Supporting Information

$Pd(PPh_3)_4$-Catalyzed Regioselective C–H *para*-Allylation of *N,N*-Dialkylanilines using Vinyl Benzoxazinanones

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Contents

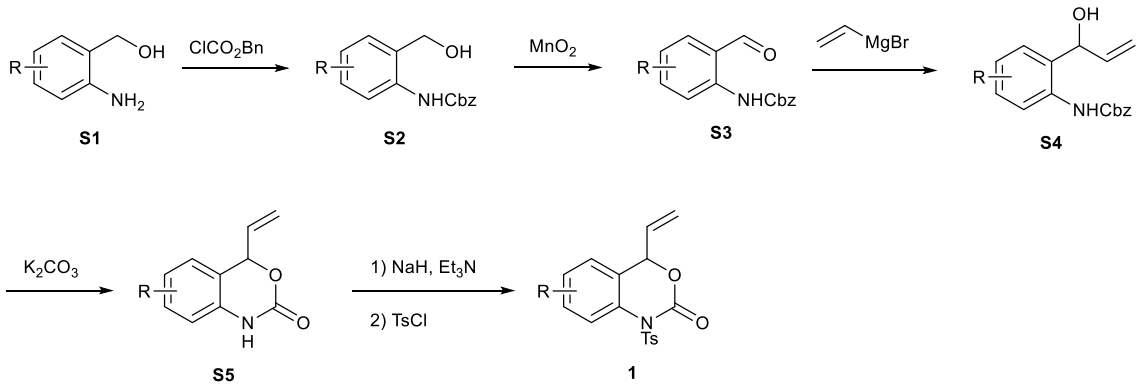
1. General Information

All commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) on glass plates coated with silica gel with a fluorescentindicator. Flash chromatography was performed on silica gel (300−400) with petroleum/EtOAc. HRMS were measured on an LTQ-Orbit. Melting points were measured using a micro melting point apparatus and are uncorrected. ^{1}H NMR (400 MHz) chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ^{13}C NMR (100 MHz) chemical shifts were reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard and ^{19}F NMR at (376 MHz) chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard.

2. Experimental Details

2.1 General Procedure for Synthesis of vinyl benzoxazinanones (1a–1c)[1].

substrates **1** were synthesized according to reported procedures. The general procedure for the synthesis of substituted vinyl benzoxazinanones were shown as below.



S1 to **S2**: To a stirring solution of 2-aminobenzyl alcohol **S1** (81.20 mmol) and K_2CO_3

(162.40 mmol) in THF (120 mL) and H_2O (120 mL), benzyl chloroformate (146.16 mmol) was slowly added dropwise. The resulting mixture was stirred at room temperature for 15 h. The reaction was quenched with saturated $NaHCO_3$ aqueous (250 mL), washed with brine (3×100 mL), dried with $MgSO_4$ and evaporated under reduced pressure. The obtained crude product **S2** was used directly without further purification.

S2 to **S3**: To a solution of crude product **S2** (81.20 mmol) mentioned above in CH_2Cl_2 (200 mL), MnO_2 (649.60 mmol) was added. The mixture was stirred at room temperature for 15 h and then filtered through a bed of silica. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (petrol ether/EtOAc = 20/1) to give product **S3** as a white or yellow solid.

S3 to **S4**: Vinyl magnesium bromide in THF (1 M, 203.00 mmol) was added to a solution of **S3** (81.20 mmol) in dry THF (200 mL) at 0 °C. Then the reacted mixture was naturally warmed to room temperature and stirred for 2.5 h. The reaction was quenched with brine (200 mL), extracted with ethyl acetate (3×100 mL) and washed with brine (3×100 mL). The combined organic layer was dried with $MgSO_4$, and evaporated under reduced pressure. The next step continued with obtained crude product **S4** directly without further purification.

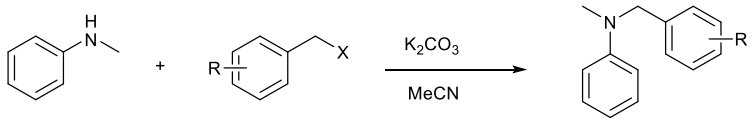
S4 to **S5**: K_2CO_3 (121.80 mmol) was added to a solution of **S4** (81.20 mmol) in methanol (250 mL), and the mixture was stirred at room temperature for 12 h. Then the mixture of reaction was quenched with saturated aqueous NH_4Cl solution (250 mL). The methanol was evaporated under reduced pressure and the residues were extracted with ethyl acetate (3×150 mL) and washed with brine (3×100 mL). Then the mixture was purified by column chromatography on silica gel (petrol ether/EtOAc =5/1). The product of **S5** was given to a white or yellow solid.

S5 to **1**: To a solution of **S5** (81.20 mmol) and triethylamine in THF (400.0 mL), NaH (162.40 mmol) was slowly added at 0 ℃. The stirred mixture was warmed to room temperature naturally and reacted for 1 h. TsCl (243.60 mmol) was added pertionwise slowly and then reacted at 60 ℃ for 36 h. The reaction was quenched with saturated aqueous NH_4Cl solution (250 mL) and washed with saturated brine (3×150 mL). Then

the organic layer was dried with $MgSO_4$. Then the mixture of production was purified by column chromatography on silica gel (petrol ether/EtOAc = 7/1). The product was given to a white solid.

2.2 General Procedure for Synthesis of *N*-methyl-*N*-benzylaniline (2m–2q)[2].

substrates **2** were synthesized according to reported procedures. The general procedure for the synthesis of substituted *N*-methyl-*N*-benzylaniline were shown as below.



S6 **S7** **2**

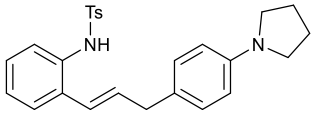
To a stirring solution of *N*-methylaniline (2.50 mmol) and K_2CO_3 (7.50 mmol) in MeCN (10.0 mL), compound **S7** (3.25 mmol) was added dropwise. The mixture was stirred at 60 °C for 8 h, and the reaction progress was monitored by TLC. Upon completion, the reaction was quenched with water (10.0 mL) and extracted with DCM (3×10.0 mL). The combined organic extracts were washed with brine (3×10.0 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography on silica gel (petrol ether/EtOAc = 10/1) afforded the product as an orange viscous oil.

2.3 General Procedure for Synthesis of 3

Under an argon atmosphere, a solution of dry HFIP (3.0 mL, 0.2 M) and *N,N*-dialkylaniline **2** (0.91 mmol, 1.5 equiv) was added dropwise simultaneously to a mixture of vinyl benzoxazinone **1** (0.61 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (0.06 mmol, 0.1 equiv). The reaction was stirred at 60 °C for 4 h, and the progress was monitored by TLC. Upon completion, the reaction mixture was quenched with saturated brine (5.0 mL) and extracted with ethyl acetate (5.0 mL × 3). The organic layer was washed with saturated brine (5.0 mL × 3), dried over anhydrous $MgSO_4$, and filtered under reduced

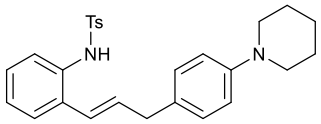
pressure. The filtrate was concentrated under reduced pressure to afford the crude product. The crude product was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to afford the product **3** as a white to off-white crystalline solid.

(*E*)-4-Methyl-*N*-(2-(3-(4-(pyrrolidin-1-yl)phenyl)prop-1-en-1-yl)phenyl)benzenesulfonamide (3a).



The title compound was purified by column chromatography (219 mg, 83%, petroleum ether/EtOAc = 5:1 v/v). Grey Solid, mp 147.4–149.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.54–7.49 (m, 2H), 7.49–7.43 (m, 1H), 7.34–7.28 (m, 2H), 7.18–7.07 (m, 2H), 7.03–6.93 (m, 3H), 6.53–6.44 (m, 3H), 6.11 (dt, J = 15.1, 7.1 Hz, 1H), 3.23 (d, J = 7.1 Hz, 2H), 3.21–3.15 (m, 4H), 2.34 (s, 3H), 1.97–1.88 (m, 4H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.5, 25.4, 38.7, 47.9, 112.2, 125.4, 126.1, 126.6, 127.2, 127.3, 127.8, 128.1, 129.5, 130.0, 131.9, 133.6, 134.6, 138.0, 143.4, 146.8 ppm; HRMS (ESI) m/z calcd for $C_{26}H_{28}N_2O_2SNa^+$[M + Na]$^+$ 455.1764, found 455.1760.

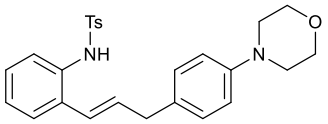
(*E*)-4-Methyl-*N*-(2-(3-(4-(piperidin-1-yl)phenyl)prop-1-en-1-yl)phenyl)benzenesulfonamide (3b).



The title compound was purified by column chromatography (196 mg, 72%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 114.8-116.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.54–7.49 (m, 2H), 7.49–7.46 (m, 1H), 7.35–7.28 (m, 2H), 7.16–7.09 (m, 2H), 7.03–6.96 (m, 3H), 6.89–6.83 (m, 2H), 6.50 (d, J = 15.6 Hz, 1H), 6.13 (dt, J = 15.1, 7.1 Hz, 1H), 3.24 (d, J = 7.1 Hz, 2H), 3.07 (t, J = 5.4 Hz, 4H), 2.33 (s, 3H), 1.65–1.57 (m, 4H), 1.55–1.47 (m, 2H) ppm ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ

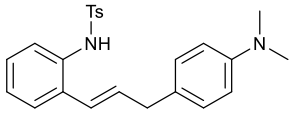
21.5, 24.4, 25.8, 38.7, 50.5, 116.6, 125.8, 126.1, 127.2, 127.3, 127.9, 128.1, 129.4, 130.0, 130.2, 131.5, 133.6, 134.5, 138.0, 143.4, 150.7 ppm; HRMS (ESI) m/z calcd for $C_{27}H_{30}N_2O_2SNa^+$[M + Na]$^+$ 469.1920, found 469.1921.

(*E*)-4-Methyl-*N*-(2-(3-(4-morpholinophenyl)prop-1-en-1-yl)phenyl)benzenesulfonamide (3c).



The title compound was purified by column chromatography (174 mg, 64%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 121.4–123.4 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.66 (s, 1H), 7.56–7.50 (m, 2H), 7.49–7.44 (m, 1H), 7.34–7.28 (m, 2H), 7.18–7.08 (m, 2H), 7.07–7.01 (m, 2H), 7.01–6.96 (m, 1H), 6.92–6.84 (m, 2H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.13 (dt, *J* = 15.6, 7.1 Hz, 1H), 3.76–3.69 (m, 4H), 3.26 (d, *J* = 7.1 Hz, 2H), 3.09–3.02 (m, 4H), 2.33 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 21.5, 38.7, 49.3, 66.6, 115.9, 125.9, 126.1, 127.2, 127.3, 127.9, 128.1, 129.5, 130.0, 131.0, 131.4, 133.6, 134.5, 137.9, 143.4, 150.0 ppm; HRMS (ESI) m/z calcd for $C_{26}H_{28}N_2O_3SNa^+$[M + Na]$^+$ 471.1713, found 471.1714.

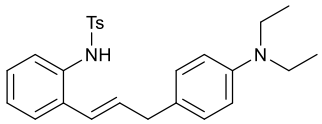
(*E*)-*N*-(2-(3-(4-(Dimethylamino)phenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3d).



The title compound was purified by column chromatography (174 mg, 70%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 131.8–133.8 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.65 (s, 1H), 7.56–7.48 (m, 2H), 7.50–7.43 (m, 1H), 7.34–7.27 (m, 2H), 7.16–7.09 (m, 2H), 7.03–6.95 (m, 3H), 6.71–6.64 (m, 2H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.12 (dt, *J* = 14.3, 7.0 Hz, 1H), 3.24 (d, *J* = 7.0 Hz, 2H), 2.88–2.82 (m, 6H), 2.33 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 21.5, 38.6, 40.9, 113.2, 125.6, 126.1, 127.2, 127.3,

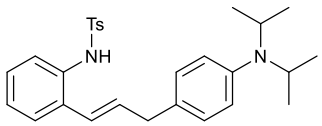
127.8, 128.1, 129.4, 130.0, 131.7, 133.6,H 134.5, 138.0, 143.4, 149.6 ppm; HRMS (ESI) m/z calcd for $C_{24}H_{26}N_2O_2SNa^+$[M + Na]$^+$ 429.1607, found 429.1607.

(*E*)-*N*-(2-(3-(4-(Diethylamino)phenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3e).



The title compound was purified by column chromatography (223 mg, 84%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 152.5–154.5 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) *δ* 9.65 (s, 1H), 7.55–7.50 (m, 2H), 7.49–7.45 (m, 1H), 7.34–7.28 (m, 2H), 7.16–7.09 (m, 2H), 7.02–6.98 (m, 1H), 6.97–6.92 (m, 2H), 6.64–6.56 (m, 2H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.11 (dt, *J* = 15.2, 7.1 Hz, 1H), 3.29 (q, *J* = 9.2, 7.3 Hz, 4H), 3.21 (d, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-*d*$_6$) *δ* 12.9, 21.5, 38.6, 44.2, 112.4, 125.5, 126.1, 126.5, 127.2, 127.3, 127.8, 128.1, 129.7, 130.0, 131.9, 133.6, 134.5, 138.0, 143.4, 146.4 ppm; HRMS (ESI) m/z calcd for $C_{26}H_{30}N_2O_2SNa^+$[M + Na]$^+$ 457.1920, found 457.1921.

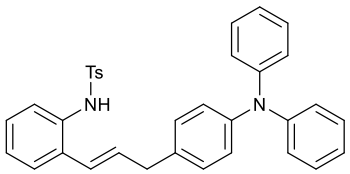
(*E*)-*N*-(2-(3-(4-(Diisopropylamino)phenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3f).



The title compound was purified by column chromatography (214 mg, 76%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 124.0–126.0 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) *δ* 9.66 (s, 1H), 7.54–7.50 (m, 2H), 7.50–7.47 (m, 1H), 7.34–7.28 (m, 2H), 7.15–7.10 (m, 2H), 7.01–6.98 (m, 1H), 6.98–6.93 (m, 2H), 6.83–6.76 (m, 2H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.14 (dt, *J* = 15.1, 7.1 Hz, 1H), 3.77–3.62 (m, 2H), 3.24 (d, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.12 (d, *J* = 6.6 Hz, 12H). ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-*d*$_6$) *δ*

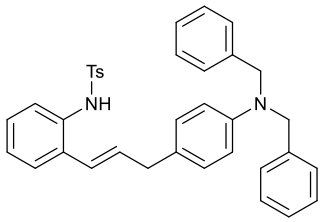
21.5, 21.7, 38.7, 47.5, 120.1, 125.7, 126.1, 127.2, 127.3, 127.8, 128.2, 128.9, 129.9, 130.0, 131.5, 133.6, 134.4, 137.9, 143.4, 146.3 ppm; HRMS (ESI) m/z calcd for $C_{28}H_{34}N_2O_2SNa^+$[M + Na]$^+$ 485.2233, found 485.2232.

(*E*)-*N*-(2-(3-(4-(Diphenylamino)phenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3g).



The title compound was purified by column chromatography (165 mg, 51%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 143.3–145.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.67 (s, 1H), 7.55–7.48 (m, 3H), 7.34–7.22 (m, 6H), 7.17–7.08 (m, 4H), 7.04–6.92 (m, 9H), 6.55 (d, J = 15.6 Hz, 1H), 6.20 (dt, J = 15.1, 7.1 Hz, 1H), 3.33 (d, J = 7.5 Hz, 2H), 2.29 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.5, 38.9, 123.1, 123.8, 124.9, 126.2, 126.4, 127.2, 127.3, 128.0, 128.2, 129.9, 130.0, 130.1, 130.7, 133.7, 134.3, 135.3, 137.9, 143.4, 145.8, 147.9 ppm; HRMS (ESI) m/z calcd for $C_{34}H_{30}N_2O_2SNa^+$[M + Na]$^+$ 553.1920, found 553.1921.

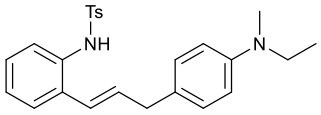
(*E*)-*N*-(2-(3-(4-(Dibenzylamino)phenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3h).



The title compound was purified by column chromatography (276 mg, 81%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 137.8–139.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.64 (s, 1H), 7.52–7.45 (m, 2H), 7.48–7.41 (m, 1H), 7.36–7.20 (m, 12H), 7.15–7.07 (m, 2H), 7.04–6.96 (m, 1H), 6.91–6.85 (m, 2H), 6.65–6.58 (m, 2H), 6.45 (d, J =

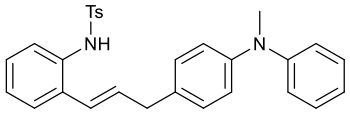
15.6 Hz, 1H), 6.09 (dt, *J* = 14.8, 7.1 Hz, 1H), 4.66 (s, 4H), 3.17 (d, *J* = 7.1 Hz, 2H), 2.25 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.4, 38.6, 54.9, 113.0, 125.6, 126.1, 127.2, 127.3, 127.6, 127.8, 128.2, 129.0, 129.5, 130.0, 131.5, 133.6, 134.4, 137.9, 139.7, 143.4, 147.1 ppm; HRMS (ESI) m/z calcd for $C_{36}H_{34}N_2O_2SNa^+$[M + Na]$^+$ 581.2233, found 581.2234.

(*E*)-*N*-(2-(3-(4-(Ethyl(methyl)amino)phenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3i).



The title compound was purified by column chromatography (198 mg, 77%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 140.5–142.5 °C;MPMP ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.66 (s, 1H), 7.54–7.50 (m, 2H), 7.49–7.45 (m, 1H), 7.34–7.27 (m, 2H), 7.15–7.08 (m, 2H), 7.02–6.93 (m, 3H), 6.67–6.61 (m, 2H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.12 (dt, *J* = 15.5, 7.1 Hz, 1H), 3.35 (q, *J* = 6.0 Hz, 2H), 3.22 (d, *J* = 7.1 Hz, 2H), 2.81 (s, 3H), 2.33 (s, 3H), 1.00 (t, *J* = 6.9 Hz, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 11.1, 21.5, 37.7, 38.6, 46.6, 113.0, 125.5, 126.1, 127.2, 127.3, 127.8, 128.1, 129.6, 130.0, 131.8, 133.6, 134.5, 138.0, 143.4, 147.8 ppm; HRMS (ESI) m/z calcd for $C_{25}H_{28}N_2O_2SNa^+$[M + Na]$^+$ 443.1764, found 443.1763.

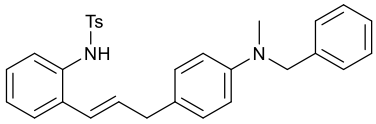
(*E*)-4-Methyl-*N*-(2-(3-(4-(methyl(phenyl)amino)phenyl)prop-1-en-1-yl)phenyl)benzenesulfonamide (3j).



The title compound was purified by column chromatography (163 mg, 57%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 121.2–123.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.67 (s, 1H), 7.56–7.47 (m, 3H), 7.34–7.28 (m, 2H), 7.27–7.19 (m, 2H), 7.18–7.08 (m, 4H), 7.03–6.95 (m, 3H), 6.96–6.89 (m, 2H), 6.90–6.82 (m, 1H), 6.54 (d, *J* = 15.7 Hz, 1H), 6.18 (dt, *J* = 15.1, 7.1 Hz, 1H), 3.32 (d, *J* = 6.7 Hz, 2H), 3.23 (s, 3H), 2.31 (s,

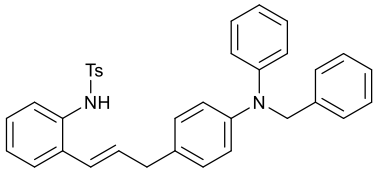
3H). ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.5, 38.8, 40.6, 119.1, 120.7, 122.1, 126.2, 126.2, 127.2, 127.3, 127.9, 128.2, 129.6, 129.9, 130.0, 131.0, 133.7, 133.9, 134.4, 137.9, 143.4, 147.3, 149.3 ppm; HRMS (ESI) m/z calcd for $C_{29}H_{28}N_2O_2SNa^+$[M + Na]$^+$ 491.1764, found 491.1764.

(*E*)-*N*-(2-(3-(4-(Benzyl(methyl)amino)phenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3k).



The title compound was purified by column chromatography (221 mg, 75%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 97.7–99.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.67 (s, 1H), 7.56–7.50 (m, 2H), 7.50–7.45 (m, 1H), 7.35–7.27 (m, 4H), 7.26–7.18 (m, 3H), 7.18–7.10 (m, 2H), 7.06–6.99 (m, 1H), 6.99–6.94 (m, 2H), 6.72–6.65 (m, 2H), 6.51 (d, J = 15.6 Hz, 1H), 6.13 (dt, J = 15.1, 7.1 Hz, 1H), 4.54 (s, 2H), 3.23 (d, J = 7.1 Hz, 2H), 2.99 (s, 3H), 2.32 (s, 3H). ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.5, 38.6, 39.2, 56.0, 112.8, 125.6, 126.1, 127.1, 127.2, 127.3, 127.5, 127.8, 128.2, 128.9, 129.5, 130.0, 131.7, 133.6, 134.5, 137.9, 139.7, 143.4, 148.1 ppm; HRMS (ESI) m/z calcd for $C_{30}H_{30}N_2O_2SNa^+$[M + Na]$^+$ 505.1920, found 505.1921.

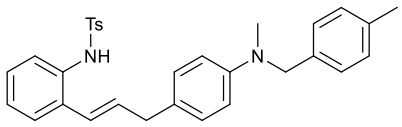
(*E*)-*N*-(2-(3-(4-(Benzyl(phenyl)amino)phenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3l).



The title compound was purified by column chromatography (223 mg, 67%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 140.3–142.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.66 (s, 1H), 7.53–7.48 (m, 3H), 7.34–7.28 (m, 6H), 7.23–7.17 (m, 3H), 7.15–7.11 (m, 2H), 7.10–7.04 (m, 4H), 7.01–6.95 (m, 3H), 6.88–6.80 (m, 1H), 6.52 (d, J = 15.7

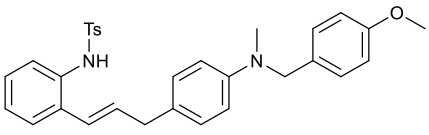
Hz, 1H), 6.17 (dt, *J* = 15.6, 7.1 Hz, 1H), 4.99 (s, 2H), 3.29 (d, *J* = 7.1 Hz, 2H), 2.28 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-*d*$_6$) *δ* 21.5, 38.8, 55.8, 119.4, 120.8, 122.1, 126.1, 126.2, 127.0, 127.2, 127.3, 127.9, 128.2, 129.0, 129.7, 129.9, 130.0, 130.9, 133.6, 133.8, 134.3, 137.9, 139.7, 143.4, 146.1, 148.3 ppm; HRMS (ESI) m/z calcd for $C_{35}H_{32}N_2O_2SNa^+$[M + Na]$^+$ 567.2077, found 567.2076.

(*E*)-4-Methyl-*N*-(2-(3-(4-(methyl(4-methylbenzyl)amino)phenyl)prop-1-en-1-yl)phenyl)benzenesulfonamide (3m).



The title compound was purified by column chromatography (251 mg, 83%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 105.7–107.7 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) *δ* 9.65 (s, 1H), 7.55–7.47 (m, 2H), 7.50–7.42 (m, 1H), 7.33–7.24 (m, 2H), 7.22–7.07 (m, 3H), 7.05–6.91 (m, 6H), 6.70–6.61 (m, 2H), 6.49 (d, *J* = 15.7 Hz, 1H), 6.11 (dt, *J* = 16.4, 8.9 Hz, 1H), 4.48 (s, 2H), 3.21 (d, *J* = 7.0 Hz, 2H), 2.96 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H). ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-*d*$_6$) *δ* 21.5, 21.6, 38.6, 39.2, 56.1, 112.8, 124.3, 125.6, 126.1, 127.2, 127.3, 127.4, 127.8, 127.9, 128.2, 128.8, 129.5, 130.0, 131.7, 133.6, 134.5, 138.0, 139.7, 143.4, 148.2 ppm; HRMS (ESI) m/z calcd for $C_{31}H_{32}N_2O_2SNa^+$[M + Na]$^+$ 519.2077, found 519.2076.

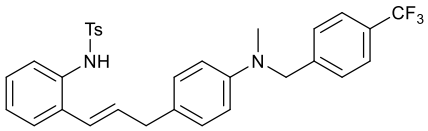
(*E*)-*N*-(2-(3-(4-((4-Methoxybenzyl)(methyl)amino)phenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3n).



The title compound was purified by column chromatography (247 mg, 79%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 115.6–117.6 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) *δ* 9.65 (s, 1H), 7.53–7.49 (m, 2H), 7.49–7.45 (m, 1H), 7.33–7.26 (m, 2H), 7.17–7.07

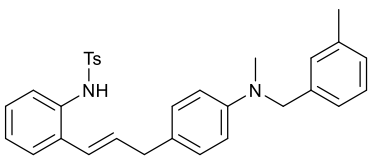
(m, 4H), 7.01–6.97 (m, 1H), 6.97–6.93 (m, 2H), 6.90–6.81 (m, 2H), 6.71–6.63 (m, 2H), 6.49 (d, J = 15.6 Hz, 1H), 6.11 (dt, J = 15.5, 7.1 Hz, 1H), 4.45 (s, 2H), 3.70 (s, 3H), 3.22 (d, J = 7.0 Hz, 2H), 2.93 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.5, 38.6, 39.0, 55.5, 113.0, 114.3, 125.6, 126.1, 127.2, 127.3, 127.5, 127.8, 128.2, 128.6, 129.5, 130.0, 131.3, 131.7, 133.6, 134.5, 137.9, 143.4, 148.2, 158.6 ppm; HRMS (ESI) m/z calcd for $C_{31}H_{32}N_2O_3SNa^+$[M + Na]$^+$ 535.2026, found 535.2027.

(*E*)-4-Methyl-*N*-(2-(3-(4-(methyl(4-(trifluoromethyl)benzyl)amino)phenyl)prop-1-en-1-yl)phenyl)benzenesulfonamide (3o).



The title compound was purified by column chromatography (178 mg, 53%, petroleum ether/EtOAc = 5:1 v/v). Pale yellow solid, mp 132.9–134.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.70–7.63 (m, 2H), 7.54–7.49 (m, 2H), 7.48–7.45 (m, 1H), 7.43–7.38 (m, 2H), 7.32–7.26 (m, 2H), 7.17–7.07 (m, 2H), 7.03–6.93 (m, 3H), 6.70–6.61 (m, 2H), 6.49 (d, J = 15.6 Hz, 1H), 6.11 (dt, J = 15.1, 7.1 Hz, 1H), 4.63 (s, 2H), 3.22 (d, J = 7.0 Hz, 2H), 3.01 (s, 3H), 2.29 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.4, 38.6, 39.3, 55.7, 112.8, 125.6, 125.8, 125.8, 126.1, 127.2, 127.3, 127.8, 127.8, 128.0, 128.2, 129.6, 130.0, 131.6, 133.6, 134.5, 137.9, 143.4, 144.9, 147.8 ppm; HRMS (ESI) m/z calcd for $C_{31}H_{29}F_3N_2O_2SNa^+$[M + Na]$^+$ 573.1794, found 573.1793.

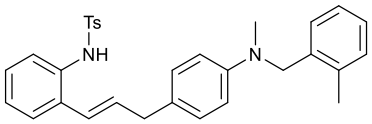
(*E*)-4-Methyl-*N*-(2-(3-(4-(methyl(3-methylbenzyl)amino)phenyl)prop-1-en-1-yl)phenyl)benzenesulfonamide (3p).



The title compound was purified by column chromatography (200 mg, 66%, petroleum

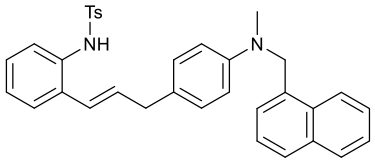
ether/EtOAc = 5:1 v/v). White solid, mp 93.6–95.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.53–7.48 (m, 2H), 7.48–7.43 (m, 1H), 7.32–7.26 (m, 2H), 7.15–7.05 (m, 6H), 7.01–6.97 (m, 1H), 6.97–6.92 (m, 2H), 6.68–6.62 (m, 2H), 6.48 (d, J = 15.6 Hz, 1H), 6.10 (dt, J = 15.0, 7.1 Hz, 1H), 4.47 (s, 2H), 3.21 (d, 2H), 2.94 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.2, 21.5, 38.6, 39.1, 55.8, 112.9, 125.6, 126.1, 127.2, 127.3, 127.3, 127.4, 127.8, 128.2, 129.5, 129.5, 130.0, 131.7, 133.6, 134.5, 136.2, 136.5, 137.9, 143.4, 148.1 ppm; HRMS (ESI) m/z calcd for $C_{31}H_{32}N_2O_2SNa^+$[M + Na]$^+$ 519.2077, found 519.2078.

(*E*)-4-Methyl-*N*-(2-(3-(4-(methyl(2-methylbenzyl)amino)phenyl)prop-1-en-1-yl)phenyl)benzenesulfonamide (3q).



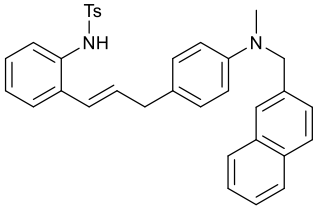
The title compound was purified by column chromatography (176 mg, 58%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 142.8–144.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.53–7.49 (m, 2H), 7.48–7.44 (m, 1H), 7.32–7.25 (m, 2H), 7.20–7.15 (m, 1H), 7.13–7.06 (m, 4H), 7.01–6.97 (m, 1H), 6.97–6.90 (m, 3H), 6.65–6.57 (m, 2H), 6.49 (d, J = 15.6 Hz, 1H), 6.12 (dt, J = 15.4, 7.2 Hz, 1H), 4.46 (s, 2H), 3.22 (d, J = 7.1 Hz, 2H), 2.97 (s, 3H), 2.29 (s, 3H), 2.28 (s, 2H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 19.1, 21.5, 38.6, 38.9, 54.1, 112.4, 125.6, 126.1, 126.2, 126.4, 126.9, 127.2, 127.3, 127.3, 127.8, 128.2, 129.6, 130.0, 130.7, 131.7, 133.6, 134.5, 136.0, 137.0, 137.9, 143.4, 148.2 ppm; HRMS (ESI) m/z calcd for $C_{31}H_{32}N_2O_2SNa^+$[M + Na]$^+$ 519.2077, found 519.2078.

(*E*)-4-Methyl-*N*-(2-(3-(4-(methyl(naphthalen-1-ylmethyl)amino)phenyl)prop-1-en-1-yl)phenyl)benzenesulfonamide (3r).



The title compound was purified by column chromatography (240 mg, 74%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 141.1–143.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 1H), 8.11–8.05 (m, 1H), 7.99–7.93 (m, 1H), 7.84–7.79 (m, 1H), 7.60–7.53 (m, 2H), 7.52–7.48 (m, 2H), 7.48–7.45 (m, 1H), 7.43–7.38 (m, 1H), 7.30–7.26 (m, 2H), 7.19–7.16 (m, 1H), 7.15–7.10 (m, 2H), 7.01–6.98 (m, 1H), 6.98–6.95 (m, 2H), 6.70–6.64 (m, 2H), 6.49 (d, J = 15.7 Hz, 1H), 6.12 (dt, J = 15.1, 7.1 Hz, 1H), 4.99 (s, 2H), 3.22 (d, J = 7.1 Hz, 2H), 3.03 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.4, 38.6, 39.0, 54.0, 112.5, 123.6, 124.1, 125.6, 126.0, 126.1, 126.3, 126.6, 127.2, 127.3, 127.5, 127.6, 127.8, 128.1, 129.1, 129.6, 130.0, 131.4, 131.7, 133.6, 134.0, 134.1, 134.5, 138.0, 143.4, 148.2 ppm; HRMS (ESI) m/z calcd for $C_{34}H_{32}N_2O_2SNa^+$[M + Na]$^+$ 555.2077, found 555.2078.

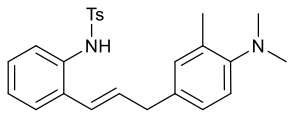
(*E*)-4-Methyl-*N*-(2-(3-(4-(methyl(naphthalen-2-ylmethyl)amino)phenyl)prop-1-en-1-yl)phenyl)benzenesulfonamide (3s).



The title compound was purified by column chromatography (266 mg, 82%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 135.0–137.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.89–7.83 (m, 2H), 7.83–7.79 (m, 1H), 7.72–7.67 (m, 1H), 7.53–7.49 (m, 2H), 7.49–7.43 (m, 3H), 7.41–7.35 (m, 1H), 7.31–7.24 (m, 2H), 7.15–7.09 (m, 2H), 7.02–6.98 (m, 1H), 6.98–6.93 (m, 2H), 6.75–6.69 (m, 2H), 6.49 (d, J = 15.6 Hz, 1H), 6.10 (dt, J = 15.1, 7.1 Hz, 1H), 4.68 (s, 2H), 3.21 (d, J = 7.1 Hz, 2H), 3.04 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.4, 38.6, 39.3, 56.4, 112.9, 125.4, 125.6, 126.0, 126.0, 126.1, 126.6, 127.2, 127.3, 127.6, 127.8, 128.0, 128.0, 128.2,

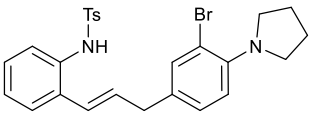
128.6, 129.6, 130.0, 131.7, 132.7, 133.5, 133.6, 134.5, 137.5, 138.0, 143.4, 148.2 ppm; HRMS (ESI) m/z calcd for $C_{34}H_{33}N_2O_2S^+[M + H]^+$ 533.2257, found 533.2260.

(*E*)-*N*-(2-(3-(4-(Dimethylamino)-3-methylphenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3t).



