Supporting Information

Electrochemical Synthesis of 3-(Sulfonyl)quinol-4-ones from *o*-Alkynyl-*N*-(Formyl)anilides and Sulfinates

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Contents

Experimental

Solvents were distilled and dried according to standard procedures. The starting materials were purchased from Sigma Aldrich and Alfa Aesar. The sulfinates **2** were prepared by literature procedures. [S1] Column chromatography was performed using silica gel (230-400 mesh), mixtures of hexane with ethyl acetate used as a mobile phase.

^{1}H and ^{13}C NMR spectra were acquired on 700 MHz spectrometers and referenced to the residual signals of the solvent (for ^{1}H and ^{13}C). The solvents used for NMR were DMSO-d_6 and $CDCl_3$. Chemical shifts are reported in parts per million (δ/ppm). Coupling constants are reported in Hertz (*J*/Hz). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; dd, doublet of doublets and br s, broad singlet.

Infrared spectra were measured on a FT/IR instrument. The wavelengths are reported in reciprocal centimeters (λ_{max}/cm^{-1}).

HRMS spectra were recorded on Bruker Maxis high-resolution mass spectrometer.

The reaction progress was monitored by TLC and the spots were visualized under UV light (254 or 365 nm).

Melting points were determined on a SMP-10 apparatus.

Electrochemical Setup

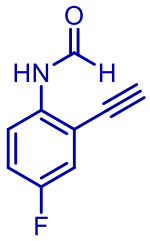
Figure S1. IKA Electrochemistry Kit ElektraSyn 2.0.

The electrochemical reactions were carried out using IKA Electrochemistry Kit ElektraSyn 2.0 with standard 10-mL vials, equipped with graphite cathode and anode and a magnetic stirring bar. Distance between the electrodes – 5 mm. Rectangular flat graphite electrodes 52 mm/8 mm/1.5 mm (length/width/thickness) were used.

Synthesis of formamides 1a-g

Corresponding *N*-(2-((trimethylsilyl)ethynyl)phenyl)formanilide (1 mmol) was dissolved in 15 ml of methanol (0.067 M), then potassium carbonate (0.276 g, 2 mmol) was added to the reaction mixture. The mixture was stirred for 30 minutes at room temperature. Upon completion methanol was evaporated, the residue was diluted with water and extracted with ethyl acetate. The organic layer was dried with sodium sulfate, and the organic solvent was removed in vacuo.

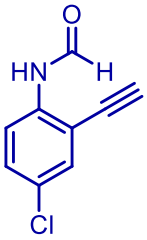
N-(2-Ethynyl-4-fluorophenyl)formamide (1a)



This compound is known. [S3]

Yellow solid, yield 160 mg (98%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.8: 0.2): δ 9.82 (d, 0.2H, *J* = 9.7 Hz), 9.72 (s, 0.8H), 8.50 (d, 0.2H, *J* = 10.8 Hz), 8.33 (s, 0.8H), 8.11 (q, 0.8H, *J* = 5.2 Hz), 7.40 (d, 0.2H, *J* = 8.8 Hz), 7.36 (q, 0.8H, *J* = 2.85 Hz), 7.33 (m, 0.2H), 7.30-7.25 (m, 1H), 4.72 (s, 0.7H), 4.58 (s, 0.3H).

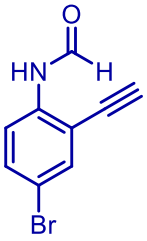
N-(4-Chloro-2-ethynylphenyl)formamide (1b)



This compound is known. [S3]

Beige solid, yield 131 mg (73%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.85: 0.15): δ 9.80 (s, 1H), 8.59 (s, 0.15H), 8.36 (s, 0.85H), 8.20 (d, 0.85H, *J* = 8.8 Hz), 7.55 (s, 1H), 7.45 (d, 1H, *J* = 8.8 Hz), 7.33 (s, 0.15H), 4.76 (s, 0.85H), 4.60 (s, 0.15H).

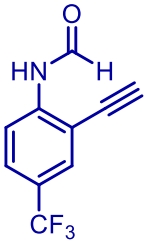
N-(4-Bromo-2-ethynylphenyl)formamide (1c)



This compound is known. [S3]

Brown solid, yield 168 mg (75%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.8: 0.2): δ 9.79 (s, 1H), 8.60 (s, 0.2H), 8.37 (s, 0.8H), 8.14 (d, 0.8H, *J* = 8.3 Hz), 7.67 (s, 1H), 7.59 (d, 1H, *J* = 7.4 Hz), 7.27 (s, 0.2H), 4.76 (s, 0.85H), 4.61 (s, 0.15H).

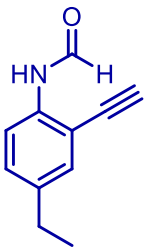
N-(2-Ethynyl-4-(trifluoromethyl)phenyl)formamide (1d)



This compound is known. [S3]

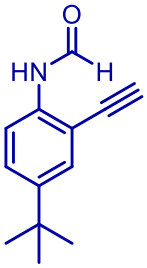
Brown solid, yield 187 mg (88%). ^{1}H NMR (DMSO-d$_6$, 700 MHz): δ 9.99 (s, 1H), 8.46 (s, 2H), 7.82 (s, 1H), 7.76 (d, 1H, *J* = 10.3 Hz), 4.81 (s, 1H).

N-(4-Ethyl-2-ethynylphenyl)formamide (1e)



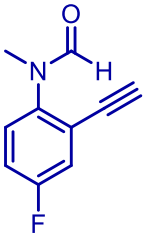
Brown solid, yield 156 mg (90%), m.p. 47-48ºC. ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.8: 0.2): δ 9.70 (s, 0.2H), 9.59 (s, 0.8H), 8.53 (s, 0.2H), 8.33 (s, 0.8H), 8.02 (d, 0.8H, *J* = 8.7 Hz), 7.34 (s, 0.2H), 7.31 (s, 0.8H), 7.25-7.19 (m, 1.2H), 4.56 (s, 0.8H), 4.42 (s, 0.2H), 2.58-2.53 (m, 2H), 1.14 (t, 3H, *J* = 7.8 Hz). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 163.4, 160.5, 140.8, 139.5, 136.8, 132.4, 131.6, 129.6, 129.1, 122.1, 121.1, 114.8, 112.3, 86.9, 85.3, 80.4, 79.4, 27.2, 15.4. HRMS (TOF ES$^+$): m/z calcd for $C_{11}H_{12}NO$ $[M+H]^+$ 174.0913; found, m/z: 174.0919. IR (KBr): 3318, 3282, 3135, 1907 cm^{-1}.

N-(4-(Tert-butyl)-2-ethynylphenyl)formamide (1f)



Dark red solid, yield 181 mg (90%), m.p. 42-43ºC. ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.75: 0.25): δ 9.72 (d, 0.25H, *J* = 11.2 Hz), 9.60 (s, 0.75H), 8.56 (d, 0.25H, *J* = 11.2 Hz), 8.33 (s, 0.75H), 8.05 (d, 0.75H, *J* = 8.4 Hz), 7.46 (s, 0.25H), 7.44-7.41 (m, 1.75H), 7.21 (d, 0.25H, *J* = 8.4 Hz), 4.55 (s, 0.75H), 4.42 (s, 0.25H), 1.25 (s, 9H). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 163.4, 160.5, 147.6, 146.3, 136.6, 129.9, 129.0, 127.2, 126.7, 121.8, 120.8, 114.4, 111.9, 86.8, 85.2, 80.6, 79.7, 34.0, 30.9, 26.3. HRMS (TOF ES$^+$): m/z calcd for $C_{13}H_{16}NO$ $[M+H]^+$ 202.1226; found, m/z: 202.1232. IR (KBr): 3284, 3112, 2102 cm^{-1}.

N-(2-Ethynyl-4-fluorophenyl)-N-methylformamide (1g)

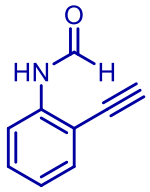


Brown oil, yield 170 mg (96%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.8: 0.2): δ 8.27 (s, 0.2H), 8.18 (s, 0.8H), 7.51-7.48 (m, 1.7H), 7.47-7.45 (m, 0.2H), 7.40-7.37 (m, 0.8H), 7.36 (d, 0.3H, *J* = 6.7 Hz), 4.58 (s, 0.8H), 4.49 (s, 0.2H), 3.25 (s, 0.4H), 3.14 (s, 2.6H). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 162.6, 162.5, 161.2, 161.1, 159.8, 159.7, 140.2, 139.1, 130.55, 129.49, 129.44, 122.42, 122.36, 121.40, 121.35, 119.9, 119.8, 119.7, 119.6, 117.6, 117.5, 117.4, 117.2, 86.6, 86.0, 78.9, 36.4, 32.6. HRMS (TOF ES$^+$): m/z calcd for $C_{10}H_9NOF$ $[M+H]^+$ 178.0663; found, m/z: 178.0668.

N-(2-Ethynylphenyl)formamide (1h)

Formic acid (121 ml, 3.2 mol) and acetic anhydride (189 ml, 2 mmol) were mixed in a round-bottom flask and stirred at heating at 60 °C for 30 minutes. Then the reaction mixture was cooled to 10 °C and the solution of 2-ethynylaniline (1 mmol) in 20 ml of THF (0.05 M) was added to the reaction mixture. The reaction mass was stirred for 3 hours at room temperature. Upon completion organic solvent was removed on a rotary evaporator. The residue was crystallized in water. The precipitate was filtered off on a Schott filter and washed with small amounts of water for three times. The product was purified by recrystallization from a mixture of dichloromethane-hexane.

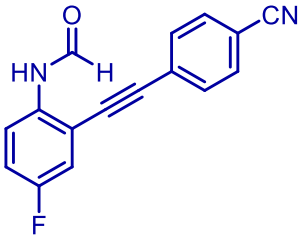
This compound is known. [S3]



Beige solid, yield 128 mg (88%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.8: 0.2): δ 9.77 (d, 0.2H, *J* = 9.6 Hz), 9.66 (s, 0.8H), 8.62 (d, 0.2H, *J* = 10.9 Hz), 8.37 (s, 0.8H), 8.16 (d, 0.8H, *J* = 8.2 Hz), 7.52-7.48 (m, 1H), 7.41-7.37 (m, 1H), 7.31 (d, 0.2H, *J* = 7.9 Hz), 7.19 (t, 0.2H, *J* = 7.4 Hz), 7.11 (t, 0.8H, *J* = 7.4 Hz), 4.61 (s, 0.8H), 4.47 (s, 0.2H).

N-(2-((4-Cyanophenyl)ethynyl)-4-fluorophenyl)formamide (1i)

In a Schlenk flask, equipped with a magnetic stirring bar, under argon atmosphere *N*-(4-fluoro-2-iodophenyl)formamide (700 mg, 2.6 mmol), 15 ml of triethylamine (0.17 M), copper (I) iodide (20 mg, 4 mmol %) and Pd(P(Ph)$_3$)$_2$Cl$_2$ (36 mg, 2 mmol. %) were mixed. Then 4-ethynylbenzonitrile (671 mg, 5.3 mmol) was added, and the reaction mixture was stirred at room temperature for 1.5 hours. Upon completion the reaction mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The product was isolated by column chromatography (eluent: hexane : ethyl acetate = 5 : 1).

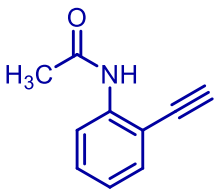


Grey solid, yield 535 mg (78%), m.p. 55-56^{o}C. ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.8: 0.2): δ 10.12 (d, 0.2H, *J* = 10.3 Hz), 9.88 (s, 0.8H), 8.60 (d, 0.2H, *J* = 10.3 Hz), 8.39 (s, 0.8H), 8.16 (q, 0.8H, *J* = 9.2 Hz), 7.94 (d, 2H, *J* = 8.1 Hz), 7.86 (d, 1.6H, *J* = 8.1 Hz), 7.78 (d, 0.4H, *J* = 8.1 Hz), 7.52-7.48 (m, 1H), 7.43-7.41 (m, 0.2H), 7.35-7.31 (m, 1H). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 163.72, 160.5, 158.4, 157.1, 153.8, 135.3, 133.3, 132.6, 132.50, 132.45, 132.3, 126.7, 123.92, 123.86, 123.37, 123.33, 119.2, 119.1, 118.7, 118.6, 118.4, 117.9, 117.8, 117.4, 117.3, 114.1, 114.0, 111.4, 94.4, 93.2, 88.8, 87.8. HRMS (TOF ES$^+$): m/z calcd for $C_{16}H_{10}N_2OF$ $[M+H]^+$ 265.0772; found, m/z: 265.0779.

N-(2-Ethynylphenyl)acetamide (1j)

2-Ethynylaniline (1 mmol) was placed in a round-bottom flask, then 10 ml of water (0.1 M) and acetic anhydride (142 ml, 1.5 mmol) were added. The reaction mixture was heated on a water bath. Reaction progress was monitored by TLC. Upon completion the mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was dried over sodium sulfate and the solvent was evaporated in vacuo. The product was isolated by column chromatography (eluent: hexane-ethyl acetate: 4:1).

This compound is known. [S4]

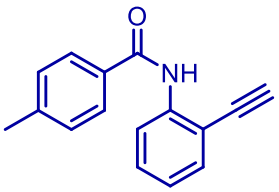


Yellow solid, yield 124 mg (78%). ^{1}H NMR (DMSO-d$_6$, 700 MHz): δ 9.33 (s, 1H), 7.77 (d, 1H, *J* = 7.7 Hz), 7.47 (d, 1H, *J* = 7.4 Hz), 7.37 (t, 1H, *J* = 7.4 Hz), 7.13 (t, 1H, *J* = 9.2 Hz), 4.47 (s, 1H), 2.09 (s, 3H).

N-(2-Ethynylphenyl)-4-methylbenzamide (1k)

2-Ethynylaniline (1 mmol) and triethylamine (175 ml, 1.25 mmol) were dissolved in dichloromethane (15 ml, 0.067M), then *p*-methylbenzoyl chloride (148 ml, 1.1 mmol) was added to the mixture at room temperature. The reaction mass was stirred at room temperature for several hours (TLC monitoring). Upon completion the reaction mass was treated with 1M HCl solution and extracted with dichloromethane (3x50 ml). The organic layer was dried with sodium sulfate, the organic solvent was evaporated in vacuo. The product was isolated by column chromatography (eluent: hexane-ethyl acetate: 5-1).

This compound is known. [S5]

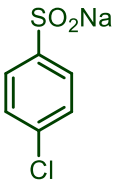


Pink solid, yield 139 mg (59%). ^{1}H NMR (DMSO-d$_6$, 700 MHz): δ 9.74 (s, 1H), 7.88 (d, 2H, *J* = 8.1 Hz), 7.76 (d, 1H, *J* = 7.9 Hz), 7.54 (d, 1H, *J* = 7.8 Hz), 7.45 (t, 1H, *J* = 7.9 Hz), 7.35 (d, 2H, *J* = 7.9 Hz), 7.23 (t, 1H, *J* = 7.6 Hz), 4.48 (s, 1H), 2.39 (s, 3H).

Synthesis of sulfinates 2a-c

Phenylsulfonyl chloride (1 mmol), sodium sulfite (0.277 g, 2.2 mmol) and sodium bicarbonate (0.168 g, 2 mmol) were mixed in a round-bottom flask and dissolved in 30 ml of water (0.033 M). The reaction mixture was stirred for 4 hours at reflux. Upon completion the solvent was removed in vacuo. Sulfinate was extracted with boiling ethanol for several times. Finally, ethanol was removed in vacuo and the product was obtained as white crystals.

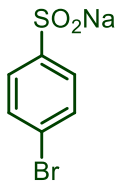
Sodium 4-chlorobenzenesulfinate (2a)



This compound is known. [S6]

White solid, yield 87 mg (87%). ^{1}H NMR (DMSO-d$_6$, 700 MHz): δ = 5.30 (d, 1H, *J* = 8.3 Hz), 5.24 (d, 1H, *J* = 8.3 Hz).

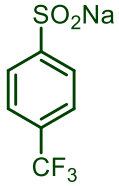
Sodium 4-bromobenzenesulfinate (2b)



This compound is known. [S7]

White solid, yield 201 mg (84%). ^{1}H NMR (DMSO-d$_6$, 700 MHz): δ = 5.55 (d, 1H, *J* = 8.1 Hz), 5.50 (d, 1H, *J* = 8.1 Hz).

Sodium 4-(trifluoromethyl)benzenesulfinate (2c)



This compound is known. [S7]

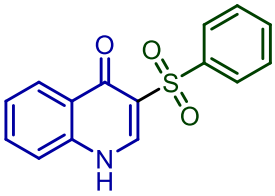
White solid, yield 207 mg (89%). ^{1}H NMR (DMSO-d$_6$, 700 MHz): δ = 5.40 (d, 1H, *J* = 8.3 Hz), 5.25 (d, 1H, *J* = 8.3 Hz).

Electrosynthesis of quinolones 3a-3o, general procedure.

N-(2-(Ethynyl)phenyl)formamide (1 mmol), sodium phenyl sulfinate (1.5 mmol), silver oxide (0.232 g, 1 mmol) and sodium tetrafluoroborate (0.110 g, 1 mmol) were mixed in a standard ElectraSyn 10 ml vial and dissolved in 5 ml of DMF (0.2 M). The electrolysis was performed in an undivided cell using a pair of graphite electrodes in a constant current mode at 20 mA*****. The mixture was stirred for 14 hours at room temperature and 15,07 F/mol of electricity were passed through the reaction mixture. Then the solvent was removed under reduced pressure. The target products 3a-3o were isolated by column chromatography on Silica: eluent hexane: ethyl acetate = 1:1.

*The reaction was carried out at 10 mA when *N*-(4-bromo-2-ethynylphenyl)formamide **1c** and sodium 4-bromobenzenesulfinate **2b** were used.

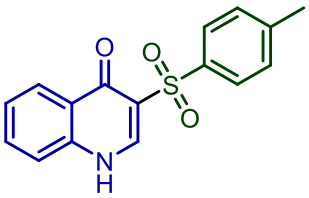
3-(Phenylsulfonyl)quinolin-4(1H)-one (3a)



This compound is known. [S8]

Beige solid, yield 212 mg (74%), m.p. 233-234ºC. ^{1}H NMR (DMSO-d_6, 700 MHz): δ 12.78 (s, 1H), 8.76 (s, 1H), 8.05-8.02 (m, 3H), 7.75 (t, 1H, *J* = 7.6 Hz), 7.69 (d, 1H, *J* = 8.1 Hz), 7.64 (t, 1H, *J* = 7.4 Hz), 7.57 (t, 2H, *J* = 7.6 Hz), 7.44 (t, 1H, *J* = 7.4 Hz). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 171.4, 143.4, 141.3, 139.5, 133.3, 133.0, 128.7 (2C), 127.8 (2C), 126.6, 125.4, 125.0, 119.3, 118.6. HRMS (TOF ES$^+$): m/z calcd for $C_{15}H_{12}NSO_3$ [M+H]$^+$ 286.0532; found, m/z: 286.0538. IR (KBr): 3193, 3164, 3134, 1615, 1351 cm^{-1}.

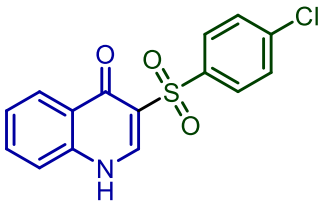
3-Tosylquinolin-4(1H)-one (3b)



This compound is known. [S8]

Beige solid, yield 215 mg (72%). m.p. 231-232ºC. ^{1}H NMR (DMSO-d_6, 700 MHz): δ 12.68 (s, 1H), 8.72 (s, 1H), 8.04 (d, 1H, *J* = 7.3 Hz), 7.89 (d, 2H, *J* = 8.4 Hz), 7.73 (t, 1H, *J* = 7.0 Hz), 7.68 (d, 1H, *J* = 8.3 Hz), 7.41 (t, 1H, *J* = 7.3 Hz), 7.36 (d, 2H, *J* = 8.0 Hz), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 171.5, 143.4, 143.2, 139.5, 138.5, 133.3, 129.1 (2C), 128.0 (2C), 126.6, 125.4, 125.1, 119.3, 119.0, 21.1. HRMS (TOF ES$^+$): m/z calcd for $C_{16}H_{14}NSO_3$ [M+H]$^+$ 300.0689; found, m/z: 300.0694. IR (KBr): 3239, 3160, 1614, 1351 cm^{-1}.

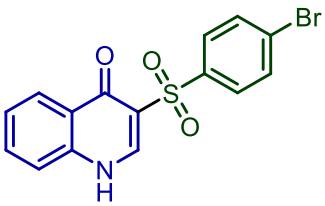
3-((4-Chlorophenyl)sulfonyl)quinolin-4(1H)-one (3c)



Beige solid, yield 214 mg (67%), m.p. 191-192ºC. ^{1}H NMR (DMSO-d_6, 700 MHz): δ 12.84 (s, 1H), 8.76 (s, 1H), 8.04 (d, 3H, *J* = 7.8 Hz), 7.76 (s, 1H), 7.70-7.64 (m, 3H), 7.45 (s, 1H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 171.5, 143.6, 140.1, 139.5, 138.0, 133.3, 129.9 (2C),

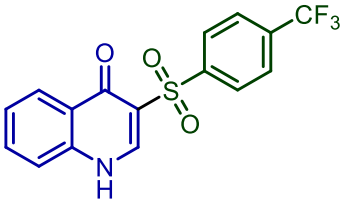
128.8 (2C), 126.6, 125.5, 125.0, 119.3, 118.2. HRMS (TOF ES$^+$): m/z calcd for $C_{15}H_{11}NSO_3Cl$ $[M+H]^+$ 320.0143; found, m/z: 320.0148. IR (KBr): 3212, 3166, 3114, 1620, 1394, 1357 cm^{-1}.

3-((4-Bromophenyl)sulfonyl)quinolin-4(1H)-one (3d)



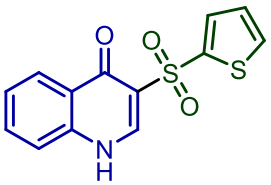
Beige solid, yield 237 mg (65%), m.p. 232-233°C. ^{1}H NMR (DMSO-d_6, 700 MHz): δ 12.87 (s, 1H), 8.75 (s, 1H), 8.05 (d, 1H, *J* = 8.0 Hz), 7.95 (d, 2H, *J* = 8.0 Hz), 7.80-7.74 (m, 2.85H), 7.70 (d, 1H, *J* = 8.1 Hz), 7.64 (t, 0.15H, *J* = 7.2 Hz), 7.57 (t, 0.15H, *J* = 7.2 Hz), 7.45 (t, 1H, *J* = 7.1 Hz). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 171.5, 143.5, 140.5, 139.5, 133.3, 131.8 (2C), 130.0 (2C), 127.1, 126.5, 125.5, 125.0, 119.3, 118.2. HRMS (TOF ES$^+$): m/z calcd for $C_{15}H_{11}NSO_3Br$ $[M+H]^+$ 363.9638; found, m/z: 363.9639. IR (KBr): 3207, 3160, 3130, 1621, 1353 cm^{-1}.

3-((4-(Trifluoromethyl)phenyl)sulfonyl)quinolin-4(1H)-one (3e)



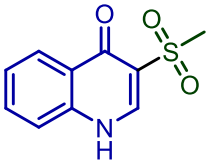
Beige solid, yield 180 mg (51%), m.p. 245-246°C. ^{1}H NMR (DMSO-d_6, 700 MHz): δ 12.90 (s, 1H), 8.80 (s, 1H), 8.24 (d, 2H, *J* = 8.4 Hz), 8.05 (d, 1H, *J* = 7.7 Hz), 7.97 (d, 2H, *J* = 8.1 Hz), 7.77 (t, 1H, *J* = 7.4 Hz), 7.71 (d, 1H, *J* = 8.1 Hz), 7.45 (t, 1H, *J* = 7.4 Hz). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 171.5, 145.2, 144.0, 139.6, 133.4, 132.6 (q, J_{CF} = 32.6), 128.8 (2C), 126.5, 125.9, 125.6, 125.0, 124.3, 122.7, 119.4, 117.5. HRMS (TOF ES$^+$): m/z calcd for $C_{16}H_{11}NSO_3F_3$ $[M+H]^+$ 354.0406; found, m/z: 354.0411. IR (KBr): 3196, 3165, 3133, 1615, 1351 cm^{-1}.

3-(Thiophen-2-ylsulfonyl)quinolin-4(1H)-one (3f)



Beige solid, trace. ^{1}H NMR (DMSO-d_6, 700 MHz): δ 12.79 (s, 1H), 8.74 (d, 1H, *J* = 6.1 Hz), 8.12 (d, 1H, *J* = 9.4 Hz), 7.98 (d, 1H, *J* = 4.7 Hz), 7.87 (d, 1H, *J* = 3.8 Hz), 7.77 (t, 1H, *J* = 8.3 Hz), 7.71 (d, 1H, *J* = 8.4 Hz), 7.47 (t, 1H, *J* = 8.1 Hz), 7.17 (t, 1H, *J* = 5.1 Hz). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 171.4, 142.9, 142.4, 139.4, 134.2, 133.8, 133.3, 127.4, 126.6, 125.5, 125.1, 119.34, 119.25. HRMS (TOF ES$^+$): m/z calcd for $C_{13}H_{10}NS_2O_3$ $[M+H]^+$ 292.0097; found, m/z: 292.0102. IR (KBr): 3215, 3094, 1621, 1343 cm^{-1}

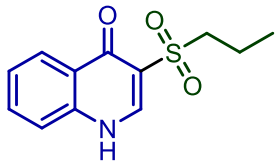
3-(Methylsulfonyl)quinolin-4(1H)-one (3g)



This compound is known. [S9]

Beige solid, yield 109 mg (49%), m.p. 238-239°C. ^{1}H NMR (DMSO-d_6, 700 MHz): δ 12.69 (s, 1H), 8.53 (s, 1H), 8.20 (d, 1H, *J* = 7.6 Hz), 7.79 (t, 1H, *J* = 6.9 Hz), 7.72 (d, 1H, *J* = 7.3 Hz), 7.50 (t, 1H, *J* = 7.3 Hz), 3.26 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 172.4, 142.4, 139.6, 133.3, 126.5, 125.3, 125.1, 119.3, 119.1, 41.9. HRMS (TOF ES$^+$): m/z calcd for $C_{10}H_{10}NSO_3$ $[M+H]^+$ 224.0376; found, m/z: 224.0383. IR (KBr): 3399, 3216, 3171, 1621, 1354 cm^{-1}.

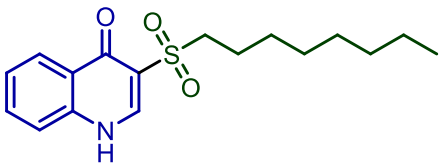
3-(Propylsulfonyl)quinolin-4(1H)-one (3h)



This compound is known. [S9]

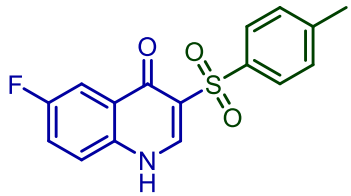
Beige solid, yield 163 mg (65%), m.p. 230-231ºC. ^{1}H NMR (DMSO-d$_6$, 700 MHz): δ 12.72 (s, 1H), 8.51 (s, 1H), 8.18 (d, 1H, *J* = 7.7 Hz), 7.79 (t, 1H, t, *J* = 7.2 Hz), 7.72 (d, 1H, *J* = 7.8 Hz), 7.49 (t, 1H, *J* = 7.2 Hz), 3.41 (t, 2H, *J* = 7.3 Hz), 1.59 (q, 2H, *J* = 6.6 Hz), 0.93 (t, 3H, *J* = 6.6 Hz). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 172.4, 143.1, 139.6, 133.3, 126.4, 125.4, 125.2, 119.3, 117.2, 54.2, 16.0, 12.8. HRMS (TOF ES$^+$): m/z calcd for $C_{12}H_{14}NSO_3$ $[M+H]^+$ 252.0689; found, m/z: 252.0694. IR (KBr): 3450, 3205, 3166, 1622, 1354 cm^{-1}.

3-(Octylsulfonyl)quinolin-4(1H)-one (3i)



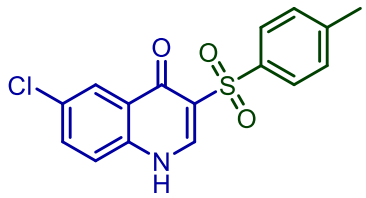
Beige solid, yield 177 mg (55%), m.p. 224-225ºC. ^{1}H NMR (DMSO-d$_6$, 700 MHz): δ 12.71 (s, 1H), 8.51 (s, 1H), 8.18 (d, 1H, *J* = 7.6 Hz), 7.79 (t, 1H, *J* = 7.4 Hz), 7.72 (d, 1H, *J* = 8.0 Hz), 7.49 (t, 1H, *J* = 7.6 Hz), 3.42 (t, 2H, *J* = 7.6 Hz), 1.60-1.54 (m, 2H), 1.31 (t, 2H, *J* = 6.2 Hz), 1.20-1.16 (m, 8H), 0.80 (t, 3H, *J* = 6.7 Hz). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 172.4, 143.1, 139.6, 133.3, 126.5, 125.4, 125.2, 119.3, 117.2, 52.3, 31.1, 28.3 (2C), 27.5, 22.1, 22.0, 13.7. HRMS (TOF ES$^+$): m/z calcd for $C_{17}H_{24}NSO_3$ $[M+H]^+$ 322.1471; found, m/z: 322.1476. IR (KBr): 3204, 3165, 1622, 1352 cm^{-1}.

6-Fluoro-3-tosylquinolin-4(1H)-one (3j)



Beige solid, yield 228 mg (72%), m.p. 237-238ºC. ^{1}H NMR (DMSO-d$_6$, 700MHz): δ 12.88 (s, 1H), 8.77 (s, 1H), 7.90 (d, 2H, *J* = 8.1 Hz), 7.78-7.76 (m, 1H), 7.70 (d, 1H, *J* = 11.7 Hz), 7.67 (t, 1H, *J* = 8.6 Hz), 7.37 (d, 2H, *J* = 8.1 Hz), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 170.6, 160.0, 158.7, 143.5, 143.1, 138.3, 136.3, 129.1 (2C), 128.0 (2C), 122.2, 122.0, 118.5, 109.6, 21.0. HRMS (TOF ES$^+$): m/z calcd for $C_{16}H_{13}NSO_3F$ $[M+H]^+$ 318.0595; found, m/z: 318.0596. IR (KBr): 3206, 3085, 1590, 1348 cm^{-1}.

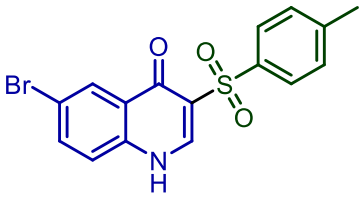
6-Chloro-3-tosylquinolin-4(1H)-one (3k)



This compound is known. [S8]

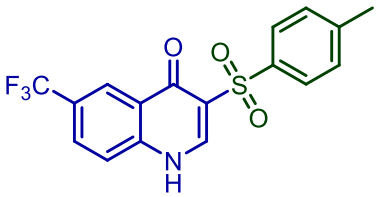
Beige solid, yield 253 mg (76%), m.p. 234-235ºC. ^{1}H NMR (DMSO-d$_6$, 700MHz): δ = 12.89 (s, 1H), 8.78 (s, 1H), 7.97 (d, 1H, *J* = 2.4 Hz), 7.89 (d, 2H, *J* = 8.4 Hz), 7.79 (d, 1H, *J* = 8.9 Hz), 7.73 (d, 1H, *J* = 8.8 Hz), 7.37 (d, 2H, *J* = 8.1 Hz), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 170.3, 143.6, 143.5, 138.3, 138.2, 133.3, 130.0, 129.2 (2C), 128.0 (2C), 127.7, 124.1, 121.7, 119.3, 21.0. HRMS (TOF ES$^+$): m/z calcd for $C_{16}H_{13}NSO_3Cl$ $[M+H]^+$ 334.0299; found, m/z: 334.0296. IR (KBr): 3245, 3194, 1677, 1353 cm^{-1}.

6-Bromo-3-tosylquinolin-4(1H)-one (3l)



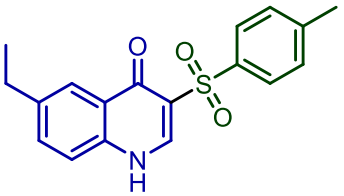
Beige solid, yield 117 mg (31%). ^{1}H NMR (DMSO-d_6, 700 MHz, a mixture of compounds 3l and 3b in a ratio of ~0.8: 0.2): δ 12.88 (s, 0.8H), 12.74 (s, 0.2H), 8.79 (d, 0.8H, *J* = 5.3 Hz), 8.74 (d, 0.2H, *J* = 5.2 Hz), 8.12(d, 0.8H, *J* = 2.1 Hz), 8.05 (d, 0.2H, *J* = 7.9 Hz), 7.91-7.89 (m, 2.7H), 7.76-7.74 (t, 0.3H, *J* = 8.2 Hz), 7.68 (d, 0.2H, *J* = 8.3 Hz), 7.66 (d, 0.8H, *J* = 8.8 Hz), 7.43 (t, 0.2H, *J* = 7.9 Hz), 7.37 (d, 2H, *J* = 8.2 Hz), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 170.2, 143.6, 138.6, 138.2, 135.9, 129.2 (2C), 129.1, 128.0, 128.0 (2C), 127.2, 121.8, 119.4, 118.1, 21.0. HRMS (TOF ES^{+}): m/z calcd for $C_{16}H_{13}NSO_3Br$ $[M+H]^{+}$ 379.9794; found, m/z: 379.9774.

3-Tosyl-6-(trifluoromethyl)quinolin-4(1H)-one (3m)



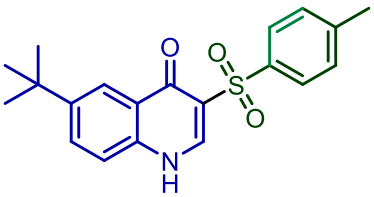
Beige solid, yield 128 mg (35%), m.p. 236-237°C. ^{1}H NMR (DMSO-d_6, 700 MHz): δ 13.1 (s, 1H), 8.86 (s, 1H), 8.29 (s, 1H), 8.07 (d, 1H, *J* = 8.6 Hz), 7.92 (d, 2H, *J* = 8.3 Hz), 7.89 (d, 1H, *J* = 8.6 Hz), 7.38 (d, 2H, *J* = 8.1 Hz), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 170.8, 144.5, 143.7, 142.0, 138.0, 129.2 (2C), 128.0 (2C), 126.2, 125.3 (q, J_{CF} = 32.4), 124.6, 123.0, 122.6, 121.1, 120.2, 21.0. HRMS (TOF ES^{+}): m/z calcd for $C_{17}H_{13}NSO_3F_3$ $[M+H]^{+}$ 368.0563; found, m/z: 368.0565. IR (KBr): 3257, 3191, 1638, 1360 cm^{-1}.

6-Ethyl-3-tosylquinolin-4(1H)-one (3n)



Beige solid, yield 229 mg (70%), m.p. 148-149°C. ^{1}H NMR (DMSO-d_6, 700 MHz): δ 12.69 (s, 1H), 8.69 (s, 1H), 7.89 (d, 2H, *J* = 6.8 Hz), 7.85 (s, 1H), 7.61 (s, 2H), 7.36 (d, 2H, *J* = 6.8 Hz), 2.69 (d, 2H, *J* = 6.7 Hz), 2.36 (s, 3H), 1.17 (t, 3H, *J* = 6.3 Hz). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 171.3, 143.3, 142.6, 141.2, 138.6, 137.7, 133.5, 129.1 (2C), 127.9 (2C), 126.6, 123.0, 119.3, 118.7, 27.8, 21.0, 15.4. HRMS (TOF ES^{+}): m/z calcd for $C_{18}H_{18}NSO_3$ $[M+H]^{+}$ 328.1002; found, m/z: 328.1009. IR (KBr): 3204, 3153, 3113, 1612, 1353 cm^{-1}.

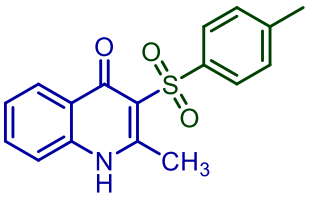
6-(Tert-butyl)-3-tosylquinolin-4(1H)-one (3o)



Beige solid, yield 220 mg (62%), m.p. 156-157°C. ^{1}H NMR (DMSO-d_6, 700MHz): δ 12.70 (s, 1H), 8.70 (s, 1H), 8.00 (d, 1H, *J* = 1.9 Hz), 7.89 (d, 2H, *J* = 8.3 Hz), 7.84 (d, 1H, *J* = 6.5 Hz), 7.63 (d, 1H, *J* = 8.8 Hz), 7.36 (d, 2H, *J* = 8.1 Hz), 2.36 (s, 3H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 171.5, 148.0, 143.3, 142.6, 138.5, 137.5, 131.3, 129.1 (2C), 127.9 (2C), 126.1, 120.2, 119.1, 118.6, 34.5, 30.9 (3C), 21.0. HRMS (TOF ES^{+}): m/z calcd for $C_{20}H_{22}NSO_3$ $[M+H]^{+}$ 356.1315; found, m/z: 356.1314. IR (KBr): 3207, 3162, 1613, 1352 cm^{-1}.

2-(Methyl)-3-tosylquinolin-4(1H)-one (3p)

N-(2-ethynylphenyl)acetamide (1 mmol), sodium *p*-tolylsulfinate (1.5 mmol), silver oxide (232 mg, 1 mmol) and sodium tetrafluoroborate (110 mg, 1 mmol) were mixed in a standard ElectraSyn 10 ml vial and dissolved in 5 ml of DMF (0.2 M). The electrolysis was performed in an undivided cell using a pair of graphite electrodes in a constant current mode at 20 mA. The mixture was stirred for 14 hours at room temperature and 15,07 F/mol of electricity were passed through the reaction mixture. Then the solvent was removed under reduced pressure. The target product was isolated by column chromatography on Silica: eluent hexane: ethyl acetate = 1:1.



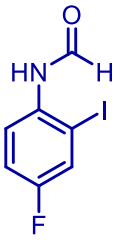
Beige solid, yield 213 mg (68%), m.p. 196-197°C. ^{1}H NMR (DMSO-d$_6$, 700 MHz): δ 12.23 (s, 1H), 7.93 (d, 1H, *J* = 7.9 Hz), 7.86 (d, 2H, *J* = 8.1 Hz), 7.70 (t, 1H, *J* = 7.1 Hz), 7.58 (d, 1H, *J* = 8.3 Hz), 7.36 (t, 1H, *J* = 7.6 Hz), 7.32 (d, 2H, *J* = 8.1 Hz), 2.90 (s, 3H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 172.2, 154.2, 142.7, 140.5, 138.6, 133.0, 128.7 (2C), 127.5 (2C), 125.3, 124.9 (2C), 118.3, 117.9, 21.0, 20.0. HRMS (TOF ES$^+$): m/z calcd for $C_{17}H_{16}NSO_3$ $[M+H]^+$ 314.0845; found, m/z: 314.0846. IR (KBr): 3388, 3272, 1654, 1342 cm^{-1}.

General procedure for preparation of products 4a-f

Sodium carbonate (159 mg, 1.5 mmol) was added to an aqueous solution of the corresponding aniline (1 mmol, 0.15 M). The mixture was stirred for 0.5 hour. Then iodine (508 mg, 2 mmol) was added and the reaction mixture was stirred for 2 hours. The reaction progress was monitored by TLC. Upon completion the reaction mixture was extracted with ethyl acetate. The organic layer was washed with a saturated solution of sodium thiosulfate, then dried over anhydrous sodium sulfate. The organic solvent was evaporated to dryness and the residue was used in next step without further purification.

On the next step formic acid (121 ml, 3.2 mmol) and acetic anhydride (189 ml, 2 mmol) were mixed in a round-bottom flask and stirred under heating (at 60 °C) for 30 minutes. Then the reaction mixture were cooled to 10°C and crude iodaniline (1 mmol) from previous step dissolved in 20 ml of THF was added (0.05 M). The reaction mixture was stirred for 3 hours at room temperature. The organic solvent was removed under reduced pressure. The residue was triturated with water. The resulting precipitate was filtered out on a Schott filter and rinsed with water. The product was recrystallized from a mixture of dichloromethane-hexane.

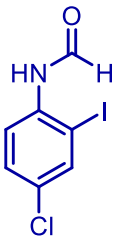
N-(4-Fluoro-2-iodophenyl)formamide (4a)



This compound is known. [S10]

Pink solid, yield 239 mg (61%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.8: 0.2): δ 9.67 (d, 0.2H, *J* = 10.7 Hz), 9.59 (s, 0.8H), 8.32 (d, 0.8H, *J* = 1.6 Hz), 8.25 (d, 0.2H, *J* = 10.7 Hz), 7.81 (q, 0.2H, *J* = 2.6 Hz), 7.77 (q, 0.8H, *J* = 3.2 Hz), 7.70 (q, 0.8H, *J* = 5.5 Hz), 7.37 (q, 0.2H, *J* = 5.5 Hz), 7.31-7.25 (m, 1H).

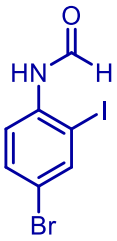
N-(4-Chloro-2-iodophenyl)formamide (4b)



This compound is known. [S10]

Violet solid, yield 231 mg (66%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.8: 0.2): δ 9.70 (d, 0.2H, *J* = 10.3 Hz), 9.59 (s, 0.8H), 8.35 (d, 1H, *J* = 17.6 Hz), 7.97 (s, 0.2H), 7.94 (d, 0.8H, *J* = 2.6 Hz), 7.81 (d, 0.8H, *J* = 8.6 Hz), 7.48-7.45 (m, 1H), 7.36 (d, 0.2H, *J* = 8.6 Hz).

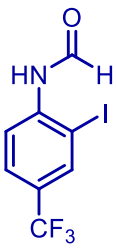
N-(4-Bromo-2-iodophenyl)formamide (4c)



This compound is known. [S10]

Dark brown solid, yield 262 mg (65%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.8: 0.2): δ 9.69 (d, 0.2H, *J* = 10.3 Hz), 9.58 (s, 0.8H), 8.35 (s, 0.8H), 8.33 (s, 0.2H), 8.08 (s, 0.2H), 8.06 (d, 0.8H, *J* = 2.4 Hz), 7.77 (d, 0.8H, *J* = 8.6 Hz), 7.60-7.56 (m, 1H), 7.30 (d, 0.2H, *J* = 8.4 Hz).

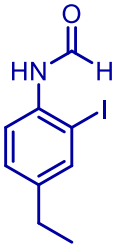
N-(2-Iodo-4-(trifluoromethyl)phenyl)formamide (4d)



This compound is known. [S10]

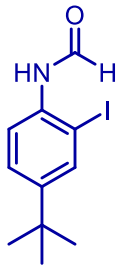
White solid, yield 277 mg (75%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.8: 0.2): δ 9.73 (s, 1H), 8.52 (s, 0.2H), 8.43 (s, 0.8H), 8.18 (s, 1H), 8.13 (d, 0.8H, *J* = 7.8 Hz), 7.76 (d, 1H, *J* = 11.6 Hz), 7.55 (s, 0.2H).

N-(4-Ethyl-2-iodophenyl)formamide (4e)



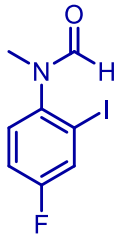
Dark brown solid, yield 261 mg (90%), m.p. 74-75°C. ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.75: 0.25): δ 9.59 (d, 0.25H, *J* = 10.3 Hz), 9.47 (s, 0.75H), 8.30 (s, 0.75H), 8.27 (d, 0.25H, *J* = 11.2 Hz), 7.75 (s, 0.25H), 7.72 (s, 0.75H), 7.62 (d, 0.75H, *J* = 8.4 Hz), 7.25-7.21 (m, 1.25H), 2.58-2.53 (m, 2H), 1.15 (t, 3H, *J* = 7.5 Hz). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 163.8, 160.2, 143.9, 142.9, 138.5, 138.1, 136.9, 136.2, 128.8, 128.1, 124.9, 124.7, 95.6, 93.2, 27.0, 15.5. HRMS (TOF ES$^+$): m/z calcd for $C_9H_{11}NOI$ $[M+H]^+$ 275.9880; found, 275.9885. IR (KBr): 3253 cm^{-1}.

