Supporting Information

Iridium-Catalyzed Enantioselective Intramolecular Hydroarylation of Allylic Aryl Ethers Devoid of a Directing Group on the Aryl Group

Toshimichi Ohmura,* Satoshi Kusaka, Michinori Suginome*

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

ohmura@sbchem.kyoto-u.ac.jp; suginome@sbchem.kyoto-u.ac.jp

Contents

1. General

All iridium- and rhodium-catalyzed reactions were performed in glove box under an atmosphere of nitrogen with magnetic stirring. Other reactions were also carried out under an atmosphere of nitrogen with magnetic stirring unless otherwise noted. Materials were weighted by an electric balance, Sartorius CPA225D or Shimadzu AP225WD (readability: 0.01 mg). Column chromatography was performed with SiliaFlash (SILICYCLE, pH 7.0, 40-63 μm, 60 Å) or Chromatolex NH-DM2035 (Fuji Silysia Chemical, 60 μm, 120 Å). Latter was used mainly for purification of silyl enol ethers and products bearing a silyloxy group. Supercritical fluid chromatography (SFC) was performed by Jasco Analytical SFC system (PU-2080-CO_2Plus, PU-2080Plus, CO-2060Plus, AS-2059Plus, UV-2075Plus, CD-2095Plus, and BP-2080Plus) and Jasco Analytical SFC system (PU-4380, PU-4185, CO-4065, AS-4350, UV-4075, CD-4095, and BP-4340). ^{1}H NMR spectra were recorded on a Varian 400-MR (399.89 MHz), JEOL JNM-ECZ400S (399.89 MHz), and JEOL JNM-ECA600P (600.17 MHz) spectrometers. ^{13}C NMR spectra were recorded on Varian 400-MR (100.55 MHz), JEOL JNM-ECZ400S (100.55 MHz), and JEOL JNM-ECA600P (150.91 MHz) spectrometers. For ^{1}H NMR spectra, chemical shifts (δ) were reported relative to residual $CHCl_3$ (δ 7.26 ppm) in $CDCl_3$ or C_6H_6 (δ 7.16 ppm) in C_6D_6. For ^{13}C NMR spectra, chemical shifts (d) were reported relative to $CDCl_3$ (δ 77.16 ppm) or C_6D_6 (δ 128.06 ppm). Following abbreviations were used for multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. High resolution mass spectra (HRMS) were recorded on JEOL JMS-MS700 (EI) or Thermo Scientific Exactive Plus (APCI) spectrometers. Optical rotation was measured by JASCO DIP-1000 polarimeter.

2. Materials

Toluene (dehydrated Super plus, Kanto) and tetrahydrofuran (THF, dehydrated Super plus, Kanto, or Super dehydrated, stabilizer free, Wako) were purchased. $[IrCl(C_2H_4)_2]_2$ was prepared according to the procedure reported previously[1] and stored at –30 ºC under nitrogen atmosphere. $[RhCl(C_2H_4)_2]_2$,[2] $[Ir(cod)_2]BAr^F{}_4$,[3] $[IrCl(cod)]_2$,[4] and $[RhCl(coe)_2]_2$[5] were prepared according to the reported methods. (*S*)-**L1** [(*S*)-DTBM-SEGPHOS, TCI], (*S*)-**L2** [(*S*)-DM-SEGPHOS, TCI], (*S*)-**L3** [(*S*)-SEGPHOS, TCI], (*S*)-**L4** [(*S*)-DTBM-MeOBIPHEP, Aldrich], (*S*)-**L5** (STREM), (*S*)-

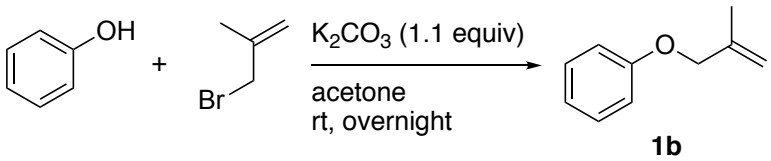
L6 (STREM), **L7** (d^Fppe, STREM), and **L8** (QuinoxP*, TCI) were used as received from commercial source. **L9** was prepared according to the reported method.[6] (±)-DTBM-SEGPHOS, which was used for synthesis of racemic compounds, was prepared according to the reported procedures.[7,8,9]

3. Preparation of Starting Materials

Allyl phenyl ether (**1a**) was purchased from TCI and distilled before use. Allylic aryl ethers **1b**-**o** were prepared by the following procedure.

3-1. Preparation of 1b and 1n

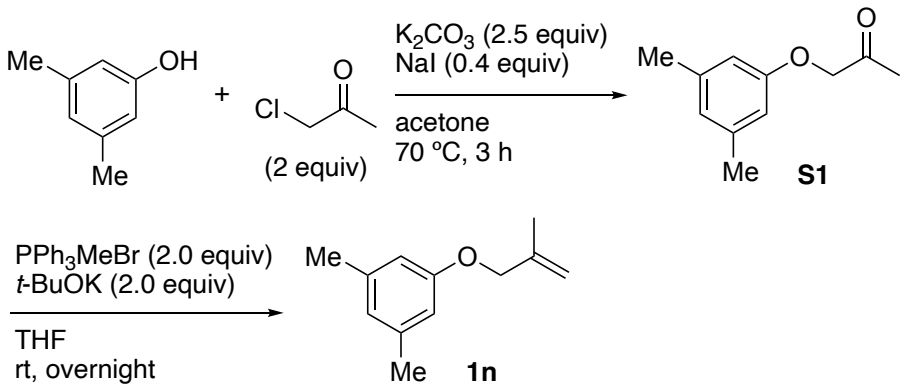
Methallyl phenyl ether (1b)



1b

An oven dried 100 mL three-neck flask, equipped with a magnetic stirring bar and a rubber septum, was charged with K_2CO_3 (nacalai, 1.52g, 11 mmol). The flask was evacuated and backfilled with nitrogen. Phenol (TCI, 940 mg, 10 mmol), acetone (5 mL), and 3-bromo-2-methyl-1-propene (TCI, 1.49 g, 11 mmol) were added to the flask, and the mixture was stirred overnight at room temperature. Water (30 mL) was added to the flask. The organic materials were extracted with EtOAc (75 mL x 3), washed with brine (75 mL), and dried over anhydrous sodium sulfate. The crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: 15% CH_2Cl_2 in hexane). **1b** (1.23 g, 8.3 mmol, 83%) was obtained as a colorless oil. **1b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.34 (m, 2H), 6.92-7.00 (m, 3H), 5.12 (s, 1H), 5.01 (s, 1H), 4.46 (s, 2H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 141.1, 129.5, 120.9, 114.9, 112.8, 71.7, 19.6. HRMS (EI, positive) *m/z* calcd for $C_{10}H_{12}O^+$ $[M]^+$: 148.0883, found: 148.0885.

Methallyl 3,5-dimethylphenyl ether (1n)



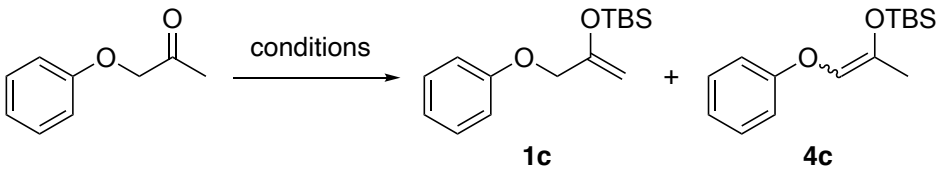
An oven dried 500 mL three-neck flask, equipped with a magnetic stirring bar and a rubber septum, was charged with NaI (nacalai, 2.40 g, 16 mmol) and K_2CO_3 (13.8 g, 100 mmol). The flask was evacuated and backfilled with nitrogen. Acetone (60 mL), 3,5-dimethylphenol (TCI, 4.89 g, 40 mmol), and chloroacetone (5.0 mL, 80 mmol) were added to the flask, and the mixture was stirred for 2 h at 70 °C. The resulting mixture was filtered through celite pad, and the crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: 30% EtOAc in hexane). **S1** (6.7 g, 37 mmol, 93%) was obtained as a colorless oil.

An oven dried 200 mL three-neck-flask, equipped with a magnetic stirring bar and a rubber septum, was charged with PPh_3MeBr (TCI, 7.14 g, 20 mmol). The powder was stirred for 1 h in vacuo at room temperature to dry. The flask was evacuated and backfilled with nitrogen. THF (20 mL) was added to the flask, and the mixture was cooled to 0 ºC by an ice/water bath. *t*-BuOK (TCI, 2.25 g, 20 mmol) was added to the flask under nitrogen flow, and the mixture was stirred at 0 ºC for 2 h. **S1** (1.79 g, 10 mmol) was added slowly to the flask. The ice/water bath was removed, and the mixture was stirred at room temperature overnight. Brine (50 mL) was added to the flask. The organic materials were extracted with hexane (50 mL x 3), washed with brine (50 mL), and dried over anhydrous magnesium sulfate. **1n** (1.10 g, 6.3 mmol, 62%) was obtained as a colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: 5% EtOAc in hexane) and Kugelrhor distillation. **1n**[10]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (s, 1H), 6.59 (s, 2H), 5.12 (s, 1H), 5.00 (s, 1H), 4.43 (s, 2H), 2.32 (s, 6H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 141.3, 139.2, 122.7, 112.58, 112.65, 71.7, 21.6, 19.6. HRMS (EI, positive) *m/z* calcd for $C_{12}H_{16}O^+$ $[M]^+$: 179.1196, found: 176.1201.

3-2. Preparation of 1c–m, 1o, and 4c

We screened reaction conditions for preparation of **1c** from phenoxyacetone (Table S1). Deprotonation of phenoxyacetone with LDA (1.2 equiv) in THF/hexane at –78 °C and following treatment with TBSCl afforded **4c** selectively (entry 1). Use of LiHMDS with or without DMPU also resulted in selective formation of **4c** (entries 2 and 3). We found that favorable formation of **1c** over **4c** (**1c**:**4c** = 62:38) was achieved by the reaction using Et_3N and TBSOTf in CH_2Cl_2 (entry 4).

Table S1. Screening of Reaction Conditions for Conversion of Phenoxyacetone to **1c**

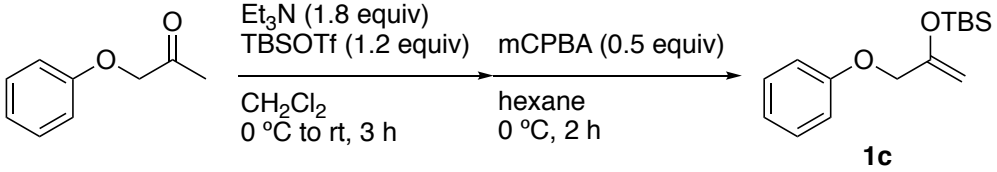


1c **4c**

entry	conditions	**1c**:**4c**
1	LDA (1.2 equiv), THF/hexane, –78 °C, 0.5 h then TBSCl (1.5 equiv), THF/hexane, –78 °C to rt, 15 h	5:95
2	LiHMDS (1.2 equiv), THF/hexane, –78 °C, 0.5 h then TBSCl (1.5 equiv), THF/hexane, –78 °C to rt, 15 h	5:95
3	LiHMDS (1.2 equiv), DMPU, THF/hexane, –78 °C, 0.5 h then TBSCl (1.5 equiv), THF/hexane, –78 °C to rt, 15 h	10:90
4	Et_3N (1.8 equiv), TBSOTf (1.2 equiv), CH_2Cl_2, 0 °C to rt, 12 h	62:38

Isolation of **1c** from the mixture of **1c** and **4c** by column chromatography was not successful. Treatment of the mixture with mCPBA in hexane at 0 °C resulted in selective conversion of **4c** to the compounds derived from the epoxide,[11] by which **1c** could be isolated by column chromatography on silica gel. This procedure was applied to preparation of **1d**–**m** and **1o**.

2-*tert*-Butyldimethylsilyloxyprop-1-ene-3-yl phenyl ether (1c)

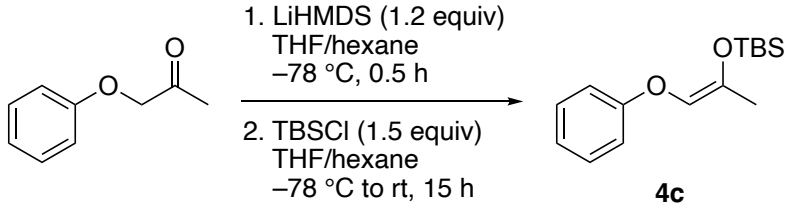


1c

An oven dried 300 mL two-neck flask, equipped with a magnetic stirring bar, was evacuated

and backfilled with nitrogen. Phenoxyacetone (Aldrich, 3.00 g, 20 mmol), CH_2Cl_2 (80 mL), and Et_3N (nacalai, 3.64 g, 36 mmol) were added to the flask, and the mixture was cooled to 0 ºC by an ice/water bath. Fleshly prepared TBSOTf (5.33 g, 24 mmol) was then added dropwise to the flask, and the resulting mixture was stirred for 3 h at room temperature. Water (50 mL) was added to the flask. The organic materials were extracted with CH_2Cl_2 (75 mL x 3), washed with brine (50 mL), and dried over anhydrous sodium sulfate. The resulting crude products were purified by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). A mixture of **1c** and an isomer **4c** was obtained (4.69 g, 17.7 mmol). The mixture was treated with mCPBA (TCI, 2.5 g, containing ca.30% water) in hexane (20 mL) at 0 ºC for 2 h, by which **4c** was converted selectively to the compounds derived from the corresponding epoxide. **1c** (2.49 g, 9.4 mmol, 47%) was obtained as a colorless oil after purification by chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). **1c**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.07-7.13 (m, 2H), 6.80-6.89 (m, 3H), 4.52 (s, 1H), 4.36 (s, 1H), 4.20 (s, 2H), 0.95 (s, 9H), 0.13 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 159.1, 154.8, 129.7, 121.2, 115.1, 92.5, 69.0, 25.8, 18.3, -4.5. HRMS (APCI, positive) *m/z* calcd for $C_{15}H_{25}O_2Si^+$ $[M + H]^+$: 265.1618, found: 265.1622.

2-*tert*-Butyldimethylsilyloxyprop-1-ene-1-yl 4-phenyl ether (**4c**)

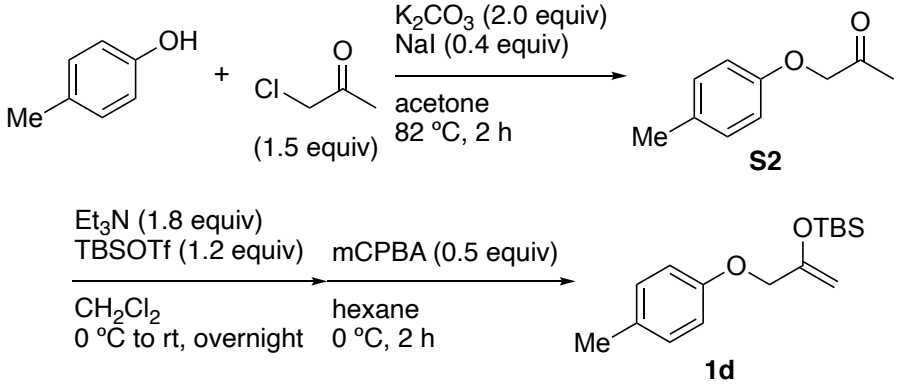


4c

An oven dried 50 mL two-neck flask, equipped with a magnetic stirring bar, was evacuated and backfilled with nitrogen. Phenoxyacetone (Aldrich, 450 mg, 3.0 mmol) and THF (5 mL) were added to the flask, and the mixture was cooled to –78 ºC by an dry ice/acetone bath. Fleshly prepared LiHMDS (3.6 mmol) in THF (2 mL) was then added dropwise to the flask, and the resulting mixture was stirred for 30 min at –78 ºC. TBSCl (540 mg, 3.6 mmol) was added to the flask, and the resulting mixture was stirred overnight at room temperature. Water (20 mL) was added to the flask. The organic materials were extracted with hexane (30 mL x 3), washed with brine (30 mL), and dried over anhydrous sodium sulfate. **4c** (*Z*:*E* = 97:3, containing 5% of **1c**, 550 mg, 2.1 mmol, 68%) was obtained as a colorless oil after purification by chromatography on silica

gel (Chromatolex NH-DM2035; eluent: hexane). (*Z*)-**4c**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.06-7.13 (m, 2H), 6.92-6.97 (m, 2H), 6.81-6.88 (m, 1H), 5.66 (q, J = 1.2 Hz, 1H), 1.58 (s, 3H), 1.00 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 158.2, 137.8, 129.8, 122.9, 122.0, 115.8, 25.9, 18.6, 18.5, –4.2. HRMS (EI, positive) *m/z* calcd for $C_{15}H_{24}O_2Si^+$ [M]$^+$: 264.1540, found: 264.1539.

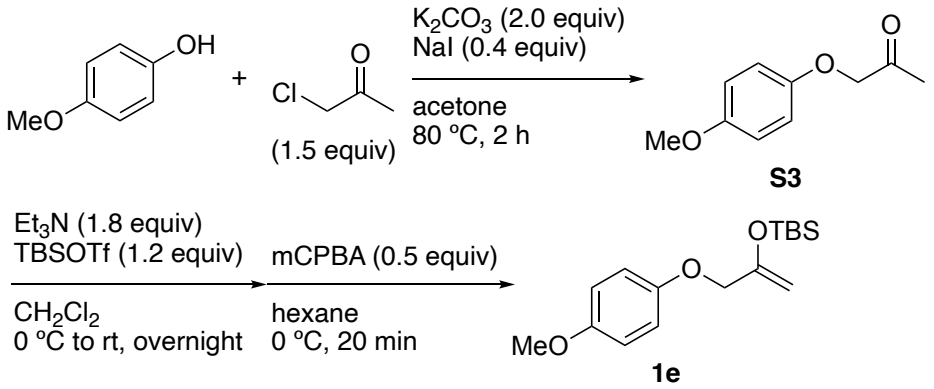
2-*tert*-Butyldimethylsilyloxyprop-1-ene-3-yl 4-methylphenyl ether (1d)



According to the procedure given for preparation of **S1** (see above), the reaction of *p*-cresol (TCI, 2.02 g, 20.0 mmol) with chloroacetone (2.4 mL, 30 mmol) was carried out for 2 h at 82 °C (reflux) in acetone (40 mL) using K_2CO_3 (5.51 g, 40 mmol) and NaI (1.20 g, 8 mmol). **S2** (2.94 g, 19 mmol, 96%) was obtained as a colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: 10% EtOAc in hexane).

According to the procedure given for preparation of **1c** (see above), **S2** (1.80 g, 10 mmol) was reacted with Et_3N (2.5 mL, 18 mmol) and TBSOTf (2.8 mL, 12 mmol) in CH_2Cl_2 (40 mL). The crude products (2.65 g, 8.9 mmol, ca. 6:4 mixture of isomers) were then treated with mCPBA (1.2 g, containing ca. 30% water) in hexane (10 mL) at 0 ºC for 4 h. **1d** (1.40 g, 5.0 mmol, 50%) was obtained as a colorless oil after purification by chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). **1d**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.90-6.96 (m, 2H), 6.81-6.87 (m, 2H), 4.56 (s, 1H), 4.37 (s, 1H), 4.23 (s, 2H), 2.10 (s, 3H), 0.96 (s, 9H), 0.14 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 157.2, 154.9, 130.2, 130.1, 115.0, 92.4, 69.2, 25.8, 20.5, 18.3, –4.5. HRMS (APCI, positive) *m/z* calcd for $C_{16}H_{27}O_2Si^+$ [M + H]$^+$: 279.1775, found: 279.1778.

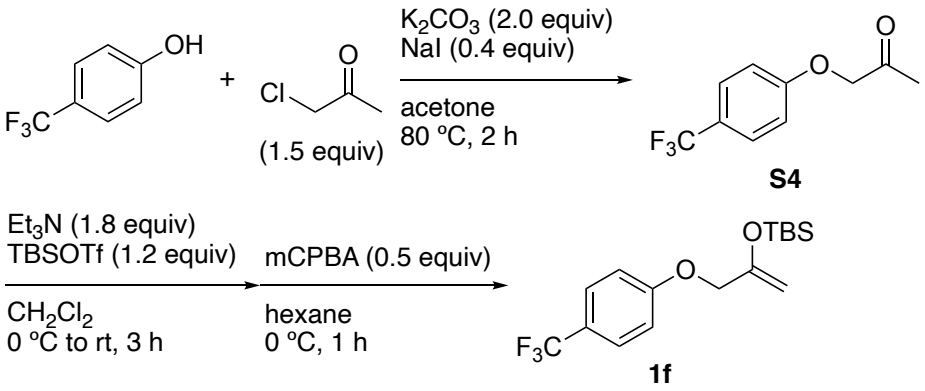
2-*tert*-Butyldimethylsilyloxyprop-1-ene-3-yl 4-methoxyphenyl ether (1e)



According to the procedure given for preparation of **S1** (see above), the reaction of 4-methoxyphenol (TCI, 2.48 g, 20.0 mmol) with chloroacetone (2.4 mL, 30 mmol) was carried out for 2 h at 80 °C in acetone (40 mL) using K_2CO_3 (5.51 g, 40 mmol) and NaI (1.20 g, 8 mmol). **S3** (3.2 g, 17.8 mmol, 89%) was obtained as colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: 10% EtOAc in hexane).

According to the procedure given for preparation of **1c** (see above), **S3** (1.80 g, 10 mmol) was reacted with Et_3N (2.5 mL, 18 mmol) and TBSOTf (2.8 mL, 12 mmol) in CH_2Cl_2 (40 mL). The crude products (2.61 g, 8.9 mmol, a 6:4 mixture of isomers) were then treated with mCPBA (890 mg, containing ca.30% water) in hexane (10 mL) for 20 min at 0 °C. **1e** (1.41 g, 4.8 mmol, 48%) was obtained as a white solid after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). **1e**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.79-6.85 (m, 2H) 6.69-6.75 (m, 2H), 4.56-4.57 (m, 1H), 4.38 (s, 1H), 4.22 (s, 2H), 3.32 (s, 3H), 0.96 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 155.1, 154.7, 153.3, 116.1, 115.0, 92.4, 69.8, 55.2, 25.8, 18.3, –4.5. HRMS (APCI, positive) *m/z* calcd for $C_{16}H_{27}O_3Si^+$ $[M+H]^+$: 295.1724, found: 295.1728.

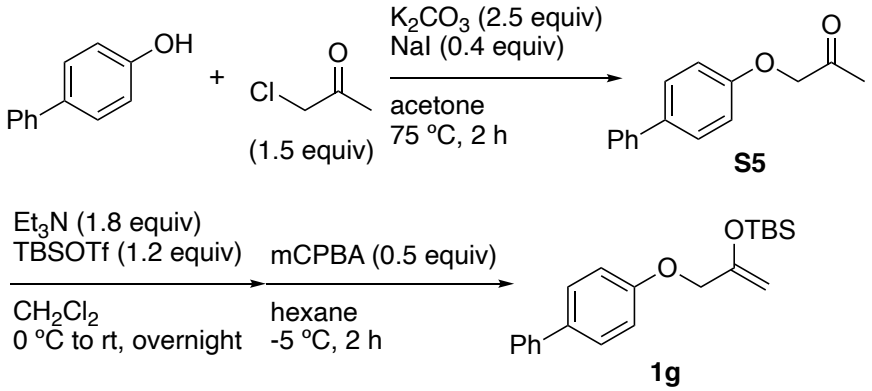
2-*tert*-Butyldimethylsilyloxyprop-1-ene-3-yl 4-trifluoromethylphenyl ether (1f)



According to the procedure given for preparation of **S1** (see above), the reaction of 4-hydroxybenzotrifluoride (TCI, 2.17 g, 13.4 mmol) with chloroacetone (2.4 mL, 30 mmol) was carried out for 2 h at 80 °C (reflux) in acetone (40 mL) using K_2CO_3 (5.51 g, 40 mmol) and NaI (1.20 g, 8 mmol). **S4** (2.71 g, 12.5 mmol, 93%) was obtained as colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: 10% EtOAc in hexane).

According to the procedure given for preparation of **1c** (see above), **S4** (2.18 g, 10 mmol) was reacted with Et_3N (2.5 mL, 18 mmol) and TBSOTf (2.8 mL, 12 mmol) in CH_2Cl_2 (40 mL). The crude products (3.00 g, 9.0 mmol, a 6:4 mixture of isomers) were then treated with mCPBA (1.1 g, containing ca.30% water) in hexane (10 mL) for 1 h at 0 °C. **1f** (1.42 g, 4.3 mmol, 43%) was obtained as a colorless oil after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane only). **1f**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.29 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 8.8 Hz, 2H), 4.38-4.41 (m, 1H), 4.31-4.33 (m, 1H), 4.04 (s, 2H), 0.94 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6, ^{1}H and ^{19}F simultaneous decoupling) δ 161.3, 154.0, 127.1, 125.3, 123.3, 115.0, 92.8, 69.1, 25.7, 18.3, –4.6. HRMS (APCI, positive) *m/z* calcd for $C_{16}H_{24}F_3O_2Si^+$ [M + H]$^+$: 333.1492, found: 333.1496.

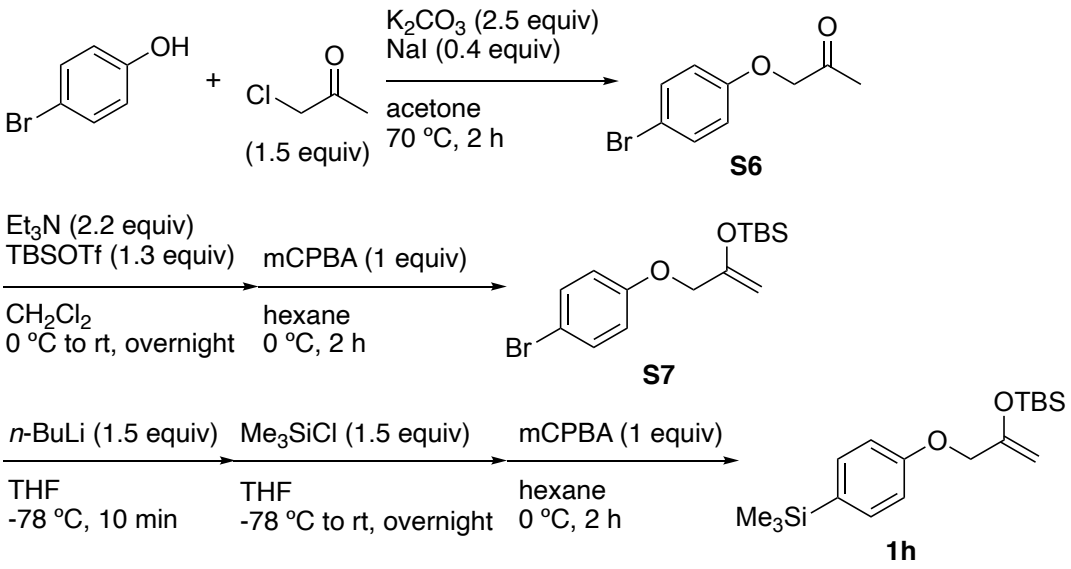
2-*tert*-Butyldimethylsilyloxyprop-1-ene-3-yl 4-phenylphenyl ether (1g)



According to the procedure given for preparation of **S1** (see above), the reaction of 4-phenylphenol (3.40 g, 20 mmol) with chloroacetone (TCI, 2.5 mL, 30 mmol) was carried out for 2 h at 75 °C in acetone using K_2CO_3 (6.81 g, 50 mmol) and NaI (1.2 g, 8.0 mmol). **S5** (3.05 g, 13 mmol, 67%) was obtained as a colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: 30% EtOAc in hexane).

According to the procedure given for preparation of **1c** (see above), **S5** (2.26 g, 10 mmol) was reacted with Et_3N (2.8 mL, 20 mmol) and TBSOTf (2.8 mL, 12 mmol) in CH_2Cl_2 (20 mL). The crude products (2.72 g, 8.0 mmol, a 6:4 mixture of isomers) were then treated with mCPBA (1.5 g, containing ca. 30% water, ca. 6 mmol) in hexane for 2 h at –5 °C. **1g** (1.40 g, 4 mmol, 41%) was obtained as a white solid after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane only). **1g**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.44-7.49 (m, 2H), 7.37-7.42 (m, 2H), 7.21-7.26 (m, 2H), 7.11-7.18 (m, 1H), 6.89-6.94 (m, 2H), 4.55-4.57 (m, 1H), 4.38-4.40 (m, 1H), 4.25 (s, 2H), 0.98 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 158.7, 154.7, 141.4, 134.6, 129.0, 128.5, 127.2, 126.9, 115.5, 92.6, 69.2, 25.8, 18.3, –4.5. HRMS (APCI, positive) *m/z* calcd for $C_{21}H_{29}O_2Si^+$ $[M + H]^+$: 341.1931, found: 341.1925.

2-*tert*-Butyldimethylsilyloxyprop-1-ene-3-yl 4-trimethylsilylphenyl ether (1h)



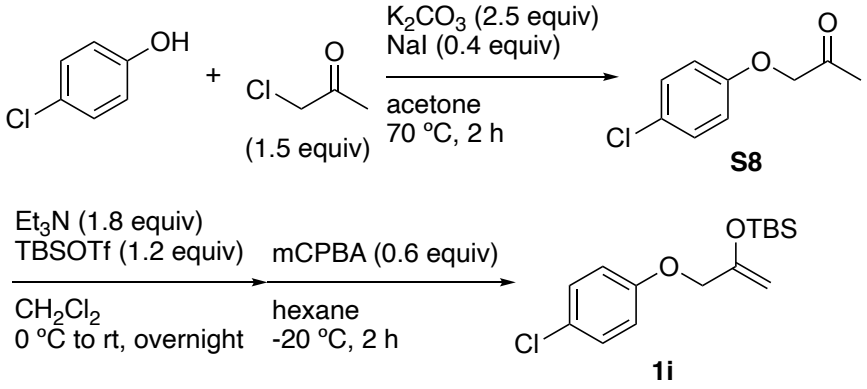
According to the procedure given for preparation of **S1** (see above), the reaction of 4-bromophenol (8.65 g, 50 mmol) with chloroacetone (TCI, 6.0 mL, 75 mmol) was carried out for 2 h at 70 °C in acetone using K_2CO_3 (17.3 g, 125 mmol) and NaI (3.00 g, 20 mmol). **S6** (10.31 g, 45 mmol, 90%) was obtained as a colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: 30% EtOAc in hexane).

According to the procedure given for preparation of **1c** (see above), **S6** (9.86 g, 43 mmol) was reacted with Et_3N (13.3 mL, 96 mmol) and TBSOTf (13.3 mL, 58 mmol) in CH_2Cl_2 (100 mL). The crude products (12.7 g, 37 mmol, a 6:4 mixture of isomers) were then treated with mCPBA (9.12 g, containing ca. 30% water, ca. 37 mmol) in hexane for 2 h at 0 °C. **S7** (5.6 g, 16 mmol, 38%, a 9:1 mixture of isomers) was obtained as a colorless oil after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane).

An oven dried 200 mL two-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, was evacuated and backfilled with nitrogen. THF (20 mL) and **S7** (1.72 g, 5 mmol, a 9:1 mixture of isomers) were added to the flask, and the mixture was cooled to –78 ºC by dry ice/acetone bath. *n*-BuLi (1.6 M in hexane, 4.7 mL, 7.5 mmol) was added slowly to the flask, and the resulting mixture was stirred for 10 min at –78 ºC. Me_3SiCl (TCI, 950 µL, 7.5 mmol) was added slowly to the flask. The dry ice/acetone bath was removed, and the mixture was stirred overnight at room temperature. Water (50 mL) was added to the flask. The organic materials were extracted with hexane (50 mL x 3), washed with brine (50 mL x 1), and dried over anhydrous

sodium sulfate. The crude product was purified by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). The mixture (1.51 g, 5 mmol, a 9:1 mixture of isomers) was then treated with mCPBA (1.23 g, containing ca. 30% water, ca. 5 mmol) in hexane for 2 h at 0 °C. **1h** (1.36 g, 4 mmol, 81%) was obtained as a colorless oil after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane) and Kugelrhor distillation. **1h**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.37-7.41 (m, 2H), 6.92-6.97 (m, 2H), 4.53-4.55 (m, 1H), 4.36-4.38 (m, 1H), 4.26 (s, 2H), 0.96 (s, 9H), 0.23 (s, 9H), 0.14 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 159.9, 154.7, 135.1, 131.6, 114.8, 92.6, 68.9, 25.8, 18.3, –0.8, –4.5. HRMS (EI, positive) *m/z* calcd for $C_{18}H_{32}O_2Si_2^+$ $[M]^+$: 336.1935, found: 336.1940.

2-*tert*-Butyldimethylsilyloxyprop-1-ene-3-yl 4-chlorophenyl ether (1i)

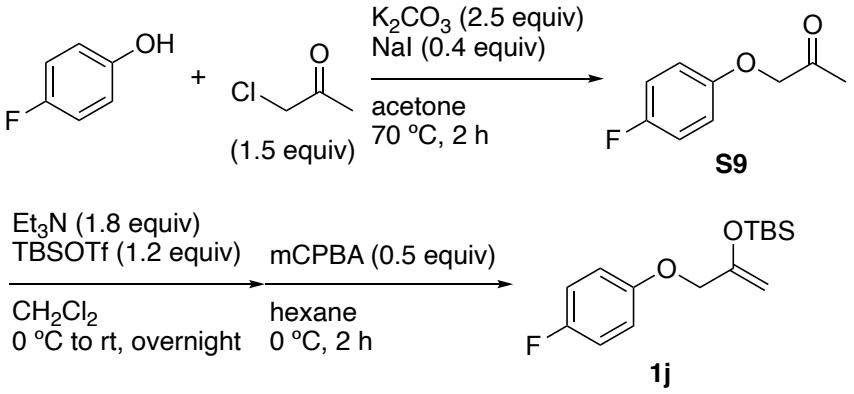


According to the procedure given for preparation of **S1** (see above), the reaction of 4-chlorophenol (1.97 mL, 20 mmol) with chloroacetone (TCI, 2.50 mL, 30 mmol) was carried out for 2 h at 70 °C in acetone using K_2CO_3 (6.9 g, 50 mmol) and NaI (1.21 g, 8 mmol). **S8** (3.02 g, 16 mmol, 82%) was obtained as a colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: hexane).

According to the procedure given for preparation of **1c** (see above), **S8** (1.85 g, 10 mmol) was reacted with Et_3N (2.6 mL, 18 mmol) and TBSOTf (2.6 mg, 12 mmol) in CH_2Cl_2 (20 mL). The crude products (2.72 g, 9 mmol, a 6:4 mixture of isomers) were then treated with mCPBA (1.23 g, containing ca. 30% water, ca. 5 mmol) in hexane for 2 h at –20 °C. Since the small amount of undesired isomer was still remained, mCPBA (120 mg, containing ca. 30% water, ca. 0.5 mmol) was added and the mixture was stirred at 0 °C for 30 min. **1i** (1.20 g, 4 mmol, 40%) was obtained

as a colorless oil after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). **1i**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.00-7.05 (m, 2H), 6.52-6.57 (m, 2H), 4.42-4.44 (m, 1H), 4.31-4.34 (m, 1H), 4.03 (s, 2H), 0.94 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 157.6, 154.3, 129.6, 126.1, 116.4, 92.6, 69.3, 25.8, 18.3, –4.6. HRMS (APCI, positive) *m/z* calcd for $C_{15}H_{24}ClO_2Si^+$ $[M + H]^+$: 299.1229, found: 299.1223.

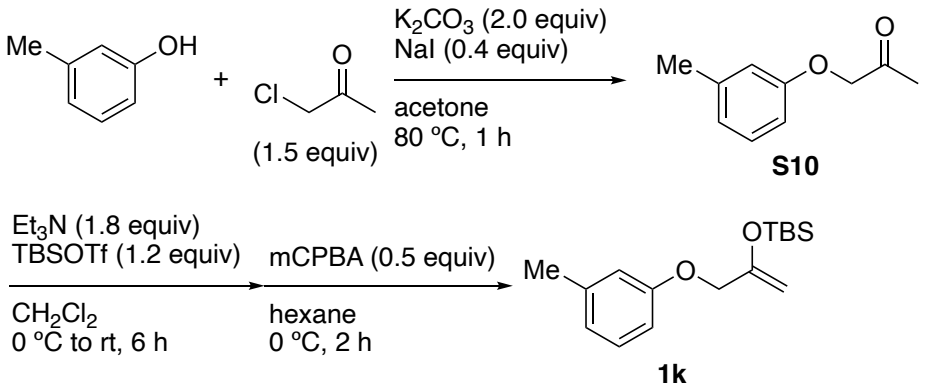
2-*tert*-Butyldimethylsilyloxyprop-1-ene-3-yl 4-fluorophenyl ether (1j)



According to the procedure given for preparation of **S1** (see above), the reaction of 4-fluorophenol (2.24 g, 20 mmol) with chloroacetone (TCI, 2.5 mL, 30 mmol) was carried out for 2 h at 70 °C in acetone using K_2CO_3 (13.8 g, 50 mmol) and NaI (1.2 g, 8 mmol). **S9** (2.86 g, 17 mmol, 85%) was obtained as a colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: hexane).

According to the procedure given for preparation of **1c** (see above), **S9** (2.52 g, 15 mmol) was reacted with Et_3N (2.73 g, 27 mmol) and TBSOTf (4.76 g, 18 mmol) in CH_2Cl_2 (30 mL). The crude products (3.52 g, 12 mmol, a 6:4 mixture of isomers) were then treated with mCPBA (1.4 g, containing ca. 30% water, ca. 5.7 mmol) in hexane for 2 h at 0 °C. **1j** (1.80 g, 6.4 mmol, 53%) was obtained as a colorless oil after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). **1j**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.70-6.77 (m, 2H), 6.56-6.62 (m, 2H), 4.46-4.48 (m, 1H), 4.33-4.35 (m, 1H), 4.08 (s, 2H), 0.95 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6, ^{1}H and ^{19}F simultaneous decoupling) δ 157.8, 155.1, 154.6, 116.1, 116.0, 92.5, 69.6, 25.8, 18.3, –4,6. HRMS (APCI, positive) *m/z* calcd for $C_{15}H_{24}FO_2Si^+$ $[M + H]^+$: 283.1524, found: 283.1518.

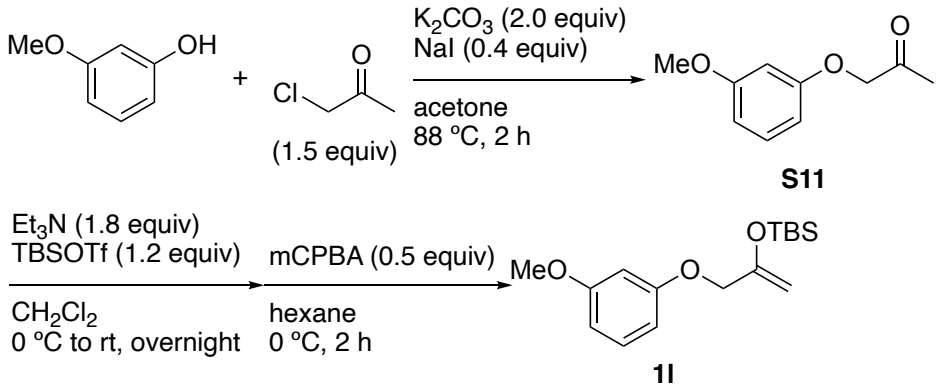
2-*tert*-Butyldimethylsilyloxyprop-1-ene-3-yl 3-methylphenyl ether (1k)



According to the procedure given for preparation of **S1** (see above), the reaction of 3-methylphenol (2.16 g, 20 mmol) with chloroacetone (TCI, 2.4 mL, 30 mmol) was carried out for 1 h at 80 °C in acetone using K_2CO_3 (5.5 g, 40 mmol) and NaI (1.2 g, 8 mmol). **S10** (3.12 g, 20 mmol, 100%) was obtained as a colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: 10% EtOAc in hexane).

According to the procedure given for preparation of **1c** (see above), **S10** (1.64 g, 10 mmol) was reacted with Et_3N (2.5 mL, 18 mmol) and TBSOTf (2.8 mL, 12 mmol) in CH_2Cl_2 (40 mL). The crude products (2.70 g, 9.7 mmol, a 6:4 mixture of isomers) were then treated with mCPBA (1.23 g, containing ca. 30% water, ca. 5 mmol) in hexane for 2 h at 0 °C. **1k** (1.34 g, 4.8 mmol, 50%) was obtained as a colorless oil after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). **1k**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.06 (t, J = 8.0 Hz, 1H), 6.78 (s, 1H), 6.74 (dd, J = 8.0, 2.4 Hz, 1H), 6.66-6.70 (m, 1H), 4.55-4.58 (m, 1H), 4.37-4.39 (m, 1H), 4.24 (s, 2H), 2.11 (s, 3H), 0.96 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 159.2, 154.9, 139.5, 129.6, 122.1, 116.0, 112.2, 92.4, 69.0, 25.8, 21.5, 18.3, –4.5. HRMS (APCI, positive) *m/z* calcd for $C_{16}H_{27}O_2Si^+$ $[M + H]^+$: 279.1775, found: 279.1778.

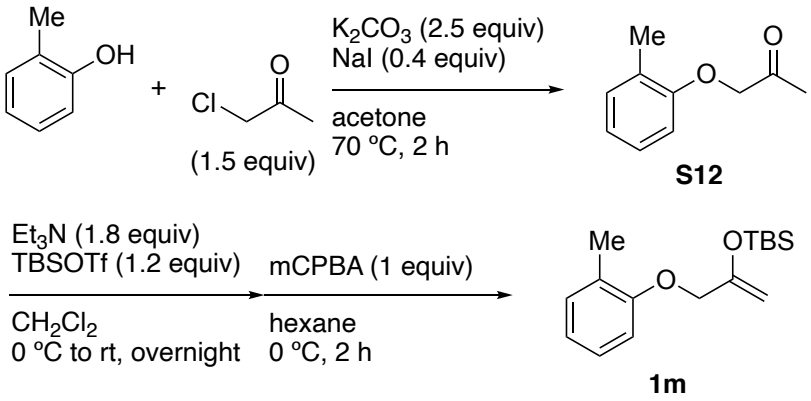
2-*tert*-Butyldimethylsilyloxyprop-1-ene-3-yl 3-methoxyphenyl ether (1l)



According to the procedure given for preparation of **S1** (see above), the reaction of 3-methoxyphenol (2.48 g, 20 mmol) with chloroacetone (TCI, 2.4 mL, 30 mmol) was carried out for 2 h at 88 °C in acetone using K_2CO_3 (5.5 g, 40 mmol) and NaI (1.2 g, 8 mmol). **S11** (3.24 g, 18 mmol, 90%) was obtained as a colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: 10% EtOAc in hexane).

According to the procedure given for preparation of **1c** (see above), **S11** (1.83 g, 10 mmol) was reacted with Et_3N (2.4 mL, 18 mmol) and TBSOTf (2.8 mL, 12 mmol) in CH_2Cl_2 (40 mL). The crude products (2.70 g, 9.2 mmol, a 7:3 mixture of isomers) were then treated with mCPBA (1.20 g, containing ca. 30% water, ca. 5 mmol) in hexane for 2 h at 0 °C. **1l** (1.27 g, 4.3 mmol, 43%) was obtained as a colorless oil after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). **1l**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.03 (t, J = 8.4 Hz, 1H), 6.64 (t, J = 2.4 Hz, 1H), 6.54 (ddd, J = 8.4, 2.4, 0.8 Hz, 1H), 6.47 (ddd, J = 8.4, 2.4, 0.8 Hz, 1H), 4.52-4.54 (m, 1H), 4.35-4.37 (m, 1H), 4.23 (s, 2H), 3.31 (s, 3H), 0.95 (s, 9H), 0.14 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 161.6, 160.5, 154.8, 130.2, 107.4, 107.0, 101.8, 92.5, 69.1, 54.8, 25.8, 18.3, –4.5. HRMS (APCI, positive) *m/z* calcd for $C_{16}H_{27}O_3Si^+$ $[M + H]^+$: 295.1724, found: 295.1726.

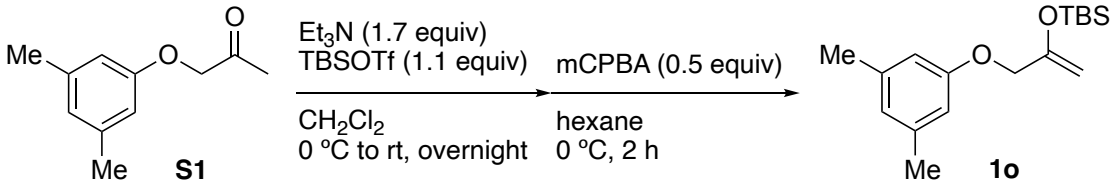
2-*tert*-Butyldimethylsilyloxyprop-1-ene-3-yl 2-methylphenyl ether (1m)



According to the procedure given for preparation of **S1** (see above), the reaction of *o*-cresol (2.16 g, 20 mmol) with chloroacetone (TCI, 2.4 mL, 30 mmol) was carried out for 2 h at 70 °C in acetone using K_2CO_3 (5.5 g, 40 mmol) and NaI (1.2 g, 8.0 mmol). **S12** (3.22 g, 20 mmol, 98%) was obtained as a colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: 10% EtOAc in hexane).

According to the procedure given for preparation of **1c** (see above), **S12** (1.64 g, 10 mmol) was reacted with Et_3N (2.5 mL, 18 mmol) and TBSOTf (2.8 mL, 12 mmol) in CH_2Cl_2 (20 mL). The crude products (2.67 g, 9.9 mmol, a 9:1 mixture of isomers) were then treated with mCPBA (1.2 g, 5.0 mmol) in hexane for 2 h at 0 °C. **1m** (1.21 g, 4.5 mmol, 45%) was obtained as a colorless oil after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). **1m**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.00-7.08 (m, 2H), 6.83 (td, J = 7.2, 0.8 Hz, 1H), 6.65 (d, J = 8.4 Hz, 1H), 4.55-4.58 (m, 1H), 4.37 (s, 1H), 4.22 (s, 2H), 2.31 (s, 3H), 0.95 (s, 9H), 0.13 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 157.2, 155.0, 131.1, 127.1, 126.9, 121.0, 111.6, 91.9, 69.0, 25.8, 18.3, 16.6, –4.6. HRMS (APCI, positive) *m/z* calcd for $C_{16}H_{27}O_2Si^+$ $[M + H]^+$: 279.1775, found: 279.1768.

2-*tert*-Butyldimethylsilyloxyprop-1-ene-3-yl 3,5-dimethylphenyl ether (1o)



According to the procedure given for preparation of **1c** (see above), **S1** (1.77 mg, 10.0 mmol)

was reacted with Et_3N (2.5 mL, 17.0 mmol) and TBSOTf (2.5 mL, 11.0 mmol) in CH_2Cl_2 (20 mL). The crude products (2.87 g, 9.80 mmol, a 6:4 mixture of isomers) were then treated with mCPBA (1.22 g, containing ca. 30% water, ca. 5 mmol) in hexane for 2 h at 0 °C. **1o** (1.27 g, 4.3 mmol, 43%) was obtained as a colorless oil after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). **1o**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.64 (s, 2H), 6.51 (s, 1H), 4.59 (s, 1H), 4.39 (s, 1H), 4.27 (s, 2H), 2.13 (s, 6H), 0.96 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 159.3, 155.0, 139.2, 123.2, 113.1, 92.4, 69.0, 25.8, 21.5, 18.3, –4.5. HRMS (EI, positive) *m/z* calcd for $C_{17}H_{28}O_2Si^+$ $[M]^+$: 292.1853, found: 292.1855.

4. Initial Findings (Scheme 2)

General procedure: In a glovebox, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with $[IrCl(C_2H_4)_2]_2$ (0.0040 mmol), (*S*)-**L1** (0.0080 mmol), **1** (0.10 mmol), and toluene (0.2 mL). The tube was sealed by the stopcock, and was taken out from the glove box. The mixture was stirred at 135 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 1–6 h, the tube was cooled to room temperature. Diphenylmethane (16 mg, 0.10 mmol, internal standard) was added, and the resulting mixture was analyzed by ^{1}H NMR to determine the yields of **3** and **4**.

The reaction of 1a (entry 1, Scheme 2a)

According to the general procedure, the reaction was carried out at 135 ºC for 1 h using $[IrCl(C_2H_4)_2]_2$ (2.4 mg, 0.0042 mmol), (*S*)-**L1** (9.7 mg, 0.0080 mmol), **1a** (15 mg, 0.10 mmol), and toluene (0.2 mL). **4a**[12] was formed in 90% yield as a *Z*/*E* mixture (61:39). No formation of **3a** was observed.

The reaction of 1b (entry 2, Scheme 2a)

According to the general procedure, the reaction was carried out at 135 ºC for 6 h using $[IrCl(C_2H_4)_2]_2$ (2.2 mg, 0.0038 mmol), (*S*)-**L1** (9.6 mg, 0.0081 mmol), **1b** (14.2 mg, 0.096 mmol), and toluene (0.2 mL). **3b**[13] and **4b**[14] were formed in 11 and 89% yields, respectively.

The reaction of 1c (entry 3, Scheme 2a)

According to the general procedure, the reaction was carried out at 135 ºC for 6 h using

$[IrCl(C_2H_4)_2]_2$ (6.6 mg, 0.012 mmol), (*S*)-**L1** (29.2 mg, 0.025 mmol), **1c** (76.6 mg, 0.29 mmol), and toluene (0.6 mL). **3c** and **4c** were formed in 89 and 7% yields, respectively. **4c** was formed as a *Z*/*E* mixture (72:28). For characterization data of **3c**, see Section 5.

The reaction of 4c (Scheme 2b)

According to the general procedure, the reaction was carried out at 135 ºC for 6 h using $[IrCl(C_2H_4)_2]_2$ (4.5 mg, 0.0080 mmol), (*S*)-**L1** (19.7 mg, 0.017 mmol), **4c** (*Z*:*E* = 97:3, containing 5% of **1c**, 50.0 mg, 0.19 mmol), and toluene (0.2 mL). Formation of only a small amount of **3c** (6%), mainly from **1c**, was observed, indicating that **4c** did not undergo intramolecular hydroarylation under the identical conditions. **4c** (69%) was recovered with the *Z*/*E* ratio of 68:32, indicating the geometrical isomerization took place under the conditions.

