Supporting Information

Thiolates Chemically Induce Redox Activation of BTZ043 and Related Potent Nitro Aromatic Anti-Tuberculosis Agents

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General Experimental Section

All anhydrous solvents, reagent grade solvents for chromatography and starting materials were purchased from either Aldrich Chemical Co. (Milwaulkee, WI) or Fisher Scientific (Suwanee, GA). All reactions were conducted under argon unless otherwise noted. Solvents were removed *in vacuo* on a rotary evaporator. All compounds are >98% pure by HPLC analysis and MIC values reported are the average of three individual measurements. Water was distilled and purified through a Milli-Q water system (Millipore Corp., Bedford, MA). General methods of purification of compounds involved the use of either silica cartridges purchased from AnaLogix, Inc. (Burlington, WI; www.ana-logix.com) or column chromatography with silica gel (230-400 mesh) purchased from Silicycle, Quebec city, Canada. The reactions were monitored by TLC on precoated Merck 60 F_{254} silica gel plates and visualized using UV light (254 nm). All compounds were analyzed for purity by HPLC and characterized by ^{1}H and ^{13}C NMR using Varian 300MHz, 500 MHz NMR and/or Bruker 400 MHz NMR spectrometers. Chemical shifts are reported in ppm (δ) relative to the residual solvent peak in the corresponding spectra; chloroform δ 7.26 and δ 77.23, methanol δ 3.31 and δ 49.00 and coupling constants (*J*) are reported in hertz (Hz) (where, s = singlet, bs = broad singlet, d = doublet, dd = double doublet, bd = broad doublet, ddd = double doublet of dublet, t = triplet, tt – triple triplet, q = quartet, m = multiplet) and analyzed using 1D NMR processor (ACD/SpecManager) purchased from ACD labs (Product version 11.03). Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The Mass spectra values are reported as *m/z* and HRMS analyses were carried out with a Bruker MicroOTOF-Q II, electrospray ionization time-of-flight mass spectrometer. All new compounds were thoroughly characterized and previously known compounds were characterized only by ^{1}H NMR.

(*S*)-(3,5-Dinitrophenyl)(2-methyl-1,4-dioxa-8-azaspiro[4.5]decan-8-yl)methanone (**11**)

S-(+)-1,2-Propanediol (2.48 g, 31.57 mmol) and the 4-piperidone monohydrate hydrochloride (5 gm, 31.57 mmol) were dissolved in 50 mL of benzene. Then *p*-TsOH (543 mg, 3.15 mmol) was added and the reaction was heated to reflux with a Dean-Stark trap on to collect the water. After 13 h, the reaction mixture was concentrated. The crude residue was dissolved in dichloromethane and washed with saturated aqueous sodium bicarbonate solution (2 X 50 mL). The organic phase was separated, dried ($MgSO_4$), filtered, and concentrated to yellow oil to obtain (*S*)-2-Methyl-1,4-dioxa-8-azaspiro[4.5]decane (**10**). The crude product was used without further purification for EDC-mediated coupling with benzoic acid analogues. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 4.20 (m, 1H), 4.03 (ddd, *J* = 5.7Hz, *J* = 8.0Hz, *J* = 9.6Hz, 1H), 3.41 (dt, *J* = 4.3Hz, *J* = 7.8Hz, 1H), 3.26 (m, 1H), 2.63 (m, 2H), 1.97 (m, 2H), 1.72 (m, 2H), 1.24 (d, *J* = 6.1Hz, 3H).

To a solution of **10** (0.16 g, 0.98 mmol) in acetonitrile (10 mL) was added EDC·HCl (0.26 gm, 1.34 mmol) and DMAP (0.22 gm,1.79 mmol) and 3,5-dinitrobenzoic acid (0.2 gm, 0.9 mmol). The reaction mixture was then stirred for 22 h at room temperature. The reaction mixture was then evaporated in vacuo. The crude residue was dissolved in dichloromethane and washed with 10% aq sodium bicarbonate solution (2x) followed by 0.5M citric acid solution (2x) and brine. The organic layer was separated, dried (Na_2SO_4), filtered and evaporated. The crude residue was purified by column over silica gel using 10% EtOAc: DCM to afford 0.18 gm (59%) of white solid (mp = 179 ºC -182 ºC). ^{1}H NMR ($CDCl_3$) δ 9.10 (t, *J* = 2.1 Hz, 1H), 8.60 (d, *J* = 2.0 Hz, 2H), 4.28 (br. s., 1H), 4.18 - 4.02 (m, 1H), 3.92 (br. s., 2H), 3.50 (br. s., 3H), 1.85 (br. s., 2 H), 1.70 (br. s., 2 H), 1.46 - 1.24 (m, 3 H). ^{13}C NMR ($CDCl_3$) δ 165.4, 148.7, 139.6, 127.5, 119.9,

106.6, 72.6, 71.0, 46.2, 41.0, 37.1, 36.2, 36.0, 35.1, 18.6. MS (HR-ESI) $C_{15}H_{17}N_3O_7$ $(M + H)^+$ calcd 352.1147, found 352.1139.

(*S*)-(2-Methyl-1,4-dioxa-8-azaspiro[4.5]decan-8-yl)(3-nitro-5-(trifluoromethyl)phenyl) methanone (**12**)

Compound **12** was synthesized in 82% yield from 3-nitro-5-(trifluoromethyl) benzoic acid using the same general procedure described for **11**. (mp = 125 ºC - 128 ºC) ^{1}H-NMR ($CDCl_3$) δ 8.53 (s, 1H), 8.44 (m, 1H), 8.01 (s, 1H), 4.26 (m, 1H), 4.09 (m, 1H), 3.87 (m, 2H), 3.50 (m, 3H), 1.83 (m, 2H), 1.70 (m, 2H), 1.29 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 166.26, 148.39, 139.05, 133.21, 132.93, 129.90, 129.87, 125.32, 123.70, 121.90, 121.87, 121.84, 121.81, 121.52, 106.72, 72.58, 71.00, 18.57. MS (HR-ESI) $C_{16}H_{17}F_3N_2O_5$ $(M + H)^+$ calcd 375.1162, found 375.1155.

(*R*)-3, 5-Dinitro-*N*-(1-phenylethyl)benzamide (**14**)[1]

Compound **14** was synthesized in 41% yield from 3,5-dinitrobenzoic acid using the same general procedure described for **11**. ^{1}H NMR (CD_3OD) δ 8.97 - 8.87 (m, 1 H), 8.64 (s, 1 H), 8.54 (s, 1 H), 7.44 - 7.13 (m, 4 H), 5.23 (q, *J* = 7.0 Hz, 1 H), 1.57 (d, *J* = 7.2 Hz, 3 H)

(*R*)-3-Nitro-*N*-(1-phenylethyl)-5-(trifluoromethyl)benzamide (**15**)[2]

Compound **15** was synthesized in 79% yield from 3-nitro-5-(trifluoromethyl) benzoic acid using the same general procedure described for **11**. ^{1}H NMR ($CDCl_3$) δ 9.12 (t, *J* = 2.1 Hz, 1 H), 9.00 (d, *J* = 2.2 Hz, 2 H), 7.43 - 7.19 (m, 5 H), 5.41 - 5.23 (m, 6 H), 1.66 (d, *J* = 6.9 Hz, 3 H)

General procedure for the reaction of thiols with compound 11

To a solution of **11** (0.075 g, 0. 21 mmol) in 9 mL of acetonitrile and 2 mL of water was added Boc-cysteamine (0.19 g, 1.07 mmol) dropwise in a 20 mL scintillation vial. The apparent pH of the reaction mixture was adjusted to pH 11-12 by dropwise addition of a 1N NaOH solution. The reaction mixture turned dark red-brown during this process. The scintillation vial was then capped tightly and the reaction mixture was stirred at room temperature and monitored by TLC and LC/MS. After 24 h, the reaction mixture was partitioned between ethyl acetate and water. The organic layer was separated and the aqueous layer was washed with ethyl acetate (2x 10 mL). The combined organic layer was washed with brine, dried (Na_2SO_4), filtered and evaporated in vacuo. The crude residue was purified by column chromatography using hexanes: EtOAc (1:1). Approximately 11 mg (15%) of the starting material was recovered after column along with **19** and **24**.

(*Z*)-1,2-bis(3-((S)-2-Methyl-1,4-dioxa-8-azaspiro[4.5]decane-8-carbonyl)-5-nitrophenyl) diazene oxide (**19**)

Yellow solid (yield = 36% , mp = 229-230 ºC) ^{1}H NMR ($CDCl_3$) δ 9.23 (d, *J* = 2.0 Hz, 1 H), 9.11 (d, *J* = 1.8 Hz, 1 H), 8.74 (d, *J* = 1.5 Hz, 1 H), 8.55 (d, *J* = 1.5 Hz, 1 H), 8.53 (d, *J* = 1.5 Hz, 1 H), 8.37 (d, *J* = 1.5 Hz, 1 H), 4.29 (br s, 2 H), 4.17 - 4.03 (m, 2 H), 3.95 (br s, 4 H), 3.66 - 3.44 (m, 6 H), 1.87 (br s, 4 H), 1.74 (br. s., 4 H), 1.27 (d, 6 H). ^{13}C NMR ($CDCl_3$) δ 166.9, 166.0, 148.7, 148.6, 148.5, 143.9, 139.1, 138.4, 129.7, 126.7, 125.7, 123.6, 121.7, 119.0, 106.9, 106.7, 72.6, 72.5, 71.0, 46.1, 40.9, 37.2, 36.3, 36.0, 35.1, 18.6. MS (HR-ESI) $C_{30}H_{34}N_6O_{11}$ $(M + H)^+$ calcd 655.2358, found 655.2337.

***tert*-Butyl 2,2'-disulfanediylbis(ethane-2,1-diyl) dicarbamate** (**24**)

White solid (yield = 0.17 g, 46 %, mp = 103-104 ºC) ^{1}H NMR ($CDCl_3$) δ 5.19 - 5.08 (m, 1 H), 3.42 (q, *J* = 6.0 Hz, 2 H), 2.77 (t, *J* = 6.4 Hz, 2 H), 1.42 (s, 9 H) ^{13}C NMR ($CDCl_3$) δ 156.0, 79.6, 39.4, 38.5, 28.5. MS (HR-ESI) $C_{14}H_{28}N_2O_4S_2$ $(M + Na)^+$ calcd 375.1383, found 375.1405.

General procedure for the reaction of thiolates with compound 11

To a solution of **11** (0.075 g, 0. 21 mmol) in 9 mL of acetonitrile and 2 mL of water was added sodium methanethiolate in a 20 mL scintillation vial and then the vial was capped tightly. The reaction mixture immediately turned dark red-brown as soon as sodium methanethiolate was added. The reaction mixture was then stirred at room temperature and monitored by TLC and LC/MS. The reaction mixture was worked up the same way as described in the general procedure for the reaction of thiols with compound **11** described above.

(*S*)-8-amino-2-(2-Methyl-1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-6-(trifluoromethyl)-4H-benzo[e][1,3]thiazin-4-one (16)

Compound **16** was isolated from the reaction of **3** (0.3 g, 0.7 mmol) with sodium methanethiolate in 17 % yield (48 mg). Yellow solid (mp = 256-257 ºC), ^{1}H NMR ($CDCl_3$) δ 8.19 (s, 1 H), 7.09 (d, *J* = 1.5 Hz, 1 H), 4.34 - 4.20 (m, 1 H), 4.08 (dd, *J* = 5.8, 8.1 Hz, 2 H), 3.98 (br. s., 3 H), 3.47 (t, *J* = 7.9 Hz, 1 H), 1.89 - 1.69 (m, 4 H), 1.28 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$) δ 169.1, 159.9, 142.2, 124.0, 118.1, 114.4, 106.9, 72.7, 71.1, 44.4, 36.6, 35.3, 18.6. MS (HR-ESI) $C_{17}H_{18}F_3N_3O_3S$ $(M + H)^+$ calcd 402.1194, found 402.1122.

(*S*)-8,8'-((E)-Diazene-1,2-diyl)bis(2-((S)-2-methyl-1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-6-(trifluoromethyl)-4H-benzo[e][1,3]thiazin-4-one) (27)

Compound **27** was isolated from the reaction of **3** (0.3 g, 0.7 mmol) with sodium methanethiolate in 2 % yield (10 mg) Yellow-orange solid, ^{1}H NMR ($CDCl_3$) δ 8.98 - 8.90 (m, 1 H), 8.15 (d, *J* = 1.8 Hz, 1 H), 4.40 - 4.23 (m, 1 H), 4.13 (dd, *J* = 5.5, 8.1 Hz, 2 H), 4.04-3.81 (m, 3H), 3.52 (t, *J* = 7.9 Hz, 1 H), 1.87 (br. s., 4 H), 1.33 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$) δ 167.5, 161.4, 147.0, 138.9, 131.0, 125.4, 116.9, 106.7, 72.8, 71.1, 33.6, 32.2, 29.9, 29.6, 23.4, 22.9, 18.6. MS (HR-ESI) $C_{34}H_{32}F_6N_6O_6S_2$ $(M + H)^+$ calcd 799.1802, found 799.1826.

Procedure for the reaction of KCN with 11.

To a solution of **11** (0.52 g, 1.47 mmol) in 20 mL of acetonitrile and 5 mL of water was added KCN (0.19 g, 2.95 mmol) in a 50 mL round bottom flask which was capped with a rubber septum. The reaction mixture immediately turned bluish-purple as soon as potassium cyanide was added. The reaction mixture was then stirred at room temperature for 3-4 h and monitored by TLC and LC/MS. The reaction mixture was then partitioned between ethyl acetate and water. The organic layer was separated and washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The crude residue was purified by column chromatography using EtOAc: Hexanes (7:3).

(*S*)-3-amino-6-(2-methyl-1,4-dioxa-8-azaspiro[4.5]decane-8-carbonyl)-4-nitrobenzo[c]isoxazole-7-carbonitrile (**31**)

Compound **31** was isolated from the reaction of **11** (0.52g, 1.47mmol) with sodium methanethiolate in 6.5% yield (37 mg) red solid, ^{1}H NMR ($CDCl_3$) δ 7.57 (s, 1 H), 7.02 (br. s., 2 H), 4.35 - 4.20 (m, 1 H), 4.17 - 4.05 (m, 1 H), 4.01 - 3.84 (m, 2 H), 3.56 - 3.41 (m, 3 H), 1.92 - 1.62 (m, 4 H), 1.30 (m, 3 H). ^{13}C NMR ($CDCl_3$) δ 166.4, 163.5, 157.1, 146.5, 146.1, 115.3,

112.3, 106.7, 91.1, 72.6, 72.6, 71.0, 45.7, 45.6, 40.7, 40.7, 37.0, 36.0, 35.9, 34.8, 18.6, 18.6. MS (HR-ESI) $C_{17}H_{17}N_5O_6$ $(M + Na)^+$ calcd 410.1071 found 410.1071.

(*S*)-(3-amino-4-nitrobenzo[c]isoxazol-6-yl)(2-methyl-1,4-dioxa-8-azaspiro[4.5]decan-8-yl)methanone (**32**)

Compound **32** was isolated from the reaction of **11** (0.52 g, 1.47 mmol) with sodium methanethiolate in 3% yield (15 mg) red solid, ^{1}H NMR ($CDCl_3$) δ 7.71 (s, 1 H), 7.54 (s, 1 H), 6.57 (br. s., 2 H), 4.27 (br. s., 1 H), 4.10 (br. s., 1 H), 4.01 - 3.50 (m, 5 H), 1.83 - 1.70 (br. s., 4 H), 1.30 (d, *J* = 5.3 Hz, 3 H) ^{13}C NMR ($CDCl_3$) δ 167.0, 165.0, 158.9, 143.9, 137.9, 119.6, 118.0, 106.9, 90.0, 72.5, 71.0, 46.0, 40.7, 37.2, 36.2, 36.0, 29.9, 18.6. MS (HR-ESI) $C_{16}H_{18}N_4O_6$ $(M + H)^+$ calcd 363.1299 found 363.1300.

Procedure for the reaction of K^{13}CN (13C, 99% atom enriched) with 3.

The reaction was carried out as described above except for using compound **3** (0.500 g, 1.16 mmol) and K^{13}CN (0.15 g, 2.31 mmol). The crude residue was purified by prep-TLC using DCM: MeOH (15:1). The reaction of **3** with KCN was also carried out for the comparison and to obtain the "simplified" 13C NMR spectra. See supporting information for both 1H and 13C NMR spectra for the products of both K^{13}CN and KCN reactions.

(*S*)-3-amino-8-(2-methyl-1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-4-(trifluoromethyl)-6H-isoxazolo[3',4':3,4]benzo[1,2-e][1,3]thiazin-6-one (**33**)

Yellow solid (96 mg, 19 %) ^{1}H NMR (DMSO-d_6) δ 8.11 (br. s., 2 H), 7.51 (br. s., 1 H), 4.14 - 4.29 (m, 1H), 4.03 - 4.14 (m, 1 H), 4.00-3.65 (br. m, 4 H), 3.44 (t, *J*=7.63 Hz, 1 H), 1.78 (br. s., 4 H), 1.22 (d, *J* = 6.16 Hz, 3 H) ^{13}C NMR (DMSO-d_6) ^{13}C NMR (151MHz ,DMSO-d_6) δ 167.8,

165.9, 159.2, 155.1, 123.8, 123.8, 123.7, 122.1, 121.9, 121.8, 120.9, 115.2, 106.3, 91.0, 90.5, 71.8, 70.1, 35.6, 34.4, 30.7, 18.4. MS (HR-ESI) $C_{17}{}^{13}CH_{17}F_3N_4O_4S$ $(M + Na)^+$ calcd 466.0804, found 466.0828.

(*S*)-3-amino-8-(2-methyl-1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-6-oxo-4-(trifluoromethyl)-6H-isoxazolo[3',4':3,4]benzo[1,2-e][1,3]thiazine-5-carbonitrile (**34**)

Yellow solid, (85 mg, 16 %).^{1}H NMR (DMSO-d_6) δ 8.80 (br. s., 2 H), 4.31 - 4.19 (m, 1 H), 4.09 (dd, *J* = 5.7, 8.1 Hz, 1 H), 4.05-3.65 (br. m, 4H), 3.45 (t, *J* = 7.8 Hz, 1 H), 1.78 (br. s., 4 H), 1.26 - 1.14 (m, 3 H) ^{13}C NMR (DMSO-d_6) δ 167.4, 165.8, 165.5, 164.5, 157.9, 153.5, 153.5, 130.6, 125.4, 122.8, 121.0, 114.1, 106.3, 97.9, 97.3, 92.6, 92.1, 71.8, 70.1, 35.5, 34.3, 29.1, 18.4. MS (HR-ESI) $C_{17}{}^{13}C_2H_{16}F_3N_5O_4S$ $(M + Na)^+$ calcd 492.0834, found 492.0823

References:

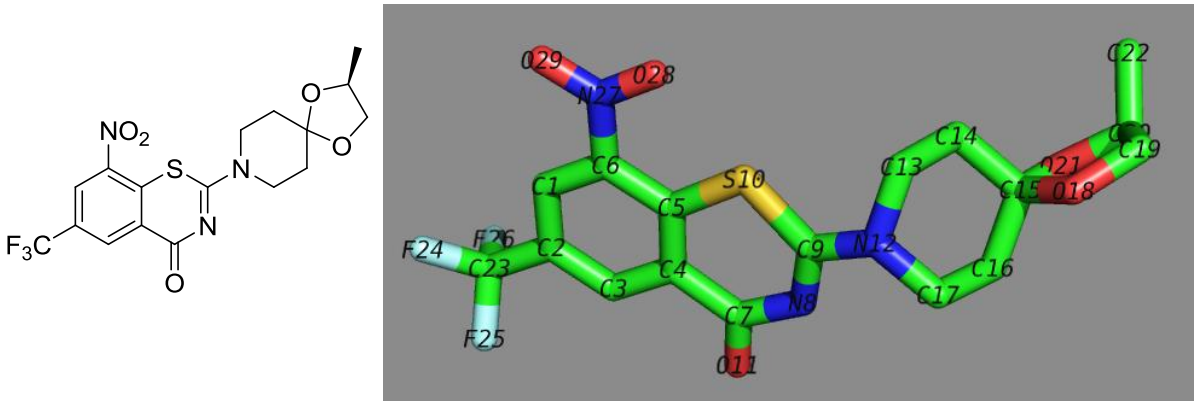
1) Huang, S.-H.; Bai, Z.-W.; Feng, J.-W. *Mag Reson Chem* **2009**, *47*, 423-427.
2) Trefzer, C.; Rengifo-Gonzalez, M.; Hinner, M. J.; Schneider, P.; Makarov, V.; Cole, S. T.; Johnsson, K. *J Am Chem Soc* **2010**, *132*, 13663-13665.

Description of the cell culture experiments of 3, 11 and 12 using *M. smegmatis* described in Scheme 3

A heavy inoculum of *M. smegmatis* was prepared by growing the organism in mycobacteria culture media for 48 h. It was then centrifuged @ 3000 rpm for 20 min. The pellet was resuspended in saline, centrifuged and resuspended in MH2 (Mueller Hinton broth 2) broth. A standard solution of test compounds was prepared in DMSO (compound **11** – 1.5 mg, compound **12** - 1.5 mg, BTZ043 – 0.5 mg) and added to 50 mL of MH2 broth in a 125 mL baffle flask. was then added to the flask. To each of the test compounds was added 3 mL of *M. smegmatis* inoculum. Separate flasks were prepared as controls with test compounds in the culture media as non-mycobacterial controls.

All of the flasks were incubated at 37ºC for 24 h in a shaker (Lab-Line® Incubator-Shaker), then the flasks were cooled on ice to stop the reaction. The test compounds with *M. smegmatis* were centrifuged @ 3000 rpm for 20 min and filtered through a 2 μ filter. The filtrate was then extracted with chloroform (50 mL). The organic layer was separated and the aqueous portion was washed with additional (2x 25mL) chloroform. The combined organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated in vacuo. The crude residue was resuspended in methanol and analysed by LC/MS.

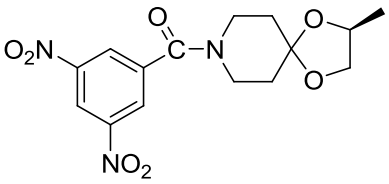
Mulliken charges calculated by AM1 for BTZ043 (**3**)

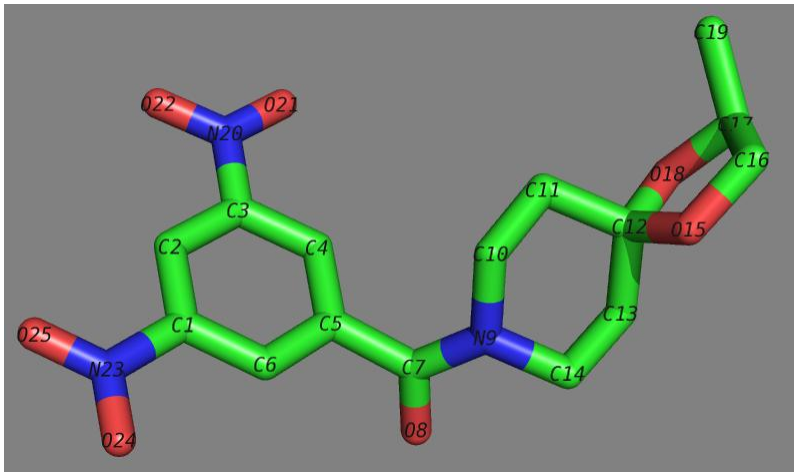


The structure was minimized by AM1 (Austin Model 1) method.
Mulliken charges with hydrogens summed into heavy atoms, the charges related to the atoms of interst are underlined.

Element number		Mulliken Charge
1	C	0.210219
2	C	-0.198556
3	C	0.226967
4	C	-0.181027
5	C	-0.178267
6	C	-0.156418
7	C	0.316634
8	N	-0.283909
9	C	-0.026508
10	S	0.506241
11	O	-0.276472
12	N	-0.208898
13	C	0.177176
14	C	0.007840
15	C	0.203827
16	C	0.050676
17	C	0.194378
18	O	-0.297603
19	C	0.157588
20	C	0.122579
21	O	-0.289048
22	C	0.035130
23	C	0.474068
24	F	-0.158655
25	F	-0.154918
26	F	-0.155915
27	N	0.570302
28	O	-0.355820
29	O	-0.331611

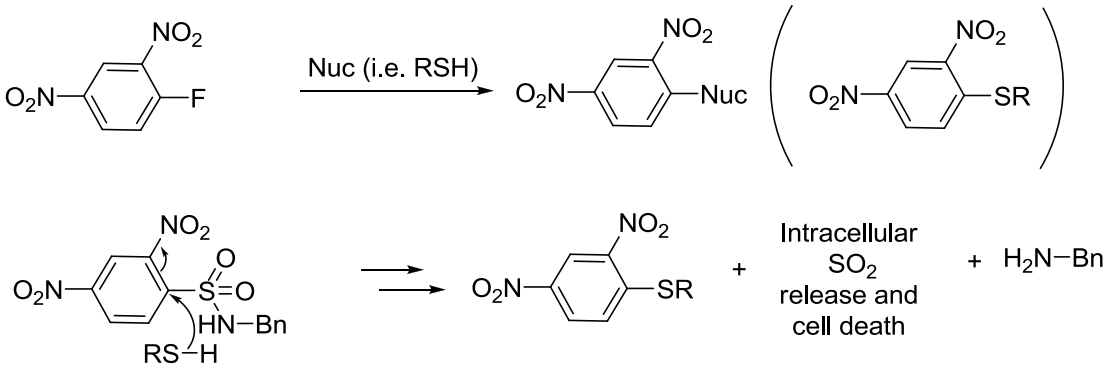
Mulliken charges calculated by AM1 for **11**



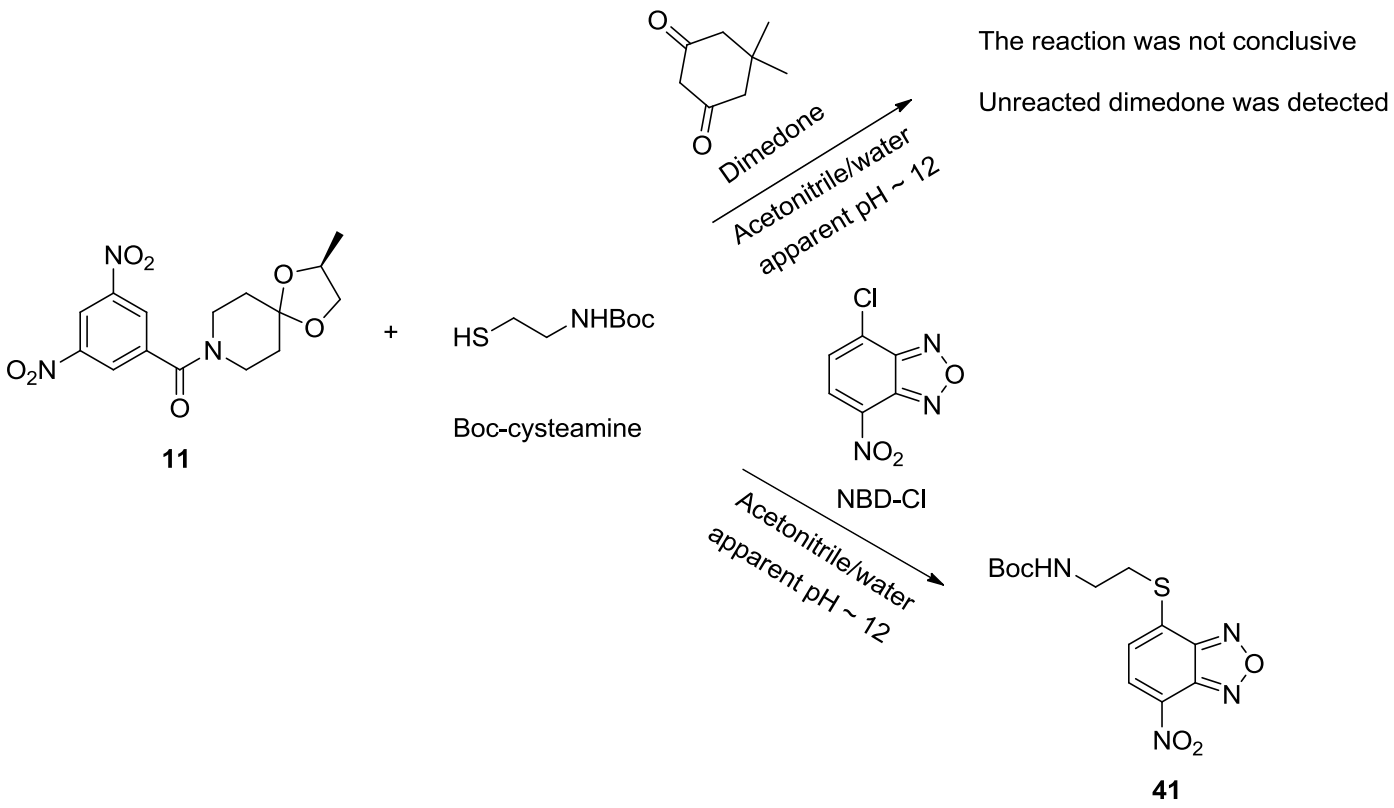


The structure was minimized by AM1 method.
Mulliken charges with hydrogens summed into heavy atoms, the charges related to the atoms of interst are underlined.

