

Supporting information

for

**Fast reductive defluorination of branched perfluorooctane
sulfonic acids by cobalt phthalocyanine: Electrochemical
studies and mechanistic insights**

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das.biswanath85@gmail.com (Dr. Biswanath Das).

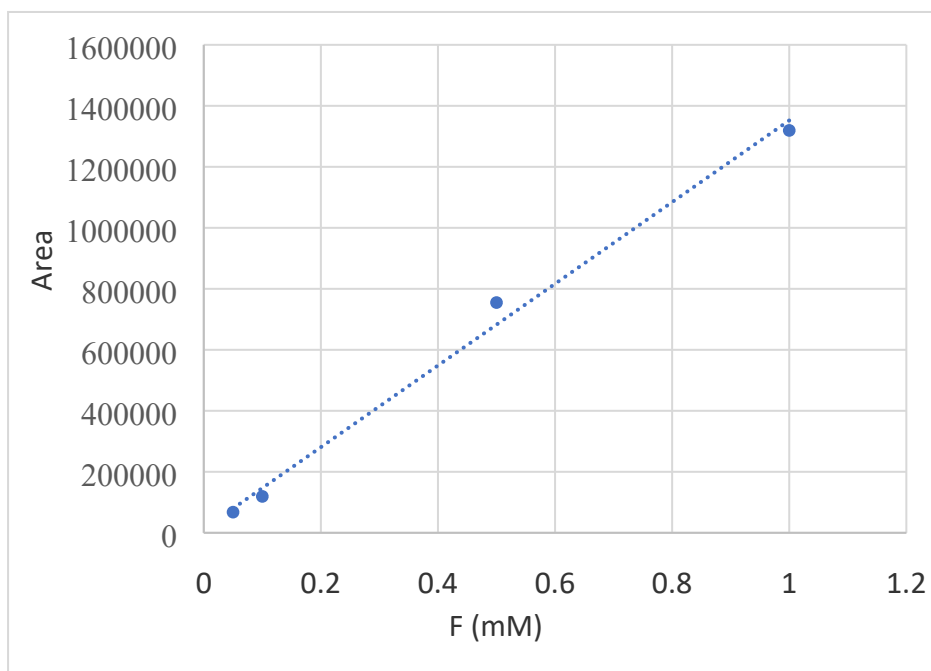


Fig. S1. Calibration curve of fluoride concentration.

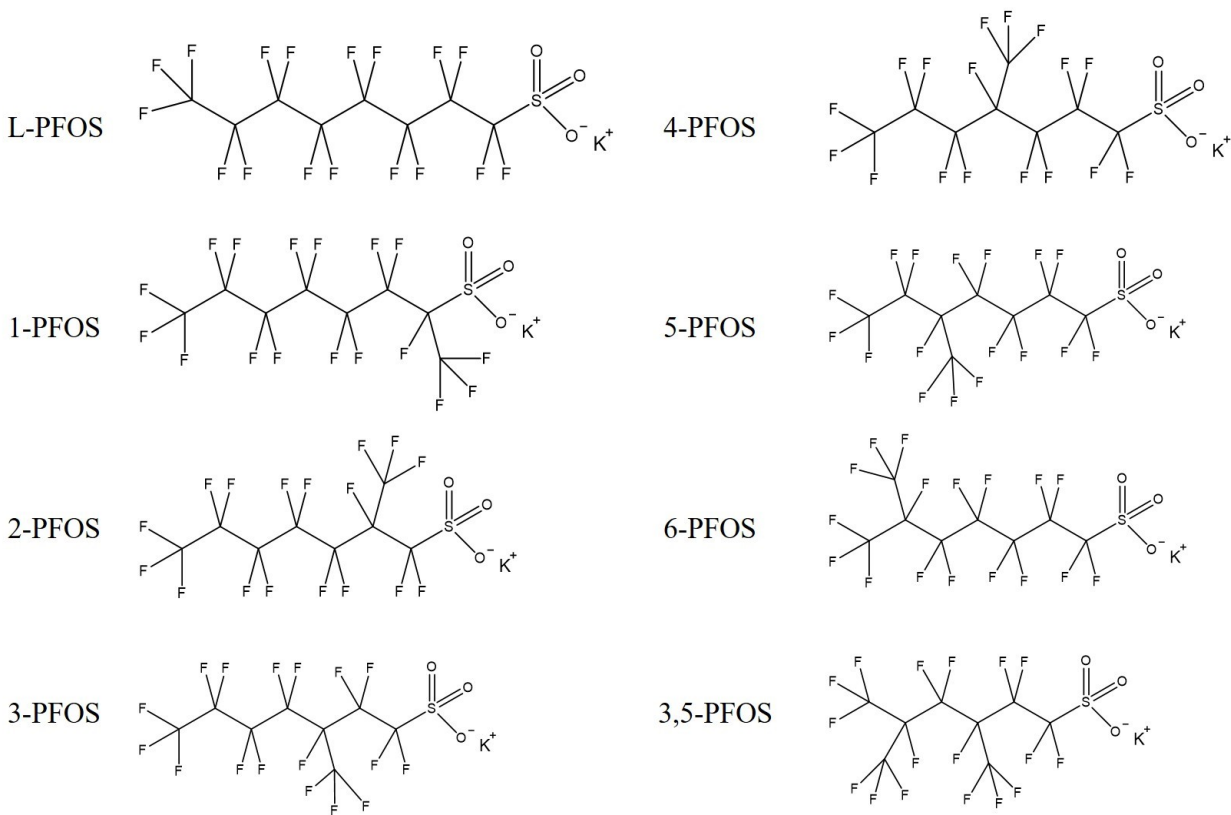
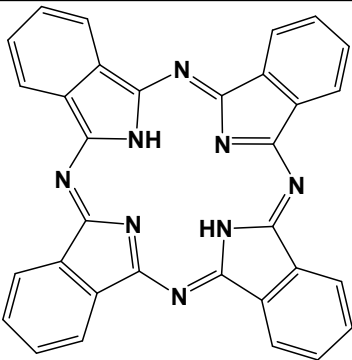
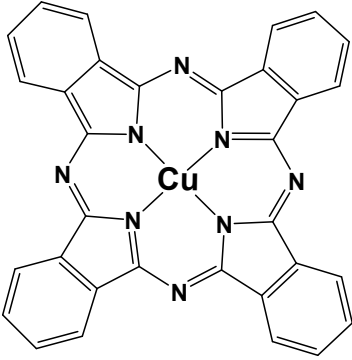
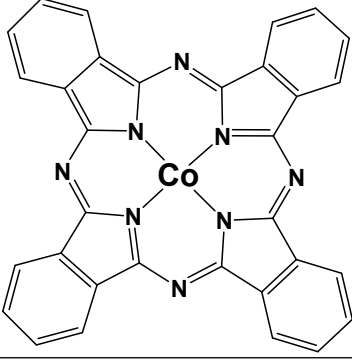
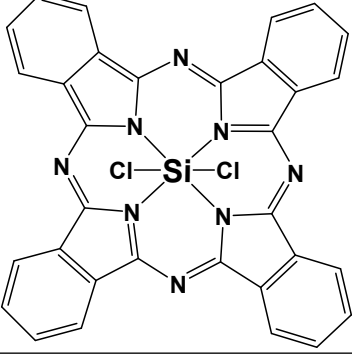
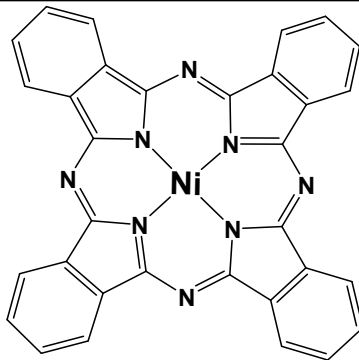


Fig. S2. Chemical structures of linear and branched isomers of PFOS.

Table S1. Chemical and structural information of the used catalysts in this study.

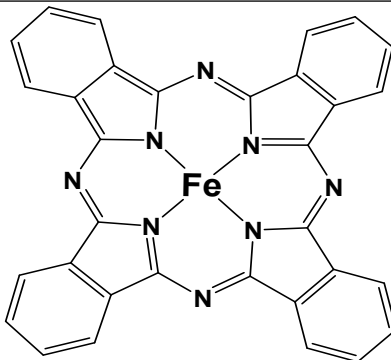
Name, symbol	Chemical structure	CAS and Supplier
29H,31H-Phthalocyanine, Pc		574-93-6 by sigma-Aldrich
Copper ^{II} phthalocyanine, CuPc		147-14-8 by sigma-Aldrich
Cobalt ^{II} phthalocyanine, CoPc		3317-67-7 by sigma-Aldrich
Silicon phthalocyanine dichloride, SiPc		19333-10-9 by sigma-Aldrich

Nickel^{II} phthalocyanine, NiPc



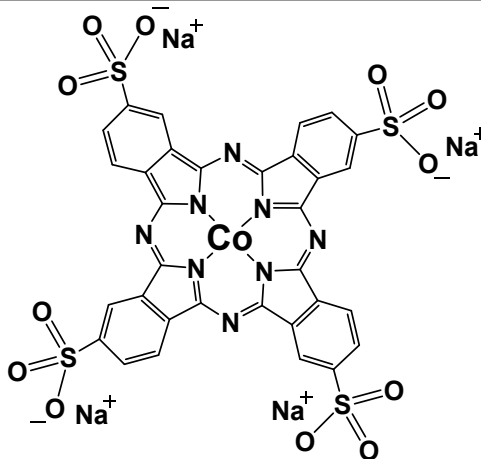
14055-02-8 by sigma-Aldrich

Iron^{II} phthalocyanine, FePc



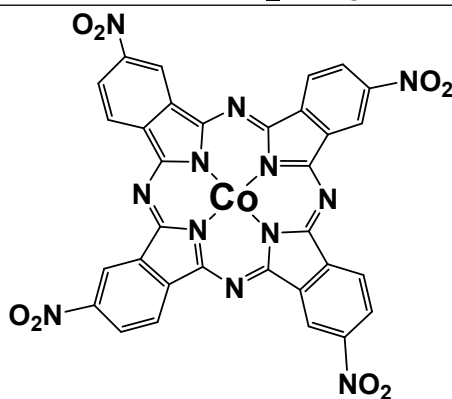
132-16-1 by sigma-Aldrich

Sodium cobalt^{II} tetrasulfophthalocyanine, CoTSPc

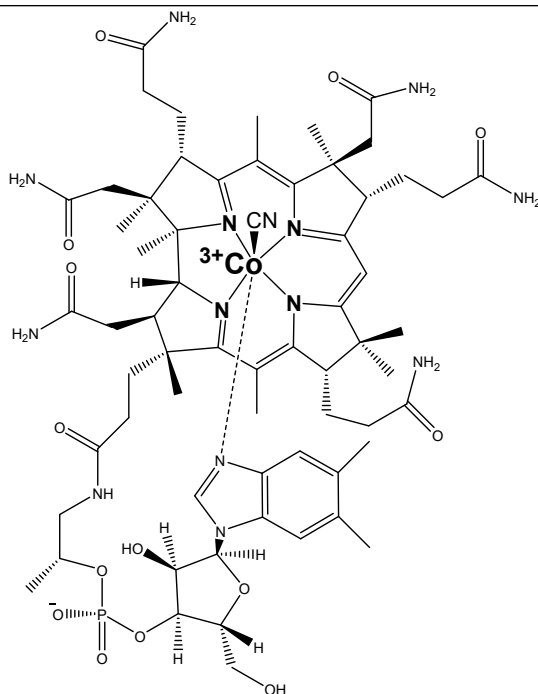


14586-48-2
Synthesized in-house

Cobalt^{II} tetranitrophthalocyanine, CoTNPc



27680-28-0
Synthesized in-house

Cyanocob^{III}alamin, VB₁₂

68-19-9 by sigma-Aldrich

Table S2. Parameter details for PFOS branched and linear isomers detection in LC–MS/MS.

Isomer name	6-methyl PFOS	5 and 3-methyl PFOS	4-methyl PFOS	3,5-dimethyl PFOS	1 and 2-methyl PFOS	L-PFOS
Precursor (m/z)	499	499	499	499	499	499
Product (m/z)	169	280	330	280	99	80
Dwell time (msec)	5	5	5	5	5	3
CE	35	35	35	35	40	41

Table S3. Isomer composition of technical PFOS used in this study based on LC–MS/MS analysis.

Isomer name	6-methyl PFOS	5-methyl PFOS	4-methyl PFOS	3-methyl PFOS	3,5-dimethyl PFOS	1 and 2-methyl PFOS	L-PFOS	Other isomers
Composition (%)	5.81	4.16	1.90	3.41	1.19	1.39	80.27	1.85

Synthesis of sodium cobalt^{II} tetrasulfophthalocyanine (CoTSPc)

Cobalt^{II} phthalocyanine (0.51 g, 0.90 mmol) in oleum (10 mL; 20% SO₃) was heated at 145 °C for 3 h. After the reaction mixture was cooled to room temperature, it was poured into cold distilled water (200 mL). Sodium chloride was then added to the solution and the dark blue precipitate was collected by vacuum filtration, washed with ethanol and dried under vacuum to give the crude product. The crude product was heated at reflux in ethanol (20 mL) for 2 h. The solution mixture

was allowed to cool to room temperature. The dark blue precipitate was collected by vacuum filtration, washed with hot ethanol and dried under vacuum to give the product as a dark blue solid (0.61 g, 0.62 mmol, 69%); mp >300.0 °C; IR (ATR): ν_{\max} 3397, 3069, 2108, 1774, 1719, 1637, 1510, 1489, 1399, 1365, 1321, 1103, 1029, 938, 803, 744, 696 cm^{-1} . The spectroscopic data agree with the literature reported values ^{1,2}.

Synthesis of cobalt^{II} tetranitrophthalocyanine (CoTNPc)

To a suspension of cobalt sulfate heptahydrate (2.22 g, 7.90 mmol), 4-nitrophthalonitrile (5.48 g, 31.63 mmol), ammonium chloride (1.80 g, 33.73 mmol), sodium hydroxide (1.46 g, 36.50 mmol) and sodium methoxide (0.17 g, 3.05 mmol) in dimethyl sulfoxide (17 mL) was heated at 180 °C for 5 h. The dark blue reaction mixture was then allowed to cool to room temperature and the dark blue precipitate was collected by vacuum filtration and washed thrice with methanol and thrice with water to give the product as a dark blue solid (3.46 g, 4.61 mmol, 58%); mp >300.0 °C; IR (ATR): ν_{\max} 3452, 3068, 2118, 1910, 1703, 1594, 1512, 1320, 1133, 1083, 901, 842, 727 cm^{-1} ; Elemental analysis: Found: C, 48.91; H, 1.84; N, 21.85%; $\text{C}_{32}\text{H}_{12}\text{N}_{12}\text{O}_8\text{Co}\cdot 2\text{H}_2\text{O}$ requires: C, 48.80; H, 2.05; N, 21.35% ³.

Preparation of catalyst stock solution

The stock solution preparation was conducted with the degassed solvents in an anaerobic chamber (Coy Lab Inc., >95% N_2 , <5% H_2). 5 mM stock solution of MPcS and VB_{12} catalysts were anaerobically dissolved in N-methyl-2-pyrrolidone (NMP).

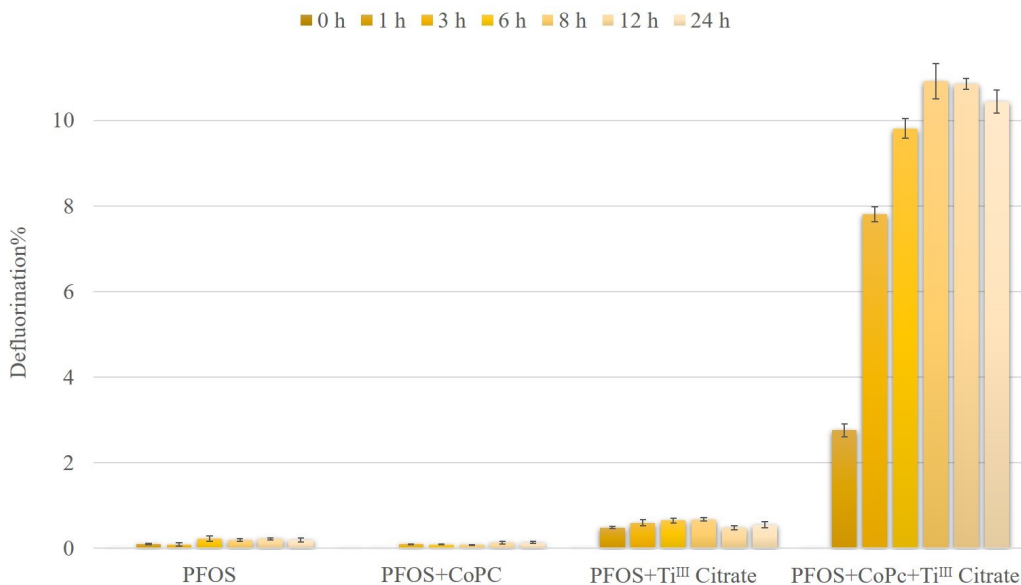


Fig. S3. Time course of technical PFOS defluorination under different experimental conditions at 65 °C and pH 9.0 within 24 hours. Experimental conditions: technical PFOS (0.1 mM), CoPc (0.25 mM), Ti^{III} citrate (40 mM), and carbonate buffer (85 mM) in Milli Q water.

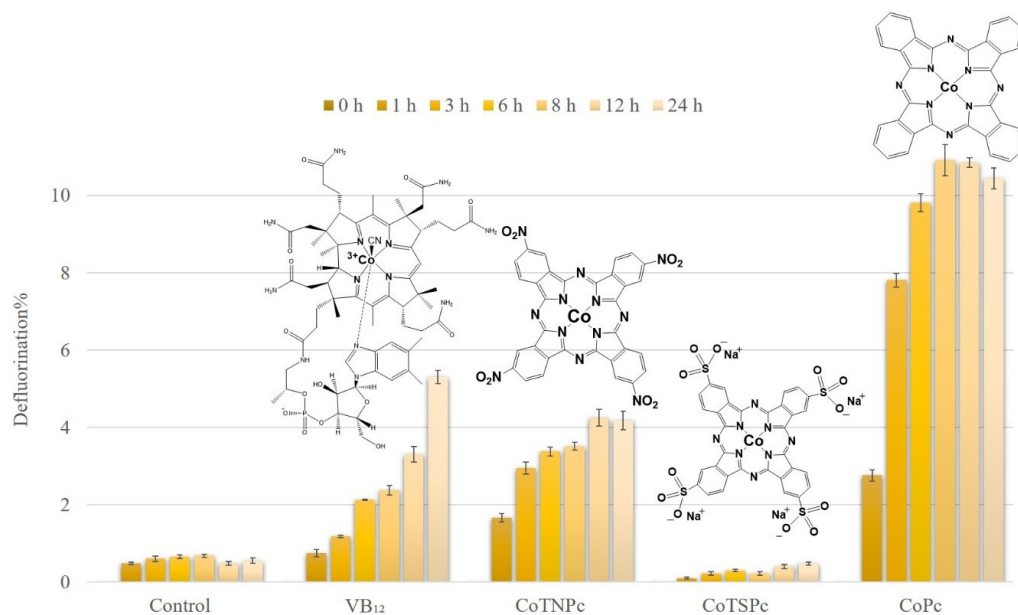


Fig. S4. Time course of technical PFOS defluorination via cobalt phthalocyanine derivatives or VB₁₂ in Ti^{III} citrate at 65 °C and pH 9.0. Experimental conditions: Technical PFOS (0.1 mM), catalyst (0.25 mM), Ti^{III} citrate (40 mM), and carbonate buffer (85 mM) in Milli Q water.

