Supporting Information

Halide-Promoted Pyridinylation of α-Acylmethylides by 2-Halo-1-methylpyridinium Iodides as Reagents

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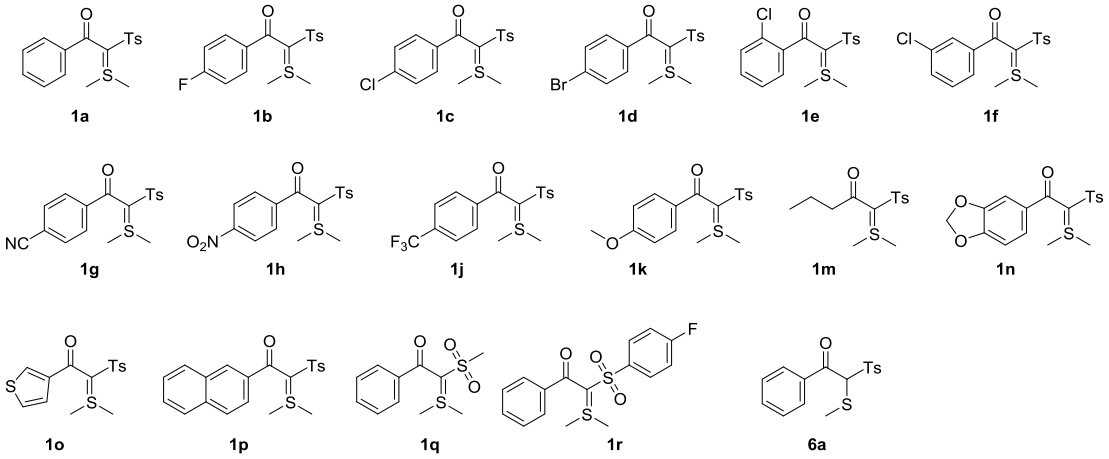
1. Experimental

1.1 General information

Unless otherwise noted, all materials were purchased from commercial suppliers. MeCN, DCE, and DCM were refluxed over CaH_2 and freshly distilled prior to use. THF and toluene (PhMe) were refluxed over sodium with benzophenone as an indicator and freshly distilled prior to use. Flash column chromatography was performed using silica gel (normal phase, 200–300 mesh) from Branch of Qingdao Haiyang Chemicals. The thin layer chromatography (TLC) silica gel preparative plates were purchased from Anhui Liangchen Silicon Material Co. Ltd. Column chromatography was performed using silica gel (normal phase, 200–300 mesh) from Branch of Qingdao Haiyang Chemical, with petroleum ether (PE, 60−90 °C fraction) and ethyl acetate (EA). Reactions were monitored by thin-layer chromatography on silica gel GF254 coated 0.2 mm plates from Institute of Yantai Chemical Industry. The plates were visualized under UV light. ^{1}H (400 MHz), ^{13}C (101 MHz), and ^{19}F NMR (377 MHz) spectra were recorded on a Bruker 400 NMR spectrometer usually with TMS as an internal standard for ^{1}H NMR, the middle peak (77.16 ppm) of $CDCl_3$ for ^{13}C NMR, and TFA (-76.55 ppm) as an external standard for ^{19}F NMR in $CDCl_3$ solution and the chemical shifts (δ) were reported in parts per million (ppm). HRMS measurements were carried out on an LC/MSD TOF mass spectrometer. Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected.

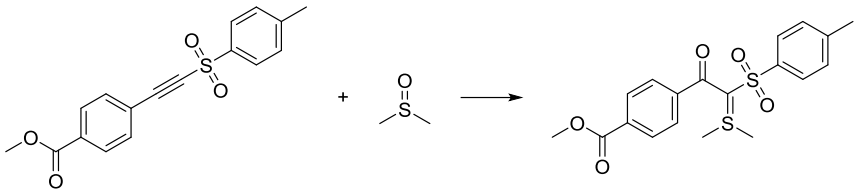
α-Acyl Sulfonylmethylides **1a**–**1h**,[1] **1j**,[1] **1k**,[1] **1m–1r**[1] and **6a**[2] were reported in our previous work.



1.2 Synthesis of α-Acyl Sulfonylmethylides 1i, 1l, 1s, 1t, 1u and 1x

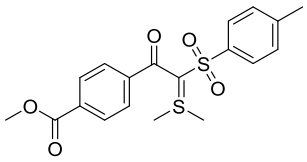
1i, **1l**, **1s** and **1x**, prepared by referring literature[1]

1.2.1 Synthesis of 1i



1i

Methyl 4-(tosylethynyl)benzoate (629 mg, 2.0 mmol, prepared by referring literature[3]) was dissolved in anhydrous DMSO (15.0 mL) in a 35 mL pressure tube without inert atmosphere (Sealed after adding). The reaction mixture was further stirred in an oil bath at 150 °C for 35 mins. After cooling and addition of water (60 mL), the mixture was extracted with DCM (3 × 20 mL), and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with a mixture of petroleum ether (60–90 °C) and ethyl acetate (2:1, *v*/v) to dichloromethane and methanol (40/1, *v*/*v*) as eluent to afford **1i**.

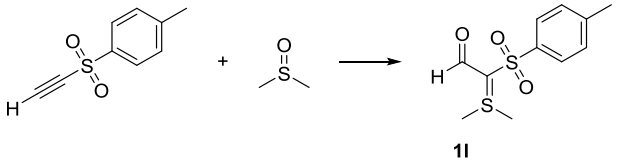


Methyl 4-(2-(dimethyl-λ^4-sulfaneylidene)-2-tosylacetyl)benzoate **(1i)**

Colorless crystals; yield: 630 mg (80%); M.p. 231–232 °C; R_f = 0.35 (DCM/MeOH 15:1, *v*/*v*).

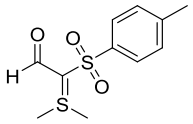
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (d, J = 7.9 Hz, 2H), 7.71 (s, 2H), 7.35 (s, 2H), 7.32 (d, J = 7.9 Hz, 2H), 3.86 (s, 3H), 3.12 (s, 6H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.6, 166.3, 146.6, 142.8, 142.4, 130.3, 129.5, 129.1, 127.7, 127.0, 81.0, 52.7, 29.4, 21.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{21}O_5S_2^+$ 393.0825, found 393.0834.

1.2.2 Synthesis of 1l



1l

1-(Ethynylsulfonyl)-4-methylbenzene (1.20 g, 6.66 mmol, prepared by referring literature[4]) was dissolved in anhydrous DMSO (25.0 mL) in a 35 mL pressure tube without inert atmosphere (Sealed after adding). The reaction mixture was further stirred in an oil bath at 150 °C for 45 mins. After cooling and addition of water (100 mL), the mixture was extracted with DCM (3 × 20 mL), and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with a mixture of petroleum ether (60–90 °C) and ethyl acetate (2:1, *v*/v) to dichloromethane and methanol (40/1, *v*/*v*) as eluent to afford **1l**.

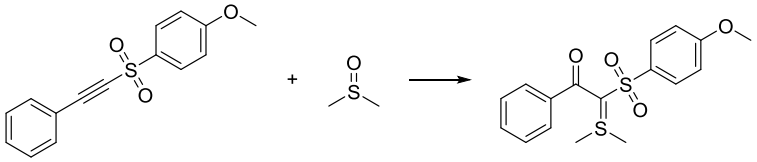


Methyl 2-(dimethyl-λ^4-sulfaneylidene)-2-tosylacetaldehyde **(1l)**

Brown crystals; yield: 1.18 g (69%); M.p. 154–155 °C; R_f = 0.75 (DCM/MeOH 10:1, *v*/*v*).

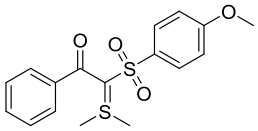
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.94 (s, 6H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.2, 142.7, 142.6, 129.8, 125.6, 79.8, 26.5, 21.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{11}H_{15}O_3S_2^+$ 259.0457, found 259.0461.

1.2.3 Synthesis of 1s



1s

1-Methoxy-4-((phenylethynyl)sulfonyl)benzene (8.59 g, 30.0 mmol, prepared by referring literature[5]) was dissolved in anhydrous DMSO (80.0 mL) in a 350 mL pressure tube without inert atmosphere (Sealed after adding). The reaction mixture was further stirred in an oil bath at 150 °C for 50 mins. After cooling and addition of water (200 mL), the mixture was extracted with DCM (4 × 100 mL), and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with a mixture of petroleum ether (60–90 °C) and ethyl acetate (2:1, *v*/v) to dichloromethane and methanol 40/1, *v*/*v*) as eluent to afford **1s**.

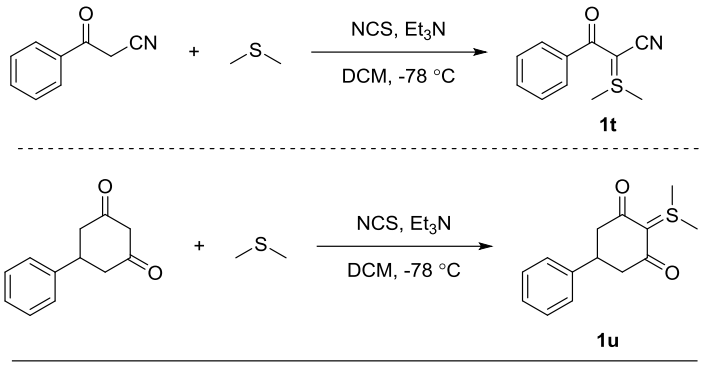


2-(Dimethyl-λ^4-sulfaneylidene)-2-((4-methoxyphenyl)sulfonyl)-1-phenylethan-1-one **(1s)**

Colorless crystals; yield: 9.48 g (87%); M.p. 169–170 °C; R_f = 0.25 (DCM/MeOH 15:1, *v*/*v*).

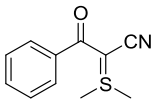
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (d, J = 8.3 Hz, 2H), 7.40–7.35 (m, 1H), 7.32 (t, J = 7.1 Hz, 2H), 7.26 (d, J = 6.9 Hz, 2H), 7.04 (d, J = 8.6 Hz, 2H) 3.83 (s, 3H), 3.12 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 185.0, 161.6, 141.6, 137.1, 129.1, 128.8, 127.7, 127.0, 113.5, 79.9, 55.5, 29.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{19}O_4S_2^+$ 351.0719, found 351.0722.

1.2.4 Synthesis of 1t and 1u



Sulfonium methylides **1t** and **1u** were prepared by referring literature.[6,7]

To a suspension of *N*-chlorosuccinimide (3.472 g, 26.0 mmol) in anhydrous dichloromethane (110 mL) was added dimethyl sulfide (2.7 mL, 36.9 mmol) dropwise at -78 °C under N_2. The resulting mixture was stirred for 1 h at the same temperature. Then, a solution of the active methylene compound (20.0 mmol) was added at the same temperature. After stirring for another 1 h, triethylamine (4.2 mL, 30.3 mmol) was added into the mixture, and the solution was stirred for additional 1 h at the same temperature. Cold brine (60 mL) was added into the mixture. The mixture was extracted with DCM (3 × 50 mL), and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with a mixture of petroleum ether (60–90 °C) and ethyl acetate (1:1, *v*/v) to dichloromethane and methanol 40/1, *v*/*v*) as eluent to afford **1t** or **1u**.

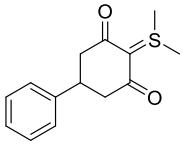


1t

2-(Dimethyl-λ^4-sulfaneylidene)-3-oxo-3-phenylpropanenitrile (**1t**)[8]

Colorless crystals; yield: 3.42 g (84%); M.p. 110–112 °C; R_f = 0.38 (DCM/MeOH 20:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.78 (m, 2H), 7.51–7.36 (m, 3H), 2.82 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.0, 138.3, 131.1, 128.1, 127.7, 119.5, 55.5, 28.0.



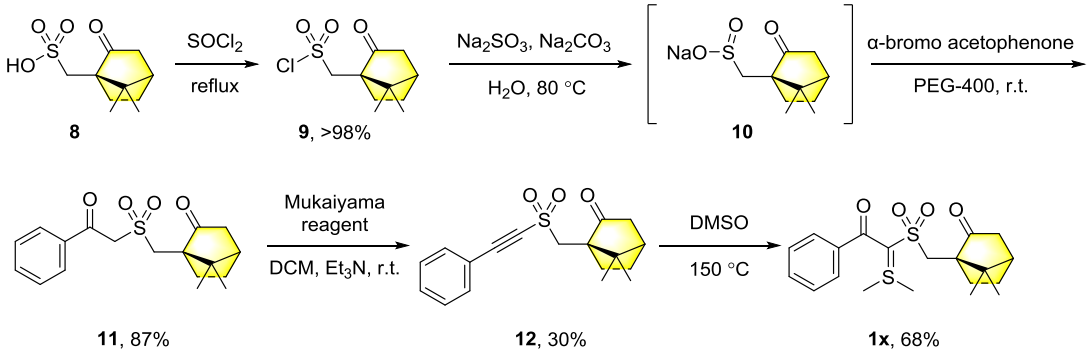
1u

2-(Dimethyl-λ^4-sulfaneylidene)-5-phenylcyclohexane-1,3-dione (**1u**)

Colorless crystals; yield: 3.11 g (78%); M.p. 180–181 °C; R_f = 0.40 (DCM/MeOH 20:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (m, 2H), 7.26–7.19 (m, 3H), 3.36 (tt, *J* = 10.6, 5.0 Hz, 1H), 2.99 (s, 6H), 2.72 (dd, *J* = 16.2, 5.0 Hz, 2H), 2.66 (dd, *J* = 16.2, 10.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 143.4, 128.8, 126.8, 126.7, 87.4, 45.2, 38.3, 25.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{17}O_2S^+$ 249.0944, found 269.0954.

1.2.5 Synthesis of 1x



Synthesis of 9 (by literature[9])

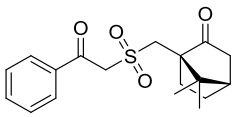
Thionyl chloride (11 mL) was added dropwise into a flask containing **8** (10.0 g, 43.1 mmol) under vigorous stirring. The resulting mixture was stirred at reflux for 2 h and then allowed to cool and poured over ice. The slurry was extracted with DCM (3 × 50 mL), dried (Na_2SO_4), and concentrated *in vacuo* to yield **9**[9] (>98%) as colorless crystals.

Synthesis of 10 (by literature[10])

To a solution of Na_2SO_3 (7.53 g, 59.8 mmol), $NaHCO_3$ (5.02 g, 59.8 mmol), and **9** (7.50 g, 29.9 mmol) in 80 mL of H_2O. The mixture was stirred at 80 °C for 7 h. After completion, the mixture was concentrated *in vacuo*. The residue was extracted with EtOH (5 × 40 mL). After drying and removal of solvent *in vacuo* crude product **10**[10] was obtained (10.3 g, accompany with NaCl, $NaHCO_3$ and Na_2SO_4).

Synthesis of 11 (by literature[11])

A mixture of the crude **10** (5.0 g) and 2-bromoacetophenone (1.99 g, 10 mmol) was taken in 50 mL of polyethylene glycol-400, and stirred at room temperature for 20 h. After completion, the reaction was poured into water (150 mL) and extracted with EtOAc (4 × 50 mL). After drying and removal of solvent *in vacuo*, the residue was purified by column chromatography with petroleum ether (60–90 °C fraction)/ EtOAc (4:1, *v*/*v*) as eluent to give the product **11**.



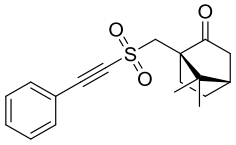
(1*R*,4*S*)-7,7-Dimethyl-1-(((2-oxo-2-phenylethyl)sulfonyl)methyl)bicyclo[2.2.1]heptan-2-one (**11**)

Light yellow oil; yield: 2.92 g (87%); R_f = 0.25 (PE/EA 4:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.97 (m, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 5.12 (d, J = 15.2 Hz, 1H), 4.81 (dd, J = 15.1, 1.3 Hz, 1H), 3.96 (d, J = 15.2 Hz, 1H), 3.05 (dd, J = 15.2, 1.3 Hz, 1H), 2.38 (ddd, J = 18.6, 4.9, 3.1 Hz, 1H), 2.30 (ddd, J = 14.8, 11.2, 3.9 Hz, 1H), 2.13 (t, J = 4.5 Hz, 1H), 2.10–1.88 (m, 3H), 1.46 (ddd, J = 12.8, 9.1, 3.9 Hz, 1H), 1.04 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.7, 189.6, 136.0, 134.4, 129.00, 128.96, 62.5, 59.5, 52.6, 49.0, 42.8, 42.7, 27.2, 26.1, 19.9, 19.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{23}O_4S^+$ 335.1312, found 335.1313.

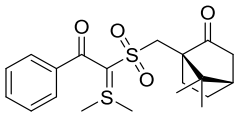
Synthesis of 12 (by literature[3])

11 (2.90 g, 8.67 mmol), 2-chloro-1-methylpyridin-1-ium iodide (CMPI) (2.66 g, 10.40 mmol), and Et_3N (6.03 mL, 43.35 mmol) were added into a 100 mL round bottom flask in turn. After addition of DCM (50 mL) the flask was sealed and the mixture was stirred at 25 °C for 12 h. After the reaction completion monitored by TLC, the mixture was washed with water and brine, dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash silica gel chromatography using petroleum ether (60–90 °C fraction)/dichloromethane and EtOAc (200:30:25, *v*/*v*/*v*) as eluent to give the product **12**.



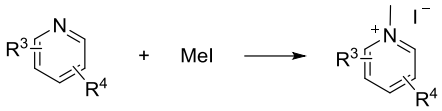
(1*R*,4*S*)-7,7-Dimethyl-1-(((phenylethynyl)sulfonyl)methyl)bicyclo[2.2.1]heptan-2-one (**12**)
Colorless crystals; yield: 810 mg (30%); M.p. 115–116 °C; R_f = 0.45 (PE/EA 4:1, *v*/*v*).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.54 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 3.91 (d, *J* = 15.1 Hz, 1H), 3.22 (d, *J* = 15.0 Hz, 1H), 2.65–2.55 (m, 1H), 2.44–2.34 (dt, *J* = 18.5, 7.5 Hz, 1H), 2.13 (t, *J* = 4.6 Hz, 1H), 2.10–2.02 (m, 1H), 1.95 (d, *J* = 18.5 Hz, 1H), 1.79 (ddd, *J* = 14.0, 9.3, 4.4 Hz, 1H), 1.45 (ddd, *J* = 13.0, 9.3, 4.0 Hz, 1H), 1.13 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.9, 132.7, 131.6, 128.8, 117.6, 91.8, 85.0, 58.8, 55.7, 48.1, 42.50, 42.47, 27.0, 24.5, 19.9, 19.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{21}O_3S^+$ 317.1206, found 317.1215.

Synthesis of 1x (by literature[1])
12 (633 mg, 2.0 mmol) was dissolved in anhydrous DMSO (20.0 mL) in a 35 mL pressure tube without inert atmosphere (Sealed after adding). The reaction mixture was further stirred in an oil bath at 150 °C for 38 mins. After cooling and addition of water (80 mL), the mixture was extracted with DCM (4 × 20 mL), and the combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with petroleum ether (60–90 °C) and ethyl acetate (2:1, *v*/v) to dichloromethane and methanol 40/1, *v*/*v*) as eluent to afford **1x**.



(1*R*,4*S*)-1-(((1-(Dimethyl-λ^4-sulfaneylidene)-2-oxo-2-phenylethyl)sulfonyl)methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-one (**1x**)
Colorless crystals; yield: 536 mg (68%); M.p. 141–142 °C; R_f = 0.32 (DCM/MeOH 20:1, *v*/*v*).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.42 (m, 2H), 7.41–7.33 (m, 3H), 3.63 (d, *J* = 14.4 Hz, 1H), 3.46 (s, 1H), 3.08 (s, 3H), 3.06 (s, 3H), 2.53–2.49 (m, 1H), 2.35 (ddd, *J* = 18.4, 4.8, 3.1 Hz, 1H), 2.08 (t, *J* = 4.5 Hz, 1H), 2.09–2.00 (m, 1H), 1.90 (d, *J* = 18.4 Hz, 1H), 1.81–1.77 (m, 1H), 1.42 (ddd, *J* = 13.1, 9.3, 3.9 Hz, 1H), 1.05 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.7, 187.4, 141.4, 129.6, 128.0, 127.1, 80.7, 59.6, 54.4, 48.3, 42.7, 42.6, 30.8, 29.6, 27.1, 25.0, 19.9, 19.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{27}O_4S_2^+$ 395.1345, found 395.1347.

1.3 Synthesis of 1-Methylpyridinium Halide Salts 2



Prepared by referring literature.[12] To the corresponding solution of pyridine (10.0 mmol) in acetonitrile (5 mL) was added methyl iodide (12 mmol) in a 10 mL pressure tube (Sealed after adding). The reaction mixture was stirred in an oil bath at 80 °C for 8 h. Then it was allowed to cool to room temperature. After removal of the solvent under reduced pressure, the residue was recrystallized from MeCN/ EtOAc as co-solvents to afford the corresponding pure product **2**.

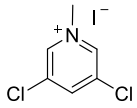
1-Methylpyridin-1-ium iodide (**2b**)[12]
Yellow crystals; yield: 2.01 g (90%).
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.03 (d, J = 5.8 Hz, 2H), 8.58 (t, J = 7.6 Hz, 1H), 8.14 (t, J = 6.8 Hz, 2H), 4.39 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.2, 144.9, 127.5, 48.1.

2-Fluoro-1-methylpyridin-1-ium iodide (**2c**)[13]
Caution: **2c** prepared and stored in the dark.
Colorless crystals; yield: 1.03 g (43%).
^{1}H NMR (400 MHz, D_2O) δ 8.83–8.72 (m, 2H), 8.05–7.92 (m, 2H), 4.37 (d, $J_{F\text{-}H}$ = 3.8 Hz, 3H). ^{13}C NMR (101 MHz, D_2O) δ 159.0 (d, J = 282.6 Hz), 151.2 (d, J = 11.4 Hz), 144.4 (d, J = 7.7 Hz), 124.3 (d, J = 3.7 Hz), 114.7 (d, J = 20.6 Hz), 42.1. ^{19}F NMR (376 MHz, D_2O) δ -77.35.

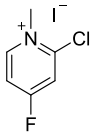
2-Bromo-1-methylpyridin-1-ium iodide (**2d**)[14]
Light gray crystals; yield: 1.80 g (60%).
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.25 (dd, J = 6.1, 1.6 Hz, 1H), 8.62 (dd, J = 8.0, 1.5 Hz, 1H), 8.16 (td, J = 7.8, 1.7 Hz, 1H), 8.07 (ddd, J = 7.7, 6.0, 1.6 Hz, 1H), 4.41 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.7, 143.9, 139.5, 126.5, 125.8, 54.6.

2-Iodo-1-methylpyridin-1-ium iodide (**2e**)[13]
Light gray crystals; yield: 1.58 g (91%) (Prepared on a 5 mmol scale).
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.24 (dd, J = 6.2, 1.6 Hz, 1H), 8.61 (dd, J = 8.0, 1.6 Hz, 1H), 8.15 (td, J = 7.8, 1.6 Hz, 1H), 8.06 (ddd, J = 7.7, 6.1, 1.6 Hz, 1H), 4.40 (s, 3H). ^{13}C NMR (101 MHz,

DMSO-d_6) δ 147.8, 143.9, 139.5, 126.6, 125.5, 54.6.



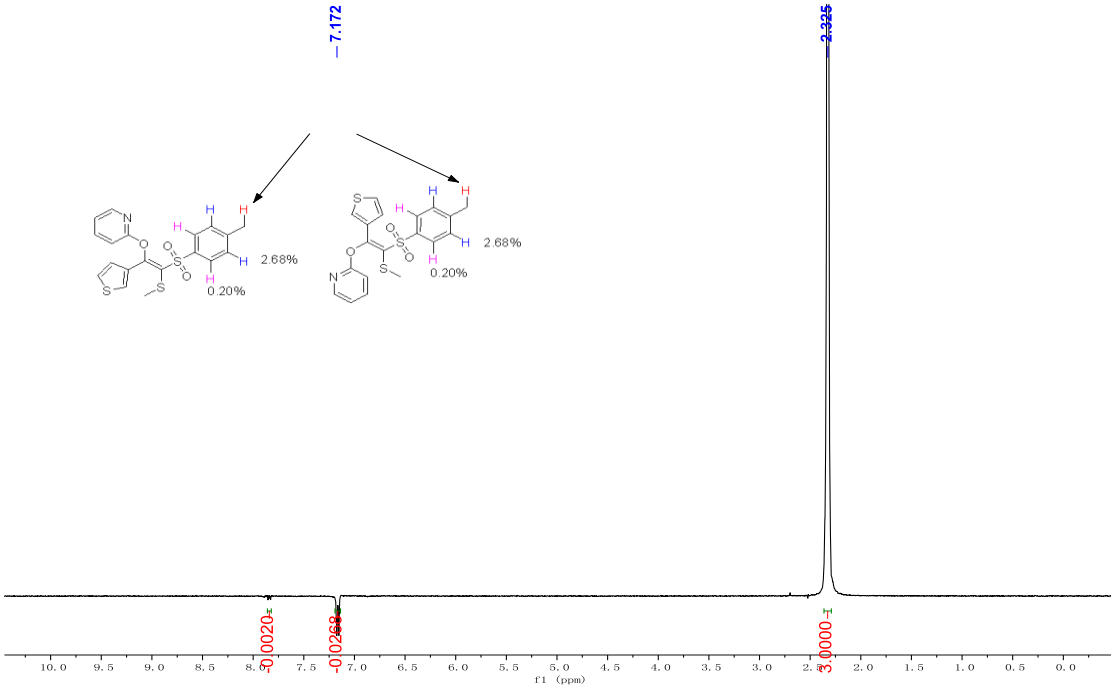
3,5-Dichloro-1-methylpyridin-1-ium (**2f**)[15]
Yellow crystals; yield: 1.50 g (52%).
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.42 (d, J = 0.4 Hz, 2H), 9.09 (s, 1H), 4.33 (s, 3H).^{13}C NMR (101 MHz, DMSO-d_6) δ 144.6, 144.4, 134.2, 49.1.



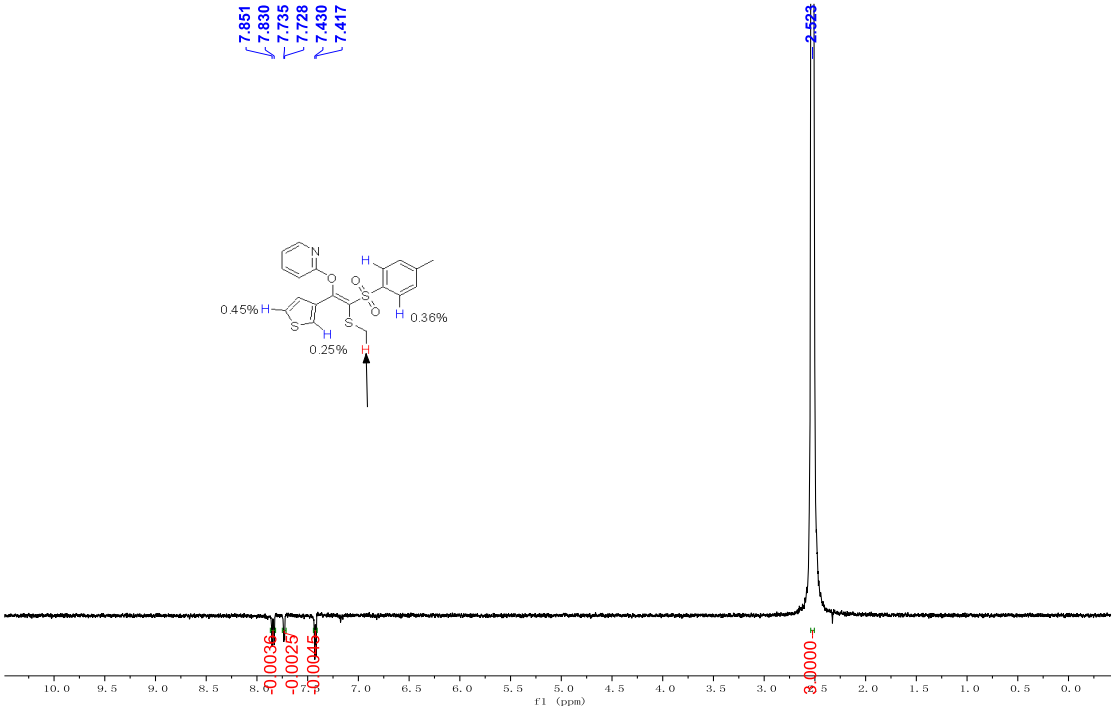
2-Chloro-4-fluoro-1-methylpyridin-1-ium iodide (**2g**)
Yellow crystals; yield: 0.92 g (34%).
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.35 (dd, J = 7.1, 5.3 Hz, 1H), 8.73 (dd, J = 6.9, 3.0 Hz, 1H), 8.12 (td, J = 7.0, 3.0 Hz, 1H), 4.38 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9 (d, J = 279.0 Hz), 151.2 (d, J = 12.6 Hz), 128.8, 126.9 (d, J = 22.7 Hz), 115.1 (d, J = 22.7 Hz), 53.7. ^{19}F NMR (376 MHz, DMSO-d_6) δ -88.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{27}O_4S_2^+$ 273.9290, found 273.9295.

1.4 Nuclear Overhauser Effect (NOE): The Configuration of 3o

We selected **3o** as the standard product for NOE experiment. (The peak positions of its ^{1}H NMR spectrum are completely separated, which is conducive to the NOE experiment). The enhancements of both α–hydrogen atoms of thiophen-3-yl were observed when methylthio was selectively irradiated, indicating the methylthio and thiophen-3-yl groups are *cis*.



(*Z*)-2-((2-(Methylthio)-1-(thiophen-3-yl)-2-tosylvinyl)oxy)pyridine (**3o**)
(Methyl on the phenyl group was irradiated selectively)

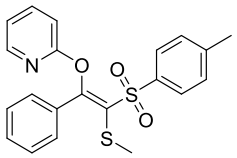


(*Z*)-2-((2-(Methylthio)-1-(thiophen-3-yl)-2-tosylvinyl)oxy)pyridine (**3o**)
(Methyl of the methylthio group was irradiated selectively)

1.5 General Procedure for the Synthesis of 3 and 4.

A 10 mL reaction tube was charged with α-arylcarbonyl sulfonylmethylide **1** (0.2 mol), 1-methylpyridinium halide **2** (0.6 mmol), and toluene (3.0 mL) under N_2. The reaction vessel was sealed and stirred at 120 °C for 5 h. After cooling, the mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with petroleum ether (60–90 °C) and ethyl acetate (5:1, *v*/v) as eluent to afford product **3** and **4**.

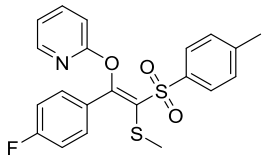
1.5.1 Analytic Date for Products 3



(*Z*)-2-((2-(Methylthio)-1-phenyl-2-tosylvinyl)oxy)pyridine (**3a**)

Colorless crystals; yield: 57 mg (71%); M.p. 84–85 °C; R_f = 0.31 (PE/EA 3:1, *v*/*v*).

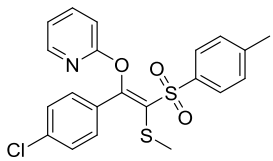
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2H), 7.82 (ddd, J = 5.0, 2.0, 0.9 Hz, 1H), 7.58–7.52 (m, 2H), 7.51 (ddd, J = 8.2, 7.3, 2.0 Hz, 1H), 7.26 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 6.85 – 6.73 (m, 2H), 2.49 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 160.9, 147.5, 143.7, 139.1, 138.6, 133.5, 130.3, 129.6, 129.1, 128.9, 128.5, 127.9, 119.1, 111.9, 21.6, 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{20}NO_3S_2^+$ 398.0879, found 398.0888



(Z)-2-((1-(4-Fluorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3b**)

Colorless crystals; yield: 50 mg (60%); M.p. 129–130 °C; R_f = 0.32 (PE/EA 3:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.1 Hz, 2H), 7.84–7.80 (m, 1H), 7.60–7.48 (m, 3H), 7.15 (d, J = 7.9 Hz, 2H), 6.94 (t, J = 8.6 Hz, 2H), 6.85–6.81 (m, 1H), 6.80 (d, J = 8.3 Hz, 1H), 2.49 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (d, J = 251.8 Hz), 161.7, 160.9, 147.5, 143.8, 139.2, 138.5, 131.8 (d, J = 8.7 Hz), 129.76, 129.73, 129.2, 128.5, 119.2, 115.2 (d, J = 22.0 Hz), 111.9, 21.6, 20.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}FNO_3S_2^+$ 416.0785, found 416.0795.

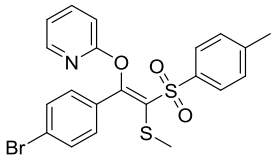


(*Z*)-2-((1-(4-Chlorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3c**)

Colorless crystals; yield: 48 mg (56%); M.p. 130–131 °C; R_f = 0.30 (PE/EA 3:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.81 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.54 (ddd, J = 8.1, 7.1, 1.9 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.82 (ddd, J = 7.2, 6.0, 0.8 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 2.49 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 160.8, 147.5, 143.9, 139.2, 138.4, 136.2, 132.2, 131.0, 129.6,

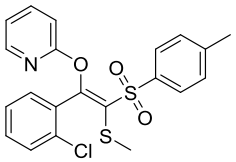
129.2, 128.5, 128.3, 119.2, 111.8, 21.6, 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}NClO_3S_2^+$ 432.0489, found 432.0488.



(*Z*)-2-((1-(4-Bromophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3d**)

Colorless crystals; yield: 58 mg (61%); M.p. 136–137 °C; R_f = 0.38 (PE/EA 3:1, *v*/*v*).

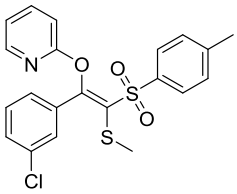
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.81 (dd, J = 5.0, 1.2 Hz, 1H), 7.54 (ddd, J = 8.2, 7.2, 2.0 Hz, 1H), 7.43 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.83 (ddd, J = 7.2, 4.9, 0.9 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H), 2.49 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 160.8, 147.5, 143.9, 139.2, 138.4, 132.7, 131.2, 131.1, 129.6, 129.2, 128.5, 124.7, 119.2, 111.8, 21.6, 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}NBrO_3S_2^+$ 475.9984, found 475.9990.



(*Z*)-2-((1-(2-Chlorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3e**)

Colorless crystals; yield: 54 mg (62%); M.p. 129–131 °C; R_f = 0.32 (PE/EA 3:1, *v*/*v*).

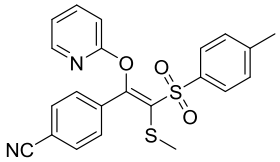
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.80 (m, 3H), 7.57–7.39 (m, 2H), 7.32–7.23 (m, 1H), 7.23–7.09 (m, 4H), 6.84 (ddd, J = 7.3, 4.9, 0.9 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 160.2, 147.3, 143.8, 139.2, 138.6, 133.6, 132.9, 132.3, 130.8, 130.1, 129.6, 129.1, 128.4, 126.0, 119.6, 112.0, 21.6, 20.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}NClO_3S_2^+$ 432.0489, found 432.0496.



(*Z*)-2-((1-(3-Chlorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3f**)

Colorless crystals; yield: 46 mg (53%); M.p. 125–126 °C; R_f = 0.42 (PE/EA 3:1, *v*/*v*).

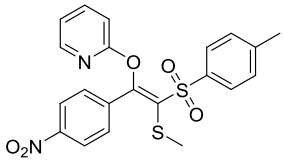
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.81 (m, 3H), 7.54 (ddt, J = 7.3, 4.4, 2.1 Hz, 2H), 7.45 (dt, J = 7.6, 1.5 Hz, 1H), 7.26–7.22 (m, 1H), 7.20 (d, J = 7.7 Hz, 1H), 7.18–7.14 (m, 2H), 6.86–6.77 (m, 2H), 2.50 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 160.7, 147.5, 143.9, 139.3, 138.4, 135.6, 133.8, 130.3, 130.2, 129.5, 129.2 (2C), 128.5, 127.8, 119.3, 111.8, 21.6, 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}NClO_3S_2^+$ 432.0489, found 432.0499.



(*Z*)-4-(2-(Methylthio)-1-(pyridin-2-yloxy)-2-tosylvinyl)benzonitrile (**3g**)

Light yellow crystals; yield: 42 mg (50%); M.p. 95–96 °C; R_f = 0.20 (PE/EA 3:1, *v*/*v*).

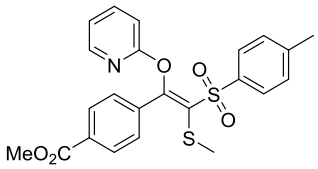
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 2H), 7.77 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.66 (d, J = 8.6 Hz, 2H), 7.58–7.52 (m, 3H), 7.19–7.10 (m, 2H), 6.90–6.75 (m, 2H), 2.52 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 160.2, 147.4, 144.1, 139.4, 138.6, 138.1, 131.6, 131.3, 130.2, 129.3, 128.5, 119.4, 118.2, 113.5, 111.7, 21.6, 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{19}N_2O_3S_2^+$ 423.0832, found 423.0836.



(*Z*)-2-((2-(Methylthio)-1-(4-nitrophenyl)-2-tosylvinyl)oxy)pyridine (**3h**)

Yellow crystals; yield: 35 mg (40%); M.p. 95–97 °C; R_f = 0.27 (PE/EA 3:1, *v*/*v*).

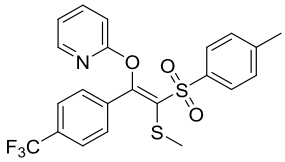
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H), 7.77 (dd, J = 5.4, 2.0 Hz, 1H), 7.72 (d, J = 8.9 Hz, 2H), 7.57 (ddd, J = 8.2, 7.3, 2.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 6.93–6.78 (m, 2H), 2.53 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 159.9, 148.3, 147.4, 144.2, 140.5, 139.5, 138.1, 131.7, 130.6, 129.3, 128.6, 123.1, 119.5, 111.7, 21.7, 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}N_2O_5S_2^+$ 443.0730, found 443.0730.



Methyl (*Z*)-4-(2-(methylthio)-1-(pyridin-2-yloxy)-2-tosylvinyl)benzoate (**3i**)

Yellowish crystals; yield: 48 mg (53%); M.p. 149–151 °C; R_f = 0.22 (PE/EA 3:1, *v*/*v*).

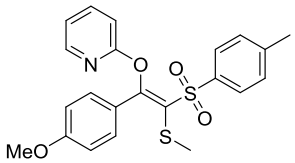
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.3 Hz, 2H), 7.79 (dd, J = 5.3, 2.3 Hz, 1H), 7.63 (d, J = 8.6 Hz, 2H), 7.53 (ddd, J = 8.2, 7.3, 2.0 Hz, 1H), 7.16 (d, J = 8.3 Hz, 2H), 6.87–6.75 (m, 2H), 3.86 (s, 3H), 2.50 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 161.4, 160.7, 147.4, 143.9, 139.2, 138.4, 138.3, 131.4, 130.3, 129.6, 129.2, 129.1, 128.5, 119.3, 111.8, 52.4, 21.6, 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{22}NO_5S_2^+$ 456.0934, found 456.0934.



(*Z*)-2-((2-(Methylthio)-2-tosyl-1-(4-(trifluoromethyl)phenyl)vinyl)oxy)pyridine (**3j**)

Colorless crystals; yield: 42 mg (45%); M.p. 152–153 °C; R_f = 0.38 (PE/EA 3:1, *v*/*v*).

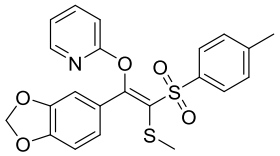
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.3 Hz, 2H), 7.80 (ddd, J = 5.0, 1.9, 0.8 Hz, 1H), 7.67 (d, J = 8.6 Hz, 2H), 7.55 (ddd, J = 8.2, 7.2, 2.0 Hz, 1H), 7.52 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.88–6.76 (m, 2H), 2.51 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 160.7, 147.5, 144.0, 139.3, 138.3, 137.6, 131.7 (q, J = 32.7 Hz), 130.8, 130.0, 129.2, 128.6, 124.9 (q, J = 3.8 Hz), 123.7 (q, J = 272.5 Hz), 119.3, 111.7, 21.6, 20.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{19}FNO_3S_2^+$ 466.0753, found 466.0745.



(*Z*)-2-((1-(4-Methoxyphenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3k**)

Colorless crystals; yield: 25 mg (29%); M.p. 163–164 °C; R_f = 0.19 (PE/EA 3:1, *v*/*v*).

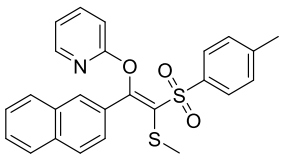
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.71 (m, 3H), 7.59–7.44 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 6.82 (ddd, J = 7.3, 4.9, 0.9 Hz, 1H), 6.79–6.73 (m, 3H), 3.75 (s, 3H), 2.49 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 161.3, 161.2, 147.7, 143.6, 139.1, 138.9, 131.5, 129.1, 128.5, 127.5, 125.5, 119.0, 113.4, 112.1, 55.3, 21.6, 20.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{22}NO_4S_2^+$ 428.0985, found 428.0987.



(*Z*)-2-((1-(Benzo[*d*][1,3]dioxol-5-yl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3n**)

Colorless crystals; yield: 59 mg (67%); M.p. 104–106 °C; R_f = 0.18 (PE/EA 3:1, *v*/*v*).

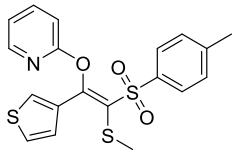
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.85 (d, J = 8.3 Hz, 2H), 7.53 (ddd, J = 8.2, 7.2, 2.0 Hz, 1H), 7.15 (d, J = 8.4, 2H), 7.08 (s, 1H), 7.07 (dd, J = 8.2, 1.8 Hz, 1H), 6.84 (ddd, J = 7.3, 4.9, 0.9 Hz, 1H), 6.77 (d, J = 8.3 Hz, 1H), 6.66 (d, J = 8.8 Hz, 1H), 5.91 (s, 2H), 2.49 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 161.1, 149.4, 147.6, 147.2, 143.7, 139.1, 138.6, 129.1, 128.4, 127.9, 127.0, 124.6, 119.1, 111.9, 110.0, 107.9, 101.6, 21.6, 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{20}NO_5S_2^+$ 442.0777, found 442.0785.



(*Z*)-2-((2-(Methylthio)-1-(naphthalen-2-yl)-2-tosylvinyl)oxy)pyridine (**3o**)

Colorless crystals; yield: 63 mg (70%); M.p. 133–134 °C; R_f = 0.25 (PE/EA 3:1, *v*/*v*).

