

Supplemental materials

A Short Step Synthesis of Peramine, a Metabolite of Endophytic Fungi

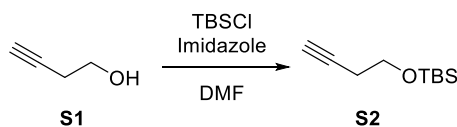
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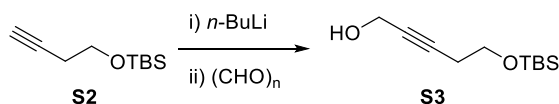
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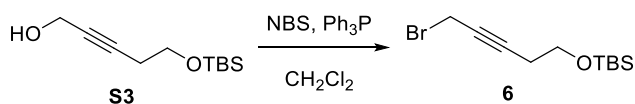
Synthesis of propargyl bromide **6**



((3-Butyn-1-yl)oxy)(*tert*-butyl)dimethylsilane (S2): 3-Butyn-1-ol (**S1**) (21.0 g, 300 mmol) was dissolved in dry THF (100 mL) and the solution was stirred to 0 °C for 1 h. To this solution were added imidazole (40.8 g, 600 mmol) and TBSCl (45.2 g, 300 mmol). After stirring at rt for 1.5 h, the mixture was extracted with Et₂O (x3), the combined organic layer was washed with H₂O (x1) and brine, dried over anhydrous Na₂SO₄, and concentrated. The residue was distilled (10 mmHg, 55-60 °C) to give **S2** (44.8 g, 83%) as a colorless oil.



5-((*tert*-Butyldimethylsilyl)oxy)pent-2-yn-1-ol (S3): Alkyne **S2** (5.70 g, 31.0 mmol) was dissolved in dry THF (70 mL) and the solution was stirred to -78 °C for 20 min. To this solution was added *n*-BuLi (1.55 M in hexane, 20.0 mL, 31.0 mmol) dropwise over 5 min. After being warmed up to 0 °C, paraformaldehyde (4.65 g, 155 mmol) was added. Stirring was continued at rt for 4 h, and then the reaction was quenched by addition of water (20 mL). The mixture was extracted with Et₂O (x3), and then the combined organic layer was washed brine, dried over anhydrous Na₂SO₄, and concentrated. The residue was purified by flash column chromatography (neutral silica gel, 200 g, hexane:Et₂O = 2:1 (R_f = 0.25)) to give compound **S3** (6.15 g, 92%) as a colorless oil.



((5-Bromopent-3-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane (6): To a solution of compound **S3** (1.86 g, 8.65 mmol) in CH₂Cl₂ (50 mL) cooled at -23 °C were added recrystallized NBS (1.71 g, 9.52 mmol) and Ph₃P (2.72 g, 10.4 mmol). After stirring at the same temperature for 1 h, the reaction was quenched with sat. NaHCO₃ solution (40 mL). The mixture was extracted with Et₂O (x3), the combined organic layer was dried over anhydrous Na₂SO₄ and concentrated. The residue was dissolved in Et₂O, and the precipitate was filtered off and rinsed with Et₂O. The filtrate was concentrated and

purified by flash column chromatography (neutral silica gel, 70 g, hexane ($R_f = 0.16$)) to give compound **6** (1.54 g, 63%) as a colorless oil.

References

- 1.

