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Supplementary Information

Epoc group: transformable protecting group with gold(III)-catalyzed fluorene formation

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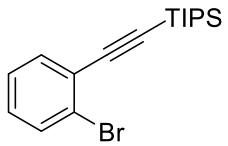
1. Synthetic protocols and characterizations

1.1 Material

All reagents were purchased from Sigma-Aldrich (St. Louis, MO, USA), Kanto Chemical Co. Inc. (Tokyo, Japan), Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan), FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan) or Watanabe Chemical Industries (Hiroshima, Japan) without further purification. Experiments dealing with air- and moisture-sensitive compounds were conducted under an atmosphere of dry nitrogen. TLC analyses (F-254) were performed with 60 Å silica gel from Merck. ^{1}H and ^{13}C NMR spectra were measured on a JEOL (AL400 400 MHz) instrument with the solvent peaks as internal standards: 7.26 and δC 77.16 for $CDCl_3$, δH 3.31 and δC 49.0 for CD_3OD, δH 2.50 and δC 39.52 for DMSO-d_6, δH 2.05 and δC 29.84 for Acetone-d_6. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quin= quintet, m = multiplet, br = broad. For ^{13}C NMR, the chemical shift shown with [] is the multiple peaks from same carbons derived from diastereomers. High-resolution mass spectra (HRMS) were obtained on a Bruker MicroTOF-QIII spectrometer® by electron spray ionization time-of-flight (ESI-TOF-MS).

1.2 Synthesis of Epoc-introducing reagents

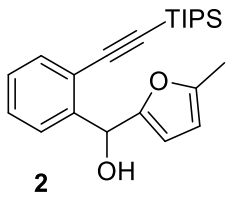


1'

Compound **1'**

To a stirred suspension of 1-bromo-2-iodobenzene (2.21 mL, 17.7 mmol, 1.0 Eq), copper(I) iodide (336.6 mg, 1.77 mmol, 0.1 Eq) and Bis(triphenylphosphine)palladium(II) dichloride (620.3 mg, 0.884 mmol, 0.05 Eq) in THF/Et_3N =1/1 (degassed by performing four freeze-pump-thaw cycles) was added (triisopropylsilyl)acetylene (5.90 mL, 26.5 mmol, 1.5 Eq). The mixture was stirred at room temperature for 1 hour and filtered with Celite. The obtained filtrate was evaporated in a vacuum. The product was purified via flash column chromatography (SiO_2, Hexane 100%) to yield compound **1'** as a colorless oil (7.66 g, quant.).

Compound **1'**: R_f= 0.70 (Hexane/EtOAc =9/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (1H, dd, *J*=8.0, 1.2 Hz), 7.50 (1H, dd, *J*=8.0, 1.6 Hz), 7.24 (1H, td, *J* =8.0, 1.2 Hz), 7.15 (1H, td, *J*= 8.0, 1.6 Hz), 1.16 (brs, 21H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.0, 132.5, 129.5, 127.0, 125.9, 125.8, 104.9, 96.3, 18.8, 11.4.

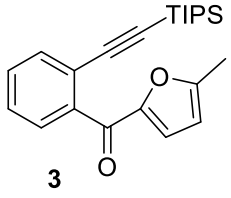


2

Compound **2**

To a stirred solution of compound **1'** (17.7 mmol) in THF (45 mL) was added *n*BuLi (12.4 mL, 1.57 M in Hexane, 19.4 mmol, 1.1 Eq) at -78 °C. The mixture solution was stirred for 1.5 hour at -78 °C, and 5-methyl2-furaldehyde (1.93 mL, 19.4 mmol, 1.1 Eq) was subsequently added. The mixture was warmed to room temperature and stirred for 1 hour. Saturated aqueous NH_4Cl was added to the mixture. The product was extracted to Et_2O. Organic layer was washed with brine, dried over Na_2SO_4, filtered and concentratedin vacuo. The product was purified via flash column chromatography (SiO_2, EtOAc: Hex 0:100 ~ 4:96) to yield compound **2** as a yellow oil (5.84 g, 15.83 mmol, 90% in 2 steps).

Compound **2**: R_f =0.60 (Hexane/EtOAc= 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (1H, d, *J*=7.6 Hz), 7.49 (1H, dd, *J*= 7.6, 1.2 Hz), 7.37 (1H, td, *J*=7.6, 1.2 Hz), 7.26 (1H, td. *J*= 7.6, 1.2 Hz), 6.24 (1H, d, *J*= 5.2 Hz), 5.84 (1H, dd, *J*= 3.2, 0.8 Hz), 5.81 (1H, d, *J*= 3.2 Hz), 2.70 (1H, d, *J* =5.2 Hz), 2.26 (3H, s), 1.08 (21H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 152.3, 143.0, 133.0, 128.8, 127.6, 126.5, 121.7, 108.9, 106.3, 104.4, 96.7, 68.6, 18.7, 13.7, 11.3; **HRMS** (ESI, pos): calcd. for $C_{23}H_{32}NaO_2Si$ $[M+Na]^+$: 391.2064 found: 391.2058.

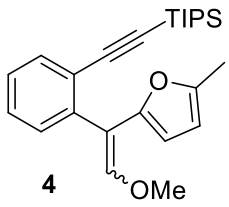


3

Compound **3**

To a stirred solution of compound **2** (5.54 g, 15.0 mmol) in EtOAc (50 mL) was added 2-iodoxybenzoic acid (12.9 g, 18.0 mmol, 39 wt% purity, 1.2 Eq). The mixture was heated to 70 °C and stirred for 3.5 h. After cooled to room temperature, the mixuture was filtered with Celite and the filtrate was evaporated. The obtained product was purified via flash column chromatography (SiO_2, EtOAc: Hex 1:99~5:95) to yield compound 3 as a yellow oil (4.58 g, 12.5 mmol, 83%).

Compound **3**: R_f =0.36 (Hexane/EtOAc= 9/1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (1H, d, *J* =8.0, 1.6 Hz), 7.46-7.36 (3H, m), 6.89 (1H, d, *J*= 3.6 Hz), 6.14 (1H, dd *J* =3.6, 0.8 Hz), 2.40 (3H, s), 0.99 (21H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.3, 159.3, 151.2, 141.8, 133.4, 130.0, 128.3, 127.8, 124.2, 121.8, 109.5, 104.2, 96.5, 18.6, 14.2, 11.3; **HRMS** (ESI, pos): calcd. for $C_{23}H_{31}O_2Si$ $[M+H]^+$: 367.2088 found: 367.2088.



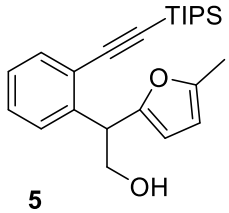
4

Compound **4**

To a stirred suspension of (methoxymethyl)triphenylphosphonuium chloride (4.71 g, 13.7 mmol, 3.4 Eq) in THF (7.0 mL) was added pottasium *tert*-butoxide solution in THF (13.7 mL, 1.0 M in THF, 13.7mmol, 3.4 Eq) at 0 °C. The mixture was warmed to room temperature and stirred for 2 hours. Compound **3** (1.48 g, 4.04 mmol)in THF (3.0 mL) was subsequently added to the mixture. The mixture was stirred for 10 min at room temperature. Water was added to the mixture and product was extracted to CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered and evaporated in a vacuum. The obtained product was purified via flash column chromatography (SiO_2, EtOAc:Hexane 0:100~3:97) to yield compound **4** as a brown oil (1.54 g, 3.91 mmol, 97%, *E/Z* mixture).

Compound **4**: R_f =0.63 (Hexane /EtOAc =9/1);**^{1}H NMR** (400 MHz, $CDCl_3$)* δ 7.53 (1H ×2, m), 7.35-7.21 (3H ×2, m), 6.82 (1H, s), 6.36 (1H, d, *J*= 3.2 Hz), 6.13 (1H, s), 5.95 (1H, dd, *J*= 3.2, 0.8 Hz), 5.82 (1H, dd, *J* =3.2, 1.2 Hz), 5.45 (1H, d, *J*= 3.2 Hz), 3.80 (3H, s), 3.67 (3H, s), 2.26 (3H, s), 2.19 (3H, s), 1.02 (21H ×2, s); **^{13}C NMR** (100 MHz, $CDCl_3$)* δ 151.6, 150.0, 150.8, 149.5, 139.6, 138.2, 134.0, 133.8, 133.2, 133.0, 131.1, 130.8, 128.3, 128.1, 127.4, 127.0, 112.0. 111.0, 109.7, 107.3, 107.1, 106.4, 106.3, 105.9, 93.5, 93.0, 60.8, 60.7, 18.7, 18.7, 13.8, 13.7, 11.6, 11.4; **MS** (ESI, pos): calcd. for $C_{25}H_{35}O_2Si$ $[M+H]^+$: 395.24 found: 395.24.

*Because compound **4** was unstable, several peaks derived from decomposition was observed in ^{1}H NMR and ^{13}C NMR whose intensity increases with longer experiment time.



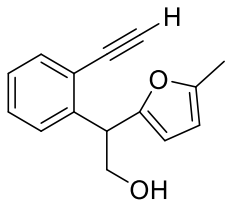
5

Compound **5**

To a stirred solution of compound **4** (310.2 mg 786.1 µmol) in acetone and water (9:1, 6.0 mL) was added 25 wt% hydrogen bromide-acetic acid solution (294 µL, 1180 µmol, 1.5 Eq). The mixture was gradually heated to 50 °C over 1 hour and stirred for 6 hours. Additional hydrogen bromide-acetic acid solution (100 µL, 401 µmol, 0.51 Eq) was added to the mixture, and the mixture was stirred at 50 °C for 1 hour. After cooled to room temperature, the mixture was quenched with saturated aqueous $NaHCO_3$ and the product was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, and evaported in a vacuum. The obtained aldehyde was unstable thus the next reaction was performed without further purification.

The obtained aldehyde (786.1 µmol) was dissolved in THF and MeOH (1:1, 8.0mL), and $NaBH_4$ (59.5 mg, 1570 µmol, 2.0 Eq) was added. The miture was stirred for 10 min at room temperature, and quenched with saturated aqueous NH_4Cl. The product was extracted with CH_2Cl_2. Organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, EtOAc:Hexane 0:100~4:96) to obtain compound **5** as brown oil (113.8 mg, 297.4 µmol, 38% for 2 steps).

Compound **5**: R_f =0.61 (Hexane/EtOAc 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (1H, d, *J*= 7.6 Hz), 7.30-7.17 (3H, m), 6.08 (1H, d, *J*= 3.2 Hz), 5.92 (1H, dd, *J*=3.2, 0.8 Hz), 4.90 (1H, t, *J*=2.8 Hz), 4.09 (2H, m), 2.27 (3H, s), 1.65 (1H, t, *J*=3.2 Hz), 1.15 (21H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) 152.7, 151.6, 141.6, 133.3, 128.8, 127.7, 126.9, 123.5, 108.1, 106.2, 105.1, 95.7, 65.0, 45.8, 18.8, 13.7, 11.5; **HRMS** (ESI, pos): calcd. for $C_{24}H_{34}NaO_2Si$ $[M+Na]^+$: 405.2220 found: 405.2226.

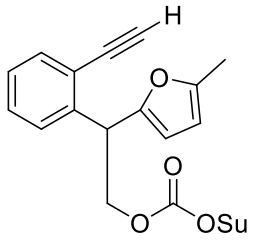


EpOH **6**

EpOH **6**

To a stirred solution of compound **5** (113.8 mg, 297.4 µmol) in THF (8.0 mL) was added 1.0 M solution of tetra-*n*-butylammonium fluoride in THF (327 µL, 327.0 µmol, 1.1 Eq) at 0 °C. The mixture was stirred for 5 min at 0 °C, and subsequently quenched with water. The product was extracted with CH_2Cl_2. Obtained organic layer was dried over Na_2SO_4, filtered and evaporated in a vacuum. The product was purified via flash column chromatography (SiO_2, EtOAc/Hexane 1:9) to yield EpOH **6** as brown oil (58.9 mg, 260.3 µmol, 88%).

Compound **6**: R_f =0.33 (Hexane/EtOAc 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) 7.53 (1H, dd, *J*=7.6, 0.8 Hz), 7.33-7.25 (2H, m), 7.21 (1H, td, *J*= 7.6, 2.0 Hz), 6.08 (1H, d, *J*=2.8 Hz), 5.92 (1H, dd, *J*= 2.8, 0.8 Hz), 4.84 (1H, t *J*=6.8 Hz), 4.13-4.00 (2H, m), 3.32 (1H, s), 2.27 (3H, s), 1.74 (1H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 151.7, 141.9, 133.3, 129.3, 127.8, 127.0, 122.1, 108.2, 106.3, 81.9, 81.9, 65.1, 45.7, 13.7; **HRMS** (ESI, pos): calcd. for $C_{15}H_{14}NaO_2$ $[M+Na]^+$: 249.0886 found: 249.0888.



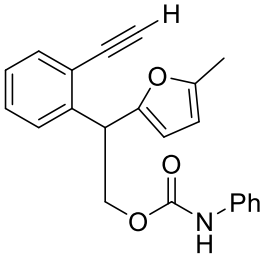
EpocOSu **7**

EpocOSu **7**

To a stirred solution of compound **6** (24.9 mg, 110 µmol) in CH_3CN (1.5 mL) was added *N,N'*-disuccinimidyl carbonate (84.6 mg, 330 µmol, 3.0 Eq) and triethylamine (46.0 µL, 330 µmol, 3.0 Eq). The mixture was stirred at room temperature for 14 hours, and subsequently quenched with 0.2 M aqueous HCl. The product was extracted to CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered and evaporated in a vacuum. The product was purified via flash column chromatography (SiO_2, EtOAc:Hexane 2:10~2:5) to yield EpocOSu **7** as a colorless oil (36.4 mg, 99.1 µmol, 90%).

Compound **7**: R_f=0.37 (Hexane/EtOAc 1/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (1H, d, *J*= 7.6 Hz), 7.33 (1H, td, *J*=7.6, 1.2 Hz), 7.26-7.22 (2H, m), 6.07 (1H, d, *J*=3.2 Hz), 5.91 (1H, dd, *J*=3.2, 1.2 Hz), 5.06 (1H, t, *J*= 7.2 Hz), 4.81 (1H, dd, *J*= 10.4, 7.2 Hz), 4.71 (1H, dd, *J*= 10.4, 7.2 Hz), 3.38 (1H, s), 2.78 (4H, s), 2.26 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 152.1, 151.4, 150.3, 140.1, 133.3, 129.4, 127.9, 127.5, 122.1, 108.6, 106.4, 82.6, 81.3, 71.6, 41.9, 25.6, 13.7; **MS** (ESI, pos): calcd. for $C_{20}H_{17}NNaO_6$ $[M+Na]^+$: 390.09 found: 390.11.

1.3 Introduction and deprotection Epoc group

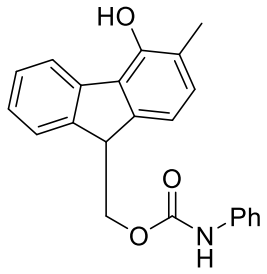


8

Compound **8**

To a sttired solution of EpOH **6** (15.9 mg, 70.3 µmol) in CH_2Cl_2 (2.0 mL) was added triethylamine (23.0 µL, 210.8 µmol, 3.0 Eq) and phenyl isocyanate (29.4 µL, 210.8 µmol, 3.0 Eq). The mixture was stirred at room temperature for 1 hour and subsequently quenched with water. The product was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered and evaporated in a vacuum. The product was purified via flash column chromatography (SiO_2, EtOAc:Hexane 0:1~4:96) to yield comopund **9** as a amorphous white solid (24.2 mg, 70.1 µmol, 99%).

Compound **8**: R_f =0.60 (Hexane/EtOAc 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (1H, dd, *J* =7.6, 1.2 Hz), 7.35-7.27 (6H, m), 7.23 (1H, td, =7.2, 2.0 Hz), 7.05 (1H, m), 6.55 (1H, brs), 6.07 (1H, d, *J*=2.8 Hz), 5.90 (1H, dd, *J*=2.8, 1.2 Hz), 5.02 (1H, t, *J*=7.6 Hz), 4.74 (1H, dd, *J*=11.2, 7.6 Hz), 4.54 (1H, dd, *J*=11.2, 7.6 Hz), 3.31 (1H, s), 2.25 (3H, d, *J*=1.2 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 151.7, 151.7, 141.5, 137.9, 133.2, 129.3, 129.2, 127.8, 127.1, 123.6, 122.2, 118.8, 107.9, 106.2, 82.0, 81.7, 66.2, 42.3, 13.7; **HRMS** (ESI, pos): calcd. for $C_{22}H_{19}NNaO_3$ $[M+Na]^+$: 368.1257 found: 368.1255.

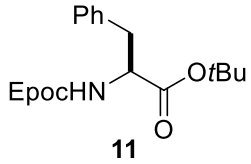


9

Compound **9**

To a stirred solution of compound **8** (8.1 mg, 23.5 µmol) in CH_2Cl_2 (1.0 mL) was added sodium tetrachloroaurate dihydrate (0.93 mg, 2.35 µmol, 50 mg/mL stock solution in MeOH). The mixture was stirred at room temperature for 5 minutes. The resulting mixuture was diluted to CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, EtOAc:Hexane 1:20~1:10 to obtain compound **9** as a white powder (6.7 mg, 19.4 µmol, 83%).

Compound **9**: R_f =0.31 (Hexane/EtOAc 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (1H, d, *J*=7.6 Hz), 7.59 (1H, d, *J*= 7.6 Hz), 7.44-7.27 (6H, m), 7.14-7.04 (3H, m), 6.63 (1H, brs), 5.09 (1H, brs), 4.53 (2H, dd+dd *J*=11.2, 6.8 Hz), 4.26 (1H, t, *J*= 6.4 Hz), 2.35 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 150.2, 144.1, 143.6, 140.6, 137.8, 129.6, 129.2, 128.0, 126.3, 124.6, 123.7, 122.1, 118.8, 117.2, 67.1, 47.3, 15.4; **HRMS** (ESI, pos): calcd. for $C_{22}H_{19}NNaO_3$ $[M+Na]^+$: 368.1257 found: 368.1250.



11

Compound **11**

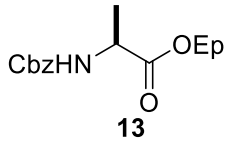
To a stirred solution of L-Phenylalanine *tert*-butyl ester hydrochloride (11.3 mg, 43.6 µmol) in THF/H_2O =3/1 (1.2 mL) was added EpocOSu **7** (16.0 mg, 43.6 µmol, 1.0 Eq) and pyridine (14.0 µL, 174.2 µmol, 4.0 Eq). The mixture was stirred at room temperature for 5 hours and subsequently quenched with saturated aqueous ammonium chloride solution. The product was extracted to CH_2Cl_2 and the organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, EtOAc:Hexane 1:9 to obtain compound **11** as colorless oil (16.7 mg, 35.3 µmol, 81%, dr~1:1).

Compound **11**: R_f =0.47 (Hexane/EtOAc=3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (1H, d, *J*= 7.2 Hz), 7.34-7.18 (6H, m), 7.10 (2H, t, *J*= 7.6 Hz), 6.04 (1H, d + d, *J*=2.8 Hz), 5.89 (1H, m), 5.13 (1H, d, *J*=8.0 Hz), 4.96 (1H, m), 4.68 (0.5H, dd. *J*=10.8, 7.6 Hz), 4.59-4.44 (2H, m), 4.38 (0.5H, dd, *J*=10.8, 7.2 Hz), 3.31 (0.5H, s), 3.29 (0.5H, s), 3.03 (1H, dd, *J*=9.6, 6.0 Hz), 2.24 (3H, s), 1.37 (9H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 155.5, 151.8, 151.6, [141.5, 141.6], 136.2, 133.2,

129.7, 129.7, 129.2, 128.4, 127.8, 127.0, [122.2, 122.2], 107.8, 106.1, 82.4, 81.9, 81.8, 66.0, 55.2, 42.3, 38.6, 28.1, 13.7; **HRMS** (ESI, pos): calcd. for $C_{29}H_{31}NaNO_5$ $[M+Na]^+$: 496.2094 found: 496.2102.

Deprotection of Compound **11**

To a stirred solution of compound **11** (23.7 mg, 50.0 µmol, 1.0 Eq) in CH_2Cl_2 (1.6 mL) was added $NaAuCl_4 \cdot 2H_2O$ (199 µg in 20 mg/mL stock solution in MeOH, 500 nmol, 0.01 Eq). The mixture was stirred at room temperature for 7 min. After the completion of the transformation of Epoc group was confirmed by TLC, piperidine (0,4 mL) was added and the mixture was stirred at room temperature for 15 min. The solvent was evaporated. the product was purified via flash column chromatography (SiO_2, EtOAc:Hexane 1:2~3:1) to obtain L-Phenylalanine *tert*-butyl ester as a white powder (9.9 mg, 44.7 µmol, 90%). The ^1H and ^{13}C NMR of the product coincided well with the previously reported one.[1]



13

Compound **13**

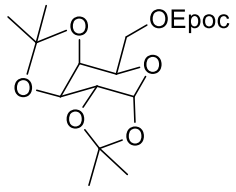
To a stirred solution of *N*-carbobenzoxy-L-alanine (14.5 mg, 65.0 µmol) in CH_2Cl_2 (2.0 mL) was added EpOH **6** (17.6 mg, 78.0 µmol,, 1.2 Eq), EDC·HCl (24.9 mg, 130 µmol, 2.0 Eq) and DMAP (15.9 mg, 130 µmol, 2.0 Eq). The mixture was stirred at room temeperature for 16 h and subsequently quenched with saturated aqueous ammonium chloride solution. The product was extracted to CH_2Cl_2 and the organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, EtOAc:Hexane 1:9) to obtain compound **13** as a colorless oil (26.0 mg, 60.2 µmol, 93%, dr~1/1).

Compound **13**: R_f=0.70 (Hexane/EtOAc=1/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (1H, m), 7.39-7.18 (8H, m), 6.02 (1H, d+d, *J*=3.2 Hz), 5.88 (1H, m), 5.26 (1H, t, J=8.8 Hz), 5.09 (2H, s+s), 5.01 (1H, t, *J*=7.2 Hz), 4.73 (0.5H, dd, *J*=11.2, 7.6 Hz), 4.61 (1H, m), 4.47 (0.5H, dd, *J*=10.8, 7.2 Hz), 4.32 (1H, quin, *J*= 6.8 Hz), 3.32 (0.5H, s), 3.31 (0.5H, s), 2.24 (3H, s), 1.24 (3H, d+d, *J*=6.8 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 155.6 [151.8, 151.7], [151.3, 151.3], [141.2, 141.0], 136.4, 133.2, 129.3, 128.7, [128.3, 128.2], 127.9, 127.8, [127.2, 127.2], [122.2, 122.1], [108.1, 108.0], 106.2, [82.1, 82.0], 81.7, 67.0, [66.3, 66.3], 49.7, [41.9, 41.8], [18.8, 18.8], 13.7; **HRMS** (ESI, pos): calcd. for $C_{26}C_{25}NaNO_5$ $[M+Na]^+$: 454.1625 found: 454.1628.

Deprotection of Compound **13**

To a stirred solution of compound **13** (21.6 mg, 50.0 µmol, 1.0 Eq) in CH_2Cl_2 (1.6 mL) was added $NaAuCl_4 \cdot 2H_2O$ (199 µg in 20 mg/mL stock solution in MeOH, 500 nmol, 0.01 Eq). The mixture was stirred at room temperature for 9 min. After the completion of the transformation of Epoc group was confirmed by TLC, piperidine (0.4 mL) was added and the mixture was stirred at room temperature for 15 min. The solvent was evaporated. The product was purified via flash

column chromatography (SiO_2, $CHCl_3$:MeOH 1:0~5:1) to obtain *N*-carbobenzoxy-L-alanine as a white powder (10.9 mg, 48.8 μmol, 98%). The ^1H and ^{13}C NMR of the product coincided well with the previously reported one.[2]



15

Compound **14**

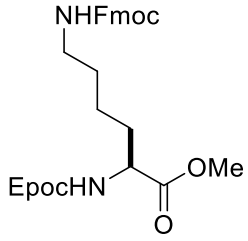
To a stirred solution of EpOH **6** (22.0 mg, 96.8 μmol, 1.2 Eq) in THF (2.0 mL) was added triphosgene (10.3 mg, 34.7 μmol, 0.43 Eq) and pyridine (9.8 μL, 121 μmol, 1.5 Eq) at 0 °C. After the mixture was stirred at room temperature for 1 hour, compound **14** (21.0 mg, 80.7 μmol, 1.0 Eq) was added. The mixture was stirred at room temperature for 3 hours and quenched with saturated aqueous NH_4Cl solution. The product was extracted to CH_2Cl_2, and the organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, Toluene:EtOAc 1:0~50:1) to obtain Compound **15** as a colorless oil (26.7 mg, 52.1 μmol, 65%, dr~1/1).

Compound **15**: R_f=0.58 (Hexane/EtOAc=3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51, (1H, dd, *J*=8.0, 1.6 Hz), 7.32-7.18 (3H, m), 6.06 (1H, d+d, *J*= 3.2 Hz), 5.88 (1H, m), 5.52 (1H, d, *J*= 4.8 Hz), 5.01 (1H, t, *J*= 7.2 Hz), 4.67 (1H, t+t, *J*= 7.6 Hz), 4.60 (1H, dd, *J*= 8.0, 2.0 Hz), 4.51 (1H, dd+dd *J*= 8.0, 6.4 Hz), 4.31 (1H, dd, *J*= 2.8, 6.0 Hz), 4.25-4.20 (3H, m), 4.03 (1H, m), 3.34 (0.5H, s), 3.33 (0.5H, s), 2.24 (3H, s), 1.51 (1.5H, s), 1.50 (1.5H, s), 1.43 (3H, s), 1.33(3H, s), 1.32 (3H, s); **^{13}C NMR** (100MHz, $CDCl_3$) δ 155.0, 151.7, 151.3, 141.0, 133.3, 129.2, 127.9, 127.2, 122.2, 109.7, 108.9, 108.2, 106.2, 96.4, 82.2, 81.6, 70.9, 70.7, 70.6, 68.8, 66.5, [65.7, 65.6], 42.1, 26.2, 26.1, 25.1, 24.6, 13.7: **HRMS** (ESI, pos): calcd. for $C_{28}H_{32}NaO_9$ $[M+Na]^+$: 535.19 39 found: 535.1944.

Deprotection of Compound **15**

To a stirred solution of compound **15** (15.8 mg, 30.8 μmol, 1.0 Eq) in CH_2Cl_2 (0.8 mL) was added $NaAuCl_4 \cdot 2H_2O$ (123 μg in 20 mg/mL stock solution in MeOH, 308 nmol, 0.01 Eq). The mixture was stirred at room temperature for 10 min. After the completion of the transformation of Epoc group was confirmed by TLC, piperidine (0.2 mL) was added and the mixture was stirred at room temperature for 5 min. The solvent was evaporated. The product was purified via flash column chromatography (SiO_2, $CHCl_3$:MeOH 1:0~5:1) to obtain *N*-Compound **15** as a colorless oil (6.0 mg, 23.1 μmol, 75%). The ^1H and ^{13}C NMR of the product coincided well with the previously reported one.[3]

1.4 Study for orthogonal deprotections

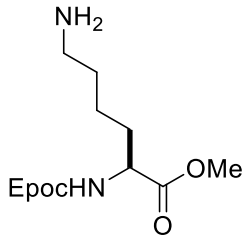


16

Compound **16**

To a stirred solution of *N*ε-Fmoc-L-lysine methyl ester hydrochloride (50.0 mg, 119.4 µmol, 1.0 Eq) in CH_2Cl_2 (2.0 mL) was added EpocOSu **7** (70.9 mg, 156.4 µmol, 1.1 Eq) and pyridine (28.3 µL, 284.4 µmol, 2.0 Eq). The mixture was stirred at room temperature for 1.5 hours and quenched with saturated aqueous NH_4Cl solution. The product was extracted to CH_2Cl_2, and the organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, EtOAc:Hexane 1:5~2:5) to obtain compound **16** as a white solid (70.9 mg, 111.7 µmol, 94%, dr~1/1).

Compound **16**: R_f =0.55 (Hexane/EtOAc =1/1); **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.85 (2H, d, *J*= 8.0 Hz), 7.68 (2H, d, *J*= 8.0 Hz), 7.51 (1H, d, *J*= 6.4 Hz), 7.43-7.23 (7H, m), 6.57 (1H, brd, *J*=8.0 Hz), 6.50 (1H, m), 6.11 (1H, m), 5.95 (1H, m), 4.94 (1H, t, *J*= 6.8 Hz), 4.63 (0.5H, dd, *J*= 10.8, 6.8 Hz), 4.56 (0.5 H, dd, *J*= 11.8, 8.0 Hz), 4.44-4.14 (5H, m), 3.93 (0.5H, s), 3.92 (0.5H, s), 3.65 (3H, s), 3.14 (2H, m), 2.18 (3H, s), 1.87-1.20 (6H, m); **^{13}C NMR** (100 MHz, Acetone-d_6) 173.6, 157.2, 156.8, 153.0, 151.9, 145.2, [142.4, 142.4], 142.1, 133.7, 129.9, 128.7, 128.5, 127.9, 126.1, 123.1, 123.1, 120.8, 108.5, 107.0, 83.9, 82.2, 66.7, 66.0, 54.9, 52.2, 48.1, 43.2, 41.1, 32.0, 23.6, 13.4; **HRMS** (ESI, pos): calcd. for $C_{38}H_{38}NaN_2O_7$ $[M+Na]^+$: 657.2571 found: 657.2577.



17

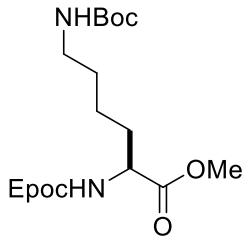
Compound **17**

To a stirred solution of compound **16** (31.7 mg, 50.0 µmol) in CH_2Cl_2 (1.6 mL) was added piperidine (0,4 mL). The mixture was stirred at room temperature for 1 hour. The product was triturated in hexane, filtered and diluted to CH_2Cl_2. The solution was washed with saturated $NaHCO_3$, dried over Na_2SO_4, filtered and evaporated. After azeotroped with toluene, compound **17** was obtained as white solid (17.8 mg, 43.2 µmol, 86%, dr~1/1).

Compound **17**: R_f =0.10 ($CHCl_3$/MeOH =4/1); **^{1}H NMR** (400 MHz, CD_3OD) δ 7.48 (1H, d, *J* =7.6 Hz), 7.34-7.19 (3H, m), 6.05 (1H, m), 5.91 (1H, m), 4.96 (1H, m), 4.64 (0.5H, dd, *J*= 10.8,

7.6 Hz), 4.54 (0.5H, dd, *J*= 11.2, 7.6 Hz), 4.60 (0.5H, dd, *J*= 10.8, 7.2 Hz), 4.38 (1H, dd, *J*= 11.2, 7.2 Hz), 4.11 (1H, dt, *J*= 9.6, 4.0 Hz), 3.76* (0.5H, s), 3.75* (0.5H, s), 3.69 (3H, s), 2.61 (2H, m), 2.21 (3H, s), 1.75 (1H, m), 1.64 (1H, m), 1.50-1.39 (2H, m)1.28-1.31 (2H, m); **^{13}C NMR** (100 MHz, CD_3OD) δ [174.6, 174.6], 158.4, 153.2, 152.5, 142.6, 134.0, 130.0, 128.8, 128.0, 123.6, 108.7, 107.1, 83.5, 82.4*, 66.8, 55.4, 52.6, 43.6, 42.1, 33.0, 32.3, 24.1, 13.4; **HRMS** (ESI, pos): calcd. for $C_{23}H_{29}N_2O_5$ $[M+H]^+$: 413.2071 found: 413.2069.

* Because the proton at terminal alkyne was substituted to deuterium in CD_3OD, its signal become lower than expected in ^{1}H NMR. In addition, the signal derived from deuterated product was also observed in ^{13}C NMR.

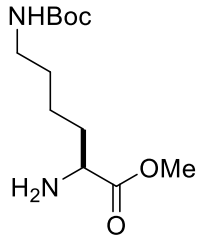


18

Compound **18**

To a stirred solution of *N*ε-Boc-L-lysine methyl ester hydrochloride (52.1 mg, 142.2 μmol, 1.0 Eq) in CH_2Cl_2 (2.0 mL) was added EpocOSu **7** (48.2 mg, 131.3 μmol, 1.1 Eq) and pyridine (19.2 μL, 238.7 μmol, 2.0 Eq). The mixture was stirred at room temperature for 1.5 hours and quenched with saturated aqueous NH_4Cl solution. The product was extracted to CH_2Cl_2, and the organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, EtOAc:Hexane 1:5~2:5) to obtain compound **18** as a white solid (69.2 mg, 135.0 μmol, 77%, dr~1/1).

Compound **18**: R_f =0.69 (Hexane/EtOAc=1/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (1H, d, *J*=7.6 Hz), 7.32-7.17 (3H, m), 6.04 (0.5H, d, *J*=2.8 Hz), 6.03 (0,5H, d, *J*= 3.2 Hz), 5.88 (1H, m), 5.18 (1H, brd, *J*= 8.0 Hz), 4.95 (1H, t, *J*= 6.4 Hz), 4.68-4.40 (3H, m), 4.30 (1H, m), 3.72 (3H, s), 3.32 (1H, s), 3.07 (2H, m), 2.23 (3H, s), 1.79 (1H, m), 1.62 (1H, m), 1.51-1.42 (11H, m), 1.36-1.23 (2H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 156.1, 155.8, [151.8, 151.8] 151.6, 141.5, 133.2, 129.2, 127.8, 127.0, 122.2, 107.8, 106.1, 81.9, 81.8, 79.3, [66.1, 66.0], 53.7, 52.5, 42.3, 40.3, 32.4, 29.6, 28.5, 22.4, 13.7; **HRMS** (ESI, pos): calcd. for $C_{28}H_{36}NaN_2O_7$ $[M+Na]^+$: 535.2415 found: 535.2425.



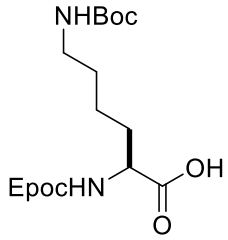
19

Compound **19** (Epoc deprotection of compound **18**)

To a stirred solution of compound **18** (25.6 mg, 50.0 μmol, 1.0 Eq) in CH_2Cl_2 (1.6 mL) was added $NaAuCl_4 \cdot 2H_2O$ (199 μg in 20 mg/mL stock solution in MeOH, 500 nmol, 0.01 Eq). The mixture was stirred at room temperature for 10 min. After the completion of the transformation of Epoc group was confirmed by TLC, piperidine (0.4 mL) was added and the mixture was stirred at room temperature for 30 min. The solvent was evaporated. The product was purified via flash column chromatography (SiO_2, $CHCl_3$:MeOH 1:0~9:1) to obtain *N*ε-Boc-L-lysine methyl ester as a white powder (11.8 mg, 45.3 μmol, 91%). The ^1H and ^{13}C NMR of the product coincided well with the previously reported one.[4]

Boc deprotection of compound **18**

To a stirred solution of compound **18** (25.6 mg, 50.0 μmol, 1.0 Eq) in CH_2Cl_2 (0.9 mL) was added trifluoroacetic acid (0.1 mL) at 0 °C. The mixture was stirred at 0 °C for 3 hours and quenched with saturated aqueous $NaHCO_3$ solution. The product was extracted to CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered and evaporated to obtain compound **17** as a white powder (17.8 mg, 43.2 μmol, 86%). The ^1H NMR and ^{13}C NMR peaks of the obtained product coincided well with the product obtained in the Fmoc deprotection of compound **16**.