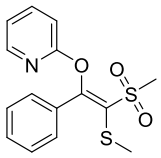
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 1.2 Hz, 1H), 7.91 (d, J = 8.3 Hz, 2H), 7.78 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.74–7.71 (m, 4H), 7.51–7.35 (m, 3H), 7.17 (d, J = 8.1 Hz, 2H), 6.84 (d, J = 8.2 Hz, 1H), 6.73 (ddd, J = 7.4, 4.9, 0.9 Hz, 1H), 2.49 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 161.0, 147.5, 143.8, 139.1, 138.6, 133.9, 132.3, 131.2, 129.6, 129.1 (2C), 128.7, 128.5, 127.7, 127.5, 127.4, 126.6, 126.5, 119.0, 111.9, 21.6, 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{22}NO_3S_2^+$ 448.1036, found 448.1041.



(*Z*)-2-((2-(Methylthio)-1-(thiophen-3-yl)-2-tosylvinyl)oxy)pyridine (**3p**)

Colorless crystals; yield: 60 mg (74%); M.p. 132–133 °C; R_f = 0.25 (PE/EA 3:1, *v*/*v*).

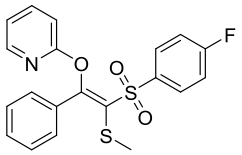
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.72 (dd, J = 3.0, 1.3 Hz, 1H), 7.56 (ddd, J = 8.1, 7.2, 1.9 Hz, 1H), 7.41 (dd, J = 5.2, 1.3 Hz, 1H), 7.20–7.10 (m, 3H), 6.86 (ddd, J = 7.2, 5.0, 0.9 Hz, 1H), 6.80 (dd, J = 8.2, 0.9 Hz, 1H), 2.51 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 157.3, 147.6, 143.7, 139.2, 138.6, 134.4, 130.3, 129.1, 128.5, 128.4, 128.2, 125.1, 119.0, 111.5, 21.6, 20.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{18}NO_3S_3^+$ 404.0443, found 404.0446.



(*Z*)-2-((2-(Methylsulfonyl)-2-(methylthio)-1-phenylvinyl)oxy)pyridine (**3q**)

Yellowish crystals; yield: 40 mg (62%); M.p. 92–93 °C; R_f = 0.15 (PE/EA 3:1, *v*/*v*).

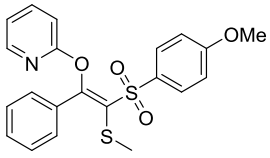
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.66–7.56 (m, 3H), 7.37–7.29 (m, 3H), 6.96 (d, J = 8.3 Hz, 1H), 6.92 (dd, J = 7.3, 4.9 Hz, 1H), 3.23 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 161.2, 147.9, 139.7, 133.2, 130.6, 129.8, 128.0, 127.4, 119.9, 112.5, 43.5, 20.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{16}NO_3S_2^+$ 322.0566, found 322.0576.



(*Z*)-2-((2-((4-Fluorophenyl)sulfonyl)-2-(methylthio)-1-phenylvinyl)oxy)pyridine (**3r**)

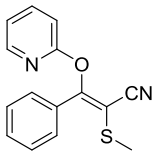
Colorless crystals; yield: 36 mg (45%); M.p. 104–105 °C; R_f = 0.42 (PE/EA 3:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.98 (m, 2H), 7.84 (ddd, J = 5.0, 2.0, 0.9 Hz, 1H), 7.61–7.51 (m, 3H), 7.32–7.21 (m, 3H), 7.04 (t, J = 8.6 Hz, 2H), 6.88–6.82 (ddd, J = 7.3, 4.9, 0.9 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4 (d, J = 255.0 Hz), 163.3, 160.8, 147.6, 139.3, 137.6 (d, J = 2.6 Hz), 133.3, 131.3 (d, J = 9.4 Hz), 130.5, 129.7, 128.6, 128.0, 119.4, 115.7 (d, J = 22.8 Hz), 111.9, 20.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -105.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{17}FNO_3S_2^+$ 402.0628, found 402.0618.

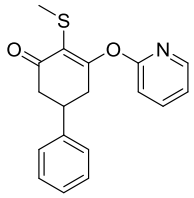


(*Z*)-2-((2-((4-Methoxyphenyl)sulfonyl)-2-(methylthio)-1-phenylvinyl)oxy)pyridine (**3s**)

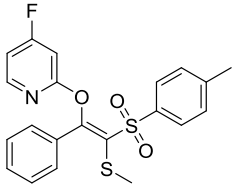
Colorless crystals; yield: 46 mg (56%); M.p. 126–127 °C; R_f = 0.20 (PE/EA 3:1, *v*/*v*).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 9.0 Hz, 2H), 7.88–7.80 (m, 1H), 7.60–7.54 (m, 2H), 7.54–7.48 (m, 1H), 7.34–7.15 (m, 3H), 6.91–6.74 (m, 4H), 3.76 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 162.4, 161.0, 147.5, 139.1, 133.6, 133.1, 130.6, 130.3, 129.6, 129.2, 127.9, 119.1, 113.7, 111.9, 55.6, 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{20}NO_4S_2^+$ 414.0828, found 414.0833.



(*E*)-2-(Methylthio)-3-phenyl-3-(pyridin-2-yloxy)acrylonitrile (**3t**)
Colorless crystals; yield: 25 mg (47%); M.p. 100–101 °C; R_f = 0.34 (PE/EA 10:1, *v*/*v*).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.77–7.70 (m, 2H), 7.67 (ddd, J = 8.3, 7.2, 2.0 Hz, 1H), 7.41–7.30 (m, 3H), 7.00 (dt, J = 8.3, 0.9 Hz, 1H), 6.95 (ddd, J = 7.2, 5.0, 1.0 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 161.1, 147.9, 139.9, 132.7, 130.6, 128.7, 128.1, 119.5, 115.3, 111.7, 99.7, 16.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{13}N_2OS^+$ 269.0743, found 269.0748.

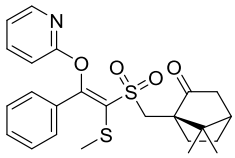


4-(Methylthio)-5-(pyridin-2-yloxy)-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (**3u**)
Sticky oil; yield: 19 mg (30%); R_f = 0.38 (PE/EA 3:1, *v*/*v*).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.74 (ddd, J = 8.2, 7.2, 2.0 Hz, 1H), 7.37–7.28 (m, 2H), 7.28–7.19 (m, 3H), 7.08 (ddd, J = 7.3, 5.0, 1.0 Hz, 1H), 7.03 (d, J = 8.2 Hz, 1H), 3.49 (tt, J = 11.9, 4.6 Hz, 1H), 3.06 (dd, J = 17.7, 11.4 Hz, 1H), 2.87 (ddd, J =16.3, 4.7, 1.6 Hz, 1H), 2.82 (dd, J = 16.6, 12.5 Hz, 1H), 2.80 (ddd, J = 17.5, 4.6, 1.6 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 171.8, 161.1, 147.9, 142.3, 140.1, 129.0, 127.3, 126.8, 122.3, 120.0, 112.9, 45.0, 39.2, 37.9, 17.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{18}NO_2S^+$ 312.1053, found 312.1059.



(*Z*)-4-Fluoro-2-((2-(methylthio)-1-phenyl-2-tosylvinyl)oxy)pyridine (**3w**)
Colorless crystals; yield: 46 mg (55%); M.p. 110–112 °C; R_f = 0.12 (PE/EA 3:1, *v*/*v*).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.3 Hz, 2H), 7.81 (dd, J = 8.6, 5.7 Hz, 1H), 7.56 (dd, J = 7.8, 1.8 Hz, 2H), 7.32–7.24 (m, 3H), 7.22–7.17 (m, 2H), 6.59 (ddd, J = 7.9, 5.7, 2.1 Hz, 1H), 6.51 (dd, J = 9.3, 2.1 Hz, 1H), 2.48 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2 (d, J =

261.7 Hz), 162.7 (d, J = 11.9 Hz), 161.9, 149.3 (d, J = 8.9 Hz), 143.9, 138.4, 133.4, 130.4, 129.6, 129.5, 129.2, 128.4, 127.9, 107.8 (d, J = 17.9 Hz), 99.4 (d, J = 21.4 Hz), 21.5, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}FNO_3S_2^+$ 416.0785, found 416.0783.

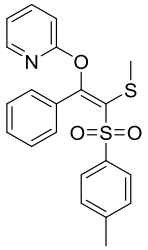


(1*R*)-7,7-Dimethyl-1-((((*Z*)-1-(methylthio)-2-phenyl-2-(pyridin-2-yloxy)vinyl)sulfonyl)methyl) bicyclo[2.2.1]heptan-2-one (**3x**)

Colorless crystals; yield: 64 mg (70%); M.p. 142–143 °C; R_f = 0.18 (PE/EA 3:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 5.0, 1.8 Hz, 1H), 7.66 (dd, J = 6.7, 3.0 Hz, 2H), 7.60 (ddd, J = 8.4, 7.2, 2.0 Hz, 1H), 7.40–7.27 (m, 3H), 6.99 (d, J = 8.1 Hz, 1H), 6.89 (ddd, J = 7.3, 4.9, 0.9 Hz, 1H), 3.96 (d, J = 14.6 Hz, 1H), 3.25 (d, J = 14.6 Hz, 1H), 2.60 (ddd, J = 14.9, 11.7, 4.1 Hz, 1H), 2.46 (s, 3H), 2.37 (ddd, J = 18.4, 4.8, 3.3 Hz, 1H), 2.08 (t, J = 4.5 Hz, 1H), 2.05–1.97 (m, 1H), 1.92 (d, J = 18.4 Hz, 1H), 1.80 (ddd, J = 14.0, 9.3, 4.6 Hz, 1H), 1.41 (ddd, J = 13.1, 9.3, 3.9 Hz, 1H), 1.09 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.7, 164.2, 161.4, 147.7, 139.5, 133.6, 130.3, 129.7, 128.5, 127.9, 119.5, 112.3, 59.3, 51.6, 48.1, 42.7, 42.6, 27.1, 25.1, 20.6, 20.1, 19.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{28}NO_4S_2^+$ 458.1454, found 458.1457.

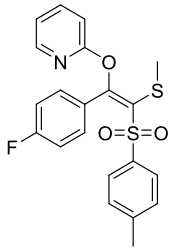
1.5.2 Analytic Date for Products 4



(*E*)-2-((2-(Methylthio)-1-phenyl-2-tosylvinyl)oxy)pyridine (**4a**)

Colorless oil; yield: 9 mg (11%); R_f = 0.48 (PE/EA 3:1, *v*/*v*).

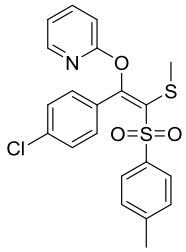
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 5.1, 1.9 Hz, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.62–7.55 (m, 1H), 7.53–7.48 (m, 2H), 7.38–7.29 (m, 1H), 7.28–77.26 (d, J = 8.4 Hz, 1H), 7.26–7.24 (m, 1H), 7.23 (d, J = 8.3 Hz, 2H), 6.91 (ddd, J = 7.3, 4.9, 1.0 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 161.6, 147.8, 143.9, 139.5, 137.8, 133.6, 130.7, 130.4, 129.2, 128.7, 128.3, 127.5, 119.6, 112.7, 21.8, 19.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{20}NO_3S_2^+$ 398.0879, found 398.0877.



(*E*)-2-((1-(4-Fluorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4b**)

Colorless oil; yield: 12 mg (15%); R_f = 0.48 (PE/EA 3:1, *v*/*v*).

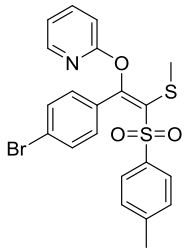
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 5.1, 1.9 Hz, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.60 (ddd, J = 8.2, 7.2, 2.0 Hz, 1H), 7.54–7.47 (m, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.00–6.91 (m, 3H), 6.87 (d, J = 8.2 Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 161.6, 161.4 (d, J = 251.2 Hz), 147.8, 144.1, 139.6, 137.7, 132.9 (d, J = 8.8 Hz), 130.8, 129.7, 129.3, 128.7, 119.7, 114.7 (d, J = 21.9 Hz), 112.6, 21.8, 19.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -109.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}FNO_3S_2^+$ 416.0785, found 416.0782.



(*E*)-2-((1-(4-Chlorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4c**)

Yellowish oil; yield: 8 mg (9%); R_f = 0.45 (PE/EA 3:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 5.0, 1.9 Hz, 1H), 7.70 (d, J = 8.1 Hz, 2H), 7.60 (ddd, J = 8.8, 7.6, 2.0 Hz, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.27–7.19 (m, 4H), 6.94 (dd, J = 7.3, 5.0 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 161.5, 147.8, 144.2, 139.7, 137.6, 136.6, 132.2, 132.0, 129.3, 129.1, 128.7, 127.8, 119.8, 112.5, 21.8, 19.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}NClO_3S_2^+$ 432.0489, found 432.0482.

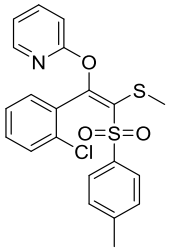


(*E*)-2-((1-(4-Bromophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4d**)

Yellowish oil; yield: 6 mg (6%); R_f = 0.44 (PE/EA 3:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (ddd, J = 5.0, 2.0, 0.9 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.60 (ddd, J = 8.2, 6.8, 2.0 Hz, 1H), 7.40 (s, 4H), 7.27–7.23 (m, 2H), 6.97–6.91 (m, 1H), 6.87 (dd, J = 8.3, 0.9 Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 161.5, 147.8, 144.2, 139.7, 137.5, 132.7, 132.2, 130.8, 129.3, 128.7, 125.0, 124.6, 119.8, 112.5, 21.8, 19.8. HRMS

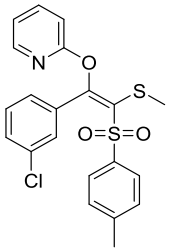
(ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}NBrO_3S_2^+$ 475.9984, found 475.9992.



(*E*)-2-((1-(2-Chlorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4e**)

Colorless oil; yield: 12 mg (14%); R_f = 0.48 (PE/EA 3:1, *v*/*v*).

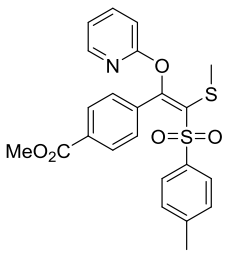
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (ddd, J = 4.9, 2.0, 0.9 Hz, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.68 (dt, J = 6.9, 1.1 Hz, 1H), 7.58 (ddd, J = 8.2, 7.2, 2.0 Hz, 1H), 7.31–7.21 (m, 5H), 7.03–6.89 (m, 2H), 2.42 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 160.9, 147.6, 144.2, 139.6, 137.4, 134.8, 132.5, 132.3, 131.2, 129.3, 129.0, 128.9, 128.7, 125.5, 120.2, 113.2, 21.8, 19.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}NClO_3S_2^+$ 432.0489, found 432.0482.



(*E*)-2-((1-(3-Chlorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4f**)

Yellow oil; yield: 5 mg (6%); R_f = 0.58 (PE/EA 3:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 5.0, 1.9 Hz, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.61 (ddd, J = 8.7, 7.3, 2.0 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.36 (s, 1H), 7.31–7.27 (m, 2H), 7.25–7.18 (m, 2H), 6.94 (dd, J = 7.2, 5.0 Hz, 1H), 6.89 (d, J = 8.2 Hz, 1H), 2.42 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 161.4, 147.8, 144.3, 139.7, 137.6, 135.4, 133.5, 130.3, 130.1, 130.0, 129.4, 129.3, 128.73, 128.65, 119.8, 112.5, 21.8, 19.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}NClO_3S_2^+$ 432.0489, found 432.0497.

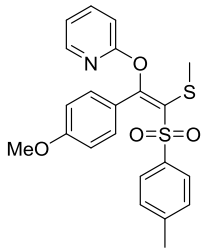


Methyl (*E*)-4-(2-(methylthio)-1-(pyridin-2-yloxy)-2-tosylvinyl)benzoate (**4i**)

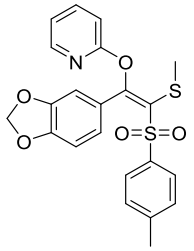
Colorless viscous oil; yield: 9 mg (10%); R_f = 0.39 (PE/EA 3:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.63–7.55 (m, 3H), 7.26 (d, J = 8.0 Hz, 2H), 6.92 (ddd, J = 7.2, 4.9, 0.9 Hz,

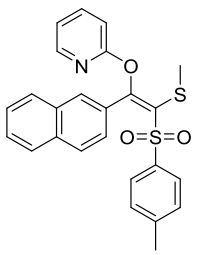
1H), 6.88 (dd, J = 8.2, 0.9 Hz, 1H), 3.89 (s, 3H), 2.42 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 164.8, 161.3, 147.8, 144.3, 139.7, 138.2, 137.5, 131.4, 130.6, 129.6, 129.4, 128.8, 128.6, 119.8, 112.6, 52.4, 21.8, 19.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{22}NO_5S_2^+$ 456.0934, found 456.0930.



(*E*)-2-((1-(4-Methoxyphenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4k**)
Colorless oil; yield: 12 mg (14%); R_f = 0.35 (PE/EA 3:1, *v*/*v*).
^{1}H NMR (400 MHz, $CDCl_3$)) δ 8.07 (ddd, J = 4.9, 2.0, 0.8 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.58 (ddd, J = 8.3, 7.2, 2.0 Hz, 1H), 7.48 (d, J = 8.9 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 6.91 (ddd, J = 7.3, 4.9, 1.0 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 6.78 (d, J = 8.9 Hz, 2H), 3.78 (s, 3H), 2.40 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 161.8, 161.5, 147.9, 143.8, 139.5, 138.0, 132.6, 129.2, 128.7, 126.7, 125.7, 119.5, 113.0, 112.6, 55.4, 21.8, 19.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{22}NO_4S_2^+$ 428.0985, found 428.0993.



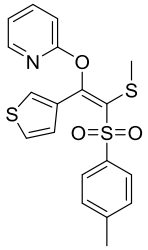
(*E*)-2-((1-(Benzo[*d*][1,3]dioxol-5-yl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4n**)
Colorless oil; yield: 13 mg (15%); R_f = 0.30 (PE/EA 3:1, *v*/*v*).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.00 (m, 1H), 7.72 (d, J = 8.3 Hz, 2H), 7.60 (ddd, J = 8.3, 7.3, 2.0 Hz, 1H), 7.24 (d, J = 8.1 Hz, 2H), 7.10 (dd, J = 8.1, 1.7 Hz, 1H), 6.94 (ddd, J = 7.2, 5.0, 0.8 Hz, 1H), 6.92 (d, J = 2.0 Hz, 1H) 6.87 (d, J = 8.3 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 5.94 (s, 2H), 2.41 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 161.7, 149.7, 147.9, 147.0, 143.9, 139.6, 137.9, 129.2, 128.7, 127.7, 127.1, 126.3, 119.6, 112.6, 110.6, 107.6, 101.6, 21.7, 19.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{20}NO_5S_2^+$ 442.0777, found 442.0770.



(*E*)-2-((2-(Methylthio)-1-(naphthalen-2-yl)-2-tosylvinyl)oxy)pyridine (**4o**)

Colorless oil; yield: 12 mg (13%); R_f = 0.38 (PE/EA 3:1, *v*/*v*).

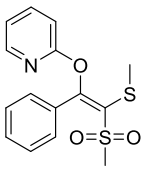
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (ddd, J = 5.8, 5.0, 0.8 Hz, 1H), 7.98 (s, 1H), 7.85–7.74 (m, 2H), 7.69 (d, J = 8.5 Hz, 1H), 7.64 (d, J = 8.3 Hz, 2H), 7.56 (ddd, J = 8.2, 3.2, 1.4 Hz, 2H), 7.50–7.45 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.2 Hz, 1H), 6.86 (ddd, J = 7.3, 4.9, 0.9 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 161.6, 147.9, 143.9, 139.5, 137.9, 134.0, 131.2, 131.0, 129.8, 129.2, 128.9, 128.8, 128.6, 127.8, 127.5, 127.3, 127.0, 126.4, 119.6, 112.6, 21.7, 19.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{22}NO_3S_2^+$ 448.1036, found 448.1046.



(*E*)-2-((2-(Methylthio)-1-(thiophen-3-yl)-2-tosylvinyl)oxy)pyridine (**4p**)

Colorless oil; yield: 10 mg (12%); R_f = 0.40 (PE/EA 3:1, *v*/*v*).

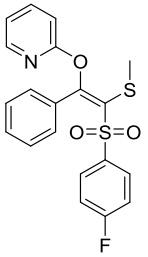
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (ddd, J = 4.9, 2.0, 0.8 Hz, 1H), 7.69–7.64 (m, 3H), 7.60 (ddd, J = 8.1, 7.2, 2.0 Hz, 1H), 7.23–7.19 (d, J = 8.0 Hz, 2H), 7.15–7.06 (m, 2H), 6.95 (ddd, J = 7.2, 5.0, 0.9 Hz, 1H), 6.85 (dd, J = 8.2, 0.9 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 161.7, 160.9, 147.9, 139.6, 137.9, 133.7, 131.0, 129.3, 129.2, 128.7, 128.4, 124.4, 119.6, 112.3, 21.8, 19.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{18}NO_3S_3^+$ 404.0443, found 404.0443.



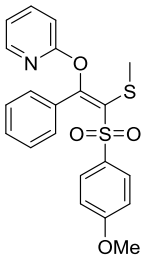
(*E*)-2-((2-(Methylsulfonyl)-2-(methylthio)-1-phenylvinyl)oxy)pyridine (**4q**)

Colorless crystals; yield: 6mg (9%); M.p. 120–121 °C R_f = 0.28 (PE/EA 3:1, *v*/*v*).

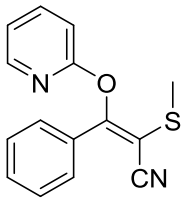
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.62 (ddd, J = 8.1, 7.3, 2.0 Hz, 1H), 7.58–7.51 (m, 2H), 7.39–7.27 (m, 3H), 6.97–6.90 (m, 2H), 3.08 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 161.6, 147.9, 139.7, 133.4, 130.7, 130.5, 127.7, 127.1, 119.7, 112.7, 42.4, 20.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{16}NO_3S_2^+$ 322.0566, found 322.0570.



(*E*)-2-((2-((4-Fluorophenyl)sulfonyl)-2-(methylthio)-1-phenylvinyl)oxy)pyridine (**4r**)
Colorless oil; yield: 4 mg (5%); R_f = 0.58 (PE/EA 3:1, *v*/*v*).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.02 (m, 1H), 7.83–7.75 (m, 2H), 7.59 (dddd, J = 8.1, 7.2, 2.0, 0.8 Hz, 1H), 7.52–7.47 (m, 2H), 7.36–7.30 (m, 1H), 7.29–7.24 (m, 2H), 7.09 (t, J = 8.6 Hz, 2H), 6.93 (ddd, J = 7.1, 4.9, 1.0 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 166.9, 165.5 (d, J =274.5 Hz), 161.6, 147.8, 139.6, 133.5, 131.4 (d, J = 9.7 Hz), 130.7, 130.6, 128.1, 127.6, 119.8, 115.8 (d, J = 22.6 Hz), 112.7, 19.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{17}FNO_3S_2^+$ 402.0628, found 402.0631.

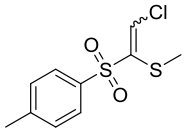


(*E*)-2-((2-((4-Methoxyphenyl)sulfonyl)-2-(methylthio)-1-phenylvinyl)oxy)pyridine (**4s**)
Colorless oil; yield: 13 mg (16%); R_f = 0.33 (PE/EA 3:1, *v*/*v*).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 5.0, 1.9 Hz, 1H), 7.92–7.97 (s, 1H), 7.74 (d, J = 8.9 Hz, 2H), 7.65–7.55 (m, 1H), 7.53–7.45 (m, 2H), 7.36–7.23 (m, 3H), 6.95–6.82 (m, 3H), 3.85 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 163.3, 161.6, 147.8, 139.5, 132.9, 130.9, 130.7, 130.4, 128.7, 127.7, 127.5, 119.6, 113.8, 112.6, 55.7, 19.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{20}NO_4S_2^+$ 414.0828, found 414.0836.



(*Z*)-2-(Methylthio)-3-phenyl-3-(pyridin-2-yloxy)acrylonitrile (**4u**)
Sticky oil; yield: 12 mg (22%); R_f = 0.32 (PE/EA 10:1, *v*/*v*).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 5.0, 1.9 Hz, 1H), 7.68–7.64 (m, 1H), 7.66–7.34 (m, 2H), 7.39–7.32 (m, 3H), 7.01 (dt, J = 8.3, 0.8 Hz, 1H), 6.96–6.90 (m, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 162.0, 147.8, 139.8, 132.3, 130.7, 129.4, 128.2, 119.5, 114.6, 111.9, 99.2, 17.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{13}N_2OS^+$ 269.0743, found 269.0754.

1.5.3 Analytic Date for Products 5



Colorless oil; yield: 46 mg (88%); R_f = 0.56 (PE/EA 10:1, *v*/*v*). (*E*)- and (*Z*)-isomers cannot be separated on silica gel column.

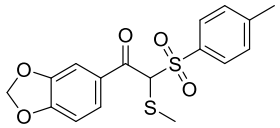
Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.84 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 2.45 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 142.4, 140.7, 135.1, 129.9, 129.0, 21.8, 18.0.

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.84 (d, J = 8.1 Hz, 2H), 7.43–7.32 (m, 2H), 2.45 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 145.2, 134.8, 129.9, 129.0, 109.0, 18.7, 18.0.

Both isomers: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{10}H_{12}ClO_2S_2^+$ 262.9962, found 262.9965.

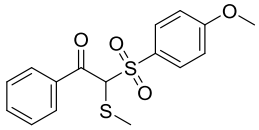
1.5.4 Analytic Date for Products 6n and 6s

Caution: NMR Spectra of **4n** contain with **6n**, **4s** contain with **6s**, unable to purify completely.



1-(Benzo[*d*][1,3]dioxol-5-yl)-2-(methylthio)-2-tosylethan-1-one (**6n**)[2]

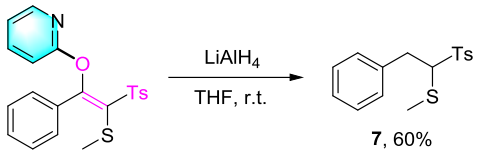
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.3 Hz, 2H), 7.59 (dd, J = 8.2, 1.8 Hz, 1H), 7.40 (d, J = 1.8 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.3 Hz, 1H), 6.07 (s, 2H), 5.41 (s, 1H), 2.45 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.8, 153.1, 148.6, 145.7, 133.3, 130.6, 129.5, 129.3, 126.1, 108.7, 108.2, 102.4, 71.4, 21.9, 15.7.



2-((4-Methoxyphenyl)sulfonyl)-2-(methylthio)-1-phenylethan-1-one (**6s**)

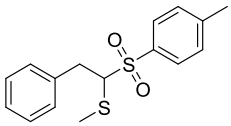
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.8 Hz, 2H), 7.62 (t, J = 7.7 Hz, 1H), 7.51–7.47 (m, 2H), 7.01 (d, J = 8.8 Hz, 2H), 6.93–6.86 (m, 2H), 5.50 (s, 1H), 3.89 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 152.7, 134.4, 133.6, 132.3, 129.12, 129.05, 128.7, 127.7, 114.0, 71.1, 15.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{10}H_{12}ClO_2S_2^+$ 337.0563, found 337.0571

1.6 Procedure for the Synthesis of 7



3a **7**, 60%

A 10 mL reaction tube was charged with **3a** (0.2 mol, 79.5 mg), THF (2.0 mL), and $LiAlH_4$ (0.6 mmol, 22.8 mg). The reaction vessel was sealed and protected by N_2. The reaction mixture was stirred at room temperature for 30 min and then quenched by addition of H_2O (3.0 mL). The resulting mixture was extracted with DCM (3 × 5 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with petroleum ether (60–90 °C) and ethyl acetate (20:1, *v*/v) as eluent to afford **7**.



Methyl(2-phenyl-1-tosylethyl)sulfane (**7**)[16]

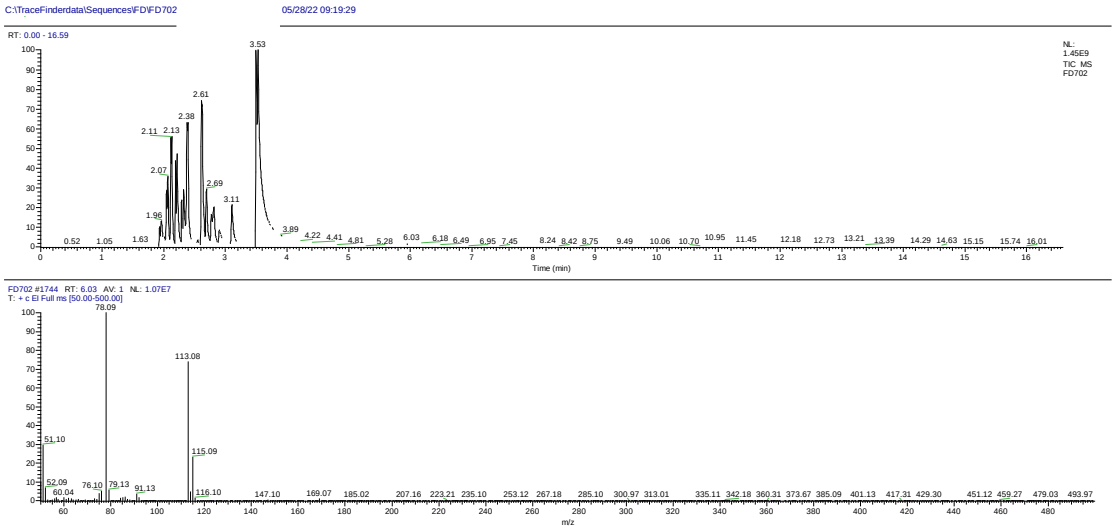
Colorless crystals; yield: 37 mg (60%); M.p. 115–116 °C; R_f = 0.70 (PE/EA 3:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.34–7.22 (m, 3H), 7.21–7.16 (m, 2H), 3.87 (dd, J = 11.7, 2.8 Hz, 1H), 3.60 (dd, J = 14.3, 2.8 Hz, 1H), 2.63 (dd, J = 14.3, 11.7 Hz, 1H), 2.47 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 136.4, 133.4, 129.9, 129.7, 129.2, 128.7, 127.2, 72.3, 34.3, 21.8, 15.9.

1.7 GC-MS Analysis

2-Chloropyridine (RT: 6.03 min)

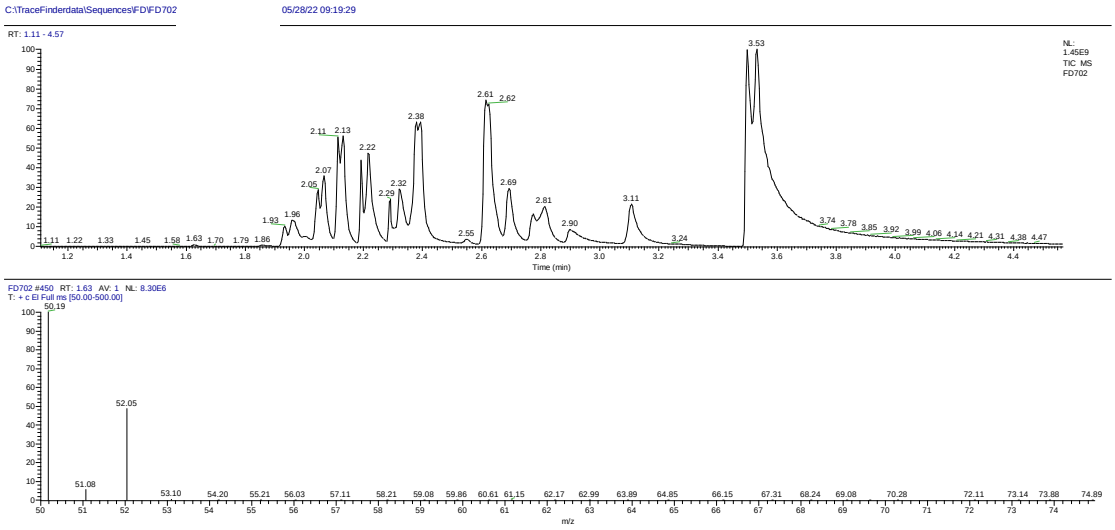
Exact Mass: 113.00



Methyl chloride (RT: 1.63 min)

MeCl

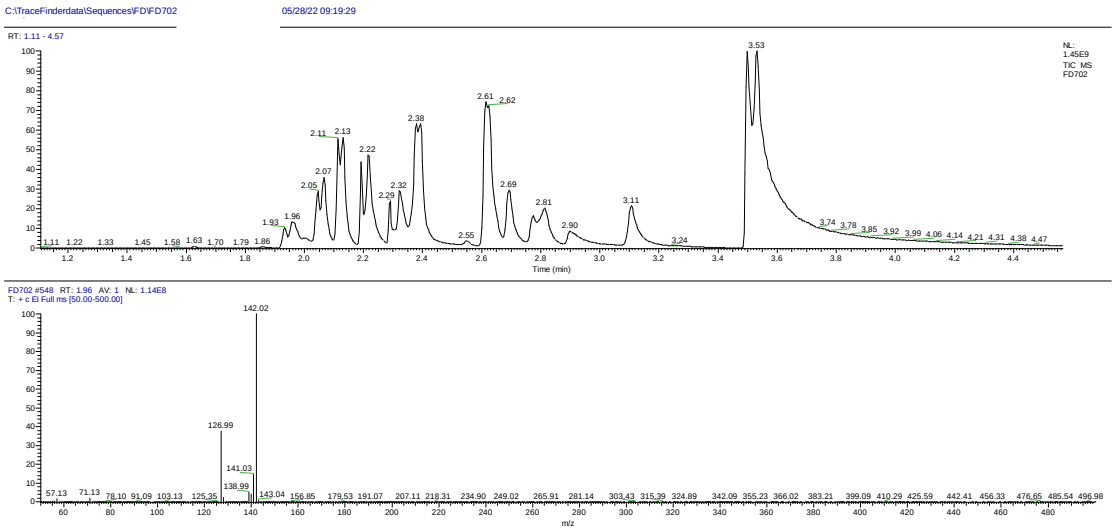
Exact Mass: 49.99



Methyl iodide (RT: 1.96 min)

MeI

Exact Mass: 141.93



1.8 References

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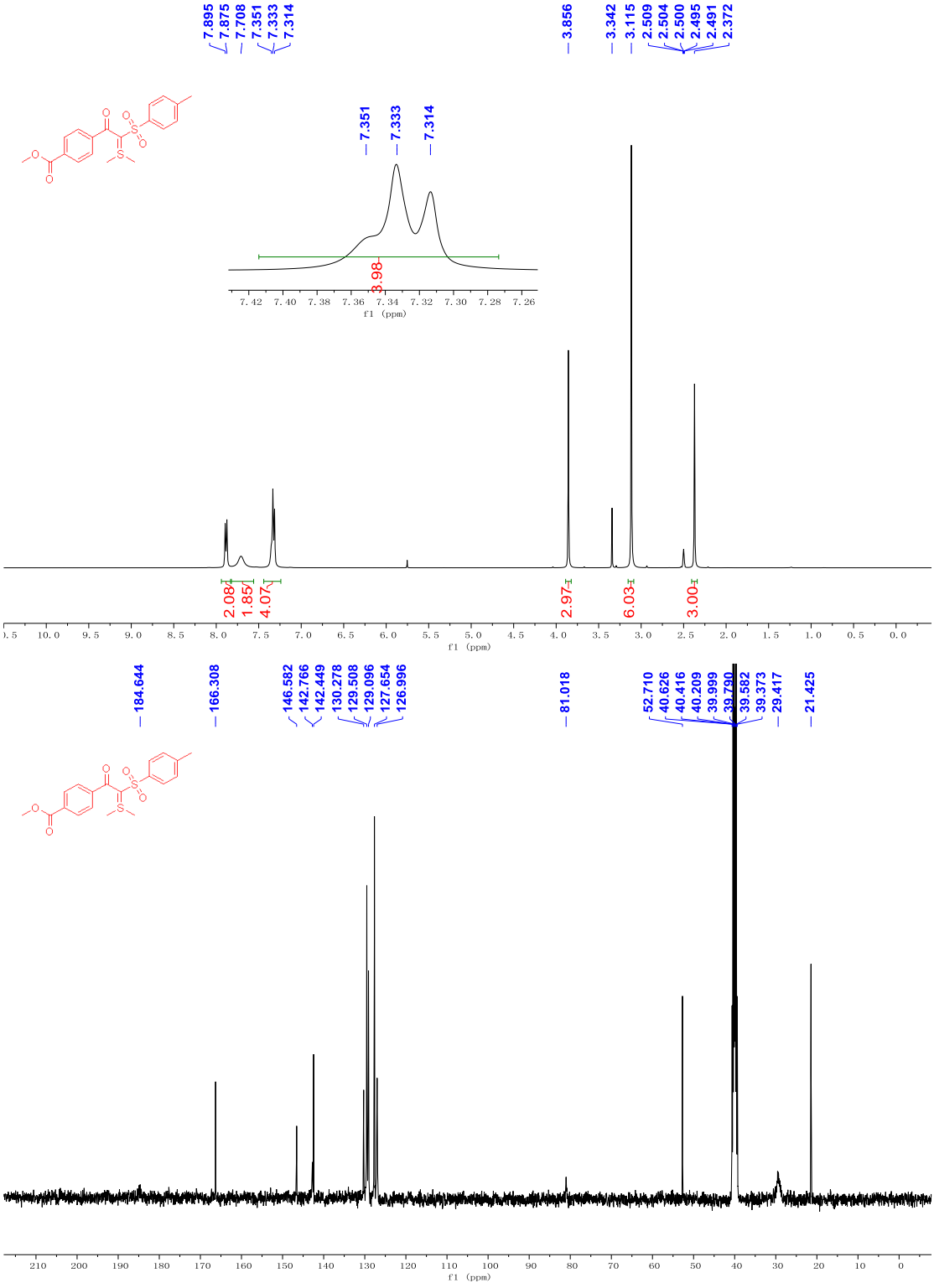
3665-3668.

