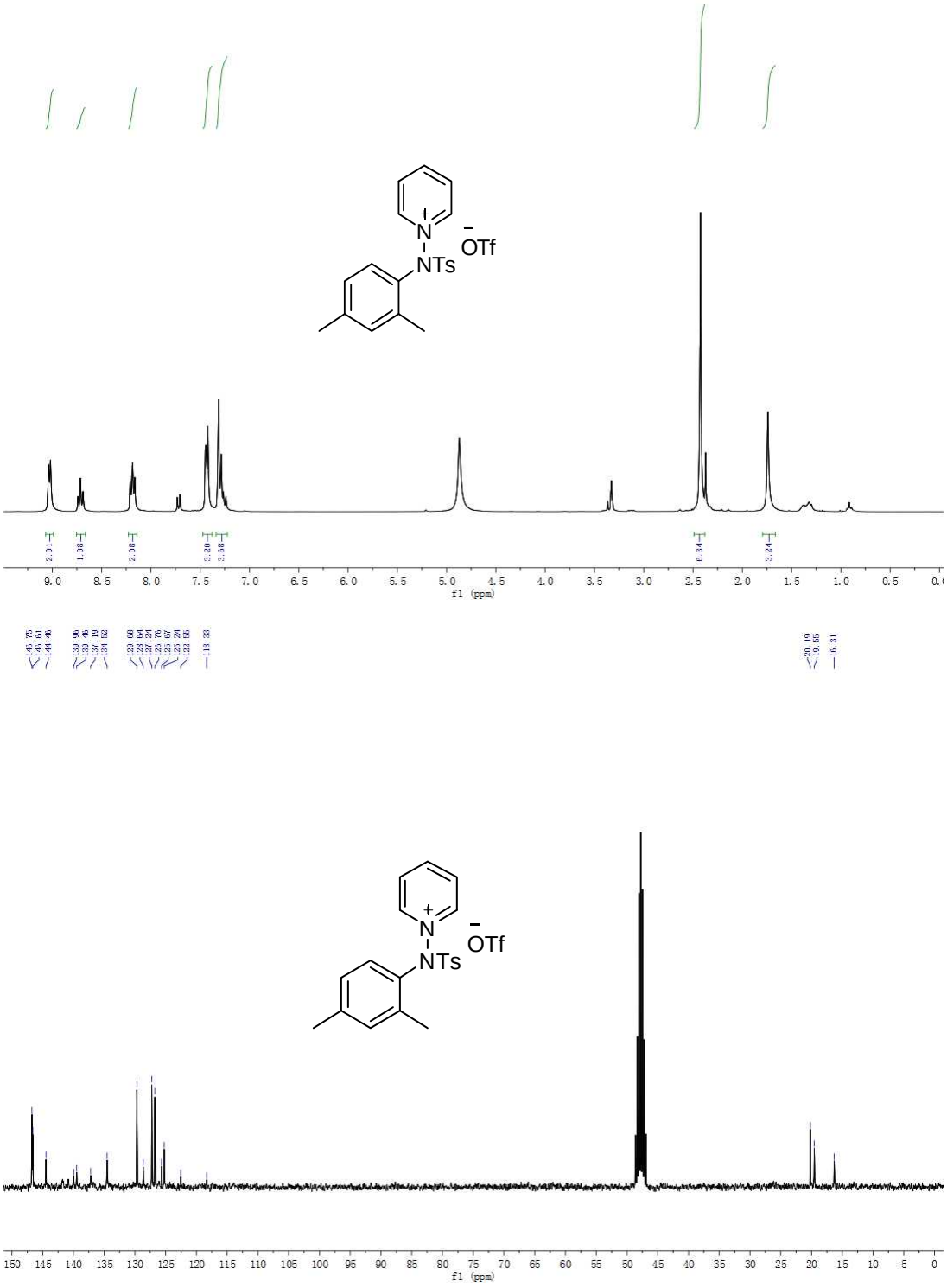
1-(4-methyl-N-(p-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3da):



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

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

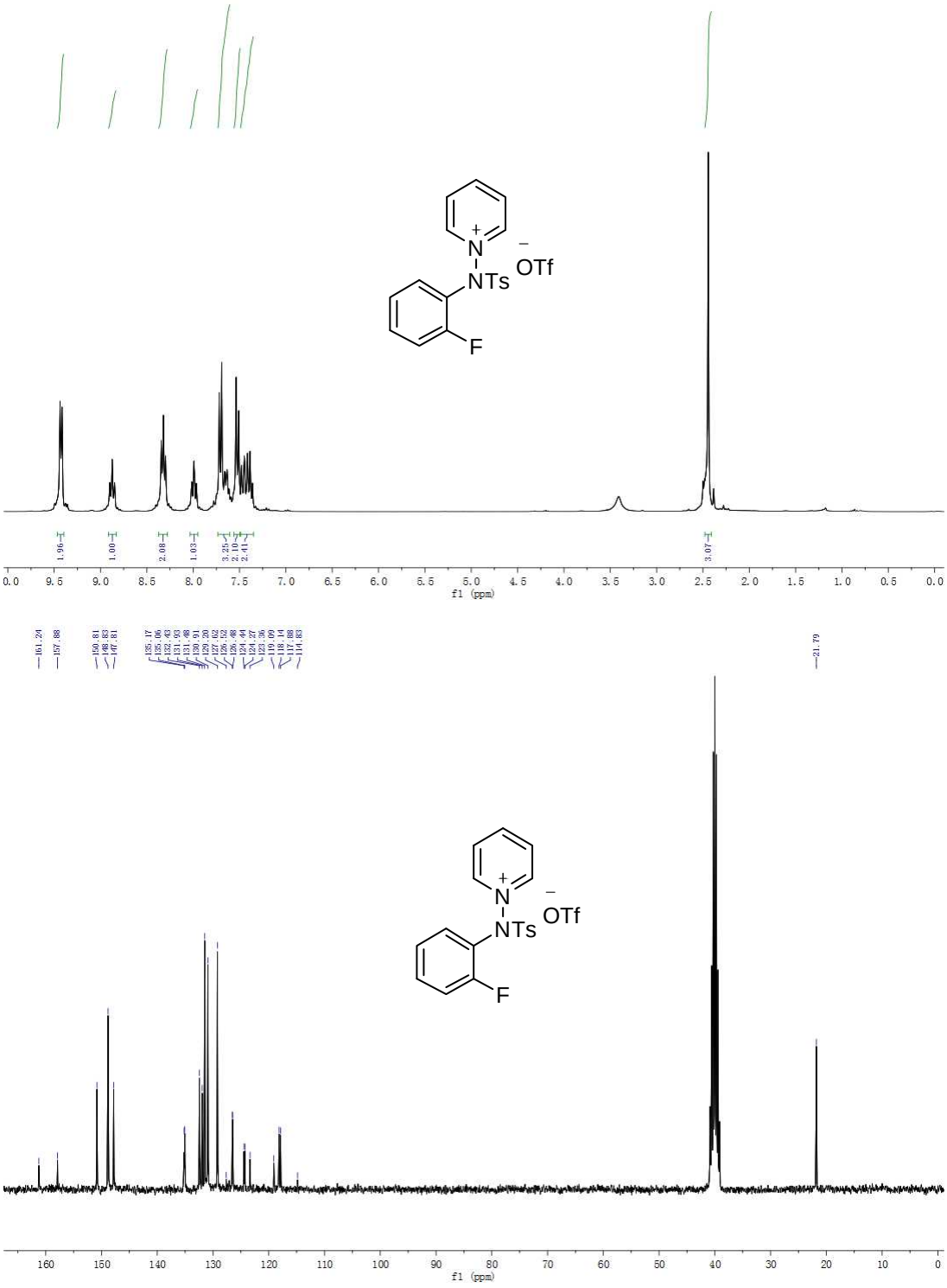
1-(N-(2,4-dimethylphenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ea)



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

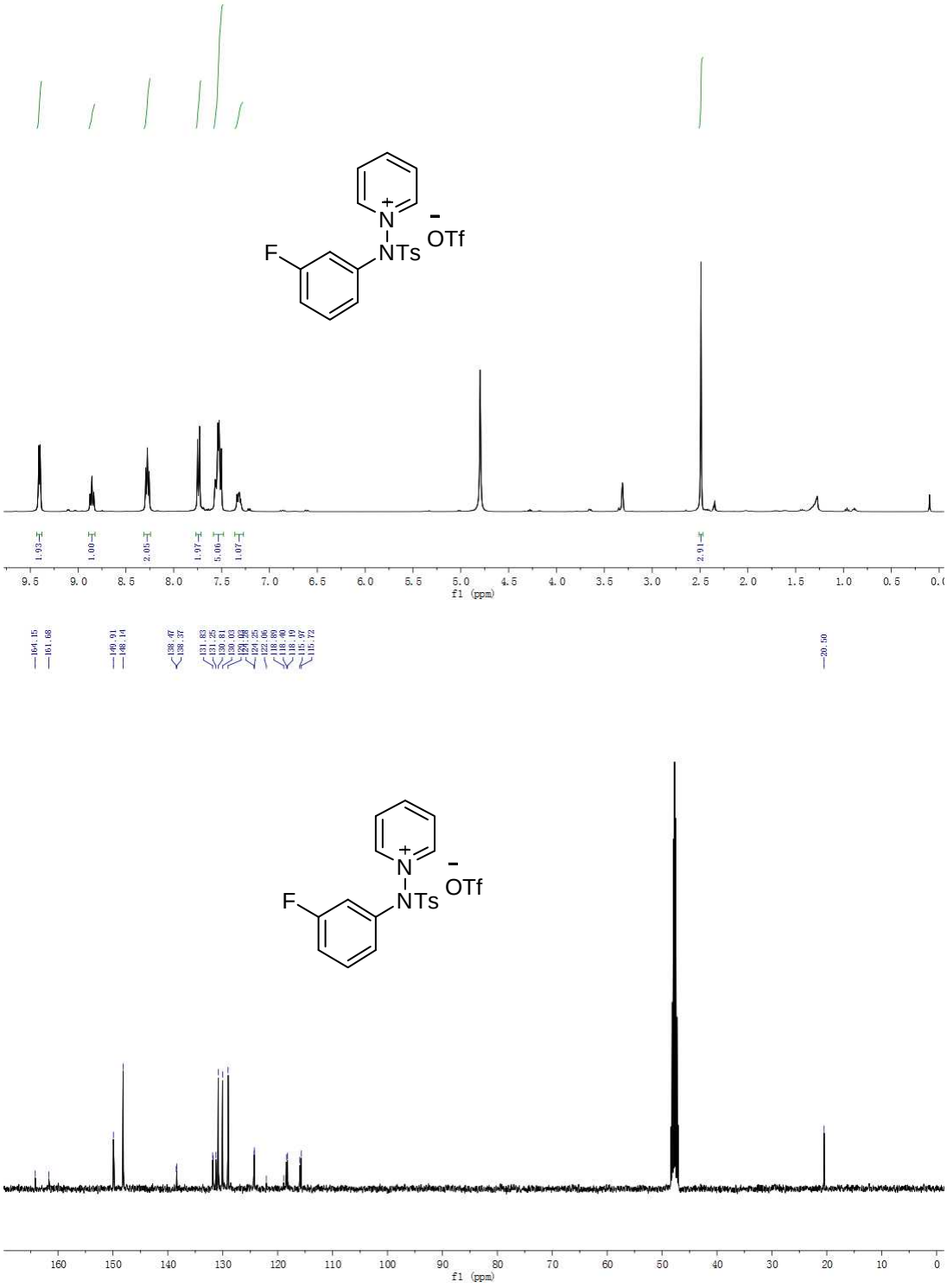
^{13}C NMR (76 MHz, METHANOL-D4) (down)

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



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

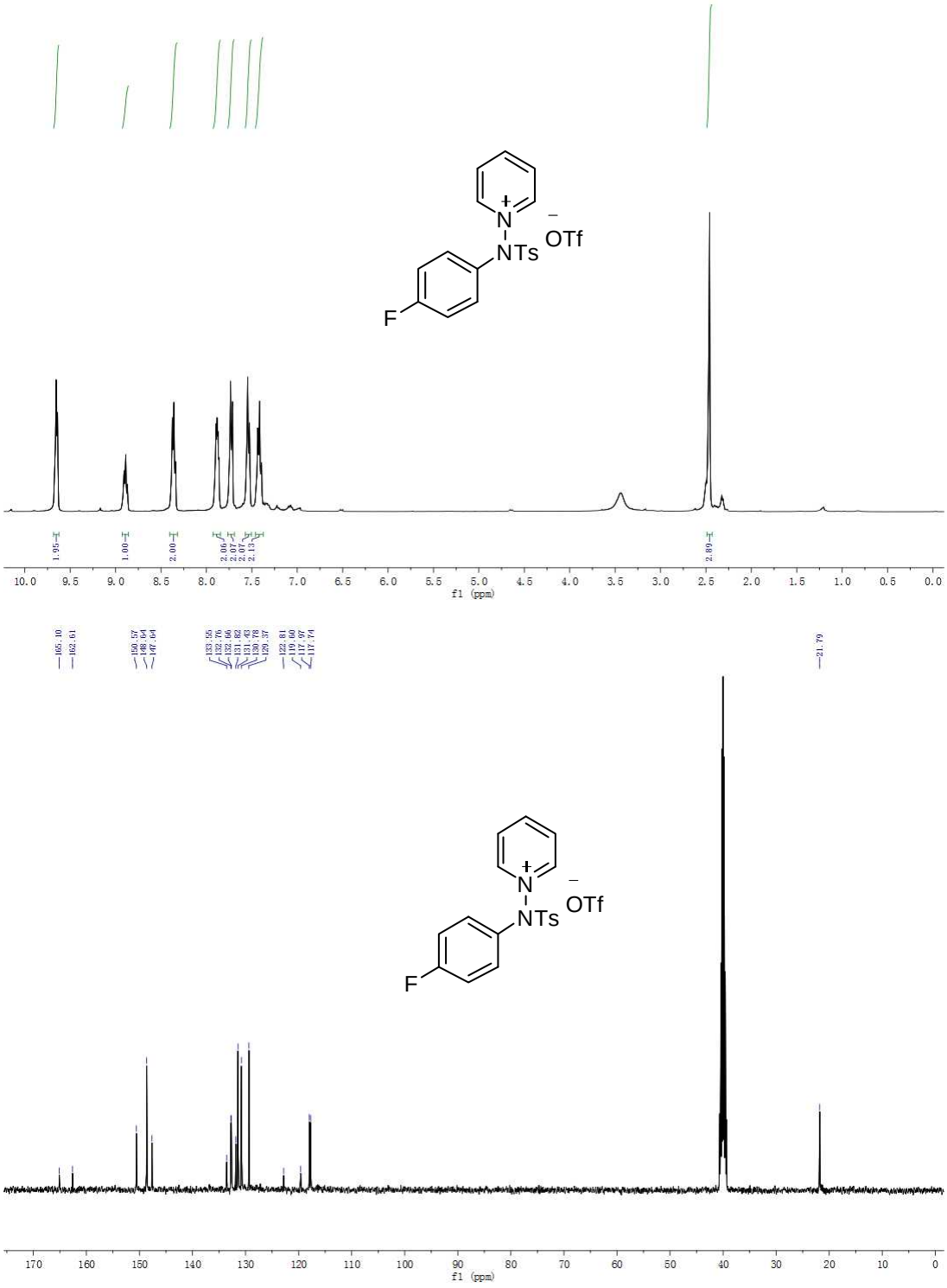
1-(N-(3-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ga)



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

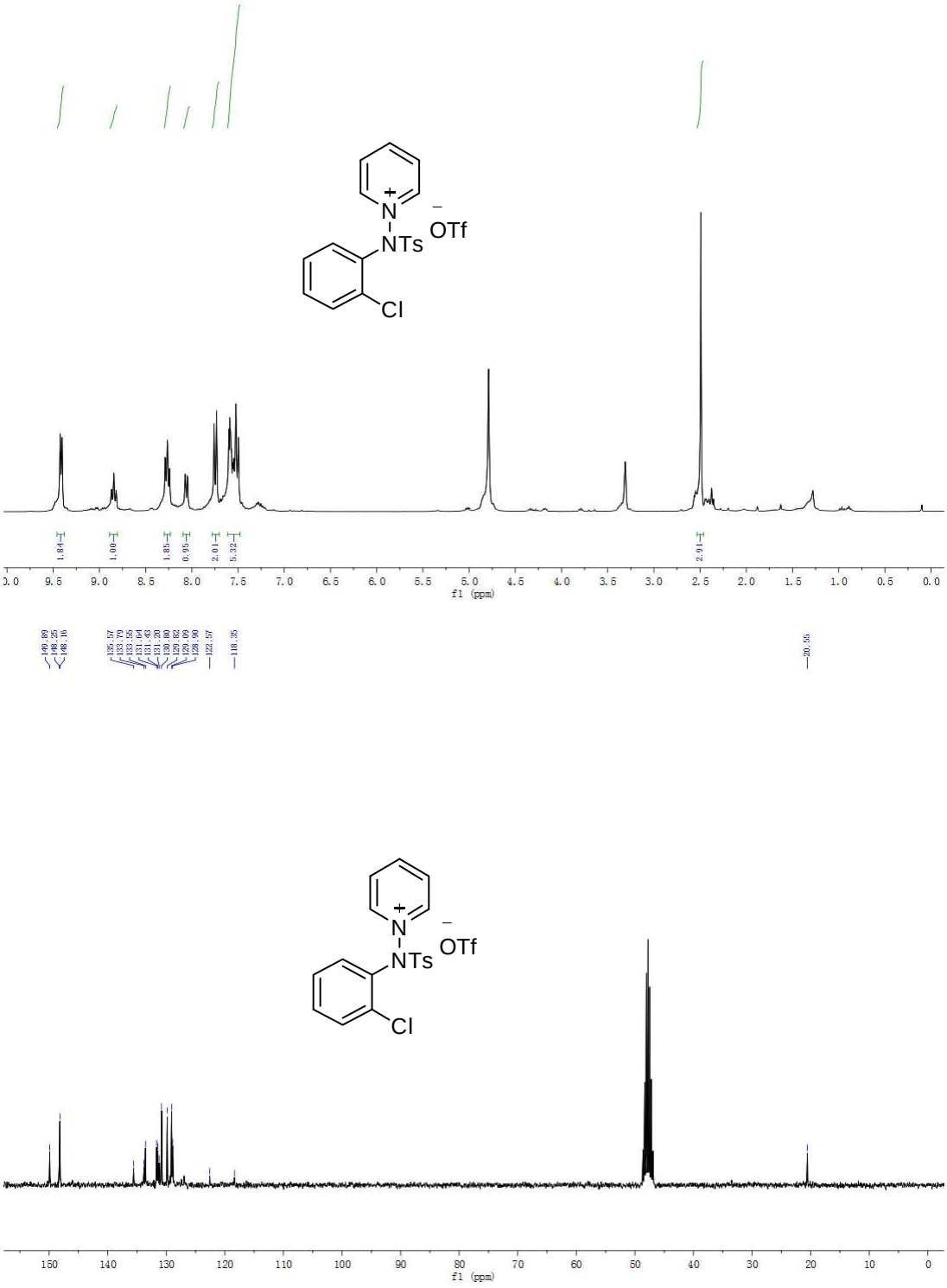
^{13}C NMR (101 MHz, METHANOL-D4) (down)

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



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

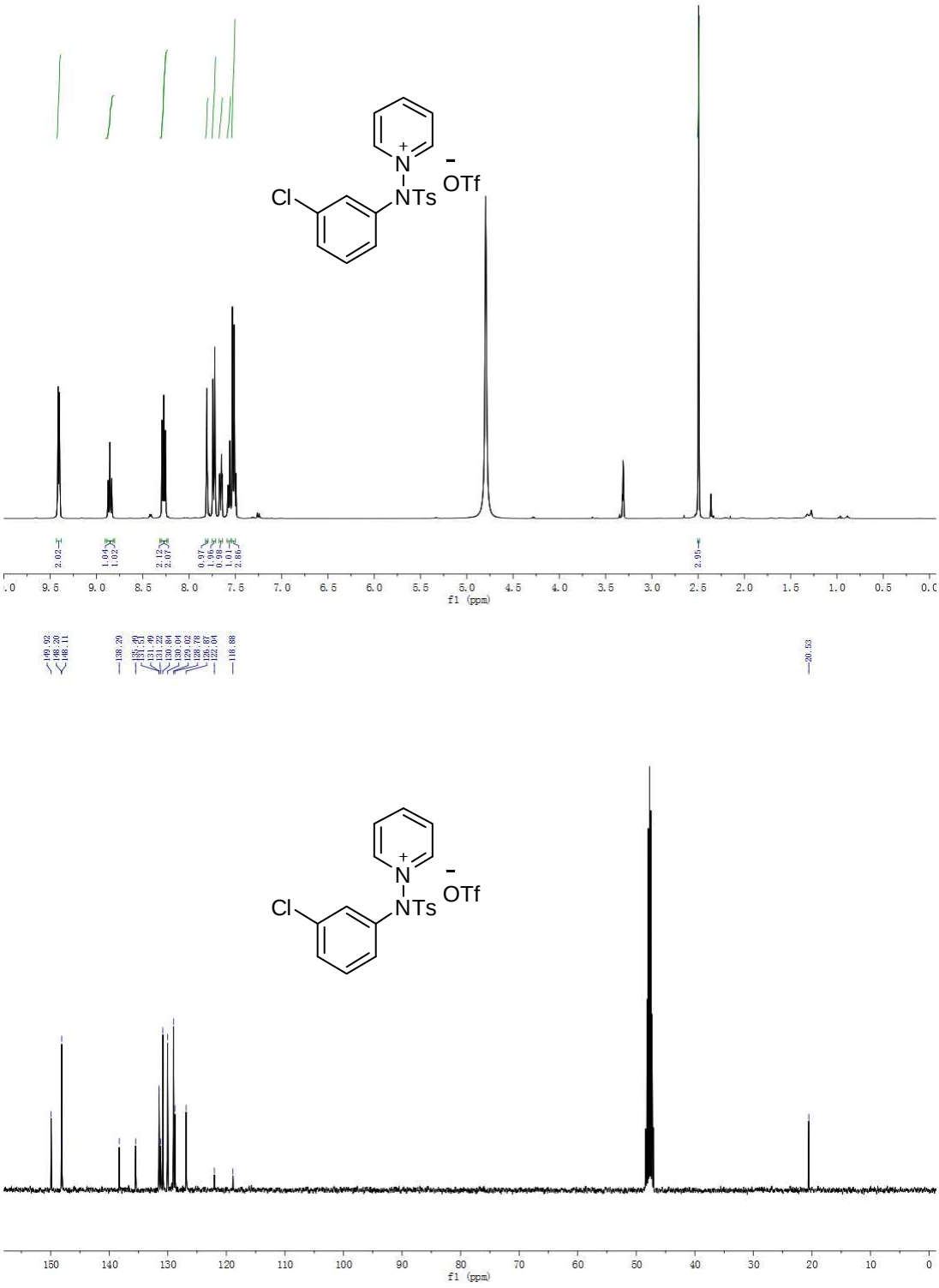
1-(N-(2-chlorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ia)



