Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Regioselective electrochemical cascade C-H sulfonylation-bromination of indolizines to access difunctionalized indolizines

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1. General considerations

Unless otherwise noted, commercial reagents were purchased from Adamas, Alfa, Aladdin, TCI, *J&K* or Macklin and used without further purification. All reactions were carried out using oven-dried glassware and all reactions proceeded without special care. Column chromatography was performed on 200-300 mesh silica gel (Huanghai, China).

^{1}H, ^{19}F and $^{13}C\{^{1}H\}$ NMR spectra were recorded on an Bruker Ascend 400 MHz spectrometer at ambient temperature. ^{1}H NMR spectra are referred to the TMS signal (δ = 0 ppm) and ^{13}C NMR spectra are referred to the residual solvent signal (δ = 77.16 ppm). Data for ^{1}H NMR are reported as follows: chemical shifts (δ ppm), multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integration.

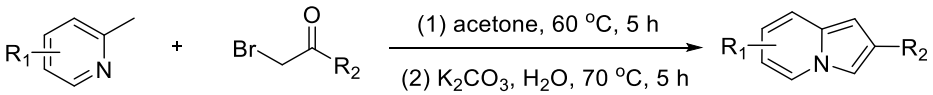
The instrument for electrolysis is ElectraSyn 2.0 Package (IKA), the anode electrode is vitreous carbon plate (52 mm×8 mm×2 mm) and cathodic electrode was platinum plate (52 mm×8 mm×2 mm); And MS-3610DS (MAISHENG), carbon plate (10 mm×10 mm×3 mm) and cathodic electrode was platinum plate (10 mm×10 mm×0.1 mm). The data of HRMS was carried out on Agilent 7250 GC/QTOF. Melting point were recorded using a SGW X-4 Melting Point Apparatus. X-ray diffraction data were collected on SuperNova, Dual, Cu at zero, AtlasS2.

2. Experimental procedures and characterization data

2.1 Experimental procedures

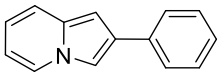
Synthesis of compounds 1 according to the following procedure[1]:

As exemplified for **1a**:



A solution of 2-picoline (0.93 g, 10 mmol, 1.0 equiv) and 2-bromoacetophenone (1.99 g, 10 mmol, 1.0 equiv) in acetone (50 mL) were added to a 100 mL round bottom flask and heated with a heating mantle for 5 hours to 60 °C. The precipitate obtained by filtration separation was redissolved in 20 mL of hot water (60 °C). Then, K_2CO_3 (2.76 g, 20 mmol, 2.0 equiv) was added and heated at 60 °C for 5 hours. After filtration and drying in vacuo, a white solid compound **1a** was obtained without further purification.

2-Phenylindolizine (1a)

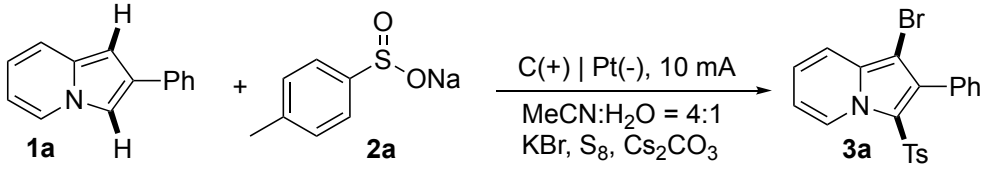


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.0 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.58 (s, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.29-7.23 (m, 1H), 6.70 (s, 1H), 6.68-6.60 (m, 1H), 6.45 (t, *J* = 6.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 133.6, 129.4, 128.7, 126.5, 126.2, 125.0, 119.0, 117.3, 110.5, 109.2, 96.6.

Indolizine derivatives **1** were known compounds and synthesized according to the known procedures, and their NMR data were in agreement with those described in the literature.[1,2]

Synthesis of products 3 and 4 according to the following procedure:

As exemplified for **3a**:

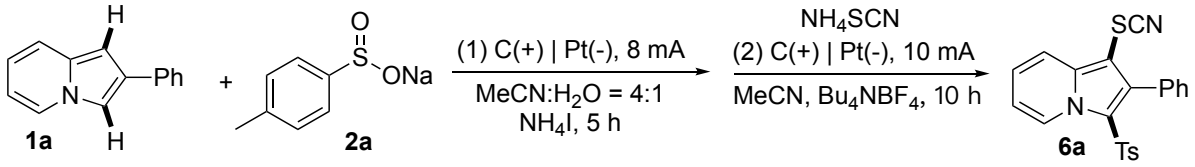


2-Phenylindolizine (0.3 mmol, 1.0 equiv), Sodium *p*-tolylsulfinate (0.6 mmol, 2 equiv), KBr (1.2 mmol), Cs_2CO_3 (0.3 mmol), S_8 (0.75 mmol, 2.5 equiv), CH_3CN (4 mL) and H_2O (1 mL) were placed in a 10 mL undivided electrolytic cell with a vitreous carbon plate anode (52 mm×8 mm×2 mm) and a platinum plate cathode (52 mm×8 mm×2 mm). The electrolysis was carried out at room temperature under a constant current of 10 mA for 10 hours. Then, the resulting solution was quenched with 10 mL brine and extracted

with ethyl acetate (3×10 mL). The extract was dried with Na_2SO_4. The solvent was removed with a rotary evaporator. The pure product **3a** was obtained by preparative TLC on silica gel (petroleum ether: ethyl acetate = 8: 1).

Synthesis of products 6 and 7 according to the following procedure:

As exemplified for **6a**:



2-Phenylindolizine (0.5 mmol, 1.0 equiv), Sodium *p*-tolylsulfinate (1.0 mmol, 2 equiv), NH_4I (2.0 mmol, 4 equiv), CH_3CN (4 mL) and H_2O (1 mL) were placed in a 10 mL undivided electrolytic cell with a vitreous carbon plate anode (52 mm×8 mm×2 mm) and a platinum plate cathode (52 mm×8 mm×2 mm). The electrolysis was carried out at room temperature under a constant current of 8 mA for 5 hours. Then, the resulting solution was quenched with 10 mL brine and extracted with ethyl acetate (3×10 mL). The extract was dried with Na_2SO_4. The solvent was removed with a rotary evaporator. The pure product **5a** was obtained by preparative TLC on silica gel (petroleum ether: ethyl acetate = 8: 1).

5a (0.2 mmol, 1.0 equiv), NH_4SCN (0.6 mmol, 3 equiv), Bu_4NBF_4 (0.8 mmol), and CH_3CN (5 mL) were placed in a 10 mL undivided electrolytic cell with a vitreous carbon plate anode (52 mm×8 mm×2 mm) and a platinum plate cathode (52 mm×8 mm×2 mm). The electrolysis was carried out at room temperature under a constant current of 10 mA for 10 hours. Then, the resulting solution was quenched with 10 mL brine and extracted with ethyl acetate (3×10 mL). The extract was dried with Na_2SO_4. The solvent was removed with a rotary evaporator. The pure product **6a** was obtained by preparative TLC on silica gel (petroleum ether: ethyl acetate = 4: 1).

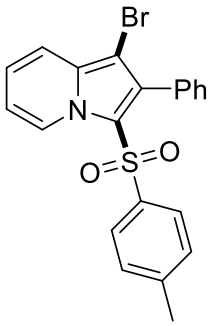
General procedure for cyclic voltammetry

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a steady vitreous carbon plate electrode, the counter electrode was a platinum plate. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. Then 10 mL electrolyte solution containing 0.05 M n-Bu_4NPF_6

the mixed solvent of MeCN and H_2O was poured into electrochemical cell. The concentration of samples was 0.01 M. The scan rate was 0.1 V/s, ranging from 0 V to 2.0 V.

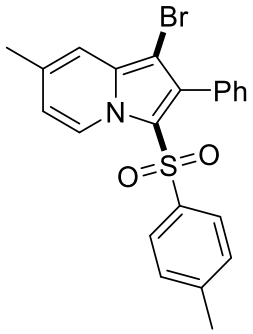
2.2 Characterization data

1-Bromo-2-phenyl-3-tosylindolizine (3a)



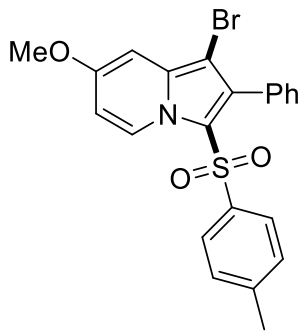
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3a**. Yellow solid (82.9 mg, 65%), mp 135.2-136.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.45 (d, *J* = 7.1 Hz, 5H), 7.37 – 7.31 (m, 2H), 7.14 (t, *J* = 9.1 Hz, 3H), 6.87 (t, *J* = 7.0 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 139.4, 135.6, 134.0, 131.8, 130.9, 129.5, 128.3, 127.5, 126.3, 125.9, 123.3, 117.8, 116.5, 113.9, 91.7, 21.5. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{21}H_{16}BrNO_2S$, 425.0085; found 425.0076.

1-Bromo-7-methyl-2-phenyl-3-tosylindolizine (3b)



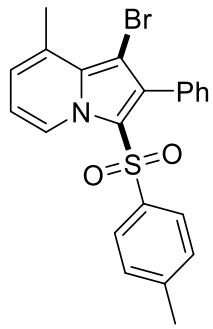
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3b**. Green solid (60.6 mg, 46%), mp 132.6-133.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 7.3 Hz, 1H), 7.47 – 7.40 (m, 5H), 7.36 – 7.31 (m, 2H), 7.29 (s, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 6.3 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 177.1, 143.8, 141.2, 139.8, 134.6, 132.1, 131.1, 129.6, 128.4, 127.6, 126.3, 125.5, 116.7, 116.2, 21.6, 21.2. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{18}BrNO_2S$, 439.0242; found 439.0247.

1-Bromo-7-methoxy-2-phenyl-3-tosylindolizine (3c)



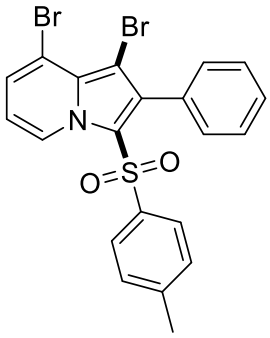
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3c**. Green solid (49.1 mg, 36%), mp 136.6-137.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.42 (m, 4H), 7.40 (s, 1H), 7.36 – 7.32 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 6.58 (d, *J* = 6.4 Hz, 1H), 3.89 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 137.5, 132.1, 131.1, 131.0, 129.9, 129.6, 129.6, 128.7, 128.4, 127.6, 127.6, 126.2, 108.9, 97.8, 94.7, 55.8, 21.6. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{18}BrNO_3S$, 455.0191; found 455.0196.

1-Bromo-8-methyl-2-phenyl-3-tosylindolizine (3d)



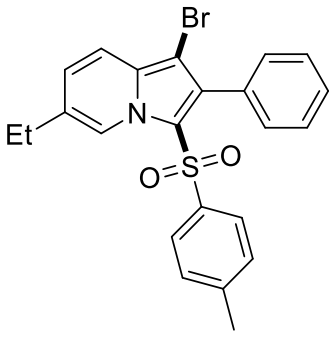
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3d**. Green solid (63.2 mg, 48%), mp 134.7-135.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 7.2 Hz, 1H), 7.50 (s, 1H), 7.47 (s, 1H), 7.45 (d, *J* = 2.5 Hz, 2H), 7.44 (s, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.28 (d, *J* = 3.7 Hz, 1H), 7.16 (s, 1H), 7.14 (s, 1H), 6.82 (d, *J* = 6.9 Hz, 1H), 6.71 (t, *J* = 7.0 Hz, 1H), 2.79 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 139.4, 136.3, 132.7, 131.0, 129.6, 129.3, 128.3, 127.6, 126.5, 124.2, 124.0, 116.9, 113.4, 100.0, 91.3, 21.6, 21.0. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{18}BrNO_2S$, 439.0242; found 439.0250.

1,8-Dibromo-2-phenyl-3-tosylindolizine (3e)



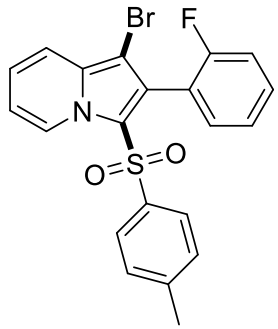
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3e**. Green solid (69.3 mg, 46%), mp 140.7-141.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 7.2 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 5H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.24 (s, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 138.9, 137.5, 133.3, 132.2, 130.9, 129.7, 128.7, 128.5, 128.2, 127.9, 127.7, 126.6, 125.5, 113.2, 112.3, 21.7. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{21}H_{15}Br_2NO_2S$, 502.9190; found 502.9189.

1-Bromo-6-ethyl-2-phenyl-3-tosylindolizine (3f)



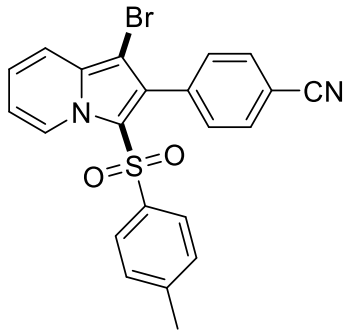
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3f**. Yellow solid (82.9 mg, 61%), mp 139.2-140.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.48 (s, 1H), 7.45 (d, *J* = 7.3 Hz, 5H), 7.34 – 7.30 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 9.1 Hz, 1H), 2.69 (q, *J* = 7.5 Hz, 2H), 2.33 (s, 3H), 1.30 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 139.6, 135.3, 133.3, 132.2, 131.1, 130.0, 129.5, 128.3, 127.6, 126.4, 125.6, 123.1, 117.4, 116.2, 91.4, 26.4, 21.6, 15.2. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{23}H_{20}BrNO_2S$, 453.0398; found 453.0395.

1-Bromo-2-(2-fluorophenyl)-3-tosylindolizine (3g)



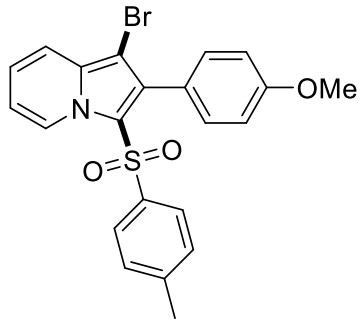
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3g**. Green solid (83.5 mg, 63%), mp 143.5-144.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 9.4 Hz, 3H), 7.51 – 7.43 (m, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.10 (m, 4H), 6.86 (t, *J* = 6.8 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 158.9, 144.2, 139.0, 134.2, 133.2, 130.7 (d, *J* = 8.0 Hz), 129.7, 129.5, 126.5, 125.7, 123.5 (d, *J* = 3.5 Hz), 123.3, 120.1 (d, *J* = 15.9 Hz), 118.0, 116.9, 115.4 (d, *J* = 21.7 Hz), 114.1, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.37 – -112.49 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{21}H_{15}BrFNO_2S$, 442.9991; 442.9988.

4-(1-Bromo-3-tosylindolizin-2-yl)benzonitrile (3h)



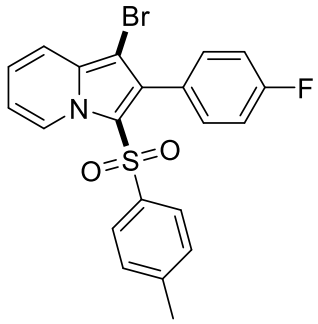
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3h**. Green solid (105.3 mg, 78%), mp 136.8-137.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.52 – 7.43 (m, 4H), 7.19 (t, *J* = 8.3 Hz, 3H), 6.93 (t, *J* = 7.0 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 139.0, 137.1, 134.3, 133.4, 131.9, 131.4, 129.8, 126.2, 125.8, 123.9, 118.9, 118.1, 116.6, 114.6, 112.2, 91.3, 21.6. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{15}BrN_2O_2S$, 450.0038; found 450.0043.

1-Bromo-2-(4-methoxyphenyl)-3-tosylindolizine (3i)



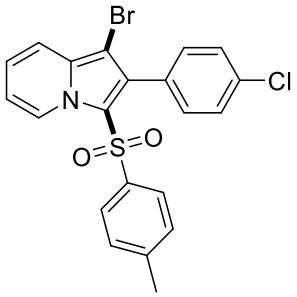
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3i**. Green solid (95.6 mg, 70%), mp 139.5-140.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.16 – 7.10 (m, 3H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.85 (t, *J* = 6.9 Hz, 1H), 3.89 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 143.9, 139.6, 135.5, 134.1, 132.4, 129.6, 126.3, 126.1, 124.0, 123.4, 117.9, 116.5, 113.9, 113.1, 92.0, 55.3, 21.6. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{18}BrNO_3S$, 455.0191; found 455.0183.

1-Bromo-2-(4-fluorophenyl)-3-tosylindolizine (3j)



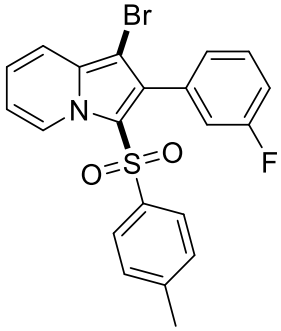
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3j**. Green solid (75.6 mg, 57%), mp 139.2-140.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, *J* = 7.2 Hz, 1H), 7.61 (q, *J* = 8.4, 5.5 Hz, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.16 – 7.12 (m, 3H), 7.08 (t, *J* = 8.6 Hz, 1H), 6.88 (t, *J* = 7.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 161.7, 144.1, 139.4, 134.6, 134.1, 132.9 (d, *J* = 8.2 Hz), 129.7, 127.8 (d, *J* = 3.3 Hz), 126.3, 126.0, 123.6, 118.0, 114.8, 114.6, 114.1, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.28. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{21}H_{15}BrFNO_2S$, 442.9991; found 442.9992.

1-Bromo-2-(4-chlorophenyl)-3-tosylindolizine (3k)



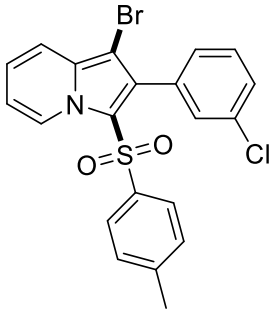
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3k**. Green solid (71.4 mg, 52%), mp 138.4-139.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.48 – 7.40 (m, 4H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.16 (t, *J* = 6.5 Hz, 3H), 6.89 (t, *J* = 7.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 139.4, 134.6, 134.4, 134.2, 132.4, 130.4, 129.7, 127.9, 126.3, 126.0, 123.6, 118.0, 116.7, 114.2, 91.7, 21.6. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{21}H_{15}BrClNO_2S$, 458.9695; found 458.9698.

1-Bromo-2-(3-fluorophenyl)-3-tosylindolizine (3l)



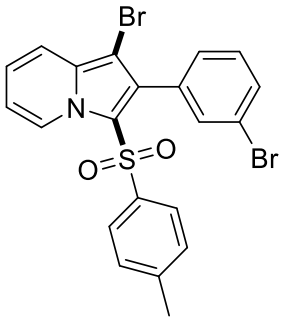
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3l**. Red solid (55.7 mg, 42%), mp 136.3-137.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.37 (m, 1H), 7.15 (t, *J* = 8.0 Hz, 5H), 7.00 (d, *J* = 9.5 Hz, 1H), 6.89 (t, *J* = 7.0 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 160.8, 144.2, 139.3, 134.1, 129.7, 129.1 (d, *J* = 8.5 Hz), 127.0 (d, *J* = 3.0 Hz), 126.4, 126.2, 126.0, 123.6, 118.0, 115.5, 115.3, 114.2, 104.3, 91.6, 21.6. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{21}H_{15}BrFNO_2S$, 442.9991; found 442.9983.

1-Bromo-2-(3-chlorophenyl)-3-tosylindolizine (3m)



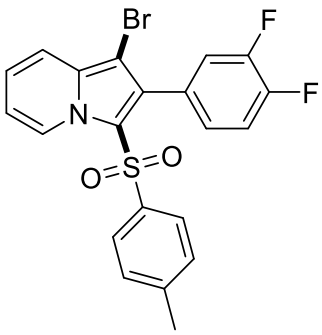
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3m**. Green solid (72.8 mg, 53%), mp 139.3-140.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 9.9 Hz, 1H), 7.49 – 7.35 (m, 5H), 7.17 (q, *J* = 7.0, 5.5 Hz, 4H), 6.90 (t, *J* = 7.0 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 139.3, 134.1, 134.0, 133.8, 133.5, 130.8, 129.7, 129.4, 128.9, 128.6, 126.4, 126.0, 123.6, 118.0, 116.9, 114.2, 91.5, 21.6. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{21}H_{15}BrClNO_2S$, 458.9695; found 458.9687.

1-Bromo-2-(3-bromophenyl)-3-tosylindolizine (3n)



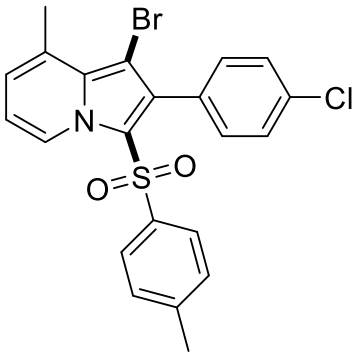
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3n**. Green solid (87.3 mg, 58%), mp 132.3-133.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (d, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 6.4 Hz, 1H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 2.9 Hz, 3H), 7.17 (d, *J* = 7.9 Hz, 3H), 6.90 (t, *J* = 7.0 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 139.3, 134.0, 133.8, 133.6, 131.4, 129.9, 129.7, 129.7, 129.2, 126.4, 126.1, 123.6, 121.5, 118.0, 117.2, 114.3, 91.6, 21.7. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{21}H_{15}Br_2NO_2S$, 502.9190; found 502.9182.

1-Bromo-2-(3,4-difluorophenyl)-3-tosylindolizine (3o)



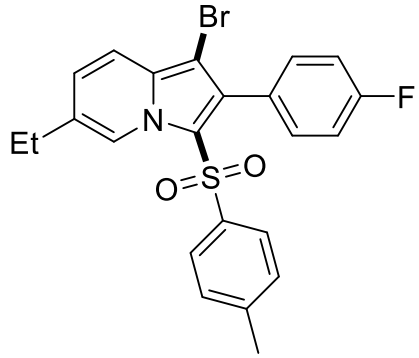
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3o**. Green solid (91.1 mg, 66%), mp 109.6-110.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 10.2 Hz, 1H), 7.19 – 7.12 (m, 4H), 7.11 – 7.06 (m, 1H), 6.90 (t, *J* = 7.0 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8 (d, *J* = 7.8 Hz), 150.8 (d, *J* = 11.5 Hz), 149.3 (d, *J* = 7.7 Hz), 148.4 (d, *J* = 11.2 Hz), 144.4, 139.3, 134.1, 133.3, 129.8, 127.6 (dd, *J* = 6.2, 3.7 Hz), 126.3, 126.0, 123.7, 120.2 (d, *J* = 17.9 Hz), 118.1, 116.6 (d, *J* = 18.0 Hz), 114.4, 91.7, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.81 – -137.98 (m), -138.26 – -138.42 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{21}H_{14}BrF_2NO_2S$, 460.9897; found 460.9899.