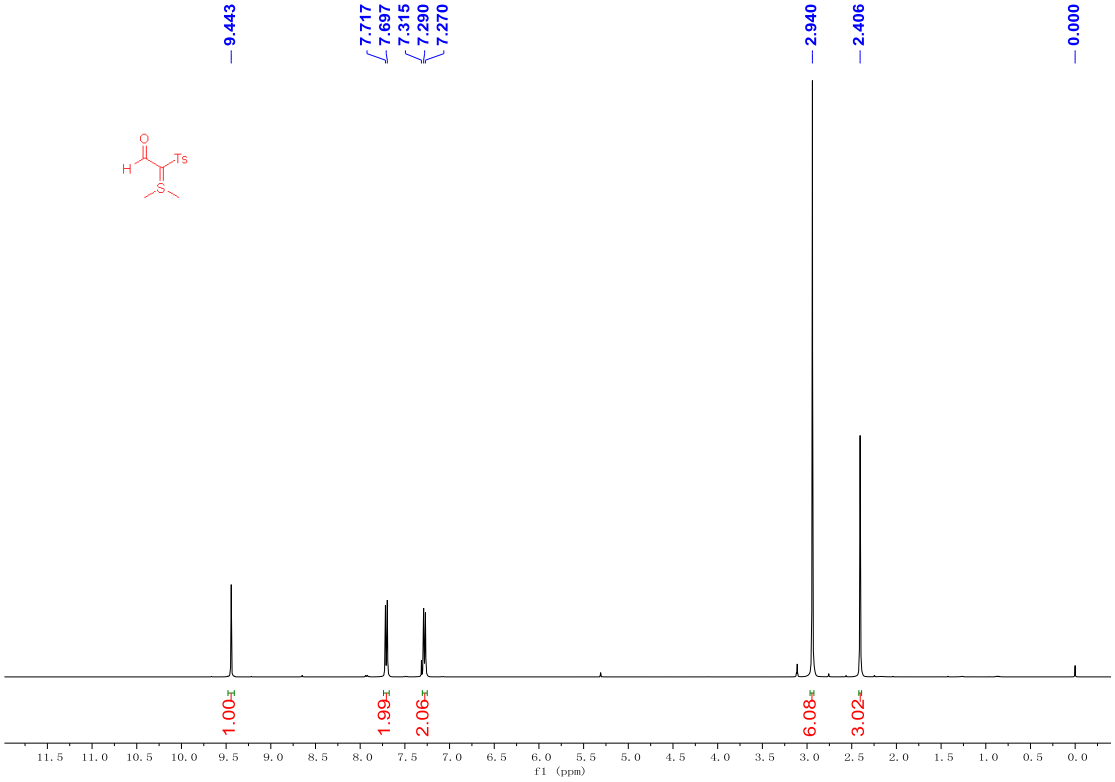
2. Copies of NMR Spectra

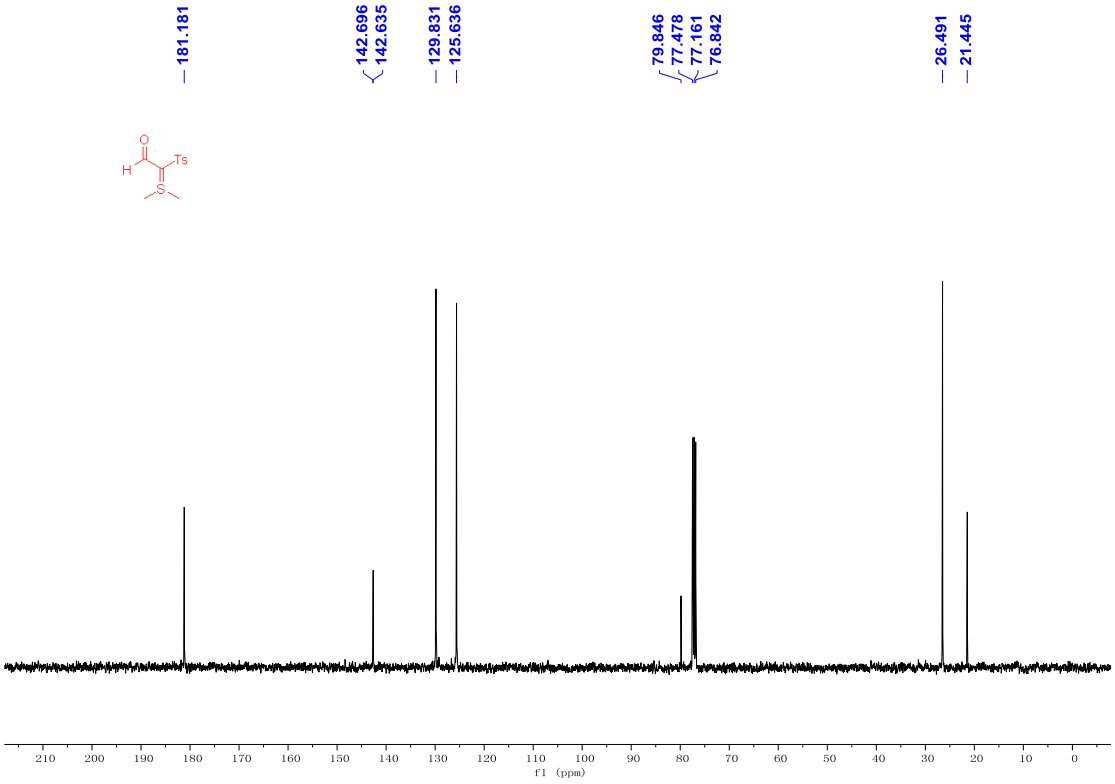
2.1 Copies of NMR Spectra for α-Acyl Sulfonylmethylides 1i, 1l, 1s, 1t, 1u and 1x

Methyl 4-(2-(dimethyl-l4-sulfaneylidene)-2-tosylacetyl)benzoate (**1i**) (DMSO-d_6)

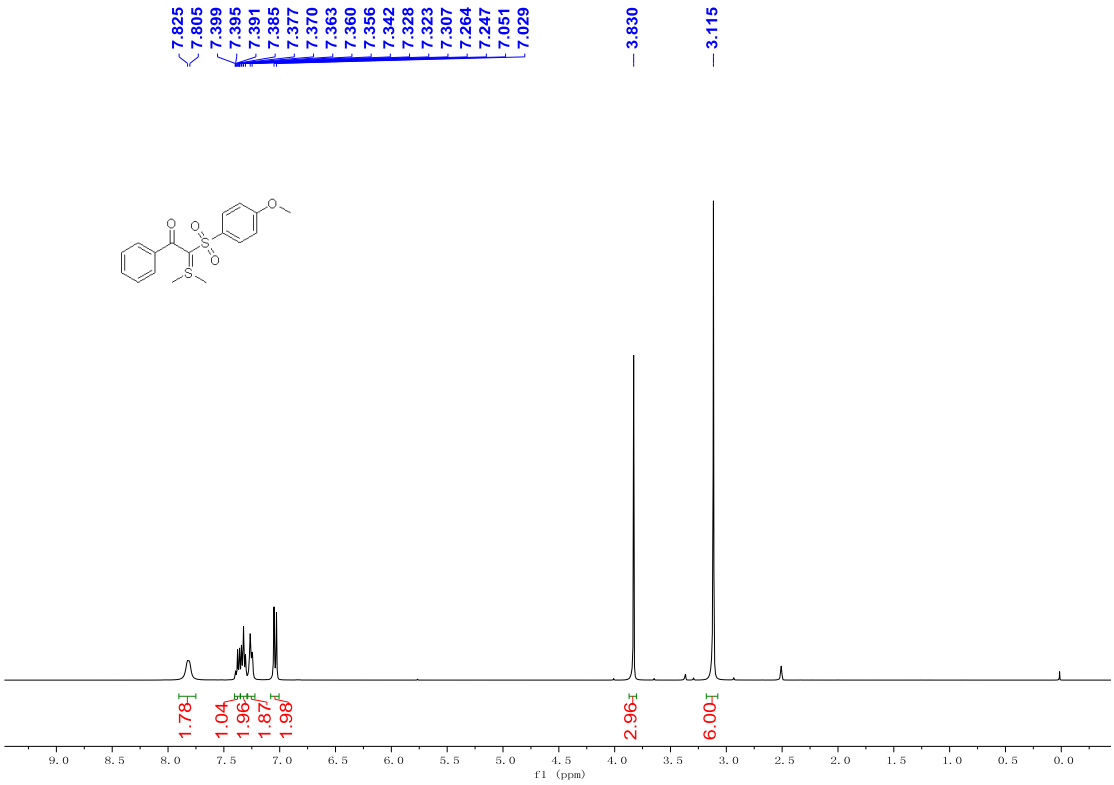


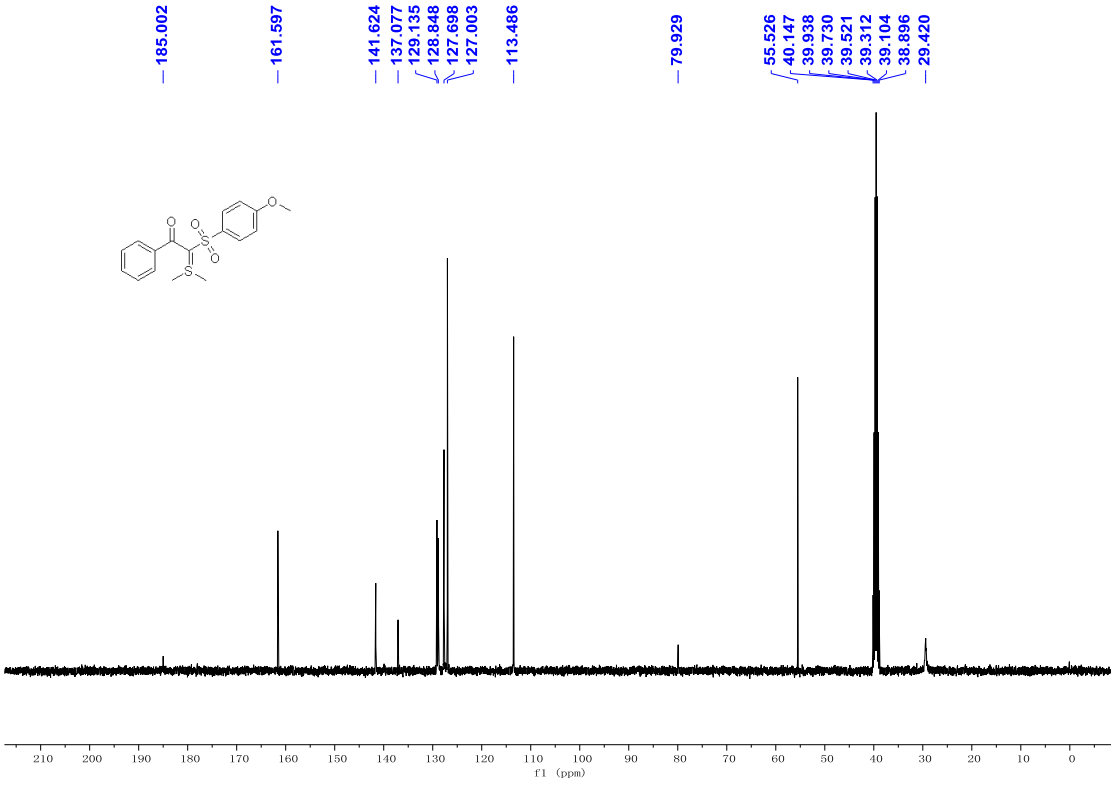
2-(Dimethyl-λ^4-sulfaneylidene)-2-tosylacetaldehyde (**1l**) ($CDCl_3$)



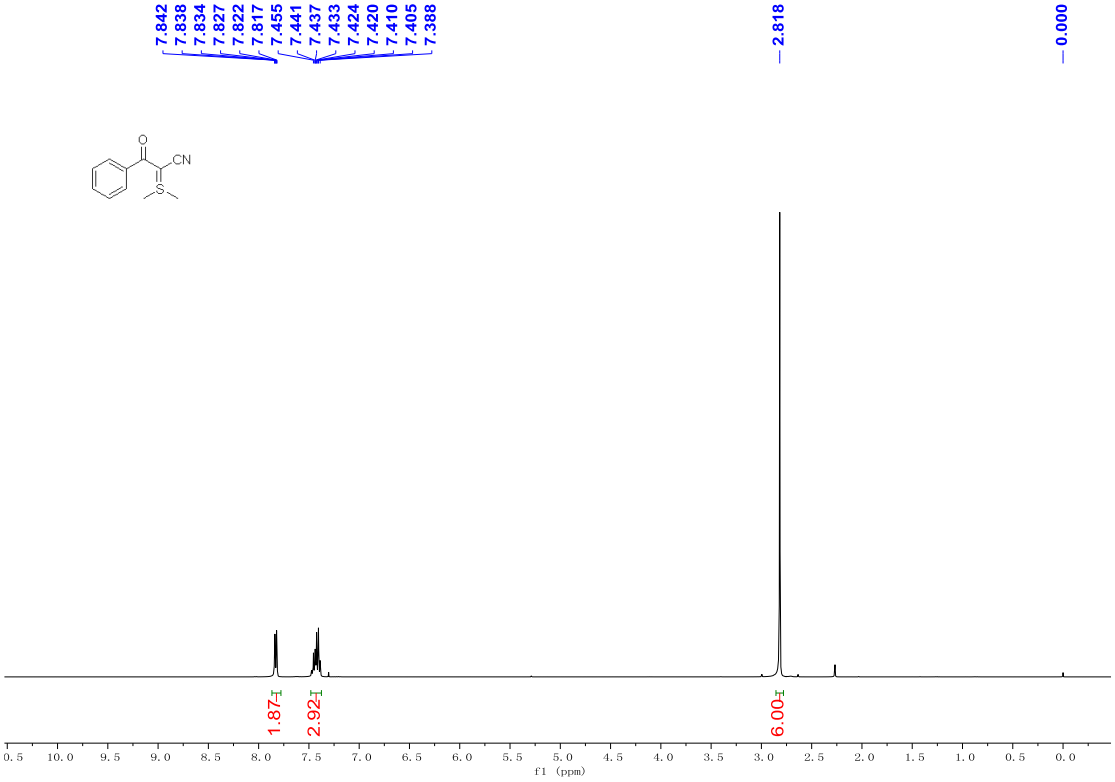


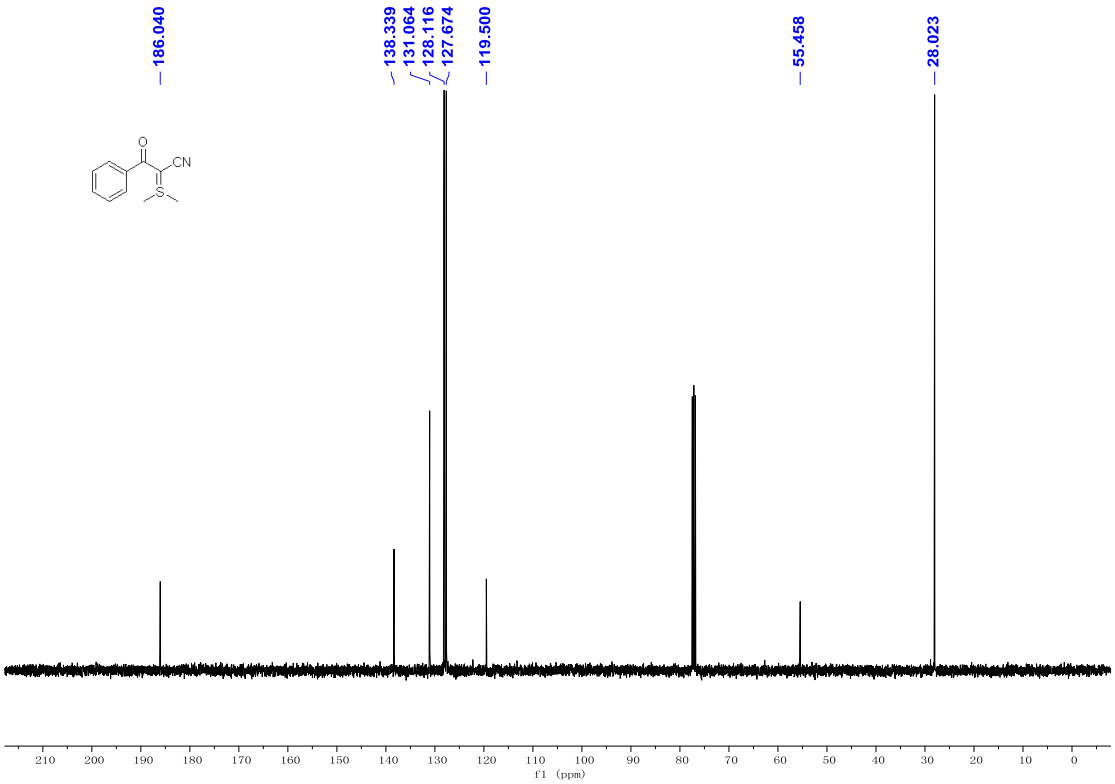
2-(Dimethyl-λ^4-sulfaneylidene)-2-((4-methoxyphenyl)sulfonyl)-1-phenylethan-1-one (**1s**) (DMSO-d_6)



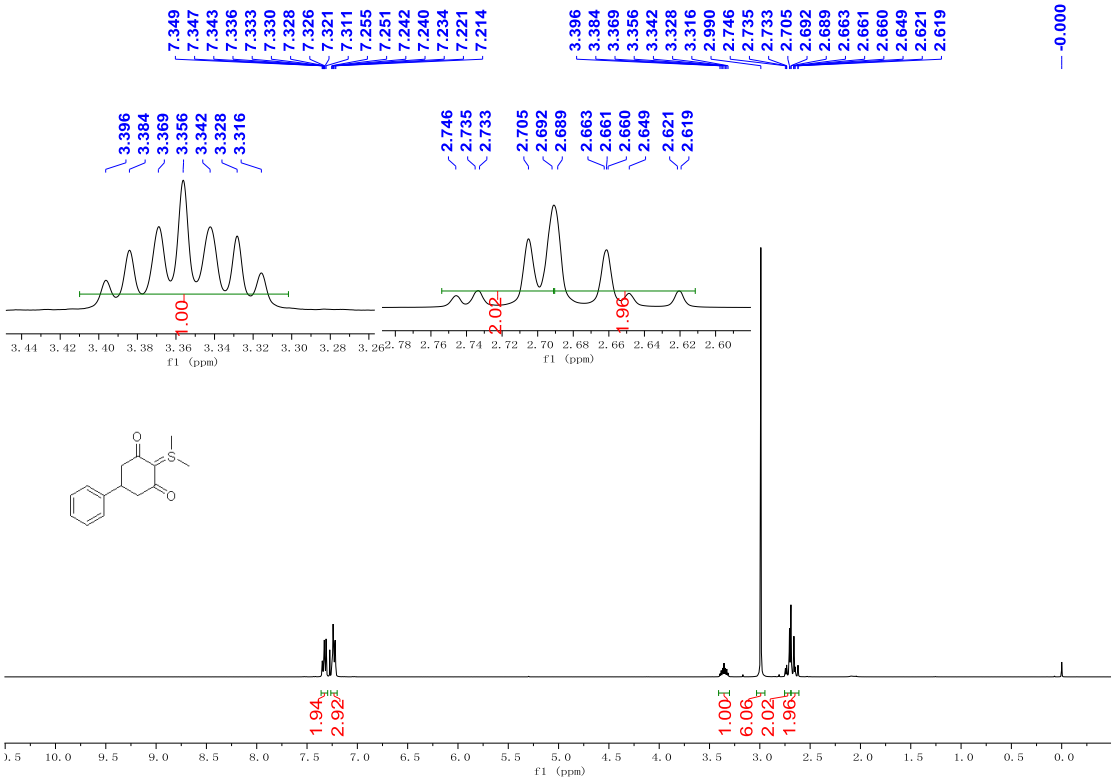


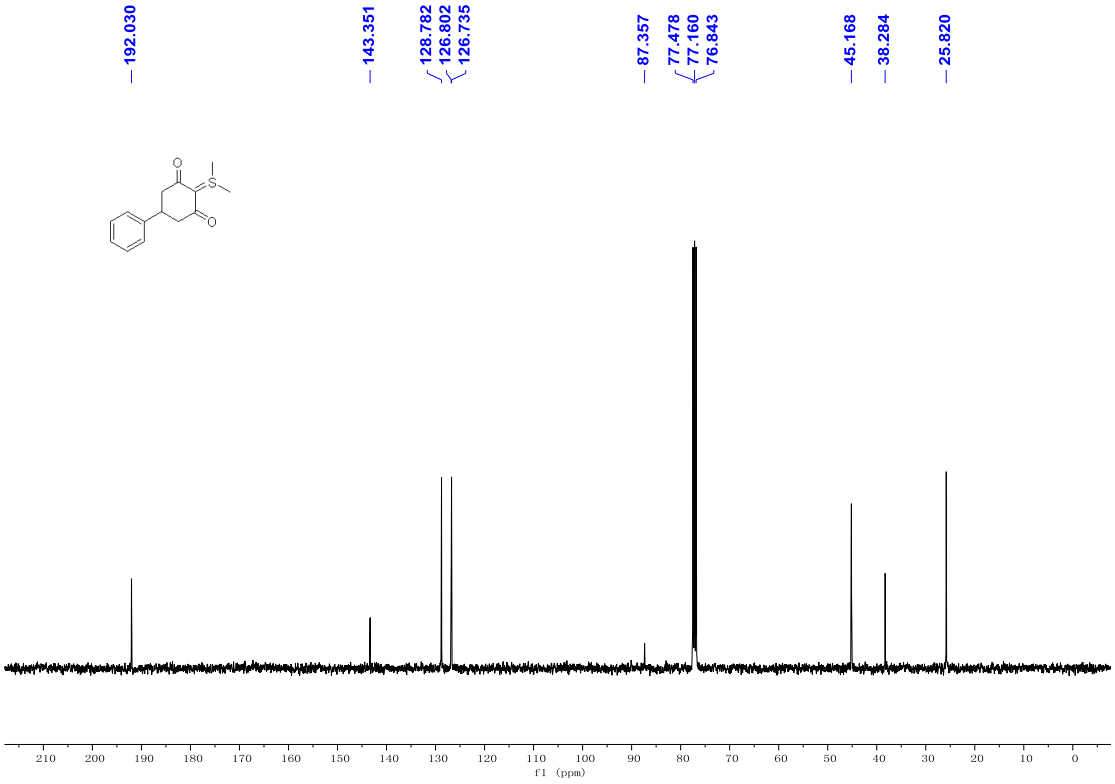
2-(Dimethyl-λ^4-sulfaneylidene)-3-oxo-3-phenylpropanenitrile (**1t**) ($CDCl_3$)



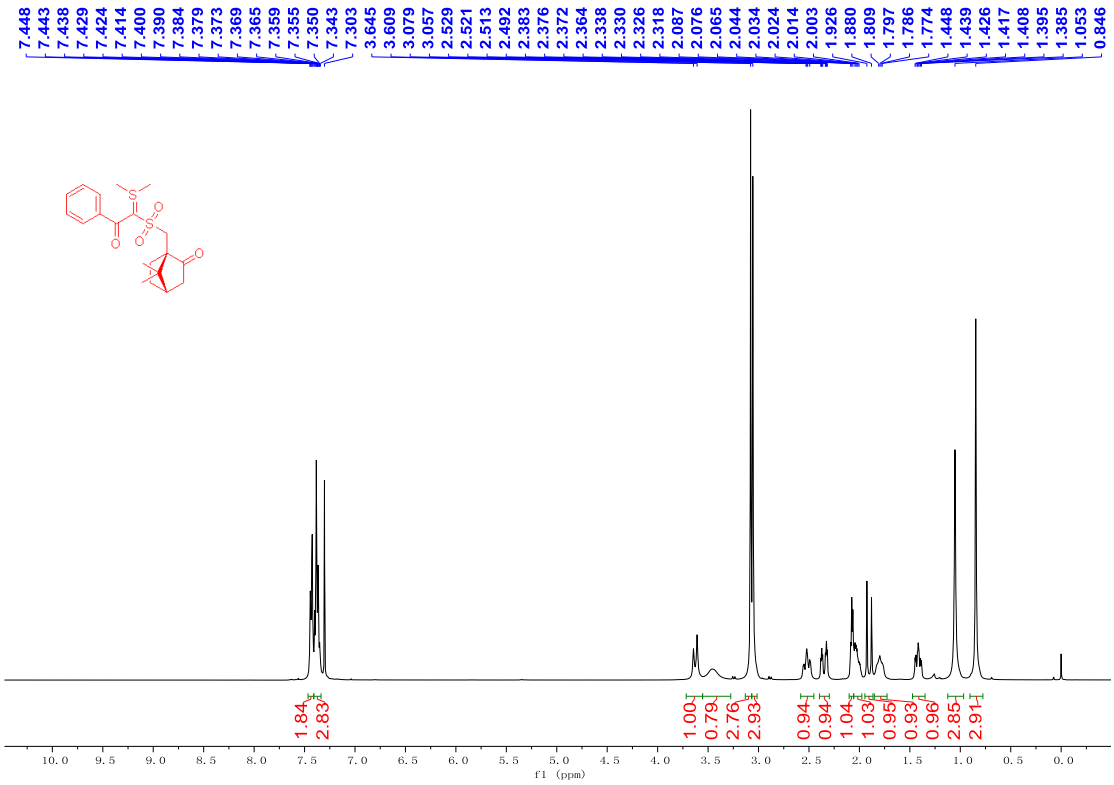


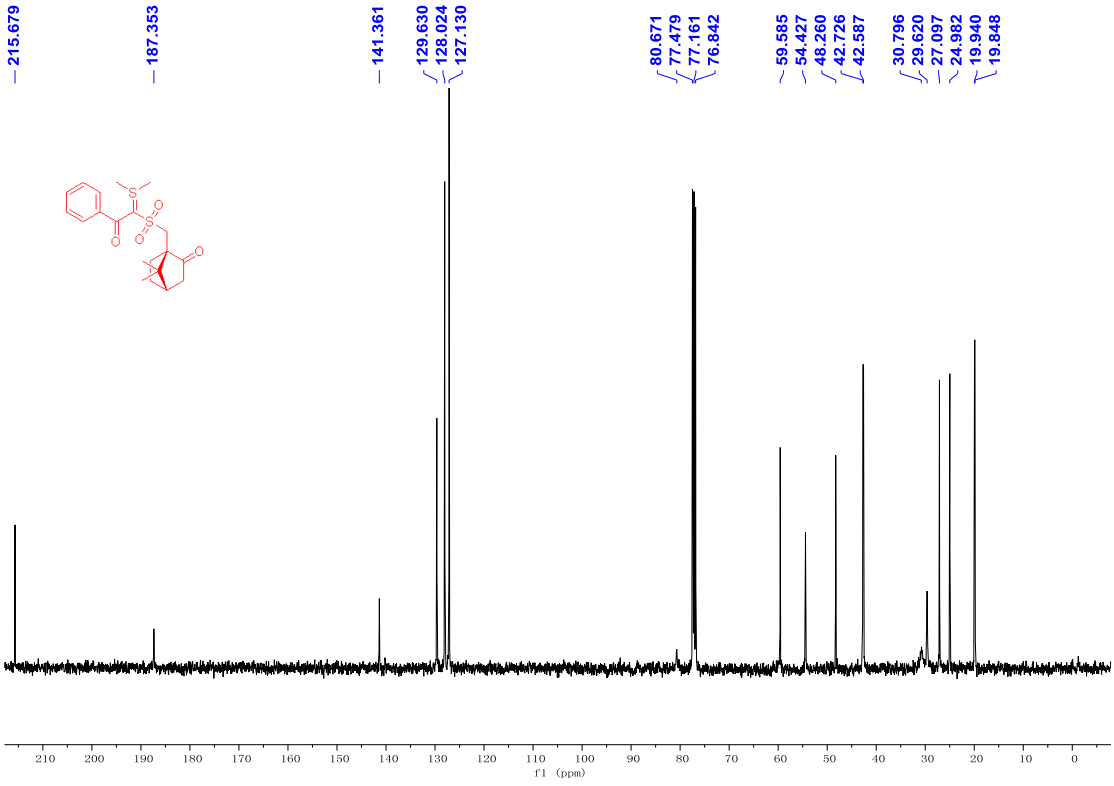
2-(Dimethyl-λ^4-sulfaneylidene)-5-phenylcyclohexane-1,3-dione (**1u**) ($CDCl_3$)





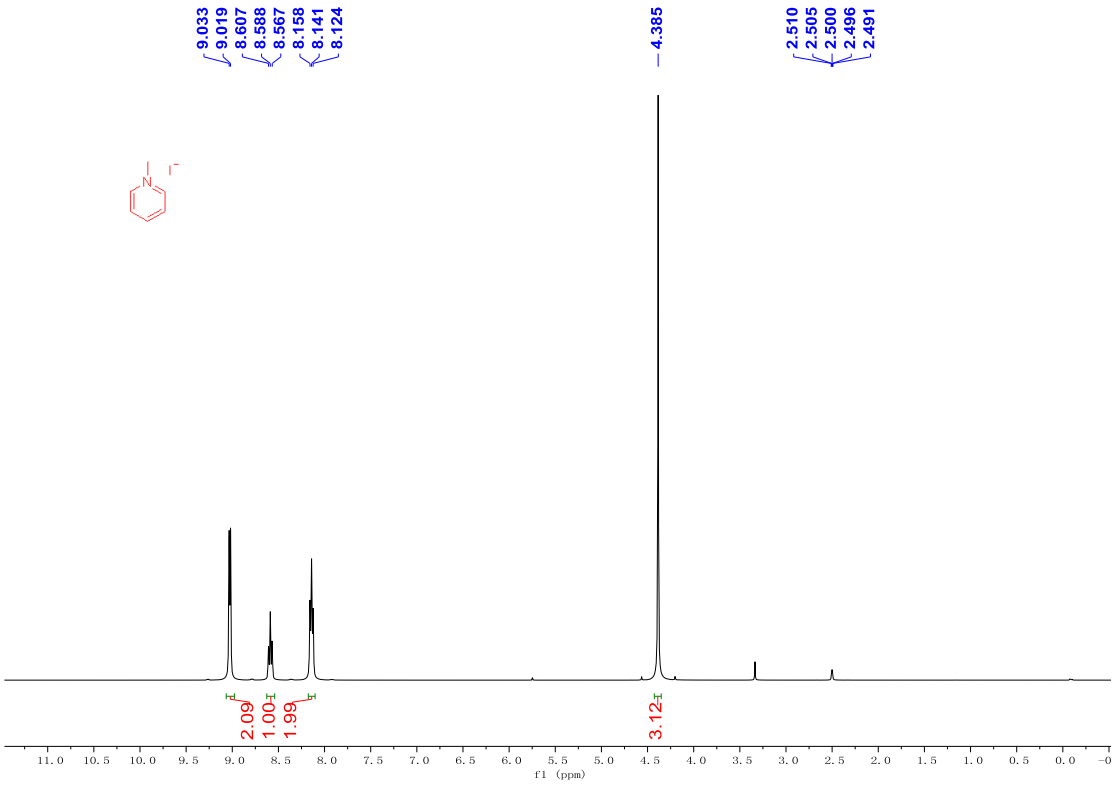
(1*R*,4*S*)-1-(((1-(Dimethyl-λ^4-sulfaneylidene)-2-oxo-2-phenylethyl)sulfonyl)methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-one (**1x**) ($CDCl_3$)

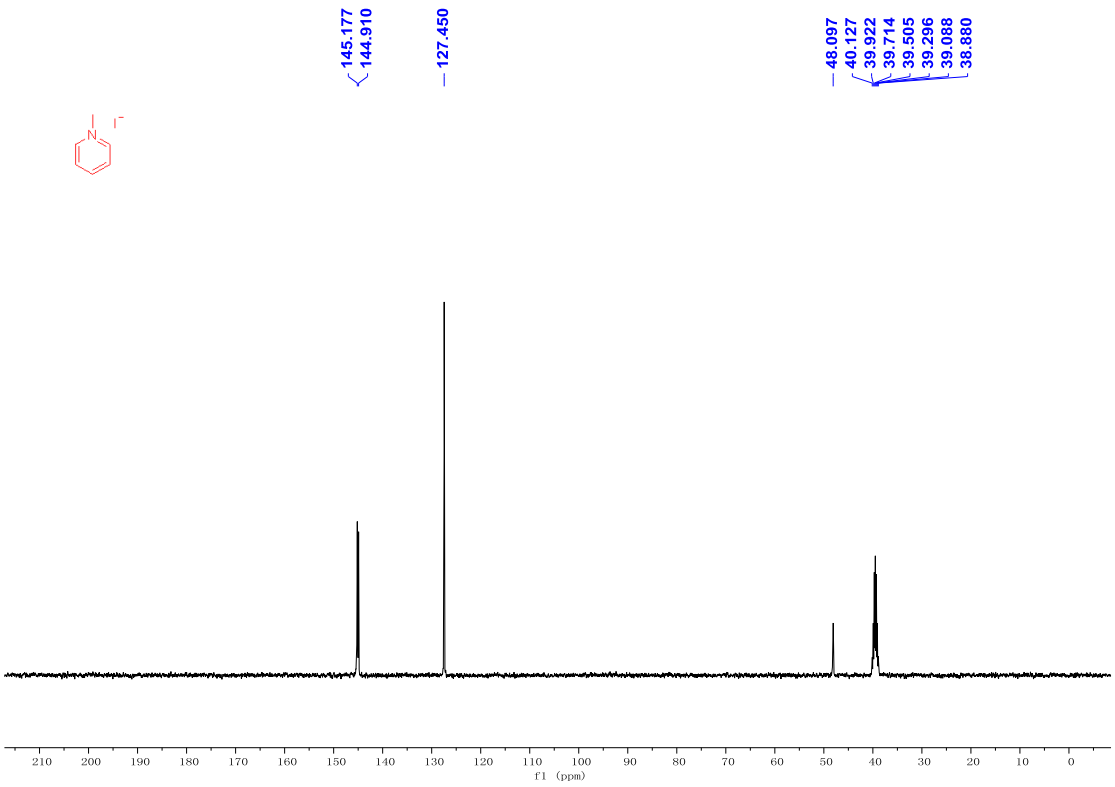




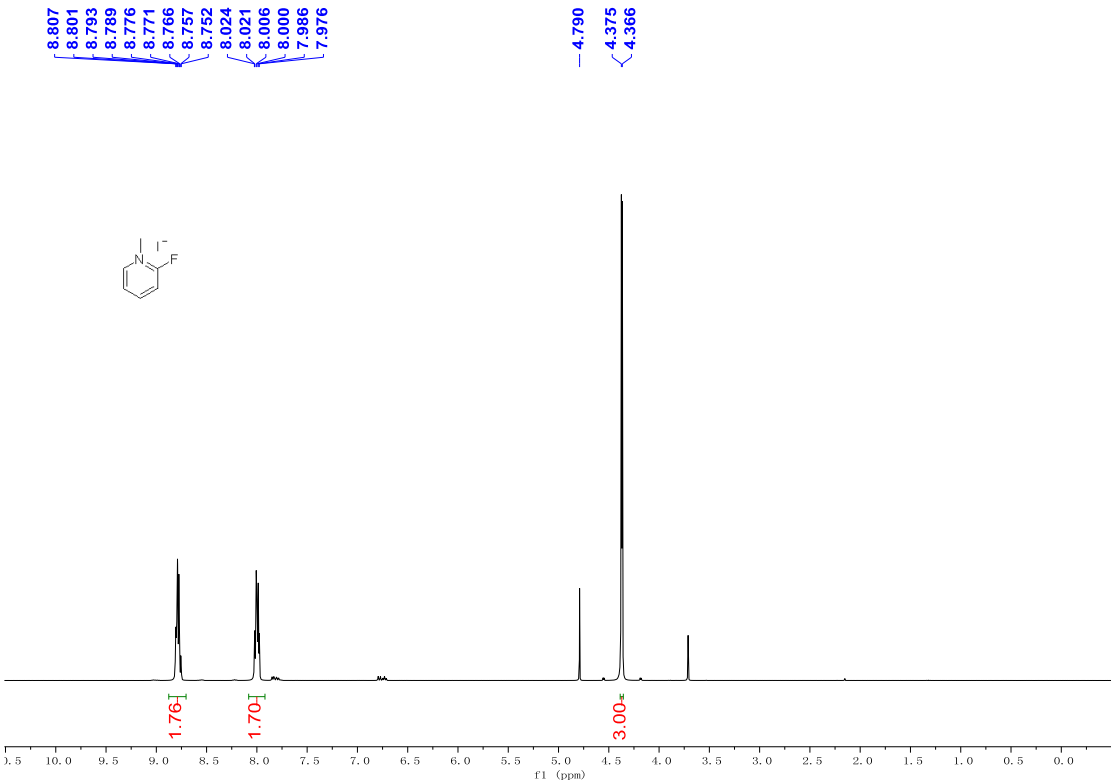
2.2 Copies of NMR Spectra for 1-Methylpyridinium Halide Salts 2

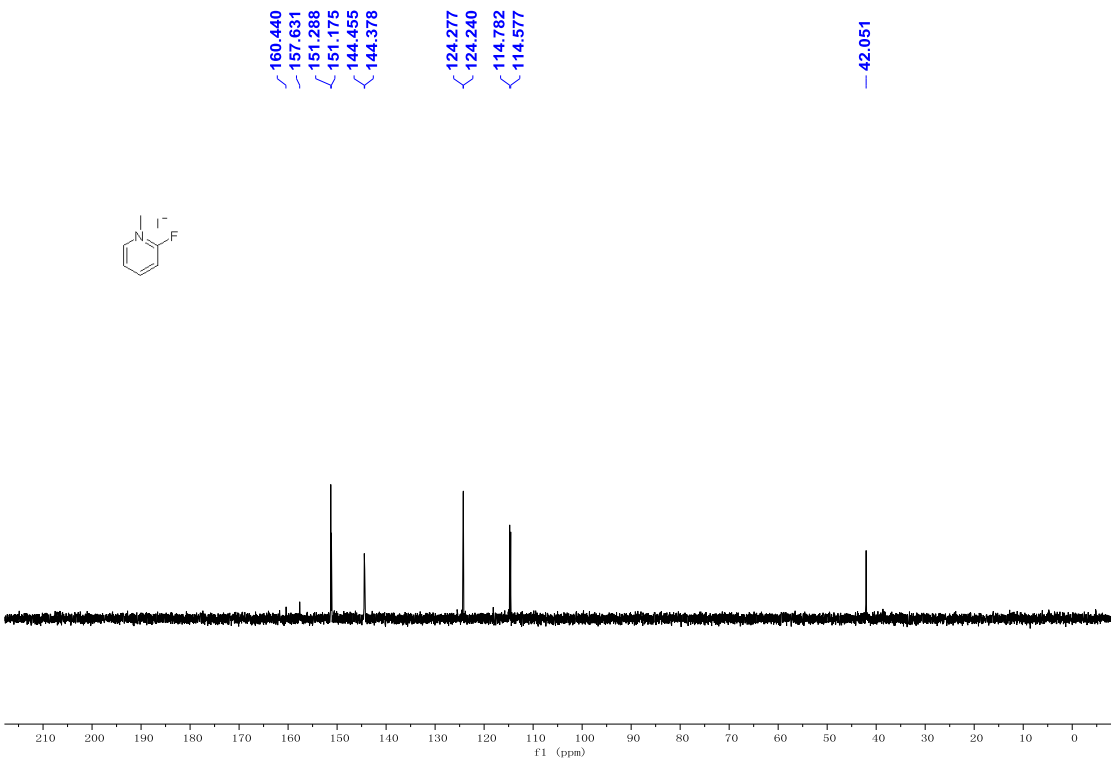
1-Methylpyridin-1-ium iodide (**2b**) (DMSO-d_6)

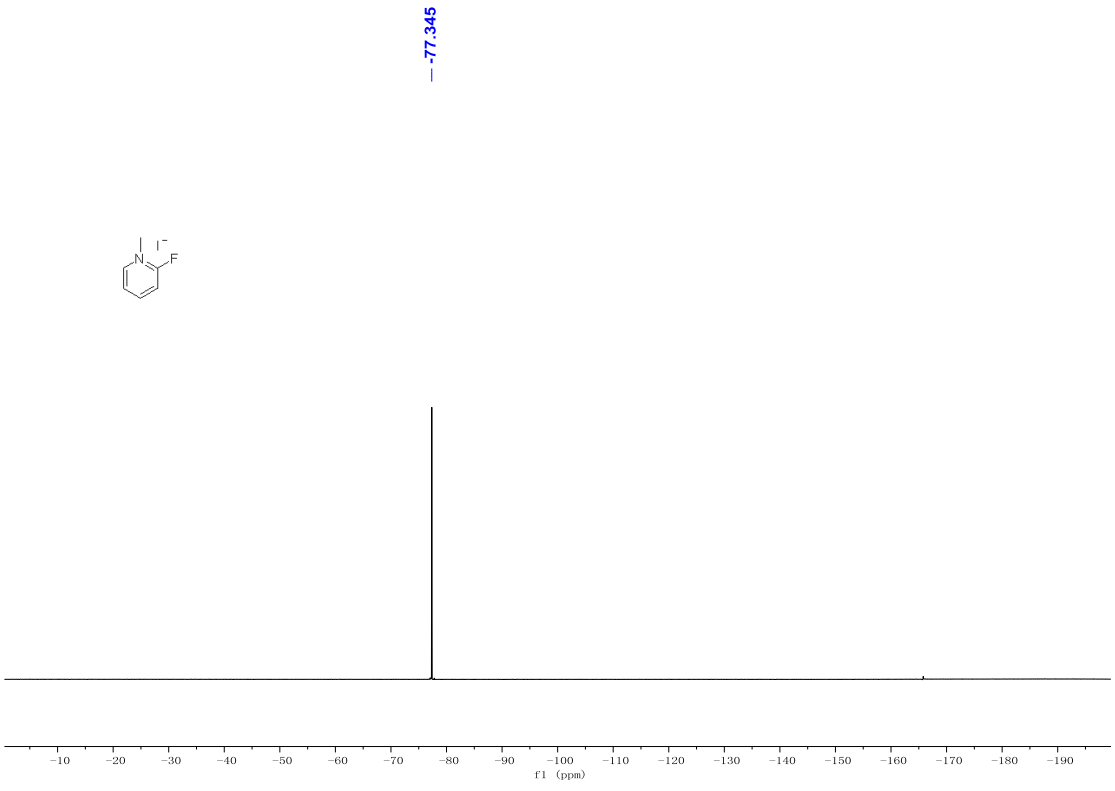




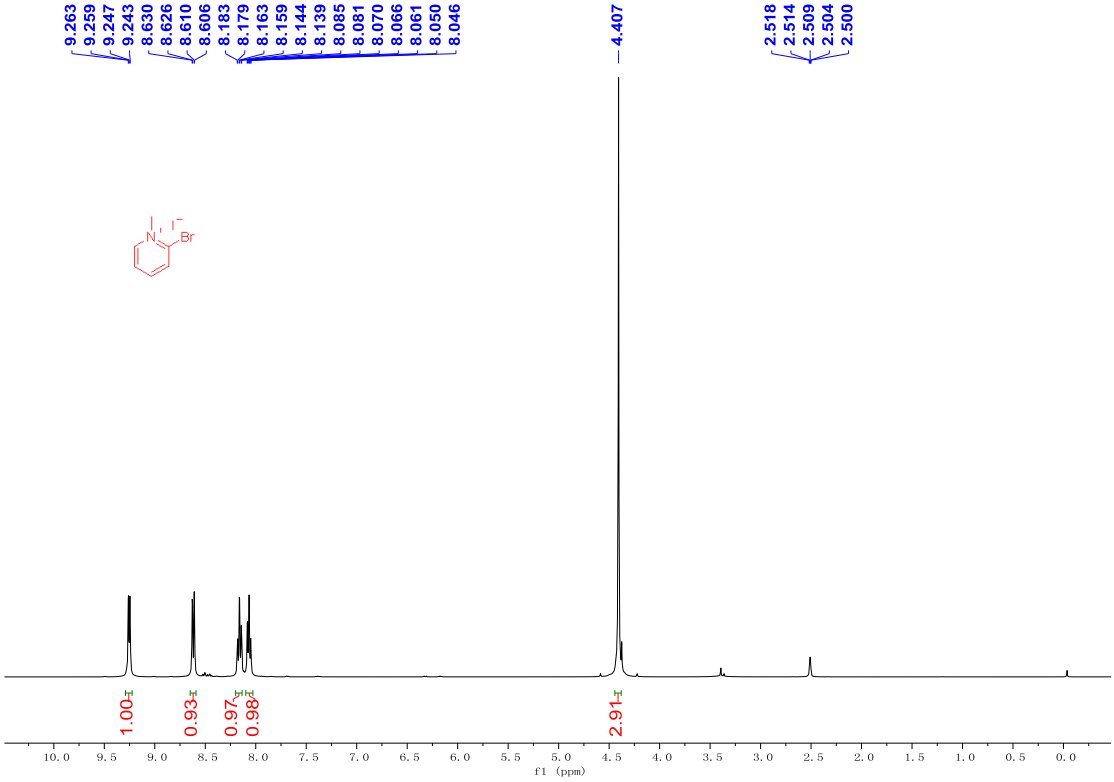
2-Fluoro-1-methylpyridin-1-ium iodide (**2c**) (D_2O)