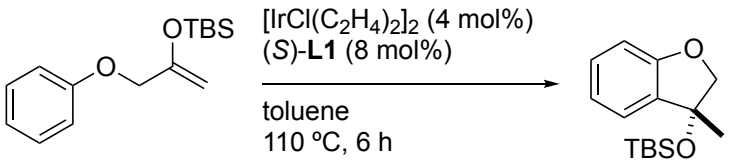
5. Optimization of Reaction Conditions (Table 1)

General procedure: In a glovebox, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with a catalyst (0.0040 mmol), a ligand (0.0080 mmol), **1c** (0.10 mmol), and toluene (0.2 mL). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 110–135 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 6 h, the tube was cooled to room temperature. Diphenylmethane (16 mg, 0.10 mmol, internal standard) was added, and the resulting mixture was analyzed by ^{1}H NMR to determine the yields of **3c** and **4c**.

*General procedure (0.2 mmol scale for isolation of **3c**)*: In a glovebox, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with a catalyst (0.0080 mmol), a ligand (0.0160 mmol), **1c** (0.20 mmol), and toluene (0.4 mL). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 135 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 6 h, the tube was cooled to room temperature. The reaction mixture was purified by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). A mixture of **3c**, **4c**, and **1c** was obtained. The mixture was then treated with mCPBA (TCI, 50 mg, containing ca.30% water) in hexane (1 mL) at rt for 30 min, by which **4c** and **1c** were converted to

the compounds derived from the corresponding epoxides. **3c** was obtained after purification by chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). Enantiomeric excess of **3c** was determined by SFC analysis [column: Daicel Chiralcel OZ-H/SFC (4.6 mm x 250 mm); eluent: CO_2; flow rate: 3.00 mL/min; detection wavelength: 220 nm; T_R = 2.2 (major), 2.6 (minor) min].

The reaction of 1c to afford 3-*tert*-Butyldimethylsilyloxy-3-methyl-2,3-dihydrobenzofuran (3c) (entry 2, Table 1)



1c **3c**

According to the general procedure, the reaction was carried out at 110 ºC for 6 h using $[IrCl(C_2H_4)_2]_2$ (4.4 mg, 0.0078 mmol), (*S*)-**L1** (19 mg, 0.016 mmol), **1c** (51 mg, 0.19 mmol), and toluene (0.4 mL). **3c** (32 mg, 62%) was obtained as a colorless oil. Enantiomeric excess of **3c** was determined to be 78% by SFC analysis [column: Daicel Chiralcel OZ-H/SFC (4.6 mm x 250 mm); eluent: CO_2; flow rate: 3.00 mL/min; detection wavelength: 220 nm; T_R = 2.2 (major), 2.6 (minor) min]. The absolute configuration of the major enantiomer was assigned as *R* based on the previous report.[13] (*R*)-**3c**[13]: ^{1}H NMR (400 MHz, C_6D_6) δ 7.12 (dd, J = 7.6, 0.8 Hz, 1H), 6.98-7.04 (m, 1H), 6.84 (d, J = 7.6 Hz, 1H), 6.75 (td, J = 7.6, 0.8 Hz, 1H), 4.33 (d, J = 10.0 Hz, 1H), 3.92 (d, J = 10.0 Hz, 1H), 1.39 (s, 3H), 0.91 (s, 9H), –0.10 (s, 3H), –0.20 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 160.9, 132.2, 130.4, 124.1, 120.7, 111.0, 84.4, 79.7, 26.7, 25.9, 18.1, –3.3, –3.7. HRMS (EI, positive) *m/z* calcd for $C_{15}H_{24}O_2Si^+$ $[M]^+$: 264.1540, found: 264.1542. $[\alpha]^{27}_D$ –33.3 (c 0.87, hexane, 78% ee).

Use of $[IrCl(cod)]_2$ as a catalyst precursor

According to the general procedure, the reaction was carried out at 135 ºC for 6 h using $[IrCl(cod)]_2$ (2.7 mg, 0.0040 mmol), (*S*)-**L1** (9.9 mg, 0.084 mmol), **1c** (27 mg, 0.10 mmol), and toluene (0.2 mL). ^{1}H NMR analysis of the crude mixture indicated that **3c** (39%), **4c** (10%, *Z*:*E* = 70:30), and a hydrogenated product $PhOCH_2CH(OTBS)CH_3$ (25%) were formed.

$PhOCH_2CH(OTBS)CH_3$: ^1H NMR (400 MHz, C_6D_6) δ 7.10-7.16 (m, 2H), 6.82-6.87 (m, 3H), 3.97-4.10 (m, 1H), 3.70 (dd, J = 9.2, 6.8 Hz, 1H), 3.50 (dd, J = 9.2, 4.4 Hz, 1H), 1.10 (d, J = 6.0 Hz, 3H), 0.99 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 159.5, 129.8, 121.0, 114.8, 73.5, 67.6, 26.1, 20.9, 18.4, –4.3, –4.6. HRMS (ESI, positive) *m/z* calcd for $C_{15}H_{26}O_2SiNa^+$ $[M + Na]^+$: 289.1594, found: 289.1596.

6. Iridium-Catalyzed Intramolecular Hydroarylation of Allylic Aryl Ethers 1 (Scheme 3)

General Procedure 1: Hydroarylation

In a glovebox, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with $[IrCl(C_2H_4)_2]_2$ (0.0080 mmol), (*S*)-**L1** (0.016 mmol), **1** (0.20 mmol), and toluene (0.4 mL). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 135 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 12 h, the tube was cooled to room temperature. The resulting solution was purified by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). A mixture of **3**, **4**, and **1** was obtained. The mixture was then treated with mCPBA in hexane for 30 min at room temperature, by which **4** and **1** were converted to the compounds derived from the corresponding epoxides. **3** was obtained after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane).

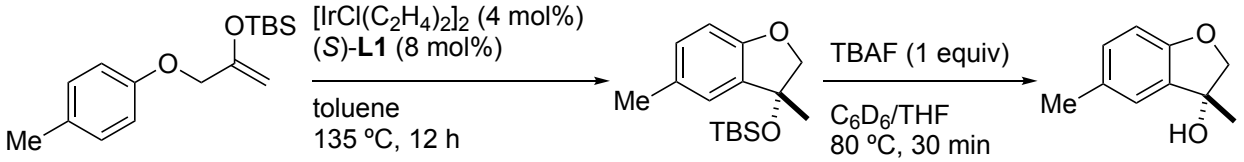
*General Procedure 2: Conversion of **3** to the alcohol **5**.*

To determine the enantiomeric excess of **3**, **3** was converted to the corresponding alcohol **5**. A 50 mL round-bottom flask, equipped with a magnetic stirrer bar, was charged with **3** and C_6D_6 (600 μL). TBAF (TCI, 1M in THF, 200 μL) was added to the flask, and the resulting mixture was stirred at 80 ºC. After 30 min, the flask was cooled to room temperature. Aqueous K_3PO_4 solution (10 mL) was added to the flask. The organic materials were extracted with EtOAc (30 mL x 3) and washed with brine (30 mL). **5** was obtained after purification by column chromatography on silica gel (SiliaFlash; eluent: hexane:AcOEt = 7:3). *Note: Aqueous workup should be performed with K_3PO_4, otherwise dehydration of **5** took place to afford 3-methylbenzofuran.*

*Notes for the SFC analysis of **5** to determine the ee: A hexane (1 mL) solution of **5** (1 mg) was prepared and used for SFC analysis. The use of i-PrOH should be avoided in this sample*

*preparation, because it induced degradation of **5**, and as a result, ee of the remaining **5** was changed. For example, when a hexane/i-PrOH (98:2) solution of **5d** (1 mg) was left at room temperature overnight, partial degradation of **5d** to 3,5-dimethylbenzofuran took place, and a 3% increase in ee of the remaining **5d** was observed. The details of this phenomenon are unclear at this moment.*

The Reaction of 1d to Afford 3-*tert*-Butyldimethylsilyloxy-3,5-dimethyl-2,3-dihydrobenzofuran (3d)

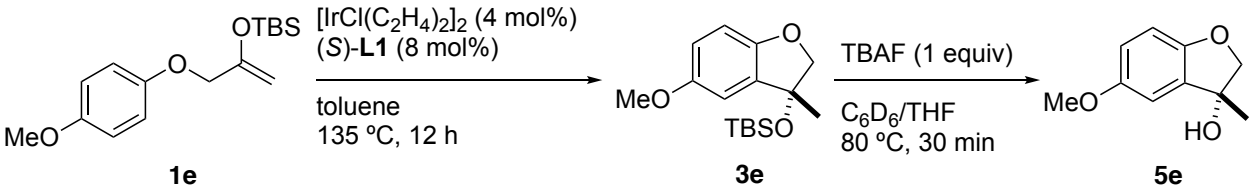


1d **3d** **5d**

According to the *General Procedure 1*, the reaction was carried out at 135 ºC for 12 h using $[IrCl(C_2H_4)_2]_2$ (4.5 mg, 0.0079 mmol), (*S*)-**L1** (19 mg, 0.016 mmol), **1d** (53 mg, 0.19 mmol), and toluene (0.4 mL). **3d** (45 mg, 85%) was obtained as a colorless oil. **3d**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.01-7.04 (m, 1H), 6.81-6.86 (m, 1H), 6.78 [d (AB pattern), J = 8.0 Hz, 1H], 4.35 (d, J = 9.6 Hz, 1H), 3.96 (d, J = 9.6 Hz, 1H), 2.12 (s, 3H), 1.43 (s, 3H), 0.92 (s, 9H), –0.06 (s, 3H), –0.17 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 159.0, 132.2, 131.0, 129.8, 124.5, 110.6, 84.5, 79.9, 26.8, 26.0, 20.8, 18.2, –3.3, –3.6. HRMS (EI, positive) *m/z* calcd for $C_{12}H_{17}O_2Si^+$ [M – *t*-Bu]$^+$: 221.0992, found: 221.0994.

According to the *General Procedure 2*, the reaction of **3d** (43 mg, 0.15 mmol) gave the product **5d** (18 mg, 0.11 mmol, 71%) as a white solid. Enantiomeric excess of **5d** was determined to be 93% by SFC analysis [column: Daicel Chiralcel OD-H/SFC (4.6 mm x 250 mm); eluent: CO_2:2-propanol = 100:2; flow rate: 3.06 mL/min; detection wavelength: 220 nm; T_R = 5.5 (major), 6.3 (minor) min]. The absolute configuration of the major enantiomer was assigned on the analogy of that of **5h** (see Section 7). (*R*)-**5d**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.90-6.93 (m, 1H), 6.81-6.86 (m, 1H), 6.78 [d (AB pattern), J = 8.0 Hz, 1H), 4.18 (d, J = 10.0 Hz, 1H), 3.94 (d, J = 10.0 Hz, 1H), 2.12 (3H, s), 1.54 (s, 1H, O*H*), 1.31 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 158.6, 132.8, 130.9, 130.0, 123.7, 110.4, 84.3, 77.8, 25.3, 20.8. HRMS (EI, positive) *m/z* calcd for $C_{10}H_{12}O_2^+$ [M]$^+$: 164.0832, found: 164.0833. $[\alpha]^{26}_D$ –29.5 (c 0.28, CH_2Cl_2, 93% ee).

The Reaction of 1e to Afford 3-*tert*-Butyldimethylsilyloxy-3-methyl-5-methoxy-2,3-dihydrobenzofuran (3e)

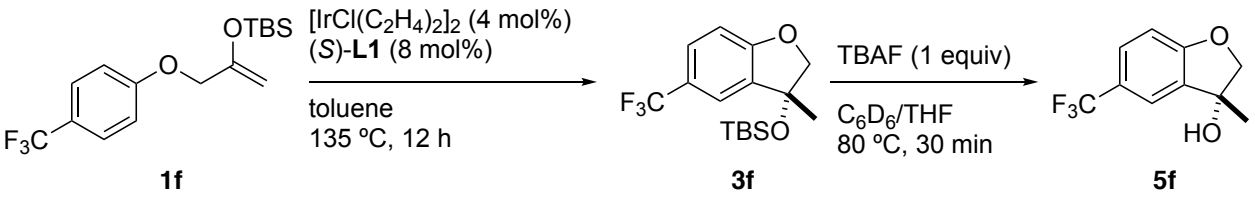


1e **3e** **5e**

According to the *General Procedure 1*, the reaction was carried out at 135 ºC for 12 h using $[IrCl(C_2H_4)_2]_2$ (4.5 mg, 0.0079 mmol), (*S*)-**L1** (21.8 mg, 0.018 mmol), **1e** (56 mg, 0.2 mmol), and toluene (0.4 mL). **3e** (40 mg, 71%) was obtained as a colorless oil. **3e**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.90 (d, J = 2.4 Hz, 1H), 6.75 [d (AB pattern), J = 8.4 Hz, 1H], 6.65 [dd (AB pattern), J = 8.4, 2.4 Hz, 1H], 4.35 (d, J = 9.6 Hz, 1H), 3.97 (d, J = 9.6 Hz, 1H), 3.35 (s, 3H), 1.41 (s, 3H), 0.91 (s, 9H), –0.05 (s, 3H), –0.16 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 154.91, 154.88, 133.0, 116.0, 111.1, 109.8, 84.6, 80.2, 55.6, 26.8, 25.9, 18.2, –3.3, –3.5. HRMS (EI, positive) *m/z* calcd for $C_{16}H_{26}O_3Si^+$ $[M]^+$: 294.1646, found: 294.1649.

According to the *General Procedure 2*, the reaction of **3e** (40 mg, 0.14 mmol) gave the product **5e** (19 mg, 0.11 mmol, 77%) as a white solid. Enantiomeric excess of **5e** was determined to be 92% by SFC analysis [column: Daicel Chiralcel OD-H/SFC (4.6 mm x 250 mm); eluent: CO_2:2-propanol = 100:2; flow rate: 3.06 mL/min; detection wavelength: 220 nm; T_R = 8.4 (major), 10.2 (minor) min]. The absolute configuration of the major enantiomer was assigned on the analogy of that of **5h** (see Section 7). (*R*)-**5e**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.81 (d, J = 2.8 Hz, 1H), 6.75 [d (AB pattern), J = 8.8 Hz, 1H], 6.66 [dd (AB pattern), J = 8.8, 2.8 Hz, 1H), 4.17 (d, J = 10.0 Hz, 1H), 3.95 (d, J = 10.0 Hz, 1H), 3.34 (s, 3H), 1.58 (s, 1H, O*H*), 1.29 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 155.0, 154.5, 133.5, 116.1, 111.0, 108.8, 84.4, 78.1, 55.6, 25.2. HRMS (EI, positive) *m/z* calcd for $C_{10}H_{12}O_3^+$ $[M]^+$: 180.0781, found: 180.0783. $[\alpha]^{25}_D$ –20.7 (c 0.61, CH_2Cl_2, 92% ee).

The Reaction of 1f to Afford 3-*tert*-Butyldimethylsilyloxy-3-methyl-5-trifluoromethyl-2,3-dihydrobenzofuran (3f)

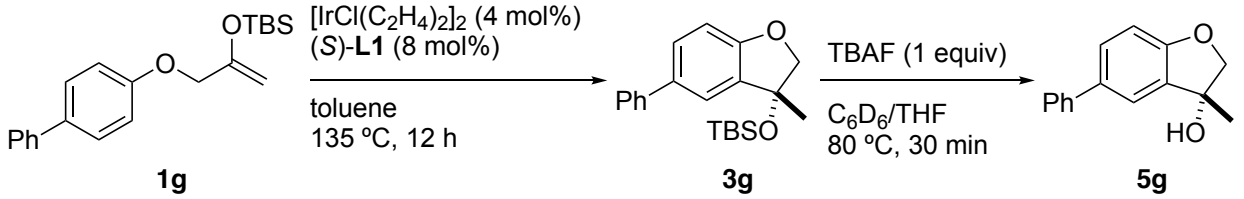


1f **3f** **5f**

According to the *General Procedure 1*, the reaction was carried out at 135 ºC for 12 h using $[IrCl(C_2H_4)_2]_2$ (6.8 mg, 0.012 mmol), (*S*)-**L1** (28.2 mg, 0.024 mmol), **1f** (105.4 mg, 0.30 mmol), and toluene (0.4 mL). **3f** (52.6 mg, 50%) was obtained as a colorless oil. The moderate yield of **3f** is due to the slower conversion of **1f** and the slightly higher formation of the double-bond migration product **4f** (ratio before isolation: **1f**:**3f**:**4f** = 24:63:13). Elongation of the reaction time to 24 h did not improve the yield of **3f**. **3f**: ^{1}H NMR (600 MHz, C_6D_6) δ 7.55 (d, J = 1.8 Hz, 1H), 7.21-7.24 (m, 1H), 6.57 (d, J = 9.0 Hz, 1H), 4.25 (d, J = 9.6 Hz, 1H), 3.80 (d, J = 9.6 Hz, 1H), 1.21 (s, 3H), 0.84 (s, 9H), –0.19 (s, 3H), –0.27 (s, 3H). ^{13}C NMR (151 MHz, C_6D_6) δ 163.2, 133.2, 128.2 (q, $^3J_{CF}$ = 3 Hz, detected by DEPT), 125.3 (q, $^1J_{CF}$ = 271 Hz), 123.3 (q, $^2J_{CF}$ = 32 Hz), 121.8 (q, $^3J_{CF}$ = 4 Hz), 111.1, 85.1, 79.0, 26.3, 25.7, 18.0, –3.4, –3.7. HRMS (EI, positive) *m/z* calcd for $C_{16}H_{23}F_2O_2Si^+$ $[M - F]^+$: 313.1430, found: 313.1429.

According to the *General Procedure 2*, the reaction of **3f** (48.3 mg, 0.15 mmol) gave the product **5f** (27.4 mg, 0.13 mmol, 87%) as a white solid. Enantiomeric excess of **5f** was determined to be 99% by SFC analysis [column: Daicel Chiralcel OD-H/SFC (4.6 mm x 250 mm); eluent: CO_2:2-propanol = 100:2; flow rate: 3.06 mL/min; detection wavelength: 220 nm; T_R = 3.2 (major), 3.8 (minor) min]. The absolute configuration of the major enantiomer was assigned on the analogy of that of **5h** (see Section 7). (*R*)-**5f**: ^{1}H NMR (600 MHz, C_6D_6) δ 7.39 (d, J = 2.4 Hz, 1H), 7.21-7.24 (m, 1H), 6.56 (d, J = 8.4 Hz, 1H), 4.04 (d, J = 10.2 Hz, 1H), 3.76 (d, J = 10.2 Hz, 1H), 1.19 (s, 1H, O*H*), 1.05 (s, 3H). ^{13}C NMR (151 MHz, C_6D_6) δ 162.9, 133.6, 128.1 (q, $^3J_{CF}$ = 4 Hz, detected by DEPT), 125.3 (q, $^1J_{CF}$ = 272 Hz), 123.4 (q, $^2J_{CF}$ = 32 Hz), 121.0 (q, $^3J_{CF}$ = 4 Hz), 111.0, 84.7, 76.8, 25.0. HRMS (EI, positive) *m/z* calcd for $C_{10}H_9F_3O_2^+$ $[M]^+$: 218.0549, found: 218.0556. $[\alpha]^{26}_D$ – 26.8 (c 0.34, CH_2Cl_2, 99% ee).

The Reaction of 1g to Afford 3-*tert*-Butyldimethylsilyloxy-3-methyl-5-phenyl-2,3-dihydrobenzofuran (3g)

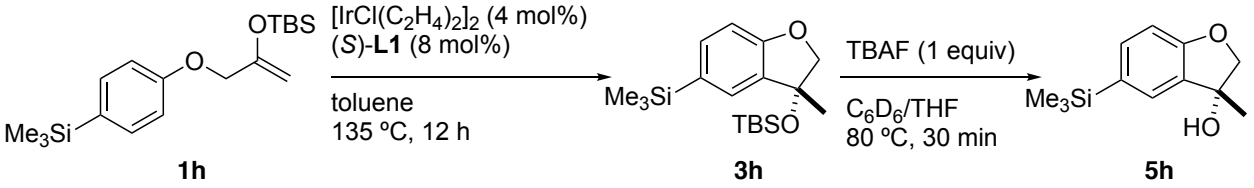


1g **3g** **5g**

According to the *General Procedure 1*, the reaction was carried out at 135 ºC for 12 h using $[IrCl(C_2H_4)_2]_2$ (4.7 mg, 0.0082 mmol), (*S*)-**L1** (19.9 mg, 0.017 mmol), **1g** (70.6 mg, 0.21 mmol), and toluene (0.4 mL). **3g** (54.9 mg, 78%) was obtained as a colorless oil. **3g**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.56 (d, J = 2.0 Hz, 1H), 7.50-7.52 (m, 1H), 7.48-7.50 (m, 1H), 7.30 (dd, J = 8.0, 2.0 Hz, 1H), 7.21-7.27 (m, 2H), 7.11-7.17 (m, 1H). 6.87 (d, J = 8.4 Hz, 1H), 4.39 (d, J = 10.0 Hz, 1H), 3.99 (d, J = 10.0 Hz, 1H), 1.44 (s, 3H), 0.91 (s, 9H), –0.06 (s, 3H), –0.16 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ160.6, 141.7, 134.7, 132.9, 129.8, 129.1, 127.2, 127.0, 123.0, 111.2, 84.9, 79.8, 26.8, 25.9, 18.2, –3.2, –3.6. HRMS (EI, positive) *m/z* calcd for $C_{21}H_{28}O_2Si^+$ $[M]^+$: 340.1853, found: 340.1858.

According to the *General Procedure 2*, the reaction of **3g** (54.9 mg, 0.16 mmol) gave the product **5g** (31.1 mg, 0.14 mmol, 86%) as a white solid. Enantiomeric excess of **5g** was determined to be 94% by SFC analysis [column: Daicel Chiralcel OD-H/SFC (4.6 mm x 250 mm); eluent: CO_2:2-propanol = 100:10; flow rate: 3.30 mL/min; detection wavelength: 220 nm; T_R = 5.1 (major), 11.7 (minor) min]. The absolute configuration of the major enantiomer was assigned on the analogy of that of **5h** (see Section 7). (*R*)-**5g**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.41-7.47 (m, 3H), 7.30 (dd, J = 8.8, 2.4 Hz, 1H), 7.22-7.28 (m, 2H), 7.12-7.18 (m, 1H), 6.86 (d, J = 8.0 Hz, 1H), 4,20 (d, J = 10.0 Hz, 1H), 3.96 (d, J = 10.0 Hz, 1H), 1.51 (s, 1H, O*H*), 1.31 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 160.2, 141.6, 134.9, 133.5, 129.5, 129.1, 127.2, 127.0, 122.2, 111.1, 84.6, 77.7, 25.3. HRMS (EI, positive) *m/z* calcd for $C_{15}H_{14}O_2^+$ $[M]^+$: 226.0988, found: 226.0990. $[\alpha]^{27}_D$ +100.4 (c 1.74, CH_2Cl_2, 94% ee).

The Reaction of 1h to Afford 3-*tert*-Butyldimethylsilyloxy-3-methyl-5-trimethylsilyl-2,3-dihydrobenzofuran (3h)

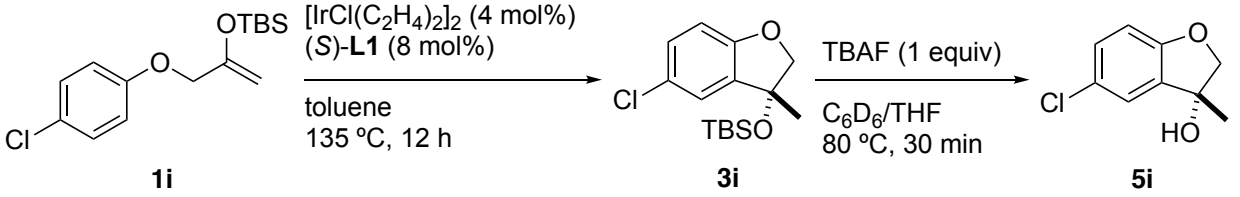


1h **3h** **5h**

According to the *General Procedure 1*, the reaction was carried out at 135 ºC for 12 h using $[IrCl(C_2H_4)_2]_2$ (4.7 mg, 0.0083 mmol), (*S*)-**L1** (20.3 mg, 0.017 mmol)), **1h** (63.3 mg, 0.19 mmol), and toluene (0.4 mL). **3h** (37.6 mg, 59%) was obtained as a colorless oil. The moderate yield of **3h** is due to the relatively fast formation of the double-bond migration product **4h** (ratio before isolation: **1h**:**3h**:**4h** = 5:64:31). **3h**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.56-7.57 (m, 1H), 7.30 (dd, J = 8.0, 1.2 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 4.36 (d, J = 10.0 Hz, 1H), 3.96 (d, J = 10.0 Hz, 1H), 1.45 (s, 3H), 0.92 (s, 9H), 0.26 (s, 9H), –0.12 (s, 3H), –0.16 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 162.0, 135.9, 131.9, 131.3, 129.2, 110.8, 84.6, 79.7, 26.8, 25.9, 18.2, –0.7, –3.3, –3.7. HRMS (EI, positive) *m*/*z* calcd for $C_{17}H_{29}O_2Si_2^+$ $[M - CH_3]^+$: 321.1701, found: 321.1704.

According to the *General Procedure 2*, the reaction of **3h** (37.6 mg, 0.11 mmol) gave the product **5h** (20.4 mg, 0.092 mmol, 84%) as a white solid. Enantiomeric excess of **5h** was determined to be 94% by SFC analysis [column: Daicel Chiralcel OD-H/SFC (4.6 mm x 250 mm); eluent: CO_2:2-propanol = 100:2; flow rate: 3.06 mL/min; detection wavelength: 220 nm; T_R = 3.8 (major), 4.2 (minor) min]. The absolute configuration of the major enantiomer was assigned as *R* based on the X-ray crystallographic analysis (see Section 7). (*R*)-**5h**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.51 (dd, J = 1.6, 0.4 Hz, 1H), 7.31 (dd, J = 8.0, 1.6 Hz, 1H), 6.92 (dd, J = 8.0, 0.4 Hz, 1H), 4.16 (d, J = 10.0 Hz, 1H), 3.92 (d, J = 10.0 Hz, 1H), 1.40 (s, 1H, O*H*), 1.32 (s, 3H), 0.25 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6) δ 161.6, 135.9, 132.7, 131.8, 128.2 (overlapping with the peaks of C_6D_6, detected by DEPT), 110.7, 84.3, 77.6, 25.3, –0.7. HRMS (EI, positive) *m/z* calcd for $C_{12}H_{18}O_2Si^+$ $[M]^+$: 222.1071, found: 222.1073. $[\alpha]^{27}_D$ –10.2 (c 0.88, CH_2Cl_2, 94% ee).

The Reaction of 1i to Afford 3-*tert*-Butyldimethylsilyloxy-3-methyl-5-chloro-2,3-dihydrobenzofuran (3i)

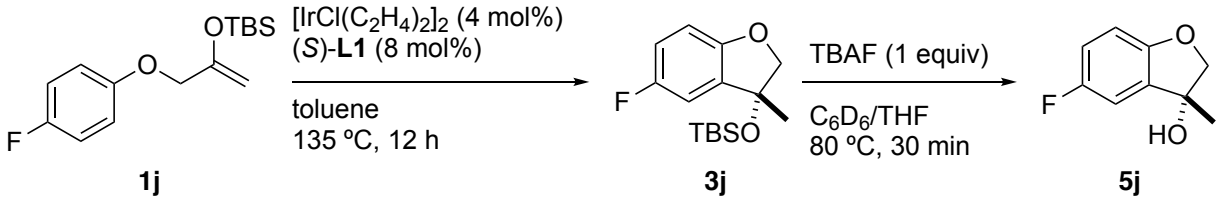


1i **3i** **5i**

According to the *General Procedure 1*, the reaction was carried out at 135 ºC for 12 h using $[IrCl(C_2H_4)_2]_2$ (4.5 mg, 0.0079 mmol), (*S*)-**L1** (19.4 mg, 0.016 mmol), **1i** (61.0 mg, 0.20 mmol), and toluene (0.4 mL). **3i** (25.1 mg, 41%) was obtained as a colorless oil. The moderate yield of **3i** is due to the relatively fast formation of the double-bond migration product **4i** (ratio before isolation: **1i**:**3i**:**4i** = 4:61:35). **3i**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.22 (d, J = 2.4 Hz, 1H), 6.95 (dd, J = 8.4,2.4 Hz, 1H), 6.52 (d, J = 8.4 Hz, 1H), 4.24 (d, J = 10.0 Hz, 1H), 3.82 (d, J = 10.0 Hz, 1H), 1.23 (s, 3H), 0.86 (s, 9H), –0.13 (s, 3H), –0.23 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 159.3, 134.2, 130.3, 125.7, 124.3, 112.1, 84.8, 79.6, 26.5, 25.8, 18.1, –3.4, –3.6. HRMS (EI, positive) *m*/*z* calcd for $C_{11}H_{14}ClO_2Si^+$ [M – *t*-Bu]$^+$: 241.0446, found: 241.0450.

According to the *General Procedure 2*, the reaction of **3i** (25.1 mg, 0.082 mmol) gave the product **5i** (8.2 mg, 0.044 mmol, 53%) as a white solid. Enantiomeric excess of **5i** was determined to be 95% by SFC analysis [column: Daicel Chiralcel OD-H/SFC (4.6 mm x 250 mm); eluent: CO_2:2-propanol=100:2; flow rate: 3.06 mL/min; detection wavelength: 220 nm; T_R = 6.8 (major), 8.0 (minor) min]. The absolute configuration of the major enantiomer was assigned on the analogy of that of **5h** (see Section 7). (*R*)-**5i**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.04 (d, J = 2.4 Hz, 1H), 6.95 (dd, J = 8.4, 2.4 Hz, 1H), 6.51 (d, J = 8.4 Hz, 1H), 4.04 (d, J = 10.0 Hz, 1H), 3.78 (d, J = 10.0 Hz, 1H), 1.23 (s, 1H), 1.09 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 158.9, 134.6, 130.2, 125.7, 123.6, 111.9, 84.5, 77.4, 25.0. HRMS (EI, positive) *m/z* calcd for $C_9H_9ClO_2^+$ [M]$^+$: 184.0286, found: 184.0289. $[\alpha]^{26}_D$ –16.0 (c 0.46, CH_2Cl_2, 95% ee).

The Reaction of 1j to Afford 3-*tert*-Butyldimethylsilyloxy-3-methyl-5-fluoro-2,3-dihydrobenzofuran (3j)

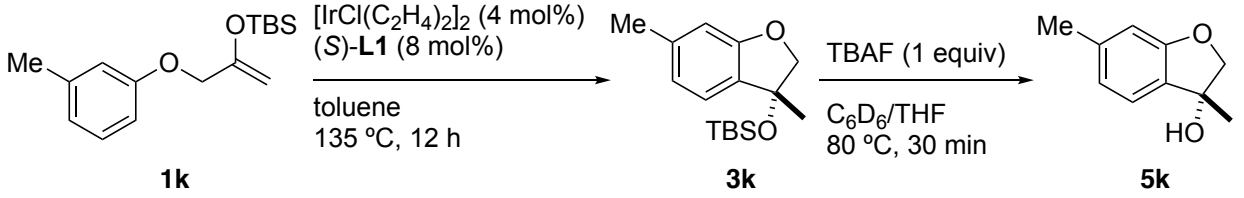


1j **3j** **5j**

According to the *General Procedure 1*, the reaction was carried out at 135 ºC for 12 h using $[IrCl(C_2H_4)_2]_2$ (4.64 mg, 0.0082 mmol), (*S*)-**L1** (20.2 mg, 0.017 mmol), **1j** (56.4 mg, 0.20 mmol), and toluene (0.4 mL). **3j** (33.8 mg, 60%) was obtained as a colorless oil. The moderate yield of **3j** is due to the slower conversion of **1j** and the slightly higher formation of the double-bond migration product **4j** (ratio before isolation: **1j**:**3j**:**4j** = 16:72:12). Elongation of the reaction time to 24 h did not improve the yield of **3j**. **3j**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.88 (dd, J = 8.0, 2.8 Hz, 1H), 6.66 (td, J = 8.8, 2.8 Hz, 1H), 6.54 (dd, J = 8.8, 4.0 Hz, 1H), 4.27 (d, J = 10.0 Hz, 1H), 3.86 (d, J = 10.0 Hz, 1H), 1.26 (s, 3H), 0.87 (s, 9H), –0.11 (s, 3H), –0.24 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6, ^{1}H and ^{19}F simultaneous decoupling) δ 157.9, 156.6, 133.6, 116.8, 111.4, 110.9, 84.8, 79.8, 26.5, 25.8, 18.1, –3.4, –3.5. HRMS (EI, positive) *m*/*z* calcd for $C_{11}H_{14}FO_2Si^+$ [M – *t*-Bu]$^+$: 225.0742, found: 225.0746.

According to the *General Procedure 2*, the reaction of **3j** (33.8 mg, 0.12 mmol) gave the product **5j** (12.9 mg, 0.08 mmol, 64%) as a white solid. Enantiomeric excess of **5j** was determined to be 84% by SFC analysis [column: Daicel Chiralcel OD-H/SFC (4.6 mm x 250 mm); eluent: CO_2:2-propanol = 100:2; flow rate: 3.06 mL/min; detection wavelength: 220 nm; T_R = 4.4 (major), 5.1 (minor) min]. The absolute configuration of the major enantiomer was assigned on the analogy of that of **5h** (see Section 7). (*R*)-**5j**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.74 (dd, J = 7.2, 2.8 Hz, 1H), 6.67 (td, J = 8.8, 2.8 Hz, 1H), 6.53 (dd, J = 8.8, 4.0 Hz, 1H), 4.07 (d, J = 10.0 Hz, 1H), 3.83 (d, J = 10.0 Hz, 1H), 1.25 (s, 1H, O*H*), 1.12 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6, ^{1}H and ^{19}F simultaneous decoupling) δ 158.0, 156.2, 134.0, 116.7, 111.2, 110.2, 84.5, 77.7, 25.0. HRMS (EI, positive) *m/z* calcd for $C_9H_9FO_2^+$ [M]$^+$: 168.0581, found: 168.0584. $[\alpha]^{26}_D$ –37.9 (c 0.67, CH_2Cl_2, 84% ee).

The Reaction of 1k to Afford 3-*tert*-Butyldimethylsilyloxy-3,6-dimethyl -2,3-dihydrobenzofuran (3k)

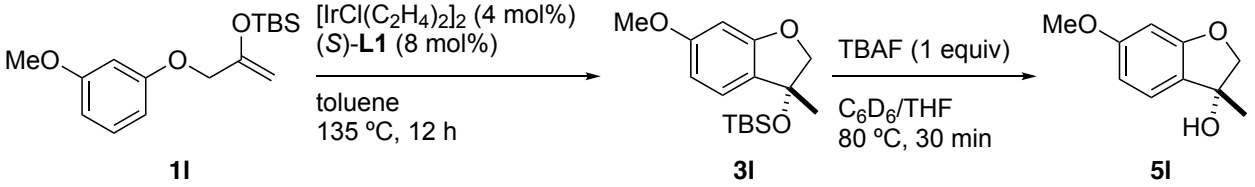


1k **3k** **5k**

According to the *General Procedure 1*, the reaction was carried out at 135 ºC for 12 h using $[IrCl(C_2H_4)_2]_2$ (4.8 mg, 0.0084 mmol), (*S*)-**L1** (19.1 mg, 0.016 mmol), **1k** (52.7 mg, 0.19 mmol), and toluene (0.4 mL). **3k** (34.2 mg, 65%) was obtained as a colorless oil. **3k**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.06 (d, J = 7.6 Hz, 1H), 6.71 (d, J = 0.8 Hz, 1H), 6.60-6.64 (m, 1H), 4.37 (d, J = 10.0 Hz, 1H), 3.97 (d, J = 10.0 Hz, 1H), 2.07 (s, 3H), 1.43 (s, 3H), 0.93 (s, 9H), –0.07 (s, 3H), –0.15 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 161.4, 140.6, 129.4, 123.8, 121.6, 111.6, 84.8, 79.6, 26.9, 26.0, 21.6, 18.2, –3.2, –3.6. HRMS (EI, positive) *m/z* calcd for $C_{16}H_{25}O_2Si^+$ $[M - H]^+$: 277.1618, found: 277.1623.

According to the *General Procedure 2*, the reaction of **3k** (26.2 mg, 0.094 mmol) gave the product **5k** (8.3 mg, 0.051 mmol, 54%) as a white solid. Enantiomeric excess of **5k** was determined to be 80% by SFC analysis [column: Daicel Chiralcel OZ-H/SFC (4.6 mm x 250 mm); eluent: CO_2:2-propanol = 100:2; flow rate: 3.06 mL/min; detection wavelength: 220 nm; T_R = 5.5 (major), 6.1 (minor) min]. The absolute configuration of the major enantiomer was assigned on the analogy of that of **5h** (see Section 7). (*R*)-**5k**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.00 (d, J = 7.6 Hz, 1H), 6.71 (d, J = 0.8 Hz, 1H), 6.60-6.64 (m, 1H), 4.19 (d, J = 10.0 Hz, 1H), 3.95 (d, J = 10.0 Hz, 1H), 2.09 (s, 3H), 1.37 (s, 1H, O*H*), 1.31 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 161.0, 140.5, 130.2, 123.0, 121.9, 111.4, 84.5, 77.5, 25.3, 21.6. HRMS (EI, positive) *m/z* calcd for $C_{10}H_{12}O_2^+$ $[M]^+$: 164.0832, found: 164.0835. $[\alpha]^{29}_D$ –29.8 (c 0.42, CH_2Cl_2, 80% ee).

The Reaction of 1l to Afford 3-*tert*-Butyldimethylsilyloxy-3-methyl-6-methoxy-2,3-dihydrobenzofuran (3l)

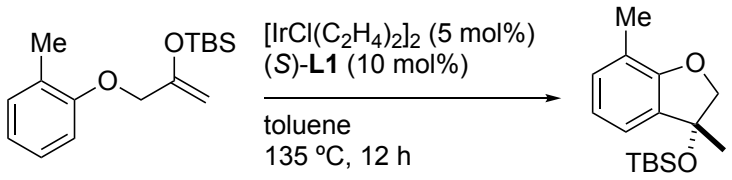


1l **3l** **5l**

According to the *General Procedure 1*, the reaction was carried out at 135 ºC for 12 h using $[IrCl(C_2H_4)_2]_2$ (4.6 mg, 0.0081 mmol), (*S*)-**L1** (19.6 mg, 0.017 mmol), **1l** (59.6 mg, 0.20 mmol), and toluene (0.4 mL). **3l** (27.5 mg, 46%) was obtained as a colorless oil. **3l**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.02 (d, J = 8.0 Hz, 1H), 6.52 [d (AB pattern), J = 2.0 Hz, 1H], 6.48 [dd (AB pattern), J = 8.0, 2.0 Hz, 1H], 4.39 [d (AB pattern), J = 10.0 Hz, 1H], 4.01 [d (AB pattern), J = 10.0 Hz, 1H], 3.23 (s, 3H), 1.43 (s, 3H), 0.94 (s, 9H), –0.05 (s, 3H), –0.13 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 162.7, 162.6, 124.5, 124.3, 107.6, 96.6, 85.5, 79.5, 55.0, 27.0, 26.0, 18.2, –3.2, –3.7. HRMS (EI, positive) *m*/*z* calcd for $C_{12}H_{17}O_3Si^+$ [M – *t*-Bu]$^+$: 237.0941, found: 237.0944.

According to the *General Procedure 2*, the reaction of **3l** (27.5 mg, 0.093 mmol) gave the product **5l** (14.7 mg, 0.082 mmol, 88%) as a white solid. Enantiomeric excess of **5l** was determined to be 78% by SFC analysis [column: Daicel Chiralcel OZ-H/SFC (4.6 mm x 250 mm); eluent: CO_2:2-propanol = 100:2; flow rate: 3.06 mL/min; detection wavelength: 220 nm; T_R = 8.4 (major), 10.2 (minor) min]. The absolute configuration of the major enantiomer was assigned on the analogy of that of **5h** (see Section 7). (*R*)-**5l**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.97 (d, J = 8.4 Hz, 1H), 6.53 [d (AB pattern), J = 2.0 Hz, 1H], 6.49 [dd (AB pattern), J = 8.4, 2.0 Hz, 1H], 4.22 (d, J = 10.0 Hz, 1H), 3.98 (d, J = 10.0 Hz, 1H), 3.27 (s, 3H), 1.31 (s, 3H), 1.29 (s, 1H, O*H*). ^{13}C NMR (101 MHz, C_6D_6) δ 162.6, 162.1, 125.1, 123.7, 107.8, 96.6, 85.2, 77.3, 55.0, 25.4. HRMS (EI, positive) *m/z* calcd for $C_{10}H_{12}O_3^+$ [M]$^+$: 180.0781, found: 180.0785. $[\alpha]^{28}_D$ –30.7 (c 0.20, CH_2Cl_2, 78% ee).

The Reaction of 1m to Afford 3-*tert*-Butyldimethylsilyloxy-3,7-dimethyl -2,3-dihydrobenzofuran (3m)



1m **3m**

According to the *General Procedure 1*, the reaction was carried out at 135 ºC for 24 h using $[IrCl(C_2H_4)_2]_2$ (5.9 mg, 0.010 mmol), (*S*)-**L1** (29 mg, 0.025 mmol), **1m** (54 mg, 0.20 mmol), and toluene (0.4 mL). **3m** (9.8 mg, 18%) was obtained as a colorless oil. Enantiomeric excess of **3m** was determined to be 33% by SFC analysis [column: Daicel Chiralcel OZ-H/SFC (4.6 mm x 250 mm); eluent: CO_2 only; flow rate: 3.00 mL/min; detection wavelength: 220 nm; T_R = 2.3 (major), 2.6 (minor) min]. The absolute configuration of the major enantiomer was assigned as *R* based on the previous report.[13] The ^{1}H NMR spectrum of **3m** is in perfect agreement with the previously reported spectrum.[13]

7. Assignment of the Absolute Configuration of 5h

The absolute configuration of the major enantiomer of **5h** was assigned by X-ray crystallographic analysis. Single crystal of **5h** was obtained from hot hexane solution and mounted in the loop. X-ray diffraction data for **5h** were collected at 153(1) K on a Rigaku Saturn 724+CCD diffractometer with Varimax Mo optics using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), and processed using CrystalClear-SM (Rigaku, Tokyo). The structures were solved using a direct method (SHELXT or SHELX97) and refined by a full-matrix least-squares method on F^2 for all reflections using the programs of SHELXL-2018. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data for the structure of **5h** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2099797. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

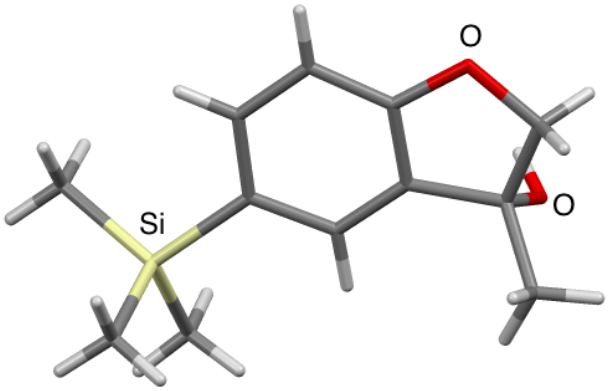


Figure S1. Crystal Structure of (*R*)-**5h**.

Table S2. Crystal Data and Structure Refinement for (*R*)-**5h**

Empirical formula	$C_{12}H_{18}O_2Si$	
Formula weight	222.35	
Temperature	143(2) K	
Wavelength	0.71075 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.7361(17) Å	α = 90°
	b = 21.906(6) Å	β = 90°
	c = 26.843(7) Å	γ = 90°
Volume	3961.0(18) $Å^3$	
Z	12	
Density (calculated)	1.119 Mg/m^3	
Absorption coefficient	0.159 mm^{-1}	
F(000)	1440	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Theta range for data collection	3.036 to 27.488°	
Index ranges	-12<=h<=12, -11<=k<=13, -29<=l<=30	
Reflections collected	32323	
Independent reflections	9056 [*R*(int) = 0.0970]	
Completeness to theta = 25.242°	99.7%	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9056 / 0 / 421	
Goodness-of-fit on F^2	1.141	
Final *R* indices [I>2sigma(I)]	*R*1 = 0.0903, *wR*2 = 0.1317	
R indices (all data)	*R*1 = 0.1287, *wR*2 = 0.1464	
Absolute structure parameter	0.04(10)	
Largest diff. peak and hole	0.220 and -0.225 e.$Å^{-3}$	

8. Substituent Effect on the Double Bond in Ir-Catalyzed Double Bond Migration (Scheme 6)

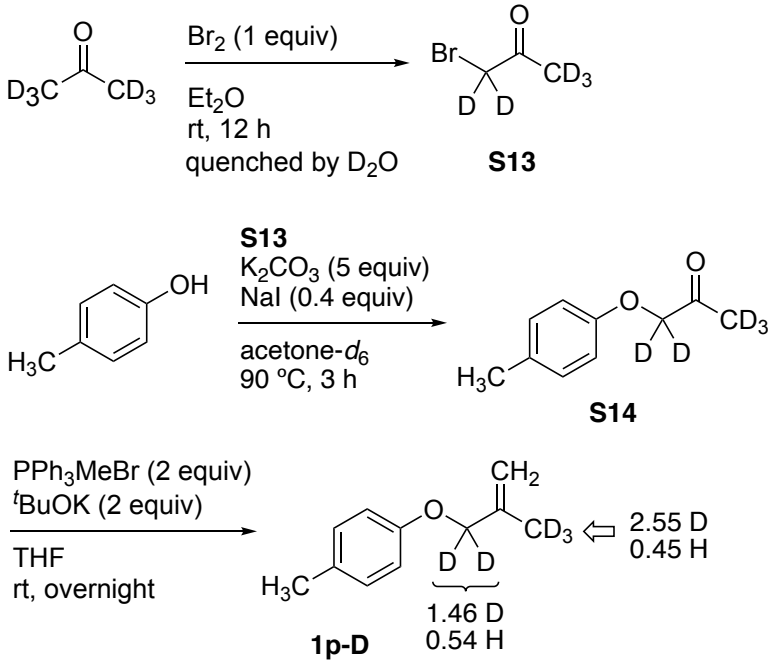
*Reaction of **1n***: According to the *General Procedure 1* described in Section 6, the reaction was carried out at 135 ºC using $[IrCl(C_2H_4)_2]_2$ (2.3 mg, 0.0040 mmol), (*S*)-**L1** (9.7 mg, 0.0080 mmol), **1n** (18 mg, 0.10 mmol), and toluene (0.2 mL). ^{1}H NMR analysis (internal standard: diphenylmethane) of the resulting mixture indicated that **4n** was formed in 73 and 88% yields after 2 and 6 h, respectively. No formation of hydroarylation product was observed.

*Reaction of **1o***: According to the *General Procedure 1* described in Section 6, the reaction was carried out at 135 ºC using $[IrCl(C_2H_4)_2]_2$ (2.3 mg, 0.0040 mmol), (*S*)-**L1** (9.6 mg, 0.0081 mmol), **1o** (26.4 mg, 0.10 mmol), and toluene (0.2 mL). ^{1}H NMR analysis (internal standard: diphenylmethane) of the resulting mixture indicated that **4o** was formed in 8% yield after 6 h. No formation of hydroarylation product was observed.

9. D-Labeling Experiments (Schemes 7 and 8)

9-1. Preparation of Deuterium-Labeled Compounds

Preparation of 1p-D



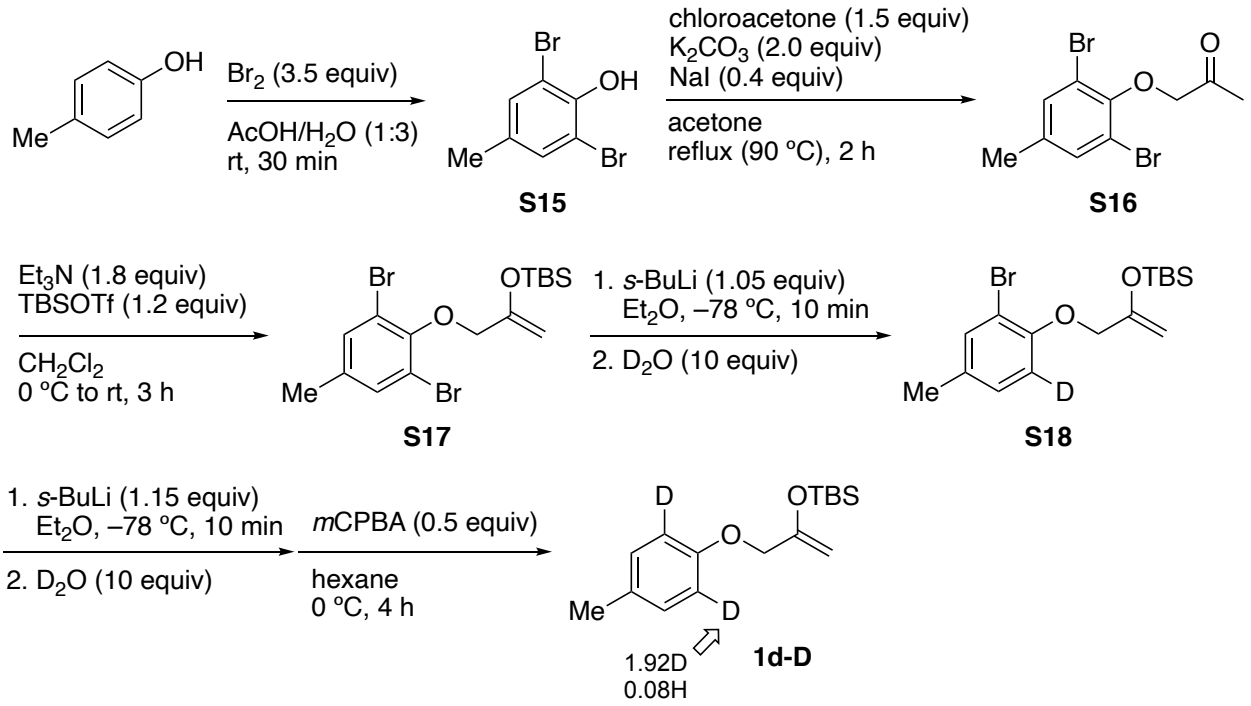
An oven dried 200 mL three-neck-flask, equipped with a magnetic stirring bar and a rubber septum, was evacuated and backfilled with nitrogen. Acetone-d_6 (Aldrich, 1.5 mL, 20 mmol) and Et_2O (40 mL) was added to the flask. Bromine (1.0 mL, 20 mmol) was added dropwise to the flask.