N-(4-(Tert-butyl)-2-iodophenyl)formamide (4f)



Brown solid, yield 221 mg (64%), m.p. 92-93°C. ^{1}H NMR (DMSO-d_6, 700 MHz, a mixture of rotamers in a ratio of ~0.75: 0.25): δ 9.60 (d, 0.25H, *J* = 10.7 Hz), 9.48 (s, 0.75H), 8.30-8.28 (m, 1H), 7.84 (s, 0.25H), 7.80 (s, 0.75H), 7.65 (d, 0.75H, *J* = 8.2 Hz), 7.43-7.40 (t, 1H, *J* = 8.2 Hz), 7.24 (d, 0.25H, *J* = 7.8 Hz), 1.25 (s, 9H); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 163.8, 160.2, 150.6, 149.7, 136.8, 136.04, 136.00, 135.0, 126.4, 125.8, 124.51, 124.45, 95.6, 93.1, 34.1, 30.9; HRMS (TOF ES^{+}): m/z calcd for $C_{11}H_{15}NOI$ $[M+H]^{+}$ 304.0193; found, 304.0198. IR (KBr): 3244 cm^{-1}.

N-(4-Fluoro-2-iodophenyl)-N-methylformamide (4aa)

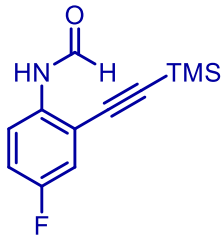


N-(4-Fluoro-2-iodophenyl)formamide (1 mmol) was dissolved in 20 ml of ethanol (0.05 M) and potassium carbonate (428 mg, 3.1 mmol) was added to the solution. The mixture was stirred for 20 minutes. Then methyl iodide (403 ml, 3 mmol) was added, and the reaction mixture was stirred for 7 hours. The reaction progress was monitored by TLC. Upon completion, water was added and reaction mass was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and solvent was removed in vacuo. The product was isolated by column chromatography (eluent: hexane-ethyl acetate: 7:1). Brown oil, yield 220 mg (79%). ^{1}H NMR (DMSO-d_6, 700 MHz, a mixture of rotamers in a ratio of ~0.75: 0.25): δ 8.32 (d, 0.05H, *J* = 1.7 Hz), 8.30 (s, 0.2H), 8.04 (s, 0.75H), 7.88-7.86 (q, 0.75H, *J* = 8.1 Hz), 7.82-7.81 (q, 0.25H, *J* = 8.1 Hz), 7.53-7.51 (q, 0.75H, *J* = 8.8 Hz), 7.39-7.33 (m, 1.25H), 3.19 (s, 0.7H), 3.04 (s, 2.3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 162.7, 162.3, 161.6, 161.3, 160.3, 160.2, 159.9, 140.7, 140.0, 130.62, 130.57, 130.25, 130.2, 126.0, 125.9, 125.7, 125.5 125.3, 116.6, 116.5, 115.5, 115.4, 100.5, 100.4, 99.38, 99.33, 36.4, 32.7; HRMS (TOF ES^{+}): m/z calcd for C_8H_8NOFI $[M+H]^{+}$ 280.9707; found, m/z: 280.9715.

Sonogashira coupling, synthesis of 5a-g, general procedure

In a Schlenk flask, equipped with a magnetic stirrer, *N*-(2-iodophenyl)formamide (1 mmol), 15 ml of triethylamine (0.067 M), copper (I) iodide (8 mg, 4 mmol %) and $Pd[P(Ph)_3]_2Cl_2$ (14 mg, 2 mmol. %) were mixed under argon atmosphere. Then trimethylsilylacetylene (284 ml, 2 mmol) was added and the reaction mass was stirred at room temperature for 1.5 hours. Upon completion the reaction mass was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate, and the organic solvent was evaporated in vacuo. The products 5a-5g were isolated by column chromatography (eluent: hexane : ethyl acetate = 5 : 1).

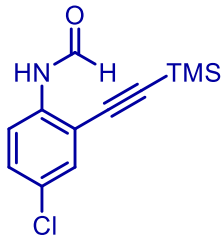
N-(4-Fluoro-2-((trimethylsilyl)ethynyl)phenyl)formamide (5a)



This compound is known. [S3]

Brown solid, yield 186 mg (74%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.75: 0.25): δ 9.76 (d, 0.25H, *J* = 10.6 Hz), 9.50 (s, 0.75H), 8.54 (d, 0.25H, *J* = 11.0 Hz), 8.36 (s, 0.75H), 8.04 (q, 0.75H, *J* = 5.2 Hz), 7.36 (d, 0.25H, *J* = 7.2 Hz), 7.32 (q, 0.75H, *J* = 5.2 Hz), 7.29-7.24 (m, 1.25H), 0.26 (s, 6.70H), 0.23 (s, 2.30H).

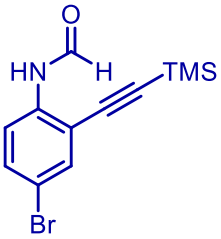
N-(4-Chloro-2-((trimethylsilyl)ethynyl)phenyl)formamide (5b)



This compound is known. [S3]

Brown solid, yield 201 mg (80%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.75: 0.25): δ 9.82 (d, 0.25H, *J* = 11.0 Hz), 9.54 (s, 0.75H), 8.65 (d, 0.25H, *J* = 10.7 Hz), 8.39 (s, 0.75H), 8.14 (d, 1H, *J* = 8.6 Hz), 7.51 (d, 0.75H, *J* = 15.4 Hz), 7.45 (q, 1H, *J* = 2.4 Hz), 7.30 (d, 0.25H, *J* = 8.4 Hz), 0.27 (s, 6.8H), 0.23 (s, 2.2H).

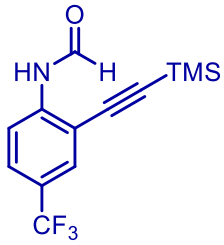
N-(4-Bromo-2-((trimethylsilyl)ethynyl)phenyl)formamide (5c)



This compound is known. [S3]

Brown solid, yield 246 mg (83%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.75: 0.25): δ 9.80 (d, 0.25H, *J* = 10.4 Hz), 9.53 (s, 0.75H), 8.67 (d, 0.25H, *J* = 10.7 Hz), 8.40 (s, 0.75H), 8.09 (d, 0.75H, *J* = 8.9 Hz), 7.65-7.63 (m, 1H), 7.56 (d, 1H, *J* = 10.9 Hz), 7.23 (d, 0.25H, *J* = 8.4 Hz), 0.27 (s, 7H), 0.23 (s, 2H).

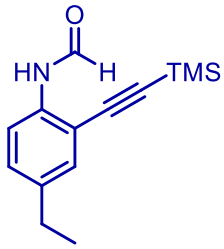
N-(4-(Trifluoromethyl)-2-((trimethylsilyl)ethynyl)phenyl)formamide (5d)



This compound is known. [S3]

Light brown solid, yield 226 mg (84%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.75: 0.25): δ 9.98 (s, 0.25H), 9.70 (s, 0.75H), 8.86 (s, 0.25H), 8.48 (s, 0.75H), 8.42 (d, 0.75H, *J* = 8.7 Hz), 7.78 (s, 1H), 7.74 (d, 1H, *J* = 8.7 Hz), 7.5 (s, 0.25H), 0.28 (s, 9H).

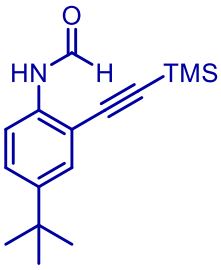
N-(4-Ethyl-2-((trimethylsilyl)ethynyl)phenyl)formamide (5e)



Brown solid, yield 196 mg (80%), m.p. 51-52°C. ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.7: 0.3): δ 9.66 (d, 0.3H, *J* = 10.8 Hz), 9.36 (s, 0.7H), 8.59 (d, 0.3H, *J* = 10.8 Hz), 8.36 (s, 0.7H), 7.98 (d, 0.7H, *J* = 8.3 Hz), 7.29 (d, 1H, *J* = 17.9 Hz), 7.23 (t, 1H, *J* = 9.4 Hz), 7.17 (d, 0.3H, *J* = 7.9 Hz), 2.57-2.53 (m, 2H), 1.14 (t, 3H, *J* = 7.6 Hz), 0.26 (s, 6.35H), 0.23 (s, 2.65H). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 163.4, 160.4, 140.7, 139.7, 136.7, 136.3,

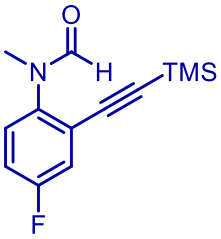
132.1, 131.6, 129.8, 129.2, 122.1, 121.5, 115.0, 113.2, 27.23, 27.18, 15.46, -0.10, -0.23. HRMS (TOF ES$^+$): m/z calcd for $C_{14}H_{20}SiNO$ $[M+H]^+$ 246.1309; found, 246.1314. IR (KBr): 3247, 3105, 2150 cm^{-1}.

N-(4-(Tert-butyl)-2-((trimethylsilyl)ethynyl)phenyl)formamide (5f)



Brown solid, yield 205 mg (75%). m.p. 72-73^{o}C. ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.7: 0.3): δ 9.66 (d, 0.3H, *J* = 10.9 Hz), 9.35 (s, 0.7H), 8.61 (d, 0.3H, *J* = 10.9 Hz), 8.36 (s, 0.7H), 7.98 (d, 0.7H, *J* = 8.6 Hz), 7.43-7.41 (m, 1.3H), 7.39 (d, 0.7H, *J* = 2.1 Hz), 7.18 (d, 0.3H, *J* = 8.4 Hz), 1.25 (s, 9H), 0.26 (s, 6.35H), 0.23 (s, 2.65H). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 163.4, 160.4, 147.5, 146.5, 136.5, 136.2, 129.4, 128.9, 127.4, 126.8, 121.8, 121.2, 114.6, 112.9, 102.3, 100.9, 100.3, 98.8, 34.1, 30.9, -0.07, -0.22. HRMS (TOF ES$^+$): m/z calcd for $C_{16}H_{24}SiNO$ $[M+H]^+$ 274.1622; found, m/z: 274.1627. IR (KBr): 3249, 3166, 3100, 2153 cm^{-1}.

N-(4-Fluoro-2-((trimethylsilyl)ethynyl)phenyl)-N-methylformamide (5g)



Brown oil, yield 194 mg (78%). ^{1}H NMR (DMSO-d$_6$, 700 MHz, a mixture of rotamers in a ratio of ~0.85: 0.15): δ 8.27 (s, 0.2H), 8.18 (s, 0.8H), 7.49-7.47 (q, 1H, *J* = 8.8 Hz), 7.45-7.43 (q, 0.85H, *J* = 9.1 Hz), 7.42-7.40 (m, 0.15H), 7.38-7.35 (m, 0.85H), 7.34-7.33 (q, 0.15H, *J* = 8.3 Hz), 7.29-7.24 (m, 1.25H), 3.25 (s, 0.3H), 3.14 (s, 2.7H), 0.21 (s, 1.5H), 0.20 (s, 7.5H). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 150 MHz): δ 162.50, 162.45, 161.0, 159.6, 140.4, 129.39, 129.33, 121.71, 121.65, 119.2, 119.1, 117.6, 117.5, 100.9, 100.2, 36.1, 32.5, -0.4, -0.5. HRMS (TOF ES$^+$): m/z calcd for $C_{13}H_{17}SiNOF$ $[M+H]^+$ 250.1058; found, m/z: 250.1063.

Cyclic Voltammetry Studies

Voltammetric studies were carried out using potentiostat P30JM with a scan rates of 0.1 $V \cdot s^{-1}$ in a temperature-controlled (25 °C) glass cell (V = 10 mL) under an argon atmosphere. A glassy carbon disk (d = 2.9 mm) was used as the working electrode (carefully polished before each measurement). A $Ag/AgNO_3$ reference electrode separated from the solution being studied by a salt bridge filled with the supporting electrolyte (0.1M Et_4NBF_4 in DMF) was used as the reference electrode. A platinum wire (l = 3 cm) was used as the counter electrode. Experiment was performed with the concentration of studied compounds of 1 mM.

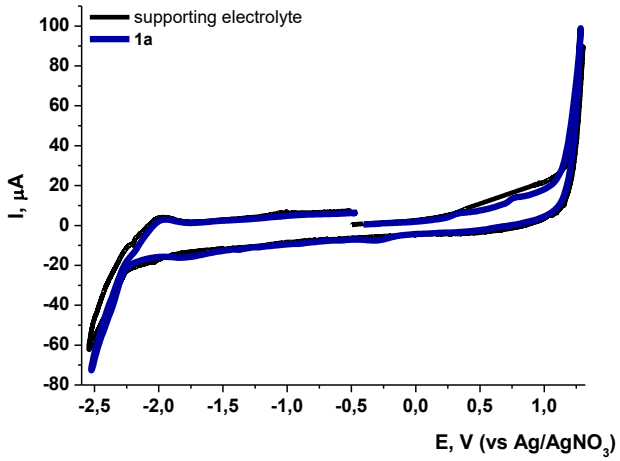


Figure S2. *N*-(2-ethynylphenyl)formamide **1a** (initial anodic scan).

Electrochemically inactive (supporting electrolyte discharge is observed)

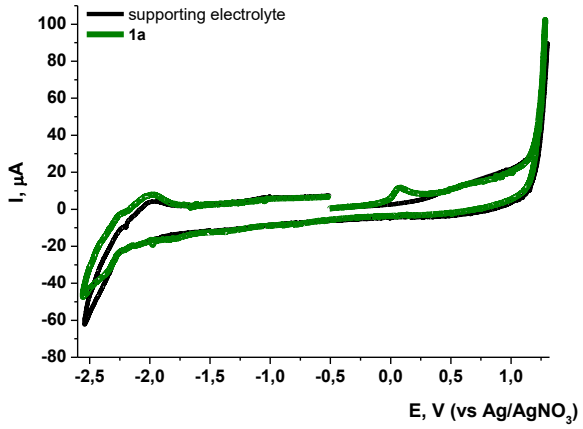


Figure S3. Phenyl sulfinate sodium **2a** (initial anodic scan).

E_p^{ox} = +0.07 V, i_p^{ox} = 11.09 µA (irreversible peak)

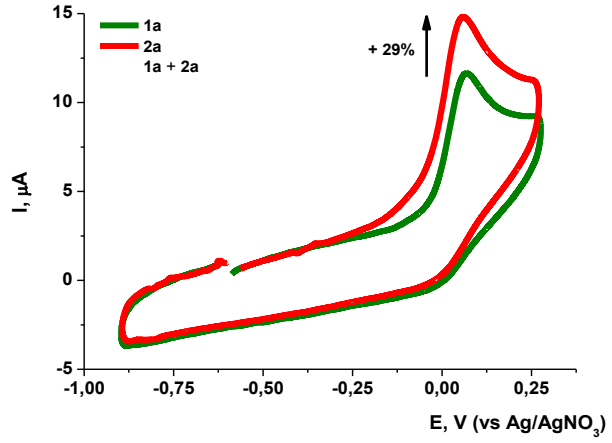
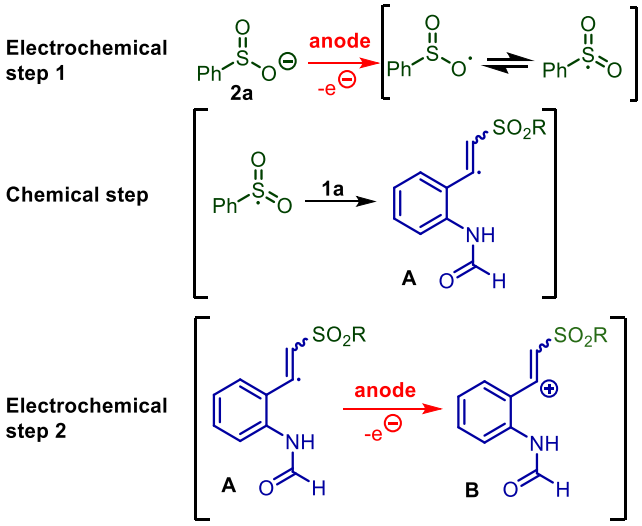


Figure S4. 1a, **2a**, mixture of **1a** and **2a** (initial anodic scan).

2a: E_p^{ox} = +0.07 V, i_p^{ox} = 11.09 µA (irreversible peak);

2a + **1a**: E_p^{ox} = +0.06 V, i_p^{ox} = 14.35 µA (29% increase in current).



Scheme S1. Proposed electrochemical steps.

Compound **1a** is electrochemically inactive, with its curve closely resembling that of the supporting electrolyte (**Figure S2**). In contrast, compound **2a** exhibits an irreversible peak at 0.07 V (**Figure S3**), indicative of the formation of the corresponding radical. Notably, the addition of **1a** to **2a** (**Figure S4**) results in a significant current increase of 29%, likely due to an increase in the number of electrochemical stages in the process. This observation aligns well with **Scheme S1**, which illustrates the anodic oxidation of **2a** to the corresponding radical, its isomerization and subsequent addition to **1a** to form radical **A**, and the anodic oxidation to cation **B**. It is noteworthy that we have previously observed a similar mechanism and voltammetric data in the reaction of anodically generated thiocyanate radicals with anilines. [S2]

X-Ray Analysis

The crystal structure of **3h** (Figure S5) was determined by X-Ray structural analysis using an automatic four-circle area-detector diffractometer Bruker KAPPA APEX II with MoKα radiation. The cell parameters were refined over the entire data set, together with data reduction using SAINT-Plus software [Bruker AXS Inc.: Madison, WI, U. SAINT, V8.40B 2020]. Absorption corrections were introduced using the SADABS program [Krause, L.; Herbst-Irmer, R.; Sheldrick, G.M.; Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Crystallogr.* **2015**, *48*, 3–10. https://doi.org/10.1107/S1600576714022985]. The structures were solved using the SHELXT-2018/2 program [Sheldrick, G.M. SHELXT-Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2015**, *71*, 3–8. https://doi.org/10.1107/S2053273314026370] and refined by full-matrix least squares on F^2 in the anisotropic approximation for all non-hydrogen atoms (SHELXL-2018/3 [Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8. https://doi.org/10.1107/S2053229614024218]). The hydrogen atoms were objectively located from the difference Fourier synthesis and refined with isotropic temperature factors equal to $1.2U_{eq}$(C, N) for CH-, CH_2- and NH- groups, and $1.5U_{eq}$(C) for CH_3-groups.

The crystal was obtained by slow cooling of hot solution of 3-(propylsulfonyl)quinoline-4(1*H*)-one **3h** in the methanol–toluene mixture.

Crystal data, data collection, and structure refinement details are summarized in Table S1. The atomic coordinates were deposited at the Cambridge Crystallographic Data Centre [Groom, C.R.; Bruno, I.J.; Lightfoot, M.P.; Ward, S.C. The Cambridge Structural Database. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* **2016**, *72*, 171–179. https://doi.org/10.1107/S2052520616003954], CCDC № 2396543**.**

Table S1. Crystal data and structure refinement for **3h.**

Identification code	**3h**
CCDC number	**2396543**
Empirical formula	$C_{12}H_{13}NO_3S$
Formula weight	251.29
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.076(12)
b/Å	7.671(8)
c/Å	12.444(12)
α/°	90
β/°	98.72(5)
γ/°	90
Volume/Å^3	1139(2)

Z	4
ρ_{calc}g/cm^3	1.465
μ/mm^1	0.279
F(000)	528.0
Crystal size/mm^3	0.28 × 0.11 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.494 to 50
Index ranges	-14 ≤ h ≤ 14, -9 ≤ k ≤ 9, -13 ≤ l ≤ 14
Reflections collected	11767
Independent reflections	1994 [R_{int} = 0.2719, R_{sigma} = 0.2011]
Data/restraints/parameters	1994/0/193
Goodness-of-fit on F^2	0.992
Final R indexes [I>=2σ (I)]	R_1 = 0.0745, wR_2 = 0.1162
Final R indexes [all data]	R_1 = 0.1881, wR_2 = 0.1605
Largest diff. peak/hole / e Å^{-3}	0.46/-0.43

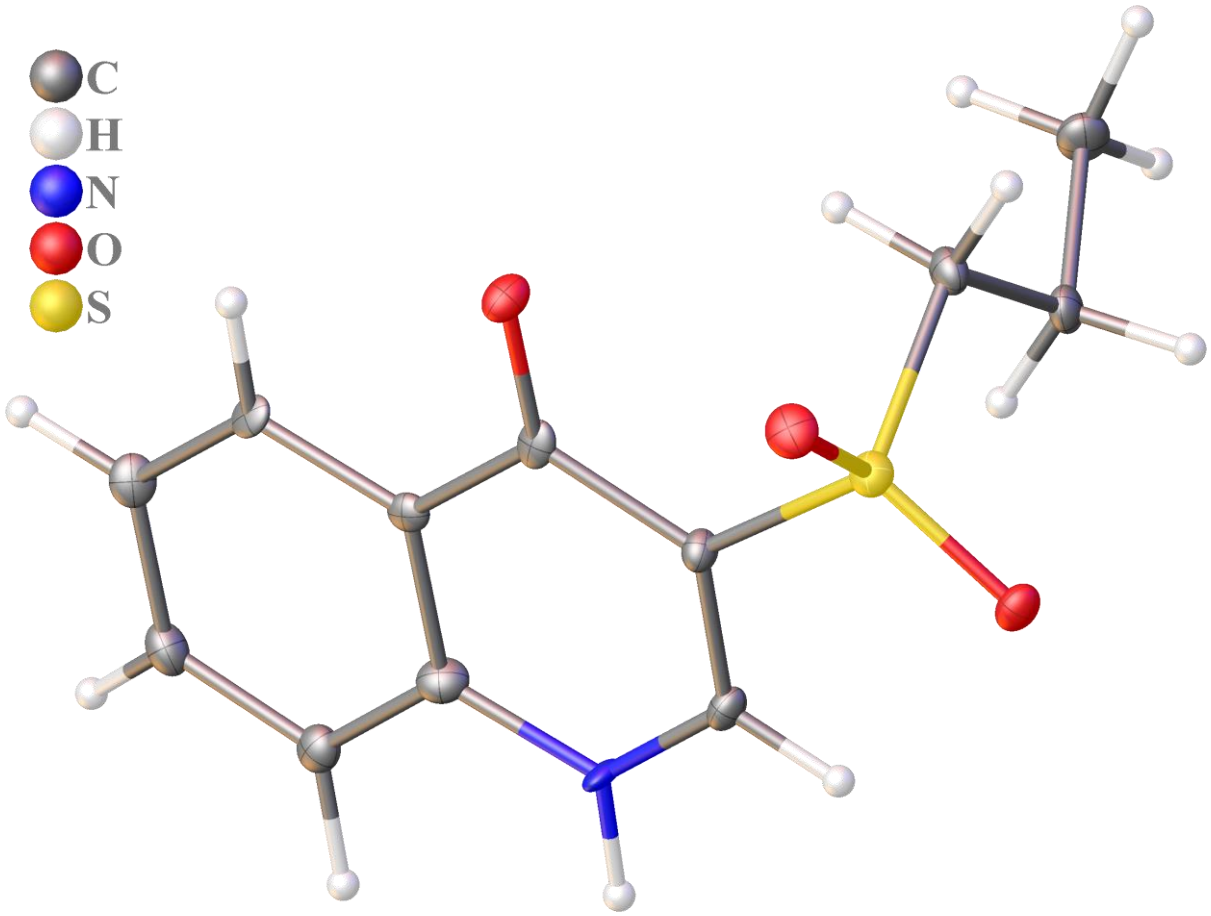


Figure S5. Molecular structure of **3h**. Displacement ellipsoids are drawn at the 50% probability level.

$H_2{}^{18}O$-labeled Experiment

N-(2-(Ethynyl)phenyl)formamide **1a** (1 mmol), sodium phenyl sulfinate **2a** (1.5 mmol), silver oxide (0.232 g, 1 mmol) and sodium tetrafluoroborate (0.110 g, 1 mmol) were mixed in a standard ElectraSyn 10 ml vial, dissolved in 5 ml of DMF (0.2 M), and 0.18 ml $H_2{}^{18}O$ (50% isotope content) was added. The electrolysis was performed in an undivided cell using a pair of graphite electrodes in a constant current mode at 20 mA. The mixture was stirred for 14 hours at room temperature and 15,07 F/mol of electricity were passed through the reaction mixture. Then the solvent was removed under reduced pressure. The target product **3b** was isolated with 59% yield by column chromatography on Silica: eluent hexane: ethyl acetate = 1:1 and submitted to HRMS using FT-ICR-MS solariX XR 15T, Bruker. Alternatively, regular water has been used in the same experiment. The resulting compound was isolated with 72% yield and submitted for HRMS. As could be seen from the Figure S6, the content of ^{18}O ion in regular water experiment is natural, but in the $H_2{}^{18}O$ experiment the content is significantly higher. Still, the incorporation of ^{18}O was very low (Figure S7).

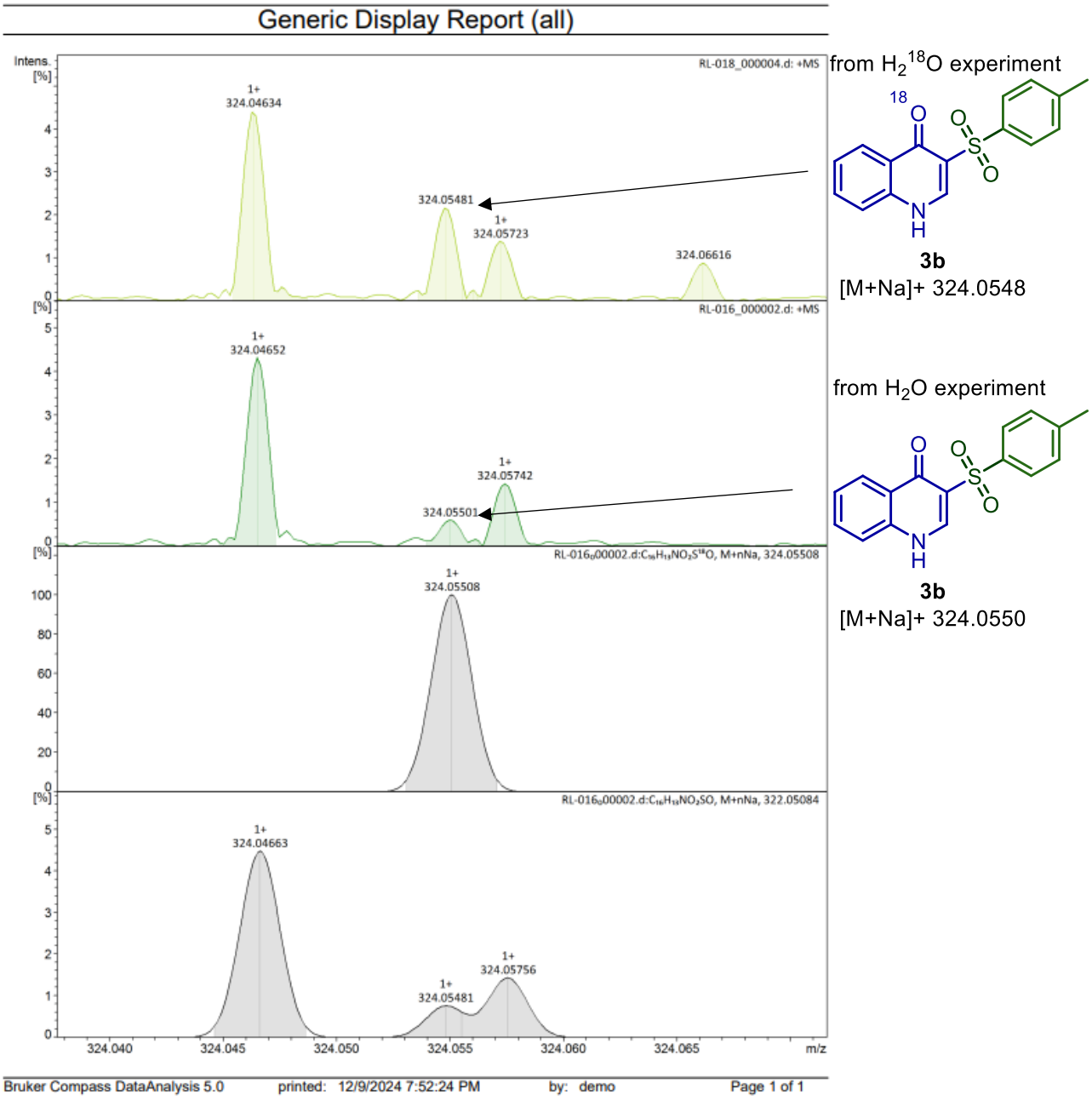


Figure S6. Zoom region of HRMS Spectra for labeled and non-labeled quinolones.

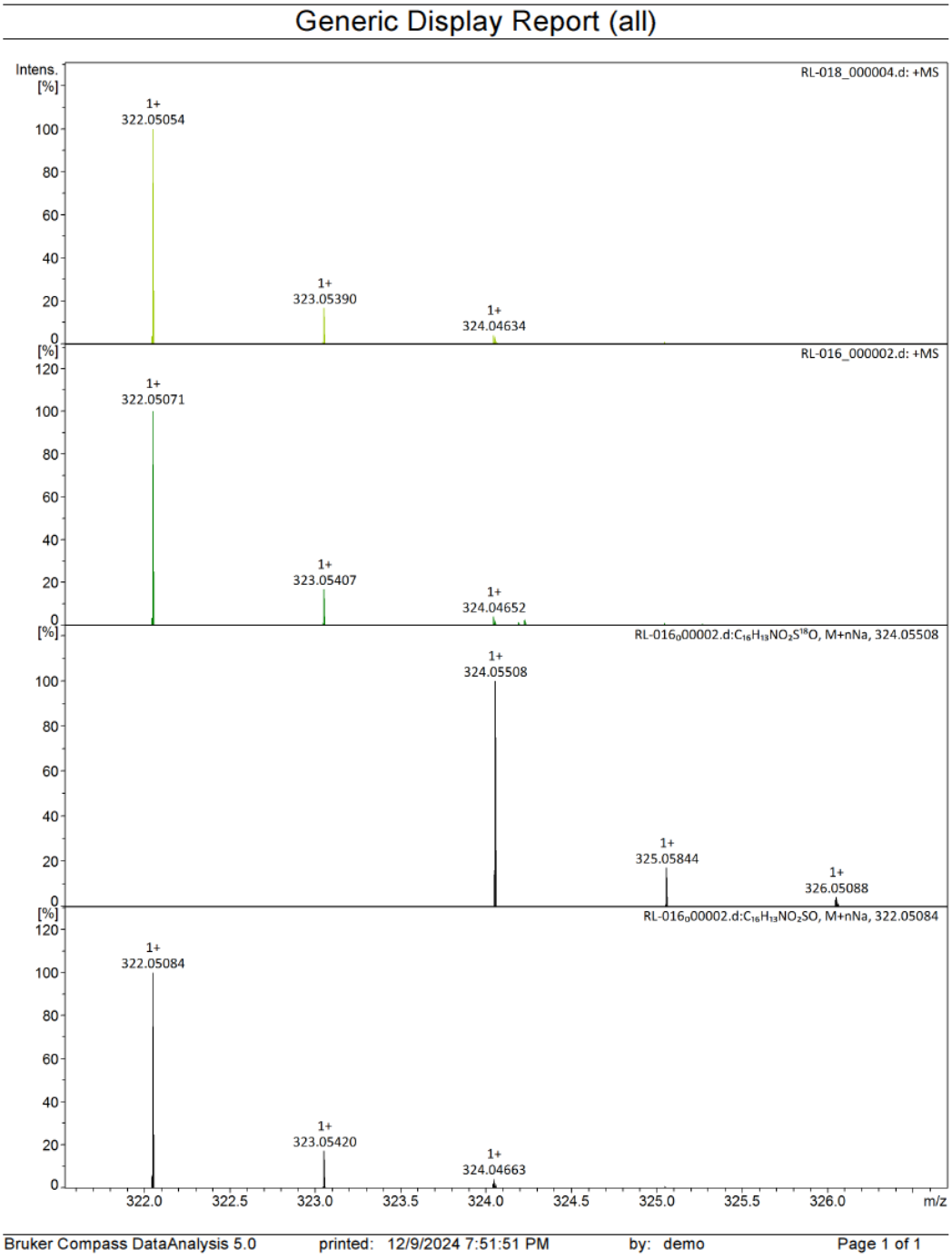


Figure S7. HRMS Spectra for labeled and non-labeled quinolones.

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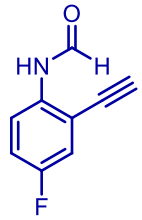
COPIES of

^{1}H and ^{13}C

SPECTRA



(1a)

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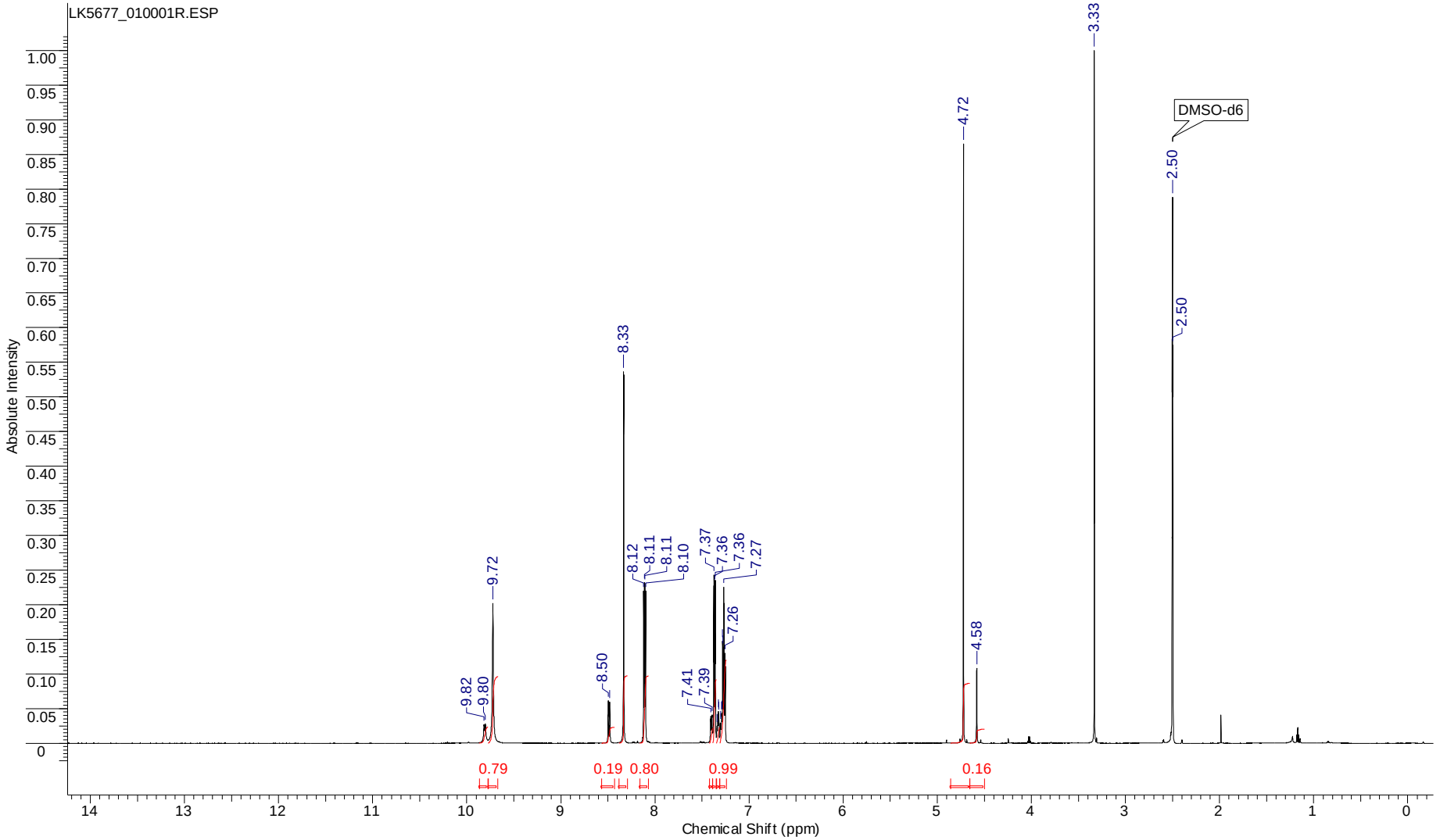

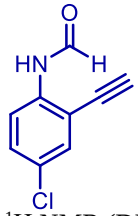

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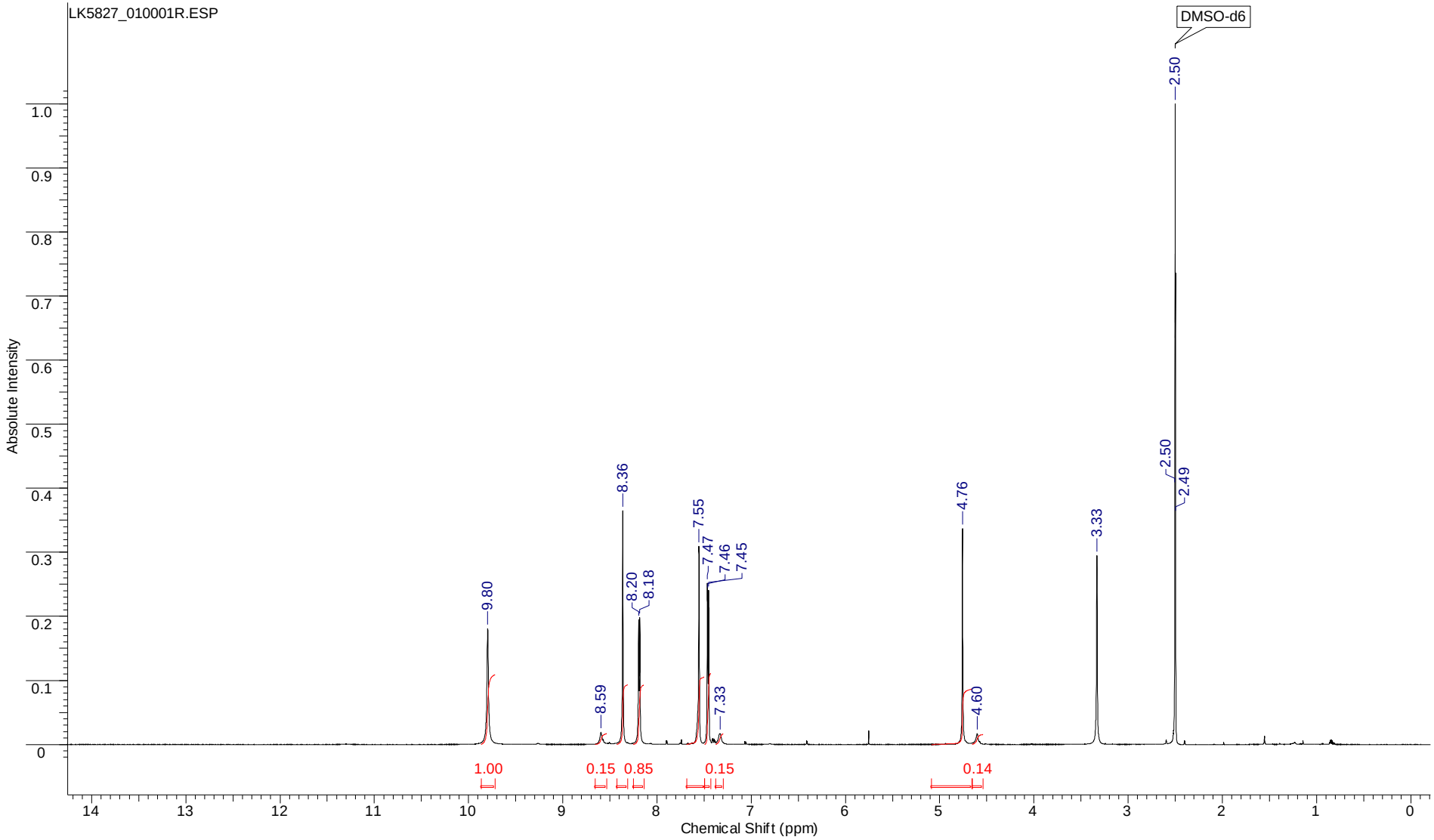
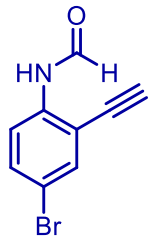
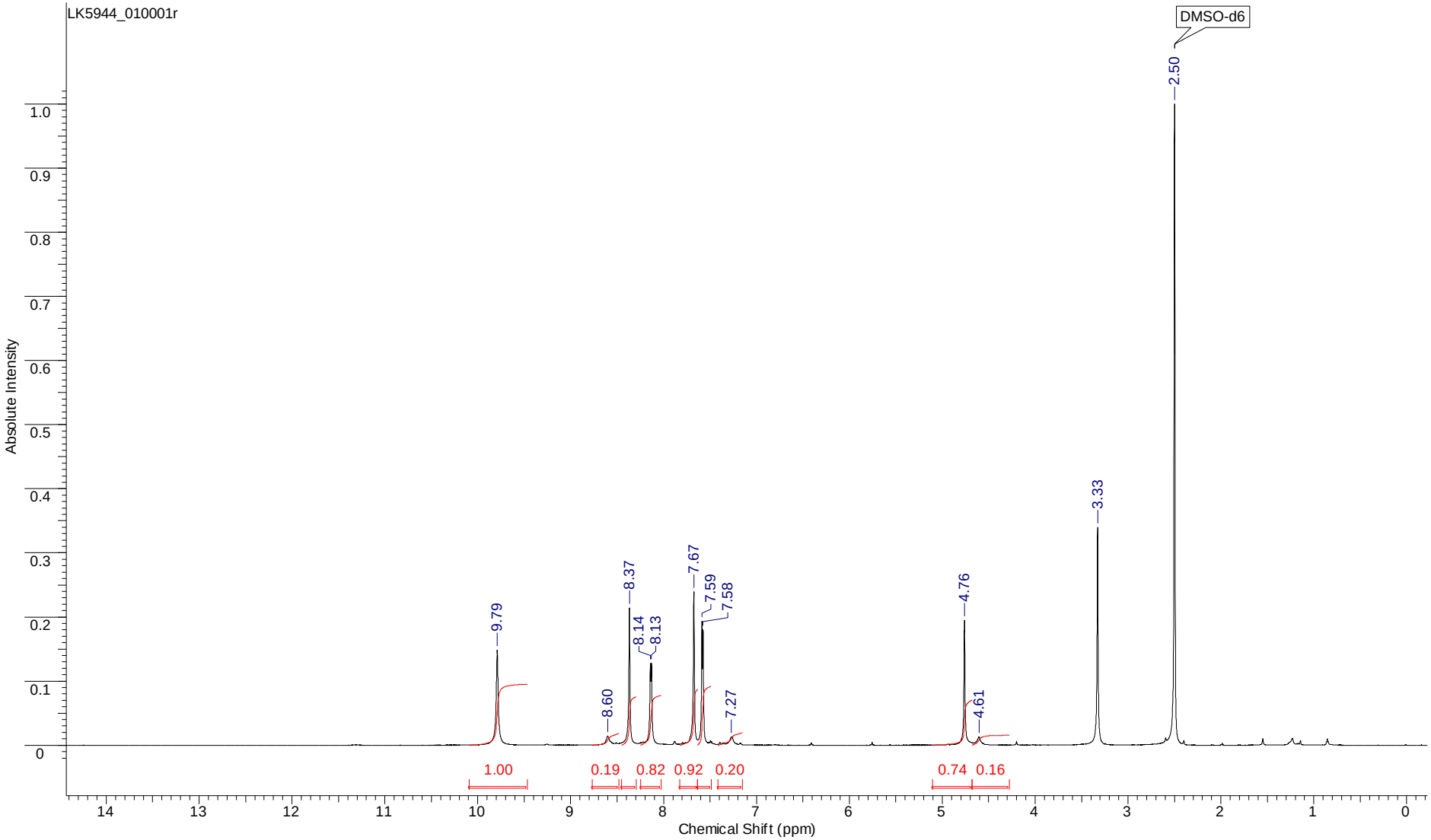
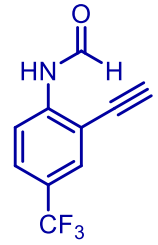




