Electronic Supplementary Information for

# Storable *N*-Phenylcarbamate Palladacycles for Rapid Functionalization of An Alkyne-Encoded Protein

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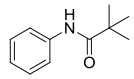
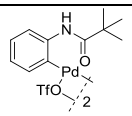
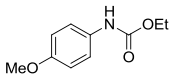
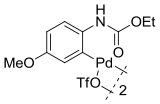
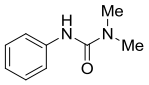
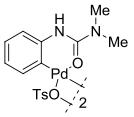
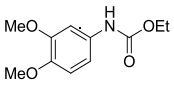
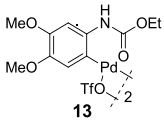
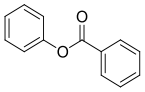
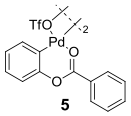
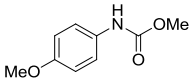
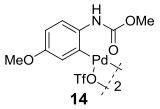
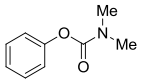
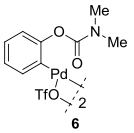
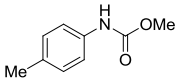
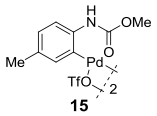
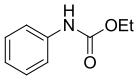
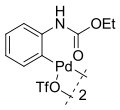
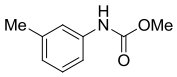
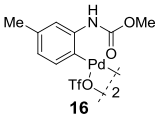
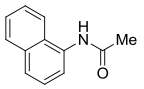
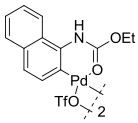
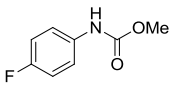
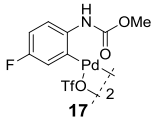
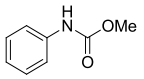
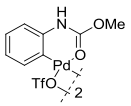
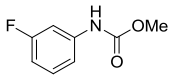
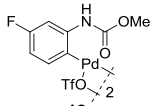
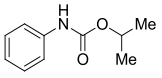
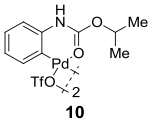
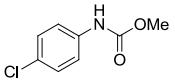
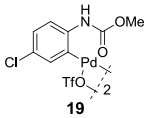
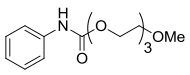
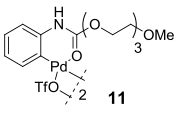
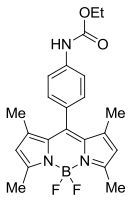
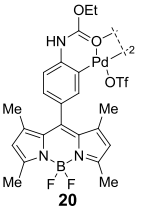
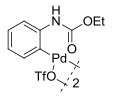
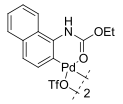
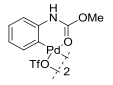
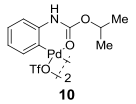
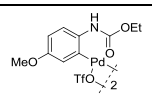
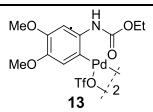
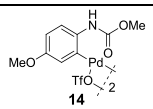
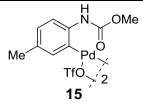
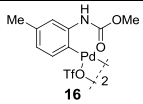
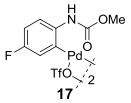
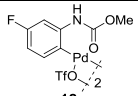
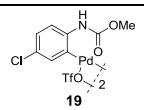
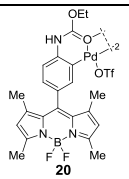
## Supplemental Tables and Figures

**Table S1.** Preparation of the palladacycles [a]

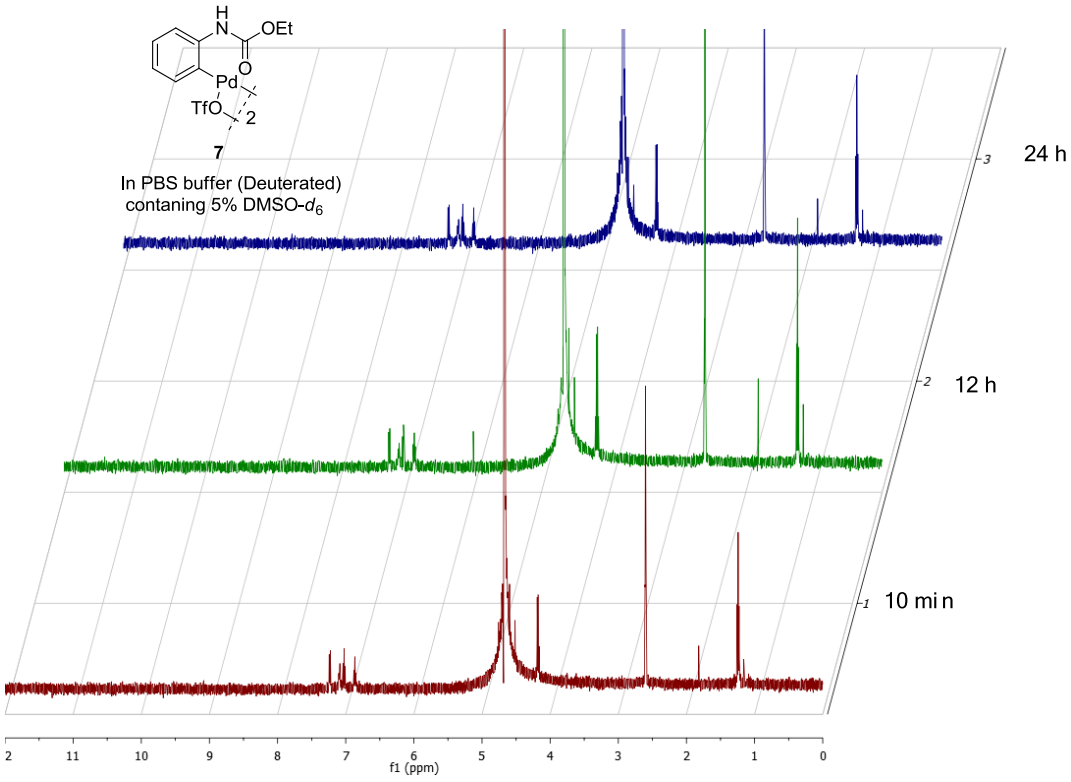
| Entry | Substrate | Palladacycle | Yield (%) | Entry | Substrate | Palladacycle | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 |  |  **3** | 76 | 10 |  |  **12** | 70 |
| 2 |  |  **4** | 87 | 11 |  |  **13** | 30 |
| 3 |  |  **5** | 51 | 12 |  |  **14** | 65 |
| 4 |  |  **6** | 73 | 13 |  |  **15** | 75 |
| 5 |  |  **7** | 75 | 14 |  |  **16** | 45 |
| 6 |  |  **8** | 60 | 15 |  |  **17** | 72 |
| 7 |  |  **9** | 80 | 16 |  |  **18** | 70 |
| 8 |  |  **10** | 80 | 17 |  |  **19** | 60 |
| 9 |  |  **11** | 90 | 18 |  |  **20** | 17 |

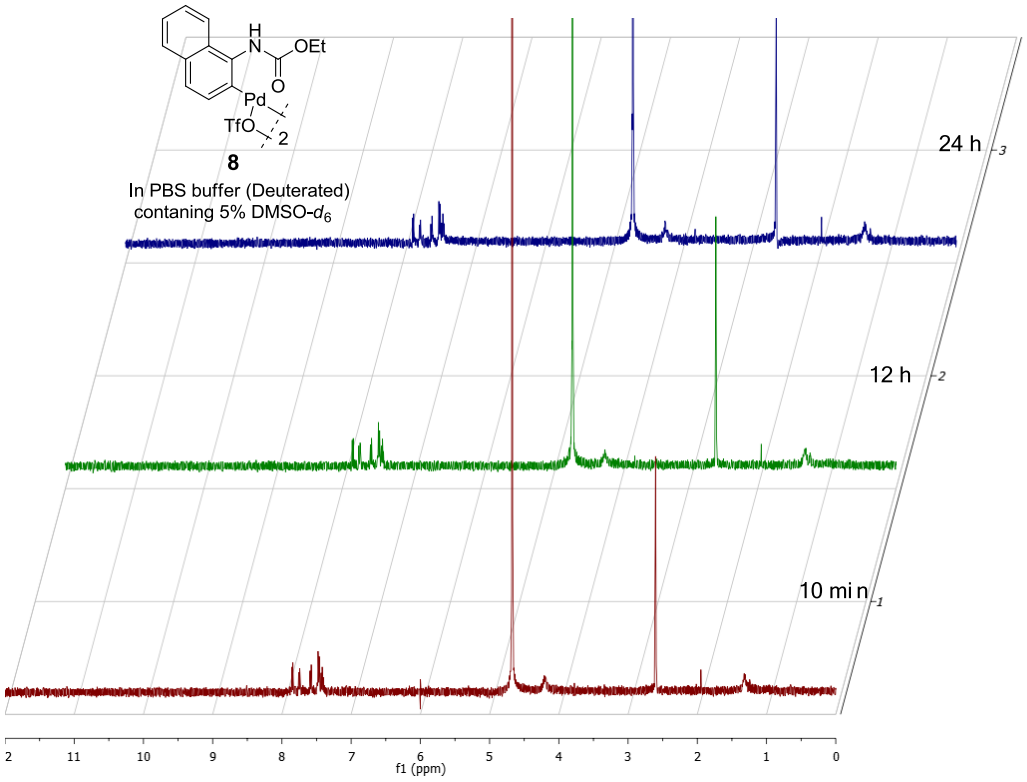
[a] Palladacycle was prepared using either Procedure A or B; see Experimental section for details.

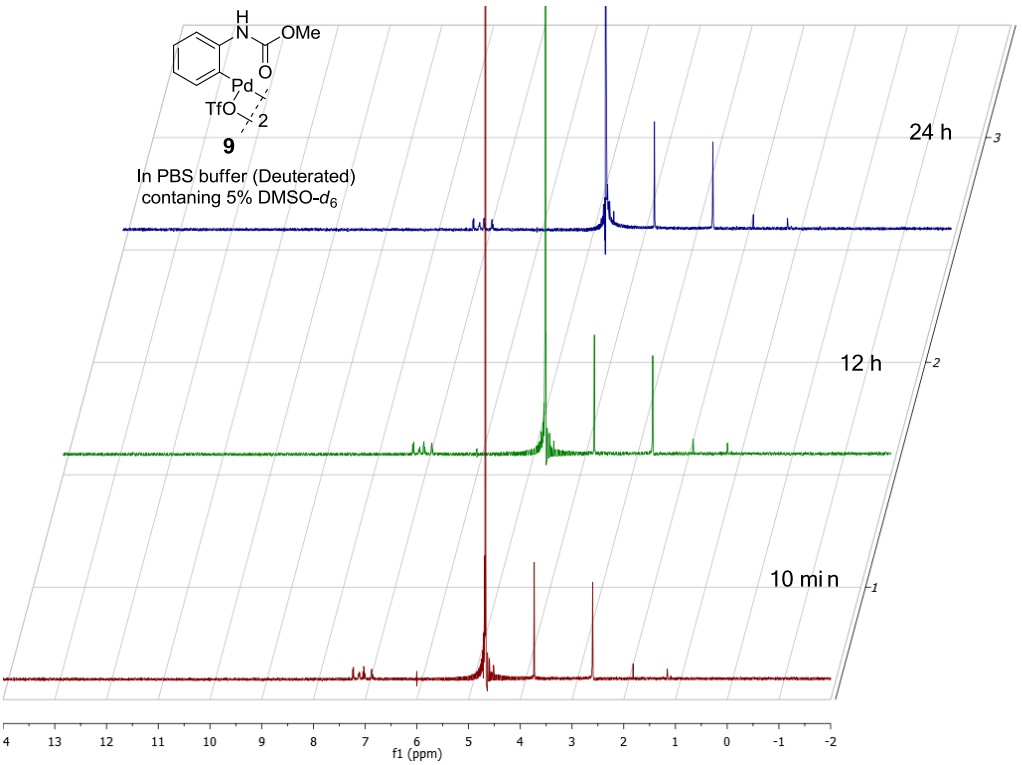
**Table S2**. Evaluation of palladacycle stability in PBS buffer by $^{1}$H NMR[a]

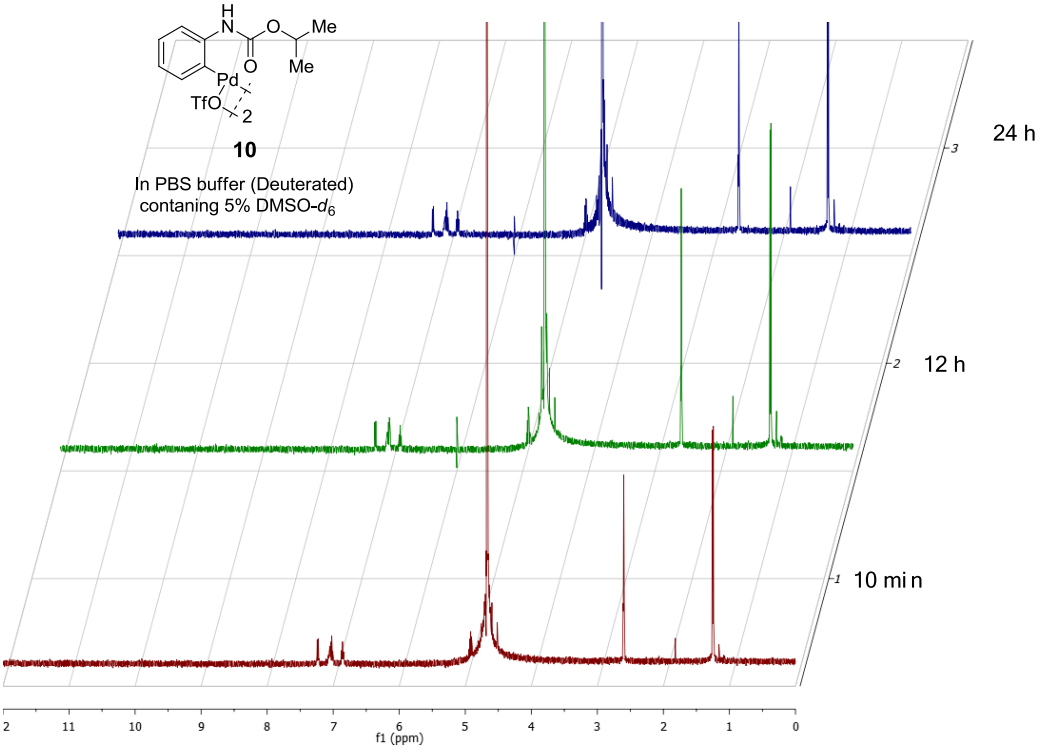
| Entry | Palladacycles | Solvent | Stability |
|---|---|---|---|
| 1 |  **7** | 95% PBS + 5% DMSO-$d_6$ | Stable for 24 h |
| 2 |  **8** | 95% PBS + 5% DMSO-$d_6$ | Stable for 24 h |
| 3 |  **9** | 95% PBS + 5% DMSO-$d_6$ | Stable for 24 h |
| 4 |  **10** | 95% PBS + 5% DMSO-$d_6$ | Stable for 24 h |
| 5 |  **12** | 95% PBS + 5% DMSO-$d_6$ | Stable for 24 h |
| 6 |  **13** | 95% PBS + 5% DMSO-$d_6$ | Stable for 24 h |
| 7 |  **14** | 95% PBS + 5% DMSO-$d_6$ | Stable for 24 h |
| 8 |  **15** | 95% PBS + 5% DMSO-$d_6$ | Stable for 24 h |
| 9 |  **16** | 95% PBS + 5% DMSO-$d_6$ | Stable for 24 h |
| 10 |  **17** | 95% PBS + 5% DMSO-$d_6$ | Stable for 24 h |
| 11 |  **18** | 95% PBS + 5% DMSO-$d_6$ | Stable for 24 h |
| 12 |  **19** | 95% PBS + 5% DMSO-$d_6$ | Stable for 24 h |
| 13 |  **20** | 40% PBS + 60% DMSO-$d_6$[b] | Stable for 24 h |

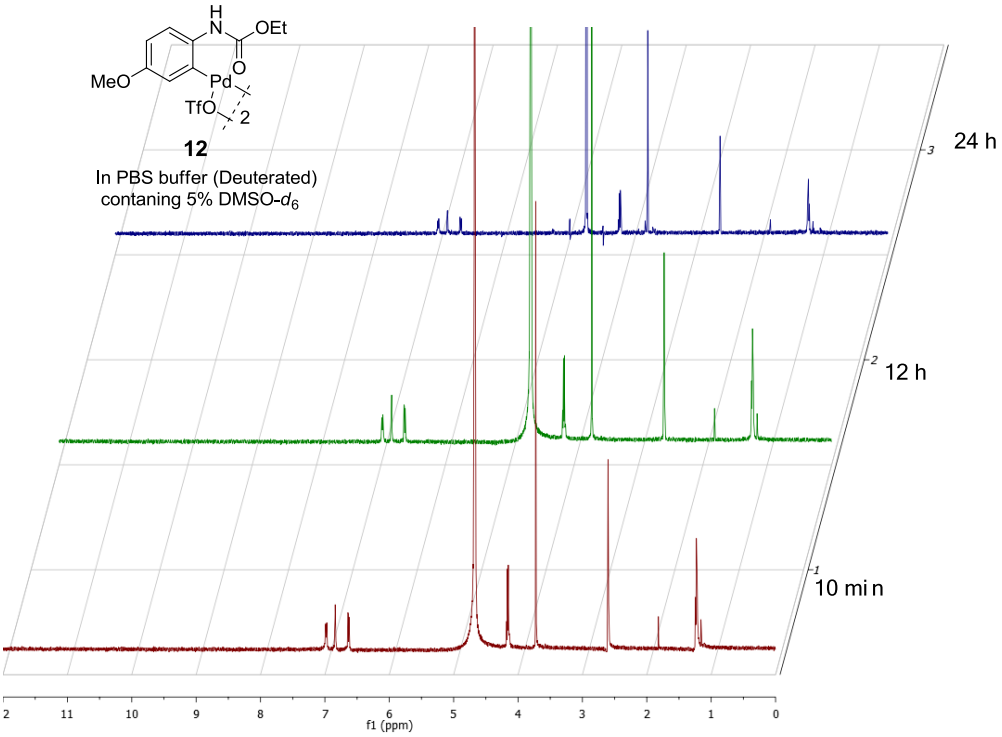
[a] Sample concentration was 1 mM. [b] Due to limited solubility, DMSO-$d_6$ content was increased to 60%.


H
N
OEt
O
Pd
TfO
2
7
In PBS buffer (Deuterated)
contaning 5% DMSO-$d_6$
24 h
12 h
10 min
f1 (ppm)


H
N
OEt
O
Pd
TfO
2
8
In PBS buffer (Deuterated)
contaning 5% DMSO-$d_6$
24 h
12 h
10 min
f1 (ppm)


H
N
OMe
O
Pd
TfO
2
9
In PBS buffer (Deuterated)
containg 5% DMSO-$d_6$
24 h
12 h
10 min
3
2
1
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


H
N
O
Me
O
Me
Pd
TfO
2
10
In PBS buffer (Deuterated)
containg 5% DMSO-$d_6$
24 h
12 h
10 min
3
2
1
2 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


H
N
OEt
O
MeO
Pd
TfO
2
12
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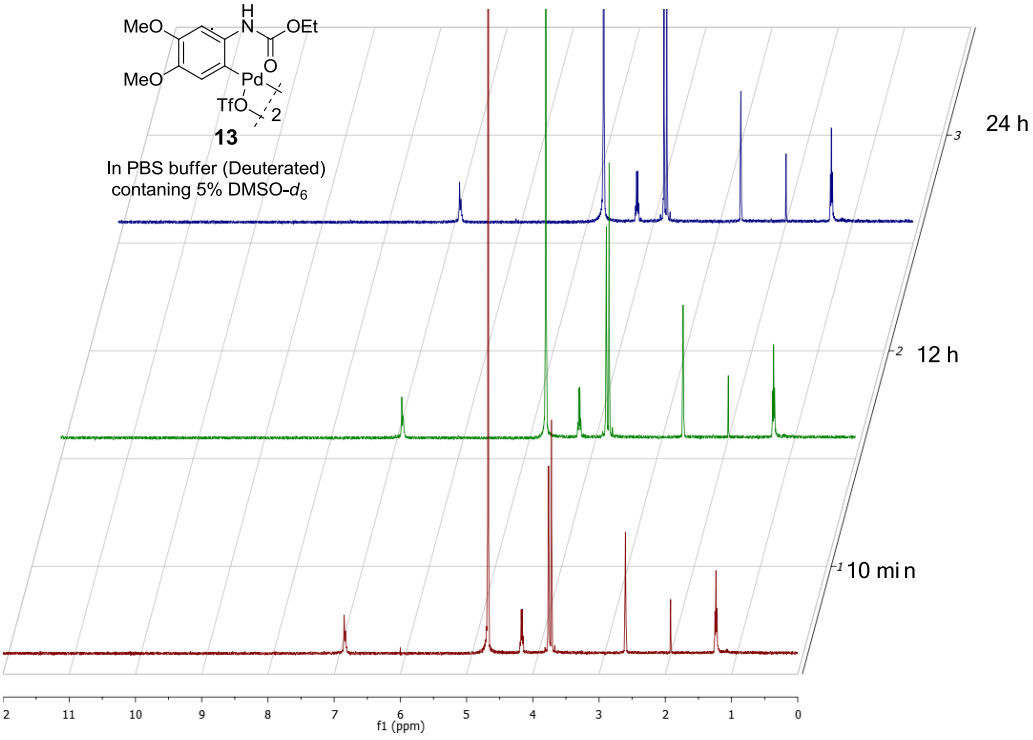
contaning 5% DMSO-$d_6$
24 h
12 h
10 min
f1 (ppm)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O
MeO
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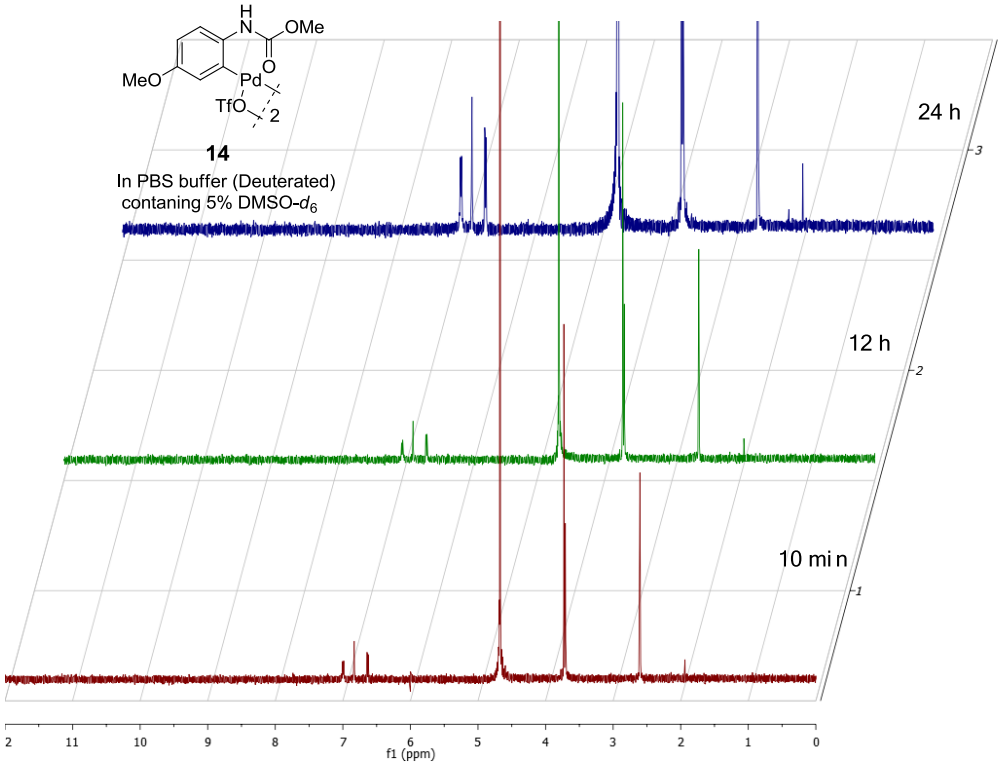
f1 (ppm)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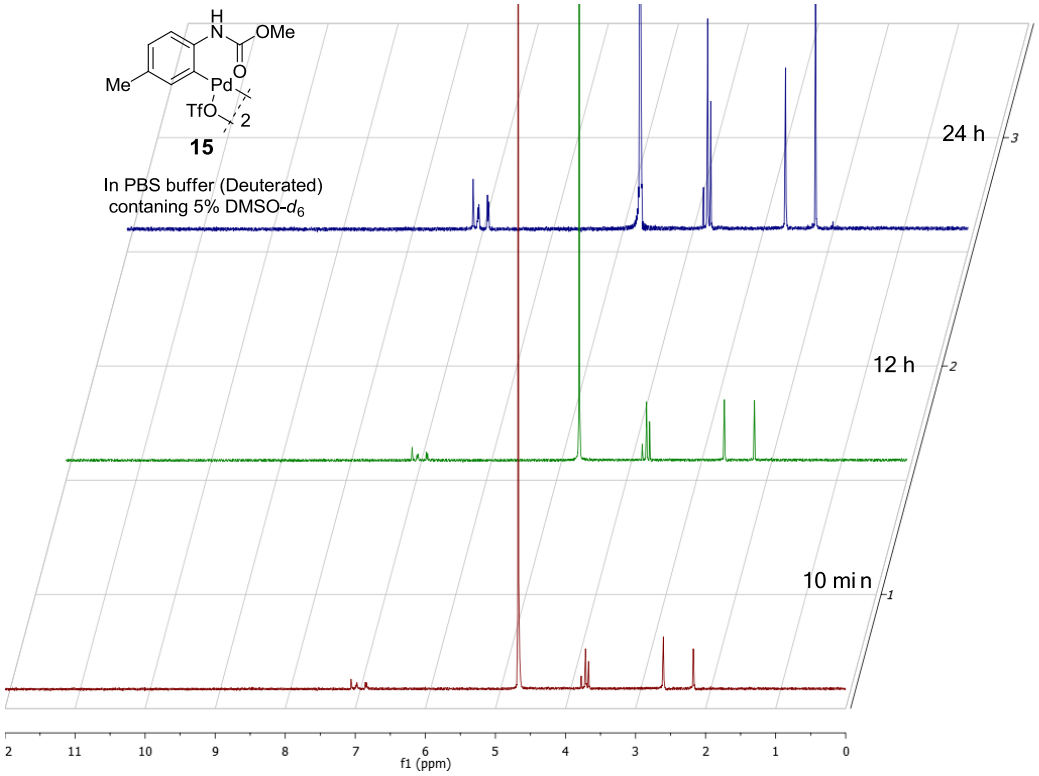
f1 (ppm)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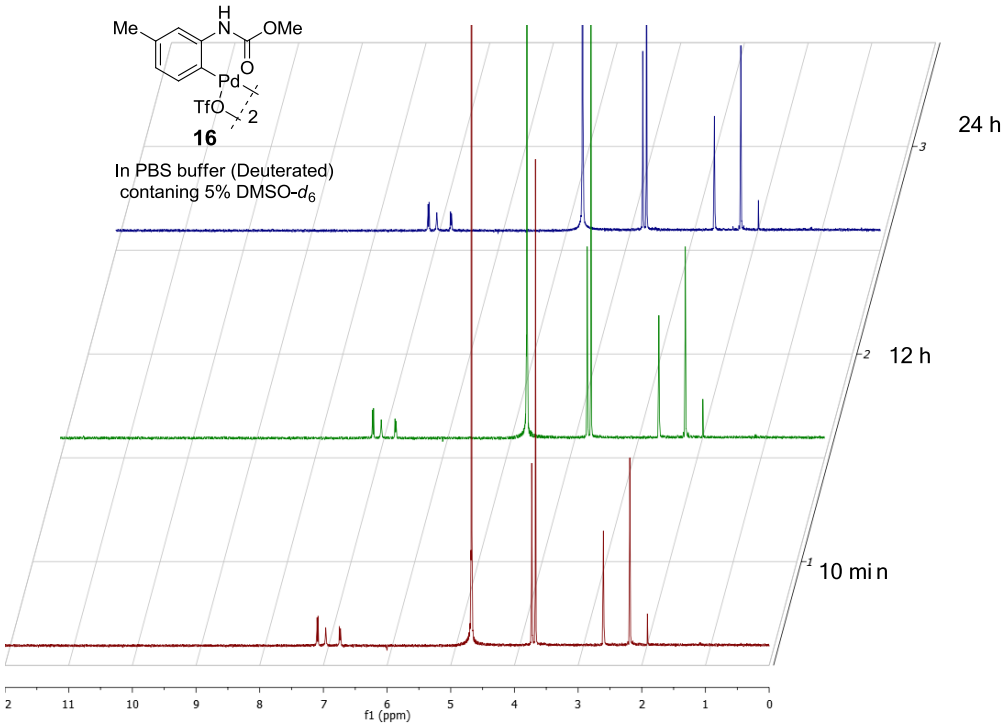
f1 (ppm)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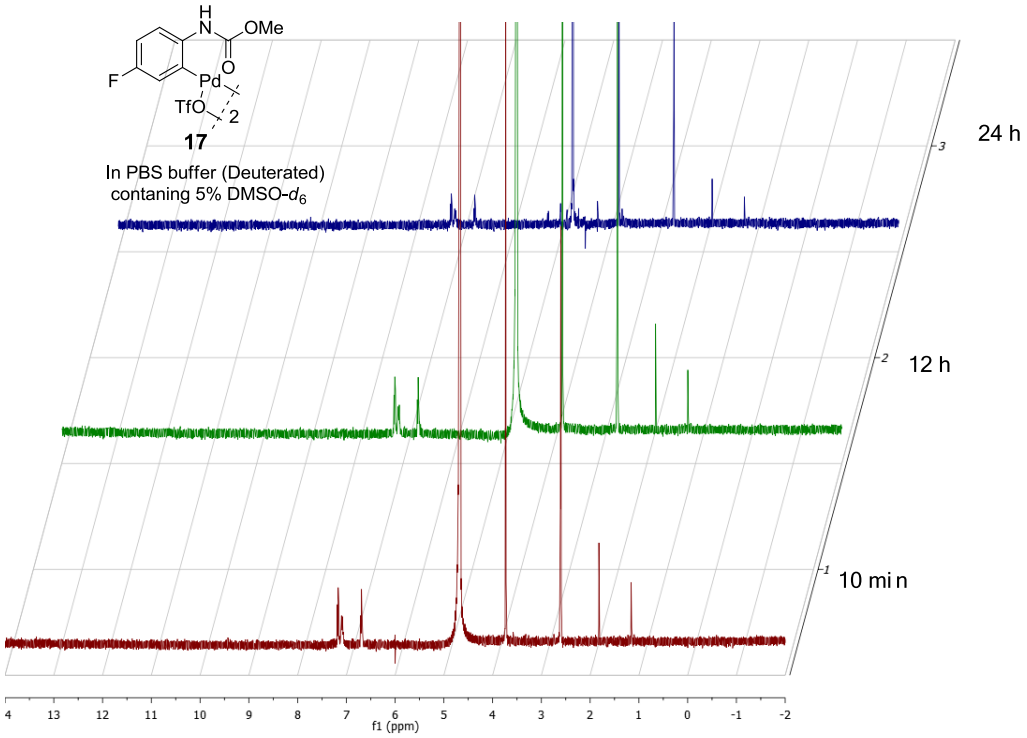
24 h
12 h
10 min
f1 (ppm)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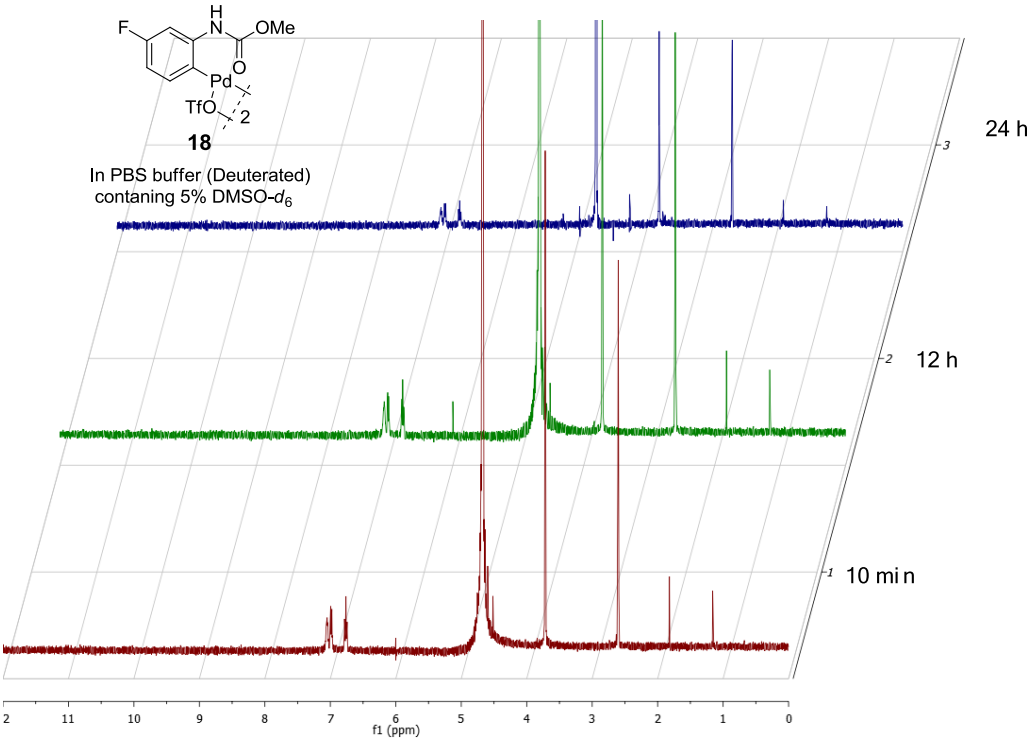
f1 (ppm)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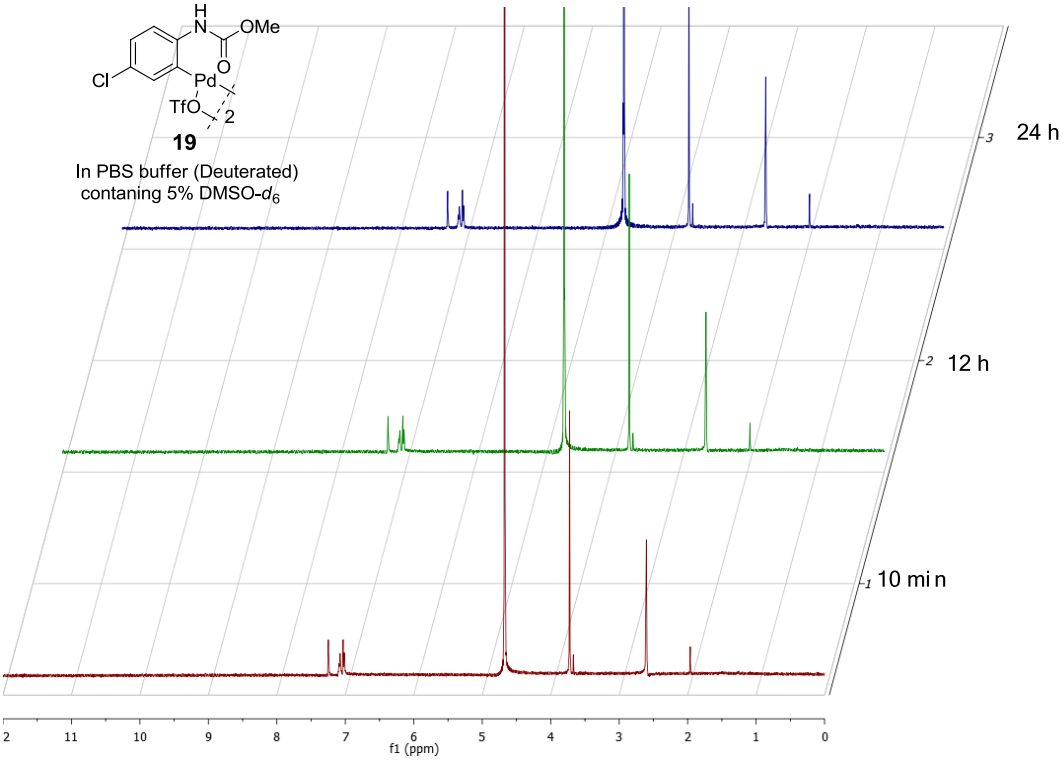
f1 (ppm)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2 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

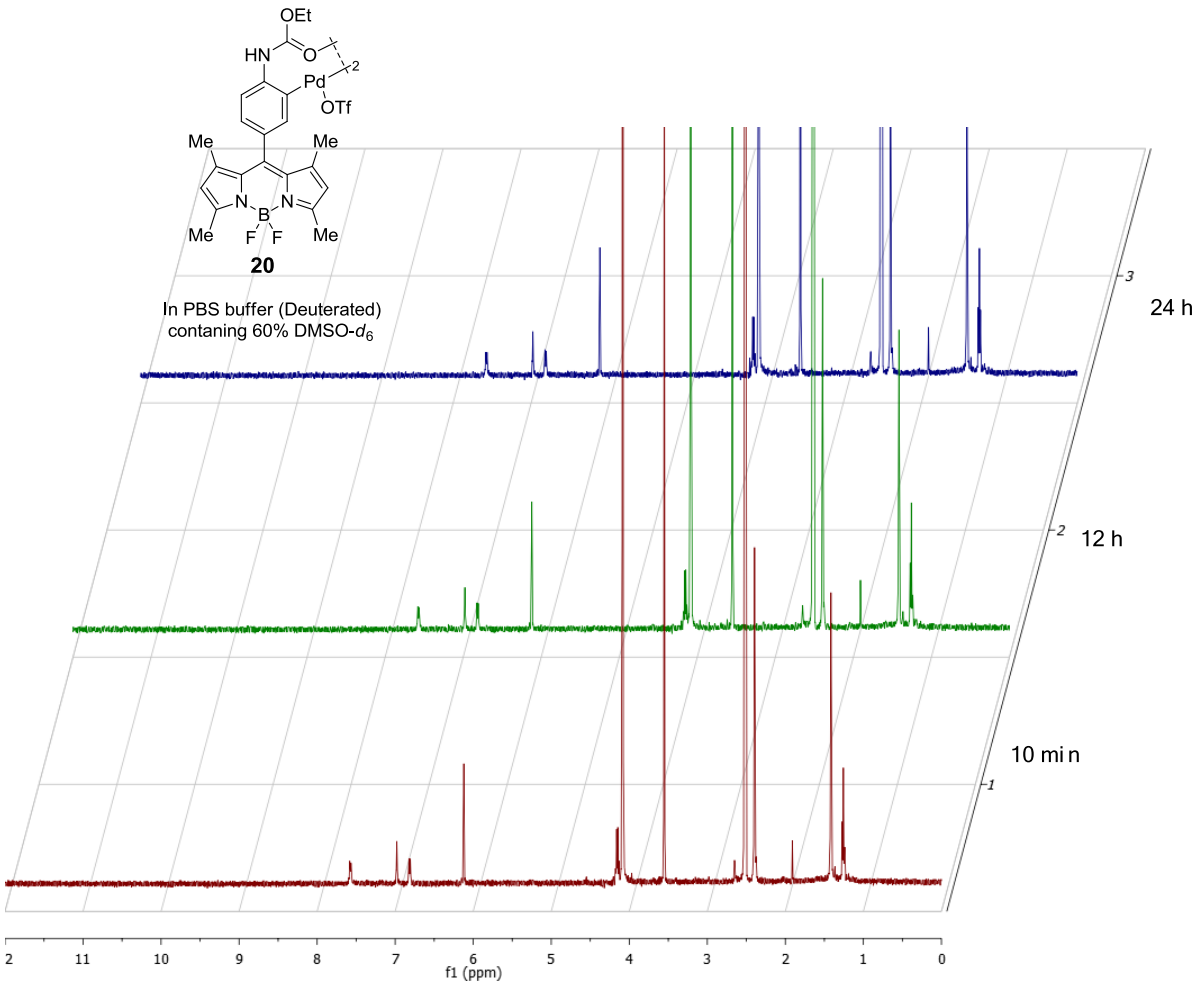
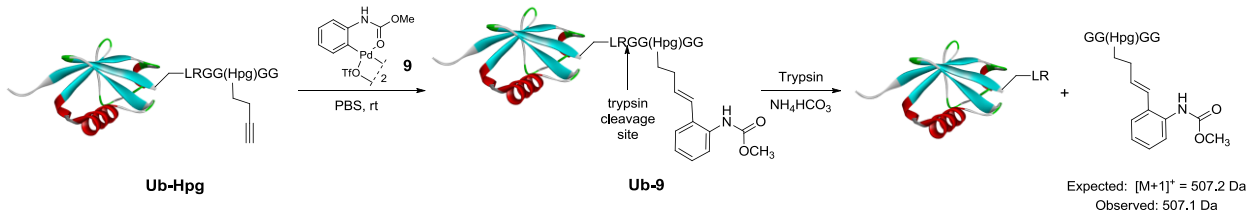



**Figure S1.** Time course of $^{1}$H NMR spectra of the palladacycles in deuterated PBS at 10 min, 12 hours, and 24 hours.

a)




b)

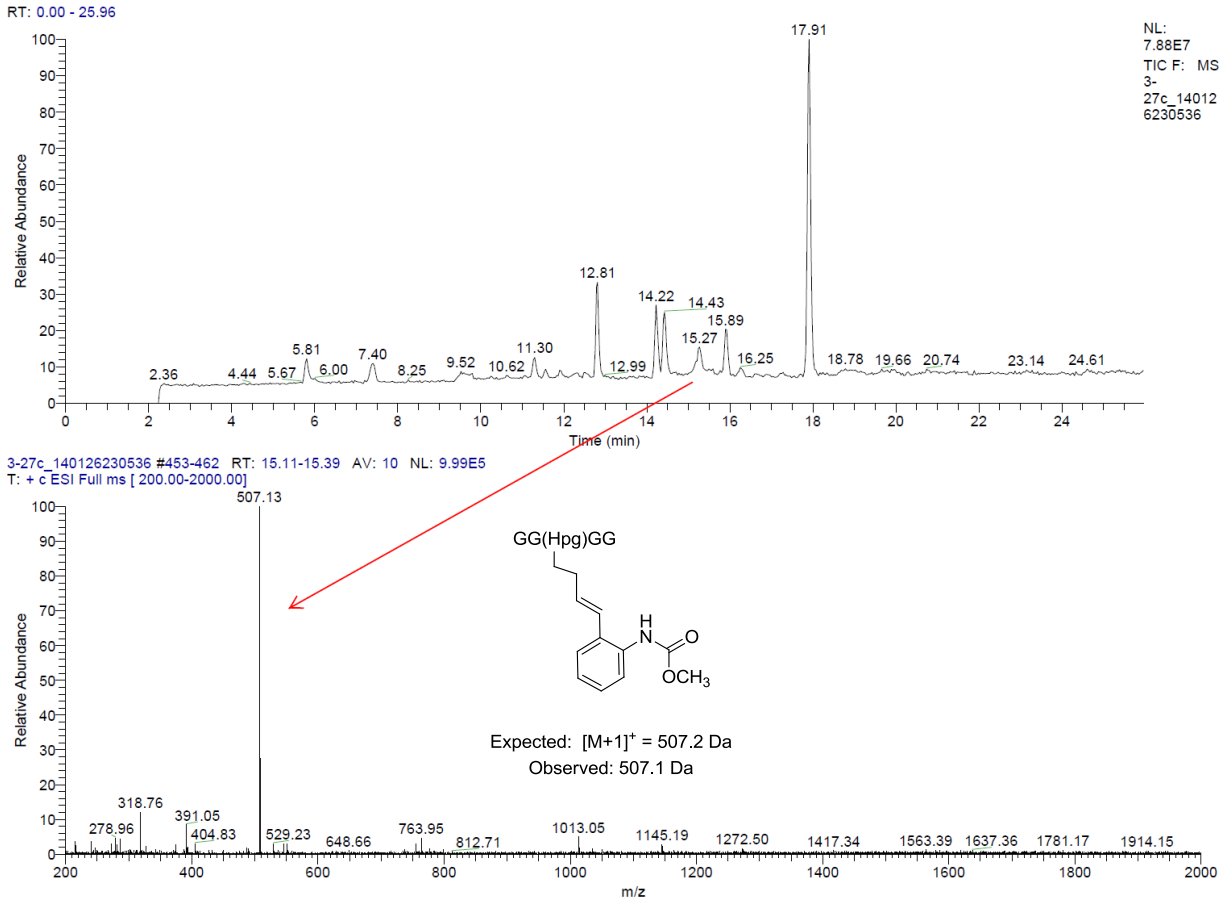
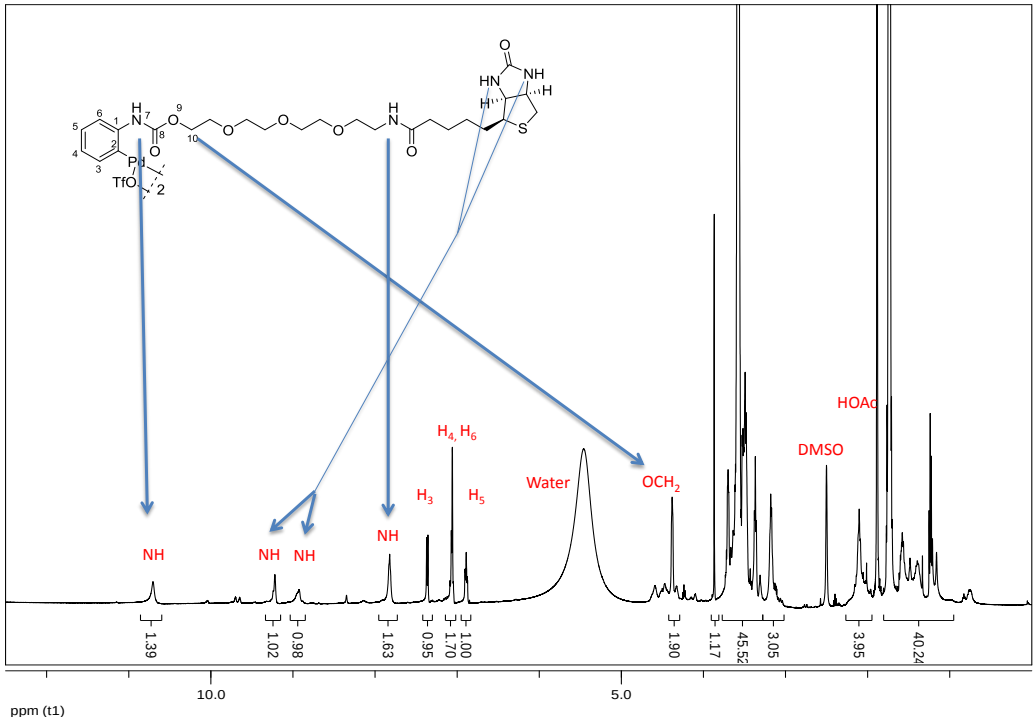



**Figure S2.** Structural analysis of the cross-coupling product derived from palladacycle **9** via trypsinization followed by LC-MS. (a) Scheme showing the bioconjugation reaction with Ub-Hpg and the subsequent trypsin digestion and LC-MS analysis of the digested fragments. (b) The LC-MS chromatogram and mass spectrum showing the positive identification of the C-terminal fragment containing the styrenyl moiety.

a)




b)

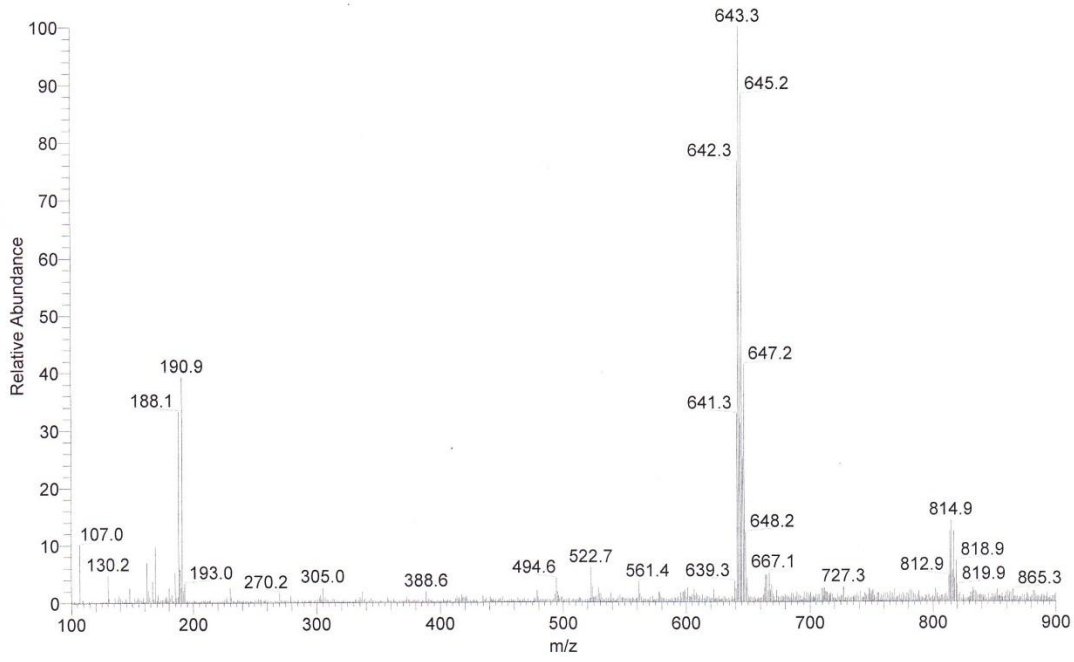
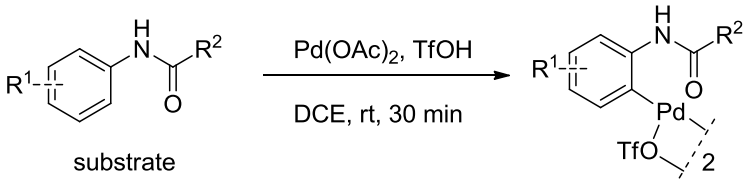



**Figure S3.** (a) $^{1}$H NMR of the biotin-containing palladacycle dissolved in DMSO-$d_6$. (b) Electrospray mass spectrum of the biotin-containing palladacycle showing the desired mass: calcd for $[M/2 - OTf]^{+}$ 643.14, found 643.3.