The resulting mixture was stirred for 24 h at room temperature. D_2O (1 mL) was added to the flask to quench the reaction. Anhydrous sodium sulfate was then added to the flask to remove the excess D_2O. After removal of Et_2O by distillation, **S13** was obtained as a crude product, which was used for the next step without further purification. (*Caution: Bromoacetone is a powerful irritant to the eyes and skin. It should be handled under a well-ventilated hood.*)

According to the procedure given for preparation of **S1** (see Section 3), the reaction of *p*-cresol (1.20 g, 10 mmol) with **S13** was carried out for 3 h at 90 °C in acetone-d_6 using K_2CO_3 (6.9 g, 50 mmol) and NaI (600 mg, 4 mmol). **S14** (1.52 g, 9.0 mmol, 90%) was obtained as a colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: 15% EtOAc in hexane).

According to the procedure given for preparation of **1n** (see Section 3), the reaction of **S14** (1.52 g, 9.0 mmol) with PPh_3MeBr (TCI, 7.14 g, 20 mmol) and *t*-BuOK (2.25 g, 20 mmol) was carried out in THF. **1p-D** (1.22 g, 7.3 mmol, 80%) was obtained as a colorless oil after purification by column chromatography on silica gel (SiliaFlash; eluent: 5% EtOAc in hexane) and Kugelrhor distillation. The D/H ratios at the allylic methyl ($CH_{0.45}D_{2.55}$) and the allylic methylene ($CH_{0.54}D_{1.46}$) were determined by ^{1}H NMR (see Figure S70). **1p-D**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.95 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 5.06-5.10 (m, 1H), 4.85-4.89 (m, 1H), 4.10-4.15 (m, 0.54H), 2.13 (s, 3H), 1.58-1.64 (m, 0.45H). ^{13}C NMR (101 MHz, C_6D_6) δ 157.4, 141.4, 130.2, 129.9, 115.0, 112.3-112.6 (m), 71.0-71.8 (m), 20.6, 18.2-19.4 (m). HRMS (EI, positive) *m/z* calcd for $C_{11}H_{10}D_4O^+$ $[M]^+$: 166.1290, found: 166.1291; *m/z* calcd for $C_{11}H_9D_5O^+$ $[M]^+$: 167.1353, found: 167.1357.

Preparation of 1d-D



A 200 mL three-neck flask, equipped with a magnetic stirring bar and a rubber septum, was charged with *p*-cresol (2.36 g, 13 mmol), AcOH (4.8 mL), distilled water (13.2 mL) under air. To the mixture bromine (2.3 mL, 45 mmol) in AcOH (32 mL) solution was added dropwise. After the stirring at room temperature for 30 min, the mixture was poured into water (80 mL) to afford white solids. The solids were collected by filtration and dried under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL). The organic materials were washed with Na_2CO_3 (50 mL), $Na_2S_2O_3$ (50 mL x 3), and brine (50 mL). The organic phase was dried over magnesium sulfate, and the solvent was removed under reduced pressure to afford **S15** (3.0 g, 11 mmol, 89% yield) as a white solid, which was used for the next step without further purification.

According to the procedure given for preparation of **S1** (see Section 3), the reaction of **S15** (1.86 g, 7.0 mmol) with chloroacetone (1.2 mL, 15 mmol) was carried out for 1.5 h at 90 °C in acetone using K_2CO_3 (1.5 g, 14 mmol) and NaI (420 mg, 2.8 mmol). **S16** (2.2 g, 6.7 mmol, 96%) was obtained as a white solid after purification by column chromatography on silica gel (SiliaFlash; eluent: 20% EtOAc in hexane).

According to the procedure given for preparation of **1c** (see Section 3), **S16** (1.61 g, 5.0 mmol) was reacted with Et_3N (1.2 mL, 9.0 mmol) and TBSOTf (1.5 mL, 6.0 mmol) in CH_2Cl_2 (20 mL).

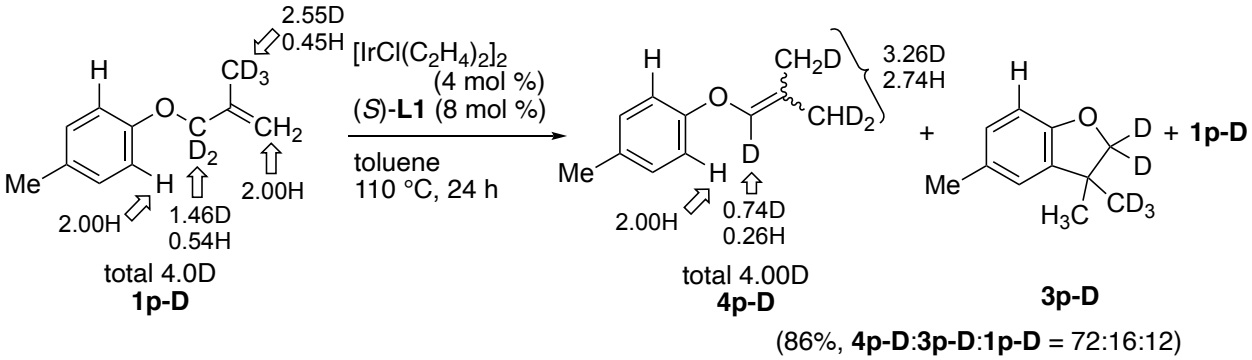
S17 (1.9 g, 4.4 mmol, ca. 9:1 mixture of isomers) was obtained as a colorless oil after purification by chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane).

An oven dried 300 mL three-neck flask, equipped with a magnetic stirring bar and a rubber septum, was charged with **S17** (1.73 g, 4.0 mmol, ca. 9:1 mixture of isomers). The flask was evacuated and backfilled with nitrogen. Et_2O (150 mL) was added to the flask, and the mixture was cooled to –78 ºC by a dry ice/acetone bath. *s*-BuLi (4.0 mL, 1.05 M in hexane, 4.2 mmol, Kanto) was added dropwise to the flask. After the stirring for 10 min at –78 ºC, D_2O (700 μL) was added to the flask. The cooling bath was removed, and the flask was allowed to warm to room temperature. Water (30 mL) was added to the flask. The organic materials were extracted with hexane (20 mL x 3), washed with brine (50 mL), and dried over anhydrous sodium sulfate. Evaporation of the volatiles afforded **S18**, which was used for the next step without further purification.

According to the procedure given above, **S18** (1.25 g, 3.5 mmol) was treated with *s*-BuLi (4.0 mL, 1.05 M in hexane, 4.2 mmol) and D_2O (700 μL) in Et_2O (150 mL). The crude products (530 mg, 1.9 mmol, a 9:1 mixture of isomers) were then treated with mCPBA (200 mg, containing ca.30% water) in hexane (10 mL) for 4 h at 0 ºC. **1d-D** (490 mg, 1.7 mmol, 92%) was obtained as a colorless oil after purification by column chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). The D/H ratio at the *ortho* positions (1.92D + 0.08H) was determined by ^{13}C NMR (see Figure S73). **1d-D**: ^1H NMR (600 MHz, C_6D_6) δ 6.93 (s, 2H), 4.54-4.56 (m, 1H), 4.36-4.38 (m, 1H), 4.23 (s, 2H), 2.11 (s, 3H), 0.96 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (151 MHz, C_6D_6) δ 157.2, 155.0, 130.2 (two non-equivalent carbons were overlapped), 114.9 (t, J = 23 Hz), 92.5, 69.3, 25.9, 20.6, 18.4, –4.4. HRMS (EI, positive) *m/z* calcd for $C_{16}H_{24}D_2O_2Si^+$ $[M]^+$: 280.1822, found: 280.1827.

9-2. Deuterium Incorporation (Scheme 7)

9-2-1. The Double Bond Migration of 1p-D to Afford 4p-D (Scheme 7a)



According to the *General Procedure 1* described in Section 6, the reaction was carried out at 110 ºC for 24 h using $[IrCl(C_2H_4)_2]_2$ (4.55 mg, 0.0079 mmol), (*S*)-**L1** (18.9 mg, 0.0160 mmol), **1p-D** (33.4 mg, 0.20 mmol), and toluene (0.4 mL). A mixture of **4p-D**, **3p-D**, and **1p-D** (28.8 mg, 86%, **4p-D**:**3p-D**:**1p-D** = 72:16:12) was obtained after purification by chromatography on silica gel (Chromatolex NH-DM2035; eluent: hexane). ^{1}H NMR analysis of the mixture focusing on the peaks of **4p-D** indicates deuterium incorporation at the allylic two carbon ($C_2H_{2.74}D_{3.26}$) and the vinylic carbon ($CH_{0.26}D_{0.74}$) (Figure S2). The H/D ratio was determined based on the methyl group (3.00H) on the benzene ring. No deuterium incorporation was observed at the aromatic carbons of **4p-D**. **4p-D**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08-7.10 (m, 2H, Ar*H*), 6.86-6.88 (m, 2H, Ar*H*), 6.18 (s, 0.26H, vinylic C*H*), 2.30 (s, 3H, ArCH_3), 1.78-1.84 (m, 0.18 H, allylic CH_3, CH_2D, and C*H*D$_2$), 1.64-1.74 (m, 2.56H, allylic CH_3, CH_2D, and C*H*D$_2$).

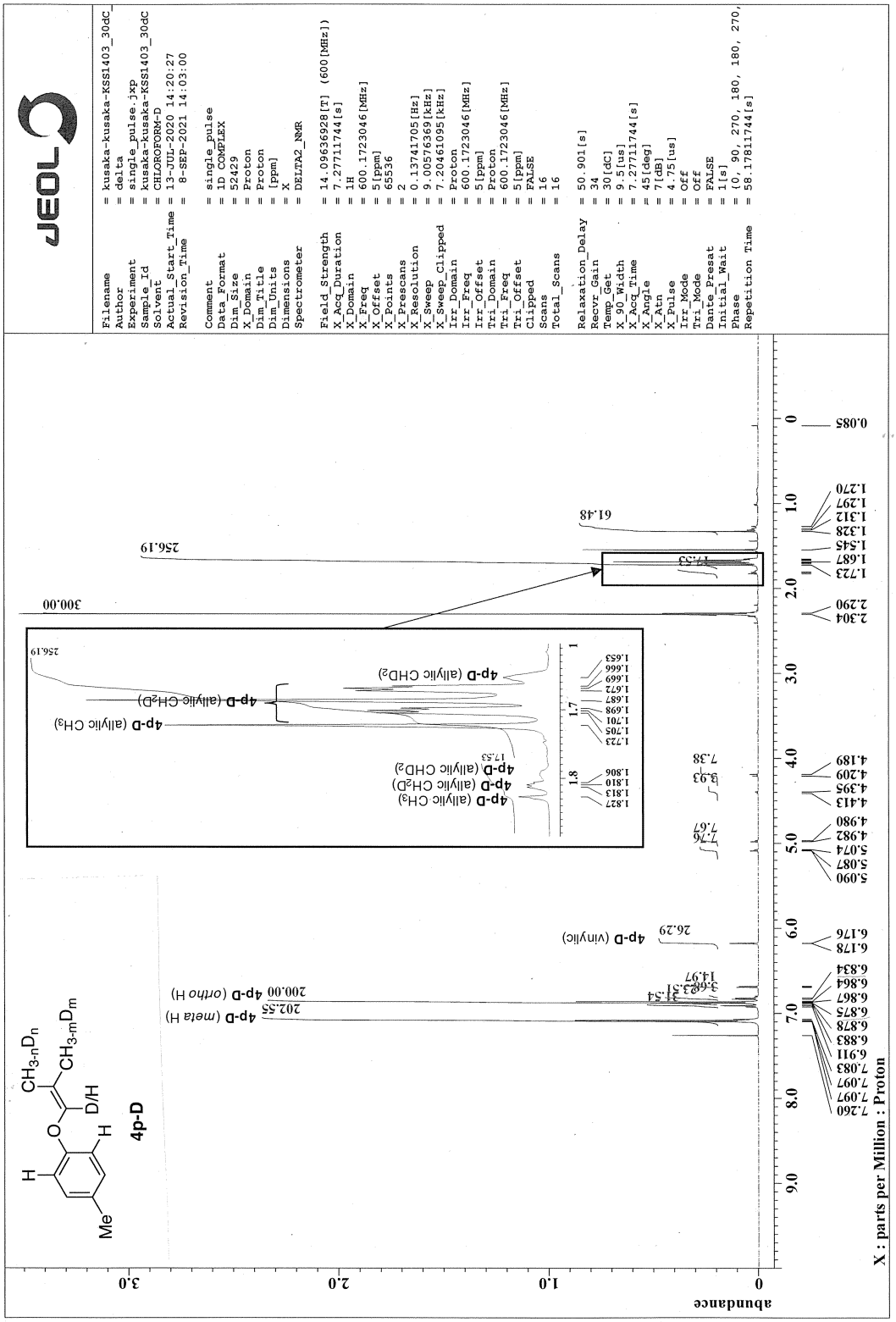
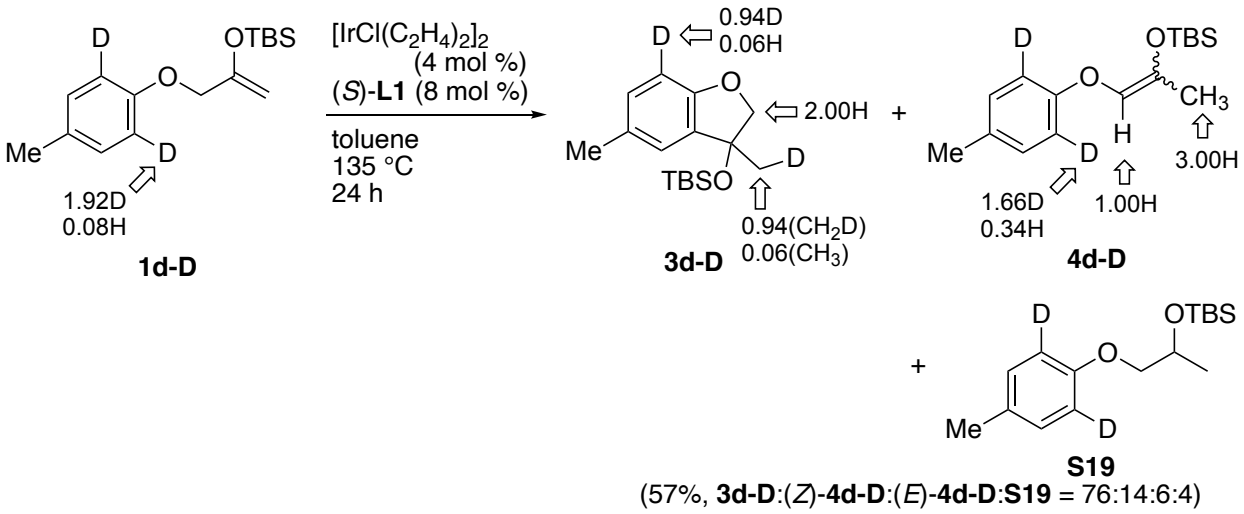


Figure S2. ^{1}H NMR Spectrum of **4p-D** (a mixture with **3p-D** and **1p-D**, **4p-D**:**3p-D**:**1p-D** = 72:16:12) (600 MHz, $CDCl_3$)

9-2-2. The Intramolecular Hydroarylation of 1d-D to Afford 3d-D (Scheme 7b)



According to the *General Procedure 1* described in Section 6, the reaction was carried out at 135 ºC for 12 h using $[IrCl(C_2H_4)_2]_2$ (6.6 mg, 0.012 mmol), (*S*)-**L1** (28.1 mg, 0.024 mmol), **1d-D** (74.1 mg, 0.26 mmol), and toluene (0.6 mL). Purification by column chromatography on silica gel (Chlomatolex NH-DM2035: eluent: hexane) afforded a mixture of hydroarylation product **3d-D**, double bond migration product **4d-D**, and hydrogenated **S19** (57%, **3d-D**:(*Z*)-**4d-D**:(*E*)-**4d-D**:**S19** = 76:14:6:4). ^{1}H NMR analysis of the mixture focusing on the peaks of **3d-D** indicated deuterium incorporation at the C3-methyl group of **3d-D** [0.94(CH_2D) + 0.06(CH_3)] (Figure S3). No deuterium incorporation was observed at the C2 methylene of **3d-D**. The H/D ratio was determined based on one of the methyl groups on the silicon atom (3.00H). The D/H ratio at the C7 position of **3d-D** (0.94D + 0.06H) was determined by ^{13}C NMR (Figure S4). ^{1}H NMR analysis of the mixture focusing on the peaks of **4d-D** indicated no deuterium incorporation at both the allylic and the vinylic carbons of **4d-D** (Figure S3). The H/D ratio was determined based on the methyl groups on the benzene ring (3.00H). The D/H ratio at the *ortho* positions of **4d-D** (1.66D + 0.34H) was determined by ^{13}C NMR (Figure S4). **3d-D**: ^{1}H NMR (600 MHz, C_6D_6) δ 7.02-7.03 (m, 1H), 6.83 (s, 1H), 4.35 (d, J = 10.2 Hz, 1H), 3.96 (d, J = 10.2 Hz, 1H), 2.12 (s, 3H), 1.41 (t, J = 1.8 Hz, 2H, CH_2D), 0.92 (s, 9H), –0.06 (s, 3H), –0.18 (s, 3H). ^{13}C NMR (151 MHz, C_6D_6) δ 158.9, 132.2, 130.9, 129.8, 124.5, 110.3 (t, J = 24 Hz, sp^2*C*D), 84.5, 79.8, 26.5 (t, J = 19 Hz, *C*H_2D), 26.0, 20.8, 18.2, –3.3, –3.6. HRMS (EI, positive) *m/z* calcd for $C_{16}H_{24}D_2O_2Si^+$ $[M]^+$: 280.1822, found: 280.1823.

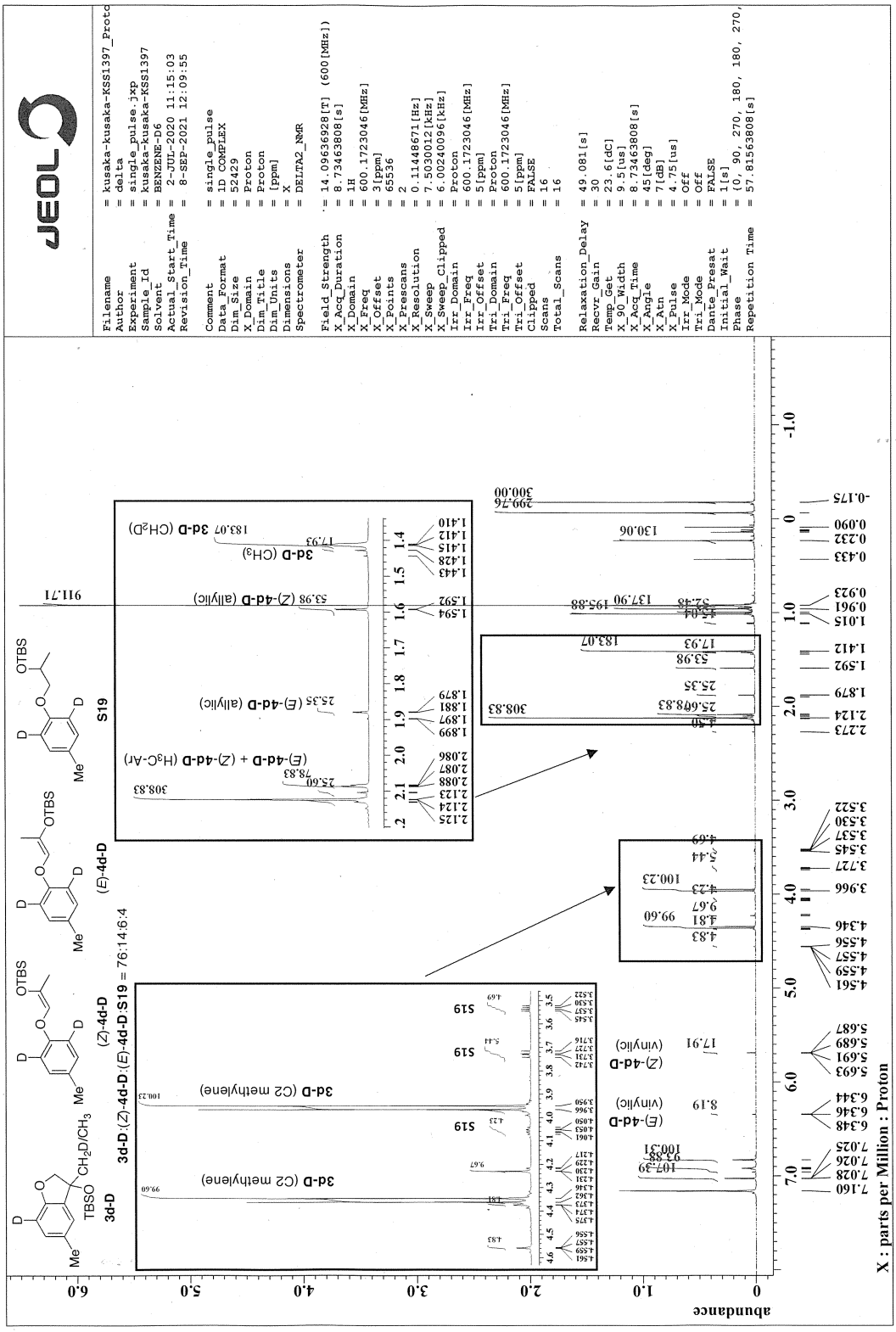


Figure S3. ^{1}H NMR Spectrum of **3d-D** [a mixture with **4d-D** and **S19**, **3d-D**:(*Z*)-**4d-D**:(*E*)-**4d-D**:**S19** = 76:14:6:4] (600 MHz, C_6D_6)

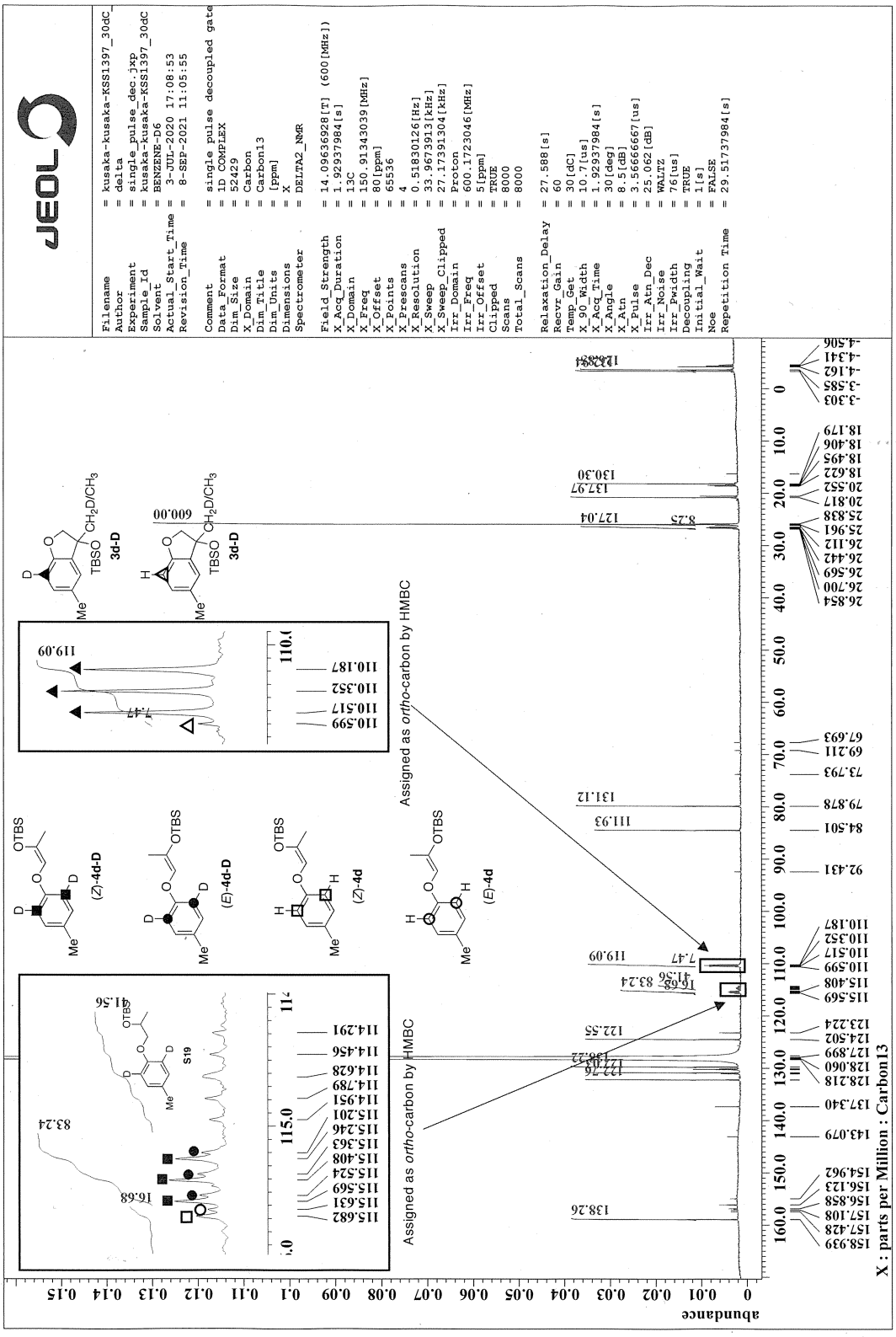


Figure S4. ^{13}C NMR Spectrum of **3d-D** [a mixture with **4d-D** and **S19**, **3d-D**:(*Z*)-**4d-D**:(*E*)-**4d-D**:**S19** = 76:14:6:4] (151 MHz, C_6D_6, inverse gated ^{1}H decoupling)

9-3. Kinetic Isotope Effect (Scheme 8)

*Reaction Tracing of **1d***: In a glovebox, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with $[IrCl(C_2H_4)_2]_2$ (2.25 mg, 0.0040 mmol), (*S*)-**L1** (9.43 mg, 0.0078 mmol), **1d** (54.5 mg, 0.20 mmol), toluene (1.0 mL), and dibenzyl ether (26.68 mg, 0.13 mmol, internal standard). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 135 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 10 min, the tube was removed from the heating block and was cooled immediately by ice/water. The tube was brought into a glove box. A part of the reaction mixture (100 μL) was transferred to NMR sample tube, diluted with C_6D_6 (500 μL), and performed ^1H NMR analysis to determine conversion of **1d**. The operation of heating for 10 min and sampling was repeated three times using the remaining reaction solution. The conversions for every 10 min were obtained as follows: 9.2% (10 min), 15.3% (20 min), 20.4% (30 min), and 25.0% (40 min).

*Reaction Tracing of **1d-D***: According to the procedure described above, **1d-D** (56.1 mg, 0.20 mmol) was reacted using $[IrCl(C_2H_4)_2]_2$ (2.26 mg, 0.0040 mmol), (*S*)-**L1** (9.44 mg, 0.0078 mmol), toluene (1.0 mL), and dibenzyl ether (22.59 mg, 0.11 mmol, internal standard). The conversions for every 15 min were obtained as follows: 11.6% (15 min), 17.4% (30 min), 21.4% (45 min), and 25.3% (60 min).

Time vs. $\ln([\mathbf{1d}]/[\mathbf{1d}]_0)$ and $\ln([\mathbf{1d\text{-}D}]/[\mathbf{1d\text{-}D}]_0)$ are shown in Fig. S5. A gradient of the approximate straight lines are obtained as -6.3×10^{-3} for **1d** (blue line) and -3.7×10^{-3} for **1d-D** (red line). Hence k_H/k_D is obtained as 1.7.

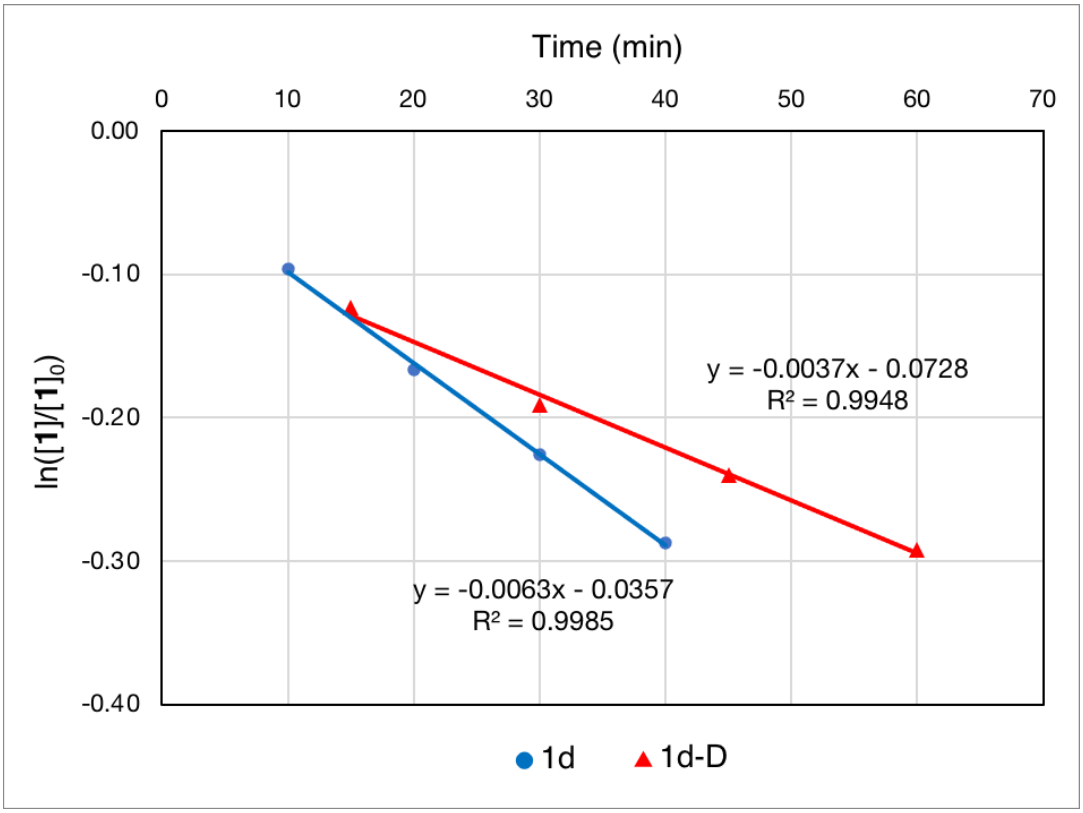


Figure S5. Time vs. ln([**1**]/[**1**]$_0$)

10. References

1 M. A. Arthurs, J. Bickerton, S. R. Stobart, J. Wang, *Organometallics* 1998, **17**, 2743.
2 R. Cramer, J. A. Mccleverty, J. Bray, *Inorg. Synth.* 1990, **28**, 86.
3 G. E. M. Crisenza, N. G. McCreanor, J. F. Bower, *J. Am. Chem. Soc.* 2014, **131**, 10258.
4 J. L. Herde, J. C. Lambert, C. V. Senoff, M. A. Cushing, *Inorg. Synth.* 1974, **15**, 18.
5 A. van der ENT, A. L. Onderdelinden. *Inorg. Synth.* 1990, **28**, 90.
6 A. Alexakis, S. Rosset, J. Allamand, S. March, F. Guillen, C. Benhaim, *Synlett* 2001, 1375.
7 C. S. Sevov, J. F. Hartwig, *J. Am. Chem. Soc.* 2014, **136**, 10625.
8 Y. Suto, R. Tsuji, M. Kanai, M. Shibasaki, *Org. Lett.* 2005, **7**, 3757.
9 M.-L. Ma, Z.-H. Peng, L. Chen, Y. Guo, H. Chen, X.-J. Li, *Chin. J. Chem.* 2006, **24**, 1391.
10 A. Sinha, S. Khatua, M. Bhattacharjee *J. Organomet. Chem.* 2014, **770**, 116.
11 G. M. Rubottom, M. A. Vazquez, D. R. Pelegrina, *Tetrahedron Lett.* 1974, 4319.
12 (a) P. Golborn, F. Scheinmann, *J. Chem. Soc. Perkin Trans. 1*, 1973, 2870. (b) D. Baudry, M. Ephritikhine, H. Felkin, *J. Chem. Soc. Chem. Commun.* 1978, 694. (c) J. V. Crivello, S. Kong, *J. Org. Chem.* 1998, **63**, 6745. (d) S. Krompiec, N. Kuznik, R. Penezek, J. Rzepa, J. Mrowiec-Bialon, *J. Mol. Catal. A* 2004, **219**, 29.
13 T. Ohmura, S. Kusaka, T. Torigoe, M. Suginome, *Adv. Synth. Catal.* 2019, **361**, 4448.
14 (a) H. A. J. Carless, D. J. Haywood, *J. Chem. Soc., Chem. Commun.* 1980, 980. (b) W. Gao, X. Zhang, X. Xie, S. Ding, *Chem. Commun.* 2020, **56**, 2012.

11. ^{1}H and ^{13}C NMR Spectra of New Compounds

^{1}H and ^{13}C NMR spectra of **1c-m**, **1o**, **4c**, **3c-l**, **5d-l**, **1p-D**, and **1d-D** are given in following pages.

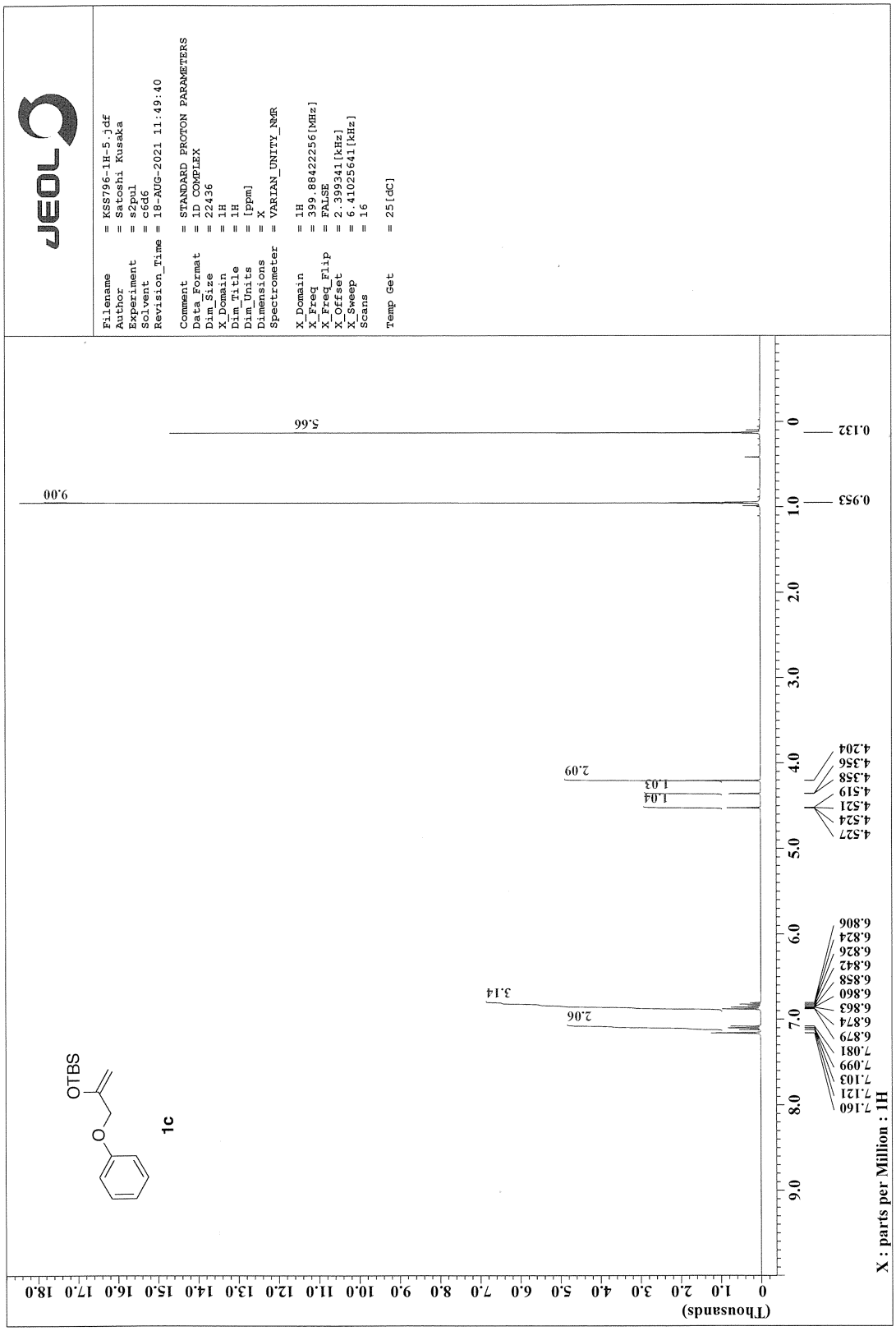


Figure S6. ^{1}H NMR Spectrum of **1c** (400 MHz, C_6D_6)

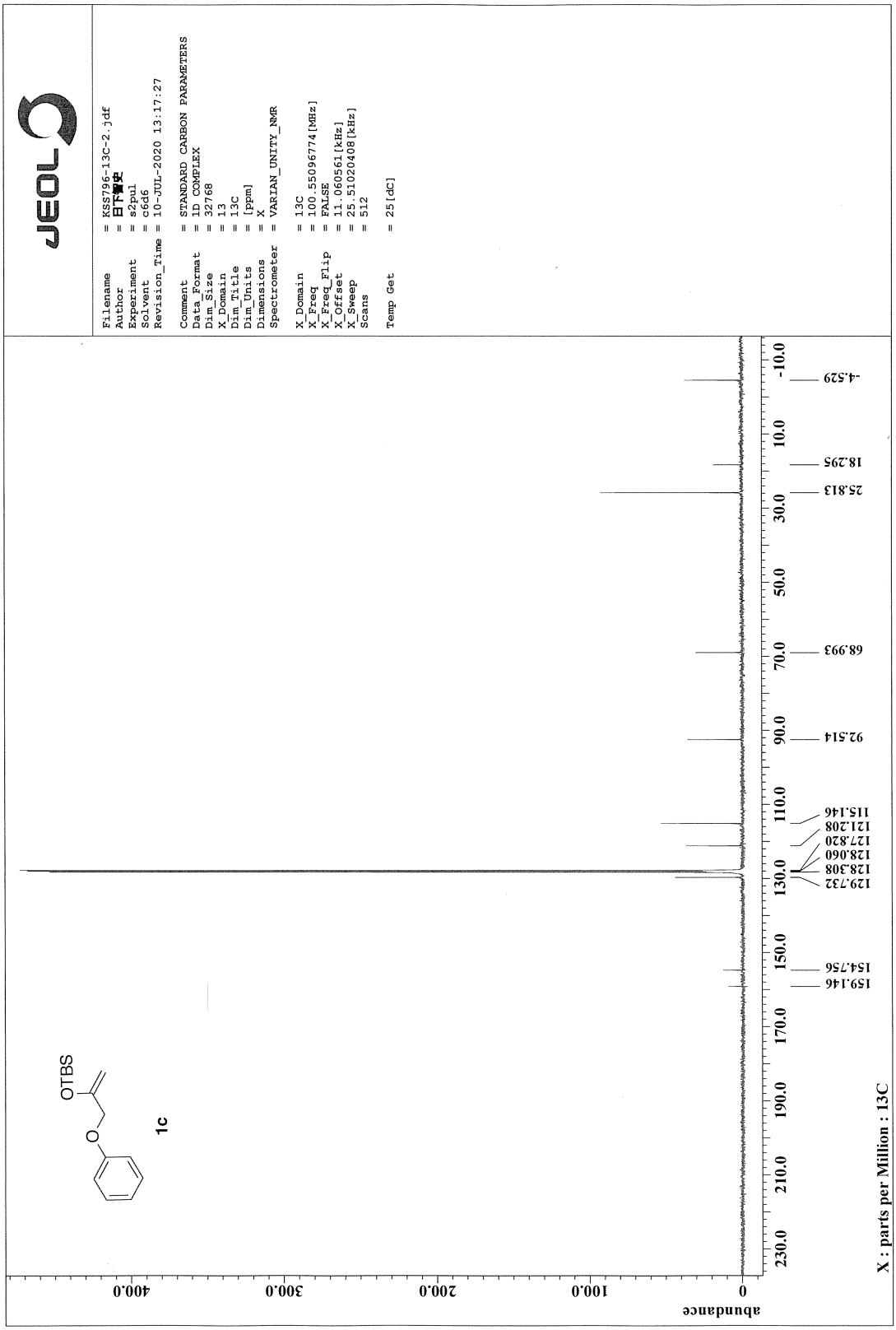


Figure S7. ^{13}C NMR Spectrum of **1c** (101 MHz, C_6D_6)

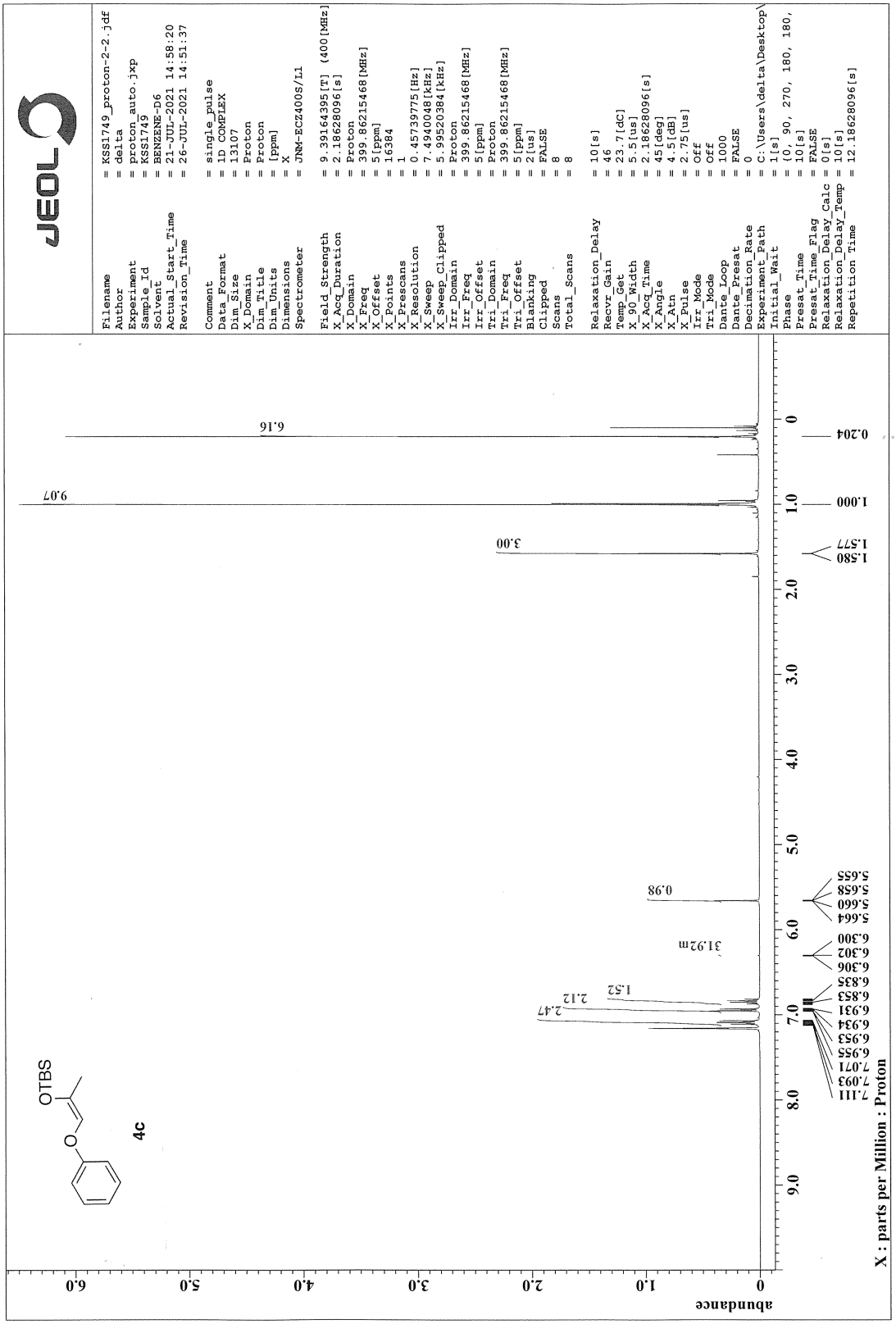


Figure S8. ^{1}H NMR Spectrum of (*Z*)-**4c** (400 MHz, C_6D_6)

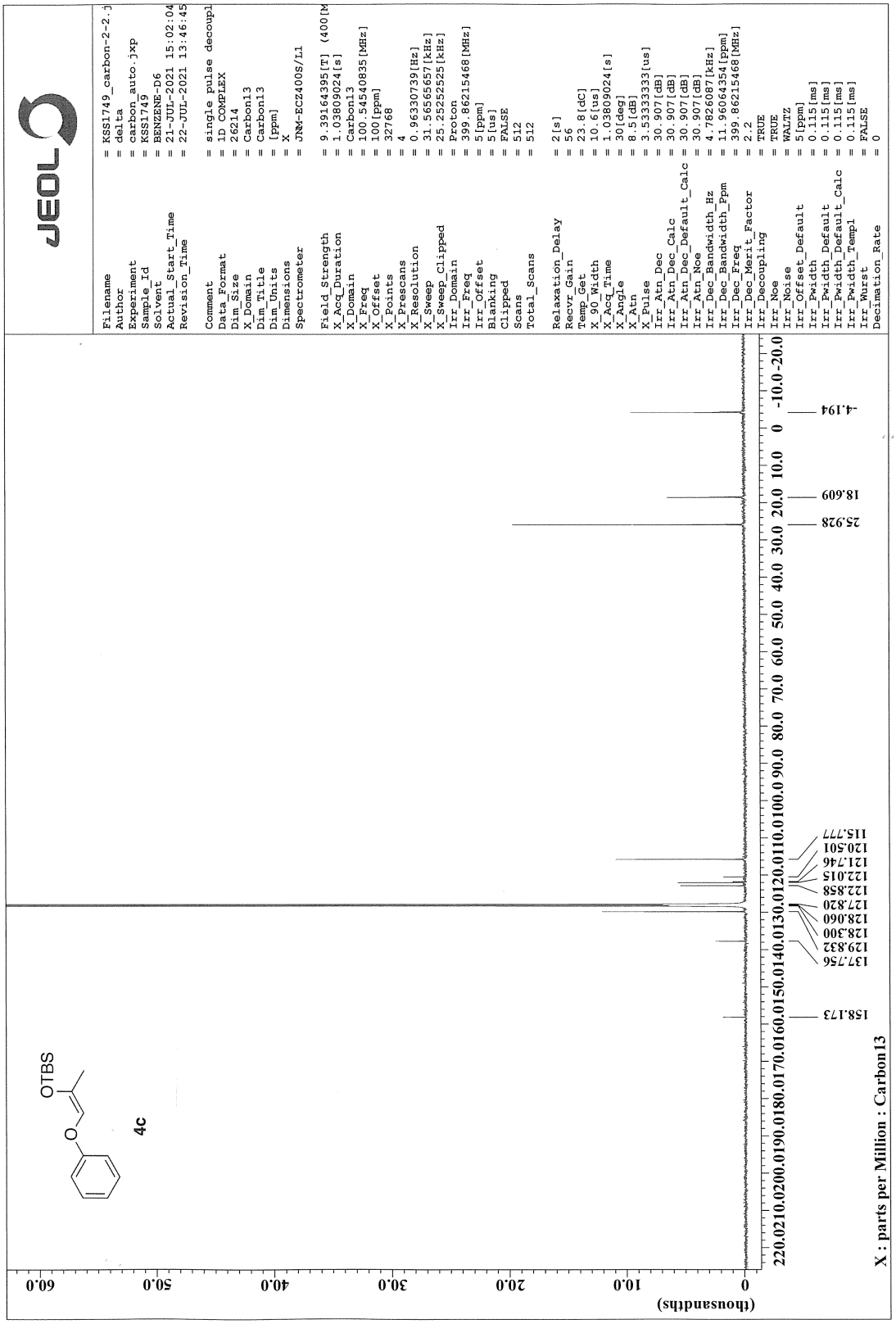


Figure S9. ^{13}C NMR Spectrum of (*Z*)-**4c** (101 MHz, C_6D_6, inverse gated ^{1}H decoupling)