Element number		Mulliken Charge
1	C	-0.146277
2	C	0.205977
3	C	-0.147038
4	C	0.172547
5	C	-0.121670
6	C	0.199720
7	C	0.336145
8	O	-0.335082
9	N	-0.306542
10	C	0.173958
11	C	0.003857
12	C	0.206237
13	C	0.044310
14	C	0.200909
15	O	-0.296153
16	C	0.157641
17	C	0.122766
18	O	-0.290659
19	C	0.036280
20	N	0.572789
21	O	-0.346568
22	O	-0.336439
23	N	0.572806
24	O	-0.339979
25	O	-0.339535

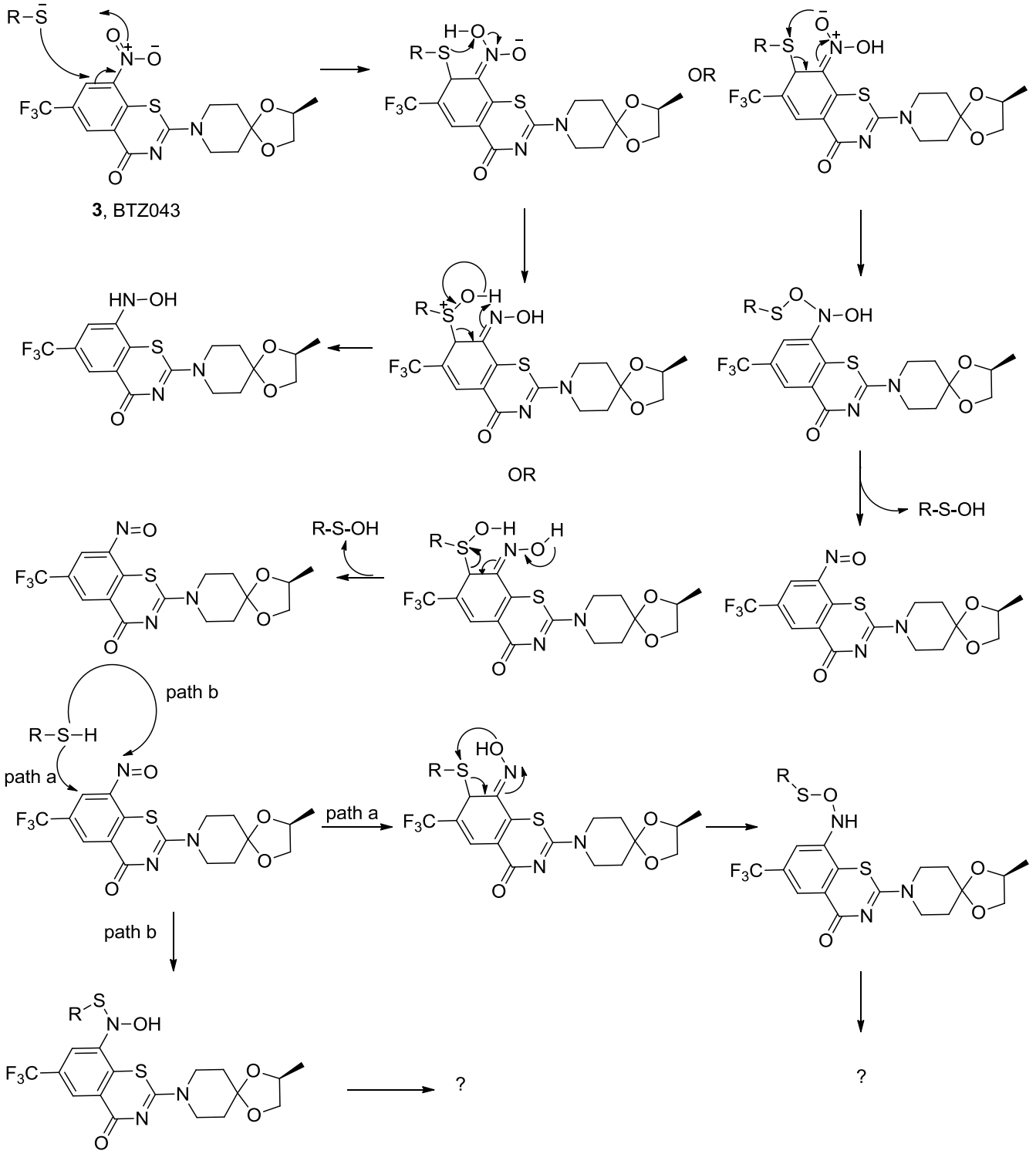


Scheme S1: Classical nucleophilic aromatic substitution at nitroaromatic compounds such as 2,4-dinitrofluorobenzene (Sangers reagent) and 2,4-dinitrobenzenesulfonamide with thiols.



Scheme S2: Reaction of **11** with sulfenic acid trapping agents such as dimedone and NBD-Cl and synthesis of compound **41**.

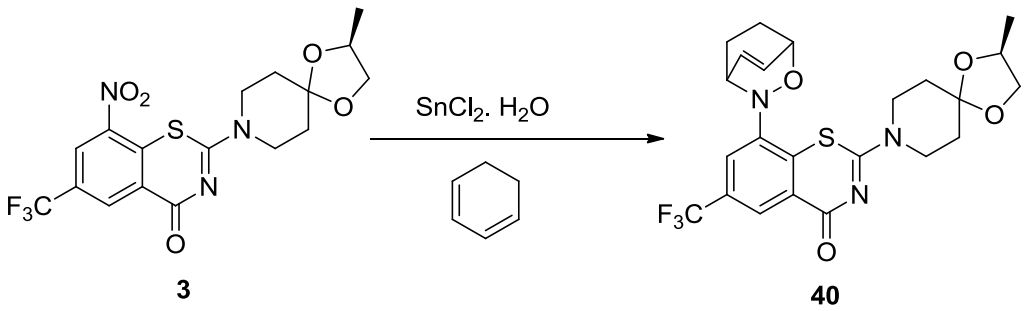
The reaction of **11** with NBD-Cl in presence of Boc-cysteamine at apparent pH 12 indicated the formation of **41** by TLC analysis and LCMS. The formation of **41** was separately confirmed by the reacting Boc-cysteamine (0.100g, 0.56 mmol) with NBD-Cl (0.226 g, 1.13 mmol) in acetonitrile/water solvent system at apparent pH 12. The reaction was complete in 5 h, the reaction mixture was partitioned between ethyl acetate and dilute ammonium chloride solution. The organic layer was separated, dried (Na_2SO_4) and concentrated in vacuo. The crude residue was purified by column over silica gel using hexanes: EtOAc (1:1) to afford 0.095 g (49%) of **37**. ^{1}H NMR ($CDCl_3$) δ 8.47 (d, *J* = 7.8 Hz, 1 H), 7.55 (d, *J* = 7.8 Hz, 1 H), 3.56 - 3.40 (m, 4 H), 1.53 - 1.41 (m, 9 H) ^{13}C NMR ($CDCl_3$) δ 149.5, 142.7, 140.5, 131.2, 121.4, 80.5, 77.6, 76.9, 39.4, 31.3, 28.5.



Scheme S3: Possible reactions of enzyme thioloates (active site cysteine) with BTZ043 (**3**) to initiate enzyme inactivating process.[a]

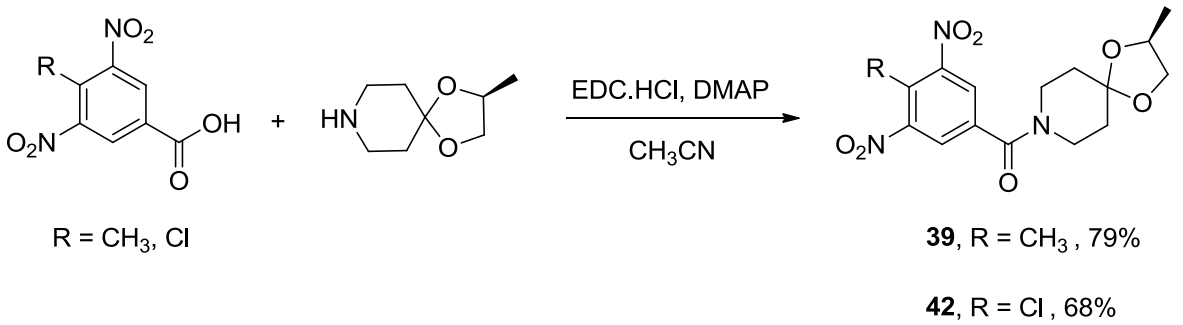
[a] In all case, generation of oxidized thiol would give and unstable enzyme intermediate and inactivate enzyme targe.

General procedure for the formation of N-O cycloadducts (nitroso trapping experiments) using stannous chloride and 1,3-cyclohexadiene : the example synthesis of compound **40**.



Scheme S4: Syntheses of compounds **40**.

To a solution of **3** (0.02 g, 0.05 mmol) in 5 mL DMF was added 1,3-Cyclohexadiene (0.06 μL, 0.5 mmol) dropwise followed by the solution of stannous chloride (0.01 g, 0.05 mmol) in 2.5 mL DMF. The reaction mixture was then stirred at rt and monitored by LC/MS for the formation of the hetero Diels-Alder cycloadducts. After 24 h, of the reaction significant amount of the starting material was still detected along with the desired cycloadduct along with the reduced amine by product of **3**. Therefore an additional amount of stannous chloride (0.011g, 0.05 mmol) dissolved in 2.5 mL of DMF was added and the reaction was ran for additional 2 days at room temperature. The reaction mixture was then diluted with 20 mL water and then extracted with 20 mL DCM. The DCM extract was further washed with 2 x with 20 mL water. The organic layer was separated and concentrated in vacuo. The crude residue was purified by preparative HPLC to obtain **40** (5.9 mg, 26%). ^{1}H NMR (DMSO) δ 8.16 (d, *J* = 1.5 Hz, 1 H), 7.43 (d, *J* = 2.1 Hz, 1 H), 6.88 (ddd, *J* = 1.5, 6.1, 8.0 Hz, 1 H), 6.11 (ddd, *J* = 1.3, 6.2, 8.0 Hz, 1 H), 4.88 (td, *J* = 2.1, 3.8 Hz, 1 H), 4.29 (d, *J* = 4.1 Hz, 1 H), 4.26 (dt, *J* = 6.1, 7.5 Hz, 1 H), 4.10 (dd, *J* = 5.7, 8.1 Hz, 1 H), 4.01 – 3.82 (m, 4H), 3.46 (td, *J* = 1.5, 7.8 Hz, 1 H), 2.29 - 2.22 (m, 2 H), 2.14 - 2.07 (m, 2 H), 1.54 - 1.43 (m, 2 H), 1.42 - 1.33 (m, 2 H), 1.23 (d, *J* = 6.2 Hz, 3 H). MS (LR-EI) $C_{23}H_{24}F_3N_3O_4S$ $(M + H)^+$ calcd 496.15, found 496.12.



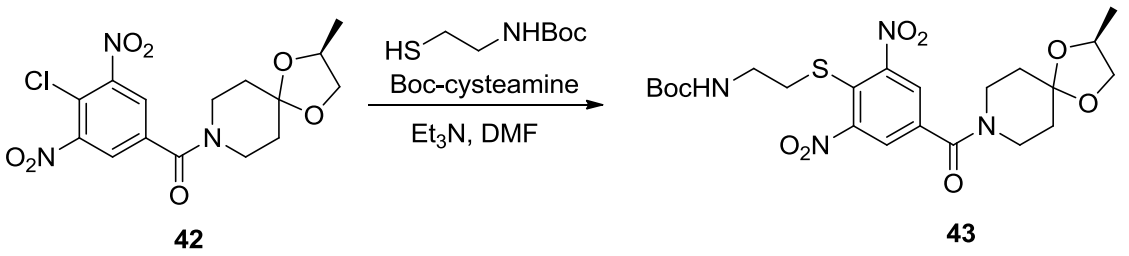
Scheme S5: Syntheses of compounds **35** and **42**.

(*S*)-(4-Methyl-3,5-dinitrophenyl)(2-methyl-1,4-dioxa-8-azaspiro[4.5]decan-8-yl)methanone (**39**)

Compound **39** was synthesized in 79% yield from 4-methyl-3,5-dinitrobenzoic acid using the same general procedure described for **11**. (mp = 143 ºC -145 ºC)^{1}H NMR ($CDCl_3$) δ 8.05 (s, 2 H), 4.28 (br. s., 1 H), 4.11 (br s, 1 H), 3.88 (br s, 2 H), 3.51 (br s, 3 H), 2.62 (s, 3 H), 1.67-1.92 (m, 4 H), 1.38 - 1.26 (m, 3 H). ^{13}C NMR ($CDCl_3$) δ 165.4, 151.7, 136.0, 128.8, 126.3, 106.7, 72.6, 71.0, 46.1, 41.0, 37.2, 36.0, 35.0, 18.6, 15.2. MS (HR-ESI) $C_{16}H_{19}N_3O_7$ $(M + H)^+$ calcd 366.1296, found 366.1298.

(*S*)-(4-Chloro-3,5-dinitrophenyl)(2-methyl-1,4-dioxa-8-azaspiro[4.5]decan-8-yl)methanone (**42**)

Compound **42** was synthesized in 68% yield from 4-chloro-3,5-dinitrobenzoic acid using the same general procedure described for **11** without using DMAP. (mp = 112 ºC -115 ºC) ^{1}H NMR ($CDCl_3$) δ 8.04 (s, 2 H), 4.27 (br s, 1 H), 4.09 (t, *J* = 6.3 Hz, 1 H), 3.85 (br s, 2 H), 3.63 - 3.34 (m, 3 H), 1.95 - 1.75 (m, 2 H), 1.70 (br s, 2 H), 1.29 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$) δ 164.5, 149.7, 136.8, 127.9, 126.7, 121.8, 106.5, 72.6, 71.0, 46.1, 41.0, 37.1, 36.1, 35.9, 35.0, 18.5. MS (HR-ESI) $C_{15}H_{16}ClN_3O_7$ $(M + H)^+$ calcd 386.0750, found 386.0775.



Scheme S6: Synthesis of compound **43**.

(*S*)-*tert*-butyl (2-(4-(2-methyl-1,4-dioxa-8-azaspiro[4.5]decane-8-carbonyl)-2,6-dinitrophenylthio)ethylcarbamate (**43**)

To a solution of **42** (0.100 g, 0.26 mmol) in 2 mL DMF was added Boc-cysteamine (0.07 g, 0.39 mmol) dissolved in 1 mL DMF dropwise. The reaction mixture was then stirred at rt for 1.5 h. The reaction mixture was then quenched with ice water and then partitioned between ethyl acetate and water. The organic layer was separated, washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The crude residue was purified by column over silica gel using hexanes: EtOAc (3:1) to afford **43** (0.100 g, 73%). ^{1}H NMR ($CDCl_3$) δ 7.89 (s, 2 H), 4.83 (br. s., 1 H), 4.28 (br. s., 1 H), 4.10 (br. s., 1 H), 3.88 (br. s., 2 H), 3.54 (br. s., 1 H), 3.50 (br. s., 2 H), 3.33 (br. s., 2 H), 3.10 (s, 2 H), 1.84 (br. s., 2 H), 1.72 (br. s., 2 H), 1.43 (s, 9 H), 1.31 (d, *J* = 5.9 Hz, 3 H). ^{13}C NMR ($CDCl_3$) δ 164.9, 155.1, 138.3, 125.2, 106.6, 72.6, 71.0, 54.0, 46.1, 41.0, 40.0, 37.8, 37.1, 36.0, 35.0, 29.9, 29.5, 28.5, 18.6. MS (HR-ESI) $C_{22}H_{30}N_4O_9S$ $(M + Na)^+$ calcd 549.1626, found 549.1598.

Table S1: *In vitro* evaluation of compounds in $H_{37}R_V$-TB and M.smegmatis in various assays and media (MIC in μM) and VERO cell toxicity (IC50 in μM)

Comps	CLogp	$H_{37}R_V$-TB				M. smegmatis	VERO
		GAS	GAST	7H12	LORA		
11	0.56	nd	0.5	0.8	>10	50	>100
12	1.69	nd	>50	>50	>50	500	>50
14	2.48	0.55	nd	0.25	49	0.78	>64
15	4.32	1.76	nd	0.95	>64	3.13	>64
INH	nd	0.22	0.48	0.37	>512	nd	>128
RMP	nd	0.11	0.10	0.05-0.06	0.62	nd	100-125

Comps, Compounds; CLogP, calculated LogP value (ChemBioDraw Ultra 12.0.2.1076);GAS, glycerol-alanine-salts media; GAST, iron deficient glycerol-alanine-salts with Tween 80 media; 7H12, 7H9 broth base media with BSA, casein hydrolysate, catalase, palmitic acid; LORA, low oxygen recover assay; VERO, African green monkey kidney cell line, nd, not determined,. Values reported are the average of three individual measurements.

Description of TB (GAS[54], GAST[55], 7H12[54]) by Microplate Alamar Blue assay (MABA) to determine MIC values against replicating TB and low-oxygen recovery assay (LORA) to determine activity against non-replicating *M. tuberculosis*[56]:

All these assays were performed as per the published protocols. [1-3]

References

(1) Collins, L.; Franzblau, S. G. *Antimicrobial Agents Chemother* **1997**, *41*, 1004-9.

(2) De Voss, J. J.; Rutter, K.; Schroeder, B. G.; Su, H.; Zhu, Y.; Barry, C. E., 3rd *Proc Natl Acad Sci U S A* **2000**, *97*, 1252-7.

(3) Cho, S. H.; Warit, S.; Wan, B.; Hwang, C. H.; Pauli, G. F.; Franzblau, S. G. *Antimicrobial Agents Chemother* **2007**, *51*, 1380-5.

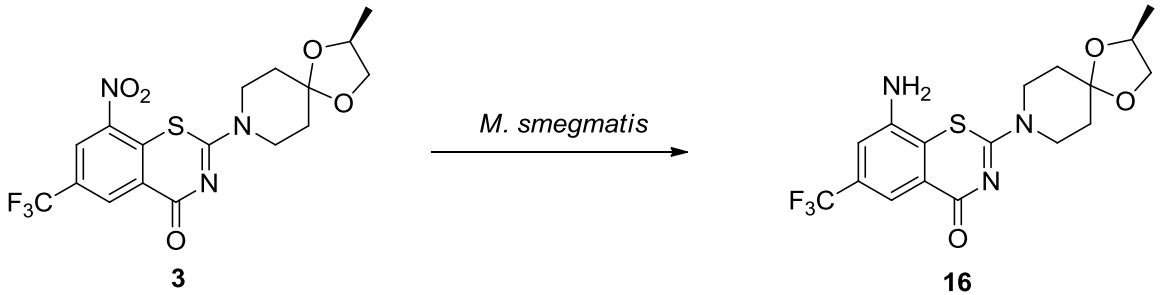
Experimental procedure for the antibiotic susceptibility testing by the broth microdilution method in M. smegmatis.

Antibacterial activity of the compounds was determined by measuring their minimum inhibitory concentrations (MIC_{90}'s) using the broth microdilution method according to the Clinical and Laboratory Standards Institute (CLSI, formerly the NCCLS) guidelines.[1] Each well of a 96-well microtiter plate was filled with 50 μL of sterile MHII broth. Each test compound was dissolved in DMSO making a 1mg/ml solution, then diluted with sterile MHII broth to 40ug/ml. Exactly 50 μL of the compound solution was added to the first well of the microtiter plate and 2-fold serial dilutions were made down each row of the plate. Exactly 50 μL of bacterial (IN BROTH) inoculum (5×10^5 CFU/mL) was then added to each well giving a total volume of 100 μL/well and a compound concentration gradient of 10ug/ml –0.0049ug/ml. The plate was incubated at 37 ºC for 18-20 h and then each well was examined for bacterial growth. The MIC_{90} was recorded as the lowest compound concentration required to inhibit 90% of bacterial growth as judged by turbidity of the culture media relative to a row of wells filled with a DMSO standard. Ciprofloxacin was included in a control row at a concentration gradient of 5ug/ml-.0025ug/ml.

References

1. *Methods for Dilution Antimicrobial Susceptibility Tests for Bacteria that Grow Aerobically*, 8th ed. (Villanova, PA, USA), Clinical and Laboratory Standards Institute (CLSI), **2009**, approved standard document M07-A7.

Cell culture experiments of compounds **3**



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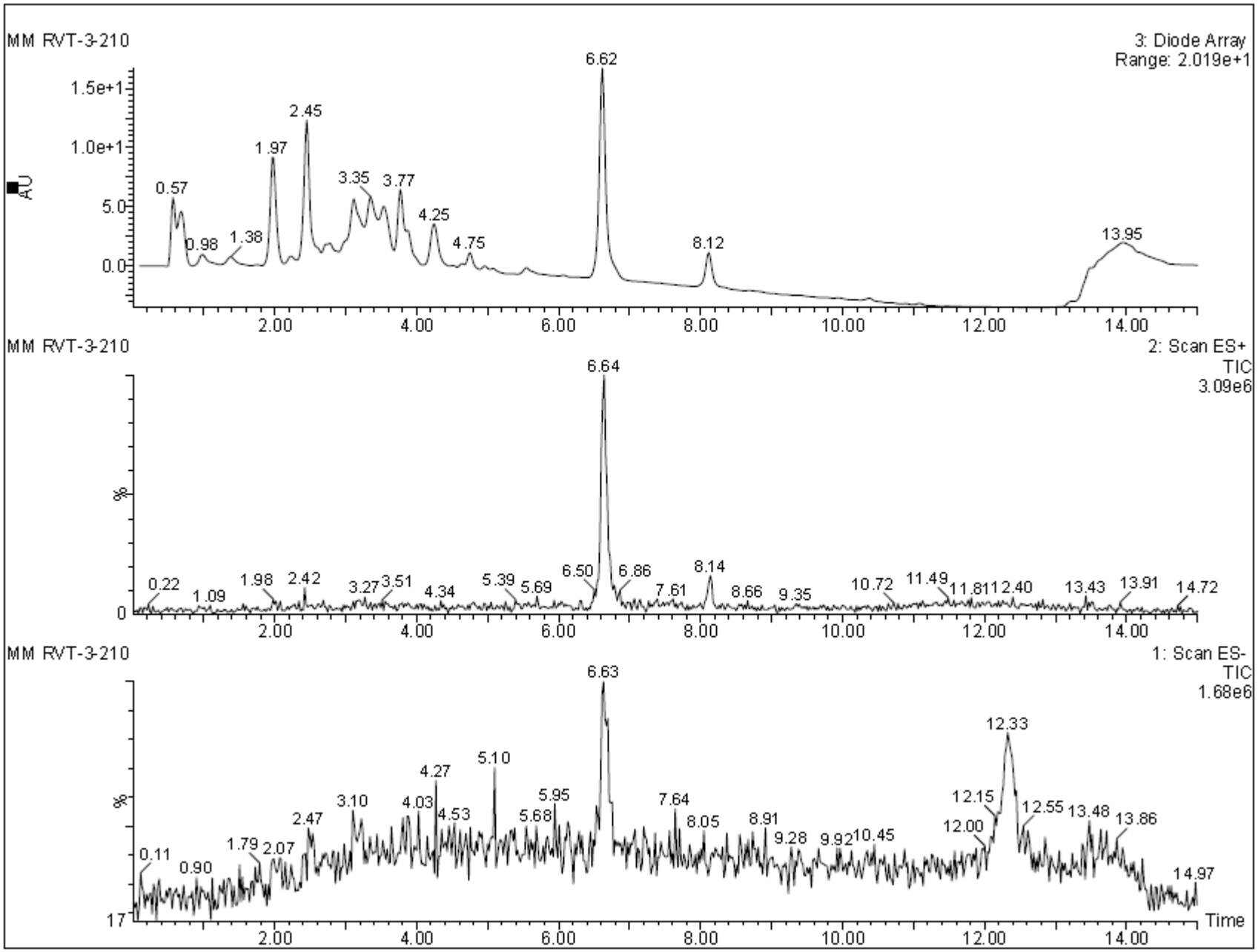
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3.77
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4.75
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10.00
12.00
14.00
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4.34
5.39
5.69
6.50
6.64
6.86
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9.35
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12.40
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13.91
14.72
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4.53
5.10
5.68
5.95
6.63
7.64
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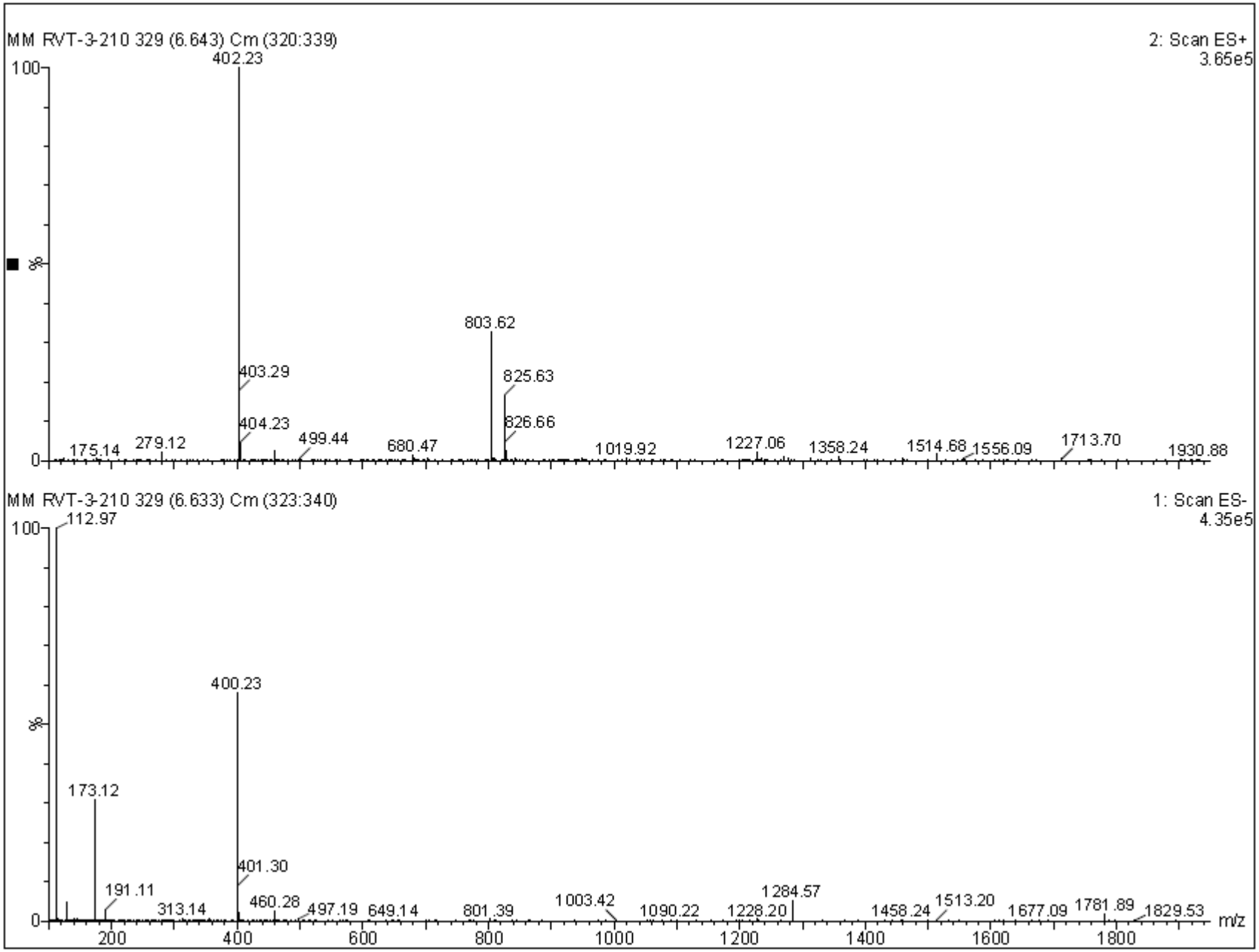
13.48
13.86
14.97
Time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%
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826.66
175.14
279.12
499.44
680.47
1019.92
1227.06
1358.24
1514.68
1556.09
1713.70
1930.88
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%
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401.30
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497.19
649.14
801.39
1003.42
1090.22
1284.57
1228.20
1458.24
1513.20
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800
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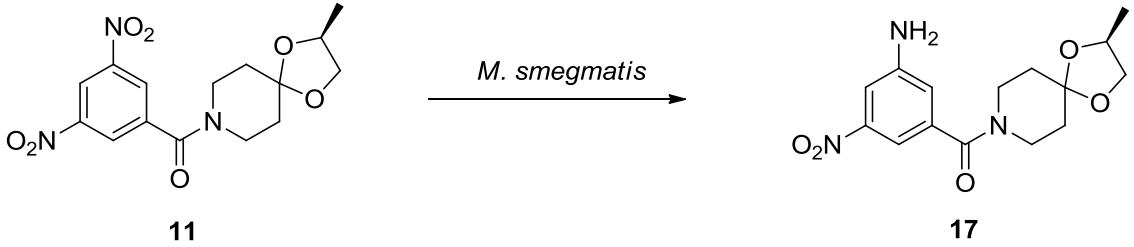
1400
1600
1800
m/z