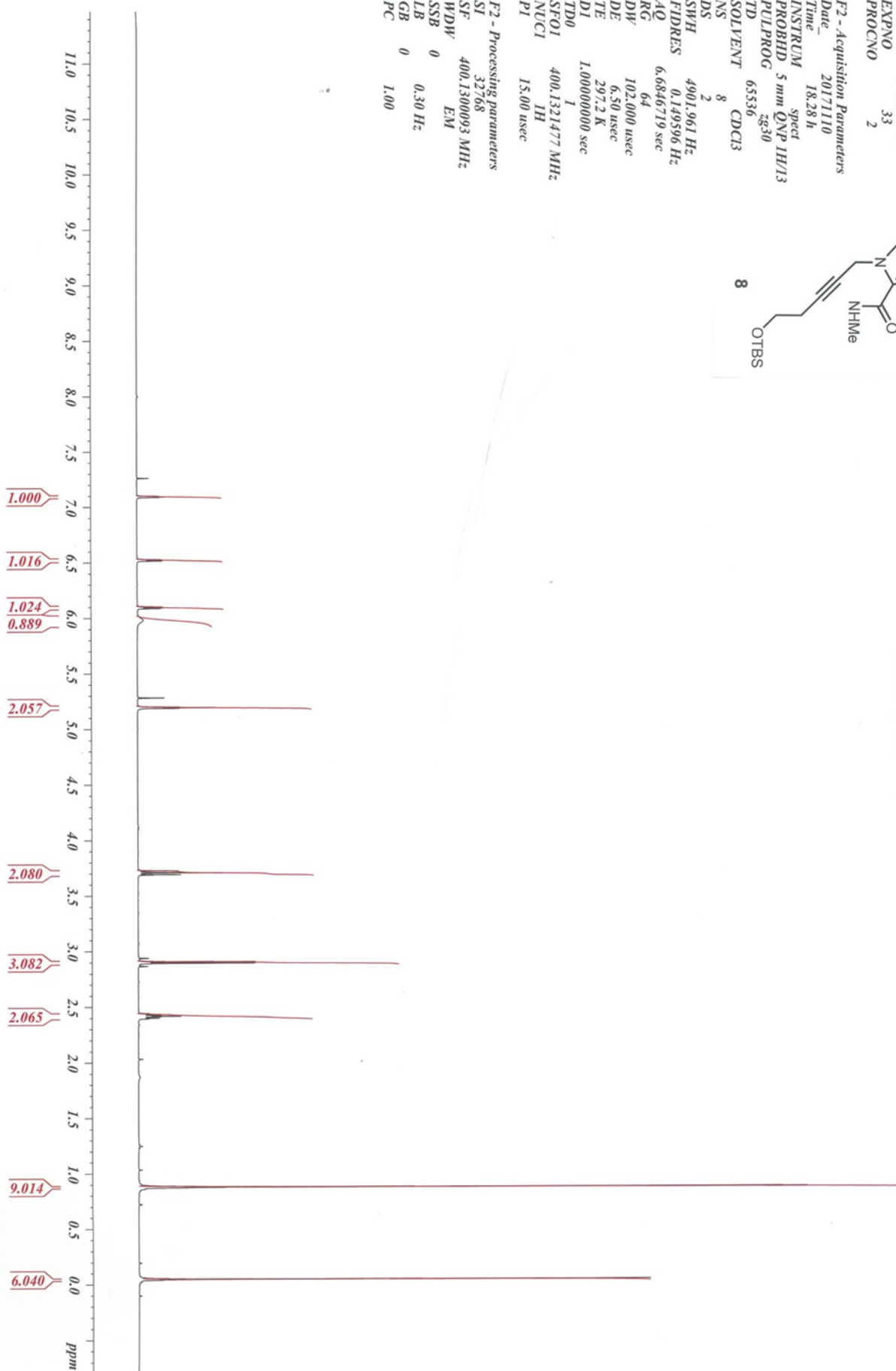
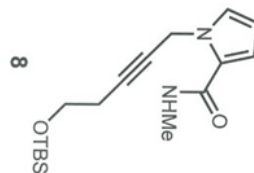
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 FIDRES 0.365918 Hz

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TE 297.2 K

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TD0 1

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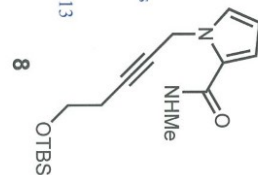
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18.36