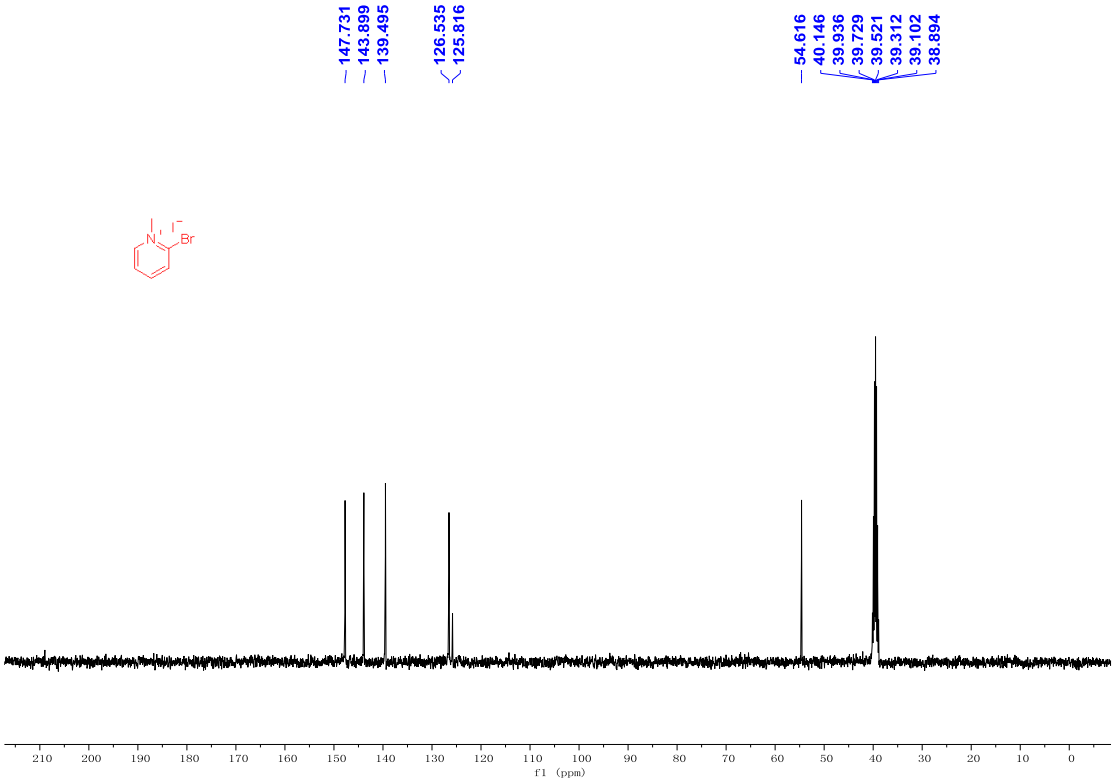




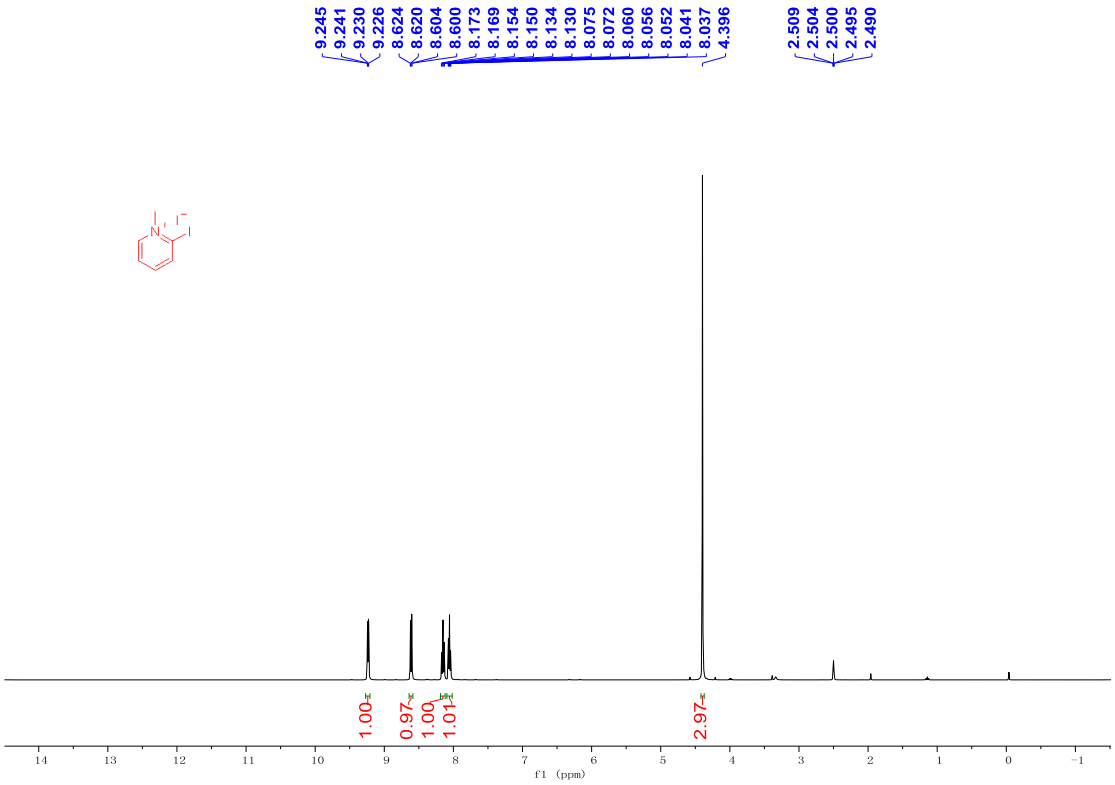

-77.345
N
I⁻
F
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

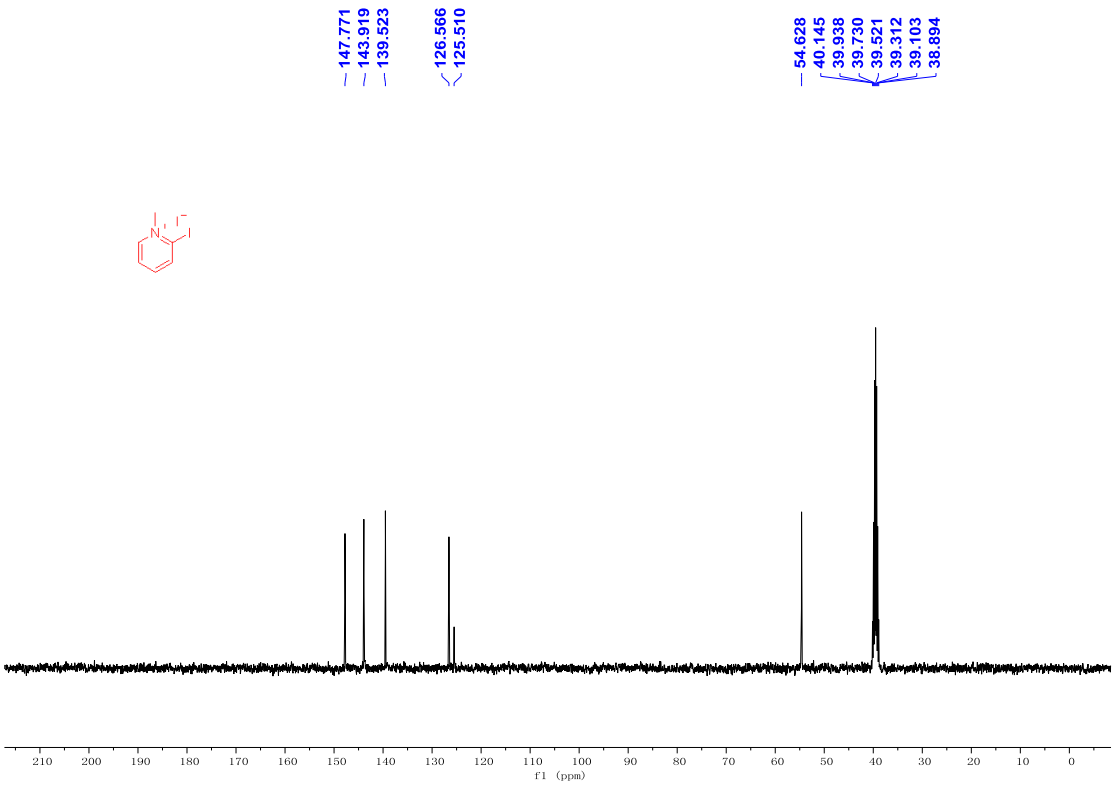
2-Bromo-1-methylpyridin-1-ium iodide (**2d**) (DMSO-d_6)



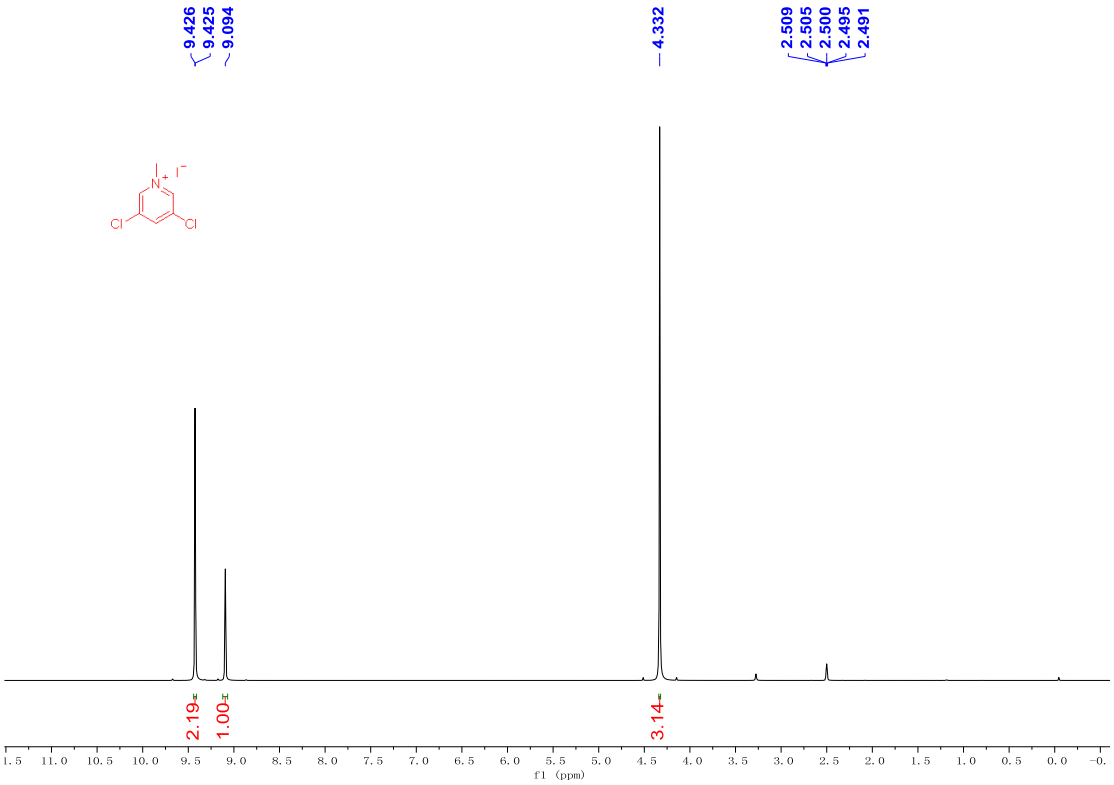


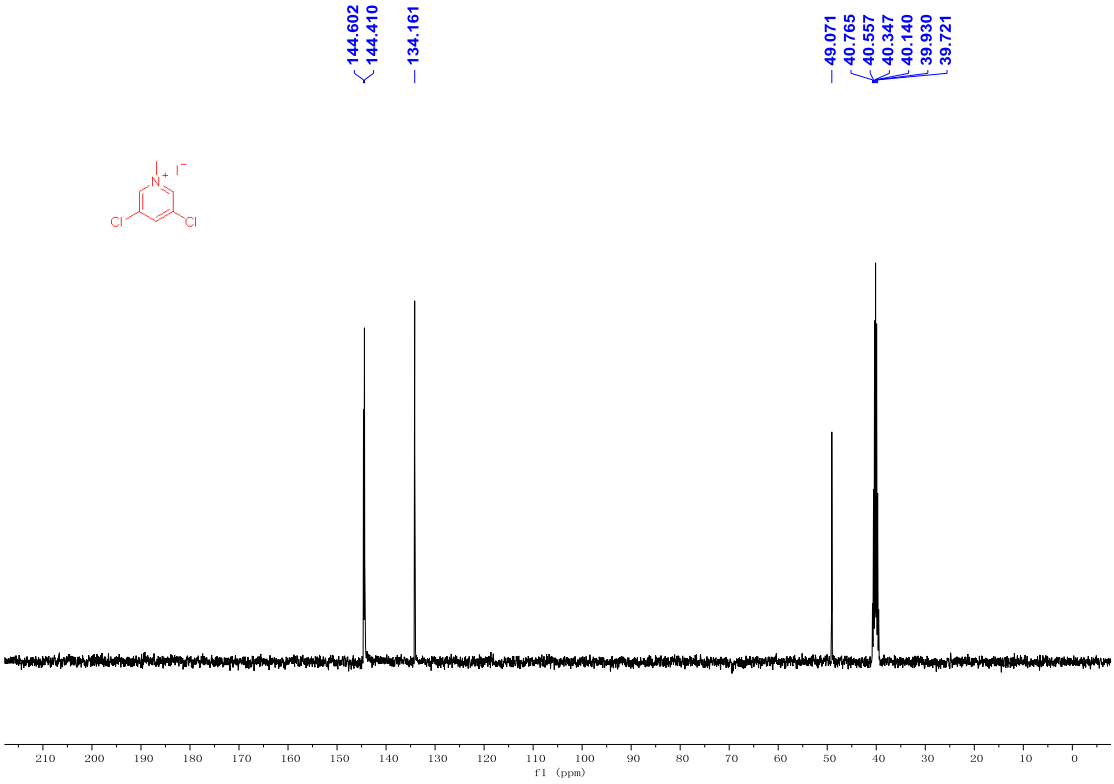
2-Iodo-1-methylpyridin-1-ium iodide (**2e**) (DMSO-d_6)



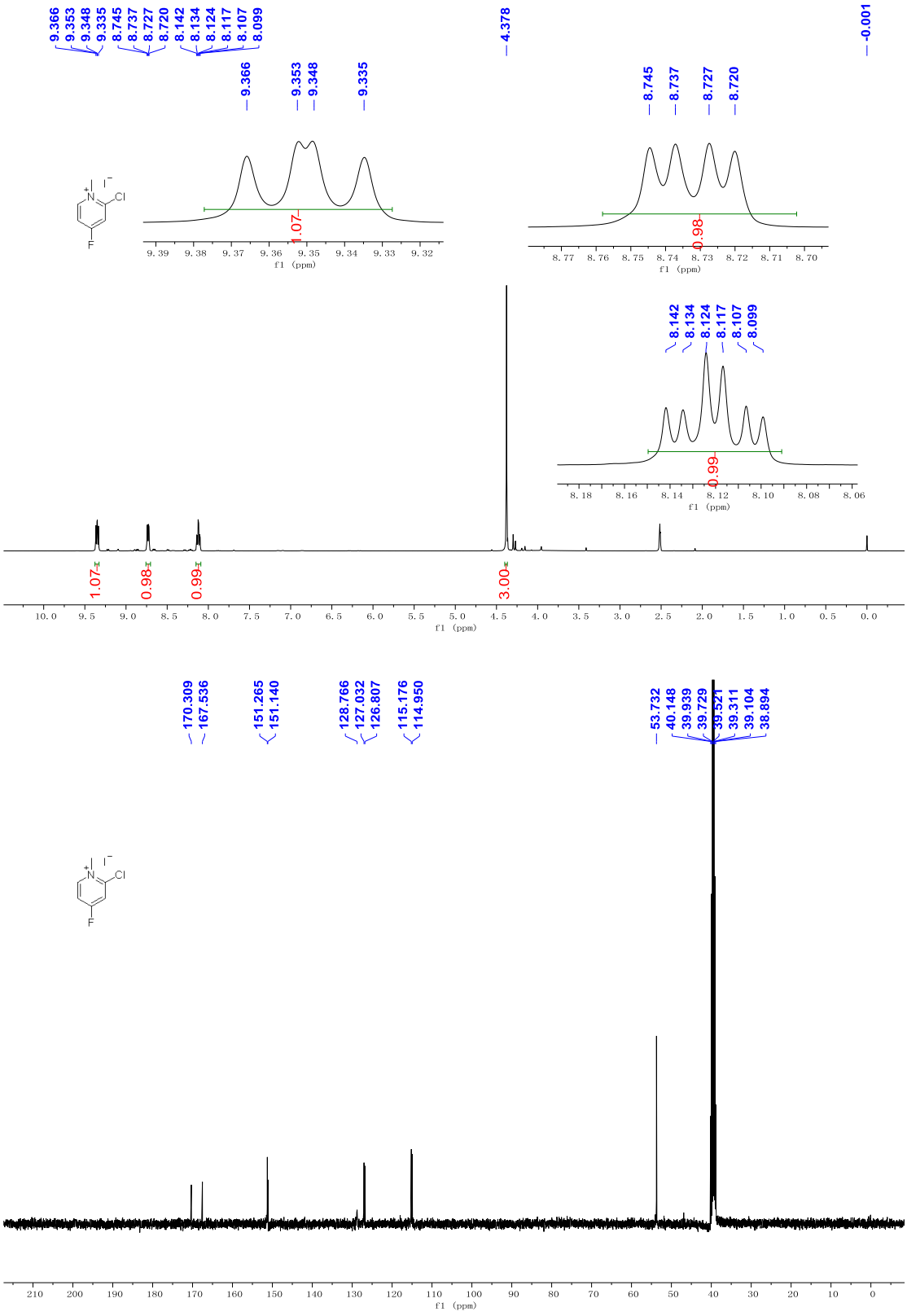


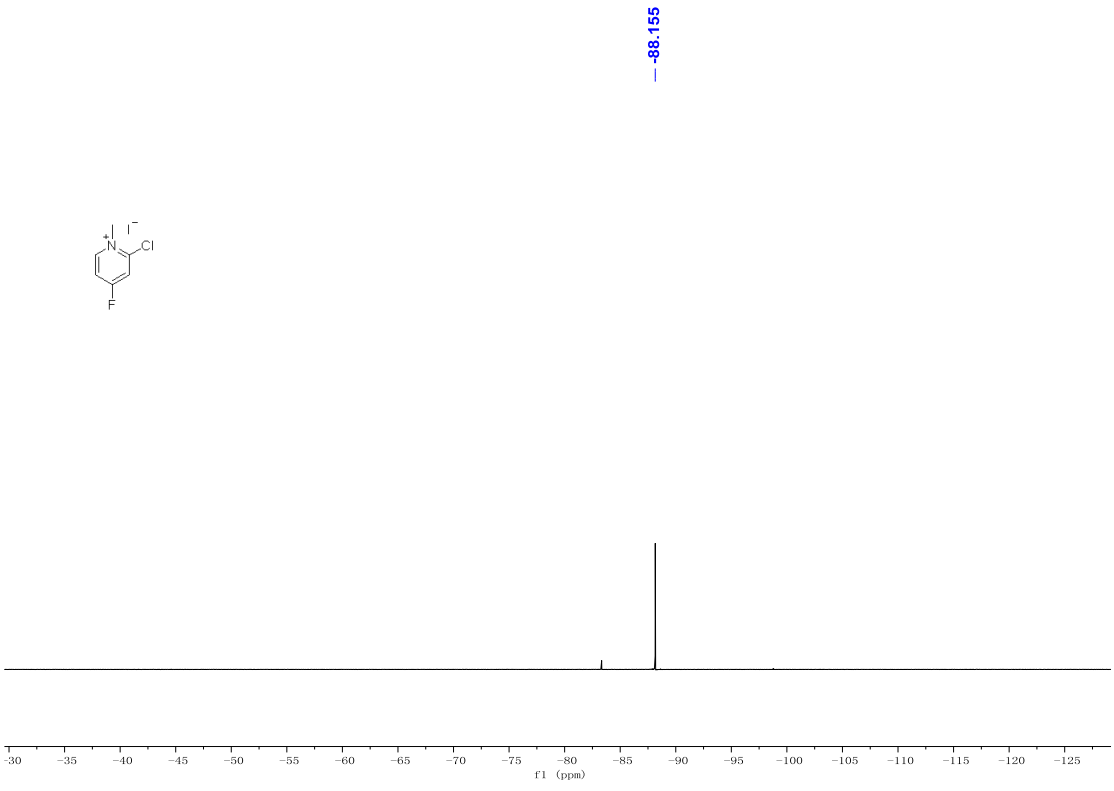
3,5-Dichloro-1-methylpyridin-1-ium (**2f**) (DMSO-d_6)





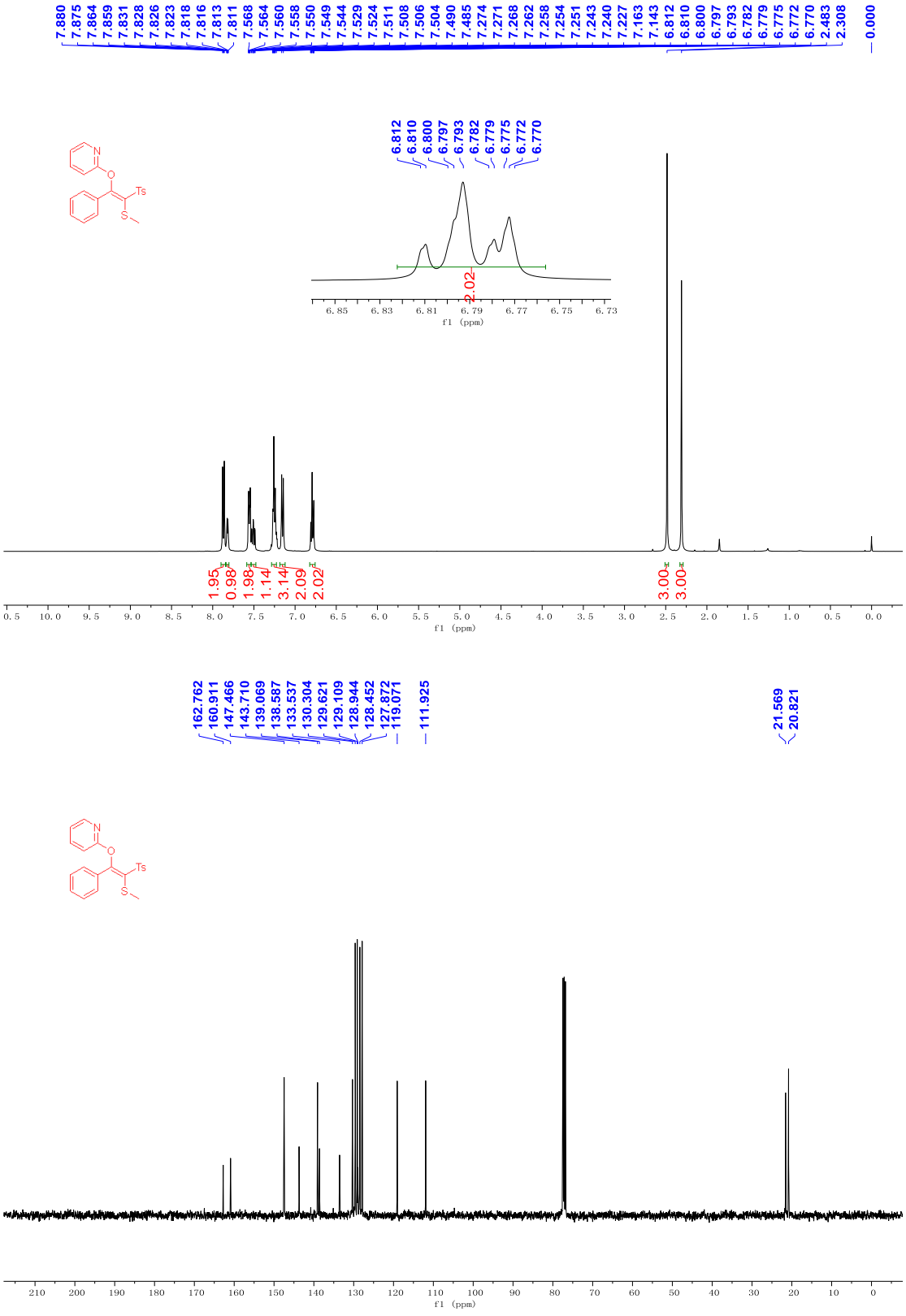
2-Chloro-4-fluoro-1-methylpyridin-1-ium iodide (**2g**) (DMSO-d_6)



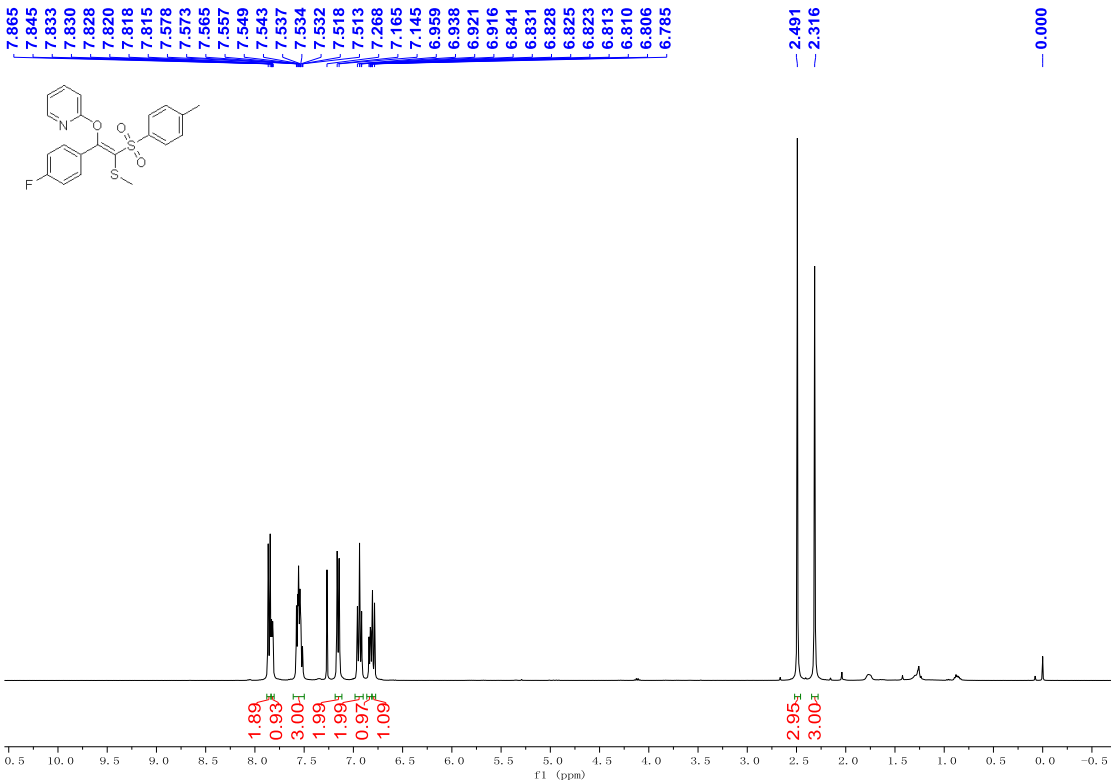

-88.155
I⁻
N⁺
Cl
F
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
f1 (ppm)

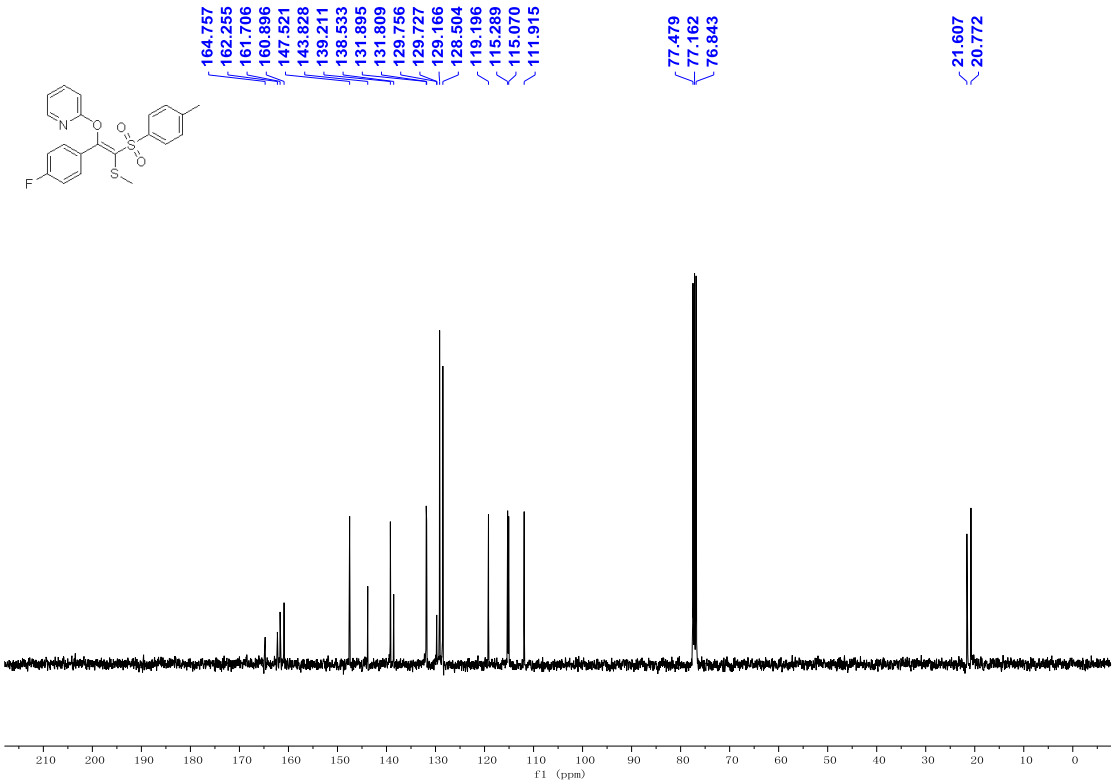
2.3 Copies of NMR Spectra for Products 3

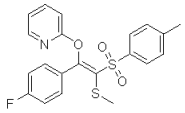
(*Z*)-2-((2-(Methylthio)-1-phenyl-2-tosylvinyl)oxy)pyridine (**3a**) ($CDCl_3$)



(Z)-2-((1-(4-fluorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3b**) ($CDCl_3$)

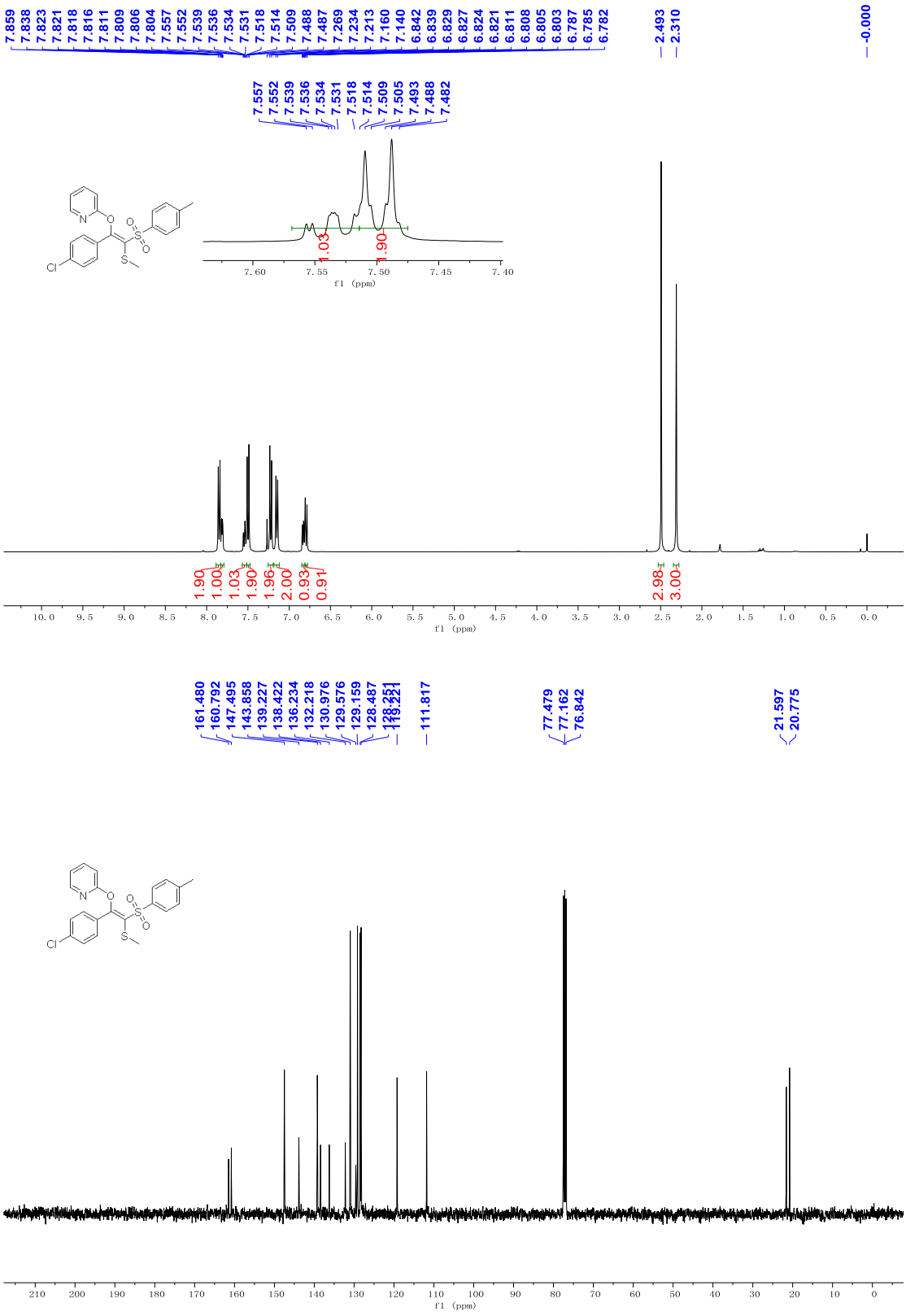




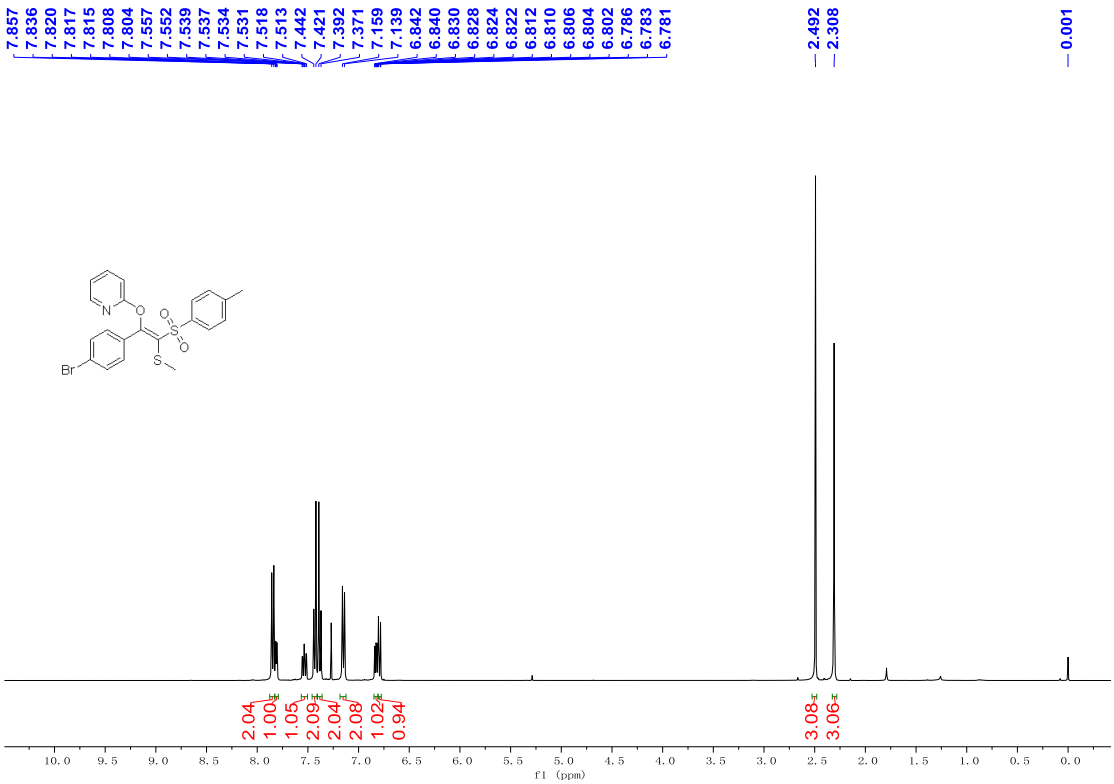

N
O
O
S
O
F
S

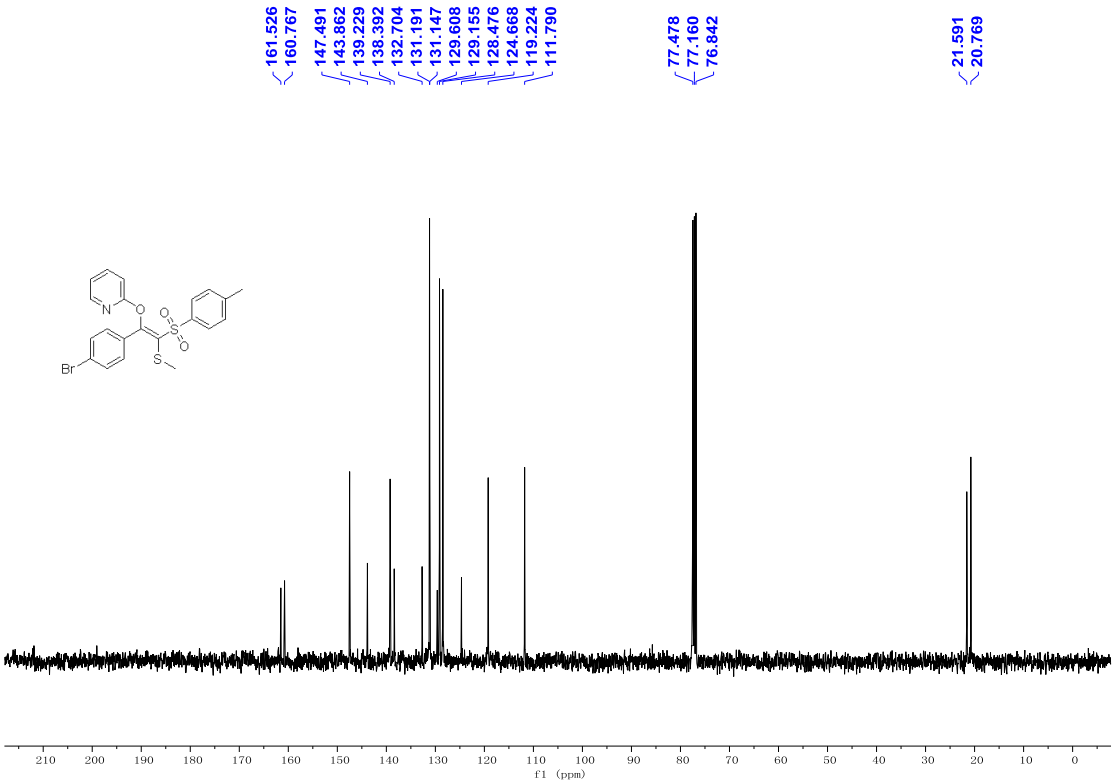
-108.707
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

(*Z*)-2-((1-(4-chlorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3c**) ($CDCl_3$)

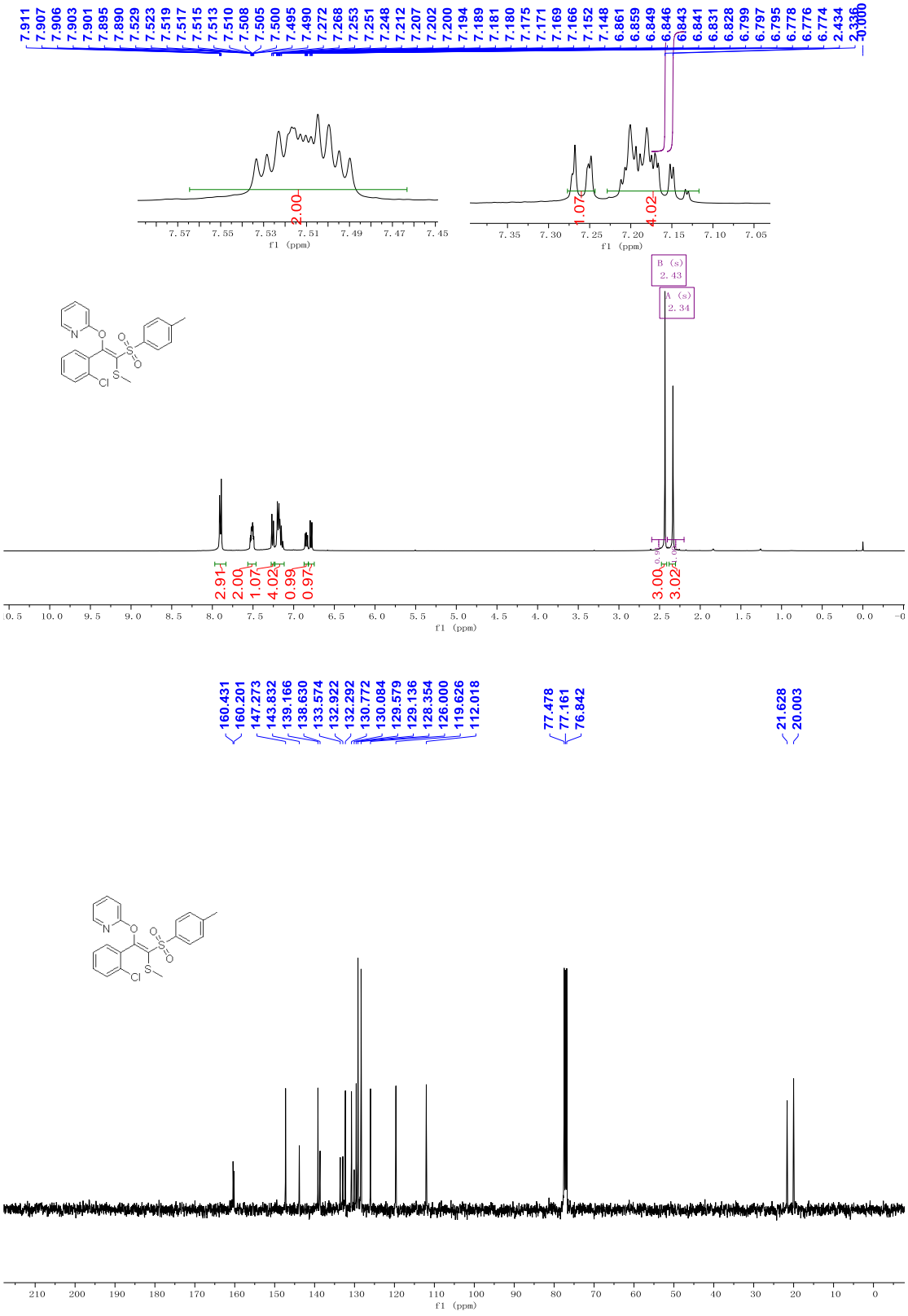


(*Z*)-2-((1-(4-bromophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3d**) ($CDCl_3$)