1-Bromo-2-(4-chlorophenyl)-8-methyl-3-tosylindolizine (3p)



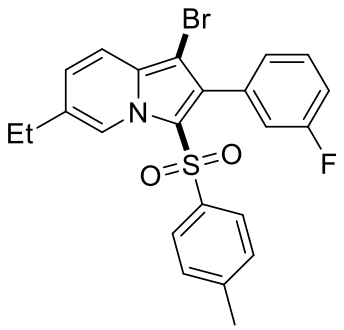
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3p**. Green solid (80.7 mg, 57%), mp 116.3-117.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 7.1 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 6.8 Hz, 1H), 6.72 (t, *J* = 7.1 Hz, 1H), 2.79 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 139.2, 135.0, 134.5, 132.9, 132.4, 131.9, 131.2, 129.7, 129.6, 129.4, 127.9, 127.8, 126.4, 124.2, 113.7, 21.6, 20.9. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{17}BrClNO_2S$, 472.9852; found 472.9858.

1-Bromo-6-ethyl-2-(4-fluorophenyl)-3-tosylindolizine (3q)



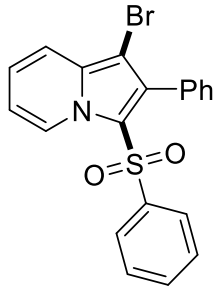
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3q**. Green solid (79.1 mg, 56%), mp 110.1-110.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.48 – 7.41 (m, 3H), 7.34 – 7.28 (m, 2H), 7.16 – 7.12 (m, 4H), 7.06 (d, *J* = 9.1 Hz, 1H), 2.69 (q, *J* = 7.5 Hz, 2H), 2.34 (s, 3H), 1.30 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 139.5, 136.6, 132.9, 132.9, 130.3, 129.6, 129.4, 128.0, 127.7, 126.3, 125.8, 123.1, 117.4, 114.8, 114.6, 26.4, 21.6, 15.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.50. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{23}H_{19}BrFNO_2S$, 471.0304; found 471.0303.

1-Bromo-6-ethyl-2-(3-fluorophenyl)-3-tosylindolizine (3r)



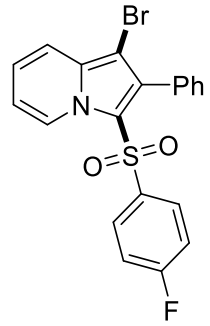
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **3r**. Green solid (84.8 mg, 60%), mp 108.6-109.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.50 – 7.44 (m, 3H), 7.43 – 7.37 (m, 1H), 7.15 (t, *J* = 8.9 Hz, 4H), 7.06 (d, *J* = 9.1 Hz, 1H), 7.00 (d, *J* = 9.5 Hz, 1H), 2.70 (q, *J* = 7.5 Hz, 2H), 2.34 (s, 3H), 1.30 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 160.8, 144.1, 136.6, 130.3, 129.6, 129.1 (d, *J* = 8.4 Hz), 127.7, 127.0 (d, *J* = 2.9 Hz), 126.4, 125.8, 123.0, 118.2, 117.9, 117.5, 115.3 (d, *J* = 21.0 Hz), 26.4, 21.6, 15.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.97. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{23}H_{19}BrFNO_2S$, 471.0304; found 471.0310.

1-Bromo-2-phenyl-3-(phenylsulfonyl)indolizine (4a)



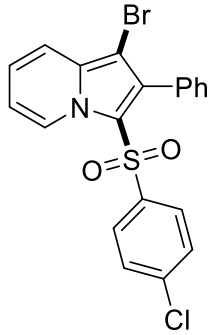
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **4a**. Green solid (89.8 mg, 73%), mp 146.4-147.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 3H), 7.45 (d, *J* = 6.0 Hz, 4H), 7.33 (t, *J* = 7.3 Hz, 4H), 7.15 (t, 1H), 6.88 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 135.9, 134.3, 133.0, 131.8, 131.0, 130.6, 129.0, 128.5, 127.6, 126.3, 126.1, 123.6, 118.0, 114.1, 91.9. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{20}H_{14}BrNO_2S$, 410.9929; found 410.9921.

1-Bromo-3-((4-fluorophenyl)sulfonyl)-2-phenylindolizine (4b)



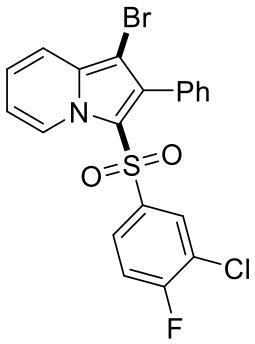
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **4b**. Green solid (89.9 mg, 70%), mp 150.1-150.7 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 7.2 Hz, 1H), 7.58 – 7.49 (m, 3H), 7.47 – 7.42 (m, 3H), 7.32 – 7.28 (m, 2H), 7.19 – 7.14 (m, 1H), 7.00 – 6.95 (m, 2H), 6.92 – 6.87 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 164.0, 138.5 (d, *J* = 3.1 Hz), 135.8, 134.3, 131.7, 131.0, 129.1 (d, *J* = 9.5 Hz), 128.6, 127.7, 126.0, 123.7, 118.0, 116.1 (d, *J* = 22.6 Hz), 114.2, 91.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.50. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{20}H_{13}BrFNO_2S$, 428.9834; found 428.9832.

1-Bromo-3-((4-chlorophenyl)sulfonyl)-2-phenylindolizine (4c)



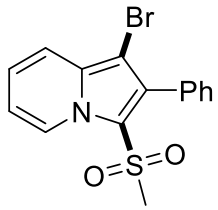
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **4c**. Green solid (78.6 mg, 59%), mp 186.6-187.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.48 – 7.43 (m, 5H), 7.32 – 7.27 (m, 3H), 7.17 (t, 1H), 6.90 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 139.6, 136.0, 134.5, 131.6, 131.1, 129.2, 128.9, 128.6, 127.8, 127.7, 126.1, 123.8, 118.1, 114.3, 92.1. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{20}H_{13}BrClNO_2S$, 444.9539; found 444.9533.

1-Bromo-3-((3-chloro-4-fluorophenyl)sulfonyl)-2-phenylindolizine (4d)



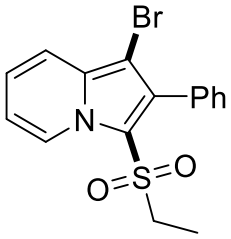
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **4d**. Green solid (105.3 mg, 76%), mp 122.3-122.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.49 – 7.45 (m, 3H), 7.42 (s, 1H), 7.40 – 7.35 (m, 1H), 7.30 – 7.27 (m, 2H), 7.21 – 7.16 (m, 1H), 7.04 (t, *J* = 8.5 Hz, 1H), 6.95 – 6.90 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 159.4, 139.5 (d, J = 3.8 Hz), 136.1, 134.6, 131.4, 131.0, 129.5, 128.8, 127.8, 126.8 (d, *J* = 8.6 Hz), 126.1, 124.0, 122.1 (d, *J* = 18.8 Hz), 118.1, 117.1 (d, *J* = 22.4 Hz), 114.5, 92.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.80. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{20}H_{12}BrClFNO_2S$, 462.9445; found 462.9439.

1-Bromo-3-(methylsulfonyl)-2-phenylindolizine (4e)



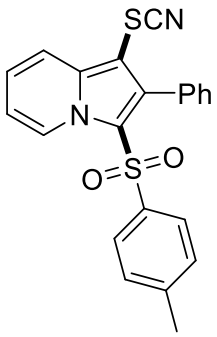
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **4e**. Green solid (71.0 mg, 68%), mp 121.6-122.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.46 (d, *J* = 5.3 Hz, 5H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.89 (t, *J* = 6.9 Hz, 1H), 2.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 134.0, 131.7, 130.8, 128.7, 128.0, 126.2, 123.5, 118.0, 116.0, 114.1, 91.4, 45.3. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{15}H_{12}BrNO_2S$, 348.9772; found 348.9781.

1-Bromo-3-(ethylsulfonyl)-2-phenylindolizine (4f)



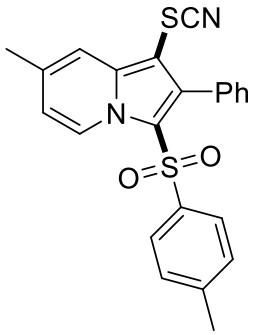
Preparative TLC on silica gel (eluent: PE/EA = 8/1, v/v) to afford **4f**. Green solid (68.4 mg, 63%), mp 106.8-107.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 7.2 Hz, 1H), 7.58 (t, 2H), 7.45 (d, *J* = 2.9 Hz, 4H), 7.18 (t, 1H), 6.87 (t, *J* = 7.0 Hz, 1H), 2.94 (q, *J* = 7.4 Hz, 2H), 1.11 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 133.5, 131.7, 130.9, 128.7, 128.7, 128.2, 127.8, 126.3, 123.5, 118.0, 114.0, 51.4, 7.3. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{16}H_{14}BrNO_2S$, 362.9929; found 362.9932.

2-Phenyl-1-thiocyanato-3-tosylindolizine (6a)



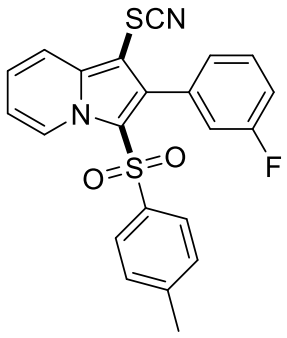
Preparative TLC on silica gel (eluent: PE/EA = 4/1, v/v) to afford **6a**. Yellow solid (67.0 mg, 83%), mp 223.9-224.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.51 – 7.45 (m, 5H), 7.40 – 7.37 (m, 1H), 7.36 – 7.32 (m, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.07 – 7.03 (m, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 140.7, 138.8, 138.5, 130.9, 130.8, 129.8, 128.9, 127.8, 126.9, 126.6, 126.0, 119.4, 117.4, 115.1, 111.2, 91.1, 21.6. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{16}N_2O_2S_2$, 404.0653; found 404.0655.

7-Methyl-2-phenyl-1-thiocyanato-3-tosylindolizine (6b)



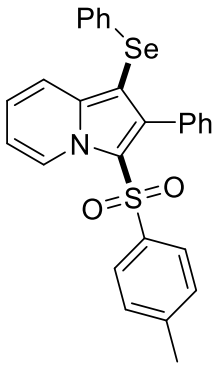
Preparative TLC on silica gel (eluent: PE/EA = 4/1, v/v) to afford **6b**. Black solid (68.5 mg, 82%), mp 226.3-226.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 7.3 Hz, 1H), 7.58 (s, 1H), 7.51 – 7.43 (m, 5H), 7.37 – 7.32 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.88 (dd, *J* = 7.3, 1.8 Hz, 1H), 2.48 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 140.9, 139.1, 139.0, 137.5, 130.9, 130.9, 129.7, 128.8, 127.8, 126.5, 126.3, 118.5, 117.7, 115.8, 111.5, 89.4, 21.6, 21.4. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{23}H_{18}N_2O_2S_2$, 418.0810; found 418.0813.

2-(3-Fluorophenyl)-1-thiocyanato-3-tosylindolizine (6c)



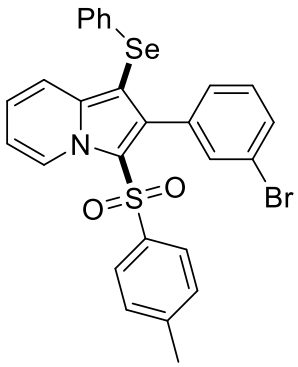
Preparative TLC on silica gel (eluent: PE/EA = 4/1, v/v) to afford **6c**. Green liquid (67.5 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.43 (m, 3H), 7.41 – 7.36 (m, 1H), 7.24 – 7.17 (m, 3H), 7.16 – 7.13 (m, 1H), 7.09 – 7.02 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 160.8, 144.8, 139.0 (d, *J* = 2.2 Hz), 138.5 (d, *J* = 9.9 Hz), 132.8 (d, *J* = 8.5 Hz), 129.8, 129.4 (d, *J* = 8.4 Hz), 126.7, 126.7 (d, *J* = 3.1 Hz), 126.6, 126.1, 119.4, 117.9 (d, *J* = 22.6 Hz), 117.3, 115.9 (d, *J* = 20.9 Hz), 115.3, 110.9, 90.9, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.10 (td, *J* = 9.0, 5.9 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{15}FN_2O_2S_2$, 422.0559; found 422.0562.

2-Phenyl-1-(phenylselanyl)-3-tosylindolizine (7a)



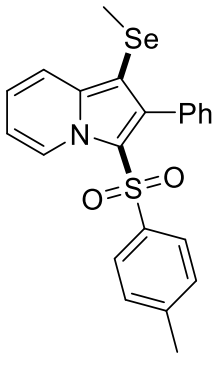
Preparative TLC on silica gel (eluent: PE/EA = 5/1, v/v) to afford **7a**. Green solid (90.5 mg, 90%), mp 177.8-178.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.24 – 7.21 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 3H), 7.10 – 7.07 (m, 2H), 7.02 – 6.98 (m, 2H), 6.94 – 6.89 (m, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 141.8, 139.5, 139.4, 133.3, 133.1, 131.0, 129.6, 129.0, 129.0, 128.1, 127.2, 126.5, 126.4, 126.0, 124.3, 119.2, 117.7, 114.2, 99.5, 21.6. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{27}H_{21}NO_2SSe$, 503.0458; found 503.0452.

2-(3-Bromophenyl)-1-(phenylselanyl)-3-tosylindolizine (7b)



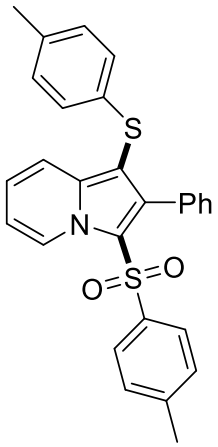
Preparative TLC on silica gel (eluent: PE/EA = 5/1, v/v) to afford **7b**. Yellow oil (102.0 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 3H), 7.24 – 7.16 (m, 5H), 7.15 (d, *J* = 1.5 Hz, 1H), 7.12 – 7.08 (m, 3H), 7.02 – 6.98 (m, 2H), 6.94 (td, *J* = 7.0, 1.4 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 139.7, 139.4, 135.2, 133.6, 132.9, 131.0, 129.8, 129.7, 129.4, 129.1, 128.8, 126.5, 126.4, 126.3, 124.4, 121.2, 119.3, 118.0, 114.4, 99.6, 21.7. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{27}H_{20}BrNO_2SSe$, 580.9563; found 580.9559.

1-(Methylselanyl)-2-phenyl-3-tosylindolizine (7c)



Preparative TLC on silica gel (eluent: PE/EA = 5/1, v/v) to afford **7c**. Yellow oil (74.9 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 5.4 Hz, 3H), 7.34 – 7.29 (m, 2H), 7.13 (d, *J* = 7.7 Hz, 3H), 6.87 (t, *J* = 6.9 Hz, 1H), 2.33 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 141.0, 139.7, 138.7, 133.6, 131.0, 129.5, 128.0, 127.3, 126.5, 126.2, 123.5, 119.3, 113.8, 104.4, 101.1, 21.6, 9.6. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{19}NO_2SSe$, 441.0302; found 441.0311.

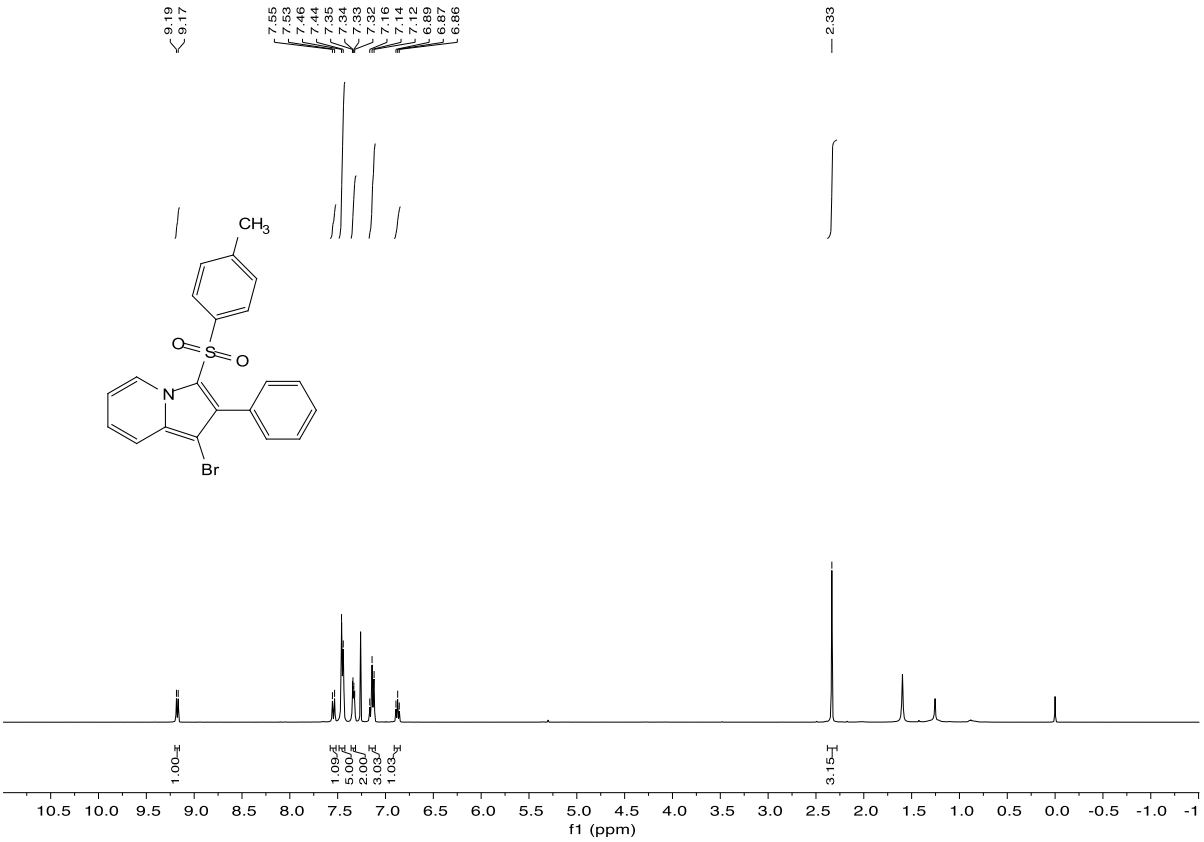
2-Phenyl-1-(p-tolylthio)-3-tosylindolizine (7d)

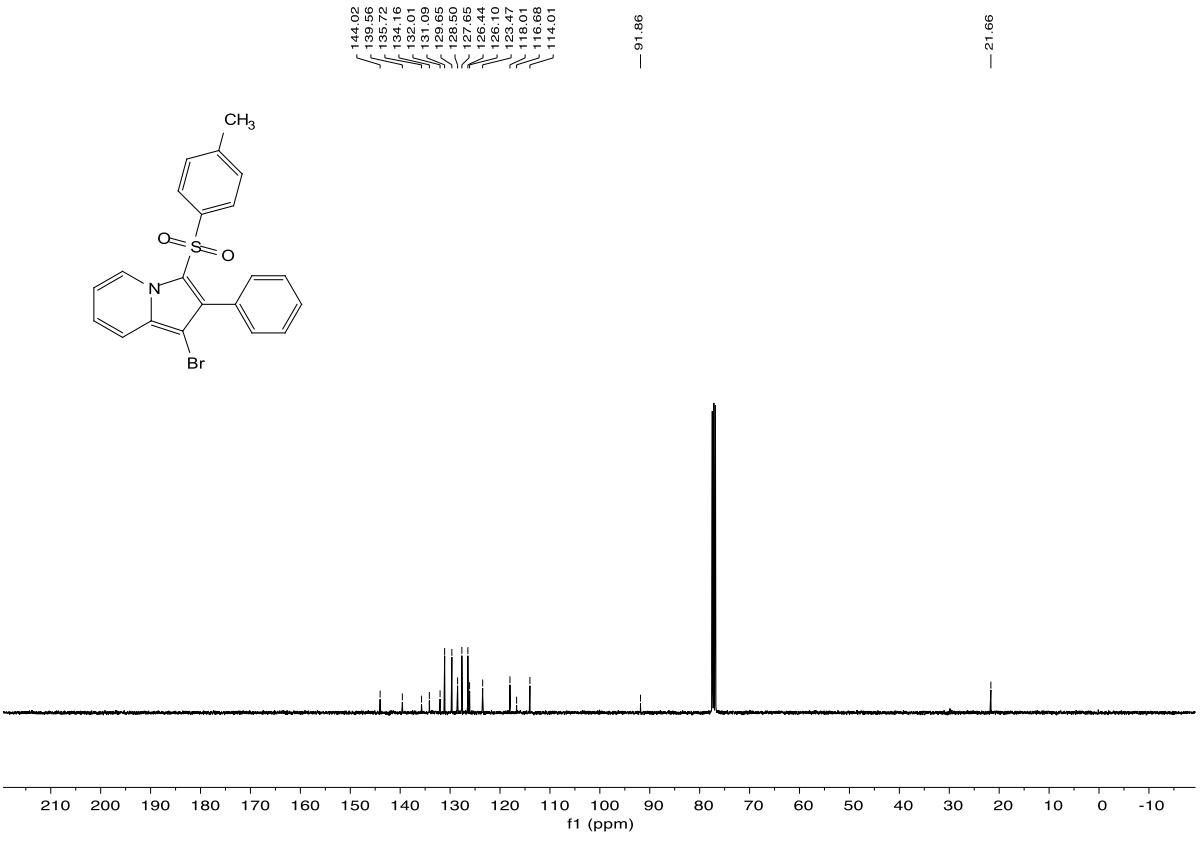


Preparative TLC on silica gel (eluent: PE/EA = 6.5/1, v/v) to afford **7d**. Green solid (75.9 mg, 81%), mp 190.6-191.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.31 (m, 3H), 7.30 – 7.21 (m, 2H), 7.18 – 7.11 (m, 3H), 6.97 – 6.87 (m, 3H), 6.78 (d, *J* = 8.2 Hz, 2H), 2.35 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 141.5, 139.5, 139.1, 135.0, 134.8, 132.1, 131.0, 129.6, 129.5, 128.1, 127.2, 126.5, 126.4, 126.4, 124.3, 118.2, 117.4, 114.3, 102.9, 21.6, 20.9. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{28}H_{23}NO_2S_2$, 469.1170; found 469.1180.