-5.24

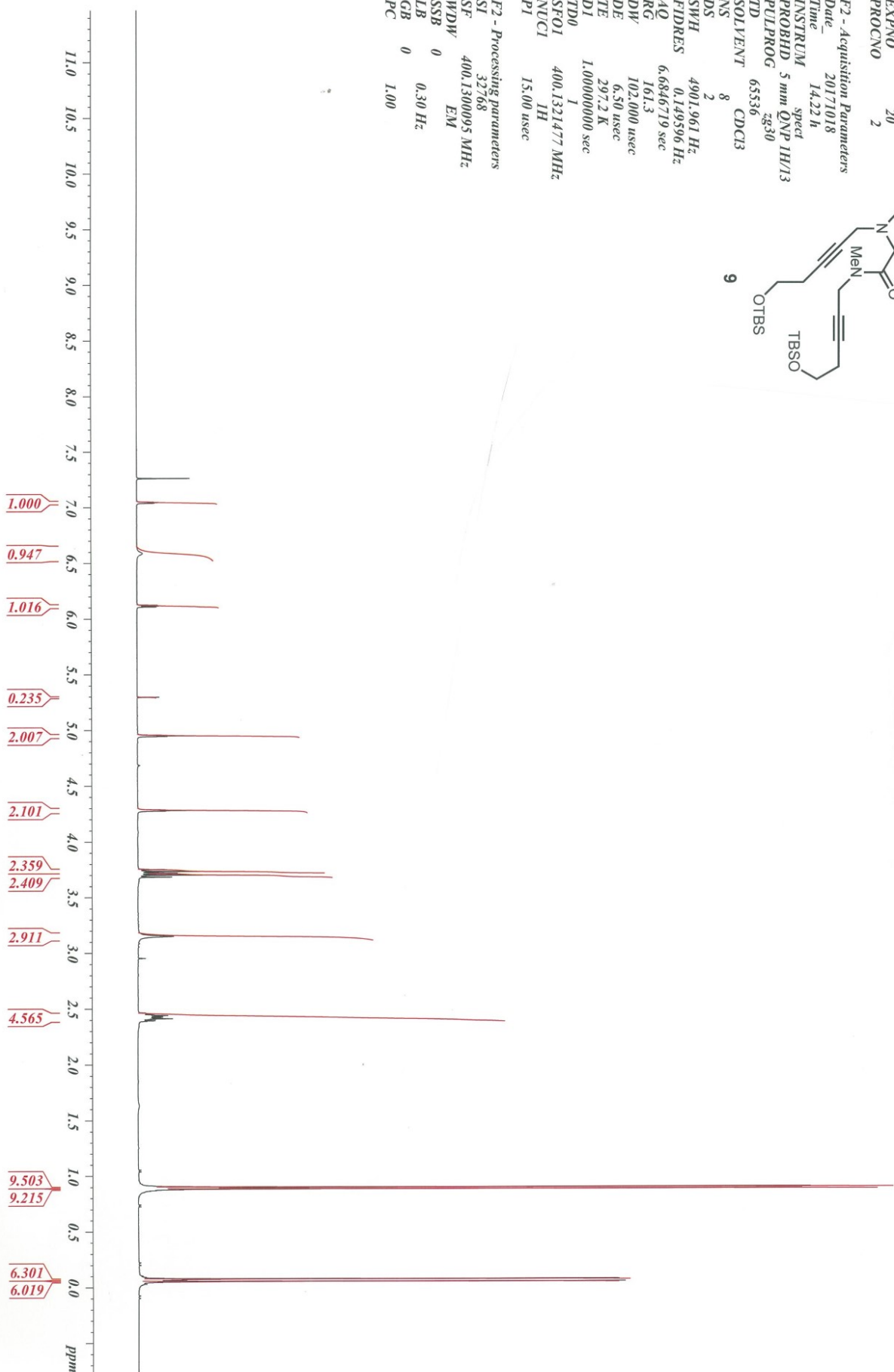
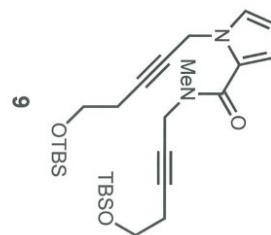