(1c)

^{1}H NMR (DMSO, 700 MHz):





(1d)

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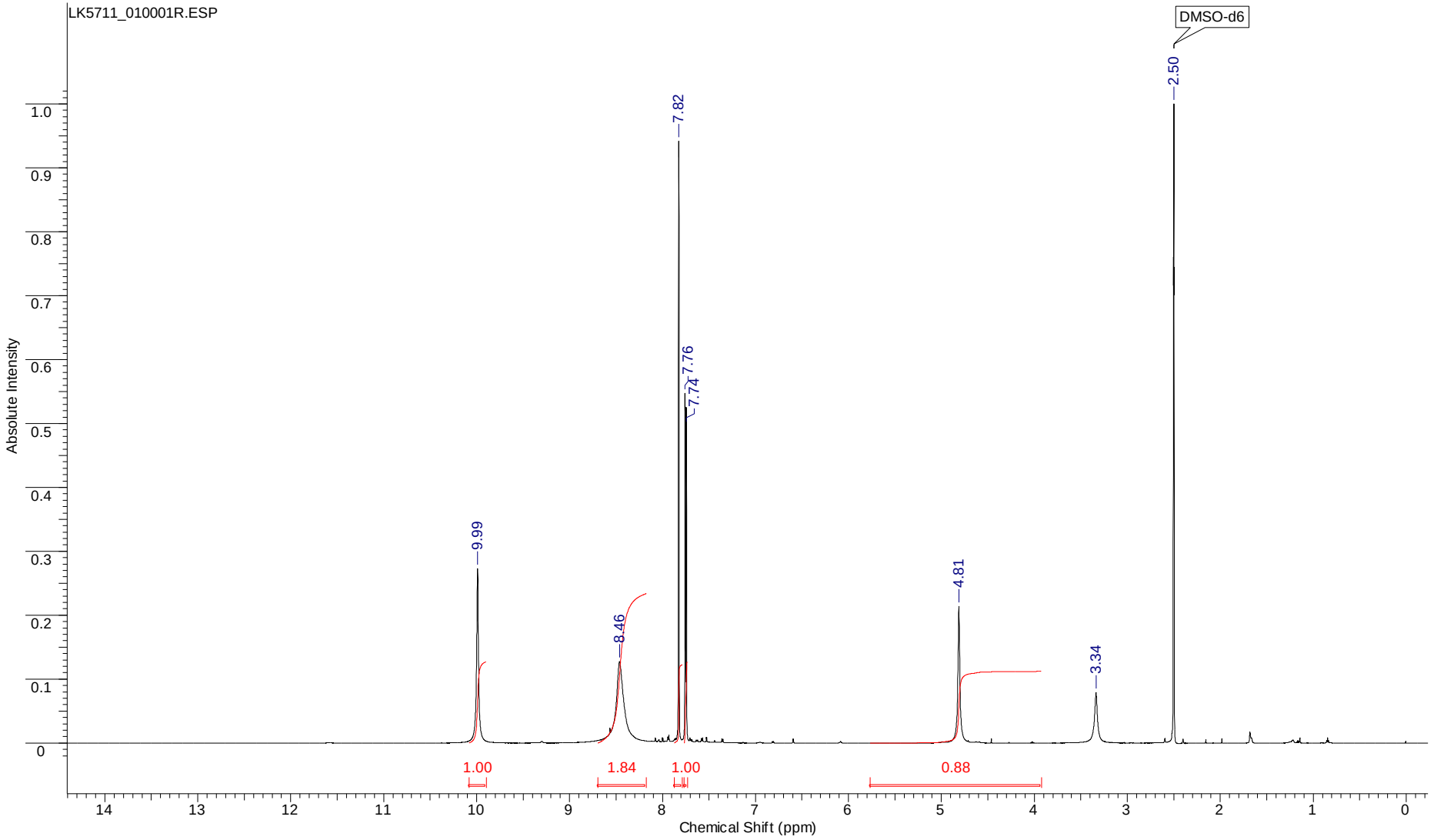

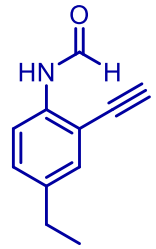

(1e)

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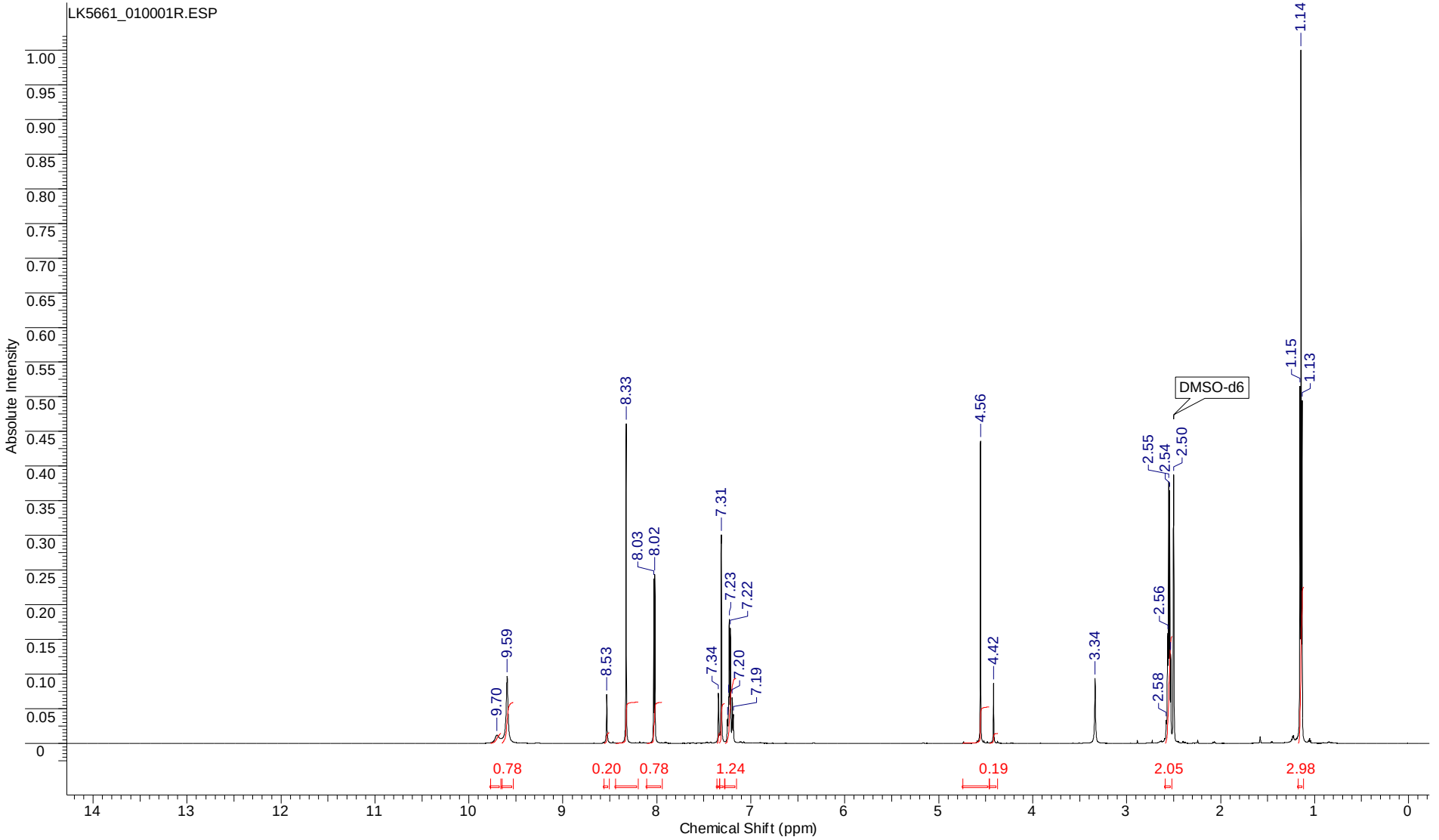
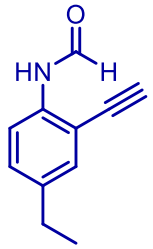
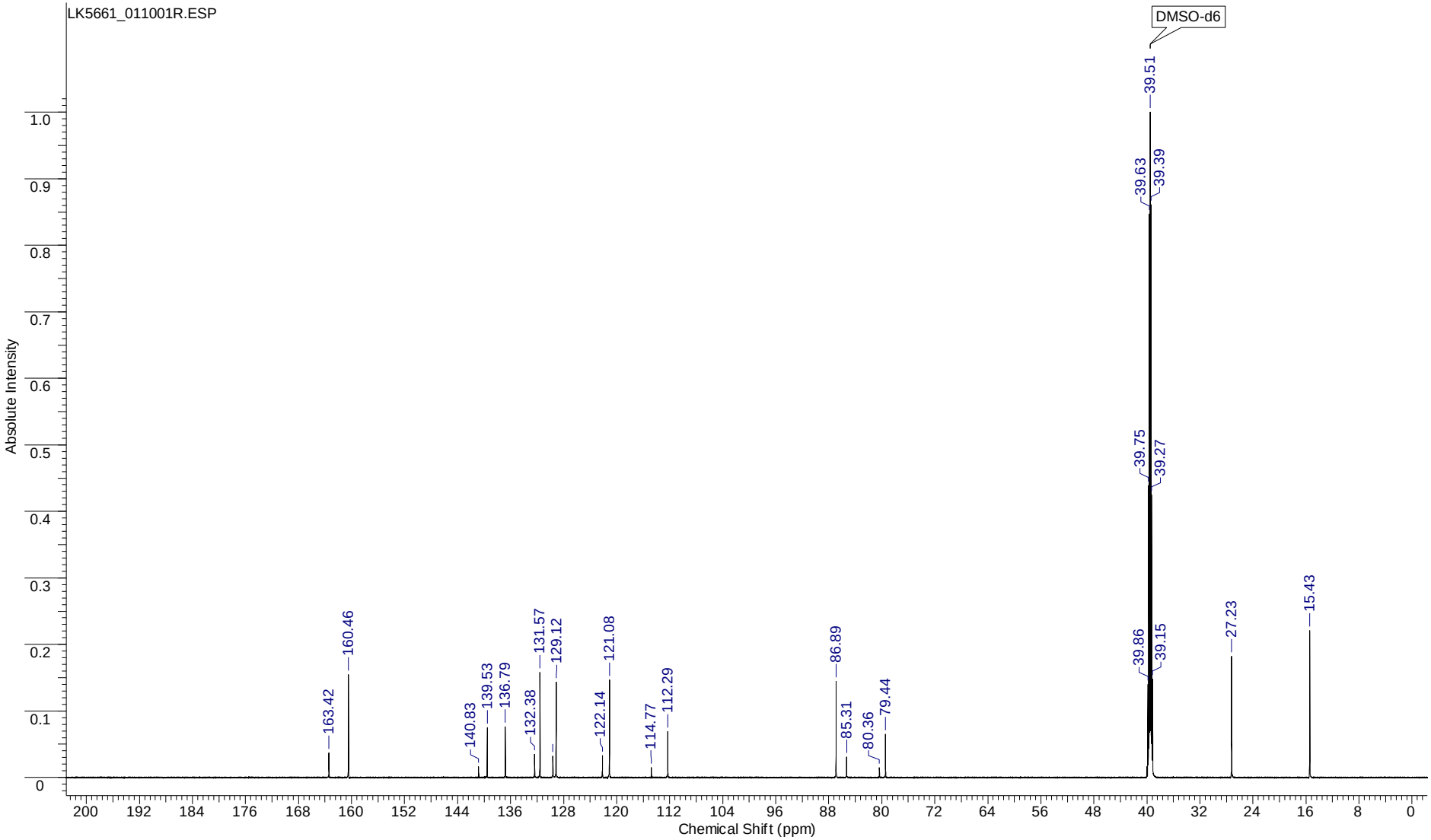
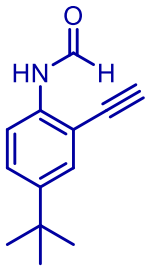




(1e) ^{13}C NMR (DMSO, 150 MHz):





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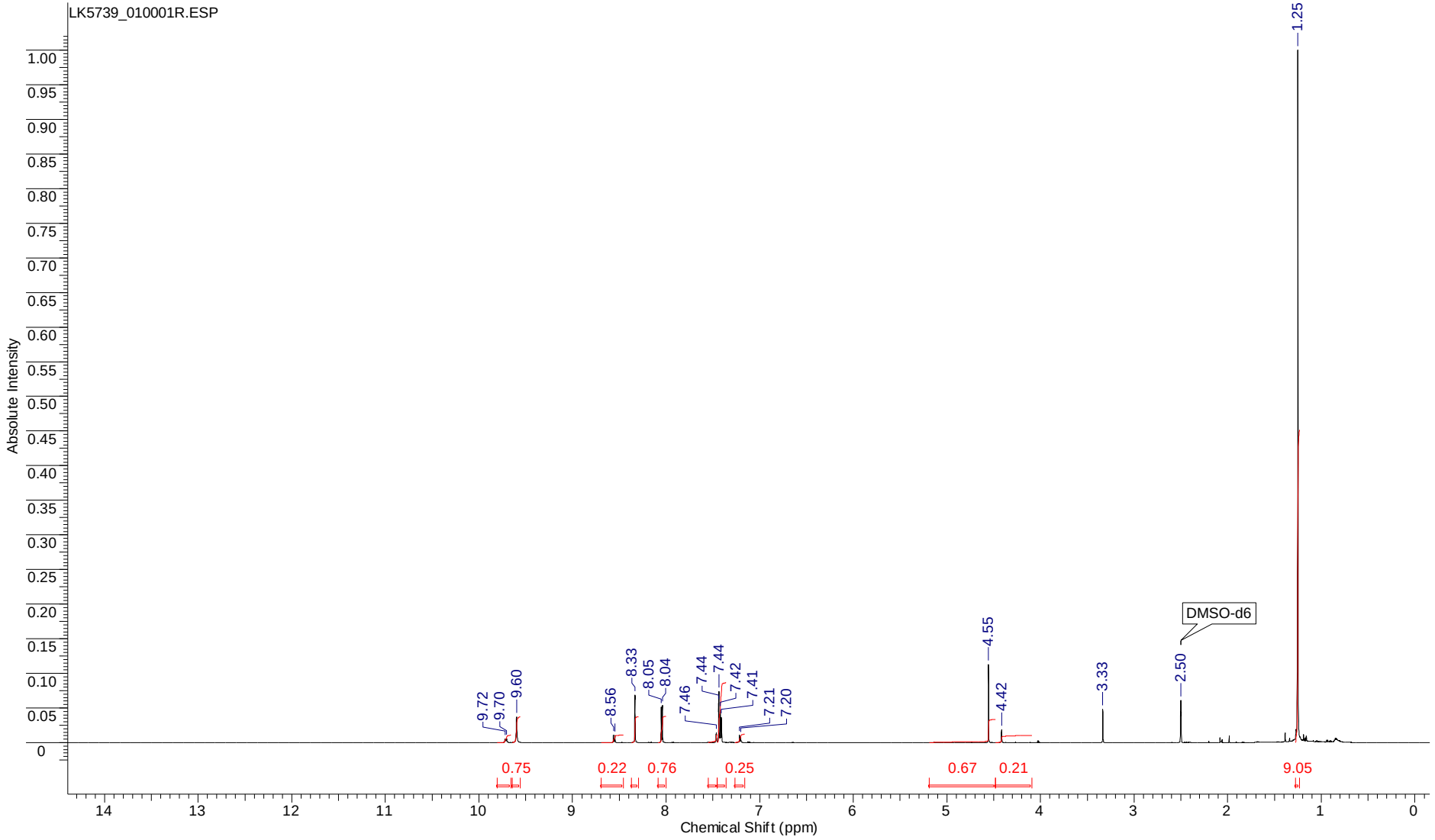

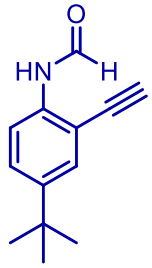

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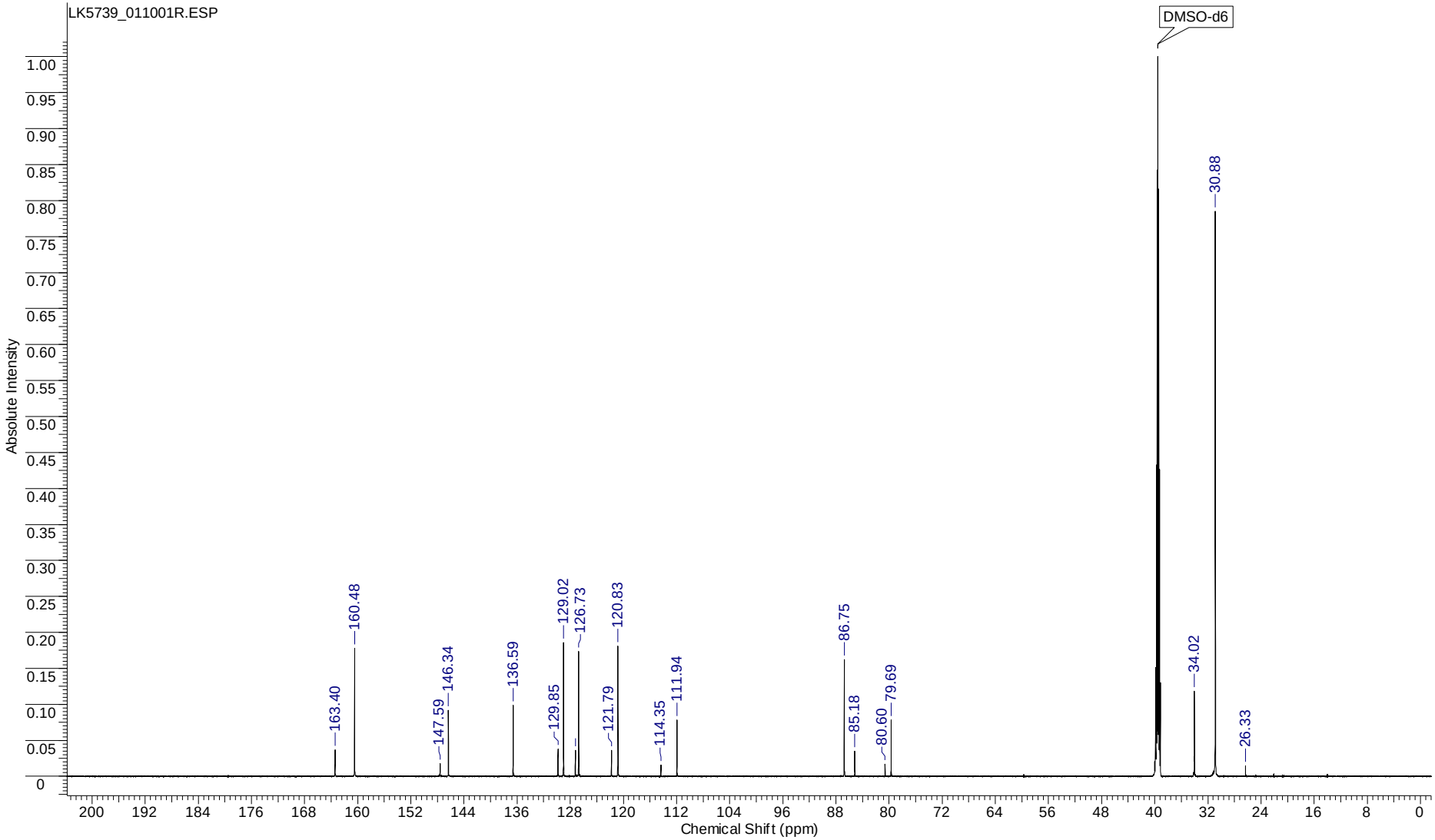

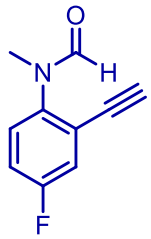

(1g)

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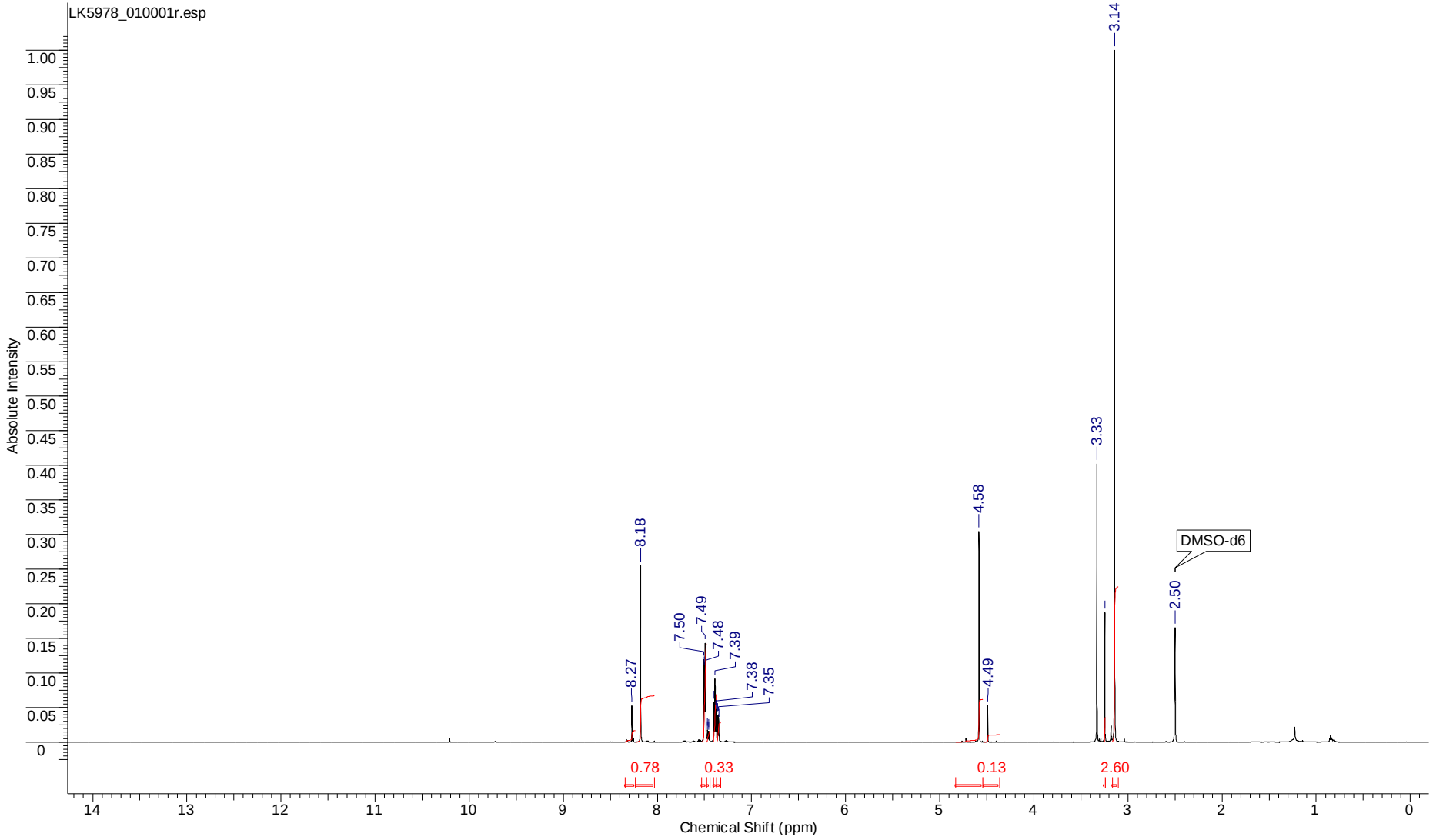

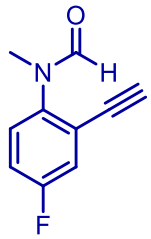

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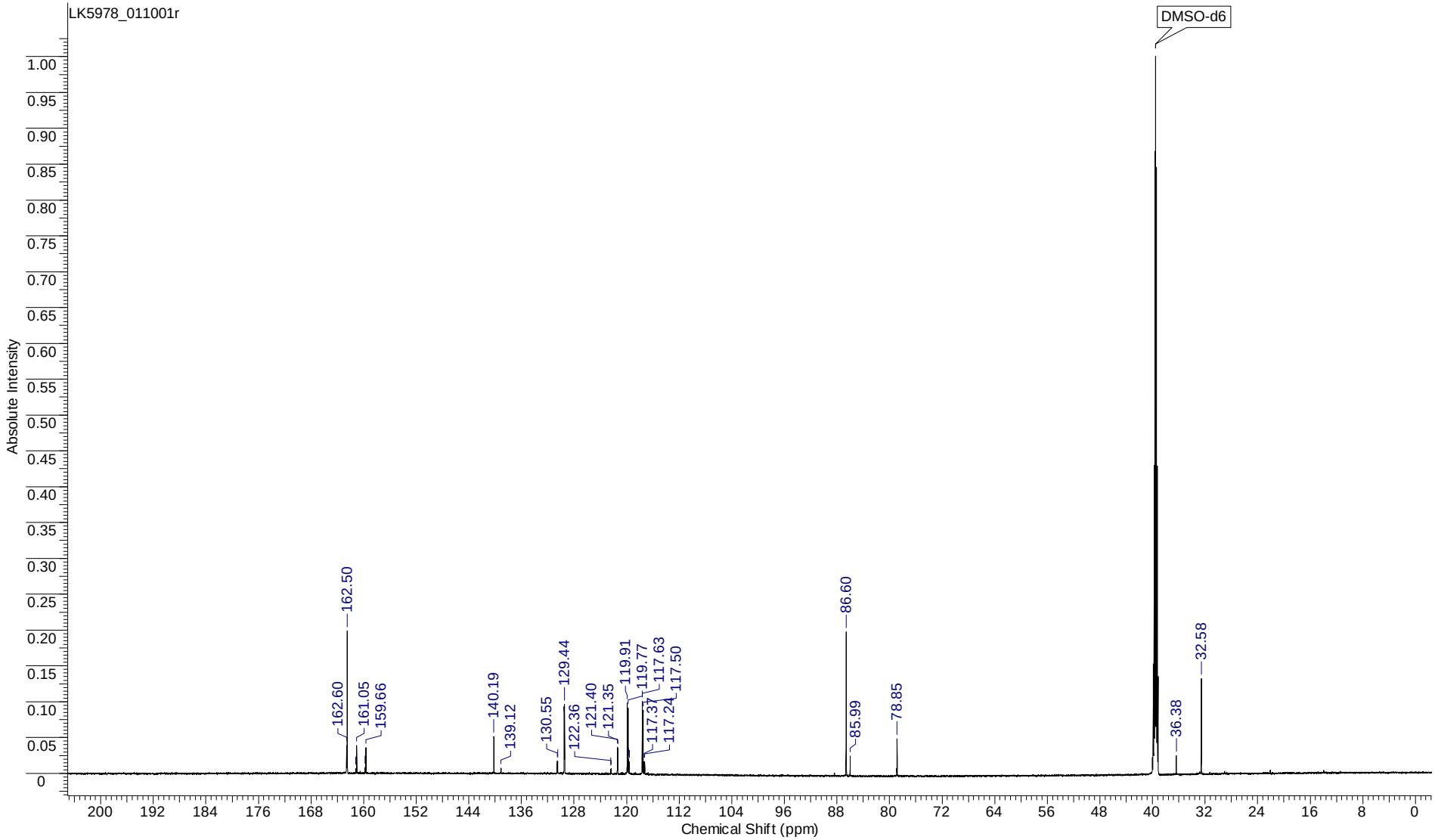

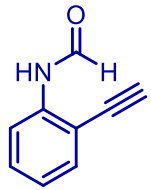

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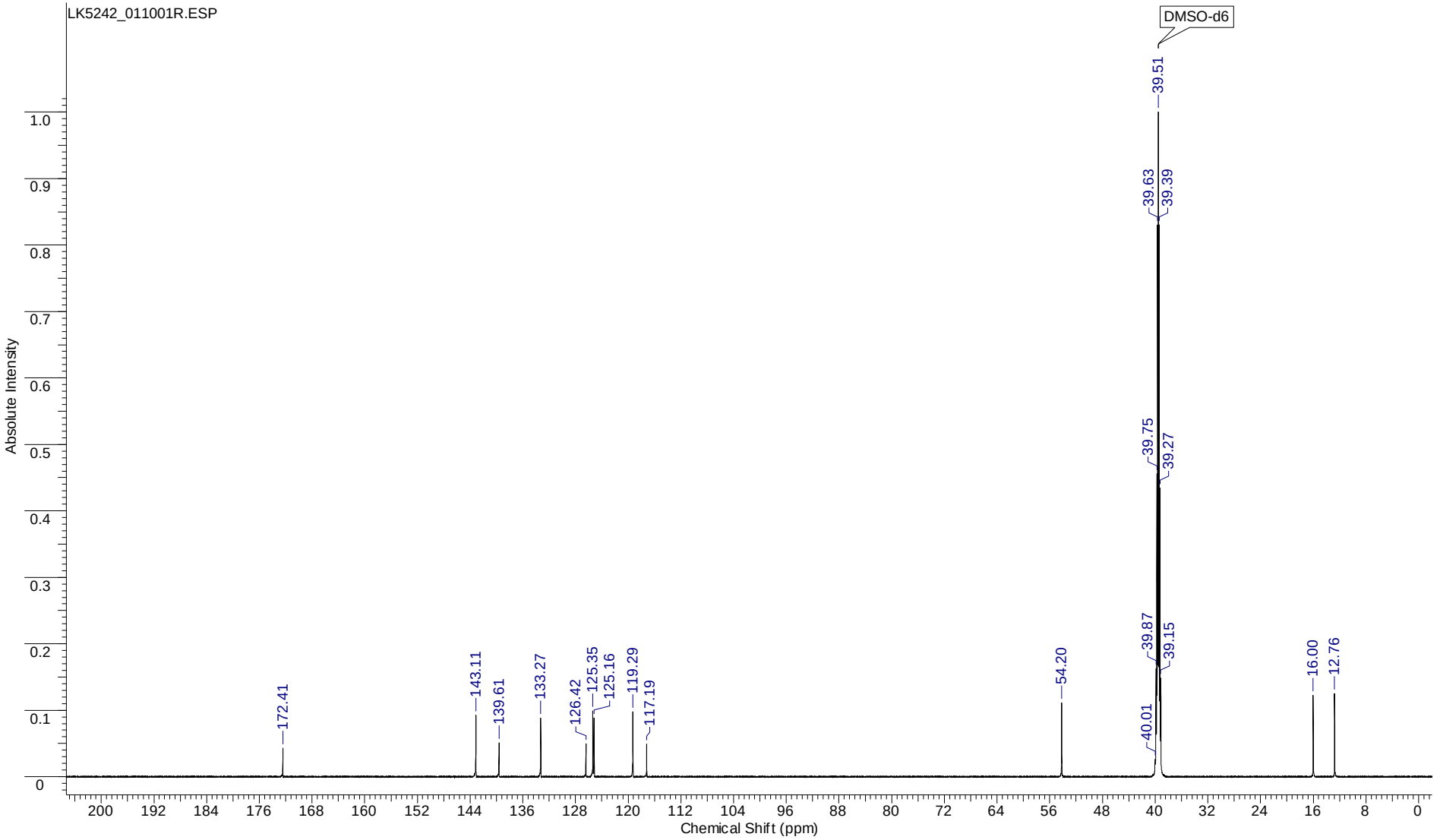
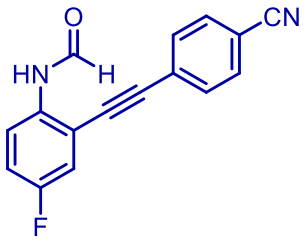
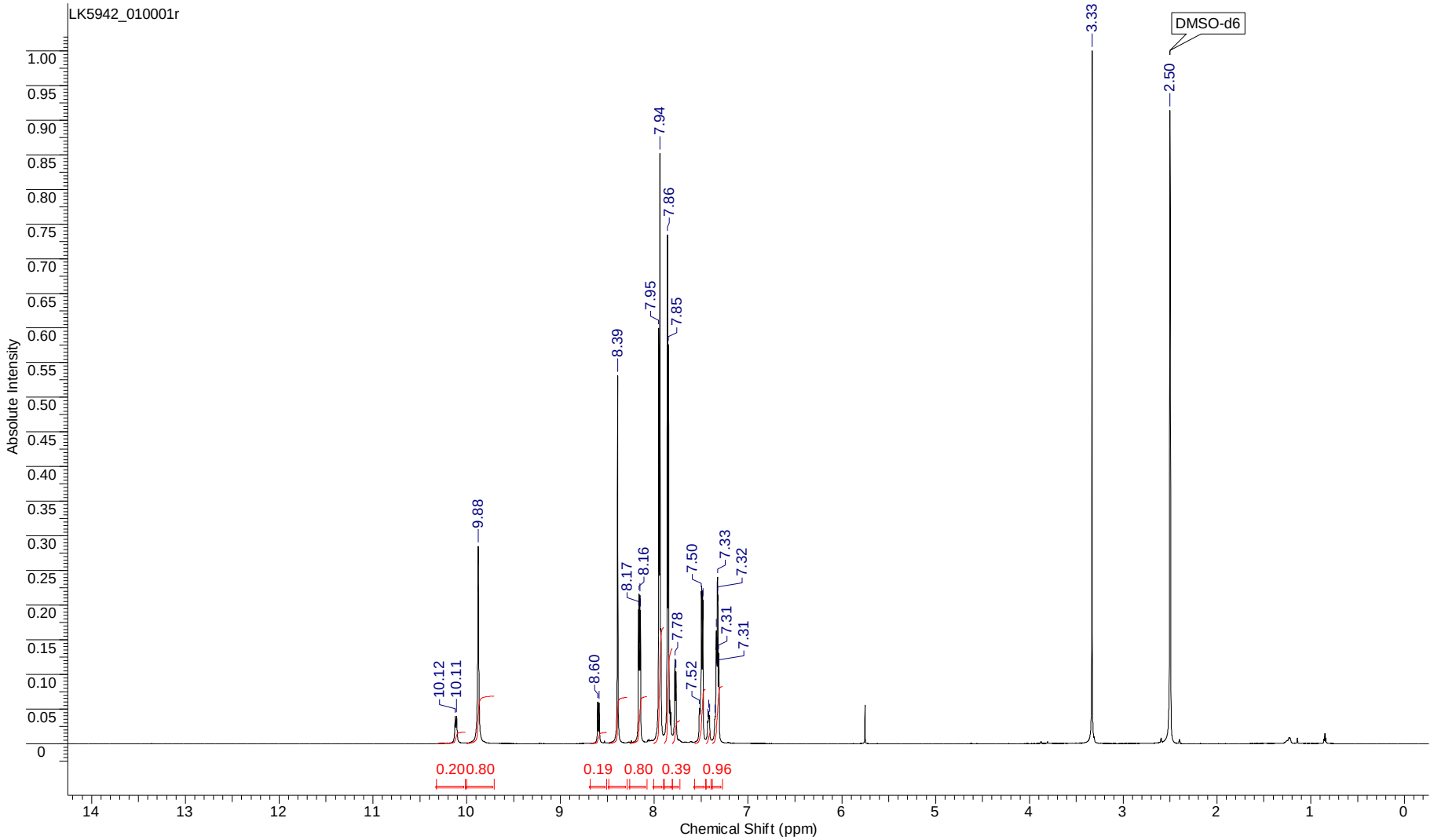
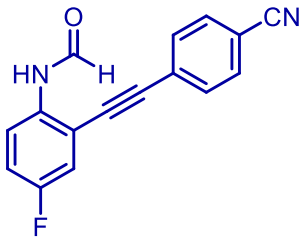




(1i)

^{1}H NMR (DMSO, 700 MHz):





(1i)

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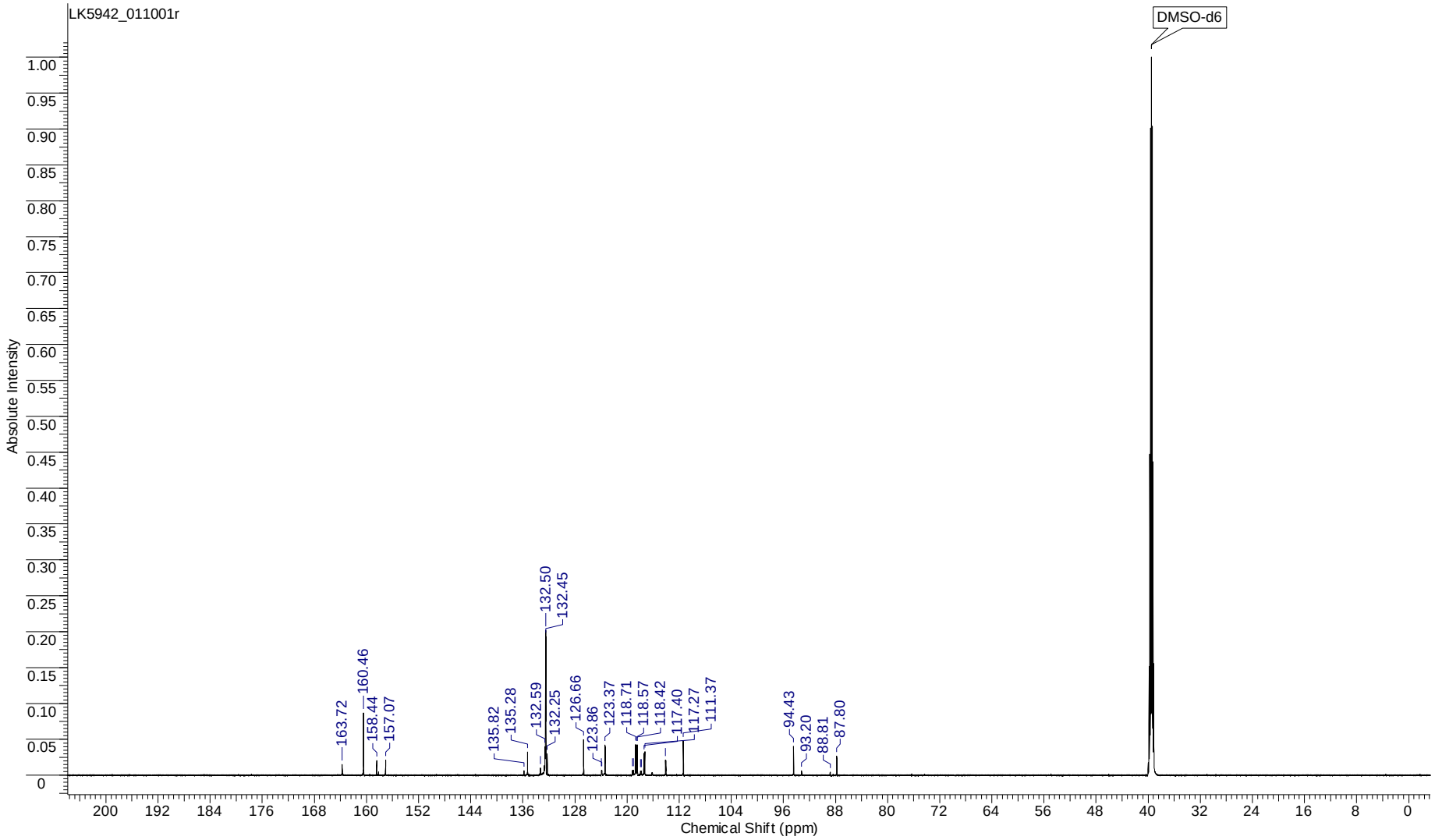

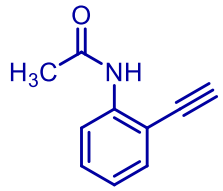

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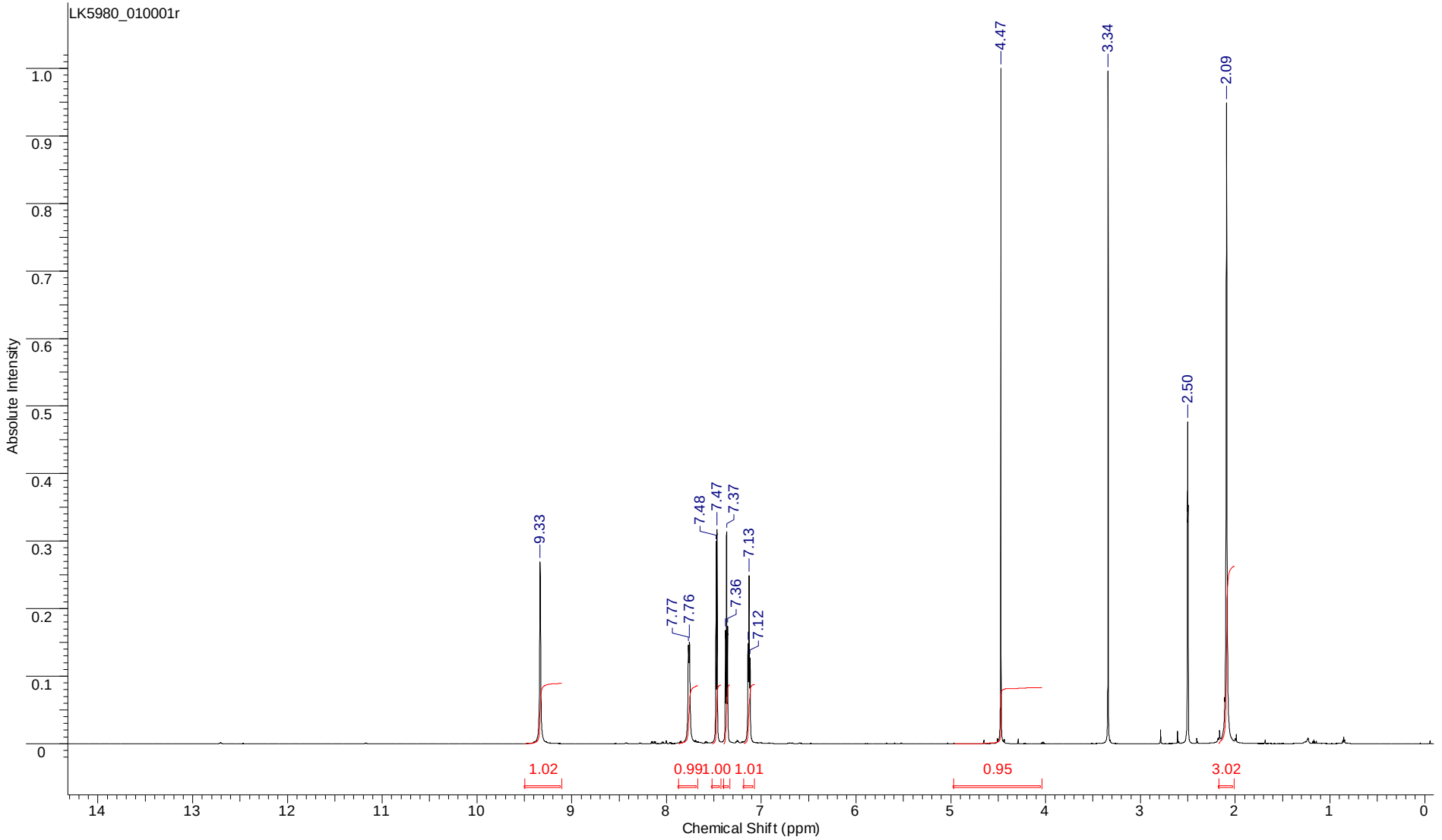