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

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

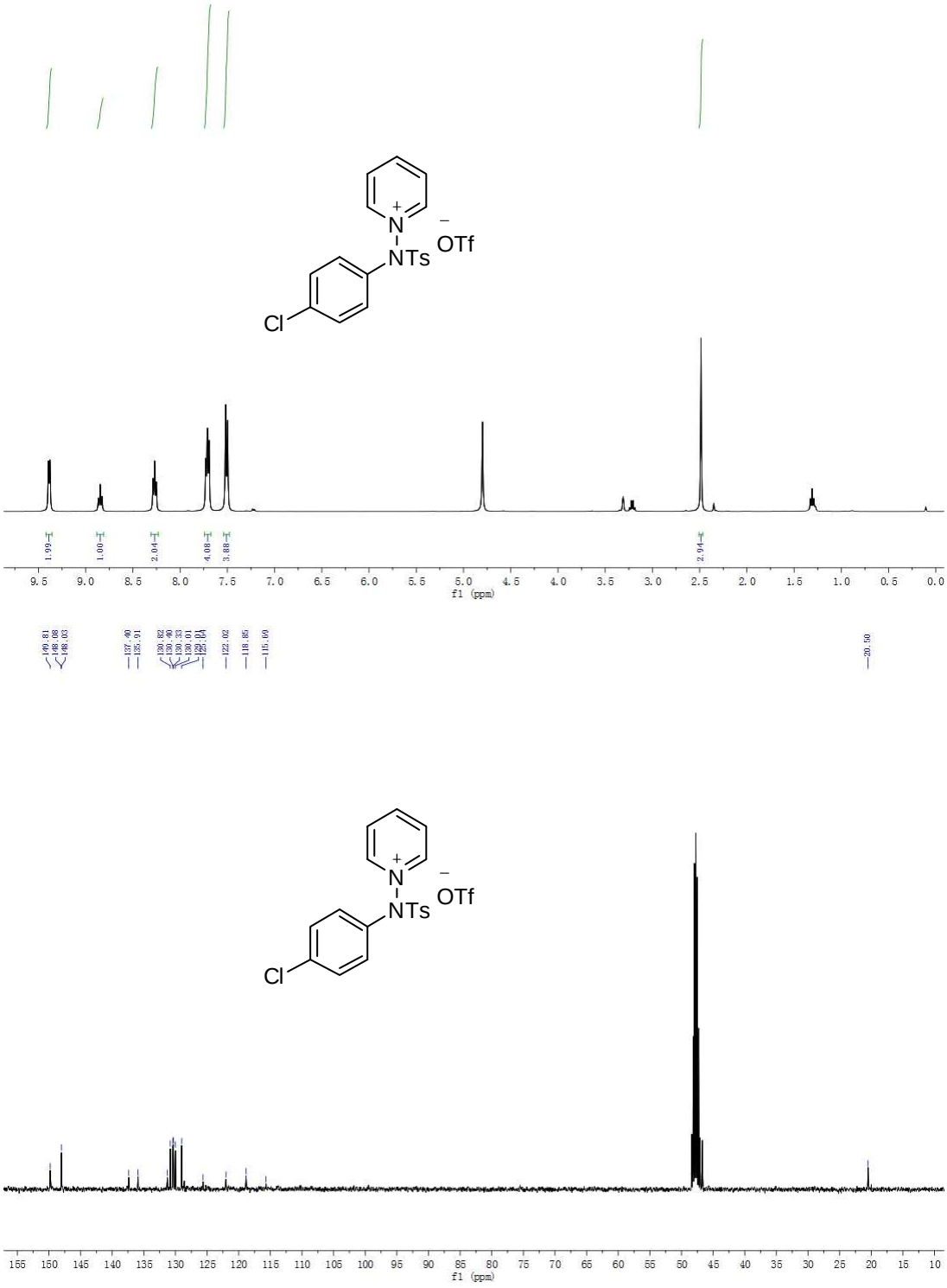
1-(N-(3-chlorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ja)



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

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

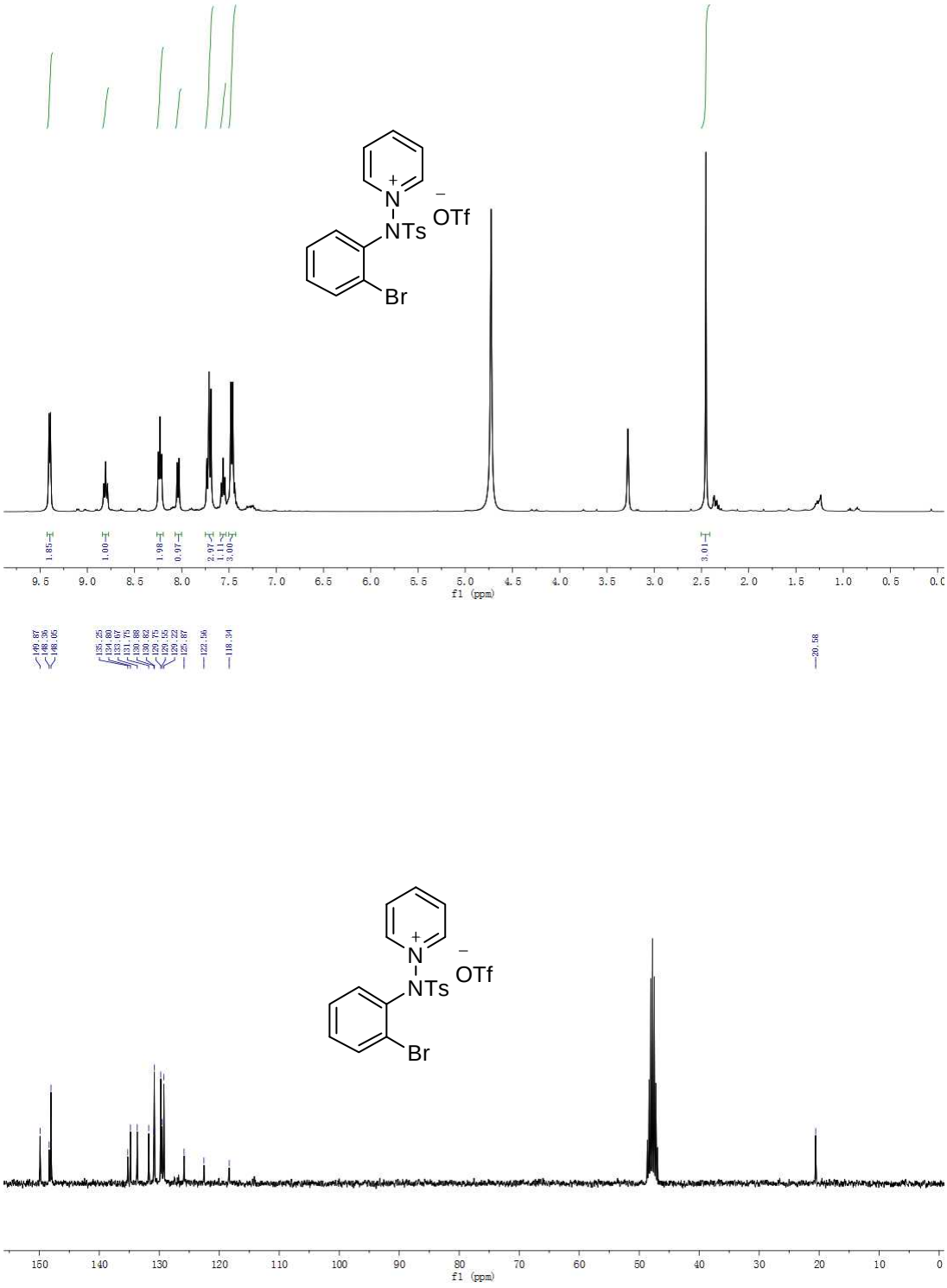
1-(N-(4-chlorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ka)



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

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

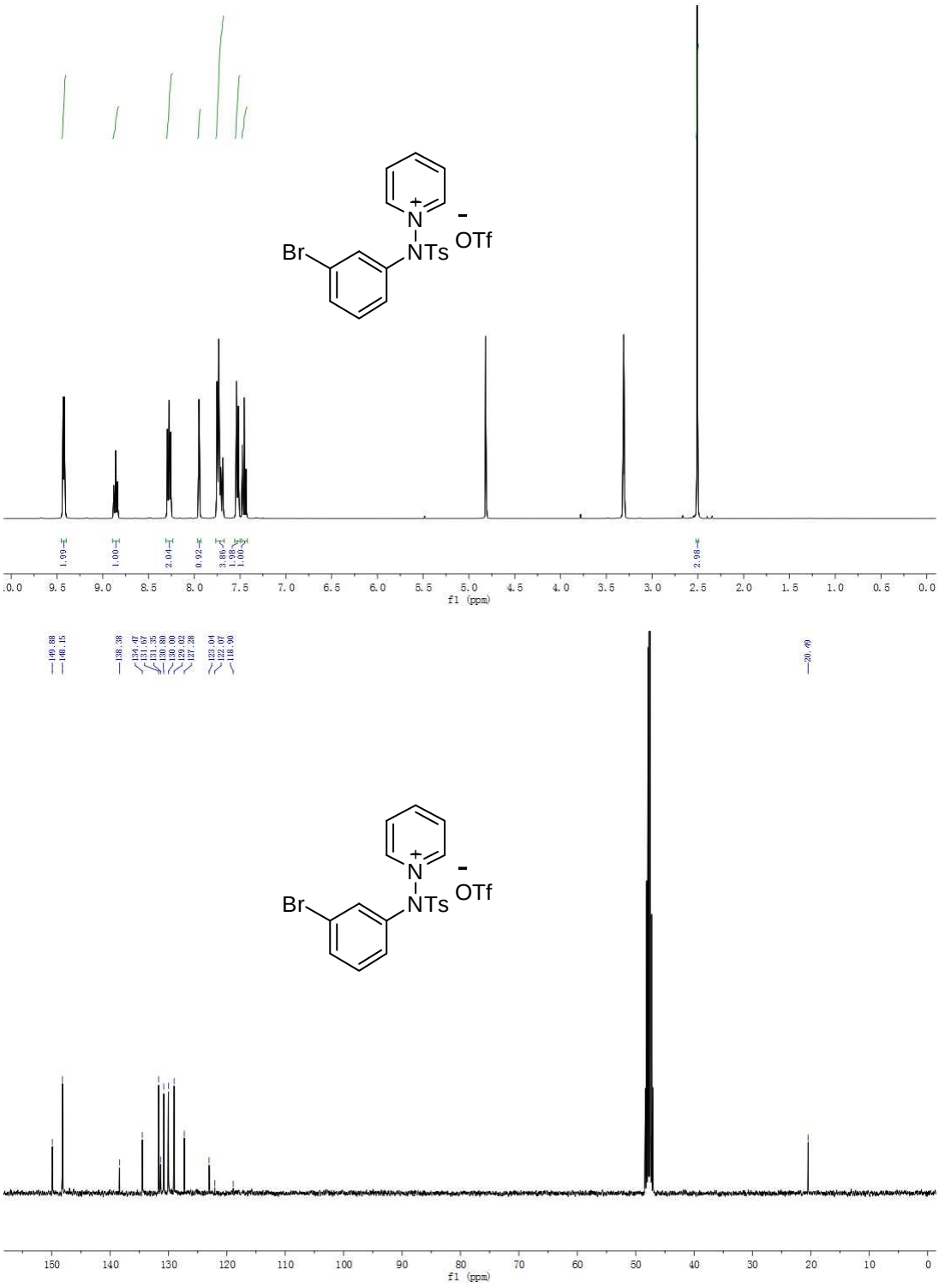
1-(N-(2-bromophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3la)



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

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

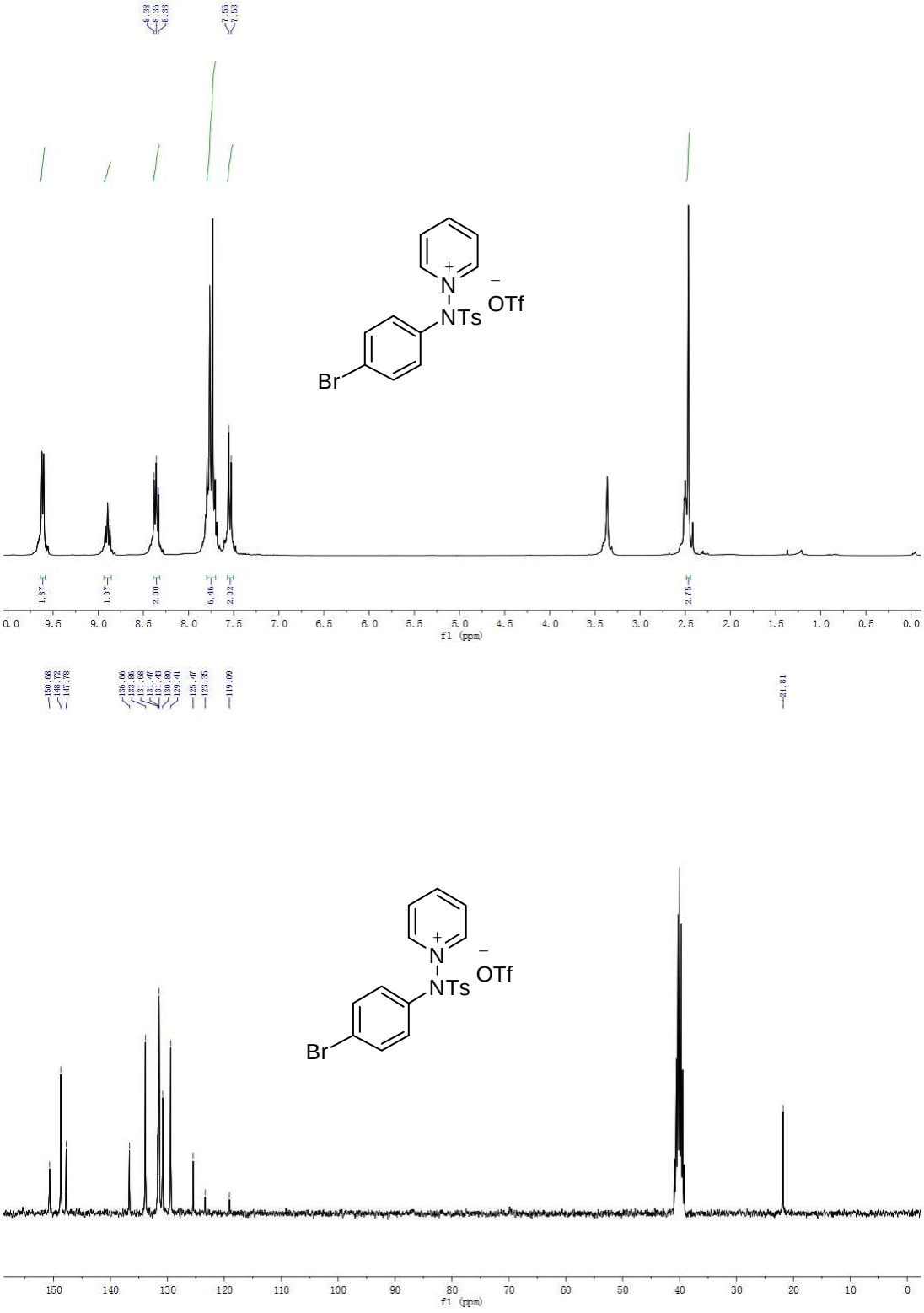
1-(N-(3-bromophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ma)



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

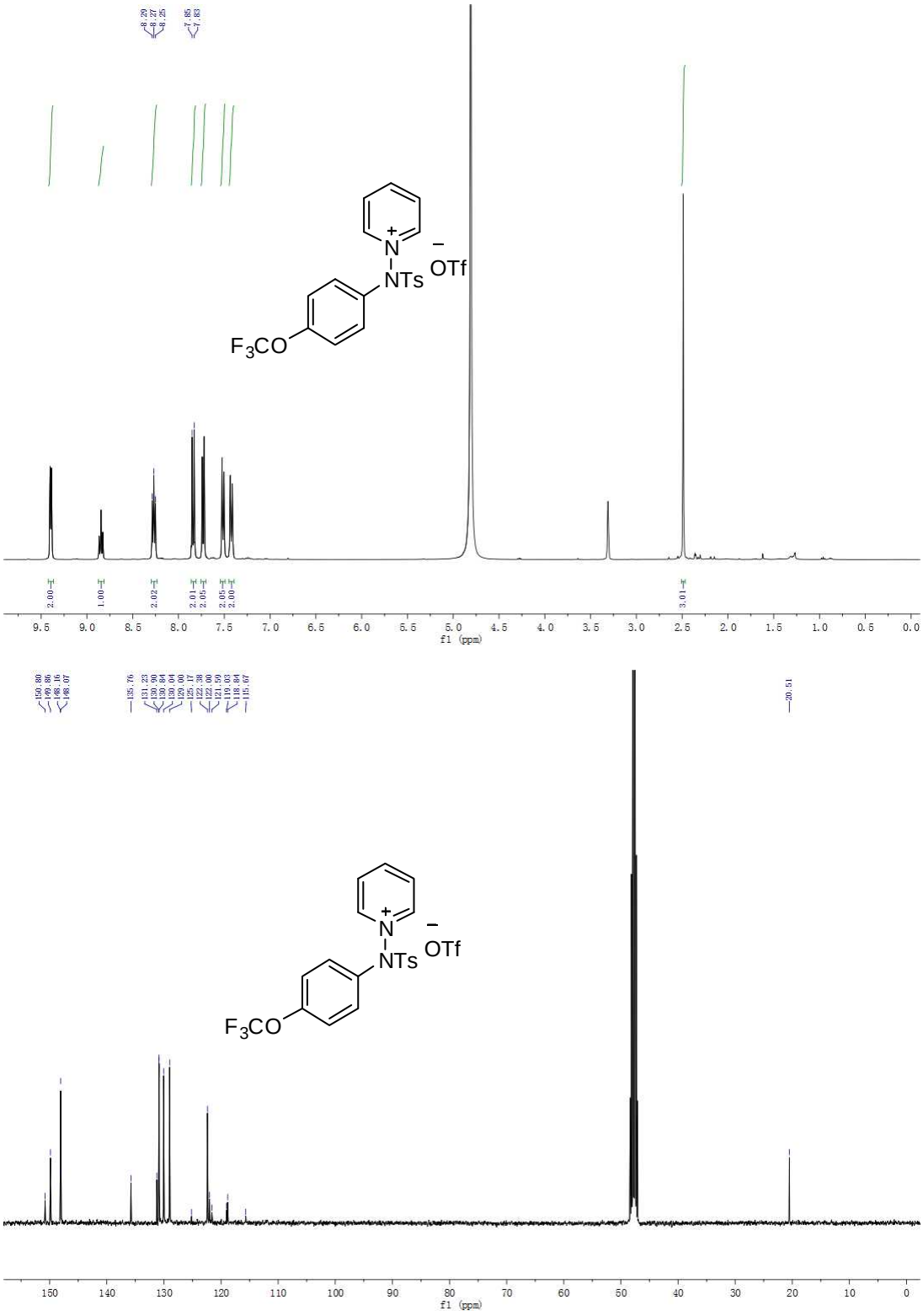
^{13}C NMR (101 MHz, METHANOL-D4) (down)

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



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

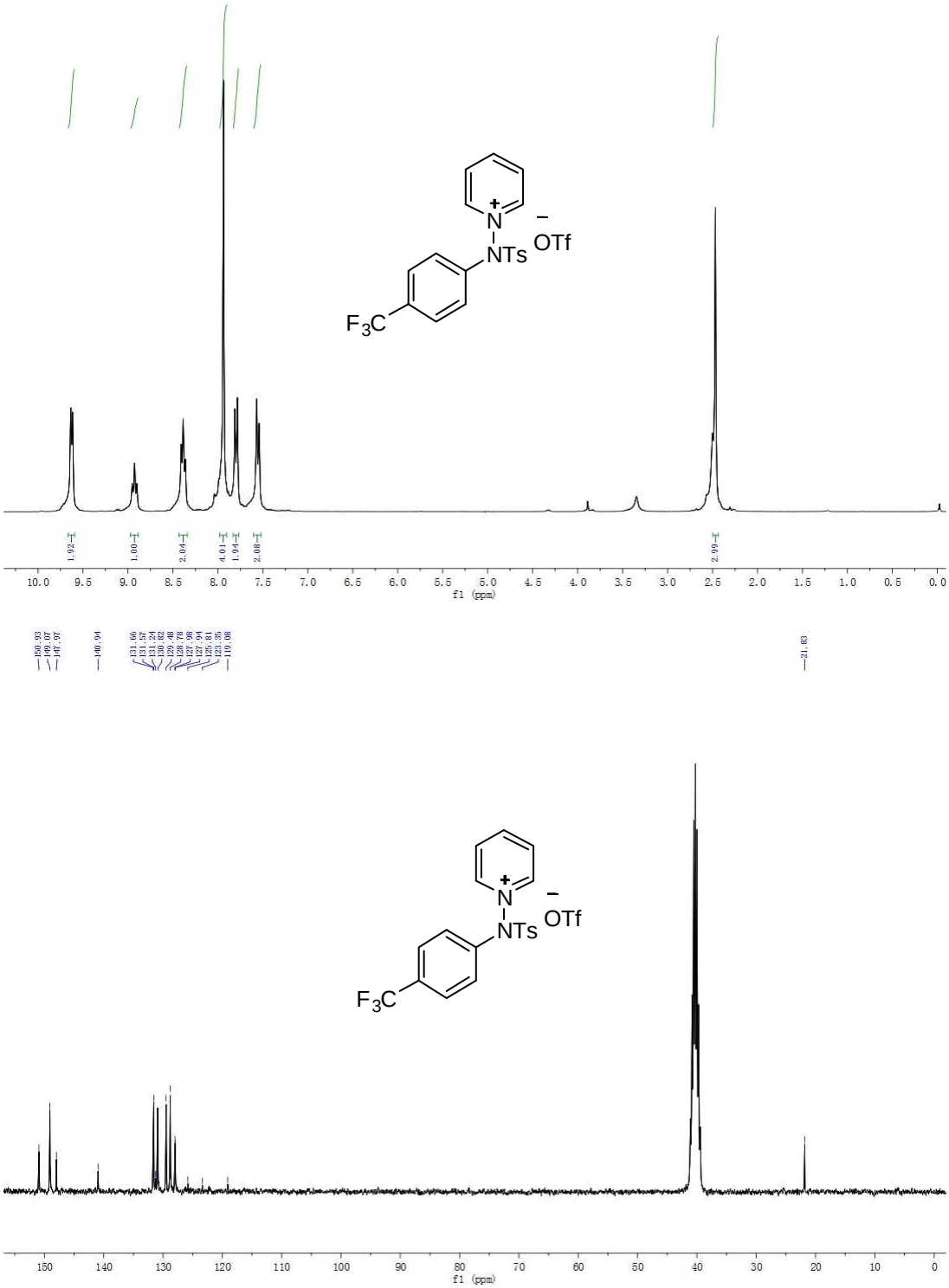
1-(4-methyl-N-(4-(trifluoromethoxy)phenyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3oa)



