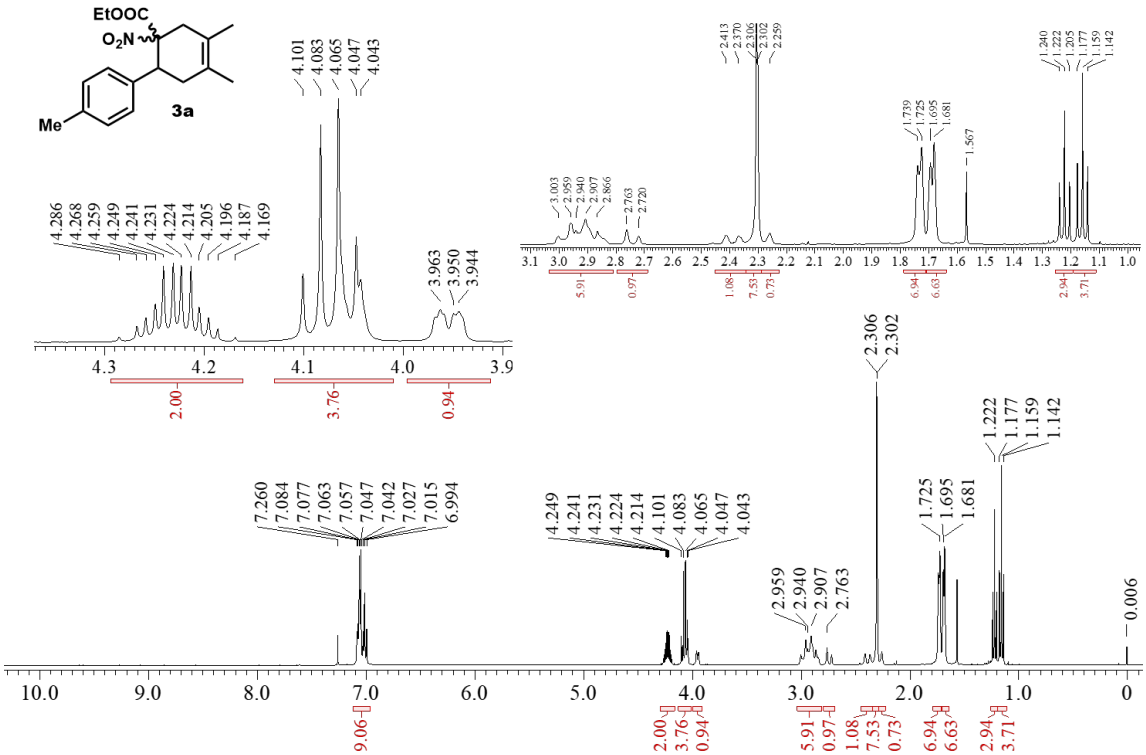
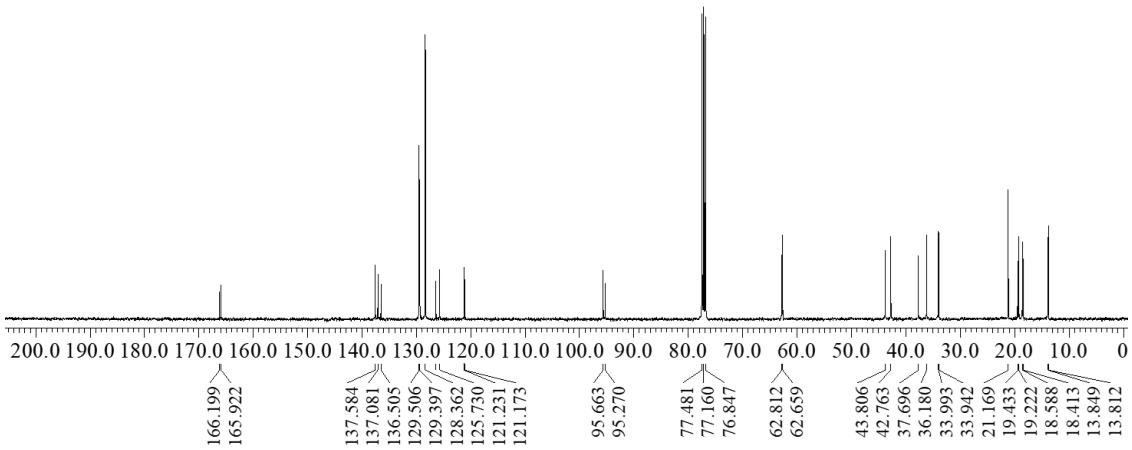
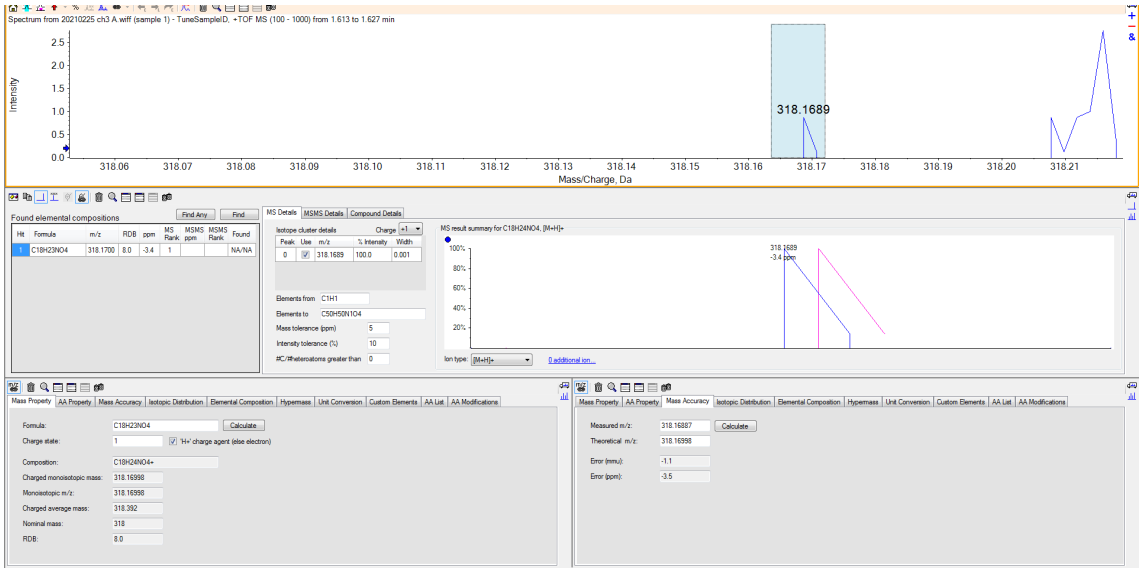
Supporting Information



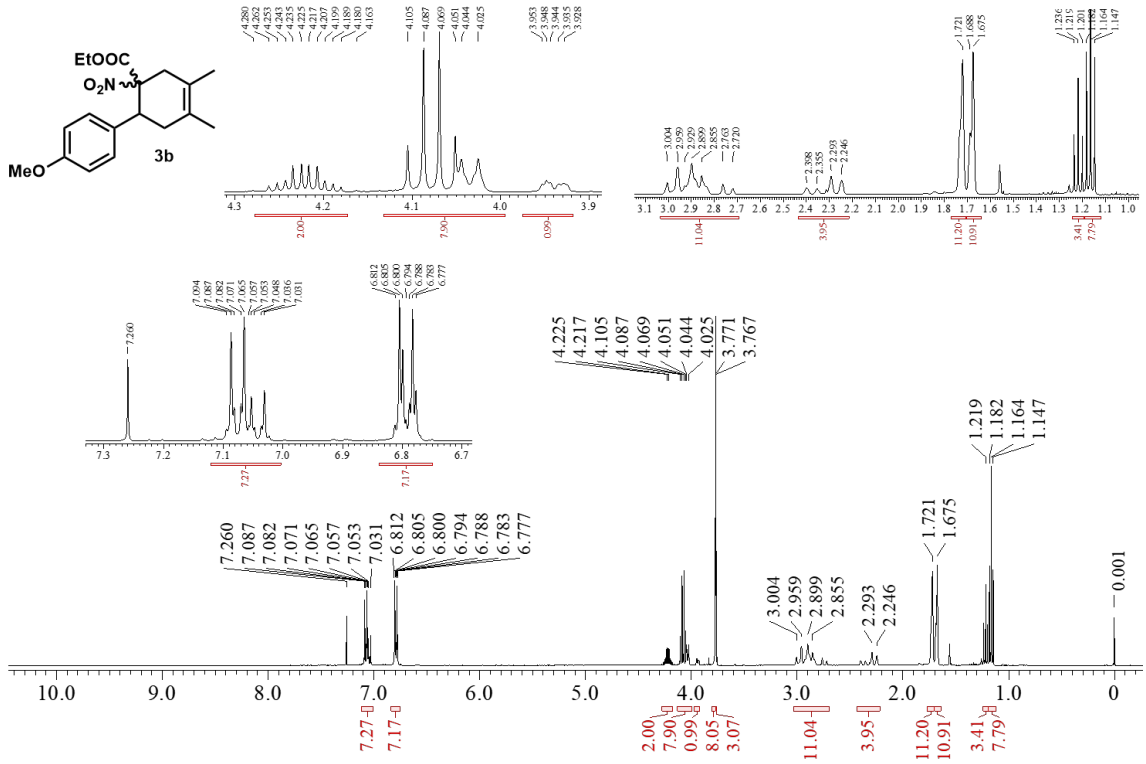
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3a**



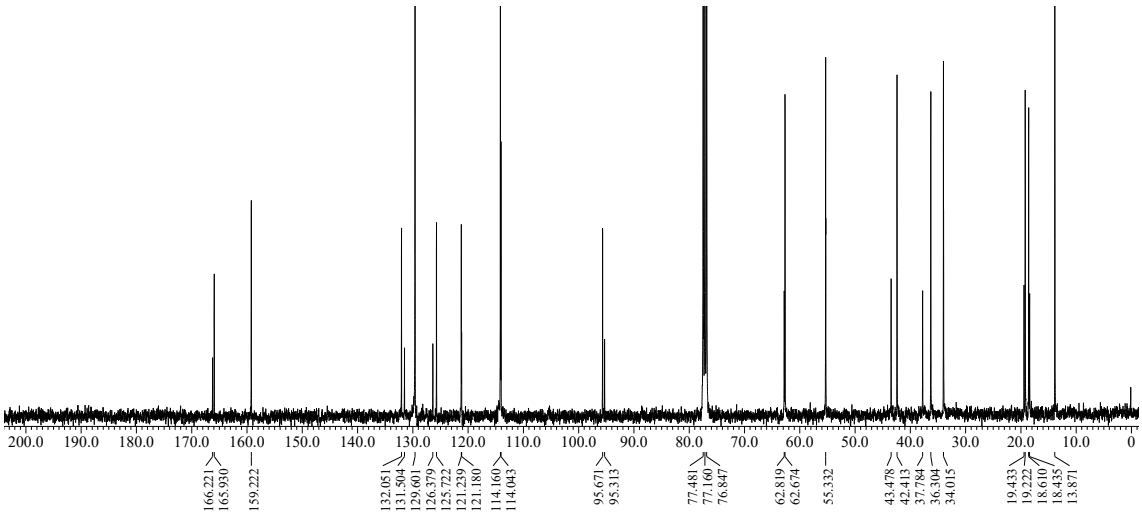
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **3a**


Spectrum from 20210225 ch3 A wiff (sample 1) - TuneSampleID, +TOF MS (100 - 1000) from 1.613 to 1.627 min
Intensity
318.1689
Mass/Charge, Da
Found elemental compositions
Hit Formula m/z RDB ppm MS Rank MSMS ppm MSMS Rank Found
1 C18H23NO4 318.1700 8.0 -3.4 1 NA/NA
MS Details MSMS Details Compound Details
Isotope cluster details
Peak Use m/z % Intensity Width
0 318.1689 100.0 0.001
MS result summary for C18H24NO4, [M+H]+
Elements from C1H1
Elements to C50H50N1O4
Mass tolerance (ppm) 5
Intensity tolerance (%) 10
#C/#heteroatoms greater than 0
Ion type [M+H]+
0 additional ion...
Mass Property AA Property Mass Accuracy Isotopic Distribution Elemental Composition Hypermass Unit Conversion Custom Elements AA List AA Modifications
Formula: C18H23NO4
Calculate
Charge state: 1
H+ charge agent (else electron)
Composition: C18H24NO4+
Charged monoisotopic mass: 318.16998
Monoisotopic m/z: 318.16998
Charged average mass: 318.392
Nominal mass: 318
RDB: 8.0
Measured m/z: 318.16887
Theoretical m/z: 318.16998
Error (mmu): -1.1
Error (ppm): -3.5

