

Supplementary Material

Synthesis of Fluorinated Aromatic Compounds by One-pot Benzyne Generation/Nucleophilic Fluorination

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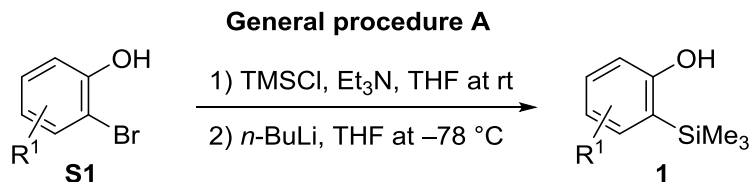
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General considerations:

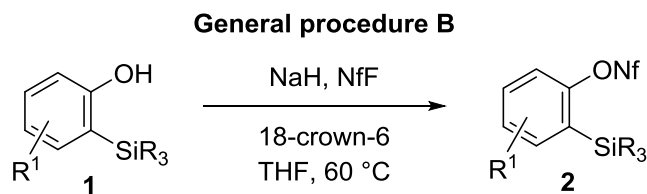
Reagents: All reactions were carried out under an argon or nitrogen atmosphere. A round-bottomed flask, a pear-shaped flask, or a test tube, each of which contained a stir-bar and was equipped with a three-way stopcock, was used as a reactor. 1.6 M and 2.6 M *n*-BuLi in hexane and 1.0 M *s*-BuLi in *n*-hexane was purchased from Kanto Chemical Co. Anhydrous THF, MeCN, CH₂Cl₂ and diethyl ether (Et₂O) were obtained from Wako Pure Chemical or Kanto Chemical Co Industries and used without further purification. 18-Crown-6 was purified by recrystallization from MeCN. Bu₄NF(*t*-BuOH)₄^[1], 4,5-dimethoxy-2-(trimethylsilyl)phenol (**1a**)^[2] and 2-(*t*-butyldimethylsilyl)-4-(1,3-dioxolan-2-yl)-6-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (**2f**)^[3] were prepared according to the literature. All other reagents were purchased from Wako Pure Chemical Industries, Tokyo Chemical Industry Co., Aldrich Chemical Co., and Kishida Chemical Co. and used without further purification. Flash chromatography^[4] was performed with Silica gel 60N, spherical neutral (40–50 μm) purchased from Kanto Chemical Co.

Analytical methods: Melting points were recorded on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were obtained on a JASCO WS/IR-8000 or a SHIMADZU FTIR-8400S. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL JMN-ECA-500 (¹H: 500 MHz, ¹³C: 125 MHz, ¹⁹F: 470 MHz) or a JEOL JMN-ECS-400 (¹H: 400 MHz, ¹³C: 100 MHz, ¹⁹F: 376 MHz) or a JEOL AL-300 (¹H: 300 MHz, ¹³C: 75 MHz) instrument with chemical shifts reported in ppm relative to the residual deuterated solvent. GC spectra were taken on SHIMADZU GC-2010. The mass spectra were recorded on a Bruker micrOTOF-Q (ESI) or a JEOL JMS-S3000 (MALDI), or a JEOL JMS-700 (FAB) spectrometer or a JMS-T100TD (APCI) spectrometer. Yield refers to isolated yields of compounds greater than 95% purity as determined by ¹H NMR analysis. ¹H NMR and melting points (where applicable) of all known compounds were taken. All new products were further characterized by high resolution mass spectrum (HRMS).

Synthesis of benzyne precursor 1 and 2:

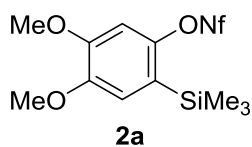


General procedure A for synthesis of 2-(trimethylsilyl)phenol 1 (Table 3).^[2] An oven dried flask was charged with 2-bromophenol derivative **S1** (1.0 equiv) and capped with an inlet adapter with a 3-way stopcock and then evacuated and back-filled with argon. Anhydrous THF (0.10–0.50 M), Et₃N (1.5 equiv) and TMSCl (1.5 equiv) were added via syringes and the reaction mixture was stirred for a few hours at room temperature. The reaction mixture was concentrated under reduced pressure. *n*-Hexane was added to the residue and filtrated through celite cake and washed with *n*-hexane. The solution was evaporated to give 2-bromophenyl trimethylsilyl ether. Without purification of the obtained material, anhydrous THF (0.10–0.33 M) was added to the flask and the mixture was cooled to –78 °C. *n*-BuLi (1.6 M *n*-hexane solution, 1.2 equiv) was added dropwise at –78 °C and the reaction was allowed to warm up to room temperature and stirred for several hours. To the reaction mixture was added a saturated aqueous solution of NH₄Cl for quenching. The mixture was extracted with EtOAc (this process was repeated three times) and combined organic phase was dried over anhydrous Na₂SO₄. The organic phase was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc) to provide 2-(trimethylsilyl)phenol **1**.

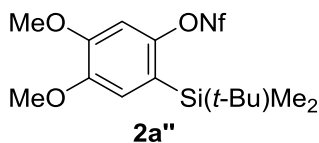


General procedure B for synthesis of 2-(trialkylsilyl)phenyl nonafluorobutanesulfonate 2 (Table 2). An oven dried flask was charged with 2-(trialkylsilyl)phenol **1**^[2] (1.0 equiv), 18-crown-6 (1.0 equiv) and capped with rubber septum, and then evacuated and back-filled with argon. Anhydrous THF (0.10 M) and NaH (60% in mineral oil, 1.5 equiv) was added into the flask, and the reaction mixture was stirred for a few minutes. NfF (1.5 equiv) was added via a syringe, and the

resulting mixture was stirred at 60 °C. After the reaction completed, water was added into the reaction mixture. The mixture was extracted with hexane (this process was repeated three times), and the combined organic phase was dried over anhydrous Na₂SO₄. The organic phase was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc) to afford 2-(trialkylsilyl)phenyl nonafluorobutane sulfonate **2**.



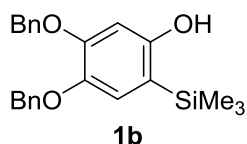
4,5-Dimethoxy-2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (2a) (**Table 1**): Following general procedure B, a mixture of 4,5-dimethoxy-2-(trimethylsilyl)phenol (**1a**)^[2] (0.50 g, 2.2 mmol), NaH (60% in mineral oil, 0.13 g, 3.3 mmol), 18-crown-6 (0.58 g, 2.2 mmol) and NfF (0.77 mL, 4.4 mmol) was stirred in THF (22 mL, 0.1 M) at 60 °C for 1 h. The titled compound **2a** was obtained as a colorless oil (1.0 g, 91%). Rf: 0.2 (hexane/EtOAc = 5:1). ¹H NMR (500 MHz, CDCl₃) δ: 0.36 (9 H, s), 3.88 (3 H, s), 3.90 (3 H, s), 6.84 (1 H, s), 6.90 (1 H, s). ¹³C NMR (125 MHz, CDCl₃) δ: -0.8, 56.0, 56.1, 104.4, 107.2–118.8 (4 C, m), 116.5, 123.1, 147.9, 148.5, 150.6. ¹⁹F NMR (376 MHz, CDCl₃) δ: -125.94–(-125.63) (m), -121.00–(-120.74) (m), -109.92–(-109.67) (m), -80.83–(-80.51) (m). IR (neat): 1603, 1509, 1422 cm⁻¹. HRMS (FAB, NBA): *m/z* calcd for C₁₅H₁₇F₉O₅SSi [M]⁺: 508.0417, found: 508.0414.



2-(*t*-Butyldimethylsilyl)-4,5-dimethoxyphenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (2a'') (**Table 2, entry 1**): An oven dried recovery flask (100 mL) was charged with *t*-butyldimethylsilyl 2-bromo-4,5-dimethoxyphenyl ether^[5] (3.6 g, 10 mmol) and capped with an inlet adapter with a 3-way stopcock and then evacuated and back-filled with argon. Anhydrous THF (35 mL, 0.30 M) was added via syringes and cooled down to -78 °C. *n*-BuLi (1.6 M *n*-hexane solution, 8.5 mL, 13 mmol) was added dropwise at -78 °C and the reaction was allowed to warm up to room

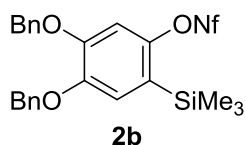
temperature. To the reaction mixture was added a saturated aqueous solution of NH_4Cl for quenching. The mixture was extracted with EtOAc (this process was repeated three times) and combined organic phase was dried over anhydrous Na_2SO_4 . The organic phase was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to provide 2-(*t*-butyldimethylsilyl)-4,5-dimethoxyphenol (**1a''**) as a light brown solid (2.3 g, 83%). Rf: 0.3 (hexane/EtOAc = 10:1). Mp: 120–122 °C. ^1H NMR (400 MHz, CDCl_3) δ : 0.32 (6 H, s), 0.90 (9 H, s), 3.83 (3 H, s), 3.84 (3 H, s), 6.35 (1 H, s), 6.78 (1 H, s). ^{13}C NMR (100 MHz, CDCl_3) δ : -4.7, 17.7, 26.7, 55.7, 56.8, 100.3, 111.8, 119.2, 142.7, 151.1, 155.5. IR (neat): 3457, 1600, 1517 cm^{-1} . HRMS (FAB, NBA): m/z calcd for $\text{C}_{14}\text{H}_{24}\text{NaO}_3\text{Si}$ [$\text{M}+\text{Na}$] $^+$: 291.1387, found: 291.1400.

Following general procedure B, a mixture of 2-(*t*-butyldimethylsilyl)-4,5-dimethoxyphenol (**1a''**) (0.53 g, 2.0 mmol), NaH (60% in mineral oil, 0.24 g, 6.0 mmol), 18-crown-6 (0.53 g, 2.0 mmol) and NfF (1.5 mL, 6.0 mmol) was stirred in THF (6.6 mL, 0.30 M) at 60 °C for 19 h. The crude reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to provide the titled compound **2a''** as a colorless oil (0.92 g, 85%). Rf: 0.4 (hexane/EtOAc = 6:1). ^1H NMR (400 MHz, CDCl_3) δ : 0.37 (6 H, s), 0.89 (9 H, s), 3.88 (6 H, s), 6.88 (1 H, s), 6.89 (1 H, s). ^{13}C NMR (100 MHz, CDCl_3) δ : -4.7, 17.6, 26.5, 55.9, 56.1, 103.9, 106.9–119.7 (4 C, m), 117.8, 120.0, 147.4, 149.2, 150.5. ^{19}F NMR (376 MHz, CDCl_3) δ : -125.82–(-125.64) (m), -120.00–(-120.85) (m), -109.80–(-109.63) (m), -80.76–(-80.54) (m). IR (neat): 1602, 1505, 1418 cm^{-1} . HRMS (FAB, NBA): m/z calcd for $\text{C}_{18}\text{H}_{23}\text{FO}_5\text{SSi}$ [$\text{M}+\text{H}$] $^+$: 551.0965, found: 551.0964.

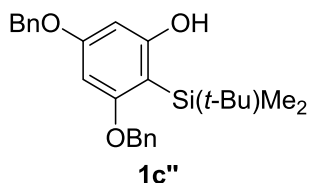


4,5-Dibenzyloxy-2-(Trimethylsilyl)phenol (1b) (Table 3, entry 2): Following general procedure A, a mixture of 2-bromo-4,5-dibenzyloxyphenol^[6] (6.0 g, 17 mmol), Et_3N (0.67 mL, 4.8 mmol), TMSCl (0.41 mL, 4.8 mmol) was stirred in anhydrous THF (10 mL, 0.30 M) for 1 h at room temperature. To the obtained 2-bromophenyl trimethylsilyl ether were added THF (10 mL, 0.33 M) and *n*-BuLi (1.6 M *n*-hexane solution, 2.4 mL, 3.8 mmol), and stirred for 0.5 h at room temperature. The crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 2:1)

to give the titled compound **1b** as a brown oil (0.60 g, 66%). Rf: 0.6 (hexane/EtOAc = 2:1). ¹H NMR (300 MHz, CDCl₃) δ: 0.26 (9 H, s), 5.07 (2 H, s), 5.08 (2 H, s), 6.34 (1 H, s), 6.93 (1 H, s), 7.29–7.43 (10 H, m). ¹³C NMR (75 MHz, CDCl₃) δ: –0.9, 70.8, 73.3, 102.5, 116.1, 123.7, 127.2, 127.7, 127.8, 128.3, 128.5, 136.9, 137.7, 142.3, 151.4, 155.8. IR (neat): 1643, 1510, 1398 cm⁻¹. HRMS (FAB, NBA): *m/z* calcd for C₂₃H₂₆O₃Si [M+H]⁺: 379.1724, found: 379.1705.



4,5-Dibenzyloxy-2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (2b) (Table 2, entry 2): Following general procedure B, a mixture of 4,5-dibenzyloxy-2-(trimethylsilyl)phenol (**1b**) (0.74 g, 8.0 mmol), NaH (60% in mineral oil, 0.48 g, 12 mmol), 18-crown-6 (0.52 g, 8.0 mmol) and NfF (0.50 mL, 12 mmol) was stirred in THF (20 mL, 0.10 M) at 60 °C for 10 h. The crude reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 20:1) to provide the titled compound **2b** as a colorless oil (0.26 g, 97%). Rf: 0.6 (hexane/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃) δ: 0.29 (9 H, s), 5.18 (4 H, s), 6.89 (1 H, s), 6.95 (1 H, s), 7.31–7.46 (10 H, m). ¹³C NMR (100 MHz, CDCl₃) δ: –0.8, 71.3, 71.8, 107.2, 108.3–118.5 (4 C, m), 120.9, 123.8, 127.2, 127.4, 128.0, 128.1, 128.58, 128.63, 136.1, 136.8, 147.5, 148.8, 150.5. ¹⁹F NMR (376 MHz, CDCl₃) δ: –125.75–(–125.60) (m), –120.89–(–120.77) (m), –109.78–(–109.63) (m), –80.57–(–80.49) (m). IR (neat): 1601, 1505, 1422 cm⁻¹. HRMS (FAB, NBA): *m/z* calcd for C₂₇H₂₅F₉NaO₅SSi [M+Na]⁺: 683.0940, found: 683.0953.



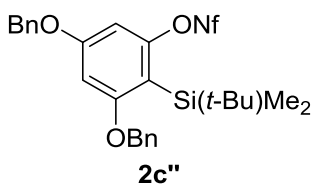
3,5-Bis(benzyloxy)-2-(t-butyl dimethylsilyl)phenol (1c'') (Table 3, entry 4): 1,3,5-Tris(benzyloxy)benzene (3.5 g, 8.7 mmol), 10% Pd/C (0.35 g, 10 wt%), MeOH (26 mL) and EtOAc (260 mL) were loaded into the flask and evacuated and back-filled with H₂ (This process was

repeated three times). The mixture was stirred at room temperature for 3.5 h with H₂ balloon. The reaction mixture was filtered through Celite cake using EtOAc and the filtrate was concentrated under reduced pressure. The residue was purified by the column chromatography on silica gel (hexane/EtOAc = 4:1) to provide 3,5-bis(benzyloxy)phenol^[7] (1.1 g, 40%). ¹H NMR (400 MHz, CDCl₃) δ: 4.98 (4 H, s), 6.10 (2 H, d, *J* = 2.0 Hz), 6.24 (1 H, d, *J* = 2.0 Hz), 7.30–7.41 (10 H, m). ¹³C NMR (100 MHz, CDCl₃) δ: 70.2, 95.0, 95.5, 127.6, 128.1, 128.7, 136.8, 157.3, 16.9.

An oven dried flask was charged with 3,5-bis(benzyloxy)phenol (1.1 g, 3.5 mmol) and NBS (0.63 g, 3.5 mmol), and evacuated and back-filled with N₂. CH₂Cl₂ (35 mL) was added to the reaction flask and stirred at –78 °C for 2 h. A saturated solution of NaHCO₃ was added to the mixture and the reaction was allowed to warm up to room temperature. The mixture was extracted with CH₂Cl₂ (this process was repeated three times) and combined organic phase was dried over anhydrous Na₂SO₄. The organic phase was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 4:1) to provide 3,5-bis(benzyloxy)-2-bromophenol^[7] (1.1 g, 83%). Mp: 90–92 °C. ¹H NMR (400 MHz, CDCl₃) δ: 4.98 (2 H, s), 5.07 (2 H, s), 5.67 (OH, s), 6.24 (1 H, d, *J* = 2.5 Hz), 6.35 (1 H, d, *J* = 2.5 Hz), 7.36–7.43 (10 H, m). ¹³C NMR (100 MHz, CDCl₃) δ: 70.4, 70.9, 92.1, 94.7, 94.8, 127.1, 127.7, 128.1, 128.3, 128.7, 128.8, 136.4, 136.5, 154.0, 156.0, 159.8.

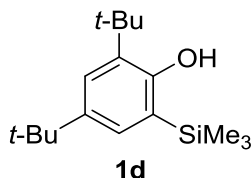
An oven dried flask was charged with 3,5-bis(benzyloxy)-2-bromophenol (1.1 g, 2.9 mmol), TBDMSCl (0.66 g, 4.5 mmol) and imidazole (0.31 g, 4.5 mmol) and evacuated and back-filled with N₂. DMF (30 mL, 0.10 M) was added to the reaction flask and stirred at room temperature for 9 h. A saturated solution of NaHCO₃ was added to the mixture. The mixture was evaporated under reduced mixture. The mixture was extracted with hexane (this process was repeated three times) and combined organic phase was dried over anhydrous Na₂SO₄. The organic phase was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to provide 3,5-bis(benzyloxy)-2-bromophenyl *t*-butyldimethylsilyl ether as a colorless solid (1.4 g, 95%). Rf: 0.5 (hexane/EtOAc = 10:1). Mp: 82–84 °C. ¹H NMR (400 MHz, CDCl₃) δ: 0.19 (6 H, s), 1.02 (9 H, s), 4.97 (2 H, s), 5.09 (2 H, s), 6.15 (1 H, d, *J* = 2.5 Hz), 6.28 (1 H, d, *J* = 2.5 Hz), 7.31–7.46 (10H, m). ¹³C NMR (100 MHz, CDCl₃) δ: –4.1, 18.5, 25.9, 70.4, 70.9, 95.5, 97.4, 100.0, 127.1, 127.5, 127.9, 128.2, 128.6, 128.8, 136.6, 136.7, 154.3, 156.8, 158.9. IR (neat): 1583, 1431 cm⁻¹. HRMS (APCI): *m/z* calcd for C₂₆H₃₁BrO₃Si [M+H]⁺ 499.1299, found: 499.1325.

An oven dried recovery flask (100 mL) was charged with 3,5-bis(benzyloxy)-2-bromophenyl *t*-butyldimethylsilyl ether (1.4 g, 2.7 mmol) and capped with an inlet adapter with a 3-way stopcock and then evacuated and back-filled with argon. Anhydrous THF (15 mL, 0.30 M) was added via a syringe and cooled down to $-78\text{ }^{\circ}\text{C}$. *n*-BuLi (1.6 M *n*-hexane solution, 1.9 mL, 3.0 mmol) was added dropwise at $-78\text{ }^{\circ}\text{C}$ and the reaction was allowed to warm up to room temperature. To the reaction mixture was added a saturated aqueous solution of NH_4Cl for quenching. The mixture was extracted with Et_2O (this process was repeated three times) and combined organic phase was dried over anhydrous Na_2SO_4 . The organic phase was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to provide 3,5-bis(benzyloxy)-2-(*t*-butyldimethylsilyl)phenol (**1c''**) as a colorless solid (0.50 g, 31%). Rf: 0.4 (hexane/EtOAc = 5:1). Mp: 77–80 $^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ : 0.09 (6 H, s), 0.98 (9 H, s), 5.07 (2 H, s), 5.11 (2 H, s), 6.44 (1 H, s), 7.08 (1 H, s), 7.29–7.44 (10 H, m). ^{13}C NMR (125 MHz, CDCl_3) δ : -4.2 , 18.4, 25.8, 70.3, 70.8, 95.4, 97.3, 99.9, 127.0, 127.4, 127.8, 128.1, 128.5, 128.6, 136.5, 136.6, 154.2, 156.7, 158.7. IR (neat): 1581, 1431 cm^{-1} . HRMS (FAB, NBA): m/z calcd for $\text{C}_{26}\text{H}_{32}\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 421.2193, found: 421.2212.

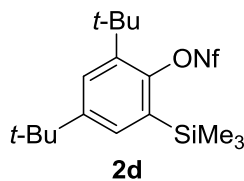


3,5-Bis(benzyloxy)-2-(*t*-butyldimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (2c''**) (Table 1):** Following general procedure B, a mixture of 3,5-bis(benzyloxy)-2-(*t*-butyldimethylsilyl)phenol (**1c''**) (0.30 g, 0.70 mmol), NaH (60% in mineral oil, 84 mg, 2.1 mmol), 18-crown-6 (0.19 g, 0.70 mmol) and NfF (0.37 mL, 2.1 mmol) was stirred in THF (7.0 mL, 0.10 M) under reflux for 14 h. Then 18-crown-6 (0.19 g, 0.70 mmol) was added and refluxed for 0.6 h. The crude reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to provide the titled compound **2c''** as a colorless oil (0.46 g, 94%). Rf: 0.6 (hexane/EtOAc = 5:1). ^1H NMR (400 MHz, CDCl_3) δ : 0.26 (6 H, s), 0.85 (9 H, s), 4.96 (2 H, s), 5.01 (2 H, s), 6.28 (1 H, d, $J = 2.0$ Hz), 6.48 (1 H, d, $J = 2.0$ Hz), 7.34–7.39 (10 H, m). ^{13}C NMR (125 MHz, CDCl_3) δ : -1.8 , 18.4, 27.0, 70.4, 71.0, 98.5, 98.7, 105.3–121.4 (4 C, m), 109.5, 127.6, 128.2, 128.3, 128.6,

128.7, 135.8, 135.9, 157.2, 161.5, 165.5. ^{19}F NMR (376 MHz, CDCl_3) δ : -125.72–(-125.57) (m), -120.96–(-120.82) (m), -109.50–(-109.23) (m), -80.64–(-80.47) (m). IR (neat): 1603, 1562, 1420 cm^{-1} . HRMS (FAB, NBA): m/z calcd for $\text{C}_{30}\text{H}_{31}\text{F}_9\text{O}_5\text{SSi}$ $[\text{M}+\text{Na}]^+$: 725.1410, found: 725.1400.

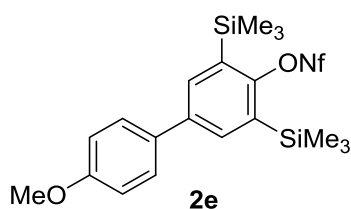


2,4-Di(*t*-butyl)-6-(trimethylsilyl)phenol (1d) (Table 3, entry 5):^[8] Following general procedure A, a mixture of 2-bromo-4,6-di(*t*-butyl)phenol^[9] (34 g, 0.12 mol), Et_3N (25 mL, 0.18 mol), TMSCl (23 mL, 0.18 mol) was stirred in anhydrous THF (250 mL, 0.50 M) for 1 h at room temperature. To the obtained 2-bromophenyl trimethylsilyl ether were added THF (500 mL, 0.30 M) and *n*-BuLi (2.6 M *n*-hexane solution, 47 mL, 0.12 mol), and stirred for 2 h at room temperature. The crude mixture was purified by flash column chromatography on silica gel (hexane) to give the titled compound **1d** as a colorless solid (33 g, 98%). Rf: 0.5 (hexane). Mp: 59–61 °C. ^1H NMR (300 MHz, CDCl_3) δ : 0.33 (9 H, s), 1.30 (9 H, s), 1.41 (9 H, s), 7.36 (1 H, d, $J = 2.5$ Hz), 7.50 (1 H, d, $J = 2.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ : -0.3, 30.2, 31.5, 34.3, 34.4, 125.1, 125.6, 129.5, 133.8, 142.3, 157.0. IR (neat): 3636, 1581, 1427 cm^{-1} . HRMS (FAB, NBA): m/z calcd for $\text{C}_{17}\text{H}_{30}\text{OSi}$ $[\text{M}]^+$: 278.2060, found: 278.2055.



2,4-Di(*t*-butyl)-6-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (2d) (Table 2, entry 4): Following general procedure B, a mixture of 2,4-di(*t*-butyl)-6-(trimethylsilyl)phenol (**1d**) (1.0 g, 3.6 mmol), NaH (60% in mineral oil, 0.21 g, 5.3 mmol), 18-crown-6 (0.95 g, 3.6 mmol) and NfF (0.95 mL, 5.4 mmol) was stirred in THF (12 mL, 0.30 M) at reflux for 16 h. The crude reaction mixture was purified by flash column chromatography on silica

gel (hexane) to provide the titled compound **2d** as a colorless solid (1.8 g, 84%). Rf: 0.7 (hexane). Mp: 57–60 °C. ¹H NMR (400 MHz, CDCl₃) δ: 0.36 (9 H, s), 1.33 (9 H, s), 1.44 (9 H, s), 7.39 (1 H, d, *J* = 3.0 Hz), 7.53 (1 H, d, *J* = 3.0 Hz). ¹³C NMR (100 MHz, CDCl₃) δ: 1.10, 31.3, 31.9, 34.6, 36.4, 103.9–123.8 (4 C, m), 128.8, 132.1, 135.6, 142.5, 145.9, 149.5. ¹⁹F NMR (470 MHz, CDCl₃) δ: –125.75–(–125.59) (m), –120.83–(–120.70) (m), –107.53–(–107.35) (m), –80.60–(–80.50) (m). IR (neat): 1581, 1478, 1394 cm⁻¹. HRMS (FAB, NBA): *m/z* calcd for C₂₁H₂₉F₉O₃SSiNa [M+Na]⁺: 583.1355, found: 583.1346.