## General Information

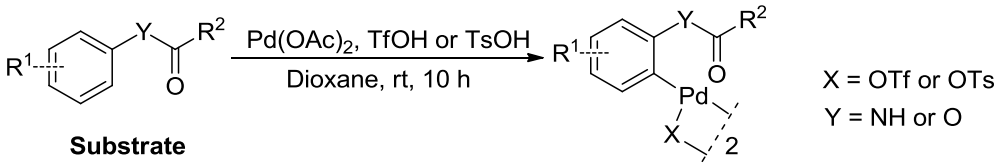
Solvents and chemicals were purchased from commercial sources and used directly without further purification. Flash chromatography was performed with SiliCycle P60 silica gel (40-63 μm, 60Å).[1]H NMR spectra were recorded with Inova-300, -400 or -500 MHz spectrometers and chemical shifts were reported in ppm using either TMS or deuterated solvents as internal standards ($CDCl_3$, 7.26; DMSO-$d_6$, 2.50). Multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. $^{13}C$ NMR spectra were recorded at 75 MHz, and chemical shifts were reported in ppm using the deuterated solvents as internal standards ($CDCl_3$, 77.0; DMSO-$d_6$, 39.5). Electrospray LC-MS analysis was performed using a Finnigan LCQ Advantage IonTrap mass spectrometry coupled with a Surveyor HPLC system. Protein liquid chromatography was performed using a Phenomenex Jupiter C4 column (5 μm, 300 Å, 2.00 × 50 mm) with a flow rate of 200 μL/min and a linear gradient of 10-90% ACN/$H_2O$ containing 0.1% HCOOH. High resolution mass spectrometry was performed on a Bruker solariX XR Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS).

## General procedure for the preparation of palladacycles 5-9, 11-19 (Procedure A)



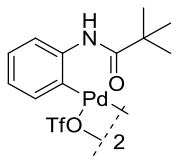

To a 5 mL vial was sequentially added $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), substrate (0.2 mmol), and DCE (0.5 mL). The vial was stirred at room temperature for 5 min and then triflic acid (18 μL, 0.2 mmol) was added. The reaction mixture was stirred at room temperature under open air for 30 min. The reaction mixture was filtered and washed with DCE and dioxane to give the desired palladacycle product.

## General procedure for the preparation of palladacycles 3, 4, 20 and 21 (Procedure B)



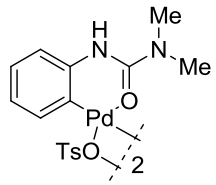

A solution of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) in dioxane (400 μL) was added triflic acid (5.3 μL, 0.06 mmol) or tosylic acid (0.06 mmol), and substrate (0.05 mmol). The mixture was stirred for 10 h at room temperature. Afterwards, the mixture was either filtered or concentrated to afford the desired palladacycle.

Palladacycles **1**, **2**[1] and **6**[2] were prepared as reported previously.



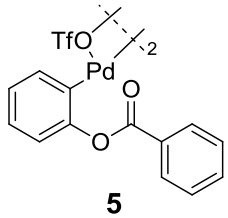
**3**

**Di-$\mu$-trifyloxy-bis (2-pivalamido-phenyl-*2C,O*)dipalladium(II) (3)** (Table 1, entry 3): The title compound was obtained as a yellow solid in 76% yield according to general procedure B: $^{1}$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 10.9 (s, 1H), 7.57 (d, $J$ = 7.5 Hz, 1H), 7.27 (d, $J$ = 7.5 Hz, 1H), 7.19 (t, $J$ = 7.2 Hz, 1H), 7.02 (t, $J$ = 7.2 Hz, 1H), 1.37 (s, 9H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 176.9, 134.7, 132.2, 126.8, 125.4, 121.3, 121.1 (q, $^{1}J_{C\text{-}F}$ = 320.3 Hz), 118.8, 27.7; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{13}H_{17}N_2OPd$ [M/2 - (OTf) + $(CH_3CN)$]$^+$ 323.0376, found 323.0375.



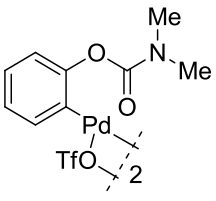
**4**

**Di-$\mu$-tosyloxy-bis(3,3-dimethylureido-phenyl-*2C,O*)dipalladium(II) (4)** (Table 1, entry 4): The title compound was obtained as a yellow solid in 87% yield according to general procedure B: $^{1}$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 9.51 (s, 1H), 7.47 (d, $J$ = 7.5 Hz, 2H), 7.38 (d, $J$ = 8.0 Hz, 1H), 7.13-7.00 (m, 4H), 7.38 (t, $J$ = 8.0 Hz, 1H), 3.09 (s, 6H), 2.26 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.4, 146.1, 138.1, 136.3, 134.4, 128.5, 126.5, 125.9, 123.9, 123.3, 118.4, 37.9, 21.2; MS (ESI) calcd for $C_{11}H_{14}N_3OPd$ [M/2 - (OTs) + $(CH_3CN)$]$^+$ 310.0172, found 310.0167.



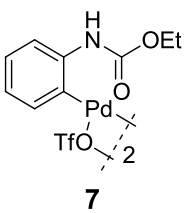
**5**

**Di-$\mu$-tosyloxy-bis(2-benzoyloxy-phenyl-*2C,O*)dipalladium(II)(5)** (Table 1, entry 5): The title compound was obtained as a yellow solid in 51% yield according to general procedure A: $^{1}$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 8.31 (d, $J$ = 7.5 Hz, 2H), 7.78 (t, $J$ = 7.5 Hz, 1H), 7.65 (t, $J$ = 7.5 Hz, 2H), 7.43 (d, $J$ = 7.5 Hz, 1H), 7.20 (t, $J$ = 7.5 Hz, 1H), 7.12-7.00 (m, 2H); $^{13}$C NMR (DMSO-$d_6$, 300 MHz) $\delta$ 165.7, 153.5, 136.5, 134.5, 132.1, 130.5, 129.9, 129.5, 127.0, 126.2, 122.9; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{15}H_{12}NO_2Pd$ [M/2 - (OTf) + $(CH_3CN)$]$^+$ 343.9903, found 343.9897.



**6**

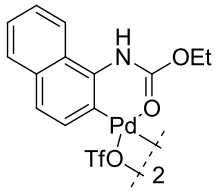
**Di-$\mu$-trifyloxy-bis(2-(dimethylcarbamoyl)oxy-phenyl-*2C,O*) dipalladium(II) (6)**[2] (Table 1, entry 6): The title compound was obtained as a yellow solid in 73% yield according to general procedure A: $^{1}$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 7.36 (d, $J$ = 7.5 Hz, 1H), 7.14 (t, $J$ = 7.5 Hz, 1H), 7.03 (t, $J$ = 7.5 Hz, 1H), 6.89 (d, $J$ = 7.5 Hz, 1H), 3.25 (s, 3H), 3.02 (s, 3H).



**7**

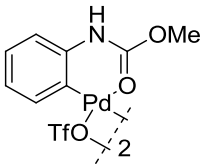
**Di-$\mu$-trifyloxy-bis(2-ethoxycarbonylamino-phenyl-*2C,O*)dipalladium(II) (7)** (Table 1, entry 7): The title compound was obtained as a yellow solid in 75% yield according to general procedure A: $^{1}$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 10.8 (s, 1H), 7.38 (d, $J$ = 8.0 Hz, 1H), 7.10-6.97 (m, 2H), 6.91 (t, $J$ = 8.0 Hz, 1H), 4.32 (q, $J$ = 7.2 Hz, 2H), 1.32 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.5,138.2, 134.9, 126.7, 124.9, 124.2, 121.1 (q, $^{1}J_{C\text{-}F}$ = 320.6 Hz), 119.0,

63.6, 14.9; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{11}H_{13}N_2O_2Pd$ [M/2 - (OTf) + $(CH_3CN)]^+$ 311.0012, found 311.0008.



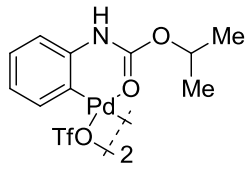
**8**

**Di-$\mu$-trifyloxy-bis(1-(ethoxycarbonylamino)naphthalen-2-yl-*2C,O*) dipalladium(II) (8)** (Table 1, entry 8): The title compound was obtained as a black solid in 60% yield according to general procedure A: $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 9.75 (s, 1H), 7.88 (d, $J$ = 8.0 Hz, 1H), 7.83 (d, $J$ = 7.5 Hz, 1H), 7.63-7.60 (m, 2H), 7.50-7.43 (m, 2H), 4.26 (brs, 2H), 1.35 (brs, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.9, 136.2, 135.2, 132.8, 132.1, 130.1, 128.3, 126.3, 125.9, 125.6, 122.6, 61.5, 15.2; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{15}H_{15}N_2O_2Pd$ [M/2 - (OTf) + $(CH_3CN)]^+$ 361.0168, found 361.0174.



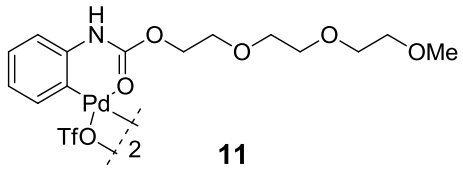
**9**

**Di-$\mu$-trifyloxy-bis(2-methoxycarbonylamino-phenyl-*2C,O*)dipalladium(II) (9)** (Table 2, entry 1): The title compound was obtained as a yellow solid in 80% yield according to general procedure A: $^1$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 10.7 (s, 1H), 7.37 (d, $J$ = 7.5 Hz, 1H), 7.12-7.03 (m, 2H), 6.98-6.93 (m, 1H), 3.85 (s, 3H; $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.7, 138.7, 134.9, 126.7, 125.8, 124.2, 121.1 (q, $^1J_{C\text{-}F}$ = 320.6 Hz), 119.6, 54.2; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{10}H_{11}N_2O_2Pd$ [M/2 - (OTf) + $(CH_3CN)]^+$ 296.9855, found 296.9850.



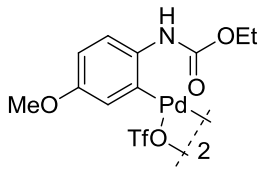
**10**

**Di-$\mu$-trifyloxy-bis(2-isopropoxycarbonylamino-phenyl-*2C,O*) dipalladium(II) (10)** (Table 2, entry 2): The title compound was obtained as a black solid in 80% yield according to general procedure A: $^1$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 10.7 (s, 1H), 7.37 (d, $J$ = 7.8 Hz, 1H), 7.10-6.97 (m, 2H), 6.90 (t, $J$ = 7.8 Hz, 1H), 5.0 (m, 1H), 1.33 (d, $J$ = 6.3 Hz, 6H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.2, 137.9, 134.9, 126.7, 124.3, 124.2, 119.0, 72.0, 22.4; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{12}H_{15}N_2O_2Pd$ [M/2 - (OTf) + $(CH_3CN)]^+$ 325.0168, found 325.0162.



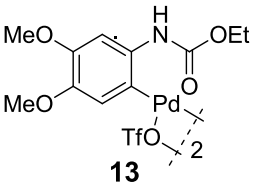
**11**

Palladacycle **11** (Table 2, entry 3): Following general procedure B, the mixture was concentrated and dried under vacuum to give the title compound as a black solid in 90% yield: $^1$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 10.7 (s, 1H), 7.38 (d, $J$ = 8.0 Hz, 1H), 7.11-7.03 (m, 2H), 6.98-6.95 (m, 1H), 4.41 (m, 2H), 3.72 (m, 2H), 3.64-3.48 (m, 6H), 3.42 (m, 2H), 3.24 (m, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.4, 138.5, 134.9, 126.7, 125.7, 124.3, 119.6, 71.7, 70.2(2C), 70.1, 68.8, 66.8, 66.6, 21.5; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{14}H_{20}NO_5Pd$ [M/2 - (OTf)]$^+$ 388.0376, found 388.0378.



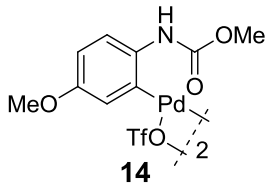

**12**

**Di-*μ*-trifyloxy-bis(5-methoxy-2-ethoxycarbonylamino-phenyl-*2C,O*) dipalladium(II) (12)** (Table 2, entry 4): The title compound was obtained as a yellow solid in 70% yield according to general procedure A: $^{1}$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 10.5 (s, 1H), 6.96 (s, 1H), 6.91 (d, $J$ = 8.4 Hz, 1H), 6.68 (d, $J$ = 8.4 Hz, 1H), 4.29 (q, $J$ = 6.9 Hz, 2H), 3.68 (s, 3H), 1.30 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.5, 155.1, 131.5, 126.3, 121.1 (q, $^{1}J_{C\text{-}F}$ = 320.6 Hz), 119.9, 119.4, 112.1, 63.6, 55.7, 14.9; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{12}H_{15}N_2O_3Pd$ [M/2 - (OTf) + $(CH_3CN)]^+$ 341.0118, found 341.0125.



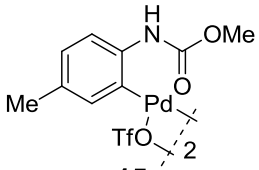

**13**

**Di-*μ*-trifyloxy-bis(4, 5-dimethoxy-2-methoxycarbonylamino-phenyl-*2C,O*)dipalladium(II) (13)** (Table 2, entry 5): The title compound was obtained as a black solid in 30% yield according to general procedure A: $^{1}$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 10.4 (s, 1H), 6.99 (s, 1H), 6.71 (s, 1H), 4.31 (q, $J$ = 6.9 Hz, 2H), 3.69 (s, 3H), 3.67 (s, 3H), 1.31 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.4, 147.8, 144.7, 130.8, 121.1 (q, $J$ = 320.6 Hz), 117.1, 112.8, 107.2, 63.6, 56.3, 55.9, 14.9; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{13}H_{17}N_2O_4Pd$ [M/2 - (OTf) + $(CH_3CN)]^+$ 371.0223, found 371.0226.



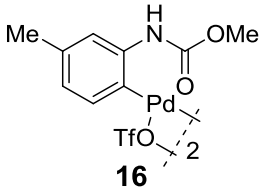

**14**

**Di-*μ*-trifyloxy-bis(4-methoxy-2-methoxycarbonylamino-phenyl-*2C,O*) dipalladium(II) (14)** (Table 2, entry 6): The title compound was obtained as a yellow solid in 65% yield according to general procedure A: $^{1}$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 10.4 (s, 1H), 6.98-6.90 (m, 2H), 6.68 (d, $J$ = 8.1 Hz, 1H), 3.84 (s, 3H), 3.68 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.8, 155.1, 132.0, 126.7, 121.1 (q, $J$ = 320.6 Hz), 120.3, 119.5, 112.0, 55.7, 54.1; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{11}H_{13}N_2O_3Pd$ [M/2 - (OTf) + $(CH_3CN)]^+$ 326.9961, found 326.9957.




**15**

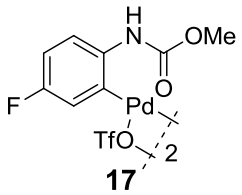
**Di-*μ*-trifyloxy-bis(5-methyl-2-methoxycarbonylamino-phenyl-*2C,O*) dipalladium(II) (15)** (Table 2, entry 7): The title compound was obtained as a yellow solid in 75% yield according to general procedure A: $^{1}$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 10.4 (s, 1H), 7.17 (d, 1H), 6.96 (d, $J$ = 7.8 Hz, 1H), 6.88 (d, $J$ = 7.8 Hz, 1H), 3.84 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.7, 136.2, 135.1, 133.2, 127.3, 126.1, 119.4, 54.1, 21.0; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{11}H_{13}N_2O_2Pd$ [M/2 - (OTf) + $(CH_3CN)]^+$ 311.0012, found 311.0016.




**16**

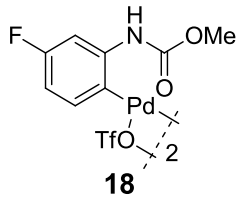
**Di-*μ*-trifyloxy-bis(4-methyl-2-methoxycarbonylamino-phenyl-*2C,O*) dipalladium(II) (16)** (Table 2, entry 8): The title compound was obtained as a black solid in 45% yield according to general procedure A: $^{1}$H NMR

(DMSO-$d_6$, 300 MHz) $\delta$ 10.5 (s, 1H), 7.23 (d, $J$ = 7.5 Hz, 1H), 6.89 (s, 1H), 6.73 (d, $J$ = 7.5 Hz, 1H), 3.84 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.8, 138.2, 135.9, 134.6, 125.2, 121.2, 120.0, 54.4, 20.7; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{11}H_{13}N_2O_2Pd$ [M/2 - (OTf) + $(CH_3CN)]^+$ 311.0012, found 311.0016.



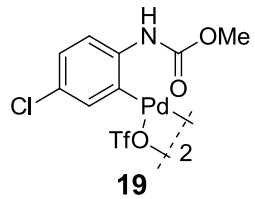
**17**

**Di-$\mu$-trifyloxy-bis(5-fluoro-2-methoxycarbonylamino-phenyl-*2C,O*) dipalladium(II) (17)** (Table 2, entry 9): The title compound was obtained as a yellow solid in 72% yield according to general procedure A: $^1$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 10.4 (s, 1H), 7.33 (t, $J$ = 8.4 Hz, 1H), 7.12 (dd, $J$ = 8.7, 2.4 Hz, 1H), 6.77 (td, $J$ = 8.7, 2.4 Hz, 1H), 3.81 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 161.7 (d, $^1J_{C\text{-}F}$ = 238.1 Hz), 156.1, 140.8 (d, $^3J_{C\text{-}F}$ = 9.2 Hz), 135.8 (d, $^3J_{C\text{-}F}$ = 9.2 Hz), 121.1 (q, $^1J_{C\text{-}F}$ = 320.6 Hz), 120.1, 110.2 (d, $^2J_{C\text{-}F}$ = 20.6 Hz), 106.5 (d, $^2J_{C\text{-}F}$ = 25.2 Hz), 53.7; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8, -118.1; HRMS (ESI) calcd for $C_{10}H_{10}FN_2O_2Pd$ [M/2 - (OTf) + $(CH_3CN)]^+$ 314.9761, found 314.9765.



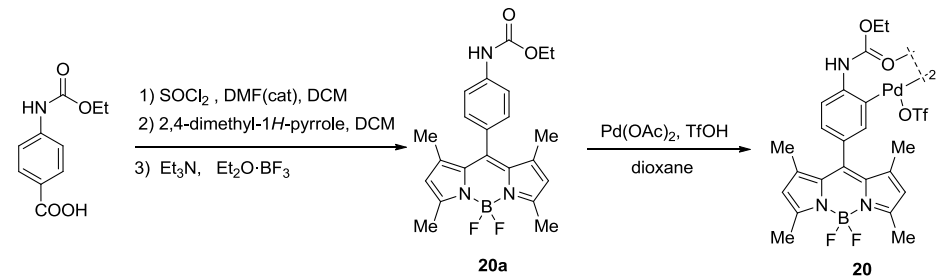
**18**

**Di-$\mu$-trifyloxy-bis(4-fluoro-2-methoxycarbonylamino-phenyl-*2C,O*) dipalladium(II) (18)** (Table 2, entry 10): The title compound was obtained as a yellow solid in 70% yield according to general procedure A: $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 10.5 (s, 1H), 7.21 (dd, $J$ = 10.0, 3.0 Hz, 1H), 7.09 (dd, $J$ = 9.0, 5.5 Hz, 1H), 6.96 (td, $J$ = 8.5, 3.0 Hz, 1H), 3.86 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 157.3 (d, $^1J_{C\text{-}F}$ = 243.8 Hz), 156.7, 135.6, 128.2, 121.1 (q, $^1J_{C\text{-}F}$ = 320.6 Hz), 120.8 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 120.3, 113.1 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 54.2; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8, -118.3; HRMS (ESI) calcd for $C_{10}H_{10}FN_2O_2Pd$ [M/2 - (OTf) + $(CH_3CN)]^+$ 314.9761, found 314.9766.



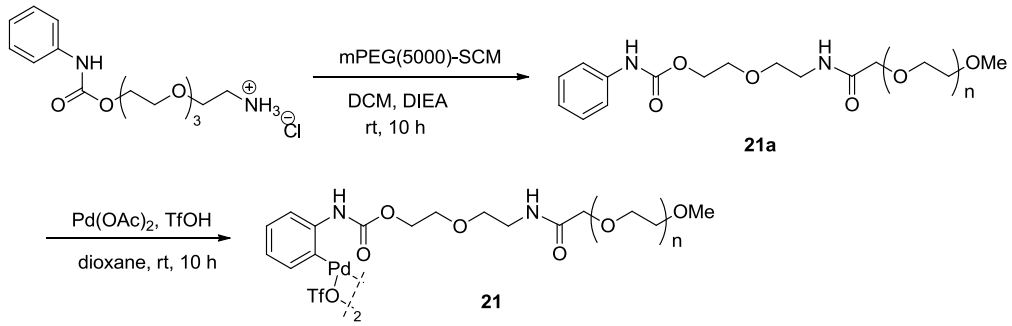
**19**

**Di-$\mu$-trifyloxy-bis(5-chloro-2-methoxycarbonylamino-phenyl-*2C,O*) dipalladium(II) (19)** (Table 2, entry 11): The title compound was obtained as a yellow solid in 60% yield according to general procedure A: $^1$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 10.5 (s, 1H), 7.38 (s, 1H), 7.13 (m, 2H), 3.83 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.5, 138.4, 133.8, 128.0, 127.0, 126.3, 120.5, 54.1; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8; HRMS (ESI) calcd for $C_{10}H_{10}ClN_2O_2Pd$ [M/2 - (OTs) + $(CH_3CN)]^+$ 330.9466, found 330.9469.



To a slurry of 4-(ethoxycarbonyl)amino-benzoic acid in 4 mL DCM, 1 mL thionyl chloride was added dropwise at 0°C under argon, followed by the addition of 6 µL DMF. This mixture was stirred at room temperature for 4 h and a clear solution was obtained. The solvent and excess amount of thionyl chloride was removed under reduced pressure to afford a yellow solid. The yellow solid was re-dissolved in 10 mL DCM, and to the solution was added 2, 4-dimethyl pyrrole under argon. After stirring at room temperature for 4 h, the reaction mixture was cooled to 0°C, and $Et_3N$ and $BF_3{\cdot}OEt_2$ was added at 0°C. The mixture was stirred overnight at room temperature under argon. Afterwards, the solvent was removed under reduced pressure and the residue was purified through column chromatography on silica gel (1:2 hexanes/DCM) to afford an orange powder **20a** (210 mg, 26% yield): $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.54 (d, $J$ = 7.8 Hz, 2H), 7.21 (d, $J$ = 7.8 Hz, 2H), 6.77 (s, 1H), 5.98 (s, 2H), 4.26 (q, $J$ = 6.9 Hz, 2H ), 2.56 (s, 6H), 1.43 (s, 6H), 1.33 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 155.4, 153.4, 143.1, 141.4, 138.8, 131.6, 129.6, 128.8, 121.2, 118.7, 61.5, 14.6, 14.5; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ –146.1 (q, $J$ = 32.7 Hz); HRMS (ESI) calcd for $C_{22}H_{24}BF_2N_3NaO_2$ $[M+Na]^+$ 434.1827, found 434.1828.

Following the general procedure B, a solution of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) in dioxane (400 µL) was added triflic acid (5.3 µL, 0.06 mmol), followed by *N*-phenylcarbamate (0.05 mmol). The mixture was stirred at room temperature for 10 h. Afterward, the mixture was filtered and washed with dioxane (300 µL) to afford palladacycle **20** as a brown powder (11 mg, 17% yield): $^1$H NMR (DMSO-$d_6$, 300 MHz) $\delta$ 11.0 (s, 1H), 7.24 (m, 2H), 7.08 (d, $J$ = 7.8 Hz, 1H), 6.14 (s, 1H), 4.37 (q, $J$ = 6.9 Hz, 2H), 2.42 (s, 6H), 1.39 (s, 6H), 1.34 (t, $J$ = 6.6 Hz, 3H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ 156.5, 155.1, 143.4, 142.5, 138.9, 133.8, 131.3, 129.1, 126.1, 125.0, 121.6, 118.4, 64.0, 14.9, 14.7, 14.6; $^{19}$F NMR (DMSO-$d_6$, 282.4 MHz) $\delta$ -77.8, -127 (brs); HRMS (ESI) calcd for $C_{24}H_{26}BF_2N_4O_2Pd$ $[M/2 - (OTf) + (CH_3CN)]^+$ 557.1152, found 557.1185.




A solution of 2-(2-((phenylcarbamoyl)oxy)ethoxy)ethanaminium chloride (4.9 mg, 0.2 mmol), mPEG-SCM (~5 kDa; 30 mg, 0.006 mmol) and DIEA (15 µL) in 2 mL DCM was stirred at room temperature for 10 h. The solvent was removed under the reduced pressure, and the residue was purified through preparative HPLC to give the PEGylated carbamate **21a** as a white solid (10 mg, 30% yield): $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 8.20 (brs, 1H), 7.45 (d, $J$ = 7.2 Hz, 2H), 7.31 (t, $J$ =

7.2 Hz, 2H), 7.24 (brs, 1H), 7.07 (t, *J* = 7.0 Hz, 1H), 4.34-4.30 (m, 2H), 4.03 (s, 3H), 3.81 (m, 2H), 3.79-3.56 (m, 428H), 3.52 (m, 4H), 3.40 (s, 3H).

Palladacycle **21**: Following the general procedure B, a solution of $Pd(OAc)_2$ (0.4 mg, 1.8 μmol) in dioxane (200 μL) was added triflic acid (0.2 μL, 2.1 μmol) and **21a** (10 mg, 1.8 μmol). After stirring at room temperature for 10 h, the solvent was removed under the reduced pressure. The desired palladacycle was obtained as a sticky black solid after drying under vacuum overnight: $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 11.7 (s, 1H), 7.60 (m, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 7.05 (m, 1H), 6.95 (m, 1H), 4.37 (m, 2H), 3.82 (s, 2H), 3.80-3.10 (m, 265H).

**Expression and purification of Hpg-encoded ubiquitin (Ub-Hpg)**

Ub-Hpg was expressed and purified as described previously.[3] Finally, the protein was desalted to 1×PBS buffer and concentrated to 0.14 mM .

**General procedures for the reaction of palladacycles with Ub-Hpg (for Table 1, Table 2, Figure 1 and Figure 2).**

To a 0.6-mL microcentrifuge tube was added 48 μL PBS buffer solution and Ub-Hpg (0.9 μL, 0.14 mM). Then the palladacycle stock solution (2 μL, 0.25 mM in DMSO) was added under vigorous stirring at room temperature. After reacted for the indicated time, the samples were immediately quenched with 10 μL of 3-mercaptopropanoic acid (4% v/v in water) and injected into LC-MS for analysis.

Final concentration of this reaction before quenching:
Ub-Hpg: 2.5 μM
Palladacycle: 10 μM
DMSO: 4%
Buffer: 1 × PBS, pH =7.4

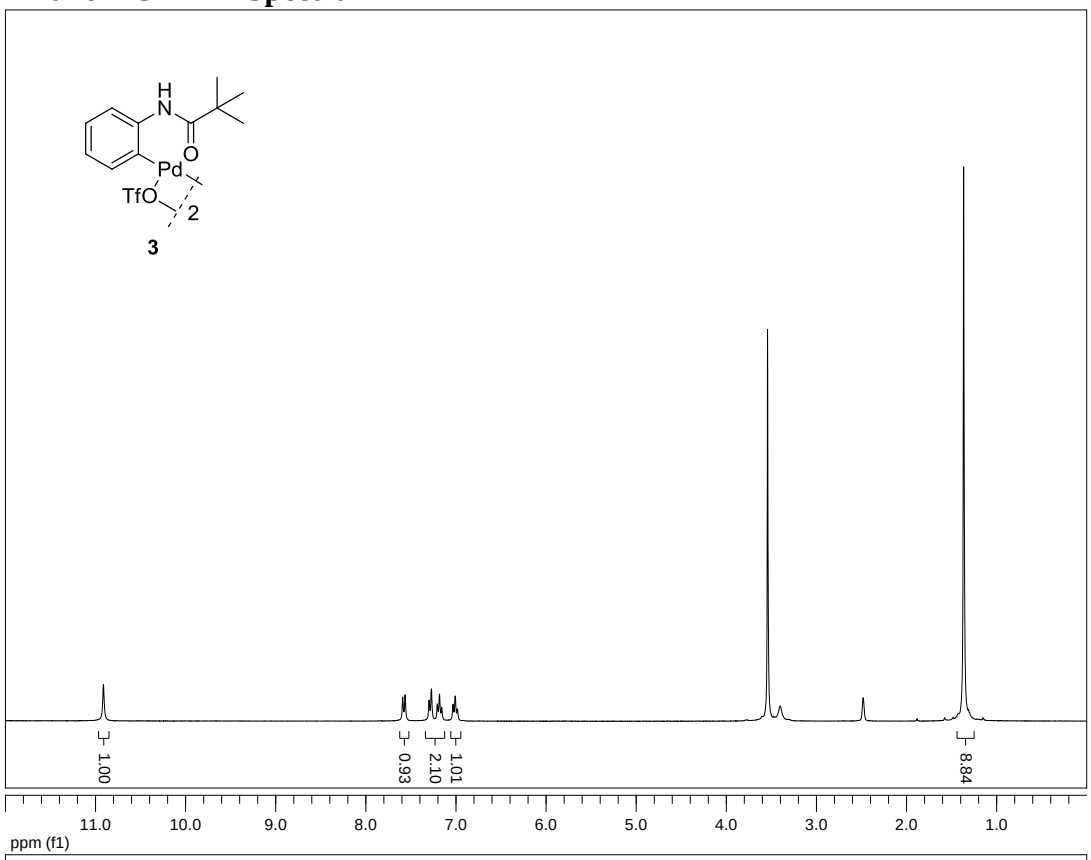
**Reference:**

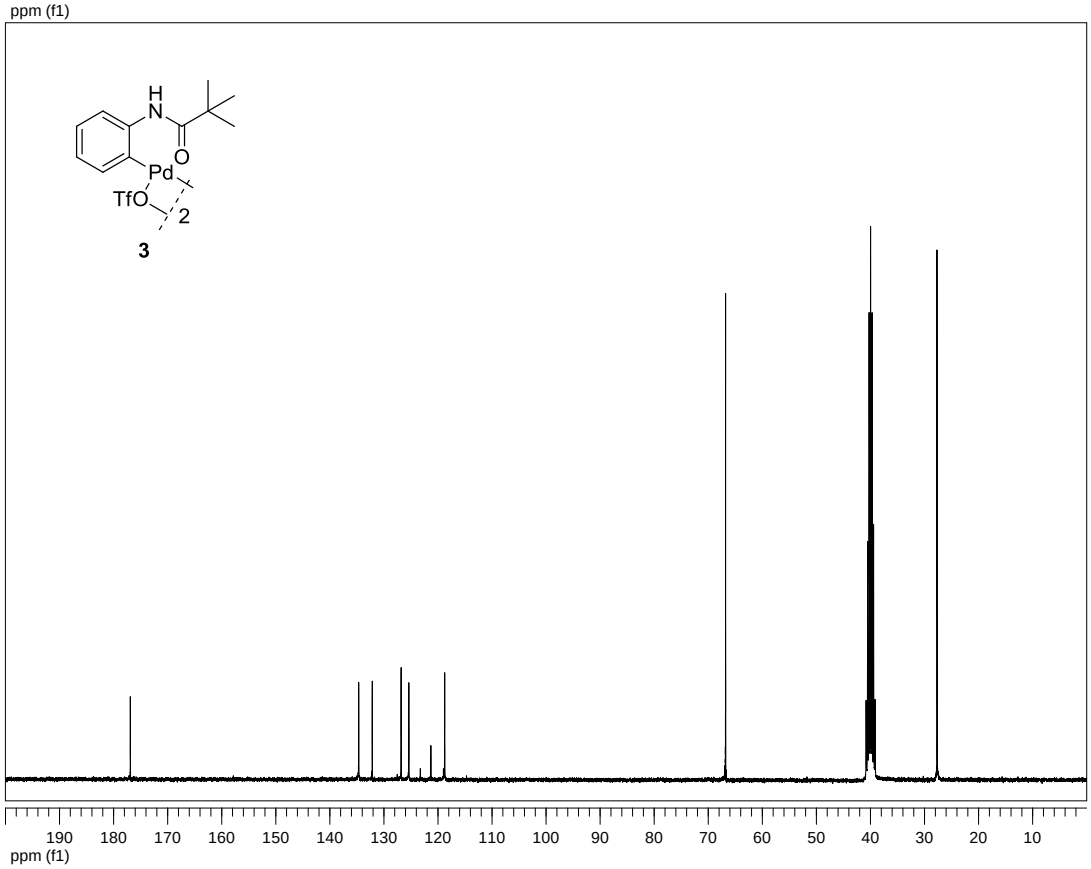
[1] Cheng, G.; Lim, R. K.; Li, N.; Lin, Q. *Chem. Commun.* **2013**, *49*, 6809.

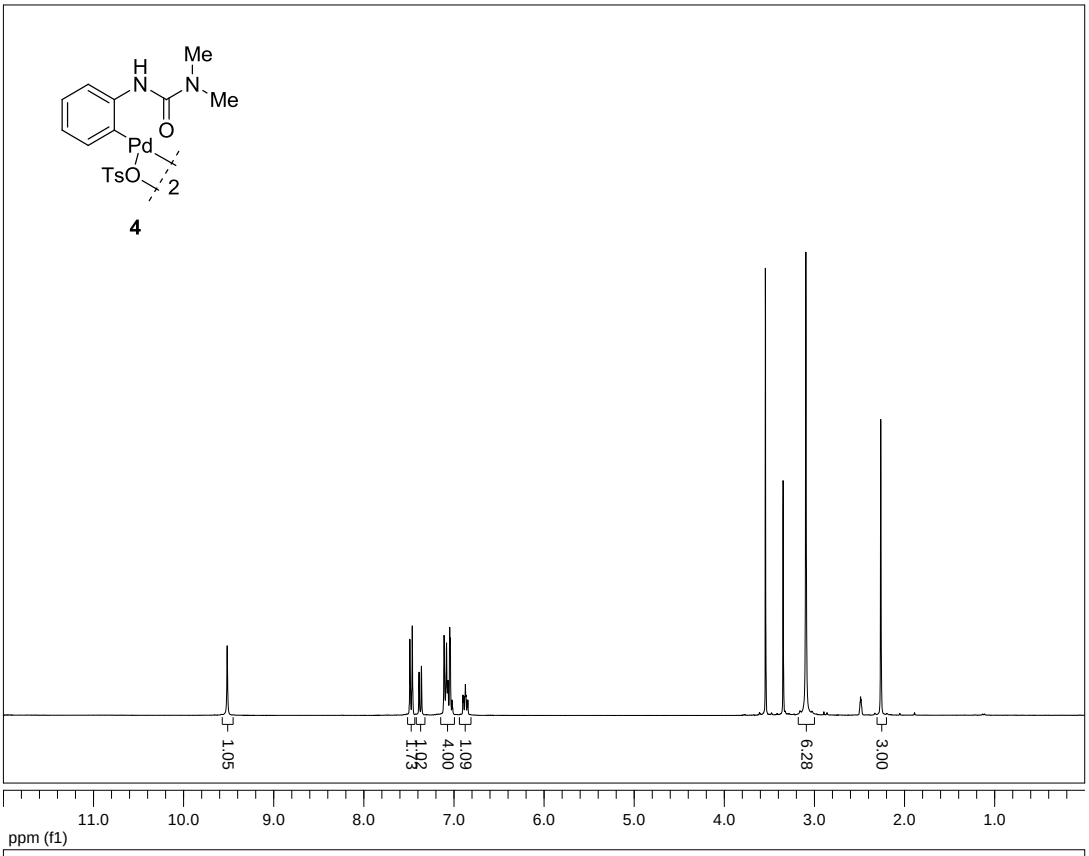
[2] John, A.; Nicholas, K. M. *J. Org. Chem.* **2012**, *77*, 5600.

[3] Li, N.; Lim, R. K.; Edwardraja, S.; Lin, Q. *J. Am. Chem. Soc.* **2011**, *133*, 15316.

