Supplementary Information

Asymmetric synthesis of δ-amino acid derivatives via diastereoselective vinylogous Mannich reactions between *N-tert*-butanesulfinyl imines and dioxinone-derived lithium dienolate

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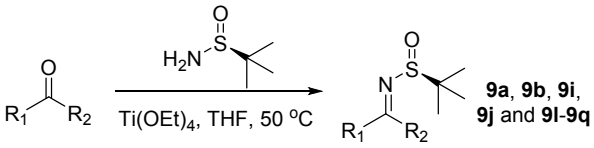
1. General information

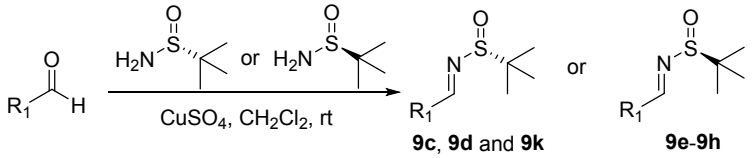
Melting points were obtained on a XT-4 melting-point apparatus and were uncorrected. The infrared (IR) spectra were measured on a Nicolet iS10 FTIR spectrometer with 4 cm^{-1} resolution and 32 scans between wavenumber of 4000 cm^{-1} and 400 cm^{-1}. Samples were prepared as KBr disks with 1 mg of samples in 100 mg of KBr. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained on a Bruker Avance 400 spectrometers at 400 MHz. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) was obtained on Bruker Avance 400 spectrometers at 100 MHz. Chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. High Resolution Mass spectra were taken on AB QSTAR Pulsar mass spectrometer or Aglient LC/MSD TOF mass spectrometer. Optical rotations were recorded on a JASCO P-2000 polarimeter. All products were characterized by IR, ^{1}H NMR, ^{13}C NMR and HRMS. All substrates were characterized by ^{1}H NMR and ^{13}C NMR. Silica gel (200–300 mesh) for column chromatography and silica GF_{254} for TLC were produced by Merch Chemicals Co. Ltd. (Shanghai). THF used in the reactions were dried by distillation over metallic sodium and benzophenone. Starting materials and reagents used in reactions were obtained commercially from Acros, Aldrich, Adamas-beta®, and were used without purification, unless otherwise indicated. All moisture-sensitive reactions were conducted in dried glassware under a positive pressure of dry nitrogen or argon. Reagents and starting materials were accordingly transferred via syringe or cannula. Unless otherwise stated, all other reactions were also performed under a dry nitrogen atmosphere.

2. Experimental section

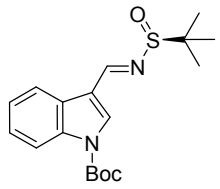
2.1 Synthesis of *N*-*tert*-butanesulfinyl imines



General procedure for heterocyclic aldehydes (9a, 9b, 9i, and 9j) and aromatic ketones (9l-9q). A mixture of heterocyclic aldehydes or aromatic ketones (1 equivalent), (*S*)-*tert*-butanesulfonamine (1.2 equivalents) and titanium ethoxide (1 equivalents) in tetrahydrofuran (0.4 M) was stirred at 50 ^{o}C for 12 h. The reaction was quenched with water and the resulting suspension was filtered through a short pad of Silica gel (200–300 mesh). The solid cake was washed with ethyl acetate, and the separated organic layer was washed with brine. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography eluting with petroleum ether/ethyl acetate (5:1) to afford sulfinimines.

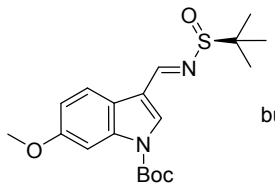


General procedure for aliphatic aldehydes (9i) and phenyl aldehydes (9c-9h). A mixture of aliphatic aldehyde or phenyl aldehydes (1 equivalent), (*S*)-*tert*-butanesulfonamine or (*R*)-*tert*-butanesulfonamine (1.2 equivalents)and copper(II) sulfate (5 equivalents) in dichloromethane (0.3 M) was stirred at room temperature for 12 h. The resulting mixture was filtered through celite. After evaporating solvent under reduced pressure, the residue was purified by flash column chromatography eluting with petroleum ether/ethyl acetate (5:1) to afford sulfinimines.



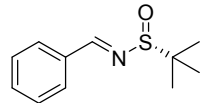
tert-butyl (*S*,*E*)-3-(((*tert*-butylsulfinyl)imino)methyl)-1*H*-indole-1 carboxylate **9a**

9a: Off-white syrup, 92% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 8.73 (s, 1H), 8.30 (d, J = 7.2 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.07 (s, 1H), 7.42 (dt, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.36 (dt, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 1.70 (s, 9H), 1.29 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*): δ 156.18, 149.09, 136.35, 133.19, 127.08, 125.97, 124.32, 122.46, 117.95, 115.41, 85.33, 57.48, 28.25, 22.65. The spectra were identical to those reported in the literature.[1]



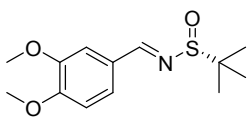
tert-butyl (*S*,*E*)-3-(((*tert*-butylsulfinyl)imino)methyl)-6-methoxy-1*H*-indole-1-carboxylate **9b**

9b: White solid, 91% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 8.67 (s, 1H), 8.14 (d, J = 8.8 Hz, 1H), 7.94 (s, 1H), 7.75 (brs, 1H), 6.97 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 3.88 (s, 3H), 1.69 (s, 9H), 1.27 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*): δ 158.83, 156.12, 149.14, 137.46, 132.02, 122.89, 120.62, 118.01, 113.47, 99.38, 85.11, 57.42, 55.72, 28.21, 22.61. The spectra were identical to those reported in the literature.[1]



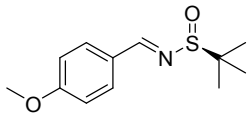
(*R*,*E*)-*N*-benzylidene-2-methylpropane-2-sulfinamide **9c**

9c: Pale oil, 97% yield. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.98 – 7.73 (m, 2H), 7.61 – 7.38 (m, 3H), 1.26 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 162.78, 134.07, 132.46, 129.41, 128.96, 57.80, 22.63. The spectra were identical to those reported in the literature.[2]

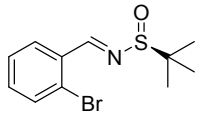


(*R*,*E*)-*N*-(3,4-dimethoxybenzylidene)-2-methylpropane-2-sulfinamide **9d**

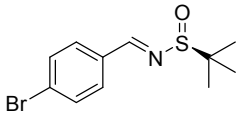
9d: White solid, 84% yield. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 7.46 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.95 (s, 6H), 1.27 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 161.96, 152.82, 149.39, 127.40, 125.09, 110.62, 109.65, 57.60, 56.07, 55.92, 22.58. The spectra were identical to those reported in the literature.[3]


(*S*,*E*)-*N*-(4-methoxybenzylidene)-2-methylpropane-2-sulfinamide **9e**

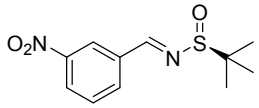
9e: White solid, 95% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 7.79 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.16, 161.86, 131.39, 127.43, 114.44, 57.66, 55.59, 22.68. The spectra were identical to those reported in the literature.[4]


(*S*,*E*)-*N*-(2-bromobenzylidene)-2-methylpropane-2-sulfinamide **9f**

9f: White solid, 83% yield. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.97 (s, 1H), 8.04 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.63 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.45 – 7.29 (m, 2H), 1.27 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 162.17, 133.66, 133.35, 132.84, 129.64, 127.72, 126.44, 58.04, 22.72. The spectra were identical to those reported in the literature.[5]

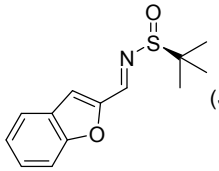

(*S*,*E*)-*N*-(4-bromobenzylidene)-2-methylpropane-2-sulfinamide **9g**

9g: Yellow syrup, 62% yield. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 1.25 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 161.70, 32.96, 132.39, 130.77, 127.33, 58.02, 22.72. The spectra were identical to those reported in the literature.[4]



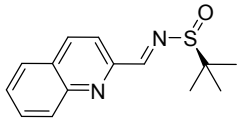
(*S*,*E*)-2-methyl-*N*-(3-nitrobenzylidene) propane-2-sulfinamide **9h**

9h: Yellow syrup, 72% yield. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 8.65 (s, 1H), 8.36 (d, *J* = 7.2 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 1.28 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 160.70, 148.83, 135.52, 135.12, 130.28, 126.66, 123.63, 58.44, 22.77.



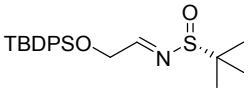
(*S*,*E*)-*N*-(benzofuran-2-ylmethylene)-2-methylpropane-2-sulfinamide **9i**

9i: Yellow solid, 88% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.56 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.36 – 7.28 (m, 2H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.37, 151.62, 151.06, 128.04, 127.62, 123.98, 122.88, 115.49, 112.39, 58.48, 22.76. The spectra were identical to those reported in the literature.[6]



(*S*,*E*)-2-methyl-*N*-(quinolin-2-ylmethylene)propane-2-sulfinamide **9j**

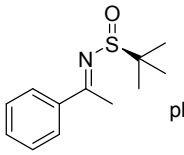
9j: Yellow solid, 62% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.87 (s, 1H), 8.28 – 8.10 (m, 3H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.77 (t, *J* = 7.2 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 164.40, 152.63, 148.20, 136.94, 130.39, 130.31, 129.09, 128.47, 127.78, 119.05, 58.30, 22.86. The spectra were identical to those reported in the literature.[7]



(*R*,*E*)-*N*-(2-((*tert*-butyldiphenylsilyl)oxy)ethylidene)-2-methylpropane-2-sulfinamide **9k**

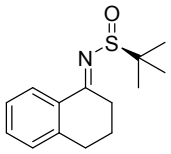
9k: Colorless oil, 84% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.76 – 7.69 (m, 4H), 7.44 – 7.40 (m, 6H), 4.58 (s, 2H), 1.20 (s, 9H), 1.11 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.31, 135.59, 135.58, 132.80, 130.01, 127.90,

127.89, 66.18, 56.94, 26.78, 22.41, 19.33. The spectra were identical to those reported in the literature.[8]



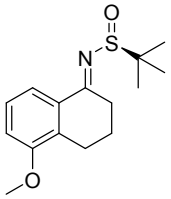
(*S*,*E*)-2-methyl-*N*-(1-phenylethylidene)propane-2-sulfinamide **9l**

9l: Yellow solid, 75% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 2.77 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 176.57, 138.94, 131.79, 128.60, 127.39, 57.59, 22.68, 19.96. The spectra were identical to those reported in the literature.[9]



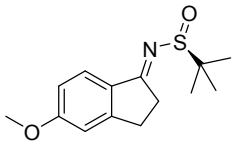
(*S*,*E*)-*N*-(3,4-dihydronaphthalen-1(2*H*)-ylidene)-2-methylpropane-2-sulfinamide **9m**

9m: Yellow solid, 38% yield. **^{1}H NMR** (Chloroform-*d*, 300 MHz) δ 8.17 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.39 (td, *J* = 7.4, 1.5 Hz, 1H), 7.30 – 7.12 (m, 2H), 3.40 – 2.97 (m, 2H), 2.88 (dd, *J*=7.1, 4.9 Hz, 2H), 2.09 – 1.87 (m, 2H), 1.33 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.02, 142.25, 133.05, 132.03, 128.95, 127.05, 126.51, 57.18, 32.43, 29.54, 22.71, 22.51. The spectra were identical to those reported in the literature.[10]



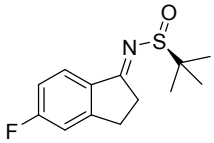
(*S*,*E*)-*N*-(5-methoxy-3,4-dihydronaphthalen-1(2*H*)-ylidene)-2-methylpropane-2-sulfinamide **9n**

9n: Yellow solid, 59% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 3.85 (s, 3H), 3.23 (ddd, *J* = 16.7, 9.4, 4.5 Hz, 1H), 3.03 (ddd, *J* = 16.9, 7.7, 4.2 Hz, 1H), 2.92 – 2.72 (m, 2H), 2.08 – 1.88 (m, 2H), 1.32 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 177.45, 156.91, 134.27, 131.60, 126.57, 118.99, 112.96, 57.39, 55.79, 32.04, 22.66, 22.62, 22.18.



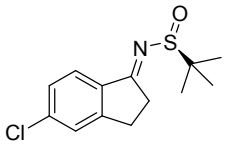
(*S*,*E*)-*N*-(5-methoxy-2,3-dihydro-1*H*-inden-1-ylidene)-2-methylpropane-2-sulfinamide **9o**

9o: Yellow solid, 39% yield. **^{1}H NMR** (Chloroform-*d*, 400 MHz) δ 7.62 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.75 (s, 1H), 3.68 (s, 3H), 3.34-2.26 (m, 1H), 2.99-2.94 (m, 2H), 2.92-2.86 (m, 1H), 1.21 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.39, 164.24, 153.55, 131.84, 124.88, 115.11, 108.86, 56.62, 55.41, 32.02, 28.91, 22.18.



(*S*,*E*)-*N*-(5-fluoro-2,3-dihydro-1*H*-inden-1-ylidene)-2-methylpropane-2-sulfinamide **9p**

9p: Yellow solid, 37% yield. **^{1}H NMR** (Chloroform-*d*, 400 MHz) δ 7.67 (dd, *J* = 8.5, 5.4 Hz, 1H), 7.06 – 6.83 (m, 2H), 3.36 (ddd, *J* = 18.6, 6.9, 4.5 Hz, 1H), 3.13 – 2.87 (m, 3H), 1.21 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.19, 167.42, 164.90, 153.29 (153.20), 135.30 (135.28), 125.42 (125.32), 115.33 (115.10), 112.42 (112.19), 57.05, 31.91, 28.92 (28.90), 22.28.

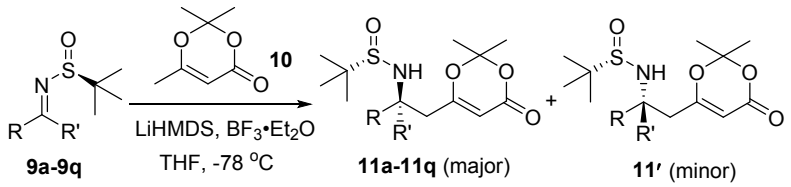


(*S*,*E*)-*N*-(5-chloro-2,3-dihydro-1*H*-inden-1-ylidene)-2-methylpropane-2-sulfinamide **9q**

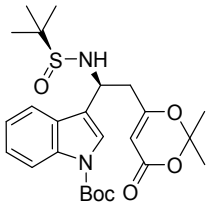
9q: Yellow solid, 43% yield. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.2 Hz, 1H), 7.26 (s, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 3.47 – 3.27 (m, 1H), 3.06 – 2.89 (m, 3H), 1.22 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 182.12, 152.03, 139.31, 137.70, 127.79, 125.89, 124.49, 57.29, 31.73, 28.85, 22.41.

2.2 Vinylogous Mannich reaction

2.2.1 Synthesis of products 11a-11q

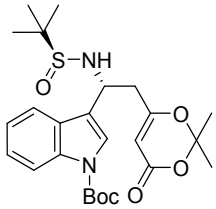


General procedure for aldimines and phenyl kteimines (11a-11q). To a solution of sulfinimines **9** (1.0 mmol) in THF (10 mL) was added BF_3•Et_2O (0.13 mL, 1.0 mmol) at –78 °C. In the mean time, to a stirred solution of dioxinone **10** (284 mg, 2.0 mmol) in THF (10 mL) was added lithium bis(trimethylsilyl)amide (1.0 M in THF, 2.4 mL, 2.4 mmol) at –78 °C. The resulting mixtures were stirred at –78 °C for 1 h. Then, the solution of dioxinone-derived lithium dienolate was cannulated to the solution of sulfinimine at –78 °C. Stirring was continued at –78 °C for 3 h. The reaction was then quenched with saturated *aq.* NH_4Cl (3 mL) at –78 °C. The cooling bath was removed and the mixture was warmed to rt, followed by extraction with EtOAc (3 x 15 mL). The combined organic layers were washed with brine (15mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with petroleum ether/EtOAc (5:1 to 2:1) or purified by preparative chromatography to afford sulfinamides **11** and their diasteromer **11'**. Caution: 2 mmol BF_3•Et_2O was added for quinoline-derived *N*-*tert*-butanesulfinyl aldimine **9j**. All yields represent isolated yields.



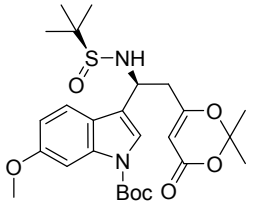
tert-butyl 3-((*S*)-1-(((*S*)-*tert*-butylsulfinyl)amino)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)ethyl)-1*H*-indole-1-carboxylate **11a**

11a: White solid, m.p.: 110-112 ^{o}C, 86% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3440, 2979, 2928, 1753, 1735, 1644, 1607, 1475, 1453, 1379, 1308, 1272, 1155, 1096, 1041, 1015, 759. [α]20 D= 31.1 (*c*=1.02, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.61 (s, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 6.9 Hz, 1H), 5.21 (s, 1H), 5.01 (td, *J* = 7.3, 3.0 Hz, 1H), 3.62 (d, *J* = 2.5 Hz, 1H), 3.09 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.93 (dd, *J* = 14.3, 7.9 Hz, 1H), 1.68 (s, 9H), 1.67 (s, 3H), 1.56 (s, 3H), 1.22 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.66, 160.81, 149.44, 135.86, 127.98, 125.19, 124.05, 123.08, 119.54, 119.37, 115.73, 106.85, 95.80, 84.44, 56.12, 48.91, 40.13, 28.27, 25.62, 24.73, 22.69. **HRMS** (ESI) *m/z* calcd for $C_{25}H_{34}N_2O_6S$ $[M+Na]^+$: 513.2030; Found: 513.2028.



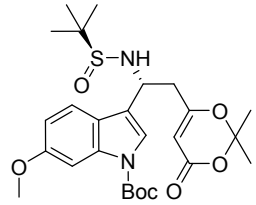
tert-butyl 3-((*R*)-1-(((*S*)-*tert*-butylsulfinyl)amino)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)ethyl)-1*H*-indole-1-carboxylate **11a'**

11a': Yellow oil, 2% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3440, 2977, 2926, 1734, 1633, 1453, 1309, 1273, 1256, 1157, 1091, 10454, 1016, 767, 749. [α]20 D= 50.3 (*c*=0.62, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 5.22 (s, 1H), 4.94 (td, *J* = 7.0, 3.3 Hz, 1H), 3.71 (s, 1H), 3.00 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.90 (dd, *J* = 14.5, 6.5 Hz, 1H), 1.68 (s, 3H), 1.66 (s, 9H), 1.63 (s, 3H), 1.19 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.29, 160.62, 149.45, 136.21, 127.99, 125.04, 124.81, 122.80, 119.90, 118.75, 115.82, 107.19, 95.85, 84.31, 55.87, 49.73, 40.87, 28.32, 25.42, 25.10, 22.71. **HRMS** (ESI) *m/z* calcd for $C_{25}H_{34}N_2O_6S$ $[M+Na]^+$: 513.2030; Found: 513.2032.



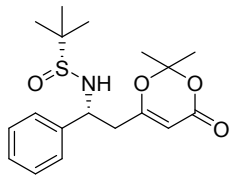
tert-butyl 3-((*S*)-1-(((*S*)-*tert*-butylsulfinyl)amino)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)ethyl)-6-methoxy-1*H*-indole-1-carboxylate **11b**

11b: White solid, m.p.: 79-81 °C, 85% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 2977, 1733, 1633, 1491, 1444, 1381, 1275, 1157, 1050, 807. [α]20 D= 50.2 (*c*=1.08, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.44 (s, 1H), 6.87 (dd, *J* = 8.7, 2.4 Hz, 1H), 5.18 (s, 1H), 4.91 (td, *J* = 7.2, 3.2 Hz, 1H), 3.84 (s, 3H), 3.61 (d, *J* = 3.2 Hz, 1H), 3.03 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.87 (dd, *J* = 14.4, 7.8 Hz, 1H), 1.64 (d, *J* = 2.8 Hz, 12H), 1.53 (s, 3H), 1.17 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.69, 160.76, 158.31, 149.46, 136.93, 122.56, 121.61, 120.01, 119.38, 112.47, 106.77, 99.65, 95.71, 84.18, 56.05, 55.62, 48.94, 40.09, 28.21, 25.59, 24.66, 22.64. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{36}N_2O_7S$ $[M+Na]^+$: 543.2135; Found: 543.2136.



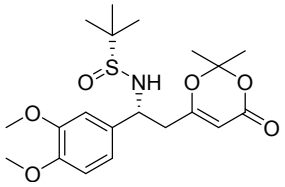
tert-butyl 3-((*R*)-1-(((*S*)-*tert*-butylsulfinyl)amino)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)ethyl)-6-methoxy-1*H*-indole-1-carboxylate **11b'**

11b': Colorless oil, 2% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 2973, 2926, 1735, 1630, 1561, 1444, 1384, 1274, 1229, 1158, 1093, 1050, 808. [α]20 D= 45.3 (*c*=0.22, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.45 (d, *J* = 8.9 Hz, 2H), 6.86 (dd, *J* = 8.6, 2.1 Hz, 1H), 5.21 (s, 1H), 4.89 (s, 1H), 3.88 (s, 3H), 3.68 (s, 1H), 2.93 (ddd, *J* = 40.3, 14.0, 6.3 Hz, 2H), 1.69 (s, 3H), 1.66 (s, 9H), 1.63 (s, 3H), 1.18 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.33, 158.26, 149.53, 137.34, 123.50, 120.43, 118.68, 112.39, 107.18, 99.69, 95.85, 84.14, 55.73, 49.78, 40.93, 28.32, 25.46, 25.11, 22.75. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{36}N_2O_7S$ $[M+Na]^+$: 543.2135; Found: 543.2135.



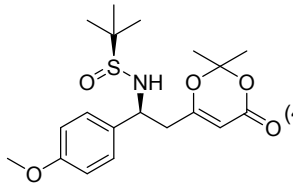
(*R*)-*N*-((*R*)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl) 1-phenylethyl)-2-methylpropane-2-sulfinamide **11c**

11c: White solid, m.p.: 116-118 ℃, 96% yield, dr > 40:1. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3438, 3234, 3090, 3063, 3031, 2959, 2868, 1724, 1635, 1456, 1390, 1273, 1204, 1057, 1014, 902, 808, 701. [α]20 D= -66.4 (*c*=0.55, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.30-7.34 (m, 5H), 5.09 (s, 1H), 4.72-4.66 (m, 1H), 3.50 (d, *J* = 3.4 Hz, 1H), 2.98 (dd, *J* = 14.2, 6.4 Hz, 1H), 2.65 (dd, *J* = 14.3, 8.4 Hz, 1H), 1.58 (s, 3H), 1.48 (s, 3H), 1.20 (s, 9H).**^{13}C NMR** (75 MHz, Chloroform-*d*) δ 167.60, 160.83, 140.20, 129.11, 128.81, 127.20, 106.77, 95.67, 56.20, 41.12, 25.53, 24.67, 22.66. **HRMS** (ESI) *m/z* calcd for $C_{18}H_{25}NO_4S$ $[M+Na]^+$: 374.1397; Found: 374.1403.



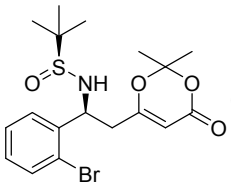
(*R*)-*N*-((*R*)-1-(3,4-dimethoxyphenyl)-2-(2,2-dimethyl-4-oxo -4*H*-1,3-dioxin-6-yl)ethyl)-2-methylpropane-2-sulfinamide **11d**

11d: White solid, m.p.: 86-88 ℃, 95% yield, dr > 40:1. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3428, 3274, 2961, 2838, 1710, 1632, 1519, 1463, 1393, 1257, 1204, 1156, 1016, 905, 807, 733. [α]20 D= -54.6 (*c*=0.17, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 6.68 – 6.56 (m, 3H), 4.95 (s, 1H), 4.39 (d, *J* = 5.6 Hz, 1H), 3.75 (brs, 1H), 3.62 (s, 3H), 3.59 (s, 3H), 2.71 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.45 (dd, *J* = 14.2, 7.5 Hz, 1H), 1.40 (s, 3H), 1.30 (s, 3H), 0.96 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 167.57, 160.31, 148.48, 148.32, 132.61, 118.73, 110.61, 109.92, 106.08, 94.96, 55.91, 55.61, 55.36, 55.28, 40.59, 25.03, 23.98, 22.10. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{29}NO_6S$ $[M+Na]^+$: 434.1608; Found: 434.1606.



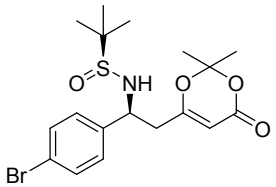
(*S*)-*N*-((*S*)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfinamide **11e**

11e: Colourless syrup, 89% yield, dr > 40:1. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3445, 3243, 2957, 2834, 1732, 1634, 1614, 1586, 1515, 1463, 1392, 1250, 1204, 1114, 1014, 902, 831, 744. [α]20 D= 85.4 (*c*=1.1, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.16 (s, 0H), 5.08 (s, 1H), 4.65 (t, *J* = 9.0 Hz, 1H), 3.78 (s, 3H), 3.40 (s, 1H), 2.97 (dd, *J* = 14.2, 6.2 Hz, 1H), 2.62 (dd, *J* = 14.2, 8.6 Hz, 1H), 1.59 (s, 3H), 1.48 (s, 3H), 1.19 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.75, 160.83, 159.83, 132.24, 128.43, 114.41, 106.75, 95.65, 56.11, 55.63, 55.39, 41.12, 25.59, 24.71, 22.67. **HRMS** (ESI) *m/z* calcd for $C_{19}H_{27}NO_5S$ $[M+Na]^+$: 404.1500; Found: 404.1502.



(*S*)-*N*-((*S*)-1-(2-bromophenyl)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)ethyl)-2-methylpropane-2-sulfinamide **11f**

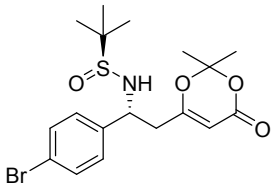
11f: Pale yellow syrup, 90% yield, dr = 87:13. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3432, 3260, 2990, 2966, 1724, 1633, 1473, 1461, 1389, 1252, 1205, 1043, 1013, 923, 817, 760. [α]20 D= -39.8 (*c*=0.15, CH_2Cl_2). **^{1}H NMR** (Chloroform-*d*, 300 MHz) δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 6.9 Hz, 1H), 5.27 (s, 1H), 5.10 (d, *J* = 7.3 Hz, 1H), 4.33 (d, *J* = 7.4 Hz, 1H), 2.89-2.74 (m, 2H), 1.65 (s, 3H), 1.52 (s, 3H), 1.19 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 167.44, 160.72, 139.37, 133.12, 129.51, 128.50, 127.74, 122.89, 106.56, 95.31, 56.31, 56.12, 40.13, 25.28, 24.21, 22.38. **HRMS** (ESI) m/z calcd for $C_{18}H_{24}BrNO_4S$ $[M+Na]^+$: 452.0502; Found: 452.0499.



(*S*)-*N*-((*S*)-1-(4-bromophenyl)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)ethyl)-2-methylpropane-2-sulfinamide **11g**

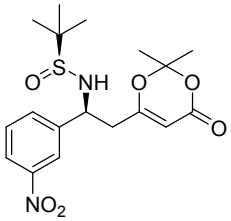
11g: Pale yellow syrup, 77% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3100, 2981, 2870, 1732, 1636, 1489, 1391, 1376, 1273, 1203, 1072, 1012, 900, 825. [α]20 D= -29.2 (*c*=0.24, CH_2Cl_2). **^{1}H NMR** (Chloroform-*d*, 400 MHz) δ 7.45 (d, *J* = 8.5 Hz, 2H),

7.25 (d, *J* = 8.4 Hz, 2H), 5.18 (s, 1H), 4.63 (q, *J* = 7.1 Hz, 1H), 4.07 (d, *J* = 6.1 Hz, 1H), 2.91 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.63 (dd, *J* = 14.4, 7.3 Hz, 1H), 1.63 (s, 3H), 1.55 (s, 3H), 1.18 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.23, 160.44, 139.65, 131.65, 128.61, 121.95, 106.45, 95.37, 56.09, 56.05, 40.87, 25.22, 24.38, 22.34. **HRMS** (ESI) m/z calcd for $C_{18}H_{24}BrNO_4S$ $[M+Na]^+$: 452.0502; Found: 452.0501.



(*S*)-*N*-((*R*)-1-(4-bromophenyl)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)ethyl)-2-methylpropane-2-sulfinamide **11g'**

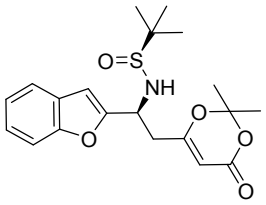
11g': Pale yellow syrup, 14% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3224, 2960, 2868, 1720, 1636, 1488, 1390, 1376, 1274, 1204, 1054, 1012, 902, 823, 734. [α]20 D= -56.3 (*c*=0.29, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 5.17 (s, 1H), 4.66 – 4.59 (m, 1H), 3.79 (d, *J* = 2.5 Hz, 1H), 2.75 (dd, *J* = 14.4, 7.7 Hz, 1H), 2.65 (dd, *J* = 14.4, 6.3 Hz, 1H), 1.63 (s, 3H), 1.59 (s, 3H), 1.15 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.72, 160.44, 139.06, 132.01, 129.20, 122.40, 107.13, 95.91, 55.93, 55.44, 42.25, 25.15, 22.50. **HRMS** (ESI) m/z calcd for $C_{18}H_{24}BrNO_4S$ $[M+Na]^+$: 452.0502; Found: 452.0500.



(*S*)-*N*-((*S*)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)-1-(3-nitrophenyl)ethyl)-2-methylpropane-2-sulfinamide **11h**

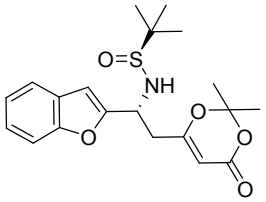
11h: White solid, m.p.: 138-139 ℃, 89% yield, dr > 40:1. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3431, 3278, 3120, 2980, 1707, 1641, 1532, 1416, 1352, 1256, 1202, 1072, 1017, 925, 817, 740. [α]20 D= -39.2 (*c*=0.17, CH_2Cl_2). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 8.09 (d, *J* = 7.1 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.50 (qd, *J* = 8.0, 2.9 Hz, 1H), 5.18 (s, 1H), 4.84 – 4.67 (m, 1H), 4.16 – 3.94 (m, 1H), 2.93 (dd, *J* = 12.9, 6.9 Hz, 1H), 2.64 (dd, *J* = 13.2, 5.6 Hz, 1H), 1.59 (s, 3H), 1.53 (s, 3H), 1.15 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.84, 160.50, 148.35, 143.12, 133.48,

130.00, 123.32, 121.86, 106.88, 95.87, 56.60, 56.44, 41.15, 25.36, 24.72, 22.53. **HRMS** (ESI) *m/z* calcd for $C_{18}H_{24}N_2O_6S$ [M+Na]$^+$: 419.1247; Found: 419.1252.



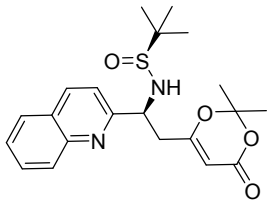
(*S*)-*N*-((*S*)-1-(benzofuran-2-yl)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)ethyl)-2-methylpropane-2-sulfinamide **11i**

11i: White solid, m.p.: 133-135℃, 73% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3424, 3247, 3004, 2924, 1732, 1641, 1492, 1390, 1273, 1201, 1059, 1014, 901, 860, 756. [α]20 D= 1.1 (*c*=1.1, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.77 (s, 1H), 5.28 (s, 1H), 4.86 (q, *J* = 7.2 Hz, 1H), 3.79 (t, *J* = 5.9 Hz, 1H), 2.91 (qd, *J* = 14.6, 7.2 Hz, 2H), 1.63 (s, 3H), 1.58 (s, 3H), 1.22 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.01, 160.68, 155.77, 154.98, 127.85, 124.79, 123.22, 121.49, 111.28, 106.92, 104.92, 95.94, 56.76, 51.75, 39.52, 25.70, 24.69, 22.64. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{25}NO_5S$ [M+Na]$^+$: 414.1344; Found: 414.1346.



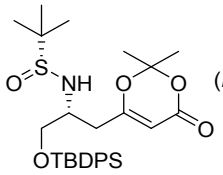
(*S*)-*N*-((*R*)-1-(benzofuran-2-yl)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)ethyl)-2-methylpropane-2-sulfinamide **11i'**

11i': Pale yellow syrup, yield 7%. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3445, 3219, 2983, 2869, 1714, 1634, 1455, 1393, 1273, 1204, 1057, 1014, 902, 804, 752. [α]20 D= 35.7 (*c*=1.7, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 5.28 (s, 1H), 4.90 (q, *J* = 6.5 Hz, 1H), 3.91 (d, *J* = 5.8 Hz, 1H), 3.06-2.96 (m, 2H), 1.62 (s, 3H), 1.58 (s, 3H), 1.21 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.60, 160.49, 155.11, 154.90, 127.62, 124.69, 123.12, 121.25, 111.19, 106.97, 104.96, 95.83, 56.28, 51.45, 39.44, 25.27, 24.87, 22.46. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{25}NO_5S$ [M+Na]$^+$: 414.1344; Found: 414.1346.



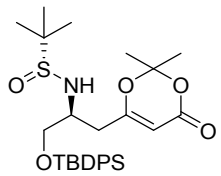
(*S*)-*N*-((*S*)-2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)-1-(quinolin-2-yl)ethyl)-2-methylpropane-2-sulfinamide **11j**

11j: Pale yellow syrup, 86% yield, dr > 40:1. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3432, 3143, 2964, 1727, 1640, 1389, 1274, 1204, 1040, 1016, 902, 836, 760. [α]20 D= -13.2 (*c*=1.1, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 6.9 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 5.49 (d, *J* = 6.4 Hz, 1H), 5.21 (s, 1H), 4.93 (q, *J* = 7.1, 6.3 Hz, 1H), 2.92 – 2.72 (m, 2H), 1.58 (s, 3H), 1.54 (s, 3H), 1.26 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.78, 160.78, 159.06, 147.03, 137.25, 129.90, 129.04, 127.63, 127.50, 126.78, 119.62, 106.66, 95.89, 57.09, 56.38, 41.79, 25.40, 24.83, 22.82. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{26}N_2O_4S$ $[M+Na]^+$: 425.1503; Found: 425.1505.



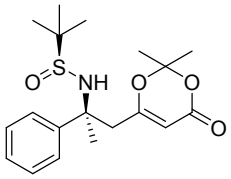
(*R*)-*N*-((*R*)-1-((*tert*-butyldiphenylsilyl)oxy)-3-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)propan-2-yl)-2-methylpropane-2-sulfinamide **11k**

11k: Yellow syrup, 32% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3448, 3285, 3071, 2931, 2858, 1735, 1637, 1589, 1473, 1389, 1273, 1204, 1112, 1070, 939, 902, 823, 702. [α]20 D= -1.3 (*c*=0.33, CH_2Cl_2). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67-7.64 (m, 4H), 7.41-7.38 (m, 6H), 5.22 (s, 1H), 4.06 (d, *J* = 6.6 Hz, 1H), 3.90-3.88 (m, 1H), 3.69 (d, *J* = 7.2 Hz, 2H), 2.59-2.43 (m, 2H), 1.62 (s, 3H), 1.55 (s, 3H), 1.22 (s, 9H), 1.09 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.17, 160.62, 135.53, 135.40, 132.65, 132.30, 129.99, 129.95, 127.85, 127.82, 106.48, 95.34, 66.23, 55.98, 54.32, 37.47, 26.82, 26.75, 25.17, 22.53, 22.47, 19.21. **HRMS** (ESI) *m/z* calcd for $C_{29}H_{41}NO_5SSi$ $[M+Na]^+$: 566.2367; Found: 566.2369.



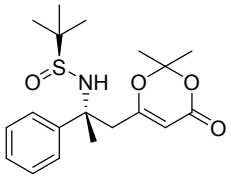
(*R*)-*N*-((*S*)-1-((*tert*-butyldiphenylsilyl)oxy)-3-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)propan-2-yl) 2-methylpropane-2-sulfinamide **11k'**

11k': Pale yellow syrup, 5% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3258, 3071, 3049, 2930, 2858, 1731, 1636, 1589, 1472, 1428, 1390, 1272, 1204, 1112, 1071, 1014, 935, 901, 823, 741, 702. [α]20 D= -21.9 (*c*=0.21, CH_2Cl_2). **^{1}H NMR** (Chloroform-*d*, 400 MHz) δ 7.64-7.61 (m 4H), 7.44-7.37 (m, 6H), 5.29 (s, 1H), 3.72-3.60 (m, 4H), 2.79 (d, *J* = 6.4 Hz, 2H), 1.64 (s, 3H), 1.56 (s, 3H), 1.18 (s, 9H), 1.07 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.06, 160.77, 135.59, 132.78, 132.59, 130.22, 130.11, 128.05, 127.98, 106.81, 95.55, 65.37, 56.22, 55.24, 37.33, 26.94, 25.24, 25.05, 22.57, 19.37. **HRMS** (ESI) *m/z* calcd for $C_{29}H_{41}NO_5SSi$ $[M+Na]^+$: 566.2367; Found: 566.2369.



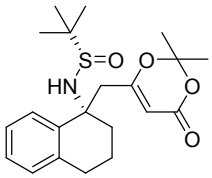
(*S*)-*N*-((*S*)-1-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)-2-phenylpropan-2-yl)-2-methylpropane-2-sulfinamide **11l**

11l: Pale yellow syrup, 20% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3438, 3241, 3091, 3062, 2991, 2941, 1729, 1628, 1446, 1388, 1278, 1247, 1204, 1045, 1015, 903, 828, 765. [α]20 D= 38.3 (*c*=0.06, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.41 – 7.28 (m, 3H), 5.12 (s, 1H), 4.05 (s, 1H), 3.07 (d, *J* = 14.1 Hz, 1H), 2.84 (d, *J* = 14.1 Hz, 1H), 1.81 (s, 3H), 1.52 (s, 3H), 1.39 (s, 3H), 1.27 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 167.59, 160.53, 143.85, 128.42, 127.75, 126.22, 106.43, 96.77, 60.59, 56.27, 47.25, 28.72, 25.20, 24.40, 22.65. **HRMS** (ESI) *m/z* calcd for $C_{19}H_{27}NO_4S$ $[M+Na]^+$: 388.1558; Found: 388.1553.



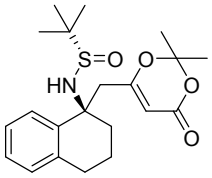
(*S*)-*N*-((*R*)-1-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)-2-phenylpropan-2-yl)-2-methylpropane-2-sulfinamide **11l'**

11l': Pale yellow syrup, 17% yield. **FTIR** (KBr, thin film) ν_{max}(cm^{-1}): 3319, 3238, 3090, 3061, 2979, 2869, 1720, 1629, 1447, 1318, 1273, 1202, 1109, 1014, 939, 901, 831, 768, 732. [α]20 D= 34.6 (*c*=0.19, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.36 (m, 5H), 5.23 (s, 1H), 4.31 (s, 1H), 2.99 (q, *J* = 14.7 Hz, 2H), 1.85 (s, 3H), 1.52 (s, 3H), 1.36 (s, 3H), 1.28 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 167.75, 160.49, 144.16, 128.41, 127.63, 125.92, 106.60, 96.82, 60.00, 56.25, 47.73, 28.45, 25.13, 24.43, 22.76. **HRMS** (ESI) m/z calcd for $C_{19}H_{27}NO_4S$ [M+Na]$^+$: 388.1558; Found: 388.1553.



(*S*)-*N*-((*S*)-1-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-2-methylpropane-2-sulfinamide **11m**

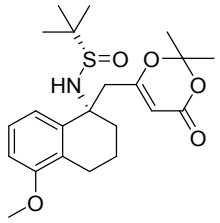
11m: White solid, m.p.: 136-137 ℃, 24% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3443, 3258, 2924, 1735, 1630, 1437, 1388, 1277, 1047, 1012, 901, 765. [α]20 D= 66.7 (*c*=0.8, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 – 7.47 (m, 1H), 7.22 – 7.19 (m, 2H), 7.10 – 7.08 (m, 1H), 5.18 (s, 1H), 3.84 (s, 1H), 3.08 (d, *J* = 14.2 Hz, 1H), 2.93 (d, *J* = 14.1 Hz, 1H), 2.85 – 2.79 (m, 1H), 2.75 – 2.67 (m, 1H), 2.27 – 2.23 (m, 1H), 2.12 – 2.05 (m, 1H), 1.96 – 1.80 (m, 2H), 1.45 (s, 3H), 1.41 (s, 3H), 1.19 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.90, 160.77, 137.82, 137.12, 129.65, 128.76, 128.20, 126.11, 106.54, 97.17, 58.80, 56.35, 46.32, 36.77, 30.01, 25.09, 24.71, 22.82, 18.69. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{29}NO_4S$ [M+Na]$^+$: 414.1715; Found: 414.1712.



(*S*)-*N*-((*R*)-1-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-2-methylpropane-2-sulfinamide **11m'**

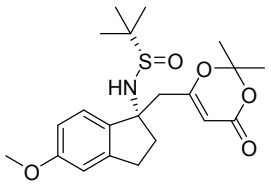
11m': Pale yellow syrup, 7% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3440, 3322, 3253, 2945, 1732, 1633, 1455, 1373, 1272, 1203, 1054, 1014, 901, 808, 753. [α]20 D= 47.1 (*c*=0.7, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.35 (m, 1H),

7.20 – 7.18 (m, 2H), 7.11 – 7.09 (m, 1H), 5.21 (s, 1H), 3.95 (s, 1H), 2.98 – 2.89 (m, 2H), 2.87 – 2.83 (m, 1H), 2.74 – 2.71 (m, 1H), 2.38 – 2.35 (m, 1H), 2.17 – 2.10 (m, 1H), 2.03 – 2.00 (m, 1H), 1.80 – 1.75 (m, 1H), 1.56 (s, 3H), 1.53 (s, 3H), 1.20 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.63, 160.63, 138.17, 138.14, 129.72, 127.96, 127.86, 126.37, 106.86, 97.23, 59.46, 56.56, 47.56, 35.99, 30.05, 25.38, 24.84, 22.86, 19.47. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{29}NO_4S$ $[M+Na]^+$: 414.1715; Found: 414.1712.



(*S*)-*N*-((*S*)-1-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl) methyl)-5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)-2-methylpropane-2-sulfinamide **11n**

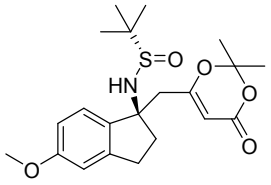
11n: Pale yellow syrup, 32% yield, dr > 40:1. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3436, 2927, 1734, 1630, 1584, 1461, 1390, 1255, 1203, 1053, 1014, 901, 778. [α]20 D= 35.9 (*c*=1.59, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 5.17 (s, 1H), 3.93 (d, *J* = 5.9 Hz, 1H), 3.81 (s, 3H), 3.09 (d, *J* = 14.2 Hz, 1H), 2.89 (d, *J* = 14.2 Hz, 1H), 2.83 (dt, *J* = 17.6, 4.4 Hz, 1H), 2.47 – 2.40 (m, 1H), 2.19 – 2.16 (m, 1H), 2.06 – 1.99 (m, 1H), 1.89 – 1.84 (m, 2H), 1.50 (s, 3H), 1.44 (s, 3H), 1.18 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.99, 160.84, 157.21, 138.15, 127.19, 126.28, 120.53, 109.05, 106.55, 97.12, 58.84, 56.41, 55.53, 46.41, 36.27, 25.04, 24.90, 23.40, 22.85, 17.90. **HRMS** (ESI) m/z calcd for $C_{21}H_{29}NO_5S$ $[M+Na]^+$: 430.1664; Found: 430.1662.



(*S*)-*N*-((*S*)-1-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-5-methoxy-2,3-dihydro-1*H*-inden-1-yl)-2-methylpropane-2-sulfinamide **11o**

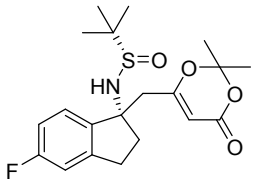
11o: Yellow syrup, 32% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3436, 3325, 2918, 2849, 2476, 2050, 1732, 1633, 1494, 1464, 1392, 1273, 1203, 1015, 964, 845, 753. [α]20 D= 45.8 (*c*=0.55, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.07 (d, *J* =

8.8 Hz, 1H), 6.77 (d, *J* = 7.4 Hz, 2H), 5.24 (s, 1H), 3.99 (s, 1H), 3.79 (s, 3H), 3.14 (dt, *J* = 15.5, 7.5 Hz, 1H), 2.90 (d, J = 14.2 Hz, 1H), 2.87 – 2.70 (m, 1H), 2.68 (d, *J* = 14.1 Hz, 1H), 2.56 – 2.51 (m, 1H), 2.43 – 2.36 (m, 1H), 1.63 (s, 3H), 1.60 (s, 3H), 1.16 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.87, 160.65, 145.77, 136.05, 124.77, 113.54, 109.78, 106.95, 97.00, 68.20, 56.18, 55.51, 45.73, 38.51, 29.98, 25.40, 24.97, 22.71. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{29}NO_5S$ [M+Na]$^+$: 430.1664; Found: 430.1662.



(*S*)-*N*-((*R*)-1-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl) methyl)-5-methoxy-2,3-dihydro-1*H*-inden-1-yl)-2-methylpropane-2-sulfinamide **11o'**

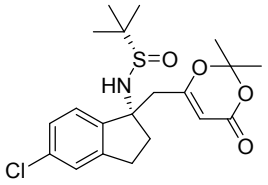
11o': Yellow syrup, 11% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3436, 2923, 2852, 1728, 1631, 1494, 1465, 1390, 1273, 1254, 1204, 1057, 1017, 904, 810. [α]20 D= 36.2 (*c*=0.17, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 7.8 Hz, 1H), 6.77 (brs, 2H), 5.29 (s, 1H), 3.93 – 3.68 (m, 4H), 3.15 (d, *J* = 12.1 Hz, 1H), 2.98 (dt, *J* = 14.7, 8.6 Hz, 1H), 2.74 (d, *J* = 13.7 Hz, 2H), 2.40 – 2.26 (m, 2H), 1.59 (s, 3H), 1.57 (s, 3H), 1.13 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.04, 160.67, 145.55, 135.76, 125.76, 112.59, 110.23, 106.71, 97.00, 67.88, 55.97, 55.53, 44.62, 40.61, 29.94, 25.45, 24.90, 22.69. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{29}NO_5S$ [M+Na]$^+$: 430.1664; Found: 430.1662.



(*S*)-*N*-((*S*)-1-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-5-fluoro-2,3-dihydro-1*H*-inden-1-yl)-2-methylpropane-2-sulfinamide **11p**

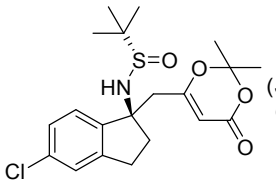
11p: Pale yellow syrup, 56% yield, dr > 40:1. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3442, 3231, 3093, 3049, 2958, 2232, 1728, 1631, 1487, 1391, 1274, 1251, 1204, 1056, 1015, 862, 817, 733. [α]20 D= 47.6 (*c*=0.13, CH_2Cl_2). **^{1}H NMR** (Chloroform-*d*, 400 MHz) δ 7.44 - 7.18 (m, 1H), 6.92 (td, *J* = 6.0, 3.1 Hz, 2H), 5.33 (d, *J* = 17.5 Hz, 1H), 4.26 (d, *J* = 44.4 Hz, 1H), 3.24 – 3.09 (m, 1H), 2.97 – 2.83 (m, 2H), 2.82 – 2.71(m, 1H), 2.67 – 2.30 (m, 2H), 1.61 (d, *J* = 12.0 Hz, 3H), 1.58 (d, *J* = 12.0 Hz, 3H), 1.15 (d,

J = 18.3 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.36, (167.21), 160.17, (160.03), 145.98, (145.89), 145.79, (145.70), 139.21, (139.01), 126.04, (125.95), 125.23, (125.14), 113.62, (113.39), 113.07, (112.85), 111.56, (111.34), 106.37, (106.15), 96.52, (96.49), 67.59, (67.18), 55.72, (55.50), 44.74, (43.72), 39.65, (37.92), 29.27, (29.24), 24.73, (24.66), 24.38, (24.30), 22.15, (22.08). **HRMS** (ESI) m/z calcd for $C_{20}H_{26}FNO_4S$ $[M+Na]^+$: 418.1464; Found: 418.1460.



(*S*)-*N*-((*S*)-5-chloro-1-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2,3-dihydro-1*H*-inden-1-yl)-2-methylpropane-2-sulfinamide **11q**

11q: Pale yellow syrup, 33% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3439, 3252, 2996, 2952, 1729, 1629, 1388, 1317, 1277, 1204, 1026, 903, 838. [α]20 D= 28.3 (*c*=0.11, CH_2Cl_2). **^{1}H NMR** (Chloroform-d, 300 MHz) δ 7.24 (d, *J* = 8.9 Hz, 1H), 7.10 (brs, 2H), 5.19 (s, 1H), 3.81 (s, 1H), 3.02 (d, *J* = 14.0 Hz, 1H), 2.93-2.83 (m, 1H), 2.74-2.70 (m, 1H), 2.64 (d, *J* = 14.0 Hz, 1H), 2.28 – 2.11 (m, 2H), 1.48 (s, 3H), 1.45 (s, 3H), 1.00 (9H, s). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.41, 160.44, 145.54, 141.99, 134.64, 126.61, 126.01, 125.24, 106.61, 96.96, 67.65, 55.92, 44.04, 40.12, 29.47, 25.21, 24.74, 22.45. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{26}ClNO_4S$ $[M+Na]^+$: 434.1169; Found: 434.1163.

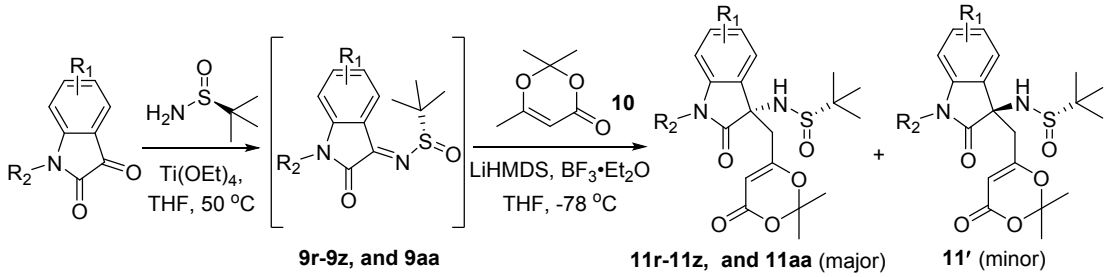


(*S*)-*N*-((*R*)-5-chloro-1-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2,3-dihydro-1*H*-inden-1-yl)-2-methylpropane-2-sulfinamide **11q'**

11q': Pale yellow syrup, 16% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3477, 3368, 3287, 3147, 2980, 1713, 1629, 1392, 1326, 1276, 1207, 1029, 906, 830. [α]20 D= 37.6 (*c*=0.32, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.13-7.03 (m, 3H), 5.19 (s, 1H), 4.10 (s, 1H), 3.05 (dt, *J* = 15.3, 8.5 Hz, 1H), 2.80 (d, *J* = 14.1 Hz, 2H), 2.60 (d, *J* = 14.2 Hz, 1H), 2.55 – 2.47 (m, 1H), 2.38 – 2.20 (m, 1H), 1.54 (s, 3H), 1.51 (s, 3H), 1.07 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 167.20, 160.25, 145.58, 142.35,

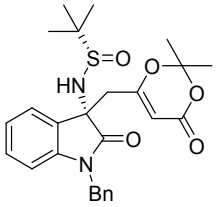
134.40, 126.87, 125.18, 125.04, 106.73, 96.84, 67.91, 56.06, 44.89, 37.87, 29.40, 25.04, 24.64, 22.38. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{26}ClNO_4S$ $[M+Na]^+$: 434.1169; Found: 434.1163.

2.2.2 Synthesis of isatin-derived products 11r-11z, and 11aa



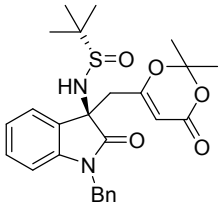
General procedure for isatin-derived ketimines (11r-11aa). A mixture of isatin-derived substrate (1.0 mmol), (*S*)-*tert*-butanesulfonamine (146 mg, 1.2 mmol) and titanium ethoxide (1.6 mL, 2.5 mmol) in dichloromethane (10 mL) was stirred under reflux for 12 h. The reaction was quenched with water and the resulting suspension was filtered through a short pad of anhydrous sodium sulfate. The solid cake was washed with dichloromethane, and the separated organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The resulting residue was dissolved in THF (10 mL). BF_3•Et_2O (0.13 mL, 1 mmol) was added at –78 °C. In the mean time, to a stirred solution of dioxinone **10** (284 mg, 2.0 mmol) in THF (10 mL) was added lithium bis(trimethylsilyl)amide (1.0 M in THF, 2.4 mL, 2.4 mmol) at –78 °C. The resulting mixtures were stirred at –78 °C for 1 h. Then, the solution of dioxinone-derived lithium dienolate was cannulated to the solution of sulfinimine at –78 °C. Stirring was continued at –78 °C for 3 h. The reaction was then quenched with saturated *aq.* NH_4Cl (3 mL) at –78 °C. The cooling bath was removed and the mixture was warmed to rt, followed by extraction with EtOAc (3 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with petroleum

ether/EtOAc (5:1 to 2:1) or purified by preparative chromatography to afford isatin-derived sulfinamides and their diasteromer. All yields represent isolated yields for two steps.



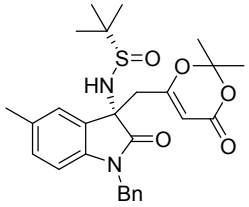
(*S*)-*N*-((*S*)-1-benzyl-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11r**

11r: Pale yellow foam, 64% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3401, 2959, 2869, 1720, 1633, 1614, 1468, 1377, 1273, 1202, 1173, 1072, 1016. [α]20 D= 52.0 (*c*=0.53, CH_2Cl_2). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.30-7.25 (m, 6H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 5.20 (s, 1H), 5.01 (d, *J* = 15.5 Hz, 1H), 4.79 (d, *J* = 15.5 Hz, 1H), 4.07 (s, 1H), 3.25 (s, 2H), 1.20 (s, 3H), 1.13 (s, 9H), 1.07 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 174.90, 165.00, 160.41, 142.89, 135.06, 130.46, 129.06, 128.15, 127.52, 126.92, 126.41, 123.01, 109.88, 106.67, 96.09, 63.07, 56.84, 44.13, 41.62, 24.47, 24.27, 22.43. **HRMS** (ESI) m/z calcd for $C_{26}H_{30}N_2O_5S$ $[M+Na]^+$: 505.1768; Found: 505.1766.