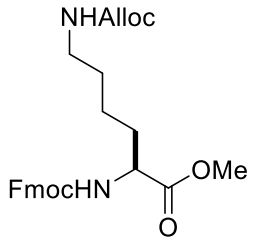


20

Compound **20** (Me deprotection of compound **18**)

To a stirred solution of compound **18** (25.6 mg, 50.0 μmol, 1.0 Eq) in THF/H_2O =3/1 (2.0 mL) was added $LiOH \cdot H_2O$ (6.4 mg, 150 μmol, 3.0 Eq). The mixture was stirred at room temperature for 1 hour and quenched with 0,1 M aqueous HCl. The product was extracted to CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via silica gel column chromatography (SiO_2, $CHCl_3$:MeOH 1:0 ~ 9:1) to obtain compound **20** as a white powder (19.3 mg, 38.7 μmol, 77%, dr ~1/1).

Compound **20**: R_f=0.42 ($CHCl_3$/MeOH =4/1) ; **^{1}H NMR** (400 MHz, CD_3OD) δ 7.48 (1H, d, *J*= 8.0 Hz), 7.32-7.21 (3H, m), 6.06 (1H, m), 5.91 (1H, m), 4.97 (1H, t+t, *J*= 7.6 Hz), 4.65 (0.5 H, dd, *J*= 10.4, 7.2 Hz), 4.51 (1H, m), 4.37 (0.5H, dd, *J*= 10.8, 7.2 Hz), 4.07 (1H, m), 3.75 (0.5H, s), 3.75 (0.5H, s), 3.02 (2H, m), 2.21 (3H, s), 1.78 (1H, m), 1.60 (1H, m), 1.54-1.24 (13H, m); **^{13}C NMR** (100 MHz, CD_3OD) δ 175.9, 158.5, 158.4, 153.2, 152.5, [142.7, 142.6], 134.0, 130.4, 128.9, 128.0, 123.6, 108.8, 107.1, 82.4, 82.4, 79.9, 66.8, 55.2, 43.6, 41.1. 32.4, 30.4, 28.8, 24.1, 13.4; **HRMS** (ESI, pos): calcd. for $C_{27}H_{34}NaN_2O_7$ $[M+Na]^+$: 521.2258 found: 521.2263.

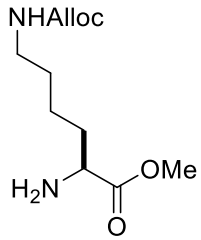


S1

Compound **S1**

To a stirred solution of *N*α-Fmoc-*N*ε-Alloc-lysine (100.0 mg, 221.0 μmol, 1.0 Eq) in DMF (5.0 mL) was added MeI (27.5 μL, 442.0 μmol, 2.0 Eq) and K_2CO_3 (61.1 mg, 442.0 μmol, 2.0 Eq). The mixture was stirred at room temperature for 2 hours and quenched with 0.2 M aqueous HCl solution. the product was extracted to CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, filtered and evaporated. The product was purified via Silica gel column chromatography (SiO_2, Hexane: EtOAc 4:1~2.5:1) to obtain compound **S1** (103.4 mg, 221.0 μmol, 100%) as a white powder.

Compound **S1**: R_f =0.72 ($CHCl_3$/MeOH =9/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (2H, d, *J*= 7.6 Hz), 7.60 (2H, m), 7.40 (2H, t, *J*= 7.6 Hz), 7.32 (2H, t, *J*= 7.6 Hz), 5.90 (1H, m), 5.37 (1H, d, *J*= 7.6 Hz), 5.28 (1H, d, *J*= 17.2 Hz), 5.18 (1H, d, *J*= 10.4 Hz), 4.76 (1H, m), 4.55 (2H, m), 4.40 (3H, m), 4.22 (1H, t, *J*=6.8 Hz), 3.75 (3H, s), 3.19 (2H, brq, *J*=6.4 Hz), 1.84 (1H, m), 1.69 (1H, m), 1.53 (2H, m), 1.39 (2H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 156.5, 156.1, 143.9, 141.5, 133.1, 127.9, 127.2, 125.2, 120.1, 117.8, 67.2, 66.7, 53.8, 52.6, 47.3, 40.6, 32.3, 29.5, 22.4; **HRMS** (ESI, pos): calcd. for $C_{26}H_{30}NaN_2O_6$ $[M+Na]^+$: 489.1996 found: 489.1999.

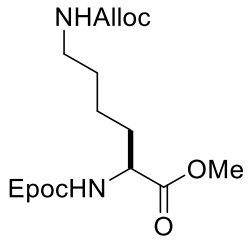


22

Compound **22**

To a stirred solution of compound **S1** (103.4 mg, 221.0 μmol, 1.0 Eq) in CH_2Cl_2 (1.6 mL) was added piperidine (0.4 mL). The mixture was stirred at room temperature for 30 minutes and evaporated. The product was purified via Silica gel column chromatography (SiO_2, $CHCl_3$:MeOH 1:0~50:1) to obtain compound **22** (51.4 mg, 210.4 μmol, 95%) as white powder.

Compound **22**: R_f=0.20 ($CHCl_3$/MeOH =9/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.91 (1H, ddd, *J*=16.8, 10.8, 5.6 Hz), 5.29 (1H, dq, *J*= 16.8, 1.6 Hz), 5.20 (1H, dq, *J*= 10.8, 1.6 Hz), 4.75 (1H, m), 4.55 (2H, d, *J*= 5.6 Hz), 3.72 (3H, s), 3,43 (1H, dd, *J*= 8.0. 5.6 Hz), 3.18 (2H, q, *J*= 6.8 Hz), 1.74 (1H, m), 1.61-1.45 (3H, m), 1.44-1.37 (2H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.6, 156.4, 133.1, 117.7, 66.6, 54.4, 52.1, 40.9, 34.6, 29.8, 23.0; **HRMS** (ESI, pos): calcd. for $C_{11}H_{21}N_2O_4$ $[M+H]^+$: 245.1496 found: 245.1497.



21

Compound **21**

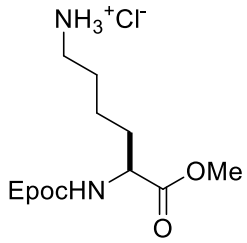
To a stirred solution of compound **22** (37.1 mg, 101.0 μmol, 1.0 Eq) in CH_2Cl_2 (2.0 mL) was added EpocOSu **7** (27.1 mg, 111.1 μmol, 1.1 Eq) and pyridine (16.3 μL, 202.0 μmol, 2.0 Eq). The mixture was stirred at room temperature for 2 hours and quenched with saturated aqueous NH_4Cl solution. The product was extracted to CH_2Cl_2, and the organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, EtOAc:Hexane 1:5~2:5) to obtain compound **21** as a colorless oil (37.6 mg, 75.7 μmol, 75%, dr~1/1).

Compound **21**: R_f=0.55 (Hexane/EtOAc= 1/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (1H, d, *J*= 7.6 Hz), 7.30-7.19 (3H, m), 6.03 (1H, m), 5.96-5.87 (2H, m), 5.29 (1H, d, *J*=17.6 Hz), 5.20 (2H, m), 4.96 (1H, t, *J*= 6.8 Hz), 4.77-4.41 (5H, m), 4.30 (1H, m), 3.72 (3H, s), 3.32 (1H, s), 3.16 (1H, m), 2.24 (3H, s), 1.80 (1H, m), 1.62 (1H, m)1.55-1.43 (2H, m), 1.36-1.22 (2H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.9 , 156.4, 155.8, 151.8, 151.6, 141.5, 133.2, 122.1, 129.2, 127.8, 127.0, 122.2, 117.8, 107.8, 106.1, 81.9, 81.8, 66.2, 65.6, 53.7, 52.5, 42.3, 40.7, 32.4, 29.5, 22.3, 13.7; **HRMS** (ESI, pos): calcd. for $C_{27}H_{32}NaN_2O_7$ $[M+Na]^+$: 519.2102 found: 519.2108.

Epoc deprotection of compound **21**

To a stirred solution of compound **21** (22.3 mg, 44.9 μmol, 1.0 Eq) in CH_2Cl_2 (1.6 mL) was added $NaAuCl_4 \cdot 2H_2O$ (179 μg in 20 mg/mL stock solution in MeOH, 449 nmol, 0.01 Eq). The mixture was stirred at room temperature for 10 min. After the completion of the transformation of Epoc group was confirmed by TLC, piperidine (0.4 mL) was added and the mixture was stirred at room temperature for 30 min. The solvent was evaporated. The product was purified via flash column chromatography (SiO_2, $CHCl_3$:MeOH 1:0~50:1) to obtain compound **22** as a white powder (11.8 mg, 45.3 μmol, 91%). The NMR spectra of this product coincided well with the one shown above for compound **22**.

Alloc deprotection of compound **21** (Compound **17'**)

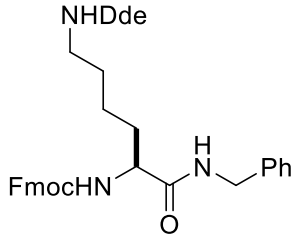


17'

To a stirred solution of compound **22** (24.9 mg, 50.1 µmol, 1.0 Eq) and dimedone (35.2 mg, 250.5 µmol, 5.0 Eq) in THF (2.0 mL) was added $Pd(PPh_3)_4$ (2.9 mg, 2.51 µmol, 0.05 Eq). The mixture was stirred at room temperature for 20 minutes and diluted to Et_2O. The product was extracted to 1M aqueous HCl solution and the solution was then poured into saturated aqueous $NaHCO_3$ solution slowly. The product was then extracted to CH_2Cl_2 and the organic layer was dried over Na_2SO_4, filtered and evaporated. To a solution of the product in Et_2O was added 1M HCl solution in Et_2O to crystalize the product as HCl salt. The product was filtered with celite, diluted to MeOH, and evaporated to obtain compound **17'** as HCl salt(16.6 mg, 37.0 µmol, 74%, dr~1/1).

Compound **17'**: R_f =0.10 ($CHCl_3$/MeOH =4/1); **^{1}H NMR** (400 MHz, CD_3OD) δ 7.48 (1H, d, *J* =8.0 Hz), 7.35-7.20 (3H, m), 6.05 (1H, m), 5.92(1H, m), 4.96 (1H, t, *J*= 7.2 Hz), 4.64 -4.54 (1H, m), 4.46-4.38 (1H, m), 4.14 (1H, quin *J*= 4.0 Hz), 3.77* (0.5H, s), 3.76* (0.5H, s), 3.70 (3H, s), 2.90 (2H, t, *J*= 7.6 Hz), 2.21 (3H, s), 1.88-1.58 (4H, m)1.50-1.32 (2H, m); **^{13}C NMR** (100 MHz, CD_3OD) δ 174.2, 158.4, 153.1, 152.6, 142.6, 134.0, 130.1, 128.8, 128.1, 123.6, 108.8, 107.1, 83.5, 82.4, 66.8, 55.0, 52.7, 43.6, 40.5, 32.0, 28.0, 23.8, 13.4; **HRMS** (ESI, pos): calcd. for $C_{23}H_{29}N_2O_5$ $[M\text{-}Cl]^+$: 413.2071 found: 413.2071.

Compound **S2**

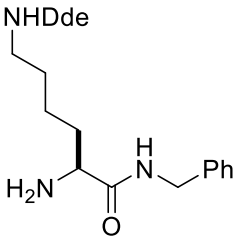


S2

To a stirred solution of *N*α-Fmoc-*N*ε-Dde-lysine (110.4 mg, 207.3 µmol, 1.0 Eq) in THF (2.0 mL) was added benzylamine (90.6 µL, 829 µmol, 4.0 Eq), EDC·HCl (79.5 mg, 415 µmol, 2.0 Eq), HOBt (56.0 mg, 415 µmol, 2.0 Eq), and *N*-methyl-morphiline (91.2 µL, 829 µmol, 4.0 Eq). The mixture was stirred at room temperature for 4 hours and quenched with 1M aqueous HCl. The product was extracted to CH_2Cl_2 and the organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, $CHCl_3$:MeOH 1:0~50:1) to obtain compound **S2** as a white powder (116.0 mg, 186.6 µmol, 90%).

Compound **S2**: R_f= 0.57 ($CHCl_3$/MeOH =9/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (2H, d, *J*= 7.6 Hz), 7.57 (2H, d, *J*= 7.6 Hz), 7.39 (2H, t, *J*=7.6 Hz), 7.32-7.20 (3H, m), 6.62 (1H, m), 5.52 (1H, d, *J*= 8.0 Hz), 4.45-4.37 (4H, m), 4.17 (2H, t, *J*= 6.8 Hz), 3.19 (2H, t, *J*= 6.8 Hz), 3.36 (2H, m), 2.53 (3H, s), 2.29 (4H, s), 1.93 (1H, m), 1.77-1.63 (3H, m), 1.55-1.41(2H, m), 0.99 (6H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.1, 196.8, 173.7, 171.4, 156.4, 143.9, 141.5, 137.9, 128.9, 127.9, 127.8, 127.8, 127.2, 125.2, 120.2, 108.0, 67.2, 54.8, 53.6, 52.4, 47.3, 43.8, 43.2, 32.3, 30.2, 28.4, 28.3 23.0, 18.1; **HRMS** (ESI, pos): calcd. for $C_{38}H_{44}N_3O_5$ $[M+H]^+$: 622.3275 found: 622.3280.

Compound **24**

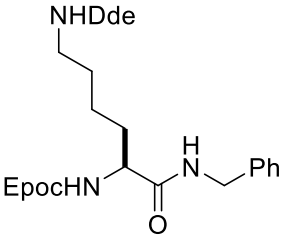


24

To a stirred solution of compound **S2** (103.4 mg, 221.0 μmol, 1.0 Eq) in CH_2Cl_2 (1.6 mL) was added piperidine (0.4 mL). The mixture was stirred at room temperature for 20 minutes and evaporated. The product was purified via Silica gel column chromatography (SiO_2, $CHCl_3$:MeOH 1:0~20:1) to obtain compound **24** (46.4 mg, 116.1 μmol, 80%) as white powder.

Compound **24**: R_f=0.29 ($CHCl_3$/MeOH =9/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (1H, t, *J*= 6.0 Hz), 7.35-7.26 (4H, m), 4.45 (2H, d, *J*= 6.0 Hz), 3.44-3.36 (3H, m), 2.55 (3H, s), 2.35 (4H, s), 1.99-1.90 (1H, m), 1.79-1.43 (5H, m), 1.03 (6H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.2, 196.9, 174.7, 173.6, 138.5, 128.8, 127.9, 127.5, 108.0, 55.0, 53.5, 52.4, 43.2, 34.7, 30.2, 29.8, 28.8, 28.4, 23.2, 18.1, ; **HRMS** (ESI, pos): calcd. for $C_{23}H_{34}N_3O_3$ $[M+H]^+$: 400.2595 found: 400.2600.

Compound **23**

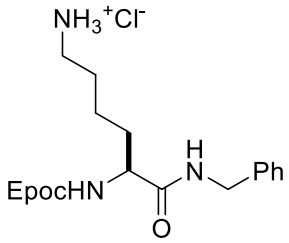


23

To a stirred solution of Compound **24** (46.4 mg, 116 μmol, 1.0 Eq) in THF (2.0 mL) was added EpocOSu **7** (55.5 mg, 151 μmol, 1.3 Eq) and Et_3N (35.9 μL, 348 μmol, 3.0 Eq). The mixture was stirred at room temperature for 1 hour and quenched with 1.0M aqueous HCl solution. The product was extracted to CH_2Cl_2, and the organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, $CHCl_3$:MeOH 1:0~50:1) to obtain compound **23** as a white solid (71.4 mg, 109.5 μmol, 94%, dr~1/1).

Compound **23**: R_f=0.53 ($CHCl_3$/MeOH =9/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (1H, d, *J*= 7.6 Hz), 7.34-7.15 (8H, m), 6.59 (1H, m), 6.00 (1H, m), 5.85 (1H, m), 5.27 (1H, m), 4.94 (1H, t, *J*= 6.8 Hz), 4.61 (1H, m), 4.47-4.39 (3H, m), 4.13 (1H, m), 3.38-3.25 (3H, m), 2.53 (3H, s), 2.31 (4H, s), 2.22 (3H, s), 1.94-1.83 (1H, m), 1.74-1.44 (3H, m), 1.49-1.35 (2H, m), 1.00 (6H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.1, 196.9, 173.7, 171.3, 156.2, 151.6, 151.6 [141.5, 141.4] 138.0, 133.2, 129.2, 128.9, 127.8, 127.8, 127.7 127.1, [122.2, 122.2], 108.0, 107.9, 107.8, 106.2, 82.0, 81.8, [66.3, 66.2], 54.7, 53.4, 52.4, 43.7, 43.2, 42.3, 32.2, 32.1, 30.2, 28.4, 23.0, 18.1, 13.7 ; **MS** (ESI, pos): calcd. for $C_{39}H_{46}N_3O_6$ $[M+H]^+$: 652.3381 found: 652.3380.

Compound **25**



25

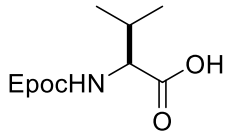
To a stirred solution of compound **23** (32.6 mg, 50.0 µmol, 1.0 Eq) in MeOH (1960 µL) was added hydrazine monohydrate (40 µL). The mixture was stirred at room temperature for 1 hour and triturated in Hexane/ Et_2O =1/1. The precipitate was filtered with Celite and dissolved in MeOH, and evaporated. To a solution of the product in Et_2O/MeOH =9/1 was added 1M HCl solution in Et_2O to crystalize the product as HCl salt. The product was filtered with celite, dissolved in MeOH, and evaporated to obtain compound **25** as a white powder (18.8 mg, 35.9 µmol, 72%, dr~1/1).

Compound **25**: R_f=0.10 ($CHCl_3$/MeOH =4/1); **^{1}H NMR** (400 MHz, CD_3OD) δ 7.47 (1H, m), 7.35-7.19 (8H, m), 6.04 (1H, d, *J*=2.8 Hz), 5.90 (1H, m), 4.96 (1H, m), 4.65 (0.5H, dd, *J*= 10.8, 7.6 Hz), 4.57 (0.5H, dd, *J*= 10.8, 7.6 Hz), 4.49-4.29 (3H, m), 4.07 (1H, m), 3.74 (1H, s ×2), 2.87 (2H, m), 2.20 (3H, s ×2), 1.78 (1H, m), 1.70-1.55 (3H, m), 1.47-1.30 (2H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5, 158.2, 153.1, 152.6, [142.6, 142.5], 139.8, 134.0, 130.1, 129.5, 128.8, [128.5, 128.5], 128.2, 128.1, 123.6, 108.8, 107.1, 83.5, [82.4, 82.4], 66.9, 56.3, 44.0, 43.5, 40.5, 32.6, 28.0, 23.8, 13.4; **MS** (ESI, pos): calcd. for $C_{29}H_{34}N_3O_4$ $[M-Cl]^+$: 488.2544 found: 488.2541.

Epoc deprotection of compound **24**

To a stirred solution of compound **24** (32.6 mg, 50.0 µmol, 1.0 Eq) in CH_2Cl_2 (1.6 mL) was added $NaAuCl_4 \cdot 2H_2O$ (199 µg in 20 mg/mL stock solution in MeOH, 500 nmol, 0.01 Eq). The mixture was stirred at room temperature for 30 min. After the completion of the transformation of Epoc group was confirmed by TLC, piperidine (0.4 mL) was added and the mixture was stirred at room temperature for 1 hour. The solvent was evaporated. The product was purified via flash column chromatography (SiO_2, $CHCl_3$:MeOH 1:0~20:1) to obtain compound **23** as a white powder (18.0 mg, 45.0 µmol, 90%). The NMR spectra of this product coincided well with the one shown above for compound **24**.

1.5 Synthesis of Epoc-protected amino acids for solid-phase peptide synthesis



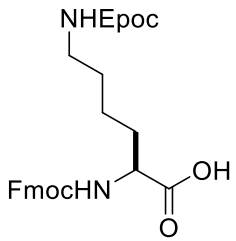
Epoc-Val-OH

Epoc-Val-OH

To a stirred solution of EpocOSu **7** (40.1 mg, 109.2 μmol, 1.0 Eq) and L-Valine (14.1 mg, 120.1 μmol, 1.1 Eq) in THF/H_2O =3/1 (2.0 mL) was added Et_3N (33.8 μL, 328 μmol, 3.0 Eq). The mixture was stirred at room temperature for 30 minutes and quenched with 0.2 M aqueous HCl solution. The product was extracted to CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, $CHCl_3$:MeOH 1:0~20:1) to obtain Epoc-Val-OH (38.0 mg, 102.9 μmol, 94%, dr~1/1) as a colorless oil.

Epoc-Val-OH: R_f=0.60 ($CHCl_3$/MeOH =4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.50 (1H, d, *J*=8.0 Hz), 7.32-7.15 (3H, m), 6.05 (1H, m), 5.88 (1H, m), 5.10 (1H, d, *J* =9.2 Hz, 4.97 (1H, t, *J*= 7.2 Hz), 4.69 (0.5H, dd, *J*=10.8, 8.0 Hz), 4.61(0.5H, dd, *J*= 10.8, 8.0 Hz), 4.51 (0.5H, dd, *J*= 10.8, 7.2 Hz), 4.43 (0,5H, dd, *J*= 10.8, 7.2 Hz), 4.27 (1H, m), 3.31 (1H, s), 2.23(3H, s), 2.22-2.12 (1H, m), 1.00-0.80 (6H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.3, 156.3, 151.8, 151.6, 141.4, 133.2, 129.2, 127.8, 127.1, 122.2, 107.9, 106.1, [82.0, 81.9], 81.7, 66.2, 58.9, [42.4, 42.1], 31.2, 19.1, 17.5, 13.7; **HRMS** (ESI, pos): calcd. for $C_{21}H_{23}NaNO_5$ $[M+Na]^+$: 392.1468 found: 392.1464.

Fmoc-Lys(Epoc)-OH

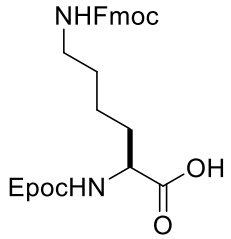


Fmoc-Lys(Epoc)-OH

To a stirred solution of EpocOSu **7** (45.1 mg, 123 μmol, 1.0 Eq) and *N*α-Fmoc-lysine hydrochloroide (54.7 mg, 135 μmol, 1.1 Eq) in THF/H_2O =3/1 (4.0 mL) was added Et_3N (50.6 μL, 491 μmol, 4.0 Eq). The mixture was stirred at room temperature for 30 minutes and quenched with 1.0 M aqueous HCl solution. The product was extracted to CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, $CHCl_3$:MeOH 50:1~7:1) to obtain Fmoc-Lys(Epoc)-OH (65.4 mg, 105.4 μmol, 86%, dr~1/1) as white powder.

Fmoc-Lys(Epoc)-OH: R_f=0.58 ($CHCl_3$/MeOH =4/1); **^{1}H NMR** (400 MHz, CD_3OD) δ7.77 (2H, d, *J*=7.6 Hz), 7.65 (2H, t, *J*= 6.4 Hz), 7.44 (1H, d, *J*=7.6 Hz), 7.37 (2H, t, *J*= 7.6 Hz), 7.32-7.23

(4H, m), 7.18 (1H, d, *J*= 7.2 Hz), 6.01 (1H, m), 5.87 (1H, m), 4.92 (1H, t, *J*= 6.4 Hz), 4.56 (1H, m), 4.45-4.29 (3H, m), 4.20 (1H, m), 4.11 (1H, m), 3.72 (1H, s), 3.04 (2H, t, *J*=6.4 Hz), 2.17 (3H, s), 1.87-1.76 (1H, m), 1.75-1.60 (1H, m), 1.51-1.30 (4H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ176.1, 158.7, 158.7, 153.3, 152.5, [145.3, 145.2], 142.7, 142.6, 134.0, 130.0, 128.8, 128.2, 128.2, 128.0, 126.3, 123.6, 120.9, 108.7, 107.0, 83.4, 82.5, 67.9, 66.6, 56.3, 48.4, 43.6, 41.3, 32.3, 30.3, 24.1, 13.4; **HRMS** (ESI, pos): calcd. for $C_{37}H_{36}NaN_2O_7$ $[M+Na]^+$: 643.2415 found: 643.2419.



Epoc-Lys(Fmoc)-OH

Epoc-Lys(Fmoc)-OH

To a stirred solution of EpocOSu **7** (109.6 mg, 298.4 μmol, 1.0 Eq) and *N*ε-Fmoc-lysine (164.9 mg, 447.5 μmol, 1.5 Eq) in THF/H_2O =5/3 (6.0 mL) was added Et_3N (166.3 μL, 1.190 mmol, 4.0 Eq). The mixture was stirred at room temperature for 30 minutes and quenched with 1.0 M aqueous HCl solution. The product was extracted to CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered and evaporated. The product was purified via flash column chromatography (SiO_2, $CHCl_3$:MeOH 1:0~20:1) to obtain Epoc-Lys(Fmoc)-OH (155.3 mg, 250.2 μmol, 84%, dr~1/1) as white powder.

Epoc-Lys(Fmoc)-OH: R_f=0.44 ($CHCl_3$/MeOH =4/1); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.88 (2H, d, *J*= 7.2 Hz), 7.68 (2H, d, *J*= 7.2 Hz), 7.49 (1H, d, *J*= 7.6 Hz), 7.43-7.20 (7H, m), 6.12 (1H, m), 5.98 (1H, m), 4.82 (1H, q, *J*= 6.4 Hz), 4.56-4.19 (6H, m), 3.81 (1H, m), 2.94 (2H, m), 2.17 (3H, s), 1.71-1.04 (6H, m) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1, 156.1, 155.8, 151.8, 150.7, 144.0, [141.1,141.0], 140.8, 132.7, 129.2, 127.6, 127.2, 127.1, 125.2, 121.7, 121.6, 120.1, [107.6, 107.55], 106.4, 81.3, 79.2, 65.2, 64.7, 54.1, 46.8, 41.8, 41.3, 30.7, 29.0, 22.8, 13.3; **HRMS** (ESI, pos): calcd. for $C_{37}H_{36}NaN_2O_7$ $[M+Na]^+$: 643.2415 found: 643.2419.

2. Solvent screening for the fluorene formation of Epoc group

2.1 HPLC product standard curves and calibration

The calibration curve for the integrated value of compound **9** was constructed using the standard solution in 1,4-dioxane to determine the yield for compound **9** from HPLC analysis (**Figure S1, S2**). For HPLC analysis, analytical 4.6 × 250 mm Cosmosil 5C_{18}-AR-300 column from Nacalai Tesque (Kyoto, Japan) was used with 1.0 mL/min flow rate. The elution method was shown in **Table S1**.

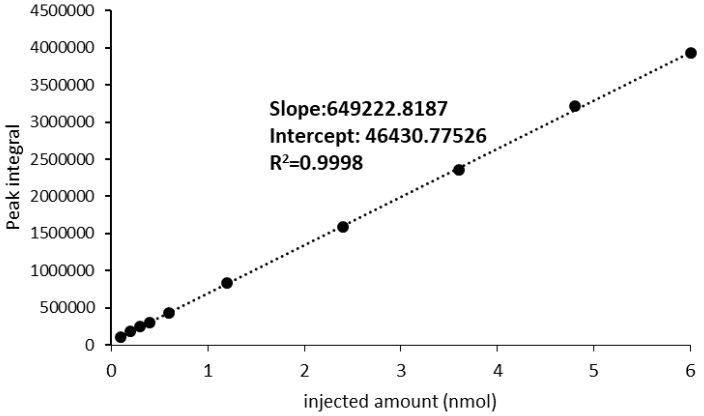


Figure S1 Calibration curve for compound **9**

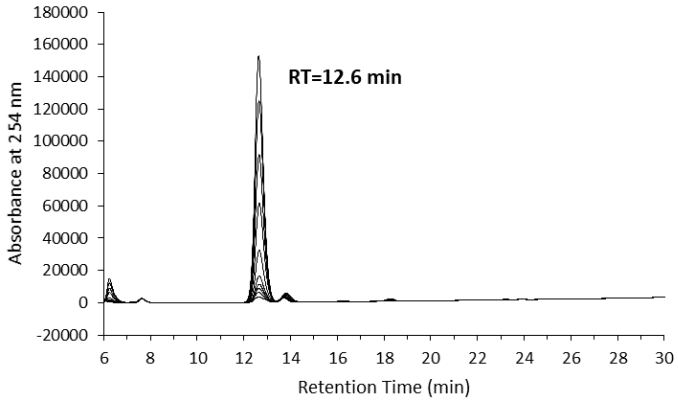


Figure S2 HPLC chart of compound **9** with different injected amount.

Table S1 HPLC method

Time (min)	Flow rate (mL/min)	H_2O with 0.1% TFA (%)	CH_3CN with 0.1% TFA (%)
0	1.0	45	55
5	1.0	45	55
30	1.0	25	75

2.2 Condition screening for fluorene formation

Compound **8** (300 nmol) from the stock solution in 1,4-dioxane (20 mg/mL, 5.2 μL) was diluted to the various solvents (192.4 μL). The stock solution of $NaAuCl_4 \cdot 2H_2O$ (3 nmol or 30 nmol) in MeOH (2.4 μL, 5 mg/mL or 0.5 mg/mL) was added to the solution of compound **8** and the total volume of the reaction solution was adjusted to 200 μL. The mixture was placed at room temperature for 1 hour and quenched with 1-dodecanethiol (50 Eq). The mixture was diluted in 5 times in volume with 1,4-dioxane, and 20 μL of this solution was injected to HPLC analysis (condition: **Table S1**, chart **Figure S3**). The yield was determined based on the calibration curve obtained above. The experiments were run in triplicate and its average was shown as the yield.

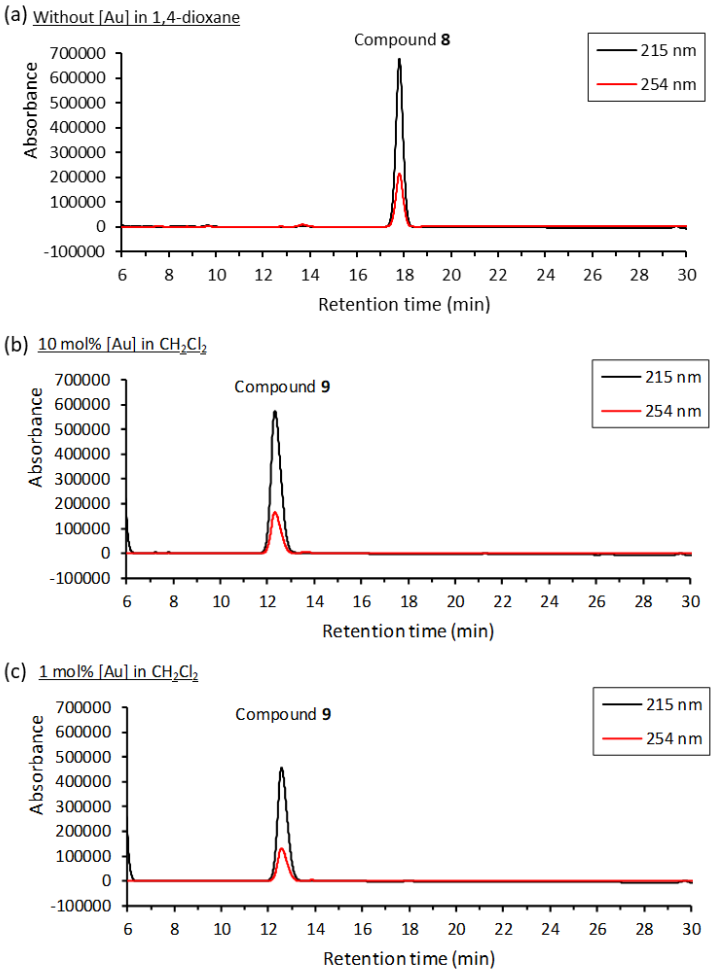


Figure S3 HPLC chart for solvent screening of fluorene formation

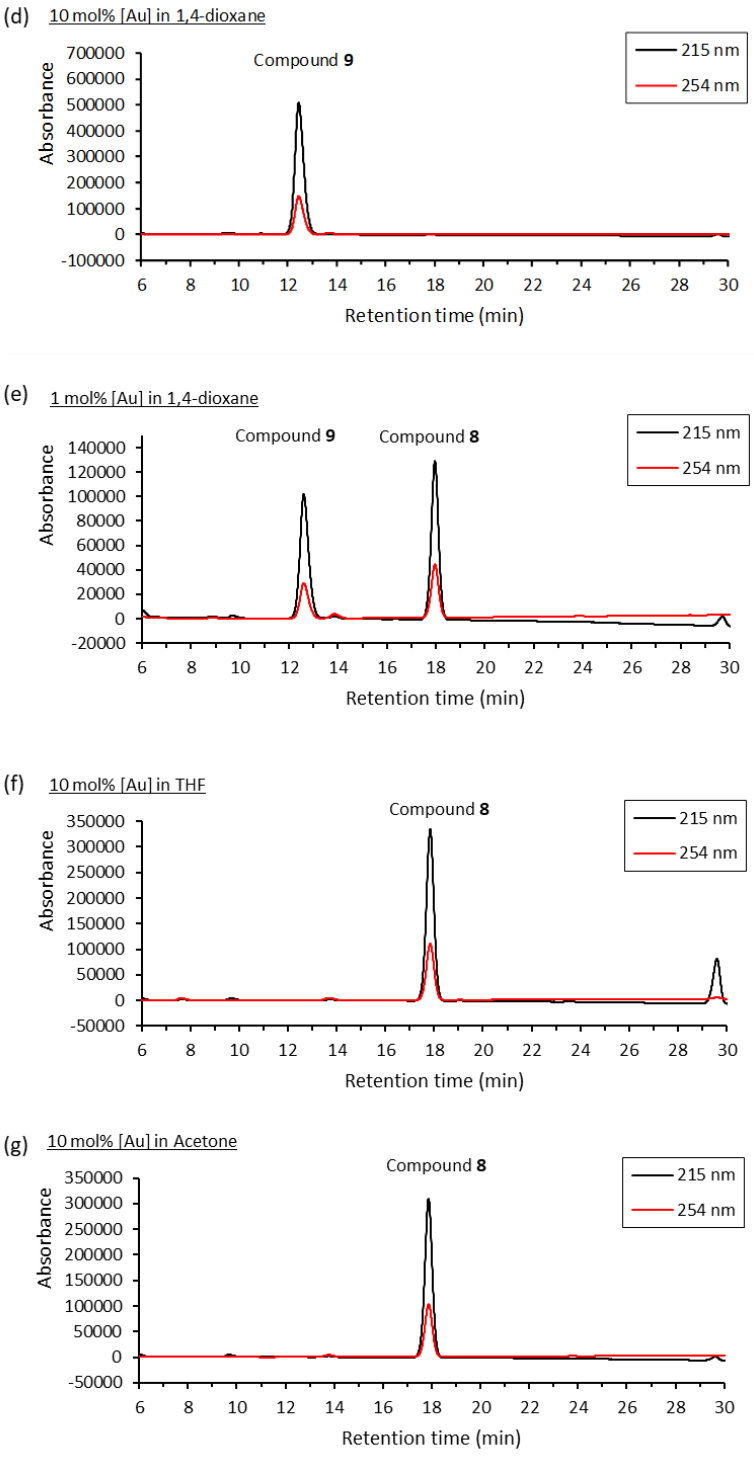
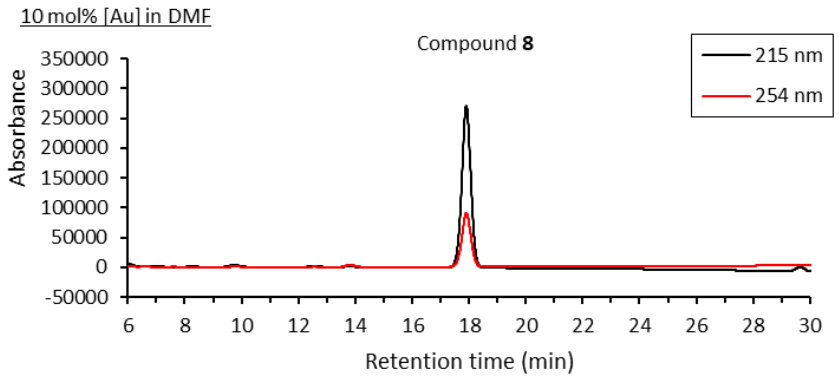
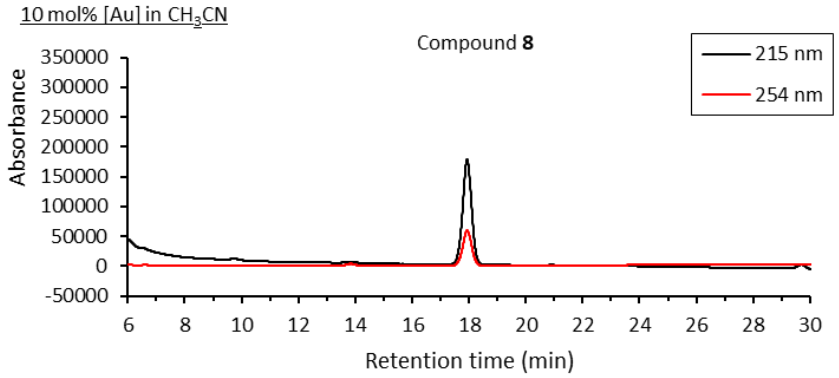


Figure S3 HPLC chart for solvent screening of fluorene formation (continued).