## $^{1}$H NMR and $^{13}$C NMR Spectra

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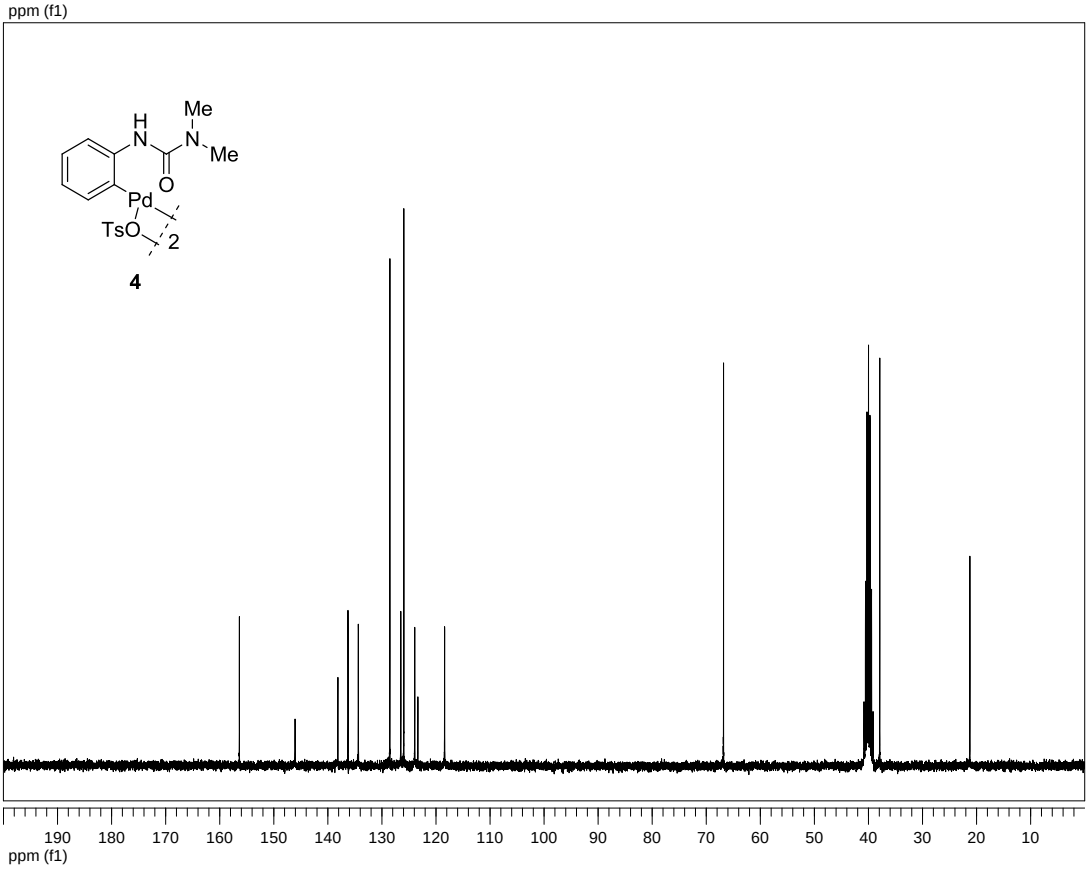
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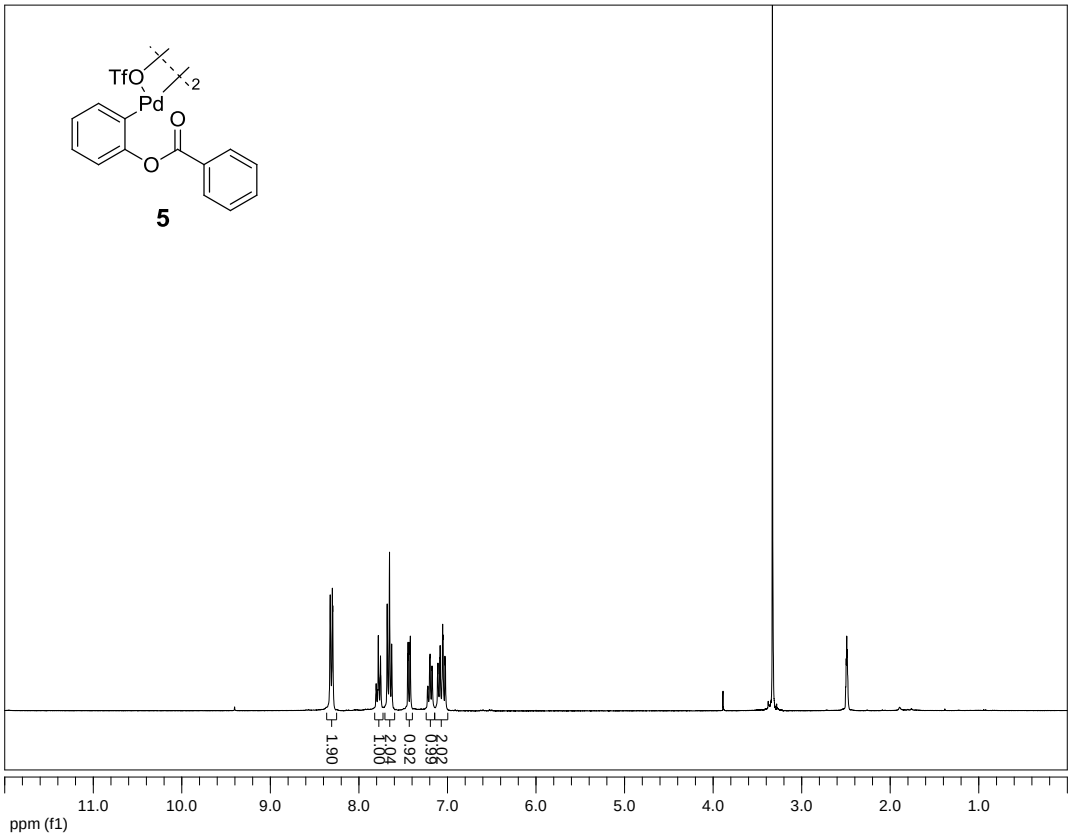
ppm (f1)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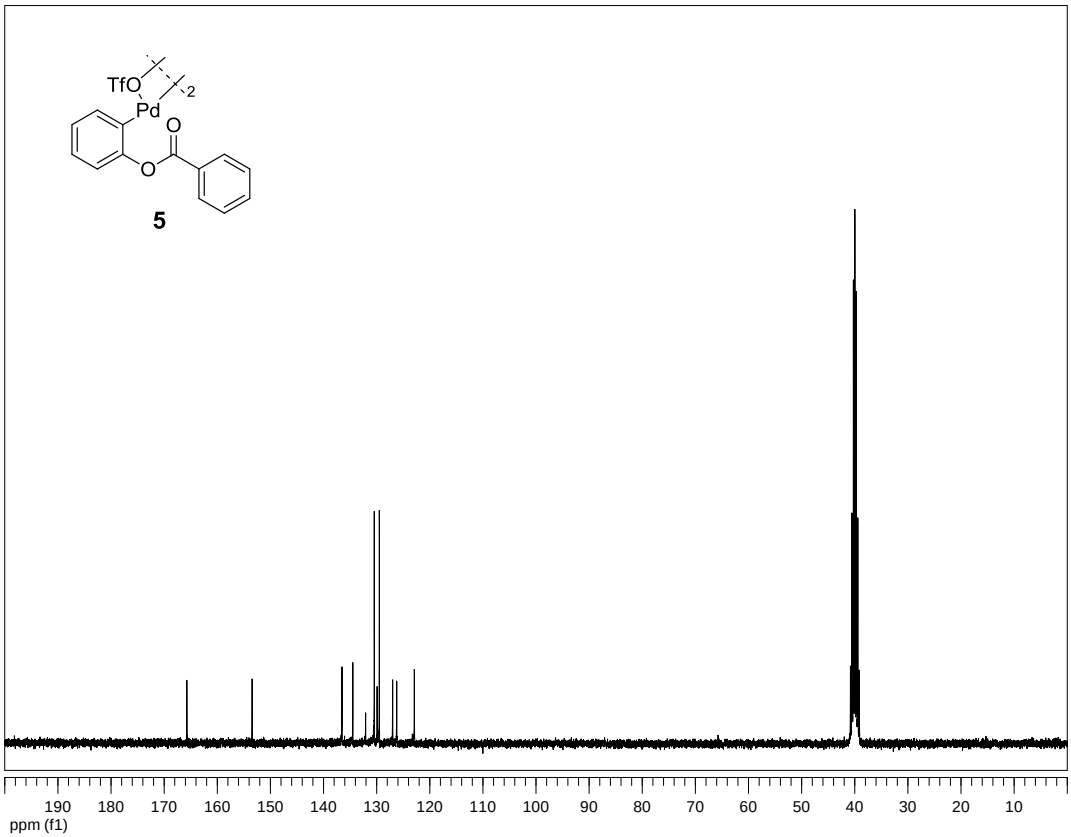
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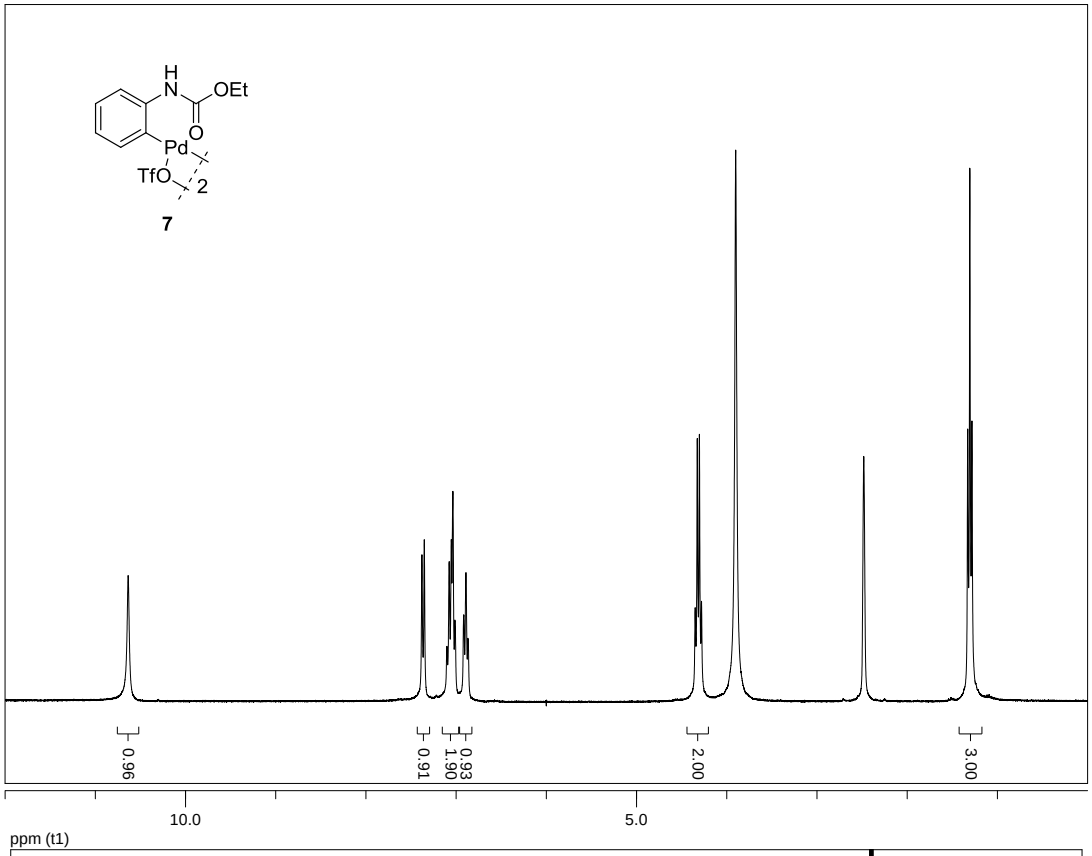
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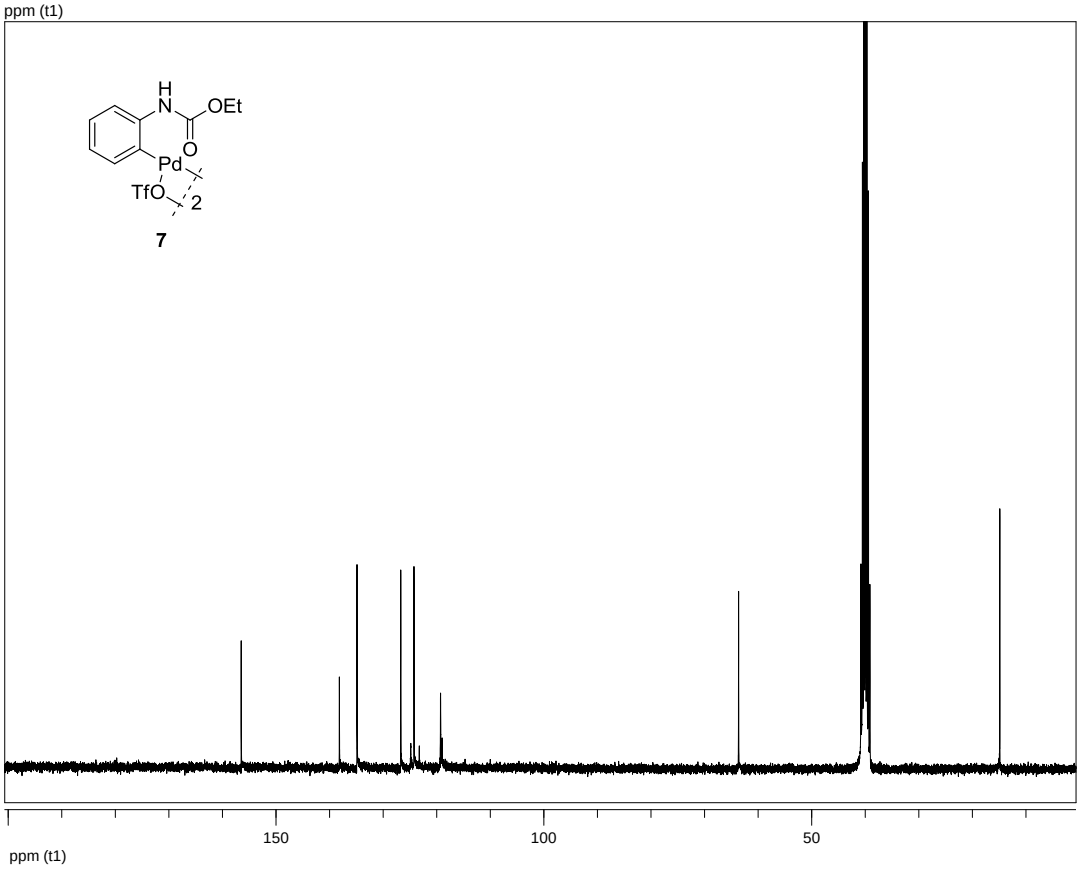
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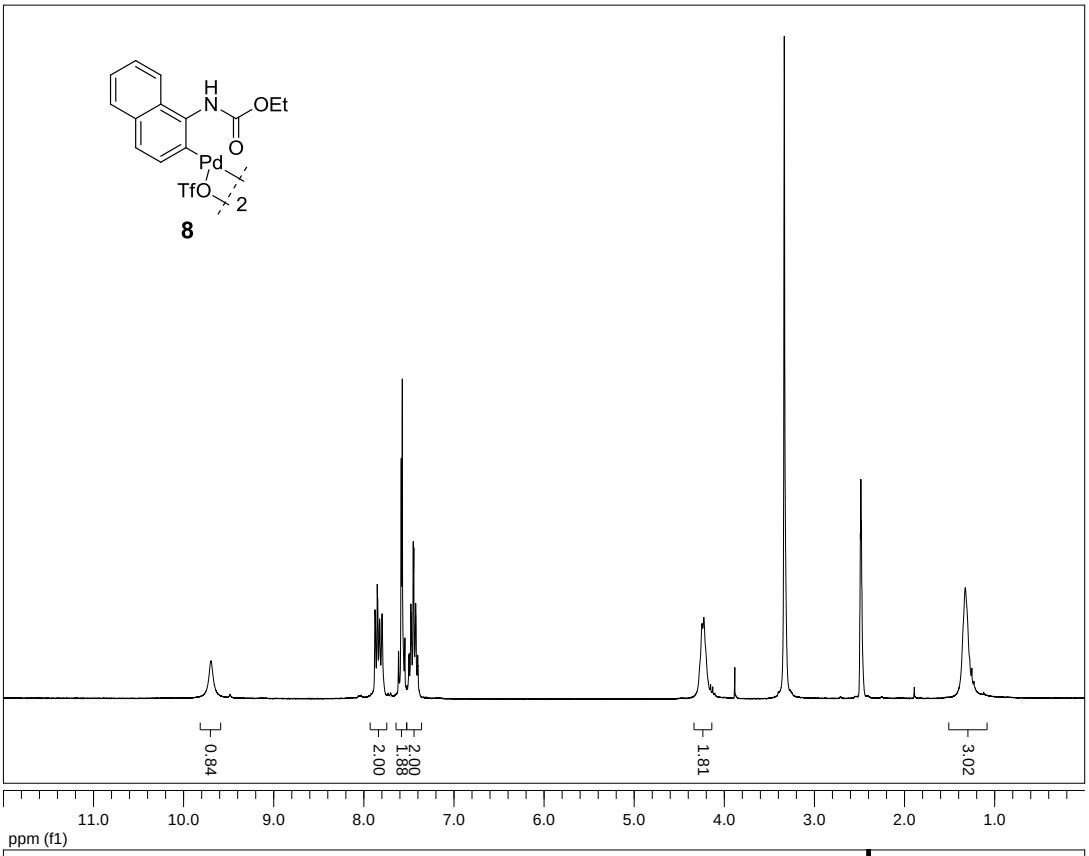
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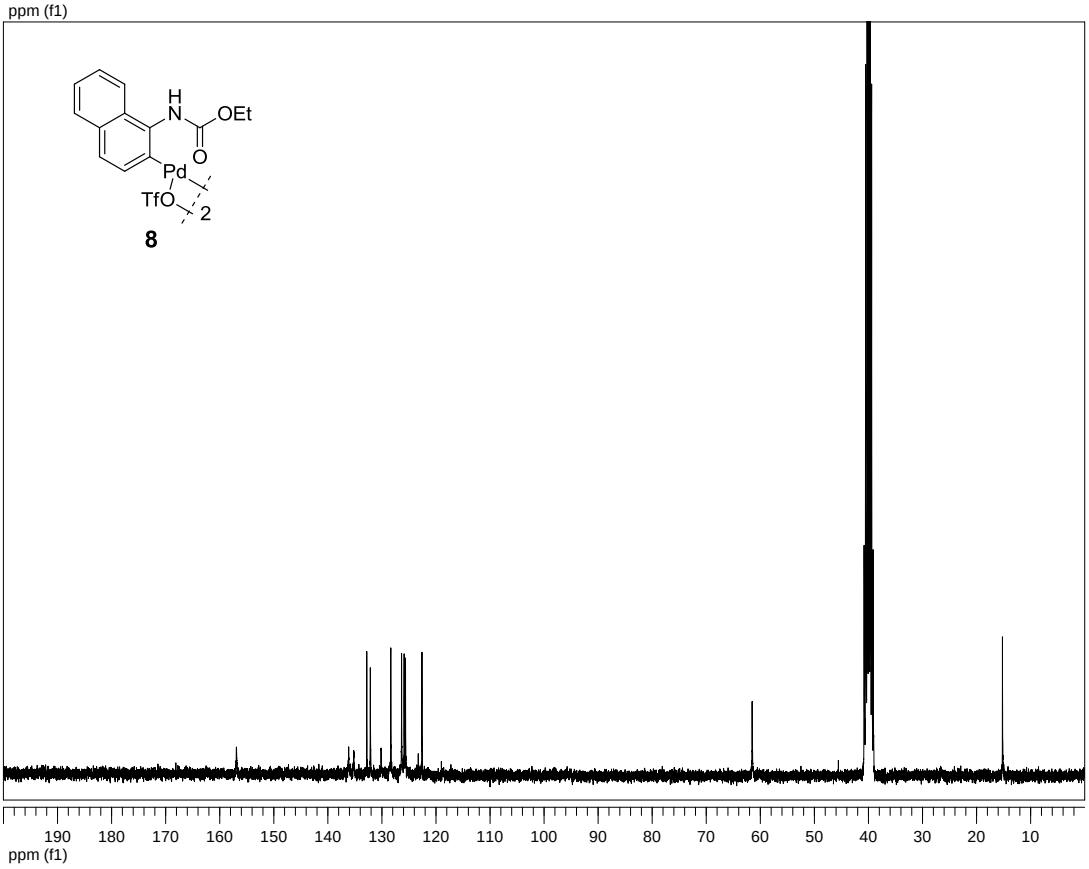
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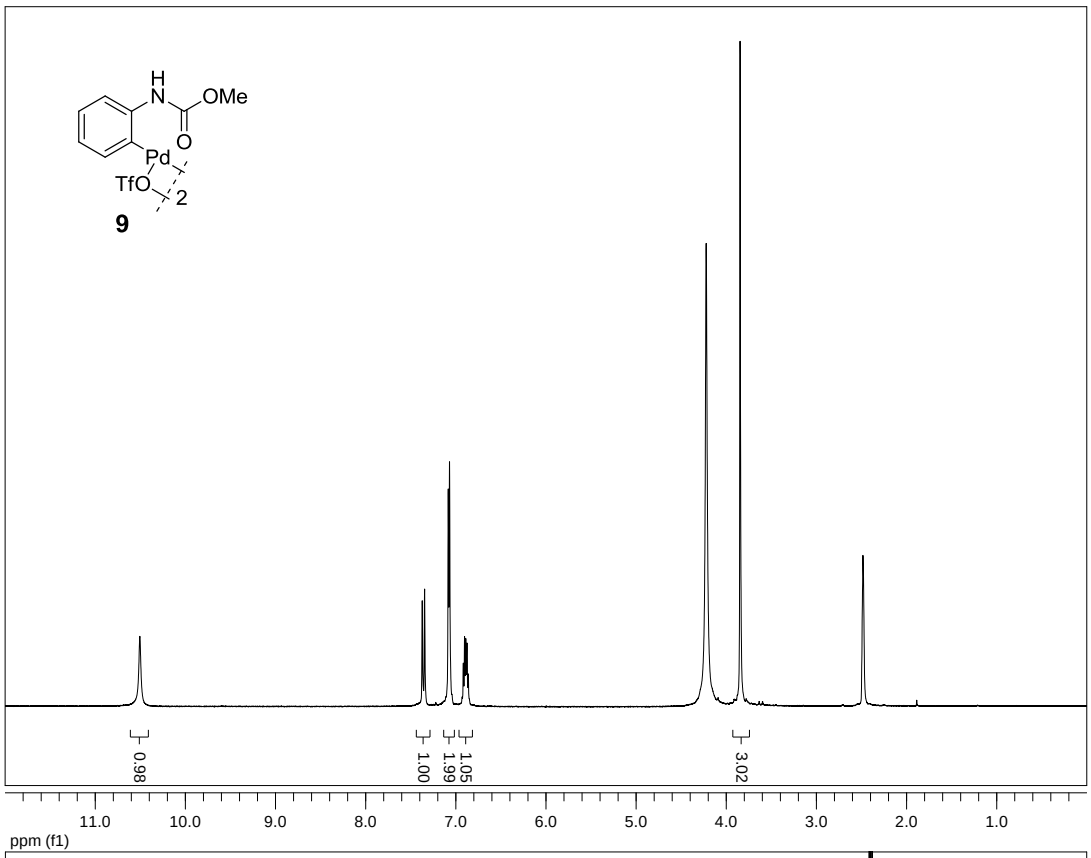
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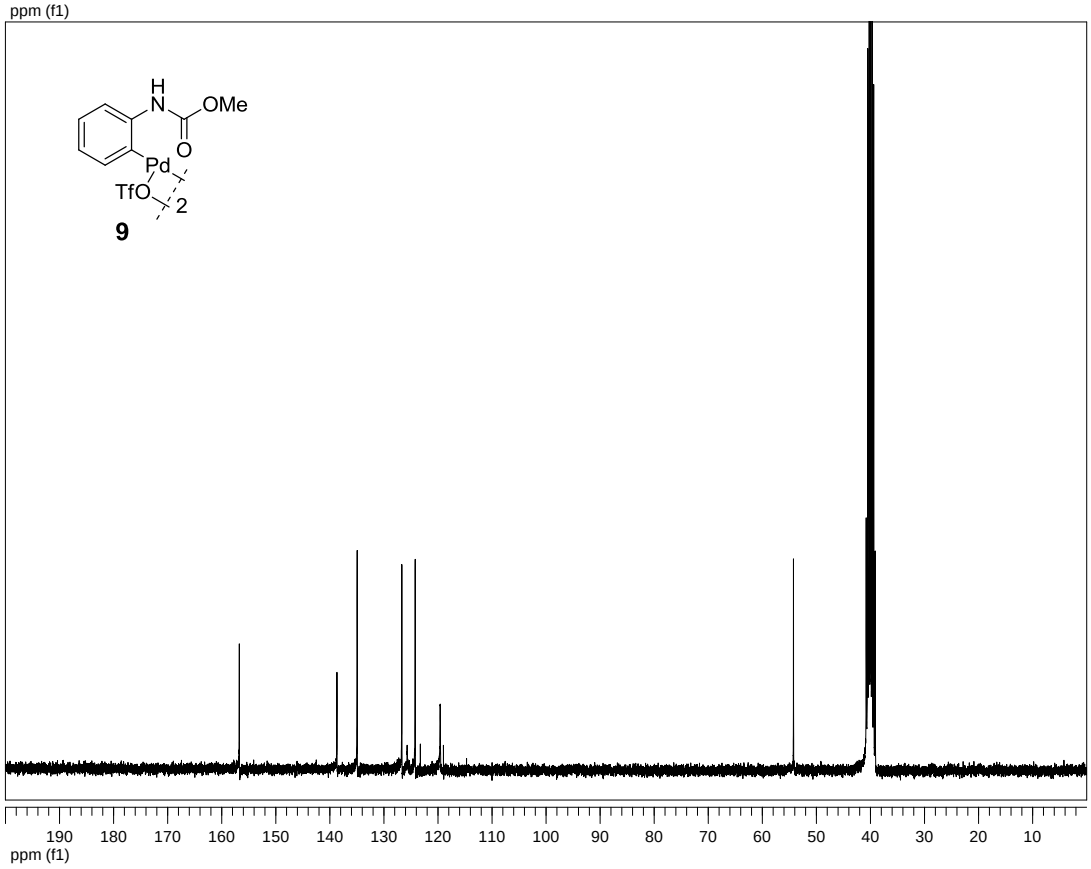
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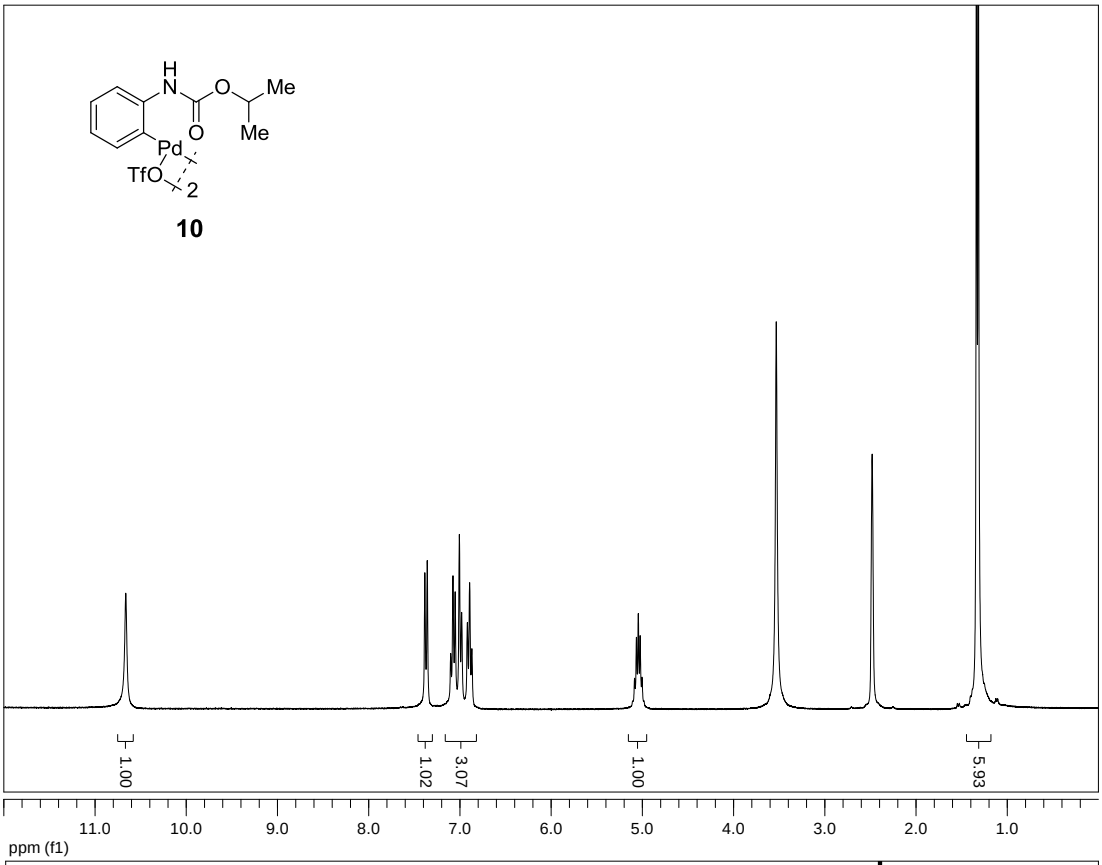
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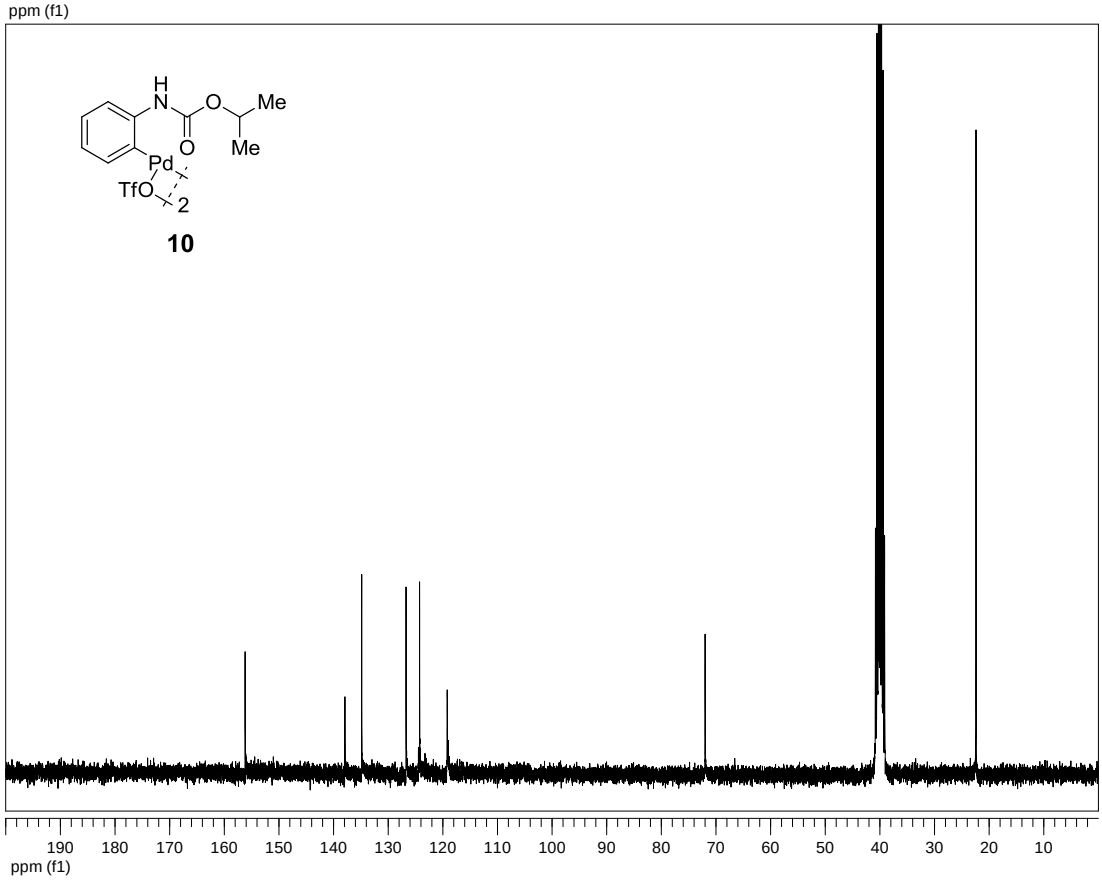
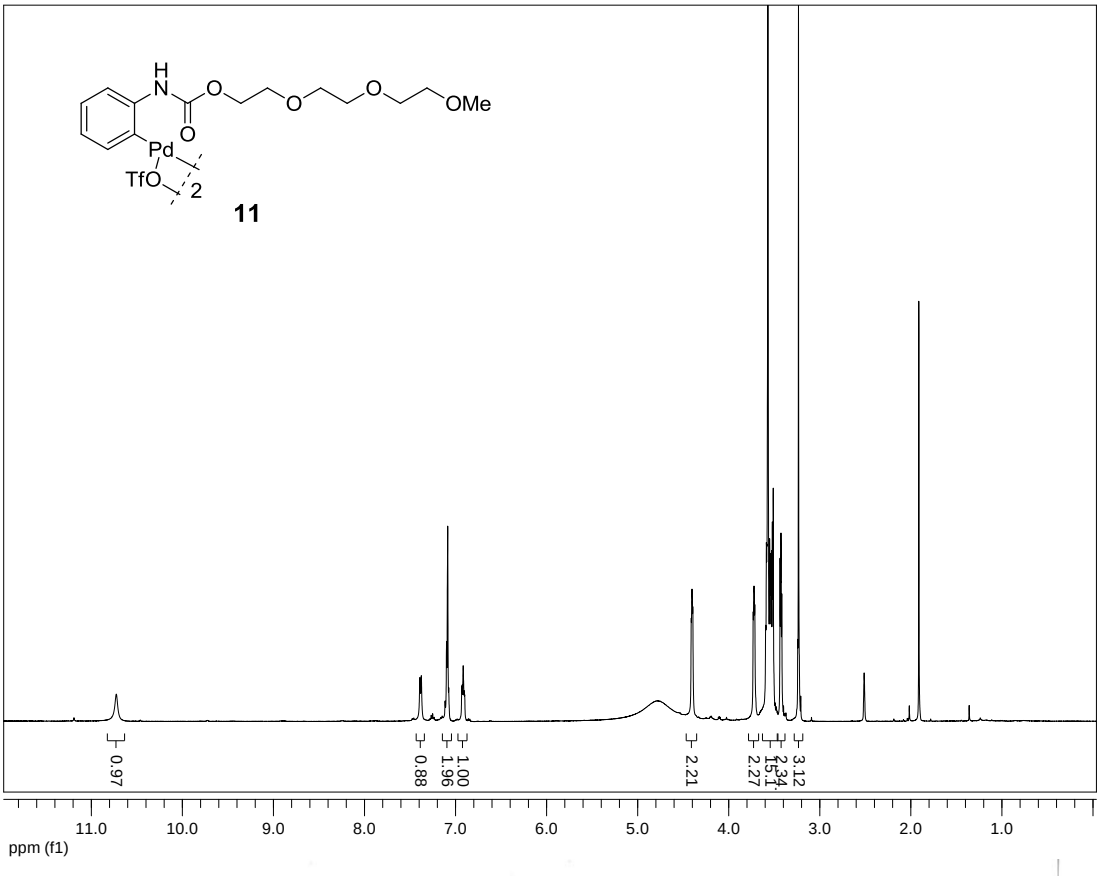
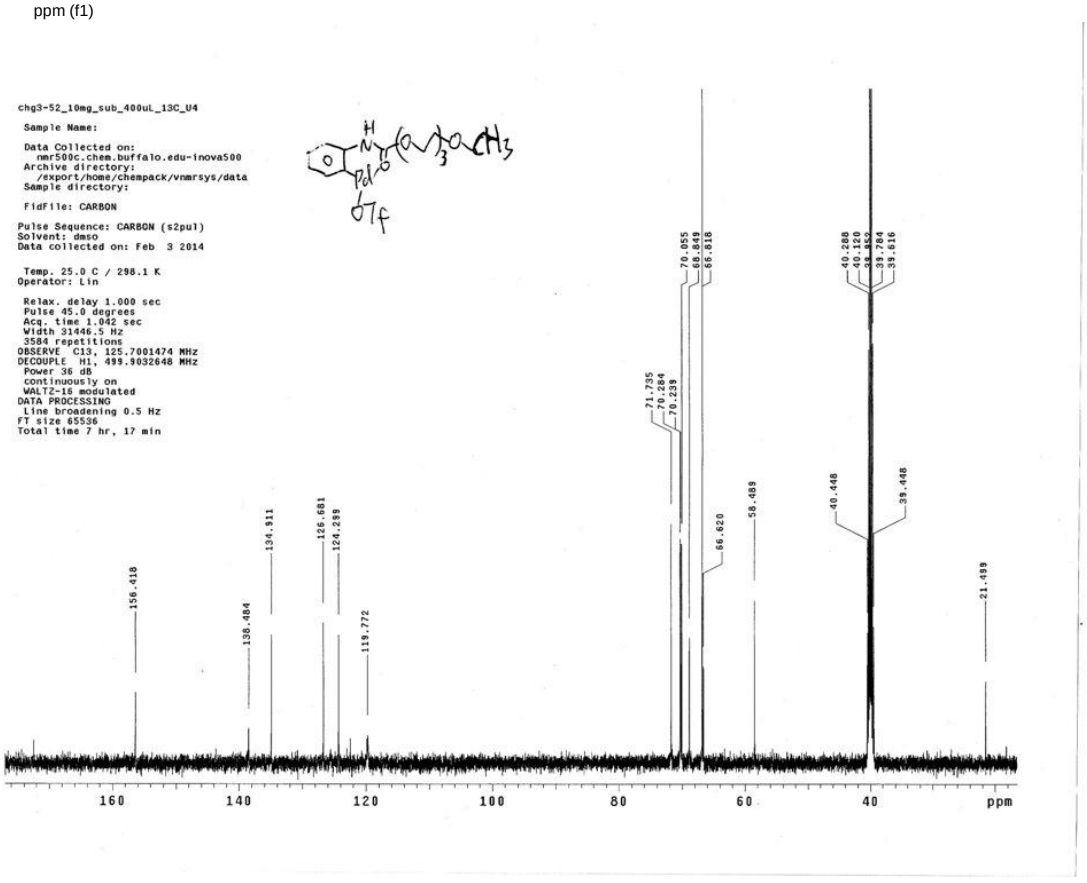
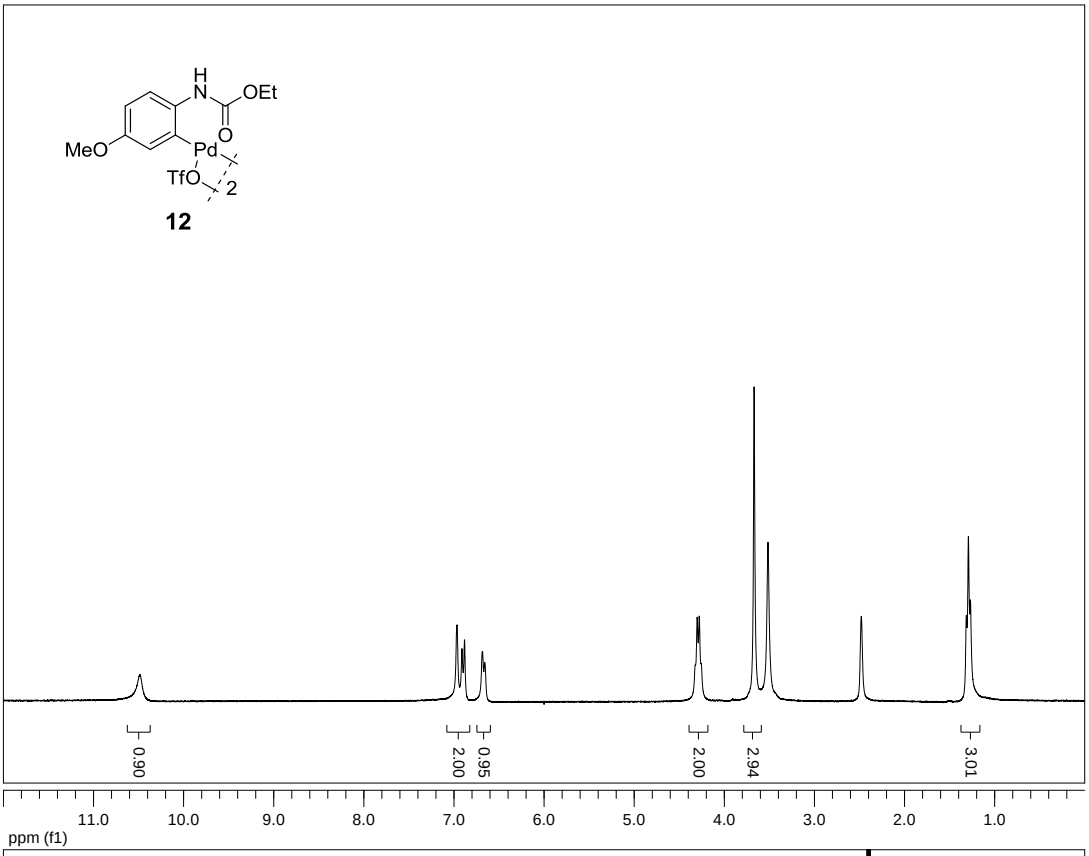
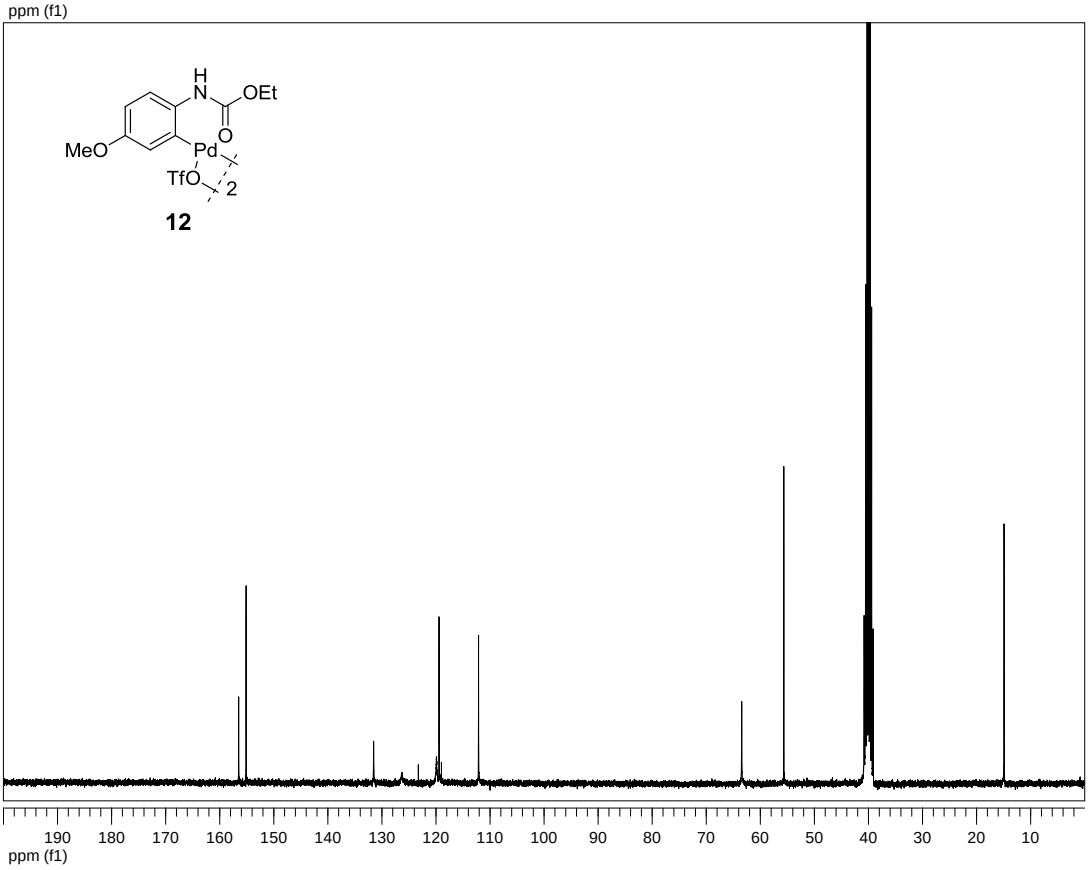
1.0
ppm (f1)

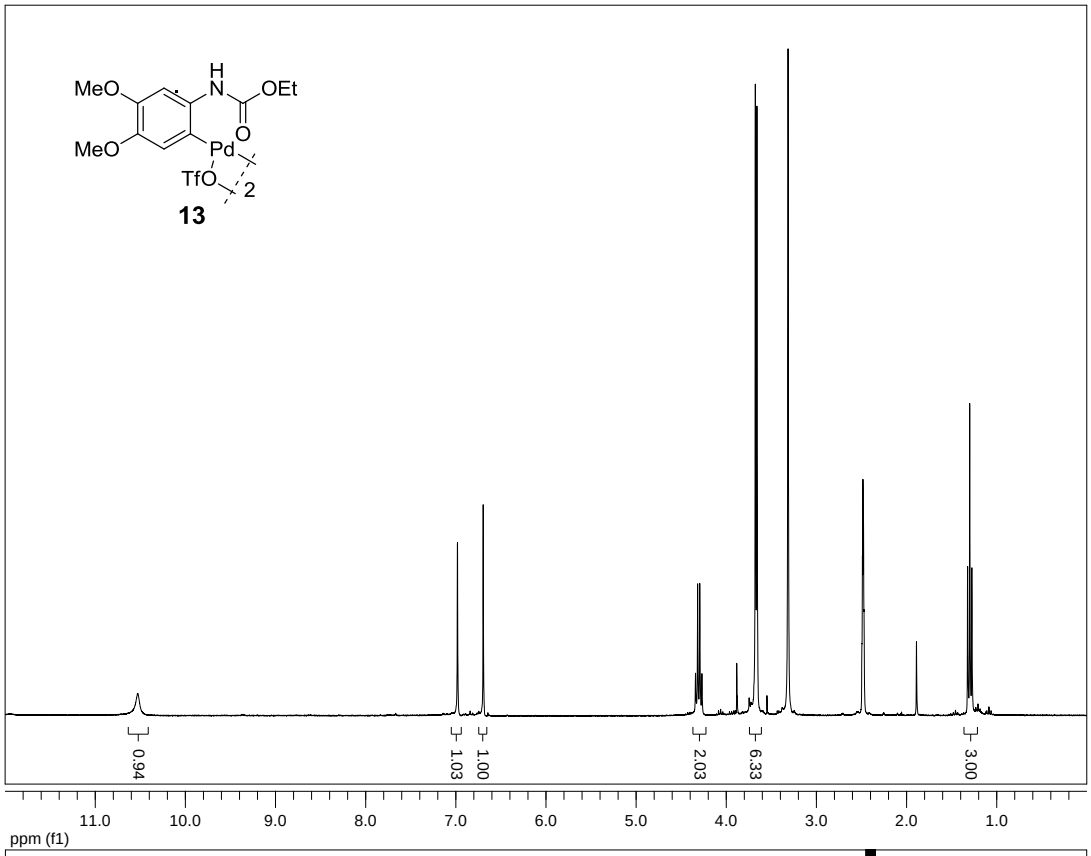

H
N
O
Me
O
Me
Pd
TfO
2
10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

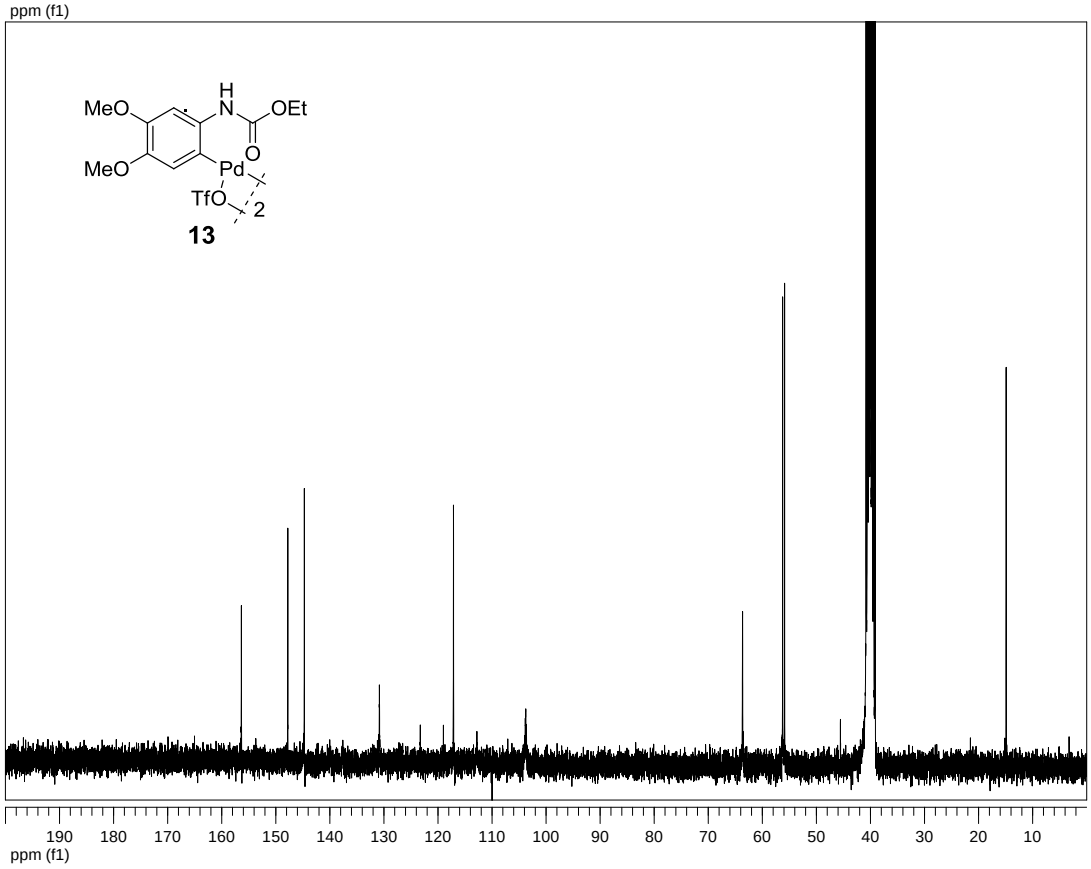

H
N
O
O
O
O
O
OMe
Pd
TfO
2
11
0.97
0.88
1.96
1.00
2.21
2.27
1.54
1.51
3.12
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

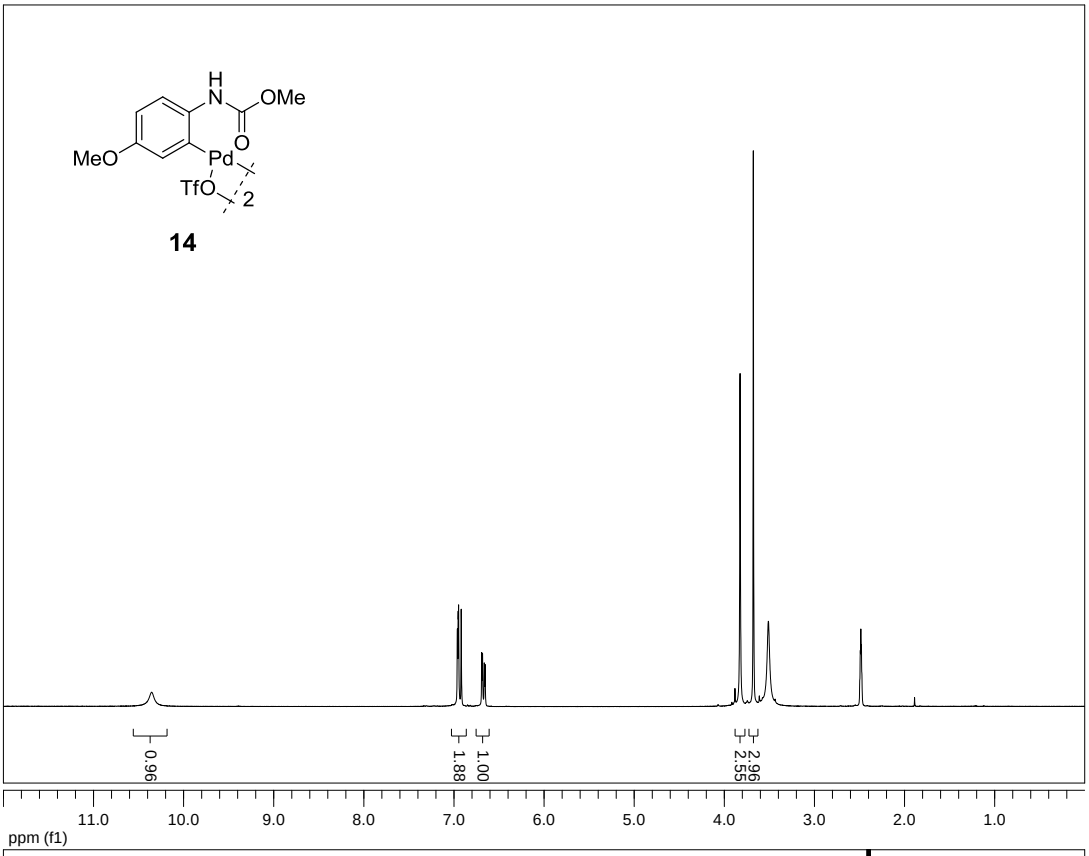

chg3-52_10mg_sub_400uL_13C_U4
Sample Name:
Data Collected on:
nmr500c.chem.buffalo.edu-inova500
Archive directory:
/export/home/chempack/vnmrsys/data
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: dmso
Data collected on: Feb 3 2014
Temp. 25.0 C / 298.1 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
3584 repetitions
OBSERVE C13, 125.7001474 MHz
DECOUPLE H1, 499.9032648 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 7 hr, 17 min
156.418
138.484
134.911
126.681
124.299
119.772
71.735
70.284
70.239
70.055
68.448
66.618
66.620
58.489
40.448
40.288
40.120
39.448
21.499
160
140
120
100
80
60
40
ppm

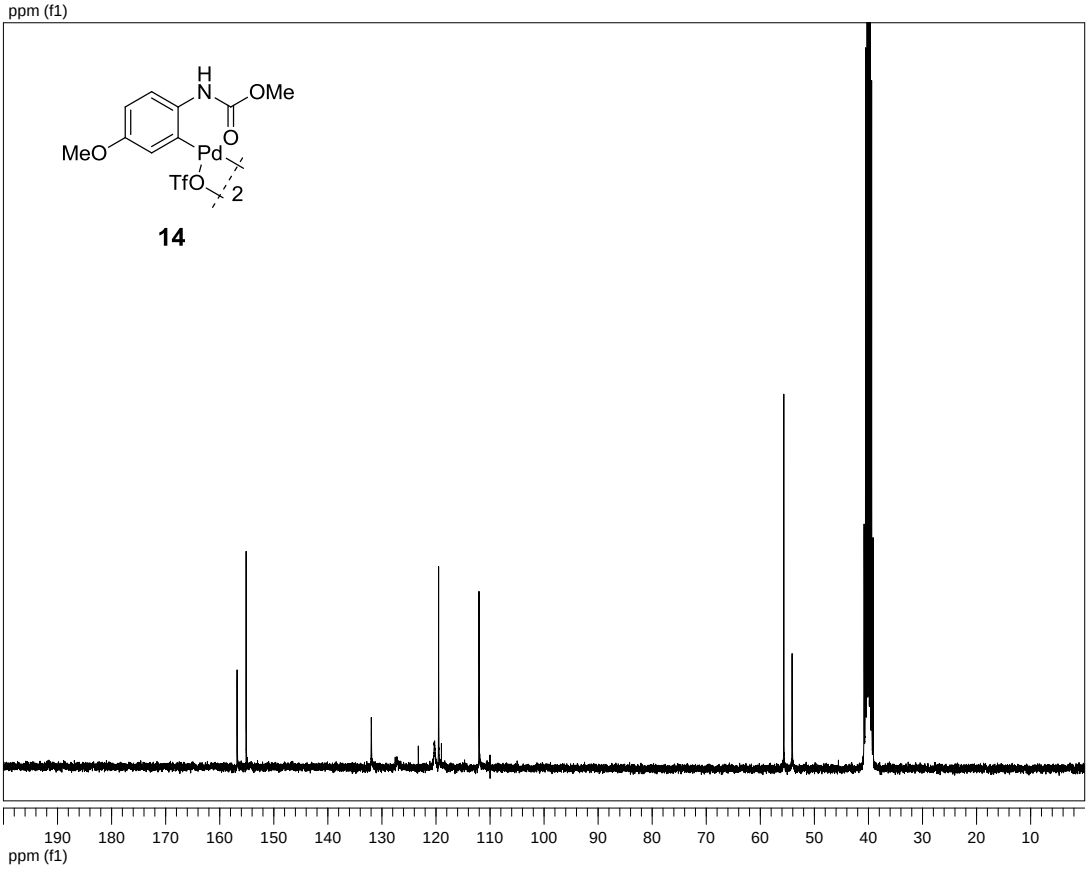

H
N
OEt
O
MeO
Pd
TfO
2
12
0.90
2.00
0.95
2.00
2.94
3.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