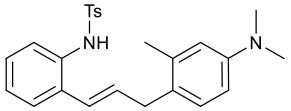
The title compound was purified by column chromatography (128 mg, 50%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 139.9–141.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.52 (d, J = 8.2 Hz, 2H), 7.50–7.46 (m, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.17–7.08 (m, 2H), 7.02–6.89 (m, 4H), 6.53 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.7, 7.1 Hz, 1H), 3.26 (d, J = 7.1 Hz, 2H), 2.59 (s, 6H), 2.32 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 18.5, 21.5, 38.9, 44.5, 118.8, 126.0, 126.2, 126.9, 127.2, 127.3, 127.9, 128.1, 130.0, 131.2, 131.5, 131.9, 133.6, 134.1, 134.5, 137.9, 143.4, 151.1 ppm; HRMS (ESI) m/z calcd for $C_{25}H_{28}N_2O_2SNa^+[M + Na]^+$ 443.1764, found 443.1763.

(*E*)-*N*-(2-(3-(3-Bromo-4-(pyrrolidin-1-yl)phenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3u).



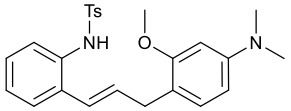
The title compound was purified by column chromatography (200 mg, 64%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 136.9–138.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.66 (s, 1H), 7.54–7.46 (m, 3H), 7.36–7.33 (m, 1H), 7.32–7.27 (m, 2H), 7.17–7.10 (m, 2H), 7.08–7.04 (m, 1H), 7.02–6.98 (m, 1H), 6.97–6.93 (m, 1H), 6.51 (d, J = 15.7 Hz, 1H), 6.13 (dt, J = 15.6, 7.1 Hz, 1H), 3.27 (d, J = 7.0 Hz, 2H), 3.25–3.20 (m, 4H), 2.32 (s, 3H), 1.91–1.79 (m, 4H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 20.9, 24.5, 37.6, 50.8, 113.5, 118.4, 125.6, 125.8, 126.7, 126.8, 127.5, 127.6, 128.2, 129.5, 130.1, 133.1, 133.4, 133.7, 137.3, 142.9, 146.5 ppm; HRMS (ESI) m/z calcd for $C_{26}H_{27}BrN_2O_2SNa^+[M + Na]^+$ 533.0869, found 533.0867.

(*E*)-*N*-(2-(3-(4-(Dimethylamino)-2-methylphenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3v).



The title compound was purified by column chromatography (139 mg, 54%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 132.3–134.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.62 (s, 1H), 7.50 (d, J = 7.8 Hz, 2H), 7.48–7.43 (m, 1H), 7.30 (d, J = 7.8 Hz, 2H), 7.15–7.08 (m, 2H), 6.98–6.93 (m, 1H), 6.93–6.89 (m, 1H), 6.57–6.49 (m, 3H), 6.07 (dt, J = 15.0, 6.9 Hz, 1H), 3.23 (d, J = 6.9 Hz, 2H), 2.84 (s, 6H), 2.34 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 20.2, 21.5, 36.3, 40.9, 111.0, 115.0, 125.6, 126.2, 126.3, 127.2, 127.3, 127.8, 128.1, 130.0, 131.3, 133.5, 134.8, 136.6, 138.0, 143.4, 149.7 ppm; HRMS (ESI) m/z calcd for $C_{25}H_{28}N_2O_2SNa^+$[M + Na]$^+$ 443.1764, found 443.1764.

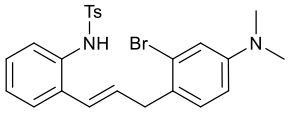
(*E*)-*N*-(2-(3-(4-(Dimethylamino)-2-methoxyphenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3w).



The title compound was purified by column chromatography (173 mg, 65%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 112.8–114.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.61 (s, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.46–7.40 (m, 1H), 7.33–7.26 (m, 2H), 7.16–7.07 (m, 2H), 6.99–6.92 (m, 1H), 6.85 (d, J = 8.3 Hz, 1H), 6.52 (d, J = 15.6 Hz, 1H), 6.35–6.29 (m, 1H), 6.28–6.22 (m, 1H), 6.08 (dt, J = 15.7, 7.1 Hz, 1H), 3.79 (s, 3H), 3.20 (d, J = 6.9 Hz, 2H), 2.87 (s, 6H), 2.33 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.5, 32.9, 41.0, 55.7, 96.9, 105.1, 116.1, 125.6, 126.1, 127.2, 127.3, 127.7, 128.0, 130.0, 130.2, 131.4, 133.5, 134.8, 138.0, 143.4, 151.1, 157.9 ppm; HRMS (ESI) m/z calcd for $C_{25}H_{28}N_2O_3SNa^+$[M + Na]$^+$ 459.1713, found 459.1712.

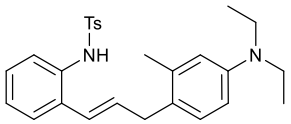
(*E*)-*N*-(2-(3-(2-Bromo-4-(dimethylamino)phenyl)prop-1-en-1-yl)phenyl)-4-

methylbenzenesulfonamide (3x).



The title compound was purified by column chromatography (225 mg, 76%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 134.4–136.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.64 (s, 1H), 7.50 (d, 2H), 7.47–7.43 (m, 1H), 7.30 (d, 2H), 7.17–7.11 (m, 2H), 7.08–7.03 (m, 1H), 7.01–6.98 (m, 1H), 6.89–6.86 (m, 1H), 6.74–6.68 (m, 1H), 6.55 (d, J = 15.7 Hz, 1H), 6.07 (dt, J = 15.6, 7.0 Hz, 1H), 3.33 (d, J = 6.6 Hz, 2H), 2.87 (s, 6H), 2.33 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.5, 38.5, 40.6, 112.7, 115.9, 124.9, 126.1, 126.2, 126.6, 127.2, 127.3, 128.0, 128.1, 129.9, 130.0, 131.2, 133.6, 134.5, 137.9, 143.4, 150.6 ppm; HRMS (ESI) m/z calcd for $C_{24}H_{25}BrN_2O_2SNa^+$[M + Na]$^+$ 507.0712, found 507.0715.

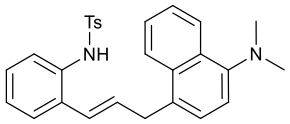
(*E*)-*N*-(2-(3-(4-(Diethylamino)-2-methylphenyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (3y).



The title compound was purified by column chromatography (213 mg, 78%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 143.5–145.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.62 (s, 1H), 7.51 (d, 2H), 7.48–7.44 (m, 1H), 7.30 (d, 2H), 7.15–7.08 (m, 2H), 7.00–6.92 (m, 1H), 6.90–6.85 (m, 1H), 6.55–6.49 (m, 1H), 6.49–6.42 (m, 2H), 6.07 (dt, J = 15.2, 7.1 Hz, 1H), 3.28 (q, J = 7.2 Hz, 4H), 3.21 (d, J = 7.0 Hz, 2H), 2.33 (s, 3H), 2.19 (s, 3H), 1.06 (t, J = 7.1 Hz, 6H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 13.0, 20.3, 21.5, 36.3, 44.1, 110.2, 114.2, 125.1, 125.5, 126.2, 127.2, 127.3, 127.7, 128.1, 130.0, 130.3, 131.4, 133.5, 134.8, 136.8, 138.0, 143.4, 146.5 ppm; HRMS (ESI) m/z calcd for $C_{27}H_{32}N_2O_2SNa^+$[M + Na]$^+$ 471.2077, found 471.2075.

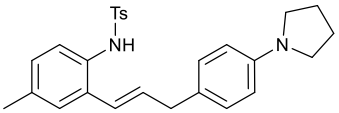
(*E*)-*N*-(2-(3-(4-(Dimethylamino)naphthalen-1-yl)prop-1-en-1-yl)phenyl)-4-

methylbenzenesulfonamide (3z).



The title compound was purified by column chromatography (148 mg, 53%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 151.5–153.5 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.67 (s, 1H), 8.25–8.17 (m, 1H), 8.10–8.03 (m, 1H), 7.58–7.47 (m, 4H), 7.46–7.42 (m, 1H), 7.29–7.23 (m, 3H), 7.15–7.06 (m, 3H), 7.02–6.95 (m, 1H), 6.71 (d, *J* = 15.7 Hz, 1H), 6.24 (dt, *J* = 15.1, 6.9 Hz, 1H), 3.74 (d, *J* = 6.9 Hz, 2H), 2.80 (s, 6H), 2.28 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 21.5, 36.4, 45.5, 124.8, 124.9, 125.4, 126.2, 126.4, 126.6, 126.7, 127.2, 127.3, 127.9, 128.0, 129.0, 130.0, 130.9, 131.0, 133.1, 133.6, 134.4, 137.9, 143.4, 149.9 ppm; HRMS (ESI) m/z calcd for $C_{28}H_{28}N_2O_2SNa^+$[M + Na]$^+$ 479.1764, found 479.1764.

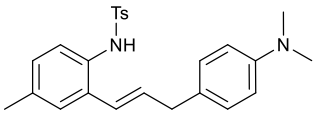
(*E*)-4-Methyl-*N*-(2-methyl-6-(3-(4-(pyrrolidin-1-yl)phenyl)prop-1-en-1-yl)phenyl)benzenesulfonamide (3ba).



The title compound was purified by column chromatography (223 mg, 82%, petroleum ether/EtOAc = 5:1 v/v). Pale brown solid, mp 170.8–172.8°C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.52 (s, 1H), 7.54–7.47 (m, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.27 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.51–6.40 (m, 3H), 6.09 (dt, *J* = 15.1, 7.1 Hz, 1H), 3.24–3.14 (m, 6H), 2.34 (s, 3H), 2.21 (s, 3H), 1.99–1.88 (m, 4H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 21.1, 21.5, 25.4, 38.7, 47.9, 112.3, 125.5, 126.4, 126.7, 127.2, 128.4, 128.5, 129.5, 130.0, 131.0, 131.6, 134.5, 136.6, 138.0, 143.3, 146.8 ppm; HRMS (ESI) m/z calcd for $C_{27}H_{30}N_2O_2SNa^+$[M + Na]$^+$ 469.1920, found 469.1921.

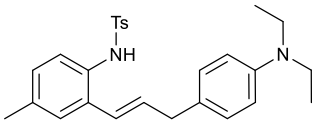
(*E*)-*N*-(2-(3-(4-(Dimethylamino)phenyl)prop-1-en-1-yl)-6-methylphenyl)-4-

methylbenzenesulfonamide (3be).



The title compound was purified by column chromatography (156 mg, 61%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 184.8–186.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.52 (s, 1H), 7.53–7.46 (m, 2H), 7.34–7.25 (m, 3H), 7.02–6.95 (m, 2H), 6.92 (d, J = 8.2 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.71–6.63 (m, 2H), 6.45 (d, J = 15.6 Hz, 1H), 6.09 (dt, J = 14.9, 7.1 Hz, 1H), 3.21 (d, J = 7.0 Hz, 2H), 2.85 (s, 6H), 2.34 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.0, 21.5, 38.6, 40.9, 113.2, 125.6, 126.4, 127.2, 127.9, 128.4, 128.5, 129.4, 130.0, 131.0, 131.4, 134.5, 136.6, 138.0, 143.3, 149.6 ppm; HRMS (ESI) m/z calcd for $C_{25}H_{28}N_2O_2SNa^+$[M + Na]$^+$ 443.1764, found 443.1765.

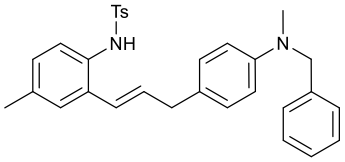
(*E*)-*N*-(2-(3-(4-(Diethylamino)phenyl)prop-1-en-1-yl)-6-methylphenyl)-4-methylbenzenesulfonamide (3bf).



The title compound was purified by column chromatography (203 mg, 74%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 132.3–134.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.53 (s, 1H), 7.51 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.28 (s, 1H), 6.98–6.89 (m, 3H), 6.89–6.82 (m, 1H), 6.63–6.56 (m, 2H), 6.45 (d, J = 15.6 Hz, 1H), 6.09 (dt, J = 15.1, 7.1 Hz, 1H), 3.29 (q, J = 7.1 Hz, 4H), 3.19 (d, J = 7.1 Hz, 2H), 2.33 (s, 3H), 2.21 (s, 3H), 1.06 (t, J = 6.9 Hz, 6H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 12.9, 21.0, 21.5, 38.6, 44.2, 112.4, 125.5, 126.4, 126.6, 127.2, 128.4, 128.5, 129.7, 130.0, 131.0, 131.5, 134.5, 136.6, 138.0, 143.3, 146.4 ppm; HRMS (ESI) m/z calcd for $C_{27}H_{32}N_2O_2SNa^+$[M + Na]$^+$ 471.2077, found 471.2077.

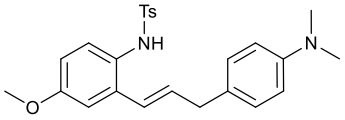
(*E*)-*N*-(2-(3-(4-(Benzyl(methyl)amino)phenyl)prop-1-en-1-yl)-6-methylphenyl)-4-

methylbenzenesulfonamide (3bk).



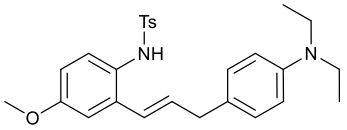
The title compound was purified by column chromatography (203 mg, 67%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 136.1–138.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.52 (s, 1H), 7.53–7.46 (m, 2H), 7.32–7.26 (m, 5H), 7.24–7.16 (m, 3H), 6.97–6.89 (m, 3H), 6.85 (d, J = 8.4 Hz, 1H), 6.70–6.63 (m, 2H), 6.43 (d, J = 15.7 Hz, 1H), 6.09 (dt, J = 15.0, 7.1 Hz, 1H), 4.53 (s, 2H), 3.19 (d, J = 7.1 Hz, 2H), 2.97 (s, 3H), 2.30 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.0, 21.5, 38.6, 39.2, 56.0, 112.8, 125.6, 126.4, 127.1, 127.2, 127.3, 127.5, 128.4, 128.5, 128.9, 129.5, 130.0, 131.0, 131.4, 134.4, 136.6, 138.0, 139.7, 143.3, 148.1 ppm; HRMS (ESI) m/z calcd for $C_{31}H_{32}N_2O_2SNa^+$[M + Na]$^+$ 519.2077, found 519.2080.

(*E*)-*N*-(2-(3-(4-(Dimethylamino)phenyl)prop-1-en-1-yl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3ce).



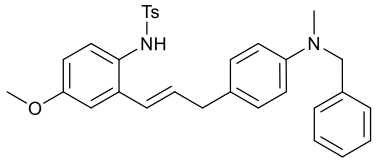
The title compound was purified by column chromatography (173 mg, 65%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 148.6–150.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.43 (s, 1H), 7.52–7.47 (m, 2H), 7.34–7.29 (m, 2H), 7.01–6.95 (m, 3H), 6.87–6.81 (m, 1H), 6.74–6.64 (m, 3H), 6.43 (d, J = 15.7 Hz, 1H), 6.17 (dt, J = 15.1, 7.1 Hz, 1H), 3.70 (s, 3H), 3.21 (d, J = 7.0 Hz, 2H), 2.85 (s, 6H), 2.34 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.5, 38.6, 40.9, 55.7, 109.9, 113.2, 114.1, 125.7, 126.4, 127.3, 127.8, 129.5, 130.0, 130.4, 131.8, 136.5, 138.0, 143.3, 149.6, 158.5 ppm; HRMS (ESI) m/z calcd for $C_{25}H_{28}N_2O_3SNa^+$[M + Na]$^+$ 459.1713, found 459.1713.

(*E*)-*N*-(2-(3-(4-(Diethylamino)phenyl)prop-1-en-1-yl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3cf).



The title compound was purified by column chromatography (232 mg, 82%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 107.9–109.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.44 (s, 1H), 7.53–7.46 (m, 2H), 7.34–7.28 (m, 2H), 7.00–6.91 (m, 3H), 6.88–6.81 (m, 1H), 6.74–6.66 (m, 1H), 6.63–6.56 (m, 2H), 6.42 (d, J = 15.6 Hz, 1H), 6.17 (dt, J = 15.0, 7.0 Hz, 1H), 3.70 (s, 3H), 3.34–3.24 (m, 4H), 3.19 (d, J = 7.0 Hz, 2H), 2.33 (s, 3H), 1.10–1.01 (m, 6H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 12.9, 21.5, 38.6, 44.2, 55.7, 109.9, 112.4, 114.1, 125.5, 126.4, 126.5, 127.3, 129.8, 130.0, 130.4, 131.9, 136.4, 137.9, 143.3, 146.4, 158.5 ppm; HRMS (ESI) m/z calcd for $C_{27}H_{32}N_2O_3SNa^+$[M + Na]$^+$ 487.2026, found 487.2030.

(*E*)-*N*-(2-(3-(4-(Diethylamino)phenyl)prop-1-en-1-yl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3ck).



The title compound was purified by column chromatography (231 mg, 72%, petroleum ether/EtOAc = 5:1 v/v). White solid, mp 113.4–115.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.43 (s, 1H), 7.52–7.45 (m, 2H), 7.32–7.27 (m, 4H), 7.25–7.16 (m, 3H), 7.00–6.91 (m, 3H), 6.88–6.81 (m, 1H), 6.74–6.62 (m, 3H), 6.41 (d, J = 15.7 Hz, 1H), 6.17 (dt, J = 15.1, 7.1 Hz, 1H), 4.53 (s, 2H), 3.70 (s, 3H), 3.19 (d, J = 7.0 Hz, 2H), 2.97 (s, 3H), 2.30 (s, 3H) ppm; ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 21.5, 38.6, 39.2, 55.7, 56.0, 109.9, 112.8, 114.1, 125.7, 126.4, 127.1, 127.3, 127.3, 127.4, 128.9, 129.6, 130.0, 130.4, 131.7, 136.4, 138.0, 139.7, 143.2, 148.1, 158.5 ppm; HRMS (ESI) m/z calcd for $C_{32}H_{34}N_2O_3SNa^+$[M + Na]$^+$ 549.2182, found 549.2183.

3. References

1 K. Wang, B. Wang, X. Liu, H. Fan, Y. Liu and C. Li, Palladium-Catalyzed Enantioselective Linear Allylic Alkylation of Vinyl Benzoxazinanones: An Inner-Sphere Mechanism, *Chin. J. Catal.*, 2021, **42**, 1227–1237.

2 (a) A. Runemark, S. C. Zacharias and H. Sundén, Visible-Light-Driven Stereoselective Annulation of Alkyl Anilines and Dibenzoylethylenes via Electron Donor–Acceptor Complexes, *J. Org. Chem.*, 2021, **86**, 1901–1910; (b) G. Perumal, M. Kandasamy, B. Ganesan, K. Govindan, H. Sathya, G. C. Senadi, Y.-C. Wu and W.-Y. Lin, Visible Light-Induced *N*-Methyl Activation of Unsymmetric Tertiary Amines, *Tetrahedron*, 2021, **80**, 131891.

4. X-Ray Structure for compounds

(1) ORTEP drawing of the X-ray crystallographic structure of compound 3a (40% probability ellipsoids)

The single crystal of compound **3a** was prepared from its solution in petrol ether/ ethyl acetate (2:1) by slow evaporation of the solvent (Table 1). Crystal structure information has been deposited at the Cambridge Crystallographic Data Centre, CCDC: 2503683.

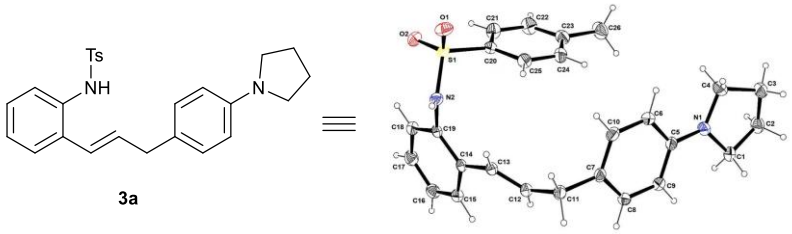


Table 1. Crystal data and structure refinement for **3a**

dentification code	**3a**
Empirical formula	$C_{26}H_{28}N_2O_2S$

Formula weight	432.56
Temperature/K	170.00
Crystal system	triclinic
Space group	P-1
a/Å	9.0572(2)
b/Å	10.2952(2)
c/Å	12.7767(2)
α/°	103.5580(10)
β/°	103.1660(10)
γ/°	91.4260(10)
Volume/Å^3	1123.87(4)
Z	2
ρ_{calc}g/cm^3	1.278
μ/mm^{-1}	0.986
F(000)	460.0
Crystal size/mm^3	0.17 × 0.11 × 0.08
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.714 to 109.97
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	25793
Independent reflections	4219 [R_{int} = 0.0375, R_{sigma} = 0.0259]
Data/restraints/parameters	4219/0/281
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0961
Final R indexes [all data]	R_1 = 0.0371, wR_2 = 0.0969
Largest diff. peak/hole / e Å^{-3}	0.45/-0.39

For detailed crystallographic data, please refer to the Cambridge Crystallographic Data

Centre at http://ccdc.cam.ac.uk.

(2) ORTEP drawing of the X-ray crystallographic structure of compound 3cf (40% probability ellipsoids)

The single crystal of compound **3cf** was prepared from its solution in petrol ether/ ethyl acetate (2:1) by slow evaporation of the solvent (Table 2). Crystal structure information has been deposited at the Cambridge Crystallographic Data Centre, CCDC: 2503680.

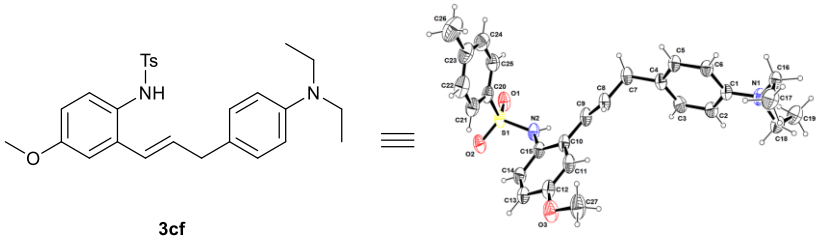


Table 2. Crystal data and structure refinement for **3cf**

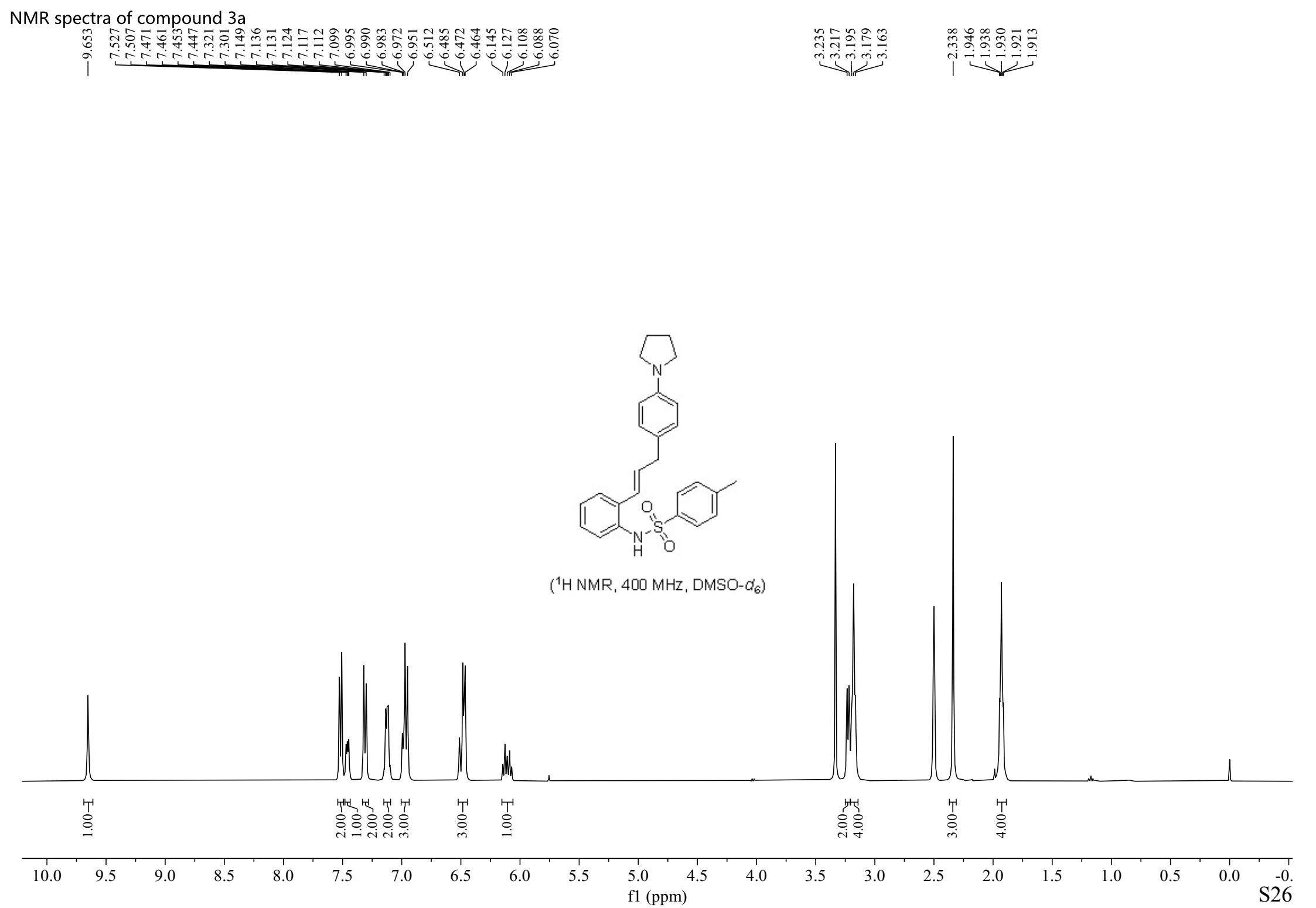
Identification code	**3cf**
Empirical formula	$C_{27}H_{32}N_2O_3$**S**
Formula weight	464.60
Temperature/K	170.00
Crystal system	triclinic
Space group	P-1
a/Å	12.2265(5)
b/Å	15.2362(7)
c/Å	21.6873(10)
α/°	99.087(2)
β/°	95.790(2)
γ/°	107.587(2)
Volume/Å^3	3755.2(3)
Z	6

$\rho_{calc}g/cm^3$	1.233
μ/mm^{-1}	0.927
F(000)	1488.0
Crystal size/mm^3	0.15 × 0.12 × 0.05
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	5.402 to 110.264
Index ranges	$-14 \leq h \leq 14$, $-18 \leq k \leq 18$, $-25 \leq l \leq 26$
Reflections collected	63335
Independent reflections	14257 [R_{int} = 0.0766, R_{sigma} = 0.0601]
Data/restraints/parameters	14257/609/1050
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0704, wR_2 = 0.1903
Final R indexes [all data]	R_1 = 0.1140, wR_2 = 0.2238
Largest diff. peak/hole / e $Å^{-3}$	0.61/-0.68

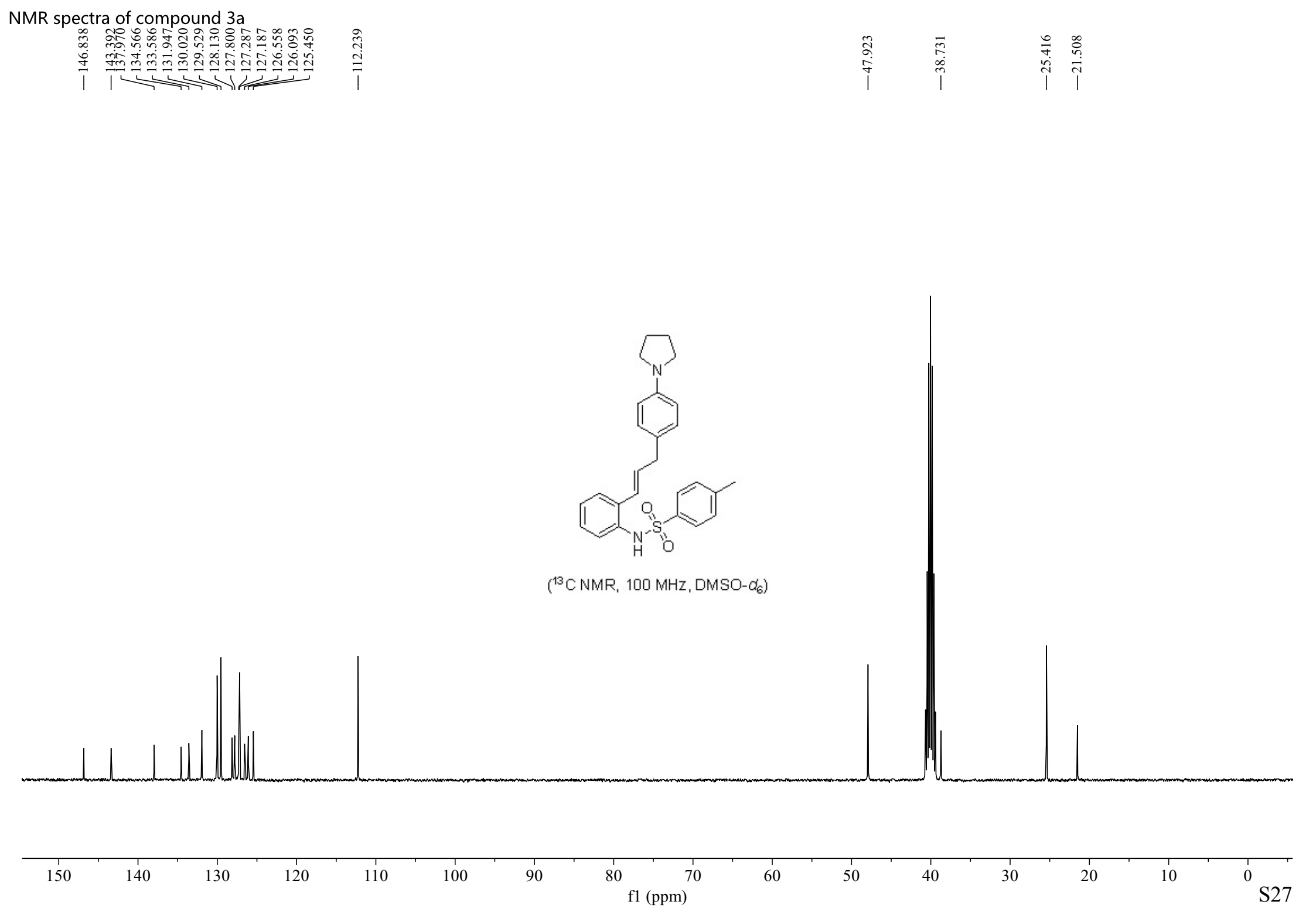
For detailed crystallographic data, please refer to the Cambridge Crystallographic Data Centre at http://ccdc.cam.ac.uk.