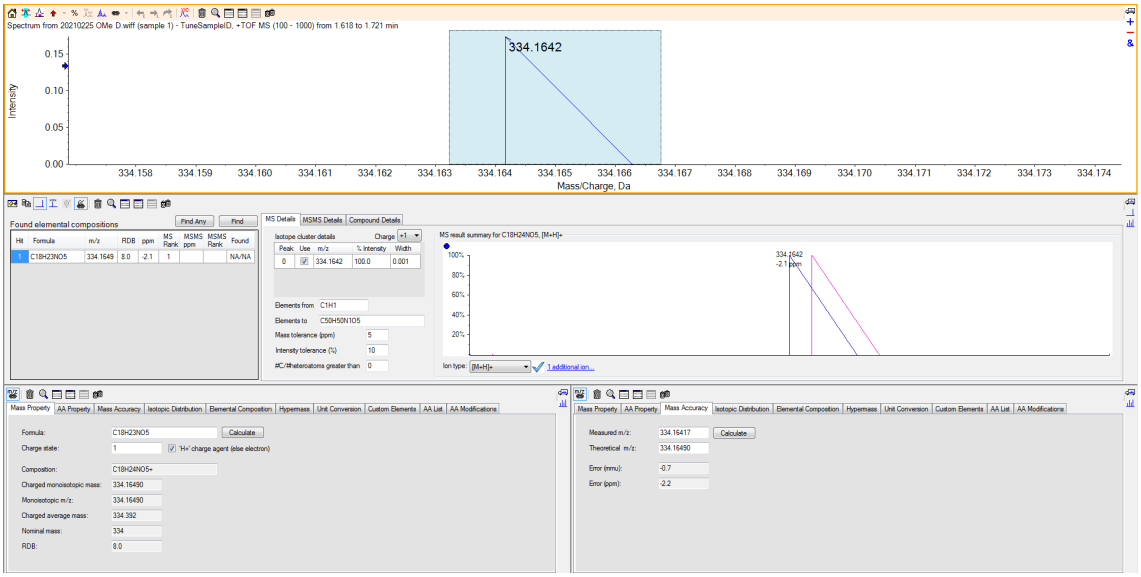
ESI-TOF MS



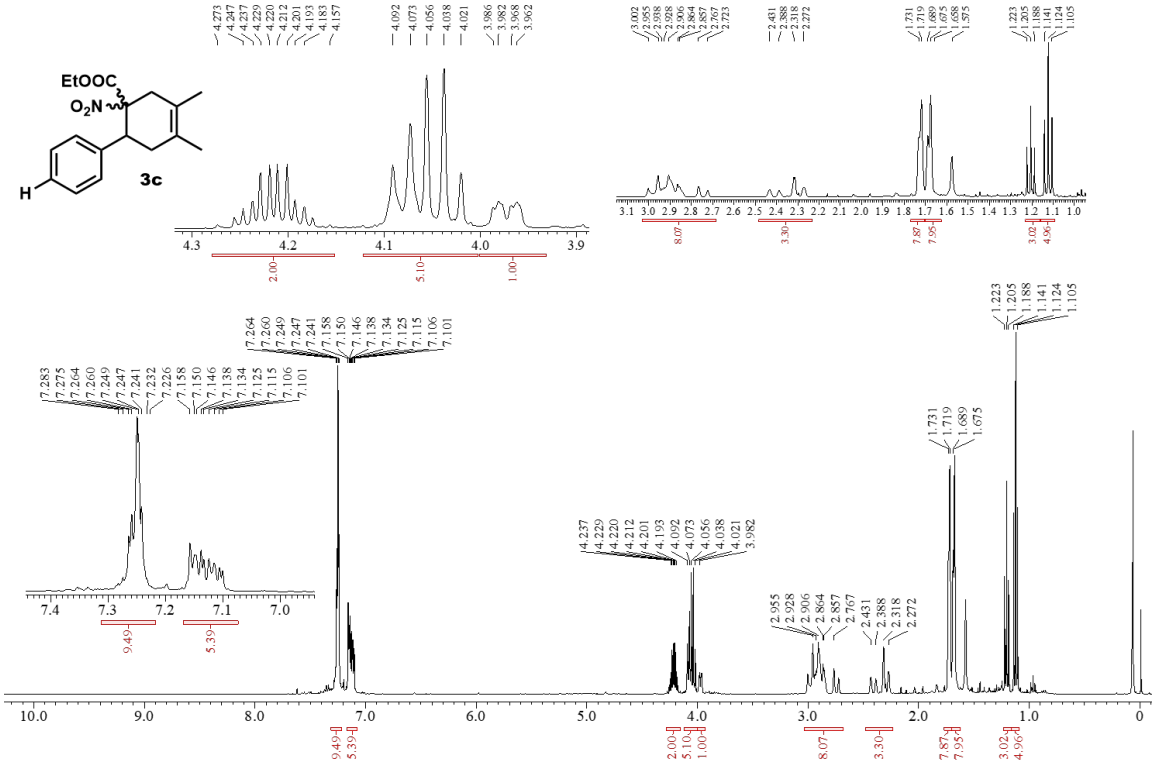
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3b**



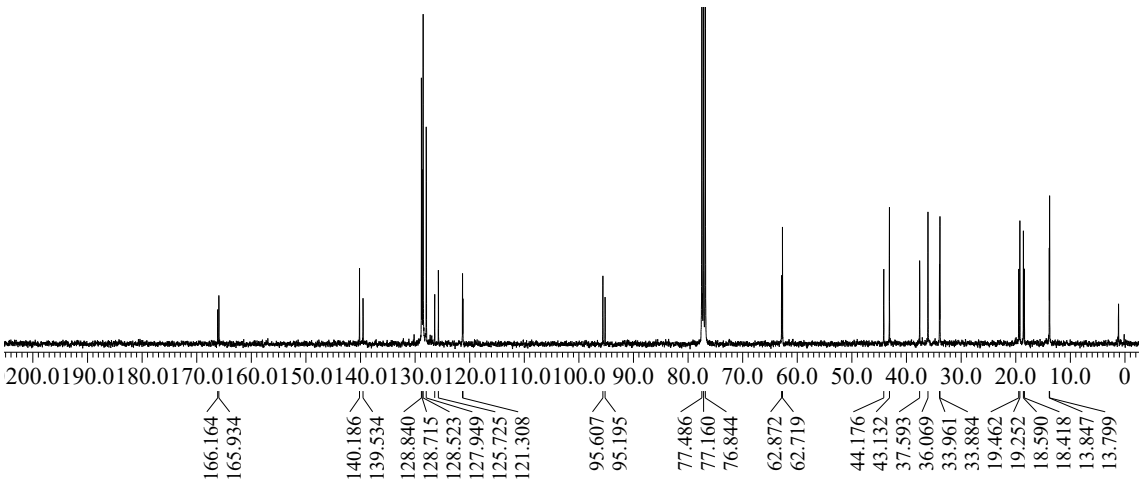
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **3b**


Spectrum from 20210225 OMe D.wiff (sample 1) - TuneSampleID, +TOF MS (100 - 1000) from 1.618 to 1.721 min
334.1642
Intensity
Mass/Charge, Da
Found elemental compositions
C18H23NO5
334.1649
8.0
-2.1
MS Details
MSMS Details
Compound Details
Isotope cluster details
334.1642
100.0
0.001
MS result summary for C18H24NO5, [M+H]+
Mass Property
AA Property
Mass Accuracy
Isotopic Distribution
Elemental Composition
Hypermass
Unit Conversion
Custom Elements
AA List
AA Modifications
Formula:
C18H23NO5
Calculate
Charge state:
Composition:
C18H24NO5+
Charged monoisotopic mass:
334.16490
Monoisotopic m/z:
334.16490
Charged average mass:
334.392
Nominal mass:
334
RDB:
8.0
Measured m/z:
334.16417
Theoretical m/z:
334.16490
Error (mmu):
-0.7
Error (ppm):
-2.2

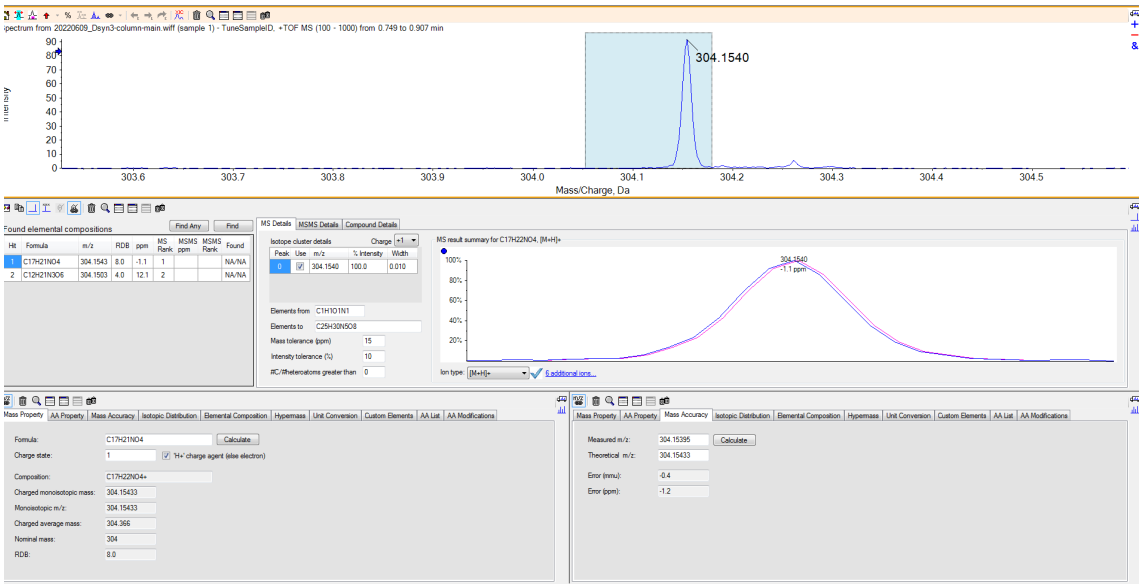
ESI-TOF MS



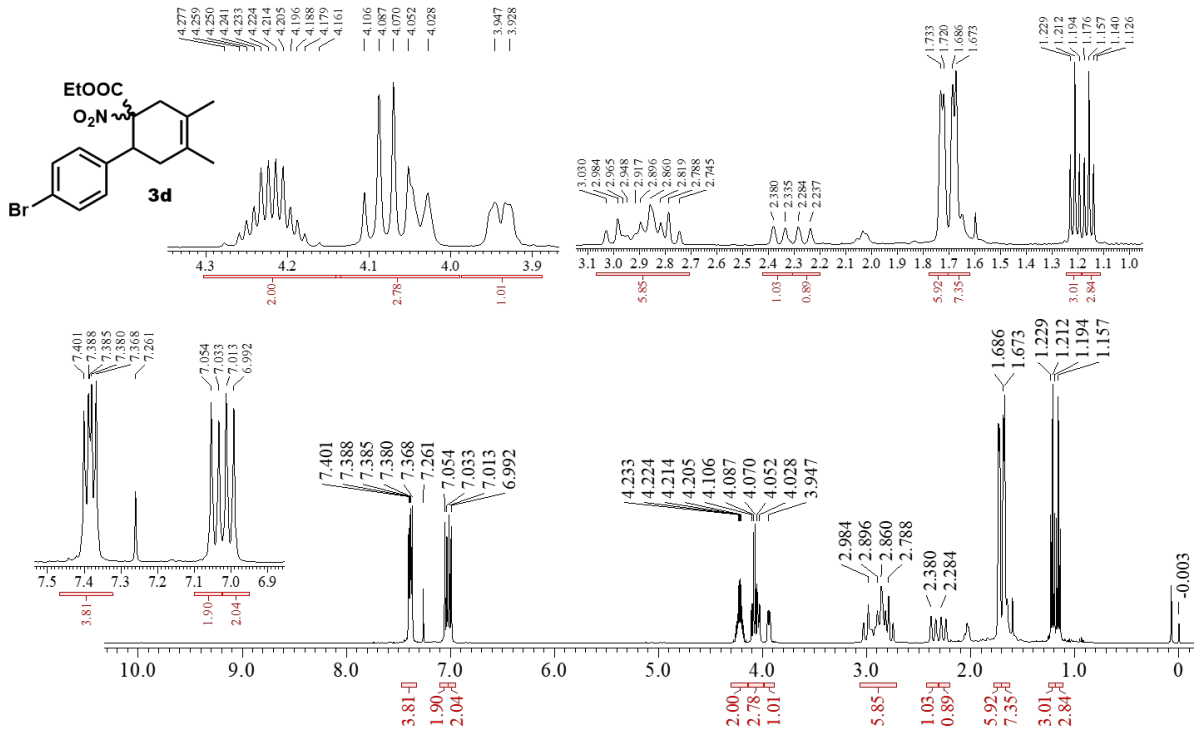
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3c**



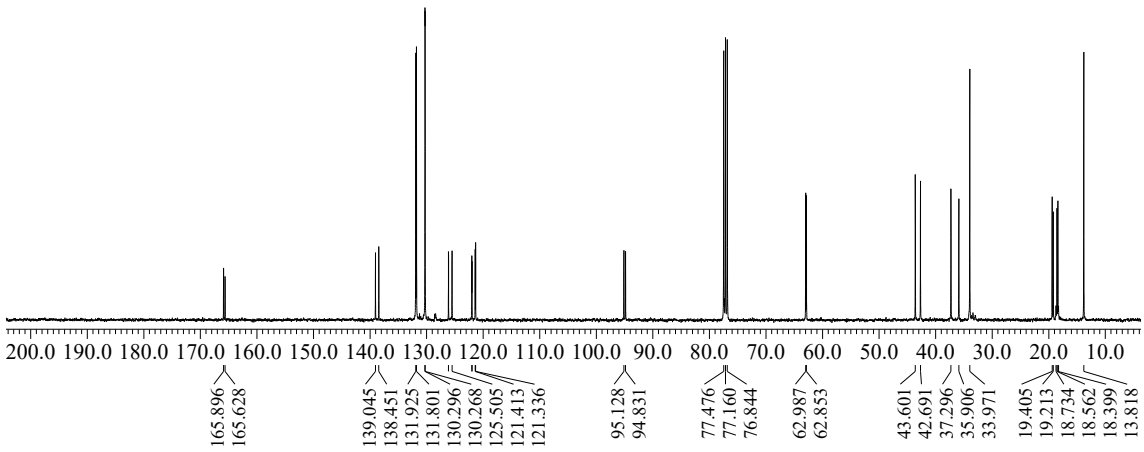
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **3c**


Spectrum from 20220609_Dsyn3-column-main.wiff (sample 1) - TuneSampleID, +TOF MS (100 - 1000) from 0.749 to 0.907 min
304.1540
Intensity
Mass/Charge, Da
Found elemental compositions
Find Any
Find
Hit Formula m/z RDB ppm MS Rank MSMS ppm MSMS Rank Found
1 C17H21NO4 304.1543 8.0 -1.1 1 NA/NA
2 C12H21N3O6 304.1503 4.0 12.1 2 NA/NA
MS Details
MSMS Details
Compound Details
Isotope cluster details
Peak Use m/z % Intensity Width
0 304.1540 100.0 0.010
Elements from C1H1O1N1
Elements to C25H30N5O8
Mass tolerance (ppm) 15
Intensity tolerance (%) 10
#C/#heteroatoms greater than 0
MS result summary for C17H22NO4, [M+H]+
304.1540
-1.1 ppm
Ion type [M+H]+
6 additional ions...
Mass Property
AA Property
Mass Accuracy
Isotopic Distribution
Elemental Composition
Hypermass
Unit Conversion
Custom Elements
AA List
AA Modifications
Formula: C17H21NO4
Calculate
Charge state: 1
'H+' charge agent (else electron)
Composition: C17H22NO4+
Charged monoisotopic mass: 304.15433
Monoisotopic m/z: 304.15433
Charged average mass: 304.366
Nominal mass: 304
RDB: 8.0
Measured m/z: 304.15395
Theoretical m/z: 304.15433
Error (mmu): -0.4
Error (ppm): -1.2

