

Supporting Information

Ag(I)-Catalyzed Oxidative Cyclization of 1,4-Diynamide-3-ols with *N*-oxide for Divergent Synthesis of 2-Substituted Furan-4-Carboxamide Derivatives.

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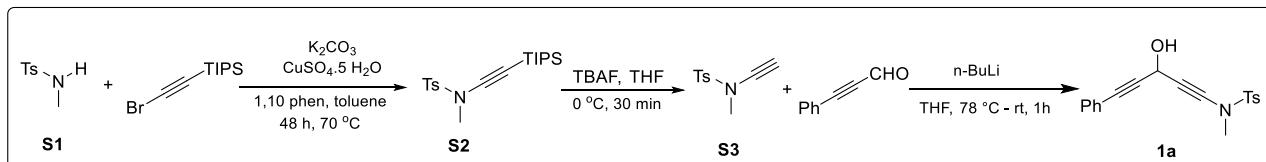
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1. Representative Synthetic Procedures:

(a) General procedure:

Unless otherwise noted, all the reactions for the preparation of the substrates were performed in oven-dried glassware under nitrogen atmosphere with freshly distilled solvents. The catalytic reactions were performed under nitrogen atmosphere. DCM, diethyl ether and toluene were distilled from CaH₂ under nitrogen. THF was distilled from Na metal under nitrogen. All other commercial reagents were used without further purification, unless otherwise indicated. ¹H NMR and ¹³C NMR spectra were recorded on a Varian 700 and 500 MHz, Bruker 400 MHz spectrometers using chloroform-*d* (CDCl₃) as the internal standard. High-resolution mass spectral analysis (HRMS) data were measured on JMST100LP4G (JEOL) mass spectrometer or a TOF mass analyzer equipped with the ESI source, JEOL Model: JMS-T200GC AccuTOF GCx equipped with FD (field desorption) source and Magnetic Sector Mass Analyzer (MStation) equipped with the EI source. Single-crystal X-ray diffraction intensity data were collected on a Bruker X8 APEX diffractometer equipped with a CCD area detector and Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 100 K; all data calculations were performed by using the PC version of the APEX2 program package.

(b) General synthetic process for *N*-(3-hydroxy-5-phenylpenta-1,4-diyn-1-yl)-N,4-dimethylbenzenesulfonamide synthesis (**1a**):



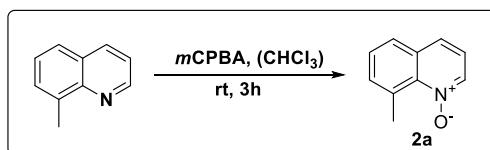
To a mixture of **S1** (3.0 g, 16.20 mmol), K₂CO₃ (4.48 g, 32.39 mmol), CuSO₄·5H₂O (404 mg, 1.62 mmol), and 1,10-phenanthroline (584 mg, 3.24 mmol) in the reaction vial was added a solution of a respective (bromoethynyl)triisopropylsilane (6.35 g, 24.29 mmol) in 30 mL toluene. The reaction mixture was capped and heated in an oil bath at 70°C for 48 h while being monitored with TLC analysis. Upon completion, the reaction mixture was cooled to room temperature and diluted with EA and filtered through celite, and the filtrate was concentrated under vacuum. The crude products were purified by flash column chromatography using silica gel (EA/Hexane= 2:98, v/v) to afford the desired product **S2** as a white solid (4.70 g, 12.86 mmol, 79 %).

To a solution of *N*,4-dimethyl-*N*-(triisopropylsilyl)ethynylbenzenesulfonamide **S2** (2.0 g, 5.47 mmol) in THF (20 mL) was added *n*-tetrabutyl ammonium fluoride (1.0 M in THF, 8.21 mL, 8.21 mmol) at 0 °C, and the resulting mixture was stirred at 0 °C for 10 mins. Then reaction mixture was quenched with water (20 ml) and extracted with ethyl acetate (3x 30 mL), Organic layer was dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash column chromatography using silica gel (ethyl acetate: hexane = 3:97, v/v) to afford the desired product **S3** as a white solid (1.00 g, 4.78 mmol, 87 %).

To a solution of **S3** (500 mg, 2.39 mmol) in anhydrous THF (10 ml) cooled to -78 °C was added n-BuLi (1.6M in Hexane, 1.79 ml, 2.87mmol). The resulting mixture was stirred at same temperature for 30 min period before the addition of 3-phenylpropiolaldehyde (373mg, 2.87mmol). The reaction mixture was warm up to room temperature and stirred for 30 min. Reaction mixture was quenched with water (20 ml) and extracted with ethyl acetate (3x 20 mL), Organic layer was dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash column chromatography using silica gel (ethyl acetate: hexane = 30:70, v/v) to afford the desired product **1a** as a yellow oil (690 mg, 2.03 mmol, 85 %).

All other 1,4-diynamide-3-ols **1b-1p** were synthesized following the same procedure as of **1a**.

(c) General synthetic procedure for Preparation of 8-methylquinoline *N*-oxide (2a**):**



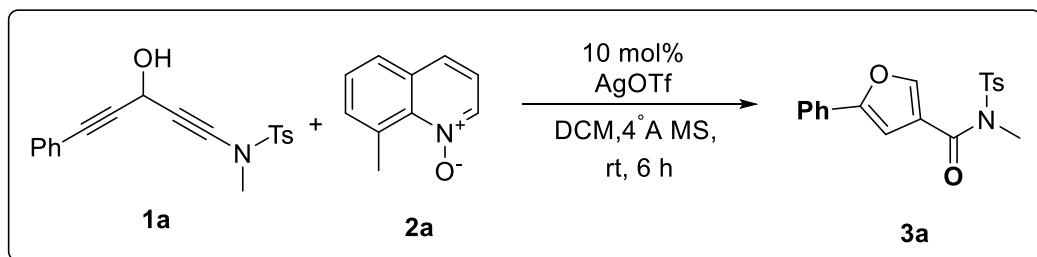
To a stirred solution of 8-methylquinoline (1.00 g, 6.98 mmol) in 20ml of chloroform was treated with *meta*-chloroperbenzoic acid (2.67 g, 7.57 mmol). The mixture was stirred for 3h at room temperature. Subsequently saturated NaHCO₃ (25 mL) and 2M NaOH (25mL) were added and the mixture was extracted with DCM. The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure yielding the desired *N*-oxide **2a** (767 mg, 4.81 mmol, 69%) as a yellow solid which was used in the following step without further purification. The analytical data agreements with the reported literature.^{s1}

References:

s1) L. Bering, A. P. Antonchick, *Org. Lett.* **2015**, *17*, 3134–3137.

2. Standard procedures for catalytic operations.

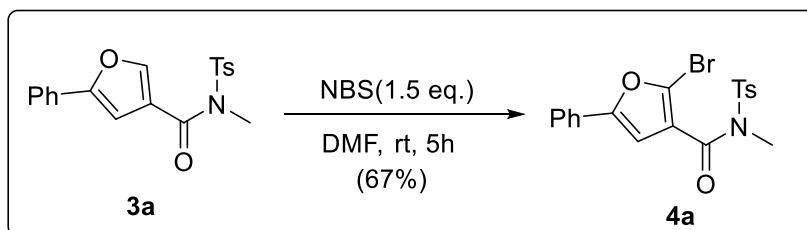
Typical procedure for the synthesis of N-methyl-5-phenyl-N-tosylfuran-3-carboxamide (**3a**):



To a stirred suspension of AgOTf (3.78 mg, 0.0147 mmol) in DCM (0.5 mL) was fitted with a N₂ balloon. To this suspension was added a DCM (1.0 mL) solution of *N*-(3-hydroxy-5-phenylpent-1,4-dien-1-yl)-*N*,4-dimethylbenzenesulfonamide **1a** (50 mg, 0.1473 mmol) and 8-methylquinoline *N*-oxide **2a** (46.90 mg, 0.2946 mmol) at room temperature. The resulting mixture was stirred at room temperature for 6 h. The solution was filtered over a short celite bed and evaporated under reduced pressure. The residue was purified on a silica gel column using ethyl acetate/hexane (15:85) as the eluent to give compound **3a** as white solid (43.50 mg, 0.1238 mmol, 83%).

(3) Chemical functionalizations of **3a**:

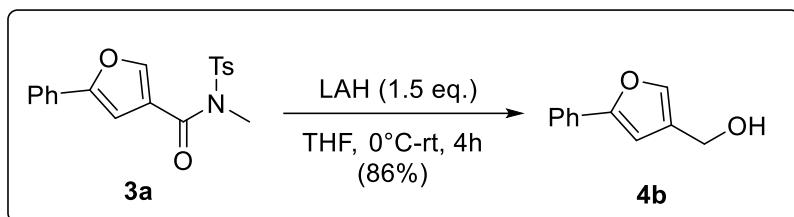
(a) Typical procedure for the synthesis of 2-bromo-*N*-methyl-5-phenyl-*N*-tosylfuran-3-carboxamide (**4a**):



To a stirred solution of *N*-methyl-5-phenyl-*N*-tosylfuran-3-carboxamide **3a** (50 mg, 0.14mmol) in DMF (2.0 mL) was added NBS (37.56 mg, 0.21 mmol) at room temperature. The resulting mixture was stirred for 5h at room temperature. The reaction mixture was quenched with water (3.0 mL) and the solution was then extracted with ethyl acetate (5.0 mL) three times. Organic phase was washed with brine, dried with MgSO₄ and concentrated under reduced pressure. The residue was

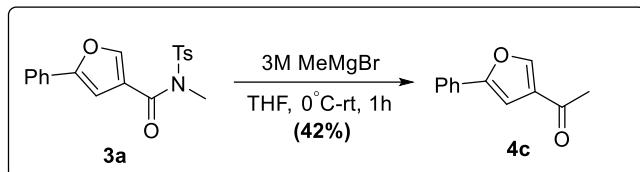
purified on a silica column using ethyl acetate/hexane (5:95) as the eluent to give compound **4a** as Yellow oil (41 mg, 0.09 mmol, 67%).

(b) Typical procedure for the synthesis of (5-phenylfuran-3-yl)methanol (**4b**):



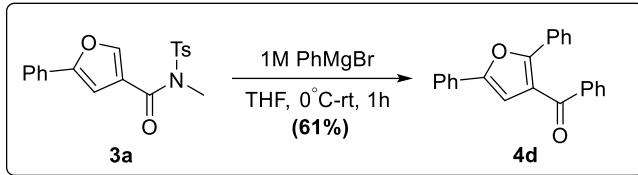
To a stirred solution of *N*-methyl-5-phenyl-*N*-tosylfuran-3-carboxamide **3a** (50 mg, 0.14mmol) in Dry THF (2.0 mL) was added LAH (1M in THF, 0.21 ml, 0.21 mmol) at 0 °C. The resulting mixture was stirred for 4h at room temperature. The reaction mixture was quenched with saturated solution of ammonium chloride (3.0 mL) and the solution was then extracted with ethyl acetate (5.0 mL) three times. Organic phase was washed with brine, dried with MgSO₄ and concentrated under reduced pressure. The residue was purified on a silica column using ethyl acetate/hexane (30:70) as the eluent to give compound **4b** as Yellow oil (21 mg, 0.12 mmol, 86%).

(c) Typical procedure for the synthesis of 1-(5-phenylfuran-3-yl)ethan-1-one (**4c**):



To a stirred solution of *N*-methyl-5-phenyl-*N*-tosylfuran-3-carboxamide **3a** (50 mg, 0.14 mmol) in THF (2.0 mL) was added MeMgBr (3M in diethyl ether, 0.19 mL, 0.56 mmol) at 0 °C. The resulting mixture was stirred for 1h at room temperature. The solution was quenched with a saturated solution of ammonium chloride (3.0 mL) at 0 °C; and the solution was then extracted with ethyl acetate (5.0 mL) three times. Organic phase was washed with brine, dried with MgSO₄ and concentrated under reduced pressure. The residue was purified on a silica column using ethyl acetate/hexane (03:97) as the eluent to give compound **4c** as white solid (11 mg, 0.059 mmol, 42%).

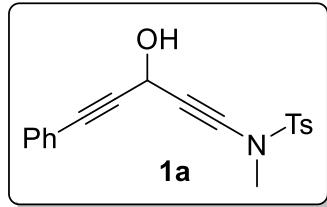
(d) Typical procedure for the synthesis of (2,5-diphenylfuran-3-yl)(phenyl)methanone (**4d**):



To a stirred solution of *N*-methyl-5-phenyl-*N*-tosylfuran-3-carboxamide **3a** (50mg, 0.14mmol) in THF (2.0 mL) was added PhMgBr (1M in THF, 0.56 mL, 0.56 mmol) at 0 °C. The resulting mixture was stirred for 1h at room temperature. The solution was quenched with a saturated solution of ammonium chloride (3.0 mL) at 0 °C; and the solution was then extracted with ethyl acetate (5.0 mL) three times. Organic phase was washed with brine, dried with MgSO₄ and concentrated under reduced pressure. The residue was purified on a silica column using ethyl acetate/hexane (03:97) as the eluent to give compound **4d** as yellow oil (28 mg, 0.086 mmol, 61%).

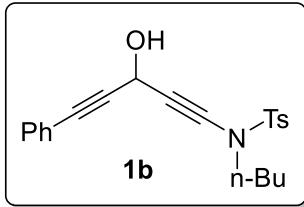
(4) Spectral data of key compounds:

Spectral data of *N*-(3-hydroxy-5-phenylpenta-1,4-diyn-1-yl)-*N*,4-dimethylbenzenesulfonamide (1a):



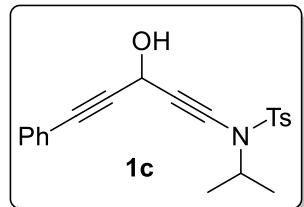
Compound **1a** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (625 mg, 1.84 mmol, 77 %); ¹H NMR (400 MHz, CDCl₃): δ 7.81 ~ 7.79 (m, 2H), 7.46 ~ 7.43 (m, 2H), 7.33 ~ 7.27 (m, 5H), 5.42 (d, *J* = 6.4 Hz, 1H), 3.07 (s, 3H), 2.58 (d, *J* = 6.8 Hz, 1H), 2.39 (s, 3H); ¹³C{¹H} NMR (175 MHz, CDCl₃): δ 144.9, 133.0, 131.8, 129.8, 128.8, 128.3, 127.8, 121.9, 86.0, 84.2, 79.8, 67.2, 52.8, 38.8, 21.6; HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. C₁₉H₁₇NO₃NSNa: 362.0827, found: 362.0827.

Spectral data of *N*-butyl-*N*-(3-hydroxy-5-phenylpenta-1,4-diyn-1-yl)-4-methylbenzenesulfonamide (1b):



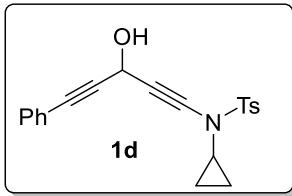
Compound **1b** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (510 mg, 1.34 mmol, 67%); ¹H NMR (700 MHz, CDCl₃): δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.45 ~ 7.44 (m, 2H), 7.34 ~ 7.30 (m, 3H), 7.26 (d, *J* = 8.2 Hz, 2H), 5.43 (d, *J* = 7.3 Hz, 1H), 3.37 ~ 3.34 (m, 1H), 3.30 ~ 3.26 (m, 1H), 2.48 (d, *J* = 7.5 Hz, 1H), 2.38 (s, 3H), 1.63 ~ 1.60 (m, 2H), 1.33 (q, *J* = 7.2 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ¹³C{¹H} NMR (175 MHz, CDCl₃): δ 144.7, 134.4, 131.8, 129.8, 128.8, 128.3, 127.7, 122.0, 86.1, 84.2, 78.5, 68.9, 52.9, 51.0, 29.9, 21.6, 19.4, 13.5; HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. C₂₂H₂₃NO₃SNa: 404.1296, found: 404.1296.

Spectral data of *N*-(3-hydroxy-5-phenylpenta-1,4-diyn-1-yl)-*N*-isopropyl-4-methylbenzenesulfonamide (1c**):**



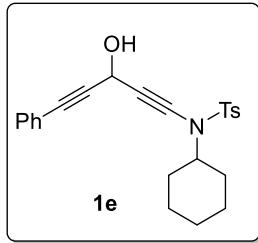
Compound **1c** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (540 mg, 1.47 mmol, 70%); ¹H NMR (700 MHz, CDCl₃): δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.44 (d, *J* = 6.3 Hz, 2H), 7.36 ~ 7.31 (m, 3H), 7.255 ~ 7.24 (m, 2H), 5.46 (d, *J* = 7.0 Hz, 1H), 4.17 ~ 4.14 (m, 1H), 2.49 (d, *J* = 7.0 Hz, 1H), 2.38 (s, 3H), 1.14 (d, *J* = 6.3 Hz, 3H), 1.09 (d, *J* = 5.6 Hz, 3H); ¹³C{¹H} NMR (175 MHz, CDCl₃): δ 144.6, 135.7, 131.8, 129.8, 128.8, 128.3, 127.5, 122.1, 86.3, 84.1, 75.7, 71.2, 53.0, 52.6, 21.6, 21.0, 20.6; HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. C₂₁H₂₁NO₃SNa: 390.1140, found: 390.1144.

Spectral data of *N*-cyclopropyl-*N*-(3-hydroxy-5-phenylpenta-1,4-diyn-1-yl)-4-methylbenzenesulfonamide (1d**):**



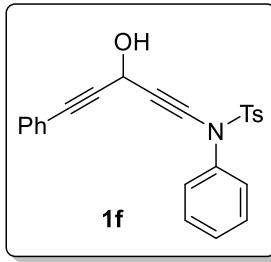
Compound **1d** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (520 mg, 1.42 mmol, 67%); ^1H NMR (700 MHz, CDCl_3): δ 7.83 (d, $J = 8.2$ Hz, 2H), 7.45 ~ 7.44 (m, 2H), 7.33 ~ 7.31 (m, 3H), 7.28 (d, $J = 8.2$ Hz, 2H), 5.42 (d, $J = 7.5$ Hz, 1H), 2.76 ~ 2.74 (m, 1H), 2.46 (d, $J = 7.6$ Hz, 1H), 2.39 (s, 3H), 0.89 ~ 0.86 (m, 1H), 0.83 ~ 0.73 (m, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (175 MHz, CDCl_3): δ 144.9, 133.7, 131.8, 129.7, 128.8, 128.3, 128.0, 122.0, 86.1, 84.2, 78.0, 68.8, 52.9, 32.6, 21.6, 6.8, 6.4; HRMS (ESI-TOF) m/z: [M+Na] $^+$ calcd. $\text{C}_{21}\text{H}_{19}\text{NO}_3\text{SNa}$: 388.0983, found: 388.0985.

Spectral data of *N*-cyclohexyl-*N*-(3-hydroxy-5-phenylpenta-1,4-diyn-1-yl)-4-methylbenzenesulfonamide (1e**):**



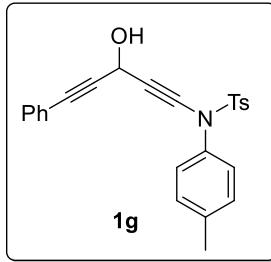
Compound **1e** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (550 mg, 1.35 mmol, 75%); ^1H NMR (700 MHz, CDCl_3): δ 7.80 (d, $J = 7.7$ Hz, 2H), 7.44 (d, $J = 6.3$ Hz, 2H), 7.32 ~ 7.31 (m, 3H), 7.23 (d, $J = 5.6$ Hz, 2H), 5.45 (s, 1H), 3.77 ~ 3.74 (m, 1H), 2.52 (bs, 1H), 2.37 (s, 3H), 1.73 ~ 1.66 (m, 4H), 1.60 ~ 1.42 (m, 3H), 1.28 ~ 1.24 (m, 2H), 1.02 (q, $J = 12.8$ Hz, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (175 MHz, CDCl_3): δ 144.5, 135.9, 131.8, 129.7, 128.8, 128.3, 127.5, 122.1, 86.3, 84.1, 76.5, 70.8, 59.5, 53.0, 31.3, 30.9, 25.4, 25.3, 24.8, 21.6; HRMS (ESI-TOF) m/z: [M+Na] $^+$ calcd. $\text{C}_{24}\text{H}_{25}\text{NO}_3\text{SNa}$: 430.1453, found: 430.1453.

Spectral data of *N*-(3-hydroxy-5-phenylpenta-1,4-diyn-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (1f**):**



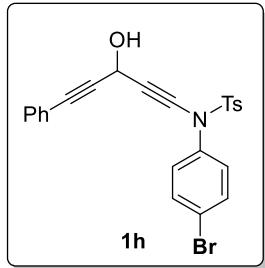
Compound **1f** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (660 mg, 1.64 mmol, 89%); ^1H NMR (700 MHz, CDCl_3): δ 7.59 (d, $J = 8.4$ Hz, 2H), 7.45 (dd, $J = 7.7, 1.4$ Hz, 2H), 7.34 ~ 7.31 (m, 6H), 7.24 ~ 7.22 (m, 2H), 7.20 (d, $J = 7.7$ Hz, 2H), 5.46 (d, $J = 6.3$ Hz, 1H), 2.43 (d, $J = 5.6$ Hz, 1H), 2.38 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (175 MHz, CDCl_3): δ 145.1, 138.3, 132.8, 131.8, 129.6, 129.1, 128.9, 128.5, 128.35, 128.32, 126.3, 121.9, 85.9, 84.4, 78.9, 68.5, 53.0, 21.7; HRMS (ESI-TOF) m/z: [M+Na] $^+$ calcd. $\text{C}_{24}\text{H}_{19}\text{NO}_3\text{SNa}$: 424.0983, found: 424.0987.

Spectral data of *N*-(3-hydroxy-5-phenylpenta-1,4-diyn-1-yl)-4-methyl-*N*-(p-tolyl)benzenesulfonamide (1g**):**



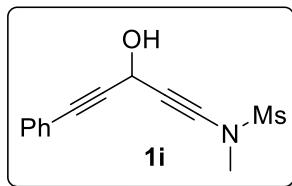
Compound **1g** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (620 mg, 1.49 mmol, 85%); ^1H NMR (700 MHz, CDCl_3): δ 7.60 (d, $J = 7.0$ Hz, 2H), 7.44 (d, $J = 7.0$ Hz, 2H), 7.32 ~ 7.31 (m, 3H), 7.20 (d, $J = 7.0$ Hz, 2H), 7.11 ~ 7.08 (m, 4H), 5.44 (s, 1H), 2.47 (s, 1H), 2.37 (s, 3H), 2.32 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (175 MHz, CDCl_3): δ 145.0, 138.7, 135.6, 132.8, 131.8, 129.8, 129.5, 128.8, 128.33, 128.32, 126.3, 121.9, 86.0, 84.3, 79.1, 68.2, 52.9, 21.6, 21.1; HRMS (ESI-TOF) m/z: [M+Na] $^+$ calcd. $\text{C}_{25}\text{H}_{21}\text{NO}_3\text{SNa}$: 438.1140, found: 438.1148.

Spectral data of *N*-(4-bromophenyl)-*N*-(3-hydroxy-5-phenylpenta-1,4-diyn-1-yl)-4-methylbenzenesulfonamide (1h**):**



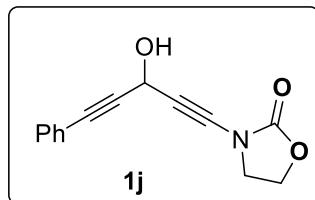
Compound **1h** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (420 mg, 0.87 mmol, 61%); ^1H NMR (700 MHz, CDCl_3): δ 7.59 (d, $J = 7.7$ Hz, 2H), 7.45 ~ 7.42 (m, 4H), 7.34 ~ 7.30 (m, 3H), 7.21 (d, $J = 7.7$ Hz, 2H), 7.11 (d, $J = 7.7$ Hz, 2H), 5.45 (d, $J = 7.0$ Hz, 1H), 2.63 (d, $J = 6.3$ Hz, 1H), 2.37 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (175 MHz, CDCl_3): δ 145.4, 137.3, 132.4, 132.3, 131.8, 129.7, 128.9, 128.4, 128.3, 127.7, 122.3, 121.9, 85.8, 84.5, 78.2, 69.0, 52.9, 21.7; HRMS (ESI-TOF) m/z: $[\text{M}+\text{Na}]^+$ calcd. $\text{C}_{24}\text{H}_{18}\text{BrNO}_3\text{SNa}$: 502.0088, found: 502.0089.

Spectral data of *N*-(3-hydroxy-5-phenylpenta-1,4-diyn-1-yl)-*N*-methylmethanesulfonamide (1i**):**



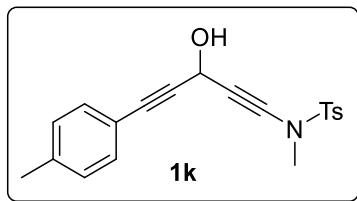
Compound **1i** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (470 mg, 1.78 mmol, 48%); ^1H NMR (700 MHz, CDCl_3): δ 7.43 (dd, $J = 7.7, 0.7$ Hz, 2H), 7.32 ~ 7.28 (m, 3H), 5.48 (d, $J = 6.3$ Hz, 1H), 3.22 (s, 3H), 3.08 (s, 3H); 2.58 (d, $J = 6.3$ Hz, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (175 MHz, CDCl_3): δ 131.8, 128.9, 128.3, 121.8, 85.7, 84.4, 78.9, 67.7, 52.8, 38.8, 37.2; HRMS (ESI-TOF) m/z: $[\text{M}+\text{Na}]^+$ calcd. $\text{C}_{13}\text{H}_{13}\text{NO}_3\text{SNa}$: 286.0514, found: 286.0513.

Spectral data of 3-(3-hydroxy-5-phenylpenta-1,4-diyn-1-yl)oxazolidin-2-one (1j**):**



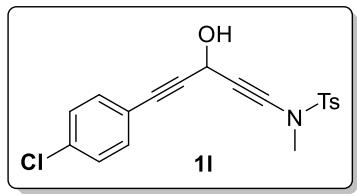
Compound **1j** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (730 mg, 3.03 mmol, 67%); ¹H NMR (700 MHz, CDCl₃): δ 7.43 (dd, *J* = 7.0 Hz, 2H), 7.31 ~ 7.27 (m, 3H), 5.51 (s, 1H), 4.41 (t, *J* = 8.4 Hz, 2H), 3.91 (t, *J* = 8.4 Hz, 2H), 3.27 (bs, 1H); ¹³C{¹H} NMR (175 MHz, CDCl₃): δ 156.1, 131.8, 128.8, 128.3, 121.9, 85.8, 84.3, 74.6, 69.4, 63.3, 52.6, 46.5; HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. C₁₄H₁₁NO₃Na: 264.0637, found: 264.0638.

Spectral data of *N*-(3-hydroxy-5-(*p*-tolyl)penta-1,4-diyn-1-yl)-*N*,4-dimethylbenzenesulfonamide (1k**):**



Compound **1k** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (720 mg, 2.04 mmol, 85%); ¹H NMR (700 MHz, CDCl₃): δ 7.78 (d, *J* = 7.0 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.27 ~ 7.26 (m, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 5.41 (d, *J* = 5.6 Hz, 1H), 3.04 (s, 3H), 2.79 (bs, 1H), 2.37 (s, 3H), 2.32 (s, 3H); ¹³C{¹H} NMR (175 MHz, CDCl₃): δ 144.9, 138.9, 132.9, 131.6, 129.8, 129.0, 127.8, 118.8, 85.4, 84.3, 79.6, 67.3, 52.7, 38.8, 21.5, 21.4; HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. C₂₀H₁₉NO₃SNa: 376.0983, found: 376.0981.

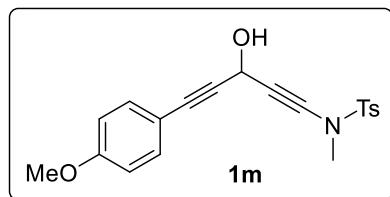
Spectral data of *N*-(5-(4-chlorophenyl)-3-hydroxpenta-1,4-diyn-1-yl)-*N*,4-dimethylbenzenesulfonamide (1l**):**



Compound **1l** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (650 mg, 1.74 mmol, 73%); ¹H NMR (700 MHz, CDCl₃): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.30 ~ 7.28 (m, 4H), 5.41 (d, *J* = 6.3 Hz, 1H), 3.07 (s, 3H), 2.45 (d, *J* = 7.0 Hz, 1H), 2.41 (s, 3H); ¹³C{¹H} NMR (175 MHz, CDCl₃): δ 145.0, 135.0, 133.1, 133.0, 129.9,

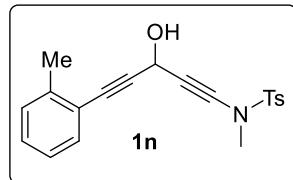
128.7, 127.8, 120.4, 86.9, 83.1, 80.0, 67.0, 52.8, 38.8, 21.6; HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. C₁₉H₁₆ClNO₃SNa: 396.0437, found: 396.0434.

Spectral data of N-(3-hydroxy-5-(4-methoxyphenyl)penta-1,4-diyn-1-yl)-N,4-dimethylbenzenesulfonamide (1m):



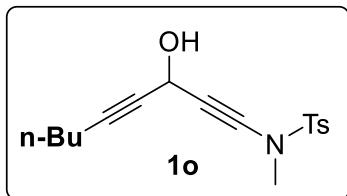
Compound **1m** was purified on silica gel column using ethyl acetate/hexane: (40: 60) as the eluent; Yellow oil (620 mg, 1.67 mmol, 70%); ¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.38 ~ 7.35 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.83 ~ 6.80 (m, 2H), 5.41 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.04 (s, 3H), 2.75 (s, 1H), 2.38 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.4, 144.9, 133.2, 132.9, 129.8, 127.8, 113.9, 84.7, 84.2, 79.5, 67.4, 55.2, 52.8, 38.8, 21.5; HRMS-ESI⁺ m/z: [M+Na]⁺ calcd. C₂₀H₁₉NO₄SNa: 392.0932, found: 392.0931.

Spectral data of N-(3-hydroxy-5-(o-tolyl)penta-1,4-diyn-1-yl)-N,4-dimethylbenzenesulfonamide (1n):



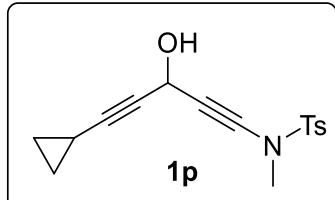
Compound **1n** was purified on silica gel column using ethyl acetate/hexane: (30:70) as the eluent; Yellow oil (450 mg, 1.27 mmol, 53%); ¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.22 ~ 7.17 (m, 2H), 7.12 (m, 1H) 5.46 (d, *J* = 6.8 Hz, 1H), 3.06 (s, 3H), 2.61 (d, *J* = 7.2 Hz, 1H), 2.41 (s, 3H), 2.38 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.9, 140.5, 133.1, 132.1, 129.8, 129.4, 128.8, 127.8, 125.5, 121.7, 89.9, 83.2, 79.7, 67.4, 52.9, 38.8, 21.5, 20.5; HRMS-ESI⁺ m/z: [M+Na]⁺ calcd. C₂₀H₁₉NO₃SNa: 376.0983, found: 376.0983.

Spectral data of *N*-(3-hydroxynona-1,4-diyn-1-yl)-*N*,4-dimethylbenzenesulfonamide (1o**):**



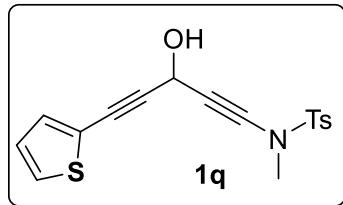
Compound **1o** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (590 mg, 1.85 mmol, 77%); ^1H NMR (700 MHz, CDCl_3): δ 7.77 (d, $J = 7.7$ Hz, 2H), 7.33 (d, $J = 7.7$ Hz, 2H), 5.18 (d, $J = 5.6$ Hz, 1H), 3.04 (s, 3H), 2.43 (s, 3H), 2.28 (d, $J = 7.0$ Hz, 1H), 2.22 (t, $J = 6.3$ Hz, 2H), 1.50 ~ 1.47 (m, 2H), 1.40 (q, $J = 7.0$ Hz, 2H), 0.89 (t, $J = 7.0$ Hz, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (175 MHz, CDCl_3): δ 144.9, 133.1, 129.8, 127.8, 85.5, 79.1, 76.8, 67.7, 52.5, 38.8, 30.4, 21.9, 21.6, 18.4, 13.6; HRMS (ESI-TOF) m/z: $[\text{M}+\text{Na}]^+$ calcd. $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{SNa}$: 342.1140, found: 342.1135.

Spectral data of *N*-(5-cyclopropyl-3-hydroxypenta-1,4-diyn-1-yl)-*N*,4-dimethylbenzenesulfonamide (1p**):**



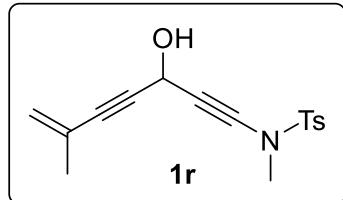
Compound **1p** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (530 mg, 1.75 mmol, 73%); ^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 5.14 (d, $J = 6.8$ Hz, 1H), 3.03 (s, 3H), 2.44 (s, 3H), 2.28 (d, $J = 6.8$ Hz, 1H), 1.29 ~ 1.24 (m, 1H), 0.81 ~ 0.69 (m, 4H); $^{13}\text{C}\{\text{H}\}$ NMR (175 MHz, CDCl_3): δ 144.9, 133.1, 129.8, 129.7, 127.9, 127.8, 88.5, 79.2, 72.5, 67.6, 52.5, 38.8, 27.3, 21.7; HRMS (ESI-TOF) m/z: $[\text{M}+\text{Na}]^+$ calcd. $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{SNa}$: 326.0827, found: 326.0824.

Spectral data of *N*-(3-hydroxy-5-(thiophen-2-yl)penta-1,4-diyn-1-yl)-*N*,4-dimethylbenzenesulfonamide (1q**):**



Compound **1q** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (610 mg, 1.77 mmol, 74%); ^1H NMR (700 MHz, CDCl_3): δ 7.79 (d, $J = 7.7$ Hz, 2H), 7.30 (d, $J = 7.7$ Hz, 2H), 7.27 (d, $J = 4.2$ Hz, 1H), 7.24 (s, 1H), 6.97 (s, 1H), 5.42 (d, $J = 6.3$ Hz, 1H), 3.06 (s, 3H), 2.55 (d, $J = 6.3$ Hz, 1H), 2.40 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (175 MHz, CDCl_3): δ 145.0, 133.0, 132.9, 129.9, 127.8, 127.0, 121.8, 89.7, 80.0, 77.7, 66.9, 52.9, 38.8, 21.6; one carbon merge with other peak; HRMS (ESI-TOF) m/z: $[\text{M}+\text{Na}]^+$ calcd. $\text{C}_{17}\text{H}_{15}\text{NO}_3\text{S}_2\text{Na}$: 368.0391, found: 368.0392.

Spectral data of *N*-(3-hydroxy-6-methylhepta-6-en-1,4-diyn-1-yl)-*N,N*-dimethylbenzenesulfonamide (1r**):**



Compound **1r** was purified on silica gel column using ethyl acetate/hexane: (30: 70) as the eluent; Yellow oil (420 mg, 1.38 mmol, 58%); ^1H NMR (700 MHz, CDCl_3): δ 7.78 (d, $J = 7.0$ Hz, 2H), 7.33 (d, $J = 7.7$ Hz, 2H), 5.34 (s, 1H), 5.31 (d, $J = 6.3$ Hz, 1H), 5.28 (d, $J = 1.4$ Hz, 1H), 3.05 (s, 3H), 2.43 (s, 3H), 2.36 (d, $J = 6.3$ Hz, 1H), 1.89 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (175 MHz, CDCl_3): δ 144.9, 133.1, 129.8, 127.9, 125.8, 123.2, 85.4, 84.9, 79.7, 67.2, 52.7, 38.8, 23.1, 21.6; HRMS (ESI-TOF) m/z: $[\text{M}+\text{Na}]^+$ calcd. $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{SNa}$: 326.0827, found: 326.0828.

5. Computational Details:

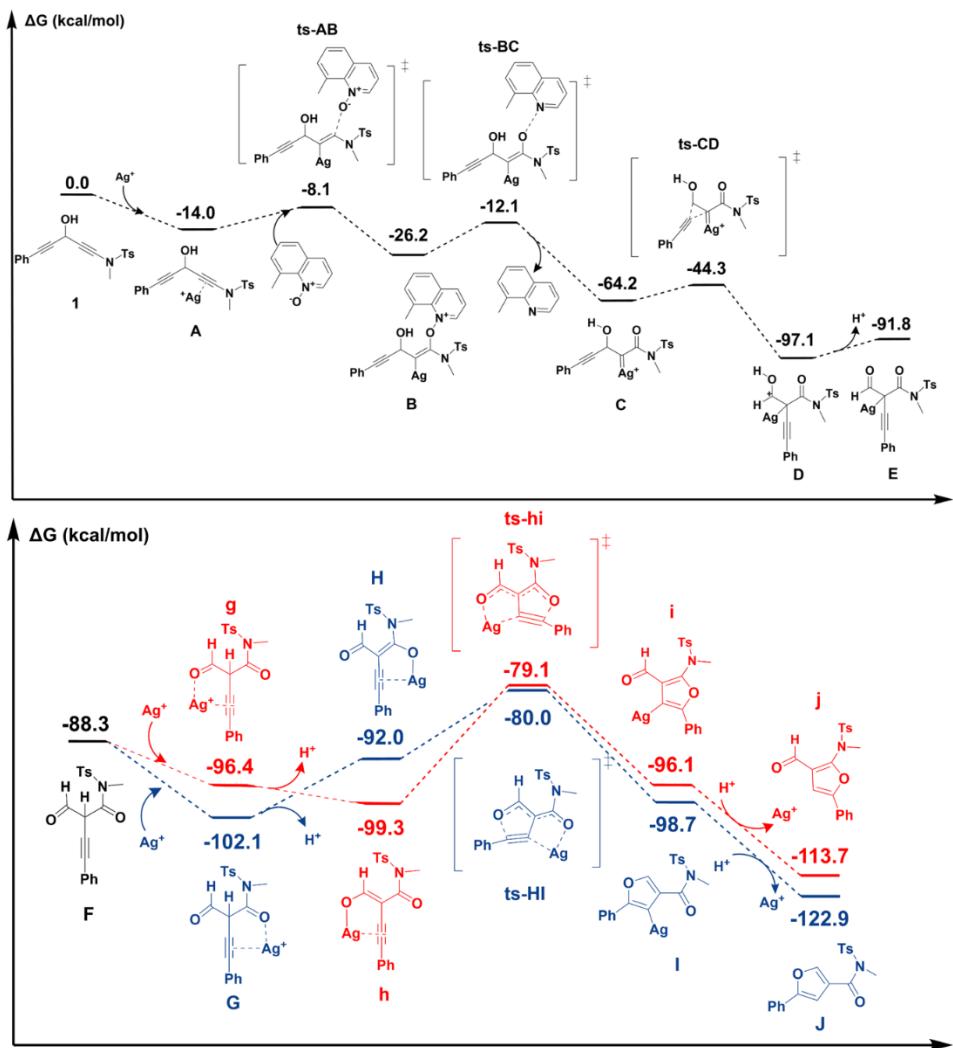
Geometries were optimized using the B3LYP-D3 functional combined with the def2-SVP basis. Hessians at these geometries provided the zero-point energy and vibrational enthalpy and entropy. Solvation free energies (G_{solv}) were computed using the CPCM continuum model. The electronic

energy E_{elec} was obtained with the same functional and the def2-TZVP basis. The Gibbs free energy of each species was computed according to the following equation:

$$G = E_{\text{elec}} + G_{\text{solv}} + ZPE + H_{\text{vib}} + 4kT - TS_{\text{vib}}$$

Table S1. The energy components to form the Gibbs free energy for each stationary point along the reaction pathway.

Species	E_{elec}	G_{solv}	$ZPE + H_{\text{vib}} + 4kT - TS_{\text{vib}}$	$G_{\text{total}}(\text{hartree})$
LAu	-1410.136904	-0.0606892	0.44085	-1409.756743
Ag^+	-146.7374663	-0.141548272	-0.016605	-146.8956195
8-methylquinoline N-oxide	-516.6425993	0.011019024	0.13396	-516.4976203
8-methylquinoline	-441.4482327	0.007996996	0.130327	-441.3099087
1a	-1413.221566	-0.01027368	0.259568	-1412.972272
A	-1560.073571	-0.07123766	0.254607	-1559.890202
B	-2076.751877	-0.07129073	0.415851	-2076.407317
C	-1635.344037	-0.07423643	0.260423	-1635.157851
D	-1635.392006	-0.08226038	0.263865	-1635.210401
E	-1635.010507	-0.03170008	0.252182	-1634.790025
F	-1488.549772	-0.01415995	0.26316	-1488.300772
G	-1635.39481	-0.08120848	0.257674	-1635.218344
H	-1635.018977	-0.02402478	0.252687	-1634.790315
I	-1635.042561	-0.01452279	0.256133	-1634.800951
J (3a)	-1488.613379	-0.01173219	0.269323	-1488.355788
g	-1635.4043	-0.07001089	0.259504	-1635.214806
h	-1635.403844	-0.07183088	0.265123	-1635.210552
i	-1635.022762	-0.02771809	0.254789	-1634.795691
j (3a')	-1488.59939	-0.011960	0.269341	-1488.3420
ts-AB	-2076.720707	-0.06924247	0.411566	-2076.378384
ts-BC	-2076.727492	-0.06840272	0.411131	-2076.384764
ts-CD	-1635.311281	-0.07686878	0.261891	-1635.126259
ts-HI	-1634.999766	-0.02400829	0.252619	-1634.771155
ts-hi	-1634.99788	-0.025608	0.253798	-1634.7697



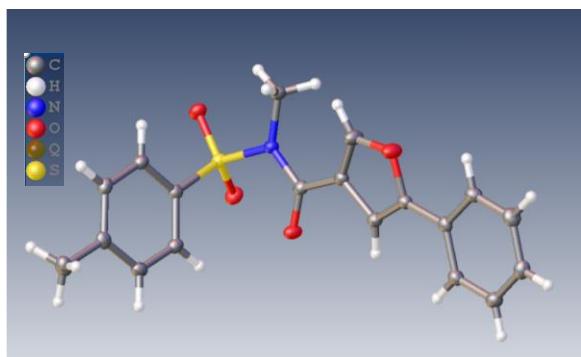
6. Figure s1: Gibbs Free Energy Profiles for two independent routes

7. X-ray crystallographic structure and data for compound 3s:

X-ray crystallographic data of compound (3a).

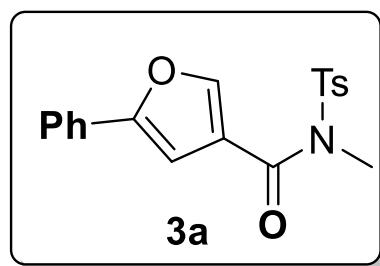
Ellipsoid contour % probability level = 50%

Experimental: The sample was dissolved in appropriate amount of Ethyl Acetate followed by the addition of pentane to furnish a saturated solution. Afterwards, the mixture was allowed to stand at room temperature to form the crystals.



CCDC-2357513

ORTEP diagram of compounds **3a**



231232LT_auto

Table s2 Crystal data and structure refinement for 231232LT_auto.