2,6-Bis(trimethylsilyl)-4-(4-methoxyphenyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (2e) (Table 2, entry 5): Following general procedure A, a mixture of 2,4,6-triiodophenol^[6] (18 g, 38 mmol), Et₃N (7.0 mL, 50 mmol), TMSCl (7.4 mL, 58 mmol) was stirred in anhydrous THF (130 mL, 0.30 M) for 1 h at room temperature. To the obtained 2,4,6-triiodophenyl trimethylsilyl ether (20 g, 97%) were added THF (130 mL, 0.30 M) and *s*-BuLi (1.0 M *n*-hexane solution, 72 mL, 72 mmol), and stirred for 9 h at room temperature. The crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 9:1) to give 2,4-diiodo-6-(trimethylsilyl)phenol as a colorless solid (13 g, 85%). Rf: 0.7 (hexane/EtOAc = 5:1). Mp: 93–95 °C. ¹H NMR (400 MHz, CDCl₃) δ: 0.27 (9 H, s), 5.43 (OH, s), 7.50 (1 H, d, *J* = 2.0 Hz), 7.90 (1 H, d, *J* = 2.0 Hz). ¹³C NMR (100 MHz, CDCl₃) δ: –1.3, 83.8, 88.0, 129.7, 144.0, 146.1, 156.4. IR (neat): 3493, 1424, 1371 cm⁻¹. HRMS (FAB, NBA): *m/z* calcd for C₉H₁₂I₂OSi [M]⁺: 417.8741, found: 417.8766.

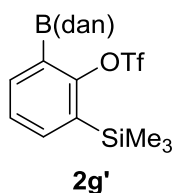
Following general procedure A, a mixture of 2,4-diiodo-6-(trimethylsilyl)phenol (13 g, 32 mmol), Et₃N (5.8 mL, 41 mmol), TMSCl (6.1 mL, 48 mmol) was stirred in anhydrous THF (110 mL, 0.30 M) for 1 h at room temperature. To the obtained 2,4-diiodo-6-(trimethylsilyl)phenyl trimethylsilyl ether (16 g, 100%) were added THF (110 mL, 0.30 M) and *s*-BuLi (1.0 M *n*-hexane solution, 61 mL, 61 mmol), and stirred for 2 h at room temperature. The crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to give 4-iodo-2,6-

bis(trimethylsilyl)phenol as a colorless solid (12 g, 99%). Rf: 0.8 (hexane/EtOAc = 10:1). Mp: 82–85 °C. ¹H NMR (400 MHz, CDCl₃) δ: 0.33 (18 H, s), 4.97 (OH, s), 7.57 (2 H, s). ¹³C NMR (100 MHz, CDCl₃) δ: –0.6, 85.5, 128.5, 144.7, 164.7. IR (neat): 3607, 1562, 1391 cm⁻¹. HRMS (FAB, NBA): *m/z* calcd for C₁₂H₂₁IOSi₂ [M]⁺: 364.0170, found: 364.0162.

Following general procedure B, a mixture of 4-iodo-2,6-bis(trimethylsilyl)phenol (1.0 g, 2.7 mmol), NaH (60% in mineral oil, 0.18 g, 4.5 mmol), 18-crown-6 (0.43 g, 2.7 mmol) and NfF (0.73 mL, 4.1 mmol) was stirred in THF (15 mL, 0.20 M) at reflux for 5 h. The crude reaction mixture was purified by flash column chromatography on silica gel (hexane) to provide 2,6-bis(trimethylsilyl)-4-iodophenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate as a colorless solid (0.26 g, 86%). Rf: 0.8 (hexane). Mp: 57–59 °C. ¹H NMR (400 MHz, CDCl₃) δ: 0.34 (18 H, s), 7.80 (2 H, s). ¹³C NMR (100 MHz, CDCl₃) δ: 0.3, 95.5, 109.8–18.3 (4C, m), 138.8, 146.7, 154.8. ¹⁹F NMR (470 MHz, CDCl₃) δ: –125.83–(–125.68) (m), –120.83–(–120.68) (m), –107.47–(–107.27) (m), –80.70–(–80.57) (m). IR (neat): 1402, 1352 cm⁻¹. HRMS (FAB, NBA): *m/z* calcd for C₁₆H₂₀F₉IO₃SSi₂Na [M+Na]⁺: 668.9465, found: 669.9484.

An oven dried flask was charged with 2,6-bis(trimethylsilyl)-4-iodophenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (0.13 g, 0.20 mmol), 4-methoxyphenyl boronic acid (30 mg, 0.20 mmol), 2 M Na₂CO₃ (0.40 mL, 0.80 mmol) and THF (2.0 mL, 0.10 M), and evacuated and back-filled with Ar. PdCl₂(dppf) (15 mg, 20 μmol) was added to the flask and stirred at 50 °C for 5 h. 1 M HCl solution was added to the reaction mixture. The mixture was extracted with hexane (this process was repeated three times) and combined organic phase was washed with brine and dried over anhydrous Na₂SO₄. The organic phase was filtered and concentrated under reduced pressure to afford a mixture of aryl iodide and **2e** (34:66). To the residue were added 4-methoxyphenyl boronic acid (15 mg, 0.25 mmol), 2 M Na₂CO₃ (0.34 L, 0.80 mmol) and PdCl₂(dppf) (15 mg, 20 μmol), and the flask was evacuated and back-filled with Ar. THF (2.0 mL, 0.10 M) was added to the flask via a syringe. After stirring at 50 °C for 12 h, 1 M HCl solution was added to the reaction mixture. The mixture was extracted with hexane (this process was repeated three times) and combined organic phase was washed with brine and dried over anhydrous Na₂SO₄. The organic phase was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane → hexane/CH₂Cl₂ = 8:1) to provide 2,6-bis(trimethylsilyl)-4-(4-methoxyphenyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (**2e**) as a yellow solid (97 mg, 77%). Rf: 0.6 (hexane). Mp: 110–111 °C. ¹H NMR (500 MHz, CDCl₃) δ: 0.36 (18 H, s), 3.84 (3 H,

s), 6.98 (2 H, d, $J = 8.5$ Hz), 7.45 (2 H, d, $J = 8.5$ Hz), 7.65 (2 H, s). ^{13}C NMR (100 MHz, CDCl_3) δ : 0.43, 55.4, 108.3–118.5 (4 C, m), 114.4, 128.4, 132.5, 135.2, 136.6, 139.7, 154.2, 159.5. ^{19}F NMR (470 MHz, CDCl_3) δ : -125.70–(-125.55) (m), -120.77–(-120.63) (m), -107.57–(-107.40) (m), -80.54–(-80.45) (m). IR (neat): 1612, 1513, 1400 cm^{-1} . HRMS (FAB, NBA): m/z calcd for $\text{C}_{23}\text{H}_{27}\text{F}_9\text{NaO}_4\text{SSi}_2$ $[\text{M}+\text{Na}]^+$: 649.0917, found: 649.0912.



2-(1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-6-(trimethylsilyl)phenyl

trifluoromethanesulfonate (2g') (Table 2, entry 8):^[10] An oven-dried round-bottomed flask was charged with 2,6-dibromophenol (10 g, 40 mmol), capped with an inlet adapter with a three-way stopcock, evacuated and back-filled with nitrogen. Anhydrous CH_2Cl_2 (100 mL) was added. Then the mixture was cooled to 0 °C. Triethylamine (6.7 mL, 48 mmol) and chlorotrimethylsilane (5.6 mL, 44 mmol) were added. The reaction mixture was stirred for 7.5 h at room temperature, and CH_2Cl_2 was evaporated. The residue was diluted with hexane, and the mixture was filtered with a pad of Celite and concentrated under reduced pressure to give (2,6-dibromophenoxy)trimethylsilane (13 g), which was used for the next reaction without further purification.

An oven-dried round-bottomed flask was charged with (2,6-dibromophenoxy)trimethylsilane (13 g), capped with an inlet adapter with a three-way stopcock, evacuated and back-filled with argon. Anhydrous THF (130 mL) was added. Then the mixture was cooled to -78 °C. 1.7 M solution of *t*-BuLi (0.10 L, 0.17 mol) in pentane was added. After 1 h at the same temperature, trimethoxyborane (20 mL, 0.18 mol) was added. The mixture was warmed up to room temperature and stirred for 20 h. A saturated aqueous NH_4Cl solution was added to the reaction mixture. After evaporation of the organic solvents under reduced pressure, the residue was extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give (2-hydroxy-3-(trimethylsilyl)phenyl)boronic acid (12 g), which was used for the next reaction without further purification.

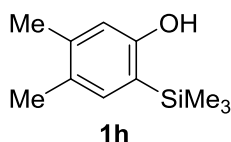
A round-bottomed flask was charged with (2-hydroxy-3-(trimethylsilyl)phenyl)boronic acid (11 g), pinacol (4.3 g, 36 mmol) and CH₂Cl₂ (50 mL). The reaction mixture was stirred overnight and H₂O was added. The reaction mixture was extracted with CH₂Cl₂. The aqueous layer was extracted twice with CH₂Cl₂. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to give 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenol (10 g), which was used for the next reaction without further purification.

An oven-dried round-bottomed flask was charged with 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenol (9.5 g), capped with an inlet adapter with a three-way stopcock, evacuated and back-filled with nitrogen. Anhydrous Et₂O (100 mL) was added. Then the mixture was cooled to -78 °C. 1.7 M *t*-BuLi (20 mL, 34 mmol) was added. After 10 min at the same temperature, trifluoromethanesulfonic anhydride (8.0 mL, 48 mmol) was added. The reaction mixture was warmed up to room temperature and stirred for 2 h at room temperature. Aqueous NH₄Cl was added, and the reaction mixture was extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was filtered through a pad of silica gel (hexane/EtOAc = 10:1) to give 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (9.1 g), which was used for the next reaction without further purification. Rf: 0.5 (hexane/EtOAc = 10:1).

A round-bottomed flask was filled with 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (8.0 g), NaIO₄ (12 g, 57 mmol) and THF/H₂O (4:1, 94 mL). The reaction mixture was stirred for 5 min at room temperature, and 1 M HCl (19 mL, 19 mmol) was added. The reaction mixture was stirred for 10 h at 60 °C, cooled to room temperature, quenched with H₂O and extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was added to a solution of NaIO₄ (12 g, 57 mmol) in THF/H₂O (4:1, 94 mL), and the reaction mixture was stirred for 5 min at room temperature. 1 M HCl (19 mL, 19 mmol) was added. The reaction mixture was stirred for 6 h at 60 °C, cooled to room temperature, quenched with H₂O and extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give

(2-((trifluoromethanesulfonyl)oxy)-3-(trimethylsilyl)phenyl)boronic acid (7.7 g), which was used for the next reaction without further purification.

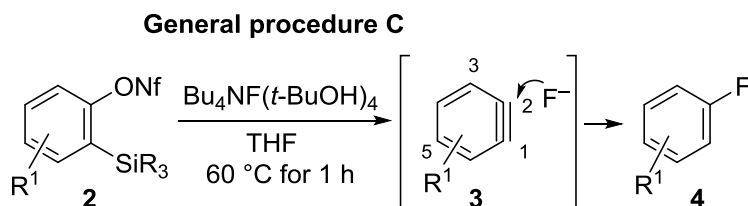
A round-bottomed flask was charged with (2-((trifluoromethanesulfonyl)oxy)-3-(trimethylsilyl)phenyl)boronic acid (7.7 g) and 1,8-diaminonaphthalene (3.0 g, 19 mmol) and CH₂Cl₂ (100 mL). The reaction mixture was stirred for 13 h at room temperature, and H₂O was added. The reaction mixture was extracted with CH₂Cl₂. The aqueous layer was extracted twice with CH₂Cl₂. The combined organic layers were washed with a saturated aqueous NaCl solution, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc = 12:1) to provide the titled compound **2g'** (6.9 g, 37% over 6 steps) as a brown solid. Rf: 0.4 (hexane/EtOAc = 10:1). Mp: 104–105 °C. ¹H NMR (500 MHz, CDCl₃) δ: 0.43 (9 H, s), 5.94 (2 NH, brs), 6.38 (2 H, d, *J* = 7.5 Hz), 7.08 (2 H, d, *J* = 7.5 Hz), 7.14 (2 H, t, *J* = 7.5 Hz), 7.44 (1 H, dd, *J* = 7.0, 7.0 Hz), 7.63 (1 H, dd, *J* = 2.0, 7.0 Hz), 7.67 (1 H, dd, *J* = 2.0, 7.0 Hz). ¹³C NMR (125 MHz, CDCl₃) δ: 0.07, 106.1, 118.1, 118.4 (q, *J* = 320 Hz), 119.8, 127.6, 127.9, 135.0, 135.5, 136.3, 138.5, 140.6, 154.7 (A carbon bearing the boron substituent could not be observed in ¹³C NMR due to quadrupolar relaxation).^[11] ¹⁹F NMR (470 MHz, CDCl₃) δ: -73.22 (s). IR (neat): 3344 cm⁻¹. HRMS (ESI): *m/z* calcd for C₂₀H₂₁BF₃N₂O₃SSi [M + H]⁺: 465.1082, found: 465.1093.



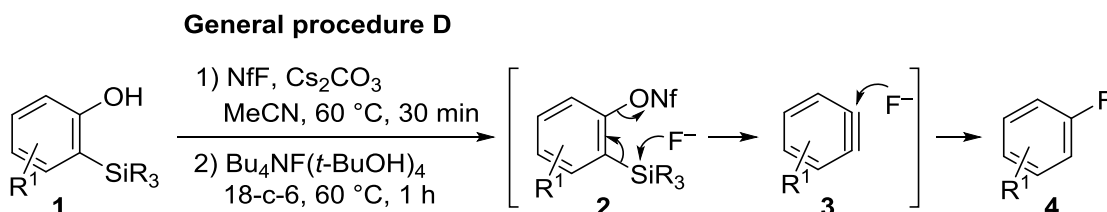
4,5-Dimethyl-2-(trimethylsilyl)phenol (1h) (Table 3, entry 3): Following general procedure A, a mixture of 4,5-dimethyl-2-bromophenol (0.26 g, 1.3 mmol), Et₃N (0.24 mL, 1.7 mmol), TMSCl (1.7 mL, 20 mmol) was stirred in anhydrous THF (4.3 mL, 0.30 M) for 1 h at room temperature. To the obtained 2-bromophenyl trimethylsilyl ether were added THF (4.3 mL, 0.30 M) and *n*-BuLi (1.6 M *n*-hexane solution, 0.98 mL, 1.6 mmol), and stirred for 1 h at room temperature. The crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to give the titled compound **1h** as a colorless oil (0.23 g, 90%). Rf: 0.5 (hexane). ¹H NMR (400 MHz, CDCl₃) δ: 0.27 (9 H, s), 2.15 (6 H, s), 6.65 (1 H, s), 7.25 (1 H, s). ¹³C NMR (100 MHz, CDCl₃) δ: 0.4, 18.7, 19.6,

111.7, 122.0, 131.1, 133.6, 136.8, 150.0. IR (neat): 3489, 1495 cm^{-1} . HRMS (MALDI): m/z calcd for $\text{C}_{11}\text{H}_{19}\text{OSi} [\text{M} + \text{H}]^+$: 192.1200, found: 192.1210.

Nucleophilic fluorination of benzyne 3 generated from 1 and 2:

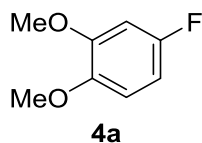


General procedure C for nucleophilic fluorination of benzyne 3 generated from 2-(trialkylsilyl)phenyl nonafluorobutanesulfonate 2 (Table 2). A flame-dried flask was charged with 2-(trialkylsilyl)phenyl nonafluorobutanesulfonate **2** (1.0 equiv) and a stir bar, capped with a rubber septum, and evacuated and back-filled with nitrogen. Anhydrous THF (0.050 M) was added by a syringe, and the mixture was heated to 60 °C. $\text{Bu}_4\text{NF}(t\text{-BuOH})_4$ (2.2 equiv) was quickly added by opening the septum. After stirring at 60 °C for 1 h, the reaction mixture was cooled down, and then passed through a short pad of silica gel using EtOAc as the solvent. The eluent was added to hexane and water, and the aqueous phase was extracted twice with hexane. The combined organic phase was washed with a saturated aqueous NaCl solution. The organic phase was dried over anhydrous Na_2SO_4 , and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (hexane, a mixture of hexane and EtOAc, or CH_2Cl_2) to afford fluorinated product **4**.



General procedure D for one-pot nucleophilic fluorination of benzyne 3 generated from 2-(trimethylsilyl)phenol 1 (Table 3). A flask was charged with Cs_2CO_3 (1.5 equiv) and a stir bar, capped with a rubber septum, and dried over a flame under reduced pressure. After cooling, the flask was charged with 2-(trialkylsilyl)phenol **1** (1.0 equiv), and the mixture was evacuated and back-filled with nitrogen. Anhydrous MeCN (0.10 M) and NfF (1.5 equiv) were sequentially added through the septum by a syringe. After the mixture was stirred at 60 °C for 30 min, $\text{Bu}_4\text{NF}(t\text{-BuOH})_4$ (1.0 equiv) and 18-crown-6 (0.60 equiv) were quickly added by opening the septum. The resealed

flask was heated at 60 °C for 1 h. The same work up and purification procedures as mentioned in the general procedure C for Table 2 afforded fluorinated product **4**.

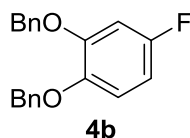


4-Fluoro-1,2-dimethoxybenzene (4a) (Table 1, entry 12, Table 2, entry 1 and Table 3, entry 1).^[12]

For Table 1, entry 12: Following the general procedure C, a mixture of **2a** (72 mg, 0.12 mmol), Bu₄NF(*t*-BuOH)₄ (0.16 g, 0.27 mmol) in THF (2.5 mL, 0.050 M) was stirred for 1 h at 60 °C. *n*-Decane (24 μL, 0.12 mmol) was added to the reaction mixture and dilute with EtOAc (ca. 2 mL). A part of the mixture was filtered through a silica gel pad and checked by GC. The crude product was purified by flash column chromatography (hexane/Et₂O = 1:1) to provide **4a** (12 mg, 64%) as a colorless oil. Rf: 0.6 (hexane/Et₂O = 6:1). ¹H NMR (500 MHz, CDCl₃) δ: 3.85 (s, 3 H), 3.86 (s, 3 H), 6.56–6.66 (2 H, m), 6.78 (1 H, dd, *J* = 5.5 and 9.0 Hz).

For Table 2, entry 1: Following the general procedure C, a mixture of **2a** (55 mg, 0.10 mmol), Bu₄NF(*t*-BuOH)₄ (0.12 g, 0.22 mmol) in THF (1.0 mL, 0.10 M) was stirred for 1 h at 60 °C. *n*-Decane (20 μL, 0.10 mmol) was added to the reaction mixture and dilute with EtOAc (ca. 2 mL). A part of the mixture was filtered through a silica gel pad and checked by GC.

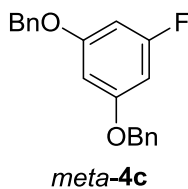
For Table 3, entry 1: Following the general procedure D, a mixture of **1a** (50 mg, 0.22 mmol), NfF (58 μL, 0.33 mmol), Cs₂CO₃ (0.11 g, 0.33 mmol), Bu₄NF(*t*-BuOH)₄ (0.15 g, 0.27 mmol), 18-crown-6 (34 mg, 0.13 mmol) in MeCN (2.2 mL, 0.10 M) was stirred for 1 h at 60 °C. *n*-Decane (45 μL, 0.22 mmol) was added to the reaction mixture and dilute with EtOAc (ca. 2 mL). A part of the mixture was filtered through a silica gel pad and checked by GC.



1,2-Dibenzyloxy-4-fluorobenzene (4b) (Table 2, entry 2 and Table 3, entry 2).

For Table 2, entry 2: Following the general procedure C, a mixture of **2b** (0.13 g, 0.19 mmol), Bu₄NF(*t*-BuOH)₄ (0.23 g, 0.42 mmol) in THF (4.0 mL, 0.050 M) was stirred for 1 h at 60 °C. *n*-Decane (38 μL, 0.19 mmol) was added to the reaction mixture and dilute with EtOAc (ca. 2 mL). A part of the mixture was filtered through a silica gel pad and checked by GC (72% GC yield). The crude product was purified by flash column chromatography (hexane/Et₂O = 10:1) to provide **4b** (38 mg, 67%) as a colorless solid. Rf: 0.5 (hexane/EtOAc = 10:1). Mp: 57–60 °C. ¹H NMR (300 MHz, CDCl₃) δ: 5.12 (2 H, s), 5.14 (2 H, s), 6.58 (1 H, ddd, *J* = 2.5, 8.5, 8.5 Hz), 6.72 (1 H, dd, *J* = 2.5, 8.5 Hz), 6.88 (1 H, dd, *J* = 5.5, 8.5 Hz), 7.30–7.48 (10 H, m). ¹³C NMR (75 MHz, CDCl₃) δ: 71.3, 72.4, 103.5 (d, *J* = 26.5 Hz), 106.9 (d, *J* = 22.5 Hz), 116.6 (d, *J* = 10.0 Hz) 127.4, 127.6, 128.0, 128.1, 128.6, 128.7, 136.7, 137.4, 145.1 (d, *J* = 3.0 Hz), 150.2 (d, *J* = 10.0 Hz), 157.9 (d, *J* = 240.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ: –119.51–(–119.40) (m). IR (neat): 1609, 1504 cm^{–1}. HRMS (MALDI): *m/z* calcd for C₂₀H₁₇FO₂ [M]⁺: 308.1207, found: 308.1207.

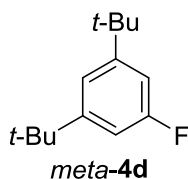
For Table 3, entry 2: Following the general procedure D, a mixture of **1b** (83 mg, 0.22 mmol), NfF (58 μL, 0.33 mmol), Cs₂CO₃ (0.11 g, 0.33 mmol), Bu₄NF(*t*-BuOH)₄ (0.15 g, 0.27 mmol), 18-crown-6 (34 mg, 0.13 mmol) in MeCN (2.2 mL, 0.10 M) was stirred for 1 h at 60 °C. The crude product was purified by flash column chromatography (hexane/EtOAc = 10:1) to provide **4b** (42 mg, 62%) as a colorless solid.



1,3-Dibenzyloxy-5-fluorobenzene (*meta*-4c) (Table 2, entry 3 and Table 3, entry 4).^[13]

For Table 2, entry 3: Following the general procedure C, a mixture of **2c''** (0.14 g, 0.20 mmol), Bu₄NF(*t*-BuOH)₄ (0.25 g, 0.44 mmol) in THF (4.0 mL, 0.05 M) was stirred for 1 h at 60 °C. The crude product was purified by flash column chromatography (hexane/Et₂O = 10:1) to provide *meta*-**4c** (39 mg, 64%) as a colorless solid. Rf: 0.5 (hexane/EtOAc = 6:1). Mp: 89–92 °C. ¹H NMR (500 MHz, CDCl₃) δ: 5.00 (4 H, s), 6.33 (2 H, dd, *J* = 2.5, 11.0 Hz), 6.41 (1 H, t, *J* = 2.5 Hz), 7.30–7.42 (10 H, m). ¹³C NMR (100 MHz, CDCl₃) δ: 70.2, 95.3 (d, *J* = 25.0 Hz), 98.0 (d, *J* = 2.5 Hz), 127.4, 127.9, 128.5, 136.3, 160.5 (d, *J* = 13.0 Hz), 164.2 (d, *J* = 242.0 Hz).

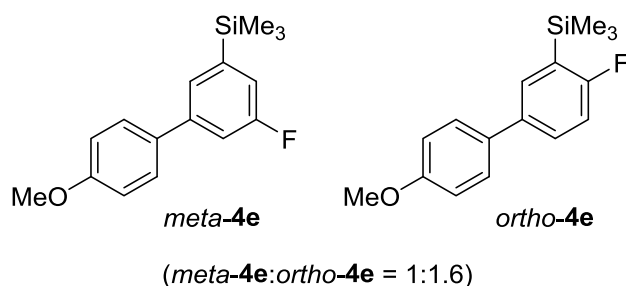
For Table 3, entry 4: Following the general procedure D, a mixture of **1c''** (83 mg, 0.22 mmol), NfF (58 μ L, 0.33 mmol), Cs₂CO₃ (0.11 g, 0.33 mmol), Bu₄NF(*t*-BuOH)₄ (0.12 g, 0.22 mmol), 18-crown-6 (34 mg, 0.13 mmol) in MeCN (2.2 mL, 0.10 M) was stirred for 1 h at 60 °C. The crude product was purified by flash column chromatography (hexane/Et₂O = 10:1) to provide **4c** (38 mg, 73%) as a colorless solid.



1,3-Di(*t*-butyl)-5-fluorobenzene (*meta*-4d**) (Table 2, entry 4 and Table 3, entry 5).^[14]**

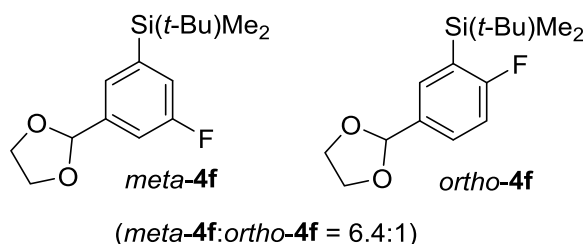
For Table 2, entry 4: Following the general procedure C, a mixture of **2d** (0.11 g, 0.20 mmol), Bu₄NF(*t*-BuOH)₄ (0.25 g, 0.44 mmol) in THF (4.0 mL, 0.050 M) was stirred for 1 h at 60 °C. The crude product was purified by preparative TLC (hexane) to provide *meta*-**4d** (24 mg, 58%) as a colorless oil. Rf: 0.4 (hexane/EtOAc = 20:1). ¹H NMR (500 MHz, CDCl₃) δ : 1.31 (18 H, s), 6.89 (2 H, dd, *J* = 1.5, 11.0 Hz), 7.17 (1 H, t, *J* = 1.5 Hz).