5. Copies of NMR Reports of New Compounds

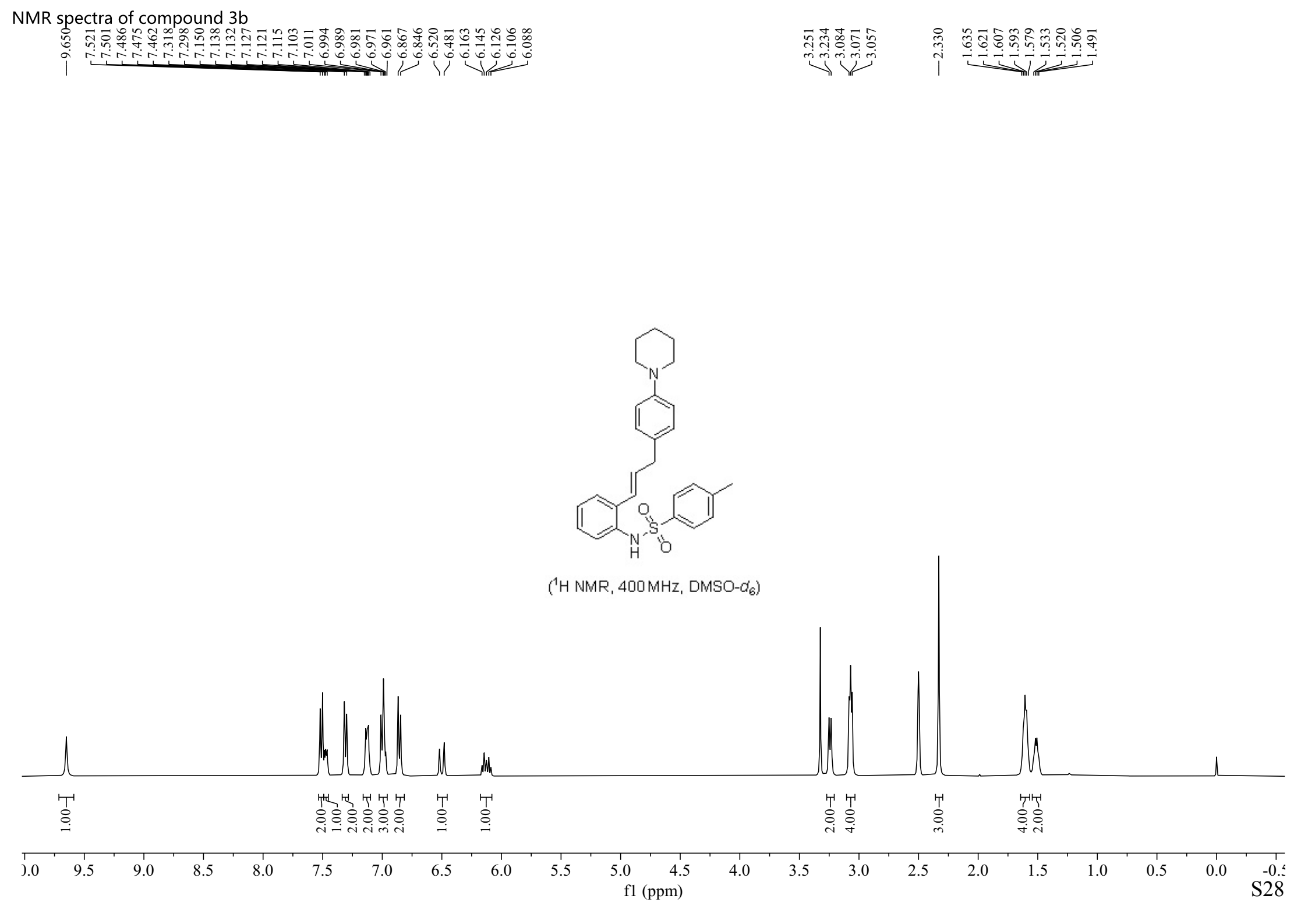
NMR spectra of compound 3a



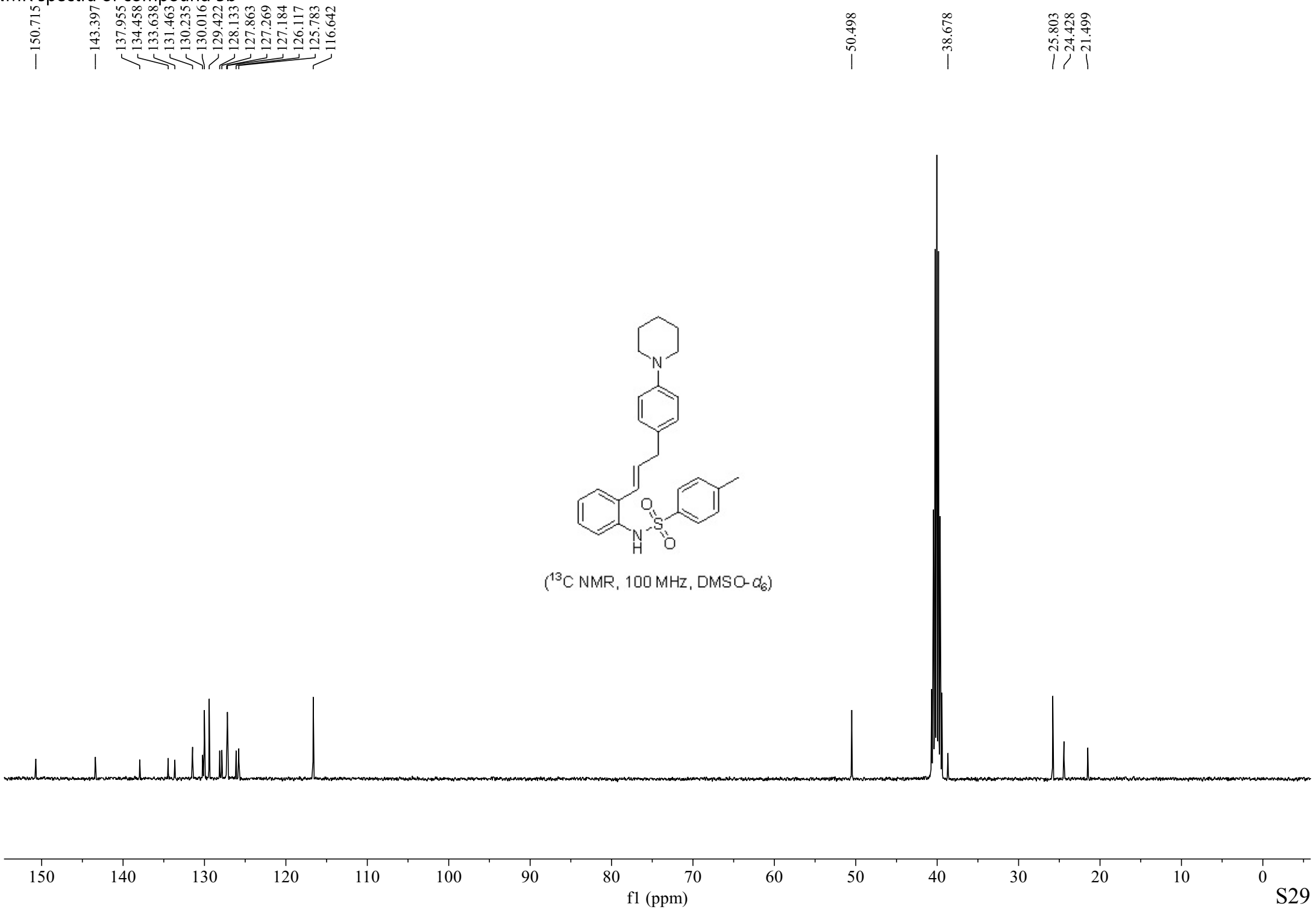
NMR spectra of compound 3a



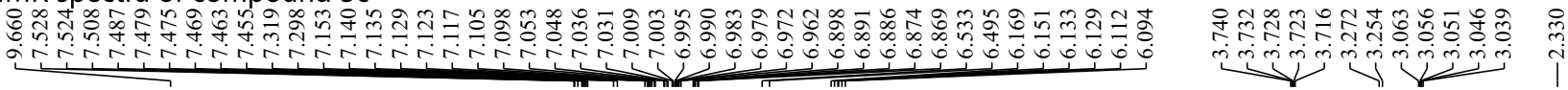
NMR spectra of compound 3b

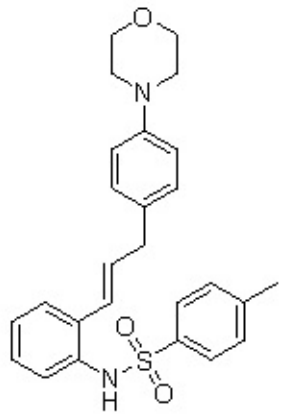


NMR spectra of compound 3b

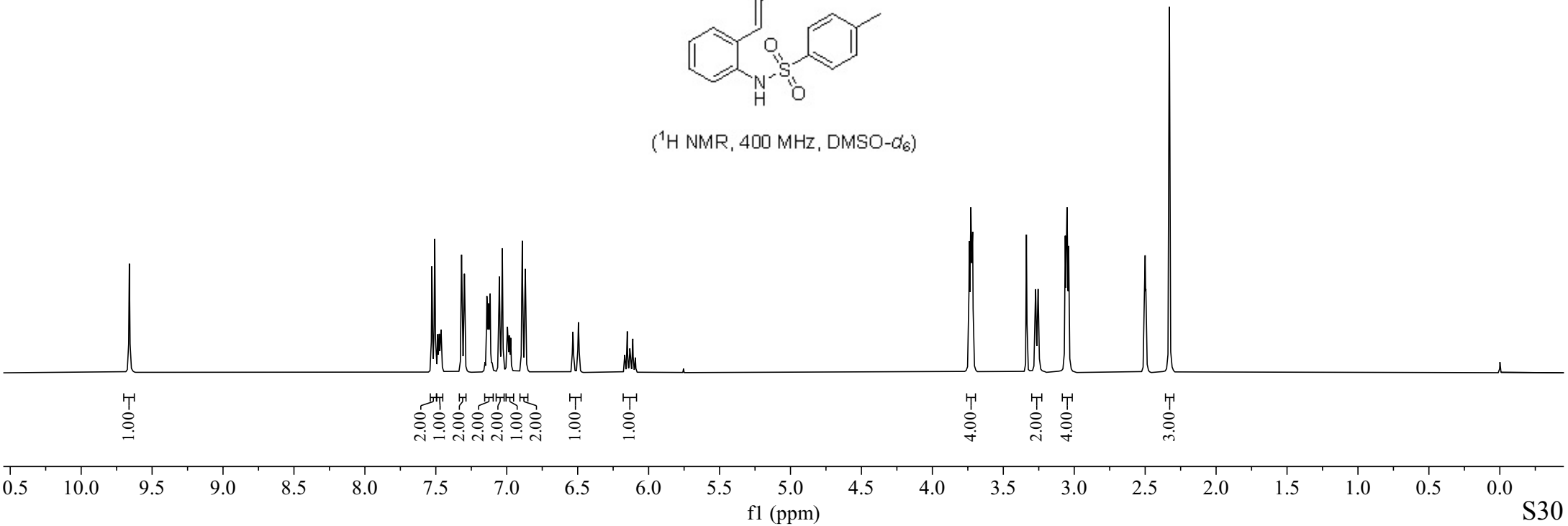


NMR spectra of compound 3c

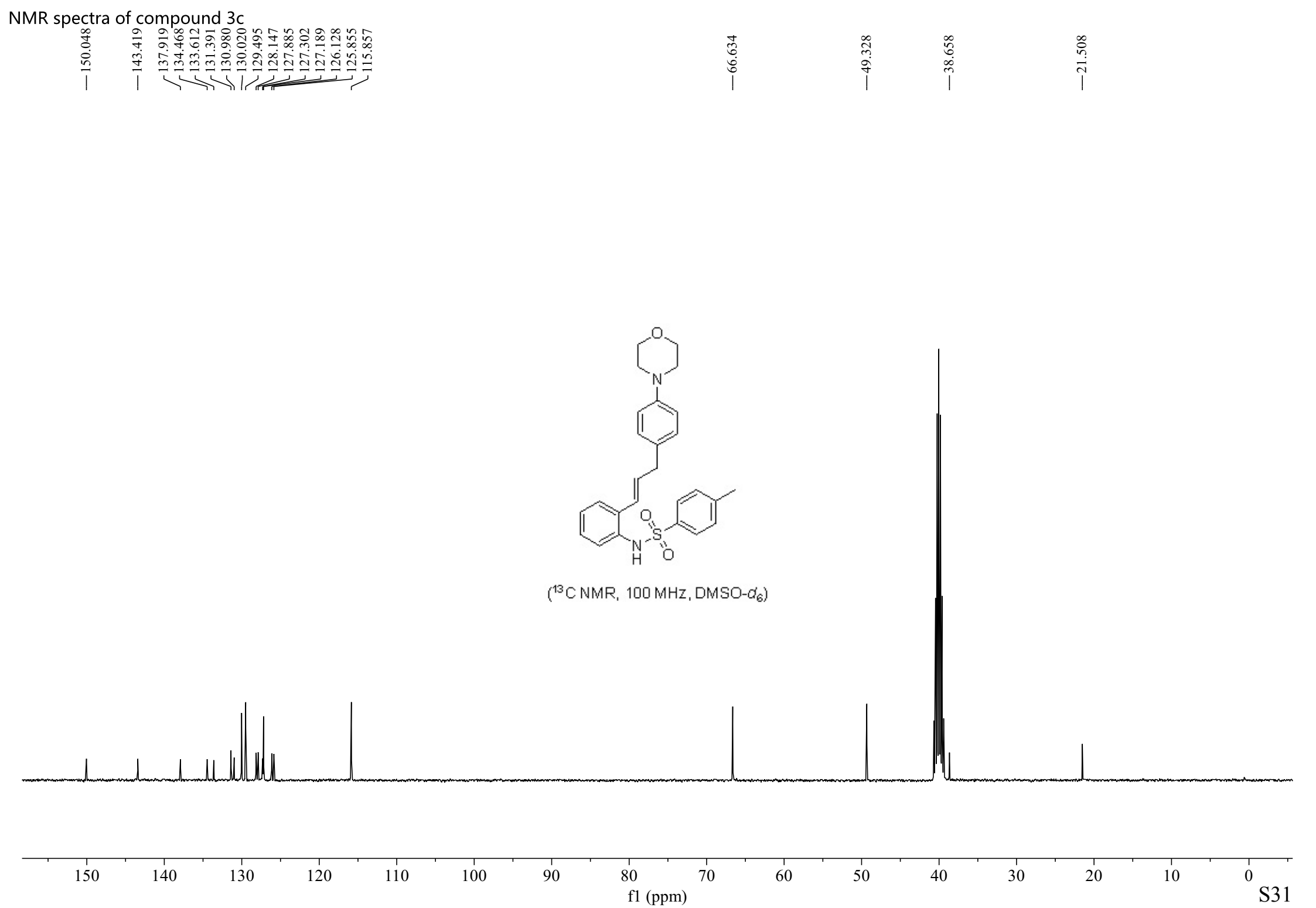




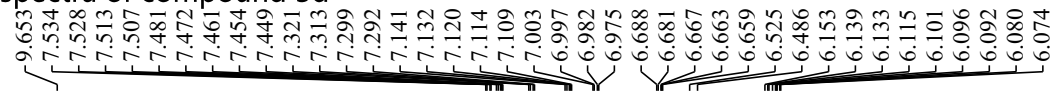
(^{1}H NMR, 400 MHz, DMSO-d_6)

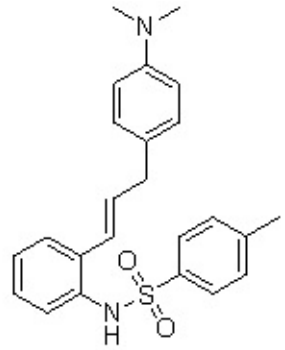


NMR spectra of compound 3c

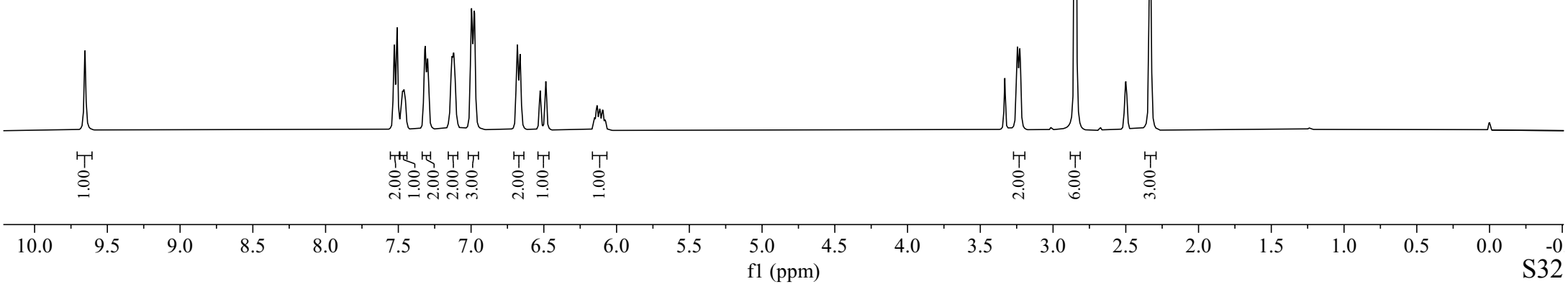


NMR spectra of compound 3d

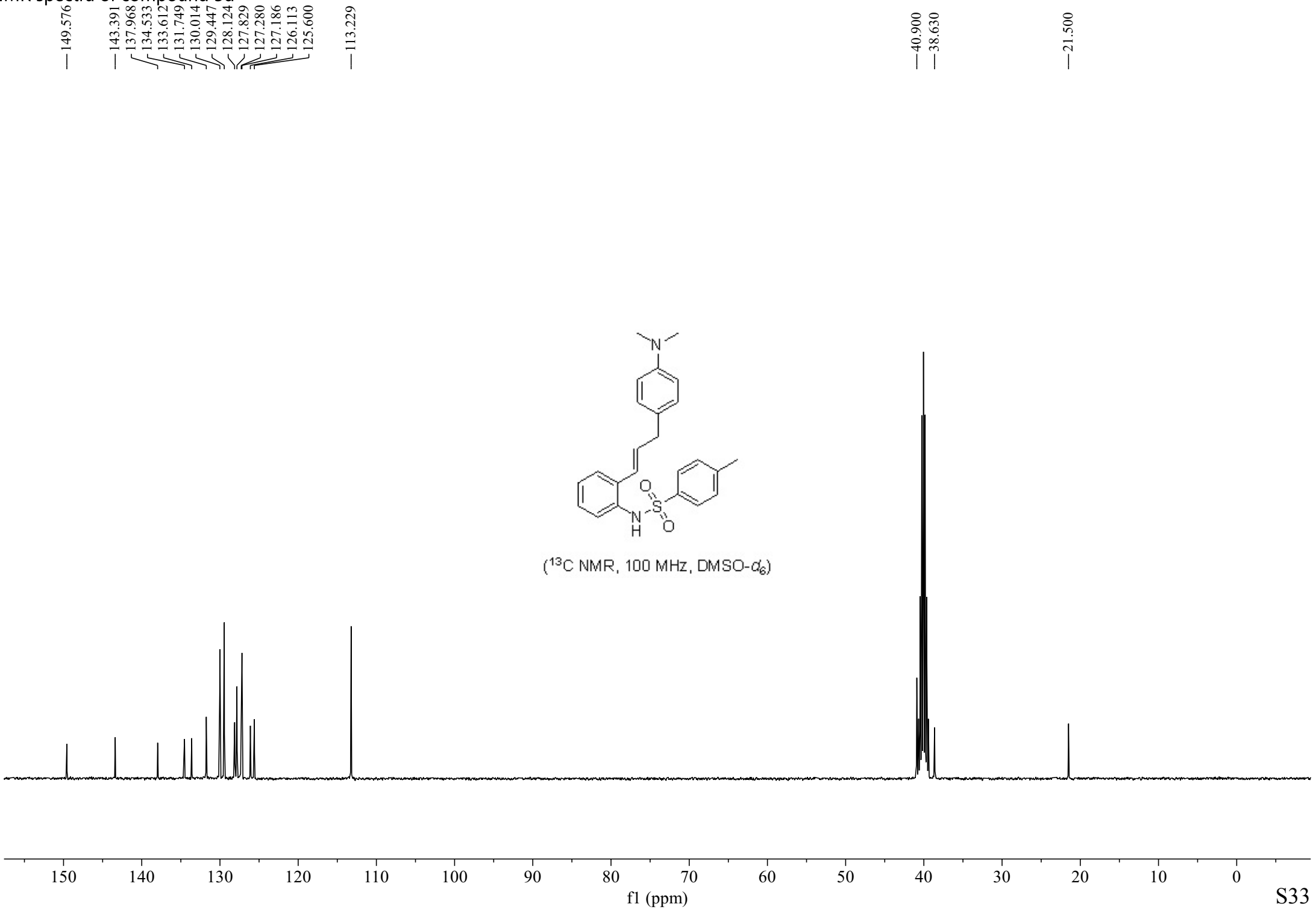




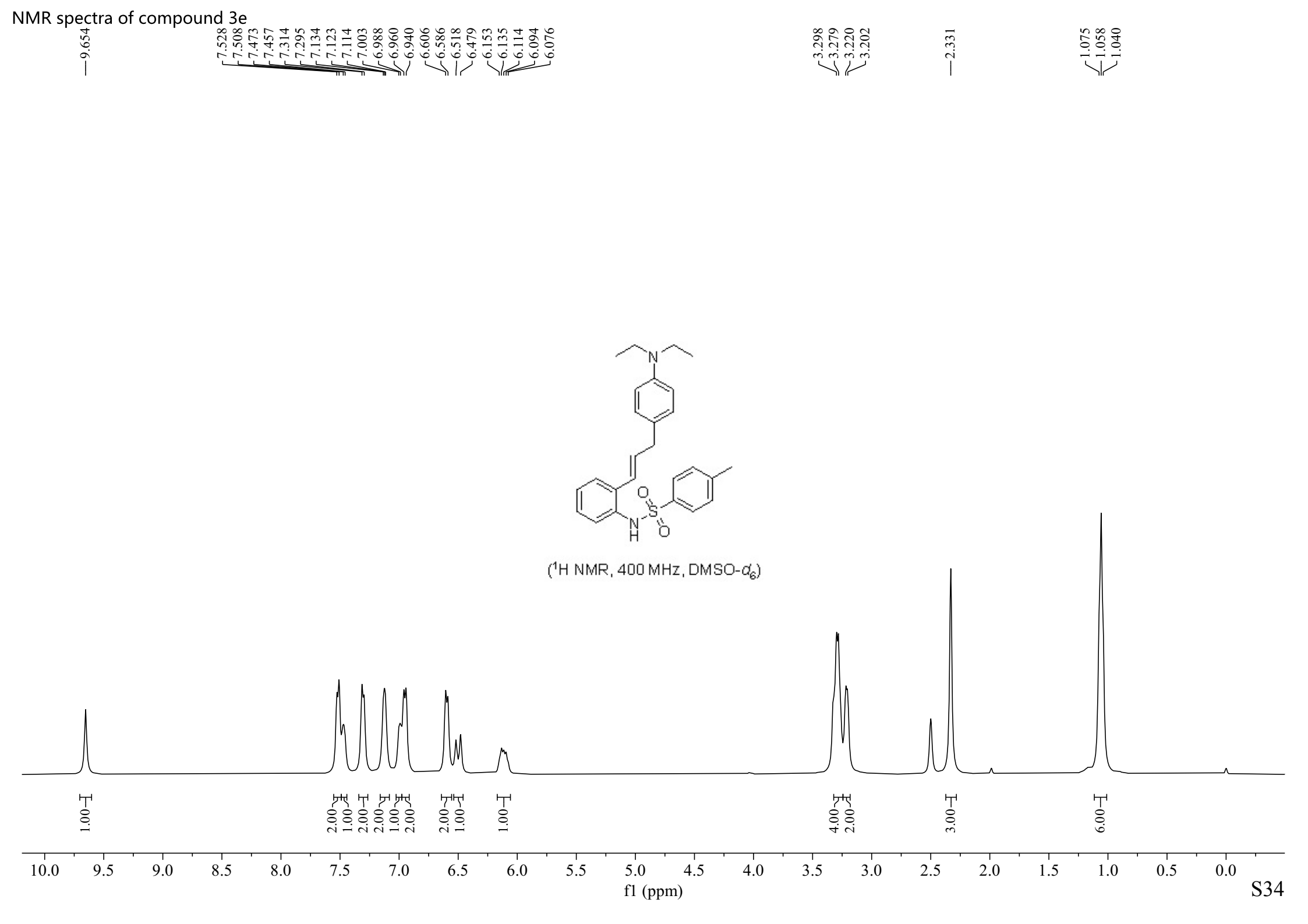
(^{1}H NMR, 400 MHz, DMSO-d_6)