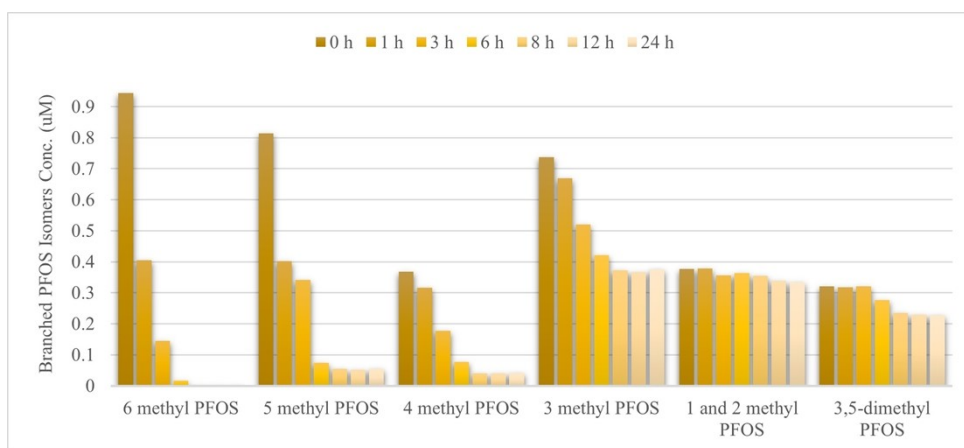


Fig. S5. Time course of branched PFOS isomers degradation in CoPc-Ti^{III} citrate system at 65 °C and pH 9.0. Experimental conditions: Technical PFOS (18.6 μM), catalyst (0.25 mM), Ti^{III} citrate (40 mM), and carbonate buffer (85 mM) in Milli Q water.

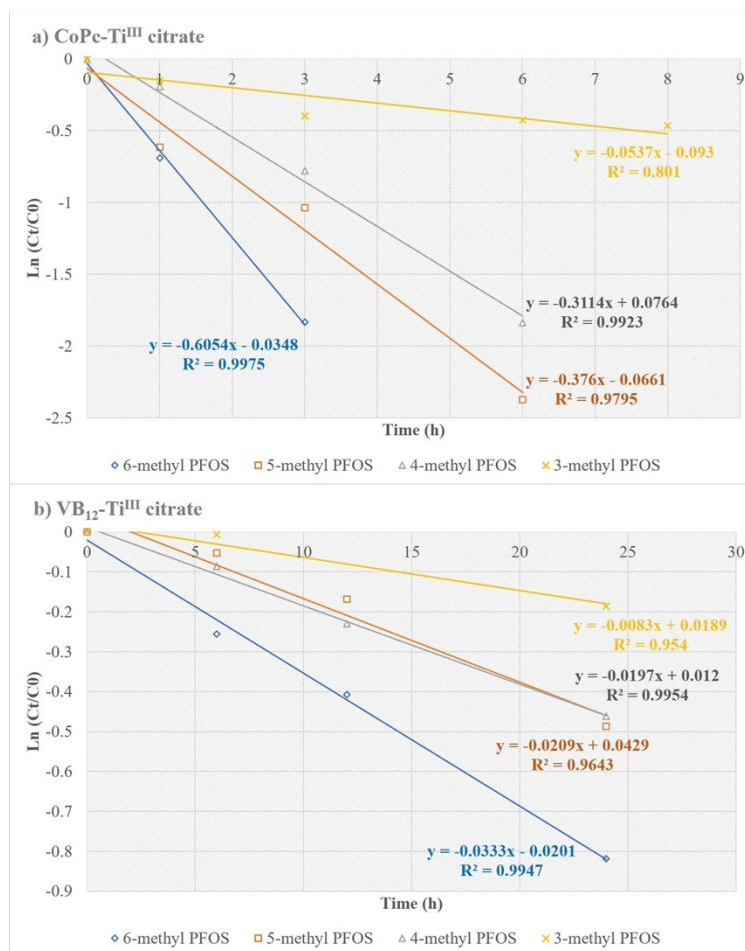
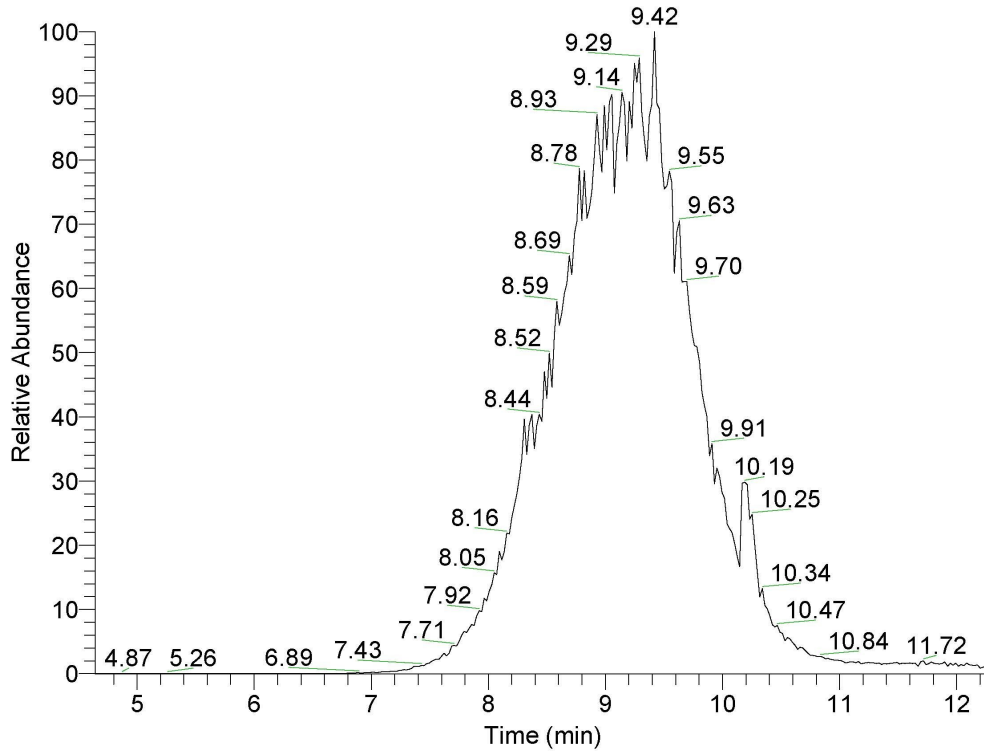
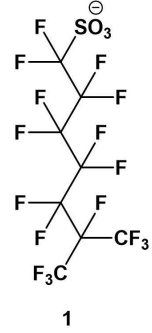


Fig. S6. Natural logarithm of the concentration ratio (C_t/C_0) when times are t and 0 which is related to the specific branched isomers for a) CoPc-Ti^{III} citrate system and b) VB₁₂-Ti^{III} citrate system. Experimental conditions: Technical PFOS (0.1 mM), CoPc/VB₁₂ (0.25 mM), Ti^{III} citrate (40 mM), and carbonate buffer (85 mM) at 65 °C.

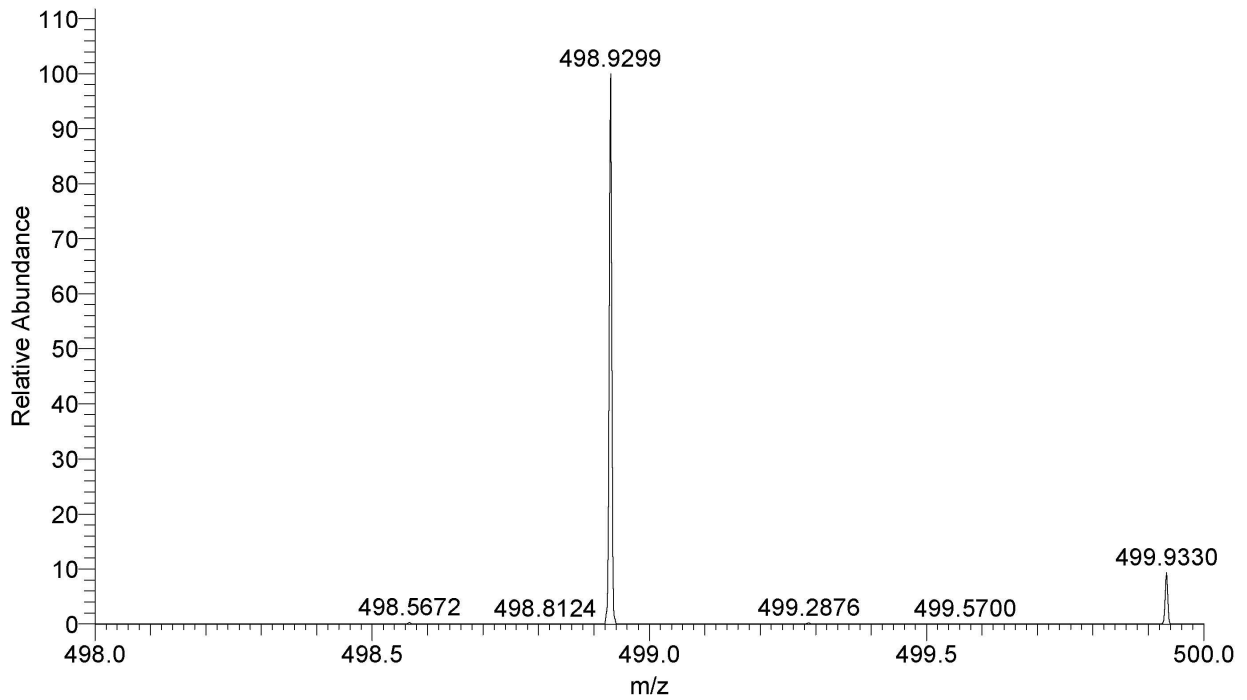
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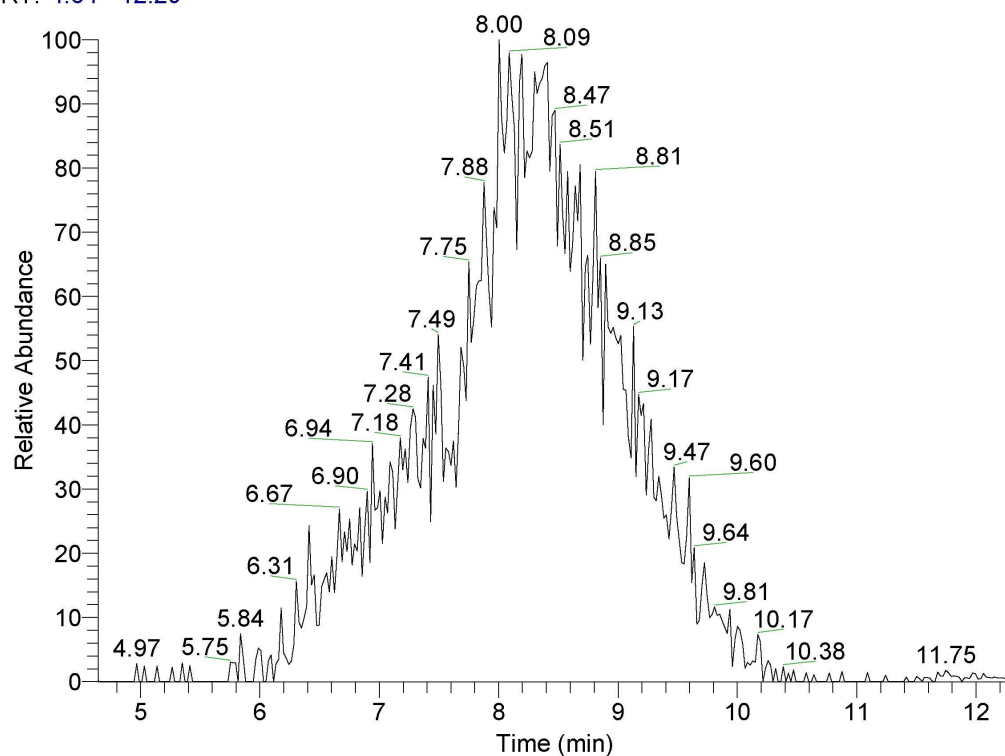
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[85.0000-1275.0000]
MS Stock50ppmPFOS



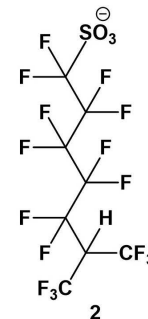
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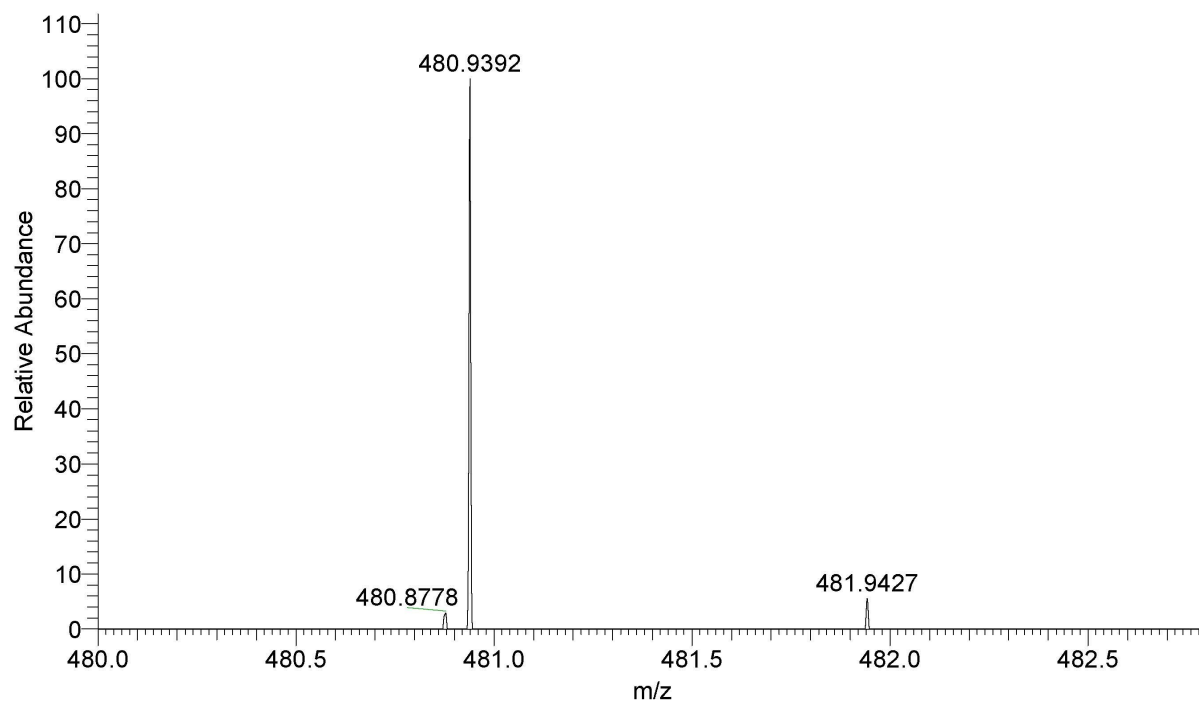
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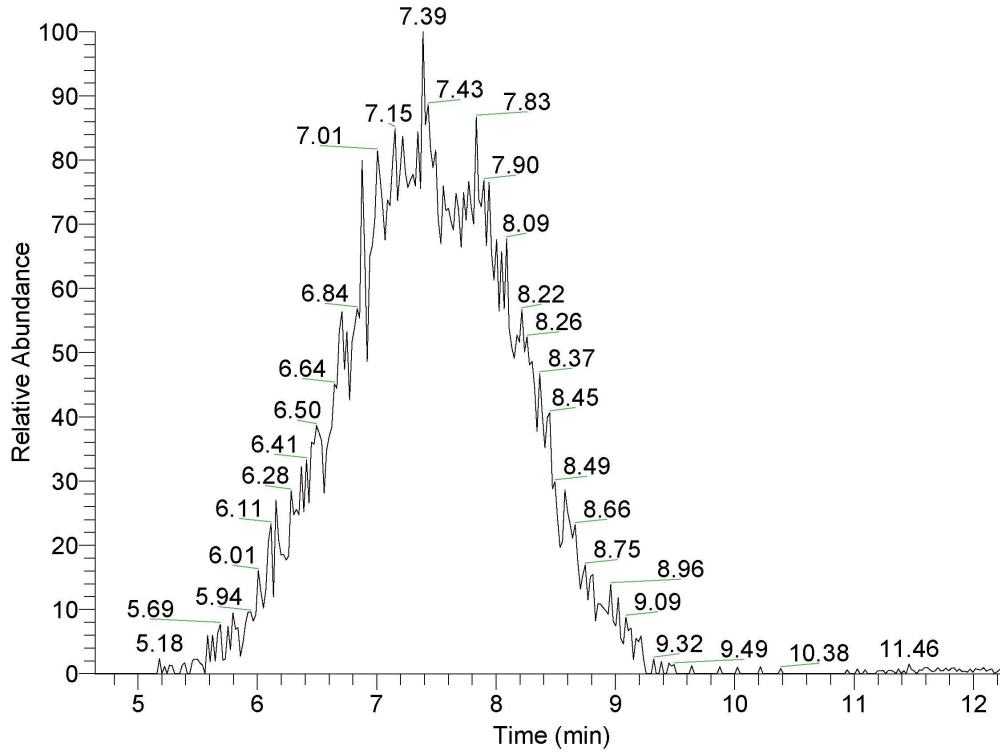
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ms
[85.0000-
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Co-Ti-3h