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

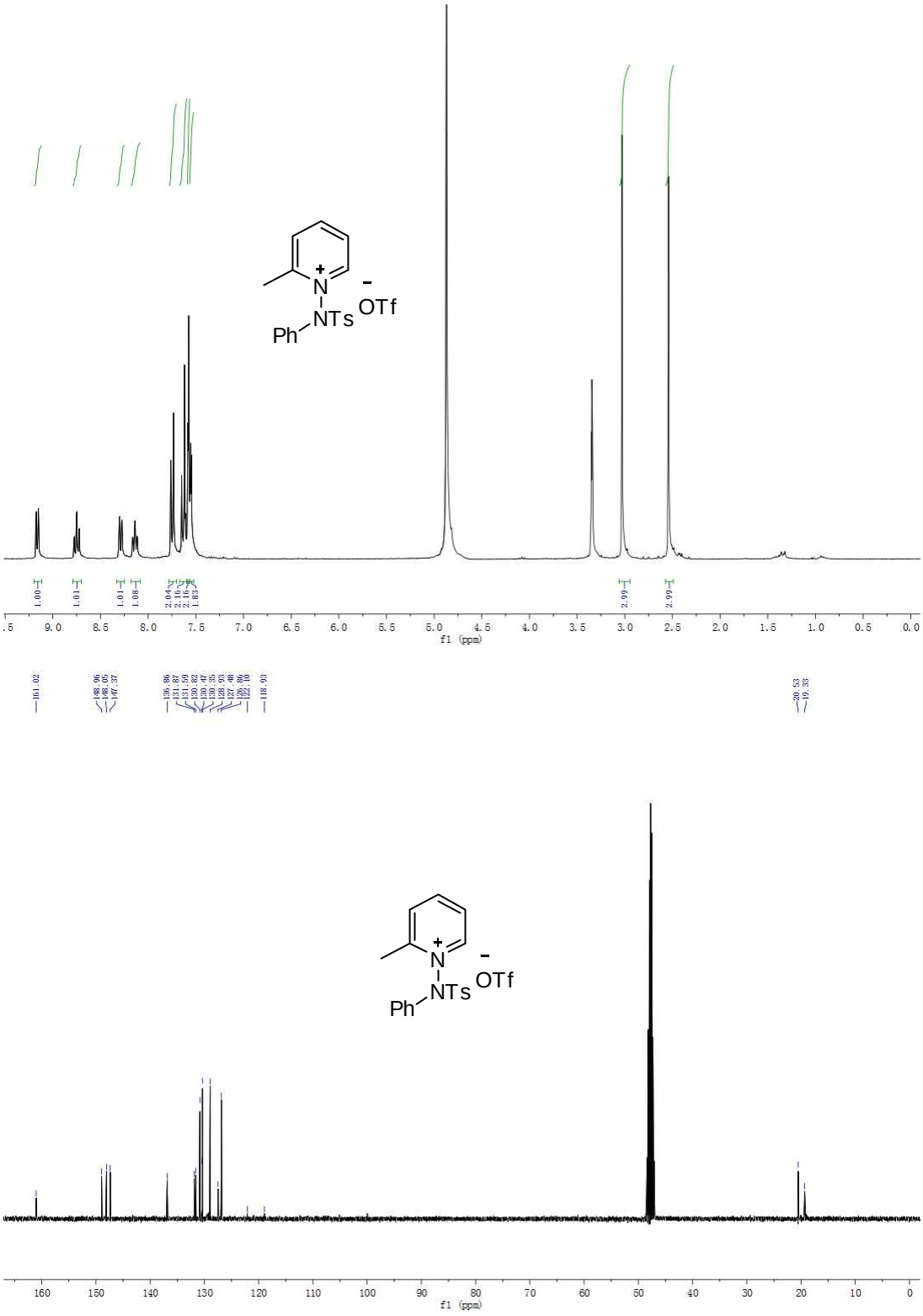
^{13}C NMR (101 MHz, METHANOL-D4) (down)

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



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

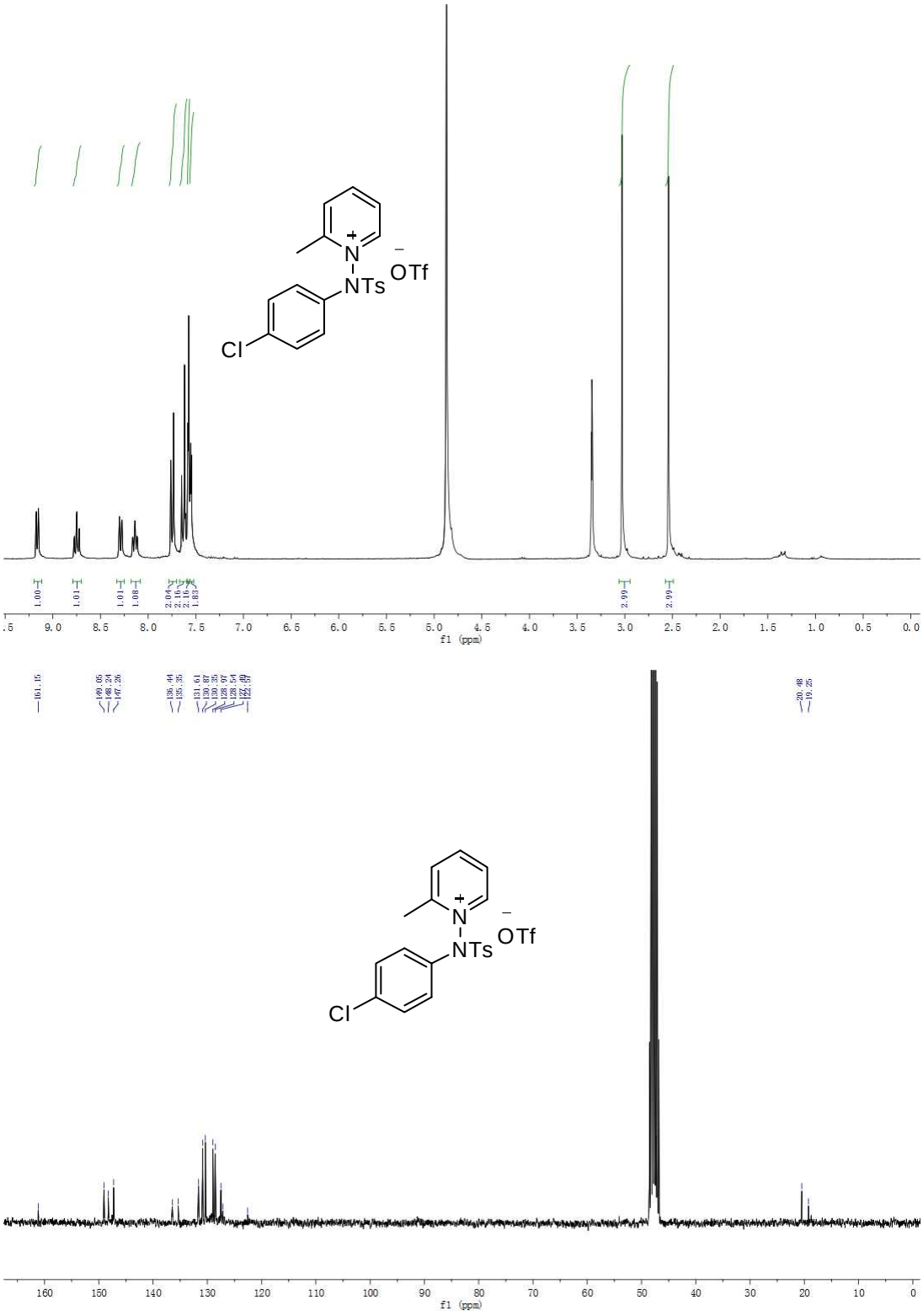
2-methyl-1-(4-methyl-N-phenylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ab)



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

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

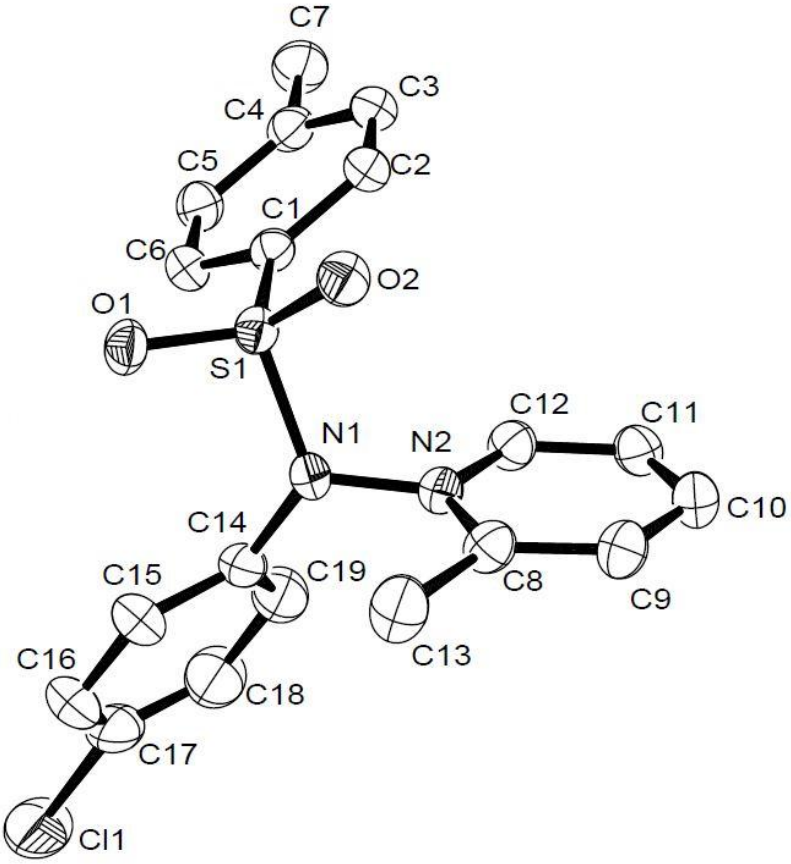
1-(N-(4-chlorophenyl)-4-methylphenylsulfonamido)-2-methylpyridin-1-ium trifluoromethanesulfonate (3kb)



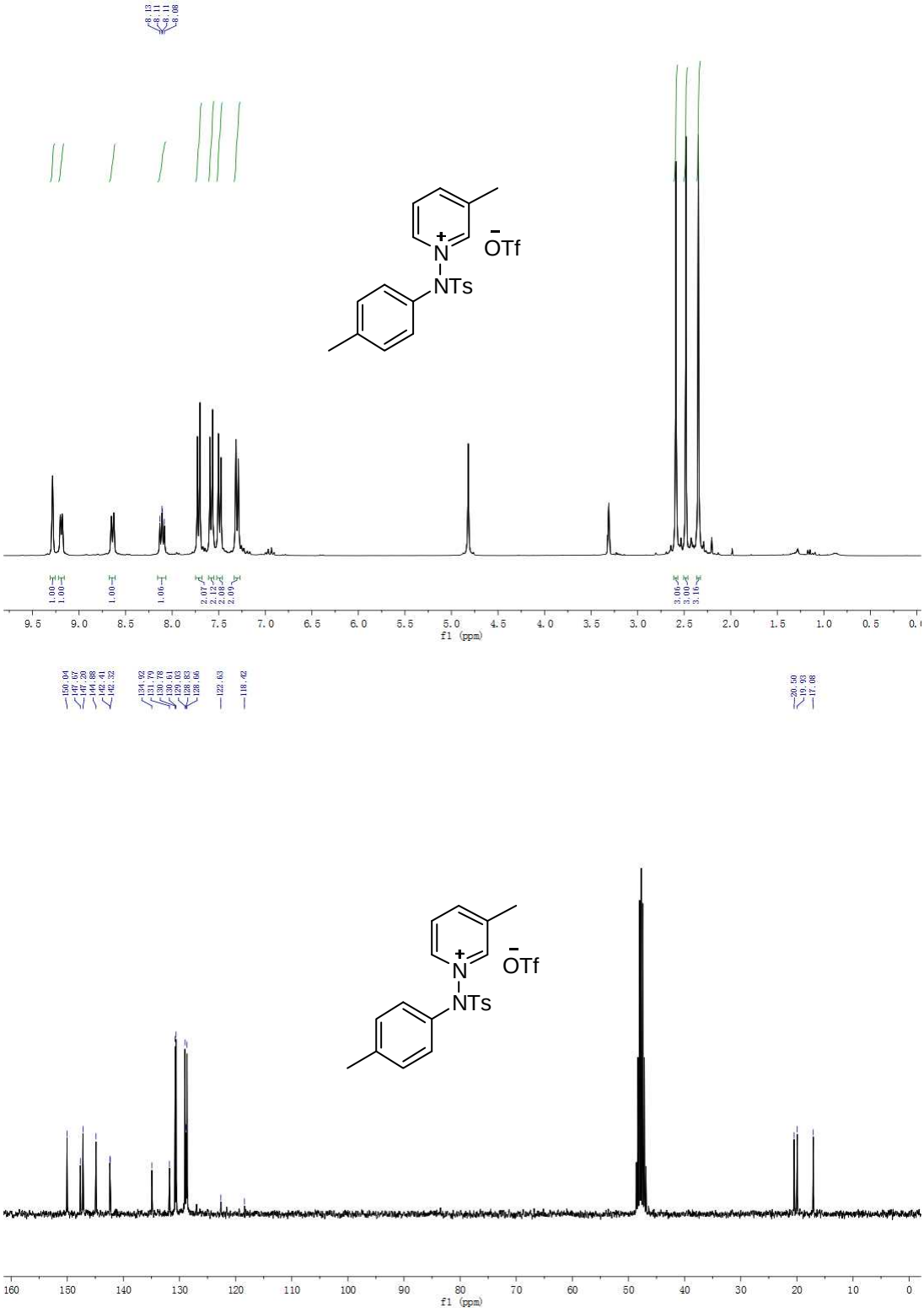
^{1}H NMR (301 MHz, METHANOL-D4) (up) and

^{13}C 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 CH_3OH. 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) $Å^3$, 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, wR2 (reflections) = 0.2084 (5129).



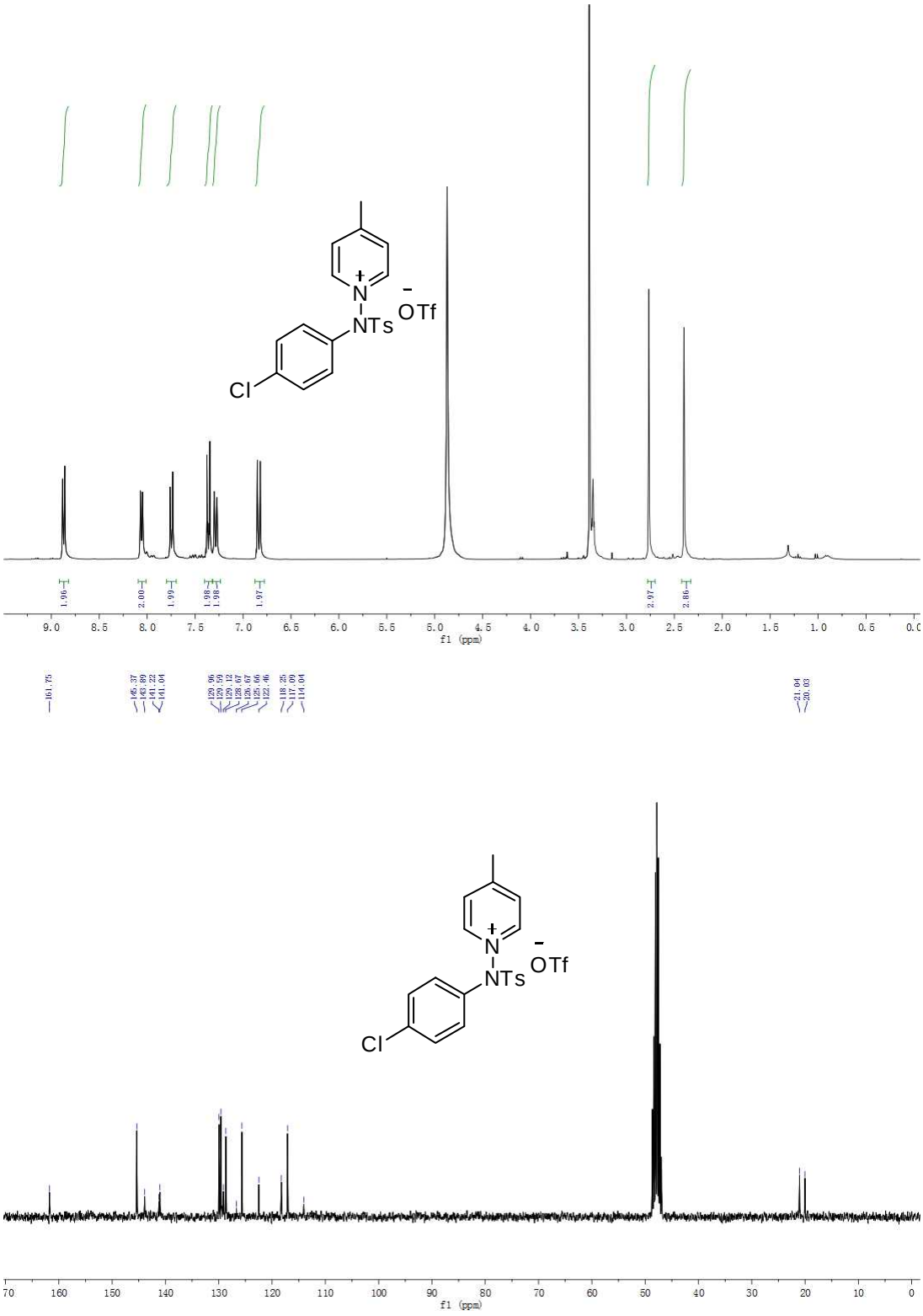
3-methyl-1-(4-methyl-N-(p-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3dc)



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

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

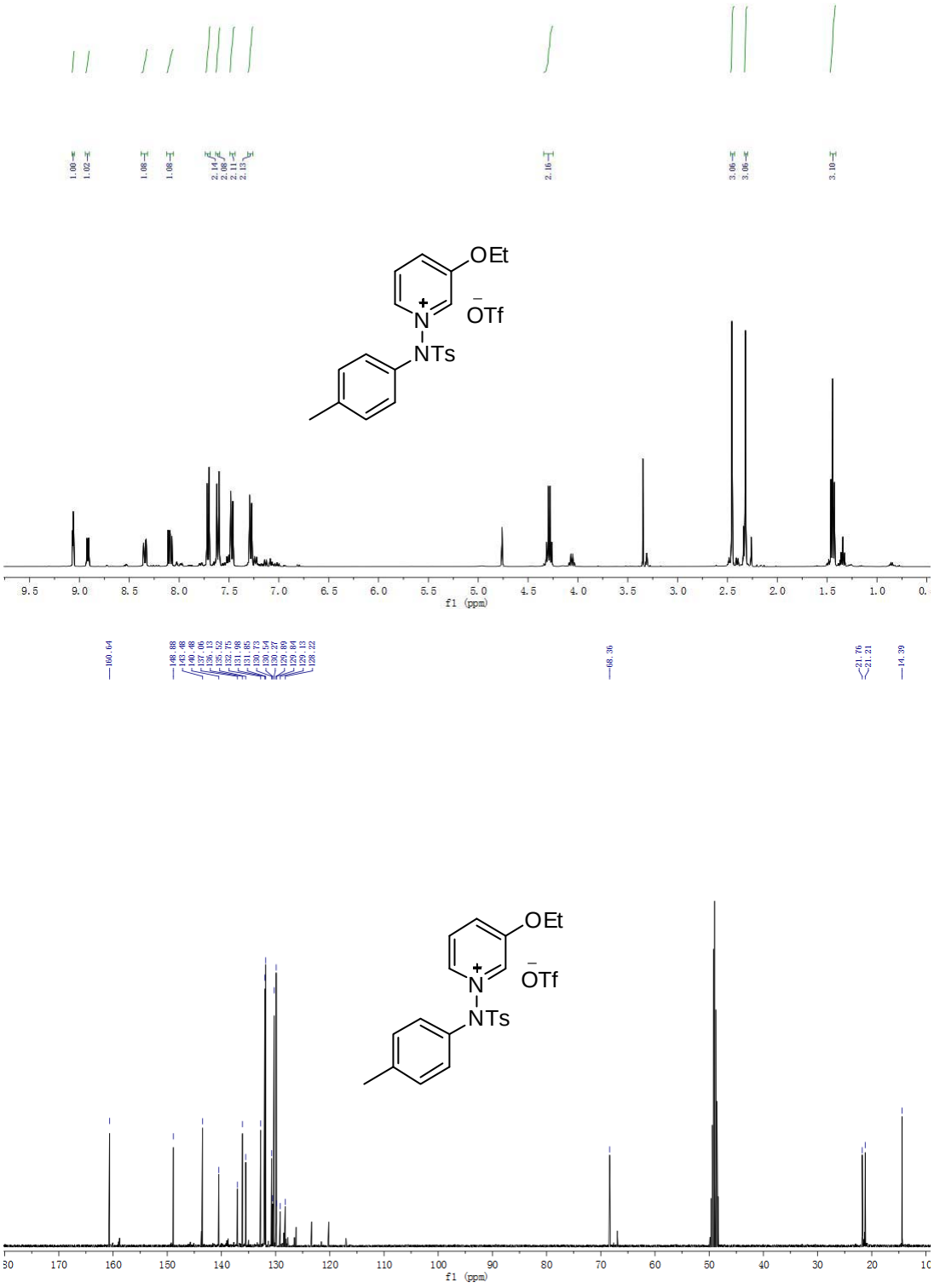
1-(N-(4-chlorophenyl)-4-methylphenylsulfonamido)-4-methylpyridin-1-ium trifluoromethanesulfonate (3kd)