For Table 3, entry 5: Following the general procedure D, a mixture of **1d** (68 mg, 0.22 mmol), NfF (58 μ L, 0.33 mmol), Cs₂CO₃ (0.11 g, 0.33 mmol), Bu₄NF(*t*-BuOH)₄ (0.15 g, 0.27 mmol), 18-crown-6 (34 mg, 0.13 mmol) in MeCN (2.2 mL, 0.10 M) was stirred for 1 h at 60 °C. Almost quantitative recovery of **1d** was observed by ¹H NMR analysis of crude reaction mixture.



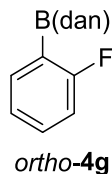
1-Fluoro-3-(4-methoxyphenyl)-5-(trimethylsilyl)benzene (*meta*-4e**) and 1-fluoro-4-(4-methoxyphenyl)-2-(trimethylsilyl)benzene (*ortho*-**4e**) (Table 2, entry 5):** Following the general procedure C, a mixture of **2e** (0.15 g, 0.20 mmol), Bu₄NF(*t*-BuOH)₄ (0.25 g, 0.44 mmol) in THF (4.0

mL, 0.050 M) was stirred for 1 h at 60 °C. The crude product was purified by flash column chromatography (hexane) and preparative TLC (hexane/EtOAc = 10:1) to provide a mixture of *meta*-**4e** and *ortho*-**4e** (18 mg, 34%) as a colorless solid. Rf: 0.6 (hexane/EtOAc = 10:1). Mp: ca. 30 °C. ¹H NMR (500 MHz, CDCl₃) δ: 0.31 (9 H×5/13, s), 0.36 (9 H×8/13, s), 3.856 (3 H×8/13, s), 3.862 (3 H×5/13, s), 6.90–7.58 (7 H, m). ¹³C NMR (125 MHz, CDCl₃) δ: -1.2, -1.0, 55.3, 112.5, 113.8, 114.2, 114.3, 114.7, 115.0, 117.6, 117.9, 126.2, 126.6, 127.1, 128.1, 128.3, 129.5, 129.7, 132.1, 133.3, 133.5, 136.6, 142.7, 143.9, 159.0, 159.5, 162.0, 164.0, 165.8, 167.7. ¹⁹F NMR (470 MHz, CDCl₃) δ: -114.38–(-114.39) (m) (F×8/13), -104.40–(-104.26) (m) (F×5/13). IR (neat): 1610, 1514, 1468 cm⁻¹. HRMS (MALDI): *m/z* calcd for C₁₆H₁₉FOSi [M]⁺: 274.1184, found: 274.1182.

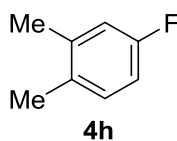


3-(1,3-Dioxolan-2-yl)-1-fluorophenyl-5-((*t*-butyl)dimethylsilyl)benzene (*meta*-4f**) and 4-(1,3-dioxolan-2-yl)-1-fluorophenyl-6-((*t*-butyl)dimethylsilyl)benzene (*ortho*-**4f**) (Table 2, entry 6):**

Following the general procedure C, a mixture of **2f** (0.25 g, 0.40 mmol), Bu₄NF(*t*-BuOH)₄ (0.49 mg, 0.88 mmol) in THF (8.0 mL, 0.05 M) was stirred for 1 h at 60 °C. The crude product was purified by flash column chromatography (hexane/CH₂Cl₂ = 3:1) to provide a mixture of *meta*-**4f** and *ortho*-**4f** (50 mg, *meta*-**4f**:*ortho*-**4f** = 6.4:1, total 44%) as a green oil. Rf: 0.4 (hexane/EtOAc = 6:1). ¹H NMR (500 MHz, CDCl₃) δ: 0.27 (6 H×6/7, s), 0.31 (6 H×1/7, s), 0.87 (9H×6/7, s), 0.89 (9H×1/7, s), 4.01–4.15 (4H, m), 5.78 (1H×1/7, s), 5.82 (1H×6/7, s), 7.00 (1H×1/7, t, *J* = 8.5 Hz), 7.18 (2H×6/7, brd, *J* = 9.5 Hz), 7.34 (1H×6/7, brs), 7.45–7.50 (2H×1/7, m). ¹³C NMR (125 MHz, CDCl₃) δ: -6.2 (6/7), -5.4 (1/7), 16.8 (6/7), 26.4 (6/7), 26.5 (1/7), 65.3, 103.0 (6/7), 103.4 (1/7), 113.6 (d, *J* = 21.5 Hz) (6/7), 114.9 (d, *J* = 27.5 Hz) (1/7), 121.6 (d, *J* = 19.0 Hz) (6/7), 128.0 (d, *J* = 2.5 Hz) (6/7), 129.5 (d, *J* = 9.5 Hz) (1/7), 132.9 (1/7), 134.8 (d, *J* = 13 Hz) (1/7), 139.5 (d, *J* = 6.0 Hz) (6/7), 141.3 (d, *J* = 3.5 Hz) (6/7), 162.3 (d, *J* = 249.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ: -114.22–(-114.11) (m) (6/7), -96.51–(-96.41) (m) (1/7). IR (neat): 1601, 1414 cm⁻¹. HRMS (APCI): *m/z* calcd for C₁₅H₂₄FO₂Si [M]⁺: 283.15240, found: 283.1540.



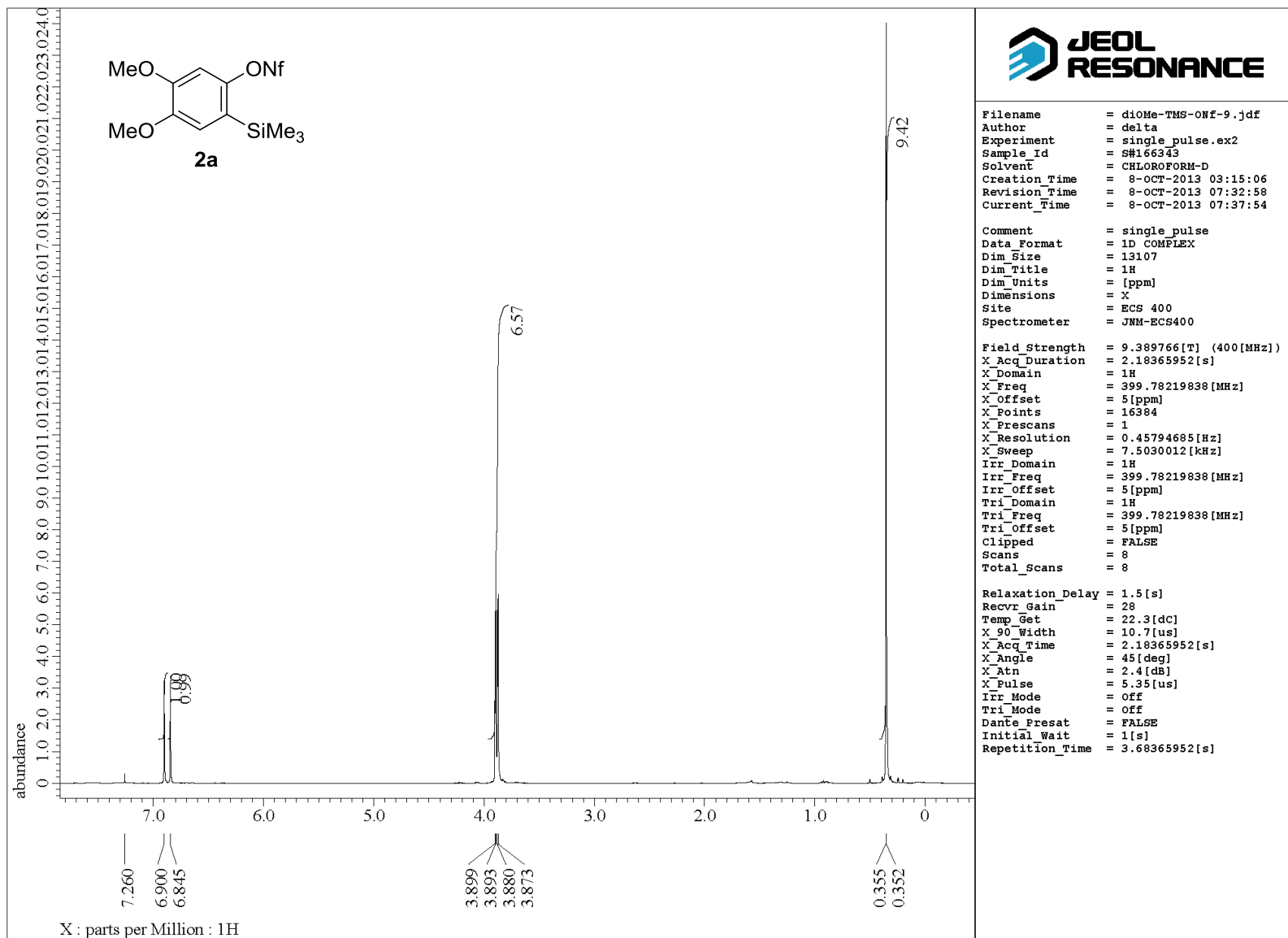
2-(2-Fluorophenyl)-2,3-dihydro-1H-naphtho[1,8-*de*][1,3,2]diazaborinine (4g) (Table 2, entry 7): Following the general procedure C, a mixture of **2g** (0.19 g, 0.40 mmol), Bu₄NF(*t*-BuOH)₄ (0.49 g, 0.88 mmol) in THF (0.80 mL, 0.050 M) was stirred for 1 h at 60 °C. The crude product was purified by flash column chromatography (hexane/EtOAc = 5:1) to provide *ortho-4g* (63 mg, 60%) as a yellow solid. Rf: 0.4 (hexane/EtOAc = 5:1). Mp: 91–93 °C. ¹H NMR (400 MHz, CDCl₃) δ: 6.27 (2NH, brs), 6.42 (2 H, dd, *J* = 7.5, 1.0 Hz), 7.08–7.26 (6 H, m), 7.43–7.49 (1 H, m), 7.53–7.57 (1 H, m). ¹³C NMR (100 MHz, CDCl₃) δ: 106.1, 115.5 (d, *J* = 25.5 Hz), 117.8, 119.9, 124.1 (d, *J* = 3.0 Hz), 127.6, 132.2 (d, *J* = 9.5 Hz), 133.2 (d, *J* = 8.5 Hz), 136.2, 140.8, 166.8 (d, *J* = 243 Hz) (A carbon bearing the boron substituent could not be observed in ¹³C NMR due to quadrupolar relaxation).^[11] ¹⁹F NMR (376 MHz, CDCl₃) δ: –105.96–(–105.84) (m). IR (neat): 3443, 3052, 1599, 1512, 1411 cm⁻¹. HRMS (FAB, NBA): *m/z* calcd for C₁₆H₁₂BFN₂ [M]⁺: 262.1072, found: 262.1078.

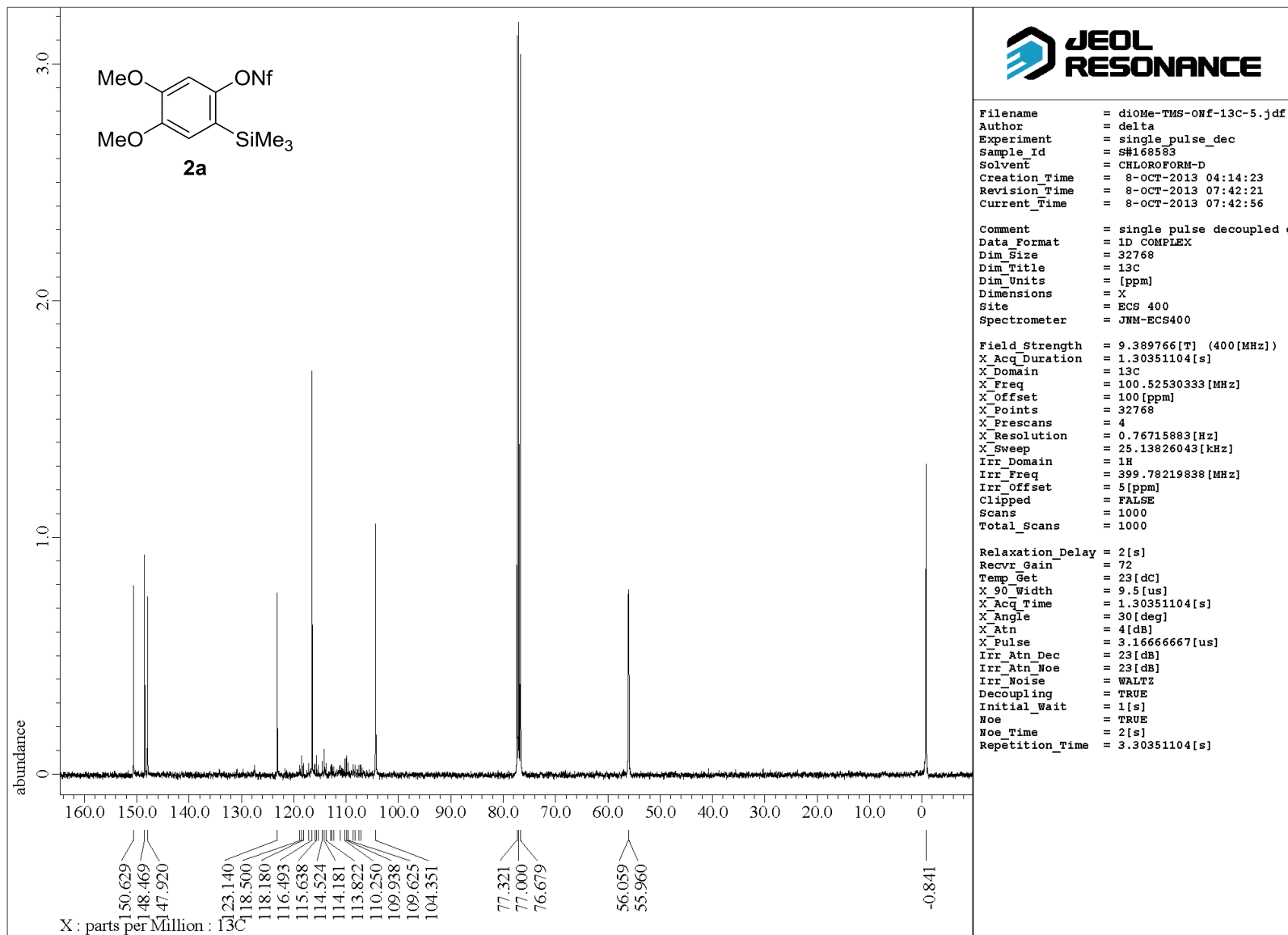


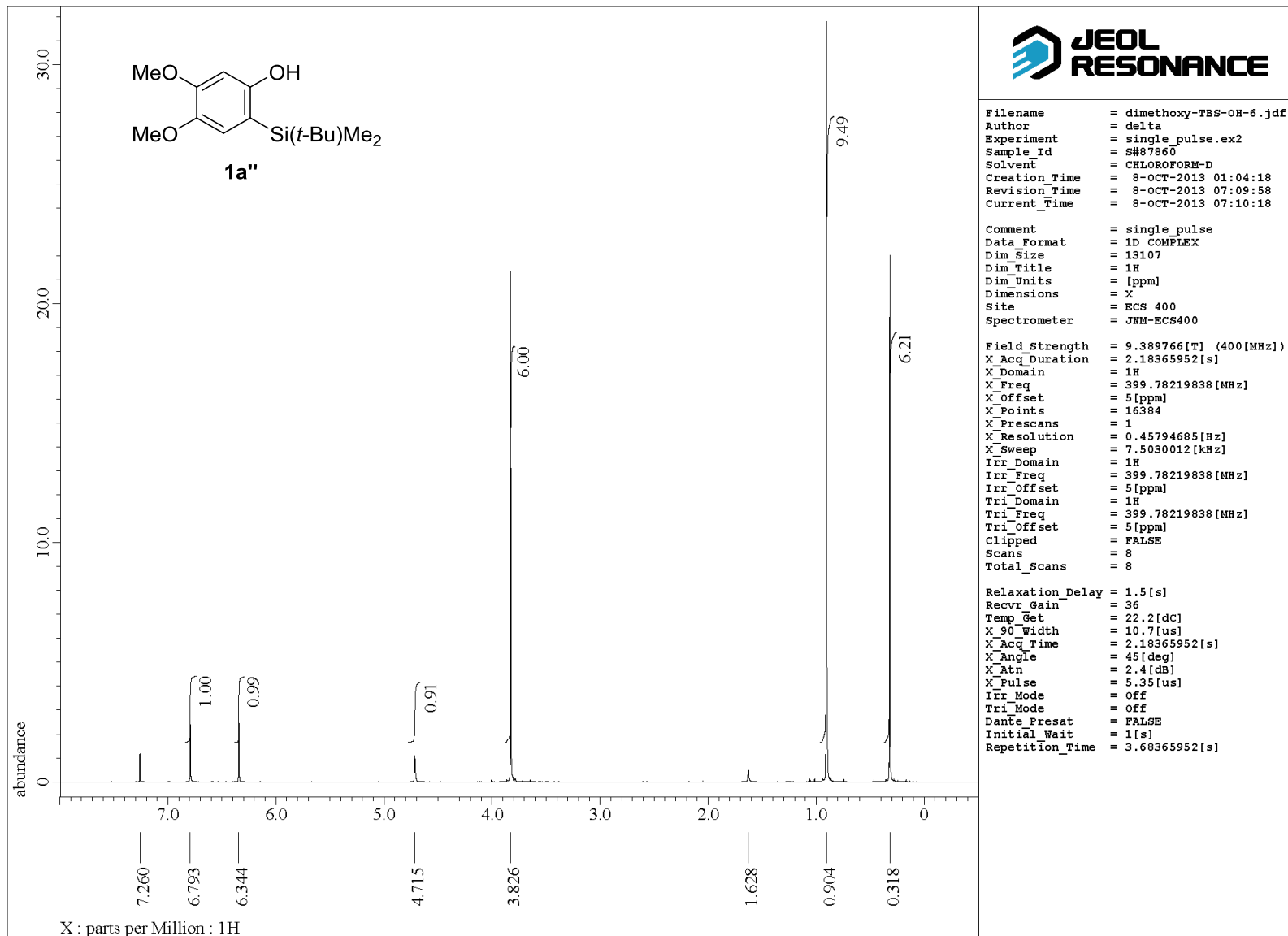
3,4-Dimethyl-fluorobenzene (4h) (Table 3, entry 3):^[12] Following the general procedure D, a mixture of **1h** (42 mg, 0.22 mmol), NfF (58 μL, 0.33 mmol), Cs₂CO₃ (0.11 g, 0.33 mmol), Bu₄NF(*t*-BuOH)₄ (0.12 g, 0.22 mmol), 18-crown-6 (34 mg, 0.13 mmol) in MeCN (2.2 mL, 0.10 M) was stirred for 1 h at 60 °C. *n*-Decane (45 μL, 0.22 mmol) was added to the reaction mixture and diluted with EtOAc (ca. 5 mL). A part of the mixture was filtered through a Celite pad and checked by GC (51% yield).