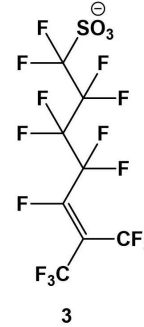
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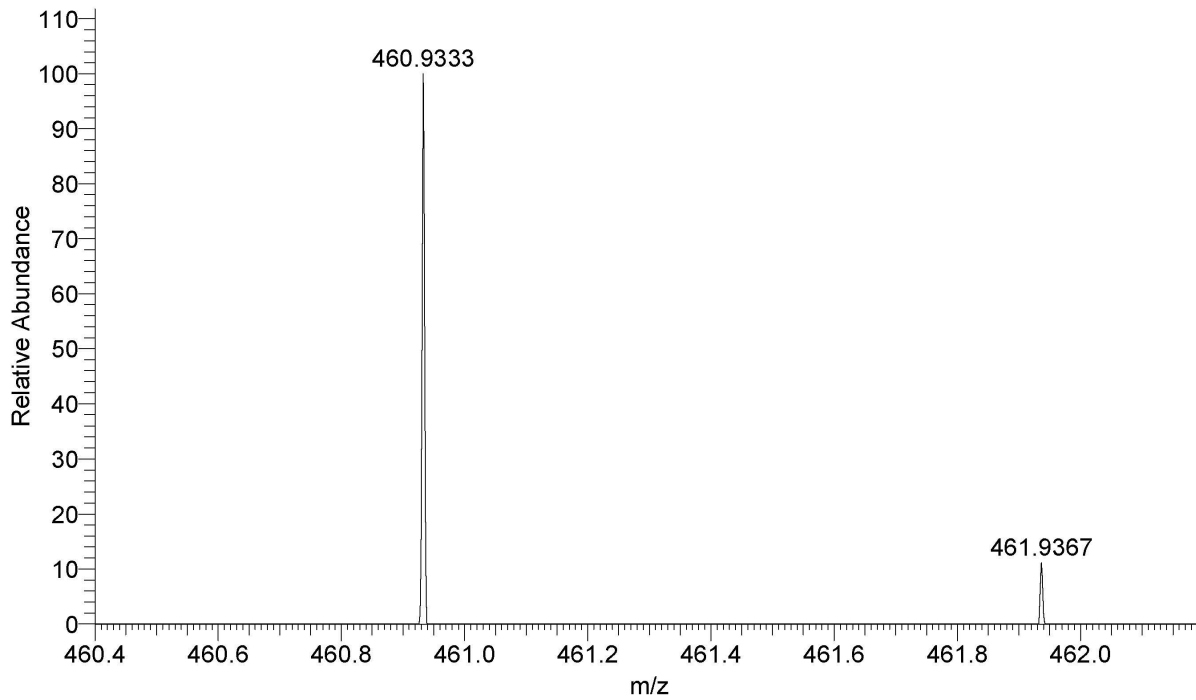
RT: 4.64 - 12.29



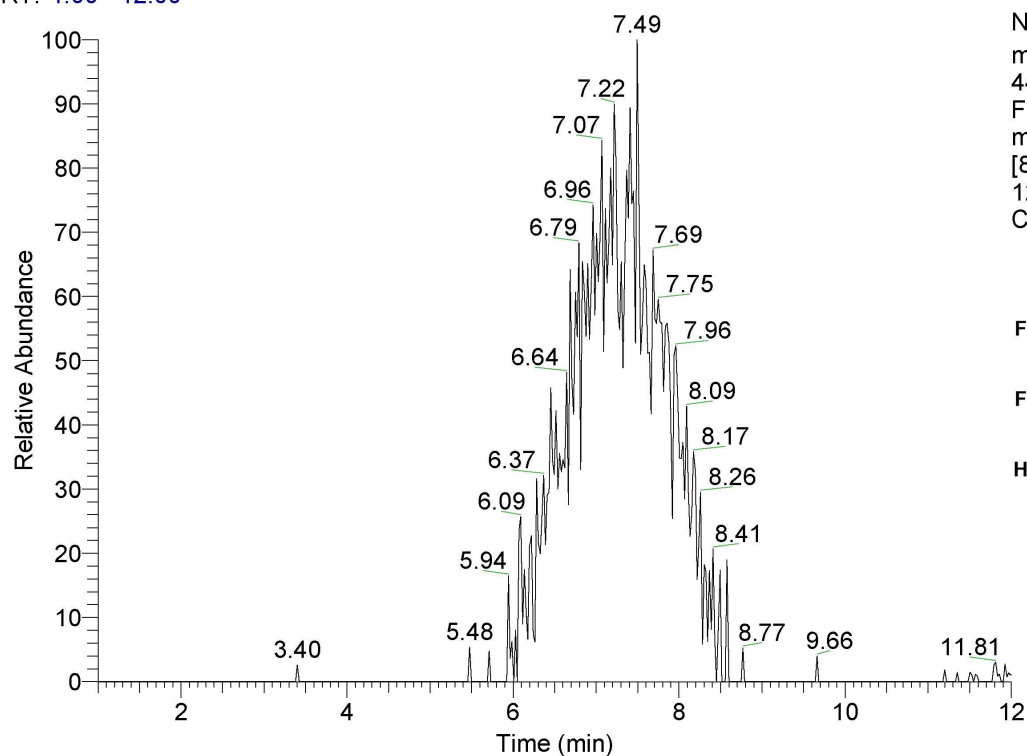
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ms
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Co-Ti-3h



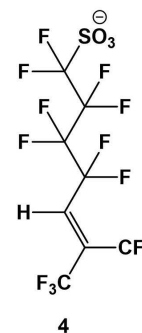
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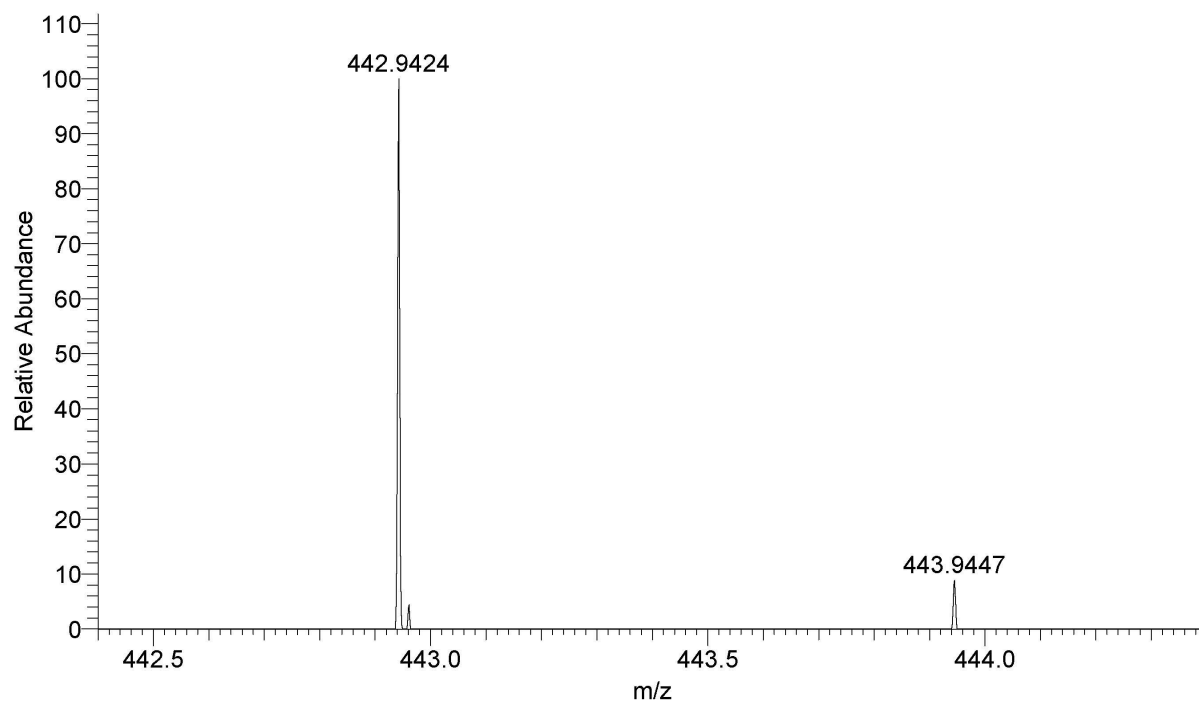
RT: 1.00 - 12.00



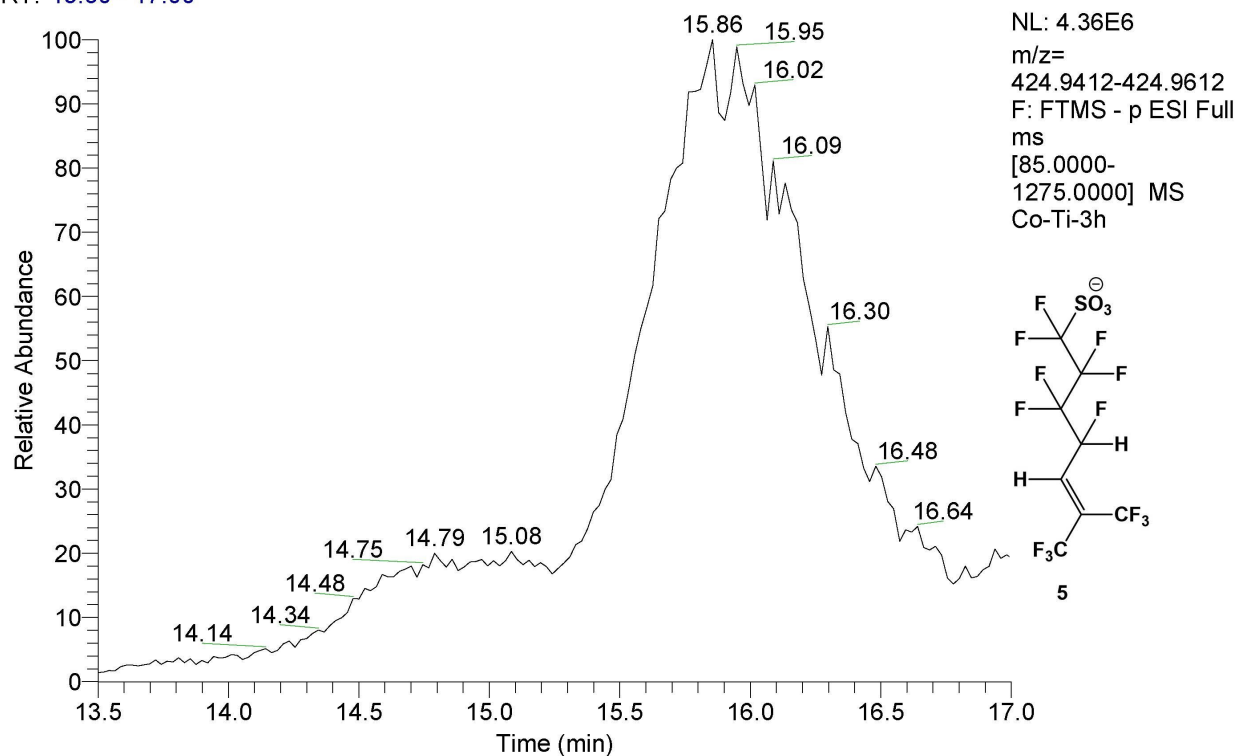
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ms
[85.0000-
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Co-Ti-3h



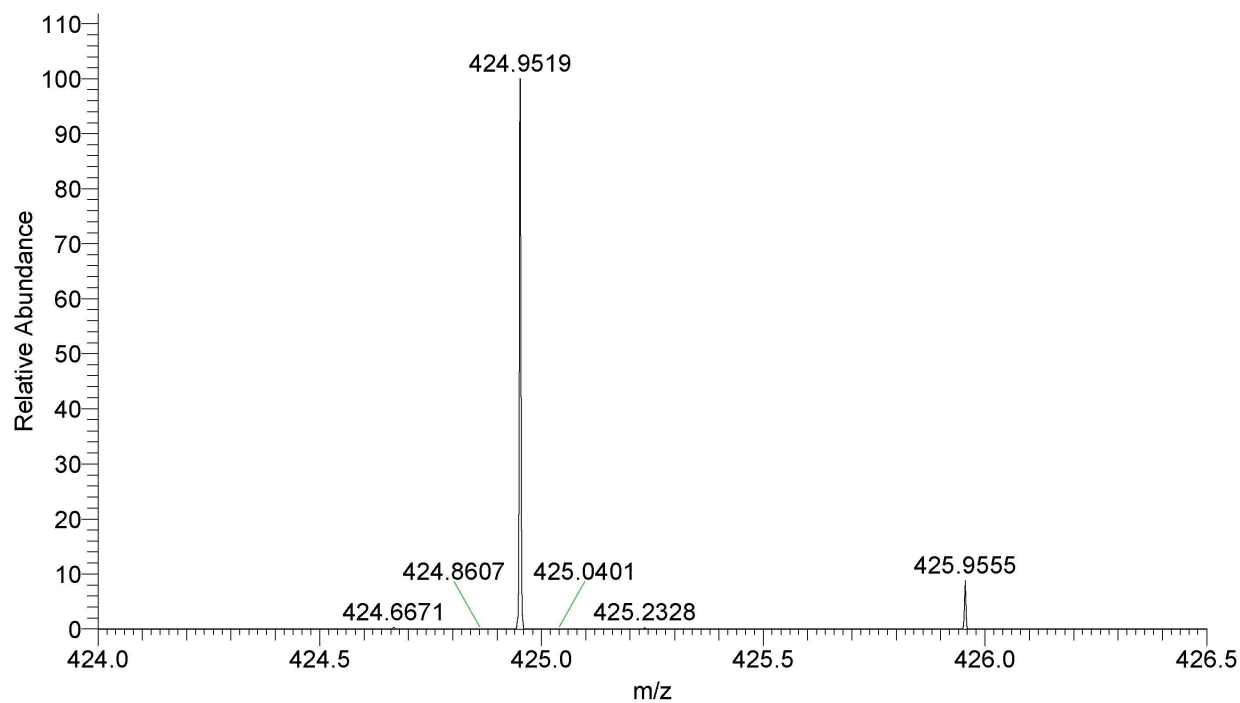
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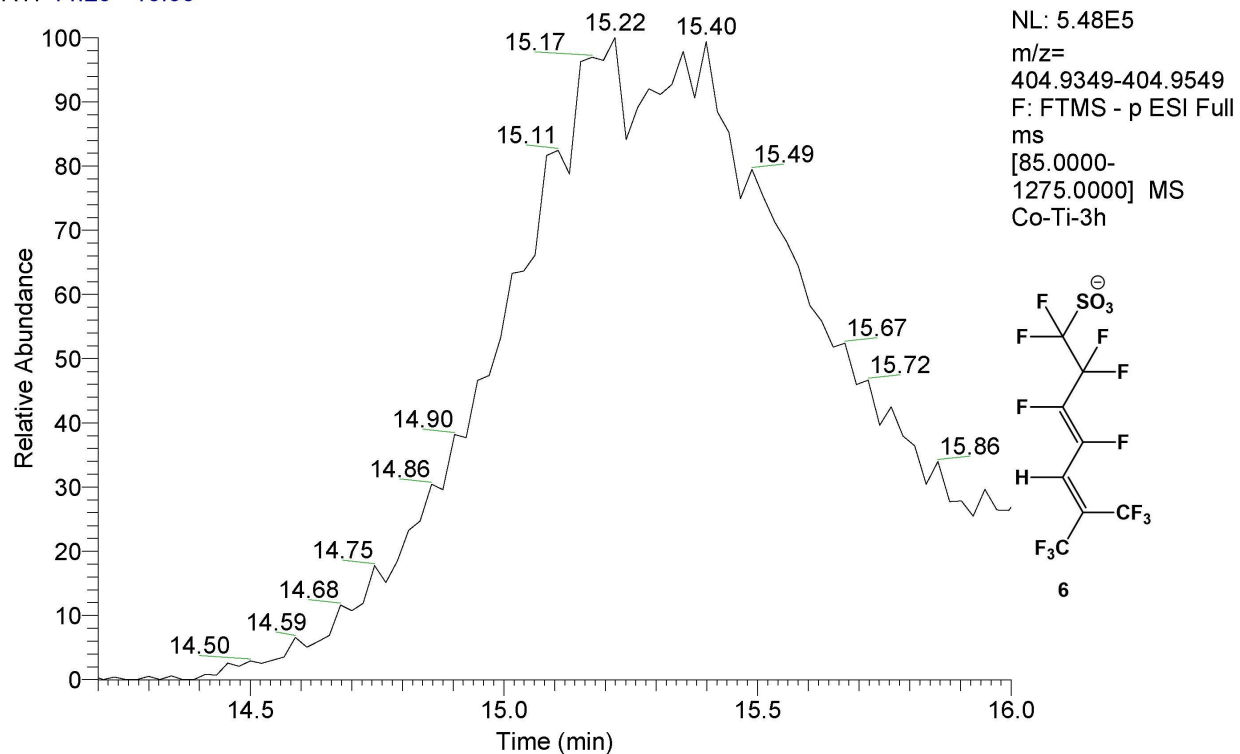
RT: 13.50 - 17.00