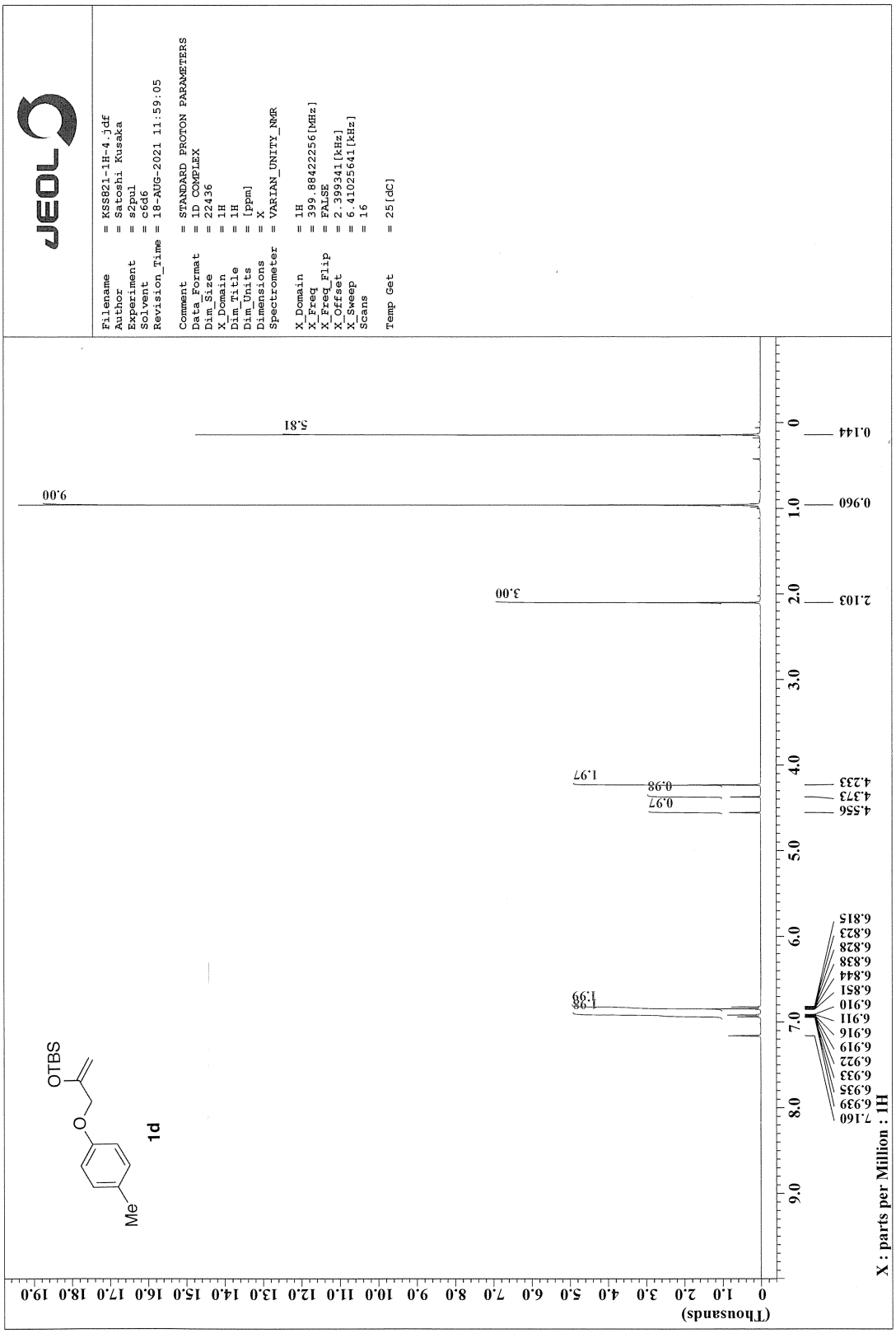


Figure S10. ^{1}H NMR Spectrum of **1d** (400 MHz, C_6D_6)

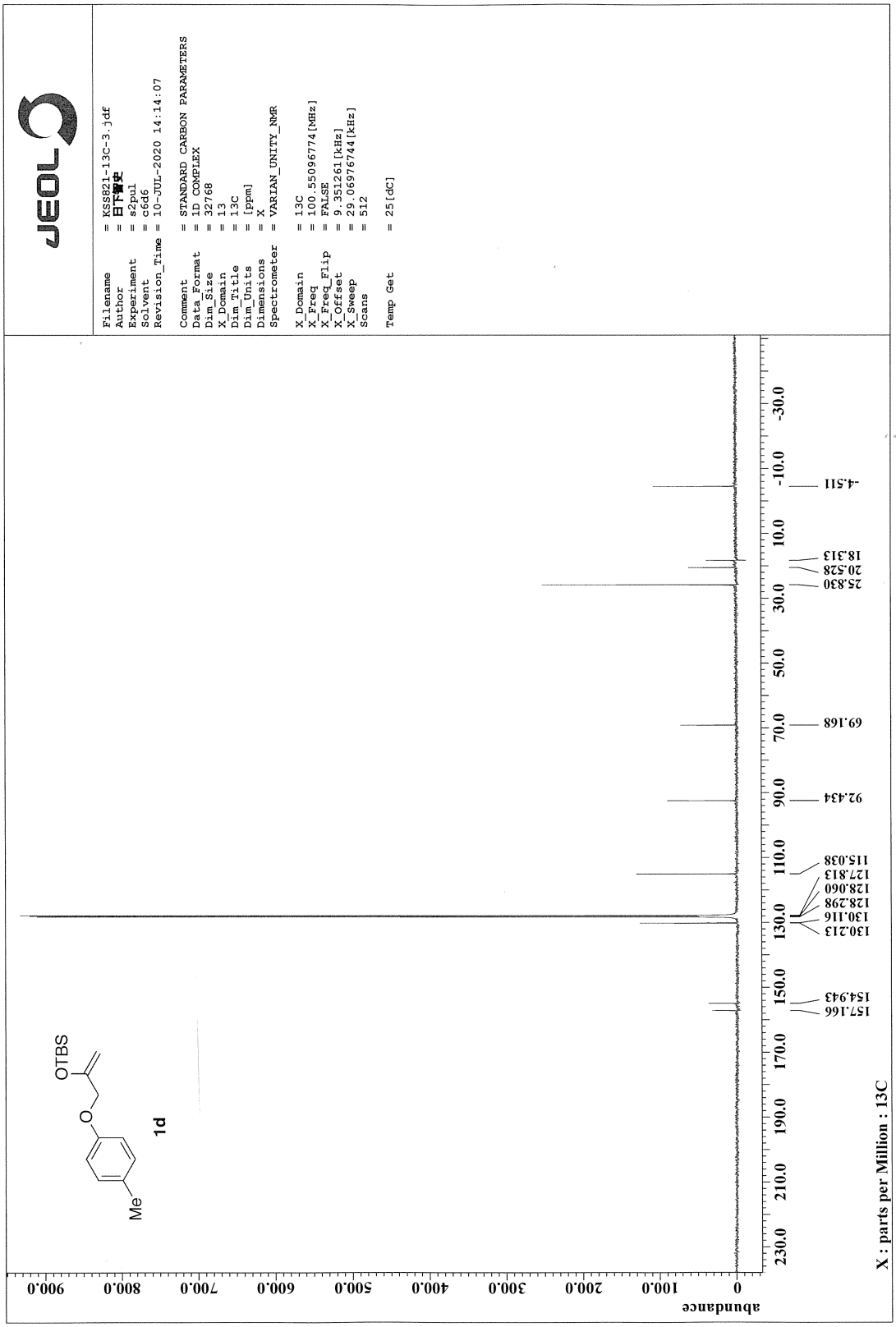


Figure S11. ^{13}C NMR Spectrum of **1d** (101 MHz, C_6D_6)

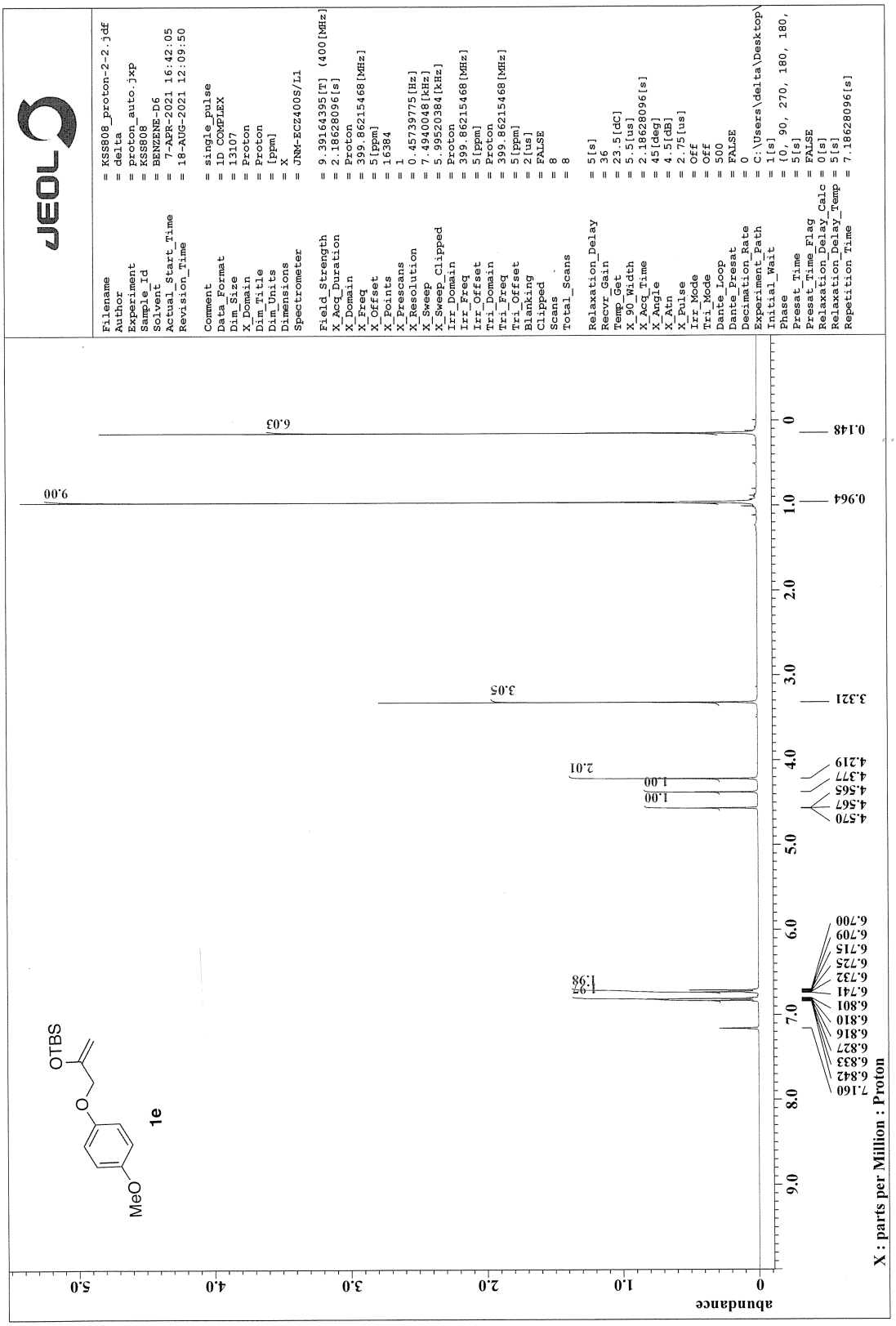


Figure S12. ^{1}H NMR Spectrum of **1e** (400 MHz, C_6D_6)

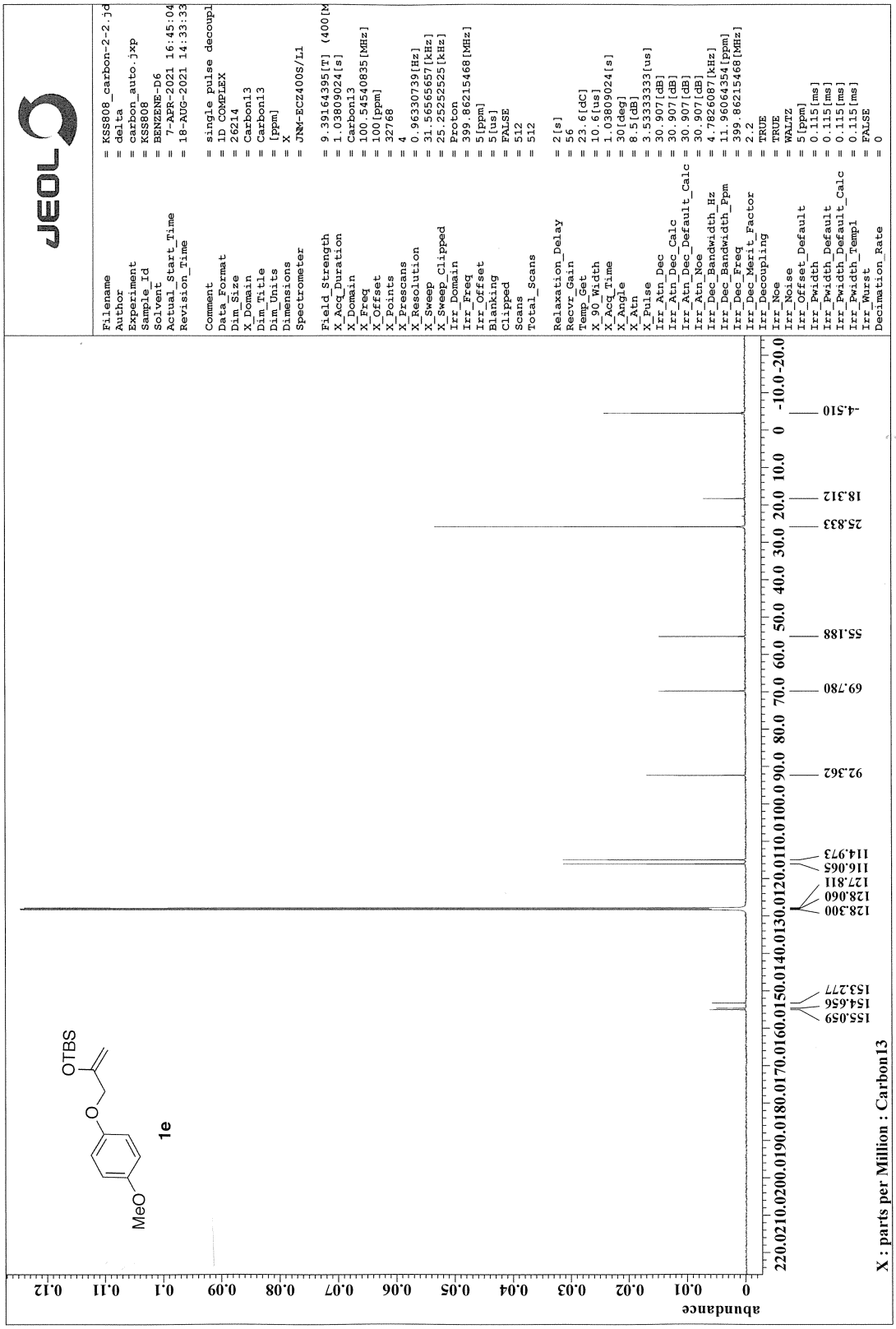


Figure S13. ^{13}C NMR Spectrum of **1e** (101 MHz, C_6D_6)

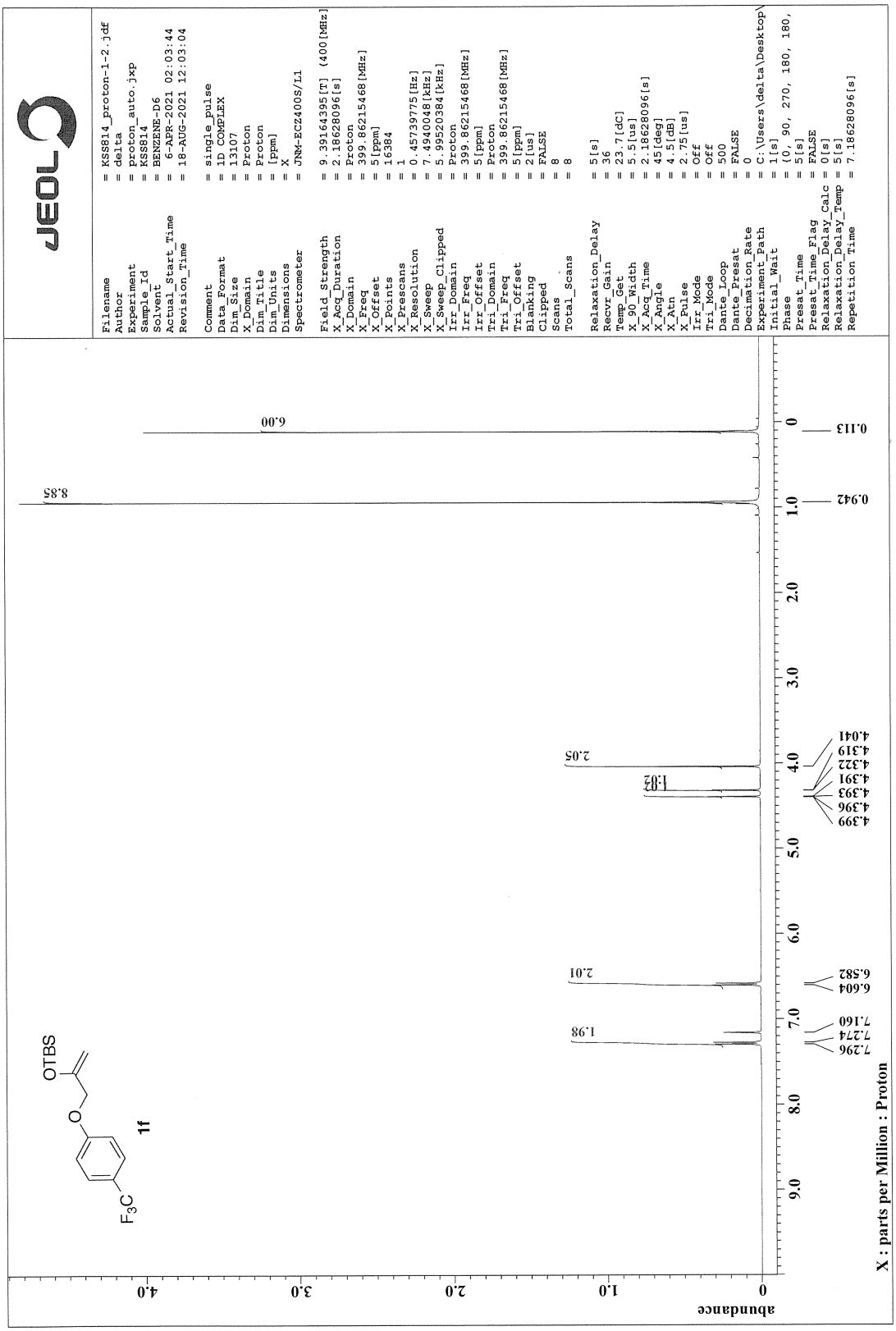


Figure S14. ^{1}H NMR Spectrum of **1f** (400 MHz, C_6D_6)

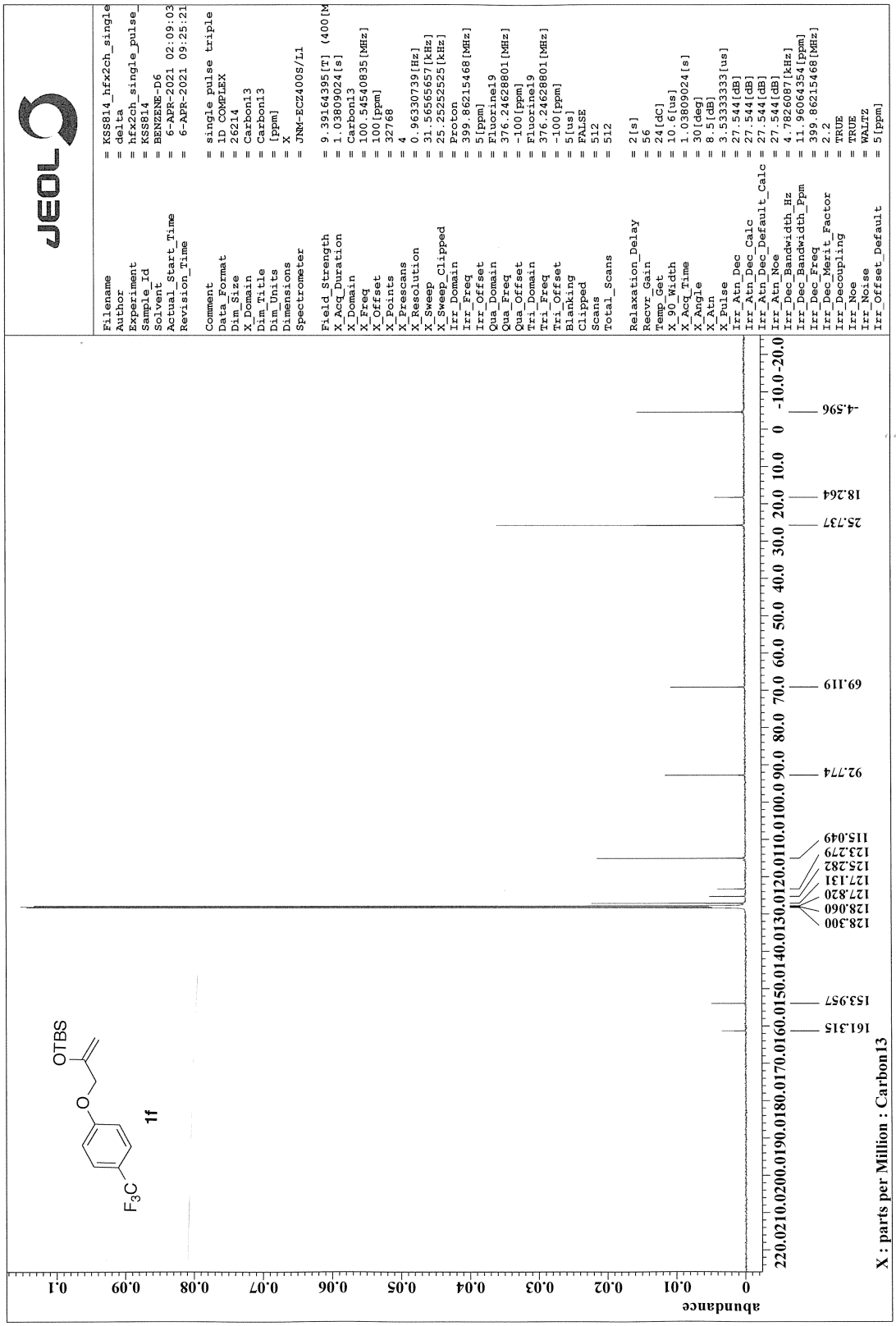


Figure S15. ^{13}C NMR Spectrum of **1f** (101 MHz, C_6D_6, ^{1}H and ^{19}F simultaneous decoupling)

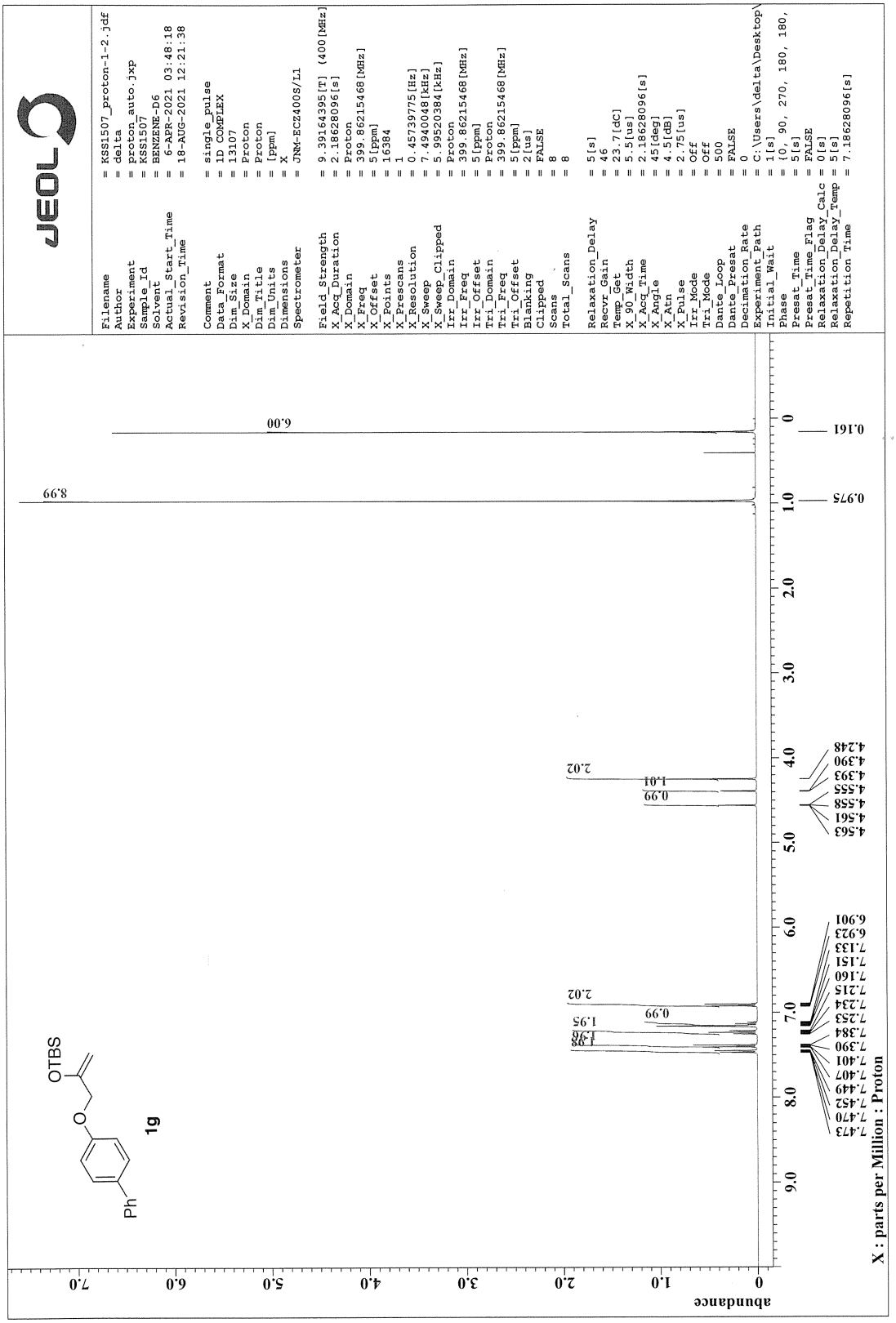


Figure S16. ^{1}H NMR Spectrum of **1g** (400 MHz, C_6D_6)

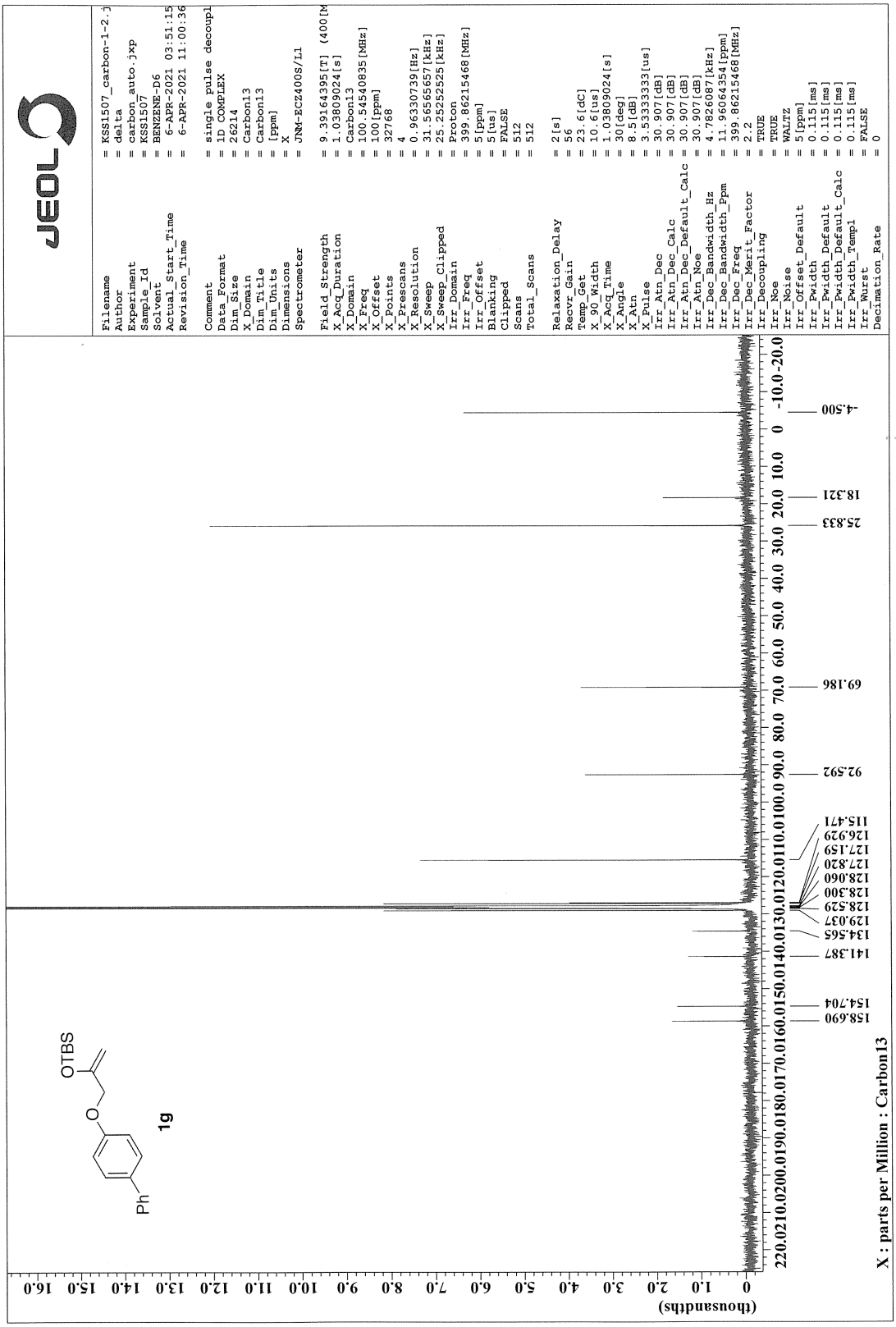


Figure S17. ^{13}C NMR Spectrum of **1g** (101 MHz, C_6D_6)

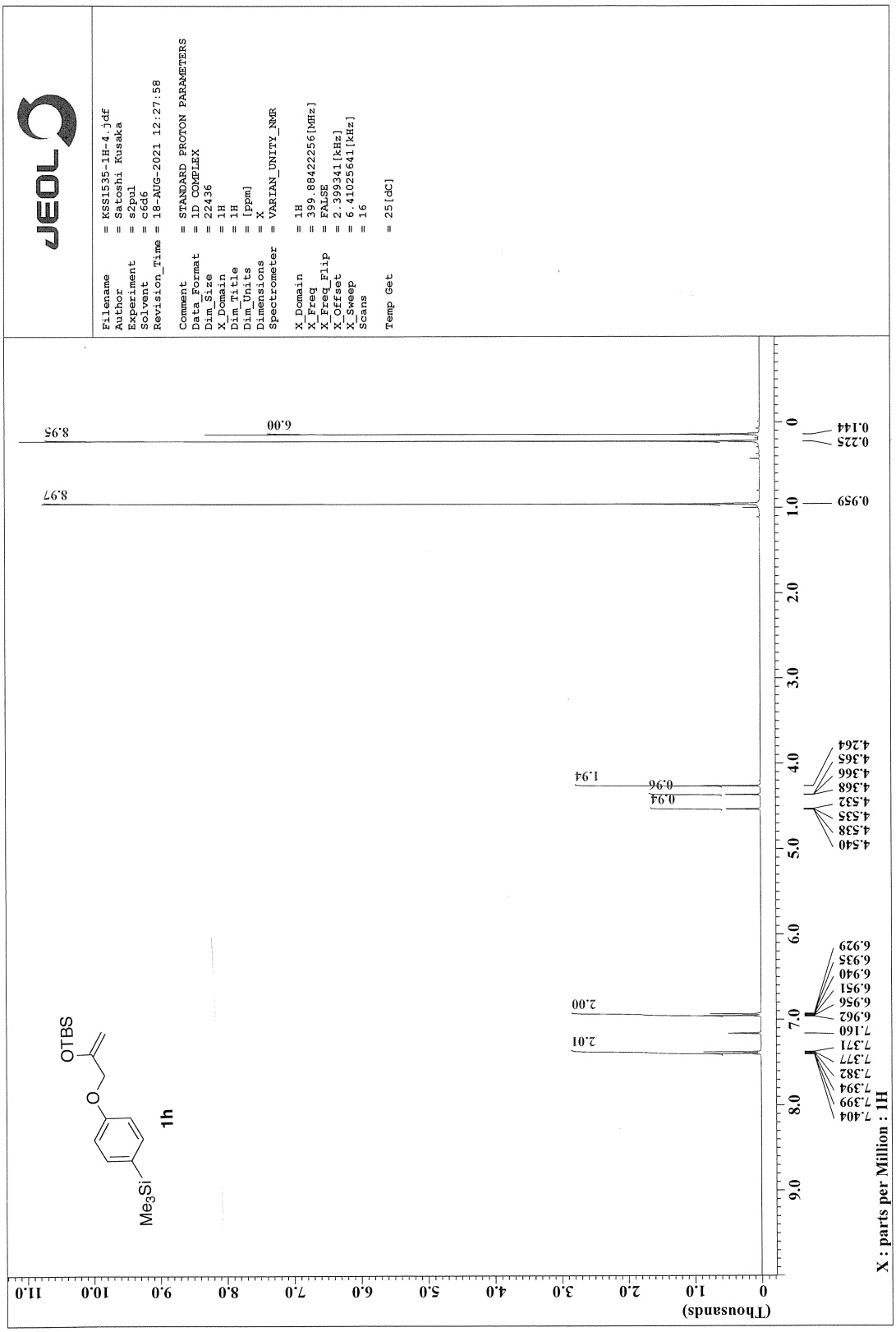


Figure S18. ^{1}H NMR Spectrum of **1h** (400 MHz, C_6D_6)

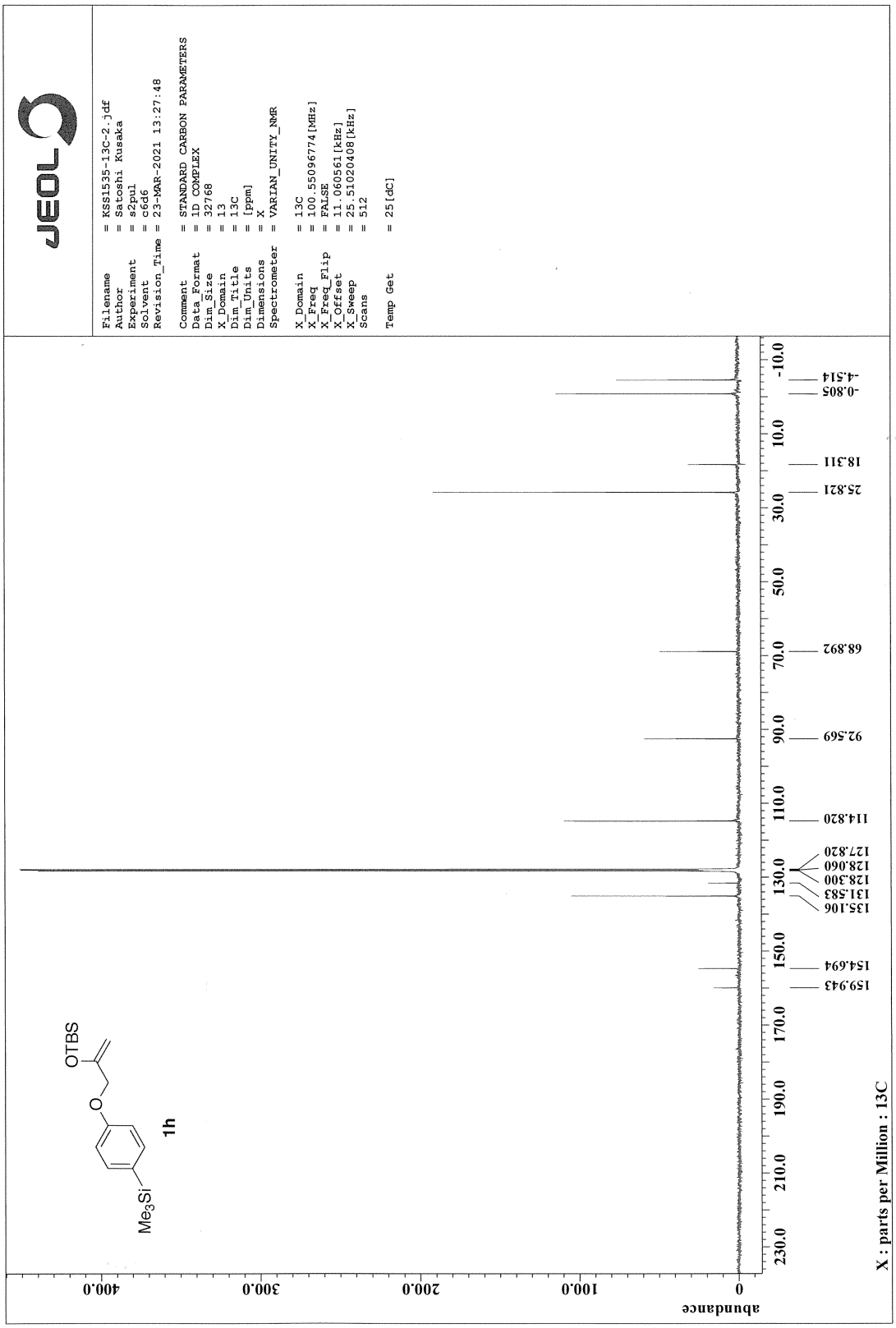


Figure S19. ^{13}C NMR Spectrum of **1h** (101 MHz, C_6D_6)

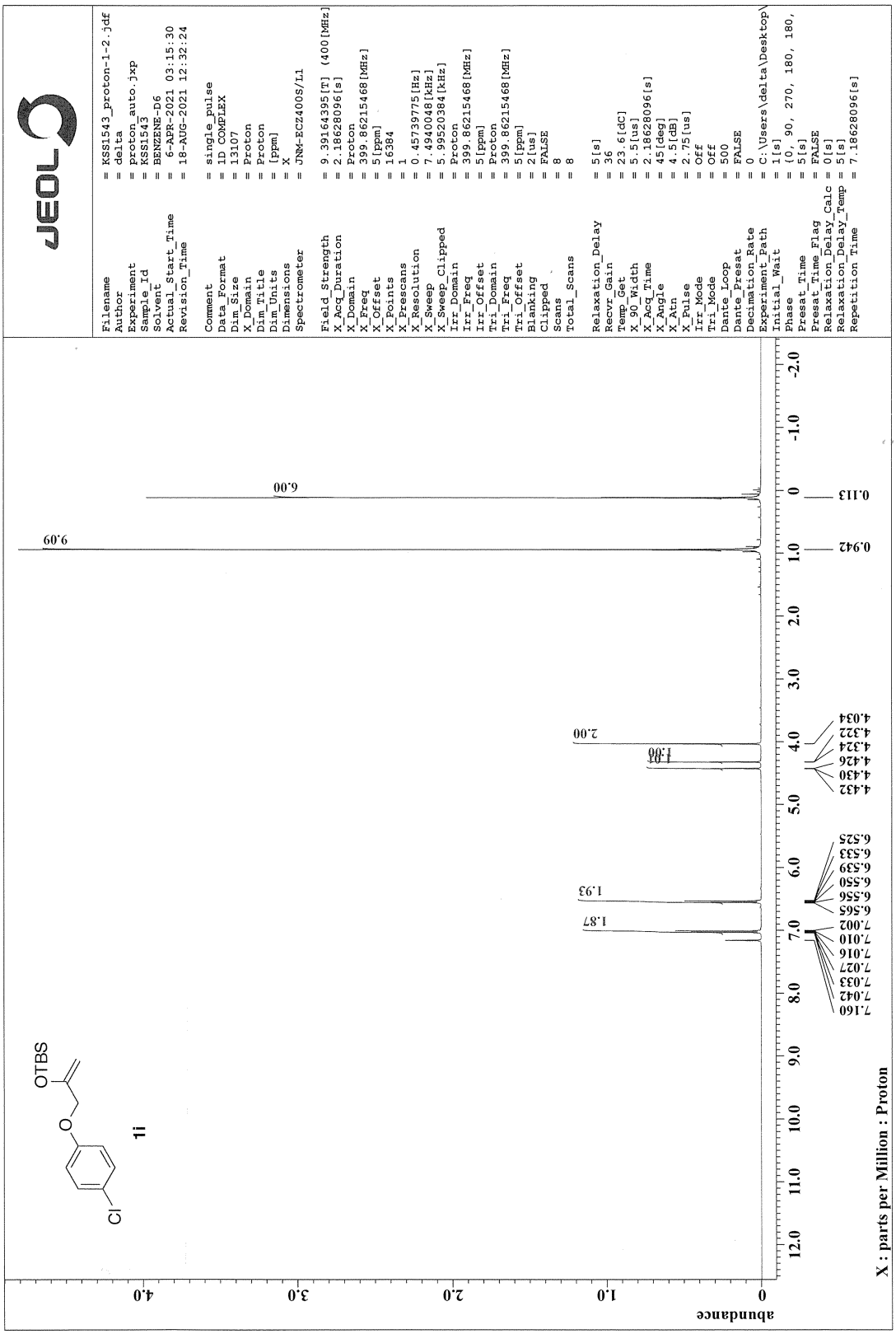


Figure S20. ^{1}H NMR Spectrum of **1i** (400 MHz, C_6D_6)

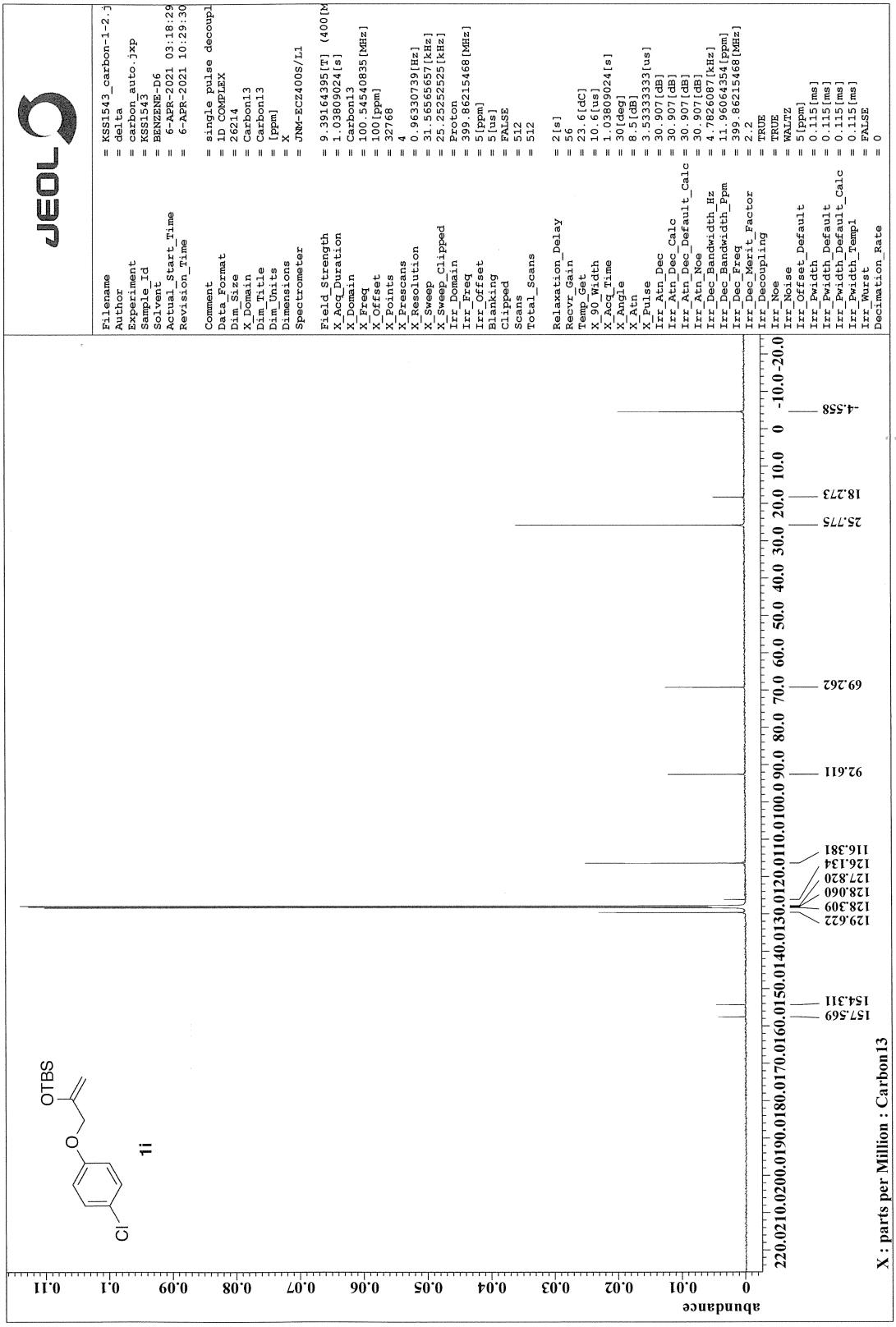


Figure S21. ^{13}C NMR Spectrum of **1i** (101 MHz, C_6D_6)

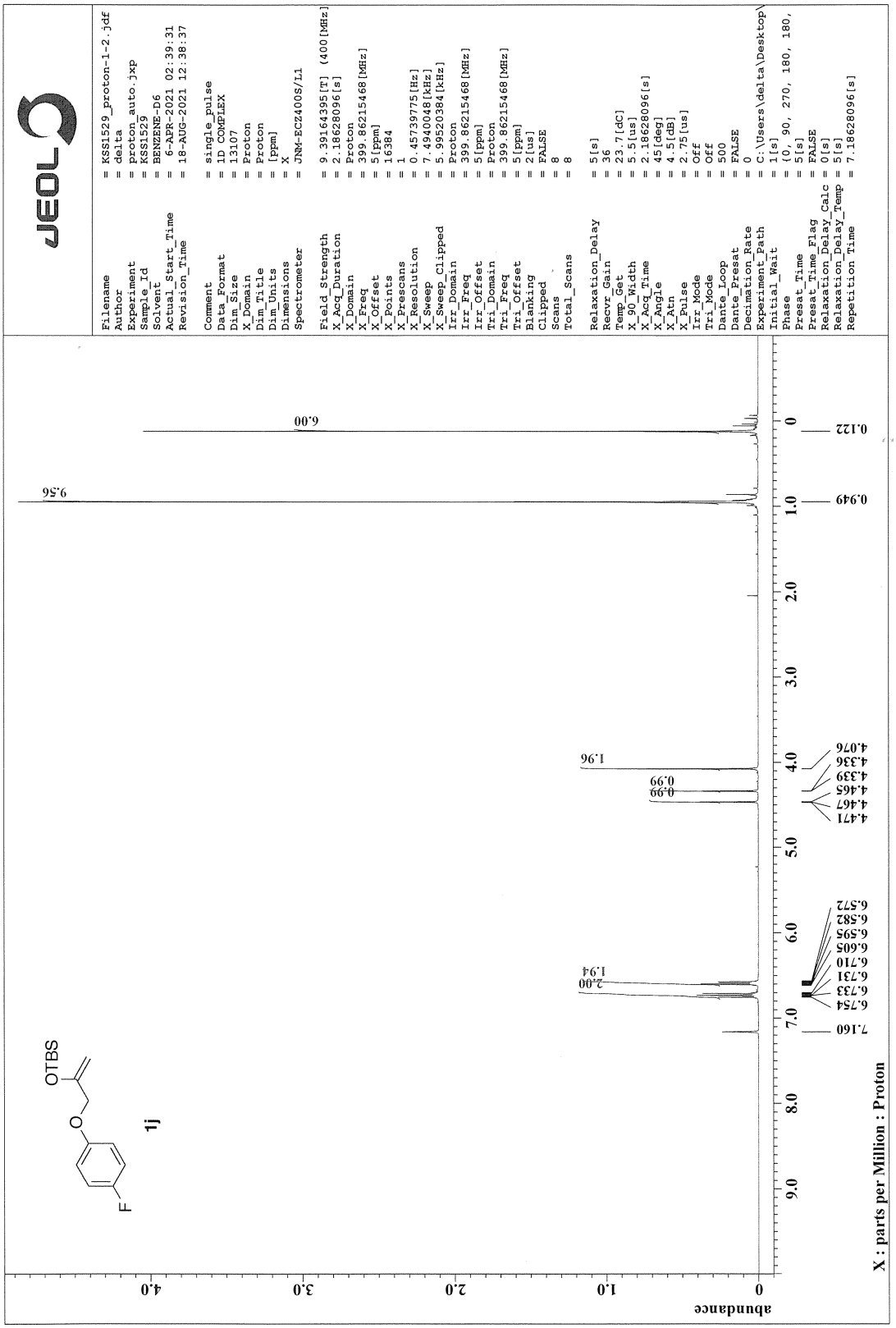


Figure S22. ^{1}H NMR Spectrum of **1j** (400 MHz, C_6D_6)