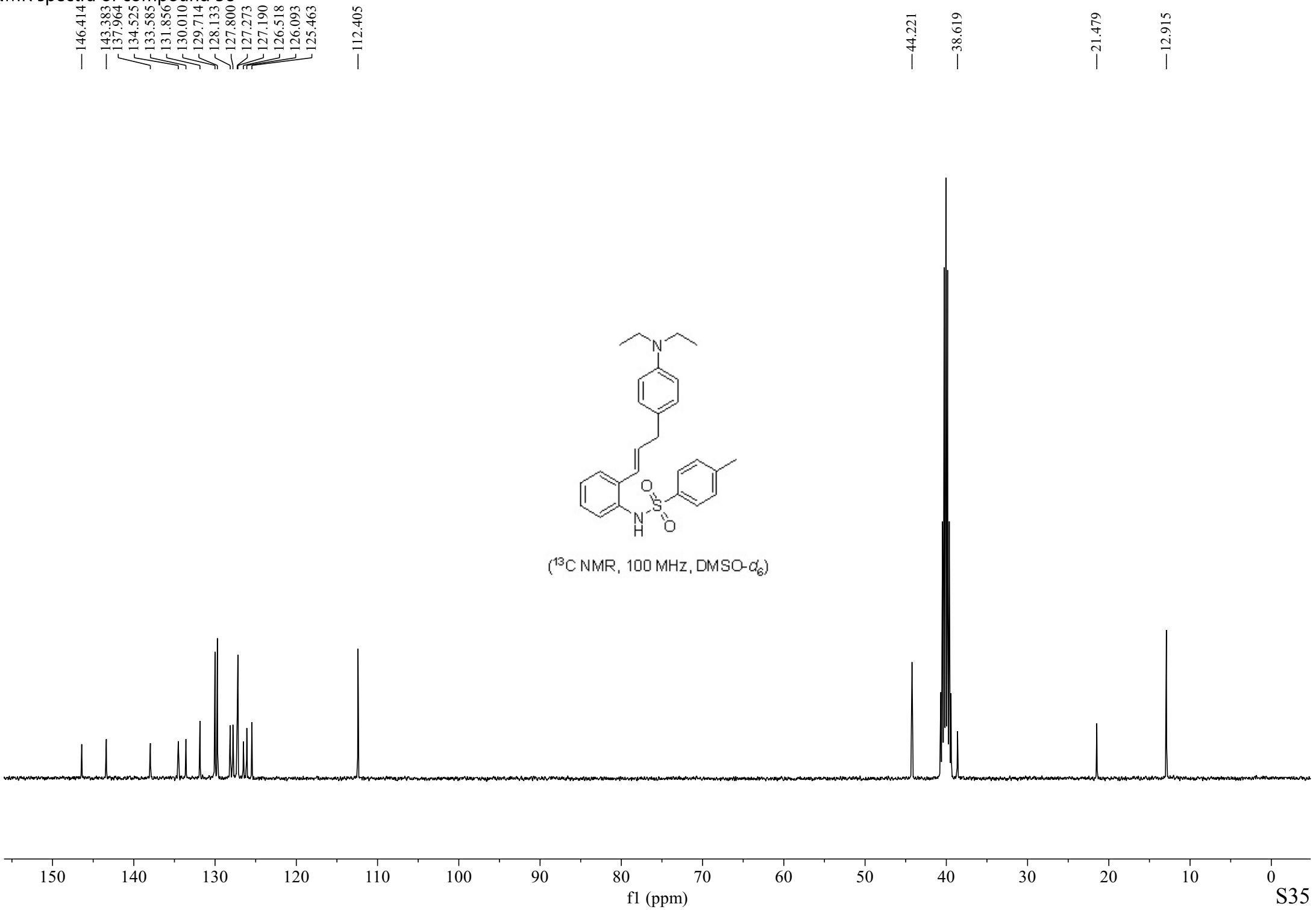
NMR spectra of compound 3d



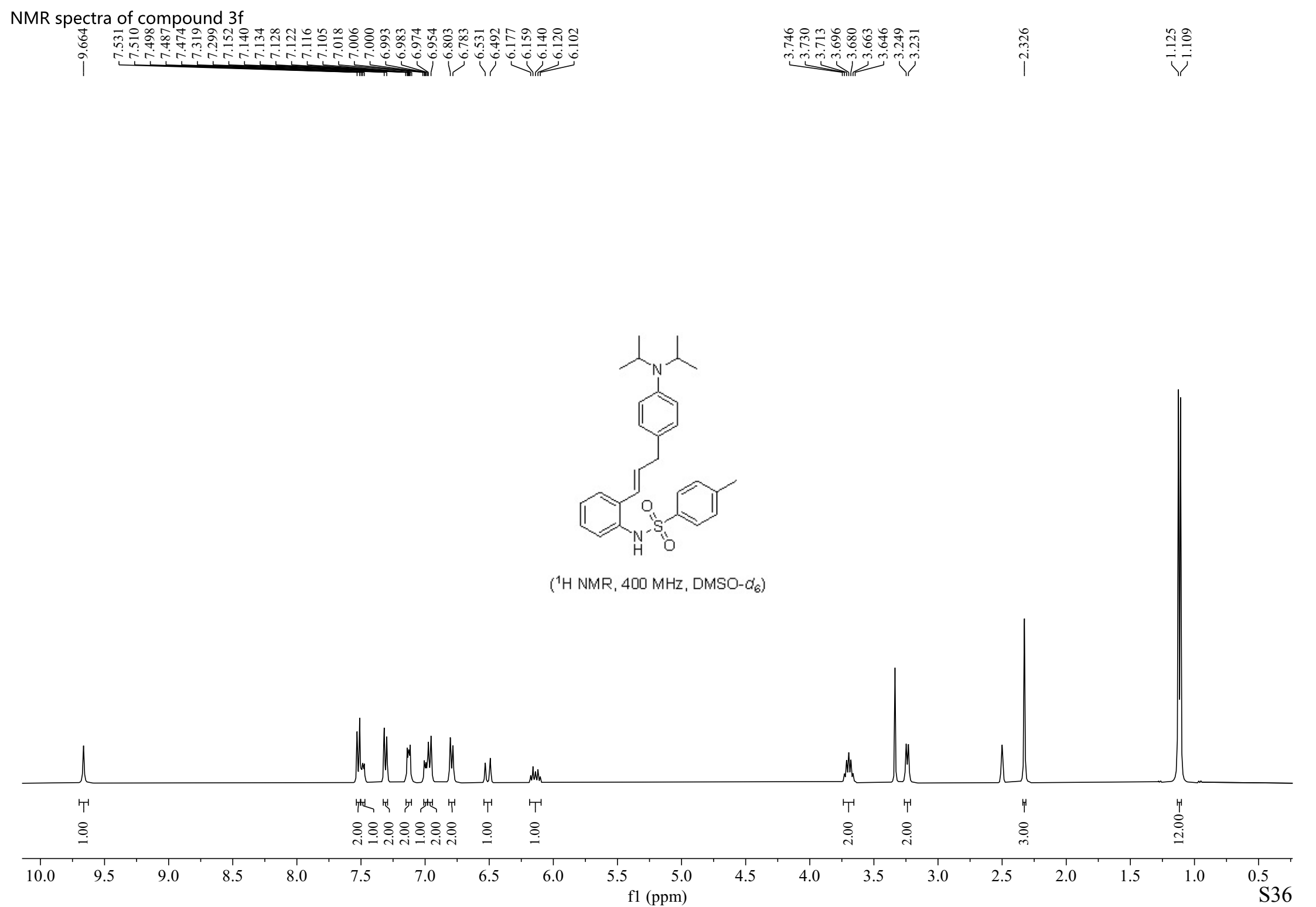
NMR spectra of compound 3e



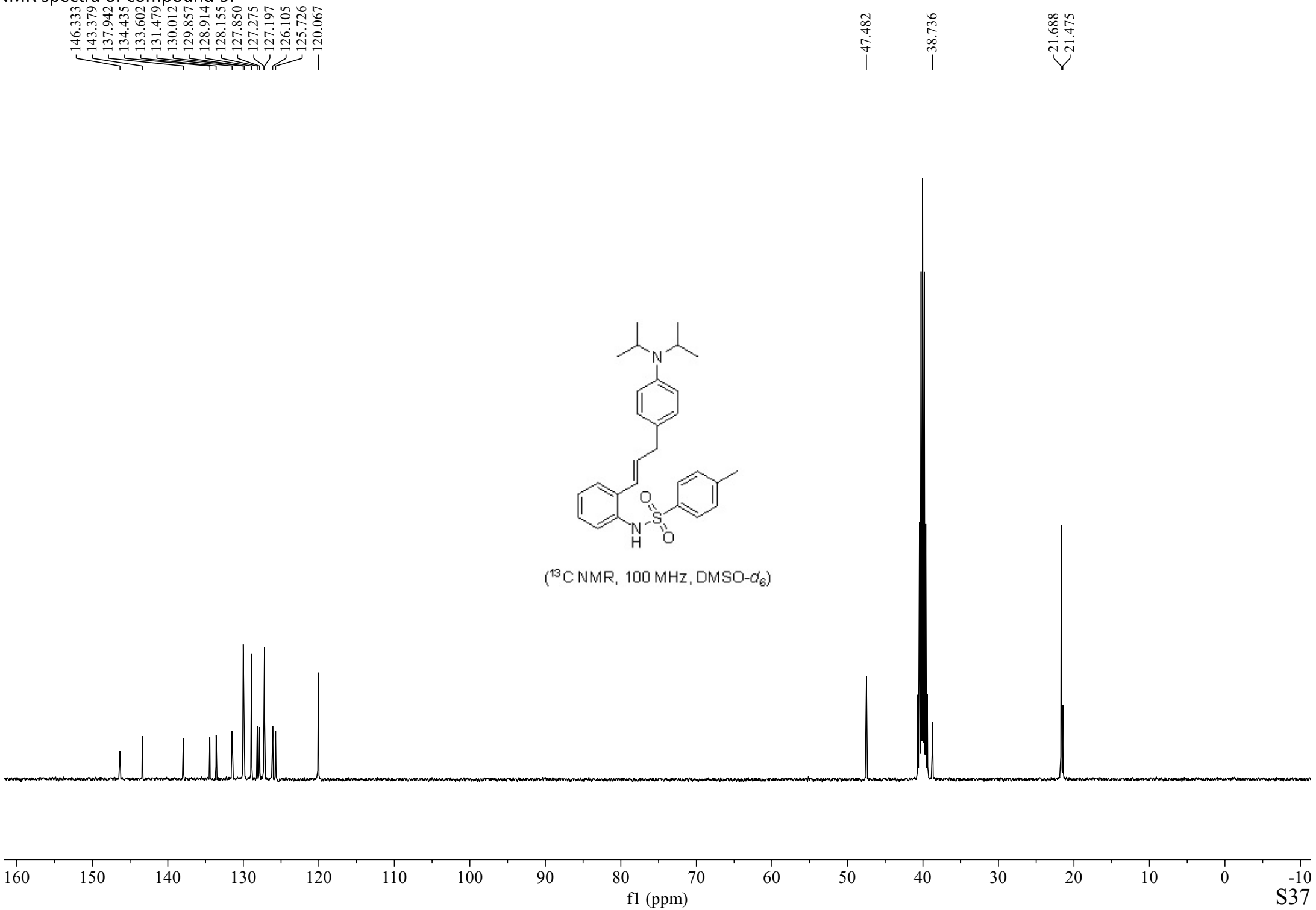
NMR spectra of compound 3e



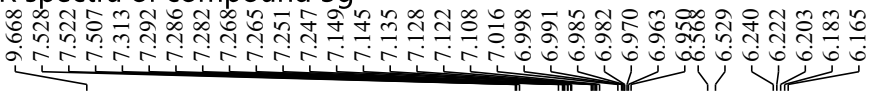
NMR spectra of compound 3f

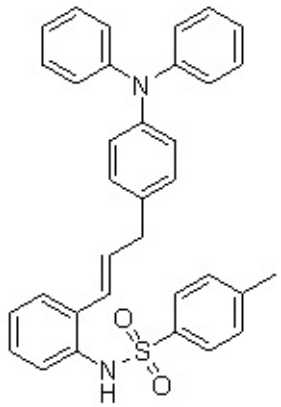


NMR spectra of compound 3f

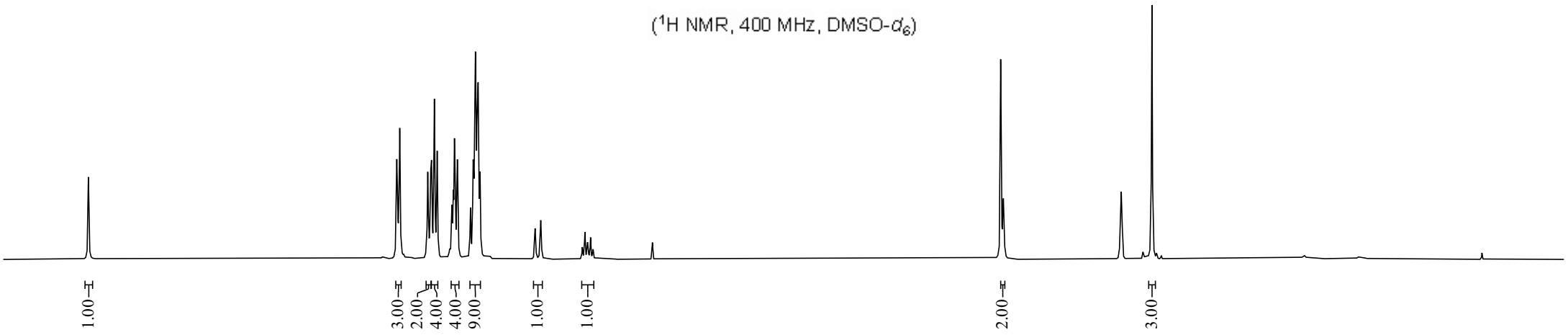


NMR spectra of compound 3g

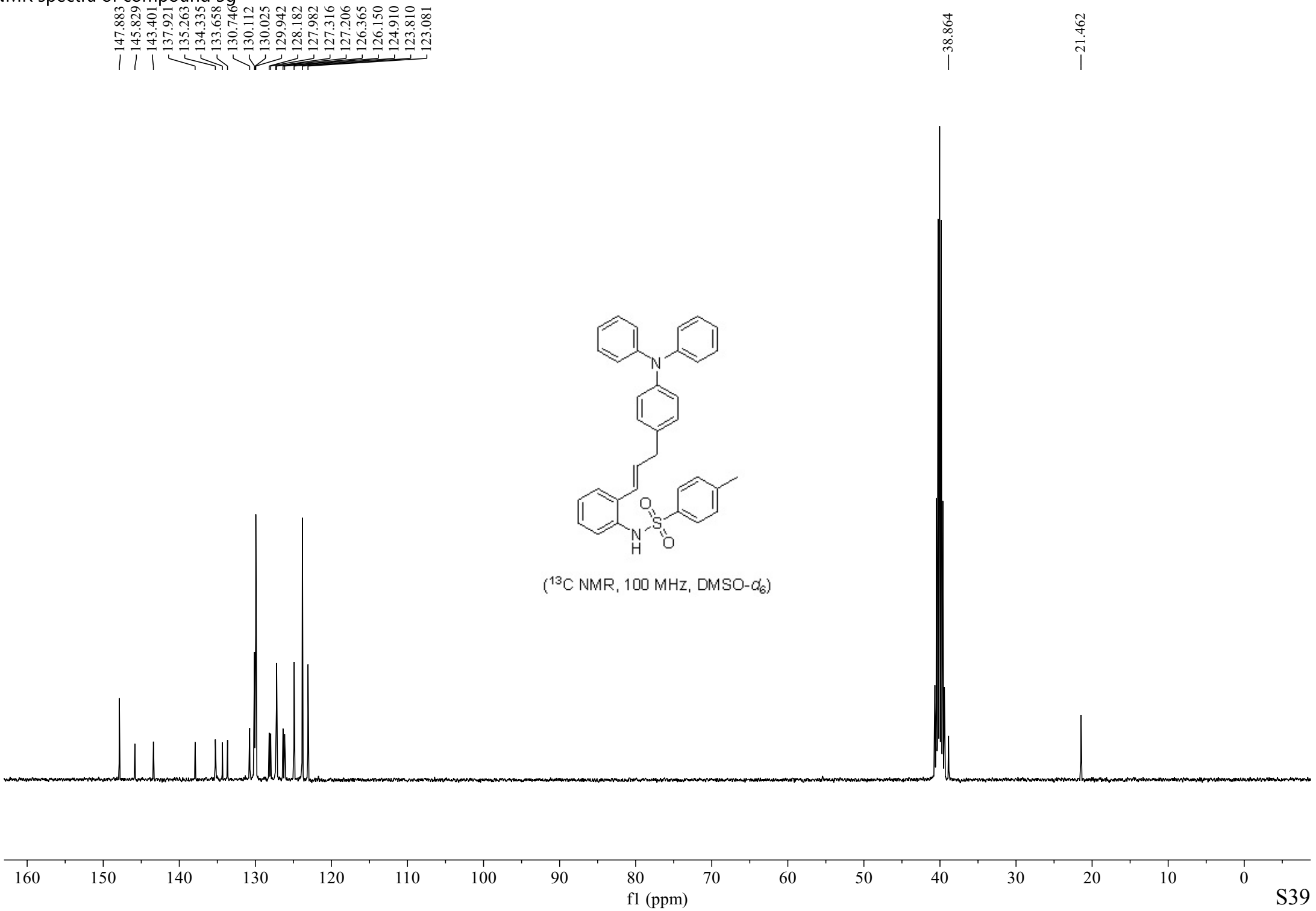




(¹H NMR, 400 MHz, DMSO-d_6)

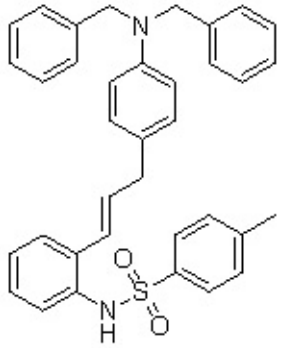


NMR spectra of compound 3g

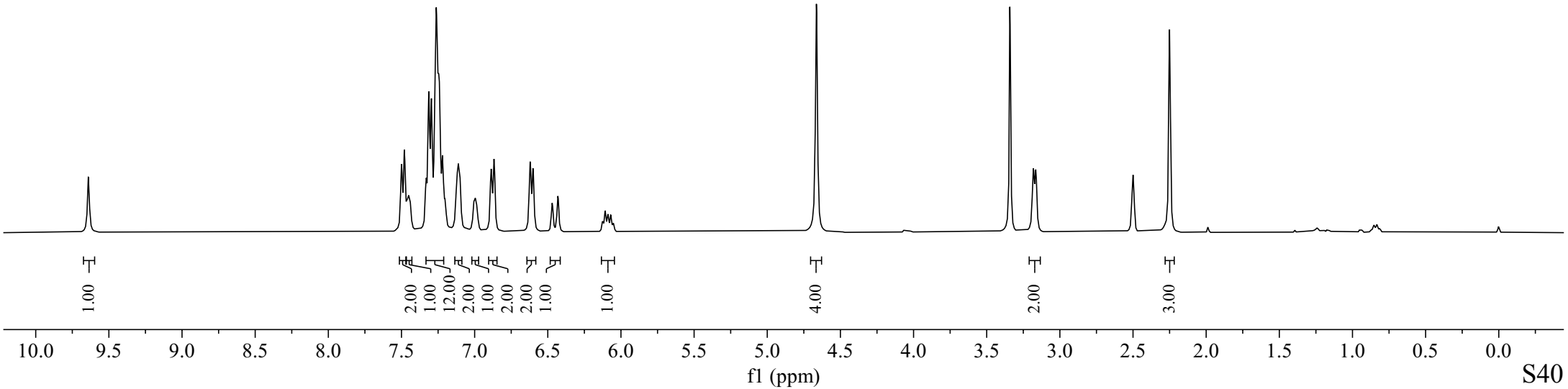


NMR spectra of compound 3h

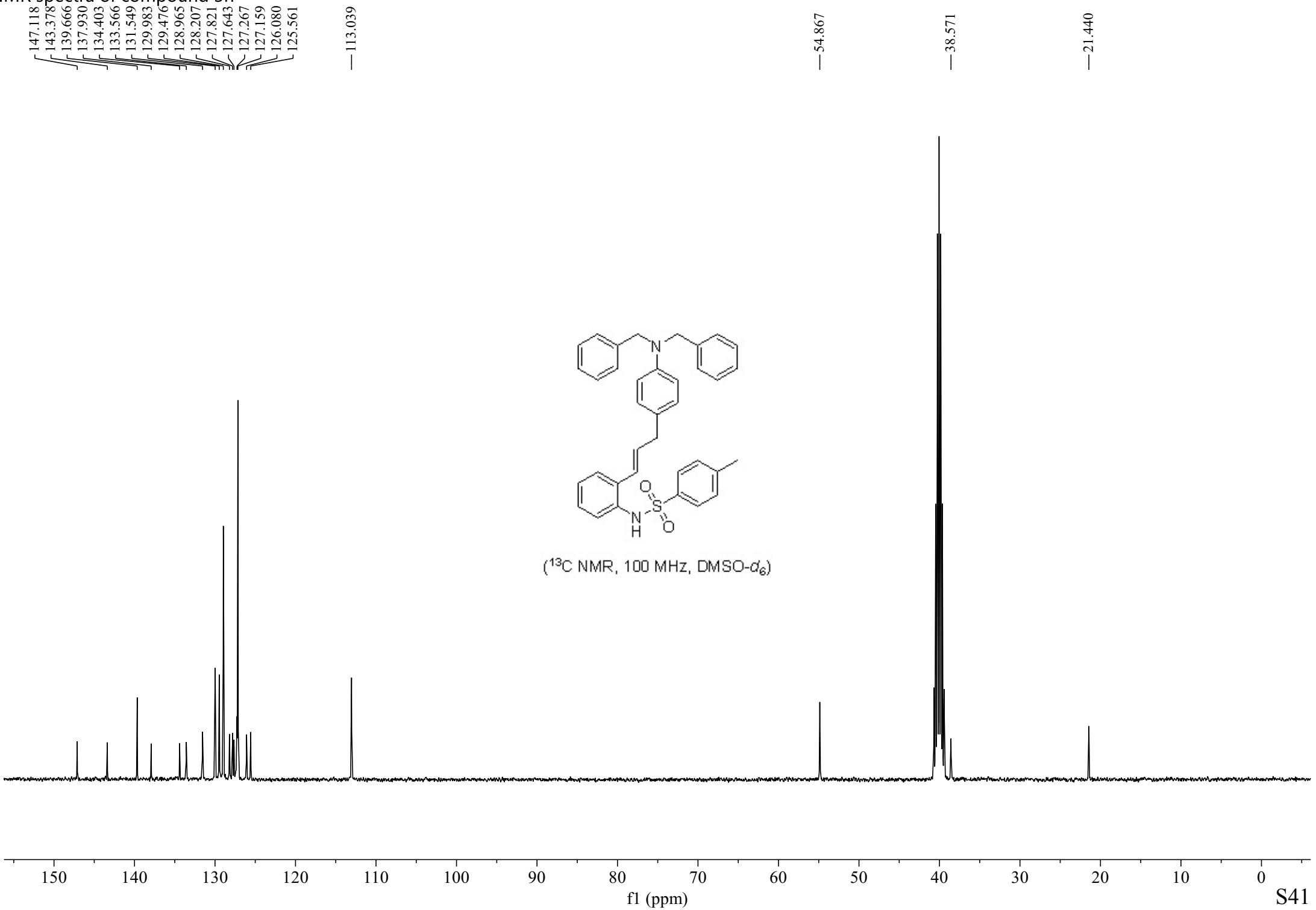
9.640 7.502 7.497 7.482 7.476 7.465 7.459 7.451 7.442 7.436 7.334 7.329 7.314 7.296 7.263 7.242 7.219 7.201 7.126 7.119 7.111 7.102 7.096 7.017 7.009 7.002 6.994 6.985 6.979 6.889 6.868 6.623 6.618 6.601 6.470 6.431 6.126 6.108 6.089 6.069 6.052 4.665 3.182 3.164 2.251



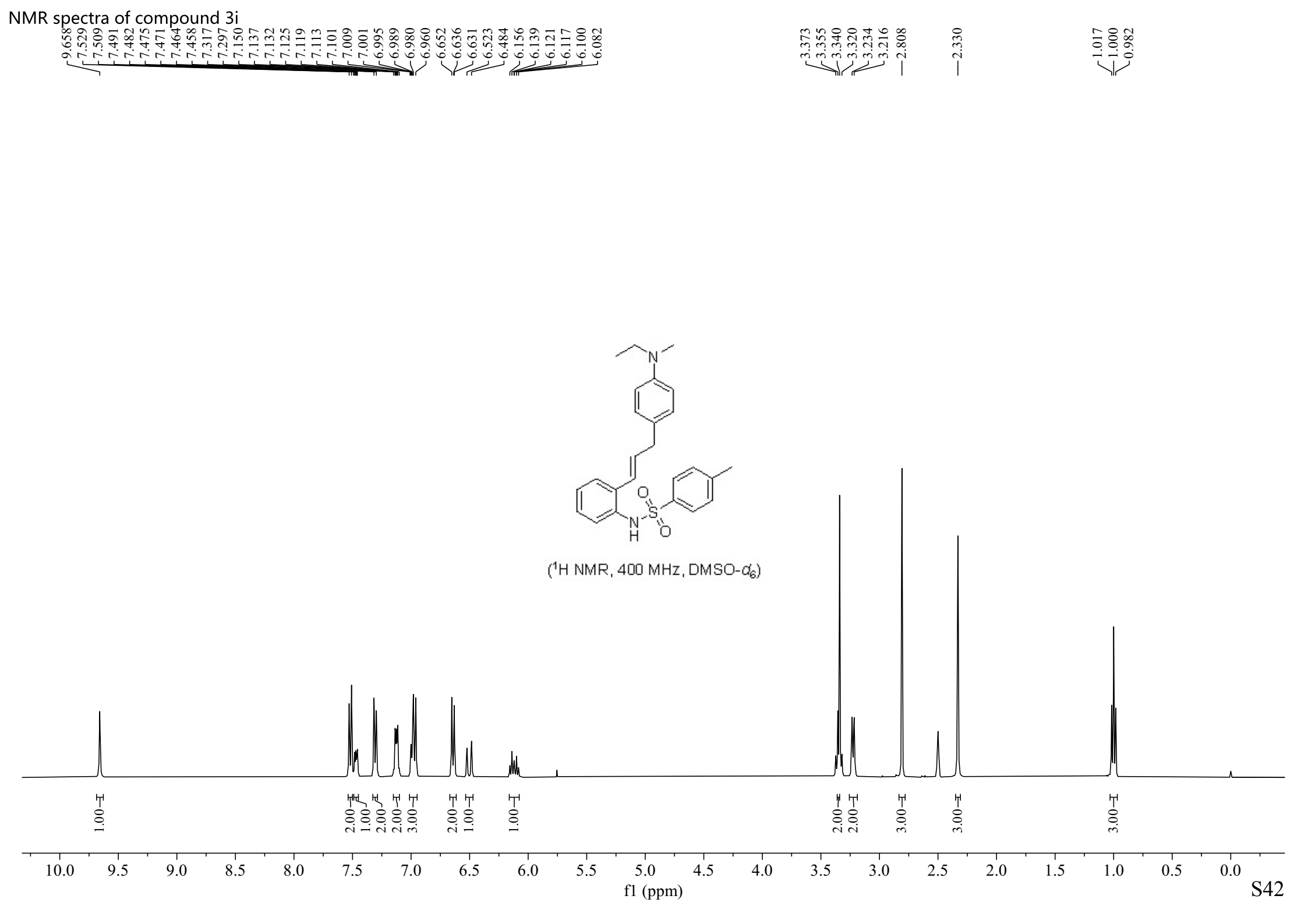
(¹H NMR, 400 MHz, DMSO-d_6)



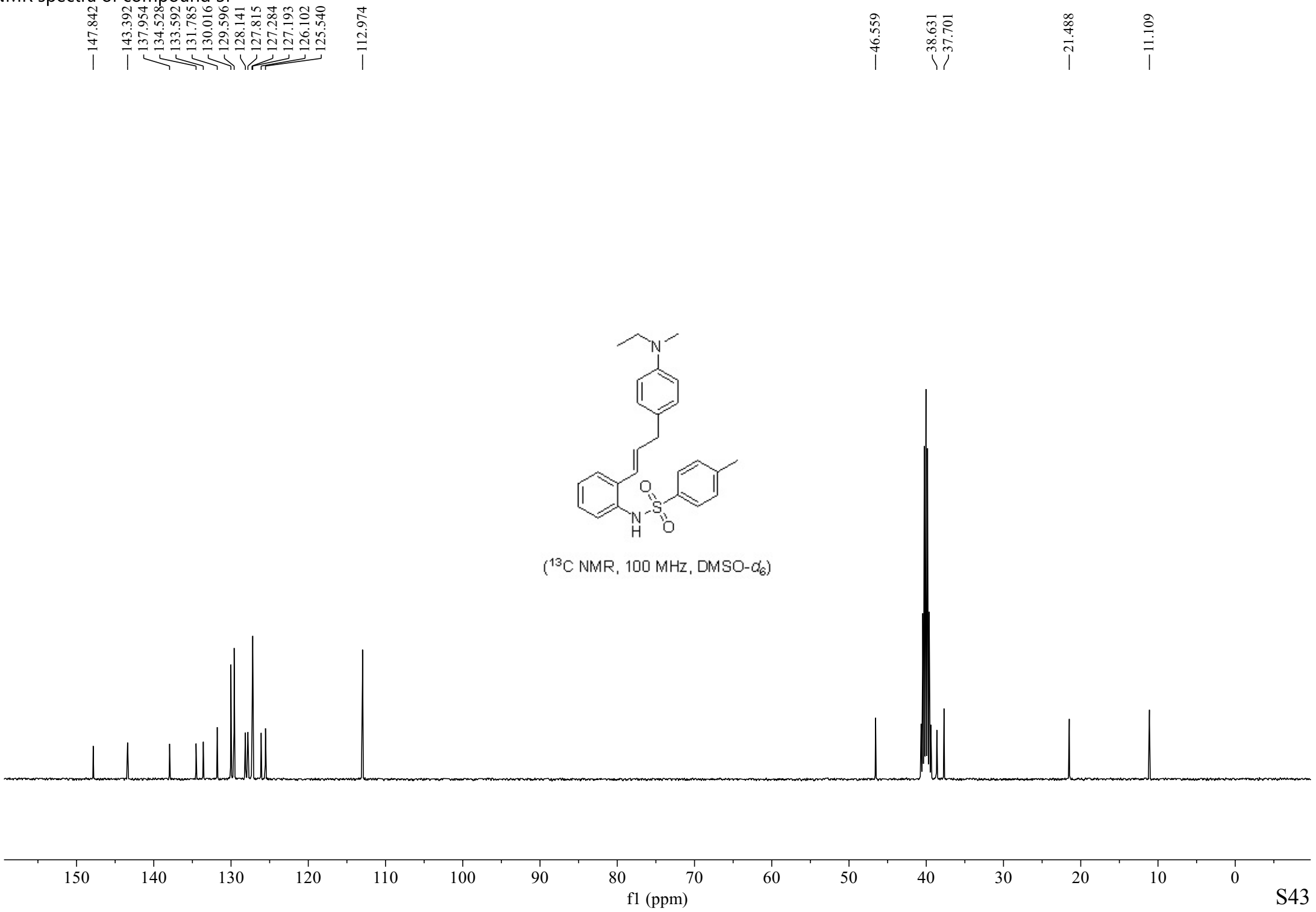
NMR spectra of compound 3h



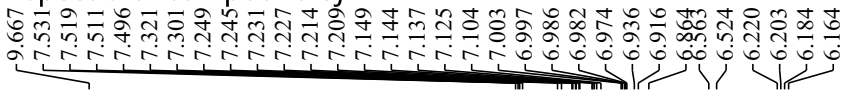
NMR spectra of compound 3i

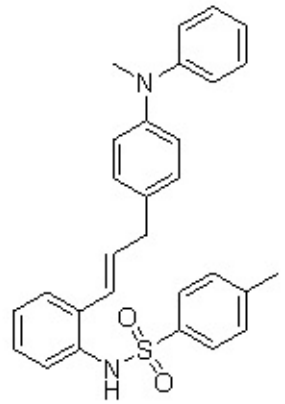


NMR spectra of compound 3i

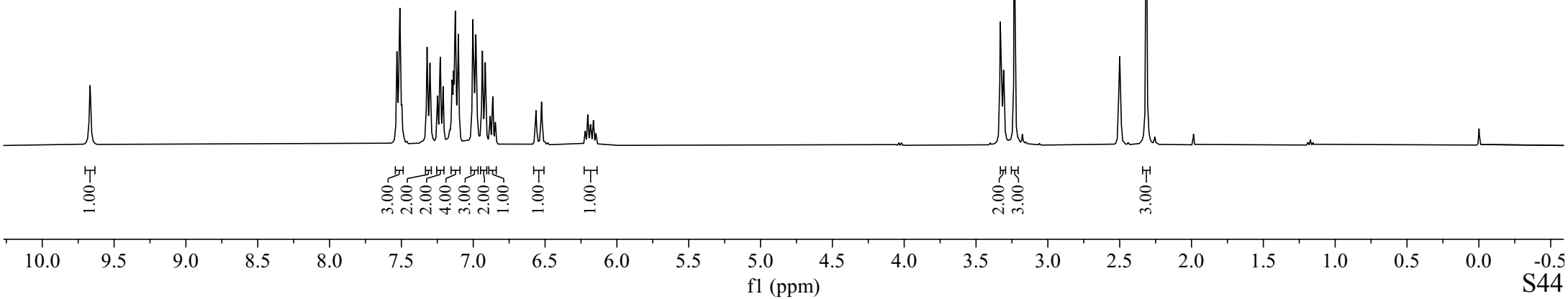


NMR spectra of compound 3j

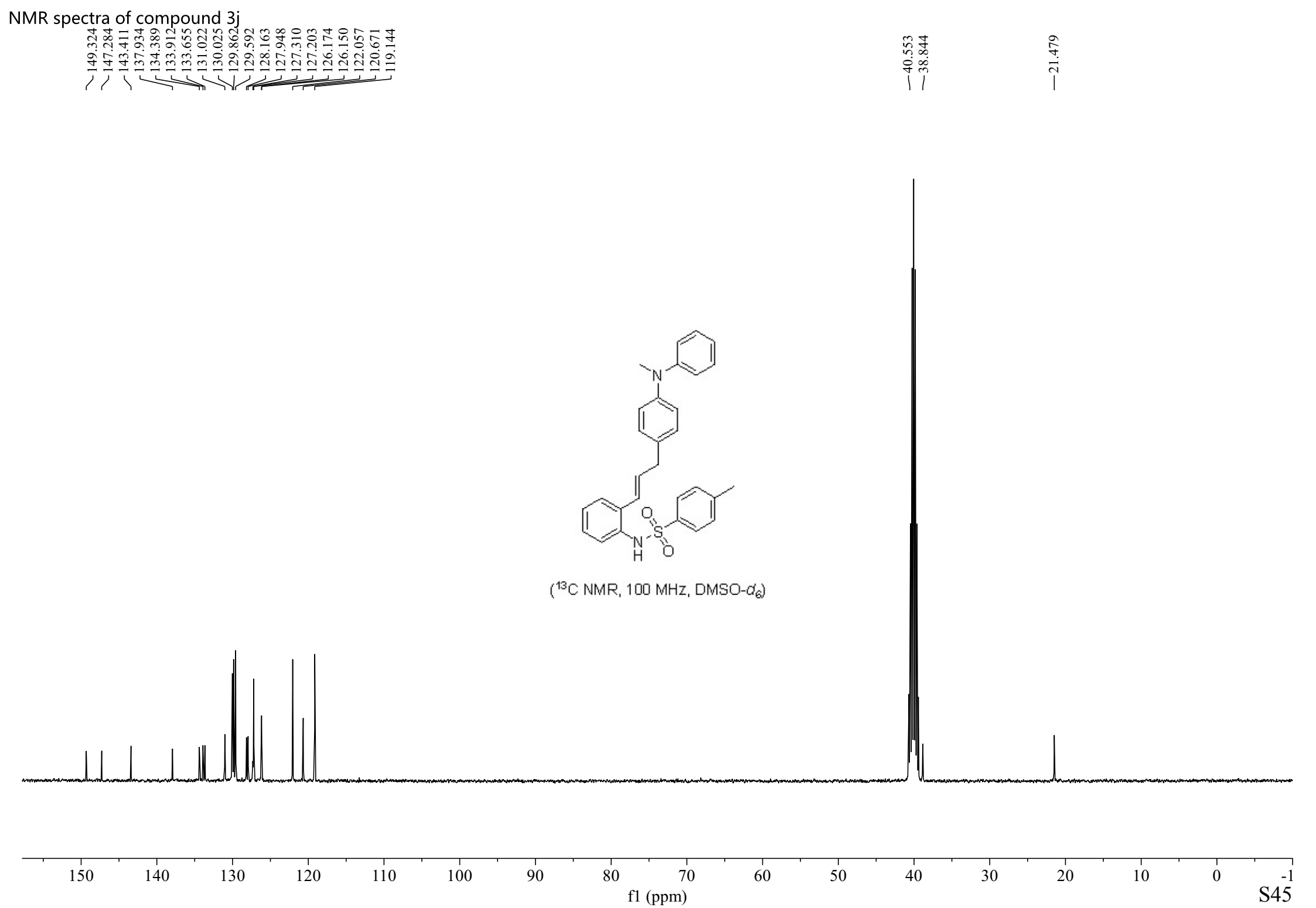




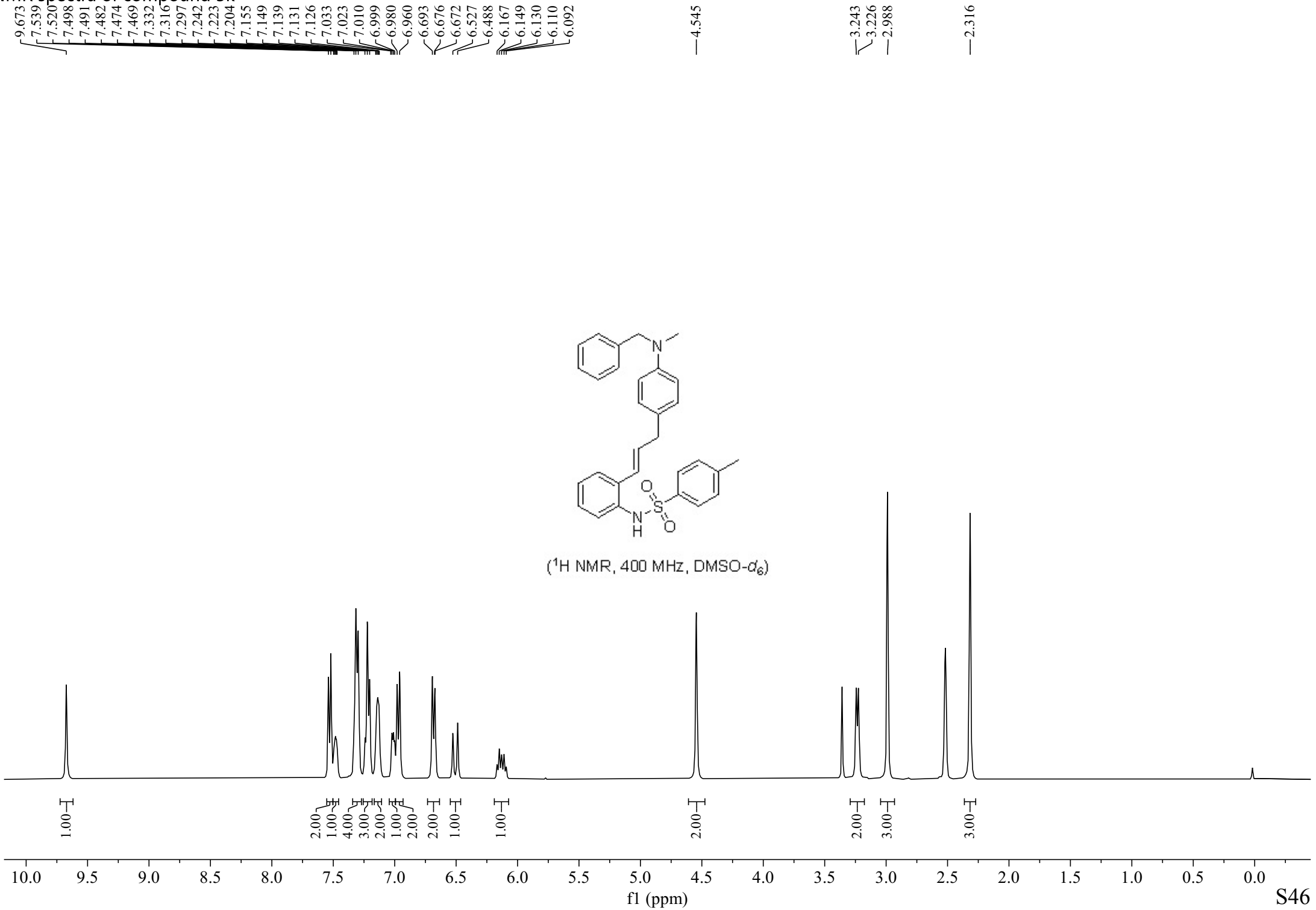
(¹H NMR, 400 MHz, DMSO-d_6)



NMR spectra of compound 3j

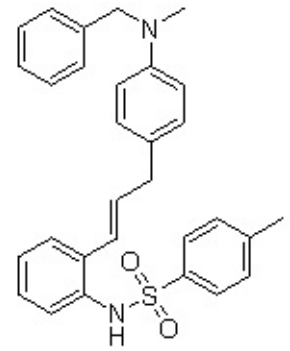


NMR spectra of compound 3k



NMR spectra of compound 3k

148.106
143.393
139.695
137.947
134.489
133.590
131.694
130.008
129.543
128.899
128.168
127.824
127.483
127.299
127.181
127.141
126.103
125.573
112.792
56.047
39.198
38.616
21.479

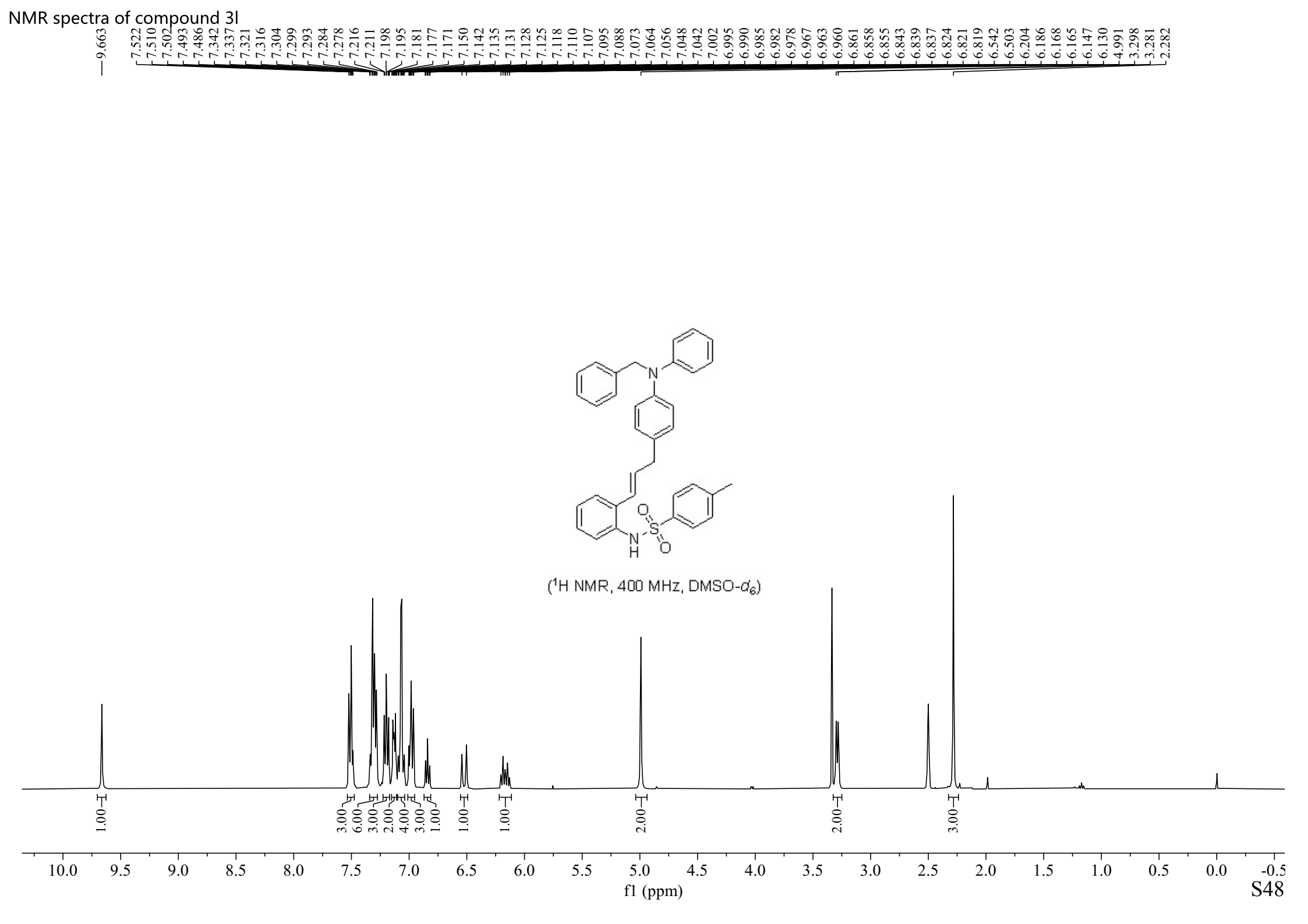


(^{13}C NMR, 100 MHz, DMSO-d_6)