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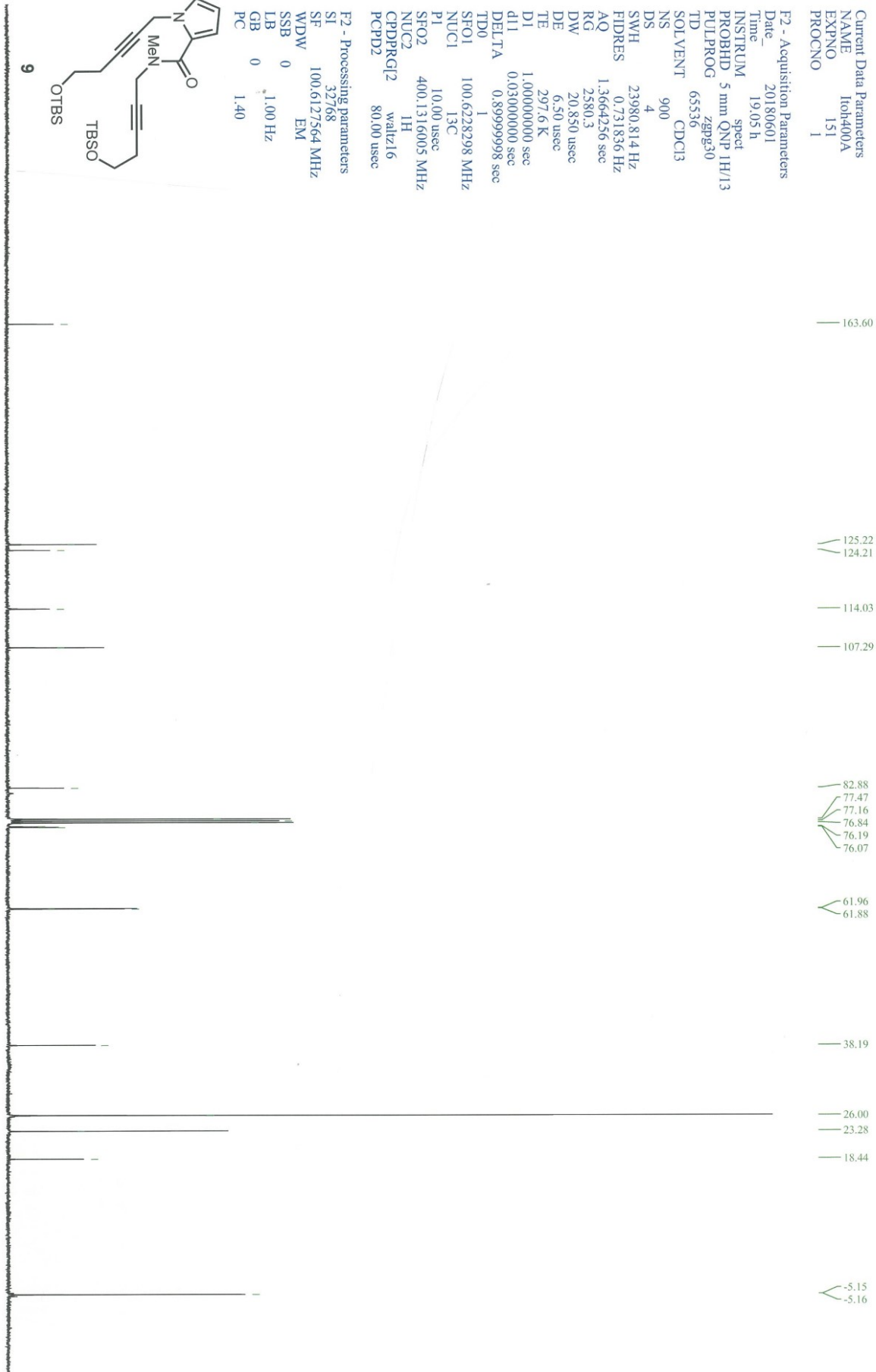
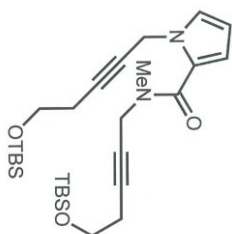
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 DE 6.50 usec
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 DELTA 0.89999998 sec
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 PROCNO 1