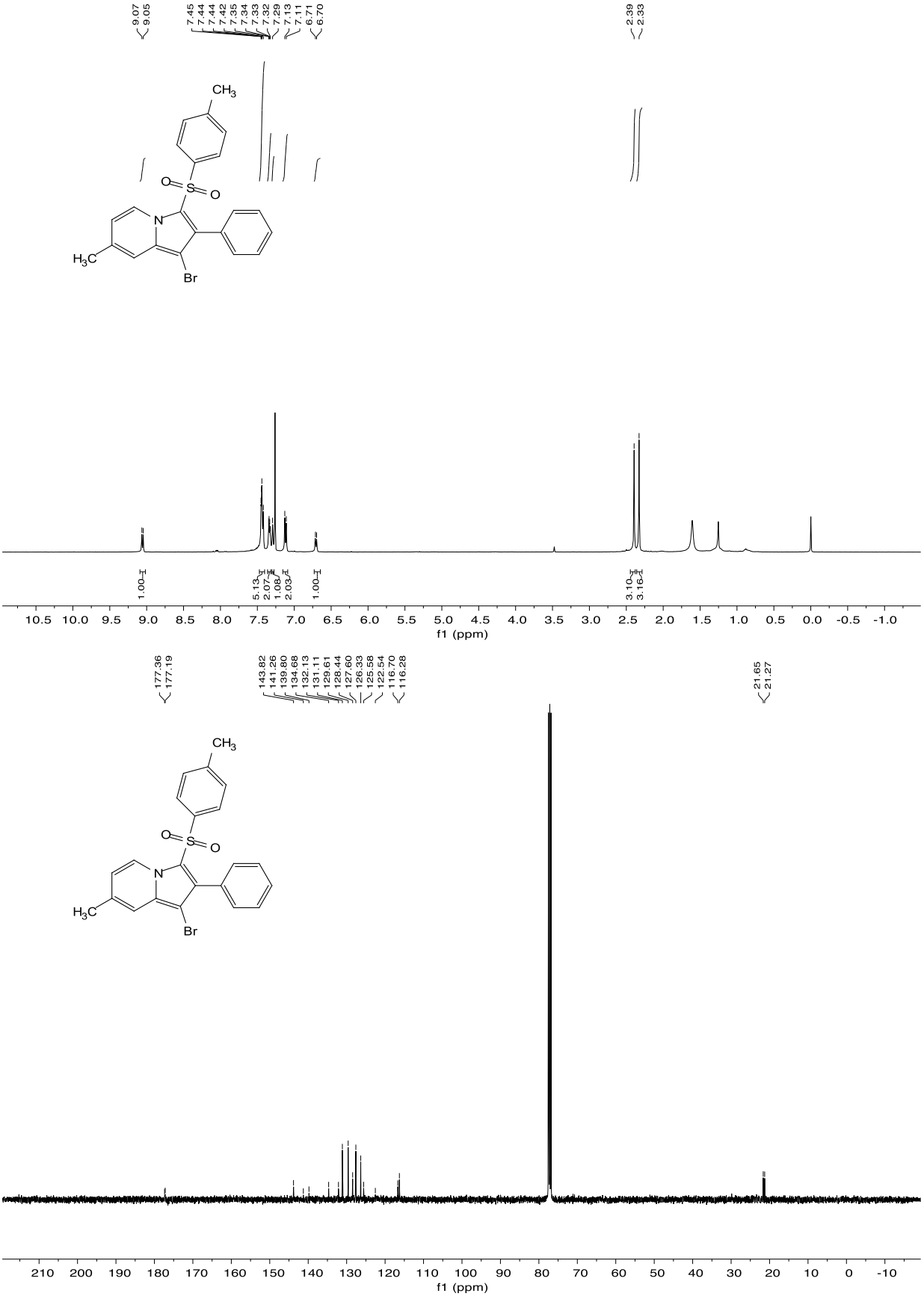
3. NMR spectra for new compounds

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3a**

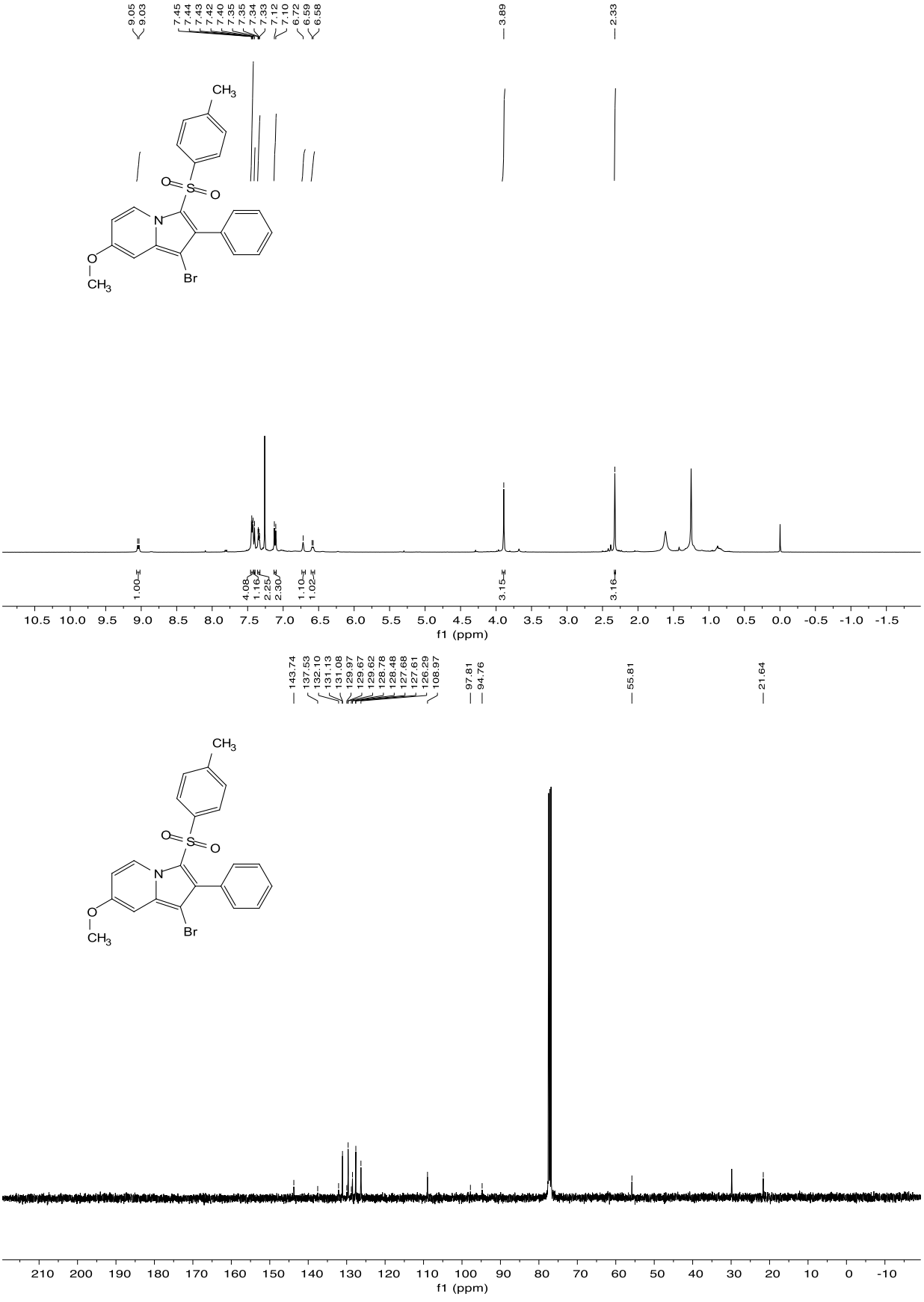




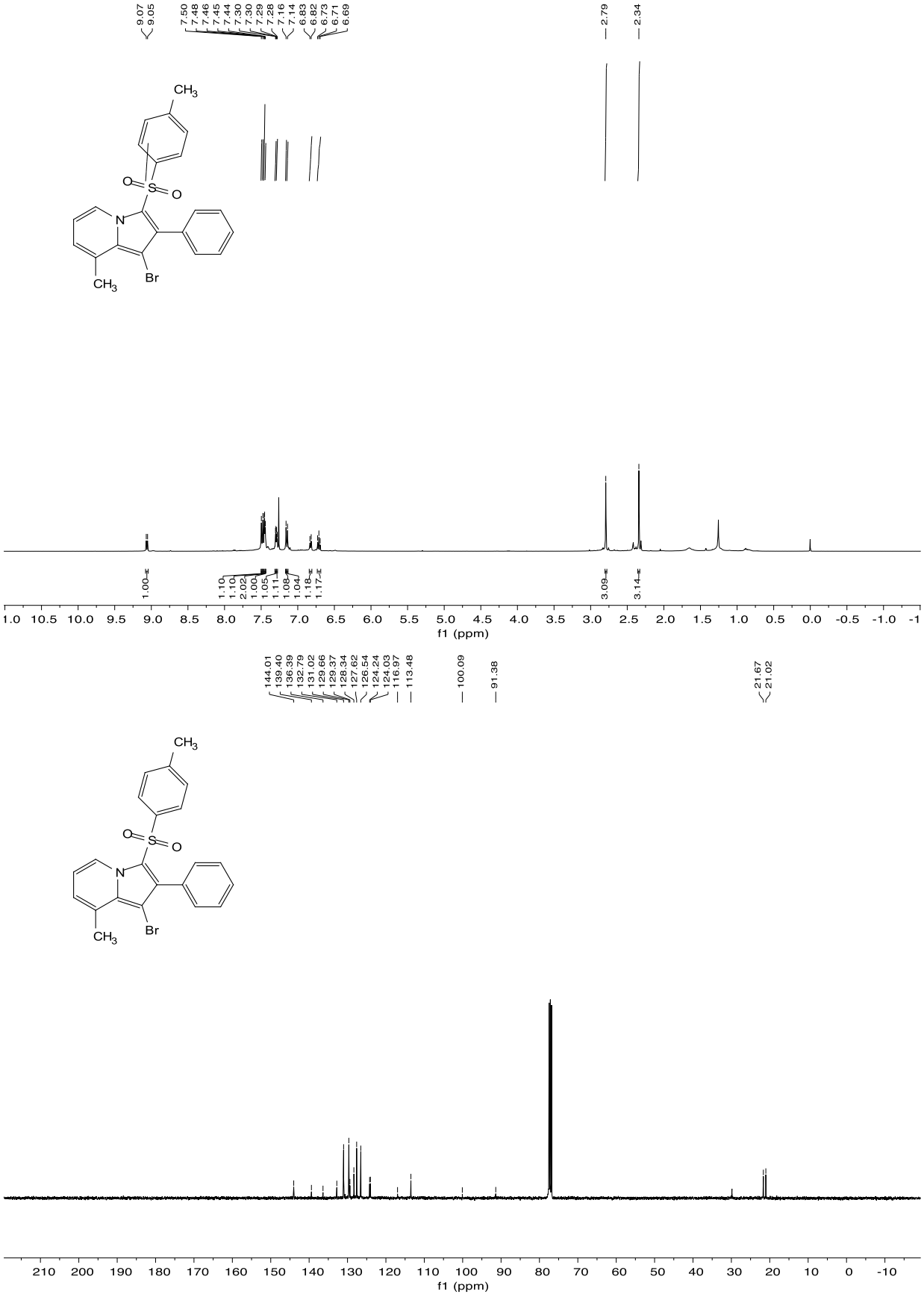
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3b**



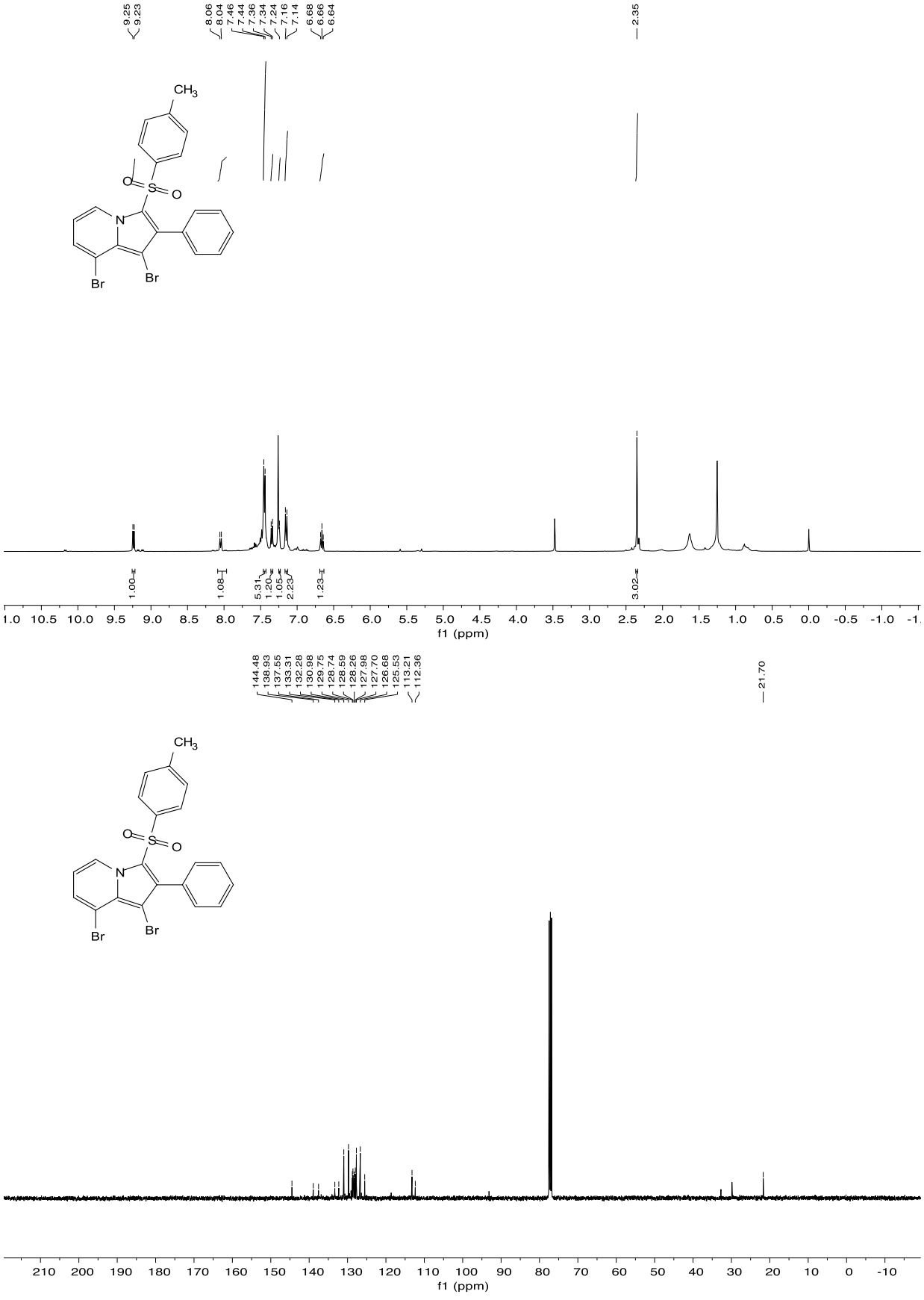
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3c**



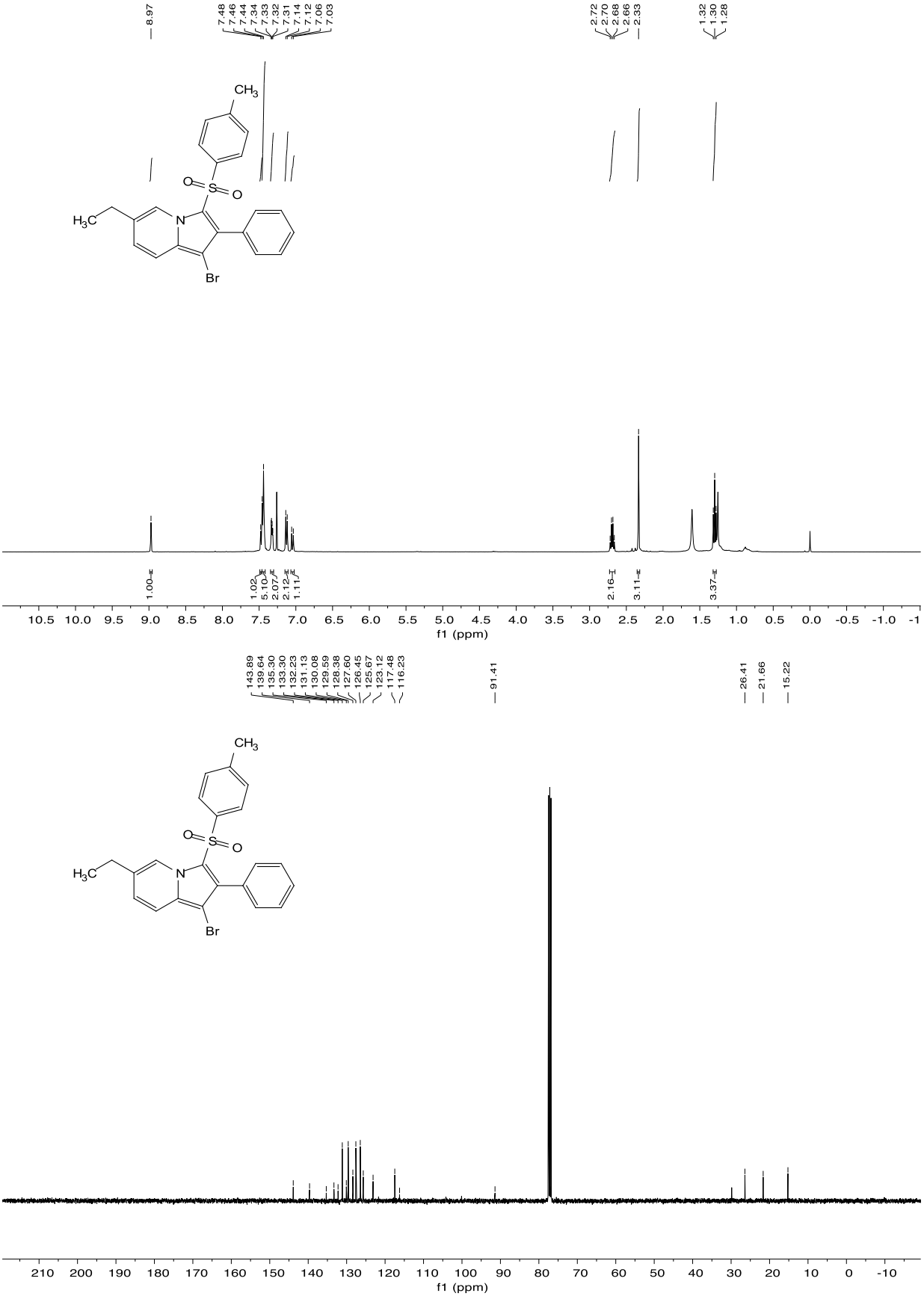
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3d**



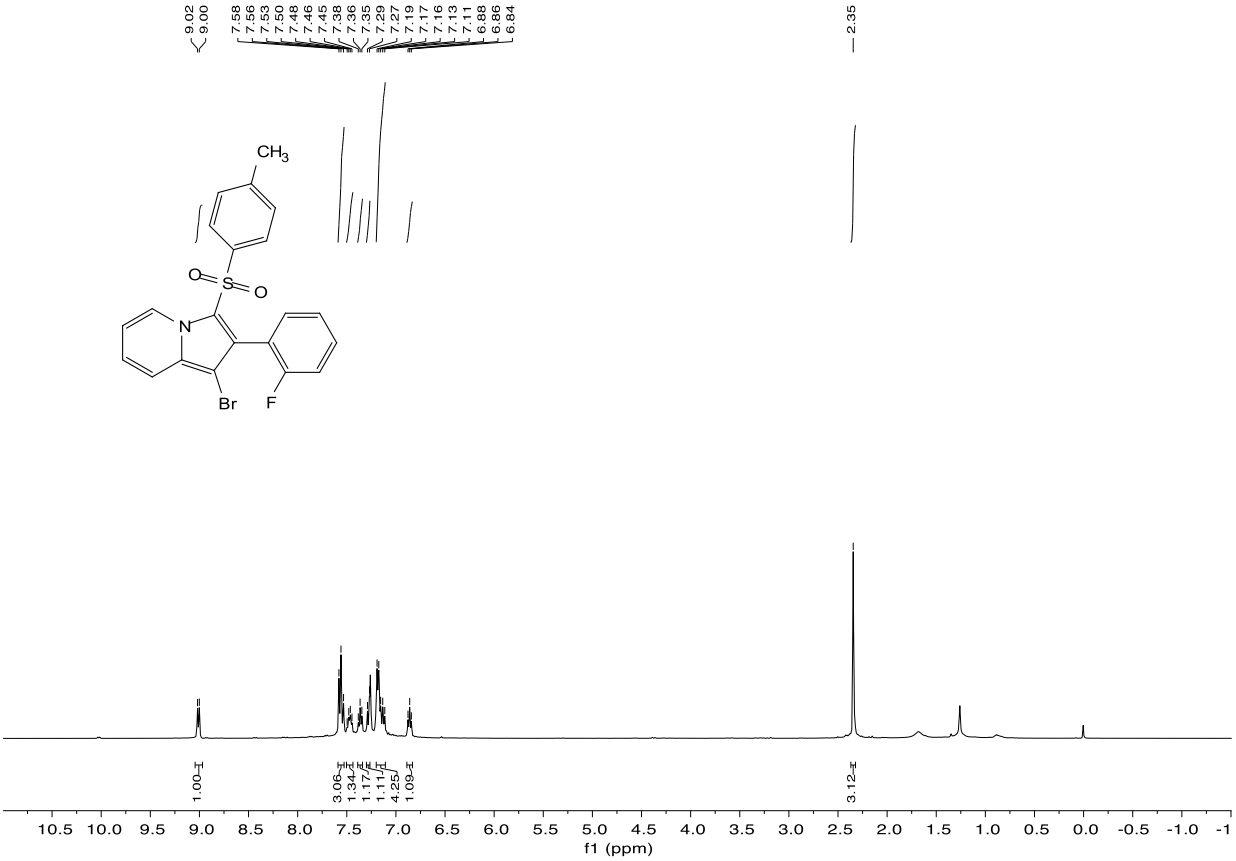
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3e**