(h)



(i)



(j)

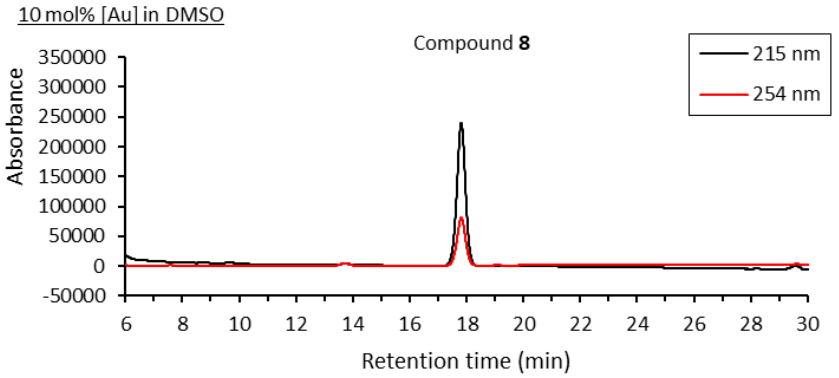


Figure S3 HPLC chart for solvent screening of fluorene formation (continued).

2.3 Fluorene formation under aqueous conditions

To a solution of $NaAuCl_4 \cdot 2H_2O$ in PBS buffer (90 μL) and 1,4-dioxane (4.82 μL) was added compound **8** (300 nmol) from the stock solution in 1,4-dioxane (20 mg/mL, 5.18 μL). The mixture was placed at 37 °C for 24 hours, and quenched with 1-dodecanethiol (50 Eq). The mixture was diluted 10 times in volume with 1,4-dioxane, and 20 μL of this solution was injected to HPLC analysis (condition: **Table S1**, chart Figure **S4**). The yield was determined based on the calibration curve obtained above. The experiments were run in triplicate and its average was shown as the yield.

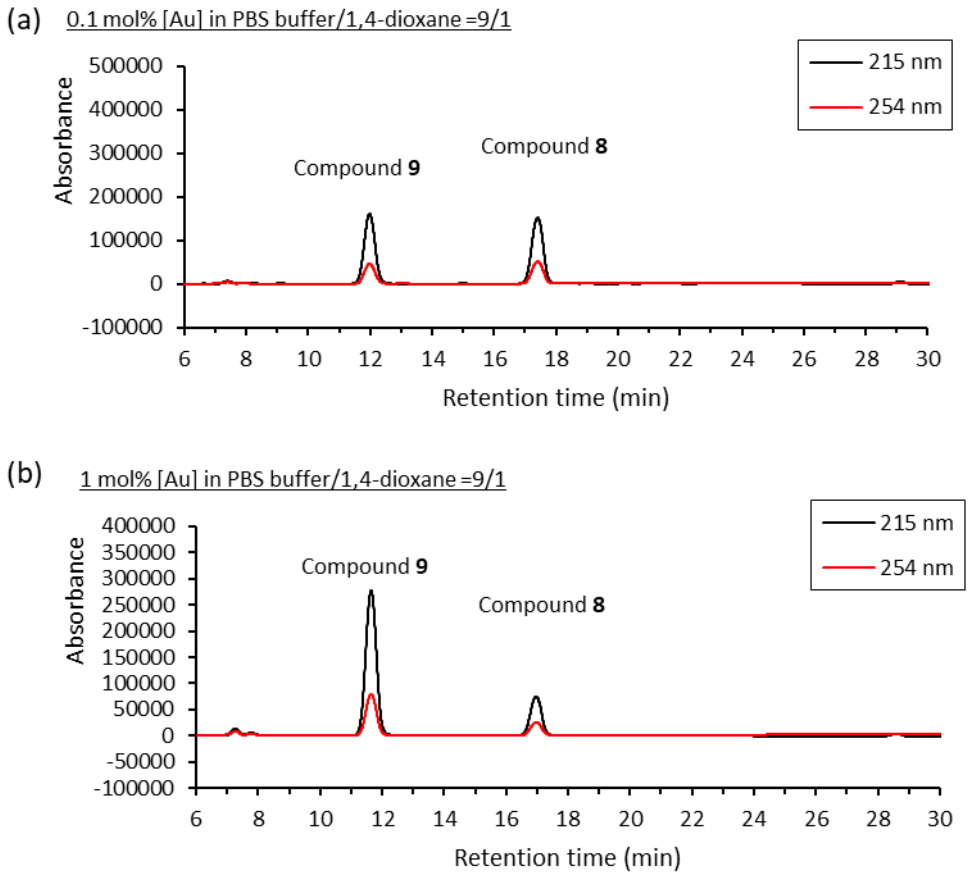


Figure S4 HPLC chart for fluorene formation under aqueous conditions.

3. Solid-phase peptide synthesis

3.1 Test for Epoc transformation on resin

2-Chlorotrityl chloride resin(1.57 mmol/g, 100-200 mesh, 1%DVB) was treated with Fmoc-Phe-OH (2.0 Eq), DIPEA (5.0 Eq) in CH_2Cl_2 for 2 hours. After washing with CH_2Cl_2/MeOH/DIPEA =17/2/1 (2 mL × 3), CH_2Cl_2 (2 mL × 3), and DMF (2 mL × 3), 20%

piperidine/DMF was added to the resin and the resin was shaken for 10 min, and washed with DMF (0.5 mL, 5 times). The amount of active N-terminal was determined by the quantification of cleaved dibenzofulvene-piperidine adduct. The coupling with Epoc-Val-OH was performed by the treatment with Epoc-Val-OH (4.0 Eq), HOBt (4.0 Eq), HBTU (4.0 Eq), and DIPEA (8.0 Eq) in DMF (500 μL) for 15 min to obtain the resin loaded with Epoc-Val-Phe-OH. After the coupling, the resins were washed with CH_2Cl_2 (1 mL, 3 times) and DMF (1 mL, 3 times).

The transformation of Epoc group was performed with the treatment of $NaAuCl_4 \cdot 2H_2O$ (0.1 Eq, 20 mg/mL stock solution in MeOH) and CH_2Cl_2 (500 μL) for 10 min. After the treatment, the resins were washed with CH_2Cl_2 (1 mL, 3 times) and DMF (1 mL, 3 times). The transformed Hmoc group was removed by the treatment of 20% piperidine/DMF for 10 min twice. The elongation was performed by the treatment with Fmoc-Gly-OH (4.0 Eq), HOBt (4.0 Eq), and DIPEA (8.0 Eq) in DMF (500 μL) for 15 min. The peptide cleaved with 1% TFA in CH_2Cl_2 showed a single major peak in HPLC analysis. The mass spectra of the peptide obtained from this fraction showed the peak derived from desired Fmoc-Gly-Val-Phe-OH **29** (**HRMS** (ESI, pos): calcd. for $C_{30}H_{32}N_2NaO_6$ $[M+Na]^+$: 539.2153 found: 539.2159). The reaction procedure of each step was monitored with the HPLC analysis of the peptide cleaved from the small portion of resin (condition: **Table S2**, chart: **Figure S5**). In this step, we used the cleavage cocktail containing thiol reagent (TFA/1-dodecanethiol/ CH_2Cl_2 =2/8/90) to quench residual gold(III) catalysts absorbed on resin and avoid the transformation after cleavage.

As a negative control, 20% piperidine/DMF was treated to Epoc-Val-Phe-OH loaded on resin for 10 min twice and the coupling reagents for Fmoc-Gly-OH were next treated, without the transformation with gold catalysis. The peptide cleaved with 1% TFA in CH_2Cl_2 showed a single major peak in HPLC analysis. The mass spectra of the peptide obtained from this fraction showed the peak derived from desired Epoc-Val-Phe-OH (**HRMS** (ESI, pos): calcd. for $C_{31}H_{34}N_3O_6$ $[M+H]^+$: 544.2442 found: 544.2440). The reaction procedure of each step was monitored with the HPLC analysis of the peptide cleaved from the small portion of resin (condition: **Table S2**, chart: **Figure S6**).

Table S2 HPLC method for monitoring the reaction procedure of the synthesis of Fmoc-Gly-Val-Phe-OH

Time (min)	Flow rate (mL/min)	H_2O with 0.1% TFA (%)	CH_3CN with 0.1% TFA (%)
0	1.0	95	5
5	1.0	95	5
10	1.0	53	47
35	1.0	53	47

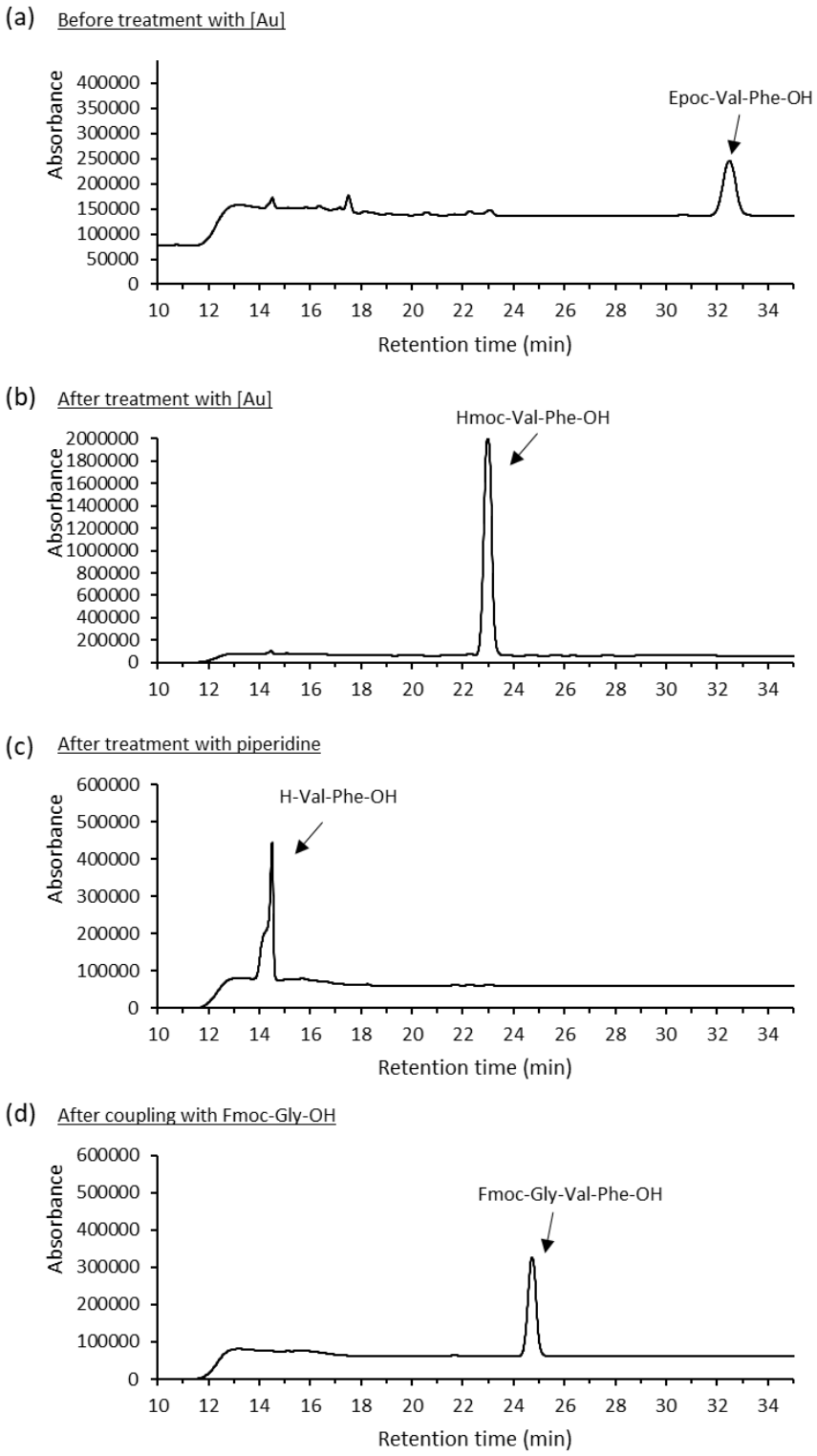


Figure S5 HPLC chart for the reaction for Epoc-Val-Phe-OH: (a) before treatment with gold catalyst, (b) after treatment with gold catalyst, (c) after treatment with piperidine, and (d) after coupling with Fmoc-Gly-OH. The peptides were identified based on the MS spectra of the collected fractions.

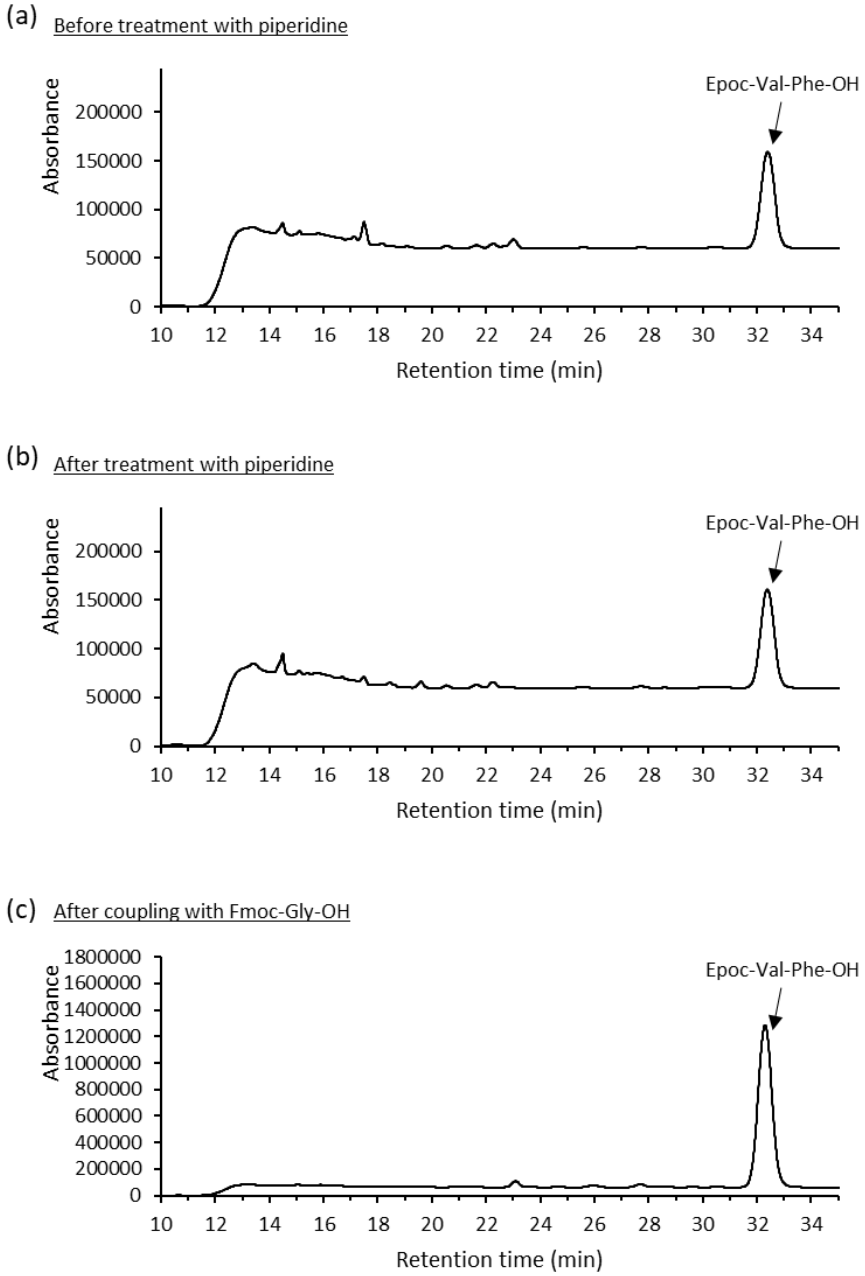


Figure S6 HPLC chart for the reaction for Epoc-Val-Phe-OH without gold catalysis (negative control): (a) before treatment with piperidine, (b) after treatment with piperidine, (c) after coupling with Fmoc-Gly-OH. The peptides were identified based on the MS spectra of the collected fractions.

3.2 Synthesis of branched peptides

The branched peptide **32** was synthesized from H-Gly-Trt(2-Cl)-resin (20.0 μmol, 0.33 mmol/g, 100-200 mesh, 1% DVB), following the standard procedure for Fmoc SPPS. The peptide chains were elongated by the treatment with protected amino acids (order: Fmoc-Tyr(*t*Bu)-OH, Fmoc-Ala-OH, Epoc-Lys(Fmoc)-OH, Fmoc-Phe-OH, Fmoc-Ser(O*t*Bu)-OH, Boc-Gly-OH, 4.0 Eq), HOBt (4.0 Eq), HBTU (4.0 Eq) and DIPEA (8.0 Eq) in DMF (500 μL). After the coupling the resins were washed with CH_2Cl_2 (1 mL, 3 times) and DMF (1 mL, 3 times). The reaction completion of the coupling was monitored with Kaiser test, and the coupling was repeated when the reaction was not completed. Fmoc group was cleaved by the treatment with 20% piperidine/DMF for 10 min after each coupling.

The transformation of Epoc group was performed by the treatment of $NaAuCl_4 \cdot 2H_2O$ (0.1 Eq, 100mg/mL stock solution in MeOH) in CH_2Cl_2 for 1 hour (1st) and 4 hours (2nd). After each treatment, the resins were washed with CH_2Cl_2 (1 mL, 3 times) and DMF (1 mL, 3 times). The reaction procedure was monitored with the HPLC analysis of the peptide cleaved from the small portion of resin. In this step, we used the cleavage cocktail containing thiol reagent (TFA/1-dodecanethiol/ CH_2Cl_2 =2/8/90) to quench residual gold(III) catalysts absorbed on resin and avoid the transformation after cleavage. After the completion of transformation, the resin was treated with 20% piperidine/DMF for 10 minutes and the completion of the removal of Hmoc was monitored by the HPLC analysis. The peptide was further elongated in the same way as above mentioned (Fmoc-Glu-(O*t*Bu)-OH, Fmoc-Trp(Boc)-OH, and Fmoc-Thr(O*t*Bu)-OH).

The obtained peptide was cleaved from resin by the treatment with the cleavage cocktail (TFA/H_2O/triisopropylsilane =90/5/5) for 2 hours, and triturated in cold Et_2O to obtain the crude peptide. The peptide was purified with preparative HPLC (20 × 250 mm Cosmosil $5C_{18}$-AR-300 column from Nacalai Tesque (Kyoto, Japan)) was used with 8.0 mL/min flow rate, isoclatic flow with 25% CH_3CN/H_2O containing 0.1% TFA to obtain the branched peptide **32** (7.7 mg, 6.8 μmol, 34%, 99% pure).

Branched peptide **32**: **HRMS** (ESI, pos): calcd. for $C_{54}H_{73}N_{12}O_{16}$ $[M+H]^+$: 1145.5262 found: 1145.5265.

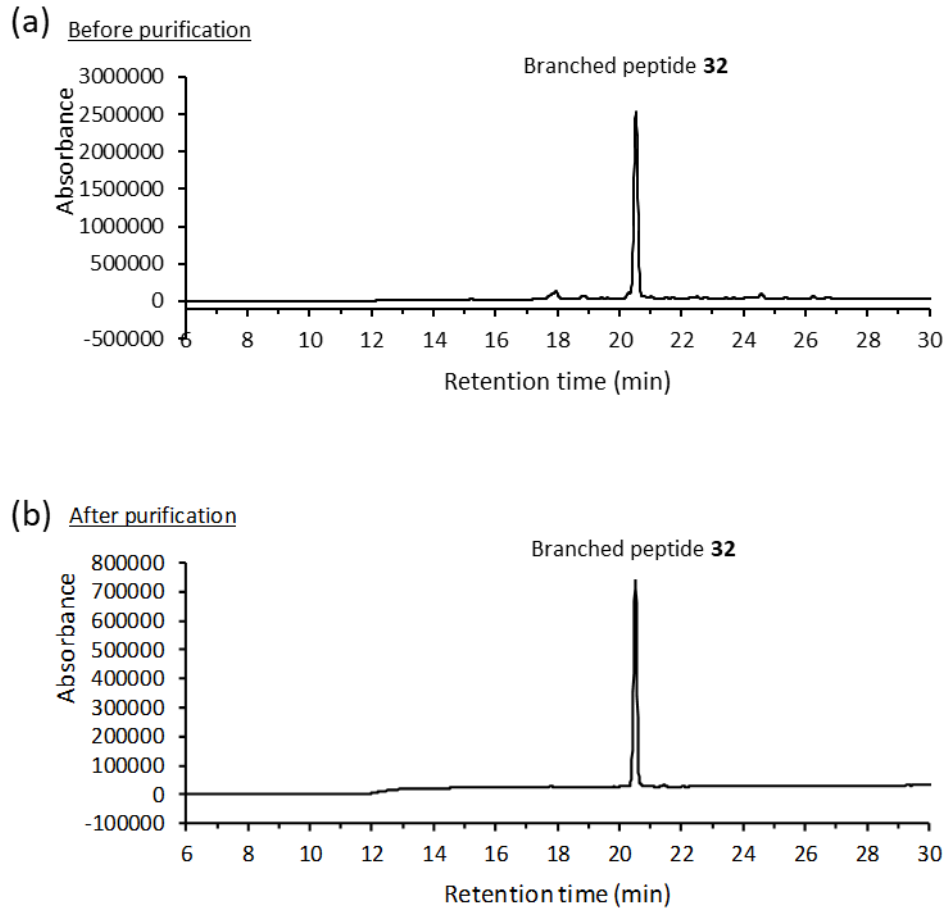


Figure S7 HPLC chart of branched peptide **32** before (a) and after (b) purification. The condition for HPLC analysis was shown in **Table S3**.

The branched peptide **35** was synthesized from H-Gly-Trt(2-Cl)-resin (20.0 μmol, 0.33 mmol/g, 100-200 mesh, 1% DVB), following the standard procedure for Fmoc SPPS. The peptide chains were elongated by the treatment with protected amino acids (order: Fmoc-Arg(Pbf)-OH, Fmoc-Met-OH, Fmoc-Gln(Trt)-OH, Fmoc-Cys(Trt)-OH, Fmoc-Leu-OH, Fmoc-Lys(Epoc)-OH, Fmoc-Ser(*t*Bu)-OH, Fmoc-His(Trt)-OH, Boc-Ala-OH, 4.0 Eq), HOBt (4.0 Eq), HBTU (4.0 Eq) and DIPEA (8.0 Eq) in DMF (500 μL). After the coupling the resins were washed with CH_2Cl_2 (1 mL, 3 times) and DMF (1 mL, 3 times). The reaction completion of the coupling was monitored with Kaiser test, and the coupling was repeated when the reaction was not completed. Fmoc group was cleaved by the treatment with 20% piperidine/DMF for 10 min after each coupling and subsequent washing with DMF (1 mL, 5 times).

The transformation of Epoc group was performed by the treatment of $NaAuCl_4 \cdot 2H_2O$ (0.1 Eq, 100mg/mL stock solution in MeOH) in CH_2Cl_2 for 1 hour (1st), 2 hours (2nd) and 2 hours (3rd). After each treatment, the resins were washed with CH_2Cl_2 (1 mL, 3 times) and DMF (1 mL, 3 times). The reaction procedure was monitored with the HPLC analysis of the peptide cleaved from the small portion of resin using the cleavage cocktail containing thiol reagent (TFA/1-dodecanethiol/ CH_2Cl_2 =2/8/90). After the completion of transformation, the resin was treated

with 10% piperidine/DMF for 15 minutes× 5 times and the completion of the removal of Hmoc was monitored by the HPLC analysis. The peptide was further elongated in the same way as above mentioned (Fmoc-Phe-OH, Fmoc-Trp(Boc)-OH, and Fmoc-Glu(O*t*Bu)-OH).

The obtained peptide was cleaved from resin by the treatment with the cleavage cocktail (TFA/ethanedithiol/H_2O/triisopropylsilane =89/1/5/5) for 2 hours, and triturated in cold Et_2O to obtain the crude peptide. The peptide was purified with preparative HPLC (20 × 250 mm Cosmosil 5C_{18}-AR-300 column from Nacalai Tesque (Kyoto, Japan)) was used with 8.0 mL/min flow rate, isoclatic flow with 25% CH_3CN/H_2O containing 0.1% TFA to obtain the branched peptide **35** (8.6 mg, 5.2 μmol, 26% yield, 95% pure).

Branched peptide **35**: **HRMS** (ESI, pos): calcd. for $C_{70}H_{107}N_{21}O_{18}S_2$ $[M+2H]^{2+}$: 796.8767 found: 796.8836.

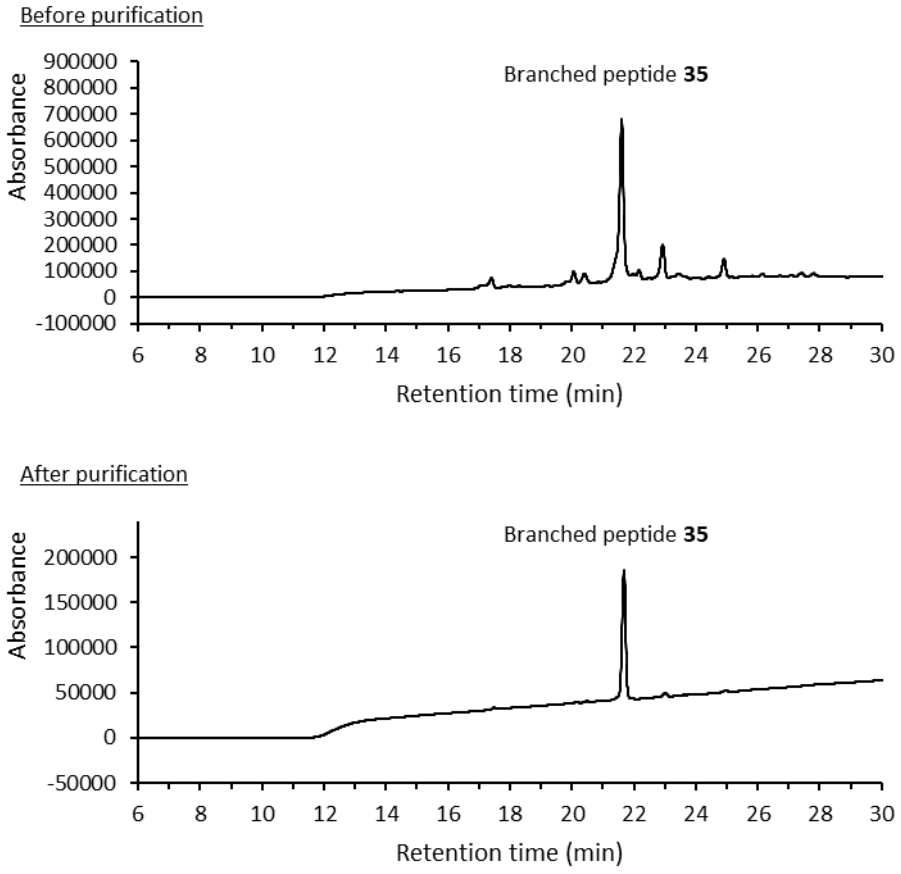


Figure S8 HPLC chart of branched peptide **31** before (a) and after (b) purification. The condition for HPLC analysis was shown in **Table S3**.

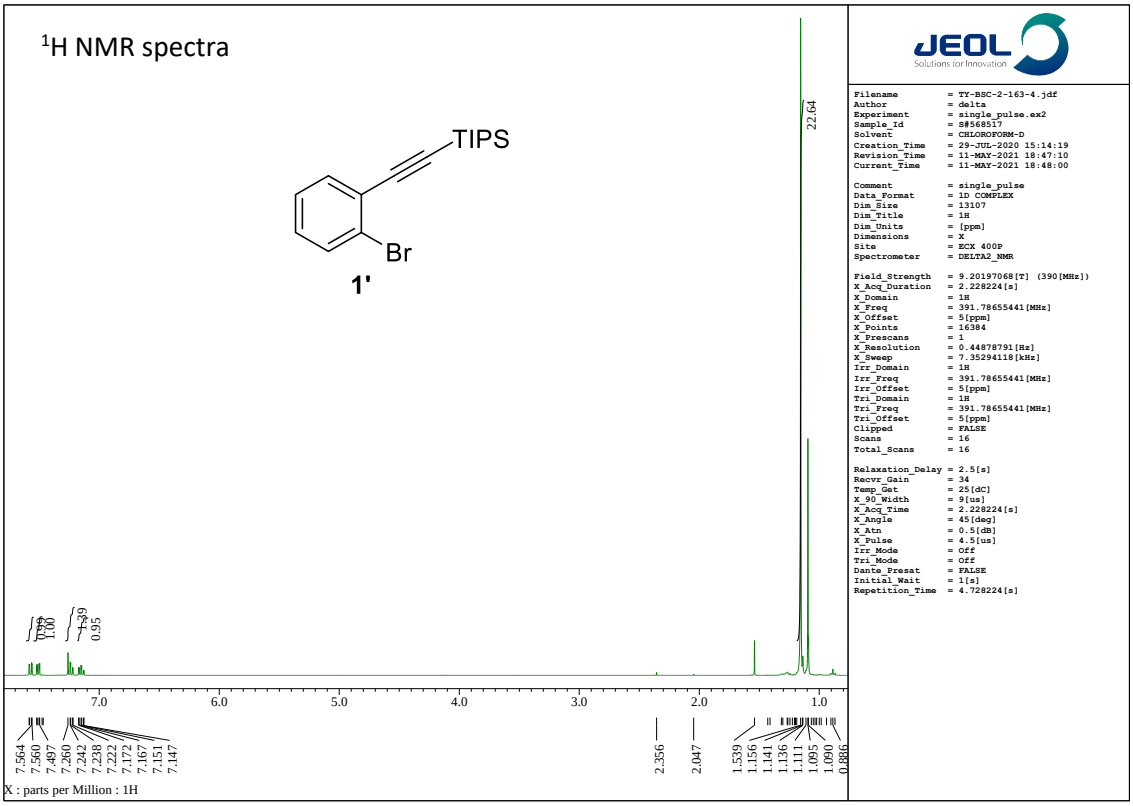
Table S3 HPLC method for the analysis of purity for branched peptides

Time (min)	Flow rate (mL/min)	H_2O with 0.1% TFA (%)	CH_3CN with 0.1% TFA (%)
0	1.0	95	5
5	1.0	95	5
30	1.0	40	60

4. References

1 A. Odriozola, M. Oiarbide and C. Palomo, *Chem. Eur. J.*, 2017, **23**, 12758–12762.
2 K. Sugimoto, K. Toyoshima, S. Nonaka, K. Kotaki, H. Ueda and H. Tokuyama, *Angew. Chem. Int. Ed.*, 2013, **52**, 7168–7171.
3 S. Meng, W. Zhong, W. Yao and Z. Li, *Org. Lett.*, 2020, **22**, 2981–2986.
4 S. K. Fehler, G. Pratsch, C. Östreicher, M. C. D. Fürst, M. Pischetsrieder and M. R. Heinrich, *Tetrahedron*, 2016, **72**, 7888–7893.