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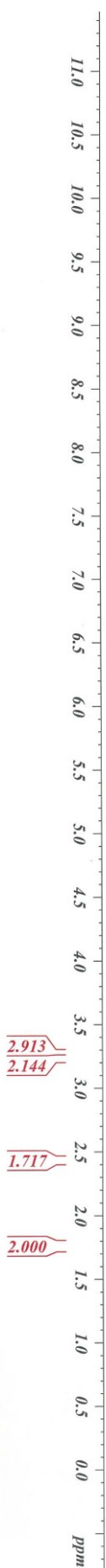
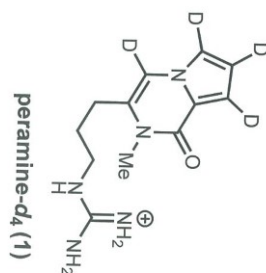
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 FIDRES 0.126314 Hz
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 RG 256
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 DE 6.50 usec
 TE 297.2 K
 D1 1.00000000 sec
 TD0 1

CHANNEL f1

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F2 - Processing parameters

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Current Data Parameters
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EXPNO 2
PROCNO 2

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SOLVENT MeOD
NS 10000
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FIDRES 0.550197 Hz
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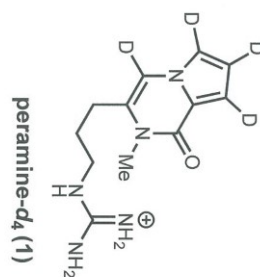
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 PROCNO 2

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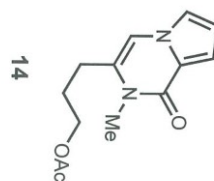
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 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
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 RG 456.1
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 DE 6.50 usec
 TE 297.2 K
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F2 - Processing parameters

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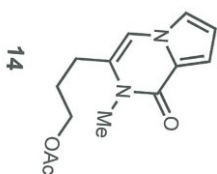


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 TD 65536
 SOLVENT MeOD
 NS 512
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 FIDRES 0.731836 Hz
 AQ 1.3664256 sec
 RG 574.7
 DW 20.850 usec
 DE 6.50 usec
 TE 297.4 K
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 d11 0.03000000 sec
 DELTA 0.89999998 sec
 TD0 1
 SFO1 100.6228298 MHz
 NUC1 13C
 P1 10.00 usec
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 80.00 usec