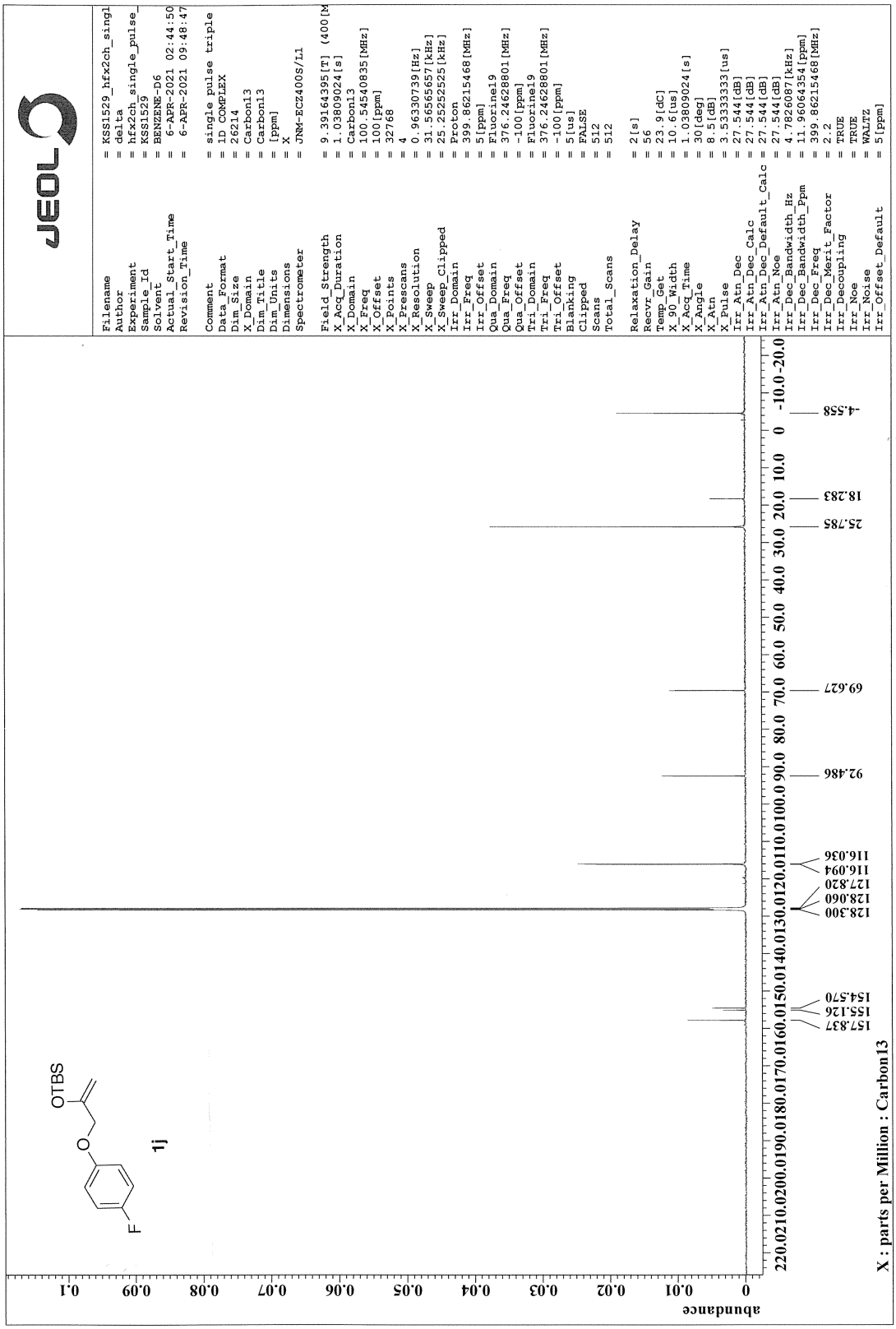


Figure S23. ^{13}C NMR Spectrum of **1j** (101 MHz, C_6D_6, ^{1}H and ^{19}F simultaneous decoupling)

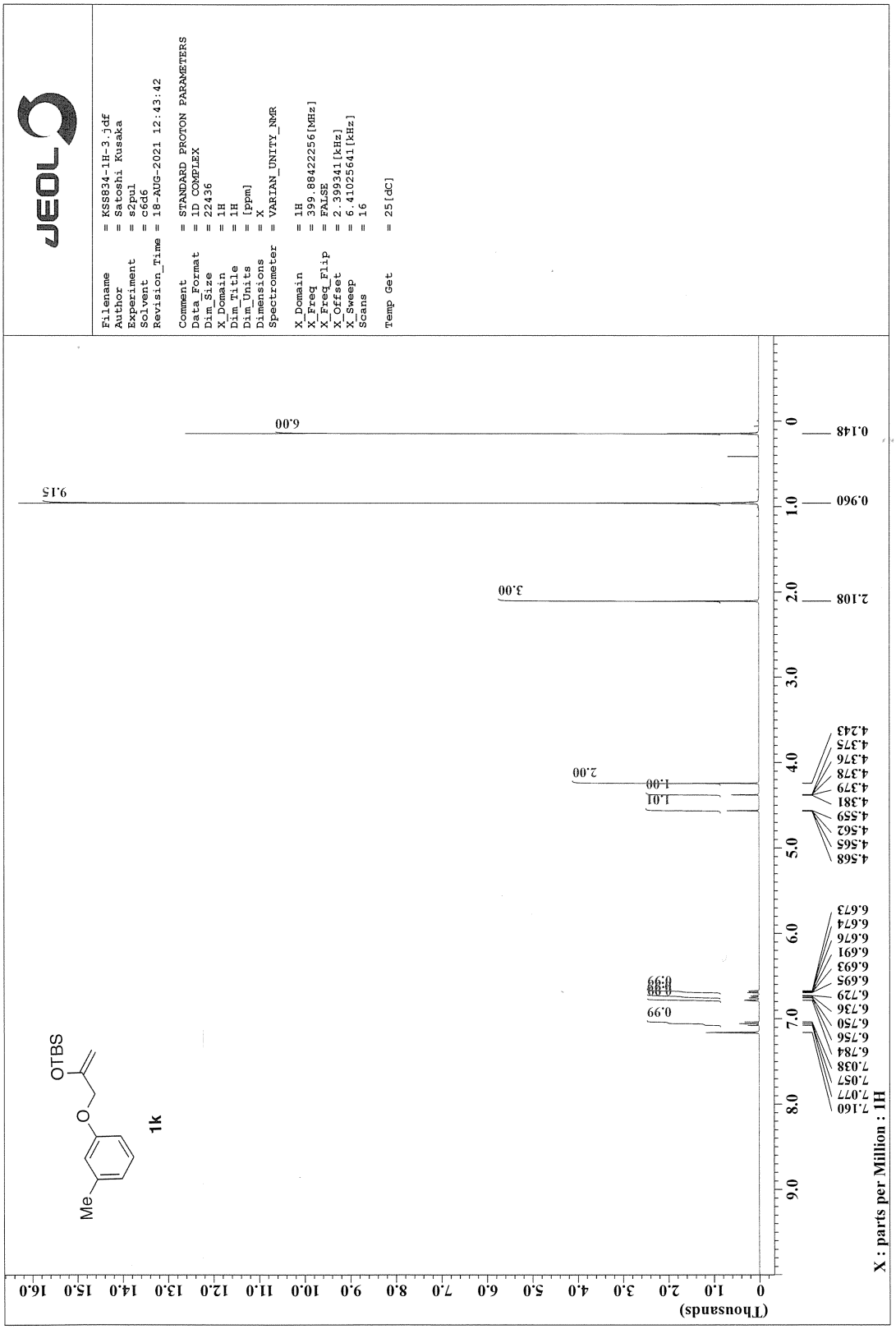


Figure S24. ^{1}H NMR Spectrum of **1k** (400 MHz, C_6D_6)

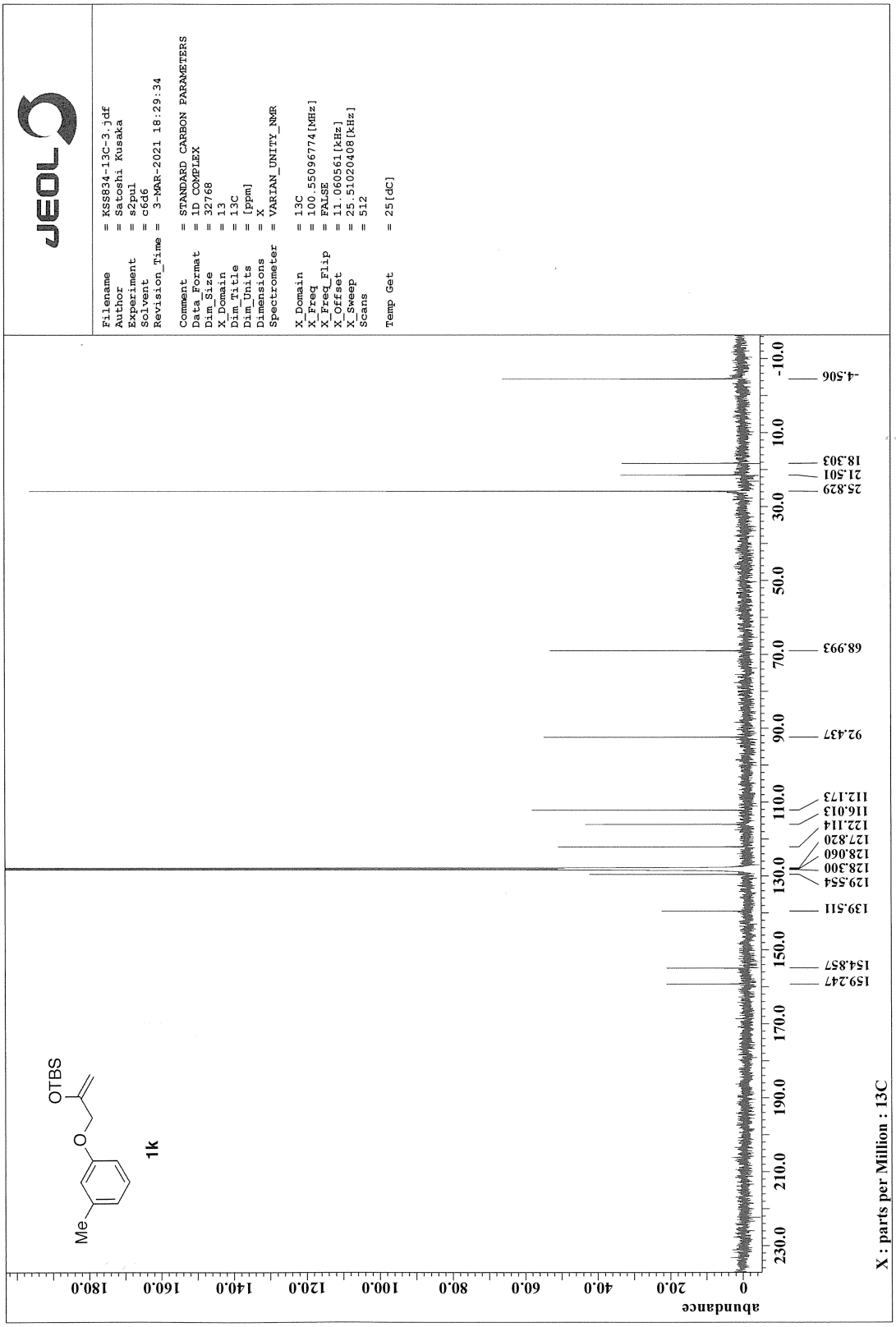


Figure S25. ^{13}C NMR Spectrum of **1k** (101 MHz, C_6D_6)

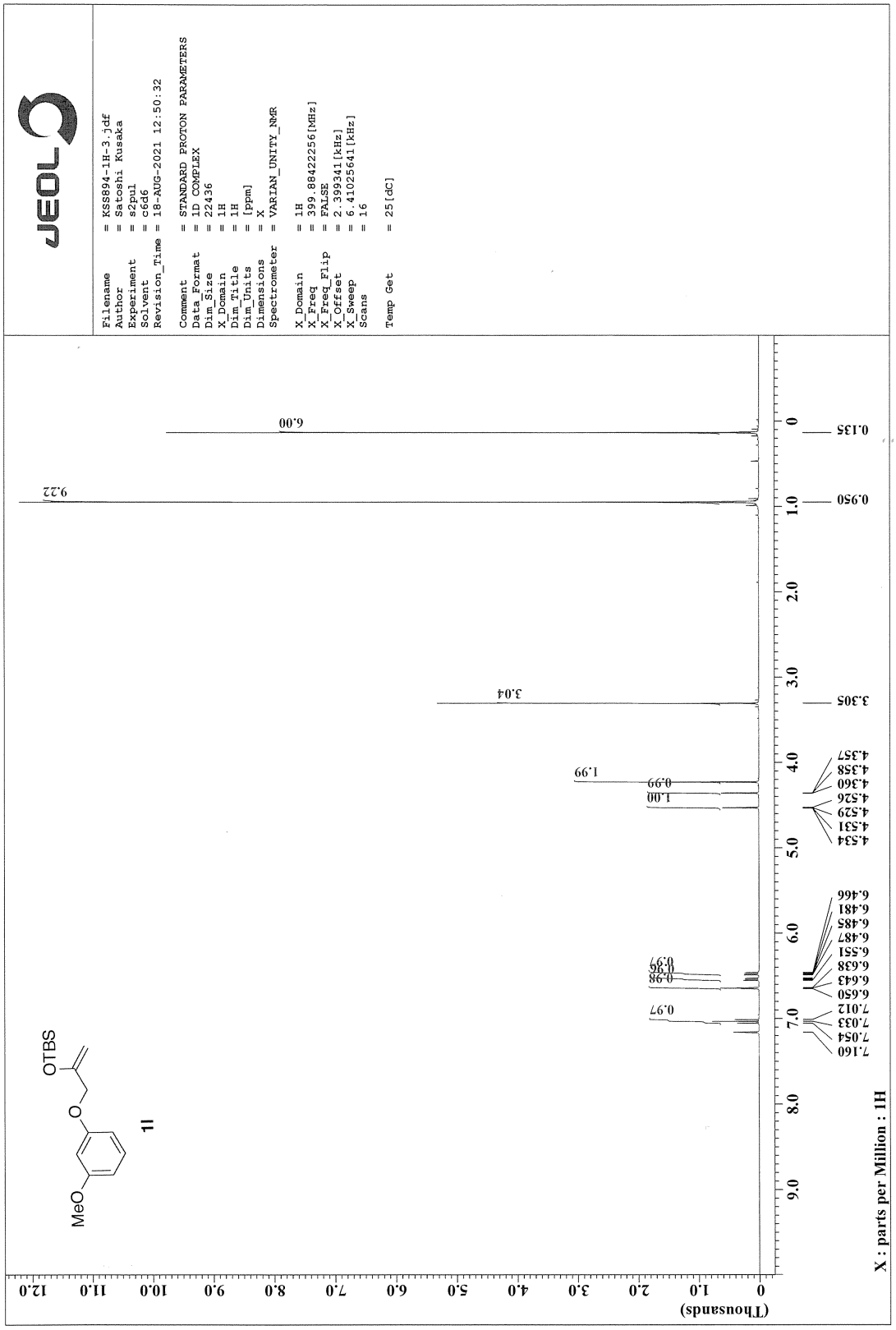


Figure S26. ^{1}H NMR Spectrum of **1l** (400 MHz, C_6D_6)

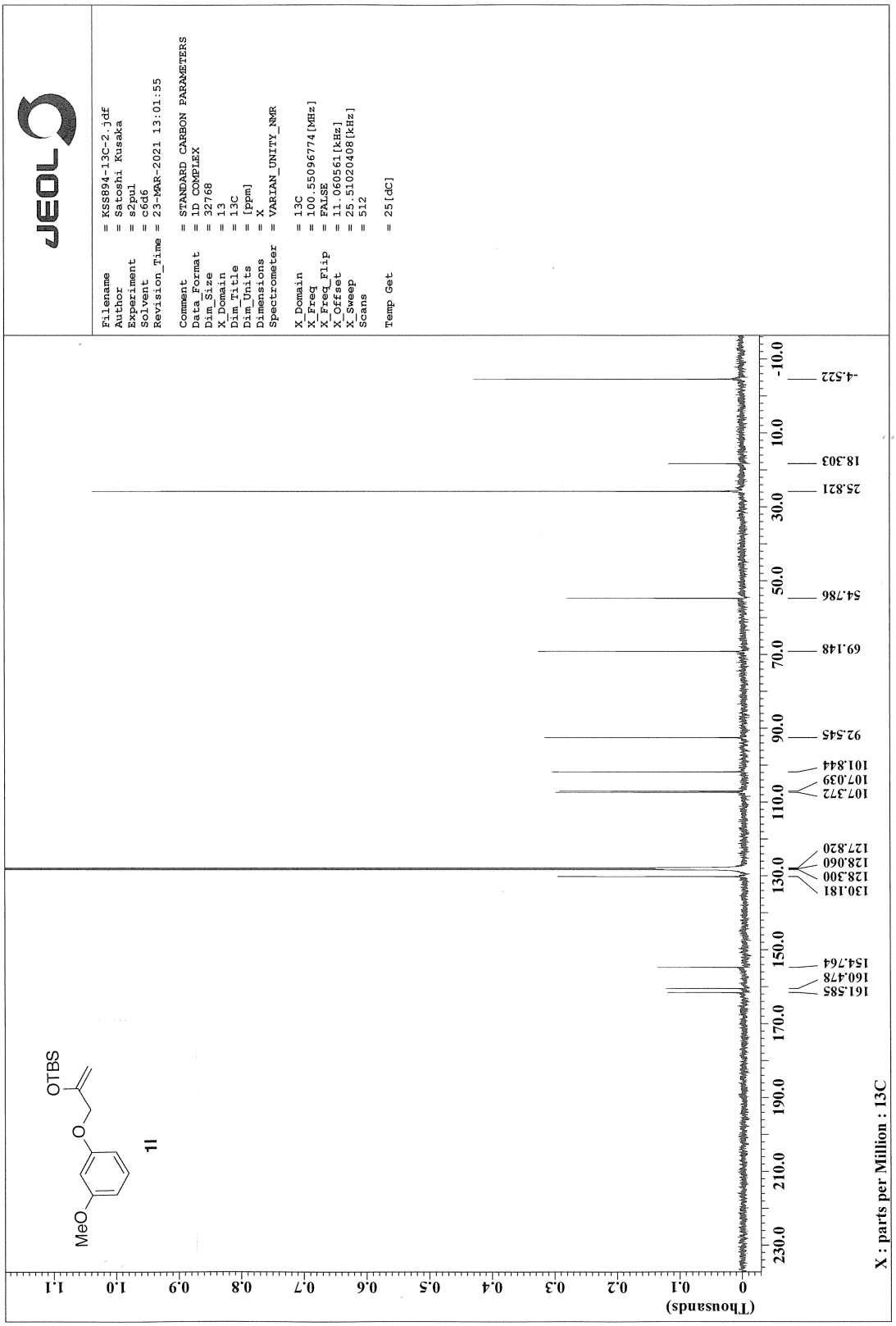


Figure S27. ^{13}C NMR Spectrum of **11** (101 MHz, C_6D_6)

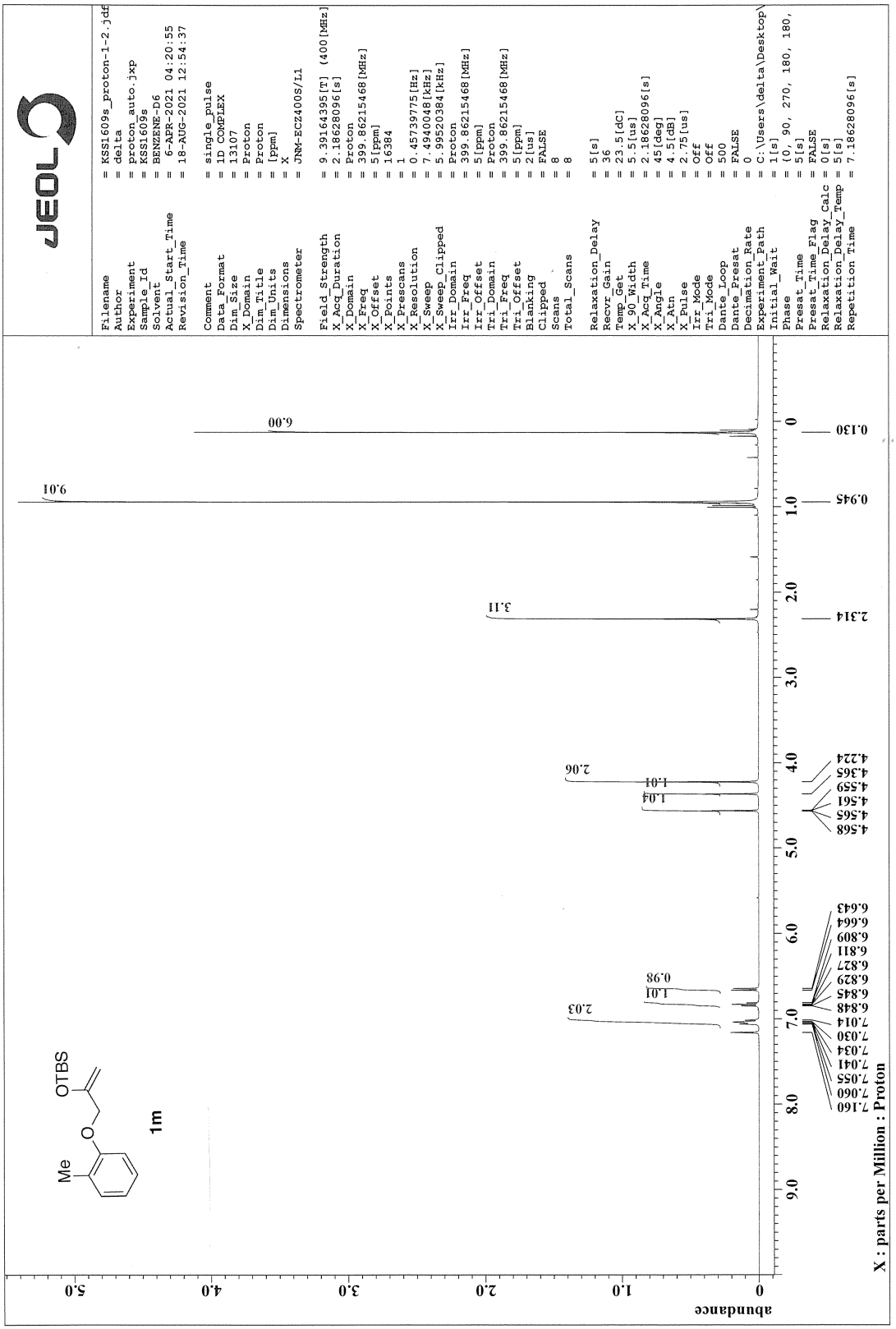


Figure S28. ^{1}H NMR Spectrum of **1m** (400 MHz, C_6D_6)

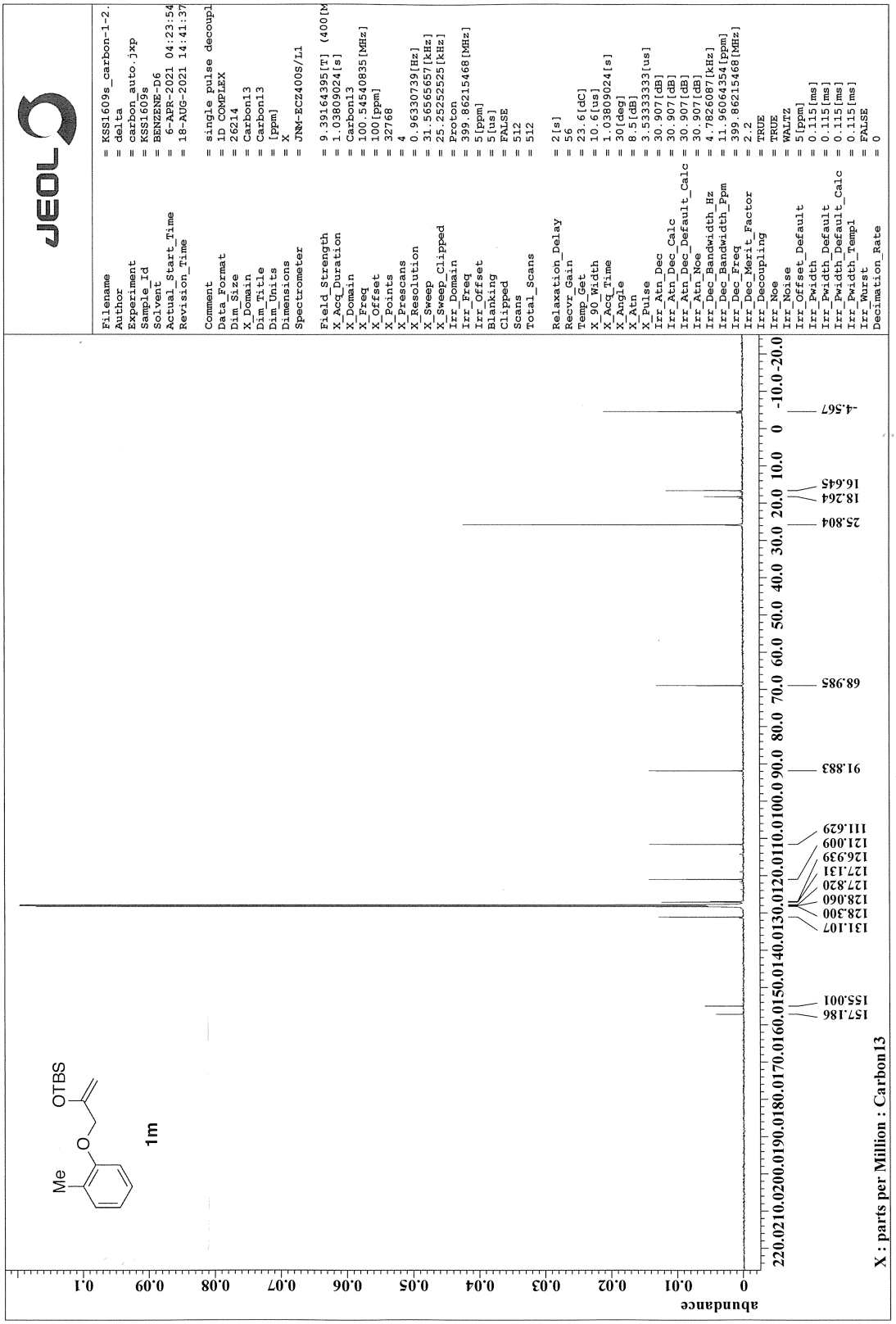


Figure S29. ^{13}C NMR Spectrum of **1m** (101 MHz, C_6D_6)

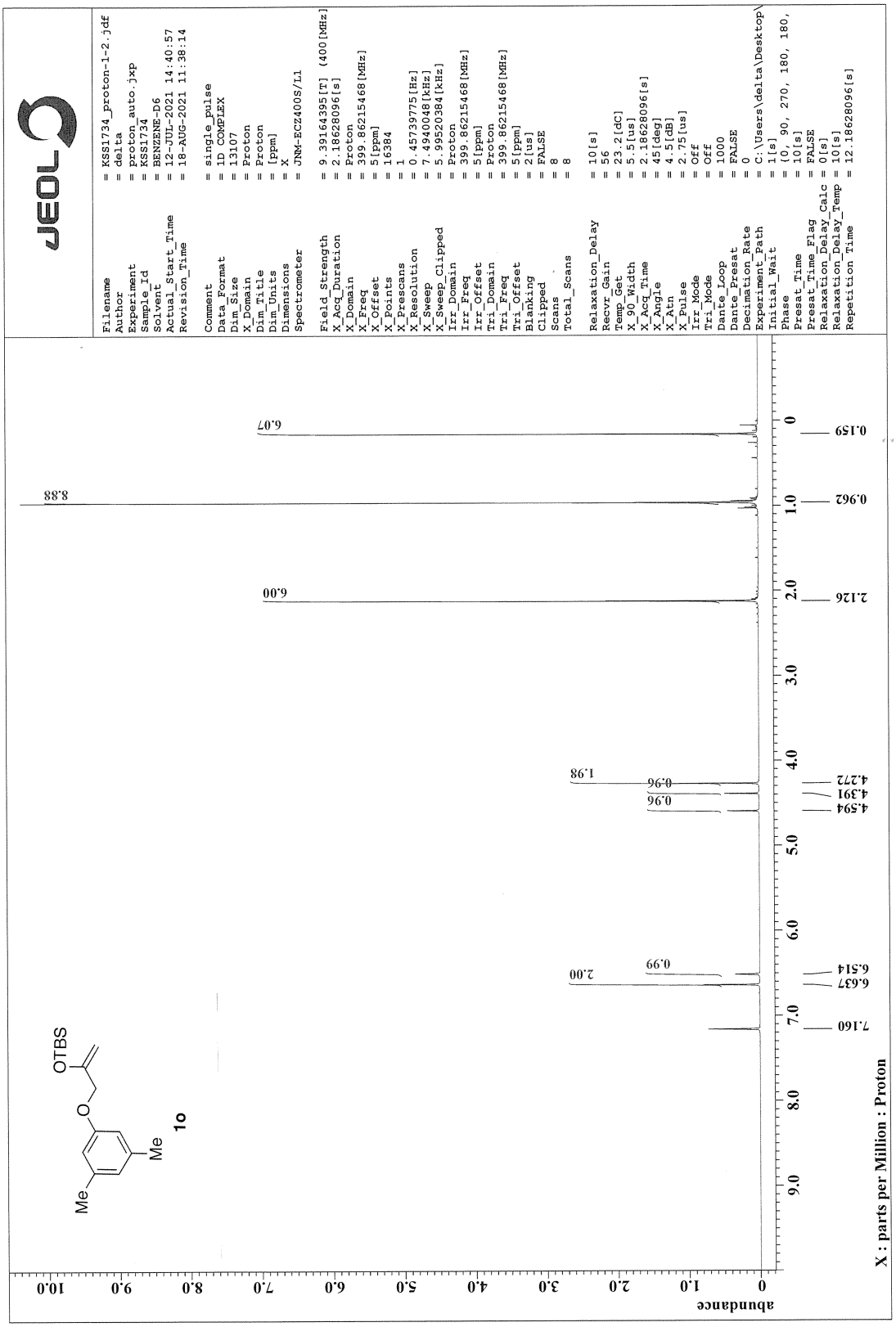


Figure S30. ^{1}H NMR Spectrum of **1o** (400 MHz, C_6D_6)

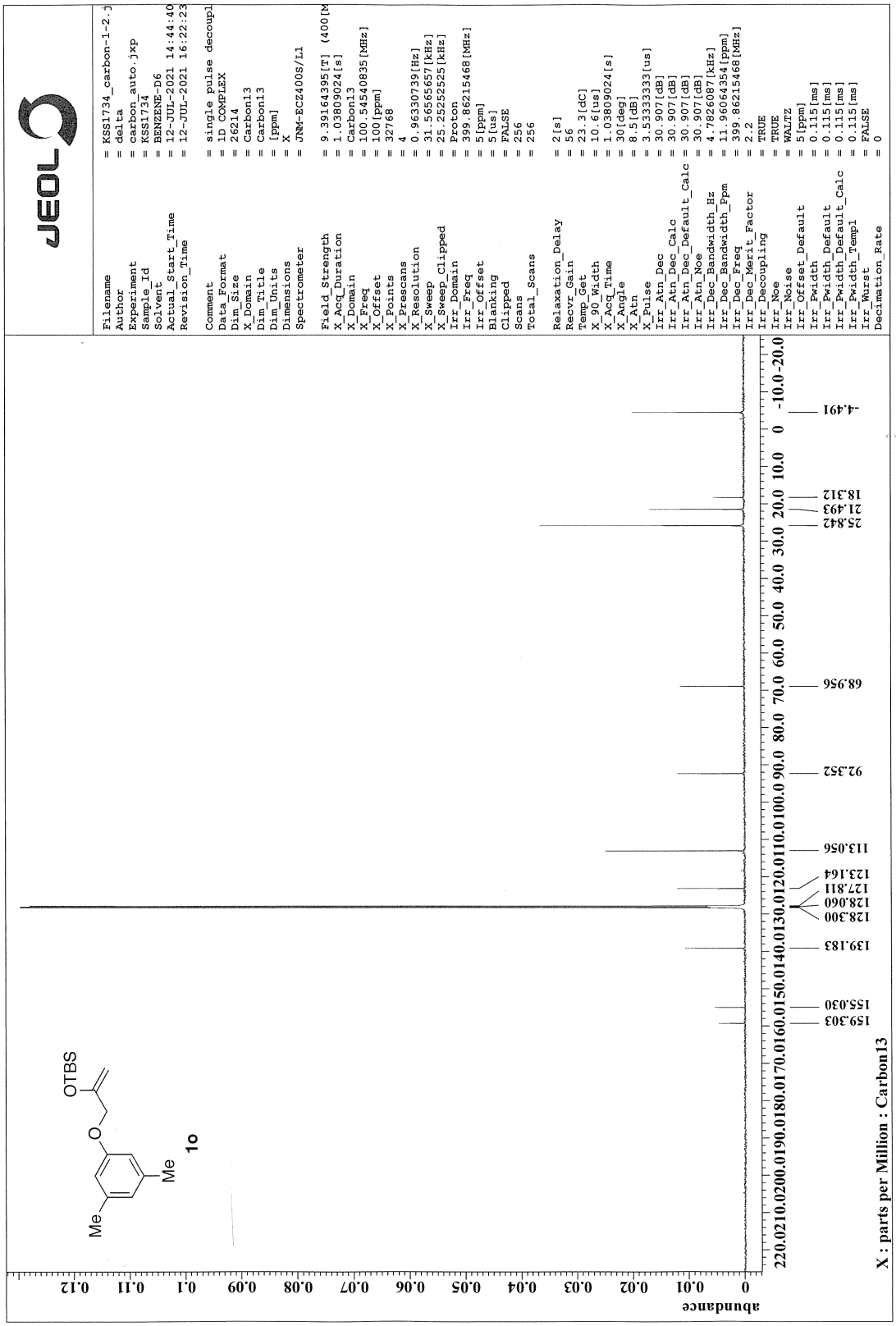


Figure S31. ^{13}C NMR Spectrum of **1o** (101 MHz, C_6D_6)

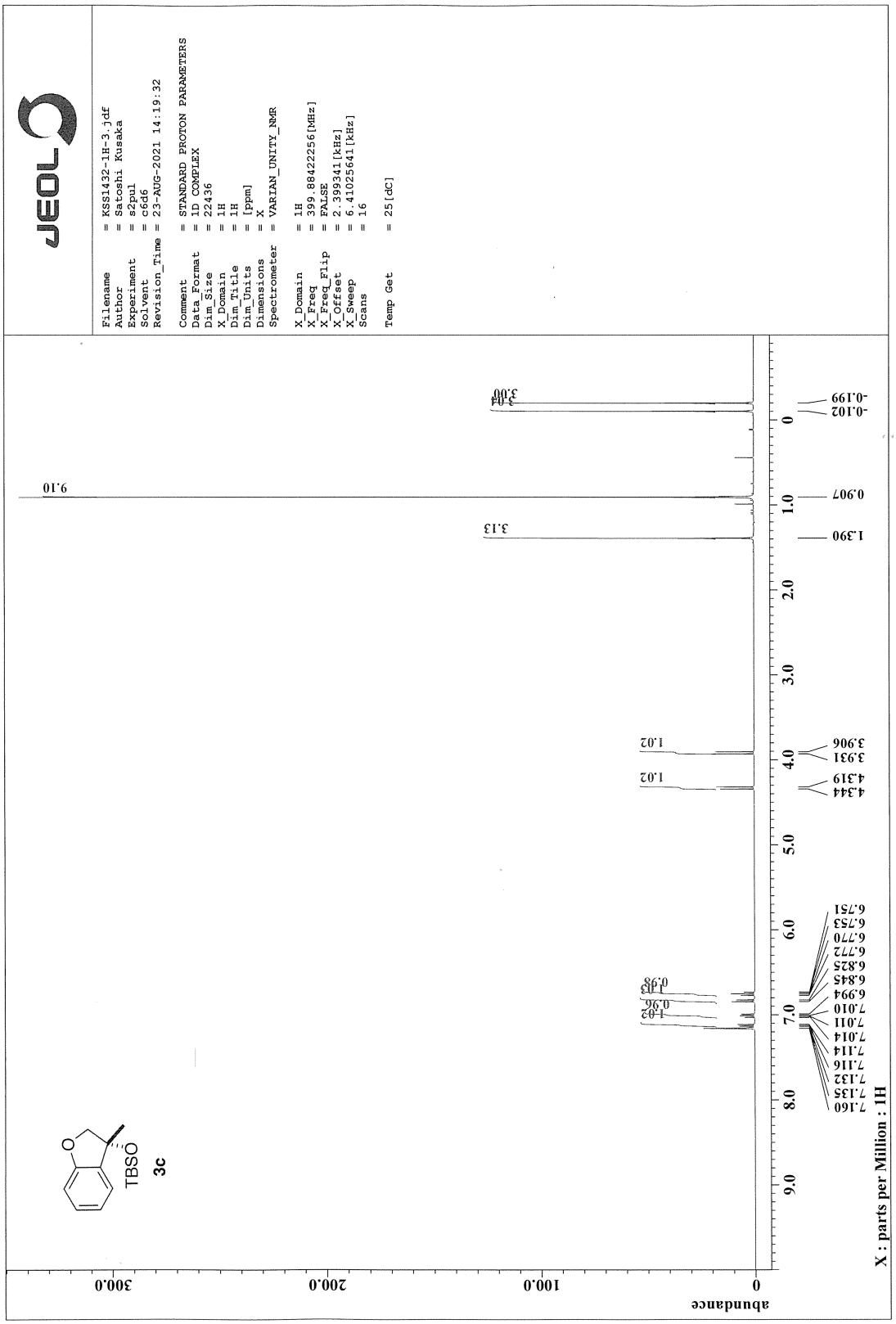


Figure S32. ^{1}H NMR Spectrum of **3c** (400 MHz, C_6D_6)

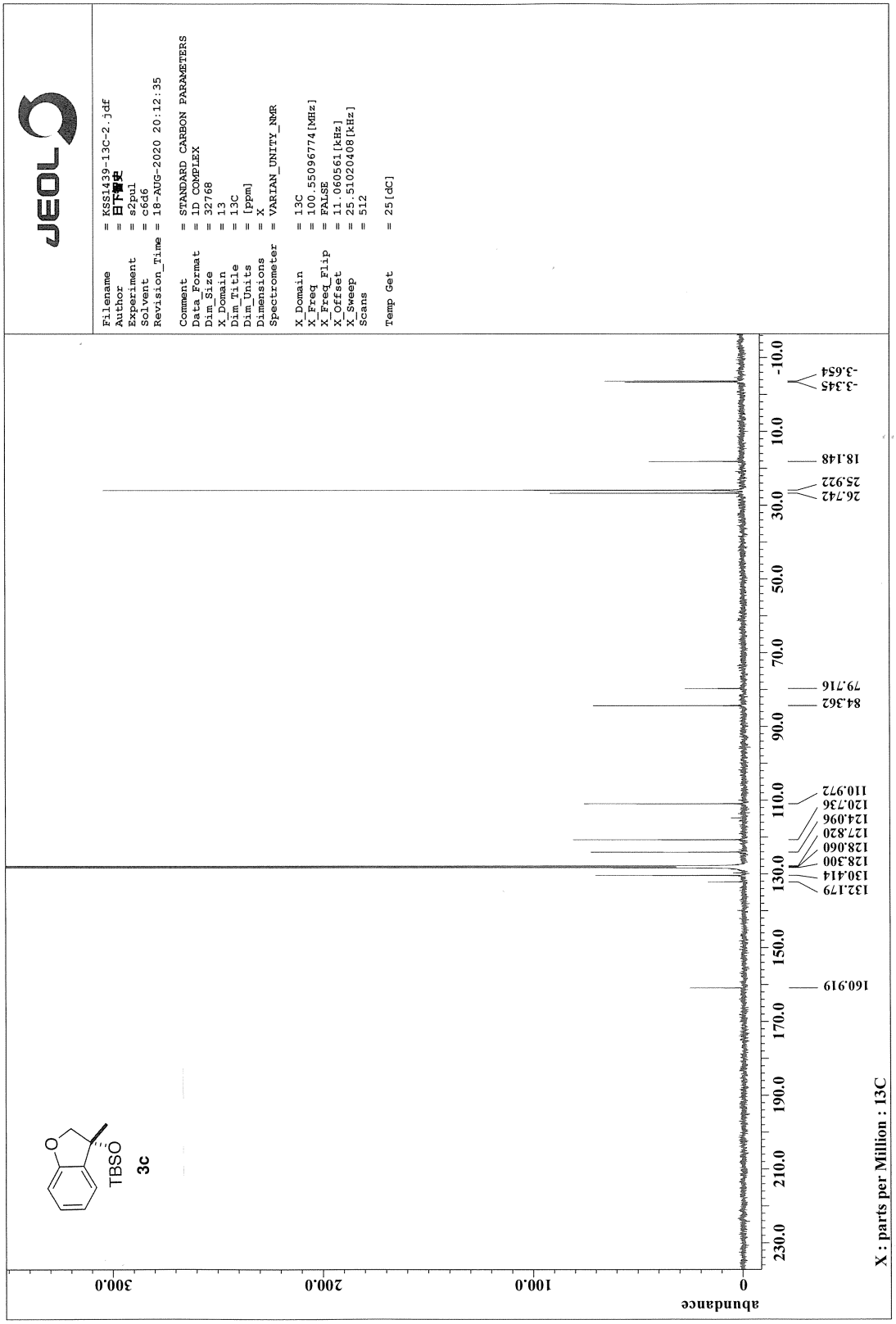


Figure S33. ^{13}C NMR Spectrum of **3c** (101 MHz, C_6D_6)

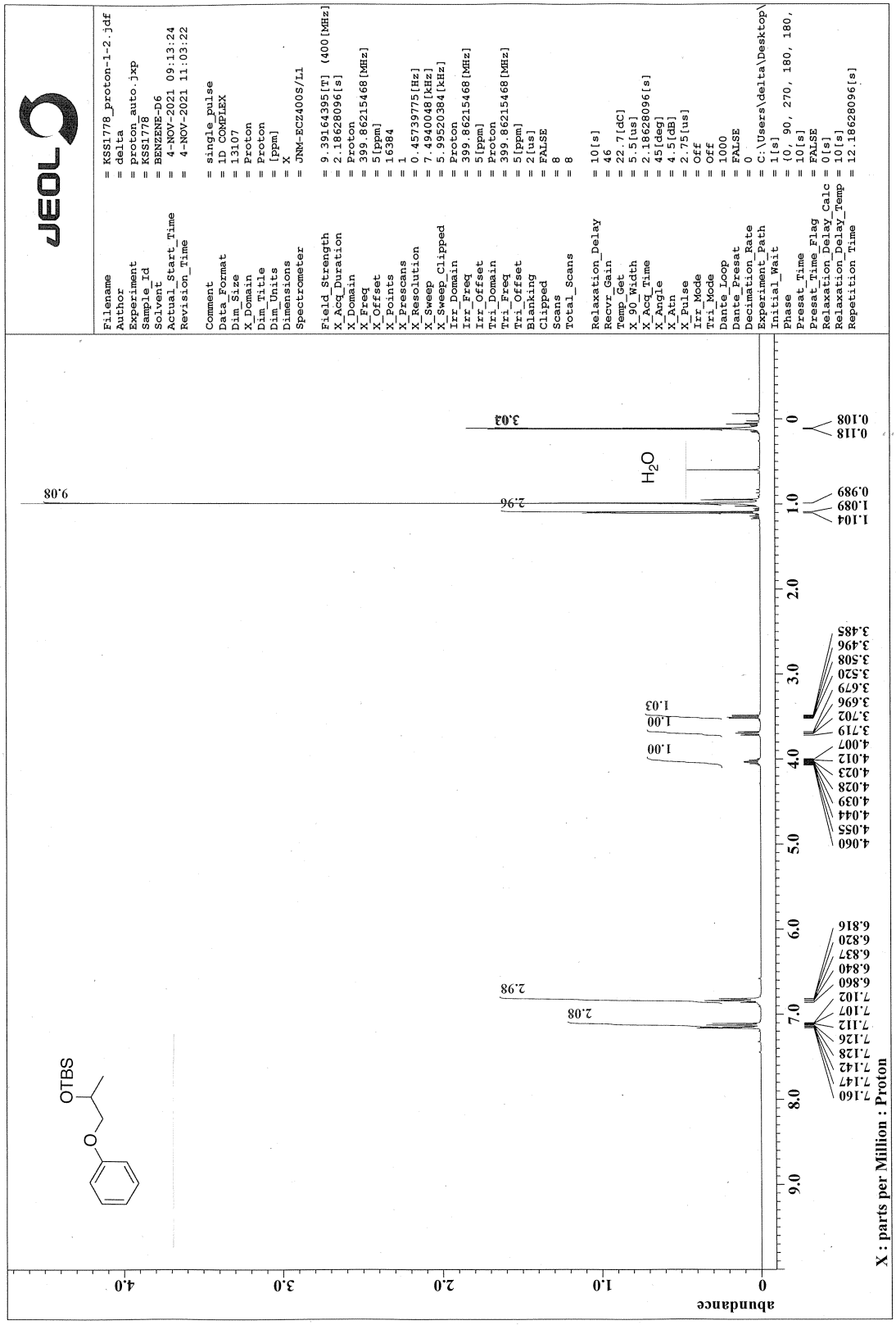


Figure S34. ^{1}H NMR Spectrum of $PhOCH_2CH(OTBS)CH_3$ (400 MHz, C_6D_6)

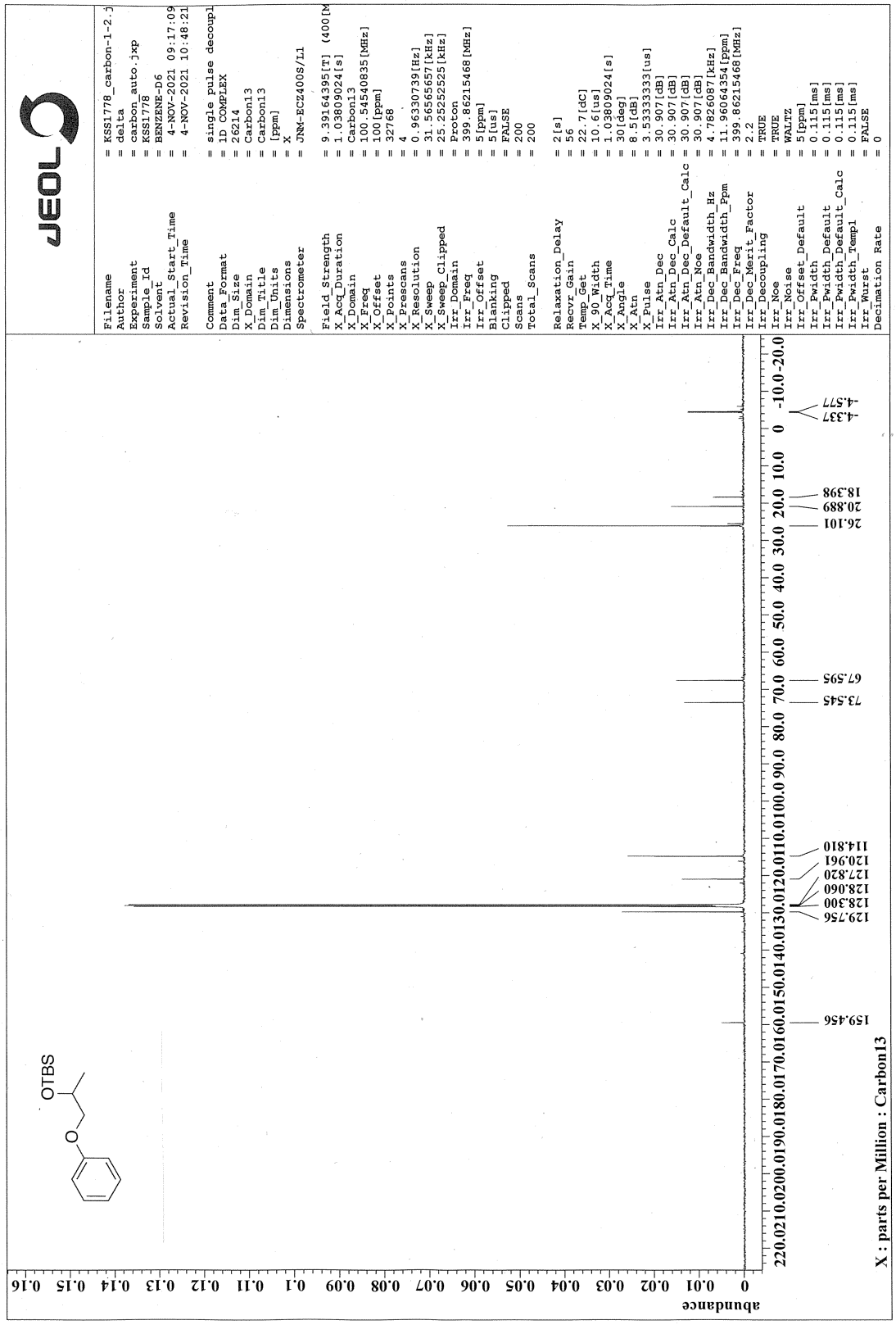


Figure S35. ^{13}C NMR Spectrum of $PhOCH_2CH(OTBS)CH_3$ (101 MHz, C_6D_6)

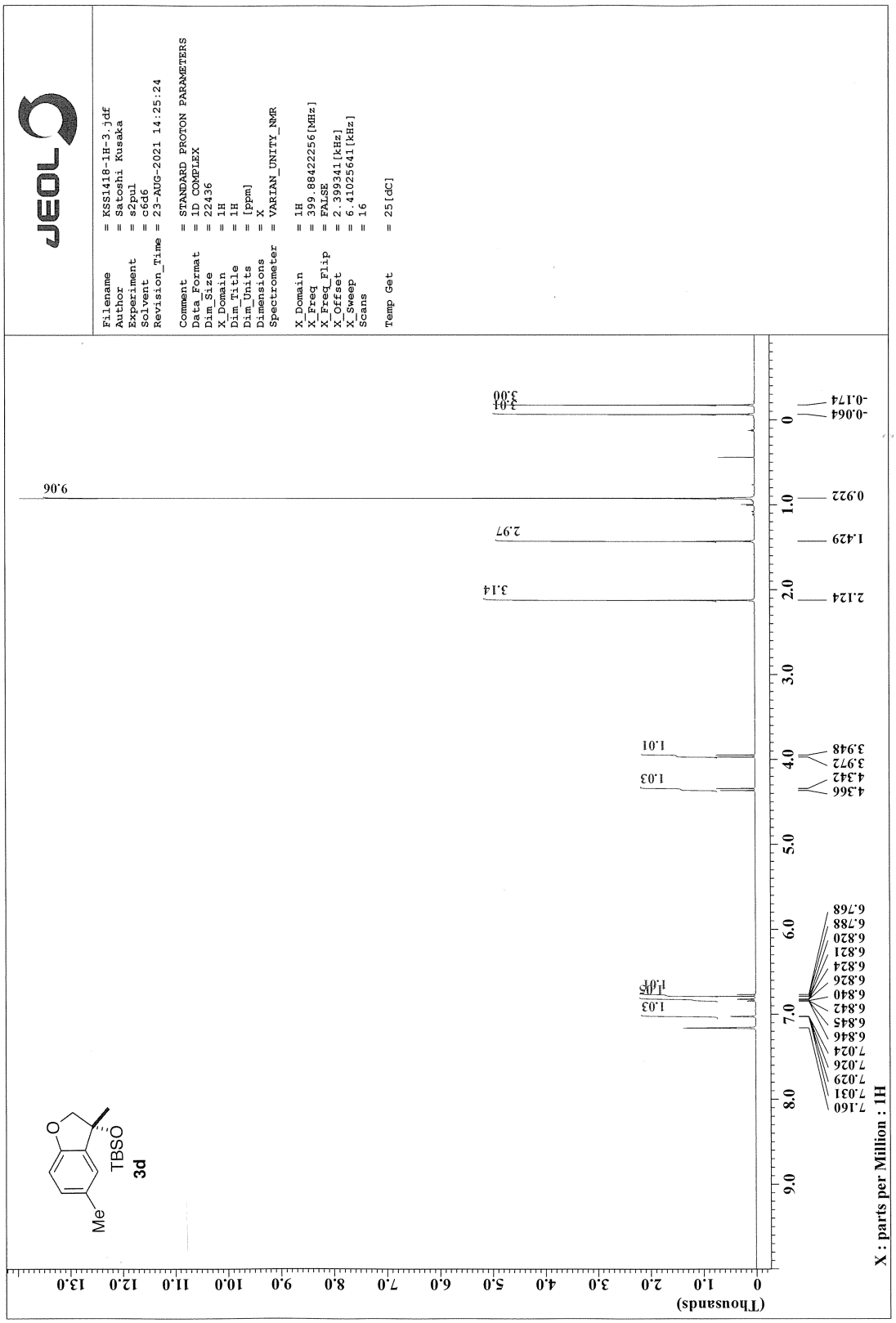


Figure S36. ^{1}H NMR Spectrum of **3d** (400 MHz, C_6D_6)