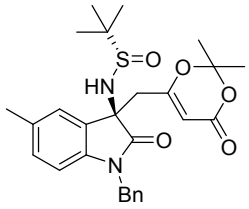
(*S*)-*N*-((*R*)-1-benzyl-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11r'**

11r': Pale yellow foam, 7% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3437, 3244, 2959, 1728, 1633, 1613, 1490, 1469, 1390, 1376, 1273, 1203, 1078, 1016, 900, 754. [α]20 D= 43.8 (*c*=0.11, CH_2Cl_2). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.36 – 7.25 (m, 5H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 5.21 (s, 1H), 4.95 (d, *J* = 15.5 Hz, 1H), 4.86 (d, *J* = 15.5 Hz, 1H), 4.36 (s, 1H), 3.10 (d, *J* = 13.7 Hz, 1H), 2.89 (d, *J* = 13.7 Hz, 1H), 1.30 (s, 3H), 1.21 (s, 9H), 1.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.26, 164.86, 160.36, 143.71, 135.27, 130.71, 129.05, 128.00, 126.24, 125.20, 122.95, 110.31, 106.75, 96.52, 62.47, 56.36, 44.75, 41.88, 24.76, 24.17, 22.71. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{30}N_2O_5S$ $[M+Na]^+$: 505.1768; Found: 505.1766.



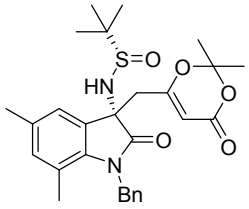
(*S*)-*N*-((*S*)-1-benzyl-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-5-methyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11s**

11s: Pale yellow syrup, 59% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3230, 2959, 1721, 1632, 1603, 1496, 1390, 1273, 1202, 1064, 902, 812, 735. [α]20 D= 54.9 (*c*=0.61, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.38 (s, 1H), 7.30 – 7.27 (m, 5H), 7.06 (d, *J* = 7.1 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.18 (s, 1H), 4.99 (d, *J* = 15.5 Hz, 1H), 4.74 (d, *J* = 15.5 Hz, 1H), 4.12 (s, 1H), 3.22 (d, *J* = 3.1 Hz, 2H), 2.34 (s, 3H), 1.22 (s, 3H), 1.15 (s, 9H), 1.09 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 174.80, 165.11, 160.48, 140.39, 135.11, 132.65, 130.68, 128.94, 128.01, 127.48, 127.43, 126.19, 109.59, 106.57, 95.95, 63.09, 56.74, 44.00, 41.54, 24.40, 24.27, 22.41, 21.16. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{32}N_2O_5S$ $[M+Na]^+$: 519.1930; Found: 519.1923.



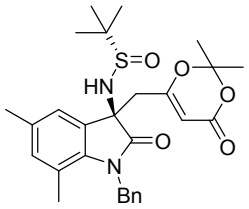
(*S*)-*N*-((*R*)-1-benzyl-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-5-methyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11s'**

11s': Pale yellow syrup, 5% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3408, 2959, 2869, 1720, 1631, 1497, 1376, 1273, 1252, 1078, 1014, 902, 811, 731. [α]20 D= 48.7(*c*=0.17, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.41 – 7.26 (m, 5H), 7.12 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.21 (s, 1H), 4.95 – 4.84 (m, 2H), 4.35 (s, 1H), 3.11 (d, *J* = 13.7 Hz, 1H), 2.88 (d, *J* = 13.7 Hz, 1H), 2.33 (s, 3H), 1.32 (s, 3H), 1.23 (s, 9H), 1.10 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 176.21, 165.01, 160.48, 141.21, 135.34, 132.60, 131.02, 129.01, 127.93, 127.75, 126.81, 125.13, 110.07, 106.70, 96.44, 62.53, 56.38, 44.69, 41.85, 24.78, 24.21, 22.71, 21.20. **HRMS** (ESI) m/z calcd for $C_{27}H_{32}N_2O_5S$ $[M+Na]^+$: 519.1930; Found: 519.1923.



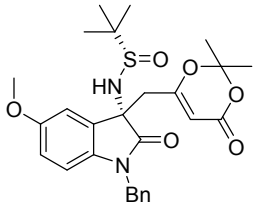
(*S*)-*N*-((*S*)-1-benzyl-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-5,7-dimethyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11t**

11t: Pale yellow syrup, 45% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3435, 3234, 2960, 2248, 1719, 1633, 1605, 1483, 1390, 1273, 1203, 1069, 904, 731. [α]20 D= 25.8 (*c*=0.25, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.31-7.24 (m, 4H), 7.15 (d, *J* = 6.4 Hz, 2H), 6.84 (s, 1H), 5.37 (d, *J* = 16.8 Hz, 1H), 5.16 (s, 1H), 4.93 (d, *J* = 16.8 Hz, 1H), 4.19 (s, 1H), 3.23 (d, *J* = 1.4 Hz, 2H), 2.31 (s, 3H), 2.21 (s, 3H), 1.34 (s, 3H), 1.29 (s, 3H), 1.17 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 175.97, 165.31, 160.51, 138.41, 136.80, 134.76, 132.70, 128.92, 127.49, 126.78, 125.61, 125.34, 120.30, 106.57, 95.81, 62.53, 56.72, 45.09, 41.75, 24.86, 24.19, 22.44, 20.84, 18.70. **HRMS** (ESI) *m/z* calcd for $C_{28}H_{34}N_2O_5S$ $[M+Na]^+$: 533.2081; Found: 533.2085.



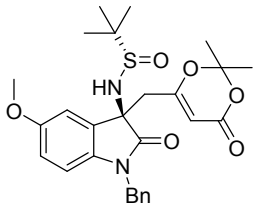
(*S*)-*N*-((*R*)-1-benzyl-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-5,7-dimethyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11t'**

11t': Pale yellow syrup, 15% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3436, 3253, 2958, 2923, 1725, 1705, 1637, 1604, 1497, 1453, 1380, 1279, 1207, 1060, 1013, 908, 863. [α]20 D= 66.2 (*c*=0.25, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.35 – 7.23 (m, 5H), 6.97 (s, 1H), 6.85 (s, 1H), 5.23 – 5.17 (m, 2H), 5.04 (d, *J* = 16.8 Hz, 1H), 4.41 (s, 1H), 3.10 (d, *J* = 13.8 Hz, 1H), 2.86 (d, *J* = 13.8 Hz, 1H), 2.29 (s, 3H), 2.18 (s, 3H), 1.41 (s, 3H), 1.35 (s, 3H), 1.22 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.39, 165.27, 160.47, 139.32, 137.27, 134.99, 132.59, 128.97, 127.31, 125.98, 124.56, 120.66, 106.70, 96.32, 61.90, 56.31, 45.84, 42.37, 24.74, 24.65, 22.71, 20.85, 18.75. **HRMS** (ESI) *m/z* calcd for $C_{28}H_{34}N_2O_5S$ $[M+Na]^+$: 533.2081; Found: 533.2084.



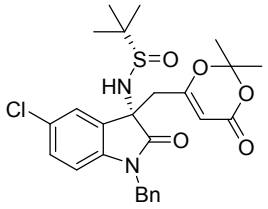
(*S*)-*N*-((*S*)-1-benzyl-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-5-methoxy-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11u**

11u: Pale yellow syrup, 63% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3437, 2957, 1725, 1632, 1495, 1390, 1275, 1203, 1047, 1014, 812. [α]20 D= 50.7 (*c*=0.06, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.28 (d, 5H), 7.17 (d, *J* = 2.5 Hz, 1H), 6.79 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.68 (d, *J* = 8.6 Hz, 1H), 5.20 (s, 1H), 4.98 (d, *J* = 15.5 Hz, 1H), 4.75 (d, *J* = 15.5 Hz, 1H), 4.15 (s, 1H), 3.77 (s, 3H), 3.22 (d, *J* = 3.2 Hz, 2H), 1.25 (s, 3H), 1.15 (s, 9H), 1.12 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 174.53, 164.98, 160.39, 156.03, 135.99, 135.06, 128.95, 128.01, 127.60, 127.41, 114.91, 113.74, 110.30, 106.60, 96.01, 63.37, 56.81, 55.96, 44.08, 41.58, 24.45, 24.31, 22.37. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{32}N_2O_6S$ $[M+Na]^+$: 535.1873; Found: 535.1876.



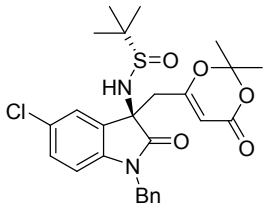
(*S*)-*N*-((*R*)-1-benzyl-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-5-methoxy-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11u'**

11u': Pale yellow syrup, 6% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3438, 3238, 2958, 2249, 1720, 1631, 1604, 1495, 1459, 1390, 1275, 1202, 1076, 1014, 903, 812, 730. [α]20 D= 43.1 (*c*=0.15, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.40 – 7.28 (m, 5H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.78 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 1H), 5.22 (s, 1H), 4.88 (d, *J* = 3.4 Hz, 2H), 4.41 (s, 1H), 3.76 (s, 3H), 3.09 (d, *J* = 13.7 Hz, 1H), 2.86 (d, *J* = 13.7 Hz, 1H), 1.35 (s, 3H), 1.22 (s, 9H), 1.14 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 175.97, 164.88, 160.41, 156.14, 136.92, 135.29, 129.02, 127.95, 127.74, 126.48, 114.81, 113.43, 110.76, 106.76, 96.51, 62.80, 56.43, 55.94, 44.77, 41.87, 24.77, 24.35, 22.70. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{32}N_2O_6S$ $[M+Na]^+$: 535.1873; Found: 535.1882.



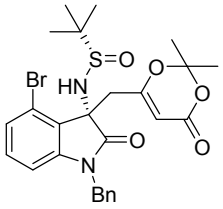
(*S*)-*N*-((*S*)-1-benzyl-5-chloro-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11v**

11v: Pale yellow syrup, 40% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3446, 3204, 2983, 1729, 1634, 1487, 1434, 1392, 1273, 1202, 1171, 1080, 901, 813, 752. [α]20 D= 78.1 (*c*=1.66, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (s, 1H), 7.31 (m, 6H), 6.70 (d, *J* = 8.4 Hz, 1H), 5.22 (s, 1H), 4.96 (d, *J* = 16.1 Hz, 1H), 4.80 (d, *J* = 15.6 Hz, 1H), 4.14 (s, 1H), 3.27 – 3.18 (m, 2H), 1.32 (s, 3H), 1.16 (s, 9H), 1.08 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 174.38, 164.49, 160.18, 141.32, 134.57, 130.30, 129.12, 128.27, 127.39, 127.16, 110.87, 106.68, 96.21, 63.20, 57.03, 44.26, 41.55, 24.71, 24.24, 22.40. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{29}N_2O_5ClS$ $[M+Na]^+$: 539.1378; Found: 539.1376.



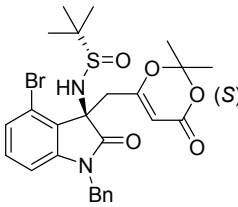
(*S*)-*N*-((*R*)-1-benzyl-5-chloro-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11v'**

11v': Pale yellow syrup, 4% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3443, 2927, 1725, 1637, 1485, 1438, 1391, 1273, 1201, 1172, 1080, 904, 812. [α]20 D= 28.2 (*c*=0.81, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.24 – 7.13 (m, 7H), 6.58 (d, *J* = 8.3 Hz, 1H), 5.15 (s, 1H), 4.85 (d, *J* = 15.4 Hz, 1H), 4.75 (d, *J* = 15.7 Hz, 1H), 4.31 (s, 1H), 2.96 (d, *J* = 13.6 Hz, 1H), 2.76 (d, *J* = 13.6 Hz, 1H), 1.33 (s, 3H), 1.14 (s, 9H), 1.03 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 175.97, 164.32, 160.17, 142.26, 134.82, 130.66, 129.20, 128.21, 127.70, 126.73, 111.39, 106.87, 96.78, 62.61, 56.61, 44.91, 41.99, 25.07, 24.32, 22.75. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{29}N_2O_5ClS$ $[M+Na]^+$: 539.1378; Found: 539.1376.



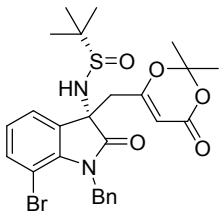
(*S*)-*N*-((*S*)-1-benzyl-4-bromo-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11w**

11w: Gray solid, m.p.: 120-122 ℃, 35% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3443, 3203, 2956, 1731, 1634, 1603, 1455, 1391, 1274, 1202, 1047, 1016, 917, 730. [α]20 D= 54.4 (*c*=0.15, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.20 – 7.08 (m, 2H), 6.71 (dd, *J* = 7.5, 1.1 Hz, 1H), 5.25 (s, 1H), 4.95 (d, *J* = 15.6 Hz, 1H), 4.81 (d, *J* = 15.6 Hz, 1H), 4.31 (s, 1H), 3.50 (d, *J* = 13.6 Hz, 1H), 3.10 (d, *J* = 13.6 Hz, 1H), 1.24 (s, 9H), 1.19 (s, 3H), 0.97 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 176.03, 164.60, 160.36, 146.14, 134.77, 132.16, 129.12, 128.13, 127.81, 127.22, 123.27, 121.89, 109.28, 106.64, 96.14, 63.93, 56.40, 45.04, 39.00, 24.38, 24.26, 22.89. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{29}BrN_2O_5S$ $[M+Na]^+$: 583.0878; Found: 583.0875.



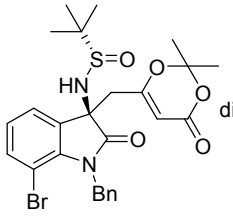
(*S*)-*N*-((*R*)-1-benzyl-4-bromo-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11w'**

11w': Gray solid, m.p.: 130-132 ℃, 17% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3454, 3158, 2955, 2865, 1734, 1634, 1603, 1581, 1454, 1388, 1270, 1202, 1168, 1051, 1014, 851, 778. [α]20 D= 49.9 (*c*=0.19, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 5H), 7.21 – 7.10 (m, 2H), 6.75 (dd, *J* = 7.6, 0.9 Hz, 1H), 5.28 (s, 1H), 4.95 (d, *J* = 15.4 Hz, 1H), 4.84 (d, *J* = 15.4 Hz, 1H), 4.12 (s, 1H), 3.40 (d, *J* = 13.6 Hz, 1H), 3.25 (d, *J* = 13.6 Hz, 1H), 1.22 (s, 9H), 1.21 (s, 3H), 0.97 (s, 3H). **^{13}C NMR** (75 MHz,Chloroform-*d*) δ 173.32, 164.32, 160.32, 144.76, 134.66, 131.74, 129.11, 128.28, 127.78, 127.30, 126.56, 120.91, 108.90, 106.60, 96.24, 64.64, 57.25, 44.57, 39.24, 24.52, 24.04, 22.29. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{29}BrN_2O_5S$ $[M+Na]^+$: 583.0878; Found: 583.0875.



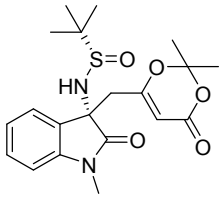
(*S*)-*N*-((*S*)-1-benzyl-7-bromo-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11x**

11x: Pale yellow syrup, 42% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3233, 2960, 2868, 1722, 1634, 1607, 1451, 1391, 1274, 1203, 1051, 1016, 901, 849, 733. [α]20 D= 14.0 (*c*=0.35, CH_2Cl_2). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 6.5 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.21 (q, *J* = 7.7 Hz, 5H), 6.98 (t, *J* = 7.8 Hz, 1H), 5.36 (s, 2H), 5.15 (s, 1H), 4.50 (s, 1H), 3.26 – 3.14 (m, 2H), 1.33 (s, 3H), 1.21 (s, 3H), 1.09 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 175.92, 164.63, 160.27, 140.45, 136.54, 136.23, 129.75, 128.64, 127.46, 126.43, 125.91, 124.36, 106.76, 103.17, 96.08, 62.41, 57.00, 55.33, 44.76, 41.49, 24.96, 24.07, 22.20. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{29}BrN_2O_5S$ $[M+Na]^+$: 583.0878; Found: 583.0875.



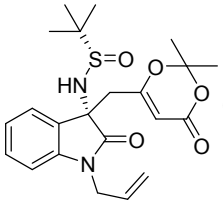
(*S*)-*N*-((*R*)-1-benzyl-7-bromo-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11x'**

11x': Yellow syrup, 18% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3444, 3206, 3091, 3064, 3033, 2868, 1720, 1633, 1609, 1578, 1497, 1390, 1273, 1202, 1163, 1062, 1014, 901, 849, 732. [α]20 D= 58.4 (*c*=0.36, CH_2Cl_2). **^{1}H NMR** (Chloroform-d, 400 MHz) δ 7.44 (1H, dd, *J* = 8.2, 1.1 Hz), 7.35 – 7.23 (6H, m), 6.97 (1H, t, *J* = 7.8 Hz), 5.43 (1H, d, *J* = 16.3 Hz), 5.27 (1H, d, *J* = 16.4 Hz), 5.20 (1H, s), 4.72 (1H, s), 3.16 (1H, d, *J* = 14.0 Hz), 2.90 (1H, d, *J* = 14.0 Hz), 1.34 (6H, s), 1.20 (9H, s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.19, 164.53, 160.11, 141.13, 136.83, 136.30, 128.81, 128.61, 128.55, 127.15, 126.55, 125.14, 124.14, 106.74, 103.21, 96.47, 61.73, 56.52, 45.34, 42.06, 24.79, 24.30, 22.65, 22.56. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{29}BrN_2O_5S$ $[M+Na]^+$: 583.0878; Found: 583.0875.



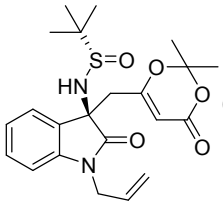
(*S*)-*N*-((*S*)-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-1-methyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11y**

11y: Pale yellow syrup, 78% yield, dr > 40:1. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3222, 2960, 2247, 1721, 1632, 1613, 1472, 1390, 1273, 1203, 1056, 902, 754, 732. [α]20 D= 66.8(*c*=0.45, CH_2Cl_2). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.14 (s, 1H), 4.23 (s, 1H), 3.24 (brs, 5H), 1.29 (s, 3H), 1.18 (s, 3H), 1.13 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 174.38, 165.01, 160.12, 143.31, 130.17, 126.46, 126.05, 122.74, 108.56, 106.18, 95.34, 62.61, 56.44, 41.35, 26.24, 24.41, 23.78, 22.09. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{26}N_2O_5S$ $[M+Na]^+$: 429.1460; Found: 429.1449.



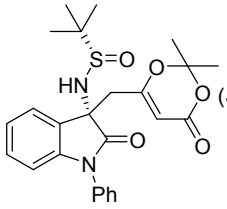
(*S*)-*N*-((*S*)-1-allyl-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11z**

11z: Pale yellow syrup, 50% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3446, 3231, 2960, 2868, 1738, 1634, 1613, 1489, 1373, 1272, 1203, 1070, 1016, 901, 847, 753. [α]20 D= 80.2 (*c*=2.46, $CHCl_3$). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.82-5.75 (m, 1H), 5.24 (d, *J* = 4.5 Hz, 1H), 5.21 (s, 1H), 5.12 (d, *J* = 1.7 Hz, 1H), 4.40 (dd, *J* = 16.2, 5.2 Hz, 1H), 4.20 (dd, *J* = 16.1, 5.3 Hz, 1H), 4.00 (s, 1H), 3.19 (s, 2H), 1.24 (s, 3H), 1.22 (s, 3H), 1.10 (s, 9H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 174.52, 165.10, 160.35, 142.93, 130.65, 130.42, 126.78, 126.53, 122.99, 118.46, 109.70, 106.65, 95.91, 63.01, 56.80, 42.65, 41.80, 24.71, 24.34, 22.41. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{28}N_2O_5S$ $[M+Na]^+$: 455.1617; Found: 455.1615.



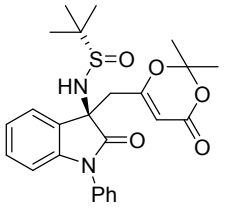
(*S*)-*N*-((*R*)-1-allyl-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **11z'**

11z': Pale yellow syrup, 25% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3439, 2924, 2853, 1726, 1633, 1613, 1491, 1391, 1274, 1203, 1074, 1016, 901, 755. [α]20 D= 56.5 (*c*=0.30, CCl_3). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.35 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 1H), 5.89-5.81 (m, 1H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.27 (d, *J* = 10.3 Hz, 1H), 5.15 (s, 1H), 4.42 (dd, *J* = 16.0, 5.2 Hz, 1H), 4.27 (s, 1H), 4.24 (d, *J* = 14.7 Hz, 1H), 3.04 (d, *J* = 13.9 Hz, 1H), 2.85 (d, *J* = 13.8 Hz, 1H), 1.35 (s, 3H), 1.31 (s, 3H), 1.20 (s, 9H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 176.00, 165.02, 143.85, 131.04, 130.82, 126.29, 125.13, 122.97, 118.84, 110.25, 106.79, 96.38, 62.38, 56.33, 43.15, 41.96, 24.80, 24.64, 22.79. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{28}N_2O_5S$ $[M+Na]^+$: 455.1617; Found: 455.1615.



(*S*)-*N*-((*S*)-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2-oxo-1-phenylindolin-3-yl)-2-methylpropane-2-sulfinamide **11aa**

11aa: Pale yellow syrup, 64% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3414, 3240, 2960, 2869, 2231, 1722, 1633, 1612, 1500, 1467, 1376, 1274, 1202, 1072, 903, 755, 730. [α]20 D= 64.1(*c*=0.28, CH_2Cl_2). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 5.24 (s, 1H), 4.14 (s, 1H), 3.39 – 3.27 (m, 2H), 1.35 (s, 3H), 1.20 (s, 3H), 1.16 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.17, 165.19, 160.40, 143.60, 133.65, 130.41, 129.92, 128.58, 126.95, 126.22, 125.98, 123.54, 110.22, 106.77, 95.93, 63.03, 56.87, 41.93, 25.02, 24.01, 22.40. **HRMS** (ESI) *m/z* calcd for $C_{25}H_{28}N_2O_5S$ $[M+Na]^+$: 491.1617; Found: 491.1615.



(*S*)-*N*-((*R*)-3-((2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)methyl)-2-oxo-1-phenylindolin-3-yl)-2-methylpropane-2-sulfinamide **11aa'**

11aa': Pale yellow syrup, 10% yield. **FTIR** (KBr, thin film) ν_{max} (cm^{-1}): 3424,

3247，2960, 2869, 2248, 1720, 1633, 1614, 1467, 1377, 1273, 1113, 1073, 848, 755, 732. [α]20 D= 50.1 (*c*=0.52, CH_2Cl_2). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.28 (m, 5H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 5.23 (s, 1H), 4.48 (s, 1H), 3.18 (d, *J* = 14.0 Hz, 1H), 2.93 (d, *J* = 14.0 Hz, 1H), 1.36 (s, 3H), 1.31 (s, 3H), 1.20 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 175.78, 165.12, 160.41, 144.79, 133.93, 130.81, 129.87, 128.51, 126.59, 126.41, 124.54, 123.39, 110.40, 106.79, 96.26, 62.38, 56.19, 41.56, 24.89, 24.36, 22.75. **HRMS** (ESI) *m/z* calcd for $C_{25}H_{28}N_2O_5S$ $[M+Na]^+$: 491.1617; Found: 491.1615.

2.3 References

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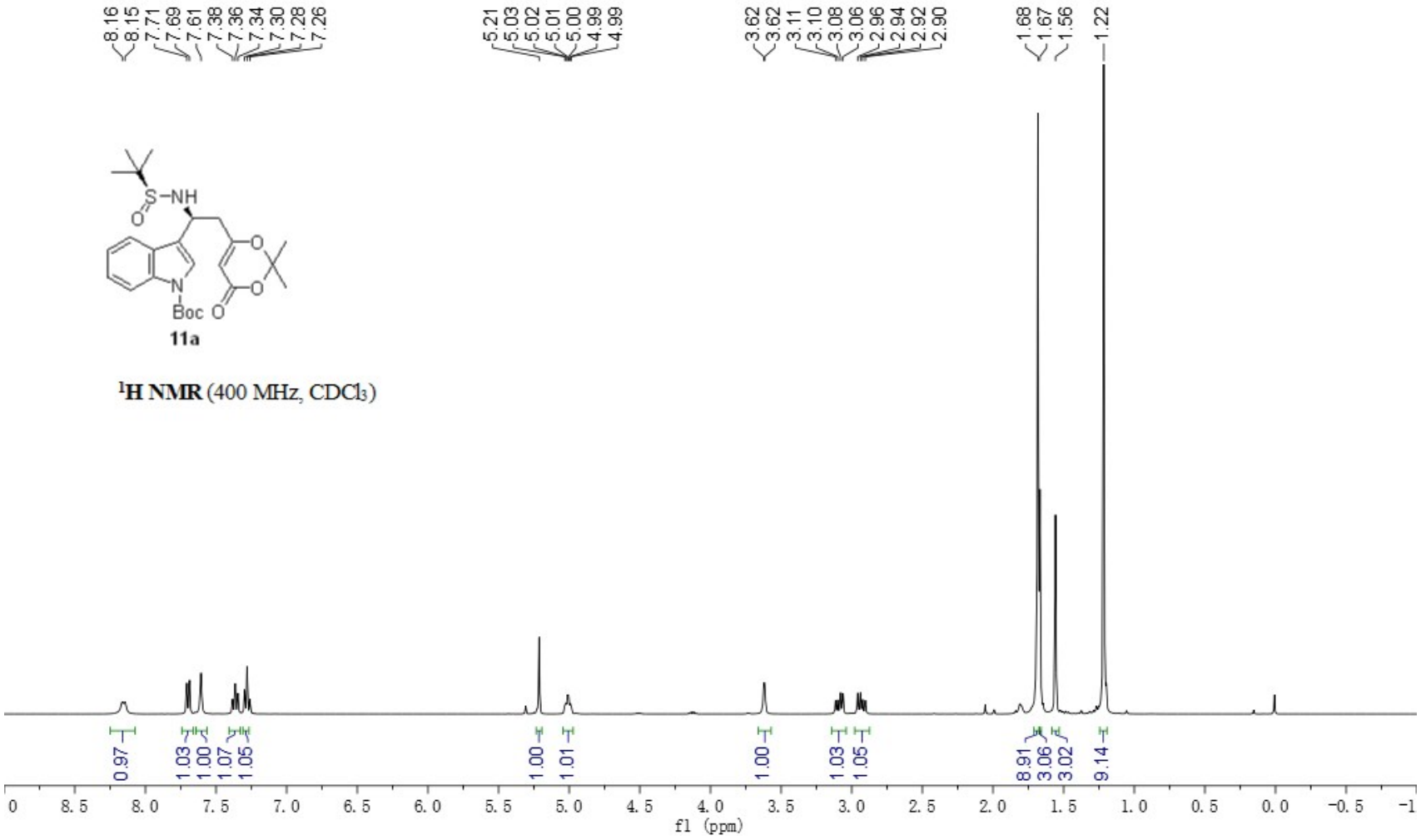
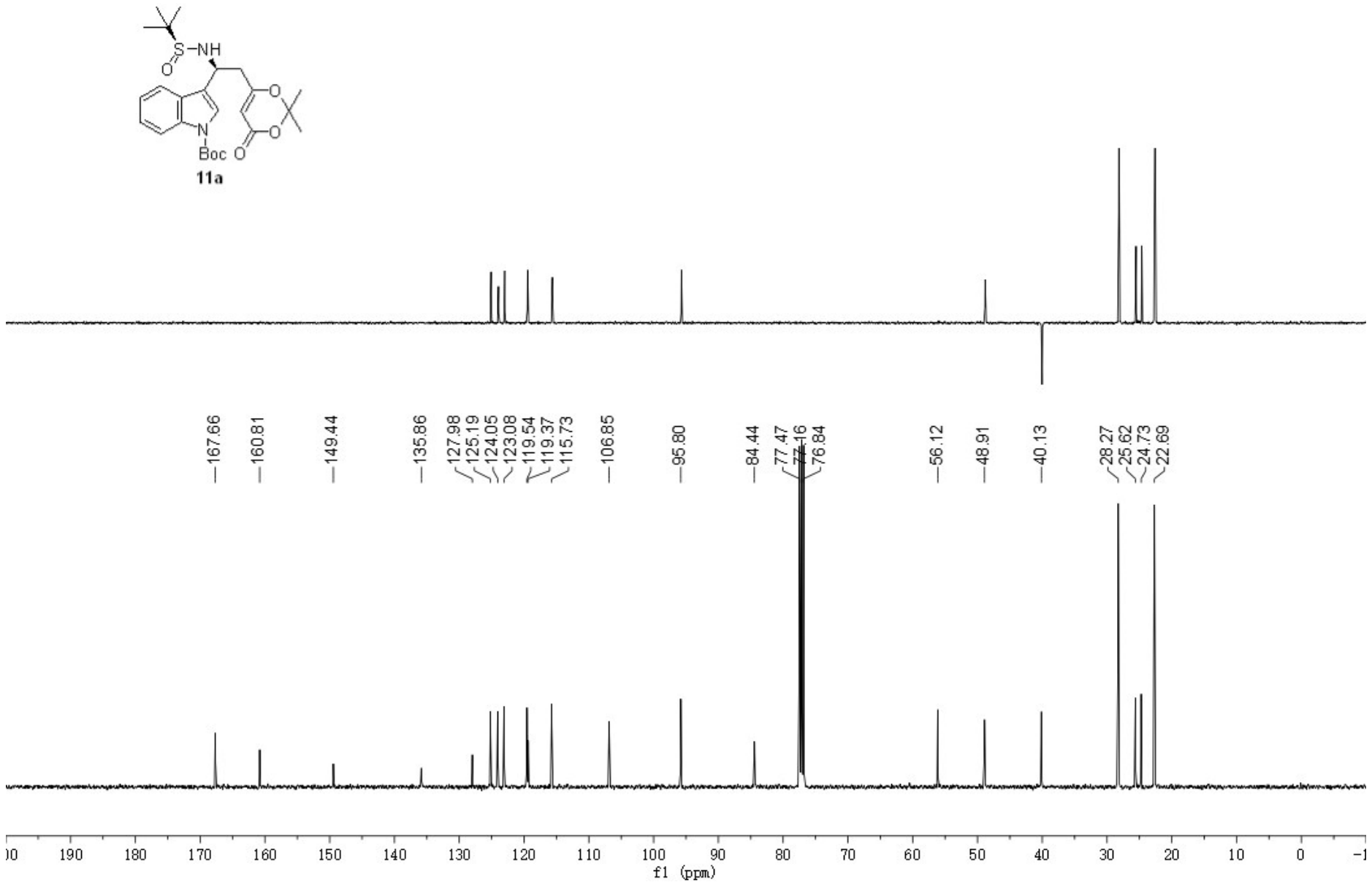
3. Copies of ^{1}H and ^{13}C NMR spectra



^{1}H NMR (400 MHz, $CDCl_3$)


S
NH
O
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N
Boc
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22.69
190
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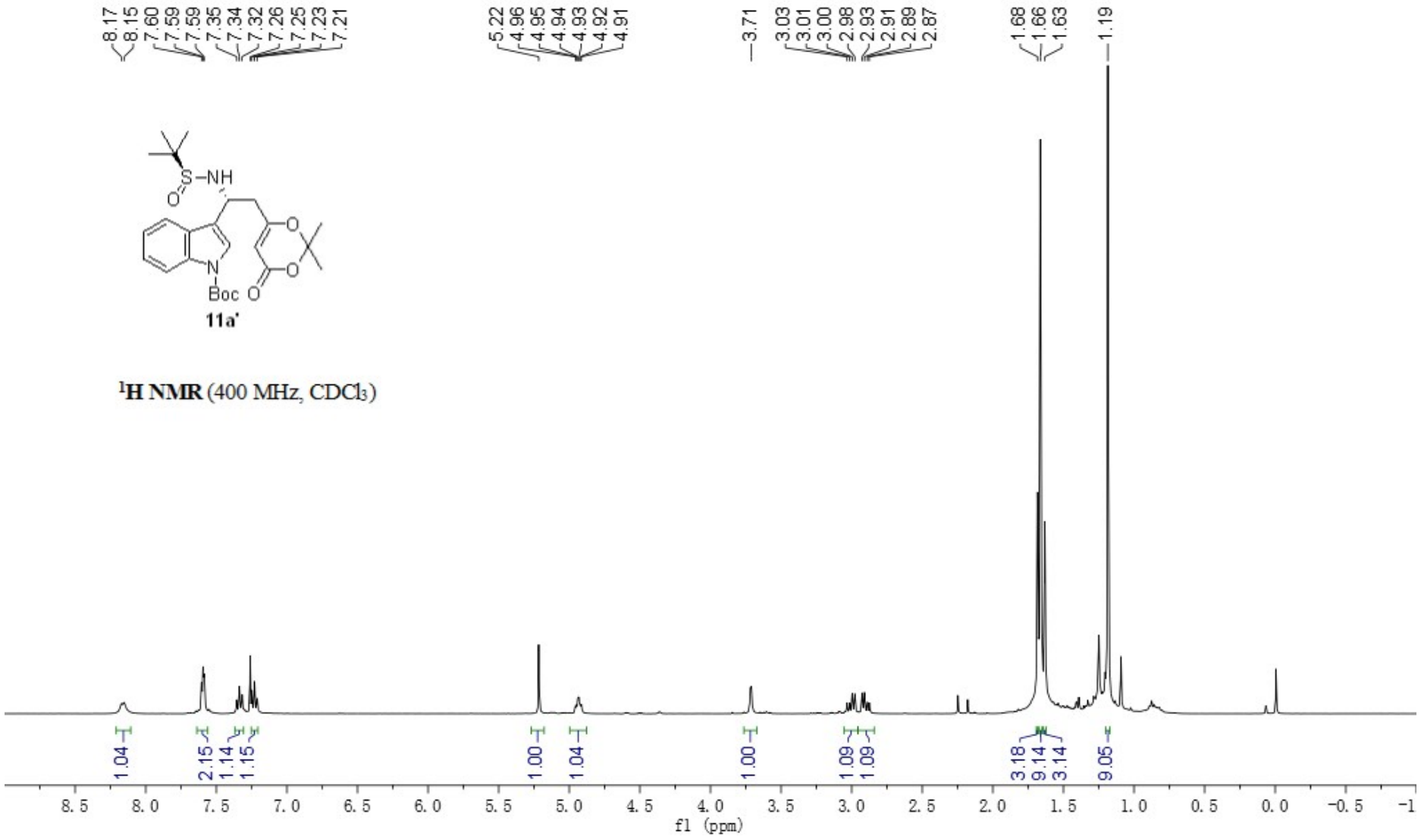
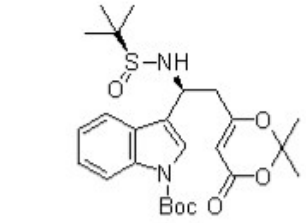
f1 (ppm)



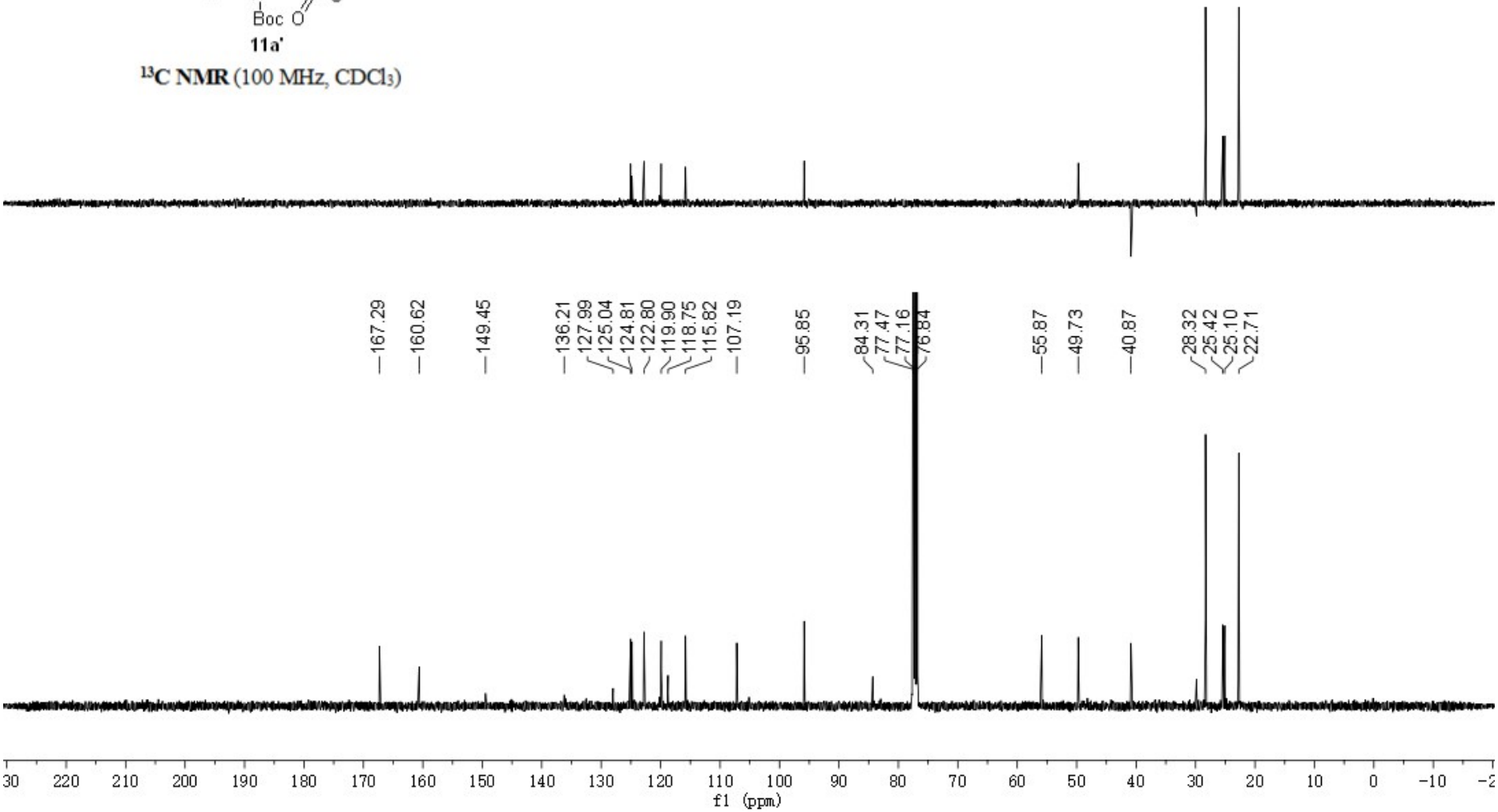
11a'

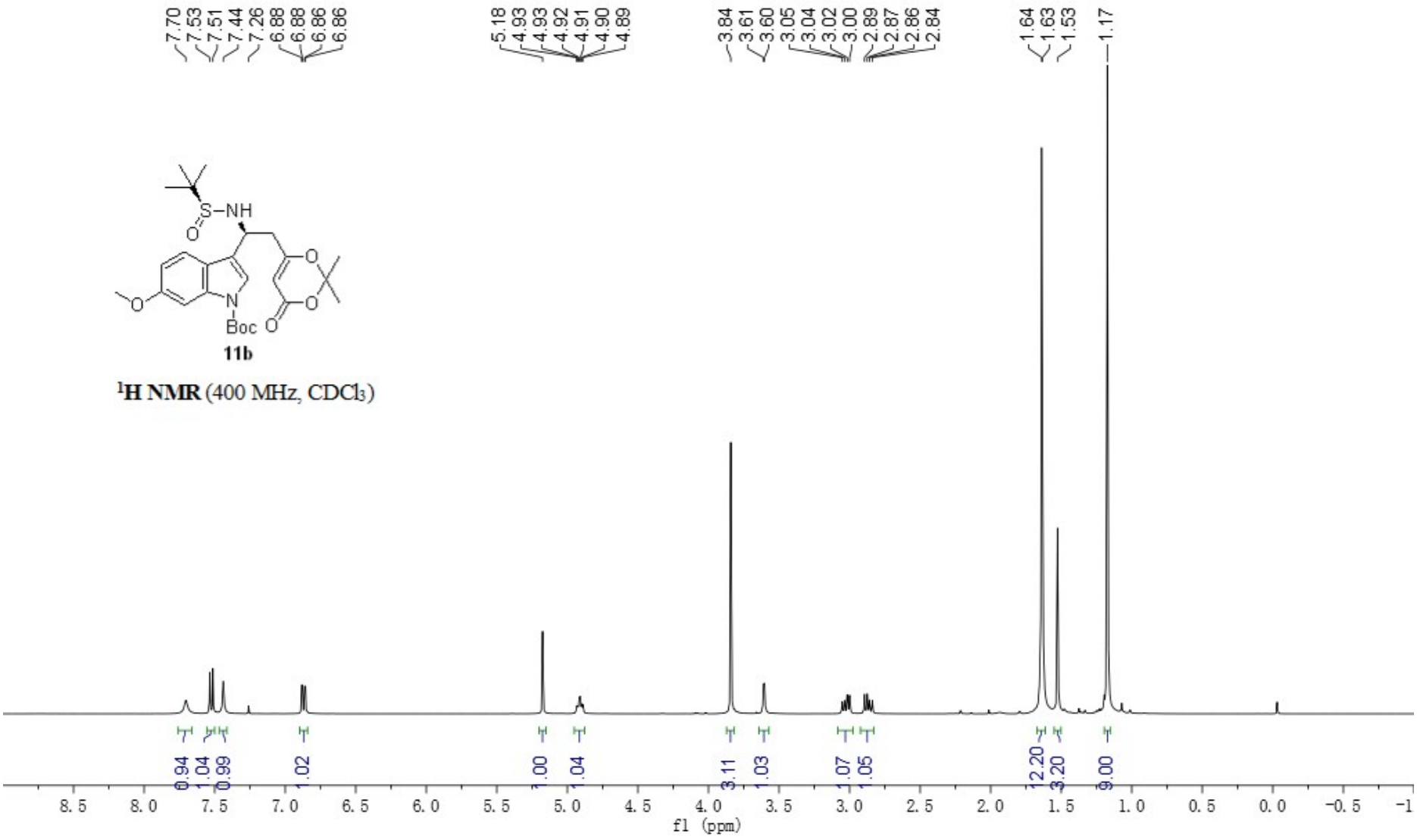
^{1}H NMR (400 MHz, $CDCl_3$)



11a'

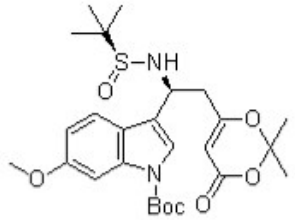
^{13}C NMR (100 MHz, $CDCl_3$)





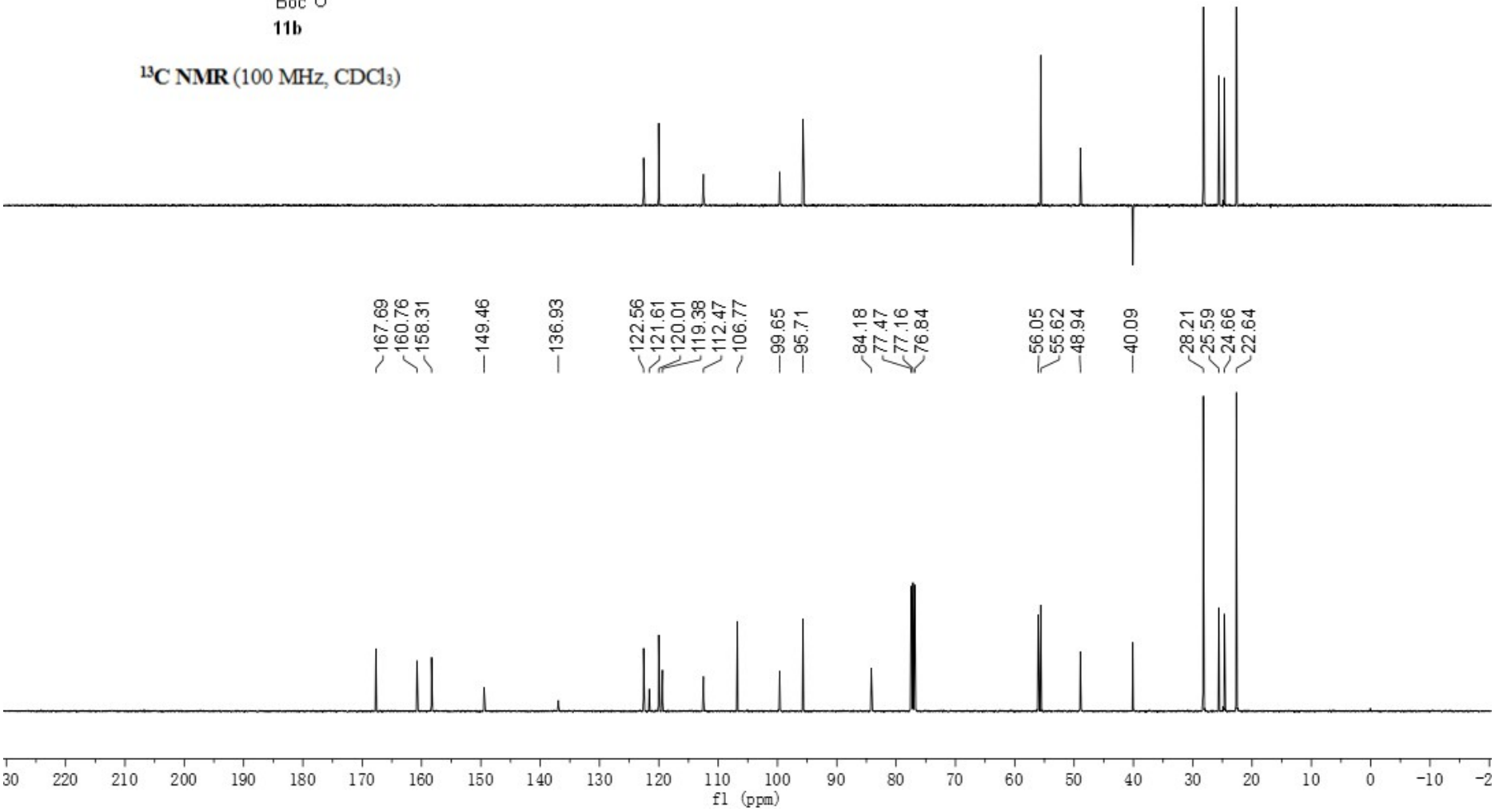
11b

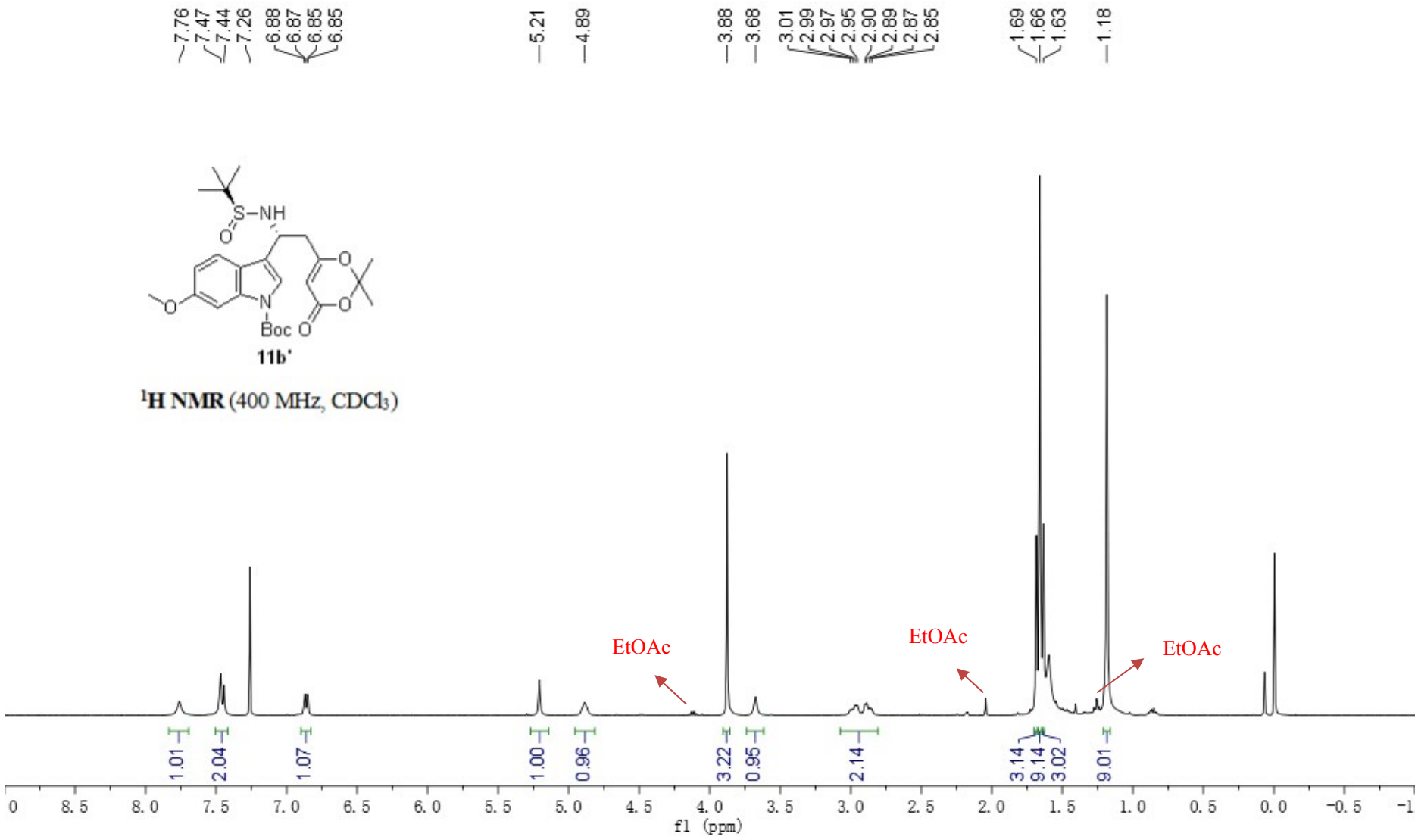
^{1}H NMR (400 MHz, $CDCl_3$)



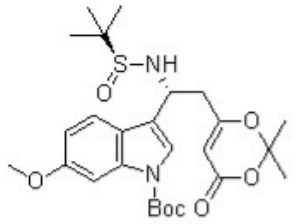
11b

^{13}C NMR (100 MHz, $CDCl_3$)



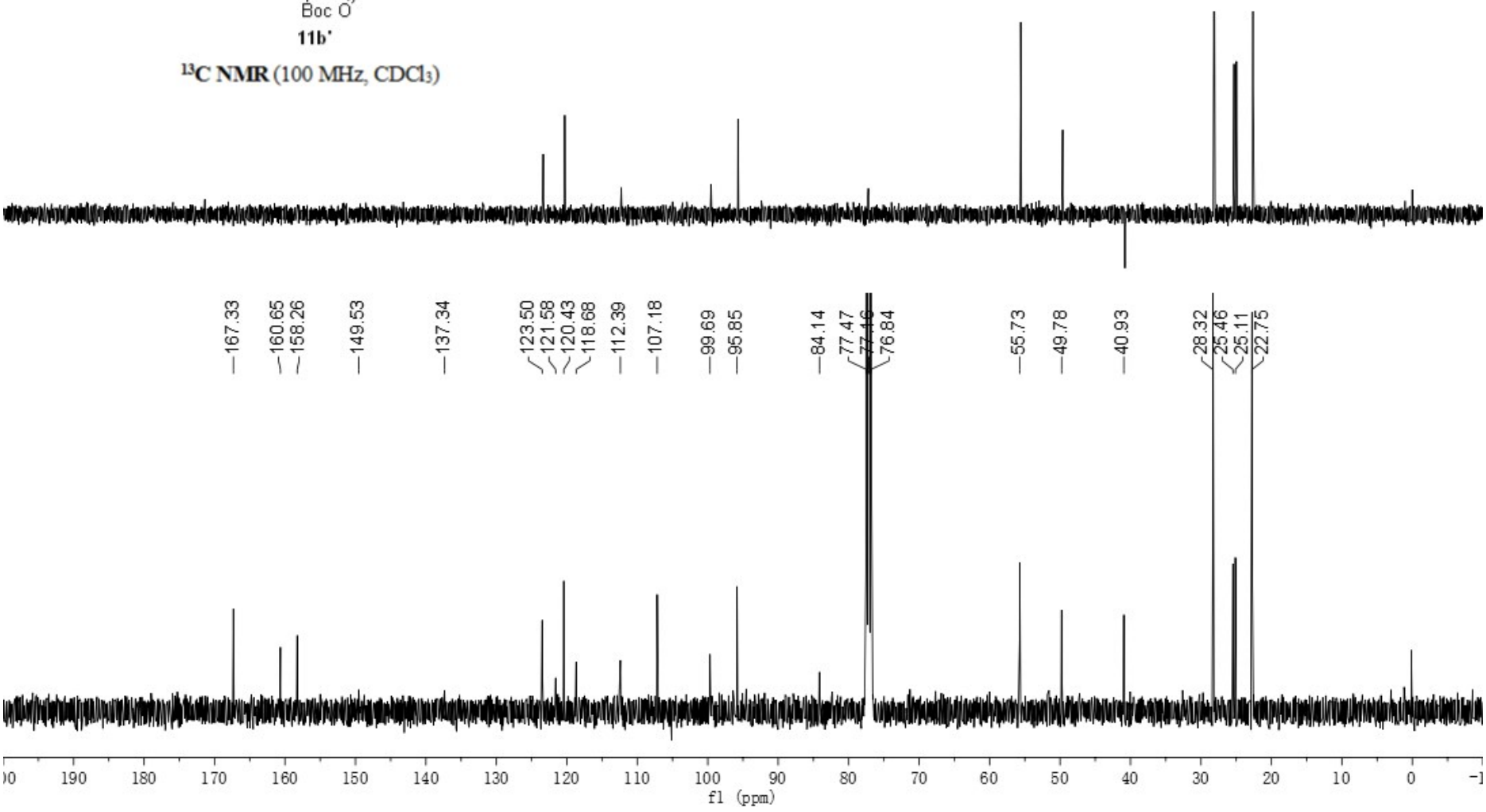


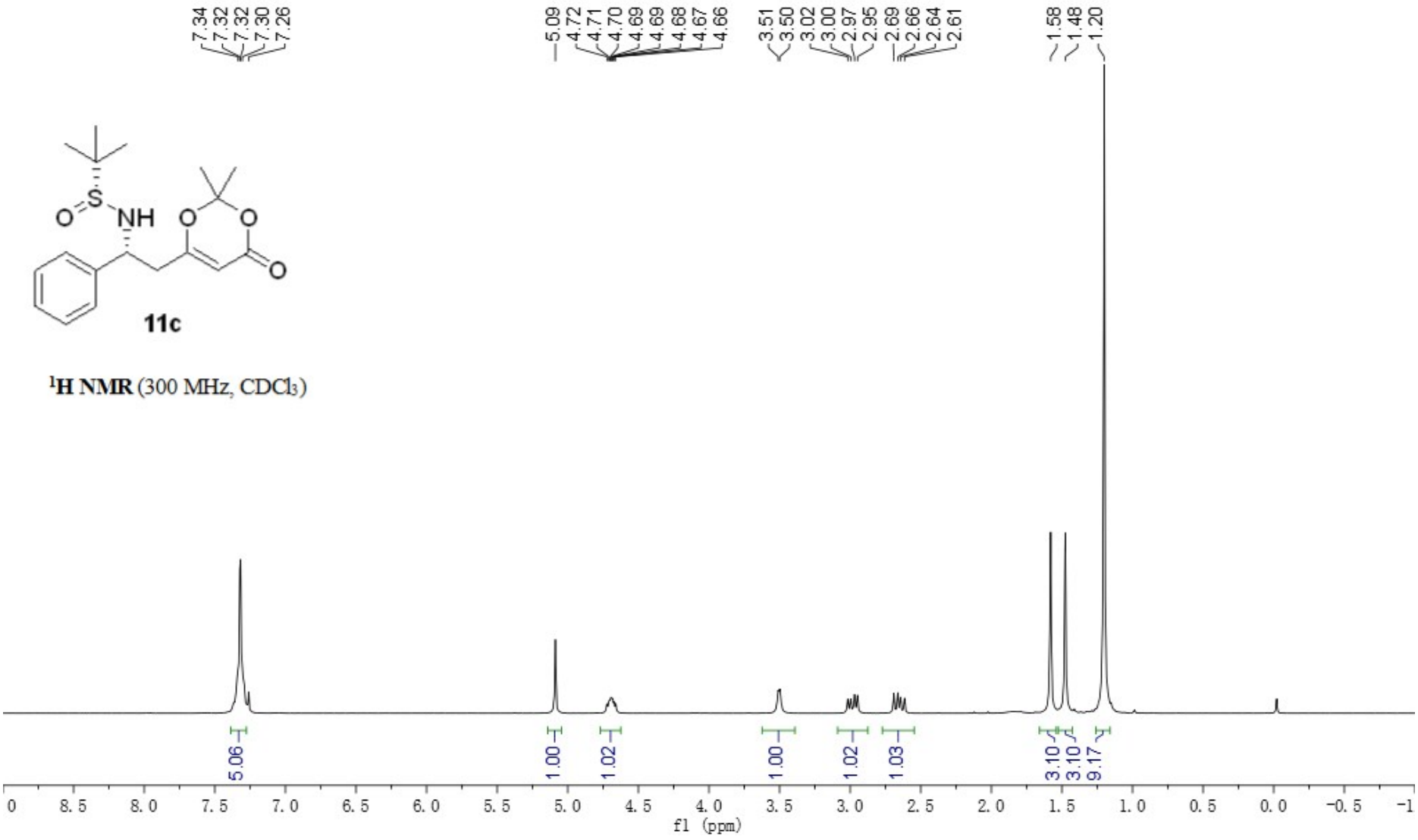
^{1}H NMR (400 MHz, $CDCl_3$)