Cell culture experiments of compounds **11**



11

Molecular Weight: 351.31

17

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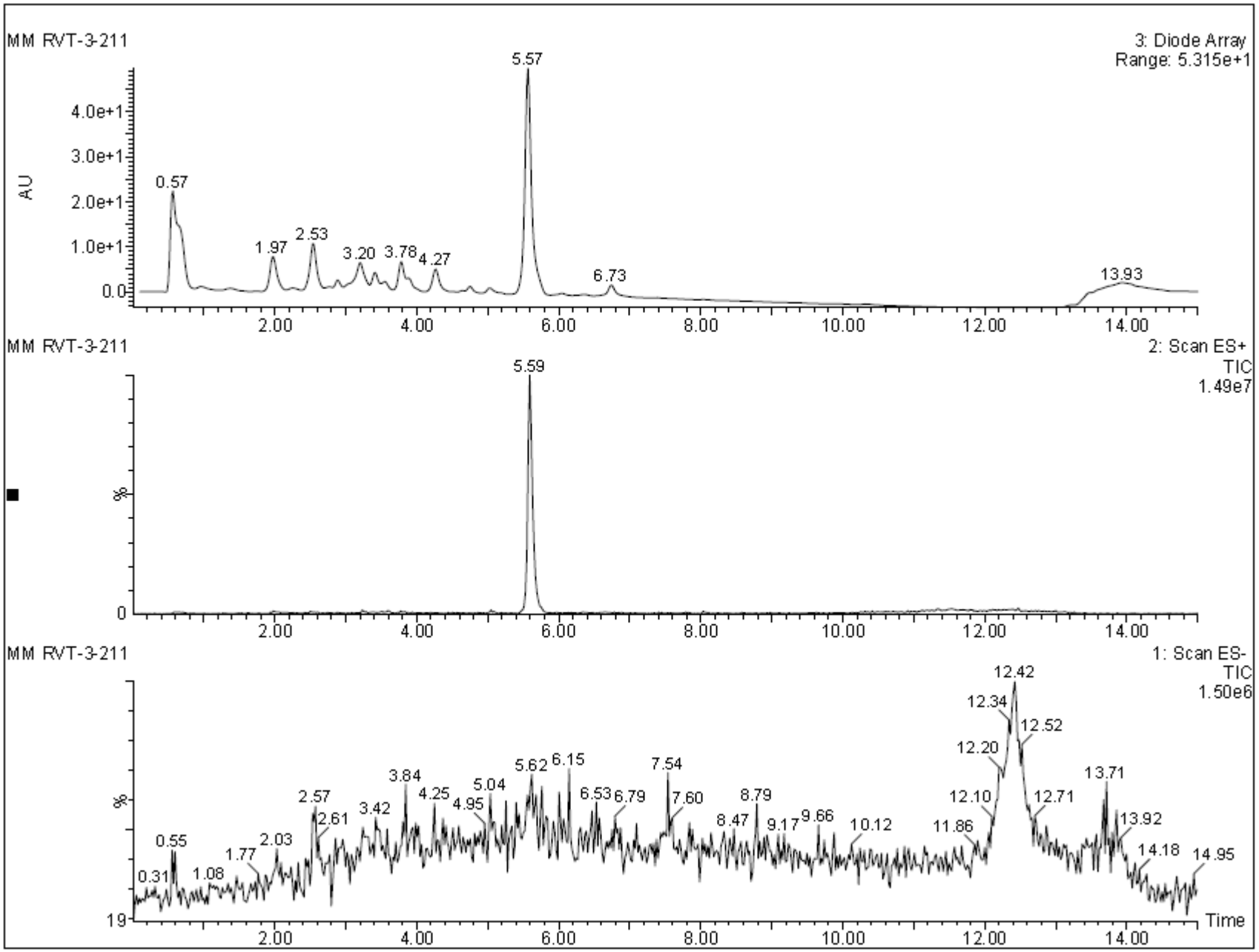
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3.78
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7.60
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10.12
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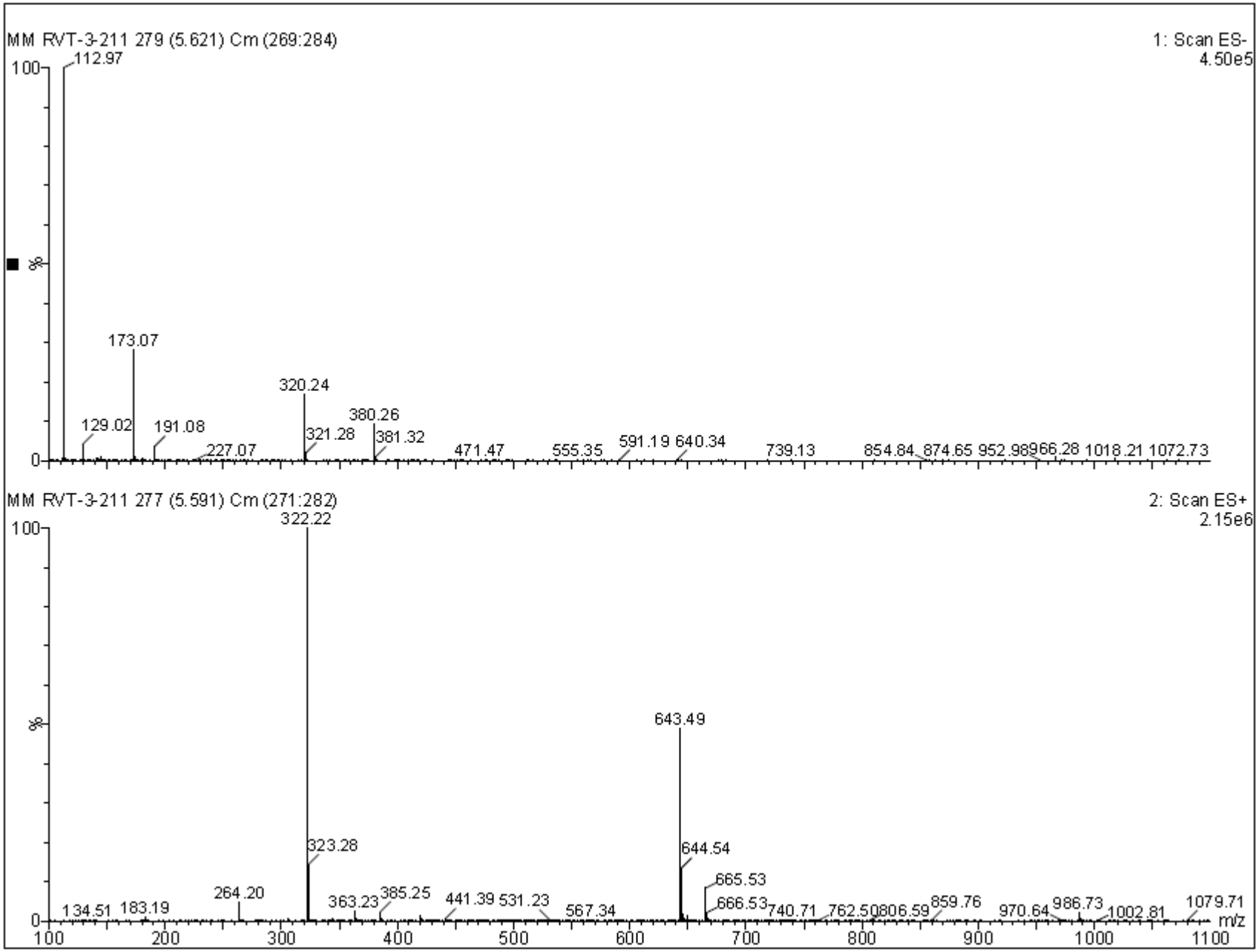
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%
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m/z
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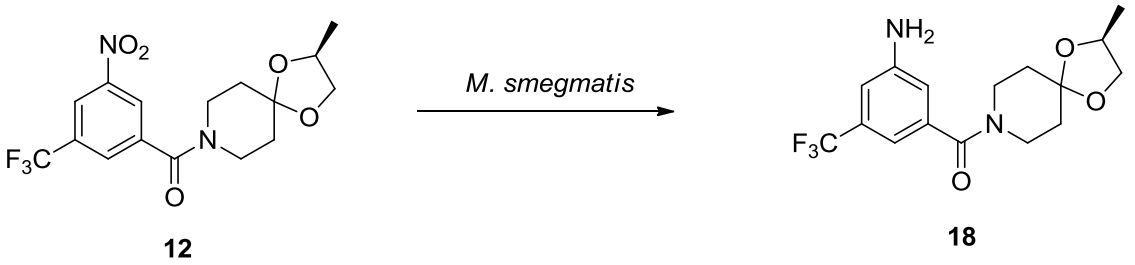
Cell culture experiments of compounds **12**



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Molecular Weight: 374.31

18

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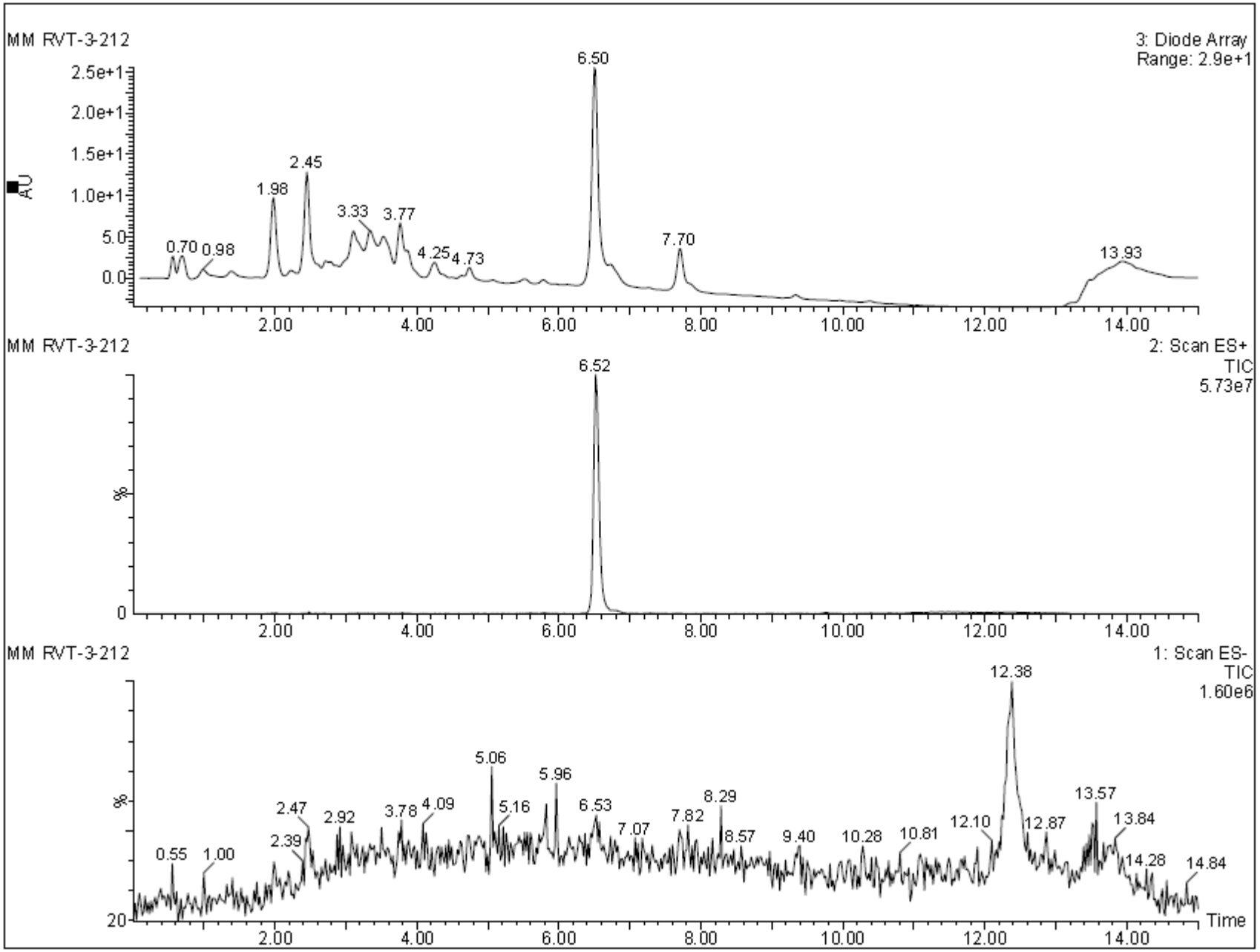
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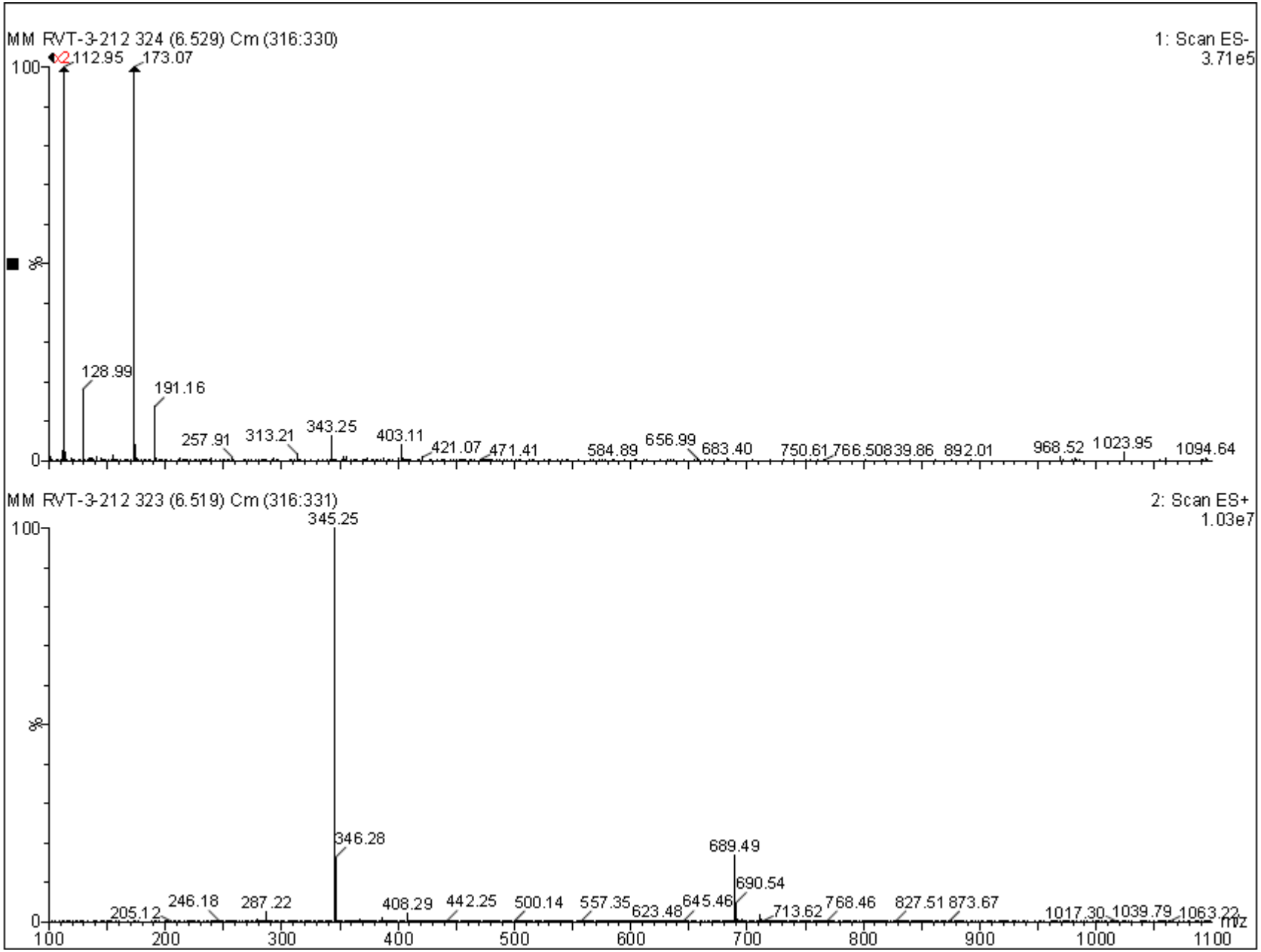
Time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200
300
400
500
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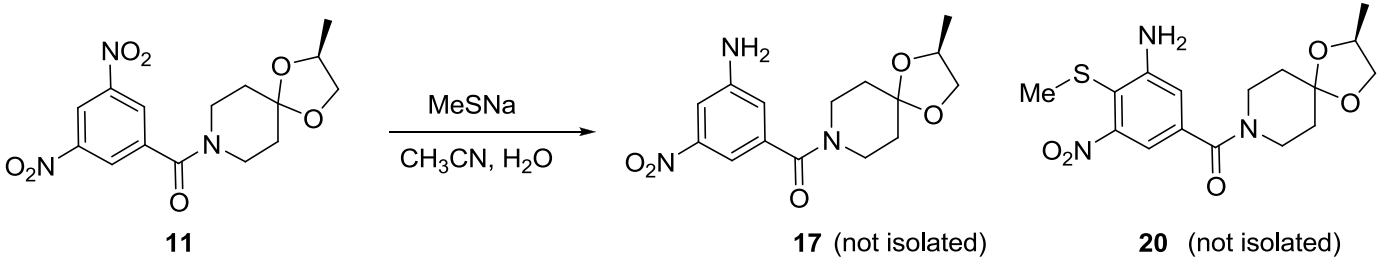
m/z

Reaction of **11** with sodium methane thiolates (Scheme 4). The structures of the products identified by LC/MS are shown along with the UV trace of the reaction.



11

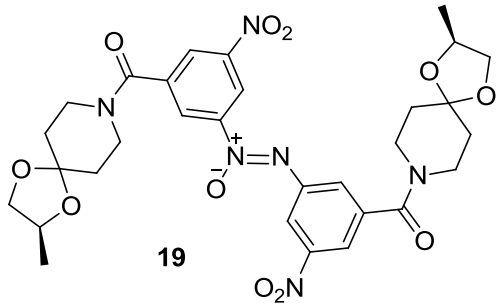
MW = 351.31138

17 (not isolated)

MW = 321.32846

20 (not isolated)

MW = 367.42004



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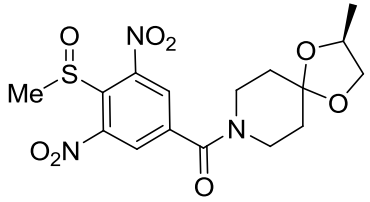
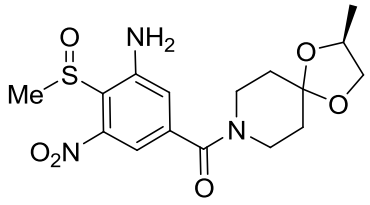
MW = 654.62456



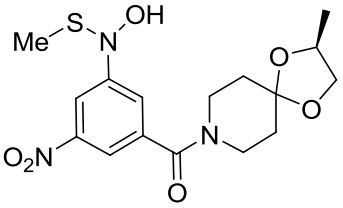
21

MW = 413.40236 (not isolated)



22

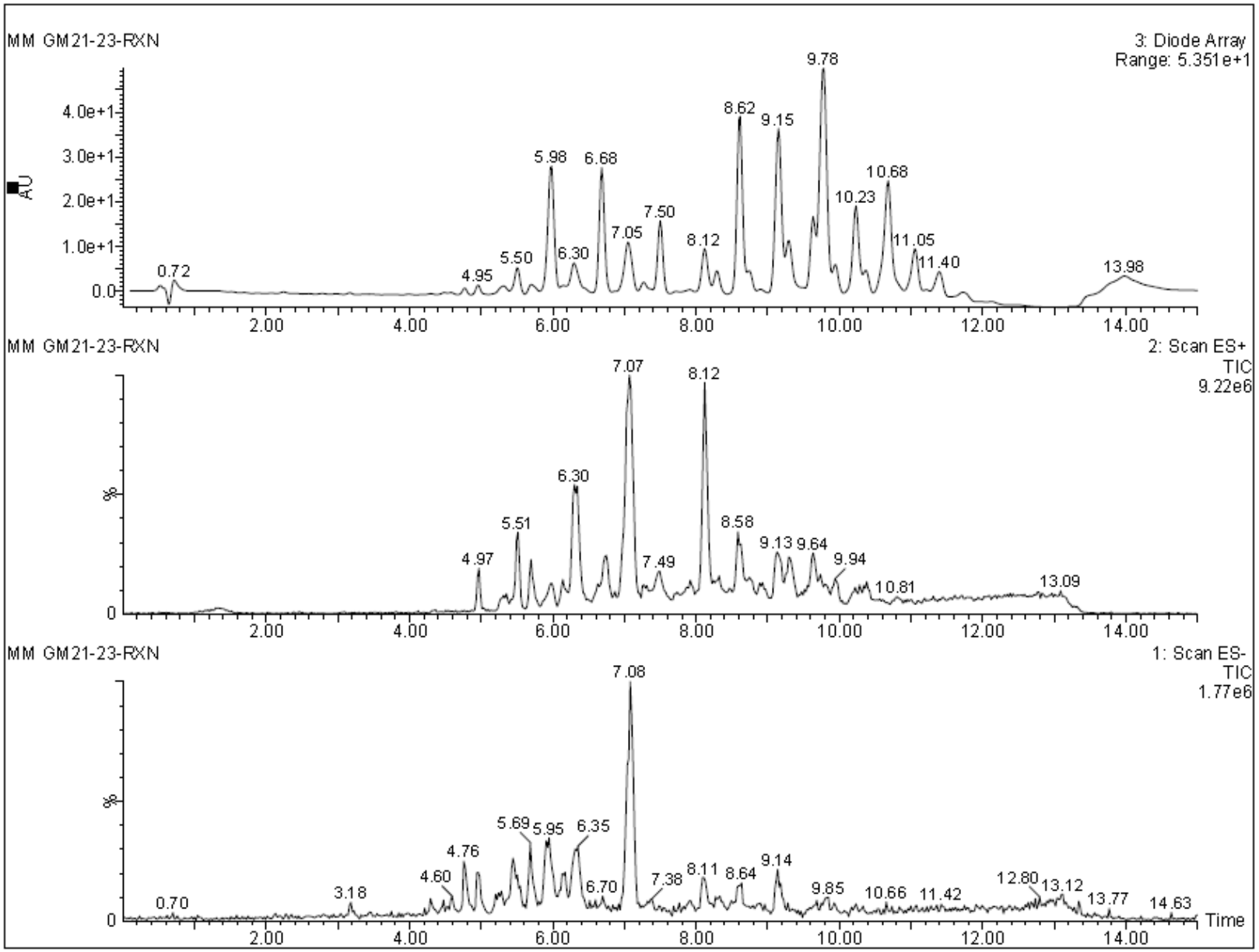
MW = 383.41944 (not isolated)



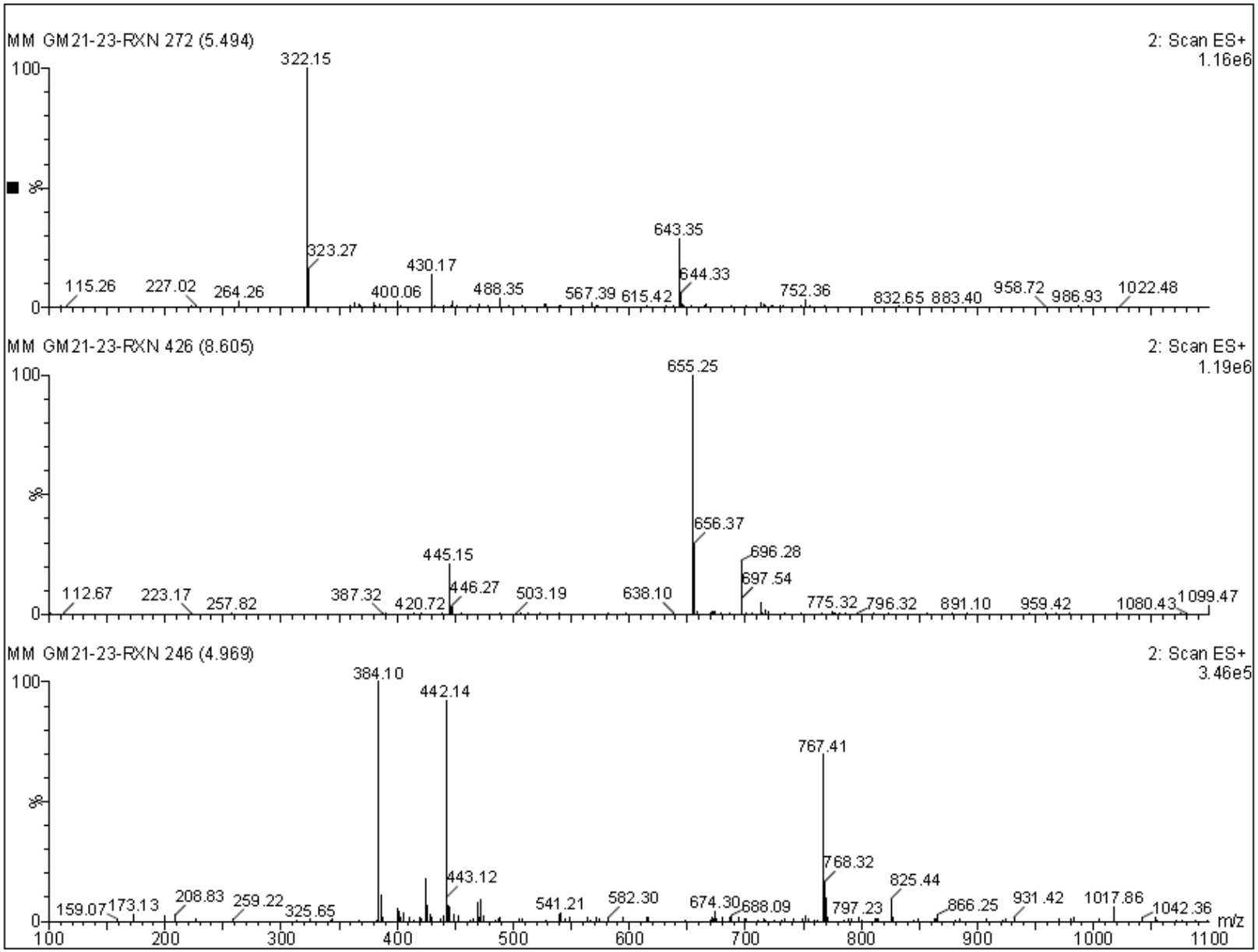
23

MW = 383.41944 (not isolated)

Chromatogram for the reaction of **11** with sodium methane thiolates (Scheme 4).



The mass spectra of the reaction of **11** with sodium methane thiolate in positive ionization mode.