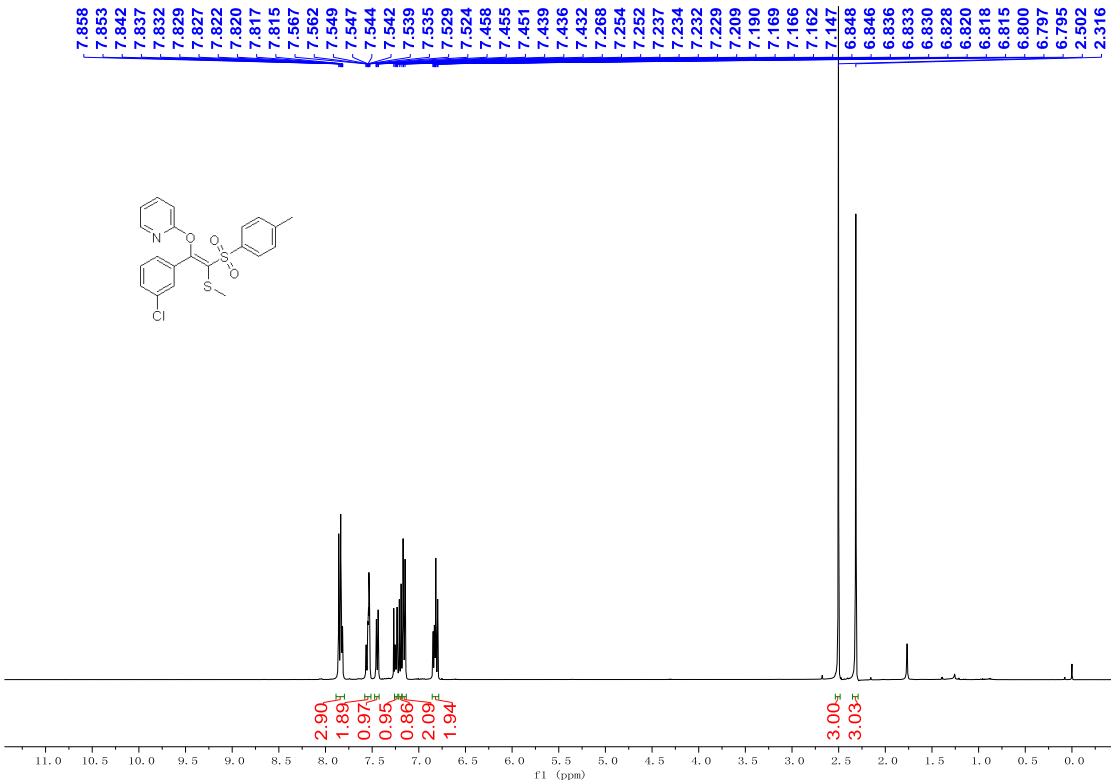


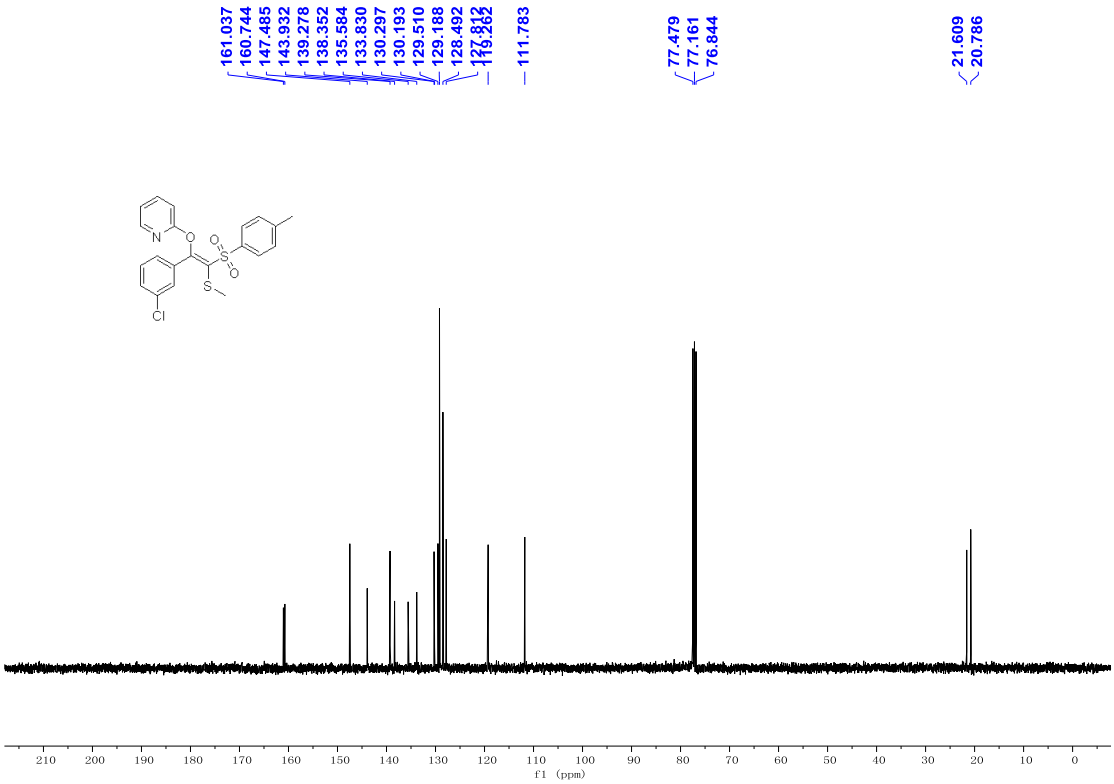


(*Z*)-2-((1-(2-Chlorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3e**)

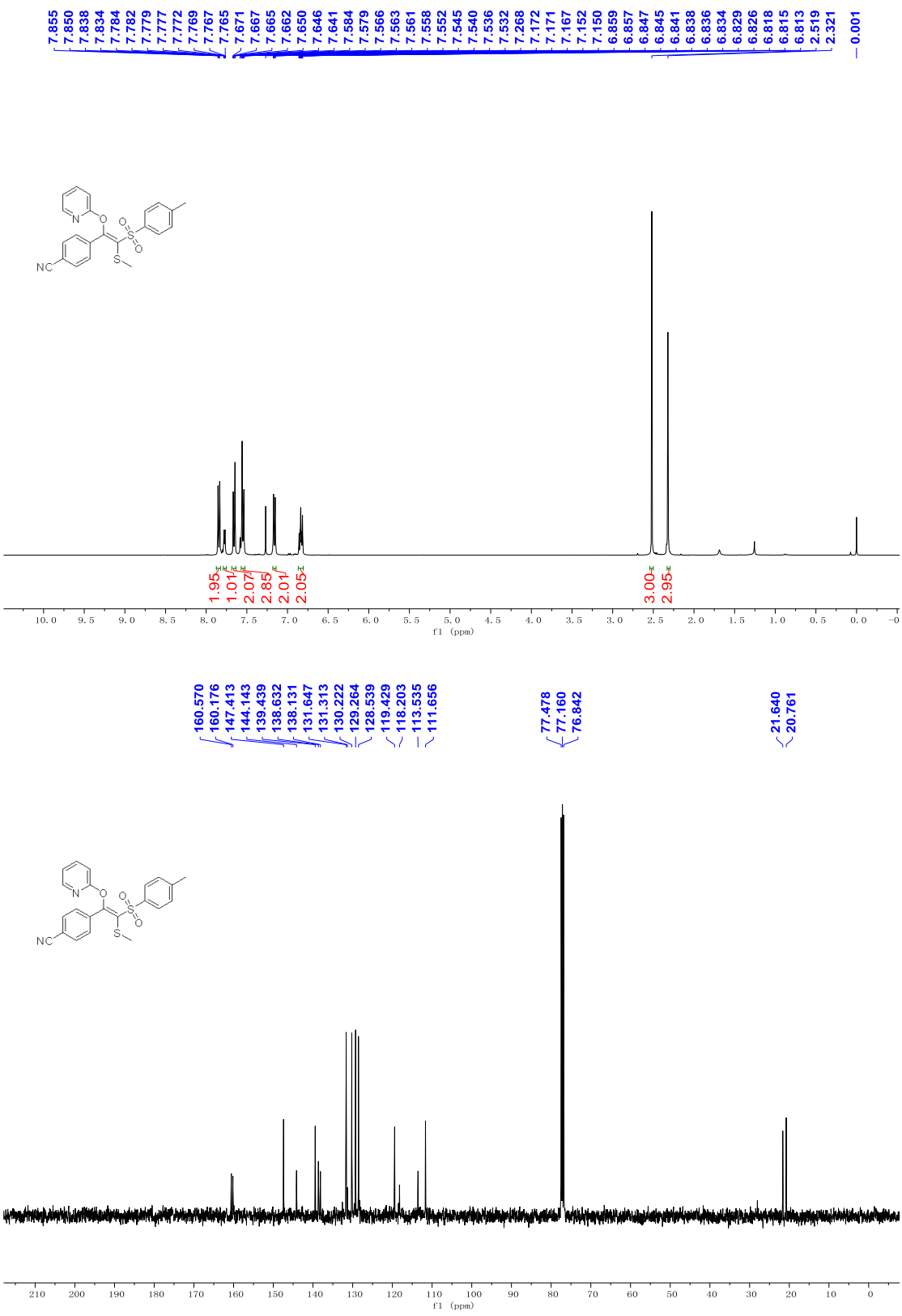


(*Z*)-2-((1-(3-Chlorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3f**) ($CDCl_3$)

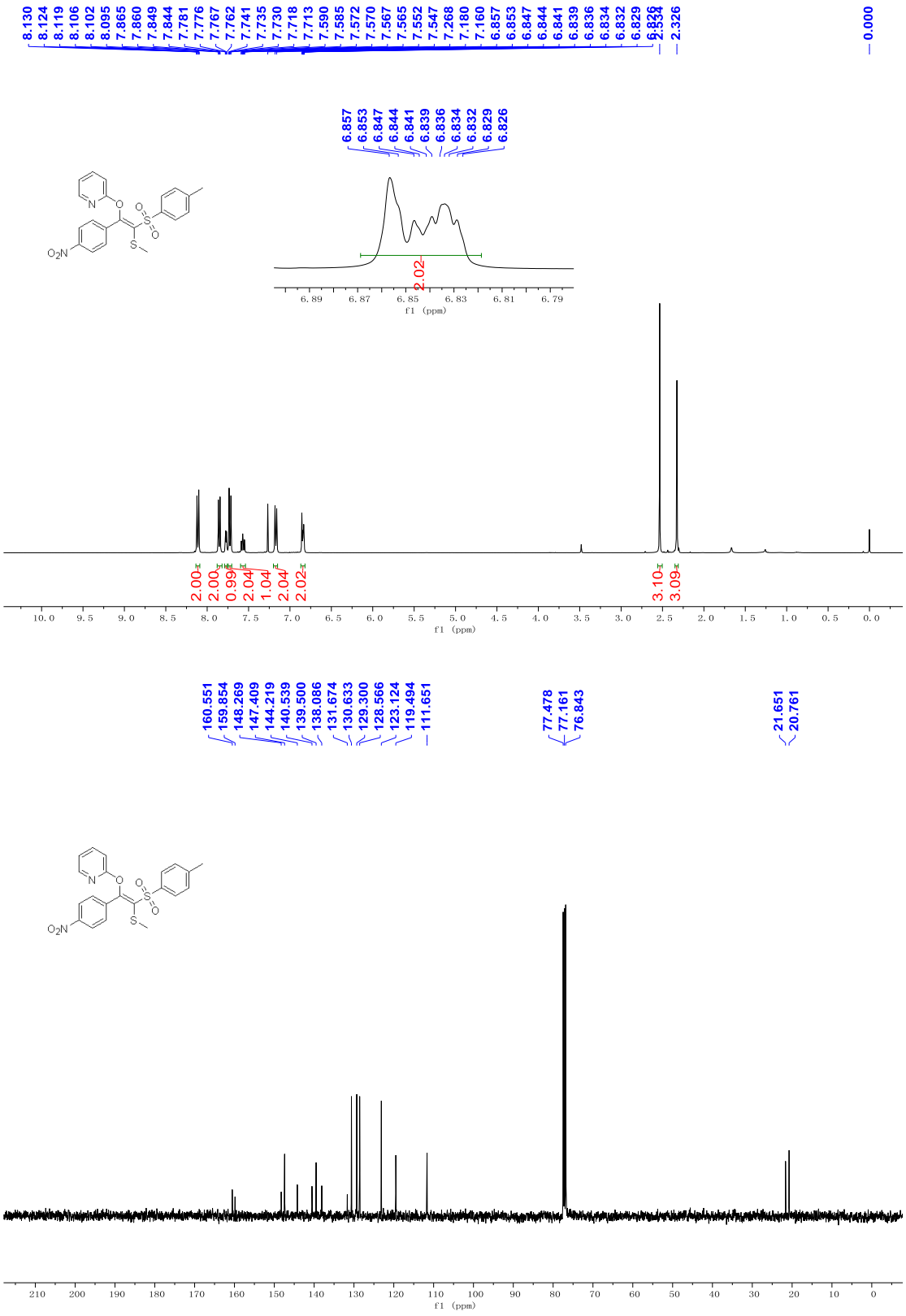




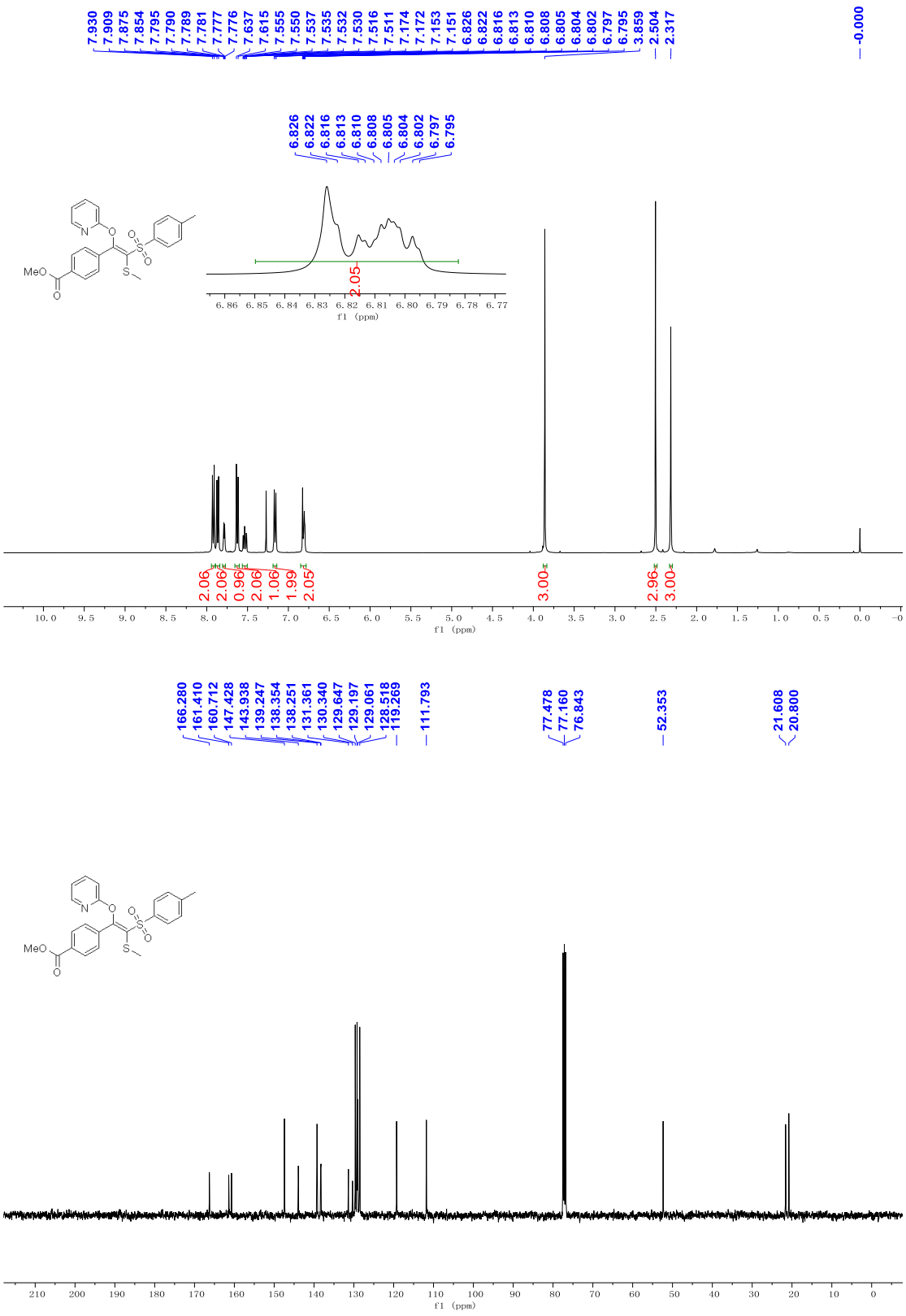
(*Z*)-4-(2-(Methylthio)-1-(pyridin-2-yloxy)-2-tosylvinyl)benzonitrile (**3g**) ($CDCl_3$)



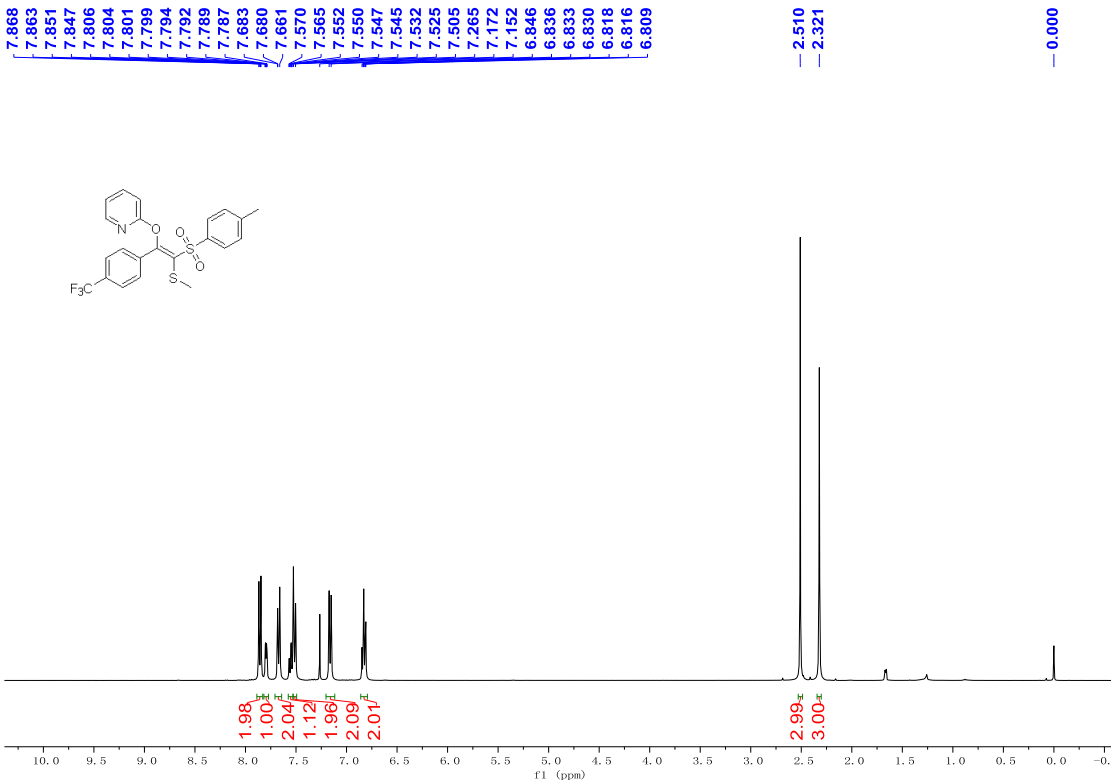
(*Z*)-2-((2-(Methylthio)-1-(4-nitrophenyl)-2-tosylvinyl)oxy)pyridine (**3h**) ($CDCl_3$)

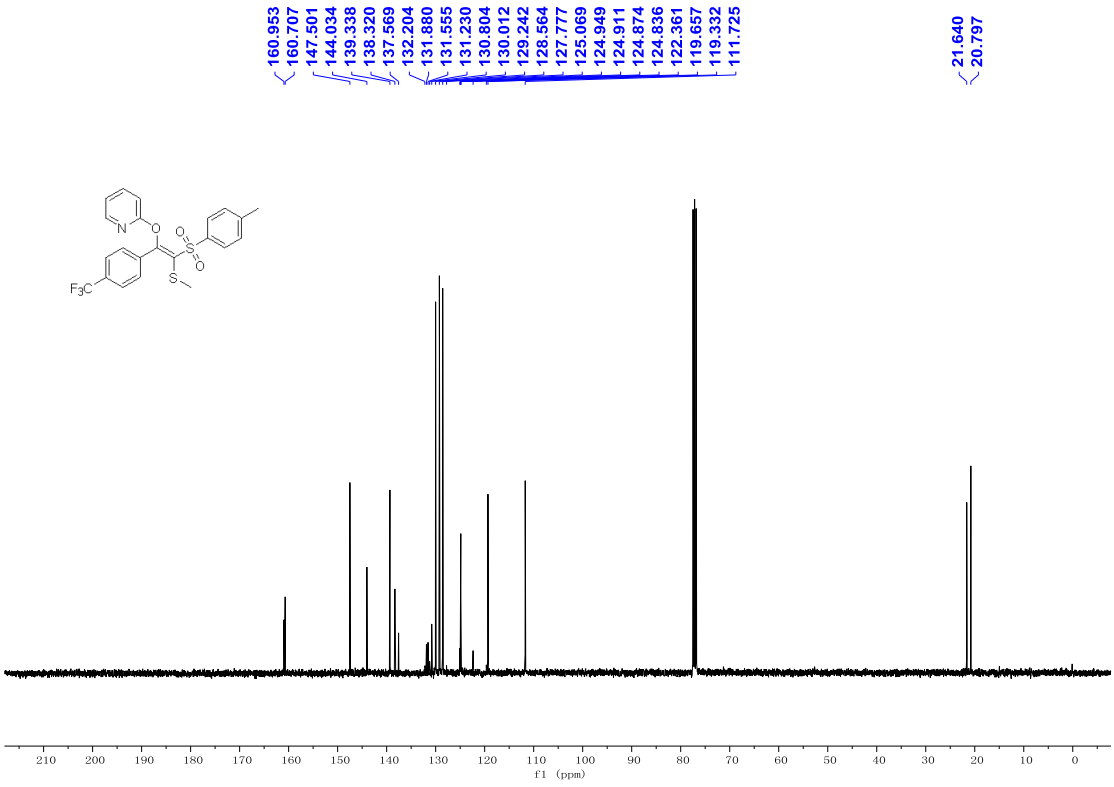


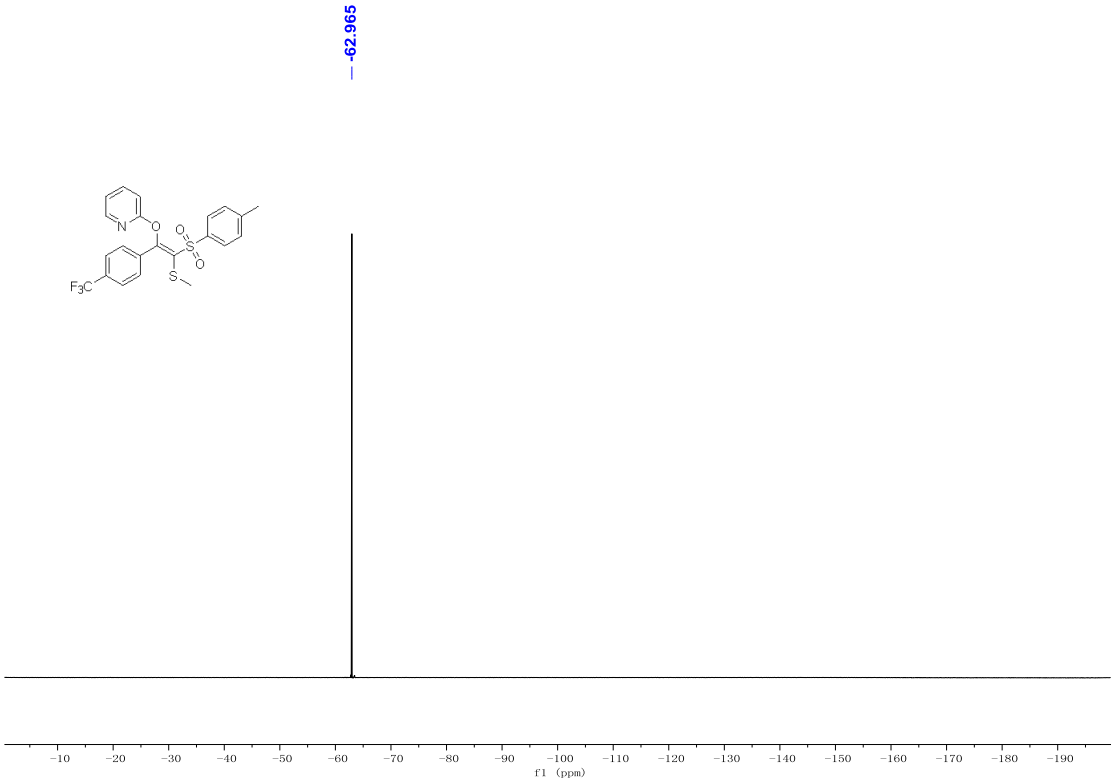
Methyl (*Z*)-4-(2-(methylthio)-1-(pyridin-2-yloxy)-2-tosylvinyl)benzoate (**3i**) ($CDCl_3$)



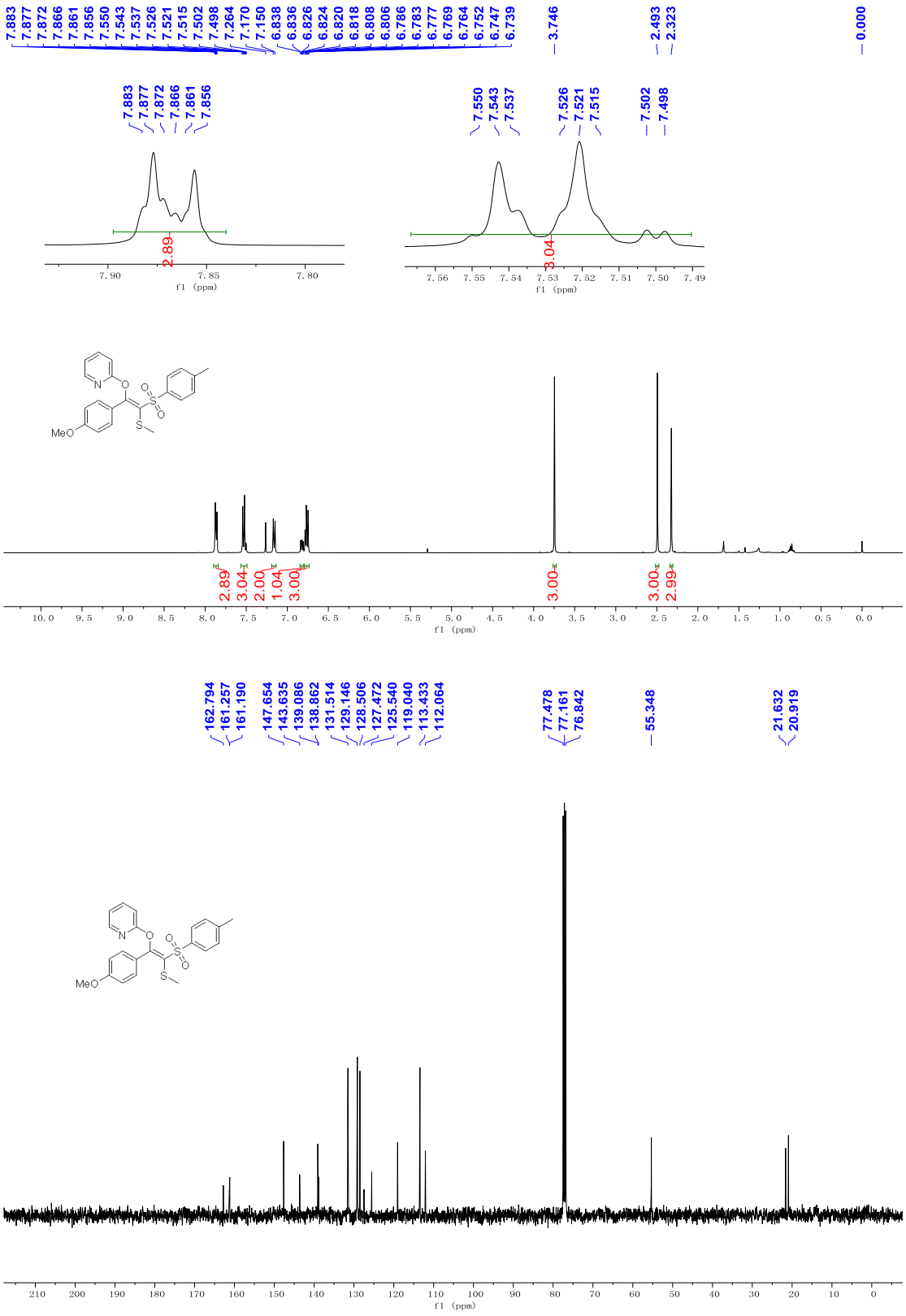
(*Z*)-2-((2-(Methylthio)-2-tosyl-1-(4-(trifluoromethyl)phenyl)vinyl)oxy)pyridine (**3j**) ($CDCl_3$)



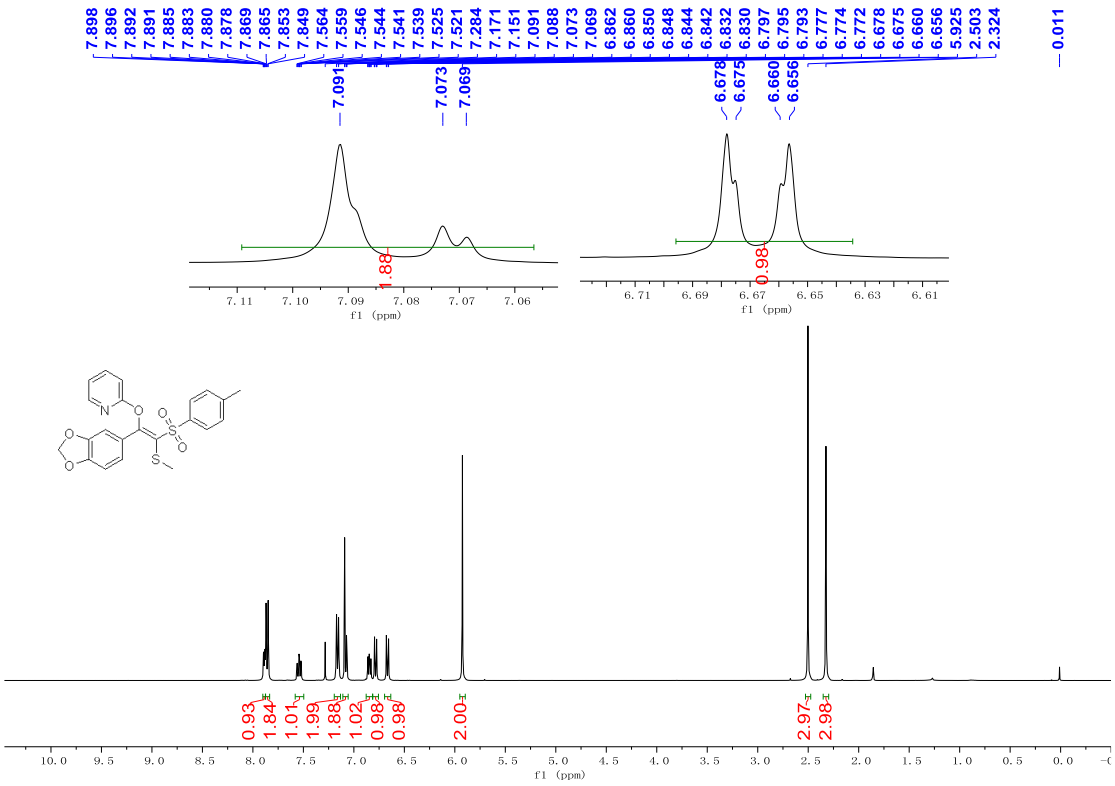


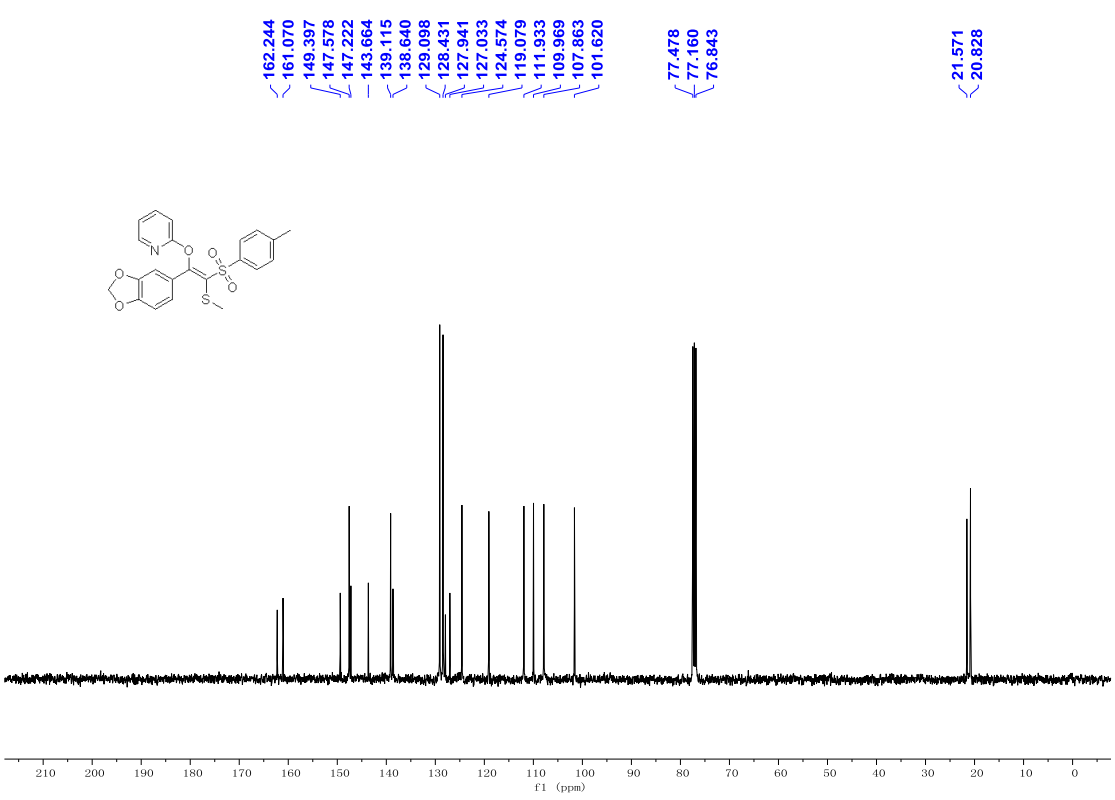

-62.965
F3C
N
O
S
O
O
S
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

(*Z*)-2-((1-(4-Methoxyphenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3k**) ($CDCl_3$)

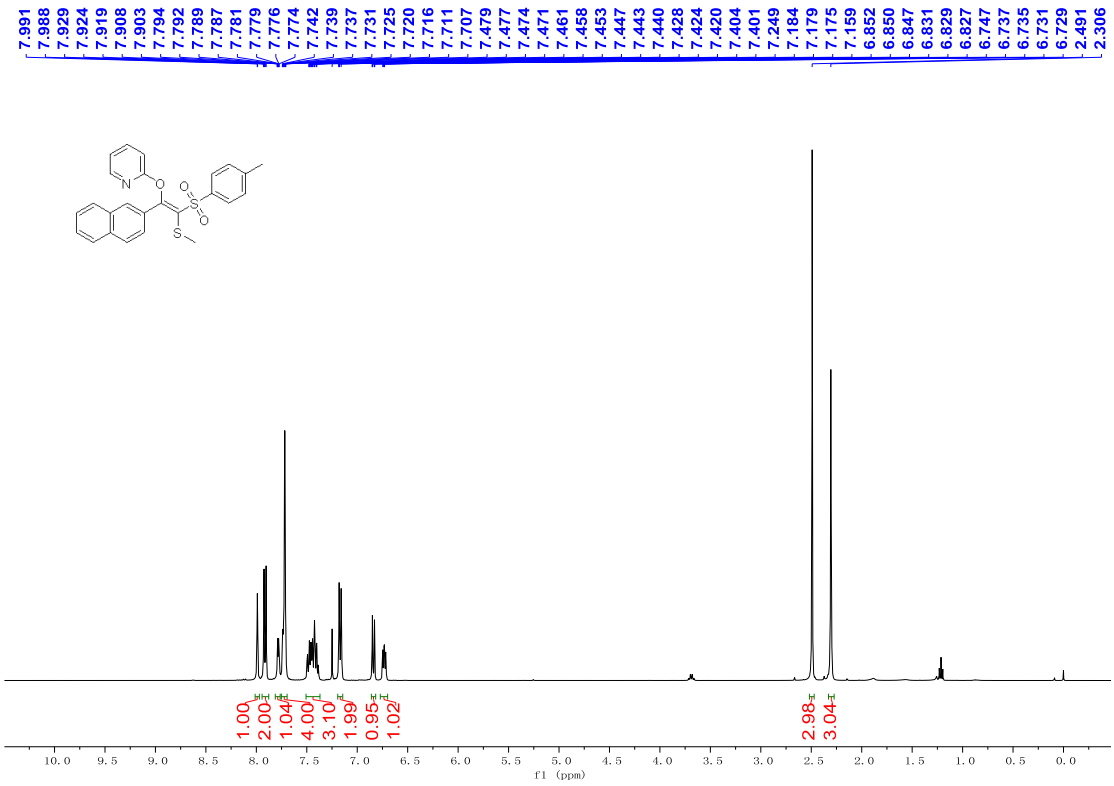


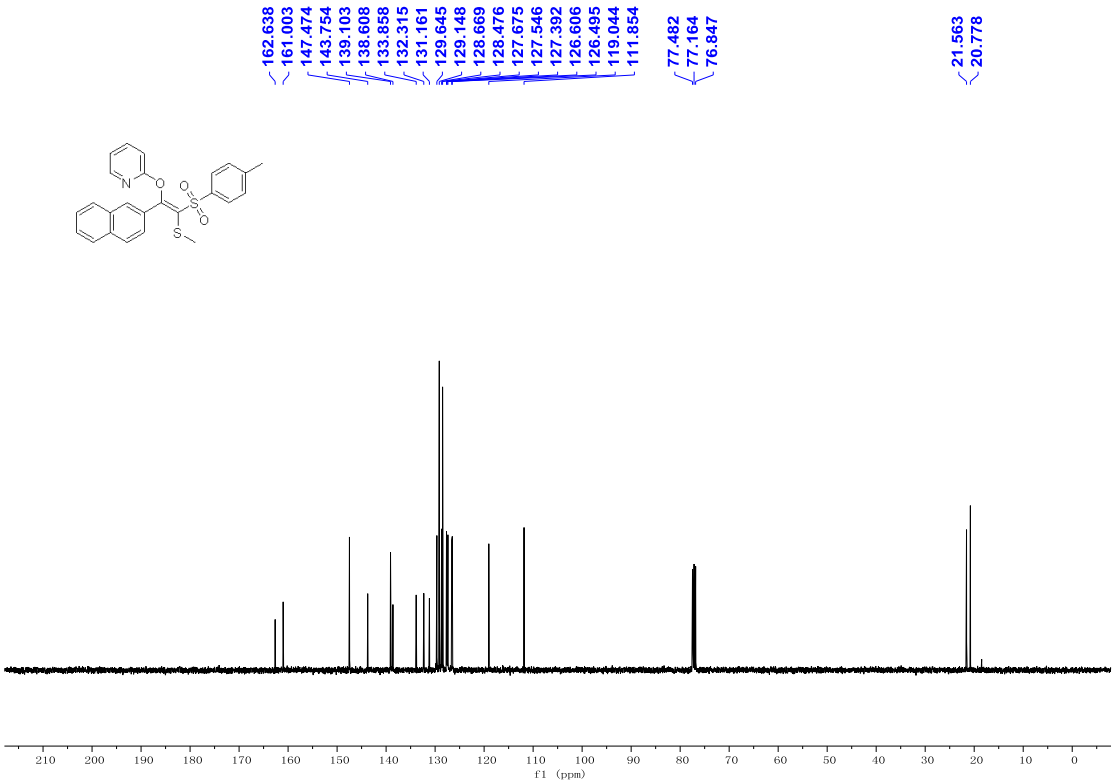
(*Z*)-2-((1-(Benzo[d][1,3]dioxol-5-yl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**3n**) ($CDCl_3$)



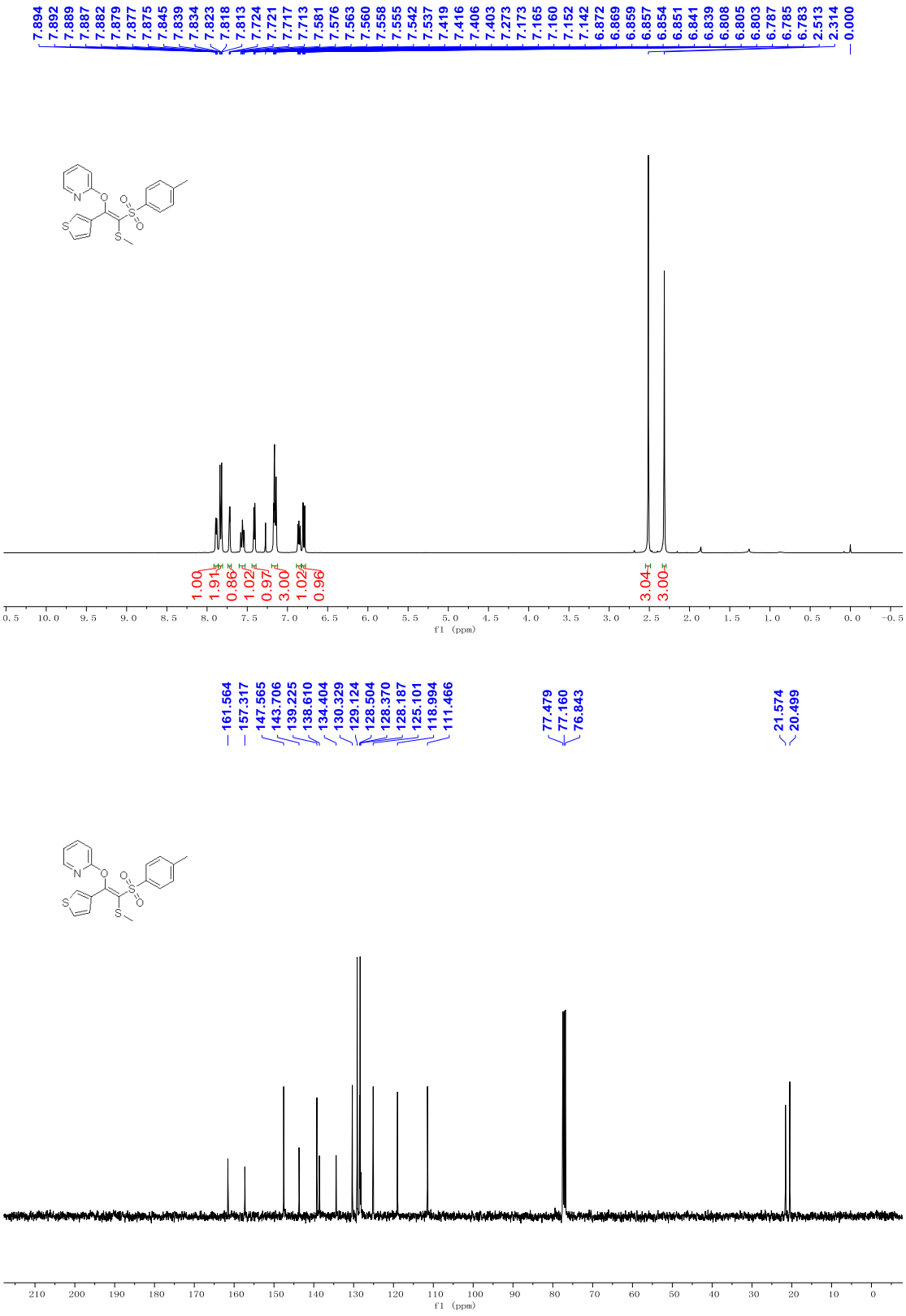


(*Z*)-2-((2-(Methylthio)-1-(naphthalen-2-yl)-2-tosylvinyl)oxy)pyridine (**3o**) ($CDCl_3$)