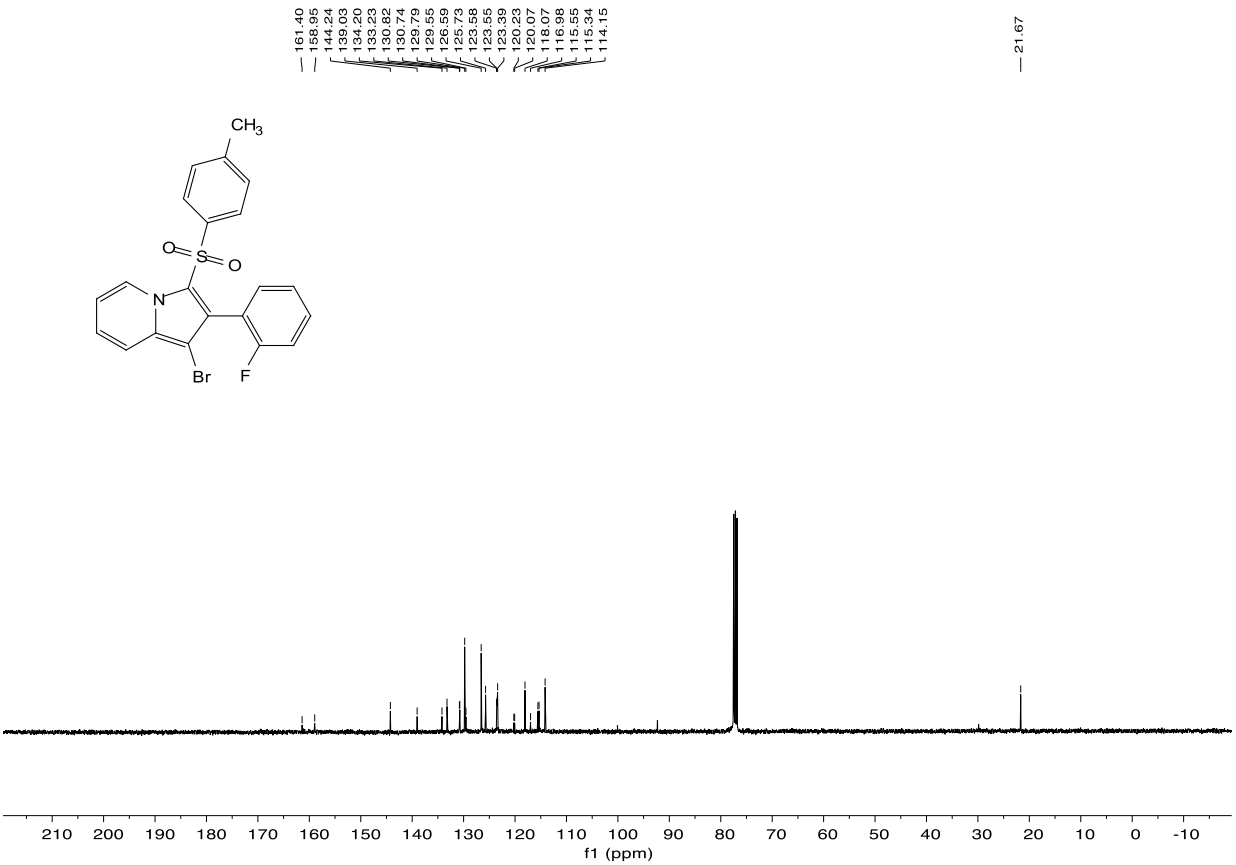


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3f**

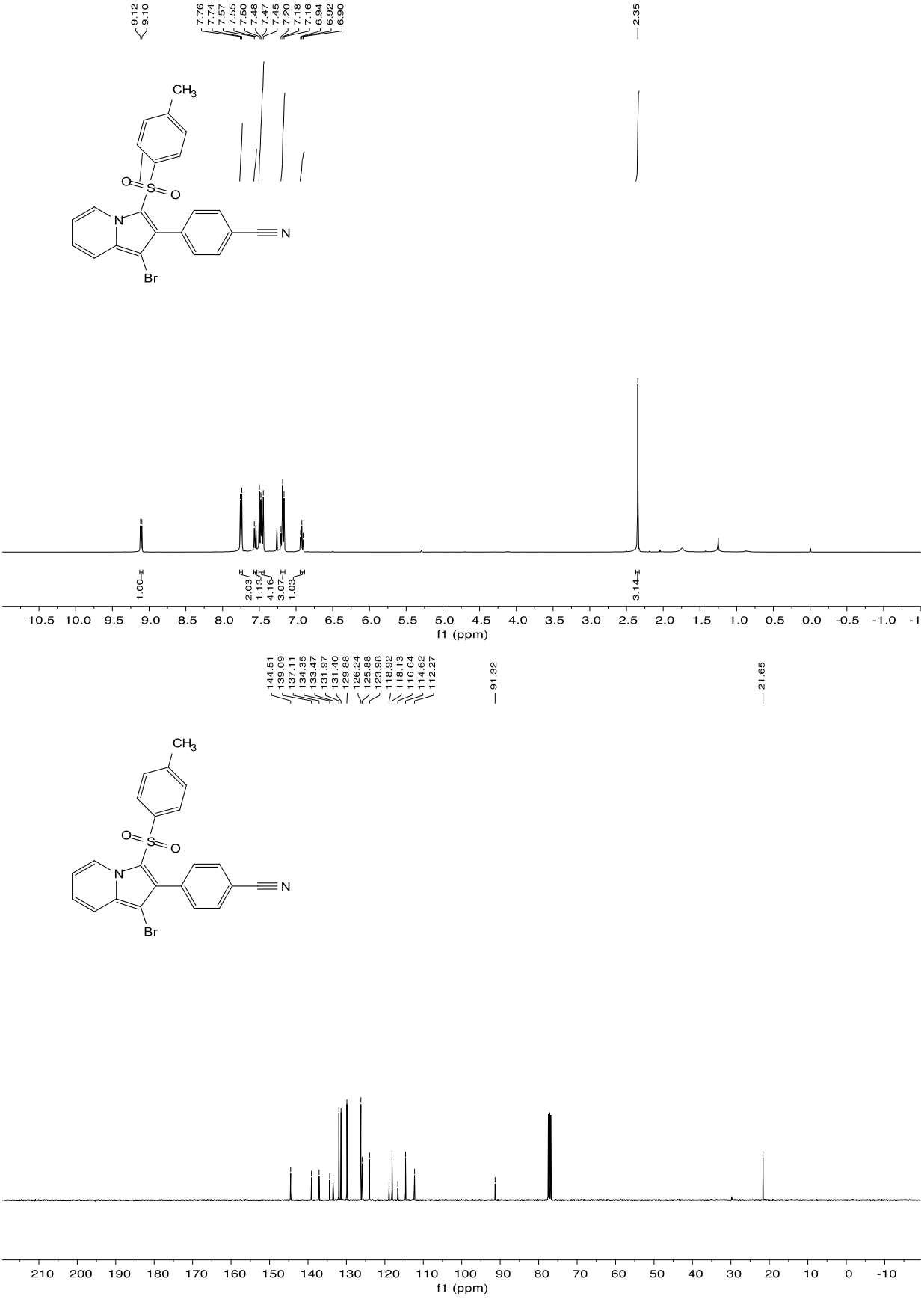


^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3g**

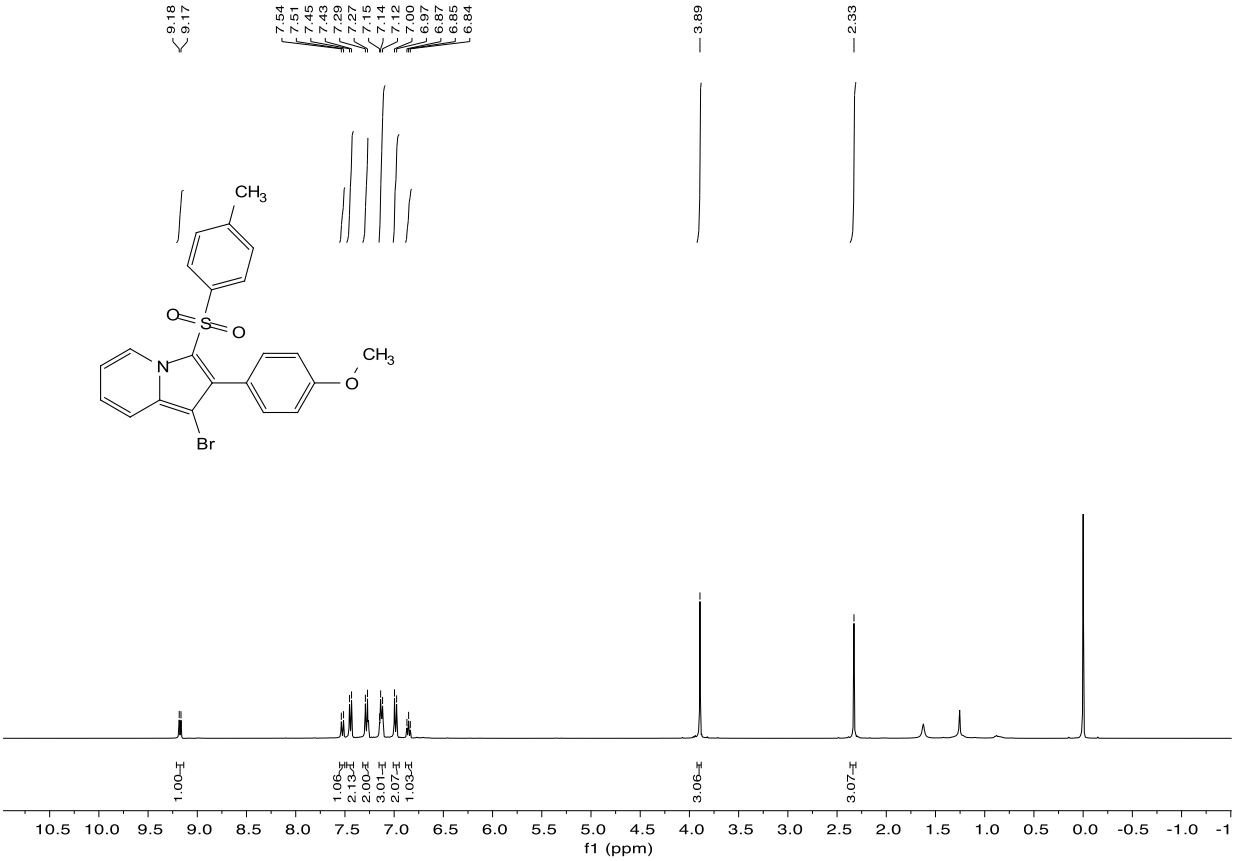


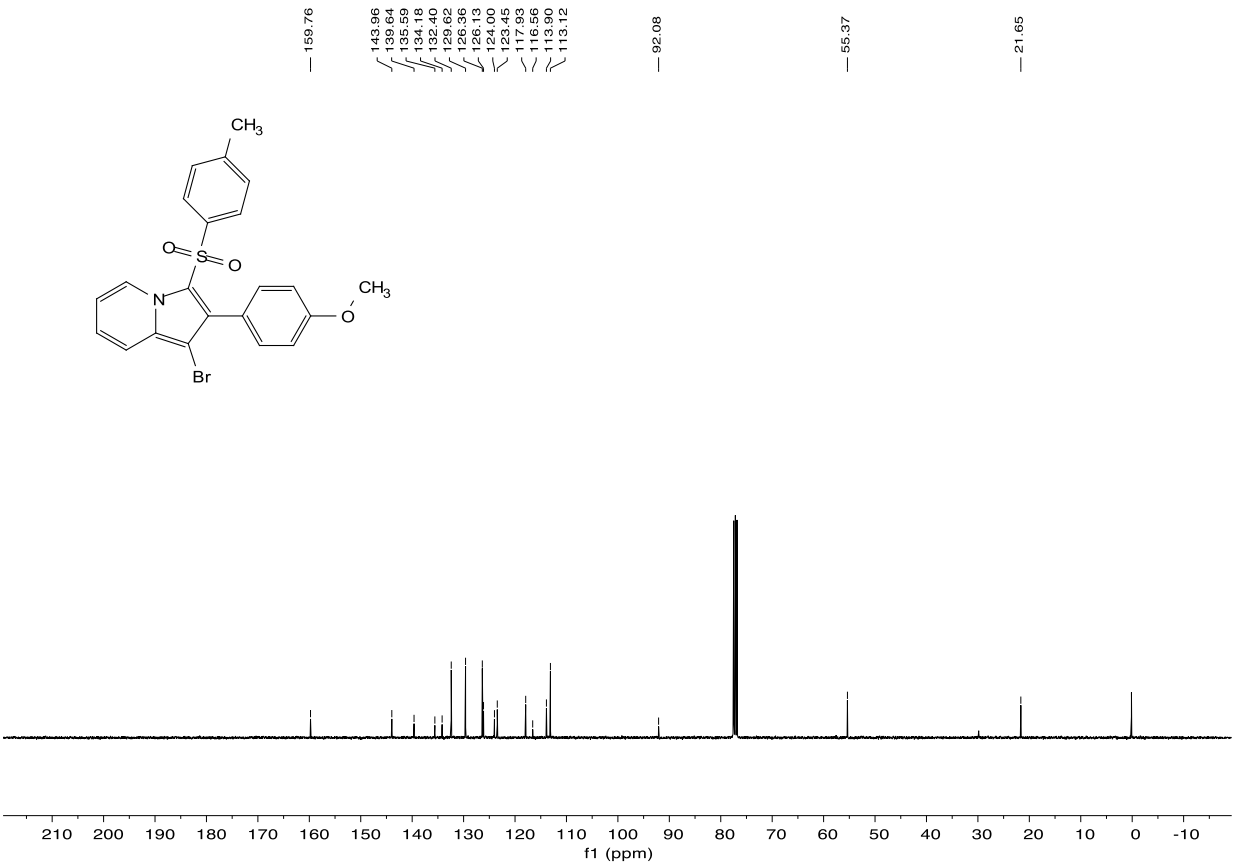


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3h**

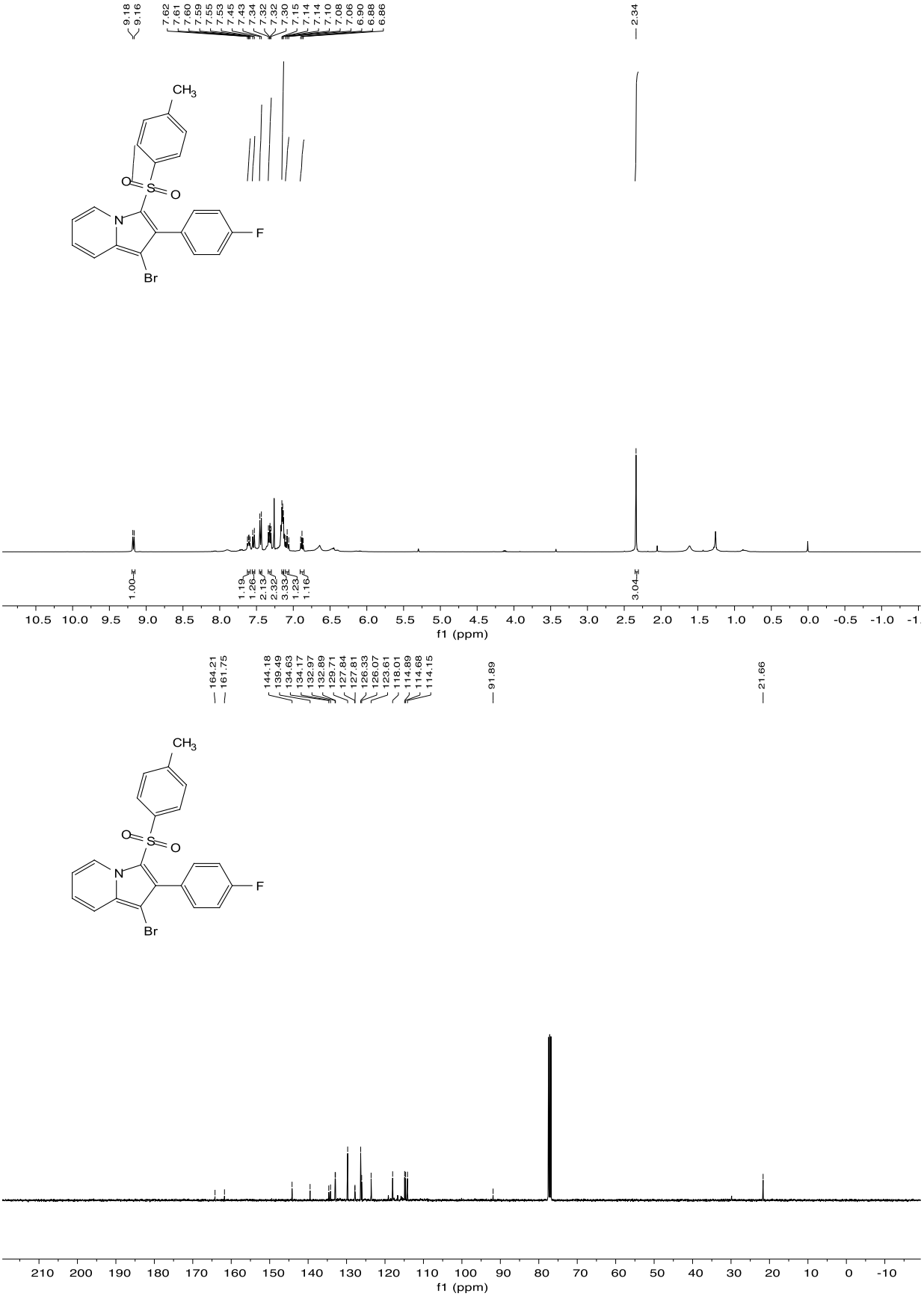


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3i**

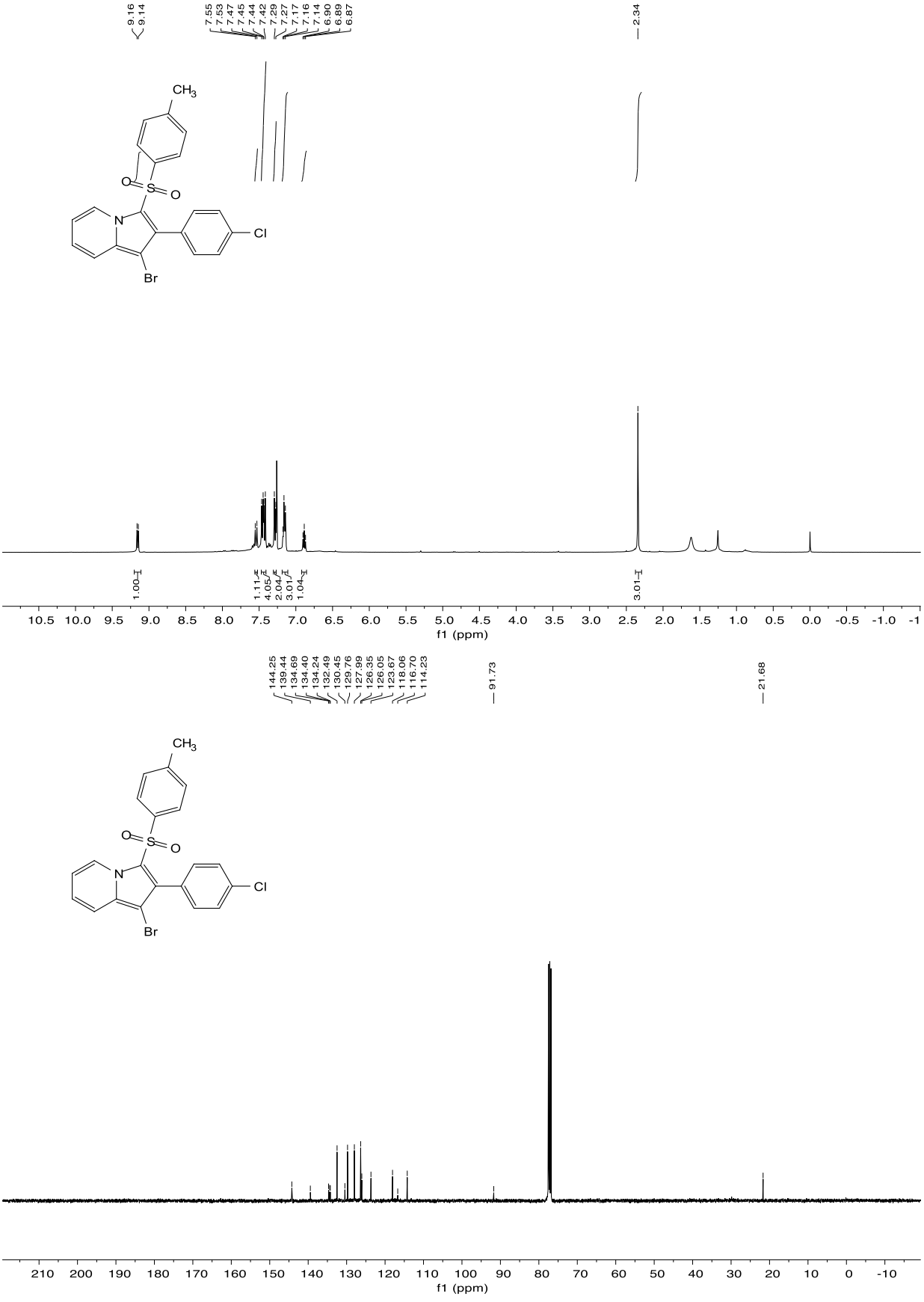




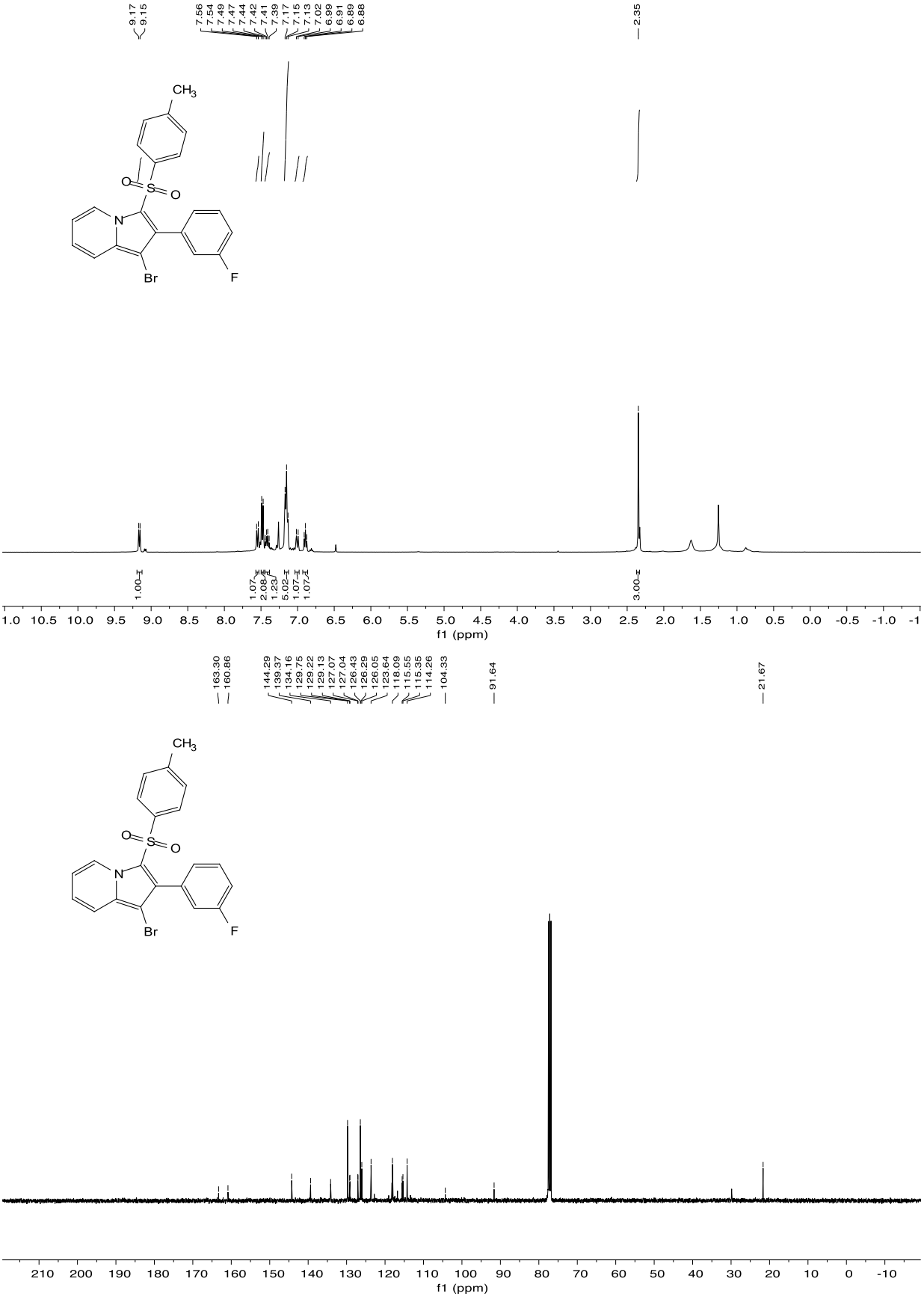