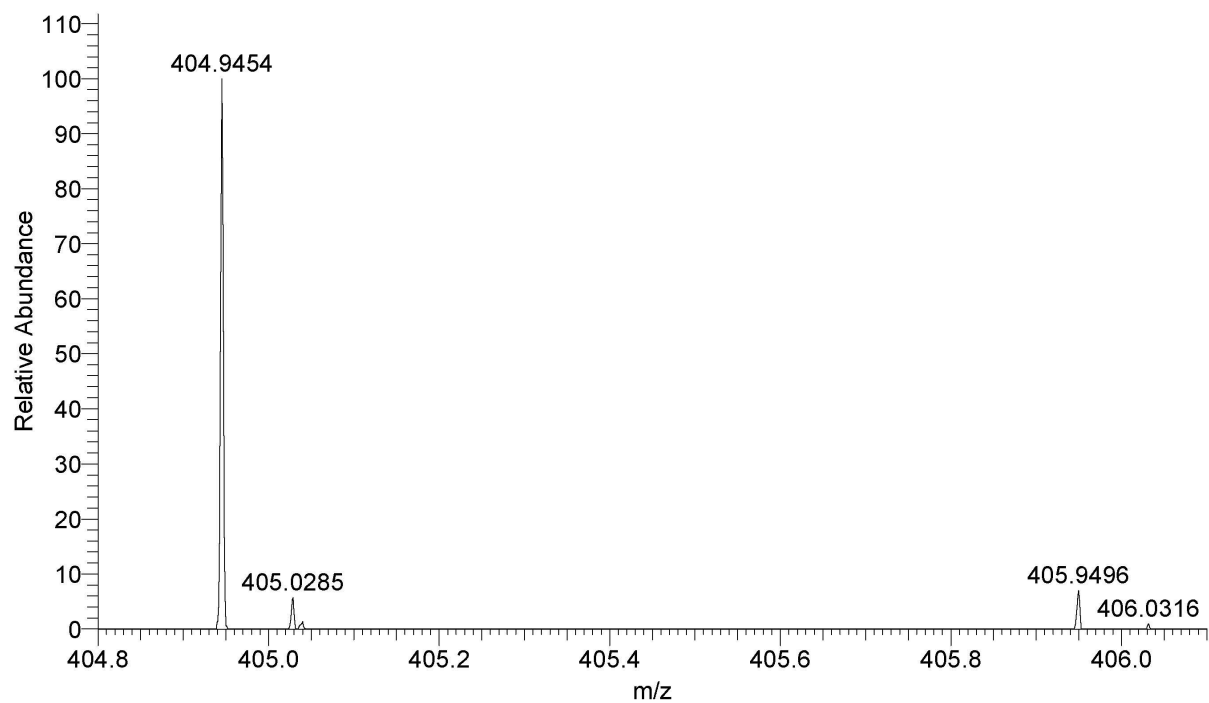
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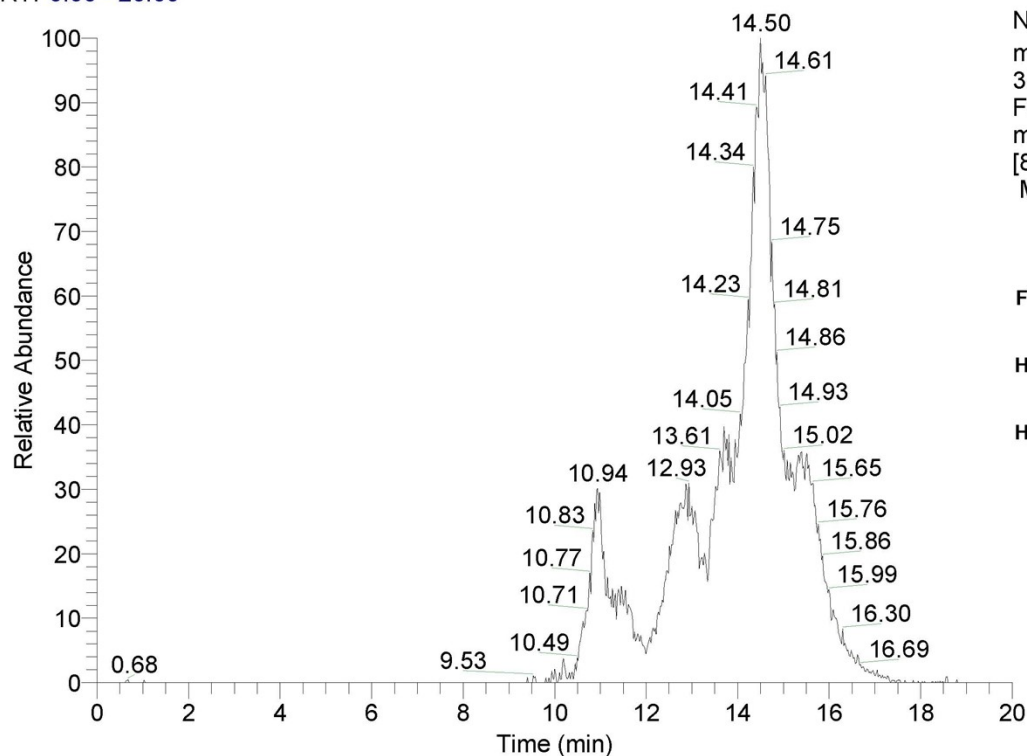
RT: 14.20 - 16.00



Co-Ti-3h #8559 RT: 16.94 AV: 1 NL: 4.98E5
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RT: 0.00 - 20.00



NL: 1.79E6

m/z=

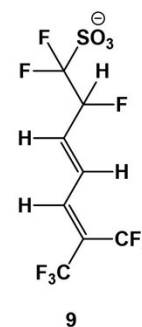
350.9632-350.9832

F: FTMS - p ESI Full

ms

[85.0000-1275.0000]

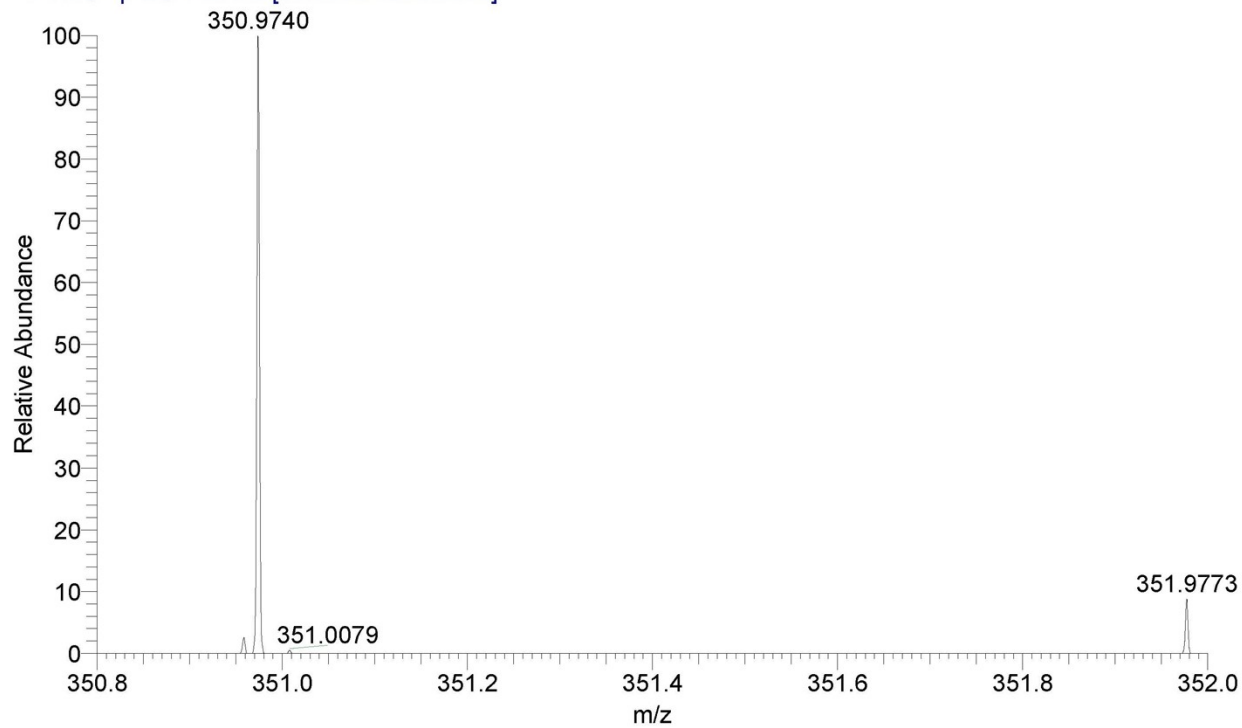
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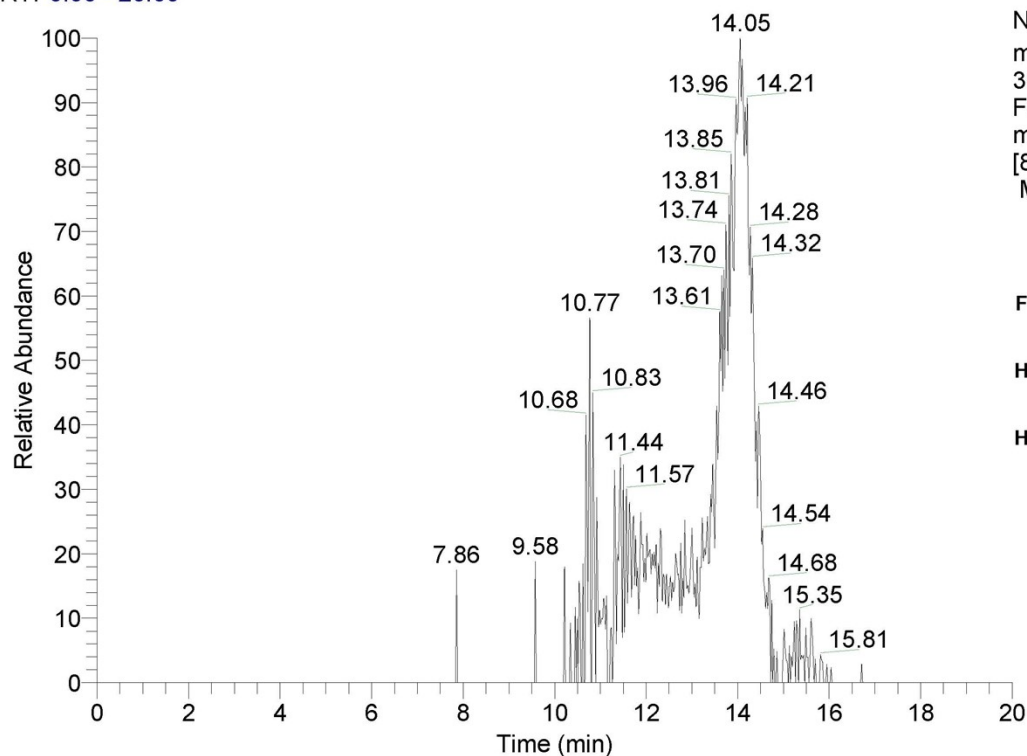
9

Co-Ti-3h #6557 RT: 12.82 AV: 1 NL: 4.59E5

T: FTMS - p ESI Full ms [85.0000-1275.0000]



RT: 0.00 - 20.00



NL: 7.00E4

m/z=

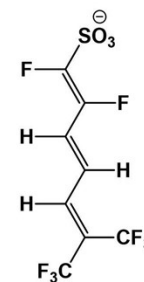
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ms

[85.0000-1275.0000]