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

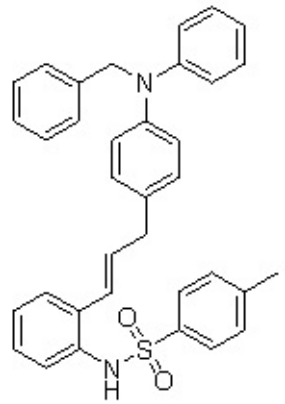
NMR spectra of compound 3l



NMR spectra of compound 3l

148.309
146.092
143.403
139.719
137.927
134.336
133.817
133.644
130.919
130.012
129.903
129.674
128.955
128.187
127.944
127.298
127.188
127.008
126.187
126.142
122.075
120.793
119.443

55.820
38.806
21.455



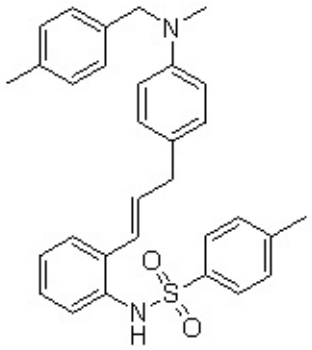
(^{13}C NMR, 100 MHz, DMSO-d_6)

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

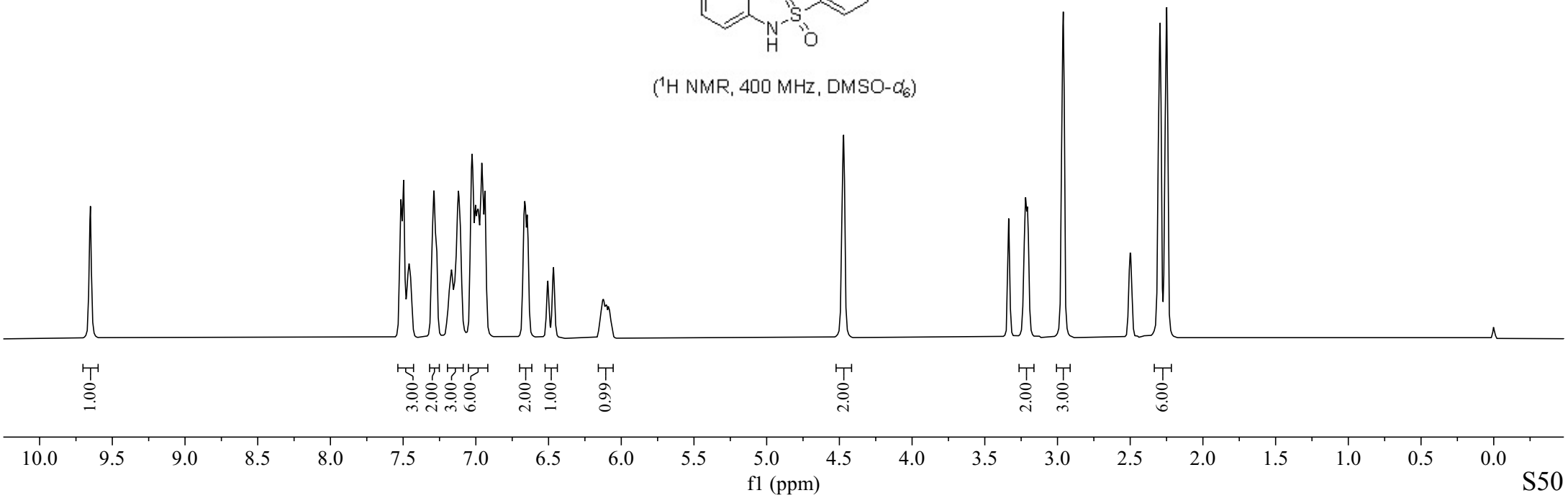
f1 (ppm)

NMR spectra of compound 3m

9.661 9.650 7.528 7.515 7.497 7.476 7.469 7.462 7.453 7.443 7.308 7.303 7.289 7.271 7.195 7.183 7.167 7.146 7.135 7.129 7.120 7.112 7.104 7.097 7.026 7.002 6.993 6.985 6.979 6.968 6.958 6.937 6.678 6.669 6.664 6.659 6.647 6.640 6.505 6.466 6.138 6.128 6.120 6.108 6.099 6.090 6.082 4.482 4.470 3.222 3.205 2.975 2.967 2.958 2.303 2.293 2.256 2.247



(¹H NMR, 400 MHz, DMSO-d_6)



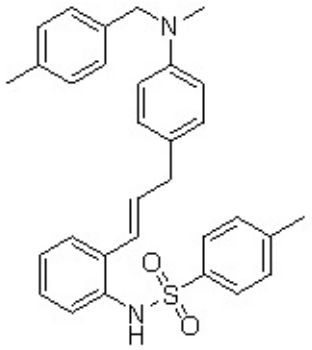
NMR spectra of compound 3m

148.188
143.380
139.744
137.977
134.495
133.588
131.702
130.000
129.530
128.805
128.165
127.860
127.825
127.440
127.276
127.175
126.105
125.575
124.350
112.756

56.141

39.212
38.608

21.610
21.466

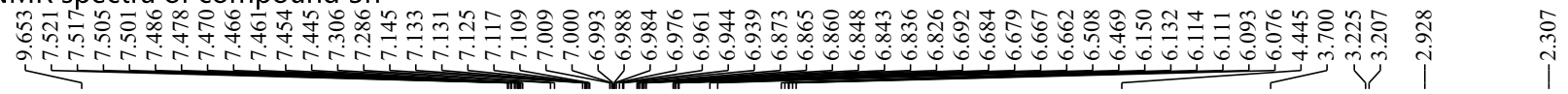


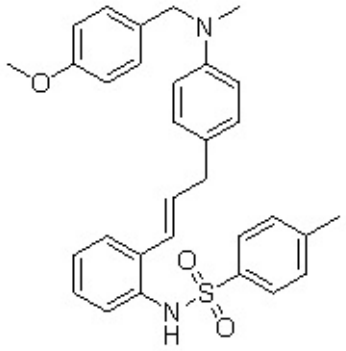
(^{13}C NMR, 100 MHz, DMSO-d_6)

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

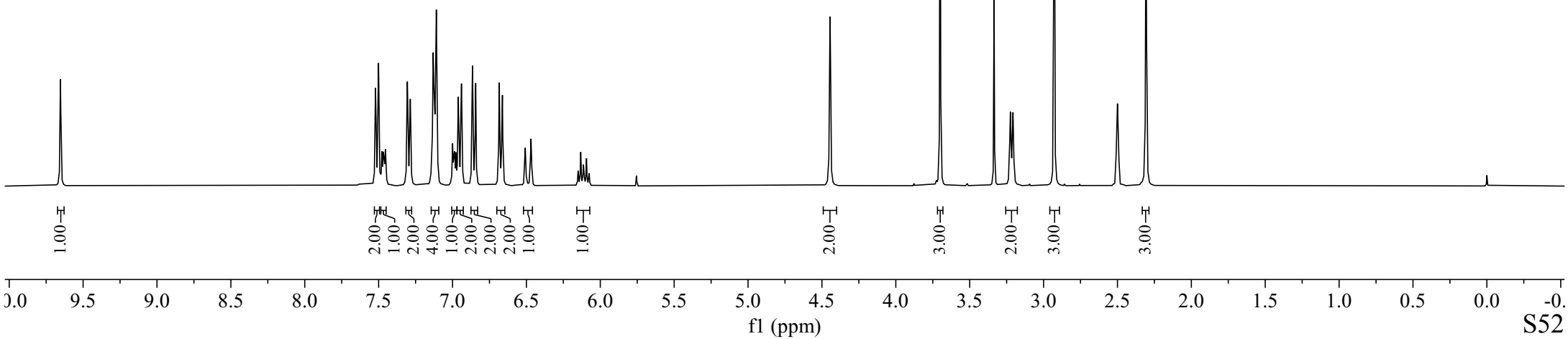
f1 (ppm)

NMR spectra of compound 3n

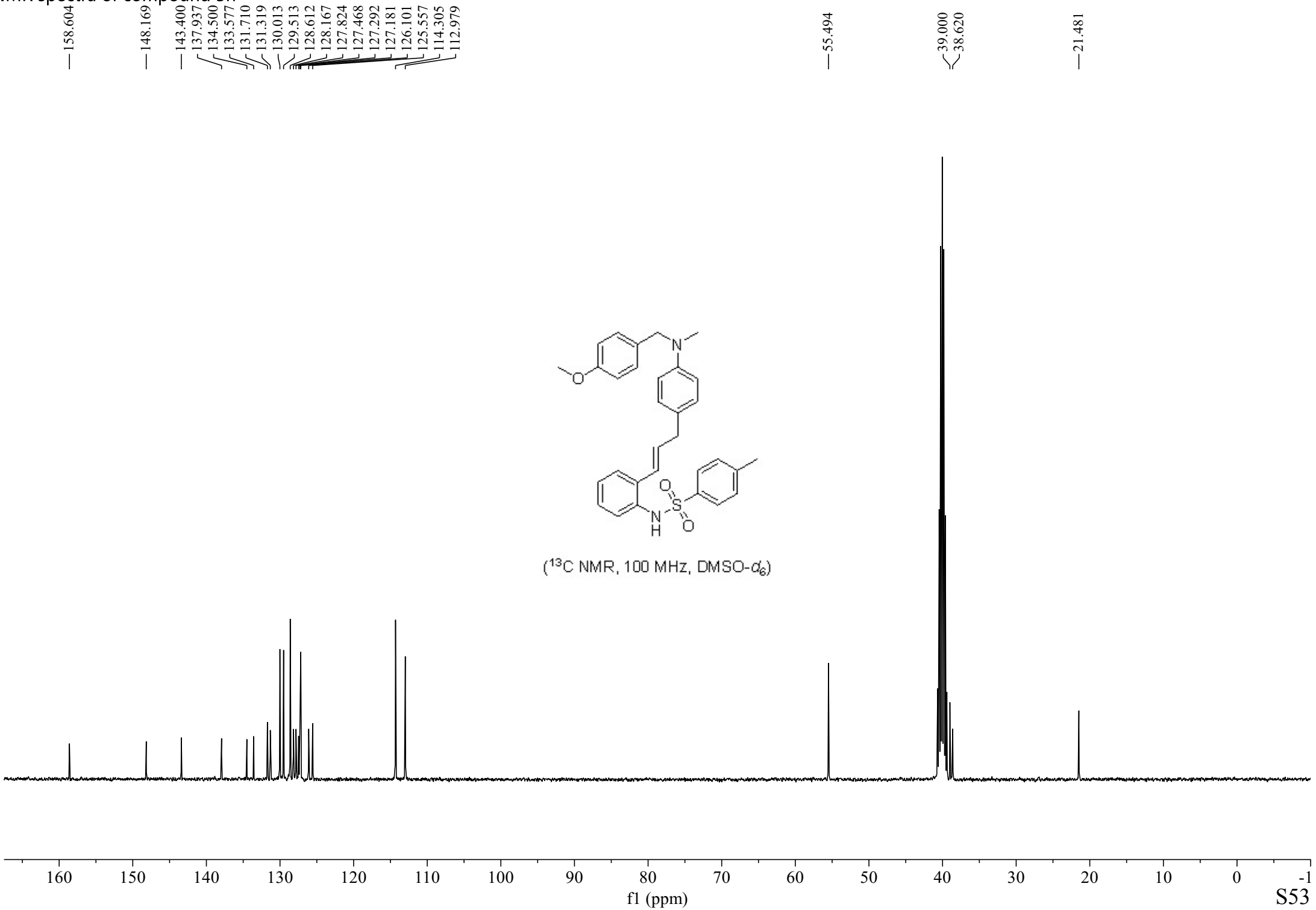




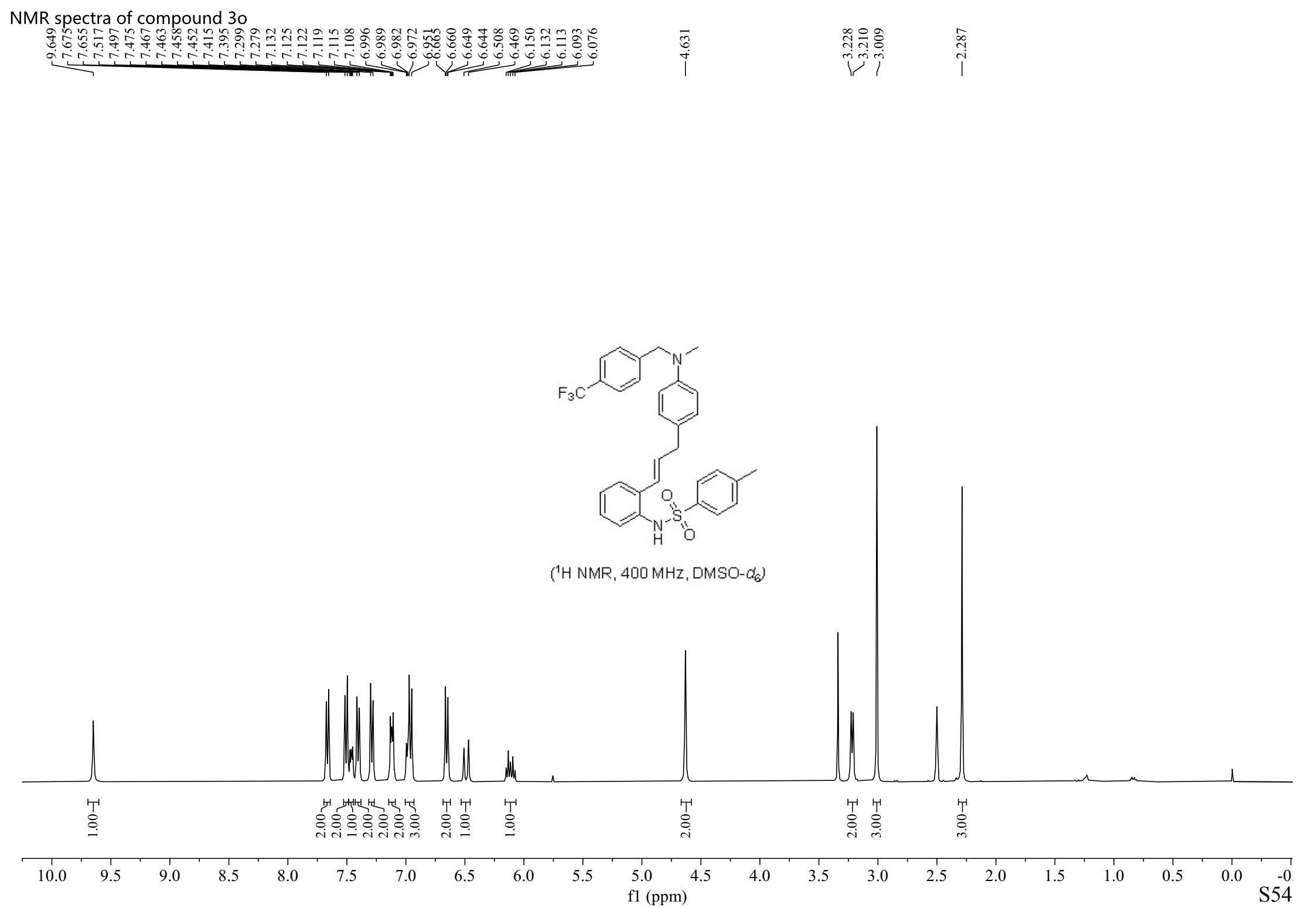
(¹H NMR, 400 MHz, DMSO-d_6)



NMR spectra of compound 3n



NMR spectra of compound 3o



NMR spectra of compound 3o

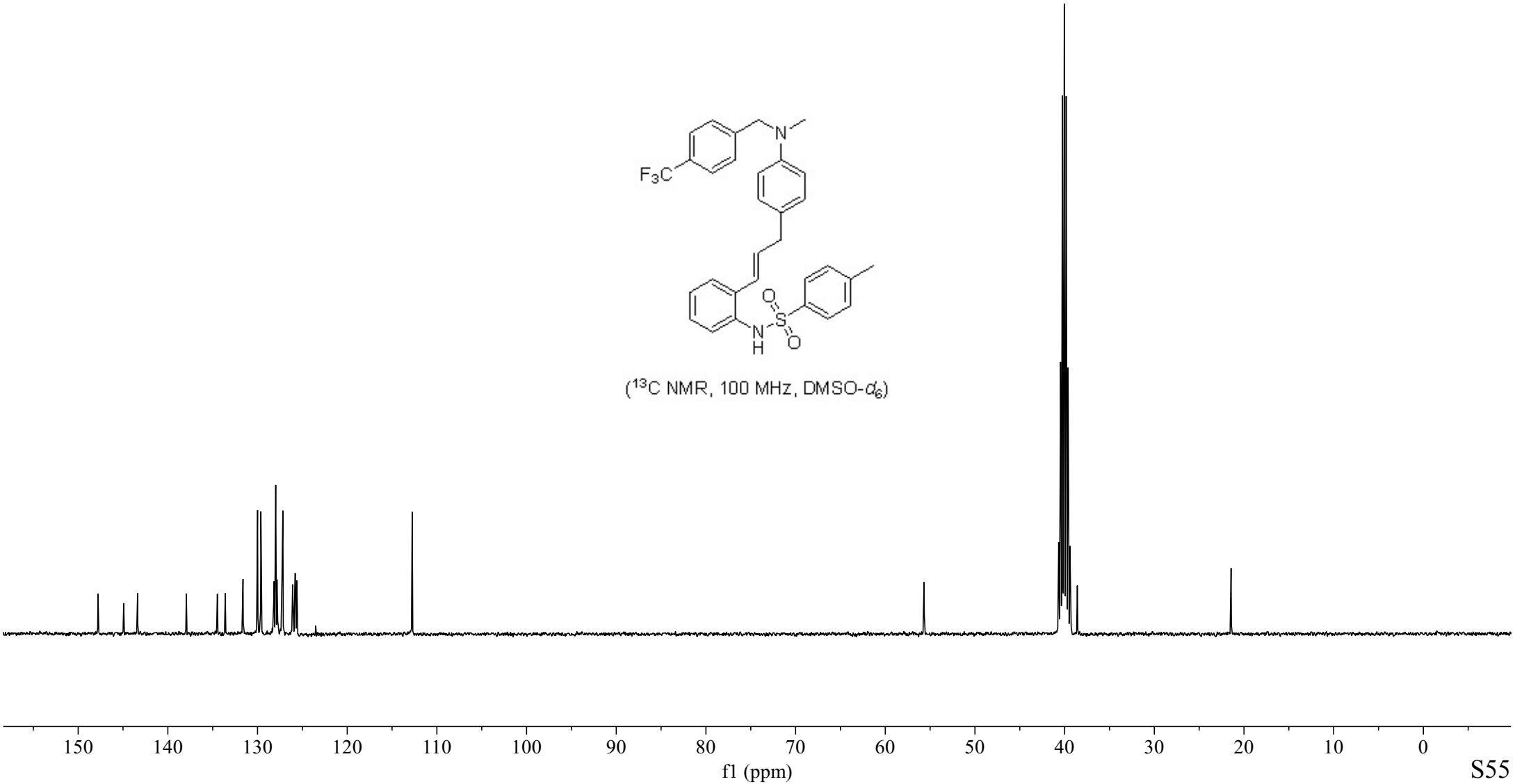
147.792
144.924
143.374
137.938
134.480
133.594
131.621
129.996
129.625
128.159
127.972
127.829
127.779
127.277
127.178
126.088
125.818
125.780
125.619
112.752

55.675

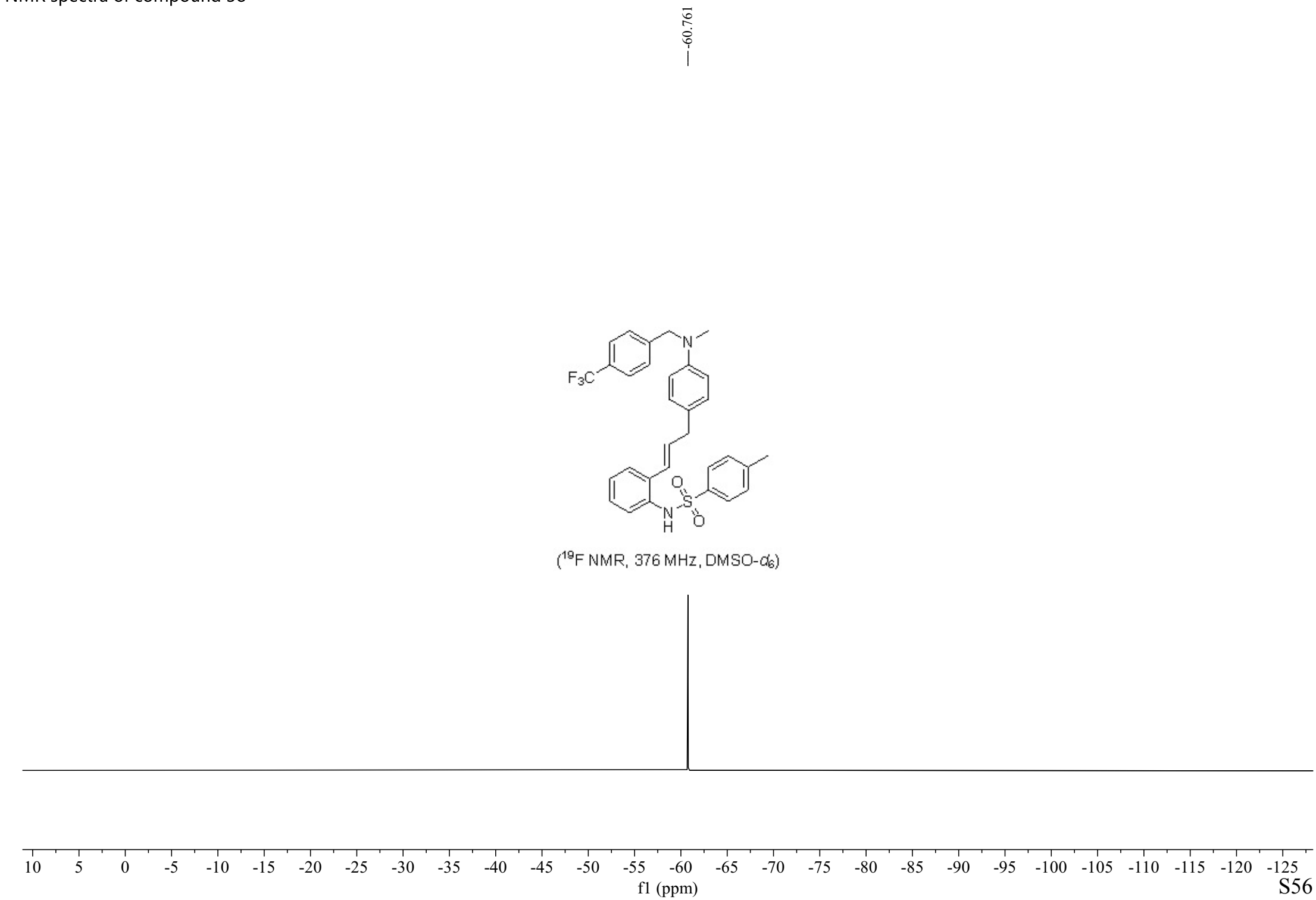
39.312
38.587

21.440

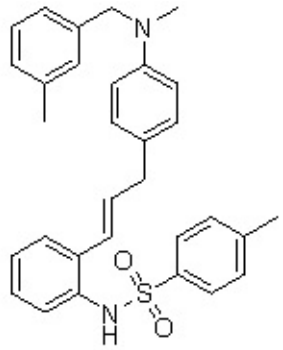
(^{13}C NMR, 100 MHz, DMSO-d_6)



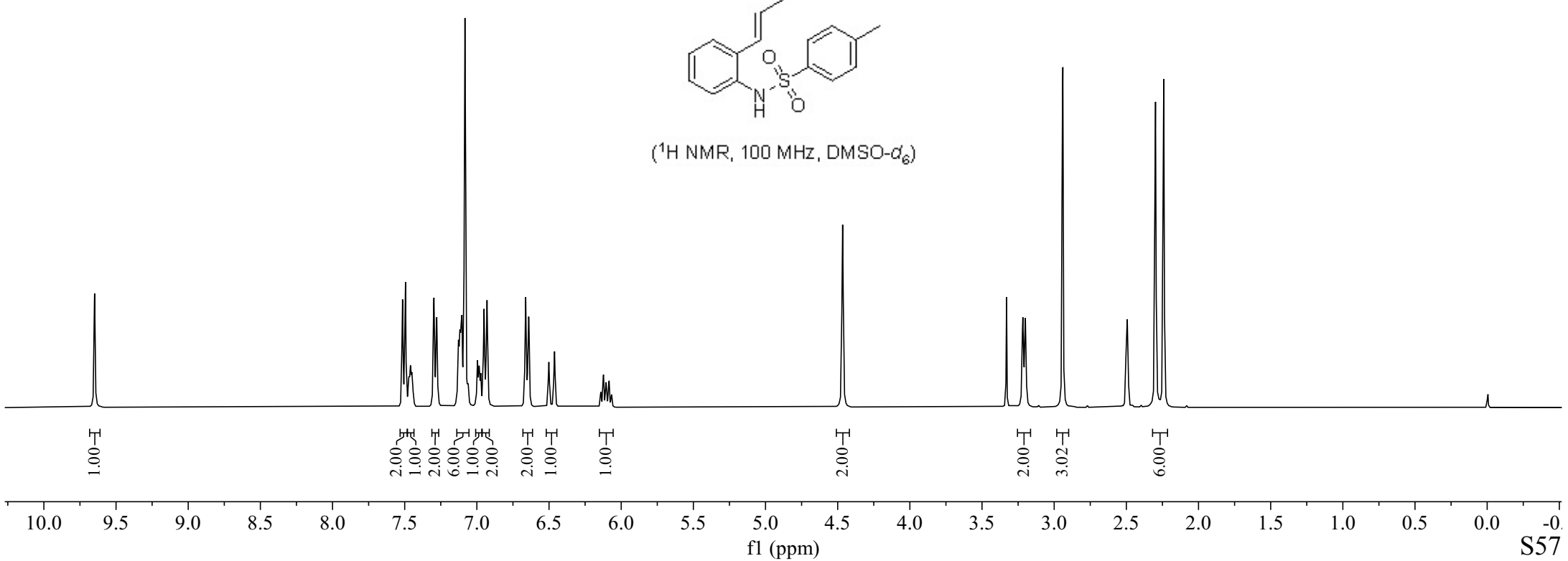
NMR spectra of compound 3o



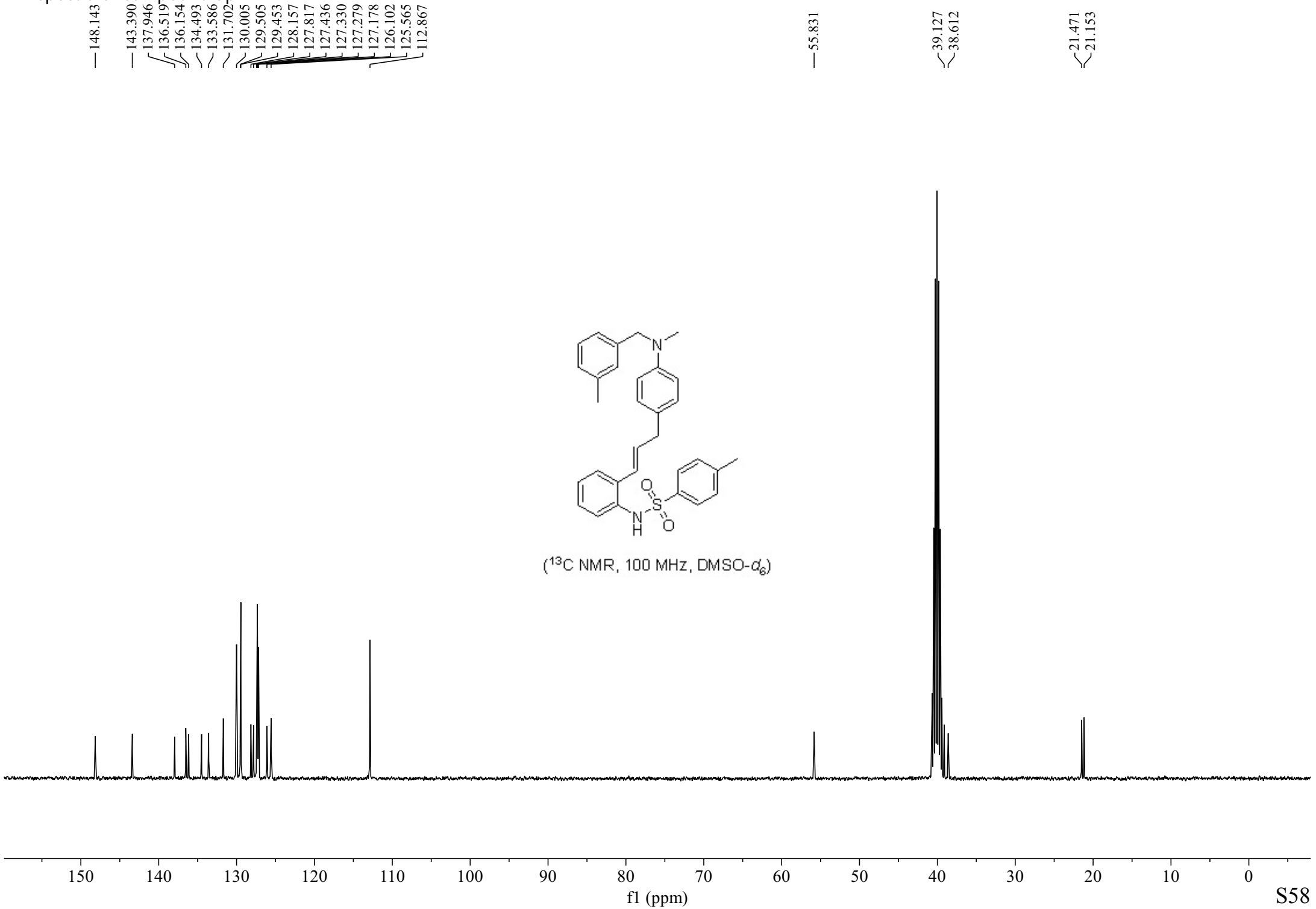
NMR spectra of compound 3p



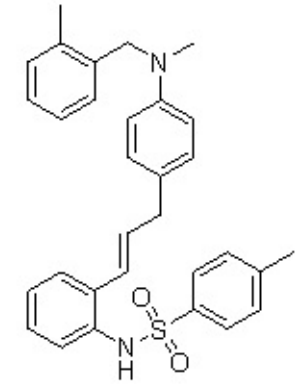
(^{1}H NMR, 100 MHz, DMSO-d_6)



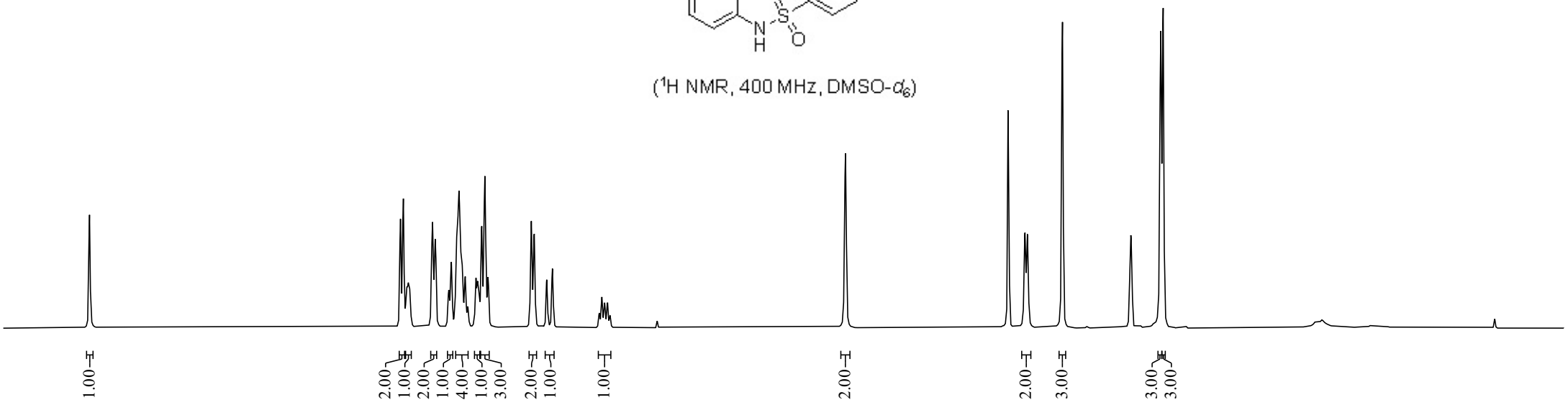
NMR spectra of compound 3p



NMR spectra of compound 3q

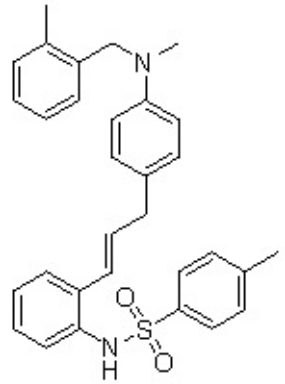


(¹H NMR, 400 MHz, DMSO-d_6)

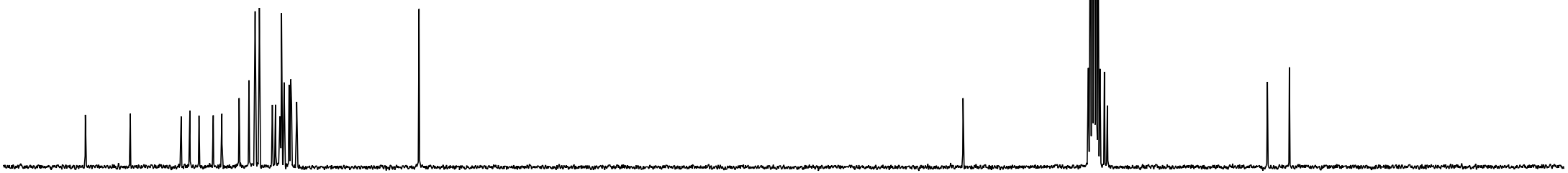


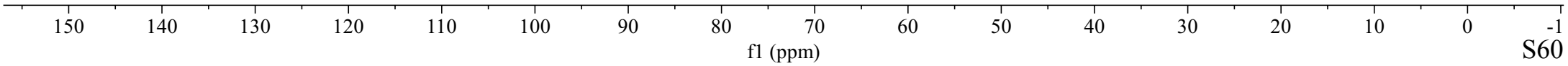
NMR spectra of compound 3q

148.213
143.391
137.937
137.003
136.027
134.496
133.575
131.723
130.667
130.008
129.557
128.162
127.824
127.334
127.290
127.180
126.896
126.368
126.183
126.101
125.555
112.435
54.097
38.943
38.623
21.462
19.104