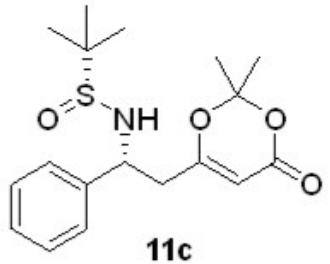
11b'

^{13}C NMR (100 MHz, $CDCl_3$)



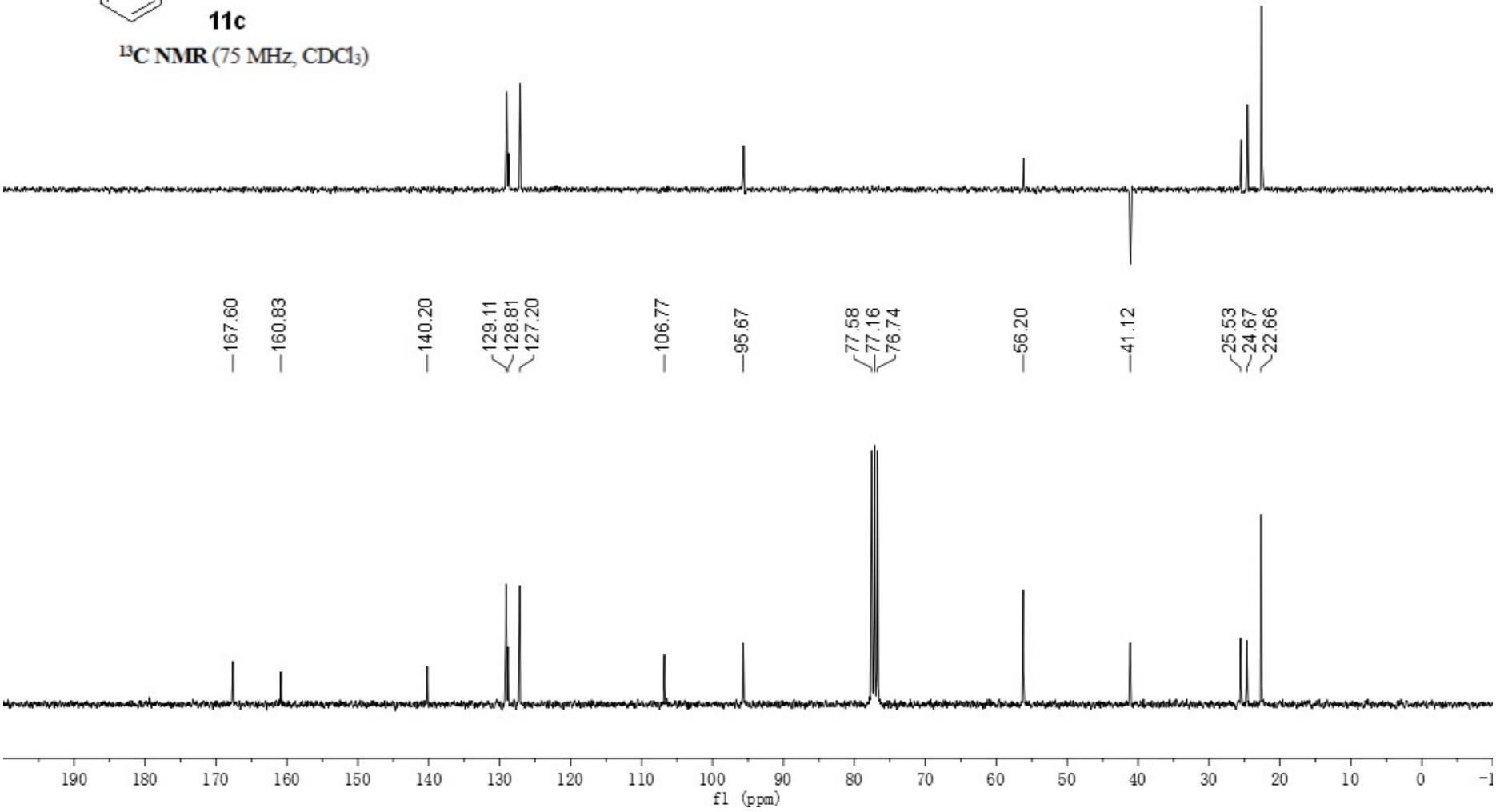


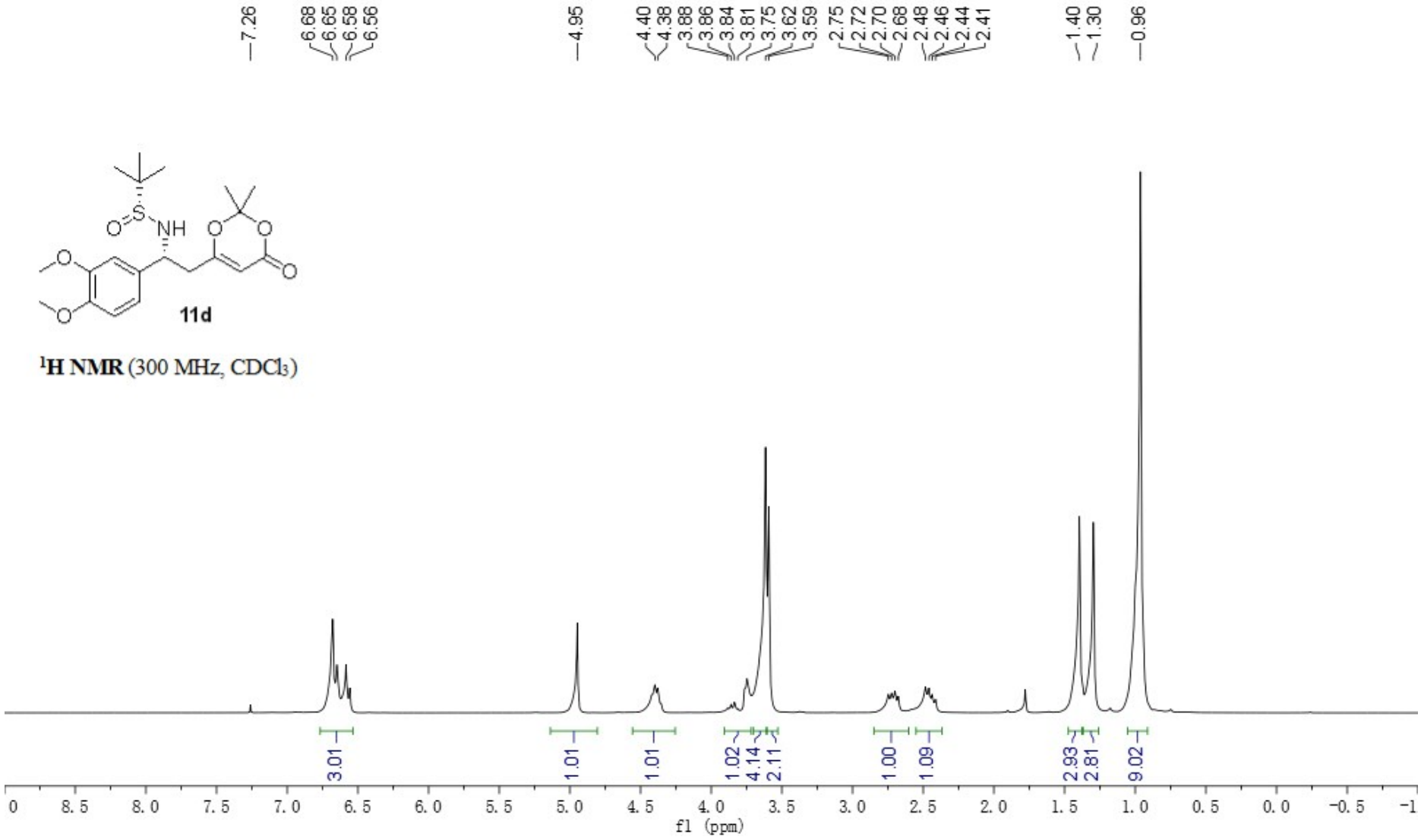
^{1}H NMR (300 MHz, $CDCl_3$)



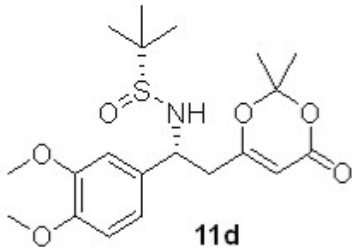
11c

^{13}C NMR (75 MHz, $CDCl_3$)



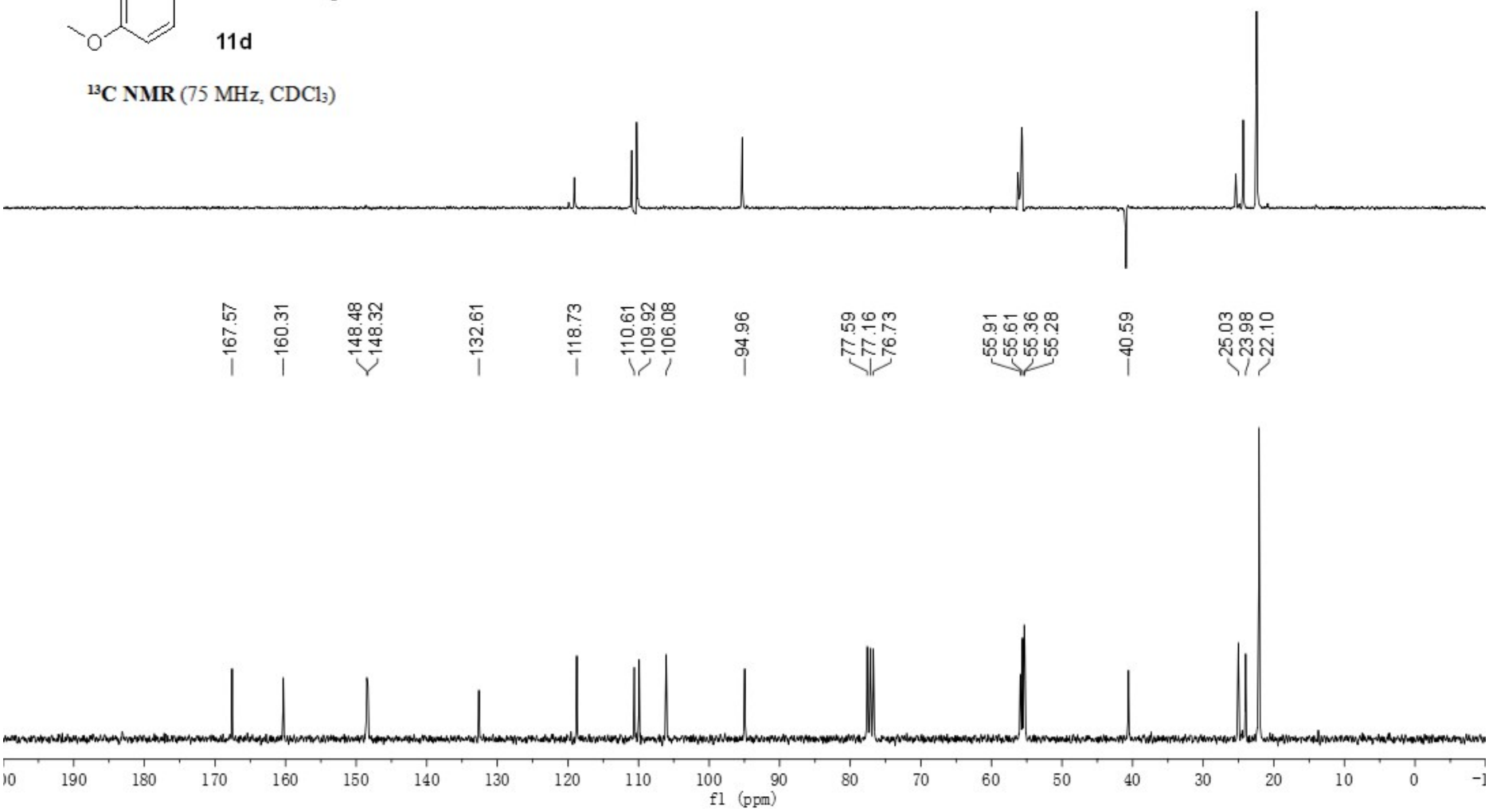


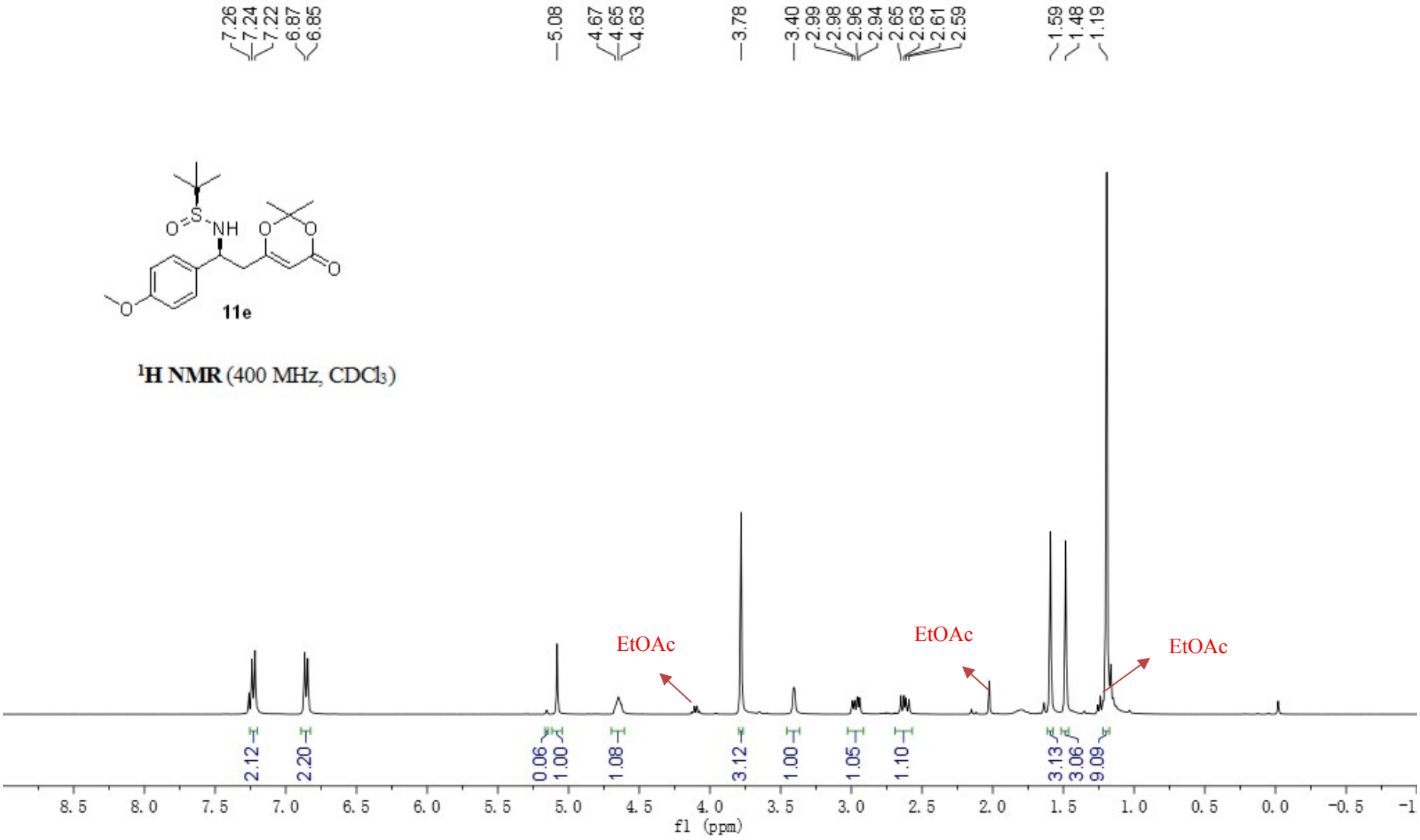
^{1}H NMR (300 MHz, $CDCl_3$)



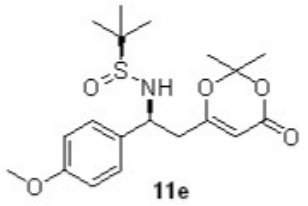
11d

^{13}C NMR (75 MHz, $CDCl_3$)



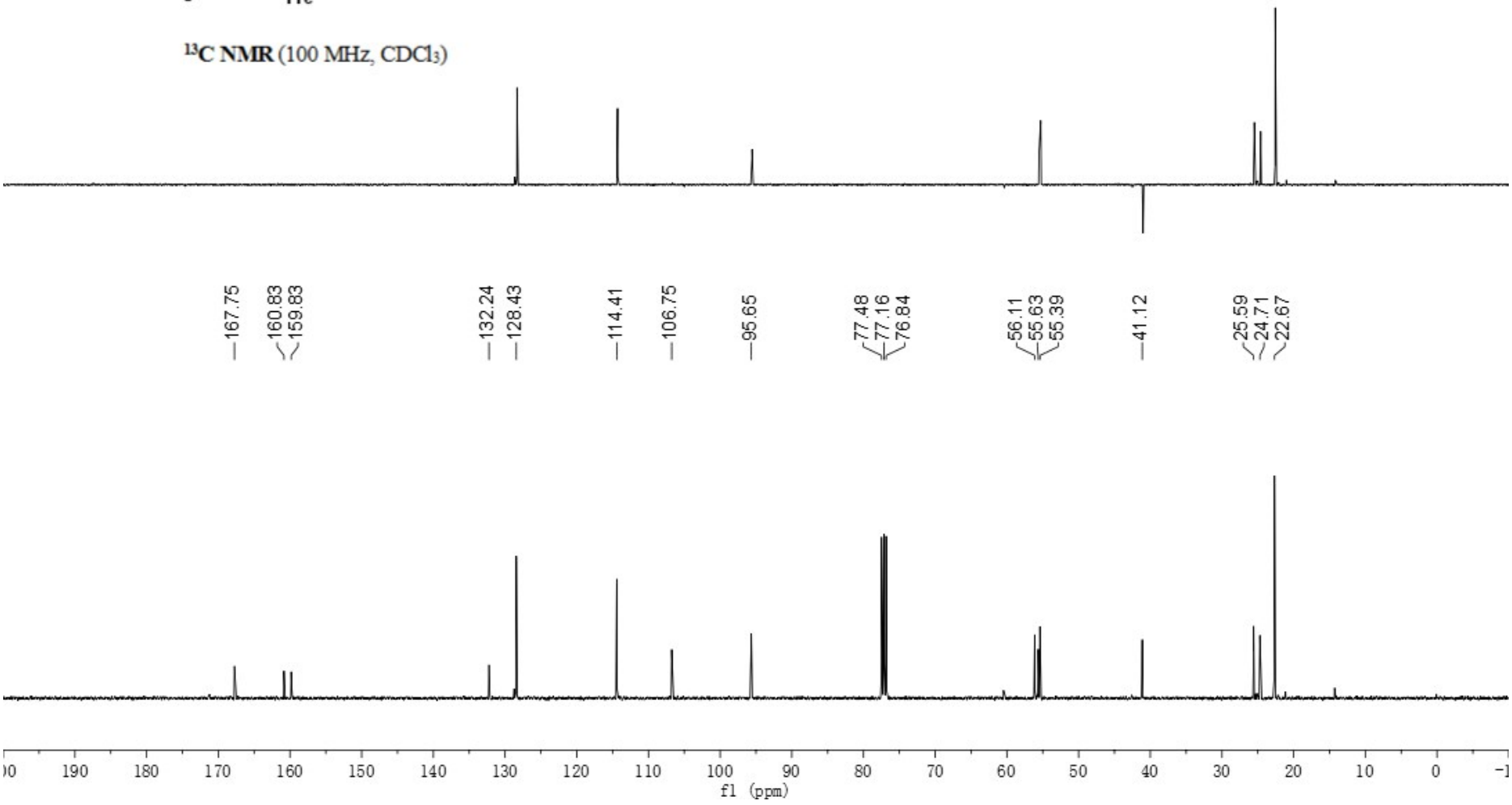


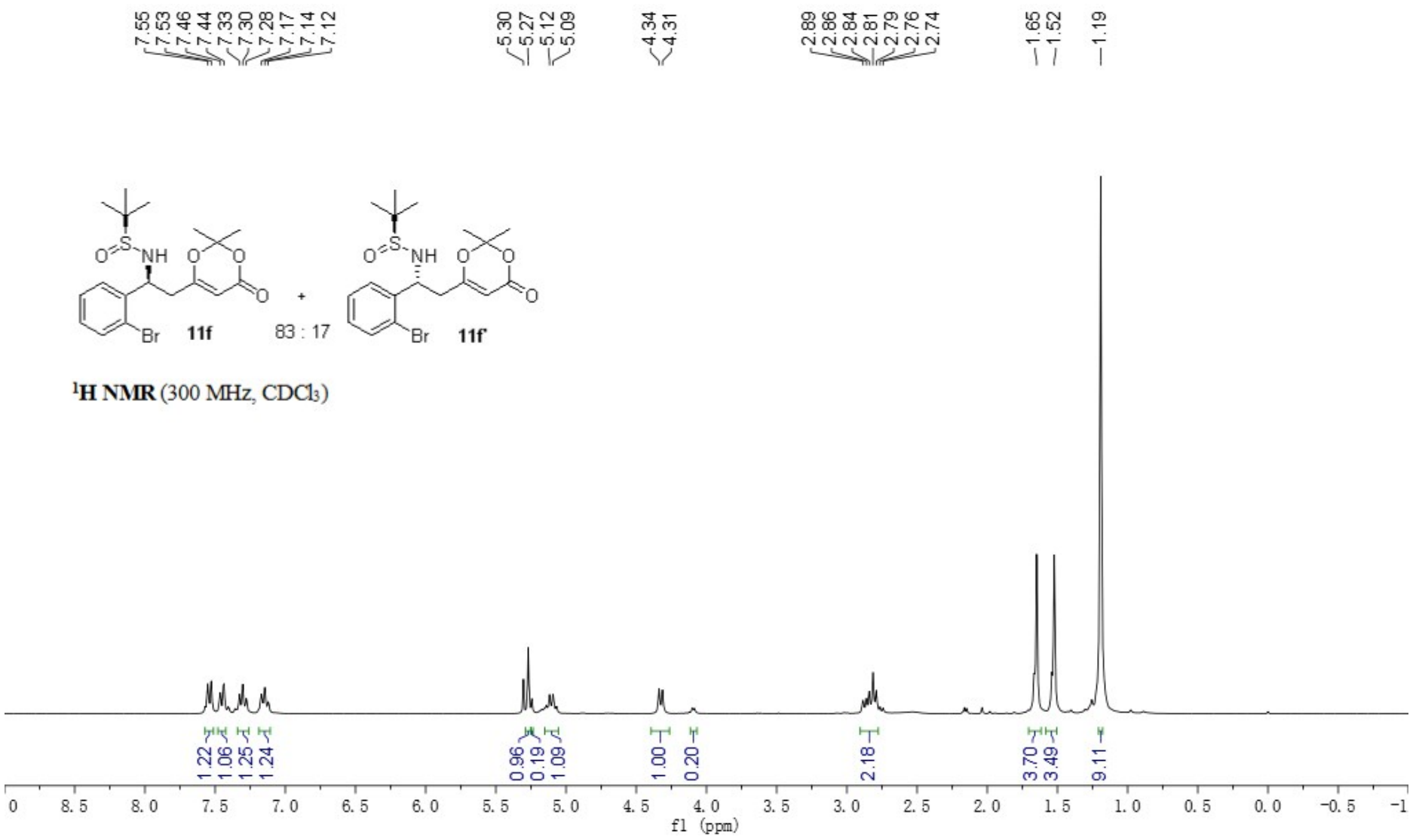
^{1}H NMR (400 MHz, $CDCl_3$)

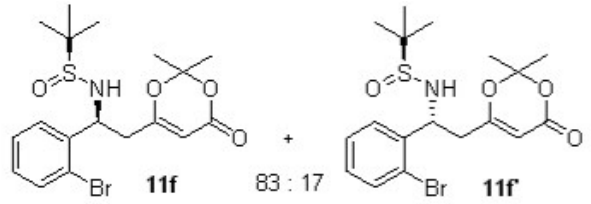


11e

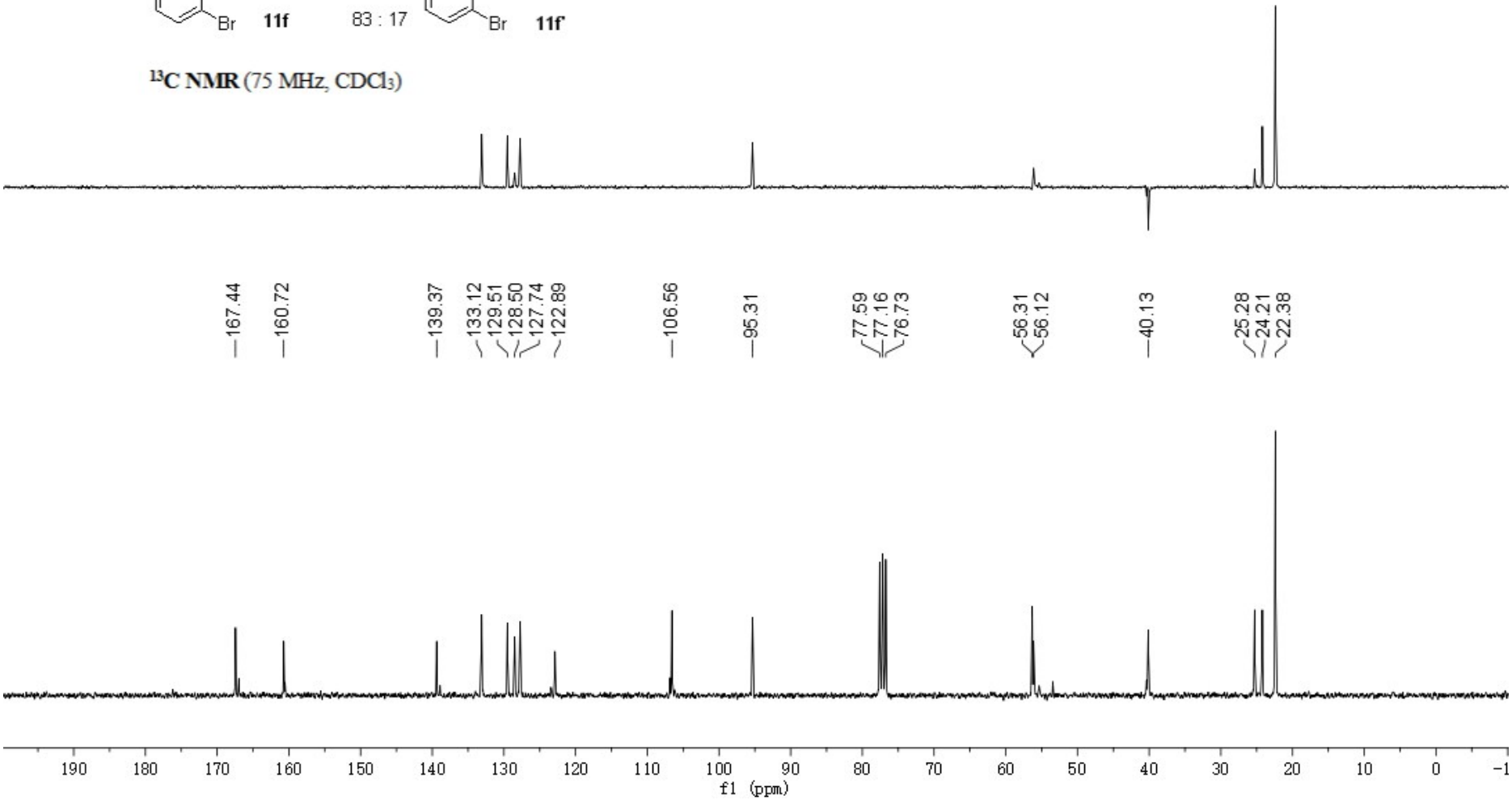
^{13}C NMR (100 MHz, $CDCl_3$)

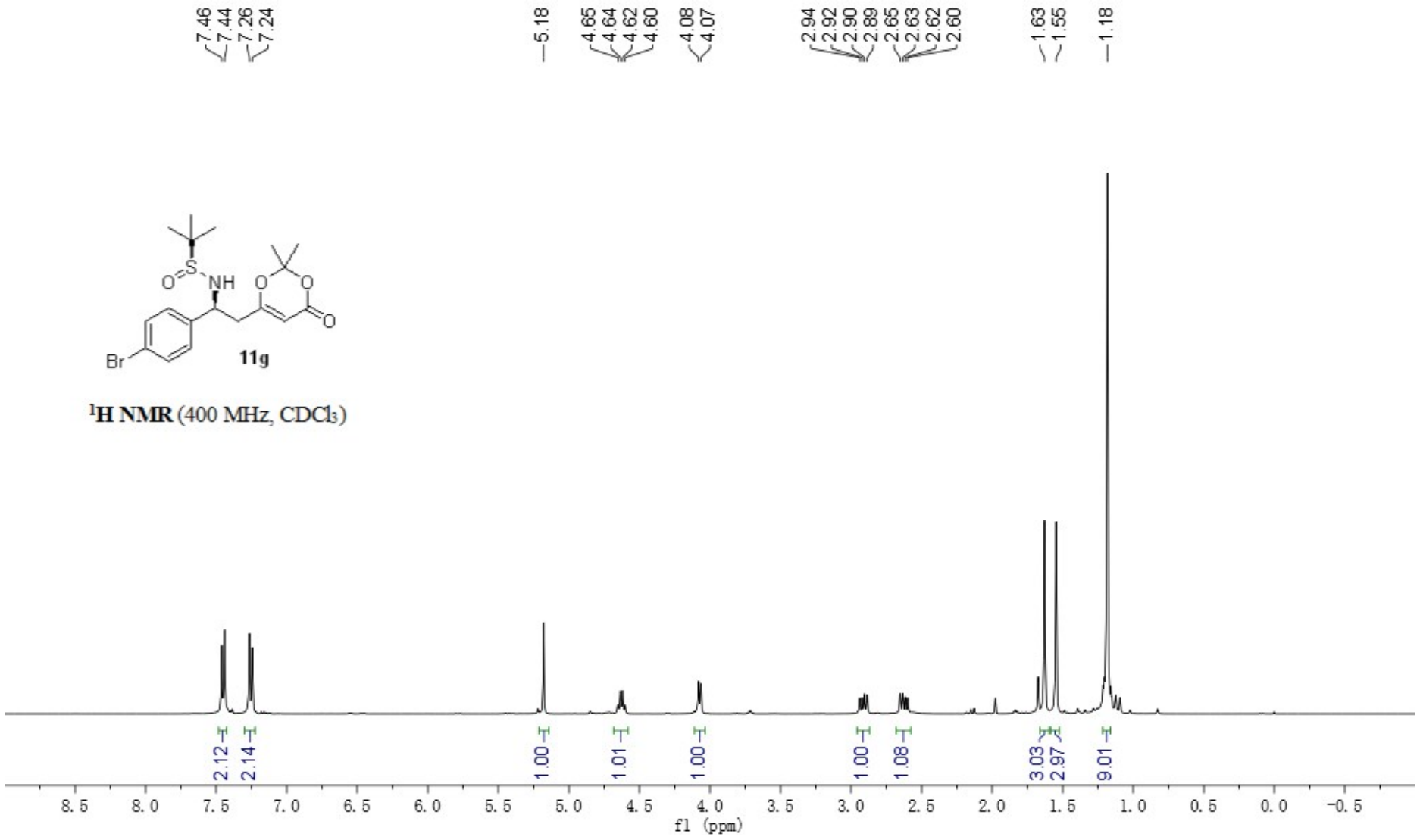



7.55
7.53
7.46
7.44
7.33
7.30
7.28
7.17
7.14
7.12
5.30
5.27
5.12
5.09
4.34
4.31
2.89
2.86
2.84
2.81
2.79
2.76
2.74
1.65
1.52
1.19
O
S
NH
O
O
O
Br
11f
83 : 17
11f'
1H NMR (300 MHz, CDCl3)
1.22
1.06
1.25
1.24
0.96
0.19
1.09
1.00
0.20
2.18
3.70
3.49
9.11
f1 (ppm)

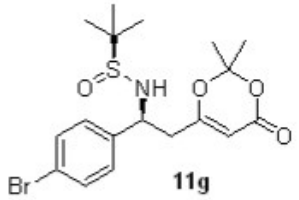


^{13}C NMR (75 MHz, $CDCl_3$)



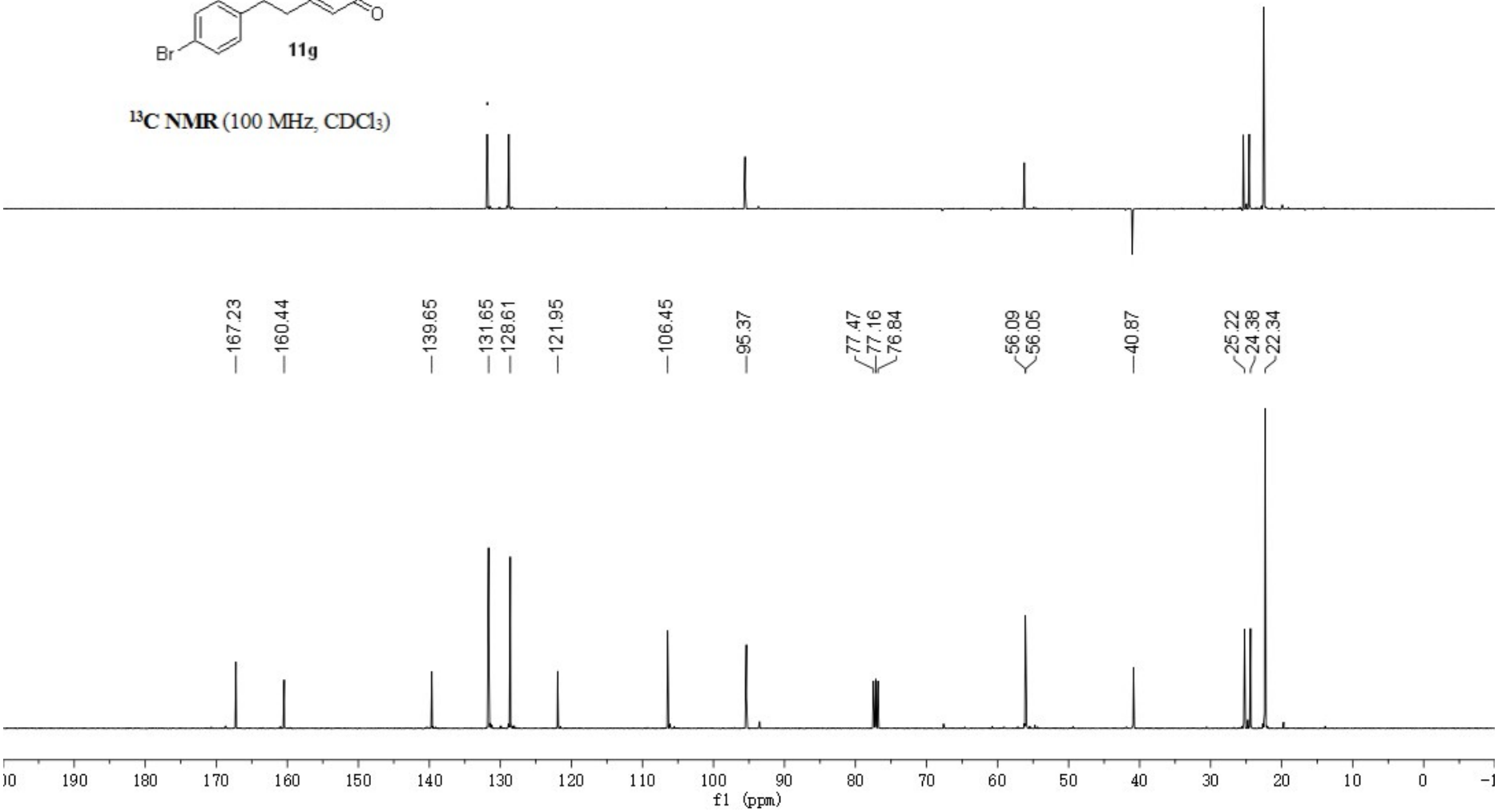


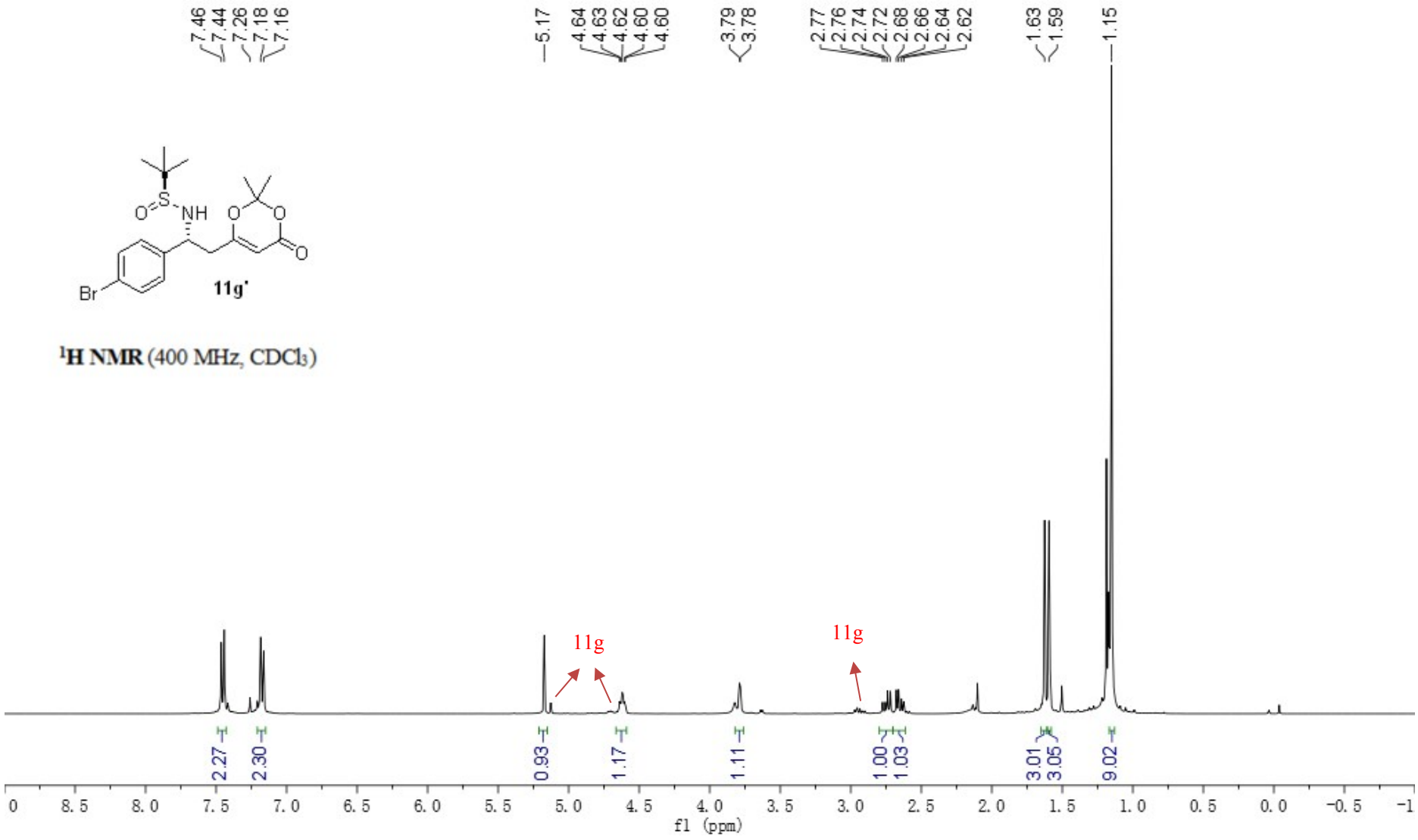
^{1}H NMR (400 MHz, $CDCl_3$)



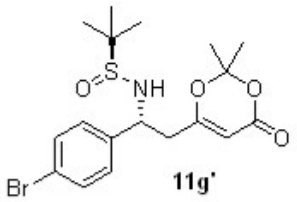
11g

^{13}C NMR (100 MHz, $CDCl_3$)



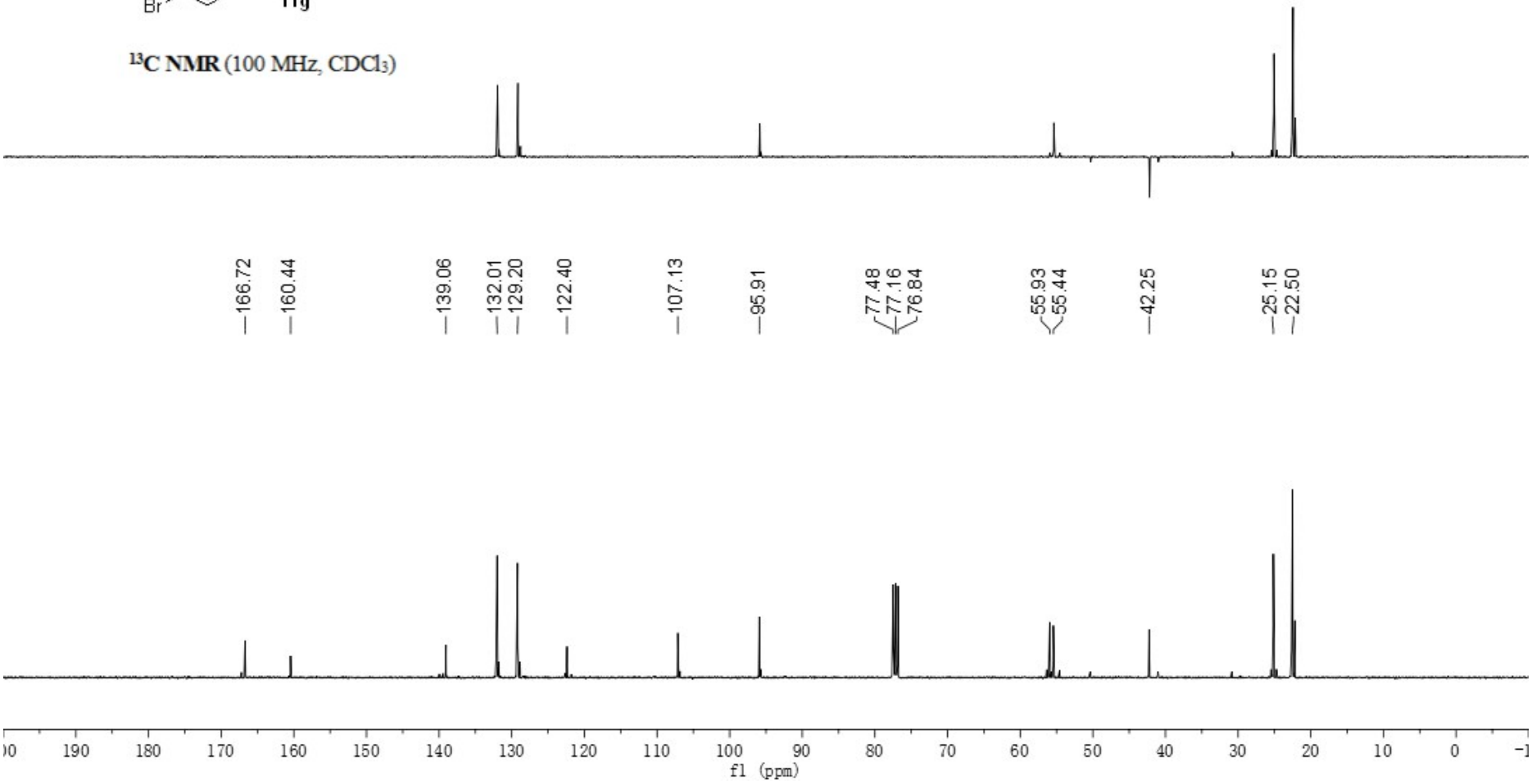


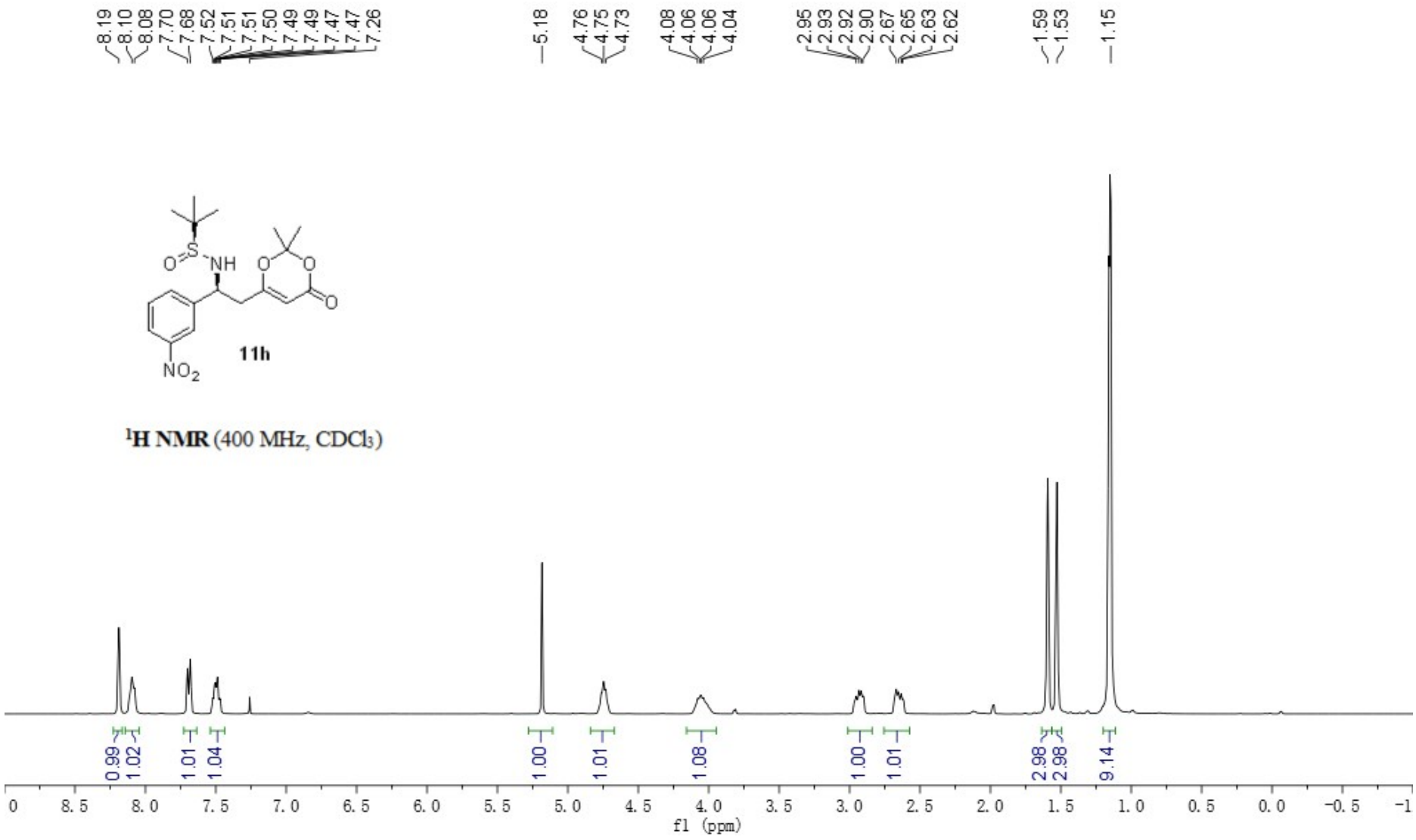
^{1}H NMR (400 MHz, $CDCl_3$)



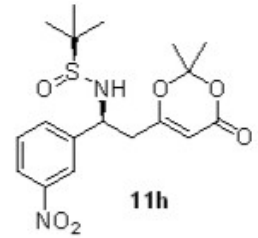
11g'

^{13}C NMR (100 MHz, $CDCl_3$)



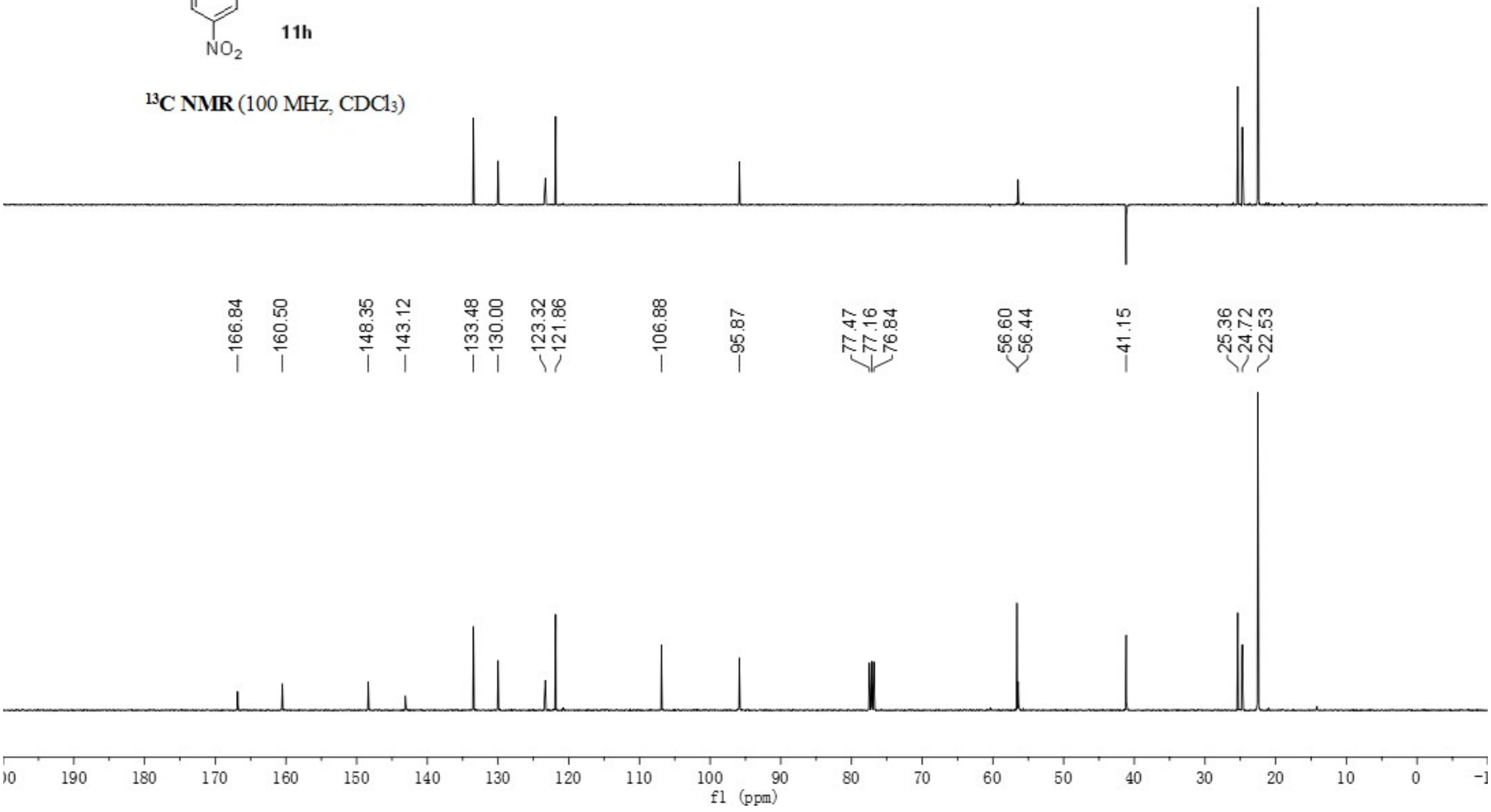


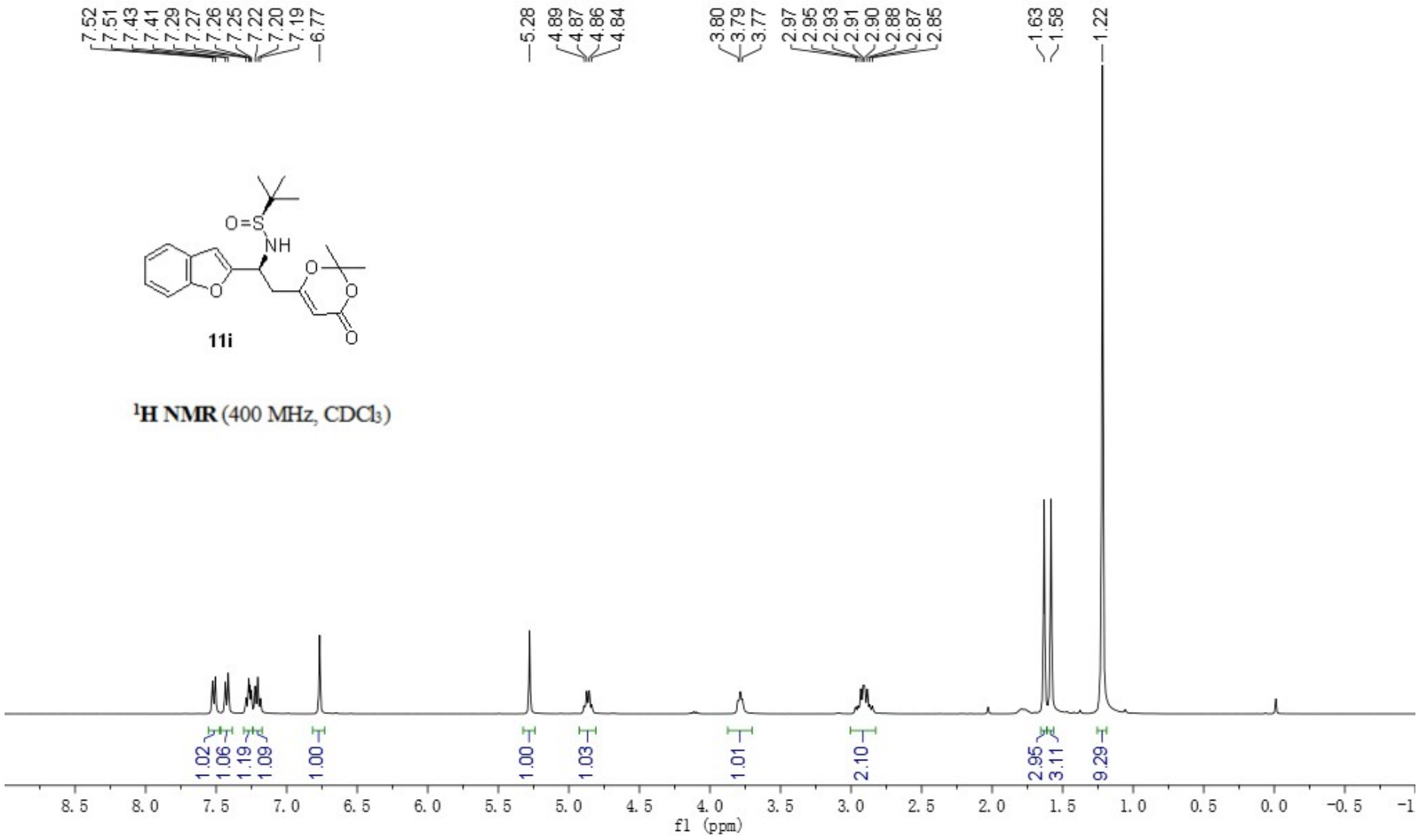
^{1}H NMR (400 MHz, $CDCl_3$)