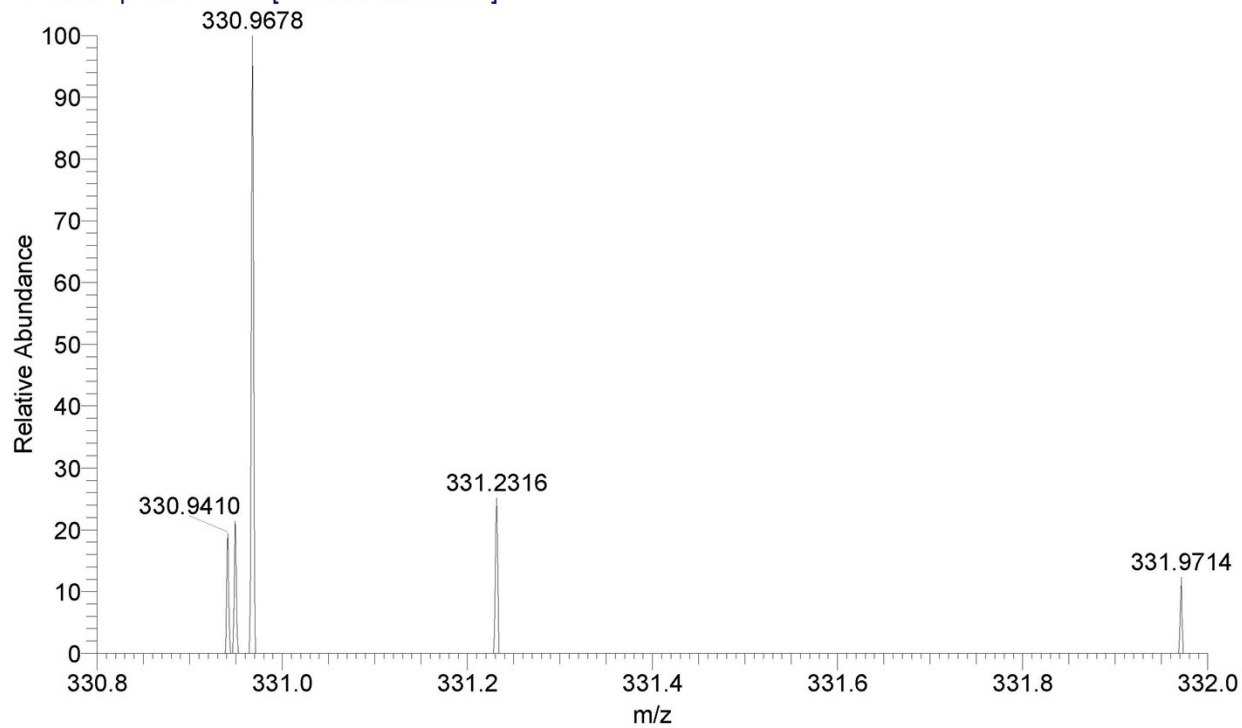
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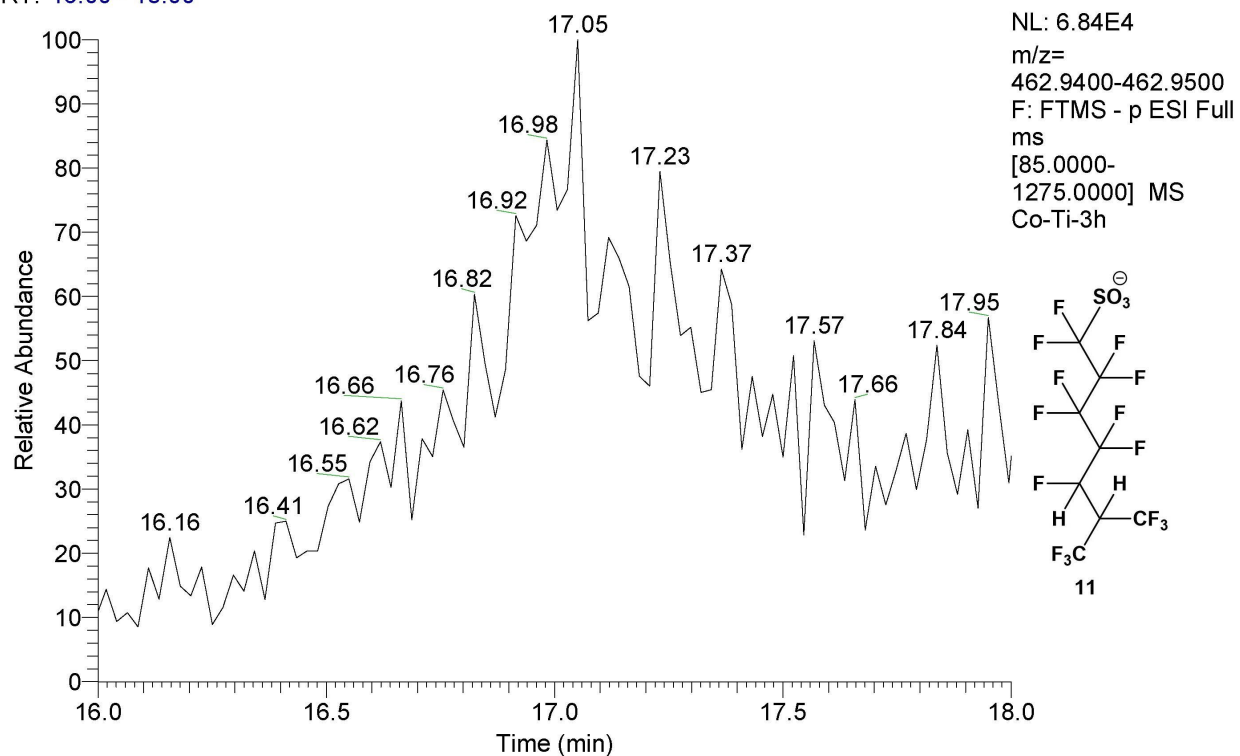
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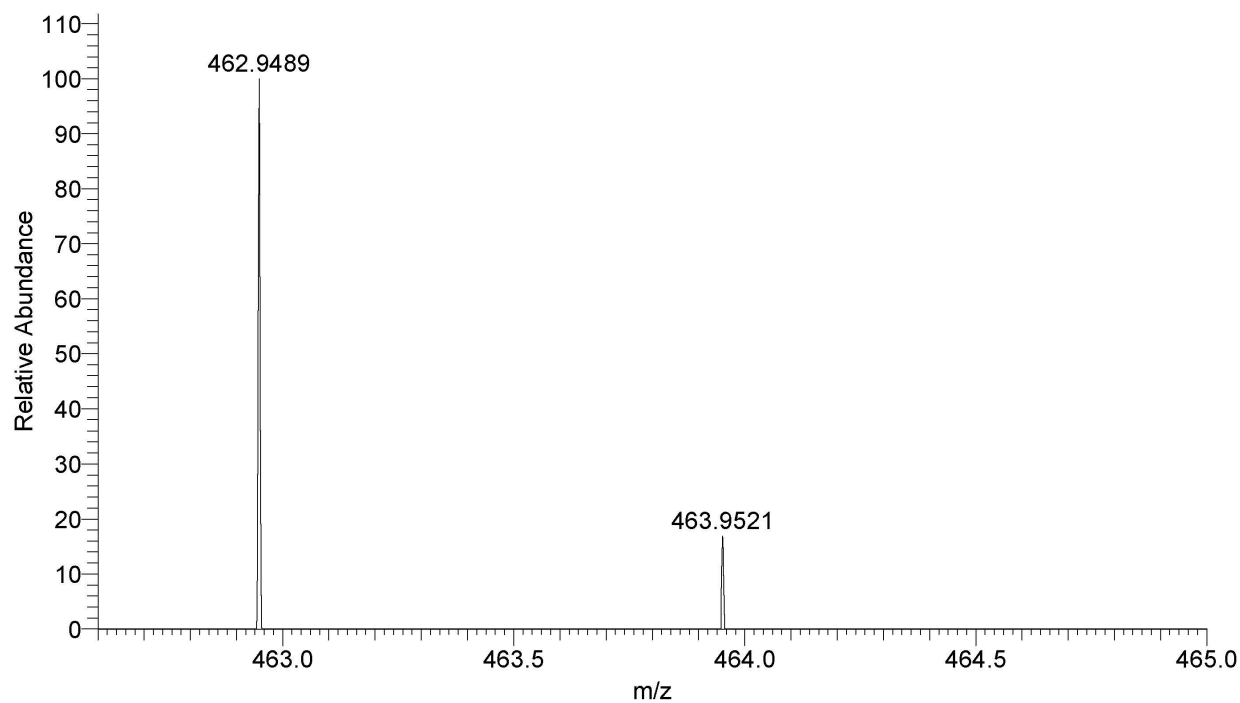
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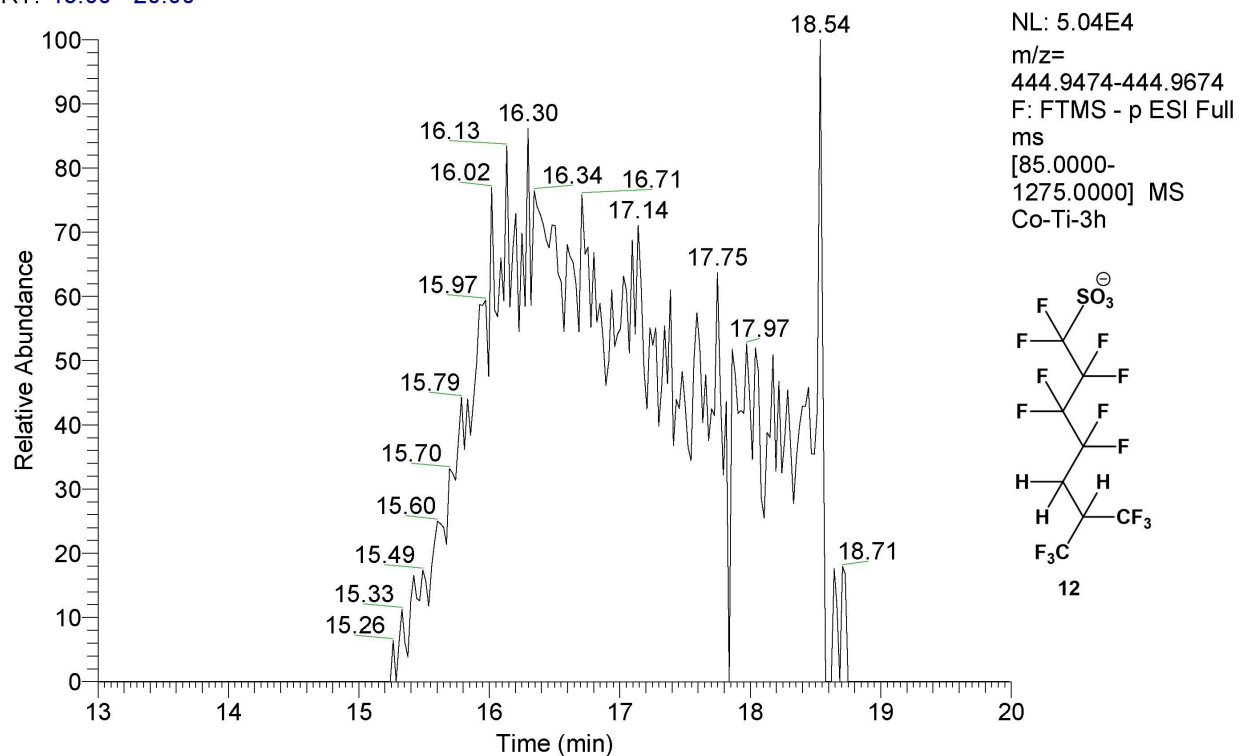
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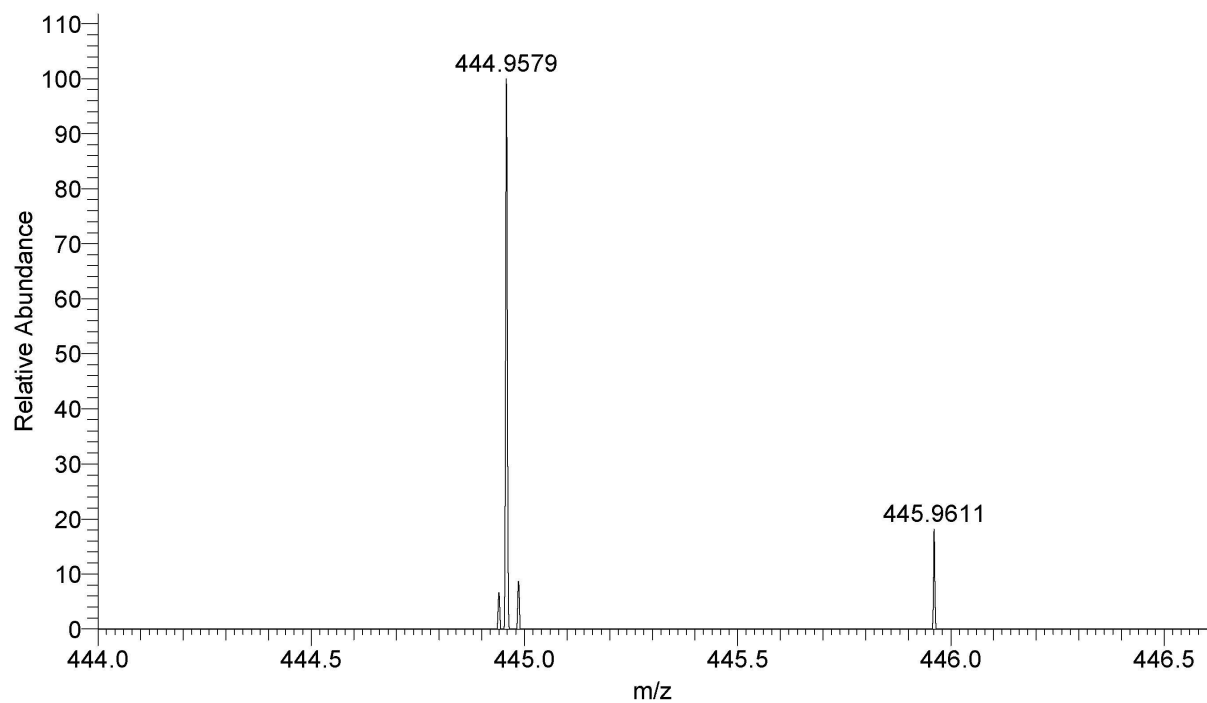
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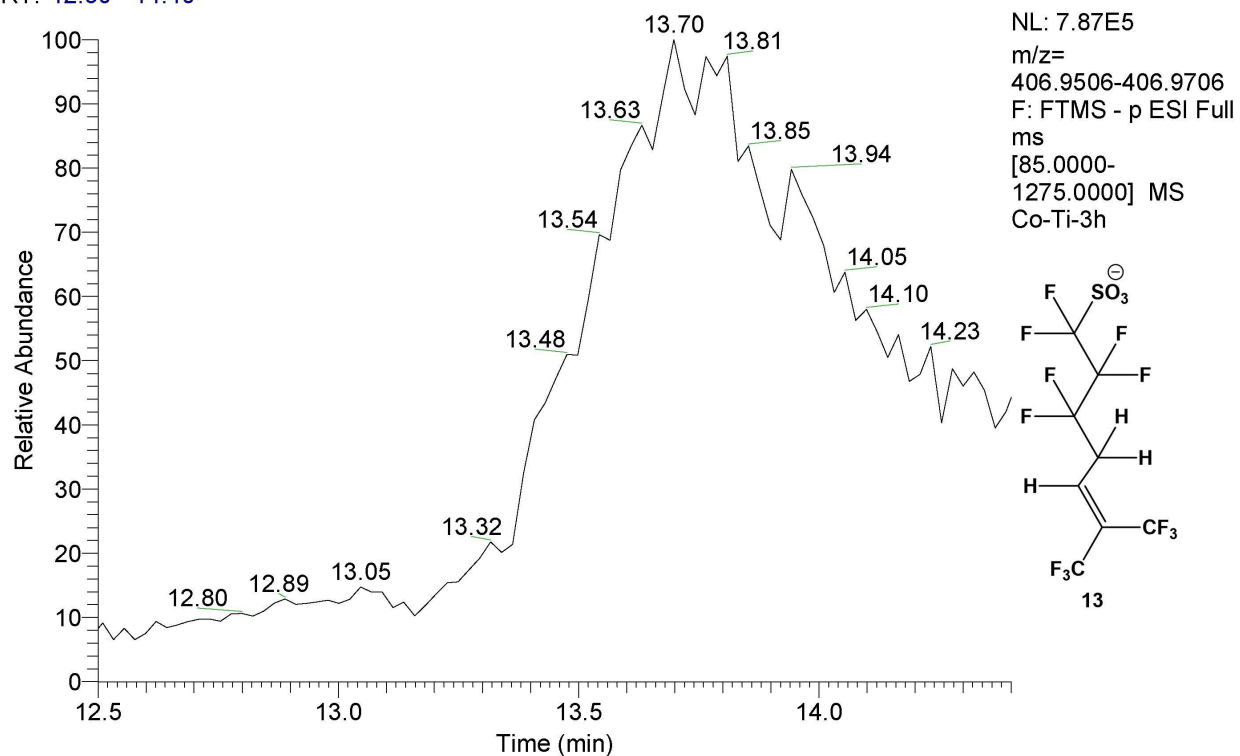
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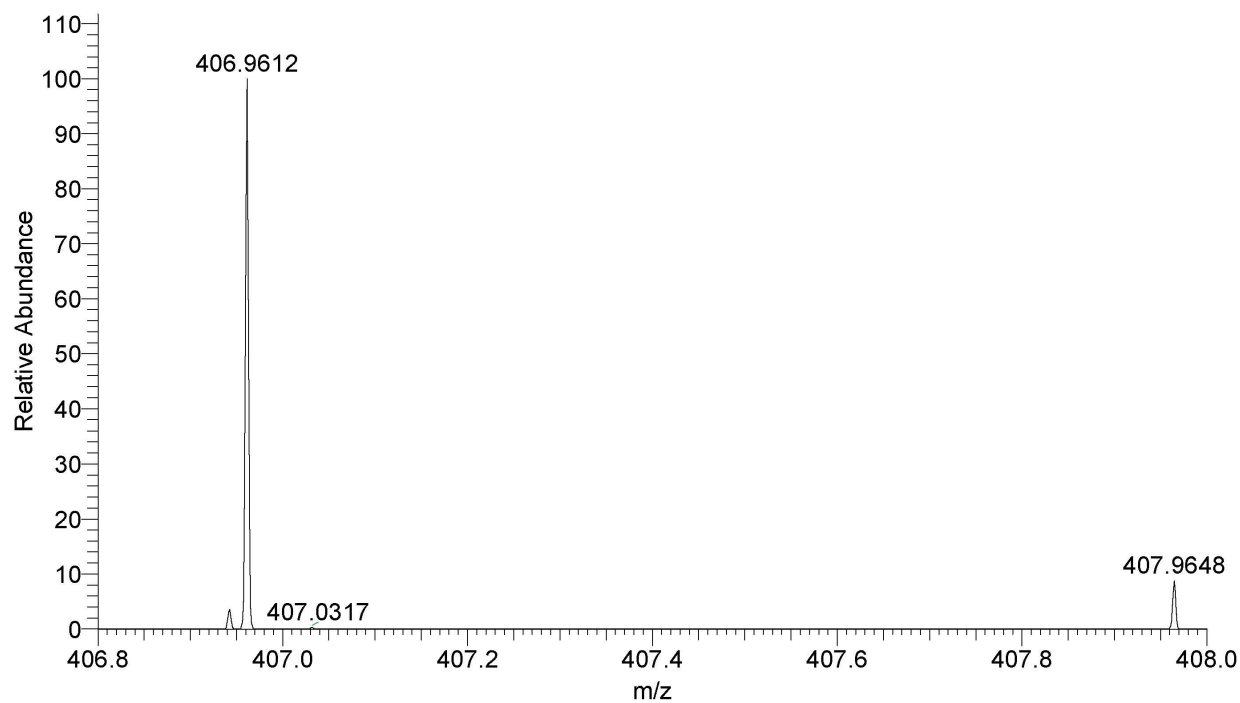
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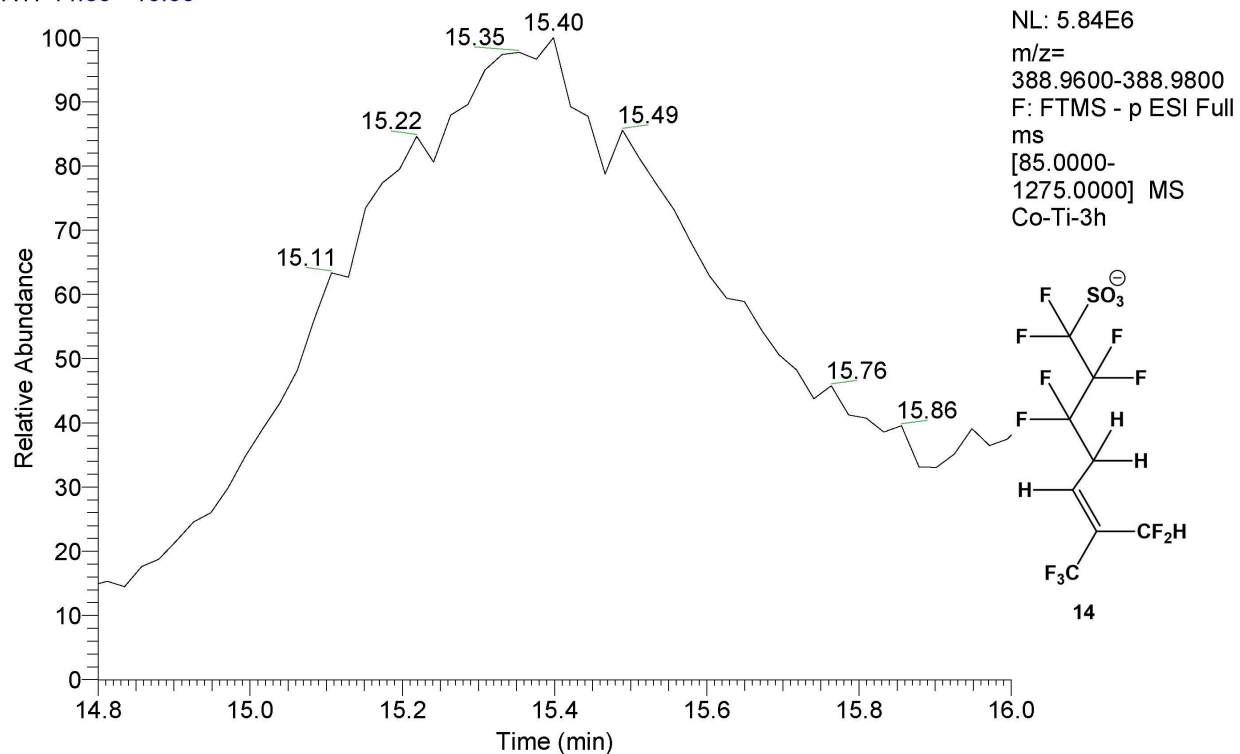
RT: 12.50 - 14.40



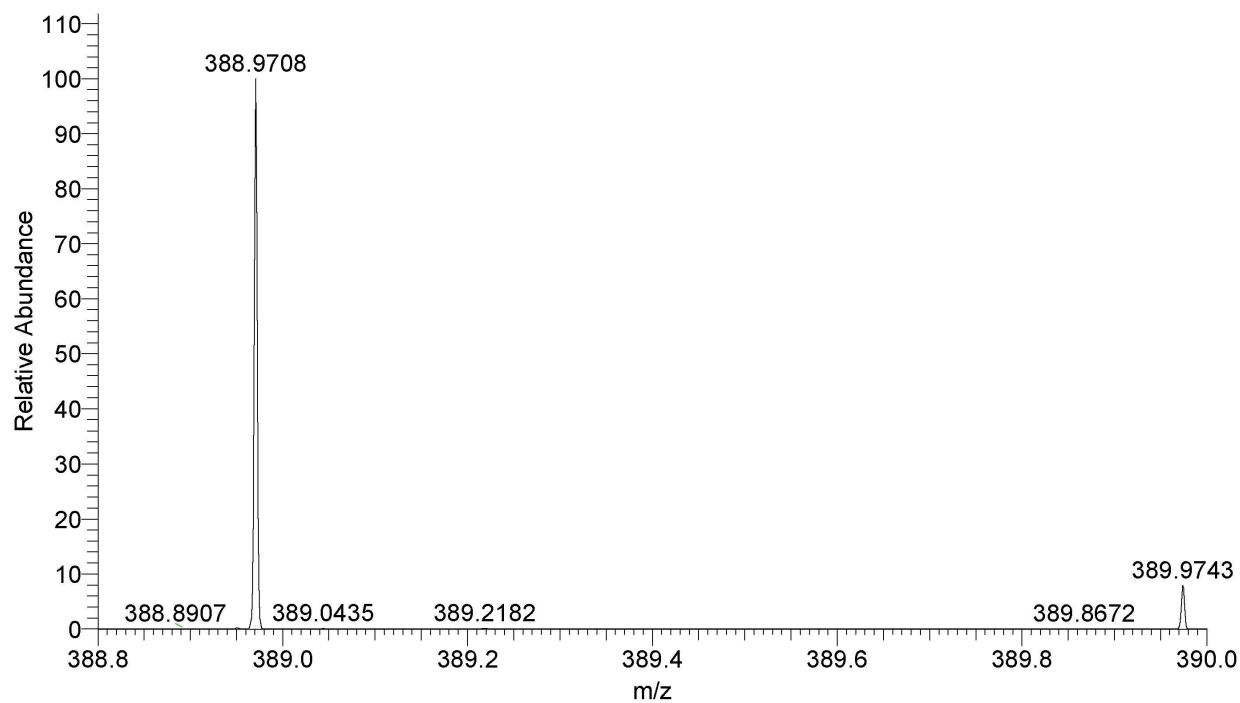
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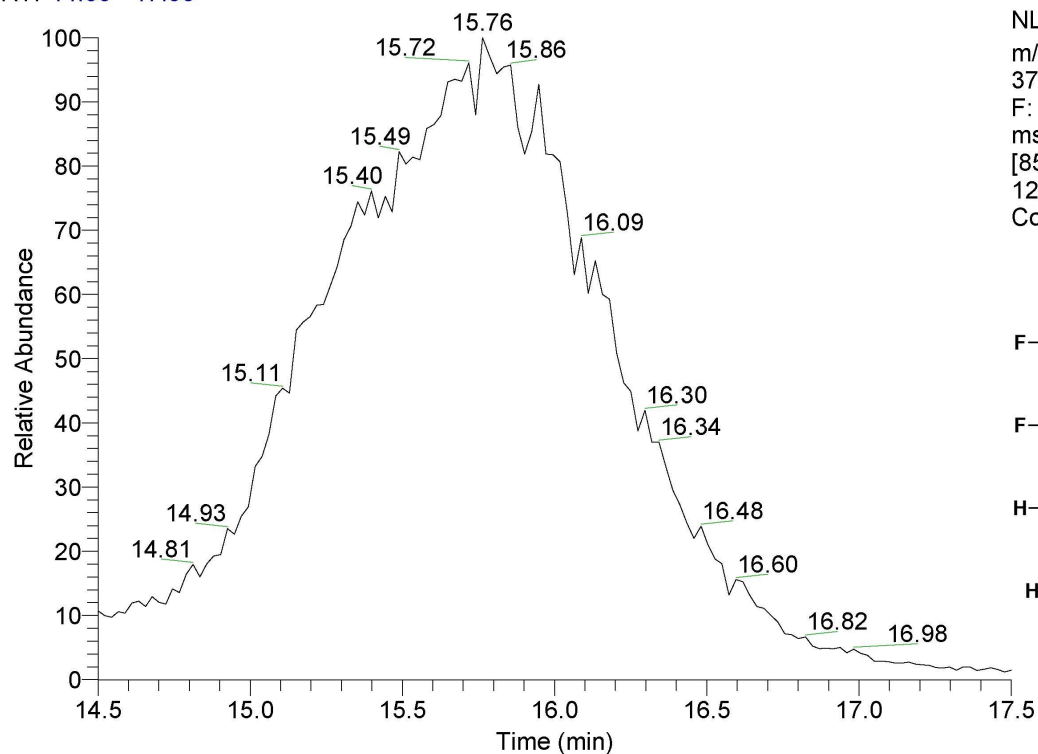
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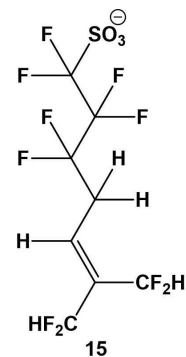
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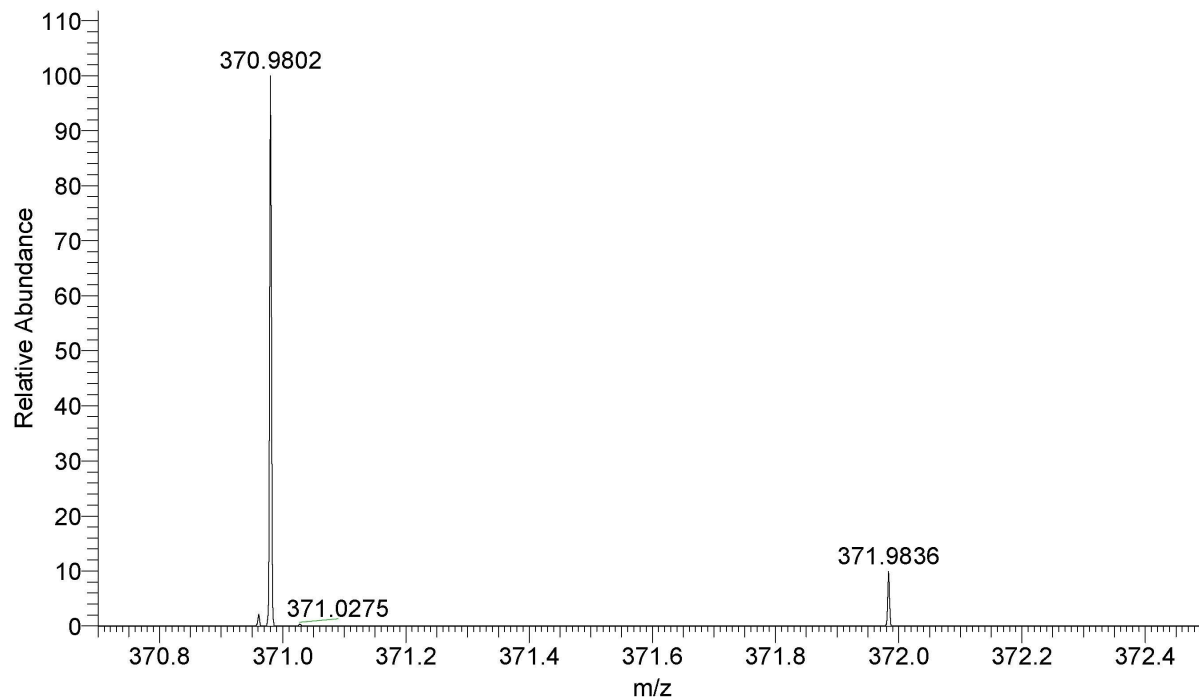
RT: 14.50 - 17.50