Identification code	231232LT_auto
Empirical formula	C ₁₉ H ₁₇ NO ₄ S
Formula weight	355.39
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	19.0633(2)
b/Å	5.70844(5)
c/Å	16.03289(17)
$\alpha/^\circ$	90
$\beta/^\circ$	108.5380(12)
$\gamma/^\circ$	90
Volume/Å ³	1654.20(3)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.427
μ/mm^{-1}	1.953
F(000)	744.0
Crystal size/mm ³	0.17 × 0.16 × 0.12
Radiation	Cu K α ($\lambda = 1.54184$)
2 Θ range for data collection/°	4.89 to 149.148
Index ranges	-23 ≤ h ≤ 21, -7 ≤ k ≤ 6, -14 ≤ l ≤ 20
Reflections collected	13685
Independent reflections	3172 [$R_{\text{int}} = 0.0180$, $R_{\text{sigma}} = 0.0148$]
Data/restraints/parameters	3172/0/228
Goodness-of-fit on F ²	1.028

Final R indexes [I>=2σ (I)]	R ₁ = 0.0323, wR ₂ = 0.0854
Final R indexes [all data]	R ₁ = 0.0334, wR ₂ = 0.0864
Largest diff. peak/hole / e Å ⁻³	0.29/-0.45

Table s3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 231232LT_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
S7	1707.2 (2)	3276.7 (6)	1305.1 (2)	15.53 (11)
O10	2955.9 (5)	1485.8 (17)	2670.5 (6)	21.1 (2)
O12	1317.7 (5)	4687.2 (18)	563.5 (6)	20.5 (2)
O13	1721.7 (5)	791.5 (18)	1202.1 (6)	20.3 (2)
O22	4828.7 (6)	6691.4 (19)	3260.4 (7)	25.9 (3)
N8	2585.1 (6)	4334 (2)	1627.7 (7)	16.3 (2)
C1	1370.7 (7)	3947 (2)	2179.0 (9)	15.4 (3)
C2	1426.5 (7)	2309 (2)	2841.2 (9)	17.4 (3)
C3	1132.1 (7)	2857 (3)	3505.4 (9)	19.0 (3)
C4	783.1 (7)	5003 (3)	3514.3 (9)	18.5 (3)
C5	741.4 (7)	6615 (2)	2846.0 (9)	18.6 (3)
C6	1033.3 (7)	6110 (2)	2176.0 (9)	17.7 (3)
C9	3103.1 (7)	3285 (2)	2348.2 (9)	16.3 (3)
C11	2728.0 (8)	6523 (3)	1225.1 (10)	22.4 (3)
C14	447.4 (8)	5563 (3)	4223.8 (9)	25.3 (3)
C15	5706.8 (7)	4421 (2)	4393.4 (9)	16.7 (3)
C16	6243.5 (8)	6163 (3)	4495.4 (9)	20.1 (3)
C17	6925.9 (8)	5957 (3)	5148.5 (10)	22.7 (3)
C18	7079.4 (8)	4034 (3)	5704.9 (9)	21.2 (3)
C19	6550.4 (8)	2279 (3)	5605.9 (9)	20.7 (3)
C20	5869.8 (8)	2476 (3)	4954.0 (9)	19.5 (3)
C21	4984.7 (7)	4605 (2)	3715.7 (9)	17.1 (3)
C23	4137.4 (8)	6502 (3)	2676.7 (10)	24.1 (3)
C24	3842.2 (7)	4361 (2)	2741.0 (9)	16.4 (3)
C25	4399.4 (8)	3152 (2)	3421.6 (9)	17.5 (3)

Table s4 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 231232LT_auto. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + 2hka^{*}b^{*}U_{12} + ...]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
S7	16.09(17)	15.83(19)	13.28(18)	-0.38(12)	2.69(13)	1.17(11)
O10	20.5(5)	18.7(5)	20.7(5)	5.6(4)	1.8(4)	-2.3(4)
O12	20.8(5)	23.8(5)	14.4(5)	2.0(4)	1.9(4)	3.3(4)
O13	21.9(5)	16.5(5)	20.1(5)	-3.6(4)	3.5(4)	0.7(4)
O22	22.2(5)	23.2(6)	27.2(6)	8.2(4)	0.6(4)	-5.7(4)
N8	16.6(5)	16.1(6)	16.0(5)	2.7(4)	5.1(4)	0.6(4)
C1	14.0(6)	16.0(6)	14.8(6)	-1.2(5)	2.6(5)	-2.1(5)
C2	15.7(6)	16.2(7)	17.8(6)	0.6(5)	2.0(5)	-1.0(5)
C3	17.5(6)	21.9(7)	15.8(6)	2.7(5)	2.7(5)	-3.2(5)
C4	13.5(6)	23.8(7)	16.4(6)	-3.7(6)	2.1(5)	-3.9(5)
C5	15.6(6)	17.2(7)	21.2(7)	-2.9(5)	3.4(5)	-0.1(5)
C6	16.9(6)	16.1(7)	19.0(6)	1.5(5)	4.0(5)	-0.6(5)
C9	17.8(6)	15.6(7)	15.6(6)	-0.1(5)	5.7(5)	2.1(5)
C11	19.8(7)	21.1(7)	26.0(7)	9.6(6)	6.7(6)	1.8(6)
C14	21.3(7)	35.1(9)	20.4(7)	-2.8(6)	7.7(6)	-0.1(6)
C15	17.4(6)	18.6(7)	15.5(6)	-2.5(5)	7.0(5)	-0.1(5)
C16	22.3(7)	18.5(7)	20.1(7)	0.2(6)	7.7(6)	-2.0(6)
C17	20.9(7)	22.6(7)	23.9(7)	-4.7(6)	6.3(6)	-6.1(6)
C18	18.8(6)	25.4(8)	17.7(7)	-4.3(6)	3.2(5)	0.6(6)
C19	22.5(7)	22.0(7)	18.0(7)	1.3(6)	6.8(6)	1.1(6)
C20	19.4(6)	19.8(7)	20.6(7)	0.0(6)	8.2(6)	-2.4(5)
C21	19.0(6)	17.4(7)	16.6(6)	1.1(5)	8.0(5)	0.6(5)
C23	22.1(7)	22.8(8)	22.6(7)	6.7(6)	0.7(6)	-2.2(6)
C24	17.9(6)	17.5(7)	14.7(6)	0.8(5)	6.6(5)	1.7(5)
C25	18.3(6)	15.9(7)	18.0(7)	1.0(5)	5.6(5)	0.6(5)

Table s5 Bond Lengths for 231232LT_auto.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
S7	O12	1.4325(10)	C4	C14	1.5063(19)
S7	O13	1.4295(10)	C5	C6	1.388(2)
S7	N8	1.6977(11)	C9	C24	1.4814(19)
S7	C1	1.7586(13)	C15	C16	1.3984(19)
O10	C9	1.2216(17)	C15	C20	1.400(2)
O22	C21	1.3790(17)	C15	C21	1.4612(18)
O22	C23	1.3564(18)	C16	C17	1.391(2)
N8	C9	1.3941(17)	C17	C18	1.386(2)
N8	C11	1.4707(18)	C18	C19	1.394(2)

Table s5 Bond Lengths for 231232LT_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.3931(19)	C19	C20	1.388(2)
C1	C6	1.3916(19)	C21	C25	1.3494(19)
C2	C3	1.388(2)	C23	C24	1.363(2)
C3	C4	1.396(2)	C24	C25	1.4346(18)
C4	C5	1.395(2)			

Table s6 Bond Angles for 231232LT_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O12	S7	N8	104.69(6)	O10	C9	N8	120.95(12)
O12	S7	C1	108.35(6)	O10	C9	C24	118.96(12)
O13	S7	O12	119.07(6)	N8	C9	C24	120.09(12)
O13	S7	N8	109.56(6)	C16	C15	C20	118.94(13)
O13	S7	C1	109.47(6)	C16	C15	C21	121.14(13)
N8	S7	C1	104.71(6)	C20	C15	C21	119.91(12)
C23	O22	C21	107.17(11)	C17	C16	C15	120.15(13)
C9	N8	S7	118.00(9)	C18	C17	C16	120.44(13)
C9	N8	C11	123.20(11)	C17	C18	C19	119.92(13)
C11	N8	S7	118.07(9)	C20	C19	C18	119.79(14)
C2	C1	S7	120.16(11)	C19	C20	C15	120.75(13)
C6	C1	S7	118.40(10)	O22	C21	C15	116.69(12)
C6	C1	C2	121.42(13)	C25	C21	O22	109.31(12)
C3	C2	C1	118.81(13)	C25	C21	C15	133.99(13)
C2	C3	C4	121.04(13)	O22	C23	C24	110.67(12)
C3	C4	C14	120.80(13)	C23	C24	C9	134.38(13)
C5	C4	C3	118.81(13)	C23	C24	C25	105.37(12)
C5	C4	C14	120.38(13)	C25	C24	C9	119.87(12)
C6	C5	C4	121.20(13)	C21	C25	C24	107.47(12)
C5	C6	C1	118.70(13)				

Table s7 Torsion Angles for 231232LT_auto.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S7	N8	C9	O10	8.76(18)	C2	C3	C4	C14	178.41(12)
S7	N8	C9	C24	170.59(10)	C3	C4	C5	C6	0.6(2)
S7	C1	C2	C3	177.72(10)	C4	C5	C6	C1	0.1(2)
S7	C1	C6	C5	177.59(10)	C6	C1	C2	C3	0.5(2)

Table s7 Torsion Angles for 231232LT_auto.

A	B	C	D	Angle/ $^{\circ}$	A	B	C	D	Angle/ $^{\circ}$
O10C9	C24C23			164.60(15)	C9	C24C25C21			174.19(12)
O10C9	C24C25			7.1(2)	C11N8	C9	O10		178.77(12)
O12S7	N8	C9		179.85(10)	C11N8	C9	C24		-0.58(19)
O12S7	N8	C11		9.62(12)	C14C4	C5	C6		178.58(12)
O12S7	C1	C2		155.27(11)	C15C16C17C18				-0.2(2)
O12S7	C1	C6		-23.01(12)	C15C21C25C24				179.30(14)
O13S7	N8	C9		-51.09(11)	C16C15C20C19				0.5(2)
O13S7	N8	C11		138.39(10)	C16C15C21O22				-7.72(19)
O13S7	C1	C2		23.95(12)	C16C15C21C25				173.37(15)
O13S7	C1	C6		154.33(10)	C16C17C18C19				0.6(2)
O22C21C25C24				0.33(16)	C17C18C19C20				-0.5(2)
O22C23C24C9				172.75(14)	C18C19C20C15				-0.1(2)
O22C23C24C25				0.17(17)	C20C15C16C17				-0.3(2)
N8 S7 C1 C2				-93.43(11)	C20C15C21O22				172.26(12)
N8 S7 C1 C6				88.29(11)	C20C15C21C25				-6.6(2)
N8 C9 C24C23				14.8(2)	C21O22C23C24				0.02(17)
N8 C9 C24C25				173.50(12)	C21C15C16C17				179.65(13)
C1 S7 N8 C9				66.23(11)	C21C15C20C19				179.50(12)
C1 S7 N8 C11				104.30(11)	C23O22C21C15				179.39(12)
C1 C2 C3 C4				0.2(2)	C23O22C21C25				-0.22(16)
C2 C1 C6 C5				-0.7(2)	C23C24C25C21				-0.31(16)
C2 C3 C4 C5				-0.7(2)					

Table s8 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 231232LT_auto.

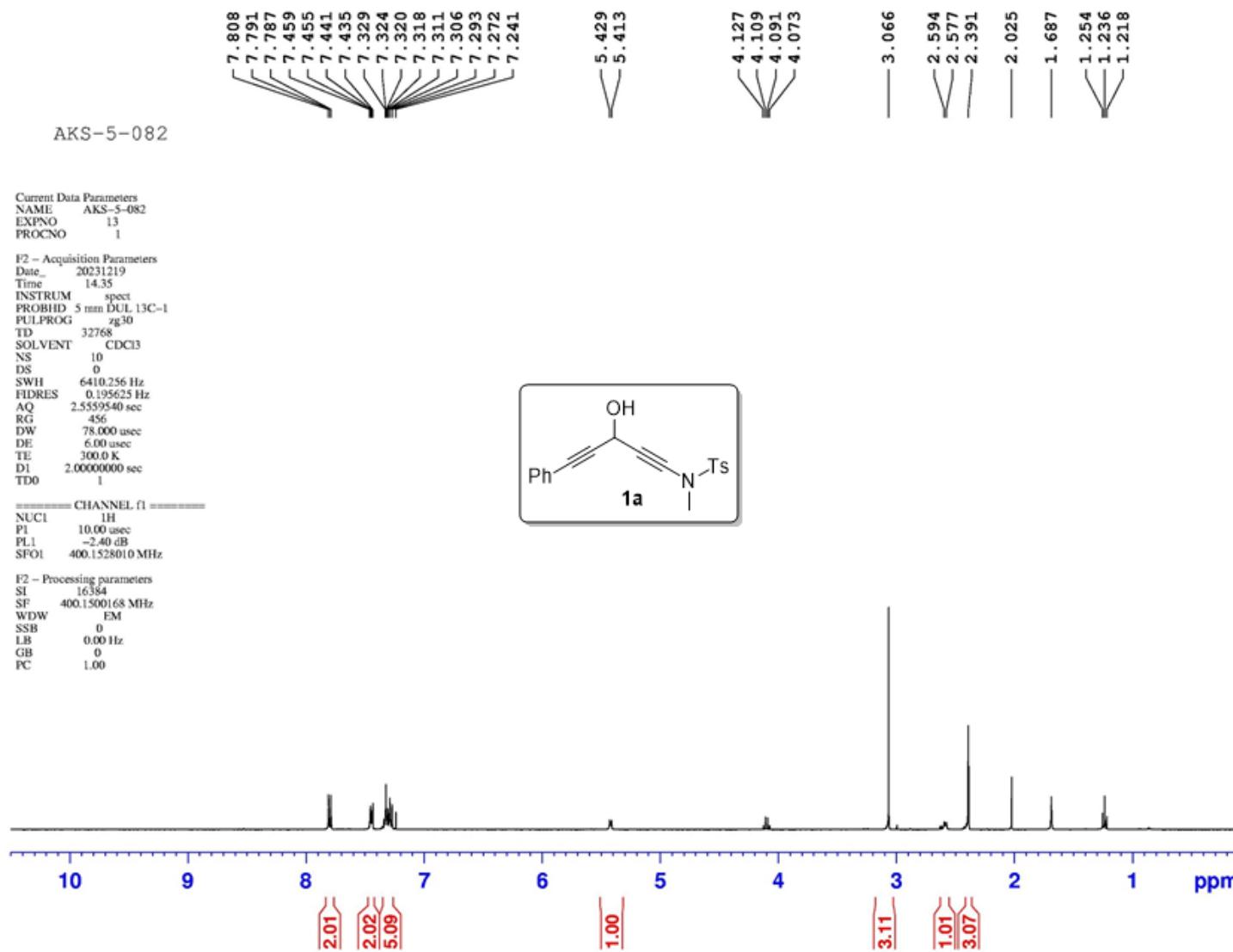
Atom	x	y	z	U(eq)
H2	1661.8	843.69	2838.26	21
H3	1168.73	1754.67	3961.16	23
H5	508.95	8085.84	2849.69	22
H6	1003.24	7219.28	1724.16	21
H11A	2326.77	6802.48	674.52	34
H11B	3198.38	6393.89	1102.37	34
H11C	2754.03	7829.8	1630.09	34

Table s8 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 231232LT_auto.

Atom	x	y	z	U(eq)
H14A	797.08	6496.96	4684.03	38
H14B	337.31	4102.72	4478.79	38
H14C	-10.75	6453.1	3970.32	38
H16	6142	7489.25	4117.97	24
H17	7288.95	7143.44	5213.4	27
H18	7544.53	3910.9	6153.19	25
H19	6655.39	953.45	5983.5	25
H20	5510.48	1277.39	4887.4	23
H23	3892.63	7697.95	2277.98	29
H25	4362.91	1610.96	3627.6	21

8. ^1H and ^{13}C spectra

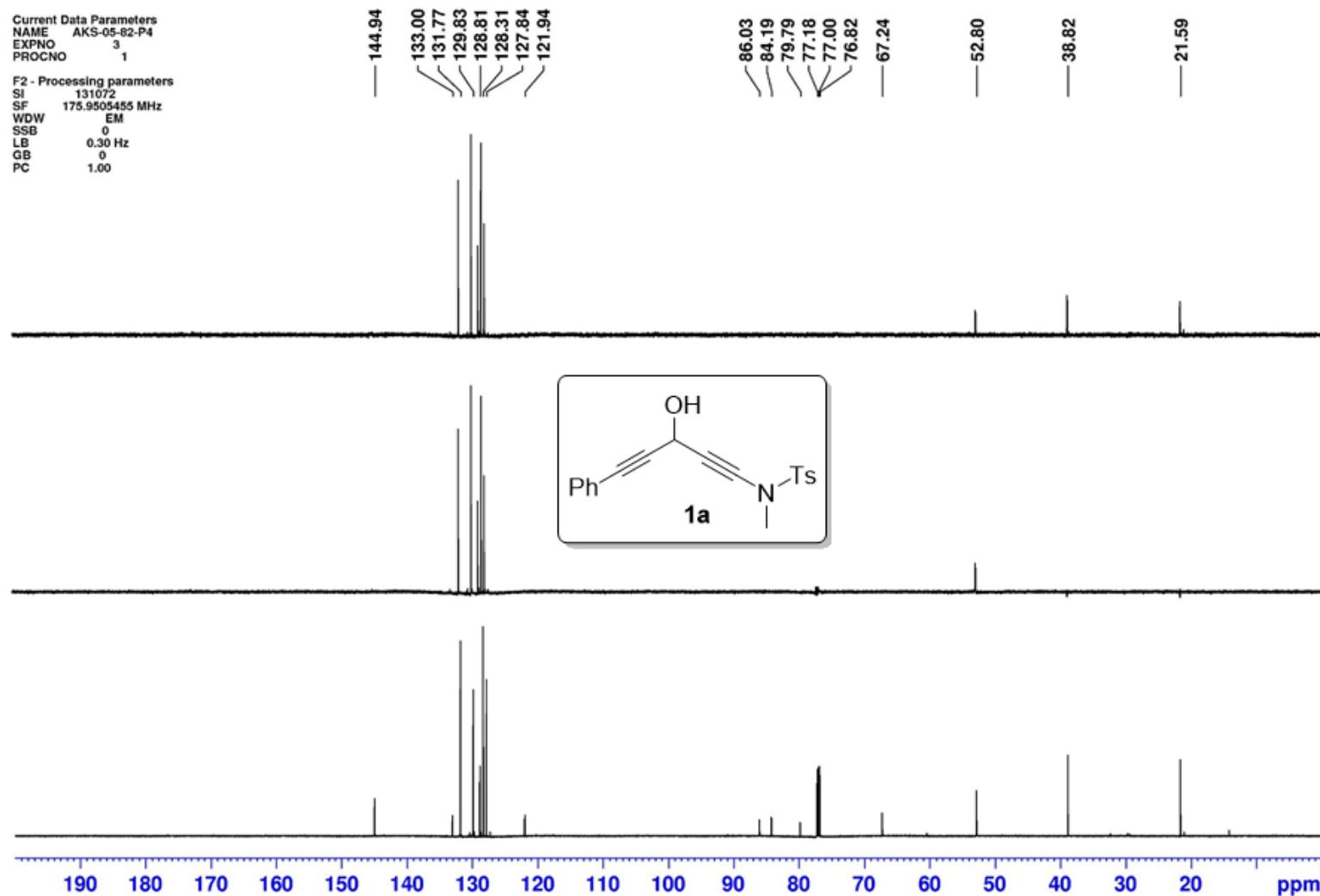
^1H NMR (CDCl_3 , 400 MHz)



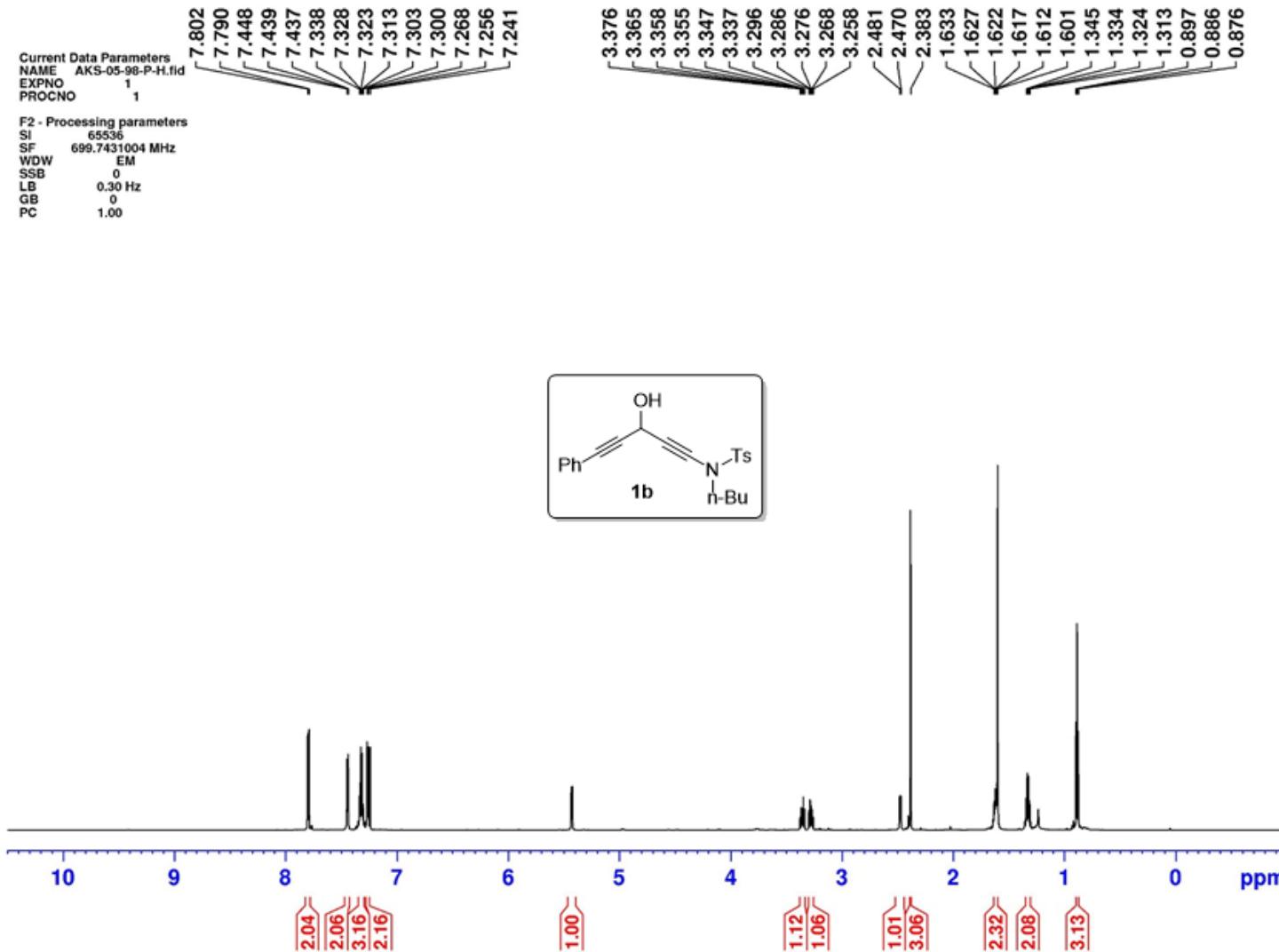
$^{13}\text{C}\{1\text{H}\}$ and DEPT NMR (CDCl_3 , 100 MHz)

Current Data Parameters
NAME AKS-05-82-P4
EXPNO 3
PROCNO 1

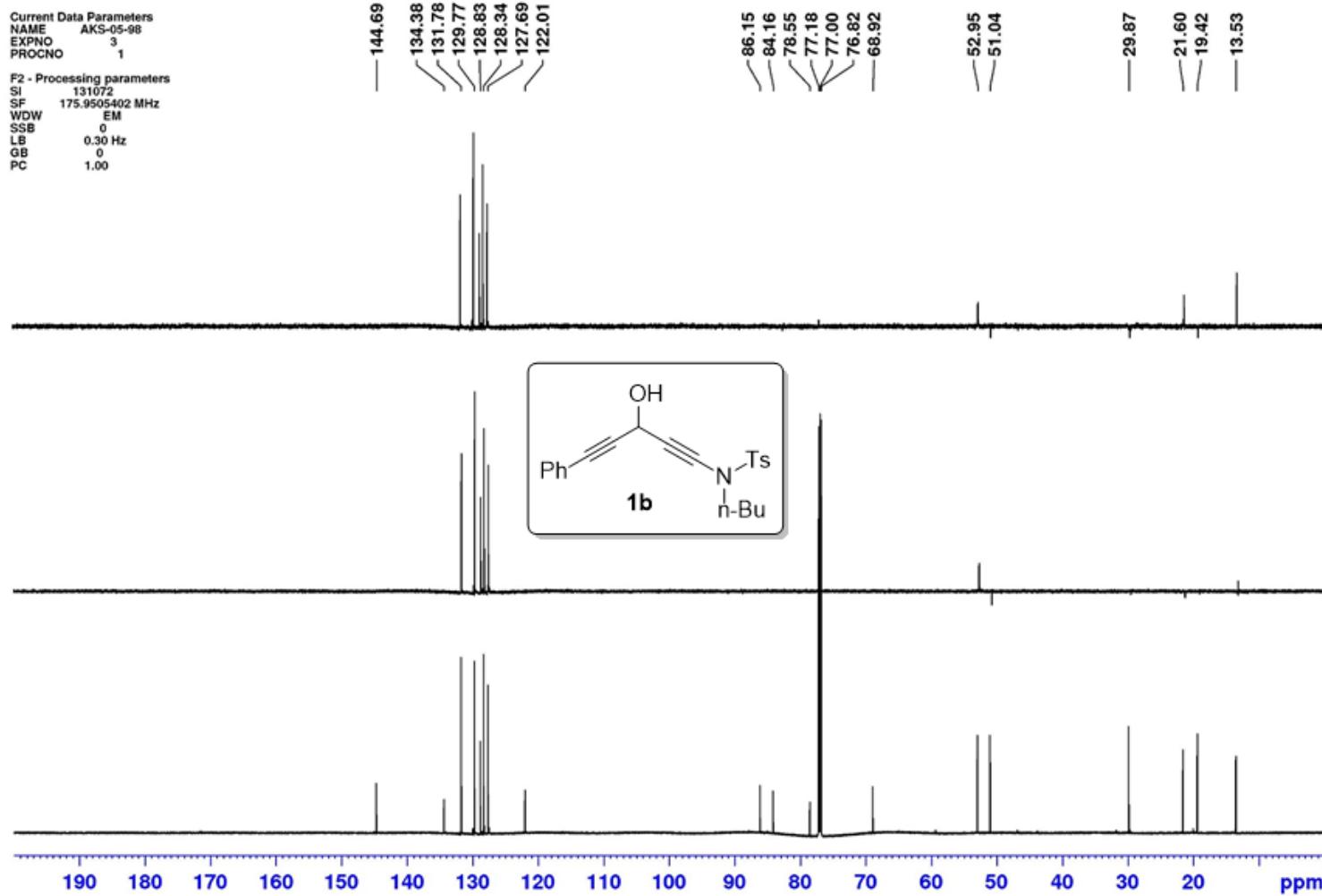
F2 - Processing parameters
SI 131072
SF 175.9505455 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



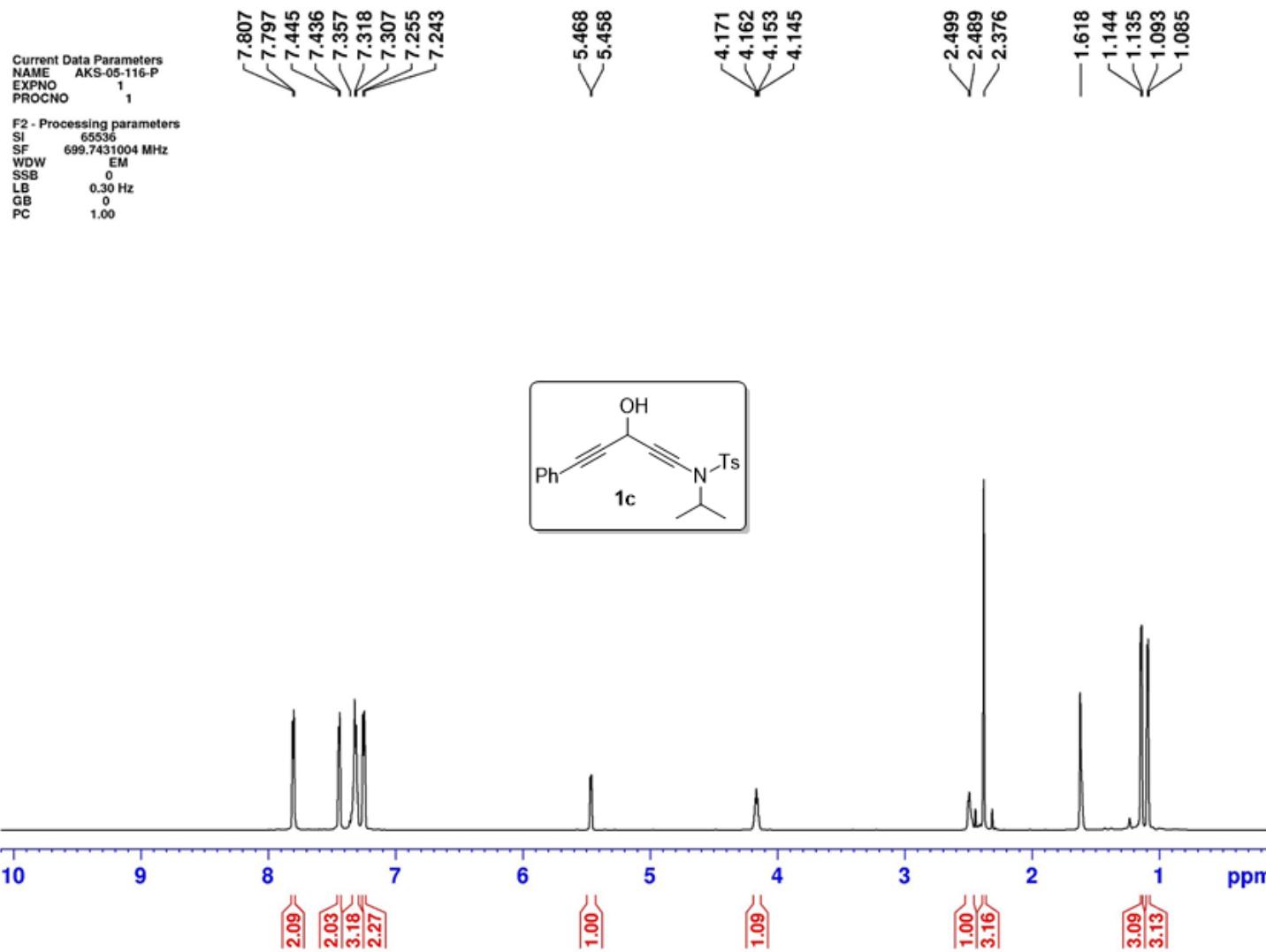
¹H NMR (CDCl₃, 700 MHz)



$^{13}\text{C}\{1\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



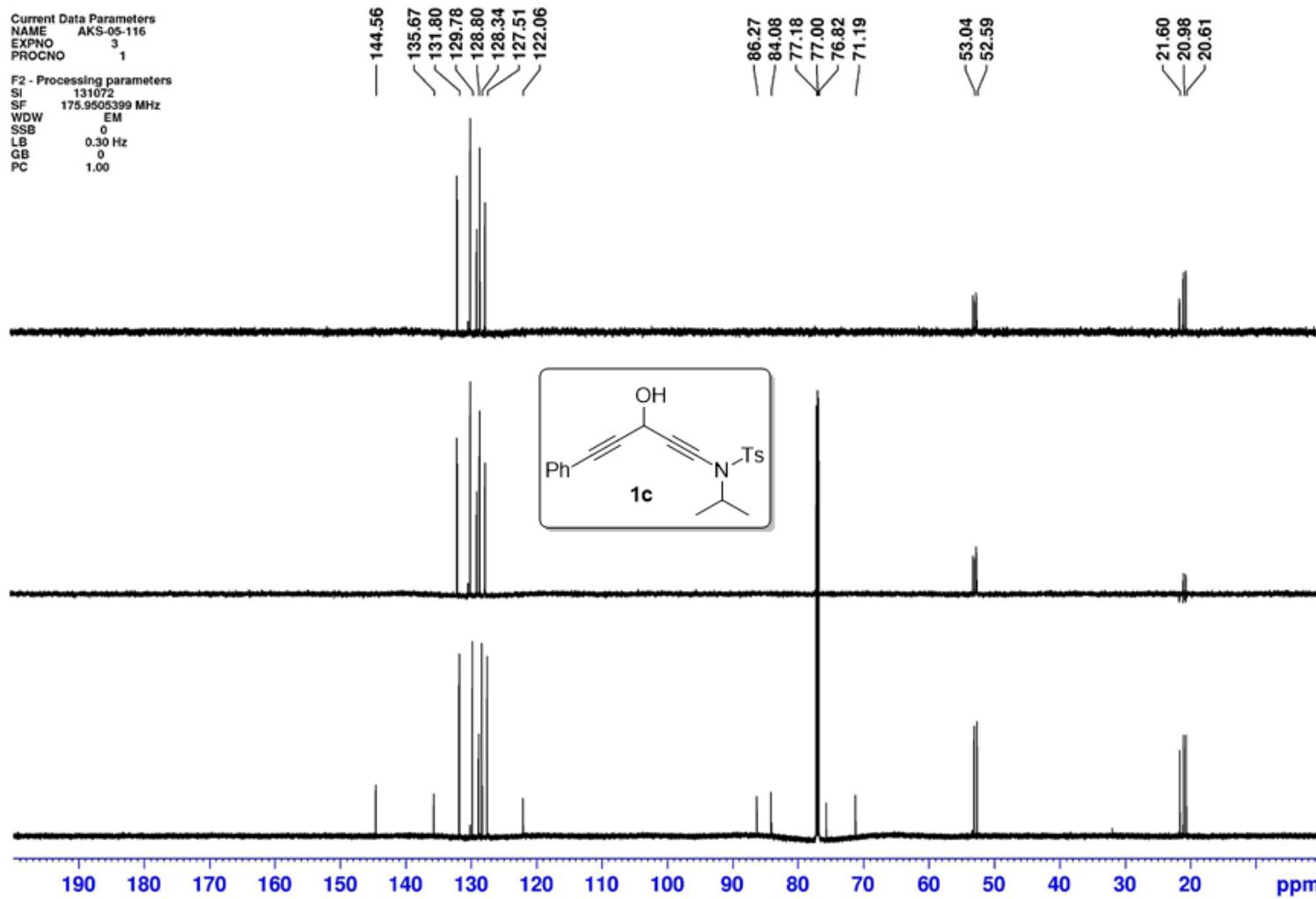
¹H NMR (CDCl₃, 700 MHz)



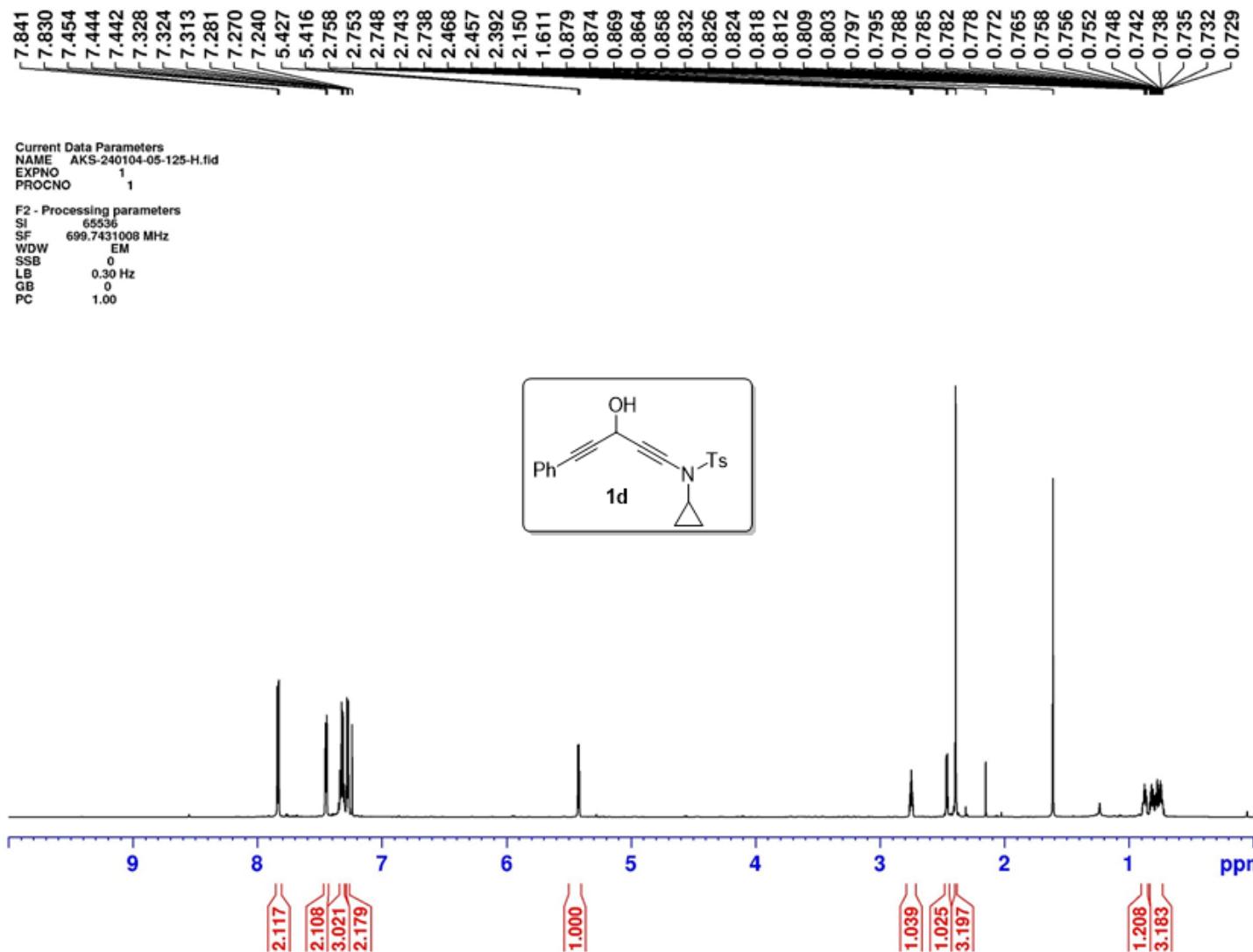
$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)

Current Data Parameters
NAME AKS-05-116
EXPNO 3
PROCNO 1

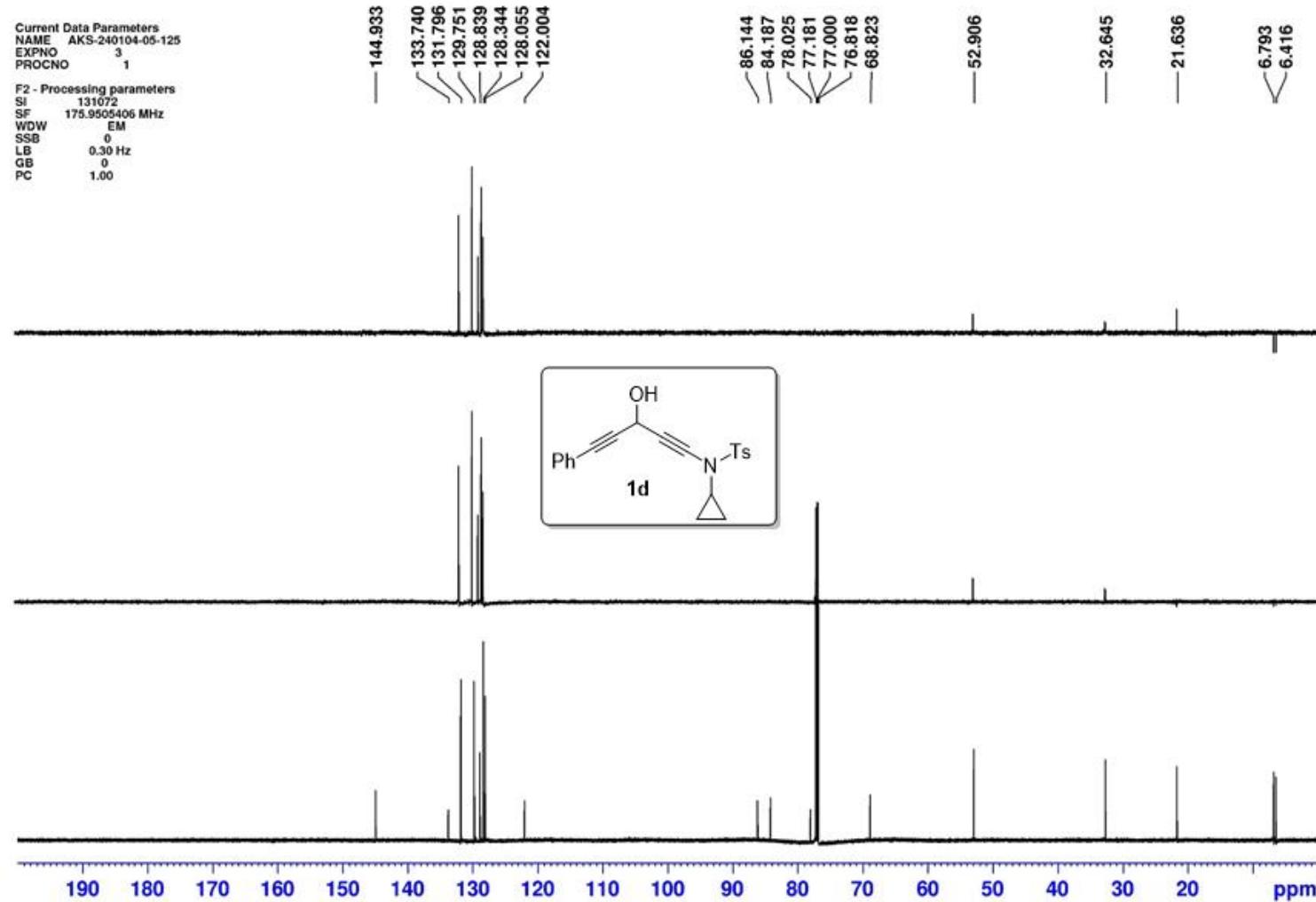
F2 - Processing parameters
SI 131072
SF 175.9505399 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



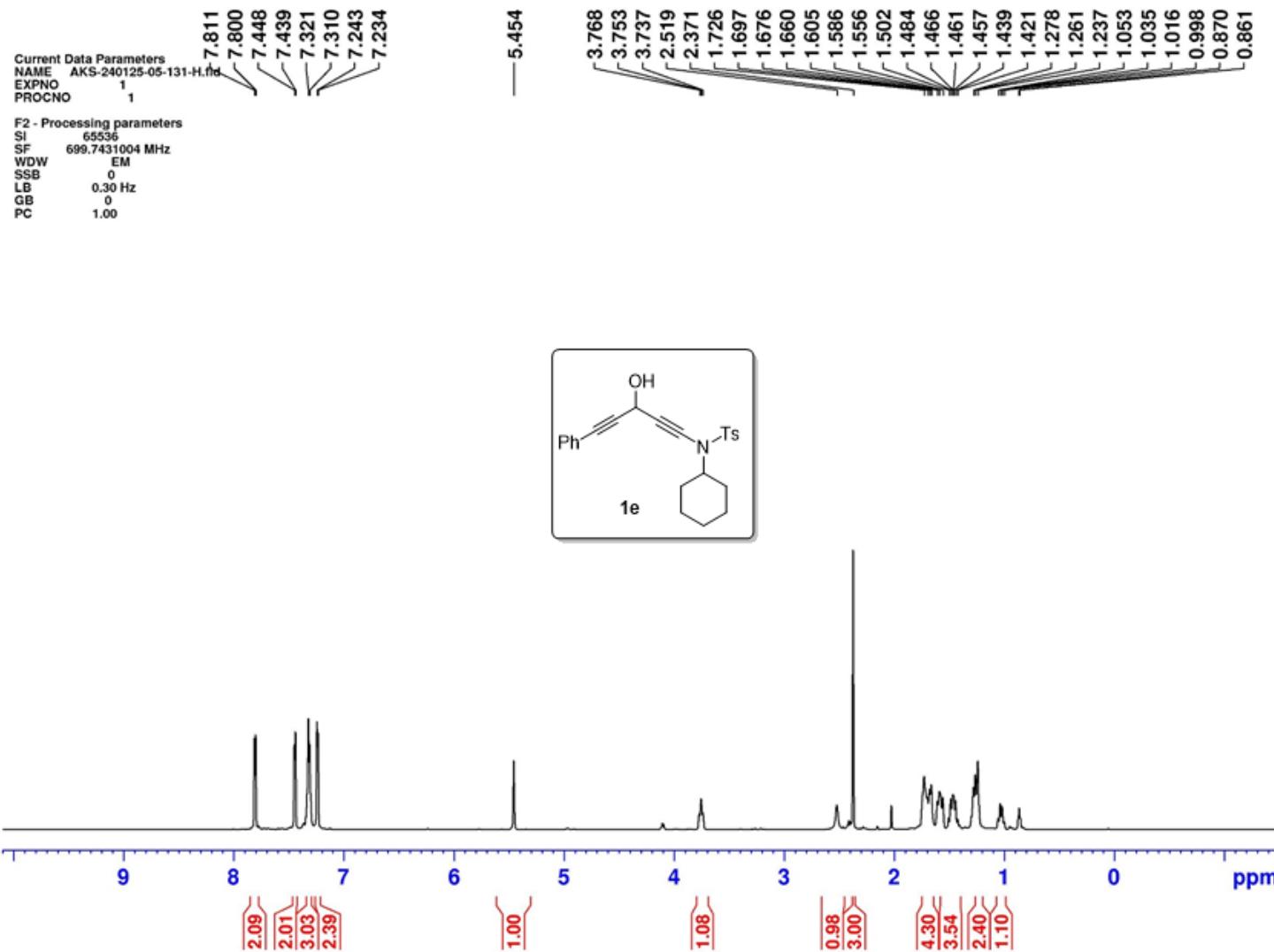
¹H NMR (CDCl₃, 700 MHz)