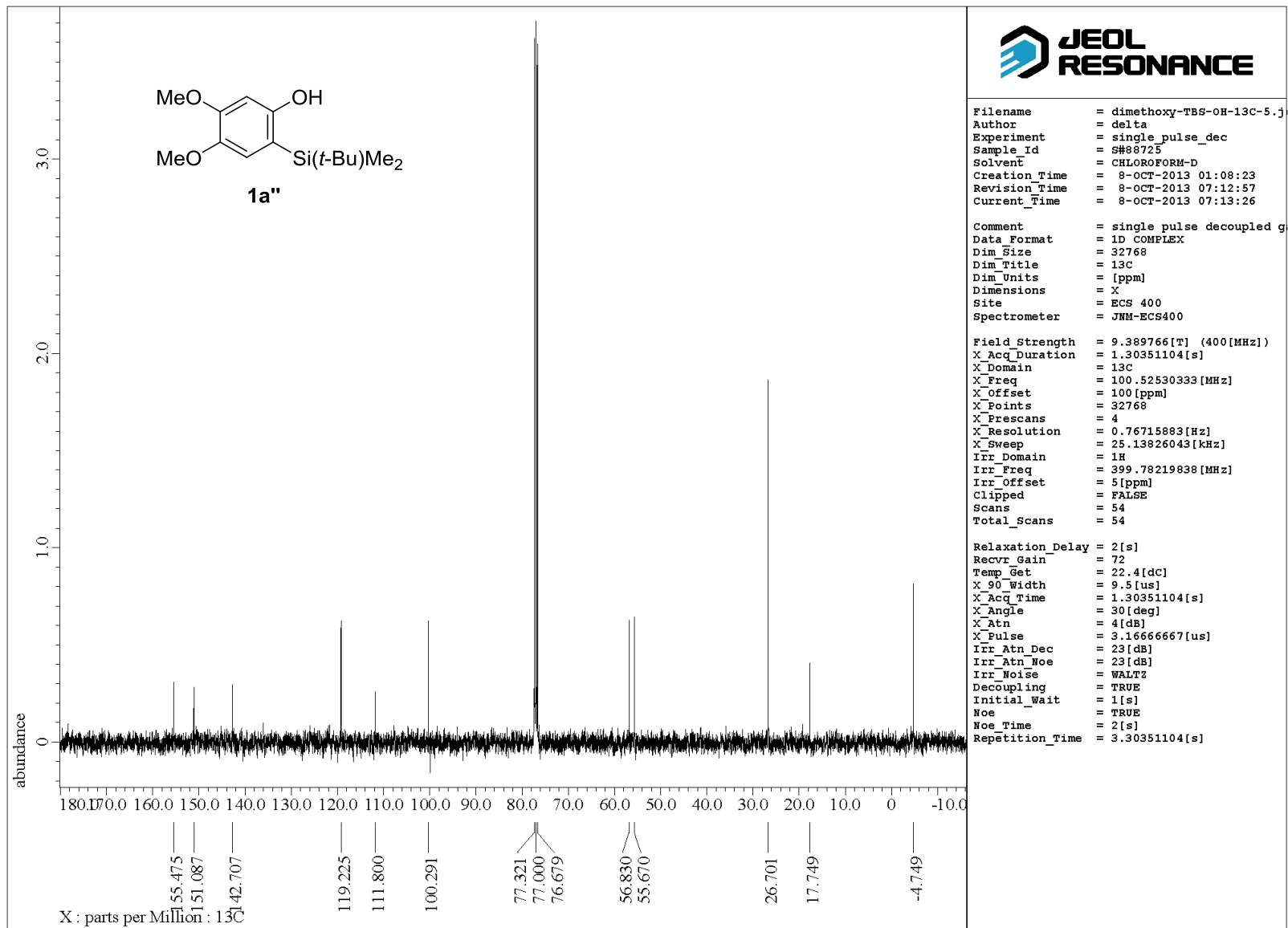
Experimental references

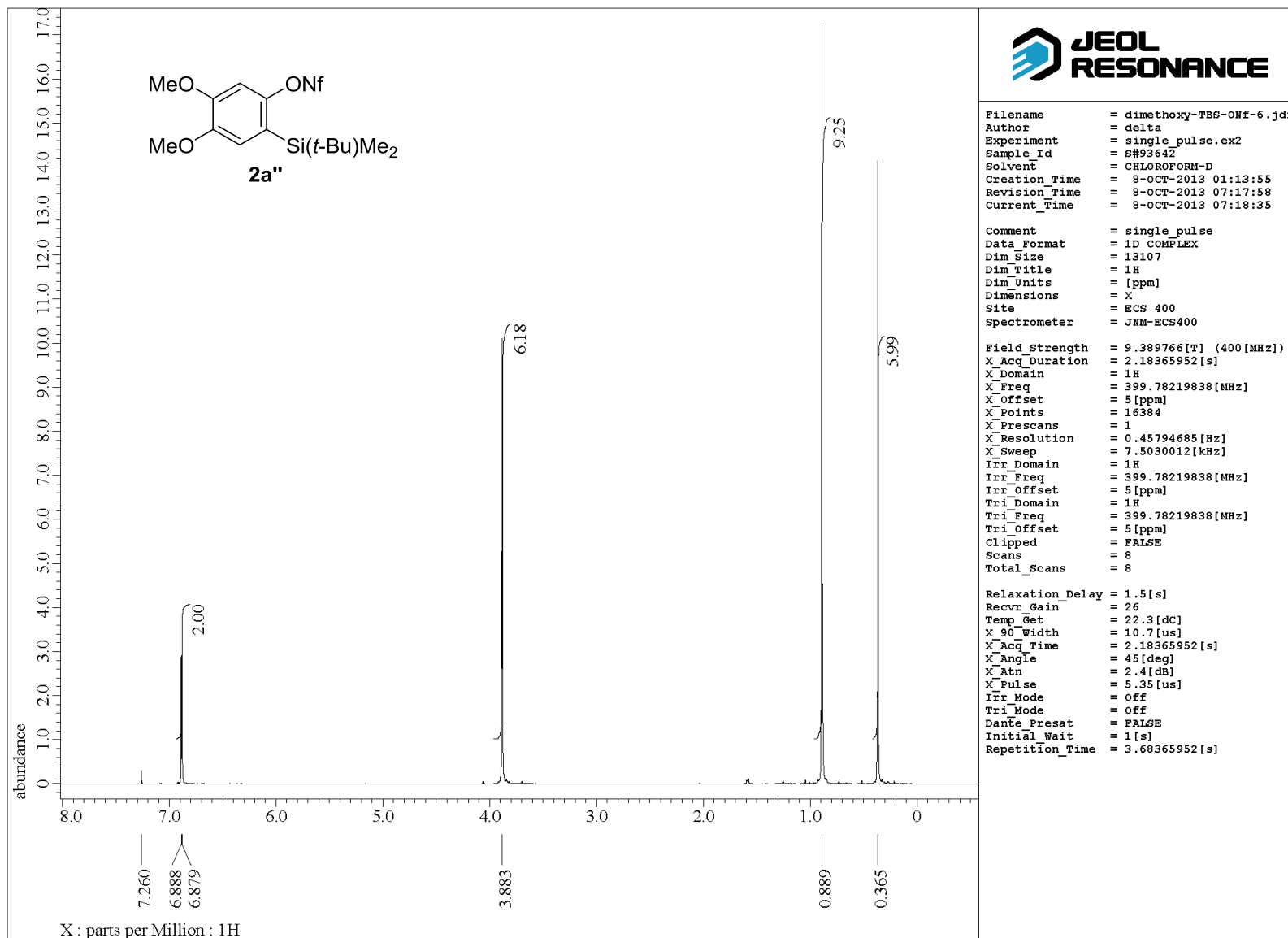
- [1] D. W. Kim, H.-J. Jeong, S. T. Lim, M.-H. Sohn, *Angew. Chem. Int. Ed.* **2008**, *47*, 8404–8406. doi:10.1002/anie.200803150
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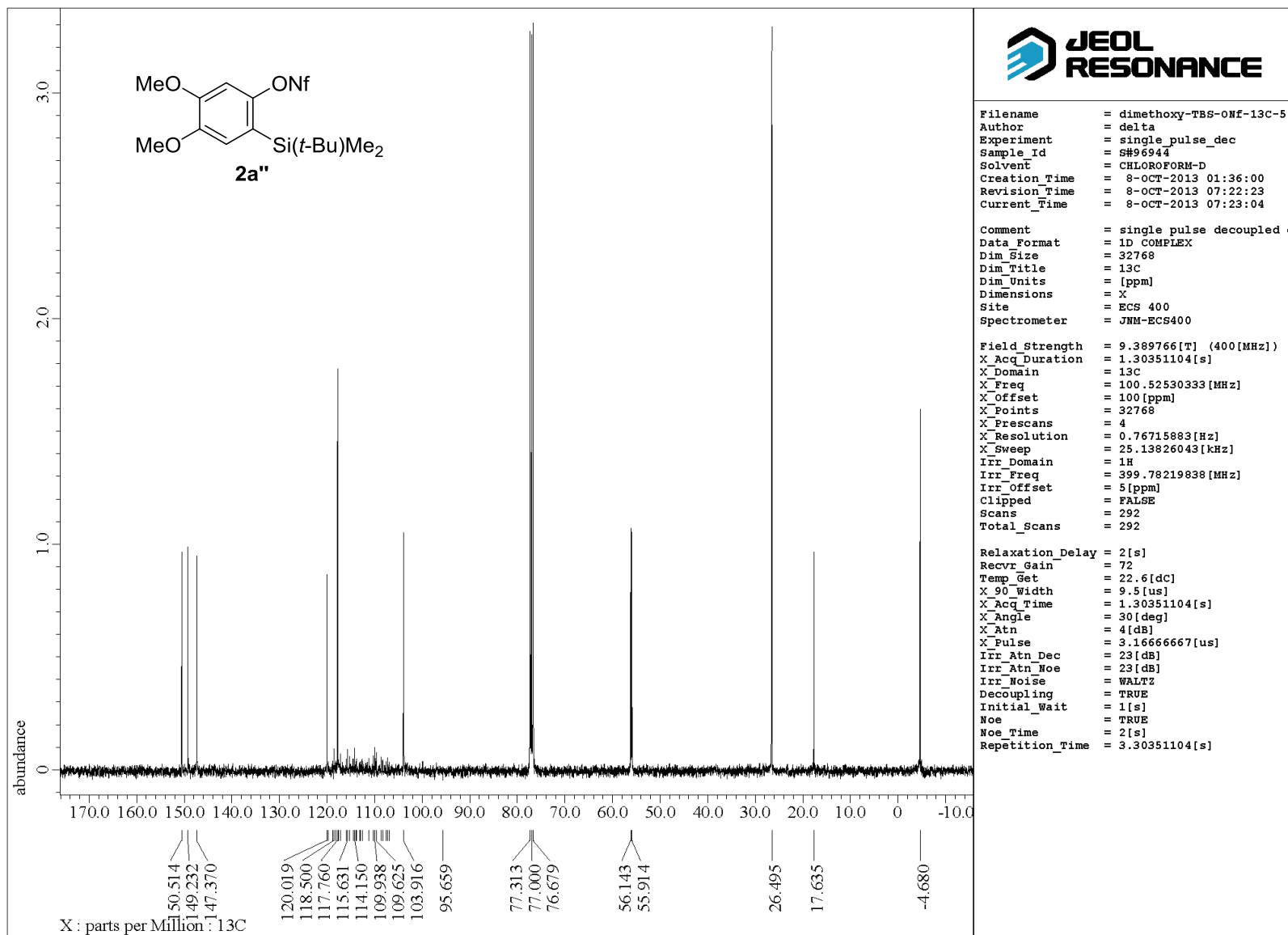


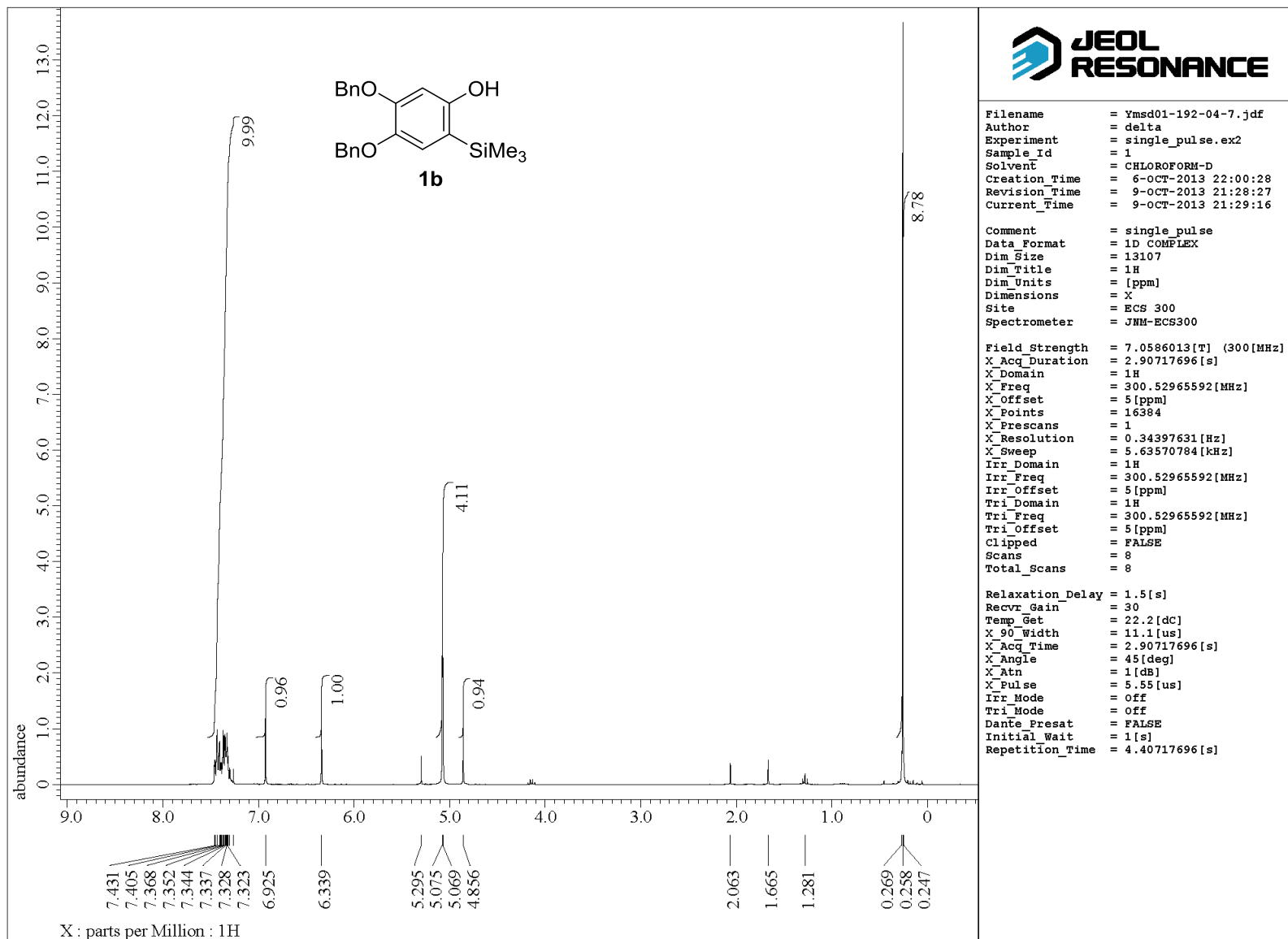


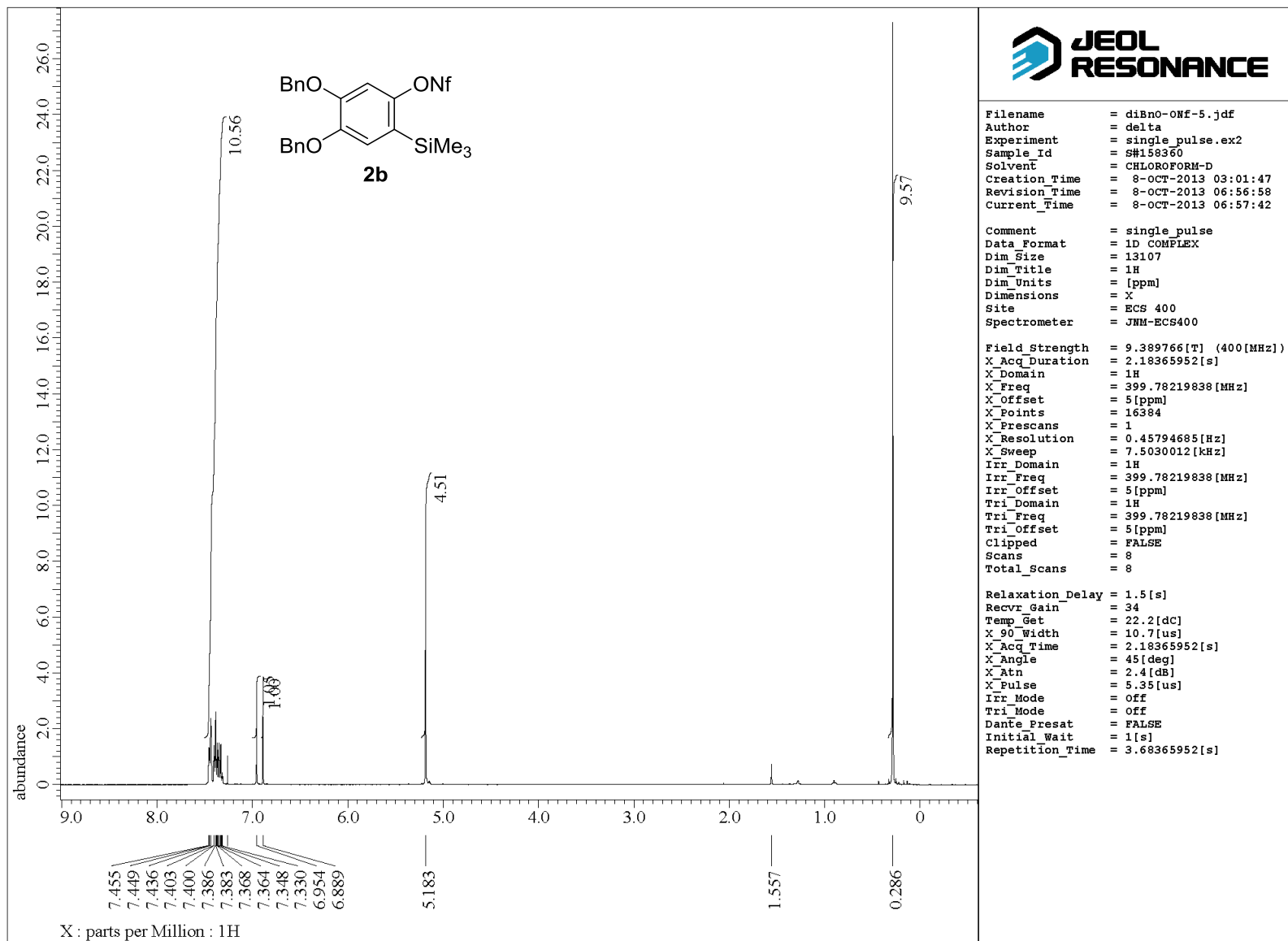












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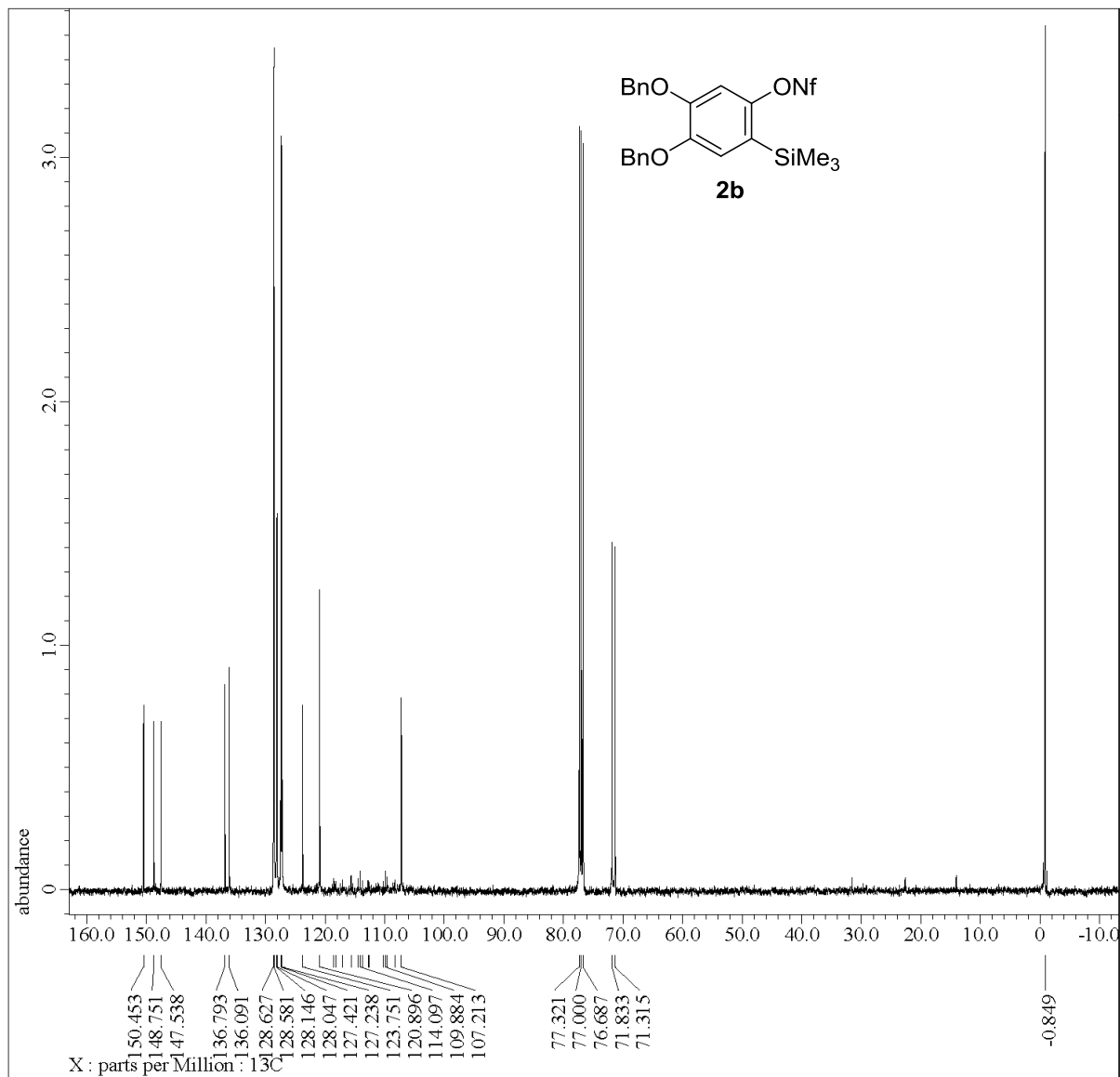
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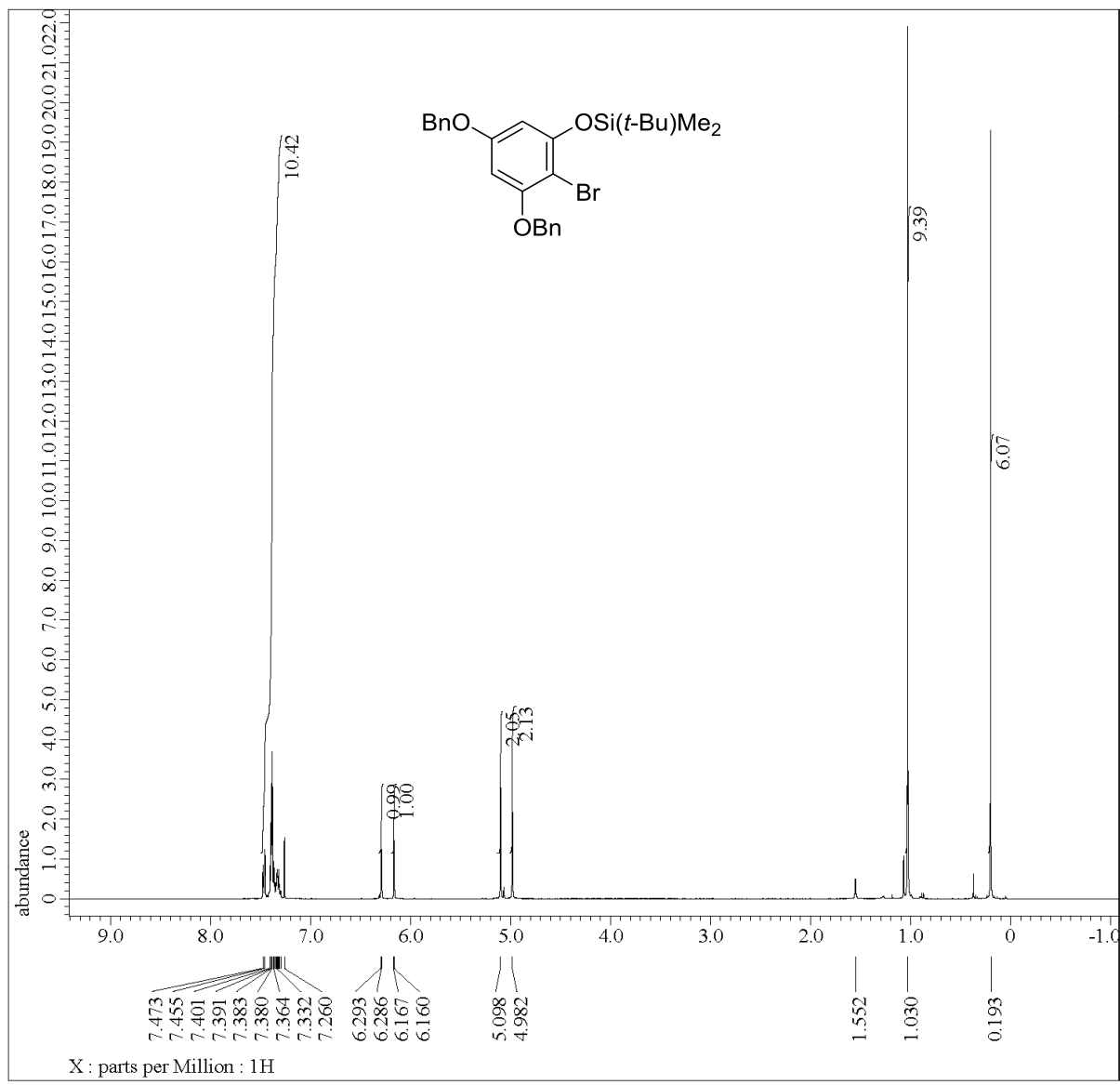