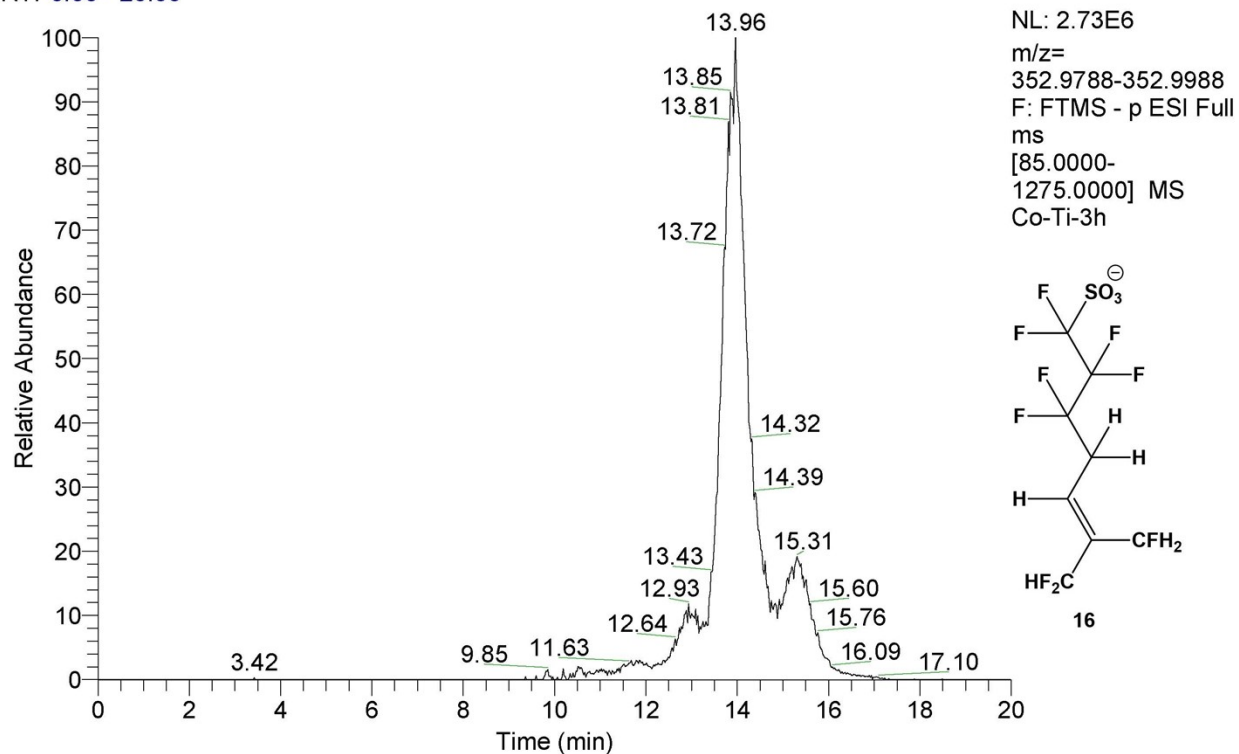
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ms
[85.0000-
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Co-Ti-3h



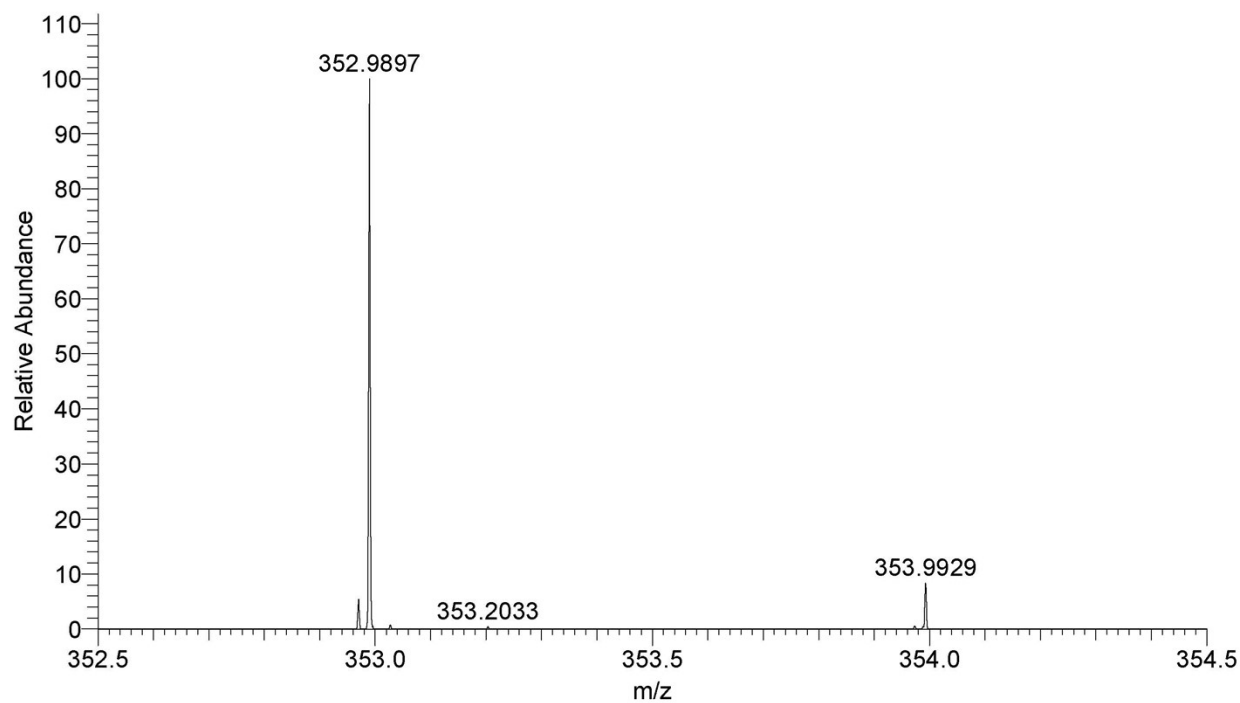
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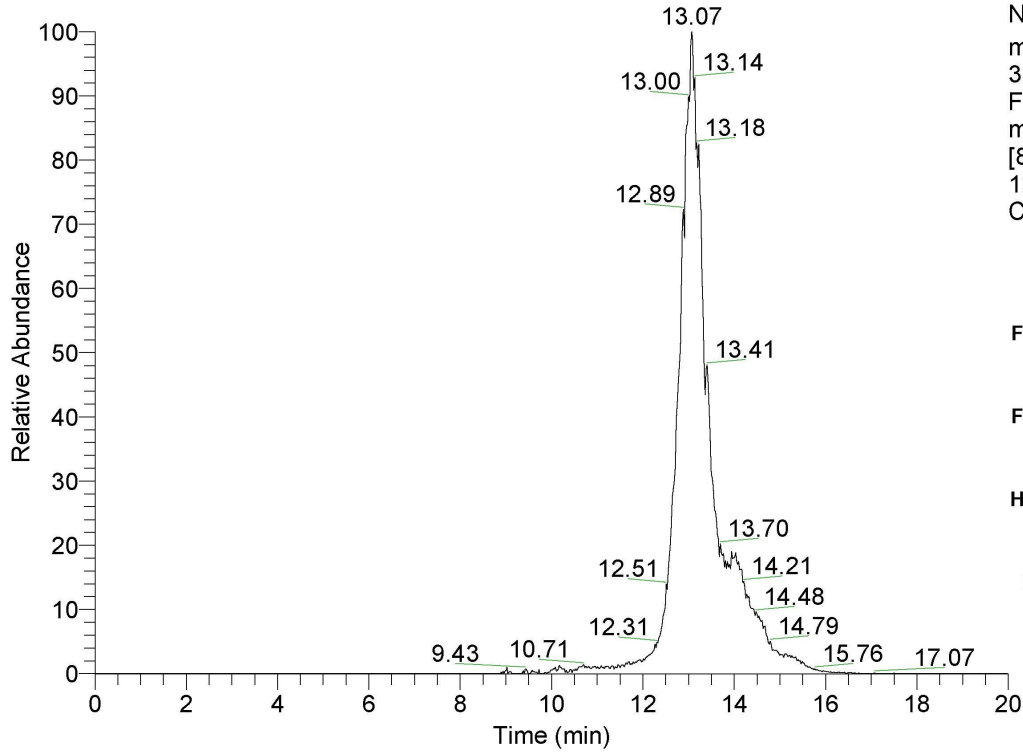
RT: 0.00 - 20.00



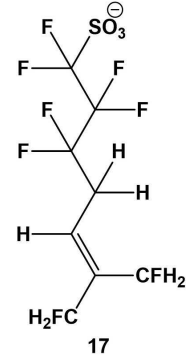
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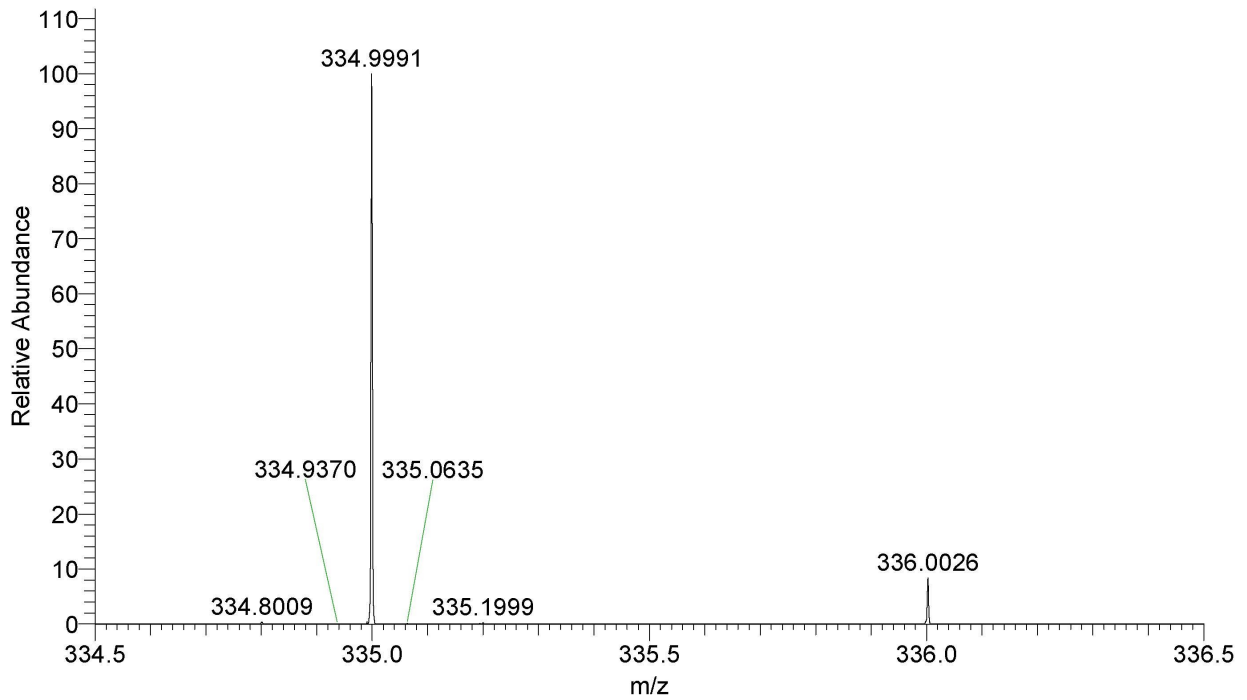
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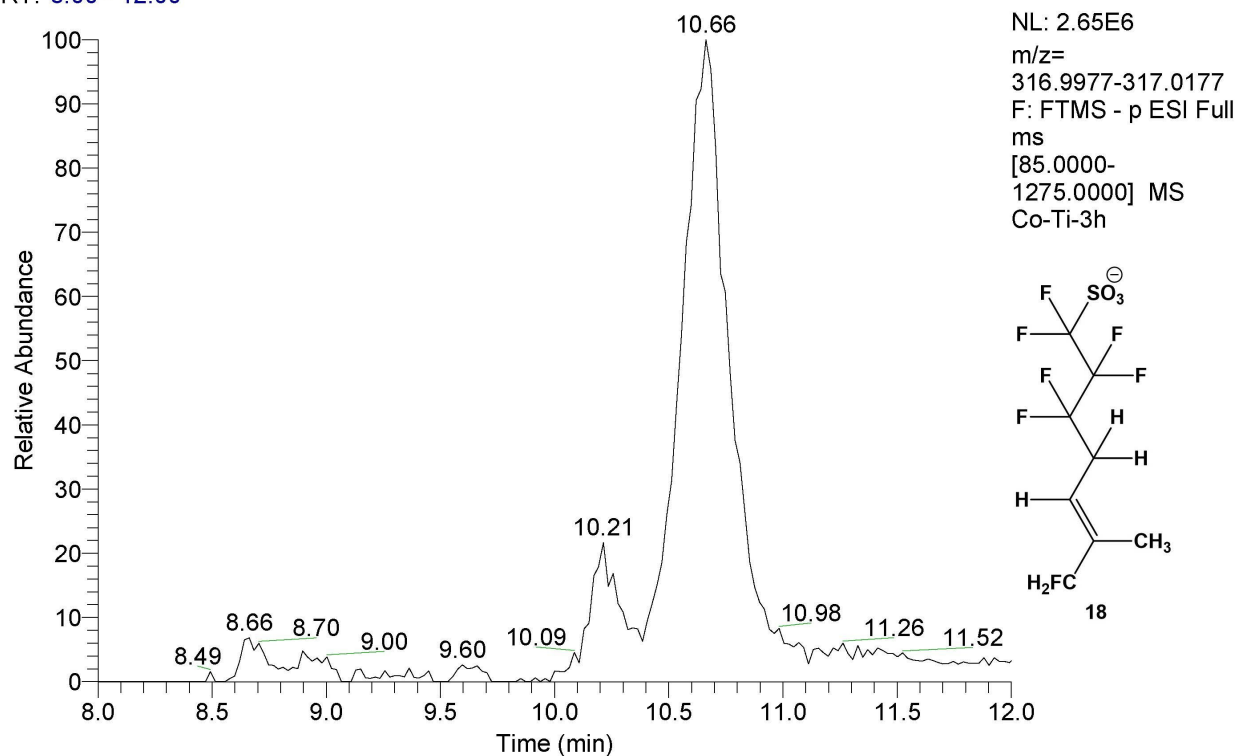
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F: FTMS - p ESI Full
ms
[85.0000-
1275.0000] MS
Co-Ti-3h