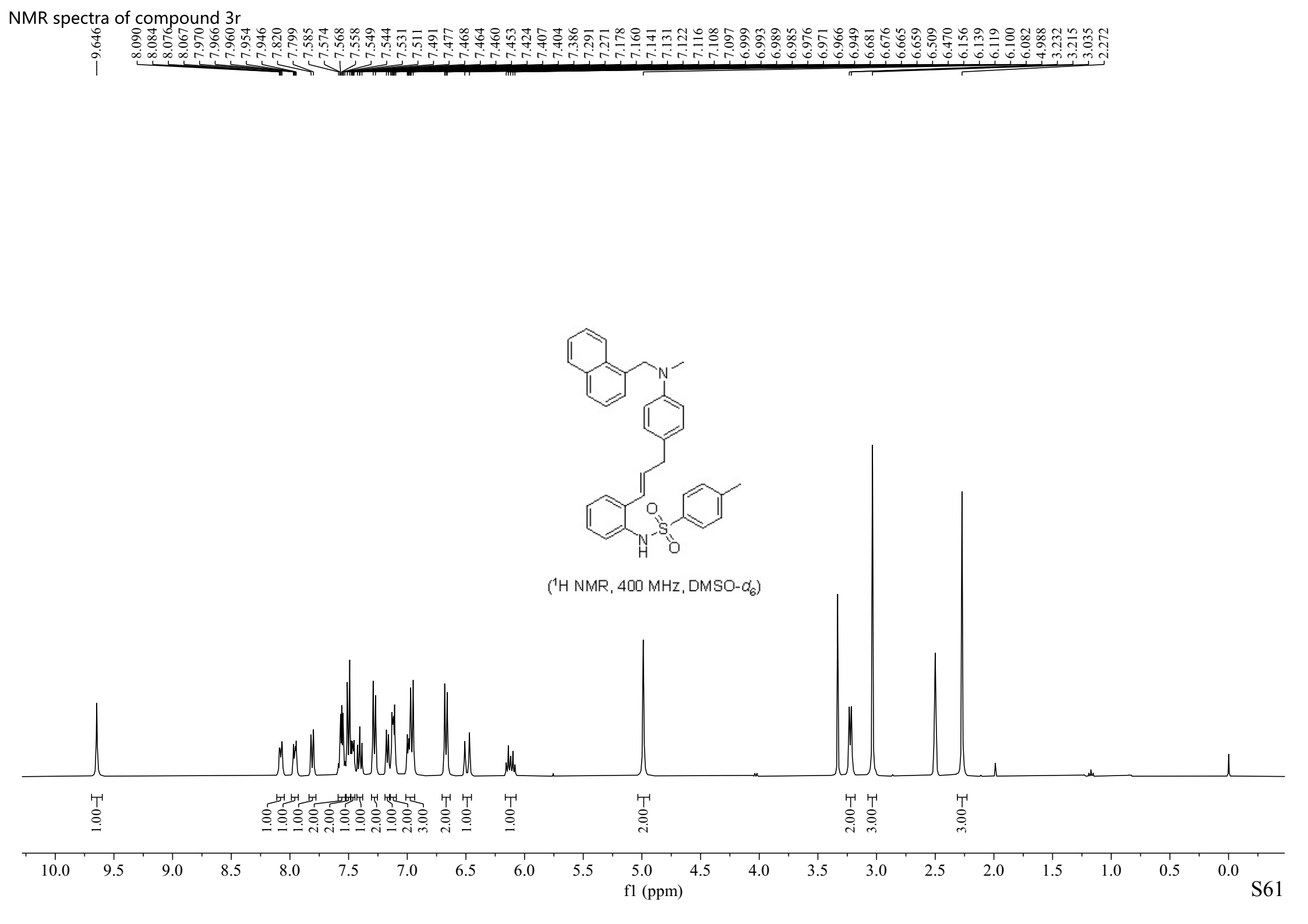


(^{13}C NMR, 100 MHz, DMSO-d_6)



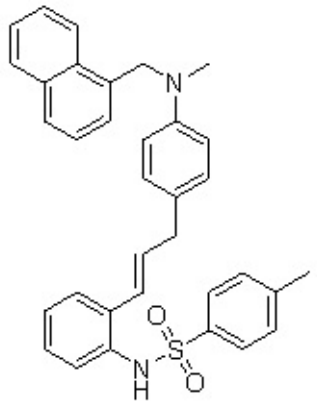


NMR spectra of compound 3r



NMR spectra of compound 3r

148.238
143.366
137.959
134.467
134.148
133.994
133.610
131.702
131.369
129.996
129.621
129.103
128.141
127.821
127.572
127.502
127.257
127.168
126.566
126.291
126.097
125.959
125.566
124.062
123.621
112.533
53.984
39.000
38.622
21.441

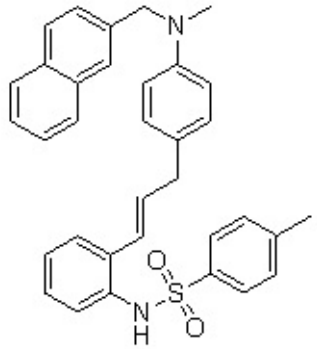


(^{13}C NMR, 100 MHz, DMSO-d_6)

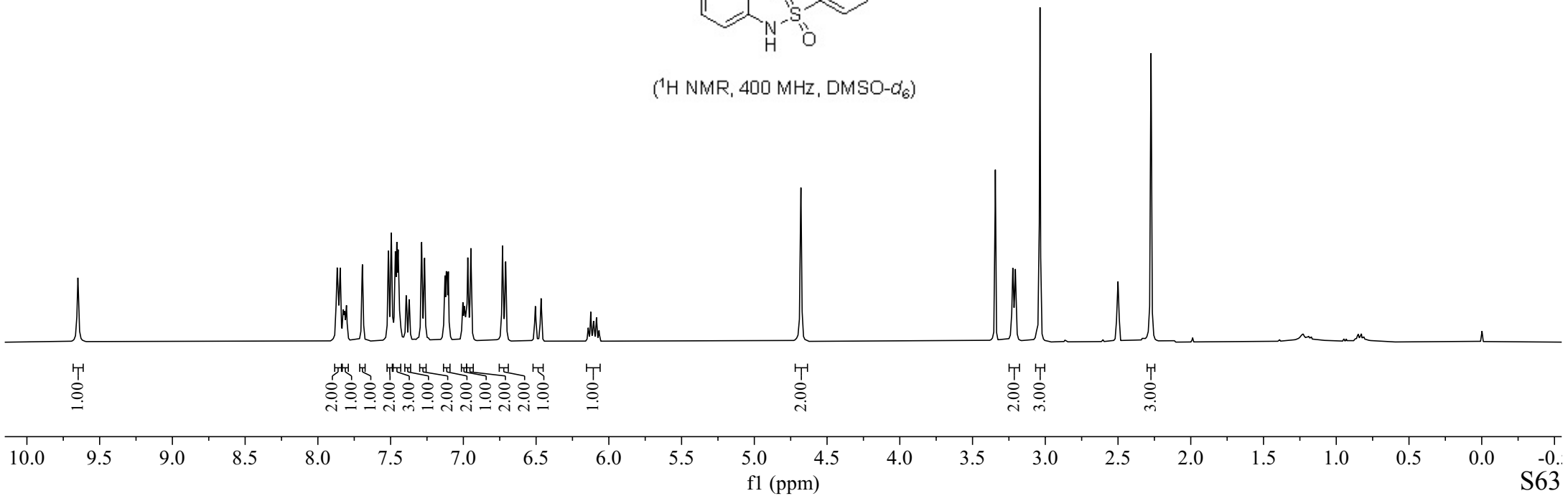
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

NMR spectra of compound 3s

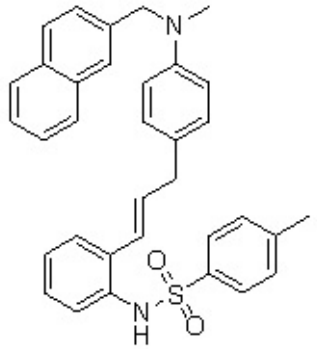


(^{1}H NMR, 400 MHz, DMSO-d_6)



NMR spectra of compound 3s

148.216
143.369
137.963
137.528
134.484
133.610
133.510
132.663
131.669
129.993
129.563
128.553
128.157
128.042
127.993
127.819
127.622
127.263
127.172
126.638
126.106
126.043
125.988
125.601
125.450
112.913
56.446
39.300
38.612
21.447

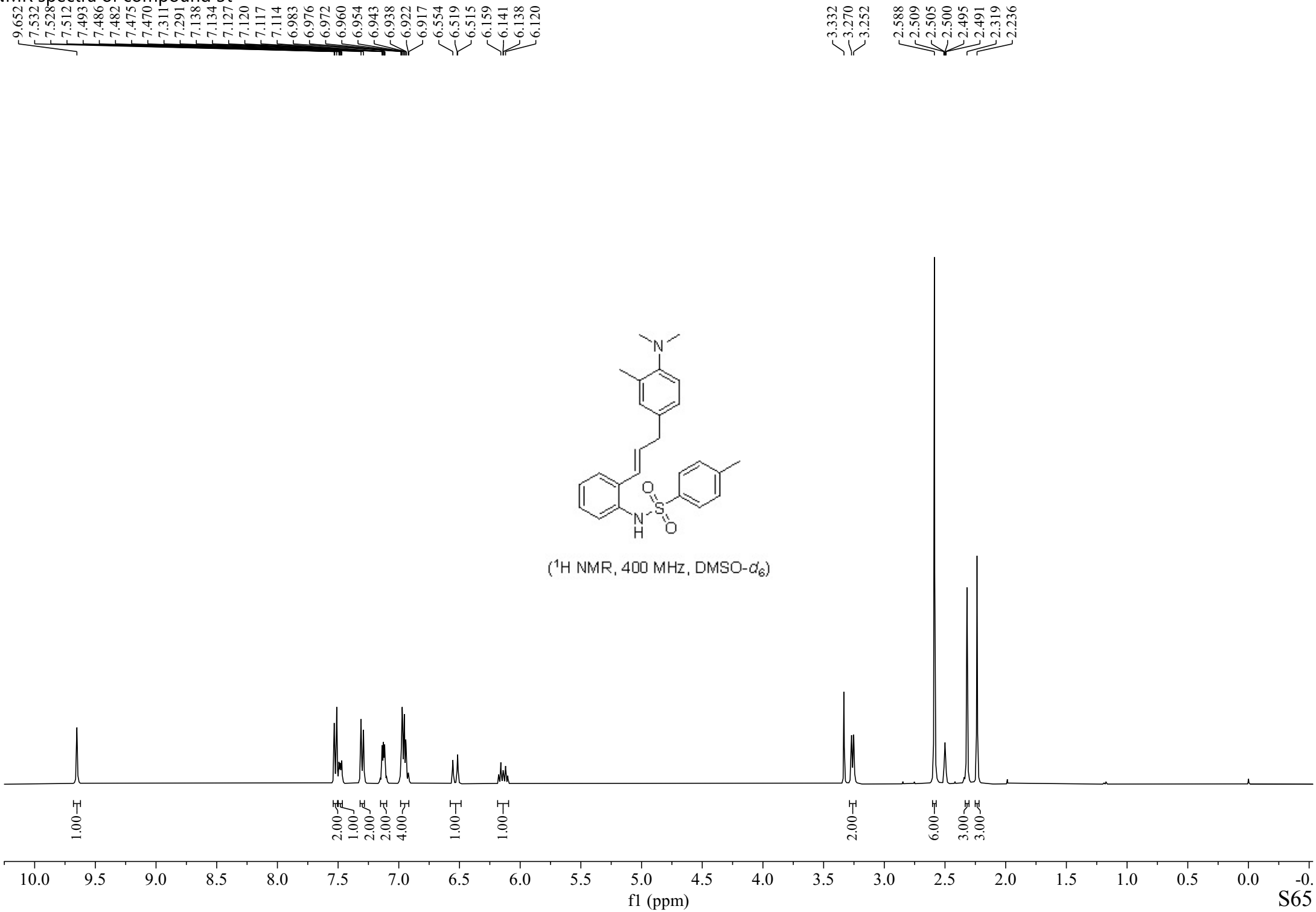


(^{13}C NMR, 100 MHz, DMSO-d_6)

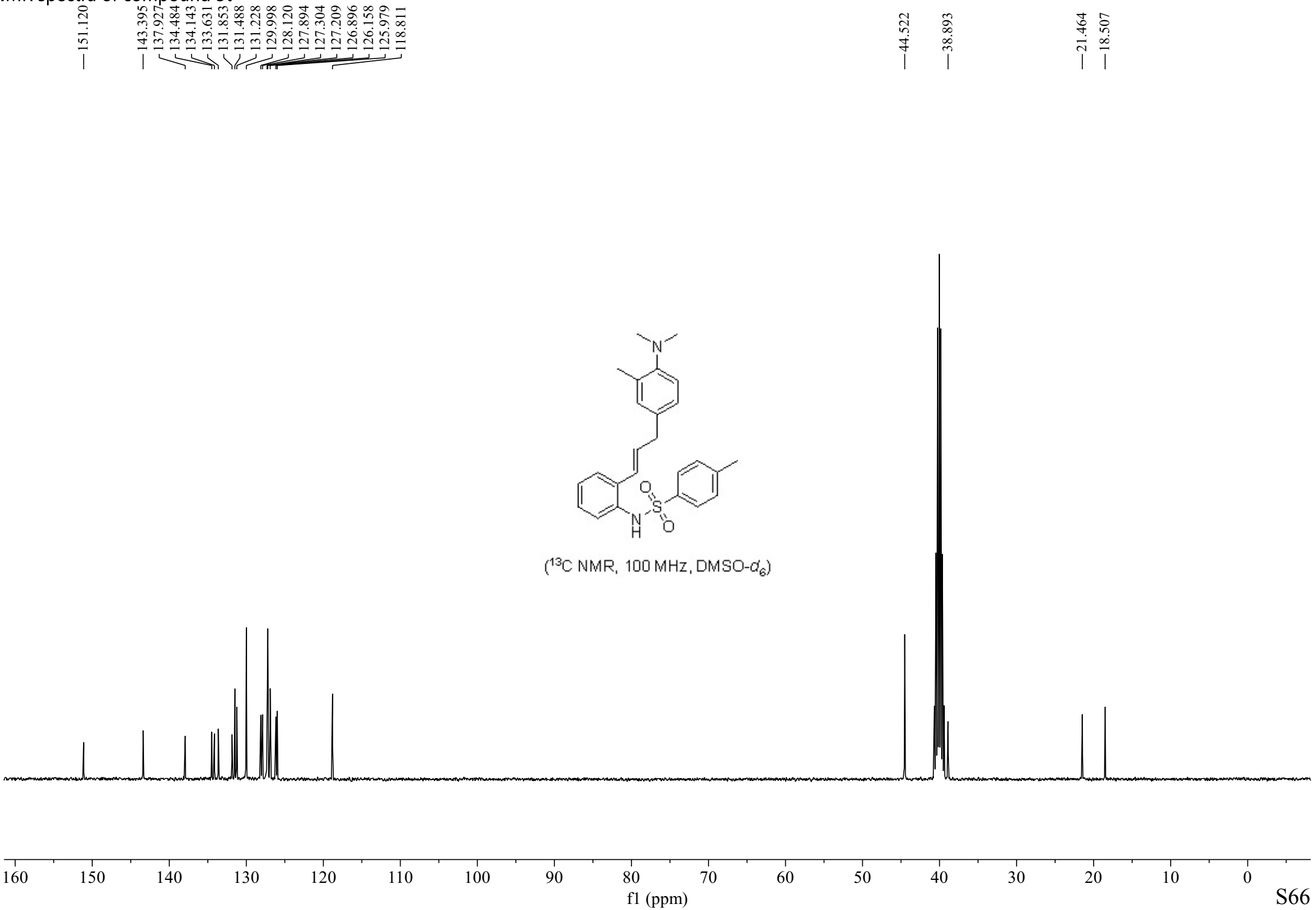
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

NMR spectra of compound 3t



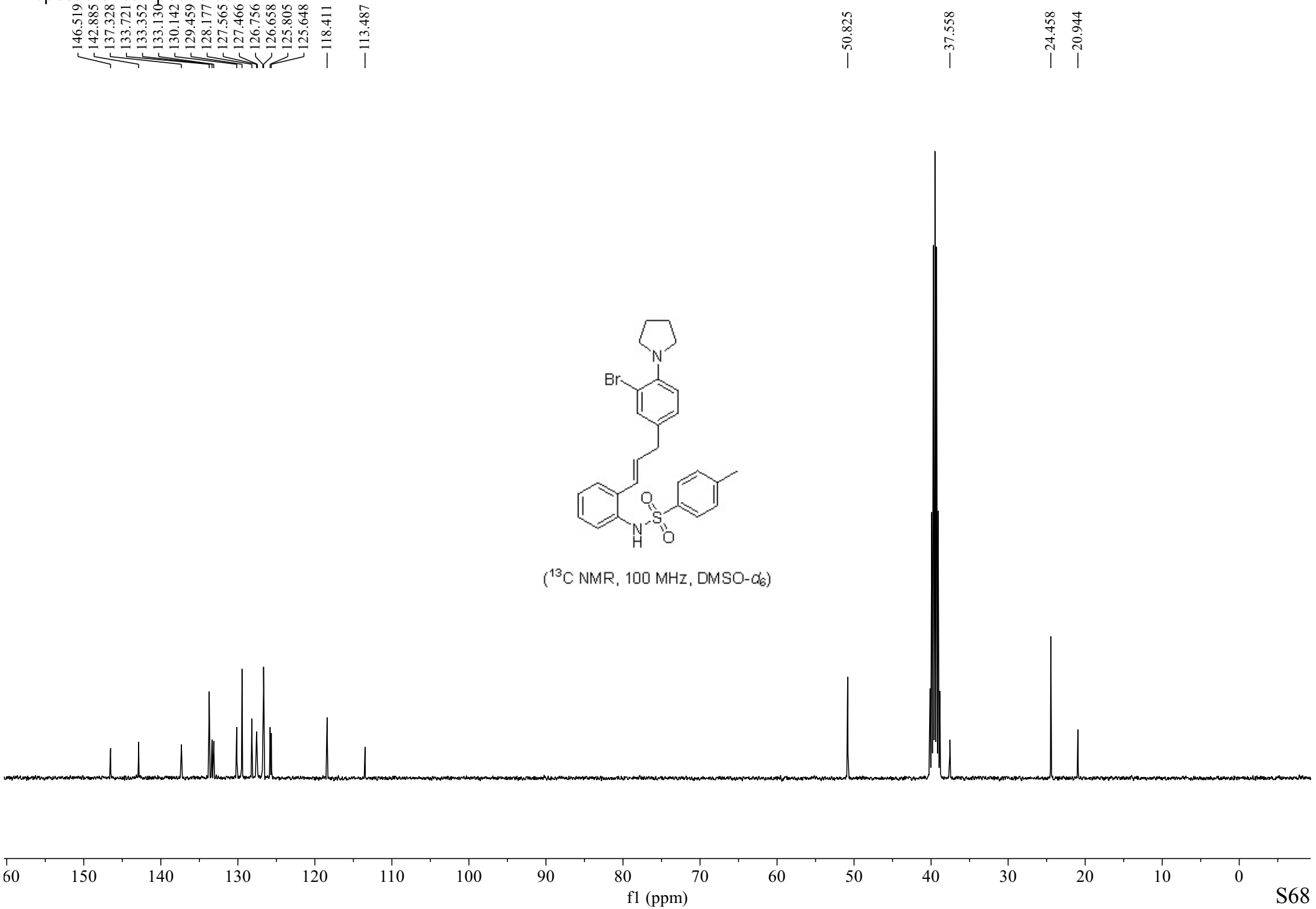
NMR spectra of compound 3t



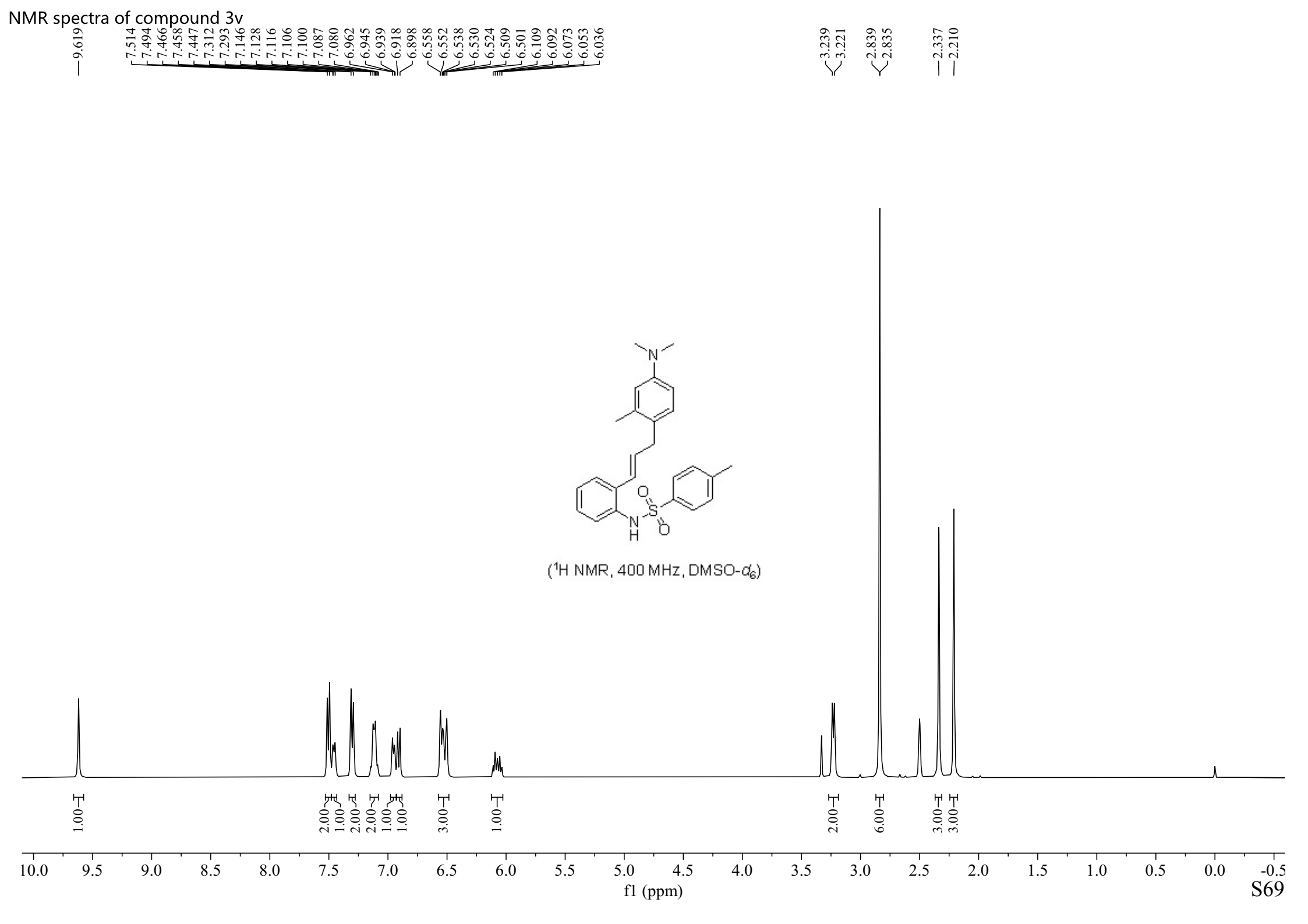
NMR spectra of compound 3u

(^{1}H NMR, 400 MHz, DMSO-d_6)

NMR spectra of compound 3u



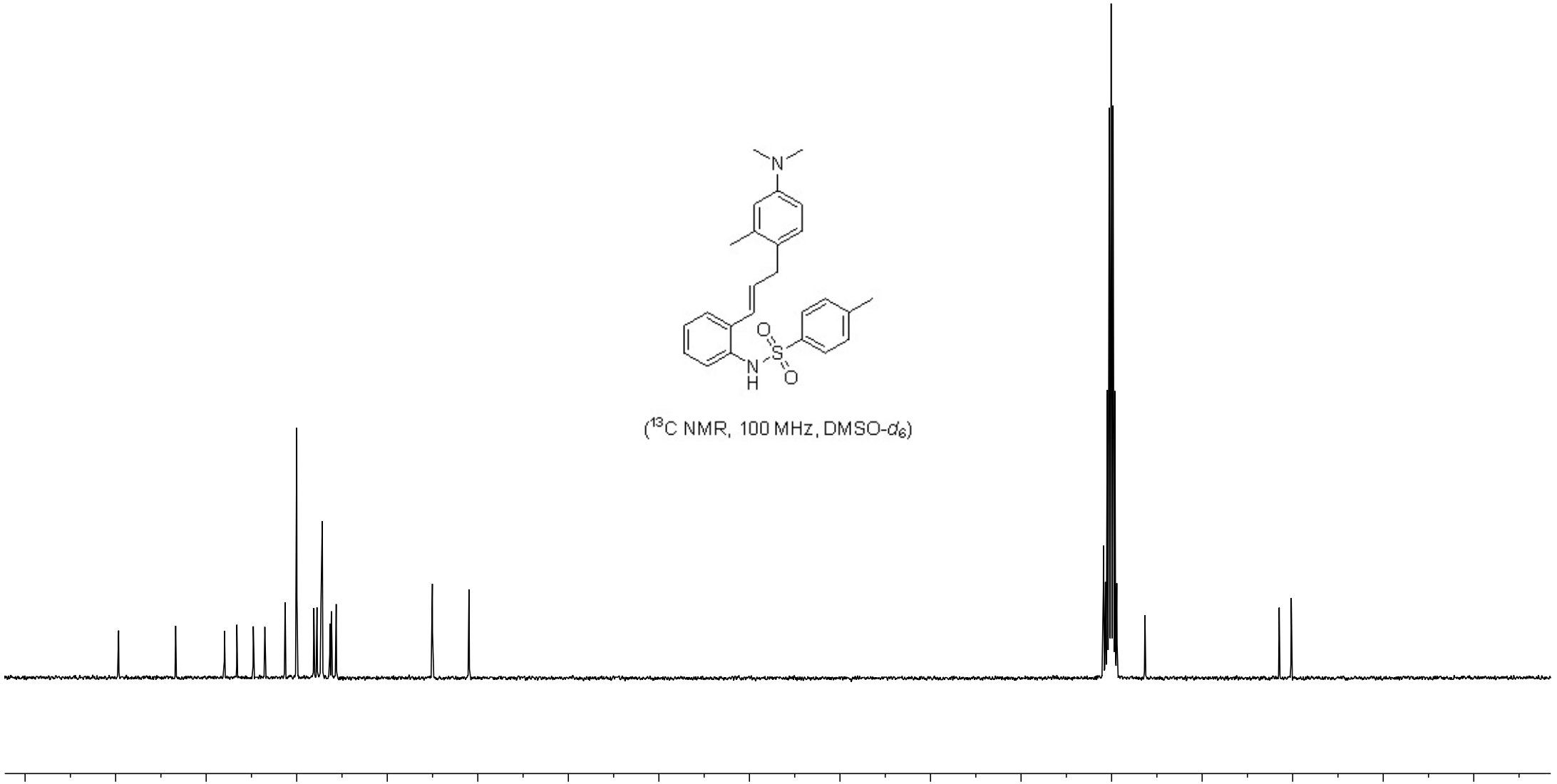
NMR spectra of compound 3v



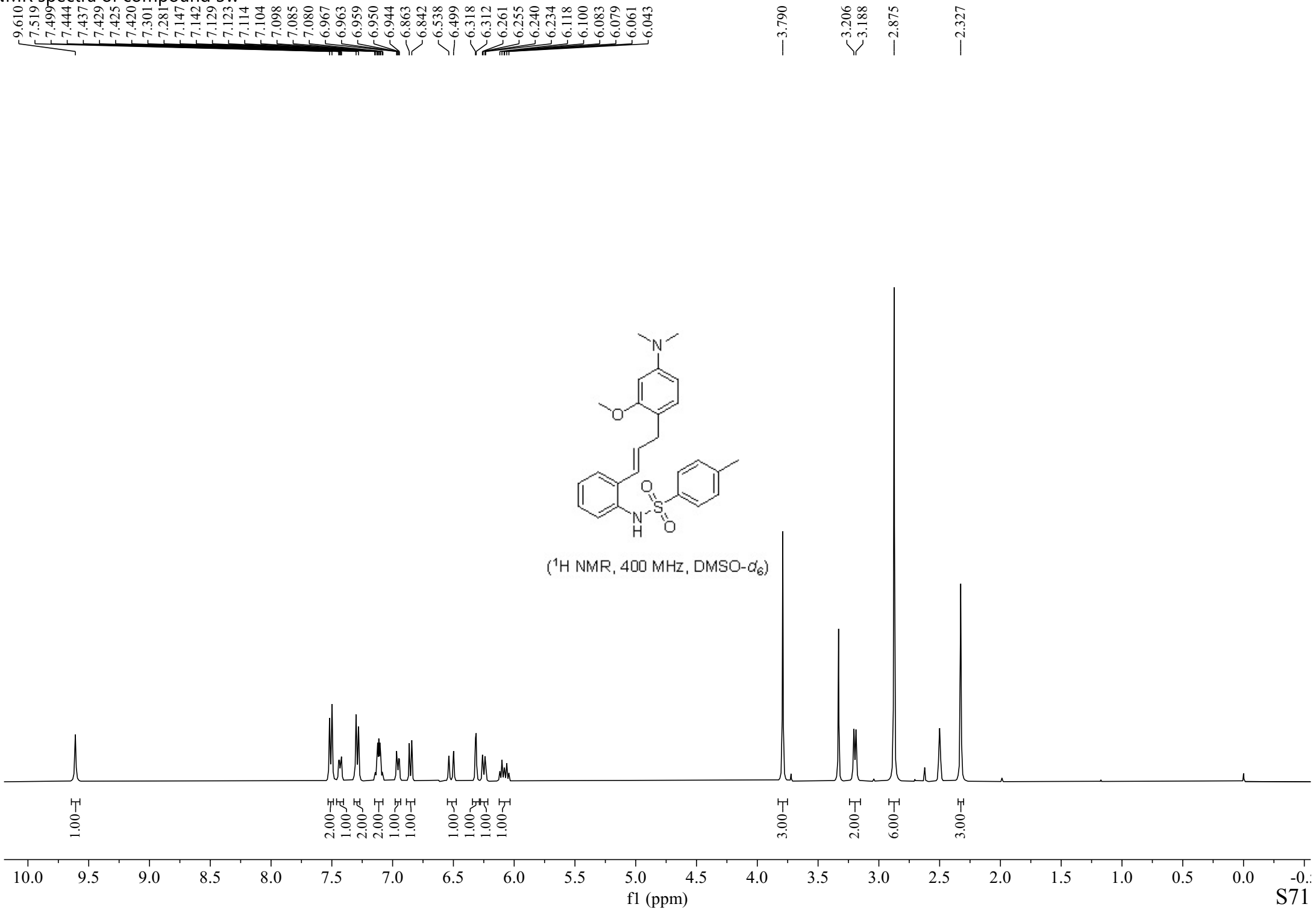
NMR spectra of compound 3v

149.675
143.370
137.976
136.614
134.798
133.521
131.277
130.002
128.104
127.762
127.325
127.176
126.337
126.171
125.641
115.020
110.970
40.897
36.315
21.491
20.162