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

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

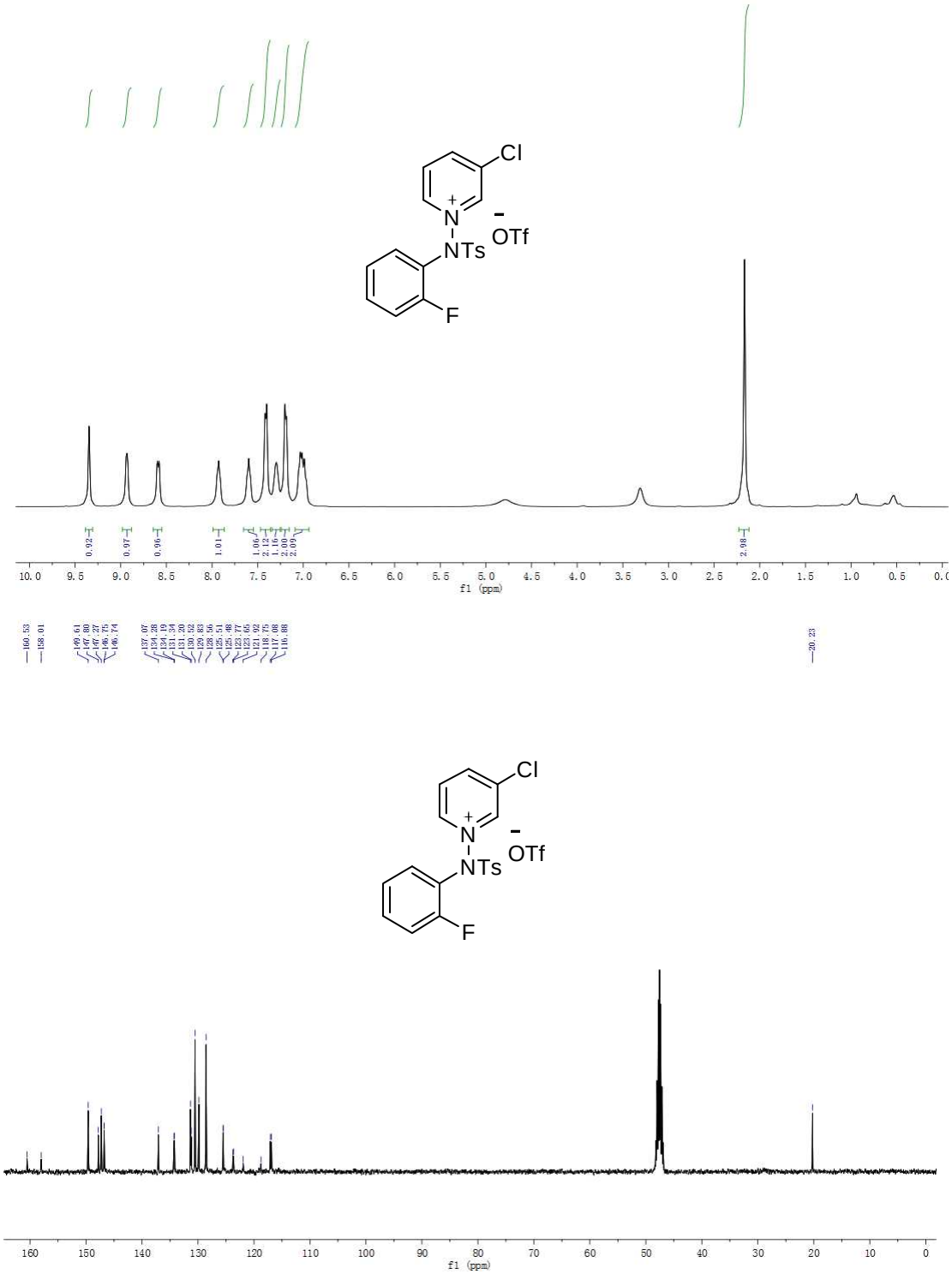
3-ethoxy-1-(4-methyl-N-(p-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3de)



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

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

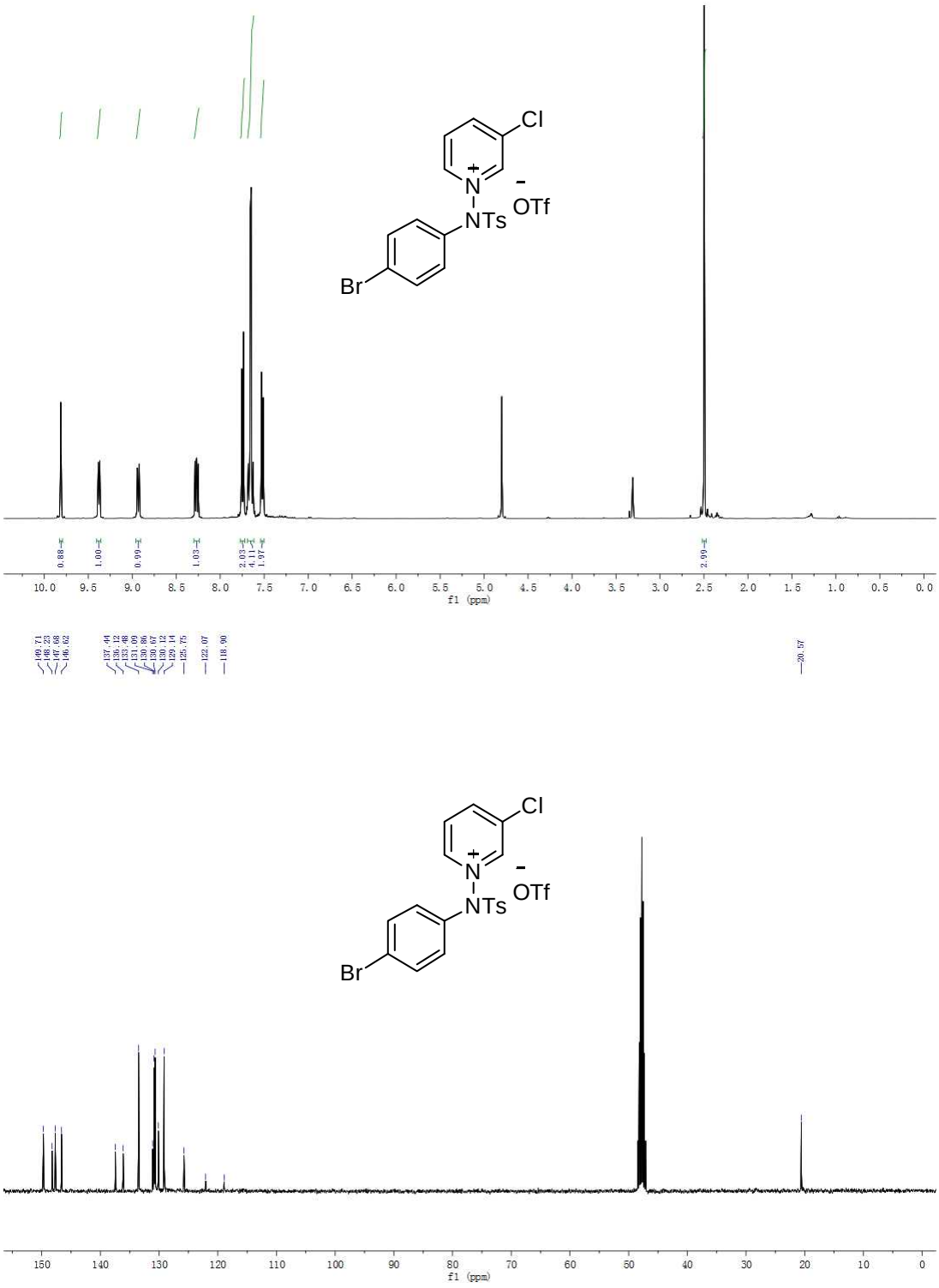
3-chloro-1-(N-(2-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ff)



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

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

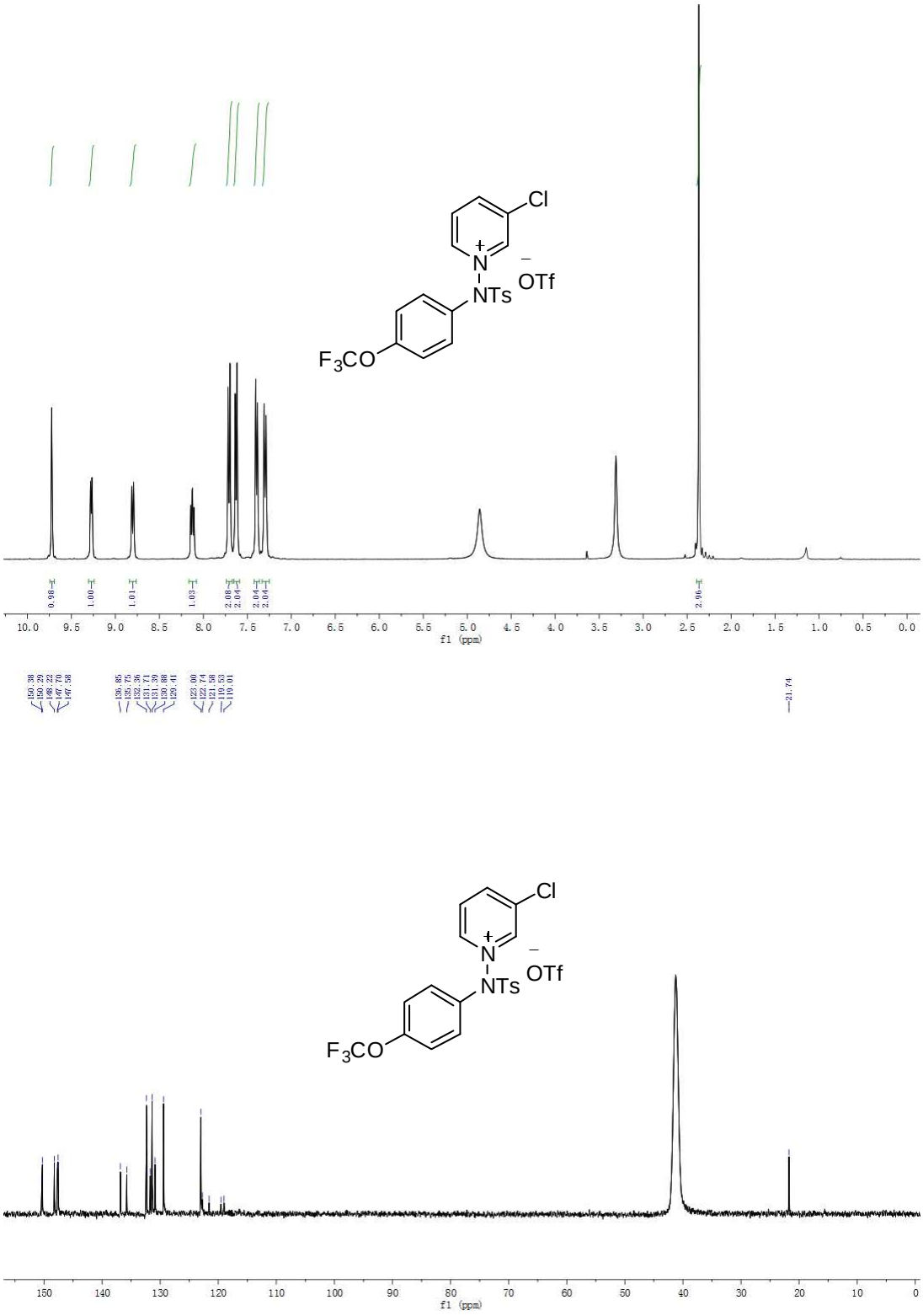
1-(N-(4-bromophenyl)-4-methylphenylsulfonamido)-3-chloropyridin-1-ium trifluoromethanesulfonate (3nf)



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

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

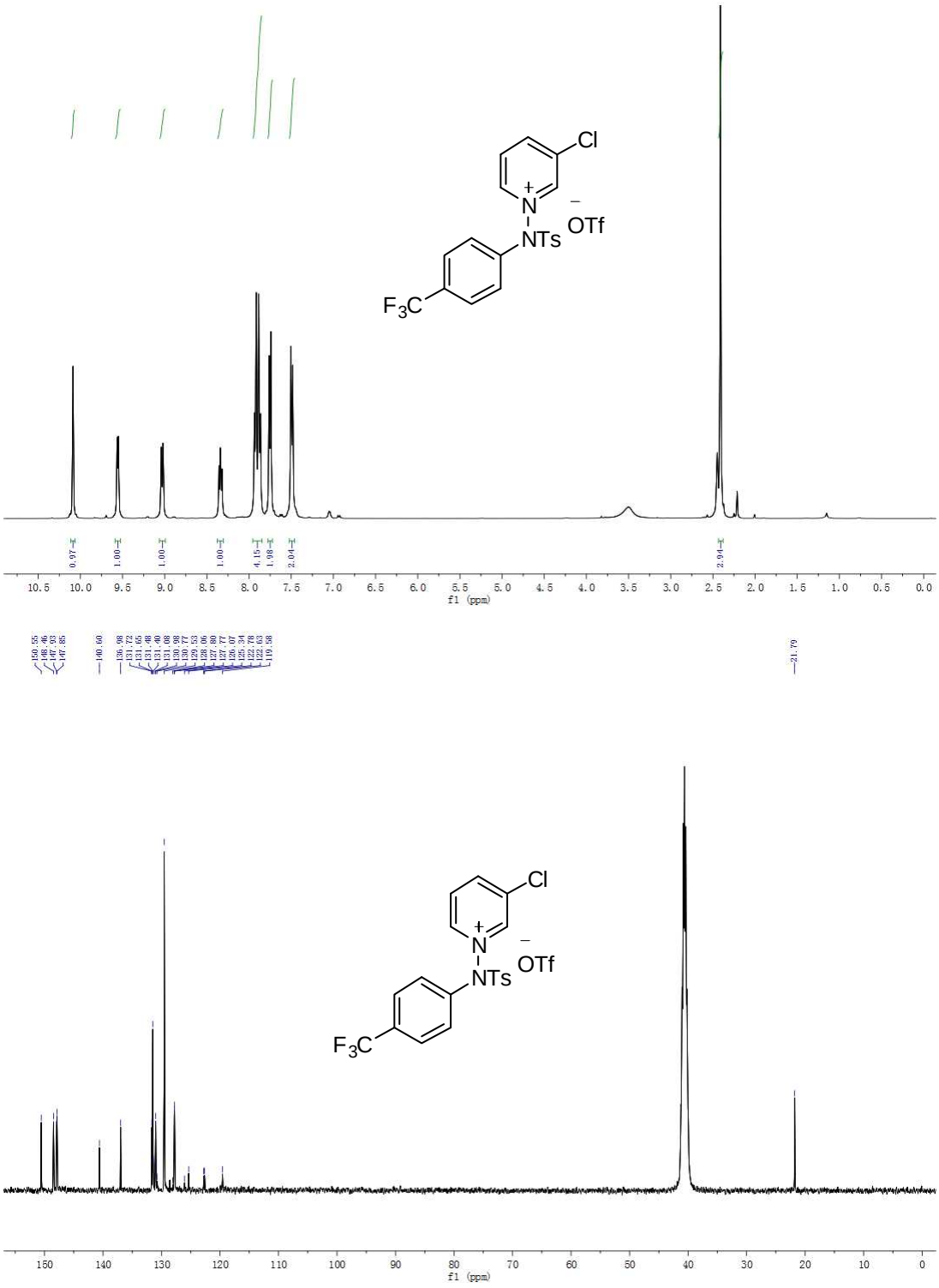
3-chloro-1-(4-methyl-N-(4-(trifluoromethoxy)phenyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3of)



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

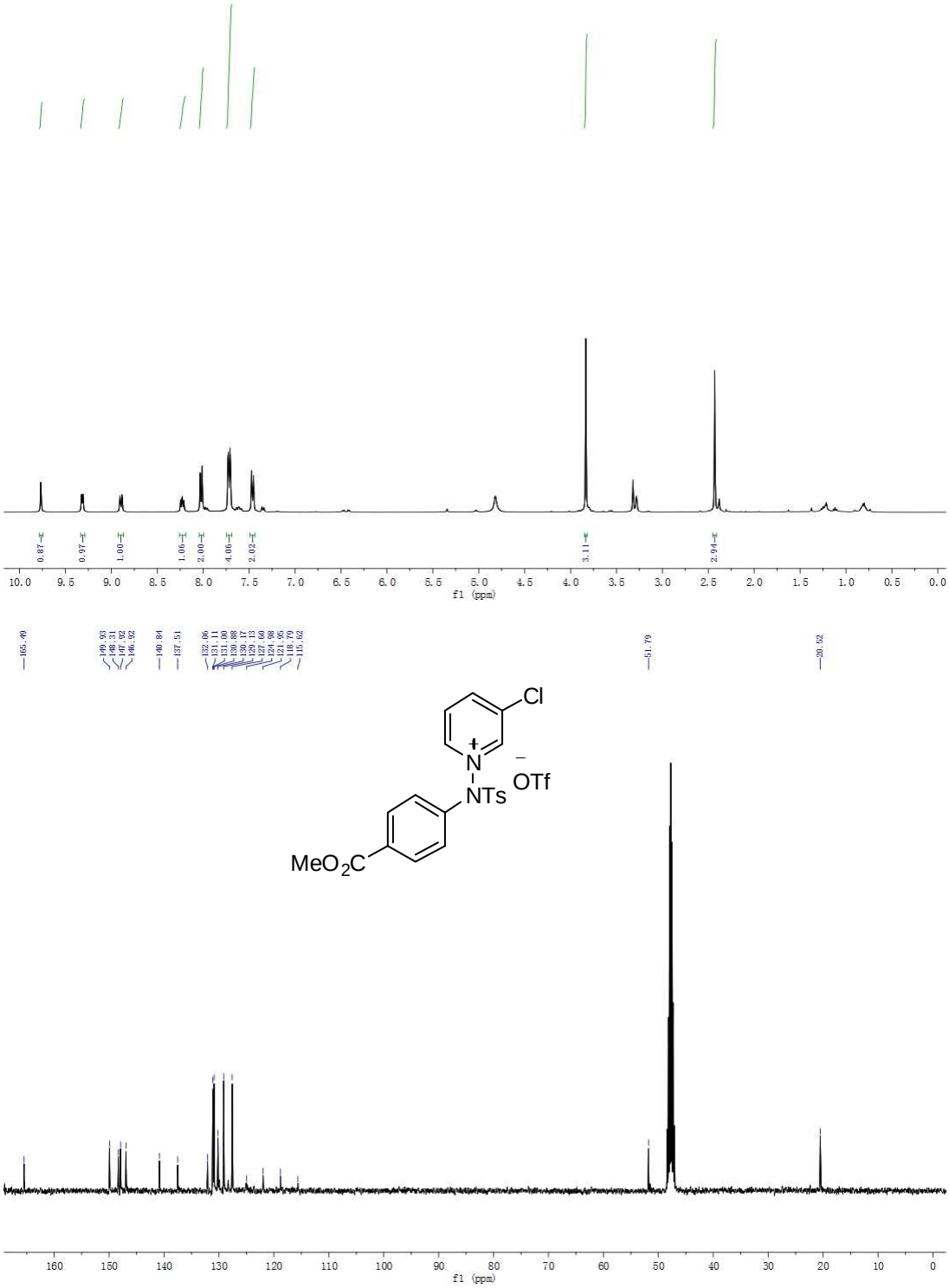
^{13}C NMR (101 MHz, DMSO-D6) (down)

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



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

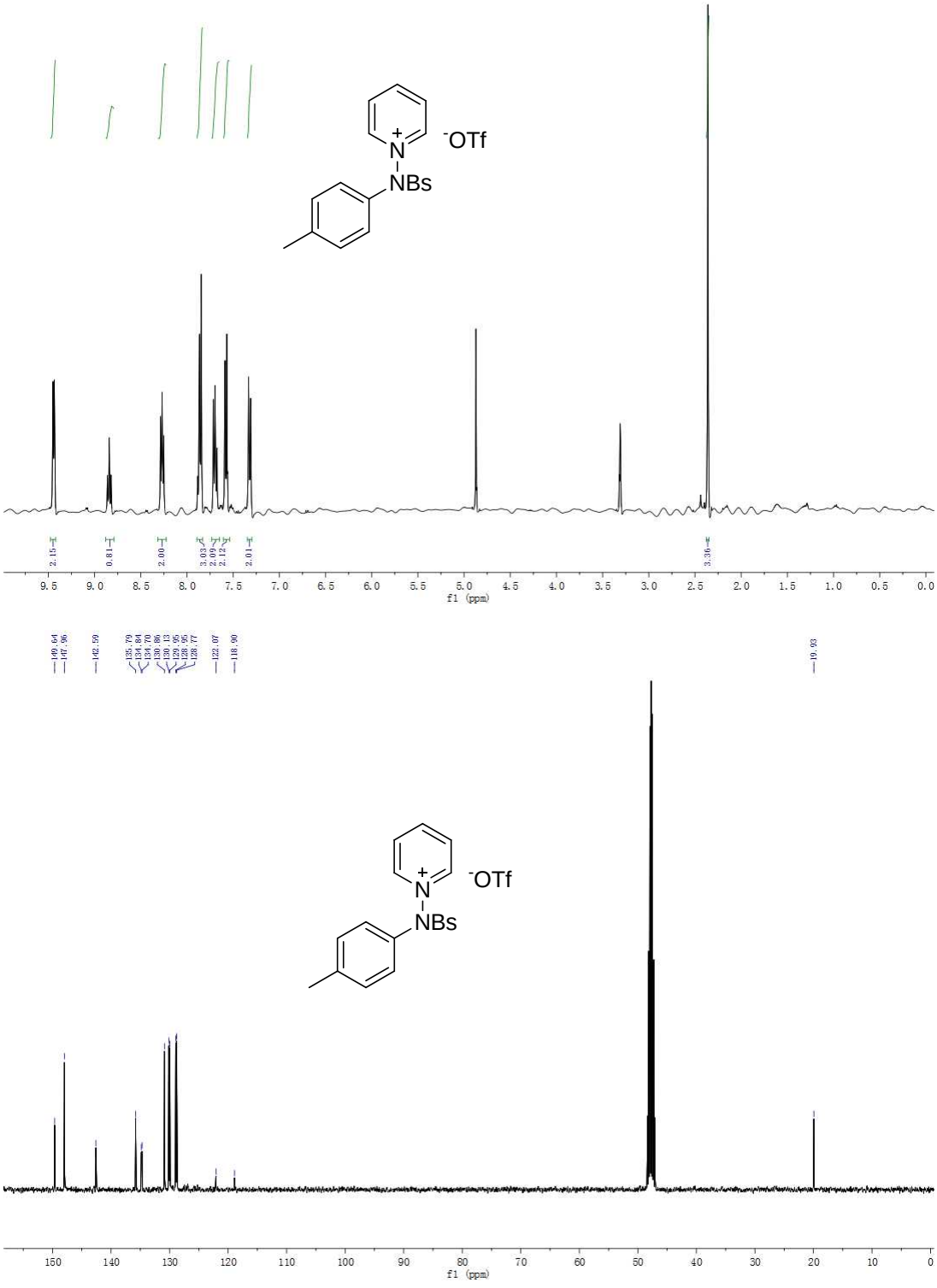
3-chloro-1-(N-(4-(methoxycarbonyl)phenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3qf)