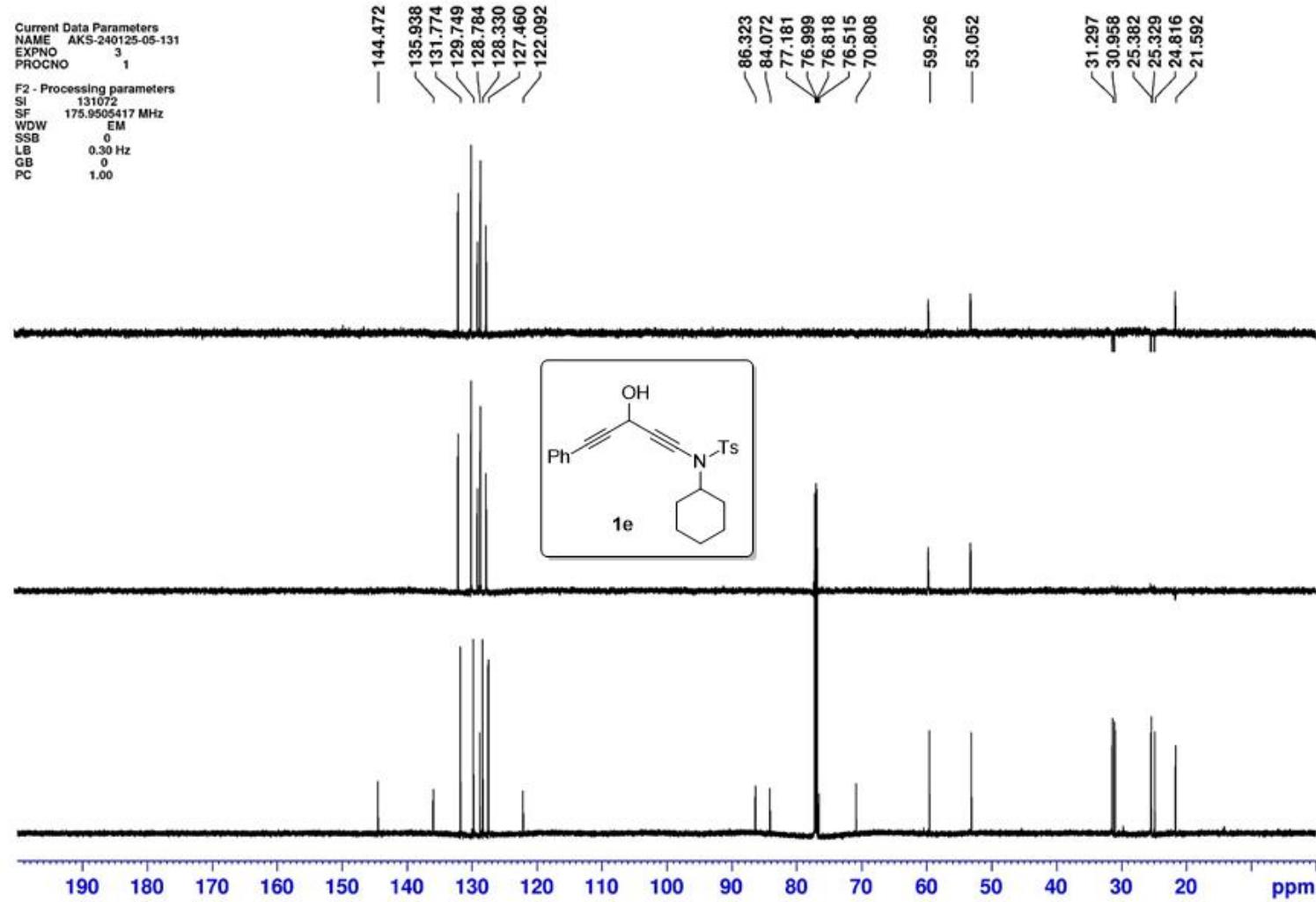
$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



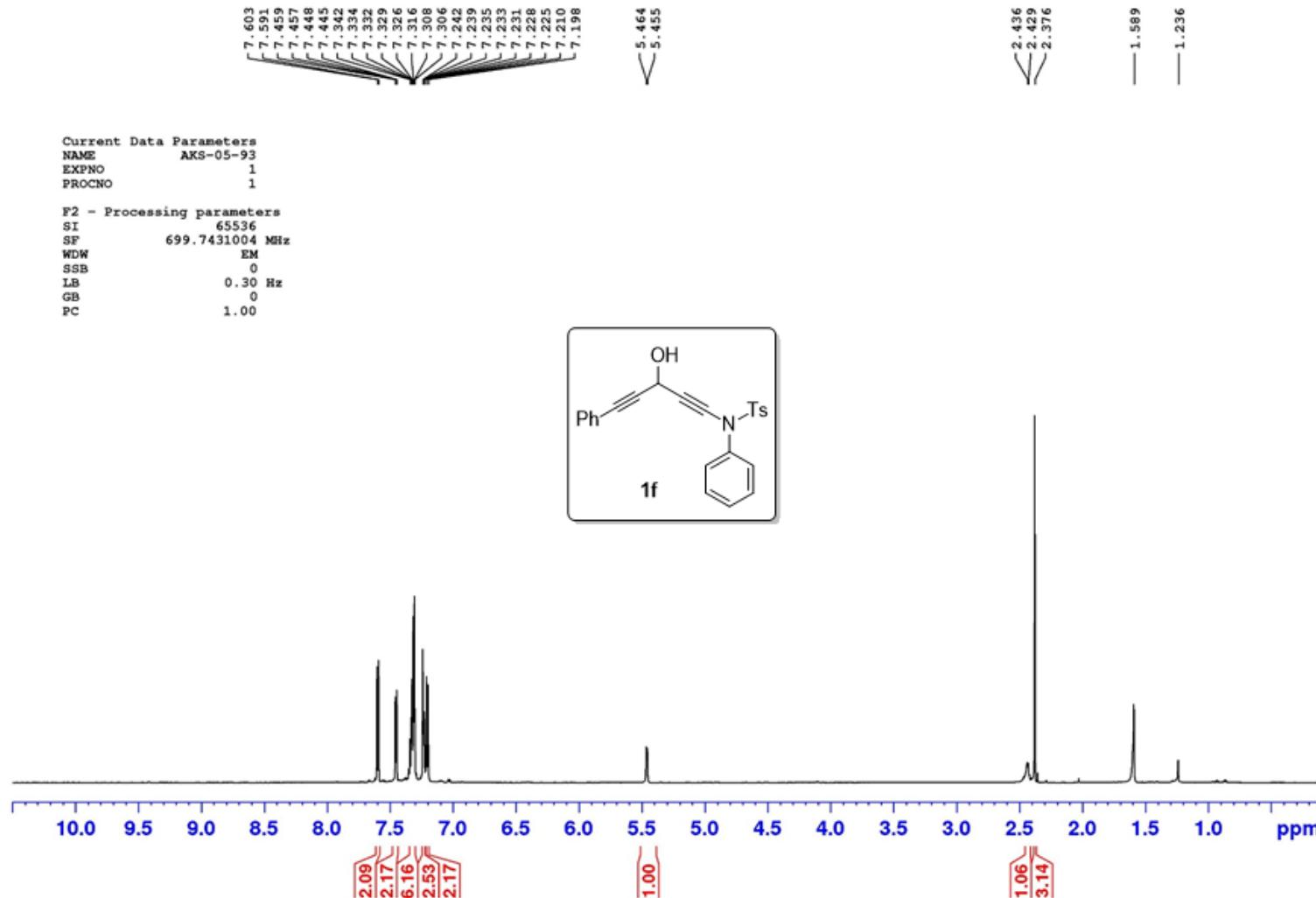
¹H NMR (CDCl₃, 700 MHz)



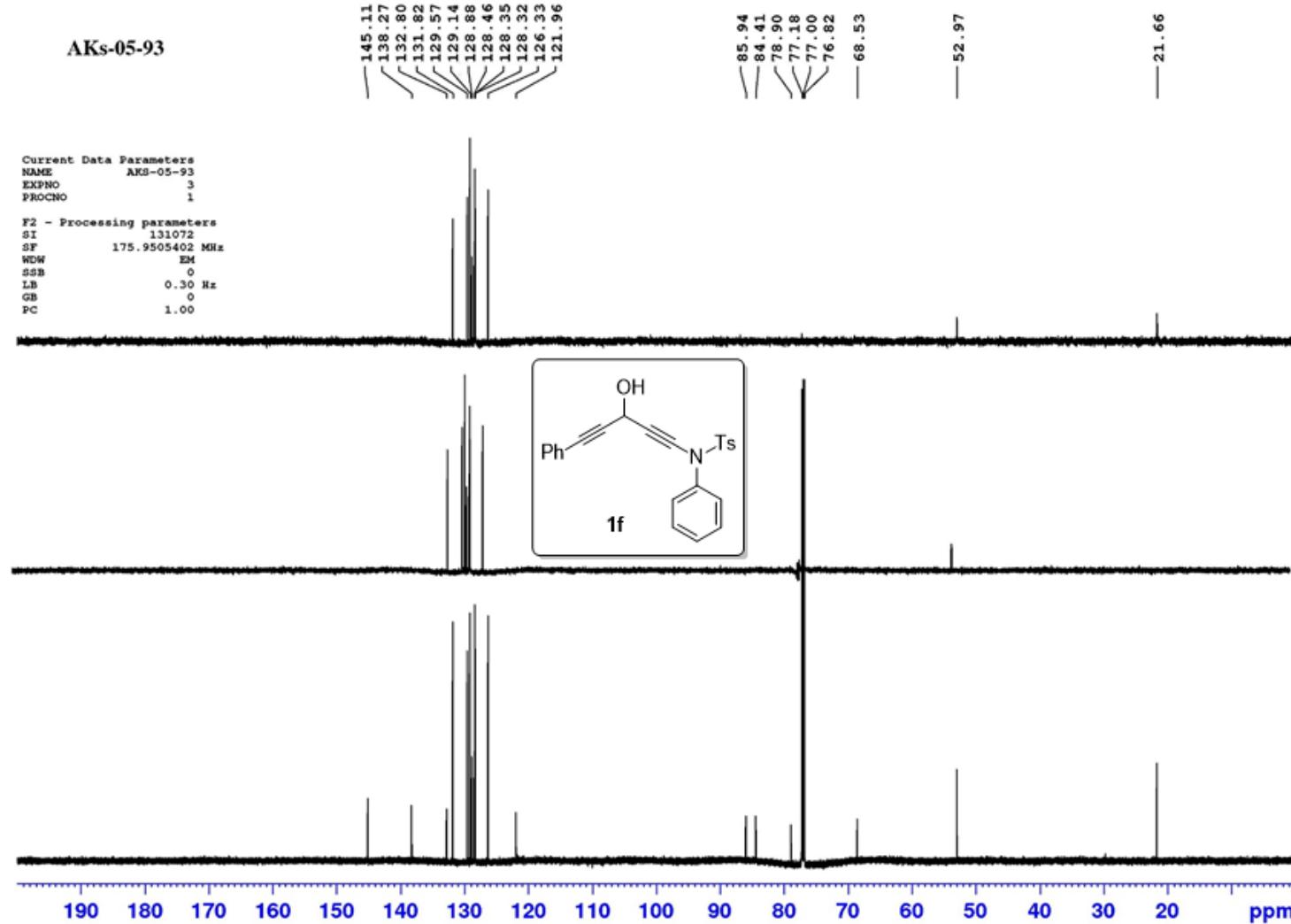
$^{13}\text{C}\{^1\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



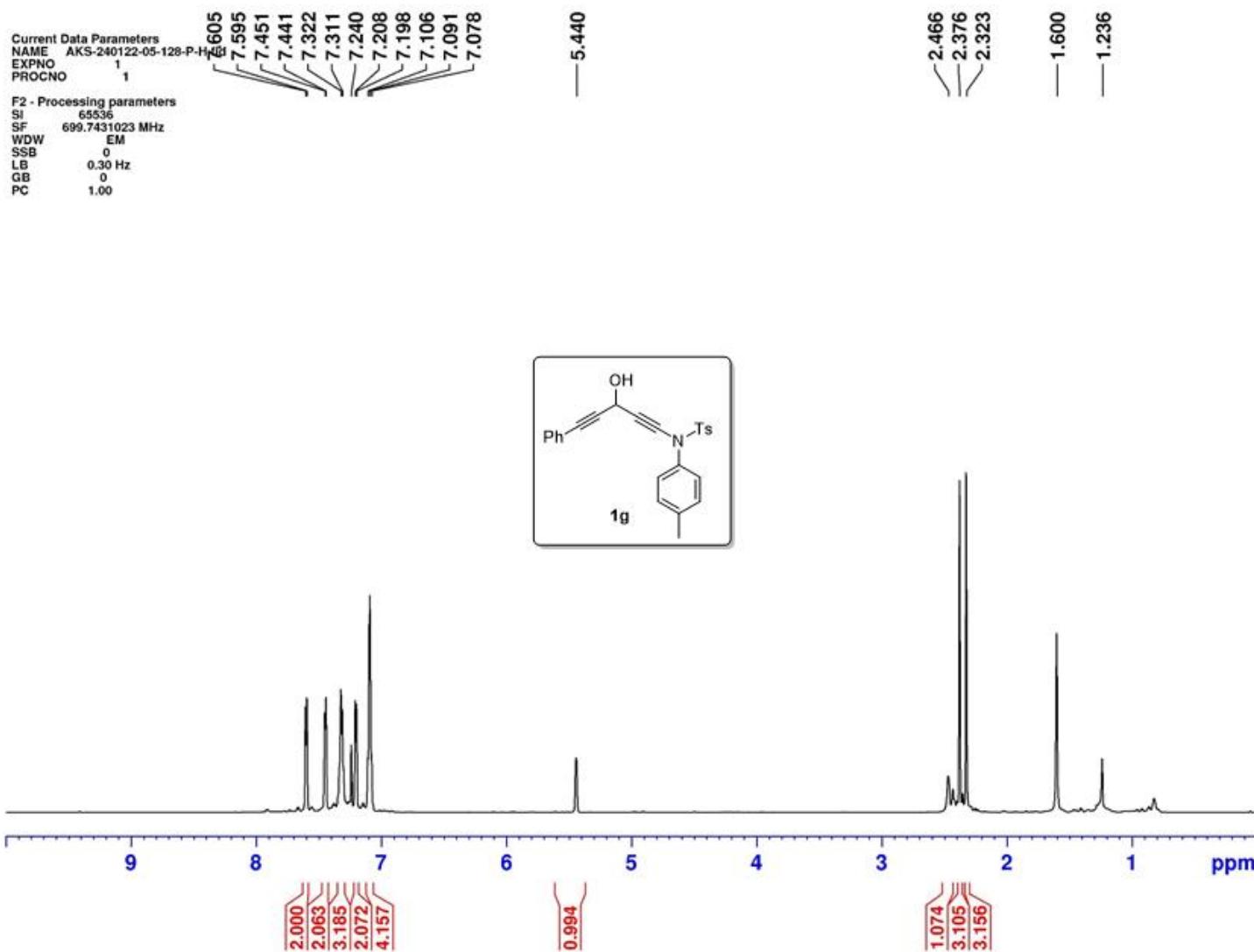
¹H NMR (CDCl₃, 700 MHz)



$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



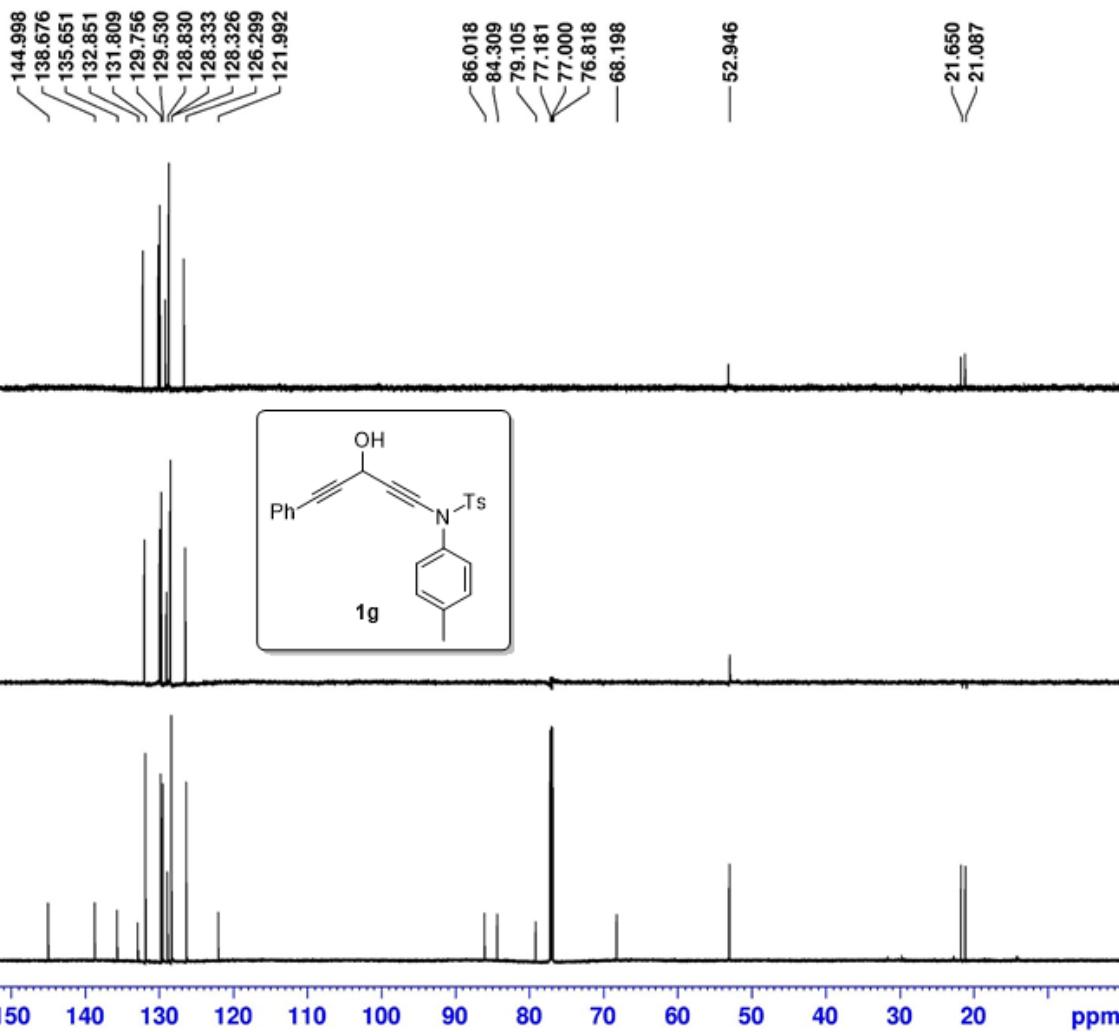
¹H NMR (CDCl₃, 700 MHz)



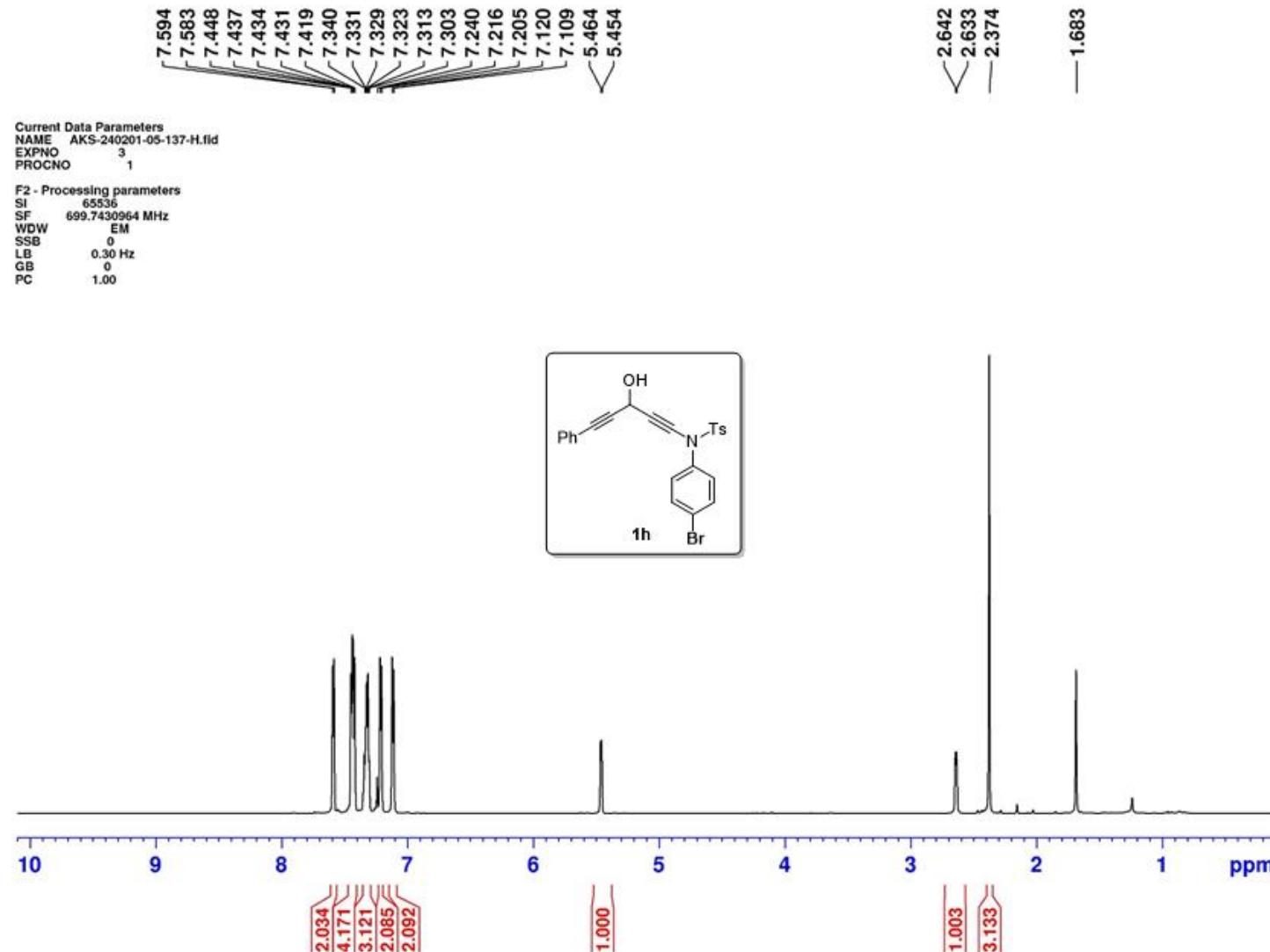
¹³C{¹H} and DEPT NMR (CDCl₃, 175 MHz)

Current Data Parameters
NAME AKS-240118-05-128
EXPNO 3
PROCNO 1

F2 - Processing parameters
SI 131072
SF 175.9505417 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



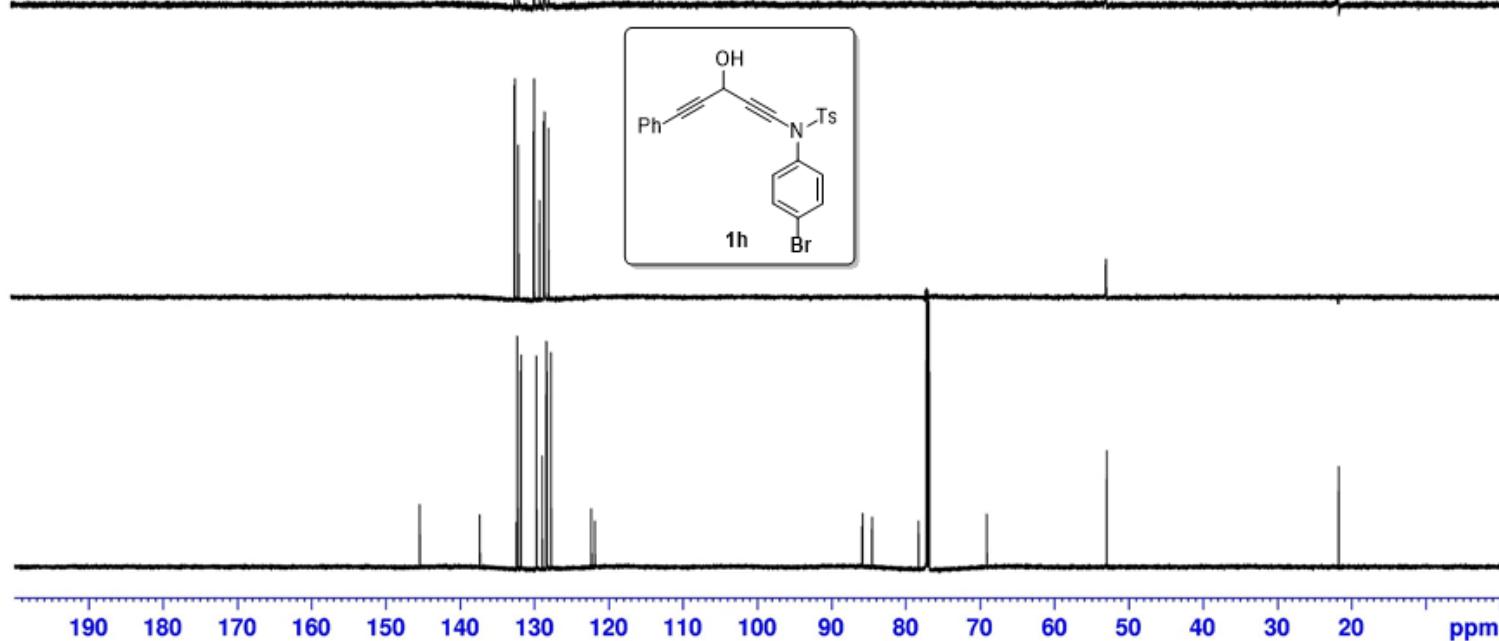
¹H NMR (CDCl₃, 700 MHz)



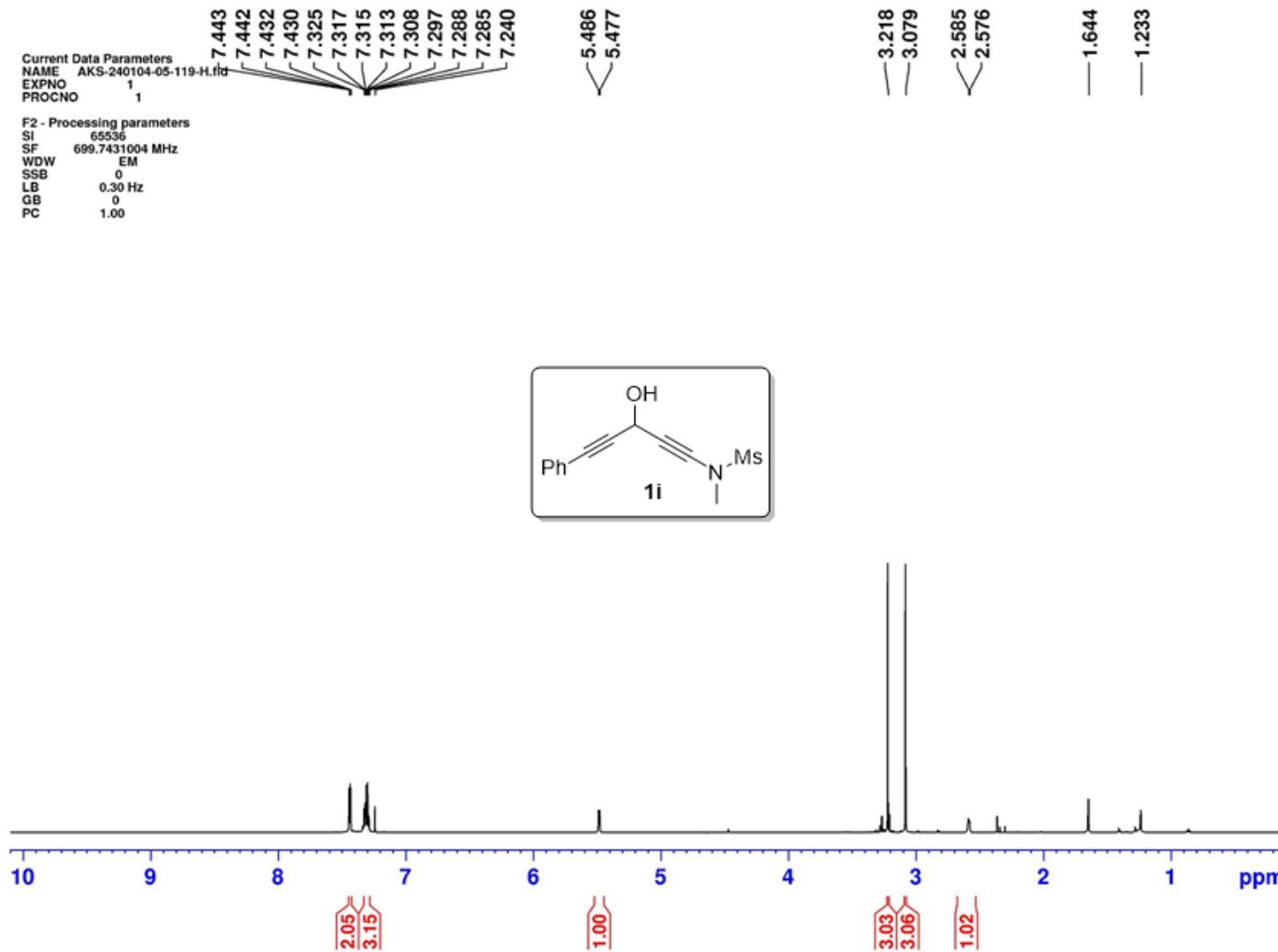
$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)

Current Data Parameters
NAME AKS-240129-05-137
EXPNO 3
PROCNO 1

F2 - Processing parameters
SI 131072
SF 175.9505417 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



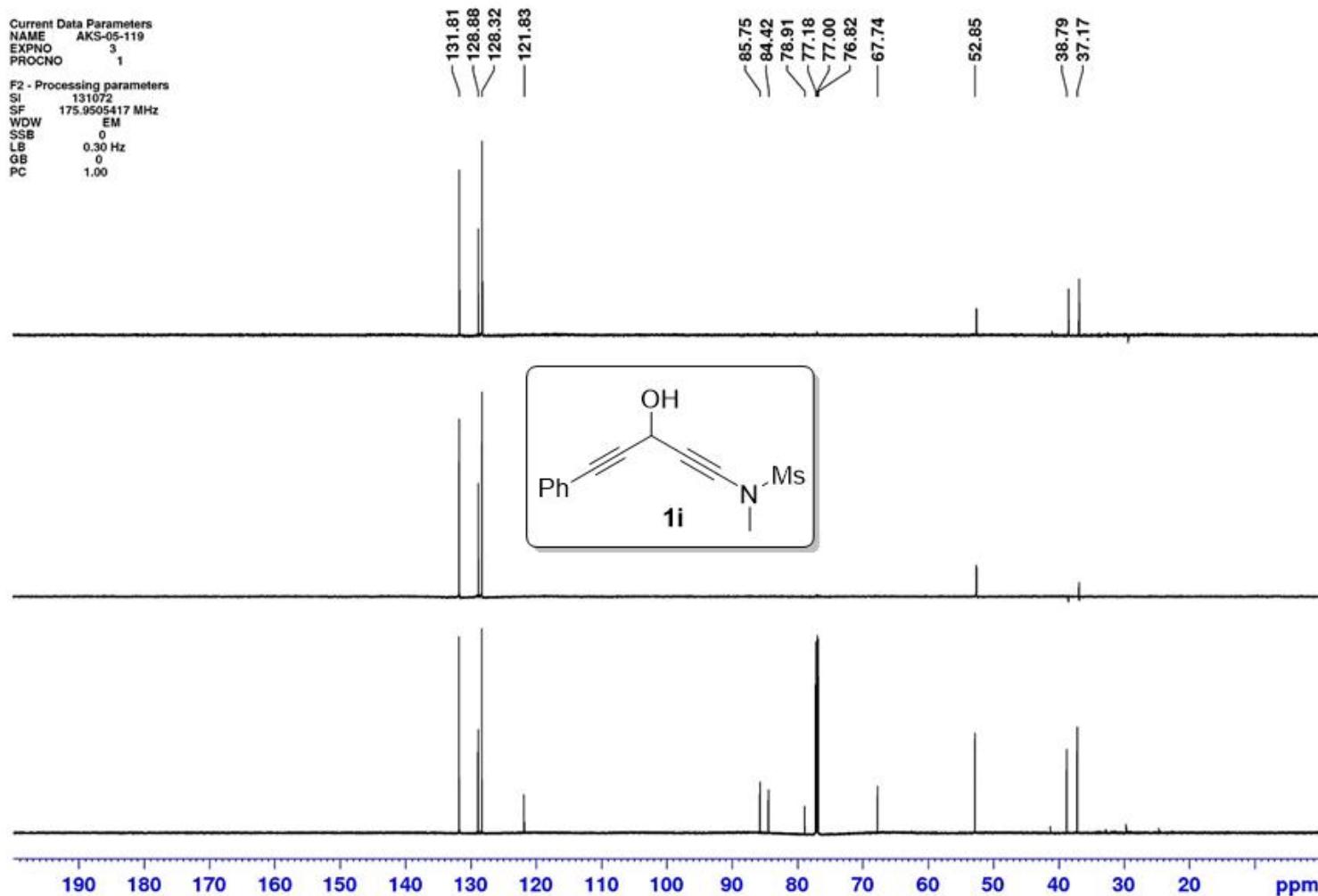
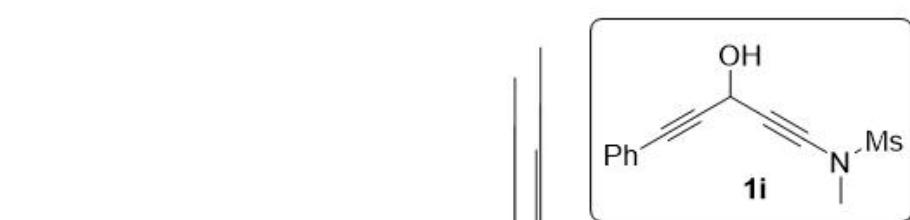
¹H NMR (CDCl₃, 700 MHz)



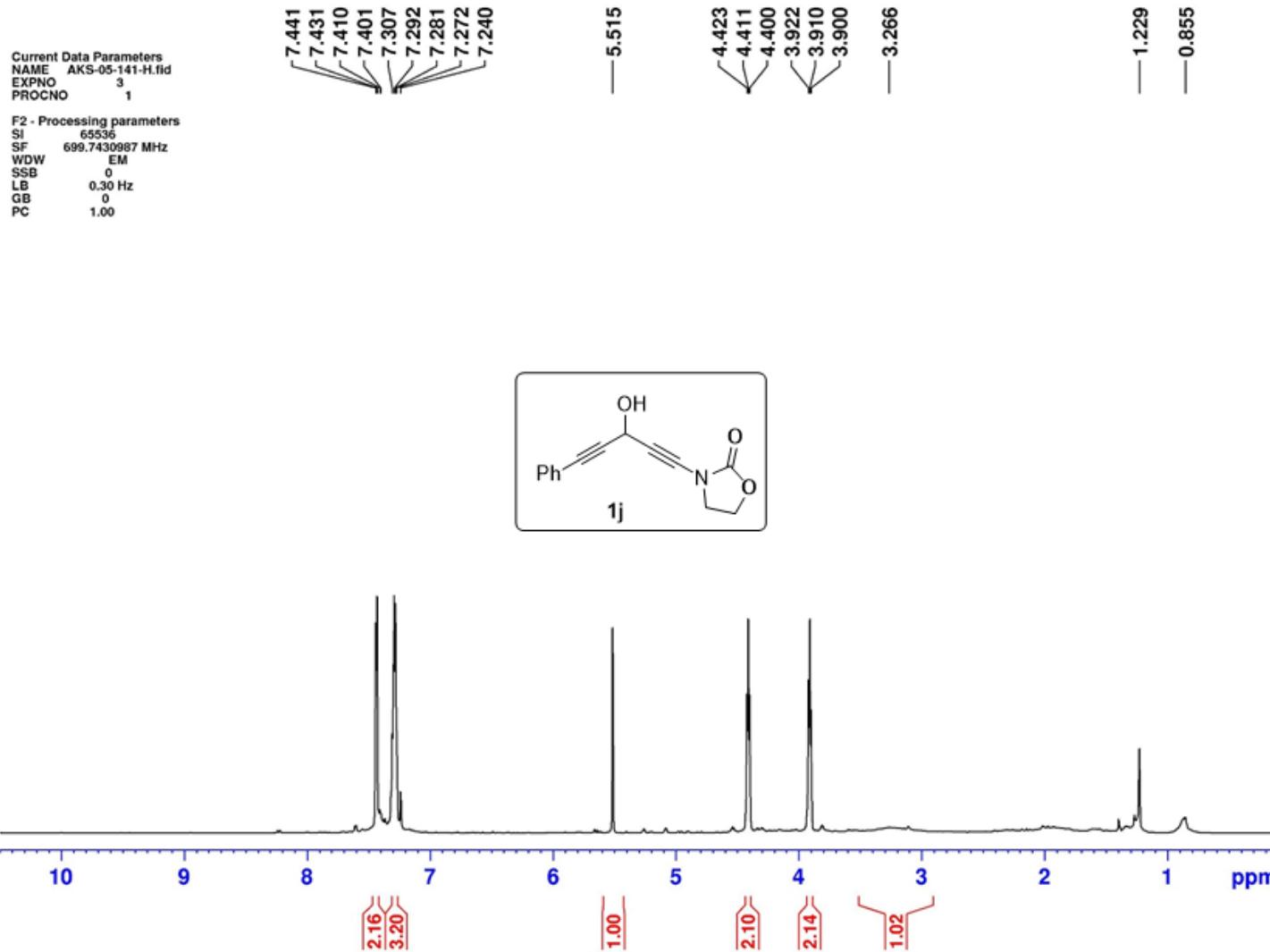
$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)

Current Data Parameters
NAME AKS-05-119
EXPNO 3
PROCNO 1

F2 - Processing parameters
SI 131072
SF 175.9505417 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



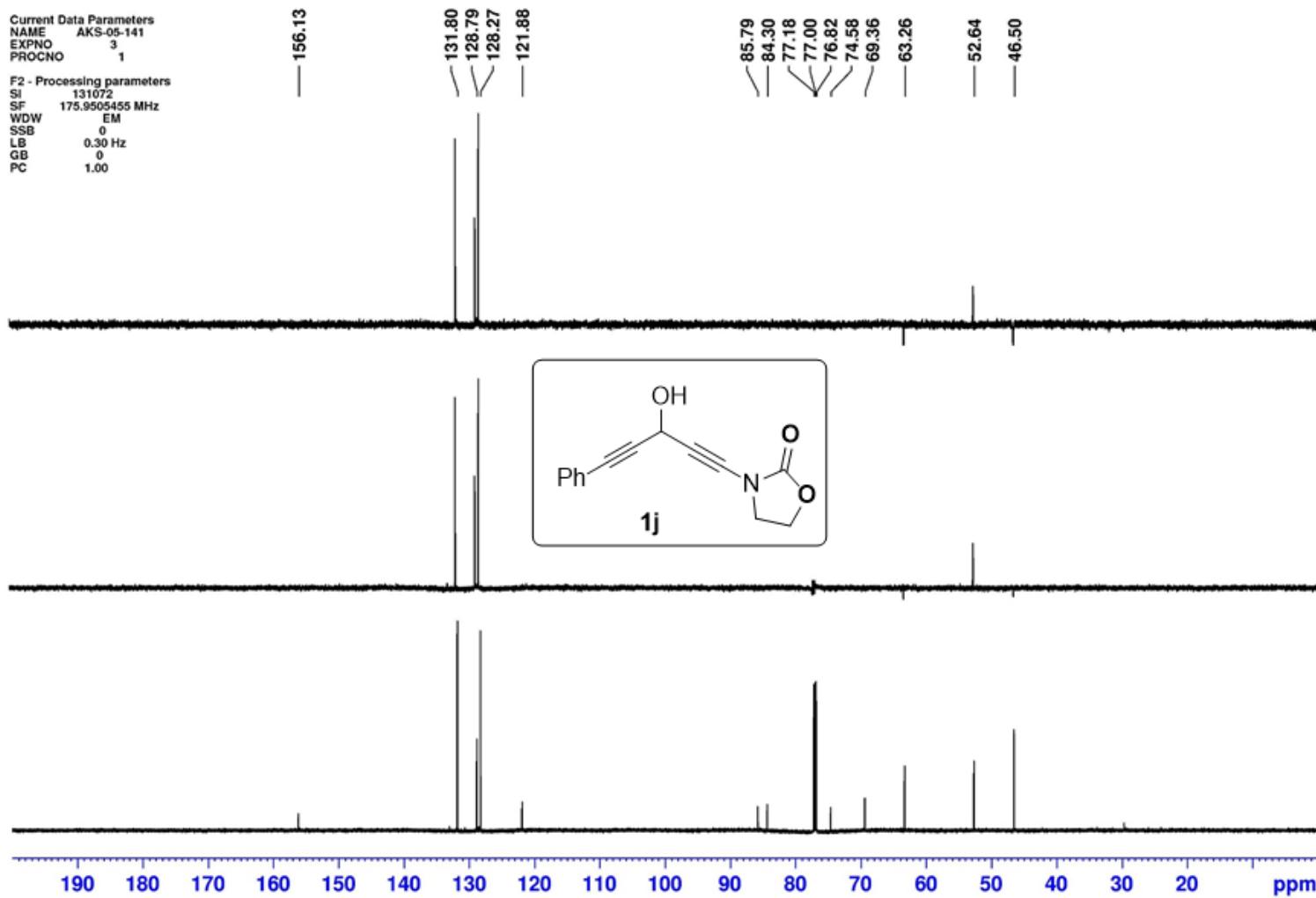
¹H NMR (CDCl₃, 700 MHz)



$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)