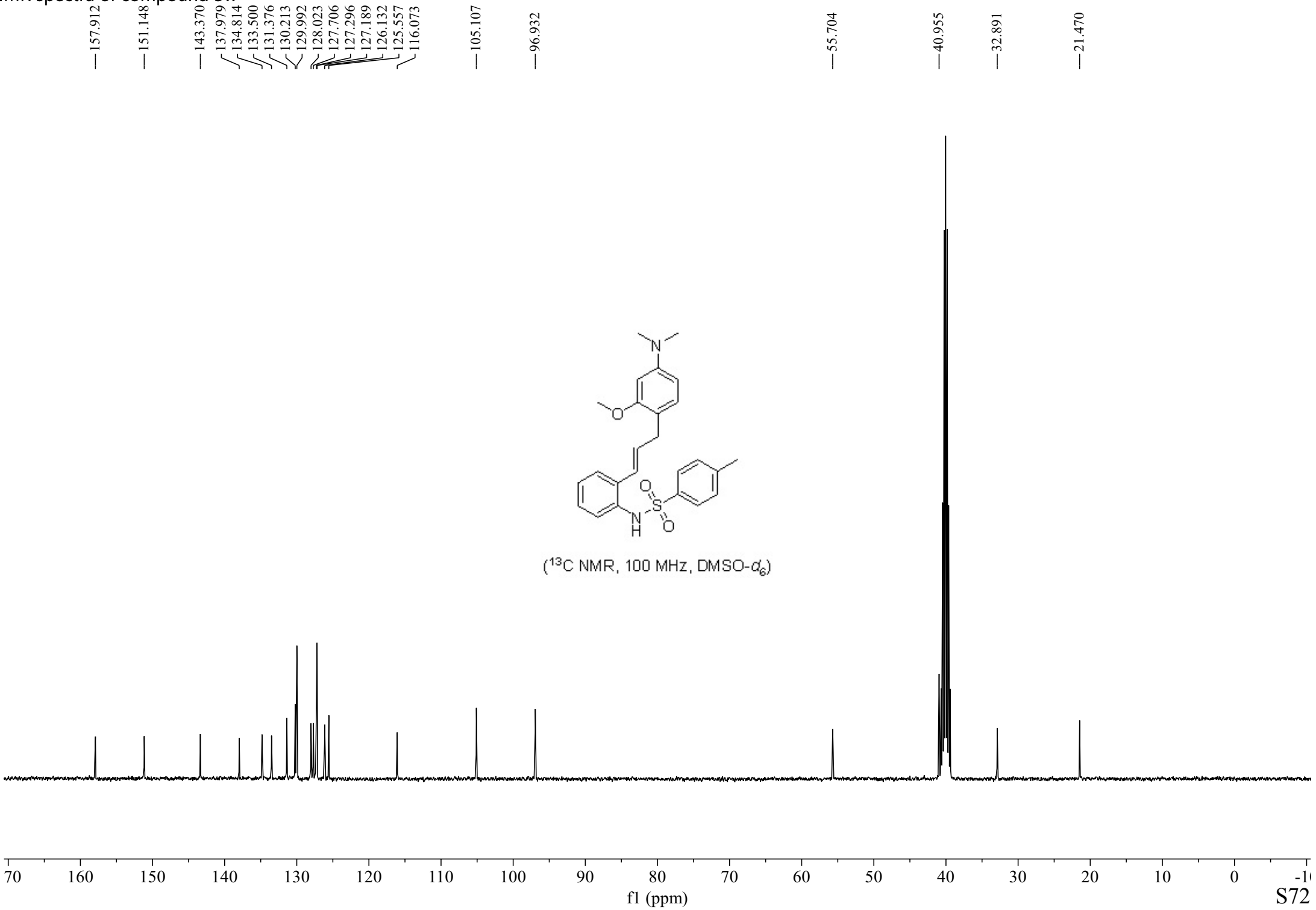
(^{13}C NMR, 100 MHz, DMSO-d_6)



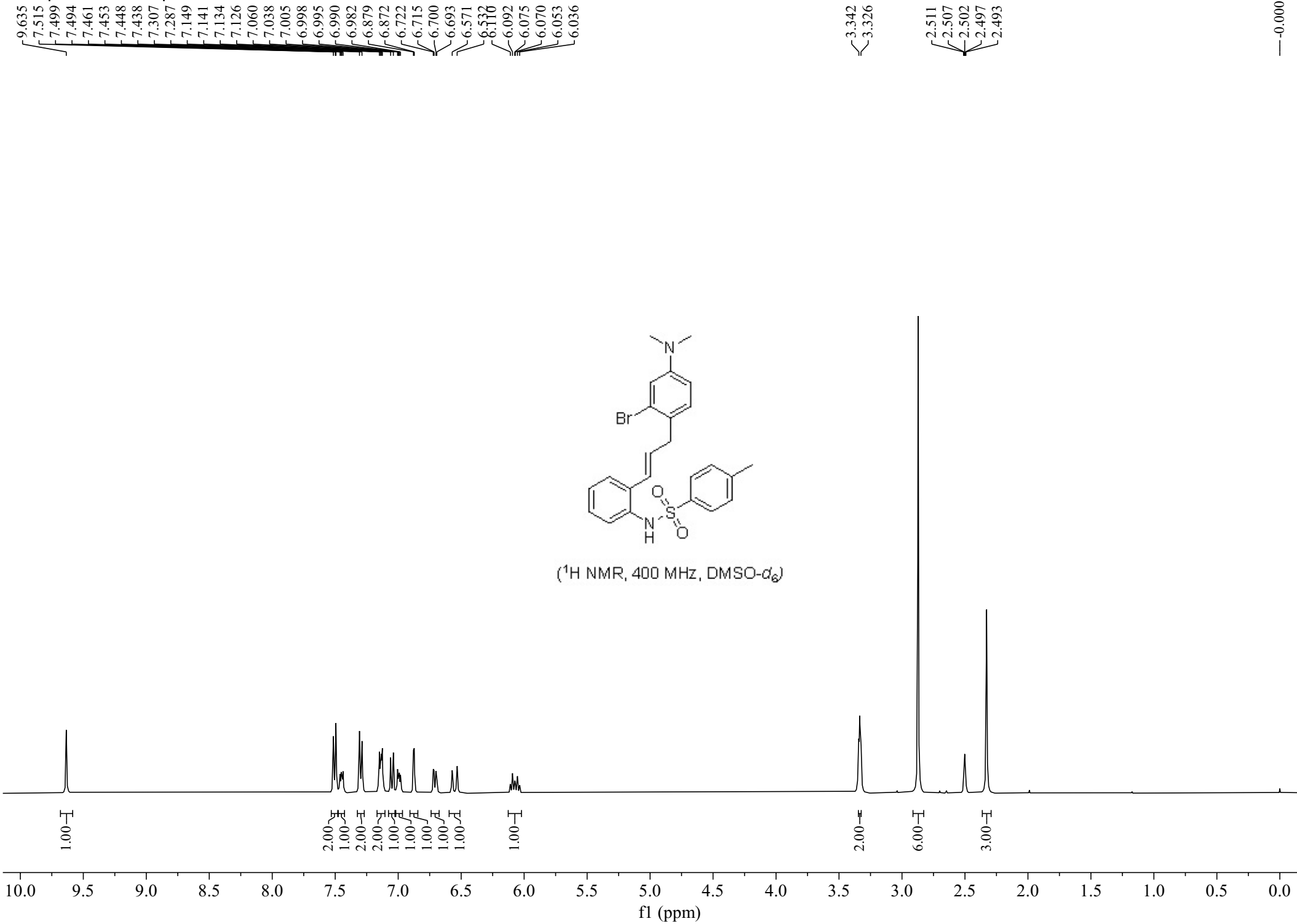
NMR spectra of compound 3w



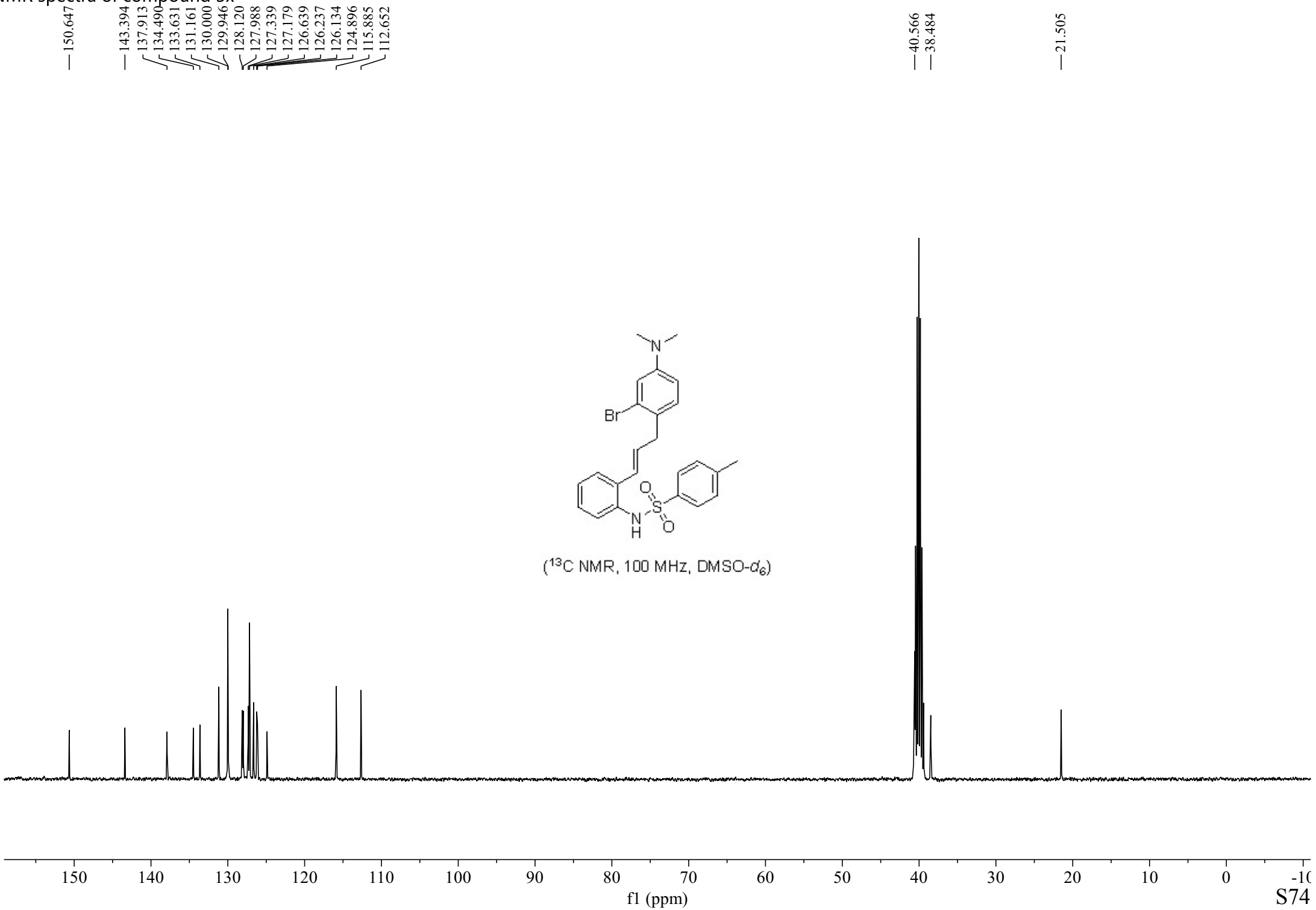
NMR spectra of compound 3w



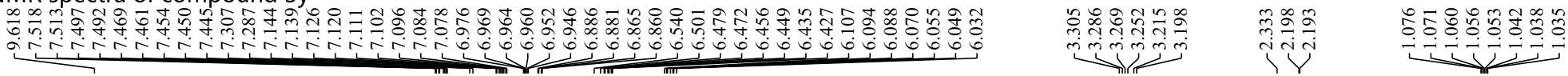
NMR spectra of compound 3x

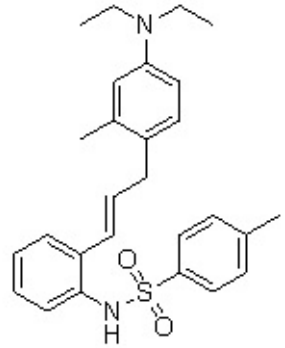


NMR spectra of compound 3x

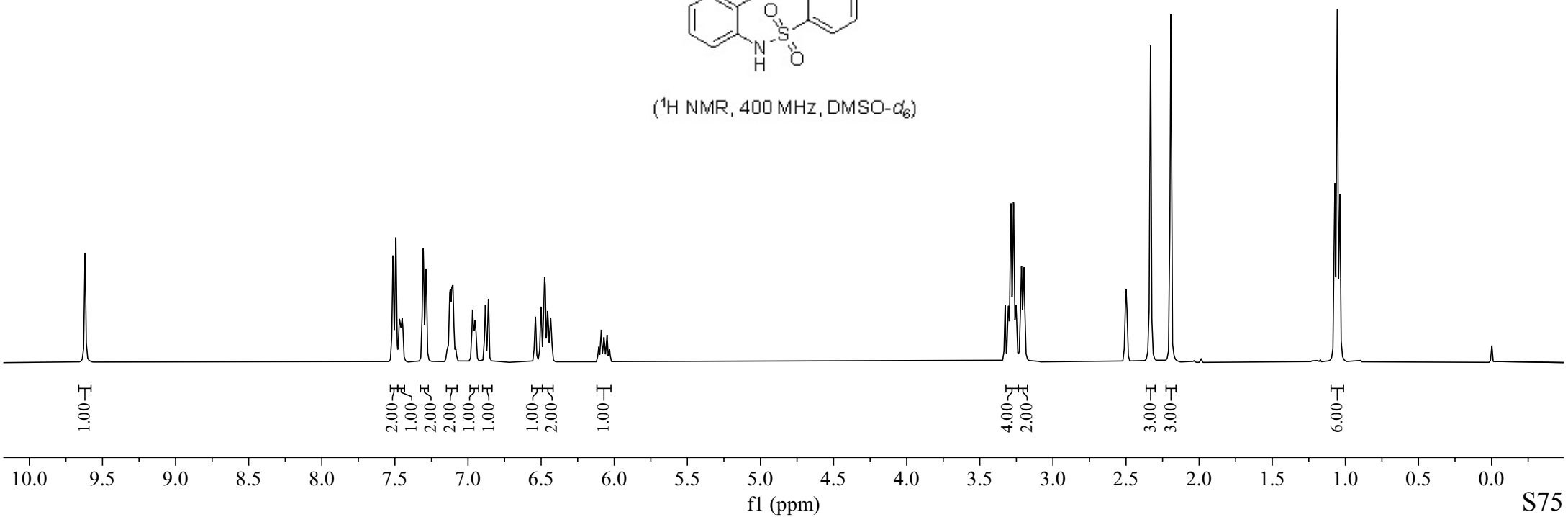


NMR spectra of compound 3y

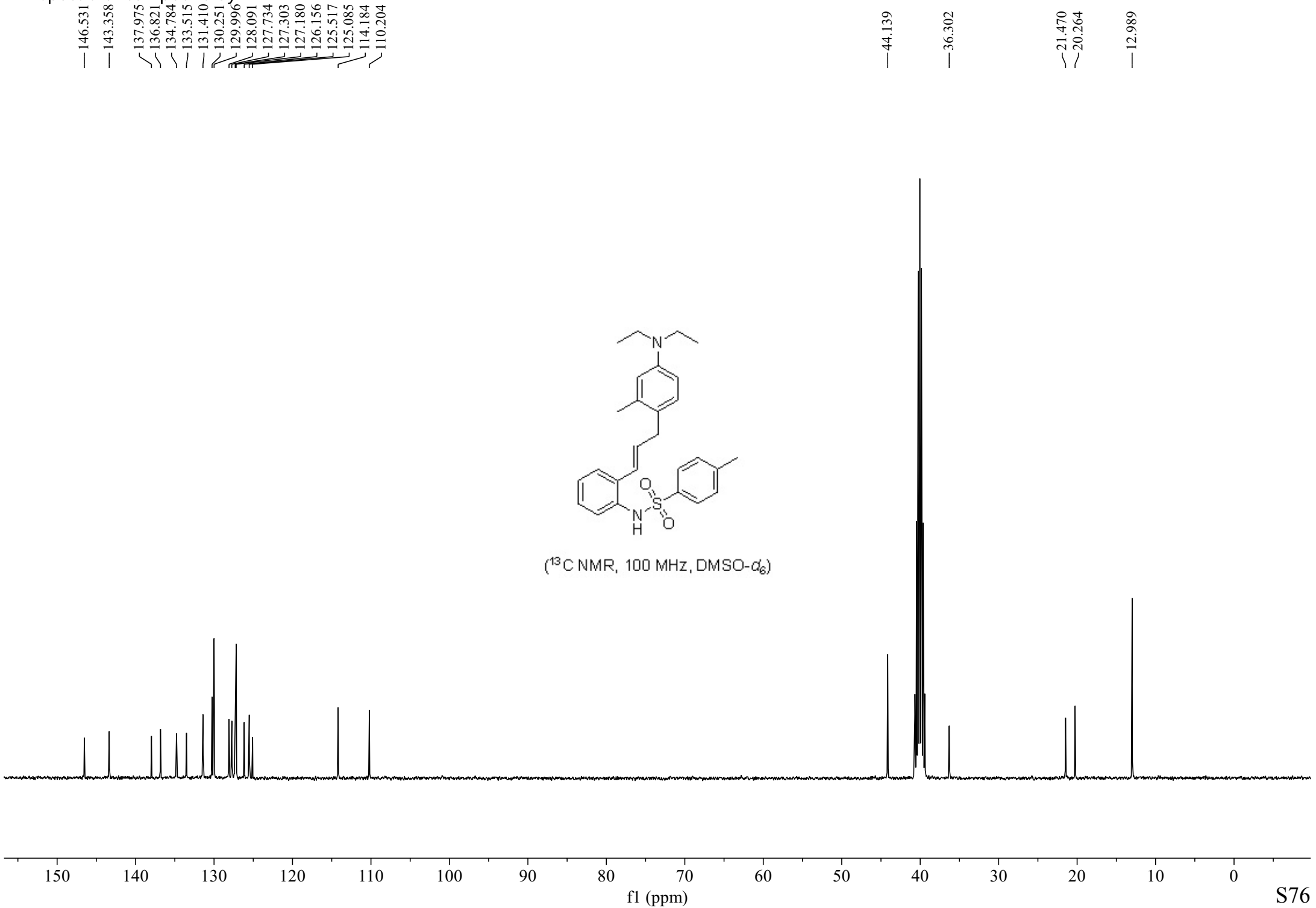




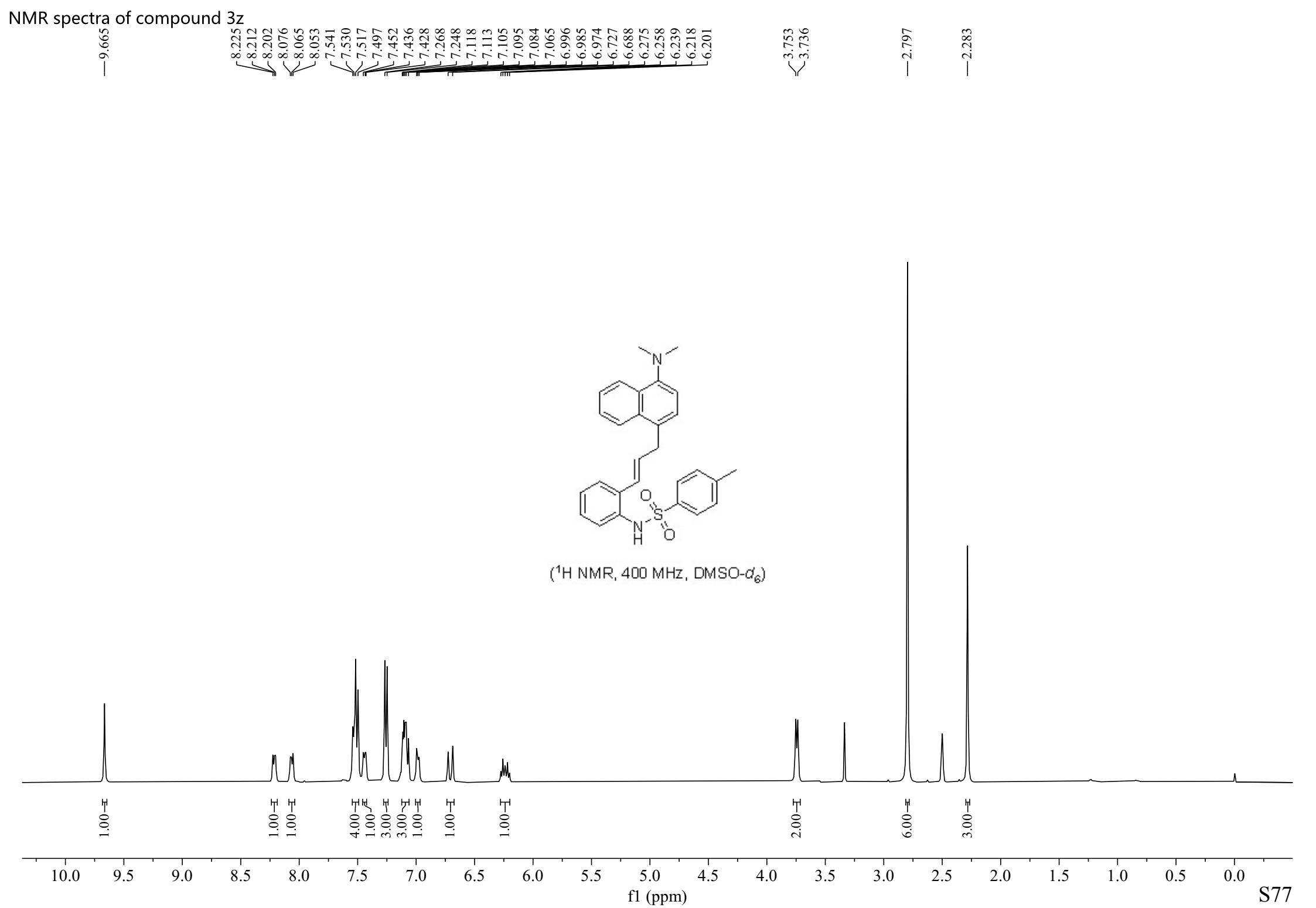
(^{1}H NMR, 400 MHz, DMSO-d_6)



NMR spectra of compound 3y

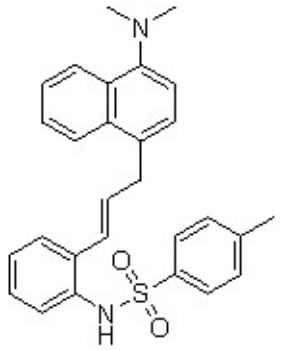


NMR spectra of compound 3z



NMR spectra of compound 3z

149.928
143.366
137.872
134.402
133.639
133.083
130.977
130.919
129.963
129.027
127.968
127.935
127.263
127.218
126.682
126.550
126.365
126.216
125.388
124.930
124.840
45.478
36.448
21.454

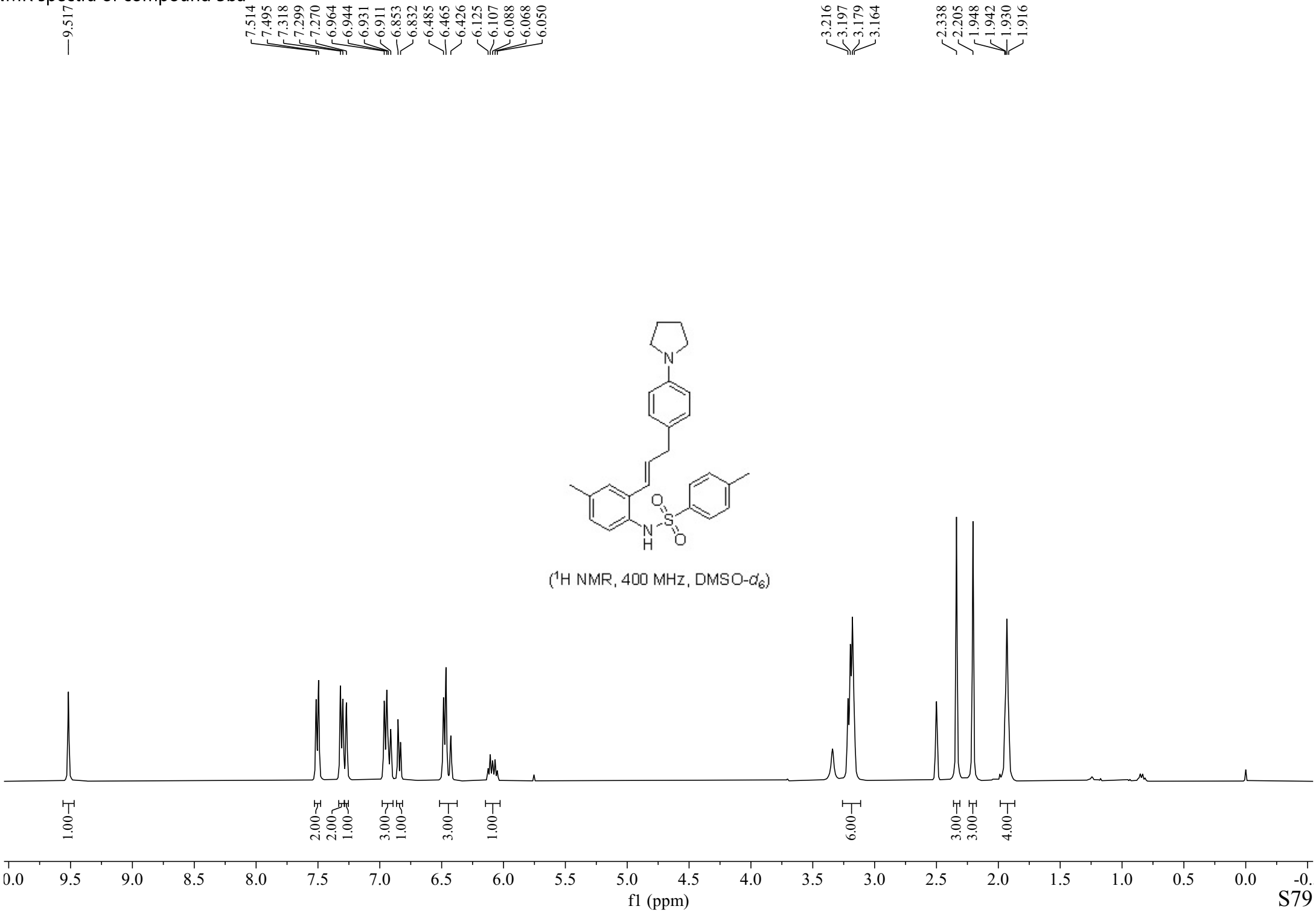


(^{13}C NMR, 100 MHz, DMSO-d_6)

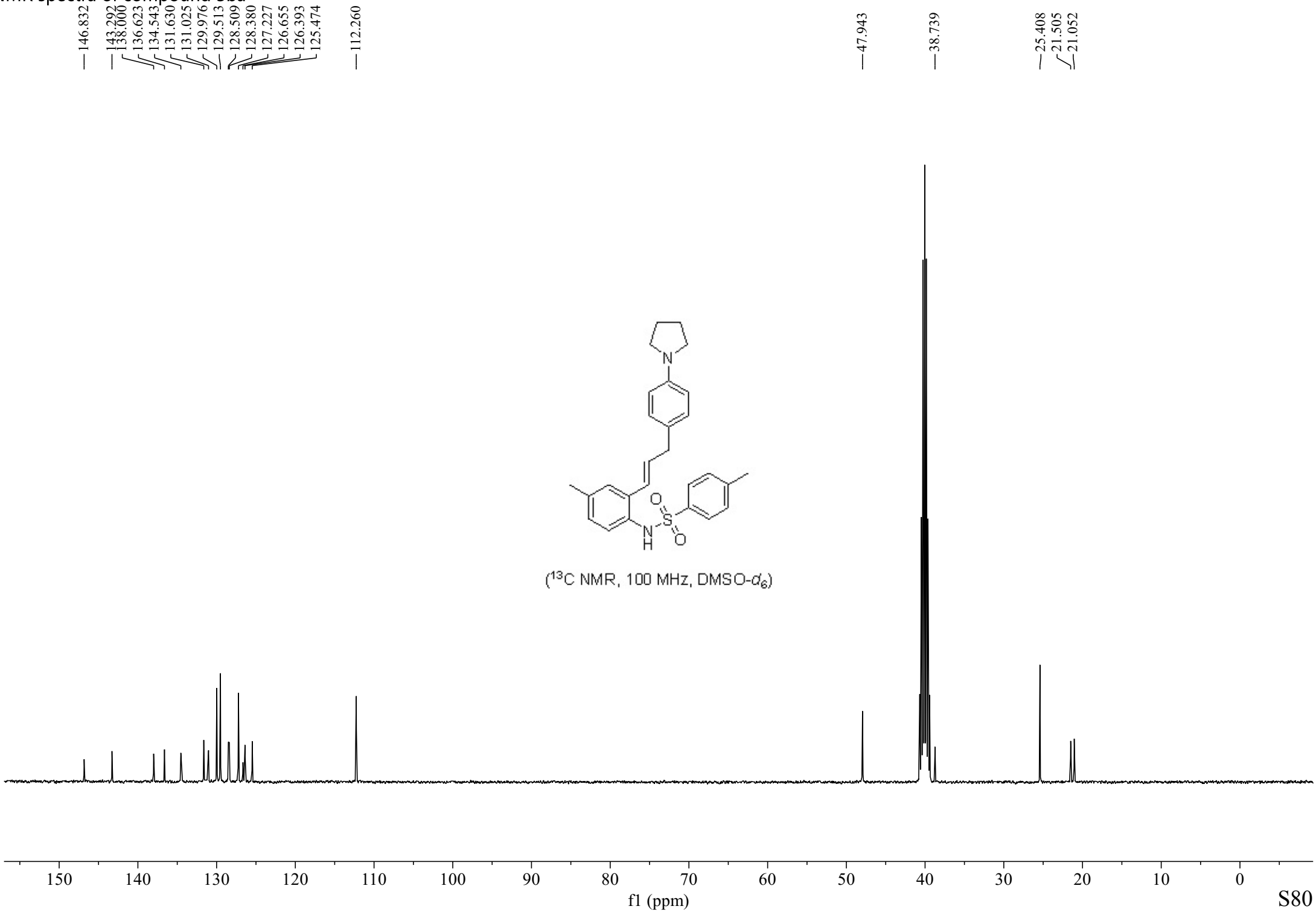
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