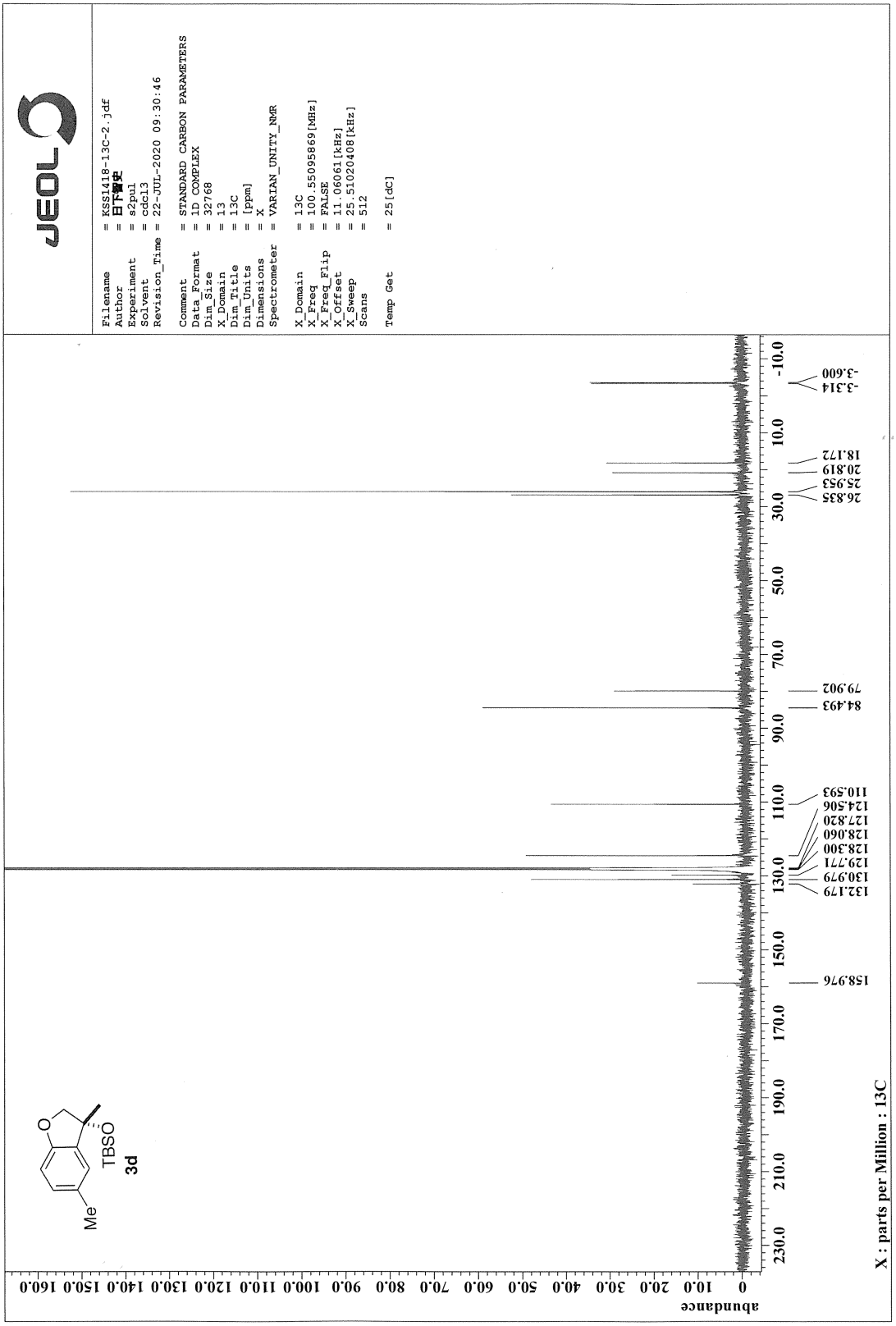


Figure S37. ^{13}C NMR Spectrum of **3d** (101 MHz, C_6D_6)

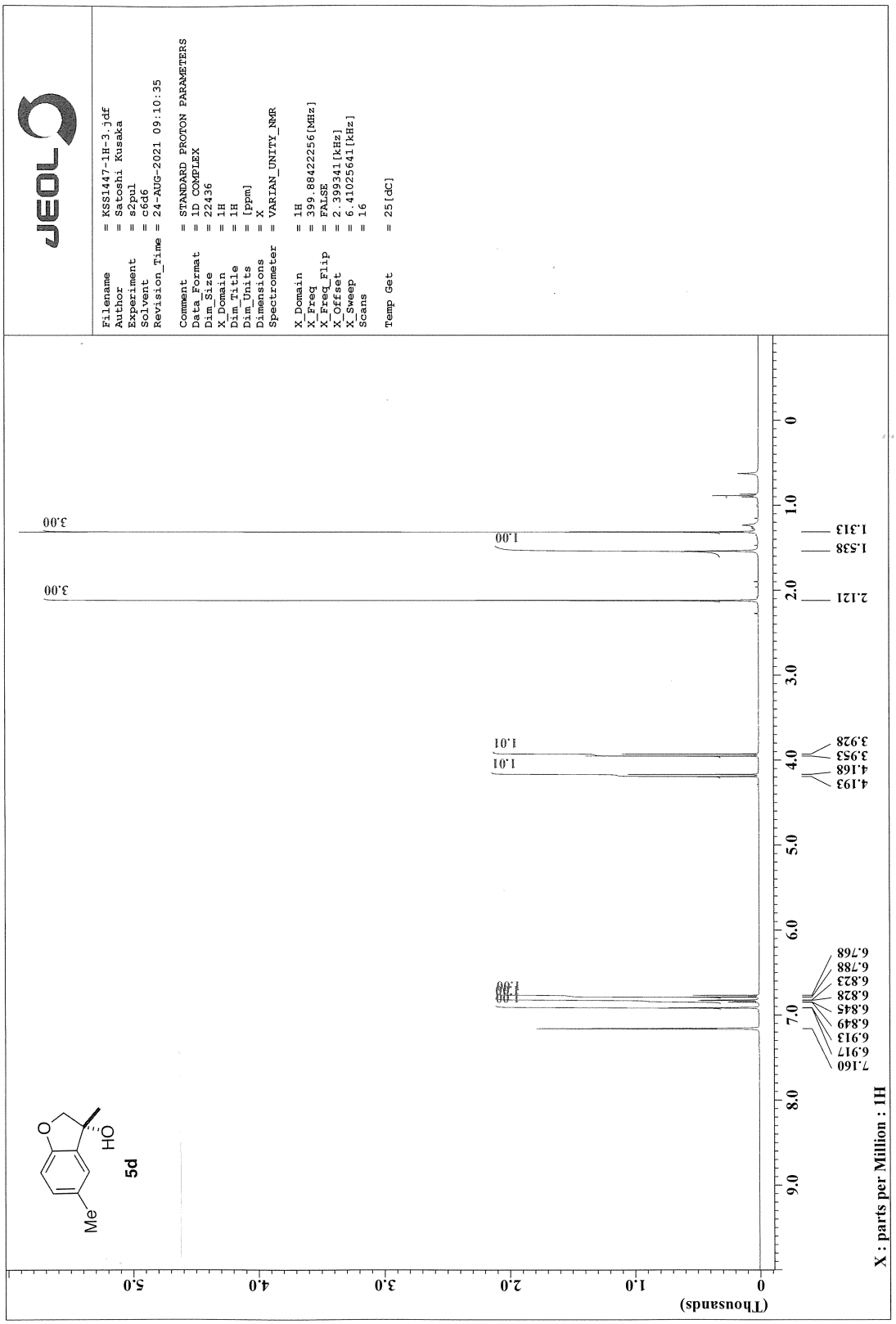


Figure S38. ^{1}H NMR Spectrum of **5d** (400 MHz, C_6D_6)

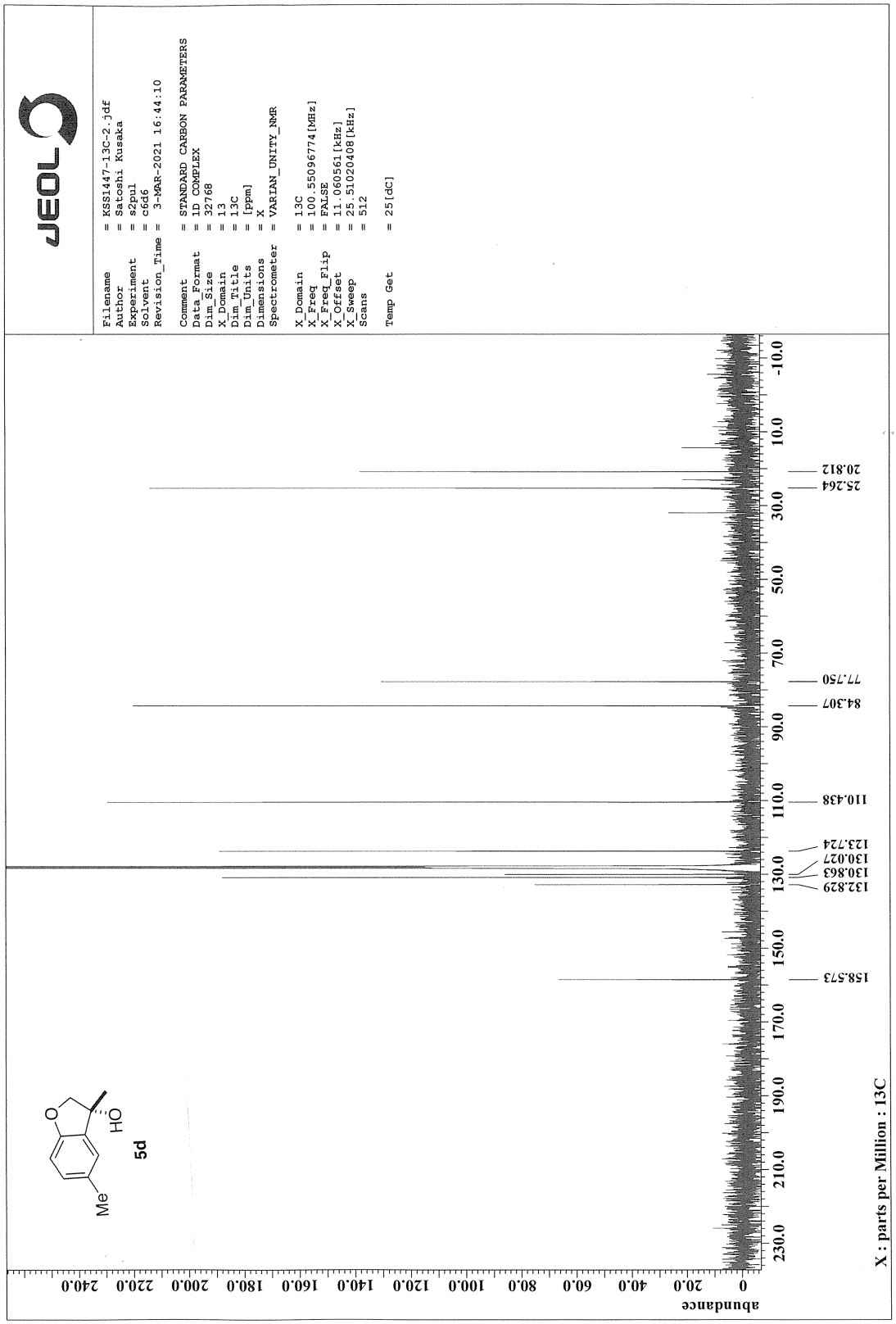


Figure S39. ^{13}C NMR Spectrum of **5d** (101 MHz, C_6D_6)

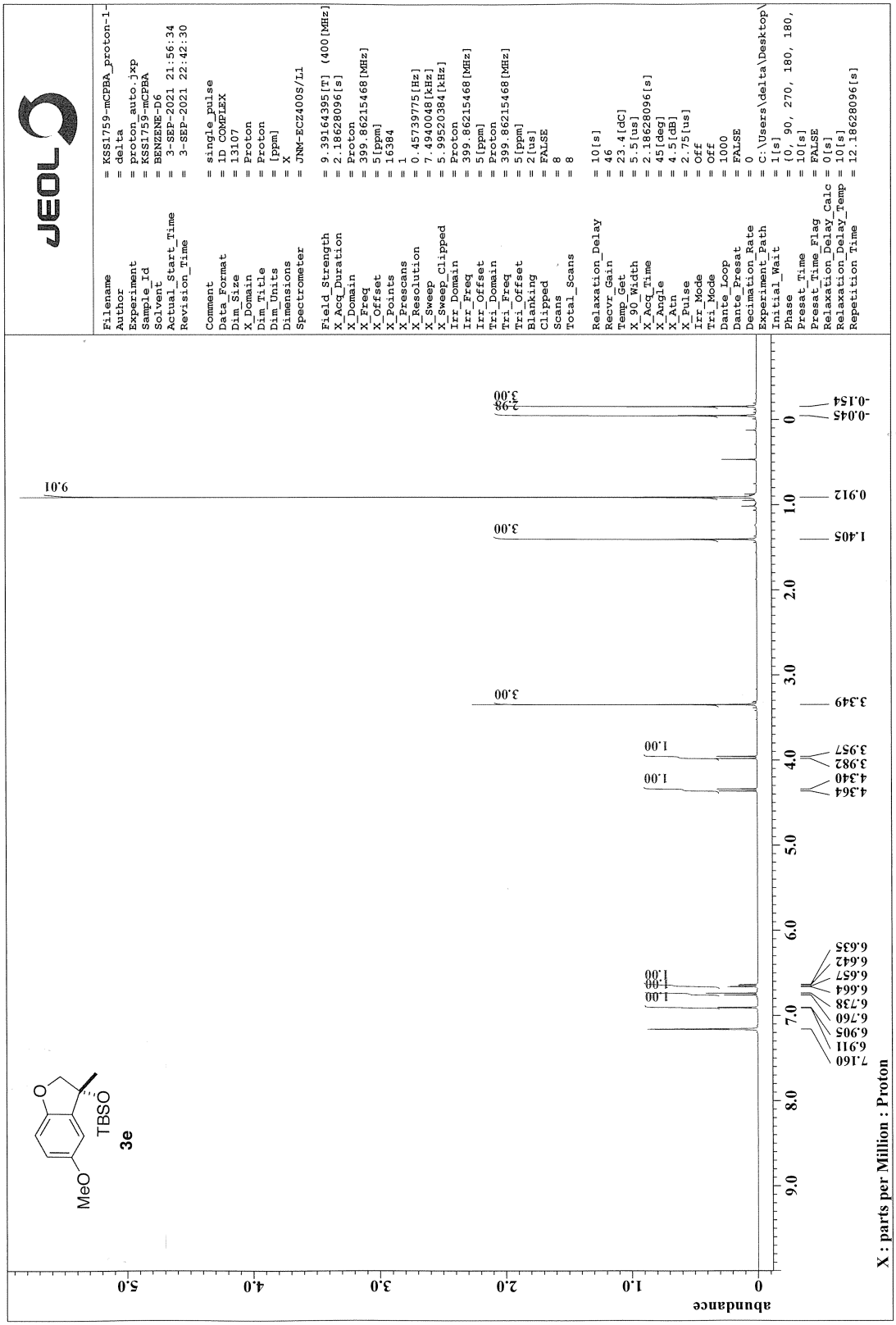


Figure S40. ^{1}H NMR Spectrum of **3e** (400 MHz, C_6D_6)

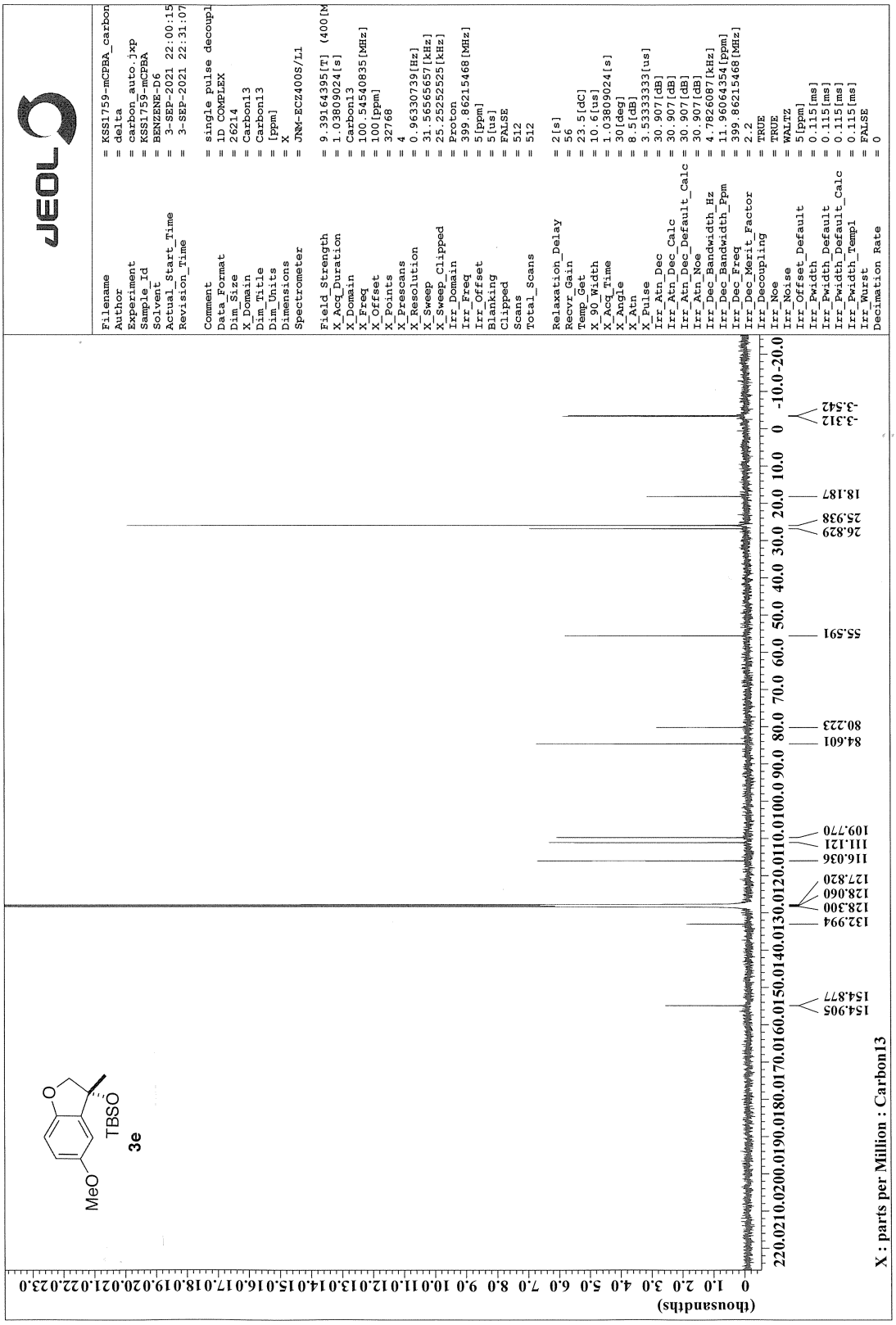


Figure S41. ^{13}C NMR Spectrum of **3e** (101 MHz, C_6D_6)

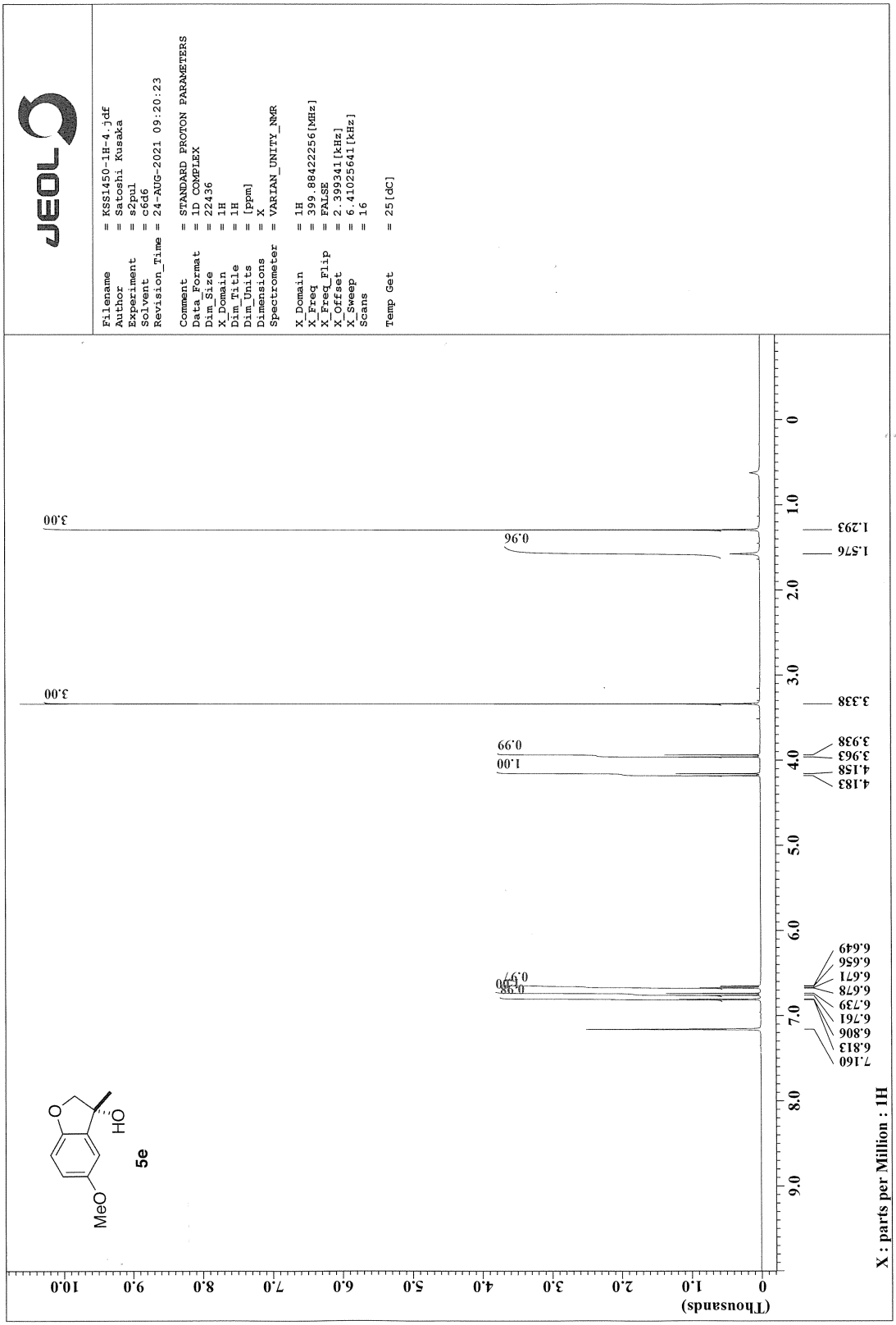


Figure S42. ^{1}H NMR Spectrum of **5e** (400 MHz, C_6D_6)

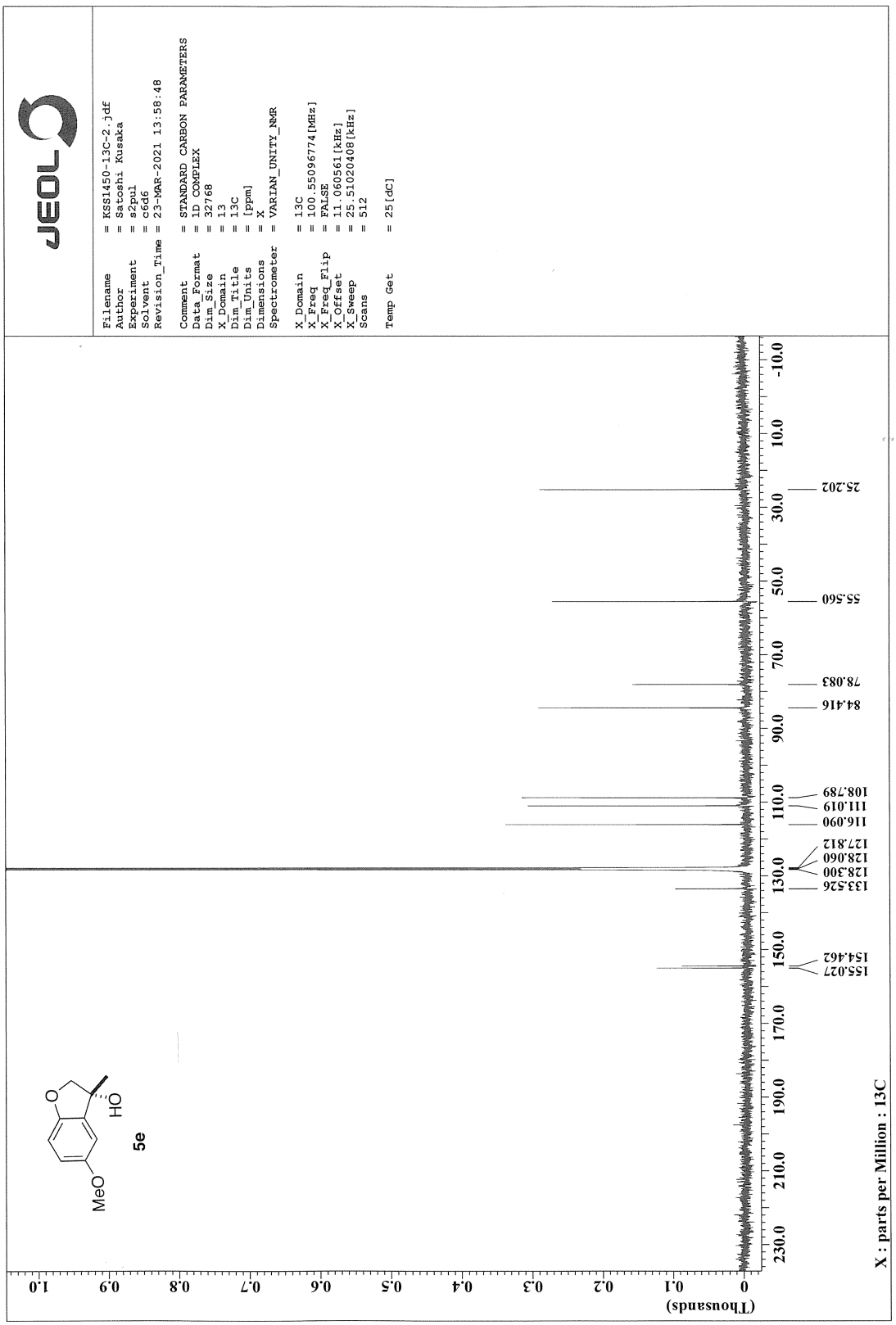


Figure S43. ^{13}C NMR Spectrum of **5e** (101 MHz, C_6D_6)

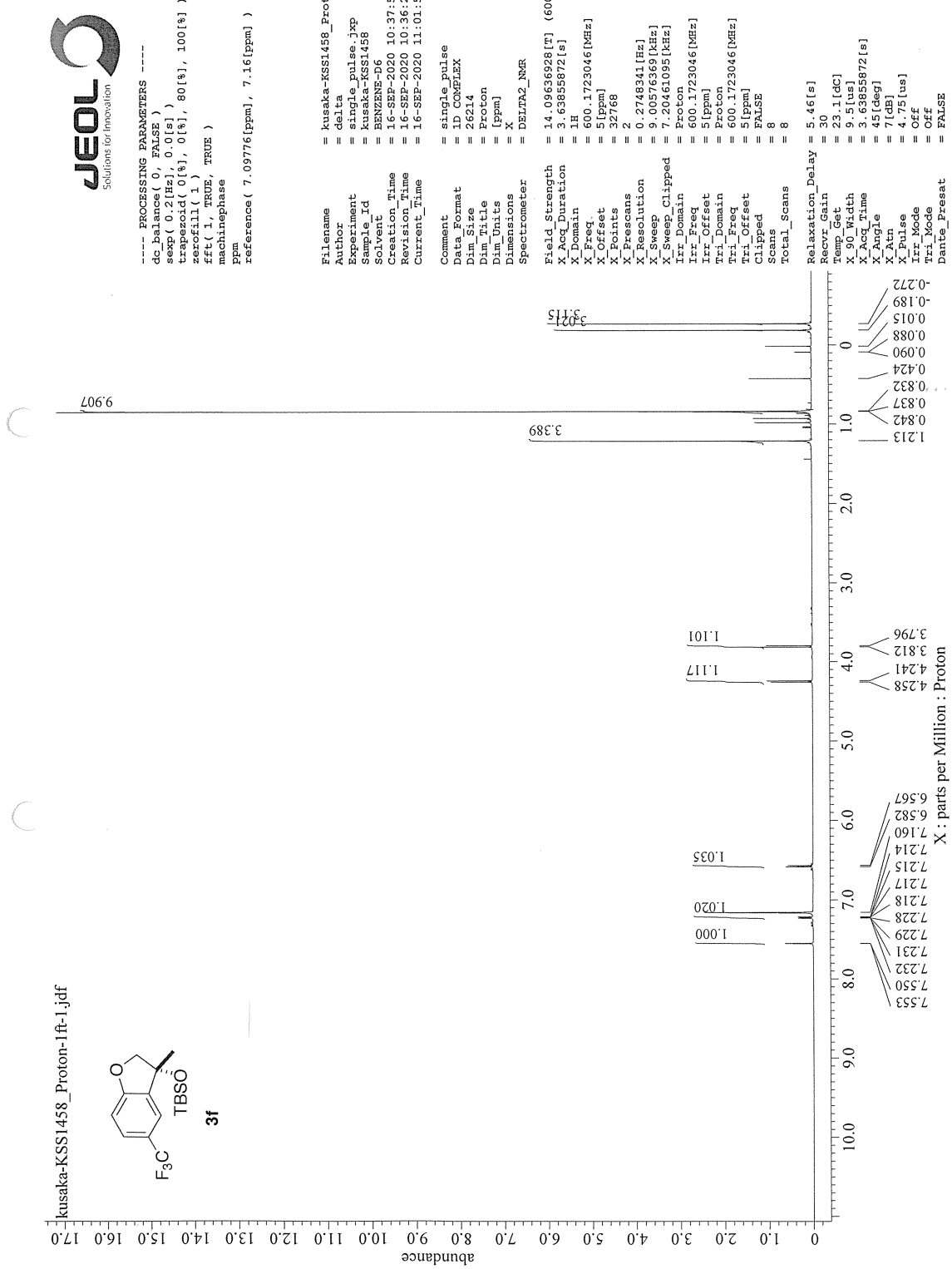


Figure S44. ^{1}H NMR Spectrum of **3f** (600 MHz, C_6D_6)

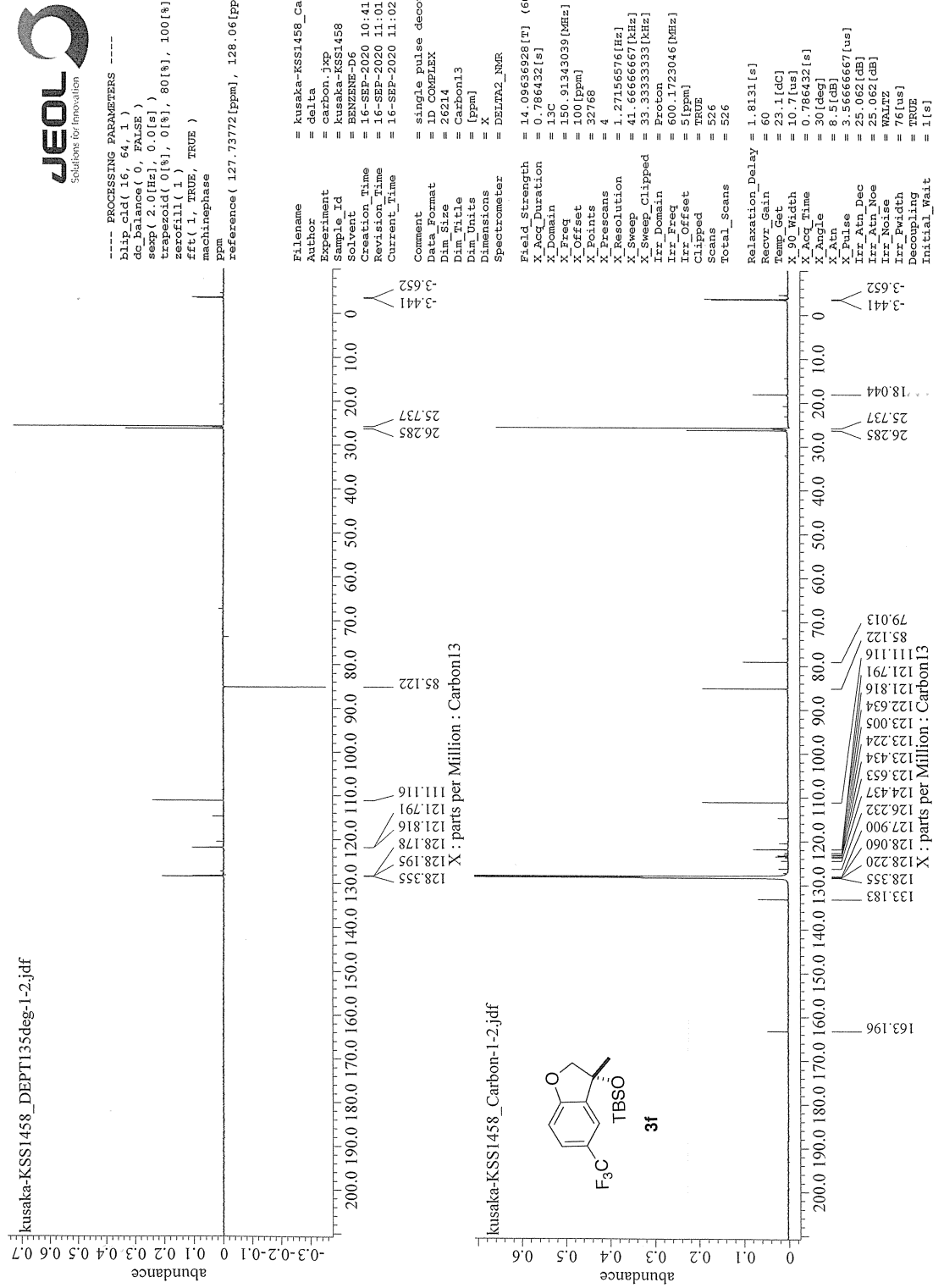


Figure S45. ^{13}C NMR Spectrum of **3f** (151 MHz, C_6D_6)

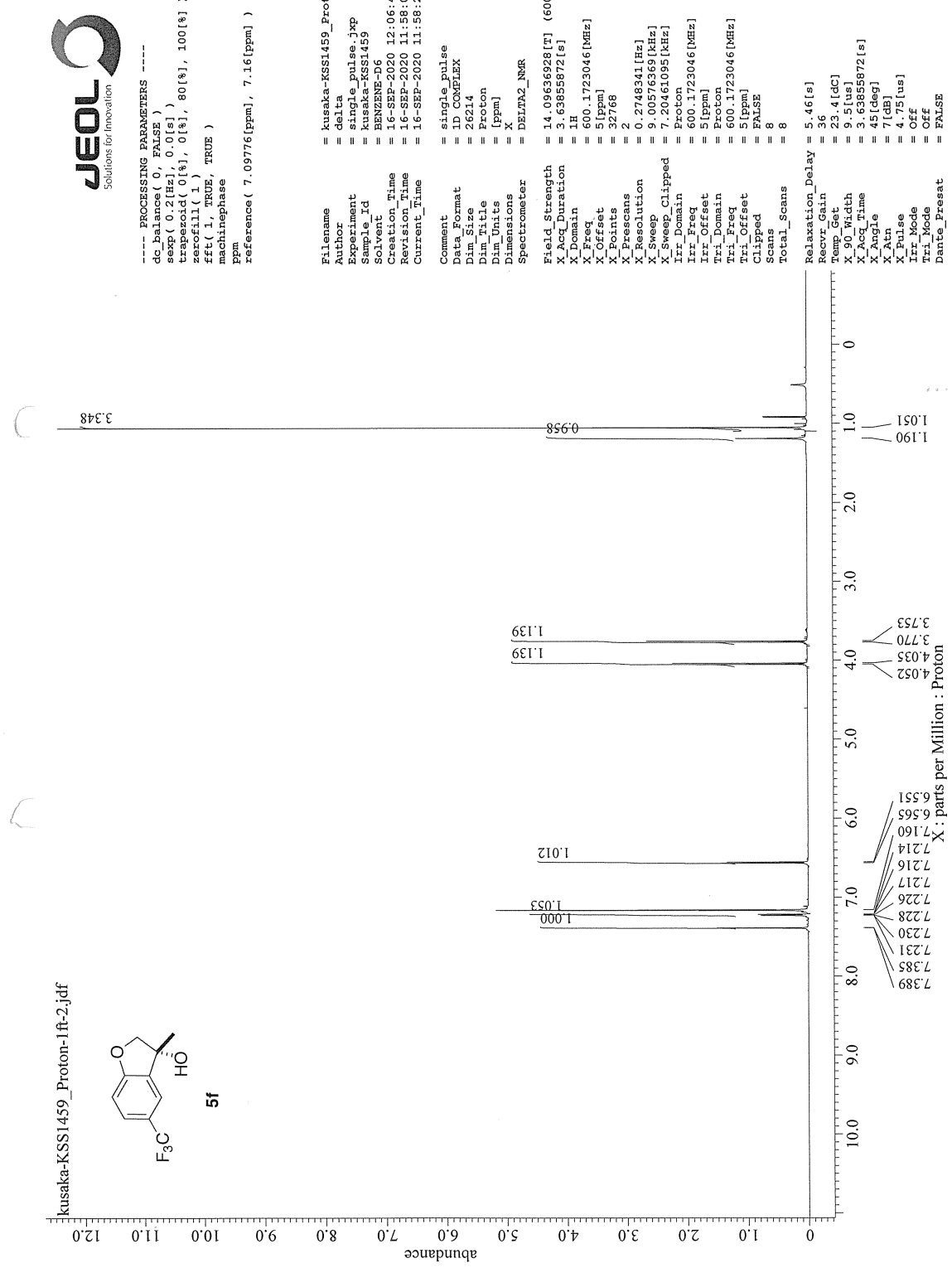


Figure S46. ^{1}H NMR Spectrum of **5f** (600 MHz, C_6D_6)

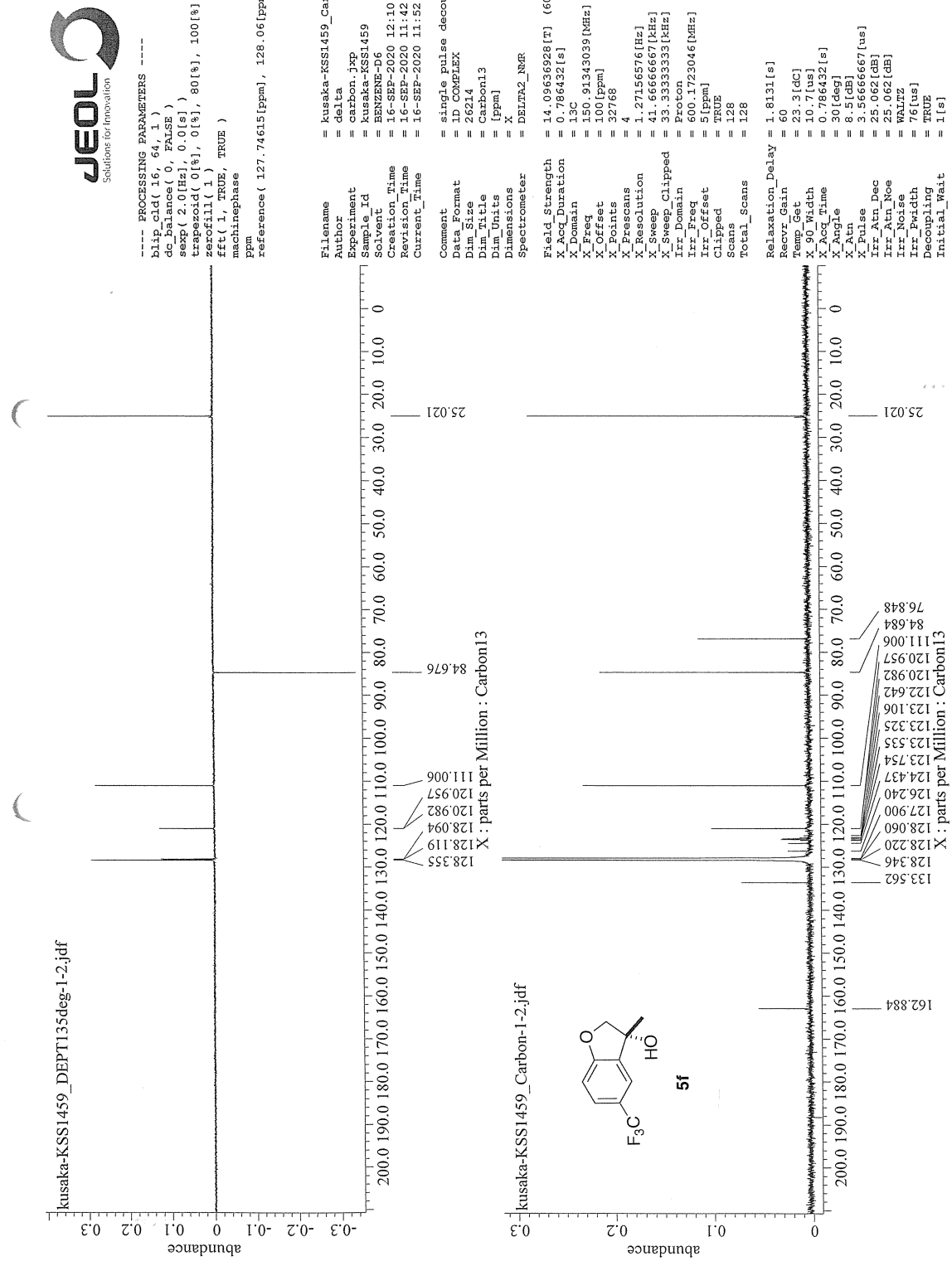


Figure S47. ^{13}C NMR Spectrum of **5f** (151 MHz, C_6D_6)

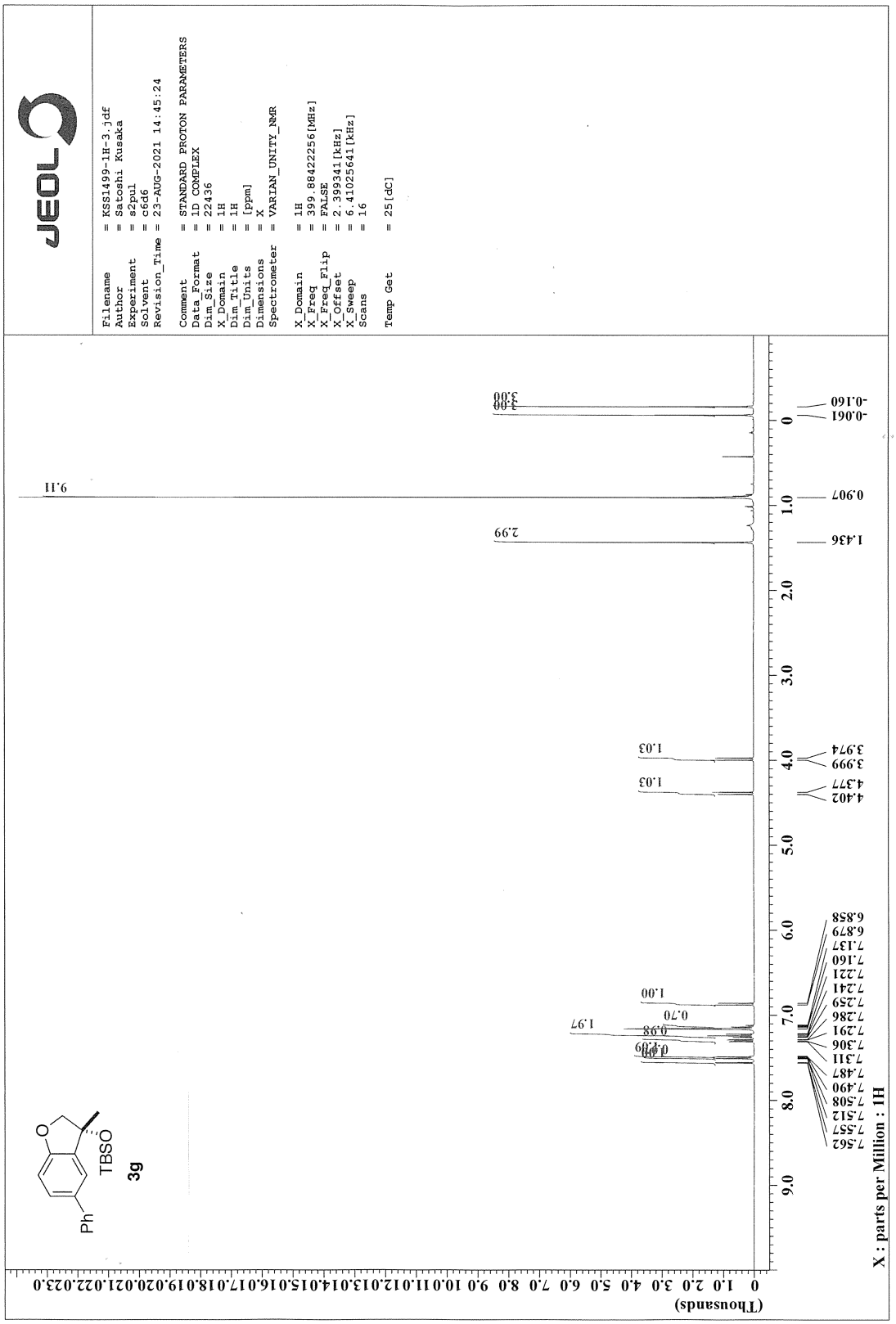


Figure S48. ^{1}H NMR Spectrum of **3g** (400 MHz, C_6D_6)

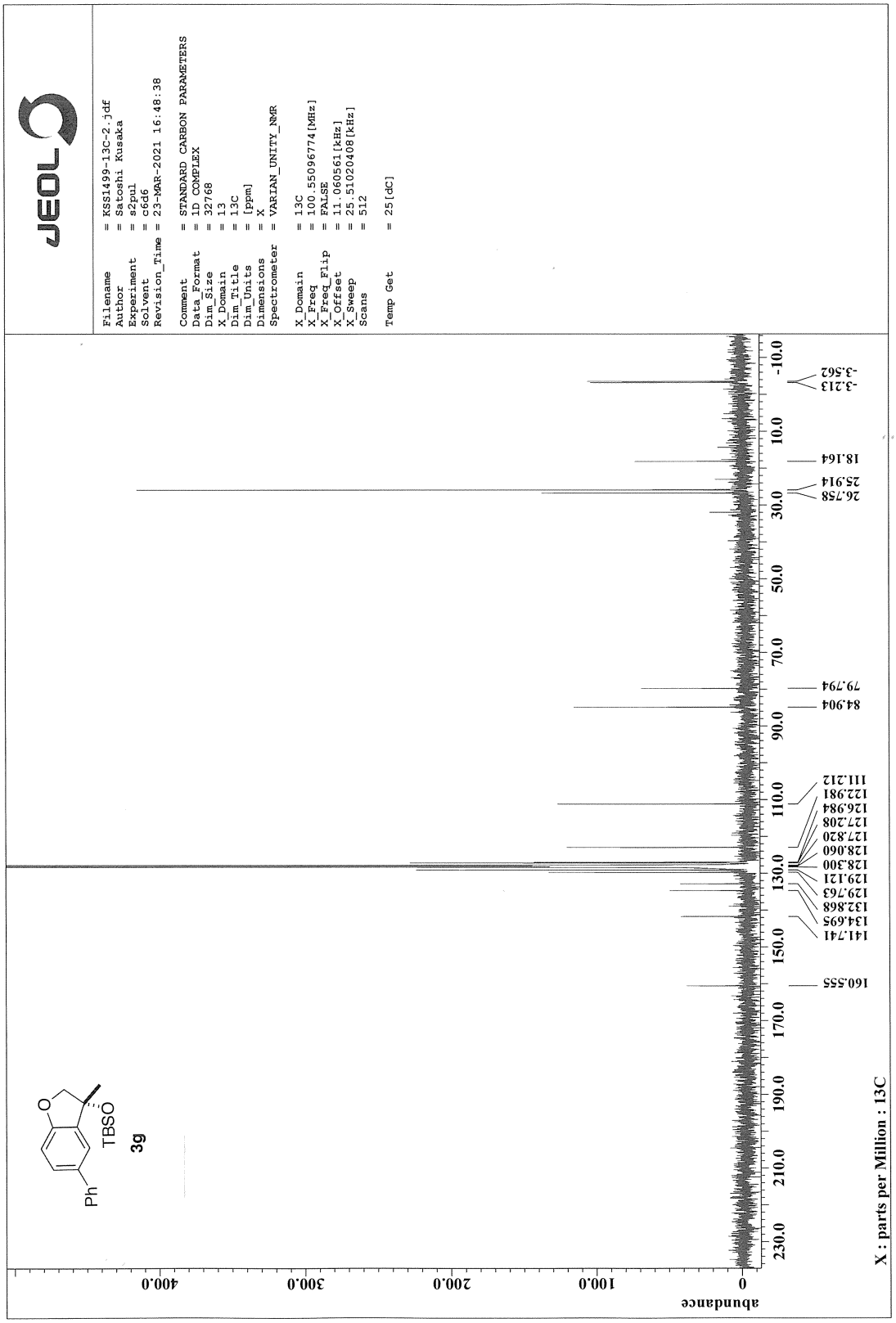


Figure S49. ^{13}C NMR Spectrum of **3g** (101 MHz, C_6D_6)