Current Data Parameters
NAME AKS-05-141
EXPNO 3
PROCNO 1

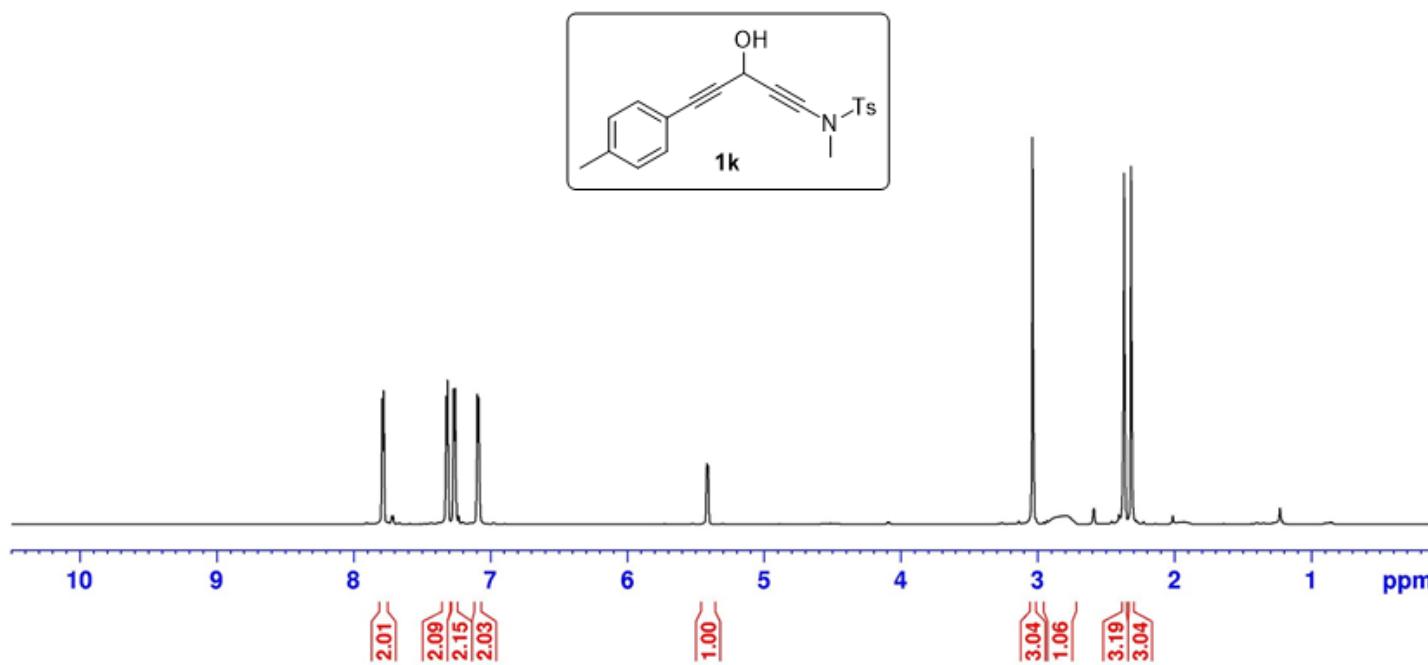
F2 - Processing parameters
SI 131072
SF 175.9505455 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



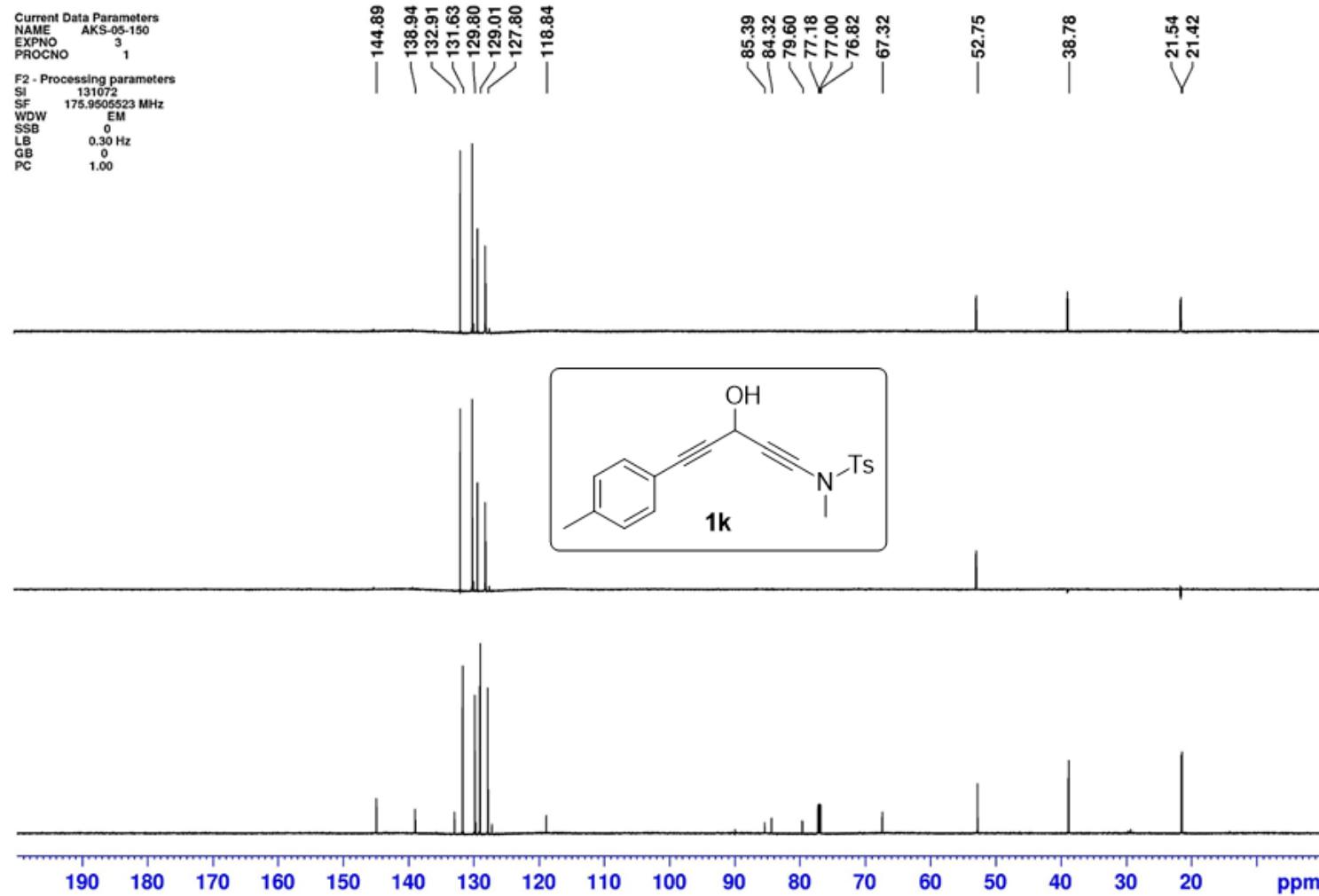
¹H NMR (CDCl₃, 700 MHz)

Current Data Parameters
NAME AKS-05-150
EXPNO 1
PROCNO 1

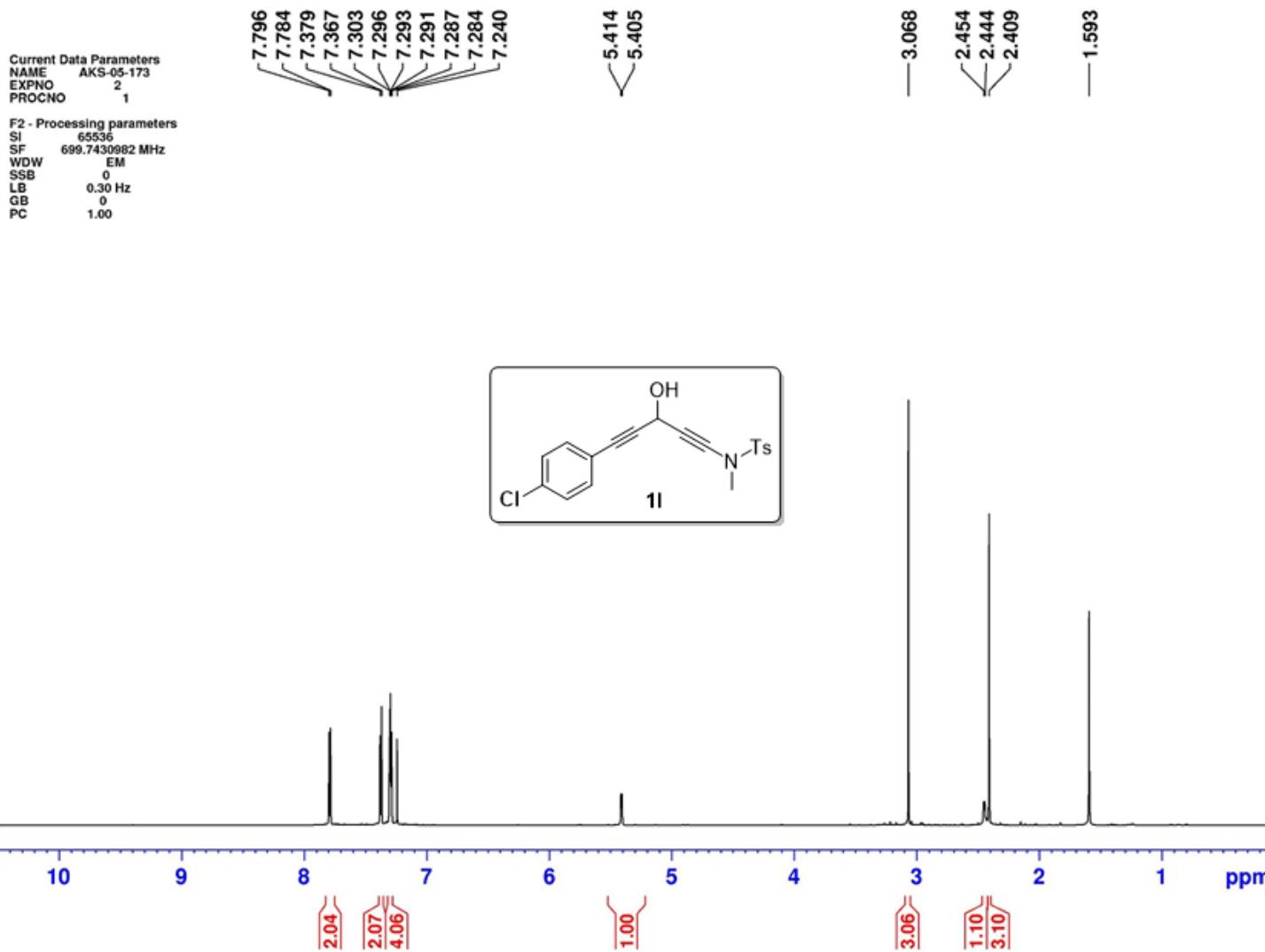
F2 - Processing parameters
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SF 699.7431004 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



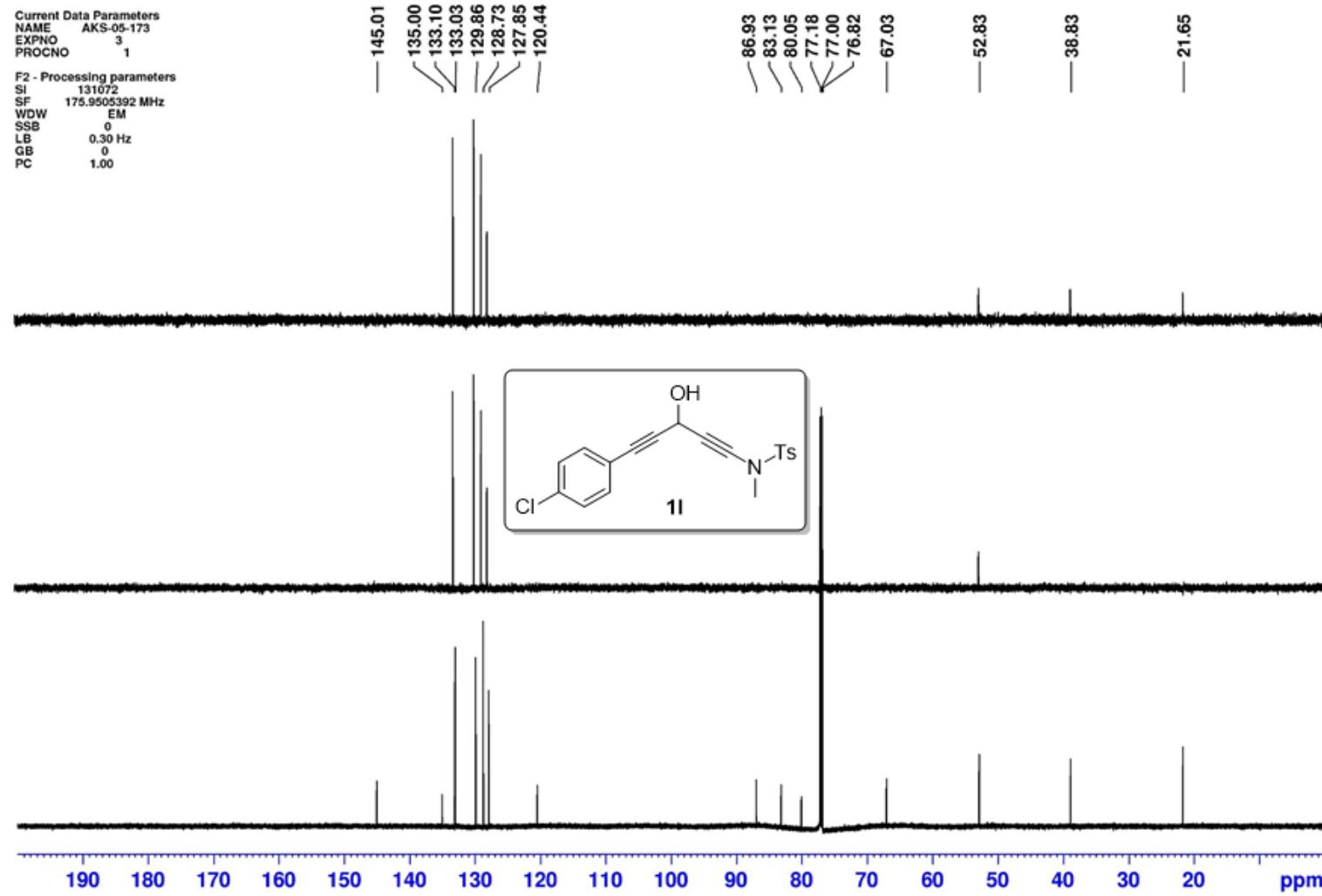
$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



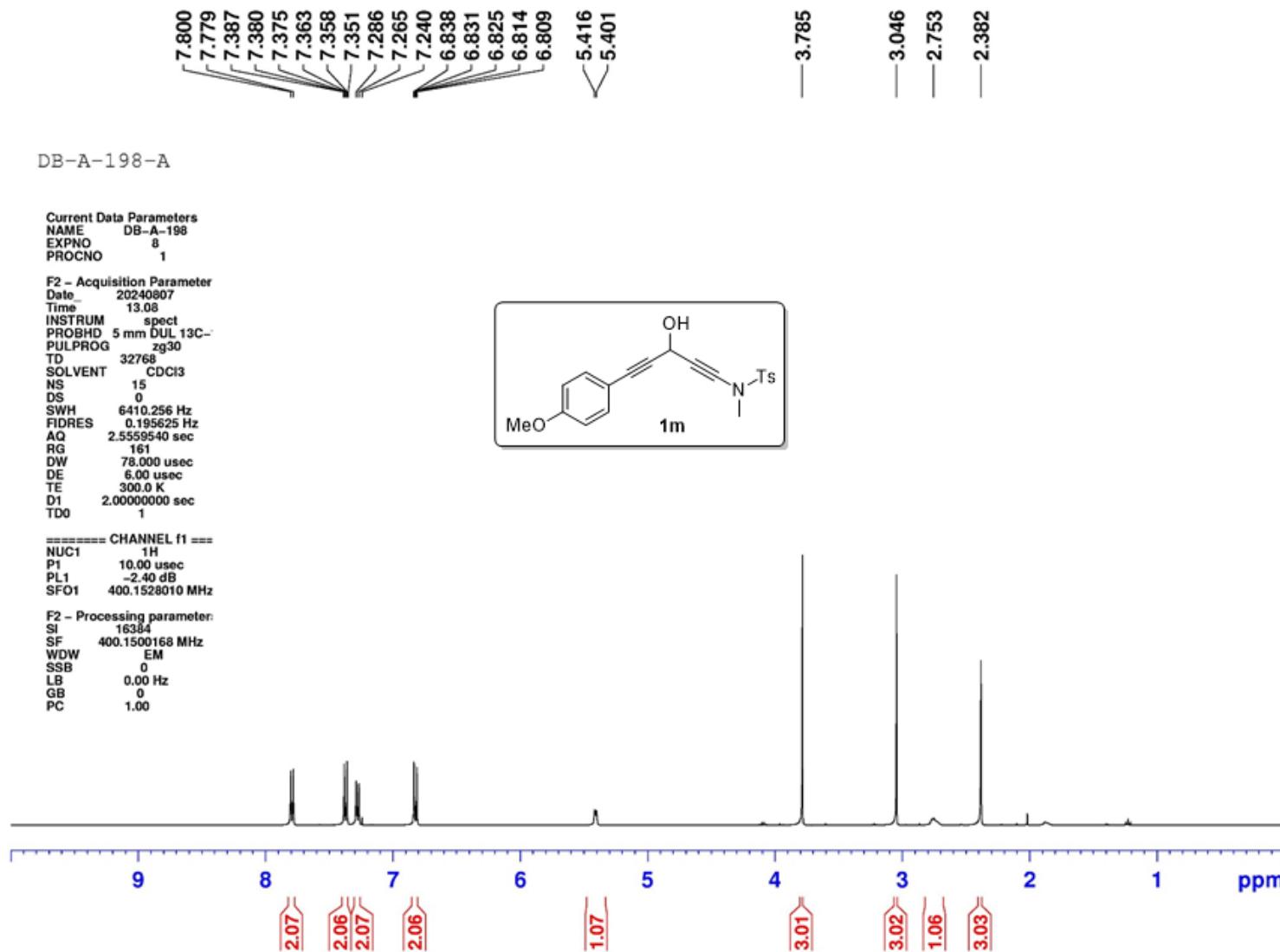
¹H NMR (CDCl₃, 700 MHz)



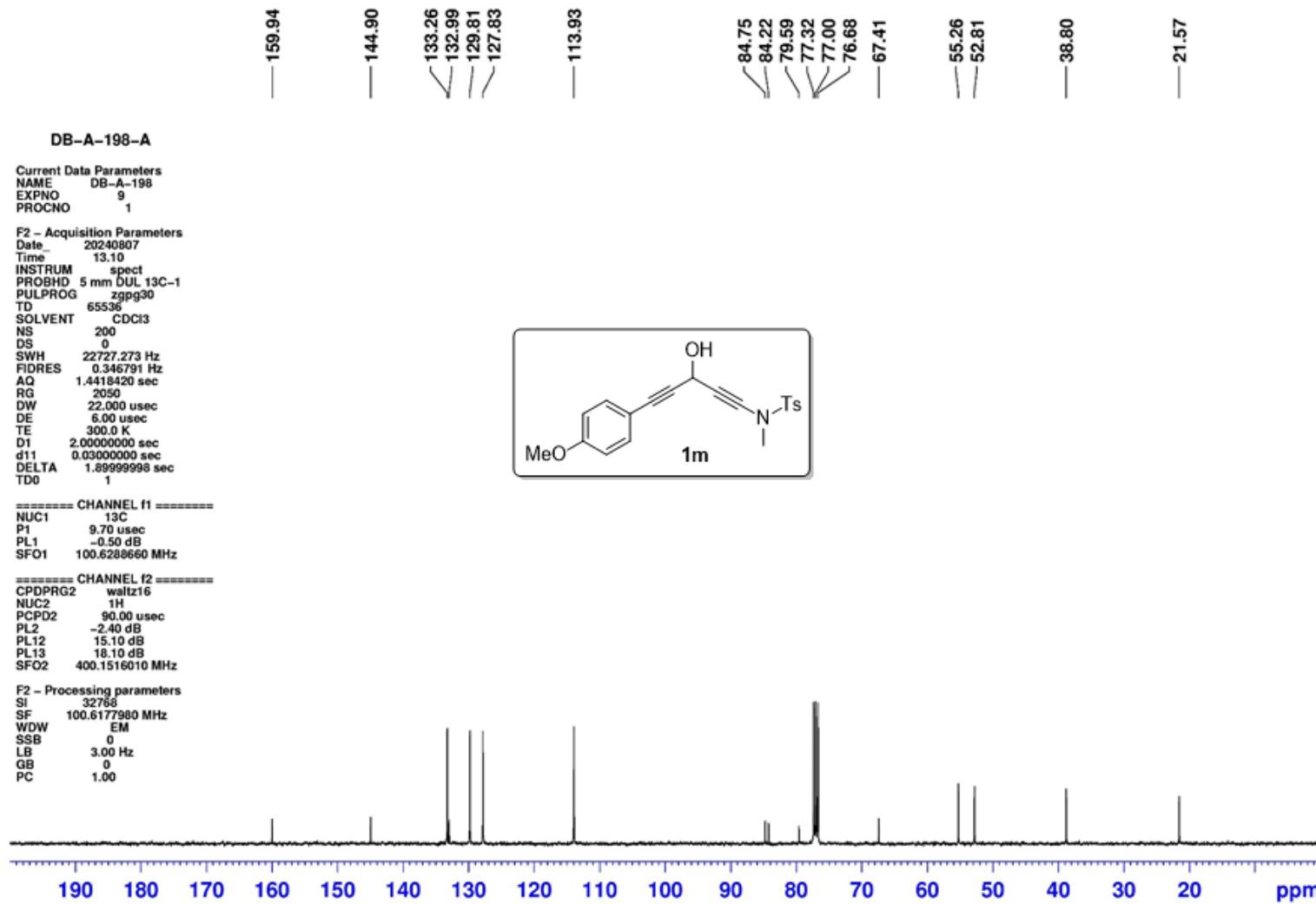
$^{13}\text{C}\{\text{1H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



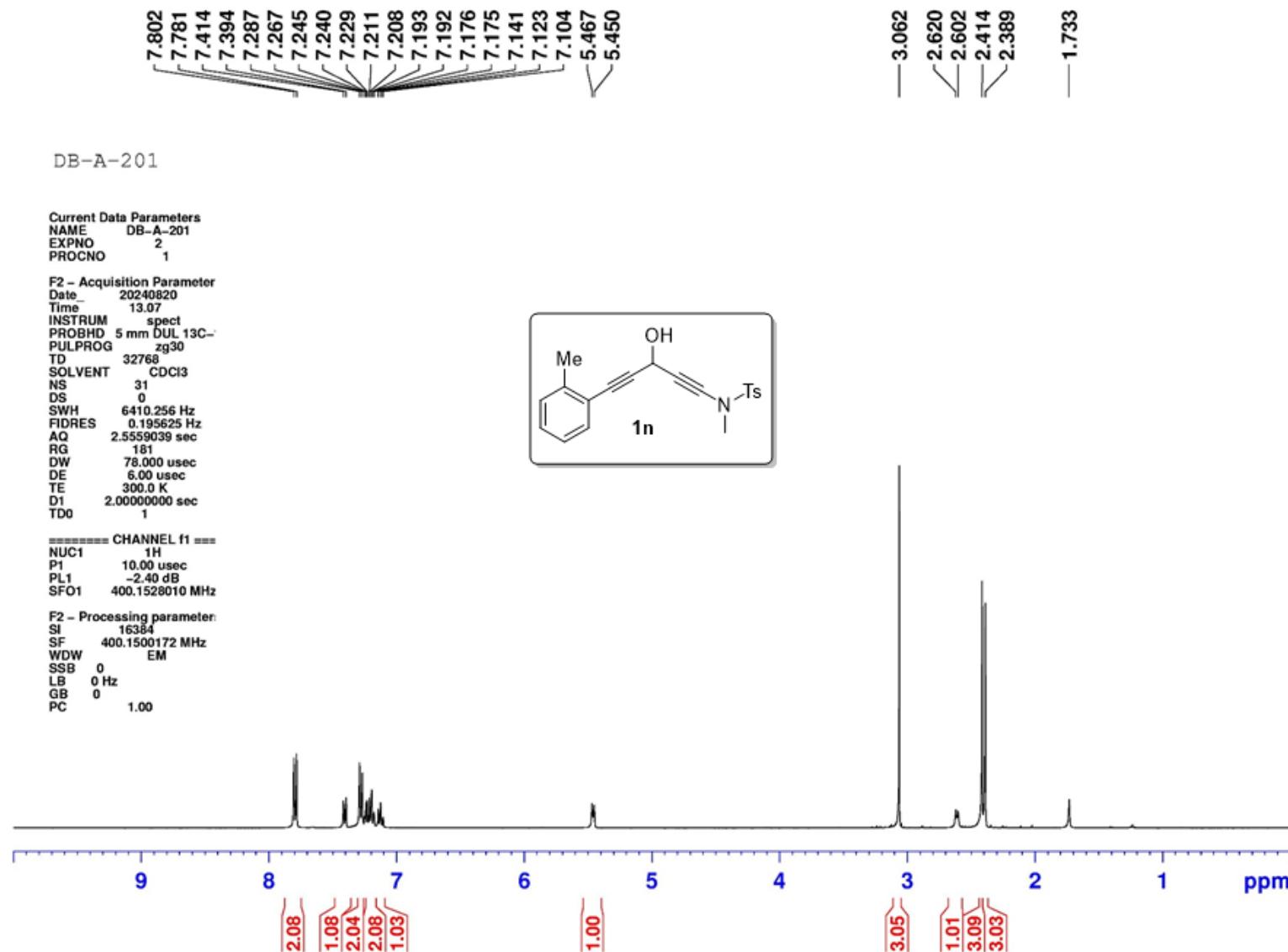
¹H NMR (CDCl₃, 400 MHz)



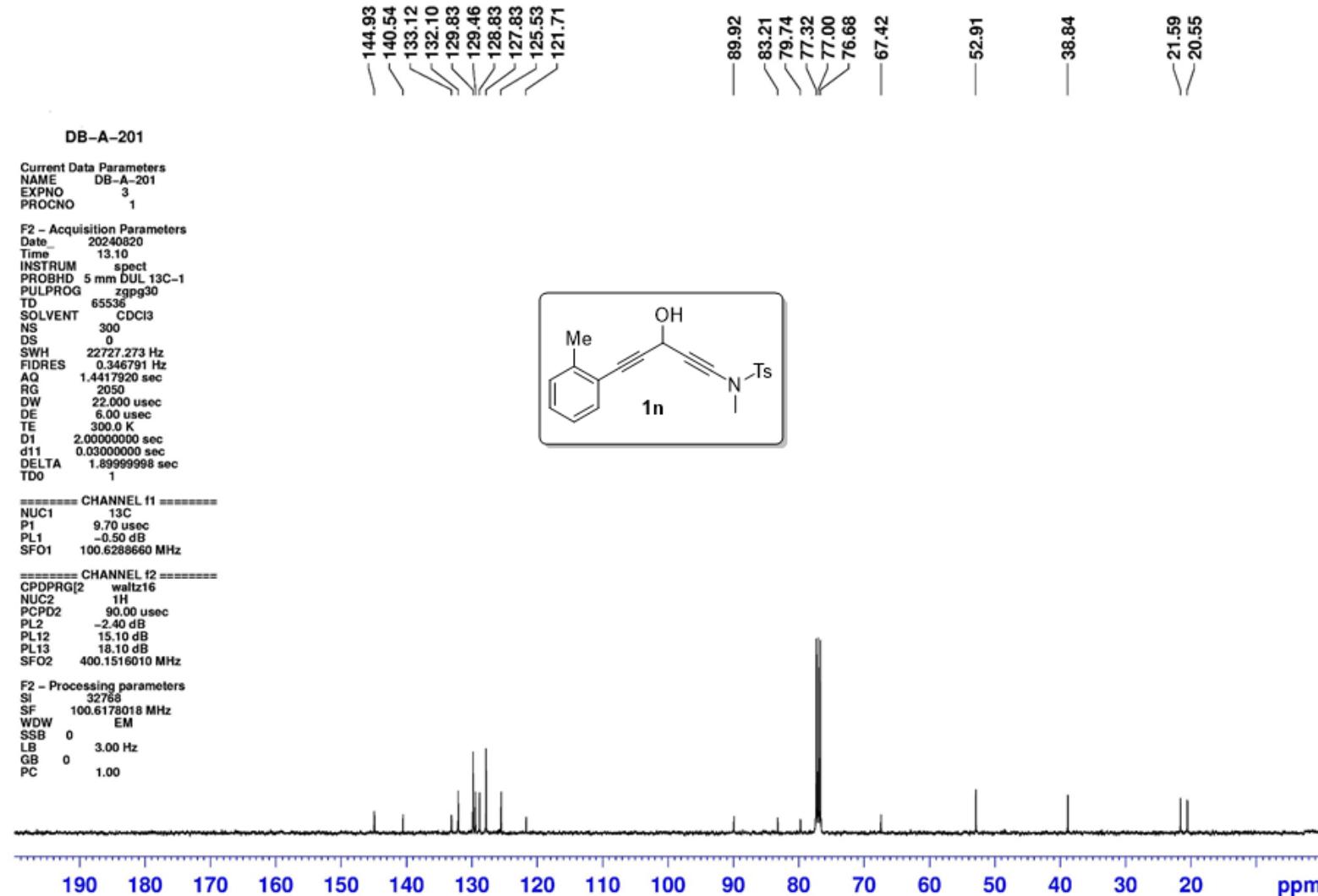
¹³C{¹H} NMR (CDCl₃, 100 MHz)



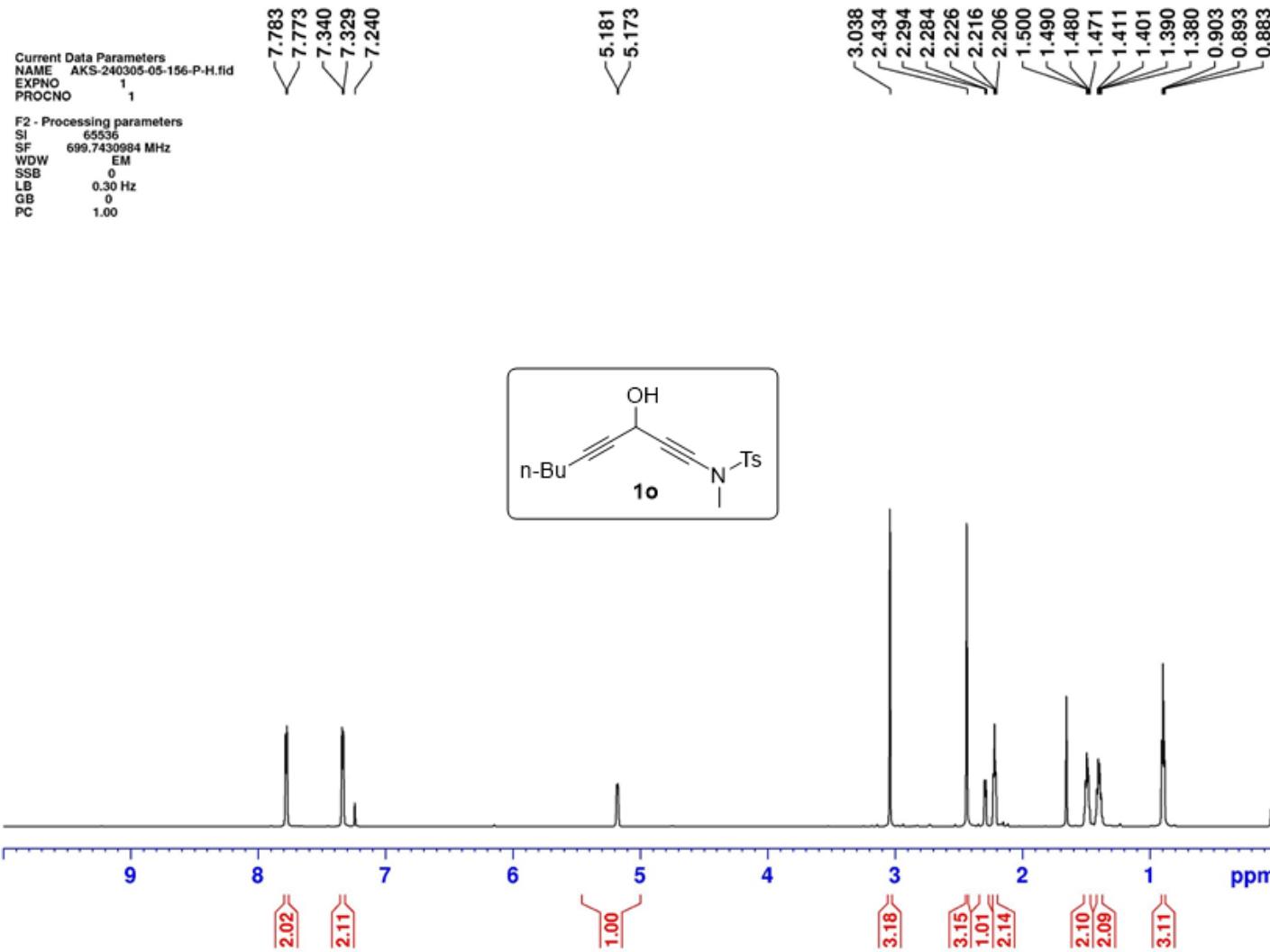
¹H NMR (CDCl₃, 400 MHz)



¹³C{¹H} NMR (CDCl₃, 100 MHz)



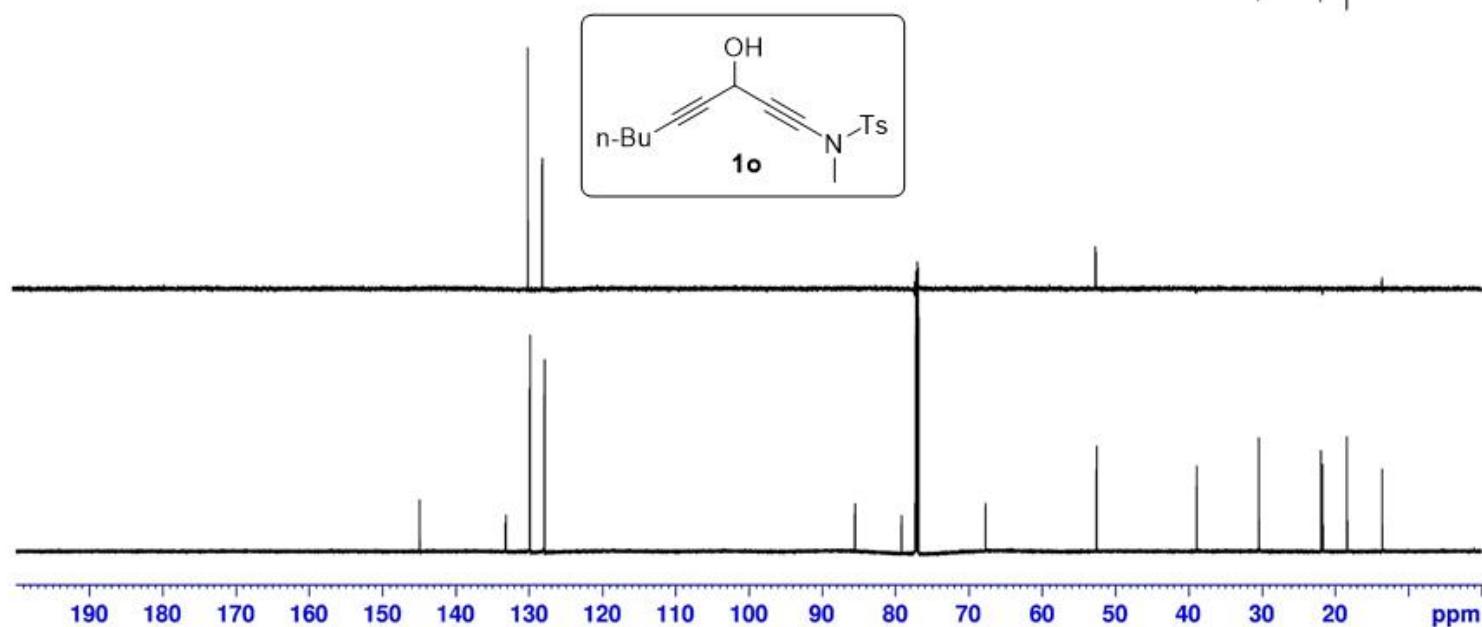
¹H NMR (CDCl₃, 700 MHz)



$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)

Current Data Parameters
NAME AKS-05-156
EXPNO 3
PROCNO 1

F2 - Processing parameters
SI 131072
SF 175.9505406 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



¹H NMR (CDCl₃, 400 MHz)

AKS-5-164

Current Data Parameters
NAME AKS-5-164
EXPNO 9
PROCNO 1

F2 – Acquisition Parameters

Date 20240321

Time 22.56

INSTRUM spect

PROBHD 5 mm DUL, 13C-1

PULPROG zg30

TD 32768

SOLVENT CDCl₃

NS 12

DS 0

SWH 6410.256 Hz

EDRRES 0.195625 Hz

AQ 2.5559540 sec

RG 406

DW 78.000 usec

DE 6.00 usec

TE 300.0 K

DI 2.0000000 sec

TDO 1

===== CHANNEL f1 =====

NUC1 1H

P1 10.00 usec

PL1 -2.40 dB

SFO1 400.1528010 MHz

F2 – Processing parameters

SI 16384

SF 400.1500168 MHz

WDW EM

SSB 0

LB 0.00 Hz

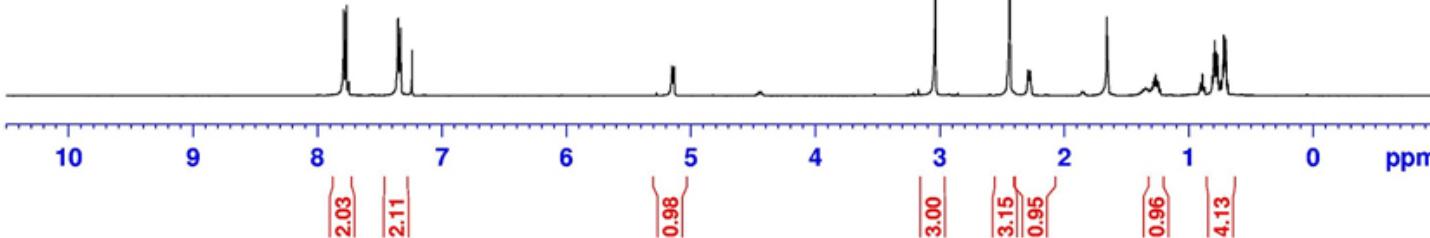
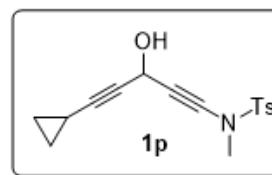
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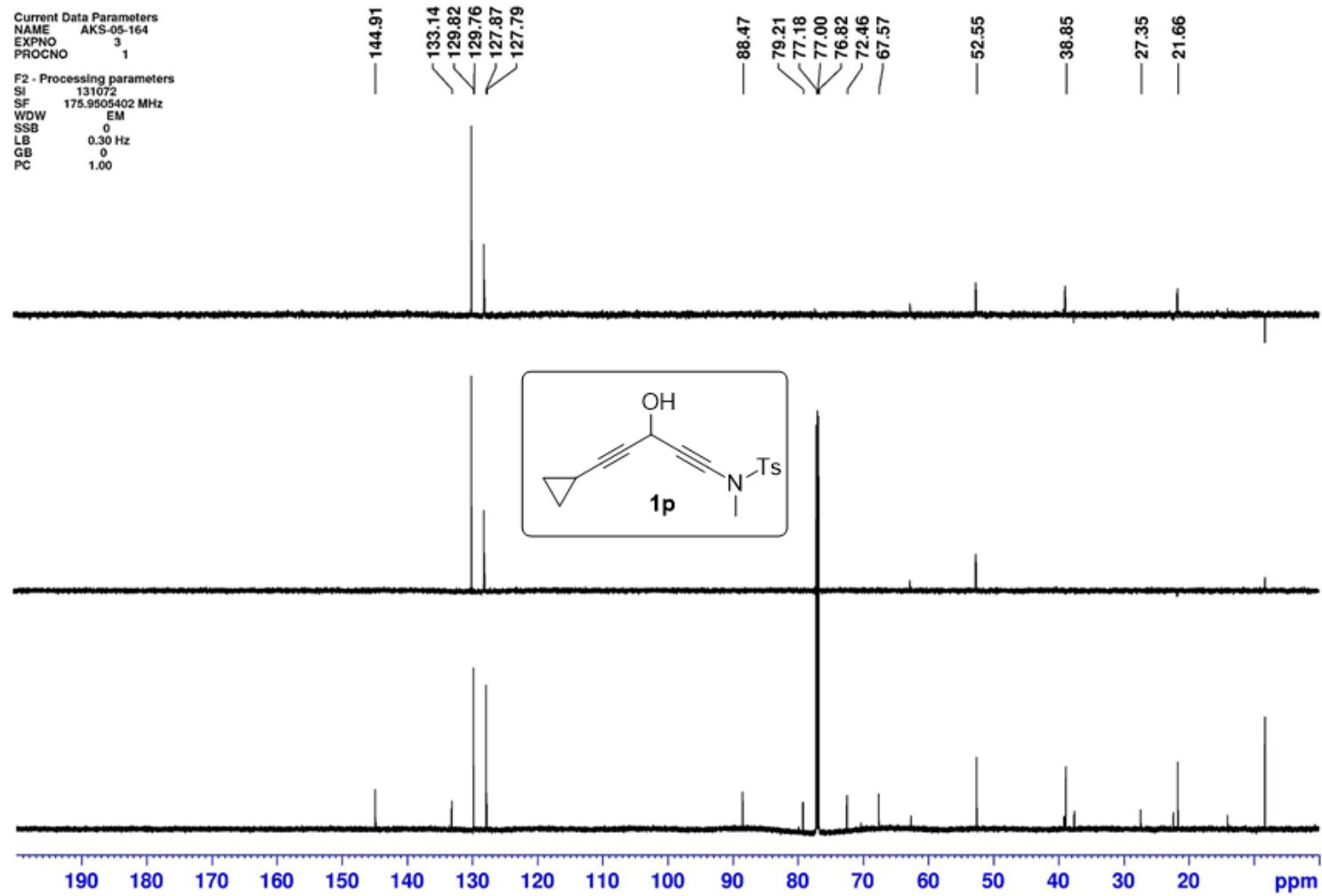
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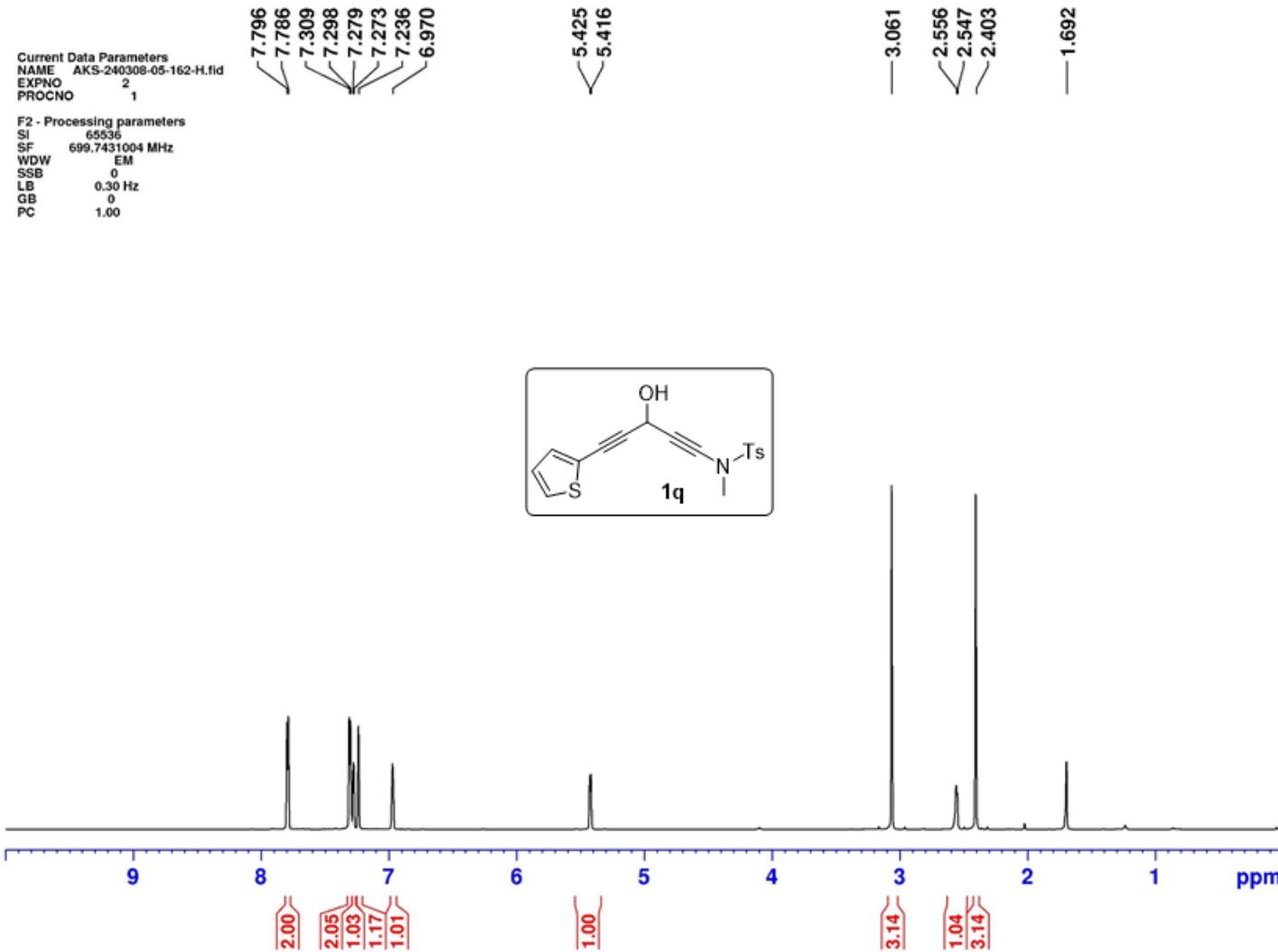
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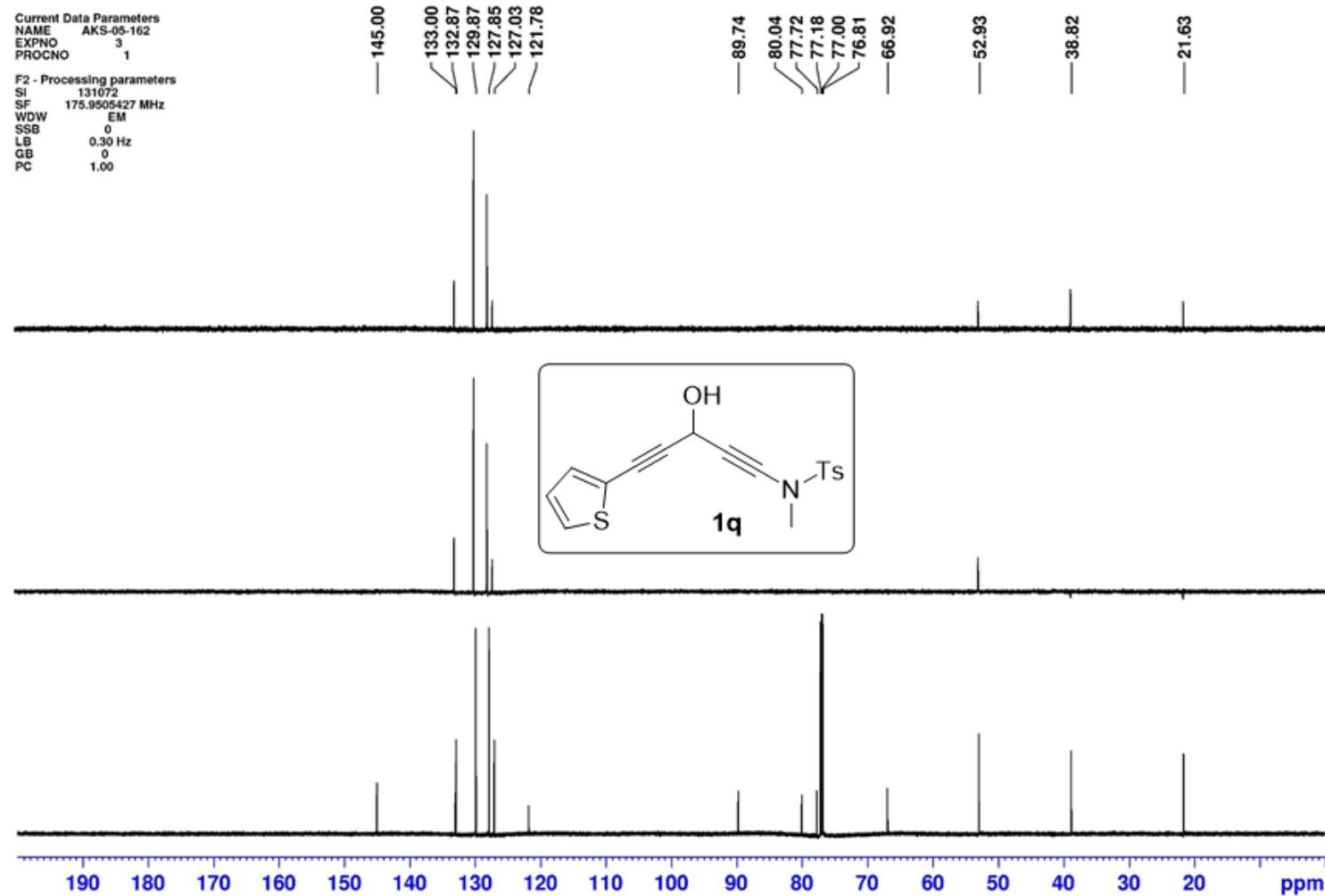
$^{13}\text{C}\{1\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