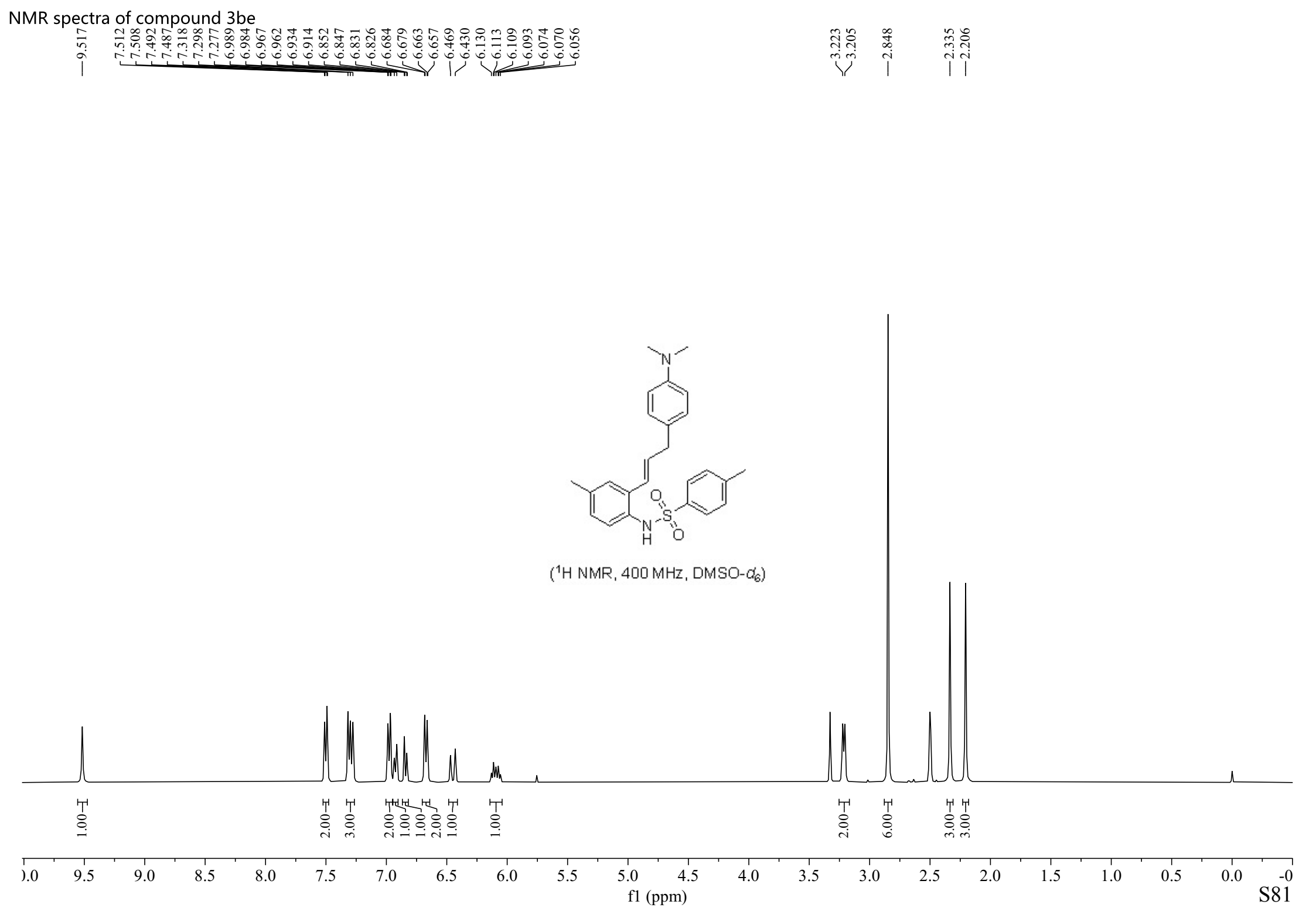
NMR spectra of compound 3ba



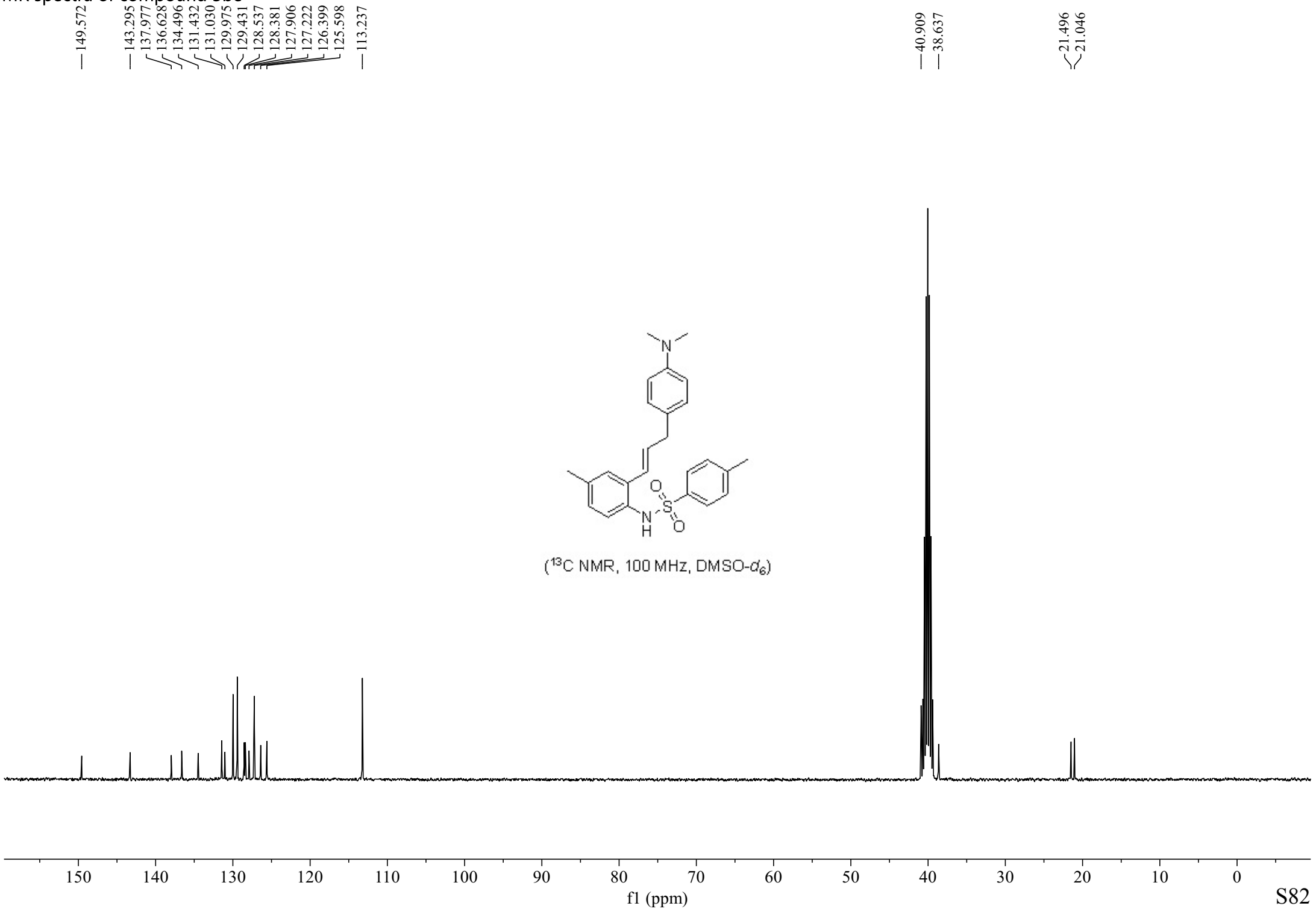
NMR spectra of compound 3ba



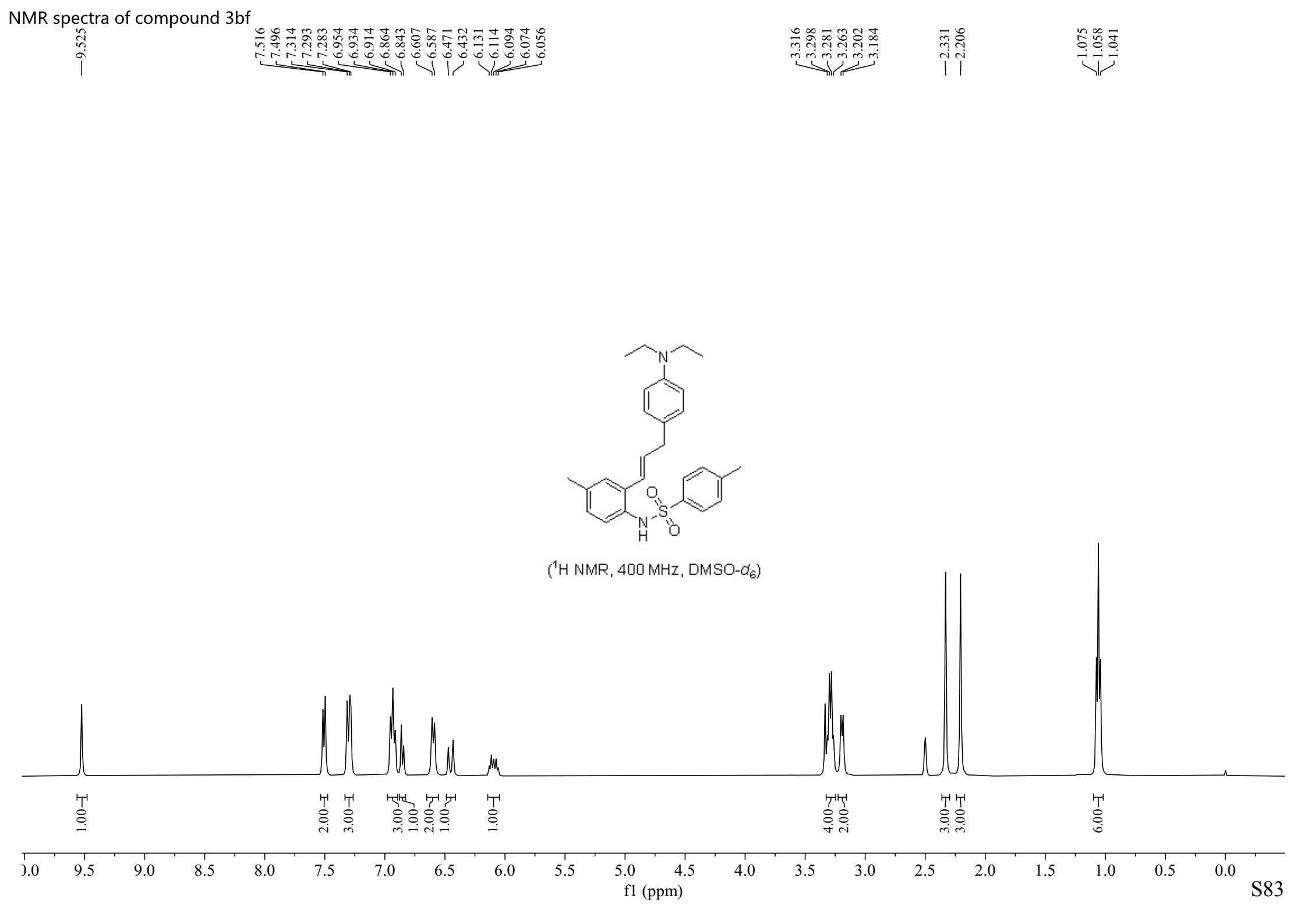
NMR spectra of compound 3be



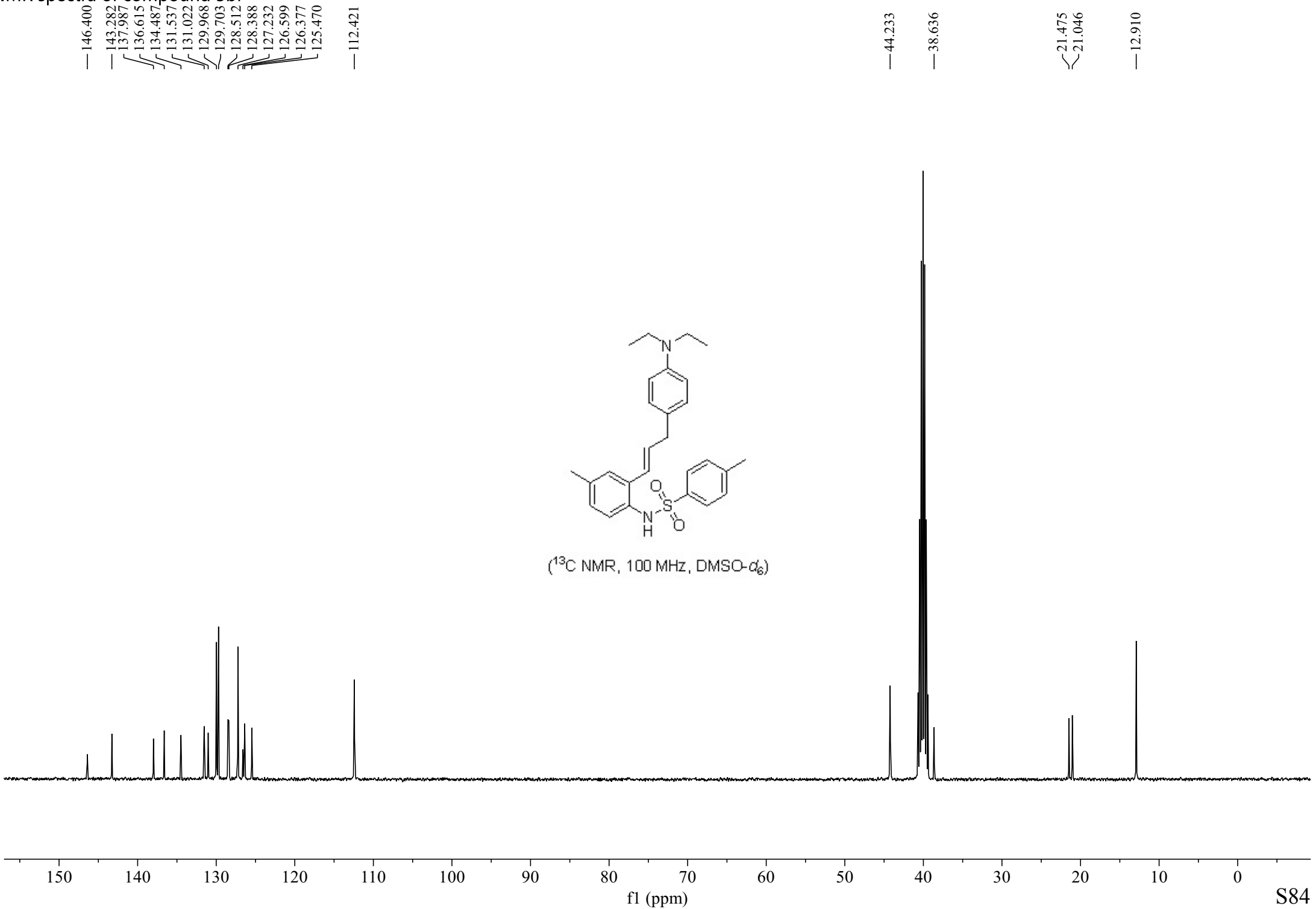
NMR spectra of compound 3be



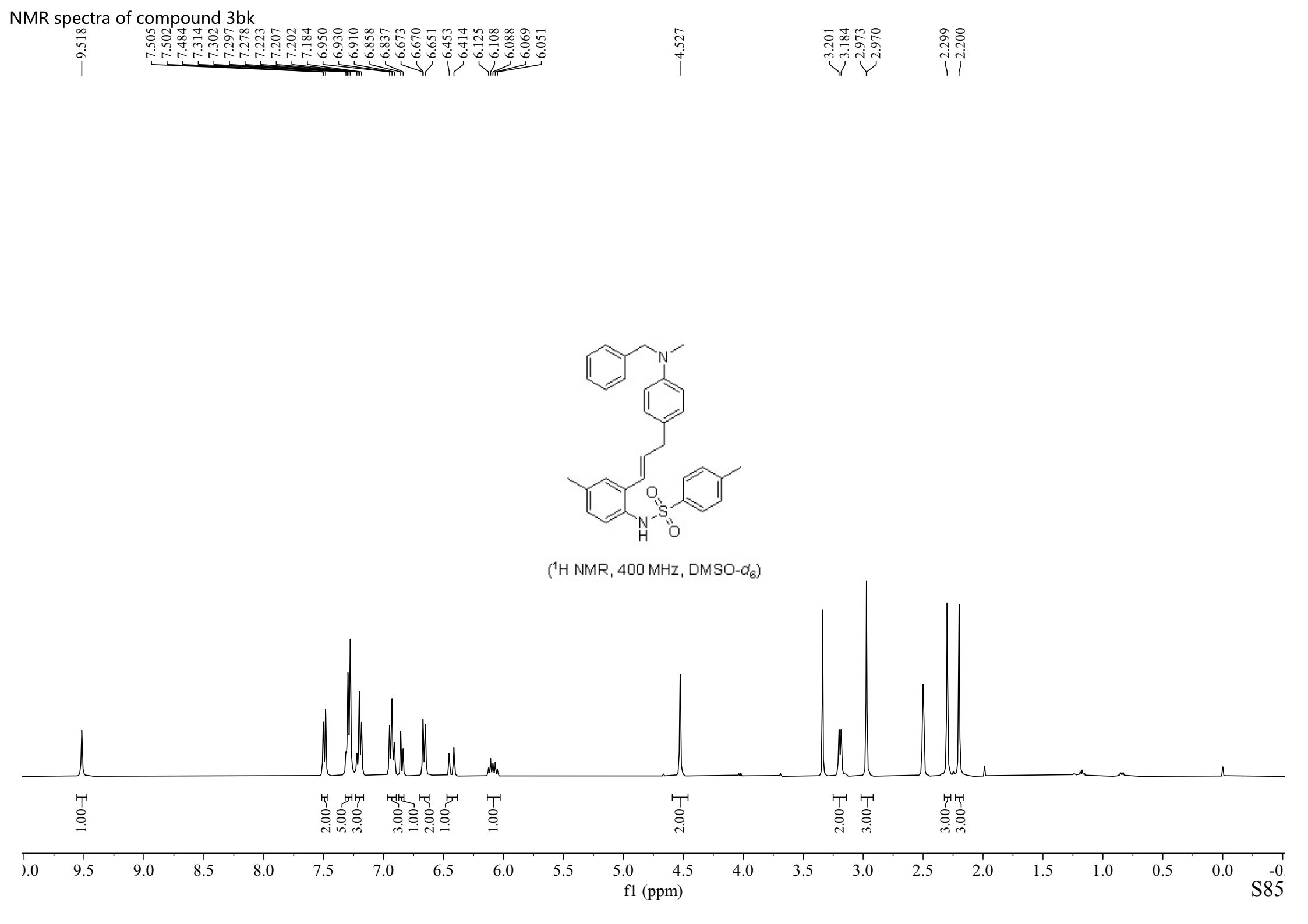
NMR spectra of compound 3bf



NMR spectra of compound 3bf



NMR spectra of compound 3bk



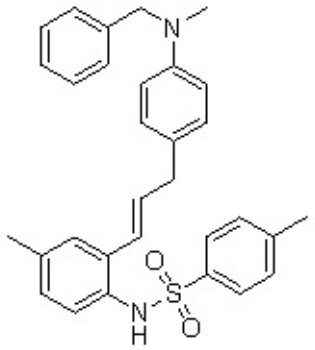
NMR spectra of compound 3bk

148.085
143.292
139.694
137.959
136.631
134.439
131.368
131.014
129.964
129.523
128.895
128.536
128.421
127.544
127.295
127.214
127.137
126.373
125.561
112.788

56.038

39.205
38.623

21.473
21.043

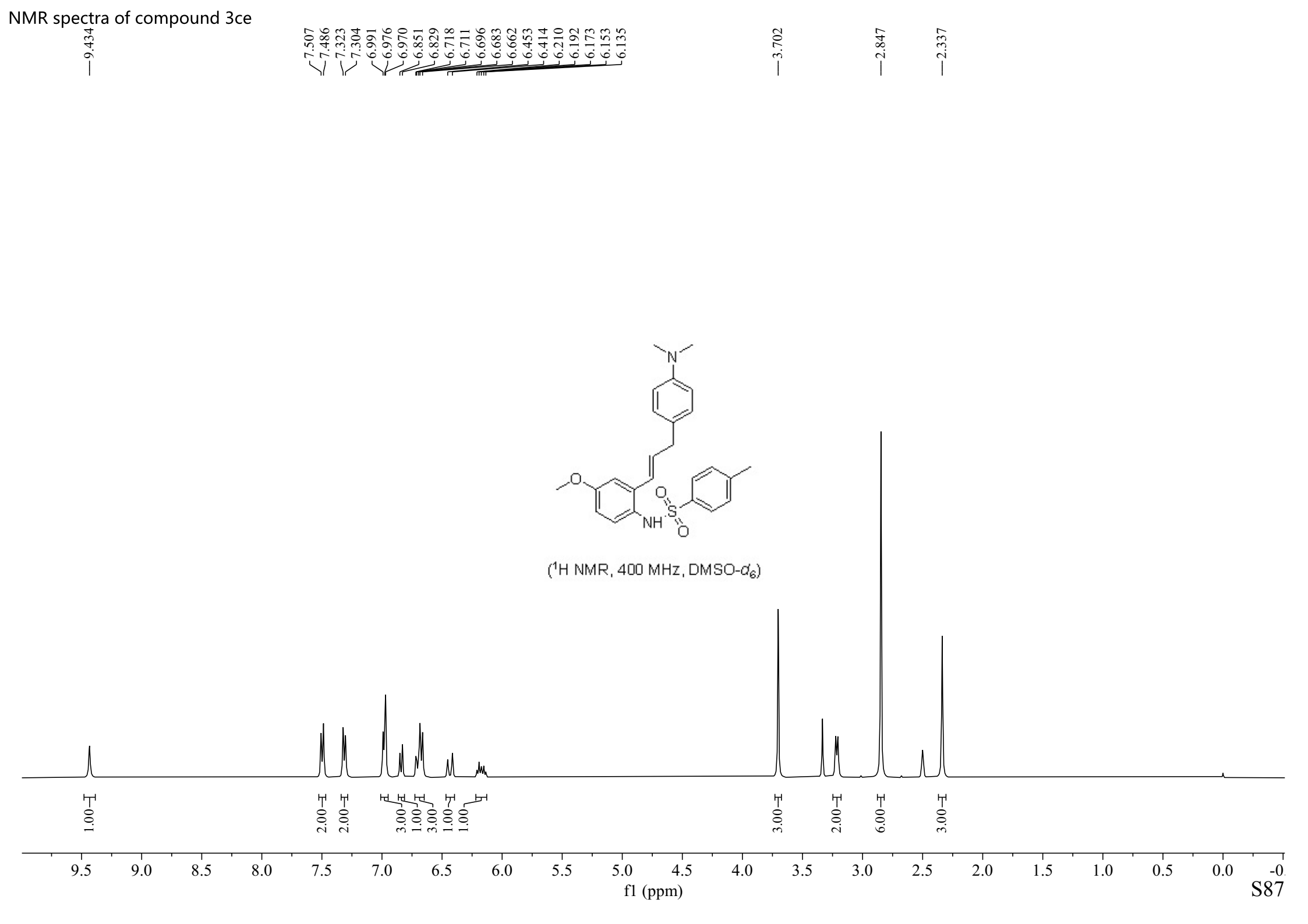


(^{13}C NMR, 100 MHz, DMSO-d_6)

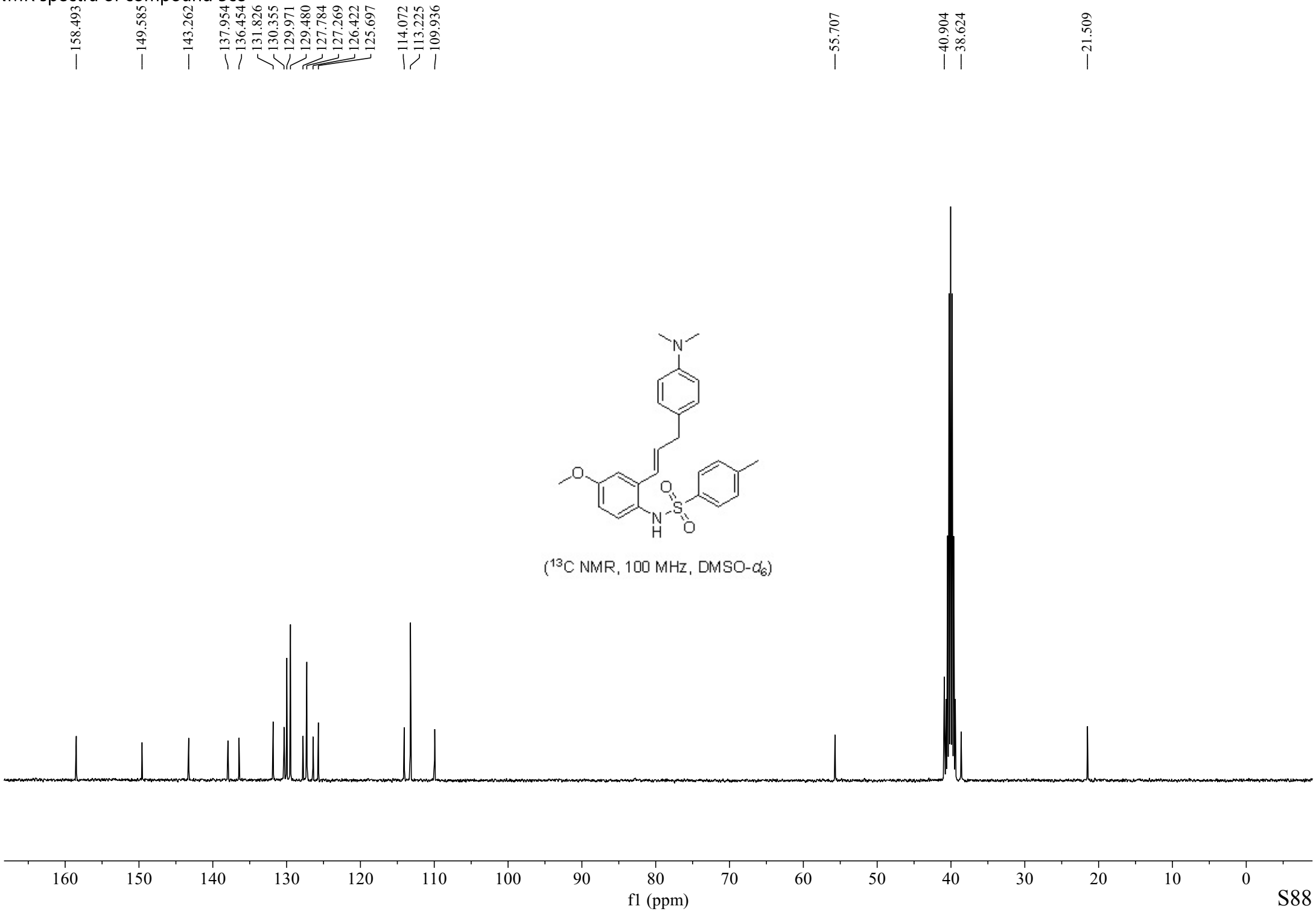
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

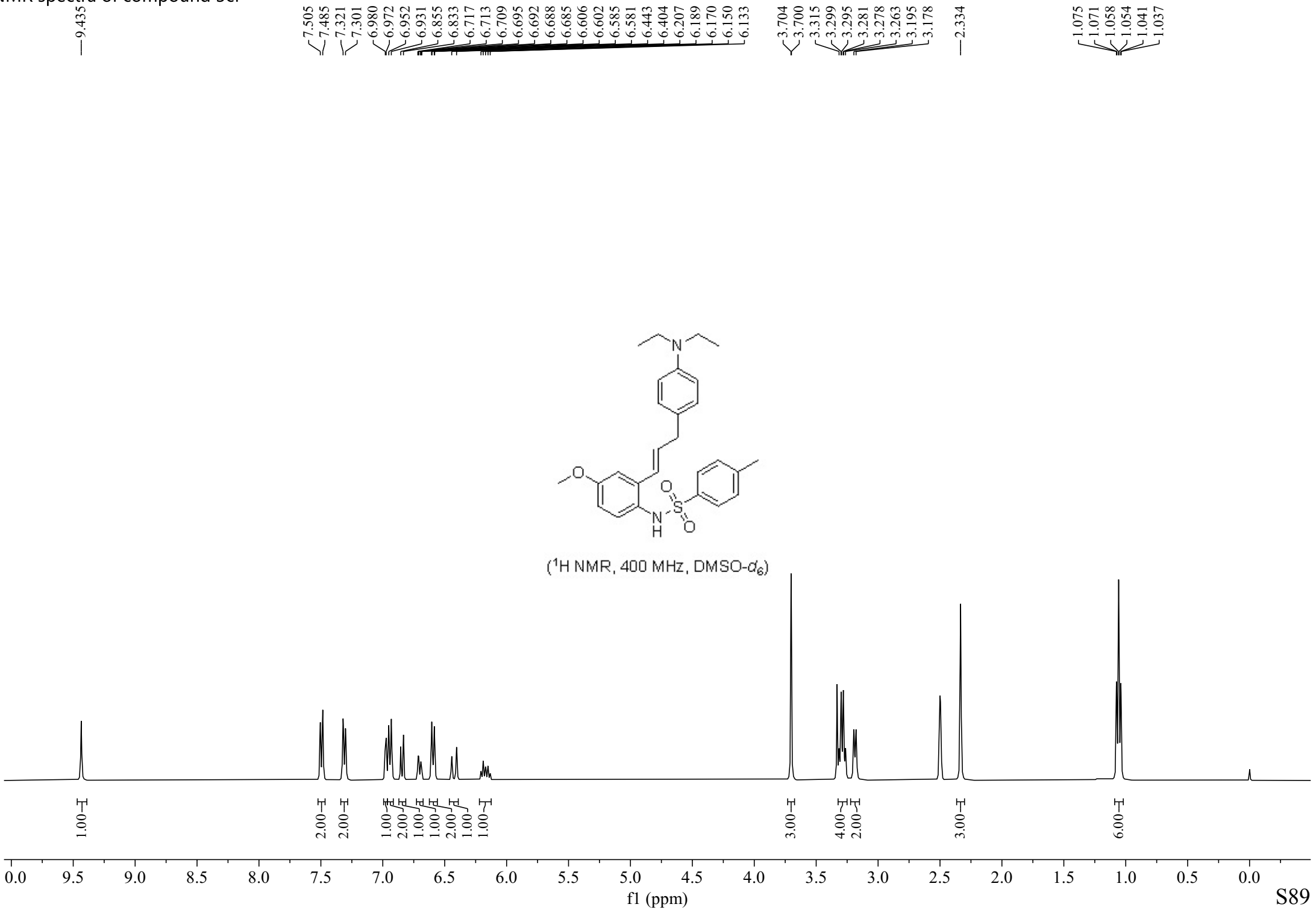
NMR spectra of compound 3ce



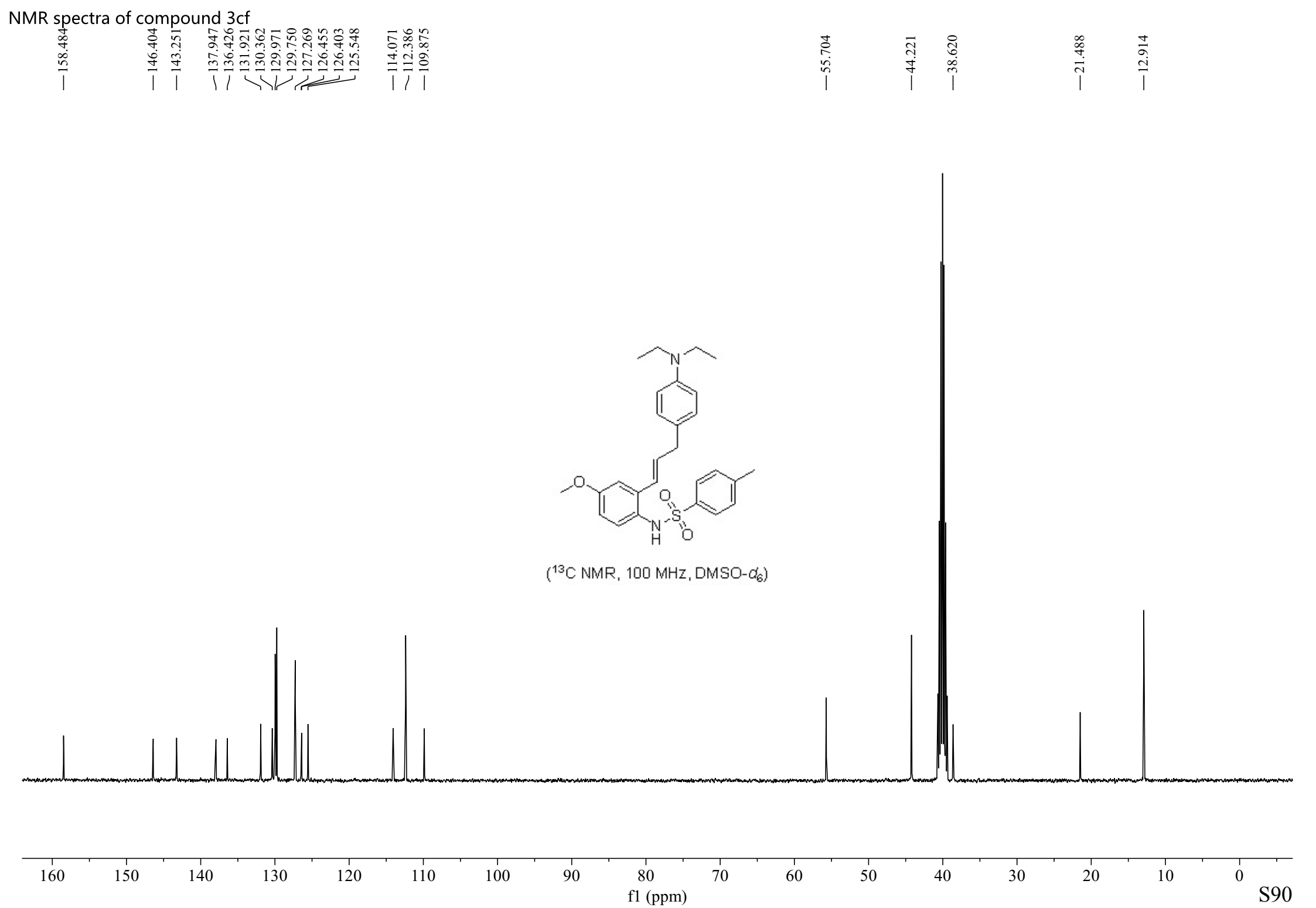
NMR spectra of compound 3ce



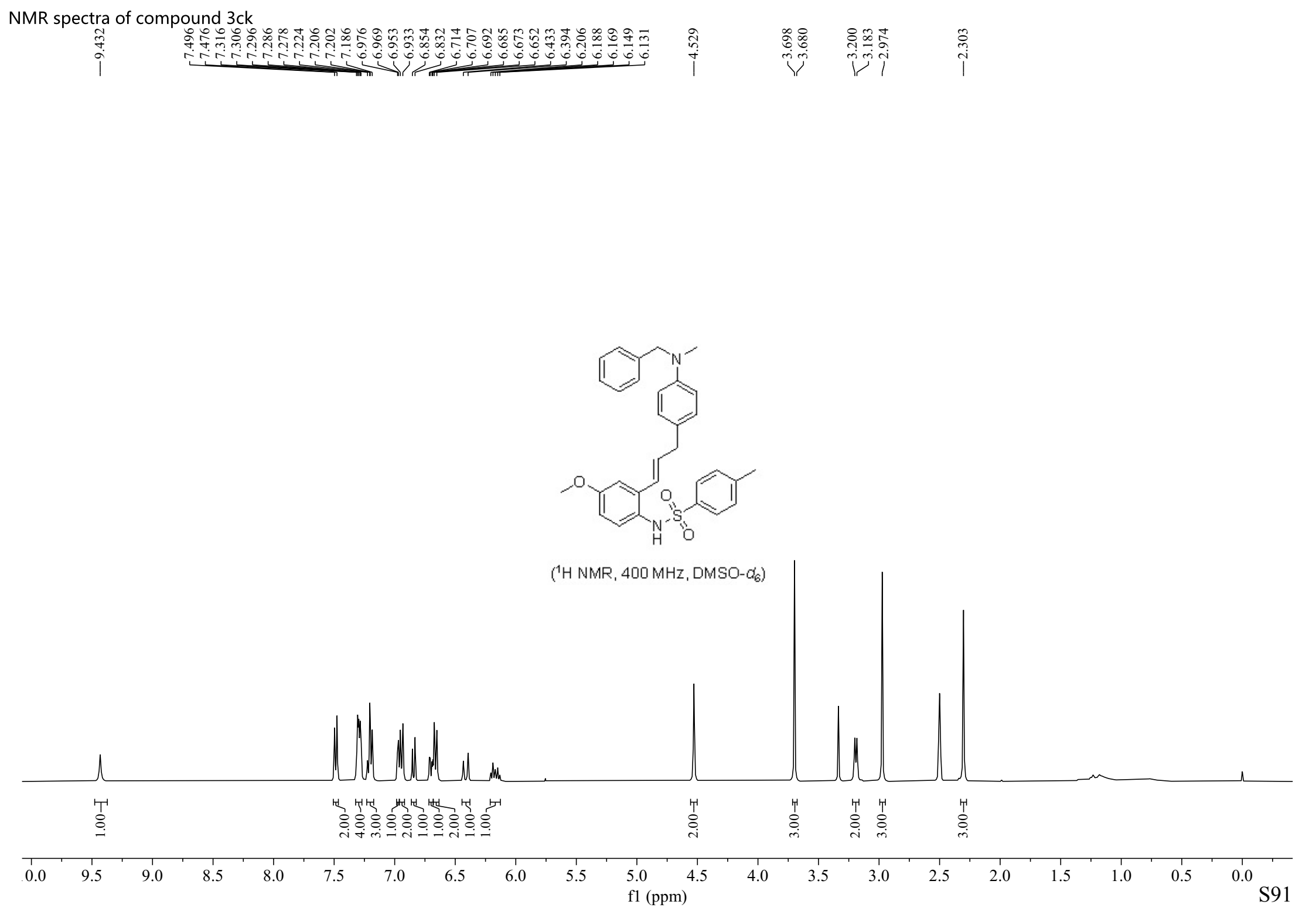
NMR spectra of compound 3cf



NMR spectra of compound 3cf



NMR spectra of compound 3ck



NMR spectra of compound 3ck

158.464
148.097
143.241
139.692
137.950
136.366
131.741
130.362
129.958
129.565
128.895
127.424
127.296
127.251
127.137
126.436
125.670
114.105
112.776
109.866
56.034
55.701
39.204
38.606
21.481

(^{13}C NMR, 100 MHz, DMSO-d_6)