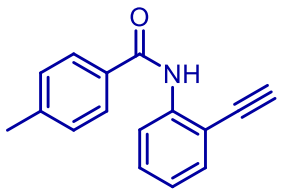

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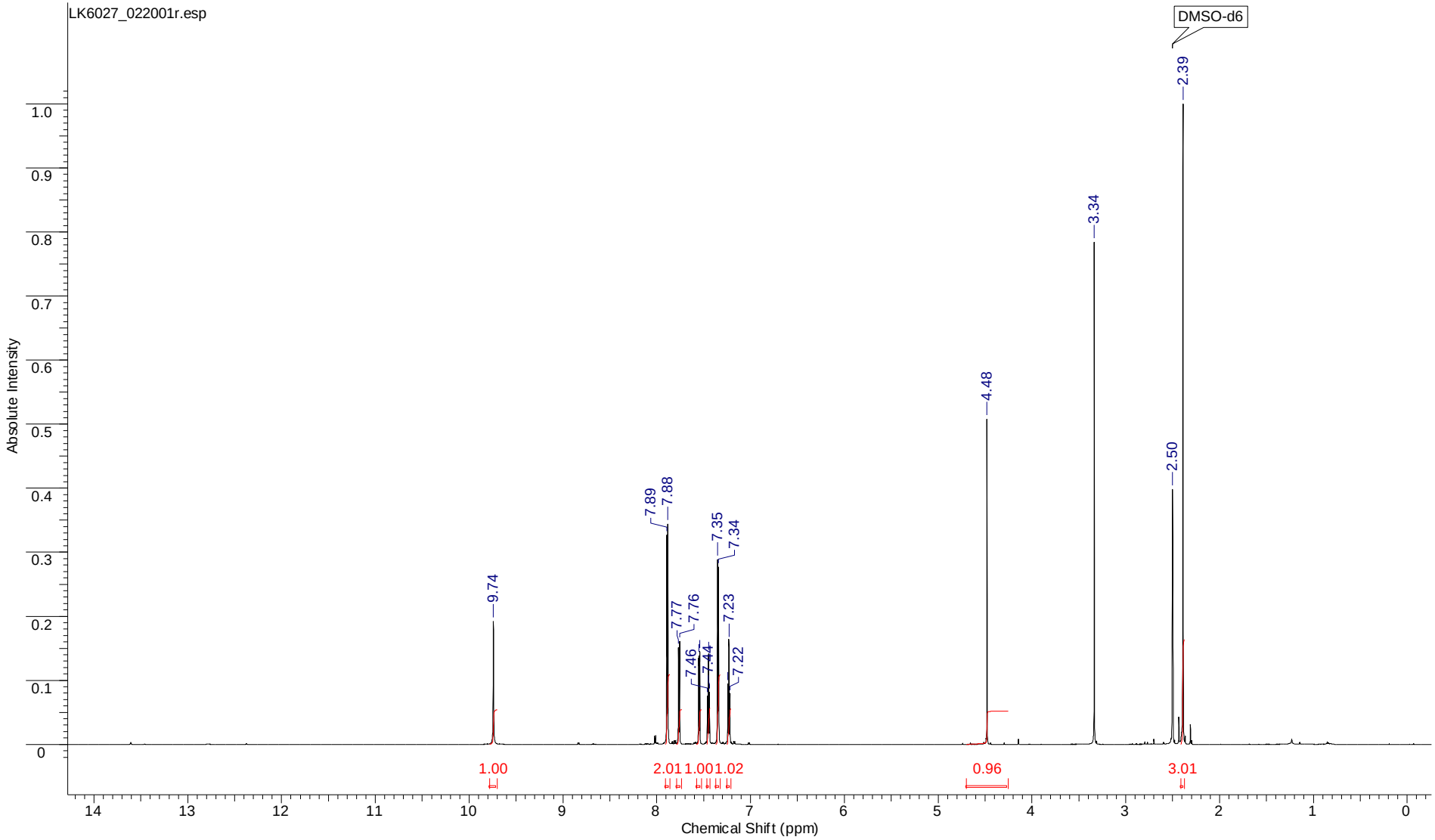

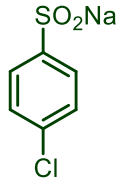

(2a)

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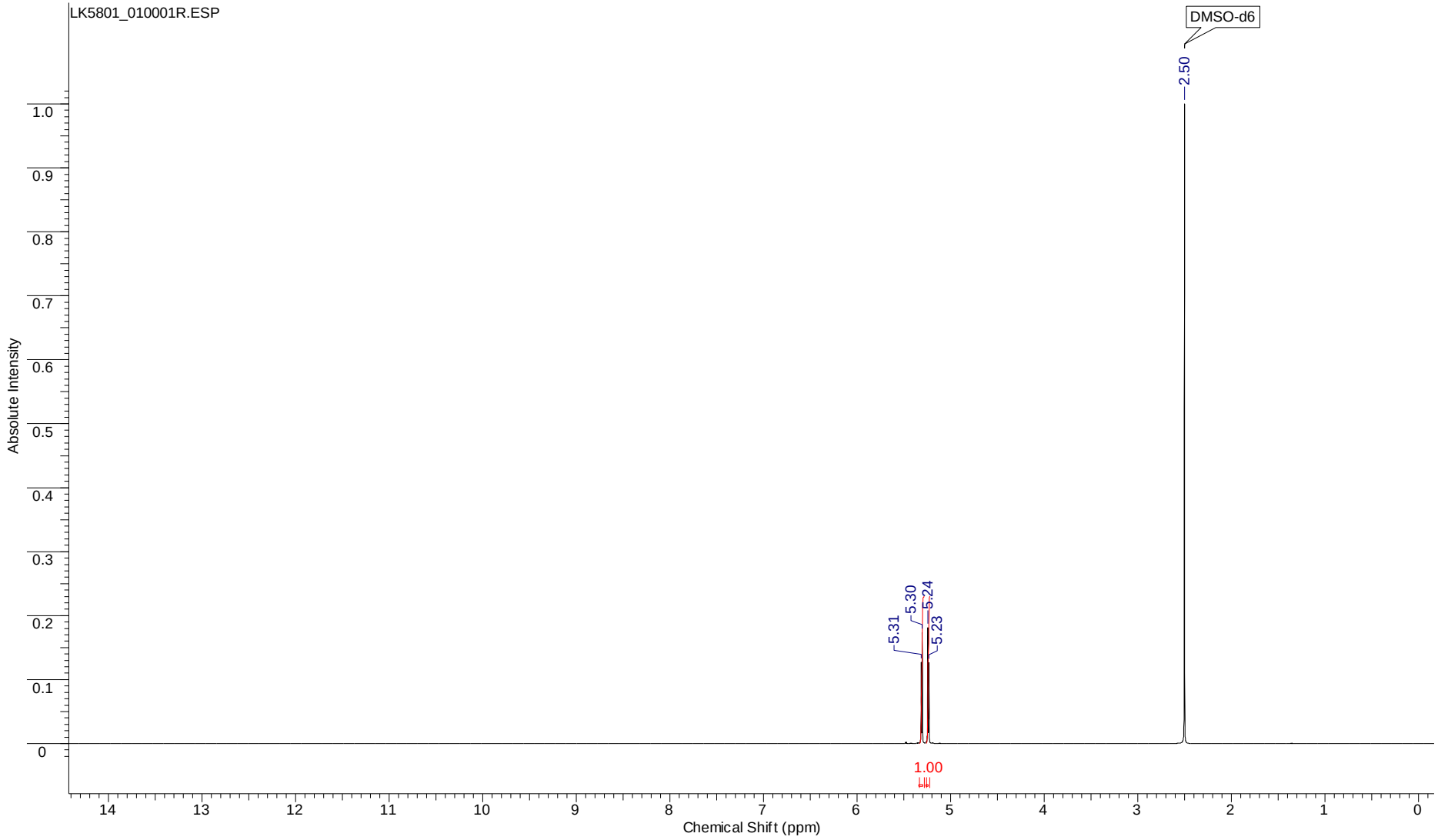
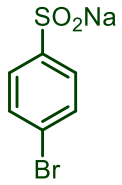
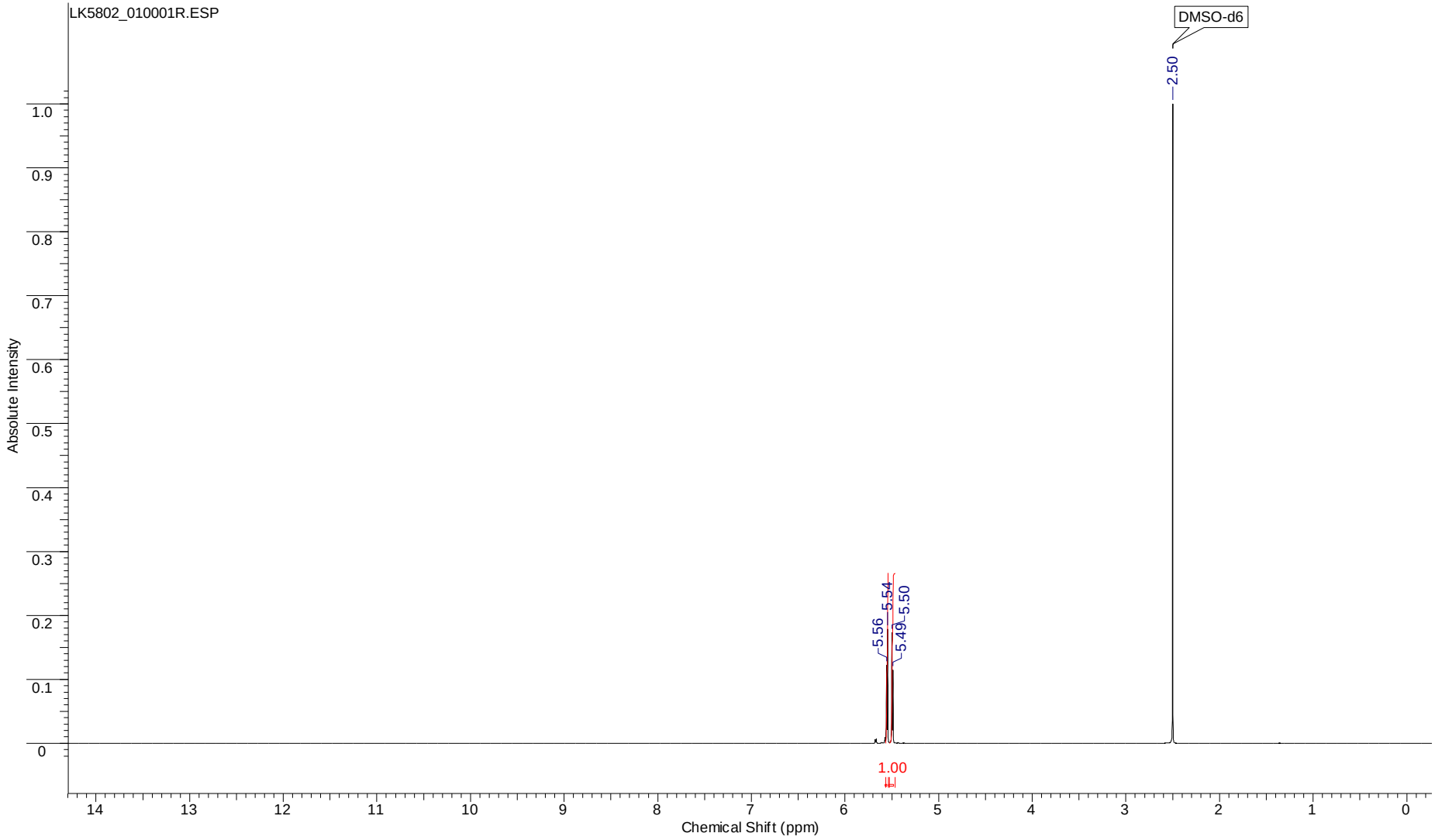
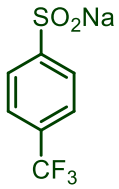




(2b)

^{1}H NMR (DMSO, 700 MHz):





(2c)

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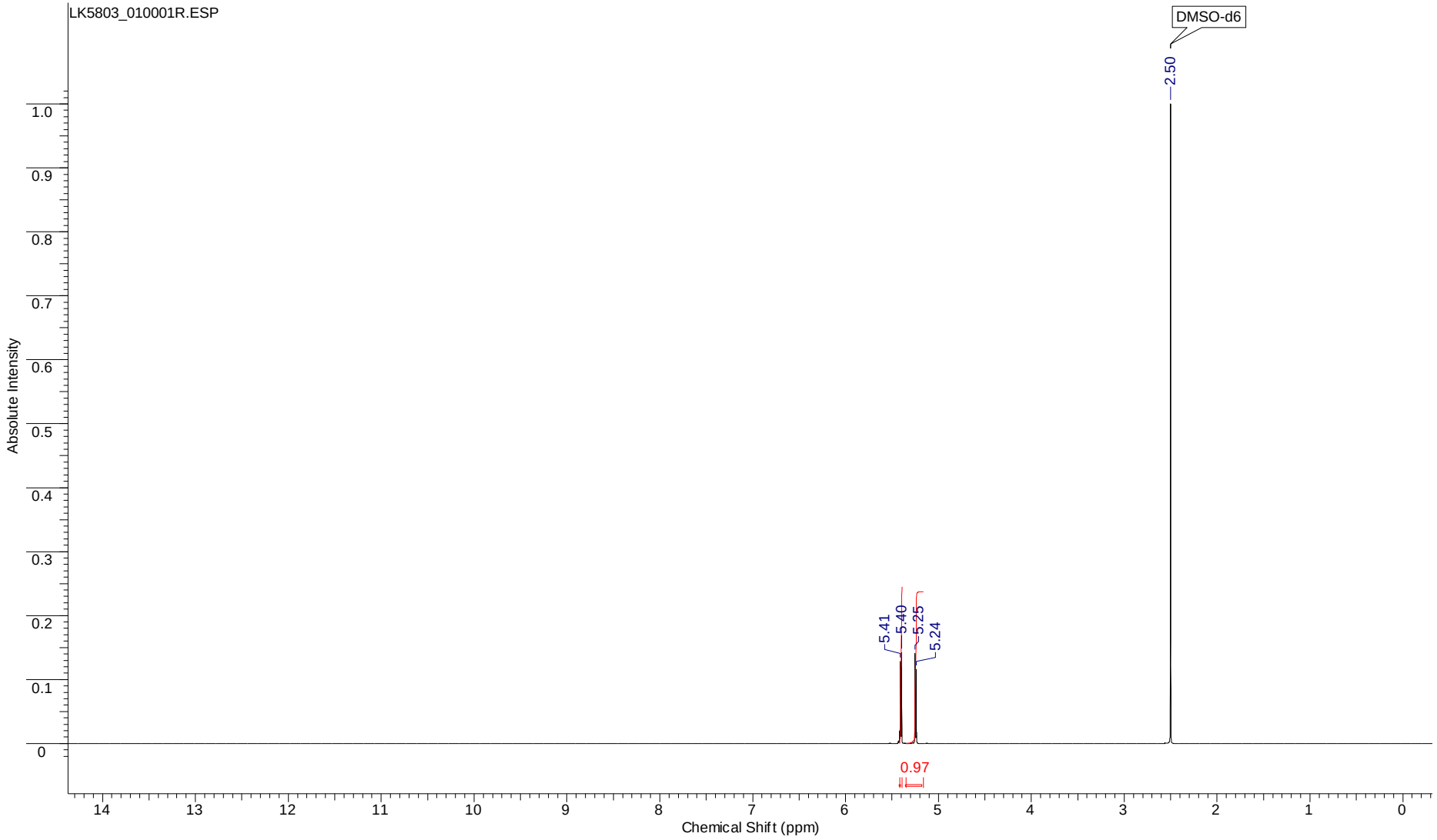

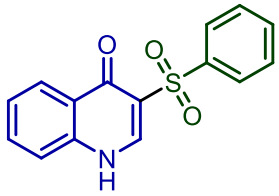

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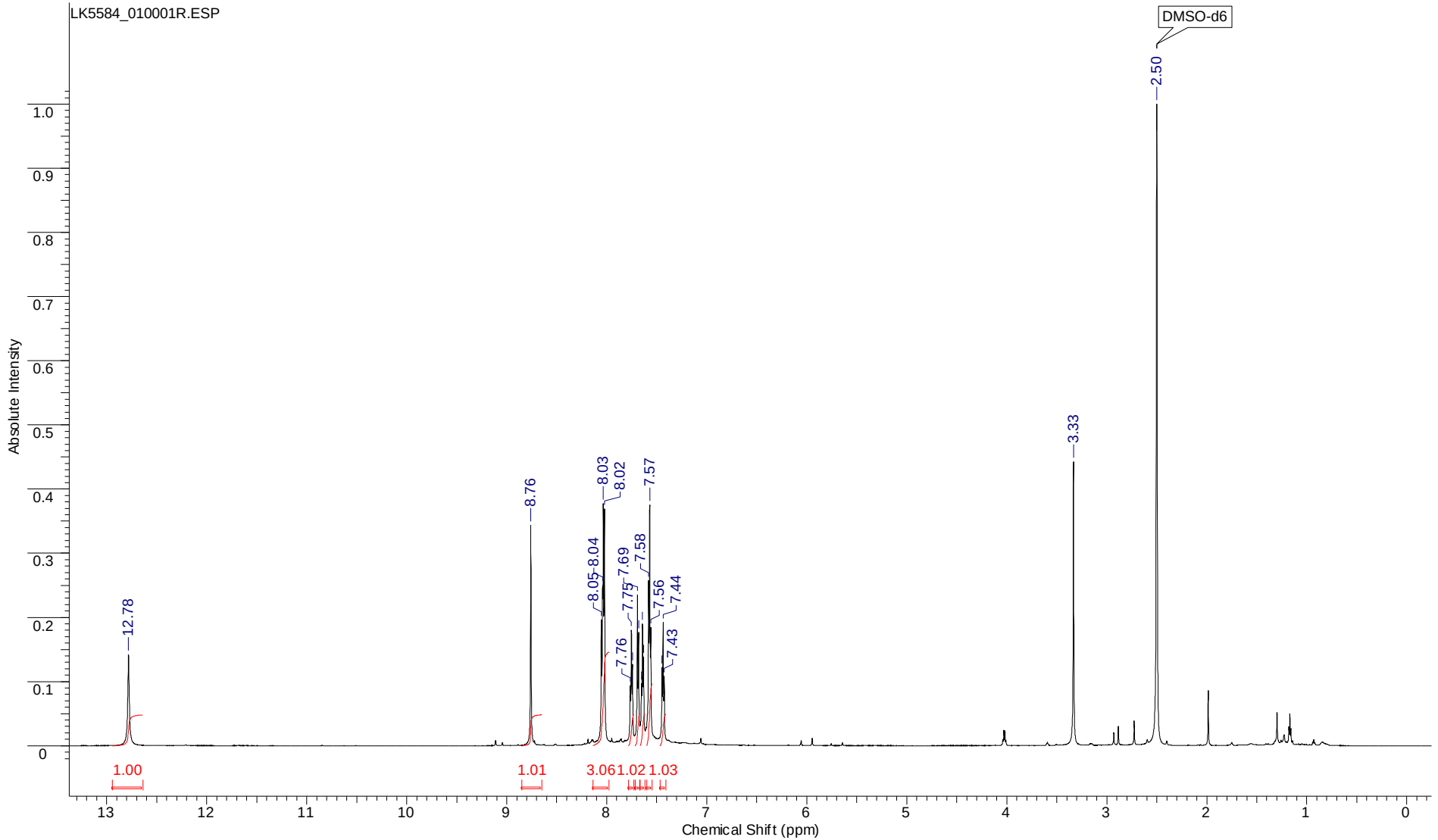

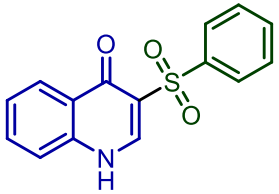

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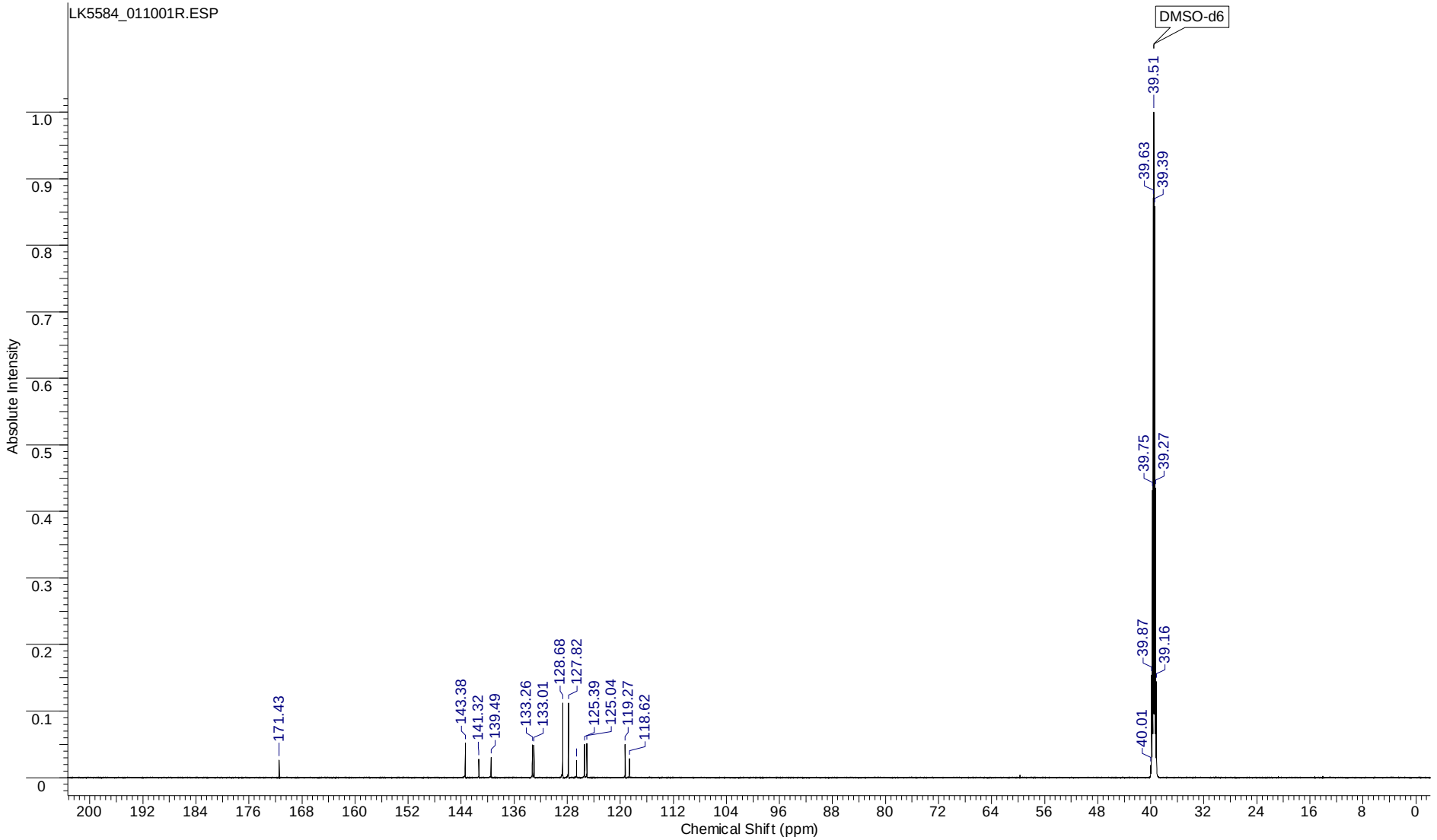
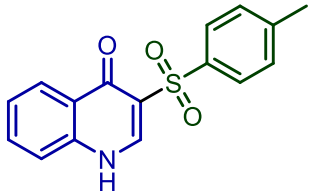
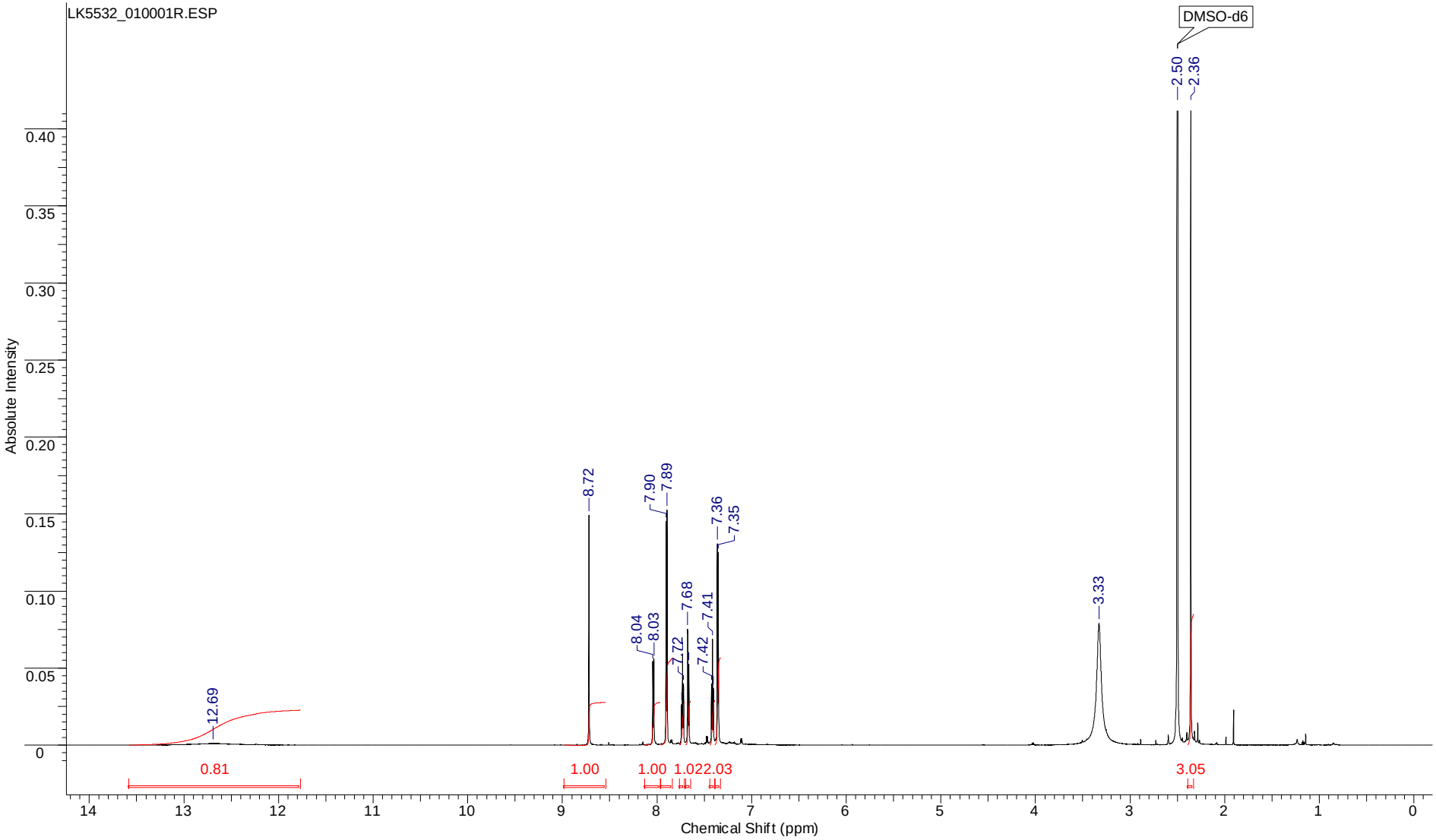
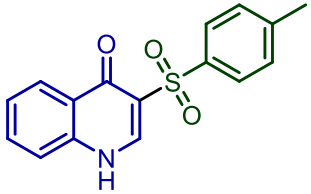




(3b)

^{1}H NMR (DMSO, 700 MHz)





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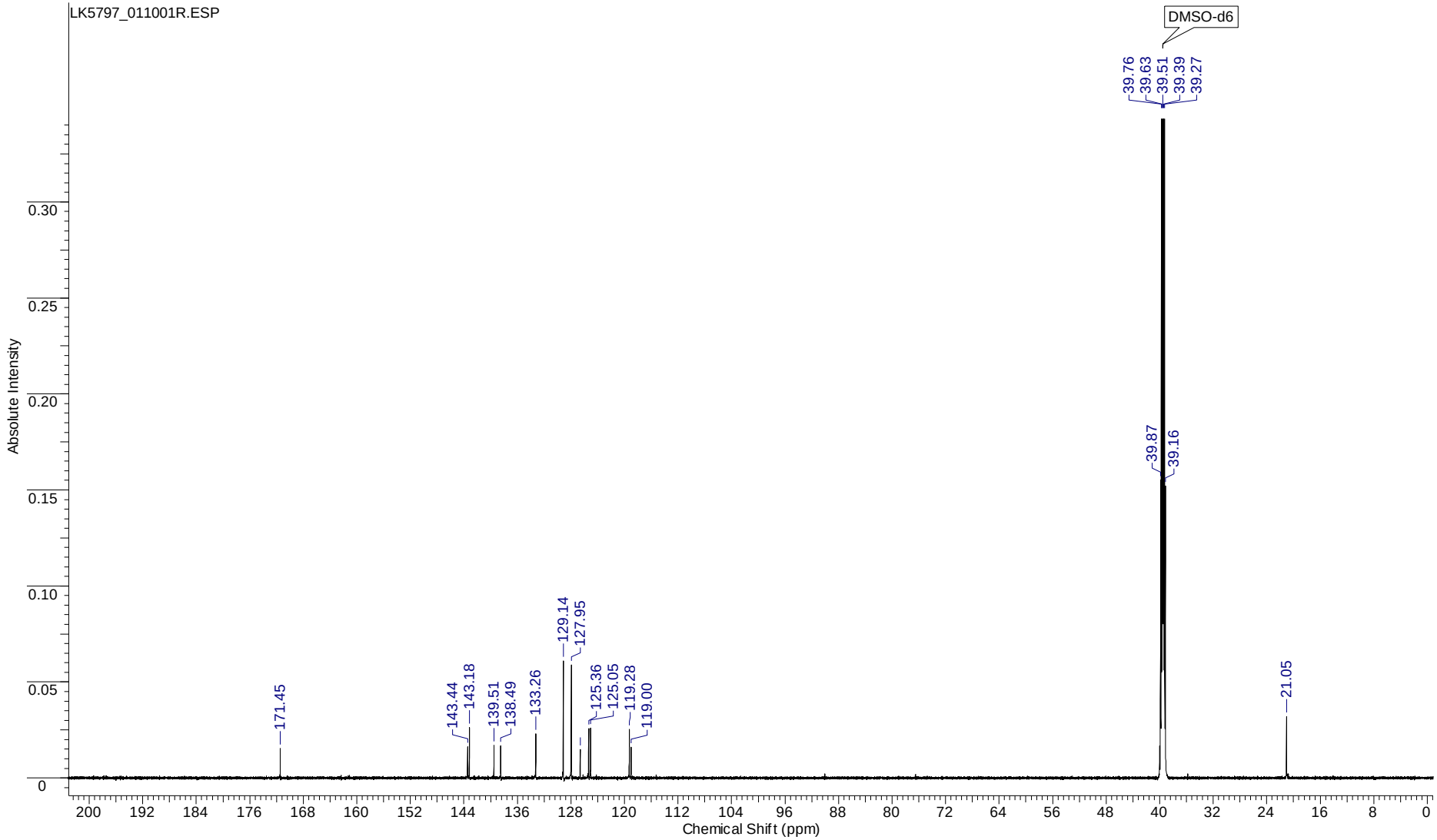
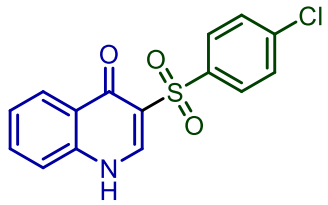
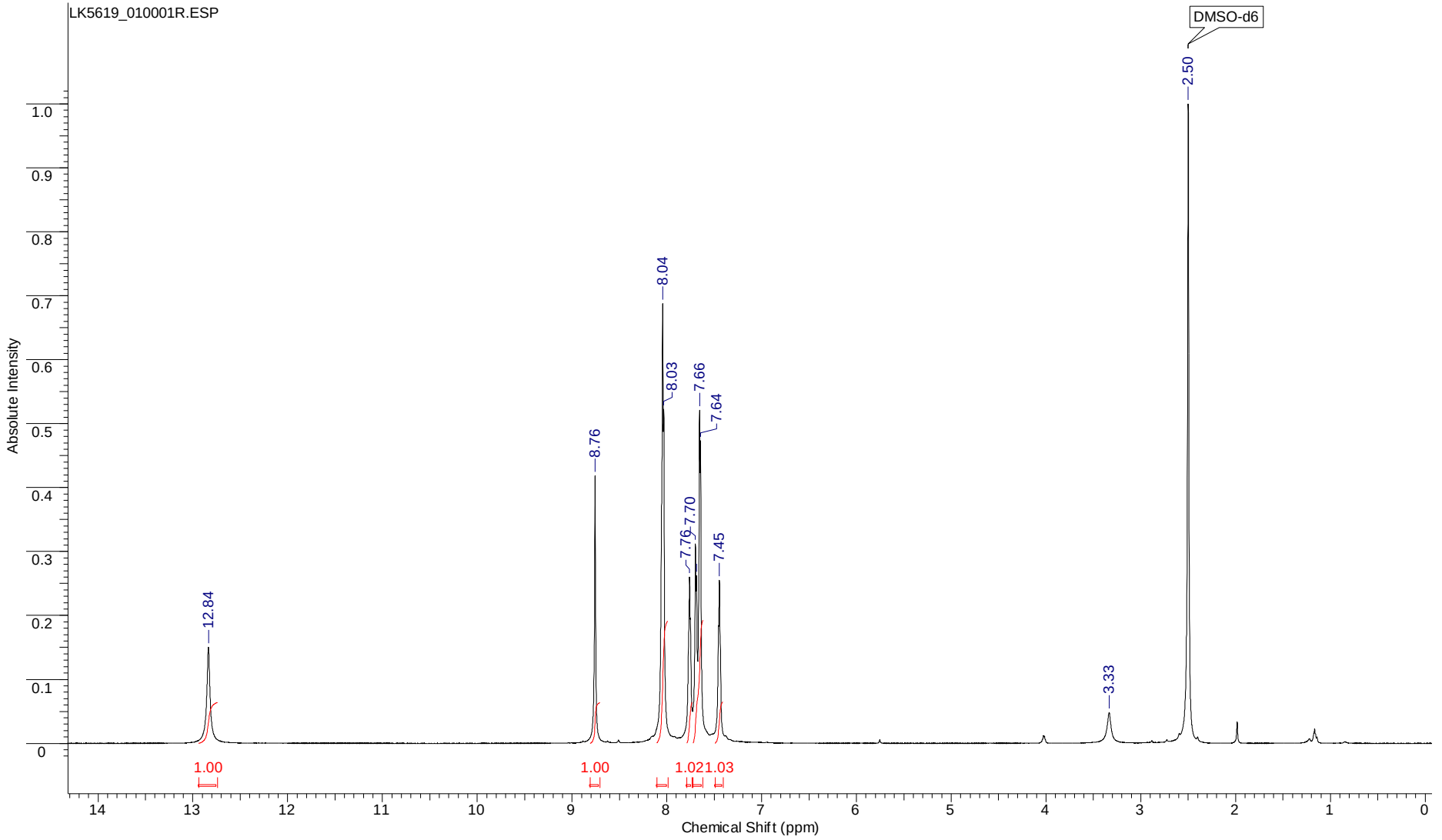
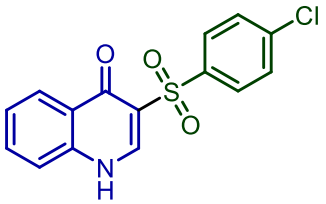




(3c)

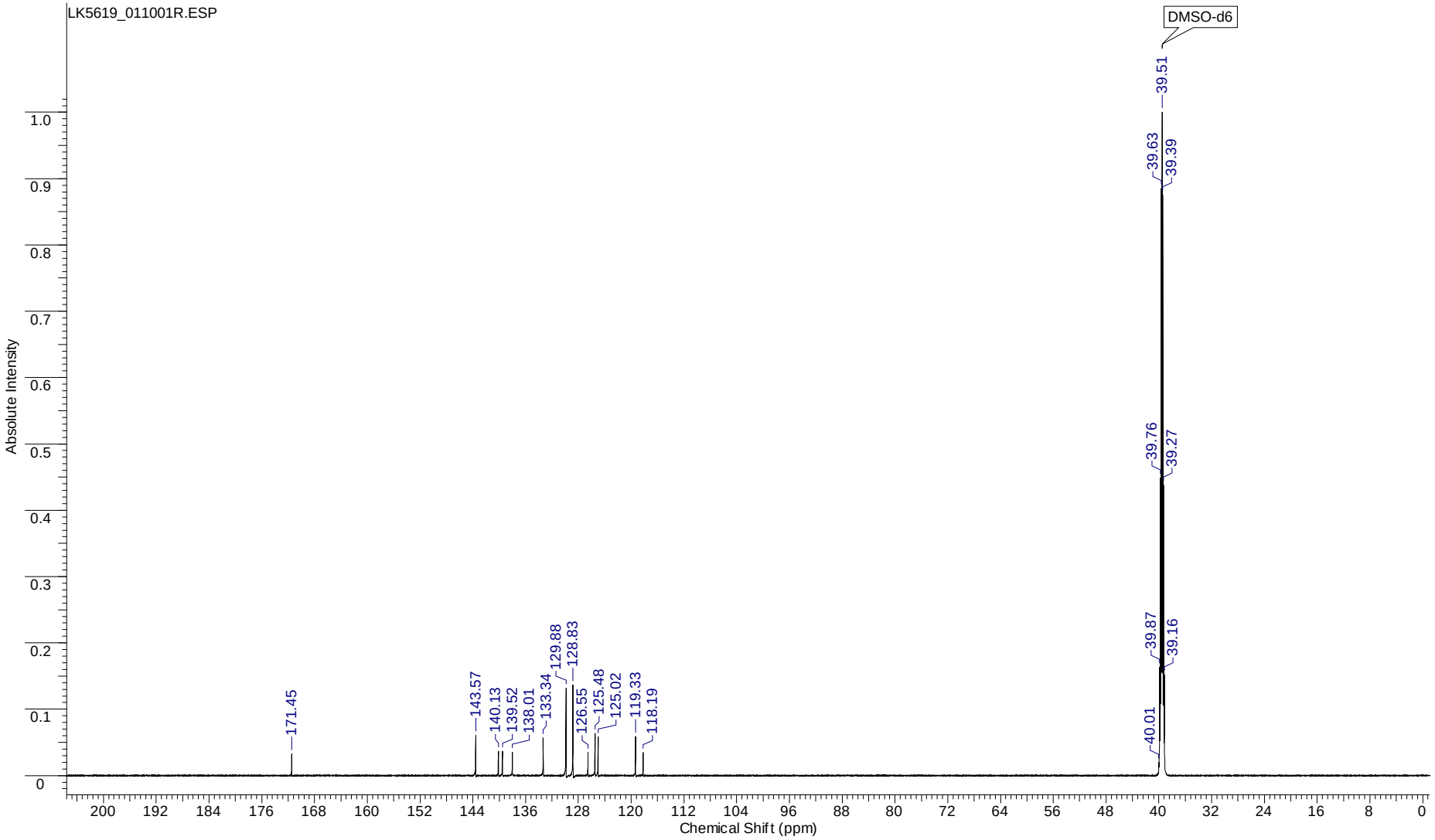
^{1}H NMR (DMSO, 700 MHz):

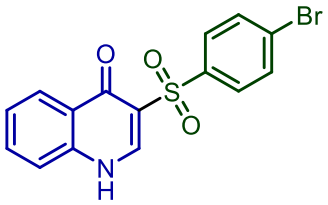




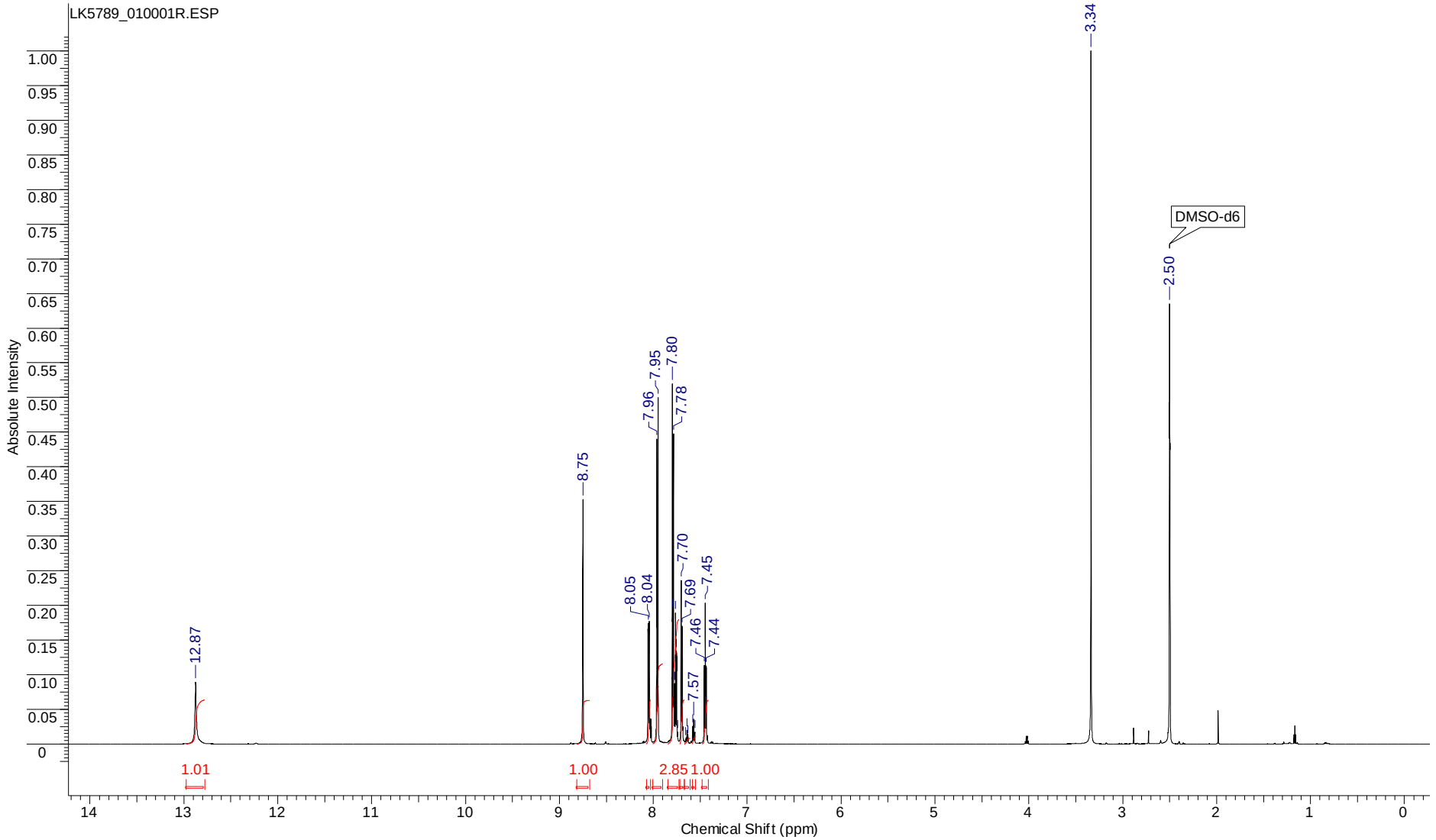
(3c)

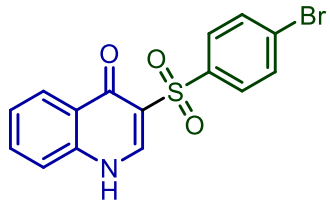
^{13}C NMR (DMSO, 150 MHz):