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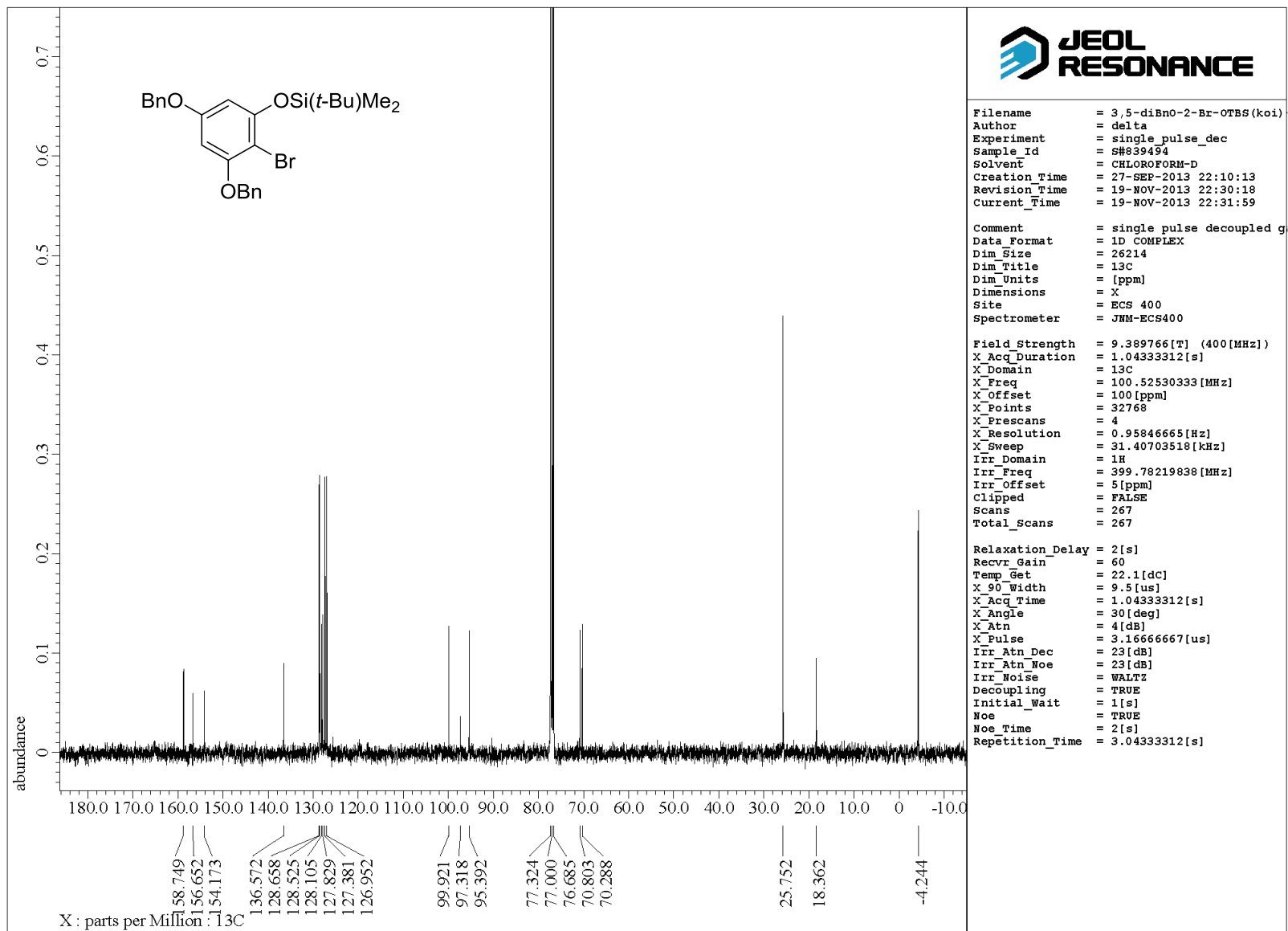
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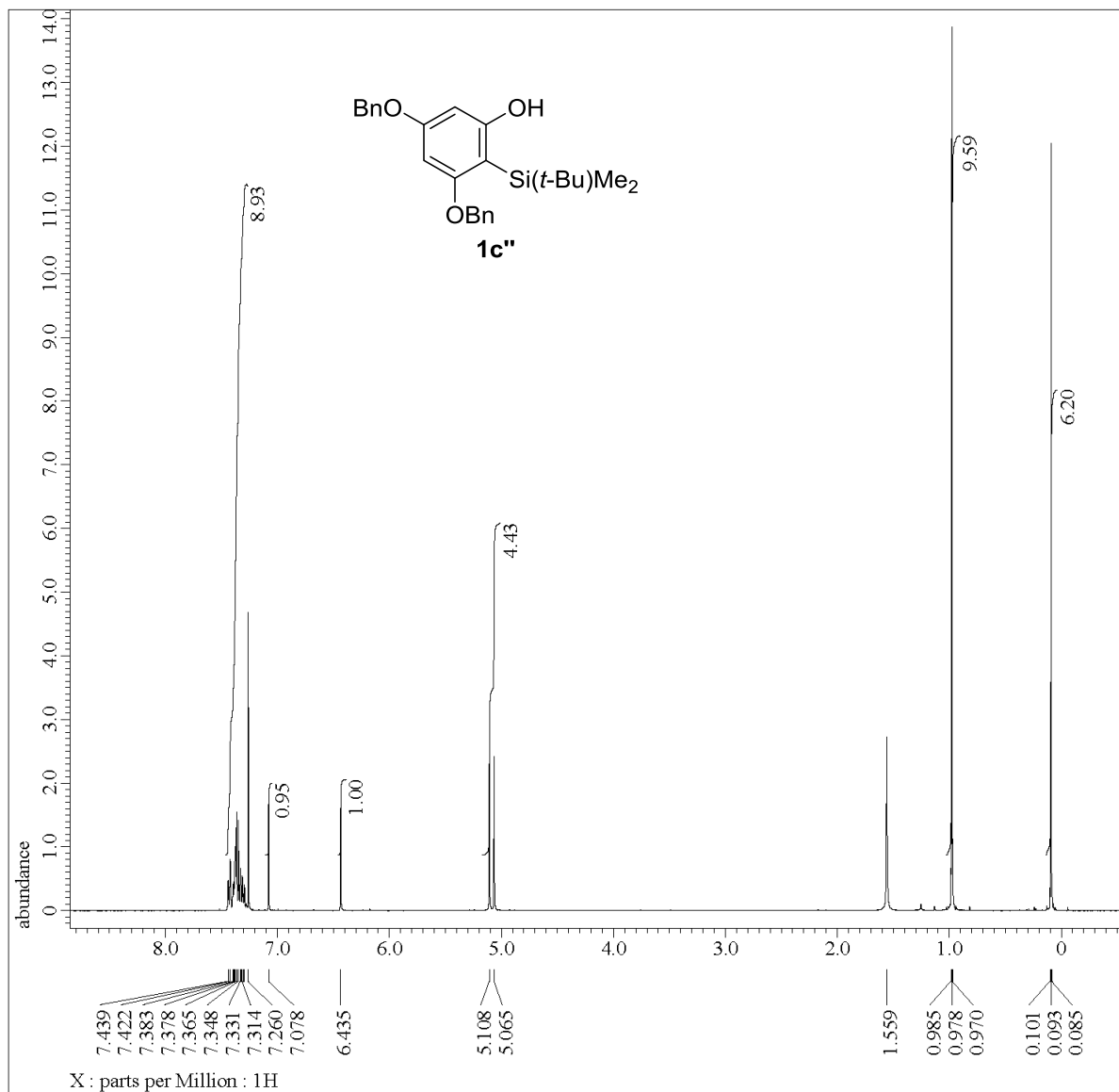
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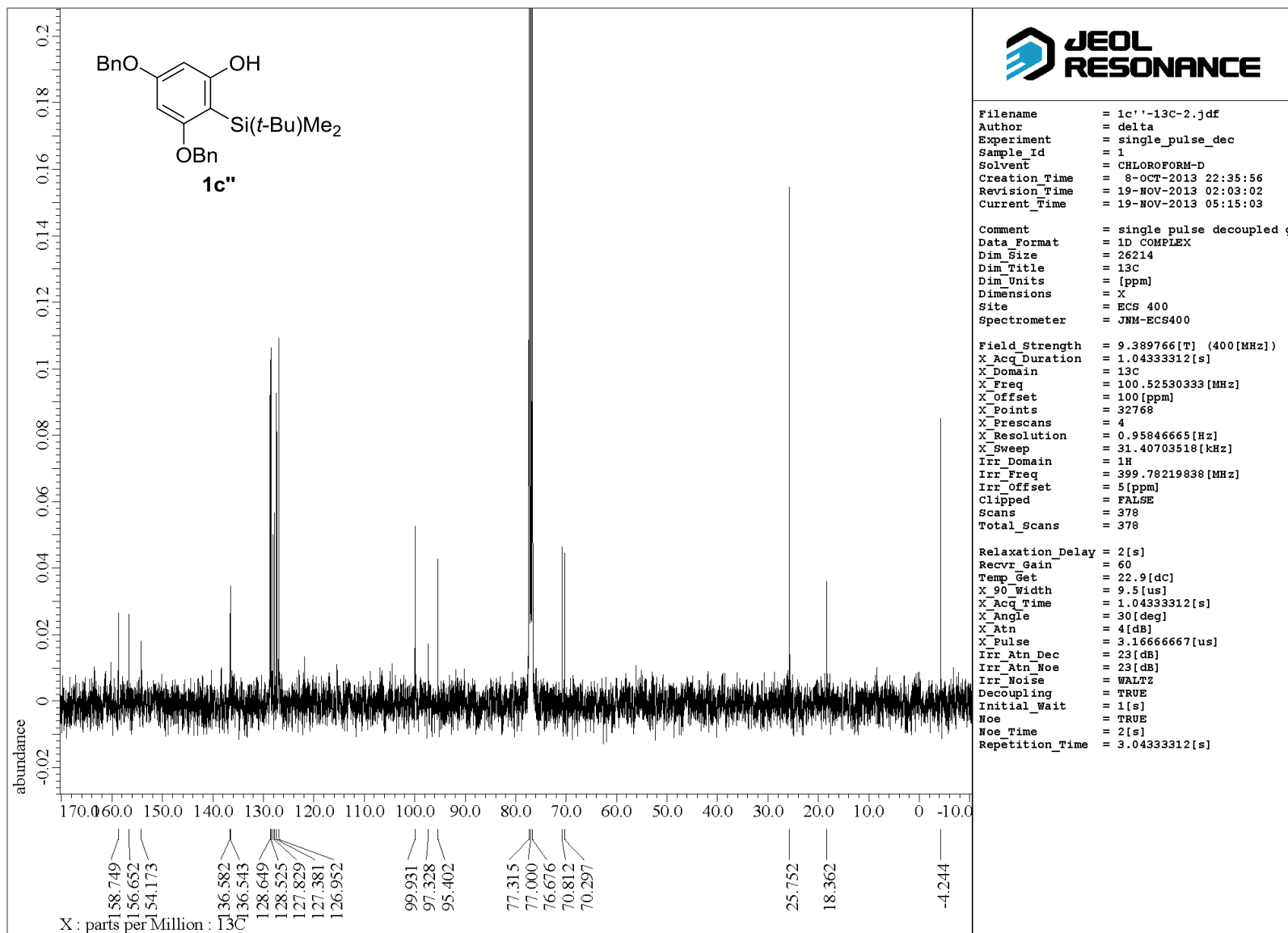
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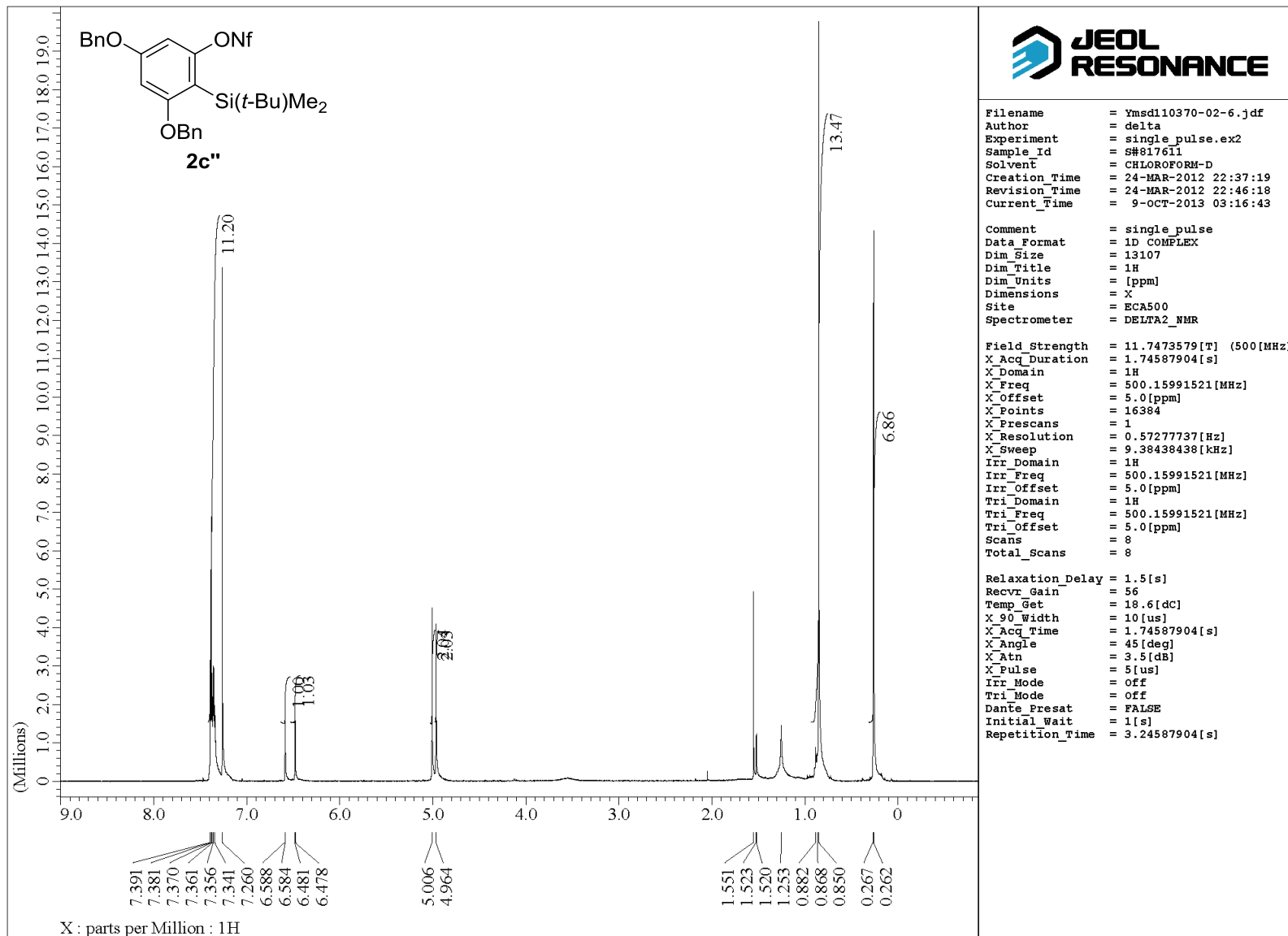
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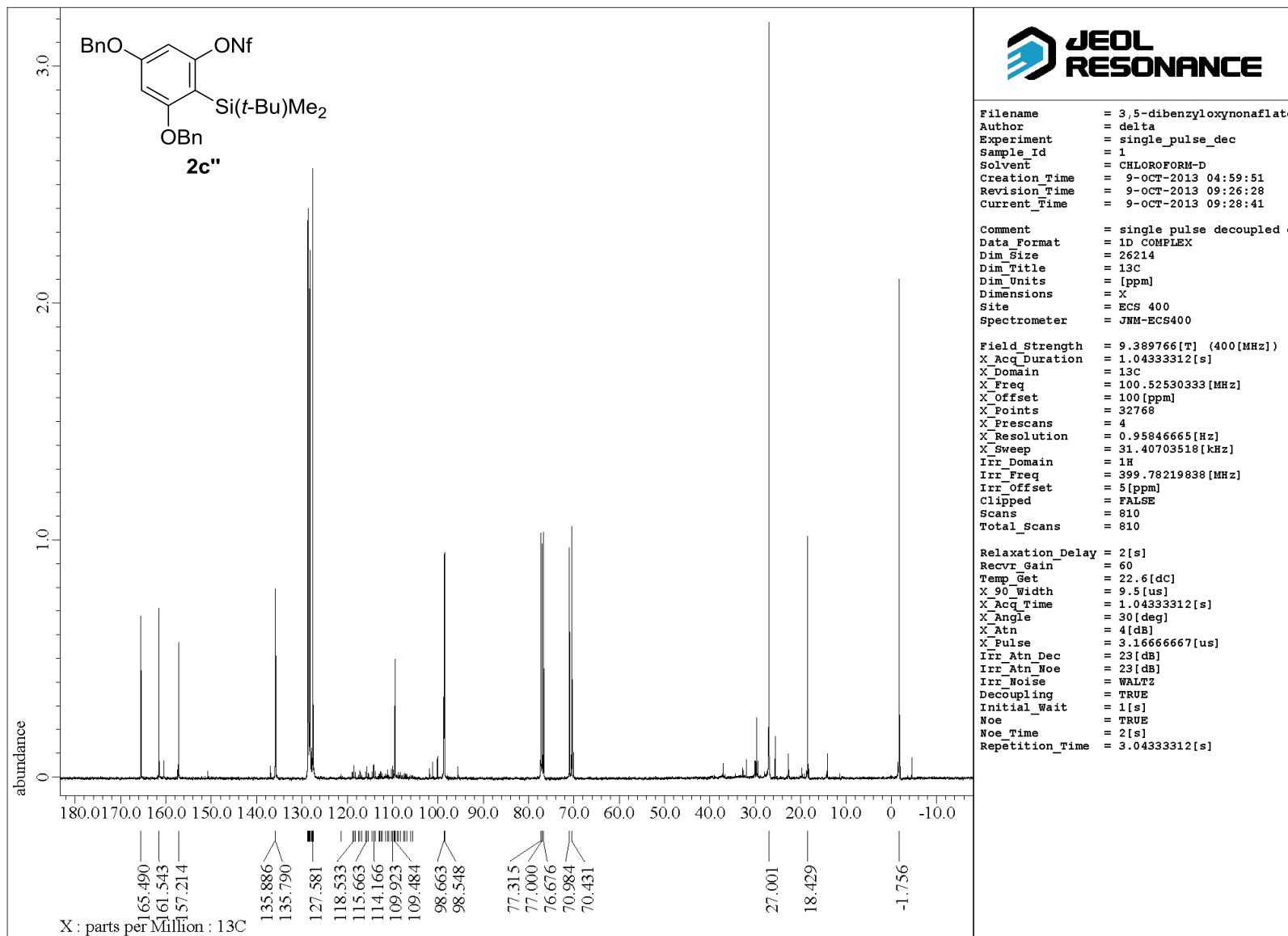
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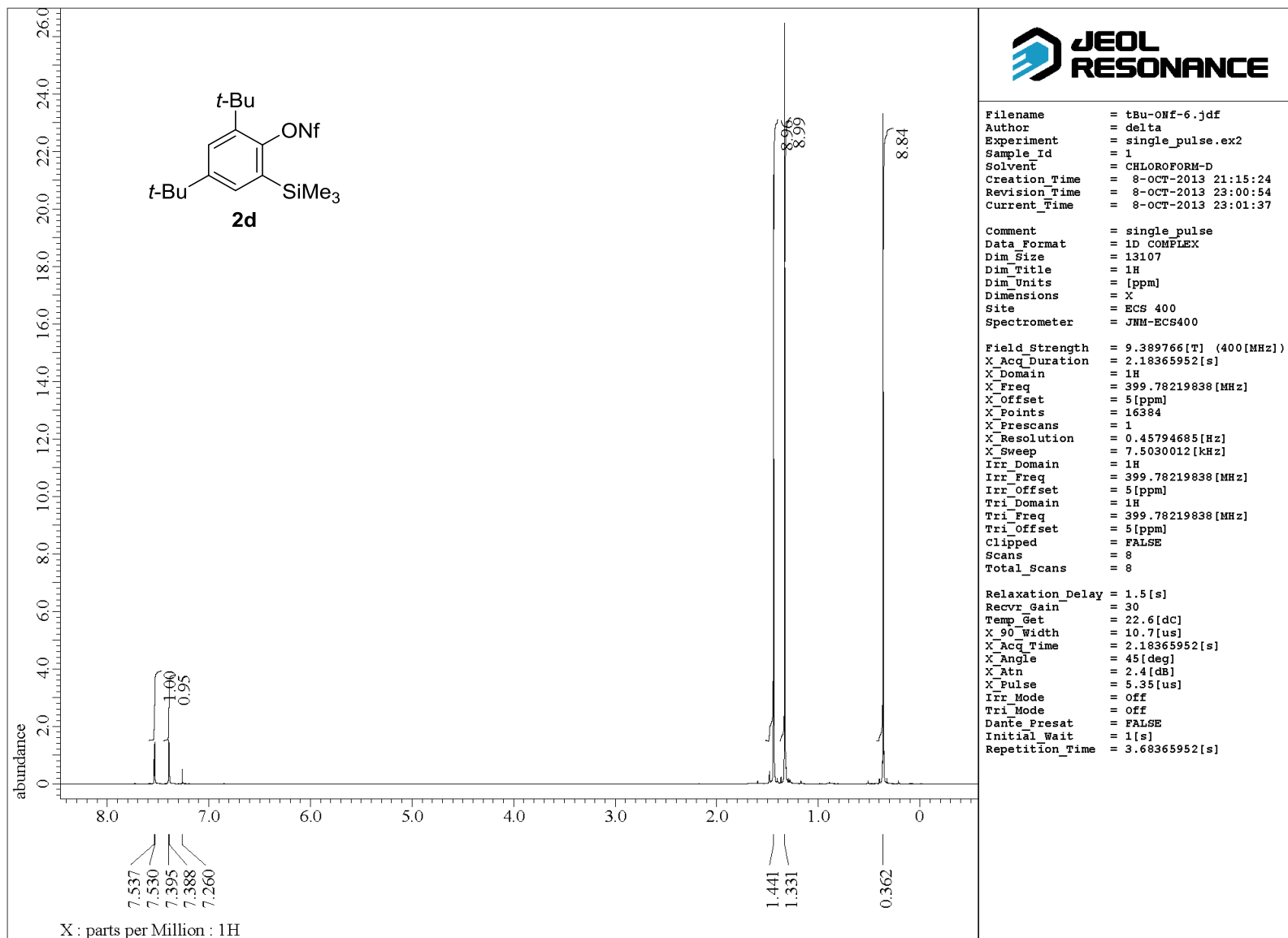
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Site         = ECA500
Spectrometer = DELTA2_NMR

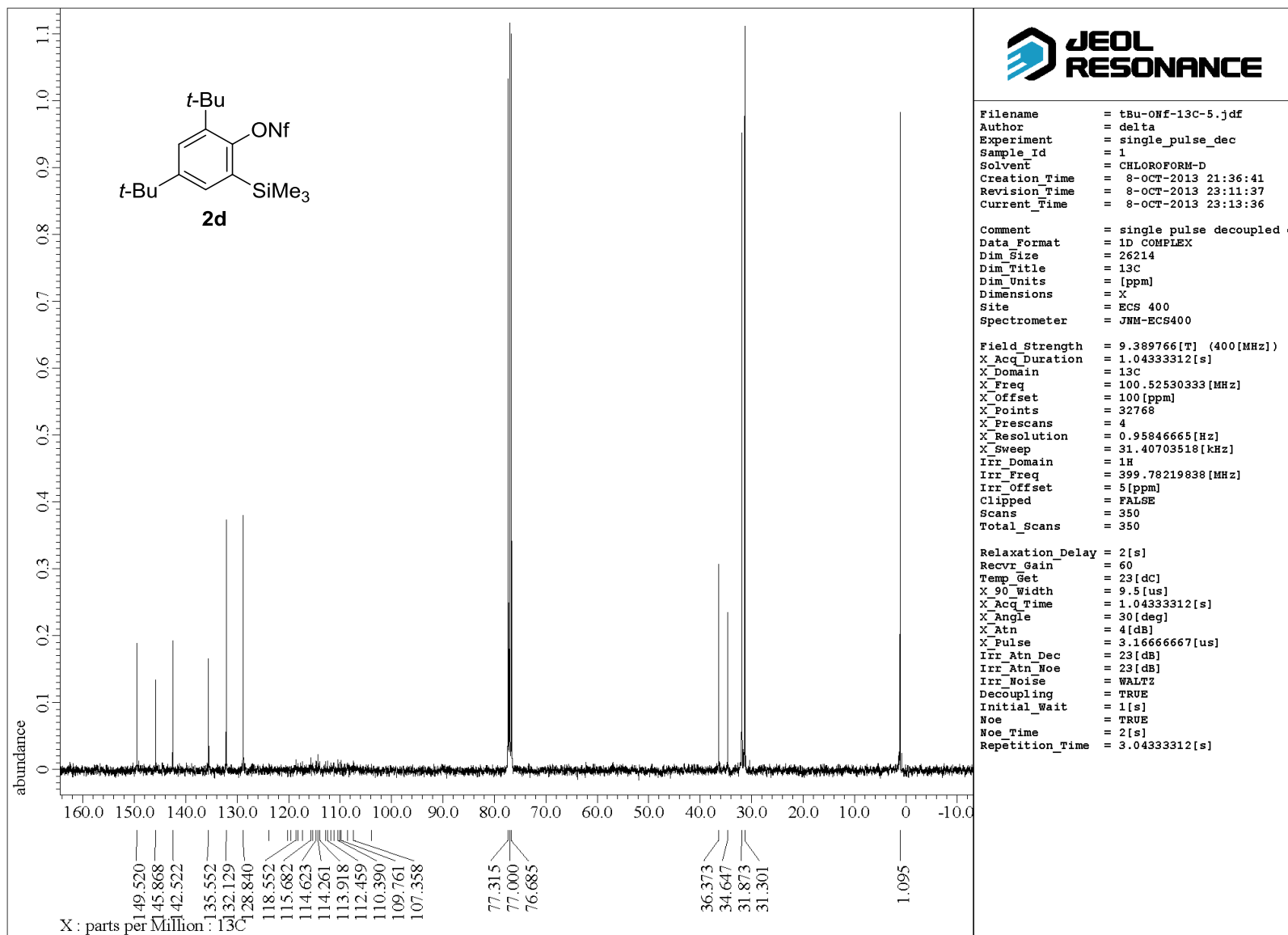
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain       = 1H
X_Freq         = 500.15991521[MHz]
X_Offset       = 5.0[ppm]
X_Points       = 16384
X_Prescans     = 1
X_Resolution   = 0.57277737[Hz]
X_Sweep        = 9.38438438[kHz]
Irr_Domain     = 1H
Irr_Freq       = 500.15991521[MHz]
Irr_Offset     = 5.0[ppm]
Tri_Domain     = 1H
Tri_Freq       = 500.15991521[MHz]
Tri_Offset     = 5.0[ppm]
Scans          = 8
Total_Scans    = 8

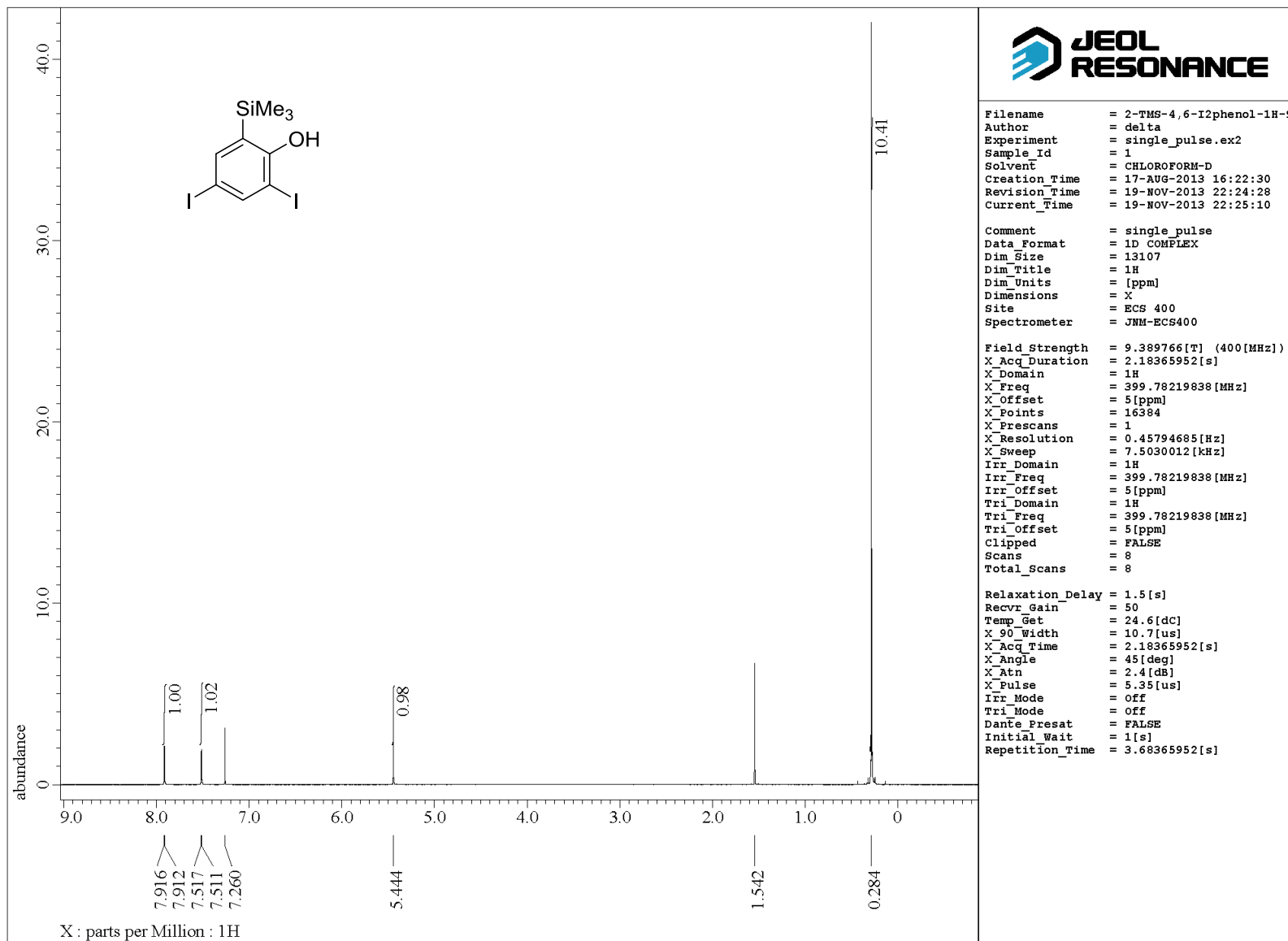
Relaxation_Delay = 1.5[s]
Recvr_Gain       = 56
Temp_Get         = 18.6[dc]
X_90_Width      = 10[us]
X_Acq_Time      = 1.74587904[s]
X_Angle         = 45[deg]
X_Atn           = 3.5[db]
X_Pulse         = 5[us]
Irr_Mode        = Off
Tri_Mode        = Off
DanE_Presat     = FALSE
Initial_Wait    = 1[s]
Repetition_Time = 3.24587904[s]