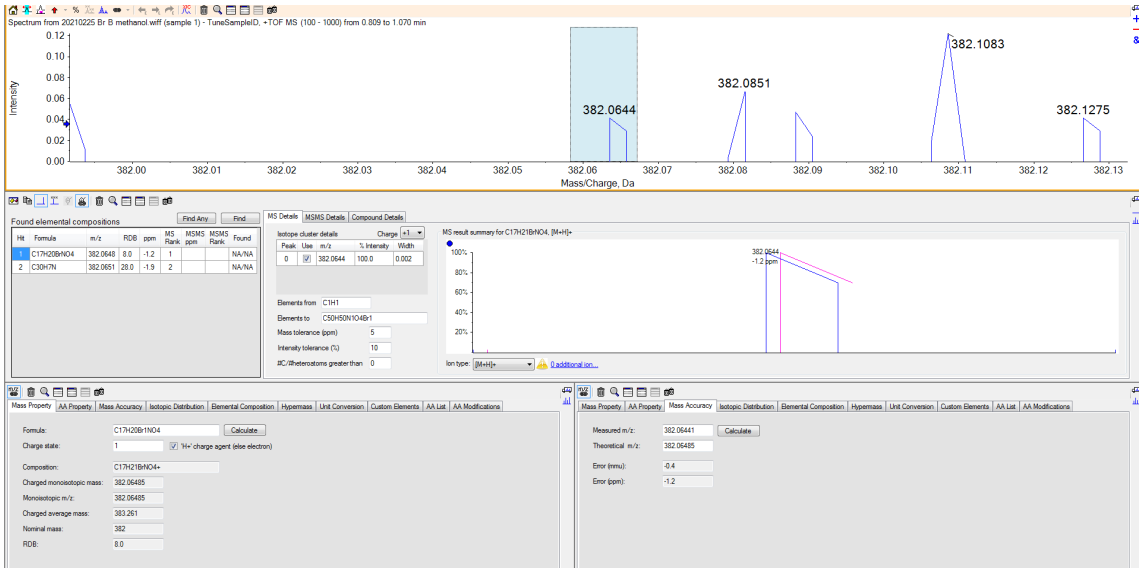
ESI-TOF MS



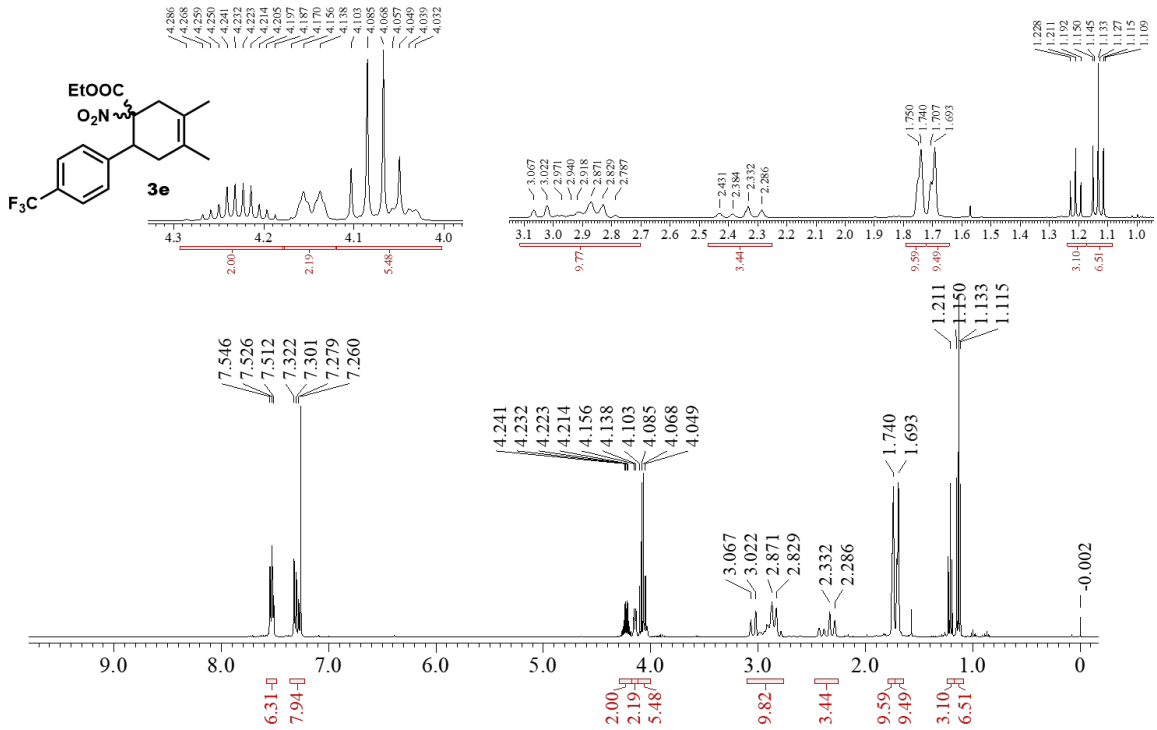
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3d**



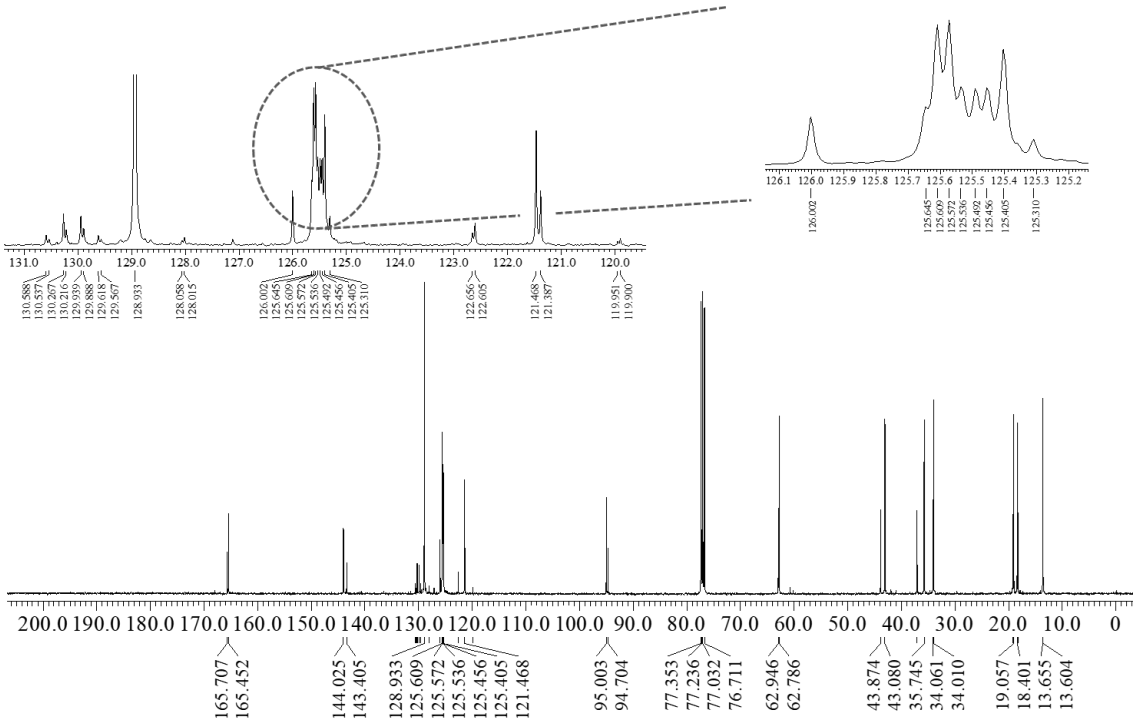
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **3d**


Spectrum from 20210225 Br B methanol.wiff (sample 1) - TuneSampleID, +TOF MS (100 - 1000) from 0.809 to 1.070 min
Intensity
Mass/Charge, Da
382.0644
382.0851
382.1083
382.1275
Found elemental compositions
Find Any
Find...
Hit
Formula
m/z
RDB
ppm
MS Rank
MSMS ppm
MSMS Rank
Found
C17H20BrNO4
382.0648
8.0
-1.2
NA/NA
C30H7N
382.0651
28.0
-1.9
MS Details
MSMS Details
Compound Details
Isotope cluster details
Charge
Peak
Use
% Intensity
Width
Elements from
C1H1
Elements to
C50H50N10O4Br1
Mass tolerance (ppm)
Intensity tolerance (%)
MS result summary for C17H21BrNO4, [M+H]+
382.0644
-1.2 ppm
Ion type:
[M+H]+
0 additional ion...
Mass Property
AA Property
Mass Accuracy
Isotopic Distribution
Elemental Composition
Hypermass
Unit Conversion
Custom Elements
AA List
AA Modifications
Formula:
C17H20Br1NO4
Calculate
Charge state:
1
'H+' charge agent (else electron)
Composition:
C17H21BrNO4+
Charged monoisotopic mass:
382.06485
Monoisotopic m/z:
382.06485
Charged average mass:
383.261
Nominal mass:
382
RDB:
8.0
Measured m/z:
382.06441
Theoretical m/z:
382.06485
Error (mmu):
-0.4
Error (ppm):
-1.2

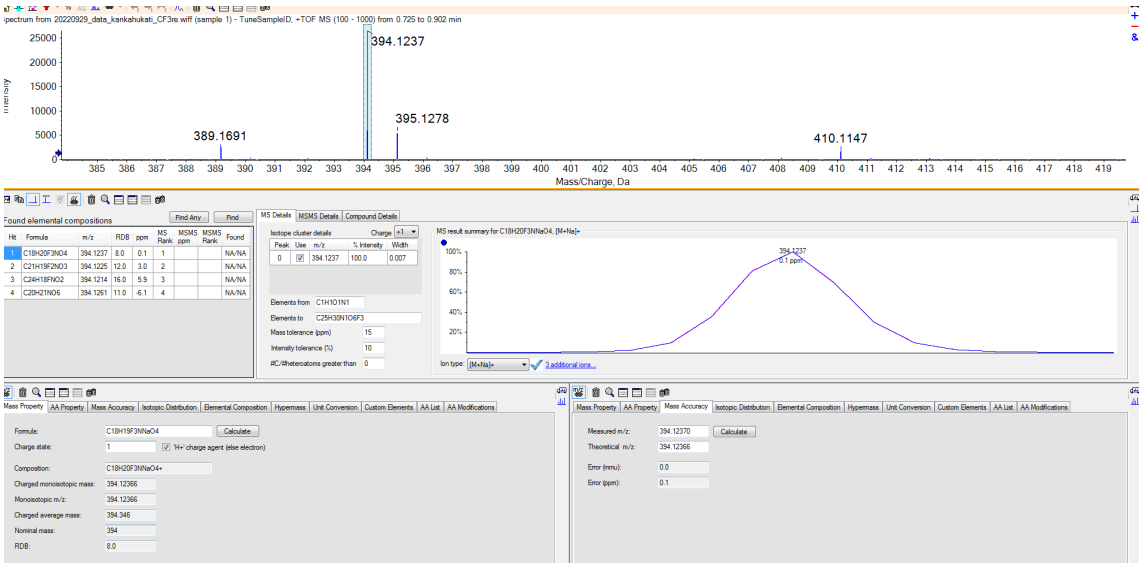
ESI-TOF MS



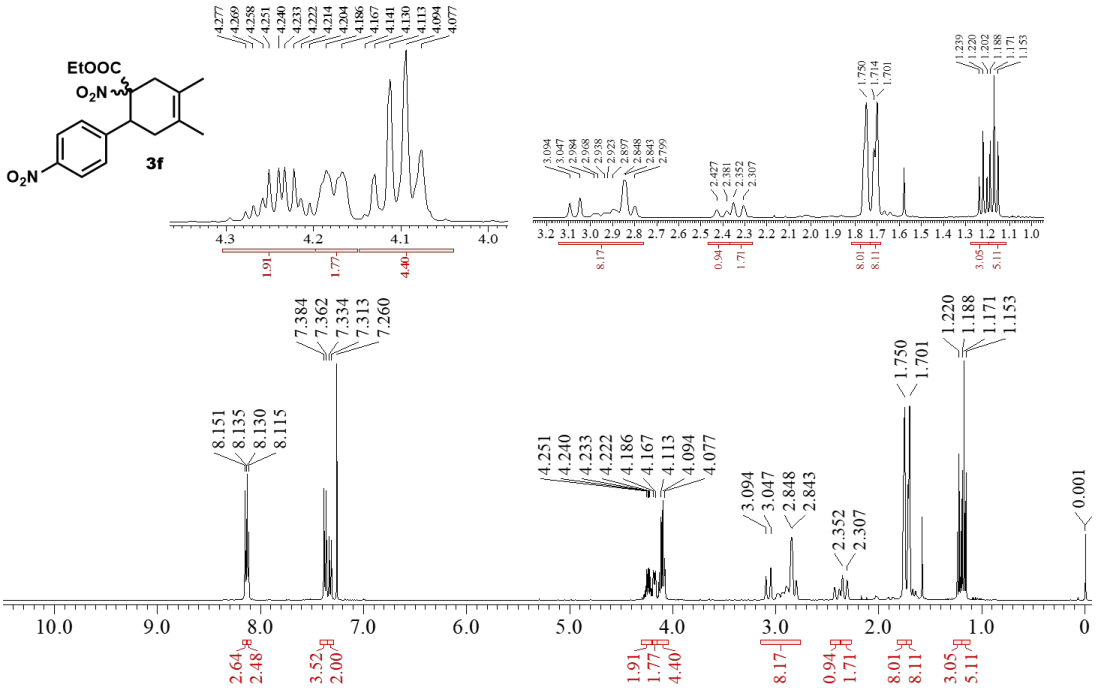
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3e**



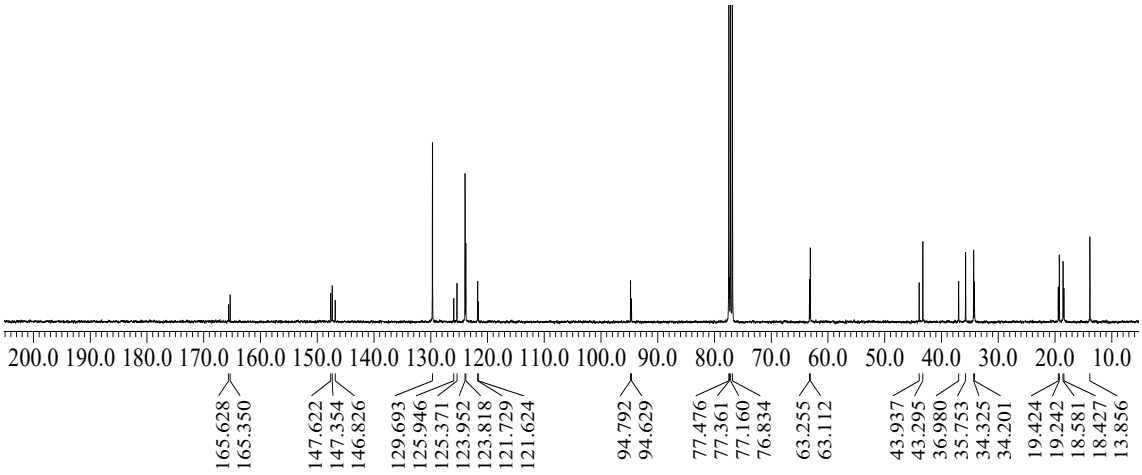
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **3e**


spectrum from 20220929_data_kankahukati_CF3re.wiff (sample 1) - TuneSampleID, +TOF MS (100 - 1000) from 0.725 to 0.902 min
394.1237
395.1278
389.1691
410.1147
Intensity
Mass/Charge, Da
Found elemental compositions
MS Details
MSMS Details
Compound Details
MS result summary for C18H20F3NNaO4, [M+Na]+
Formula:
Charge state:
Composition:
Charged monoisotopic mass:
Monoisotopic m/z:
Charged average mass:
Nominal mass:
RDB:
Measured m/z:
Theoretical m/z:
Error (mmu):
Error (ppm):