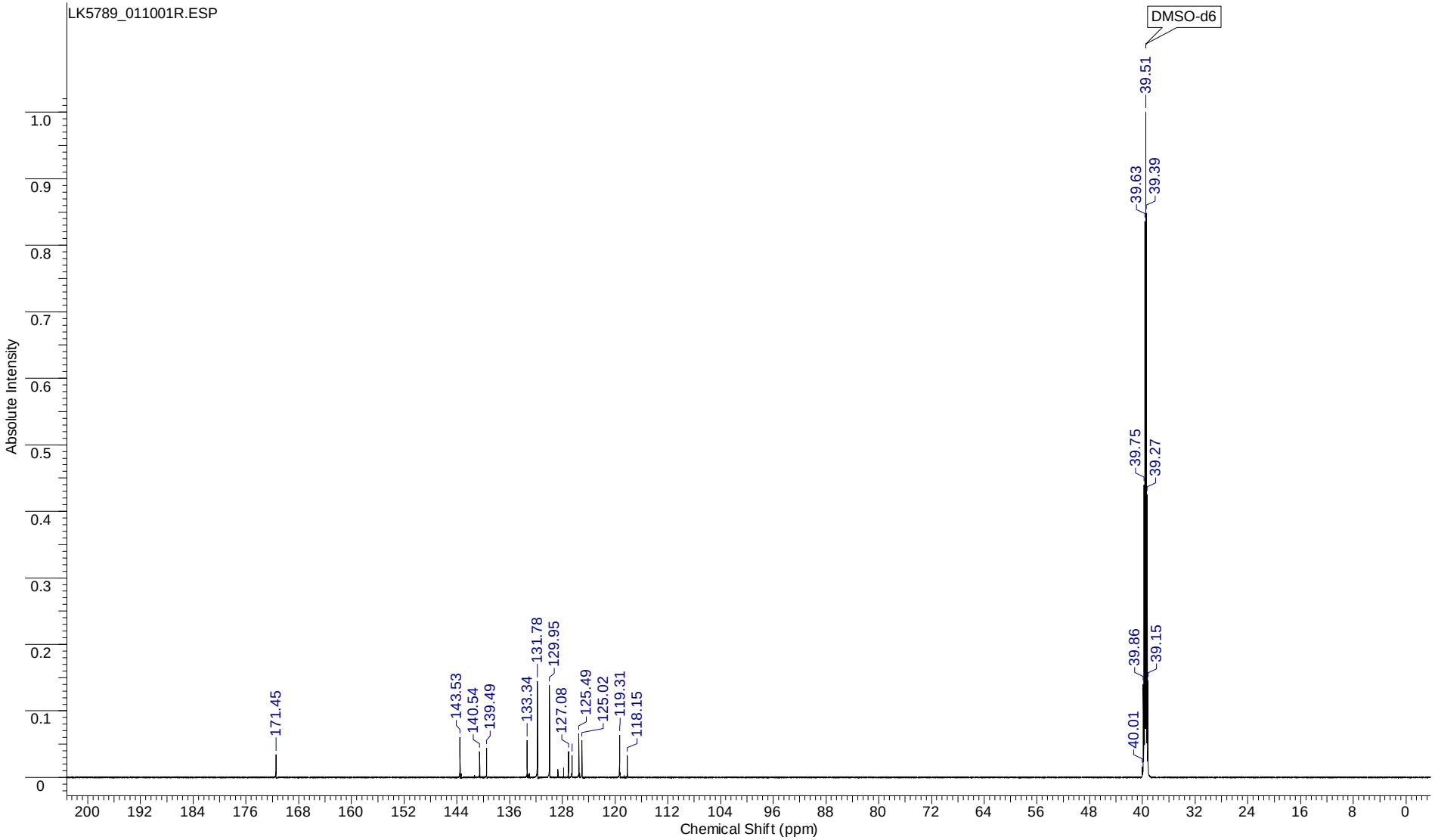


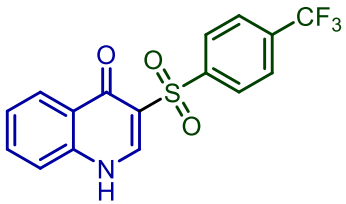
(3d) ^{1}H NMR (DMSO, 700 MHz):



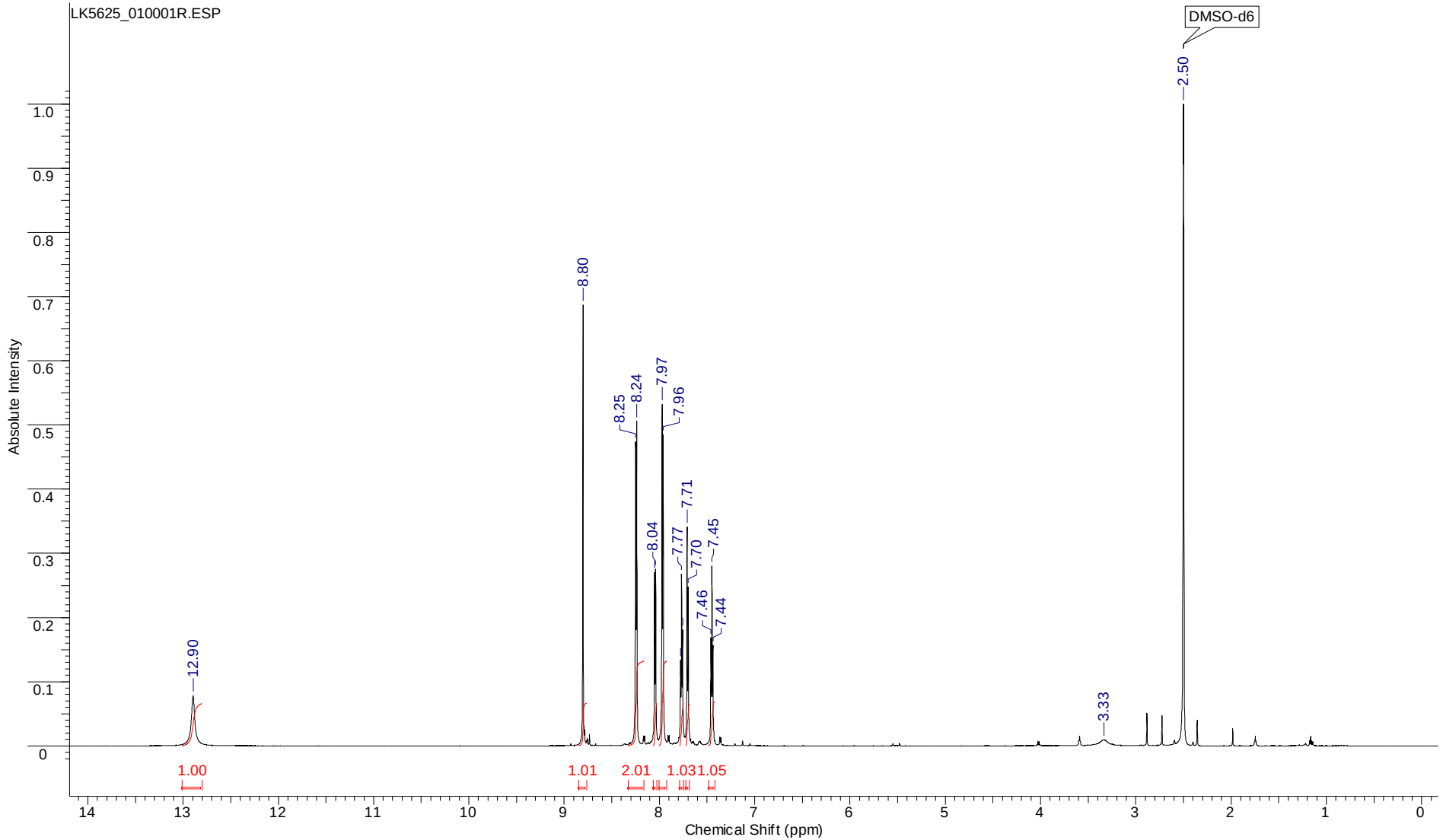


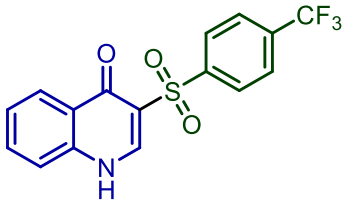
(3d) ^{13}C NMR (DMSO, 150 MHz):



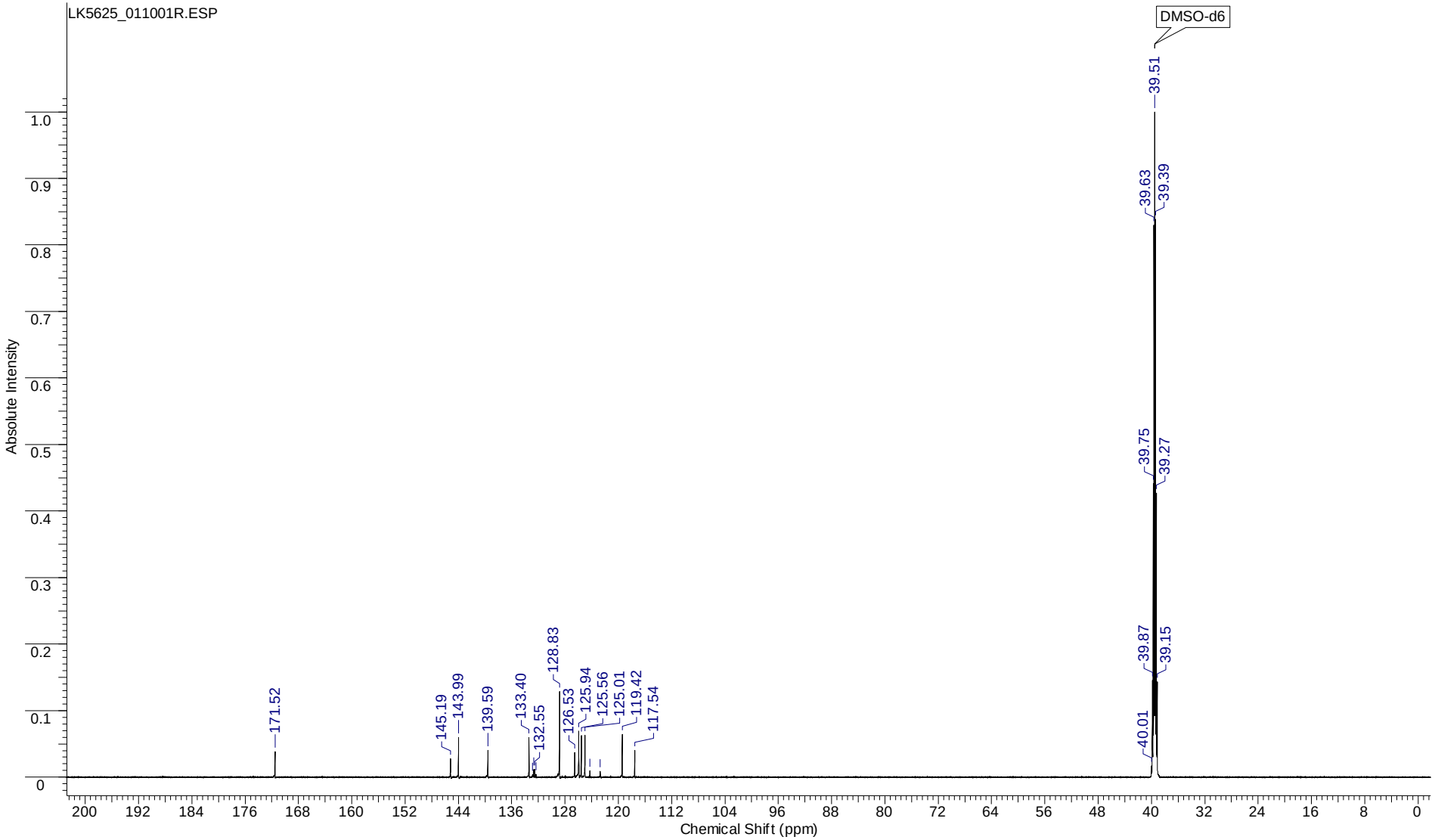


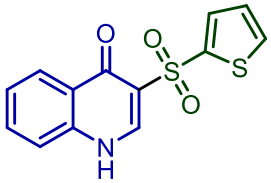
(3e) ^{1}H NMR (DMSO, 700 MHz):



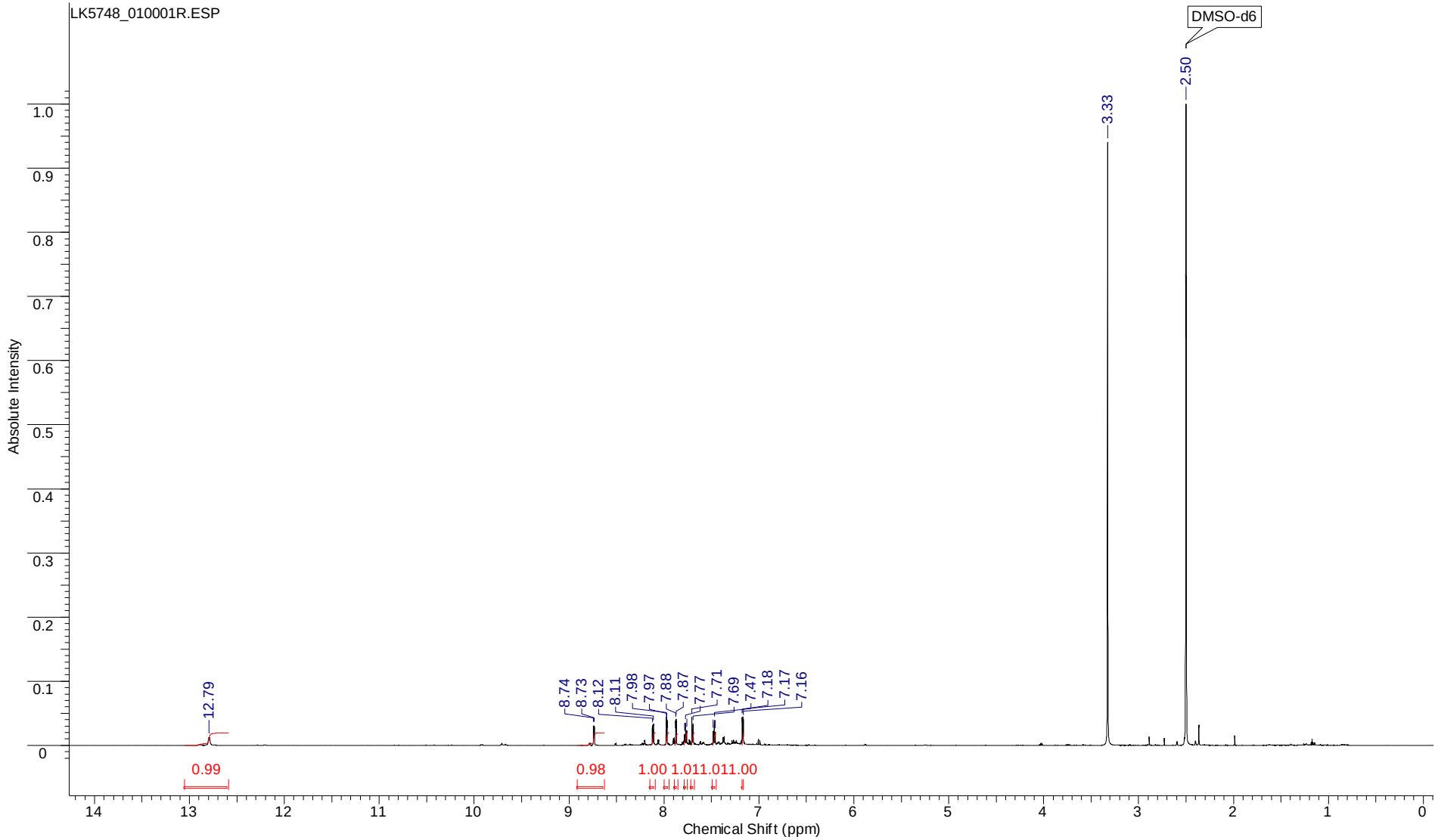


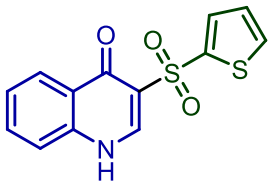
(3e) ^{13}C NMR (DMSO, 150 MHz):



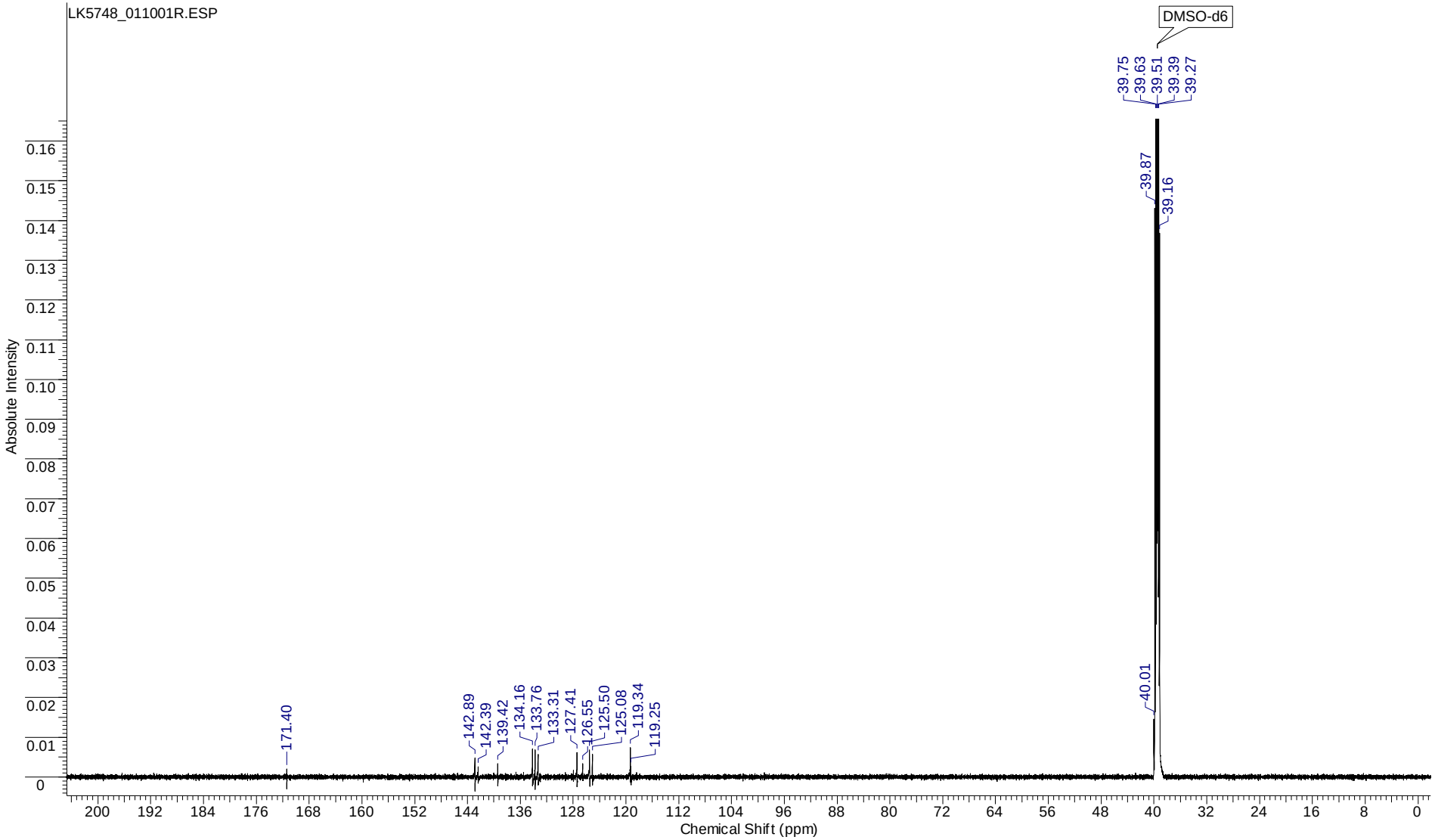


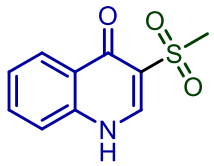
(3f) ^{1}H NMR (DMSO, 700 MHz):





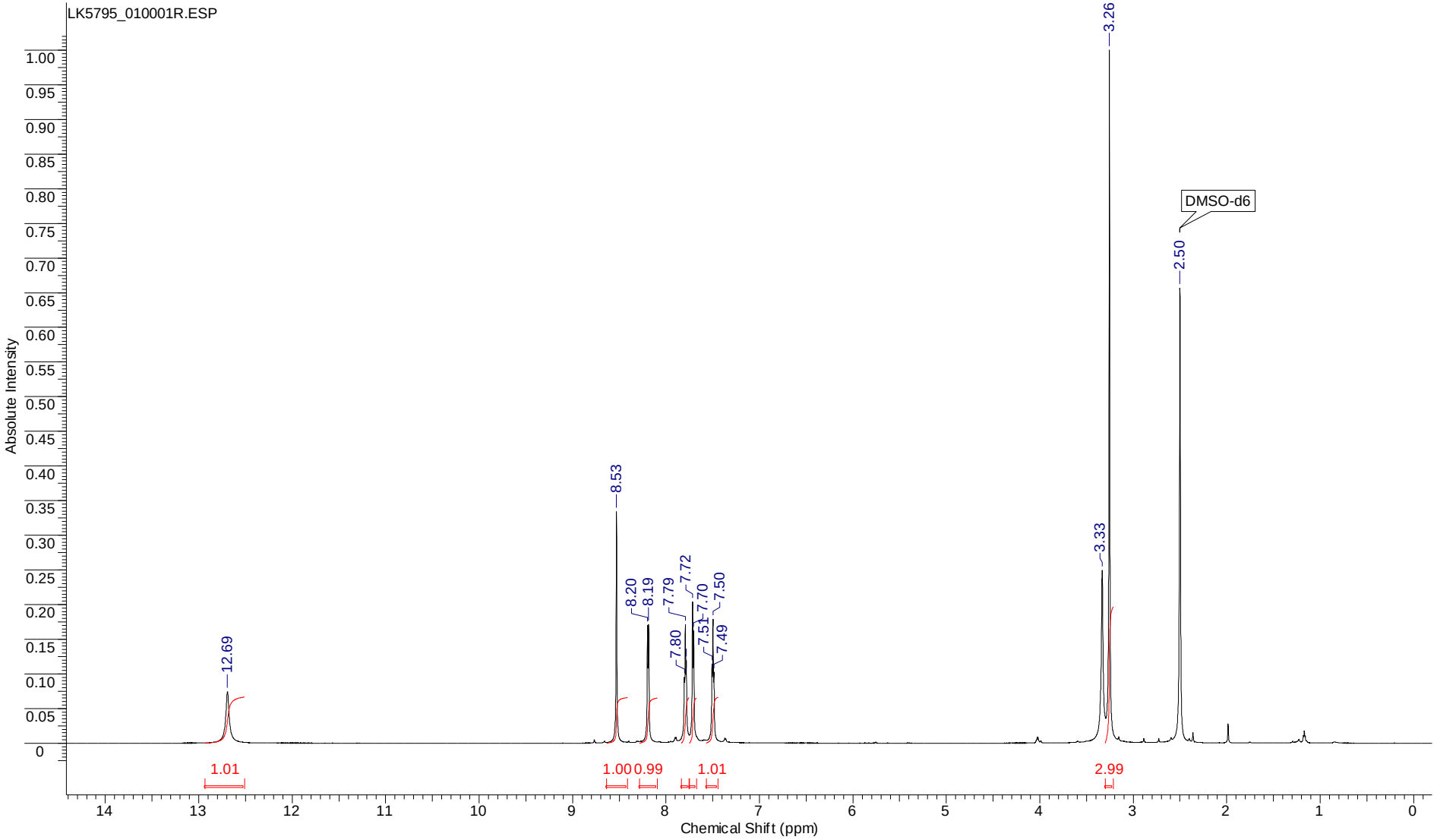
(3f) ^{13}C NMR (DMSO, 150 MHz):

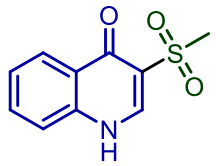




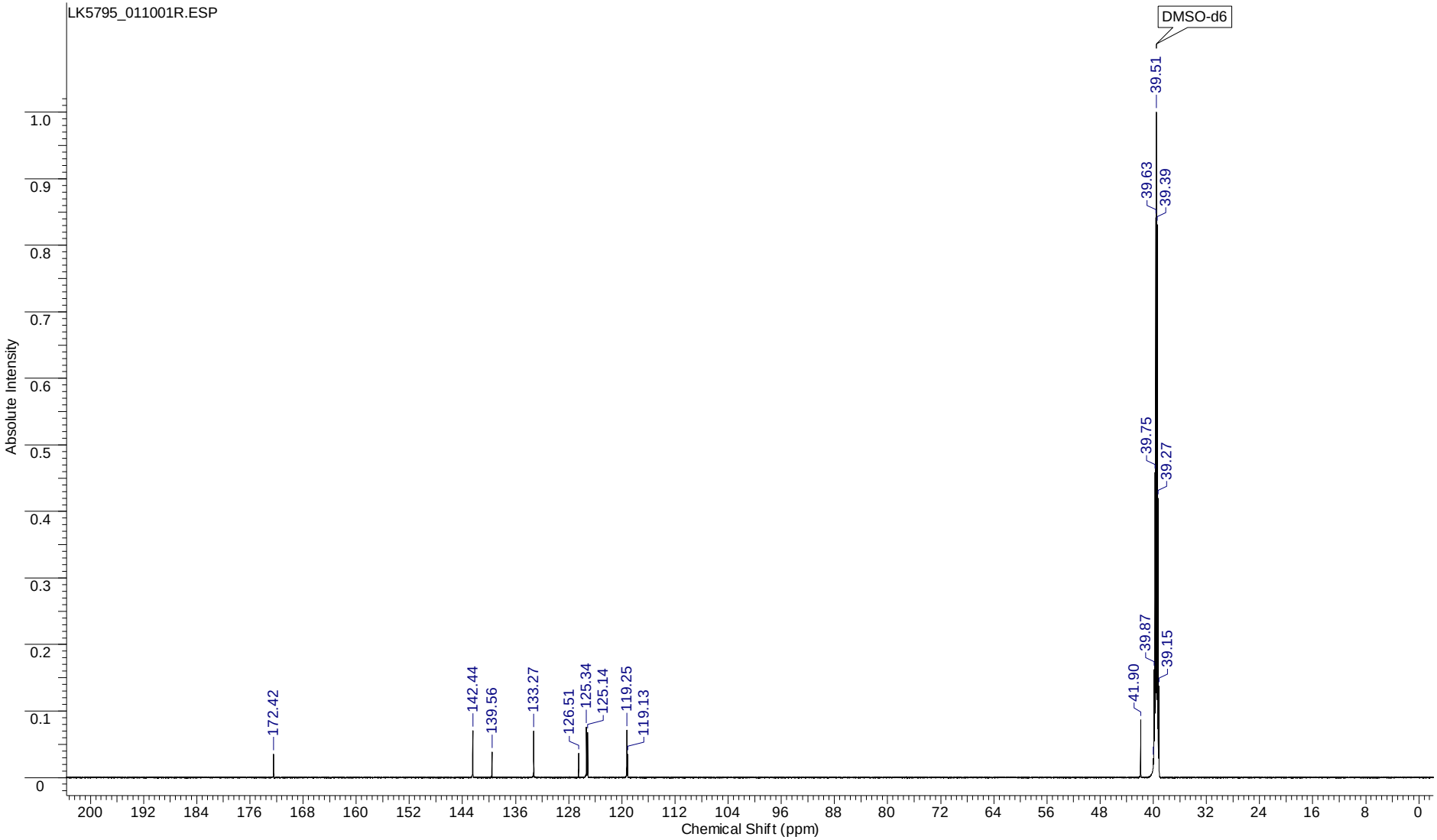
(3g)

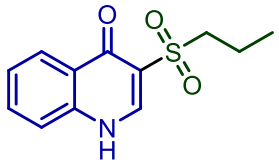
^{1}H NMR (DMSO, 700 MHz):



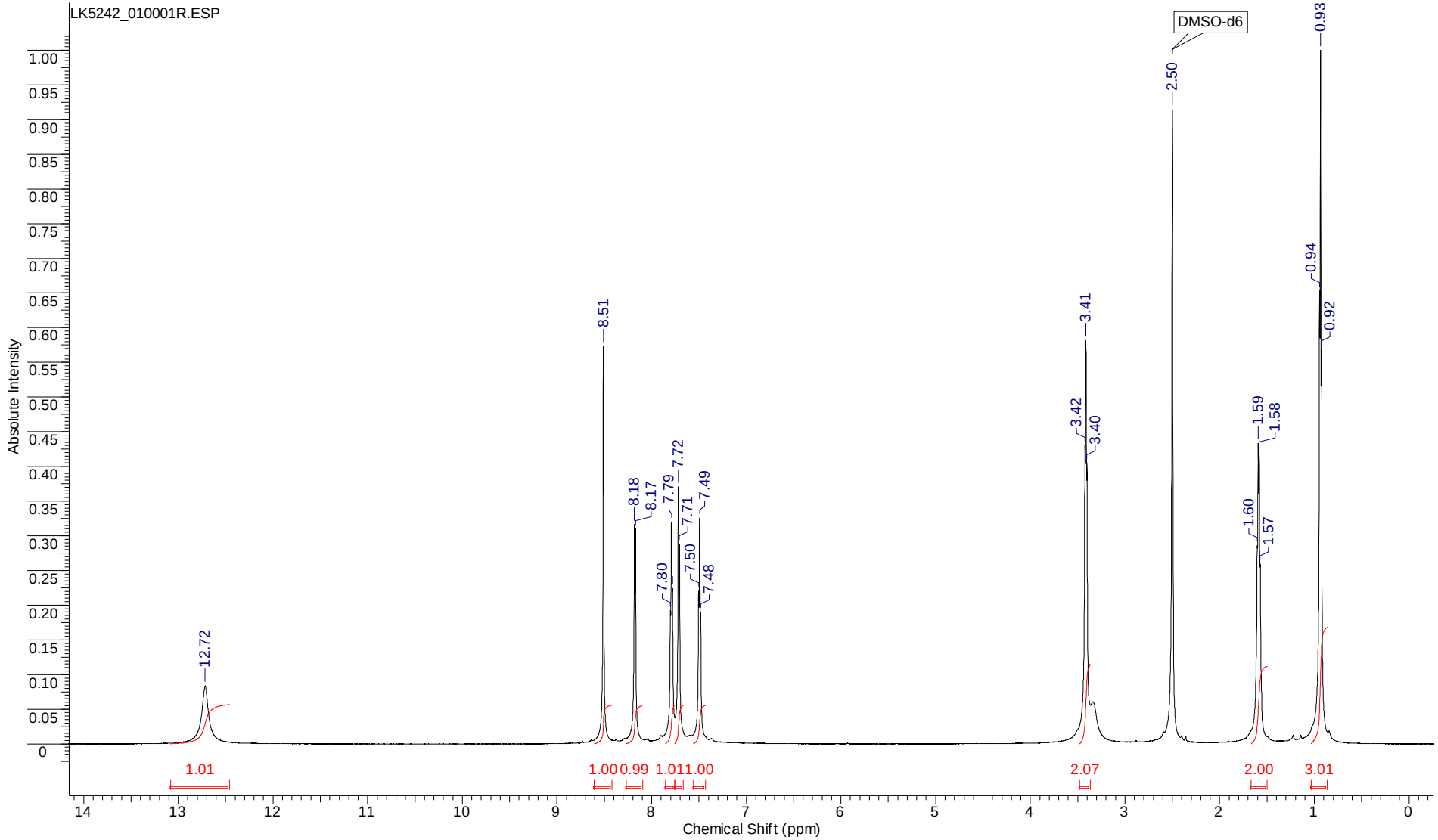


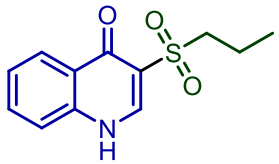
(3g) ^{13}C NMR (DMSO, 150 MHz):





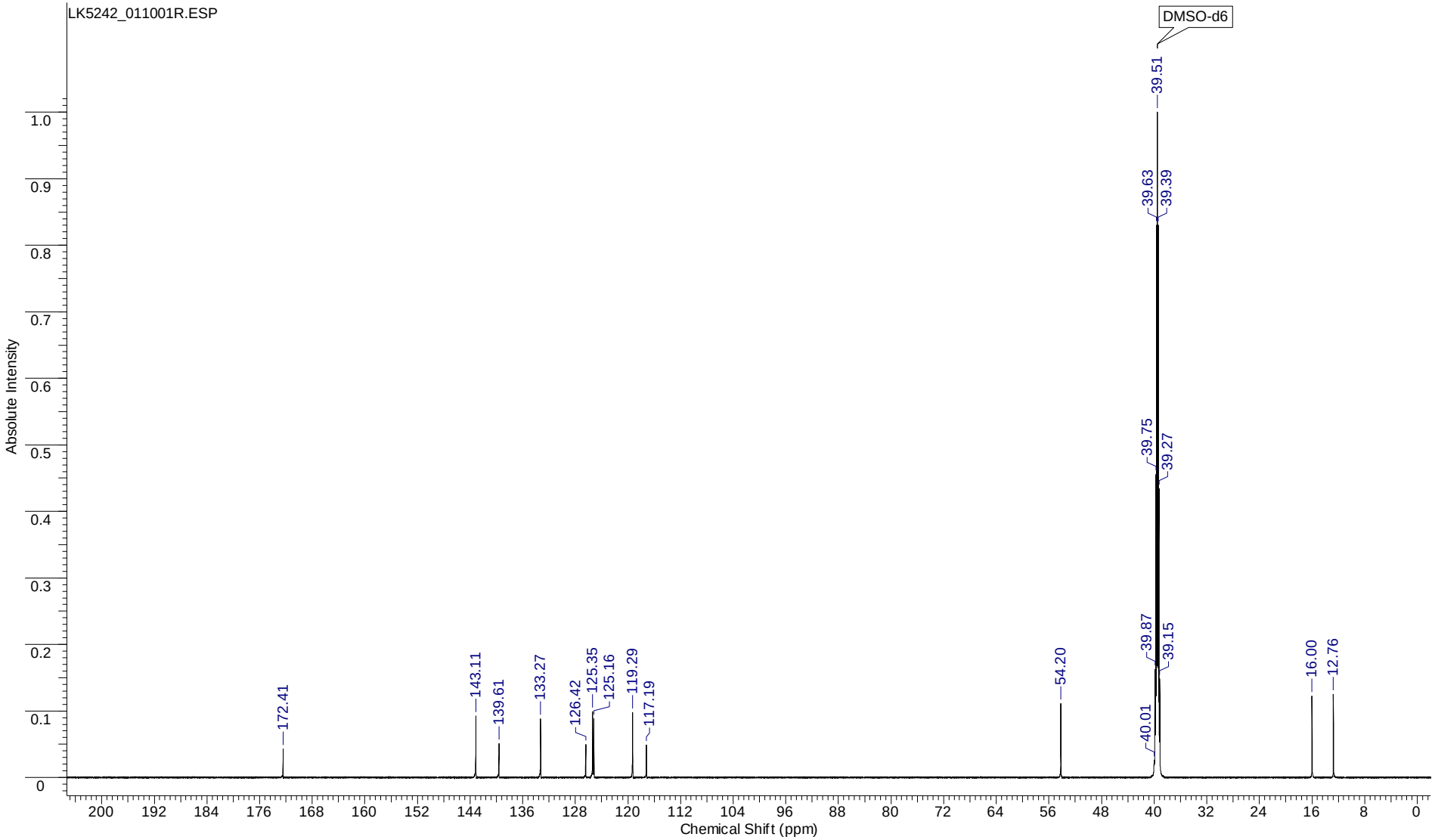
(3h) ^{1}H NMR (DMSO, 700 MHz):

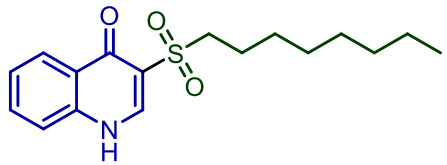




(3h)

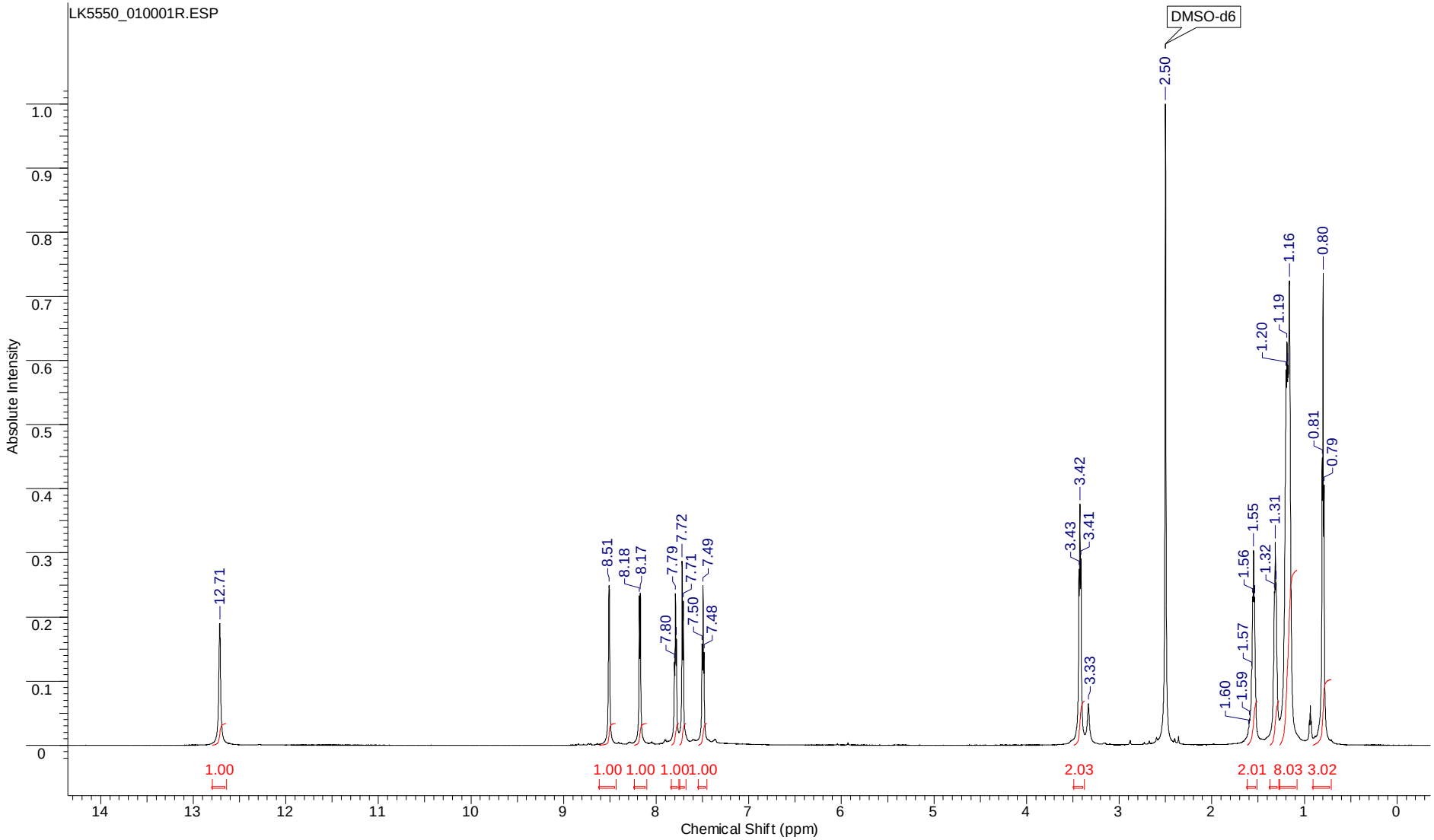
^{13}C NMR (DMSO, 150 MHz):

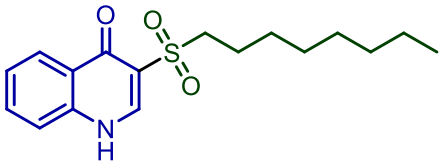




(3i)

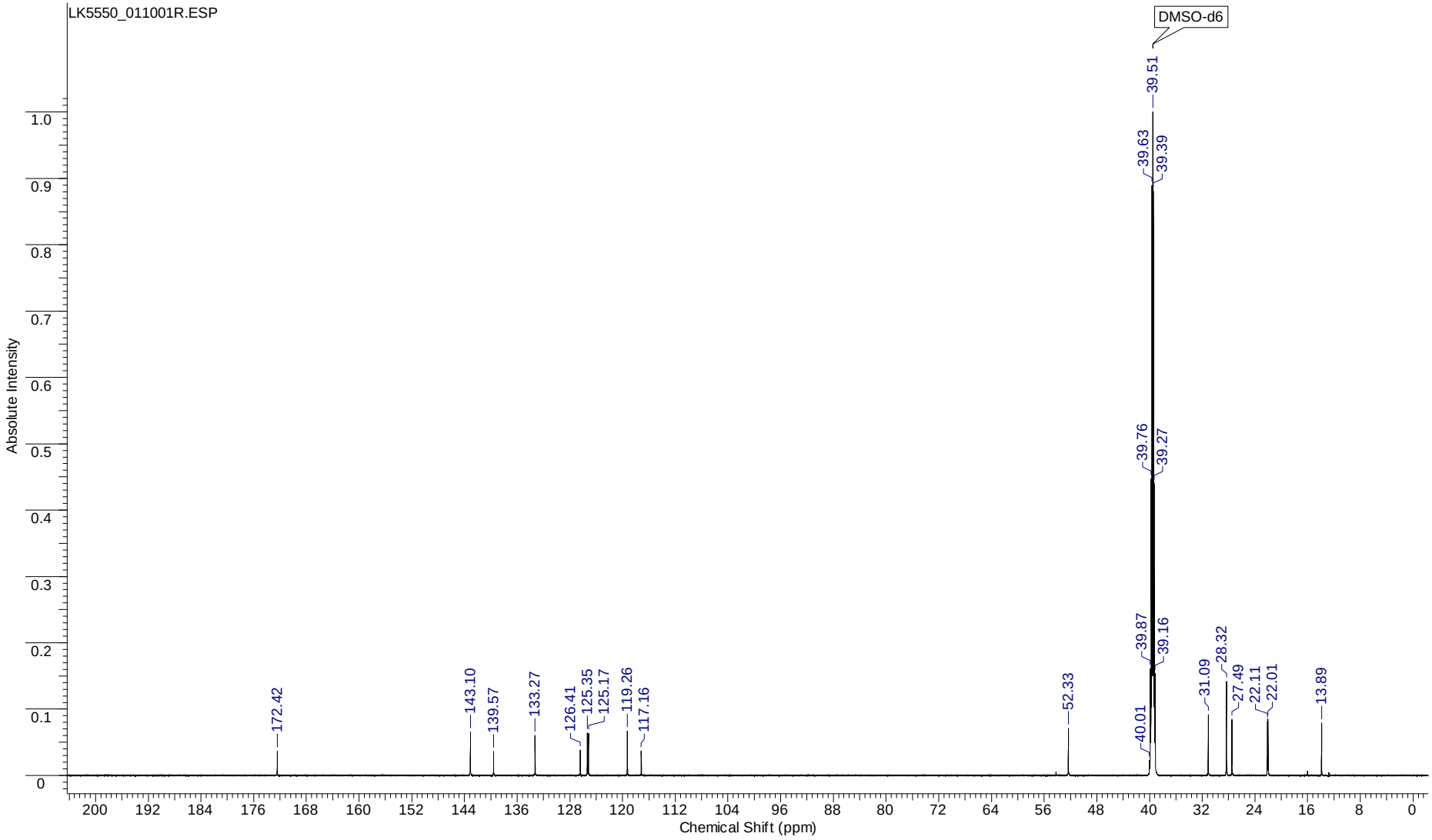
^{1}H NMR (DMSO, 700 MHz):