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

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

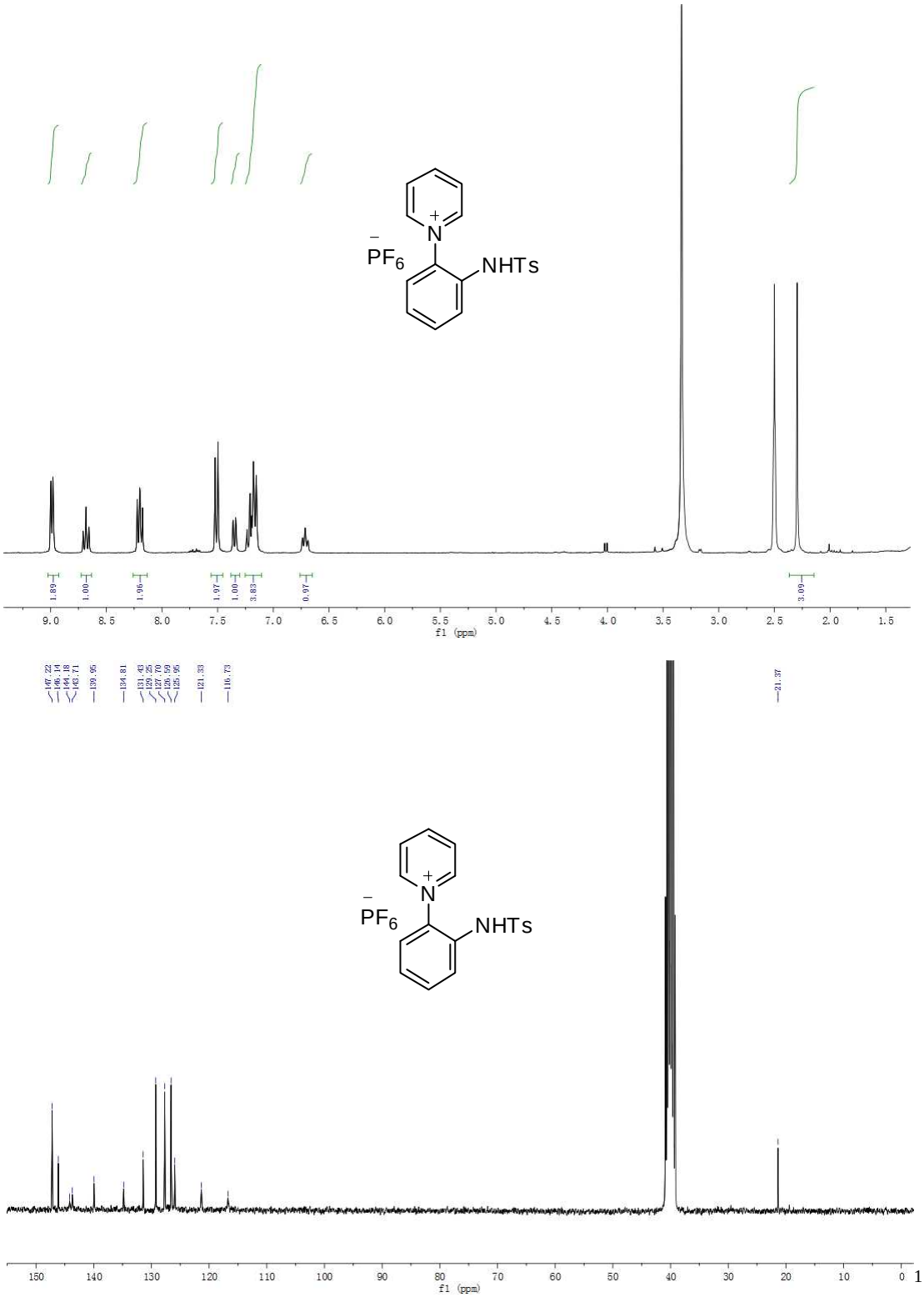
1-(N-(p-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3dg)



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

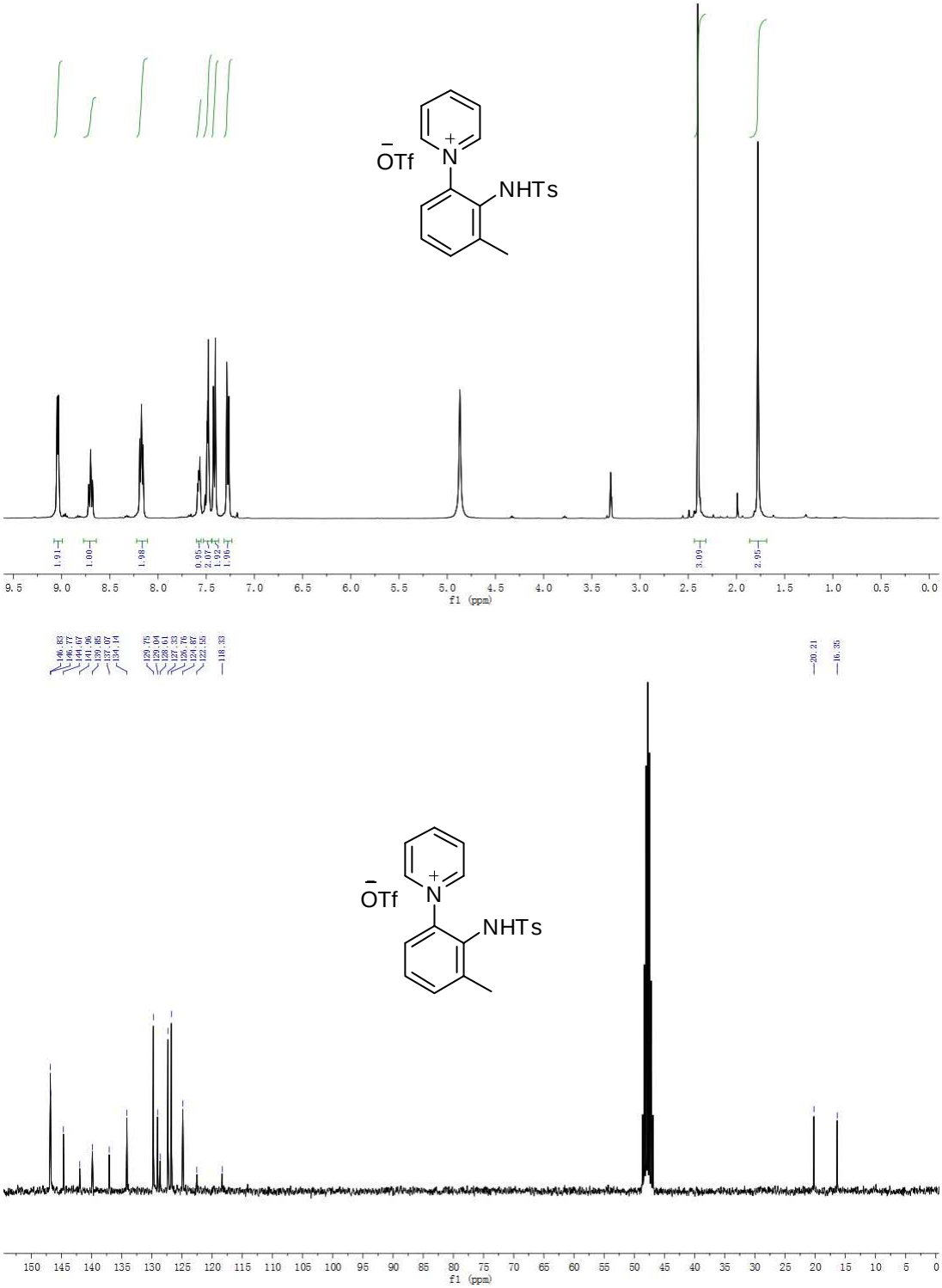
^{13}C NMR (101 MHz, METHANOL-D4) (down)

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



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

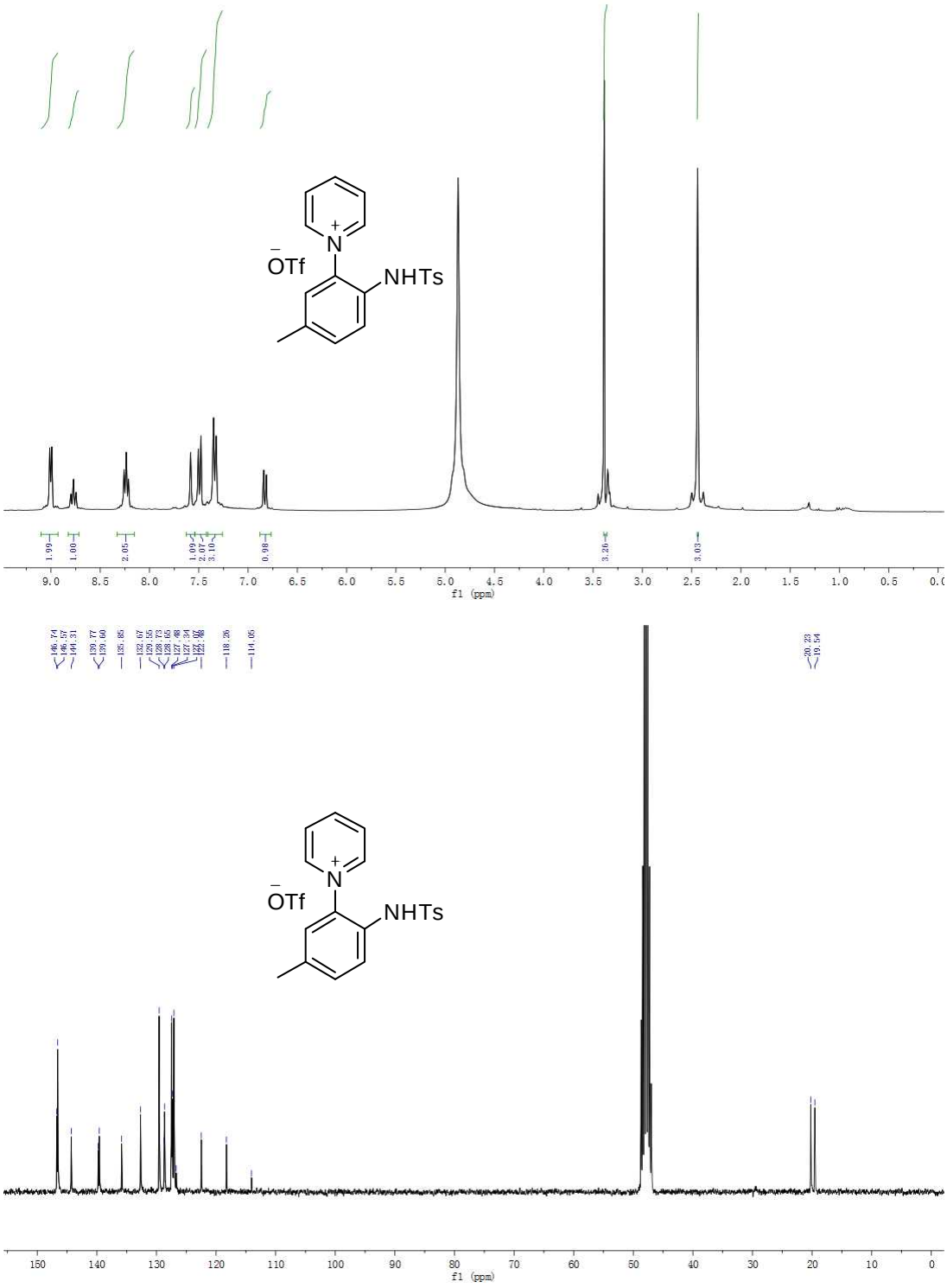
1-(3-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ba)



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

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

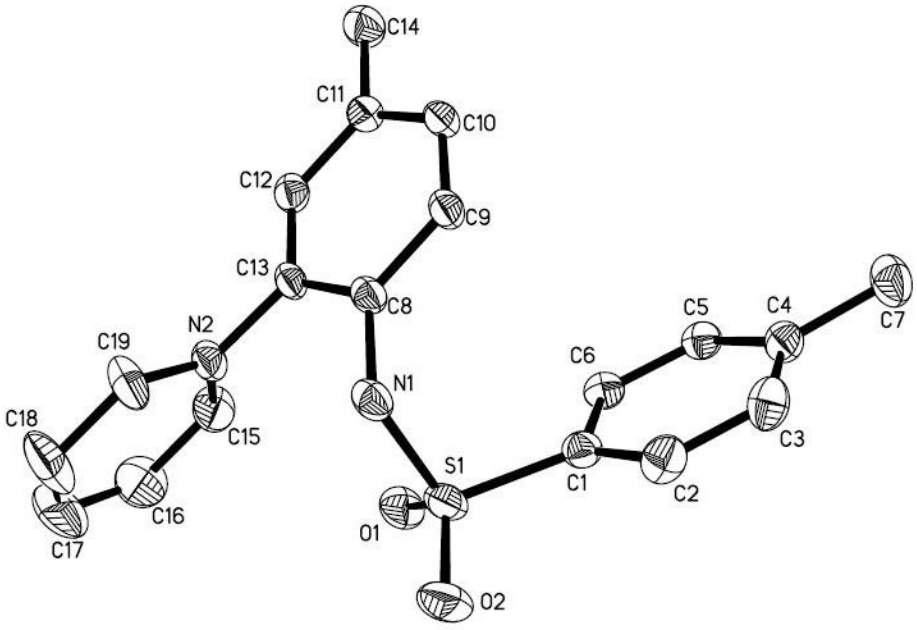
1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4da)



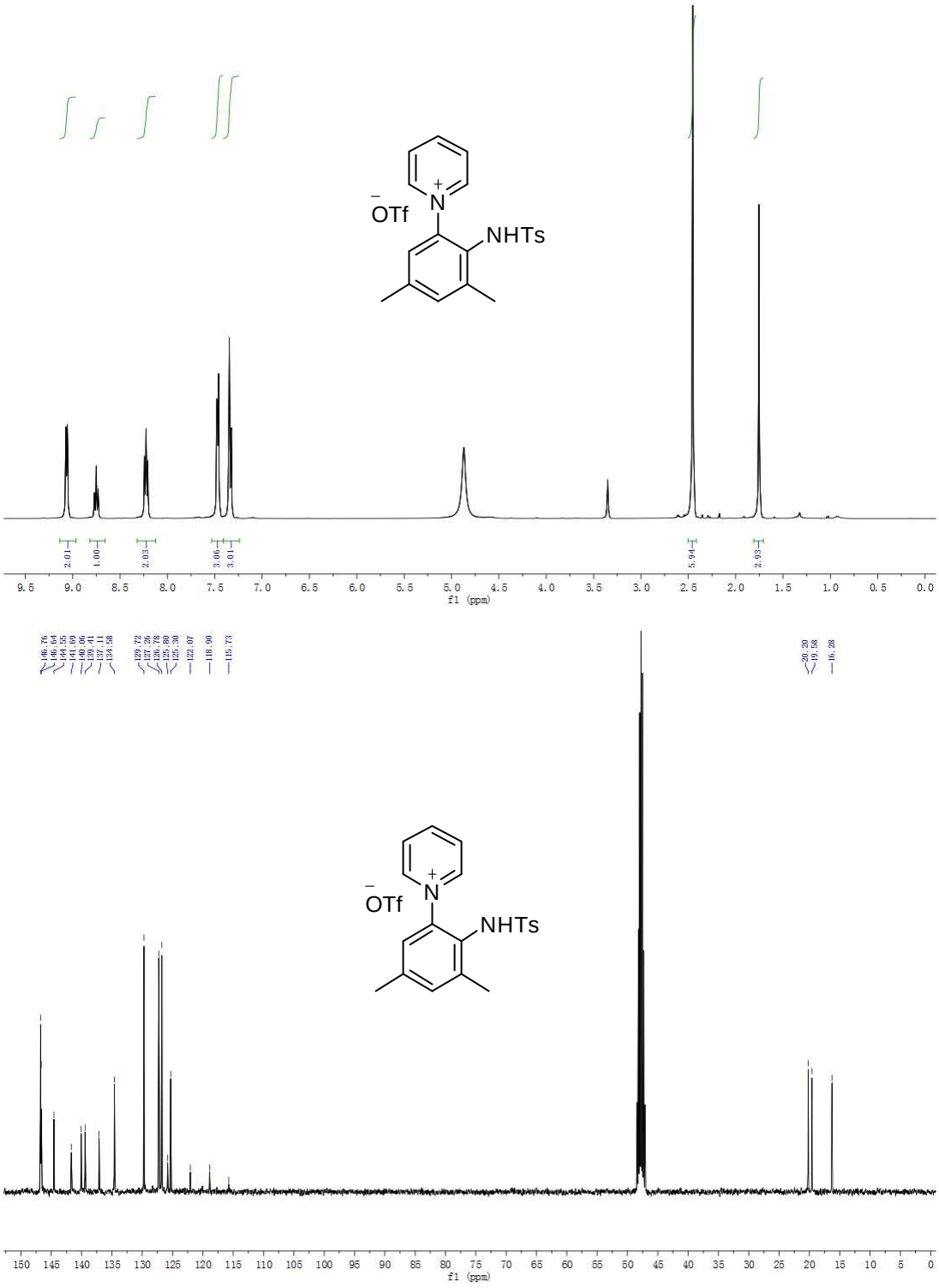
^{1}H NMR (301 MHz, METHANOL-D4) (up) and

^{13}C 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 CH_3OH. 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) $Å^3$, 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).



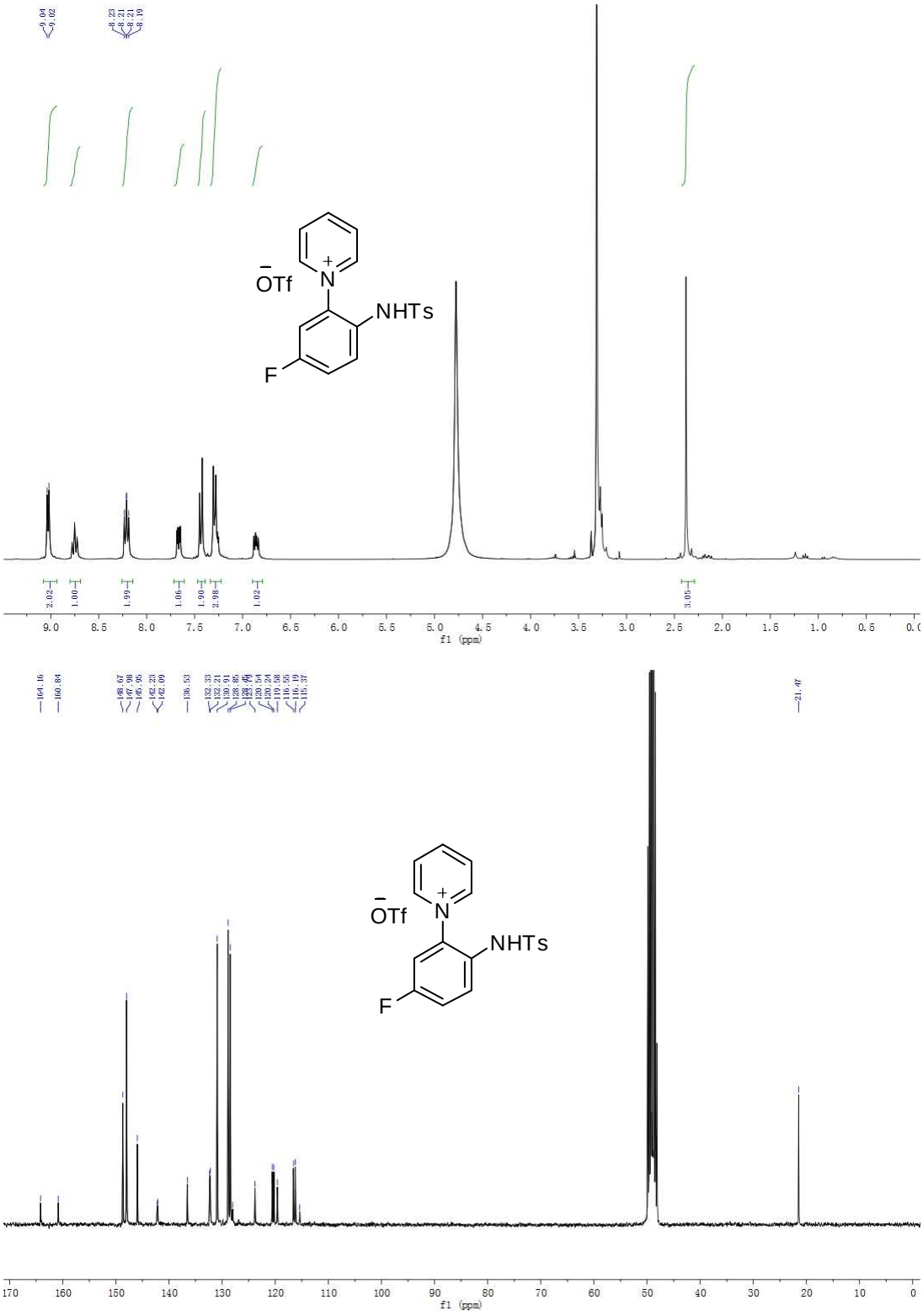
1-(3,5-dimethyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ea)



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

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

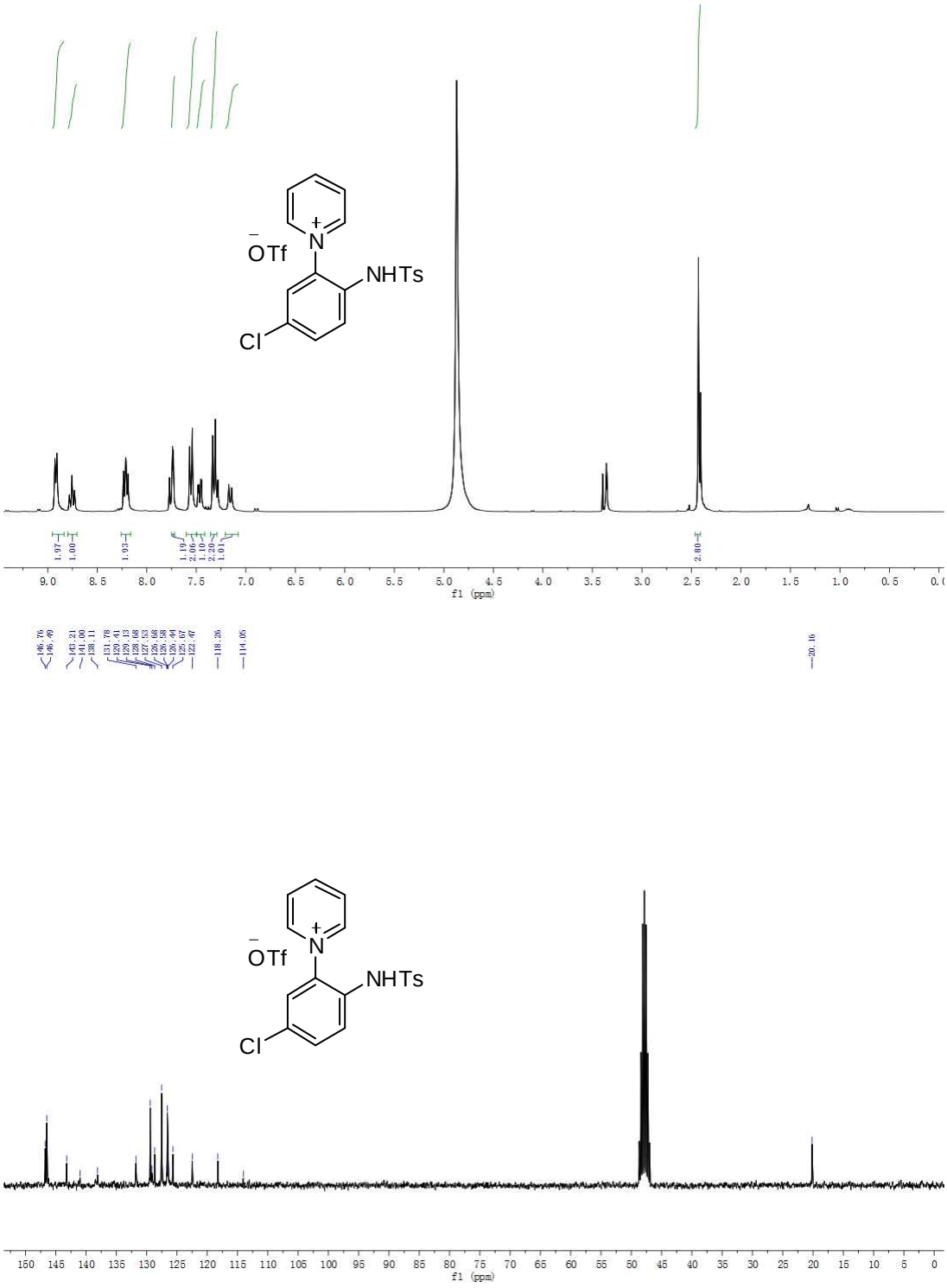
1-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ha)