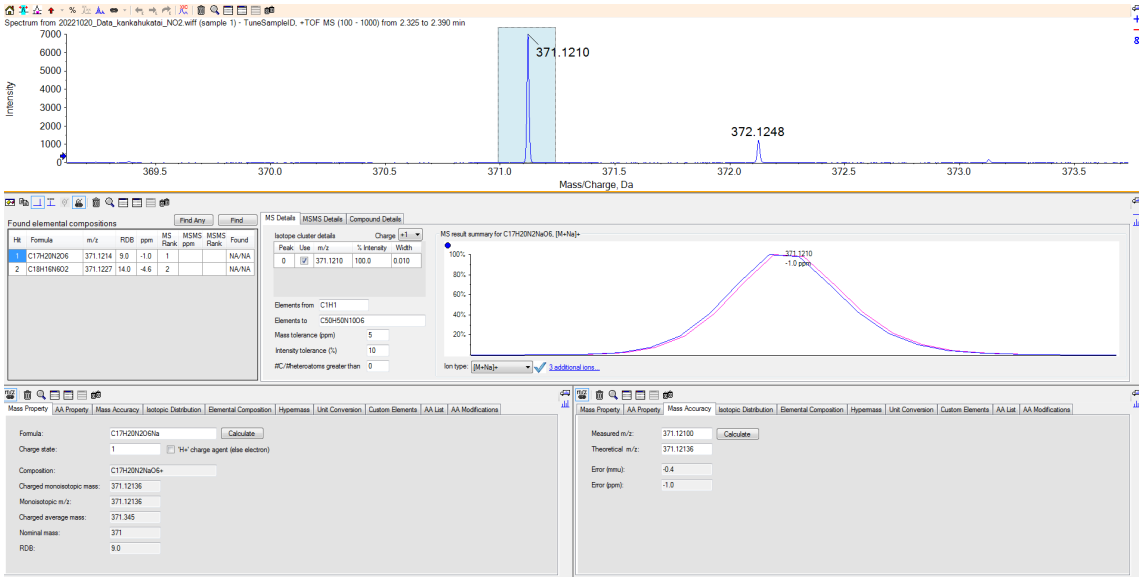
ESI-TOF MS



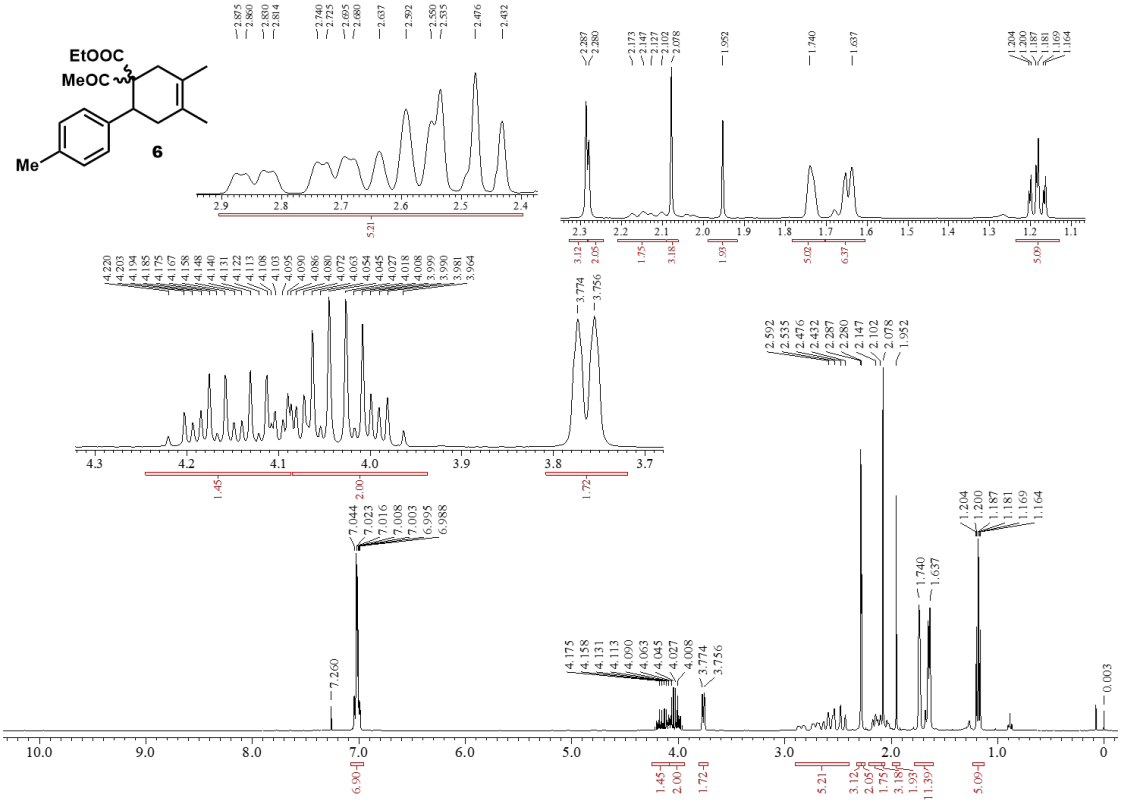
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3f**



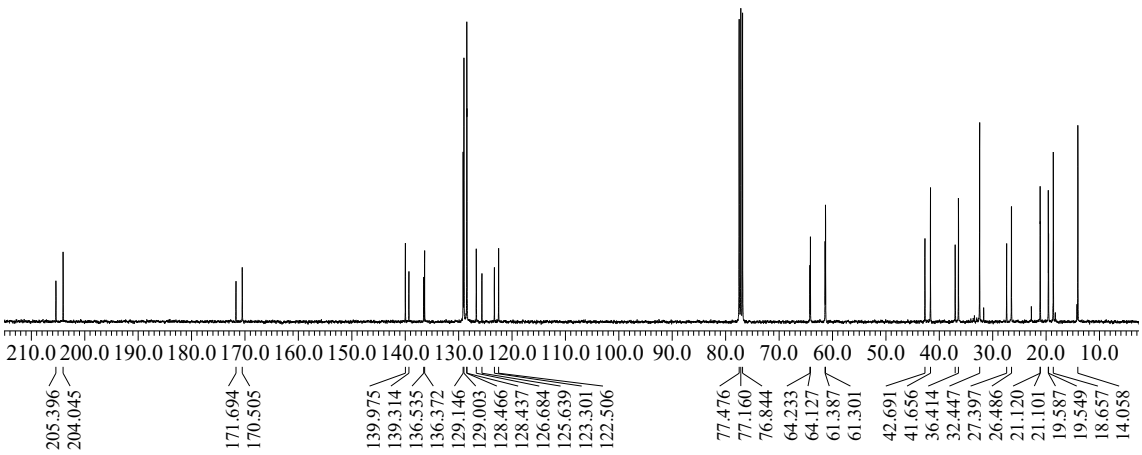
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **3f**


Spectrum from 20221020_Data_kankahukatai_NO2.wiff (sample 1) - TuneSampleID, +TOF MS (100 - 1000) from 2.325 to 2.390 min
Intensity
371.1210
372.1248
Mass/Charge, Da
Found elemental compositions
Find Any
Find
Hit Formula m/z RDB ppm MS Rank MSMS ppm MSMS Rank Found
1 C17H20N2O6 371.1214 9.0 -1.0 1 NA/NA
2 C18H16N6O2 371.1227 14.0 -4.6 2 NA/NA
MS Details
MSMS Details
Compound Details
Isotope cluster details
Charge +1
Peak Use m/z % Intensity Width
0 371.1210 100.0 0.010
Elements from C1H1
Elements to C50H50N10O6
Mass tolerance (ppm) 5
Intensity tolerance (%) 10
#C/#heteroatoms greater than 0
MS result summary for C17H20N2NaO6, [M+Na]+
371.1210
-1.0 ppm
Ion type [M+Na]+
3 additional ions...
Mass Property
AA Property
Mass Accuracy
Isotopic Distribution
Elemental Composition
Hypermass
Unit Conversion
Custom Elements
AA List
AA Modifications
Formula: C17H20N2O6Na
Calculate
Charge state: 1
'H+' charge agent (else electron)
Composition: C17H20N2NaO6+
Charged monoisotopic mass: 371.12136
Monoisotopic m/z: 371.12136
Charged average mass: 371.345
Nominal mass: 371
RDB: 9.0
Measured m/z: 371.12100
Theoretical m/z: 371.12136
Error (mmu): -0.4
Error (ppm): -1.0

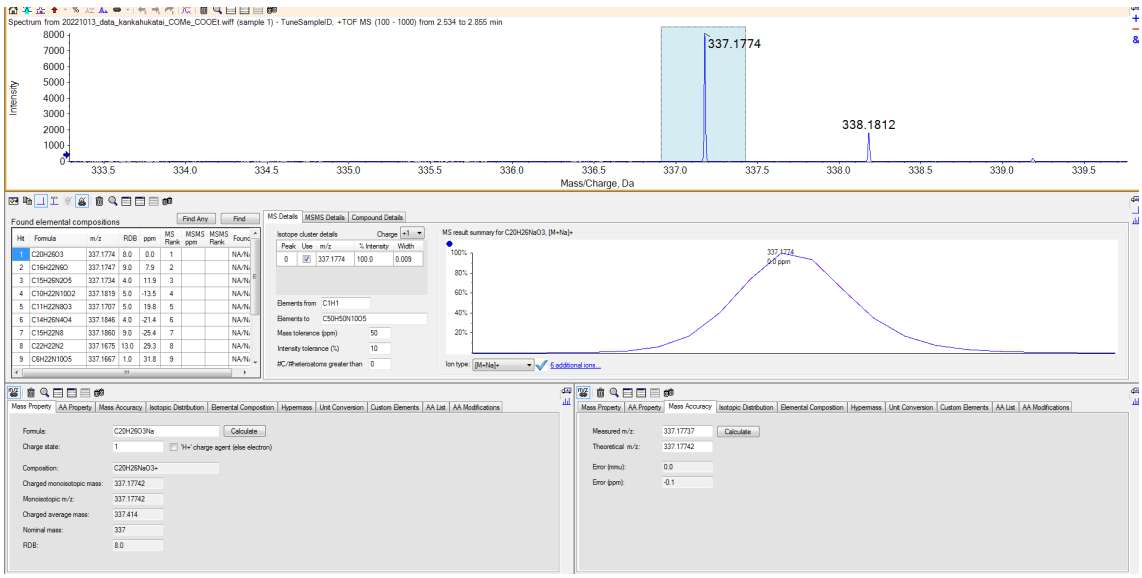
ESI-TOF MS



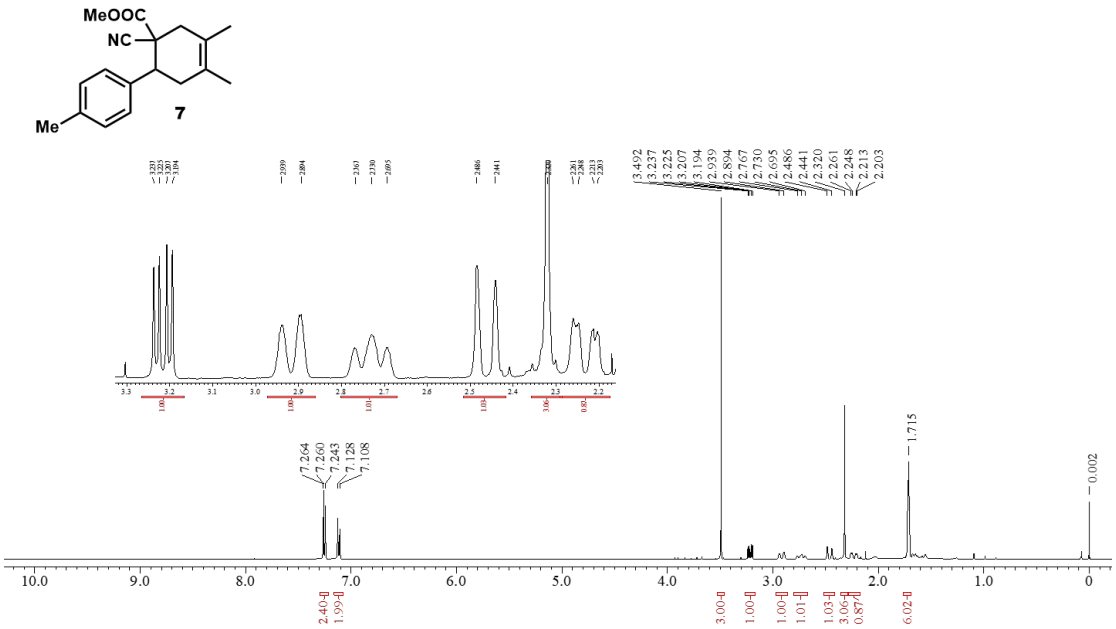
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **6**