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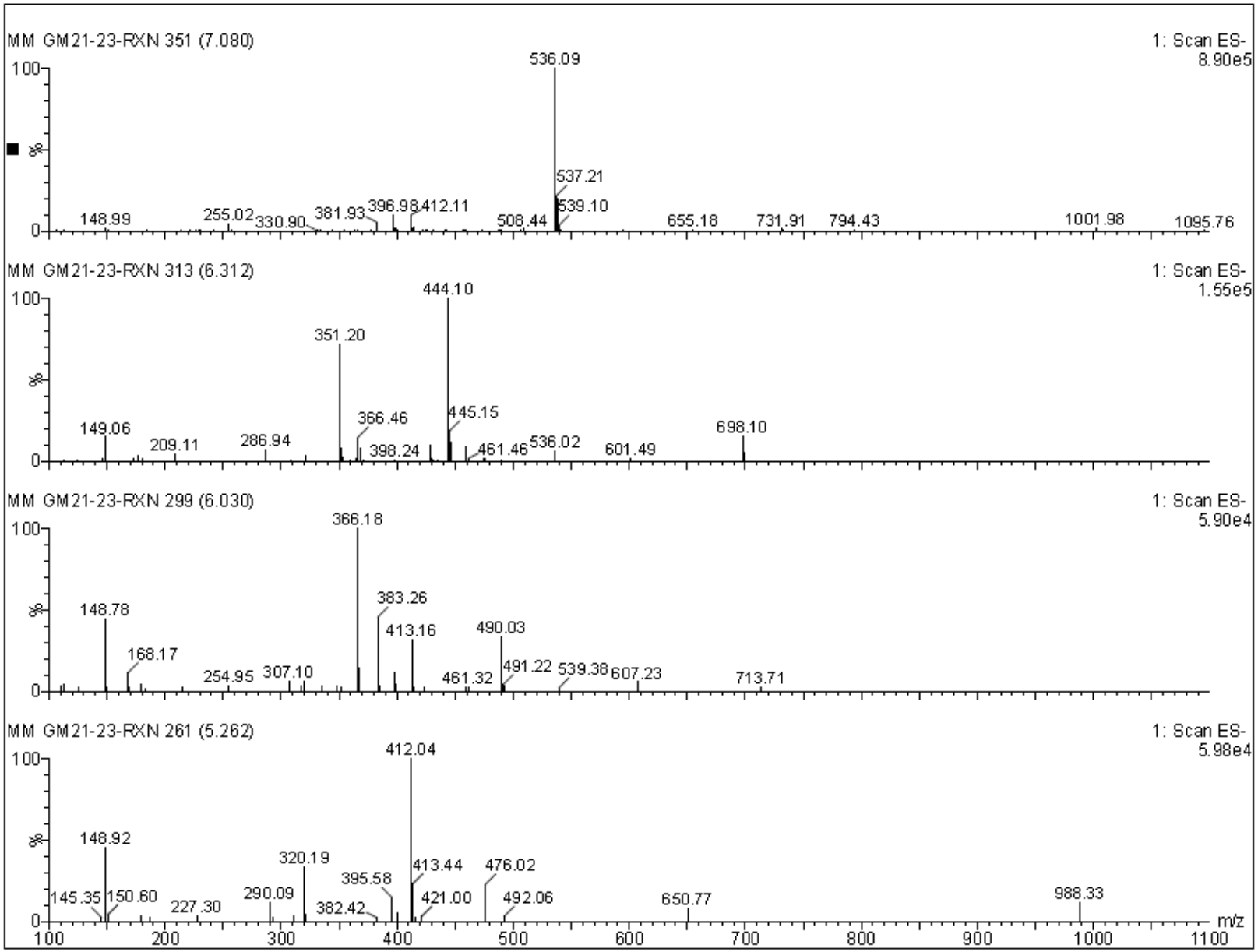
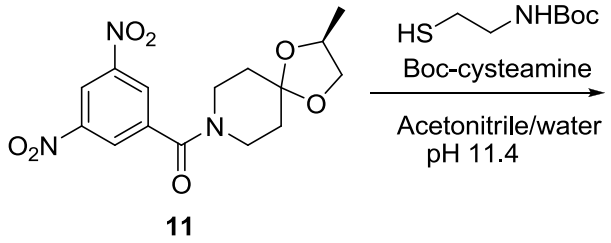
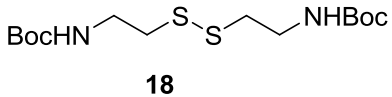


Reaction of **11** with Boc-cysteamine

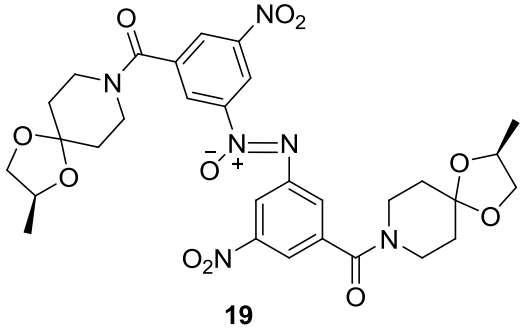




18

Chemical Formula: $C_{14}H_{28}N_2O_4S_2$
Exact Mass: 352.14905
Molecular Weight: 352.51312

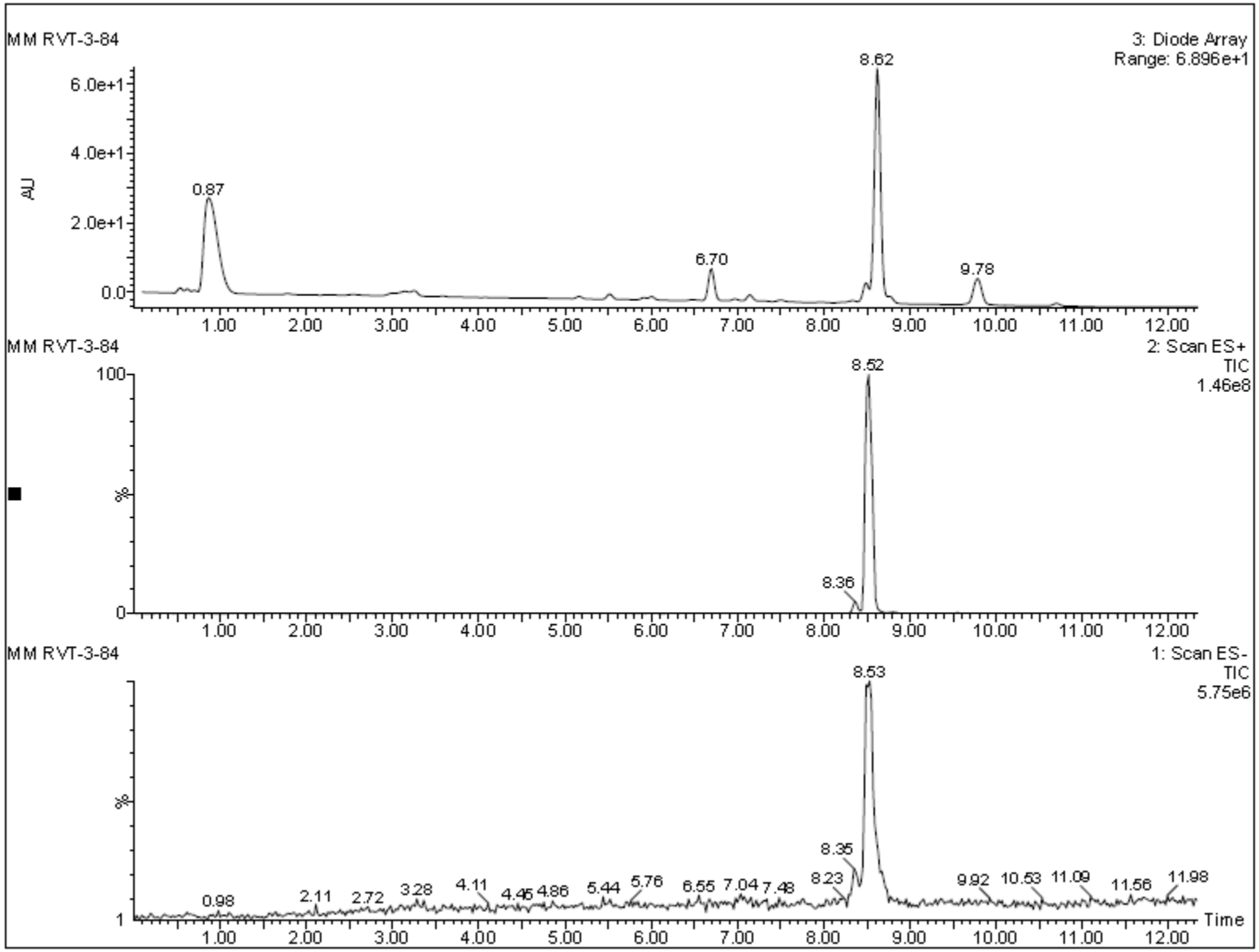
+



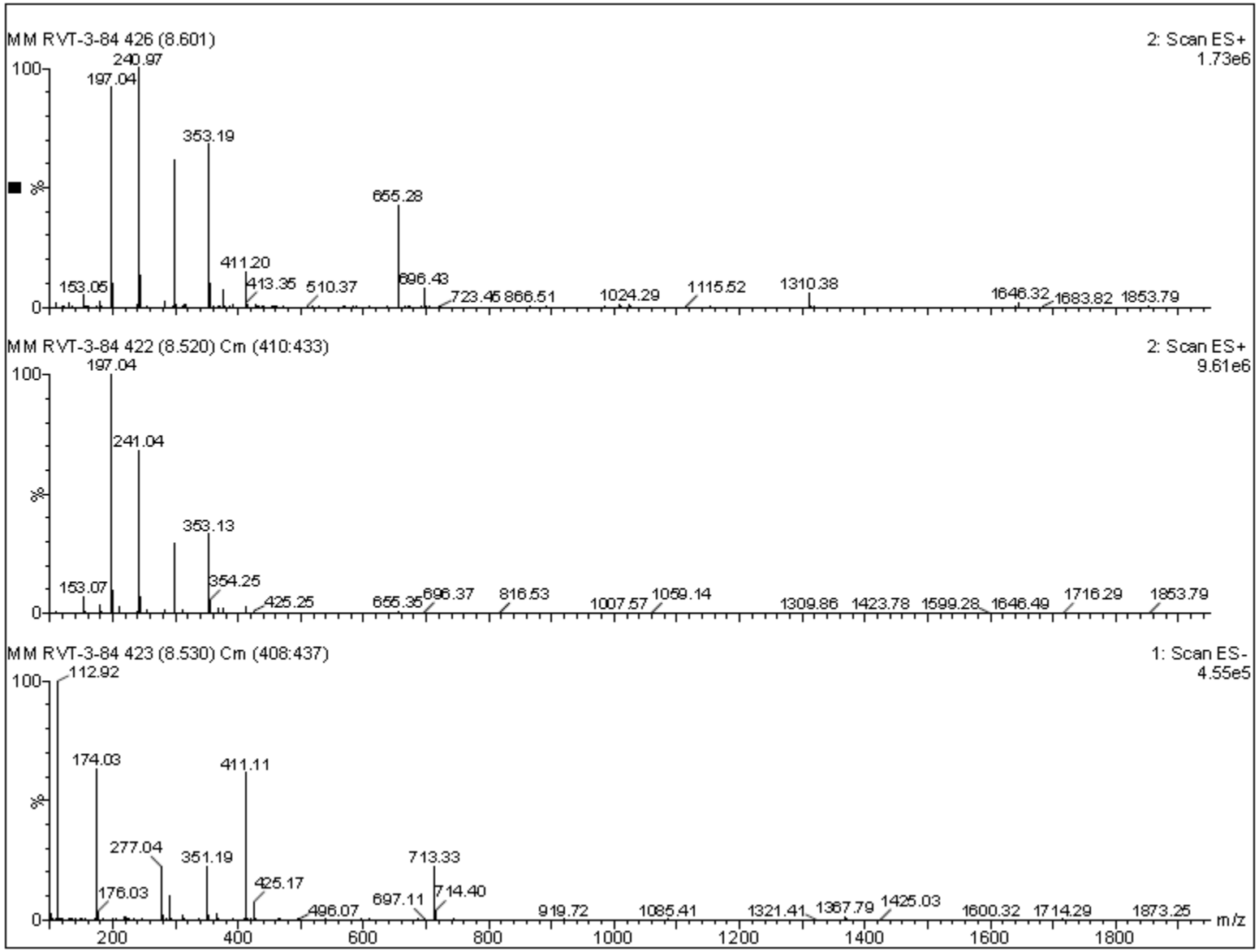
19

Chemical Formula: $C_{30}H_{34}N_6O_{11}$
Exact Mass: 654.22856
Molecular Weight: 654.62456

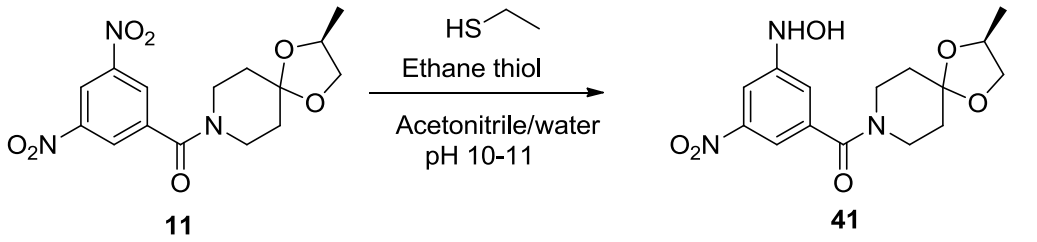
LC/MS


MM RVT-3-84
3: Diode Array
Range: 6.896e+1
AU
6.0e+1
4.0e+1
2.0e+1
0.0
0.87
6.70
8.62
9.78
1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00
MM RVT-3-84
2: Scan ES+
TIC
1.46e8
100
%
0
8.52
8.36
1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00
MM RVT-3-84
1: Scan ES-
TIC
5.75e6
%
1
8.53
8.35
0.98
2.11
2.72
3.28
4.11
4.45
4.86
5.44
5.76
6.55
7.04
7.48
8.23
9.92
10.53
11.09
11.56
11.98
Time
1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00

Mass spectra in the positive and the negative ionization mode.

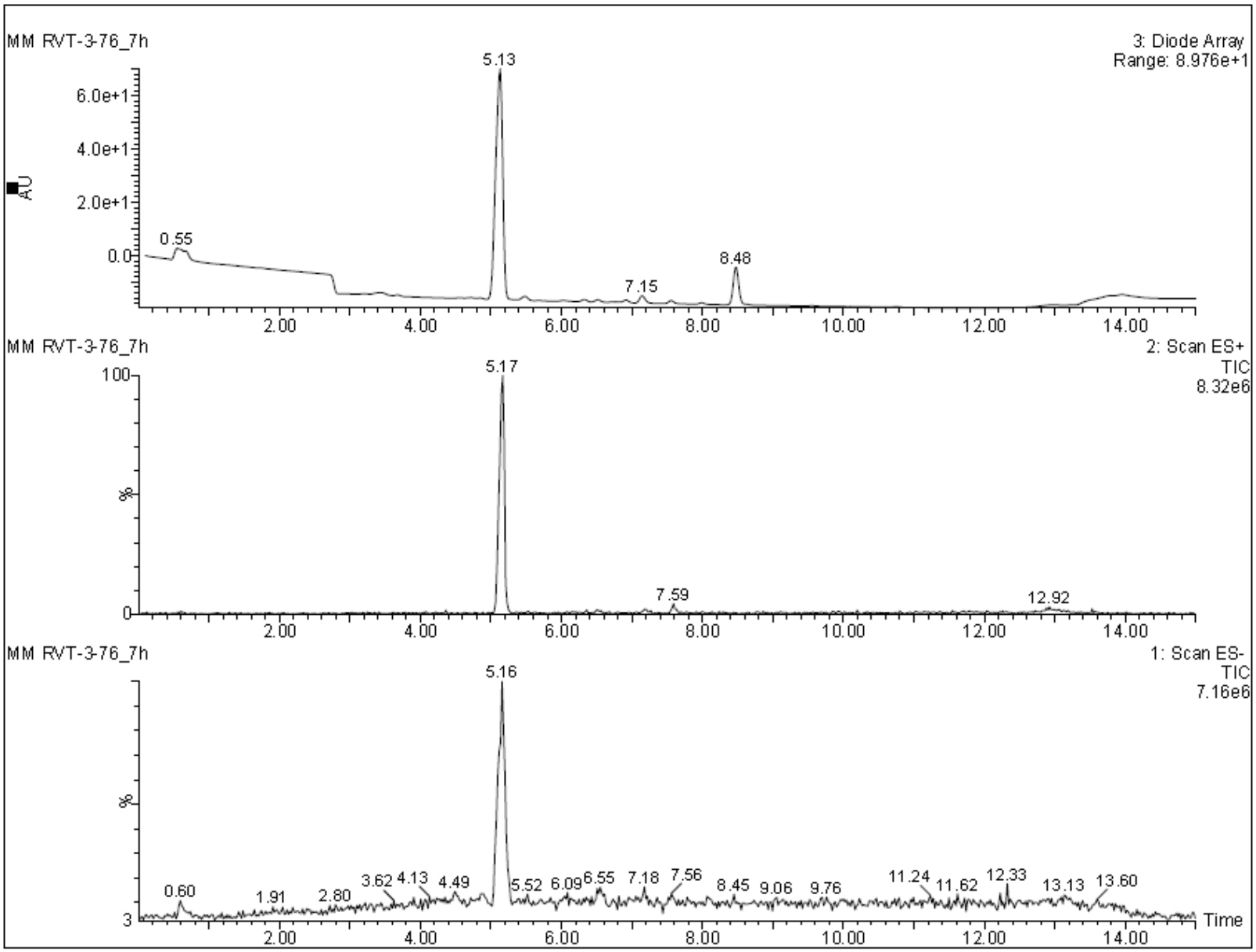


Reaction of **11** with ethane thiol at apparent pH 10-11. The starting material was completely disappeared after 7 h of reaction. Only hydroxylamine analogue (**41**) was detected under reaction condition. LC/MS is shown on the next page.

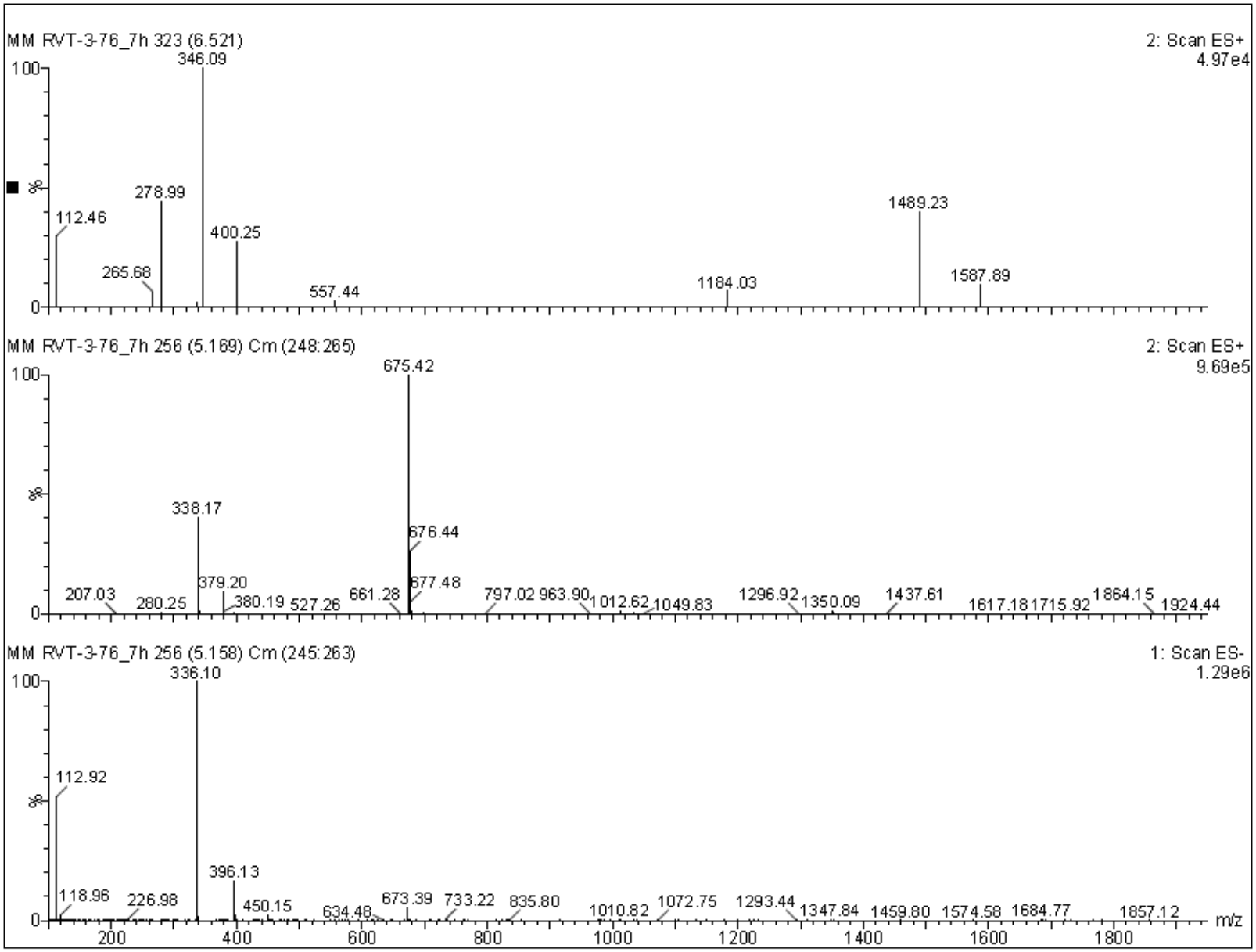


Chemical Formula: $C_{15}H_{19}N_3O_6$
Exact Mass: 337.12739
Molecular Weight: 337.32786

LC/MS

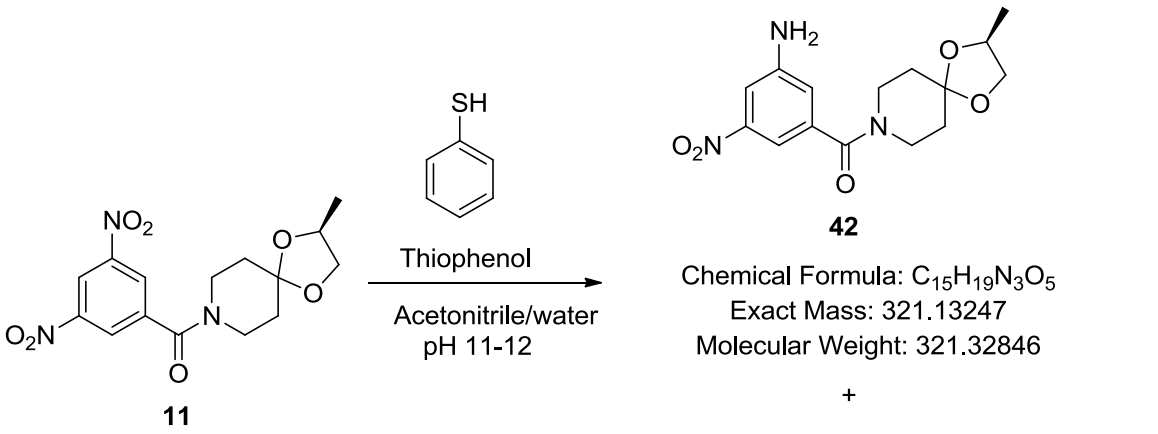

MM RVT-3-76_7h
3: Diode Array
Range: 8.976e+1
AU
6.0e+1
4.0e+1
2.0e+1
0.0
5.13
0.55
7.15
8.48
2.00
4.00
6.00
8.00
10.00
12.00
14.00
MM RVT-3-76_7h
2: Scan ES+
TIC
8.32e6
%
100
0
5.17
7.59
12.92
MM RVT-3-76_7h
1: Scan ES-
TIC
7.16e6
%
3
5.16
0.60
1.91
2.80
3.62
4.13
4.49
5.52
6.09
6.55
7.18
7.56
8.45
9.06
9.76
11.24
11.62
12.33
13.13
13.60
Time

Mass spectra in the positive and the negative ionization mode

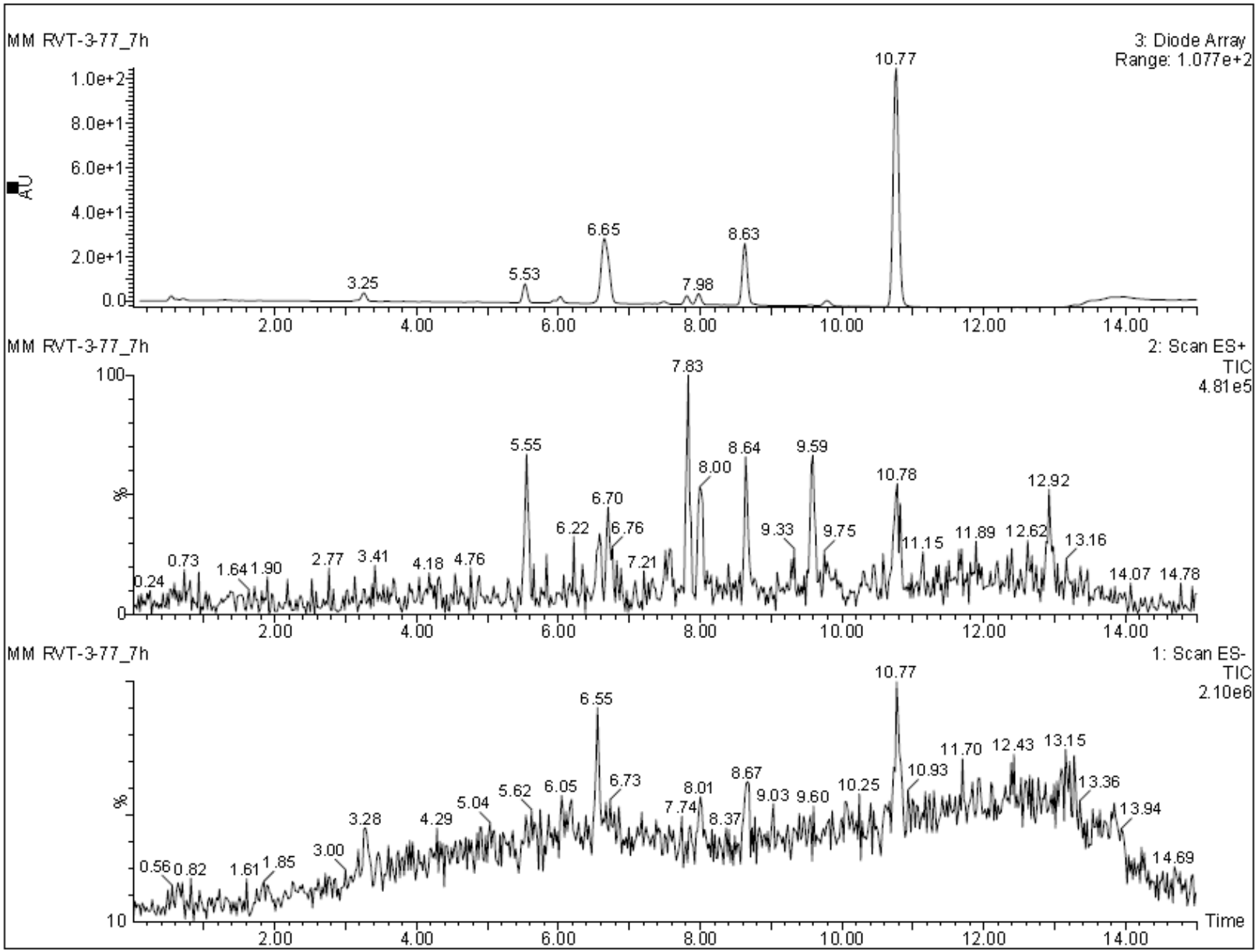


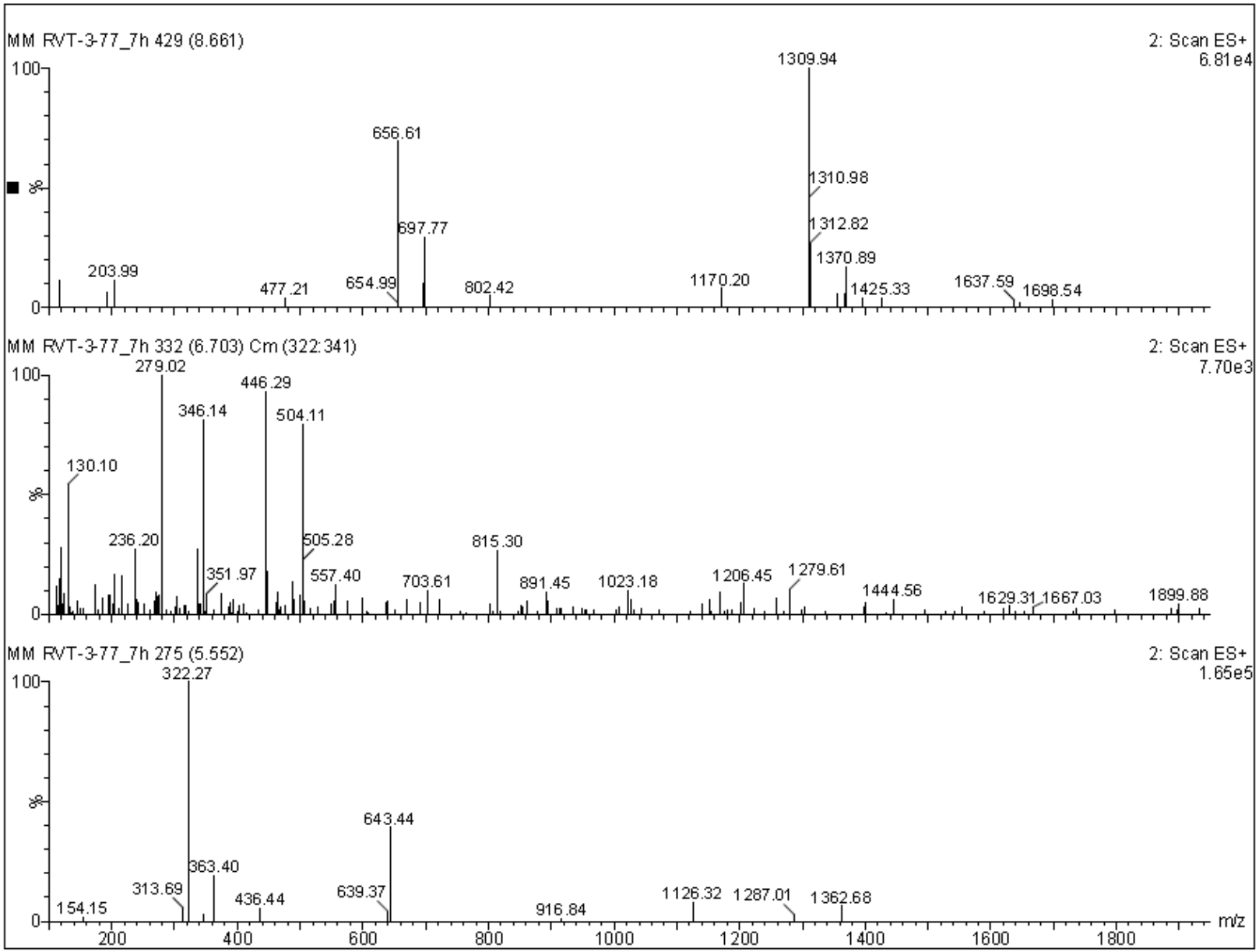
Reaction of **11** with thiophenol at apparent pH 11-12. The LC/MS of the reaction mixture indicated the formation of **42** and **19**.