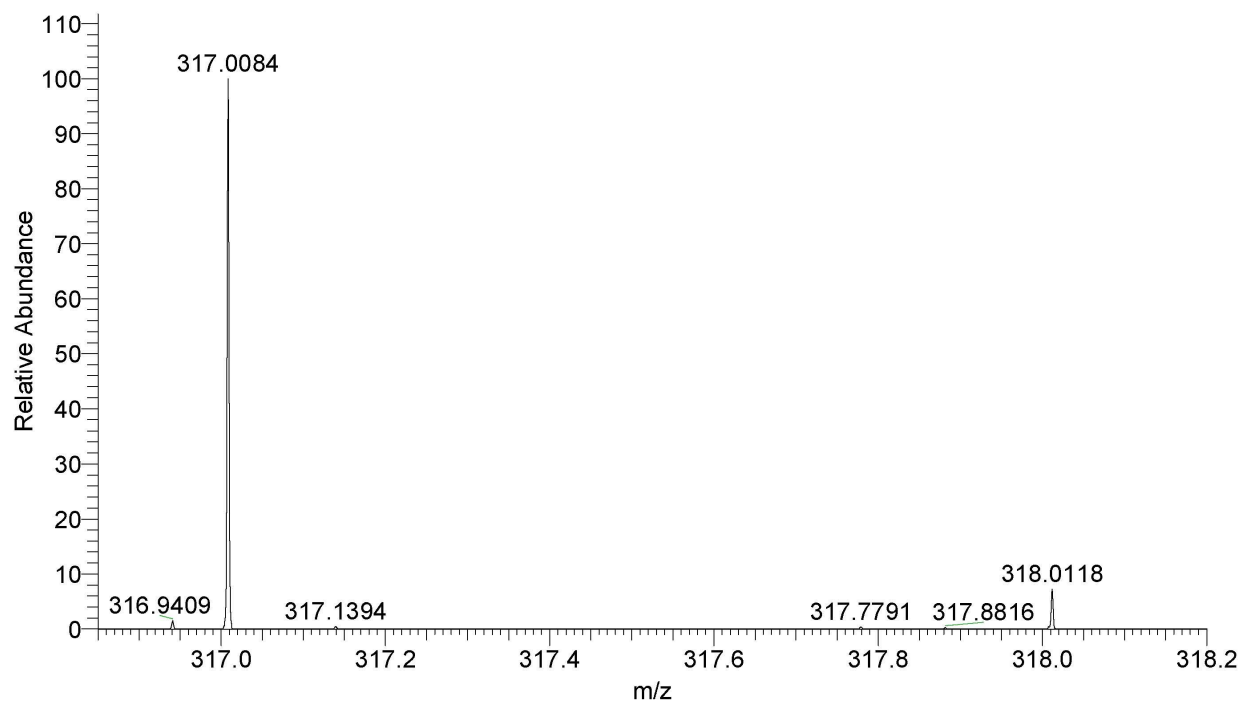
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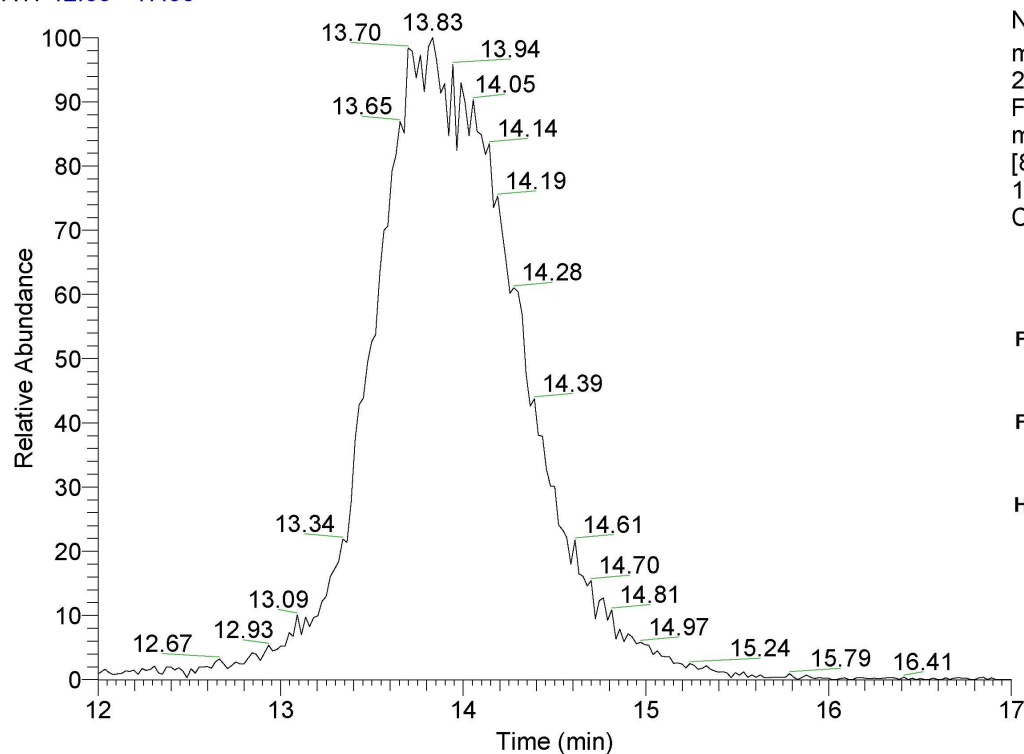
RT: 8.00 - 12.00



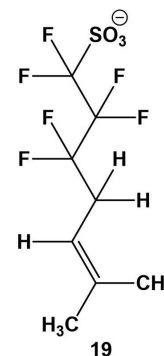
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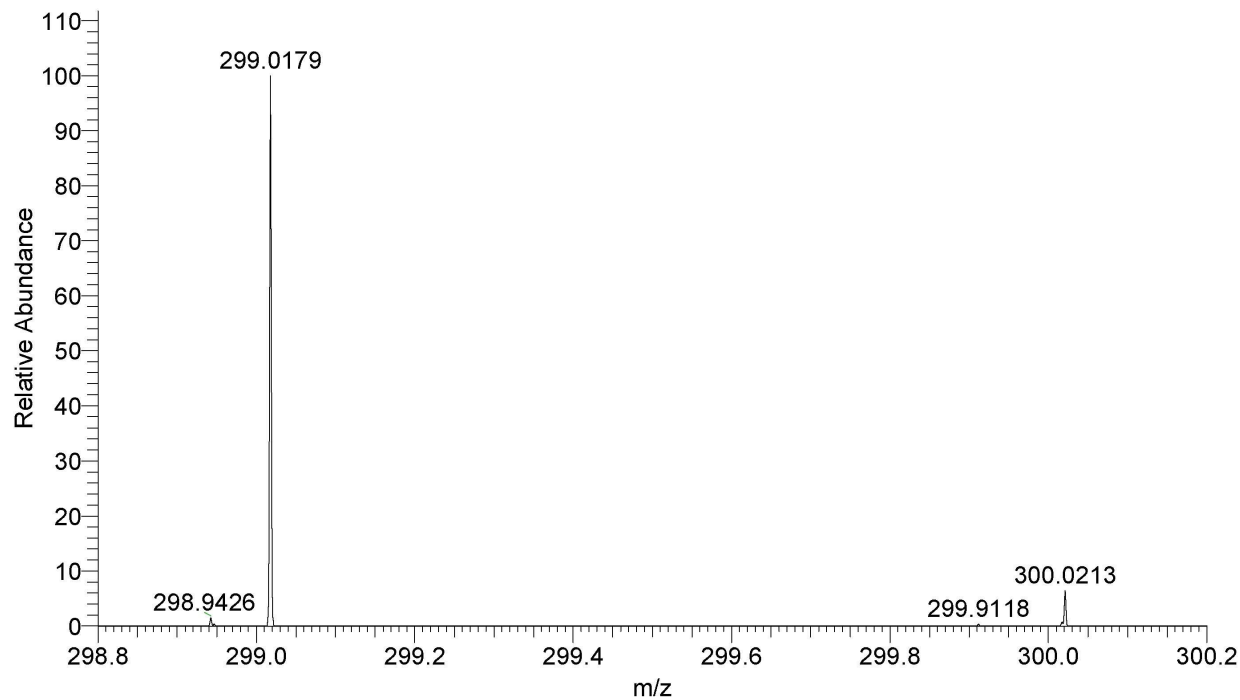
RT: 12.00 - 17.00



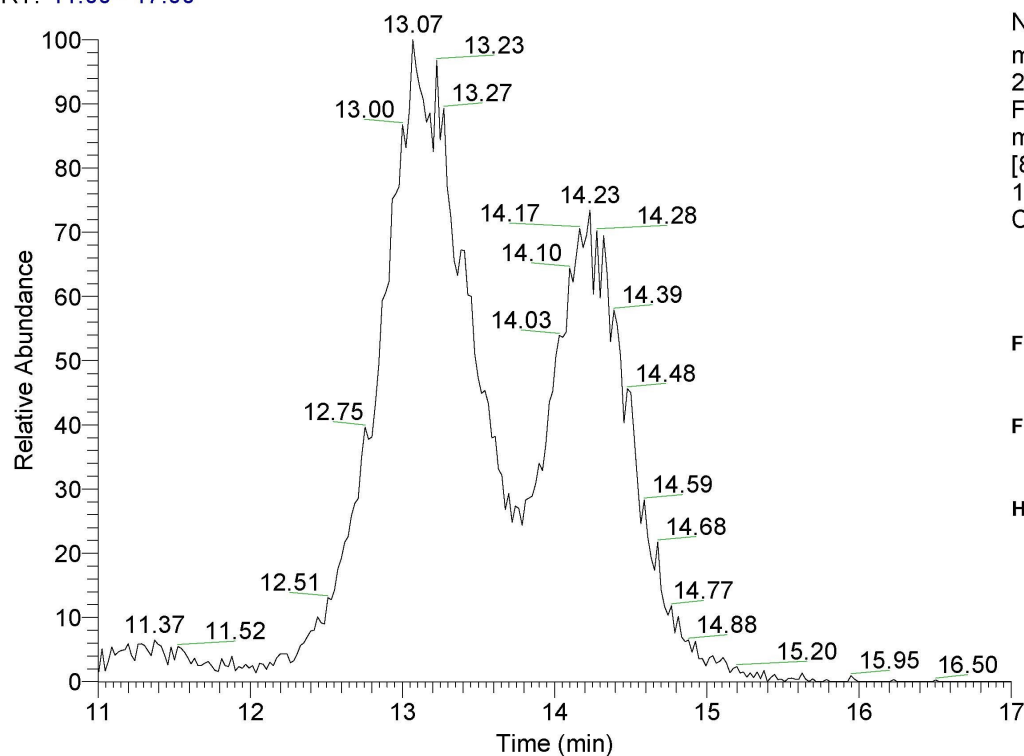
NL: 7.90E5
m/z=
299.0071-299.0271
F: FTMS - p ESI Full
ms
[85.0000-
1275.0000] MS
Co-Ti-3h



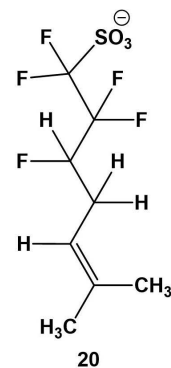
Co-Ti-3h #7063 RT: 13.85 AV: 1 NL: 7.53E5
T: FTMS - p ESI Full ms [85.0000-1275.0000]



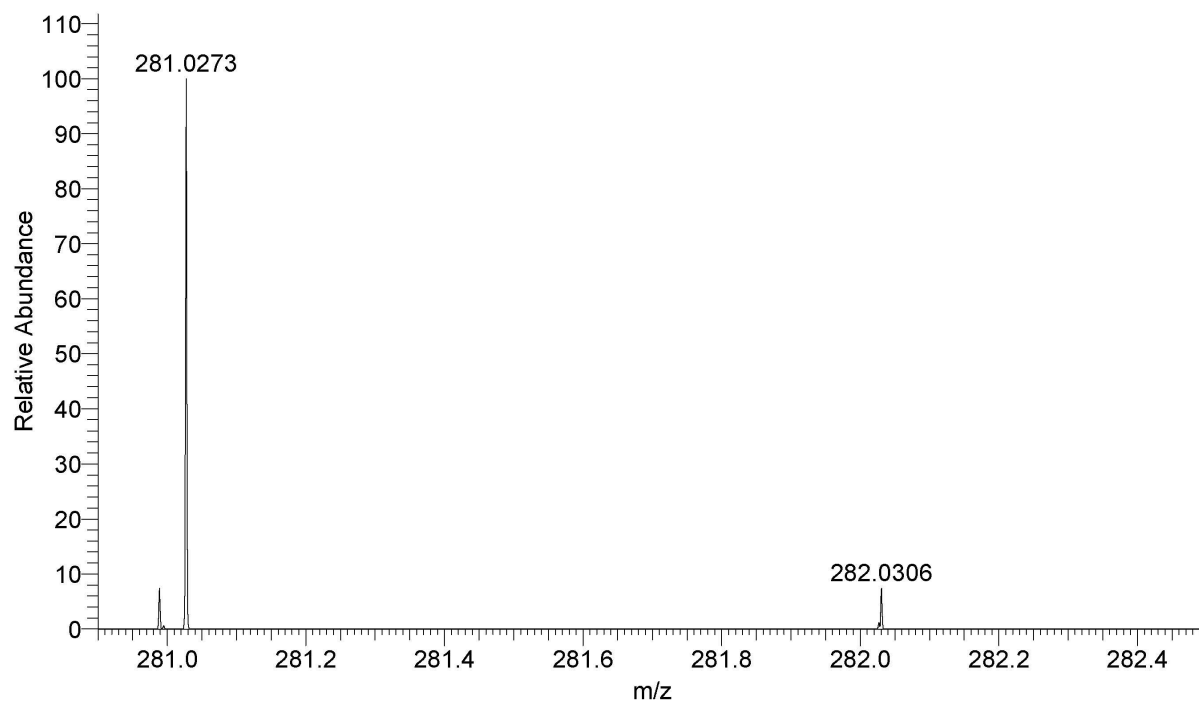
RT: 11.00 - 17.00



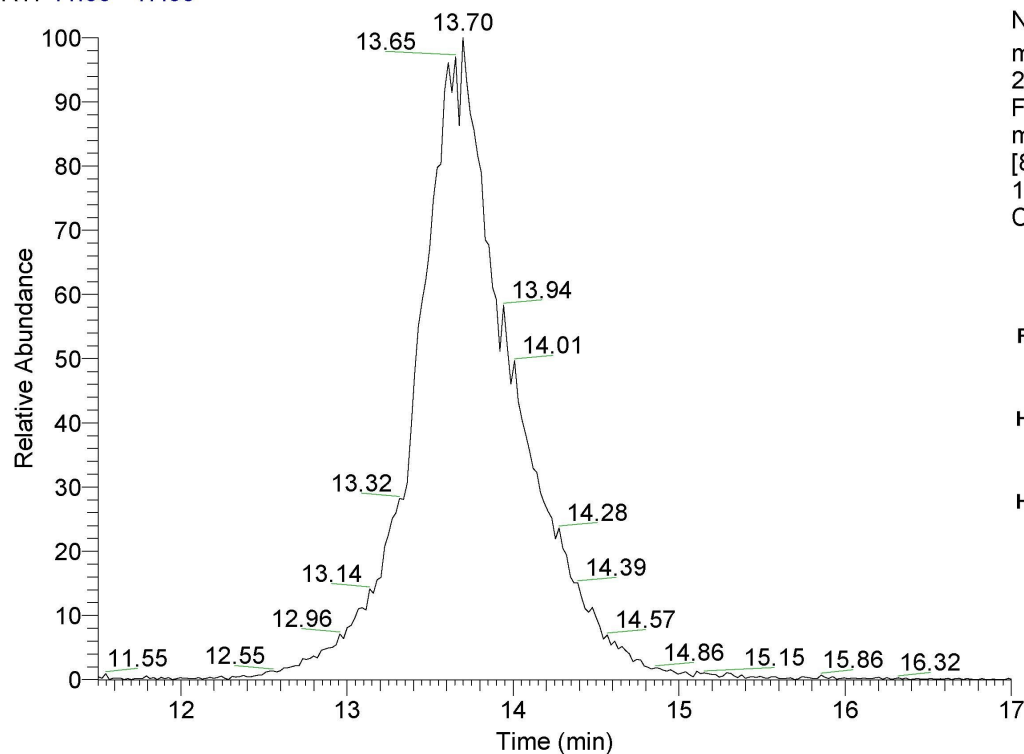
NL: 5.13E5
m/z=
281.0165-281.0365
F: FTMS - p ESI Full
ms
[85.0000-
1275.0000] MS
Co-Ti-3h



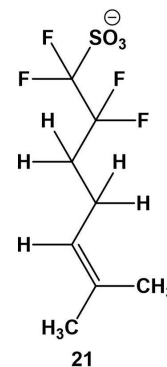
Co-Ti-3h #7283 RT: 14.30 AV: 1 NL: 3.06E5
T: FTMS - p ESI Full ms [85.0000-1275.0000]