5. NMR spectra

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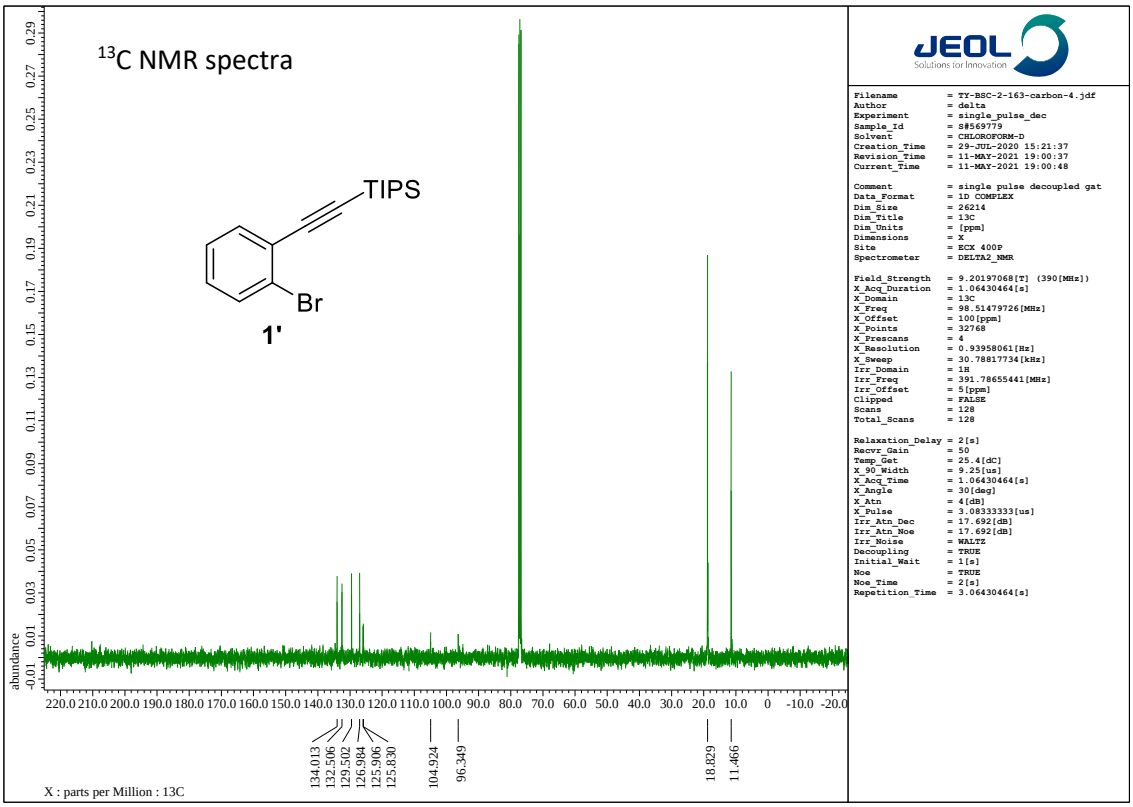


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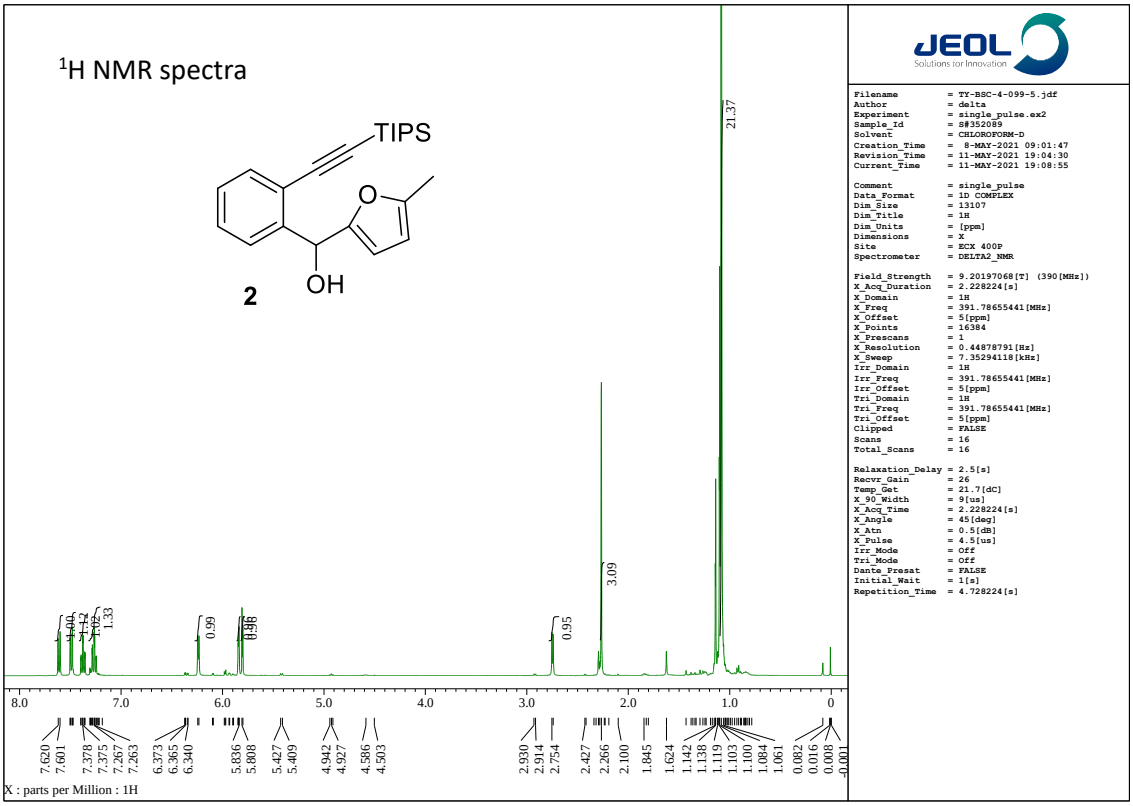
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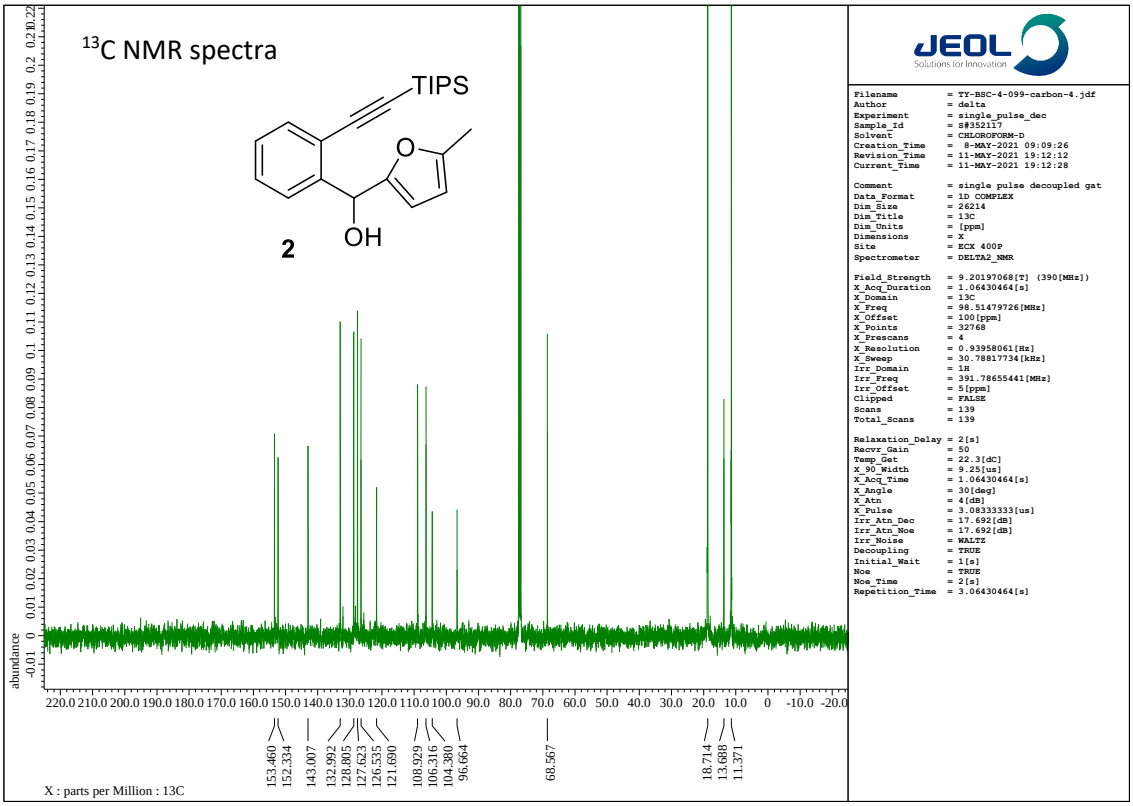
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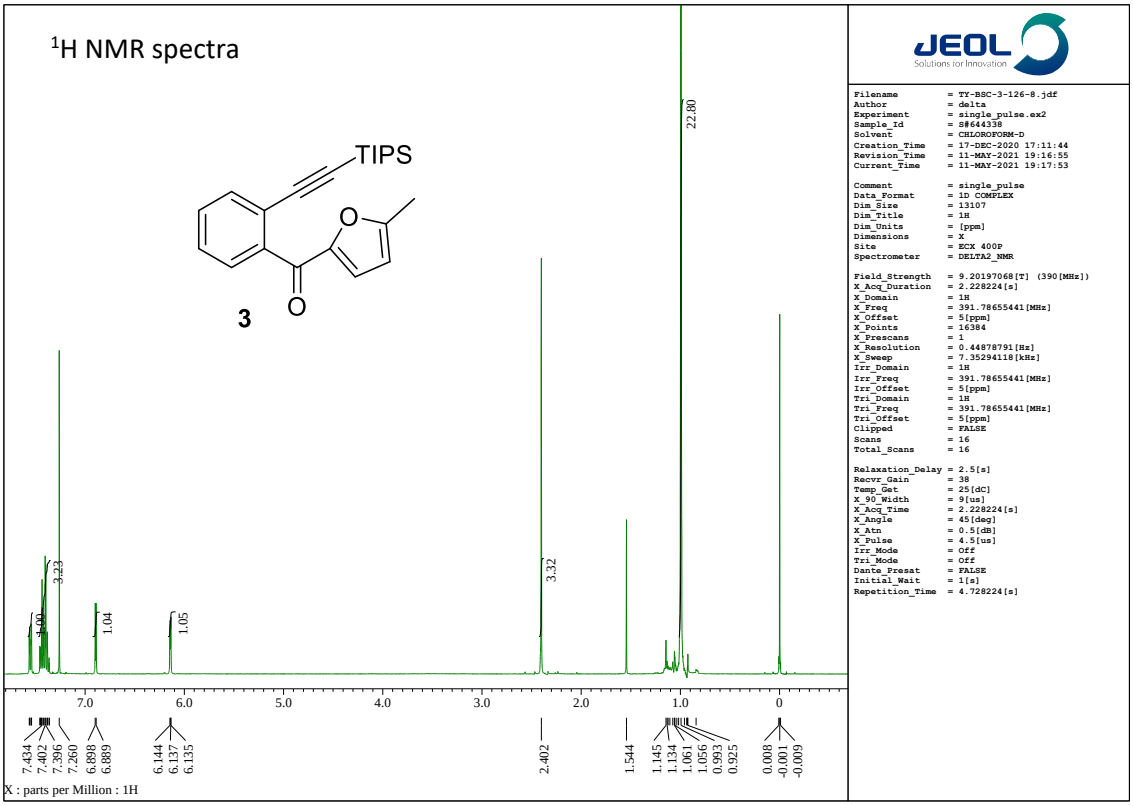
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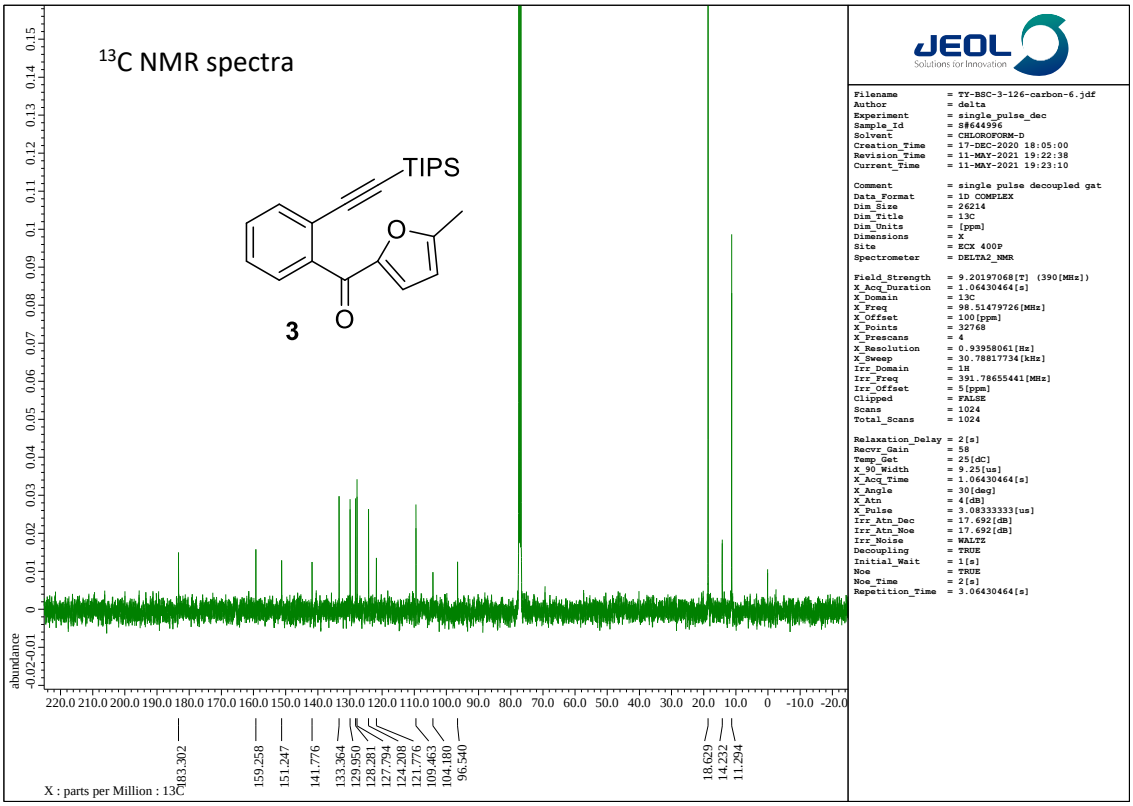
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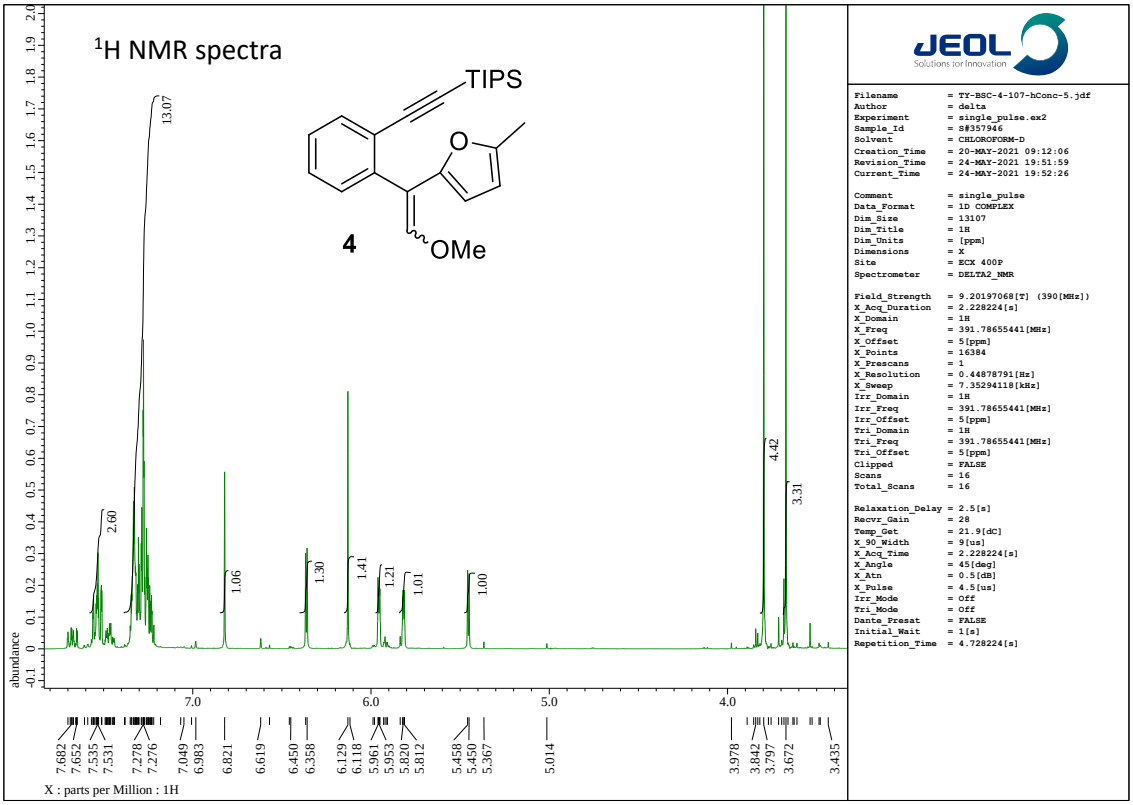
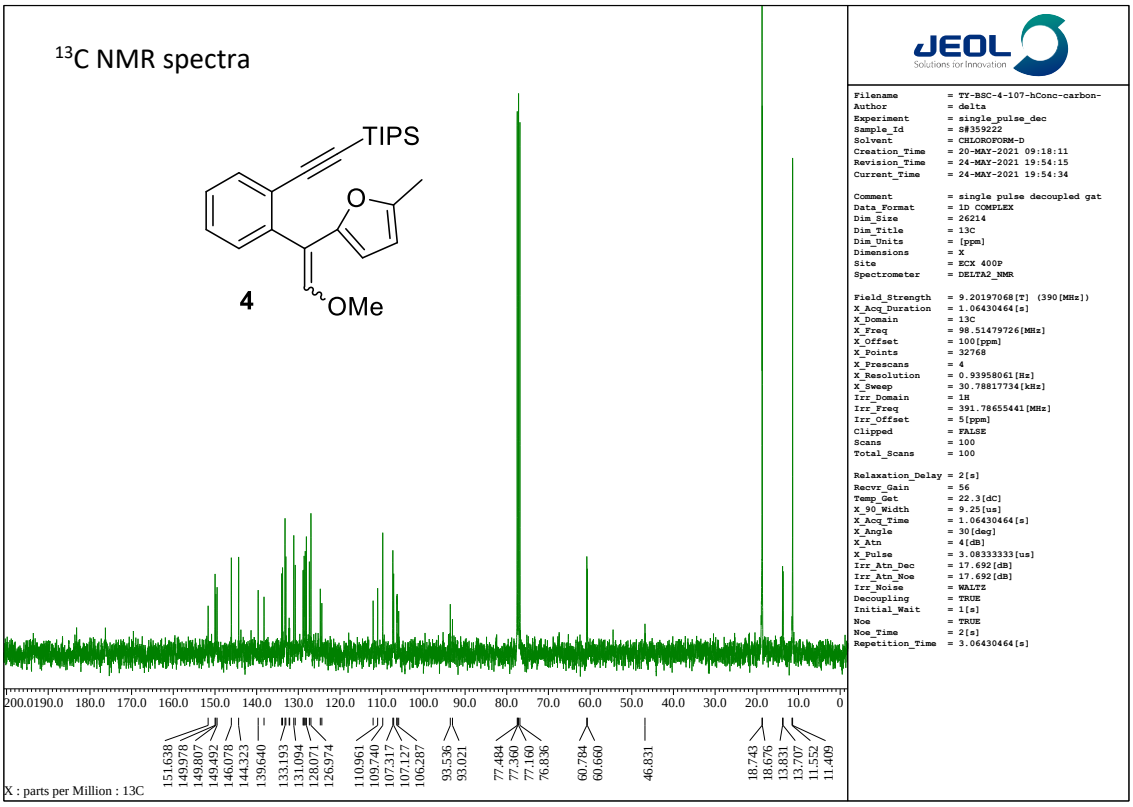
109.463
104.180
96.540
18.629
14.232
11.294
X : parts per Million : 13C

JEOL
Solutions for Innovation
Filename = TY-BSC-3-126-carbon-6.jdf
Author = delta
Experiment = single_pulse_dec
Sample_Id = S#644996
Solvent = CHLOROFORM-D
Creation_Time = 17-DEC-2020 18:05:00
Revision_Time = 11-MAY-2021 19:22:38
Current_Time = 11-MAY-2021 19:23:10
Comment = single pulse decoupled gat
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = 13C
Dim_Units = [ppm]
Dimensions = X
Site = ECX 400P
Spectrometer = DELTA2_NMR
Field_Strength = 9.20197068[T] (390[MHz])
X_Acq_Duration = 1.06430464[s]
X_Domain = 13C
X_Freq = 98.51479726[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.93958061[Hz]
X_Sweep = 30.78817734[kHz]
Irr_Domain = 1H
Irr_Freq = 391.78655441[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 58
Temp_Get = 25[dC]
X_90_Width = 9.25[us]
X_Acq_Time = 1.06430464[s]
X_Angle = 30[deg]
X_Atn = 4[dB]
X_Pulse = 3.08333333[us]
Irr_Atn_Dec = 17.692[dB]
Irr_Atn_Noe = 17.692[dB]
Irr_Noise = WALTZ
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 3.06430464[s]



JEOL Solutions for Innovation

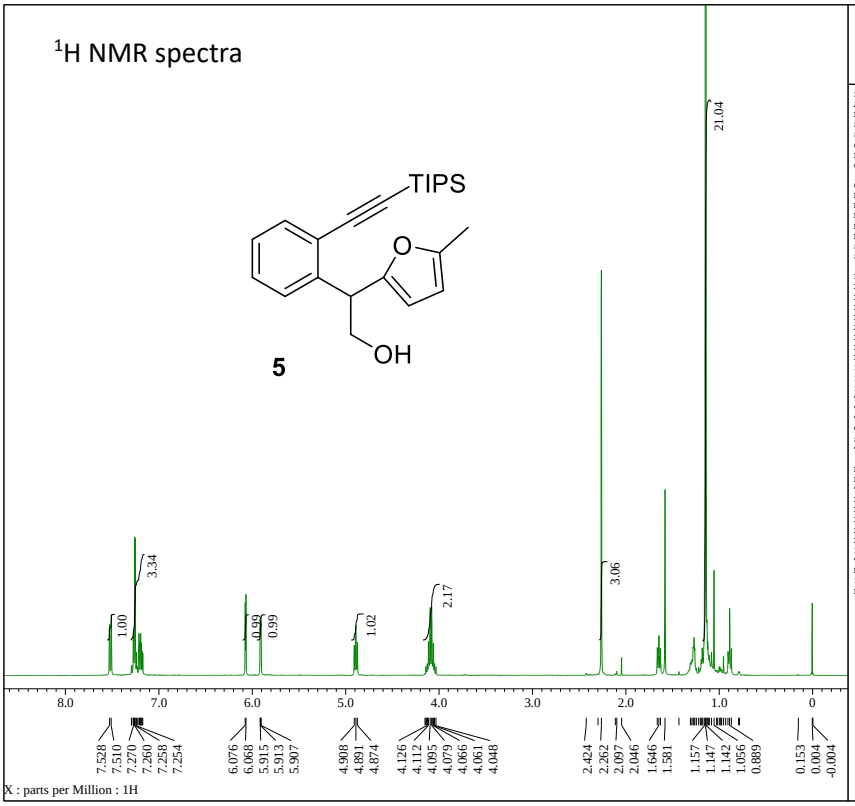
```
Filename          = TY-BSC-4-107-hConc-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#357946
Solvent           = CHLOROFORM-D
Creation_Time     = 20-MAY-2021 09:12:06
Revision_Time     = 24-MAY-2021 19:51:59
Current_Time      = 24-MAY-2021 19:52:26

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 28
Temp_Get          = 21.9[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```



JEOL Solutions for Innovation

```
Filename          = TY-BSC-4-107-hConc-carbon-
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#359222
Solvent           = CHLOROFORM-D
Creation_Time     = 20-MAY-2021 09:18:11
Revision_Time     = 24-MAY-2021 19:54:15
Current_Time      = 24-MAY-2021 19:54:34

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 100
Total_Scans       = 100

Relaxation_Delay  = 2[s]
Recvr_Gain        = 56
Temp_Get          = 22.3[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```

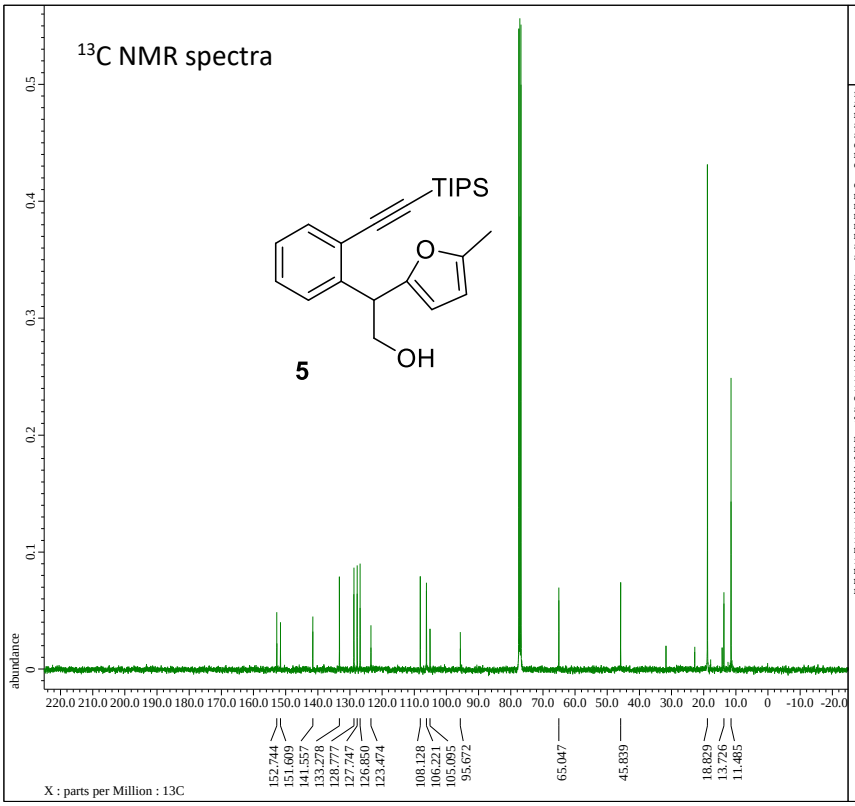
^{1}H NMR spectra



JEOL Solutions for Innovation

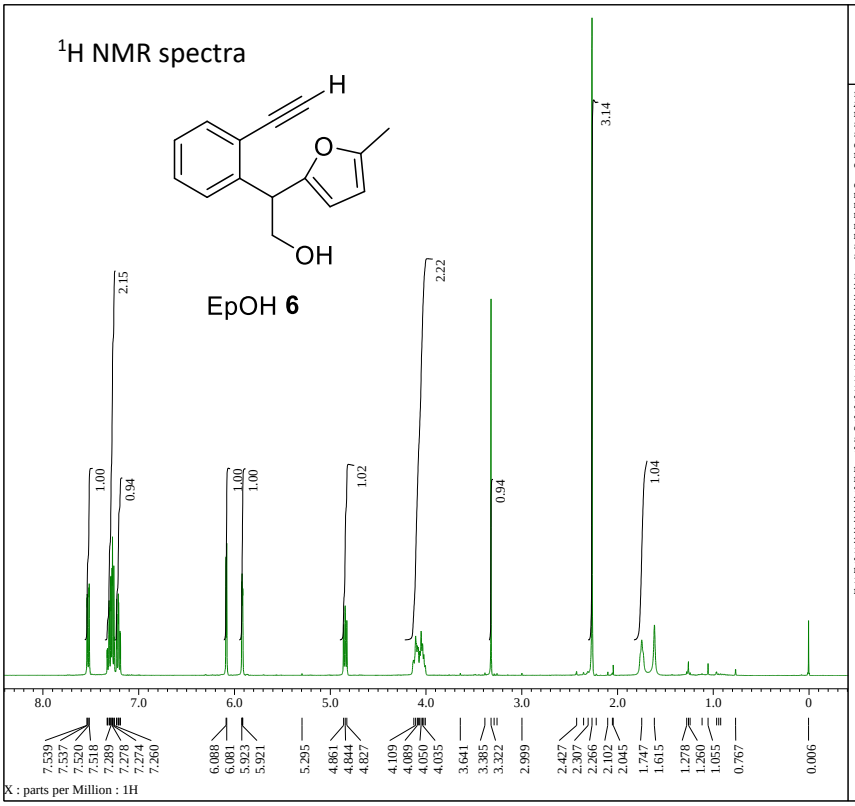
```
Filename          = TY-BSC-3-031-8.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#411749
Solvent           = CHLOROFORM-D
Creation_Time     = 11-SEP-2020 10:54:54
Revision_Time     = 11-MAY-2021 19:30:29
Current_Time      = 11-MAY-2021 19:30:51

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 32
Temp_Get          = 25.8[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```

^{13}C NMR spectra



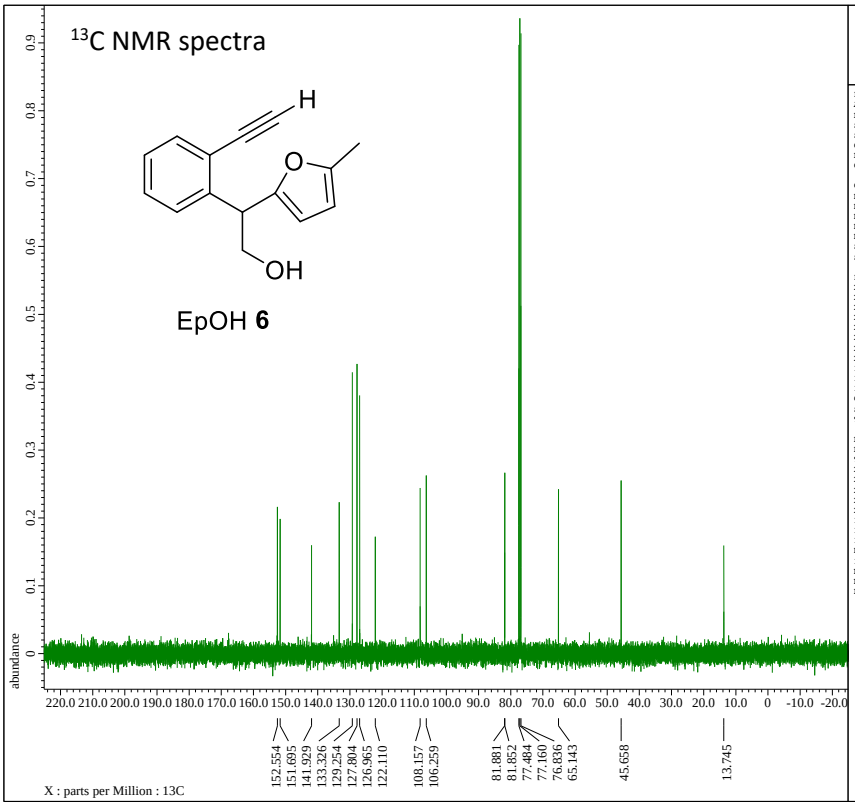
JEOL Solutions for Innovation

```
Filename          = TY-BSC-3-031-carbon-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#413029
Solvent           = CHLOROFORM-D
Creation_Time     = 11-SEP-2020 11:48:11
Revision_Time     = 11-MAY-2021 19:33:41
Current_Time      = 11-MAY-2021 19:33:53

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 56
Temp_Get          = 26.5[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```



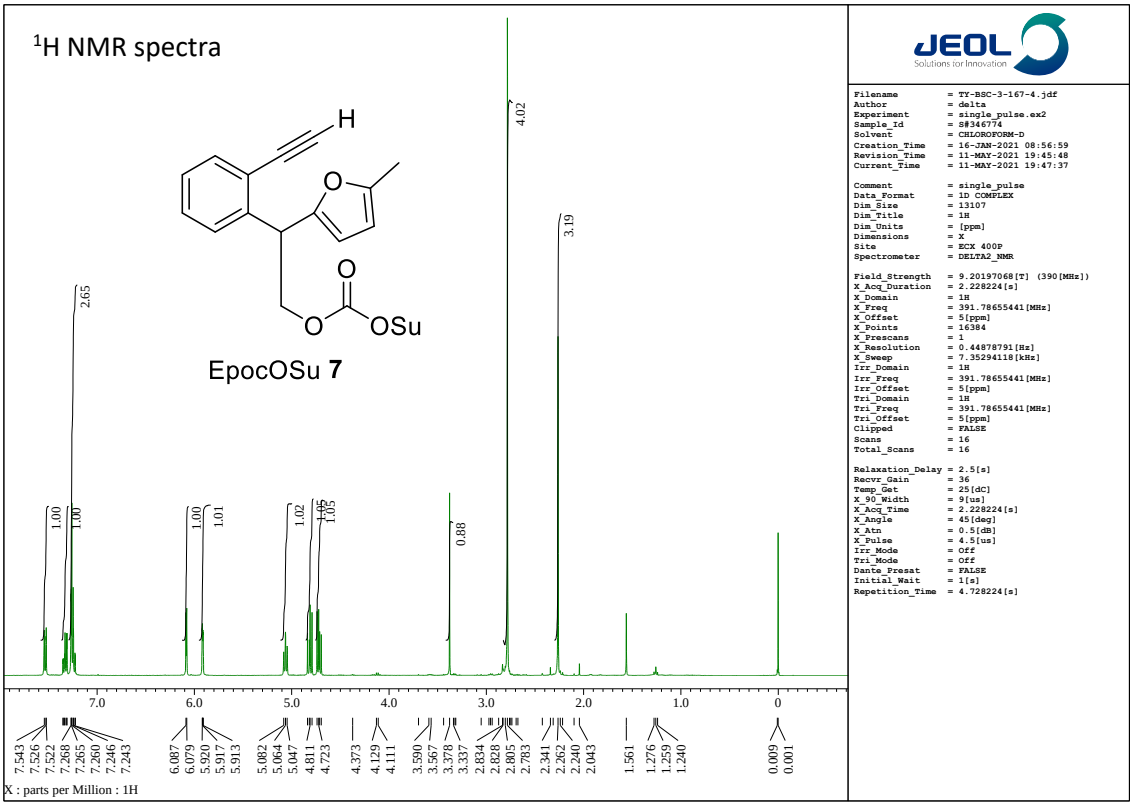
JEOL Solutions for Innovation

```
Filename          = TY-BSC-3-032-11.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#345899
Solvent           = CHLOROFORM-D
Creation_Time     = 12-SEP-2020 09:06:58
Revision_Time     = 11-MAY-2021 19:38:43
Current_Time      = 11-MAY-2021 19:38:52

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 34
Temp_Get          = 25.8[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```

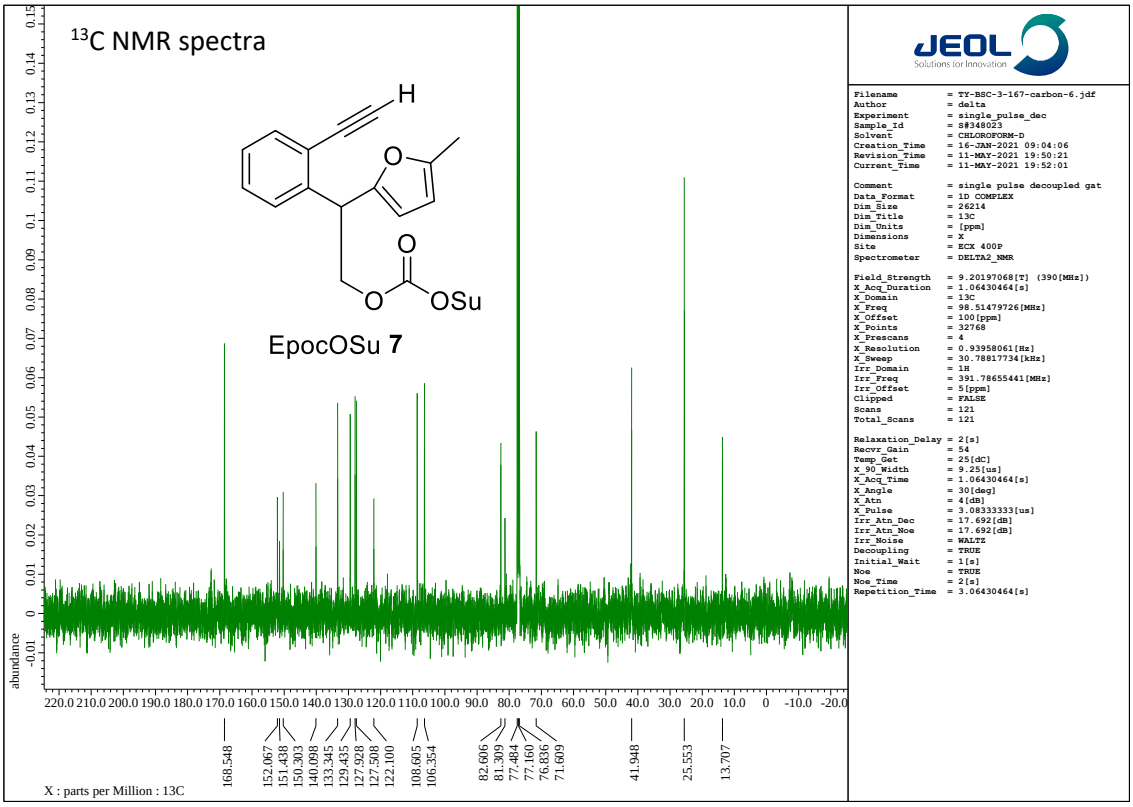


JEOL Solutions for Innovation

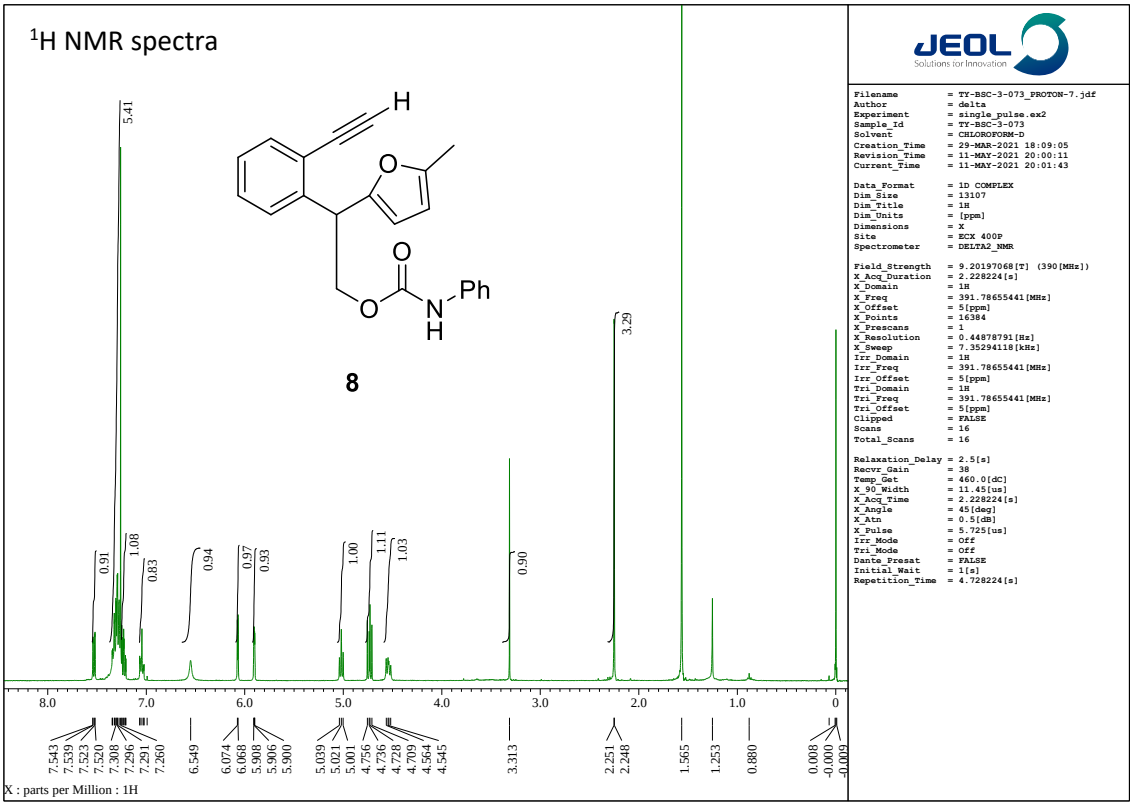
```
Filename          = TY-BSC-3-032-carbon-12.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#345931
Solvent           = CHLOROFORM-D
Creation_Time     = 12-SEP-2020 09:14:10
Revision_Time     = 11-MAY-2021 19:41:36
Current_Time      = 11-MAY-2021 19:41:56