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3j**



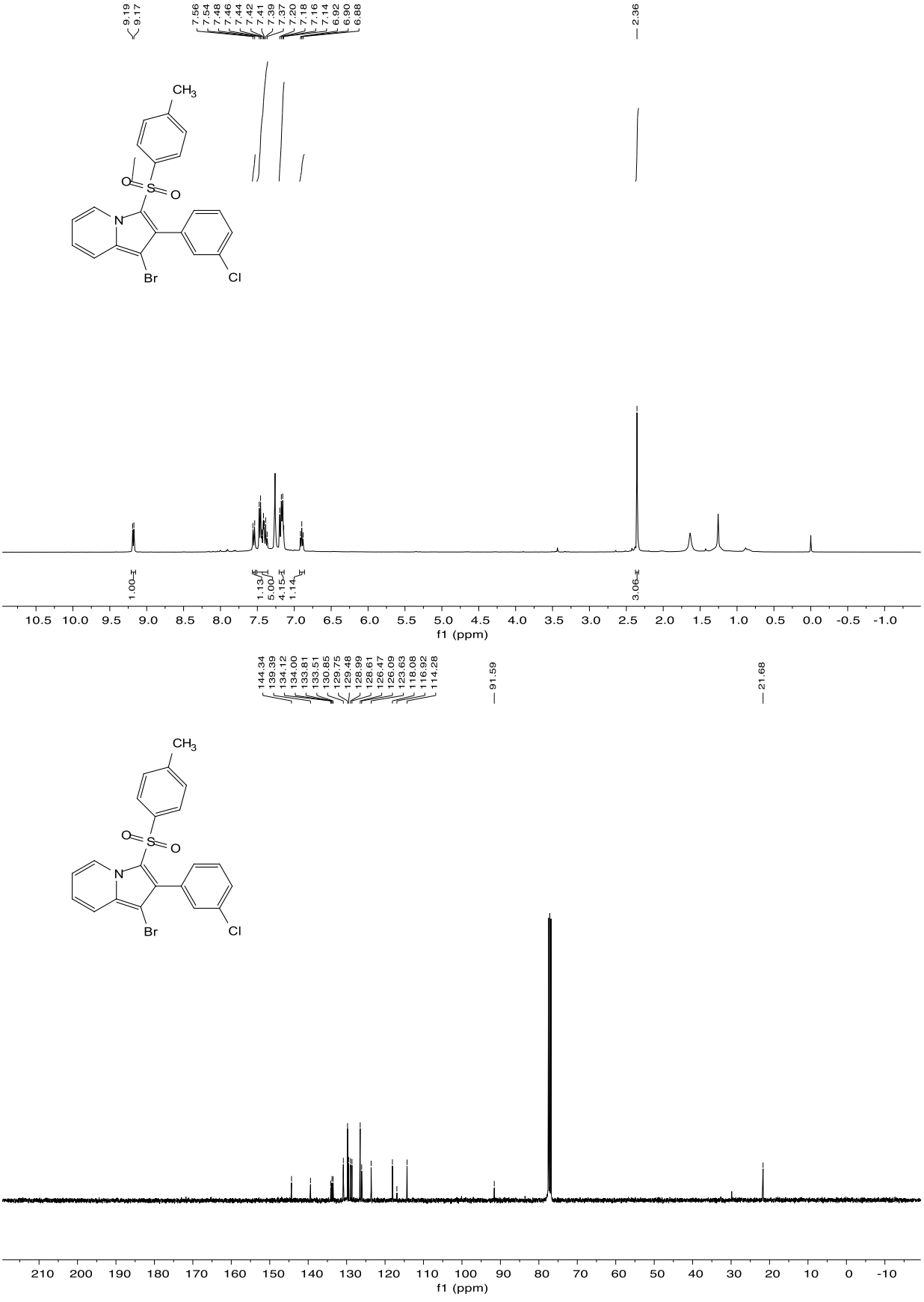
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3k**



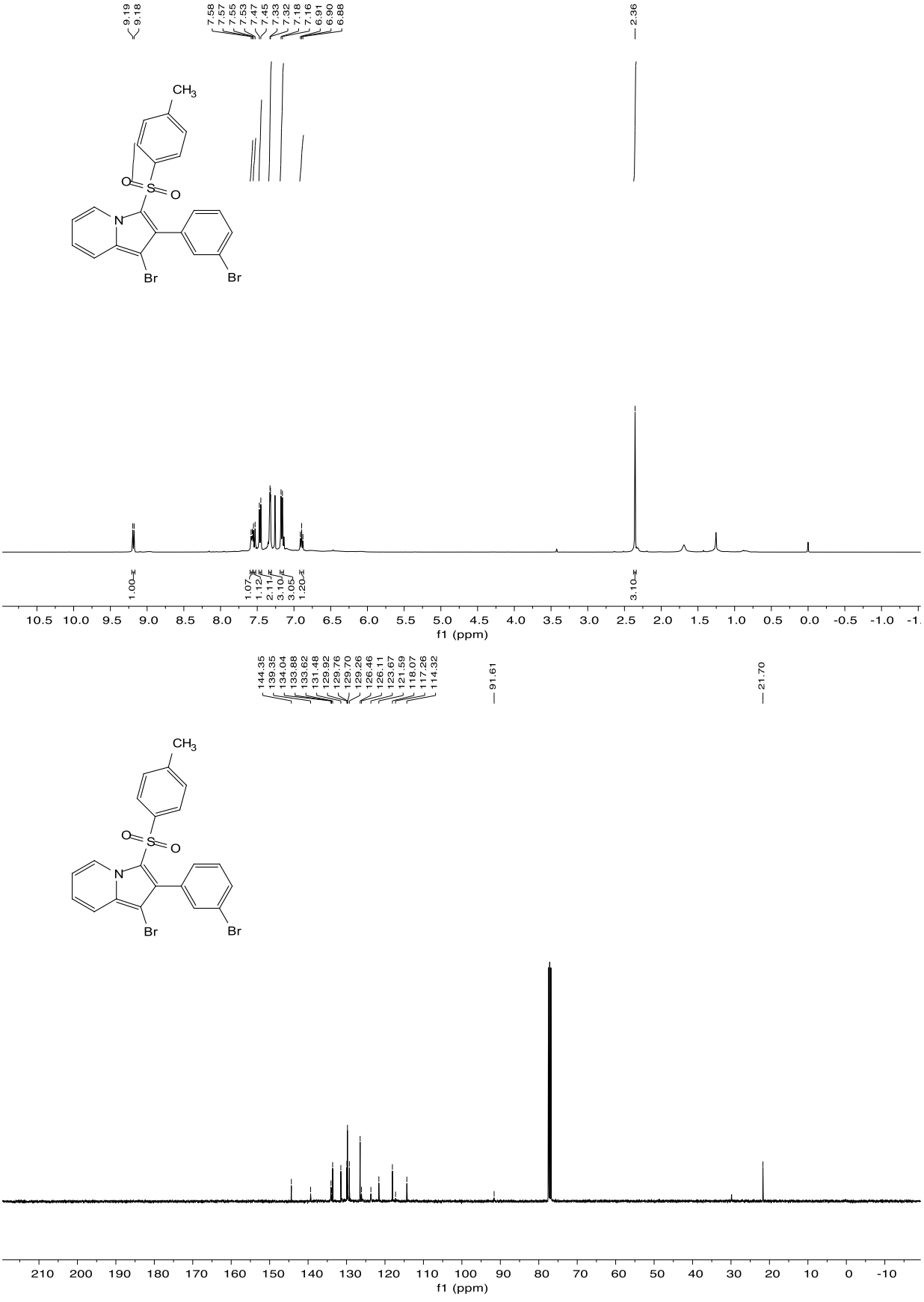
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3l**



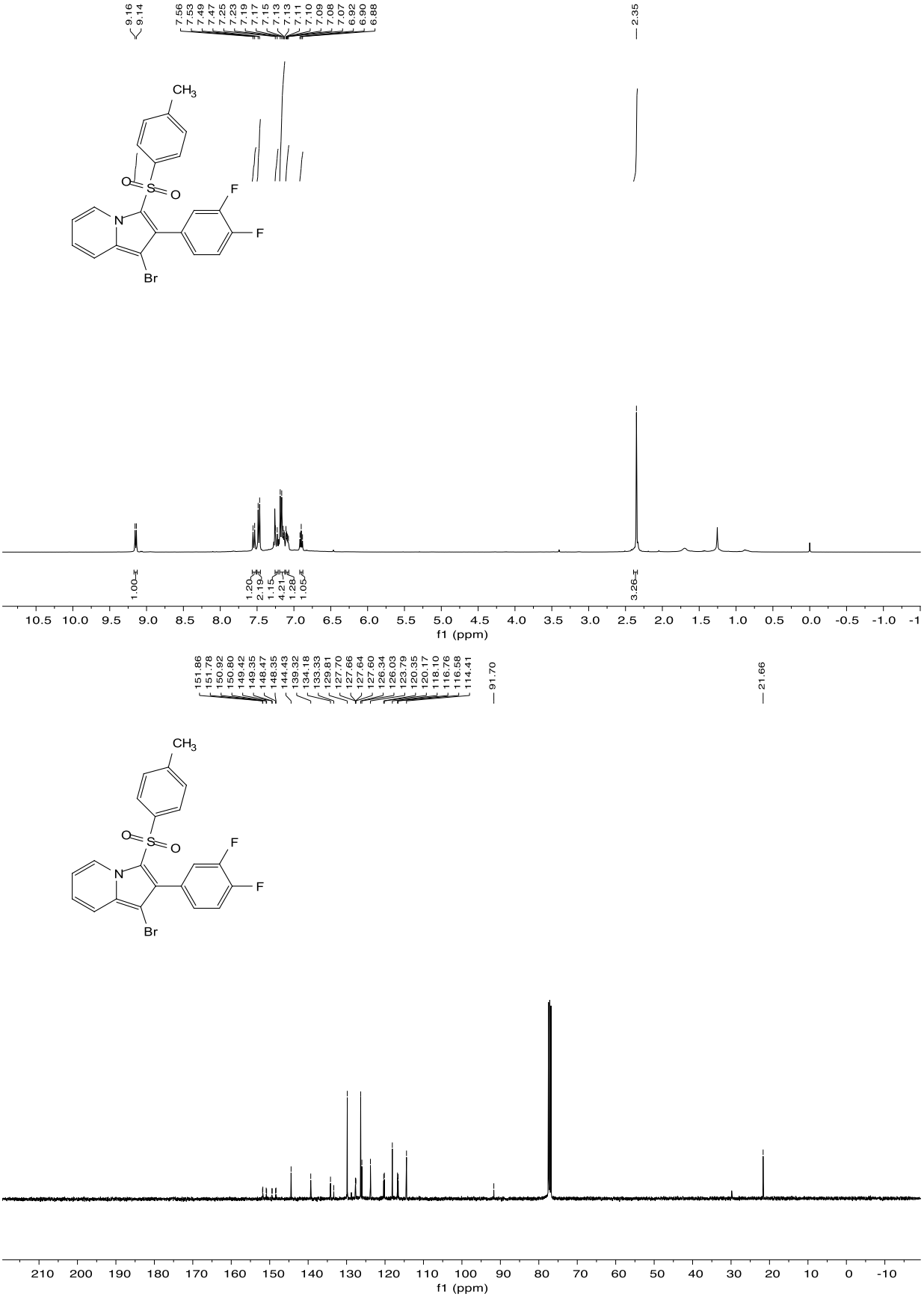
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3m**



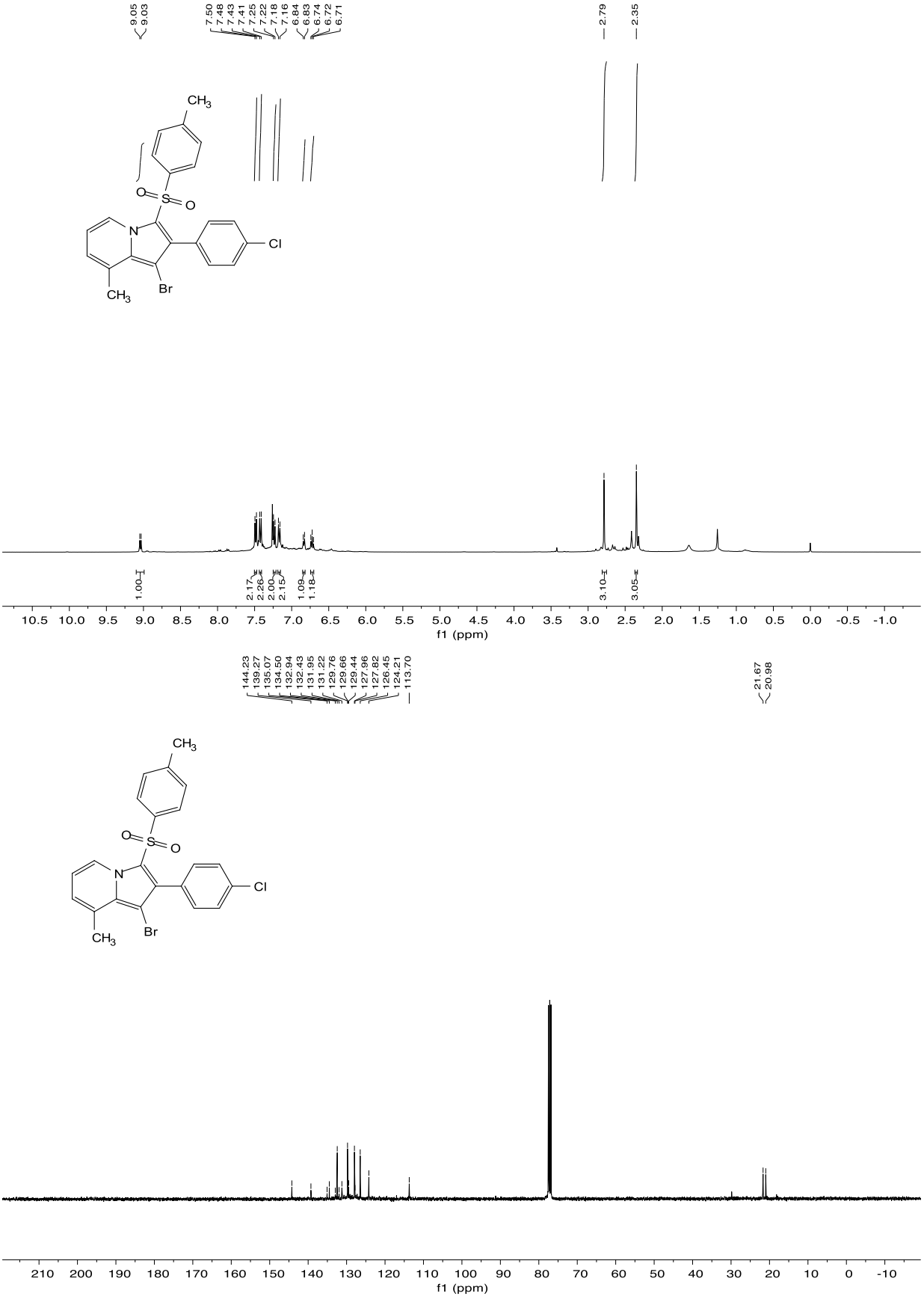
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3n**



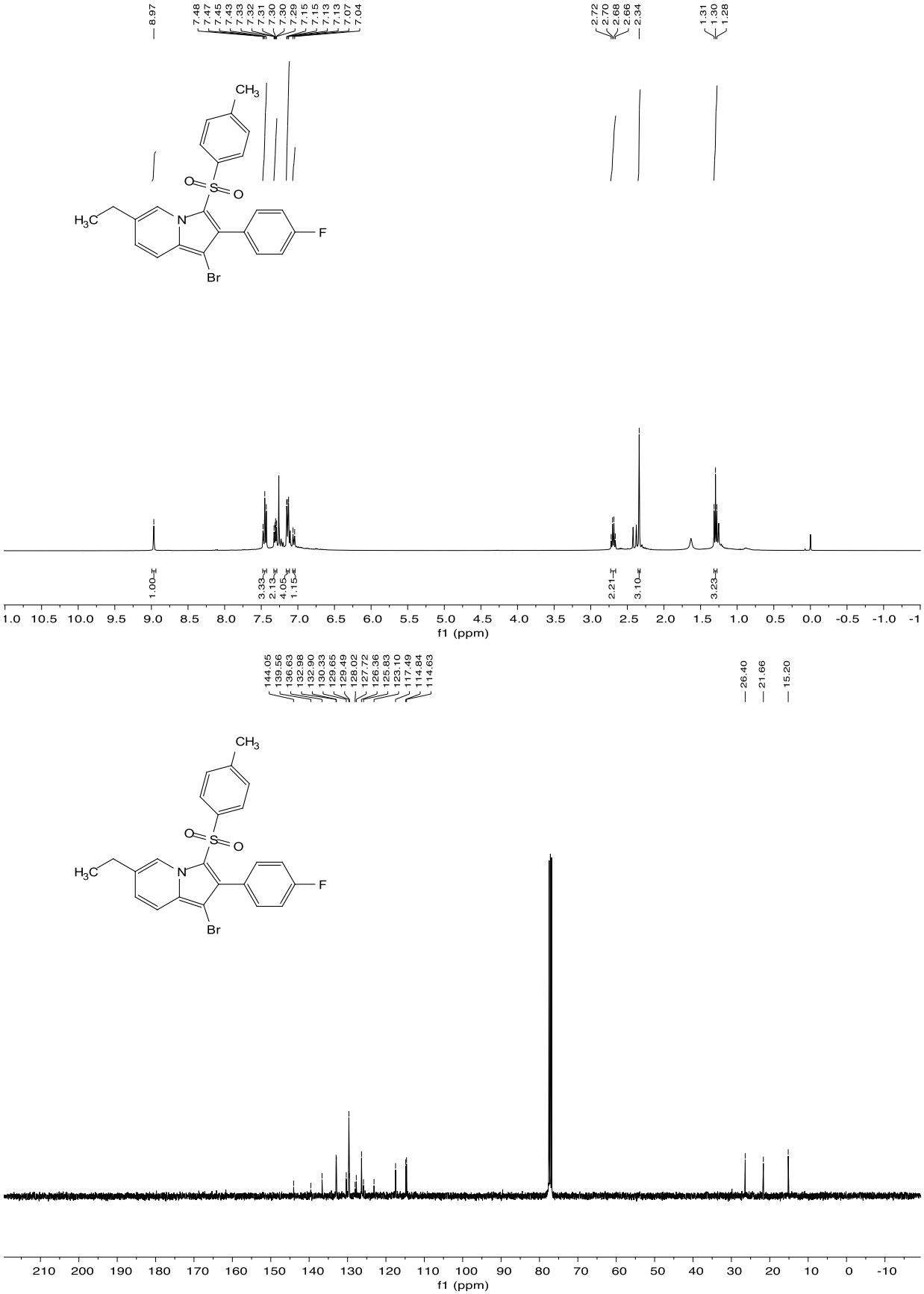
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3o**