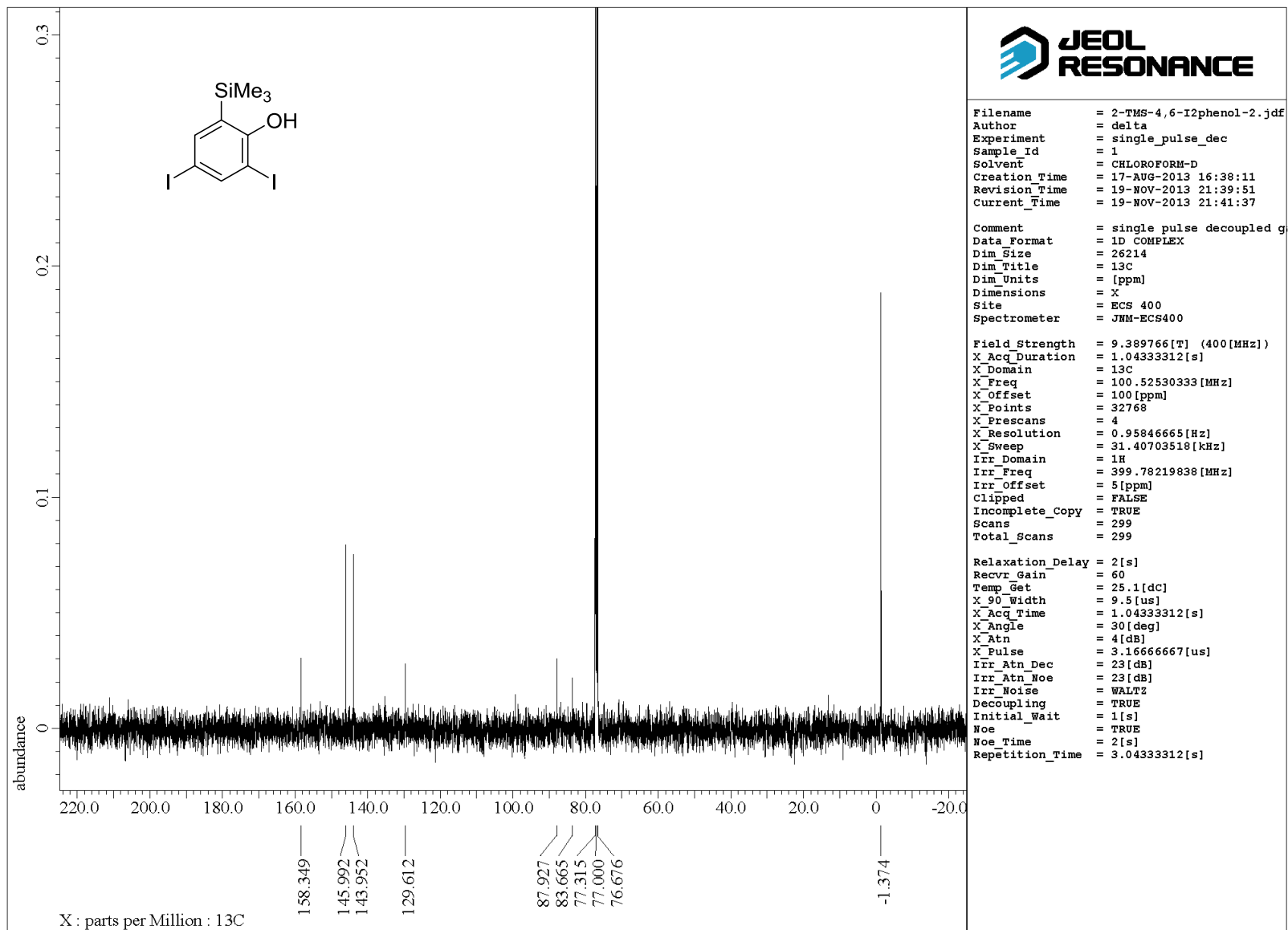
```

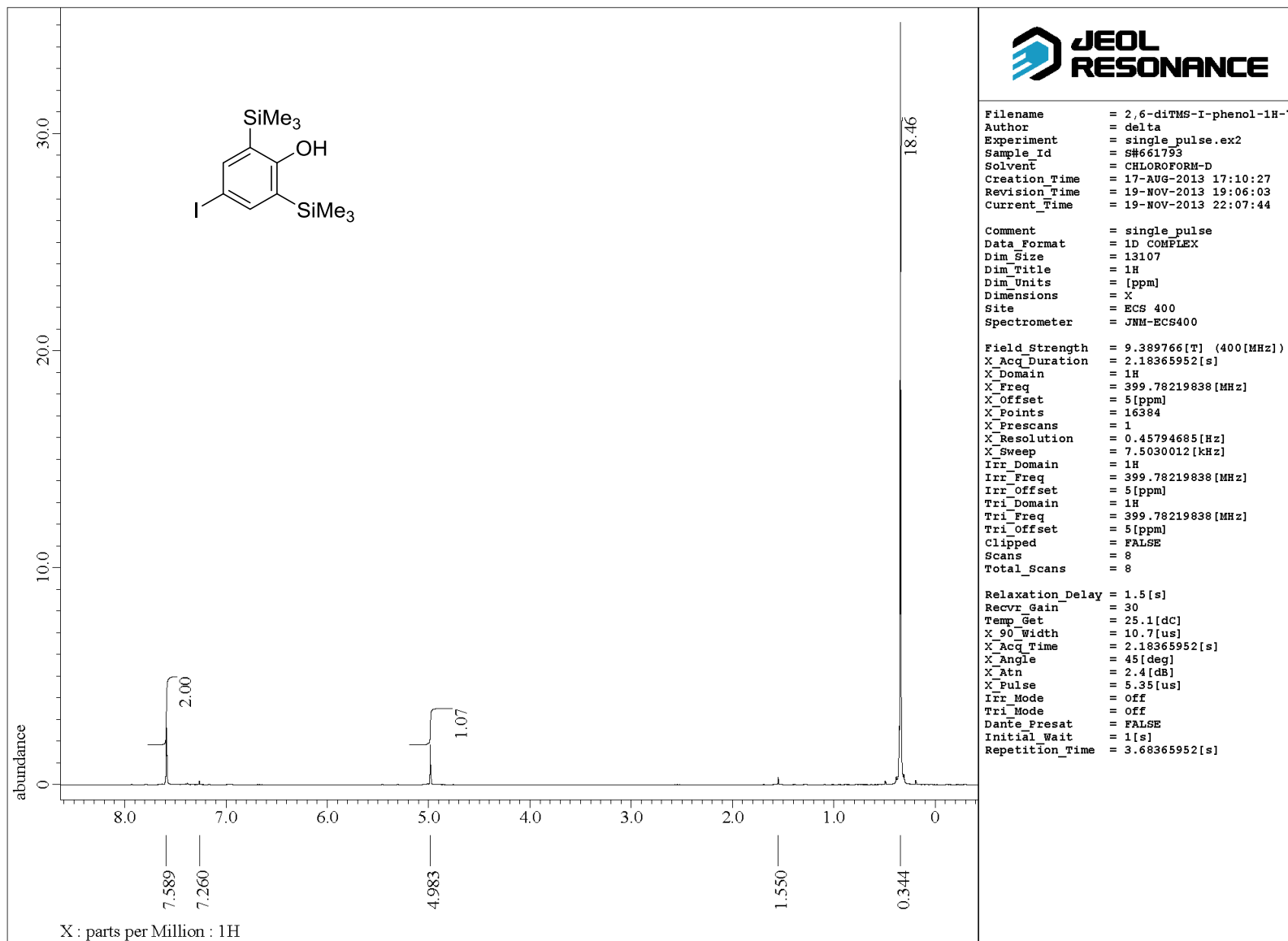


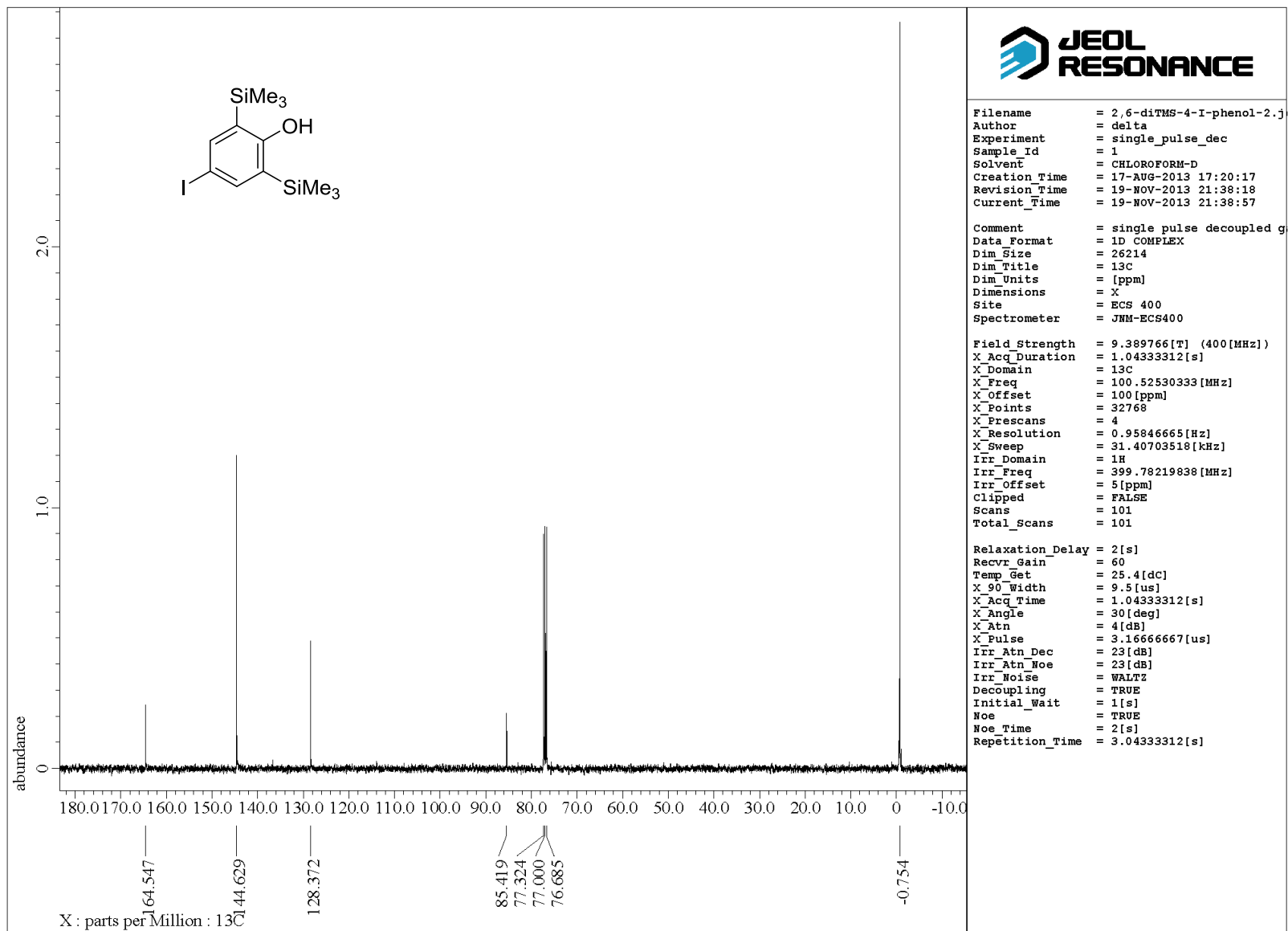


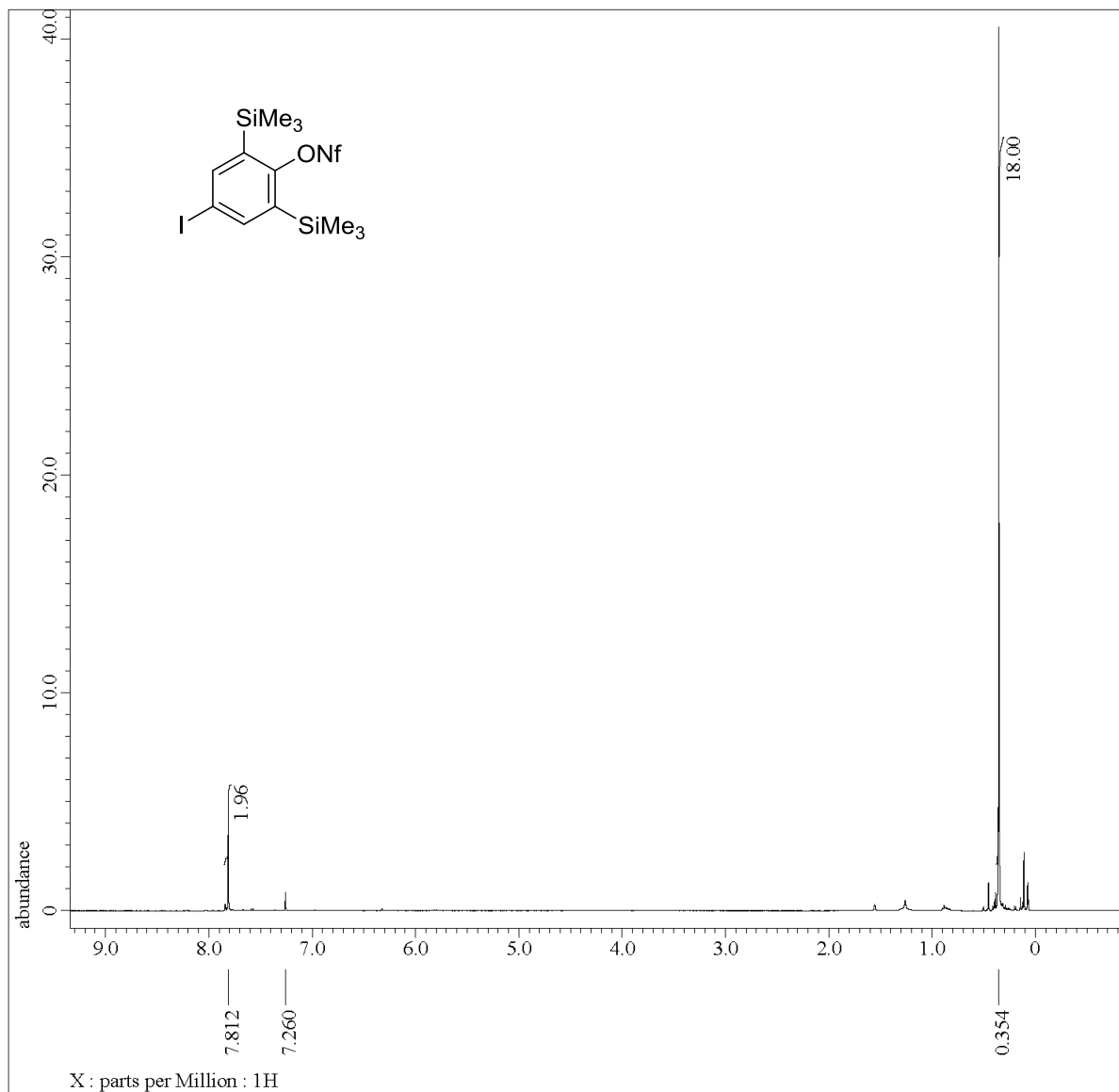










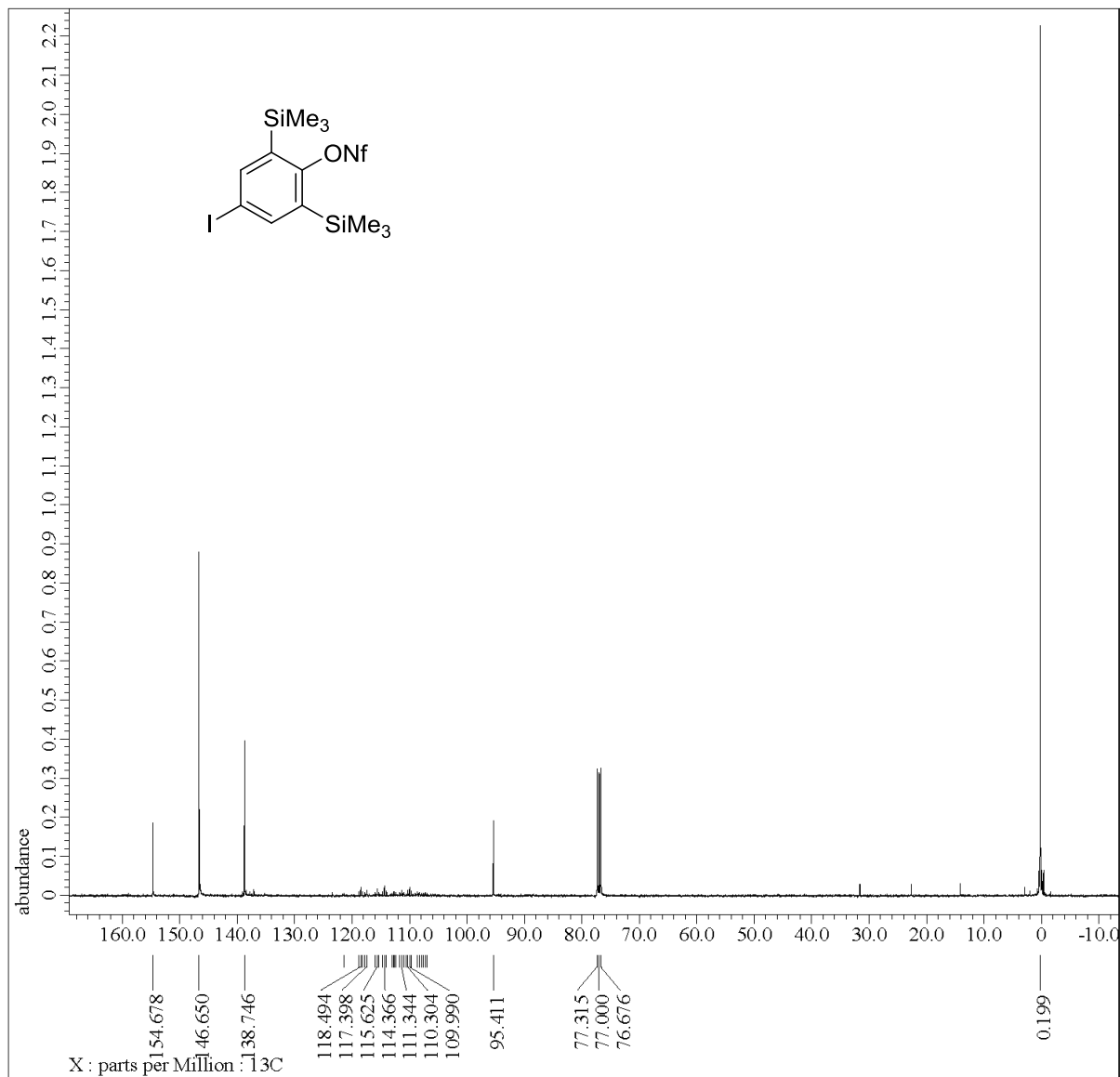


Filename = 2,6-diTMS-I-phenolONF-1H
 Author = delta
 Experiment = single_pulse.ex2
 Sample_Id = 1
 Solvent = CHLOROFORM-D
 Creation_Time = 11-NOV-2013 20:40:11
 Revision_Time = 19-NOV-2013 22:05:52
 Current_Time = 19-NOV-2013 22:06:31

Comment = single_pulse
 Data_Format = 1D_COMPLEX
 Dim_Size = 13107
 Dim_Title = 1H
 Dim_Units = [ppm]
 Dimensions = X
 Site = ECS 400
 Spectrometer = JNM-ECS400

Field_Strength = 9.389766[T] (400[MHz])
 X_Acq_Duration = 2.18365952[s]
 X_Domain = 1H
 X_Freq = 399.78219838[MHz]
 X_Offset = 5[ppm]
 X_Points = 16384
 X_Prescans = 1
 X_Resolution = 0.45794685[Hz]
 X_Sweep = 7.5030012[kHz]
 Irr_Domain = 1H
 Irr_Freq = 399.78219838[MHz]
 Irr_Offset = 5[ppm]
 Tri_Domain = 1H
 Tri_Freq = 399.78219838[MHz]
 Tri_Offset = 5[ppm]
 Clipped = FALSE
 Scans = 8
 Total_Scans = 8

Relaxation_Delay = 1.5[s]
 Recvr_Gain = 36
 Temp_Get = 19.7[dc]
 X_90_Width = 10.7[us]
 X_Acq_Time = 2.18365952[s]
 X_Angle = 45[deg]
 X_Atn = 2.4[db]
 X_Pulse = 5.35[us]
 Irr_Mode = Off
 Tri_Mode = Off
 DanE_Preset = FALSE
 Initial_Wait = 1[s]
 Repetition_Time = 3.68365952[s]



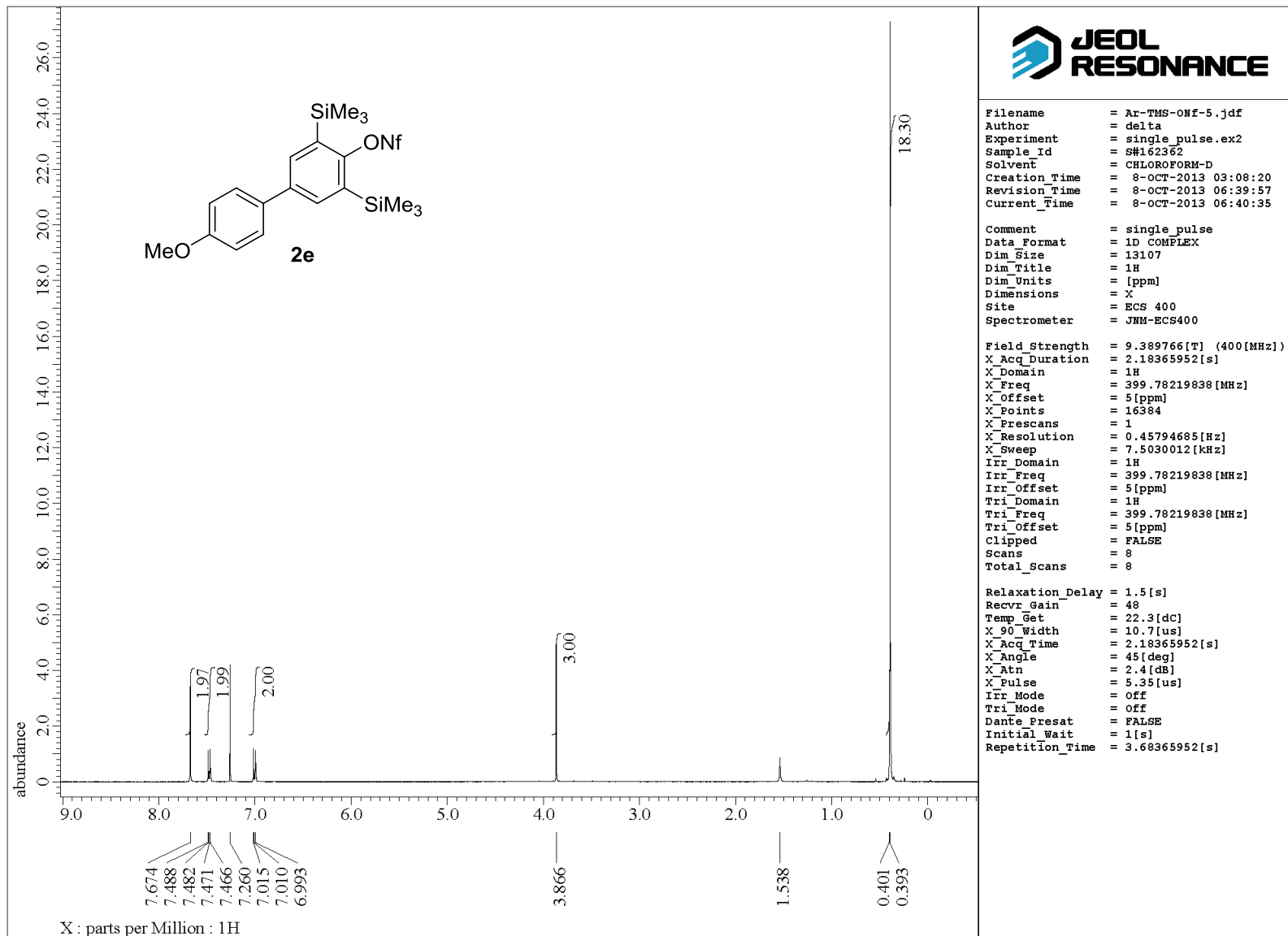
```

Filename      = TMSTMSIONf-9.jdf
Author       = delta
Experiment   = single_pulse_dec
Sample_Id    = 1
Solvent      = CHLOROFORM-D
Creation_Time = 19-NOV-2013 12:08:32
Revision_Time = 19-NOV-2013 21:24:13
Current_Time  = 19-NOV-2013 21:25:12

Comment      = single pulse decoupled g
Data_Format  = 1D COMPLEX
Dim_Size     = 26214
Dim_Title    = 13C
Dim_Units    = [ppm]
Dimensions   = X
Site         = ECS 400
Spectrometer = JNM-ECS400

Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain       = 13C
X_Freq         = 100.52530333 [MHz]
X_Offset       = 100 [ppm]
X_Points       = 32768
X_Prescans     = 4
X_Resolution   = 0.95846665 [Hz]
X_Sweep        = 31.40703518 [kHz]
Irr_Domain     = 1H
Irr_Freq       = 399.78219838 [MHz]
Irr_Offset     = 5 [ppm]
Clipped        = FALSE
Scans          = 382
Total_Scans    = 382

Relaxation_Delay = 2[s]
Recvr_Gain       = 50
Temp_Get        = 19.9 [dC]
X_90_Width      = 9.5 [us]
X_Acq_Time      = 1.04333312[s]
X_Angle         = 30 [deg]
X_Atn           = 4 [dB]
X_Pulse         = 3.16666667 [us]
Irr_Atn_Dec     = 23 [dB]
Irr_Atn_Hoe     = 23 [dB]
Irr_Noise       = WALTZ
Decoupling      = TRUE
Initial_Wait    = 1[s]
Noe              = TRUE
Noe_Time        = 2[s]
Repetition_Time = 3.04333312[s]
  
```