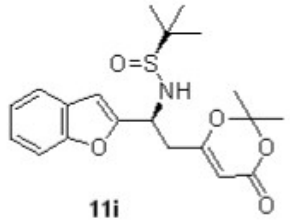
11h

^{13}C NMR (100 MHz, $CDCl_3$)



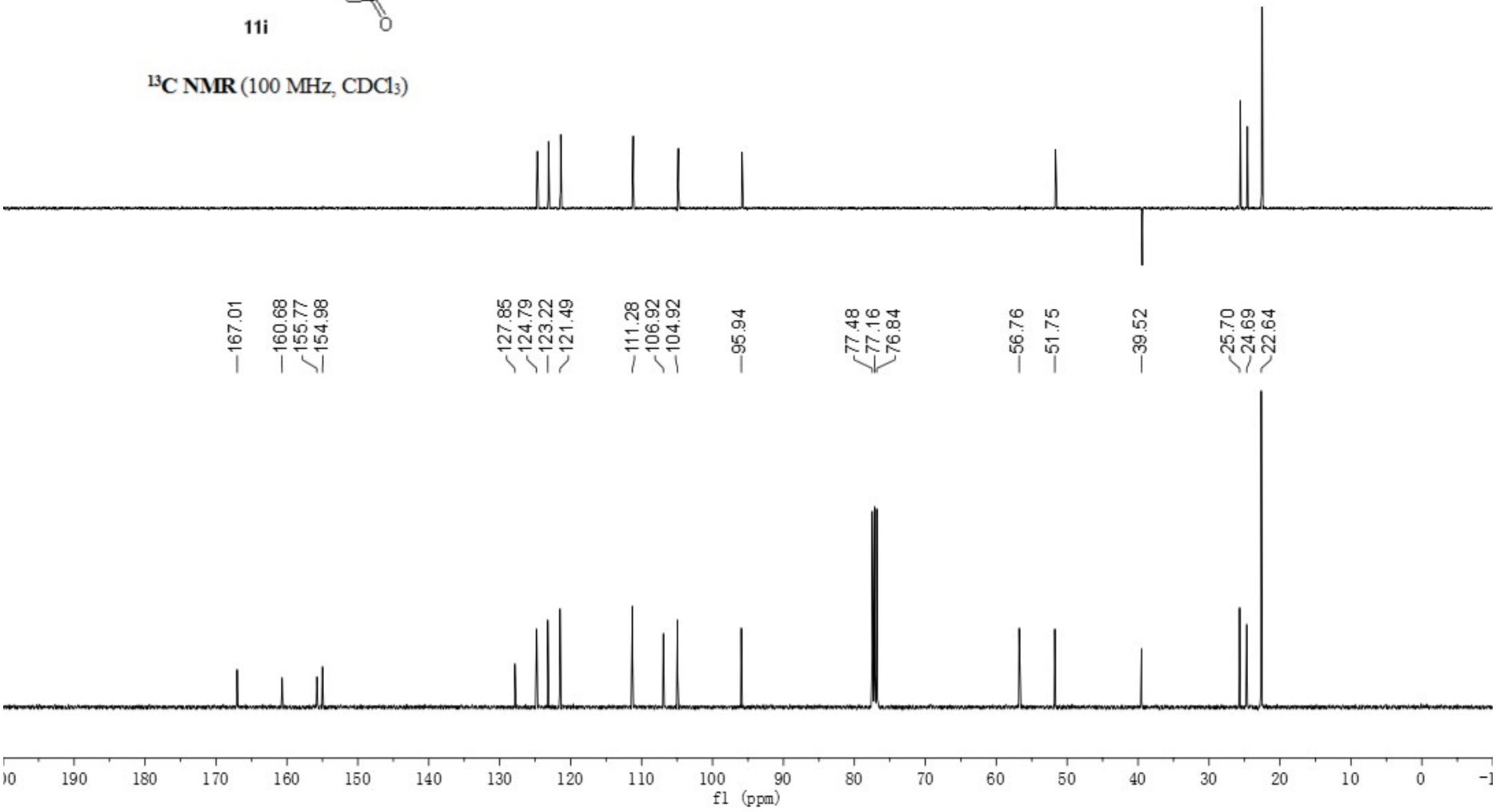


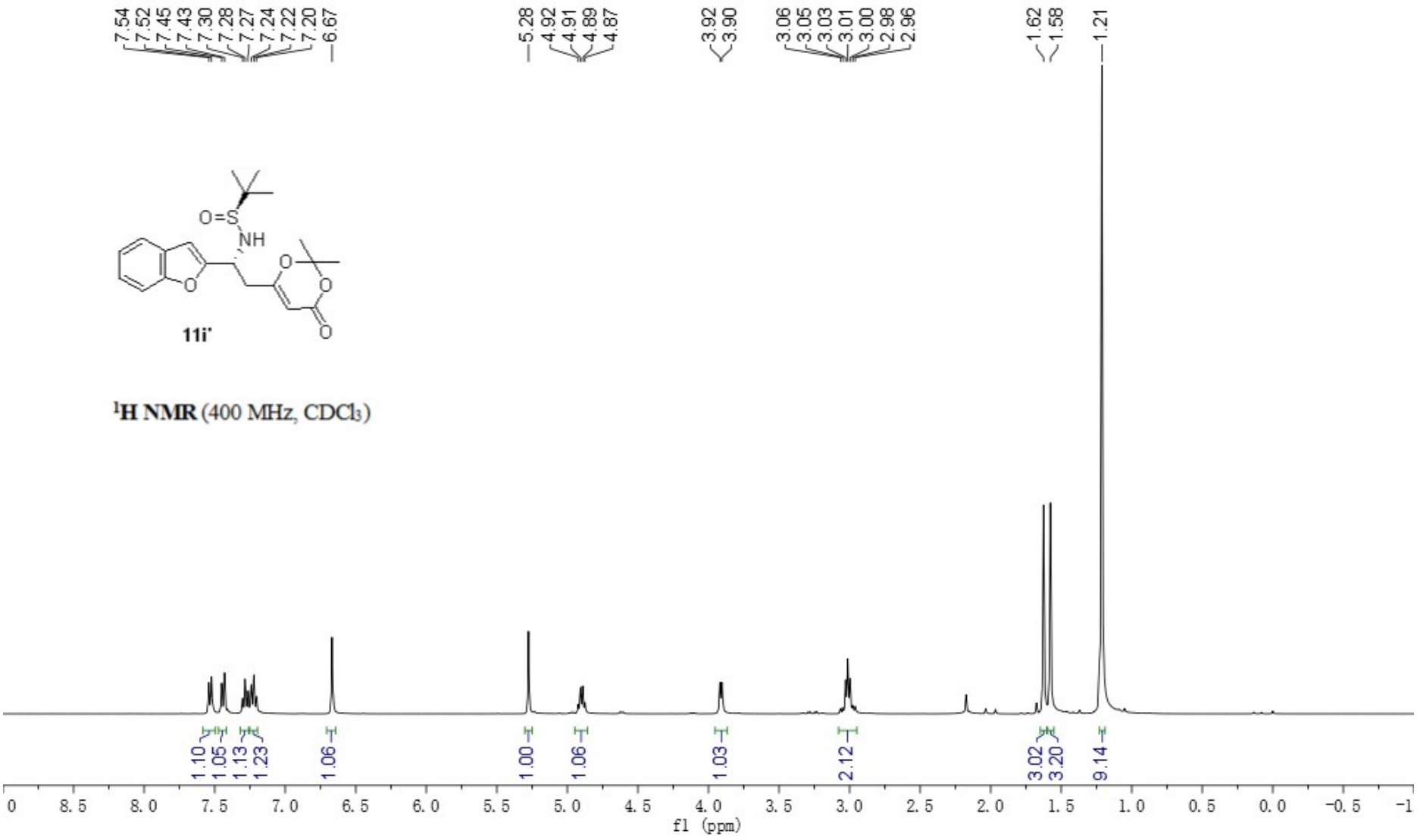
^{1}H NMR (400 MHz, $CDCl_3$)

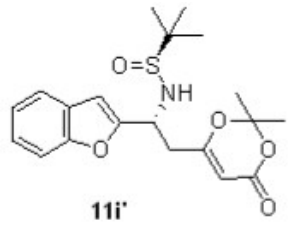


11i

^{13}C NMR (100 MHz, $CDCl_3$)

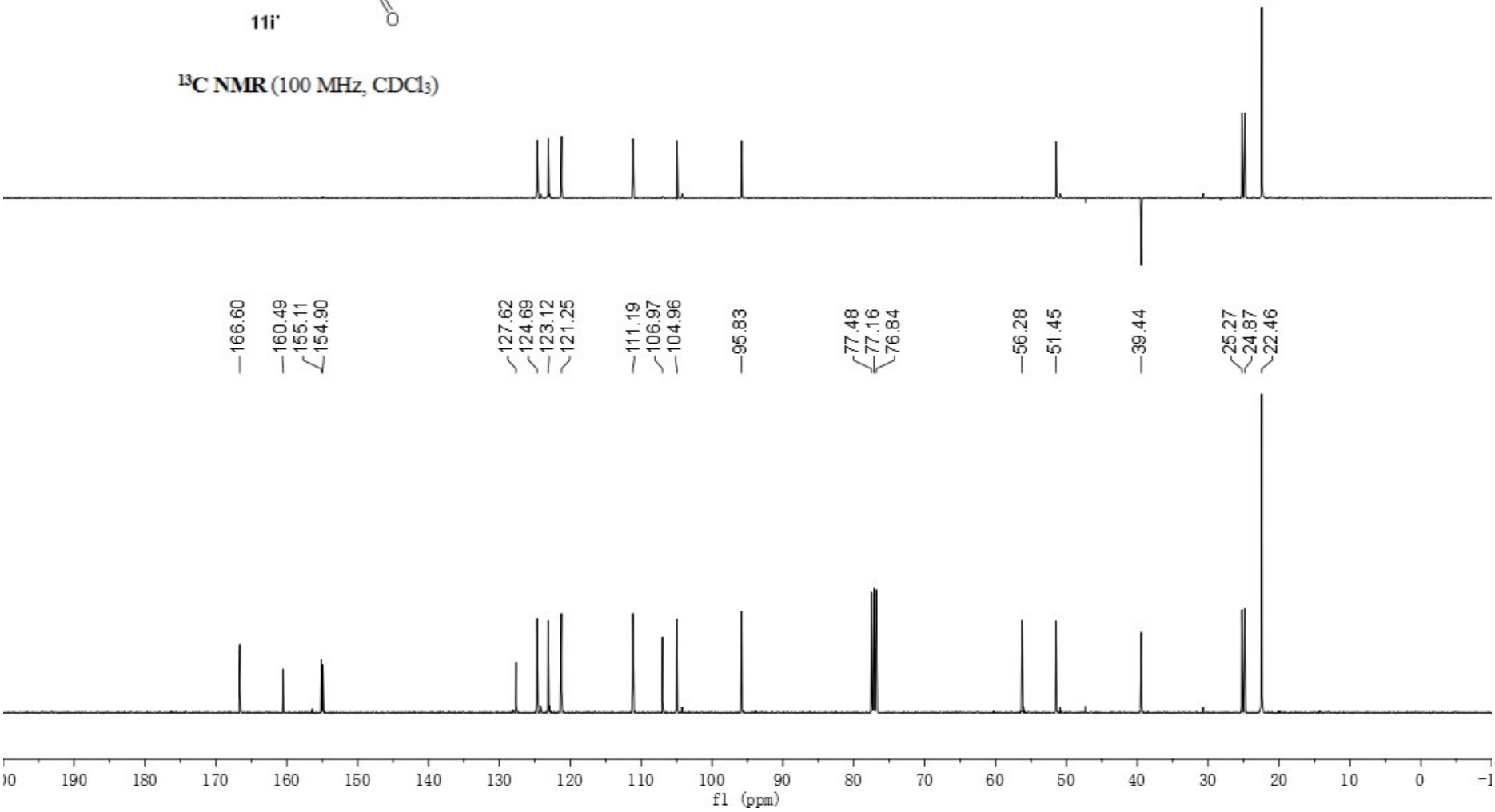


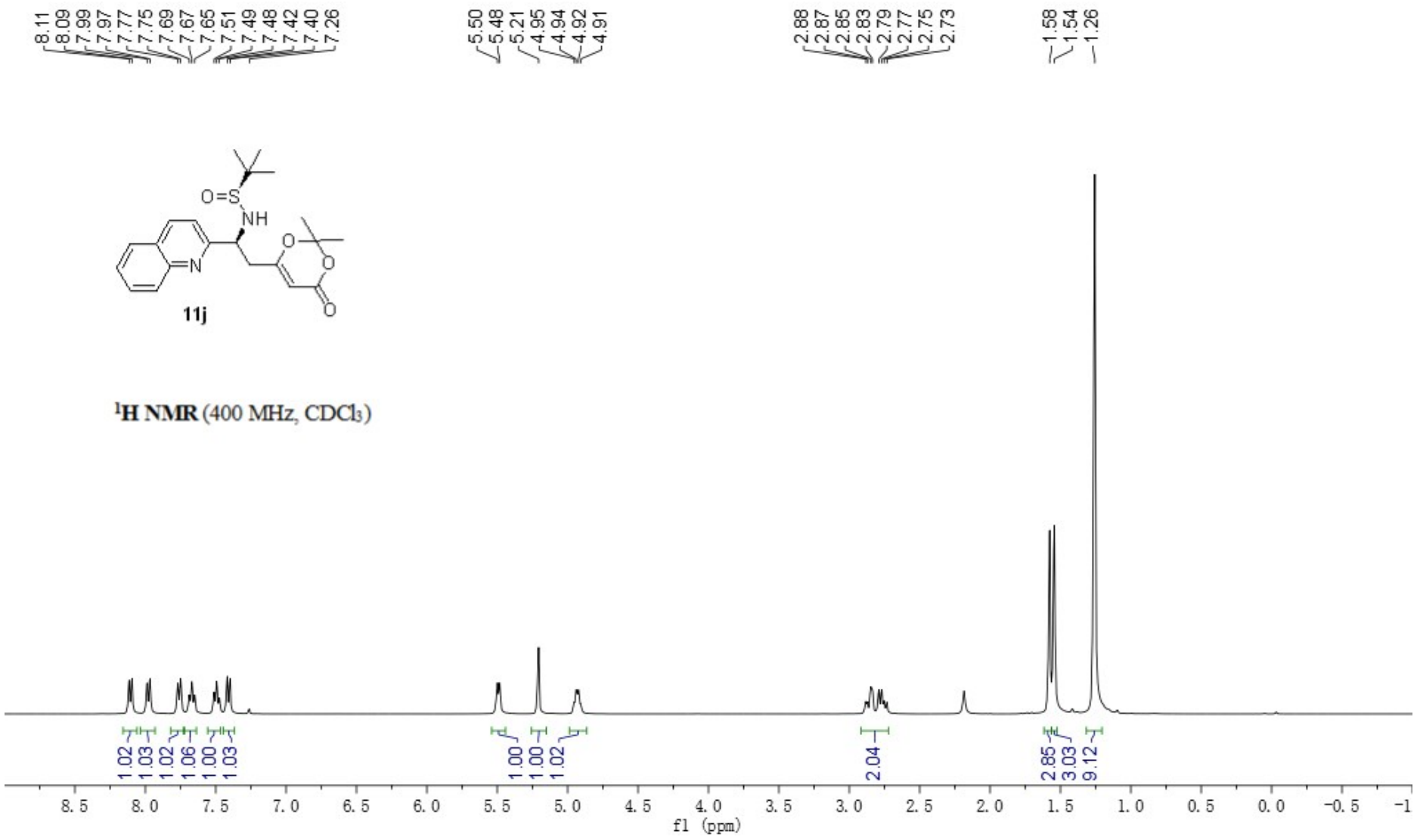

7.54
7.52
7.45
7.43
7.30
7.28
7.27
7.24
7.22
7.20
6.67
5.28
4.92
4.91
4.89
4.87
3.92
3.90
3.06
3.05
3.03
3.01
3.00
2.98
2.96
1.62
1.58
1.21
O=S
NH
O
O
O
O
11i'
1H NMR (400 MHz, CDCl3)
1.10
1.05
1.13
1.23
1.06
1.00
1.06
1.03
2.12
3.02
3.20
9.14
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

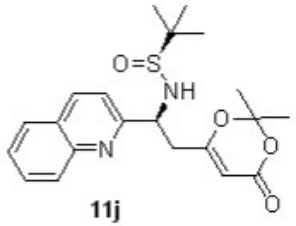


11i'

^{13}C NMR (100 MHz, $CDCl_3$)

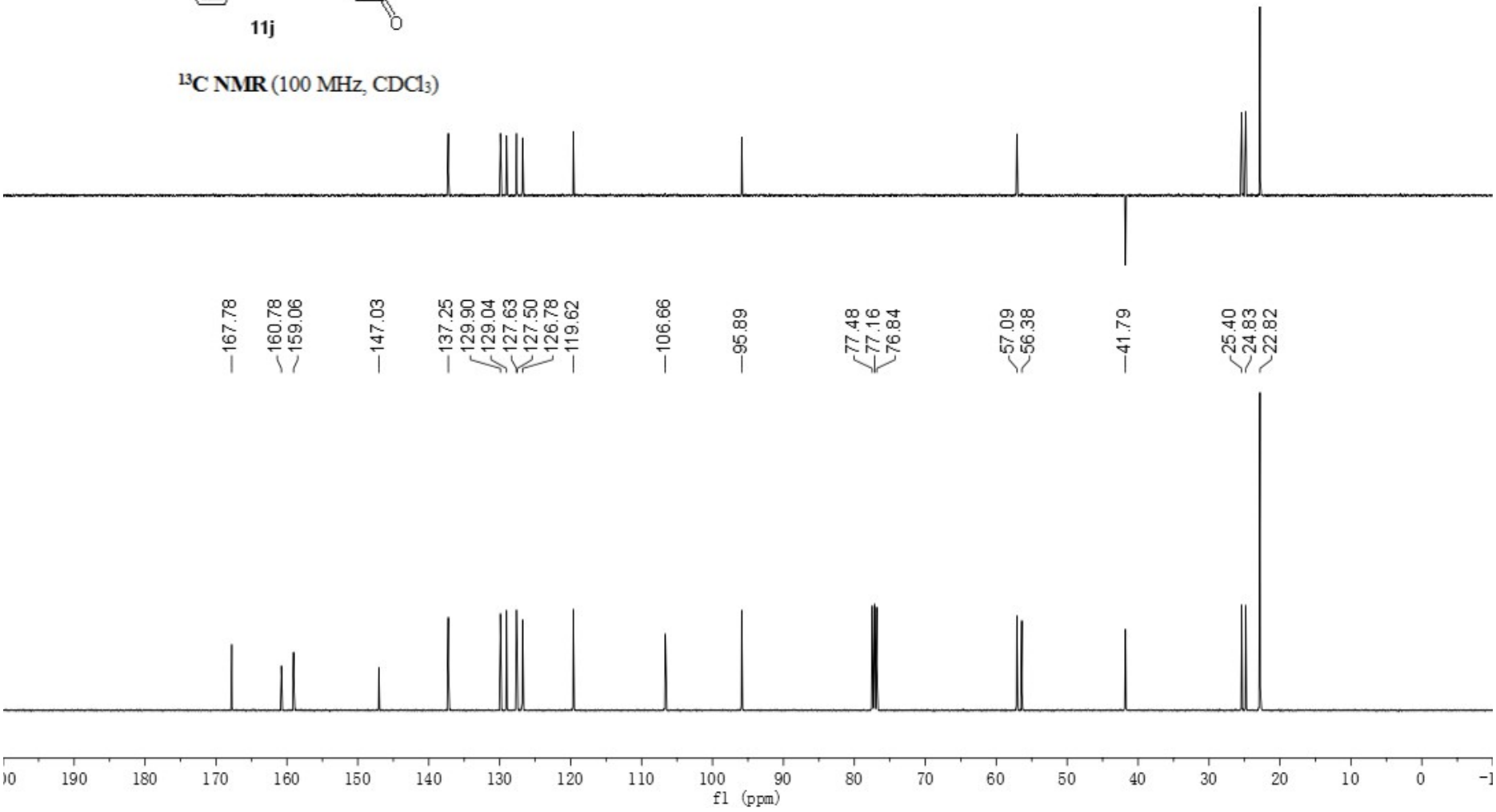


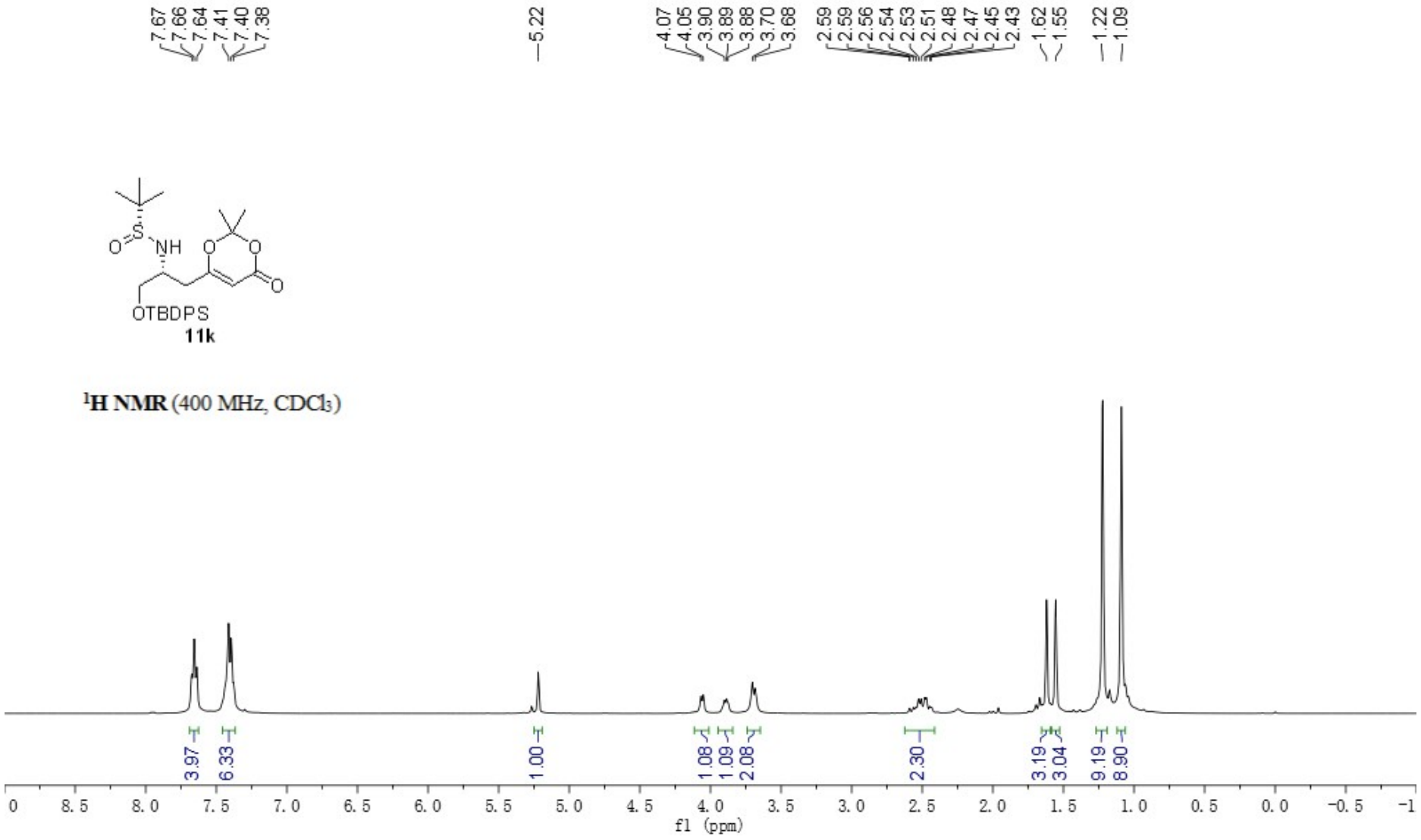

8.11
8.09
7.99
7.97
7.77
7.75
7.69
7.67
7.65
7.51
7.49
7.48
7.42
7.40
7.26
5.50
5.48
5.21
4.95
4.94
4.92
4.91
2.88
2.87
2.85
2.83
2.79
2.77
2.75
2.73
1.58
1.54
1.26
O=S
NH
N
O
O
O
11j
1H NMR (400 MHz, CDCl3)
1.02
1.03
1.02
1.06
1.00
1.03
1.00
1.00
1.02
2.04
2.85
3.03
9.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

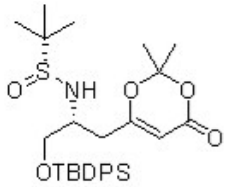


11j

^{13}C NMR (100 MHz, $CDCl_3$)

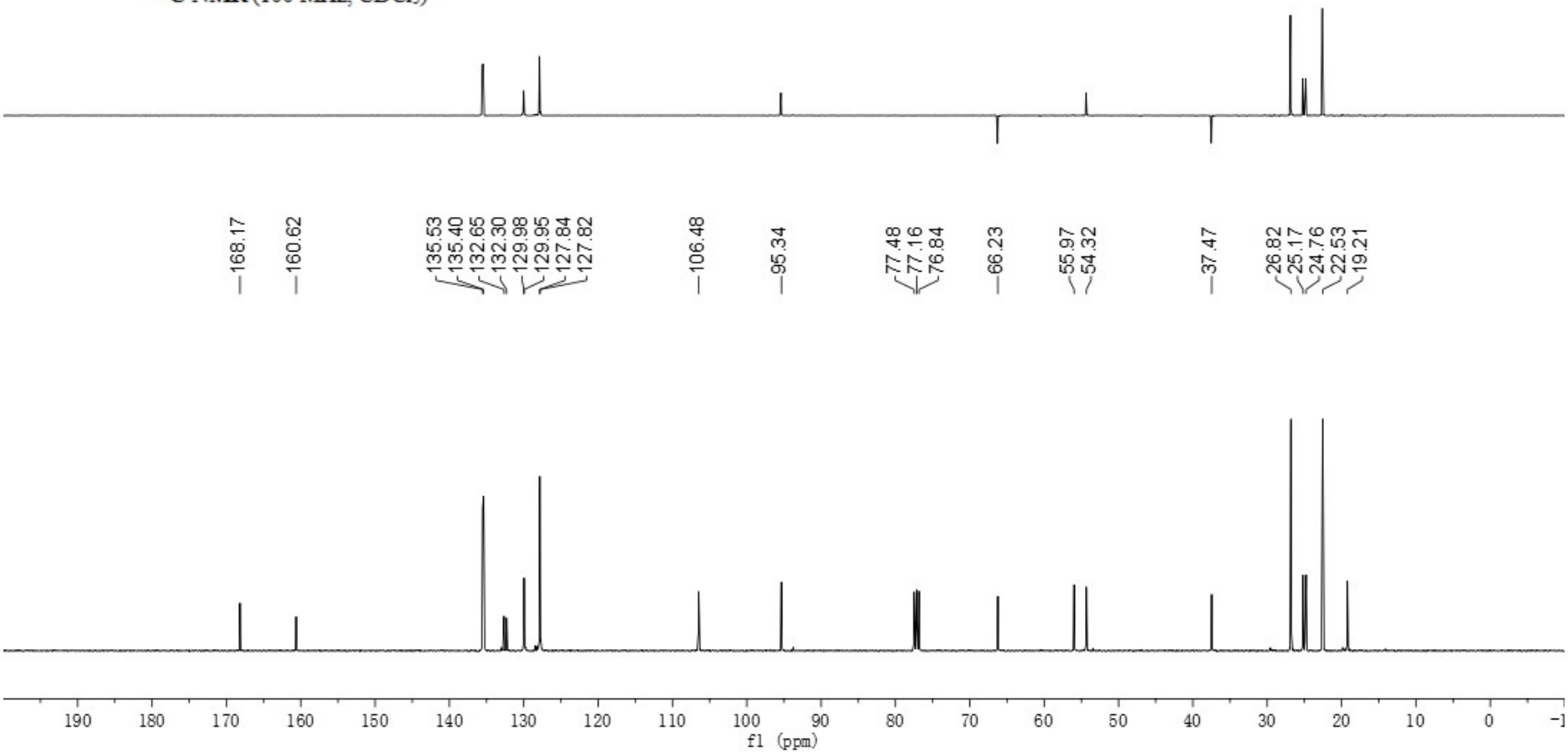


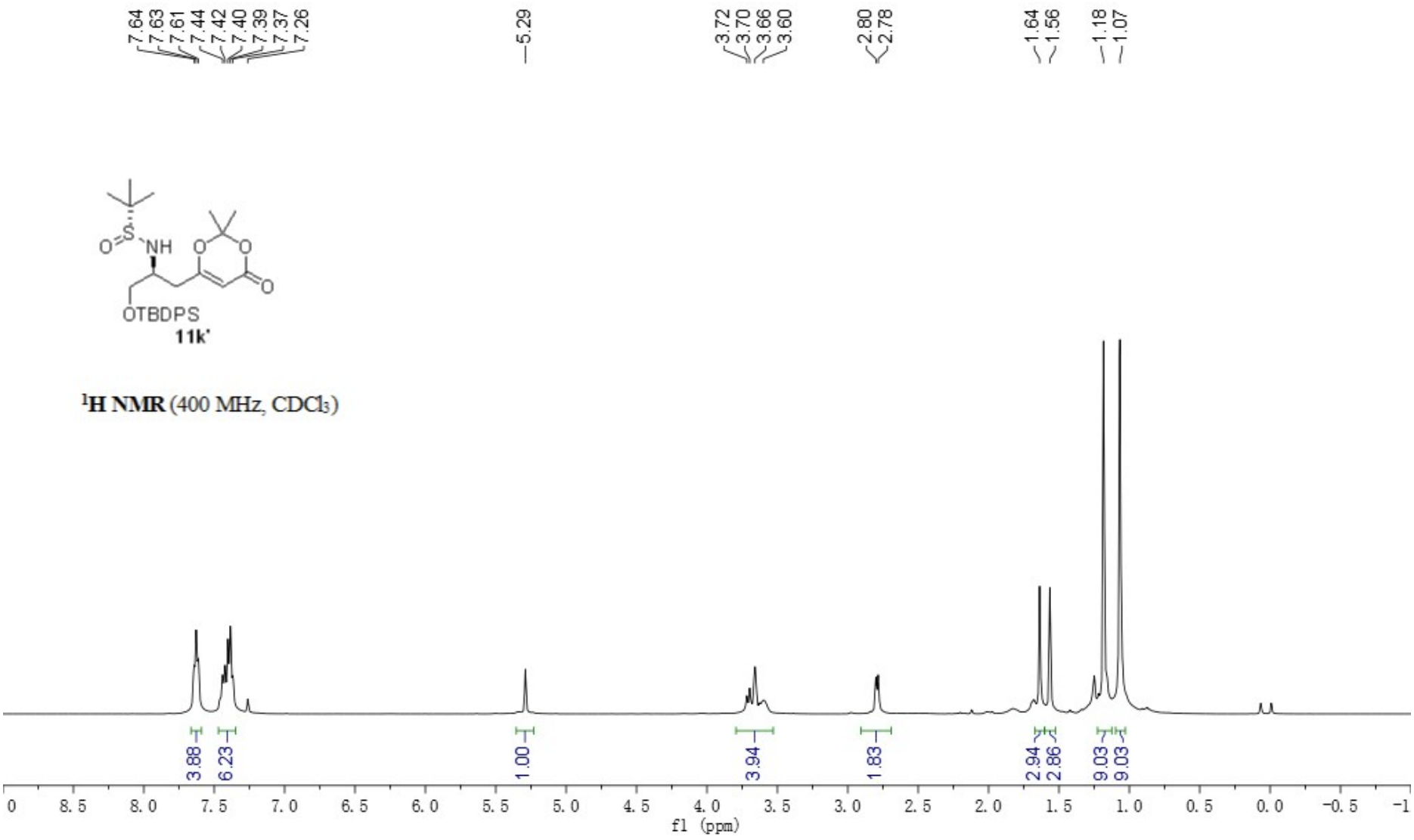

7.67
7.66
7.64
7.41
7.40
7.38
5.22
4.07
4.05
3.90
3.89
3.88
3.70
3.68
2.59
2.59
2.56
2.54
2.53
2.51
2.48
2.47
2.45
2.43
1.62
1.55
1.22
1.09
O
S
NH
O
O
O
OTBDPS
11k
1H NMR (400 MHz, CDCl3)
3.97
6.33
1.00
1.08
1.09
2.08
2.30
3.19
3.04
9.19
8.90
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)



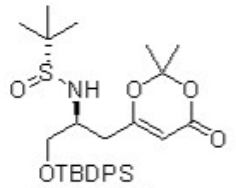
11k

^{13}C NMR (100 MHz, $CDCl_3$)



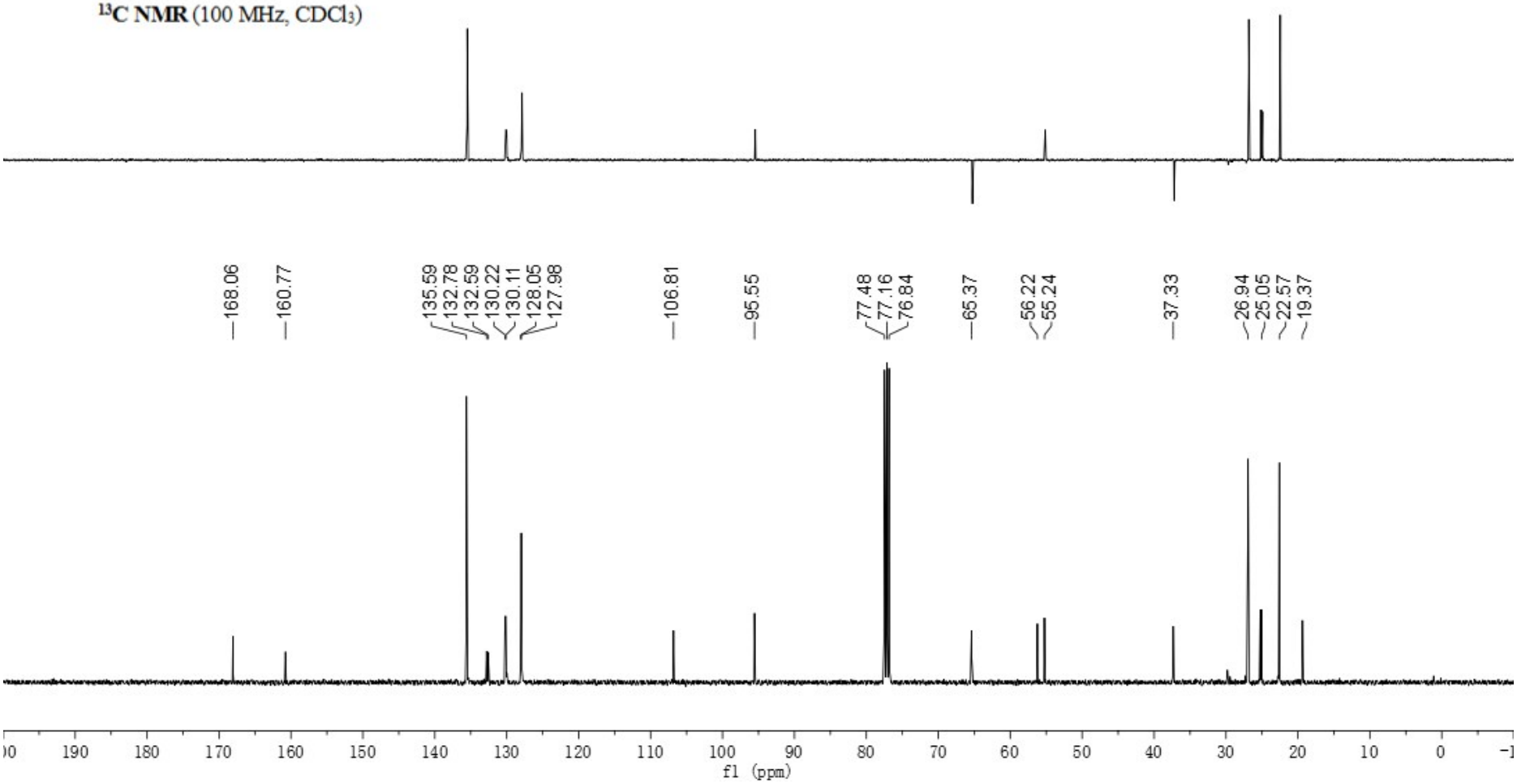


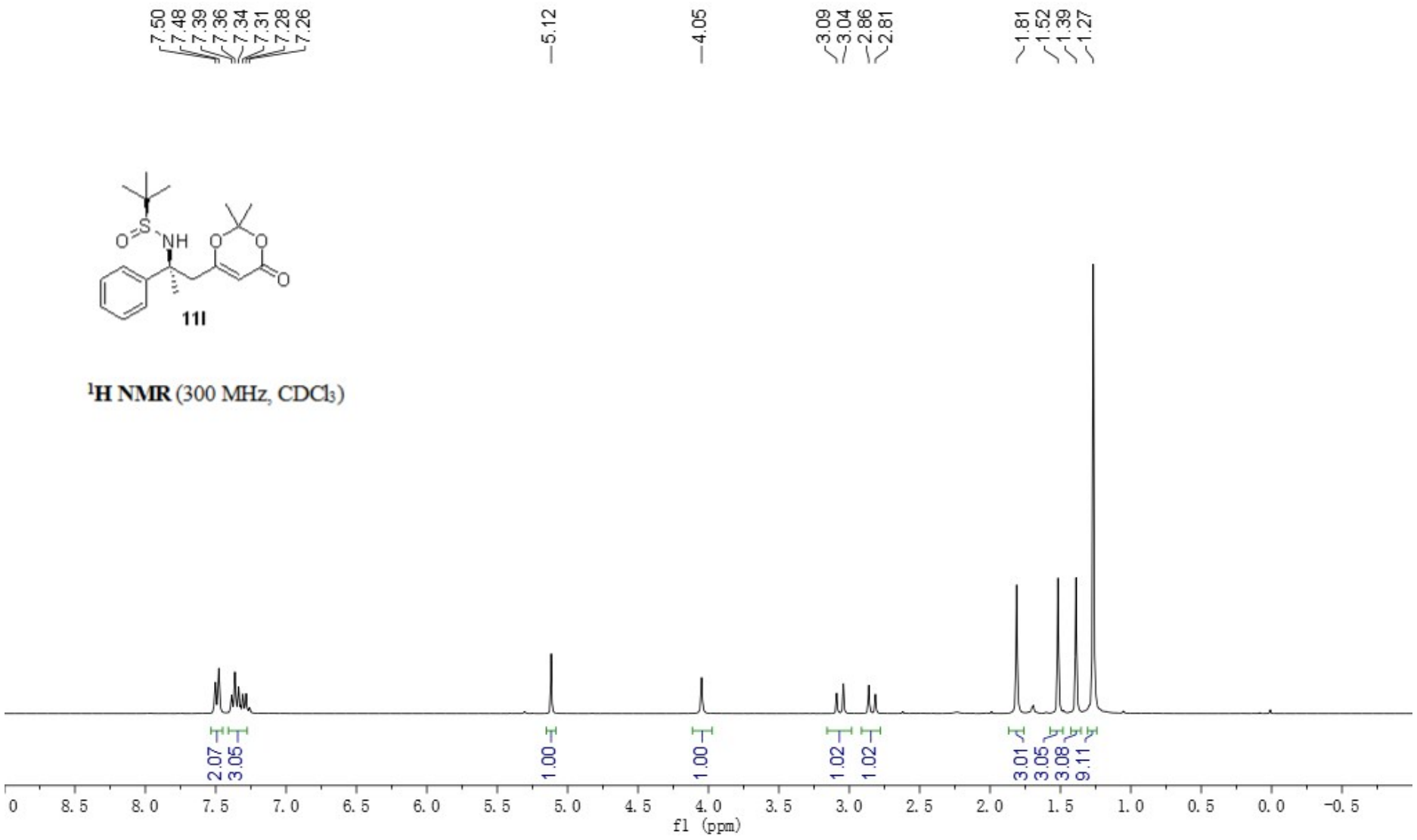
^{1}H NMR (400 MHz, $CDCl_3$)



11k'

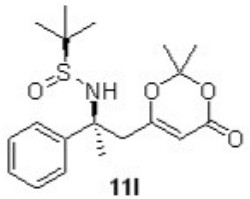
^{13}C NMR (100 MHz, $CDCl_3$)





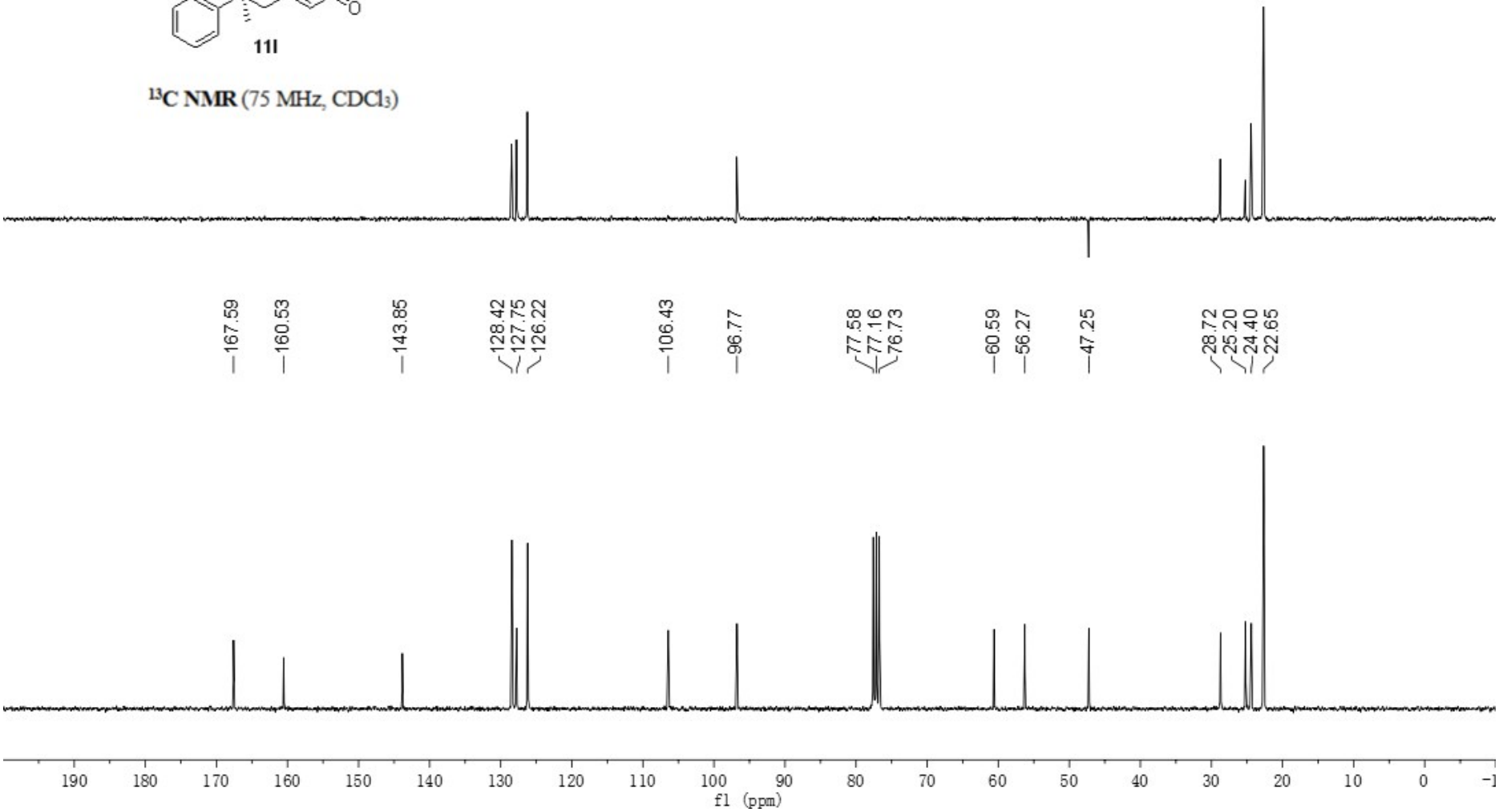
11l

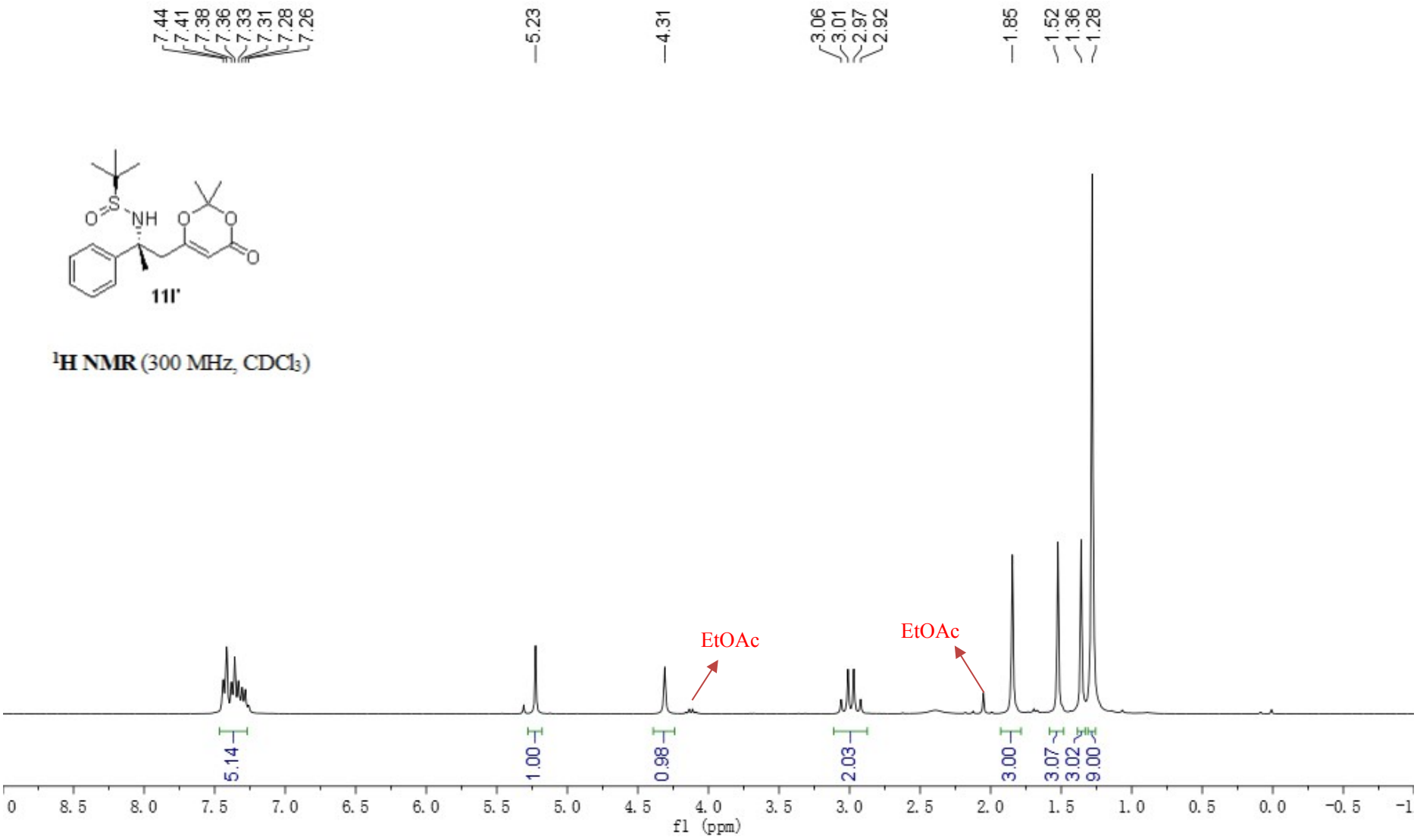
^{1}H NMR (300 MHz, $CDCl_3$)



11l

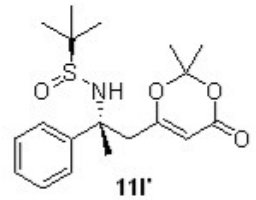
^{13}C NMR (75 MHz, $CDCl_3$)





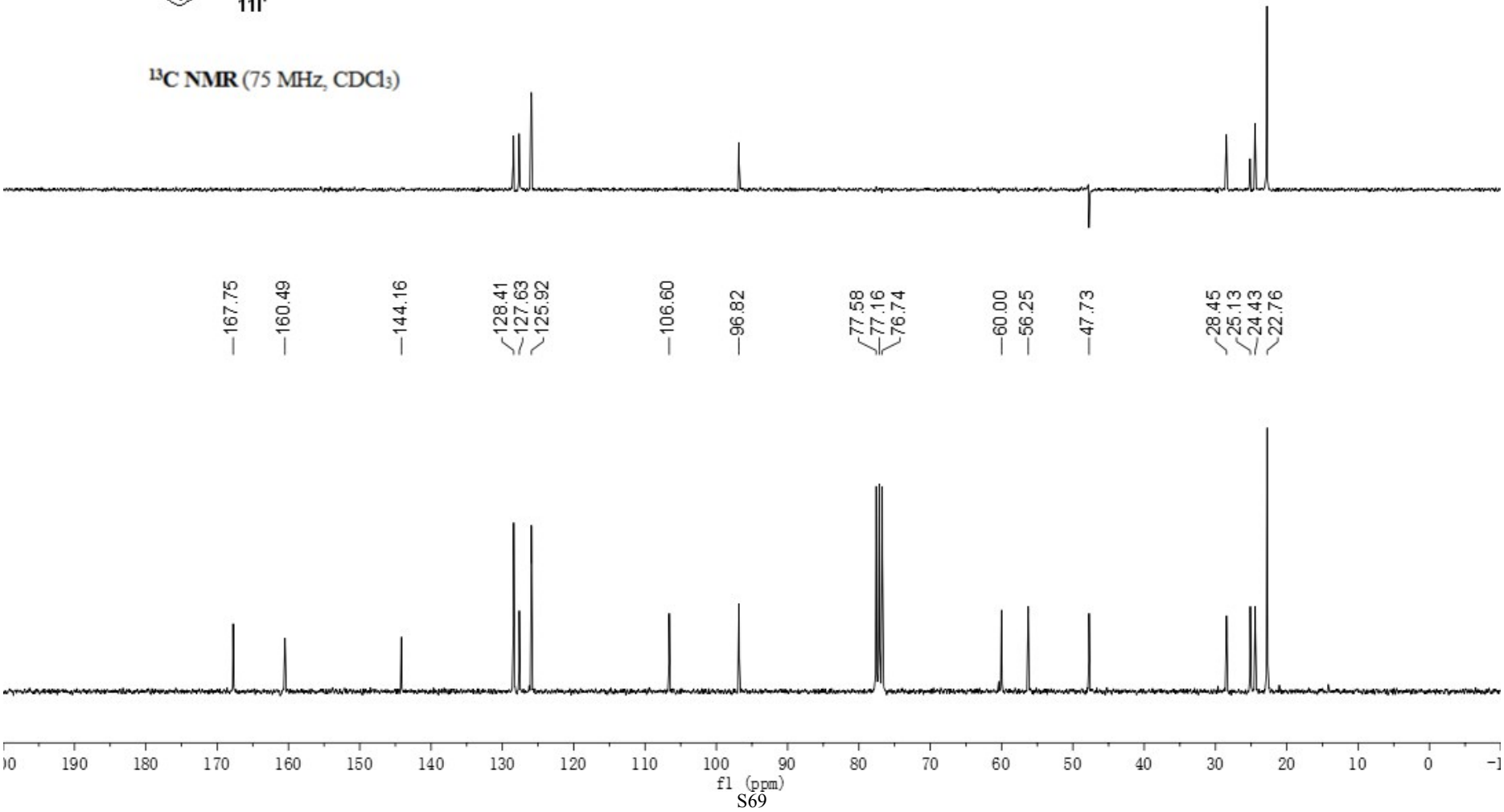
11l'