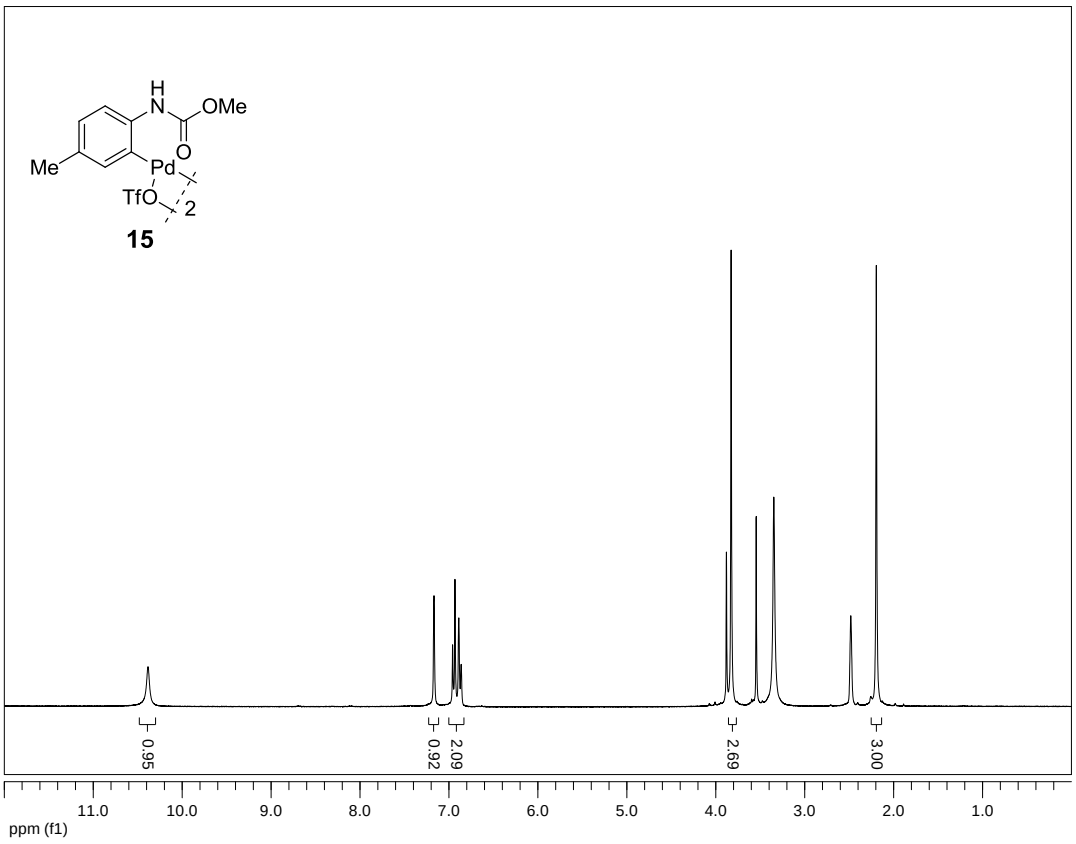

H
N
OEt
O
MeO
Pd
TfO
2
12
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

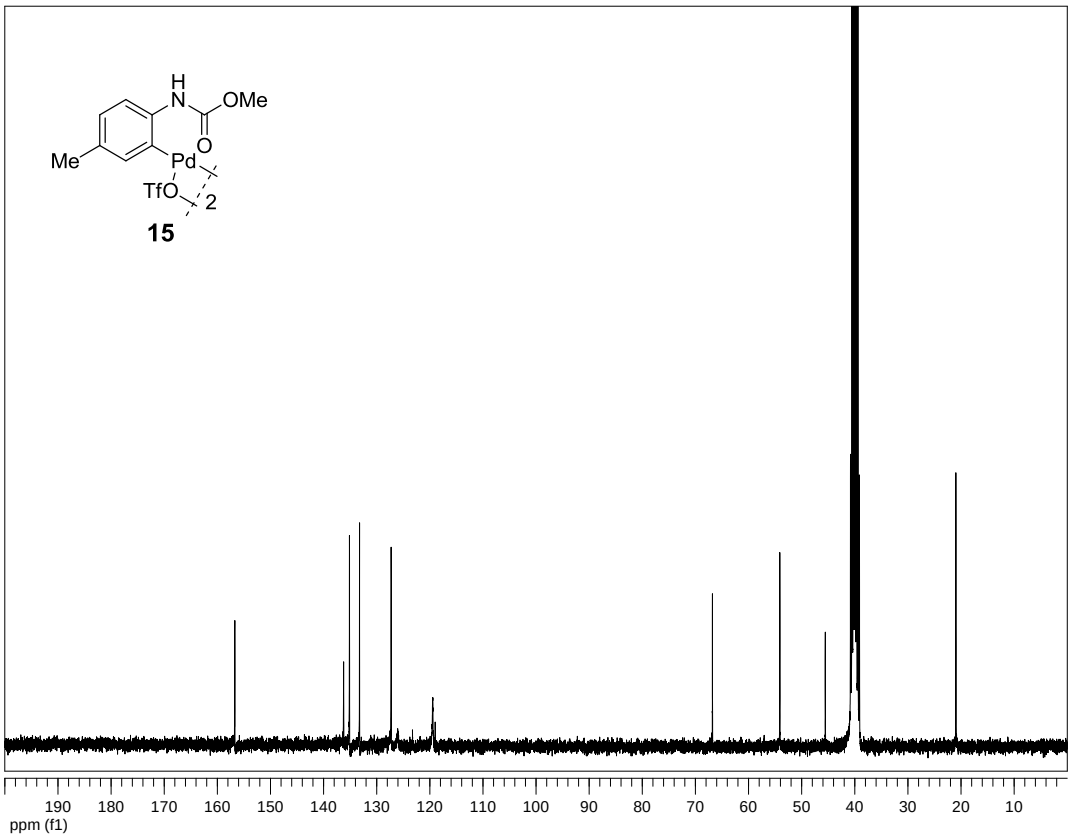

MeO
MeO
H
N
OEt
O
Pd
TfO
2
13
0.94
1.03
1.00
2.03
6.33
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

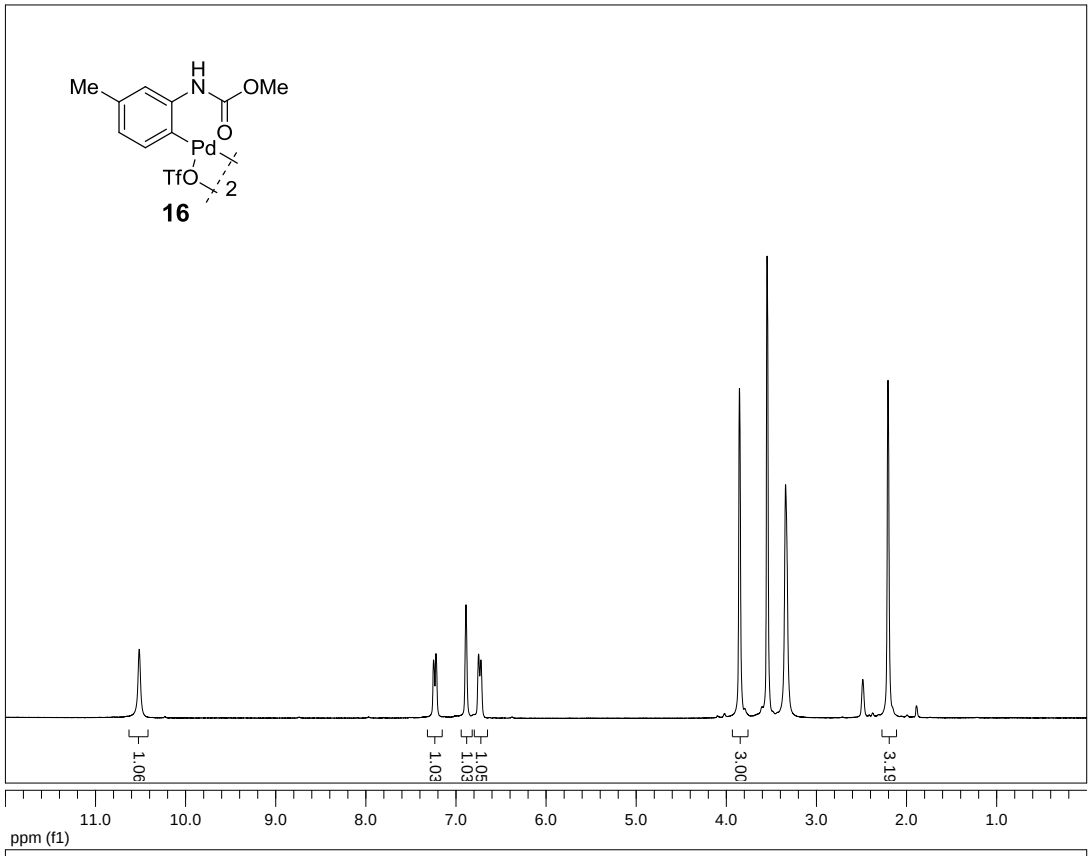

MeO
MeO
H
N
OEt
O
Pd
TfO
2
13
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

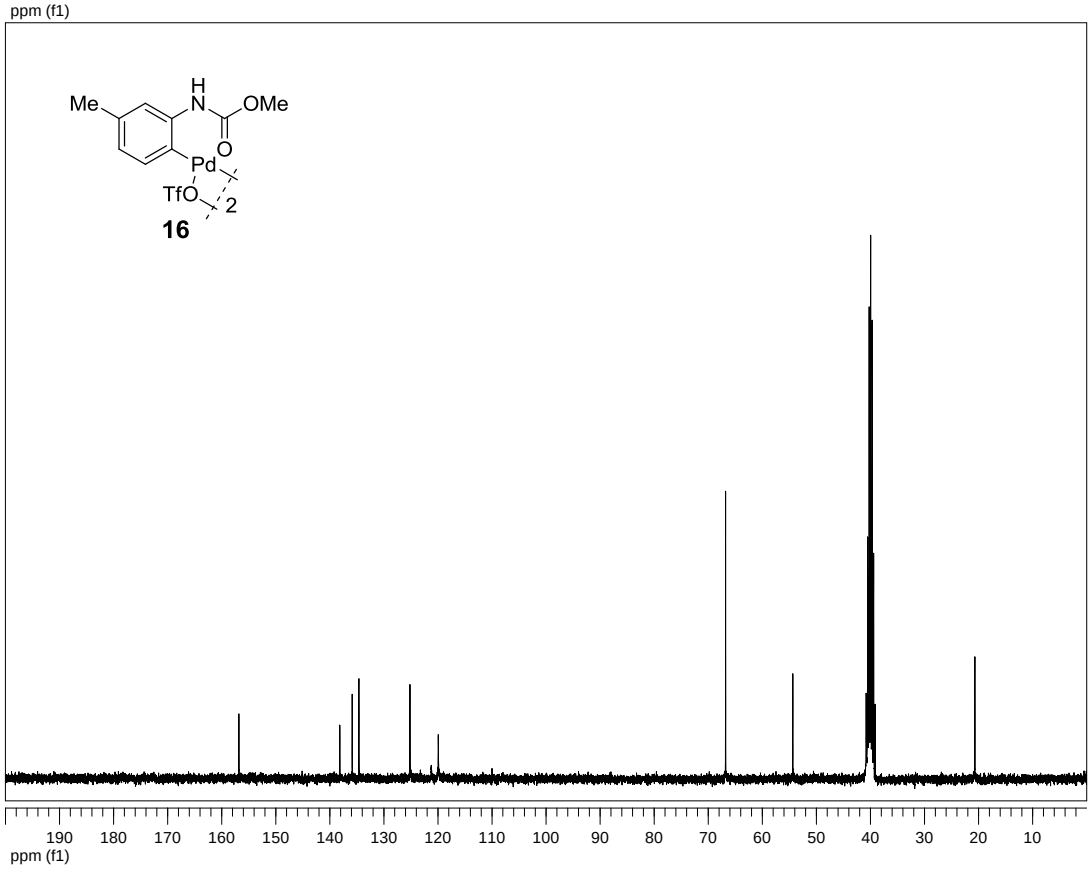

H
N
OMe
O
MeO
Pd
TfO
2
14
0.96
1.88
1.00
2.96
2.55
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

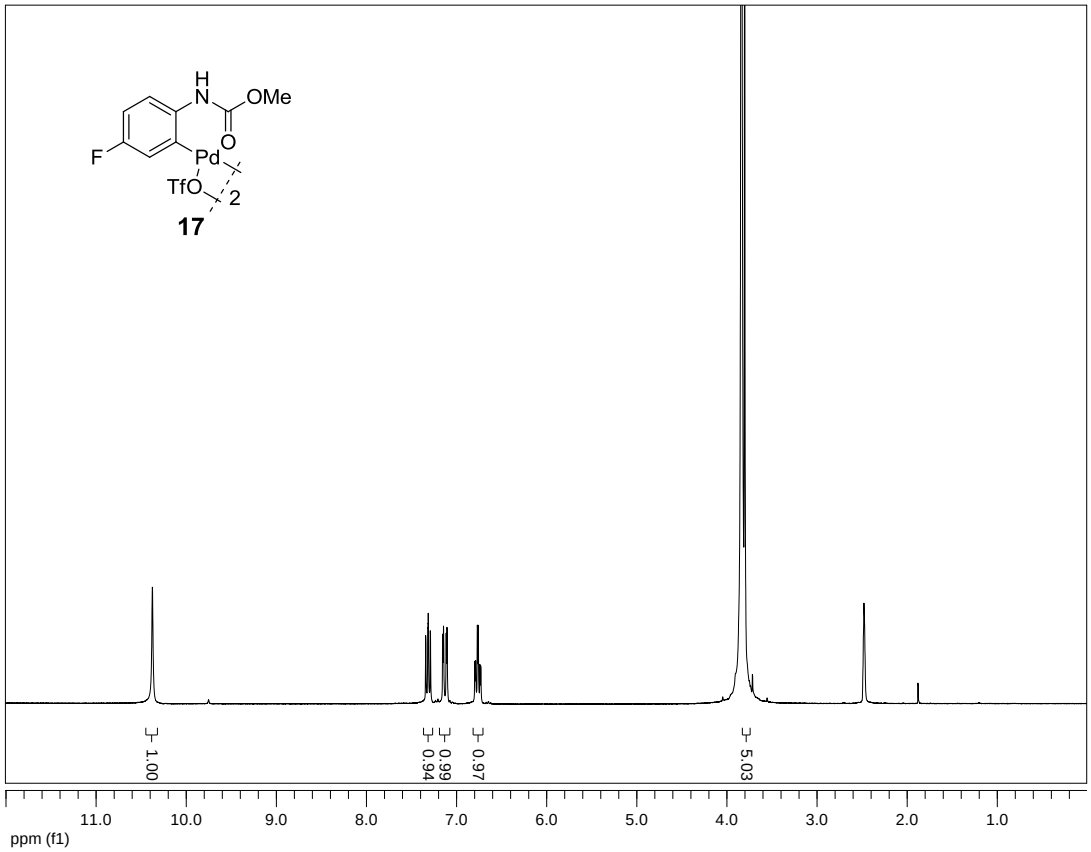

H
N
OMe
O
MeO
Pd
TfO
2
14
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

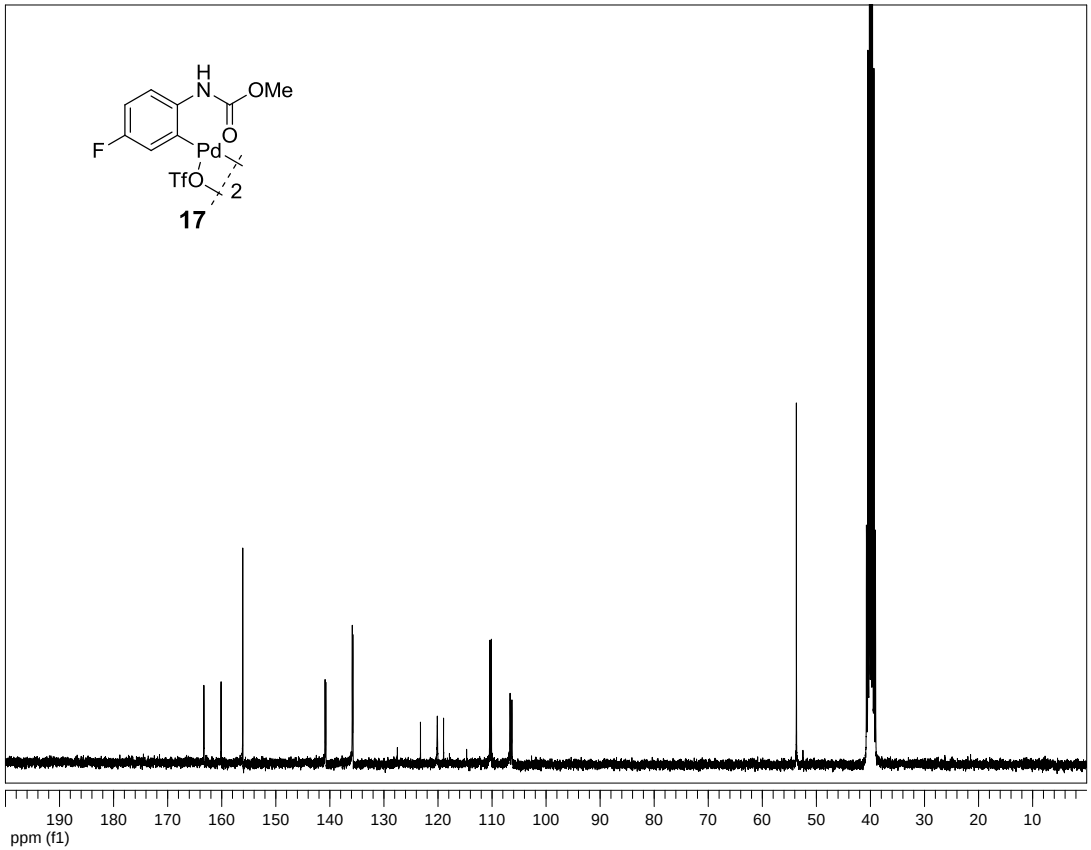

H
N
OMe
O
Me
Pd
TfO
2
15
0.95
0.92
2.09
2.69
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

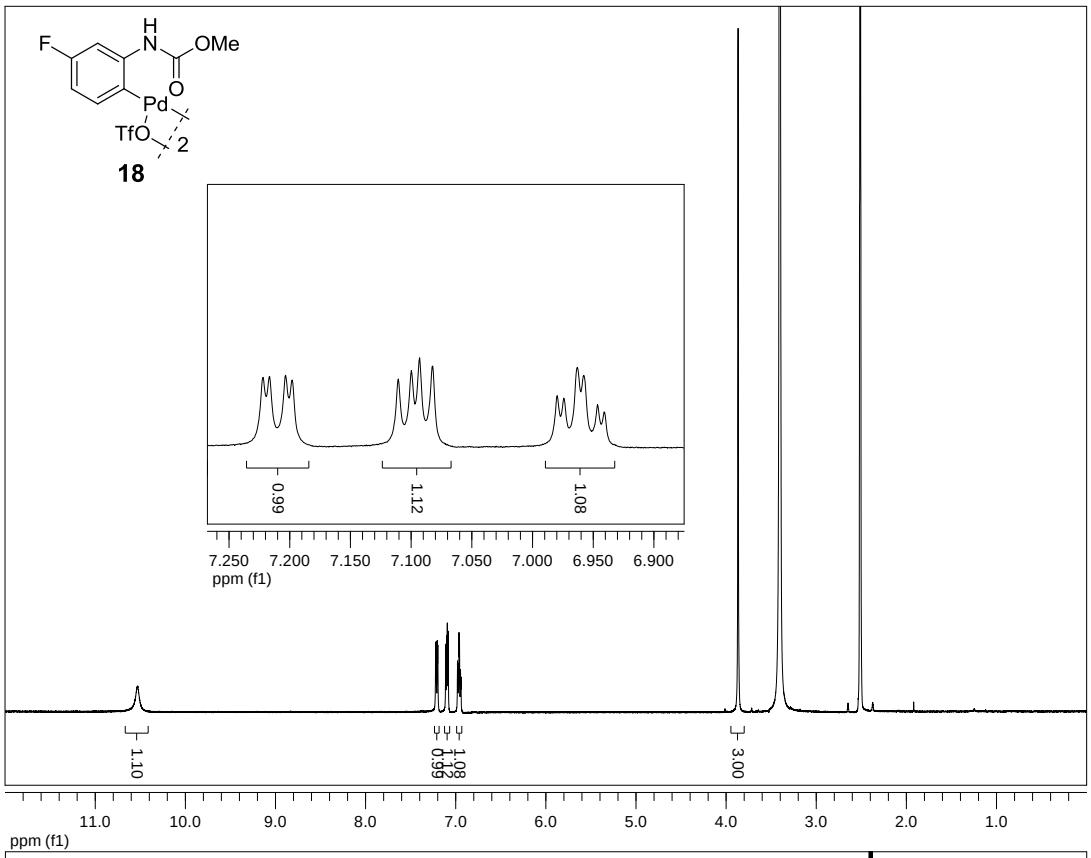

H
N
OMe
O
Me
Pd
TfO
2
15
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

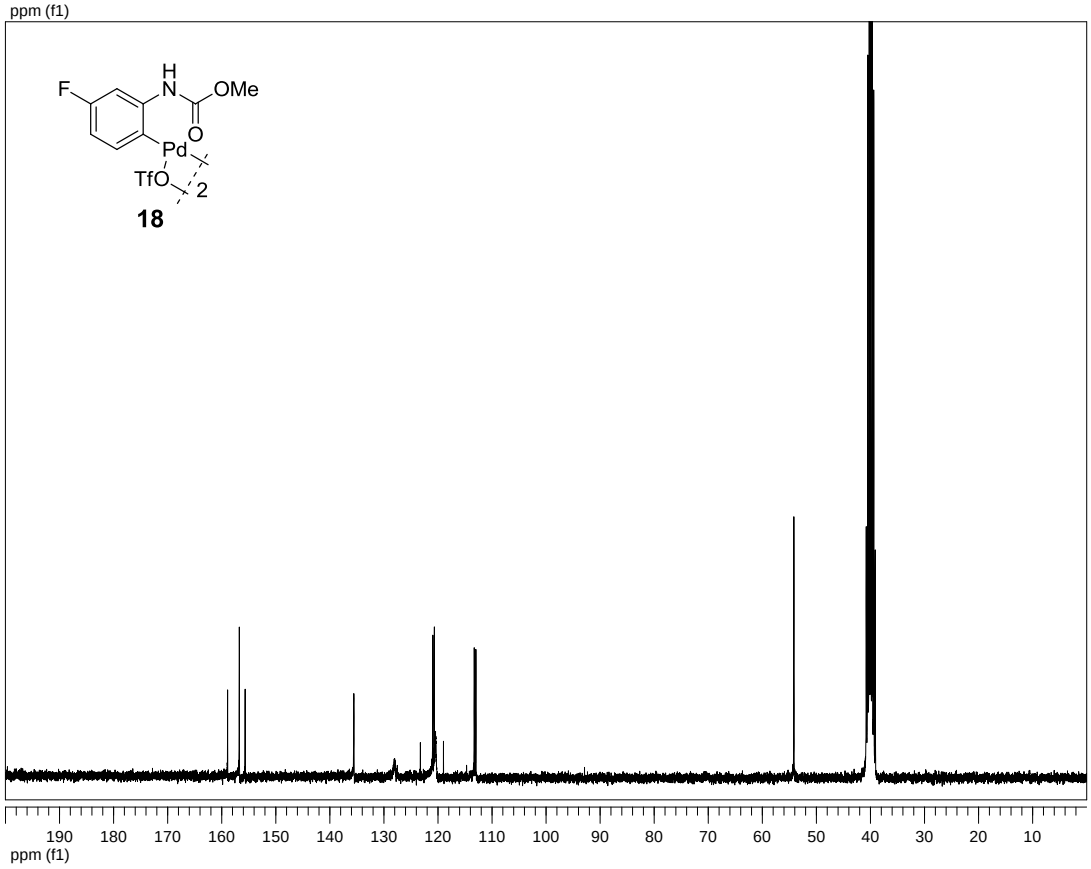

Me
H
N
OMe
O
Pd
TfO
2
16
1.06
1.03
1.03
1.05
3.00
3.19
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

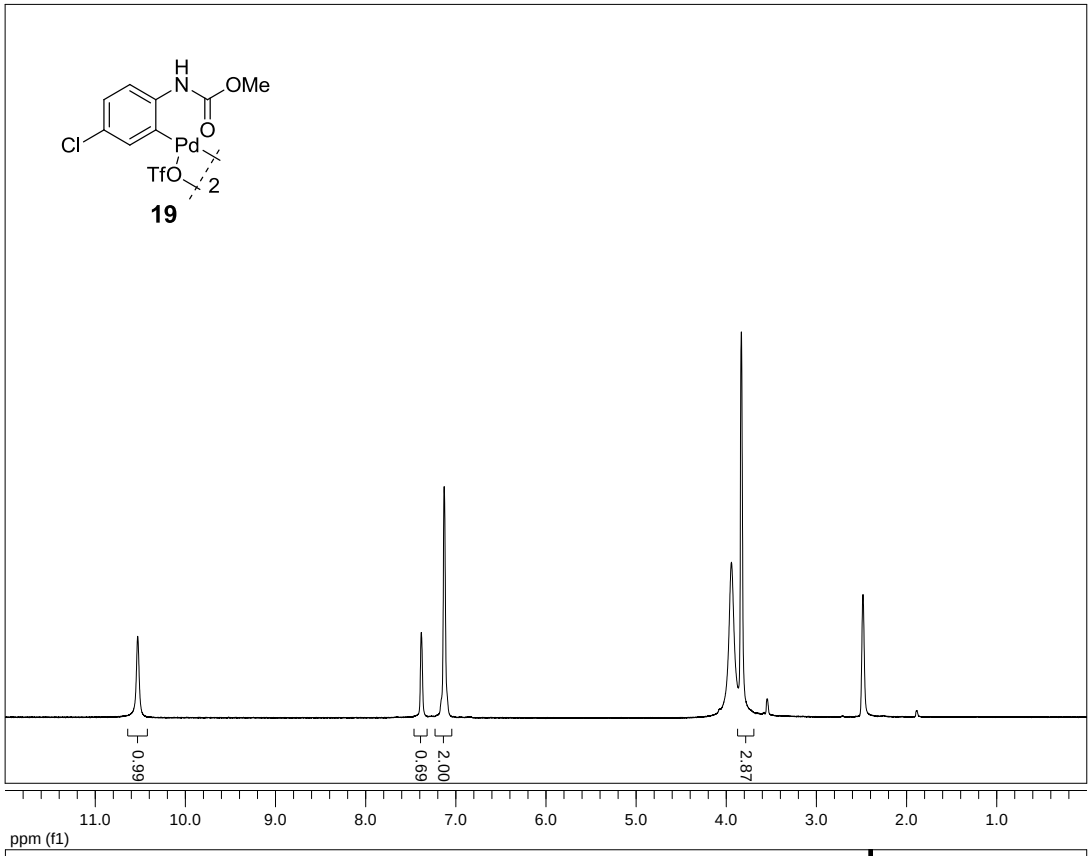

Me
H
N
OMe
O
Pd
TfO
2
16
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

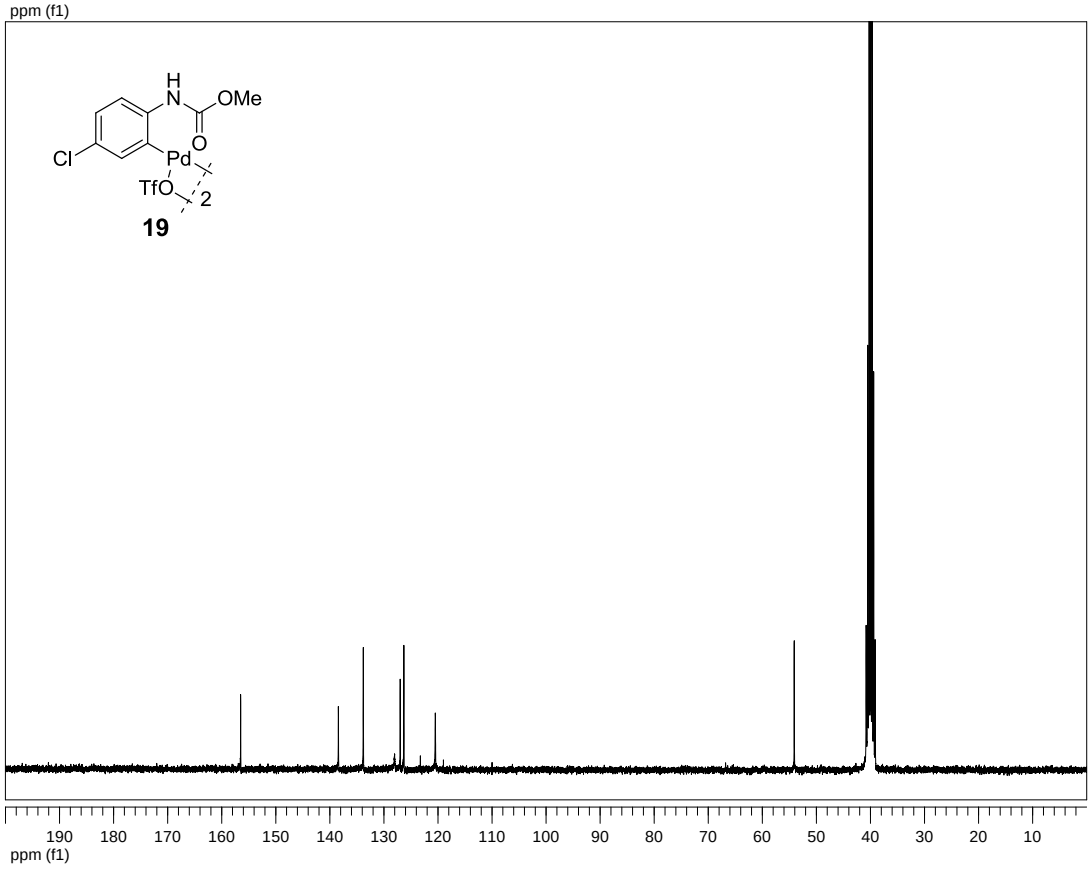

H
N
OMe
O
F
Pd
TfO
2
17
1.00
0.94
0.99
0.97
5.03
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

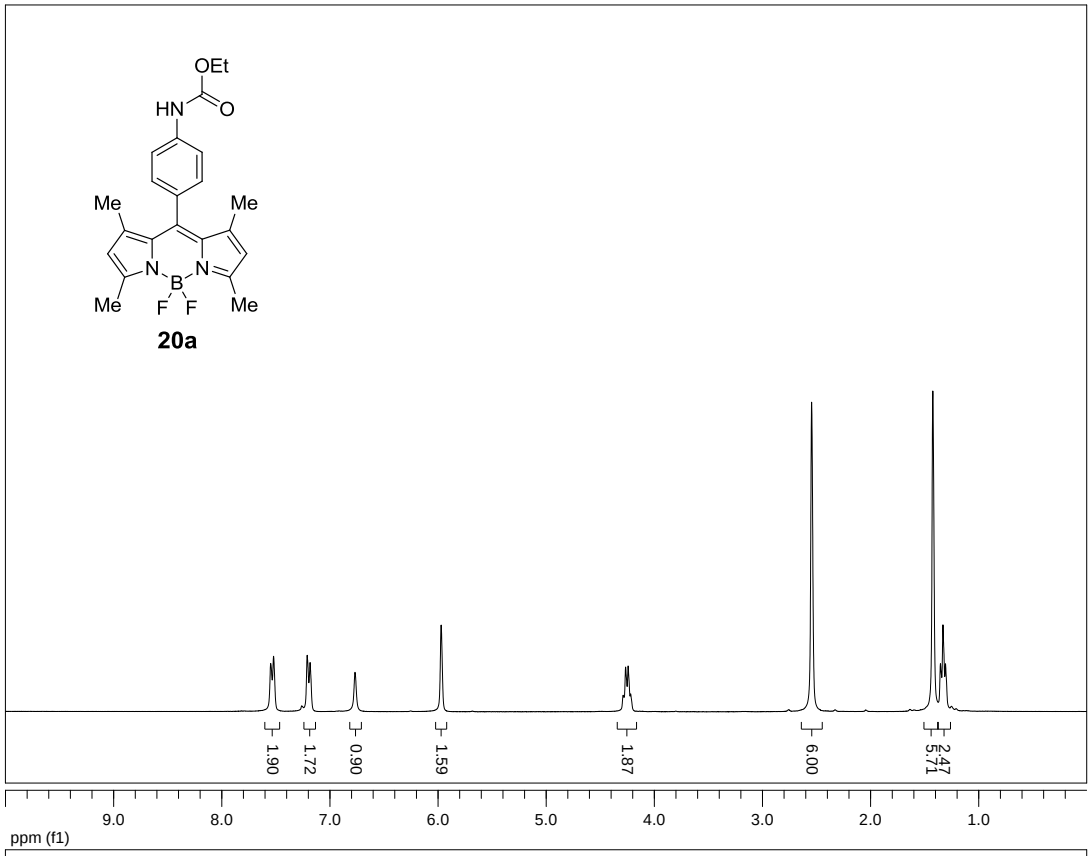

H
N
OMe
O
F
Pd
TfO
2
17
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

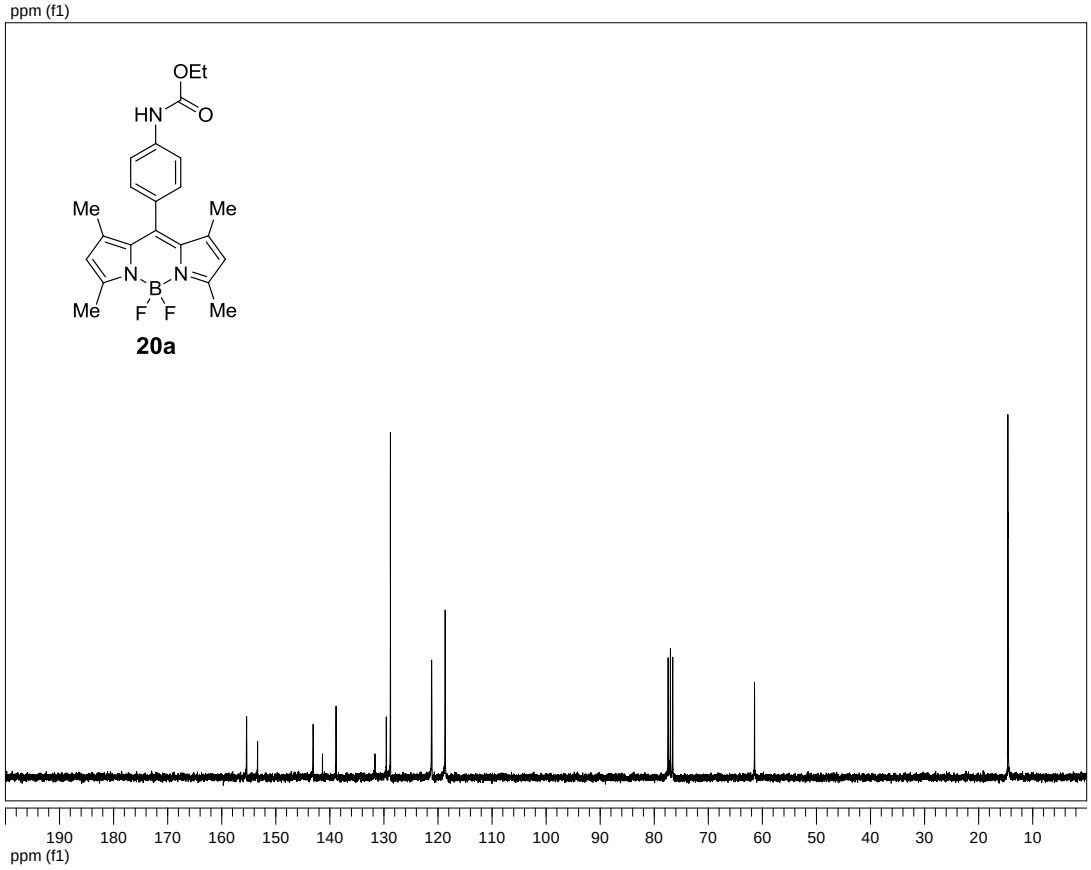

F
H
N
OMe
O
Pd
TfO
2
18
0.99
1.12
1.08
7.250 7.200 7.150 7.100 7.050 7.000 6.950 6.900
ppm (f1)
1.10
1.08
1.12
0.99
3.00
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
ppm (f1)

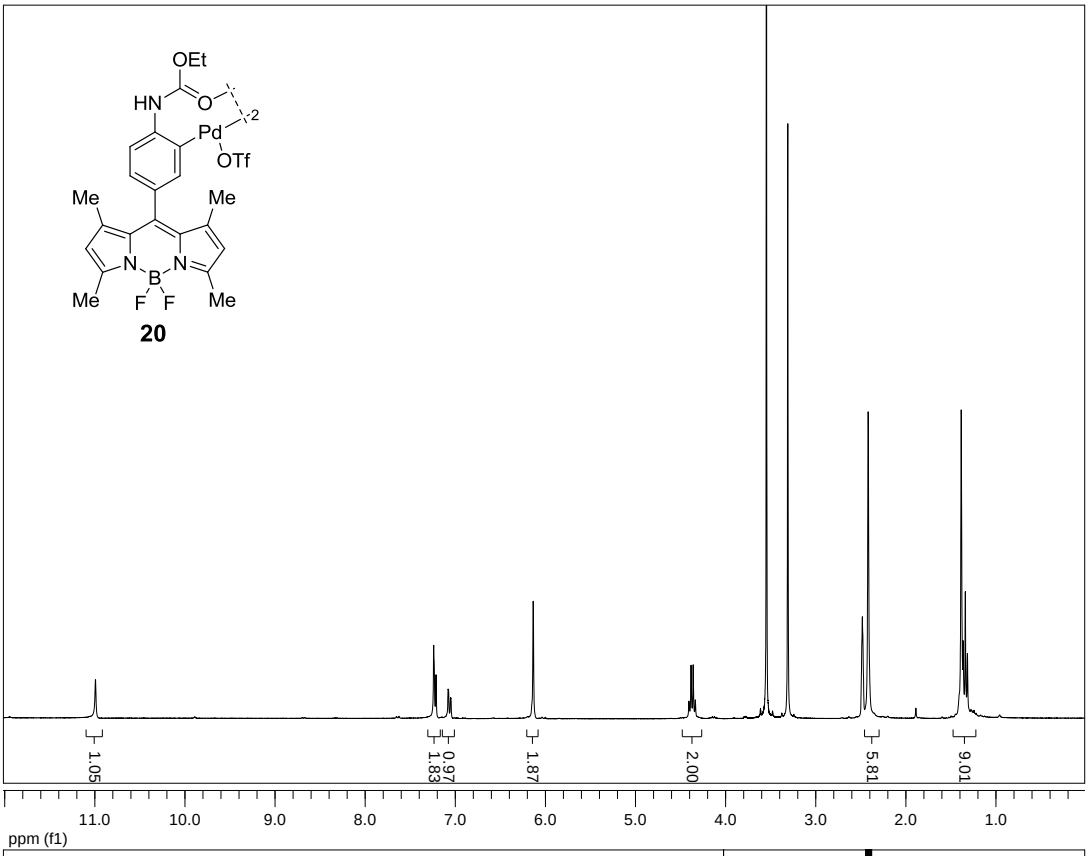

F
H
N
OMe
O
Pd
TfO
2
18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (f1)

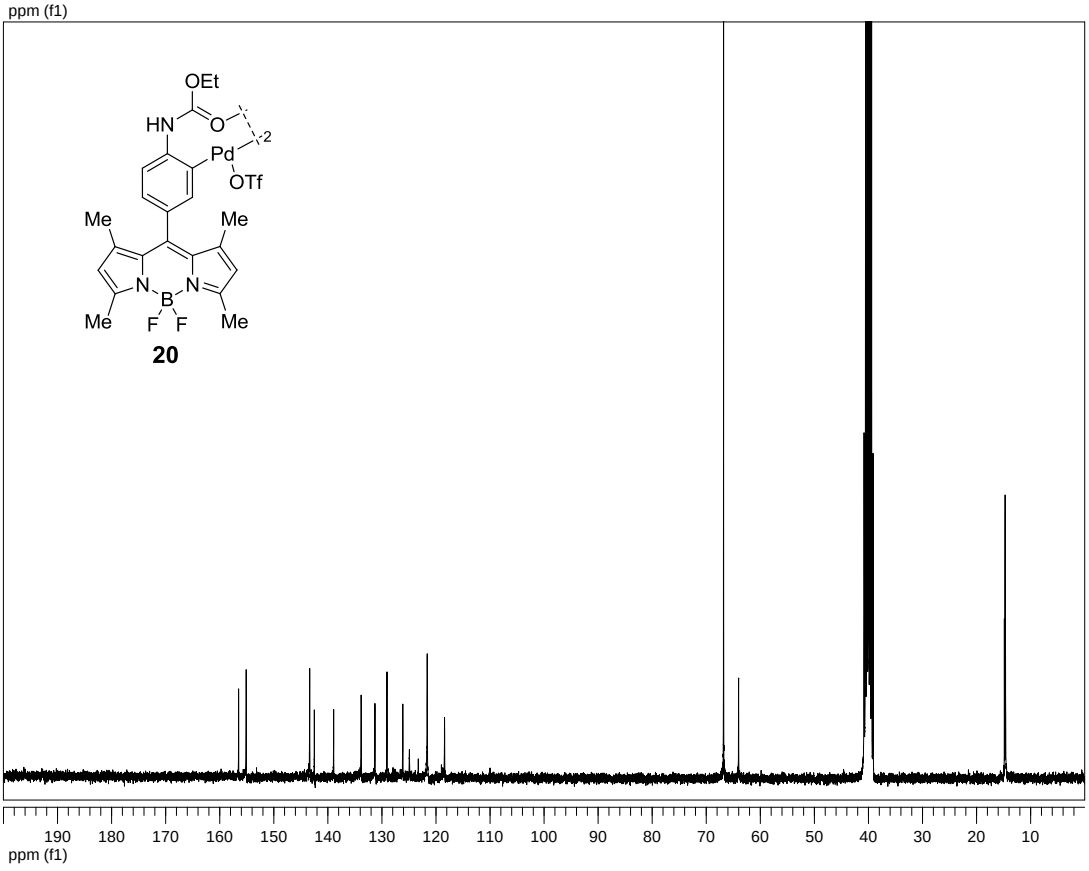

H
N
OMe
O
Cl
Pd
TfO
2
19
0.99
0.69
2.00
2.87
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

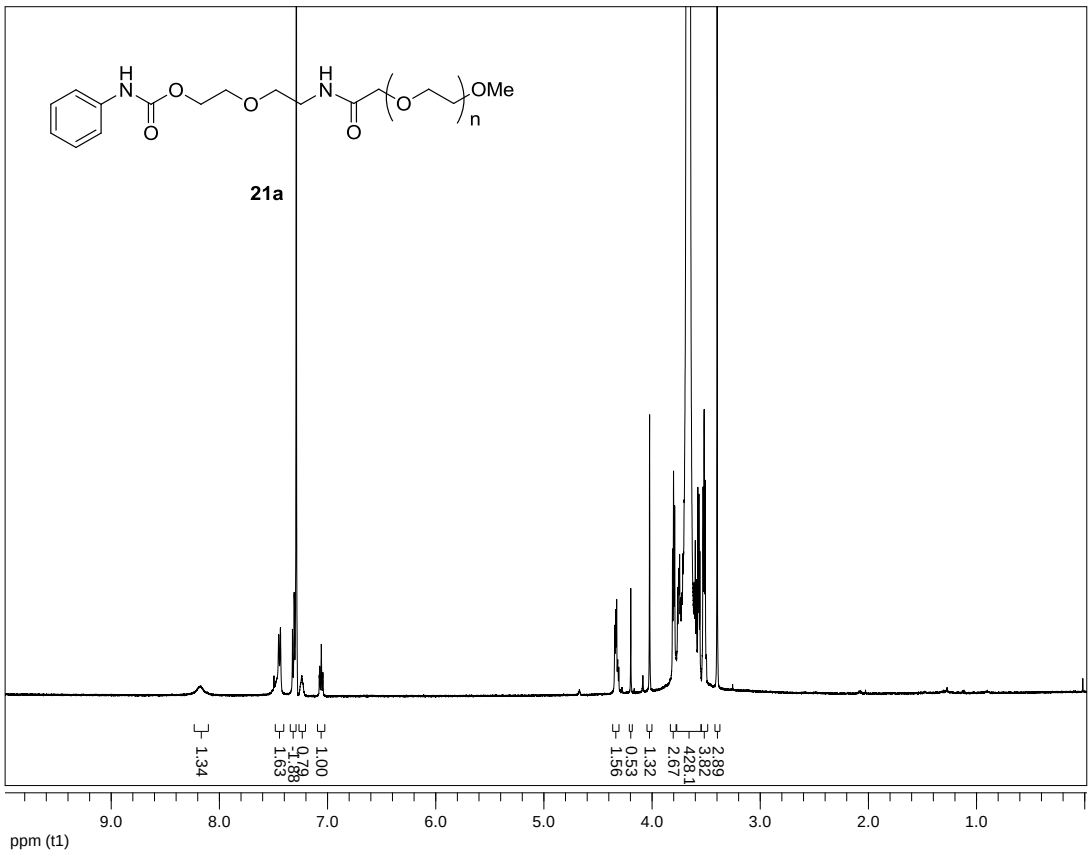

H
N
OMe
O
Cl
Pd
TfO
2
19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

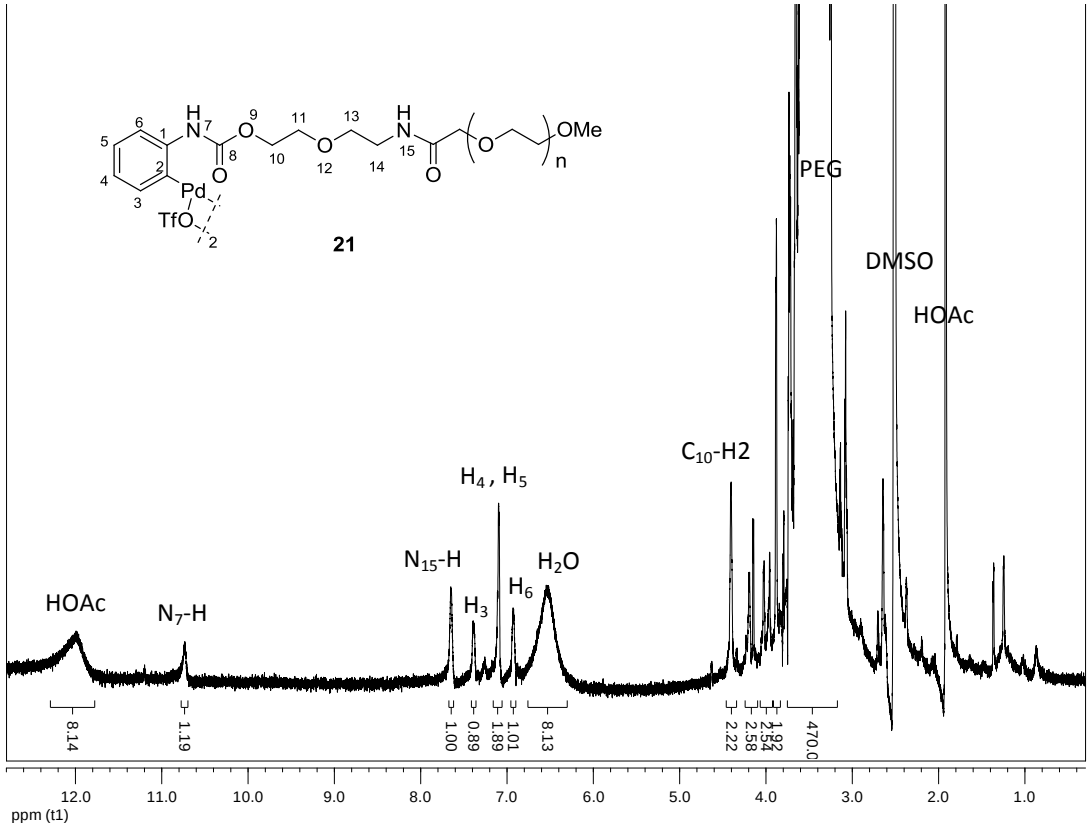

OEt
HN
O
Me
Me
N
B
N
Me
F
F
Me
20a
1.90
1.72
0.90
1.59
1.87
6.00
2.47
5.71
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


OEt
HN
O
Me
Me
N
B
N
Me
F
F
Me
20a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)


OEt
HN
O
2
Pd
OTf
Me
Me
N
B
N
Me
F
F
Me
20
1.05
0.97
1.83
1.87
2.00
5.81
9.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


OEt
HN
O
2
Pd
OTf
Me
Me
N
B
N
Me
F
F
Me
20
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

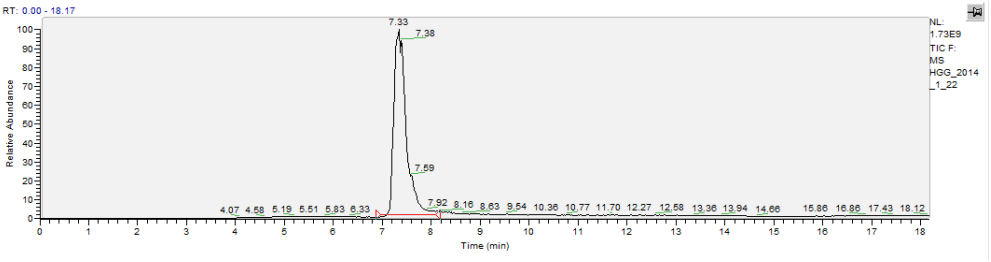

21a
1.34
1.63
0.79
0.88
1.00
1.56
0.53
1.32
2.67
428.1
3.82
2.89
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


21
PEG
DMSO
HOAc
C10-H2
H4 , H5
N15-H
H3
H6
H2O
HOAc
N7-H
8.14
1.19
1.00
0.89
1.89
1.01
8.13
2.22
2.58
470.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