```

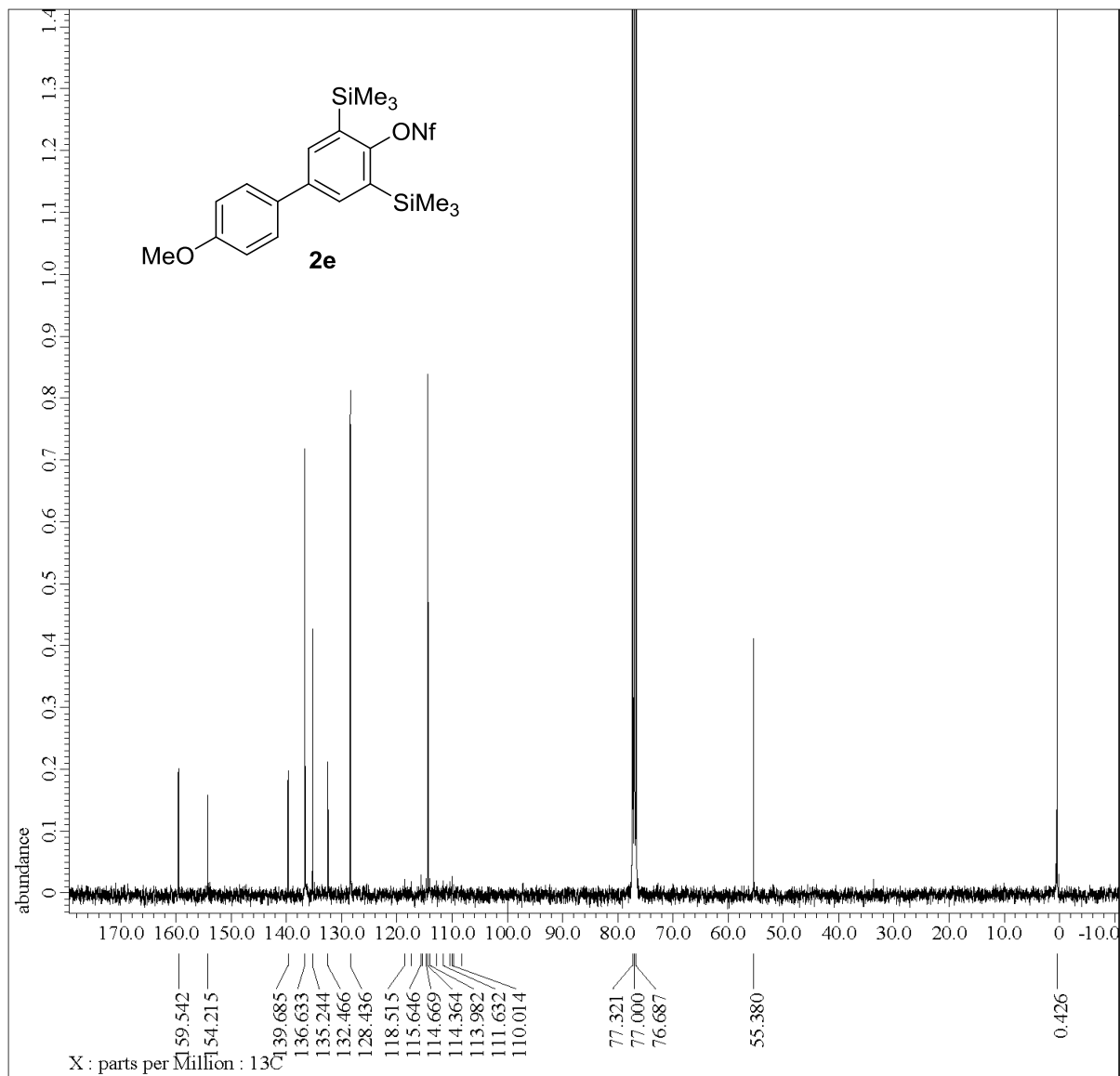
Filename      = Ar-TMS-ONf-5.jdf
Author       = delta
Experiment    = single_pulse.ex2
Sample_Id    = S#162362
Solvent      = CHLOROFORM-D
Creation_Time = 8-OCT-2013 03:08:20
Revision_Time = 8-OCT-2013 06:39:57
Current_Time  = 8-OCT-2013 06:40:35

Comment      = single_pulse
Data Format   = 1D COMPLEX
Dim_Size     = 13107
Dim_Title    = 1H
Dim_Units    = [ppm]
Dimensions   = X
Site         = ECS 400
Spectrometer = JNM-ECS400

Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 2.18365952[s]
X_Domain       = 1H
X_Freq         = 399.78219838[MHz]
X_Offset       = 5[ppm]
X_Points       = 16384
X_Prescans     = 1
X_Resolution   = 0.45794685[Hz]
X_Sweep        = 7.5030012[kHz]
Irr_Domain     = 1H
Irr_Freq       = 399.78219838[MHz]
Irr_Offset     = 5[ppm]
Tri_Domain     = 1H
Tri_Freq       = 399.78219838[MHz]
Tri_Offset     = 5[ppm]
Clipped        = FALSE
Scans          = 8
Total_Scans    = 8

Relaxation_Delay = 1.5[s]
Recvr_Gain       = 48
Temp_Get         = 22.3[dc]
X_90_Width      = 10.7[us]
X_Acq_Time      = 2.18365952[s]
X_Angle         = 45[deg]
X_Atn           = 2.4[db]
X_Pulse         = 5.35[us]
Irr_Mode        = Off
Tri_Mode        = Off
DanE_Presat     = FALSE
Initial_Wait    = 1[s]
Repetition_Time = 3.68365952[s]

```



```

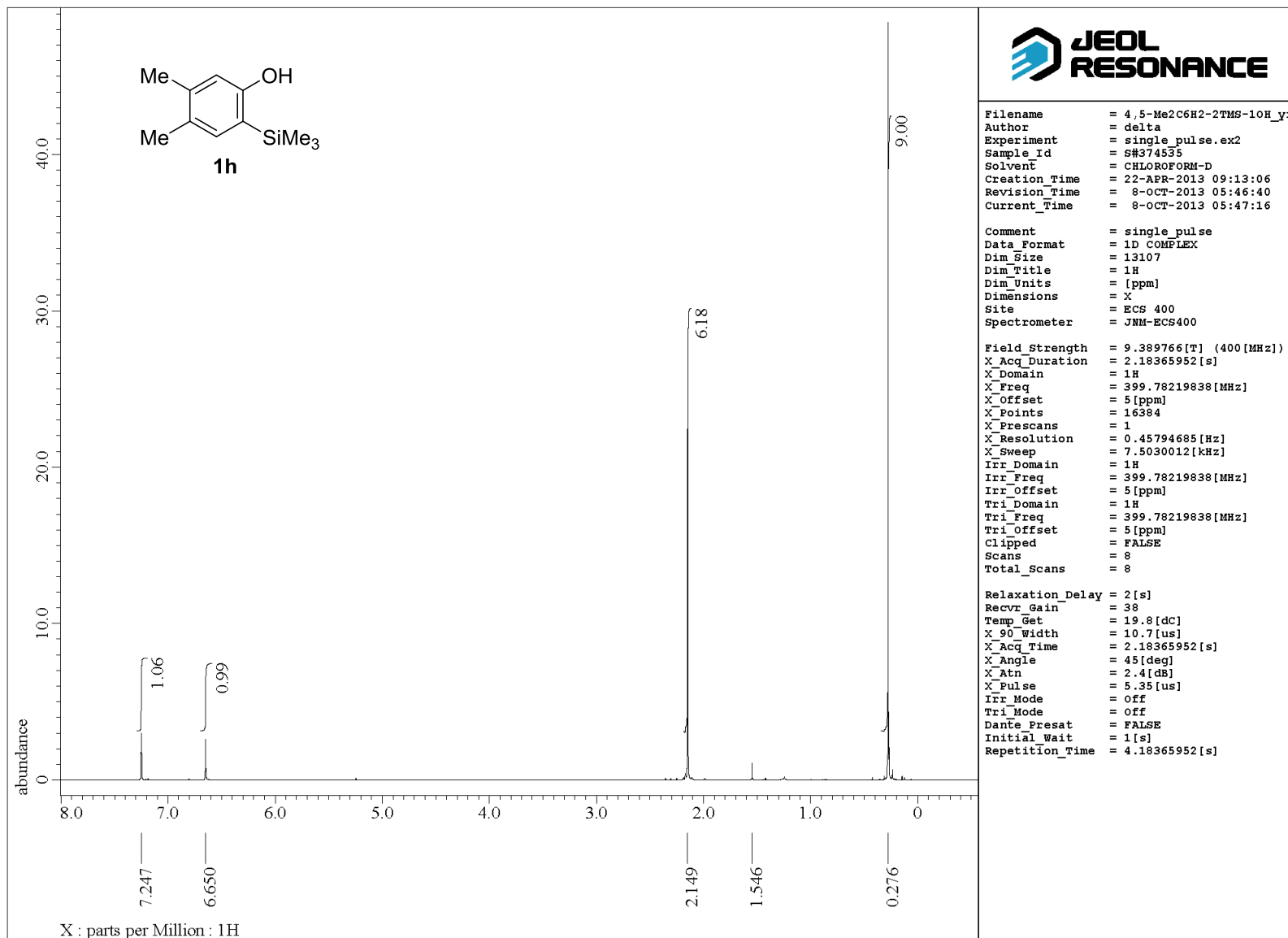
Filename      = Ar-TMS-ONf-13C-5.jdf
Author       = delta
Experiment   = single_pulse_dec
Sample_Id    = 1
Solvent      = CHLOROFORM-D
Creation_Time = 8-OCT-2013 06:36:46
Revision_Time = 8-OCT-2013 08:29:57
Current_Time = 8-OCT-2013 08:30:52

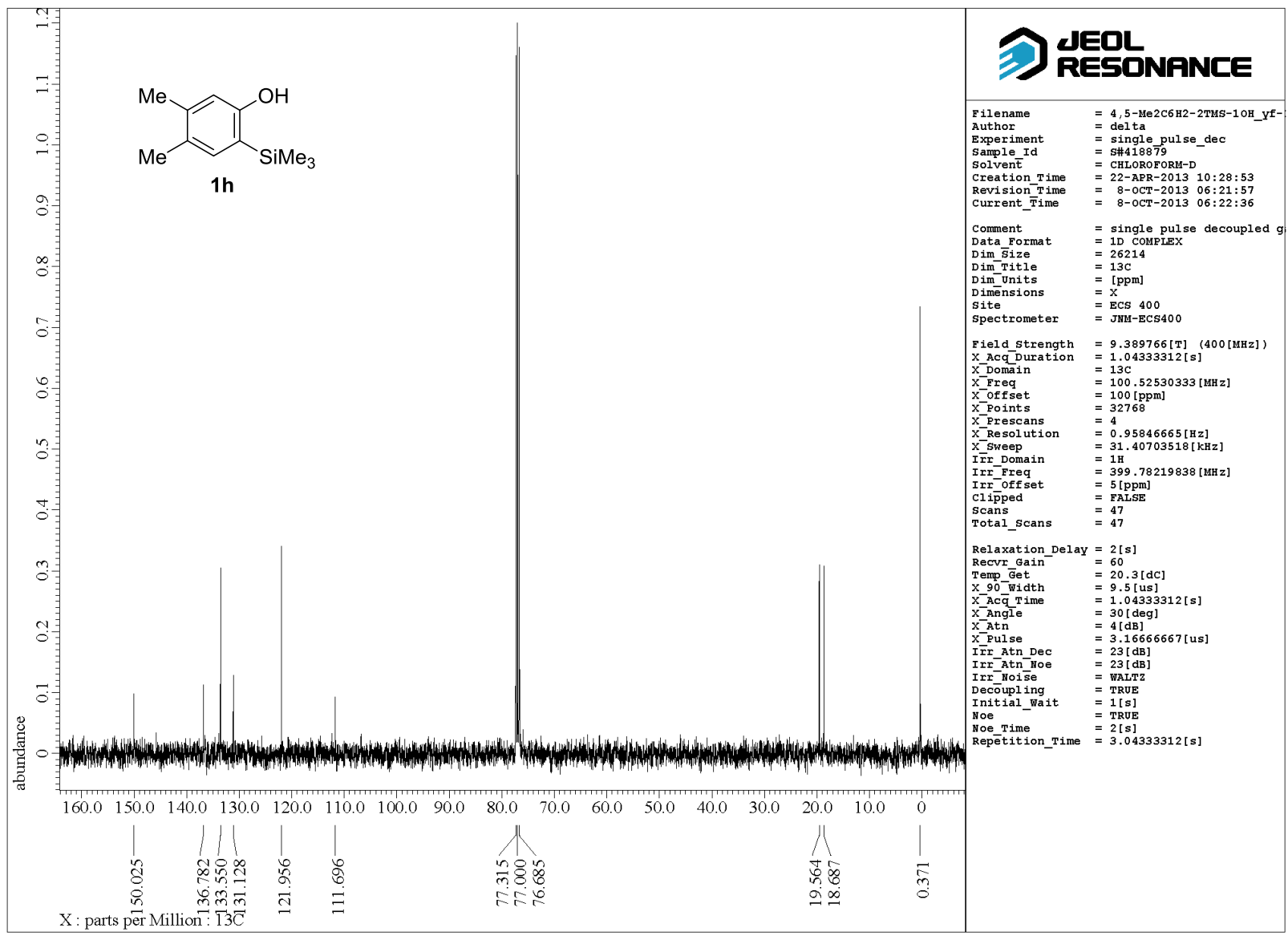
Comment      = single pulse decoupled g
Data_Format  = 1D_COMPLEX
Dim_Size     = 32768
Dim_Title    = 13C
Dim_Units    = [ppm]
Dimensions   = X
Site         = ECS 400
Spectrometer = JNM-ECS400

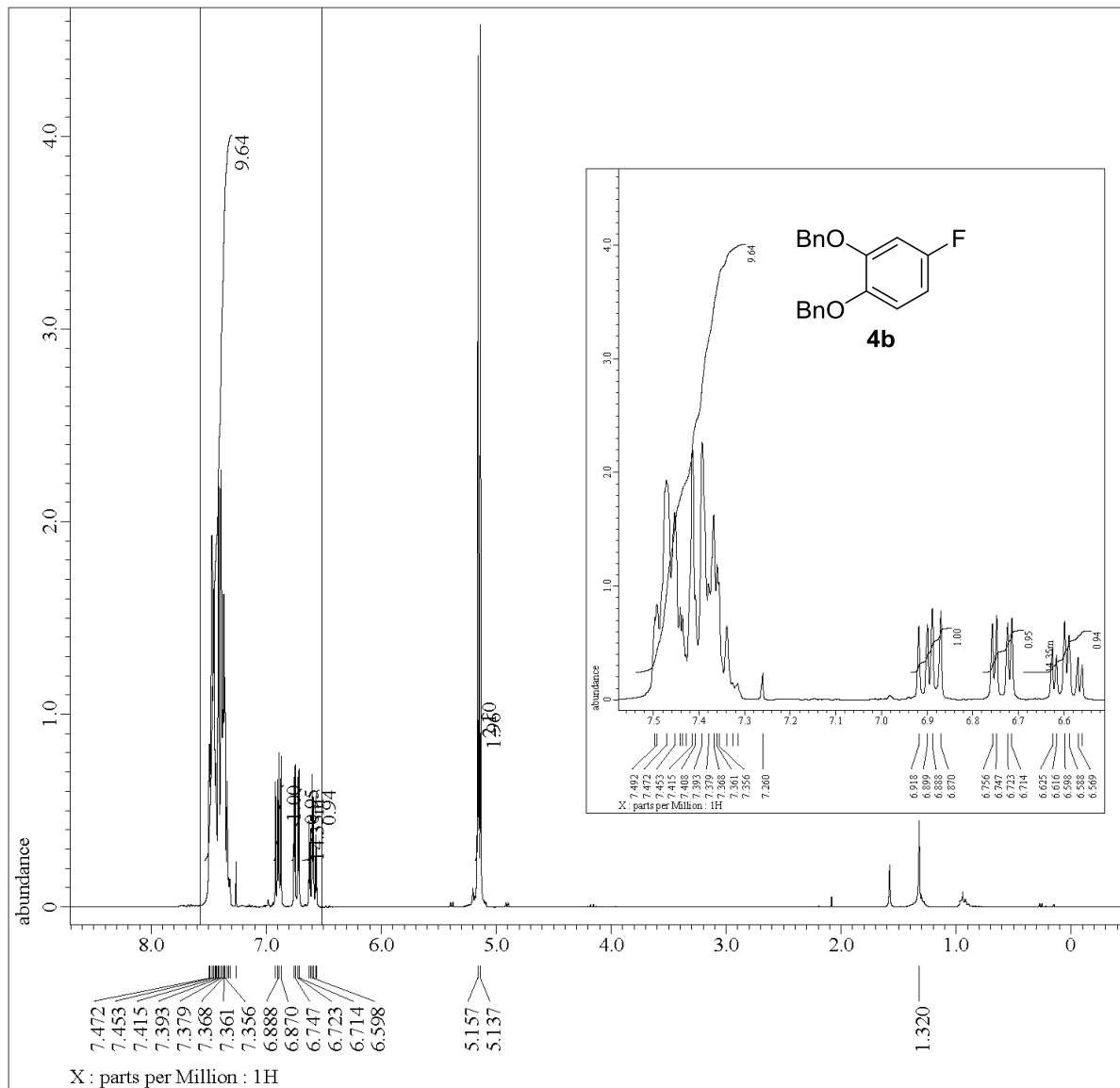
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.30351104[s]
X_Domain       = 13C
X_Freq         = 100.52530333[MHz]
X_Offset       = 100[ppm]
X_Points       = 32768
X_Prescans     = 4
X_Resolution   = 0.76715883[Hz]
X_Sweep        = 25.13826043[kHz]
Irr_Domain     = 1H
Irr_Freq       = 399.78219838[MHz]
Irr_Offset     = 5[ppm]
Clipped        = FALSE
Scans          = 1000
Total_Scans    = 1000

Relaxation_Delay = 2[s]
Recvr_Gain       = 72
Temp_Get         = 22.4[dc]
X_90_Width       = 9.5[us]
X_Acq_Time       = 1.30351104[s]
X_Angle          = 30[deg]
X_Atn            = 4[dB]
X_Pulse          = 3.16666667[us]
Irr_Atn_Dec      = 23[dB]
Irr_Atn_Hoe      = 23[dB]
Irr_Noise        = WALTZ
Decoupling       = TRUE
Initial_Wait     = 1[s]
Noe              = TRUE
Noe_Time         = 2[s]
Repetition_Time  = 3.30351104[s]

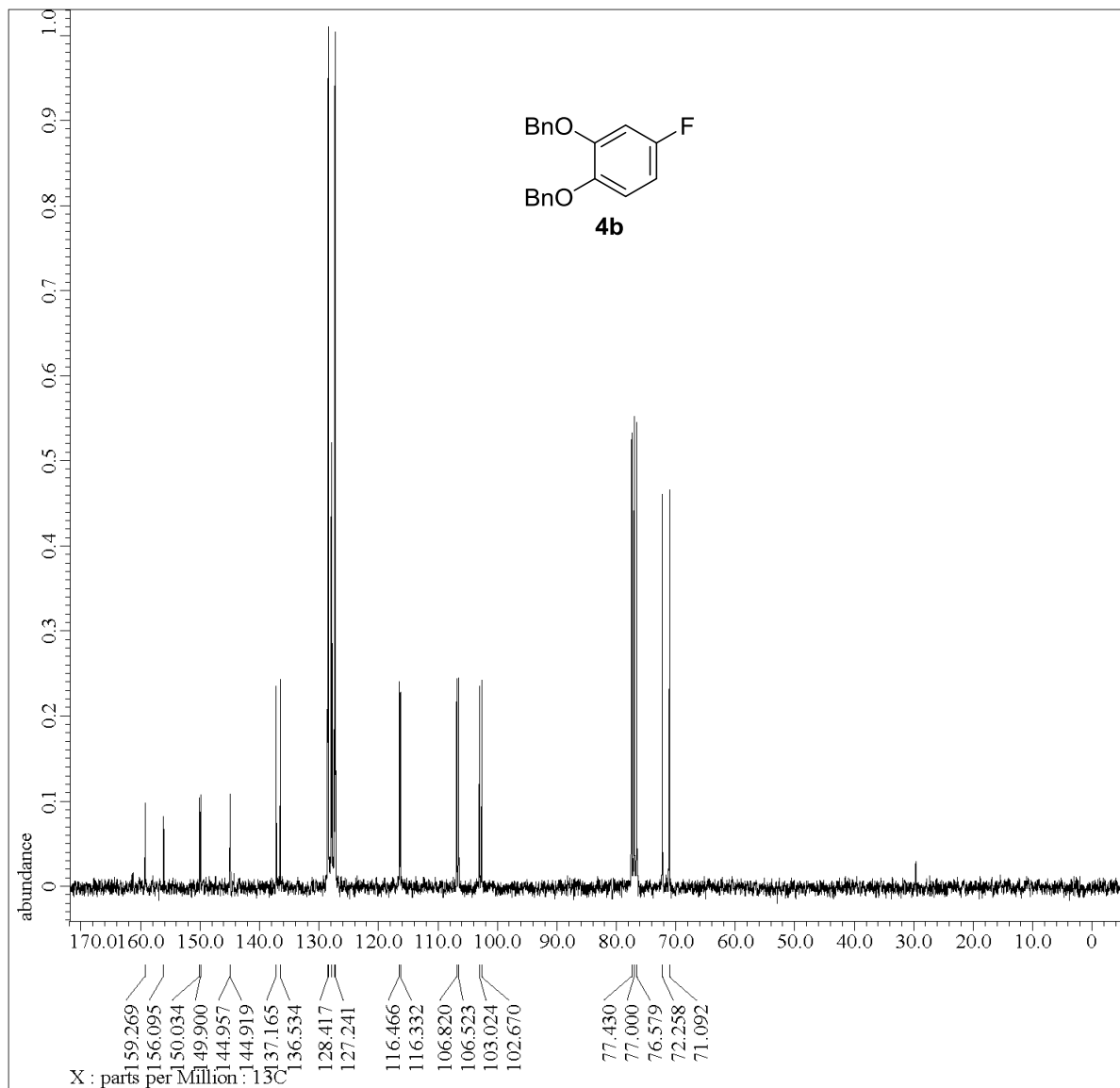
```





Filename = Ymsd01-197-02-34.jdf
 Author = delta
 Experiment = single_pulse.ex2
 Sample_Id = 1
 Solvent = CHLOROFORM-D
 Creation_Time = 8-OCT-2013 13:25:44
 Revision_Time = 8-OCT-2013 20:22:16
 Current_Time = 8-OCT-2013 20:23:50
 Comment = single_pulse
 Data_Format = 1D REAL
 Dim_Size = 13107
 Dim_Title = 1H
 Dim_Units = [ppm]
 Dimensions = X
 Site = ECS 300
 Spectrometer = JNM-ECS300
 Field_Strength = 7.0586013 [T] (300 [MHz])
 X_Acq_Duration = 2.90717696 [s]
 X_Domain = 1H
 X_Freq = 300.52965592 [MHz]
 X_Offset = 5 [ppm]
 X_Points = 16384
 X_Prescans = 1
 X_Resolution = 0.34397631 [Hz]
 X_Sweep = 5.63570784 [kHz]
 Irr_Domain = 1H
 Irr_Freq = 300.52965592 [MHz]
 Irr_Offset = 5 [ppm]
 Tri_Domain = 1H
 Tri_Freq = 300.52965592 [MHz]
 Tri_Offset = 5 [ppm]
 Clipped = FALSE
 Scans = 8
 Total_Scans = 8
 Relaxation_Delay = 1.5 [s]
 Recvr_Gain = 30
 Temp_Get = 23 [dC]
 X_90_Width = 11.1 [us]
 X_Acq_Time = 2.90717696 [s]
 X_Angle = 45 [deg]
 X_Atn = 1 [dB]
 X_Pulse = 5.55 [us]
 Irr_Mode = off
 Tri_Mode = off
 DanE_Presat = FALSE
 Initial_Wait = 1 [s]
 Repetition_Time = 4.40717696 [s]