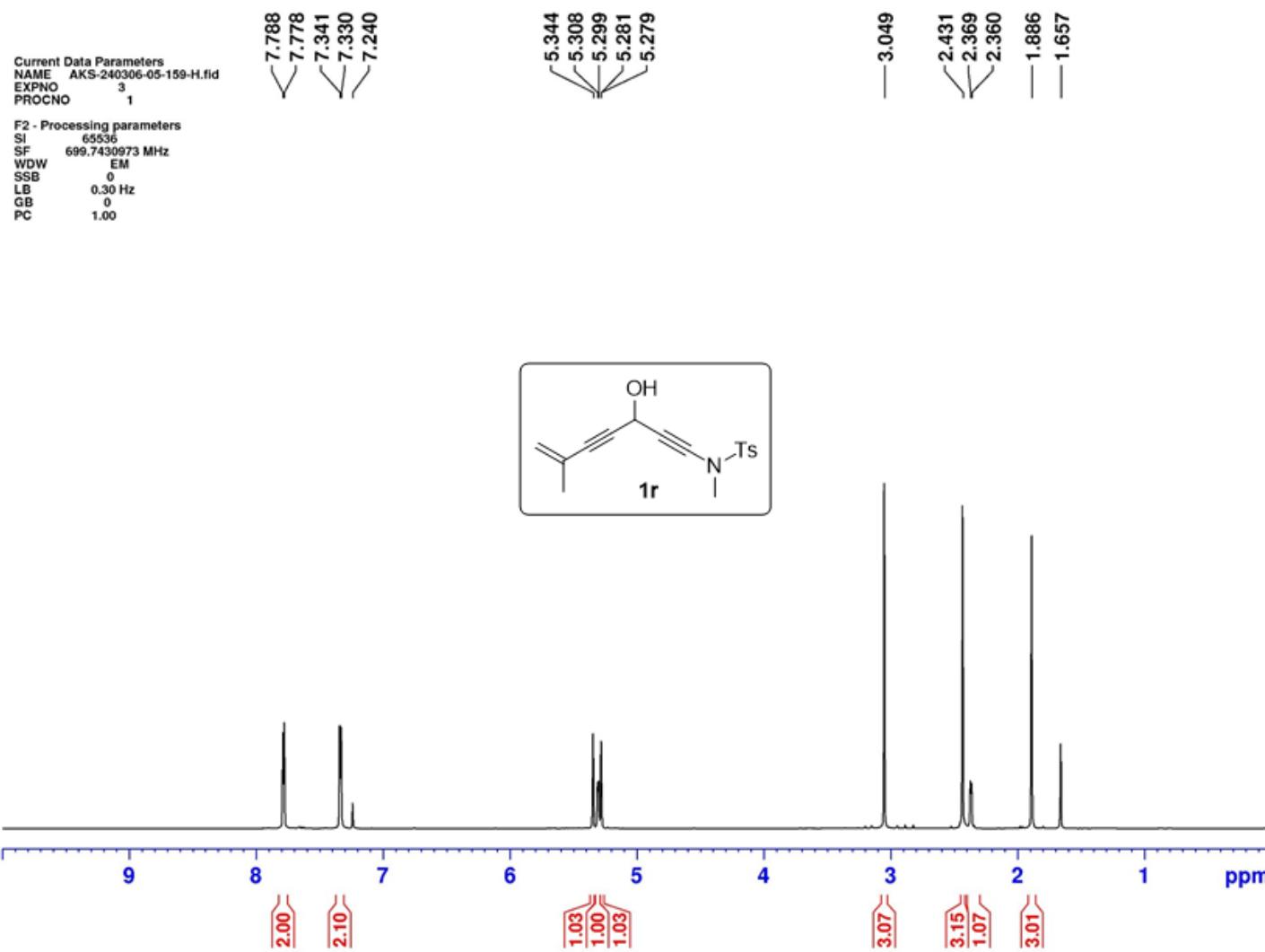
¹H NMR (CDCl₃, 700 MHz)



$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



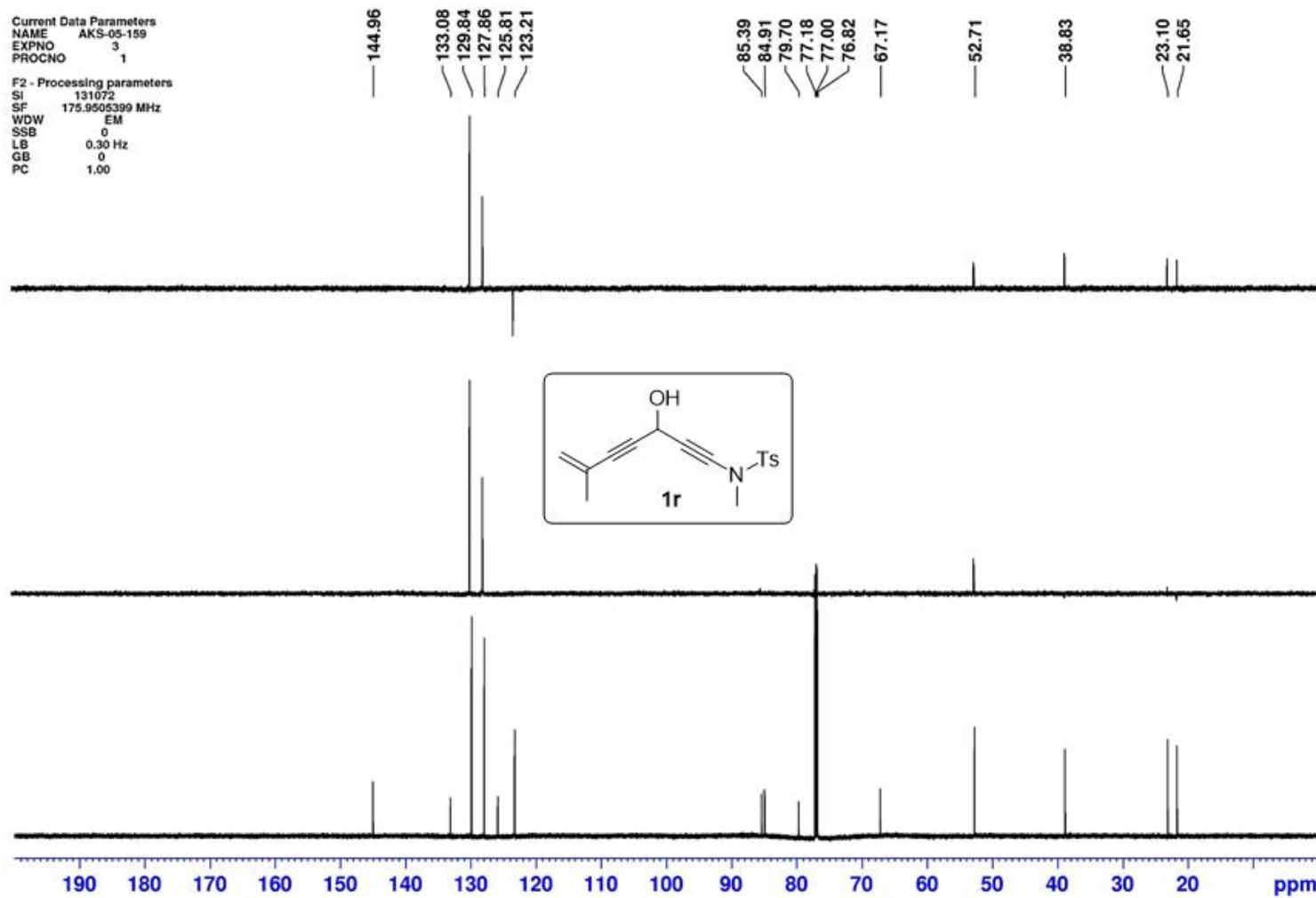
¹H NMR (CDCl₃, 700 MHz)



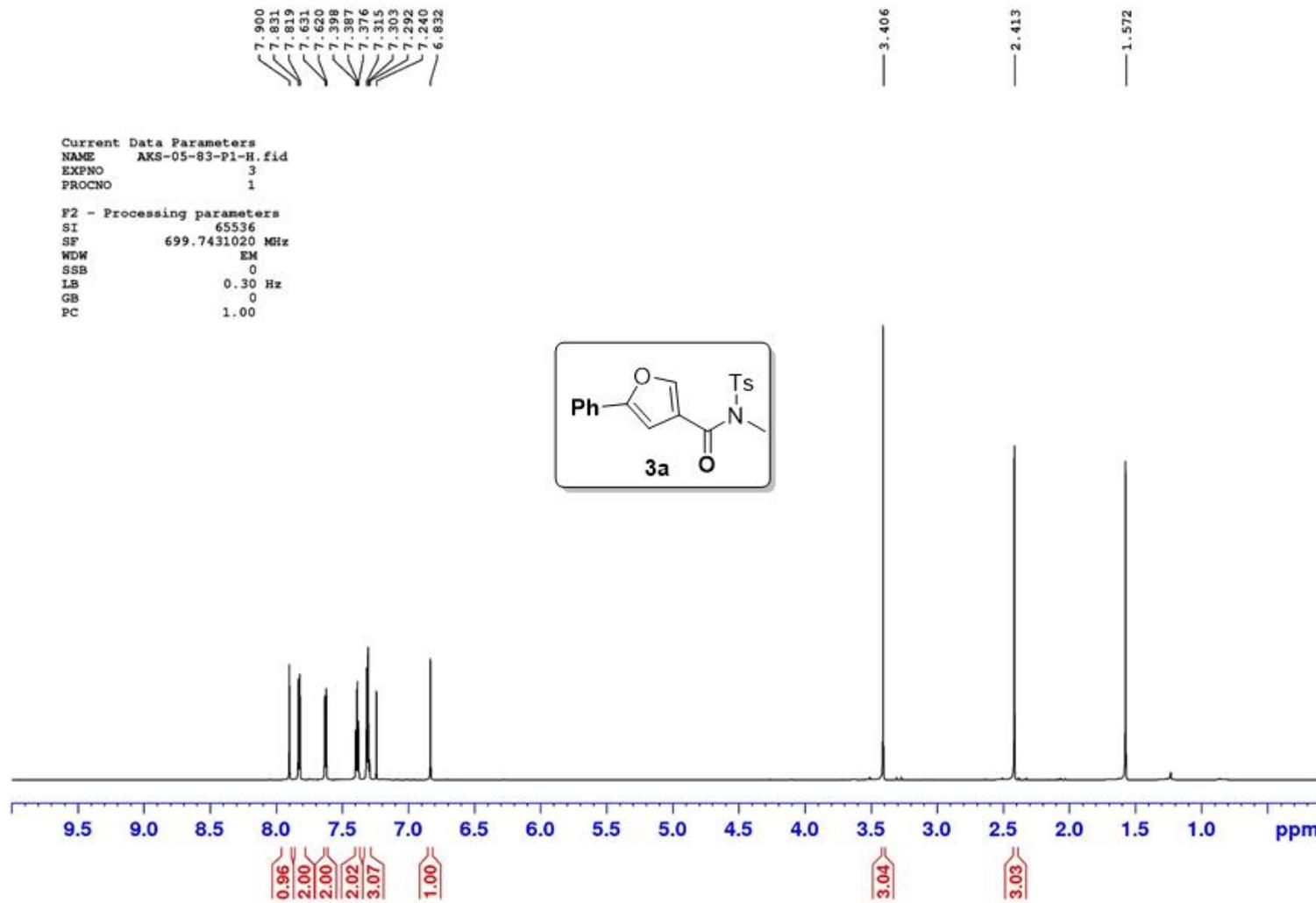
$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)

Current Data Parameters
NAME AKS-05-159
EXPNO 3
PROCNO 1

F2 - Processing parameters
SI 131072
SF 175.9505399 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



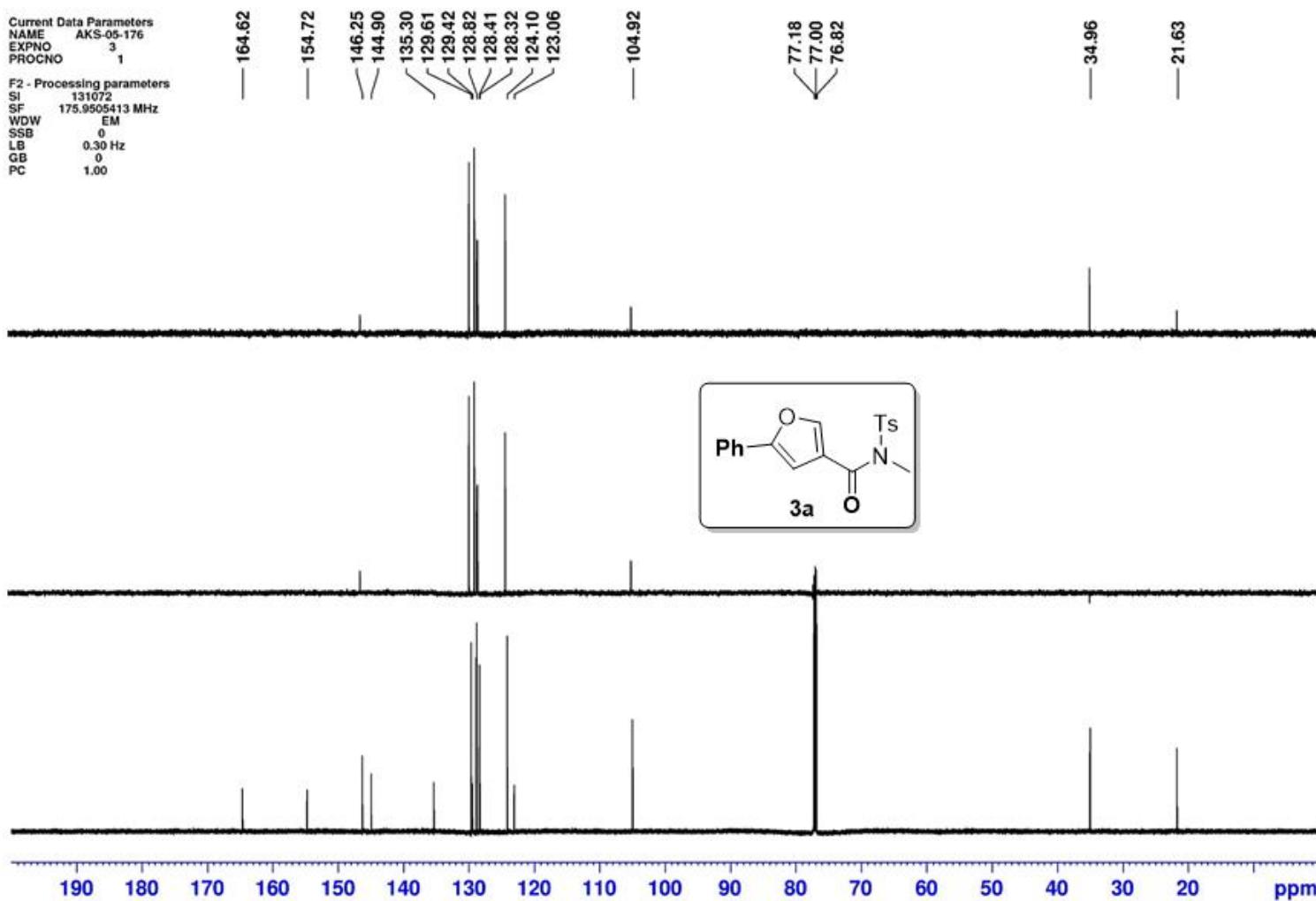
¹H NMR (CDCl₃, 700 MHz)



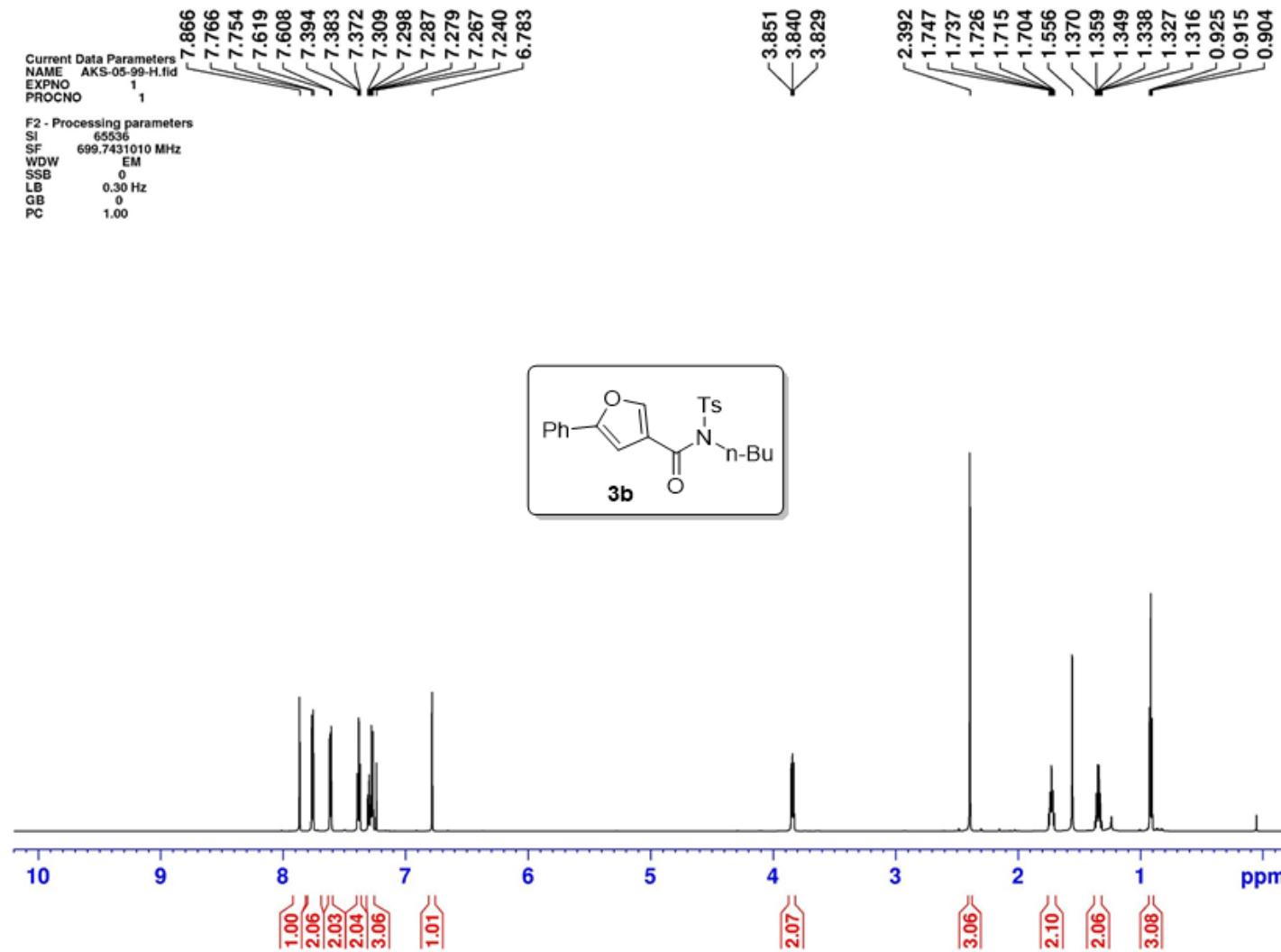
$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)

Current Data Parameters
NAME AKS-05-176
EXPNO 3
PROCNO 1

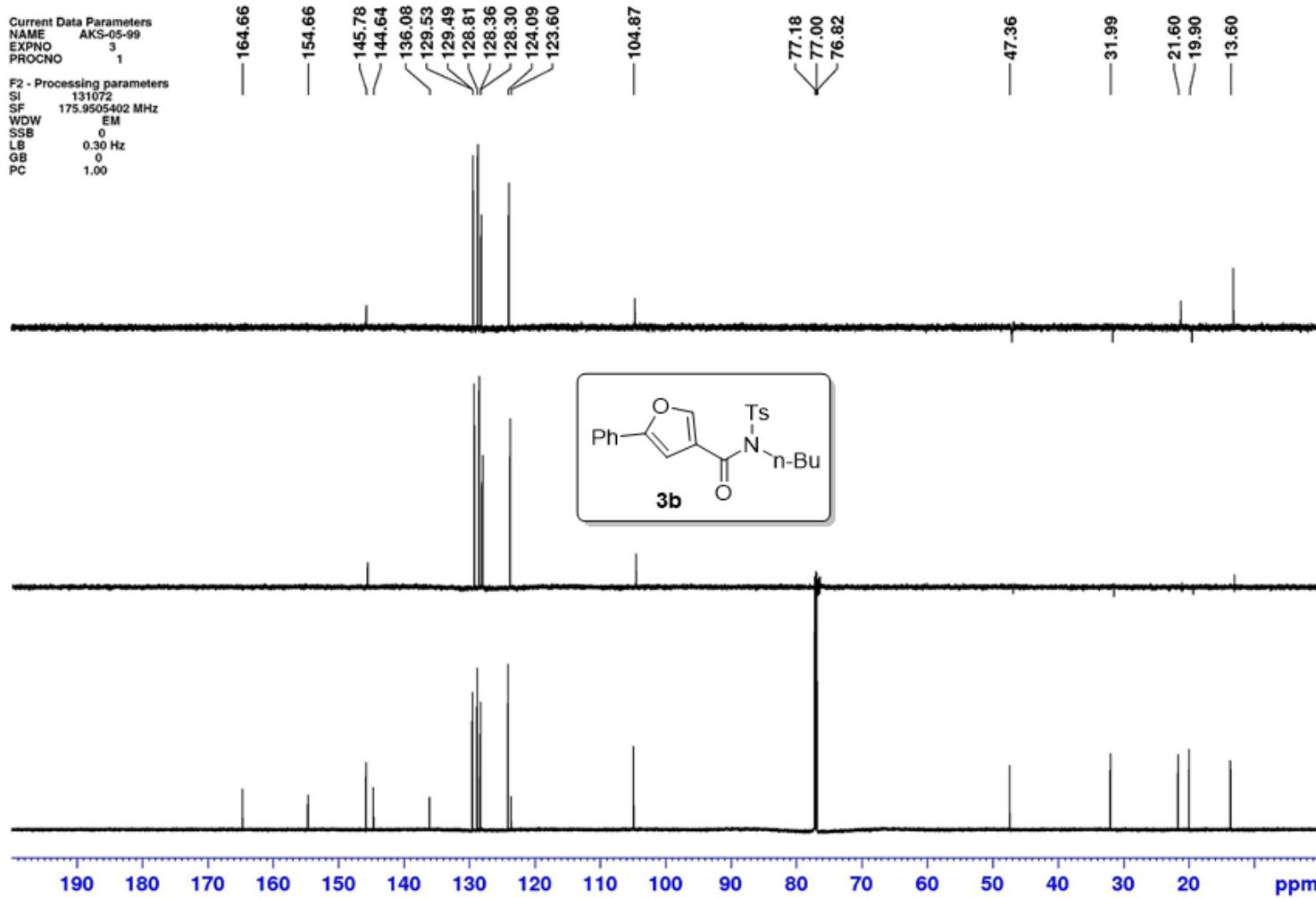
F2 - Processing parameters
SI 131072
SF 175.9505413 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



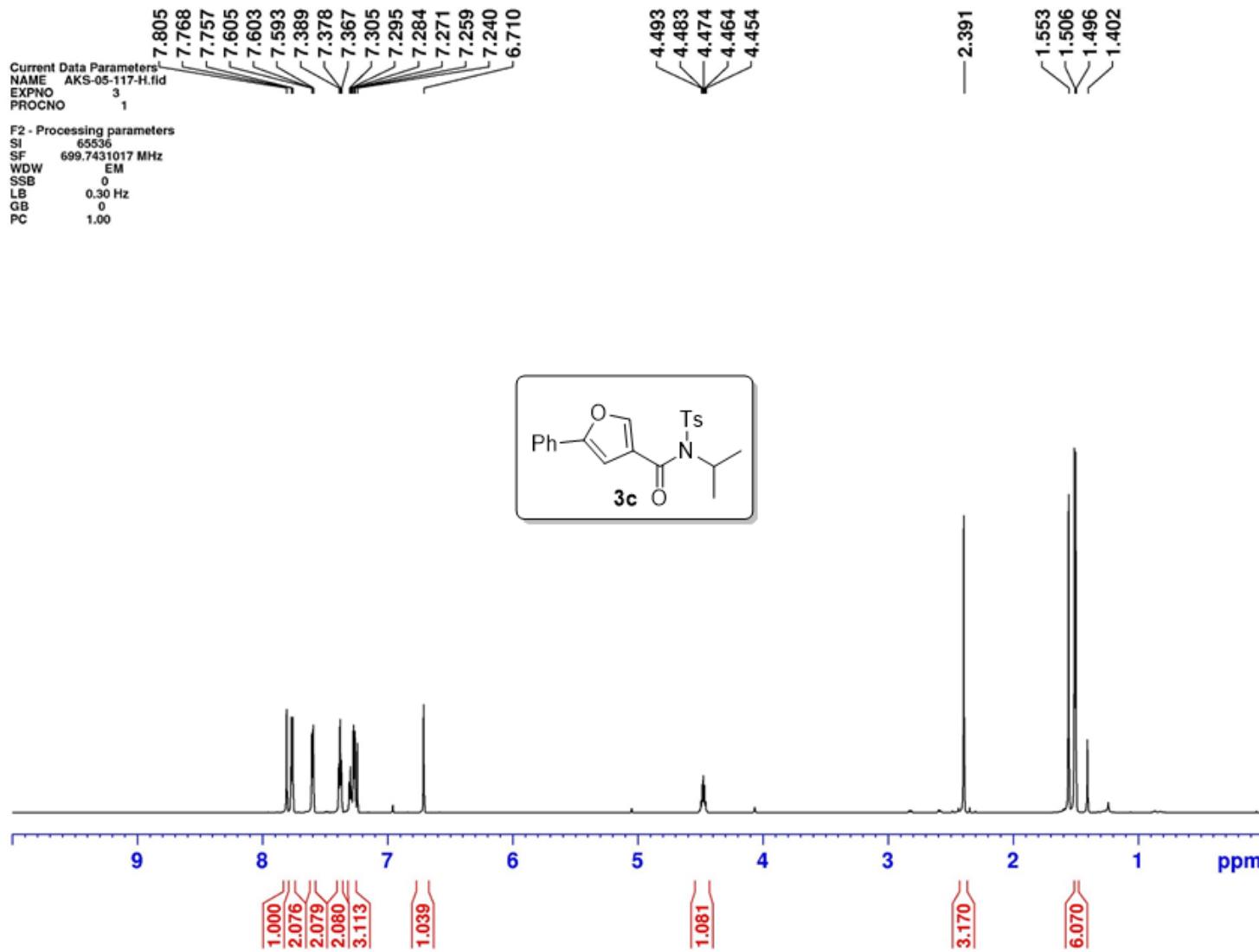
¹H NMR (CDCl₃, 700 MHz)



$^{13}\text{C}\{^1\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



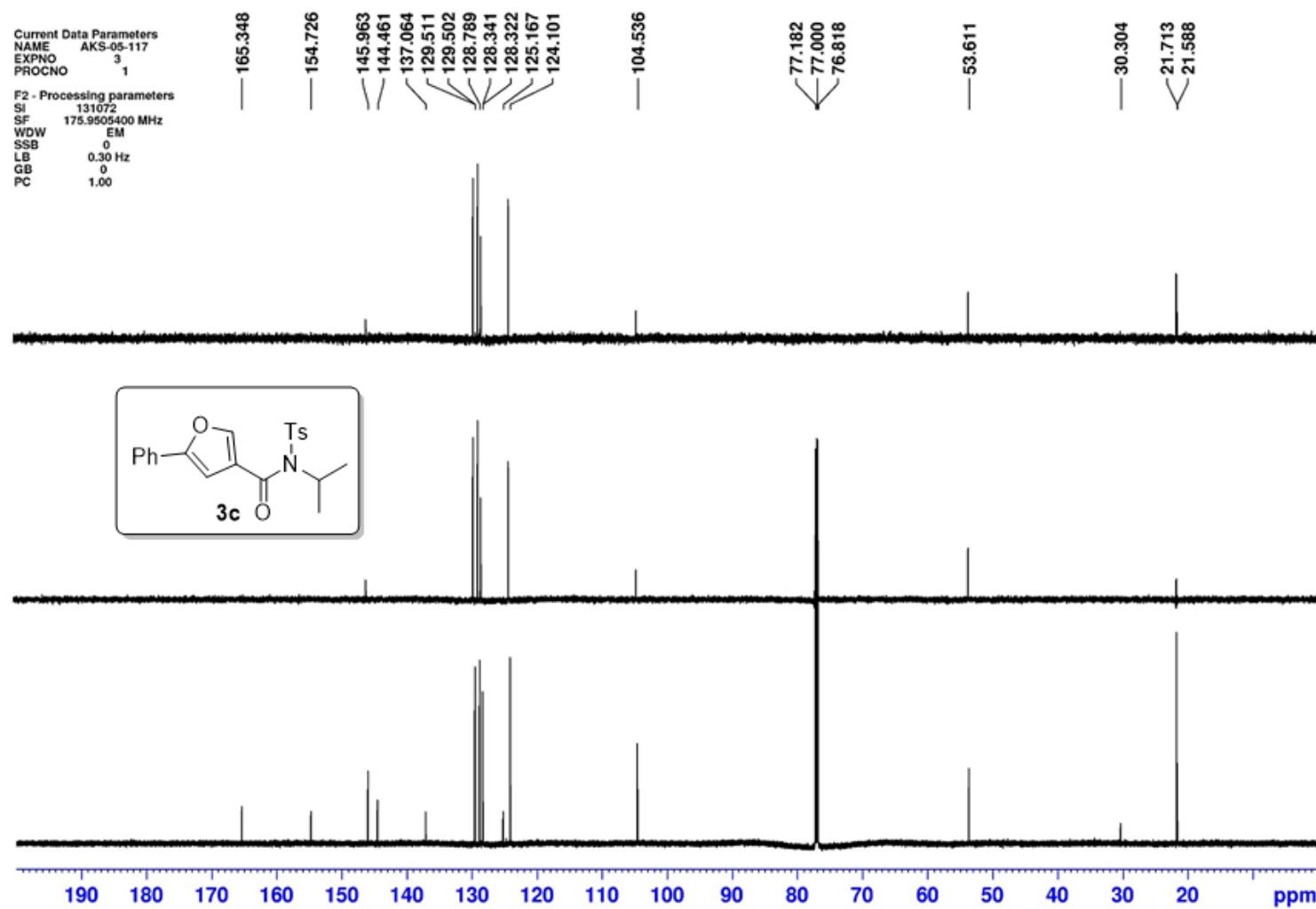
¹H NMR (CDCl₃, 700 MHz)



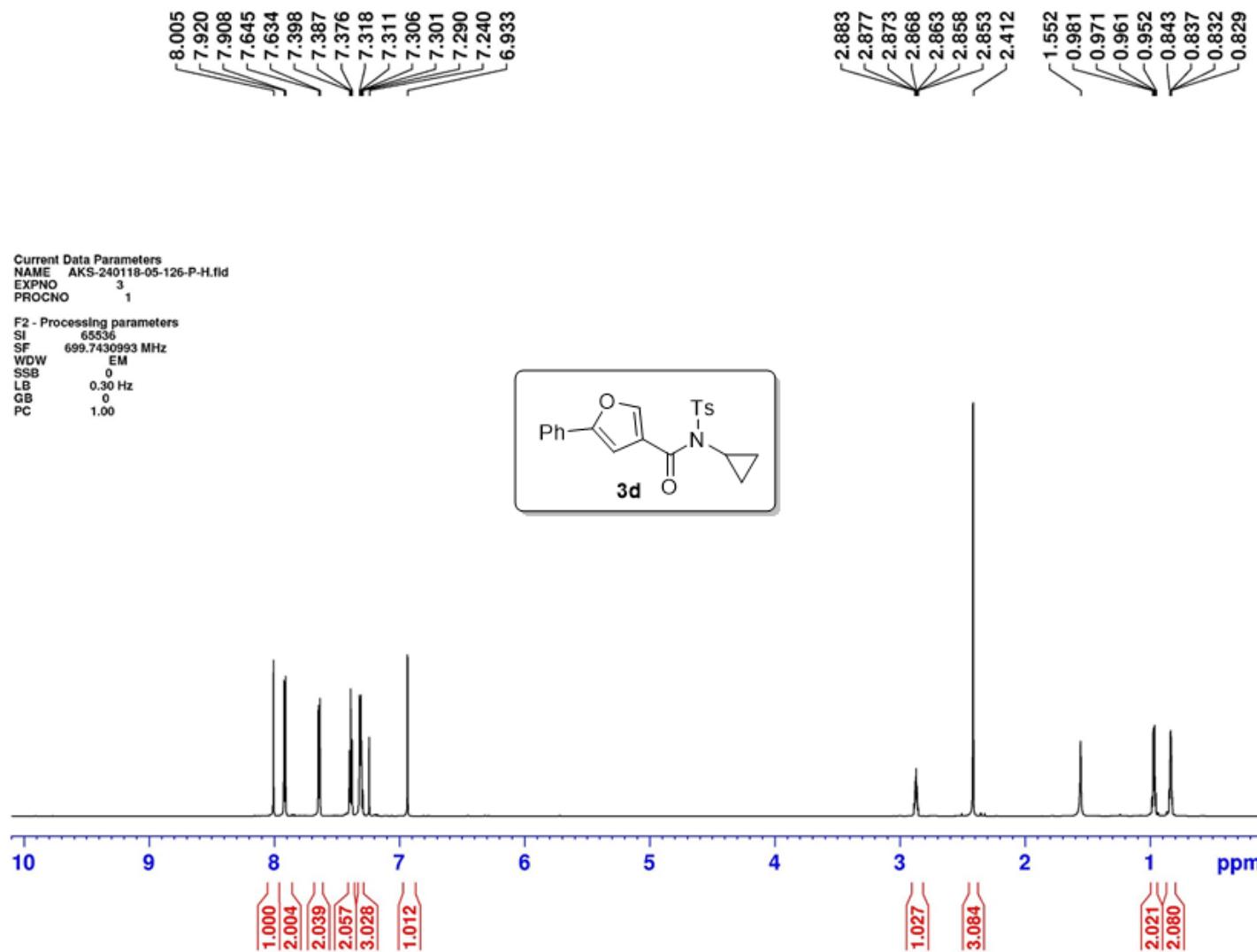
$^{13}\text{C}\{1\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)

Current Data Parameters
NAME AKS-05-117
EXPNO 3
PROCNO 1

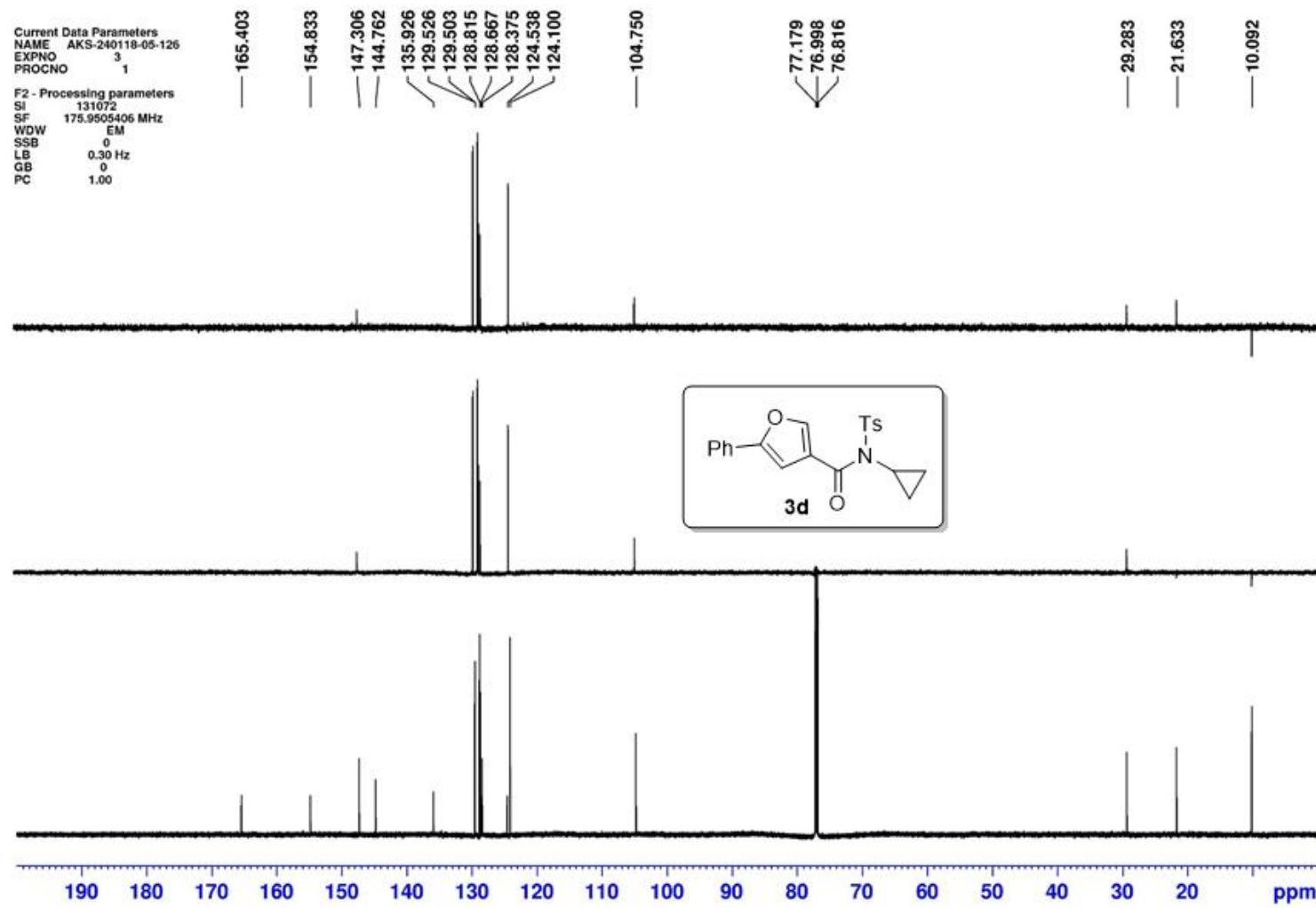
F2 - Processing parameters
SI 131072
SF 175.9505400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