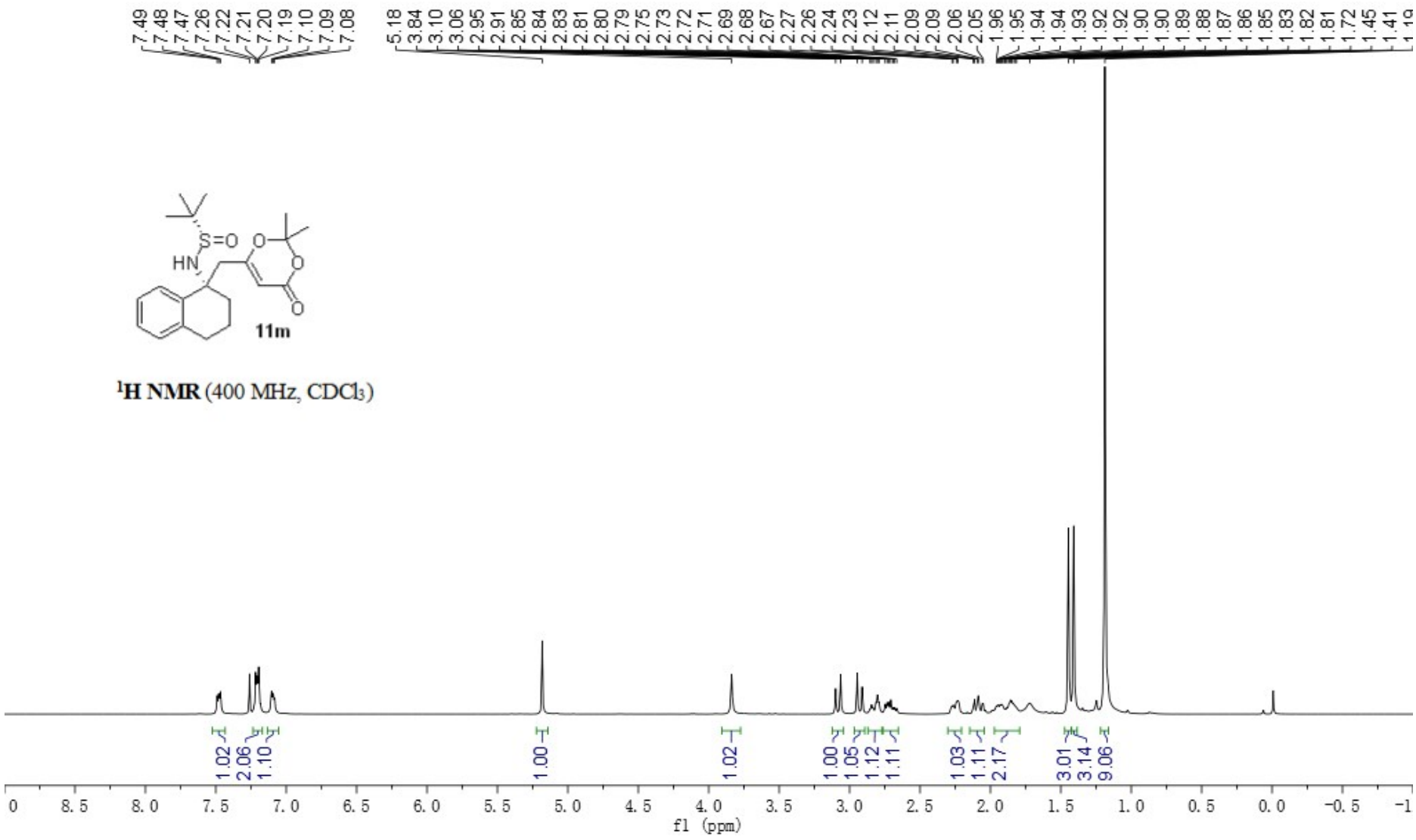
^{1}H NMR (300 MHz, $CDCl_3$)



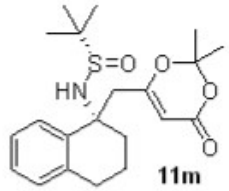
11l'

^{13}C NMR (75 MHz, $CDCl_3$)

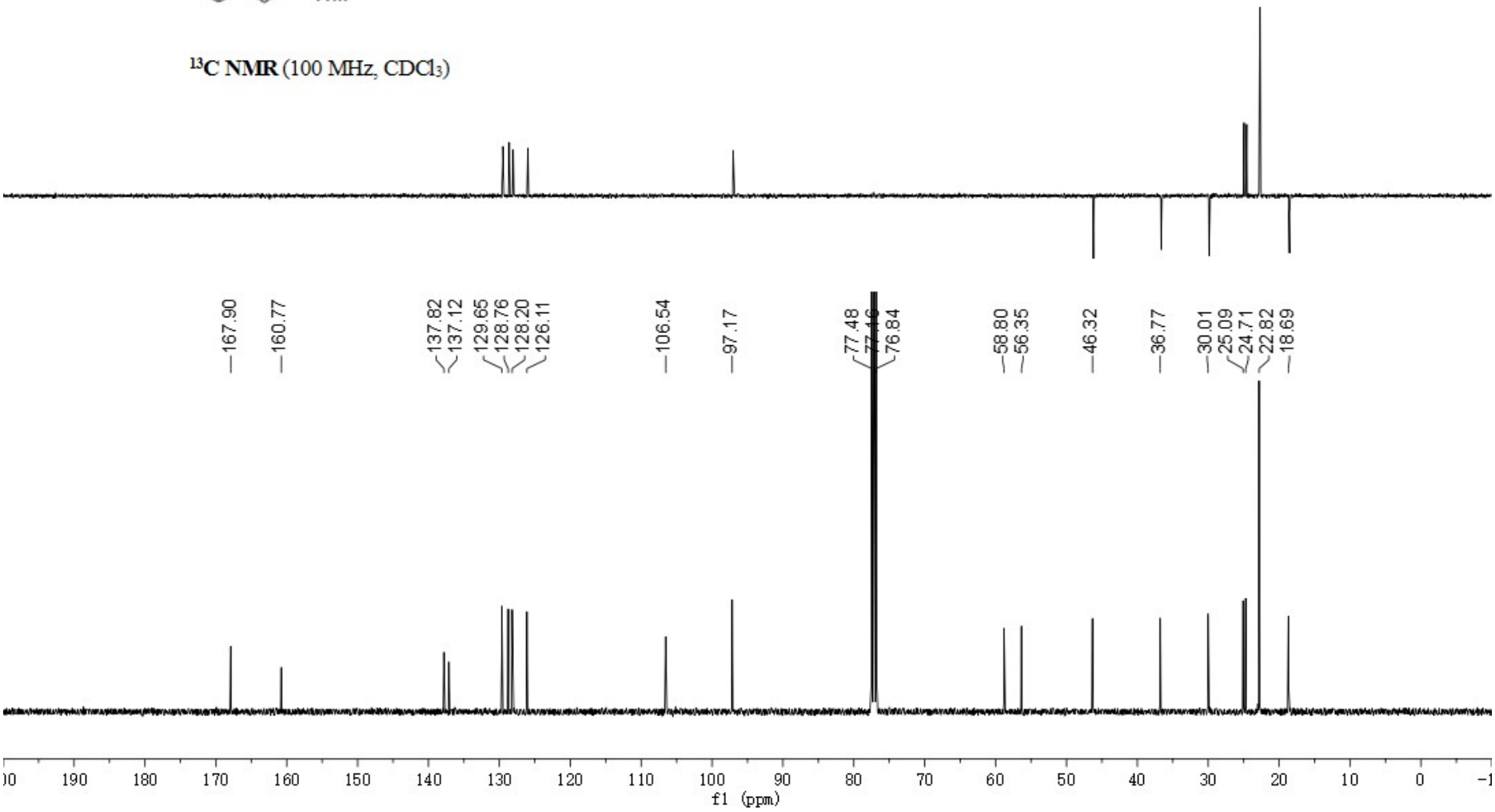


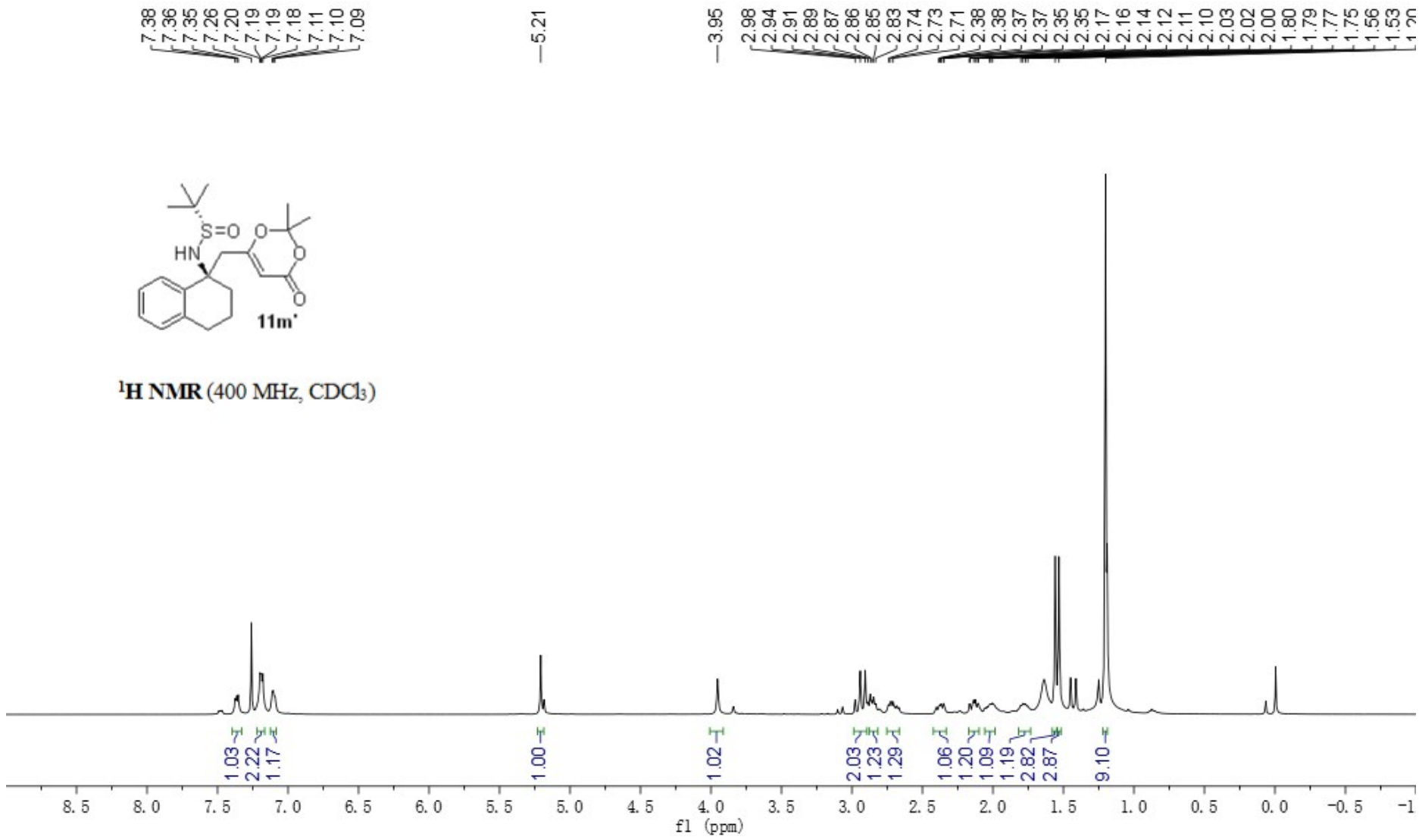


^{1}H NMR (400 MHz, $CDCl_3$)

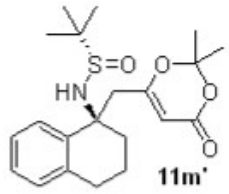


^{13}C NMR (100 MHz, $CDCl_3$)



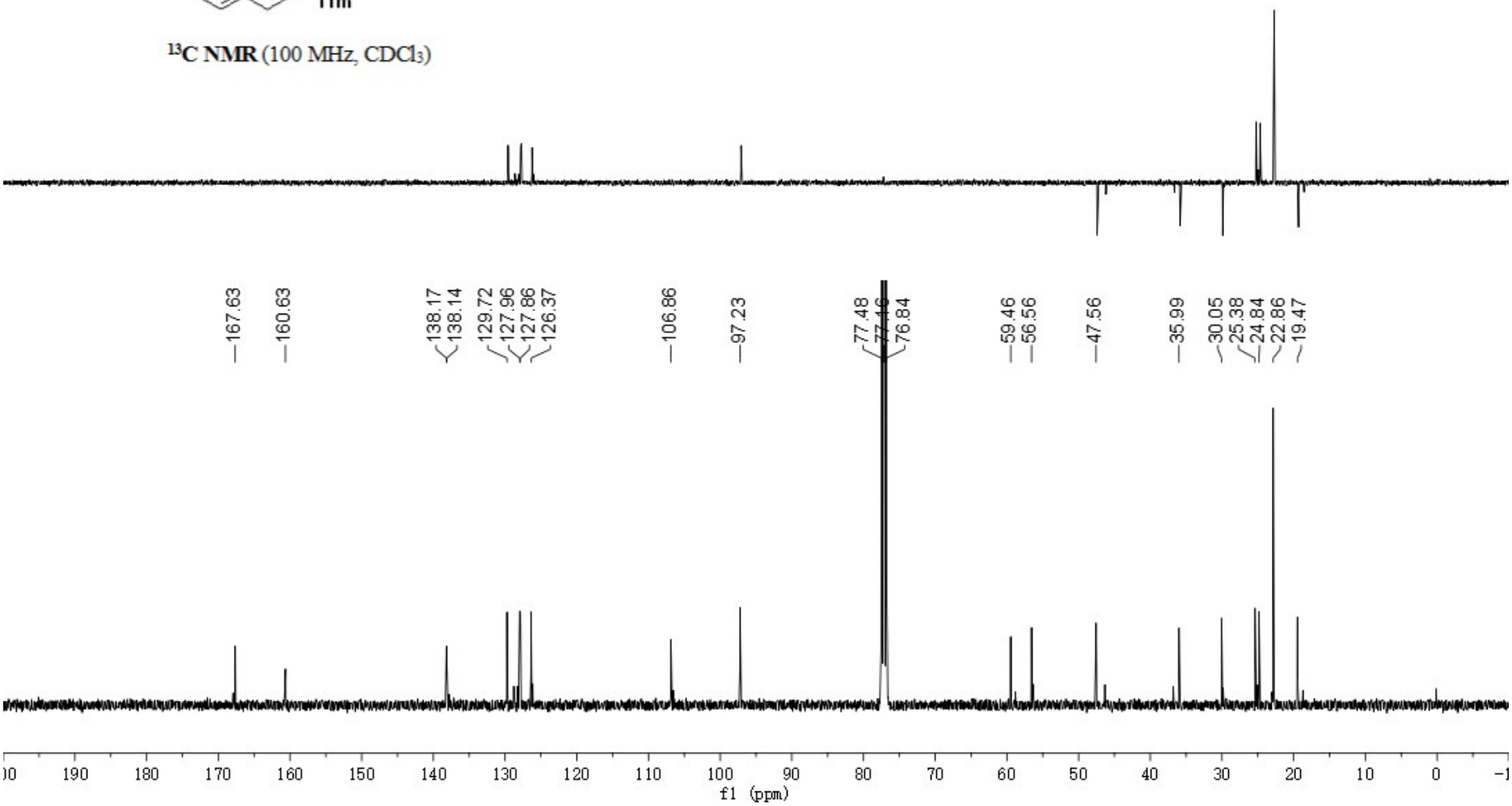


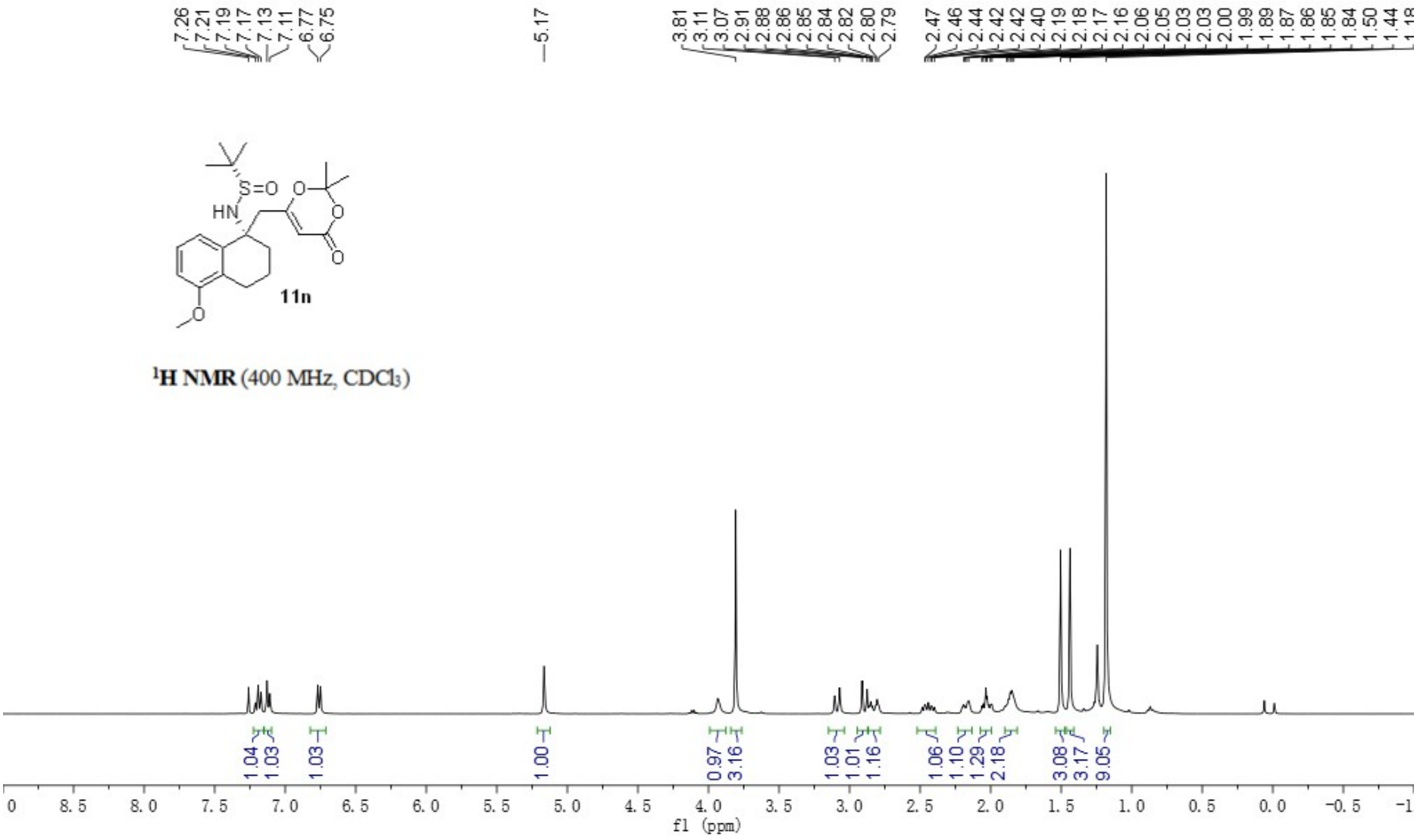
^{1}H NMR (400 MHz, $CDCl_3$)



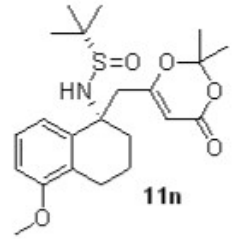
11m'

^{13}C NMR (100 MHz, $CDCl_3$)



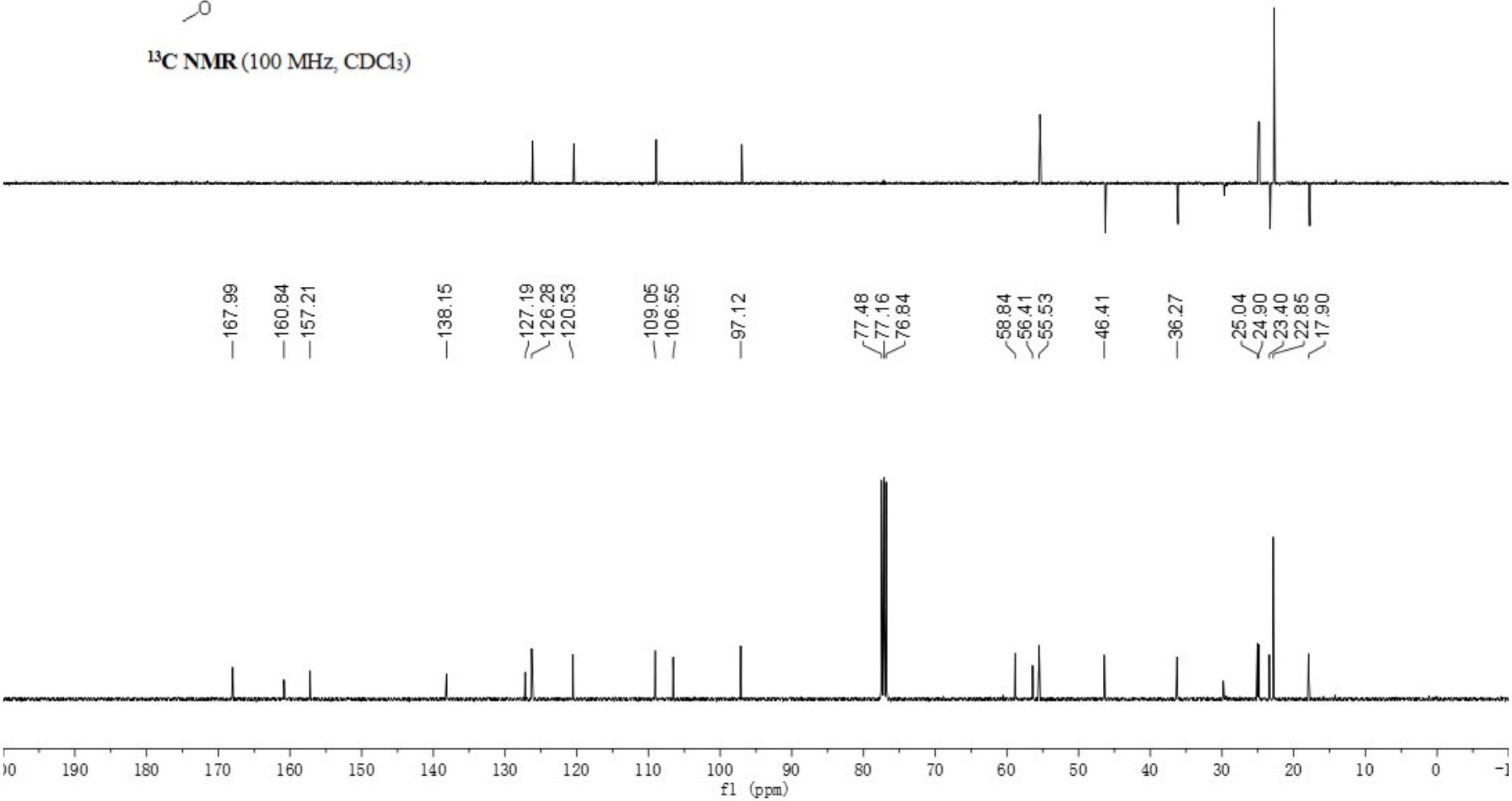


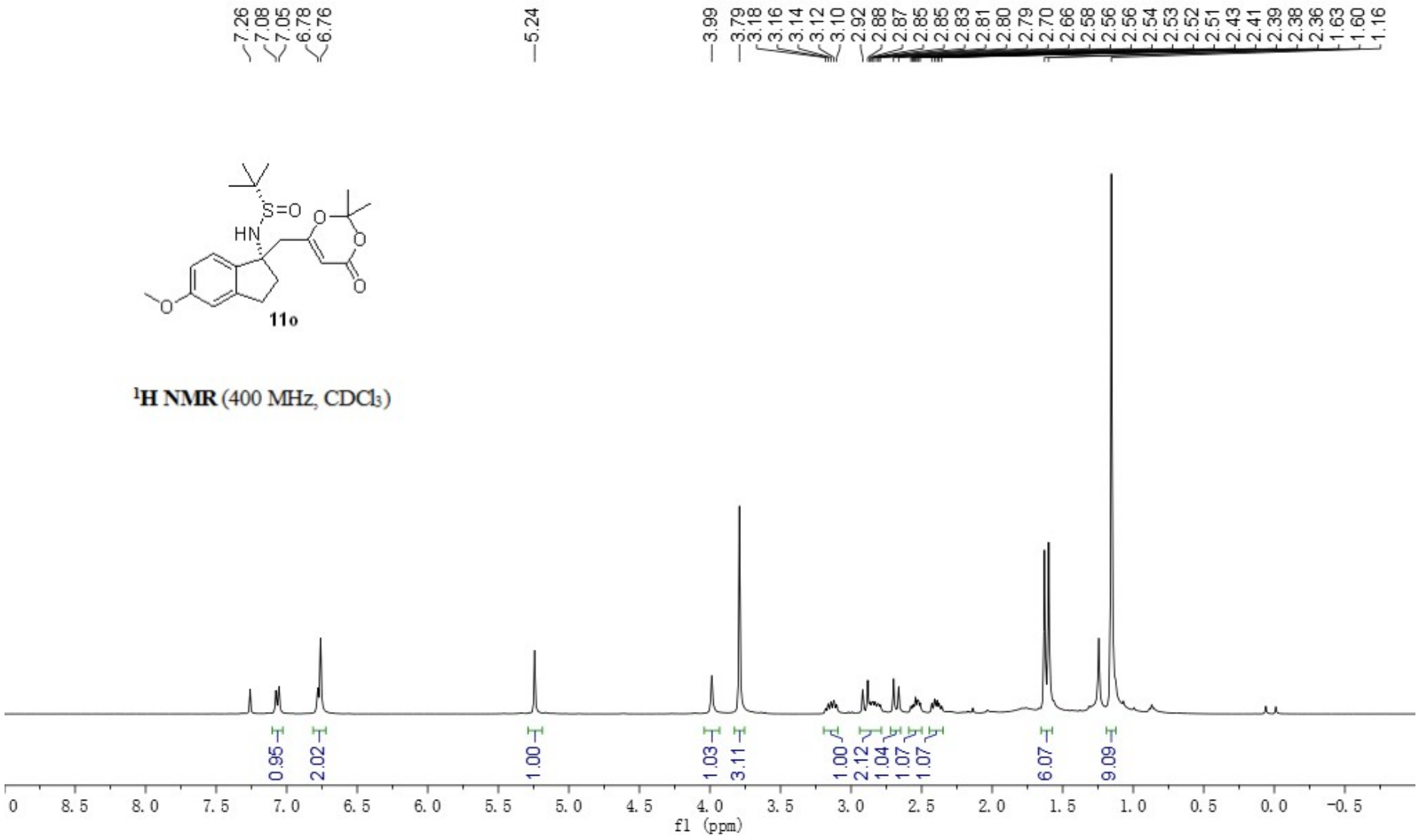
^{1}H NMR (400 MHz, $CDCl_3$)



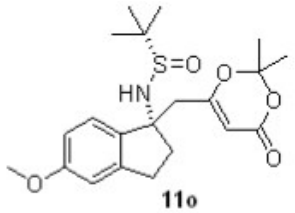
11n

^{13}C NMR (100 MHz, $CDCl_3$)



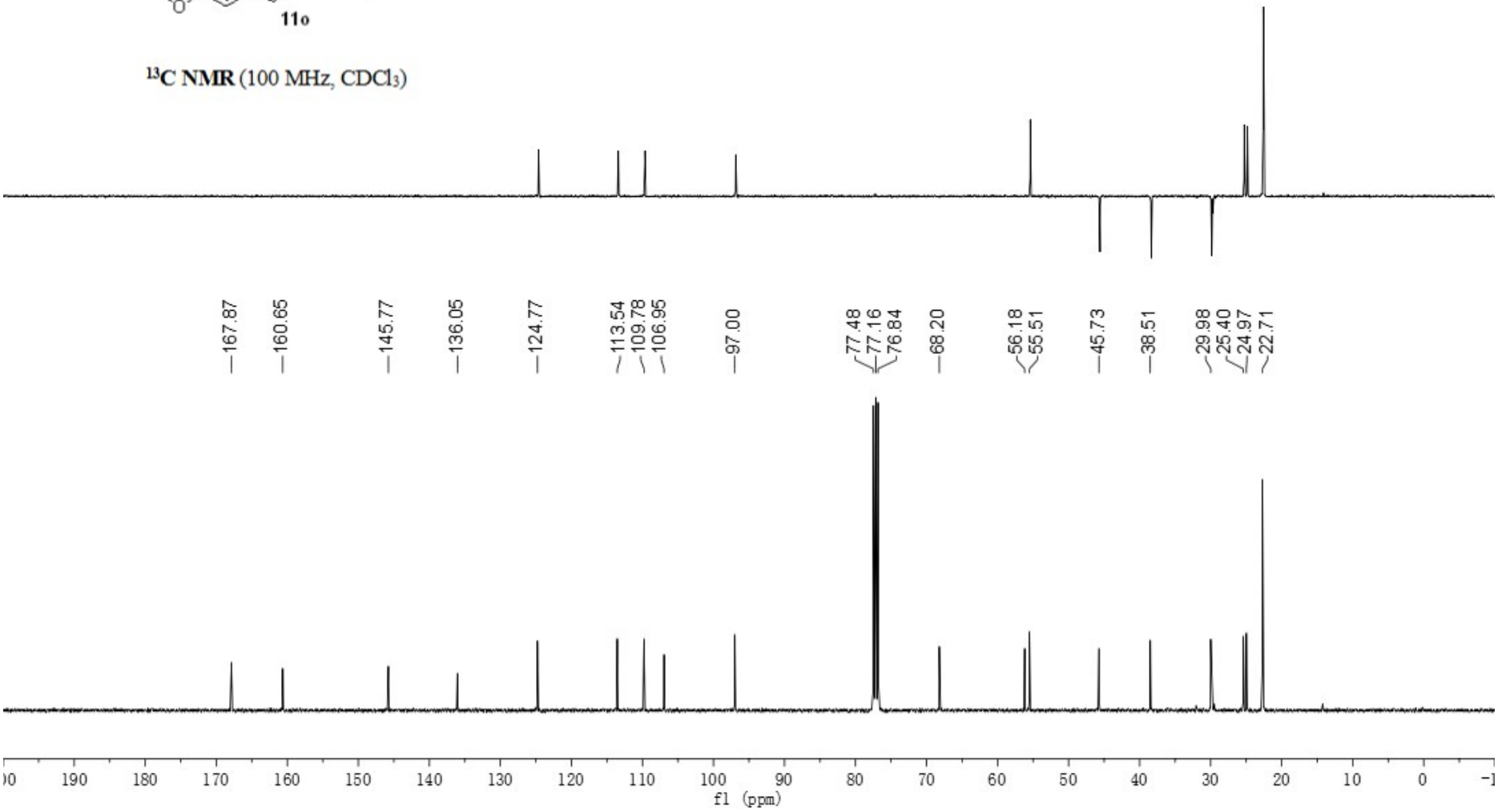


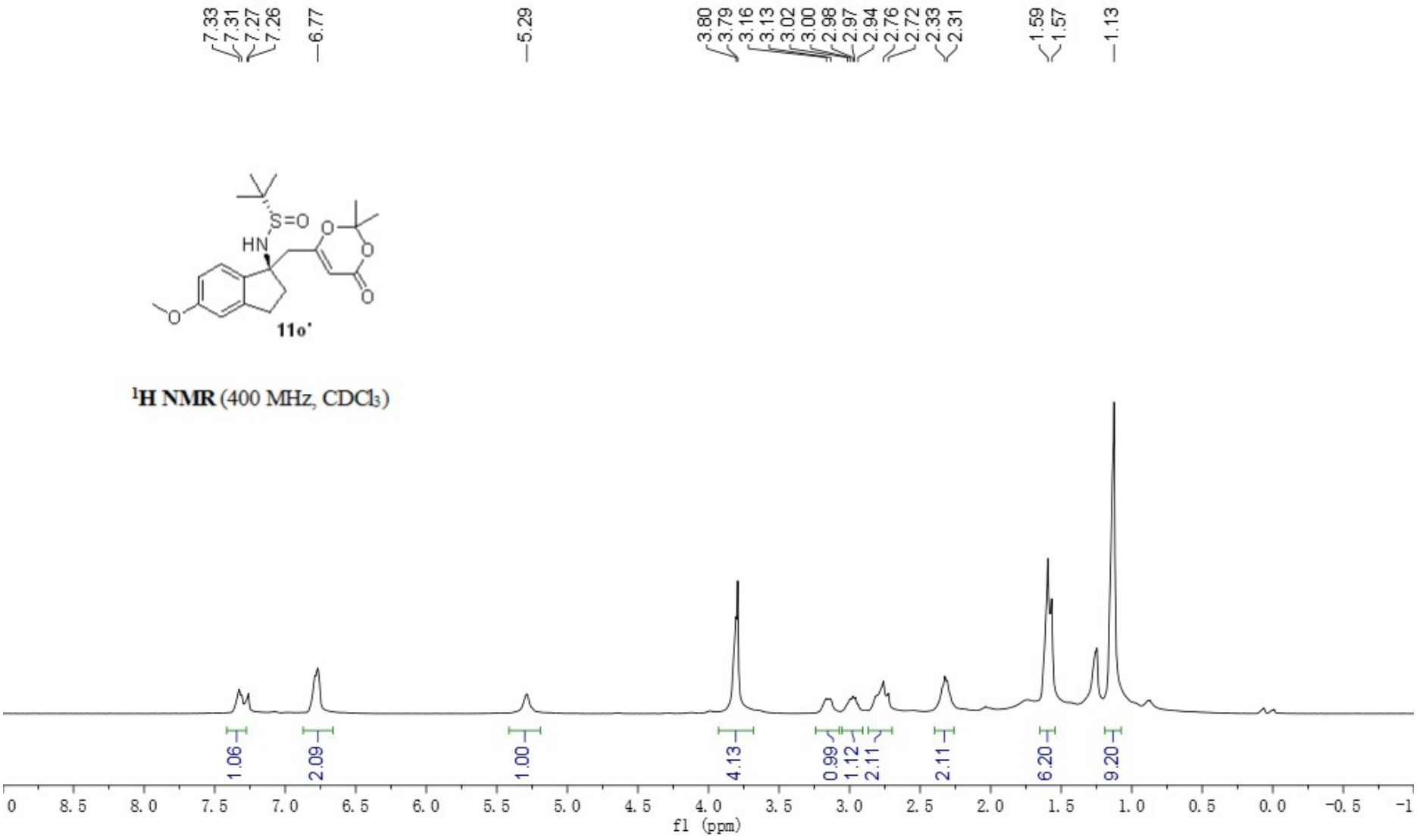
^{1}H NMR (400 MHz, $CDCl_3$)

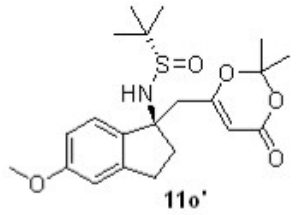


11o

^{13}C NMR (100 MHz, $CDCl_3$)

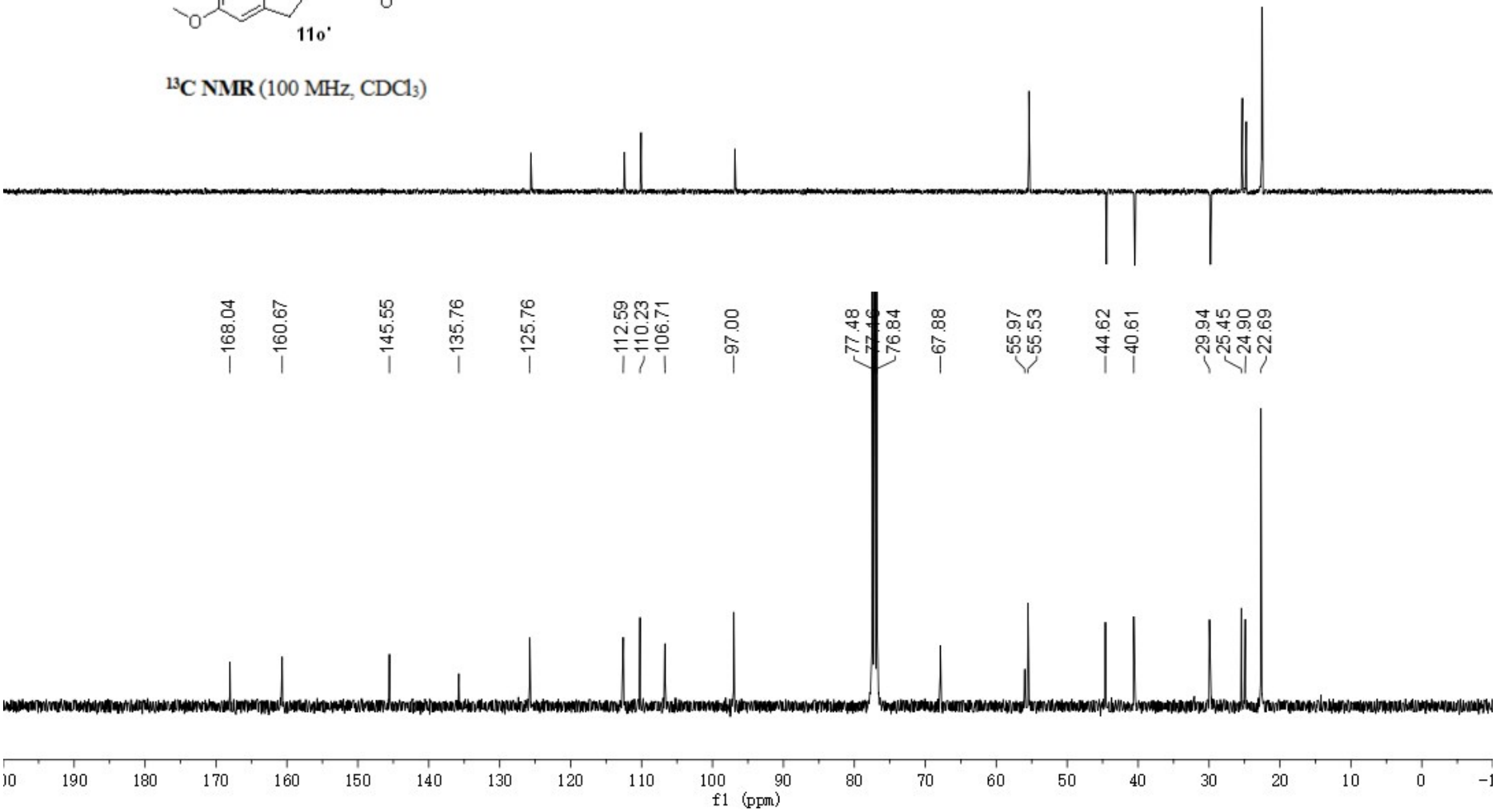


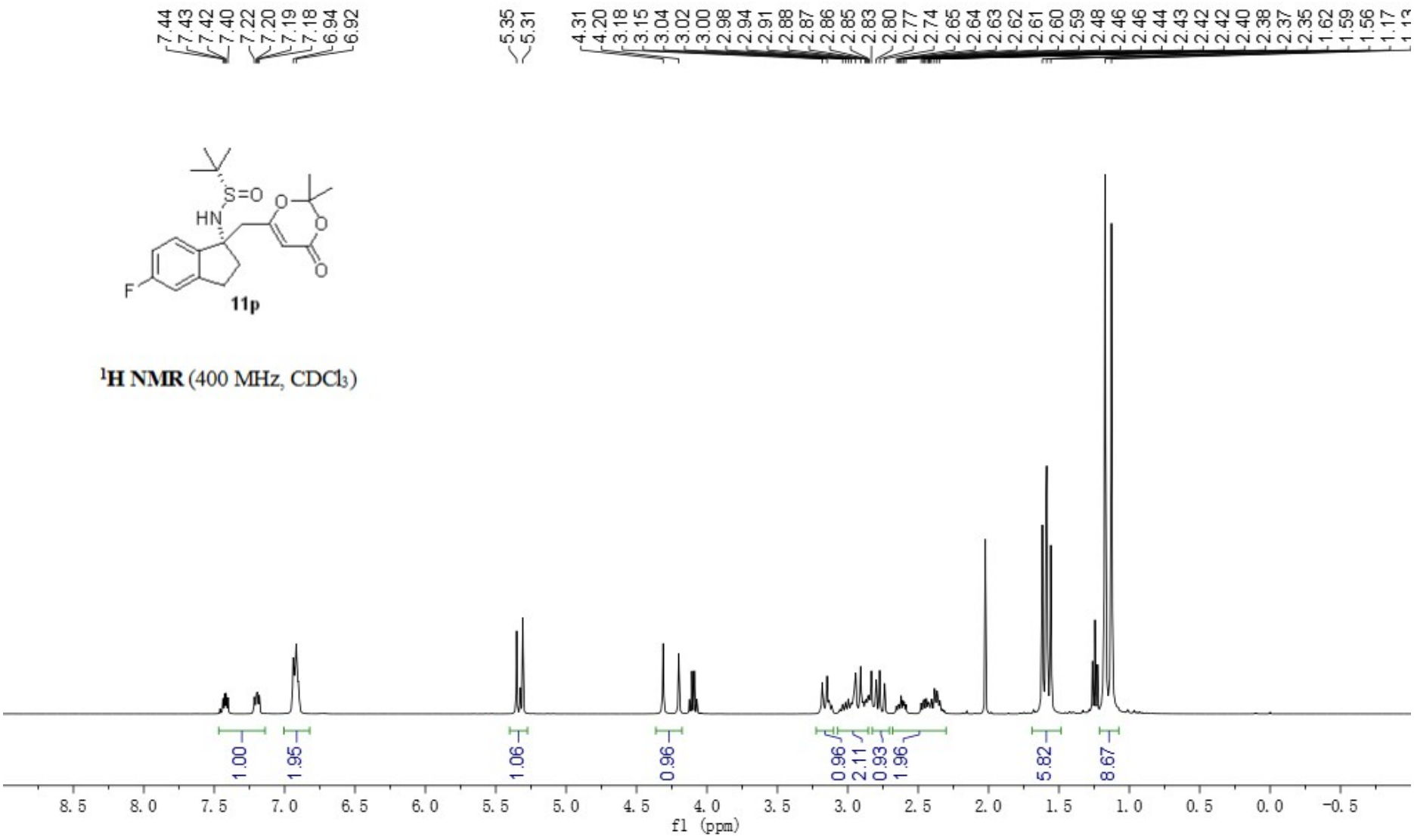

7.33
7.31
7.27
7.26
6.77
5.29
3.80
3.79
3.16
3.13
3.02
3.00
2.98
2.97
2.94
2.76
2.72
2.33
2.31
1.59
1.57
1.13
S=O
HN
O
O
O
O
11o'
1H NMR (400 MHz, CDCl3)
1.06
2.09
1.00
4.13
0.99
1.12
2.11
2.11
6.20
9.20
fl (ppm)

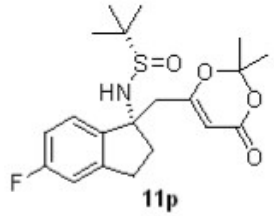


11o'

^{13}C NMR (100 MHz, $CDCl_3$)

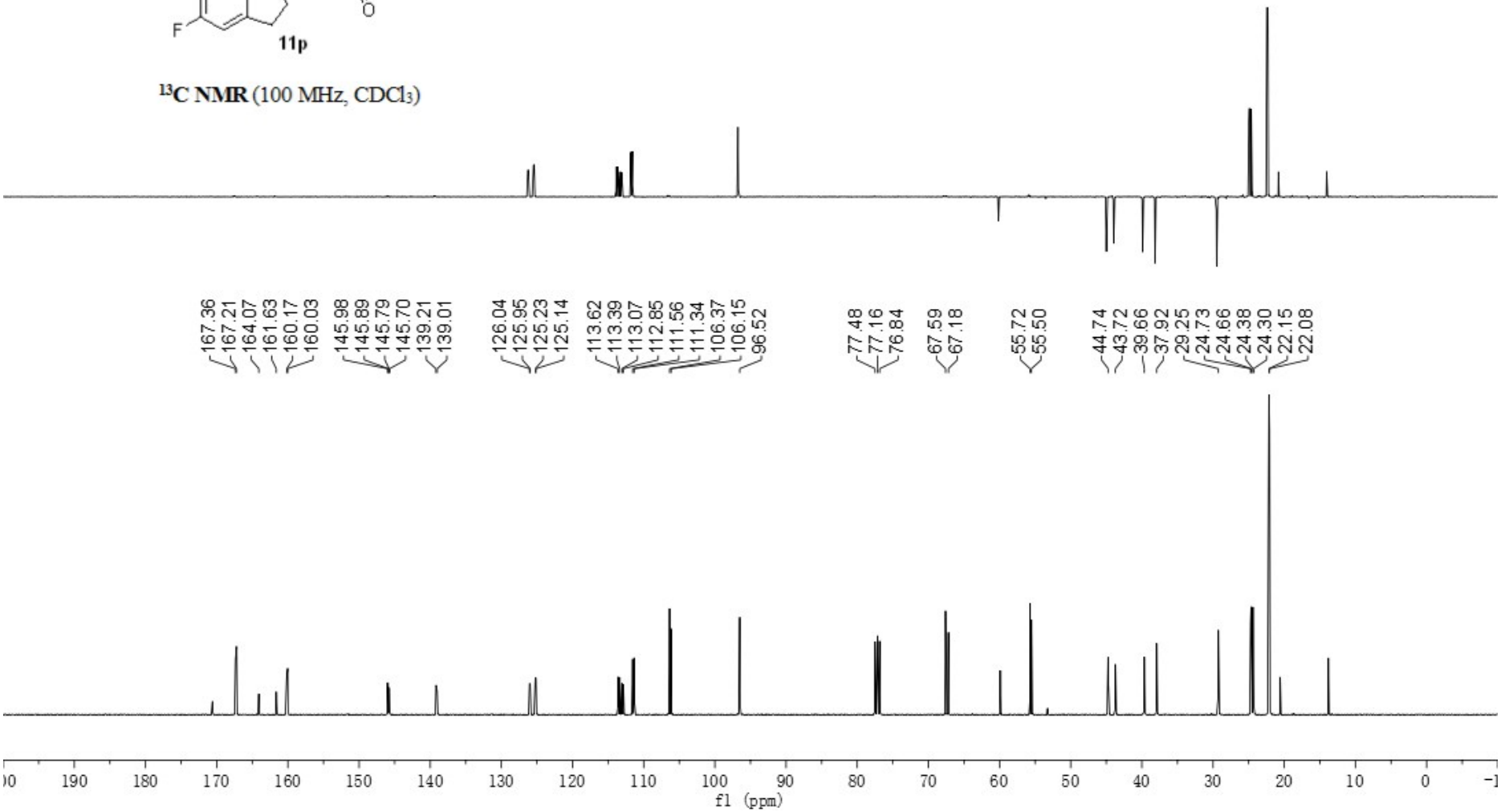


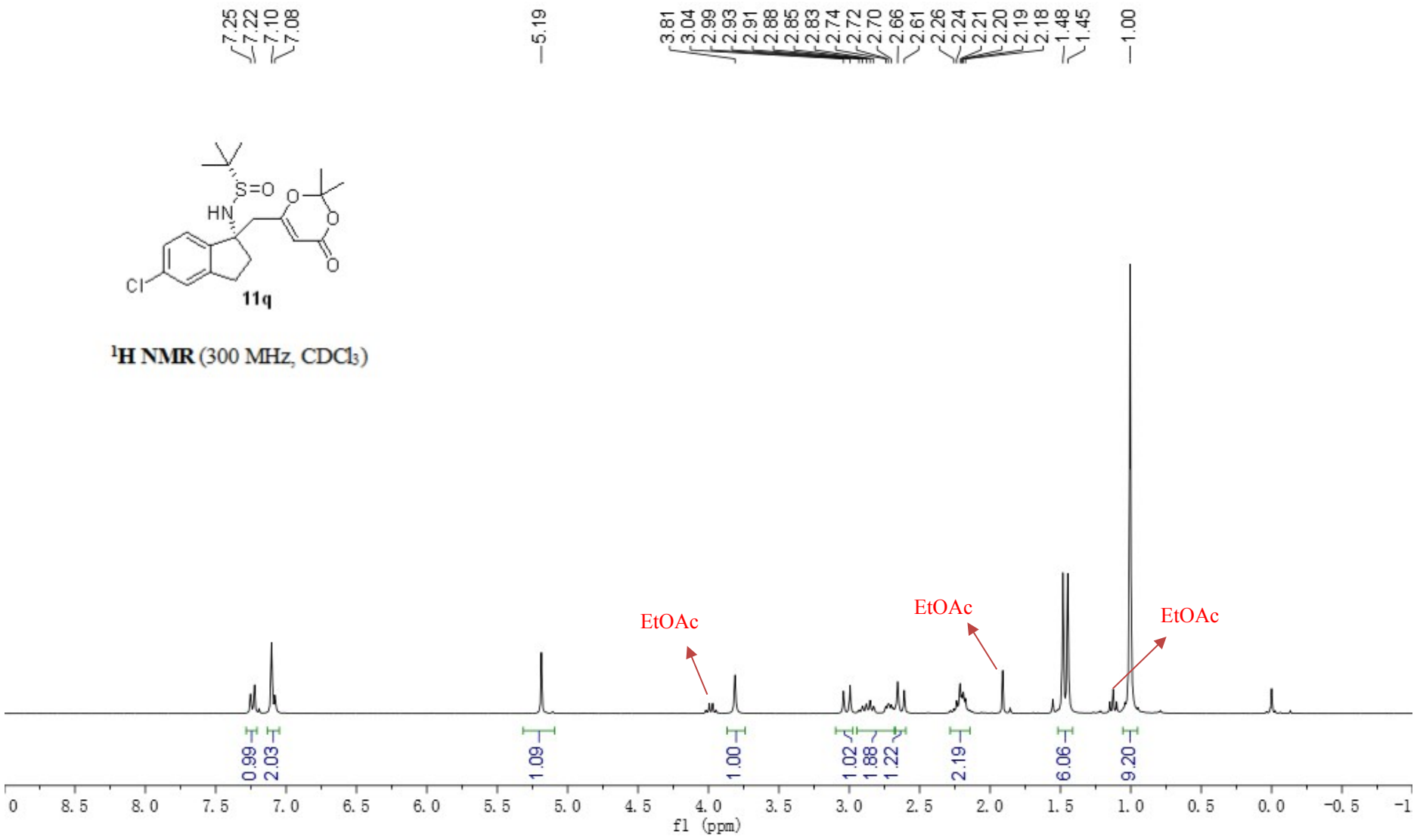

7.44
7.43
7.42
7.40
7.22
7.20
7.19
7.18
6.94
6.92
5.35
5.31
4.31
4.20
3.18
3.15
3.04
3.02
3.00
2.98
2.94
2.91
2.88
2.87
2.86
2.85
2.83
2.80
2.77
2.74
2.65
2.64
2.63
2.62
2.61
2.60
2.59
2.48
2.46
2.46
2.44
2.43
2.42
2.42
2.40
2.38
2.37
2.35
1.62
1.59
1.56
1.17
S=O
HN
O
O
O
F
11p
1H NMR (400 MHz, CDCl3)
1.00
1.95
1.06
0.96
0.96
2.11
0.93
1.96
5.82
8.67
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



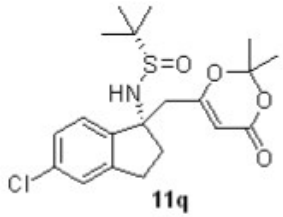
11p

^{13}C NMR (100 MHz, $CDCl_3$)