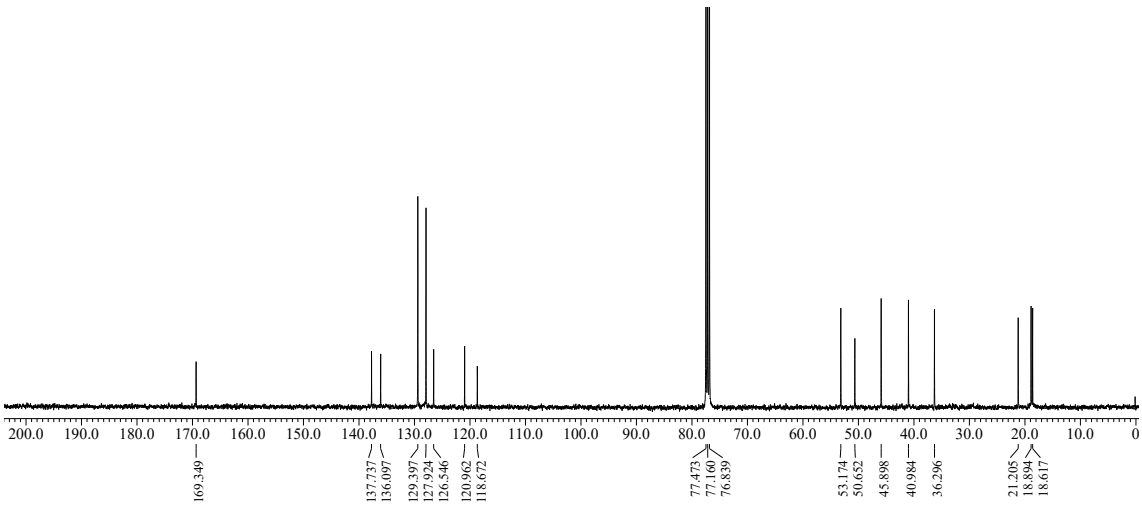
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **6**


Spectrum from 20221013_data_kankahukatai_COMe_COOEt.wiff (sample 1) - TuneSampleID, +TOF MS (100 - 1000) from 2.534 to 2.855 min
Intensity
337.1774
338.1812
Mass/Charge, Da
Found elemental compositions
MS Details
MSMS Details
Compound Details
MS result summary for C20H26NaO3, [M+Na]+
Mass Property
AA Property
Mass Accuracy
Isotopic Distribution
Elemental Composition
Hypermass
Unit Conversion
Custom Elements
AA List
AA Modifications
Formula:
Charge state:
Composition:
Charged monoisotopic mass:
Monoisotopic m/z:
Charged average mass:
Nominal mass:
RDB:
Measured m/z:
Theoretical m/z:
Error (mmu):
Error (ppm):

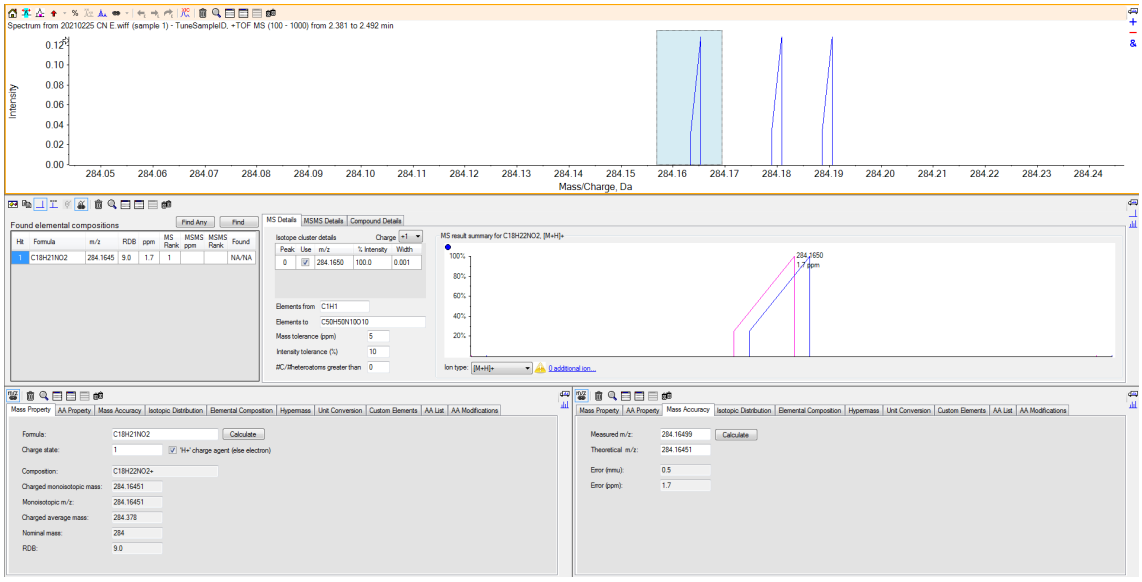
ESI-TOF MS



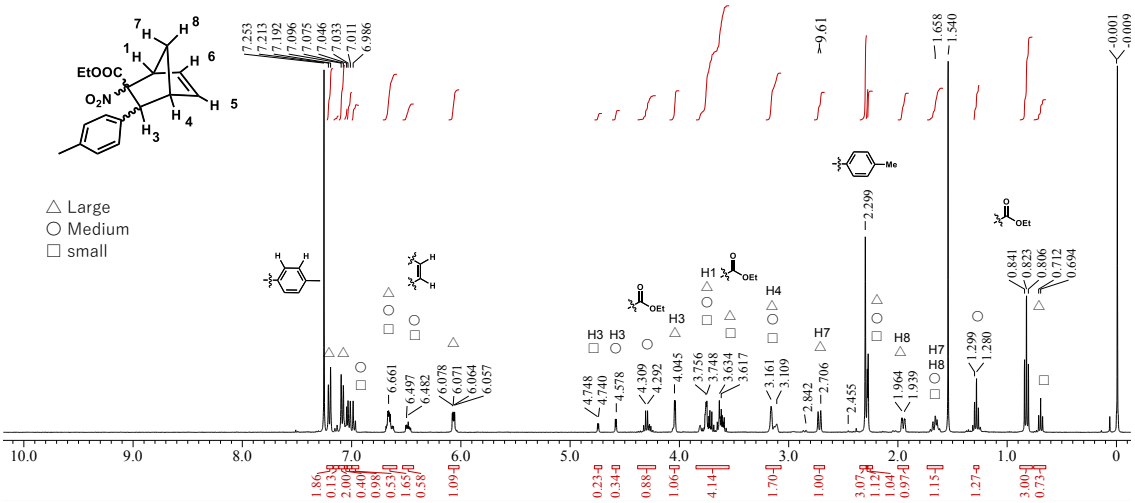
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **7**



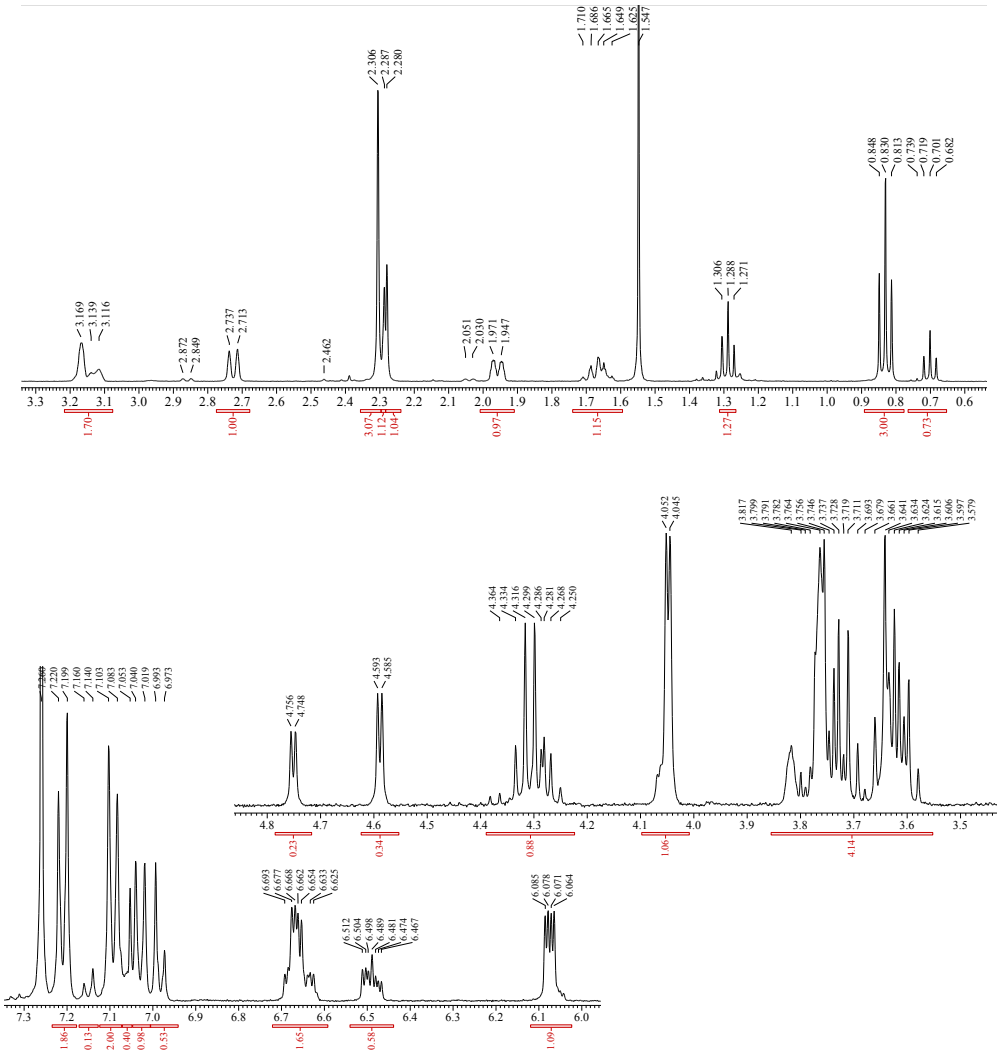
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **7**

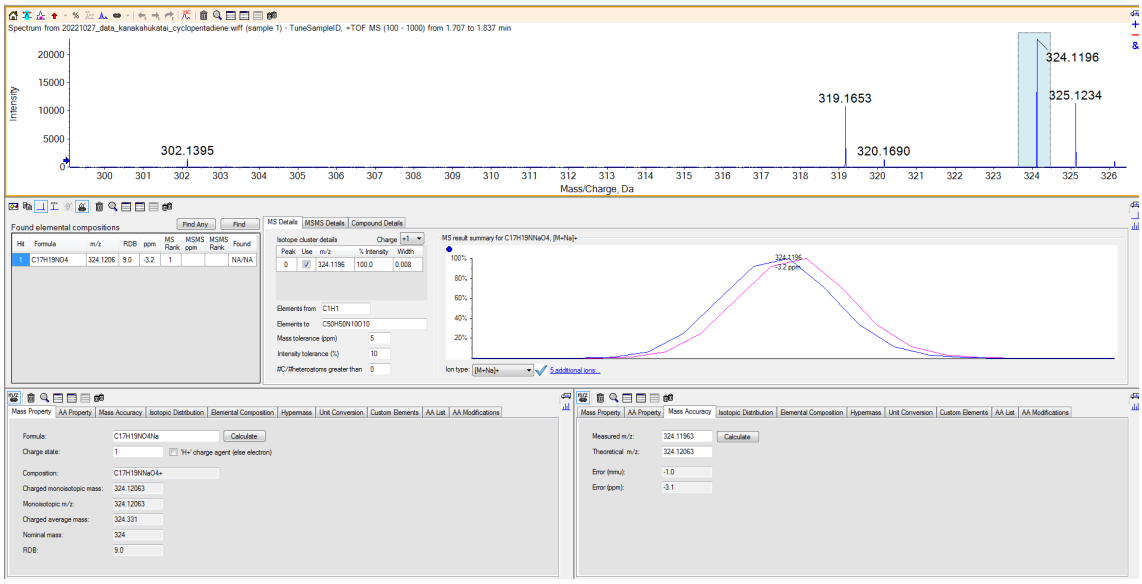

Spectrum from 20210225 CN E.wiff (sample 1) - TuneSampleID, +TOF MS (100 - 1000) from 2.381 to 2.492 min
Intensity
Mass/Charge, Da
Found elemental compositions
Find Any
Find
Hit Formula m/z RDB ppm MS Rank MSMS ppm MSMS Rank Found
1 C18H21NO2 284.1645 9.0 1.7 1 NA/NA
MS Details
MSMS Details
Compound Details
Isotope cluster details
Charge +1
Peak Use m/z % Intensity Width
0 284.1650 100.0 0.001
Elements from C1H1
Elements to C50H50N10O10
Mass tolerance (ppm) 5
Intensity tolerance (%) 10
#C/#heteroatoms greater than 0
MS result summary for C18H22NO2, [M+H]+
284.1650
1.7 ppm
Ion type [M+H]+
0 additional ion...
Mass Property
AA Property
Mass Accuracy
Isotopic Distribution
Elemental Composition
Hypermass
Unit Conversion
Custom Elements
AA List
AA Modifications
Formula: C18H21NO2
Calculate
Charge state: 1
%H+ charge agent (else electron)
Composition: C18H22NO2+
Charged monoisotopic mass: 284.16451
Monoisotopic m/z: 284.16451
Charged average mass: 284.378
Nominal mass: 284
RDB: 9.0
Measured m/z: 284.16499
Theoretical m/z: 284.16451
Error (mmu): 0.5
Error (ppm): 1.7