LC/MS is shown on the next page

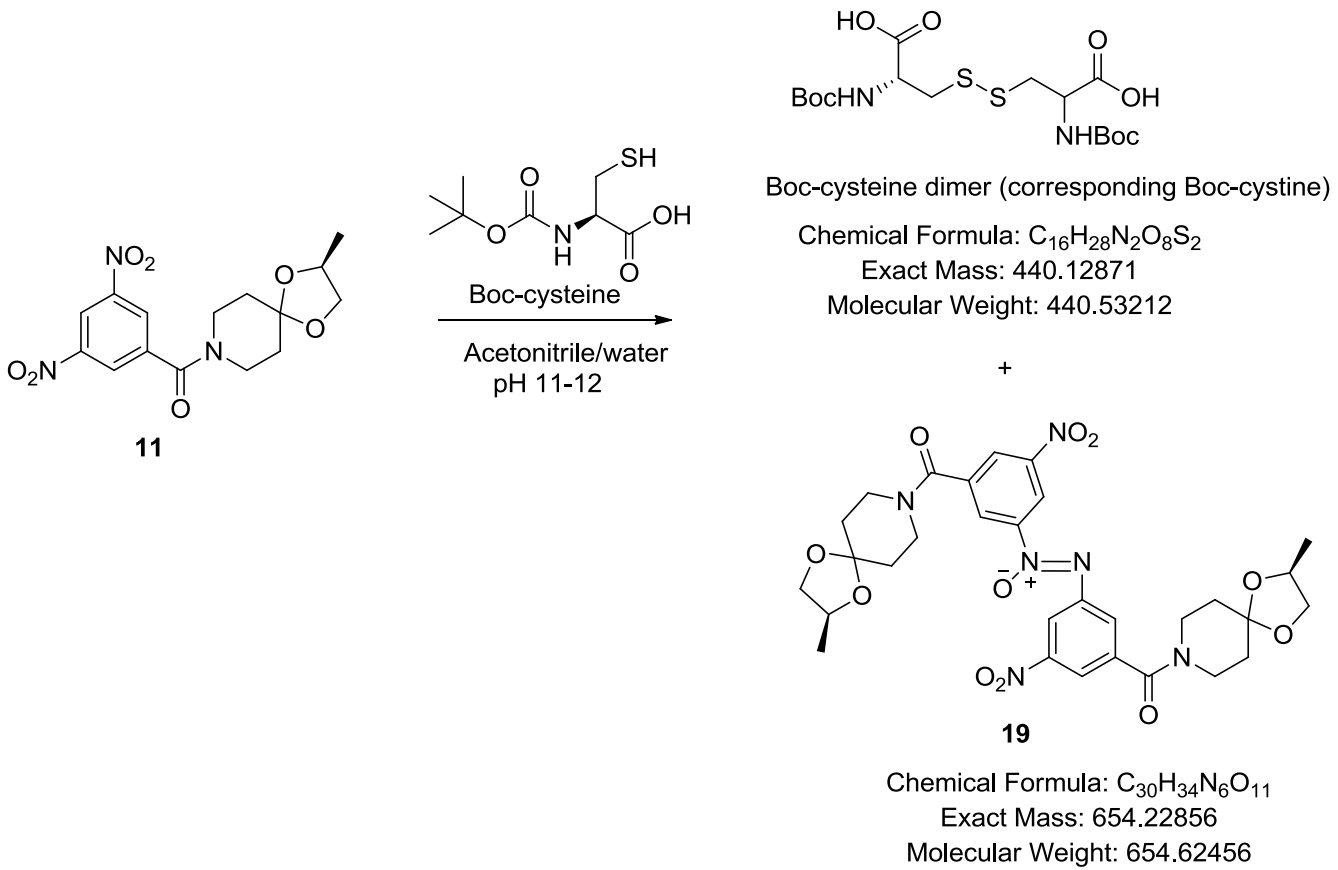


LC/MS

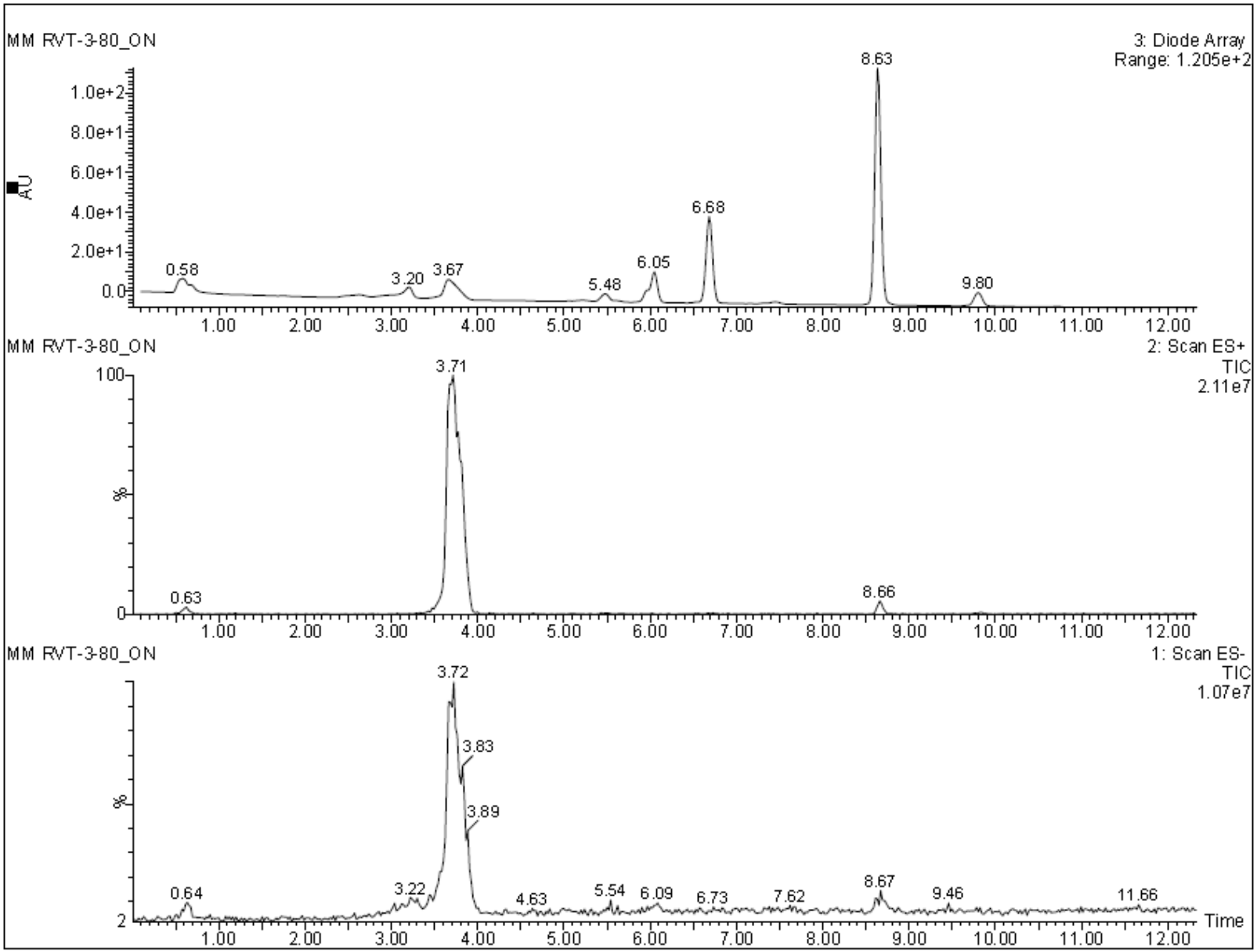

MM RVT-3-77_7h
3: Diode Array
Range: 1.077e+2
AU
10.77
6.65
8.63
3.25
5.53
7.98
MM RVT-3-77_7h
2: Scan ES+
TIC
4.81e5
%
7.83
5.55
8.64
9.59
8.00
10.78
12.92
6.70
6.22
6.76
9.33
9.75
11.15
11.89
12.62
13.16
0.24
0.73
1.64
1.90
2.77
3.41
4.18
4.76
7.21
14.07
14.78
MM RVT-3-77_7h
1: Scan ES-
TIC
2.10e6
%
10.77
6.55
11.70
12.43
13.15
10.93
6.73
8.67
8.01
13.36
5.62
6.05
9.03
9.60
10.25
5.04
7.74
8.37
13.94
3.28
4.29
0.56
0.82
1.61
1.85
3.00
14.69
Time


MM RVT-3-77_7h 429 (8.661)
2: Scan ES+
6.81e4
1309.94
656.61
1310.98
697.77
1312.82
1370.89
203.99
477.21
654.99
802.42
1170.20
1425.33
1637.59
1698.54
MM RVT-3-77_7h 332 (6.703) Cm (322:341)
2: Scan ES+
7.70e3
279.02
446.29
346.14
504.11
130.10
236.20
505.28
815.30
351.97
557.40
703.61
891.45
1023.18
1206.45
1279.61
1444.56
1629.31
1667.03
1899.88
MM RVT-3-77_7h 275 (5.552)
2: Scan ES+
1.65e5
322.27
643.44
363.40
313.69
436.44
639.37
154.15
916.84
1126.32
1287.01
1362.68
m/z
200
400
600
800
1000
1200
1400
1600
1800

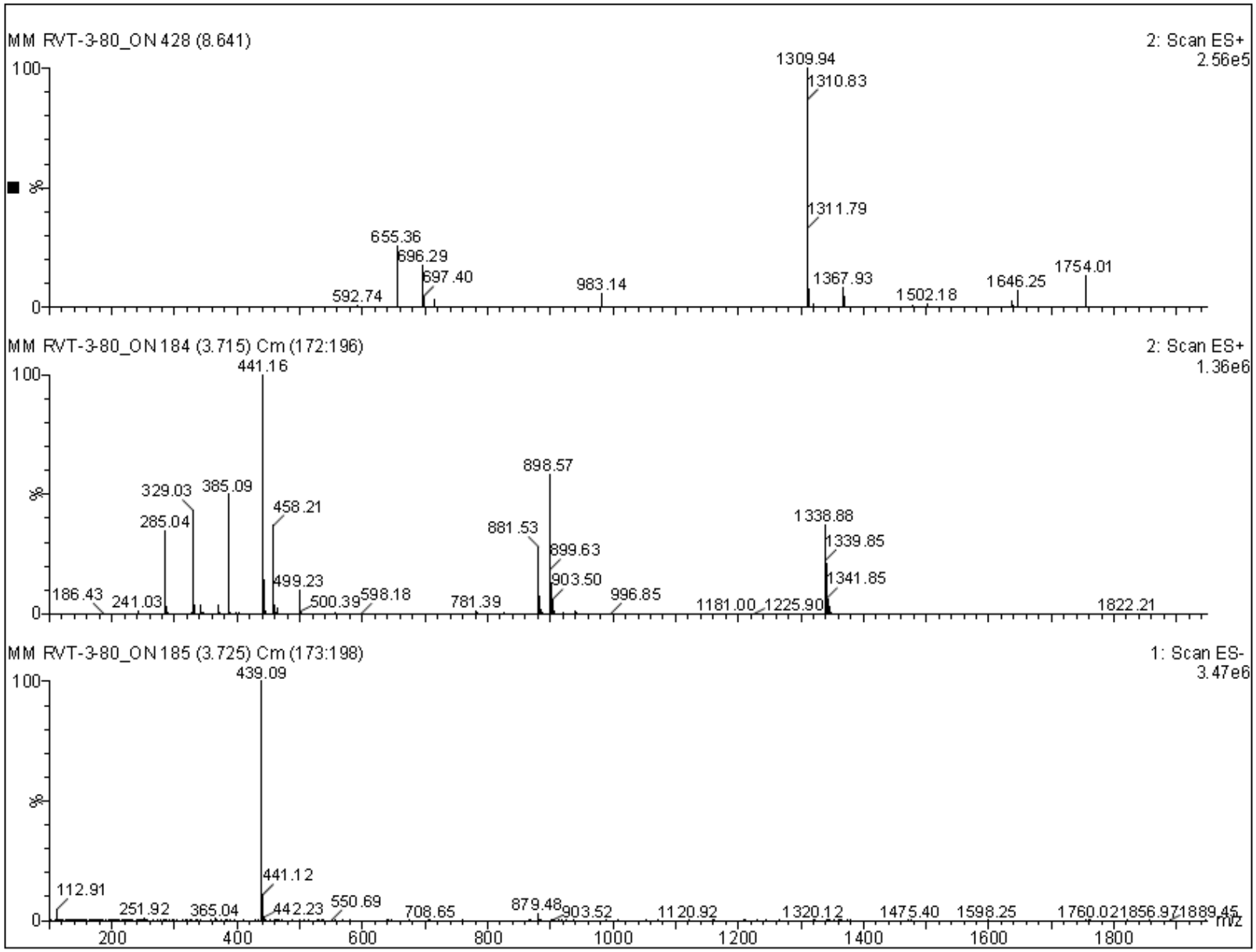
Reaction of **11** with Boc-cysteine at apparent pH 10-11. The LC/MS of the reaction mixture indicated the formation of the Boc-cysteine dimer (corresponding cysteine) and **19**. LC/MS is shown on the next page



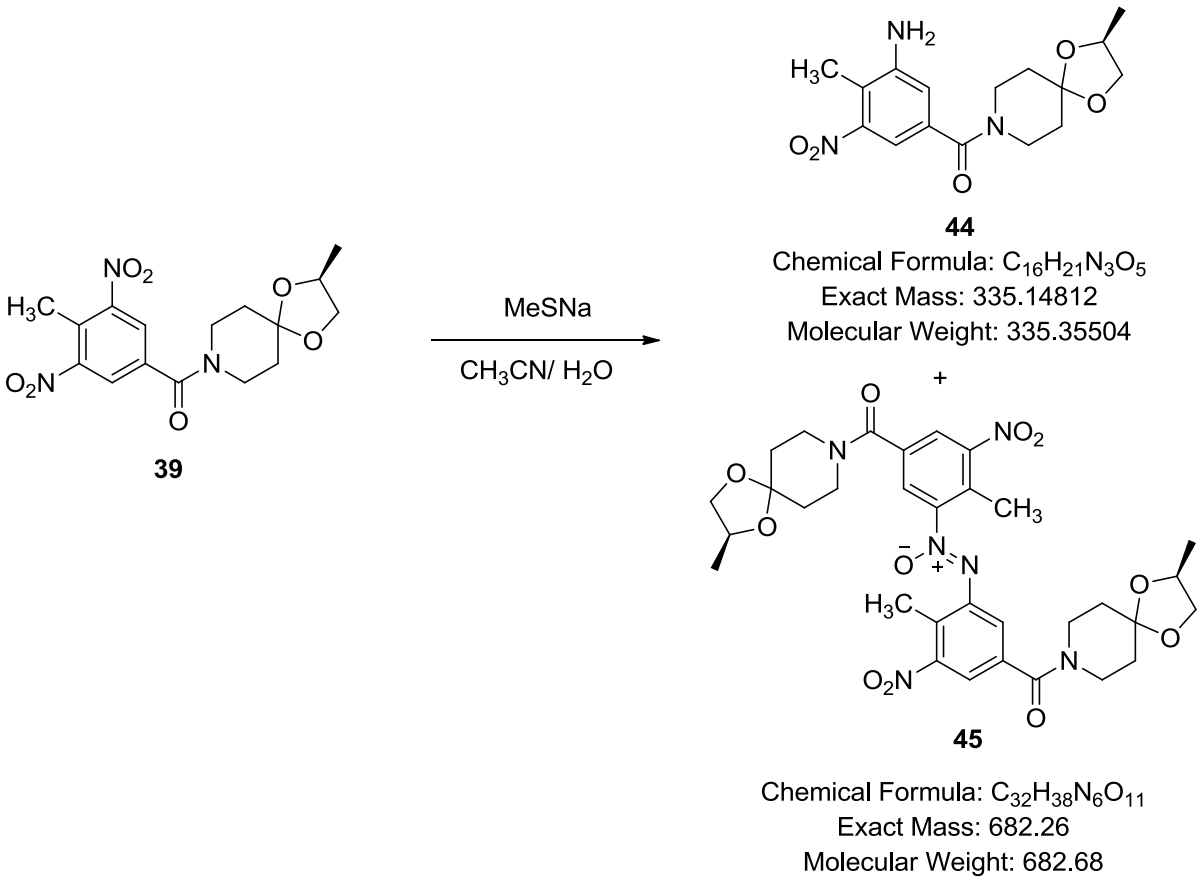
LC/MS

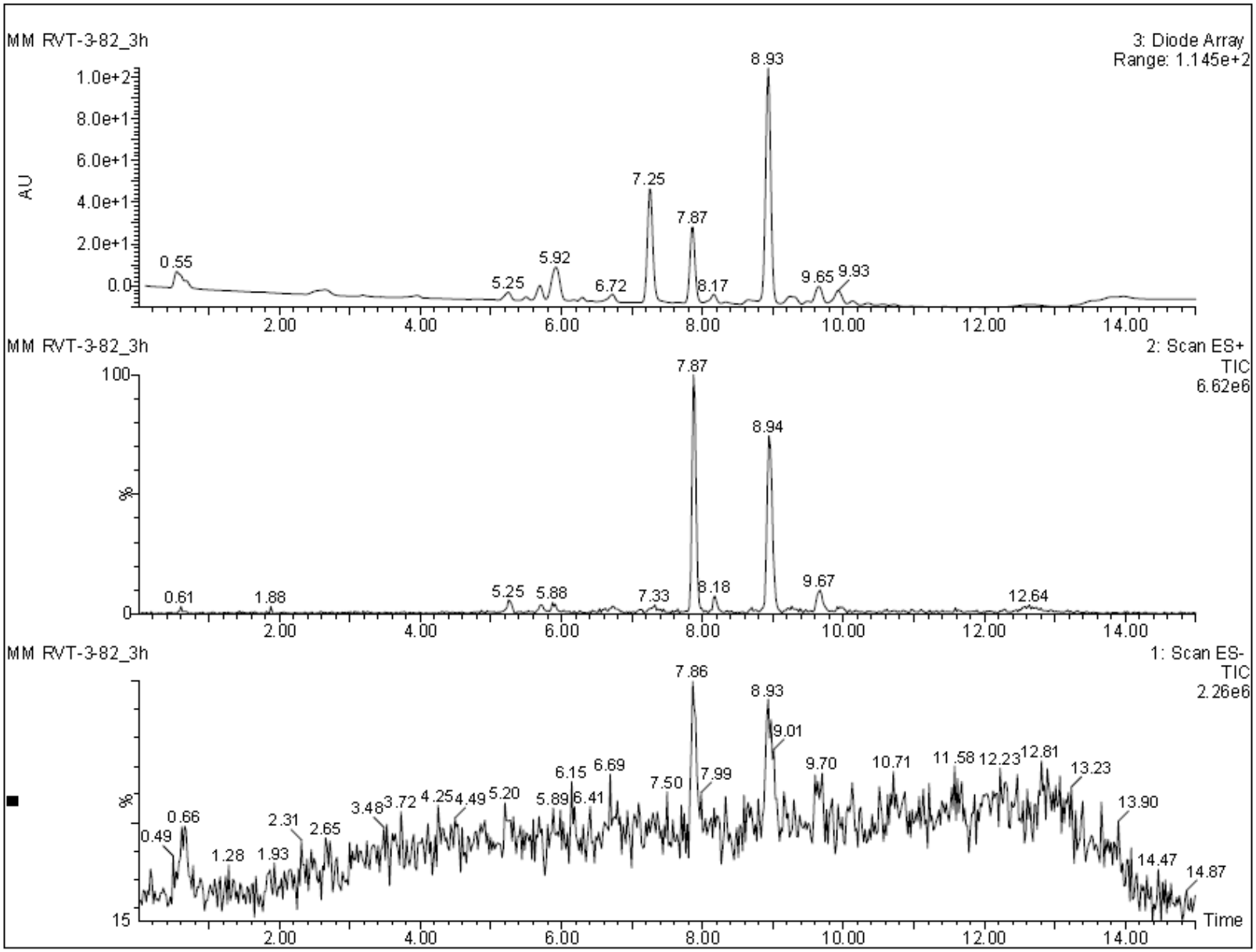

MM RVT-3-80_ON
3: Diode Array
Range: 1.205e+2
AU
1.0e+2
8.0e+1
6.0e+1
4.0e+1
2.0e+1
0.0
0.58
3.20
3.67
5.48
6.05
6.68
8.63
9.80
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
MM RVT-3-80_ON
2: Scan ES+
TIC
2.11e7
100
%
0
0.63
3.71
8.66
MM RVT-3-80_ON
1: Scan ES-
TIC
1.07e7
%
2
0.64
3.22
3.72
3.83
3.89
4.63
5.54
6.09
6.73
7.62
8.67
9.46
11.66
Time

Mass spectra in the positive and the negative ionization mode

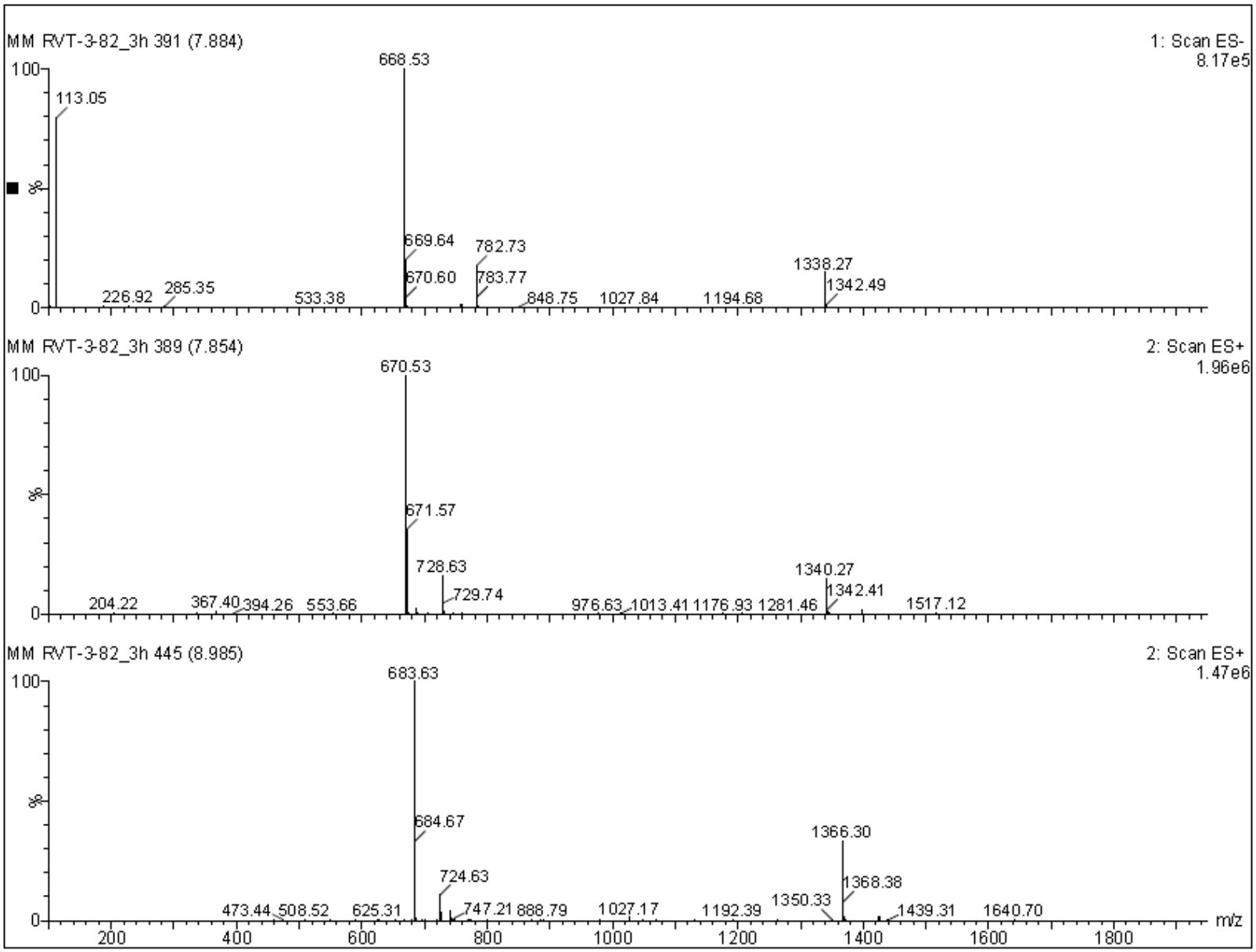


Reaction of 4-methyl analog of **11** (compound **39**) with sodium methane thiolate.

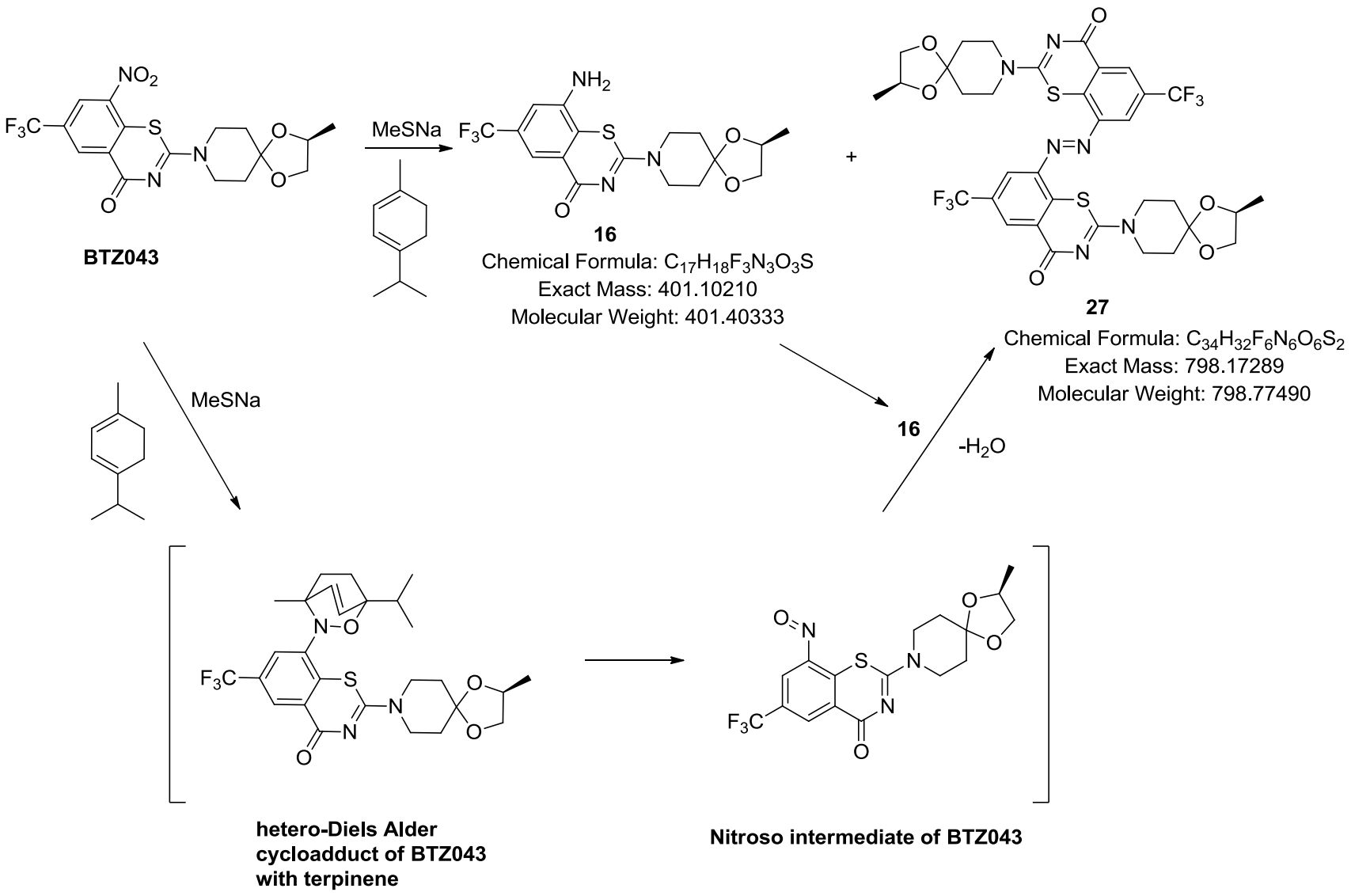



MM RVT-3-82_3h
3: Diode Array
Range: 1.145e+2
AU
1.0e+2
8.0e+1
6.0e+1
4.0e+1
2.0e+1
0.0
0.55
5.25
5.92
6.72
7.25
7.87
8.17
8.93
9.65
9.93
2.00
4.00
6.00
8.00
10.00
12.00
14.00
MM RVT-3-82_3h
2: Scan ES+
TIC
6.62e6
%
100
0
0.61
1.88
5.25
5.88
7.33
7.87
8.18
8.94
9.67
12.64
MM RVT-3-82_3h
1: Scan ES-
TIC
2.26e6
%
15
0.49
0.66
1.28
1.93
2.31
2.65
3.48
3.72
4.25
4.49
5.20
5.89
6.15
6.41
6.69
7.50
7.86
7.99
8.93
9.01
9.70
10.71
11.58
12.23
12.81
13.23
13.90
14.47
14.87
Time