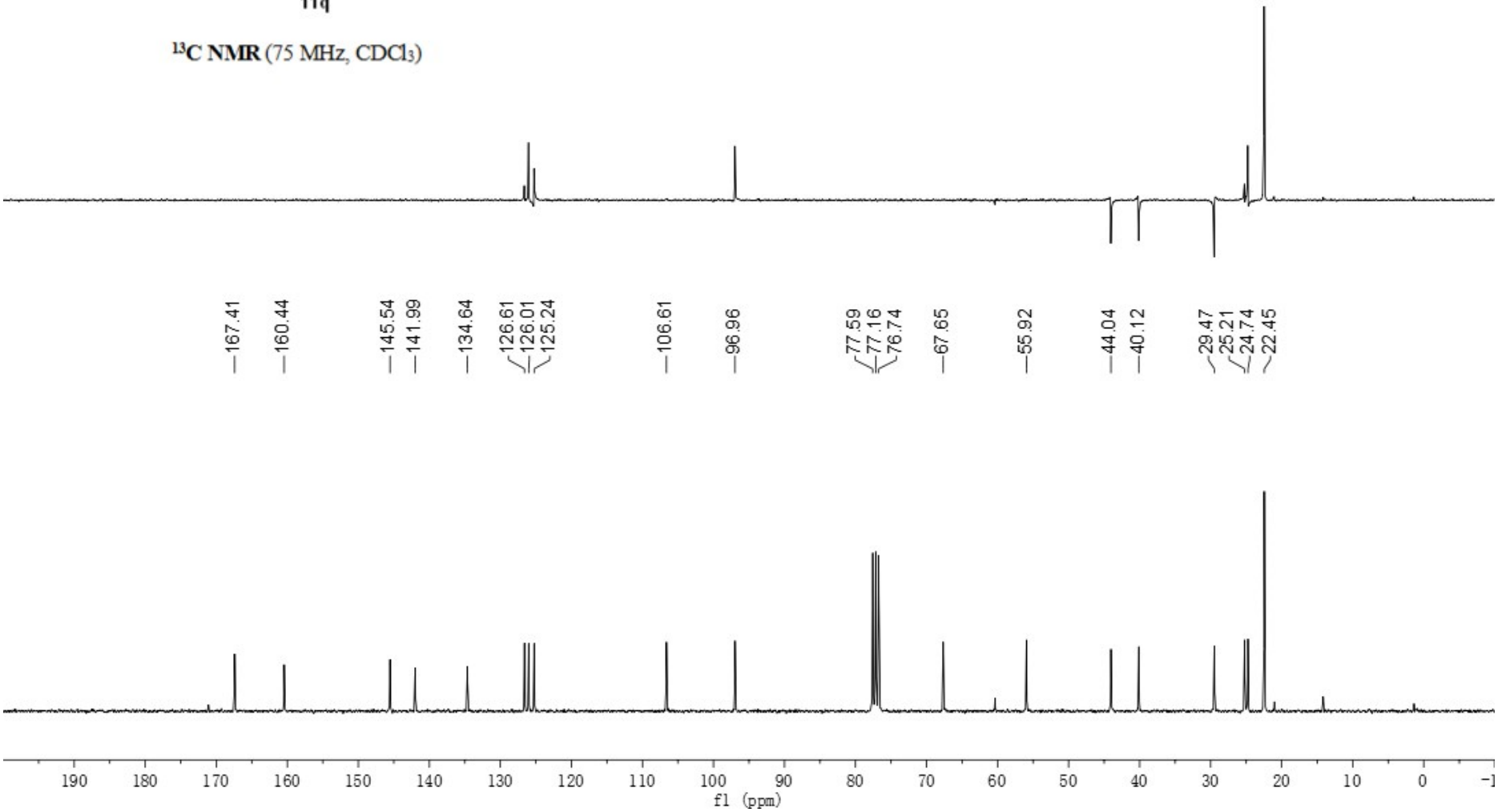


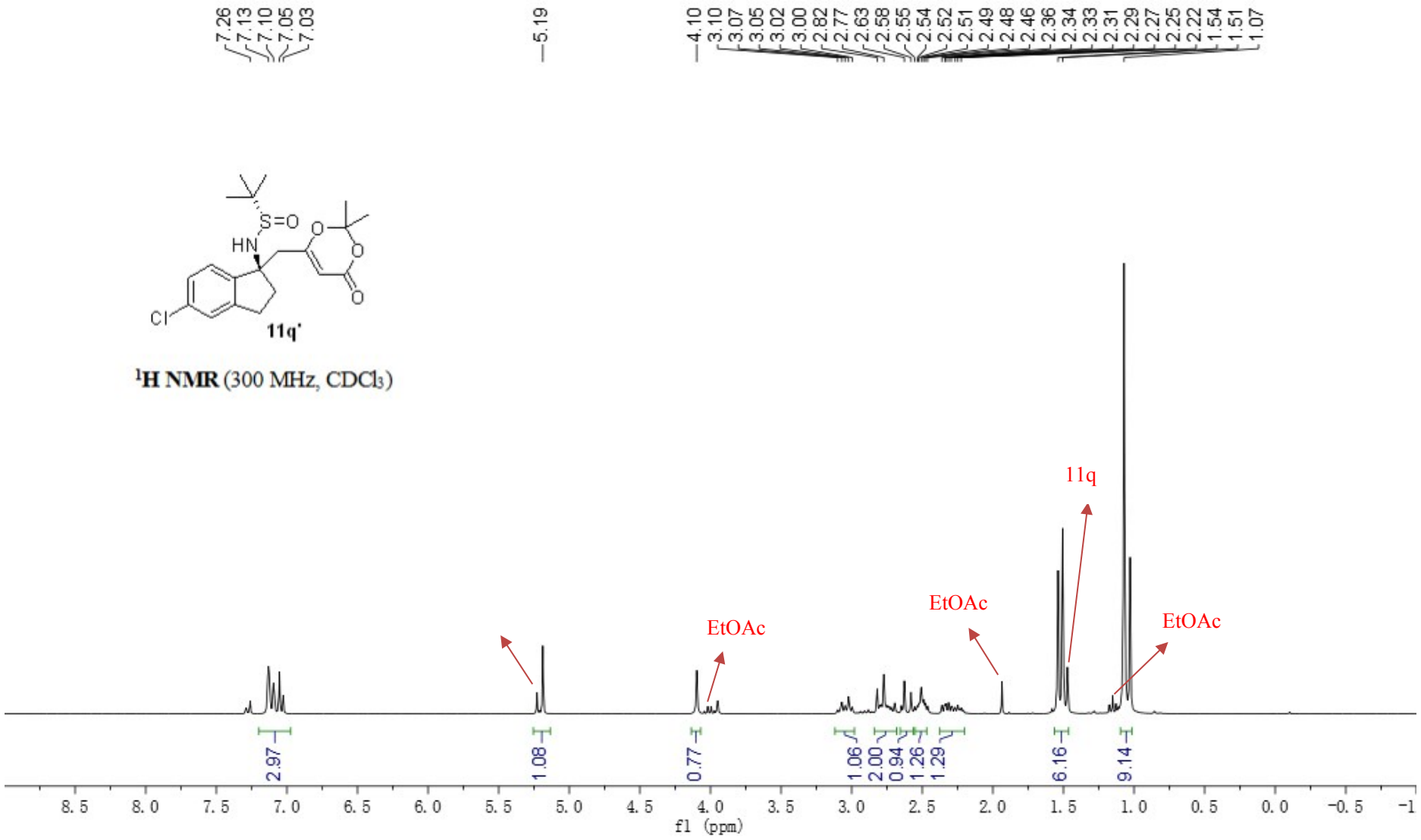
^{1}H NMR (300 MHz, $CDCl_3$)



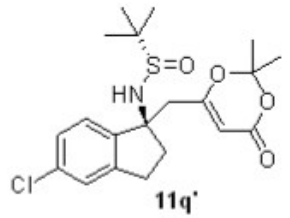
11q

^{13}C NMR (75 MHz, $CDCl_3$)



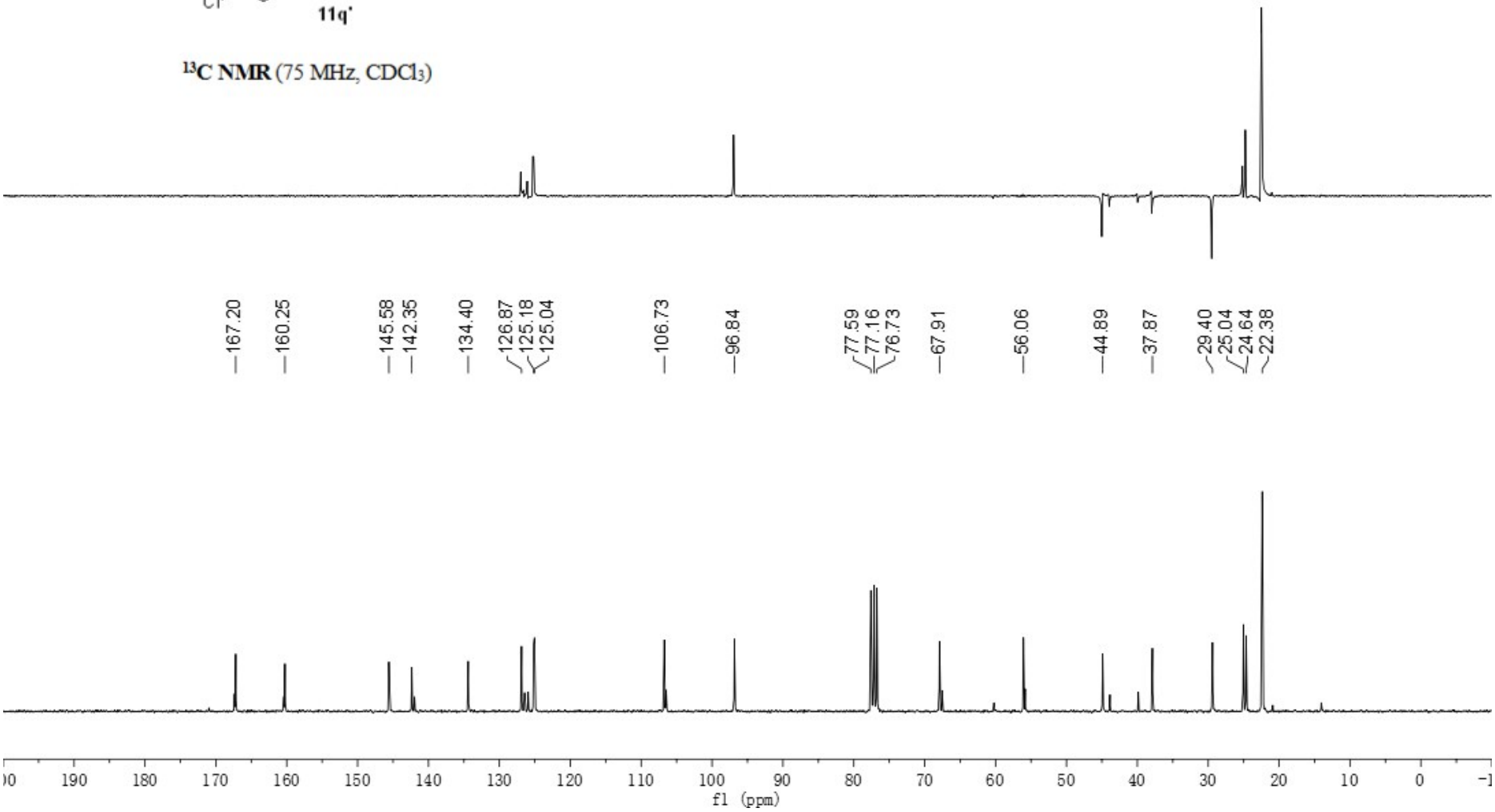


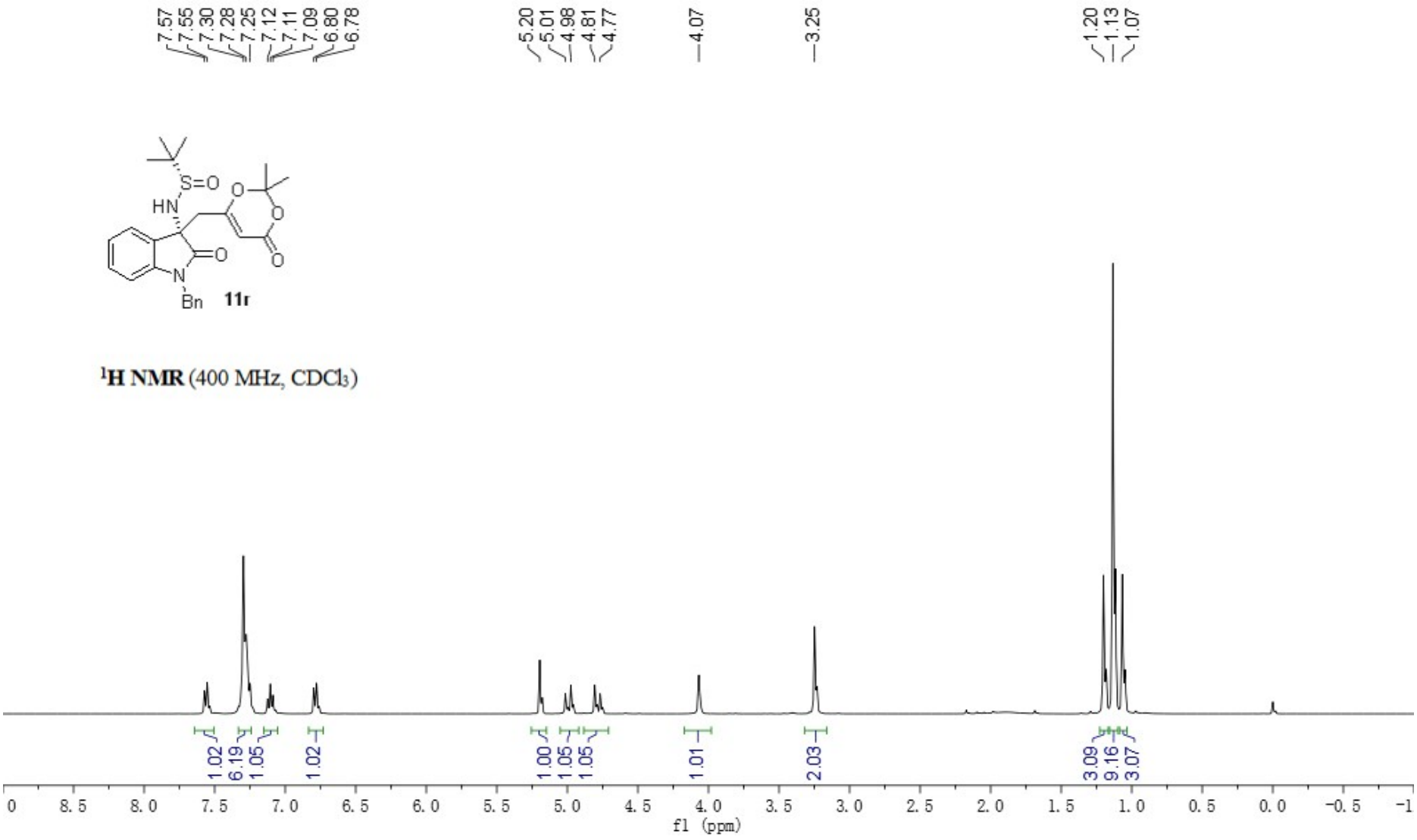
^{1}H NMR (300 MHz, $CDCl_3$)



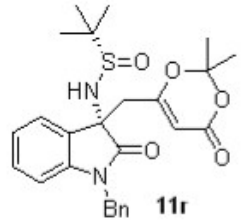
11q'

^{13}C NMR (75 MHz, $CDCl_3$)



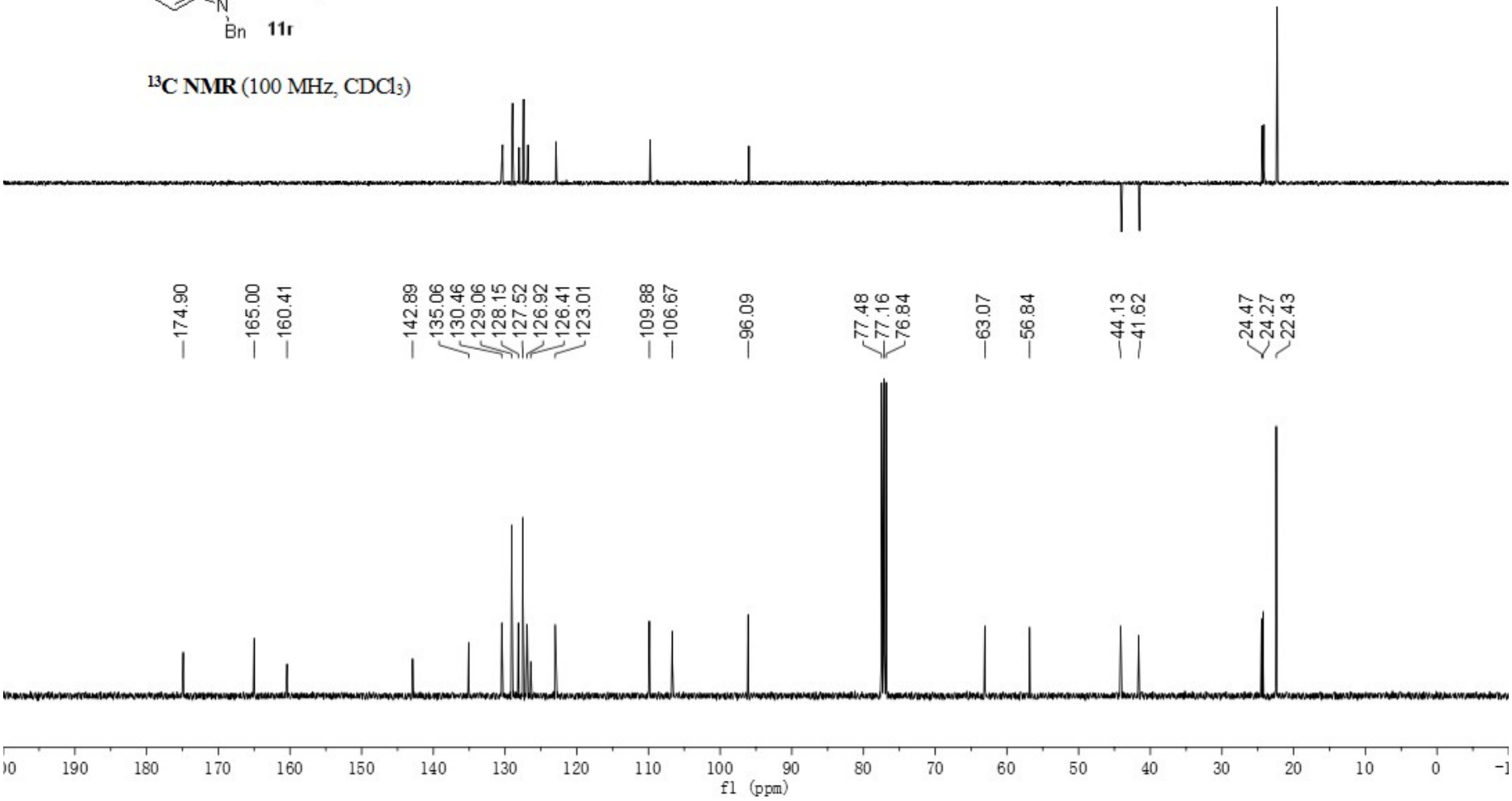


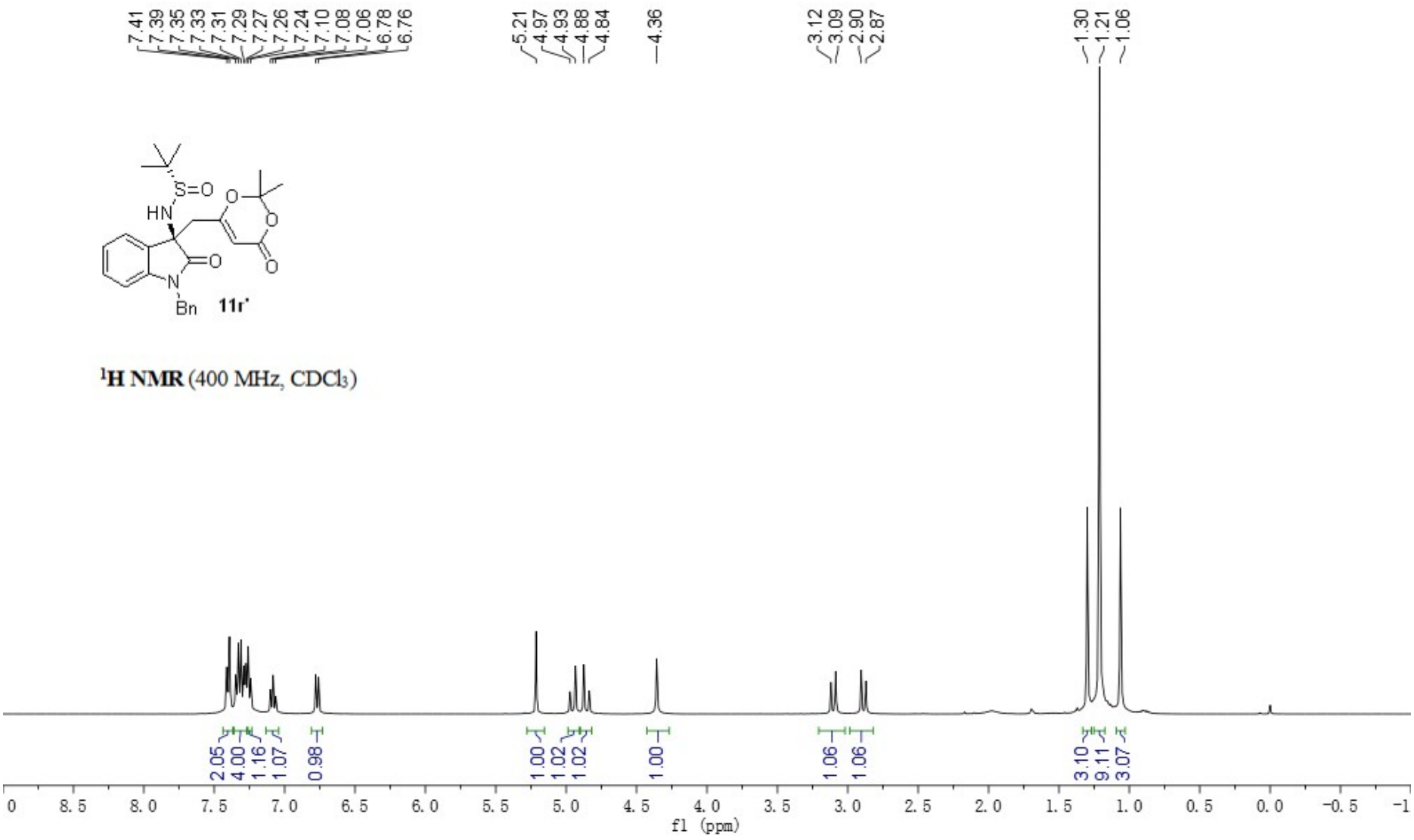
^{1}H NMR (400 MHz, $CDCl_3$)



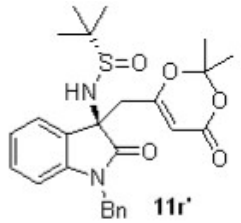
11r

^{13}C NMR (100 MHz, $CDCl_3$)



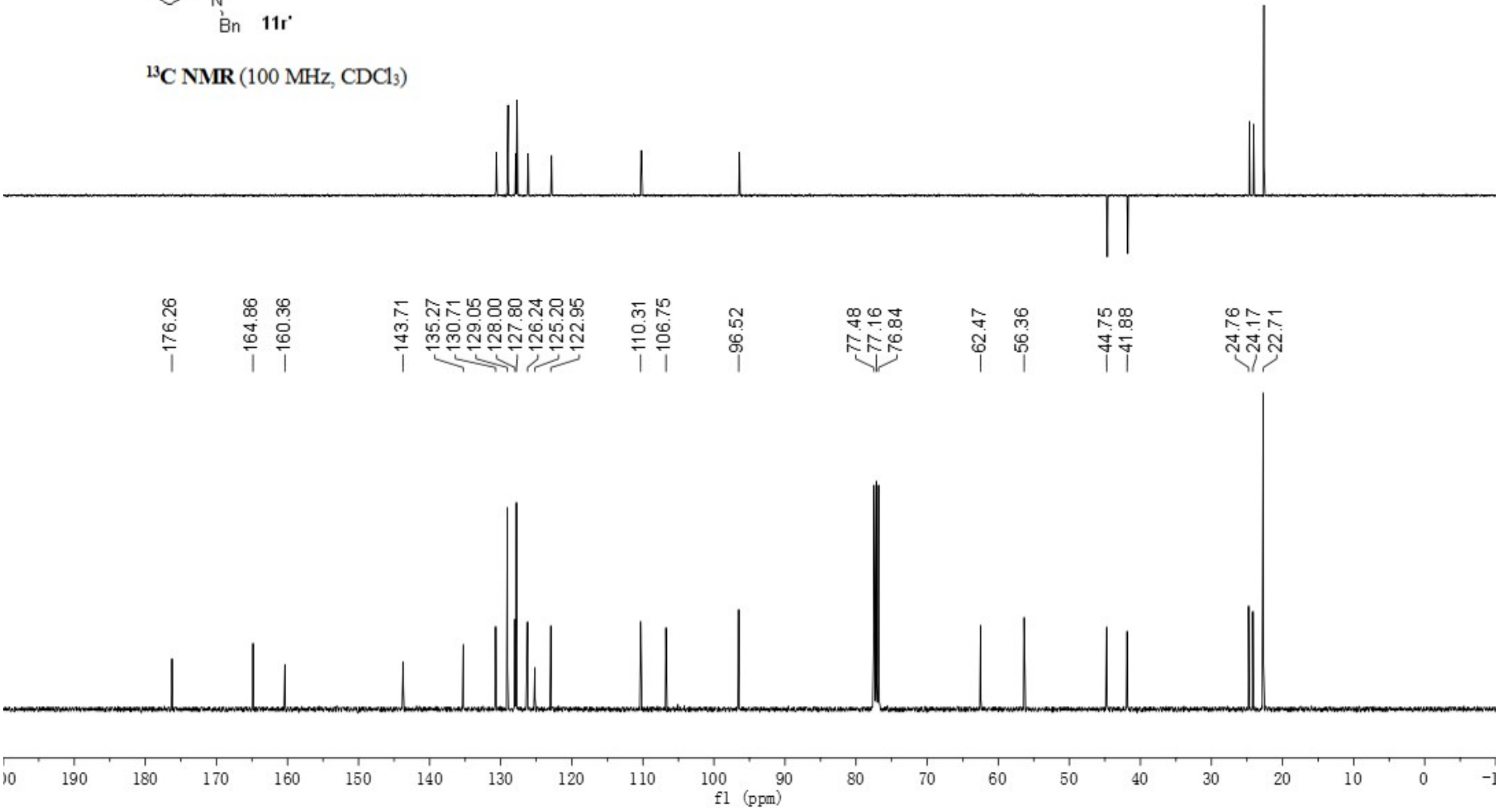


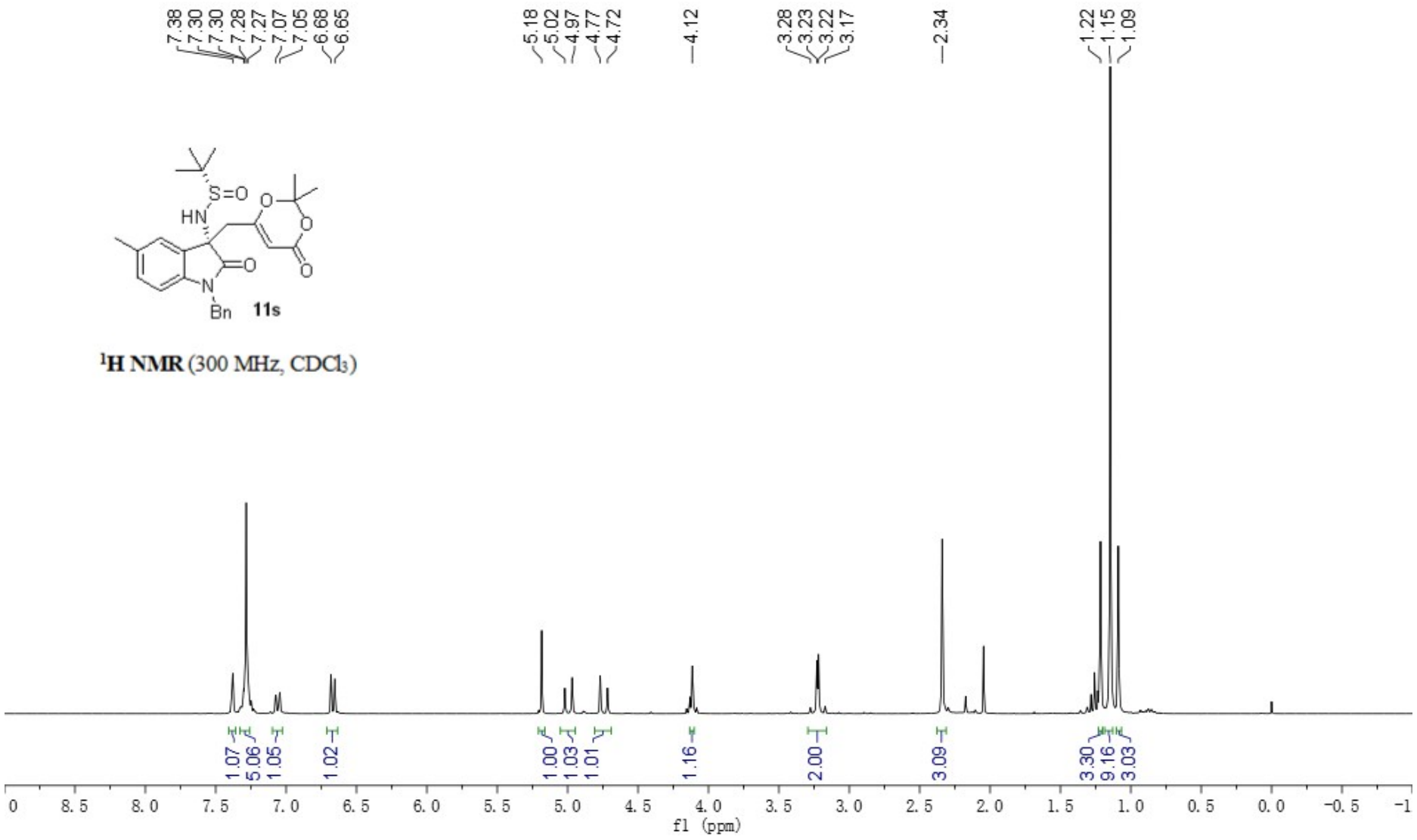
^{1}H NMR (400 MHz, $CDCl_3$)



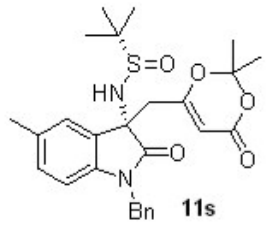
11r'

^{13}C NMR (100 MHz, $CDCl_3$)



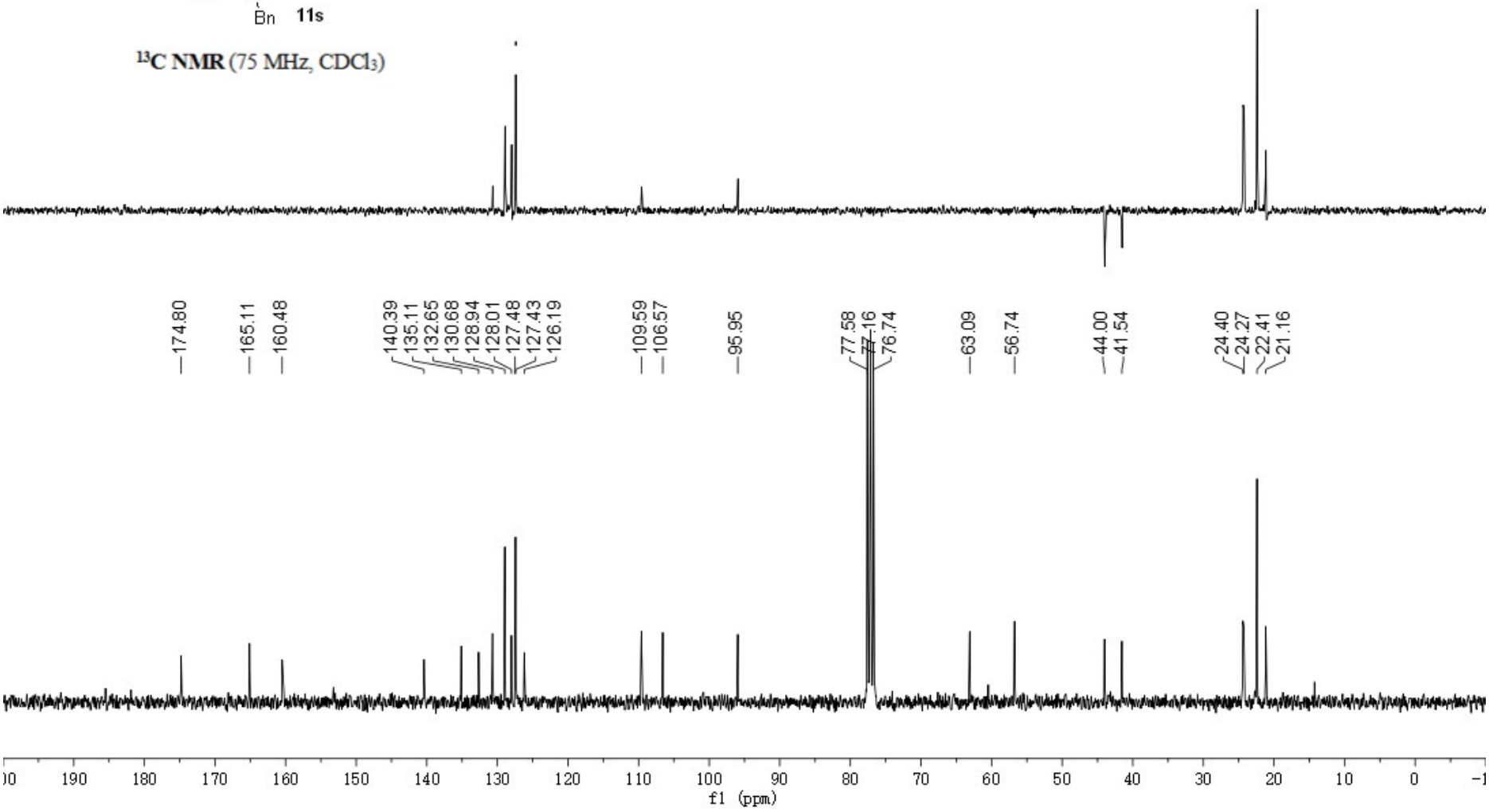


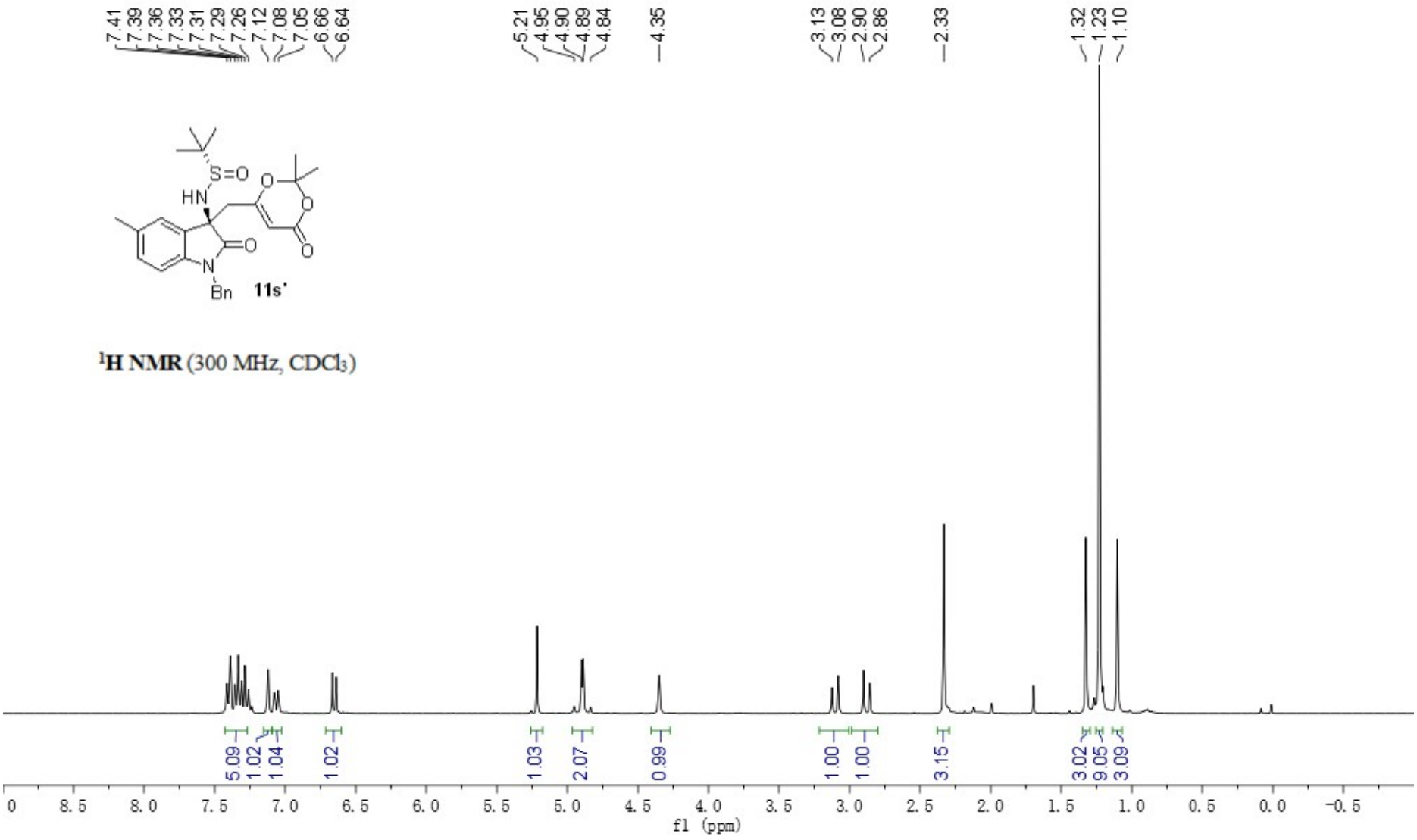
^{1}H NMR (300 MHz, $CDCl_3$)



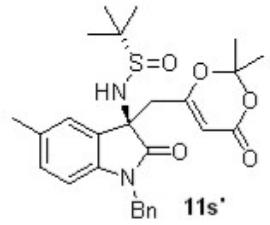
11s

^{13}C NMR (75 MHz, $CDCl_3$)



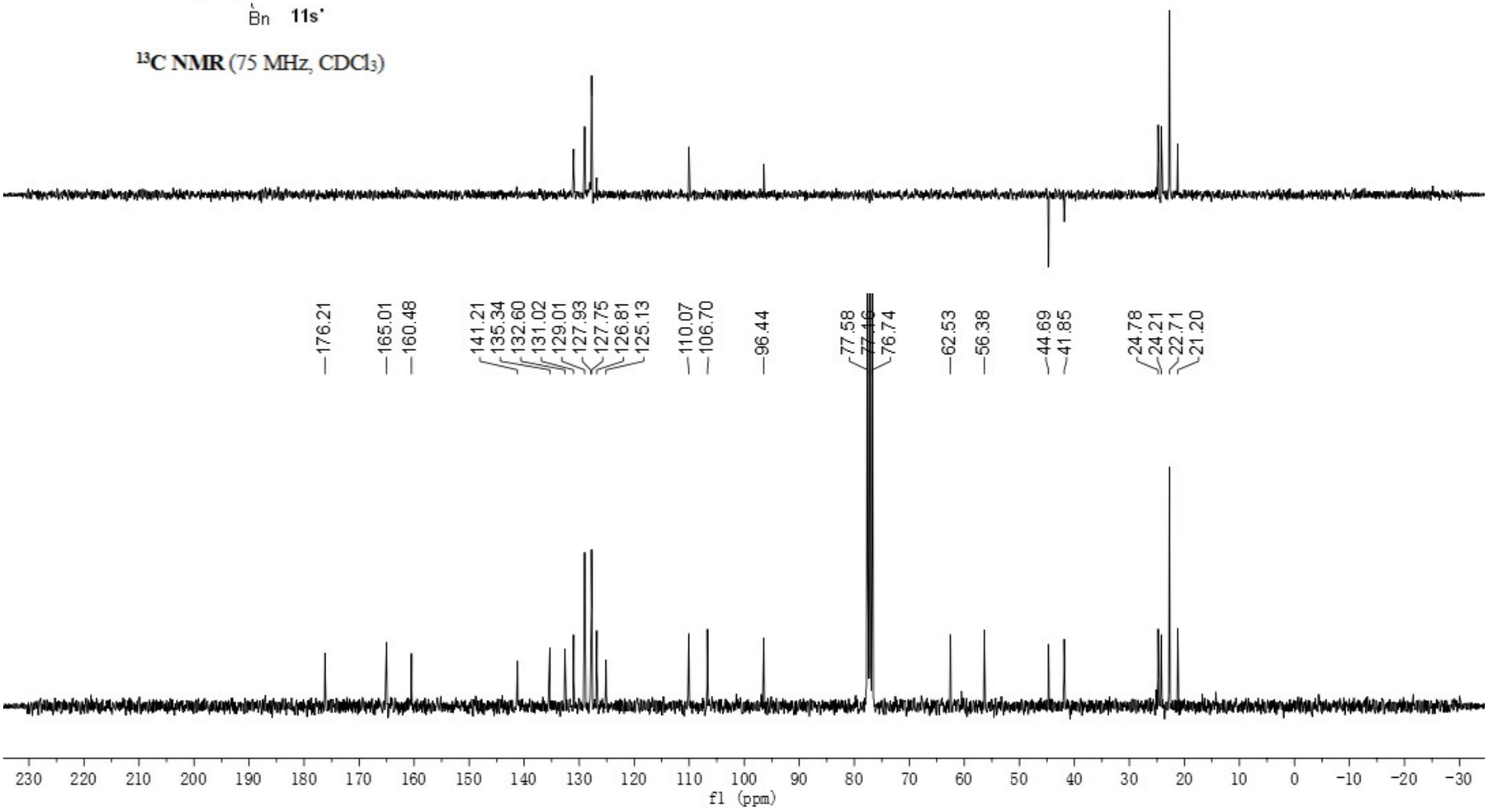


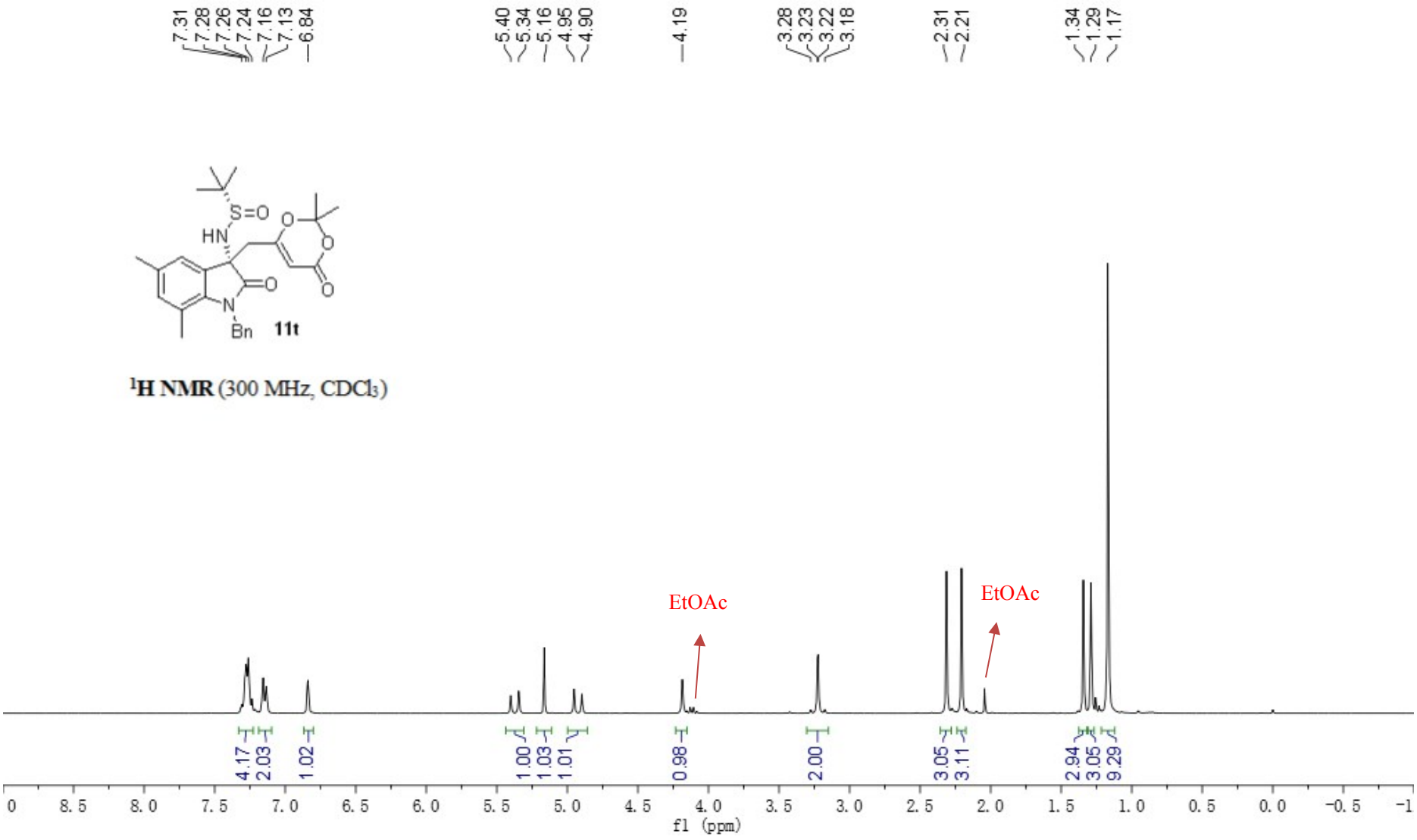
^{1}H NMR (300 MHz, $CDCl_3$)



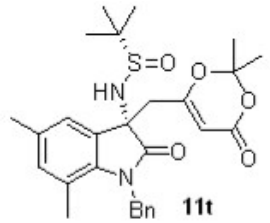
11s'

^{13}C NMR (75 MHz, $CDCl_3$)



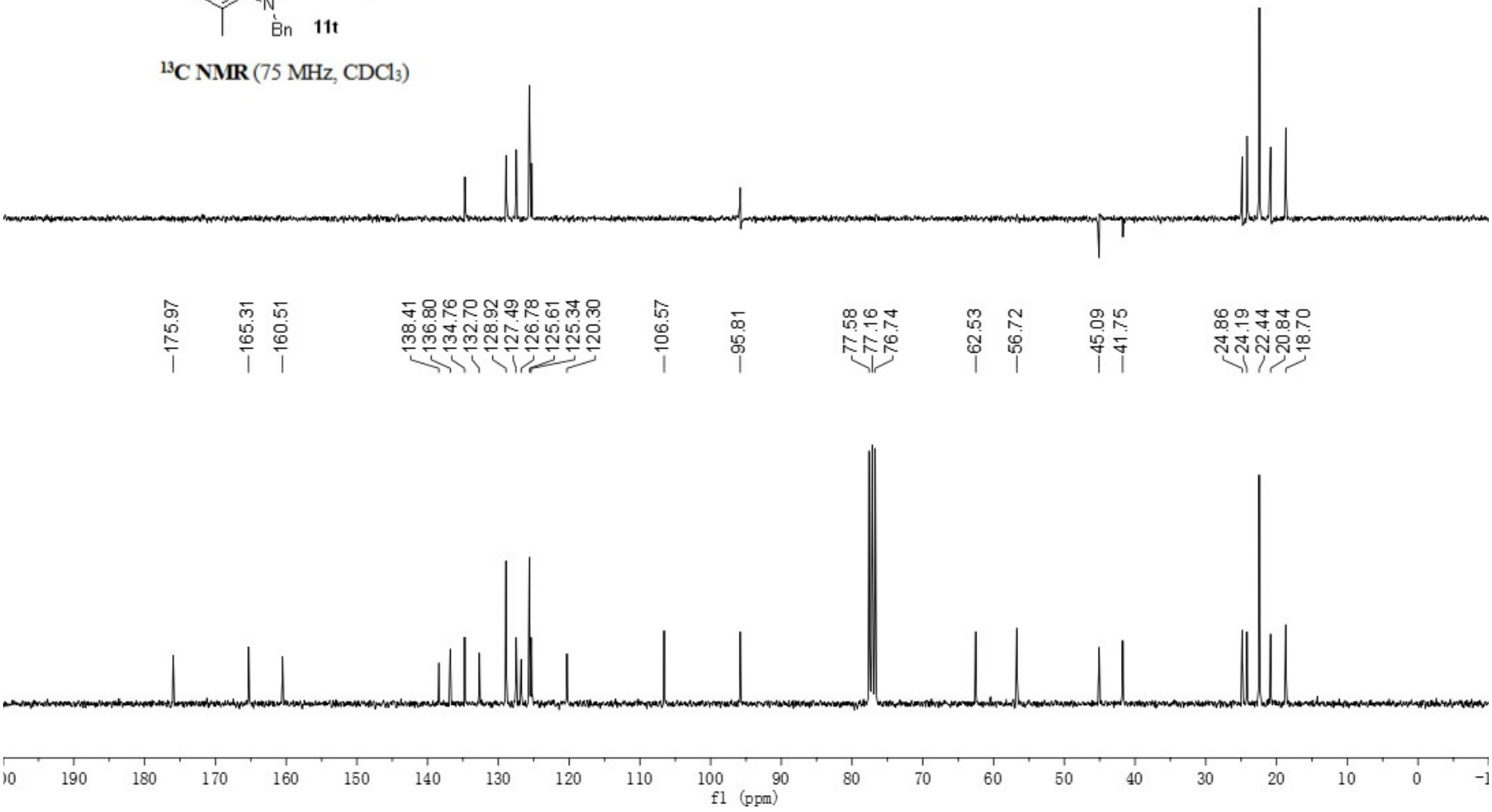


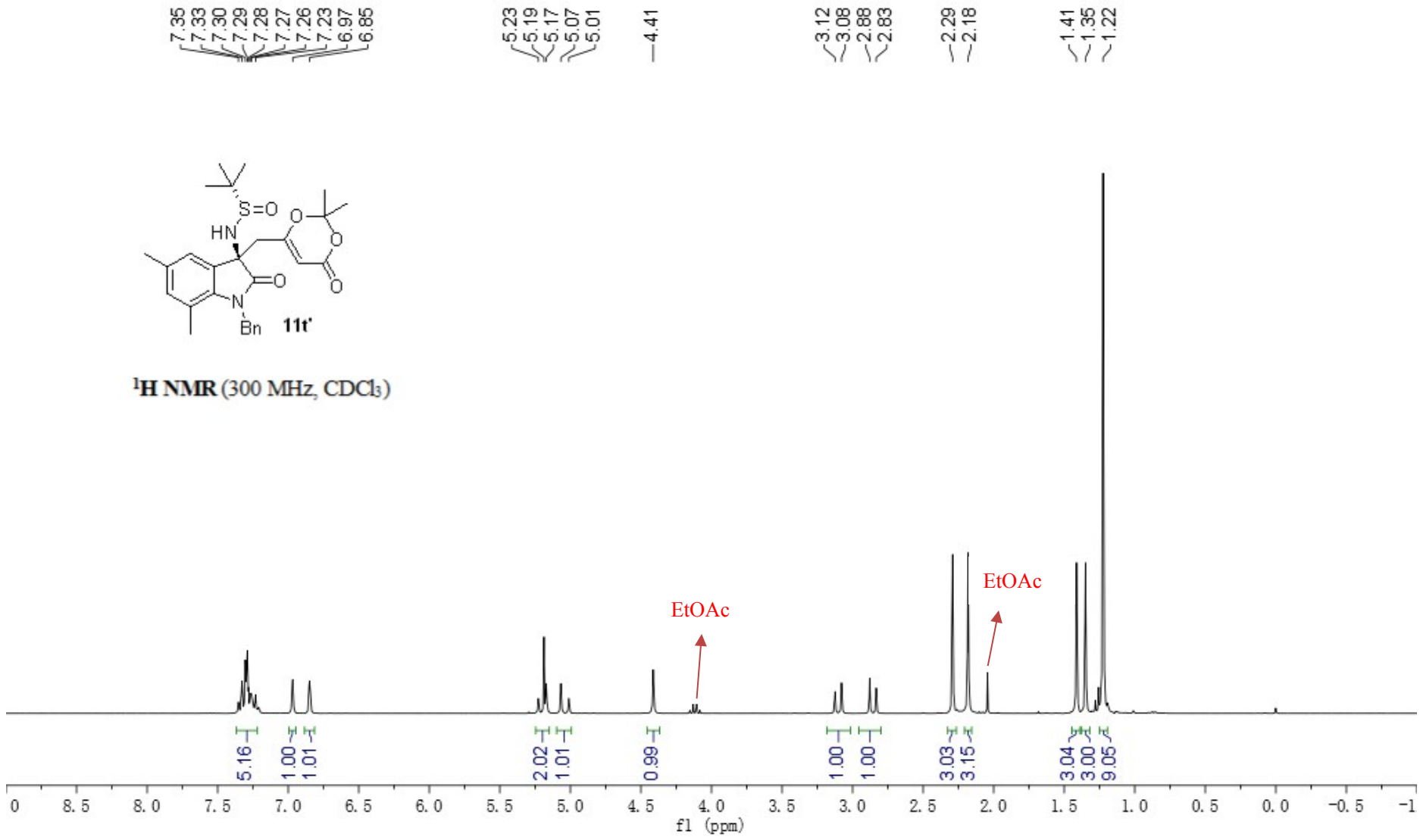
^{1}H NMR (300 MHz, $CDCl_3$)



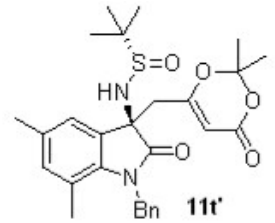
11t

^{13}C NMR (75 MHz, $CDCl_3$)