ESI-TOF MS

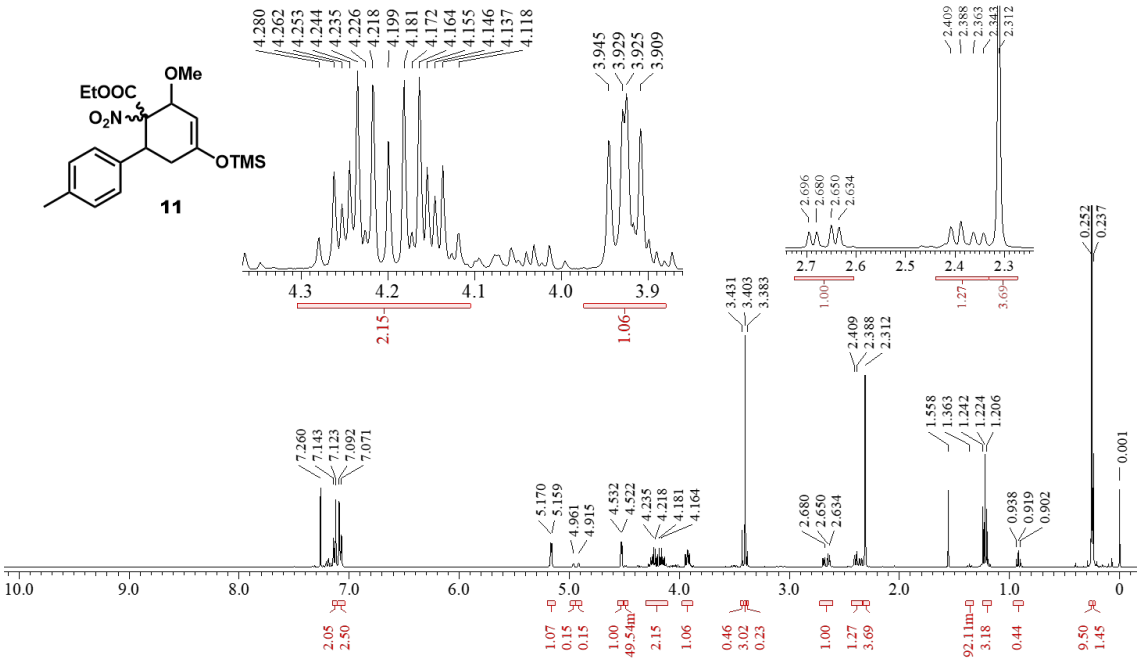


^{1}H NMR ($CDCl_3$, 400 MHz) of compound **9**

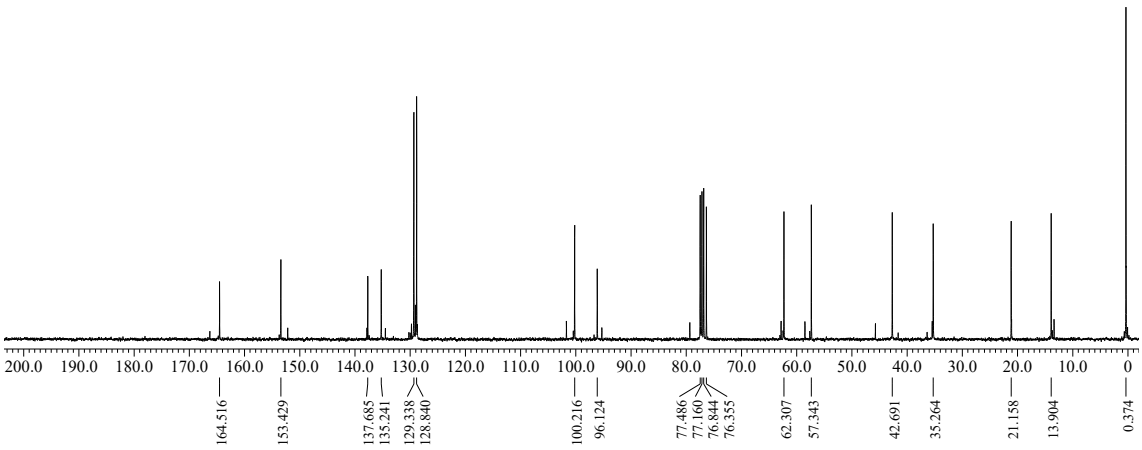



Spectrum from 20221027_data_kanakahukatai_cyclopentadiene.wiff (sample 1) - TuneSampleID, +TOF MS (100 - 1000) from 1.707 to 1.837 min
Intensity
Mass/Charge, Da
302.1395
319.1653
320.1690
324.1196
325.1234
Found elemental compositions
C17H19NO4
324.1206
9.0
-3.2
MS result summary for C17H19NNaO4, [M+Na]+
Formula: C17H19NO4Na
Composition: C17H19NNaO4+
Charged monoisotopic mass: 324.12063
Monoisotopic m/z: 324.12063
Charged average mass: 324.331
Nominal mass: 324
RDB: 9.0
Measured m/z: 324.11963
Theoretical m/z: 324.12063
Error (mmu): -1.0
Error (ppm): -3.1

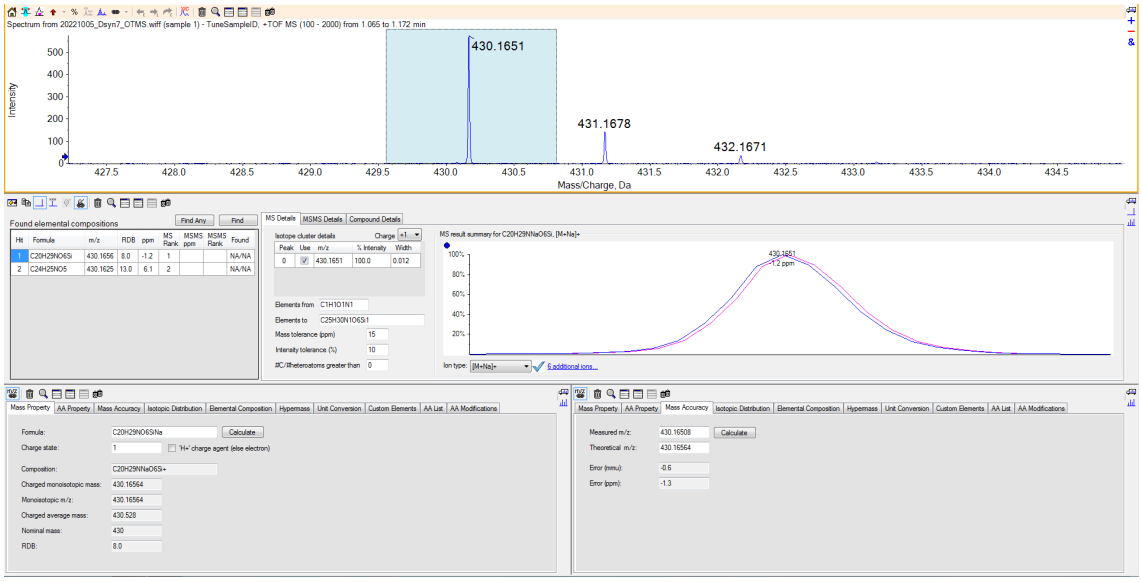
ESI-TOF MS



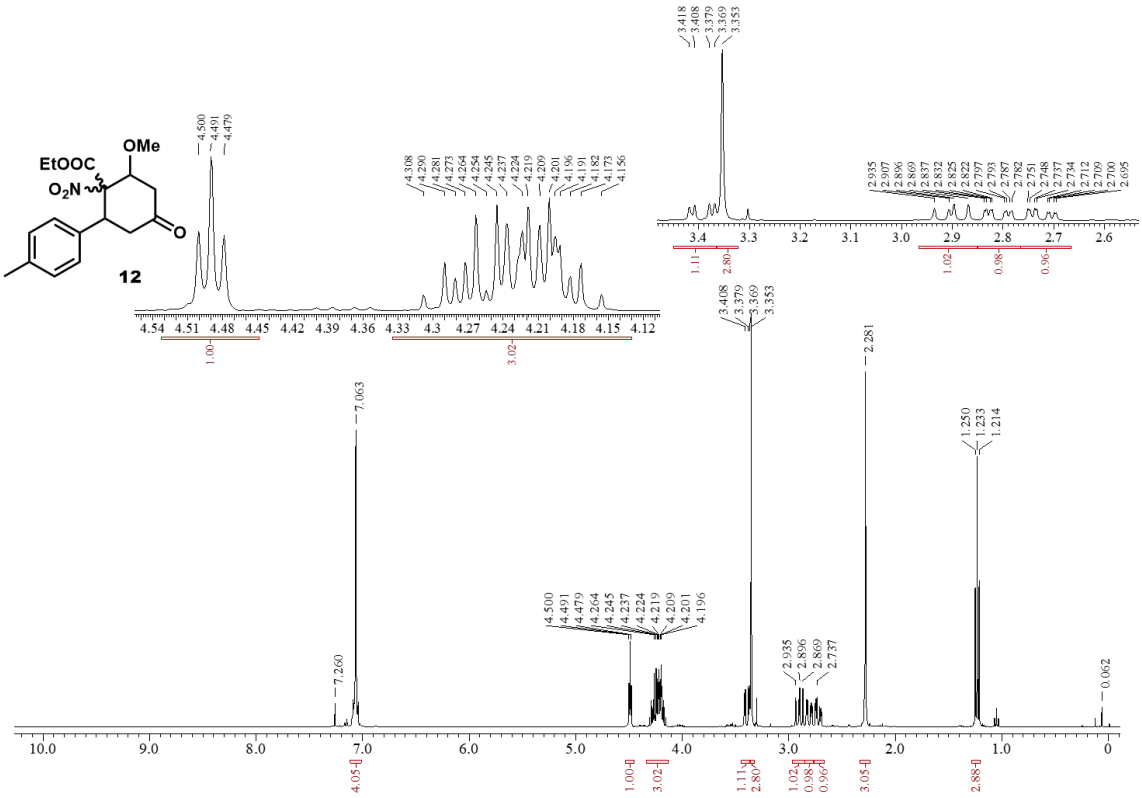
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **11**



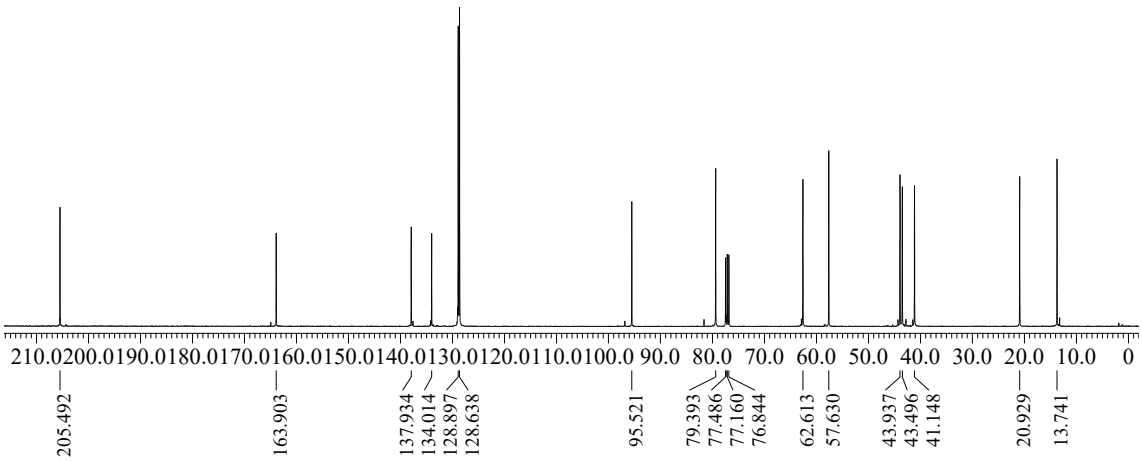
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **11**


Spectrum from 20221005_Dsyn7_OTMS.wiff (sample 1) - TuneSampleID, +TOF MS (100 - 2000) from 1.065 to 1.172 min
Intensity
430.1651
431.1678
432.1671
Mass/Charge, Da
Found elemental compositions
Hit Formula m/z RDB ppm MS Rank MSMS ppm MSMS Rank Found
1 C20H29NO6Si 430.1656 8.0 -1.2 1 NA/NA
2 C24H25NO5 430.1625 13.0 6.1 2 NA/NA
MS Details MSMS Details Compound Details
Isotope cluster details
Peak Use m/z % Intensity Width
0 430.1651 100.0 0.012
Elements from C1H1O1N1
Elements to C25H30N1O6Si1
Mass tolerance (ppm) 15
Intensity tolerance (%) 10
#C/#heteroatoms greater than 0
MS result summary for C20H29NNaO6Si, [M+Na]+
430.1651
-1.2 ppm
Ion type: [M+Na]+
6 additional ions...
Mass Property AA Property Mass Accuracy Isotopic Distribution Elemental Composition Hypermass Unit Conversion Custom Elements AA List AA Modifications
Formula: C20H29NO6SiNa
Calculate
Charge state: 1
'H+' charge agent (else electron)
Composition: C20H29NNaO6Si+
Charged monoisotopic mass: 430.16564
Monoisotopic m/z: 430.16564
Charged average mass: 430.528
Nominal mass: 430
RDB: 8.0
Measured m/z: 430.16508
Theoretical m/z: 430.16564
Error (mmu): -0.6
Error (ppm): -1.3

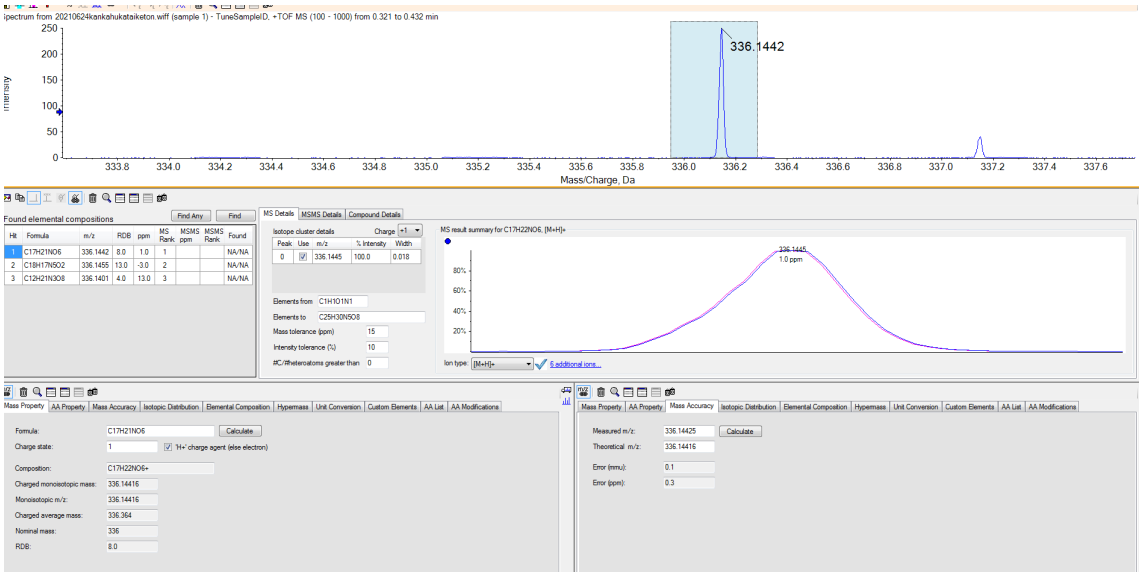
ESI-TOF MS



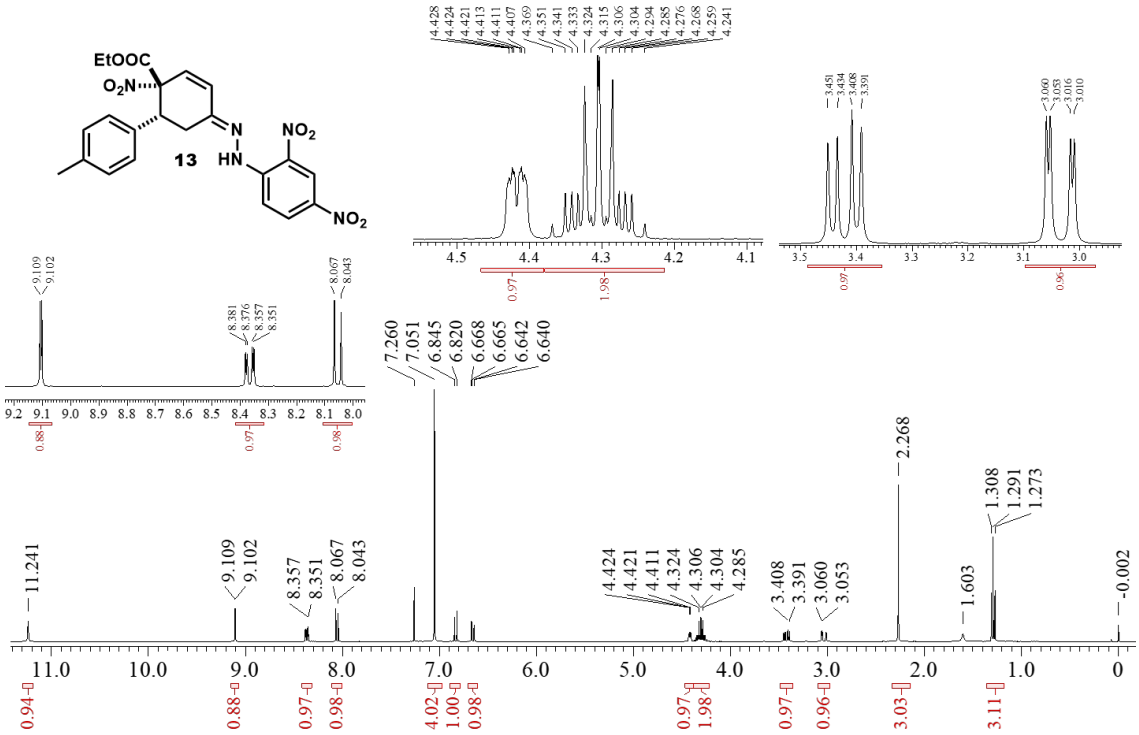
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **12**