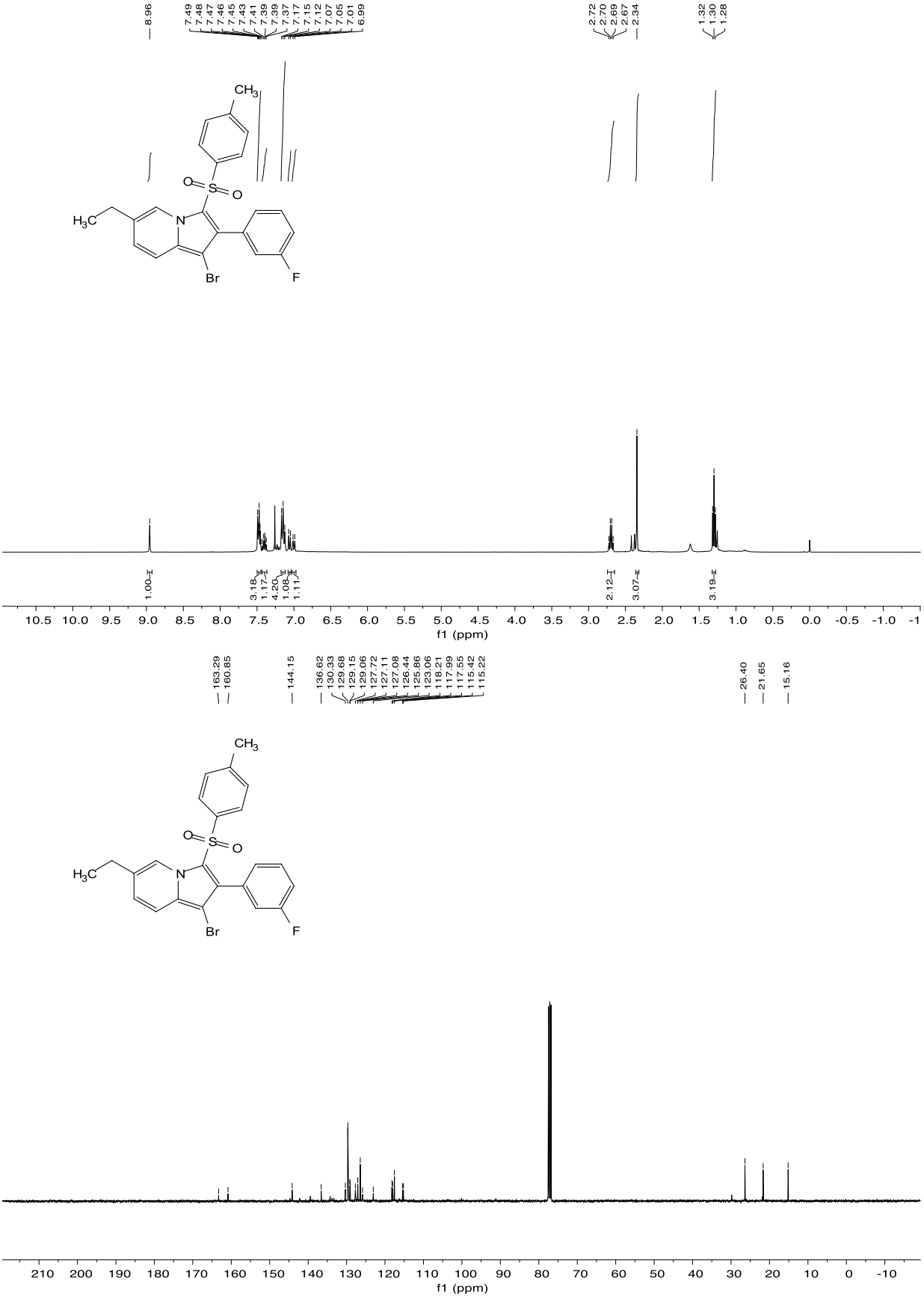
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3p**



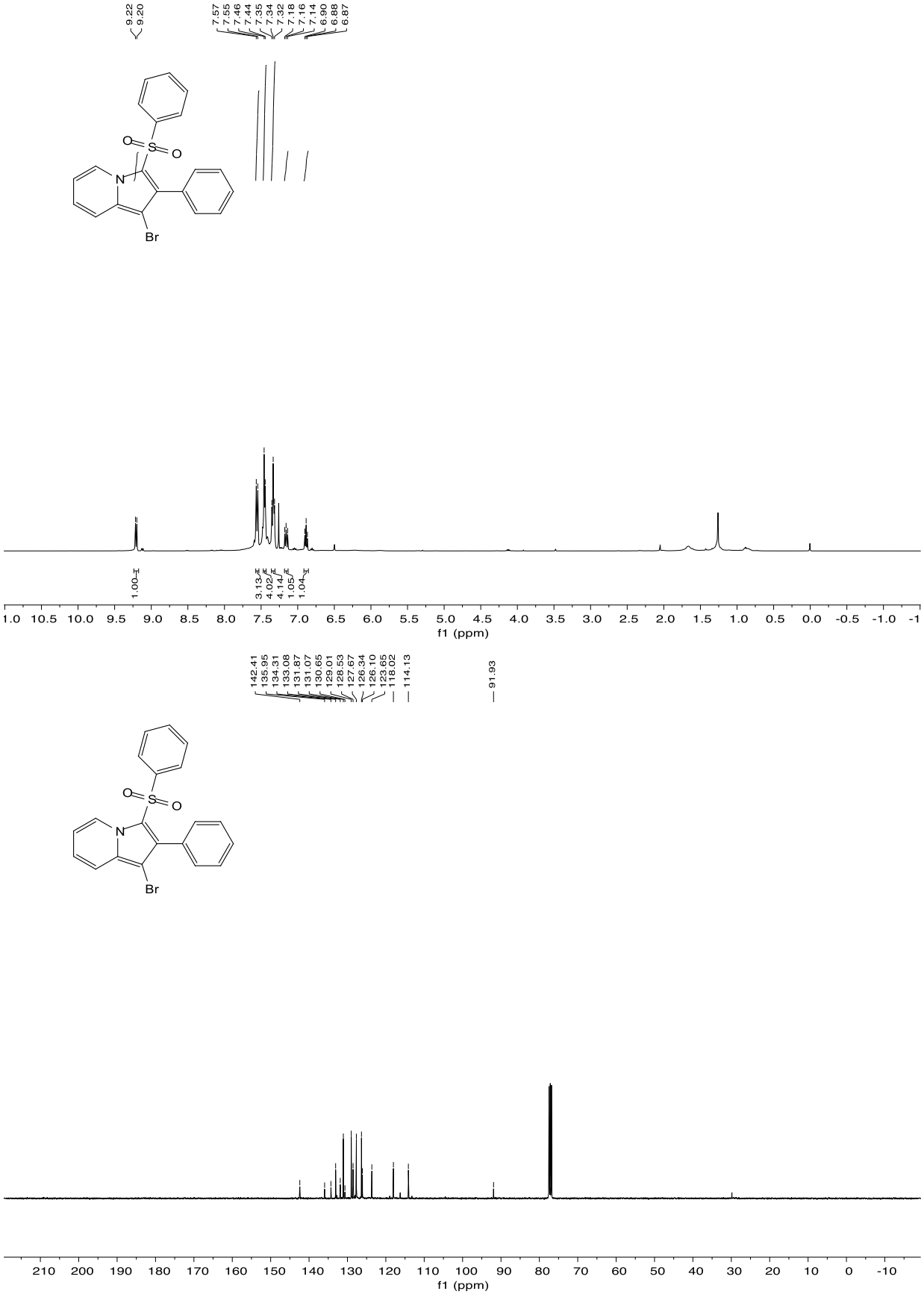
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3q**



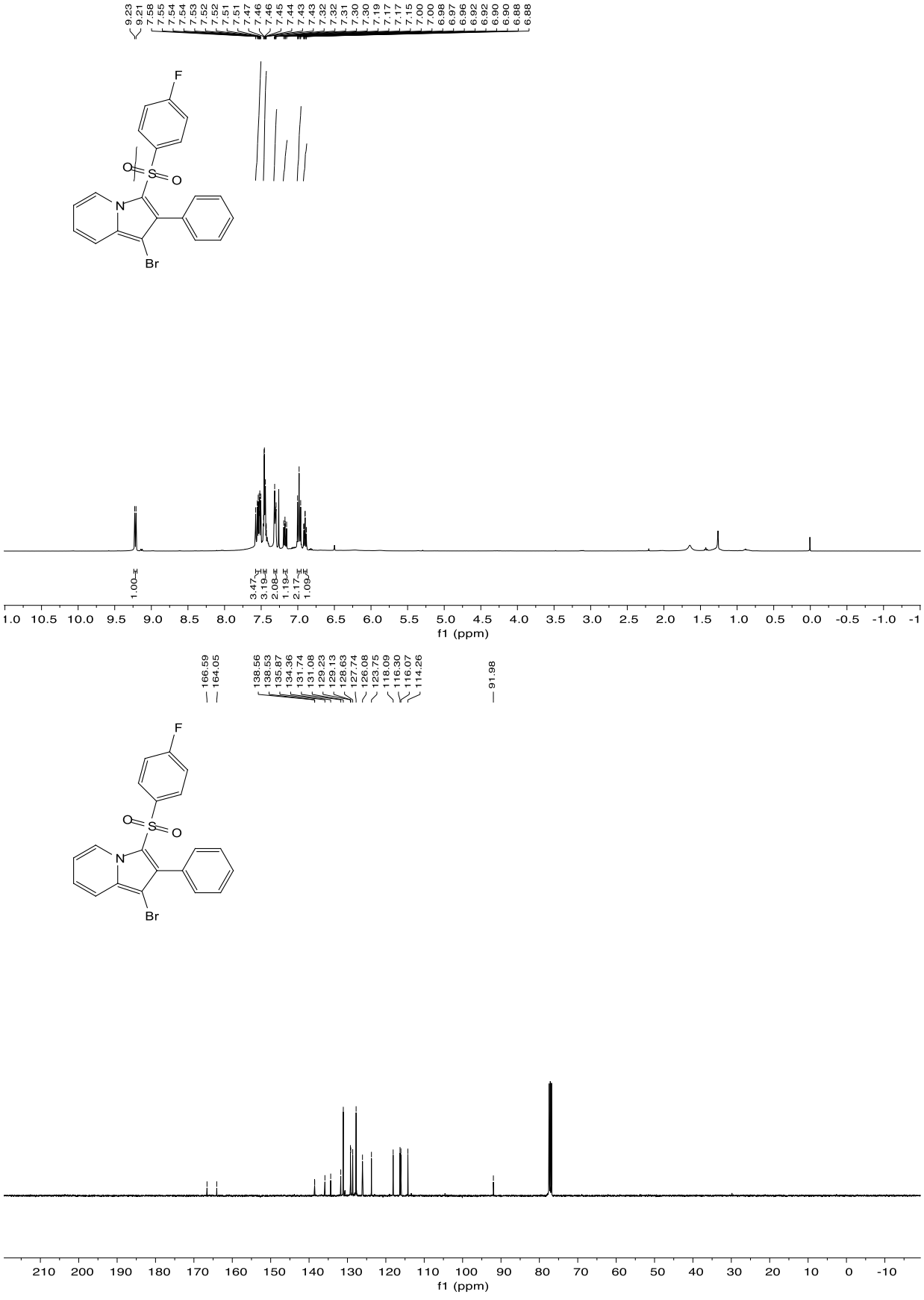
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3r**



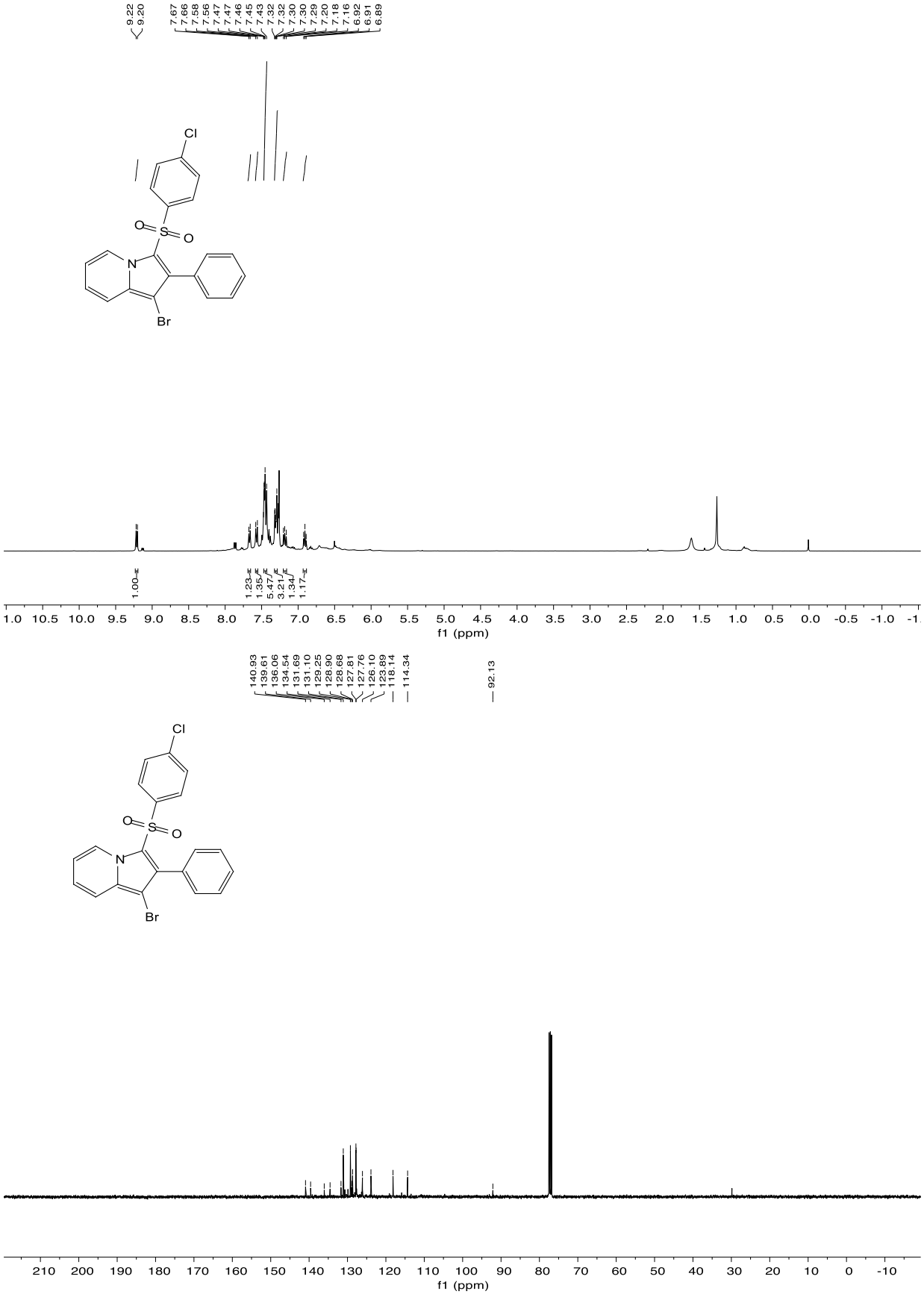
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4a**



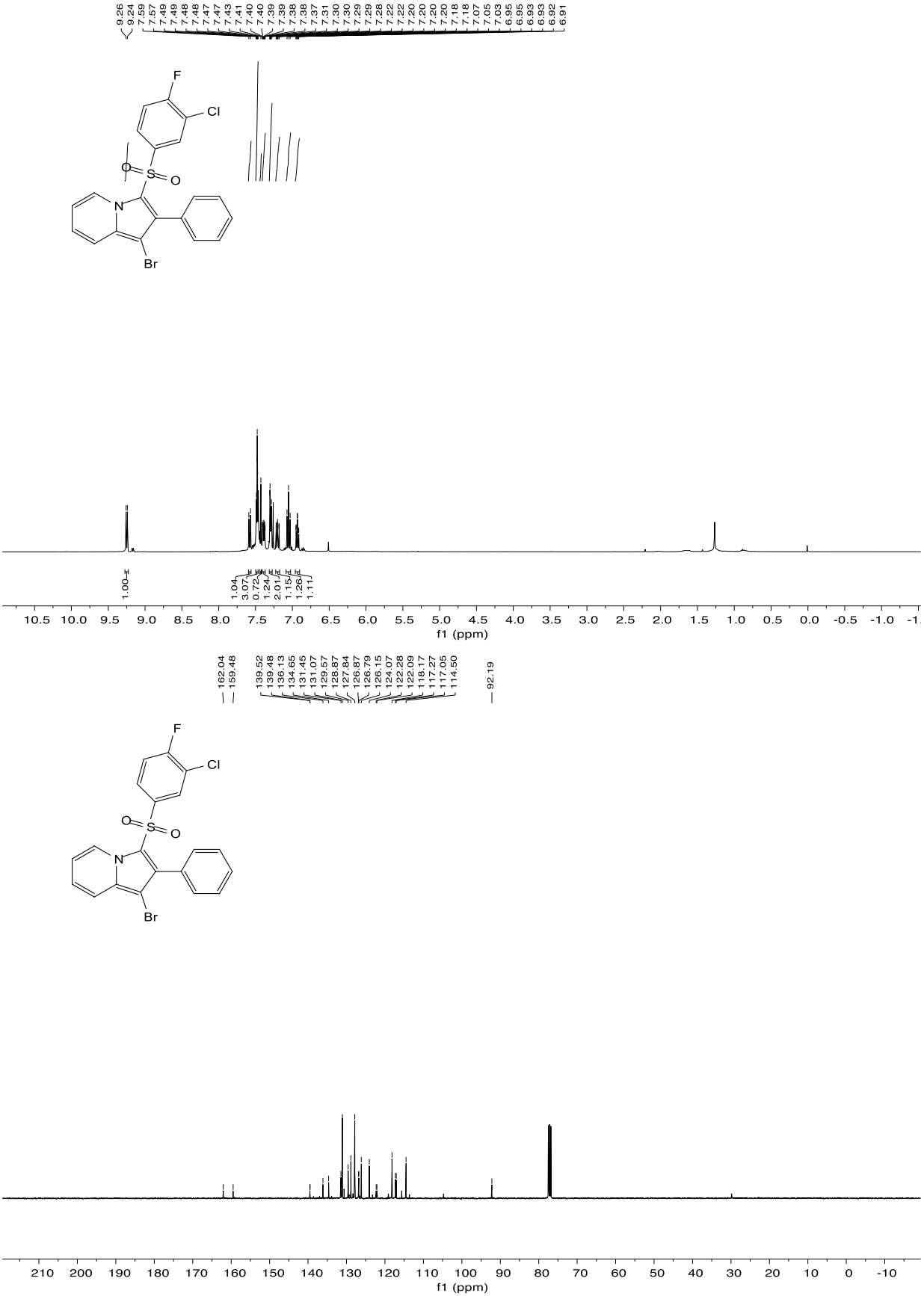
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4b**



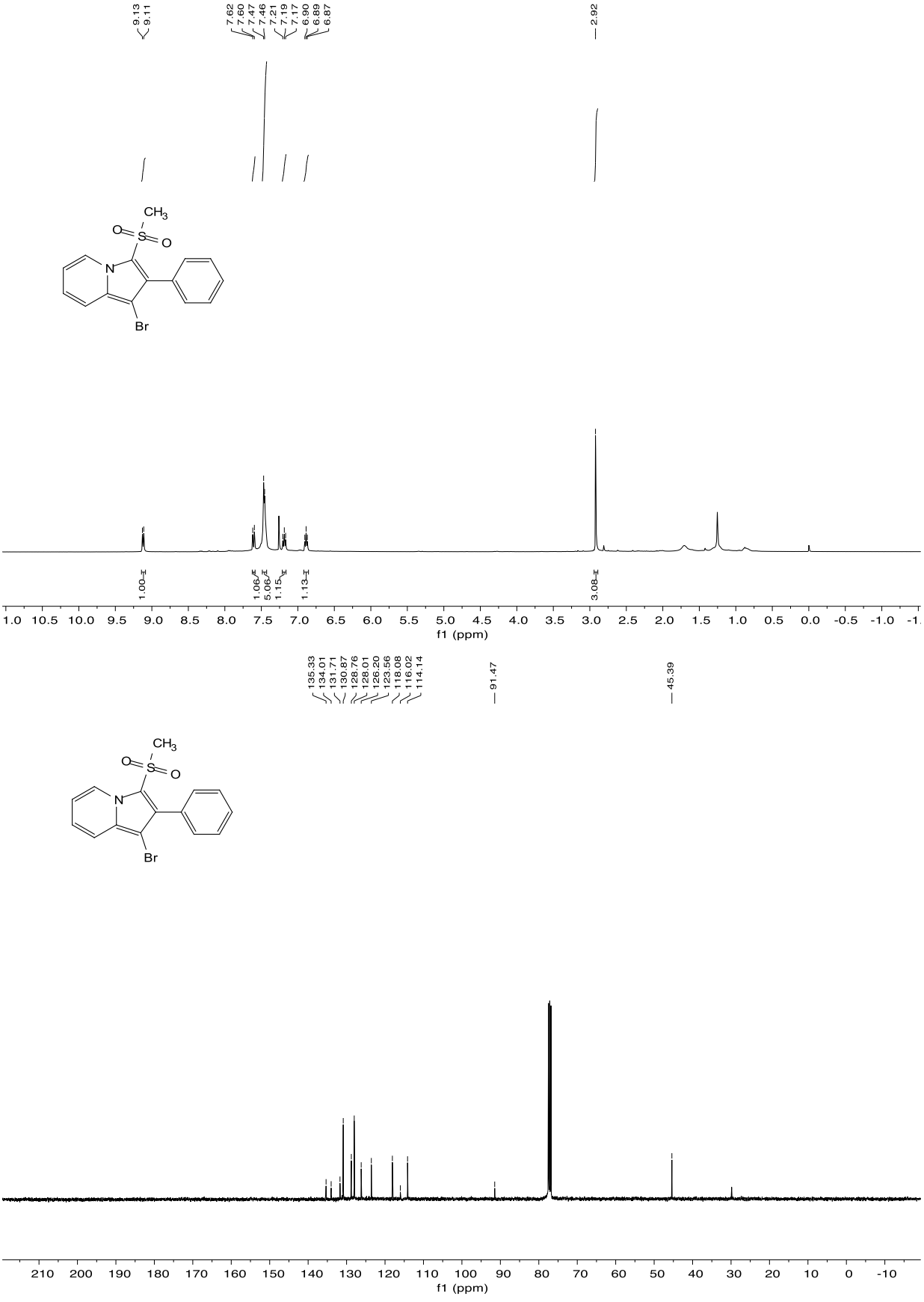
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4c**