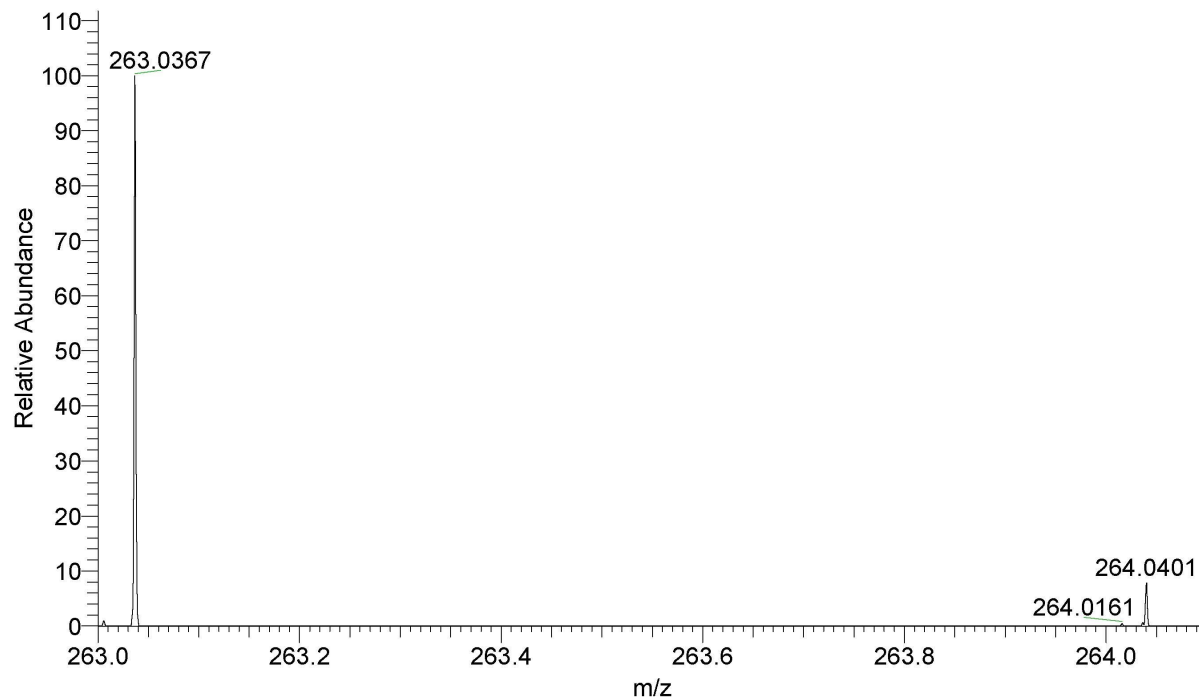
RT: 11.50 - 17.00



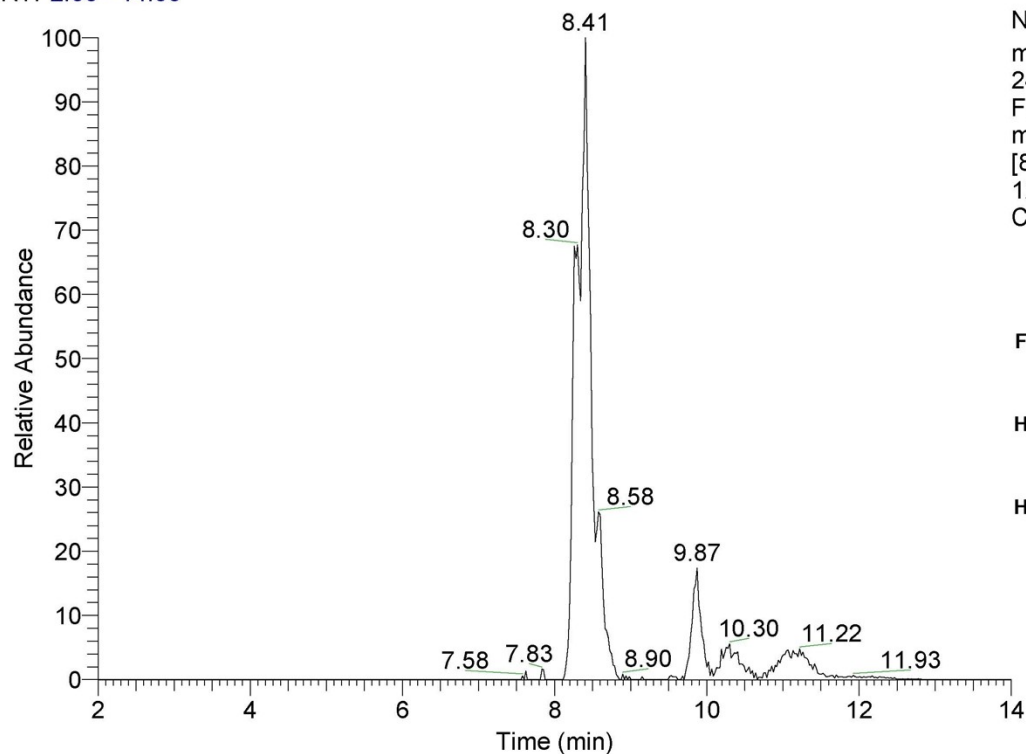
NL: 1.79E6
m/z=
263.0260-263.0460
F: FTMS - p ESI Full
ms
[85.0000-
1275.0000] MS
Co-Ti-3h



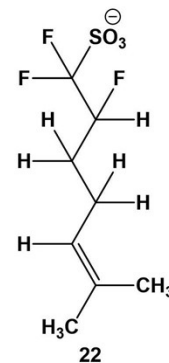
Co-Ti-3h #6953 RT: 13.63 AV: 1 NL: 1.58E6
T: FTMS - p ESI Full ms [85.0000-1275.0000]



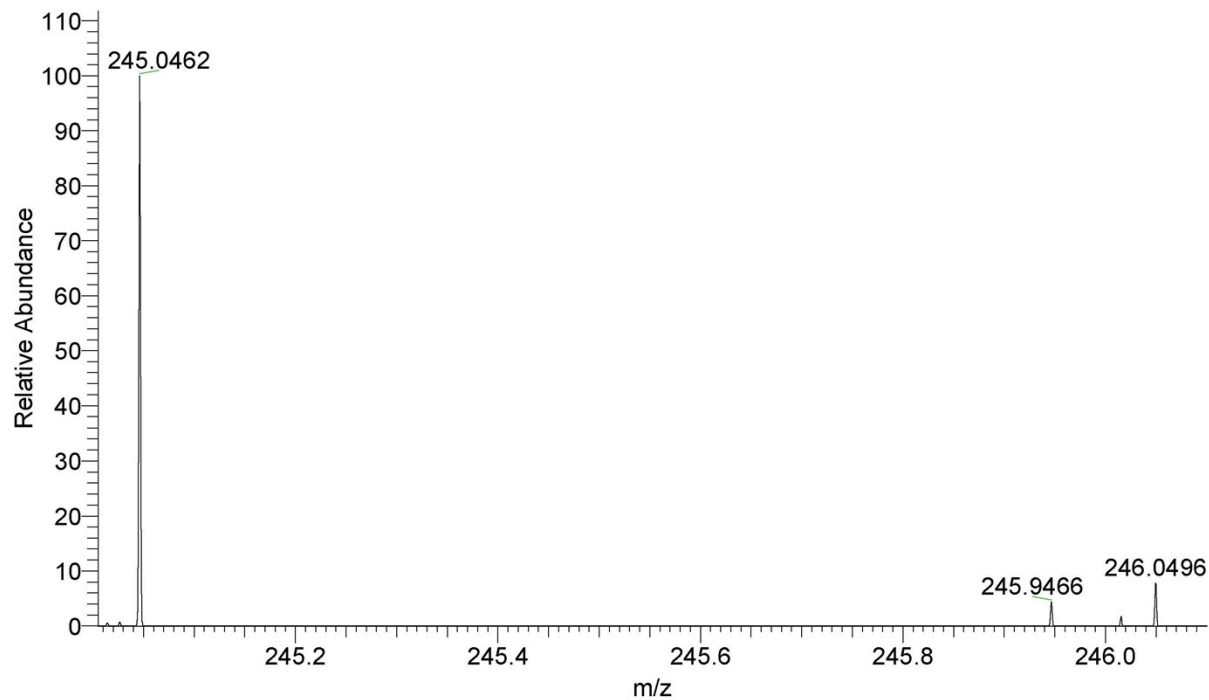
RT: 2.00 - 14.00



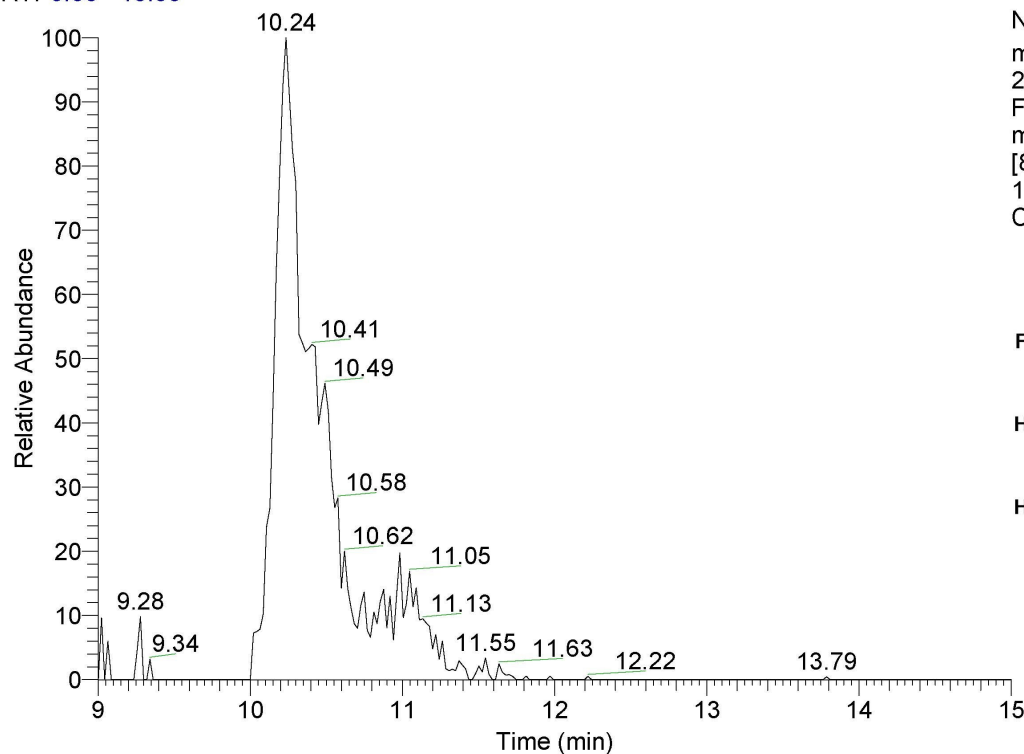
NL: 2.83E6
m/z=
245.0354-245.0554
F: FTMS - p ESI Full
ms
[85.0000-
1275.0000] MS
Co-Ti-3h



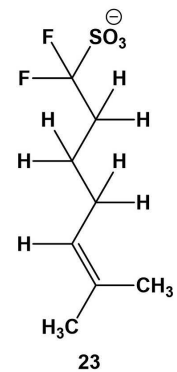
Co-Ti-3h #4313 RT: 8.41 AV: 1 NL: 2.83E6
T: FTMS - p ESI Full ms [85.0000-1275.0000]



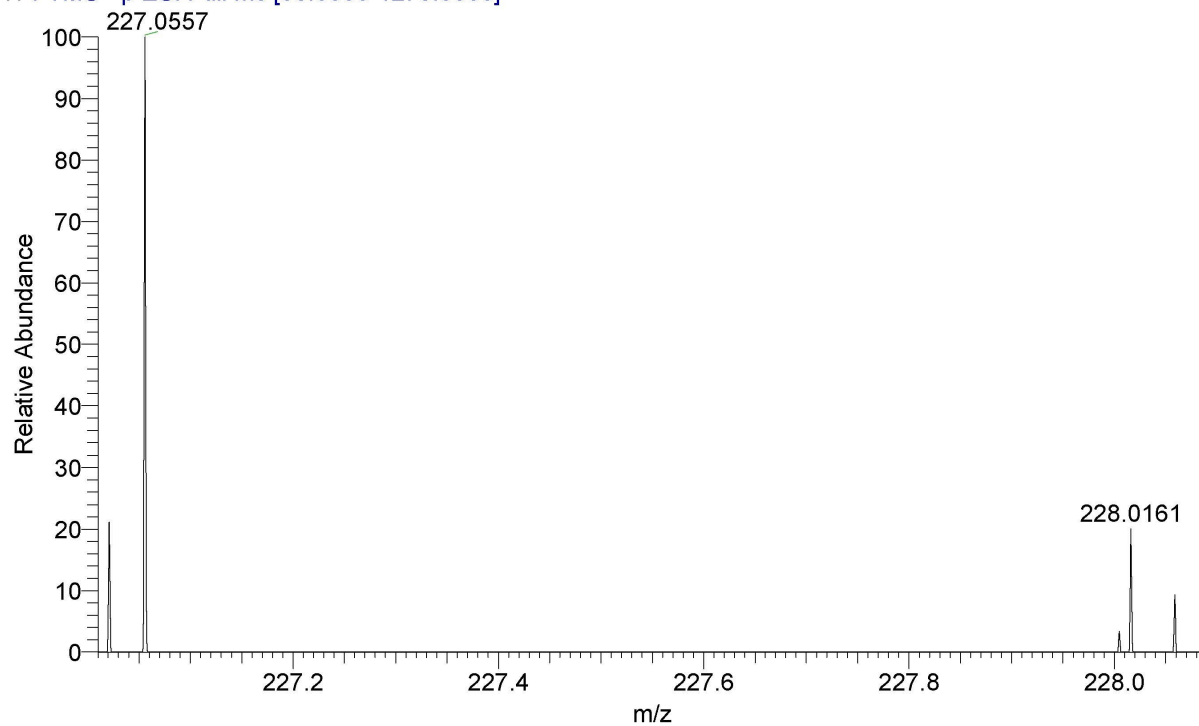
RT: 9.00 - 15.00



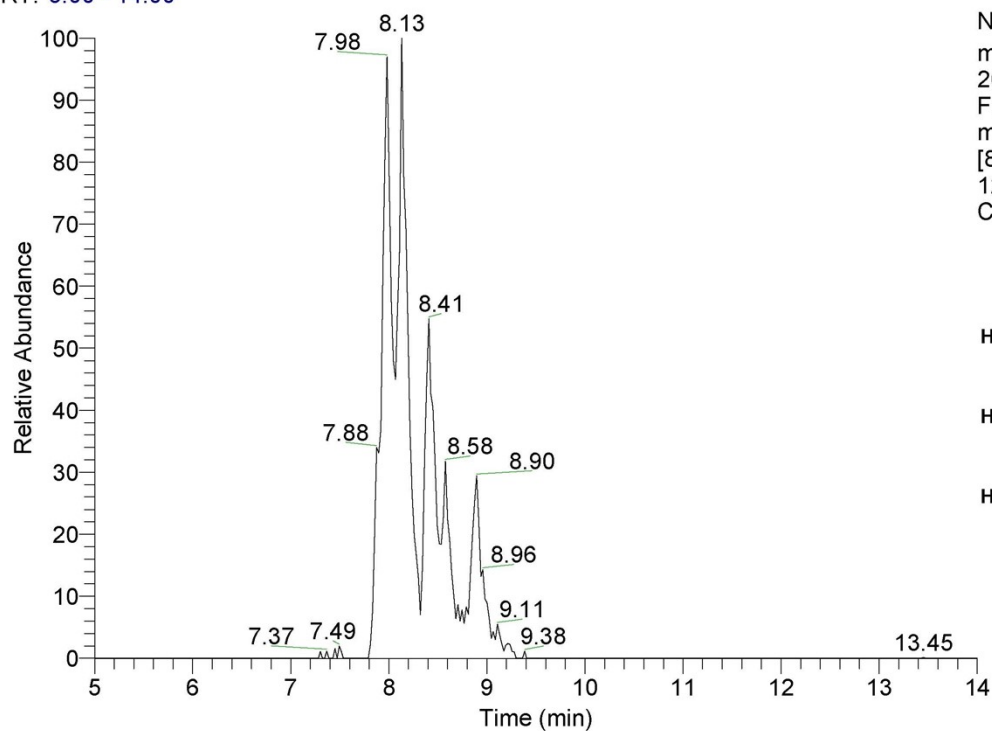
NL: 4.60E5
m/z=
227.0448-227.0648
F: FTMS - p ESI Full
ms
[85.0000-
1275.0000] MS
Co-Ti-3h



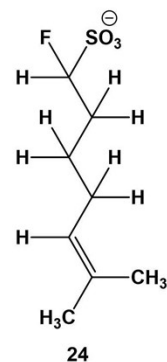
Co-Ti-3h #5292 RT: 10.30 AV: 1 NL: 3.53E5
T: FTMS - p ESI Full ms [85.0000-1275.0000]



RT: 5.00 - 14.00



NL: 1.95E6
m/z=
209.0542-209.0742
F: FTMS - p ESI Full
ms
[85.0000-
1275.0000] MS
Co-Ti-3h



Co-Ti-3h #4082 RT: 7.96 AV: 1 NL: 1.60E6
T: FTMS - p ESI Full ms [85.0000-1275.0000]

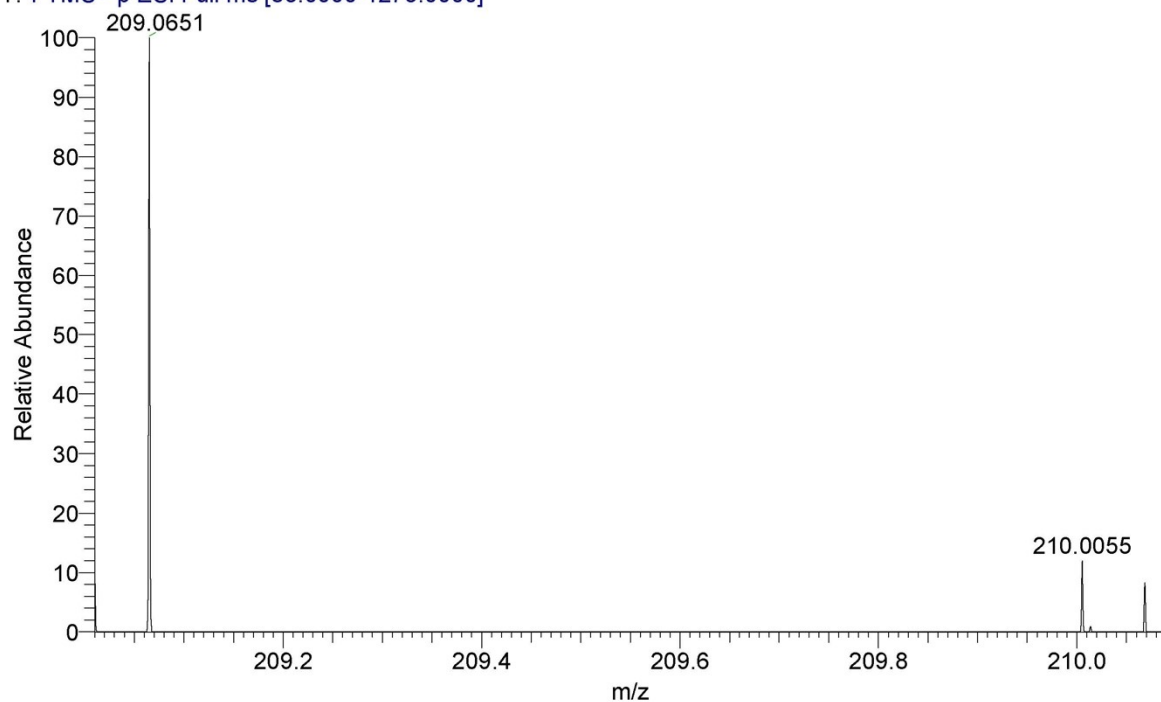


Fig. S7. Ion chromatographs and spectrums of the detected degradation products of PFOS defluorination via CoPc. Experimental conditions: Technical PFOS (0.1 mM), CoPc (0.25 mM), Ti^{III} citrate (40 mM), and carbonate buffer (85 mM) in Milli Q water.

References

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