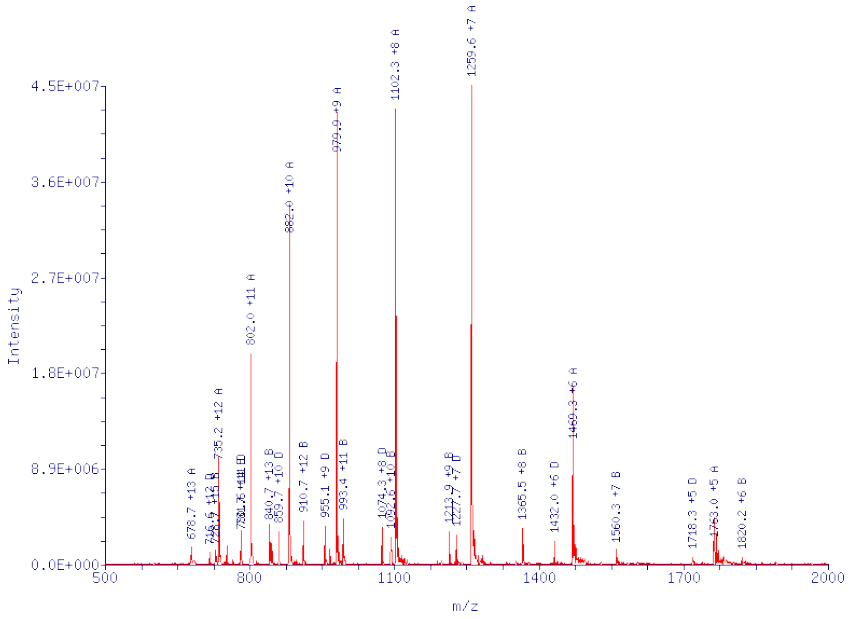
## LC-MS Data

Ub-Hpg

LC-MS




Charge ladder




Deconvoluted mass

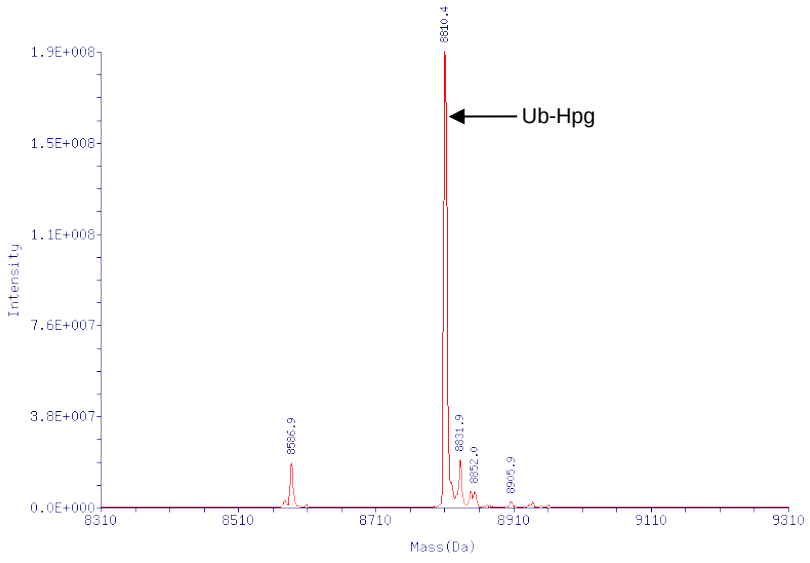
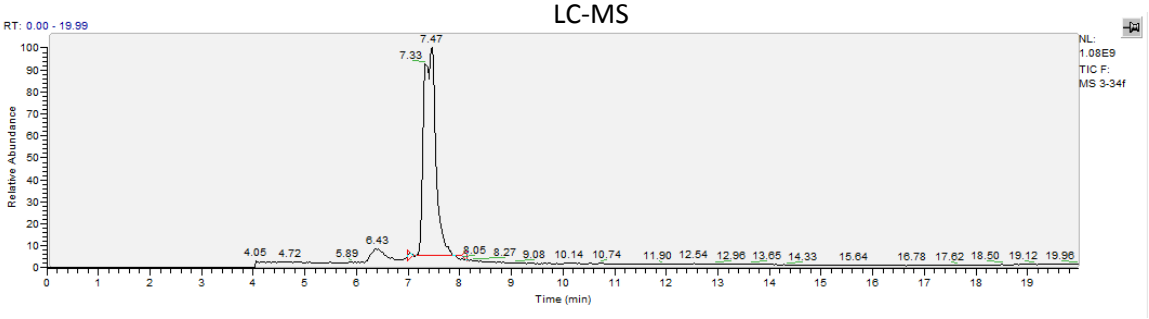
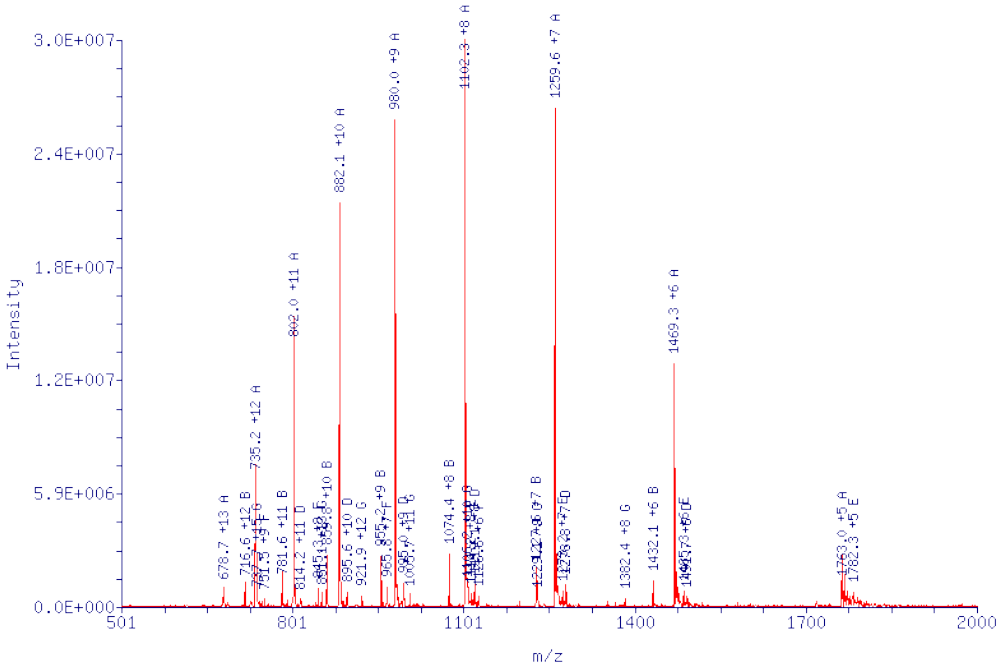


Table 1, entry 1 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

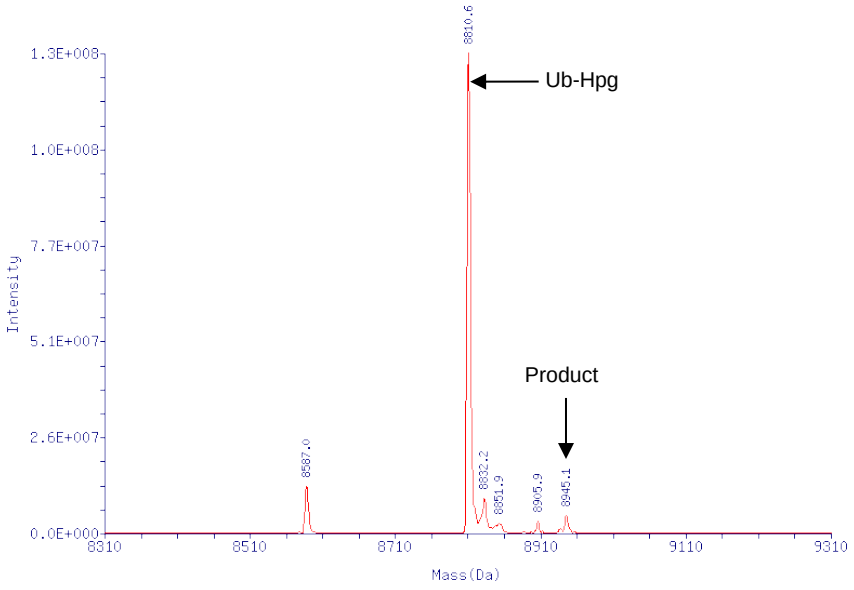
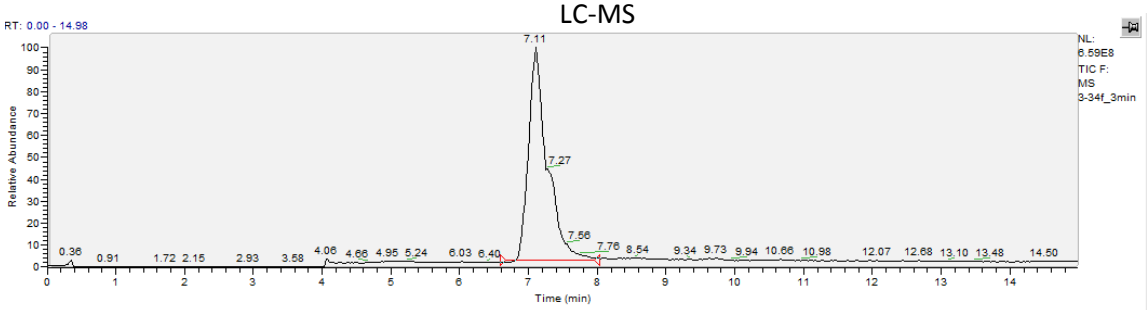
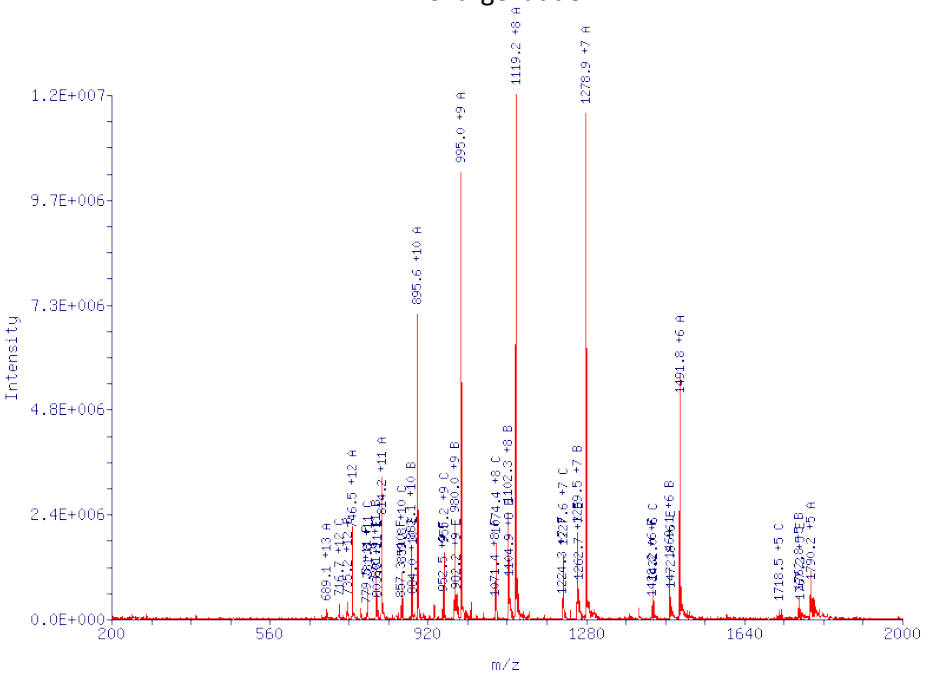


Table 1, entry 1 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

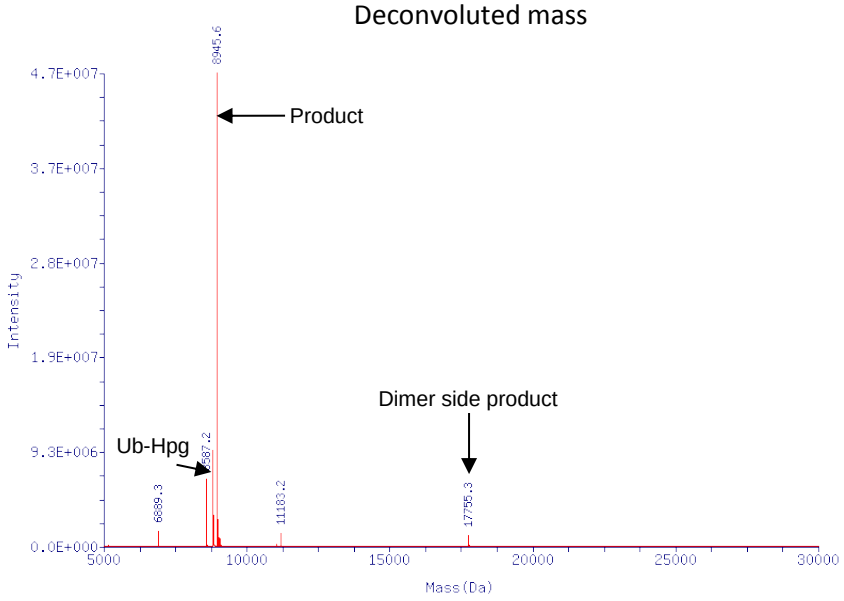
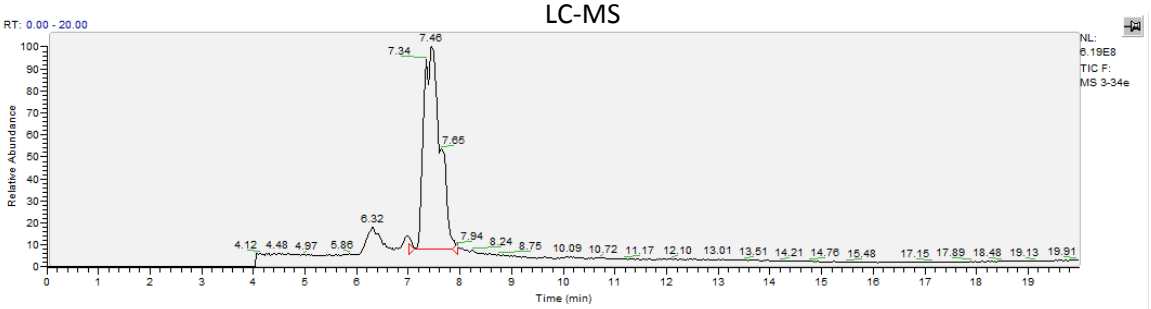
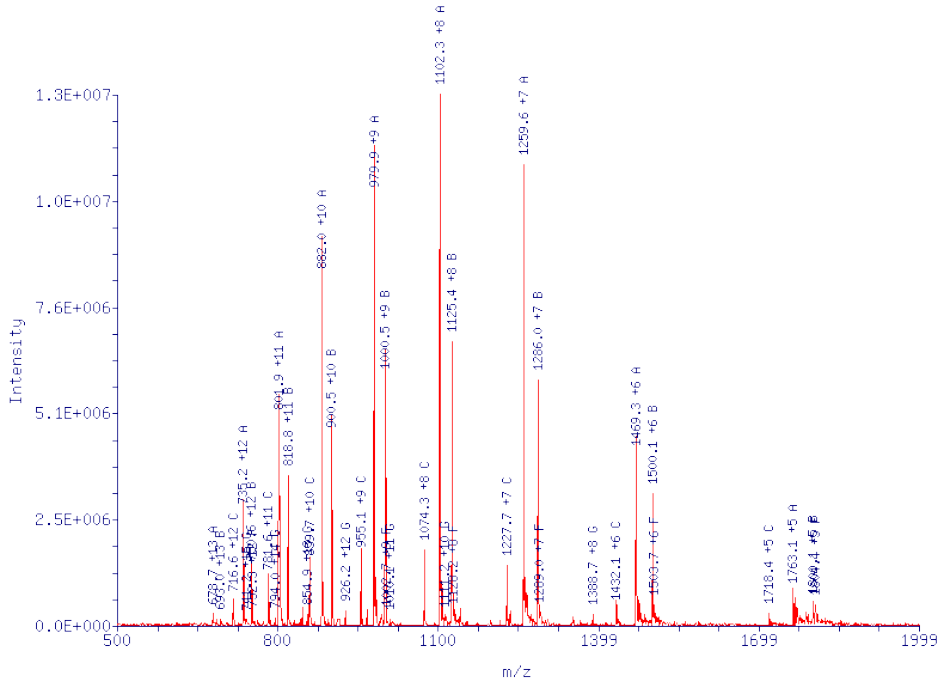


Table 1, entry 2 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

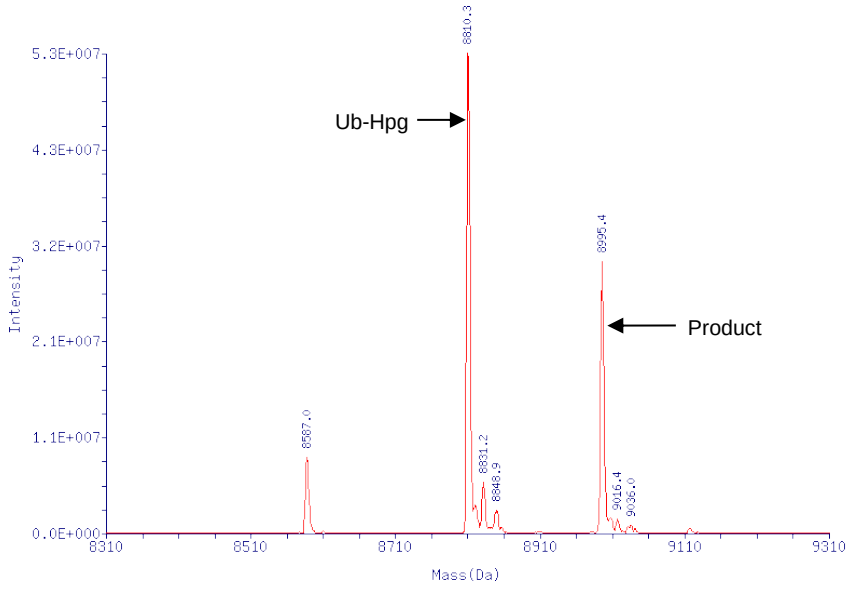
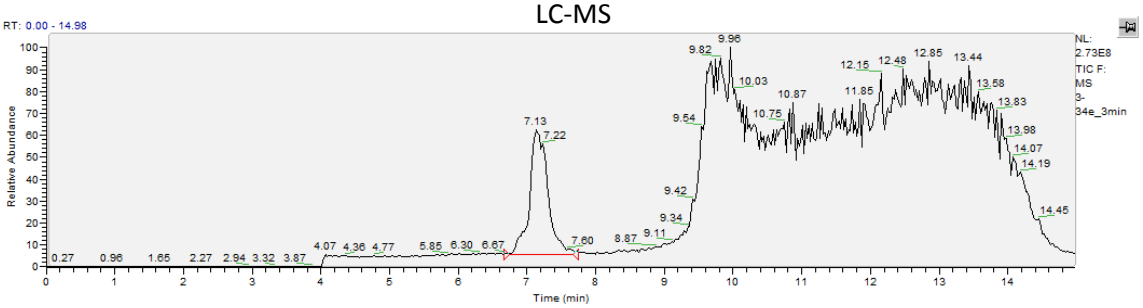
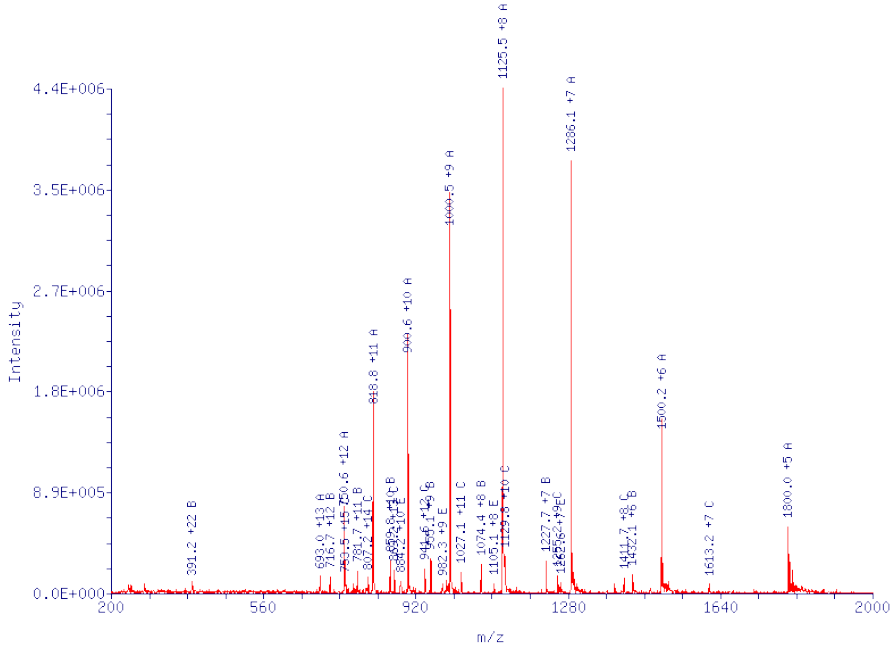


Table 1, entry 2 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

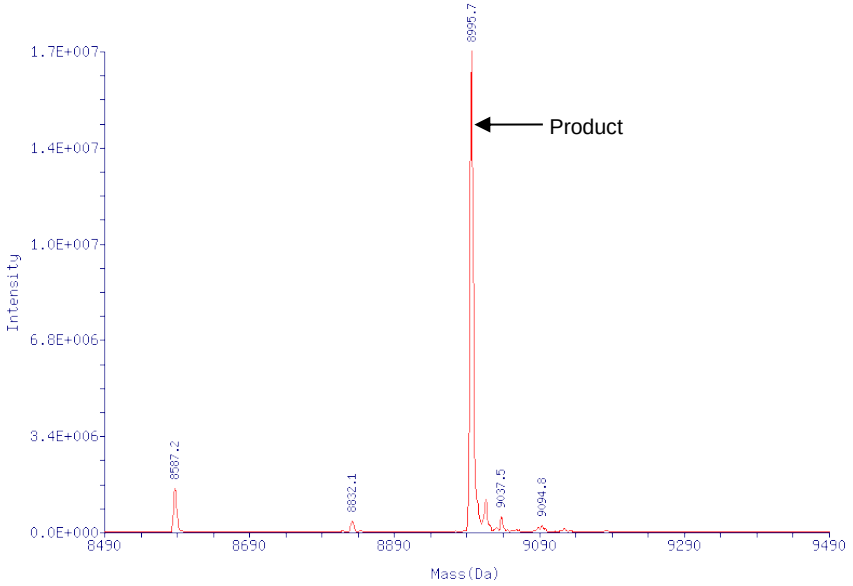
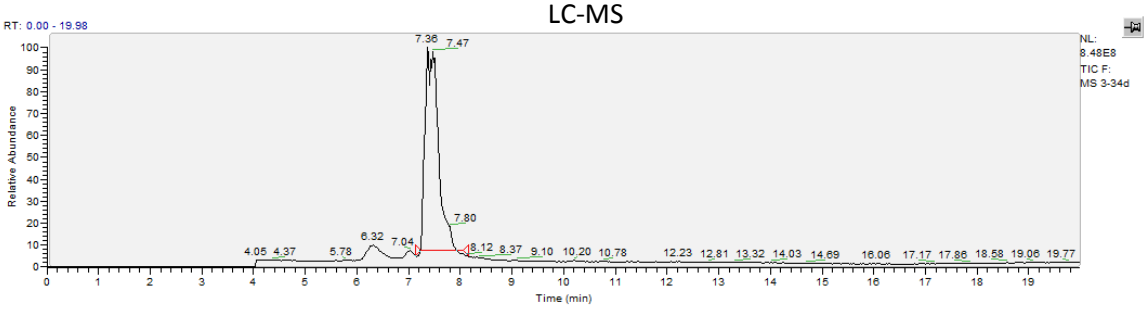
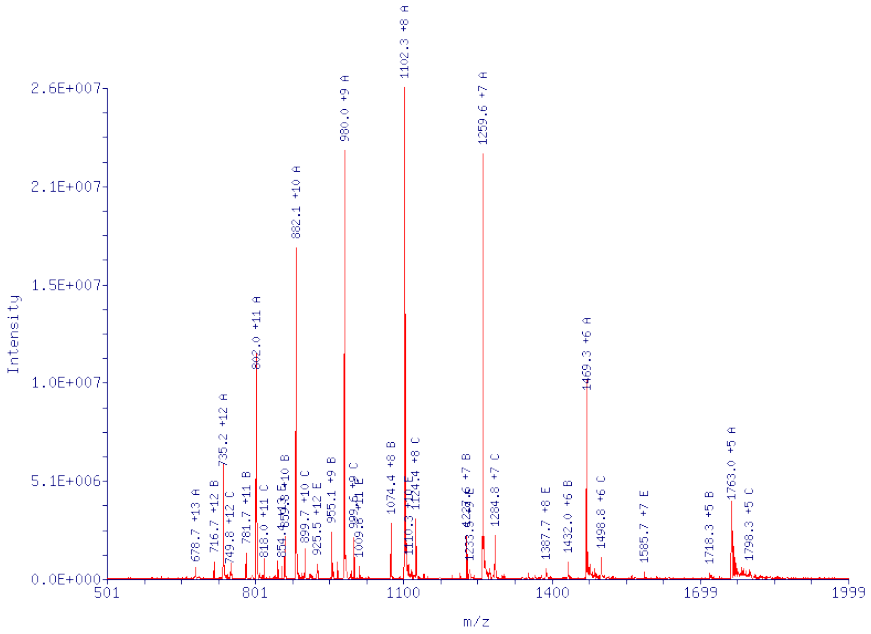


Table 1, entry 3 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

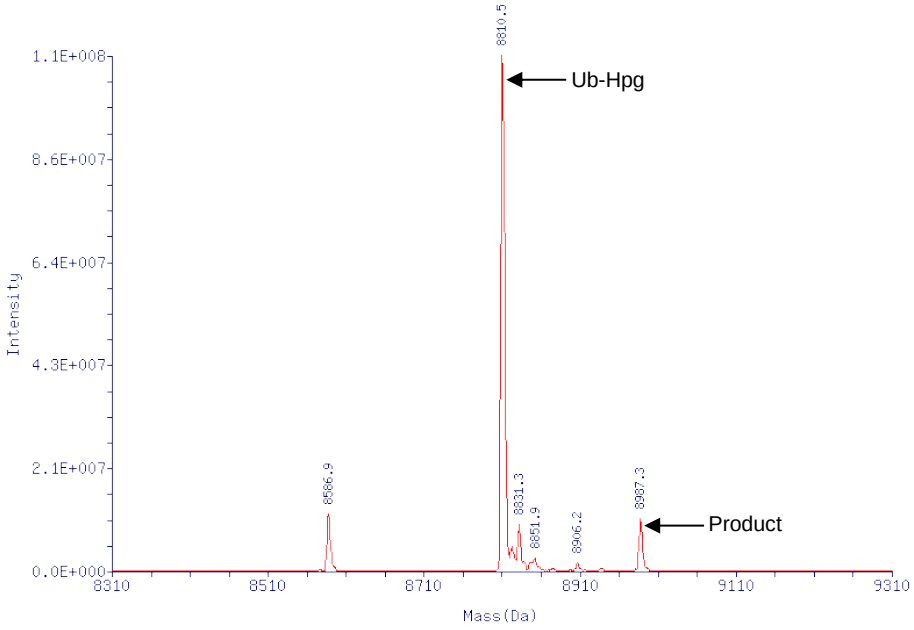
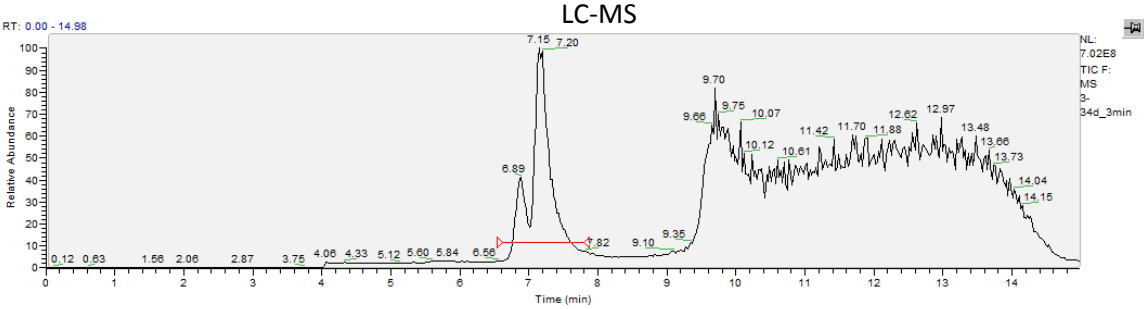
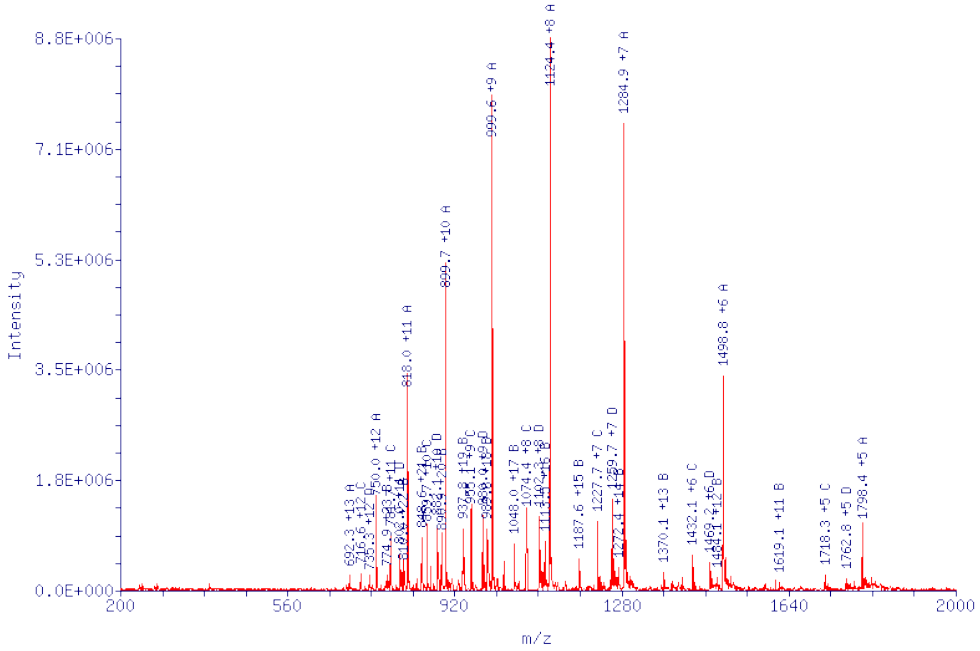


Table 1, entry 3 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

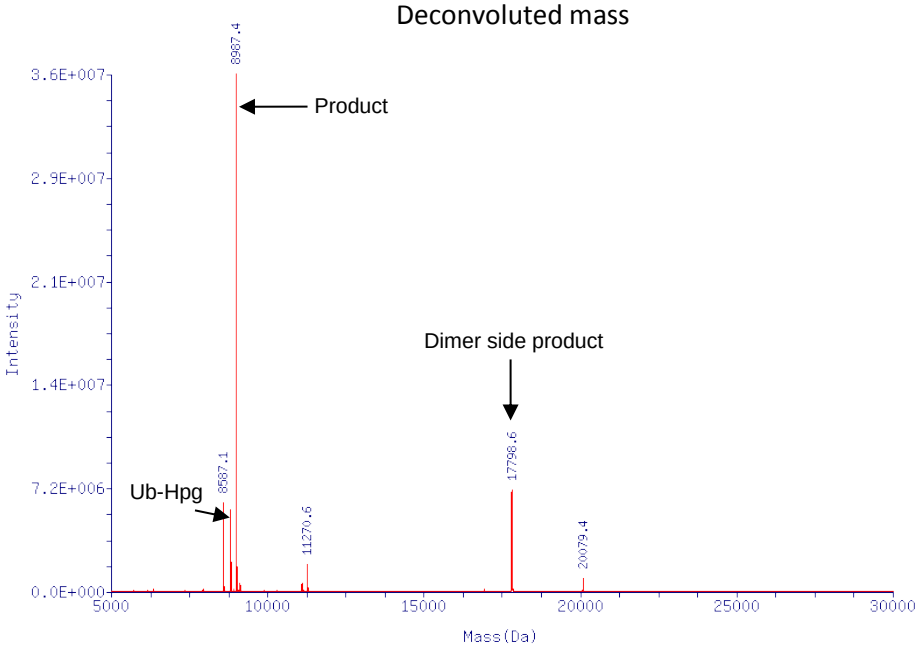
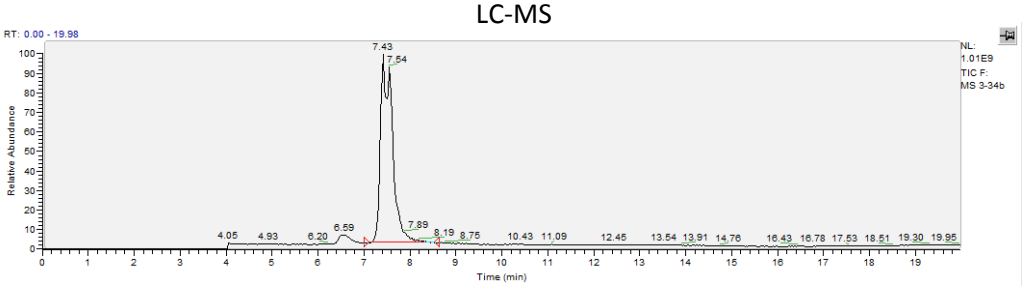
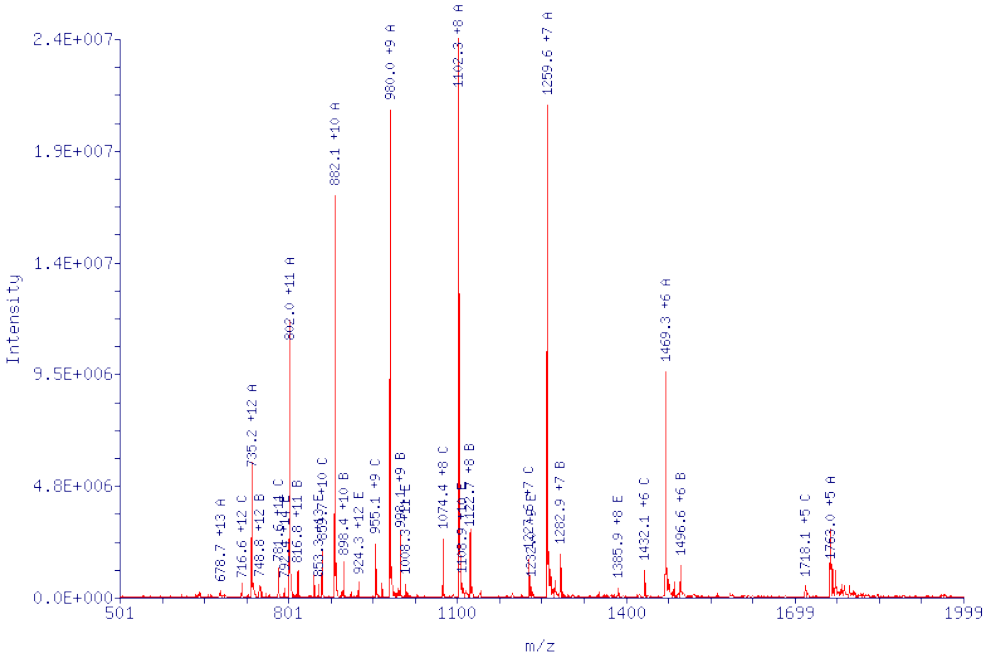


Table 1, entry 4 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

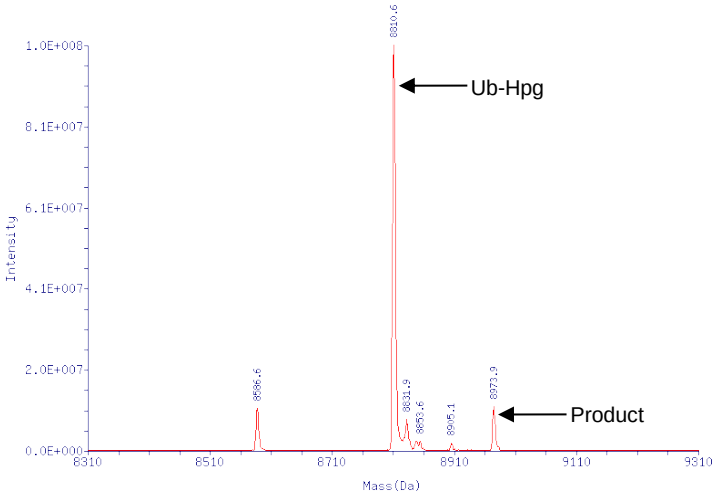
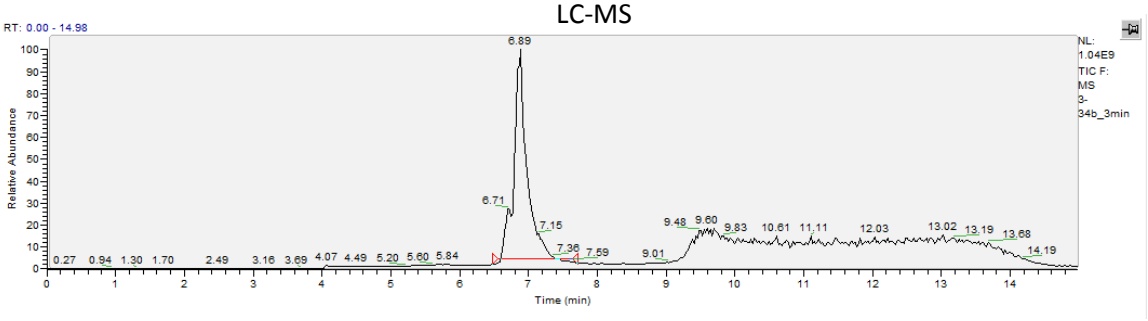
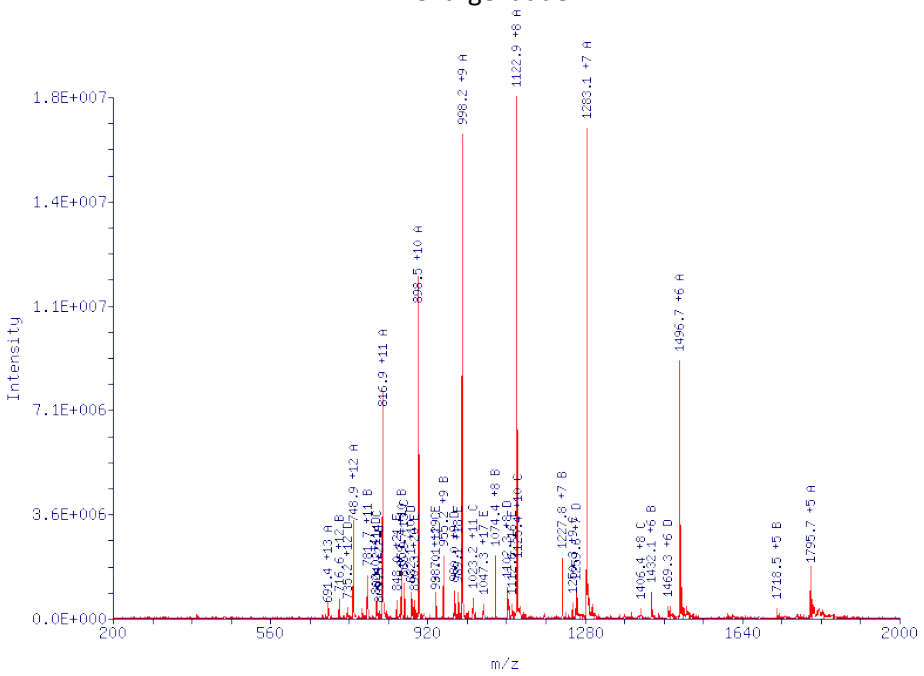


Table 1, entry 4 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

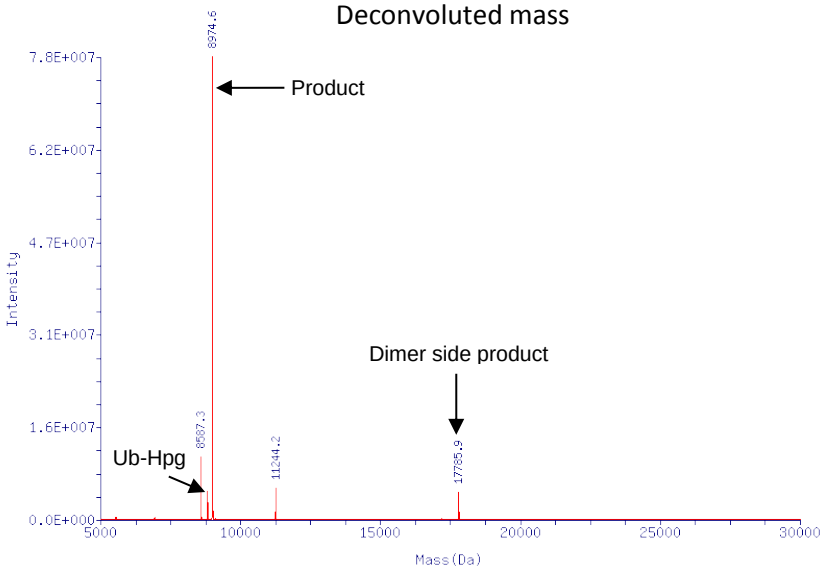
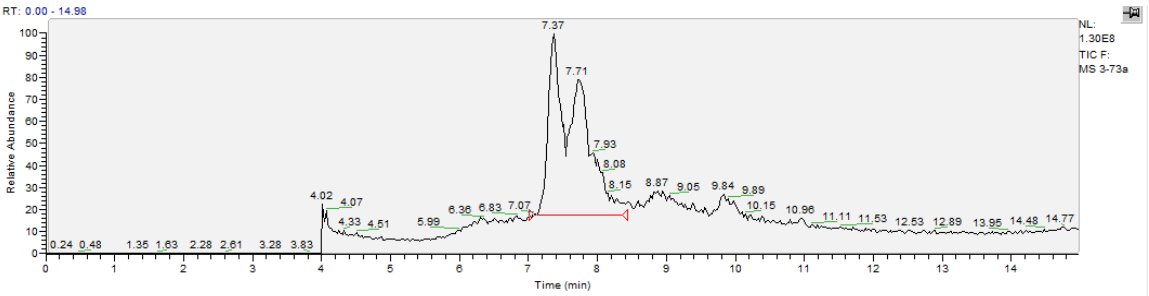
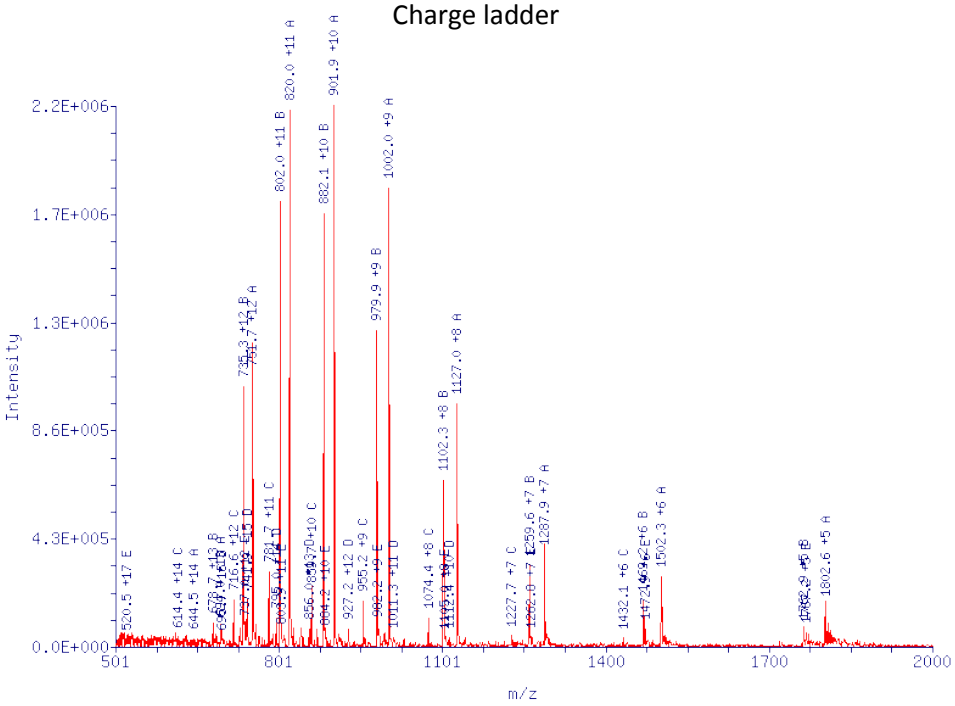


Table 1, entry 5 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

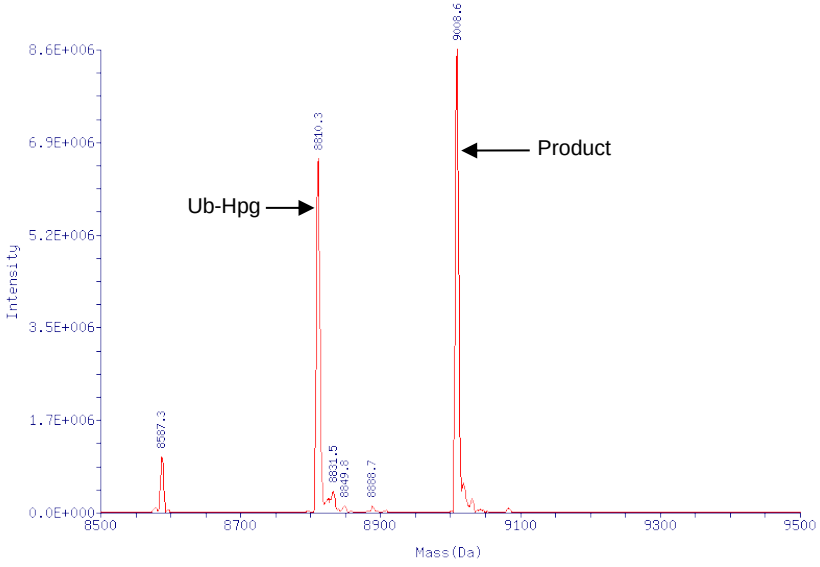
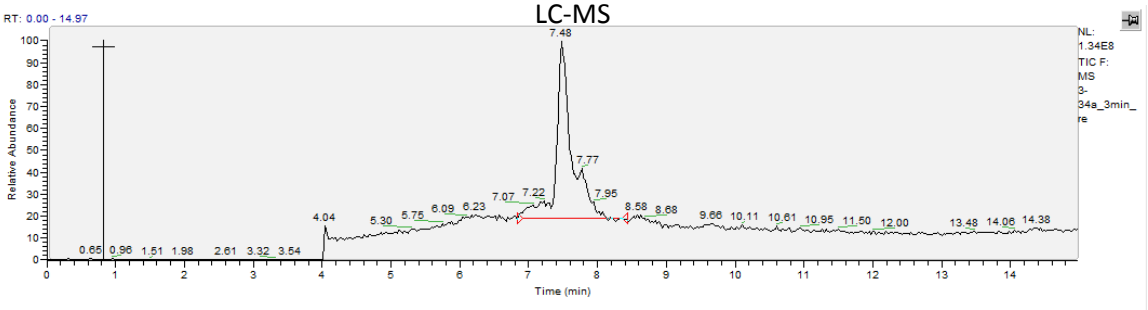
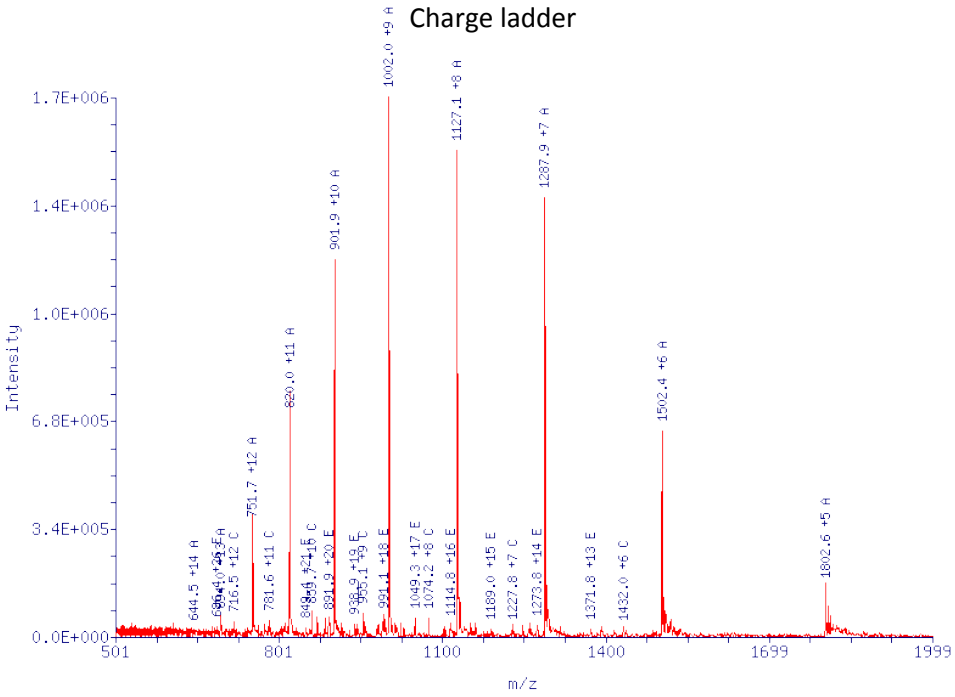