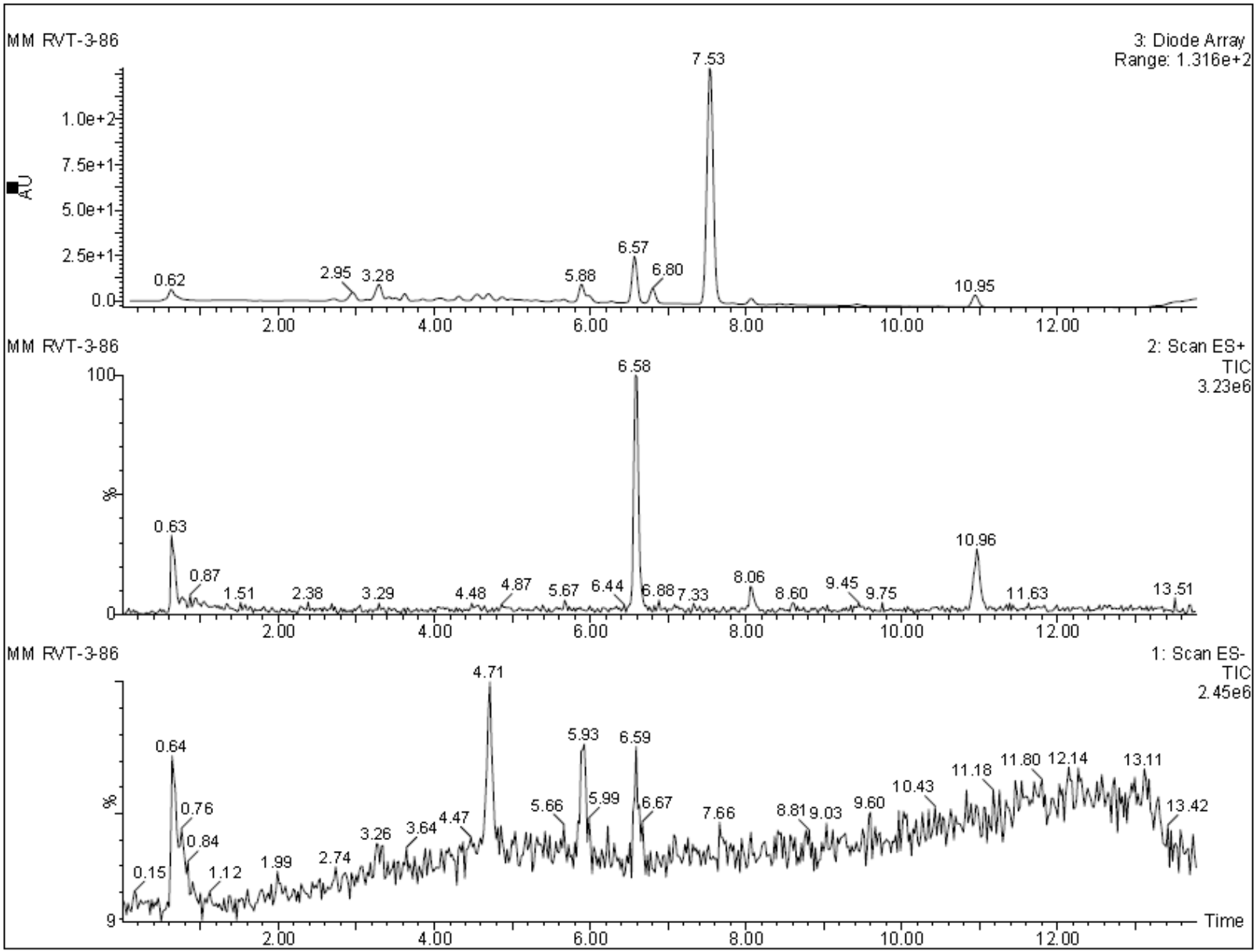
Mass spectra in the positive and the negative ionization mode



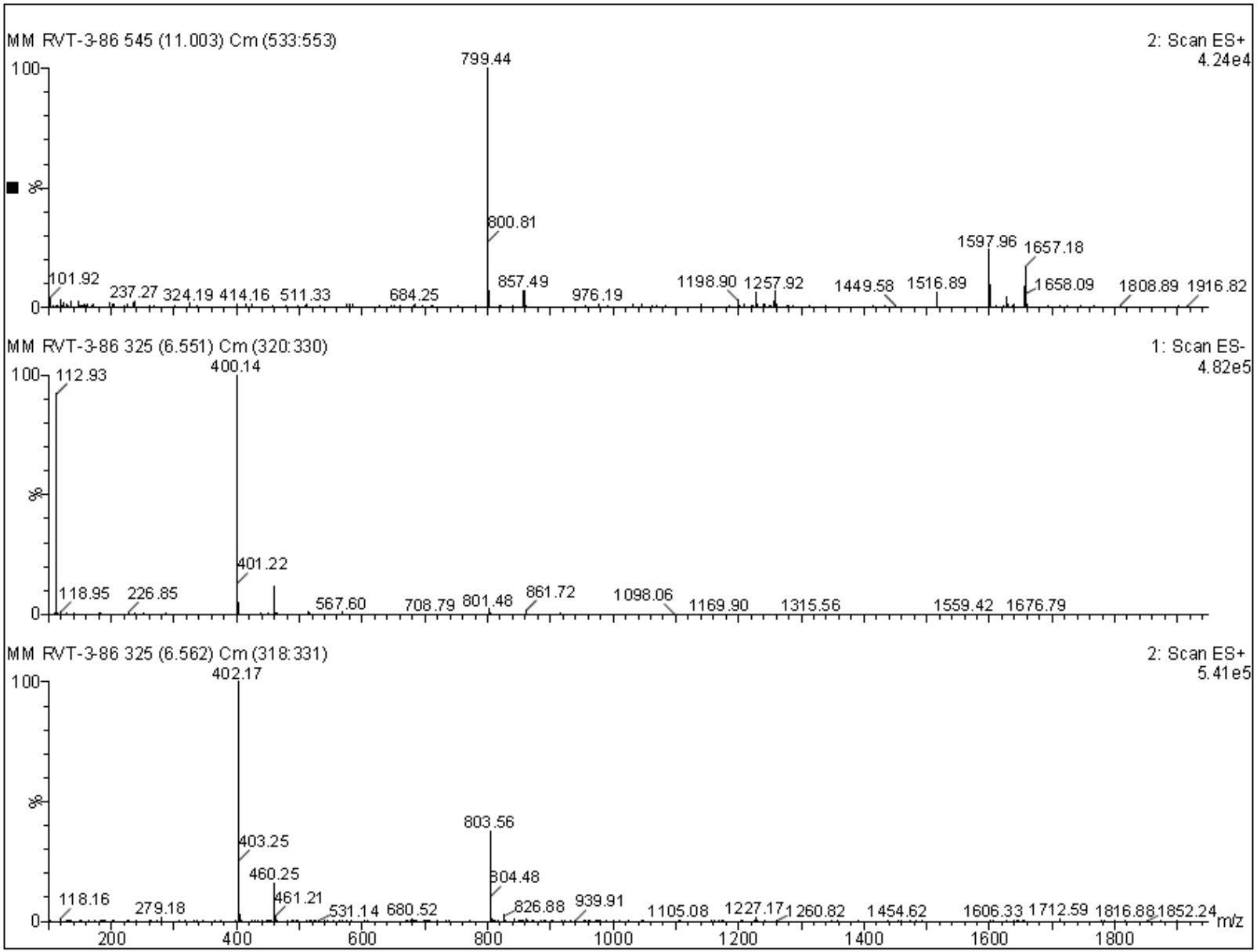
Reaction of **3** with sodium methane thiolate in the presence of terpinene. The LC/MS is shown on the next page.



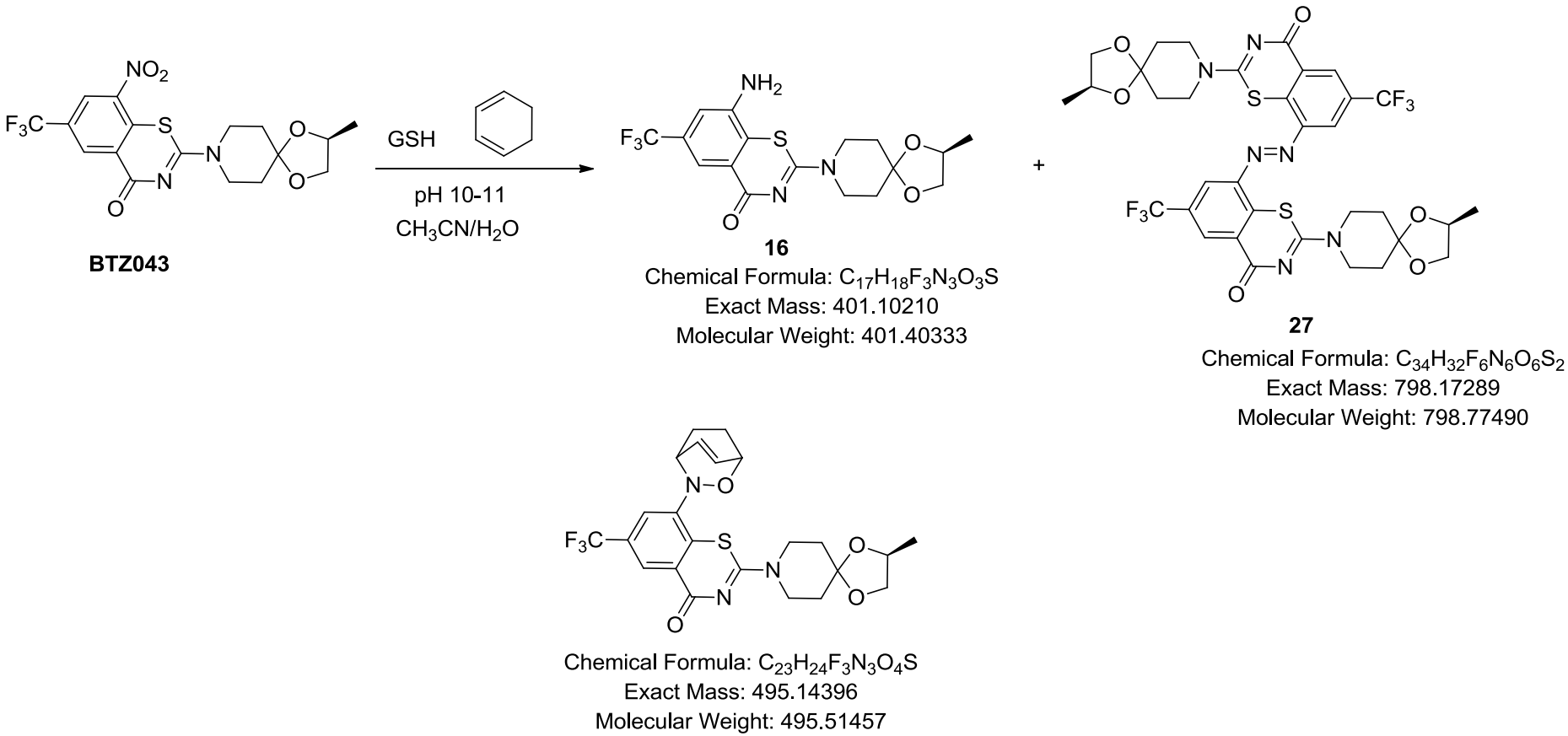
LC/MS


MM RVT-3-86
3: Diode Array
Range: 1.316e+2
AU
1.0e+2
7.5e+1
5.0e+1
2.5e+1
0.0
7.53
6.57
6.80
0.62
2.95
3.28
5.88
10.95
2.00
4.00
6.00
8.00
10.00
12.00
MM RVT-3-86
2: Scan ES+
TIC
3.23e6
100
%
0
6.58
0.63
0.87
1.51
2.38
3.29
4.48
4.87
5.67
6.44
6.88
7.33
8.06
8.60
9.45
9.75
10.96
11.63
13.51
2.00
4.00
6.00
8.00
10.00
12.00
MM RVT-3-86
1: Scan ES-
TIC
2.45e6
%
9
4.71
5.93
6.59
0.64
0.76
0.84
0.15
1.12
1.99
2.74
3.26
3.64
4.47
5.66
5.99
6.67
7.66
8.81
9.03
9.60
10.43
11.18
11.80
12.14
13.11
13.42
Time
2.00
4.00
6.00
8.00
10.00
12.00

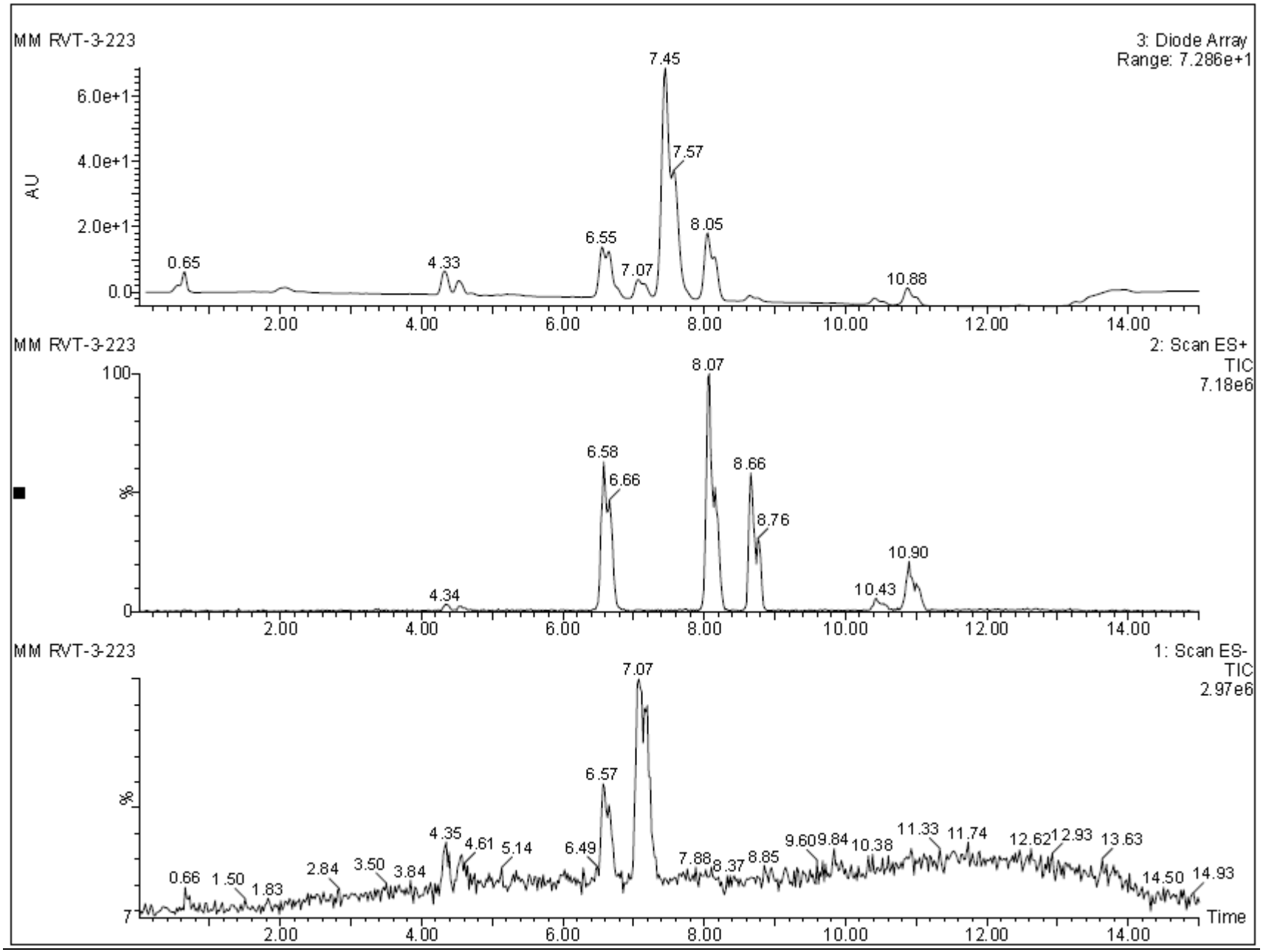
Mass spectra in the positive and the negative ionization mode

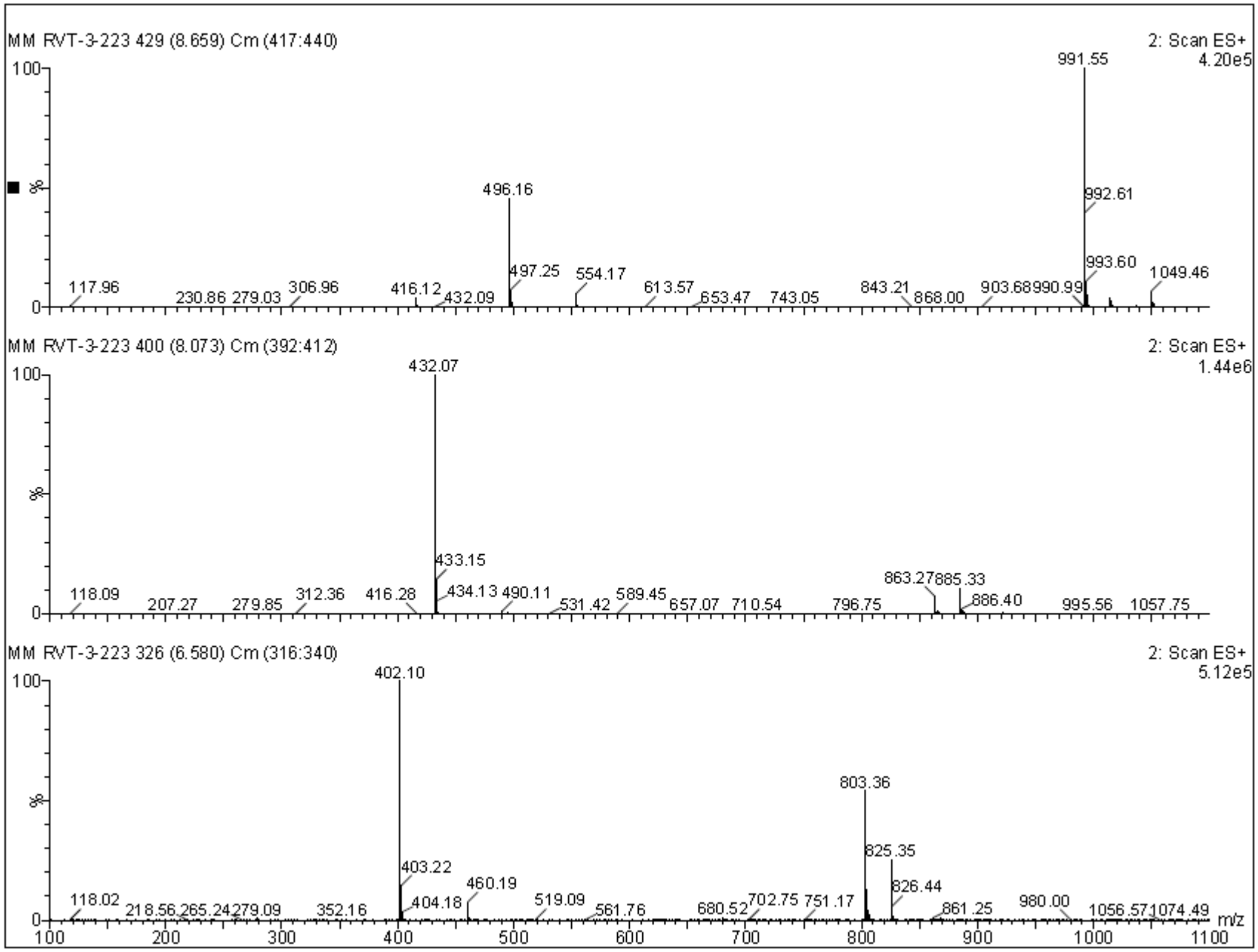


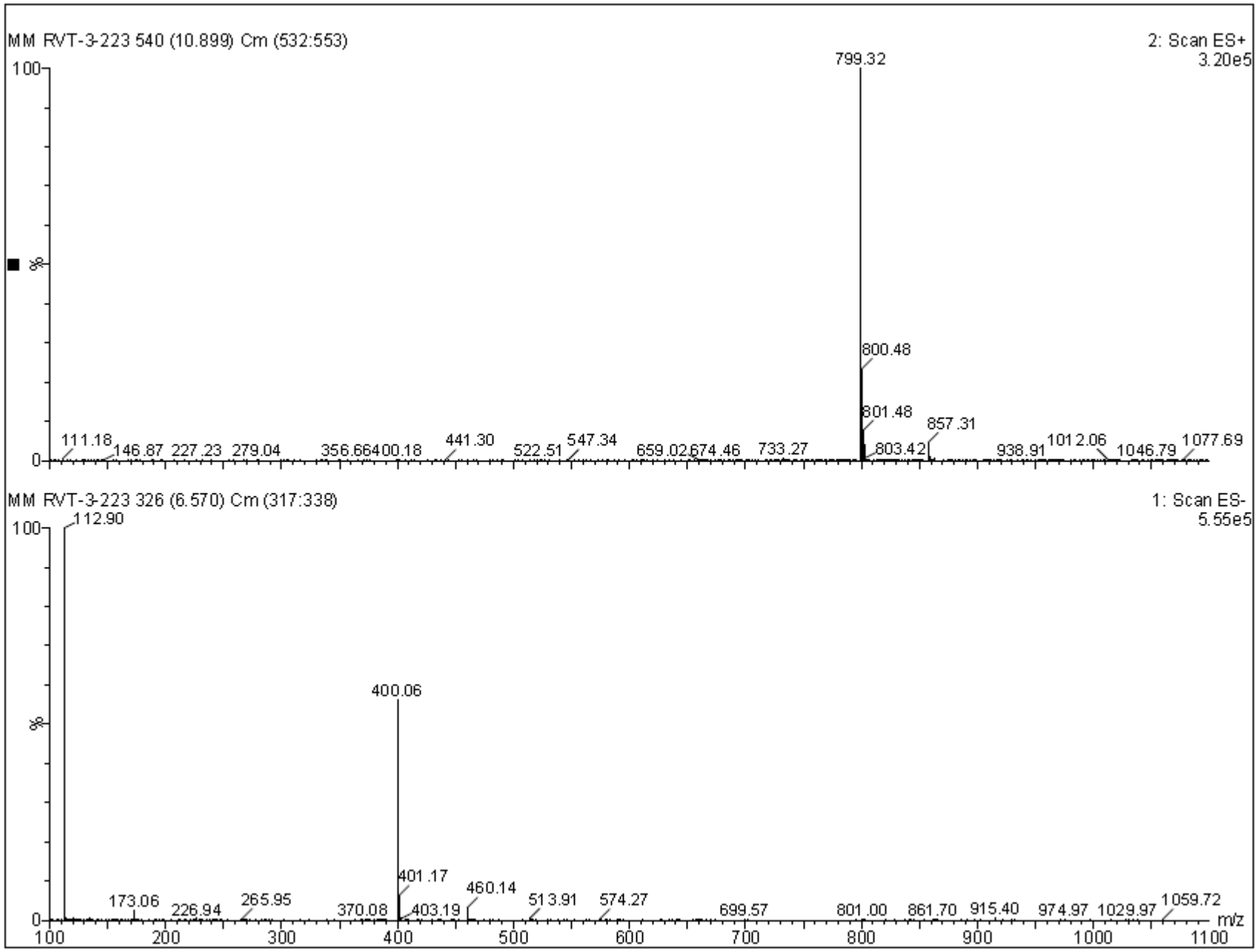
Reaction of **3** with glutathione (GSH) under apparent pH 10-11 in the presence of 1,3-cyclohexadiene. The LC/MS is shown on the next page.



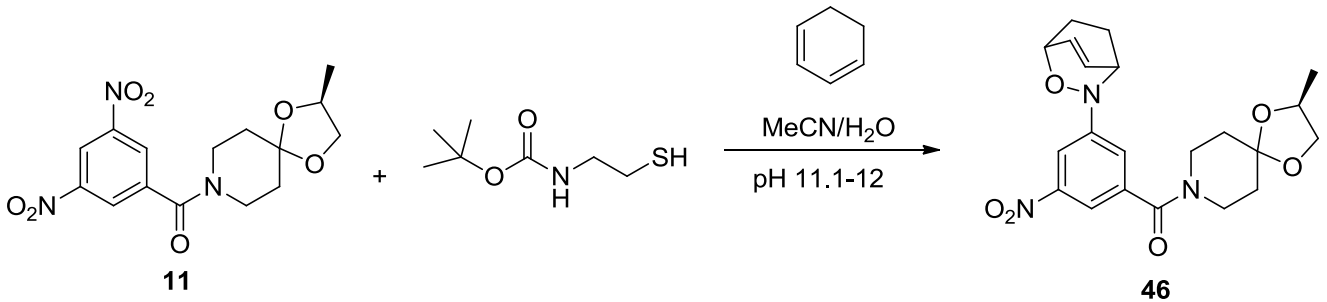
LC/MS


MM RVT-3-223
3: Diode Array
Range: 7.286e+1
AU
6.0e+1
4.0e+1
2.0e+1
0.0
7.45
7.57
8.05
6.55
7.07
0.65
4.33
10.88
2.00
4.00
6.00
8.00
10.00
12.00
14.00
MM RVT-3-223
2: Scan ES+
TIC
7.18e6
%
100
0
8.07
6.58
6.66
8.66
8.76
10.90
10.43
4.34
MM RVT-3-223
1: Scan ES-
TIC
2.97e6
%
7
7.07
6.57
4.35
4.61
5.14
6.49
0.66
1.50
1.83
2.84
3.50
3.84
7.88
8.37
8.85
9.60
9.84
10.38
11.33
11.74
12.62
12.93
13.63
14.50
14.93
Time


MM RVT-3-223 429 (8.659) Cm (417:440)
2: Scan ES+
4.20e5
991.55
496.16
992.61
993.60
497.25
554.17
1049.46
117.96
230.86
279.03
306.96
416.12
432.09
613.57
653.47
743.05
843.21
868.00
903.68
990.99
MM RVT-3-223 400 (8.073) Cm (392:412)
2: Scan ES+
1.44e6
432.07
433.15
863.27
885.33
886.40
118.09
207.27
279.85
312.36
416.28
434.13
490.11
531.42
589.45
657.07
710.54
796.75
995.56
1057.75
MM RVT-3-223 326 (6.580) Cm (316:340)
2: Scan ES+
5.12e5
402.10
803.36
825.35
403.22
826.44
460.19
118.02
218.56
265.24
279.09
352.16
404.18
519.09
561.76
680.52
702.75
751.17
861.25
980.00
1056.57
1074.49
%
m/z
100
200
300
400
500
600
700
800
900
1000
1100

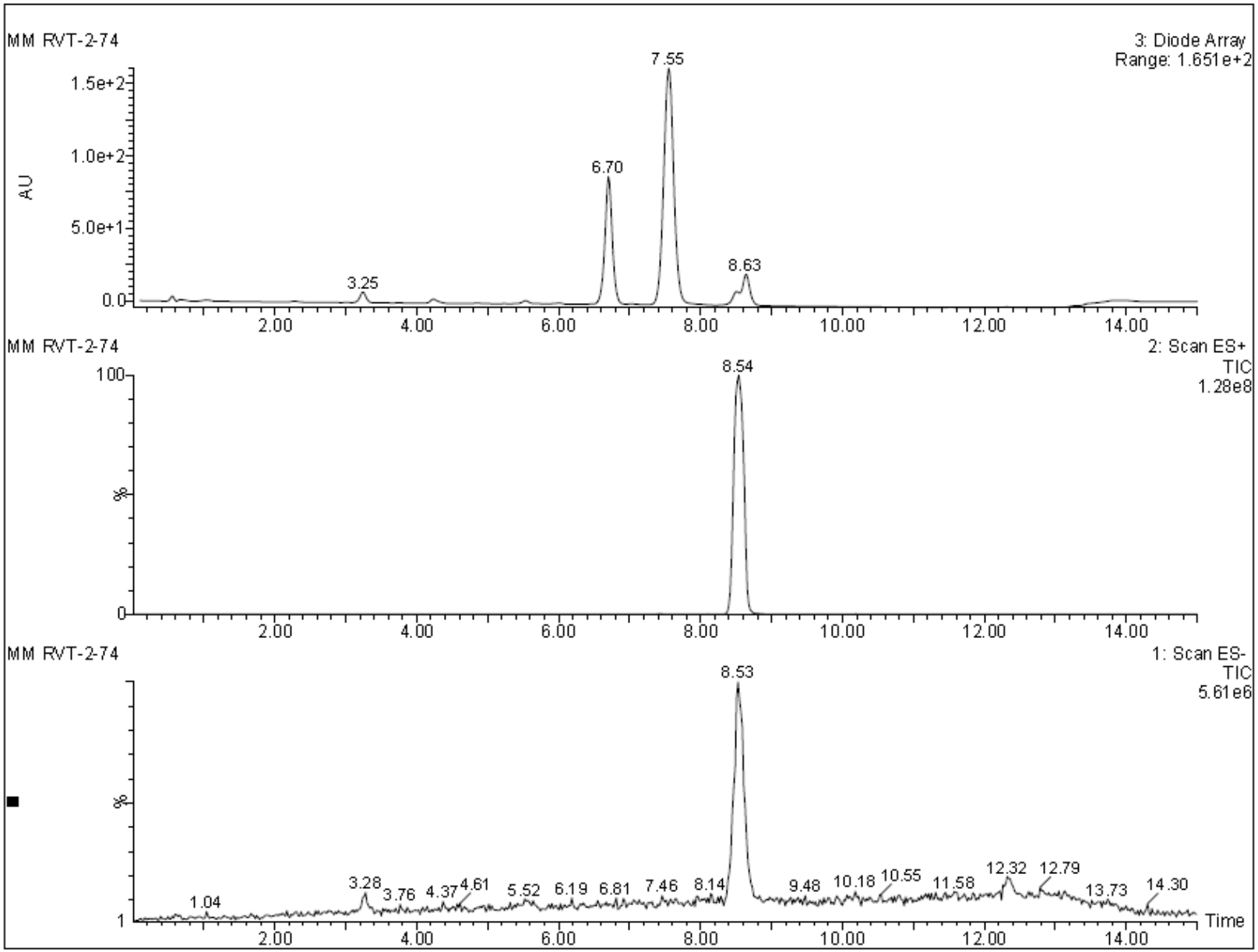

MM RVT-3-223 540 (10.899) Cm (532:553)
2: Scan ES+
3.20e5
100
%
0
799.32
800.48
801.48
857.31
111.18
146.87
227.23
279.04
356.66
400.18
441.30
522.51
547.34
659.02
674.46
733.27
803.42
938.91
1012.06
1046.79
1077.69
MM RVT-3-223 326 (6.570) Cm (317:338)
1: Scan ES-
5.55e5
100
%
0
112.90
400.06
401.17
173.06
226.94
265.95
370.08
403.19
460.14
513.91
574.27
699.57
801.00
861.70
915.40
974.97
1029.97
1059.72
m/z
100
200
300
400
500
600
700
800
900
1000
1100

Trapping of the in situ generated nitroso intermediate of **11** by Boc-cysteamine under basic conditions using 1,3-Cyclohexadiene to afford **46**.