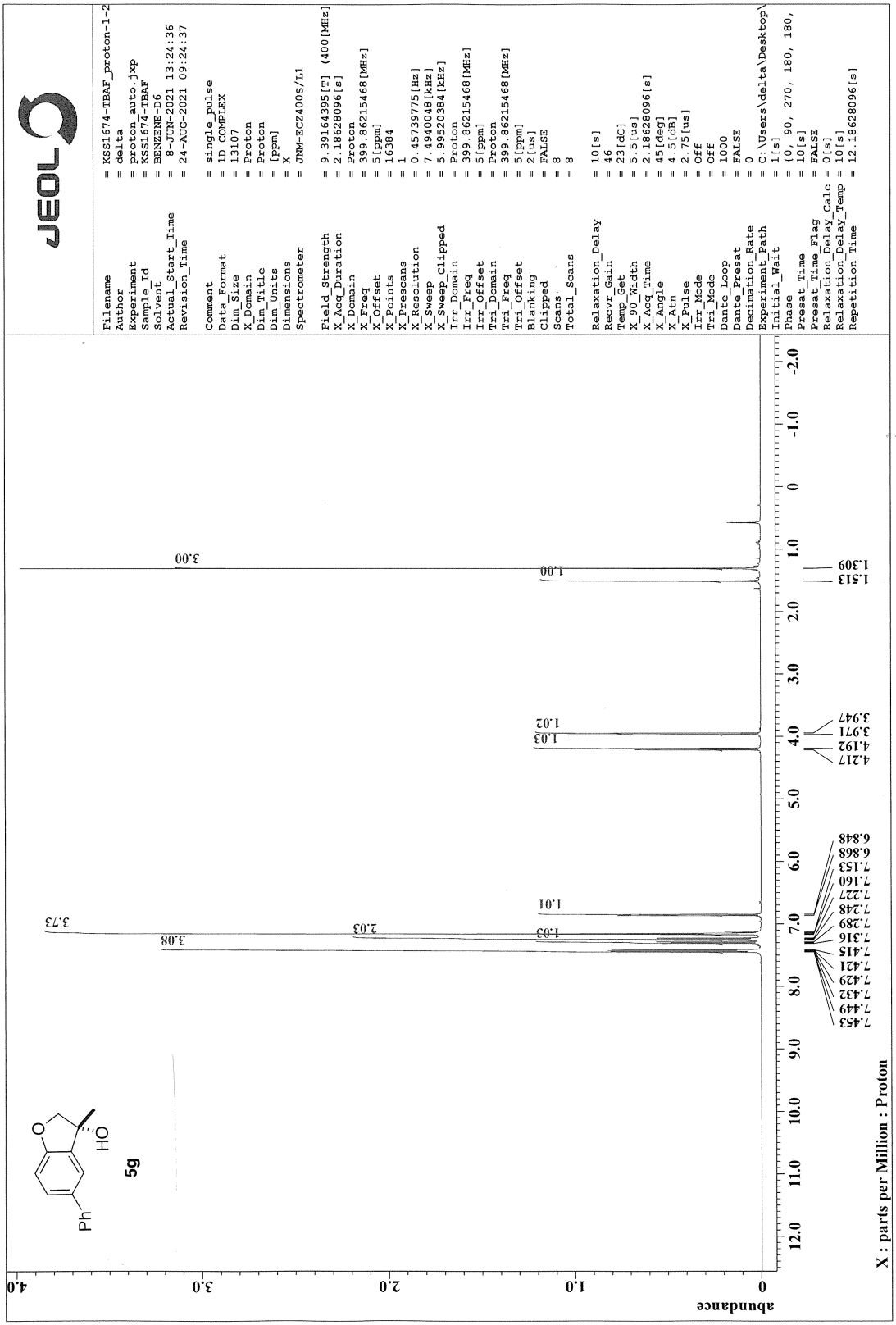


Figure S50. ^{1}H NMR Spectrum of **5g** (400 MHz, C_6D_6)

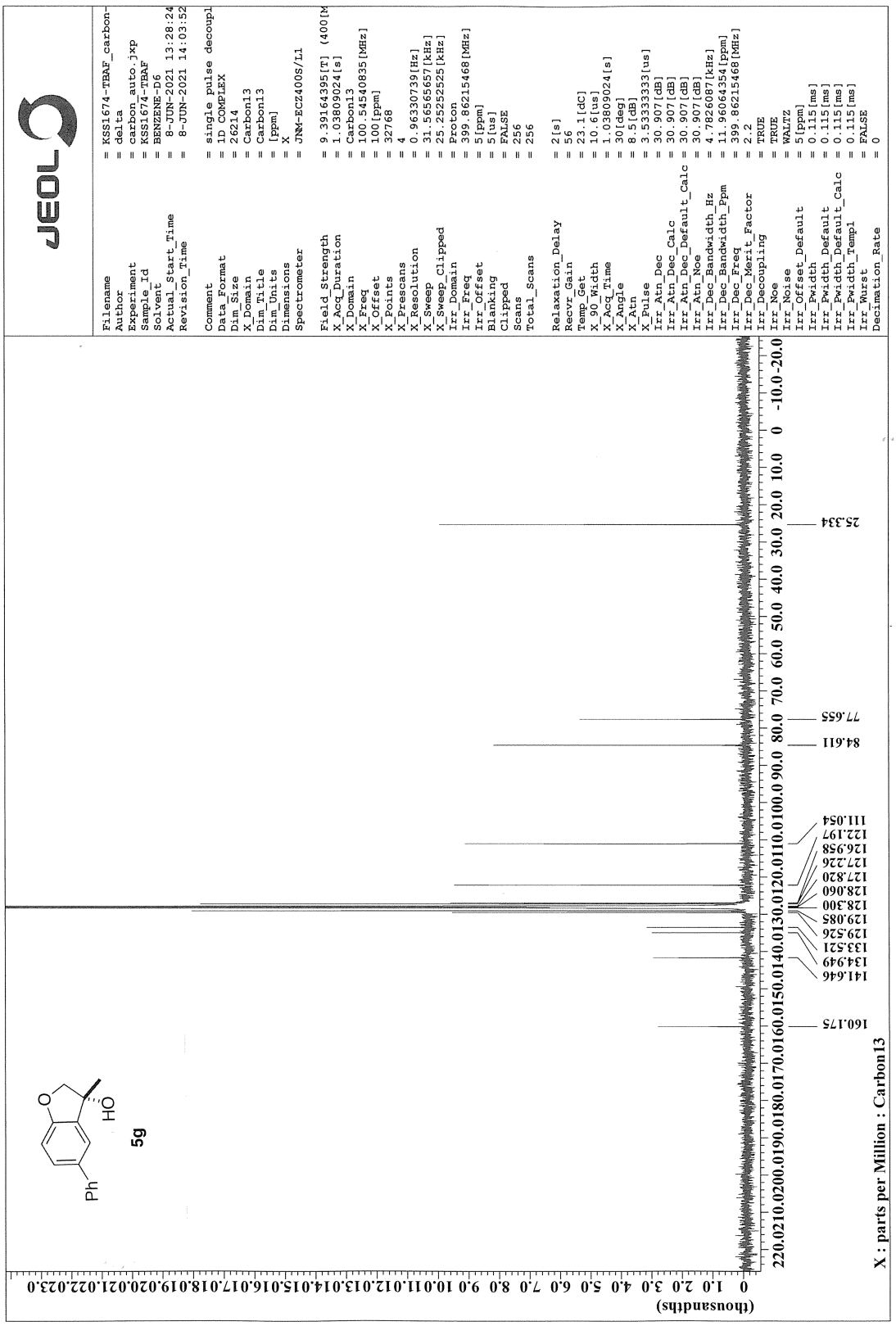


Figure S51. ^{13}C NMR Spectrum of **5g** (101 MHz, C_6D_6)

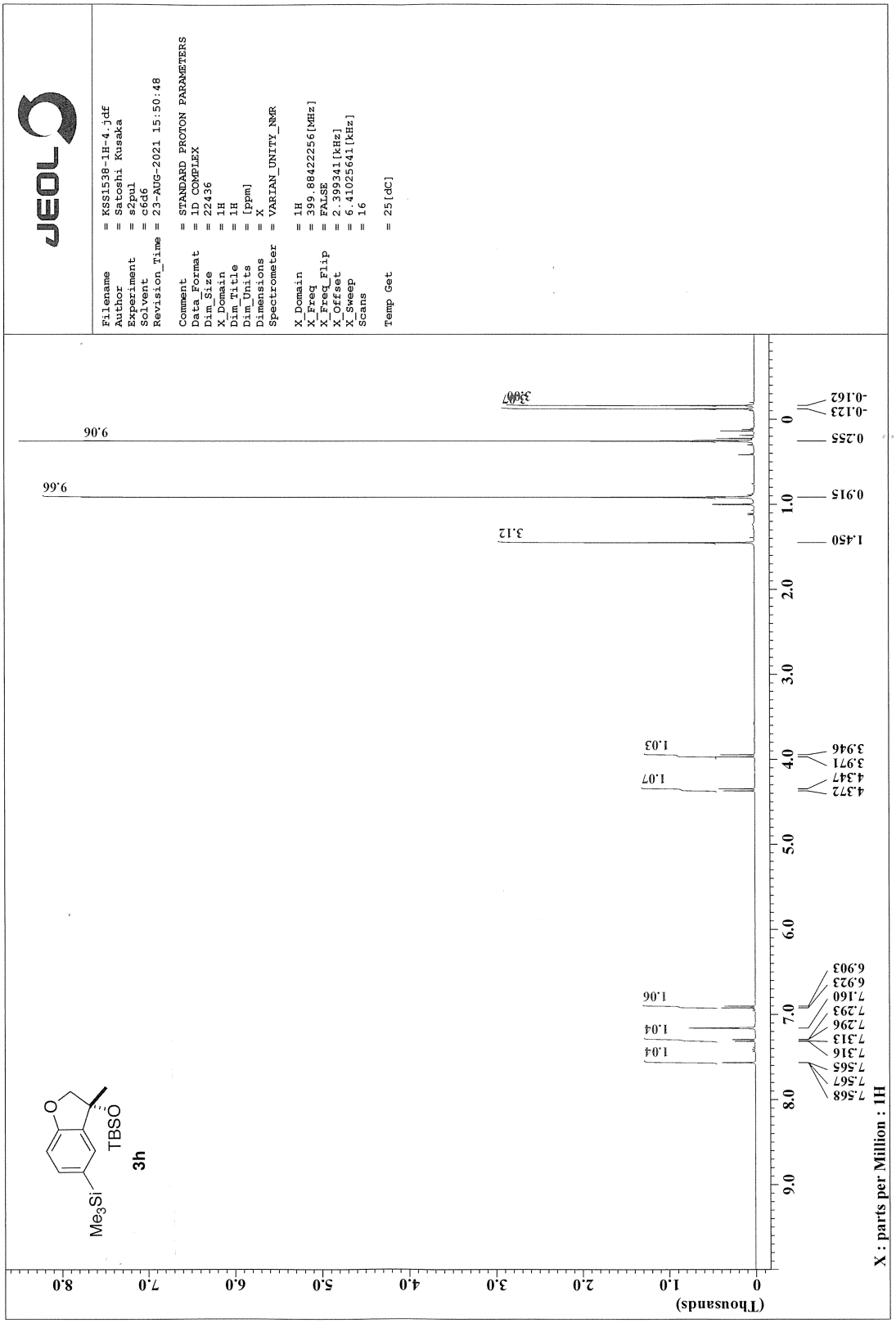


Figure S52. ^{1}H NMR Spectrum of **3h** (400 MHz, C_6D_6)

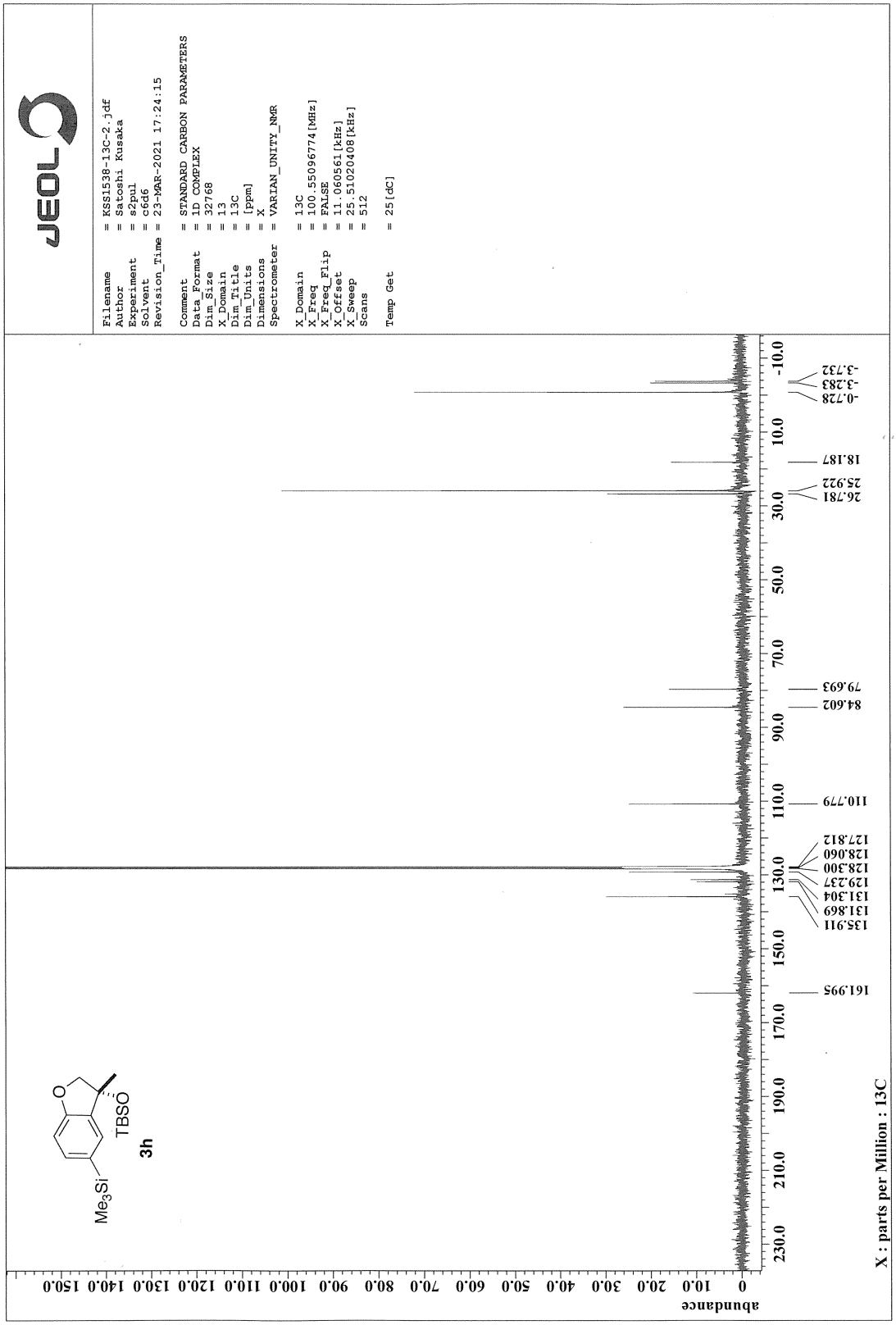


Figure S53. ^{13}C NMR Spectrum of **3h** (101 MHz, C_6D_6)

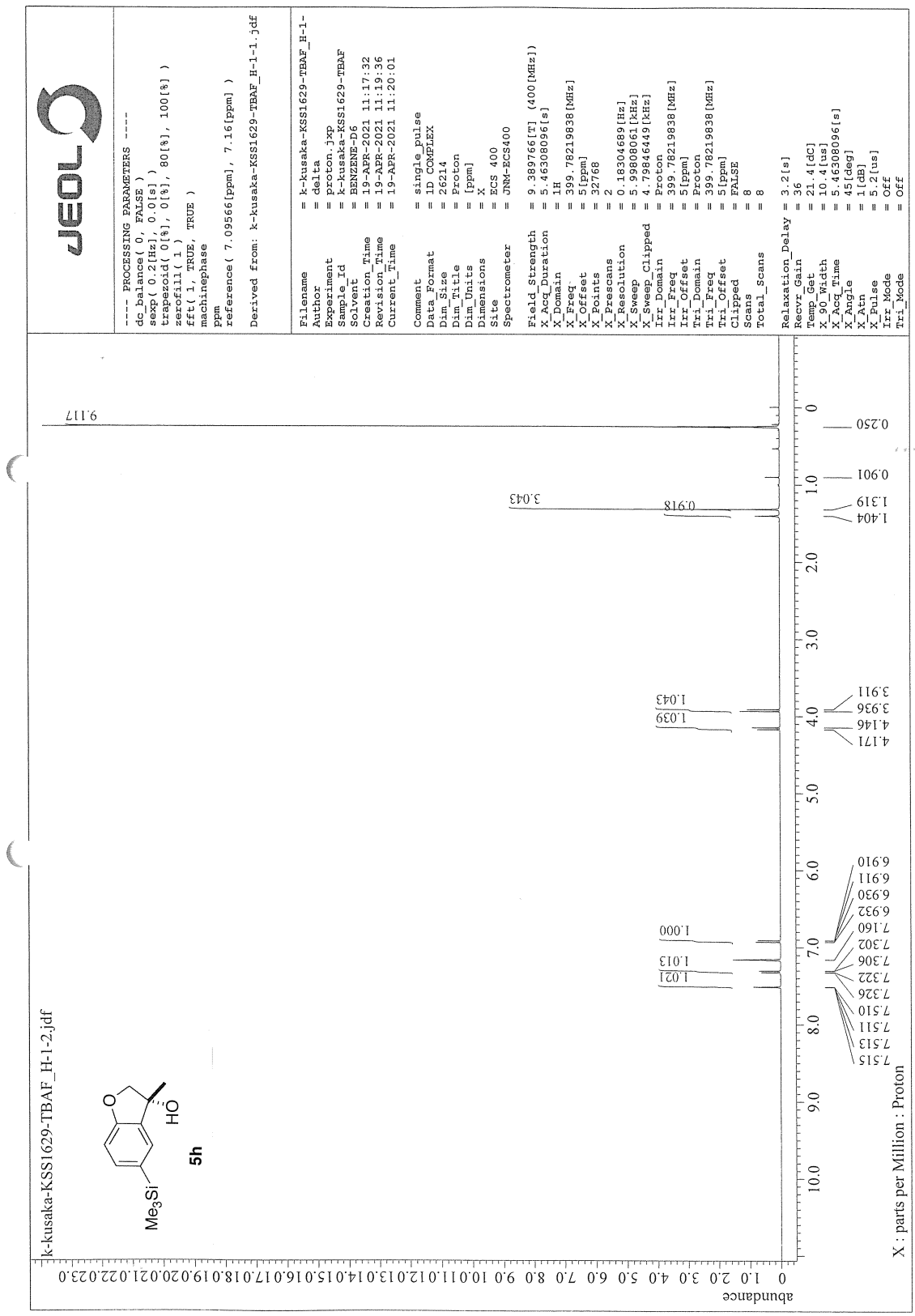


Figure S54. ^{1}H NMR Spectrum of **5h** (400 MHz, C_6D_6)

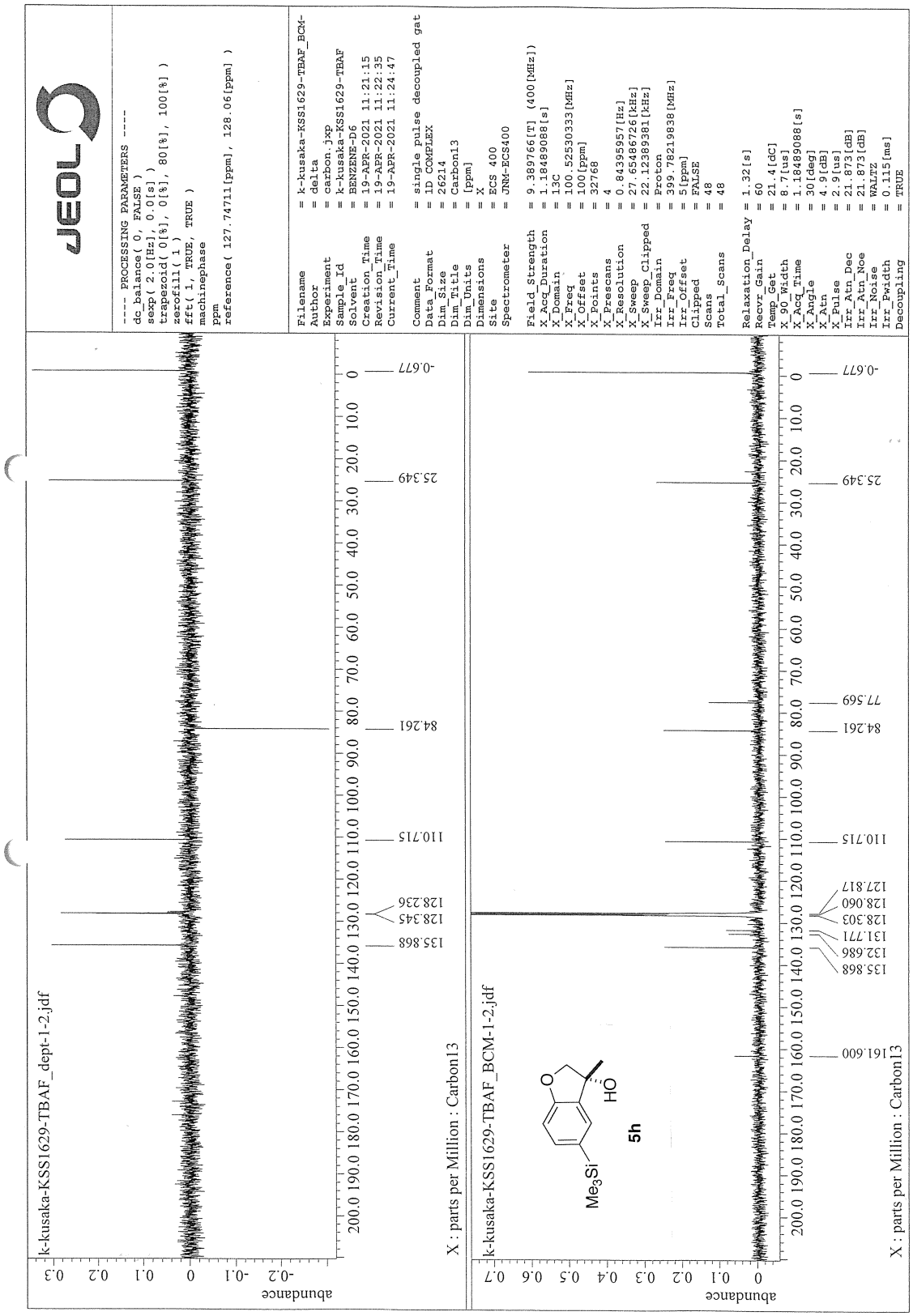


Figure S55. ^{13}C NMR Spectrum of **5h** (101 MHz, C_6D_6)

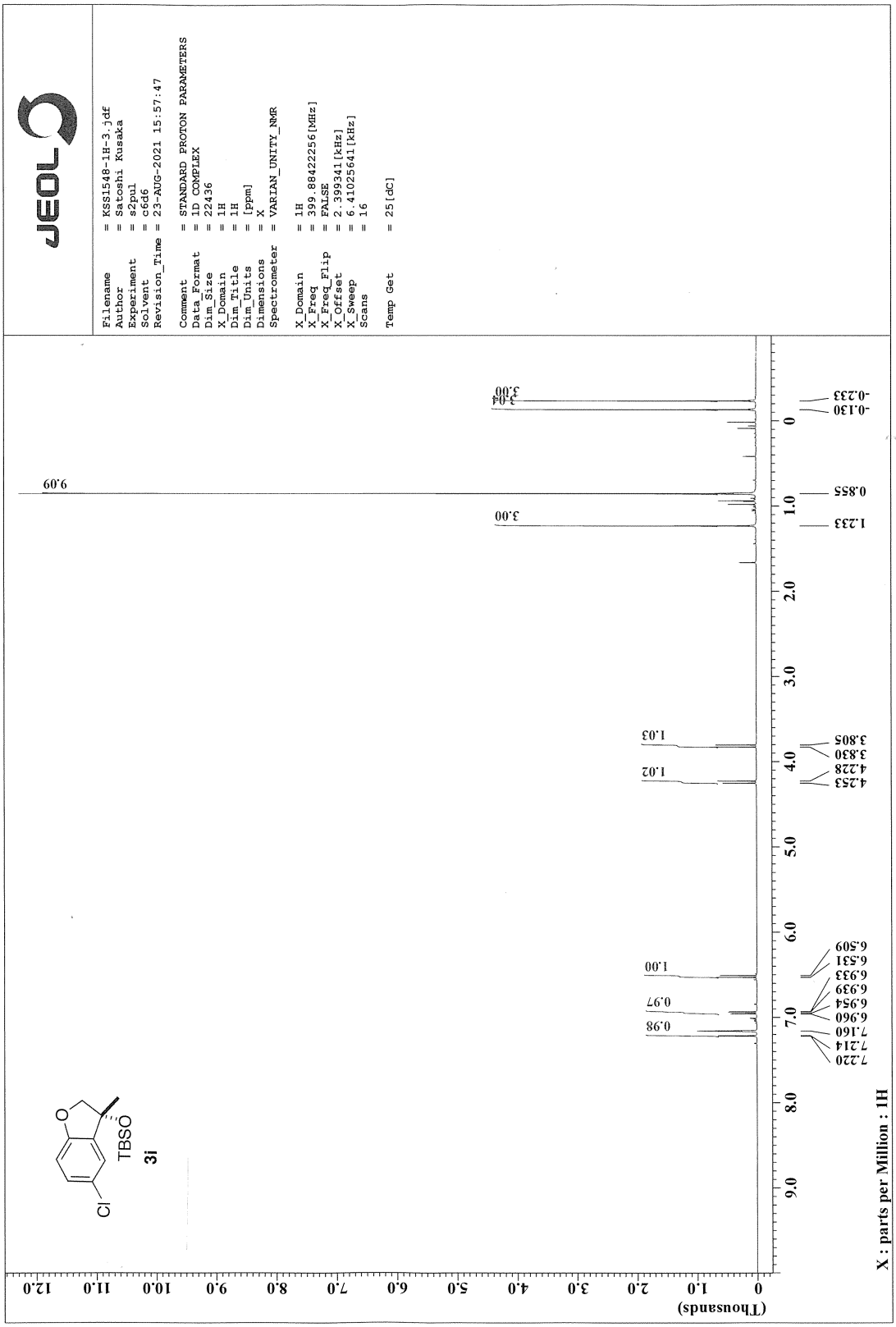


Figure S56. ^{1}H NMR Spectrum of **3i** (400 MHz, C_6D_6)

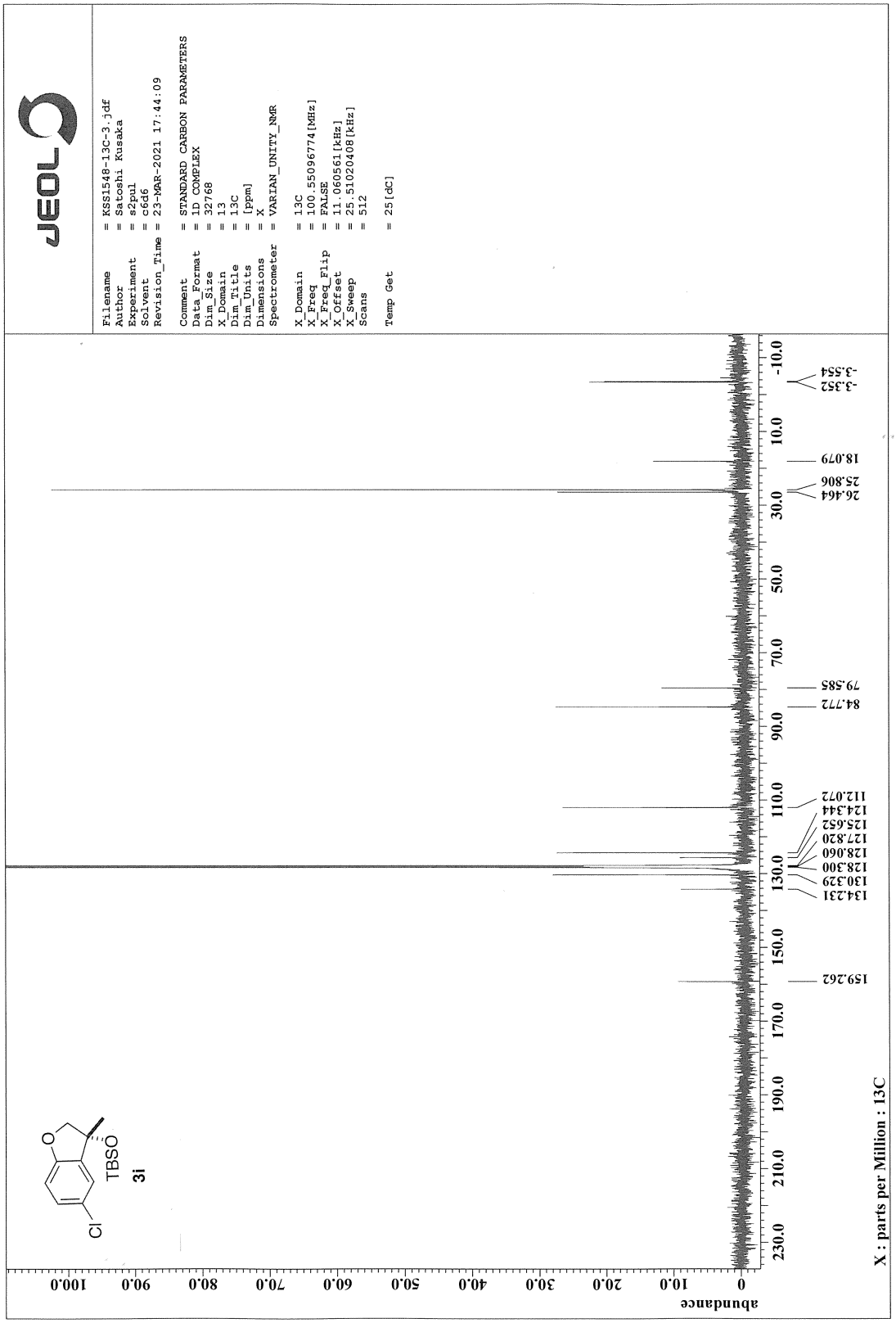


Figure S57. ^{13}C NMR Spectrum of **3i** (101 MHz, C_6D_6)

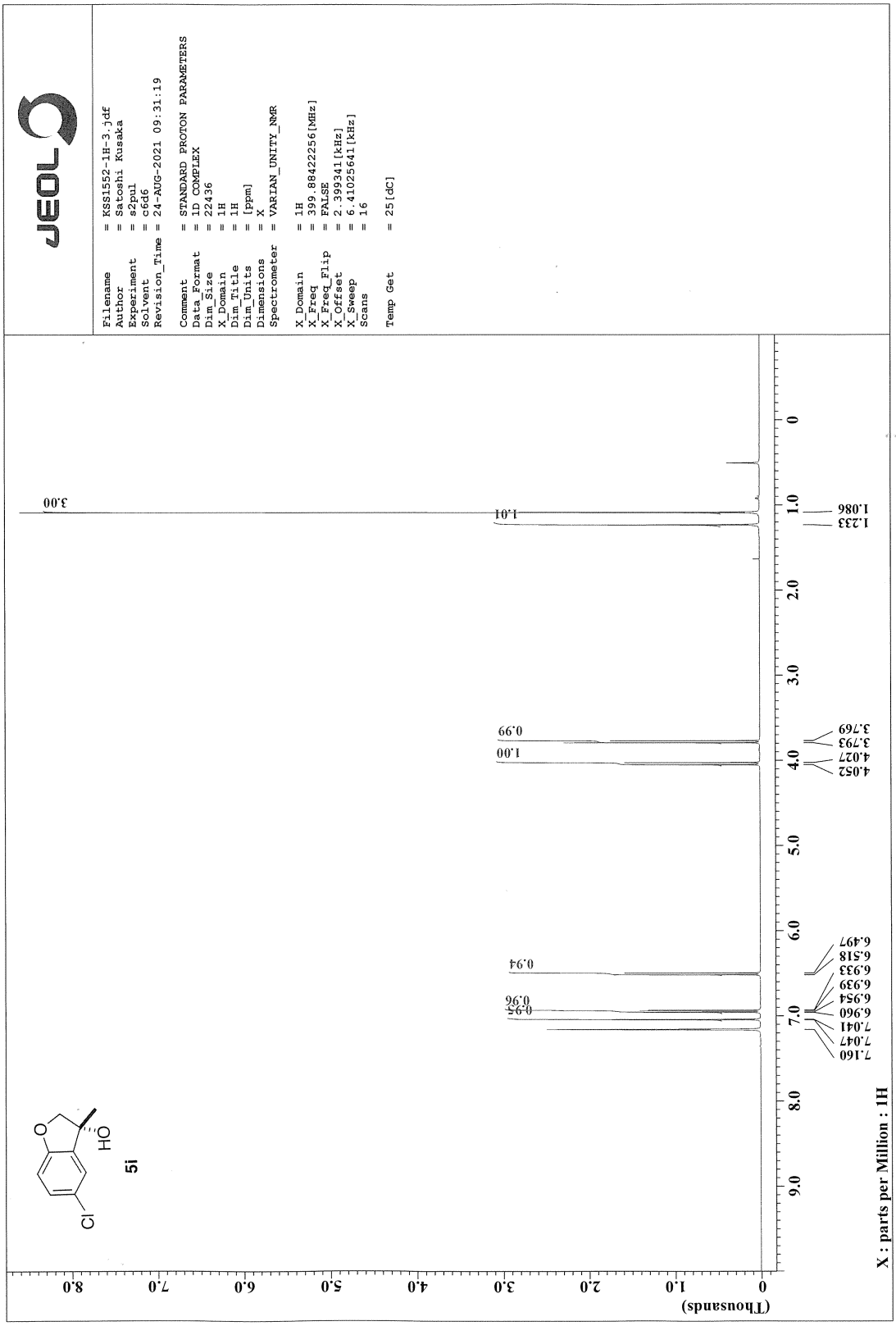


Figure S58. ^{1}H NMR Spectrum of **5i** (400 MHz, C_6D_6)

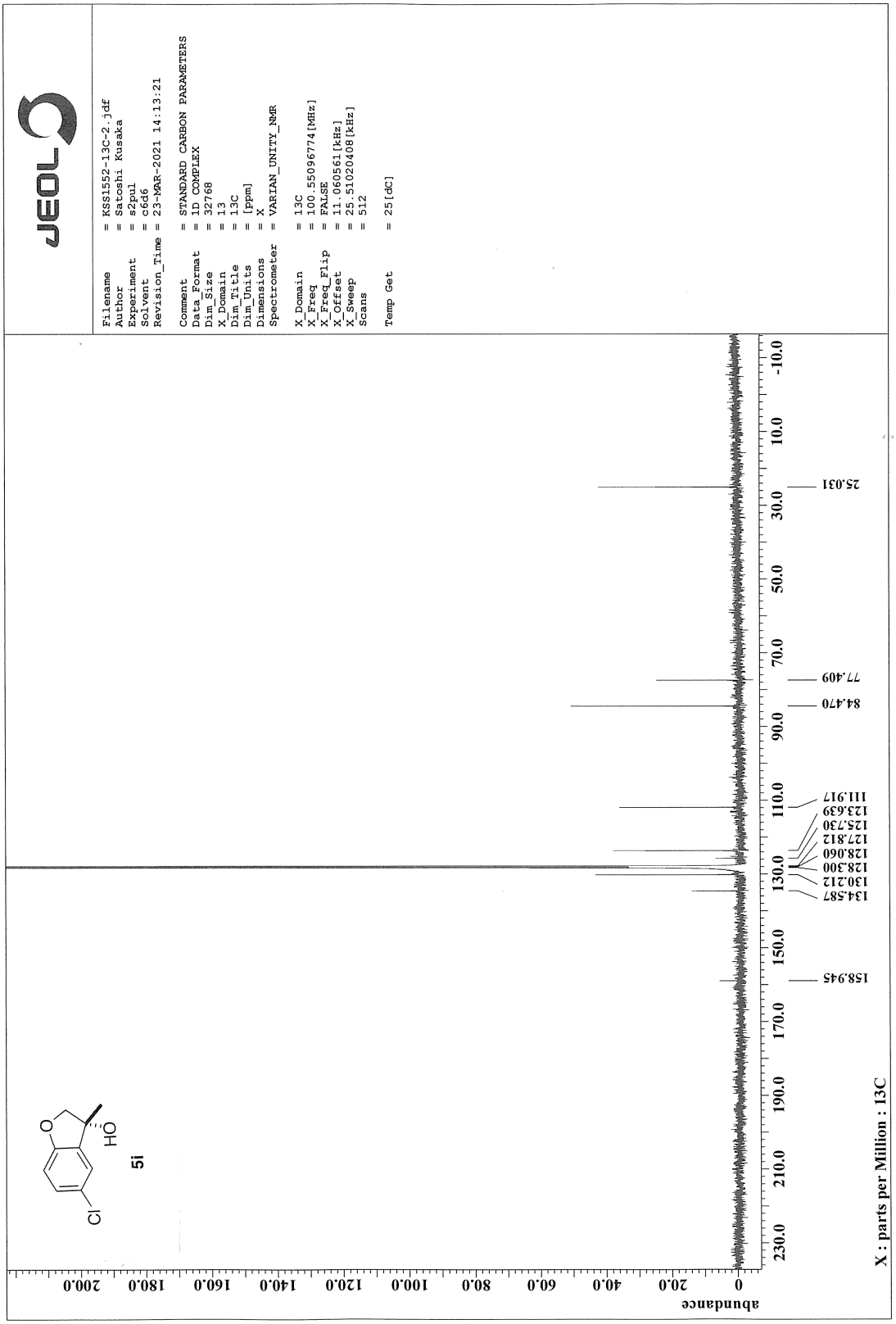


Figure S59. ^{13}C NMR Spectrum of **5i** (101 MHz, C_6D_6)

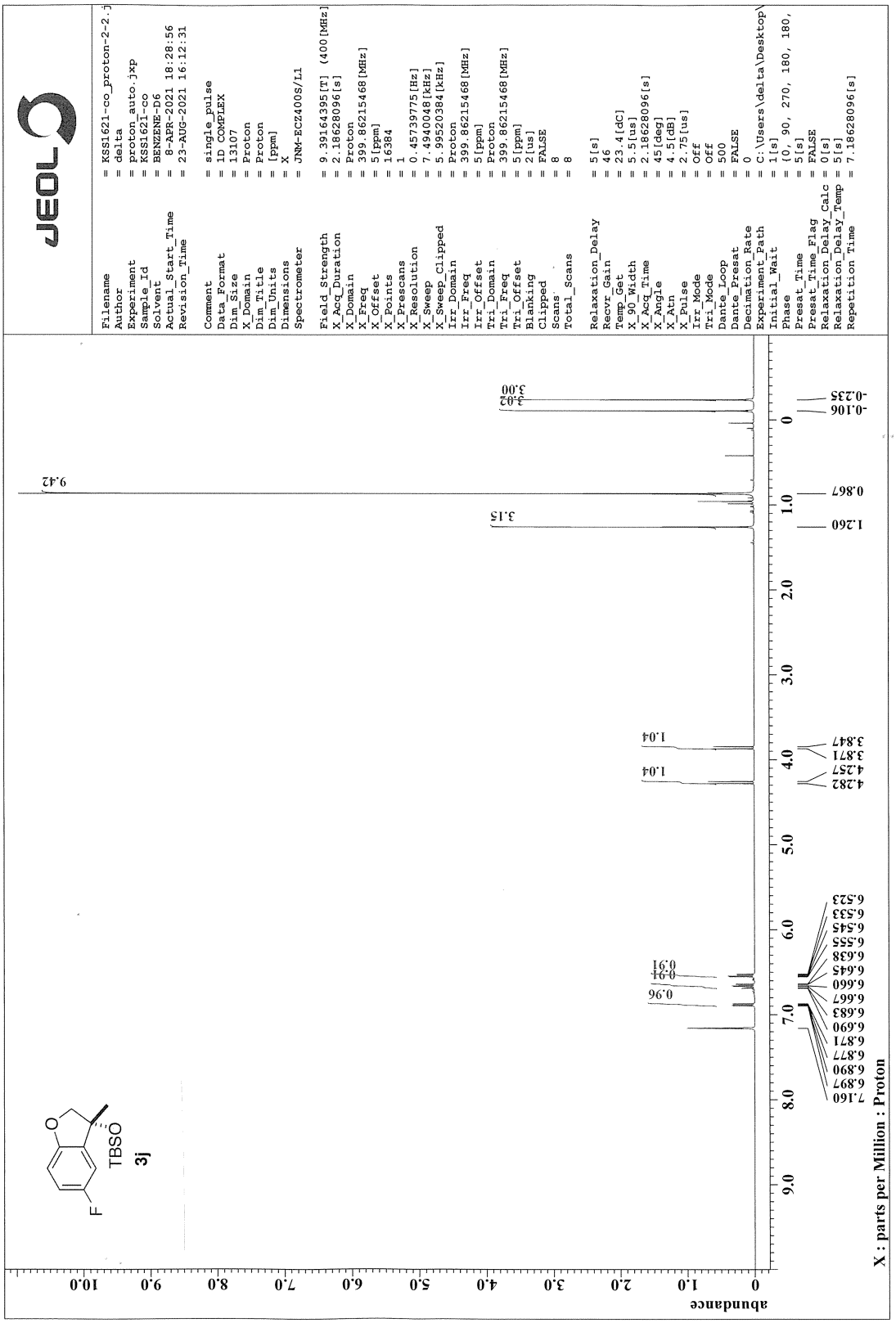


Figure S60. ^{1}H NMR Spectrum of **3j** (400 MHz, C_6D_6)

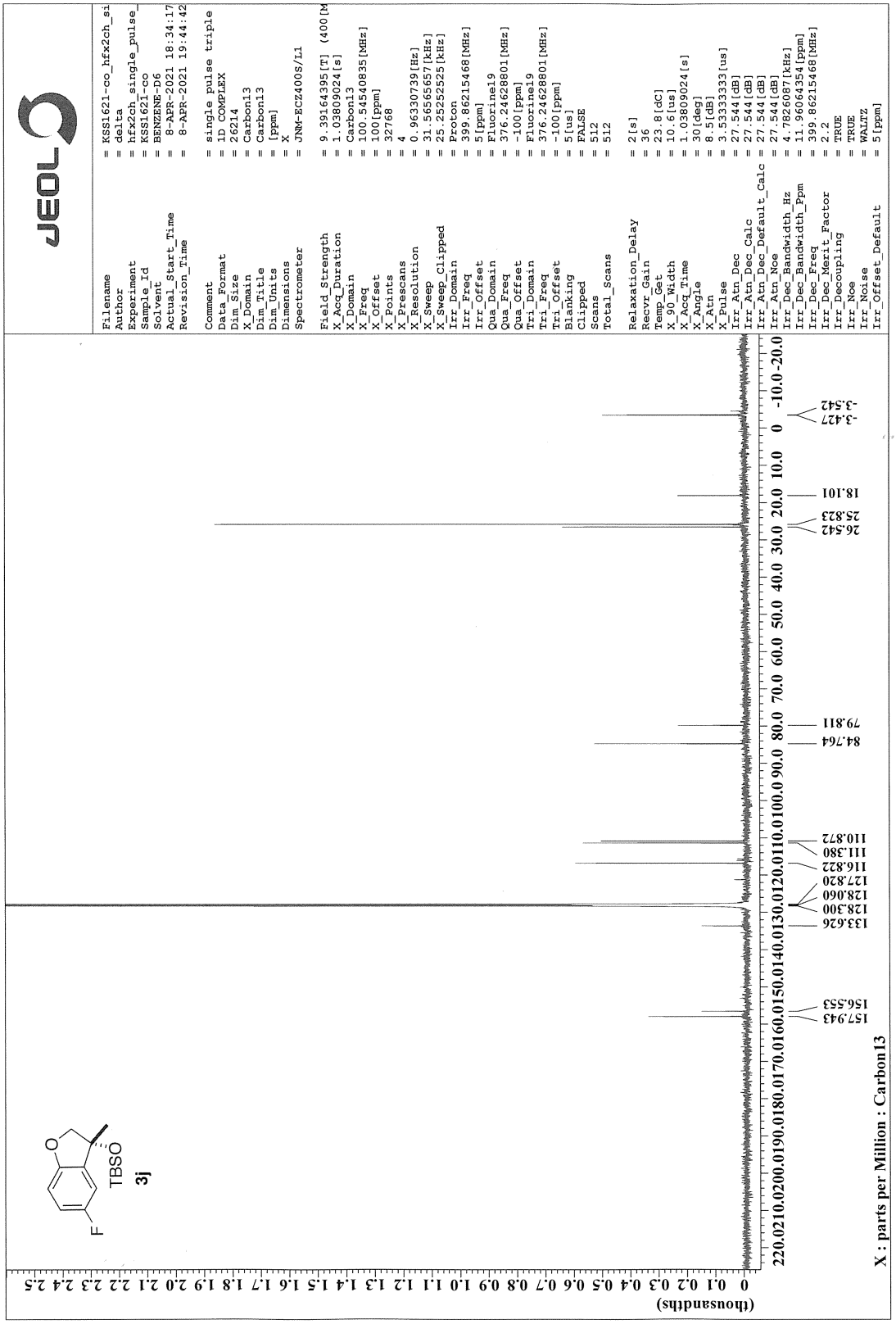


Figure S61. ^{13}C NMR Spectrum of **3j** (101 MHz, C_6D_6, ^{1}H and ^{19}F simultaneous decoupling)

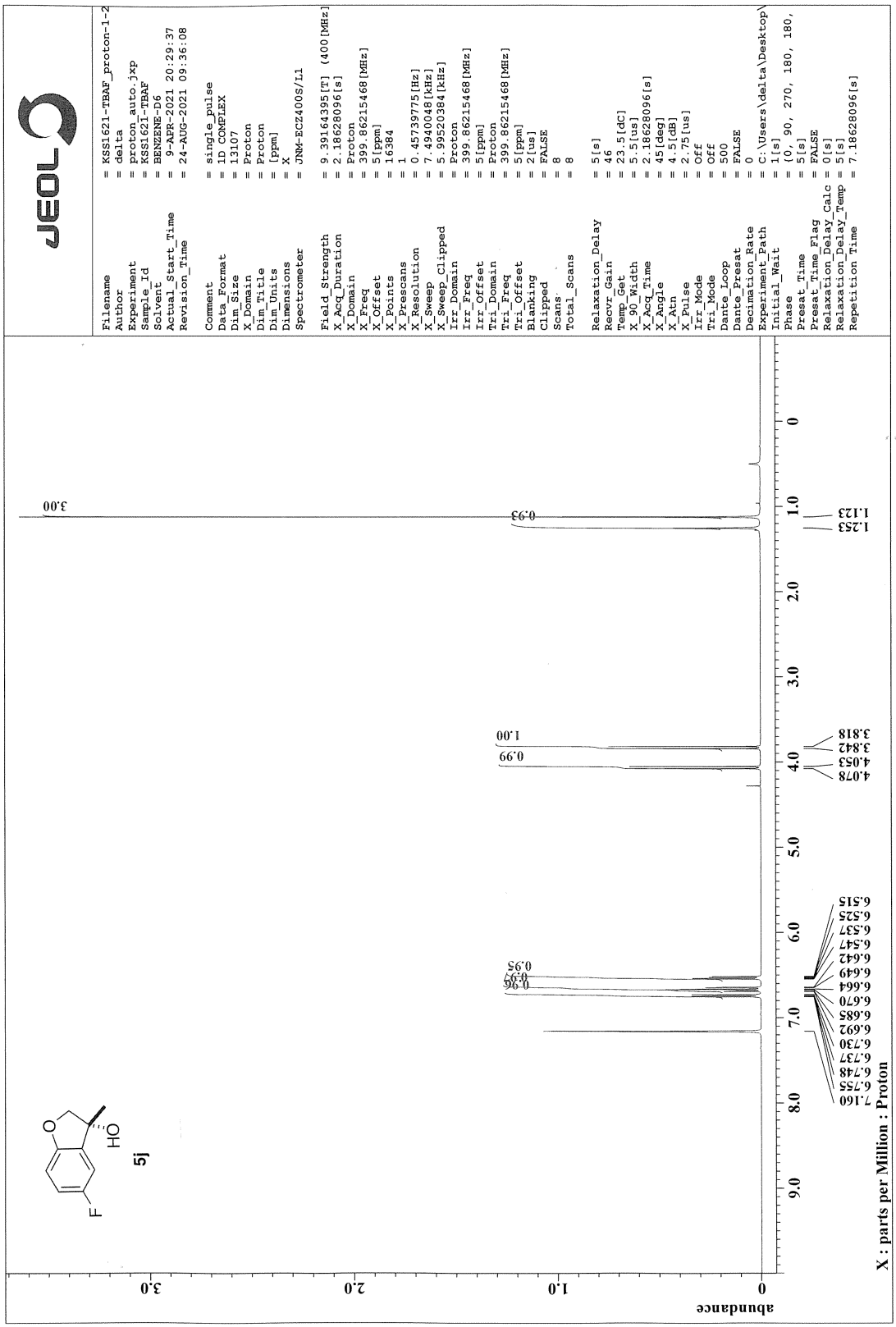


Figure S62. ^{1}H NMR Spectrum of **5j** (400 MHz, C_6D_6)