Table 1, entry 5 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

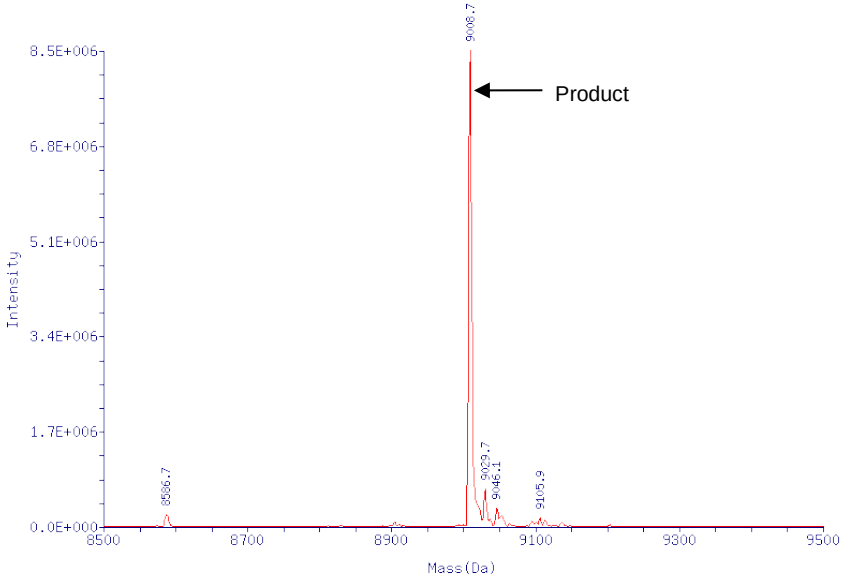
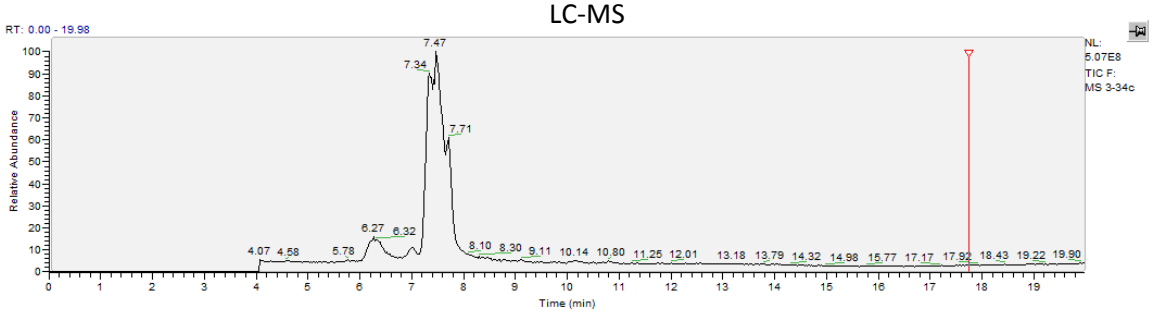
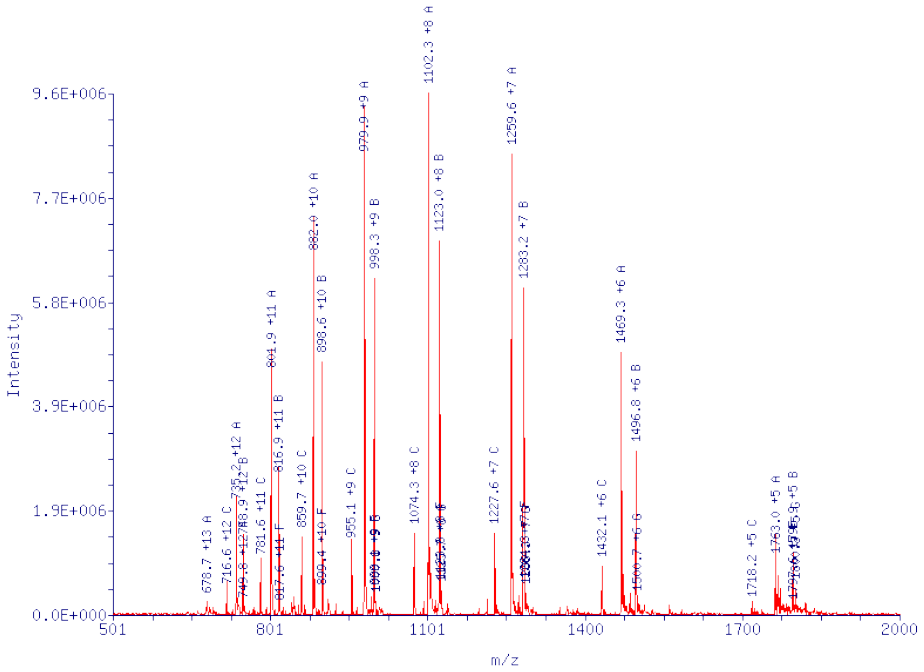


Table 1, entry 6 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

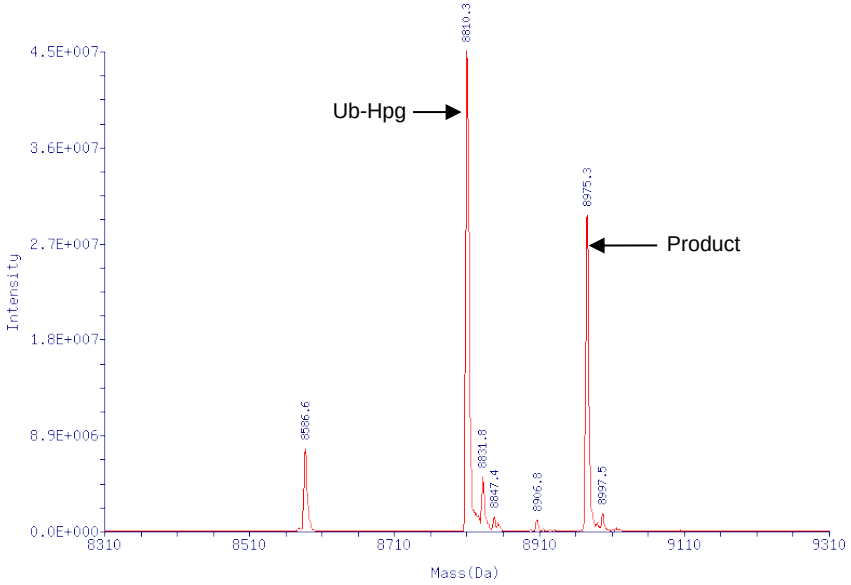
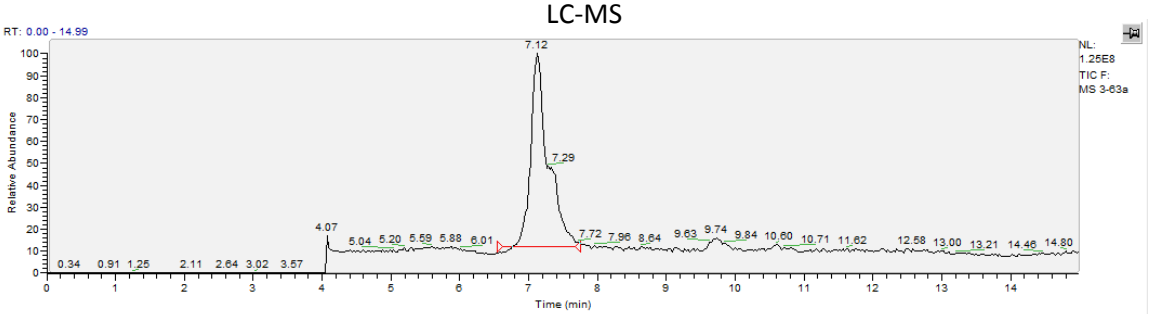
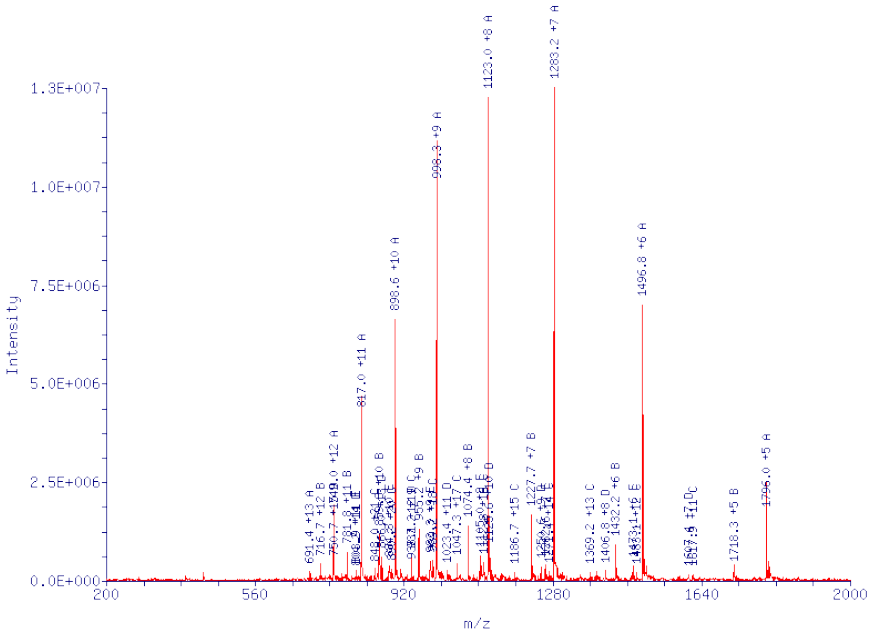


Table 1, entry 6 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

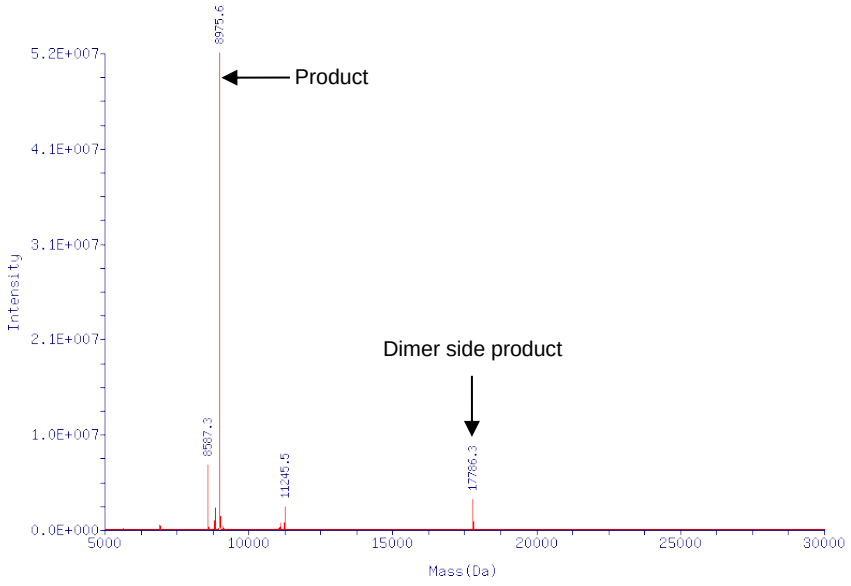
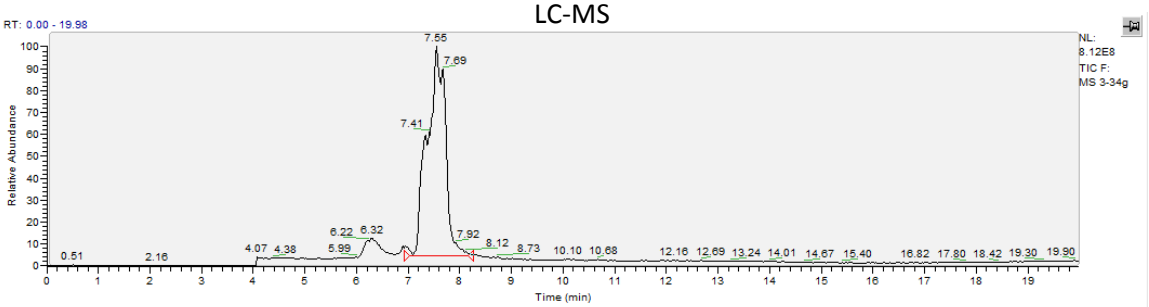
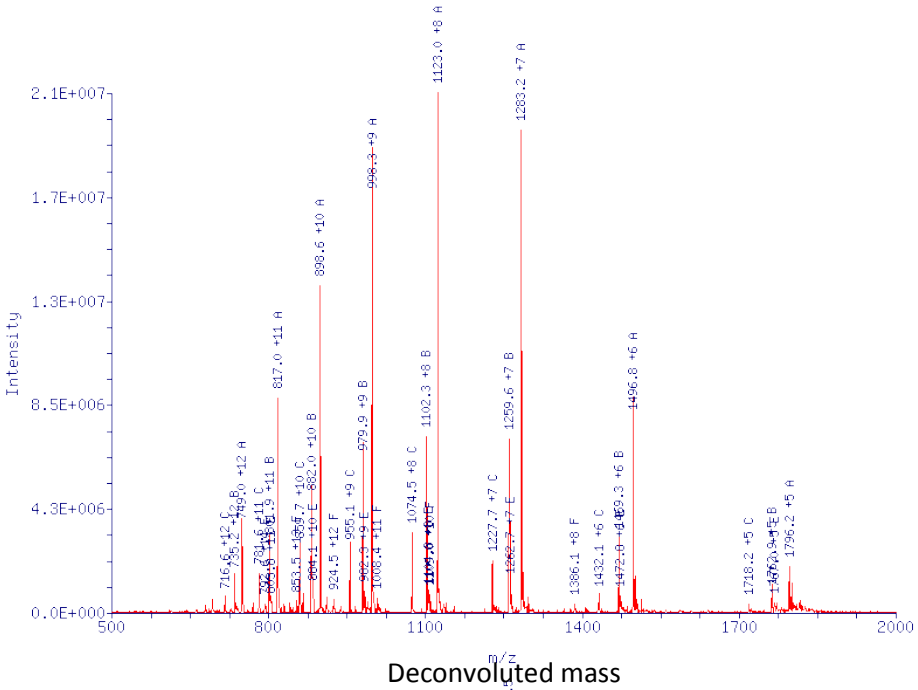


Table 1, entry 7 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

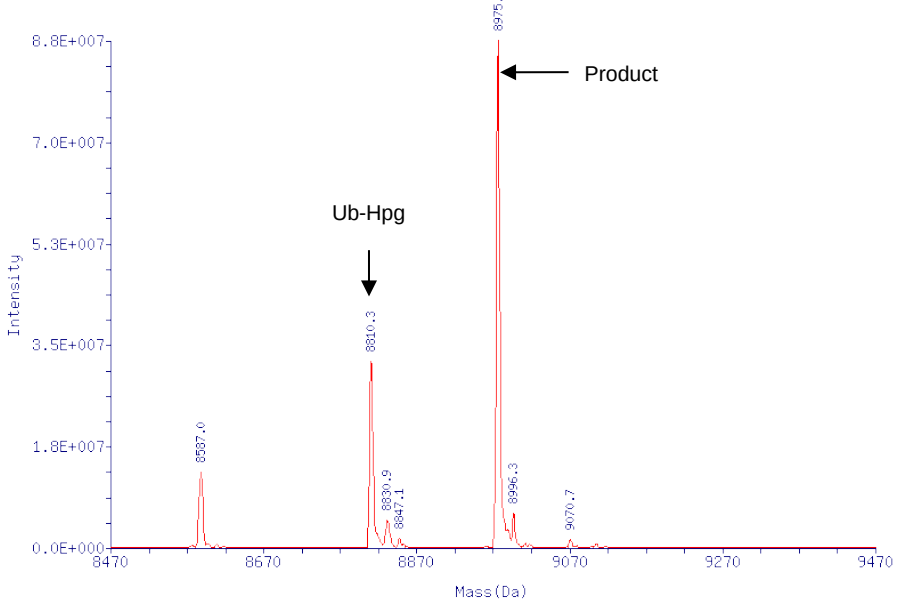
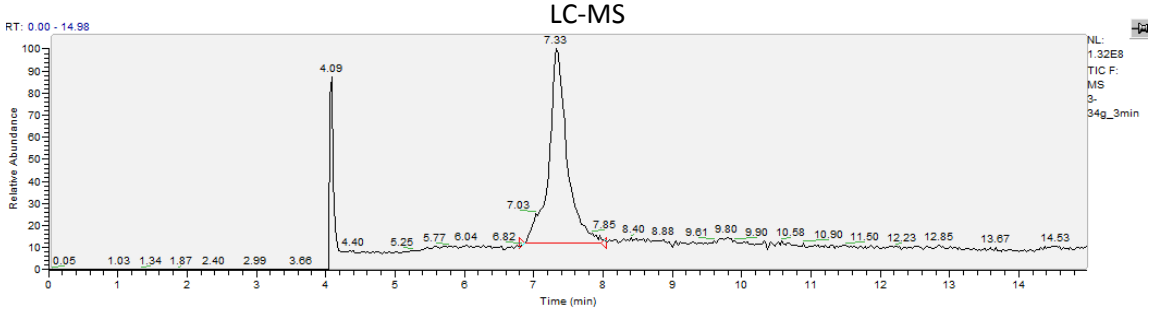
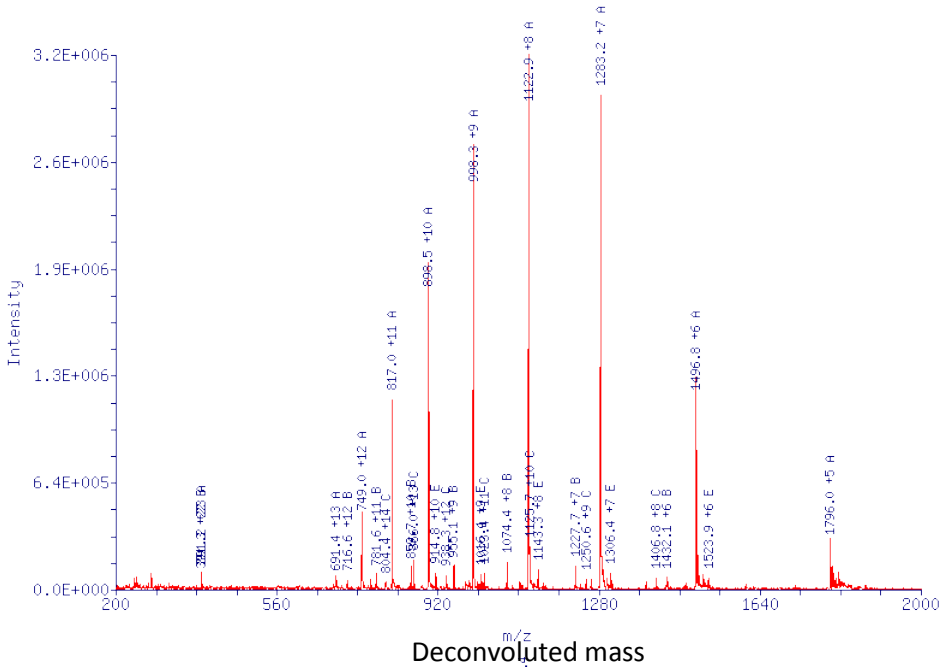


Table 1, entry 7 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

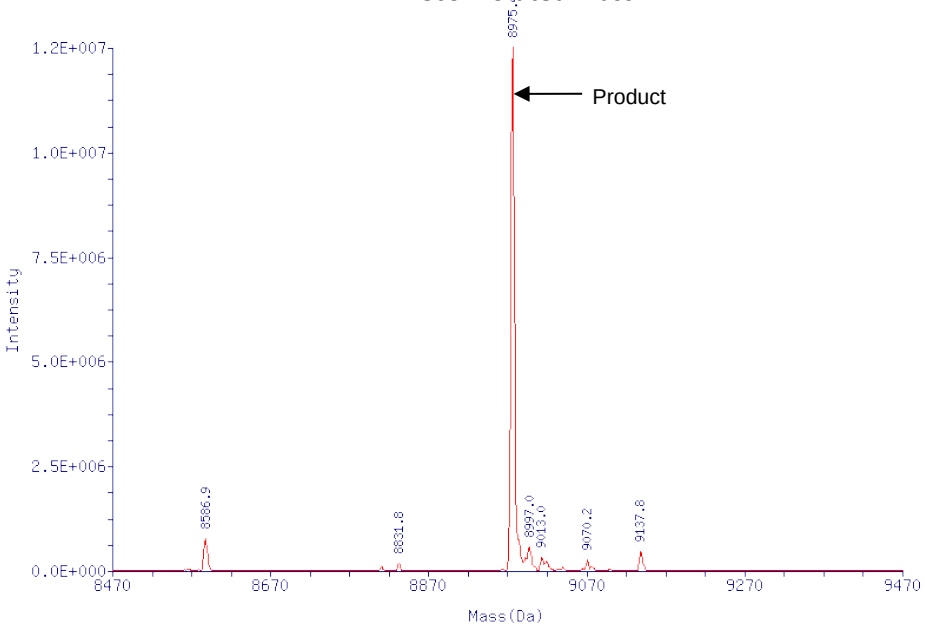
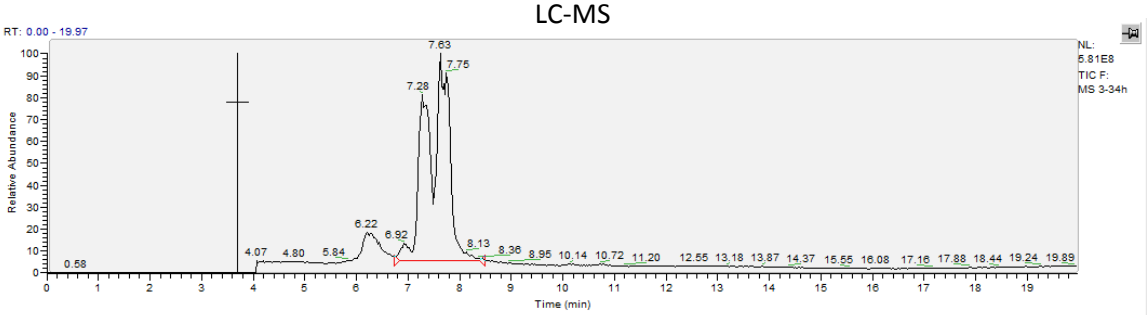
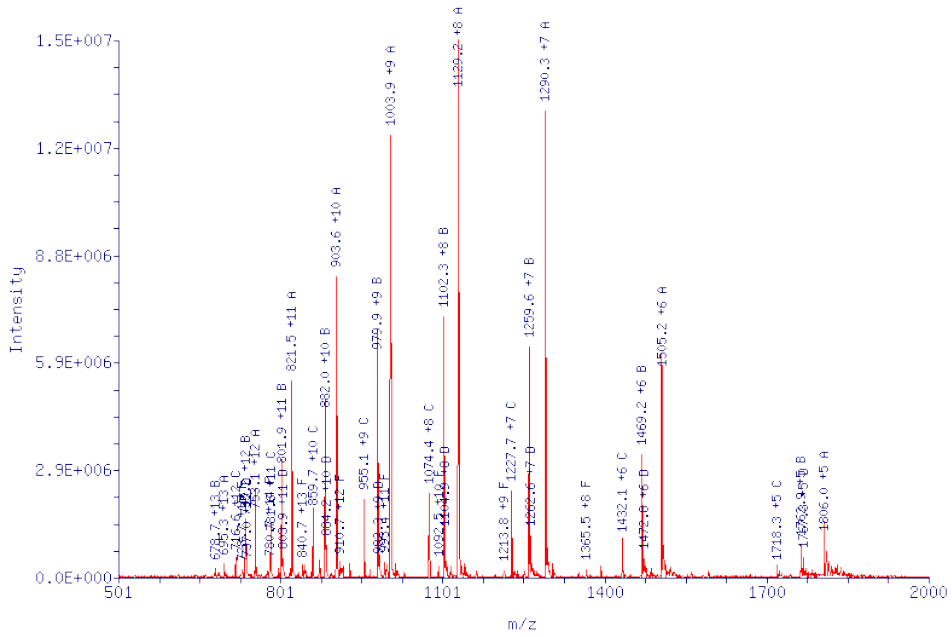


Table 1, entry 8 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

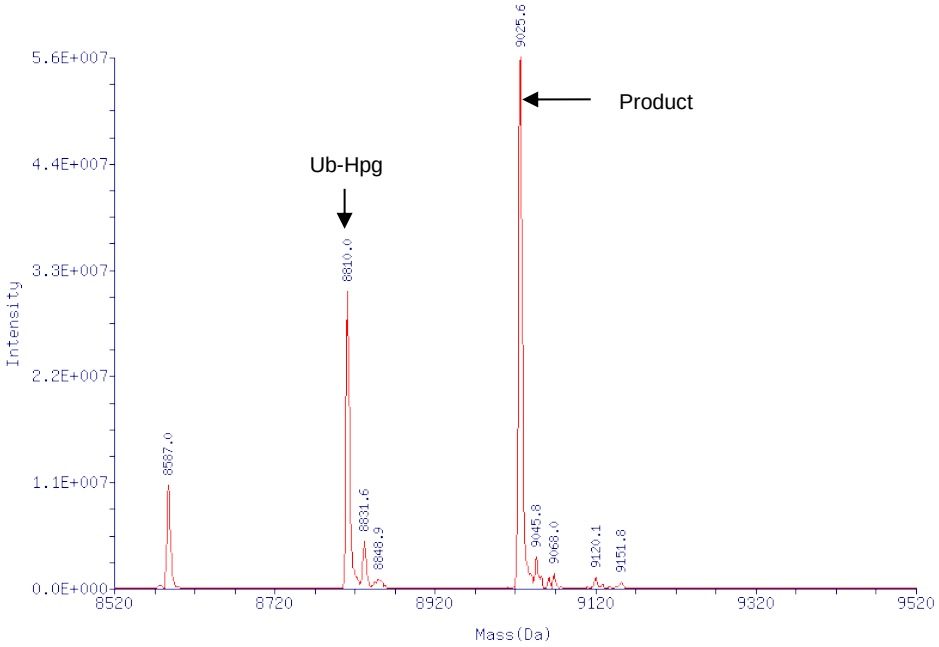
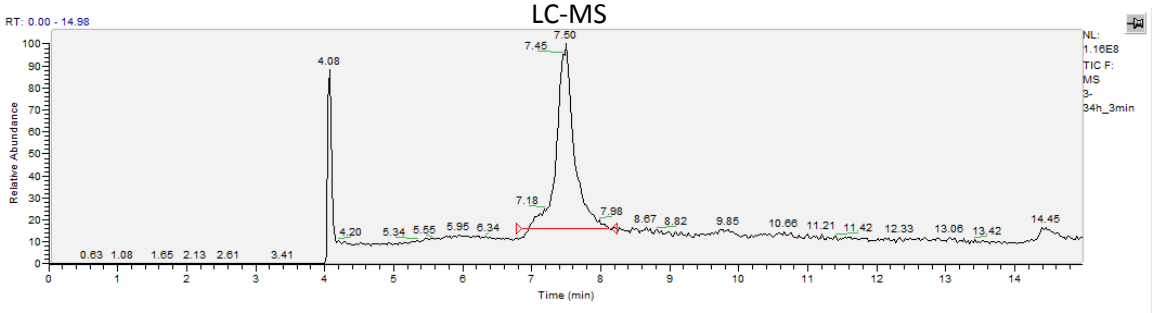
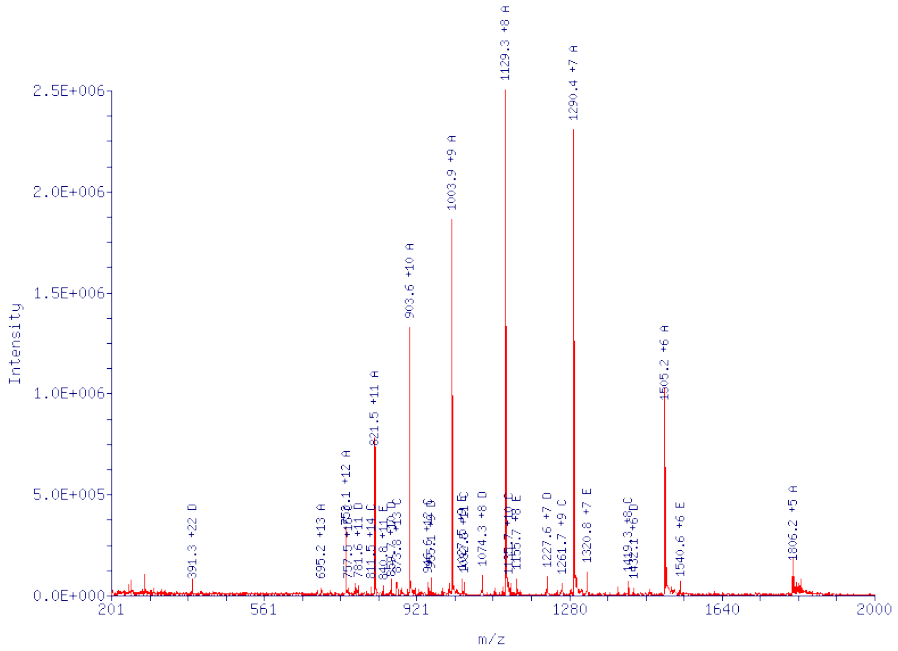


Table 1, entry 8 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

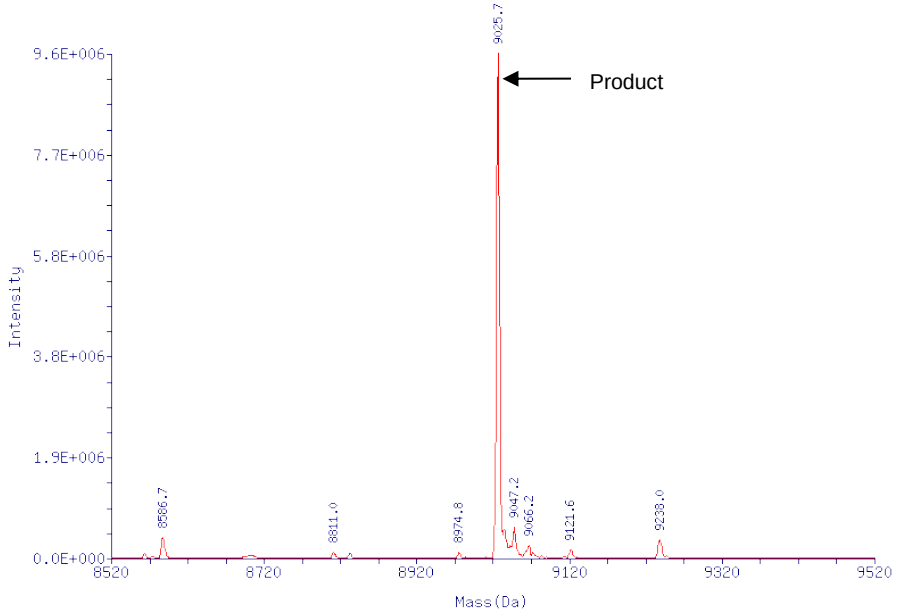
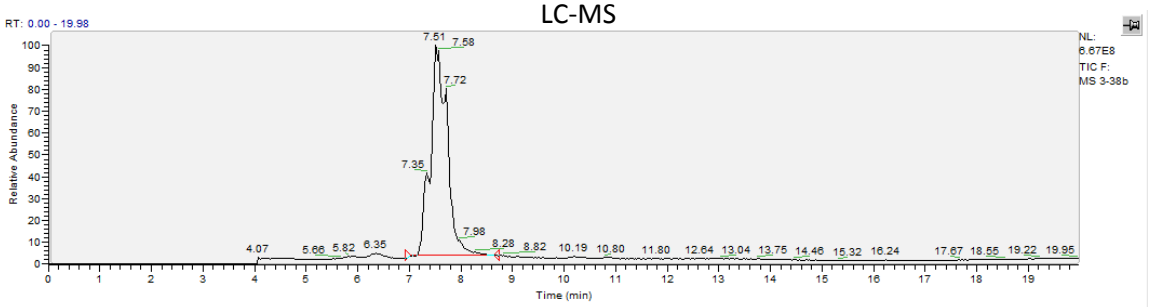
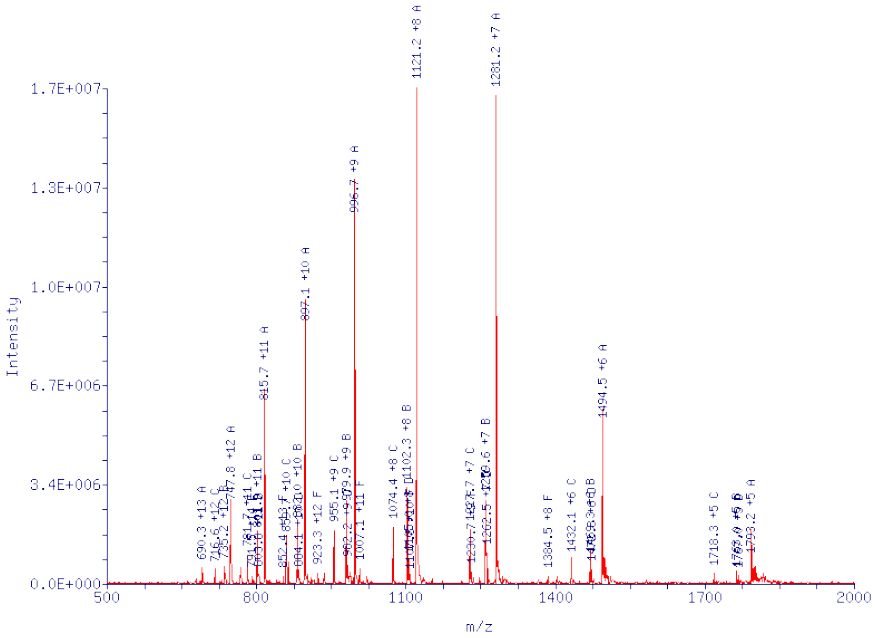


Table 2, entry 1 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

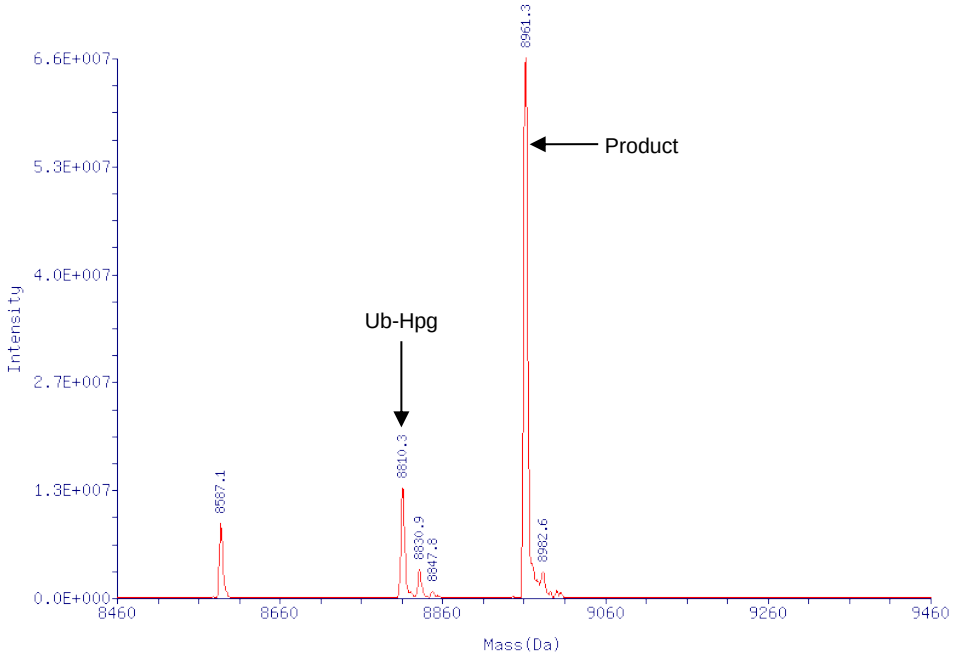
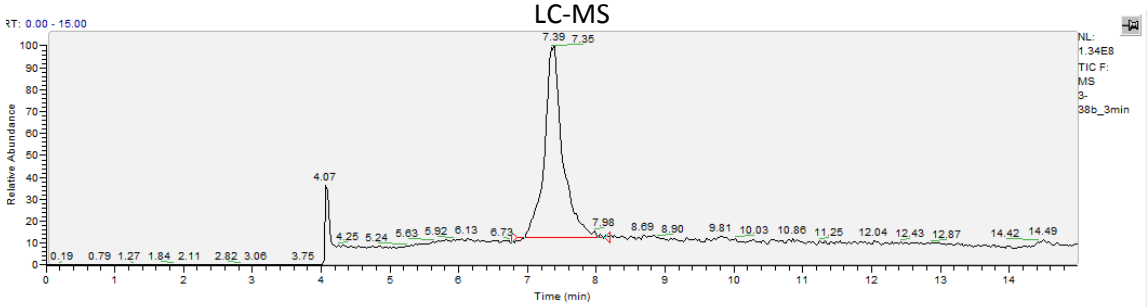
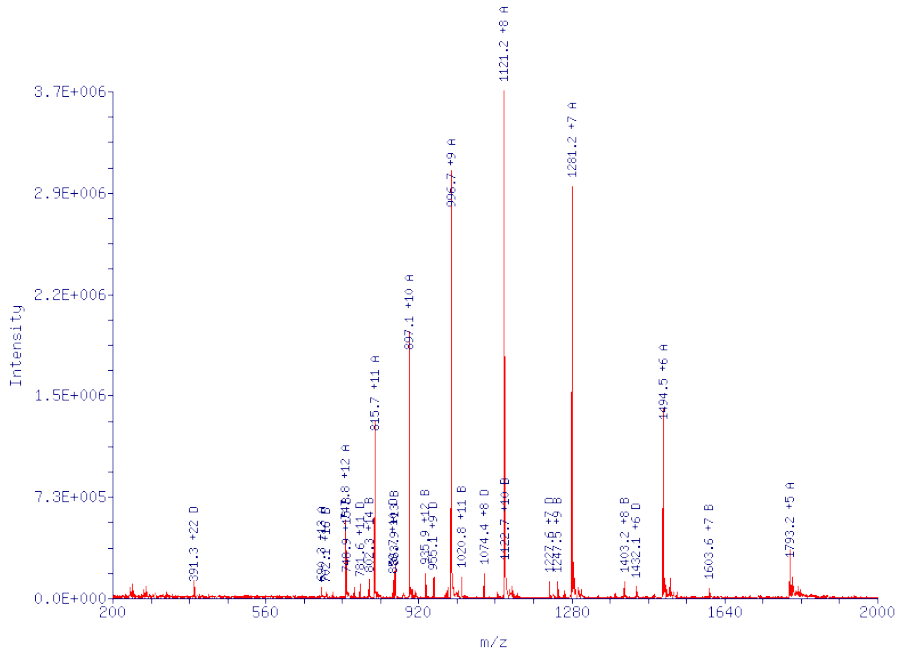


Table 2, entry 1 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

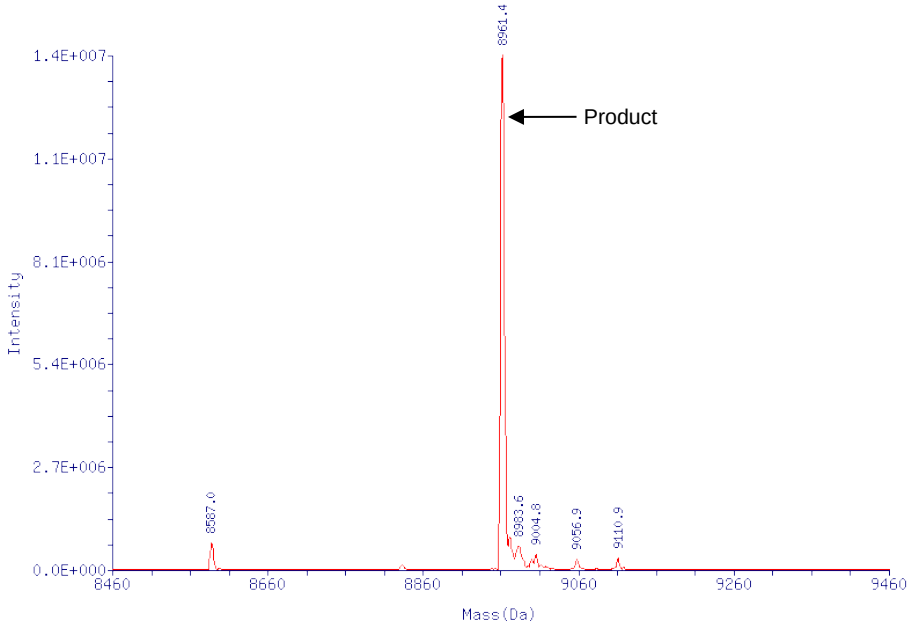
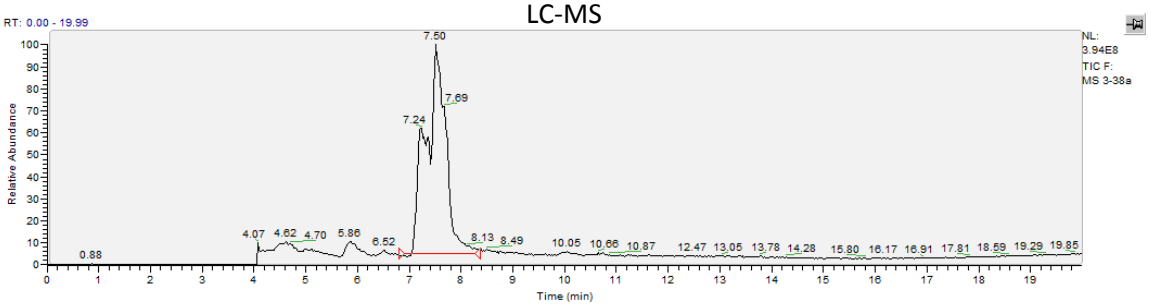
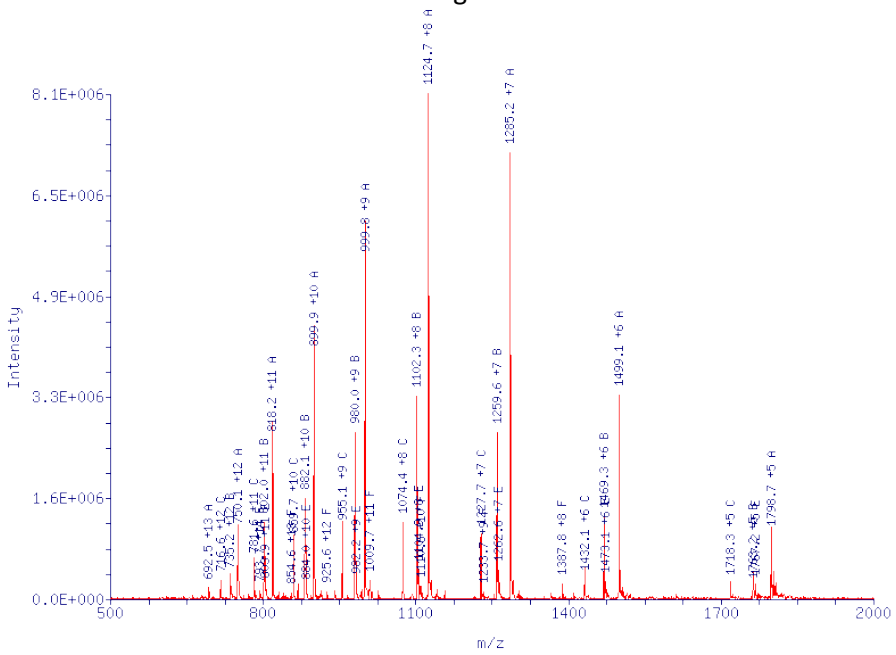


Table 2, entry 2 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

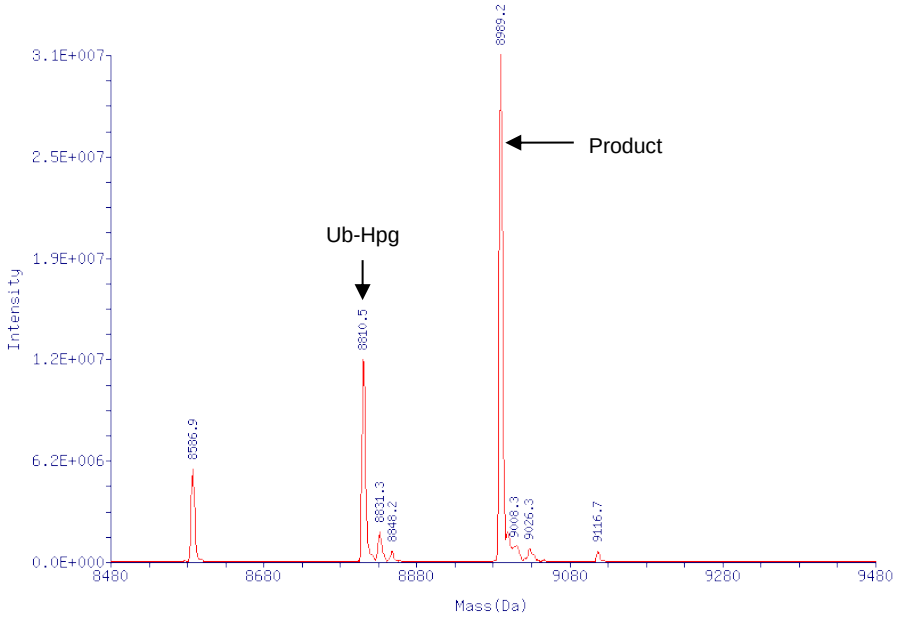
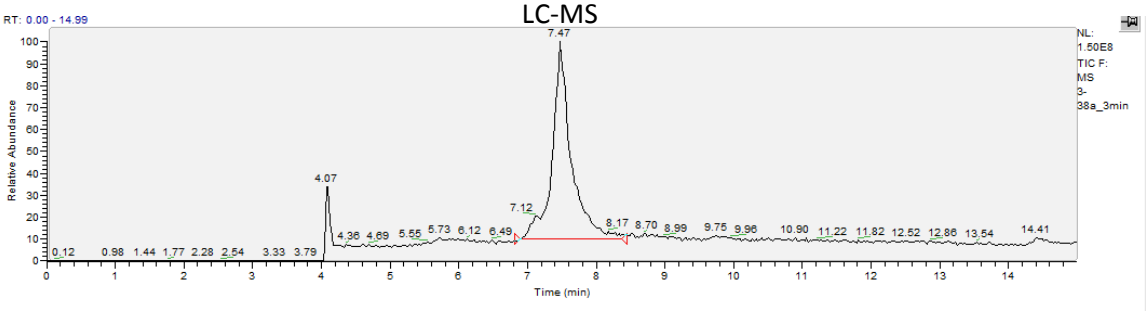
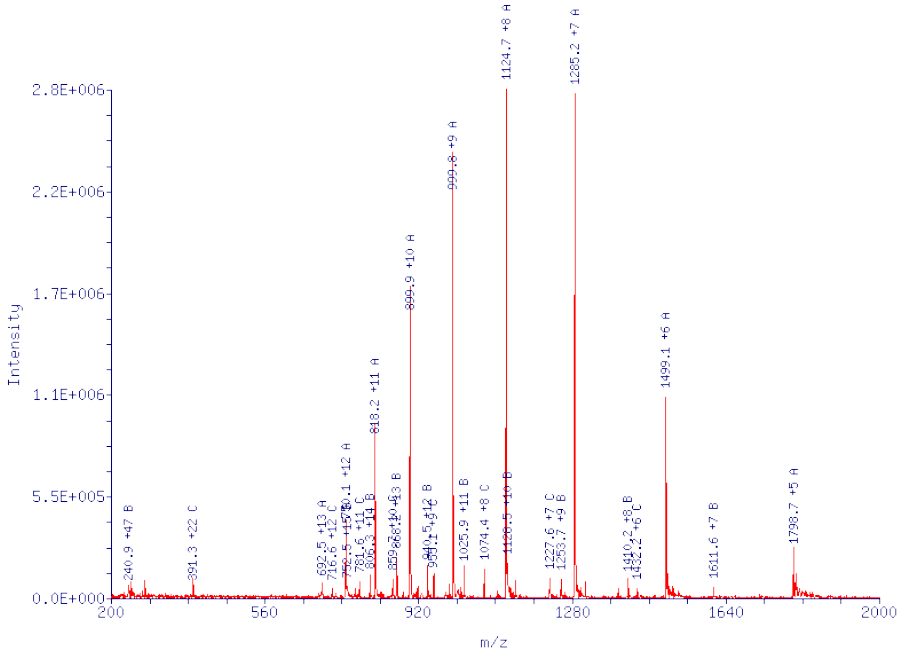