```

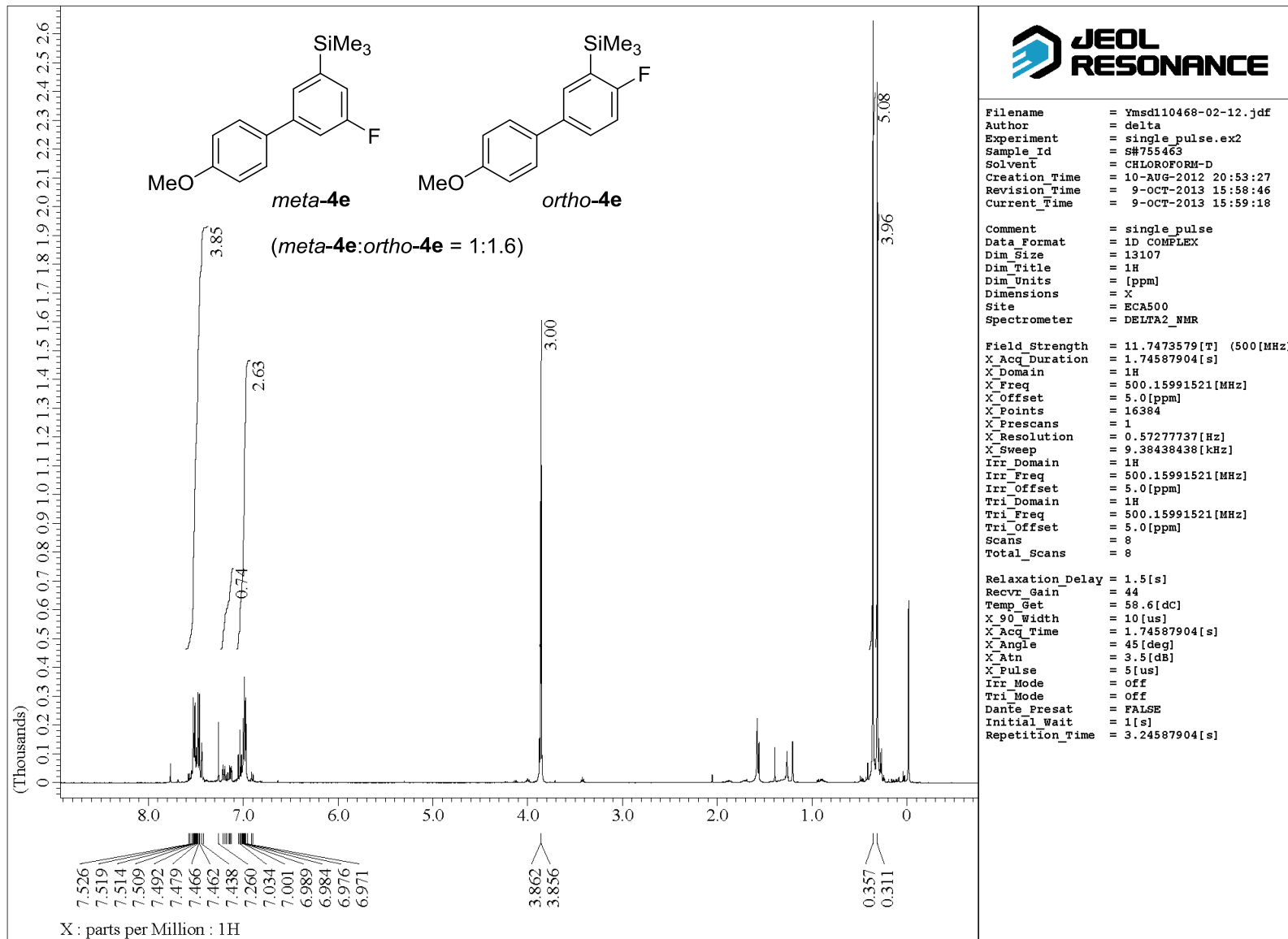
Filename      = Ymsd01-197-02c-8.jdf
Author       = delta
Experiment    = single_pulse_dec
Sample Id    = 1
Solvent      = CHLOROFORM-D
Creation Time = 8-OCT-2013 13:34:23
Revision Time = 8-OCT-2013 20:35:30
Current Time  = 8-OCT-2013 20:35:59

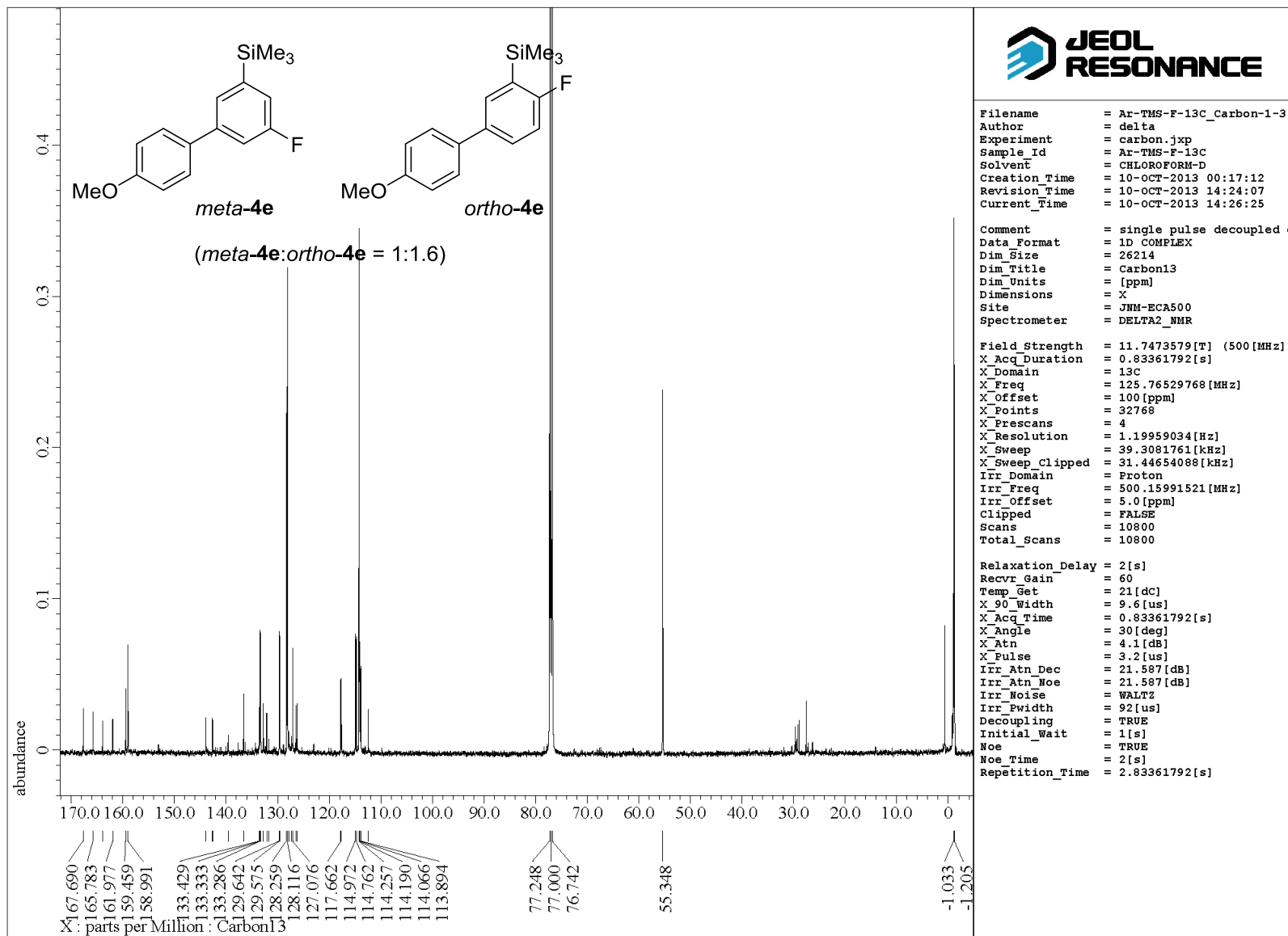
Comment      = single pulse decoupled g
Data Format   = 1D COMPLEX
Dim Size     = 26214
Dim Title    = 13C
Dim Units    = [ppm]
Dimensions   = X
Site         = ECS 300
Spectrometer = JNM-ECS300

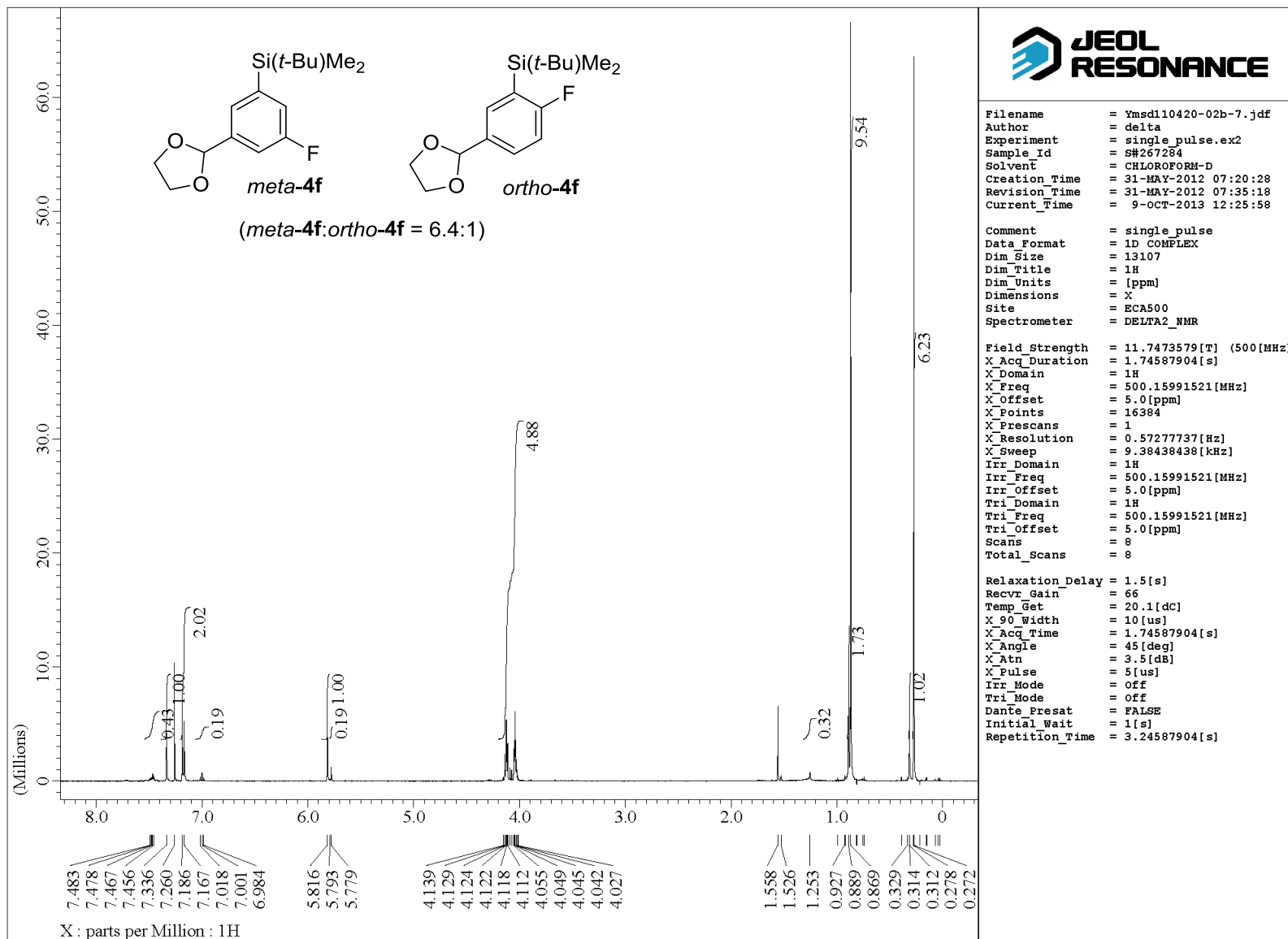
Field Strength = 7.0586013 [T] (300 [MHz])
X_Acq_Duration = 1.38412032 [s]
X_Domain      = 13C
X_Freq        = 75.56823426 [MHz]
X_Offset      = 100 [ppm]
X_Points      = 32768
X_Prescans    = 4
X_Resolution  = 0.72248054 [Hz]
X_Sweep       = 23.67424242 [kHz]
Irr_Domain    = 1H
Irr_Freq      = 300.52965592 [MHz]
Irr_Offset    = 5 [ppm]
Clipped       = FALSE
Scans         = 143
Total_Scans   = 143

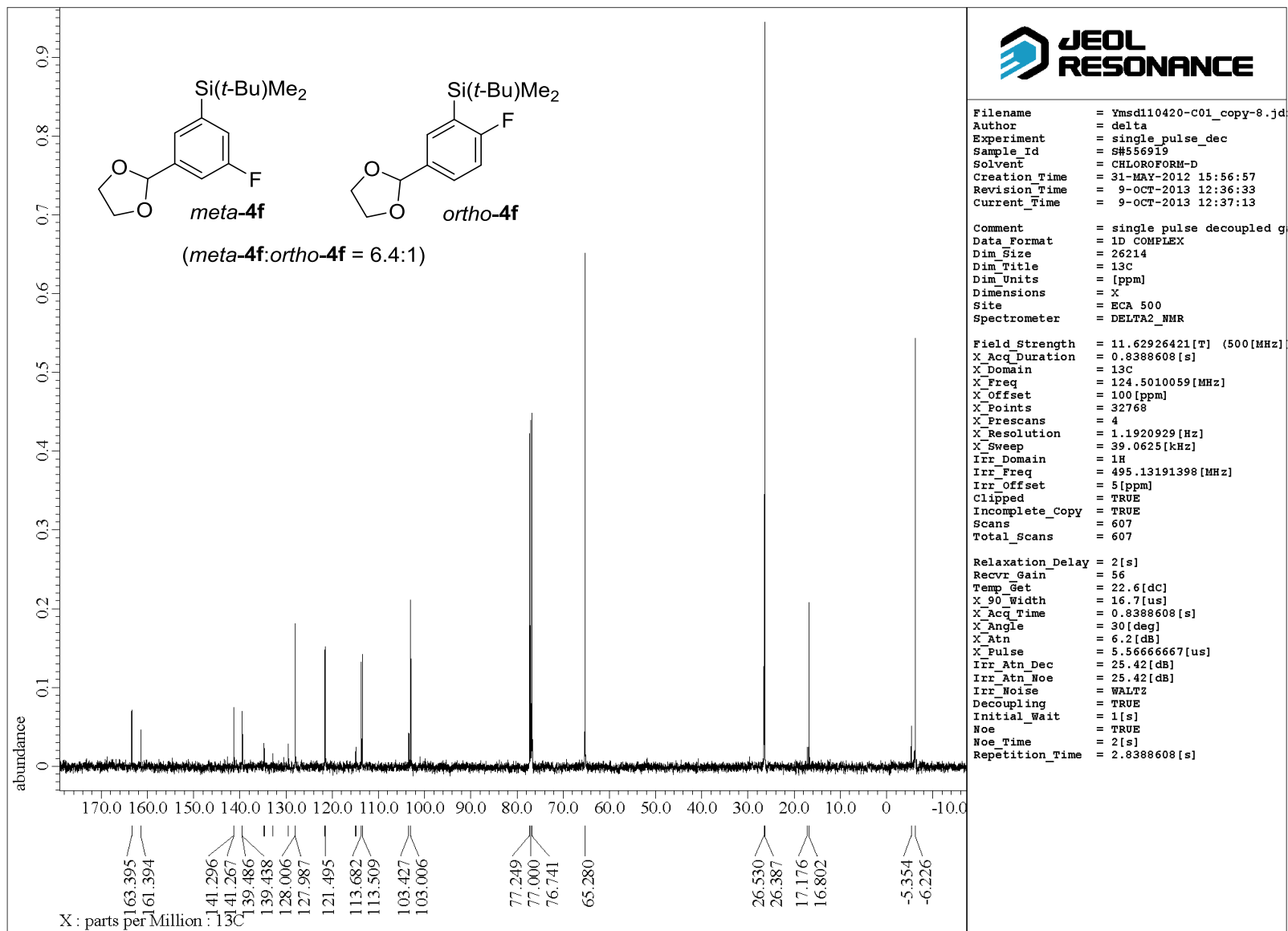
Relaxation_Delay = 2 [s]
Recvr_Gain      = 60
Temp_Get       = 23.2 [dc]
X_90_Width     = 9.4 [us]
X_Acq_Time     = 1.38412032 [s]
X_Angle        = 30 [deg]
X_Atn          = 4.6 [dB]
X_Pulse        = 3.13333333 [us]
Irr_Atn_Dec    = 24.298 [dB]
Irr_Atn_Hoe    = 24.298 [dB]
Irr_Noise     = WALTZ
Decoupling     = TRUE
Initial_Wait   = 1 [s]
Noe            = TRUE
Noe_Time       = 2 [s]
Repetition_Time = 3.38412032 [s]

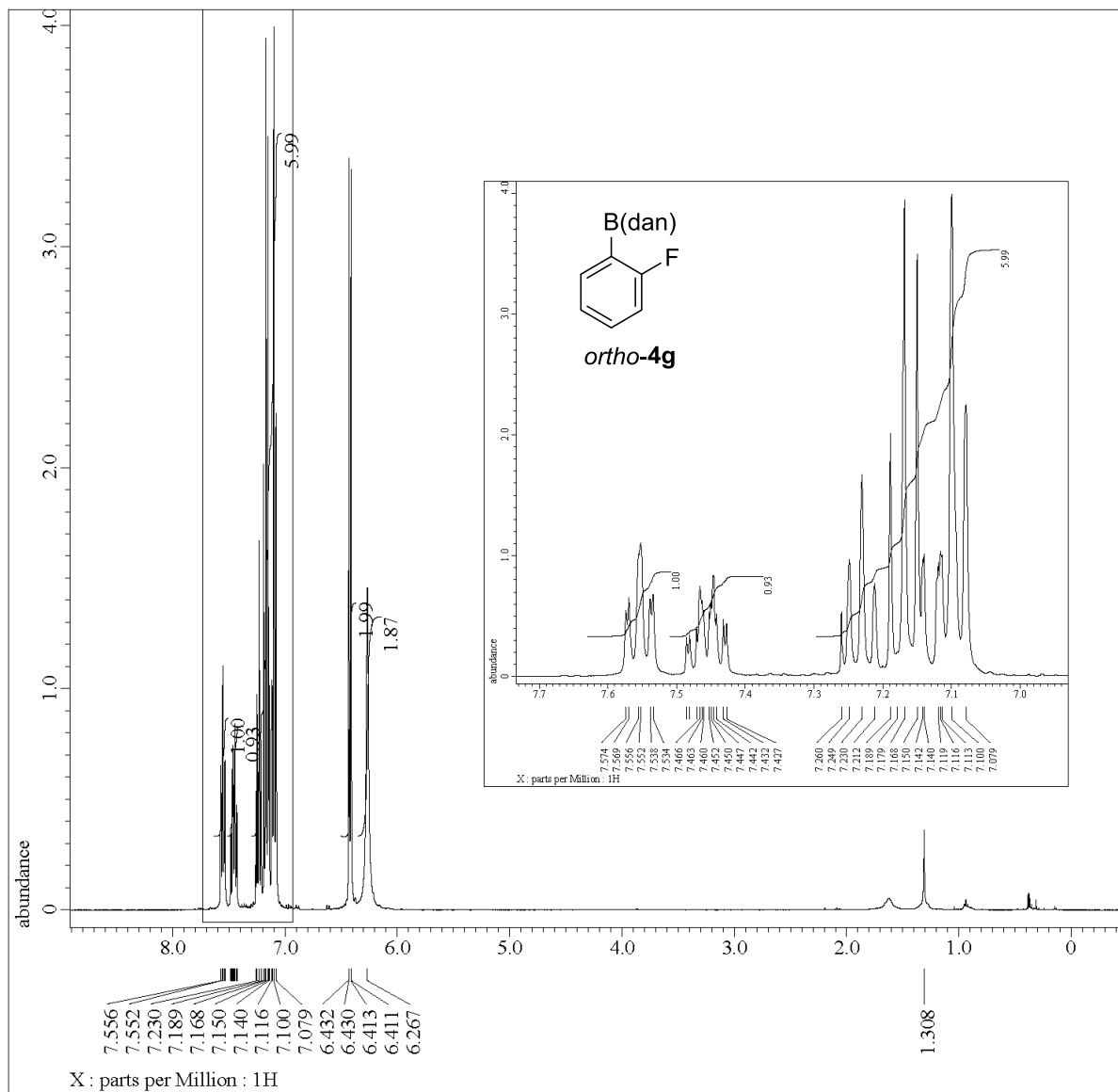
```











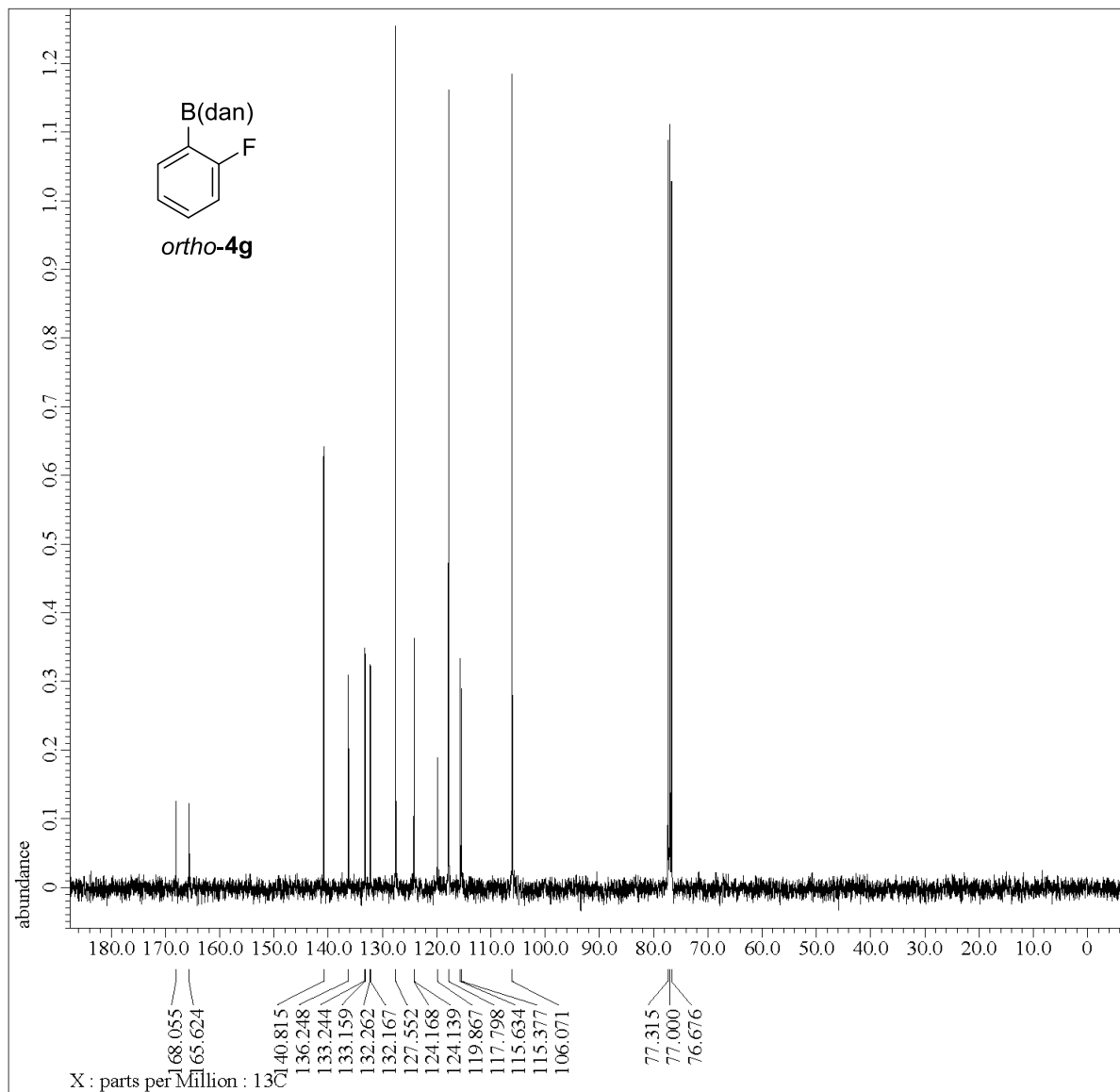
```

Filename      = Ymsd01-196-03-6.jdf
Author       = delta
Experiment   = single_pulse.ex2
Sample_Id    = 1
Solvent      = CHLOROFORM-D
Creation_Time = 8-OCT-2013 13:12:06
Revision_Time = 8-OCT-2013 20:12:32
Current_Time = 8-OCT-2013 20:13:50

Comment      = single_pulse
Data_Format  = 1D COMPLEX
Dim_Size     = 13107
Dim_Title    = 1H
Dim_Units    = [ppm]
Dimensions   = X
Site         = ECS 400
Spectrometer = JNM-ECS400

Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 2.18365952[s]
X_Domain       = 1H
X_Freq         = 399.78219838 [MHz]
X_Offset       = 5 [ppm]
X_Points       = 16384
X_Prescans     = 1
X_Resolution   = 0.45794685 [Hz]
X_Sweep        = 7.5030012 [kHz]
Irr_Domain     = 1H
Irr_Freq       = 399.78219838 [MHz]
Irr_Offset     = 5 [ppm]
Tri_Domain     = 1H
Tri_Freq       = 399.78219838 [MHz]
Tri_Offset     = 5 [ppm]
Clipped        = FALSE
Scans          = 8
Total_Scans    = 8

Relaxation_Delay = 1.5 [s]
Recvr_Gain       = 30
Temp_Get         = 22.5 [dC]
X_90_Width       = 10.7 [us]
X_Acq_Time       = 2.18365952 [s]
X_Angle          = 45 [deg]
X_Atn            = 2.4 [dB]
X_Pulse          = 5.35 [us]
Irr_Mode         = off
Tri_Mode         = off
DanE_Preset     = FALSE
Initial_Wait     = 1 [s]
Repetition_Time = 3.68365952 [s]
  
```



```

Filename      = Ymsd01-196-03C-5.jdf
Author       = delta
Experiment   = single_pulse_dec
Sample_Id    = 1
Solvent      = CHLOROFORM-D
Creation_Time = 8-OCT-2013 13:16:50
Revision_Time = 8-OCT-2013 20:16:08
Current_Time = 8-OCT-2013 20:16:47

Comment      = single pulse decoupled g
Data_Format  = 1D COMPLEX
Dim_Size     = 26214
Dim_Title    = 13C
Dim_Units    = [ppm]
Dimensions   = X
Site         = ECS 400
Spectrometer = JNM-ECS400

Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain       = 13C
X_Freq         = 100.52530333[MHz]
X_Offset       = 100[ppm]
X_Points       = 32768
X_Prescans     = 4
X_Resolution   = 0.95846665[Hz]
X_Sweep        = 31.40703518[kHz]
Irr_Domain     = 1H
Irr_Freq       = 399.78219838[MHz]
Irr_Offset     = 5[ppm]
Clipped        = FALSE
Scans          = 65
Total_Scans    = 65

Relaxation_Delay = 2[s]
Recvr_Gain       = 60
Temp_Get         = 22.7[dc]
X_90_Width      = 9.5[us]
X_Acq_Time      = 1.04333312[s]
X_Angle         = 30[deg]
X_Atn           = 4[db]
X_Pulse         = 3.16666667[us]
Irr_Atn_Dec     = 23[db]
Irr_Atn_Hoe     = 23[db]
Irr_Noise       = WALTZ
Decoupling      = TRUE
Initial_Wait    = 1[s]
Noe              = TRUE
Noe_Time        = 2[s]
Repetition_Time = 3.04333312[s]
  
```