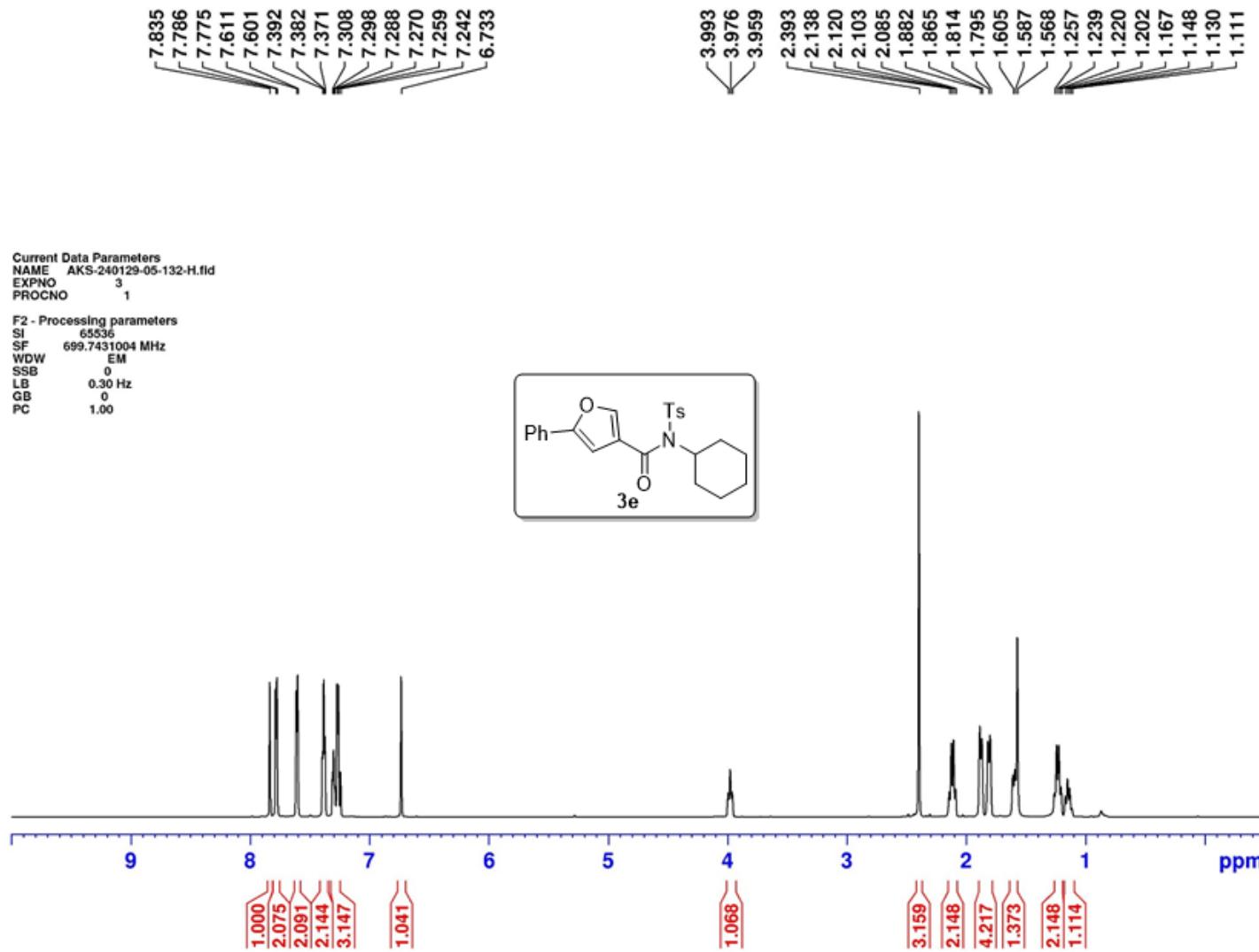
¹H NMR (CDCl₃, 700 MHz)



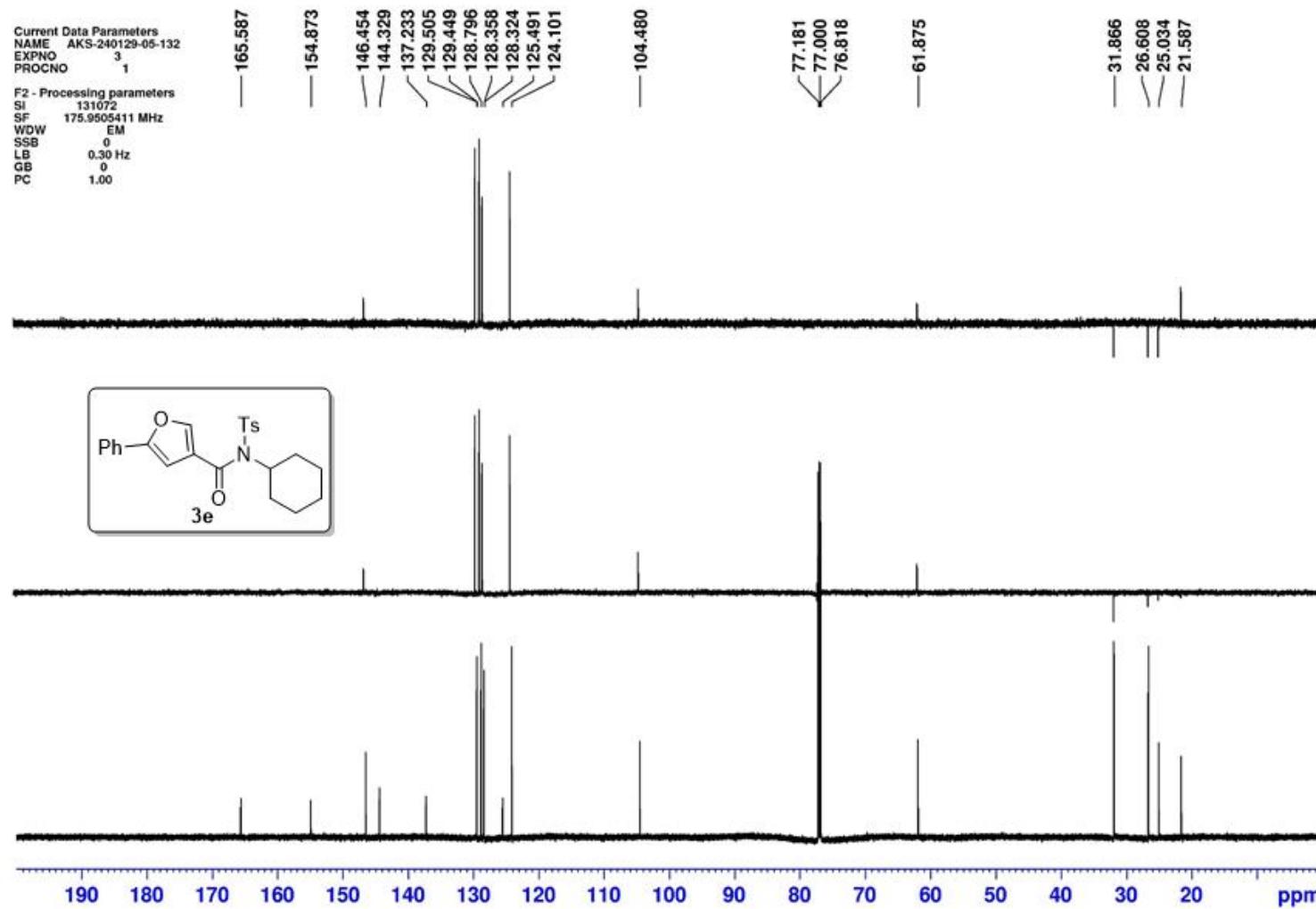
¹³C{¹H} and DEPT NMR (CDCl₃, 175 MHz)



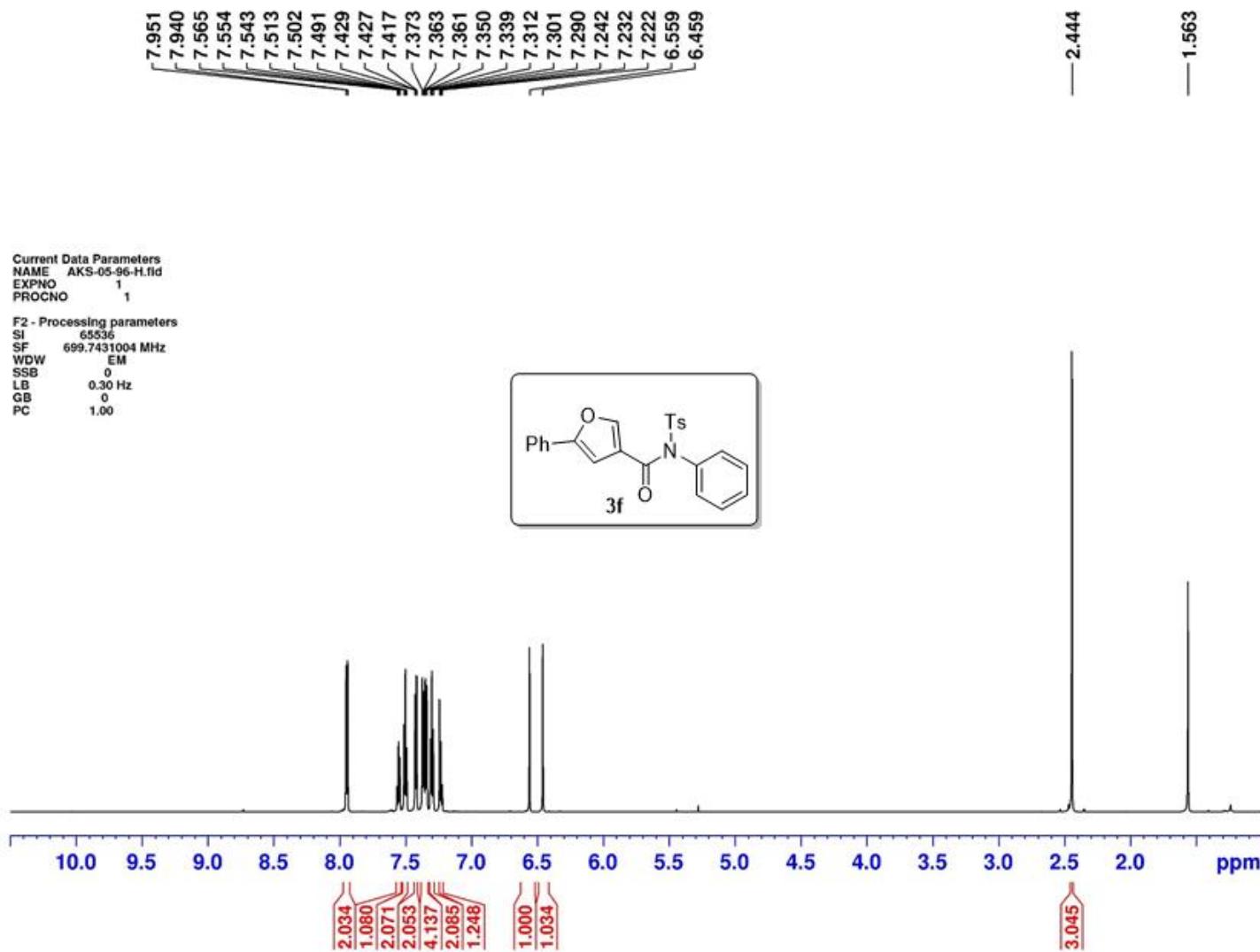
¹H NMR (CDCl₃, 700 MHz)



¹³C{¹H} and DEPT NMR (CDCl₃, 175 MHz)



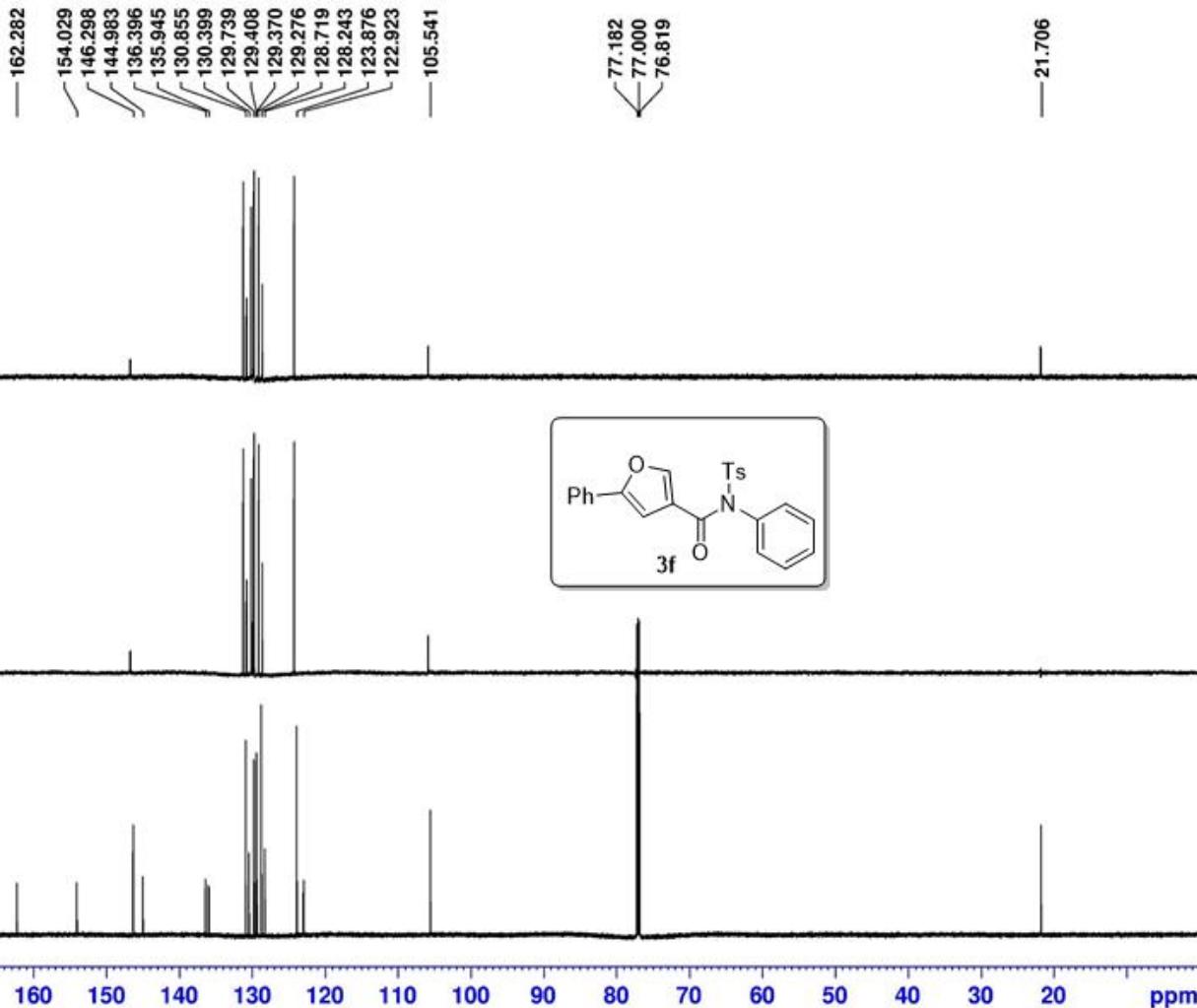
¹H NMR (CDCl₃, 700 MHz)



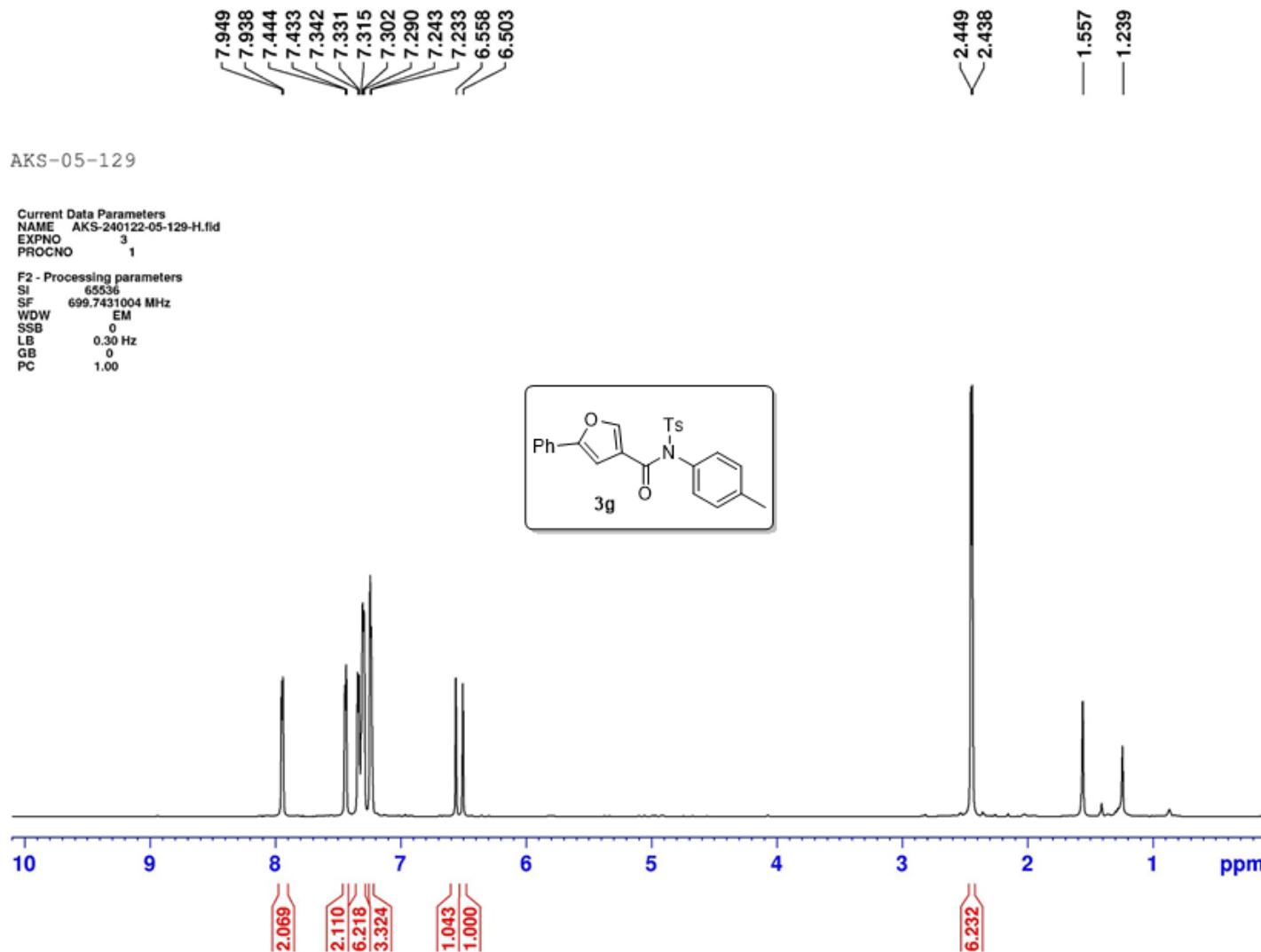
$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)

Current Data Parameters
NAME AKS-05-96
EXPNO 3
PROCNO 1

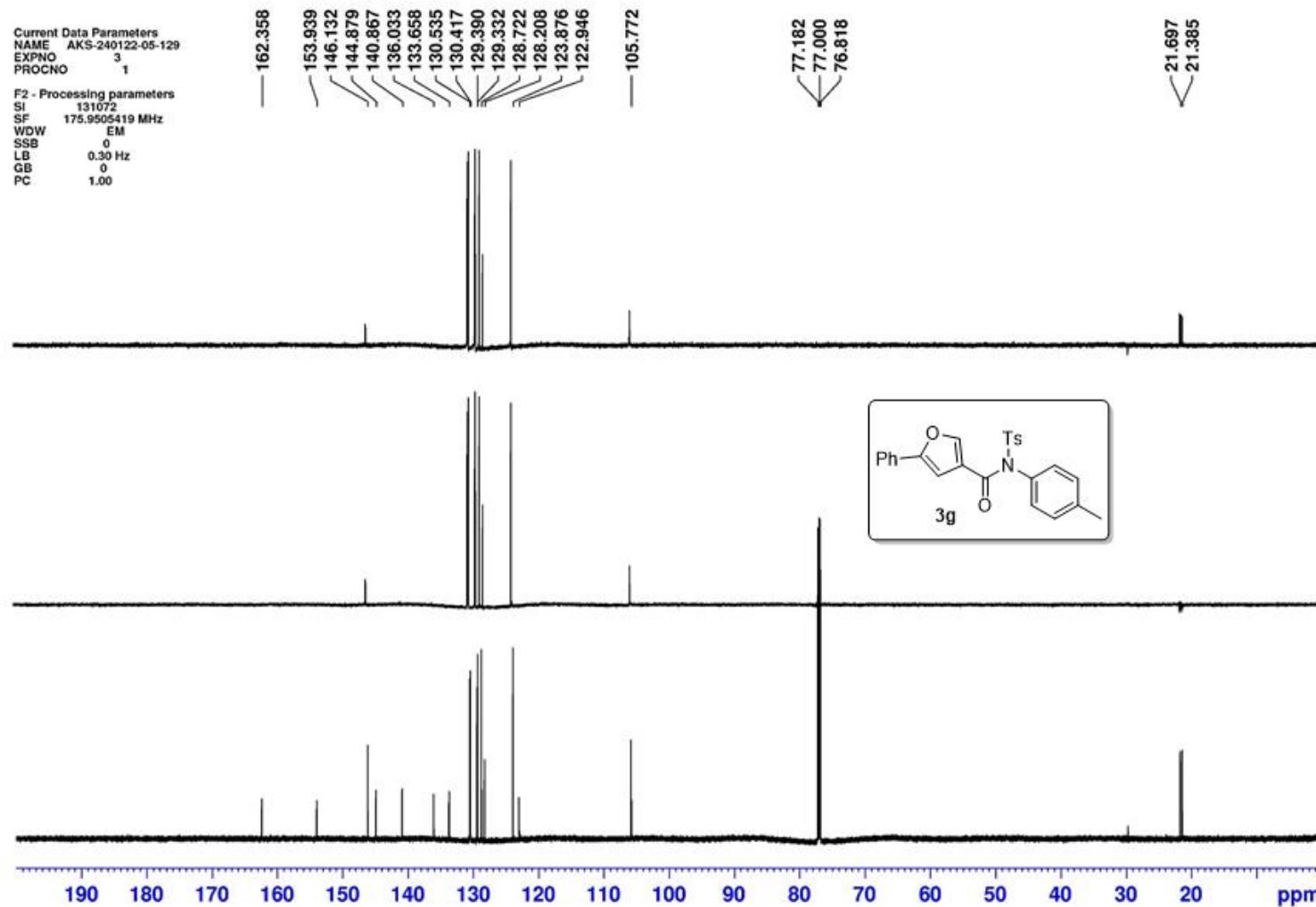
F2 - Processing parameters
SI 131072
SF 175.9505417 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



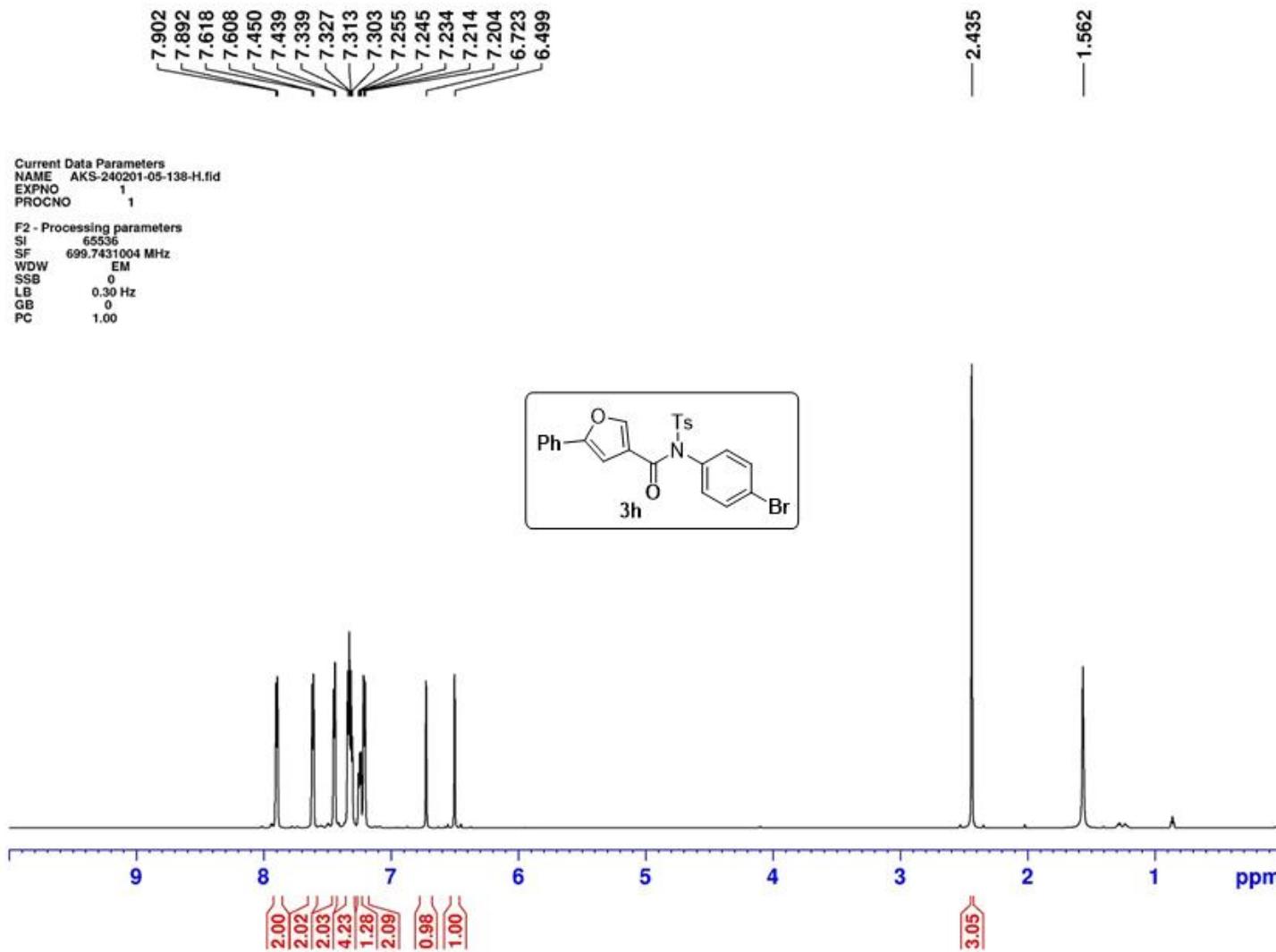
¹H NMR (CDCl₃, 700 MHz)



$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



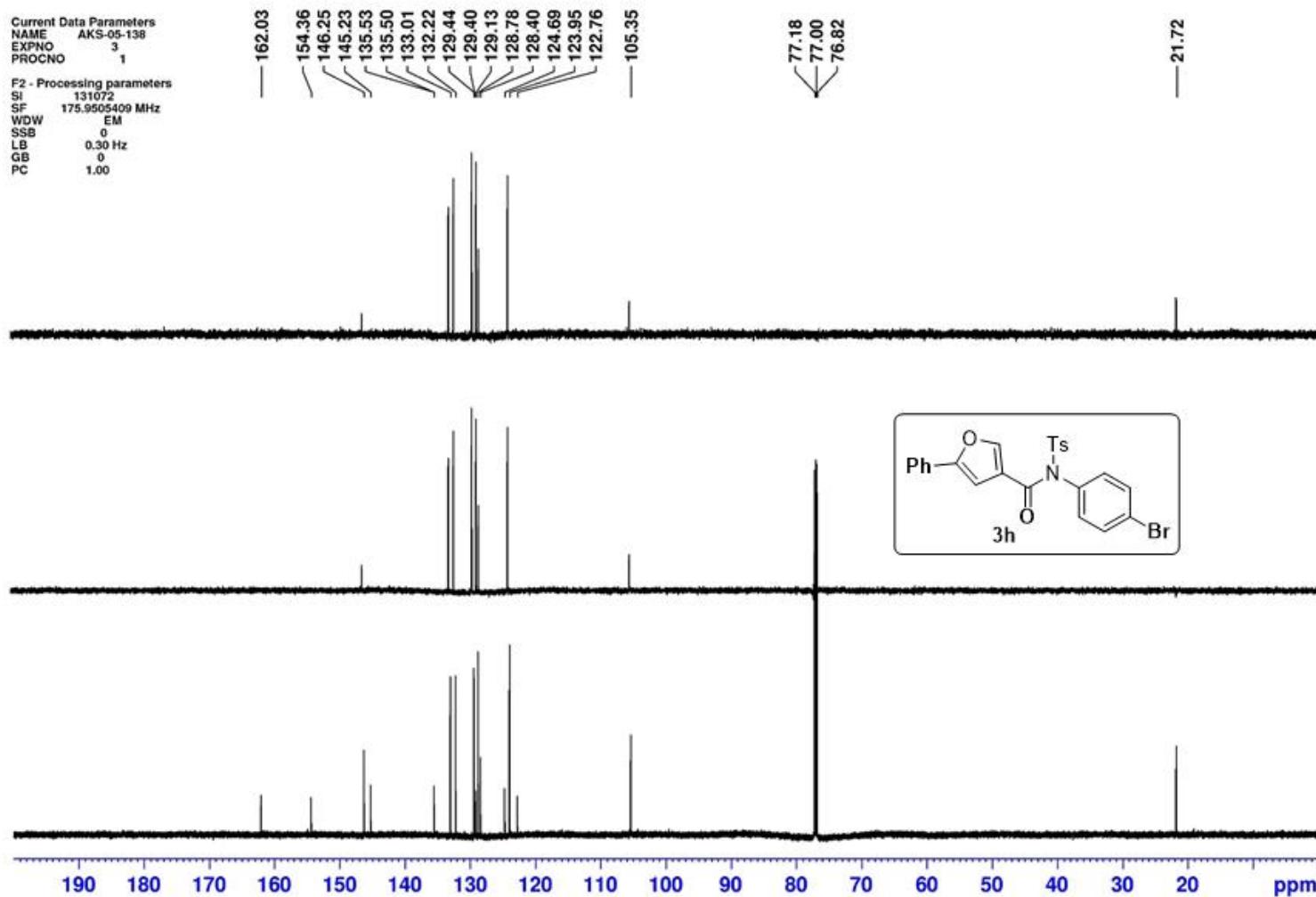
¹H NMR (CDCl₃, 700 MHz)



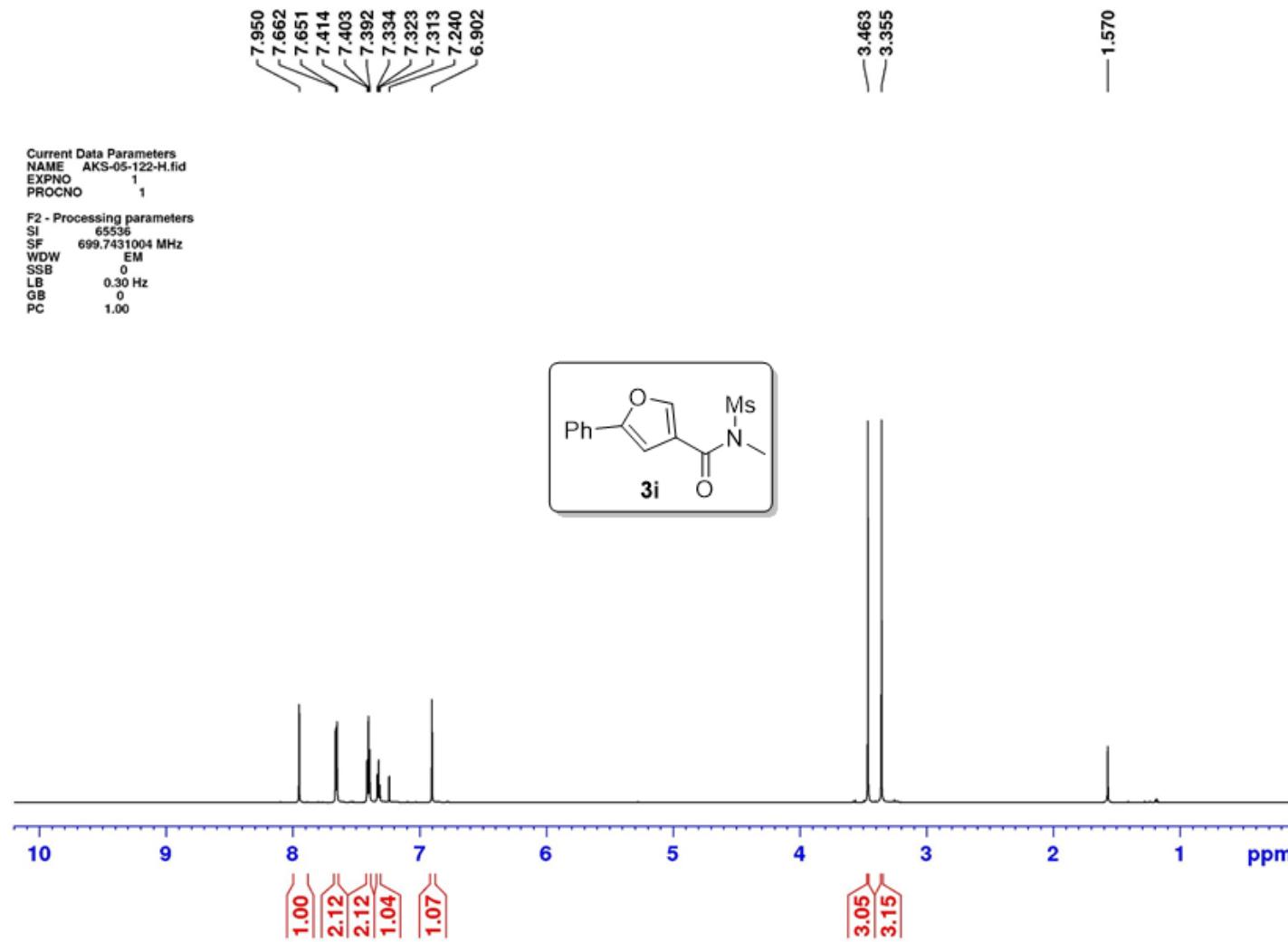
$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)

Current Data Parameters
NAME AKS-05-138
EXPNO 3
PROCNO 1

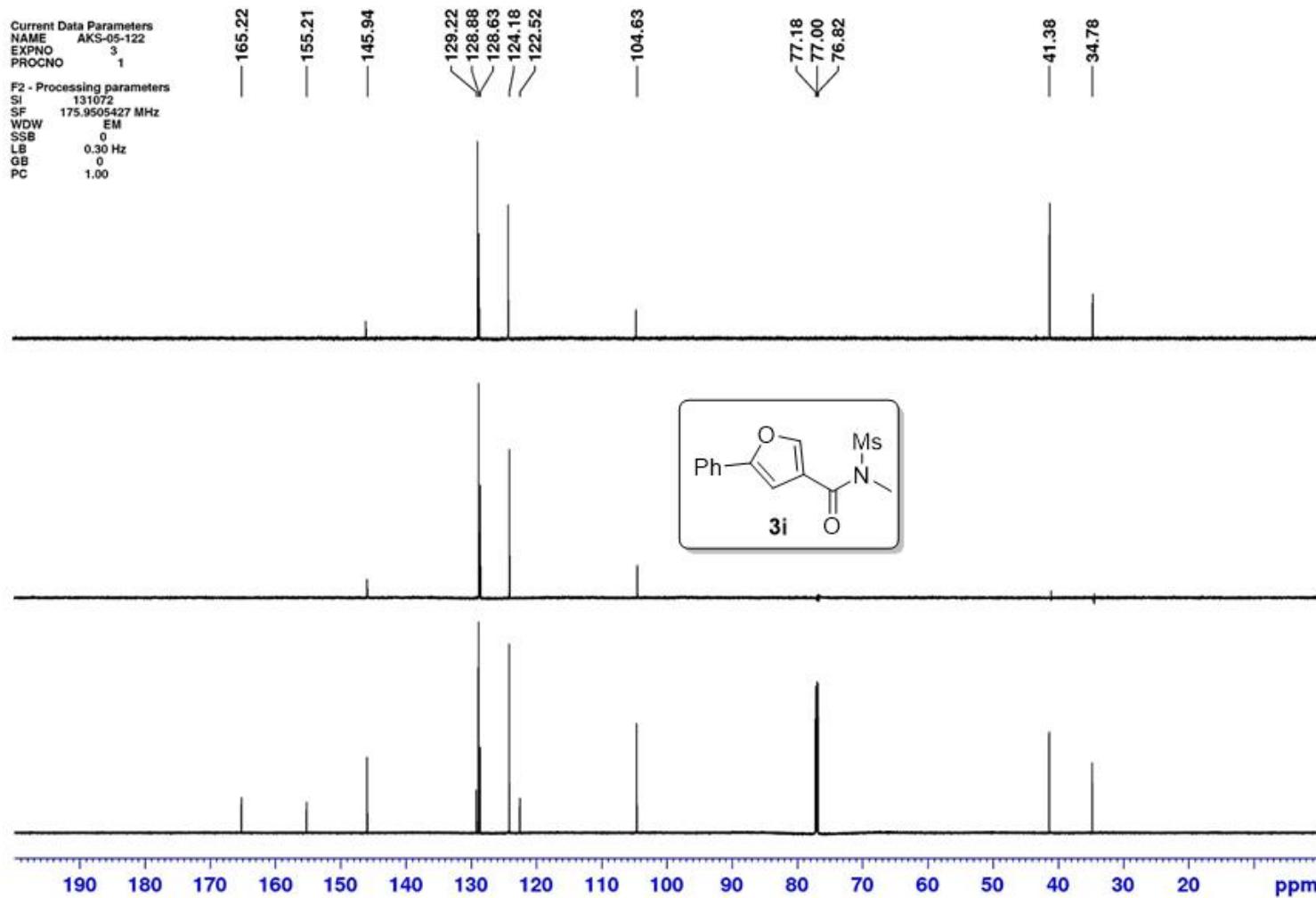
F2 - Processing parameters
SI 131072
SF 175.9505409 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



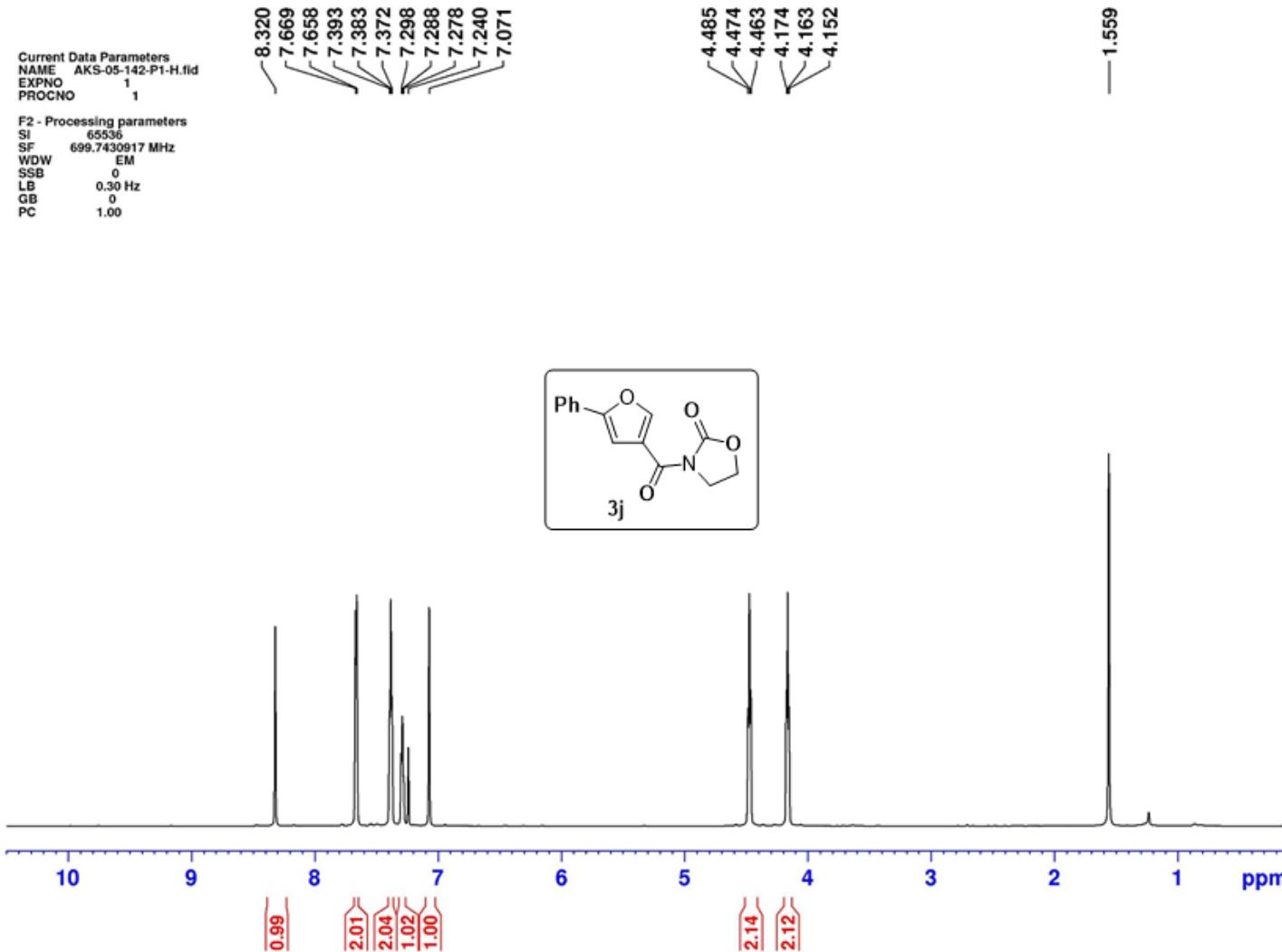
¹H NMR (CDCl₃, 700 MHz)



¹³C{¹H} and DEPT NMR (CDCl₃, 175 MHz)



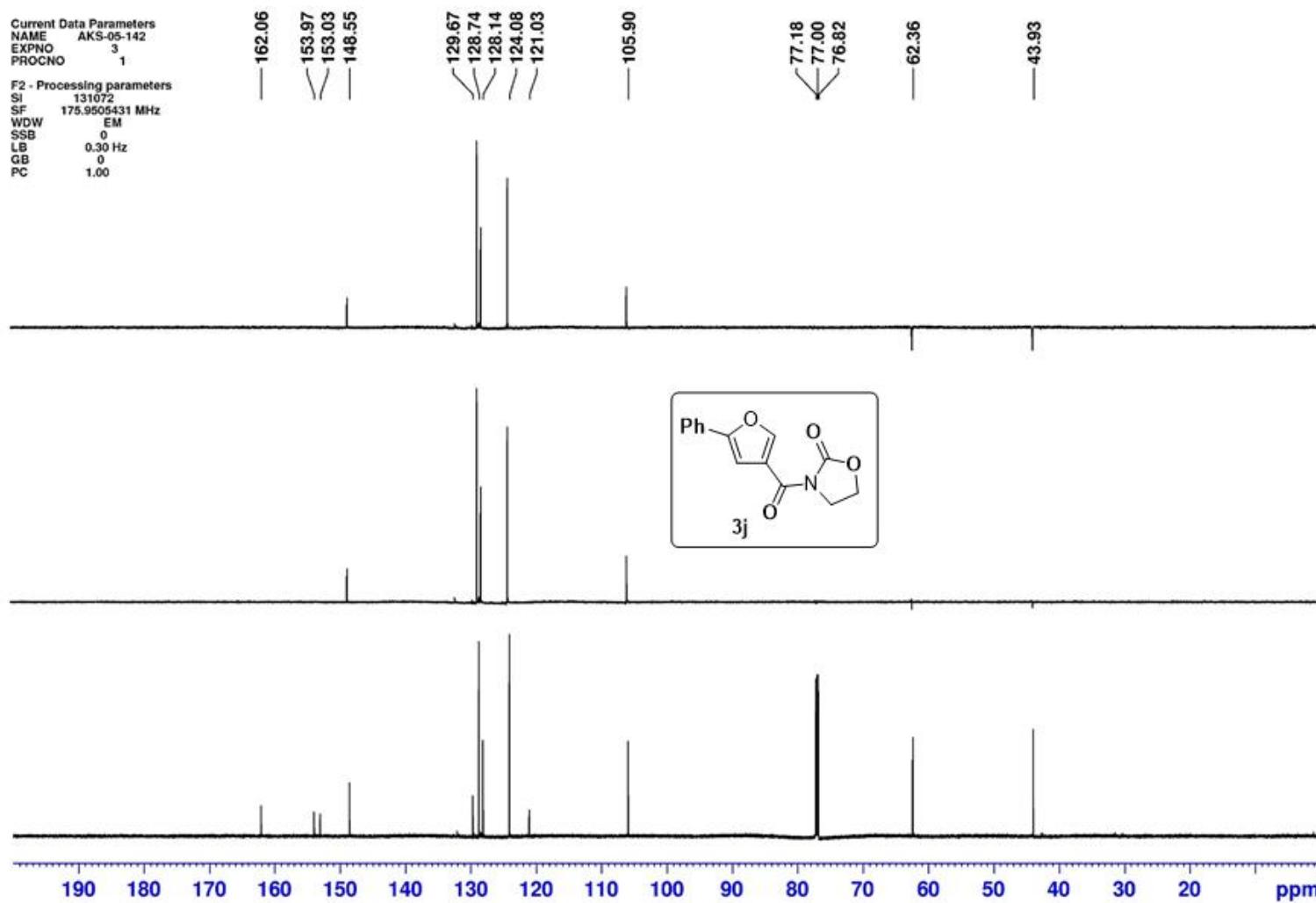
¹H NMR (CDCl₃, 700 MHz)