Table 2, entry 2 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

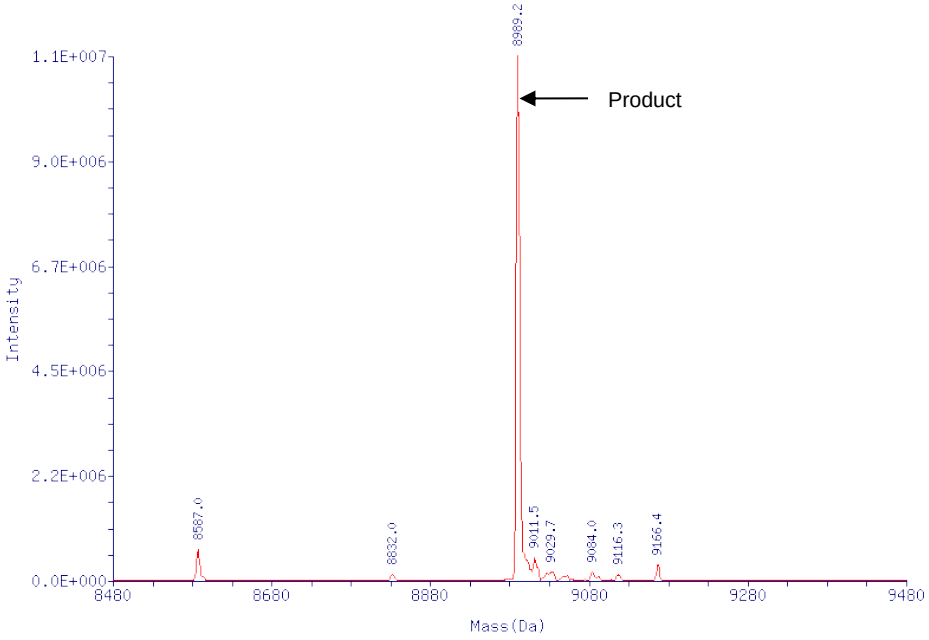
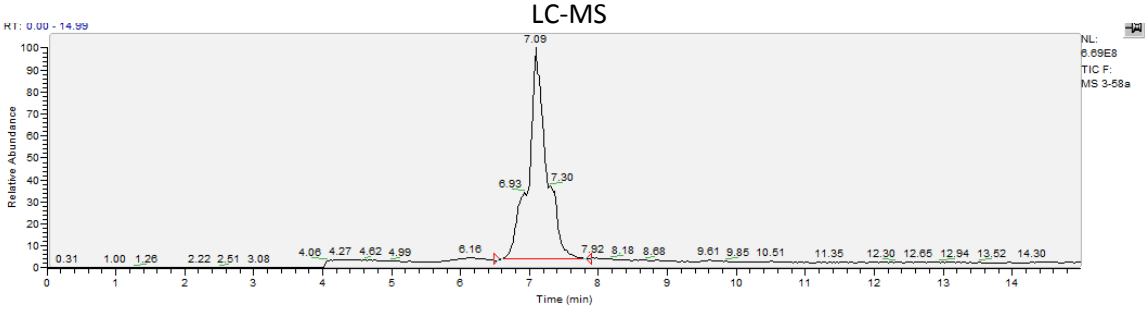
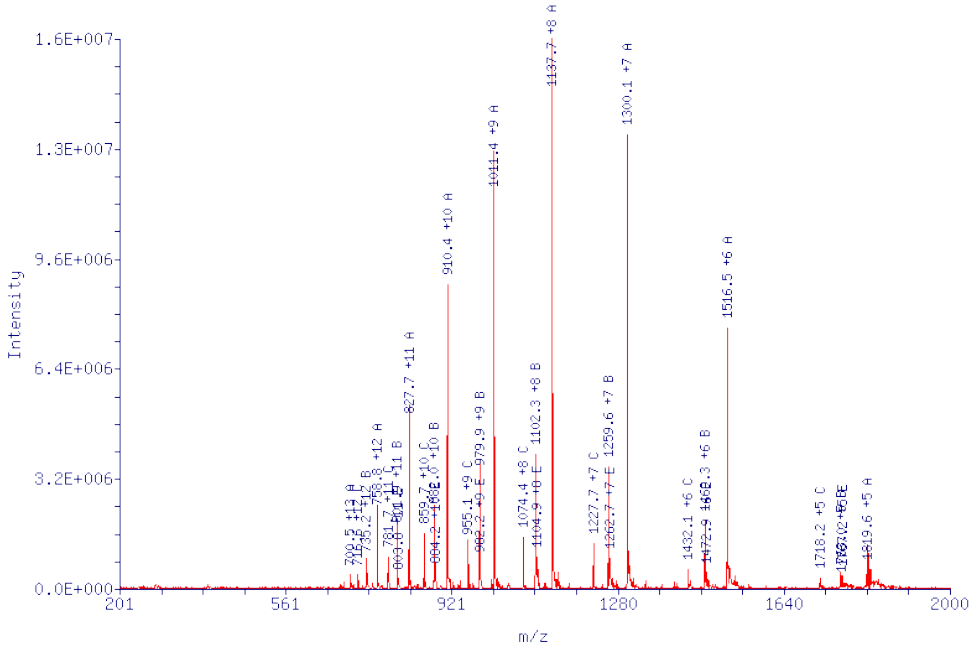


Table 2, entry 3 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

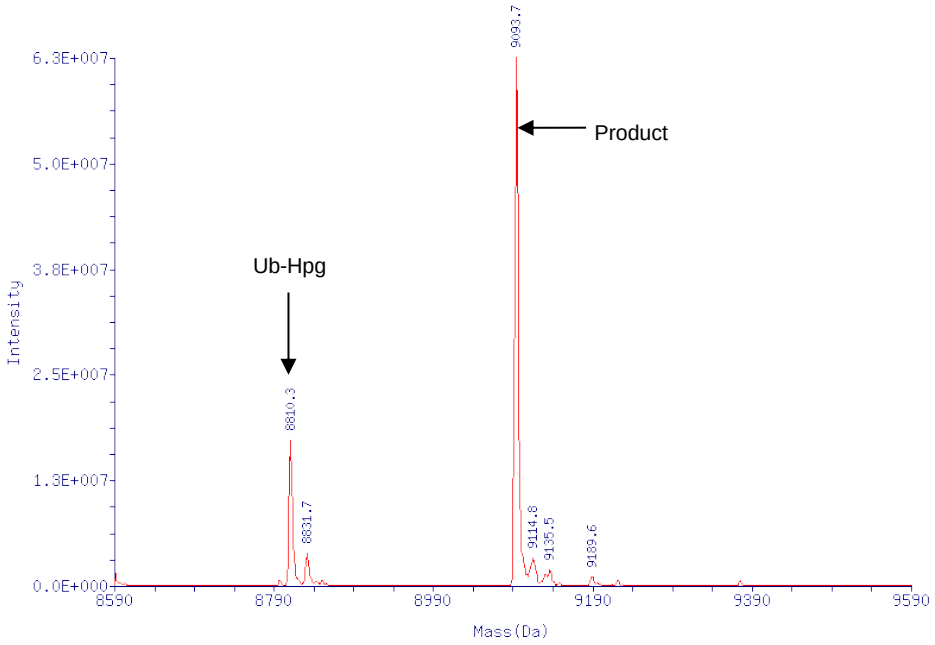
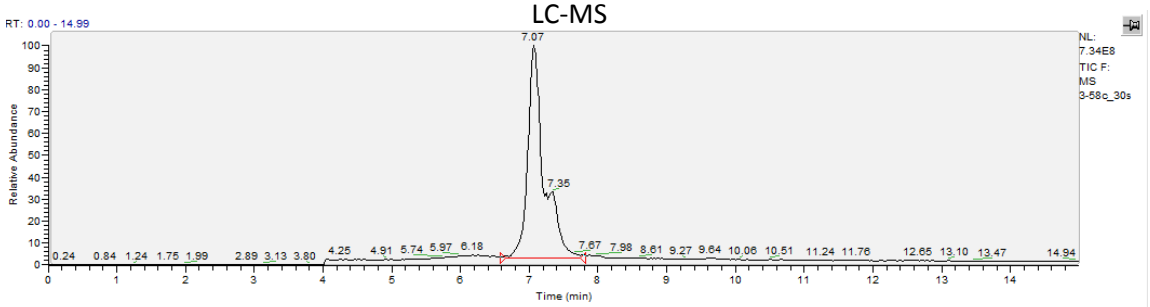
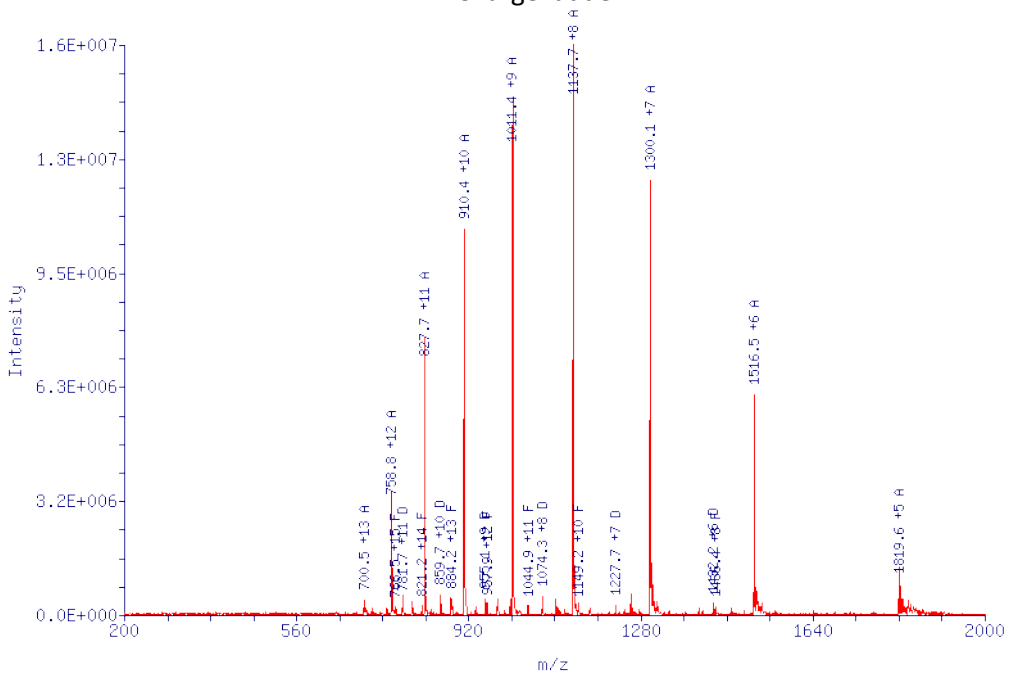


Table 2, entry 3 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

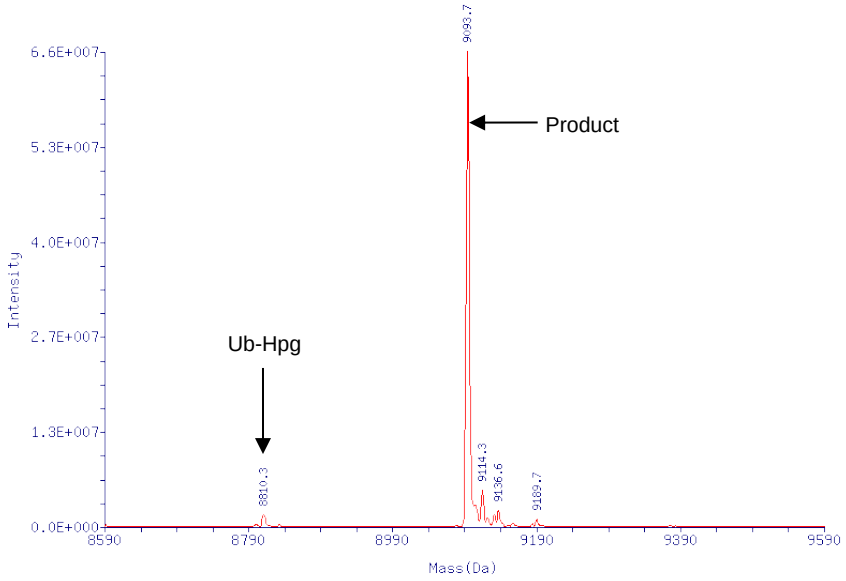
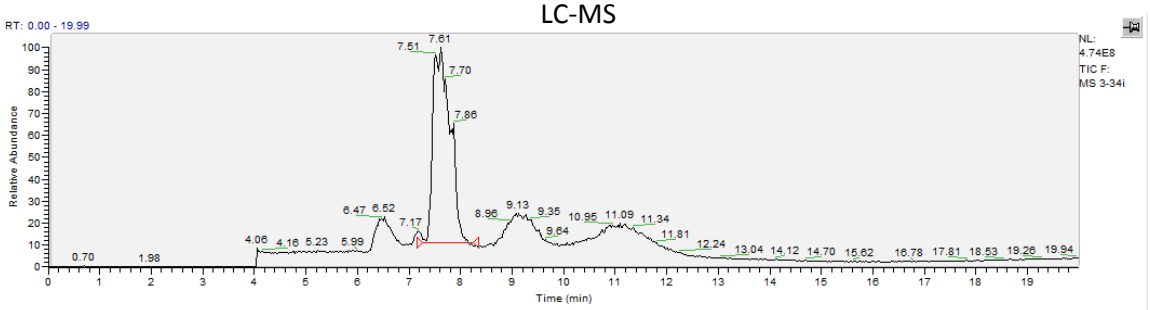
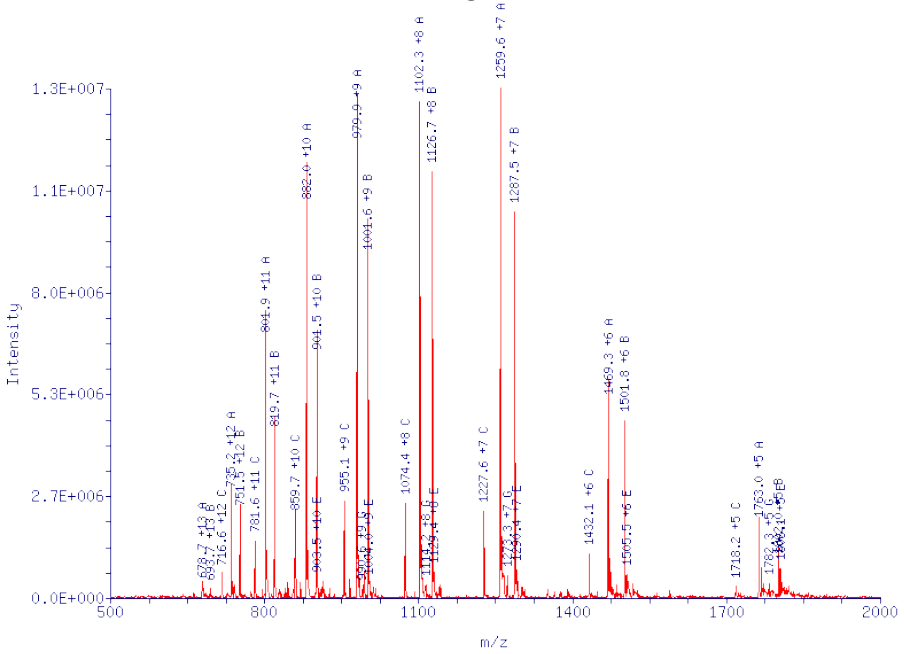


Table 2, entry 4 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

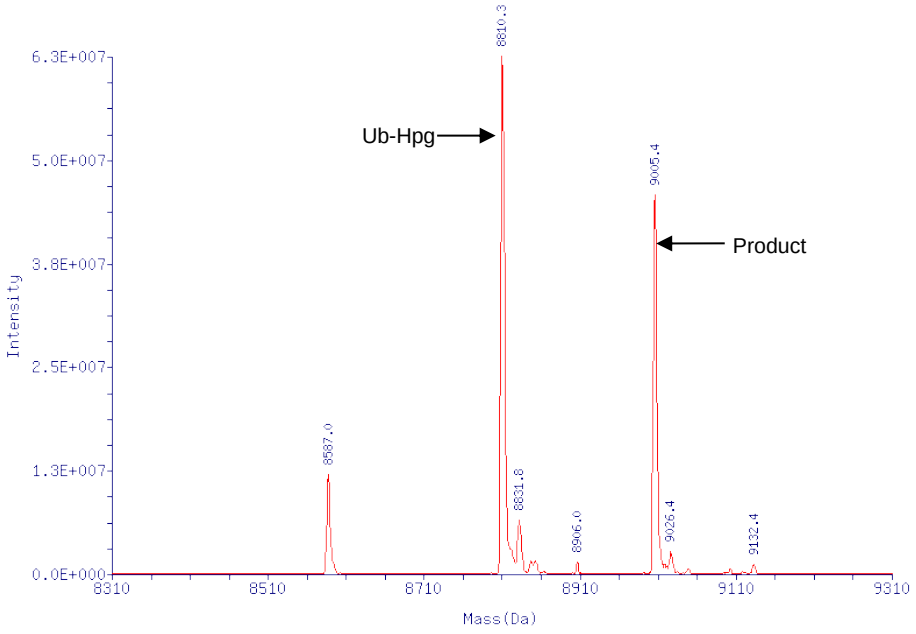
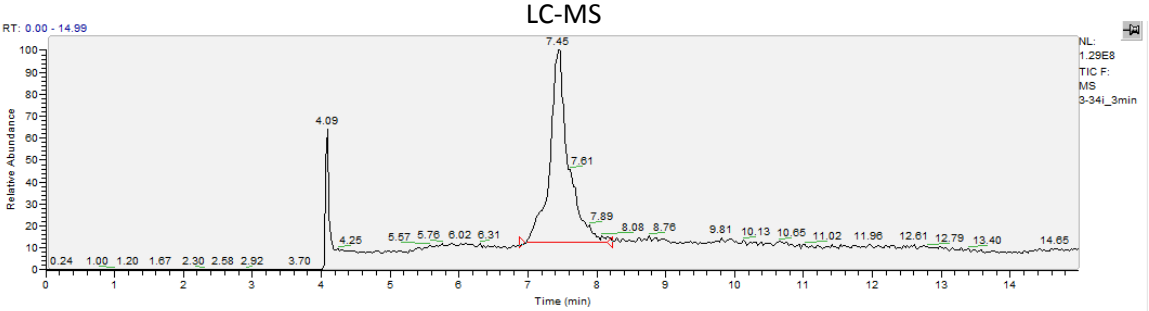
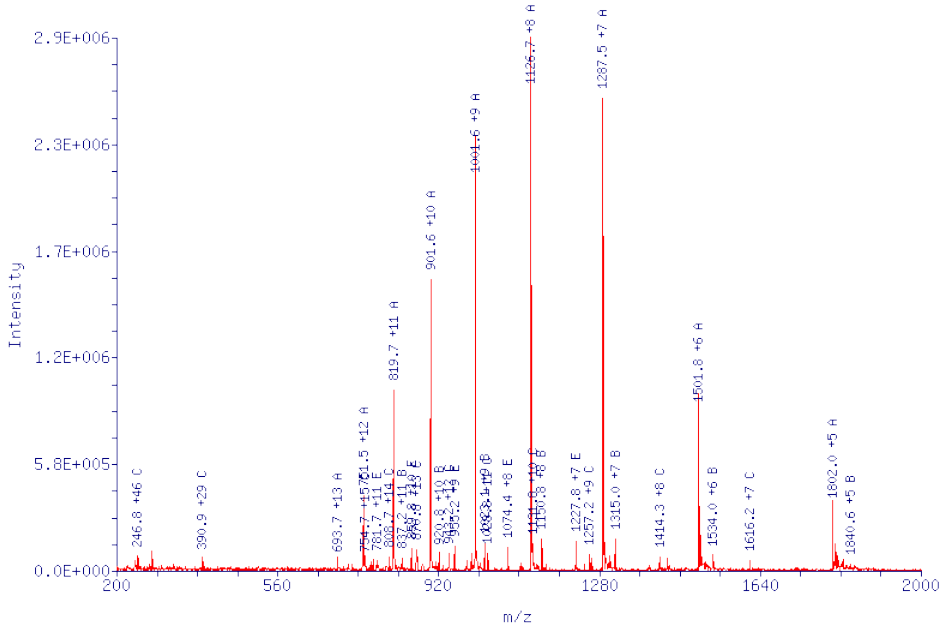


Table 2, entry 4 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

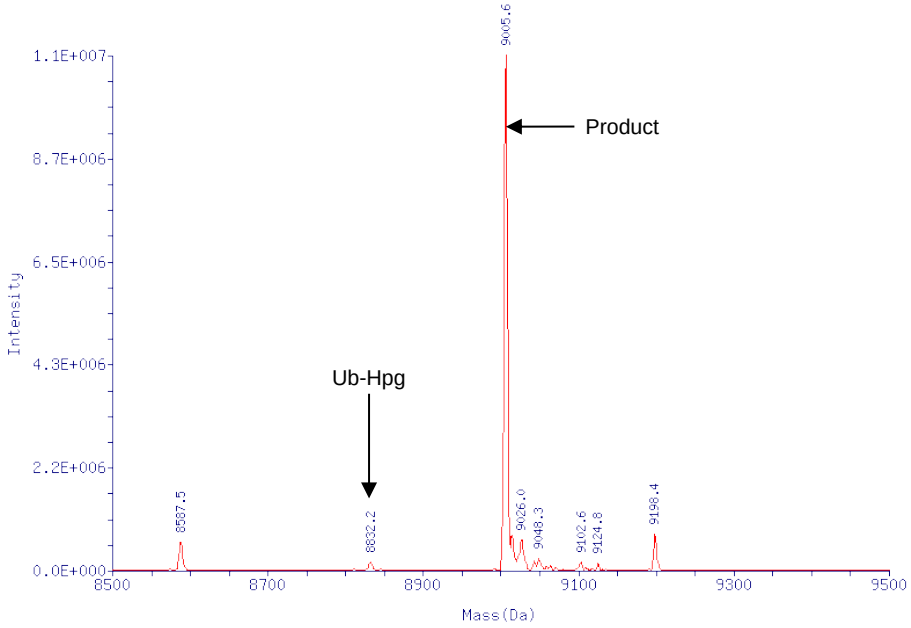
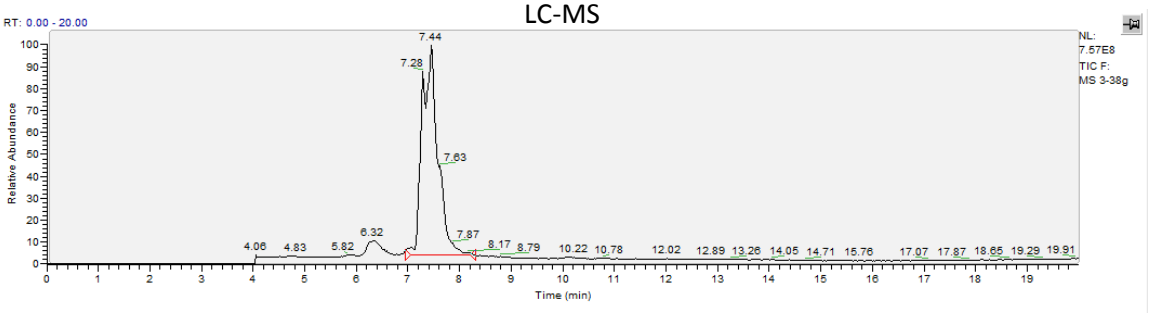
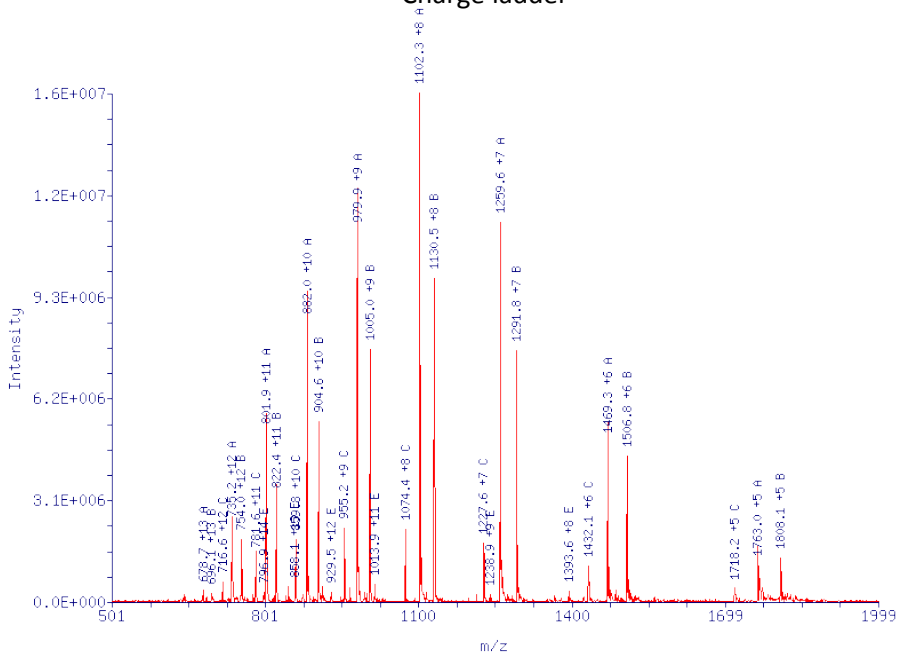


Table 2, entry 5 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

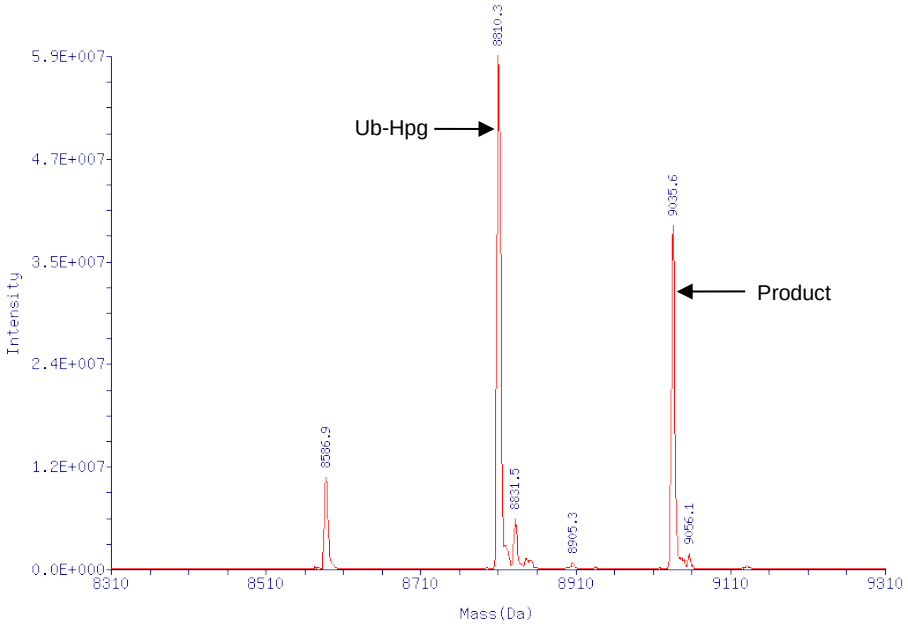
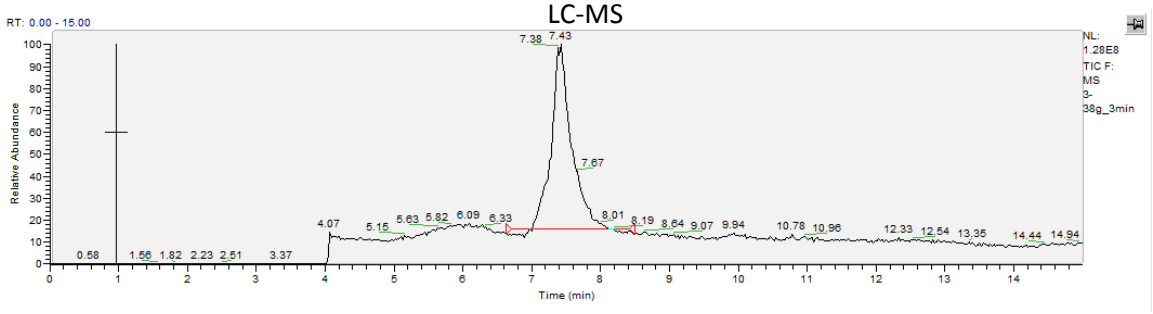
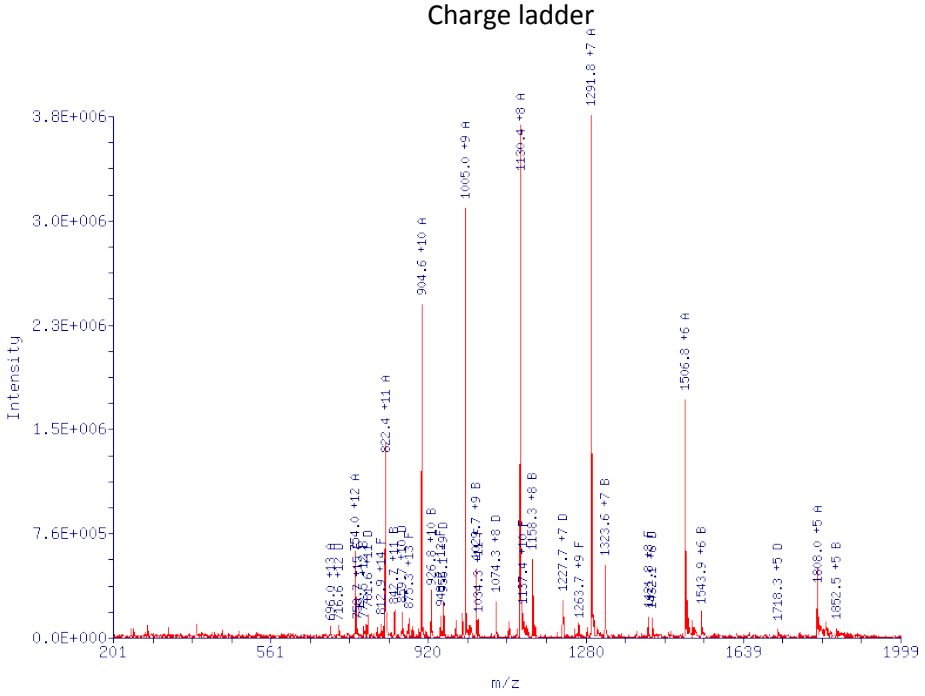


Table 2, entry 5 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

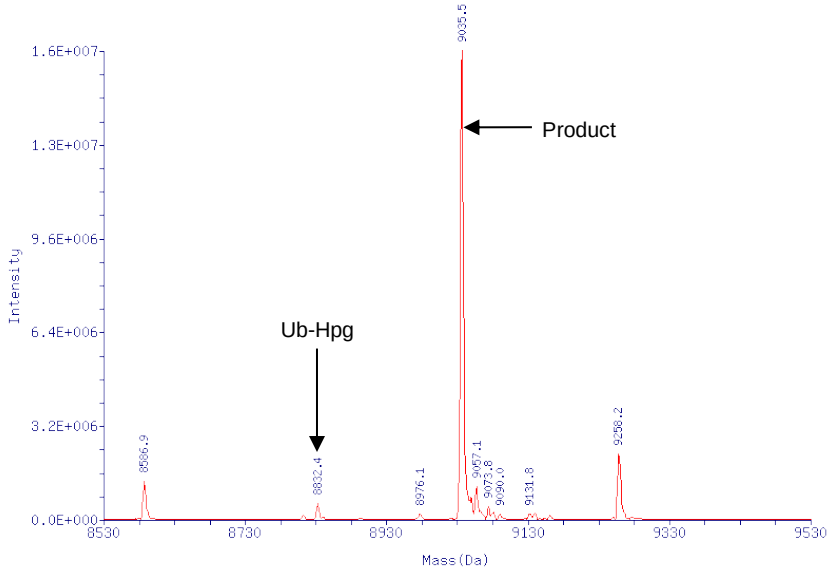
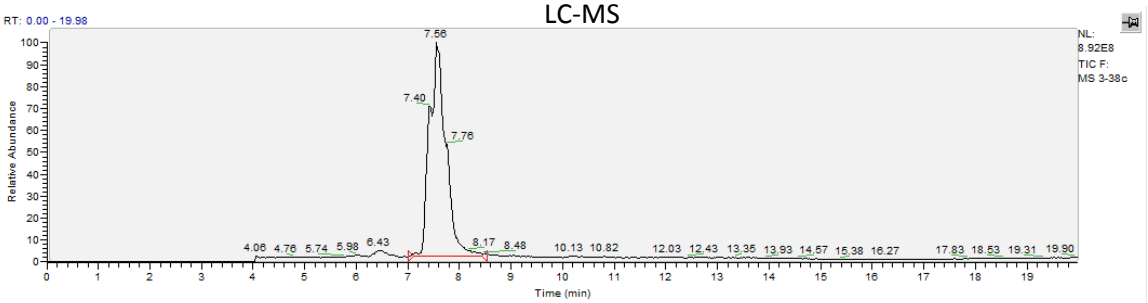
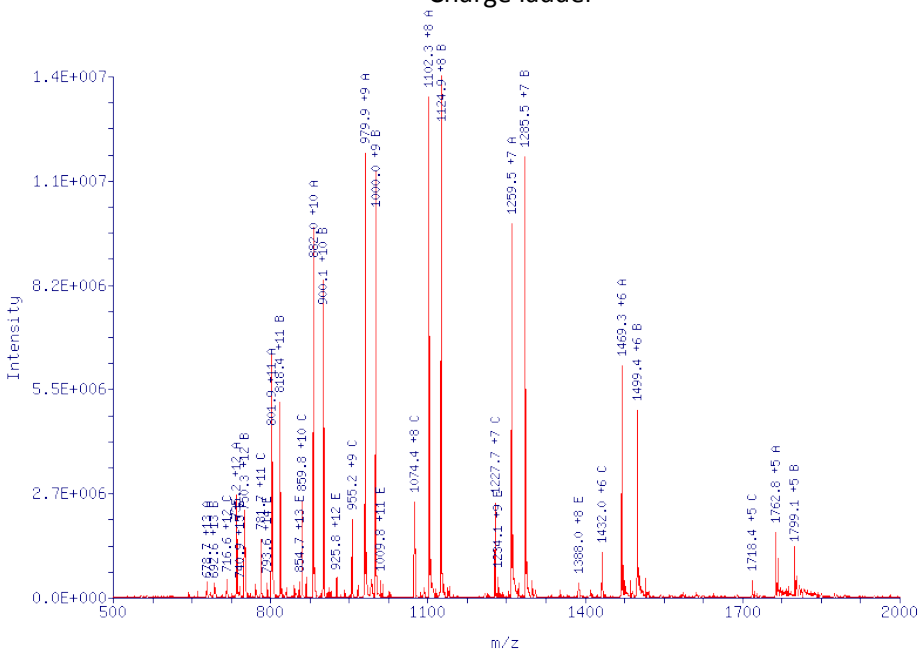


Table 2, entry 6 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

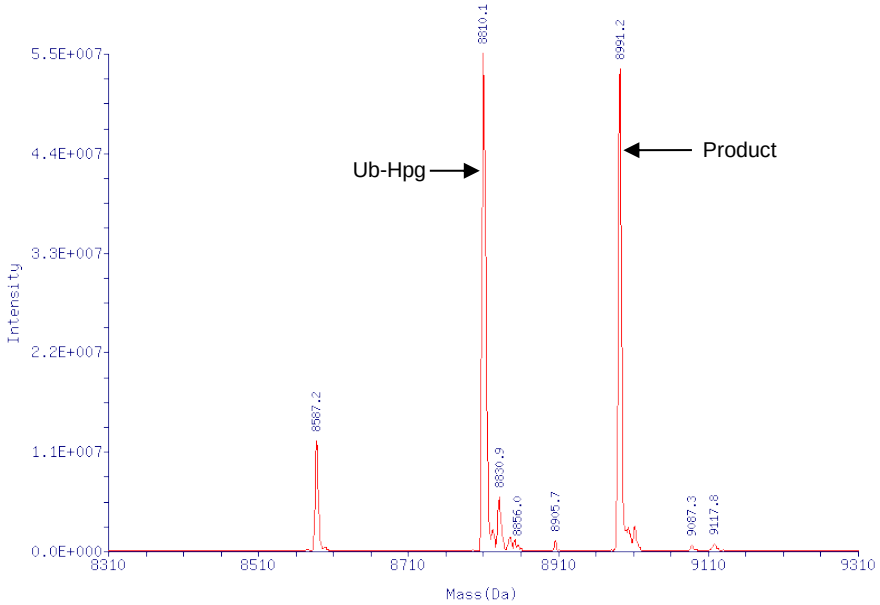
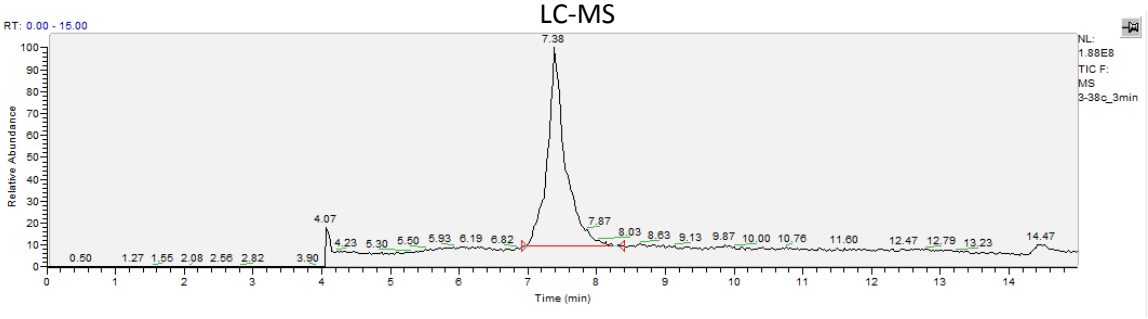
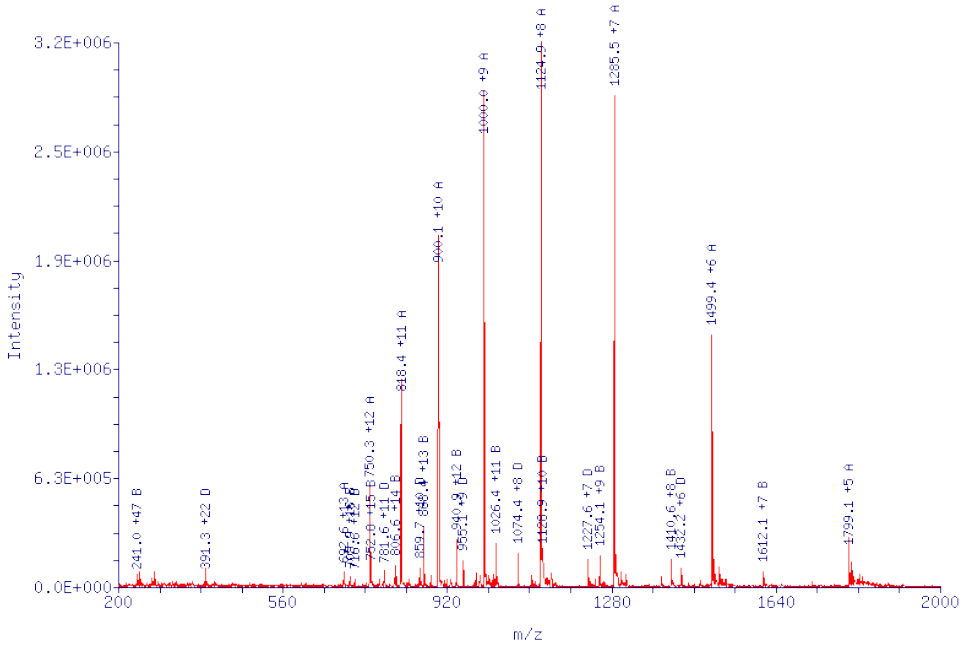


Table 2, entry 6 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

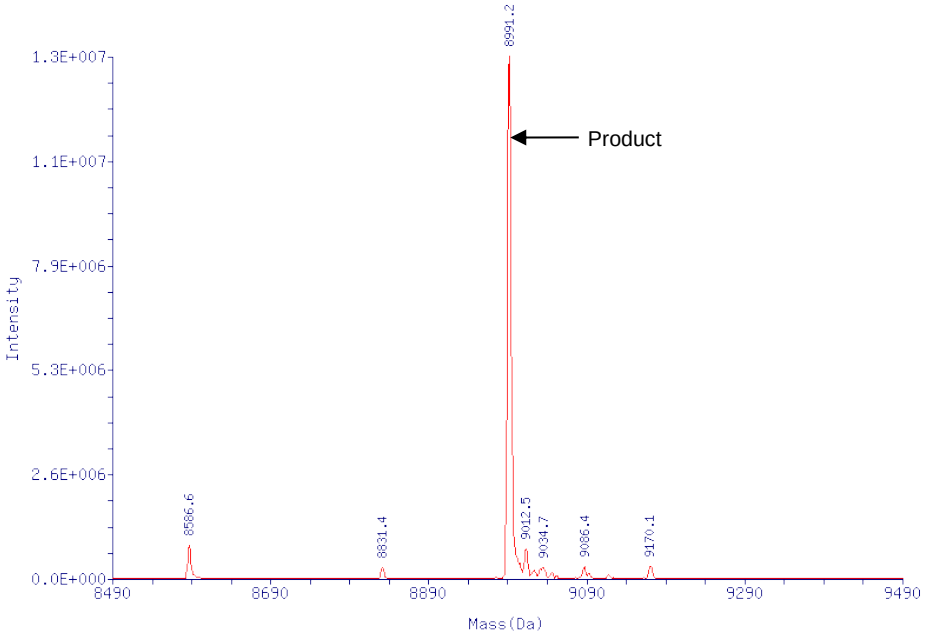
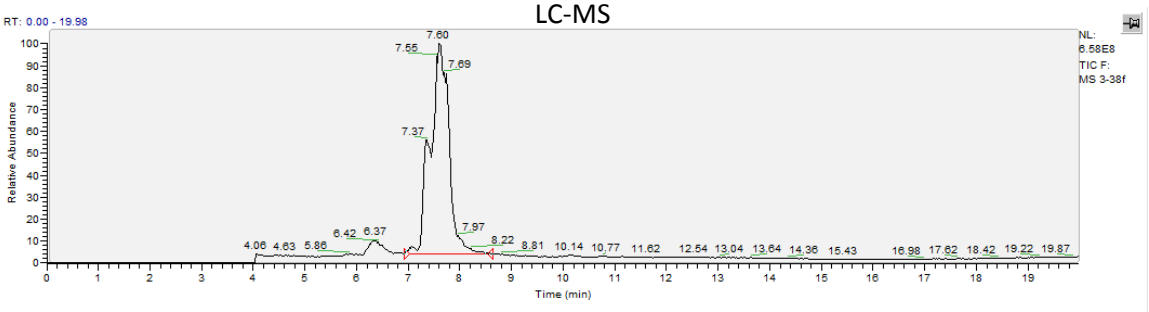
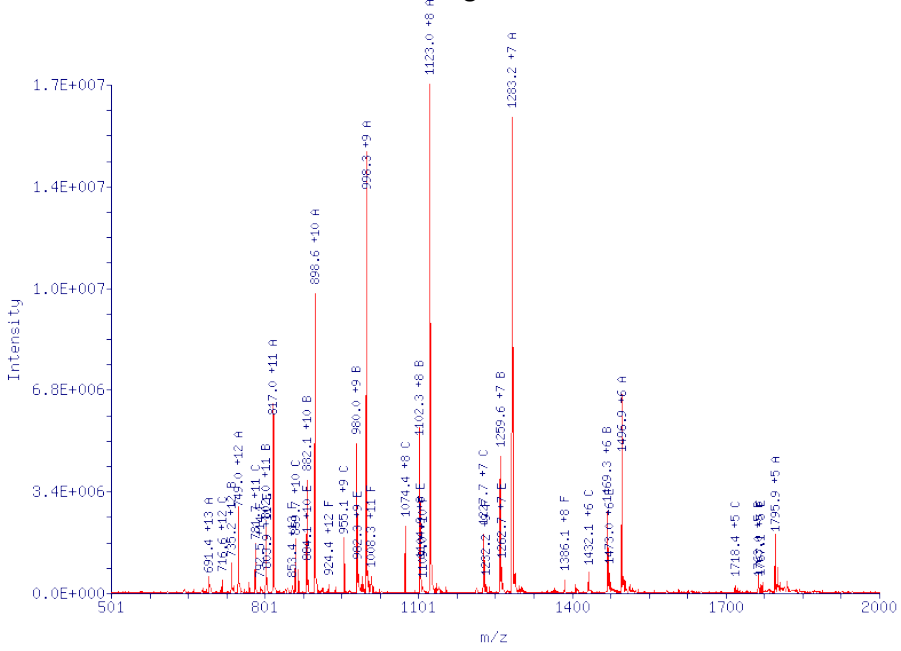


Table 2, entry 7 (10 s)

LC-MS




Charge ladder

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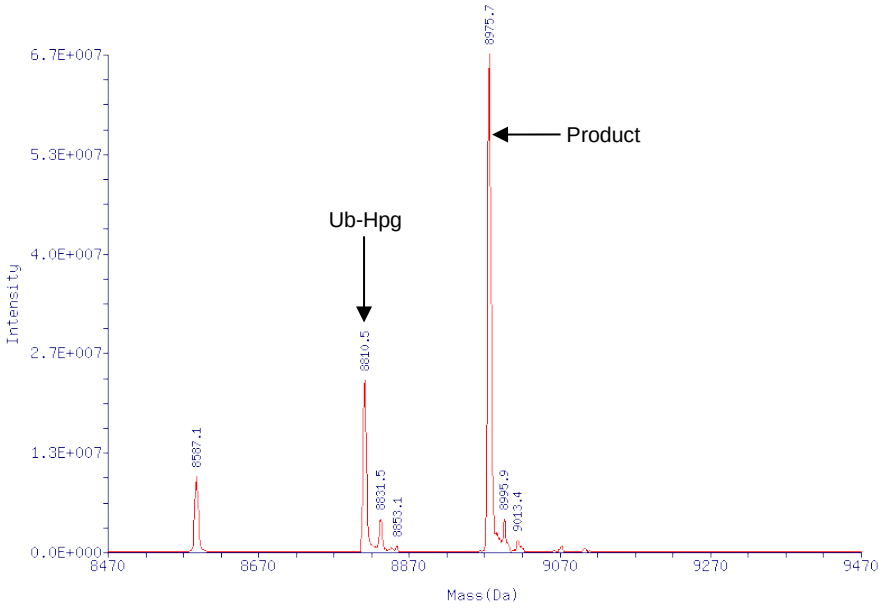
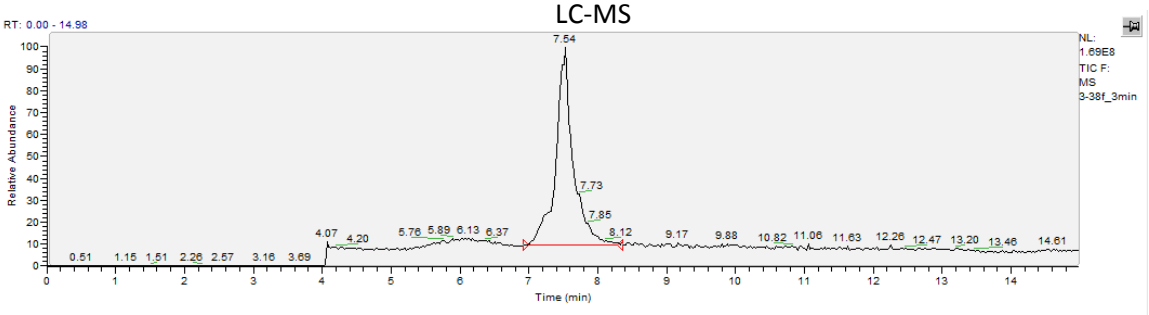
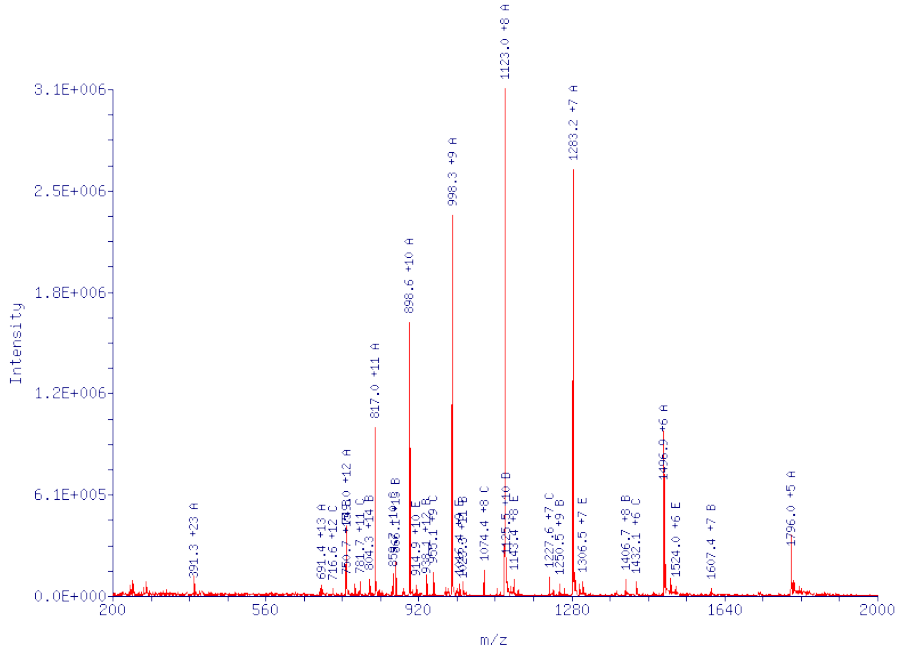