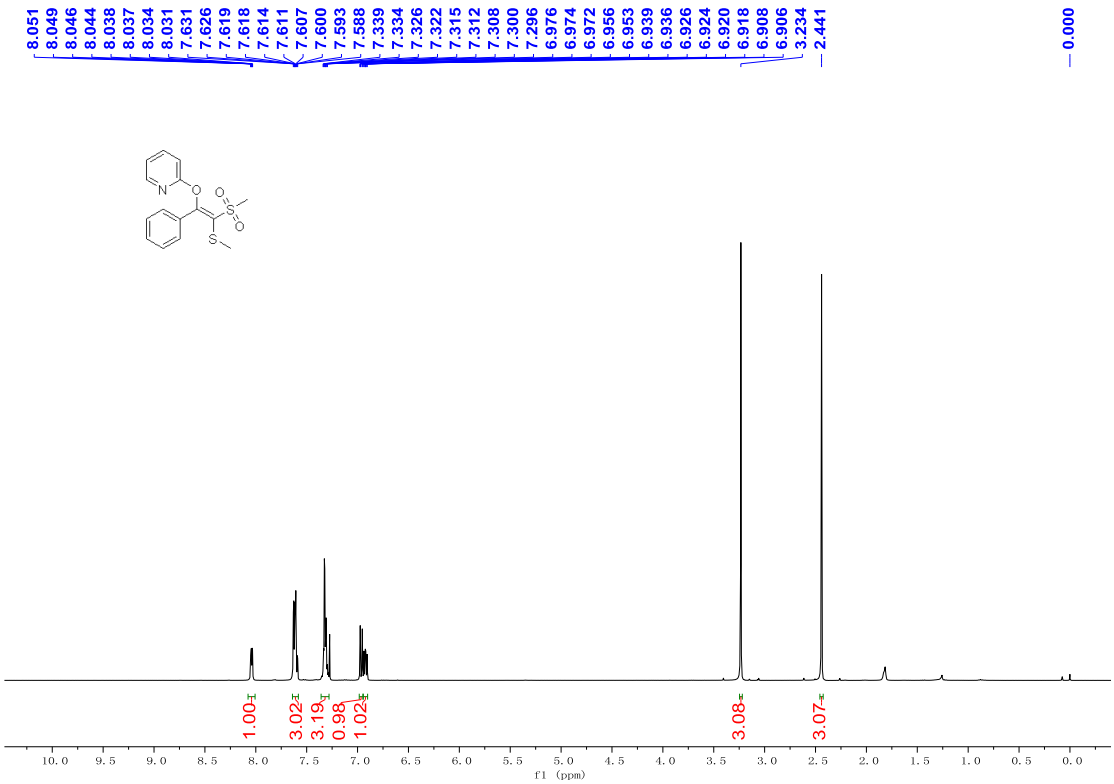


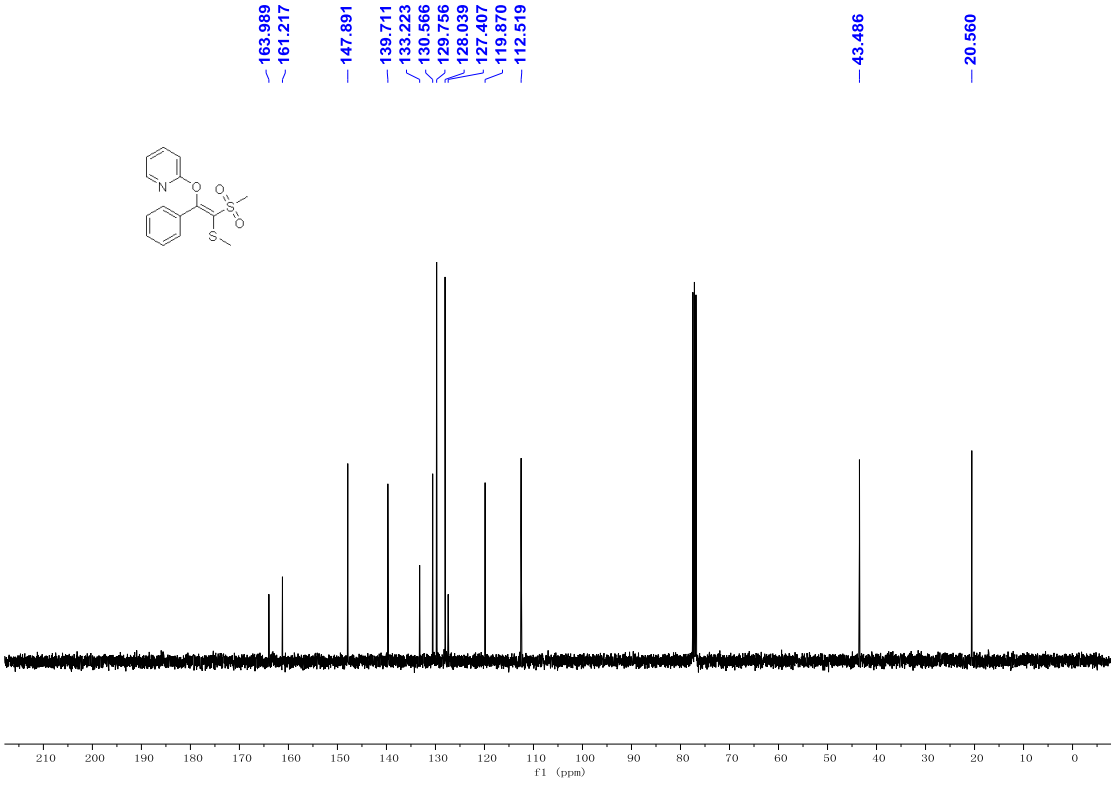


(*Z*)-2-((2-(Methylthio)-1-(thiophen-3-yl)-2-tosylvinyl)oxy)pyridine (**3p**) ($CDCl_3$)

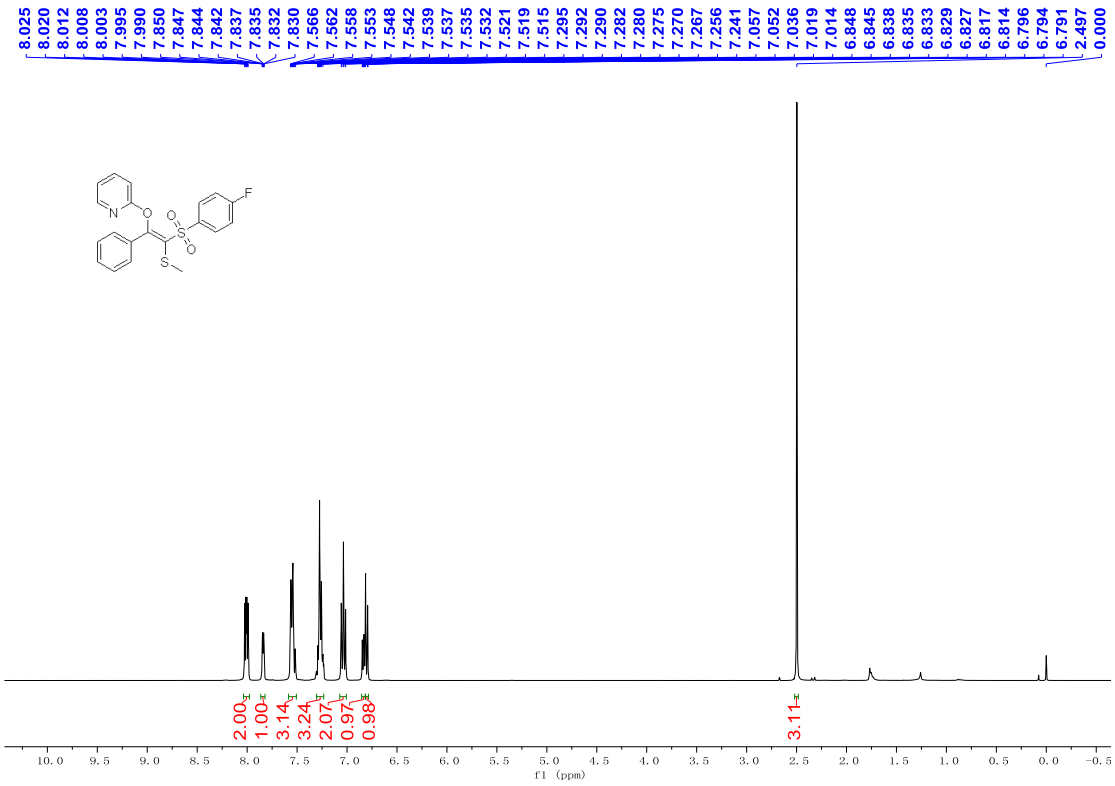


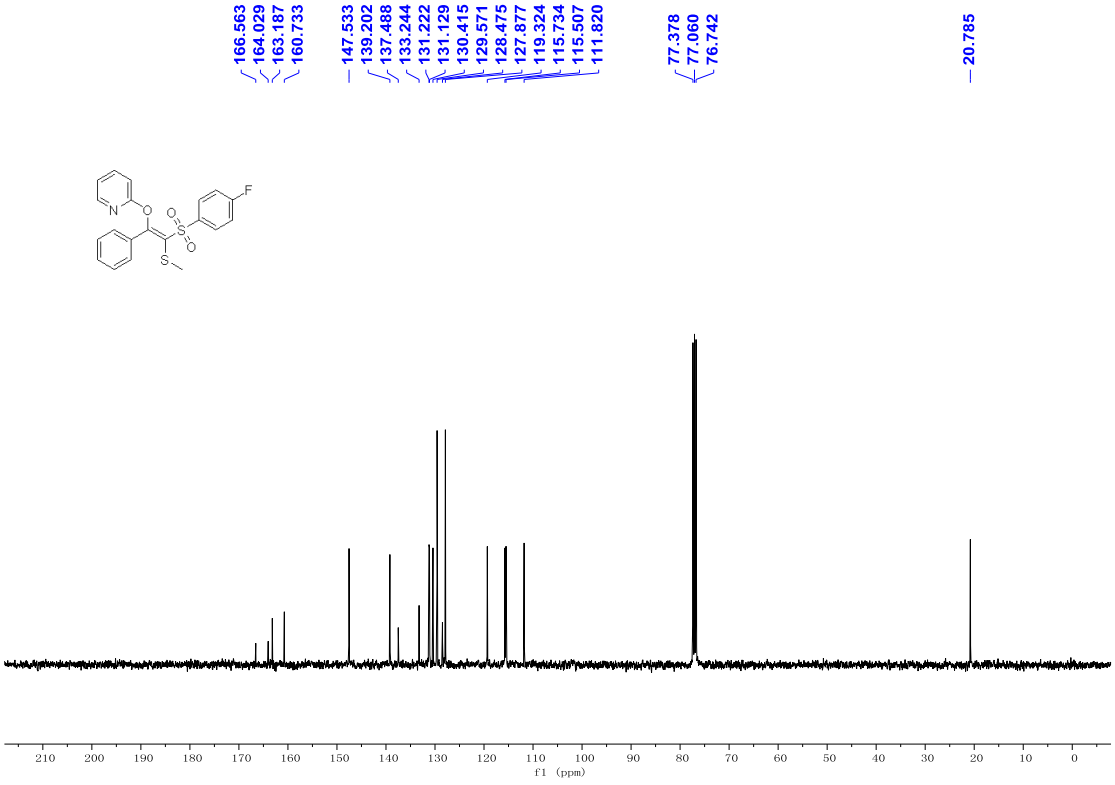
(*Z*)-2-((2-(Methylsulfonyl)-2-(methylthio)-1-phenylvinyl)oxy)pyridine (**3q**) ($CDCl_3$)

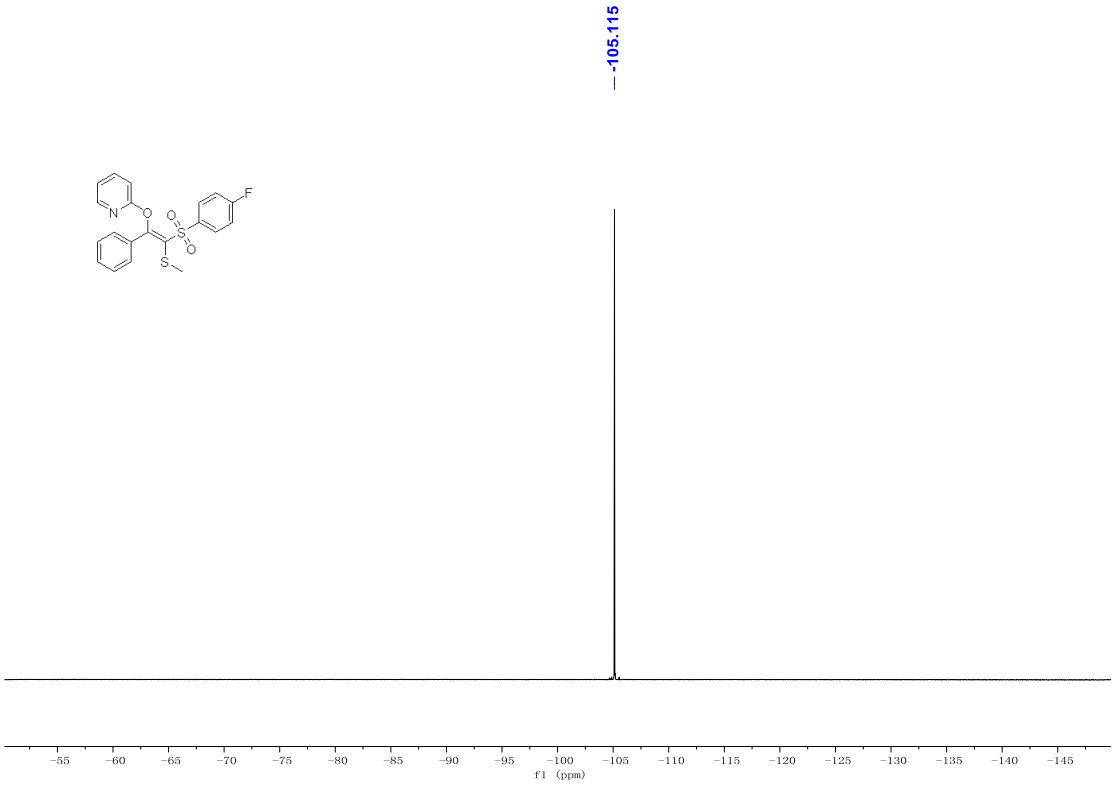




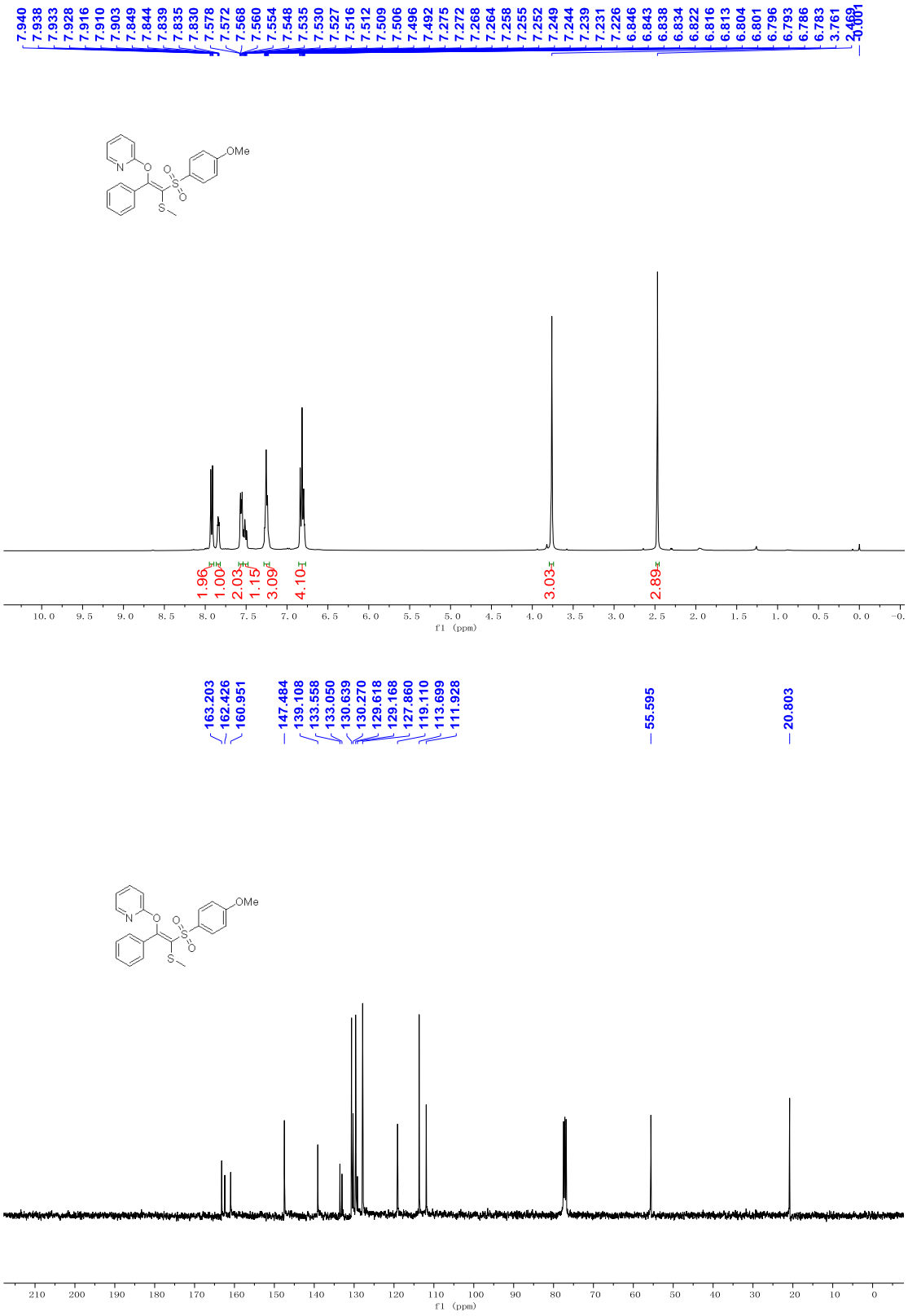
(*Z*)-2-((2-((4-Fluorophenyl)sulfonyl)-2-(methylthio)-1-phenylvinyl)oxy)pyridine (**3r**) ($CDCl_3$)



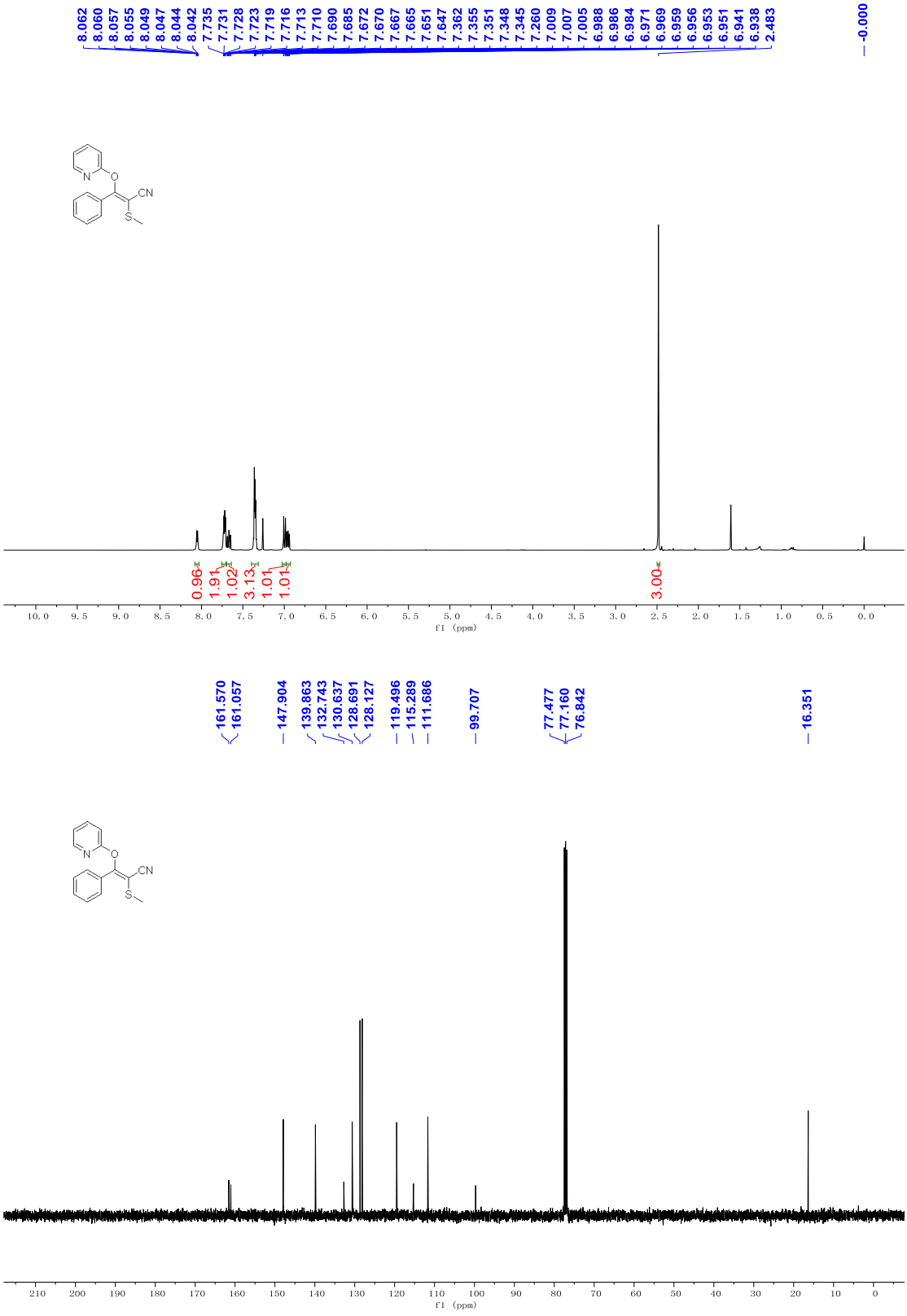



-105.115
F
N
O
O
S
O
S
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
f1 (ppm)

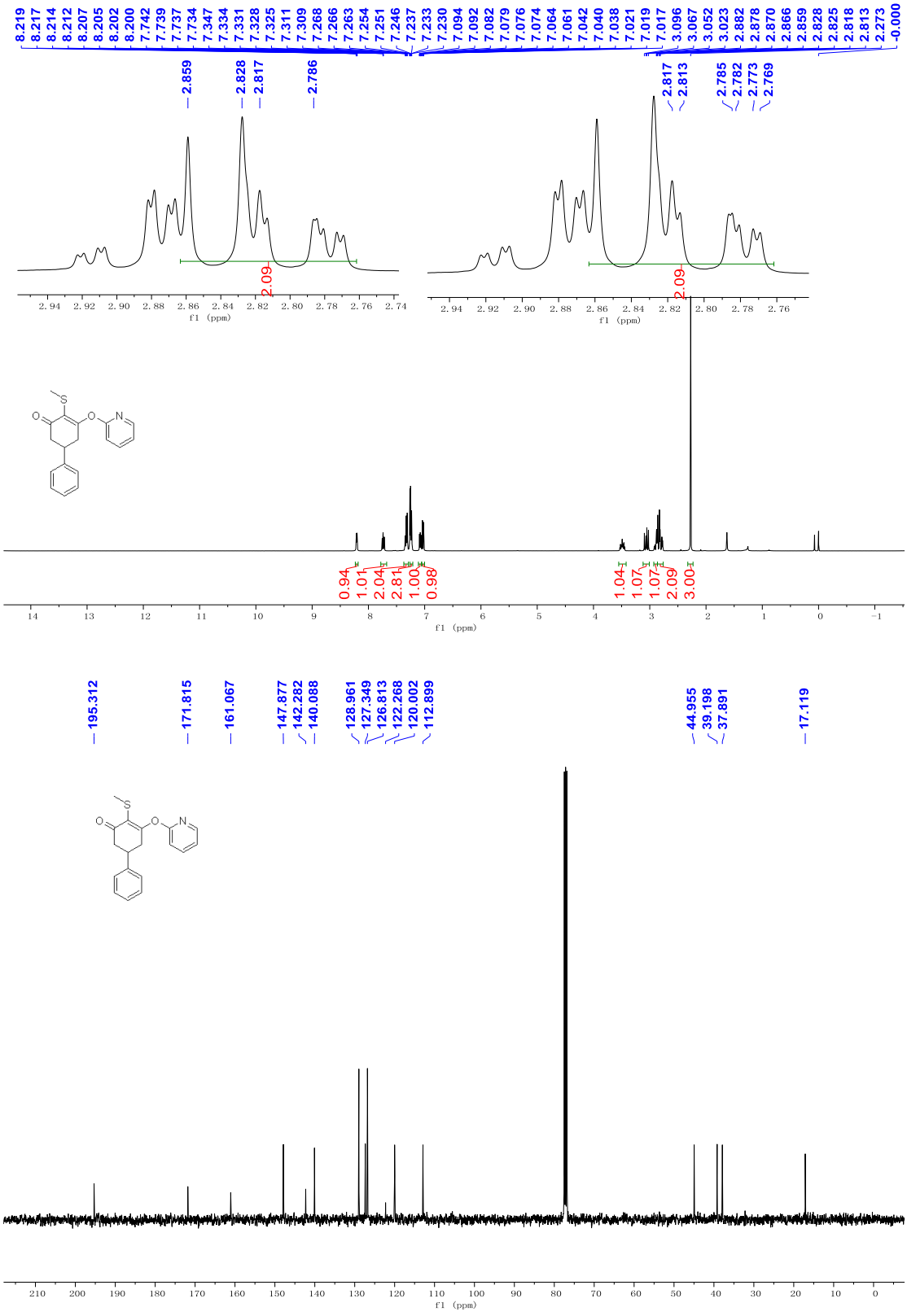
(*Z*)-2-((2-((4-Methoxyphenyl)sulfonyl)-2-(methylthio)-1-phenylvinyl)oxy)pyridine (**3s**) ($CDCl_3$)



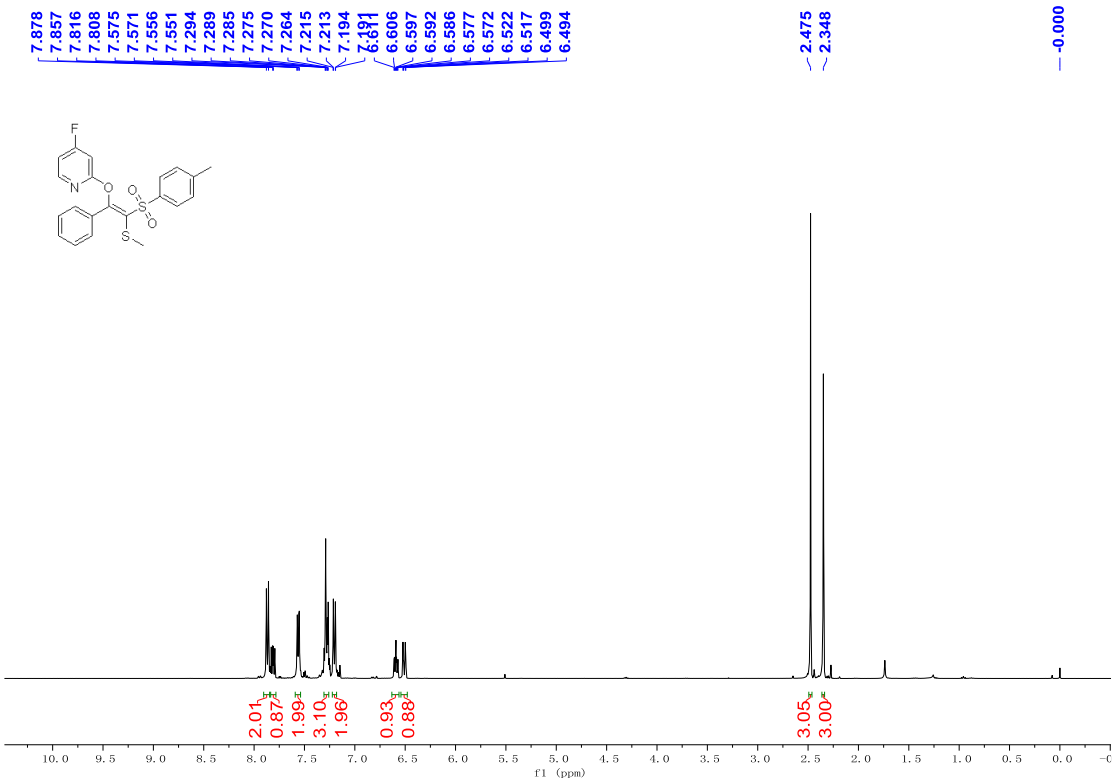
(*E*)-2-(Methylthio)-3-phenyl-3-(pyridin-2-yloxy)acrylonitrile (**3t**)

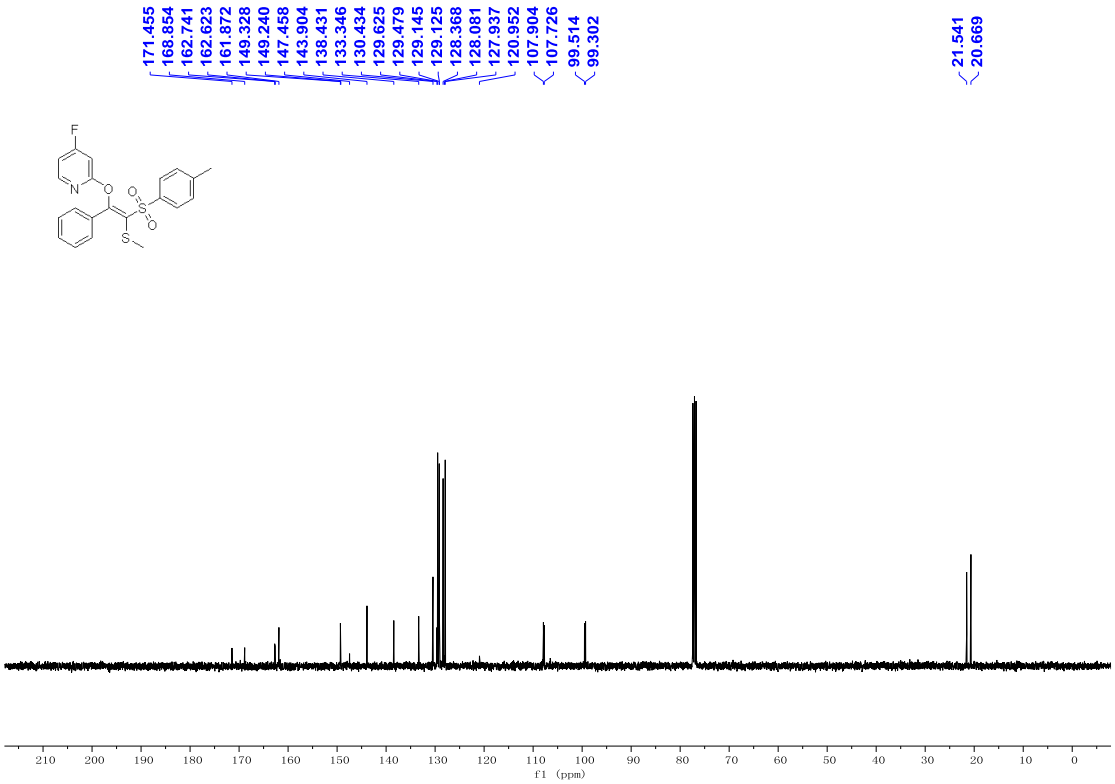


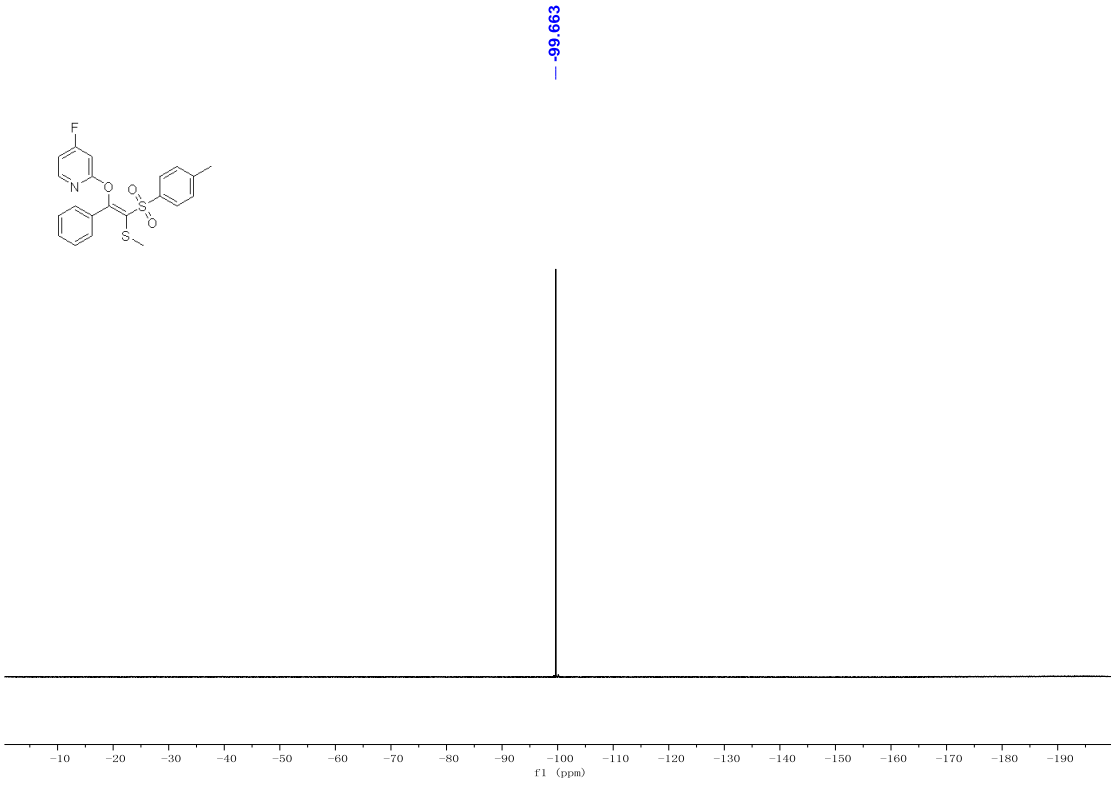
4-(Methylthio)-5-(pyridin-2-yloxy)-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (**3u**)



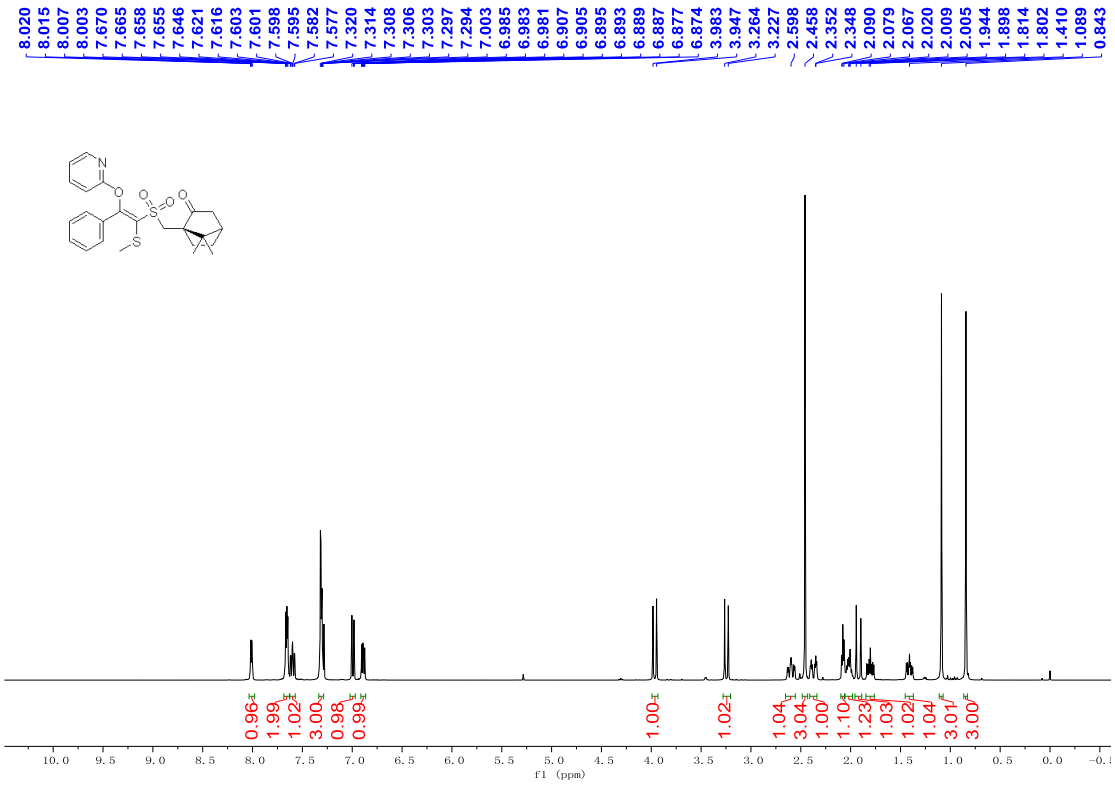
(*Z*)-4-Fluoro-2-((2-(methylthio)-1-phenyl-2-tosylvinyl)oxy)pyridine (**3w**)

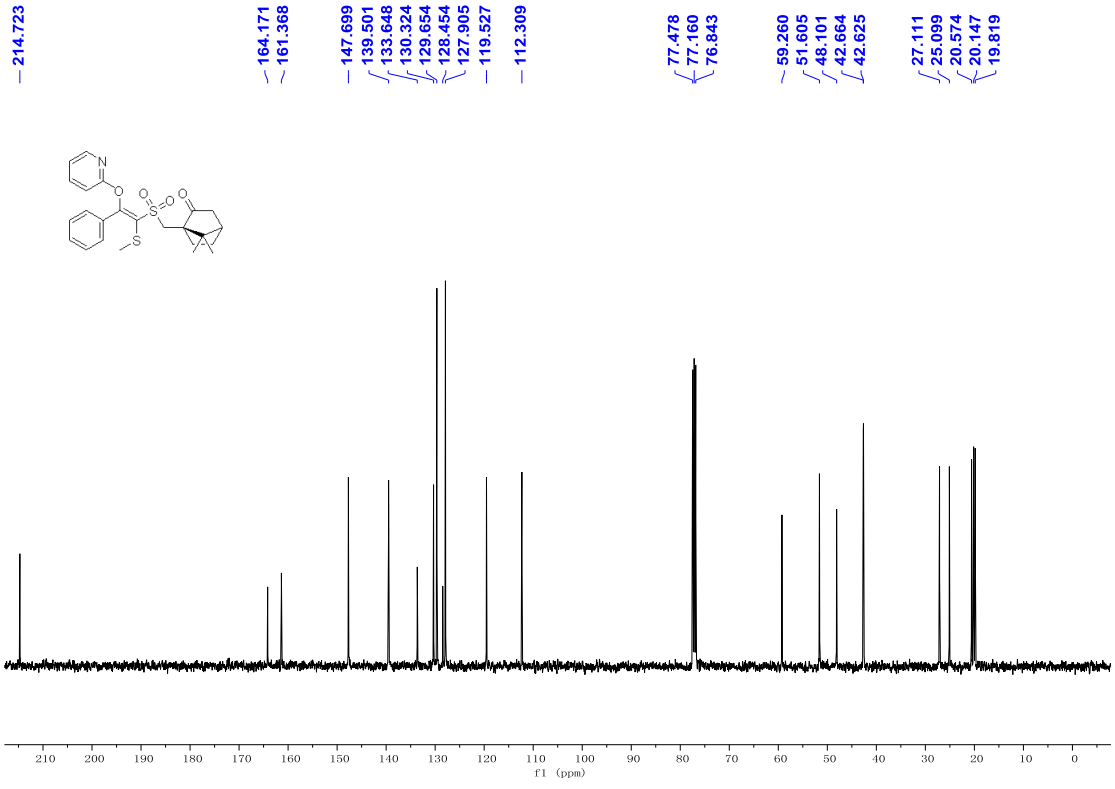





-99.663
F
N
O
S
O
O
S
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

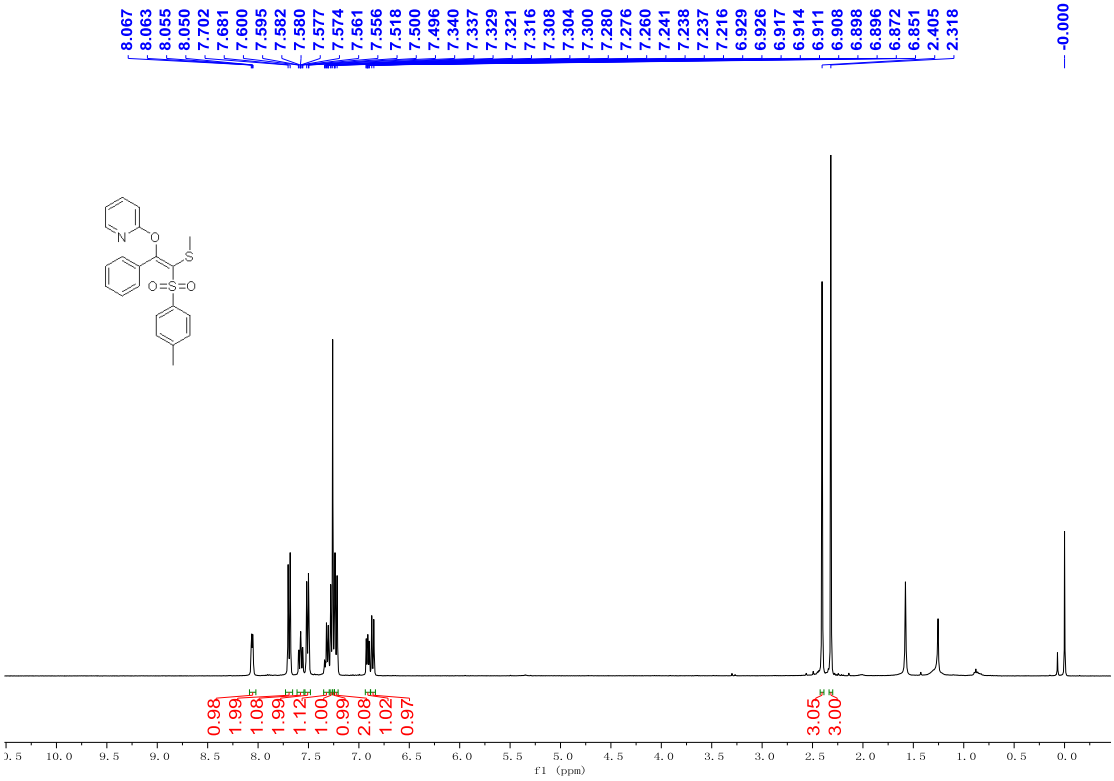
(1*R*)-7,7-Dimethyl-1-((((*Z*)-1-(methylthio)-2-phenyl-2-(pyridin-2-yloxy)vinyl)sulfonyl)methyl)bicyclo[2.2.1]heptan-2-one (**3x**) ($CDCl_3$)