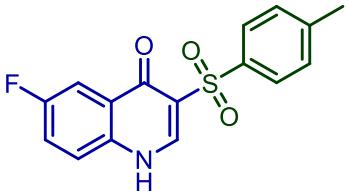




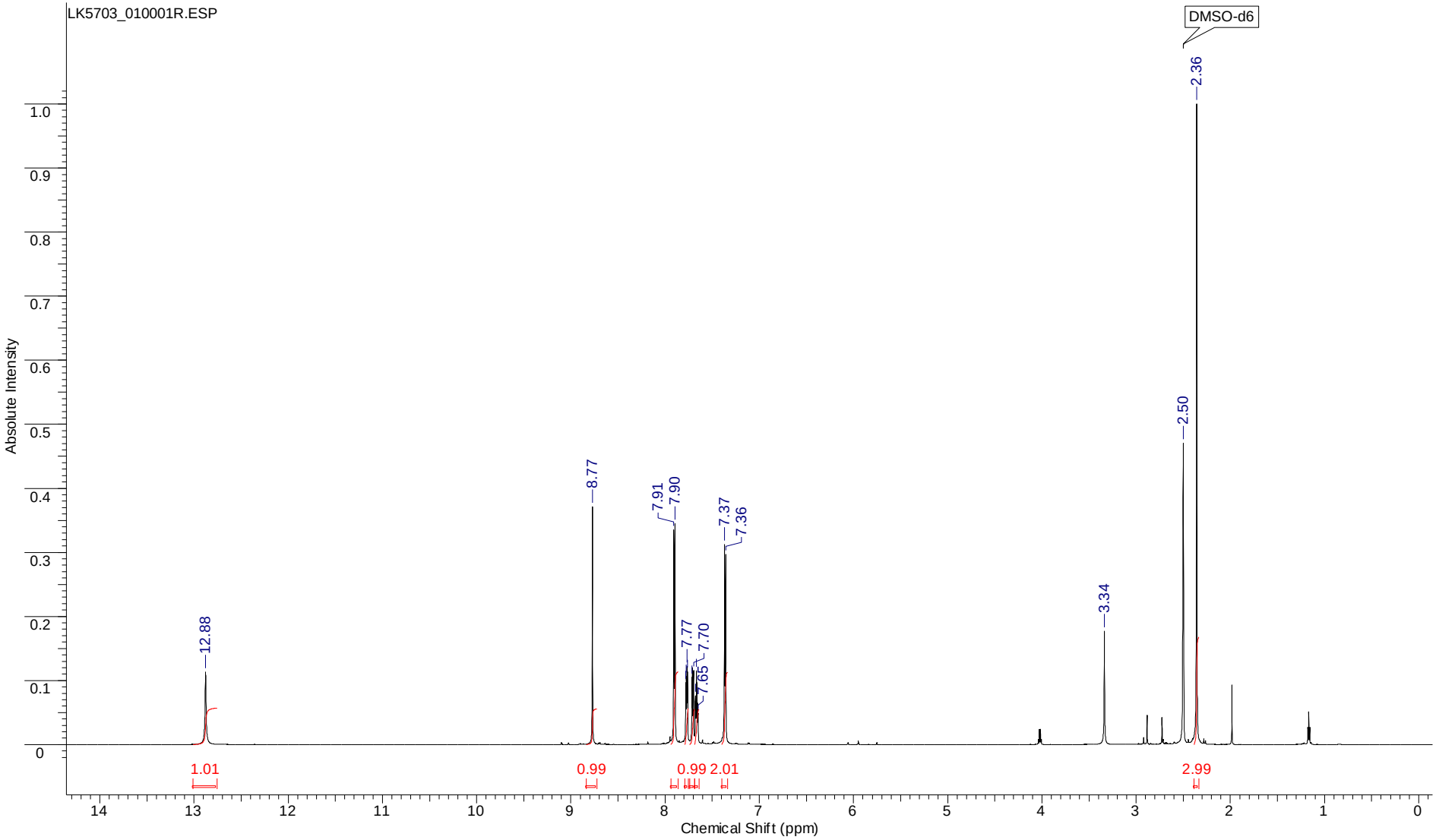
(3i)

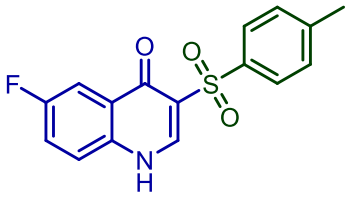
^{13}C NMR (DMSO, 150 MHz):



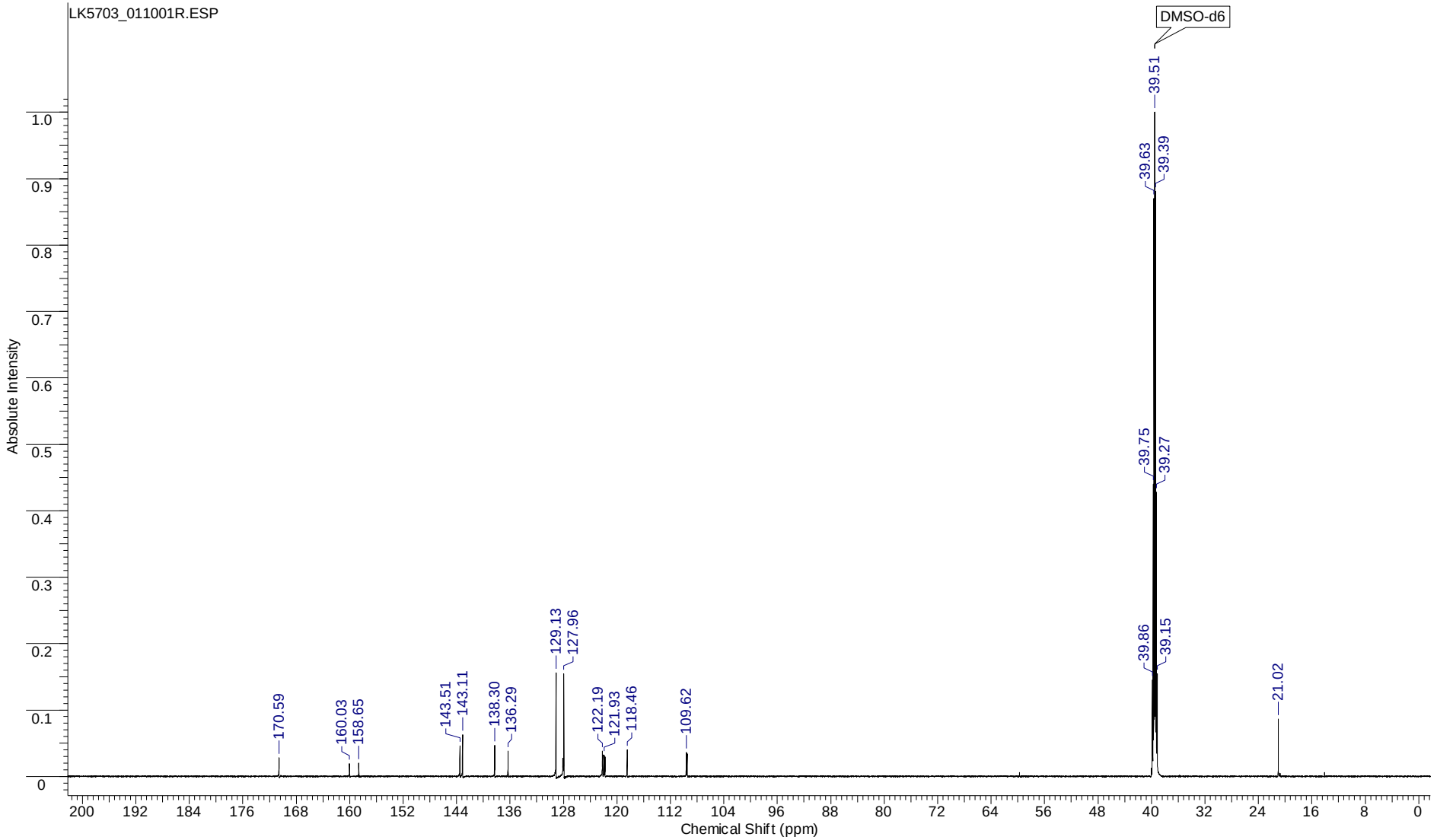


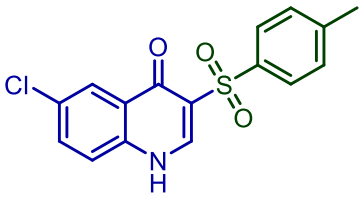
(3j) ^{1}H NMR (DMSO, 700 MHz):



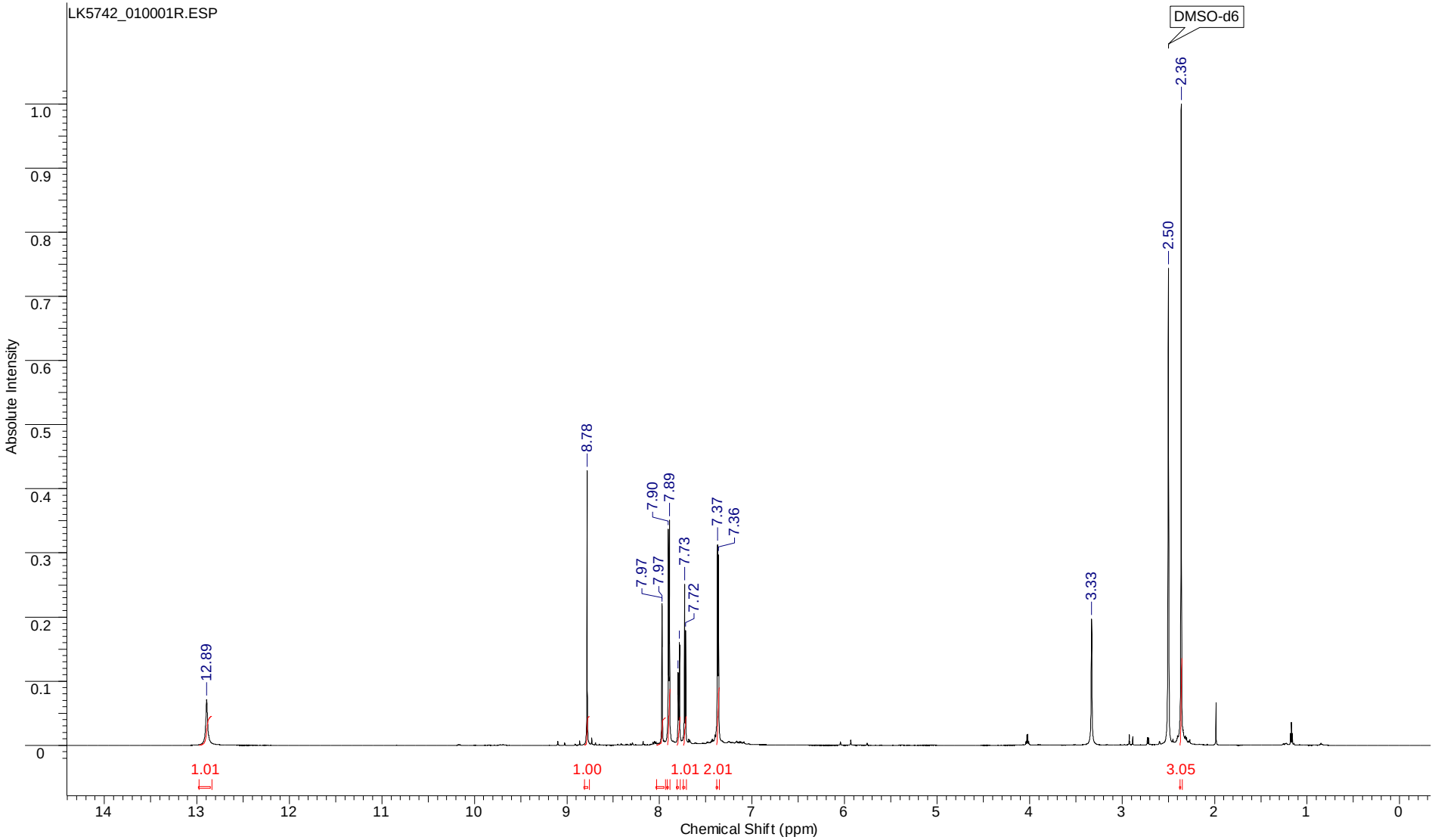


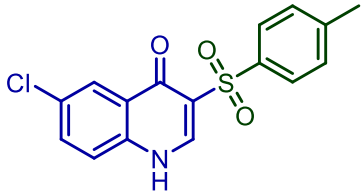
(3j) ^{13}C NMR (DMSO, 150 MHz):





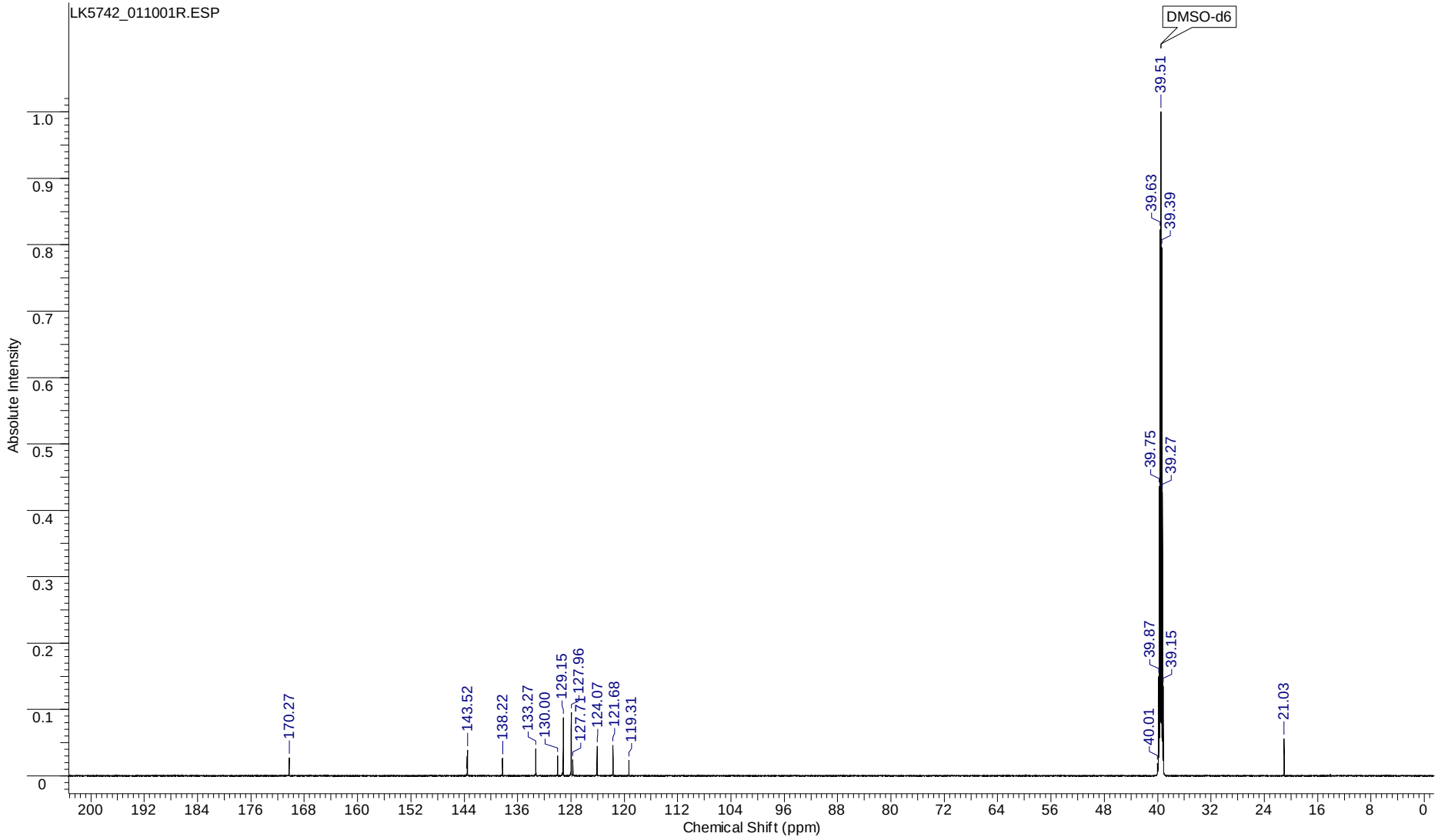
(3k) ^{1}H NMR (DMSO, 700 MHz):

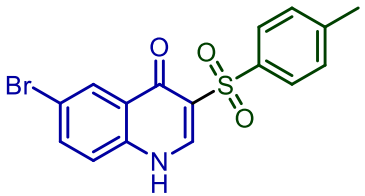




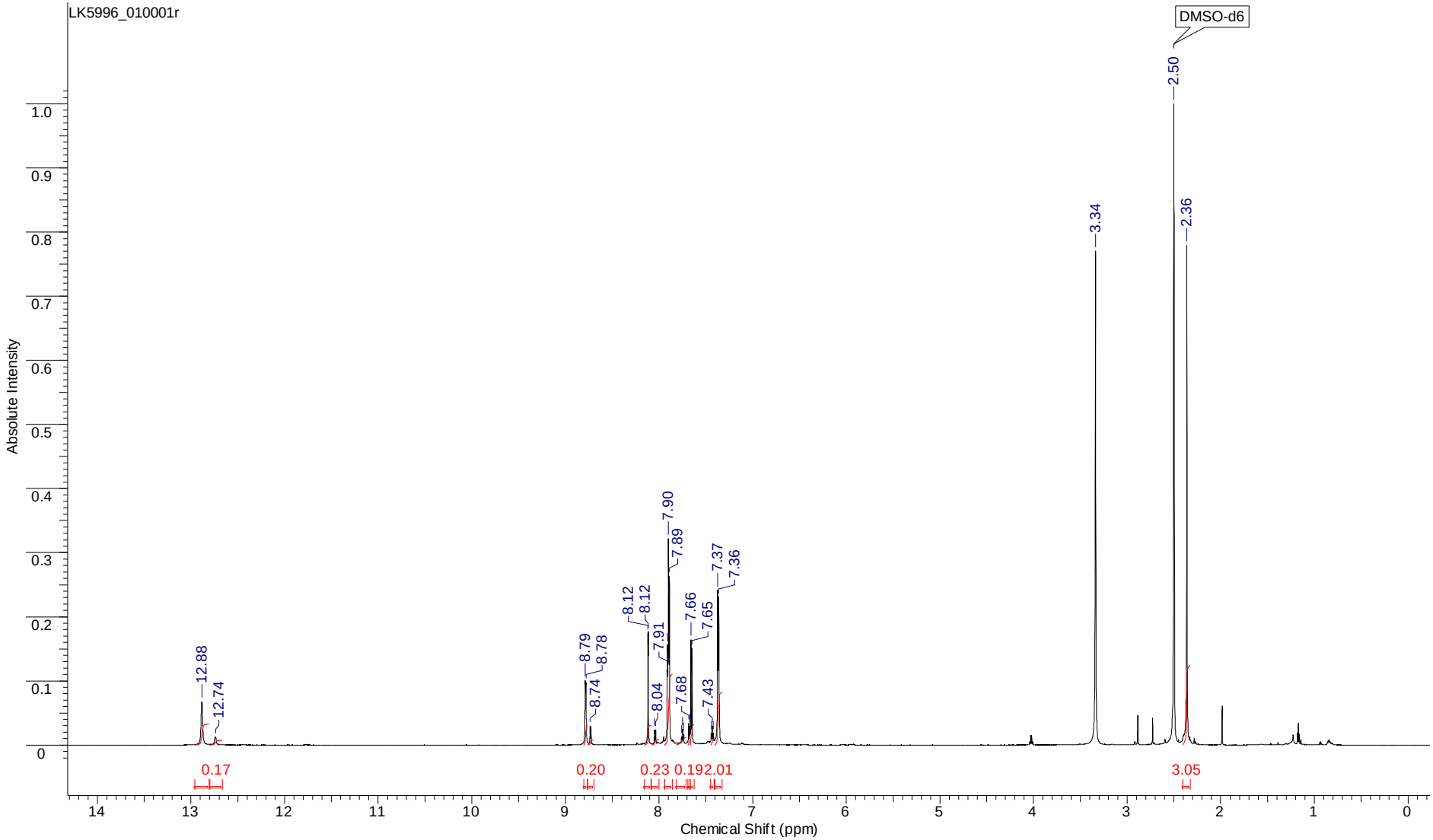
(3k)

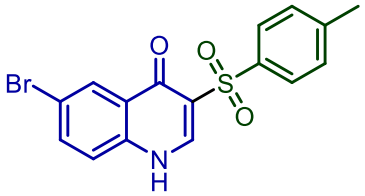
^{13}C NMR (DMSO, 150 MHz):





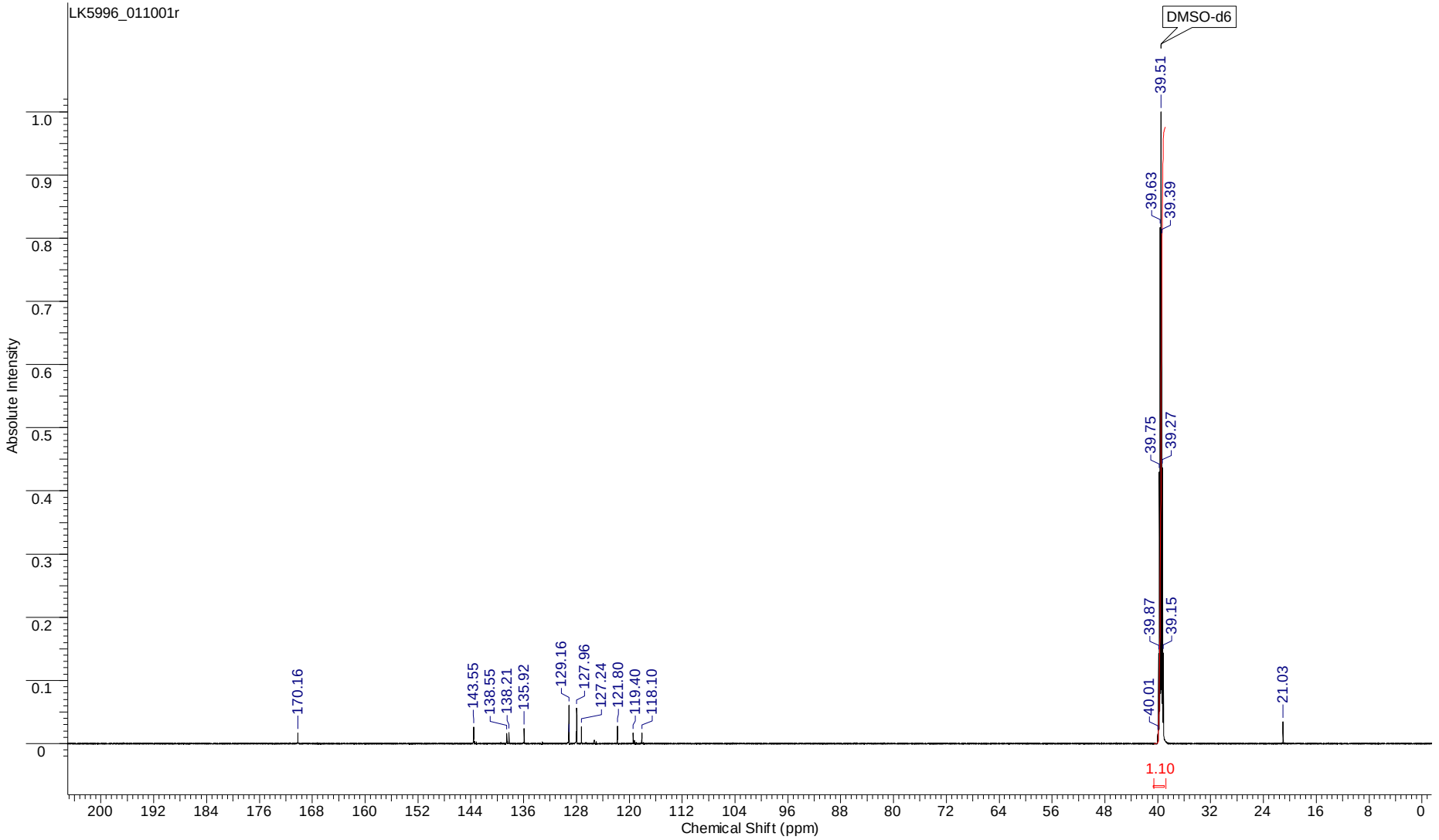
(3l) ^{1}H NMR (DMSO, 700 MHz):

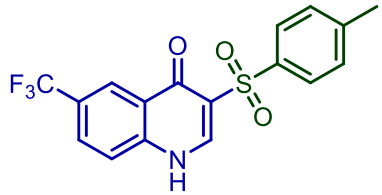




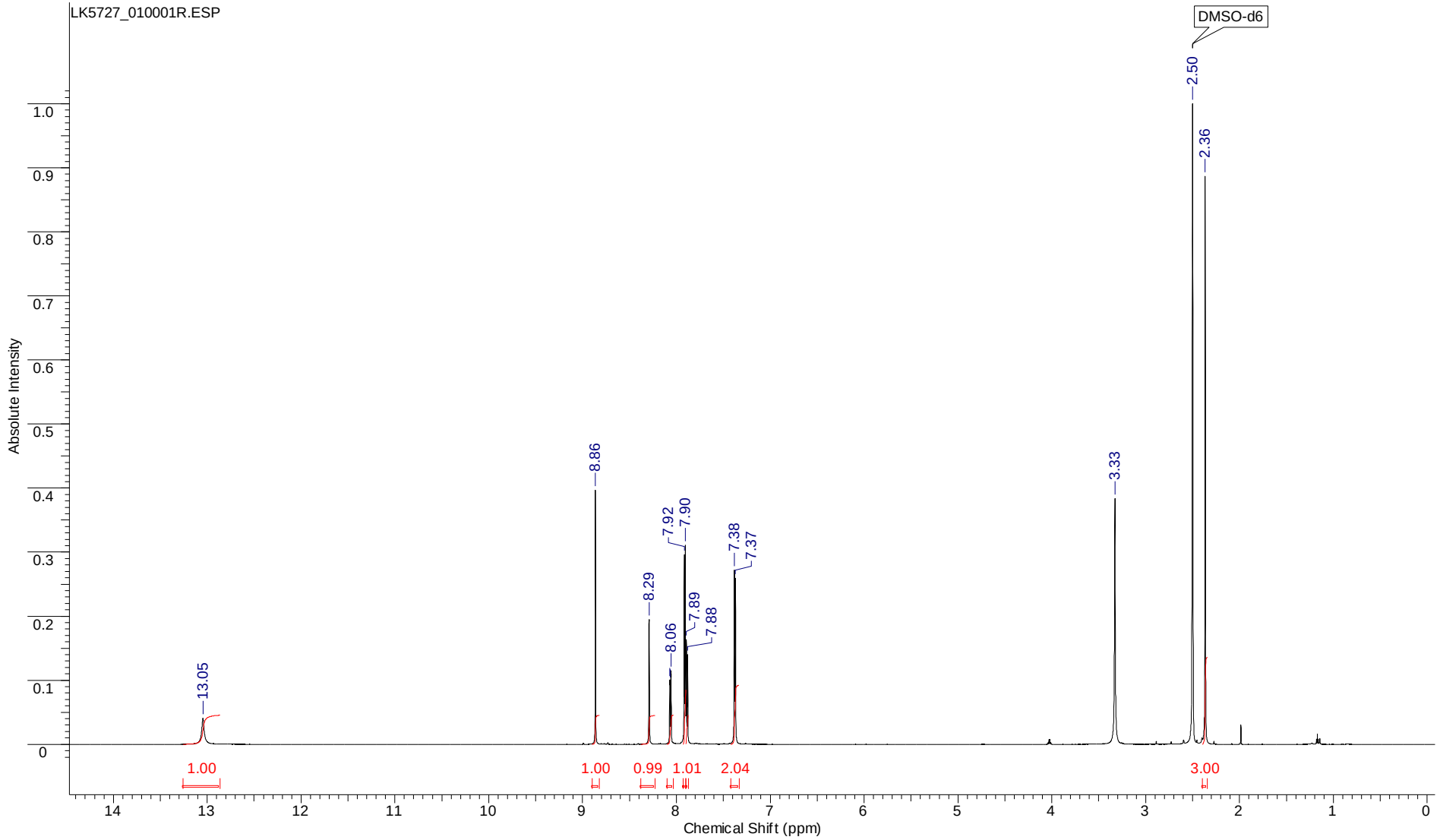
(3l)

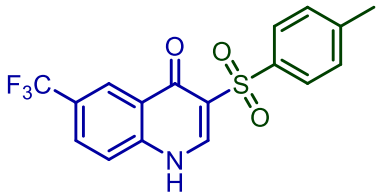
^{13}C NMR (DMSO, 150 MHz):



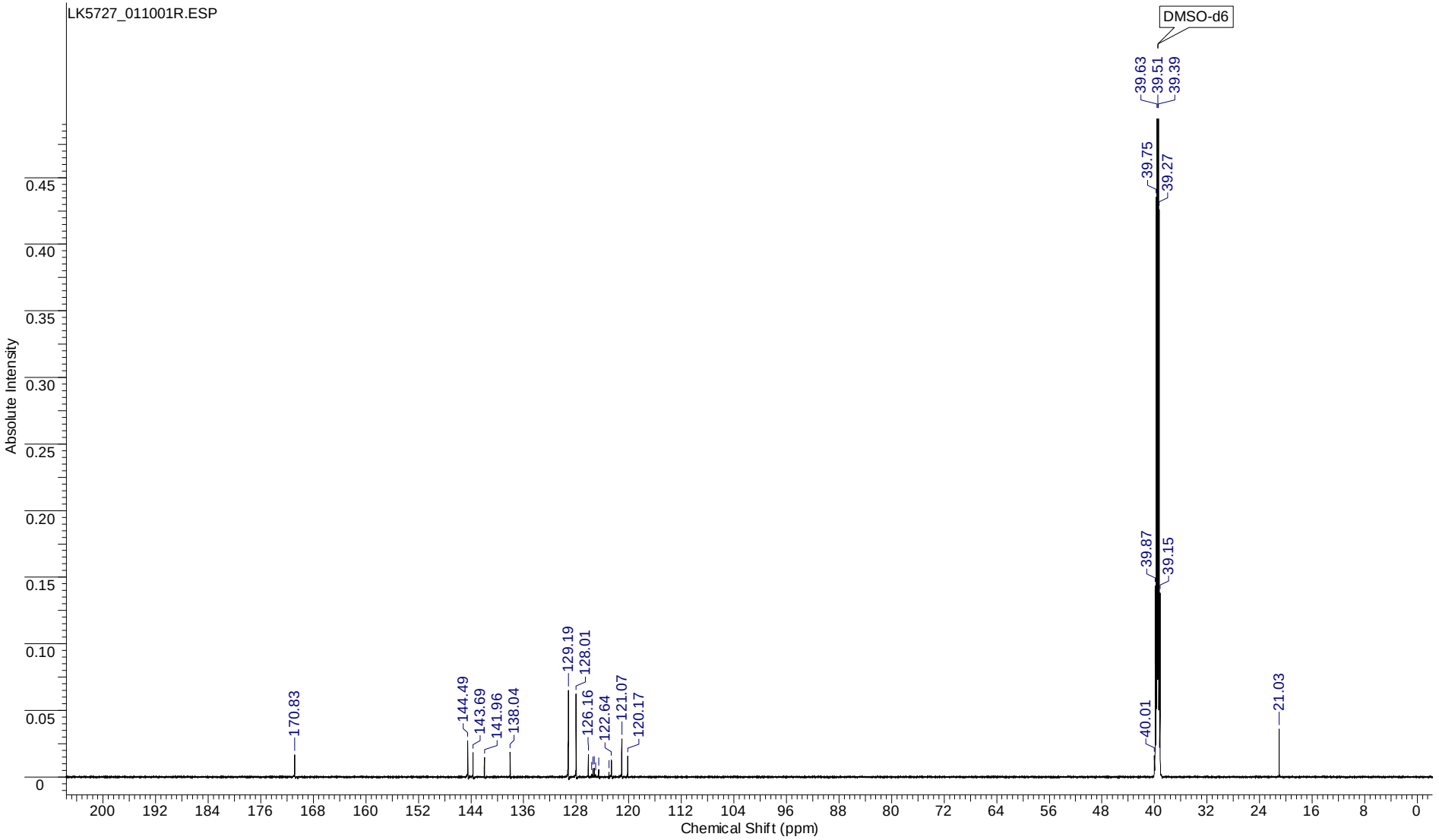


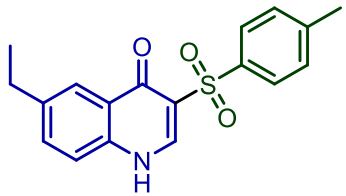
(3m) ^{1}H NMR (DMSO, 700 MHz):



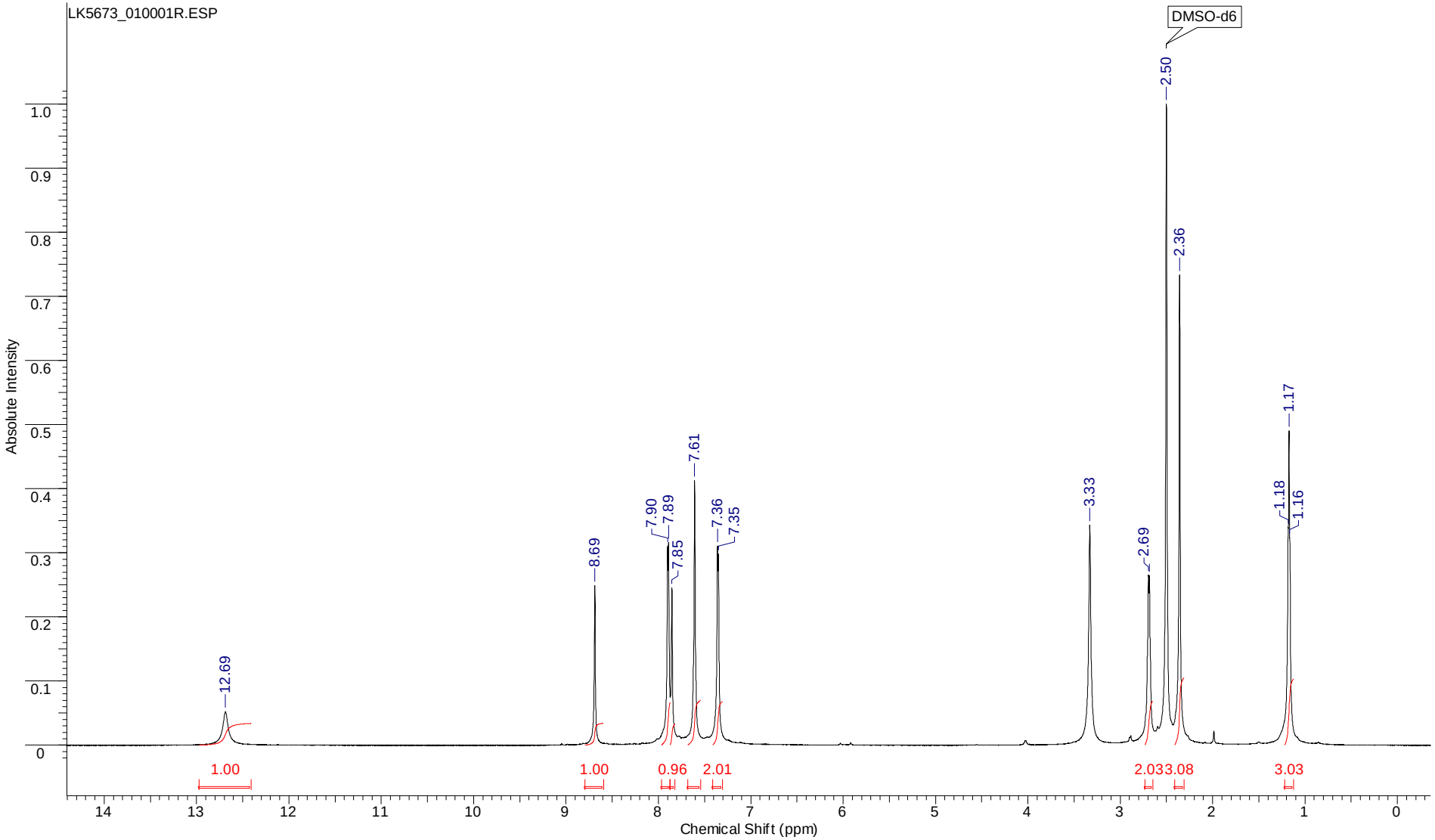


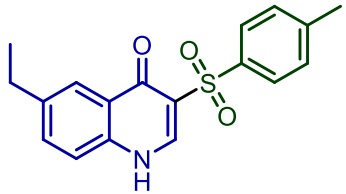
(3m) ^{13}C NMR (DMSO, 150 MHz):



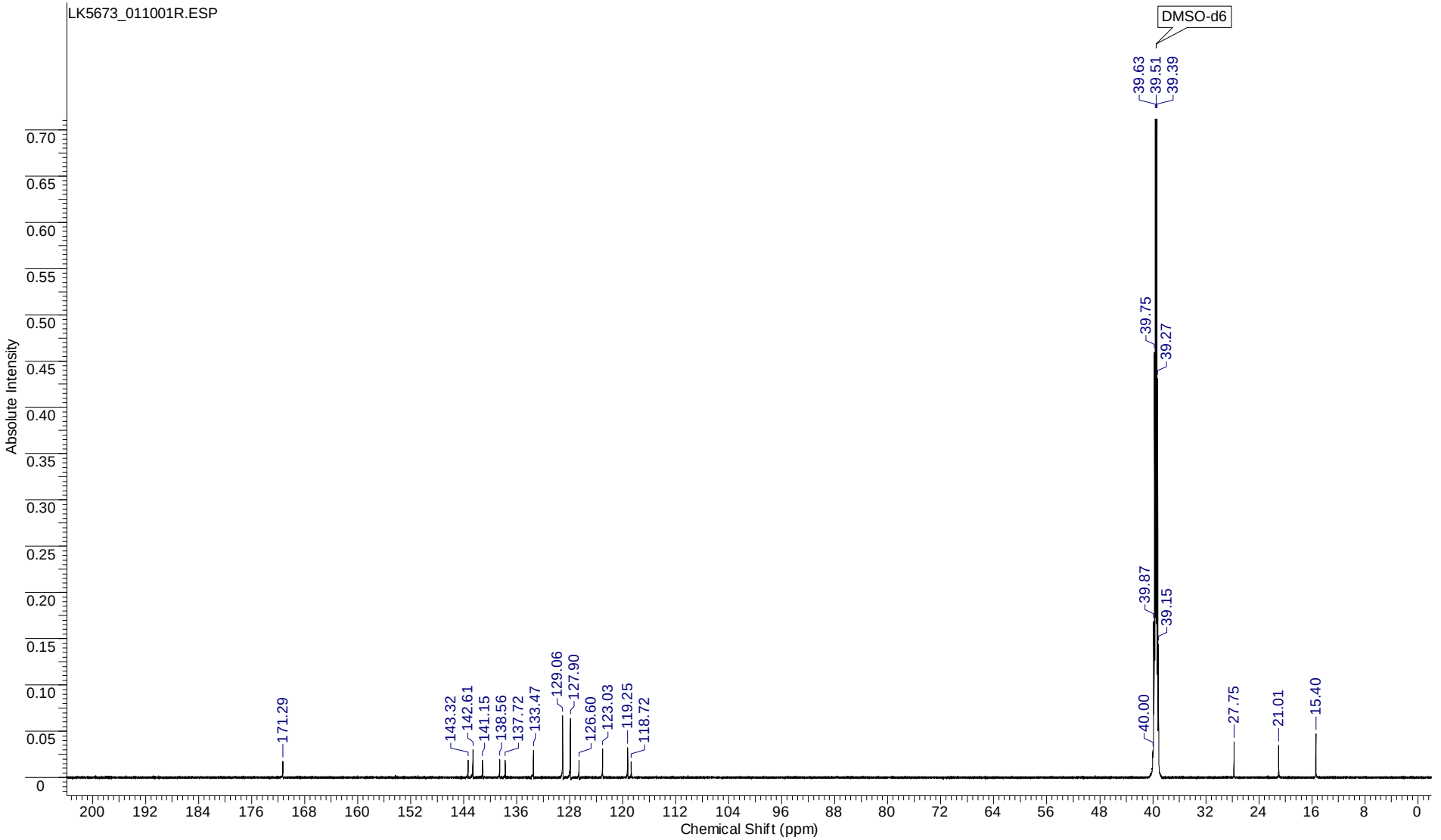


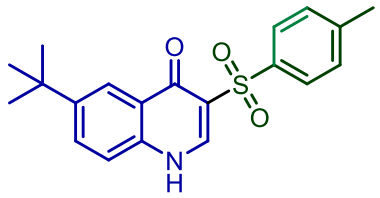
(3n) ^{1}H NMR (DMSO, 700 MHz):



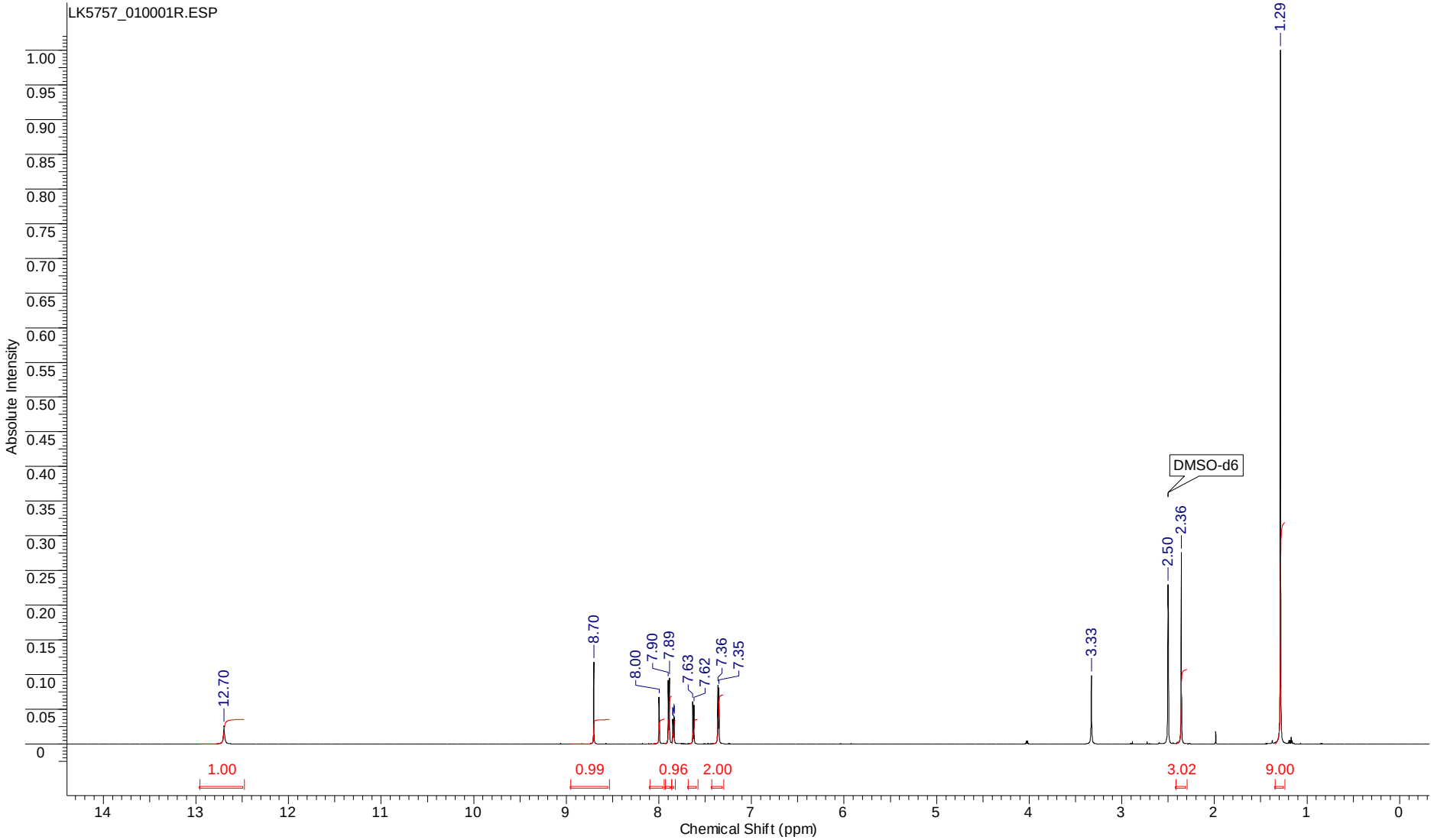


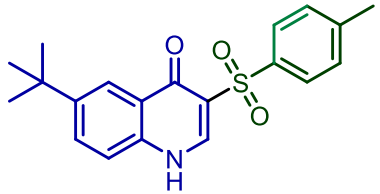
(3n) ^{13}C NMR (DMSO, 150 MHz):