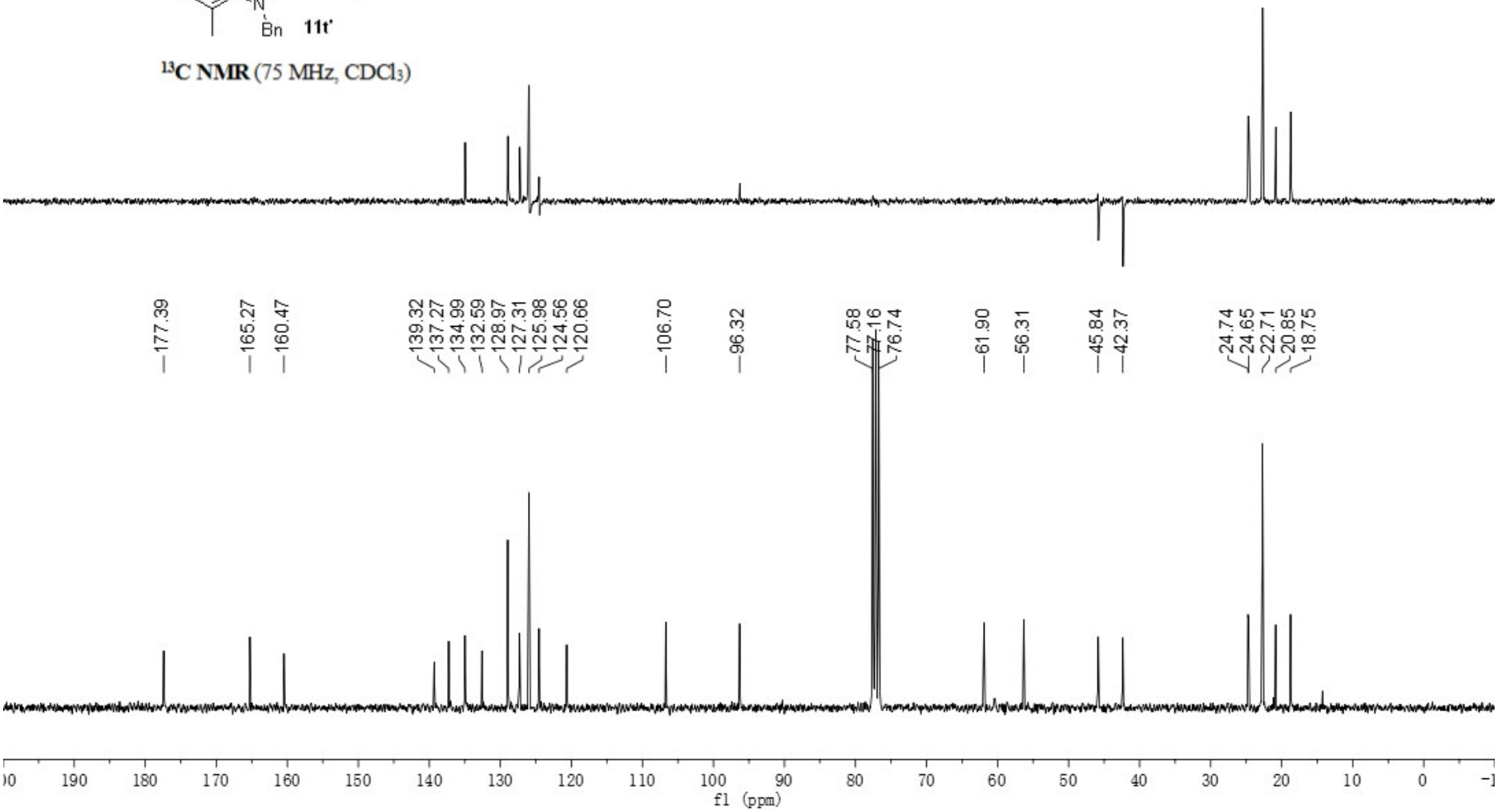


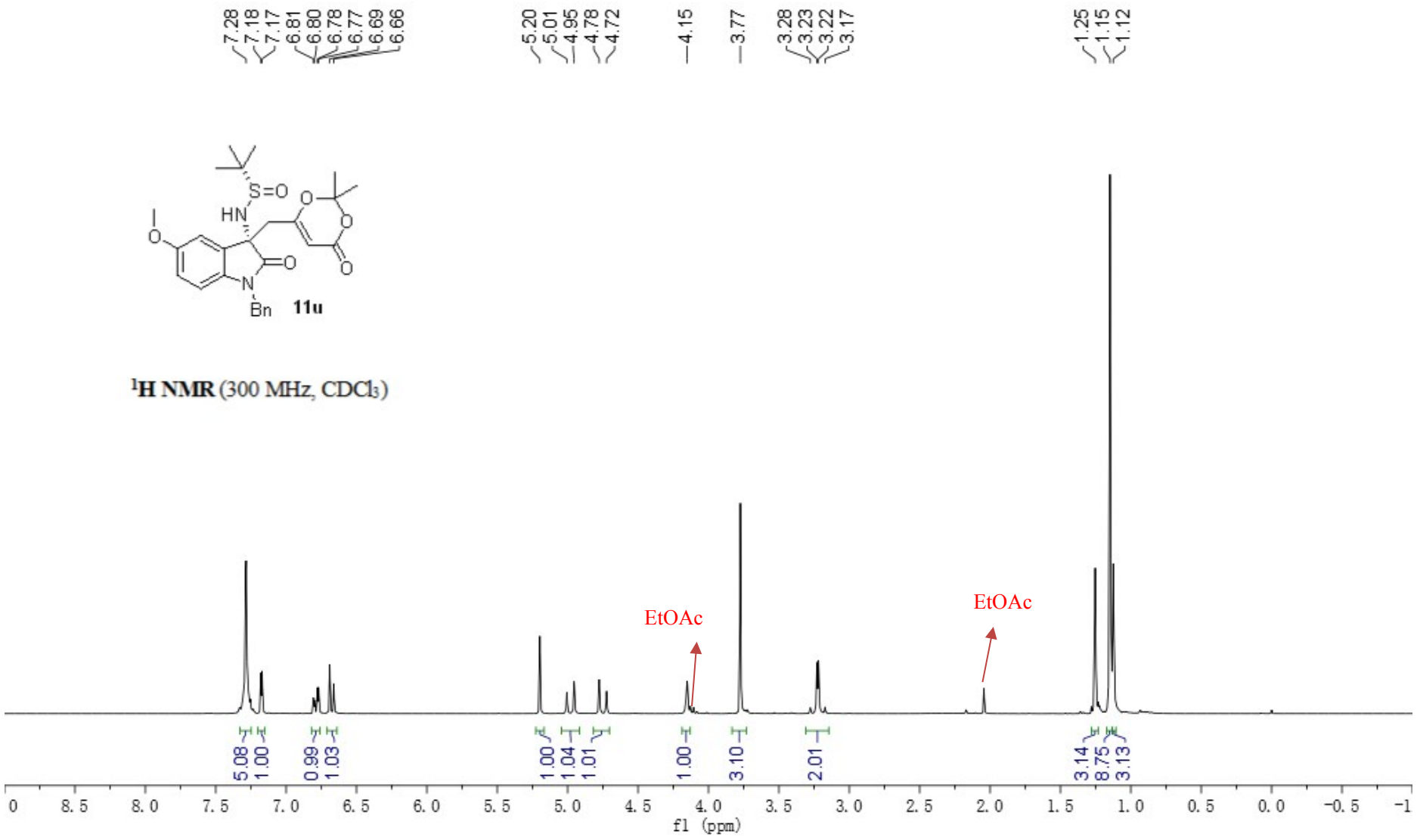
^{1}H NMR (300 MHz, $CDCl_3$)



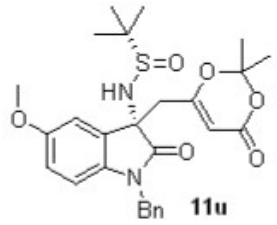
11t'

^{13}C NMR (75 MHz, $CDCl_3$)



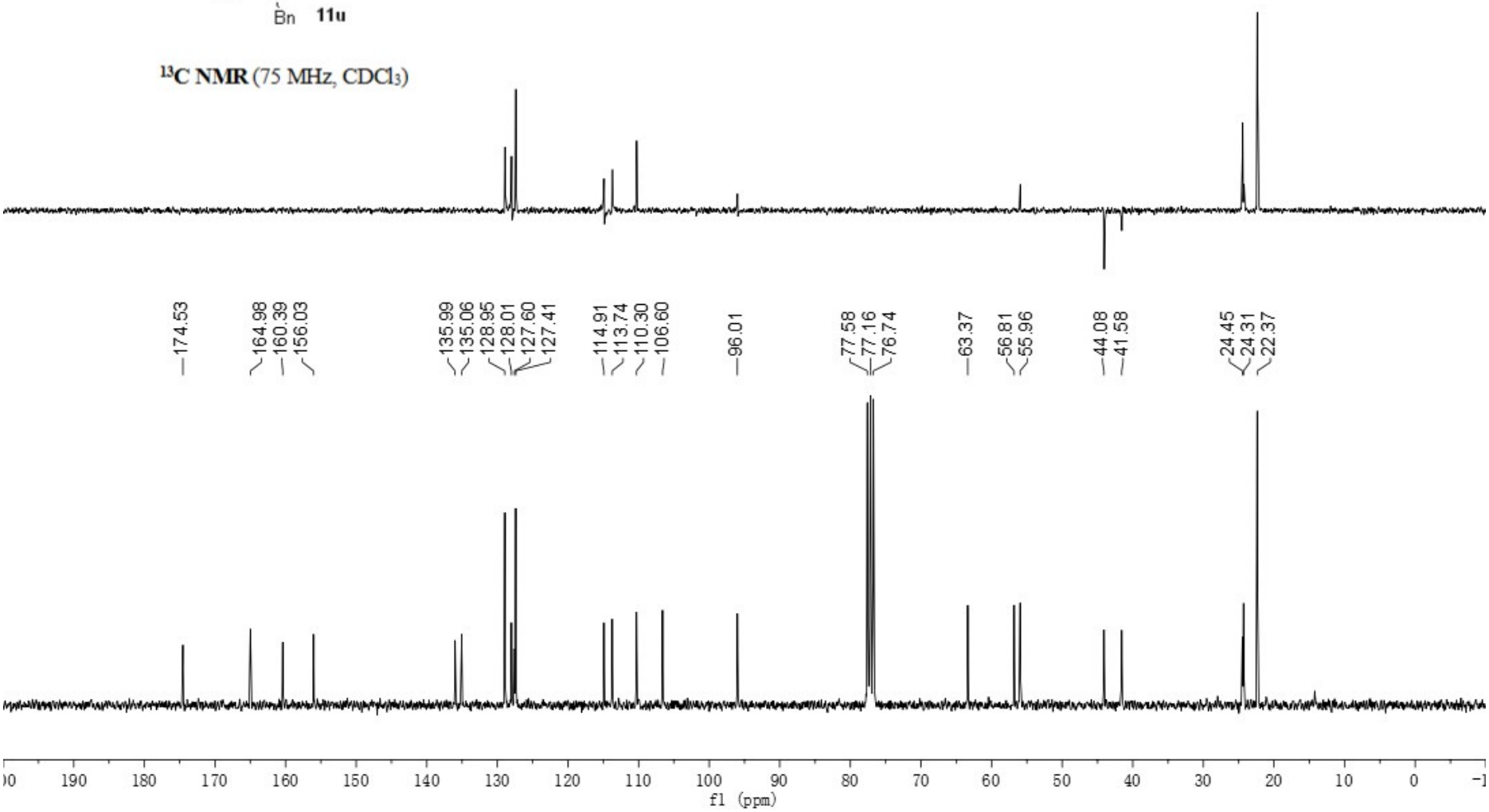


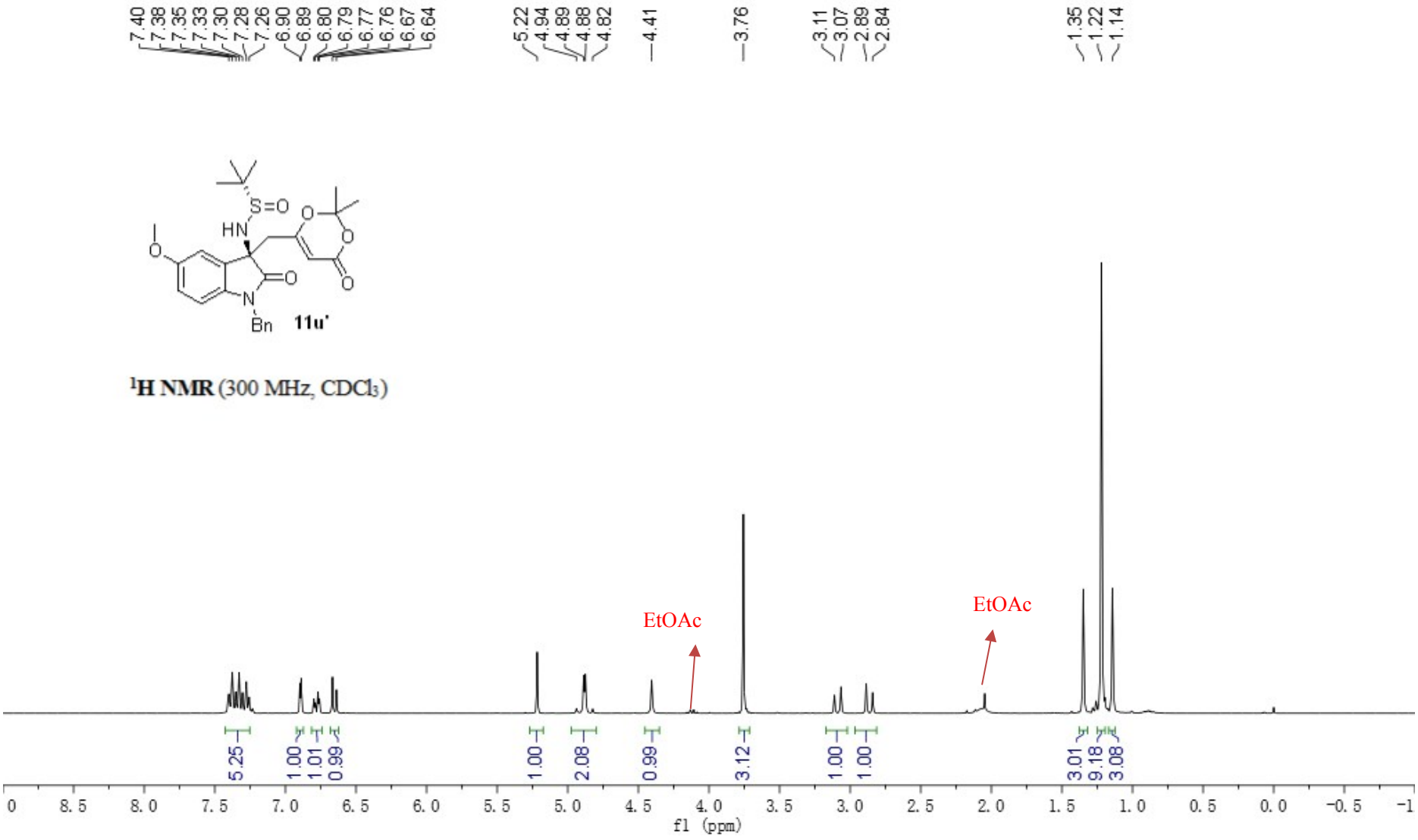
^{1}H NMR (300 MHz, $CDCl_3$)



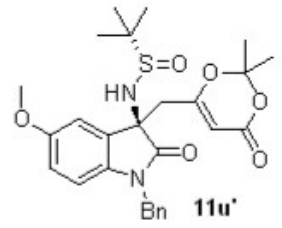
11u

^{13}C NMR (75 MHz, $CDCl_3$)



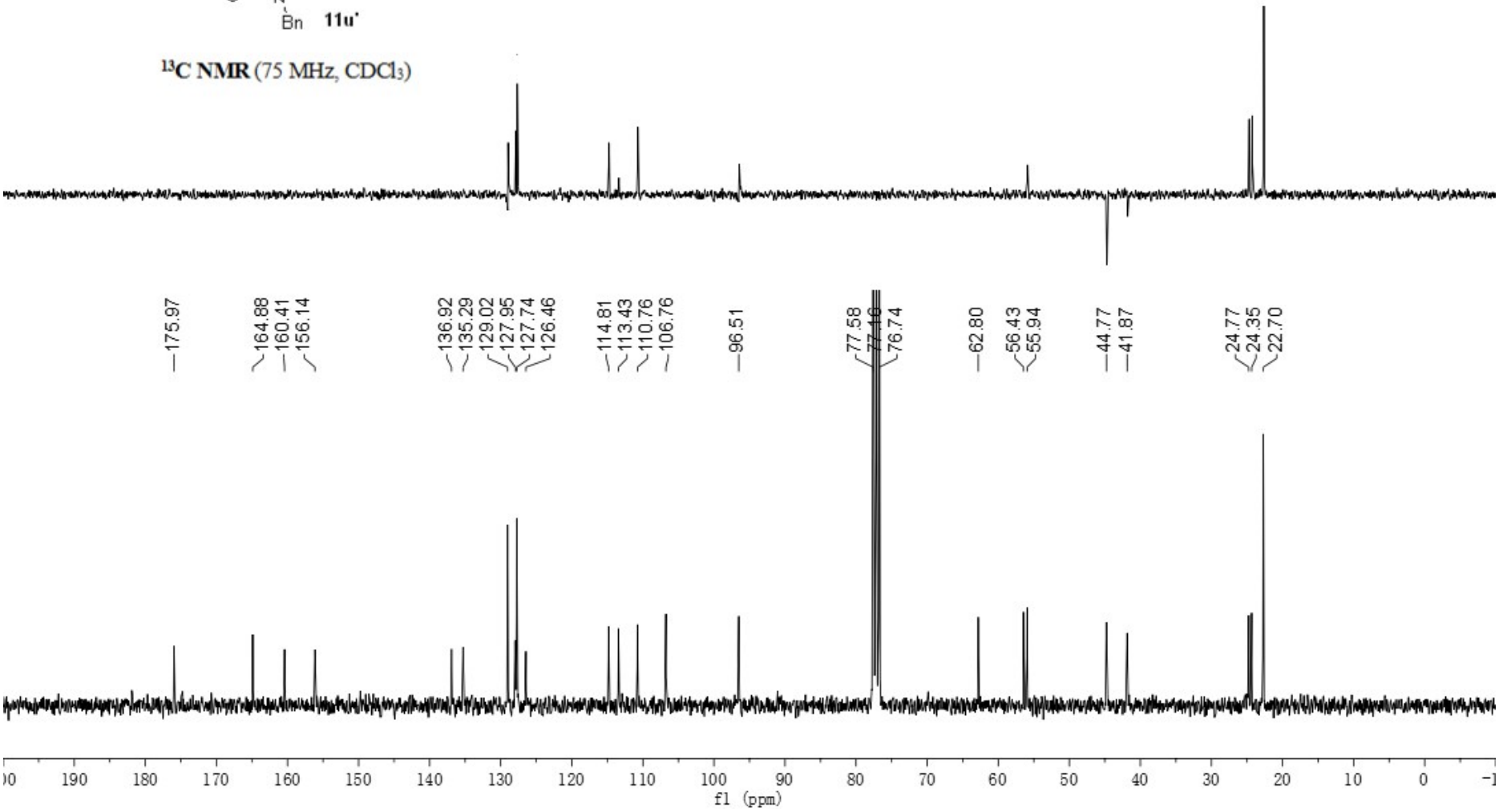


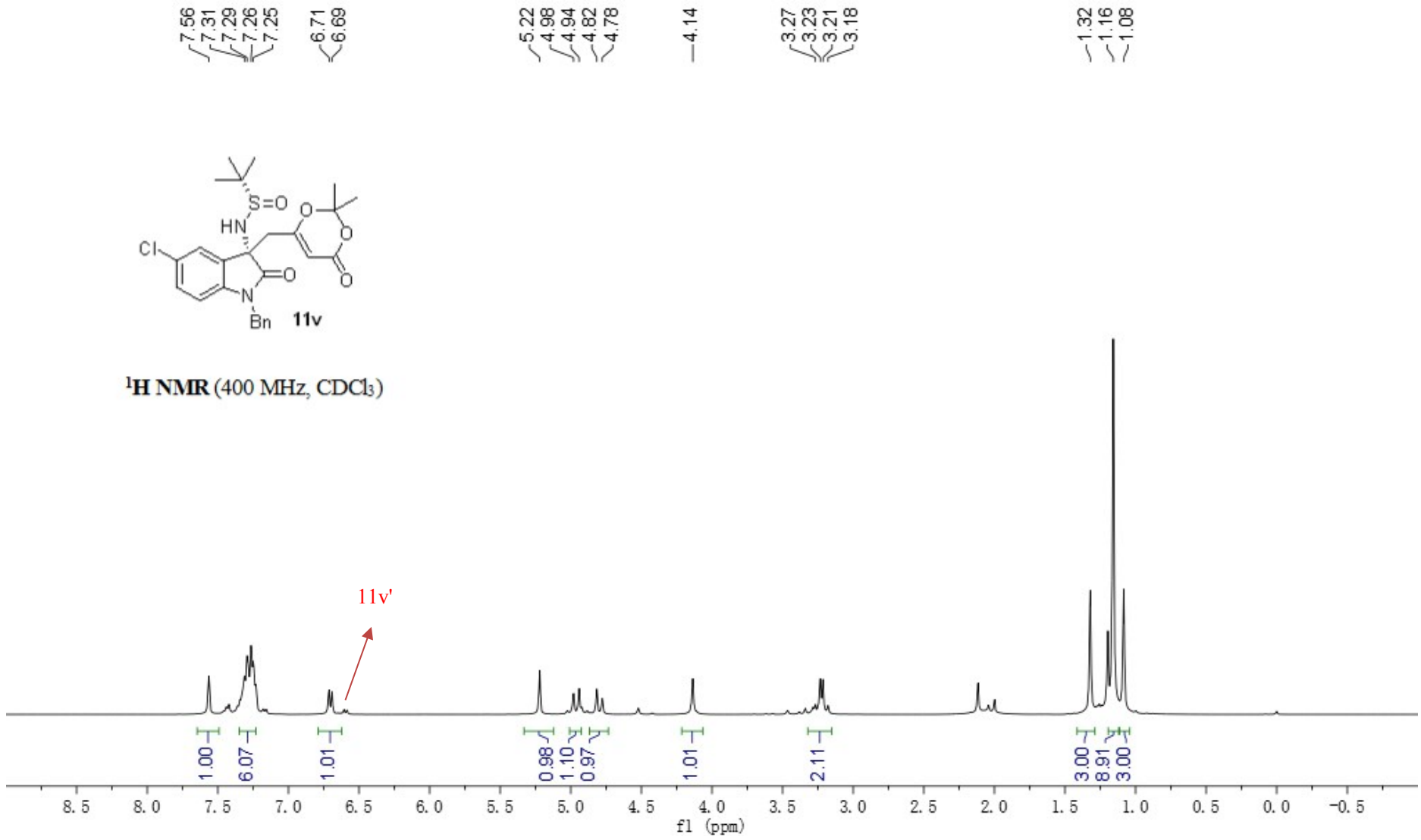
^{1}H NMR (300 MHz, $CDCl_3$)



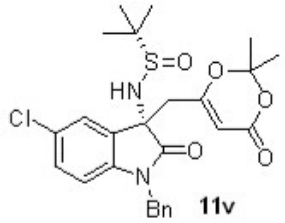
11u'

^{13}C NMR (75 MHz, $CDCl_3$)



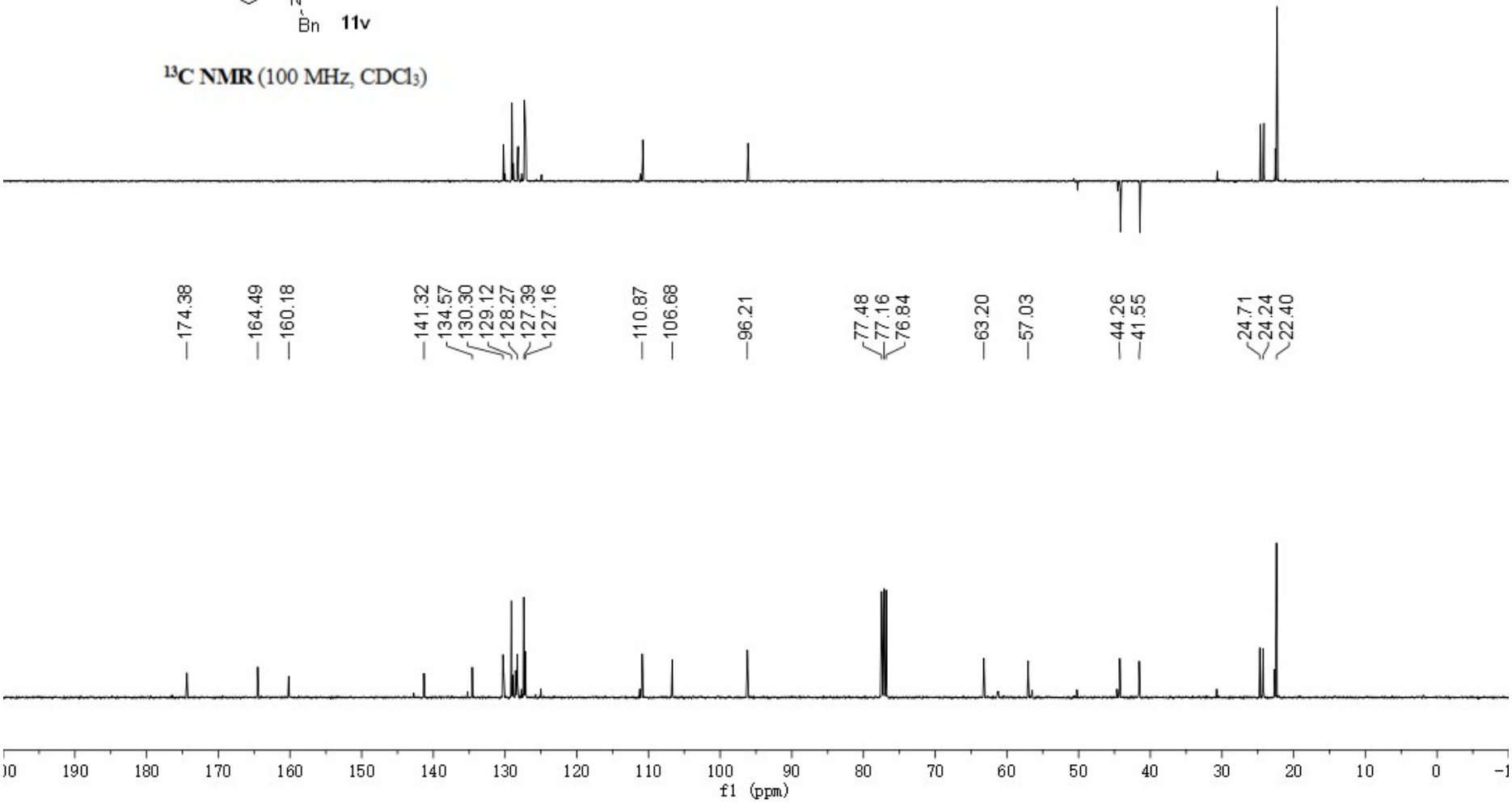


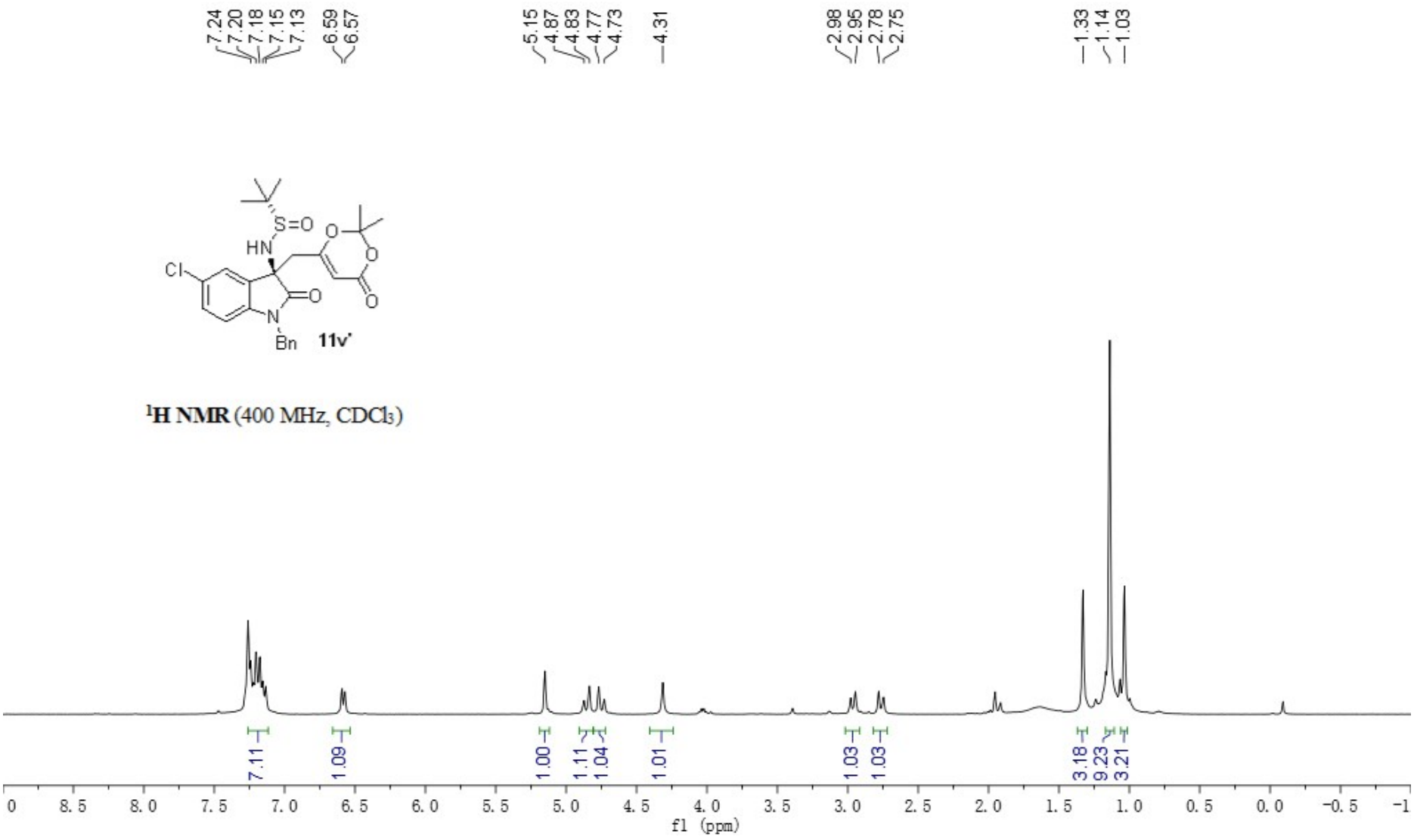
^{1}H NMR (400 MHz, $CDCl_3$)



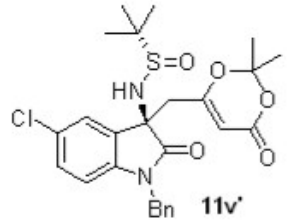
11v

^{13}C NMR (100 MHz, $CDCl_3$)



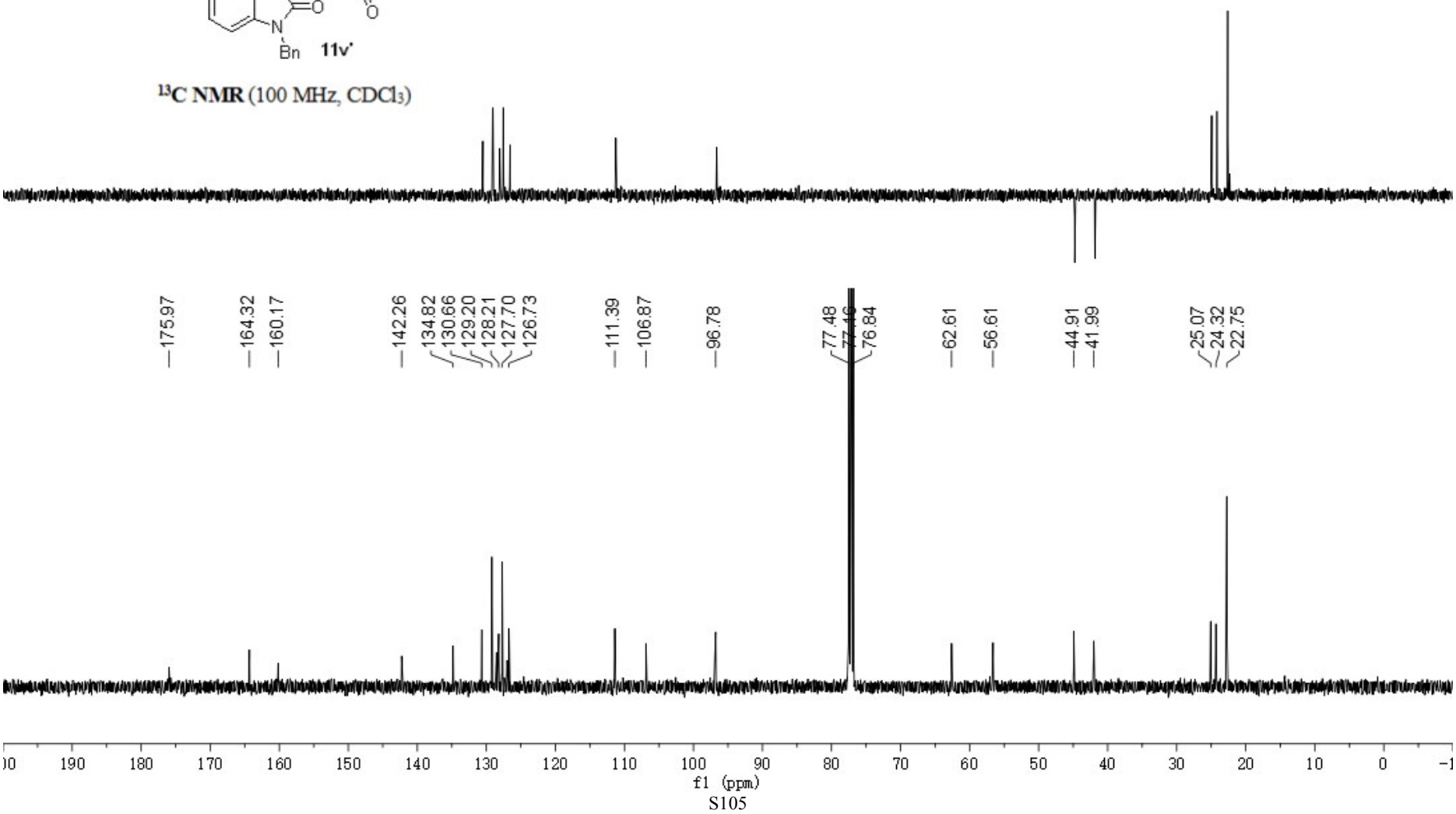


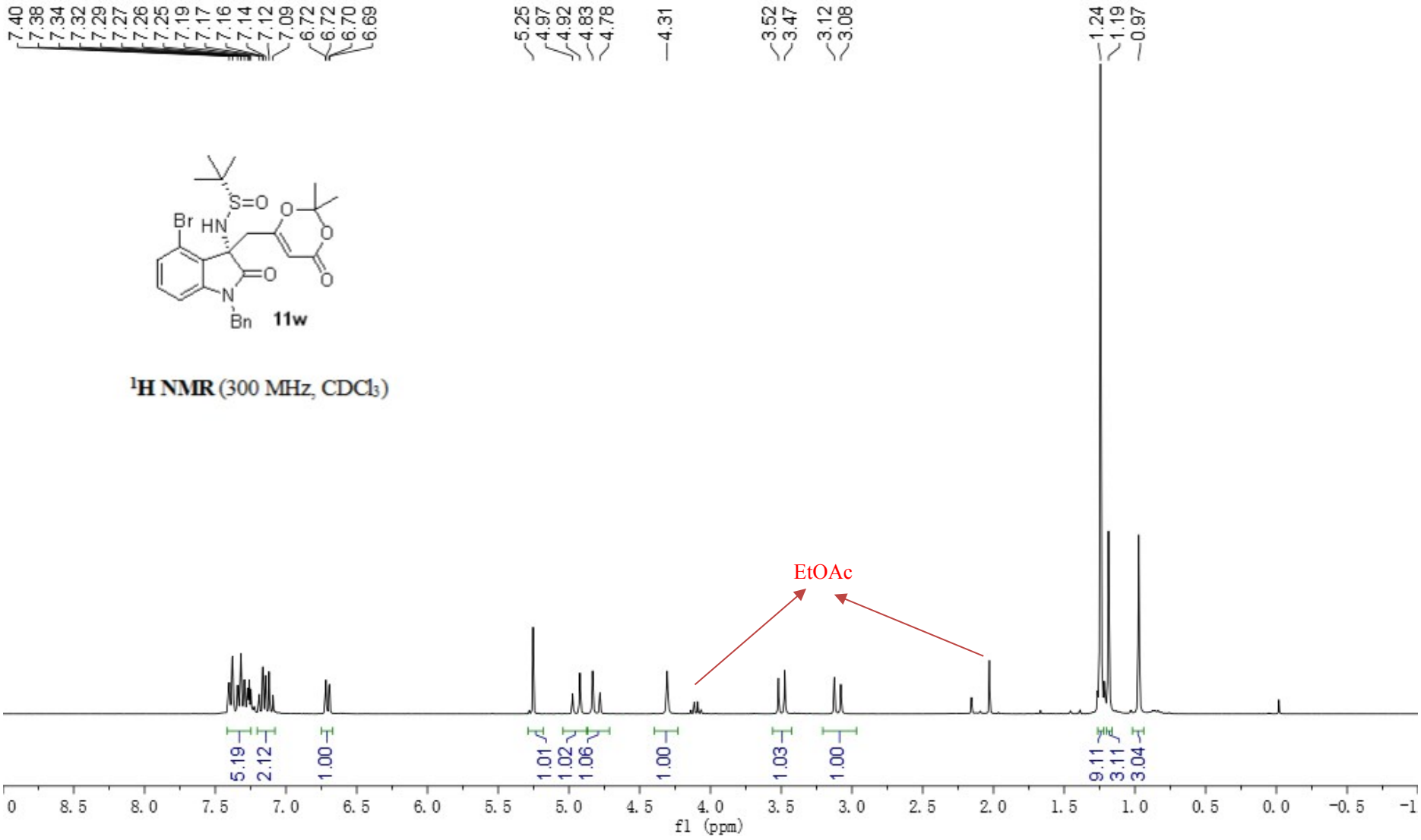
^{1}H NMR (400 MHz, $CDCl_3$)



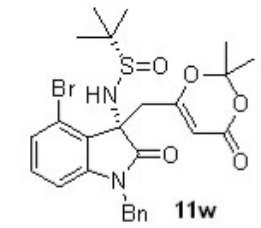
11v'

^{13}C NMR (100 MHz, $CDCl_3$)



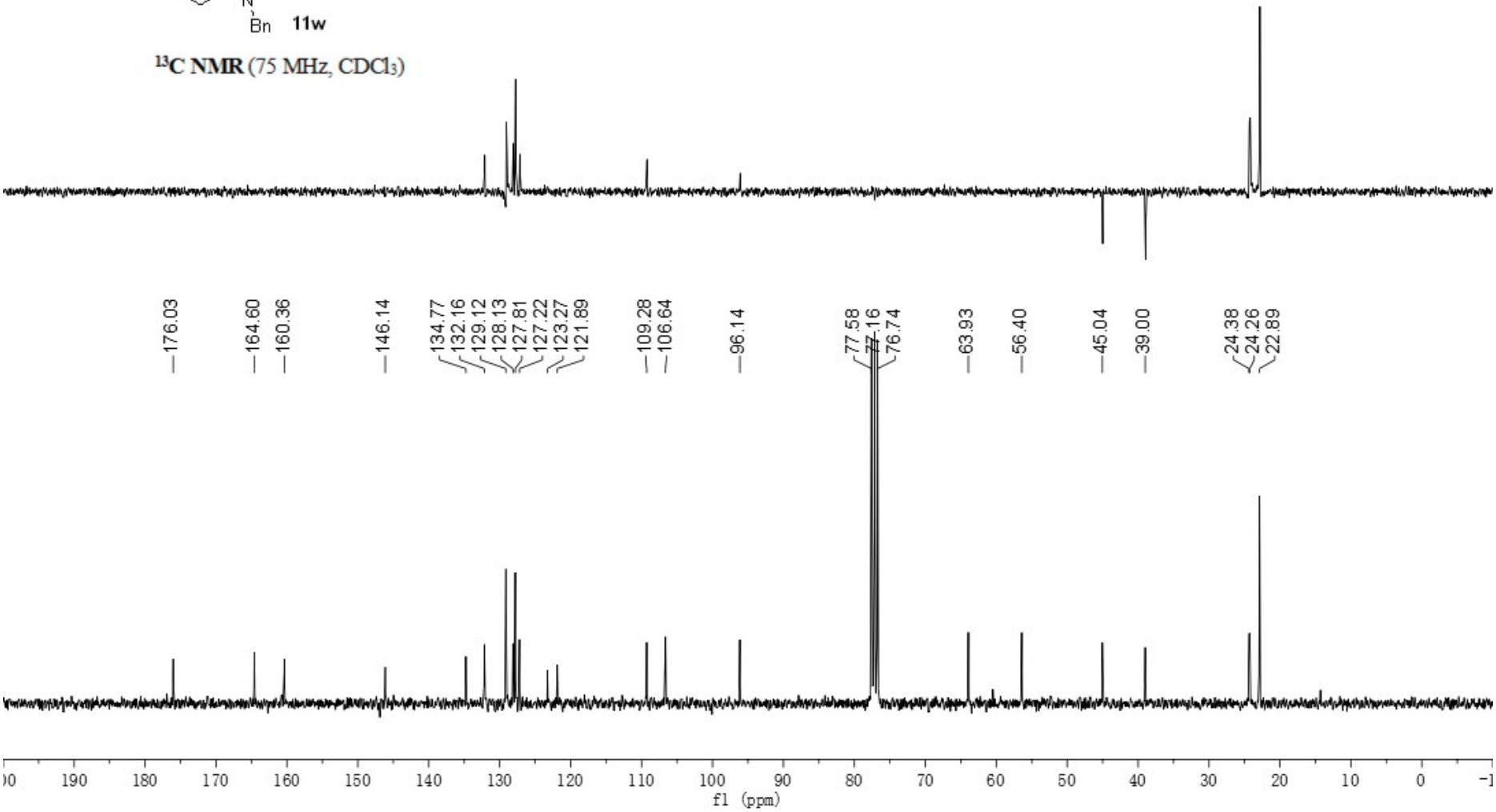


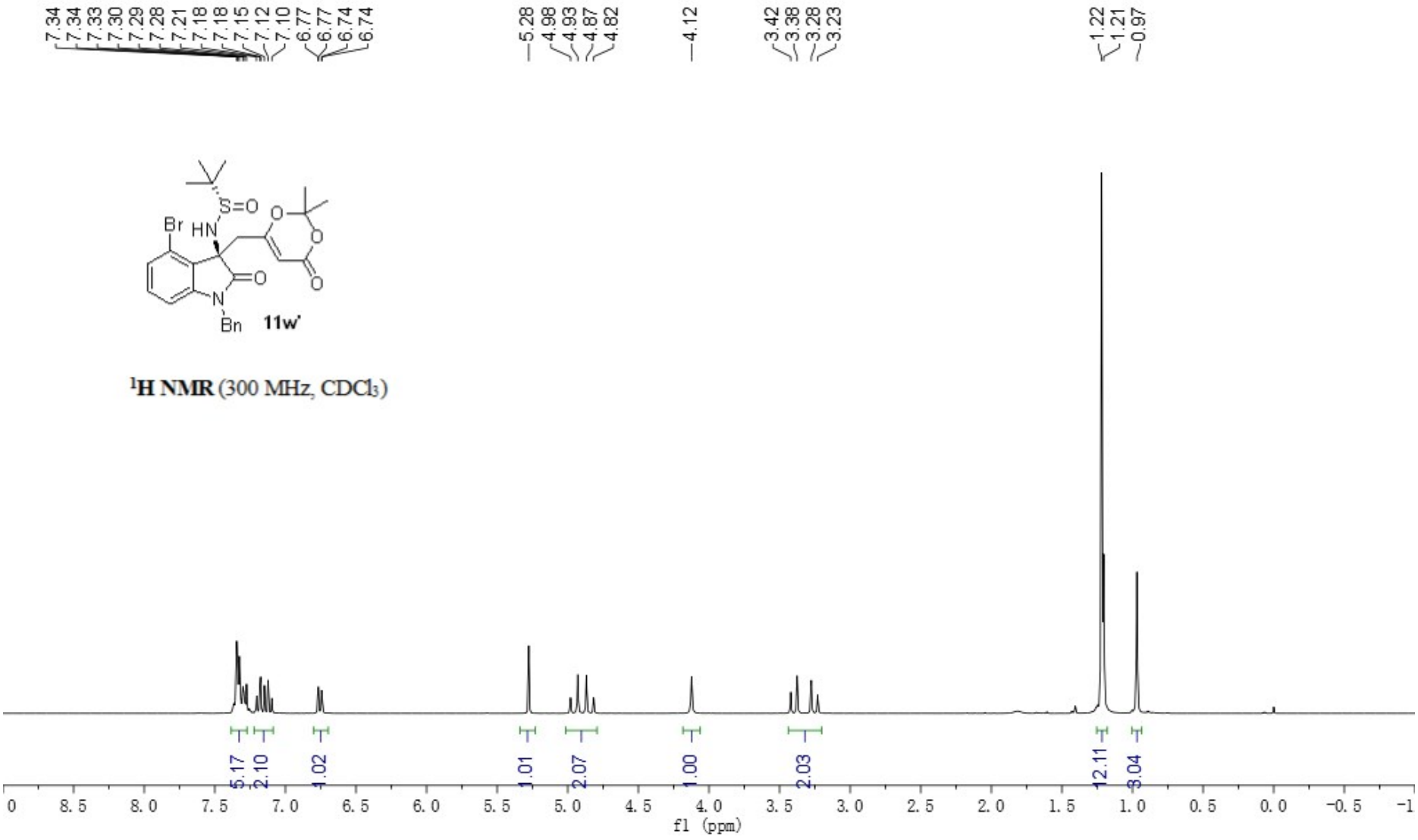
^{1}H NMR (300 MHz, $CDCl_3$)



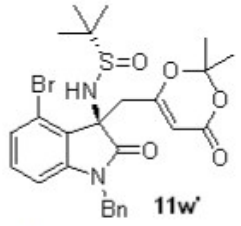
11w

^{13}C NMR (75 MHz, $CDCl_3$)



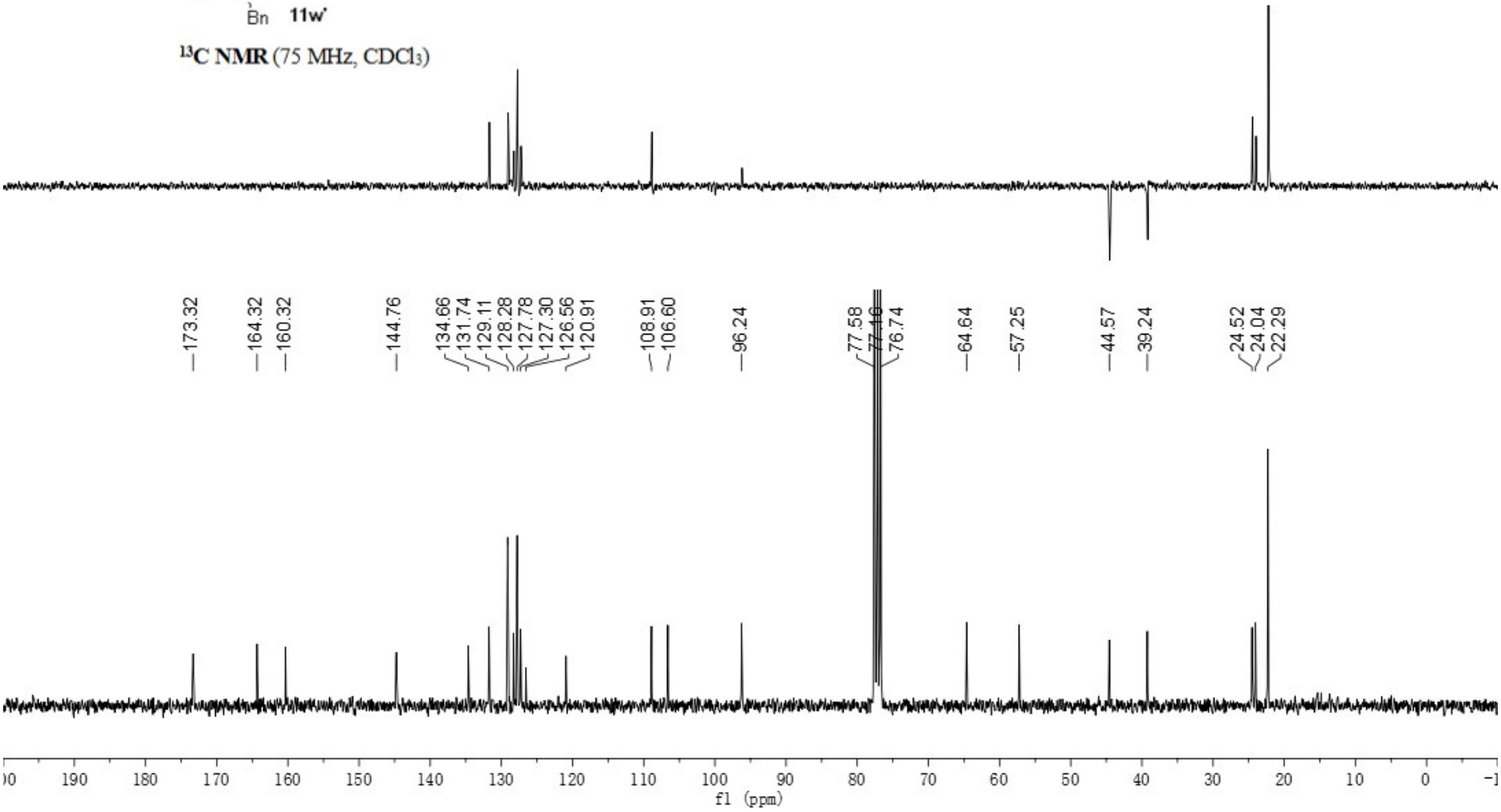


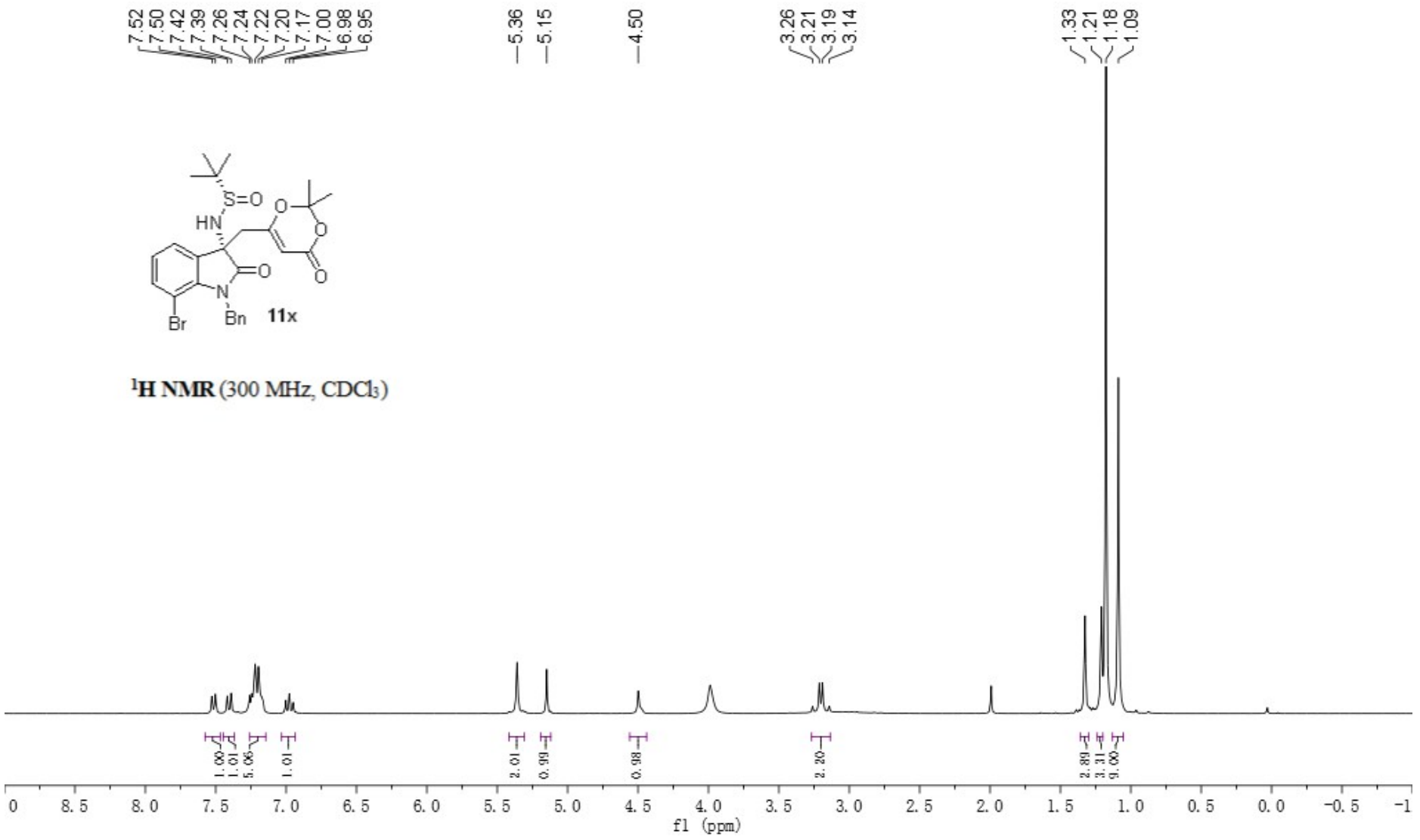
^{1}H NMR (300 MHz, $CDCl_3$)



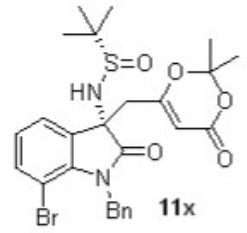
11w'

^{13}C NMR (75 MHz, $CDCl_3$)



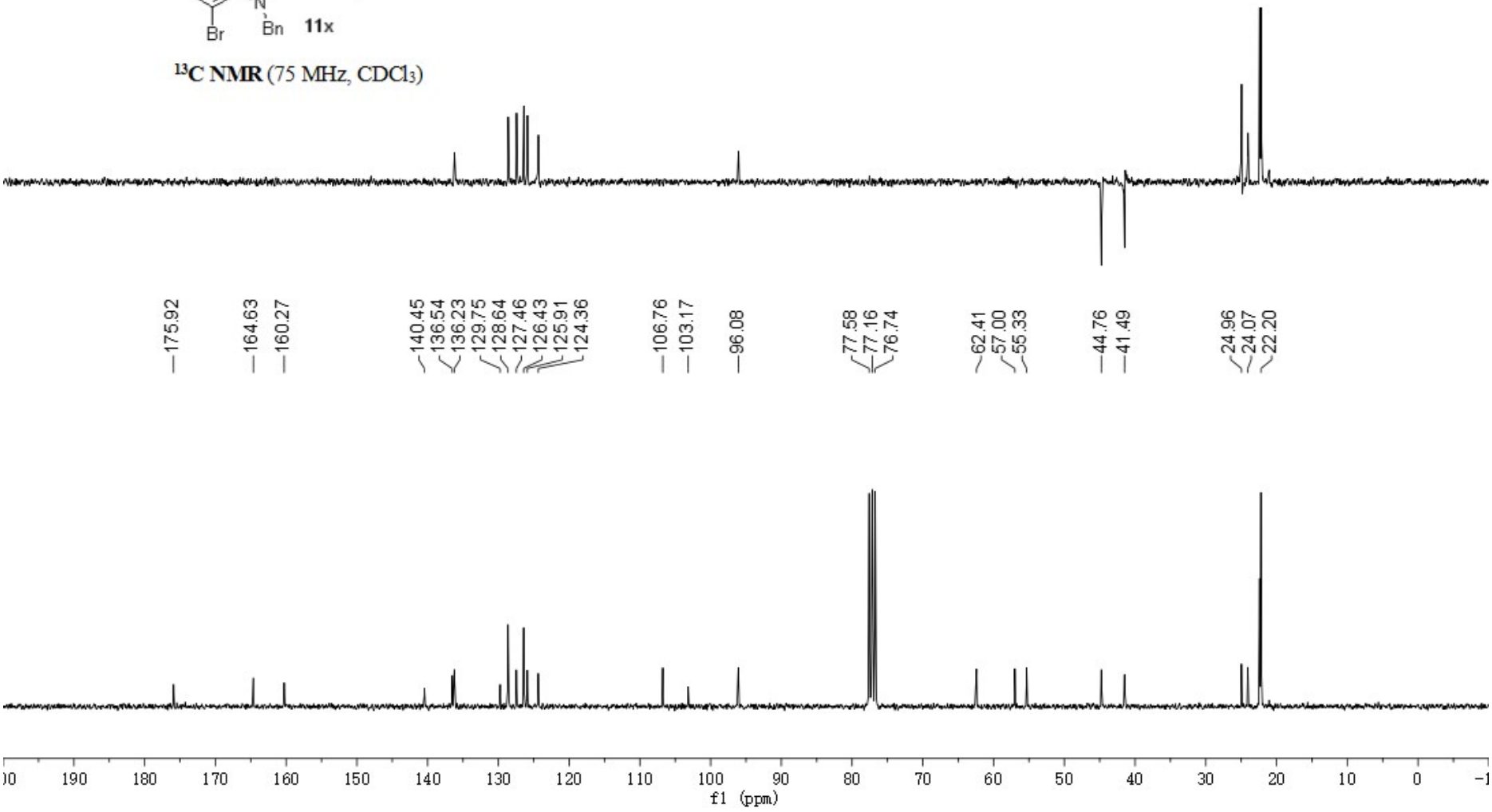


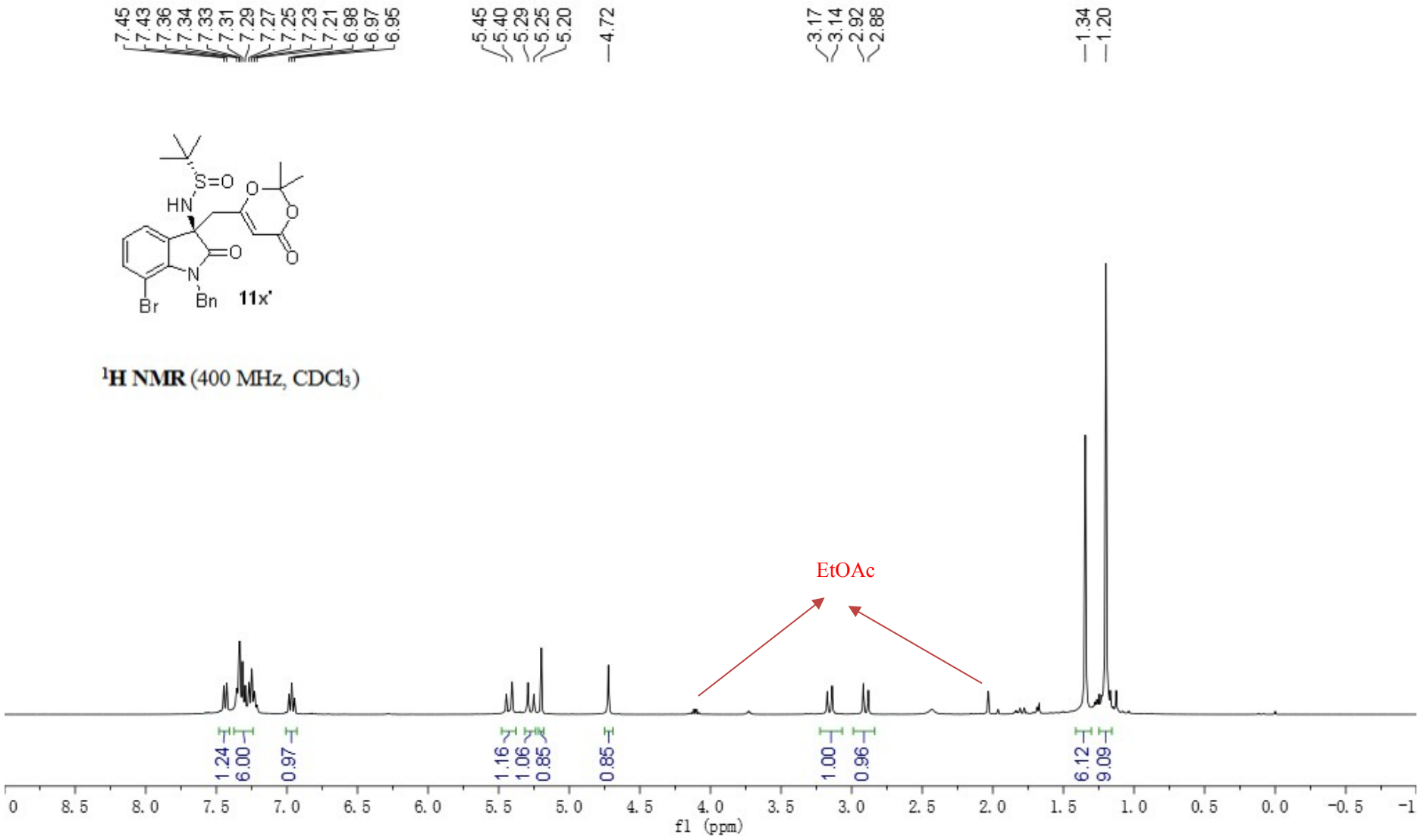
^{1}H NMR (300 MHz, $CDCl_3$)