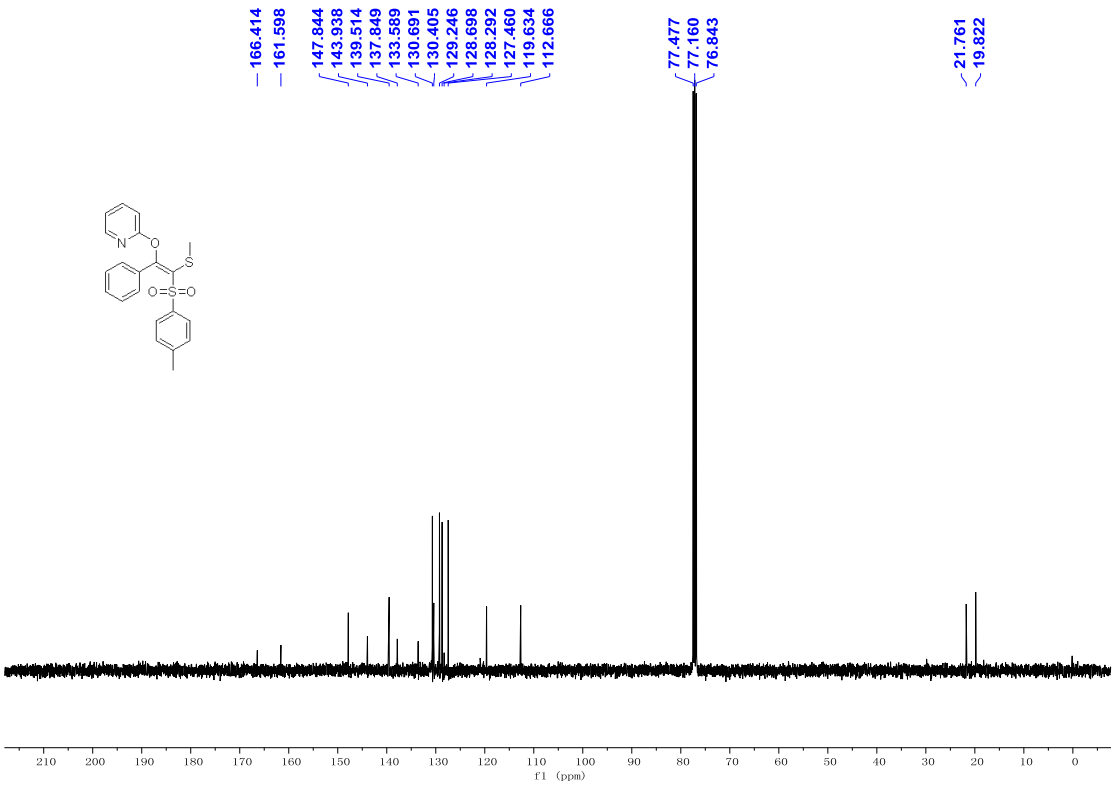




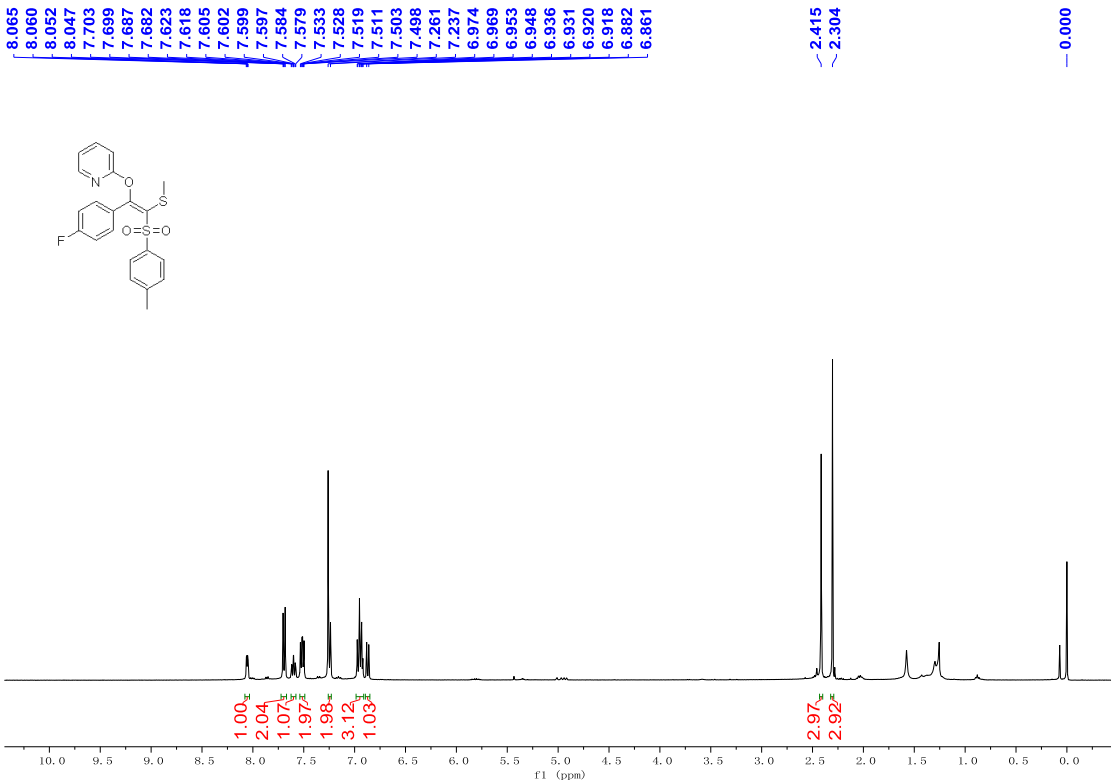
2.4 Copies of NMR Spectra for Products 4

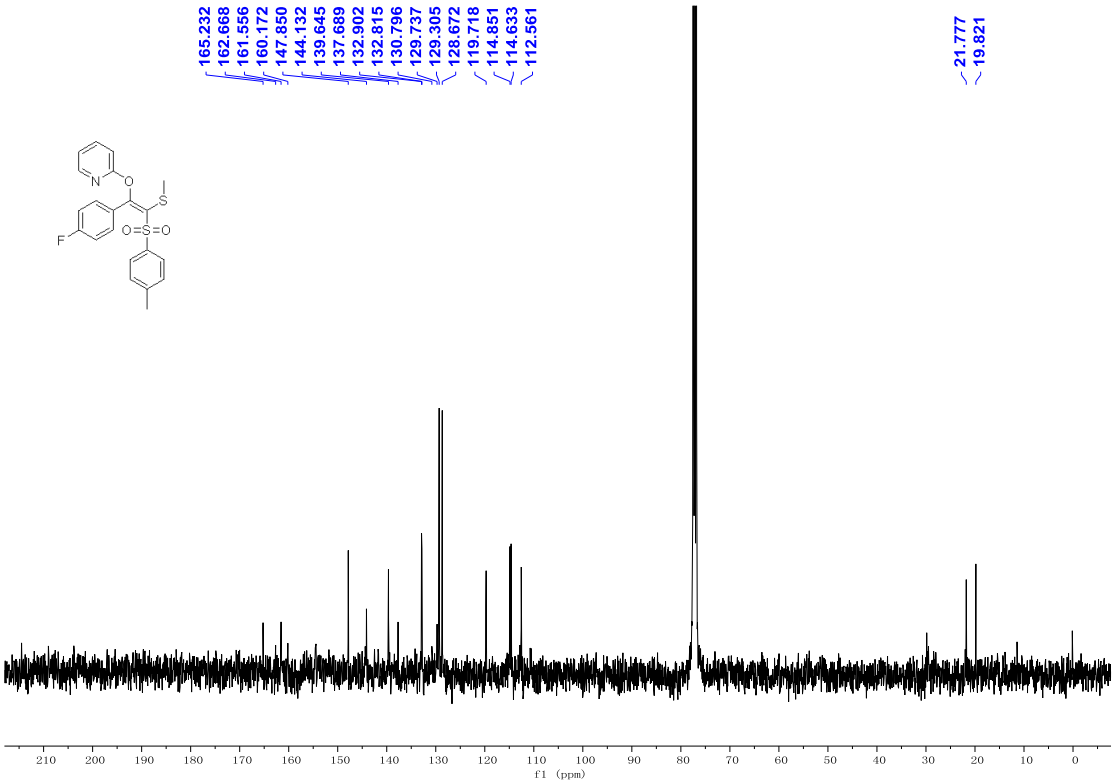
(*E*)-2-((2-(Methylthio)-1-phenyl-2-tosylvinyl)oxy)pyridine (**4a**) ($CDCl_3$)

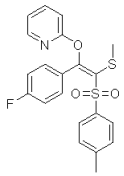




(*E*)-2-((1-(4-fluorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4b**) ($CDCl_3$)

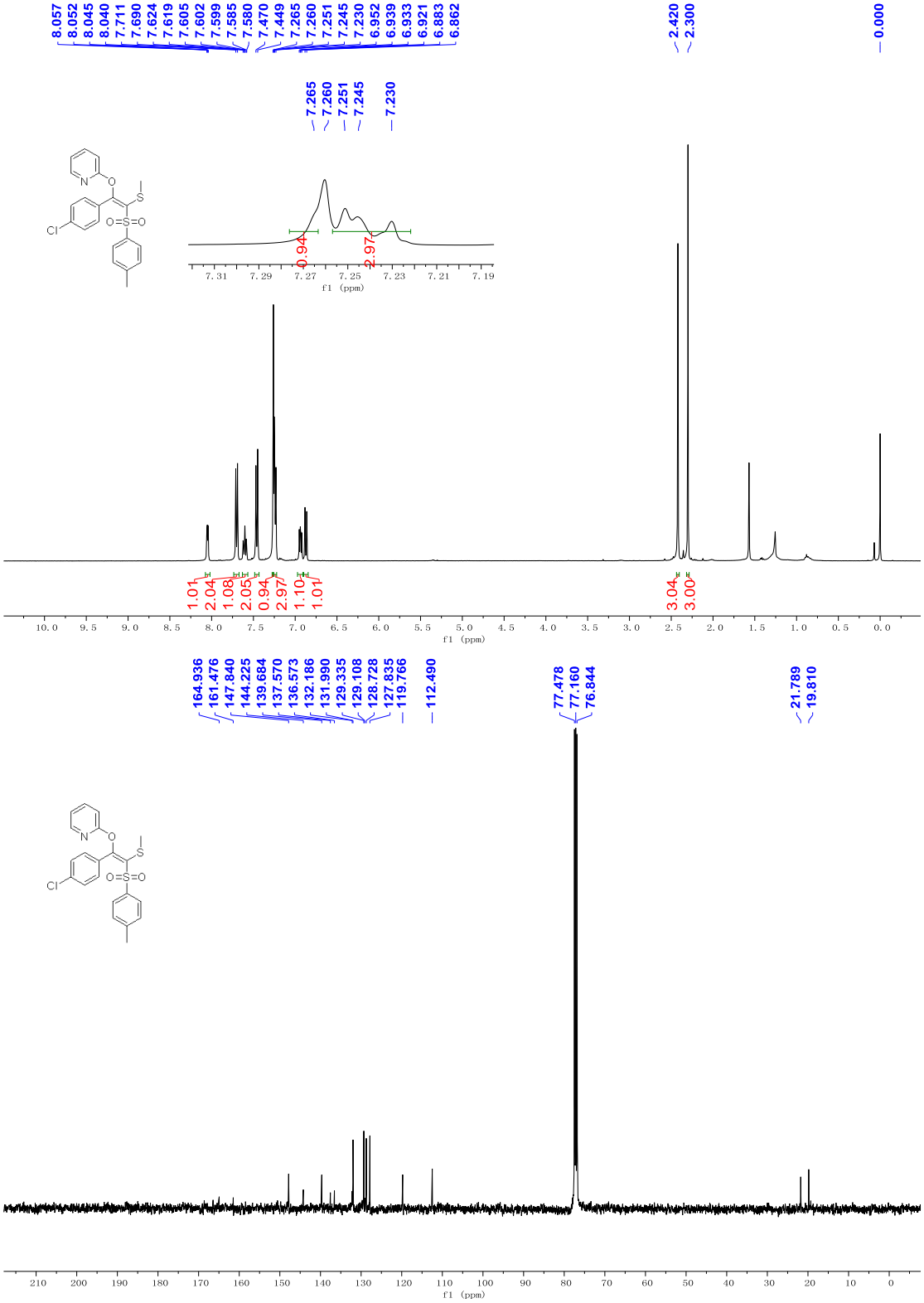




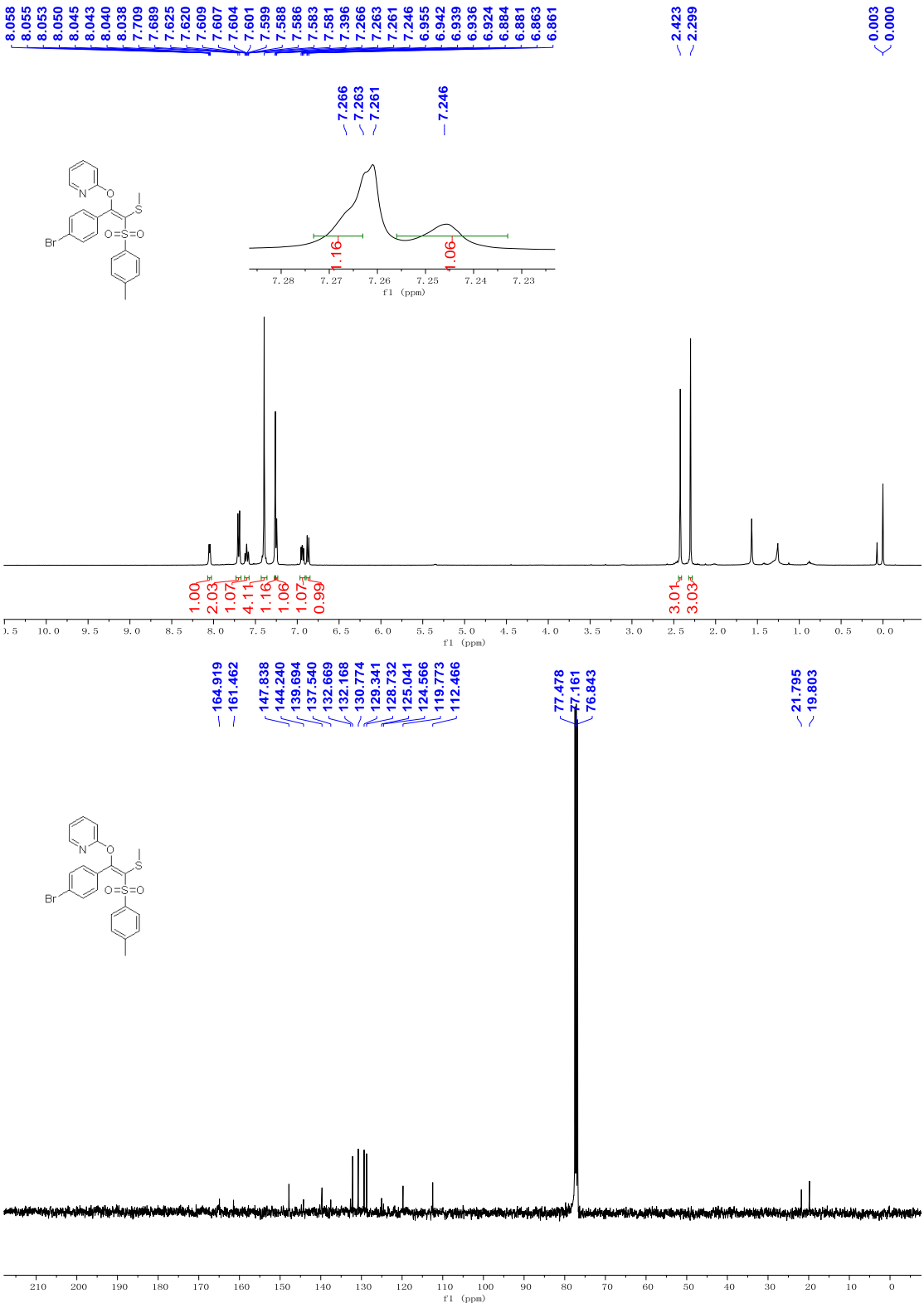

N
O
S
F
O=S=O

-109.127
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)

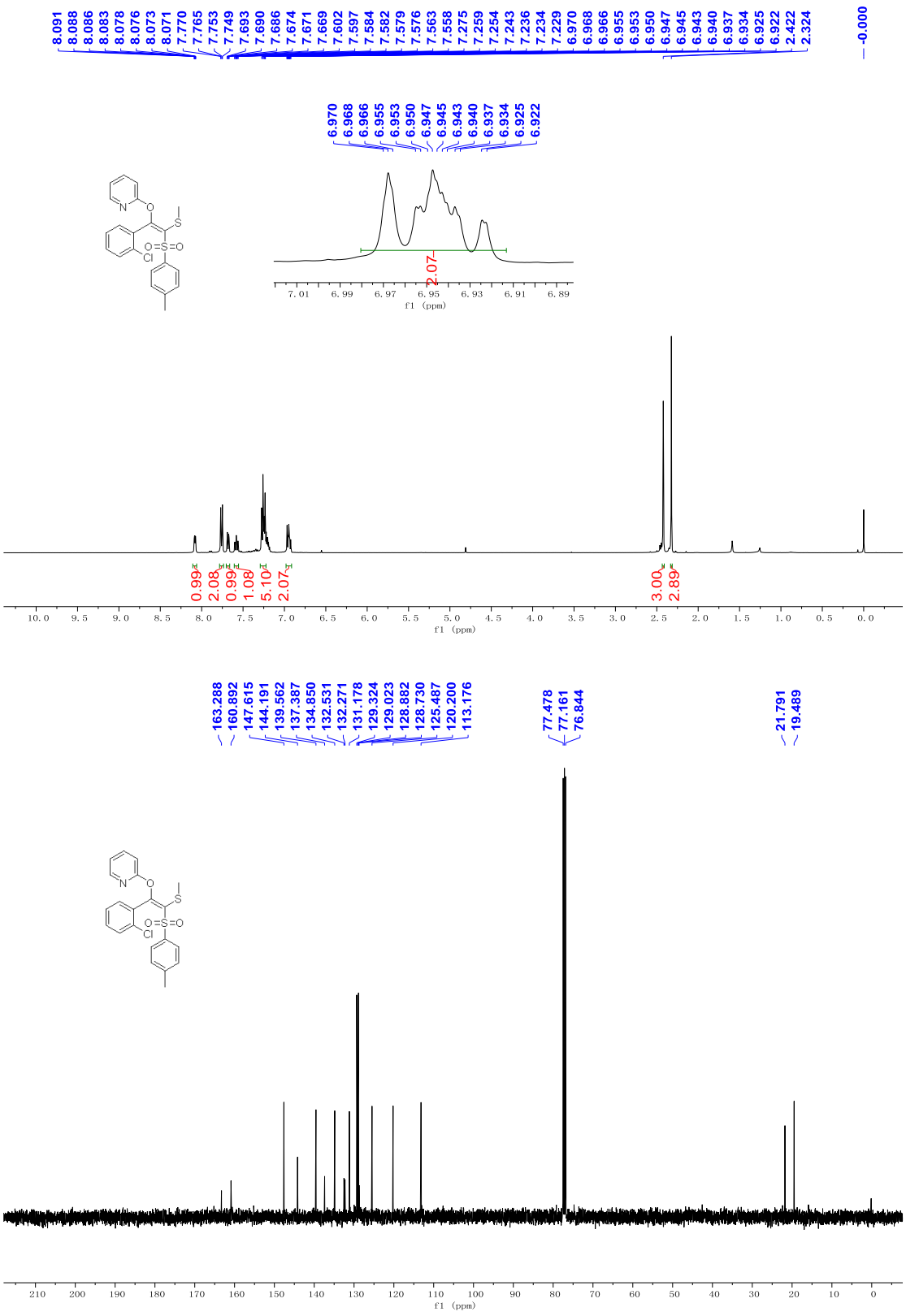
(*E*)-2-((1-(4-chlorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4c**) ($CDCl_3$)



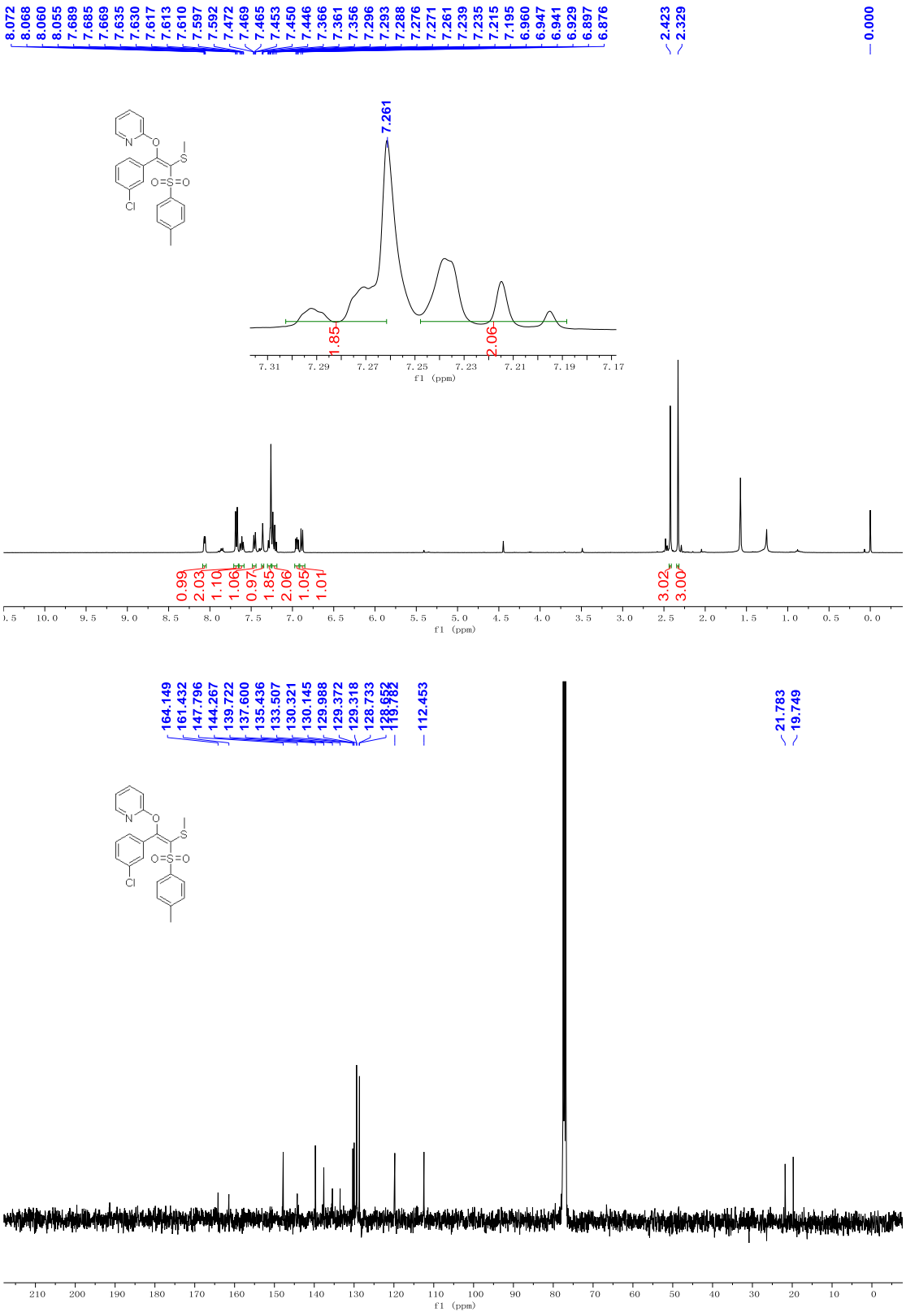
(*E*)-2-((1-(4-bromophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4d**) ($CDCl_3$)



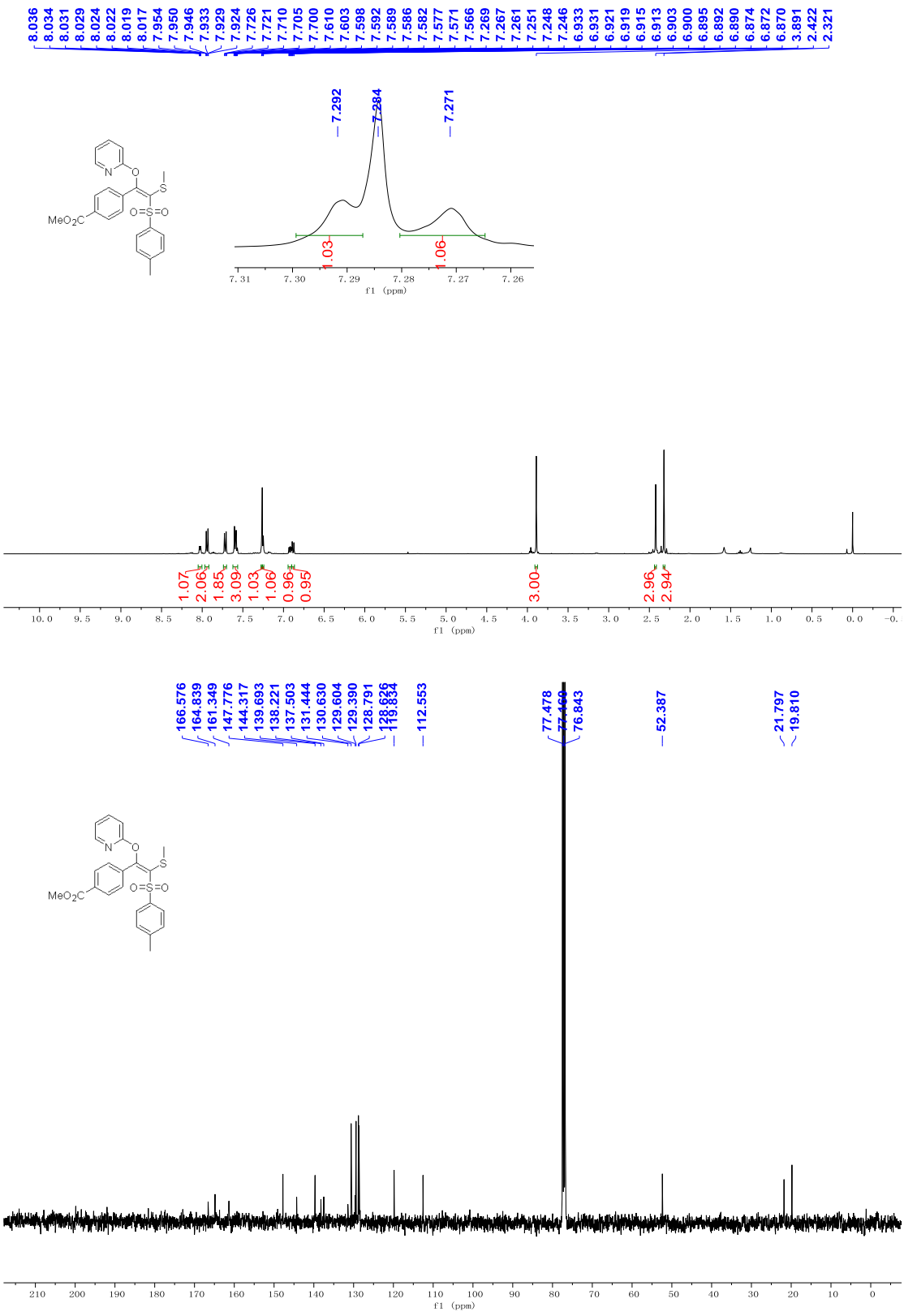
(*E*)-2-((1-(2-Chlorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4e**) ($CDCl_3$)



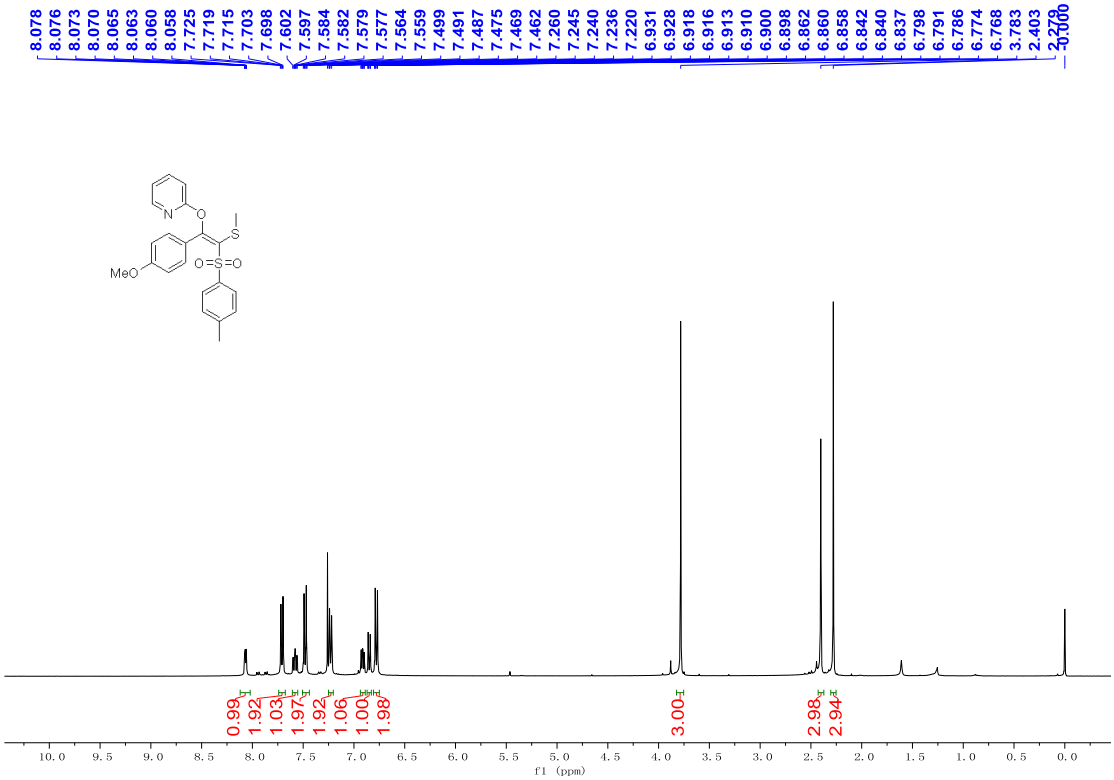
(*E*)-2-((1-(3-Chlorophenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4f**) ($CDCl_3$)

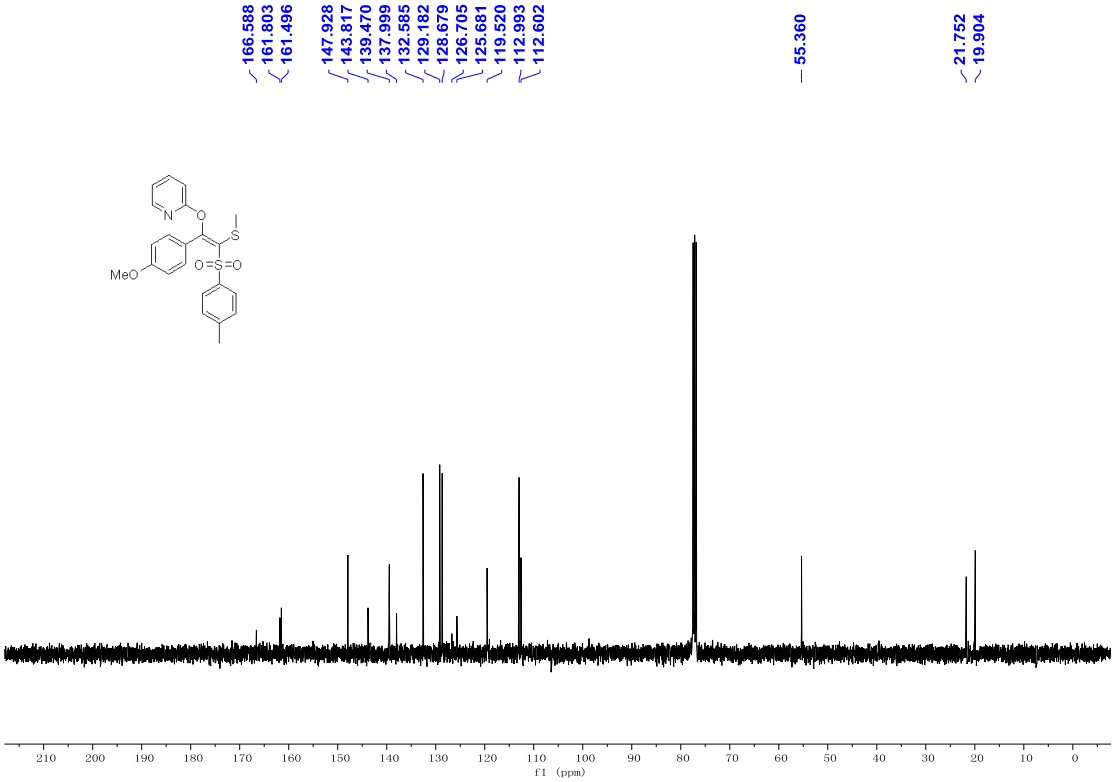


Methyl (*E*)-4-(2-(methylthio)-1-(pyridin-2-yloxy)-2-tosylvinyl)benzoate (**4i**) ($CDCl_3$)

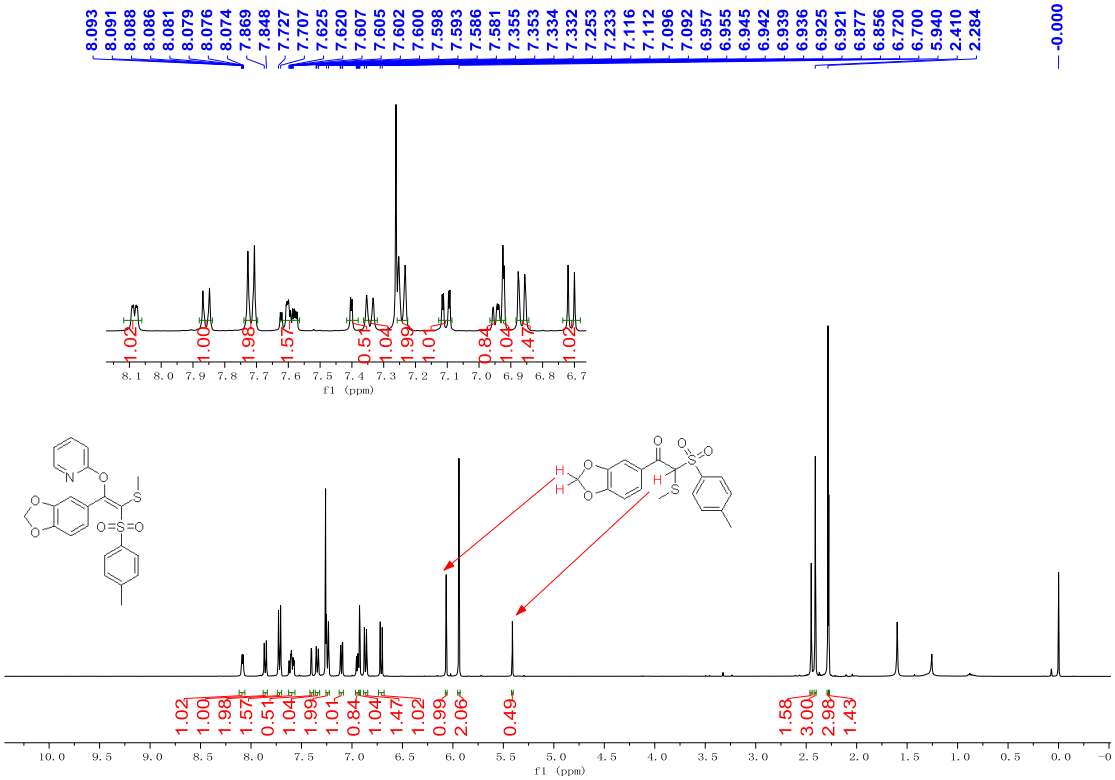


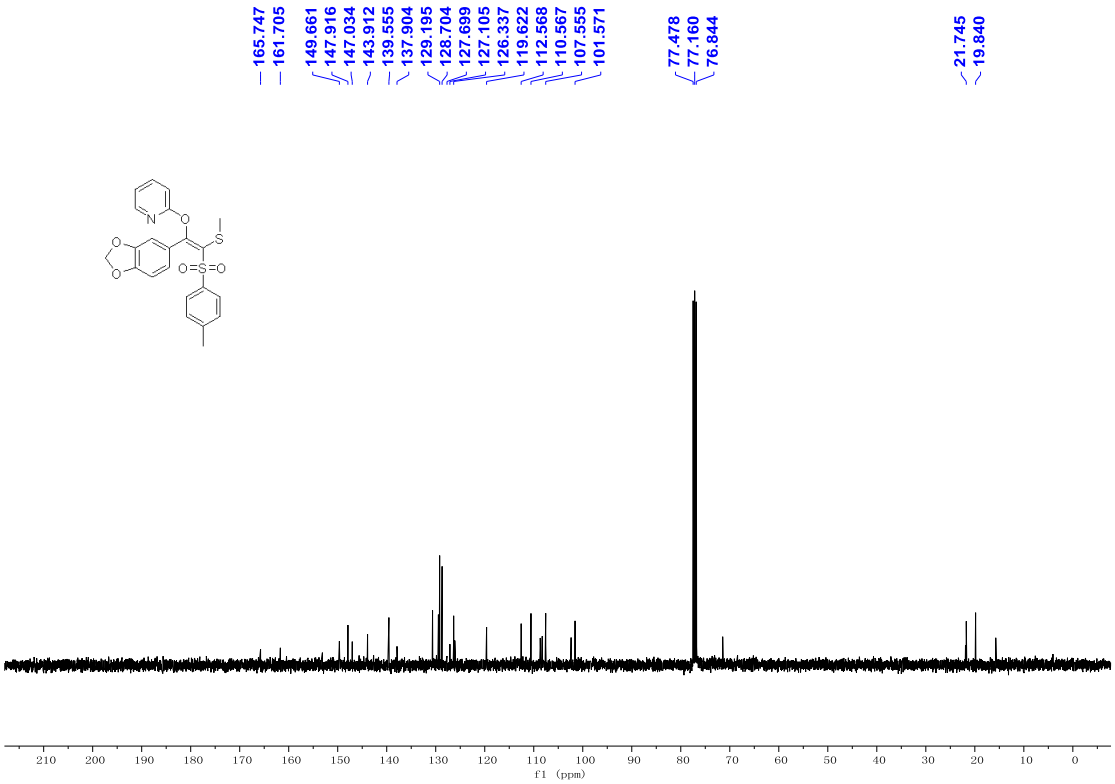
(*E*)-2-((1-(4-Methoxyphenyl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4k**) ($CDCl_3$)



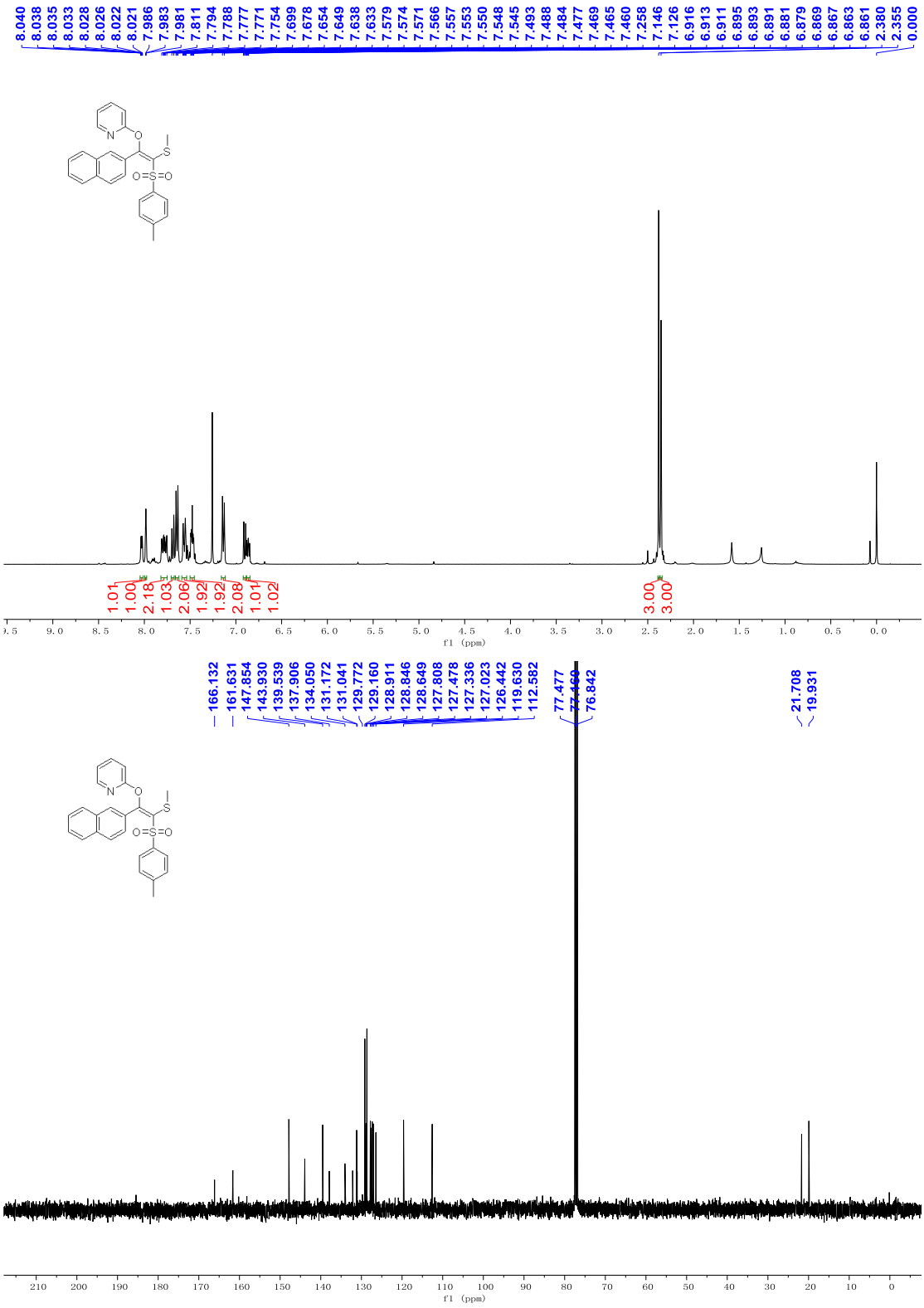


(*E*)-2-((1-(Benzo[d][1,3]dioxol-5-yl)-2-(methylthio)-2-tosylvinyl)oxy)pyridine (**4n**) ($CDCl_3$)