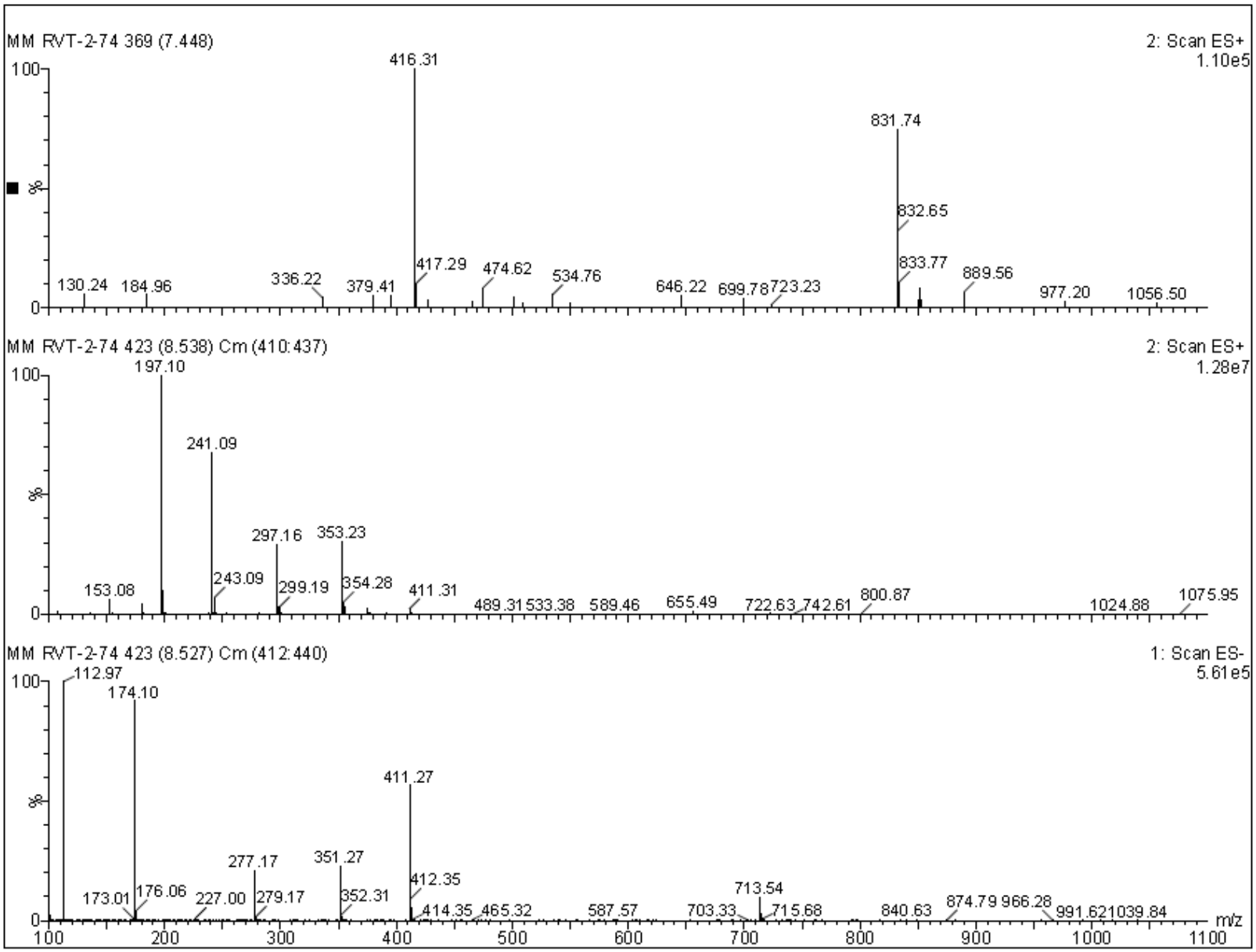


Exact Mass: 415.17434
Molecular Weight: 415.43970

LC/MS

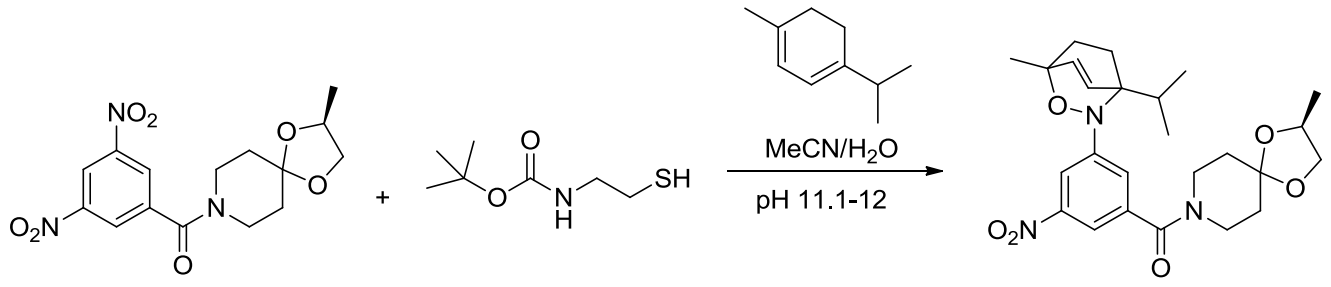

MM RVT-2-74
3: Diode Array
Range: 1.651e+2
AU
1.5e+2
1.0e+2
5.0e+1
0.0
3.25
6.70
7.55
8.63
2.00
4.00
6.00
8.00
10.00
12.00
14.00
MM RVT-2-74
2: Scan ES+
TIC
1.28e8
%
100
0
8.54
MM RVT-2-74
1: Scan ES-
TIC
5.61e6
%
1
8.53
1.04
3.28
3.76
4.37
4.61
5.52
6.19
6.81
7.46
8.14
9.48
10.18
10.55
11.58
12.32
12.79
13.73
14.30
Time

Mass spectra in the positive and the negative ionization mode



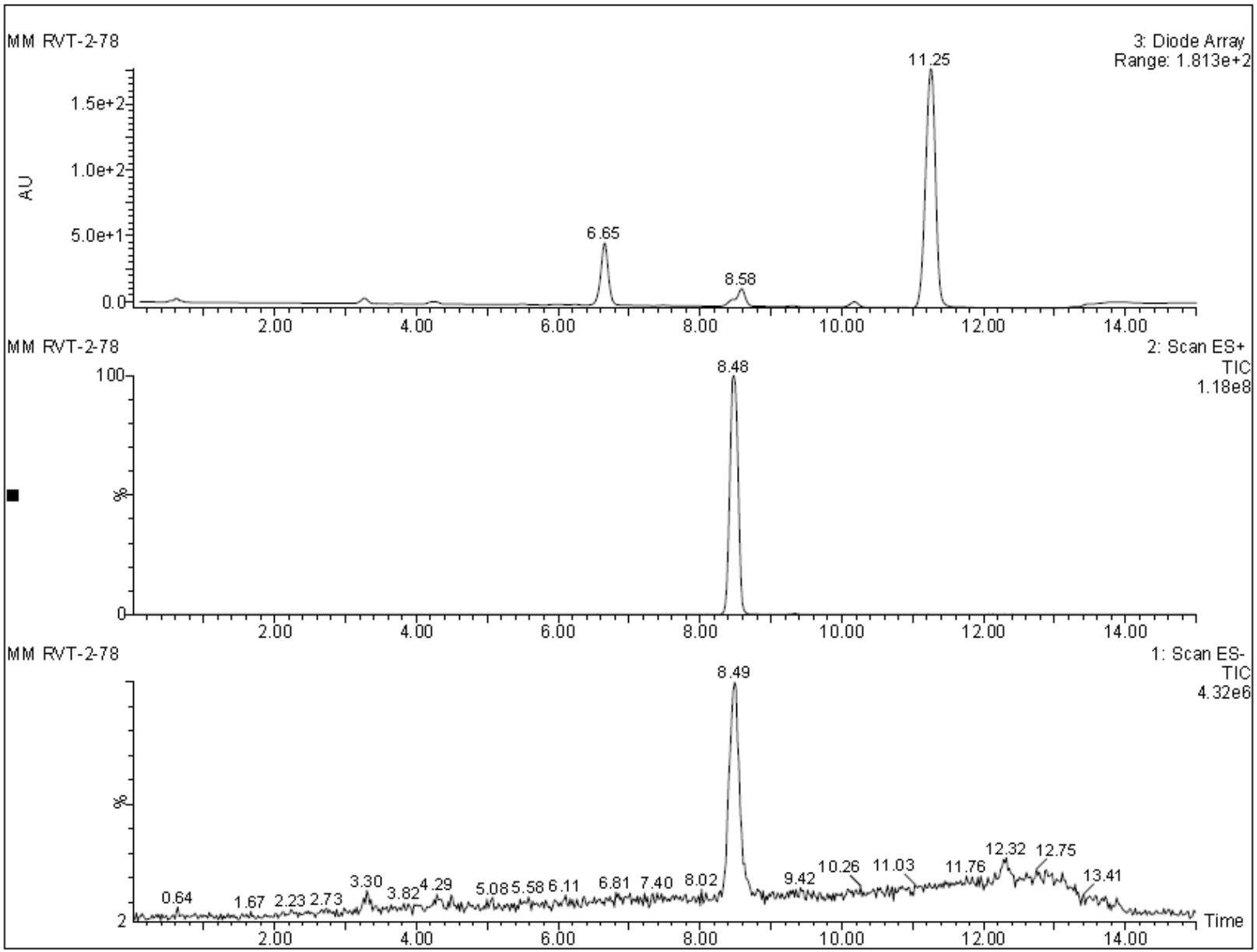
Trapping of the in situ generated nitroso intermediate of **11** by Boc-cysteamine under basic conditions using α-terpinene to obtain **40**.

as a mixture of regioisomers.

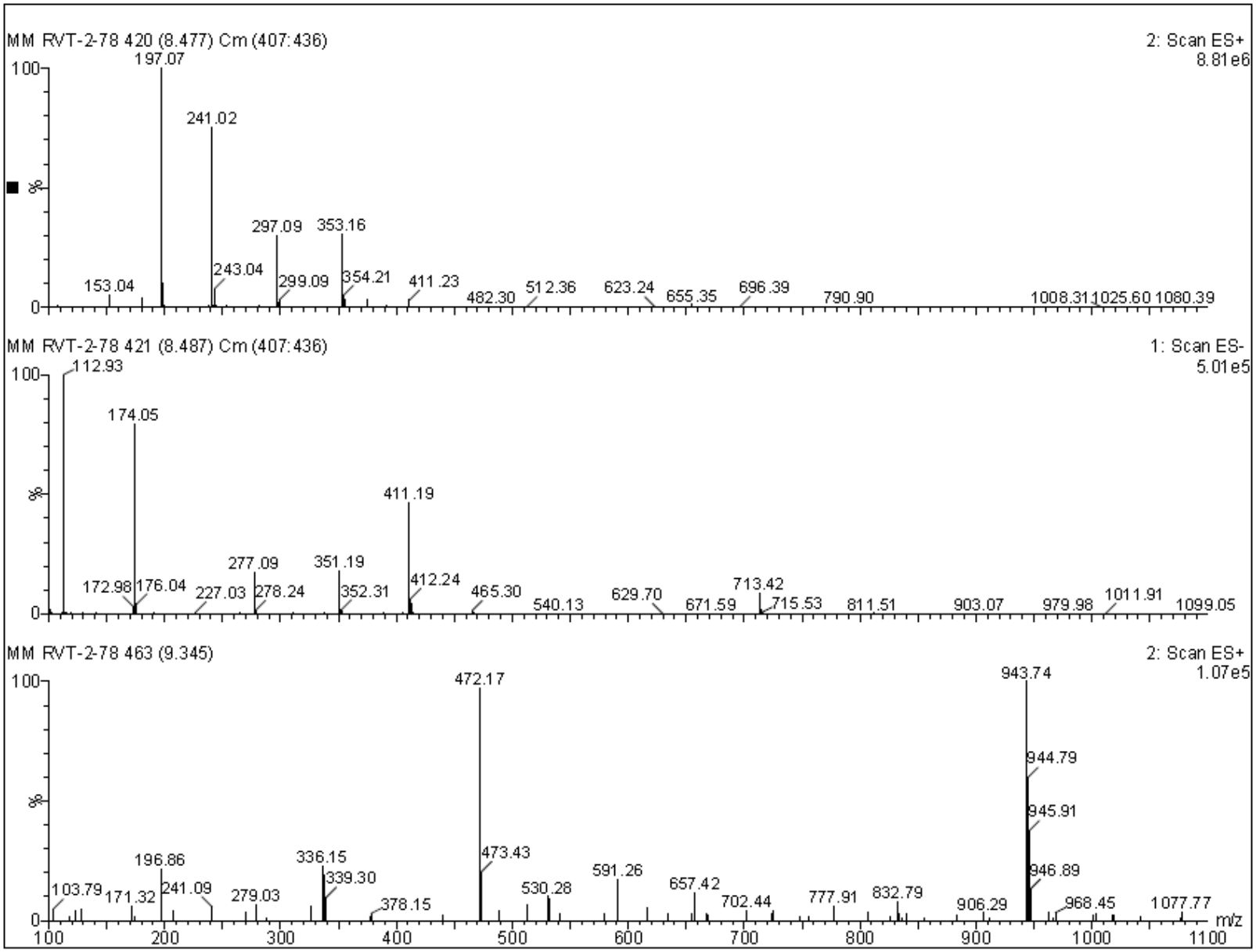


MW= 471.54602

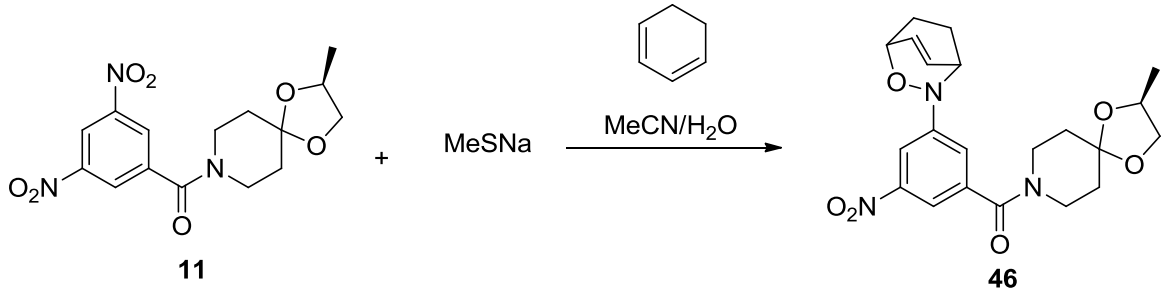
LC/MS


MM RVT-2-78
3: Diode Array
Range: 1.813e+2
AU
1.5e+2
1.0e+2
5.0e+1
0.0
11.25
6.65
8.58
2.00
4.00
6.00
8.00
10.00
12.00
14.00
MM RVT-2-78
2: Scan ES+
TIC
1.18e8
100
%
0
8.48
MM RVT-2-78
1: Scan ES-
TIC
4.32e6
%
2
8.49
0.64
1.67
2.23
2.73
3.30
3.82
4.29
5.08
5.58
6.11
6.81
7.40
8.02
9.42
10.26
11.03
11.76
12.32
12.75
13.41
Time

Mass spectra in the positive and the negative ionization mode

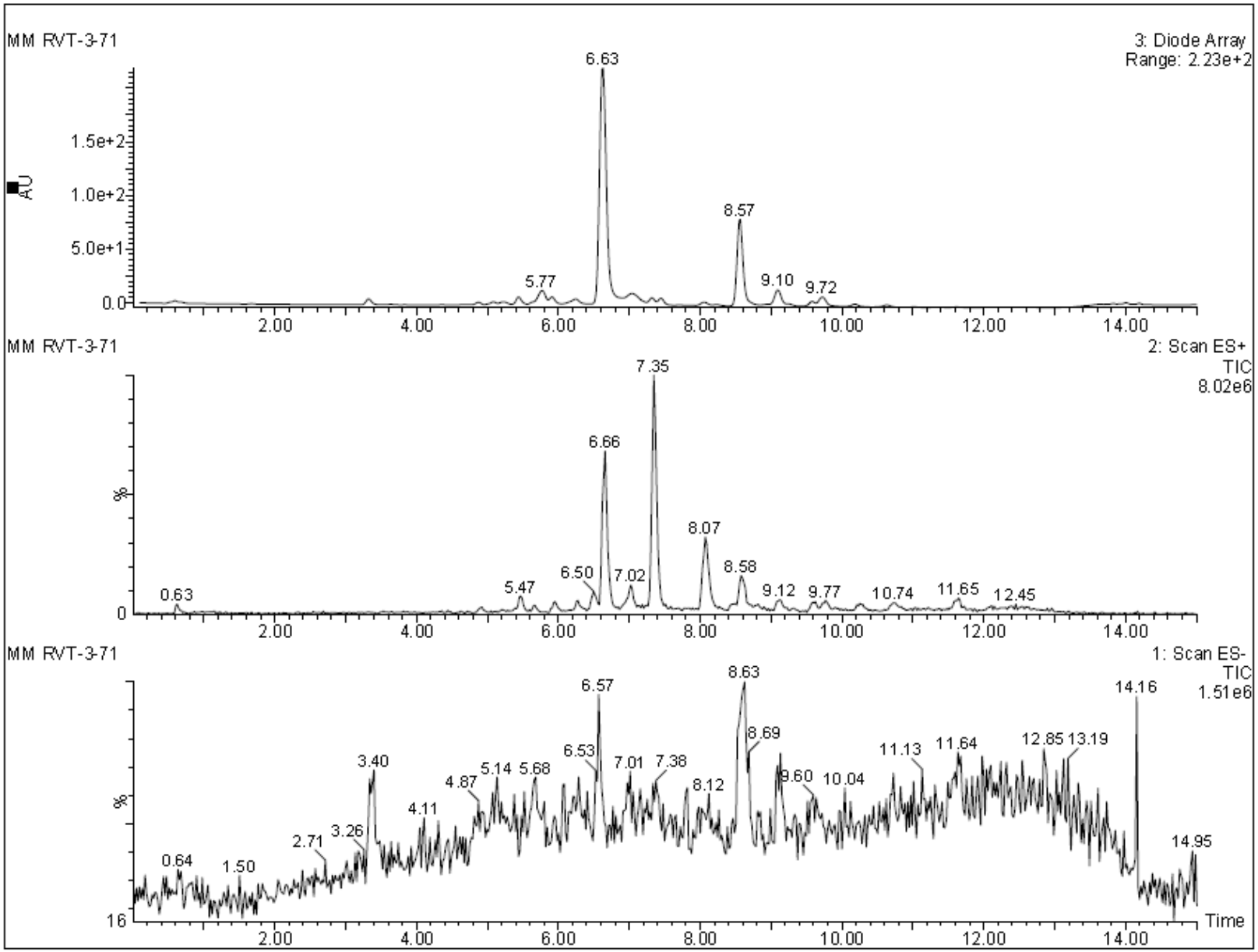


Trapping of the in situ generated nitroso intermediate of **11** by Sodium methane thiolate in a mixture of acetonitrile and water using 1,3-Cyclohexadiene to afford **46**.

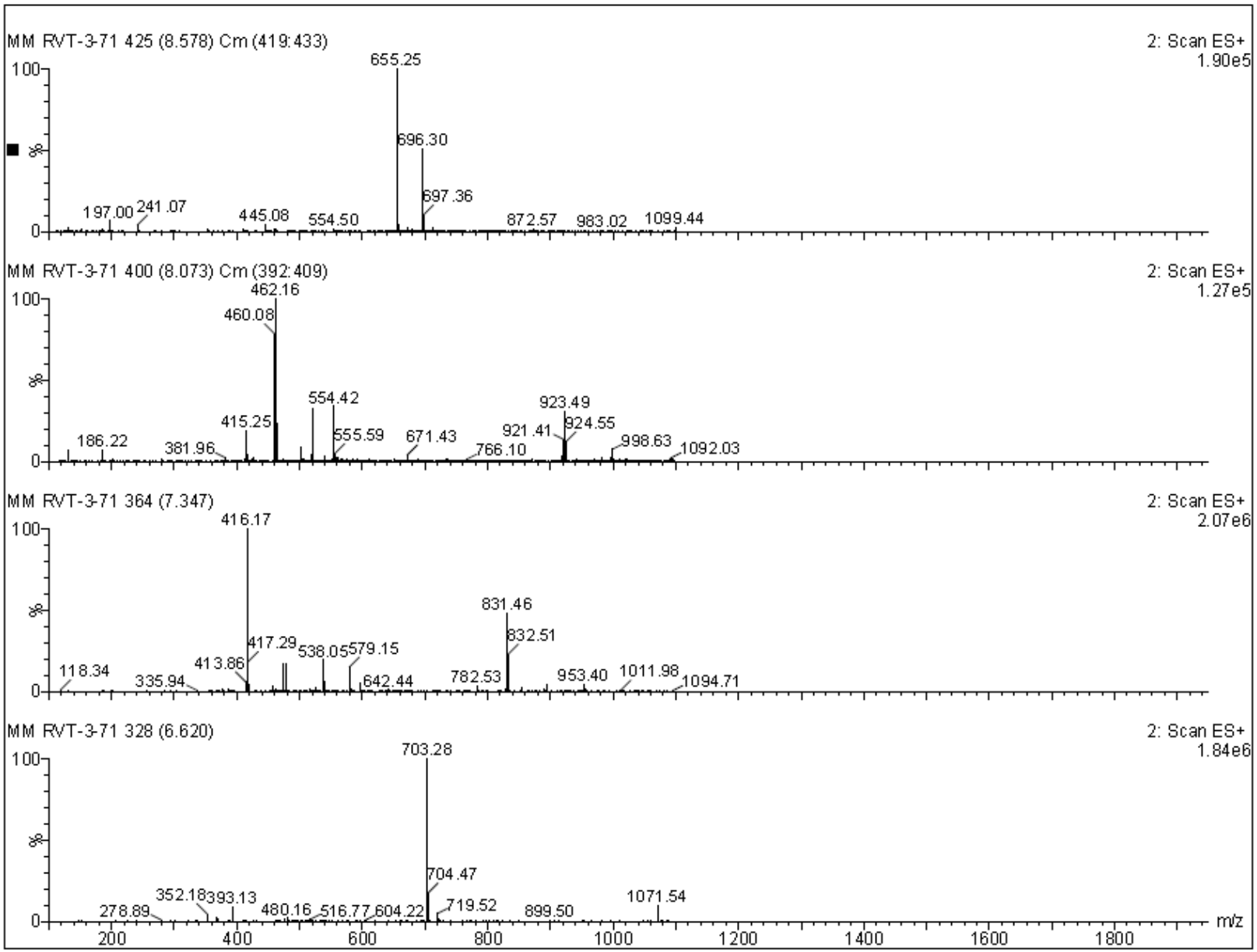


Exact Mass: 415.17434
Molecular Weight: 415.43970

LC/MS

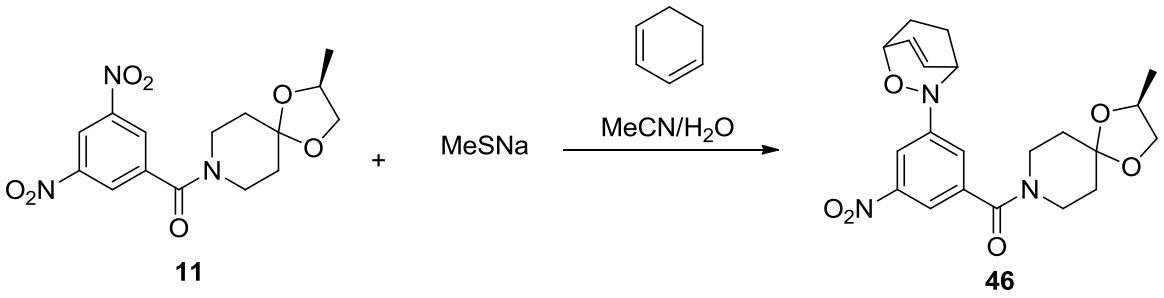

MM RVT-3-71
3: Diode Array
Range: 2.23e+2
AU
1.5e+2
1.0e+2
5.0e+1
0.0
6.63
8.57
5.77
9.10
9.72
2.00
4.00
6.00
8.00
10.00
12.00
14.00
MM RVT-3-71
2: Scan ES+
TIC
8.02e6
%
0
7.35
6.66
8.07
8.58
6.50
7.02
5.47
0.63
9.12
9.77
10.74
11.65
12.45
MM RVT-3-71
1: Scan ES-
TIC
1.51e6
%
16
8.63
6.57
14.16
8.69
3.40
6.53
7.01
7.38
5.14
5.68
4.87
11.13
11.64
12.85
13.19
4.11
8.12
9.60
10.04
3.26
2.71
14.95
0.64
1.50
Time

Mass spectra in the positive and the negative ionization mode



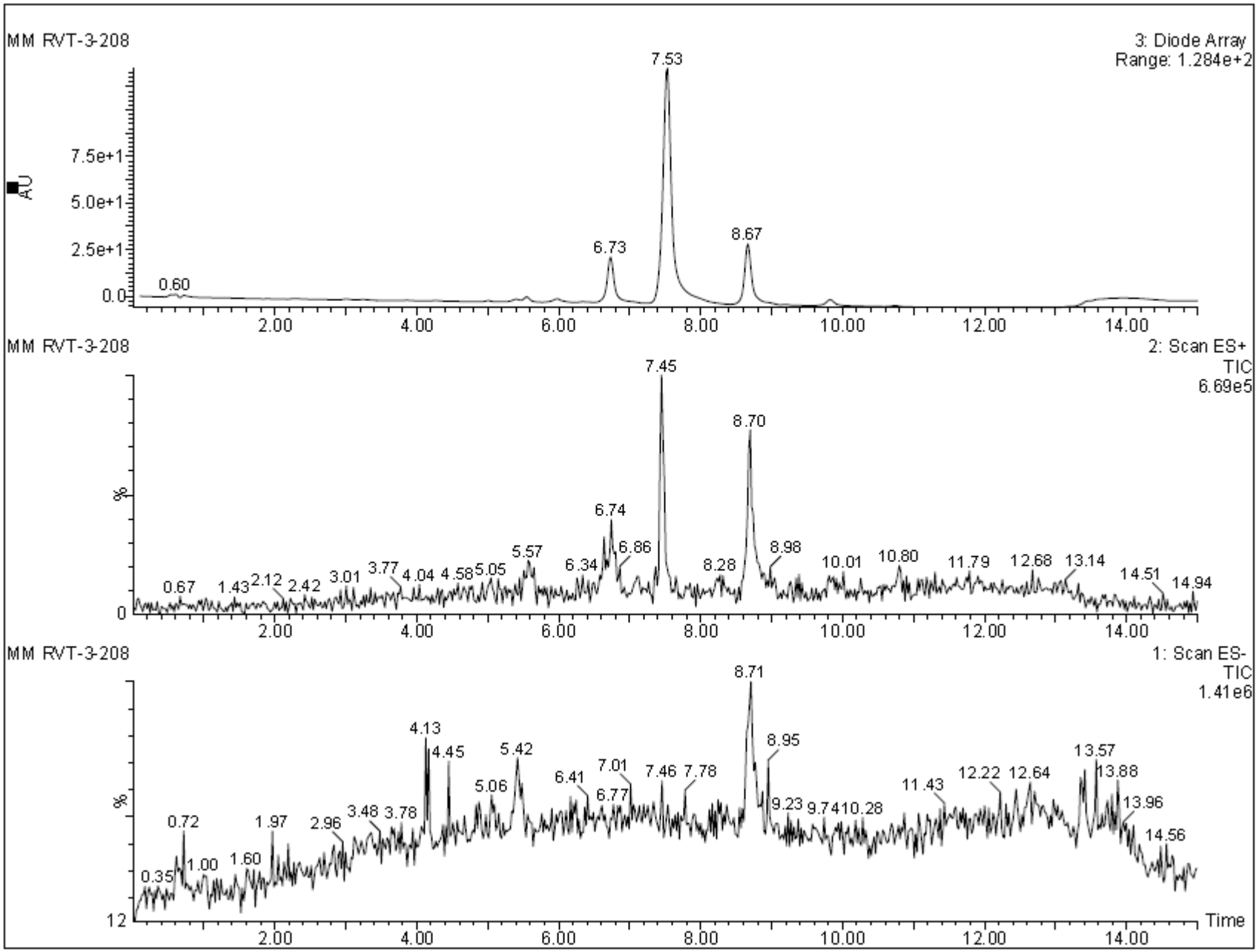
Trapping of the in situ generated nitroso intermediate of **11** by Sodium methane thiolate in a deoxygenated mixture of acetonitrile and water using 1,3-Cyclohexadiene to afford **46**.

Acetonitrile and water mixture was purged with Argon prior to the addition of the starting material. To this solvent mixture was added **11**, followed by 1,3-cyclohexadiene and NaSMe under argon flow. The reaction mixture was then stirred at room temperature under argon.