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 128
Total_Scans       = 128

Relaxation_Delay  = 2[s]
Recvr_Gain        = 54
Temp_Get          = 26.2[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```

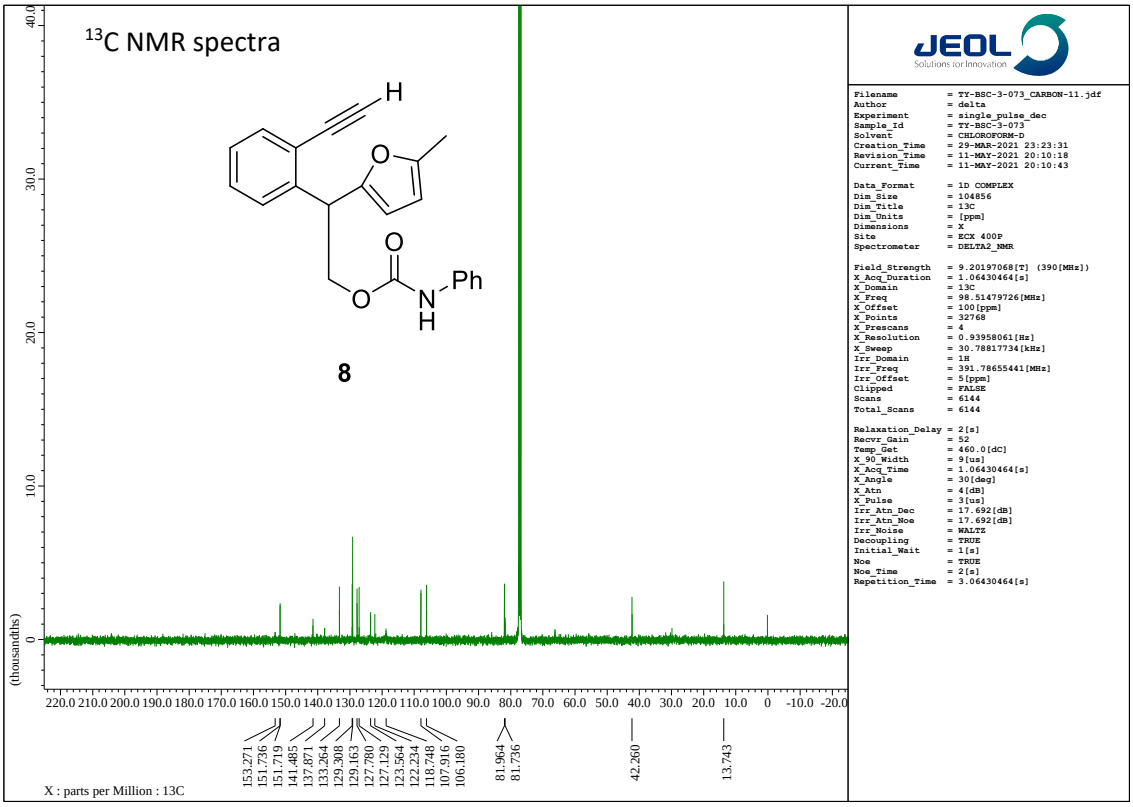


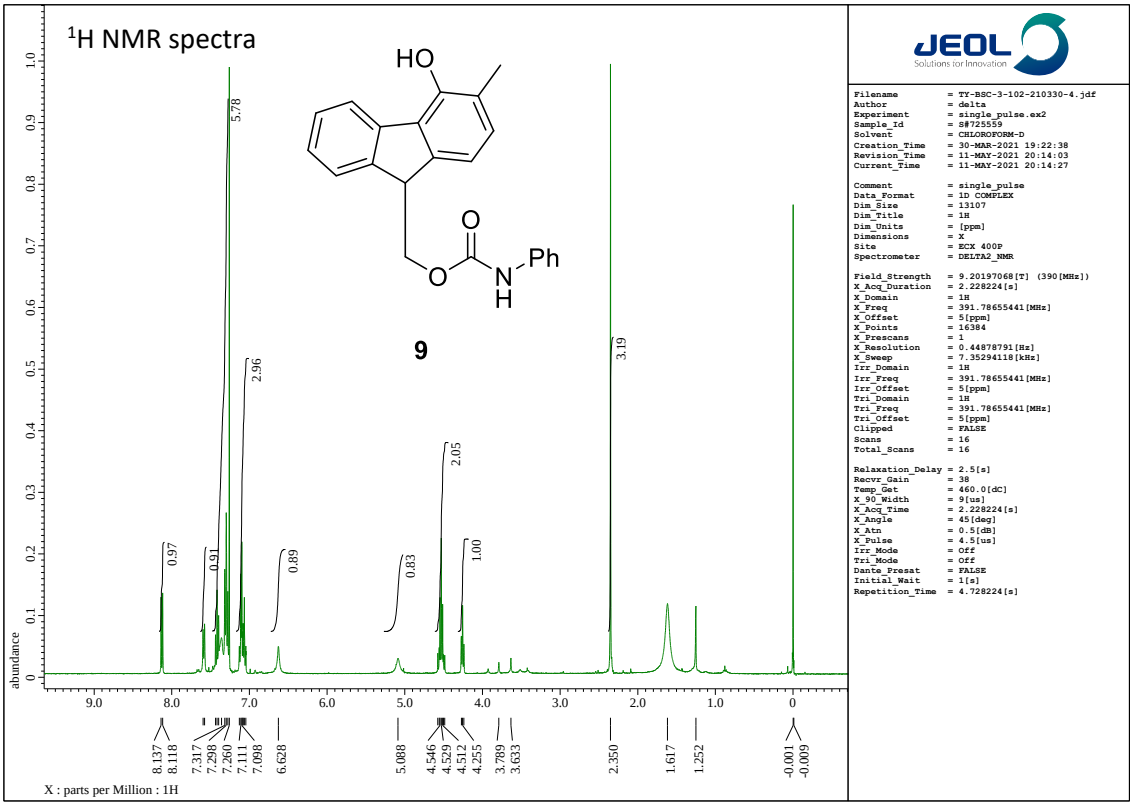

```
Filename          = TY-BSC-3-167-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#346774
Solvent           = CHLOROFORM-D
Creation_Time     = 16-JAN-2021 08:56:59
Revision_Time     = 11-MAY-2021 19:45:48
Current_Time      = 11-MAY-2021 19:47:37

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 36
Temp_Get          = 25[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```

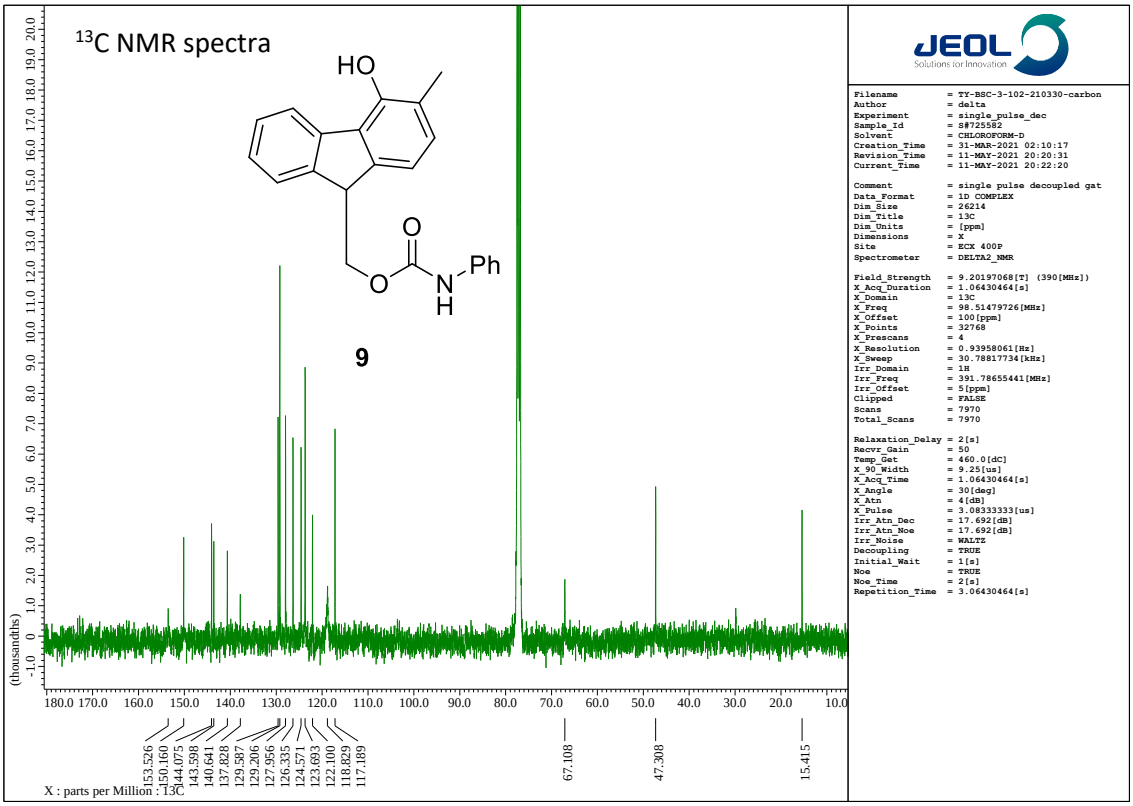


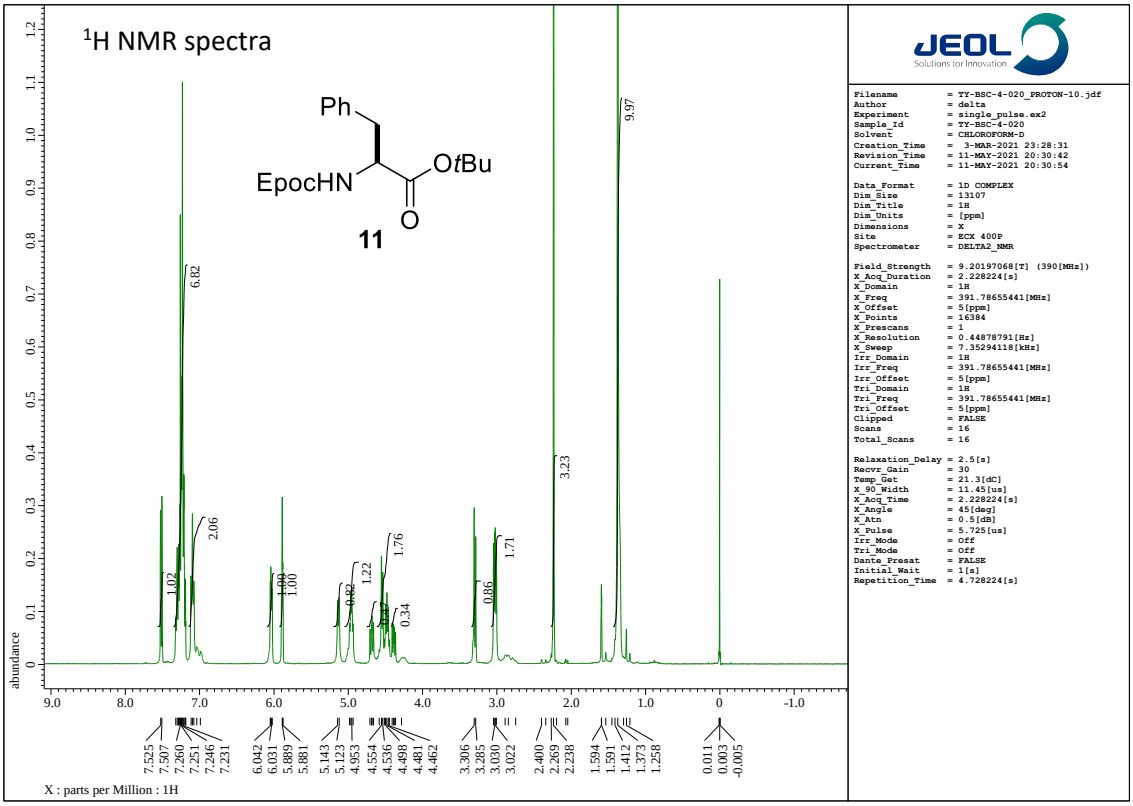

```
Filename          = TY-BSC-3-167-carbon-6.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#348023
Solvent           = CHLOROFORM-D
Creation_Time     = 16-JAN-2021 09:04:06
Revision_Time     = 11-MAY-2021 19:50:21
Current_Time      = 11-MAY-2021 19:52:01

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 121
Total_Scans       = 121

Relaxation_Delay  = 2[s]
Recvr_Gain        = 54
Temp_Get          = 25[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```


1H NMR spectra
8
X : parts per Million : 1H
Filename = TY-BSC-3-073_PROTON-7.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_Id = TY-BSC-3-073
Solvent = CHLOROFORM-D
Creation_Time = 29-MAR-2021 18:09:05
Revision_Time = 11-MAY-2021 20:00:11
Current_Time = 11-MAY-2021 20:01:43
Data_Format = 1D COMPLEX
Dim_Size = 13107
Dim_Title = 1H
Dim_Units = [ppm]
Dimensions = X
Site = ECX 400P
Spectrometer = DELTA2_NMR
Field_Strength = 9.20197068[T] (390[MHz])
X_Acq_Duration = 2.228224[s]
X_Domain = 1H
X_Freq = 391.78655441[MHz]
X_Offset = 5[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.44878791[Hz]
X_Sweep = 7.35294118[kHz]
Irr_Domain = 1H
Irr_Freq = 391.78655441[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = 1H
Tri_Freq = 391.78655441[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 16
Total_Scans = 16
Relaxation_Delay = 2.5[s]
Recvr_Gain = 38
Temp_Get = 460.0[dC]
X_90_Width = 11.45[us]
X_Acq_Time = 2.228224[s]
X_Angle = 45[deg]
X_Atn = 0.5[dB]
X_Pulse = 5.725[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 4.728224[s]

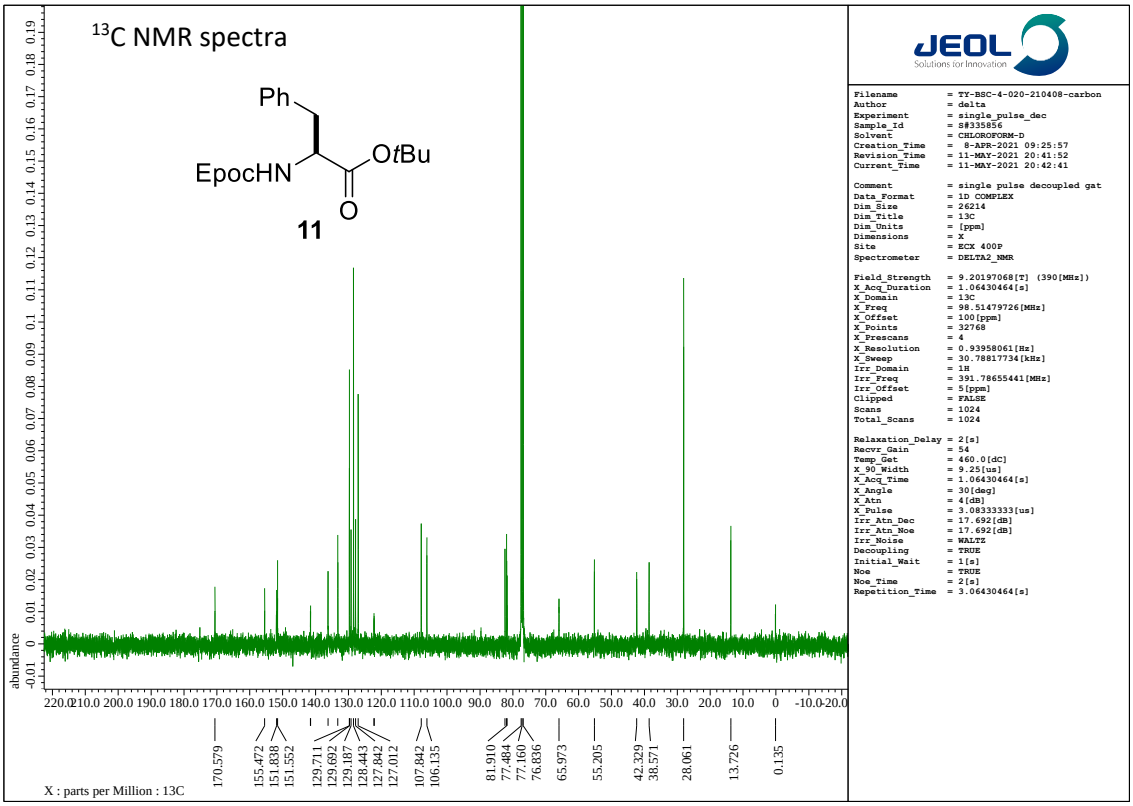

13C NMR spectra
8
X : parts per Million : 13C
Filename = TY-BSC-3-073_CARBON-11.jdf
Author = delta
Experiment = single_pulse_dec
Sample_Id = TY-BSC-3-073
Solvent = CHLOROFORM-D
Creation_Time = 29-MAR-2021 23:23:31
Revision_Time = 11-MAY-2021 20:10:18
Current_Time = 11-MAY-2021 20:10:43
Data_Format = 1D COMPLEX
Dim_Size = 104856
Dim_Title = 13C
Dim_Units = [ppm]
Dimensions = X
Site = ECX 400P
Spectrometer = DELTA2_NMR
Field_Strength = 9.20197068[T] (390[MHz])
X_Acq_Duration = 1.06430464[s]
X_Domain = 13C
X_Freq = 98.51479726[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.93958061[Hz]
X_Sweep = 30.78817734[kHz]
Irr_Domain = 1H
Irr_Freq = 391.78655441[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 6144
Total_Scans = 6144
Relaxation_Delay = 2[s]
Recvr_Gain = 52
Temp_Get = 460.0[dC]
X_90_Width = 9[us]
X_Acq_Time = 1.06430464[s]
X_Angle = 30[deg]
X_Atn = 4[dB]
X_Pulse = 3[us]
Irr_Atn_Dec = 17.692[dB]
Irr_Atn_Noe = 17.692[dB]
Irr_Noise = WALTZ
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 3.06430464[s]


^{1}H NMR spectra
HO
O
O
N
H
Ph
9
5.78
2.96
3.19
2.05
0.97
0.91
0.89
0.83
1.00
abundance
X : parts per Million : 1H

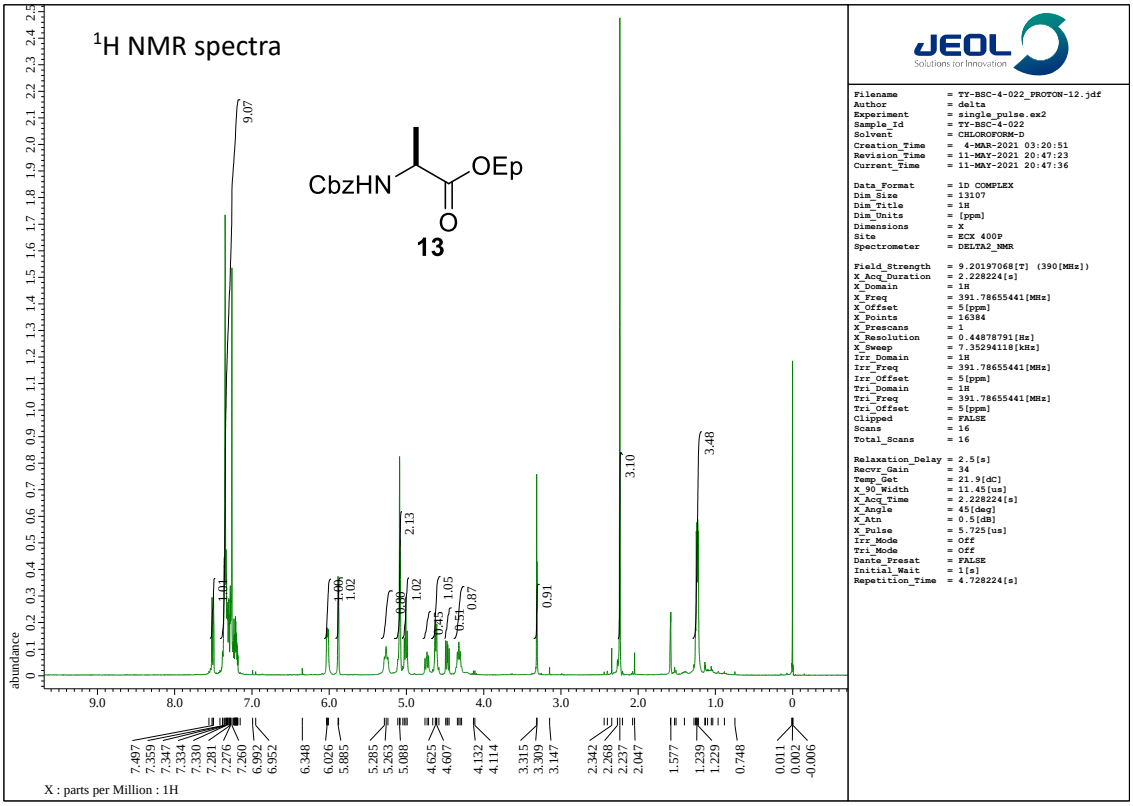

^{13}C NMR spectra
HO
O
O
N
H
Ph
9
(thousandths)
X : parts per Million : 13C




```
Filename          = TY-BSC-4-020_PROTON-10.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = TY-BSC-4-020
Solvent           = CHLOROFORM-D
Creation_Time     =  3-MAR-2021 23:28:31
Revision_Time     = 11-MAY-2021 20:30:42
Current_Time      = 11-MAY-2021 20:30:54

Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 30
Temp_Get          = 21.3[dC]
X_90_Width        = 11.45[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 5.725[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```

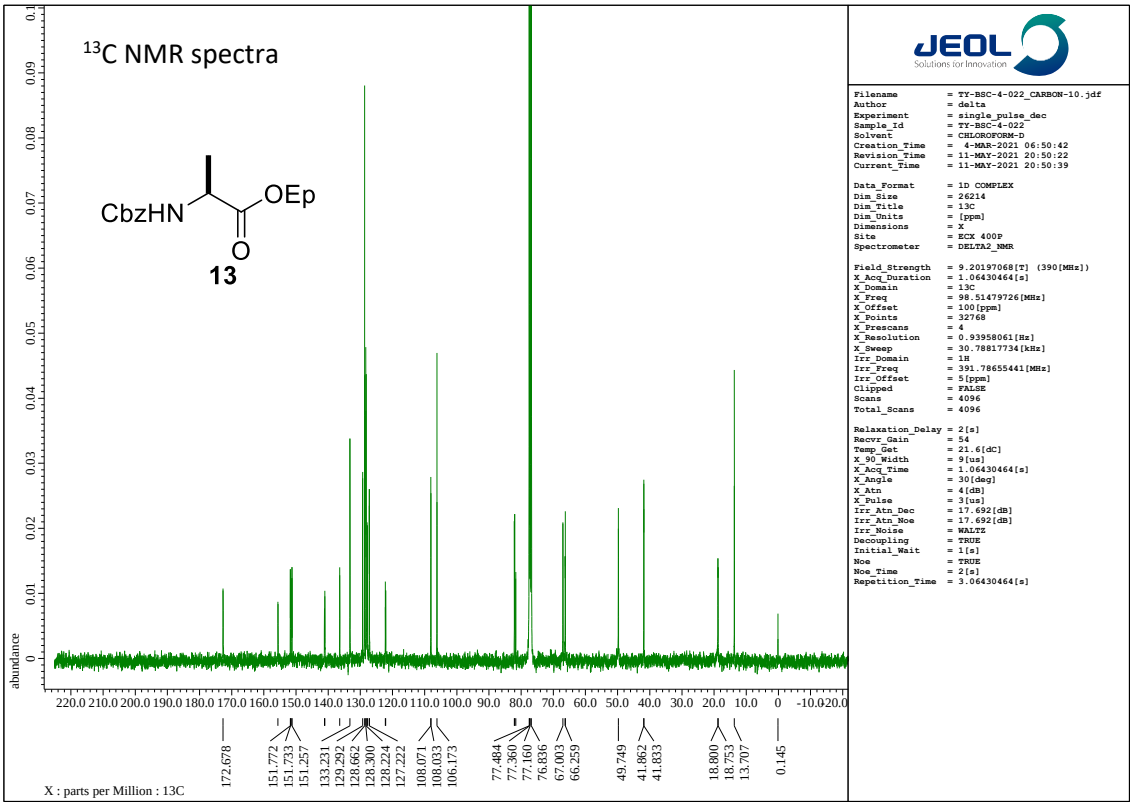



```
Filename          = TY-BSC-4-020-210408-carbon
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#335856
Solvent           = CHLOROFORM-D
Creation_Time     =  8-APR-2021 09:25:57
Revision_Time     = 11-MAY-2021 20:41:52
Current_Time      = 11-MAY-2021 20:42:41

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 54
Temp_Get          = 460.0[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```



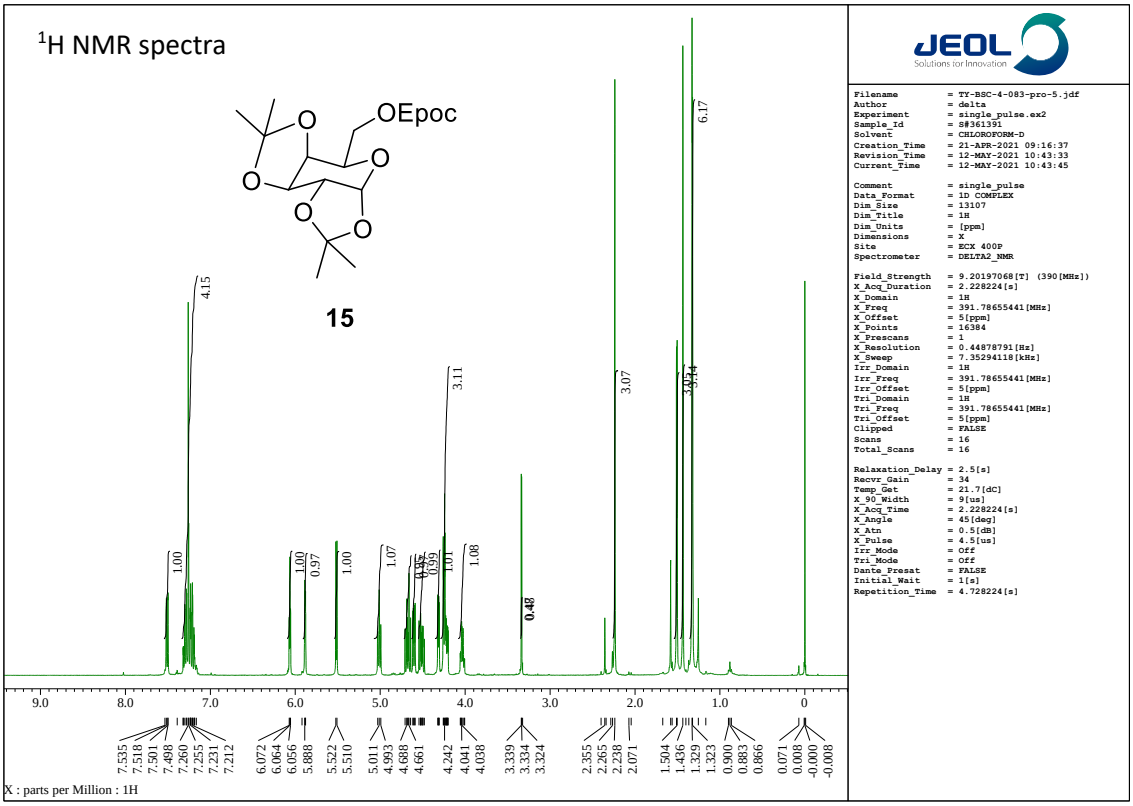
JEOL Solutions for Innovation

```
Filename          = TY-BSC-4-022_PROTON-12.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = TY-BSC-4-022
Solvent           = CHLOROFORM-D
Creation_Time     =  4-MAR-2021 03:20:51
Revision_Time     = 11-MAY-2021 20:47:23
Current_Time      = 11-MAY-2021 20:47:36

Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 34
Temp_Get          = 21.9[dC]
X_90_Width        = 11.45[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 5.725[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```

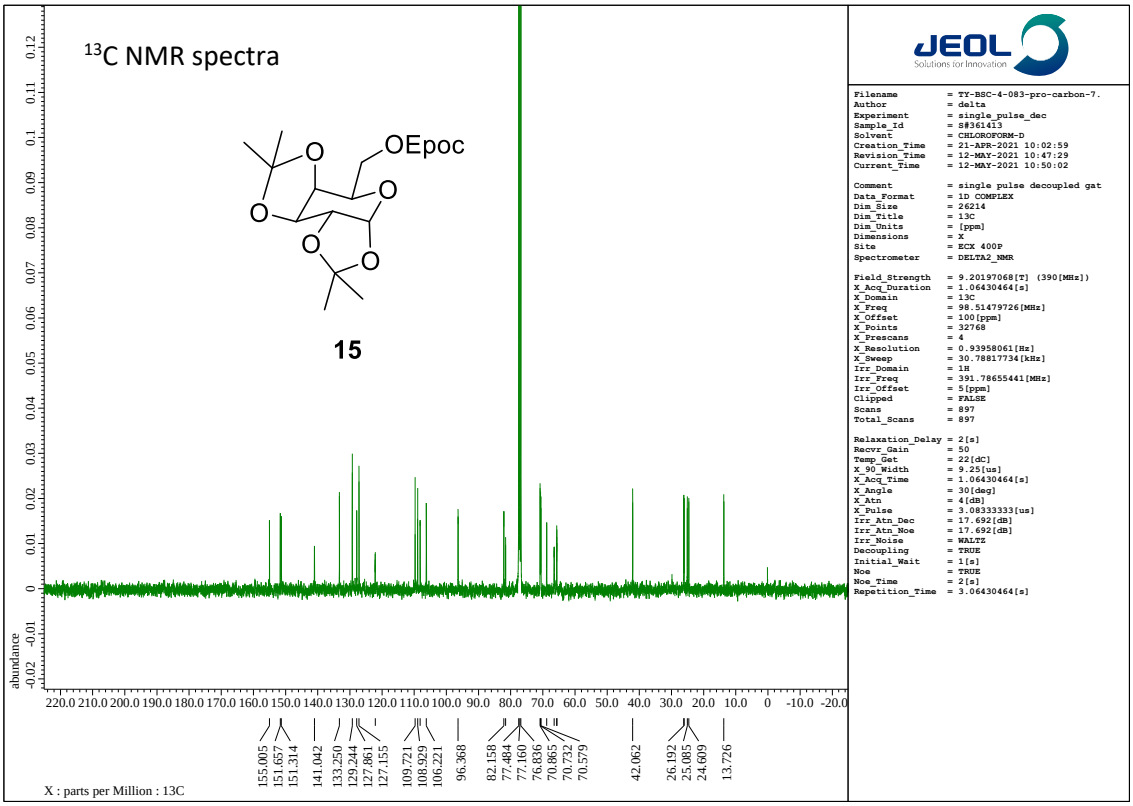


JEOL Solutions for Innovation

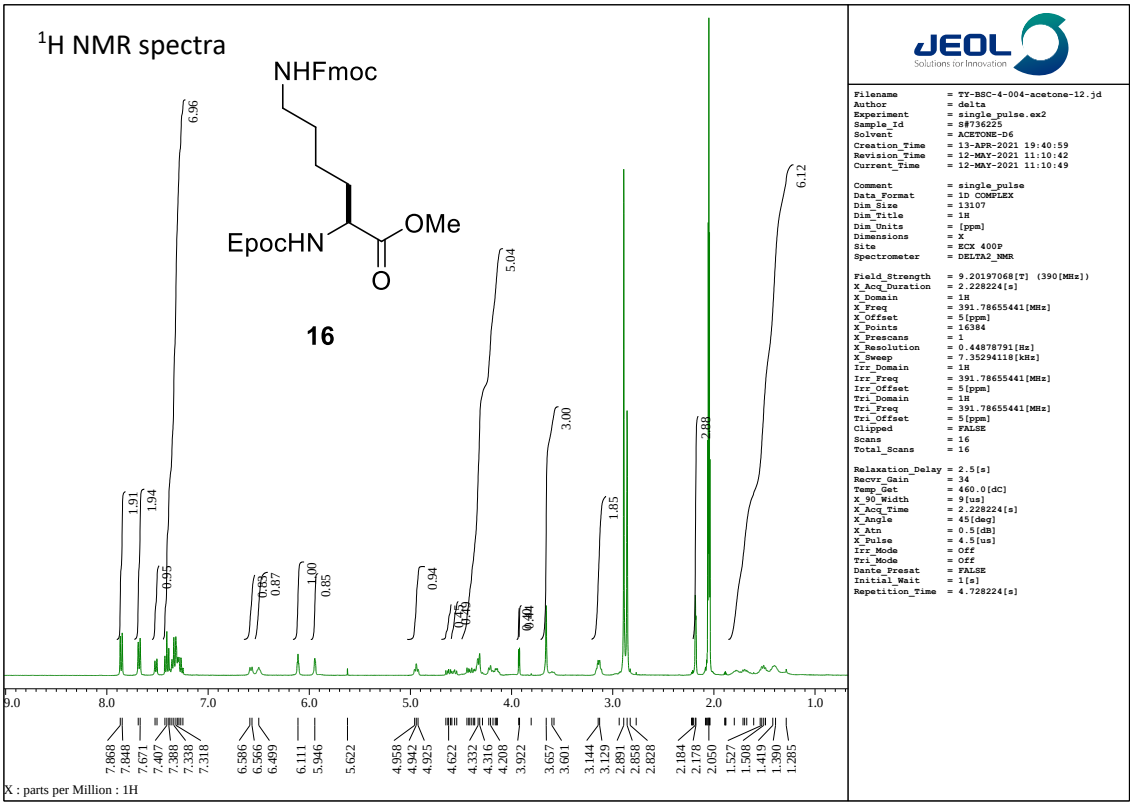
```
Filename          = TY-BSC-4-022_CARBON-10.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = TY-BSC-4-022
Solvent           = CHLOROFORM-D
Creation_Time     =  4-MAR-2021 06:50:42
Revision_Time     = 11-MAY-2021 20:50:22
Current_Time      = 11-MAY-2021 20:50:39

Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 4096
Total_Scans       = 4096

Relaxation_Delay  = 2[s]
Recvr_Gain        = 54
Temp_Get          = 21.6[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```

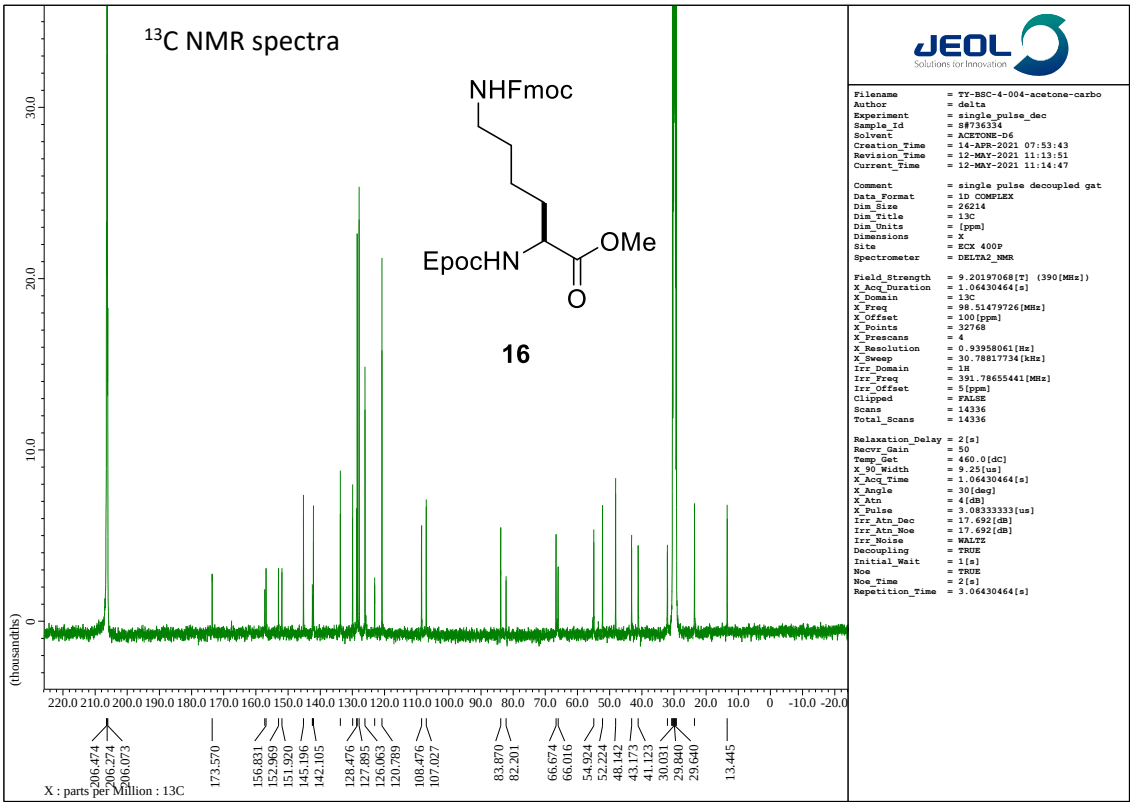


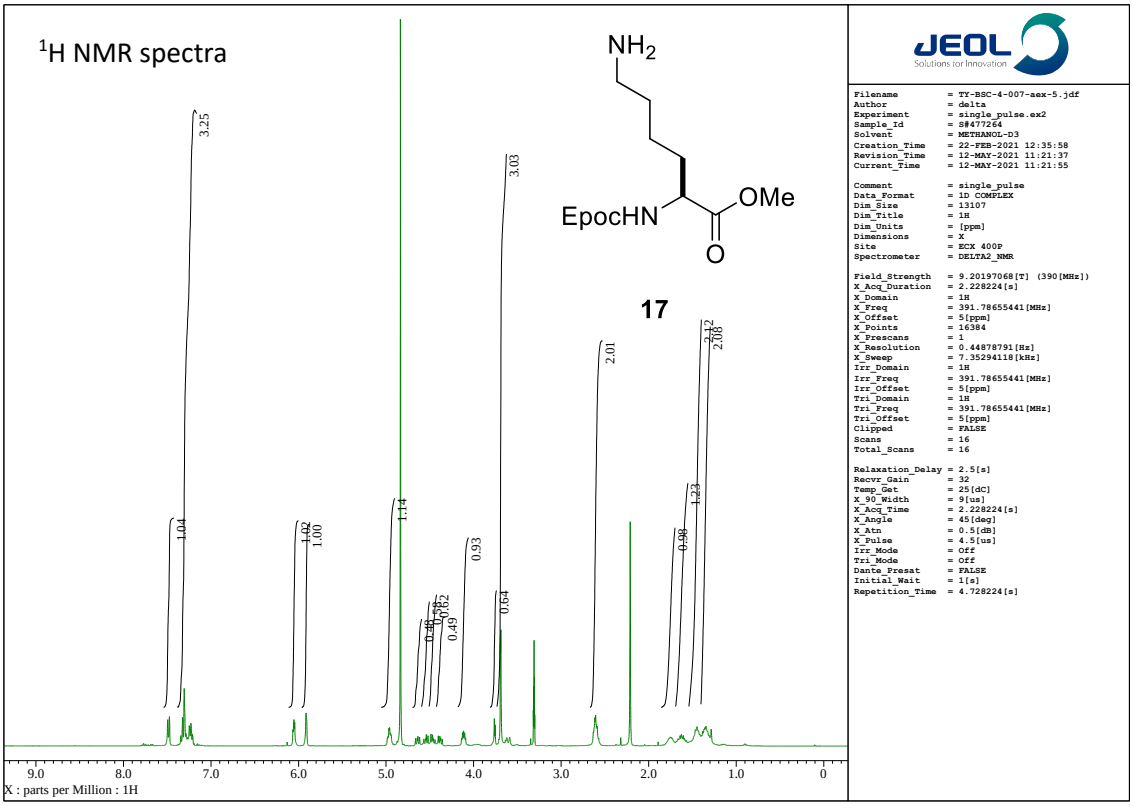

```
Filename          = TY-BSC-4-083-pro-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#361391
Solvent           = CHLOROFORM-D
Creation_Time     = 21-APR-2021 09:16:37
Revision_Time     = 12-MAY-2021 10:43:33
Current_Time      = 12-MAY-2021 10:43:45

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 34
Temp_Get          = 21.7[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```

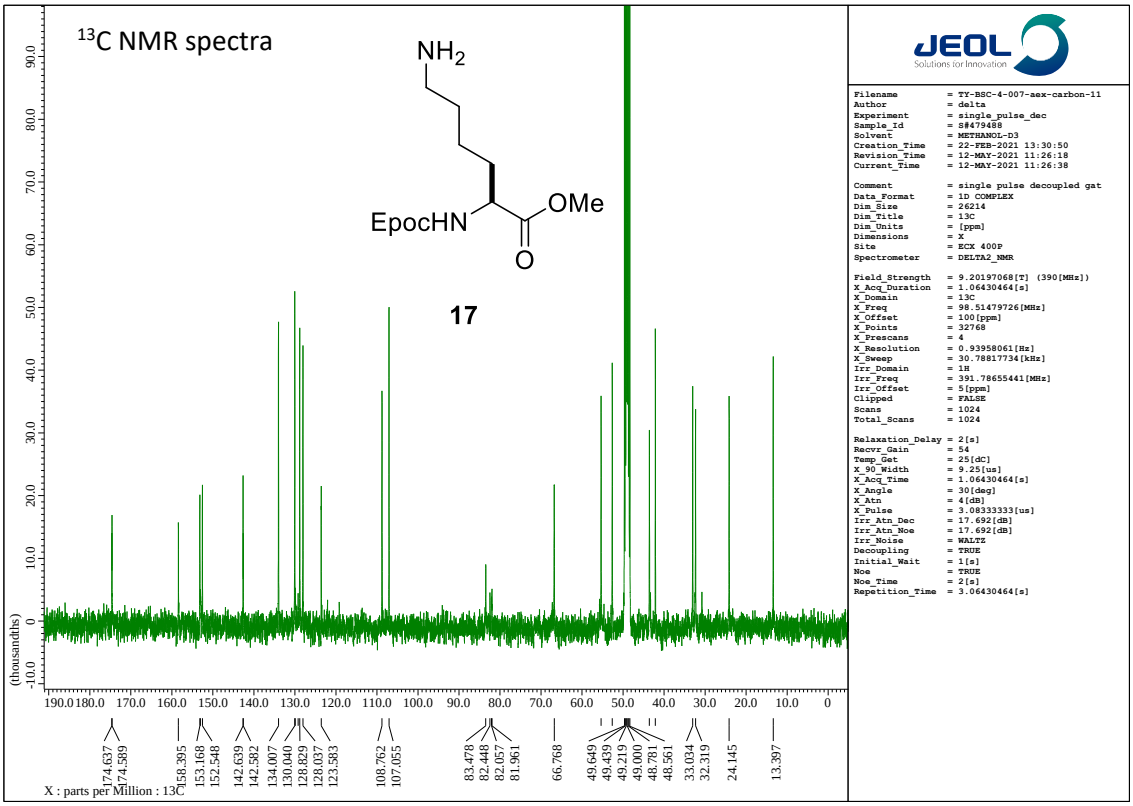

```
Filename          = TY-BSC-4-083-pro-carbon-7.
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#361413
Solvent           = CHLOROFORM-D
Creation_Time     = 21-APR-2021 10:02:59
Revision_Time     = 12-MAY-2021 10:47:29
Current_Time      = 12-MAY-2021 10:50:02

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 897
Total_Scans       = 897

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 22[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```


^{1}H NMR spectra
NHFmoc
EpocHN
OMe
O
16
6.96
5.04
6.12
3.00
2.88
1.91
1.94
0.95
1.85
1.00
0.85
0.94
0.85
0.87
0.49
0.44
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.868
7.848
7.671
7.407
7.388
7.338
7.318
6.586
6.566
6.499
6.111
5.946
5.622
4.958
4.942
4.925
4.622
4.332
4.316
4.208
3.922
3.657
3.601
3.144
3.129
2.891
2.858
2.828
2.184
2.178
2.050
1.527
1.508
1.419
1.390
1.285
X : parts per Million : 1H
JEOL
Solutions for Innovation
Filename = TY-BSC-4-004-acetone-12.jd
Author = delta
Experiment = single_pulse.ex2
Sample_Id = S#736225
Solvent = ACETONE-D6
Creation_Time = 13-APR-2021 19:40:59
Revision_Time = 12-MAY-2021 11:10:42
Current_Time = 12-MAY-2021 11:10:49
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
Dim_Title = 1H
Dim_Units = [ppm]
Dimensions = X
Site = ECX 400P
Spectrometer = DELTA2_NMR
Field_Strength = 9.20197068[T] (390[MHz])
X_Acq_Duration = 2.228224[s]
X_Domain = 1H
X_Freq = 391.78655441[MHz]
X_Offset = 5[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.44878791[Hz]
X_Sweep = 7.35294118[kHz]
Irr_Domain = 1H
Irr_Freq = 391.78655441[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = 1H
Tri_Freq = 391.78655441[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 16
Total_Scans = 16
Relaxation_Delay = 2.5[s]
Recvr_Gain = 34
Temp_Get = 460.0[dC]
X_90_Width = 9[us]
X_Acq_Time = 2.228224[s]
X_Angle = 45[deg]
X_Atn = 0.5[dB]
X_Pulse = 4.5[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 4.728224[s]

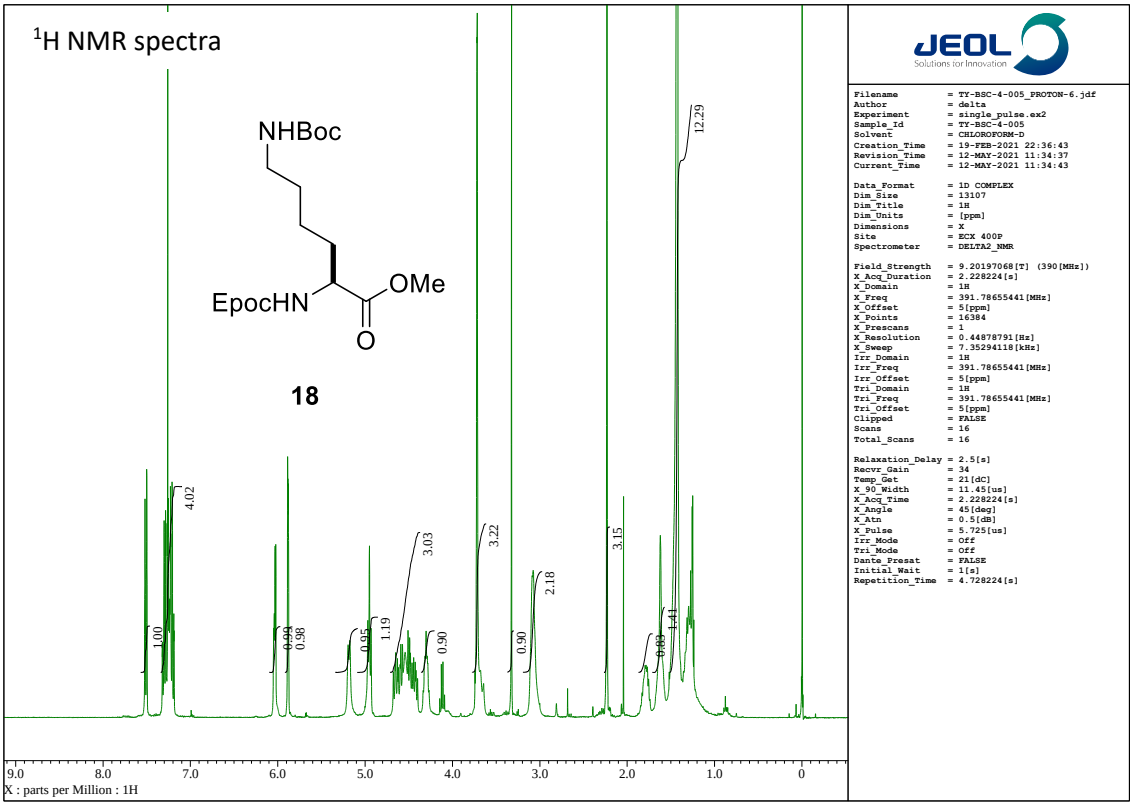

^{13}C NMR spectra
NHFmoc
EpocHN
OMe
O
16
(thousandths)
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
206.474
206.274
206.073
173.570
156.831
152.969
151.920
145.196
142.105
128.476
127.895
126.063
120.789
108.476
107.027
83.870
82.201
66.674
66.016
54.924
52.224
48.142
43.173
41.123
30.031
29.840
29.640
13.445
X : parts per Million : 13C
JEOL
Solutions for Innovation
Filename = TY-BSC-4-004-acetone-carbo
Author = delta
Experiment = single_pulse_dec
Sample_Id = S#736334
Solvent = ACETONE-D6
Creation_Time = 14-APR-2021 07:53:43
Revision_Time = 12-MAY-2021 11:13:51
Current_Time = 12-MAY-2021 11:14:47
Comment = single pulse decoupled gat
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = 13C
Dim_Units = [ppm]
Dimensions = X
Site = ECX 400P
Spectrometer = DELTA2_NMR
Field_Strength = 9.20197068[T] (390[MHz])
X_Acq_Duration = 1.06430464[s]
X_Domain = 13C
X_Freq = 98.51479726[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.93958061[Hz]
X_Sweep = 30.78817734[kHz]
Irr_Domain = 1H
Irr_Freq = 391.78655441[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 14336
Total_Scans = 14336
Relaxation_Delay = 2[s]
Recvr_Gain = 50
Temp_Get = 460.0[dC]
X_90_Width = 9.25[us]
X_Acq_Time = 1.06430464[s]
X_Angle = 30[deg]
X_Atn = 4[dB]
X_Pulse = 3.08333333[us]
Irr_Atn_Dec = 17.692[dB]
Irr_Atn_Noe = 17.692[dB]
Irr_Noise = WALTZ
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 3.06430464[s]

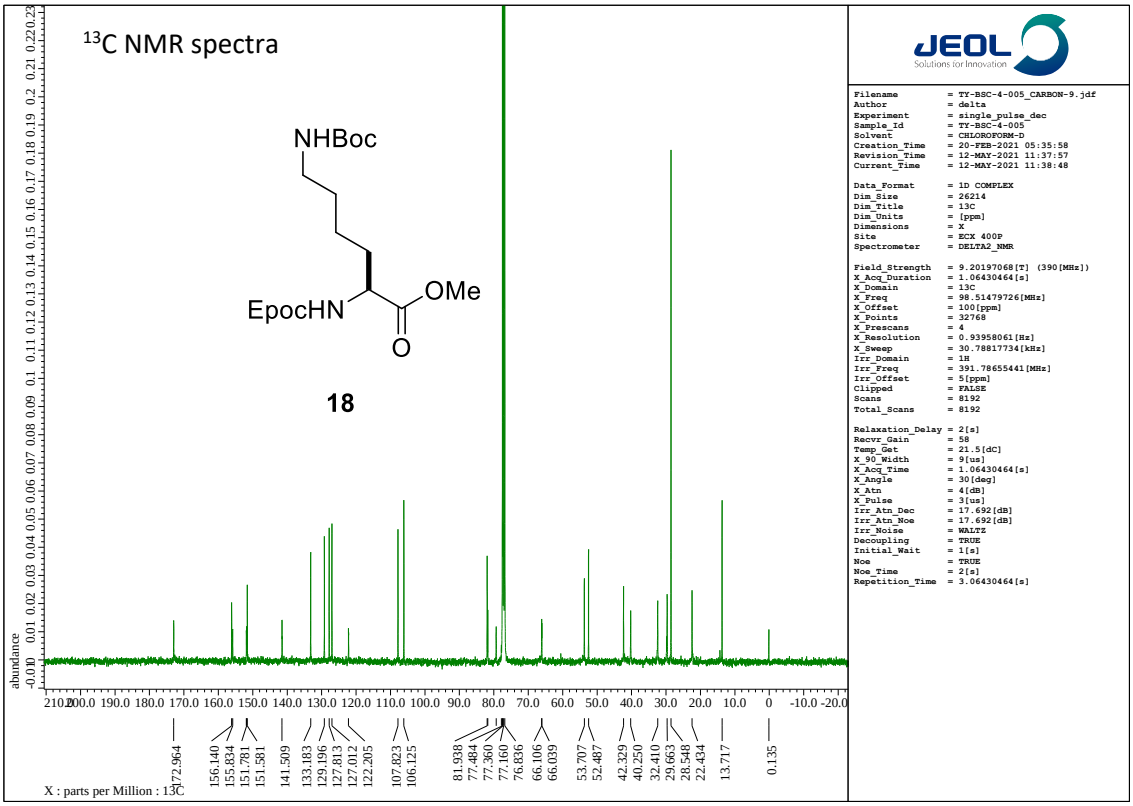



```
Filename          = TY-BSC-4-007-aex-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#477264
Solvent           = METHANOL-D3
Creation_Time     = 22-FEB-2021 12:35:58
Revision_Time     = 12-MAY-2021 11:21:37
Current_Time      = 12-MAY-2021 11:21:55

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 32
Temp_Get          = 25[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```



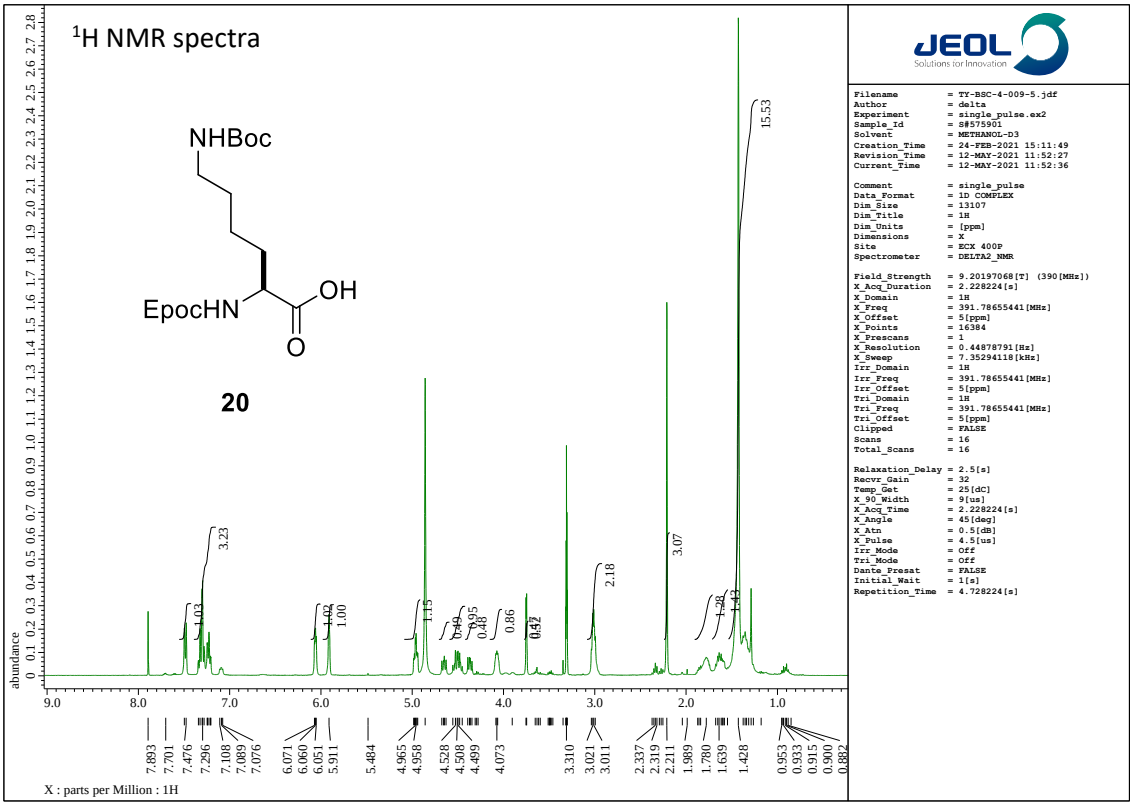

```
Filename          = TY-BSC-4-007-aex-carbon-11
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#479488
Solvent           = METHANOL-D3
Creation_Time     = 22-FEB-2021 13:30:50
Revision_Time     = 12-MAY-2021 11:26:18
Current_Time      = 12-MAY-2021 11:26:38

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 54
Temp_Get          = 25[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```

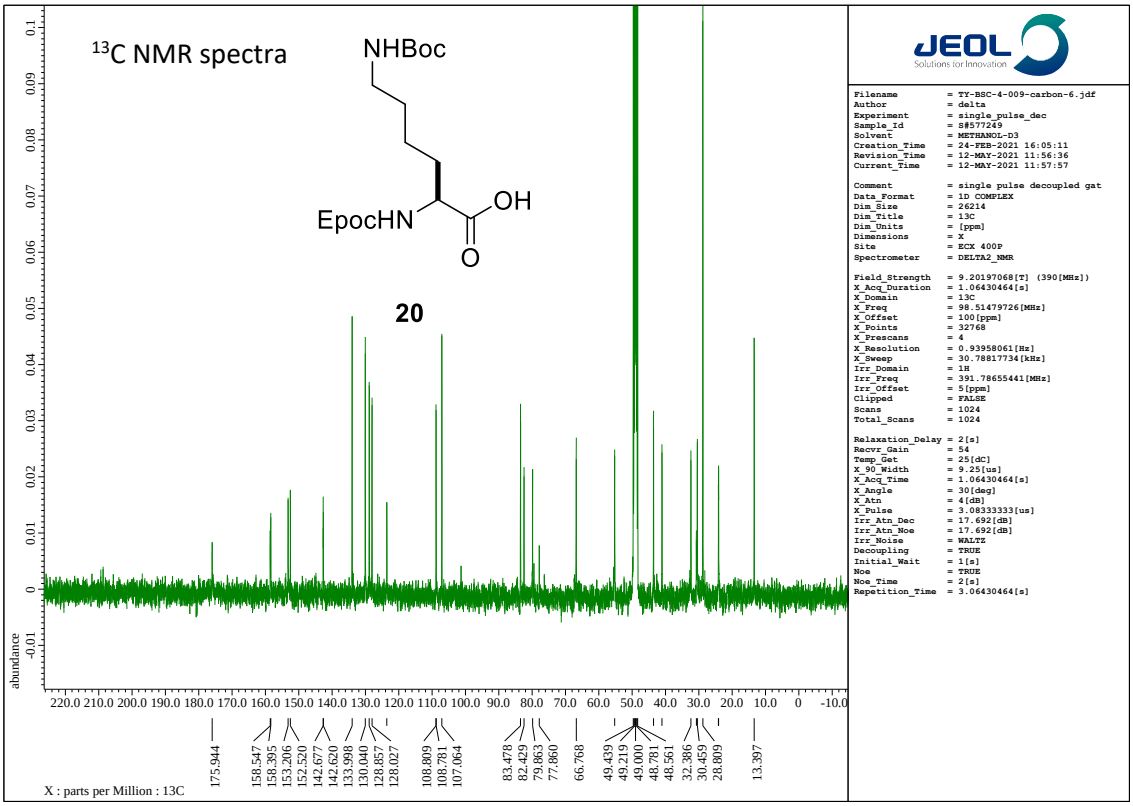


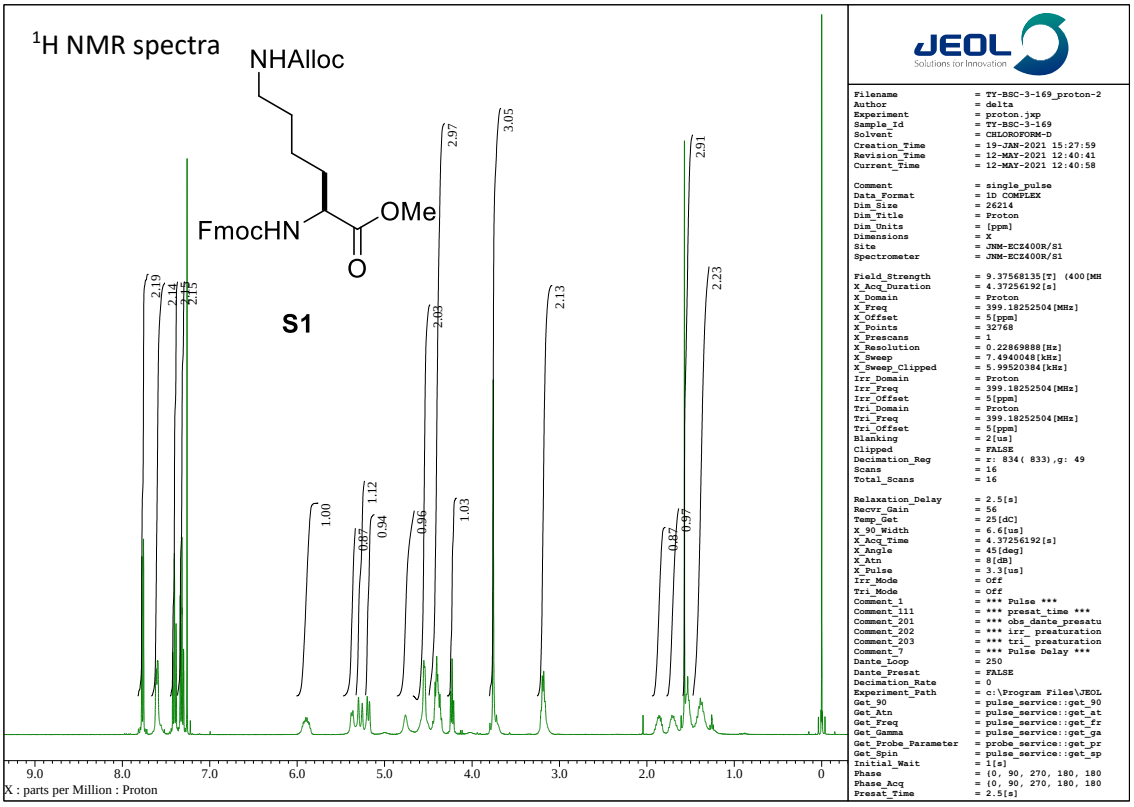



```
Filename          = TY-BSC-4-005_PROTON-6.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = TY-BSC-4-005
Solvent           = CHLOROFORM-D
Creation_Time     = 19-FEB-2021 22:36:43
Revision_Time     = 12-MAY-2021 11:34:37
Current_Time      = 12-MAY-2021 11:34:43

Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 34
Temp_Get          = 21[dC]
X_90_Width        = 11.45[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 5.725[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```

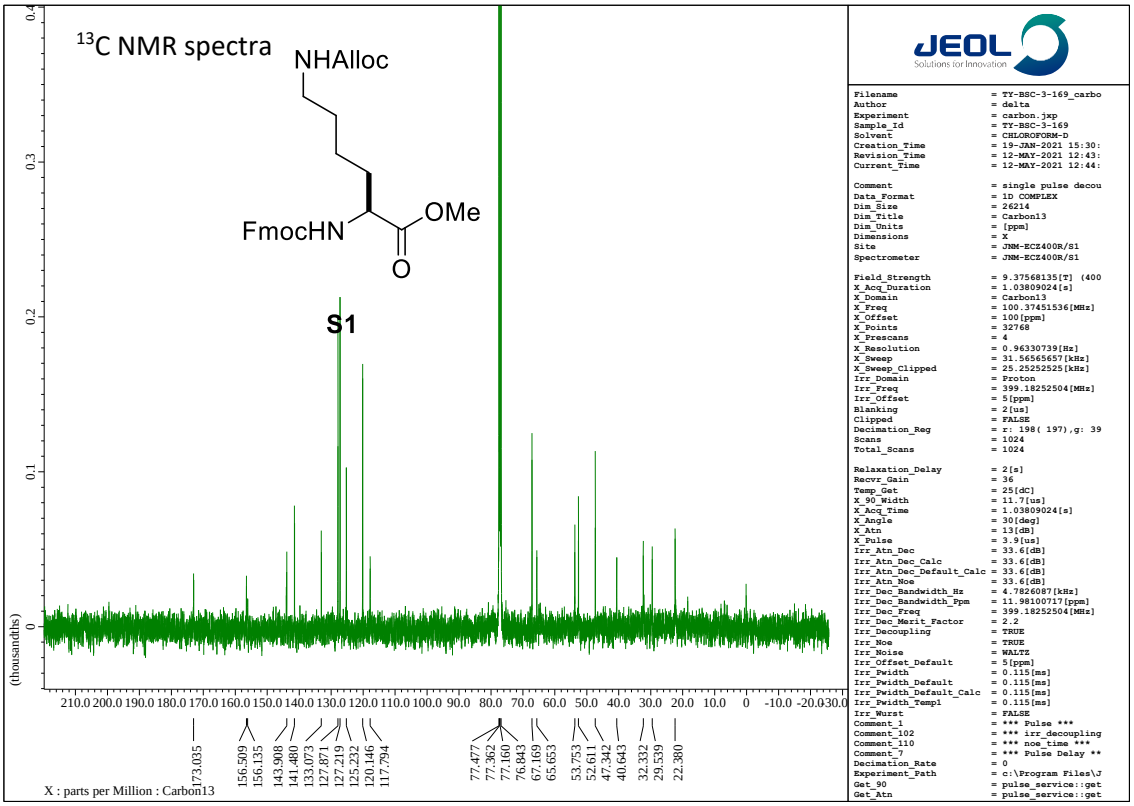
```
Filename          = TY-BSC-4-005_CARBON-9.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = TY-BSC-4-005
Solvent           = CHLOROFORM-D
Creation_Time     = 20-FEB-2021 05:35:58
Revision_Time     = 12-MAY-2021 11:37:57
Current_Time      = 12-MAY-2021 11:38:48

Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8192
Total_Scans       = 8192

Relaxation_Delay  = 2[s]
Recvr_Gain        = 58
Temp_Get          = 21.5[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```


^{1}H NMR spectra
NHBoc
EpocHN
OH
O
20
abundance
X : parts per Million : 1H
Filename = TY-BSC-4-009-5.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_Id = S#575901
Solvent = METHANOL-D3
Creation_Time = 24-FEB-2021 15:11:49
Revision_Time = 12-MAY-2021 11:52:27
Current_Time = 12-MAY-2021 11:52:36
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
Dim_Title = 1H
Dim_Units = [ppm]
Dimensions = X
Site = ECX 400P
Spectrometer = DELTA2_NMR
Field_Strength = 9.20197068[T] (390[MHz])
X_Acq_Duration = 2.228224[s]
X_Domain = 1H
X_Freq = 391.78655441[MHz]
X_Offset = 5[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.44878791[Hz]
X_Sweep = 7.35294118[kHz]
Irr_Domain = 1H
Irr_Freq = 391.78655441[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = 1H
Tri_Freq = 391.78655441[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 16
Total_Scans = 16
Relaxation_Delay = 2.5[s]
Recvr_Gain = 32
Temp_Get = 25[dC]
X_90_Width = 9[us]
X_Acq_Time = 2.228224[s]
X_Angle = 45[deg]
X_Atn = 0.5[dB]
X_Pulse = 4.5[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 4.728224[s]