Table 2, entry 7 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

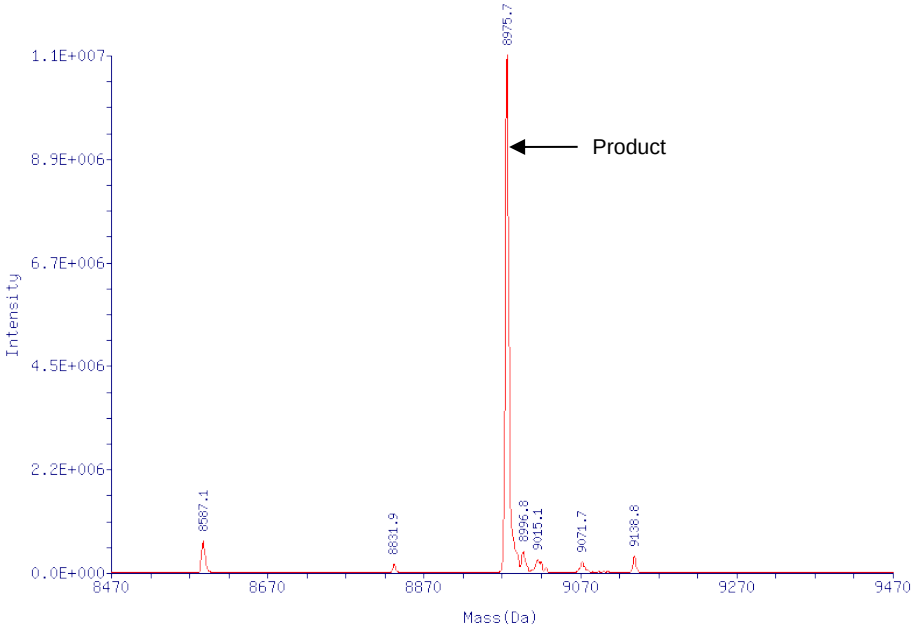
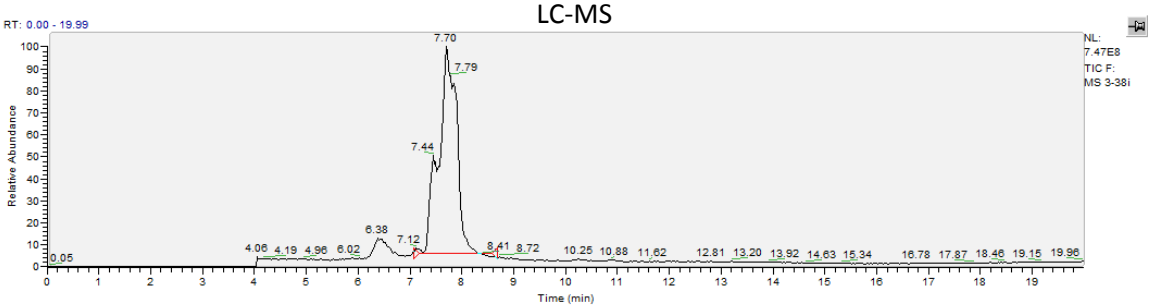
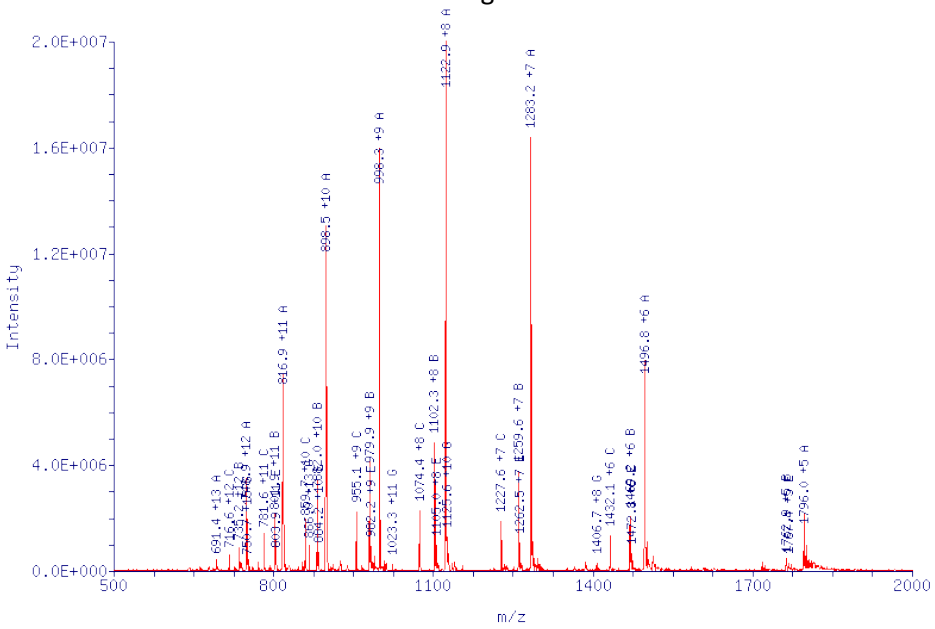


Table 2, entry 8 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

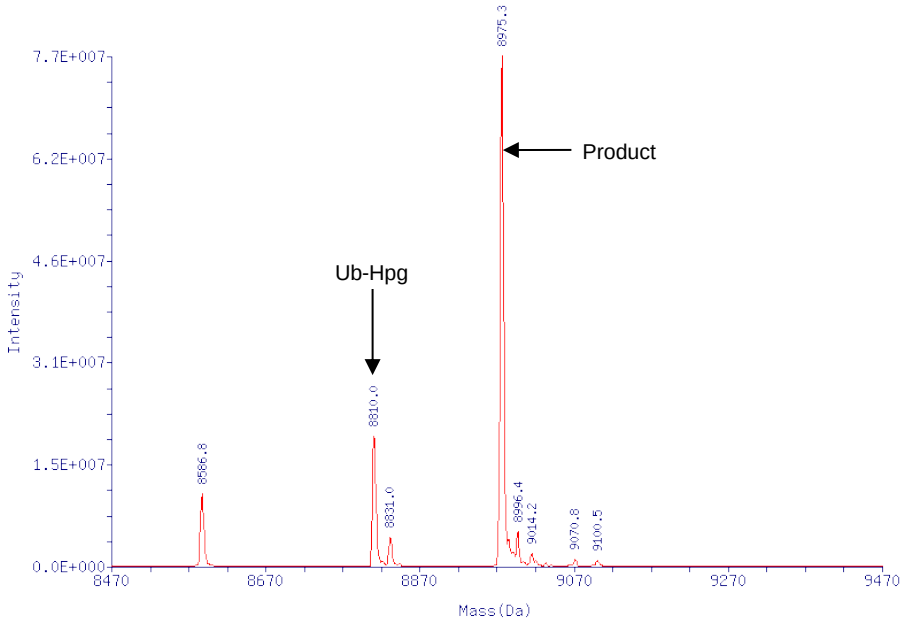
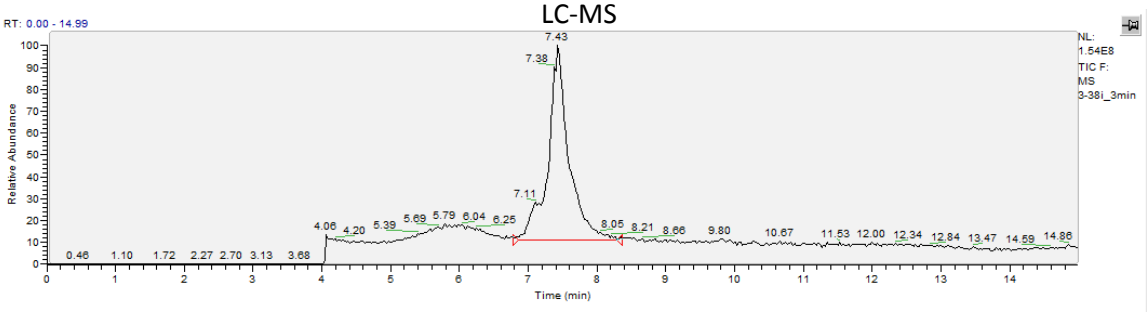
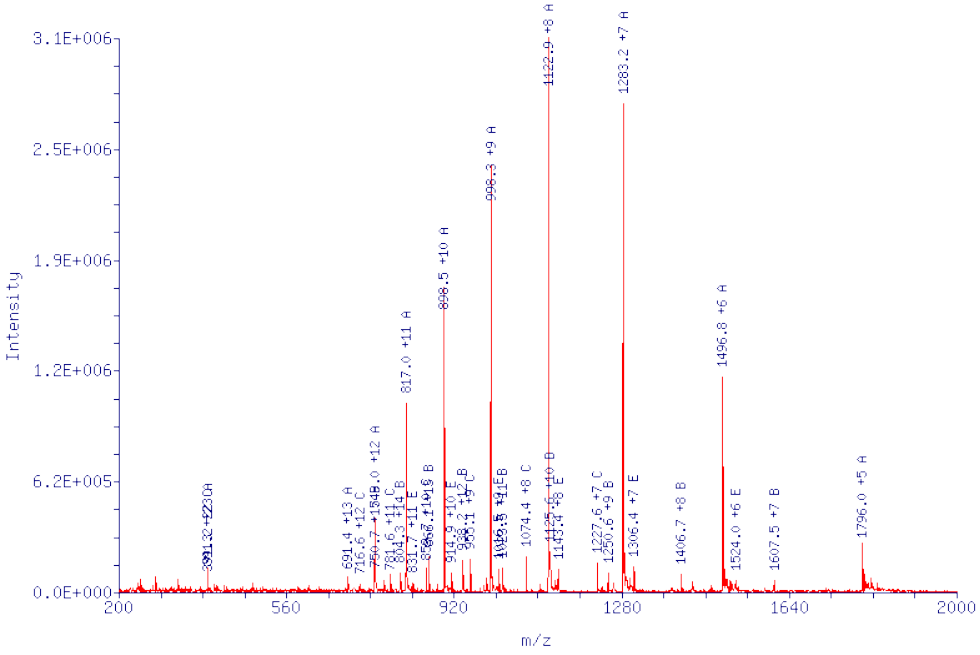


Table 2, entry 8 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

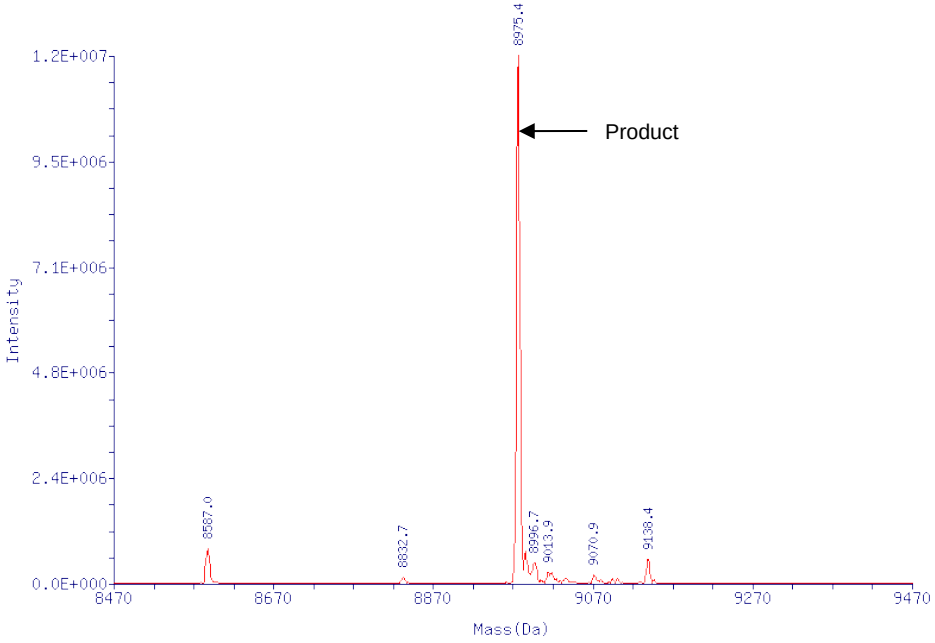
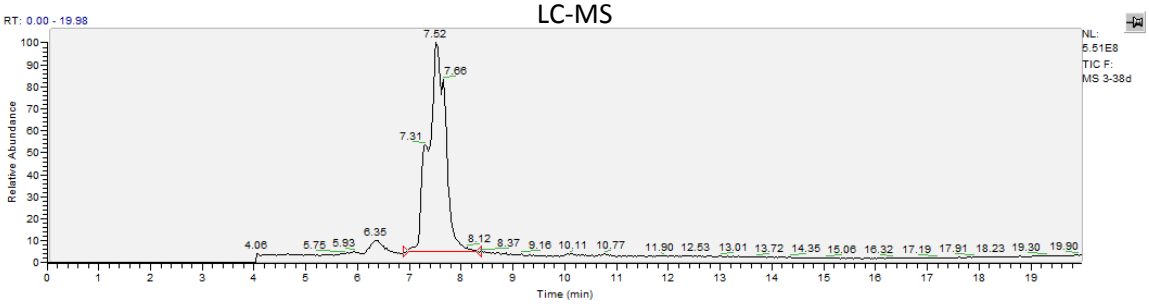
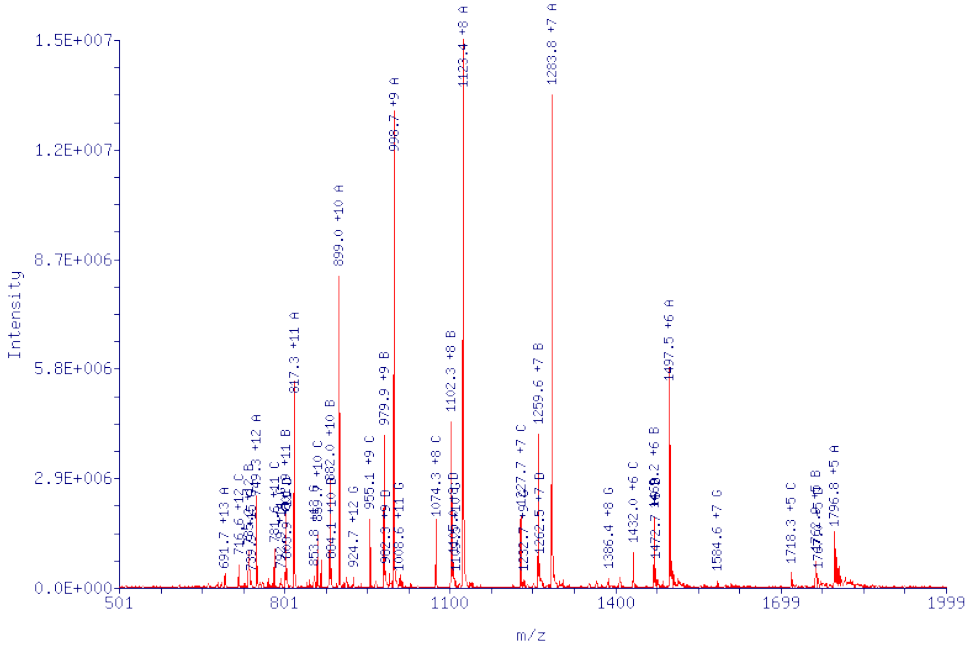


Table 2, entry 9 (10 s)

LC-MS




Charge ladder

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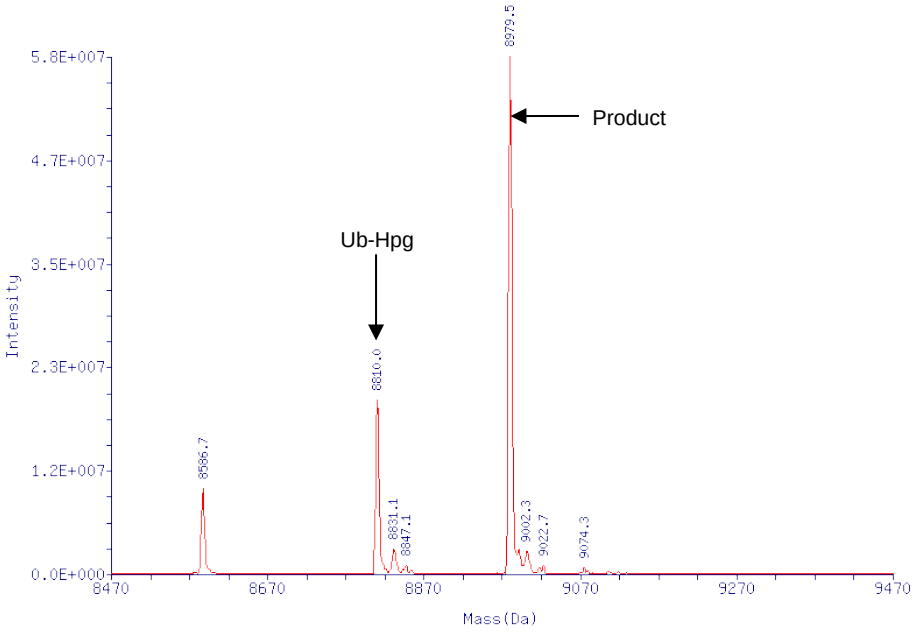
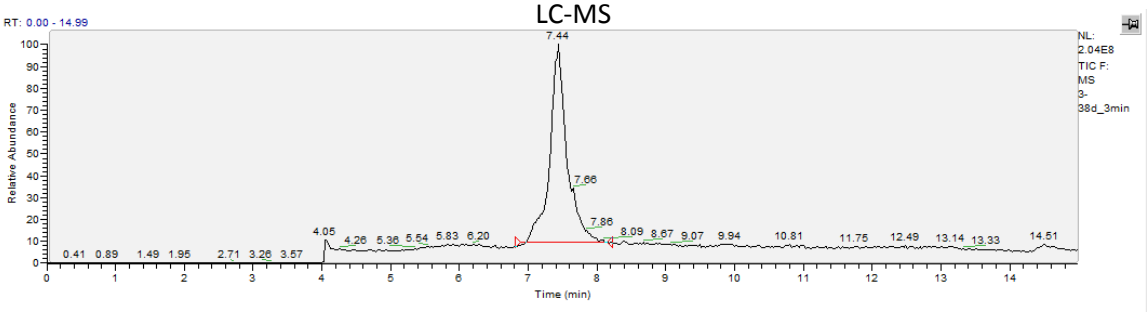
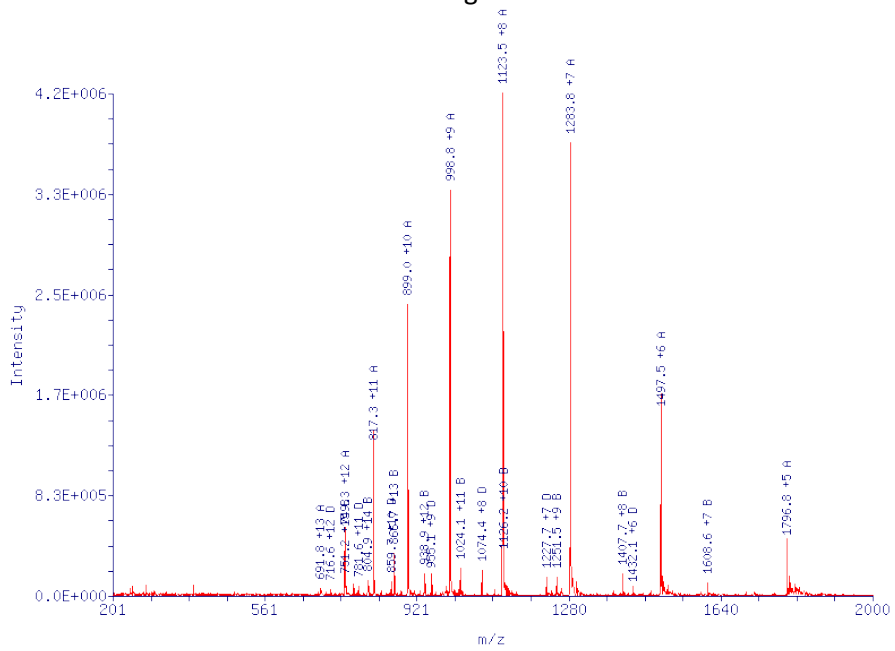


Table 2, entry 9 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

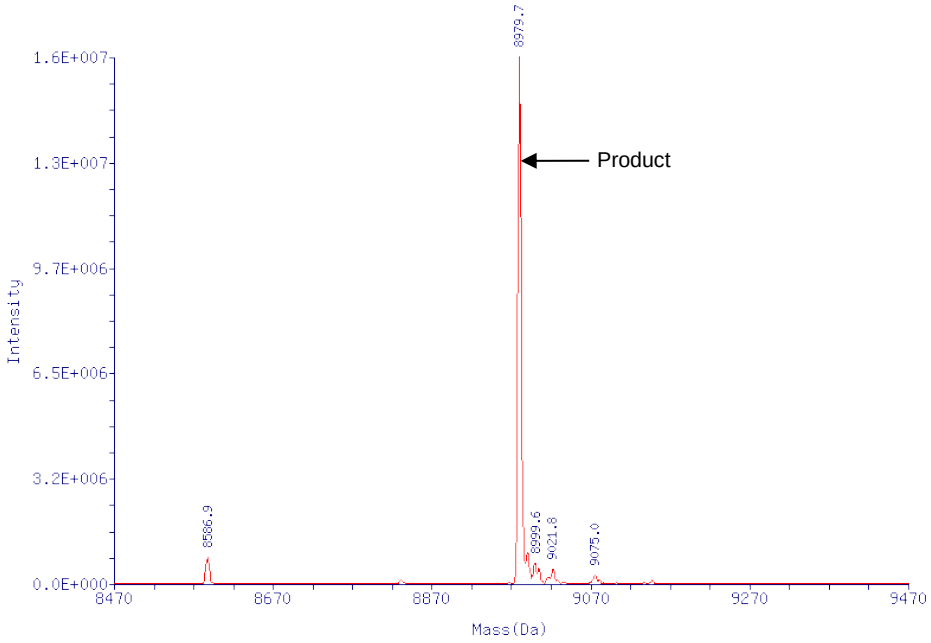
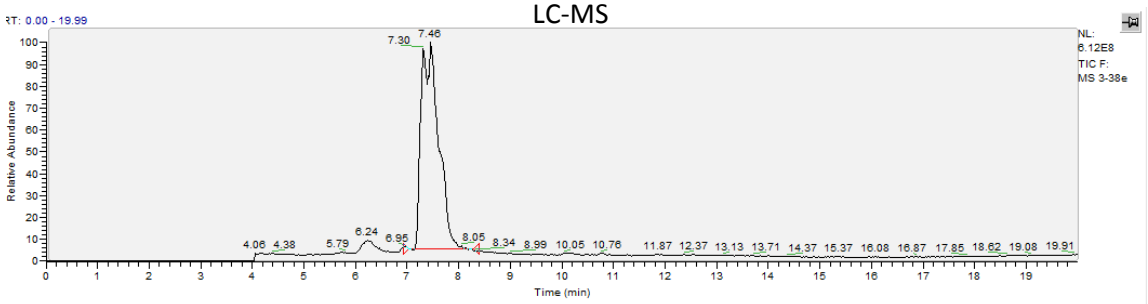
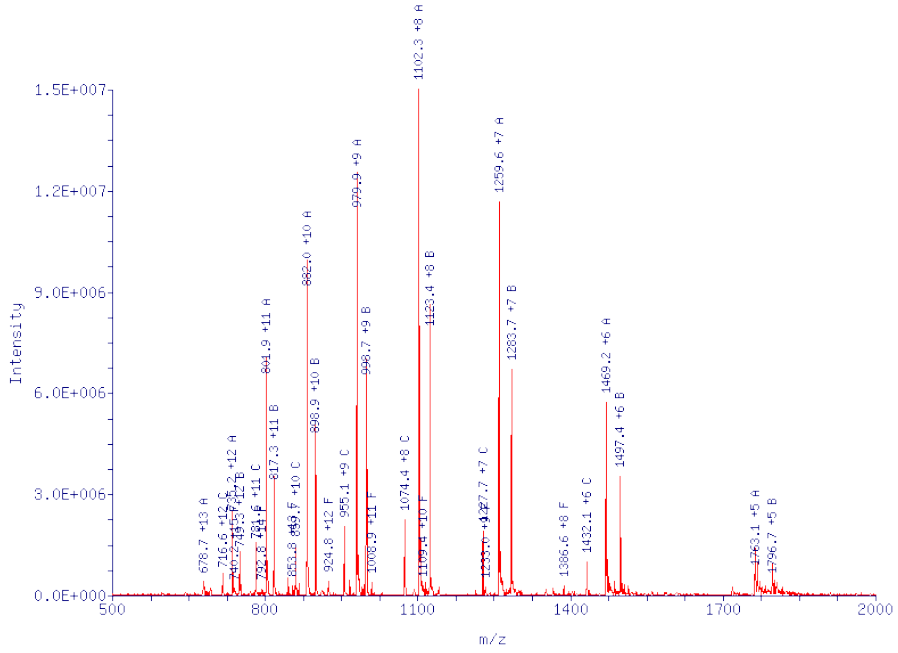


Table 2, entry 10 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

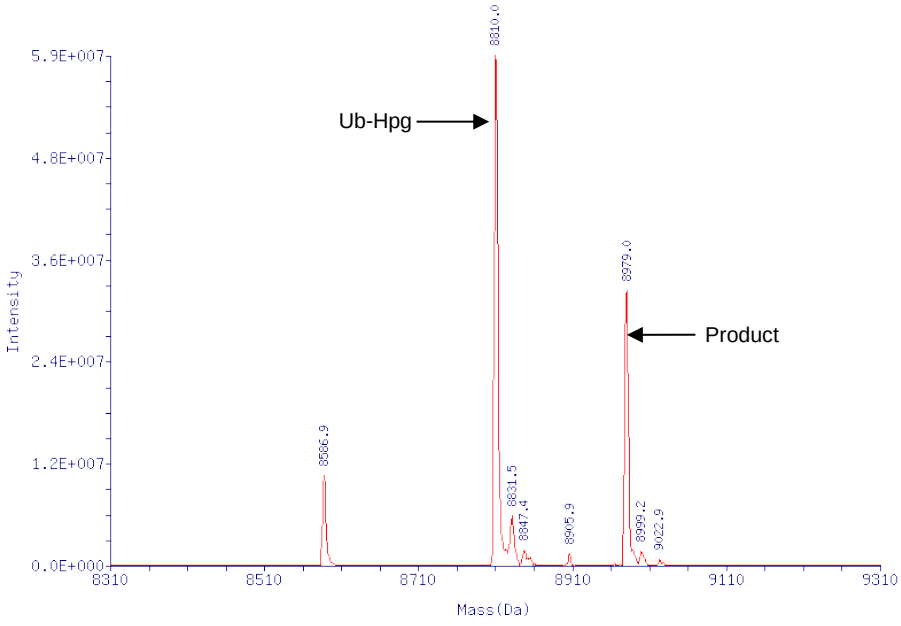
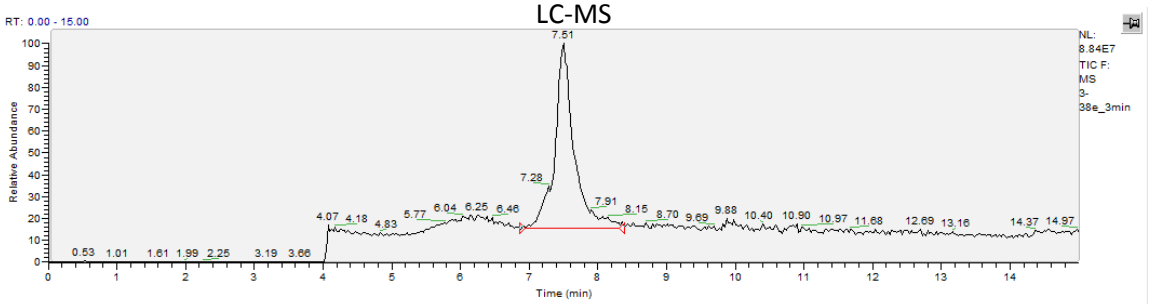
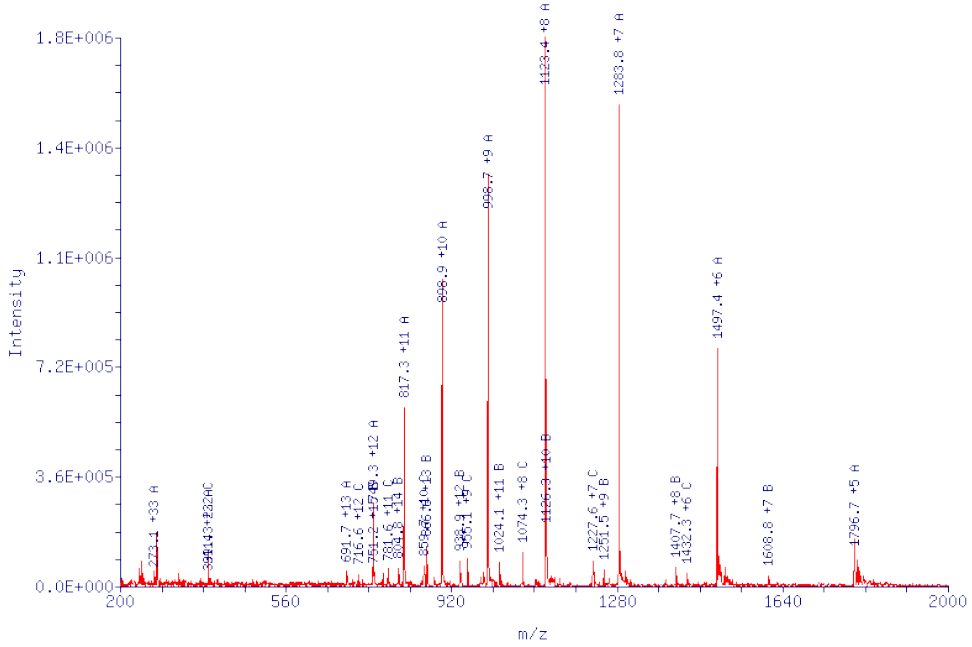


Table 2, entry 10 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

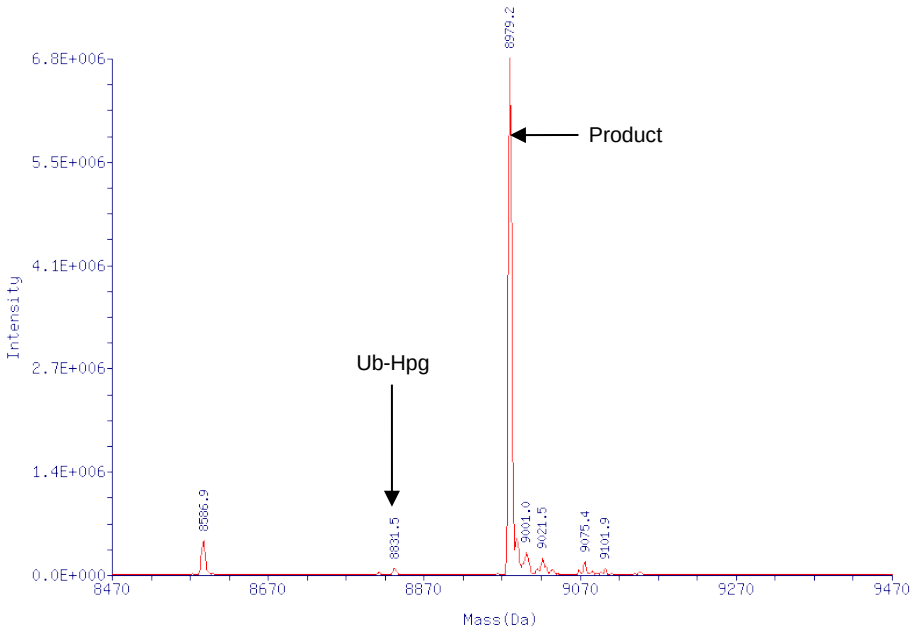
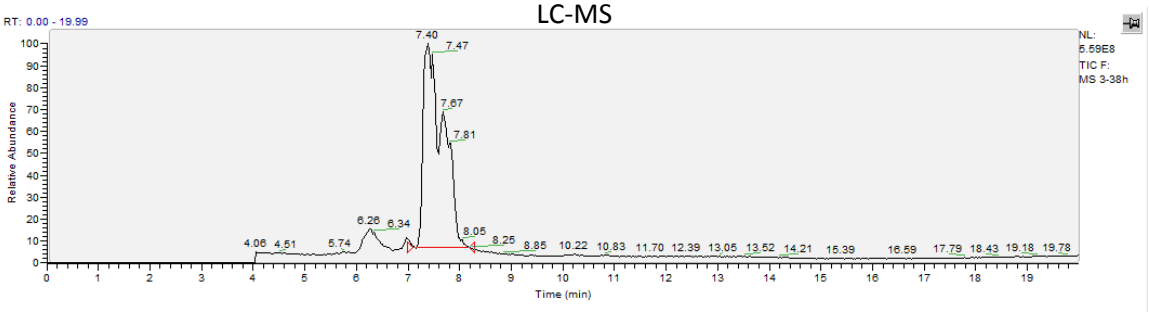
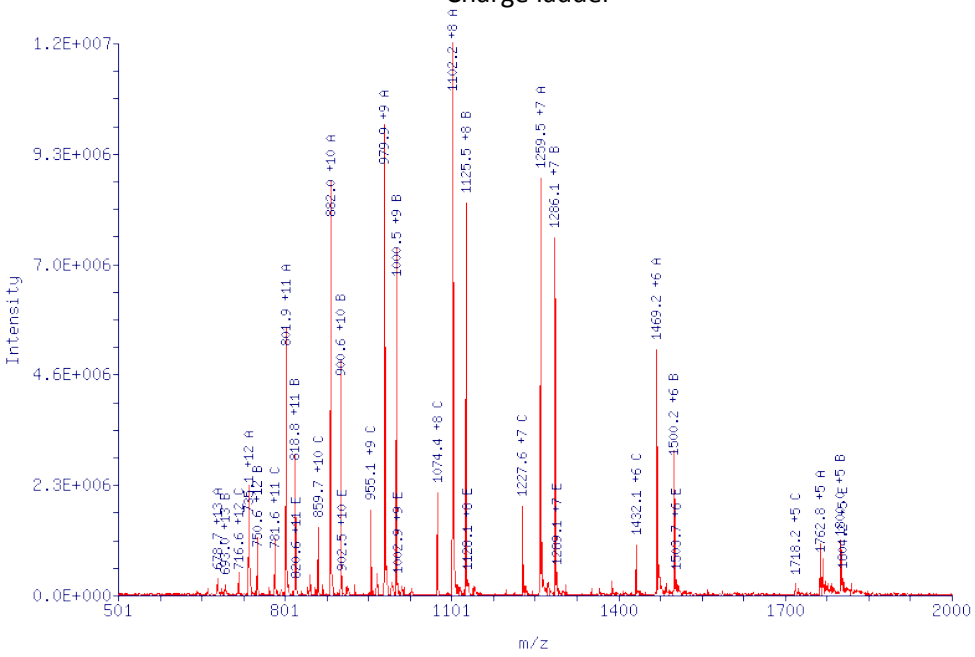


Table 2, entry 11 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

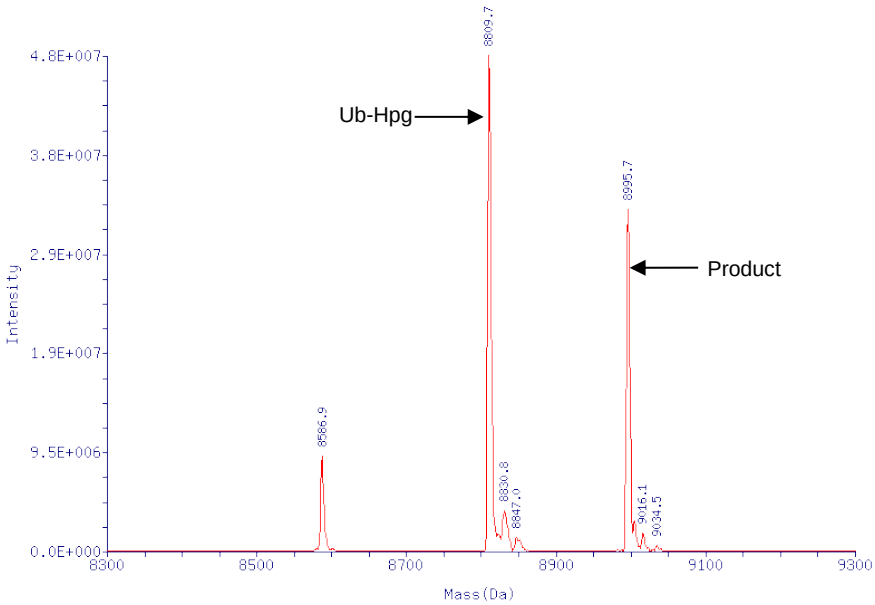
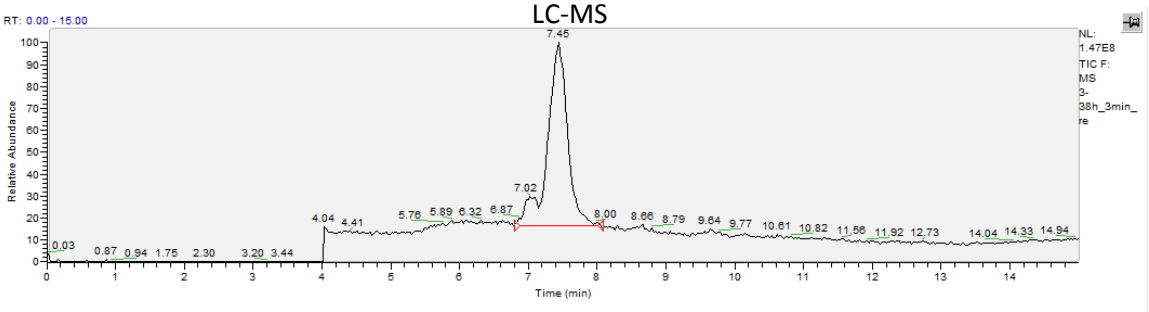
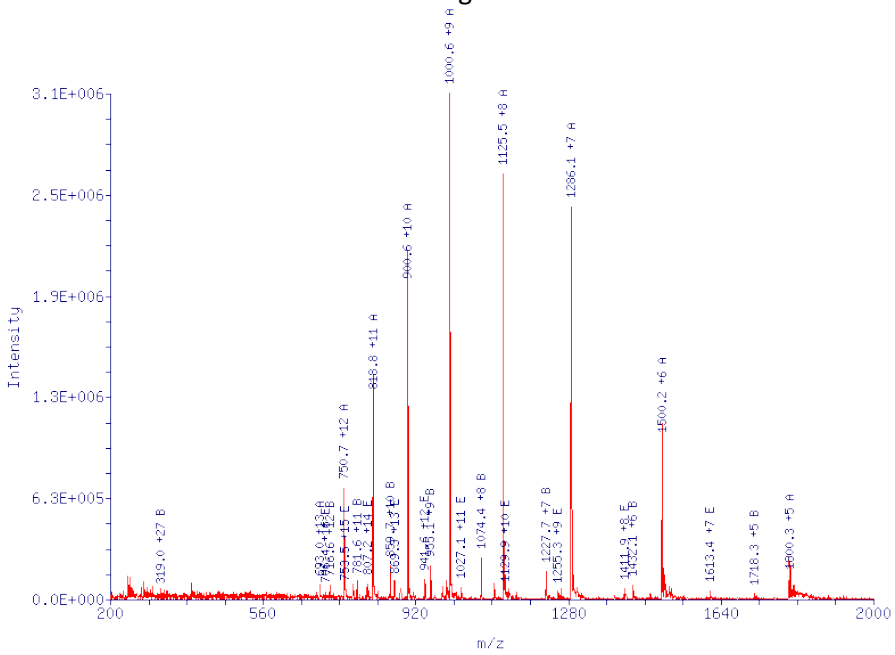


Table 2, entry 11 (3 min)

LC-MS




Charge ladder




Deconvoluted mass

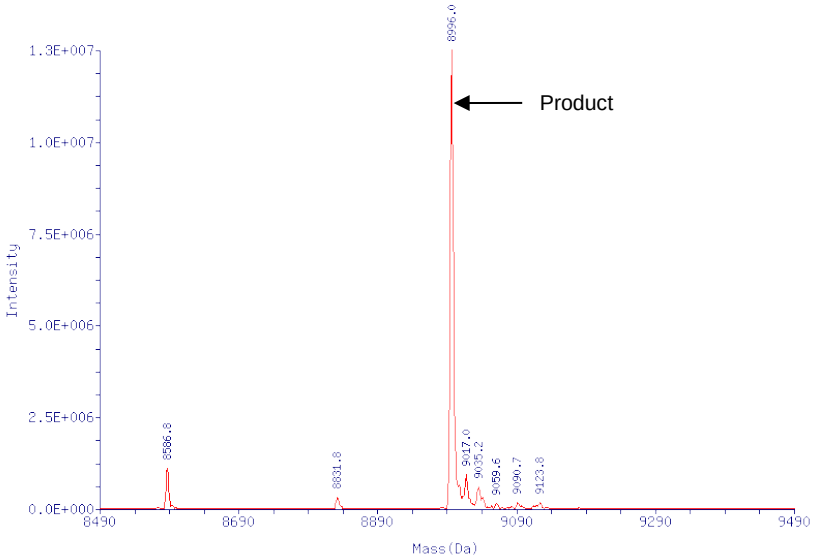
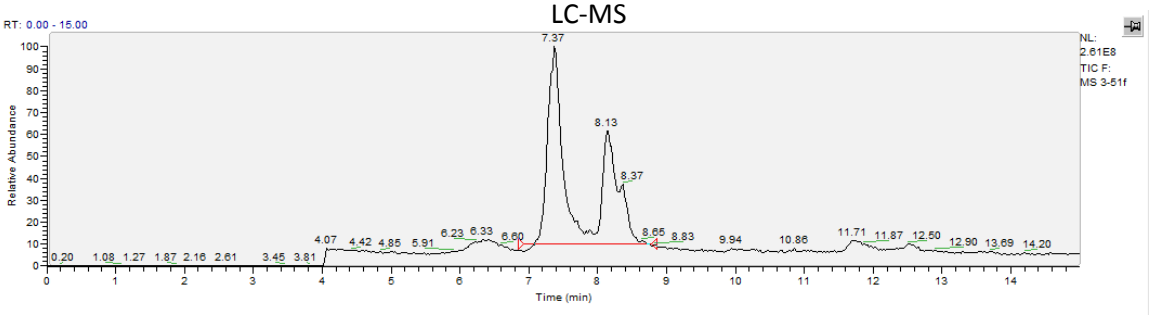
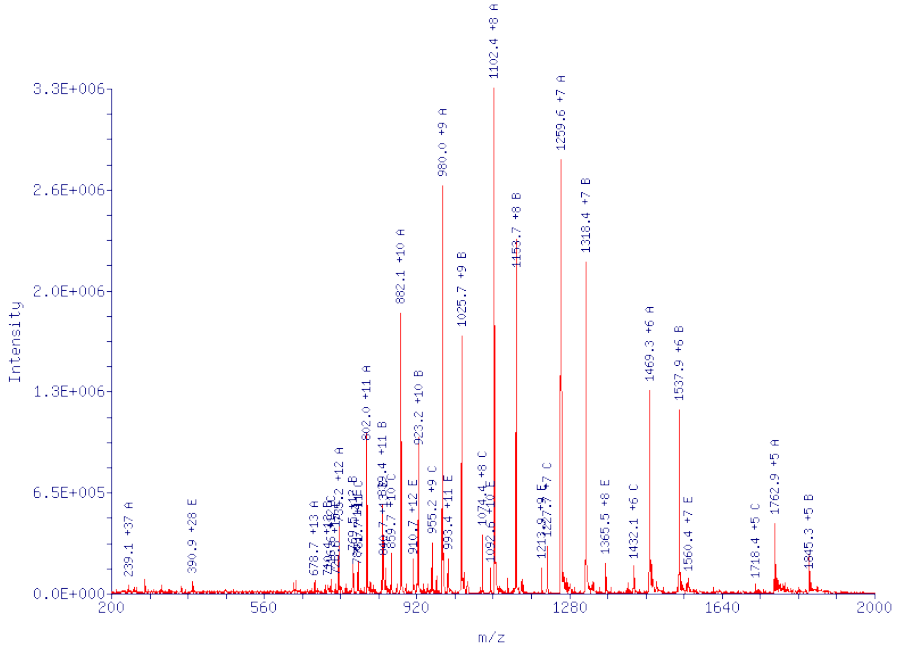


Table 2, entry 12 (10 s)

LC-MS




Charge ladder




Deconvoluted mass

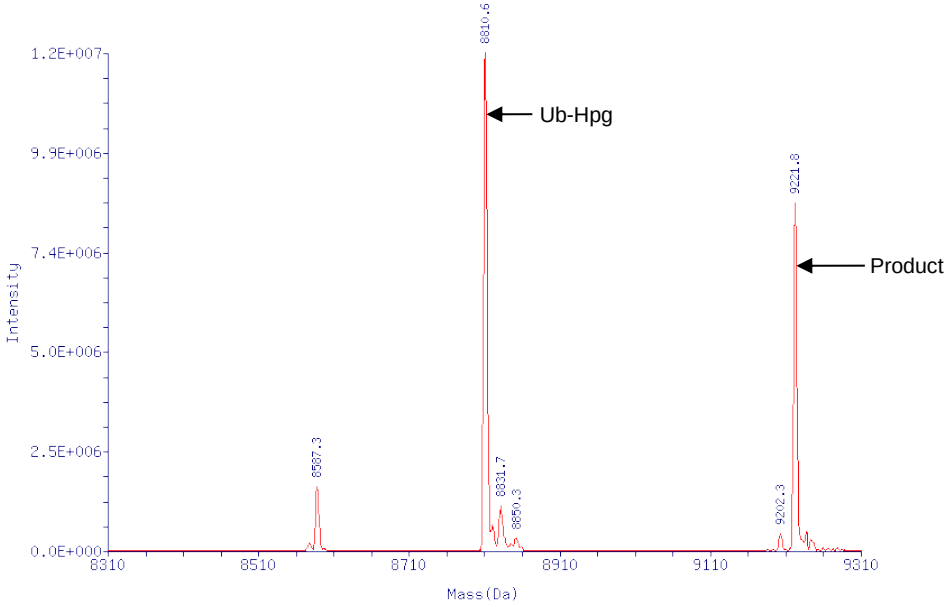
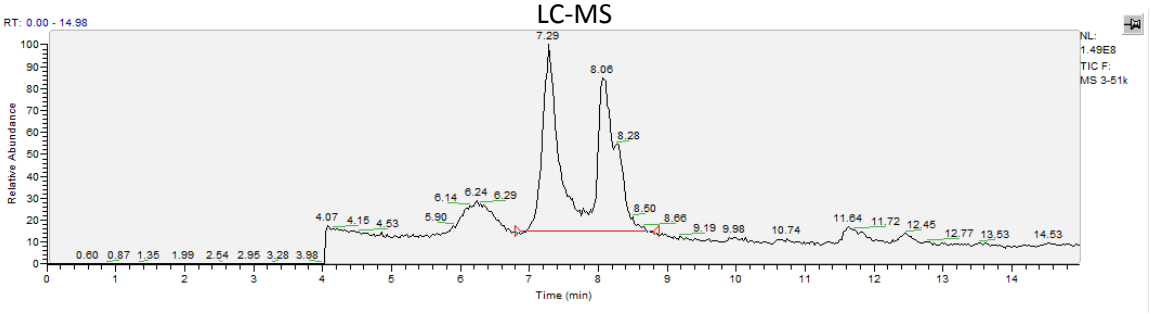
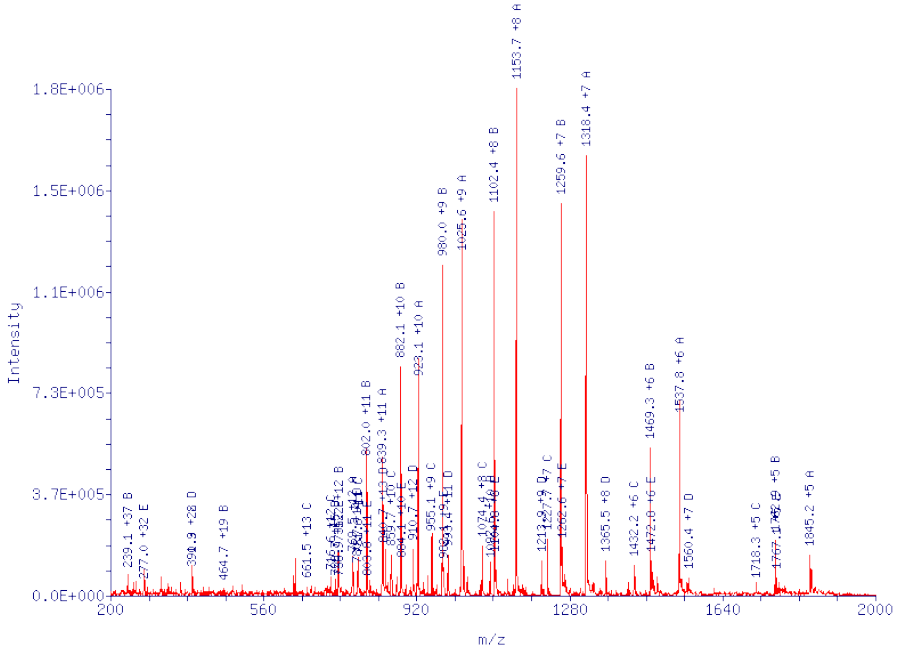


Table 2, entry 12 (3 min)

LC-MS




Charge ladder




Deconvoluted mass