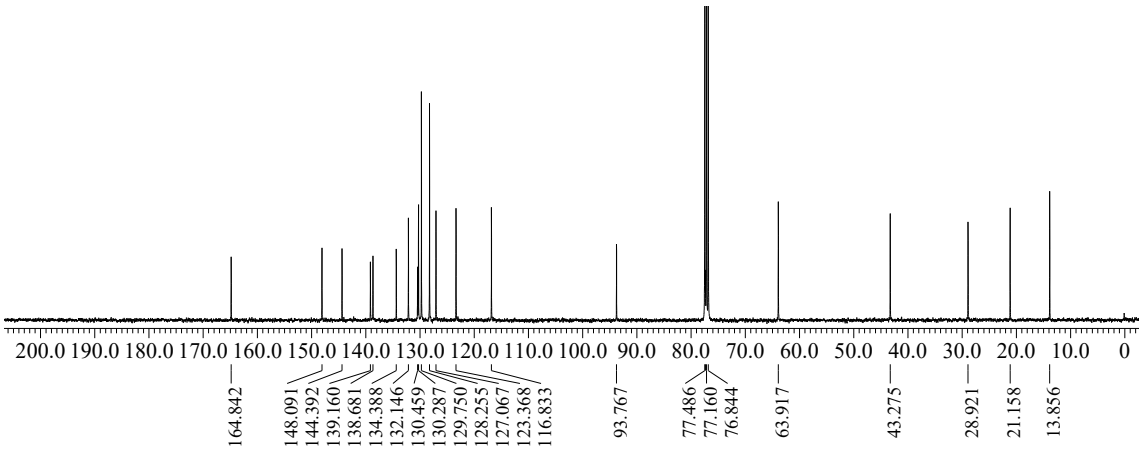
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **12**


ipectrum from 20210624kankahukataiketon.wiff (sample 1) - TuneSampleID, +TOF MS (100 - 1000) from 0.321 to 0.432 min
336.1442
Intensity
Mass/Charge, Da
Found elemental compositions
Find Any
Find
Hit Formula m/z RDB ppm MS Rank MSMS ppm MSMS Rank Found
1 C17H21NO6 336.1442 8.0 1.0 1 NA/NA
2 C18H17N5O2 336.1455 13.0 -3.0 2 NA/NA
3 C12H21N3O8 336.1401 4.0 13.0 3 NA/NA
MS Details
MSMS Details
Compound Details
Isotope cluster details
Charge +1
Peak Use m/z % Intensity Width
0 336.1445 100.0 0.018
Elements from C1H1O1N1
Elements to C25H30N5O8
Mass tolerance (ppm) 15
Intensity tolerance (%) 10
#C:#heteroatoms greater than 0
MS result summary for C17H22NO6, [M+H]+
336.1445
1.0 ppm
Ion type [M+H]+
5 additional ions...
Mass Property
AA Property
Mass Accuracy
Isotopic Distribution
Elemental Composition
Hypermass
Unit Conversion
Custom Elements
AA List
AA Modifications
Formula: C17H21NO6
Calculate
Charge state: 1
'H+' charge agent (else electron)
Composition: C17H22NO6+
Charged monoisotopic mass: 336.14416
Monoisotopic m/z: 336.14416
Charged average mass: 336.364
Nominal mass: 336
RDB: 8.0
Measured m/z: 336.14425
Calculate
Theoretical m/z: 336.14416
Error (mmu): 0.1
Error (ppm): 0.3

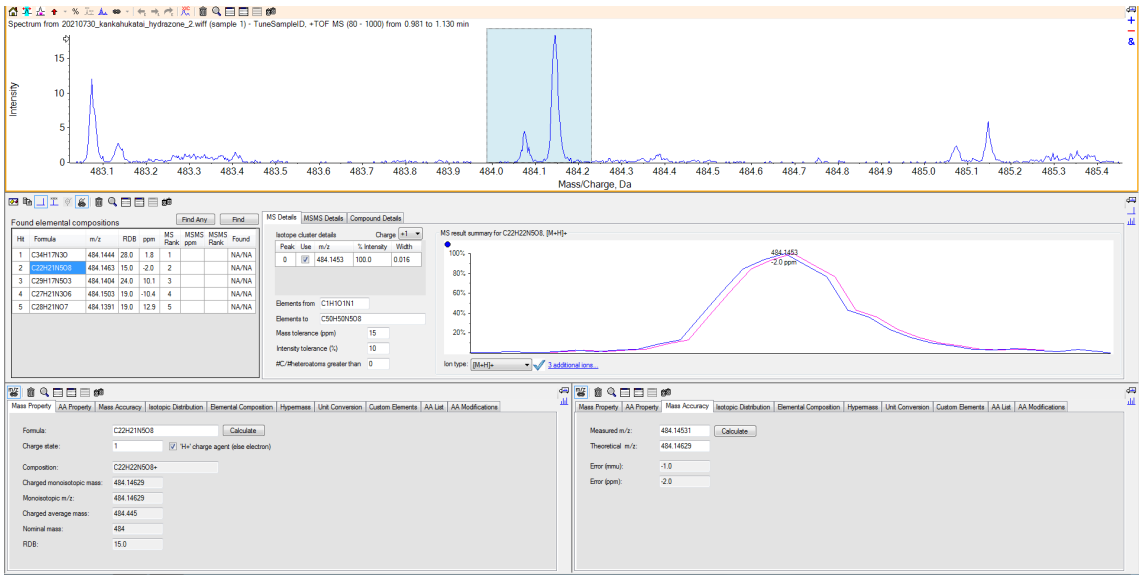
ESI-TOF MS



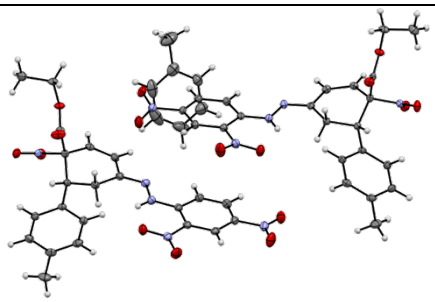
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **13**



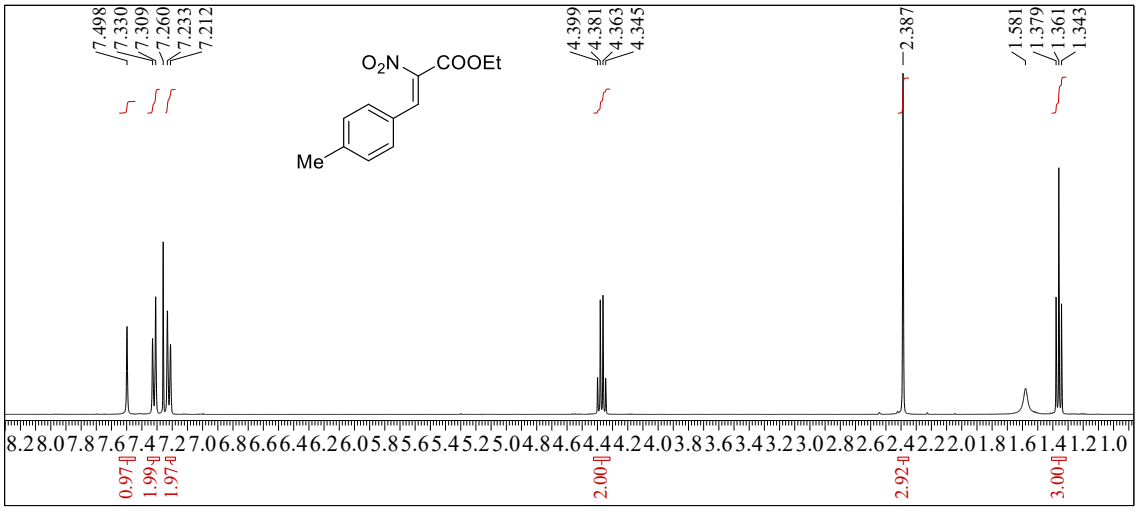
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **13**


Spectrum from 20210730_kankahukatai_hydrazone_2.wiff (sample 1) - TuneSampleID, +TOF MS (80 - 1000) from 0.981 to 1.130 min
Intensity
Mass/Charge, Da
Found elemental compositions
Find Any
Find...
Hit Formula m/z RDB ppm MS Rank MSMS ppm MSMS Rank Found
1 C34H17N3O 484.1444 28.0 1.8 1 NA/NA
2 C22H21N5O8 484.1463 15.0 -2.0 2 NA/NA
3 C29H17N5O3 484.1404 24.0 10.1 3 NA/NA
4 C27H21N3O6 484.1503 19.0 -10.4 4 NA/NA
5 C28H21NO7 484.1391 19.0 12.9 5 NA/NA
MS Details
MSMS Details
Compound Details
Isotope cluster details
Charge +1
Peak Use m/z % Intensity Width
0 484.1453 100.0 0.016
Elements from C1H1O1N1
Elements to C50H50N5O8
Mass tolerance (ppm) 15
Intensity tolerance (%) 10
#C/#heteroatoms greater than 0
MS result summary for C22H22N5O8, [M+H]+
484.1453
-2.0 ppm
Ion type [M+H]+
3 additional ions...
Mass Property
AA Property
Mass Accuracy
Isotopic Distribution
Elemental Composition
Hypermass
Unit Conversion
Custom Elements
AA List
AA Modifications
Formula: C22H21N5O8
Calculate
Charge state: 1
'H+' charge agent (else electron)
Composition: C22H22N5O8+
Charged monoisotopic mass: 484.14629
Monoisotopic m/z: 484.14629
Charged average mass: 484.445
Nominal mass: 484
RDB: 15.0
Measured m/z: 484.14531
Theoretical m/z: 484.14629
Error (mmu): -1.0
Error (ppm): -2.0

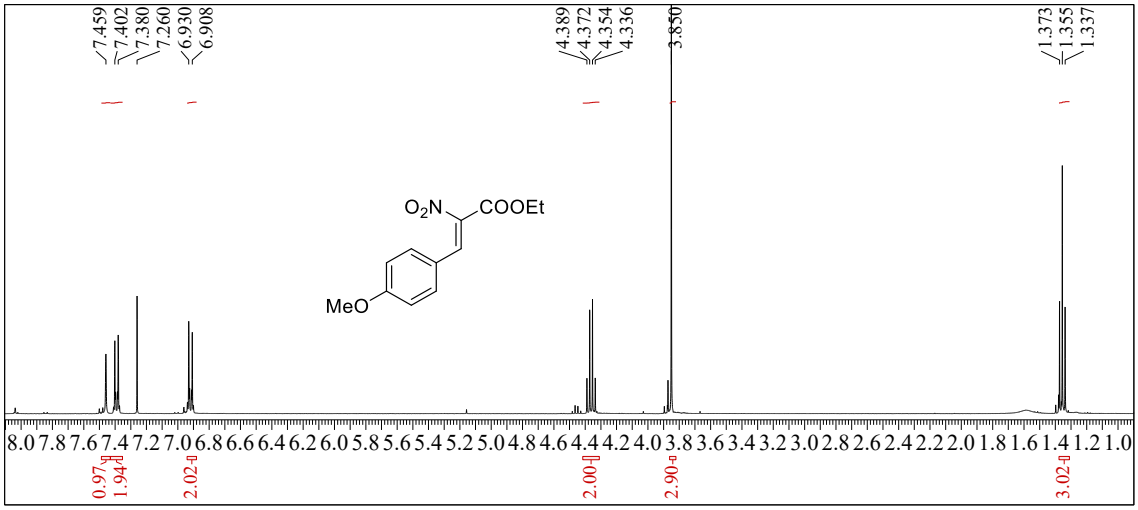
ESI-TOF MS

	
	13
Empirical formula	$2(C_{22}H_{21}N_5O_8),C_7H_8$
Formula weight	1059.01
Temperature (K)	103(2)
Crystal system	triclinic
Space group	*P*-1 (#2)
Unit cell Dimensions	a = 9.7580(1) Å, b = 13.4229(2) Å c = 20.8536(3) Å, α = 100.707(1)°, β = 96.142(1)°, γ = 108.673(1)°
Volume (Å)	2501.60(6)
Z	2
ρ_{calc} (g•cm^{-3})	1.406
Absorption coefficient (mm^{-1})	0.107
θ range (°)	2.239 to 30.195
Reflections collected	12117
Independent reflections	9643
Completeness to θ	100
Goodness-of-fit	1.083
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0415, wR_2 = 0.1095
R indices (all data)	R_1 = 0.0555, wR_2 = 0.1162
Largest diff. peak (e•Å)	0.432
Largest diff. hole (e•Å)	–0.286
CCDC number	2217872