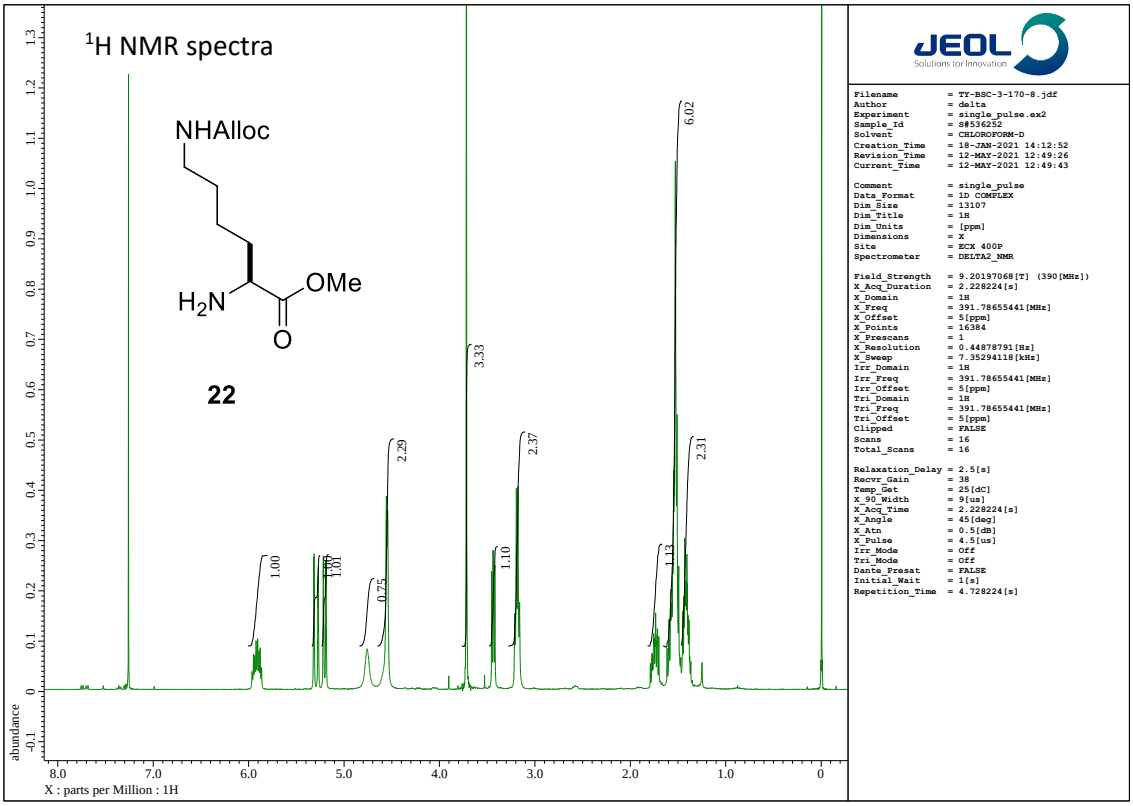

^{13}C NMR spectra
NHBoc
EpocHN
OH
O
20
abundance
X : parts per Million : 13C
Filename = TY-BSC-4-009-carbon-6.jdf
Author = delta
Experiment = single_pulse_dec
Sample_Id = S#577249
Solvent = METHANOL-D3
Creation_Time = 24-FEB-2021 16:05:11
Revision_Time = 12-MAY-2021 11:56:36
Current_Time = 12-MAY-2021 11:57:57
Comment = single pulse decoupled gat
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = 13C
Dim_Units = [ppm]
Dimensions = X
Site = ECX 400P
Spectrometer = DELTA2_NMR
Field_Strength = 9.20197068[T] (390[MHz])
X_Acq_Duration = 1.06430464[s]
X_Domain = 13C
X_Freq = 98.51479726[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.93958061[Hz]
X_Sweep = 30.78817734[kHz]
Irr_Domain = 1H
Irr_Freq = 391.78655441[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 54
Temp_Get = 25[dC]
X_90_Width = 9.25[us]
X_Acq_Time = 1.06430464[s]
X_Angle = 30[deg]
X_Atn = 4[dB]
X_Pulse = 3.08333333[us]
Irr_Atn_Dec = 17.692[dB]
Irr_Atn_Noe = 17.692[dB]
Irr_Noise = WALTZ
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 3.06430464[s]


^{1}H NMR spectra
NHAlloc
FmocHN
OMe
O
S1
2.19
2.14
2.13
2.13
2.97
3.05
2.08
2.13
2.91
2.23
1.00
1.12
0.87
0.94
0.96
1.03
0.87
0.97
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

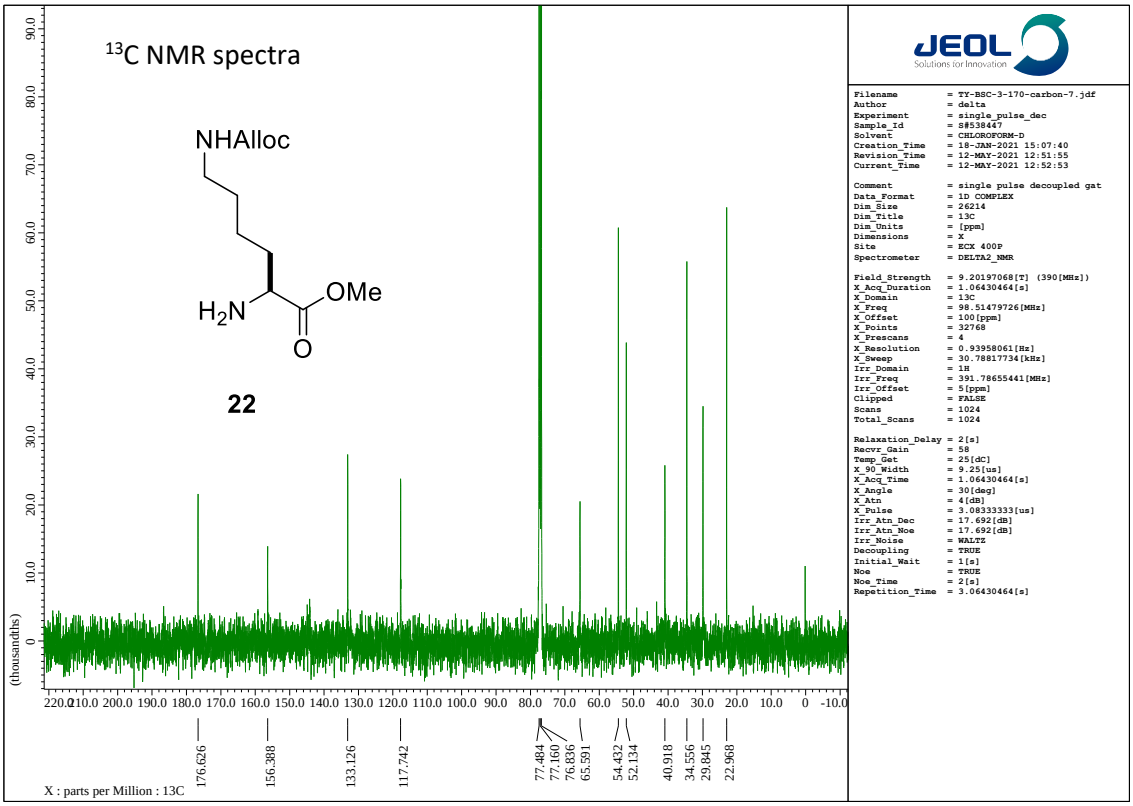
JEOL
Solutions for Innovation
Filename = TY-BSC-3-169_proton-2
Author = delta
Experiment = proton.jxp
Sample_Id = TY-BSC-3-169
Solvent = CHLOROFORM-D
Creation_Time = 19-JAN-2021 15:27:59
Revision_Time = 12-MAY-2021 12:40:41
Current_Time = 12-MAY-2021 12:40:58
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECZ400R/S1
Spectrometer = JNM-ECZ400R/S1
Field_Strength = 9.37568135[T] (400[MH
X_Acq_Duration = 4.37256192[s]
X_Domain = Proton
X_Freq = 399.18252504[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22869888[Hz]
X_Sweep = 7.4940048[kHz]
X_Sweep_Clipped = 5.99520384[kHz]
Irr_Domain = Proton
Irr_Freq = 399.18252504[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.18252504[MHz]
Tri_Offset = 5[ppm]
Blanking = 2[us]
Clipped = FALSE
Decimation_Reg = r: 834(833),g: 49
Scans = 16
Total_Scans = 16
Relaxation_Delay = 2.5[s]
Recvr_Gain = 56
Temp_Get = 25[dC]
X_90_Width = 6.6[us]
X_Acq_Time = 4.37256192[s]
X_Angle = 45[deg]
X_Atn = 8[dB]
X_Pulse = 3.3[us]
Irr_Mode = Off
Tri_Mode = Off
Comment_1 = *** Pulse ***
Comment_111 = *** presat_time ***
Comment_201 = *** obs_dante_presatu
Comment_202 = *** irr_ preaturation
Comment_203 = *** tri_ preaturation
Comment_7 = *** Pulse Delay ***
Dante_Loop = 250
Dante_Presat = FALSE
Decimation_Rate = 0
Experiment_Path = c:\Program Files\JEOL
Get_90 = pulse_service::get_90
Get_Atn = pulse_service::get_at
Get_Freq = pulse_service::get_fr
Get_Gamma = pulse_service::get_ga
Get_Probe_Parameter = probe_service::get_pr
Get_Spin = pulse_service::get_sp
Initial_Wait = 1[s]
Phase = (0, 90, 270, 180, 180
Phase_Acq = (0, 90, 270, 180, 180
Presat_Time = 2.5[s]


^{13}C NMR spectra
NHAlloc
FmocHN
OMe
O
S1
(thousandths)
0.4
0.3
0.2
0.1
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0 -30.0
173.035
156.509
156.135
143.908
141.480
133.073
127.871
127.219
125.232
120.146
117.794
77.477
77.362
77.160
76.843
67.169
65.653
53.753
52.611
47.342
40.643
32.332
29.539
22.380
X : parts per Million : Carbon13

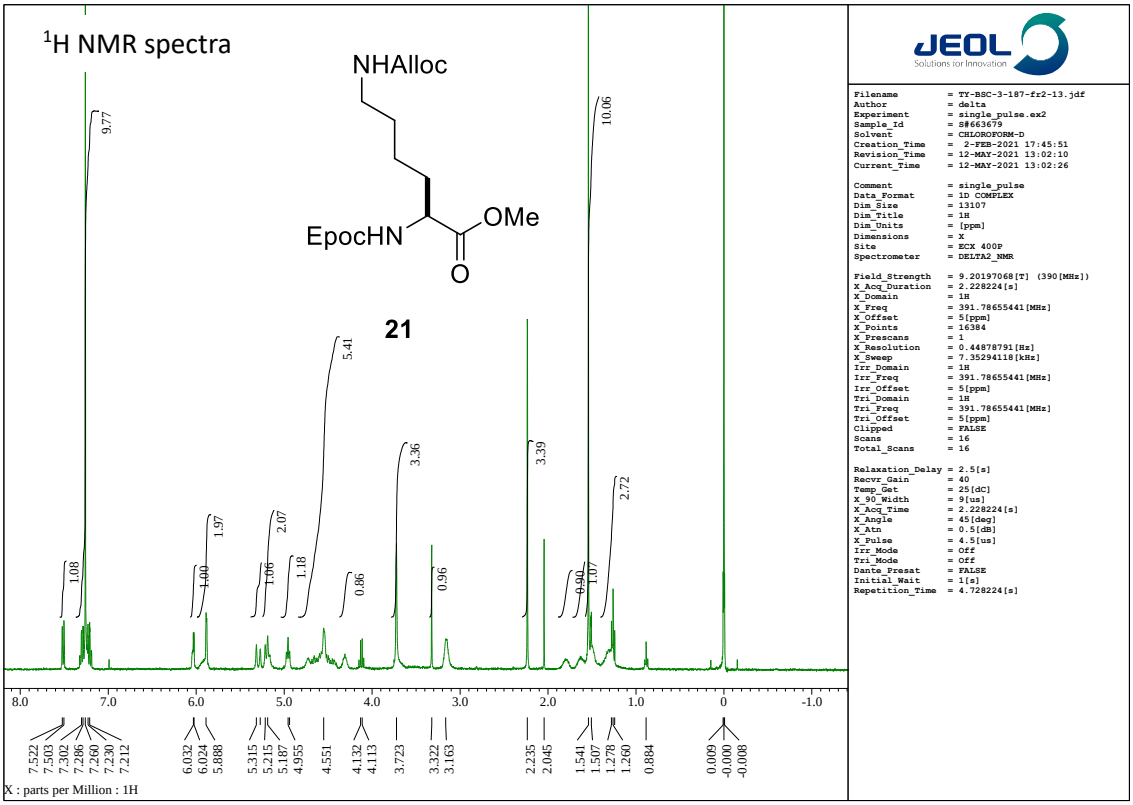
JEOL
Solutions for Innovation
Filename = TY-BSC-3-169_carbo
Author = delta
Experiment = carbon.jxp
Sample_Id = TY-BSC-3-169
Solvent = CHLOROFORM-D
Creation_Time = 19-JAN-2021 15:30:
Revision_Time = 12-MAY-2021 12:43:
Current_Time = 12-MAY-2021 12:44:
Comment = single pulse decou
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECZ400R/S1
Spectrometer = JNM-ECZ400R/S1
Field_Strength = 9.37568135[T] (400
X_Acq_Duration = 1.03809024[s]
X_Domain = Carbon13
X_Freq = 100.37451536[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.96330739[Hz]
X_Sweep = 31.56565657[kHz]
X_Sweep_Clipped = 25.25252525[kHz]
Irr_Domain = Proton
Irr_Freq = 399.18252504[MHz]
Irr_Offset = 5[ppm]
Blanking = 2[us]
Clipped = FALSE
Decimation_Reg = r: 198(197),g: 39
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 36
Temp_Get = 25[dC]
X_90_Width = 11.7[us]
X_Acq_Time = 1.03809024[s]
X_Angle = 30[deg]
X_Atn = 13[dB]
X_Pulse = 3.9[us]
Irr_Atn_Dec = 33.6[dB]
Irr_Atn_Dec_Calc = 33.6[dB]
Irr_Atn_Dec_Default_Calc = 33.6[dB]
Irr_Atn_Noe = 33.6[dB]
Irr_Dec_Bandwidth_Hz = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm = 11.98100717[ppm]
Irr_Dec_Freq = 399.18252504[MHz]
Irr_Dec_Merit_Factor = 2.2
Irr_Decoupling = TRUE
Irr_Noe = TRUE
Irr_Noise = WALTZ
Irr_Offset_Default = 5[ppm]
Irr_Pwidth = 0.115[ms]
Irr_Pwidth_Default = 0.115[ms]
Irr_Pwidth_Default_Calc = 0.115[ms]
Irr_Pwidth_Temp1 = 0.115[ms]
Irr_Wurst = FALSE
Comment_1 = *** Pulse ***
Comment_102 = *** irr_decoupling
Comment_110 = *** noe_time ***
Comment_7 = *** Pulse Delay **
Decimation_Rate = 0
Experiment_Path = c:\Program Files\J
Get_90 = pulse_service::get
Get_Atn = pulse_service::get



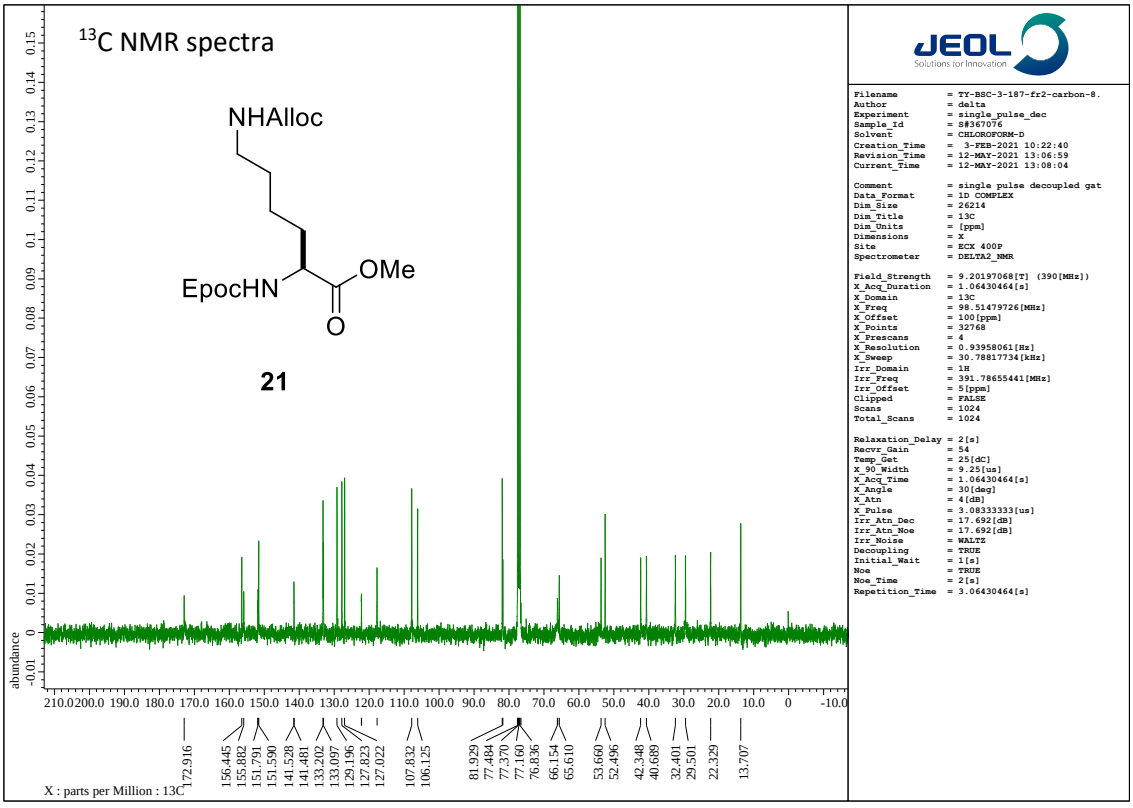

```
Filename          = TY-BSC-3-170-8.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#536252
Solvent           = CHLOROFORM-D
Creation_Time     = 18-JAN-2021 14:12:52
Revision_Time     = 12-MAY-2021 12:49:26
Current_Time      = 12-MAY-2021 12:49:43

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 38
Temp_Get          = 25[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```



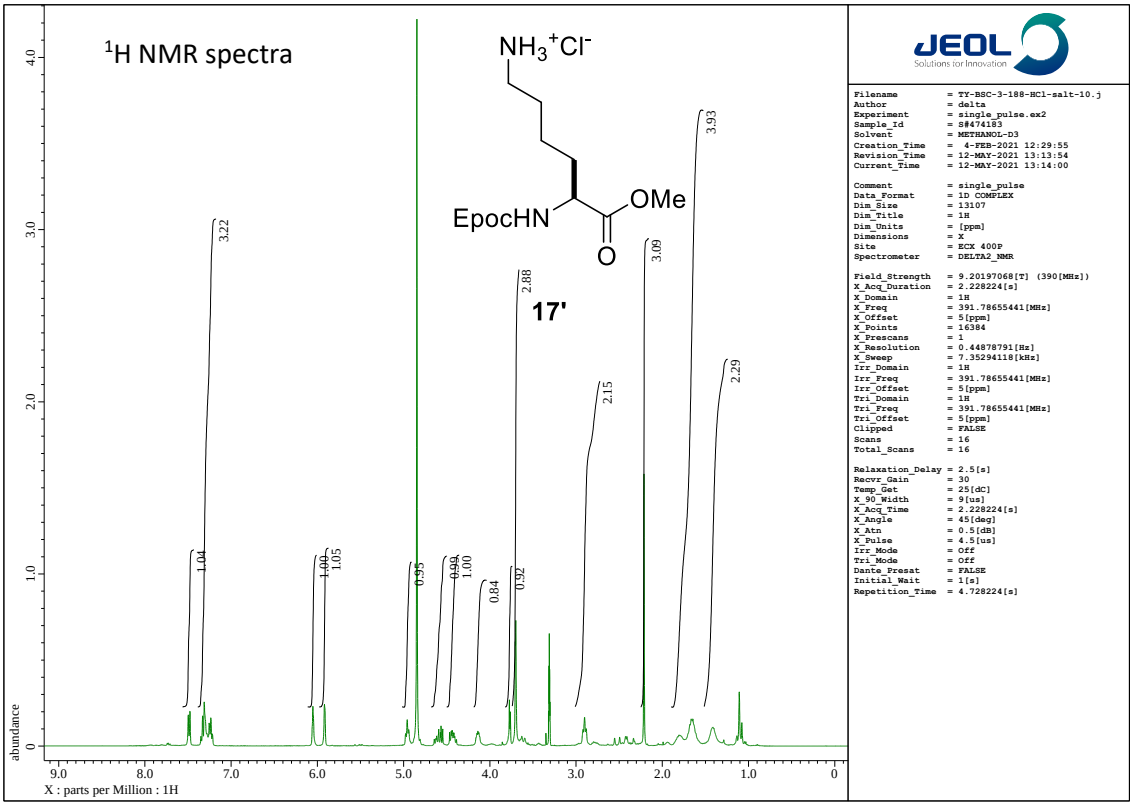

```
Filename          = TY-BSC-3-170-carbon-7.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#538447
Solvent           = CHLOROFORM-D
Creation_Time     = 18-JAN-2021 15:07:40
Revision_Time     = 12-MAY-2021 12:51:55
Current_Time      = 12-MAY-2021 12:52:53

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 58
Temp_Get          = 25[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```



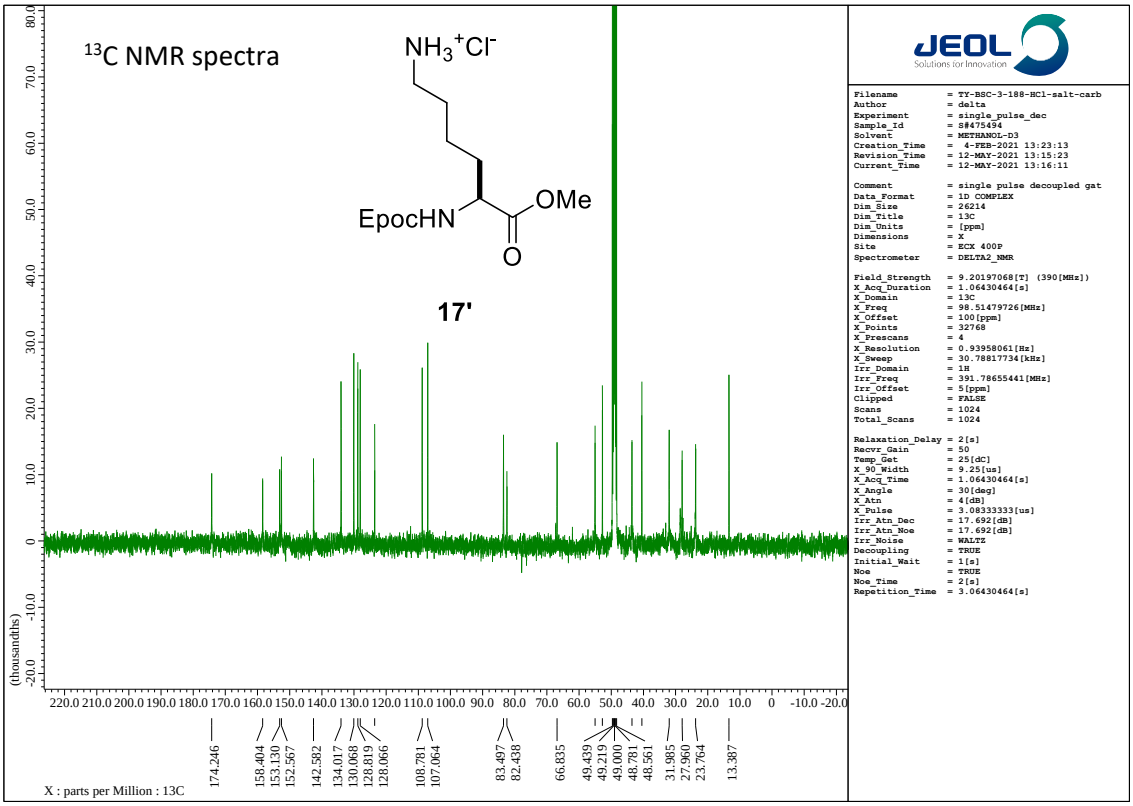

```
Filename          = TY-BSC-3-187-fr2-13.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#663679
Solvent           = CHLOROFORM-D
Creation_Time     =  2-FEB-2021 17:45:51
Revision_Time     = 12-MAY-2021 13:02:10
Current_Time      = 12-MAY-2021 13:02:26

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 40
Temp_Get          = 25[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```



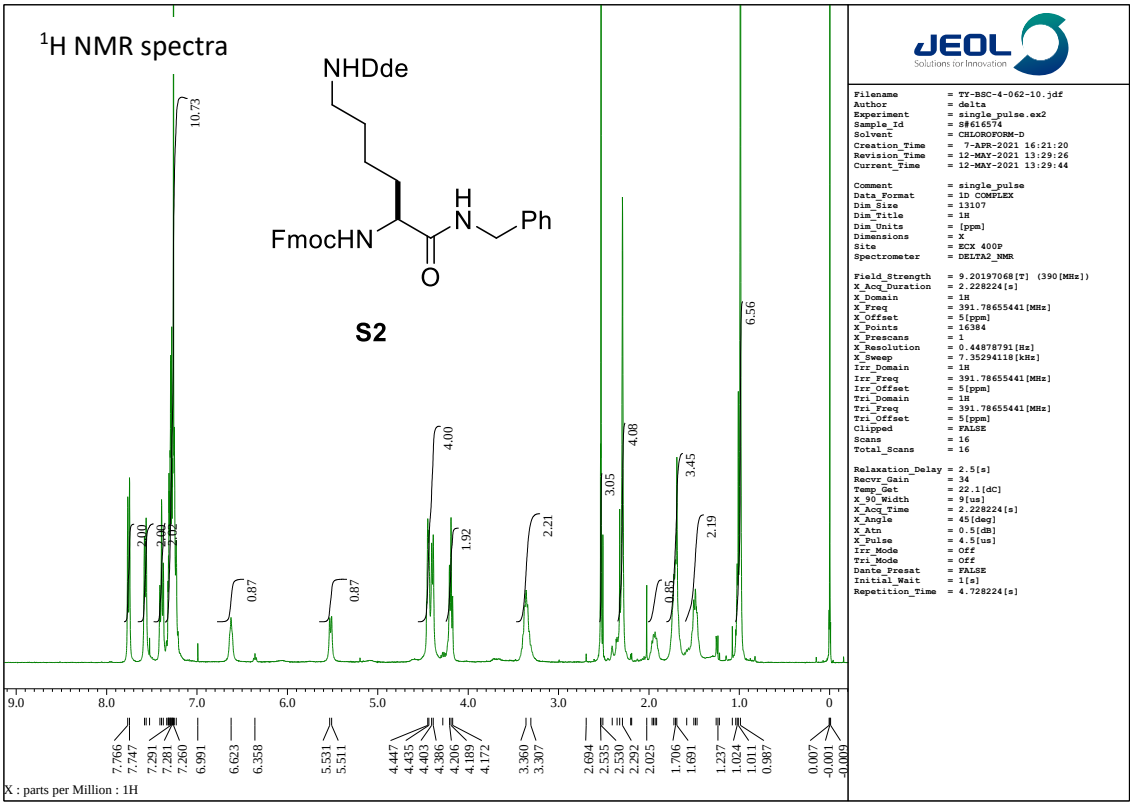

```
Filename          = TY-BSC-3-187-fr2-carbon-8.
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#367076
Solvent           = CHLOROFORM-D
Creation_Time     =  3-FEB-2021 10:22:40
Revision_Time     = 12-MAY-2021 13:06:59
Current_Time      = 12-MAY-2021 13:08:04

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 54
Temp_Get          = 25[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```




```
Filename          = TY-BSC-3-188-HCl-salt-10.j
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#474183
Solvent           = METHANOL-D3
Creation_Time     =  4-FEB-2021 12:29:55
Revision_Time     = 12-MAY-2021 13:13:54
Current_Time      = 12-MAY-2021 13:14:00

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 30
Temp_Get          = 25[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```

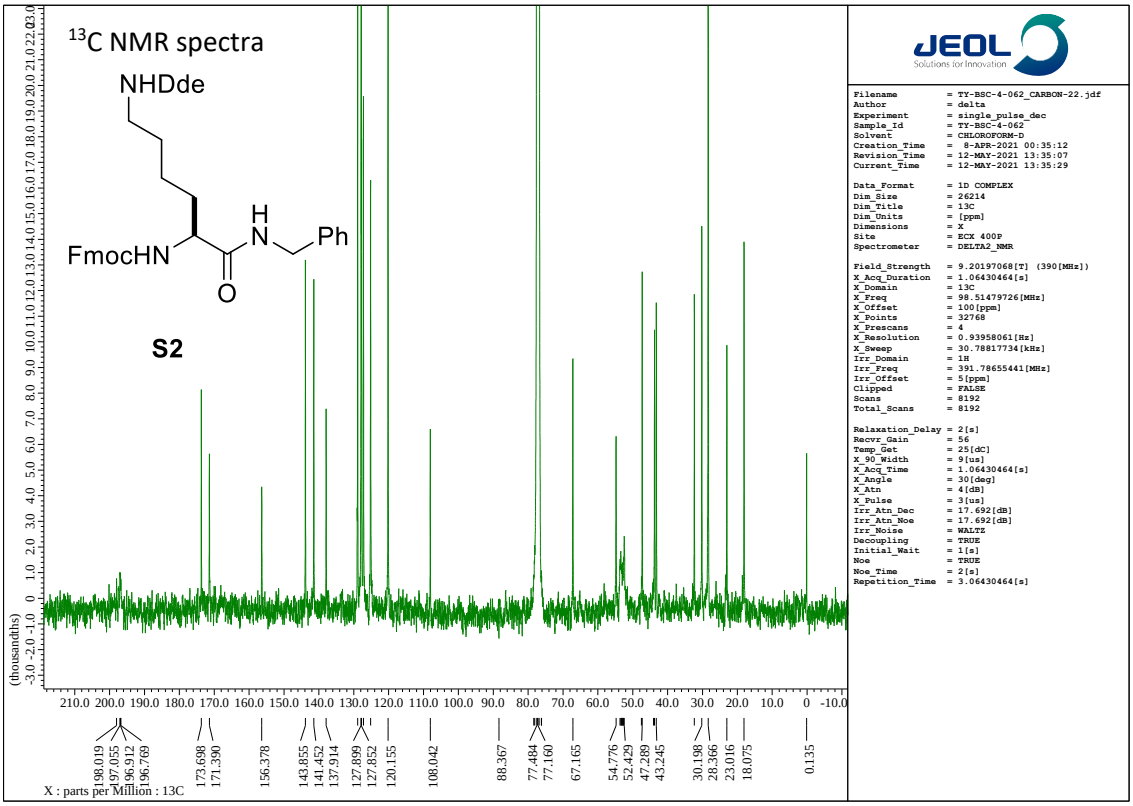



```
Filename          = TY-BSC-3-188-HCl-salt-carb
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#475494
Solvent           = METHANOL-D3
Creation_Time     =  4-FEB-2021 13:23:13
Revision_Time     = 12-MAY-2021 13:15:23
Current_Time      = 12-MAY-2021 13:16:11

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 25[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```



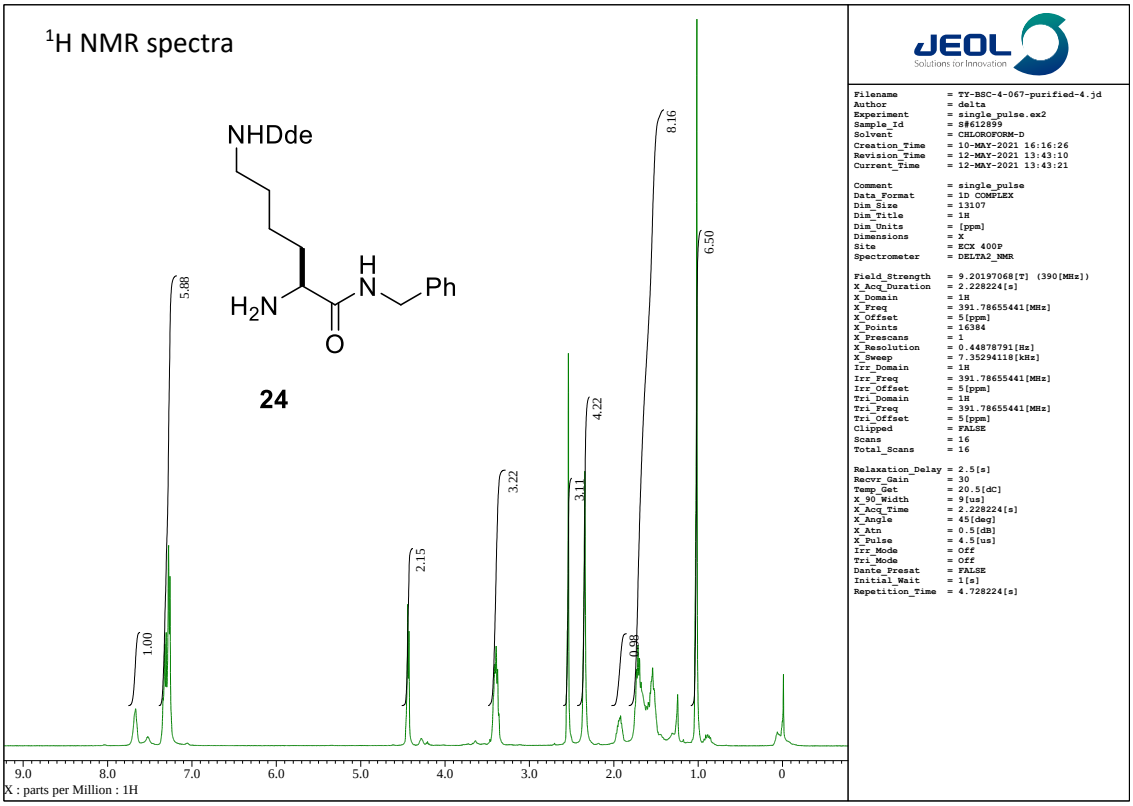
JEOL
Solutions for Innovation

```
Filename          = TY-BSC-4-062-10.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#616574
Solvent           = CHLOROFORM-D
Creation_Time     =  7-APR-2021 16:21:20
Revision_Time     = 12-MAY-2021 13:29:26
Current_Time      = 12-MAY-2021 13:29:44

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 34
Temp_Get          = 22.1[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```



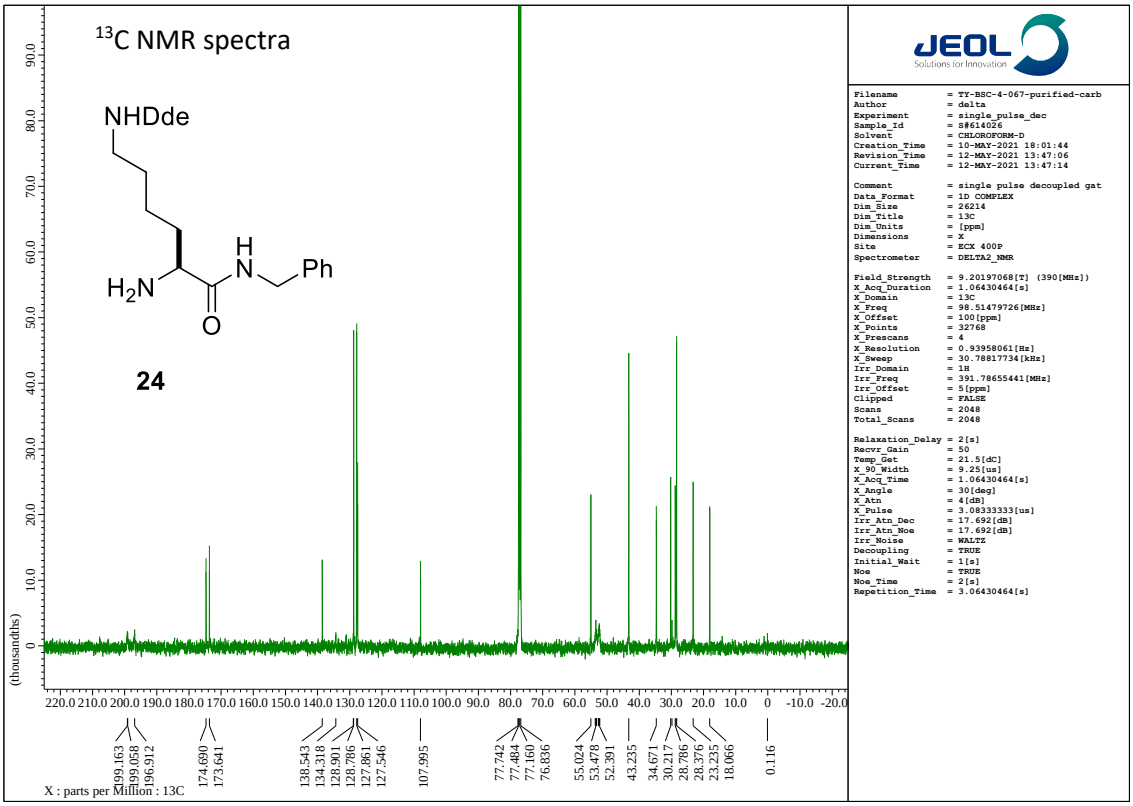
JEOL
Solutions for Innovation