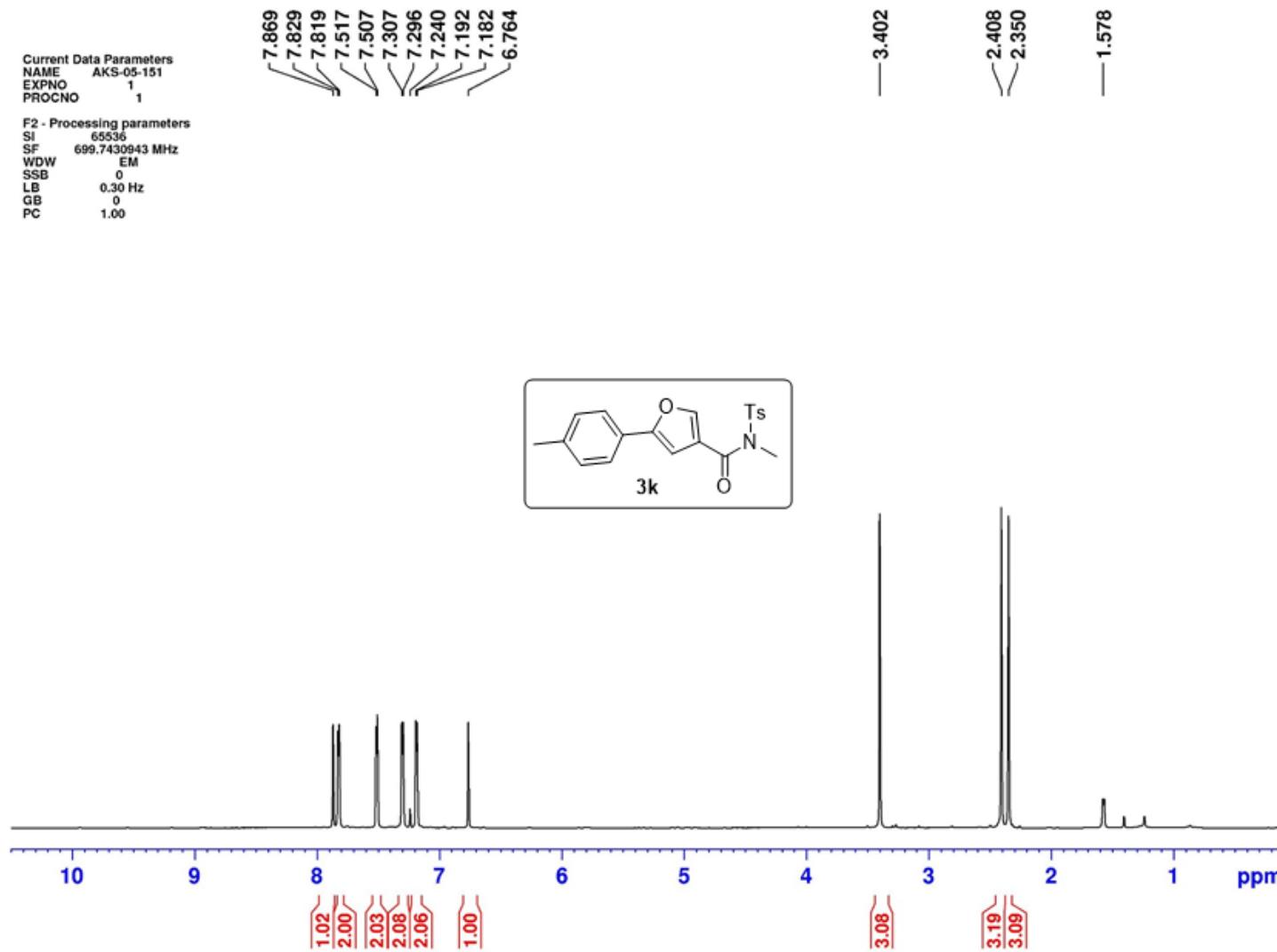
¹³C{¹H} and DEPT NMR (CDCl₃, 175 MHz)

Current Data Parameters
NAME AKS-05-142
EXPNO 3
PROCNO 1

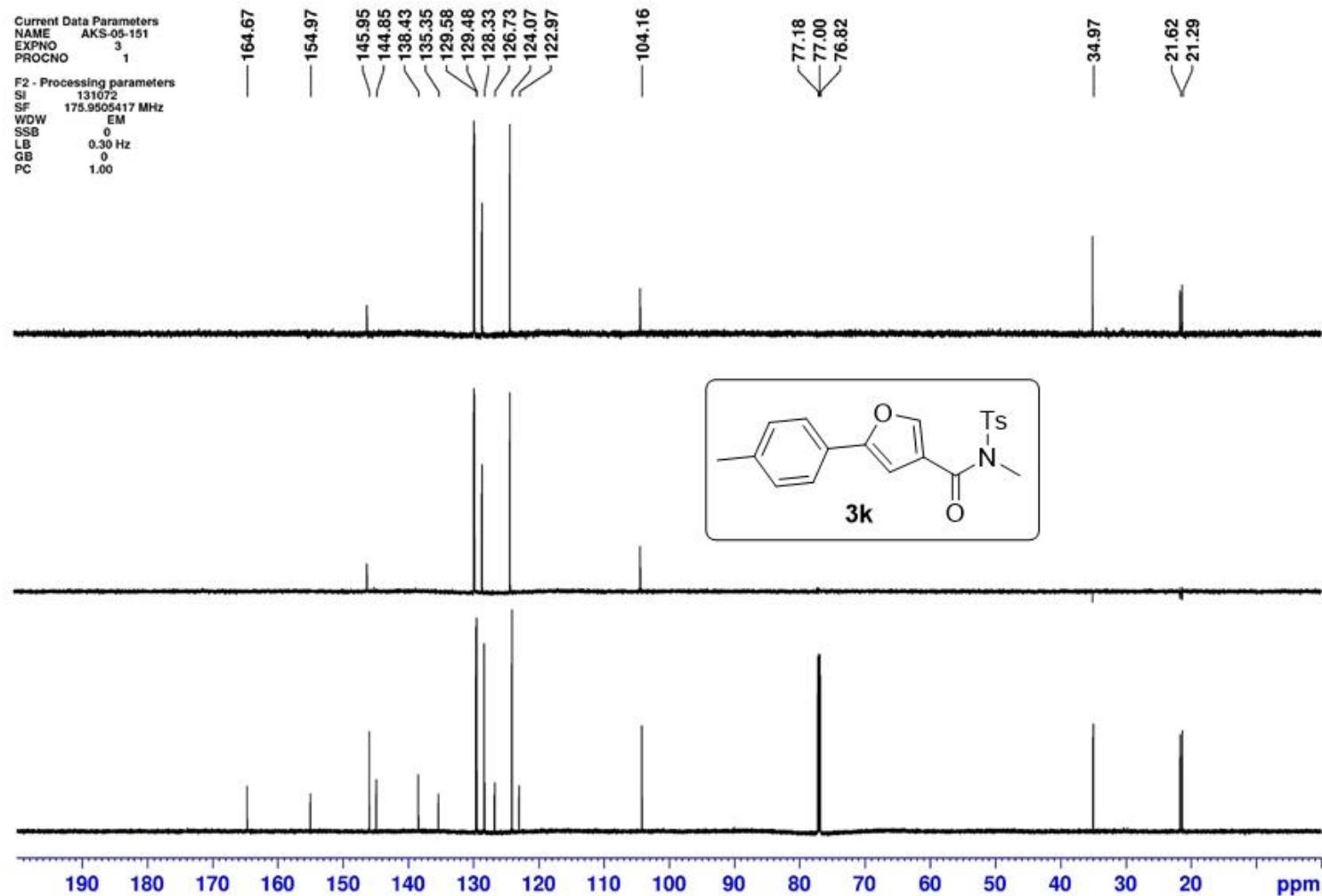
F2 - Processing parameters
SI 131072
SF 175.9505431 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



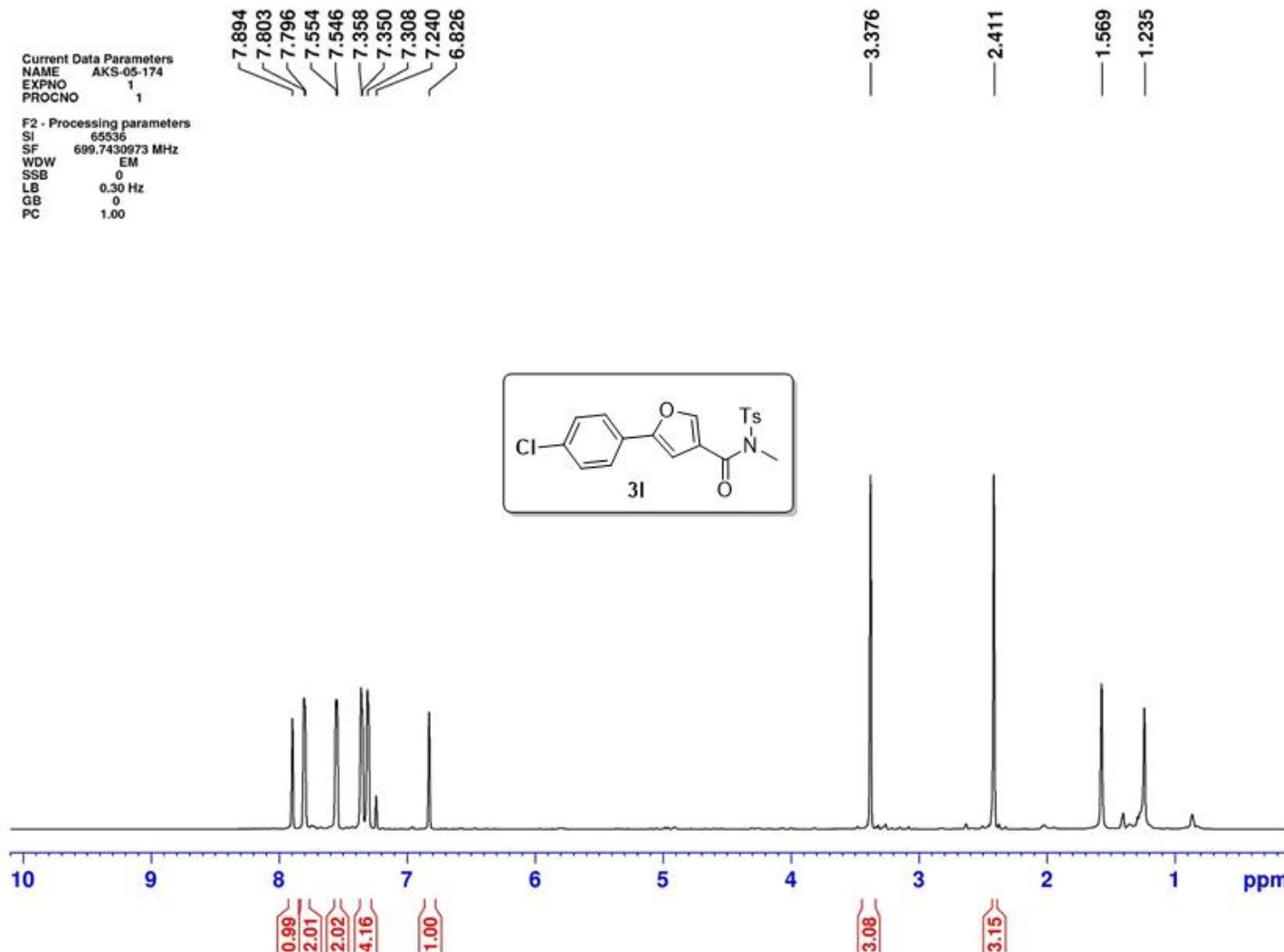
¹H NMR (CDCl₃, 700 MHz)



¹³C{¹H} and DEPT NMR (CDCl₃, 175 MHz)



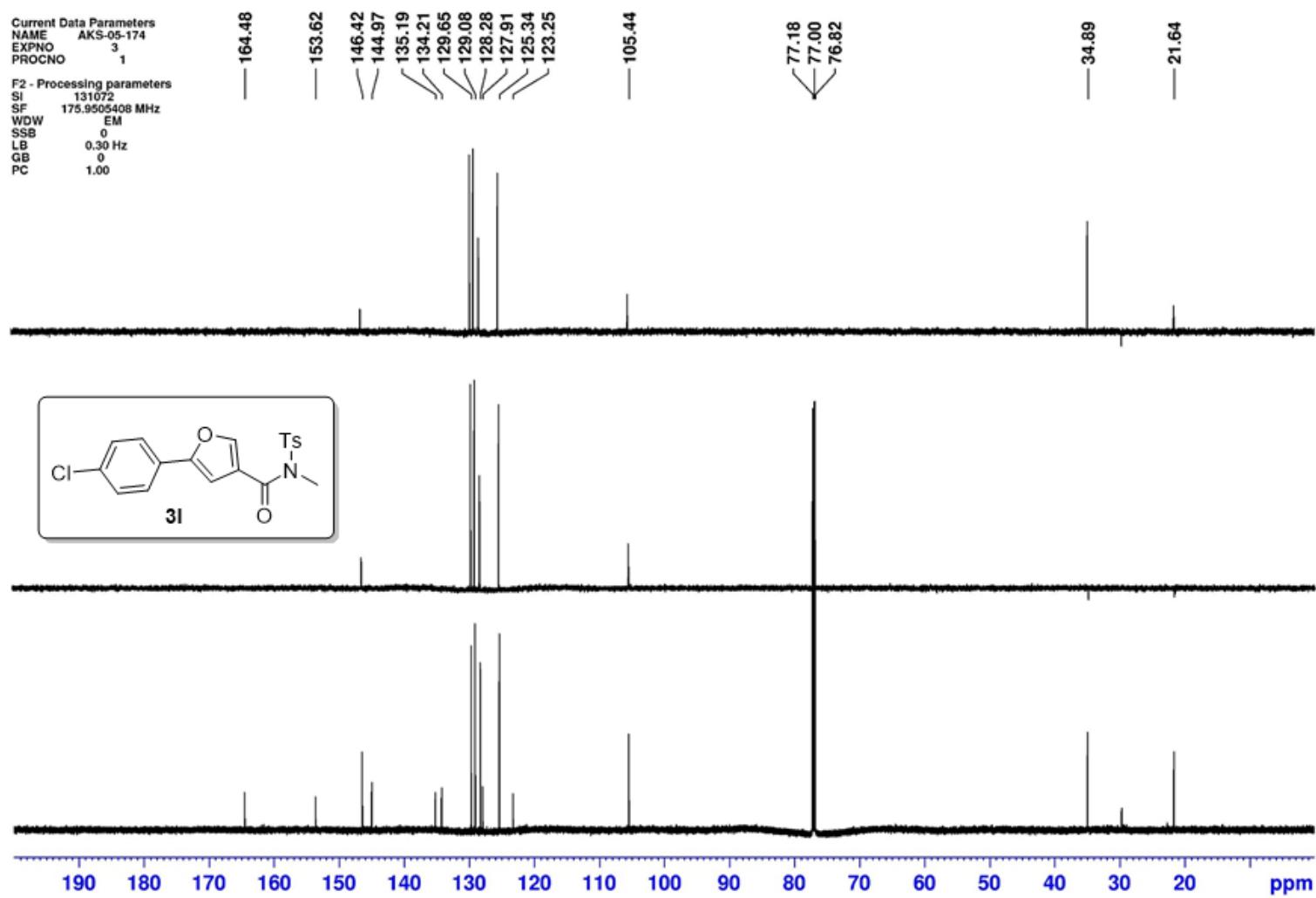
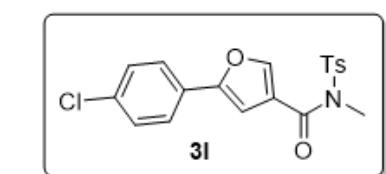
¹H NMR (CDCl₃, 700 MHz)



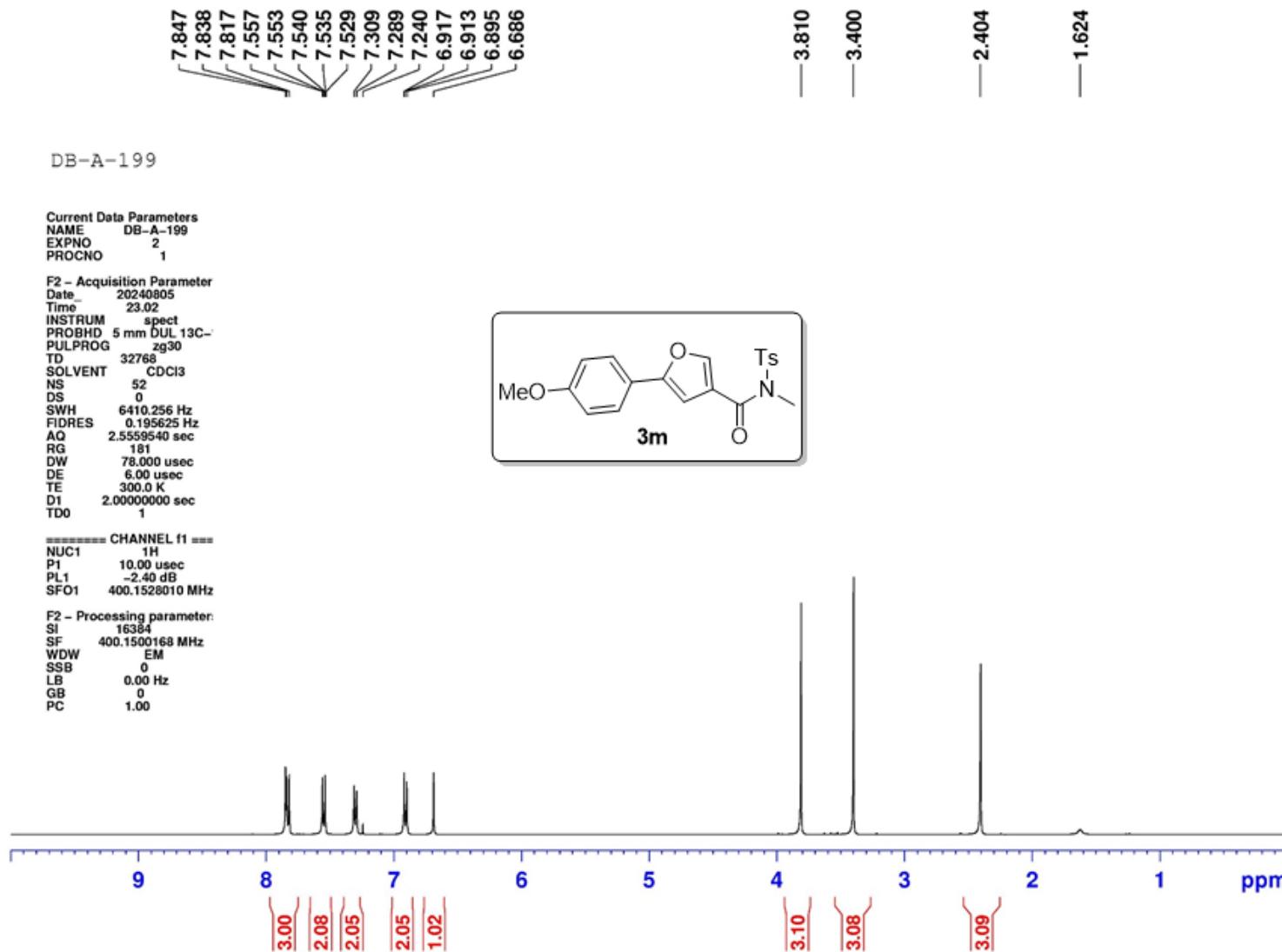
$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)

Current Data Parameters
NAME AKS-05-174
EXPNO 3
PROCNO 1

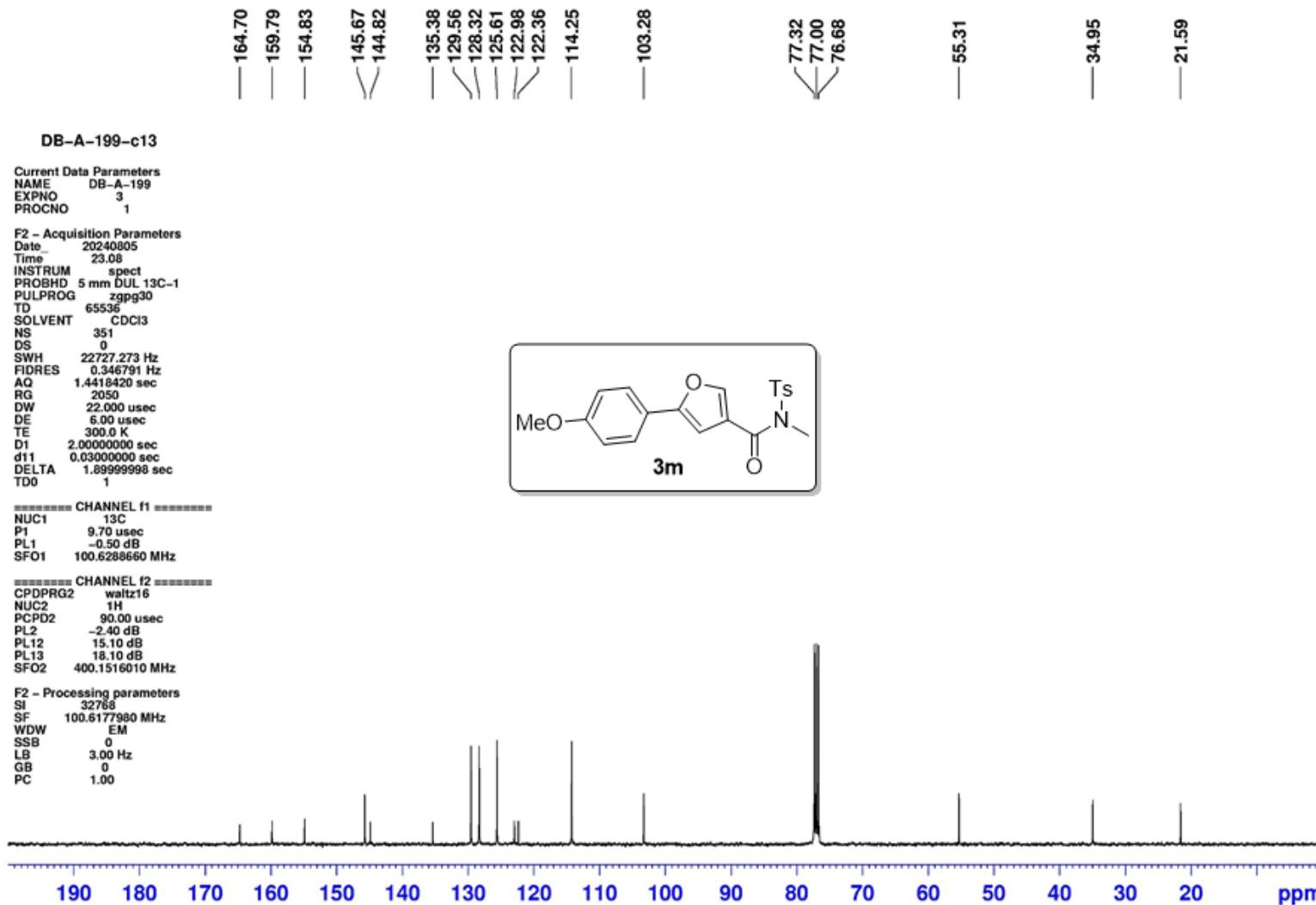
F2 - Processing parameters
SI 131072
SF 175.9505408 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



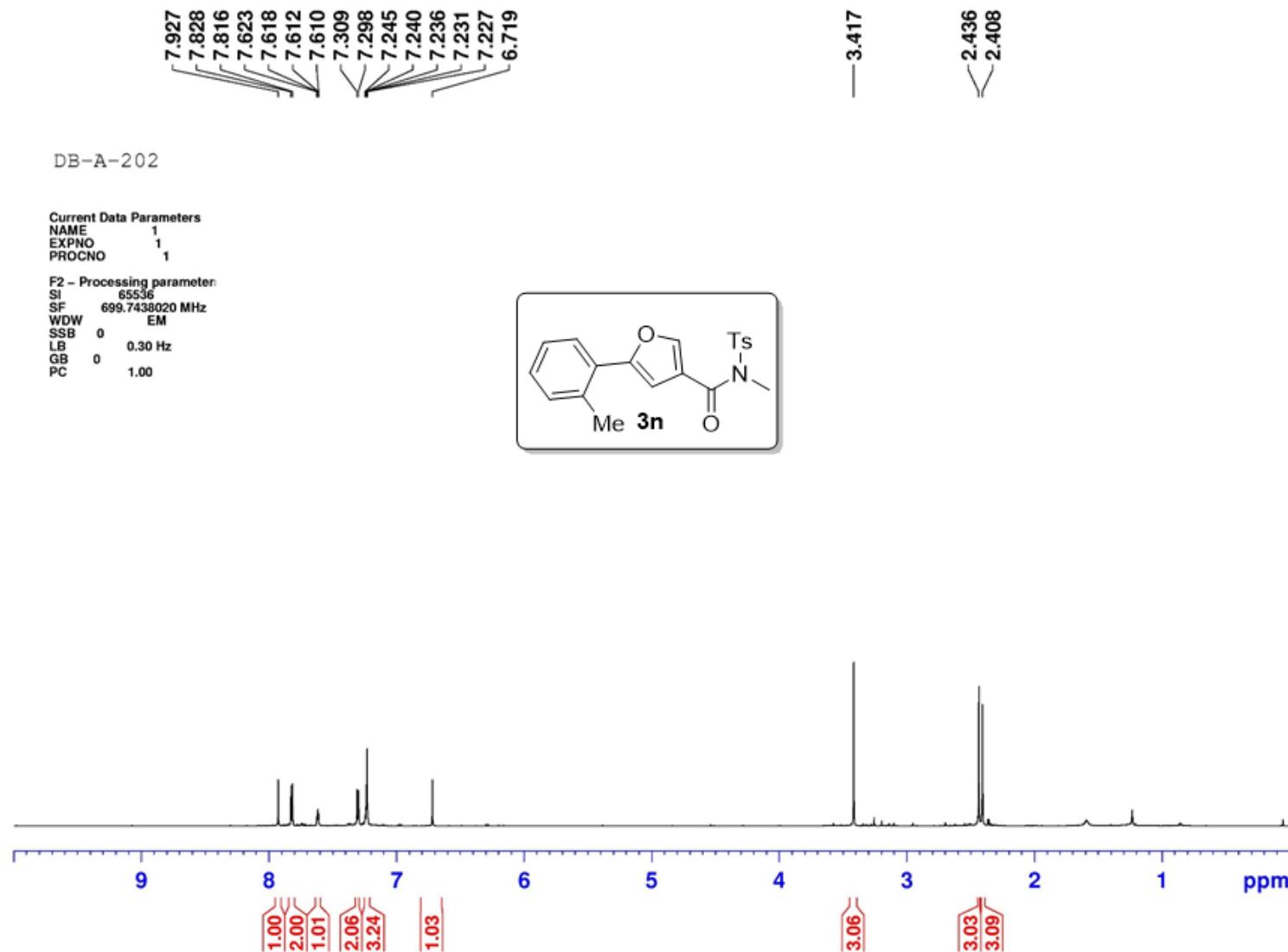
¹H NMR (CDCl₃, 400 MHz)



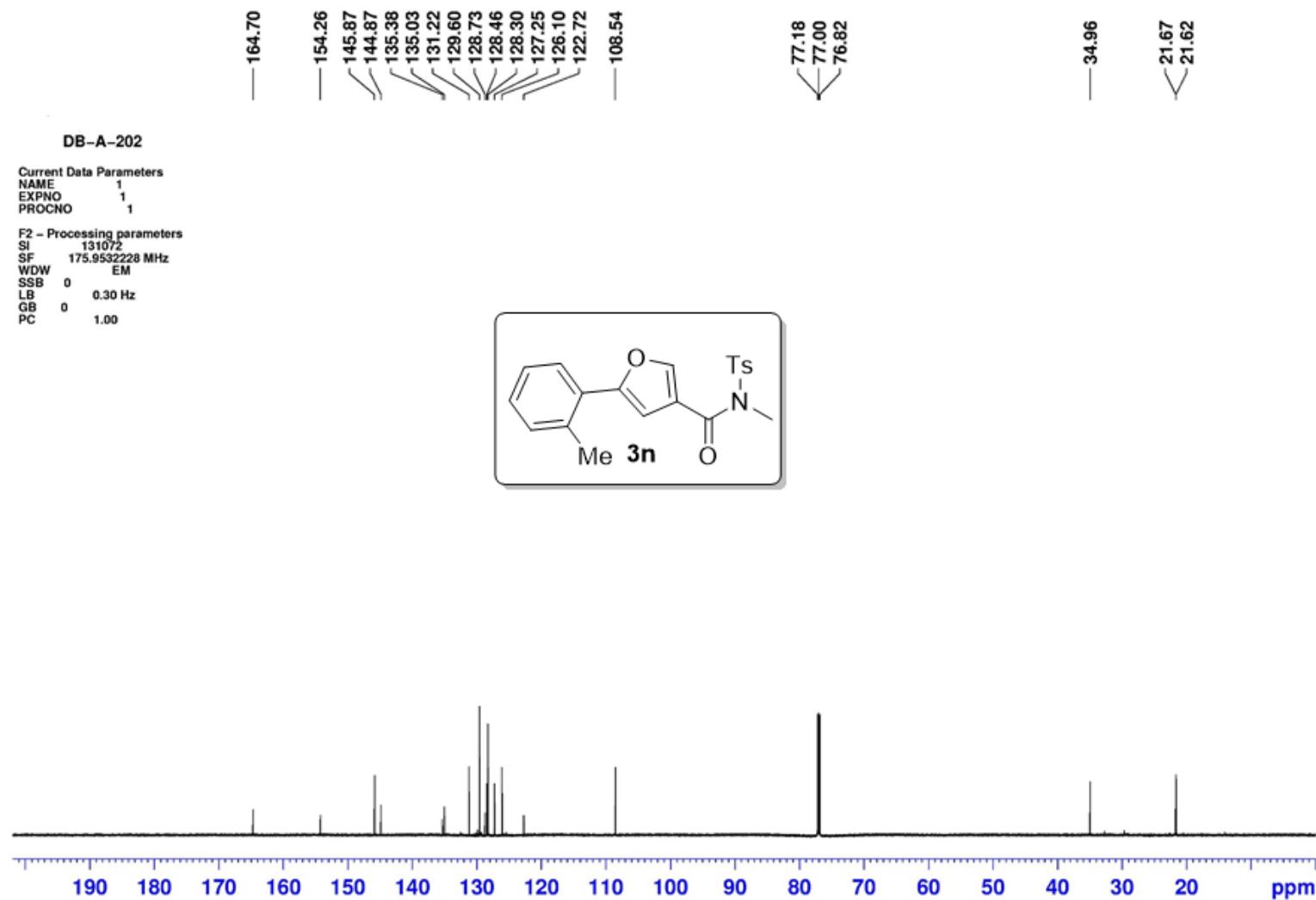
¹³C{¹H} NMR (CDCl₃, 100 MHz)



¹H NMR (CDCl₃, 700 MHz)



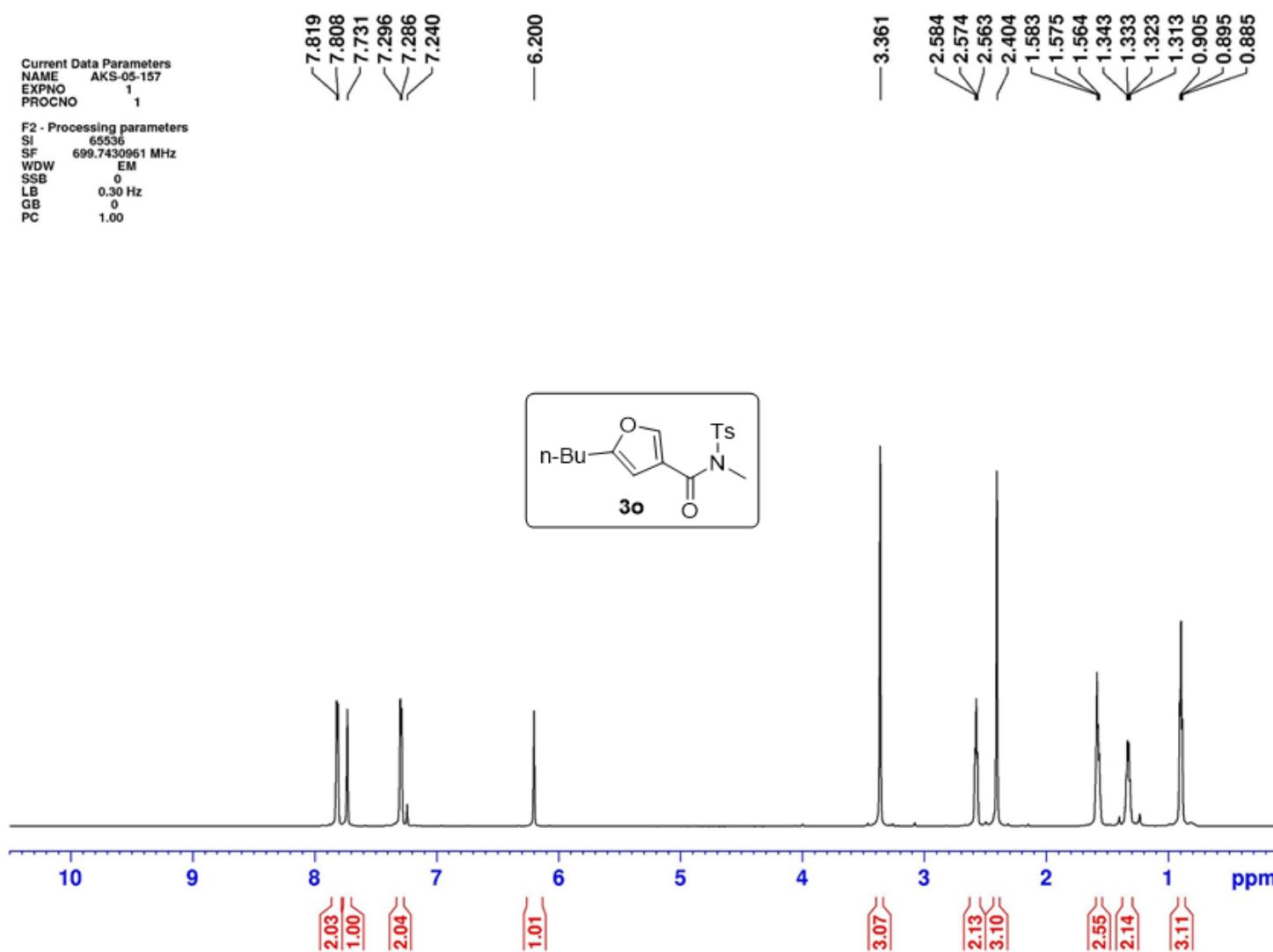
¹³C{¹H} NMR (CDCl₃, 175 MHz)



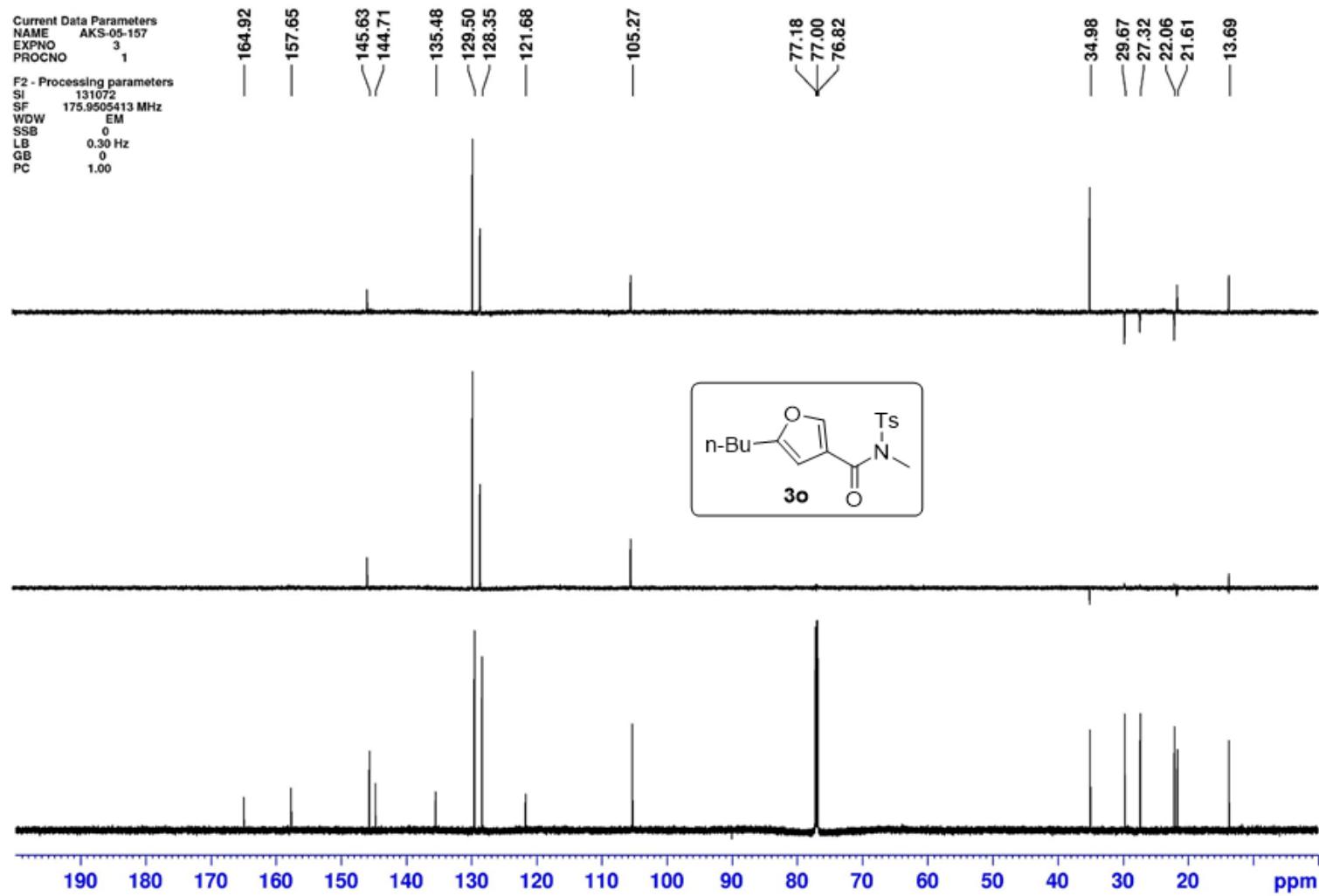
¹H NMR (CDCl₃, 700 MHz)

Current Data Parameters
NAME AKS-05-157
EXPNO 1
PROCNO 1

F2 - Processing parameters
SI 65536
SF 699.7430961 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



$^{13}\text{C}\{1\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



¹H NMR (CDCl₃, 700 MHz)

Current Data Parameters
NAME AKS-05-155
EXPNO 1
PROCNO 1

F2 - Processing parameters
SI 65536
SF 699.7431014 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

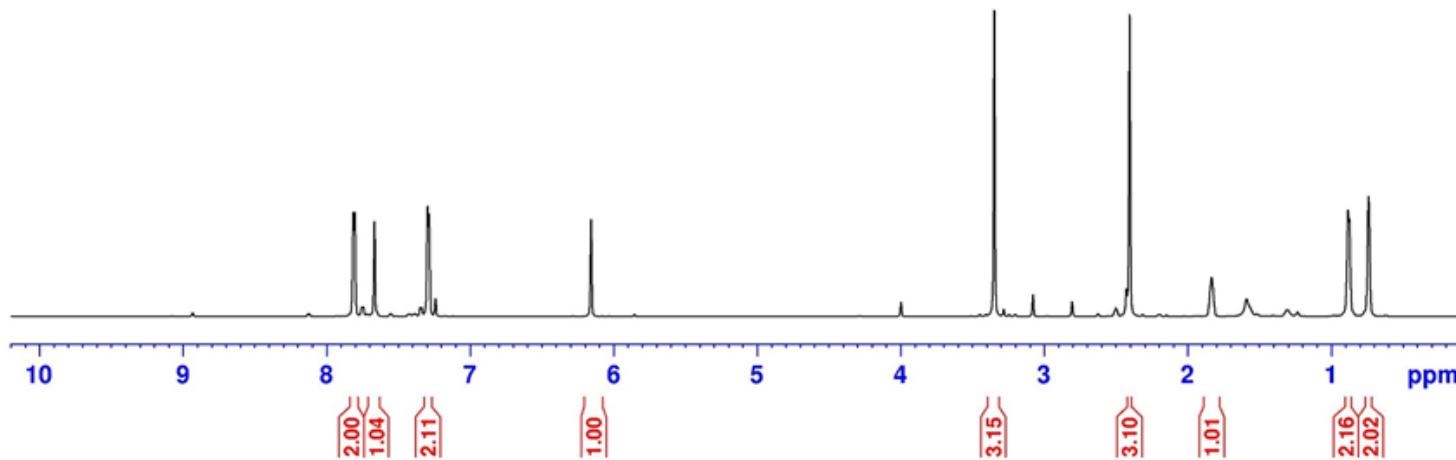
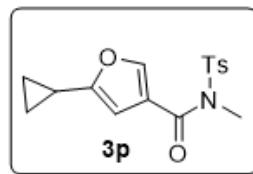
7.813
7.803
7.665
7.295
7.284
7.240