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

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

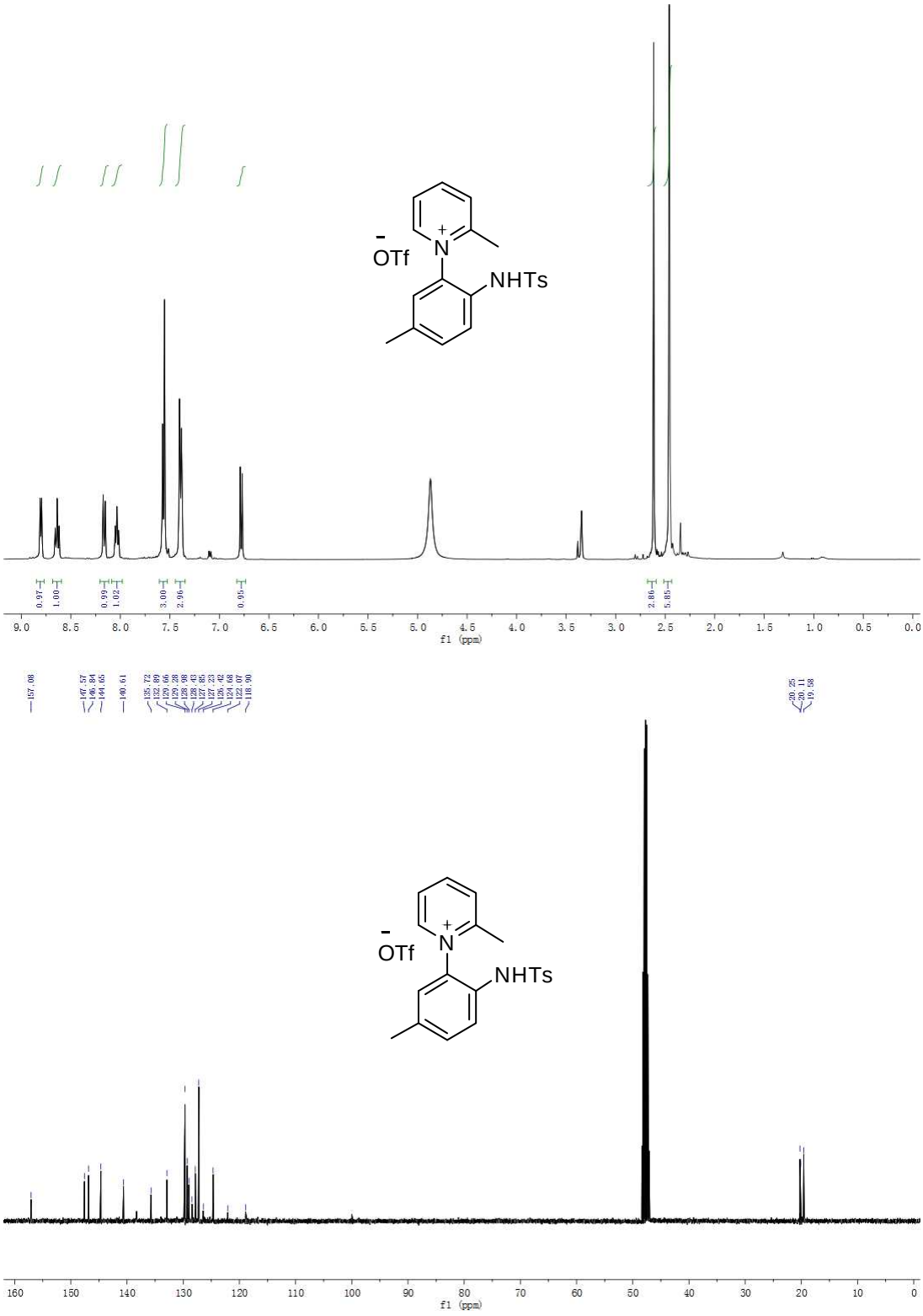
1-(5-chloro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ka)



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

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

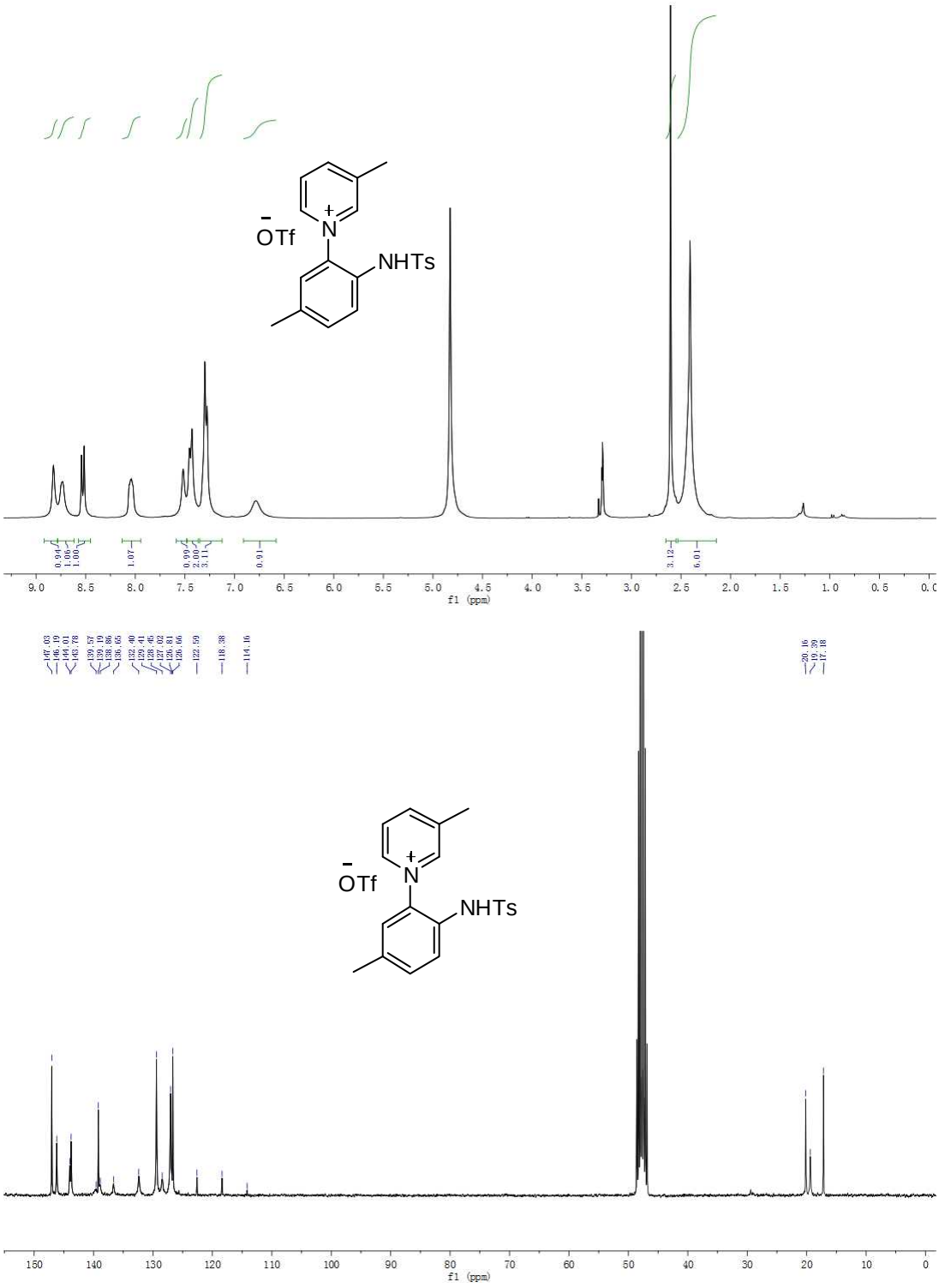
2-methyl-1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4db)



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

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

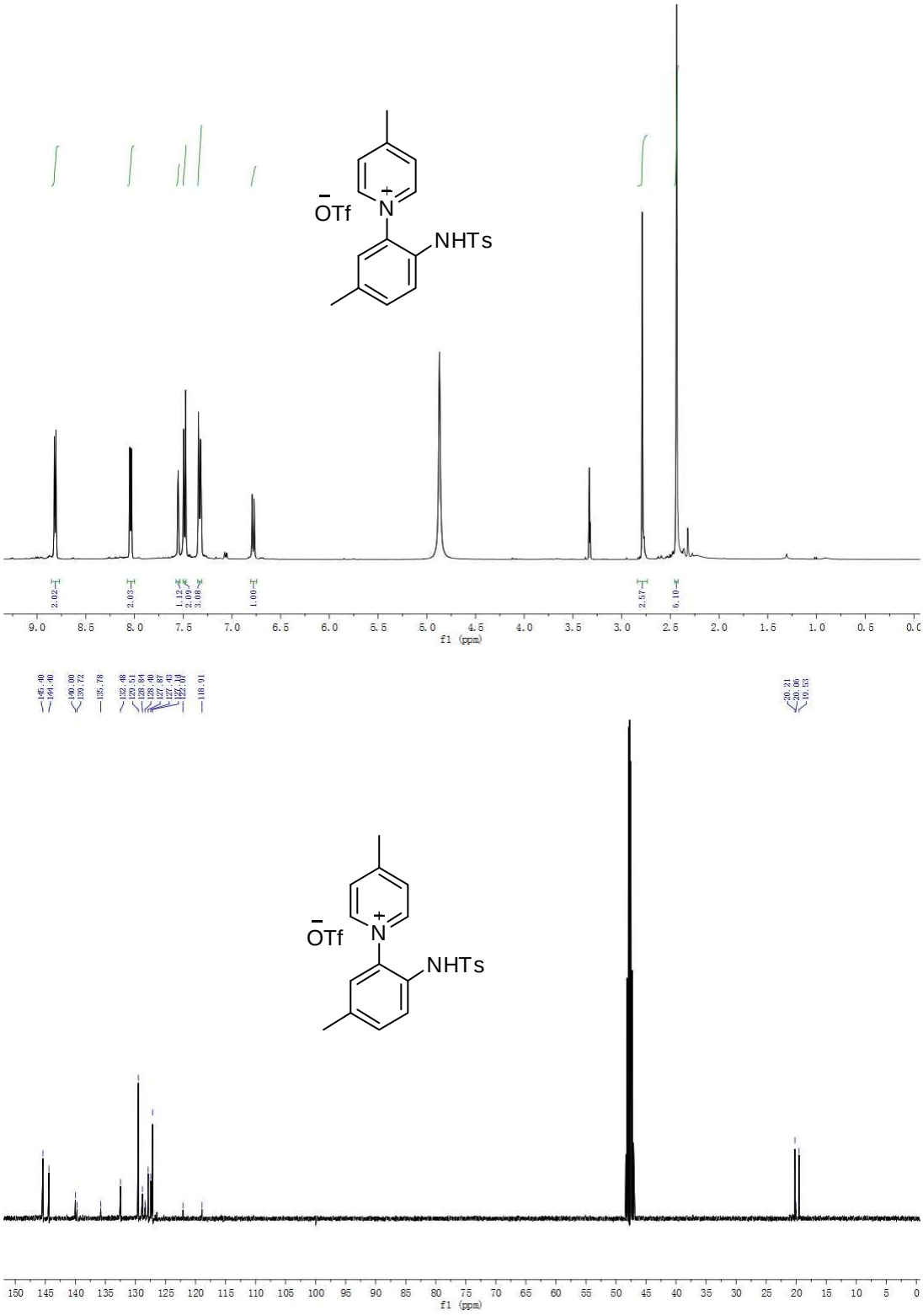
3-methyl-1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4dc)



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

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

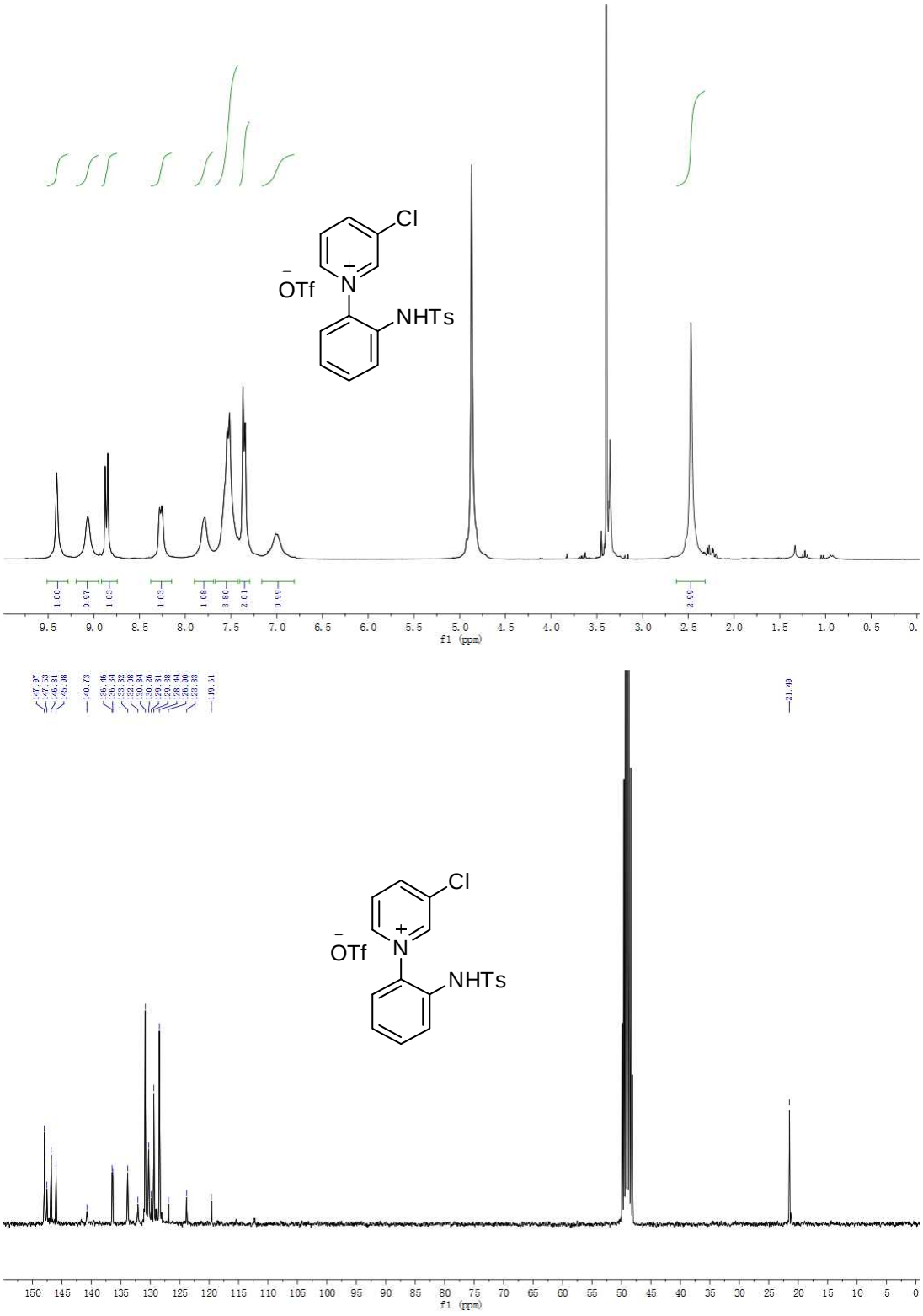
4-methyl-1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4dd)



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

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

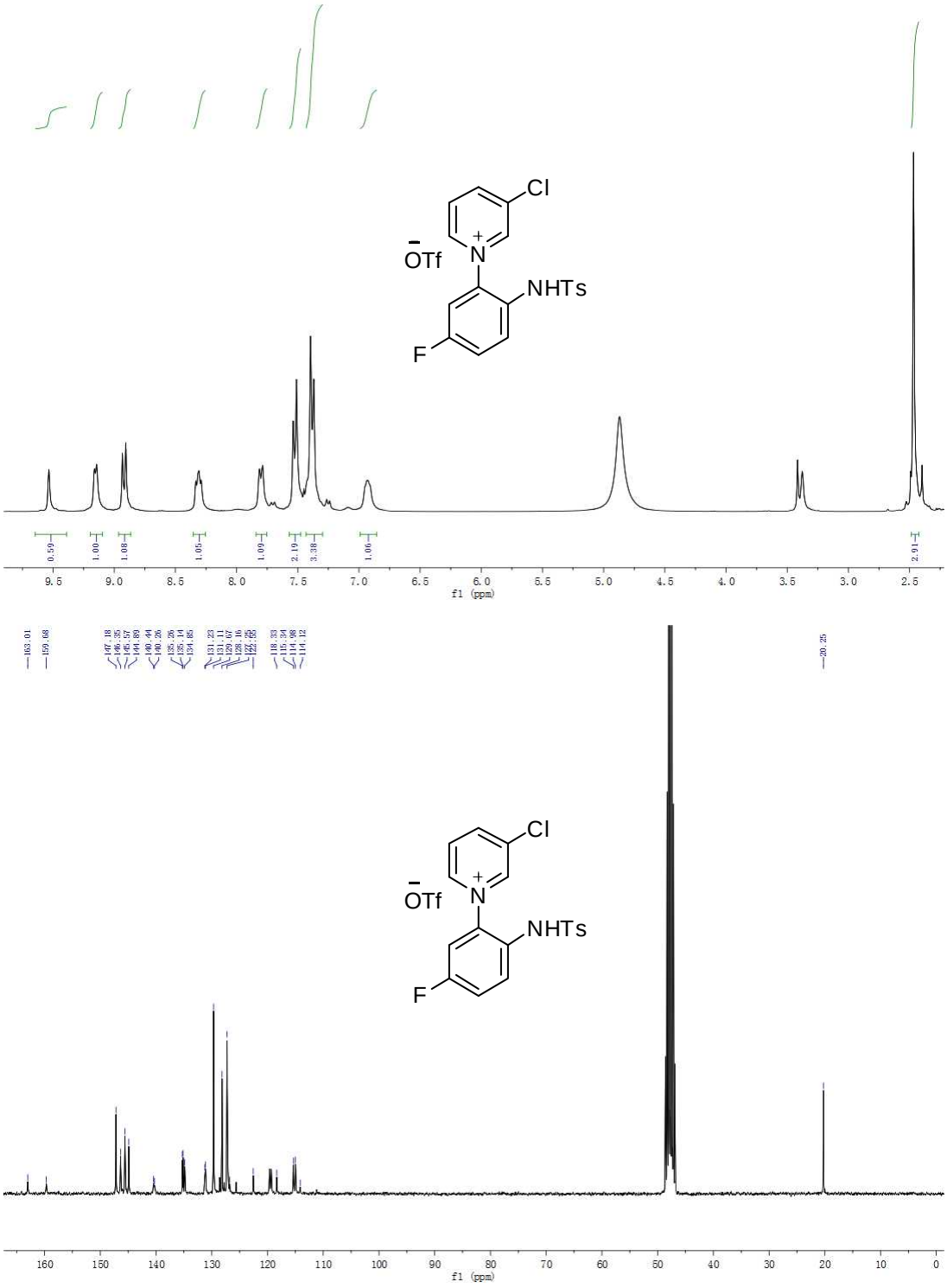
3-chloro-1-(2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4af)



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

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

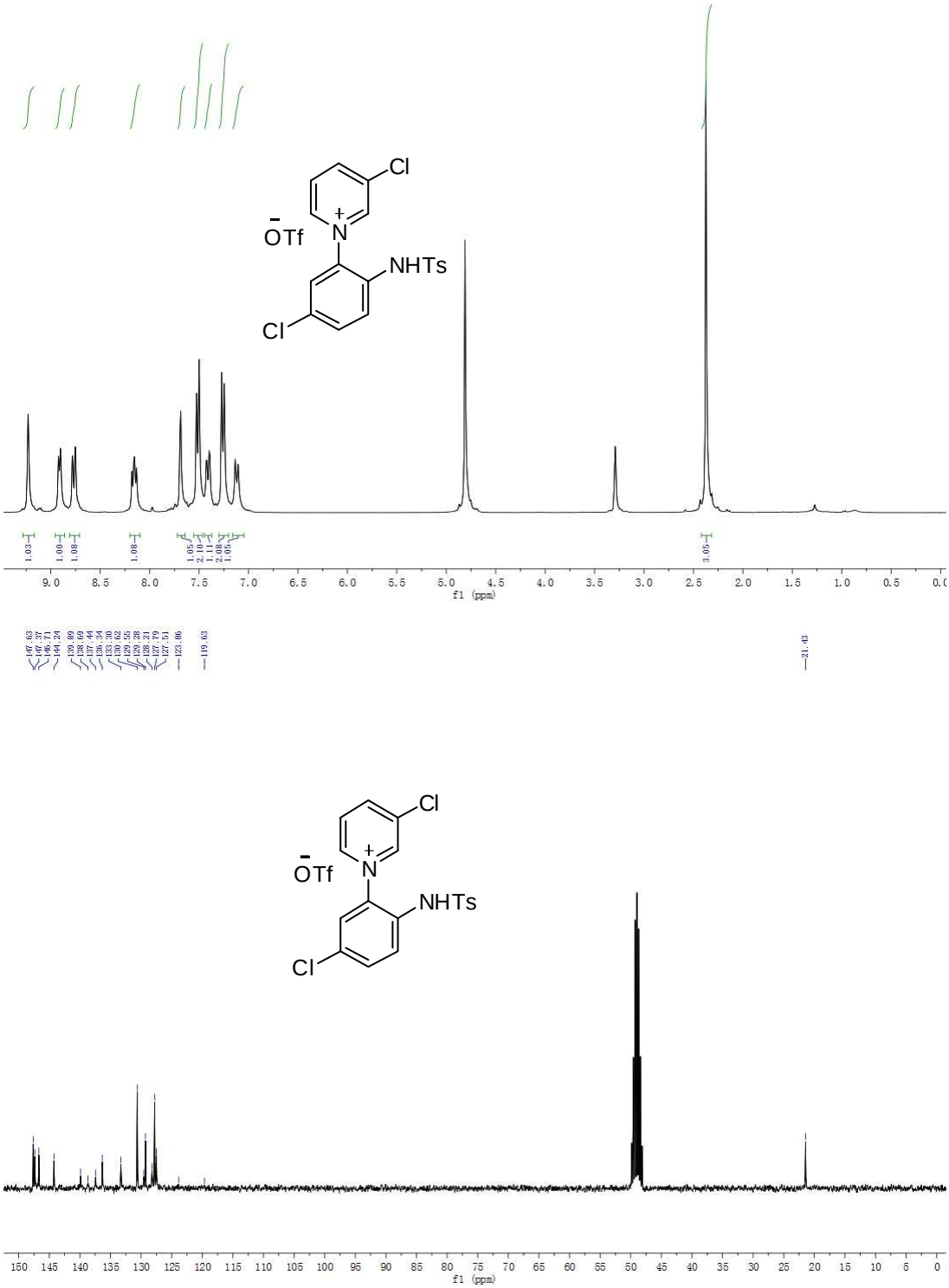
3-chloro-1-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4hf)