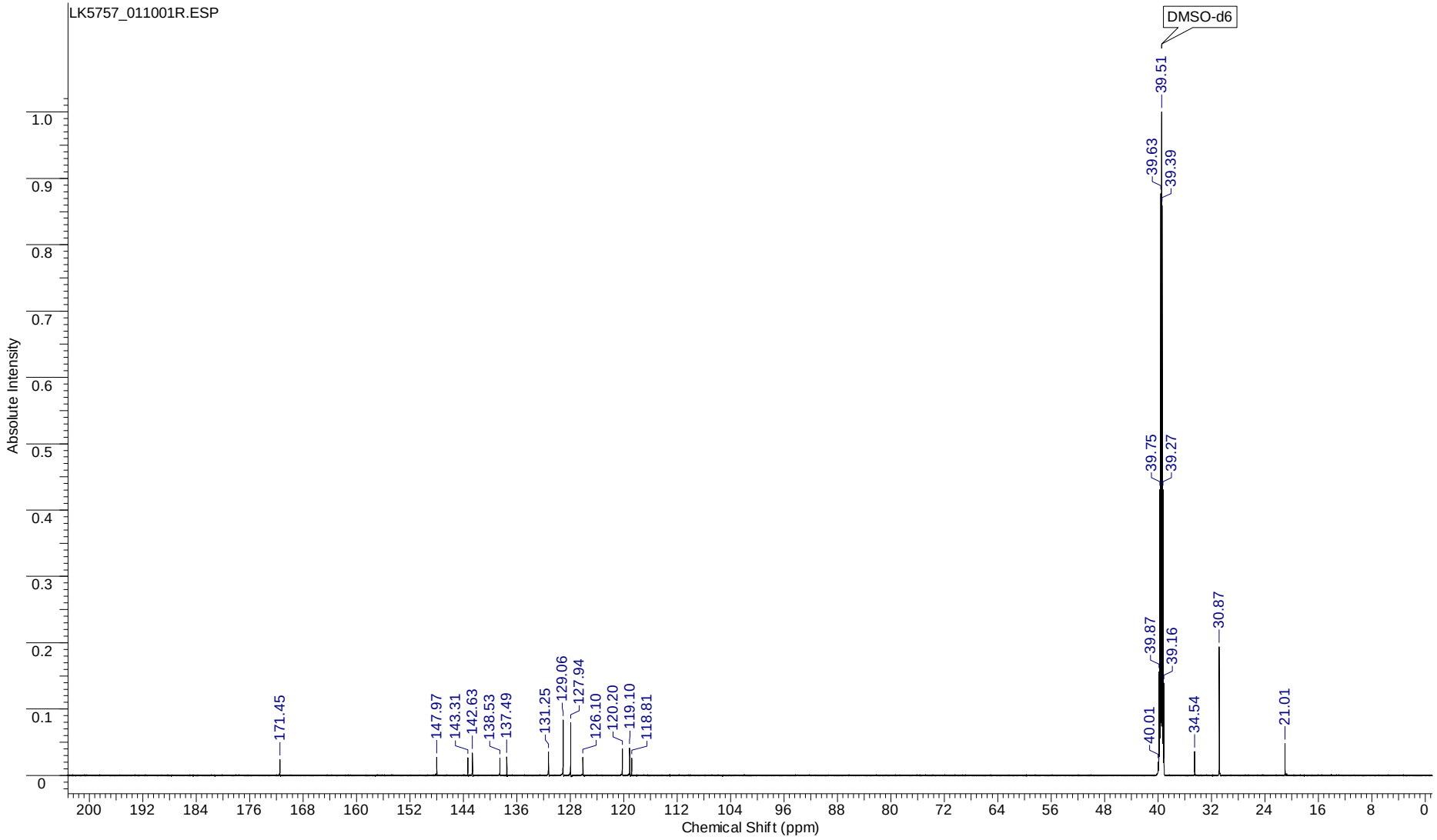
(3o) ^{1}H NMR (DMSO, 700 MHz):

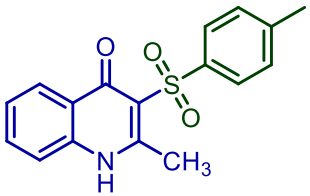




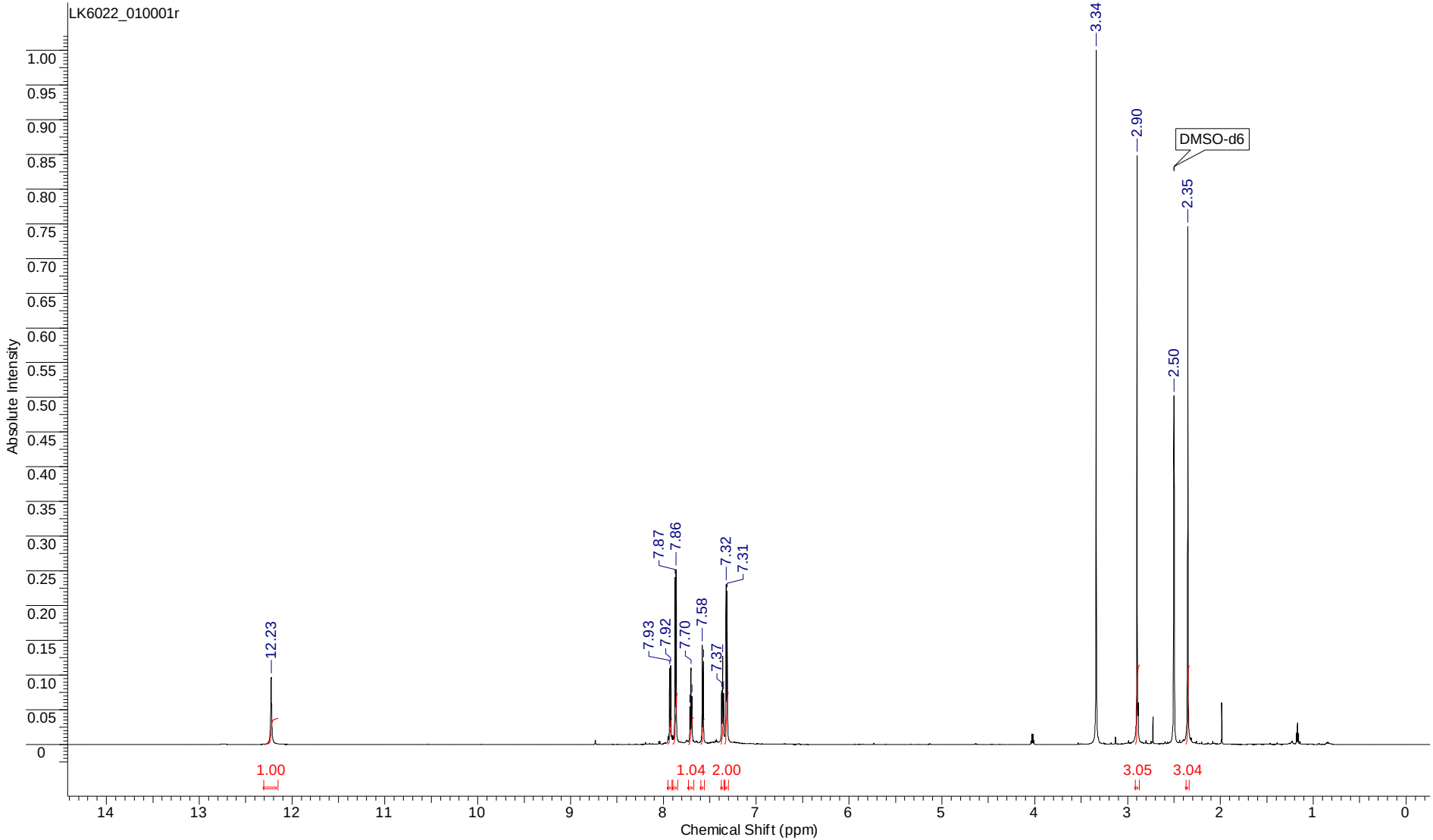
(3o)

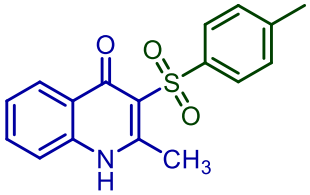
^{13}C NMR (DMSO, 150 MHz):





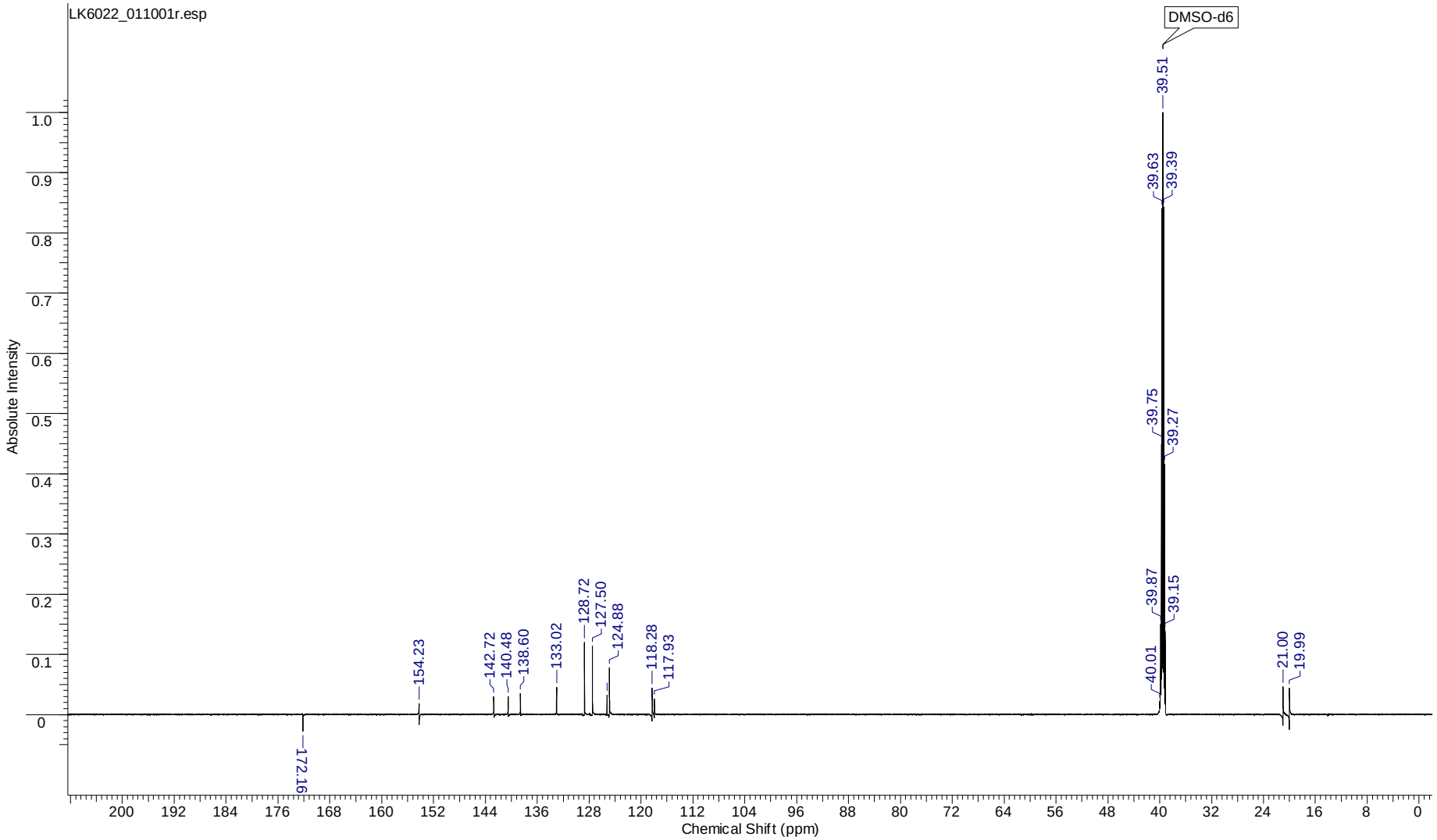
(3p) ^{1}H NMR (DMSO, 700 MHz):

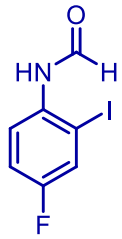




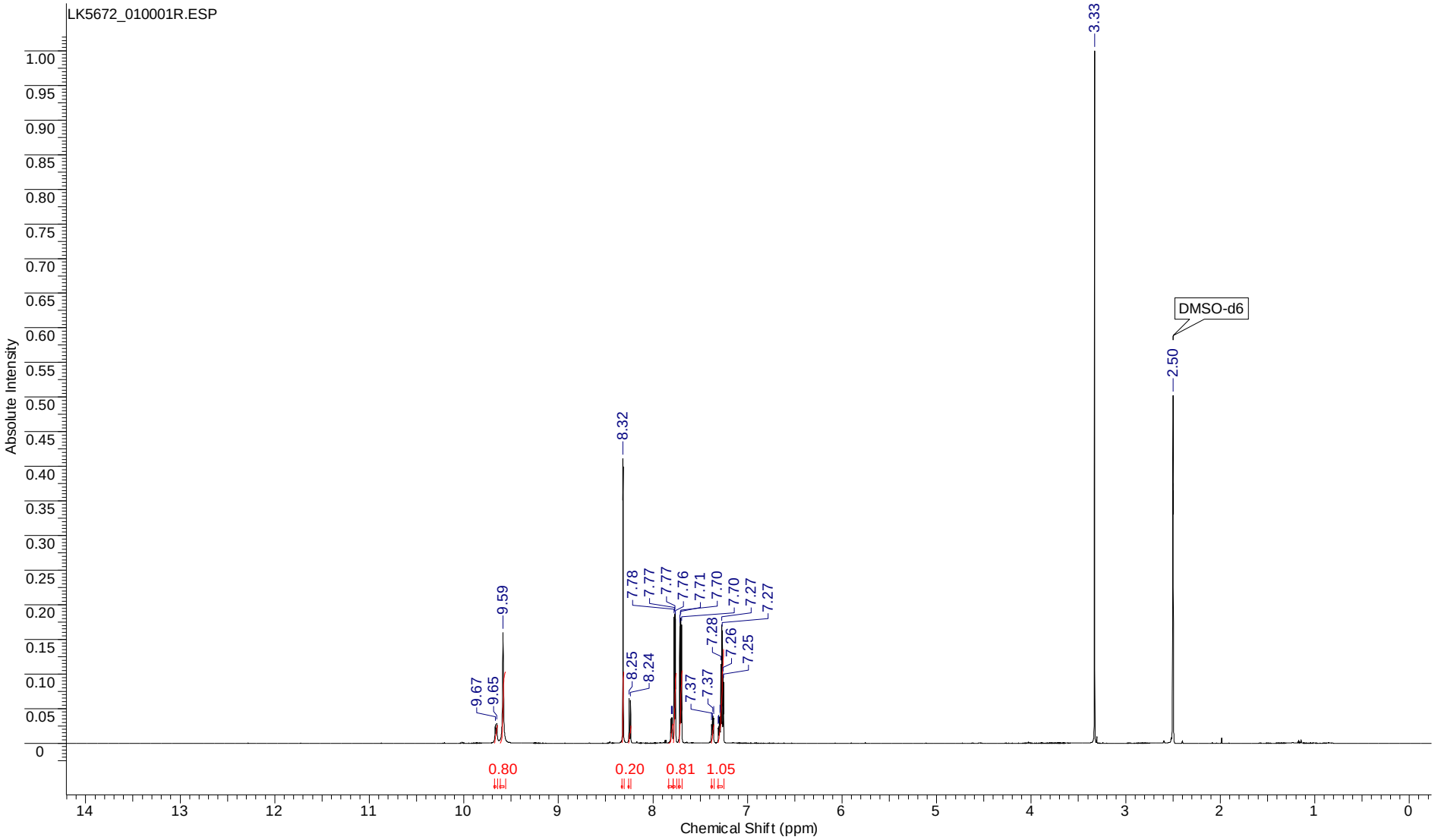
(3p)

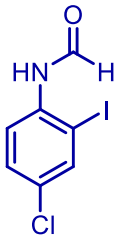
^{13}C NMR (DMSO, 150 MHz):



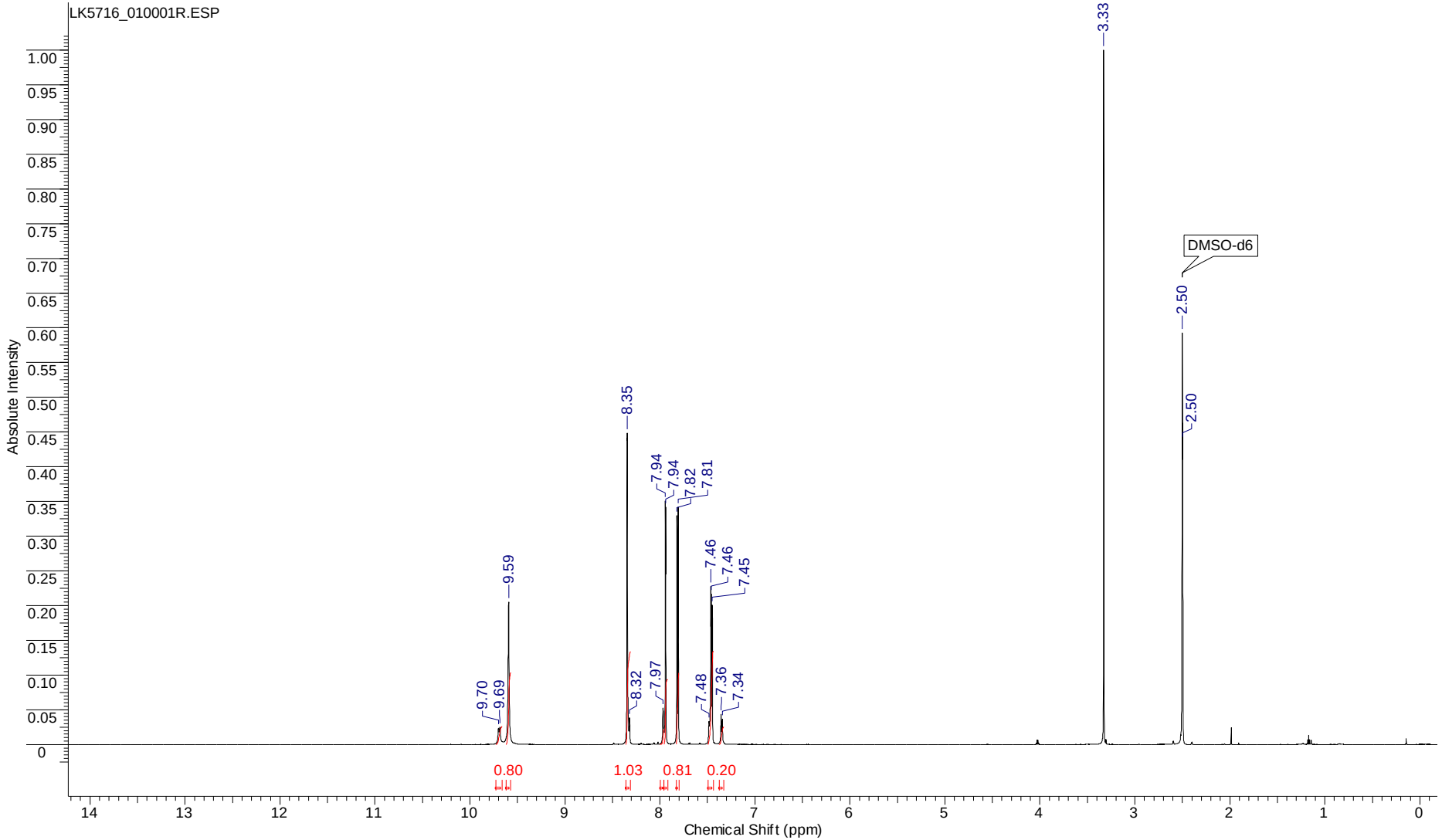


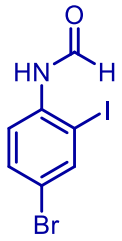
(4a) ^{1}H NMR (DMSO, 700 MHz):



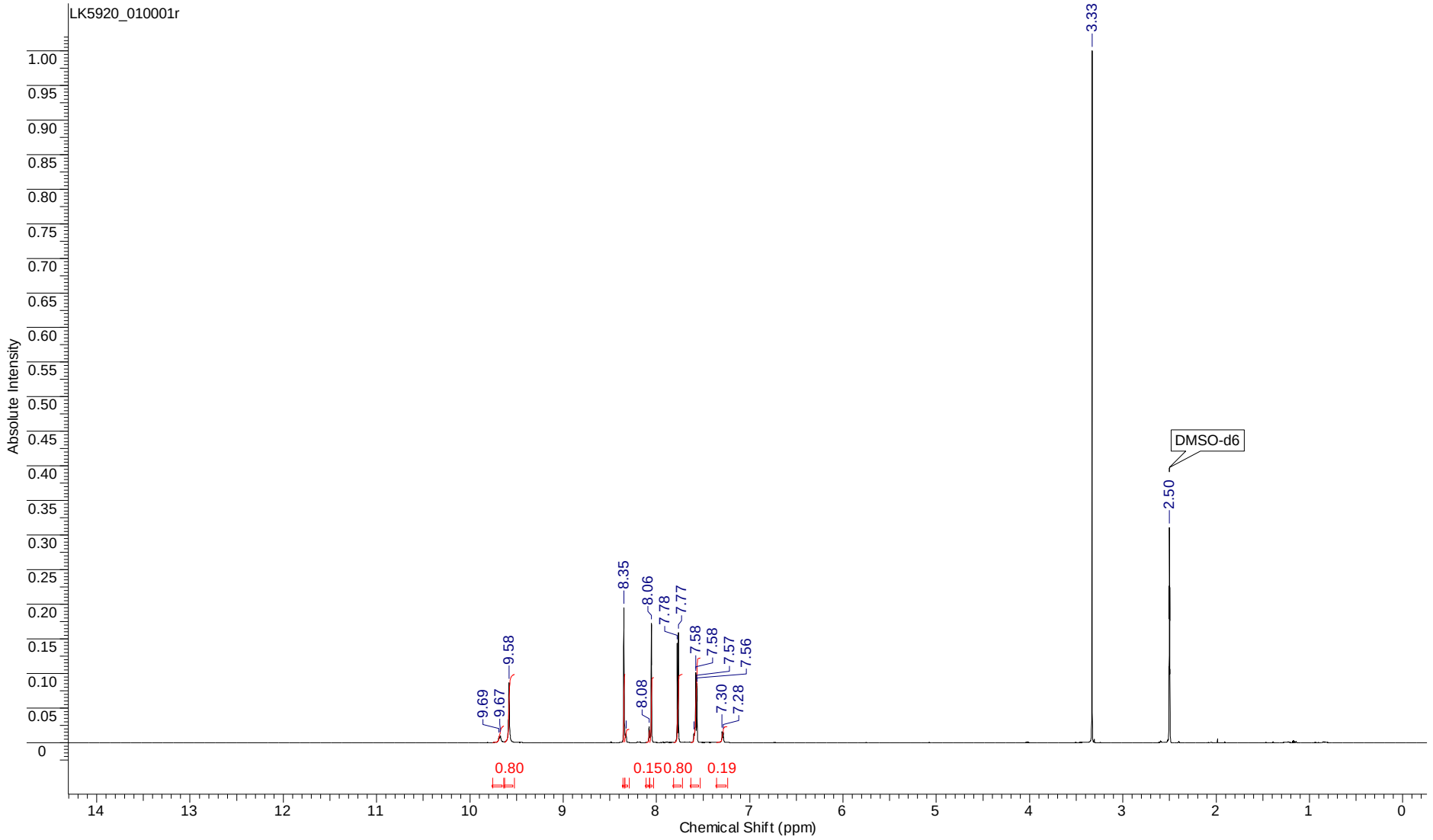


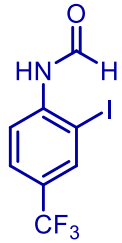
(4b) ^{1}H NMR (DMSO, 700 MHz):



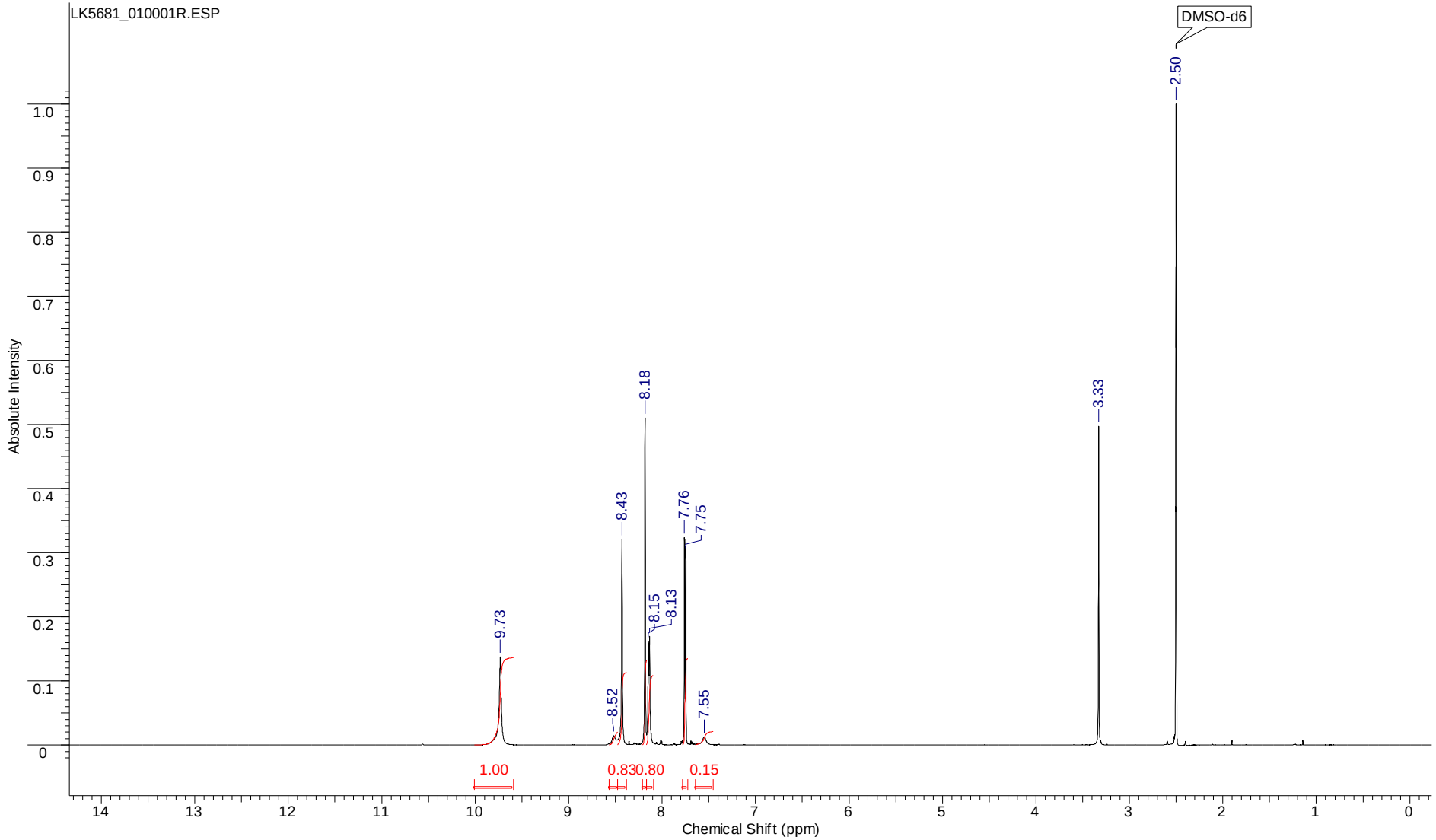


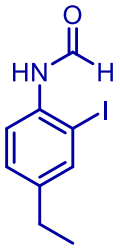
(4c) ^{1}H NMR (DMSO, 700 MHz):





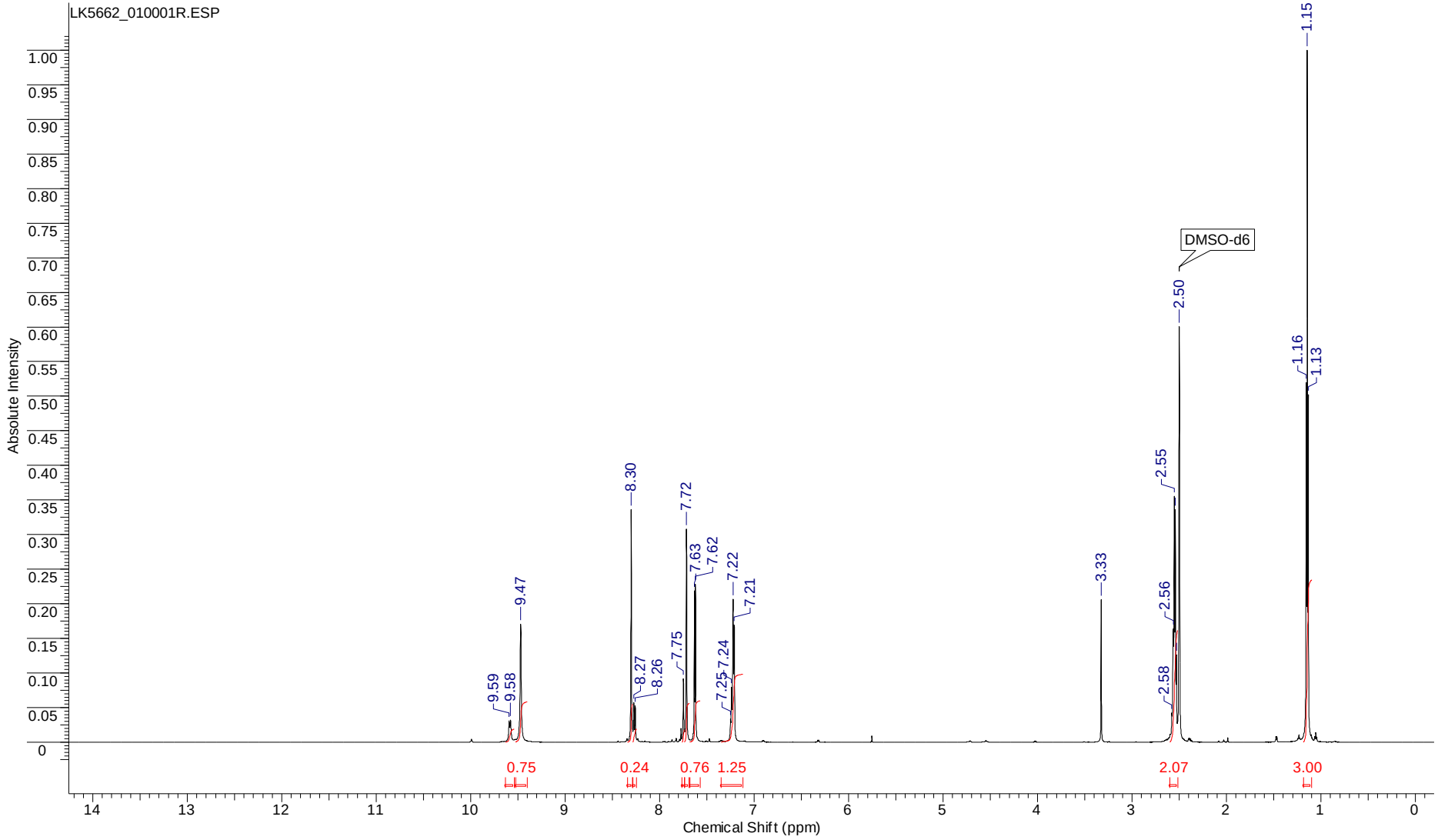
(4d) ^{1}H NMR (DMSO, 700 MHz):

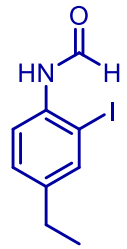




(4e)

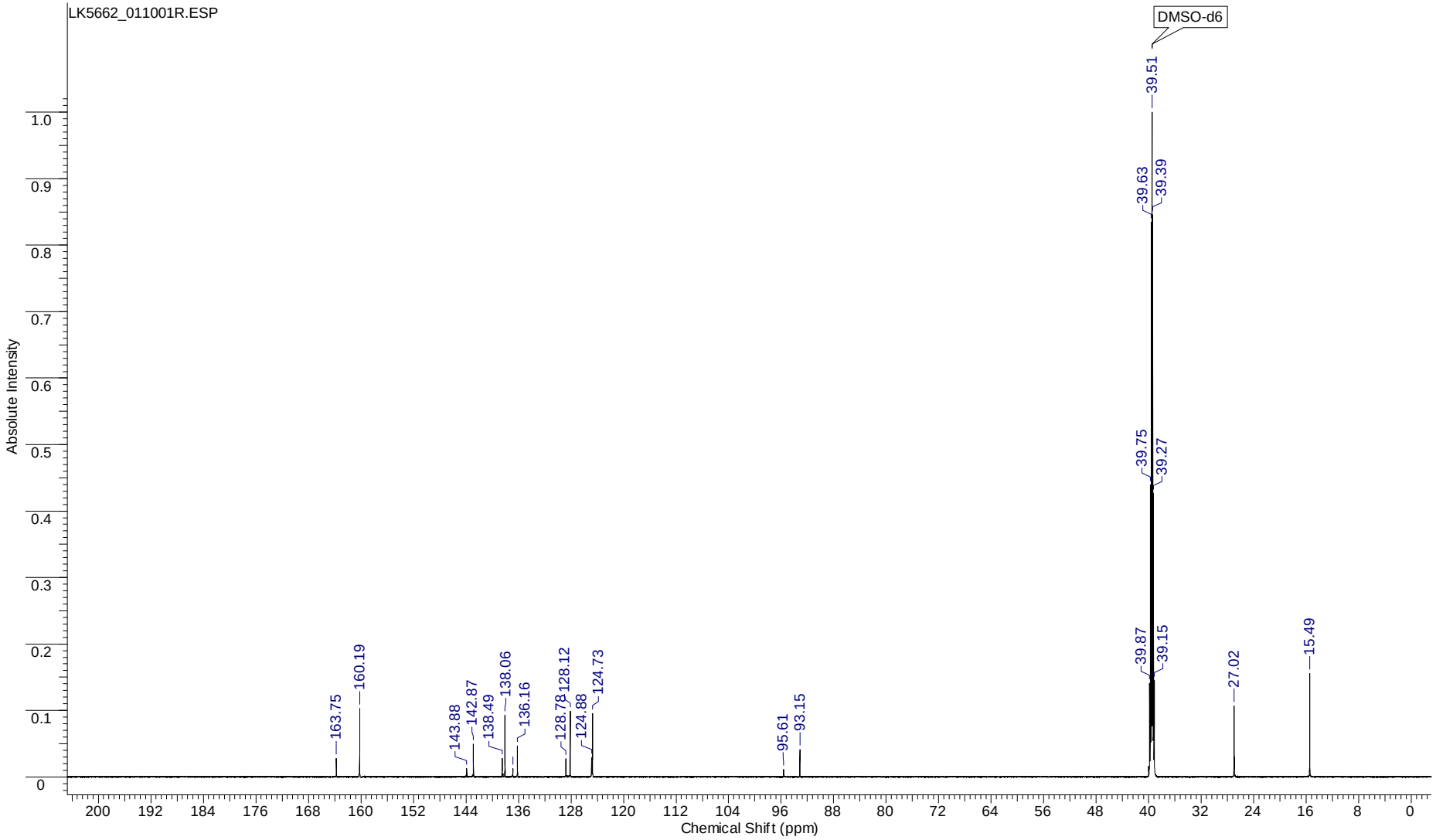
^{1}H NMR (DMSO, 700 MHz)

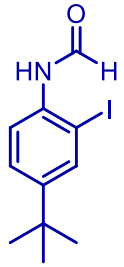




(4e)

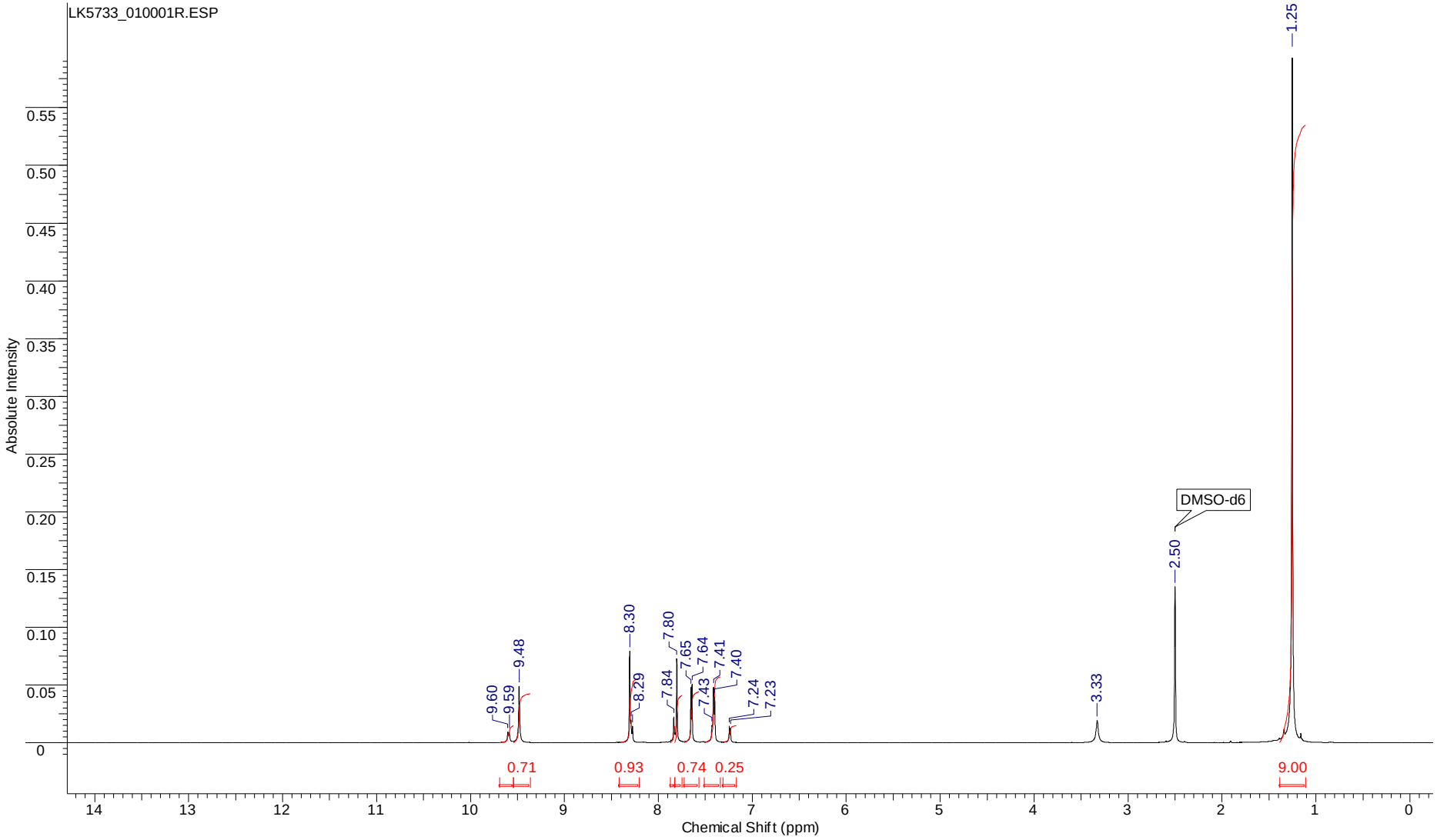
^{13}C NMR (DMSO, 150 MHz):

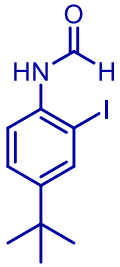




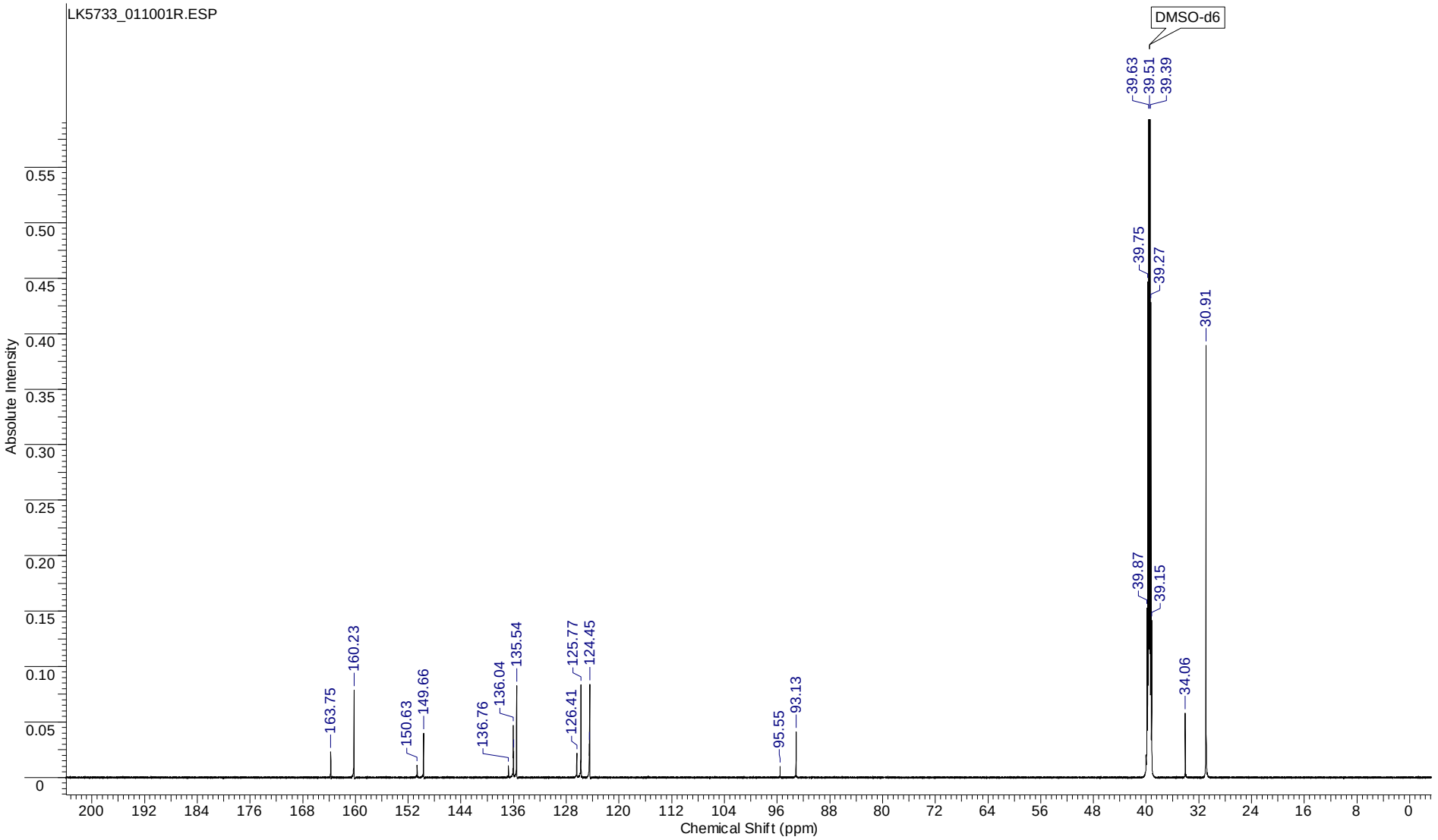
(4f)

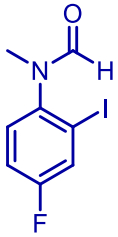
^{1}H NMR (DMSO, 700 MHz):