— 6.156

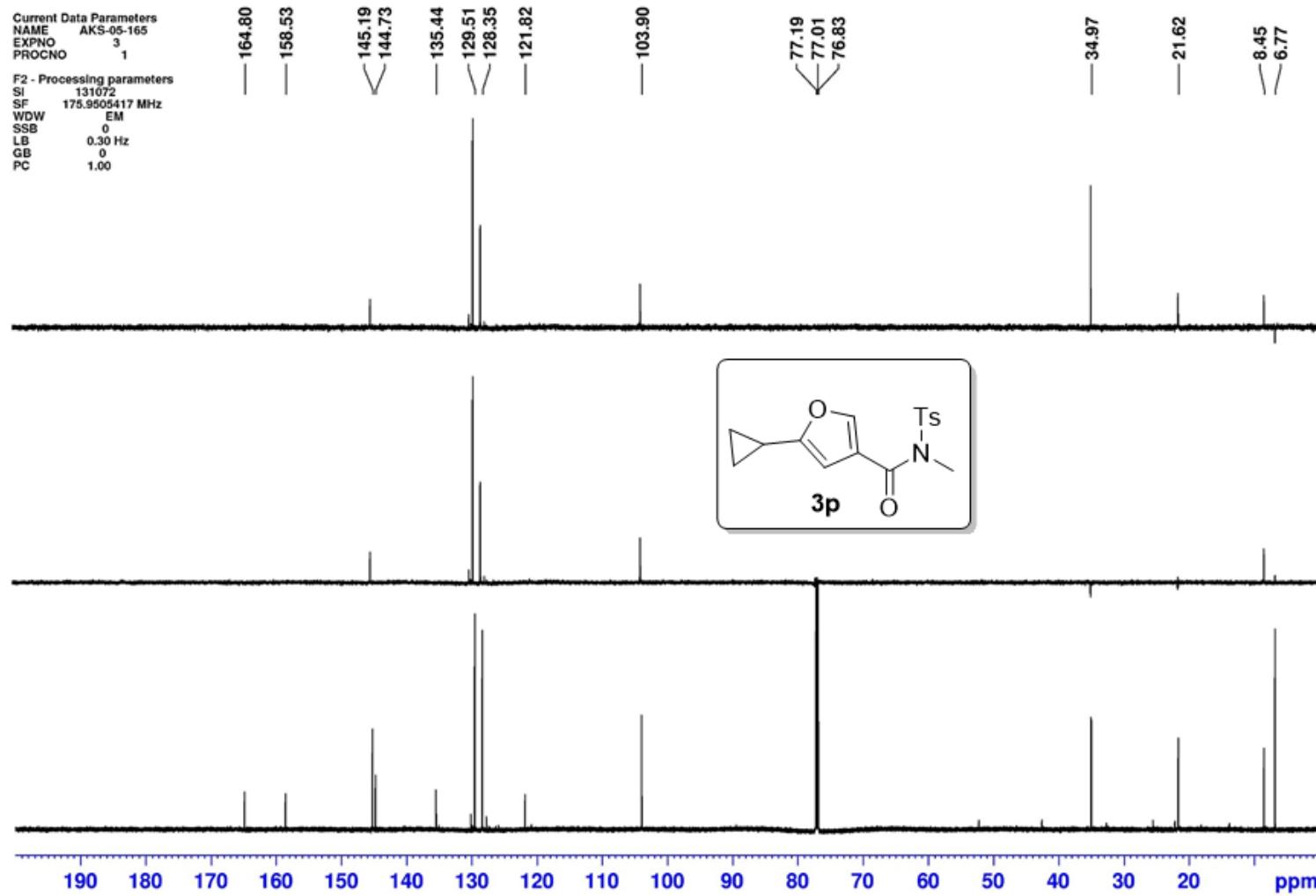
— 3.347

— 2.403
— 1.832
— 1.589

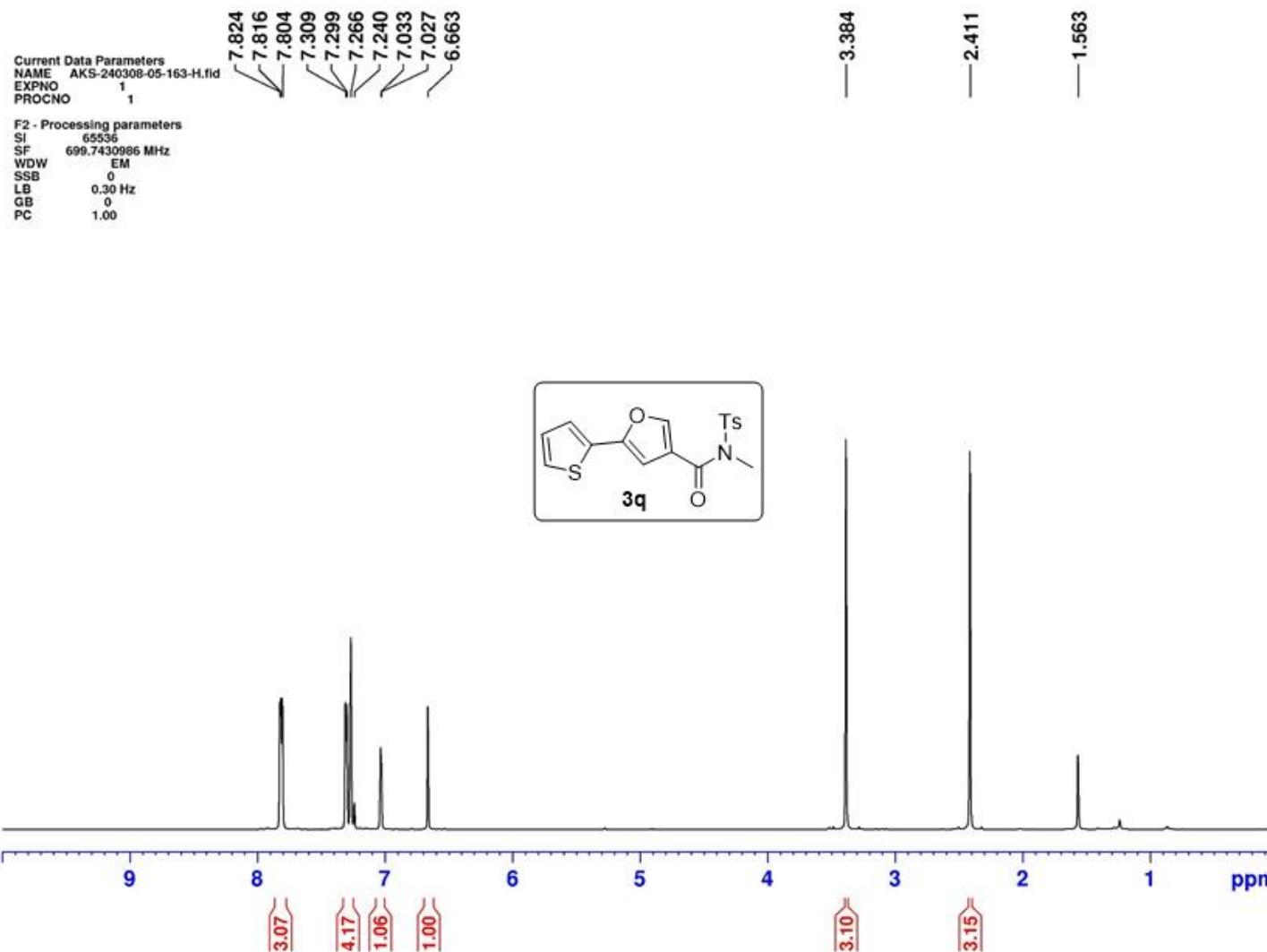
— 0.882
— 0.873
— 0.739



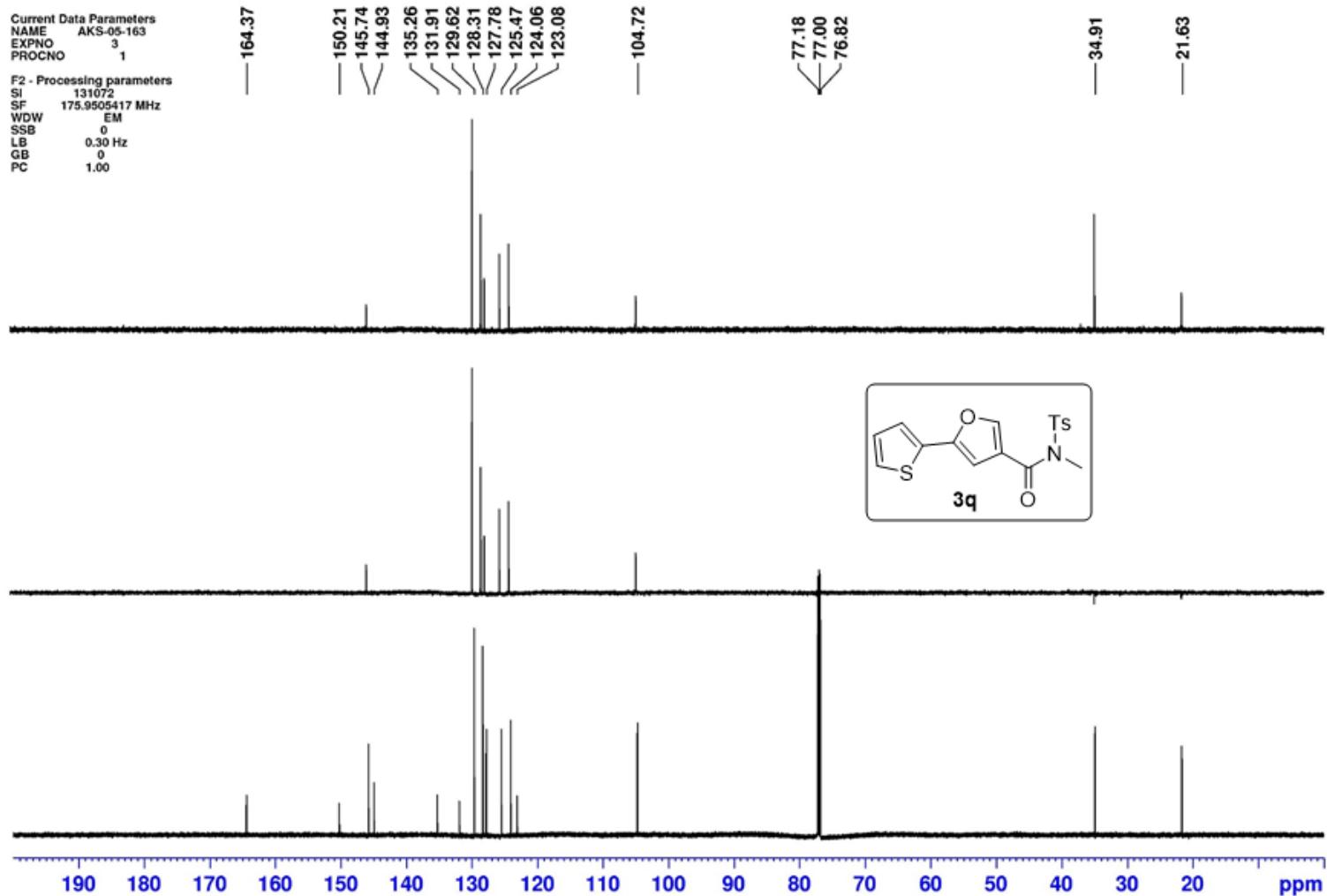
$^{13}\text{C}\{1\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



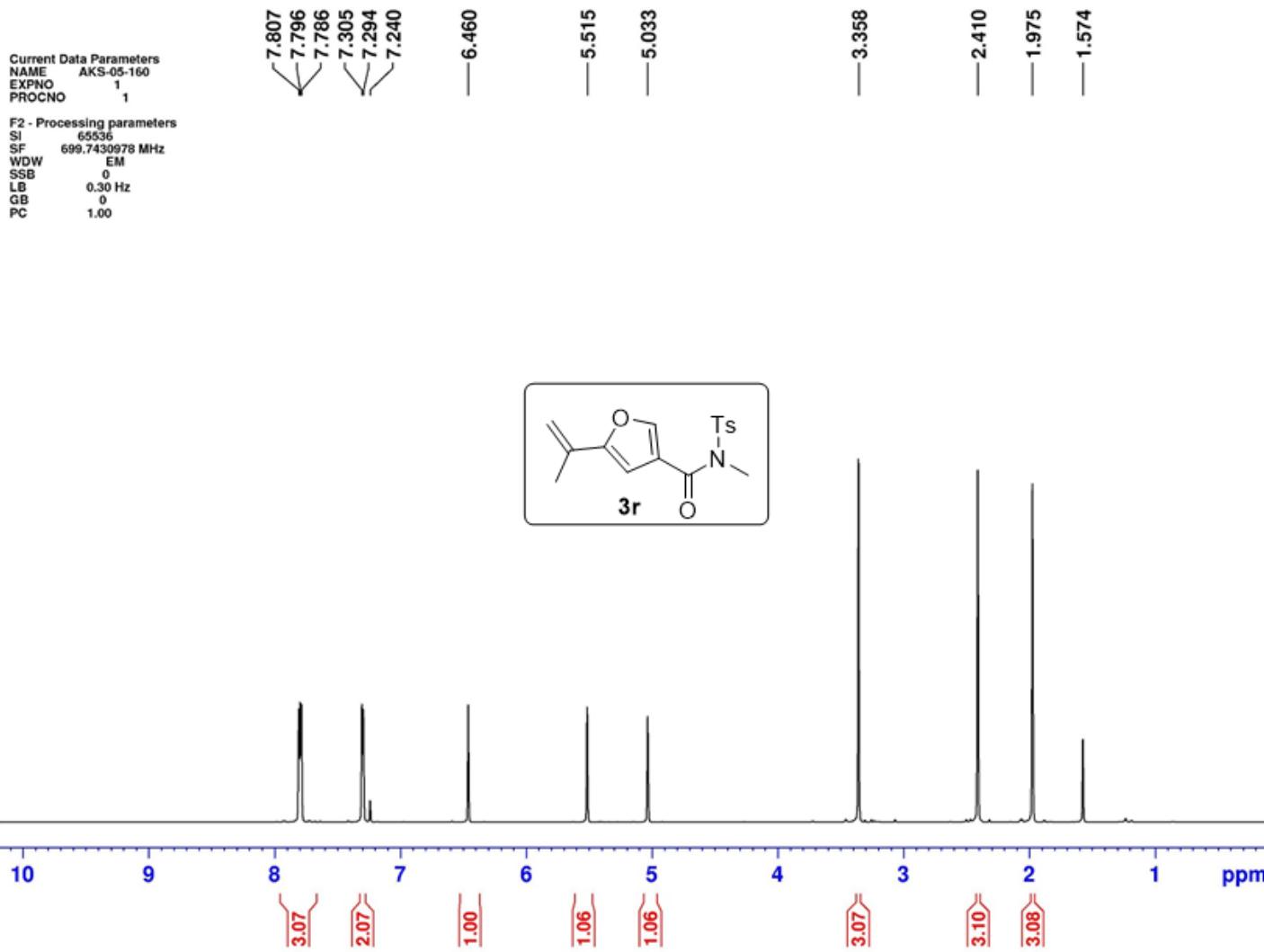
¹H NMR (CDCl₃, 700 MHz)



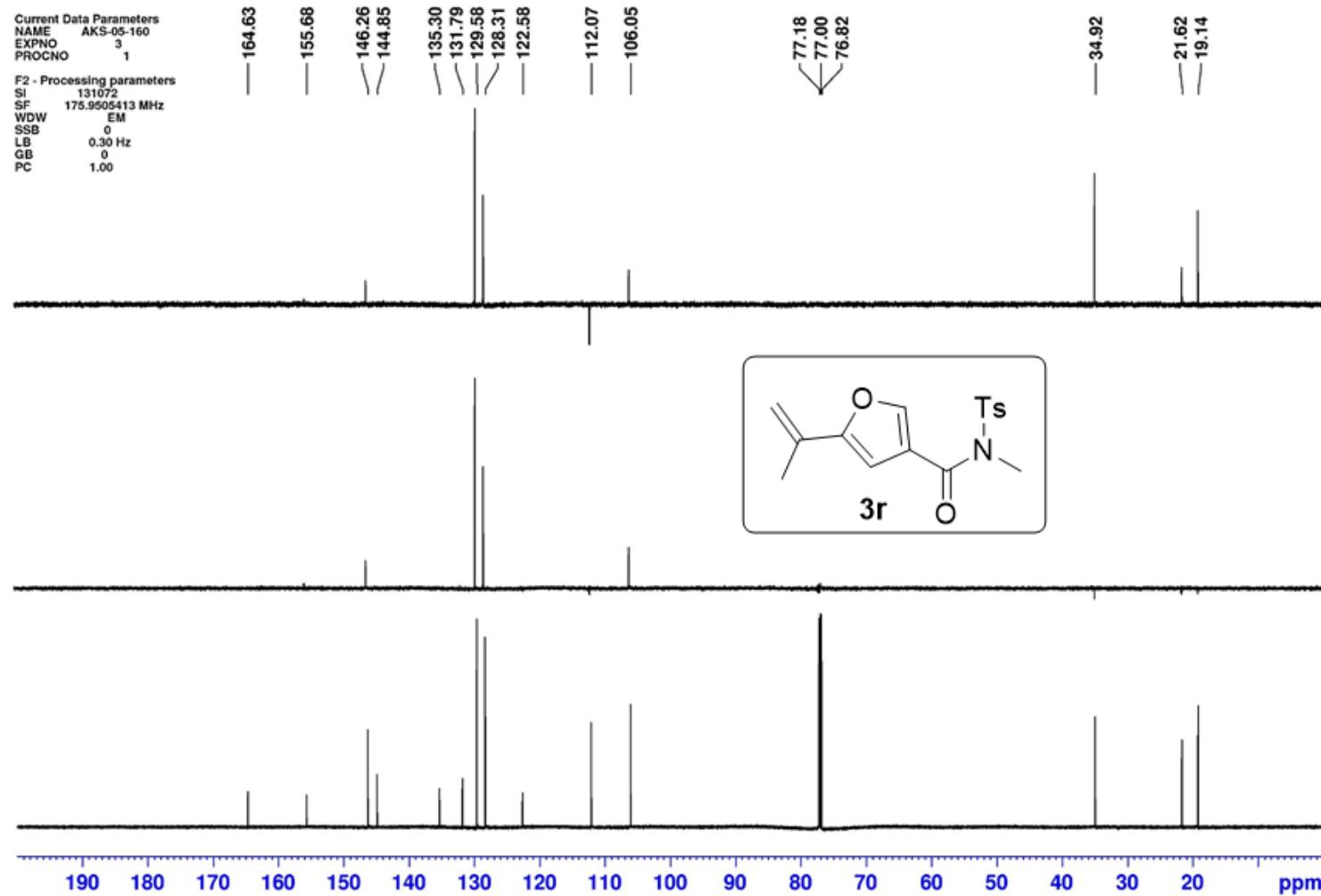
¹³C{¹H} and DEPT NMR (CDCl₃, 175 MHz)



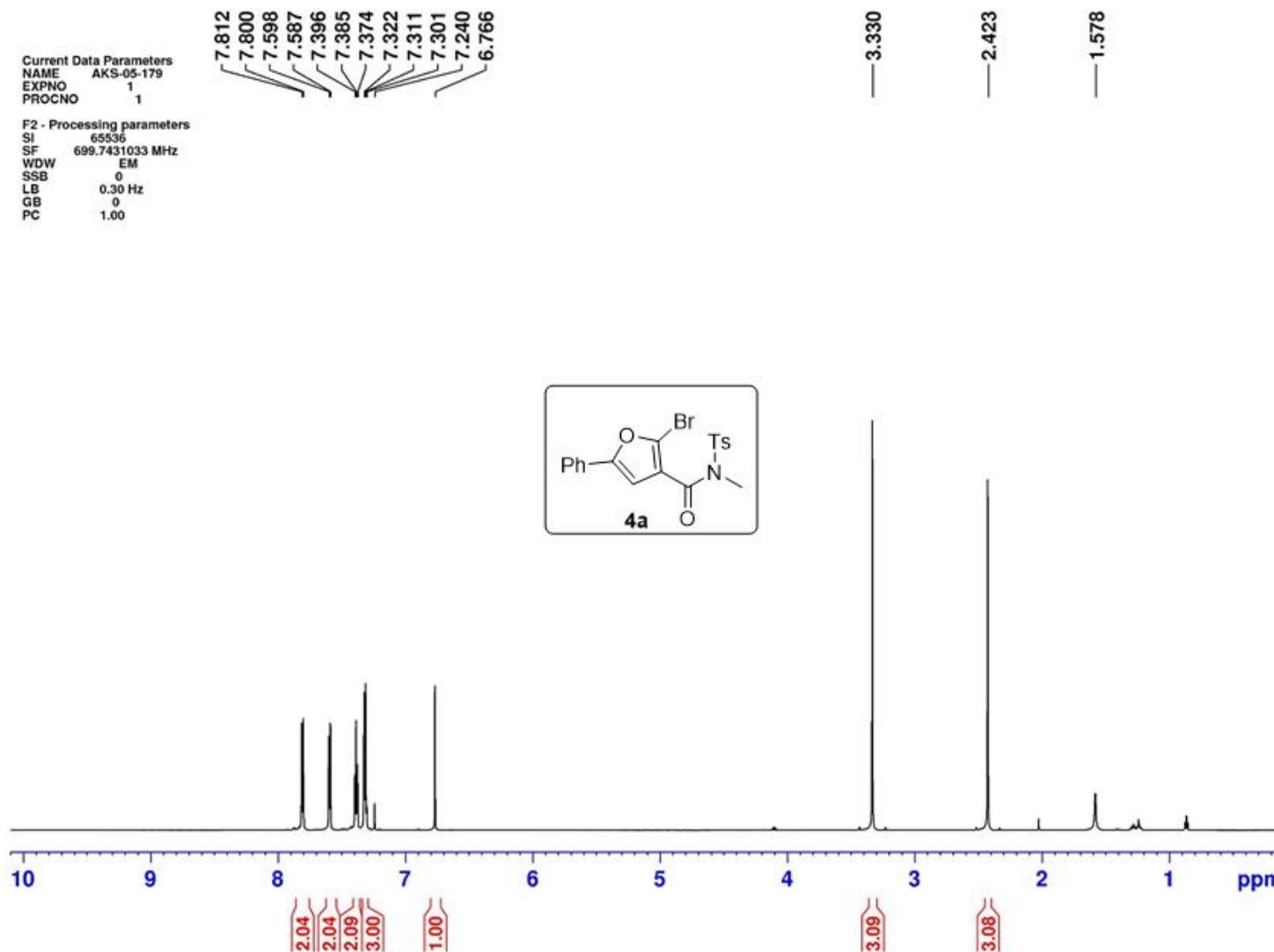
¹H NMR (CDCl₃, 700 MHz)



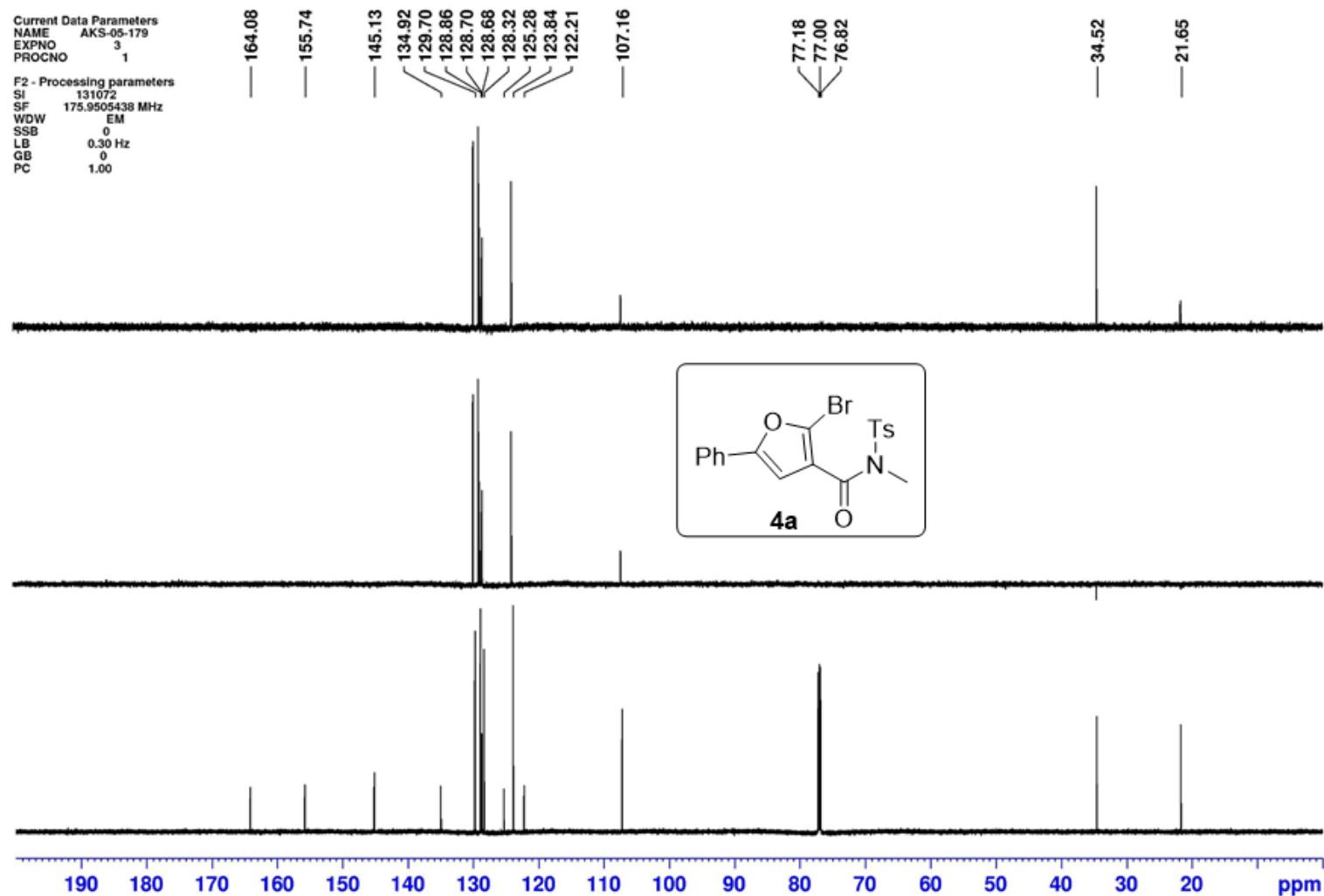
¹³C{¹H} and DEPT NMR (CDCl₃, 175 MHz)



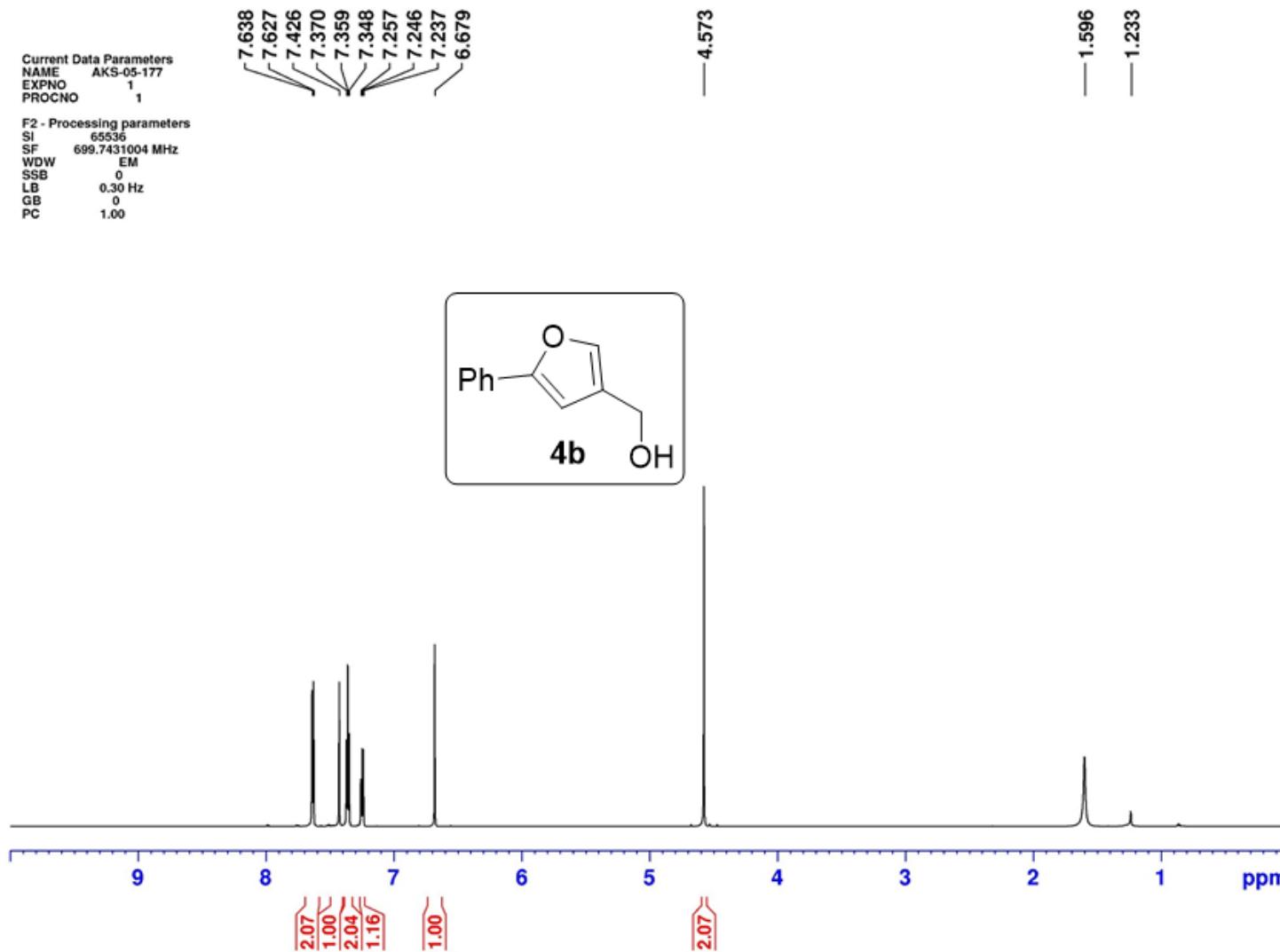
¹H NMR (CDCl₃, 700 MHz)



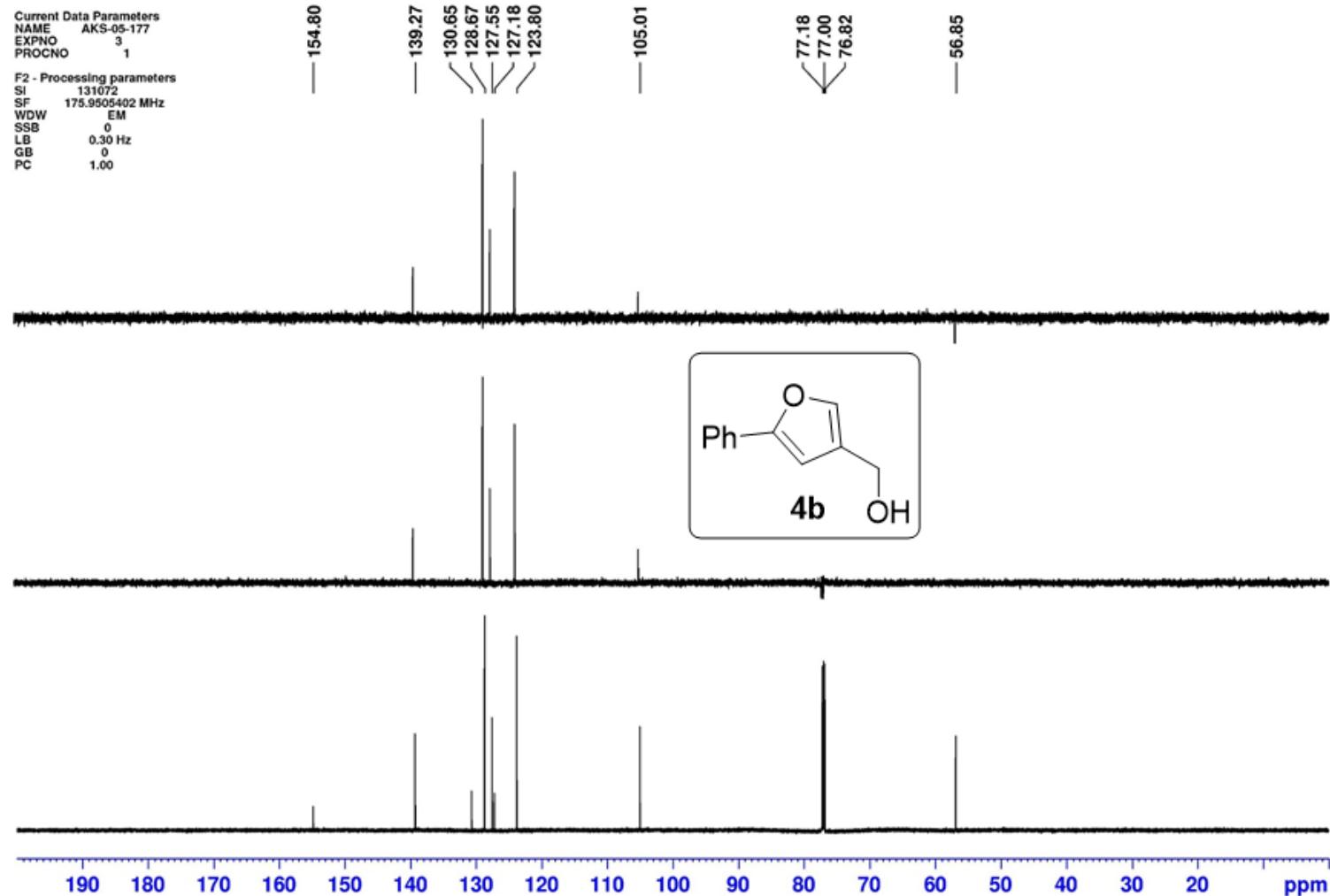
¹³C{¹H} and DEPT NMR (CDCl₃, 175 MHz)



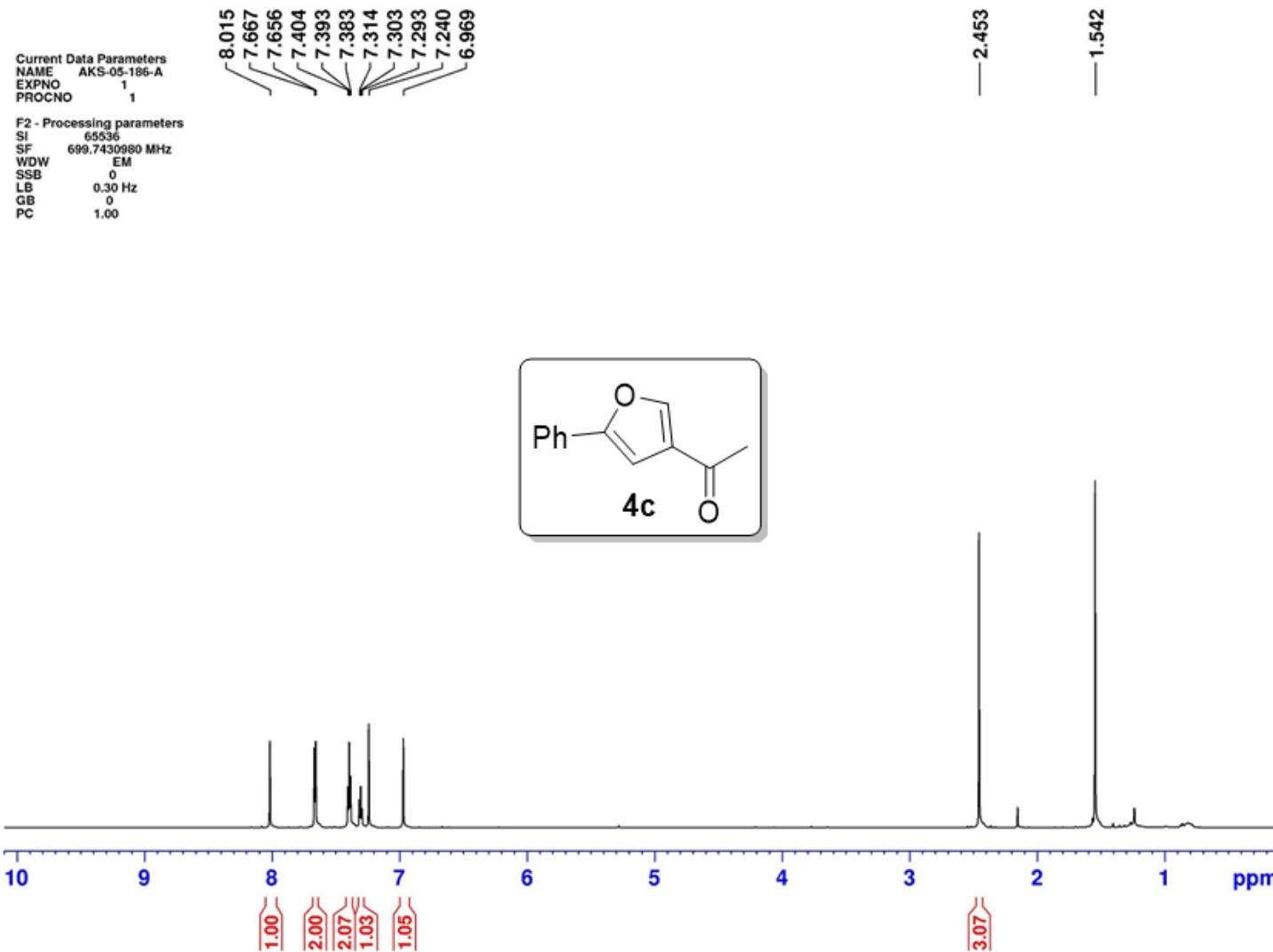
¹H NMR (CDCl₃, 700 MHz)



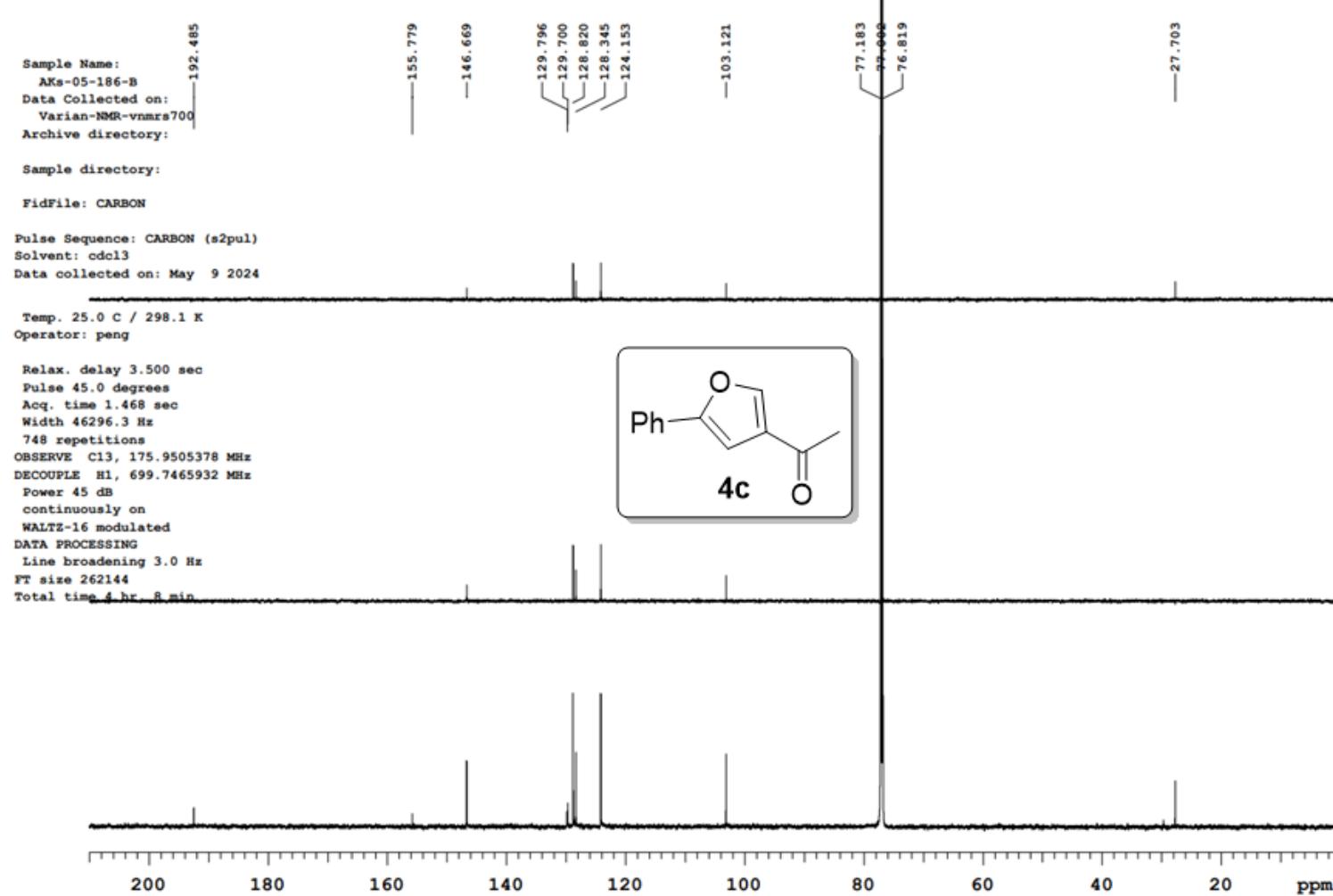
¹³C{¹H} and DEPT NMR (CDCl₃, 175 MHz)



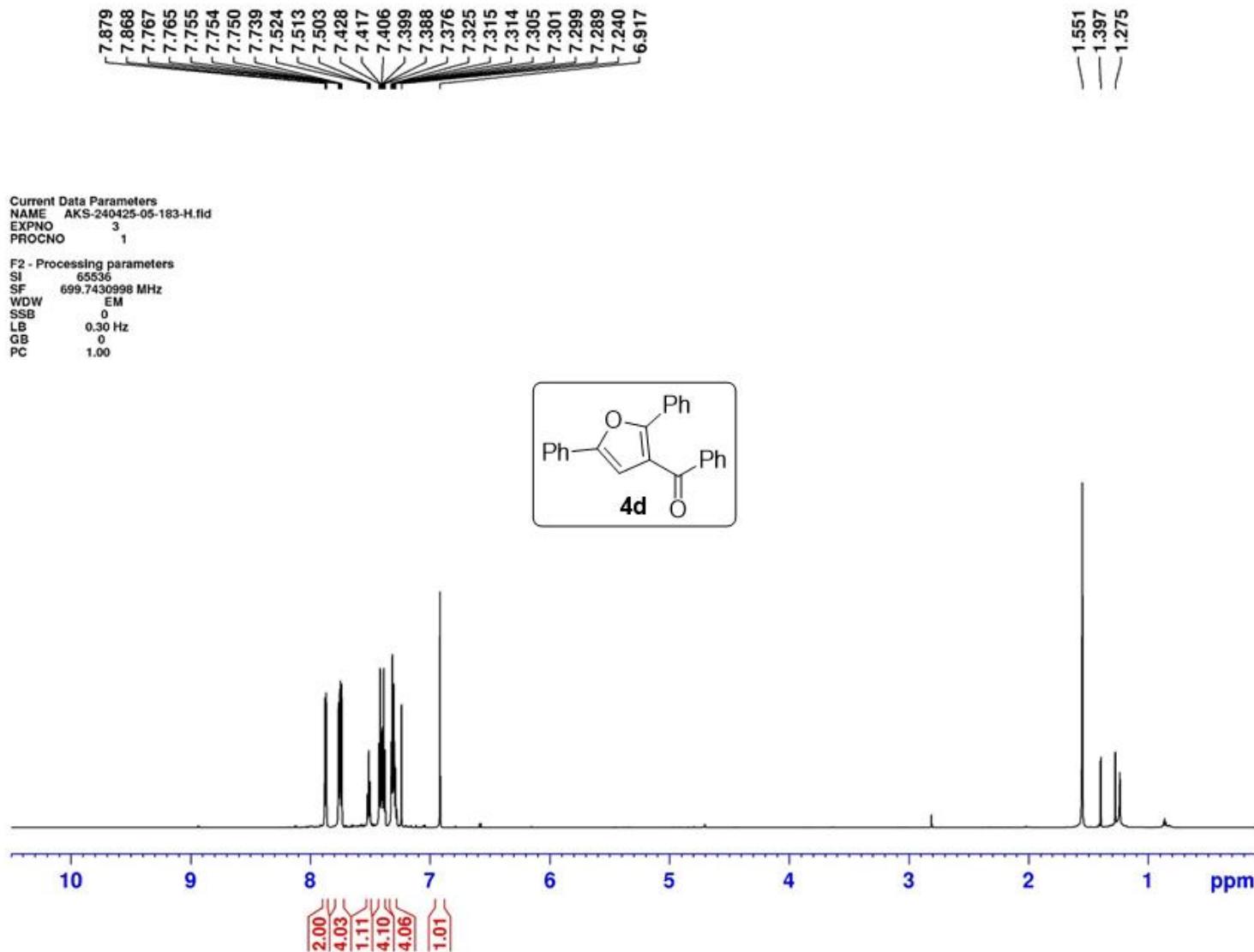
¹H NMR (CDCl₃, 700 MHz)



$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)



¹H NMR (CDCl₃, 700 MHz)



$^{13}\text{C}\{\text{H}\}$ and DEPT NMR (CDCl_3 , 175 MHz)