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

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

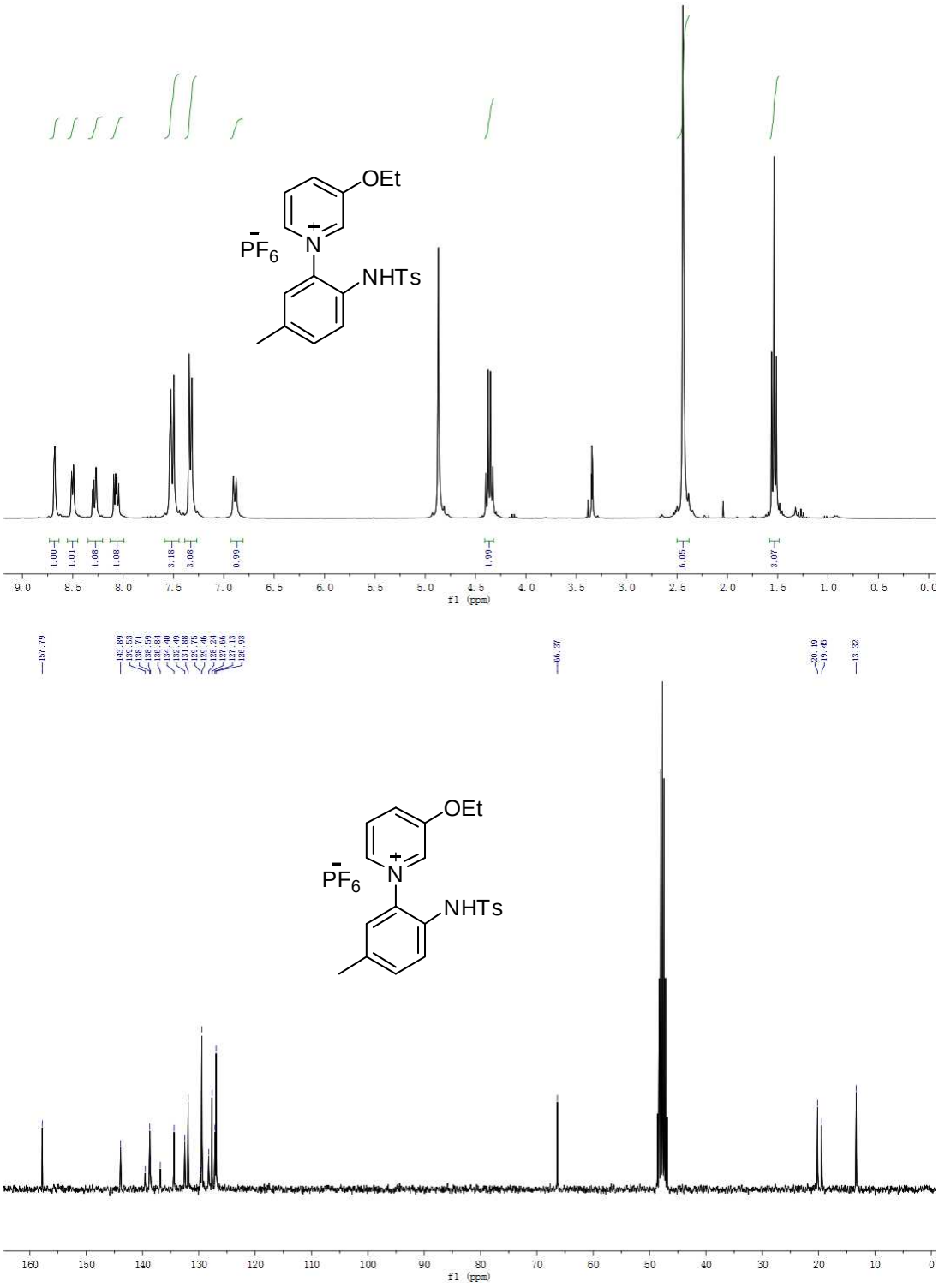
3-fluoro-1-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4kf)



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

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

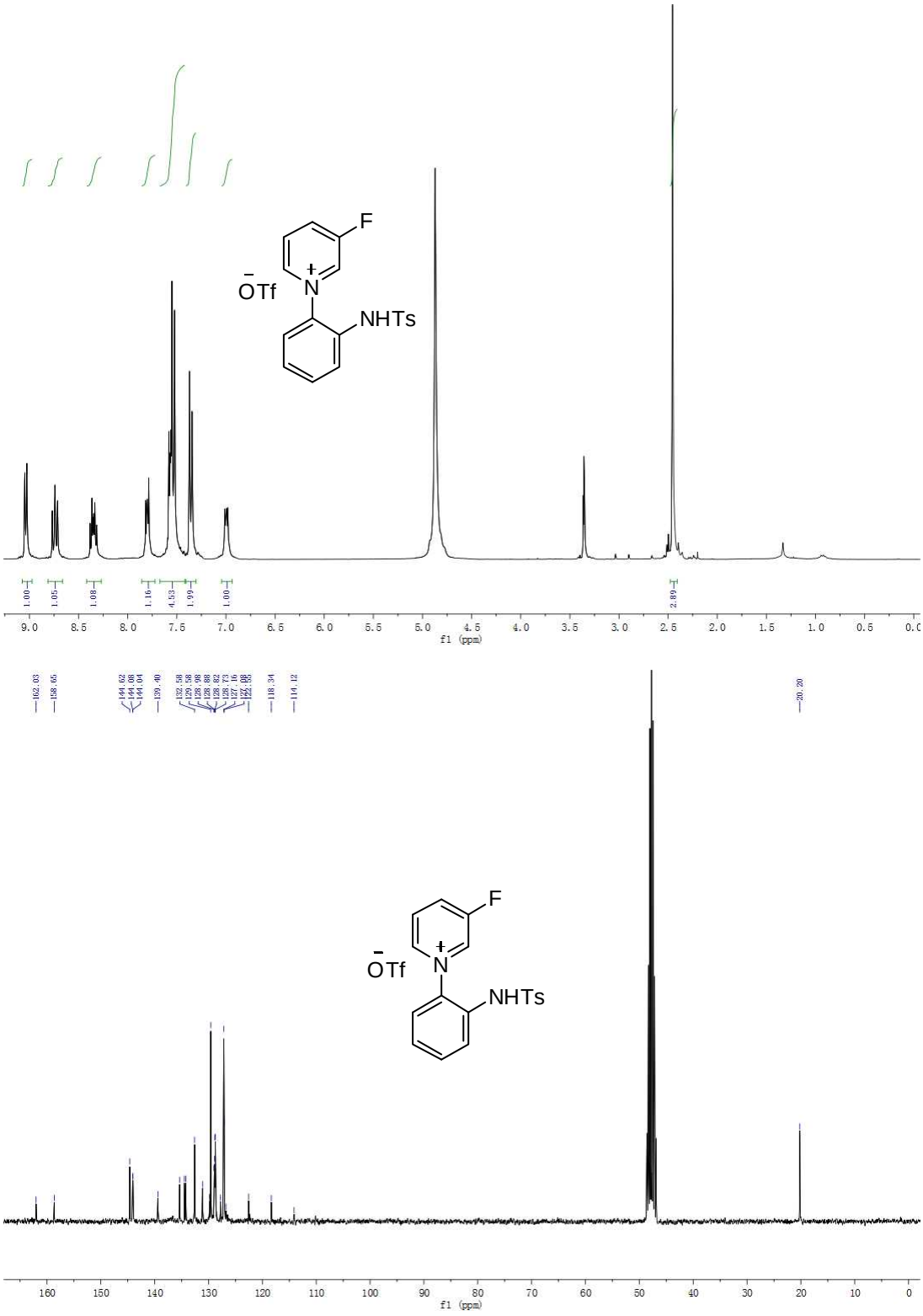
3-ethoxy-1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium hexafluorophosphate(V) (4de)



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

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

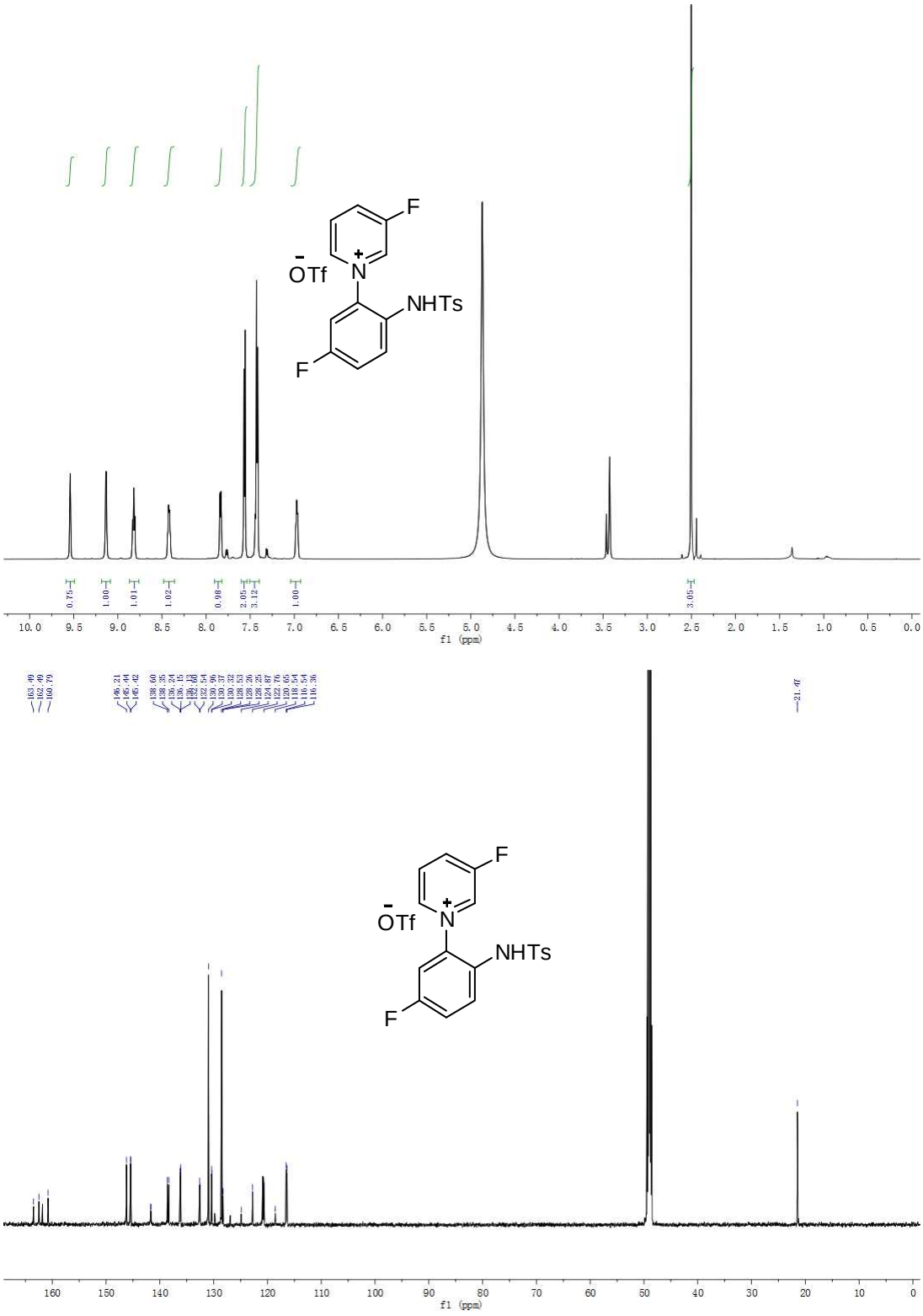
3-fluoro-1-(2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ah)



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

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

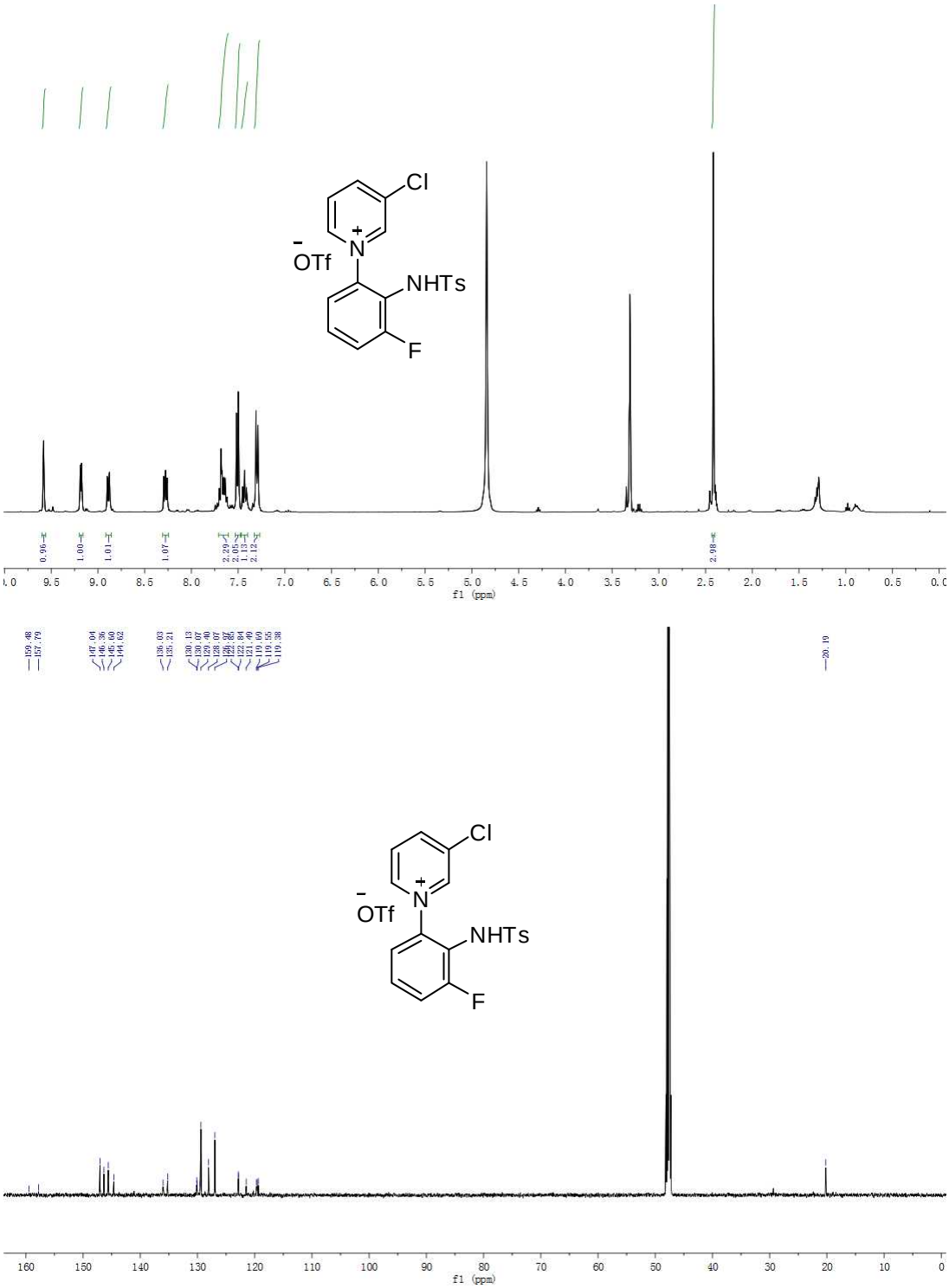
3-fluoro-1-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4hh)



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

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

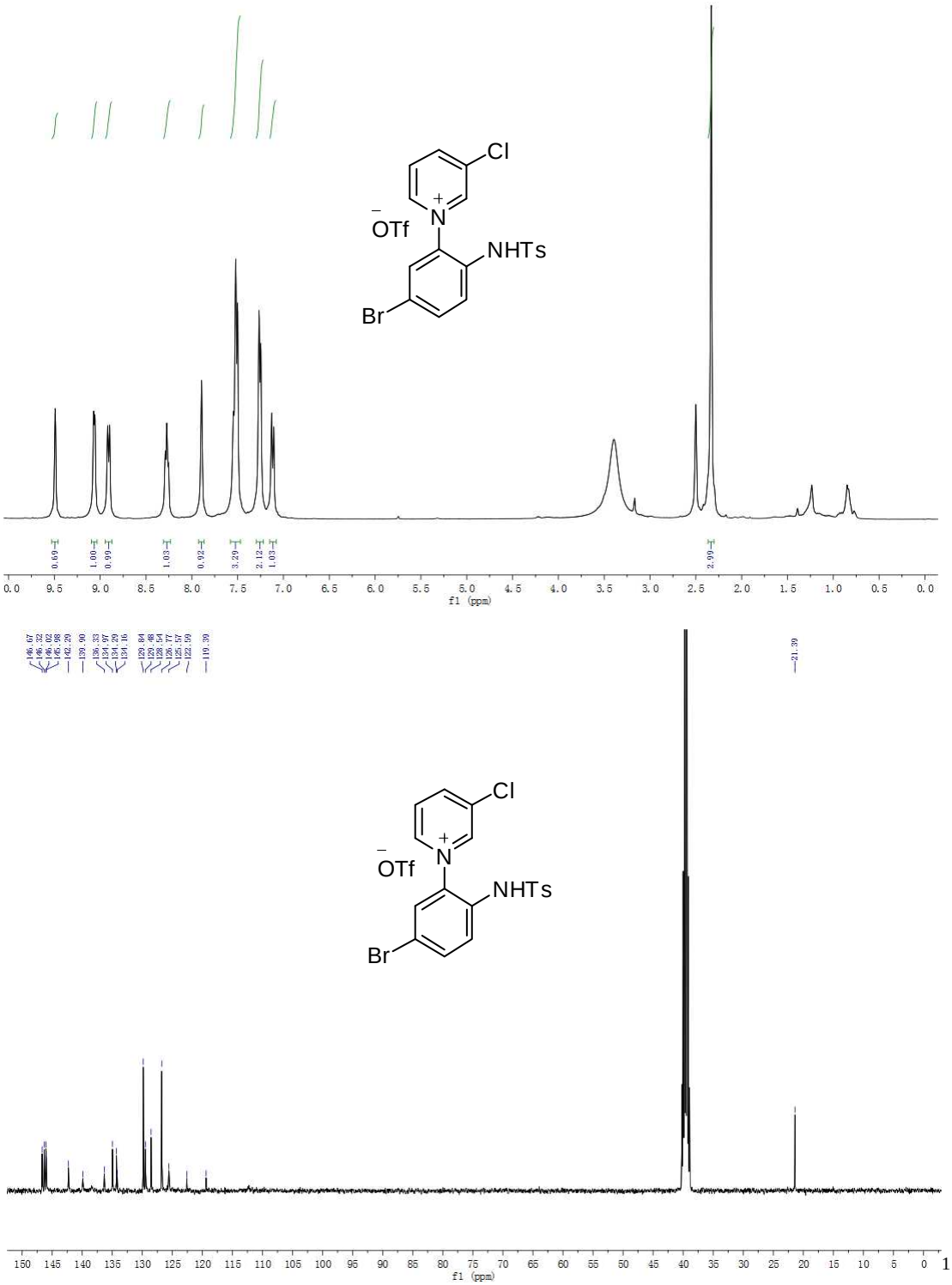
3-chloro-1-(3-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ff)