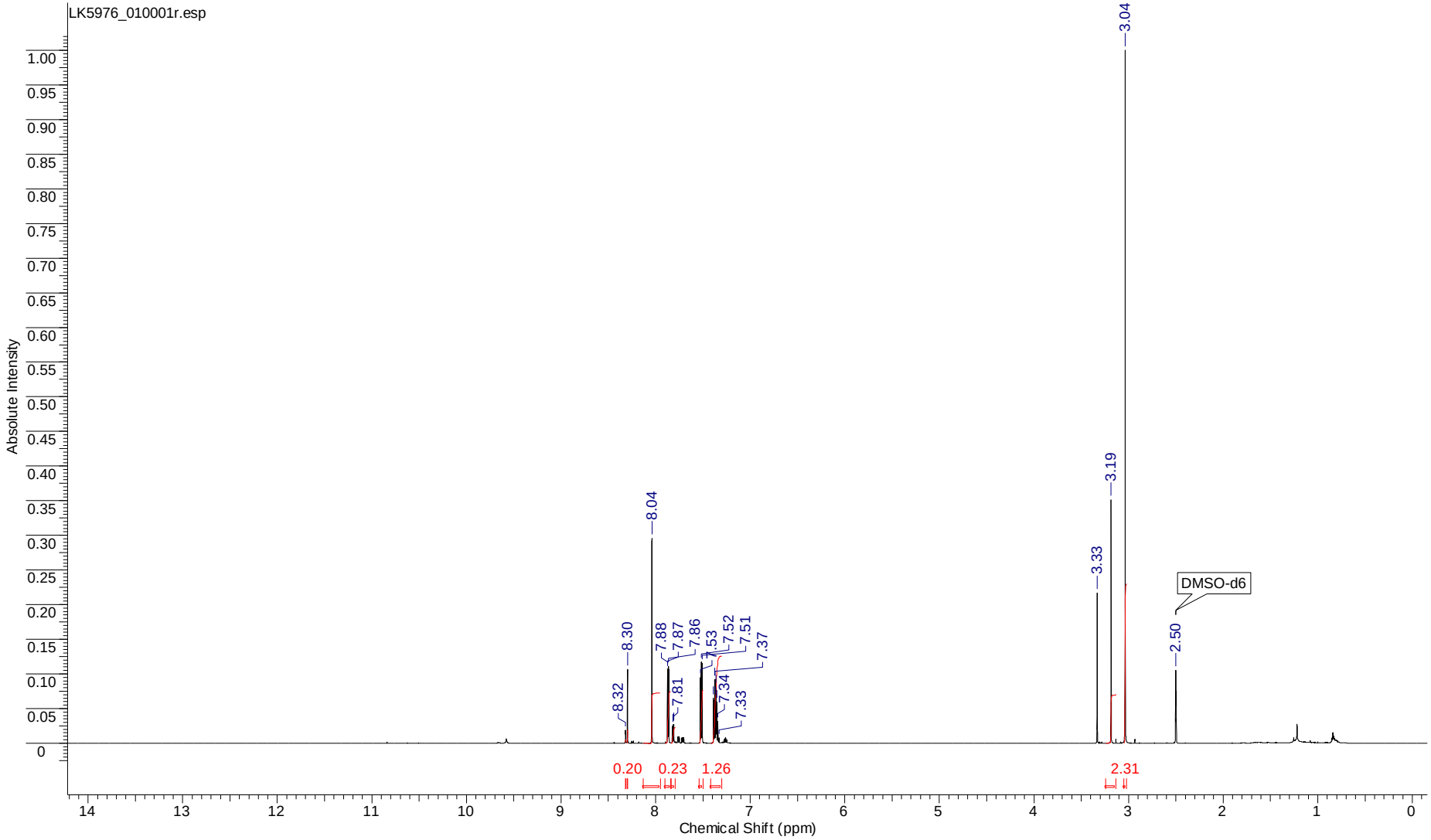
(4f) ^{13}C NMR (DMSO, 150 MHz):

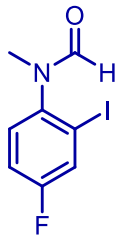




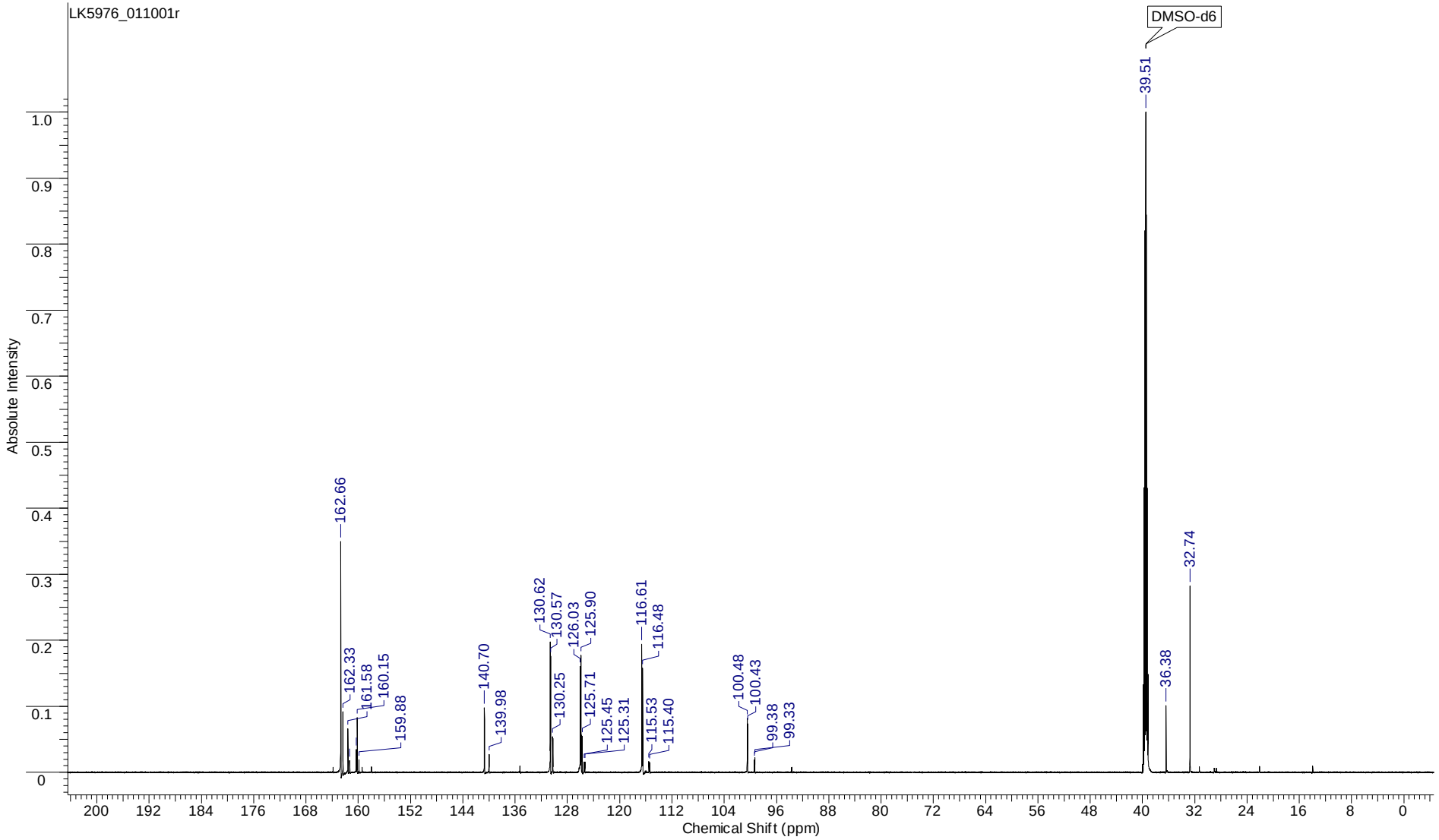
(4aa)

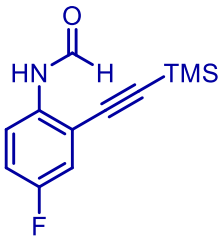
^{1}H NMR (DMSO, 700 MHz):



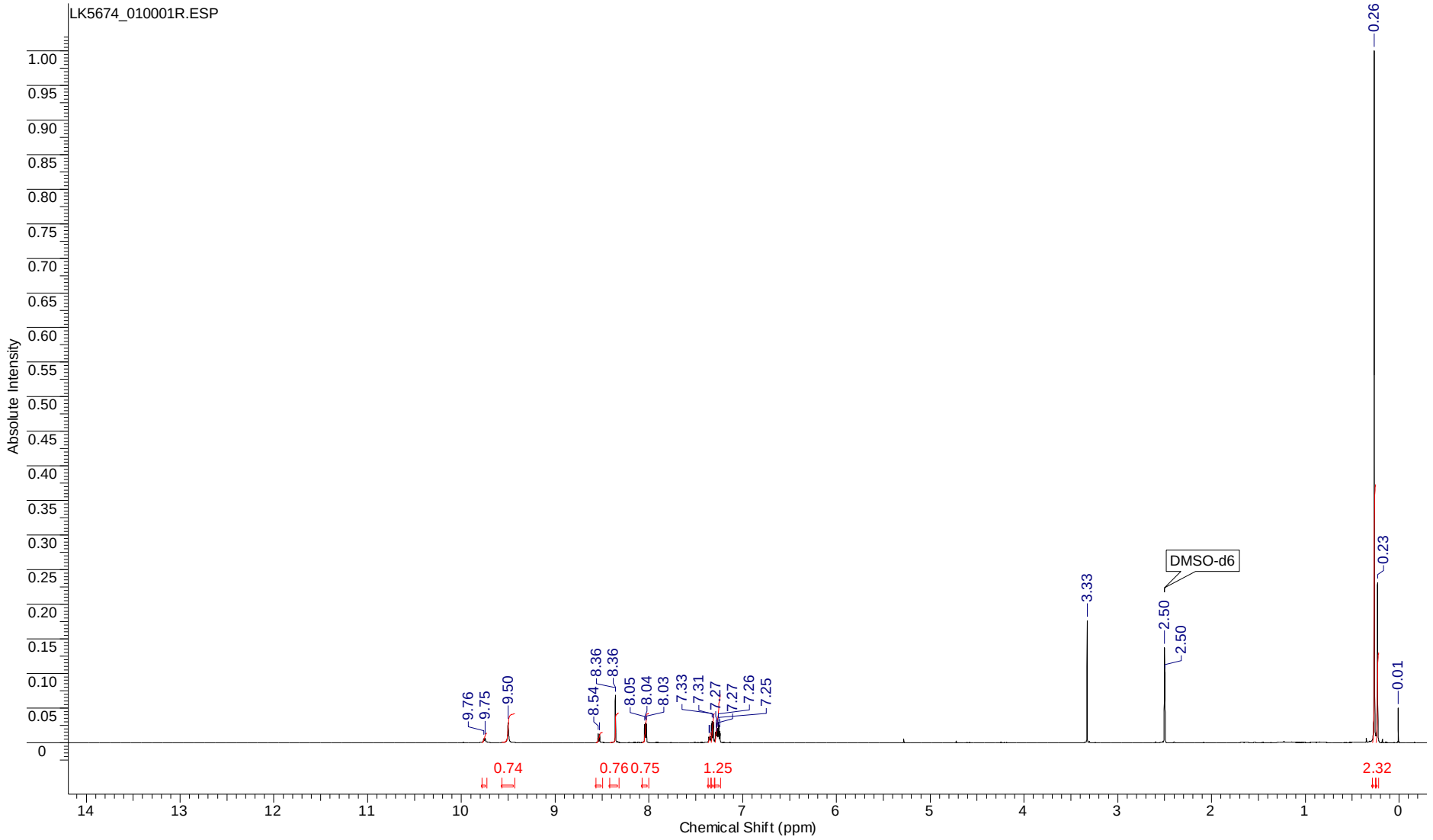


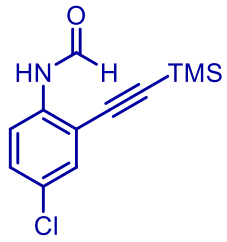
(4aa) ^{13}C NMR (DMSO, 150 MHz):



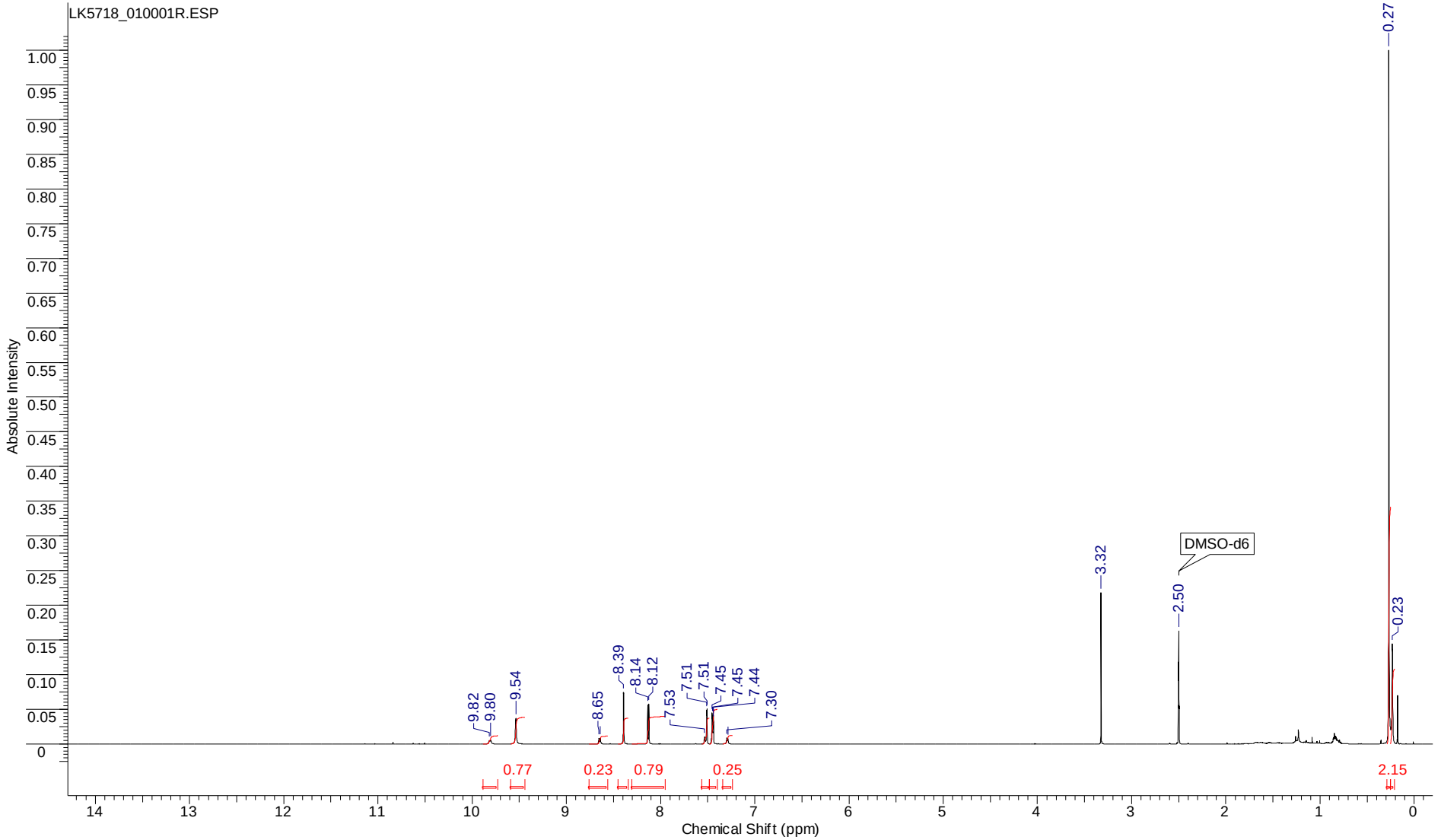


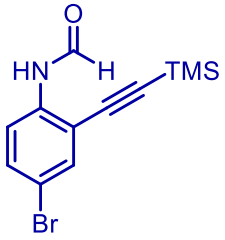
(5a) ^{1}H NMR (DMSO, 700 MHz):





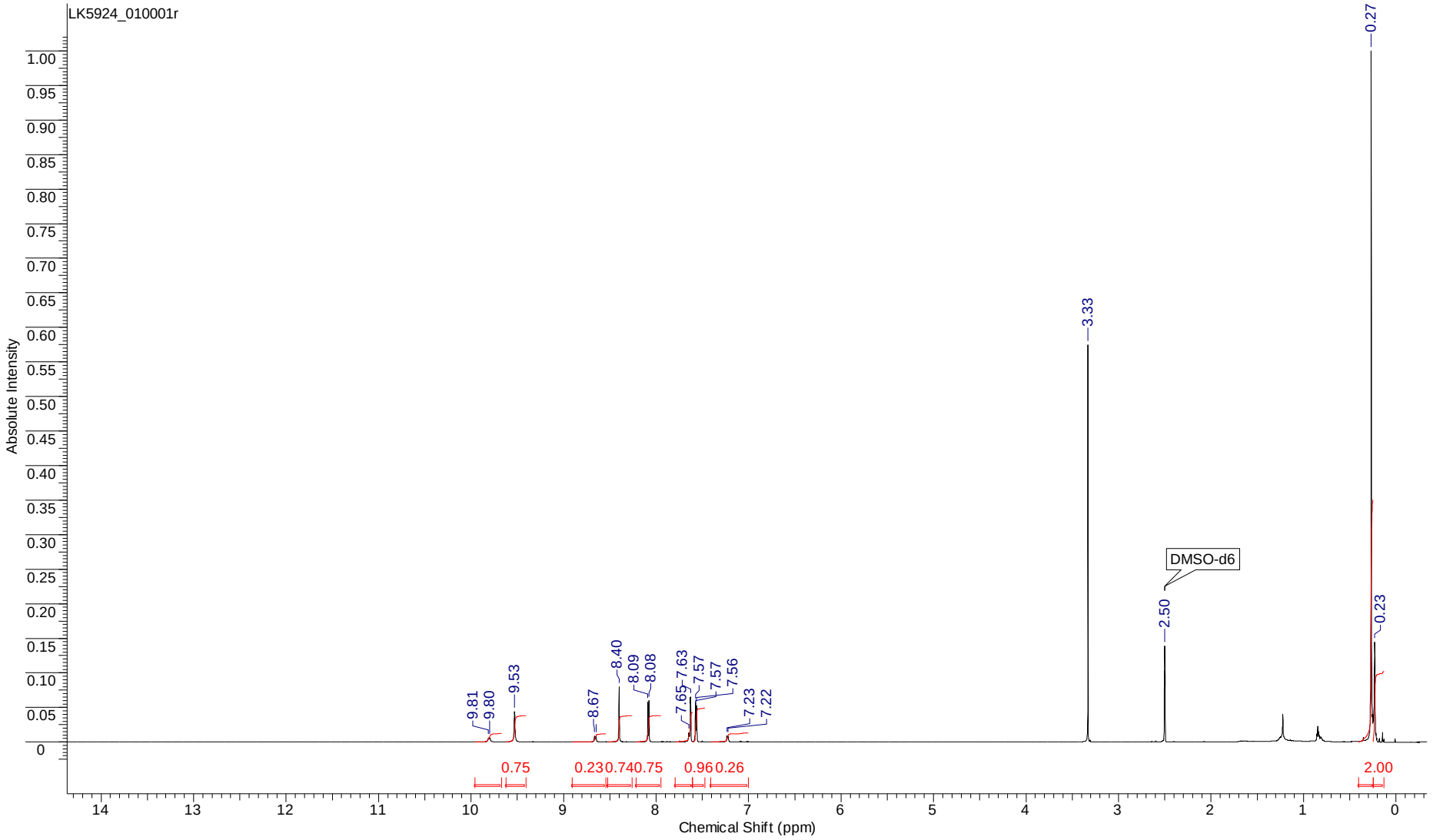
(5b) ^{1}H NMR (DMSO, 700 MHz):

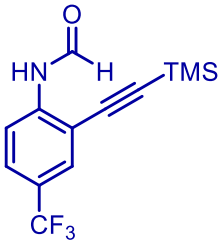




(5c)

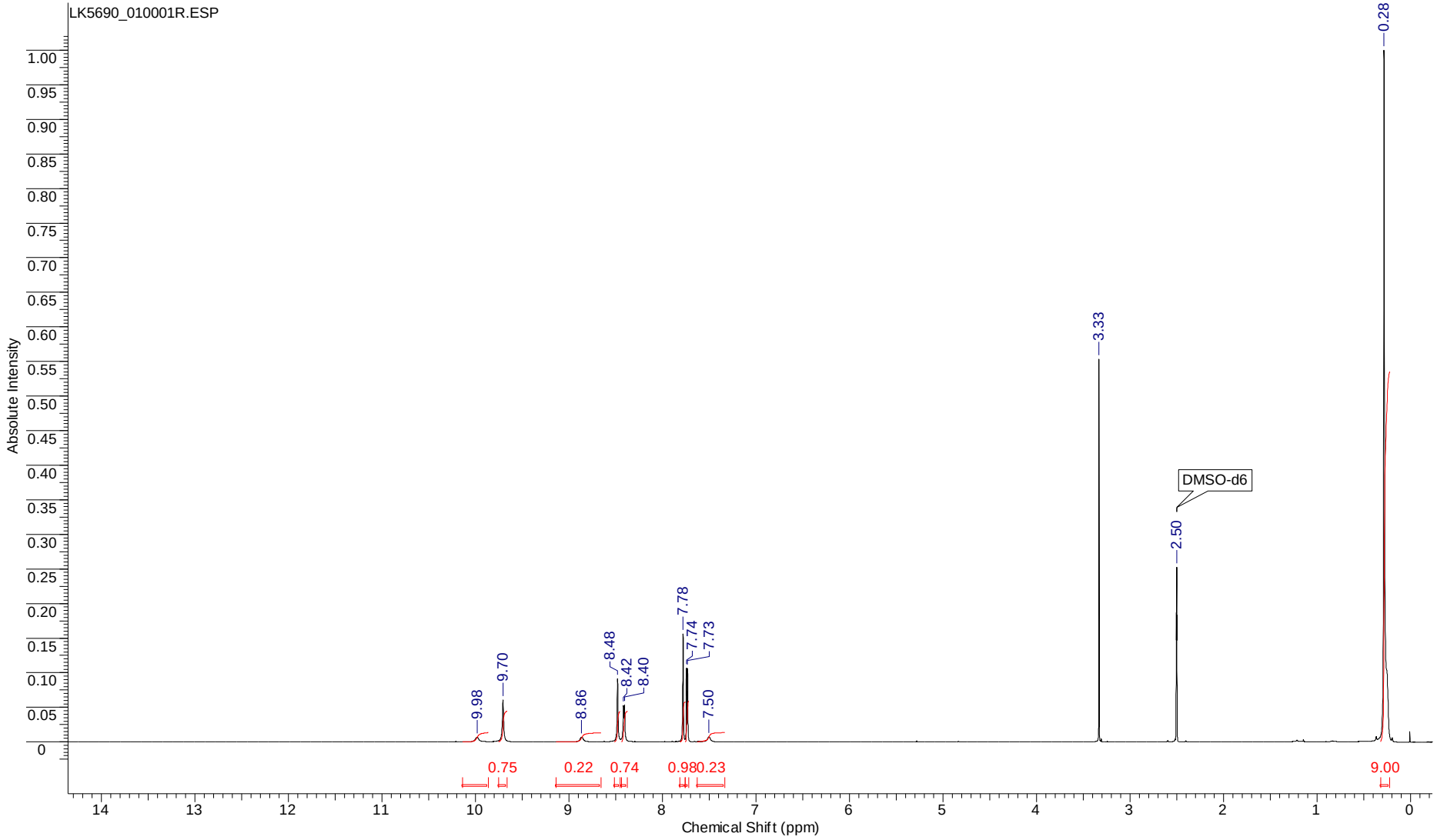
^{1}H NMR (DMSO, 700 MHz):

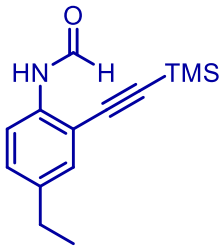




(5d)

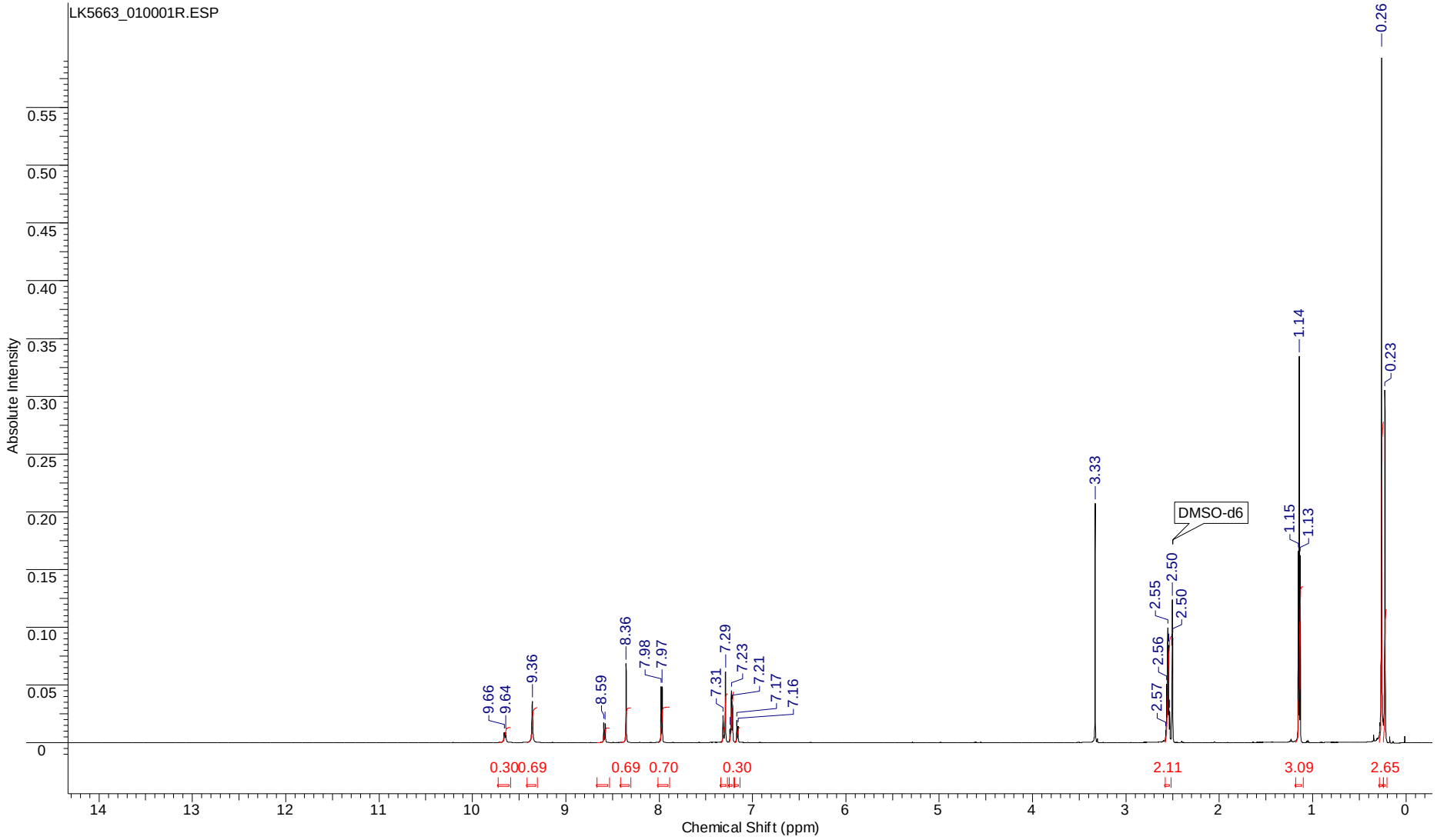
^{1}H NMR (DMSO, 700 MHz):

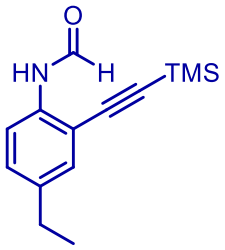




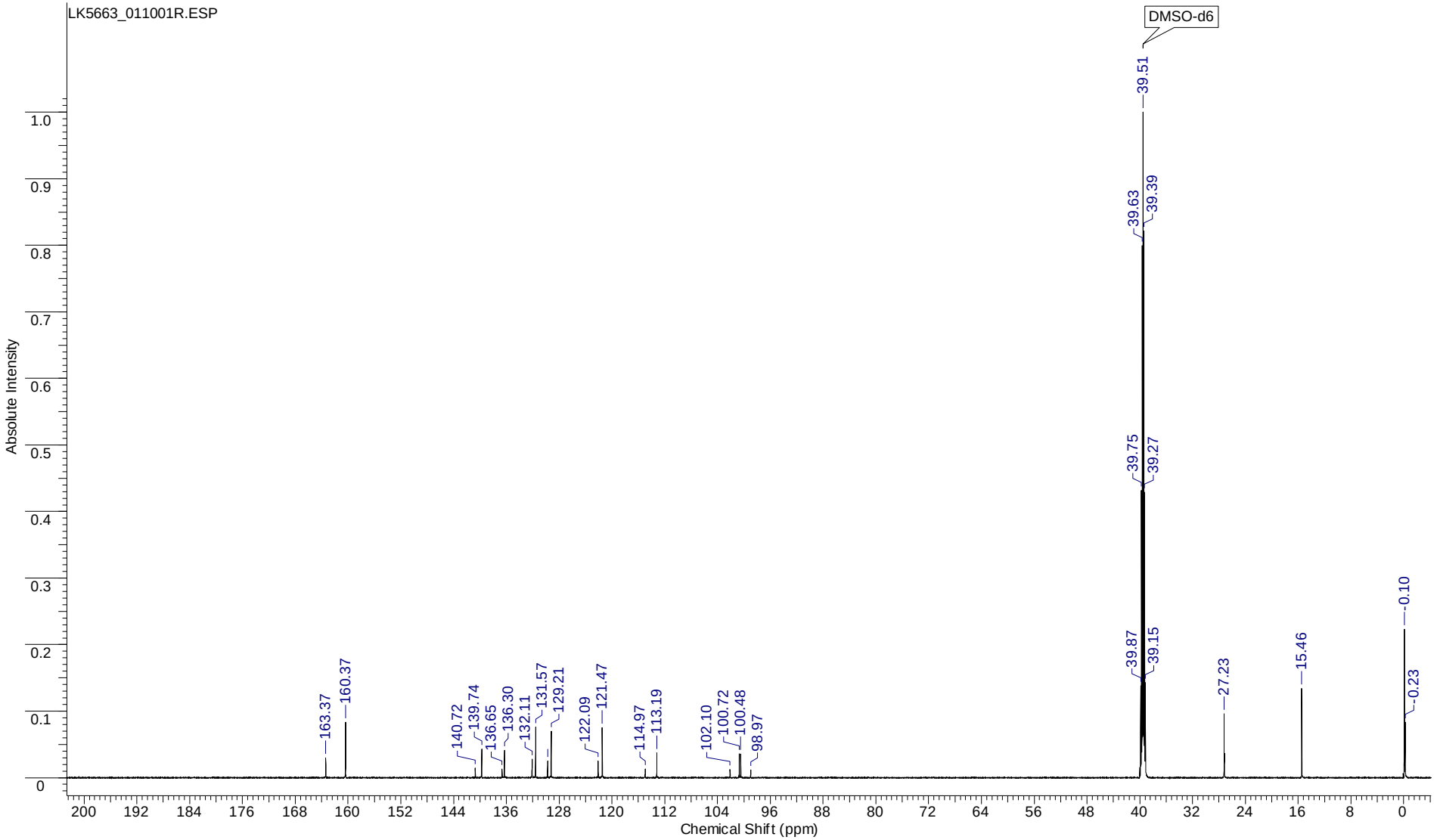
(5e)

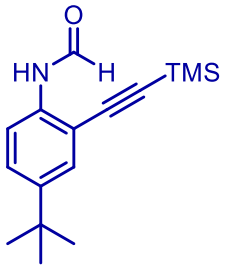
^{1}H NMR (DMSO, 700 MHz):





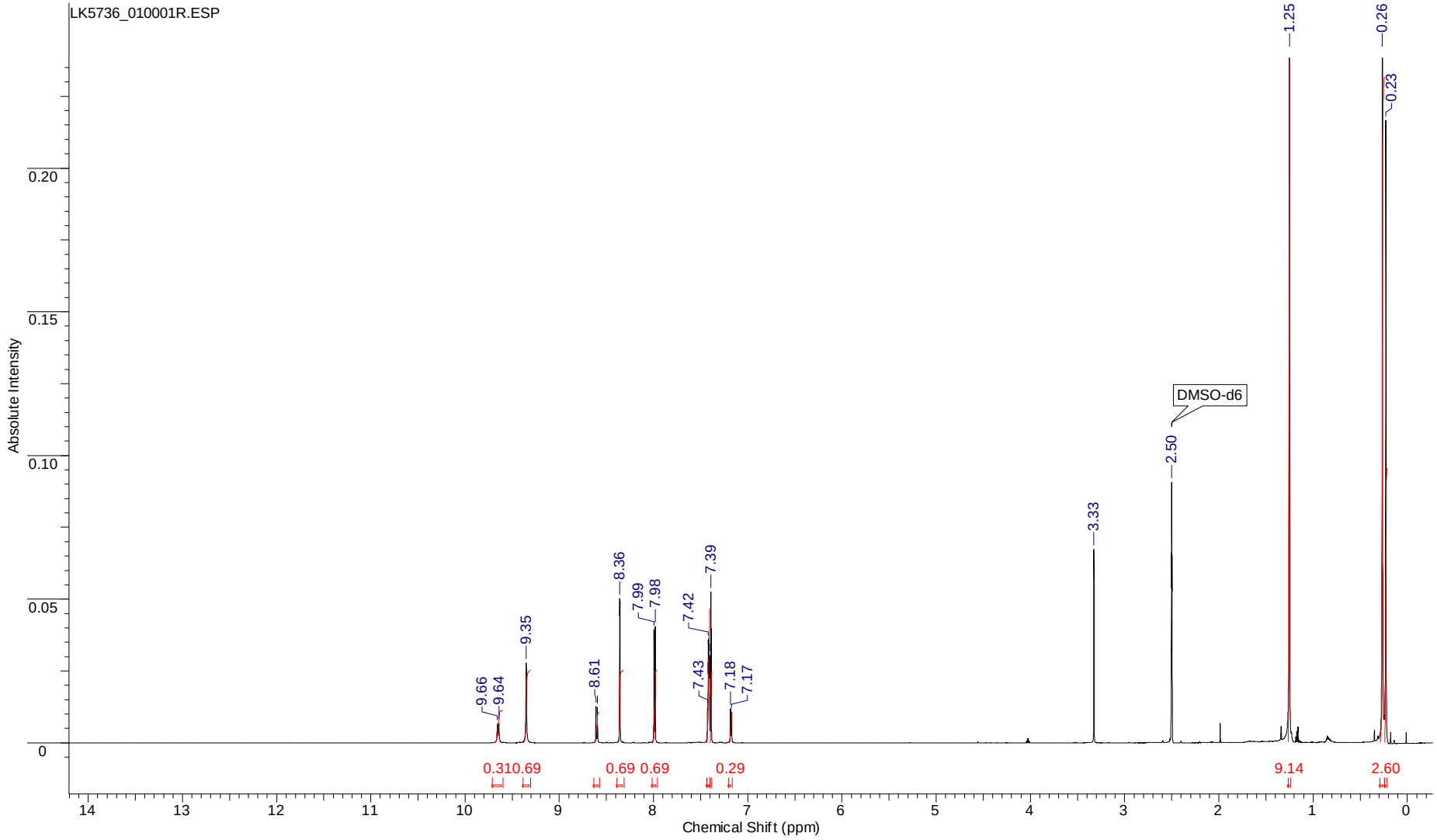
(5e) ^{13}C NMR (DMSO, 150 MHz):

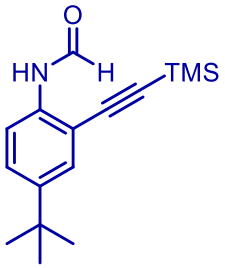




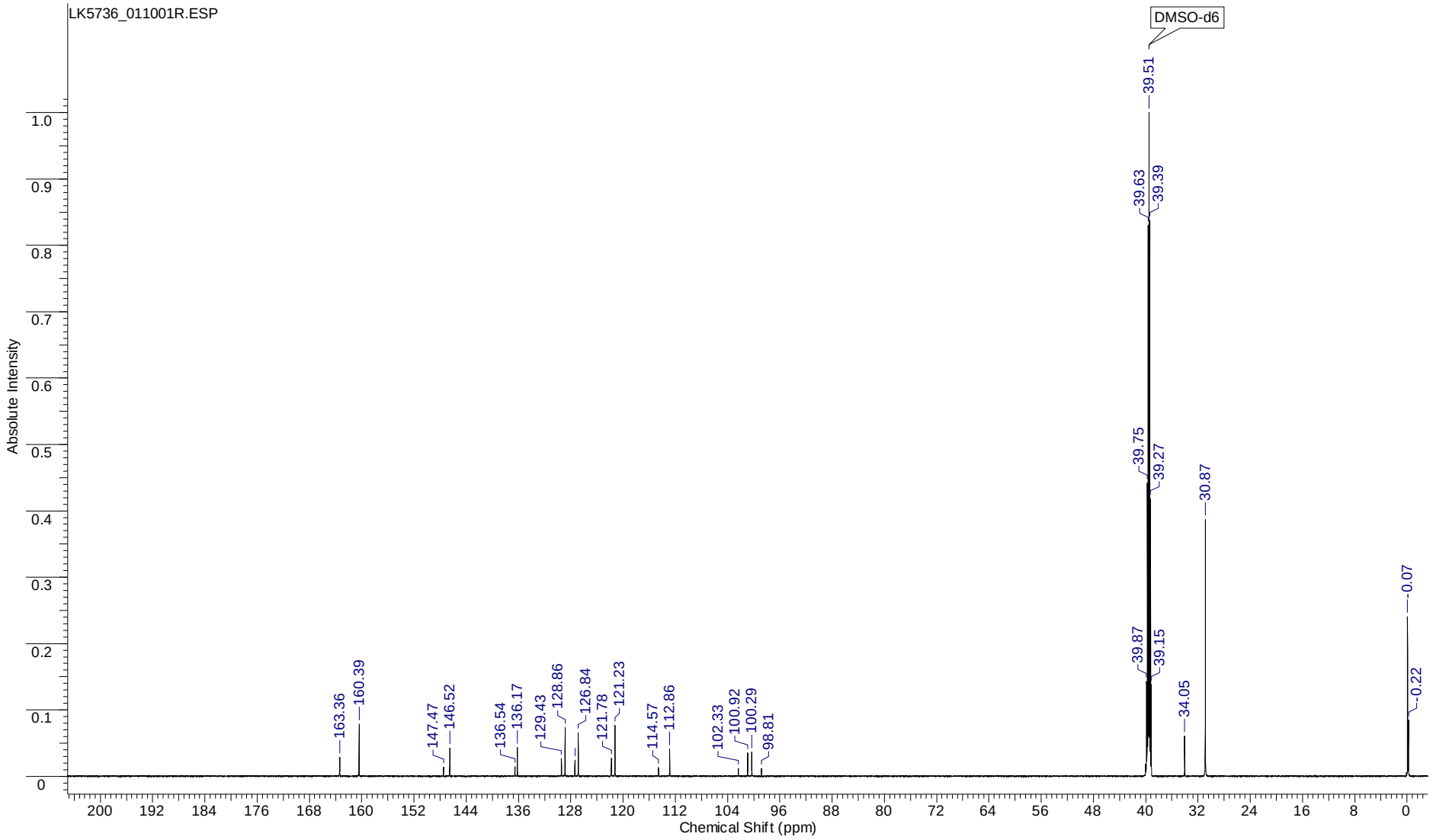
(5f)

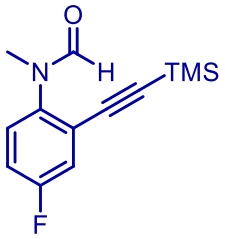
^{1}H NMR (DMSO, 700 MHz):





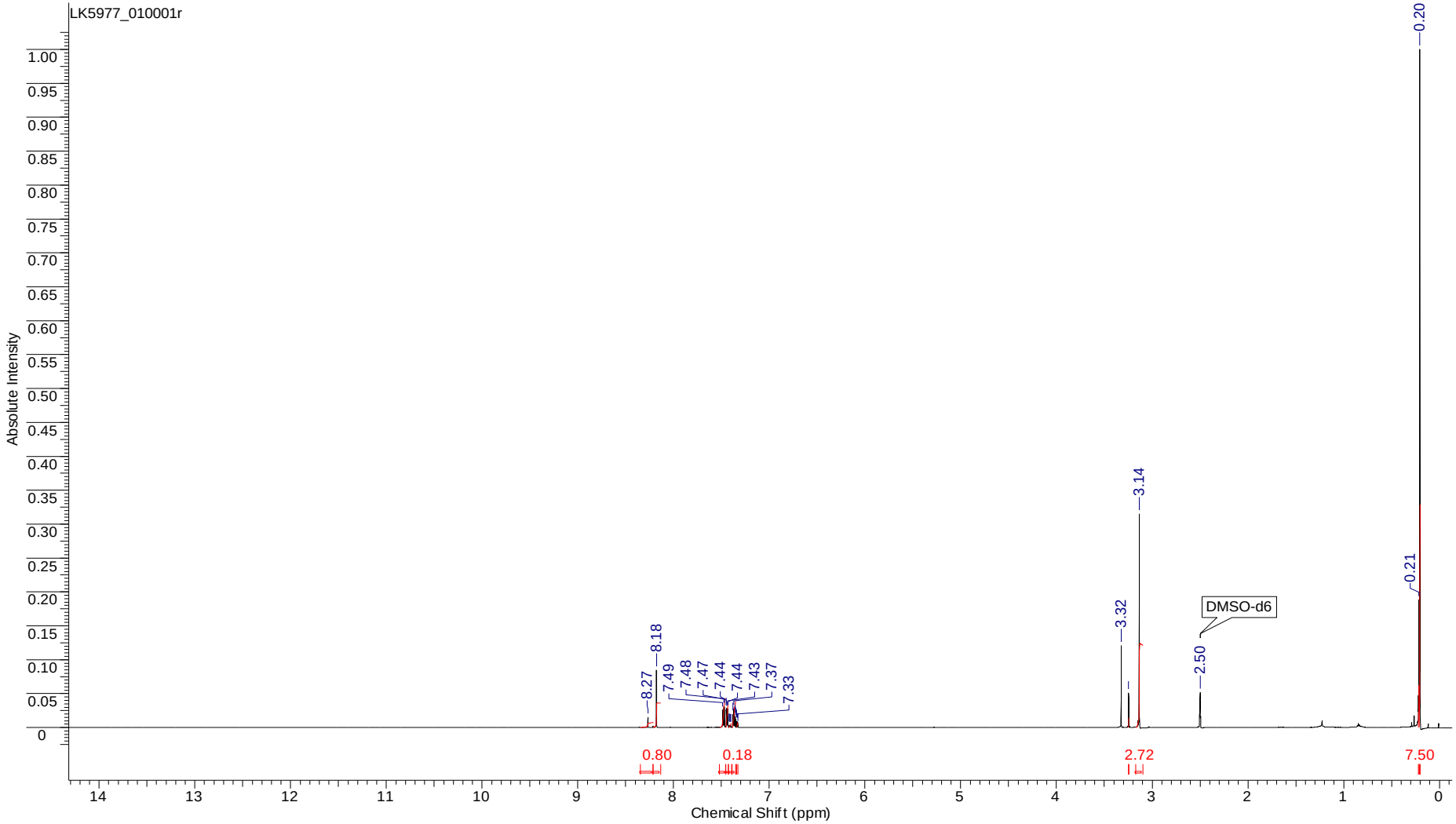
(5f) ^{13}C NMR (DMSO, 150 MHz):

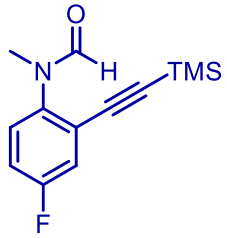




(5g)

^{1}H NMR (DMSO, 700 MHz):





(5g) ^{13}C NMR (DMSO, 150 MHz):