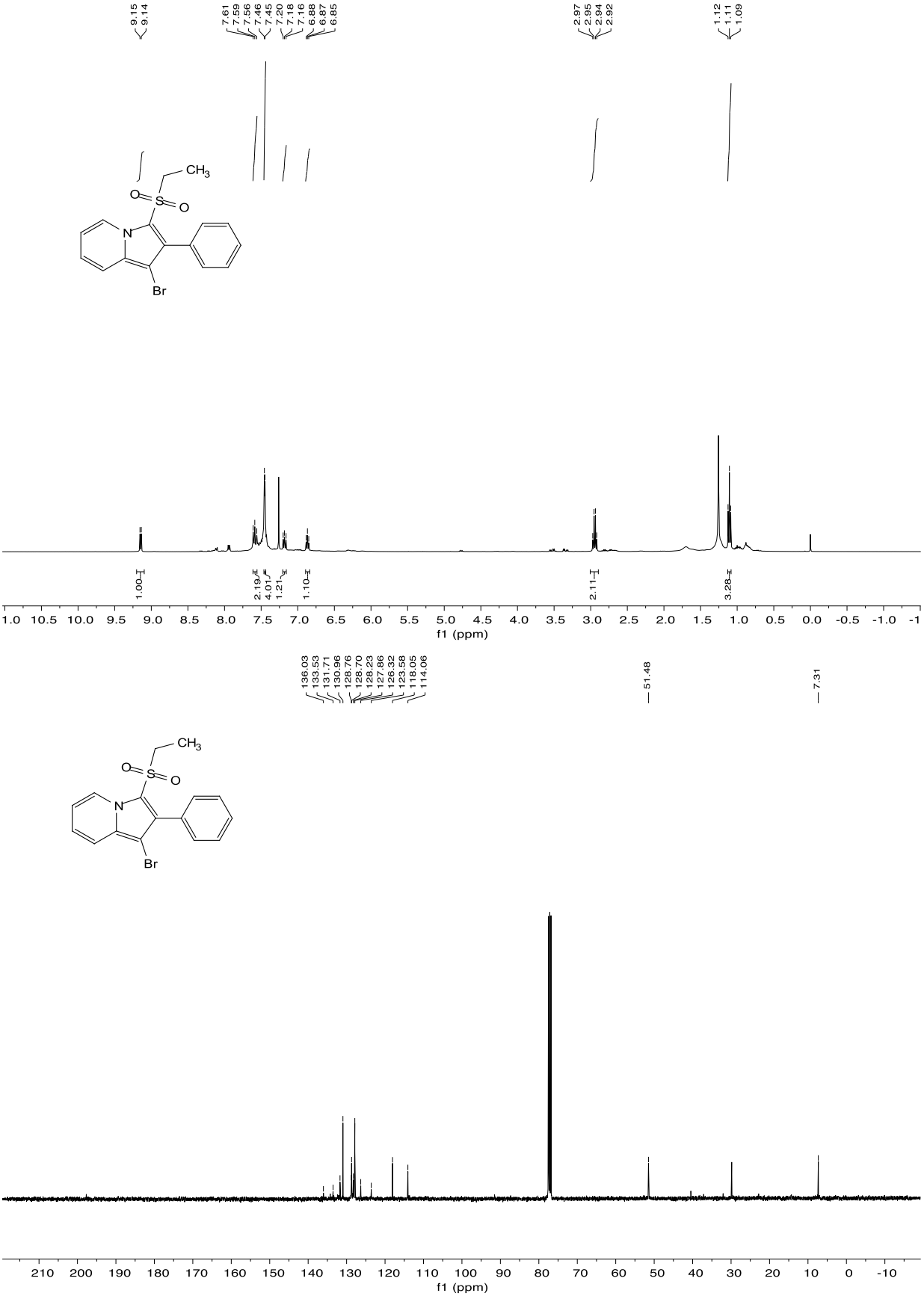
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4d**



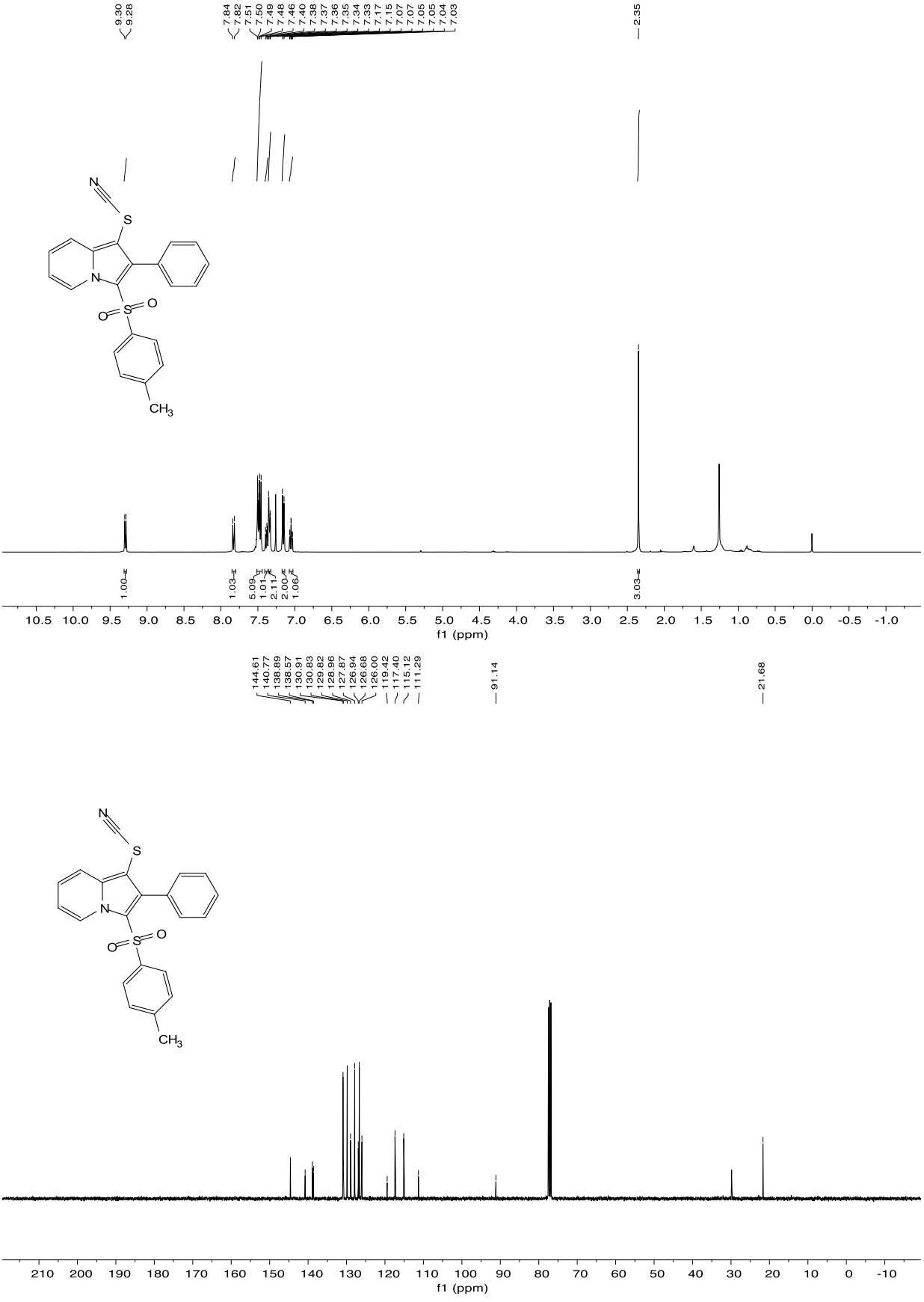
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4e**



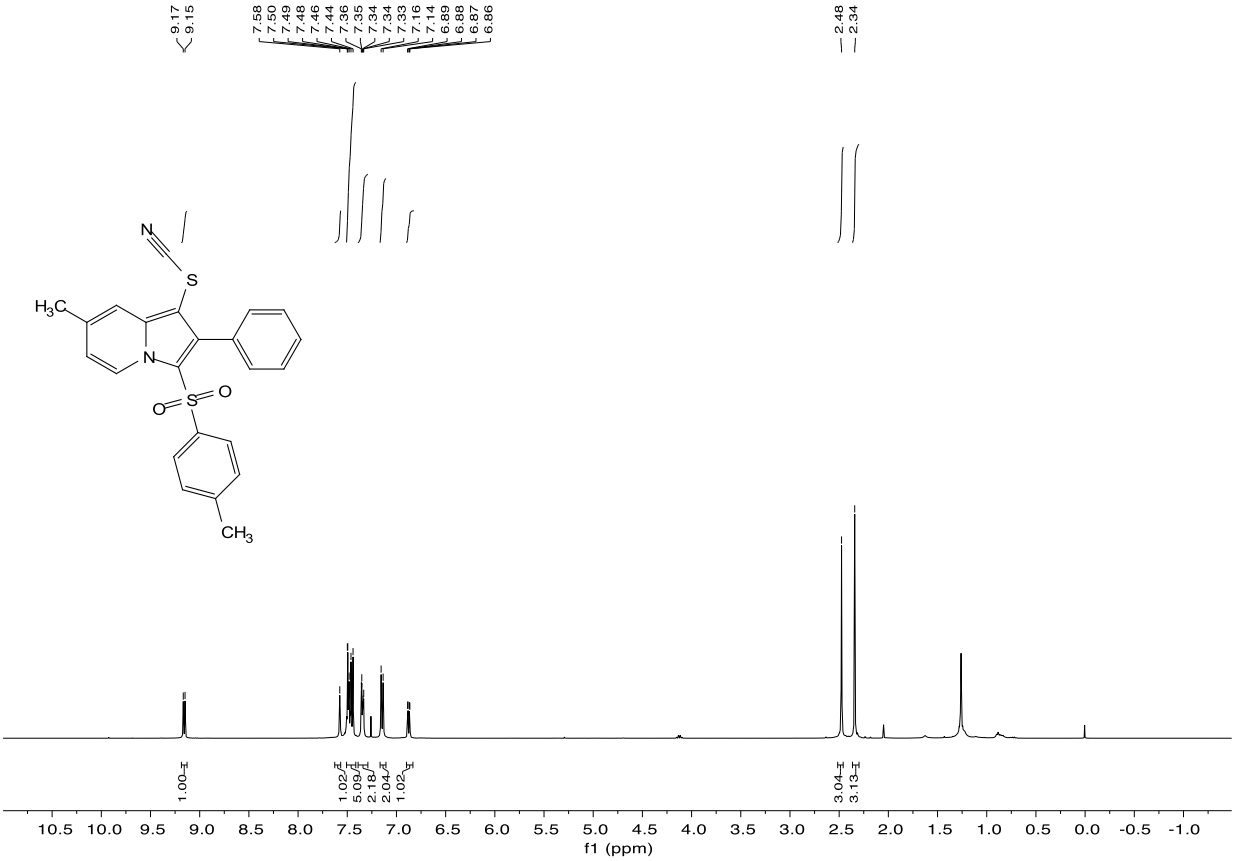
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4f**

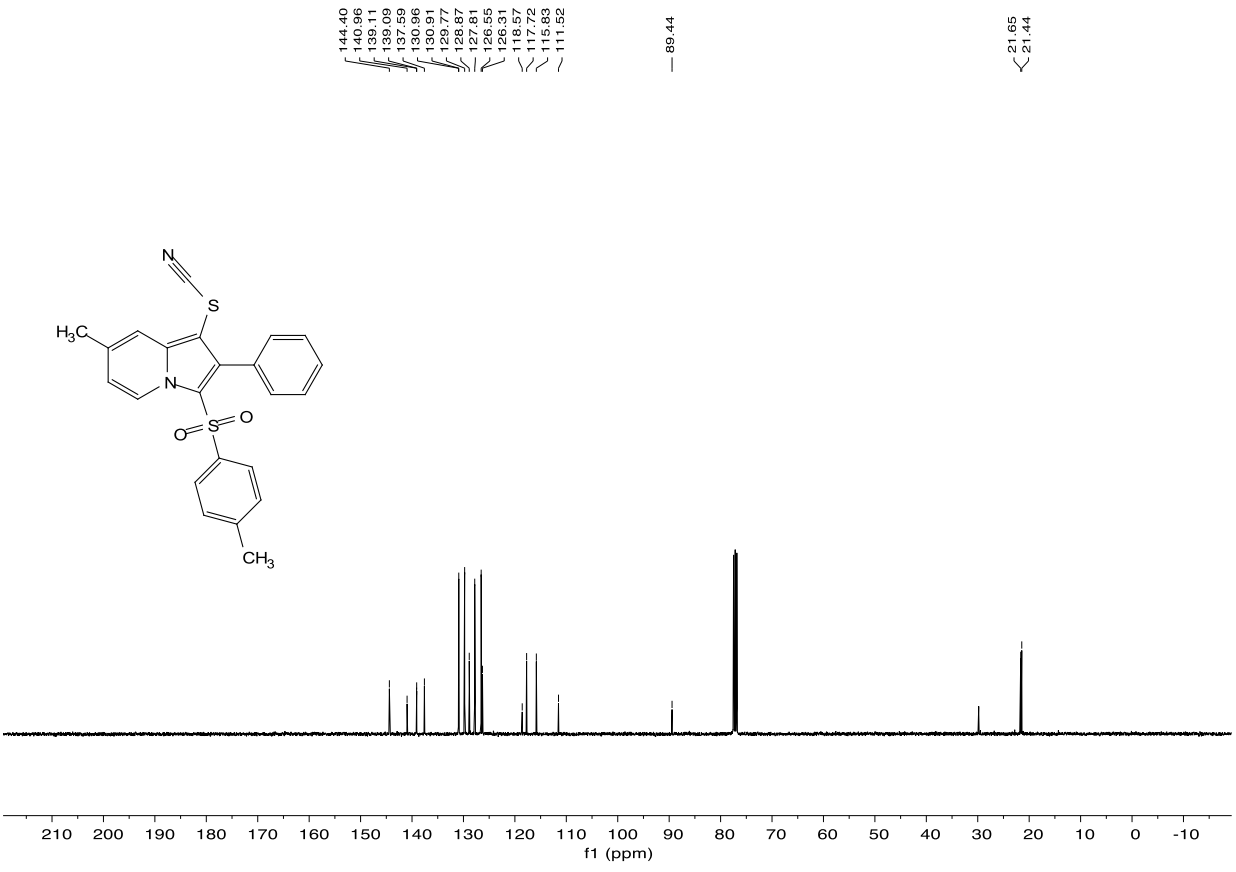


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6a**

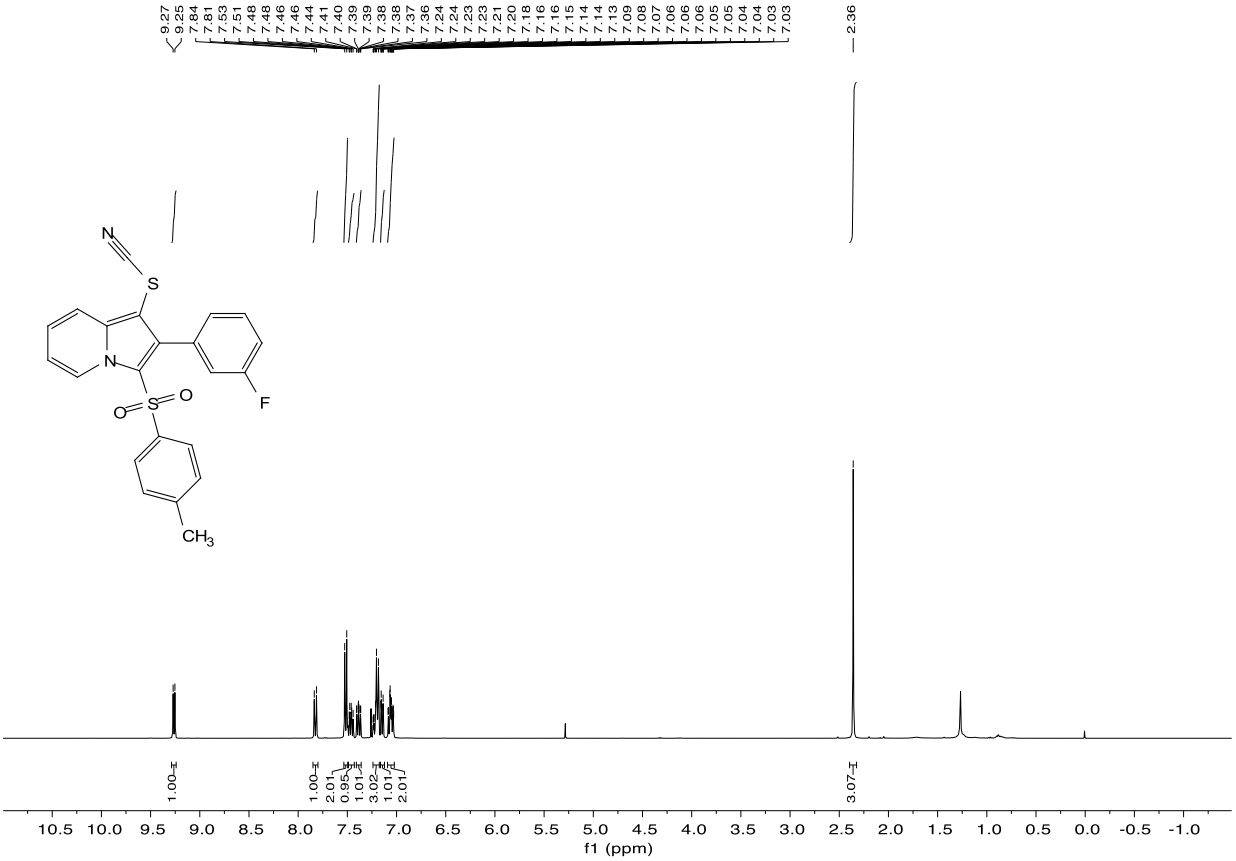


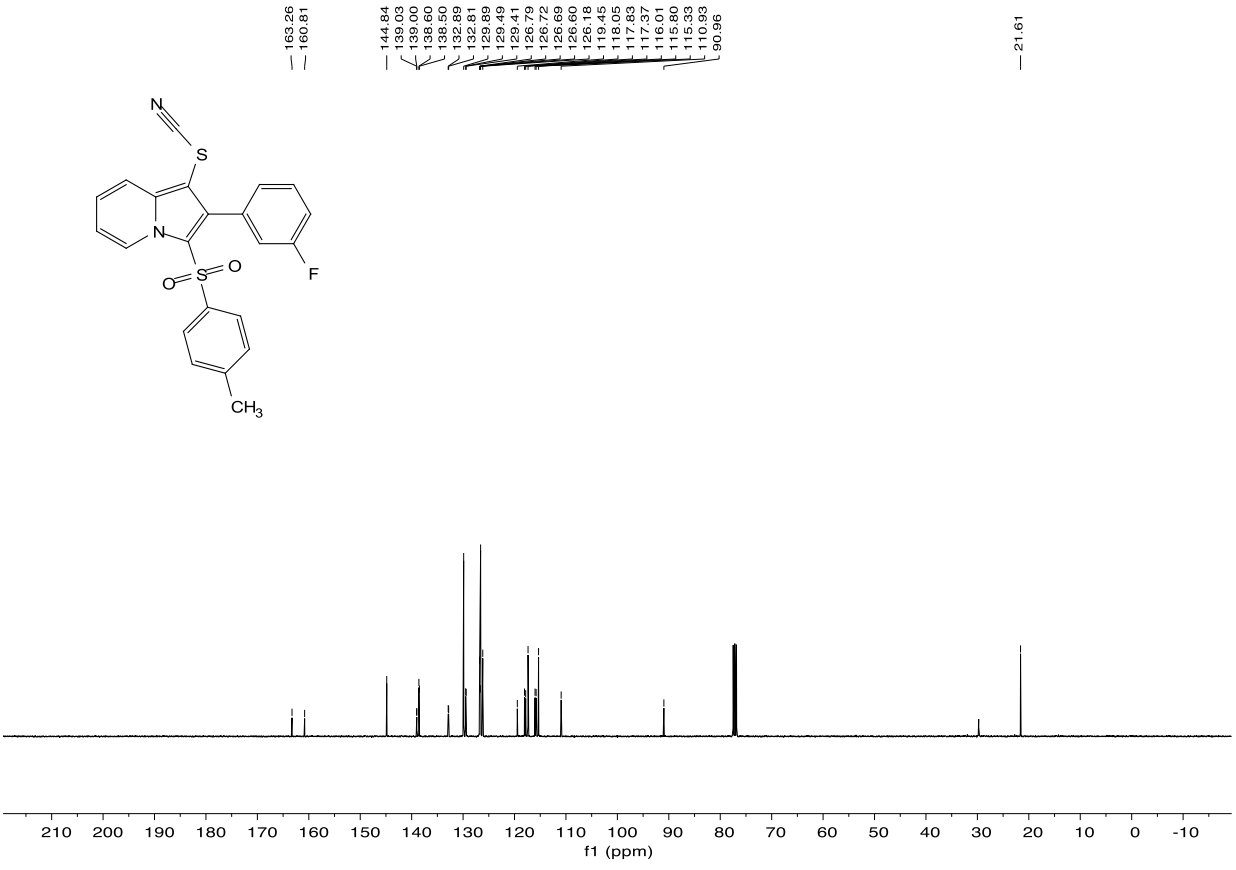
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6b**