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

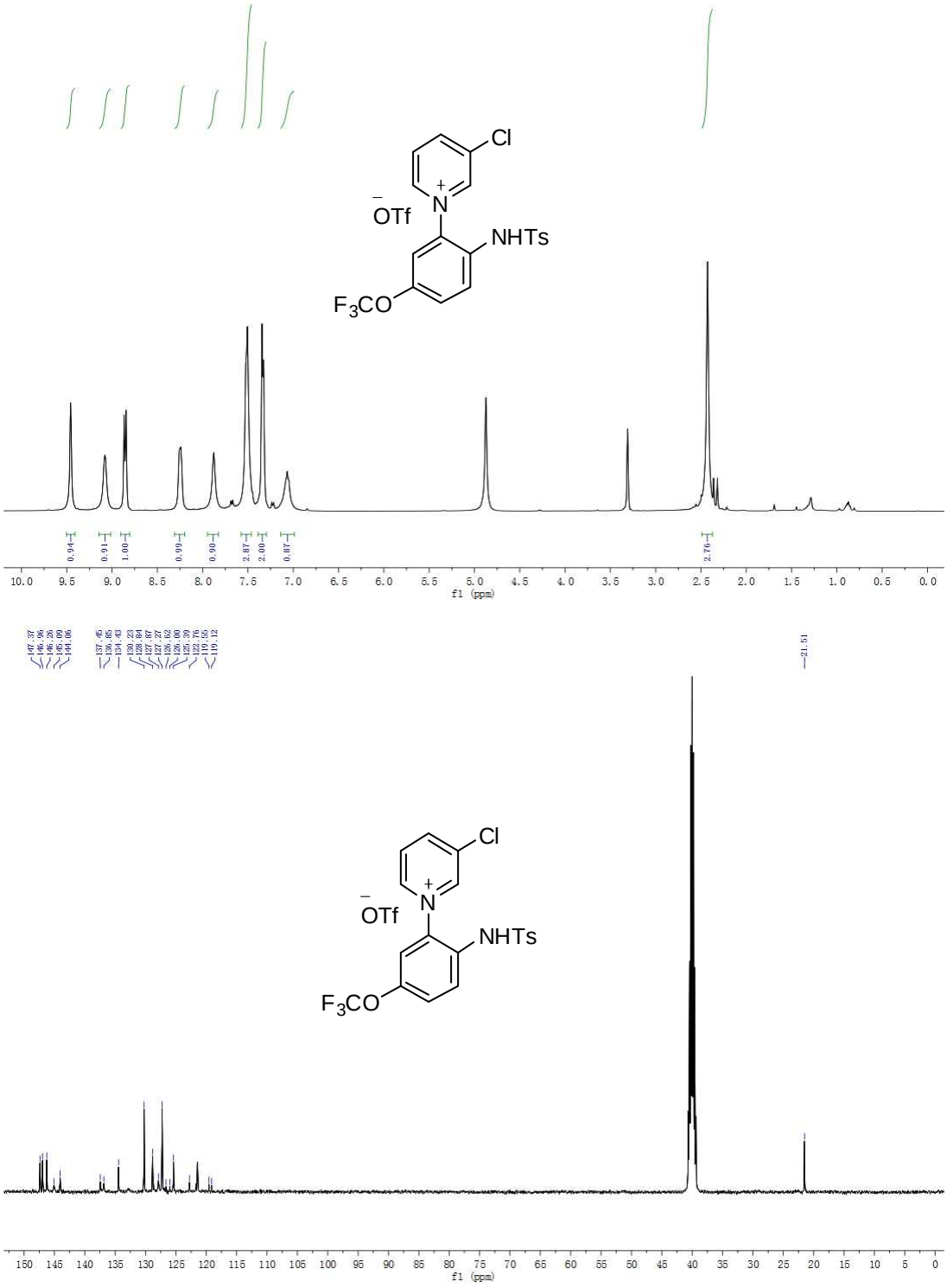
^{13}C NMR (151 MHz, METHANOL-D4) (down)

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



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

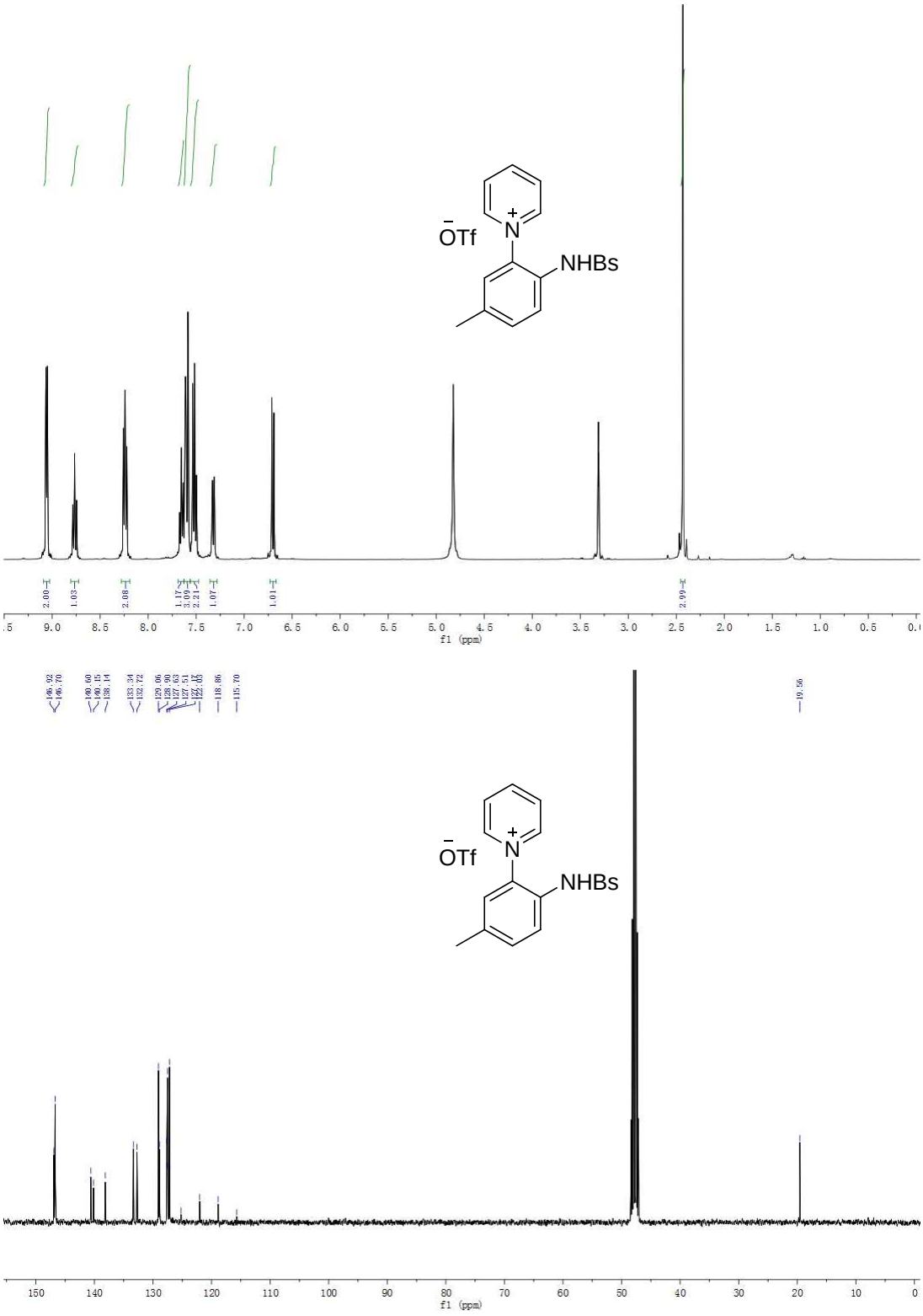
3-chloro-1-(2-(4-methylphenylsulfonamido)-5-(trifluoromethoxy)phenyl)pyridin-1-ium trifluoromethanesulfonate (4of)



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

^{13}C NMR (101 MHz, DMSO-D6) (down)

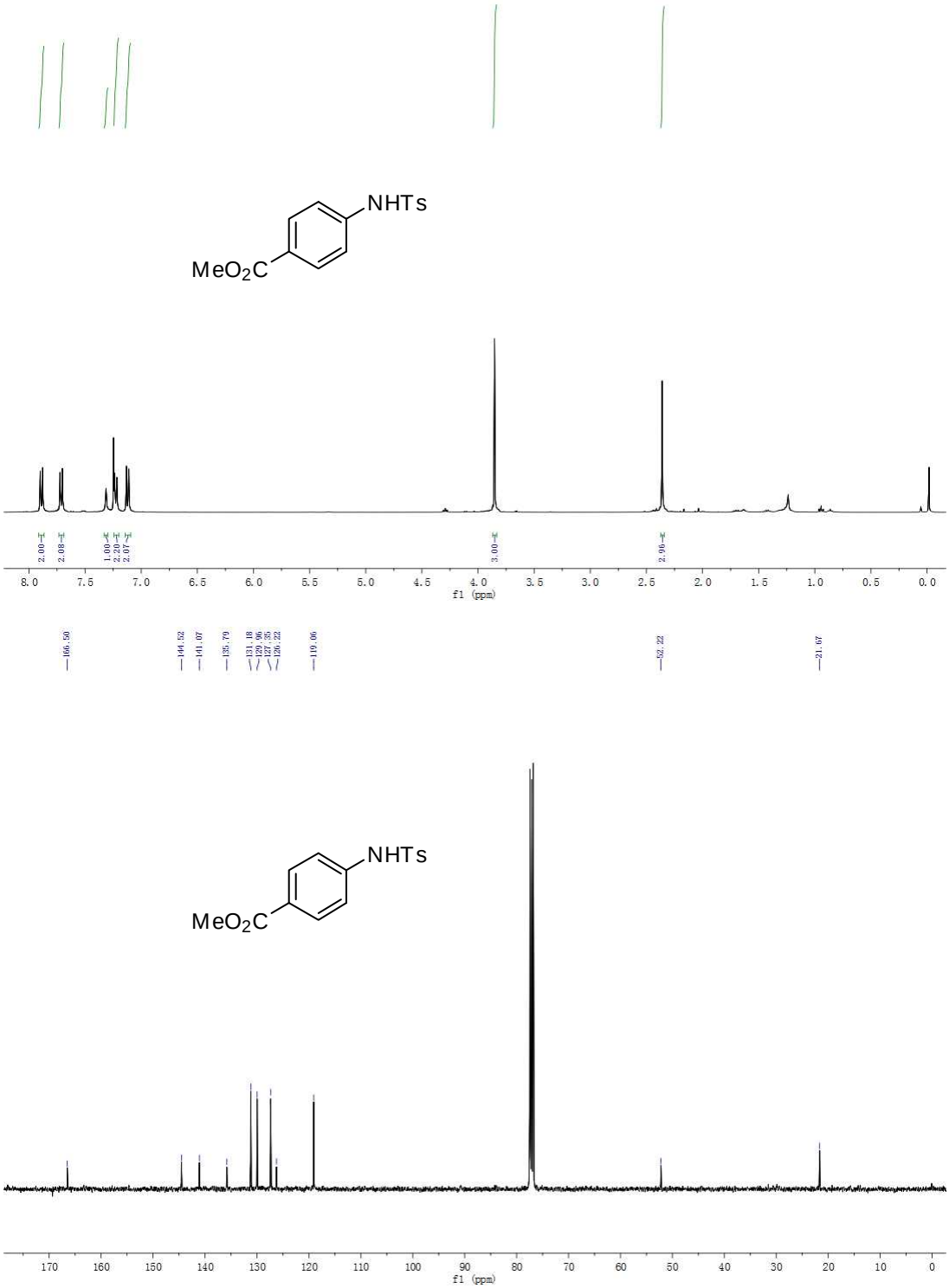
1-(5-methyl-2-(phenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4dg)



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

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

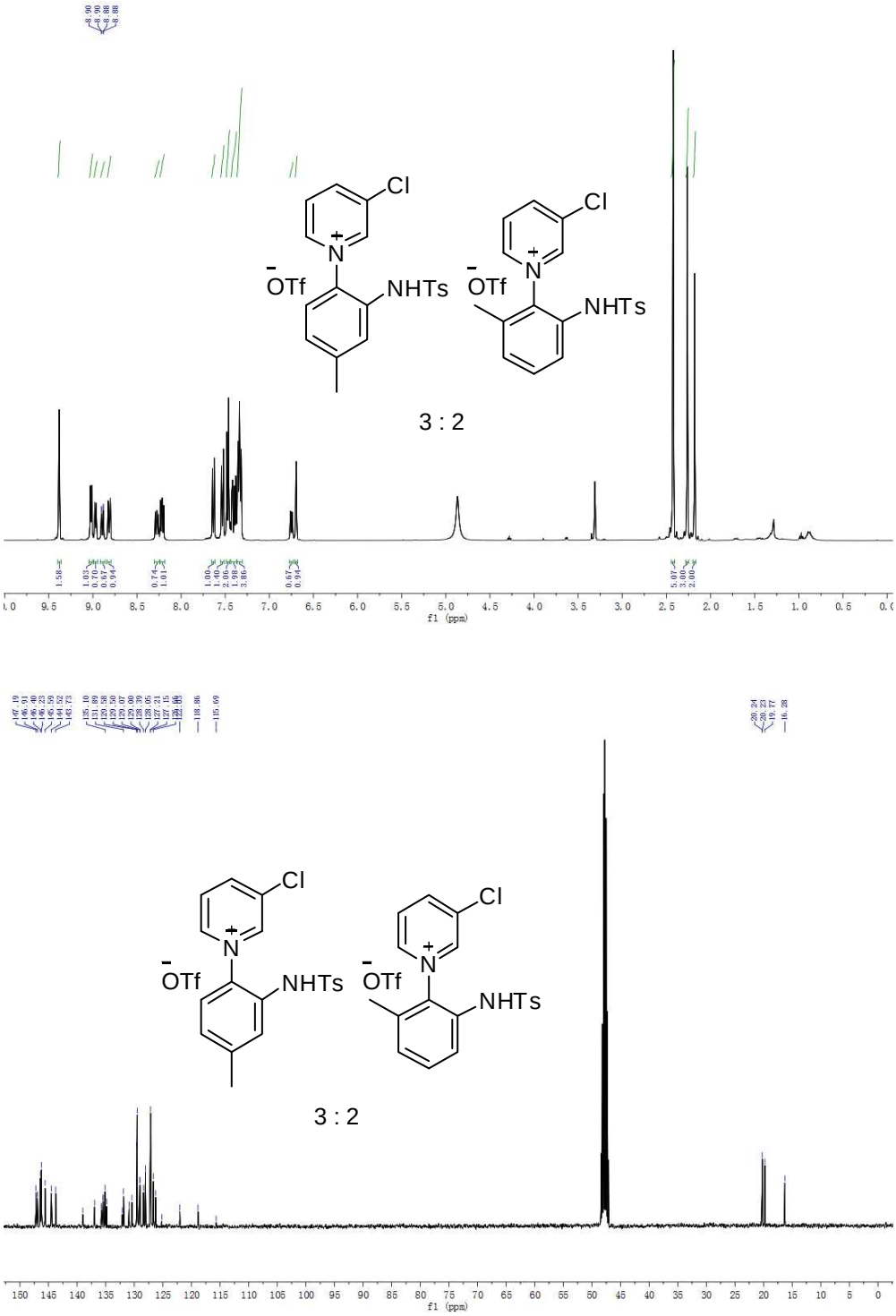
methyl 4-(4-methylphenylsulfonamido)benzoate (7)



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

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

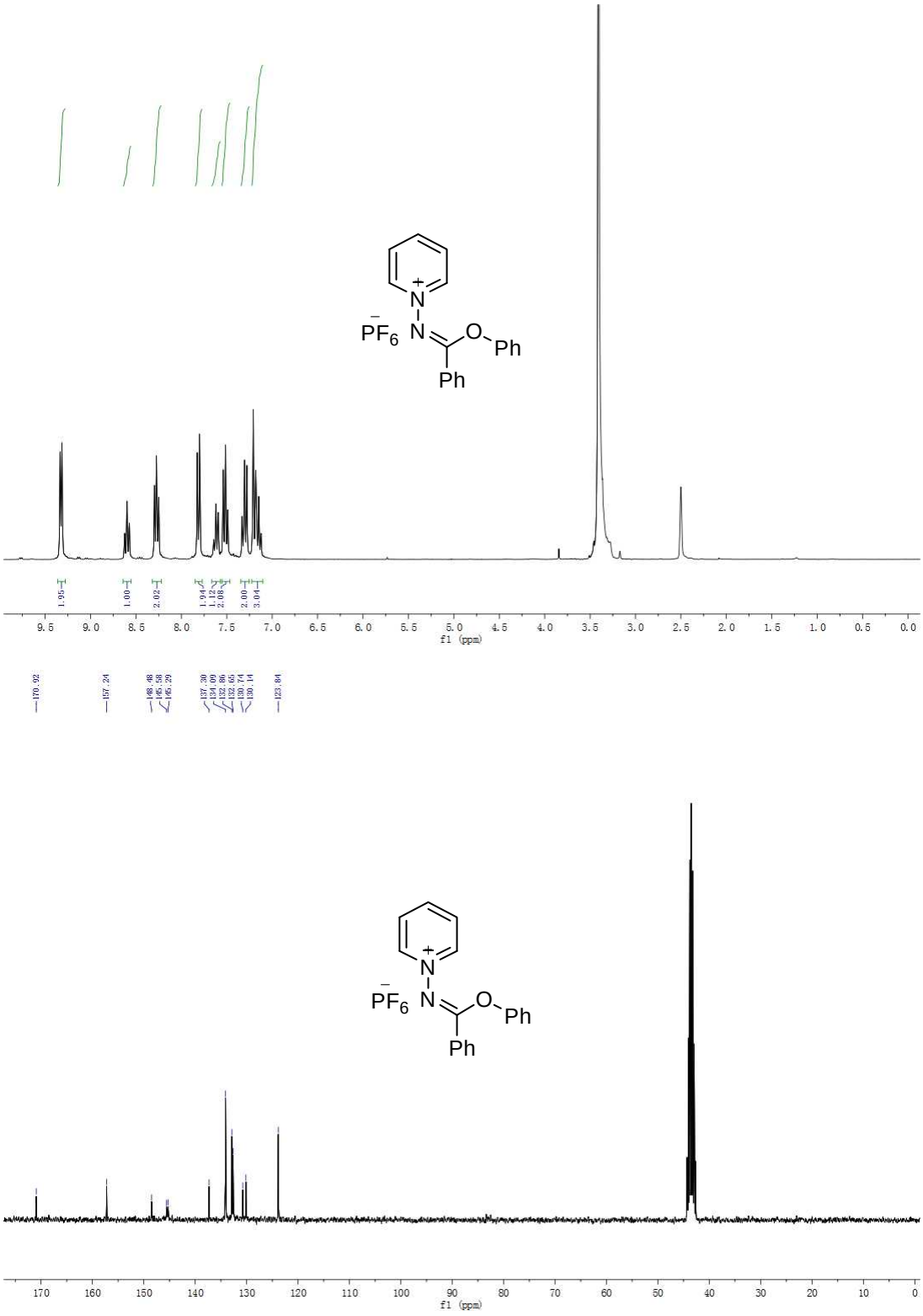
3-chloro-1-(2-methyl-6-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4cf-2)



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

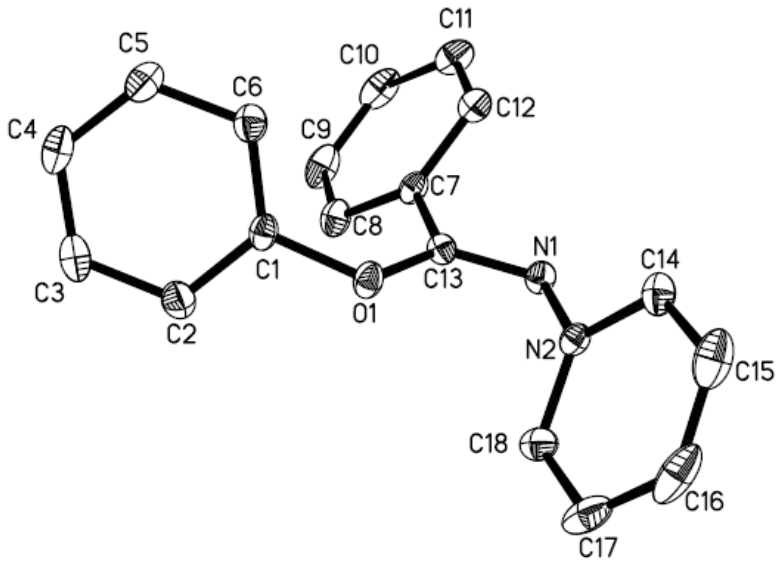
^{13}C NMR (101 MHz, METHANOL-D4) (down)

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

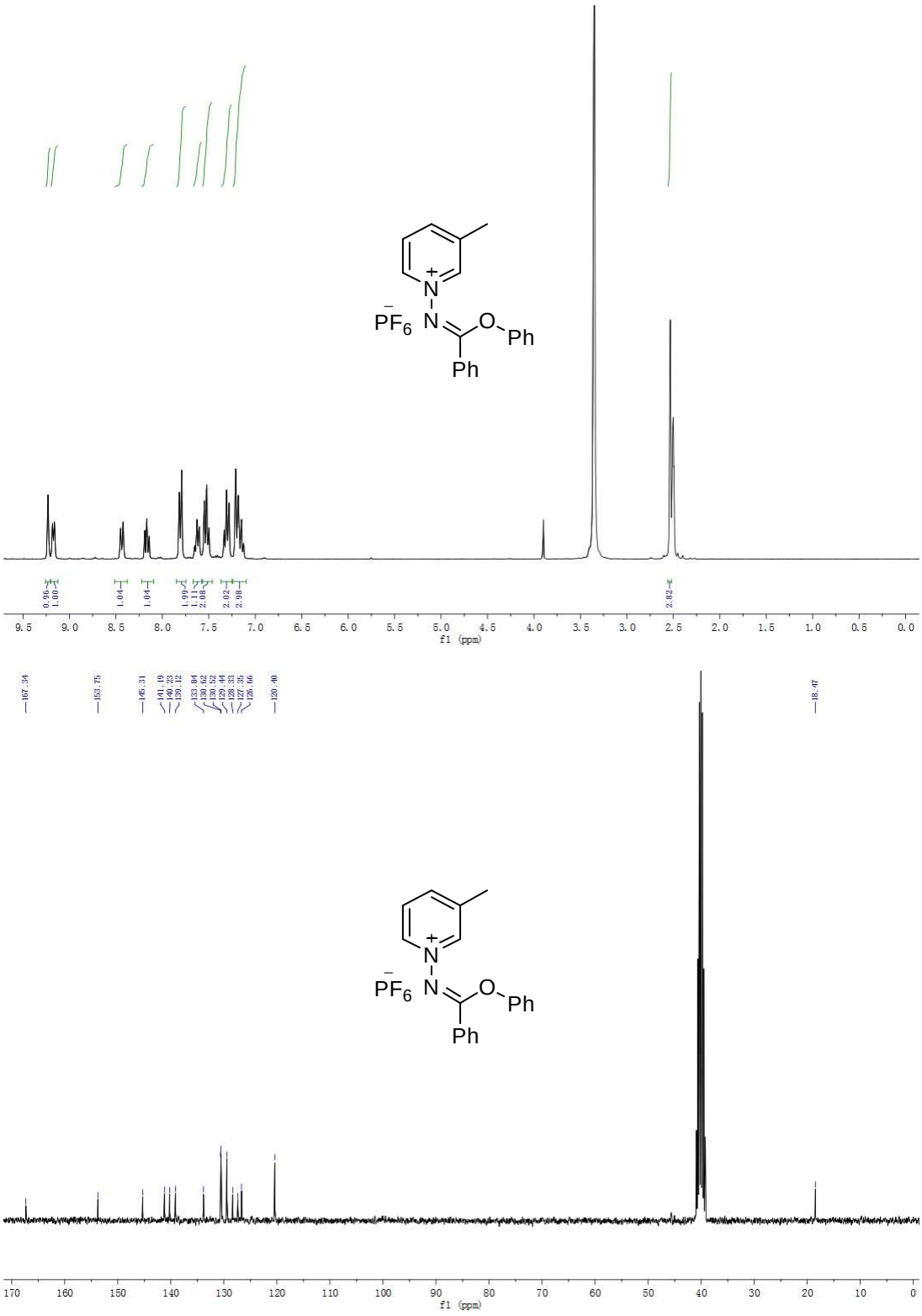


^{1}H NMR (301 MHz, DMSO-D6) (up) and ^{13}C NMR (76 MHz, DMSO-D6) (down)

X-ray crystal structure analysis of compound 6a: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in CH_3OH. 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) $Å^3$, 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)



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