```
Filename          = TY-BSC-4-062_CARBON-22.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = TY-BSC-4-062
Solvent           = CHLOROFORM-D
Creation_Time     =  8-APR-2021 00:35:12
Revision_Time     = 12-MAY-2021 13:35:07
Current_Time      = 12-MAY-2021 13:35:29

Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8192
Total_Scans       = 8192

Relaxation_Delay  = 2[s]
Recvr_Gain        = 56
Temp_Get          = 25[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```



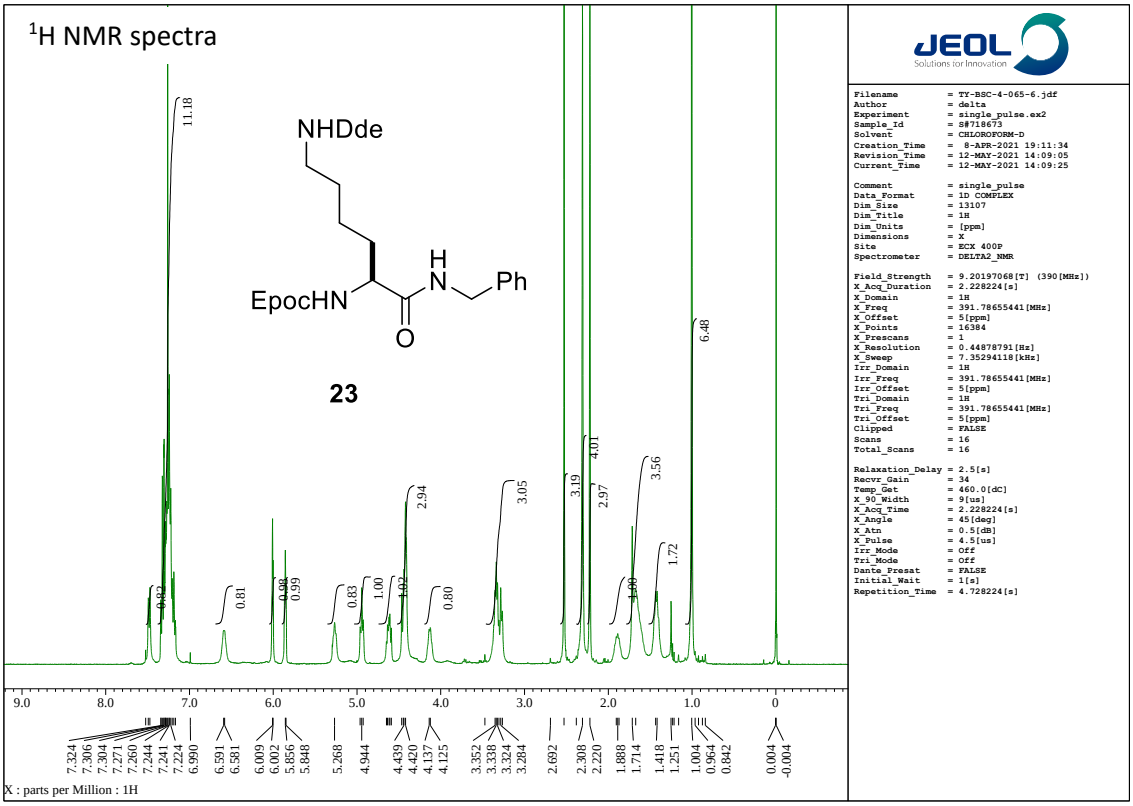
JEOL Solutions for Innovation

```
Filename          = TY-BSC-4-067-purified-4.jd
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#612899
Solvent           = CHLOROFORM-D
Creation_Time     = 10-MAY-2021 16:16:26
Revision_Time     = 12-MAY-2021 13:43:10
Current_Time      = 12-MAY-2021 13:43:21

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 30
Temp_Get          = 20.5[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```



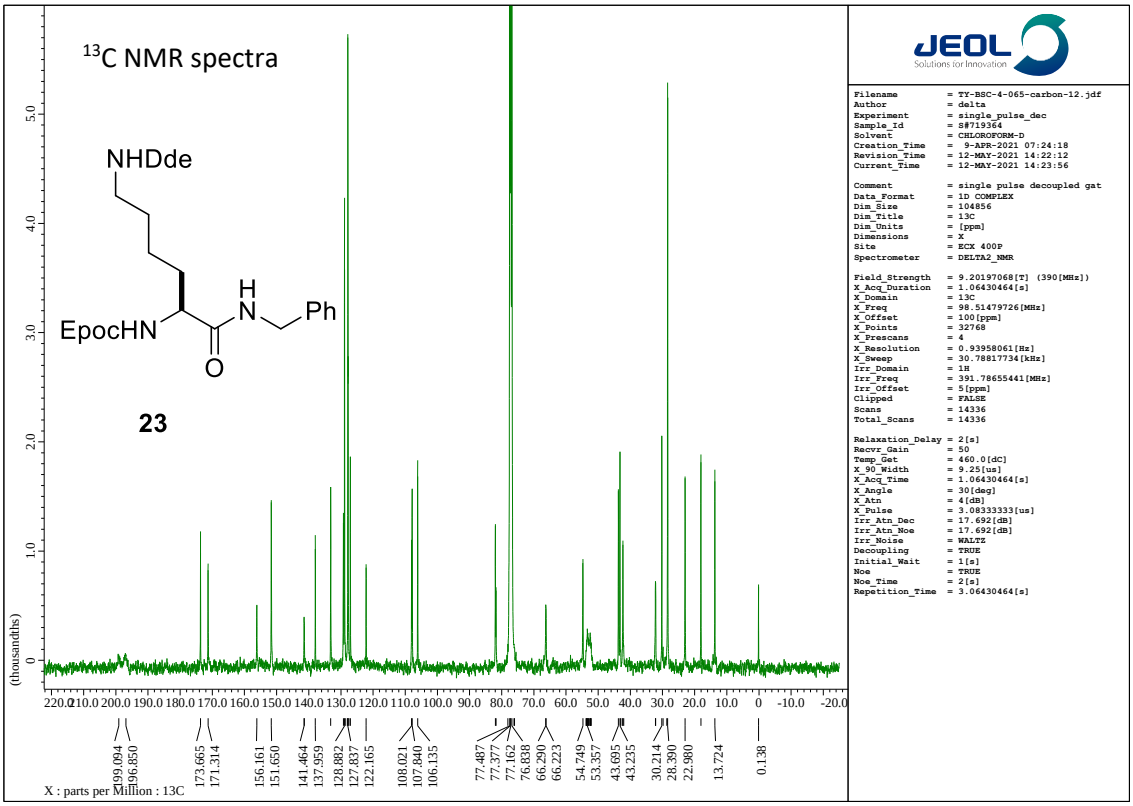
JEOL Solutions for Innovation

```
Filename          = TY-BSC-4-067-purified-carb
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#614026
Solvent           = CHLOROFORM-D
Creation_Time     = 10-MAY-2021 18:01:44
Revision_Time     = 12-MAY-2021 13:47:06
Current_Time      = 12-MAY-2021 13:47:14

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 2048
Total_Scans       = 2048

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 21.5[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```



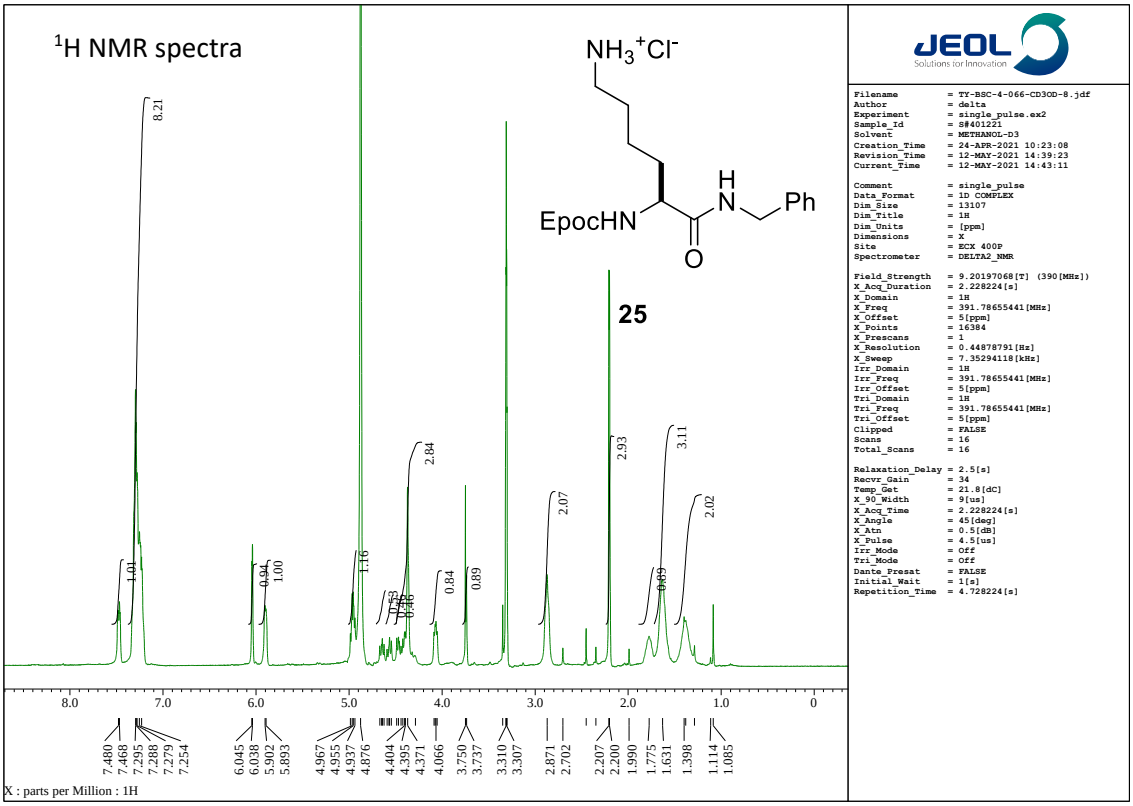
JEOL Solutions for Innovation

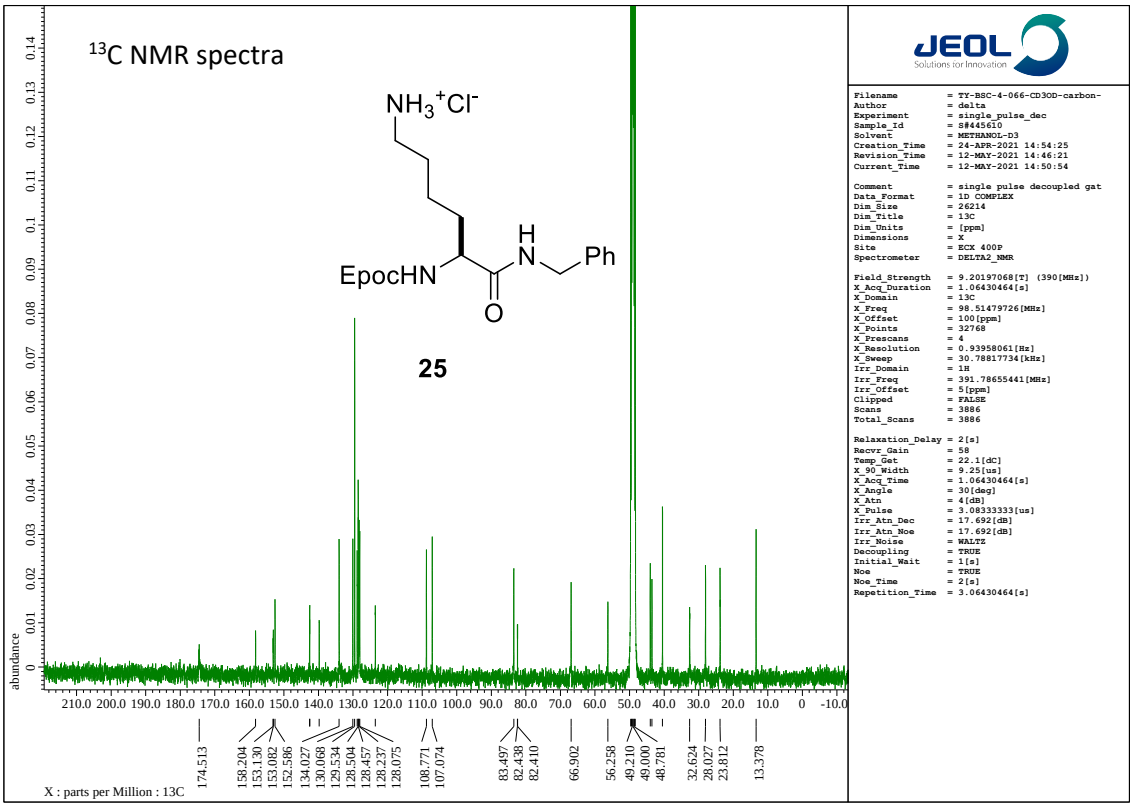
```
Filename          = TY-BSC-4-065-6.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#718673
Solvent           = CHLOROFORM-D
Creation_Time     =  8-APR-2021 19:11:34
Revision_Time     = 12-MAY-2021 14:09:05
Current_Time      = 12-MAY-2021 14:09:25

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 34
Temp_Get          = 460.0[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```



JEOL Solutions for Innovation

```
Filename          = TY-BSC-4-065-carbon-12.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#719364
Solvent           = CHLOROFORM-D
Creation_Time     =  9-APR-2021 07:24:18
Revision_Time     = 12-MAY-2021 14:22:12
Current_Time      = 12-MAY-2021 14:23:56

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 104856
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 14336
Total_Scans       = 14336

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 460.0[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```

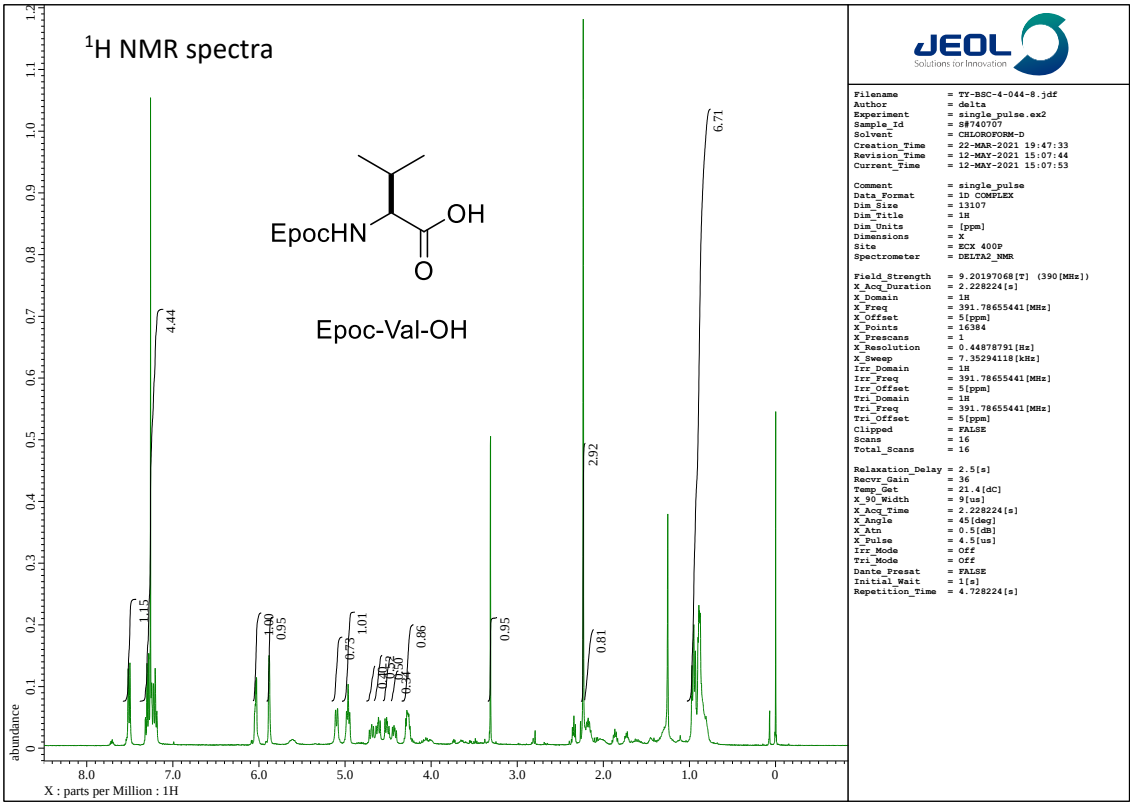





```
Filename          = TY-BSC-4-066-CD3OD-8.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#401221
Solvent           = METHANOL-D3
Creation_Time     = 24-APR-2021 10:23:08
Revision_Time     = 12-MAY-2021 14:39:23
Current_Time      = 12-MAY-2021 14:43:11

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 34
Temp_Get          = 21.8[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```

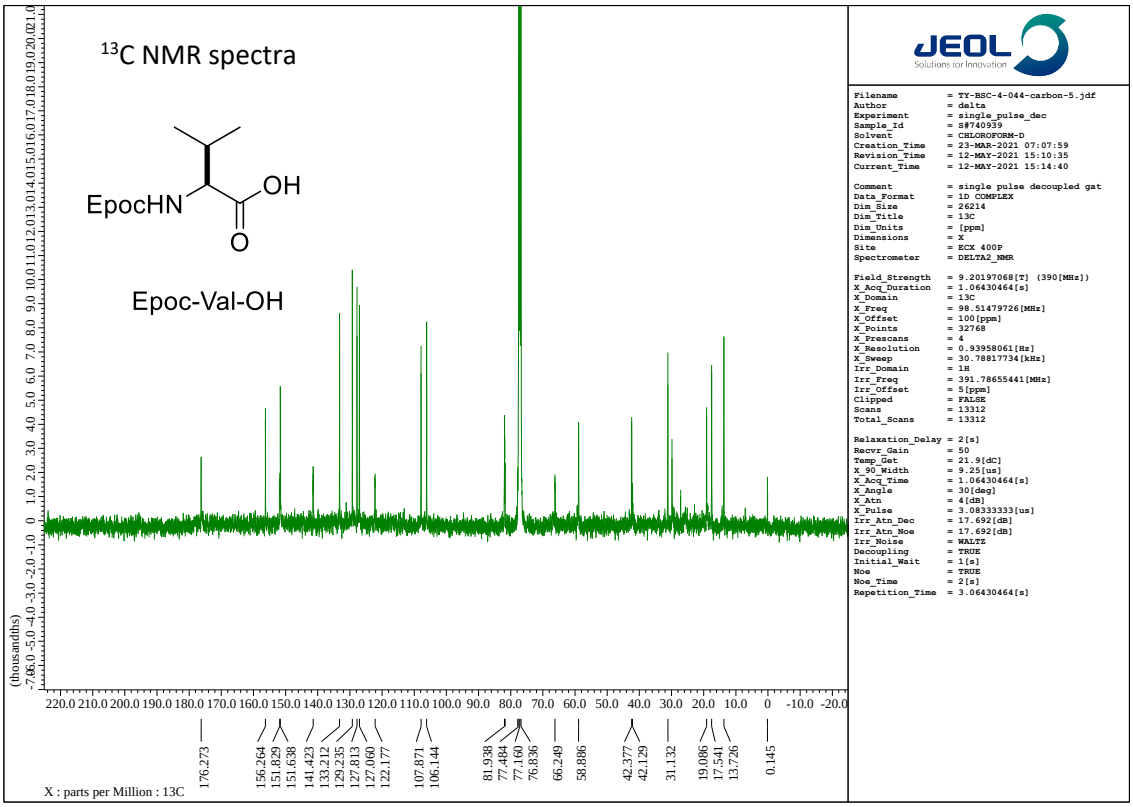


```
Filename          = TY-BSC-4-066-CD3OD-carbon-
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#445610
Solvent           = METHANOL-D3
Creation_Time     = 24-APR-2021 14:54:25
Revision_Time     = 12-MAY-2021 14:46:21
Current_Time      = 12-MAY-2021 14:50:54

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 3886
Total_Scans       = 3886

Relaxation_Delay  = 2[s]
Recvr_Gain        = 58
Temp_Get          = 22.1[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```



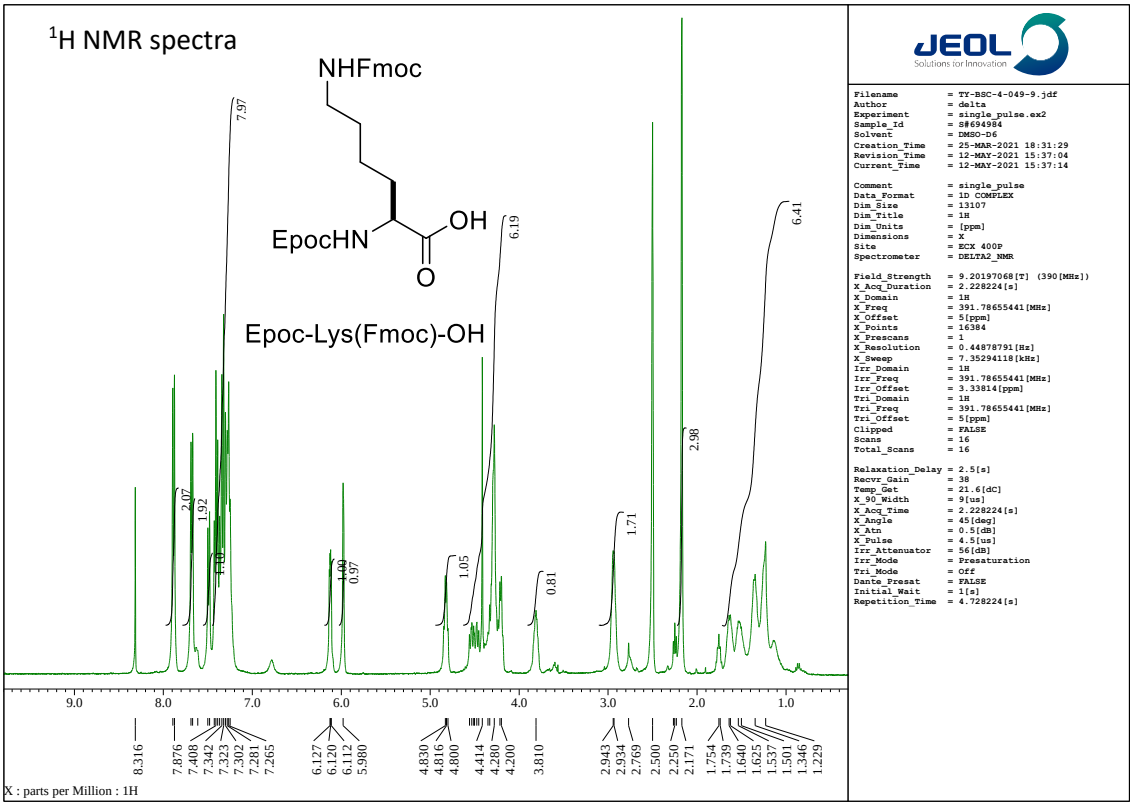
JEOL Solutions for Innovation

```
Filename          = TY-BSC-4-044-8.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#740707
Solvent           = CHLOROFORM-D
Creation_Time     = 22-MAR-2021 19:47:33
Revision_Time     = 12-MAY-2021 15:07:44
Current_Time      = 12-MAY-2021 15:07:53

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 36
Temp_Get          = 21.4[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```



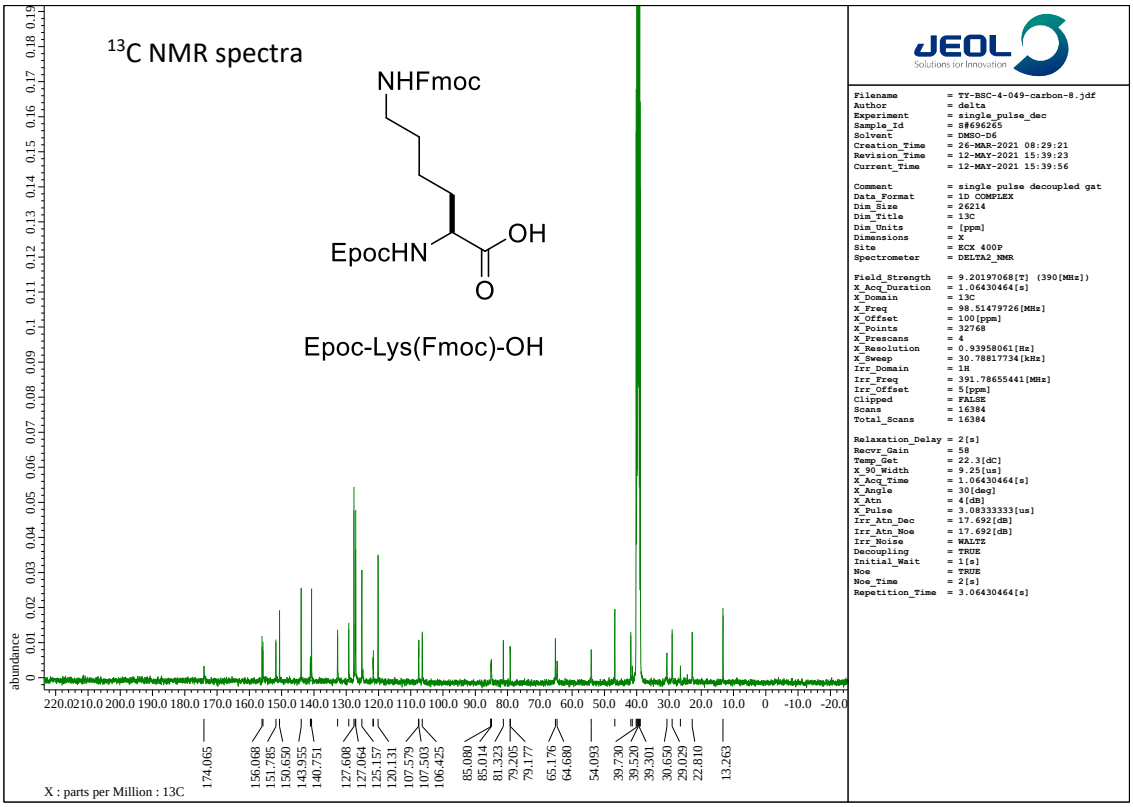
JEOL Solutions for Innovation

```
Filename          = TY-BSC-4-044-carbon-5.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#740939
Solvent           = CHLOROFORM-D
Creation_Time     = 23-MAR-2021 07:07:59
Revision_Time     = 12-MAY-2021 15:10:35
Current_Time      = 12-MAY-2021 15:14:40

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 13312
Total_Scans       = 13312

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 21.9[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```



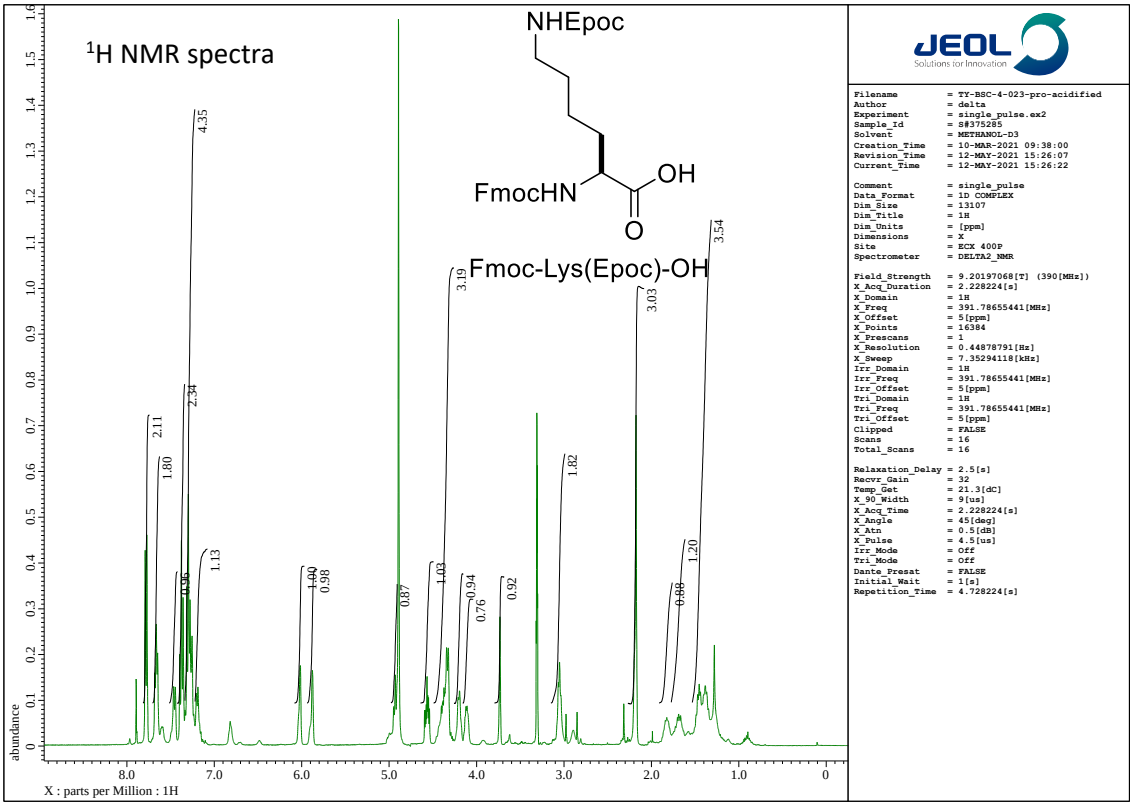
JEOL Solutions for Innovation

```
Filename          = TY-BSC-4-049-9.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#694984
Solvent           = DMSO-D6
Creation_Time     = 25-MAR-2021 18:31:29
Revision_Time     = 12-MAY-2021 15:37:04
Current_Time      = 12-MAY-2021 15:37:14

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 3.33814[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 38
Temp_Get          = 21.6[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Attenuator    = 56[dB]
Irr_Mode          = Presaturation
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```

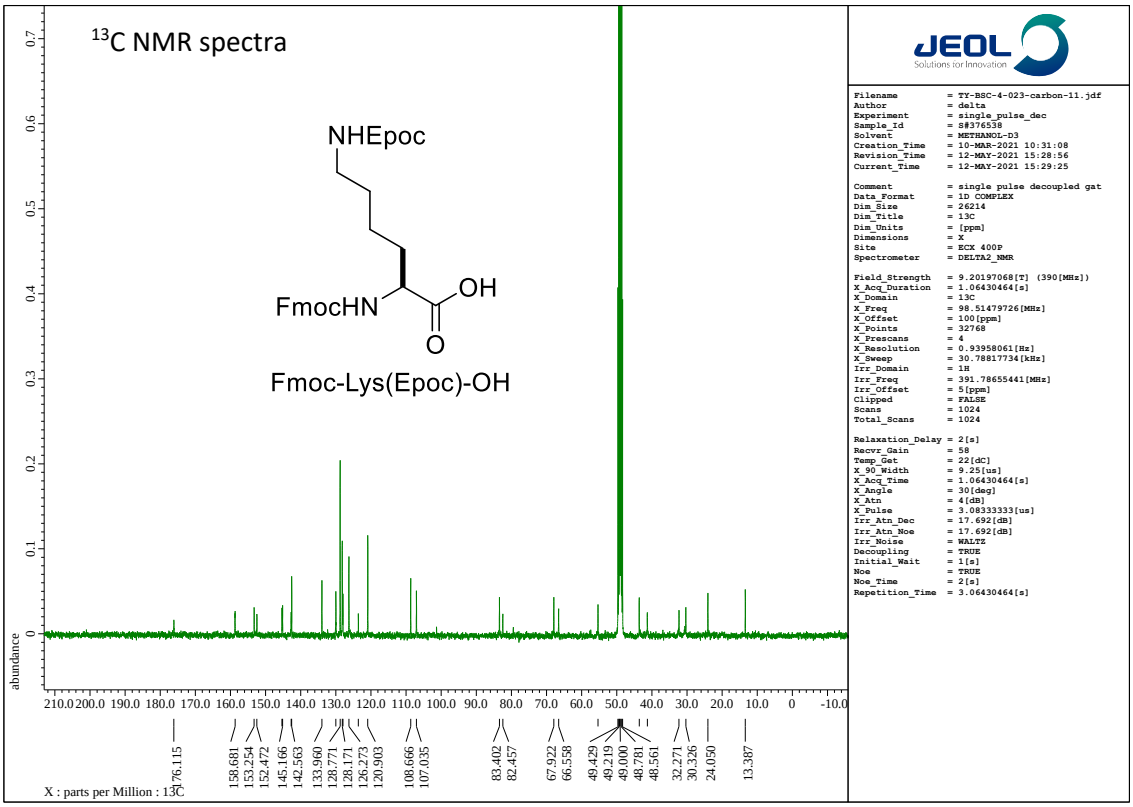


JEOL Solutions for Innovation

```
Filename          = TY-BSC-4-049-carbon-8.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#696265
Solvent           = DMSO-D6
Creation_Time     = 26-MAR-2021 08:29:21
Revision_Time     = 12-MAY-2021 15:39:23
Current_Time      = 12-MAY-2021 15:39:56

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16384
Total_Scans       = 16384

Relaxation_Delay  = 2[s]
Recvr_Gain        = 58
Temp_Get          = 22.3[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```




```
Filename          = TY-BSC-4-023-pro-acidified
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#375285
Solvent           = METHANOL-D3
Creation_Time     = 10-MAR-2021 09:38:00
Revision_Time     = 12-MAY-2021 15:26:07
Current_Time      = 12-MAY-2021 15:26:22

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 2.228224[s]
X_Domain          = 1H
X_Freq            = 391.78655441[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.44878791[Hz]
X_Sweep           = 7.35294118[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 391.78655441[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 2.5[s]
Recvr_Gain        = 32
Temp_Get          = 21.3[dC]
X_90_Width        = 9[us]
X_Acq_Time        = 2.228224[s]
X_Angle           = 45[deg]
X_Atn             = 0.5[dB]
X_Pulse           = 4.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.728224[s]
```




```
Filename          = TY-BSC-4-023-carbon-11.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#376538
Solvent           = METHANOL-D3
Creation_Time     = 10-MAR-2021 10:31:08
Revision_Time     = 12-MAY-2021 15:28:56
Current_Time      = 12-MAY-2021 15:29:25

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.20197068[T] (390[MHz])
X_Acq_Duration    = 1.06430464[s]
X_Domain          = 13C
X_Freq            = 98.51479726[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.93958061[Hz]
X_Sweep           = 30.78817734[kHz]
Irr_Domain        = 1H
Irr_Freq          = 391.78655441[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 58
Temp_Get          = 22[dC]
X_90_Width        = 9.25[us]
X_Acq_Time        = 1.06430464[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.08333333[us]
Irr_Atn_Dec       = 17.692[dB]
Irr_Atn_Noe       = 17.692[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.06430464[s]
```