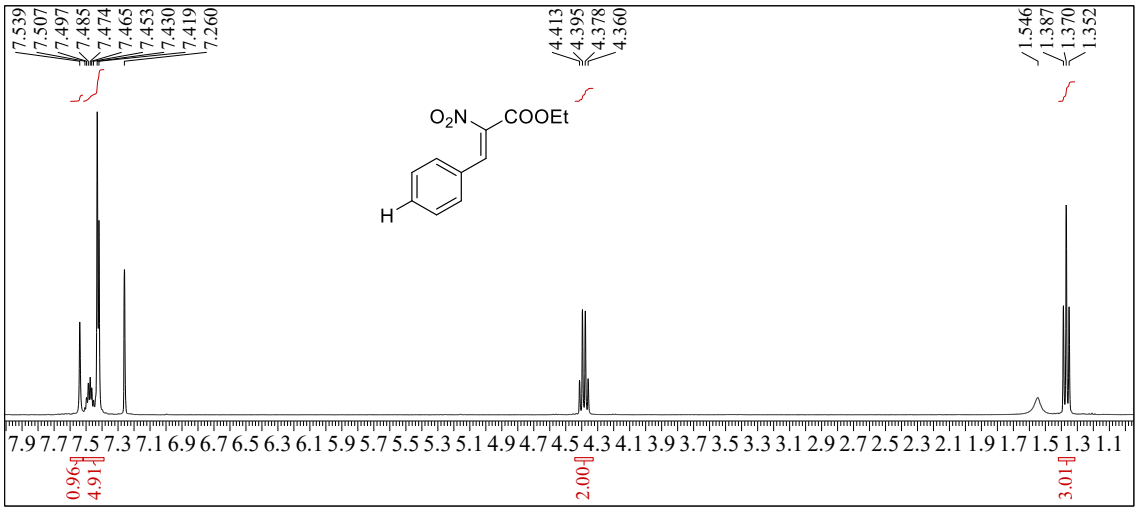
1a


7.498
7.330
7.309
7.260
7.233
7.212
4.399
4.381
4.363
4.345
2.387
1.581
1.379
1.361
1.343
O2N
COOEt
Me
0.97
1.99
1.97
2.00
2.92
3.00

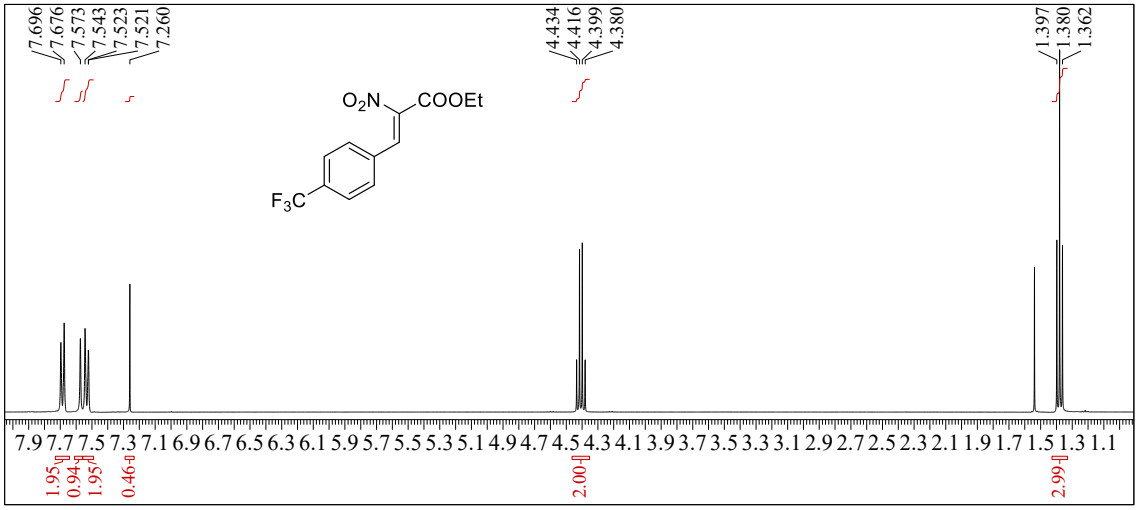
1b


7.459
7.402
7.380
7.260
6.930
6.908
4.389
4.372
4.354
4.336
3.850
1.373
1.355
1.337
O2N
COOEt
MeO
0.97
1.94
2.02
2.00
2.90
3.02

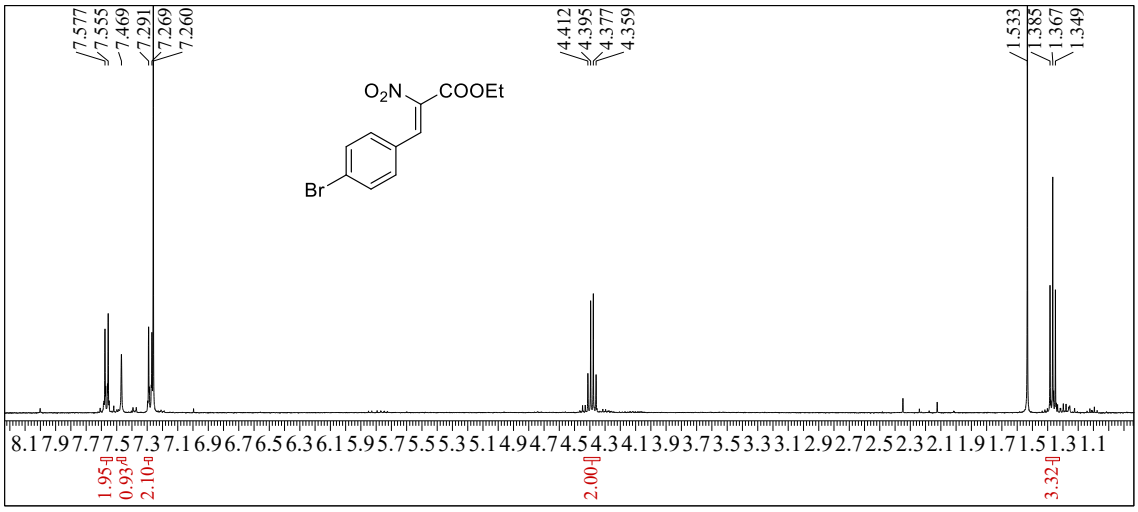
1c


7.539
7.507
7.497
7.485
7.474
7.465
7.453
7.430
7.419
7.260
4.413
4.395
4.378
4.360
1.546
1.387
1.370
1.352
O2N
COOEt
H
0.96
4.91
2.00
3.01

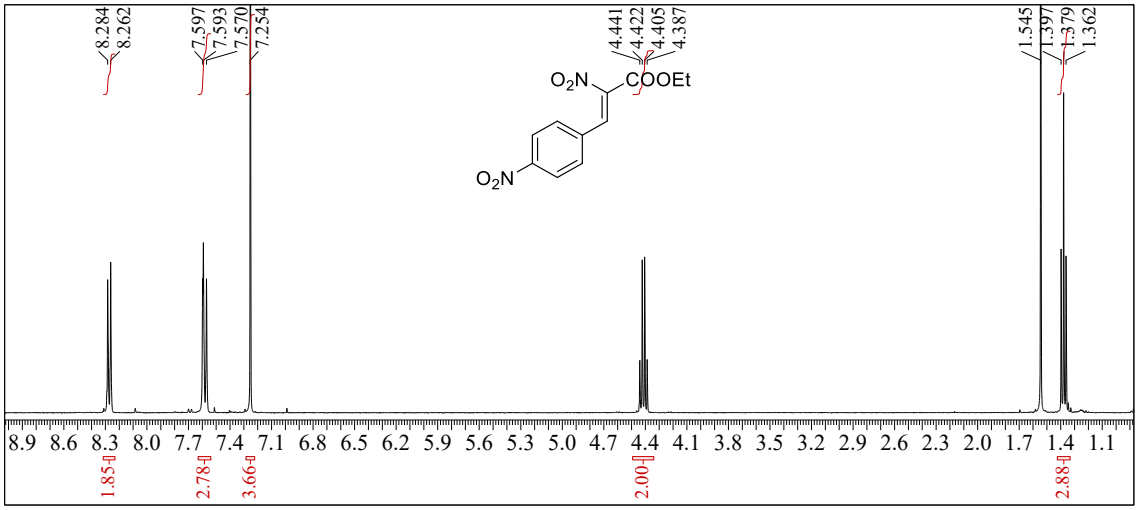
1d


7.696
7.676
7.573
7.543
7.523
7.521
7.260
4.434
4.416
4.399
4.380
1.397
1.380
1.362
O2N
COOEt
F3C
7.9 7.7 7.5 7.3 7.1 6.9 6.7 6.5 6.3 6.1 5.9 5.7 5.5 5.3 5.1 4.9 4.7 4.5 4.3 4.1 3.9 3.7 3.5 3.3 3.1 2.9 2.7 2.5 2.3 2.1 1.9 1.7 1.5 1.3 1.1
1.95
0.94
1.95
0.46
2.00
2.99

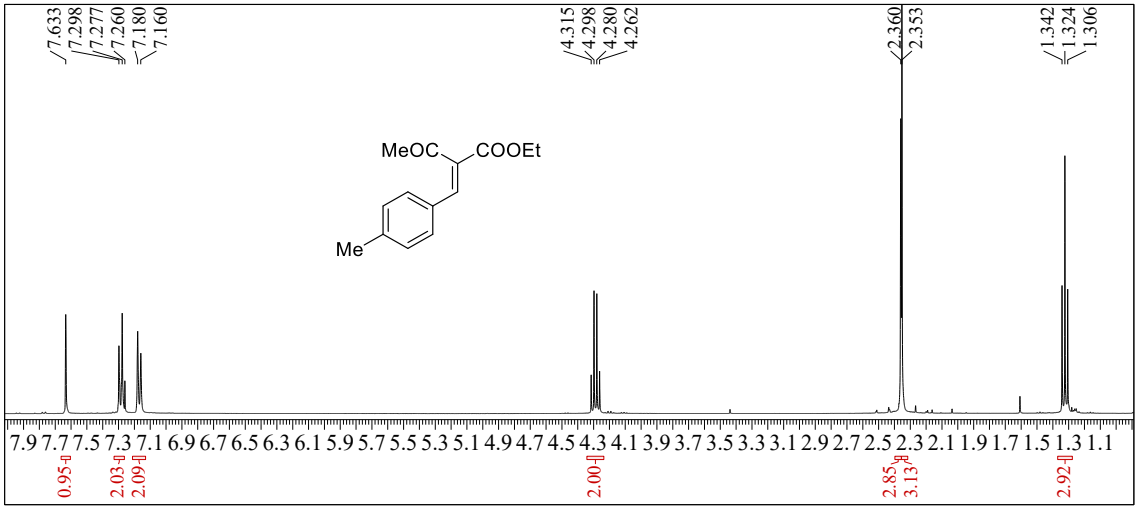
1e


7.577
7.555
7.469
7.291
7.269
7.260
4.412
4.395
4.377
4.359
1.533
1.385
1.367
1.349
O2N
COOEt
Br
8.1 7.9 7.7 7.5 7.3 7.1 6.9 6.7 6.5 6.3 6.1 5.9 5.7 5.5 5.3 5.1 4.9 4.7 4.5 4.3 4.1 3.9 3.7 3.5 3.3 3.1 2.9 2.7 2.5 2.3 2.1 1.9 1.7 1.5 1.3 1.1
1.95
0.93
2.10
2.00
3.32

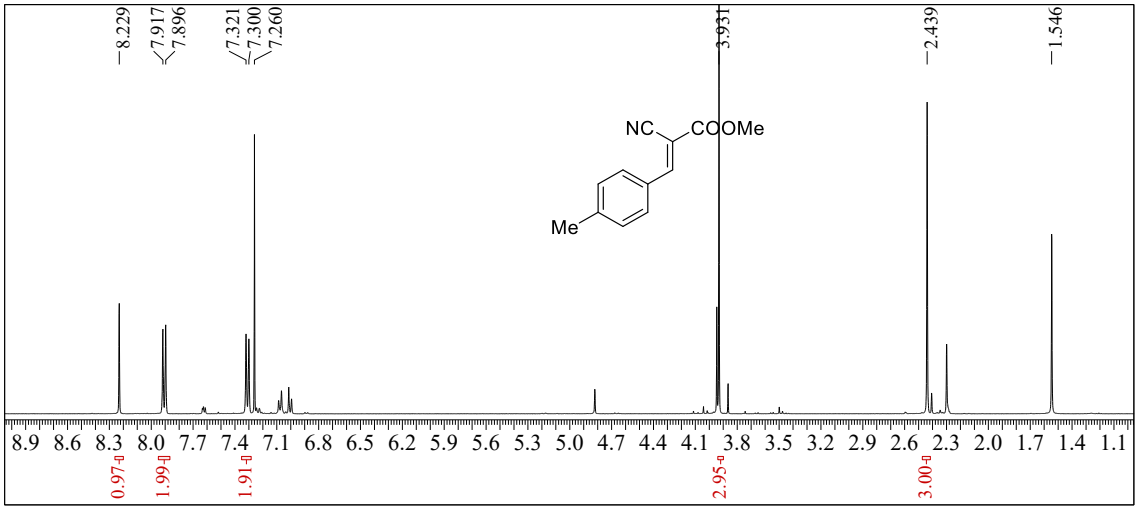
1f


8.284
8.262
7.597
7.593
7.570
7.254
4.441
4.422
4.405
4.387
1.545
1.397
1.379
1.362
O2N
COOEt
O2N
8.9 8.6 8.3 8.0 7.7 7.4 7.1 6.8 6.5 6.2 5.9 5.6 5.3 5.0 4.7 4.4 4.1 3.8 3.5 3.2 2.9 2.6 2.3 2.0 1.7 1.4 1.1
1.85
2.78
3.66
2.00
2.88

4


7.633
7.298
7.277
7.260
7.180
7.160
4.315
4.298
4.280
4.262
2.360
2.353
1.342
1.324
1.306
MeOC
COOEt
Me
7.9 7.7 7.5 7.3 7.1 6.9 6.7 6.5 6.3 6.1 5.9 5.7 5.5 5.3 5.1 4.9 4.7 4.5 4.3 4.1 3.9 3.7 3.5 3.3 3.1 2.9 2.7 2.5 2.3 2.1 1.9 1.7 1.5 1.3 1.1
0.95
2.03
2.09
2.00
2.85
3.13
2.92

5


8.229
7.917
7.896
7.321
7.300
7.260
3.931
2.439
1.546
NC
COOMe
Me
8.9 8.6 8.3 8.0 7.7 7.4 7.1 6.8 6.5 6.2 5.9 5.6 5.3 5.0 4.7 4.4 4.1 3.8 3.5 3.2 2.9 2.6 2.3 2.0 1.7 1.4 1.1
0.97
1.99
1.91
2.95
3.00