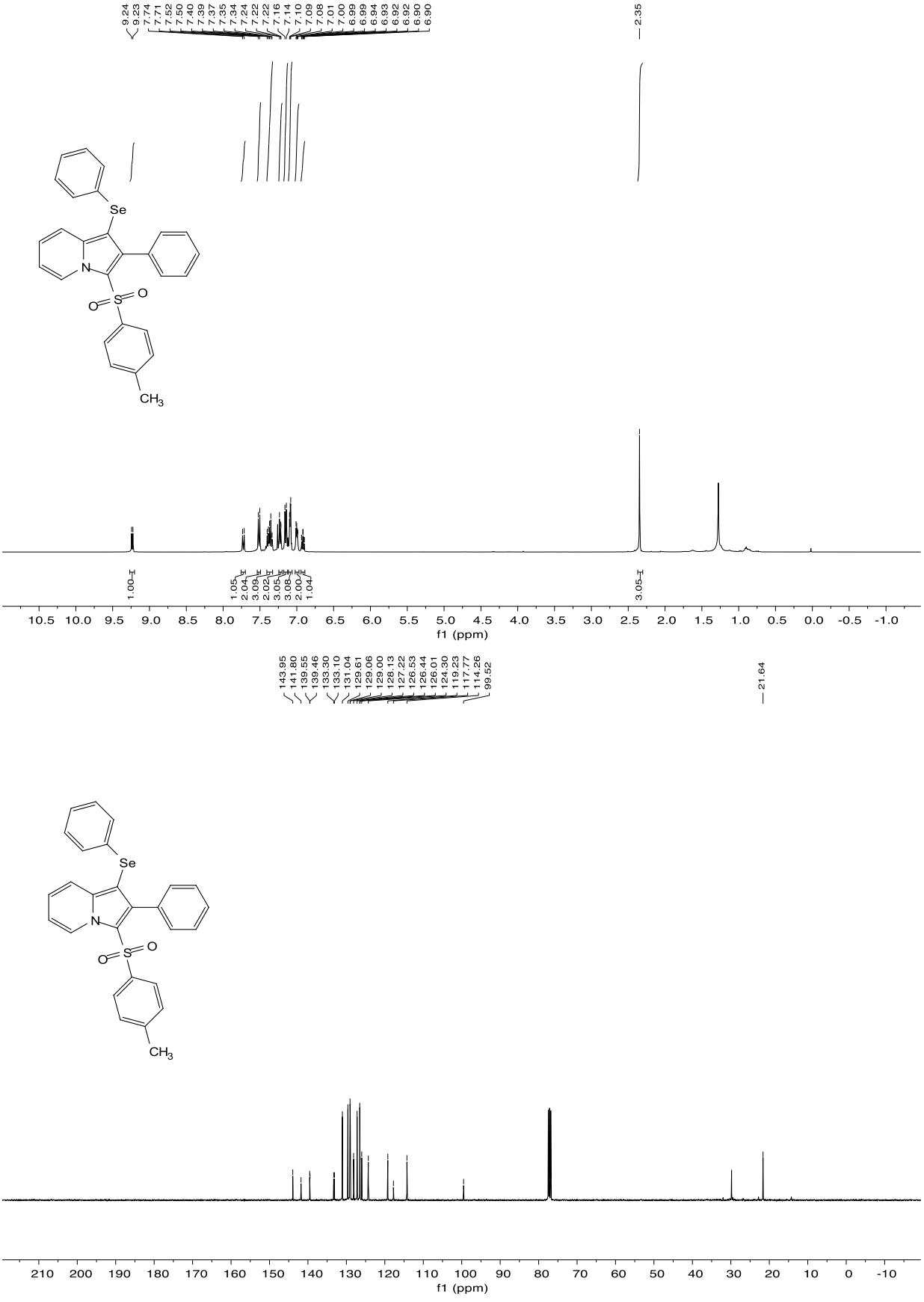


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6c**

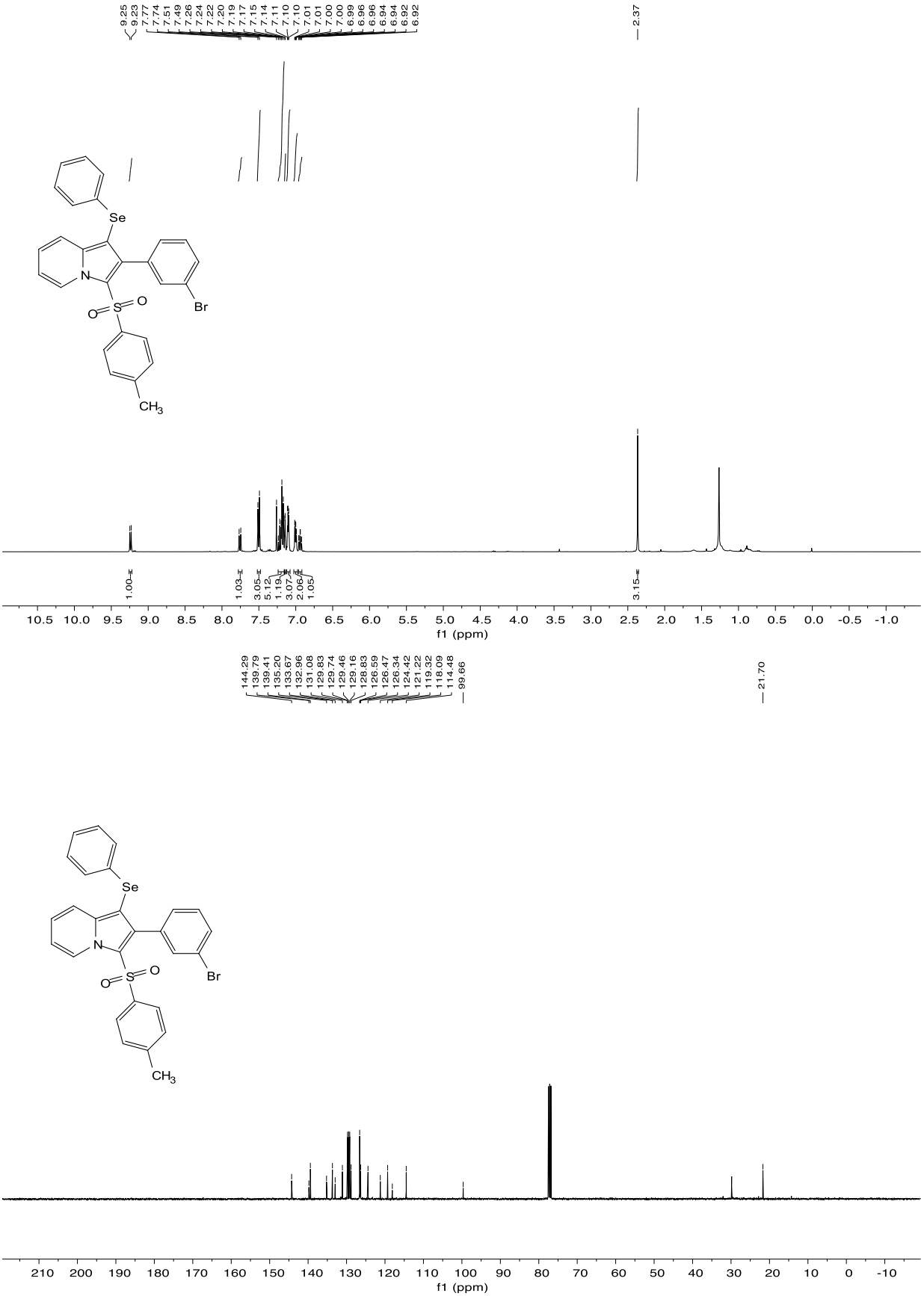




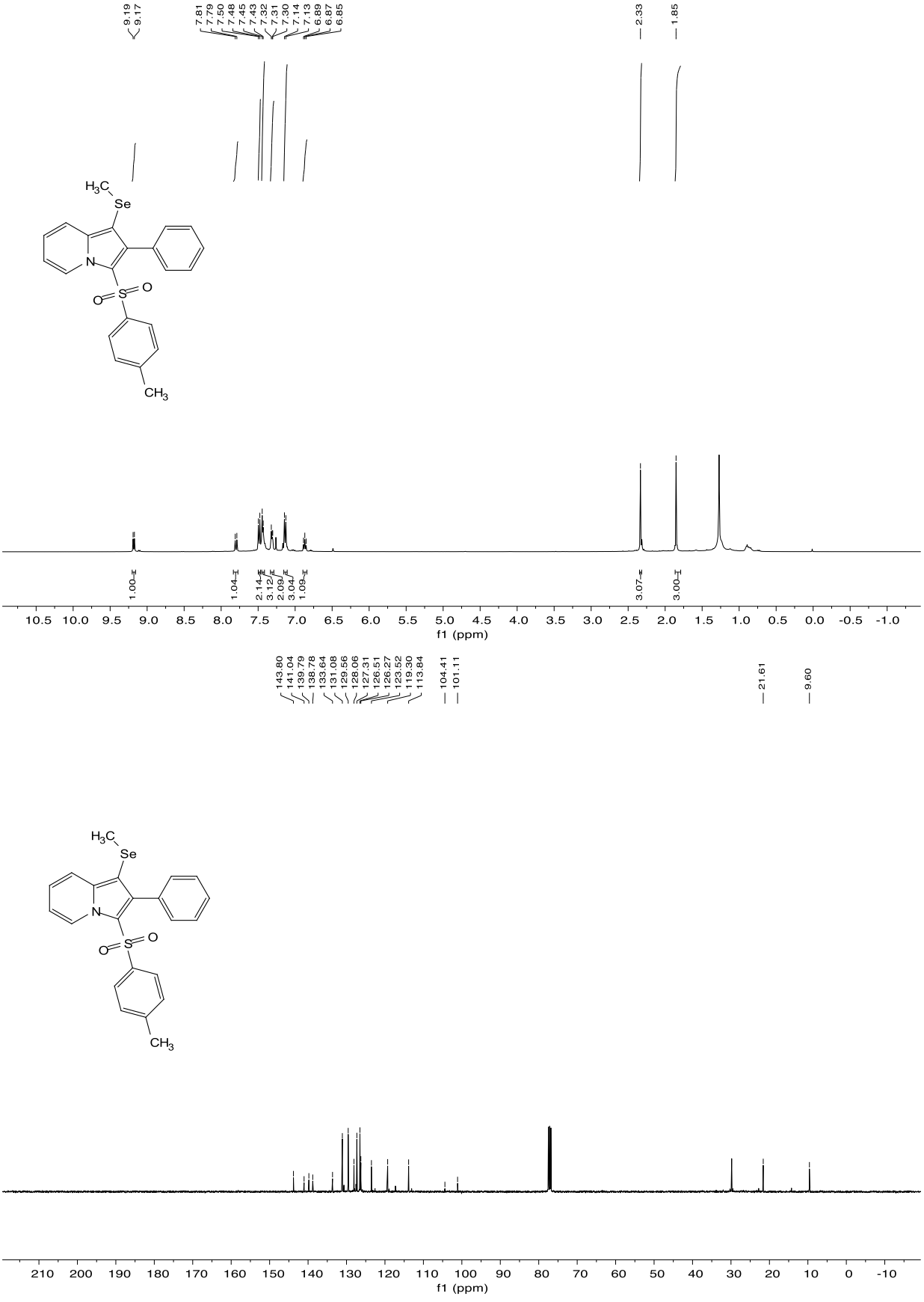
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7a**



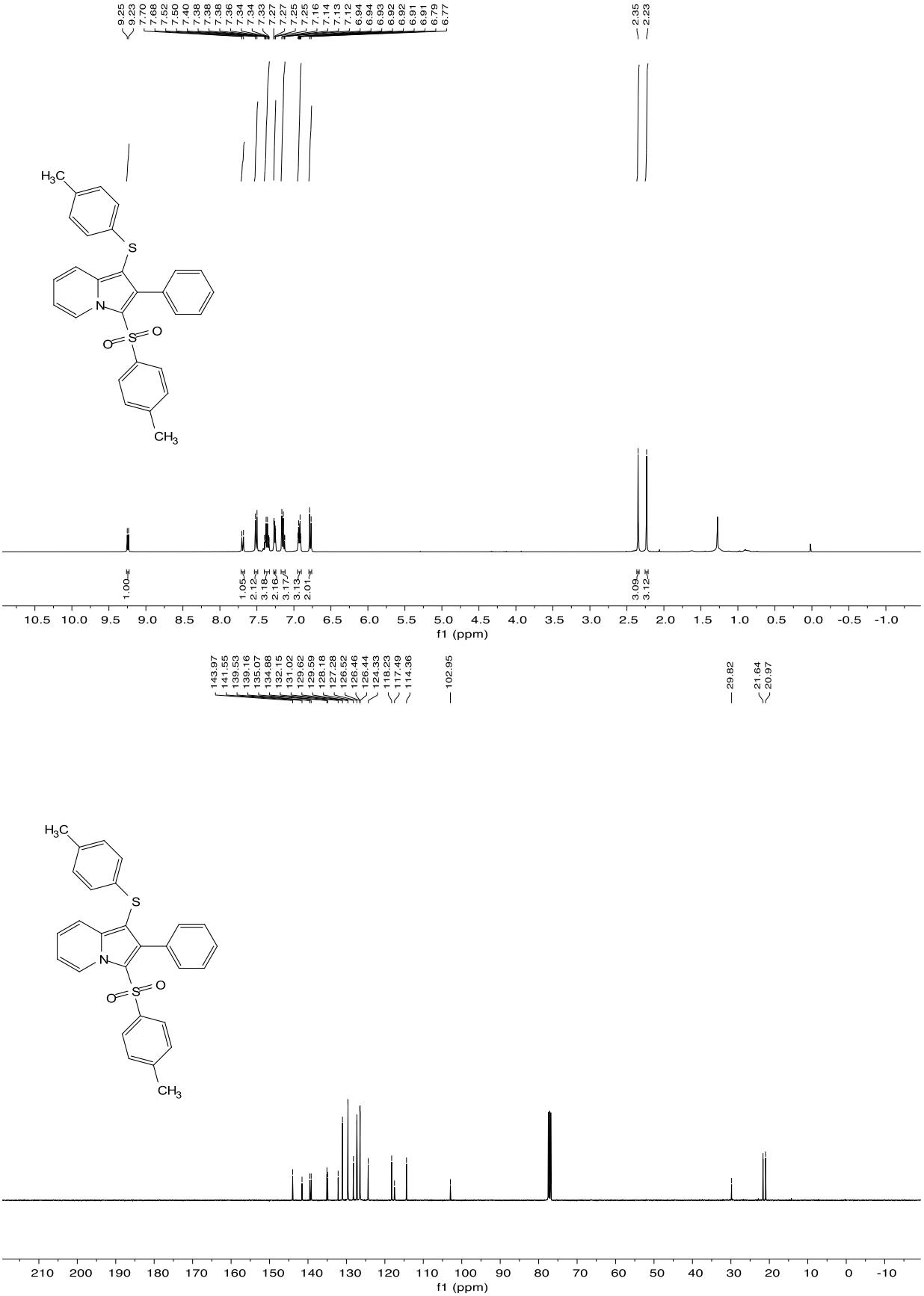
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7b**



^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7c**

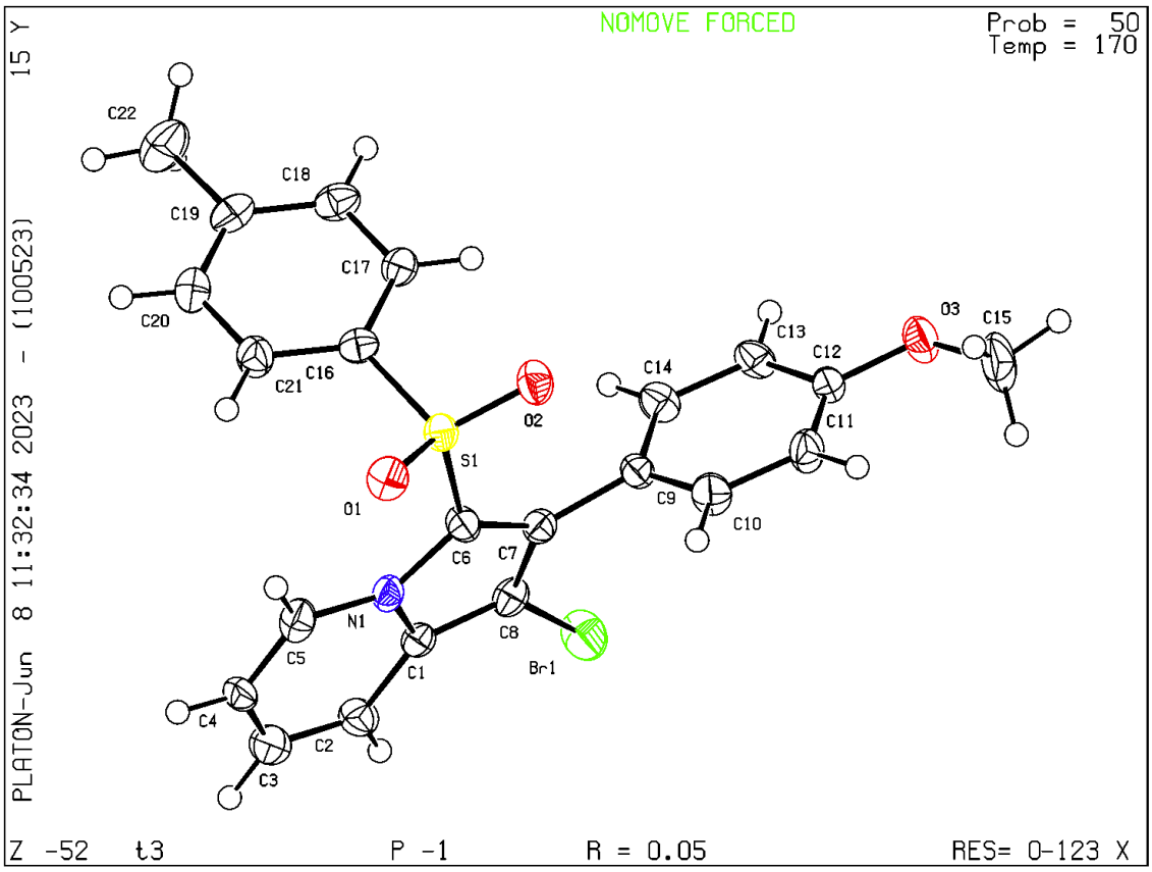


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7d**



4. X-ray crystallographic data

Figure S1 X-ray single crystal structure of **3i** (displacement ellipsoids are drawn at the 50% probability level)



Single crystals of **3i** were grown by slow evaporation of its DCM/PE solution. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC number: 2305723).

Table S1 Crystal data and structure refinement for **3i**

Identification code	T3
Empirical formula	$C_{22}H_{18}BrNO_3S$
Formula weight	456.34
Temperature/K	170.0(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.6263(11)
b/Å	10.0825(12)
c/Å	10.7578(10)
α/°	78.197(9)
β/°	80.281(9)
γ/°	85.359(10)
Volume/Å^3	1006.2(2)
Z	2
ρ_{calc}g/cm^3	1.506
μ/mm^{-1}	2.169

F(000)	464.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.916 to 49.998
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -12 ≤ l ≤ 9
Reflections collected	7103
Independent reflections	3543 [R_{int} = 0.0597, R_{sigma} = 0.0778]
Data/restraints/parameters	3543/0/255
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0484, wR_2 = 0.1089
Final R indexes [all data]	R_1 = 0.0623, wR_2 = 0.1204
Largest diff. peak/hole / e Å^{-3}	0.71/-0.44

Table S2 Bond Lengths for **3i**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C8	1.873(4)	C7	C8	1.400(5)
S1	O1	1.435(3)	C7	C9	1.480(5)
S1	O2	1.425(2)	C9	C10	1.378(5)
S1	C6	1.727(4)	C9	C14	1.384(5)
S1	C16	1.757(4)	C10	C11	1.381(5)
O3	C12	1.367(4)	C11	C12	1.377(5)
O3	C15	1.432(5)	C12	C13	1.369(5)
N1	C1	1.389(5)	C13	C14	1.384(5)
N1	C5	1.385(5)	C16	C17	1.395(5)
N1	C6	1.404(4)	C16	C21	1.377(5)
C1	C2	1.398(5)	C17	C18	1.365(5)
C1	C8	1.383(5)	C18	C19	1.393(6)
C2	C3	1.360(6)	C19	C20	1.391(6)
C3	C4	1.401(6)	C19	C22	1.495(6)
C4	C5	1.354(5)	C20	C21	1.384(6)
C6	C7	1.390(5)			

Table S3 Bond Angles for **3i**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	C6	108.64(16)	C1	C8	Br1	123.1(3)
O1	S1	C16	107.88(17)	C1	C8	C7	110.1(3)
O2	S1	O1	119.39(15)	C7	C8	Br1	126.8(3)
O2	S1	C6	107.24(17)	C10	C9	C7	119.8(3)
O2	S1	C16	108.29(16)	C10	C9	C14	118.8(3)
C6	S1	C16	104.42(18)	C14	C9	C7	121.2(3)
C12	O3	C15	116.8(3)	C9	C10	C11	120.8(3)
C1	N1	C6	109.2(3)	C12	C11	C10	119.9(4)
C5	N1	C1	120.4(3)	O3	C12	C11	124.7(3)
C5	N1	C6	130.5(3)	O3	C12	C13	115.3(3)
N1	C1	C2	119.4(3)	C13	C12	C11	120.0(3)
C8	C1	N1	106.4(3)	C12	C13	C14	120.1(3)
C8	C1	C2	134.2(4)	C13	C14	C9	120.4(4)
C3	C2	C1	120.4(4)	C17	C16	S1	118.9(3)
C2	C3	C4	118.9(4)	C21	C16	S1	121.0(3)
C5	C4	C3	122.0(4)	C21	C16	C17	120.0(4)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	C5	N1	119.0(4)	C18	C17	C16	120.1(4)
N1	C6	S1	122.4(3)	C17	C18	C19	121.0(4)
C7	C6	S1	127.9(3)	C18	C19	C22	120.9(4)
C7	C6	N1	107.6(3)	C20	C19	C18	118.2(4)
C6	C7	C8	106.8(3)	C20	C19	C22	120.9(4)
C6	C7	C9	129.6(3)	C21	C20	C19	121.2(4)
C8	C7	C9	123.6(3)	C16	C21	C20	119.4(3)

5. References

1. (a) L. Teng, X. Liu, P. Guo, Y. Yu and H. Cao, *Org. Lett.,* 2020, **22**, 3841-3845; (b) J. Zhou, X. Shi, H. Zheng, G. Chen, C. Zhang, X. Liu and H. Cao, *Org. Lett.*, 2022, **24**, 3238-3243.
2. W. Kim, H. Y. Kim and K. Oh, *J. Org. Chem.,* 2021, **86***,* 15973-15991.