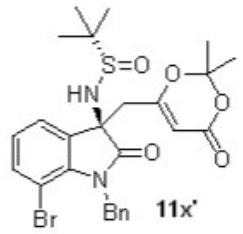
11x

^{13}C NMR (75 MHz, $CDCl_3$)



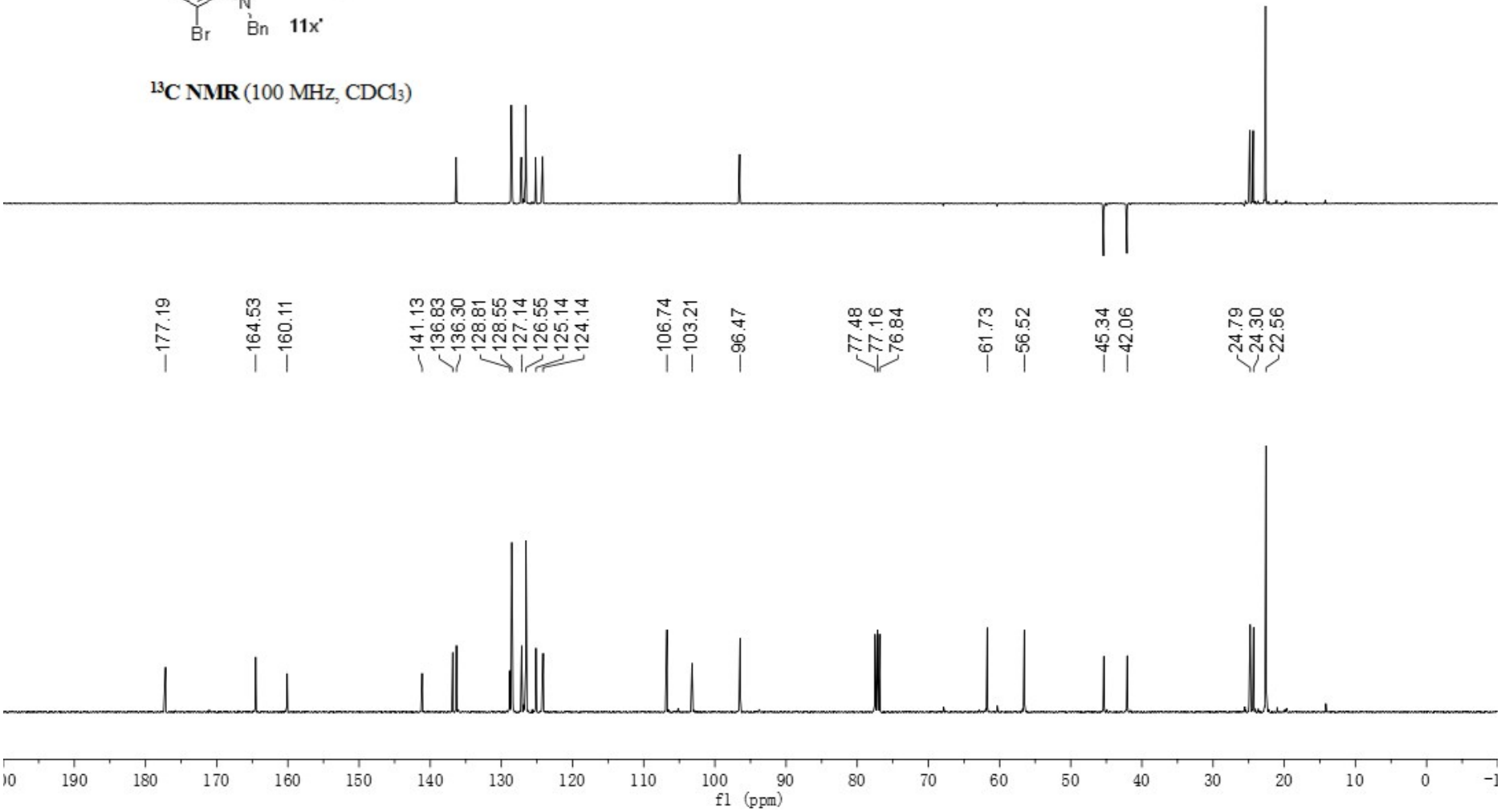


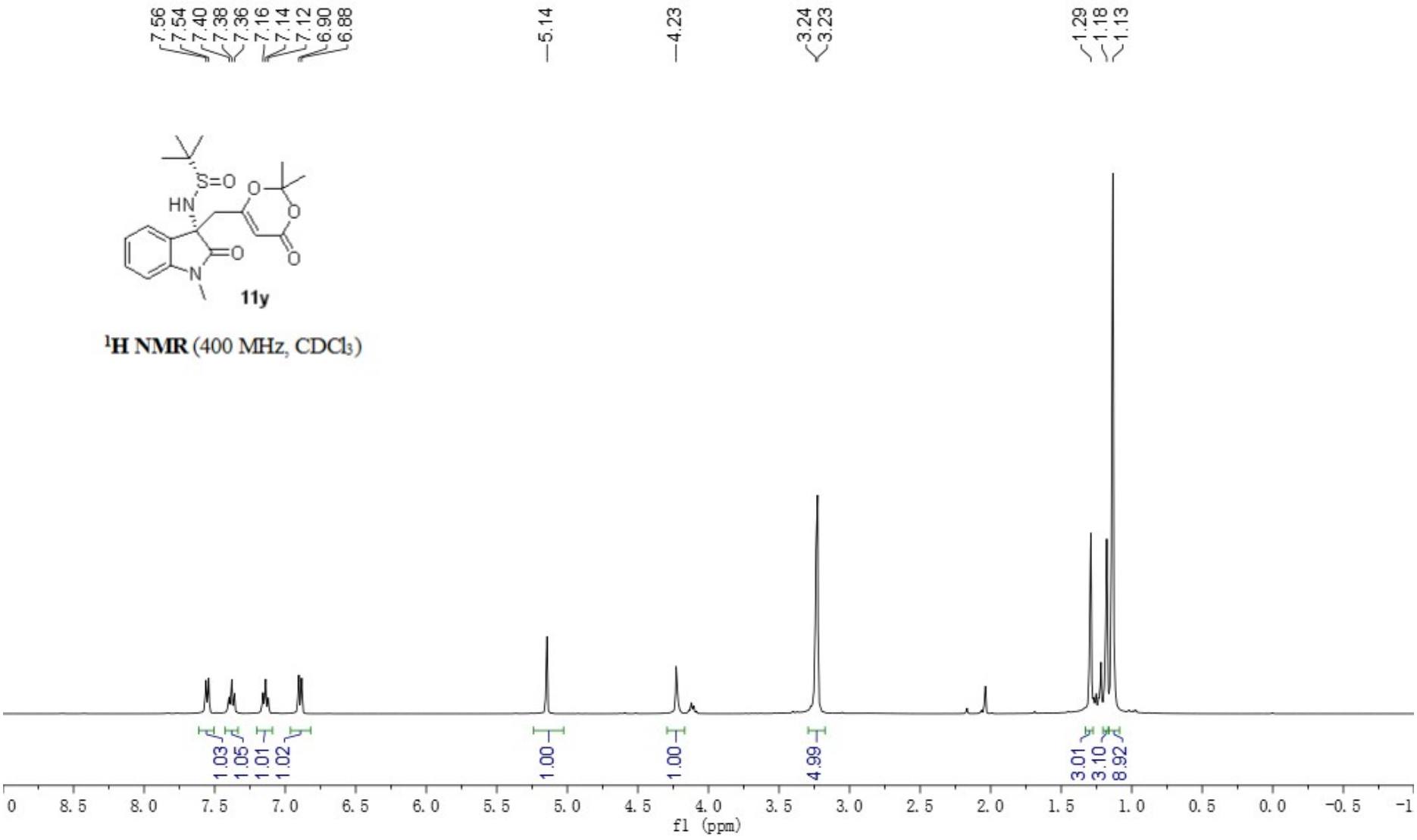
^{1}H NMR (400 MHz, $CDCl_3$)



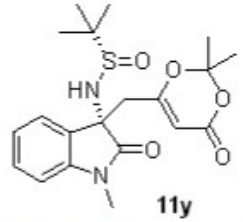
11x'

^{13}C NMR (100 MHz, $CDCl_3$)



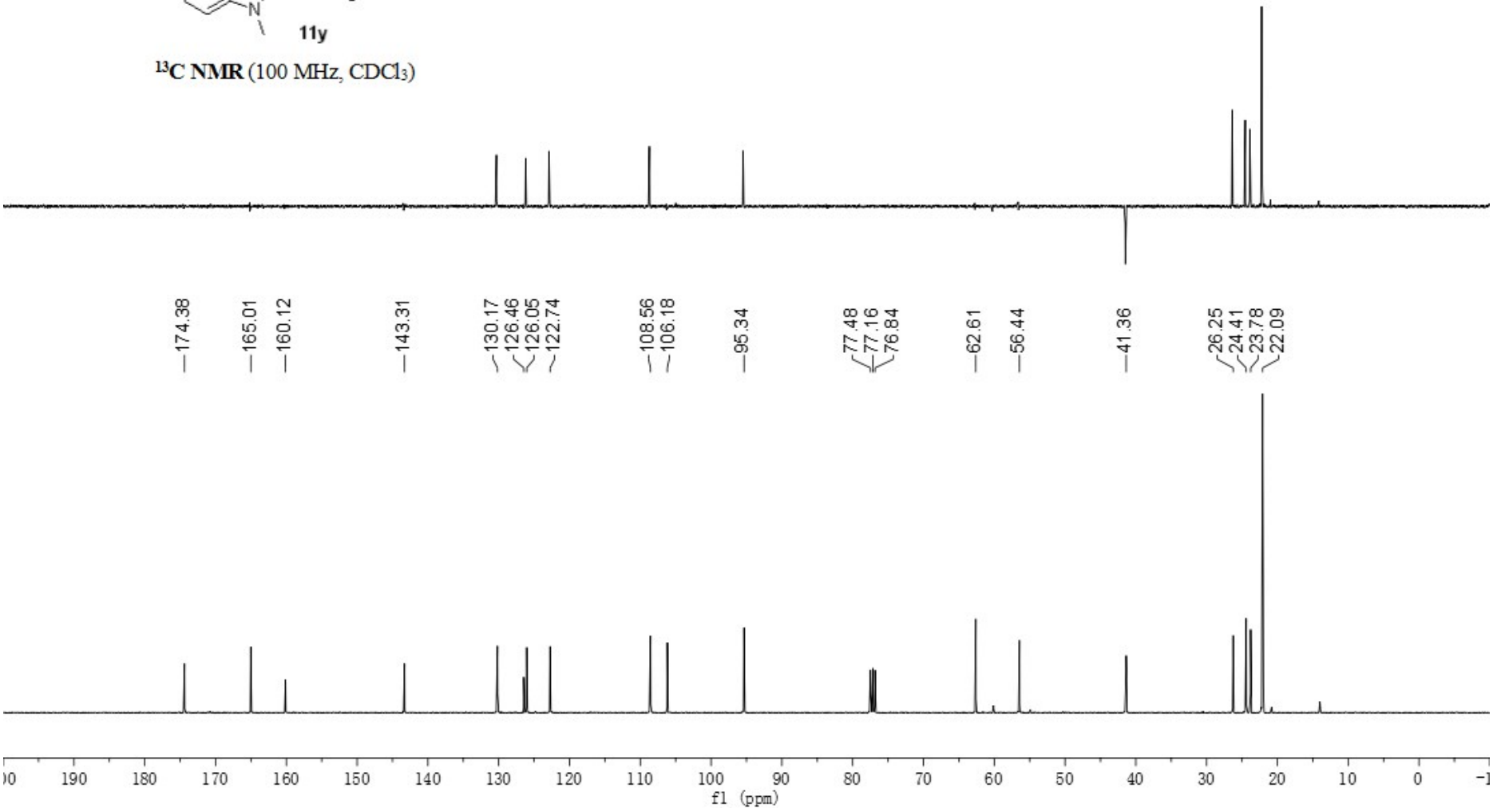


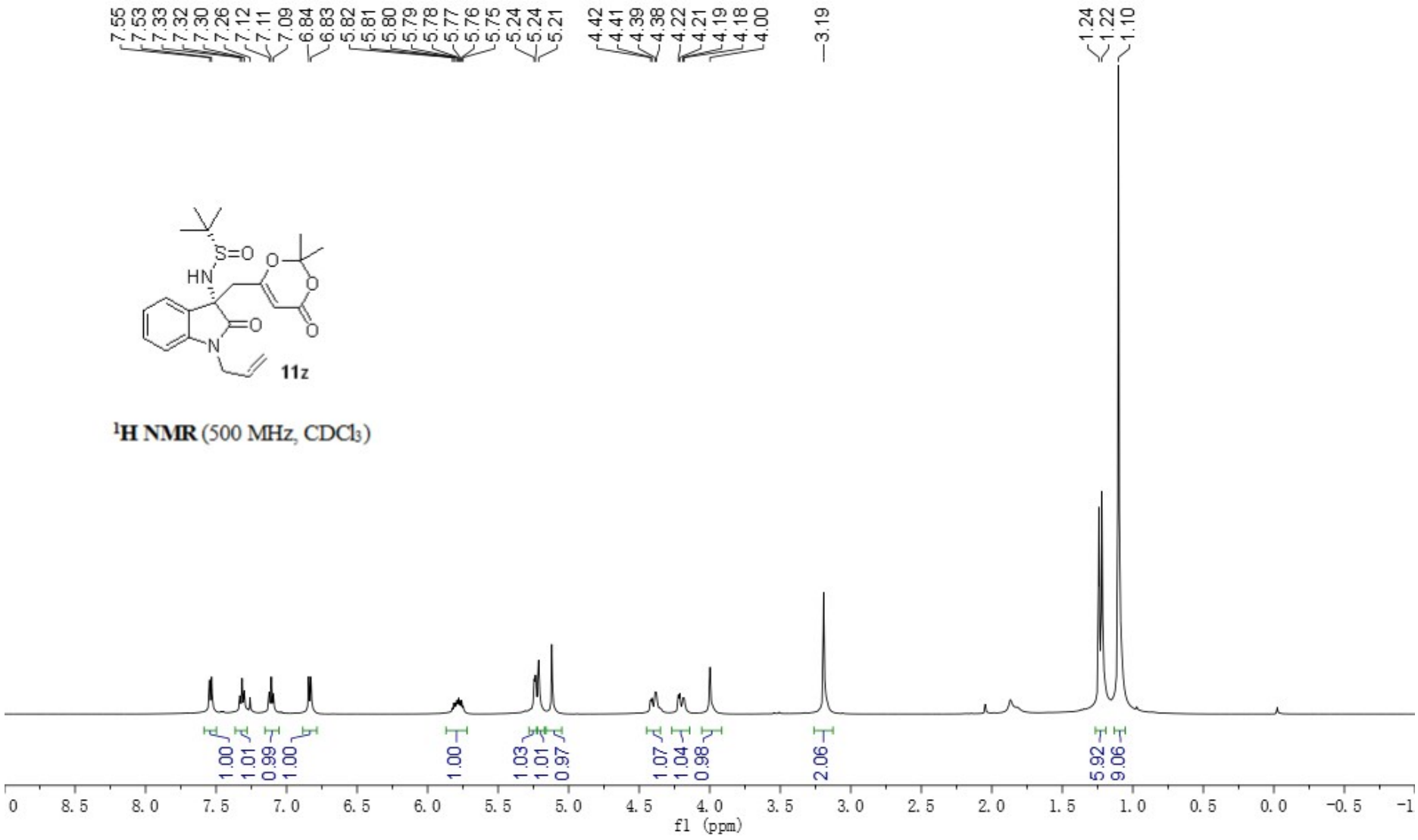
^{1}H NMR (400 MHz, $CDCl_3$)



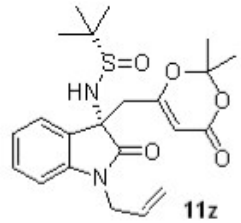
11y

^{13}C NMR (100 MHz, $CDCl_3$)



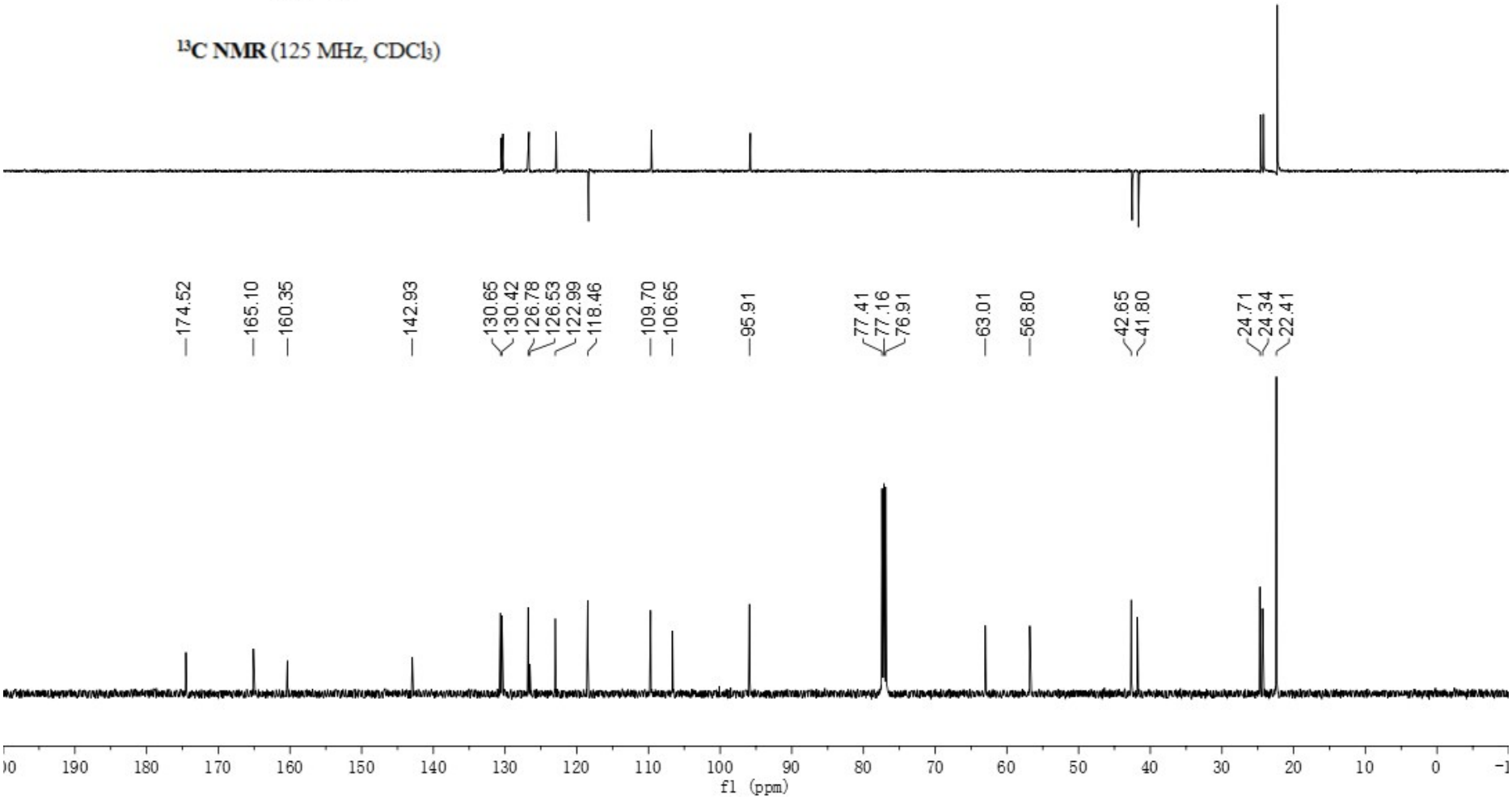


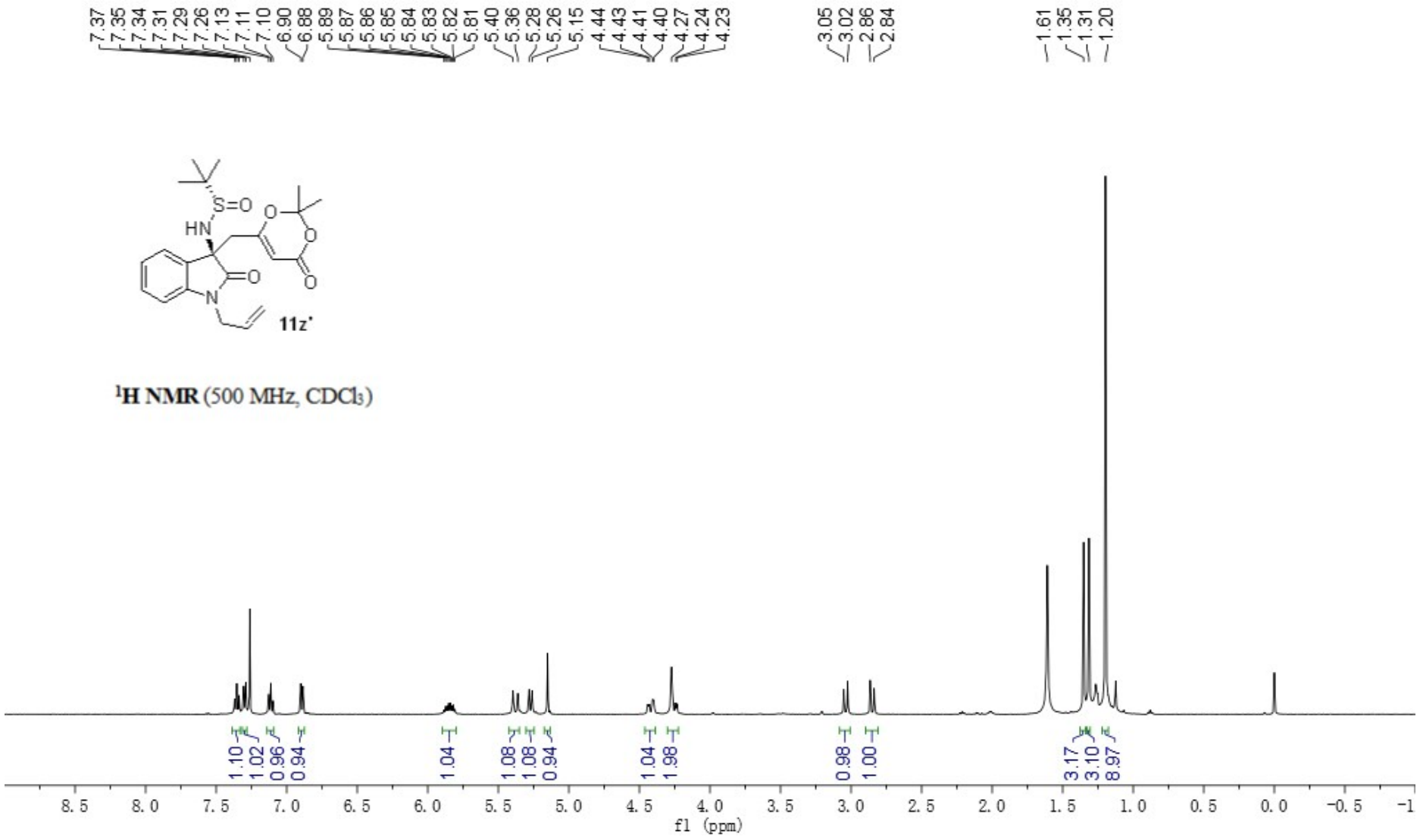
^{1}H NMR (500 MHz, $CDCl_3$)

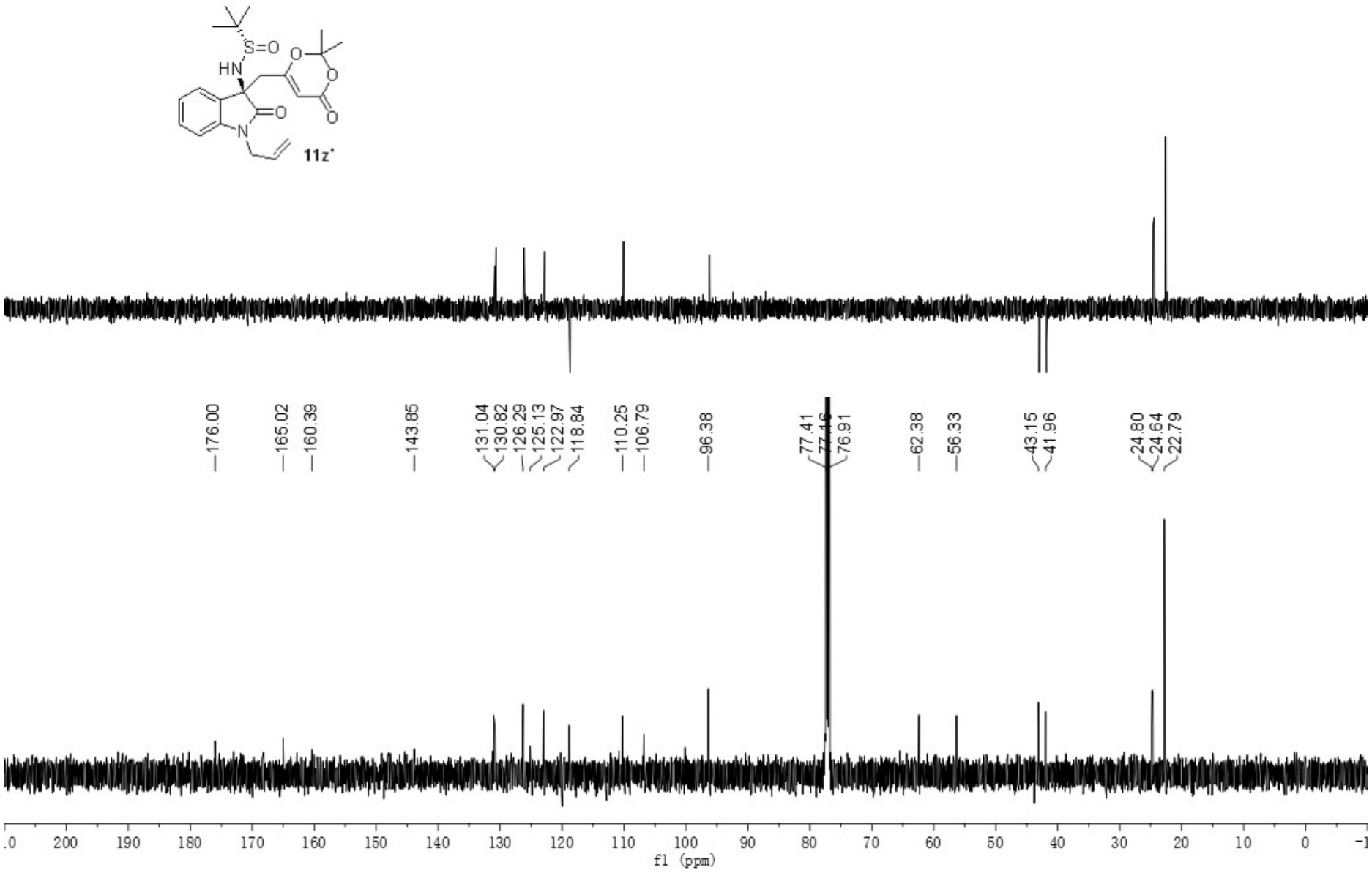


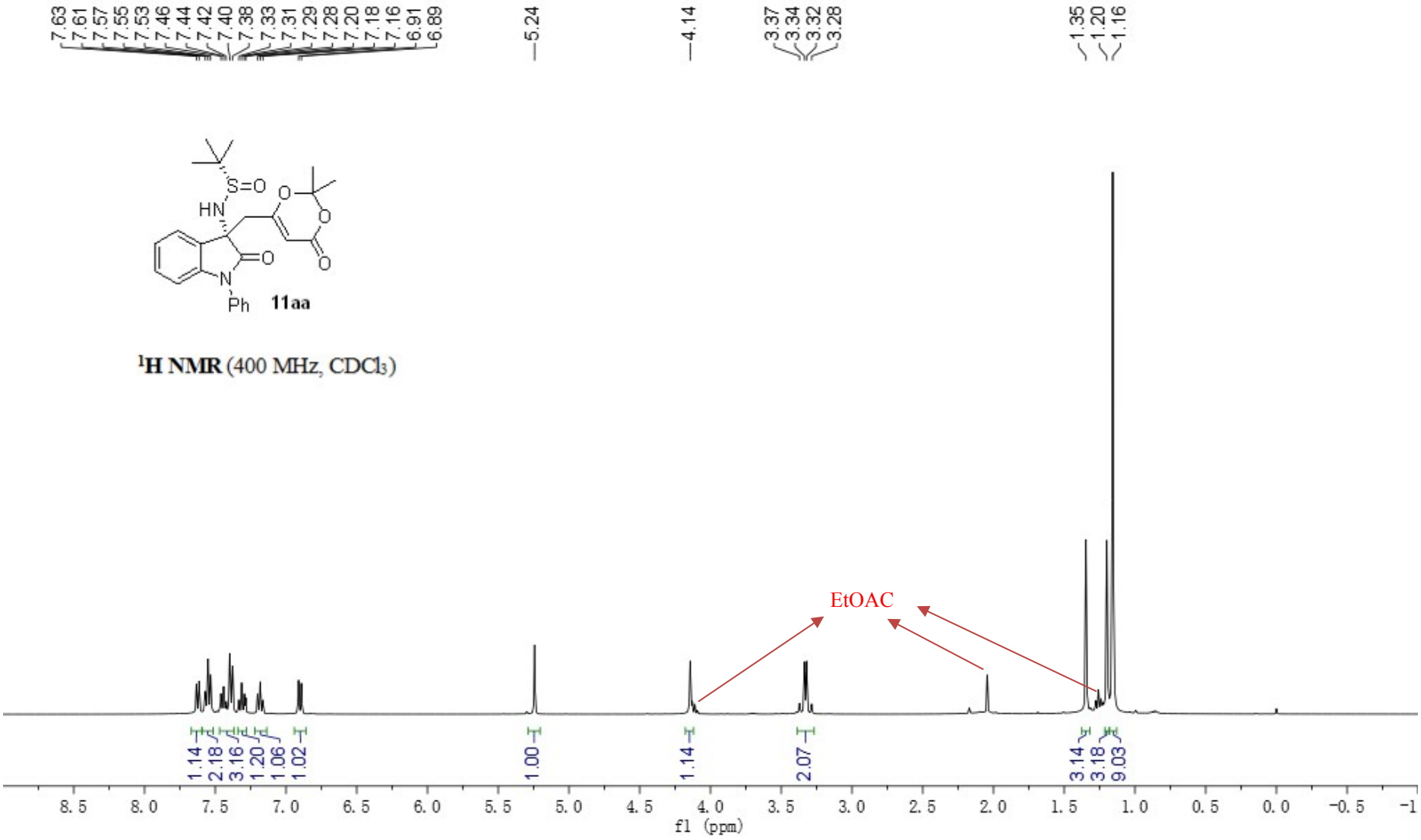
11z

^{13}C NMR (125 MHz, $CDCl_3$)

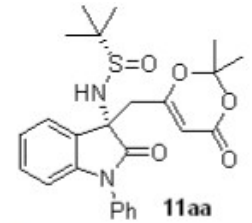



7.37
7.35
7.34
7.31
7.29
7.26
7.13
7.11
7.10
6.90
6.88
5.89
5.87
5.86
5.85
5.84
5.83
5.82
5.81
5.40
5.36
5.28
5.26
5.15
4.44
4.43
4.41
4.40
4.27
4.24
4.23
3.05
3.02
2.86
2.84
1.61
1.35
1.31
1.20
S=O
HN
O
O
O
O
N
11z'
1H NMR (500 MHz, CDCl3)
1.10
1.02
0.96
0.94
1.04
1.08
1.08
0.94
1.04
1.98
0.98
1.00
3.17
3.10
8.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


S=O
HN
O
O
O
O
N
11z'
176.00
165.02
160.39
143.85
131.04
130.82
126.29
125.13
122.97
118.84
110.25
106.79
96.38
77.41
77.16
76.91
62.38
56.33
43.15
41.96
24.80
24.64
22.79
f1 (ppm)

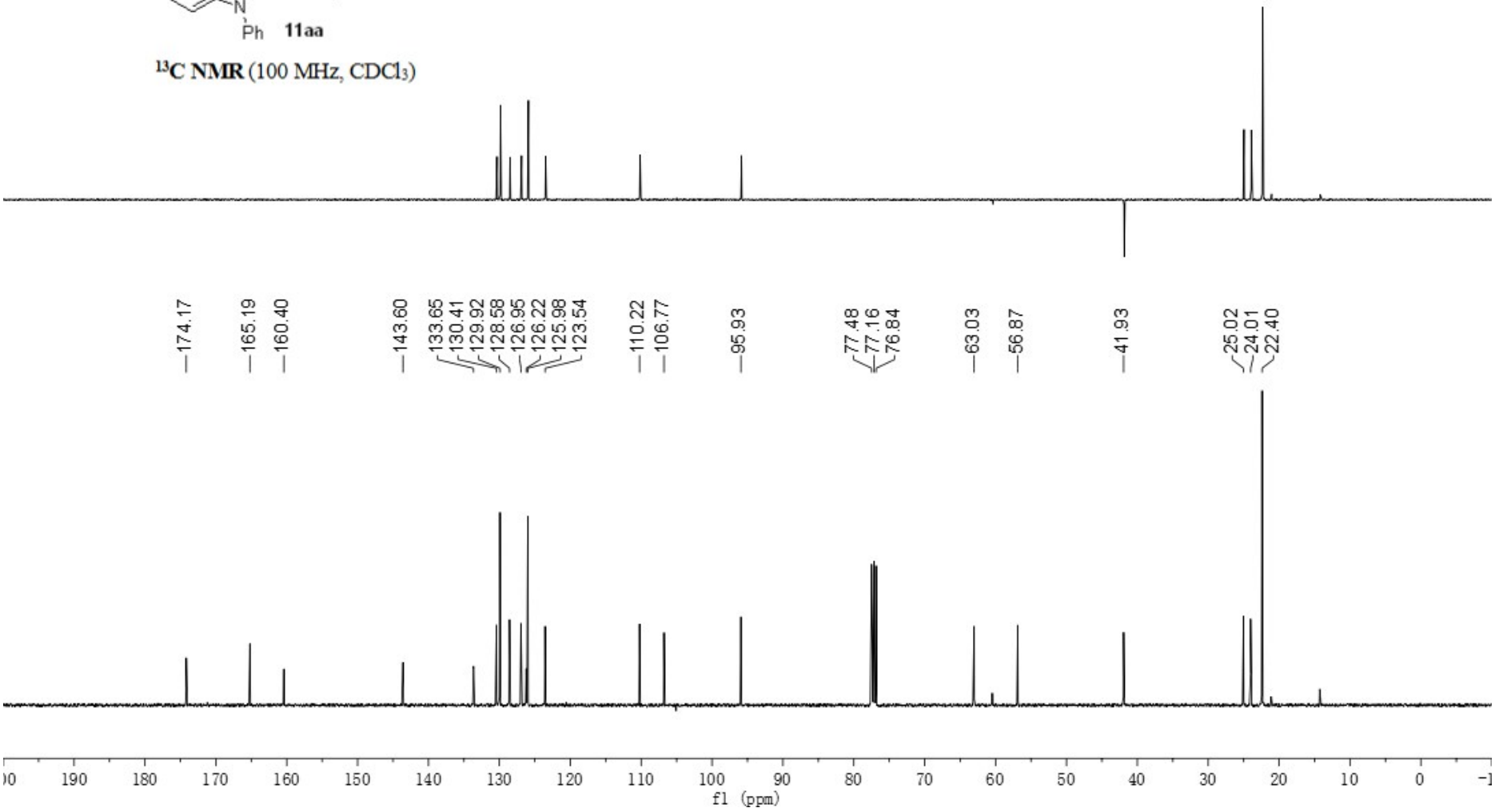


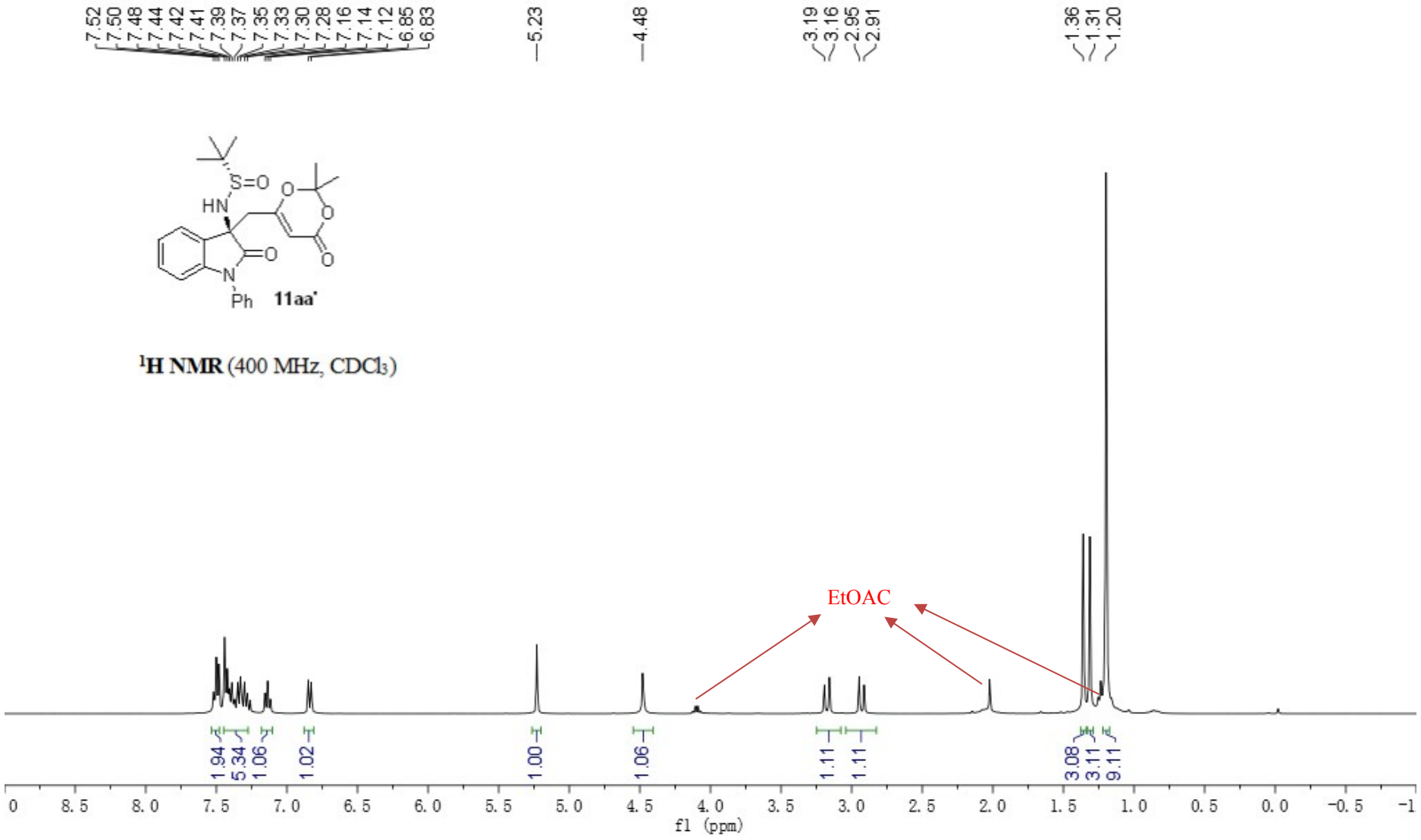
^{1}H NMR (400 MHz, $CDCl_3$)



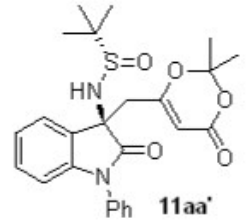
11aa

^{13}C NMR (100 MHz, $CDCl_3$)



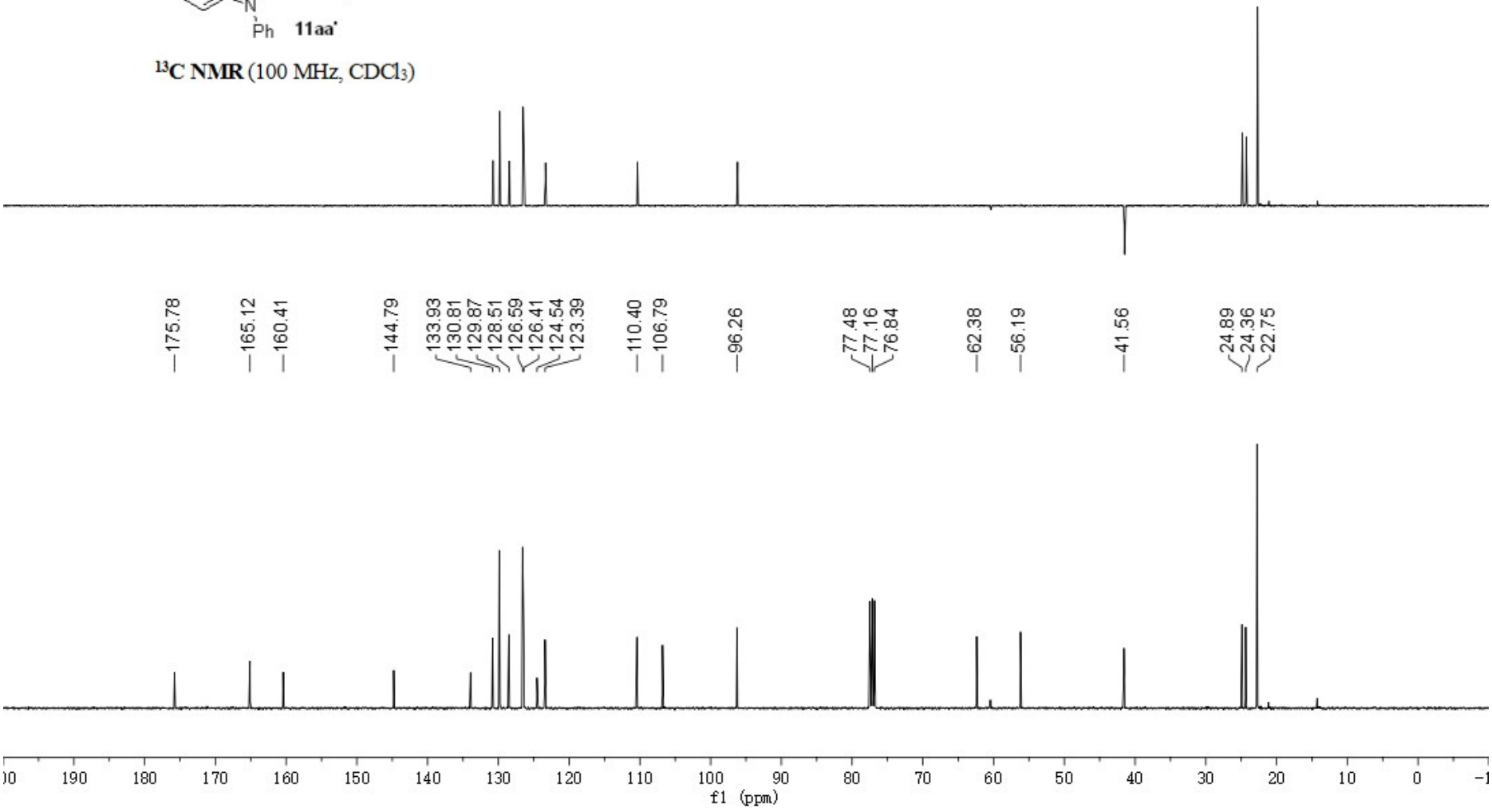


^{1}H NMR (400 MHz, $CDCl_3$)



11aa'

^{13}C NMR (100 MHz, $CDCl_3$)



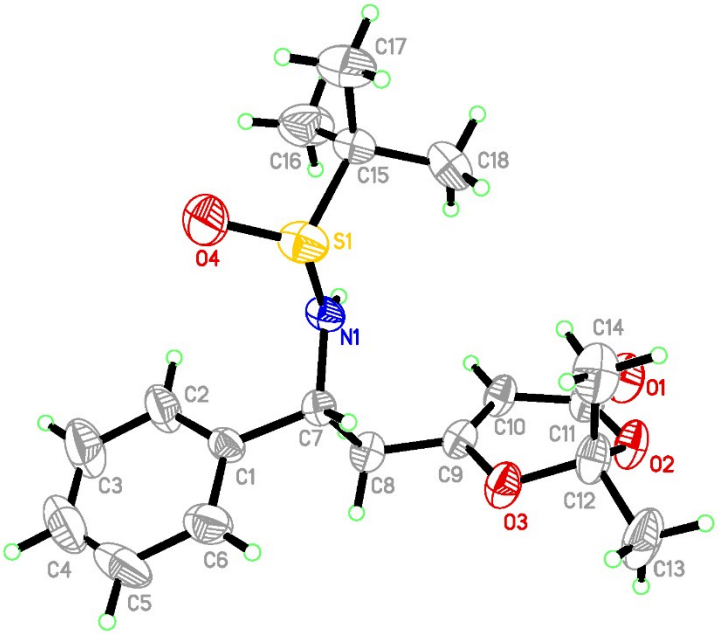
4. X-Ray Single Crystal Diffraction Data

4.1 X-Ray Single Crystal Diffraction Data for product 11c

Table S1. Crystal data and structure refinement for **11c**.

Identification code	1
Empirical formula	C18H25NO4S
Formula weight	351.45
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 10.551(7) A alpha = 90 deg.
	b = 11.366(8) A beta = 90 deg.
	c = 16.422(11) A gamma = 90 deg.
Volume	1969(2) A^3
Z, Calculated density	4, 1.185 Mg/m^3
Absorption coefficient	0.184 mm^-1
F(000)	752
Crystal size	0.330 x 0.280 x 0.150 mm
Theta range for data collection	2.179 to 24.997 deg.
Limiting indices	-12<=h<=12, -12<=k<=13, -19<=l<=19
Reflections collected / unique	11219 / 3469 [R(int) = 0.0730]
Completeness to theta = 25.242	97.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.973 and 0.942
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3469 / 0 / 222
Goodness-of-fit on F^2	0.945
Final R indices [I>2sigma(I)]	R1 = 0.0525, wR2 = 0.1073
R indices (all data)	R1 = 0.1202, wR2 = 0.1263

Absolute structure parameter	0.11(11)
Extinction coefficient	n/a
Largest diff. peak and hole	0.187 and -0.181 e.A^-3



View of product **11c** in an asymmetric unit

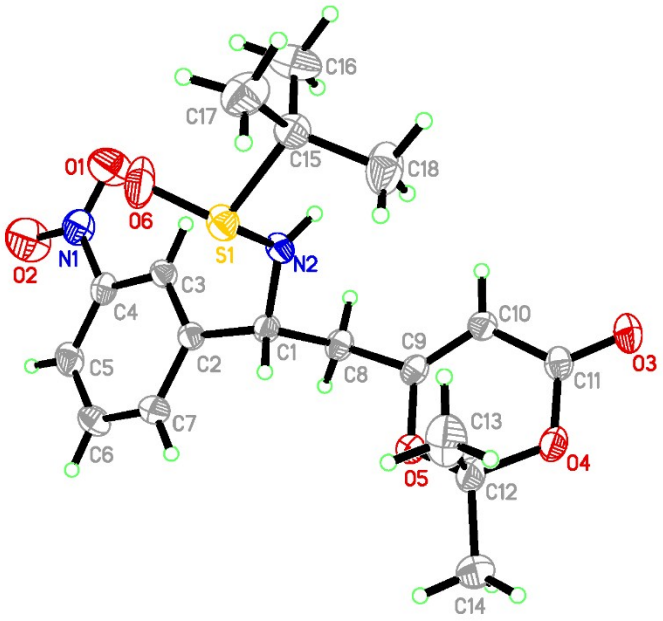
Displacement ellipsoids are drawn at the 30% probability level

4.2 X-Ray Single Crystal Diffraction Data for product 11h

Table S2. Crystal data and structure refinement for **11h**.

Identification code	1
Empirical formula	C18H24N2O6S
Formula weight	396.45
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 10.9782(13) A alpha = 90 deg.
	b = 11.2330(14) A beta = 90 deg.
	c = 16.728(2) A gamma = 90 deg.
Volume	2062.8(4) A^3
Z, Calculated density	4, 1.277 Mg/m^3
Absorption coefficient	0.192 mm^-1
F(000)	840
Crystal size	0.500 x 0.300 x 0.250 mm
Theta range for data collection	2.184 to 25.145 deg.
Limiting indices	-13<=h<=13, -13<=k<=11, -20<=l<=18
Reflections collected / unique	11642 / 3684 [R(int) = 0.0223]
Completeness to theta = 25.242	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.953 and 0.933
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3684 / 0 / 244
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0876
R indices (all data)	R1 = 0.0383, wR2 = 0.0913
Absolute structure parameter	-0.01(2)
Extinction coefficient	n/a

Largest diff. peak and hole 0.209 and -0.280 e.A^-3



View of product **11h** in an asymmetric unit

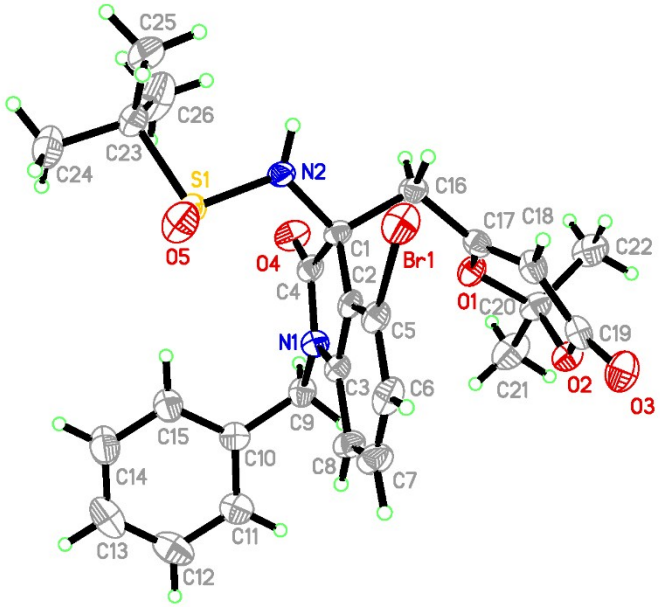
Displacement ellipsoids are drawn at the 30% probability level

4.3 X-Ray Single Crystal Diffraction Data for product 11w

Table S3. Crystal data and structure refinement for **11w**.

Identification code	1
Empirical formula	C26 H29 Br N2 O5 S
Formula weight	561.48
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 10.0662(14) A alpha = 90 deg.
	b = 15.170(2) A beta = 90 deg.
	c = 17.178(2) A gamma = 90 deg.
Volume	2623.2(6) A^3
Z, Calculated density	4, 1.422 Mg/m^3
Absorption coefficient	1.685 mm^-1
F(000)	1160
Crystal size	0.400 x 0.310 x 0.290 mm
Theta range for data collection	1.791 to 24.999 deg.
Limiting indices	-11<=h<=11, -18<=k<=17, -19<=l<=20
Reflections collected / unique	14738 / 4588 [R(int) = 0.0437]
Completeness to theta = 25.242	96.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.641 and 0.552
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4588 / 0 / 322
Goodness-of-fit on F^2	0.985
Final R indices [I>2sigma(I)]	R1 = 0.0347, wR2 = 0.0662
R indices (all data)	R1 = 0.0544, wR2 = 0.0716
Absolute structure parameter	0.018(11)
Extinction coefficient	n/a

Largest diff. peak and hole 0.280 and -0.265 e.A^-3



View of product **11w** in an asymmetric unit

Displacement ellipsoids are drawn at the 30% probability level