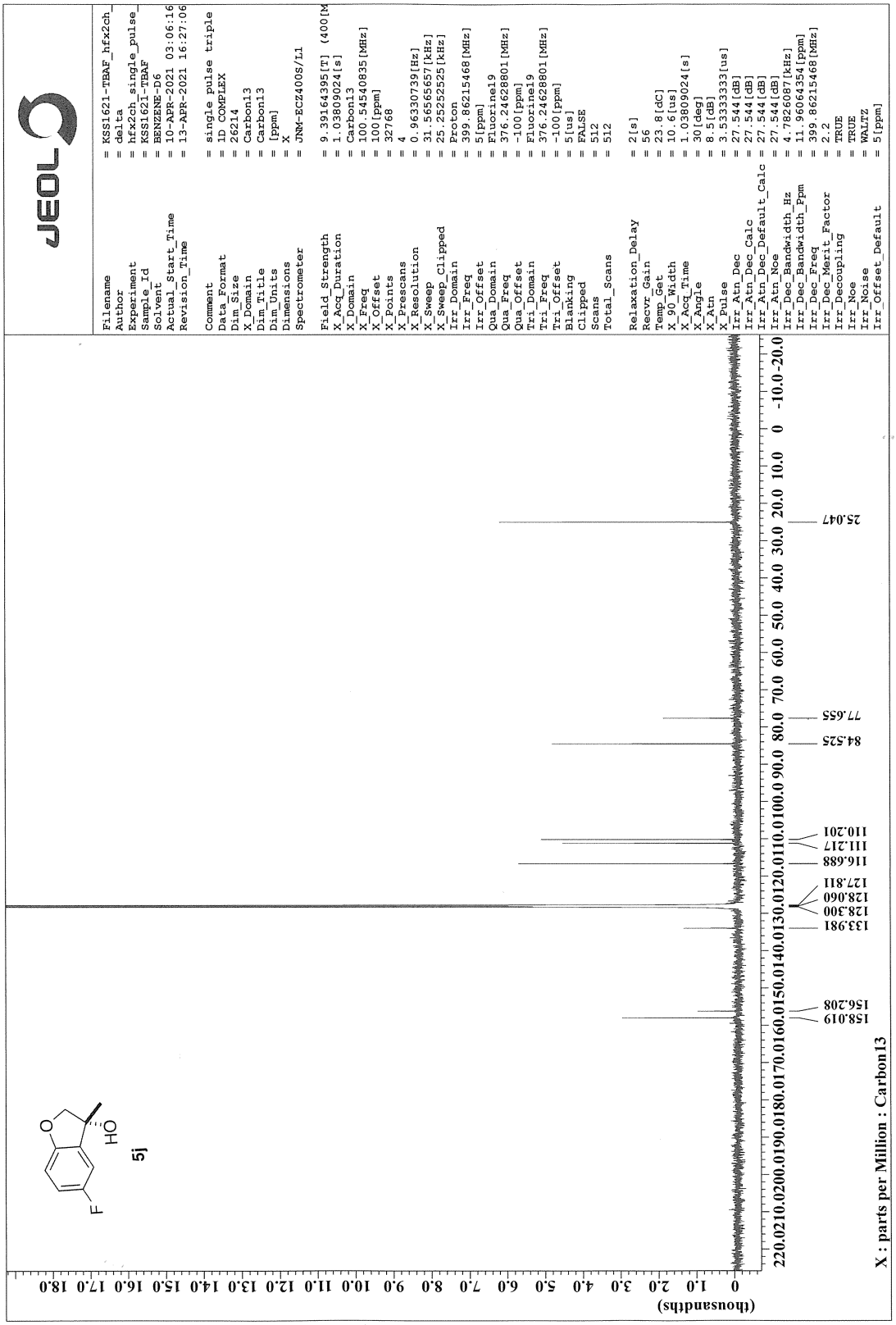


Figure S63. ^{13}C NMR Spectrum of **5j** (101 MHz, C_6D_6, ^{1}H and ^{19}F simultaneous decoupling)

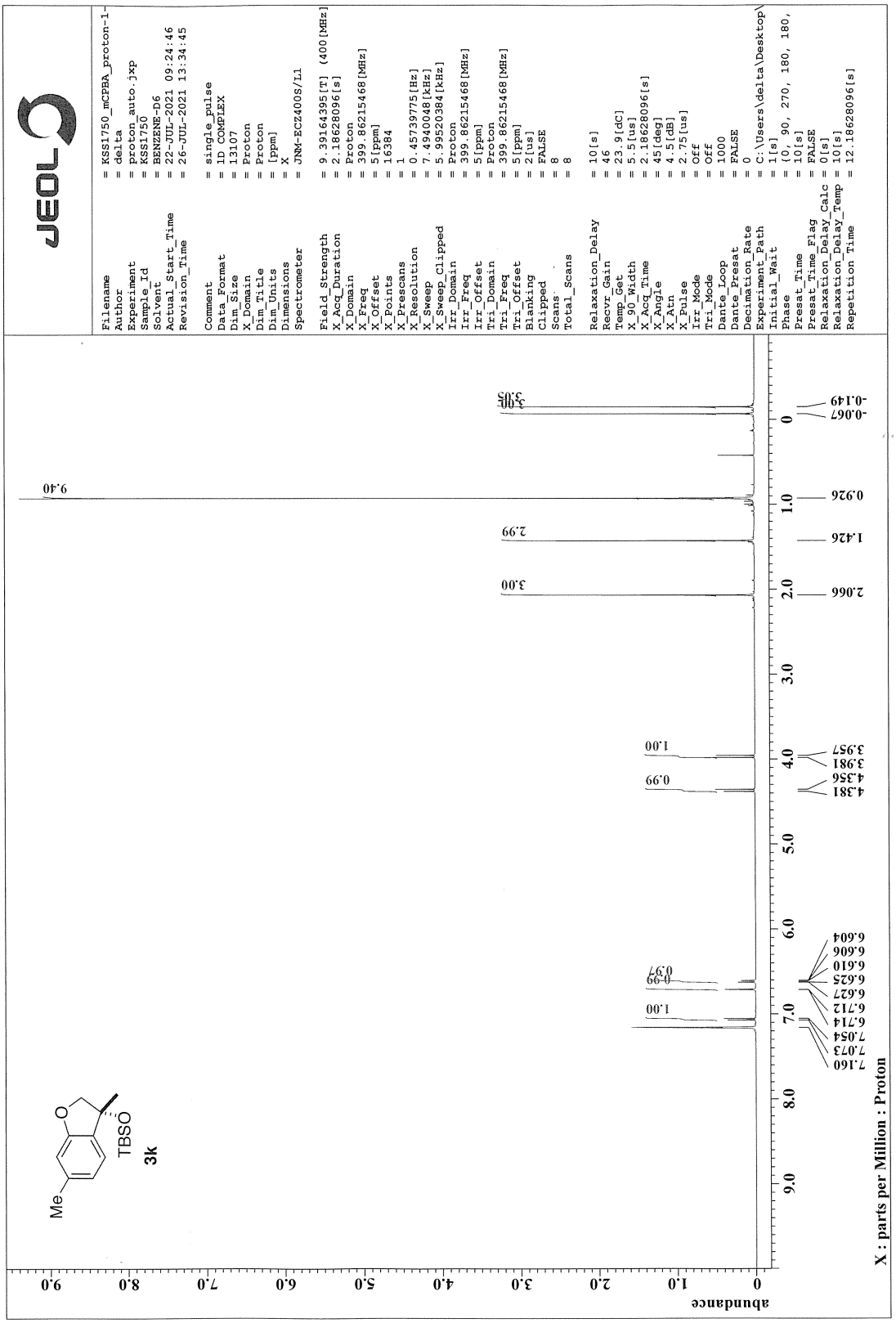


Figure S64. ^{1}H NMR Spectrum of **3k** (400 MHz, C_6D_6)

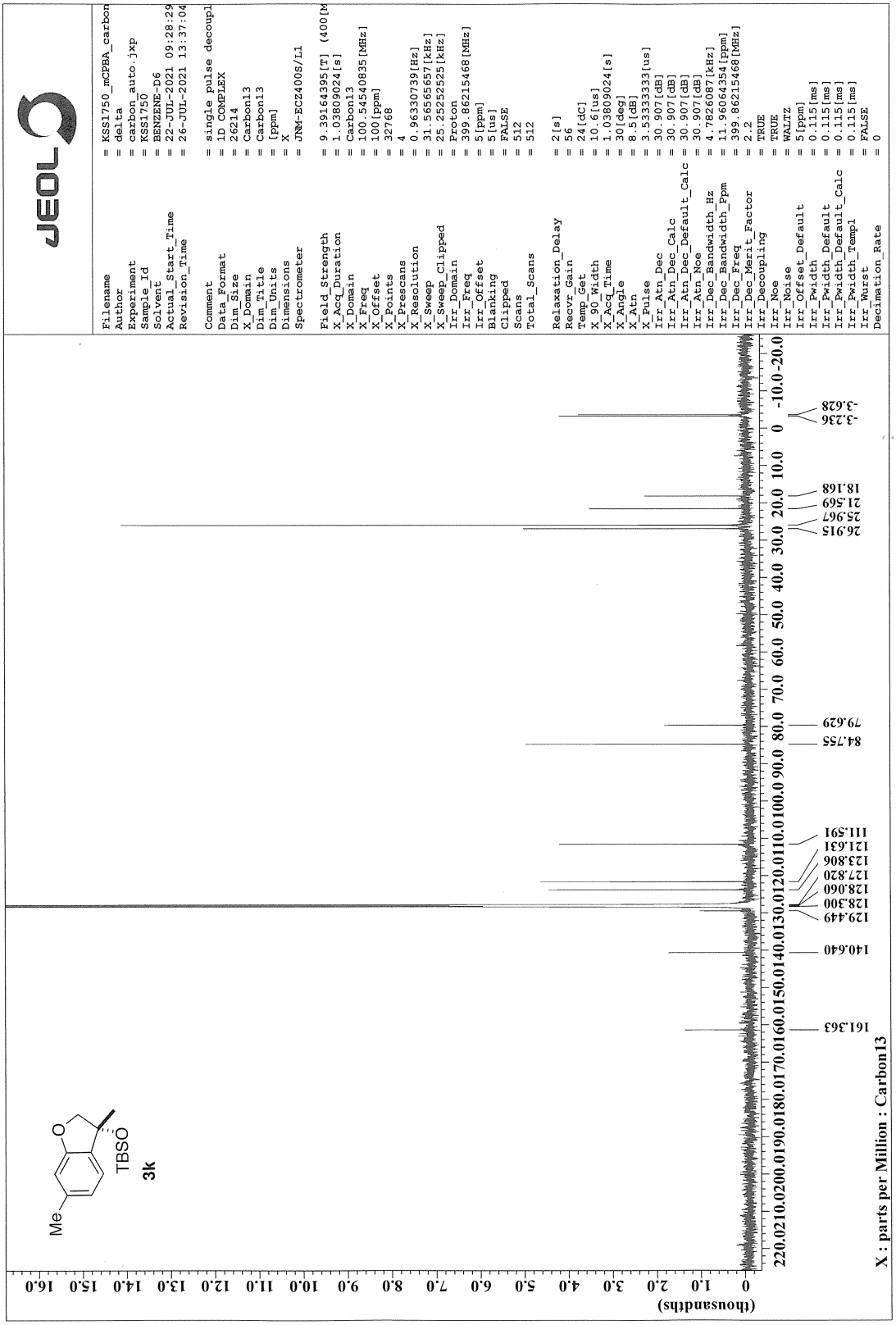


Figure S65. ^{13}C NMR Spectrum of **3k** (101 MHz, C_6D_6)

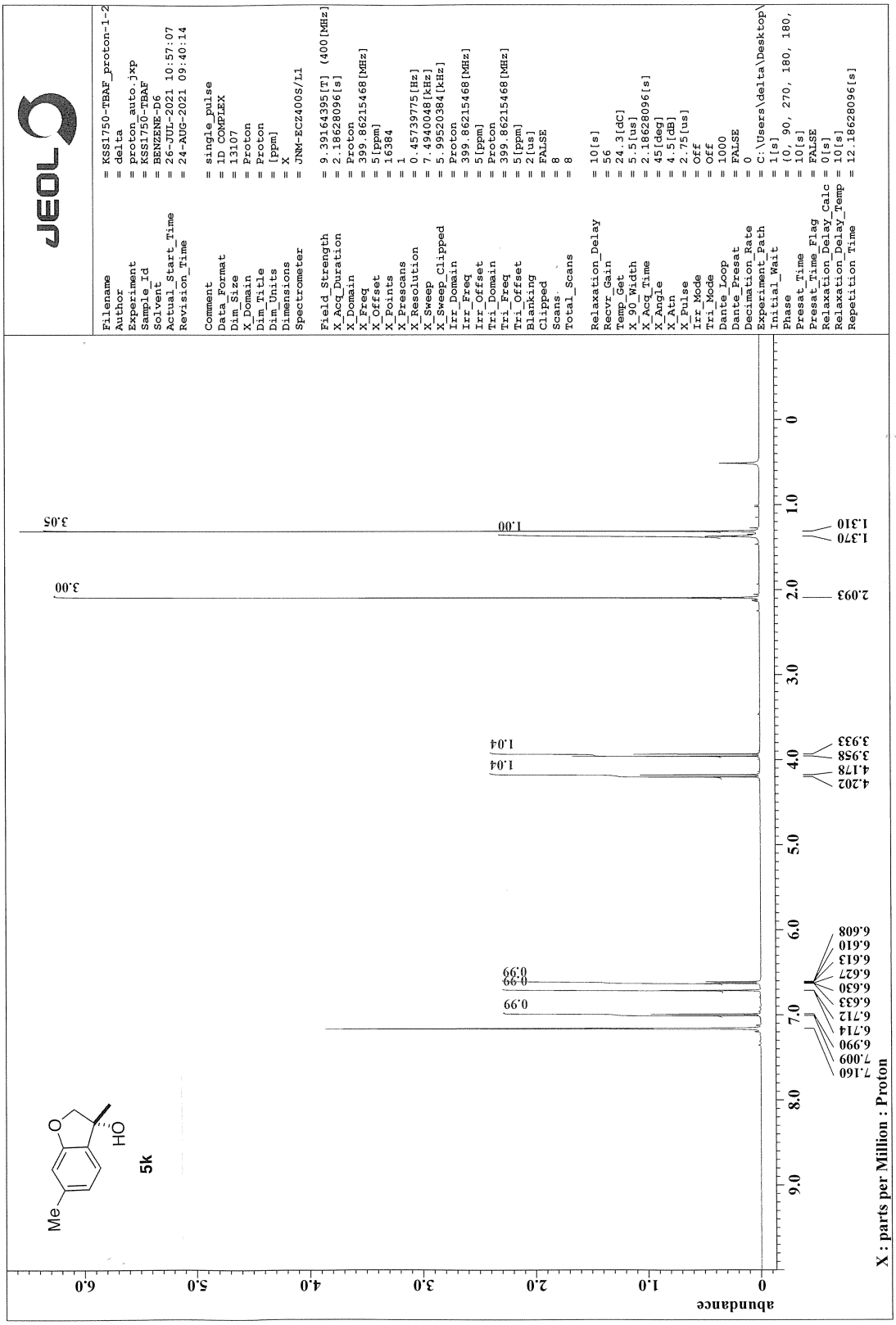


Figure S66. ^{1}H NMR Spectrum of **5k** (400 MHz, C_6D_6)

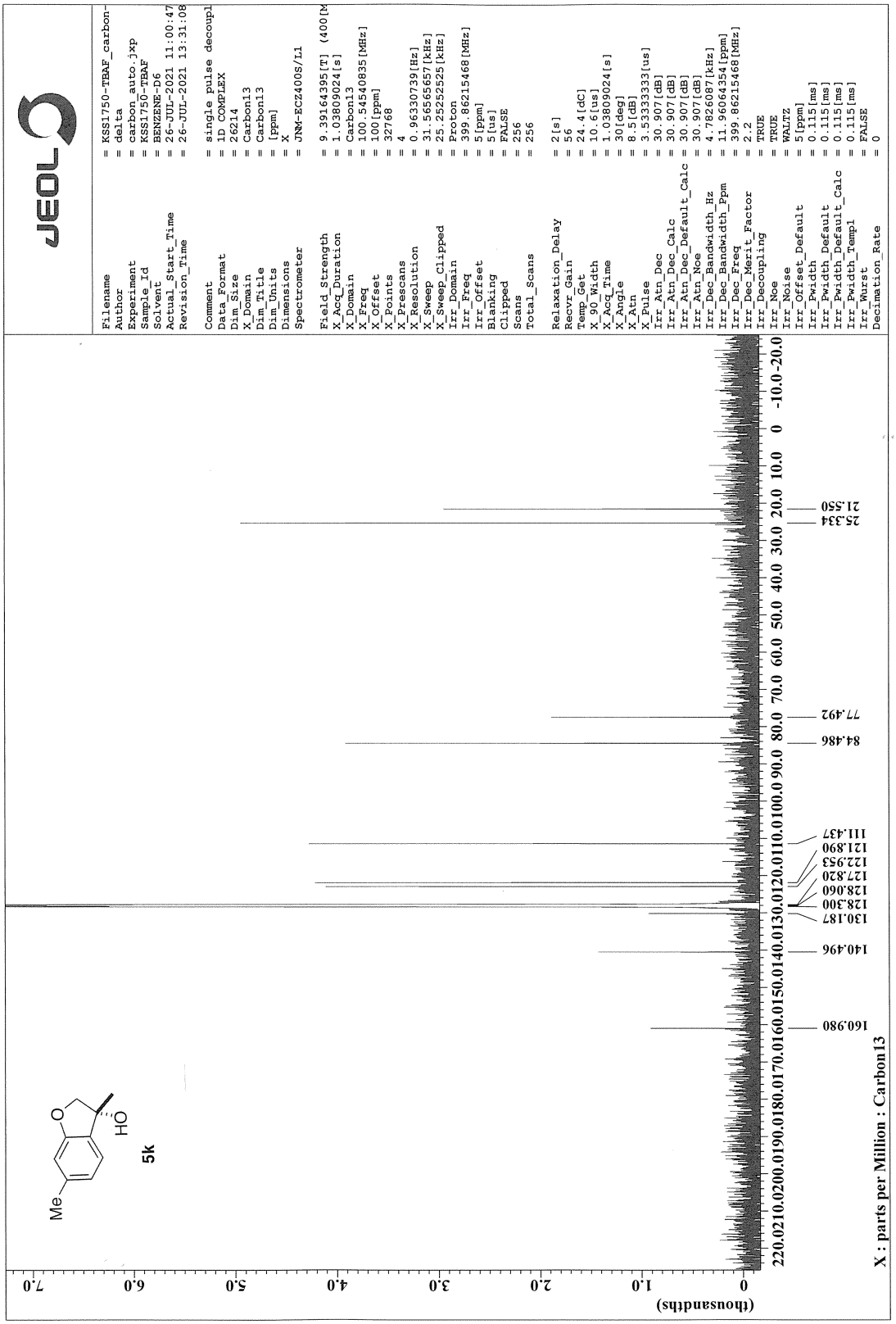


Figure S67. ^{13}C NMR Spectrum of **5k** (101 MHz, C_6D_6)

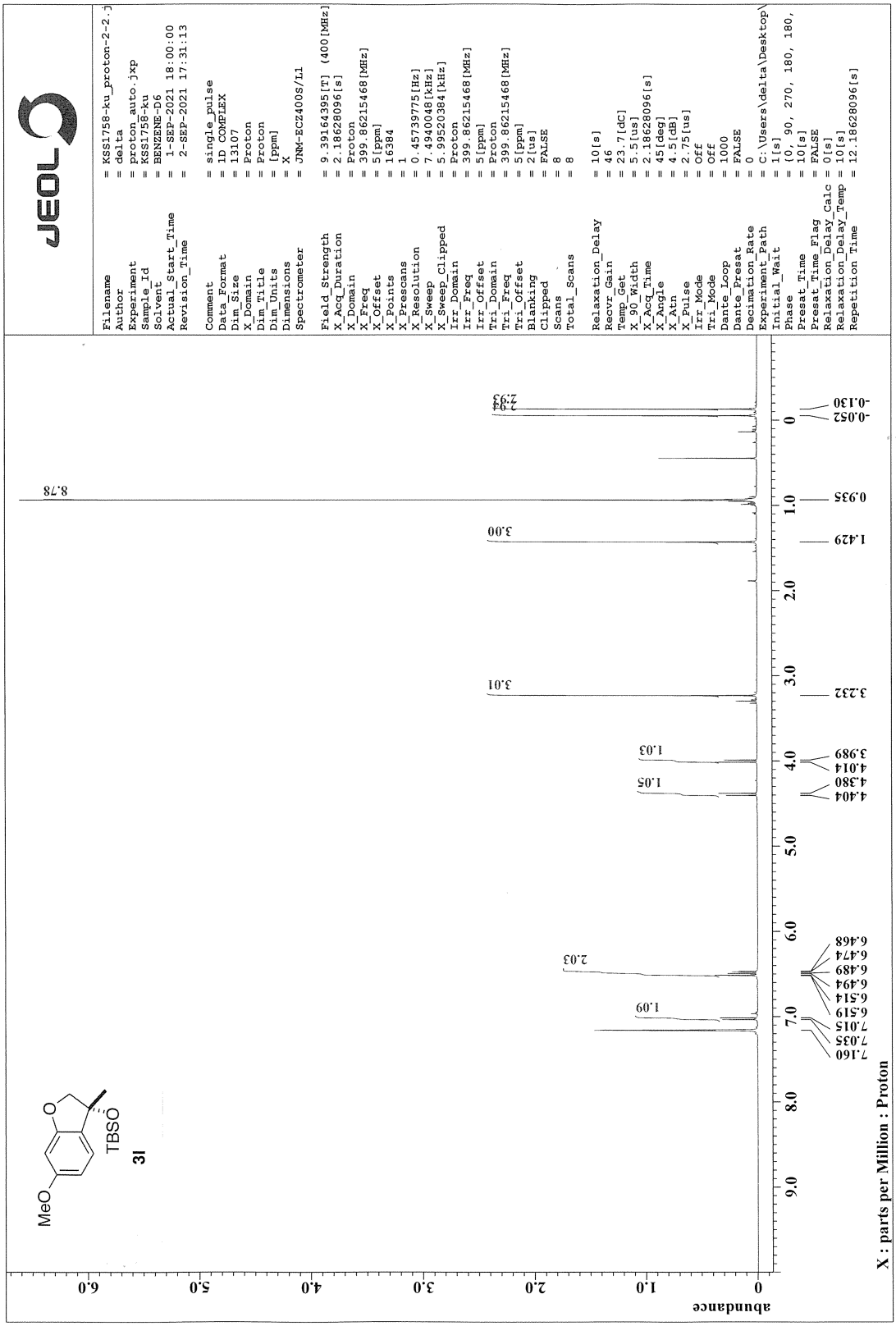


Figure S68. ^{1}H NMR Spectrum of **3l** (400 MHz, C_6D_6)

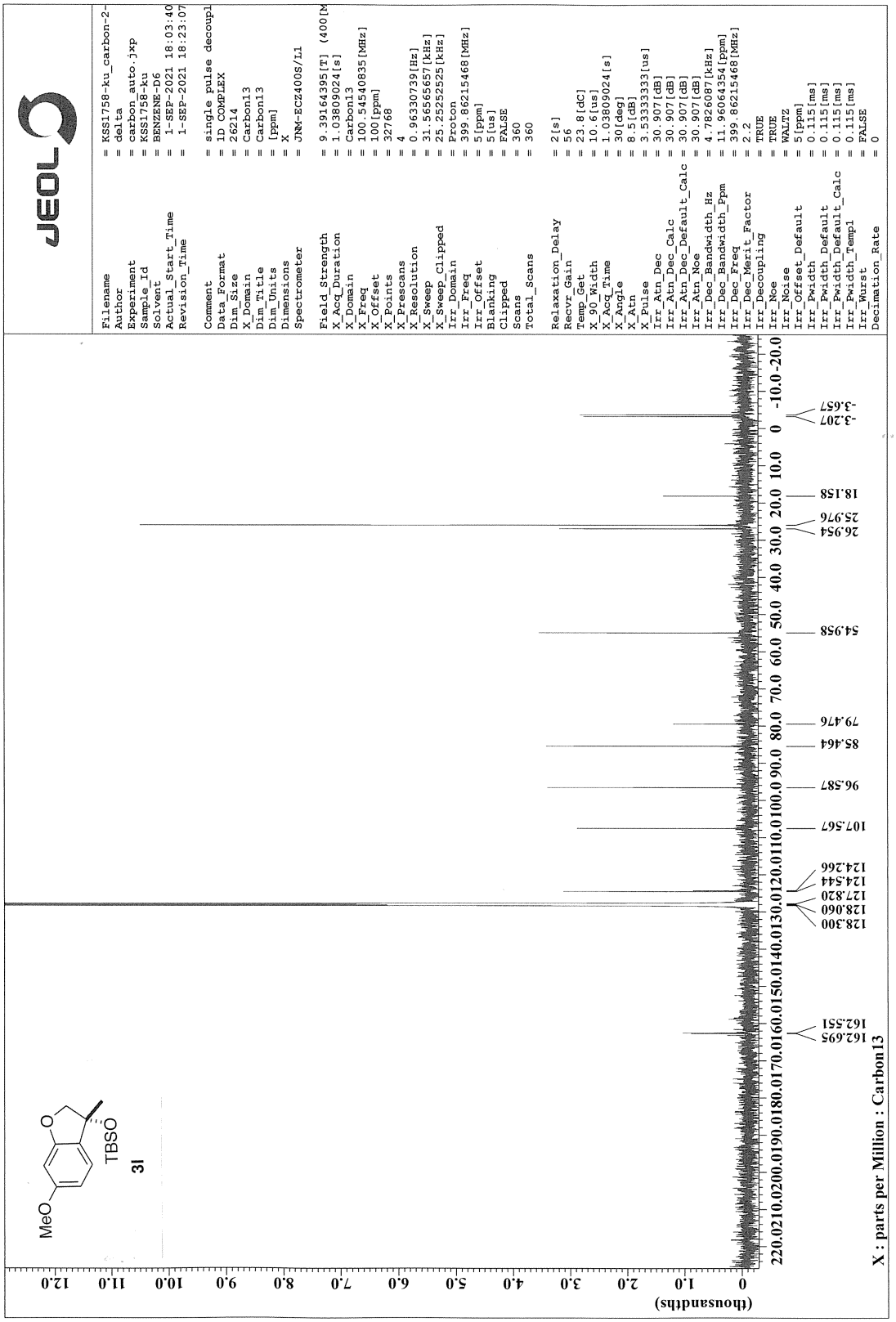


Figure S69. ^{13}C NMR Spectrum of **3l** (101 MHz, C_6D_6)

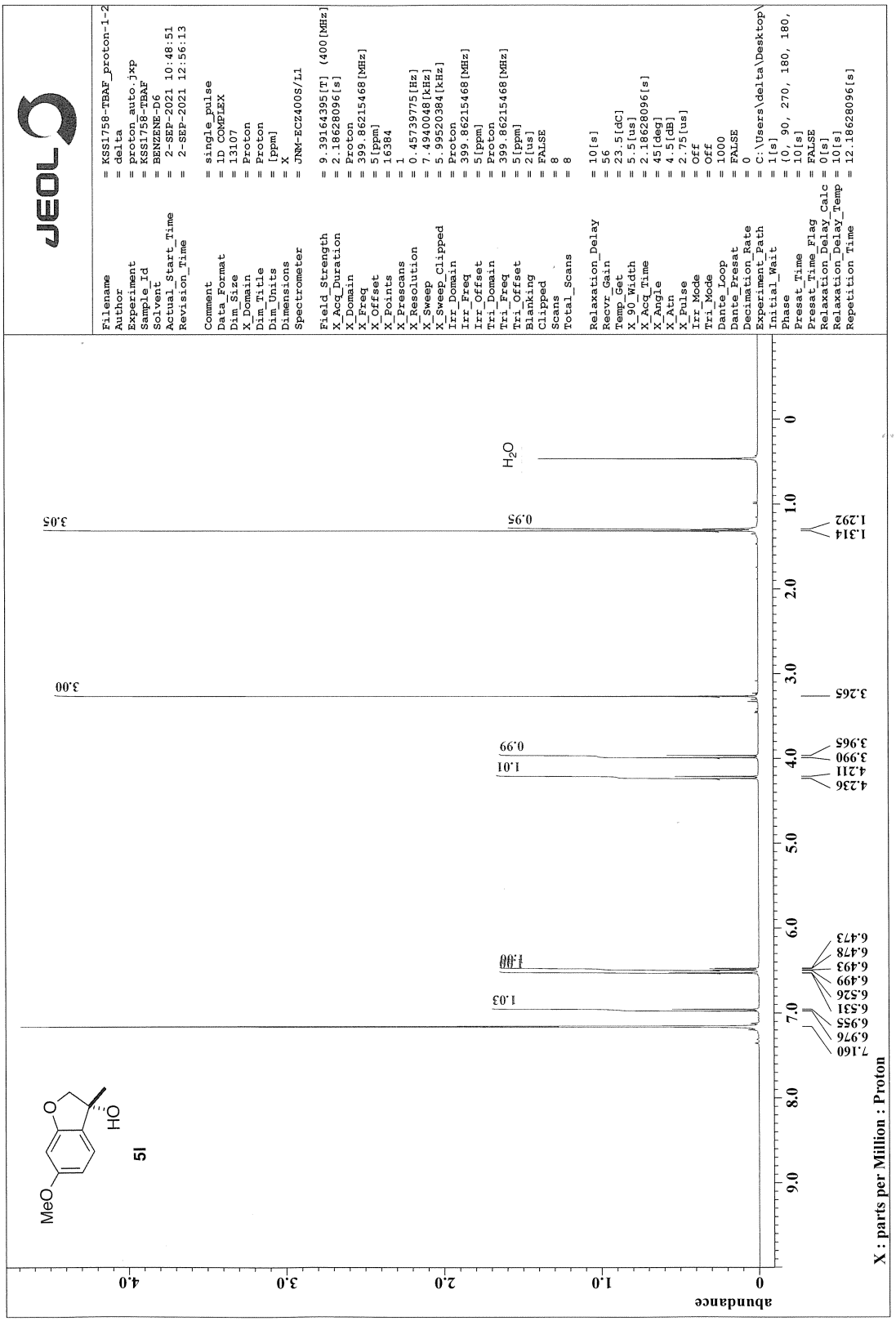


Figure S70. ^{1}H NMR Spectrum of **5l** (400 MHz, C_6D_6)

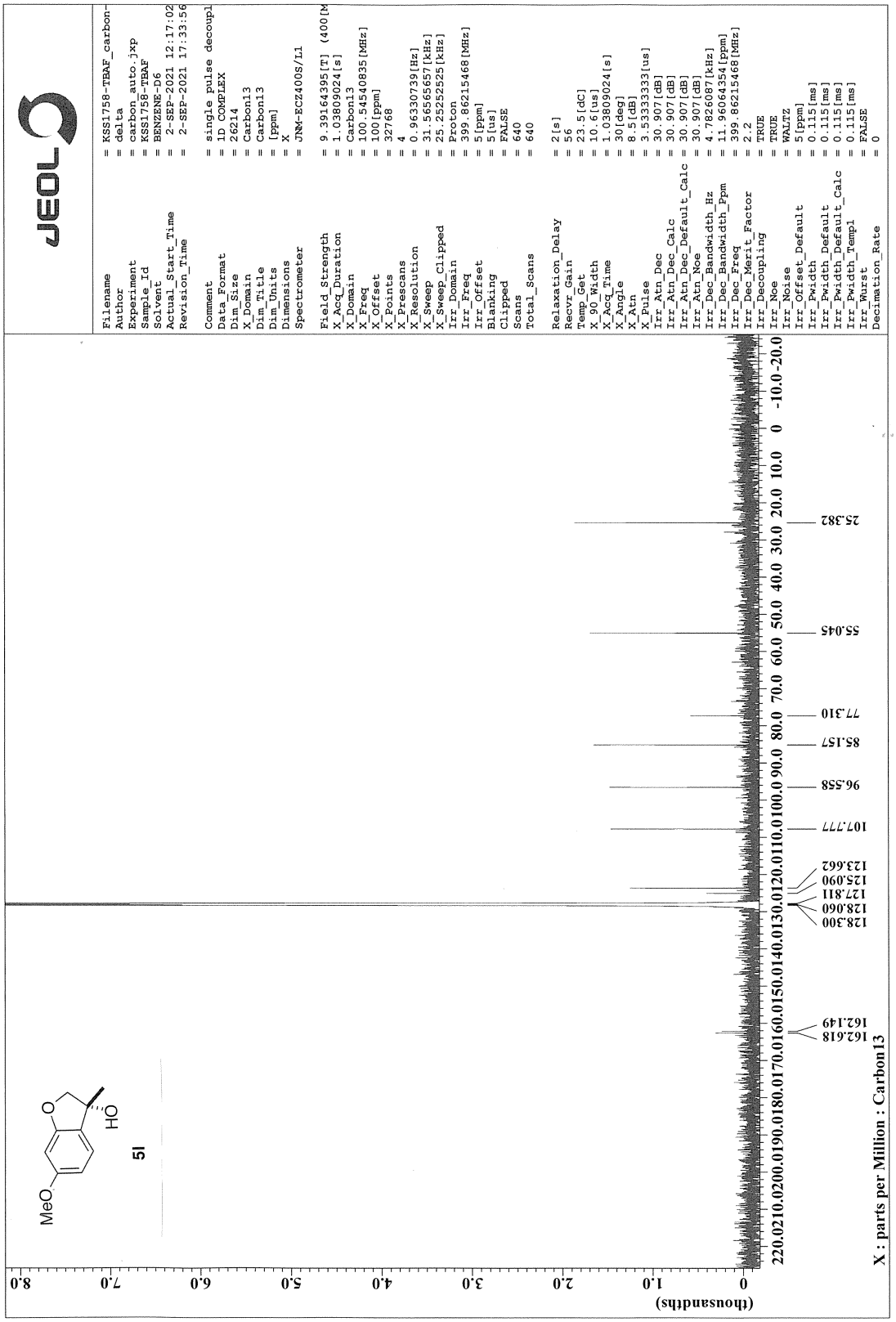


Figure S71. ^{13}C NMR Spectrum of **5l** (101 MHz, C_6D_6)

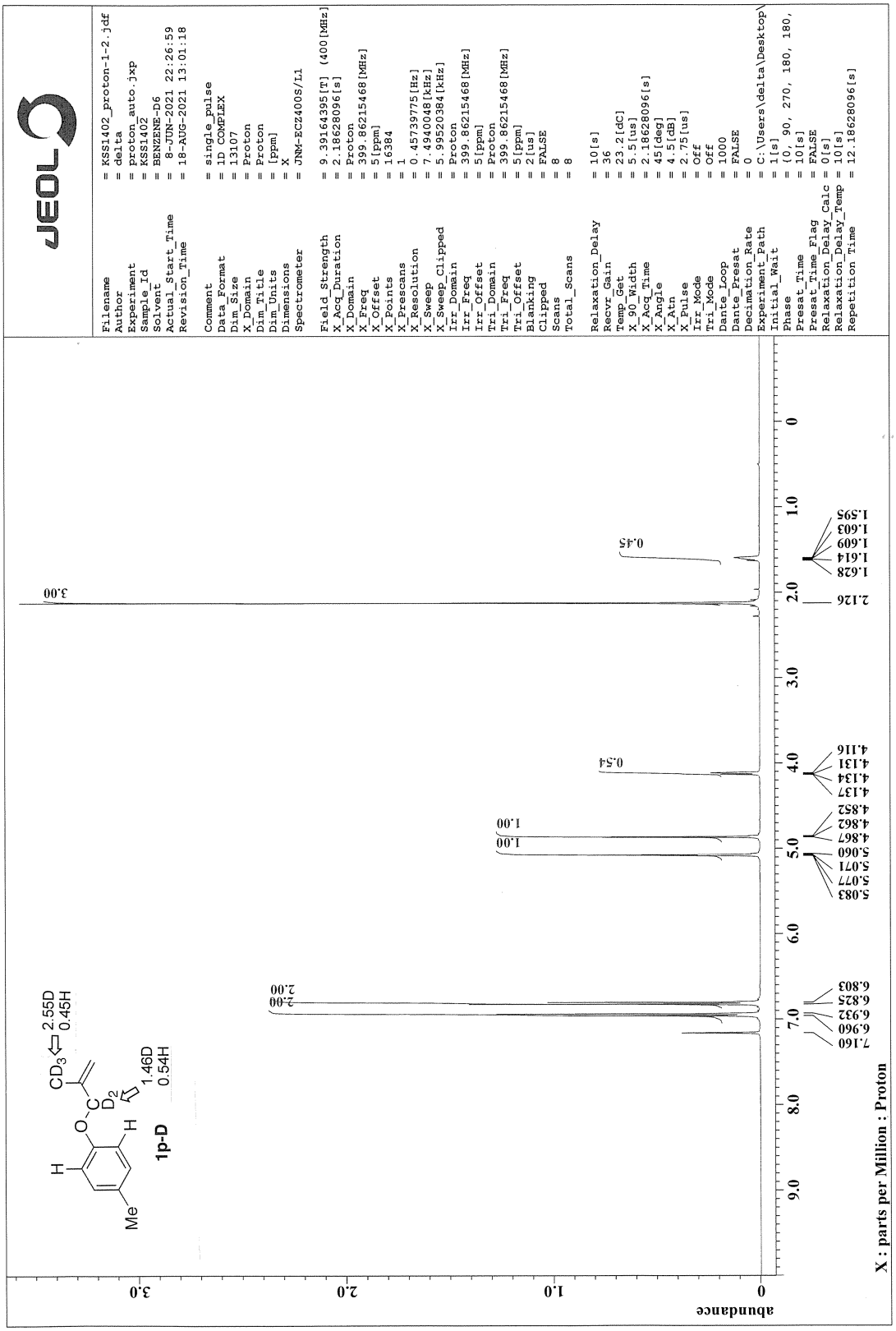


Figure S72. ^{1}H NMR Spectrum of **1p-D** (400 MHz, C_6D_6)

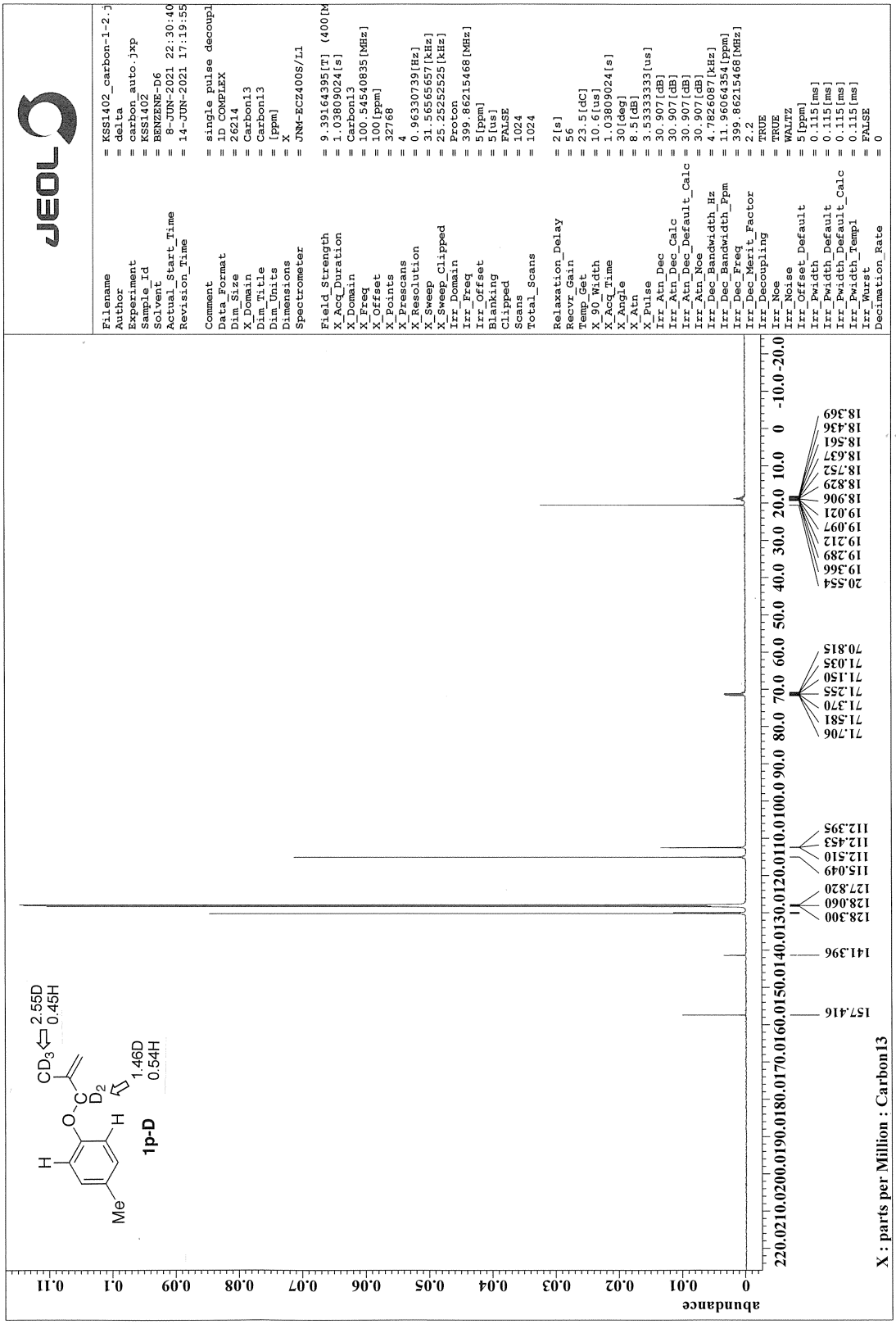


Figure S73. ^{13}C NMR Spectrum of **1p-D** (101 MHz, C_6D_6)

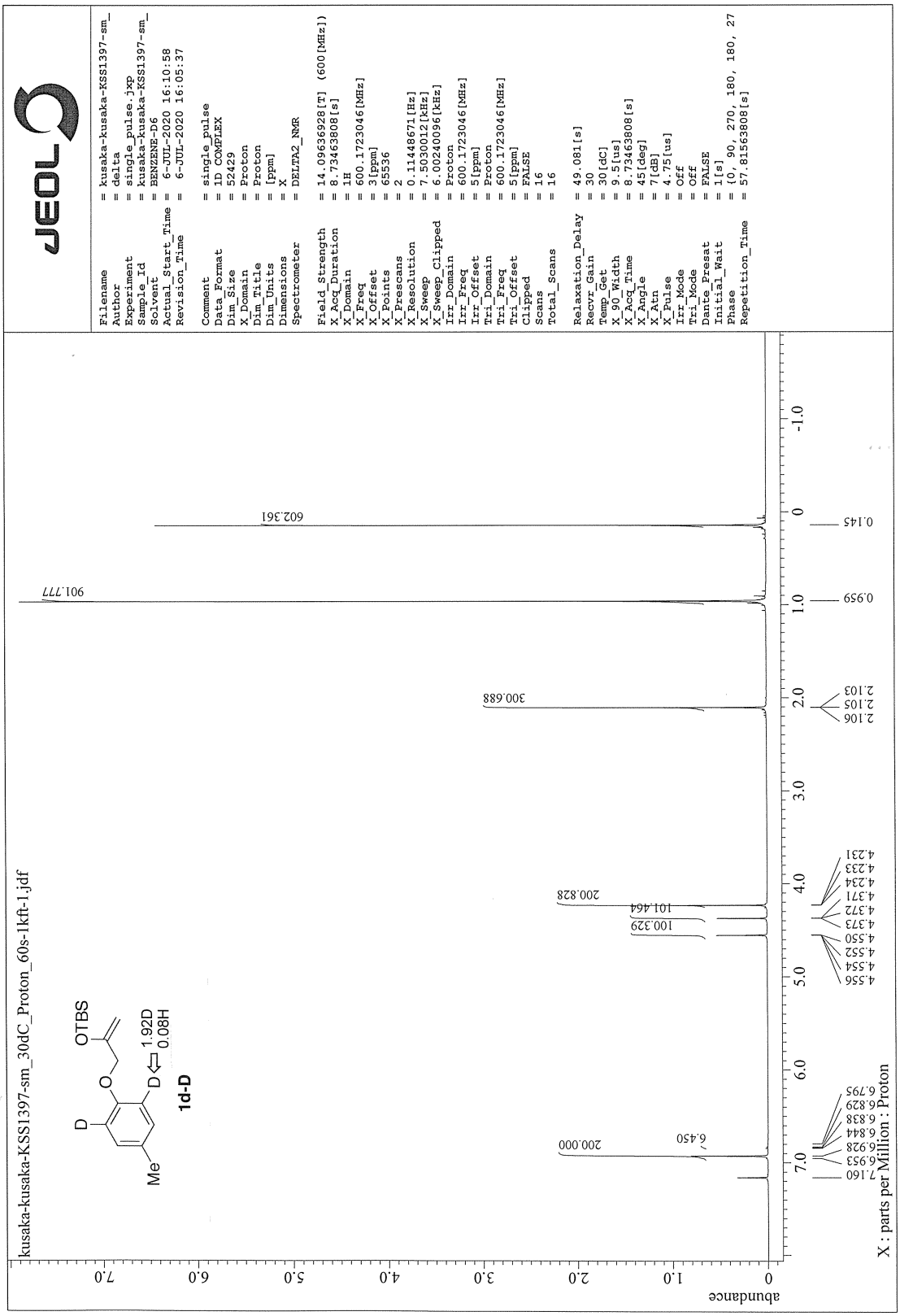


Figure S74. ^{1}H NMR Spectrum of **1d-D** (600 MHz, C_6D_6)

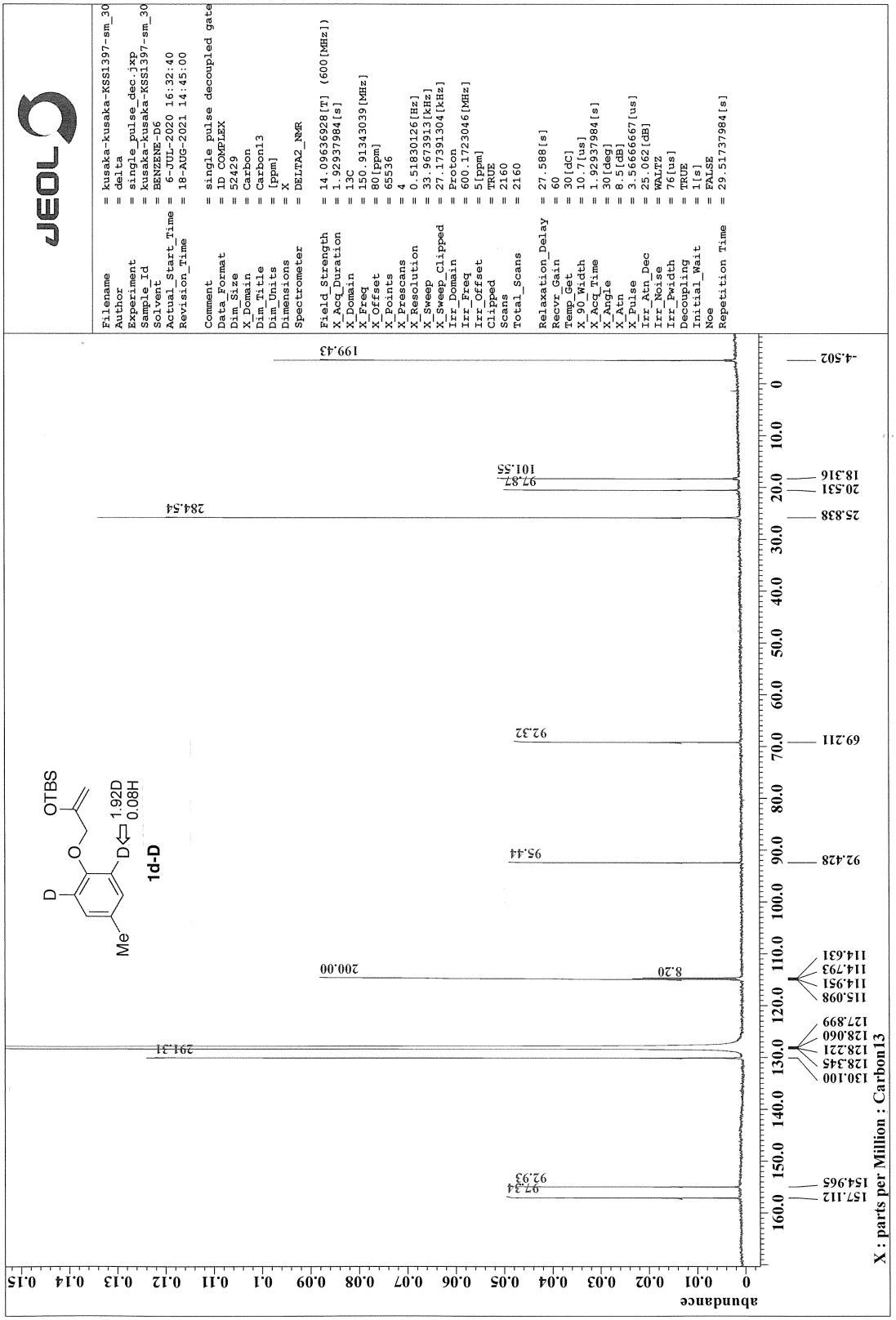


Figure S75. ^{13}C NMR Spectrum of **1d-D** (151 MHz, C_6D_6, inverse gated ^{1}H decoupling)