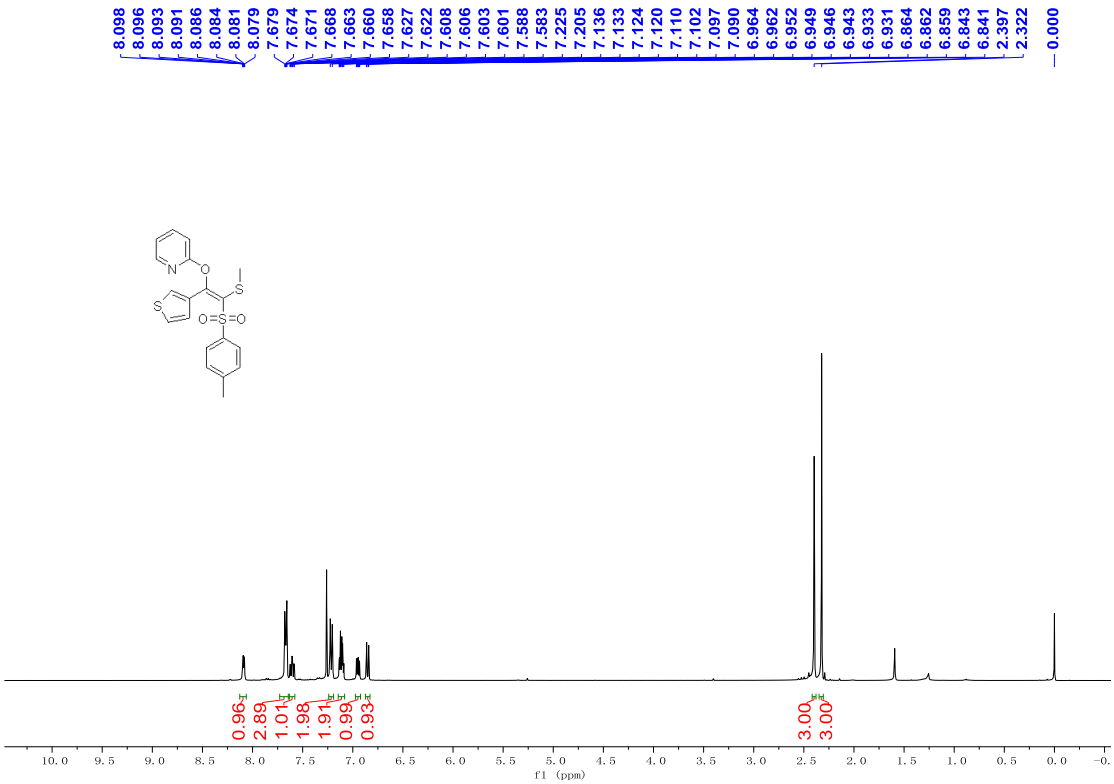


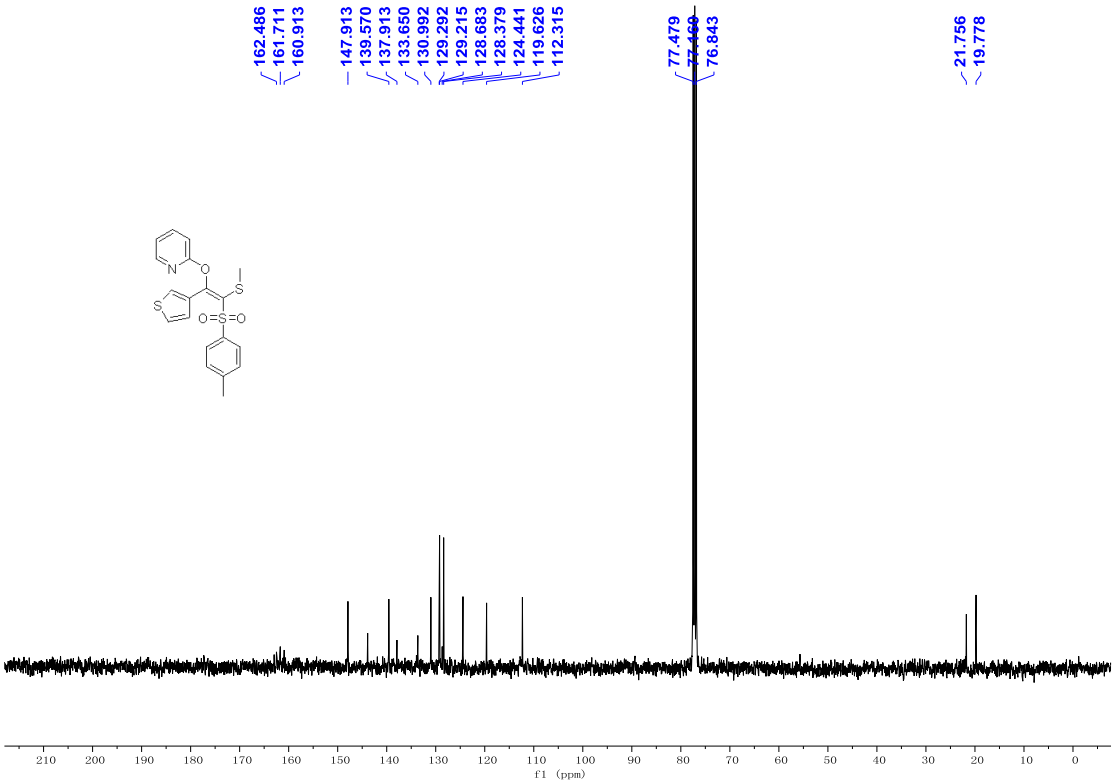


(*E*)-2-((2-(Methylthio)-1-(naphthalen-2-yl)-2-tosylvinyl)oxy)pyridine (**4o**) ($CDCl_3$)

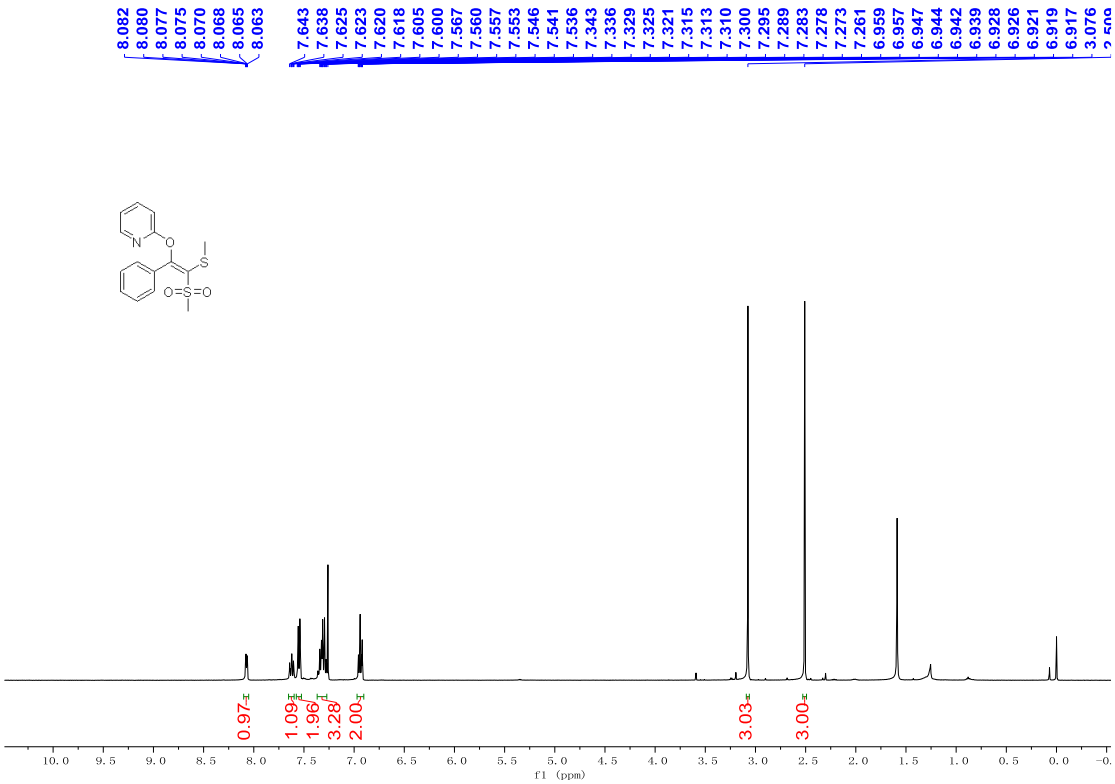


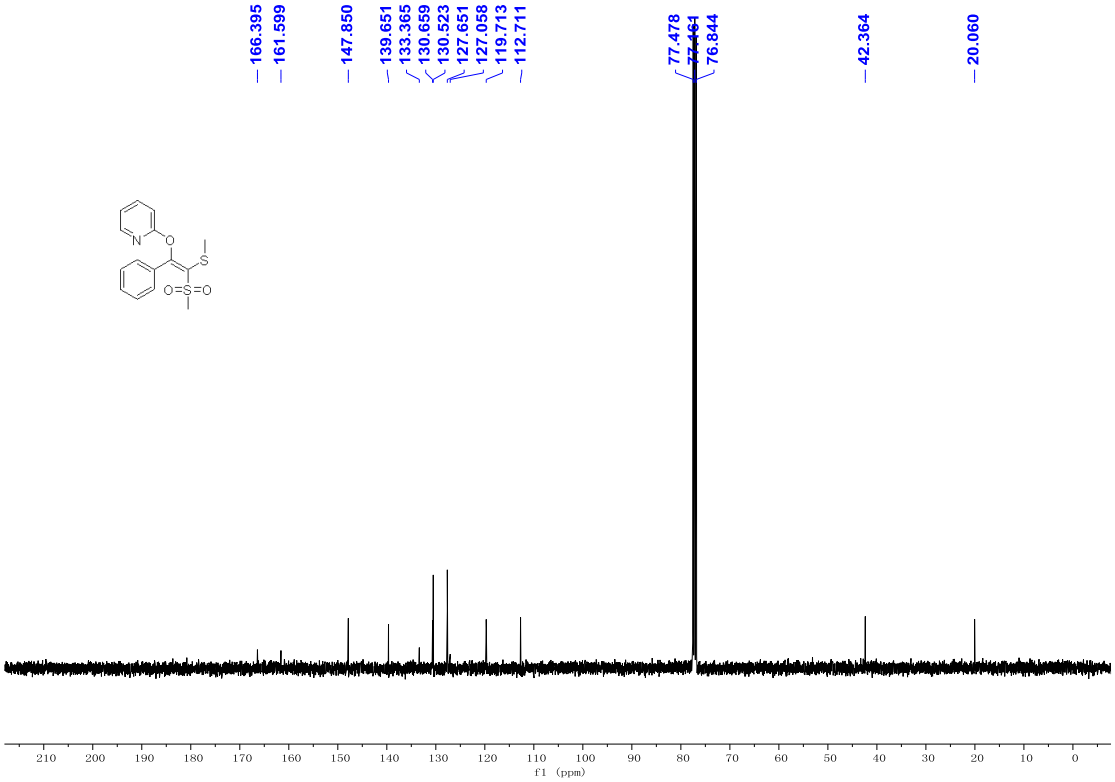
(*E*)-2-((2-(Methylthio)-1-(thiophen-3-yl)-2-tosylvinyl)oxy)pyridine (**4p**) ($CDCl_3$)



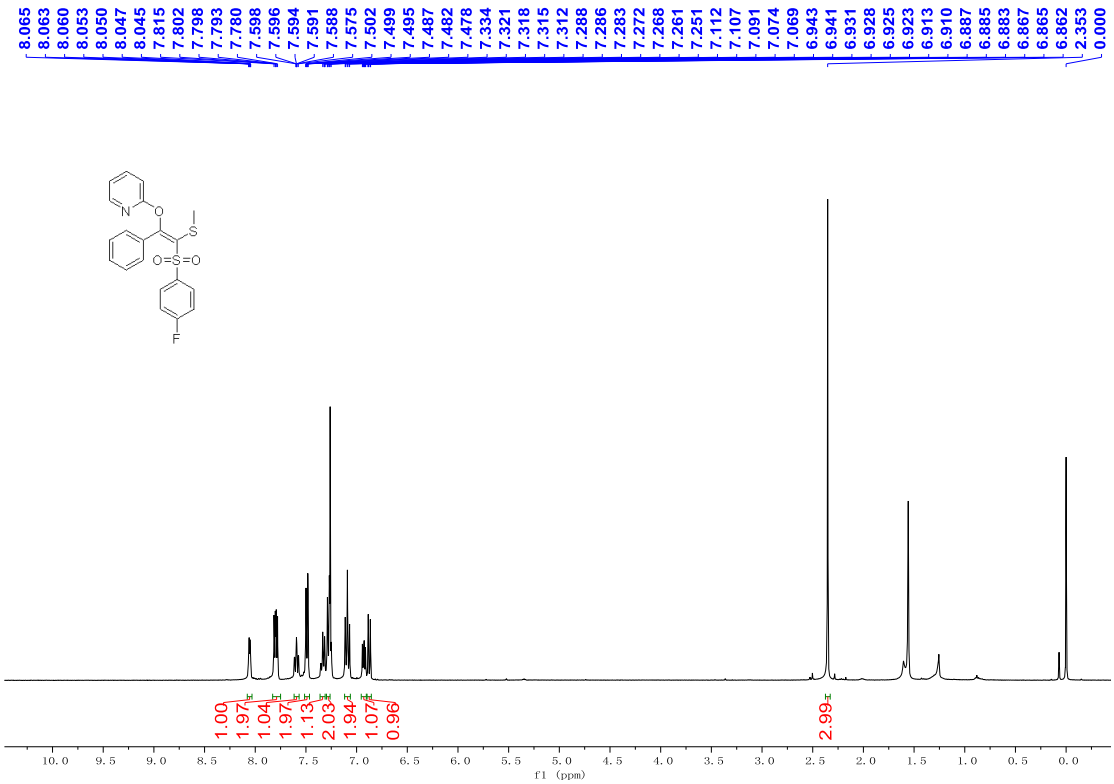


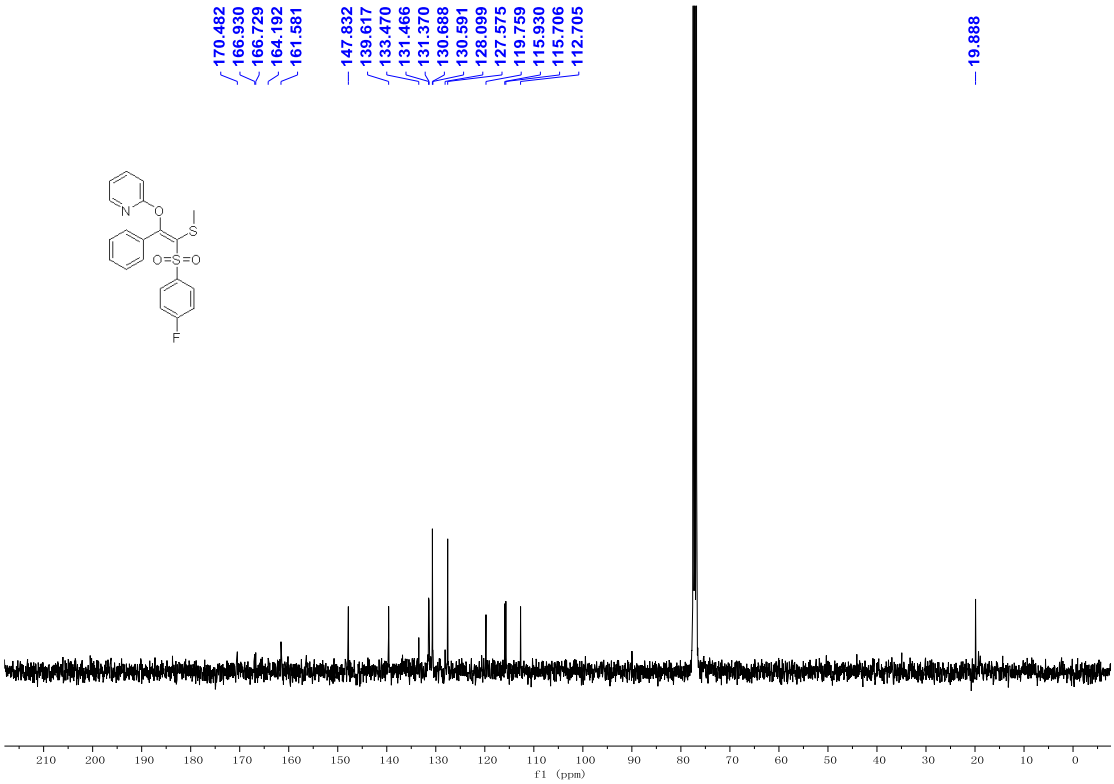
(*E*)-2-((2-(Methylsulfonyl)-2-(methylthio)-1-phenylvinyl)oxy)pyridine (**4q**) ($CDCl_3$)

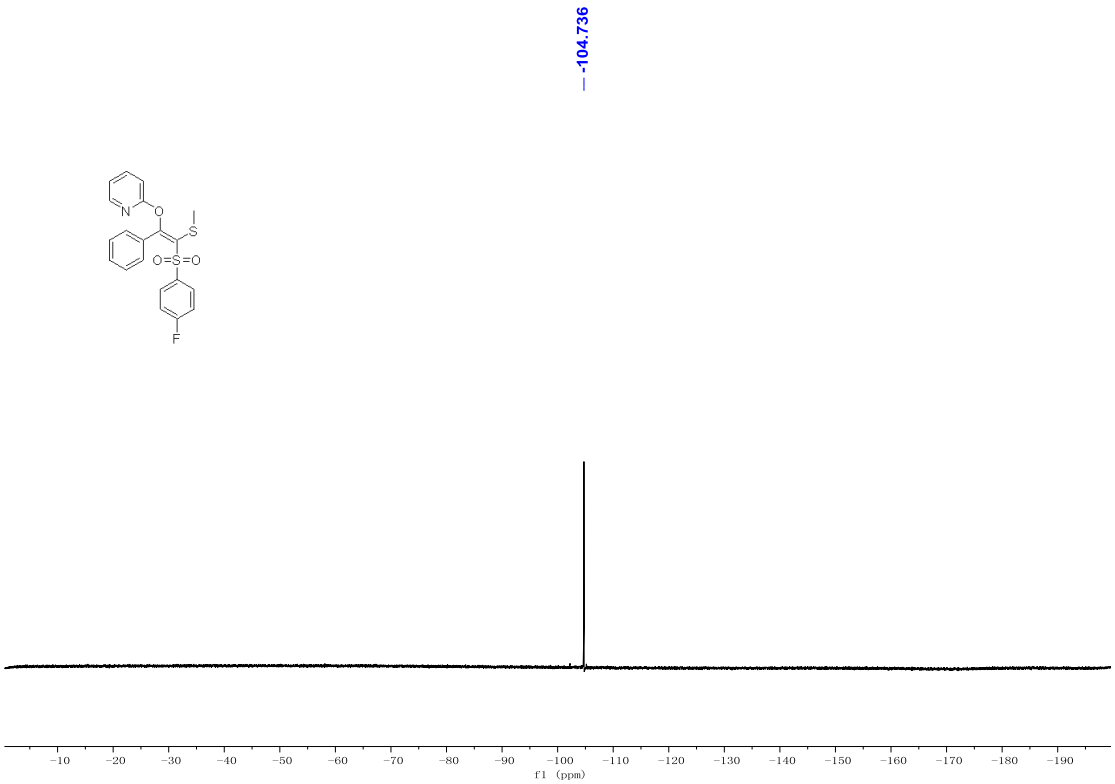




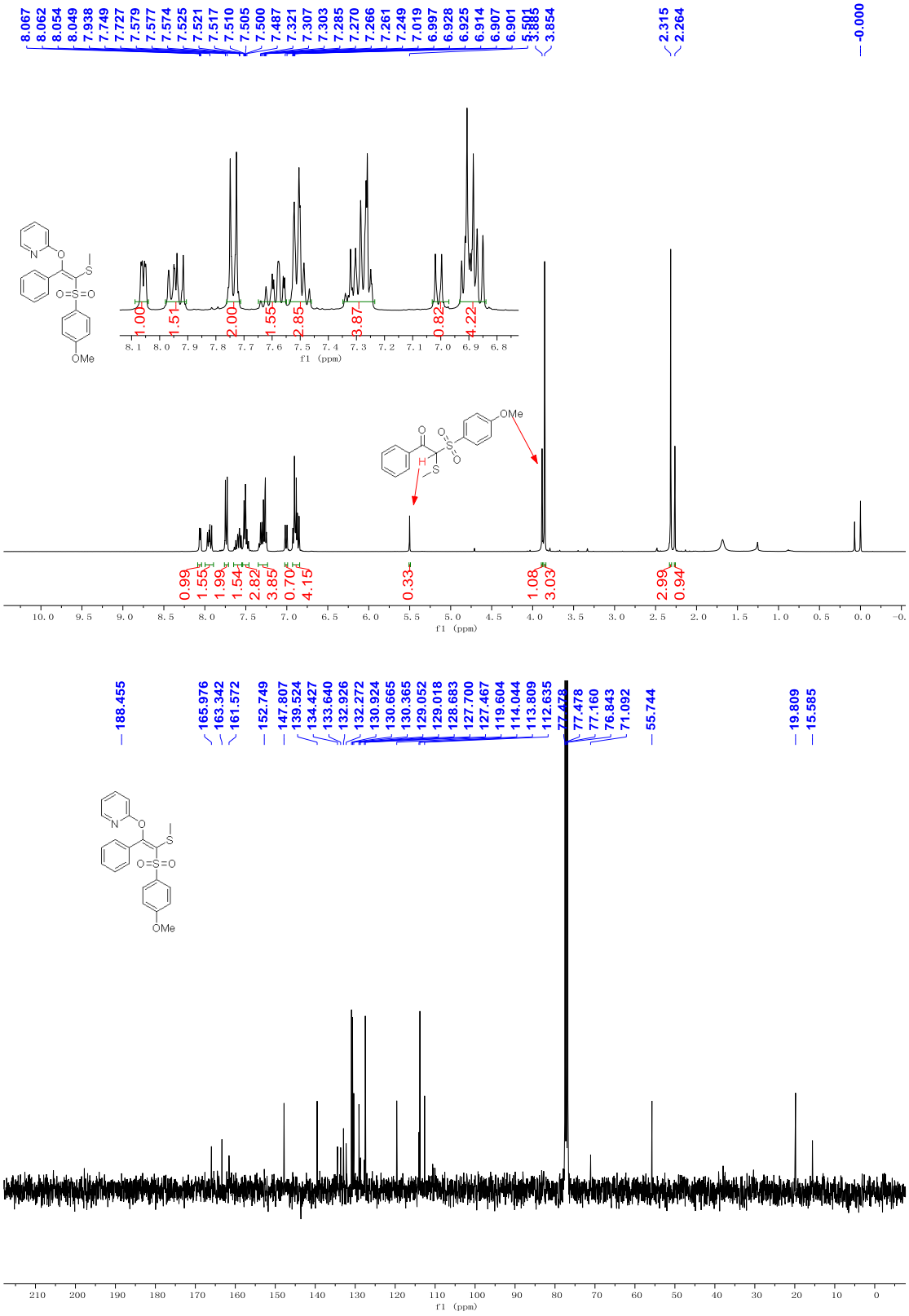
(*E*)-2-((2-((4-Fluorophenyl)sulfonyl)-2-(methylthio)-1-phenylvinyl)oxy)pyridine (**4r**) ($CDCl_3$)



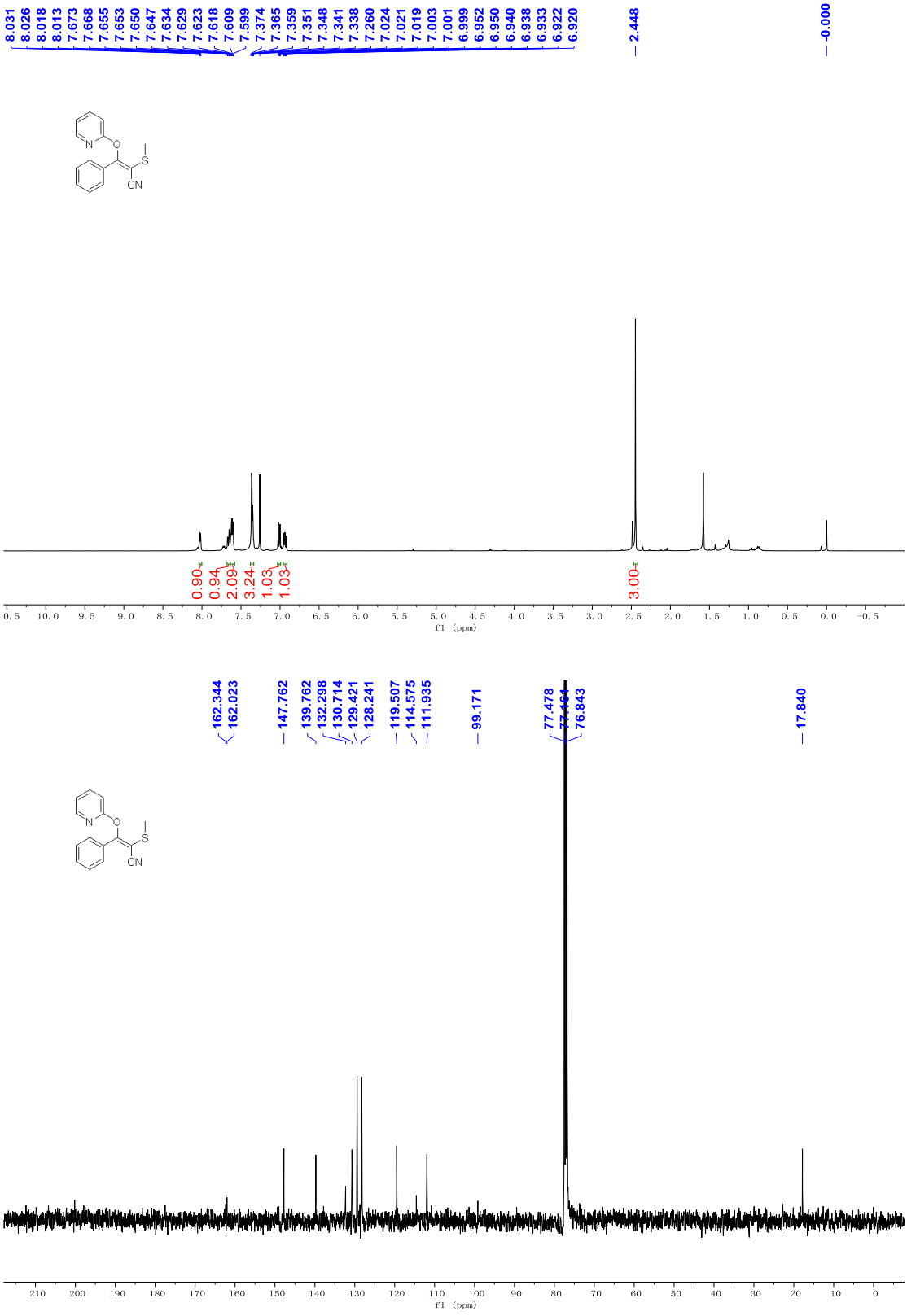



-104.736
N
O
S
O=S=O
F
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

(*E*)-2-((2-((4-Methoxyphenyl)sulfonyl)-2-(methylthio)-1-phenylvinyl)oxy)pyridine (**4s**) ($CDCl_3$)

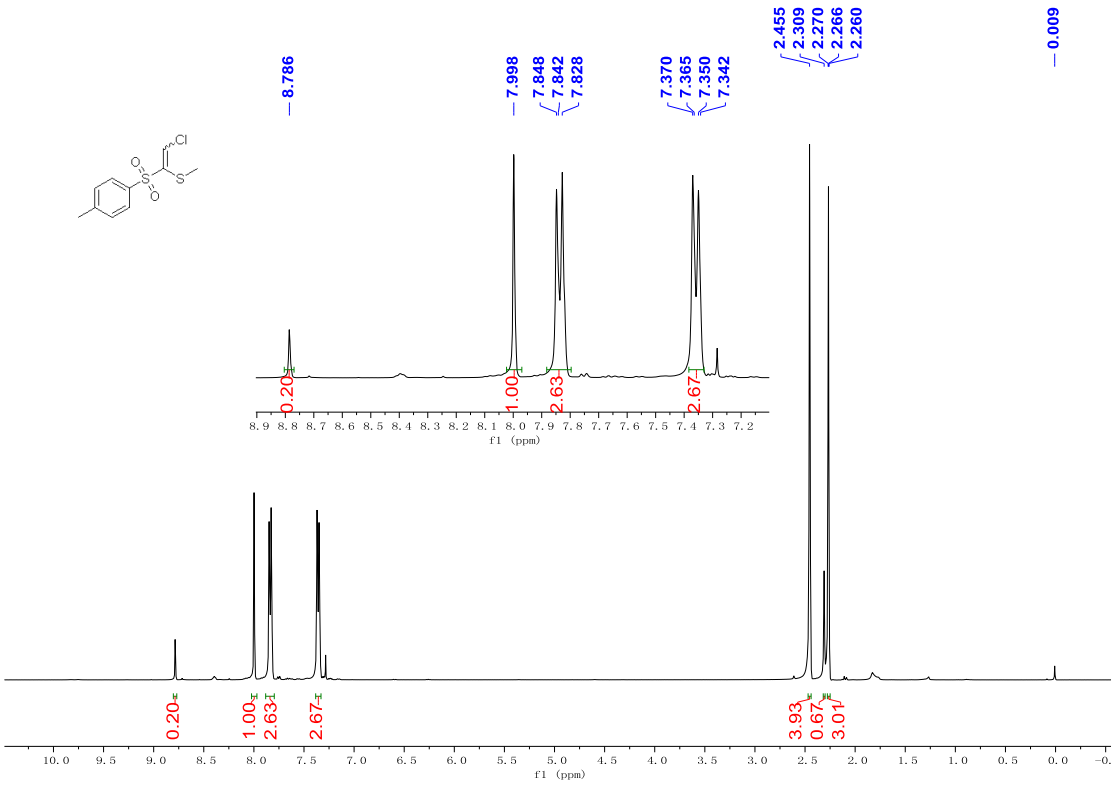


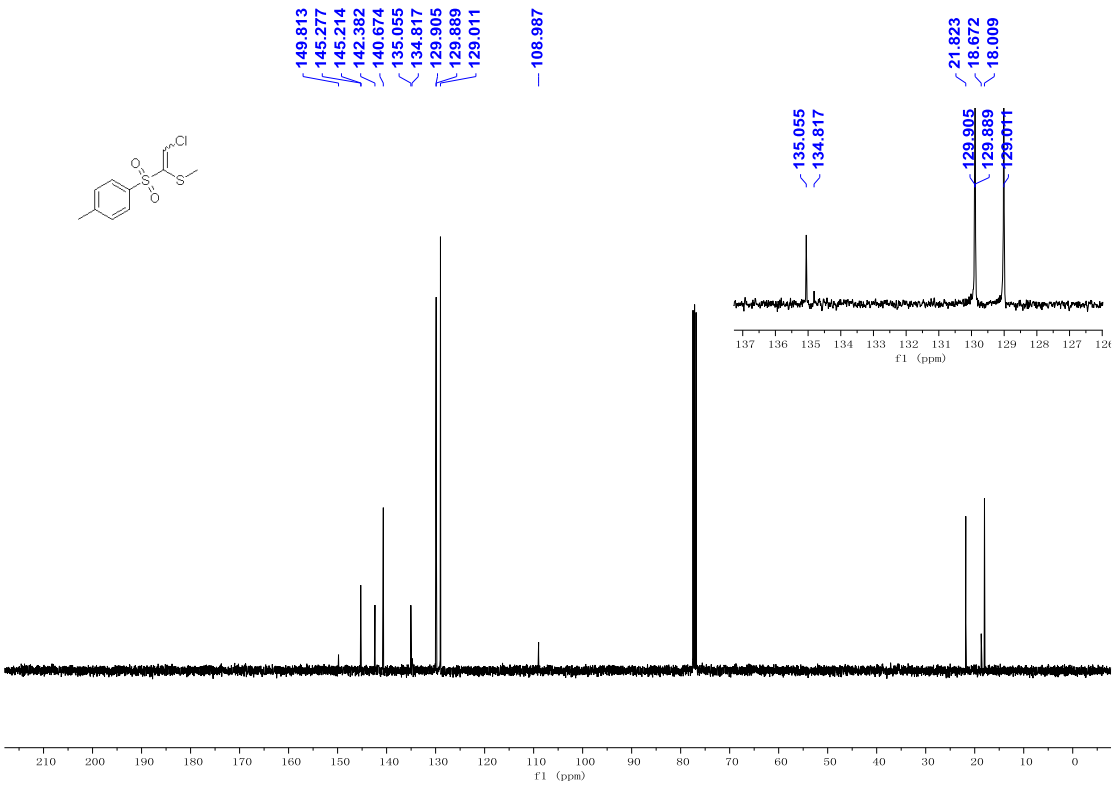
(Z)-2-(Methylthio)-3-phenyl-3-(pyridin-2-yloxy)acrylonitrile (**4u**) ($CDCl_3$)



2.5 Copies of NMR Spectra for 5

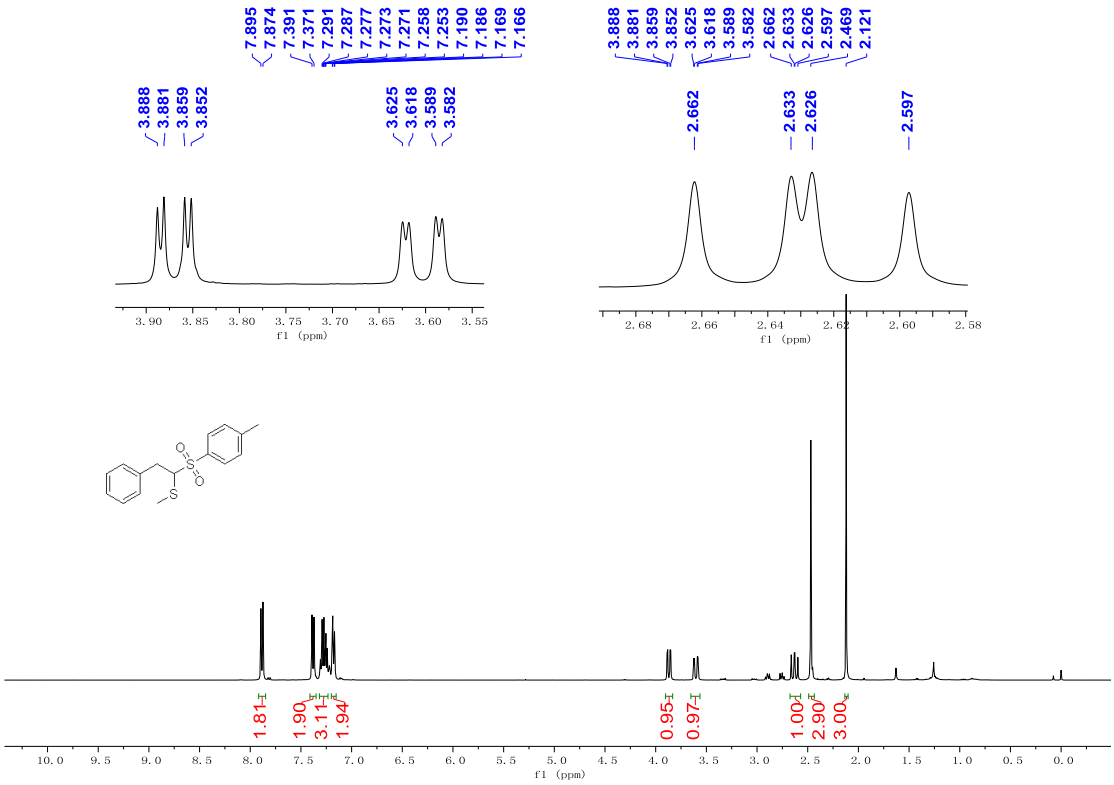
(2-Chloro-1-tosylvinyl)(methyl)sulfane (**5**) ($CDCl_3$)

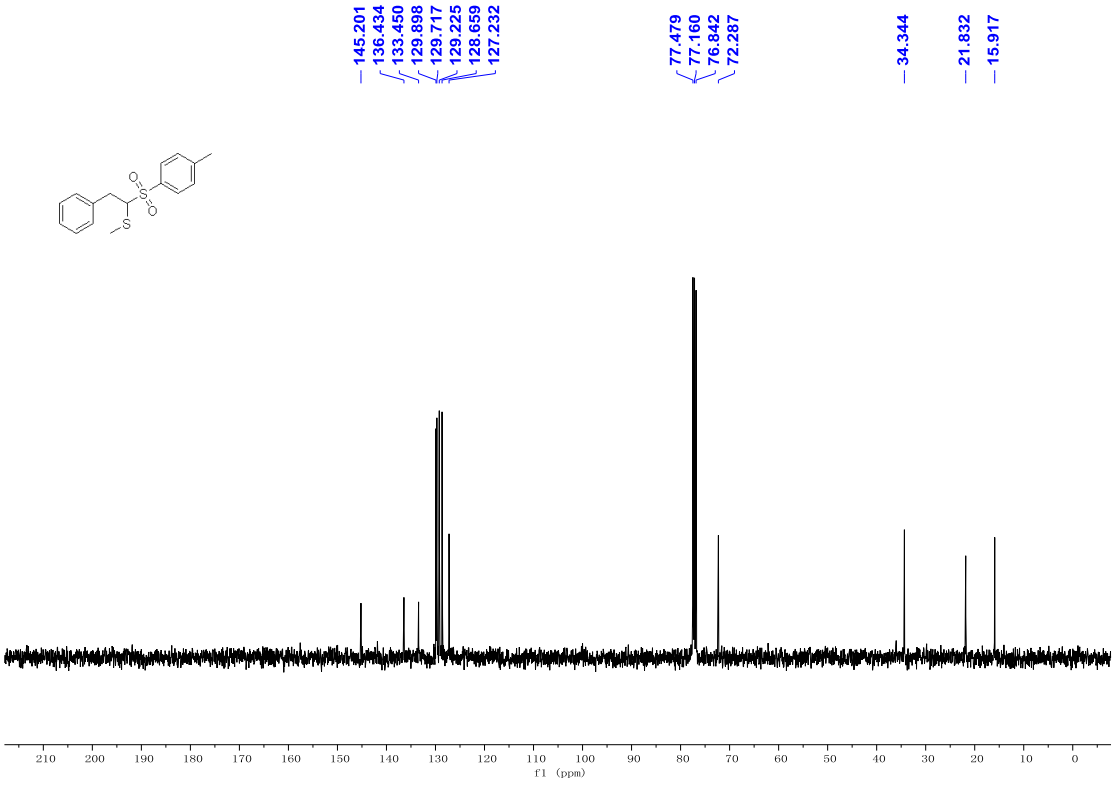




2.6 Copies of NMR Spectra for 7

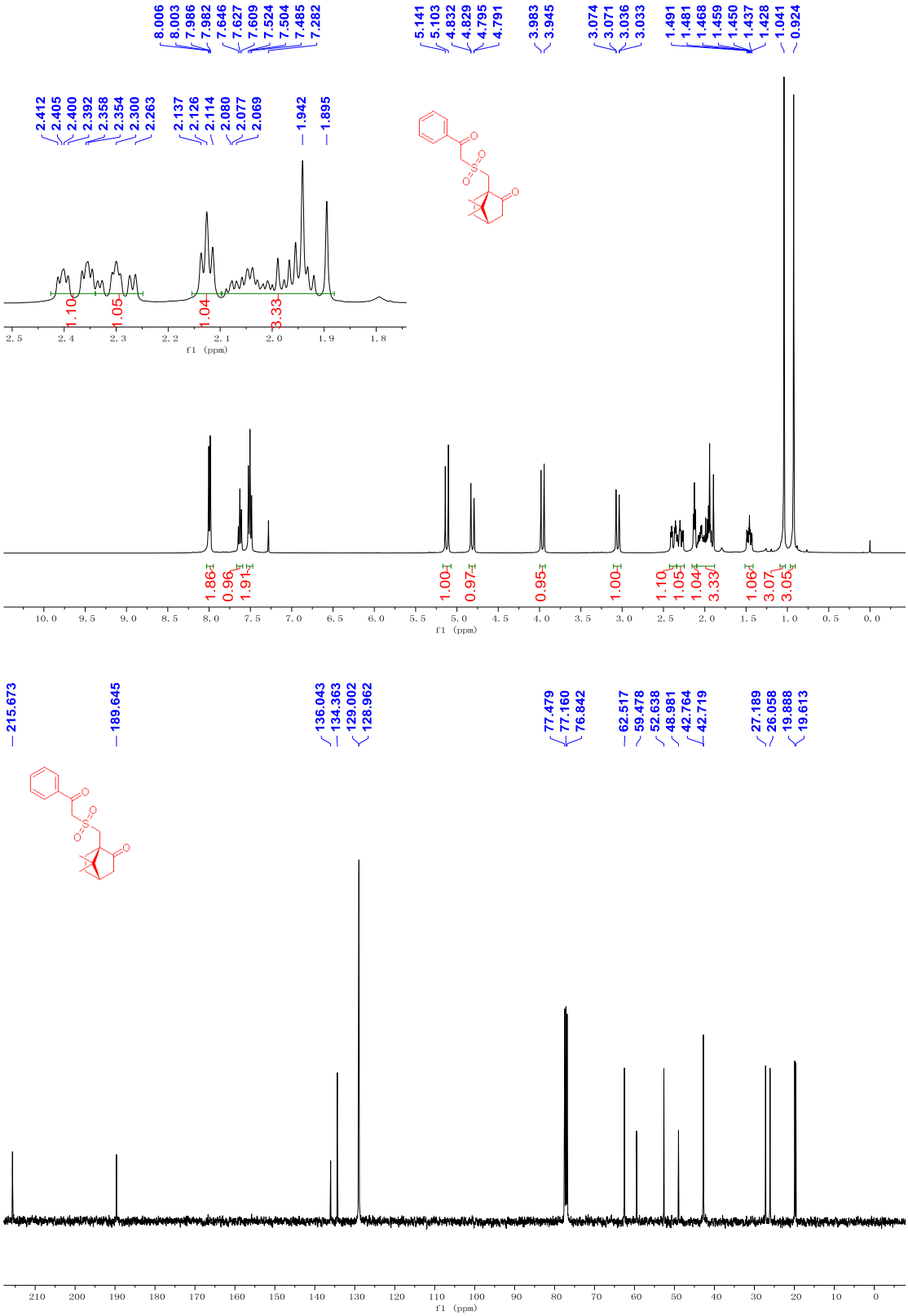
Methyl(2-phenyl-1-tosylethyl)sulfane (**7**) ($CDCl_3$)





2.7 Copies of NMR Spectra for 11 and 12

(1*R*,4*S*)-7,7-Dimethyl-1-(((2-oxo-2-phenylethyl)sulfonyl)methyl)bicyclo[2.2.1]heptan-2-one（**11**）



(1*R*,4*S*)-7,7-Dimethyl-1-(((phenylethynyl)sulfonyl)methyl)bicyclo[2.2.1]heptan-2-one (**12**)

($CDCl_3$)