F2 - Processing Parameters
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 SSB 0
 LB 1.00 Hz
 GB 0
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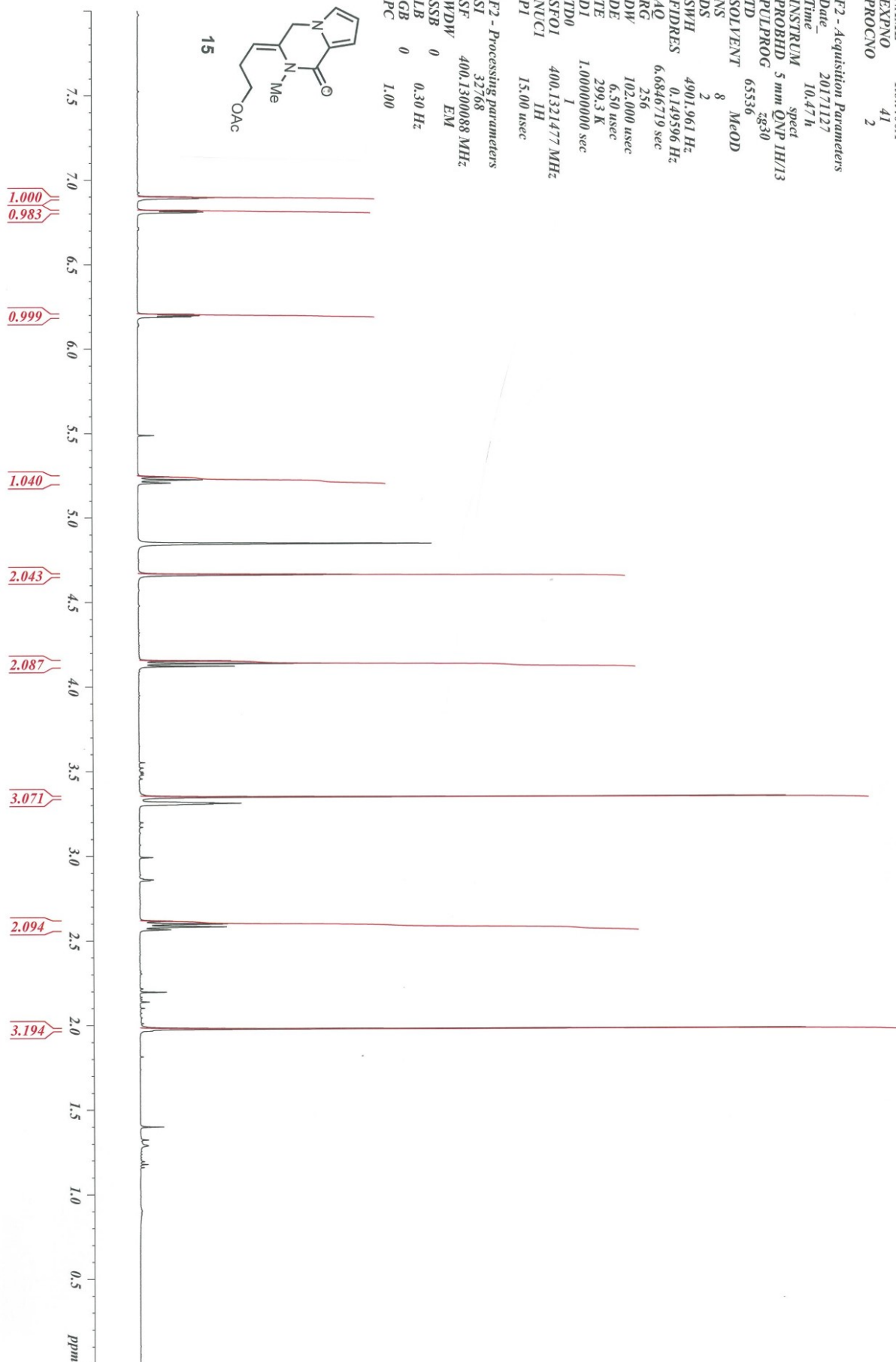
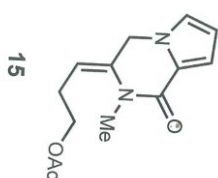
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 FIDRES 0.149596 Hz
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 RG 256
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 DE 6.50 usec
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 NUC1 1H
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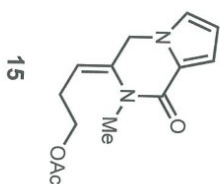
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NS 1096
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FIDRES 0.731836 Hz
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RG 574.7
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DE 6.50 usec
TE 300.6 K
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d11 0.03000000 sec
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NUC2 1H
CPDPRG2 waltz16
PCPD2 80.00 usec

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