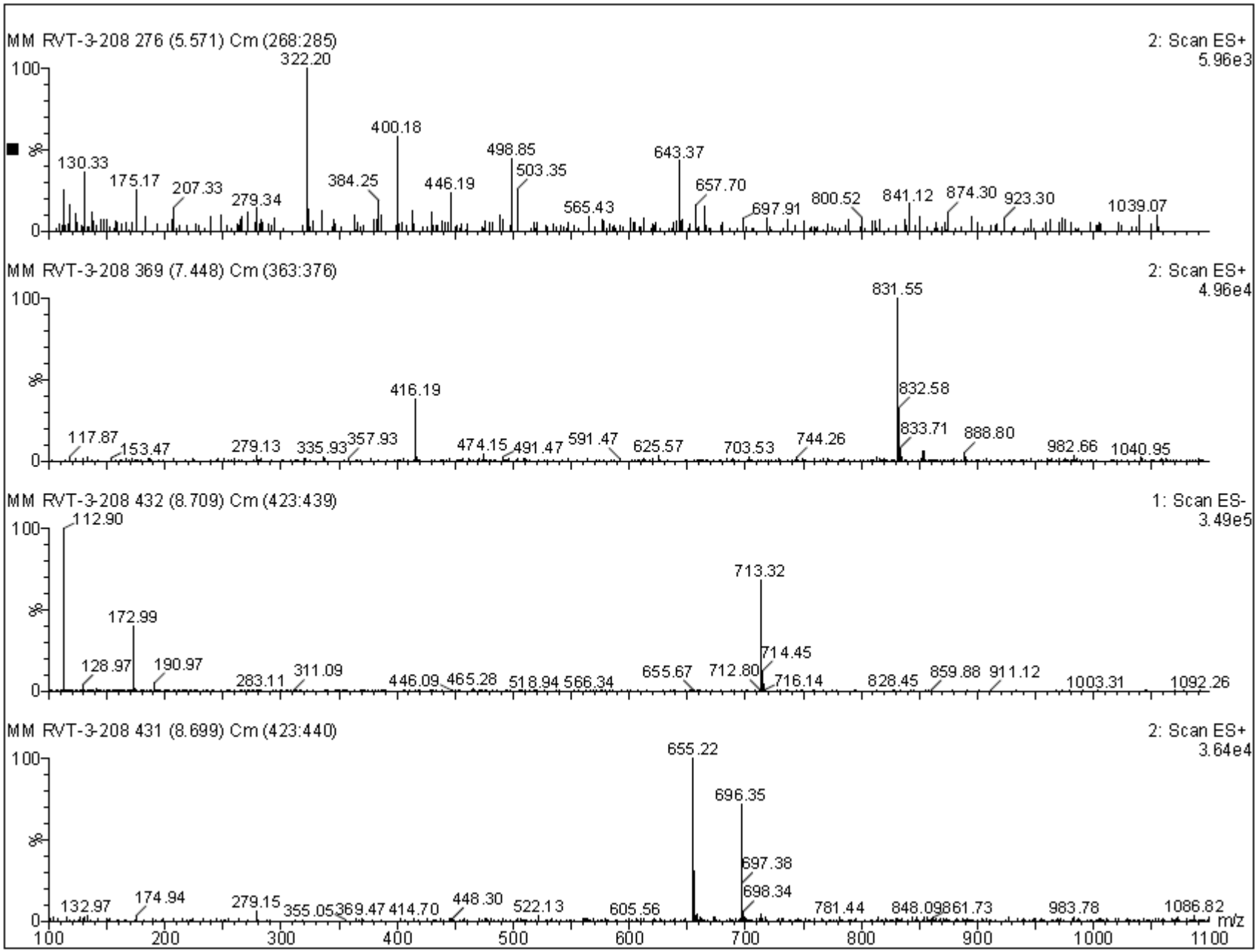


Exact Mass: 415.17434
Molecular Weight: 415.43970

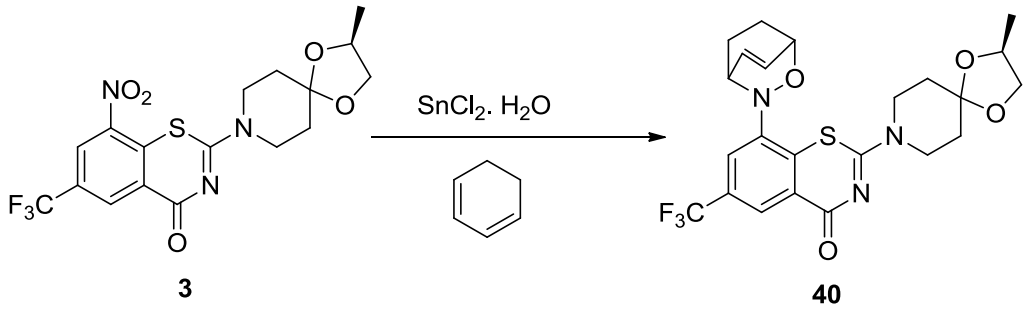
LC/MS


MM RVT-3-208
3: Diode Array
Range: 1.284e+2
AU
7.5e+1
5.0e+1
2.5e+1
0.0
0.60
6.73
7.53
8.67
2.00
4.00
6.00
8.00
10.00
12.00
14.00
MM RVT-3-208
2: Scan ES+
TIC
6.69e5
%
0
0.67
1.43
2.12
2.42
3.01
3.77
4.04
4.58
5.05
5.57
6.34
6.74
6.86
7.45
8.28
8.70
8.98
10.01
10.80
11.79
12.68
13.14
14.51
14.94
MM RVT-3-208
1: Scan ES-
TIC
1.41e6
%
12
0.35
0.72
1.00
1.60
1.97
2.96
3.48
3.78
4.13
4.45
5.06
5.42
6.41
6.77
7.01
7.46
7.78
8.71
8.95
9.23
9.74
10.28
11.43
12.22
12.64
13.57
13.88
13.96
14.56
Time

Mass spectra in the positive and the negative ionization mode



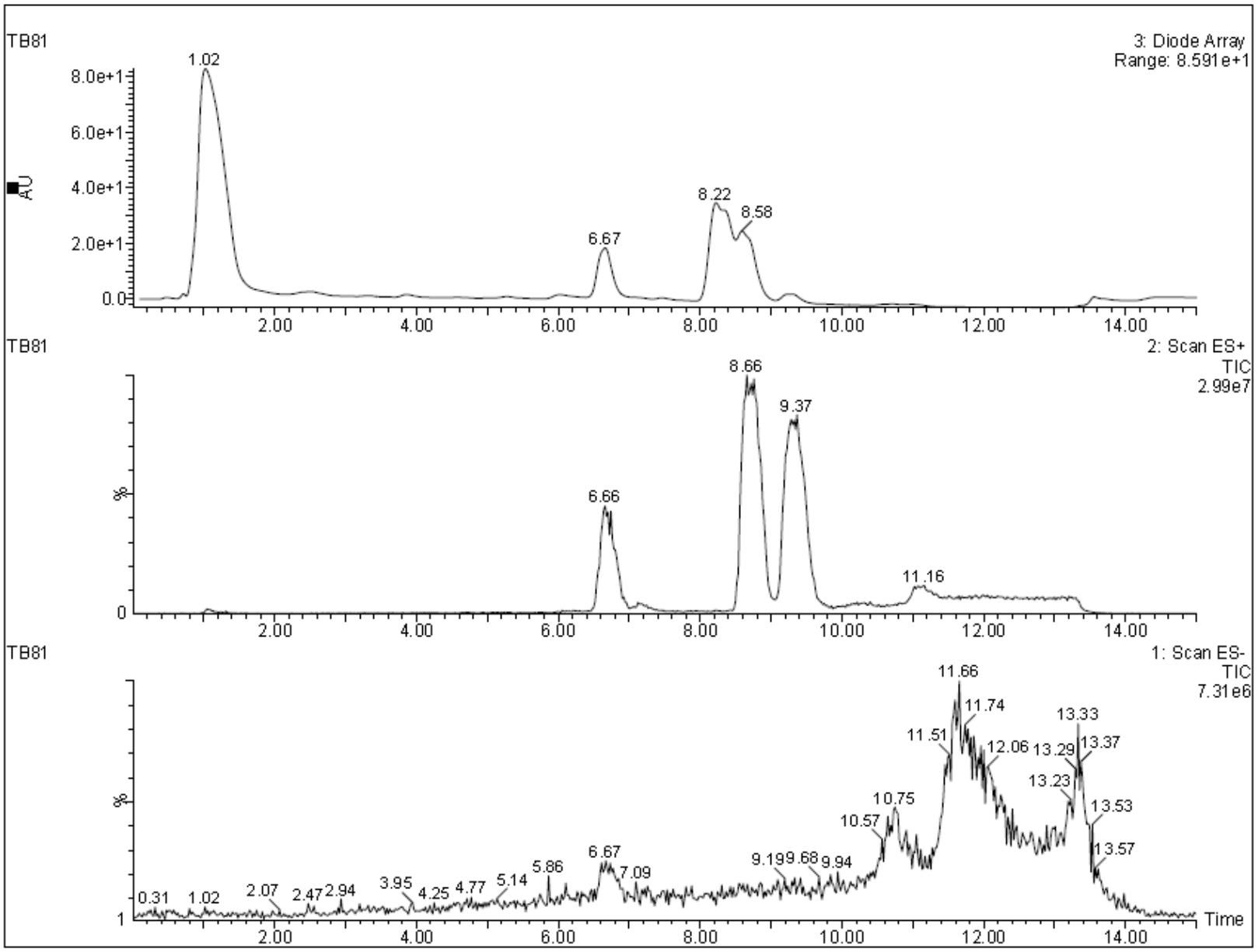
The nitroso trapping experiment of **3** by employing stannous chloride and 1,3-cyclohexadiene to afford **40**.



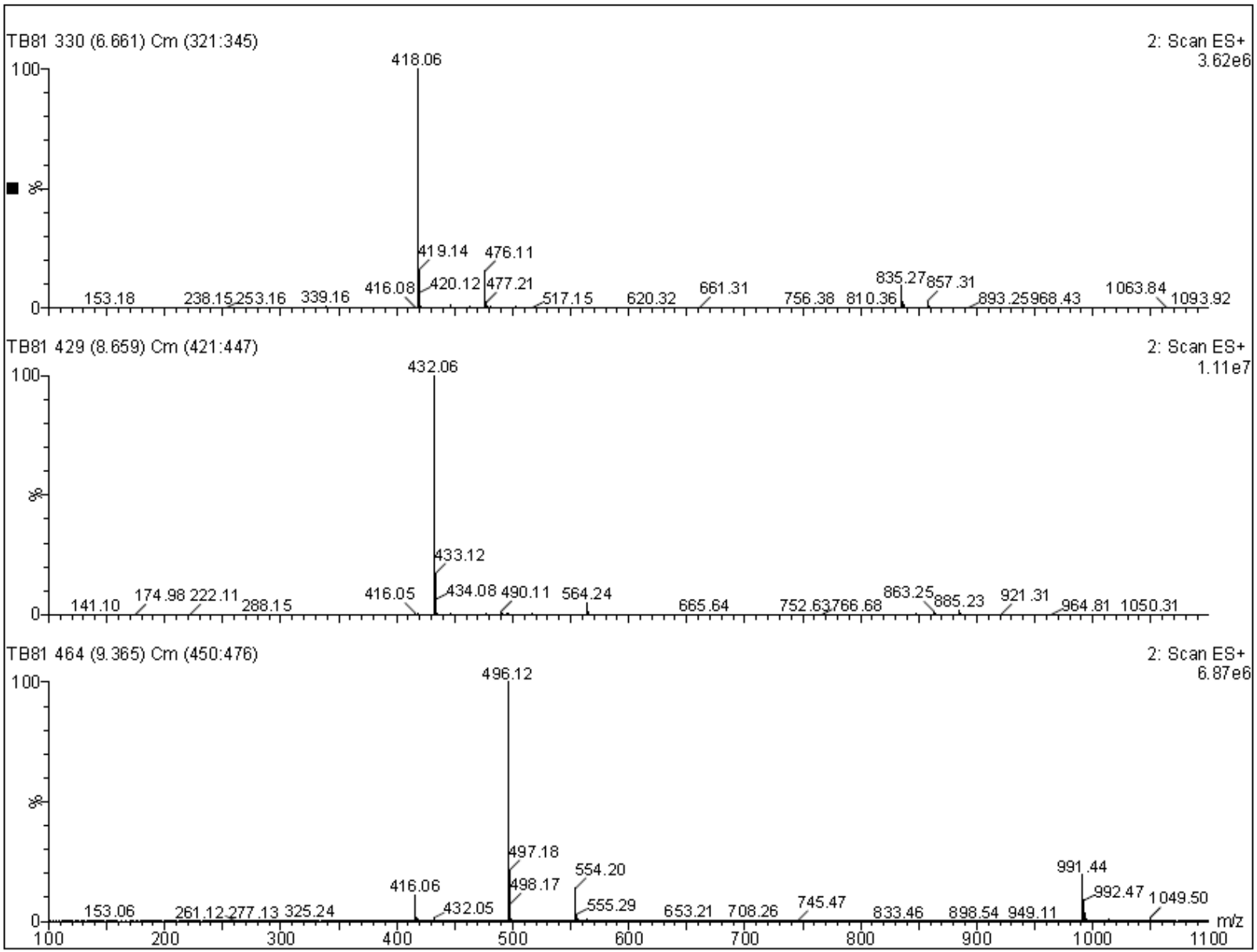
3 **40**

Chemical Formula: $C_{23}H_{24}F_3N_3O_4S$
Exact Mass: 495.1440
Molecular Weight: 495.5146

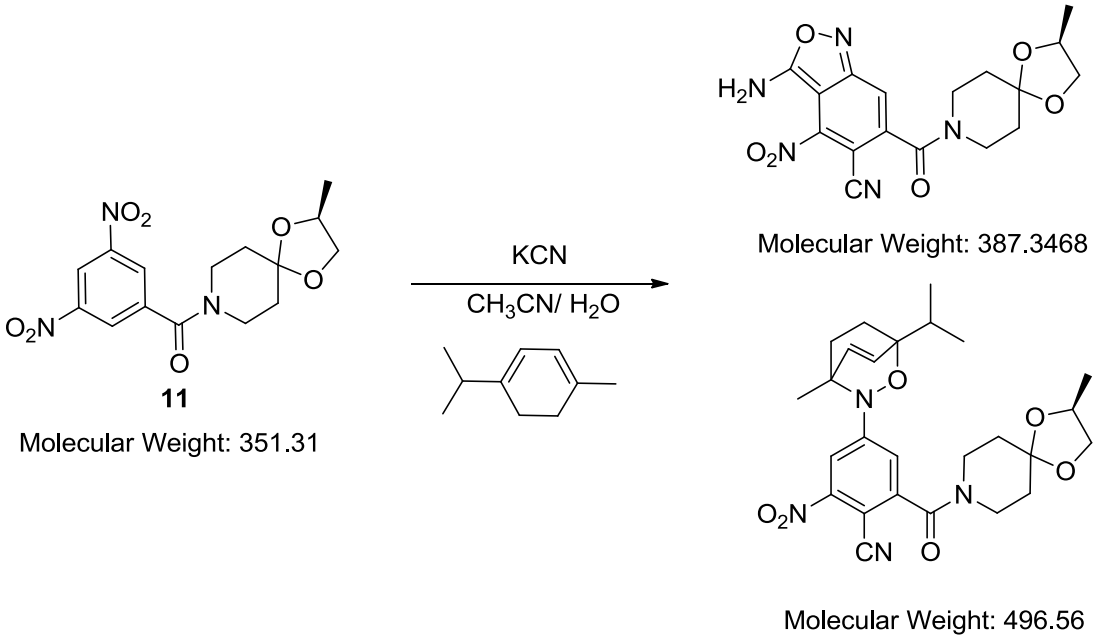
LC/MS


TB81
3: Diode Array
Range: 8.591e+1
AU
1.02
6.67
8.22
8.58
TB81
2: Scan ES+
TIC
2.99e7
%
8.66
9.37
6.66
11.16
TB81
1: Scan ES-
TIC
7.31e6
%
11.66
11.74
11.51
12.06
13.33
13.37
13.29
13.23
13.53
13.57
10.75
10.57
6.67
7.09
9.19
9.68
9.94
5.86
0.31
1.02
2.07
2.47
2.94
3.95
4.25
4.77
5.14
Time

Mass spectra in the positive ionization mode

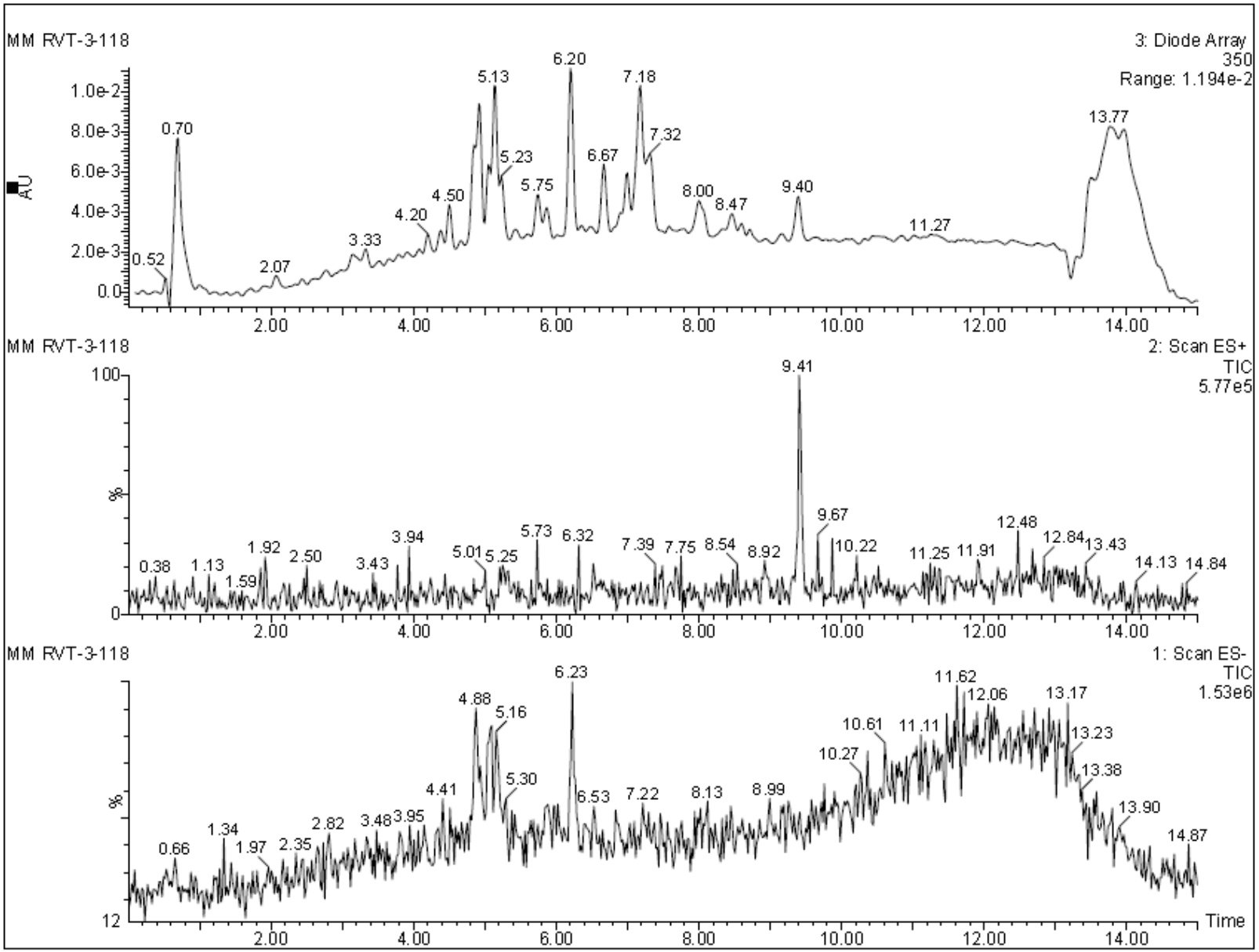


Reaction of **11** with potassium cyanide in presence of terpinene at rt in CH_3CN/H_2O.

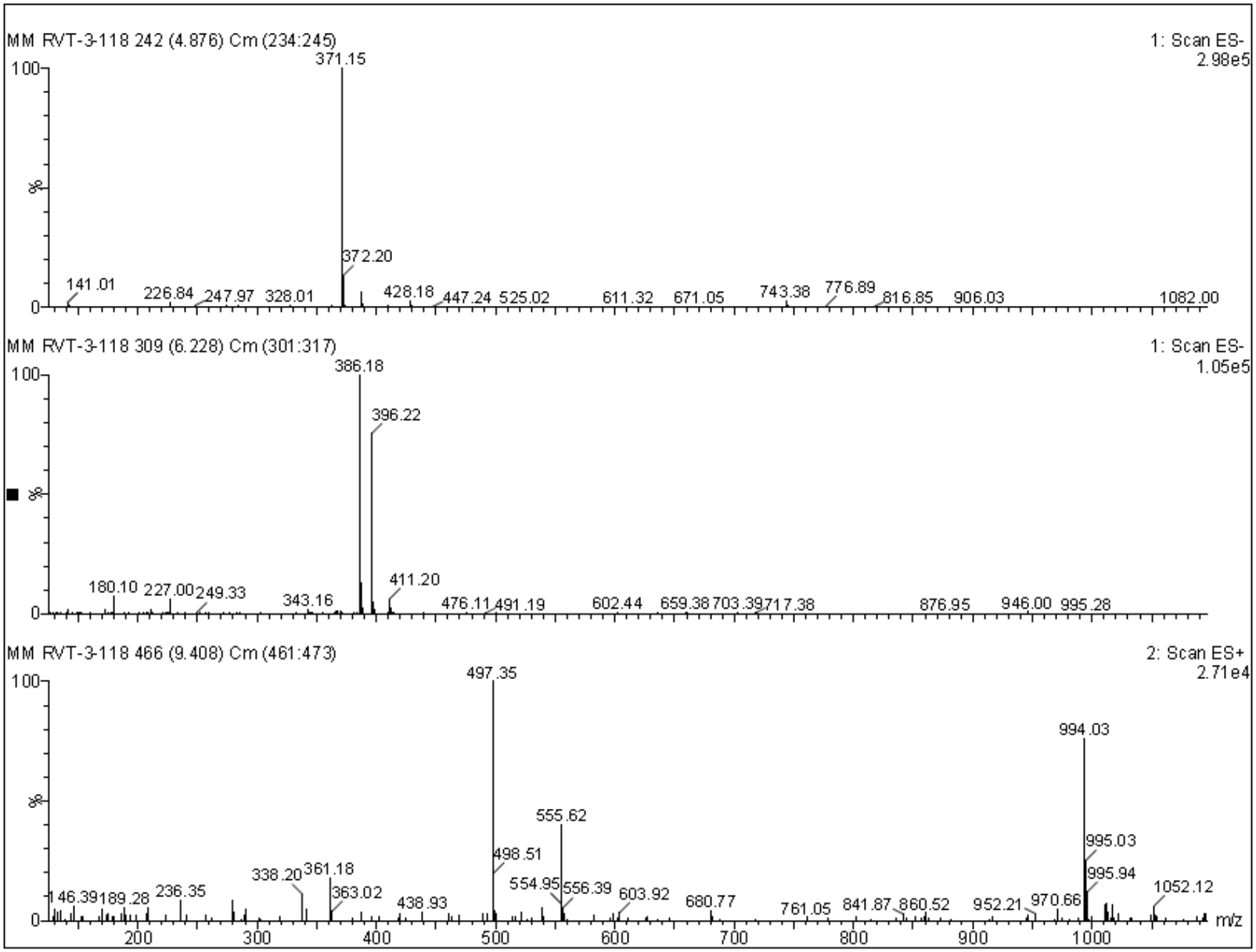


Molecular Weight: 351.31

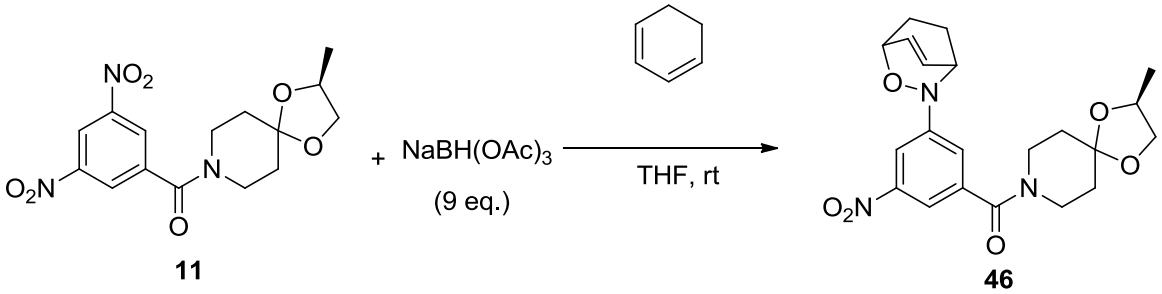
LC/MS


MM RVT-3-118
3: Diode Array
350
Range: 1.194e-2
AU
1.0e-2
8.0e-3
6.0e-3
4.0e-3
2.0e-3
0.0
0.52
0.70
2.07
3.33
4.20
4.50
5.13
5.23
5.75
6.20
6.67
7.18
7.32
8.00
8.47
9.40
11.27
13.77
2.00
4.00
6.00
8.00
10.00
12.00
14.00
MM RVT-3-118
2: Scan ES+
TIC
5.77e5
%
100
0
0.38
1.13
1.59
1.92
2.50
3.43
3.94
5.01
5.25
5.73
6.32
7.39
7.75
8.54
8.92
9.41
9.67
10.22
11.25
11.91
12.48
12.84
13.43
14.13
14.84
2.00
4.00
6.00
8.00
10.00
12.00
14.00
MM RVT-3-118
1: Scan ES-
TIC
1.53e6
%
12
0.66
1.34
1.97
2.35
2.82
3.48
3.95
4.41
4.88
5.16
5.30
6.23
6.53
7.22
8.13
8.99
10.27
10.61
11.11
11.62
12.06
13.17
13.23
13.38
13.90
14.87
Time
2.00
4.00
6.00
8.00
10.00
12.00
14.00

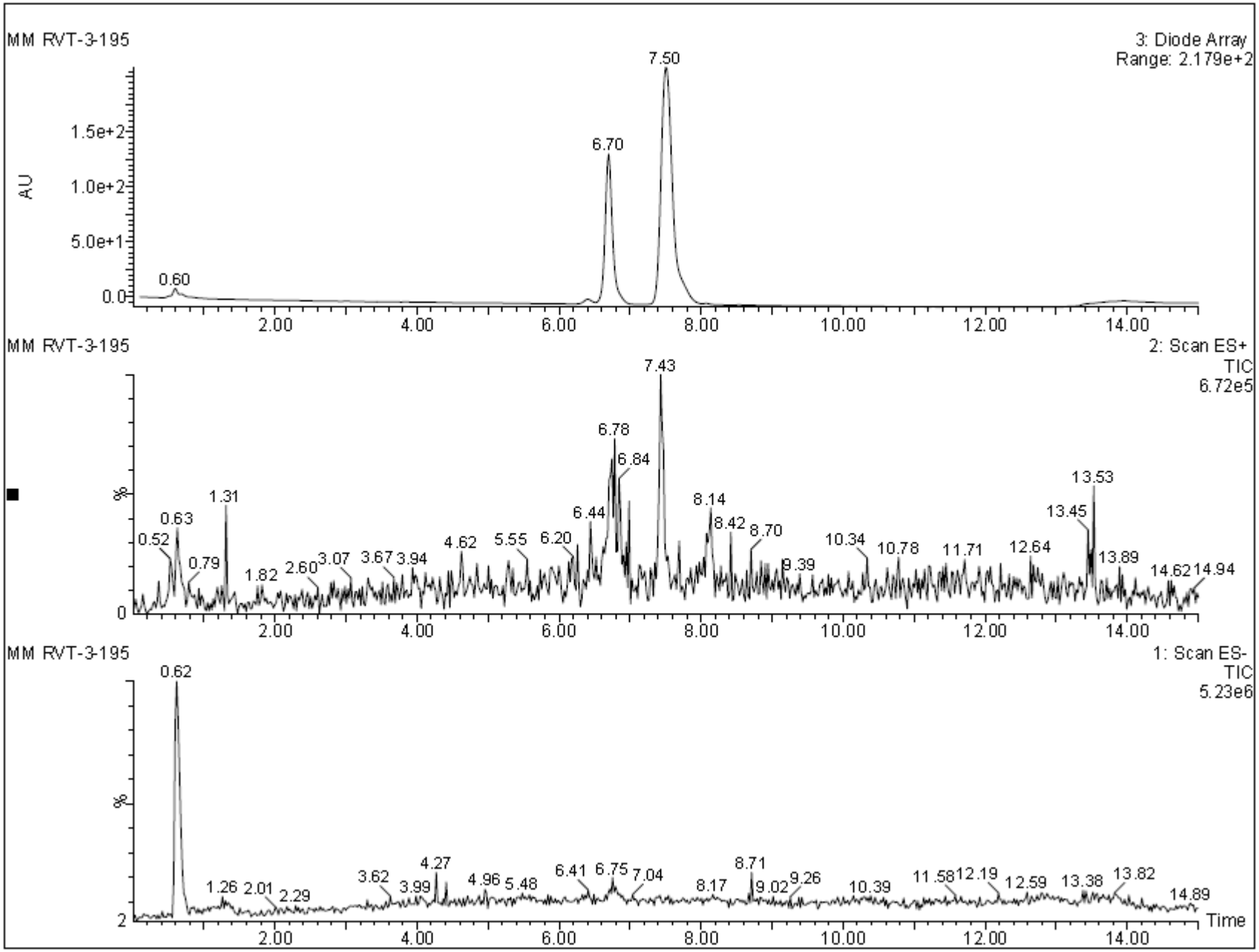
Mass spectra in the positive and the negative ionization mode

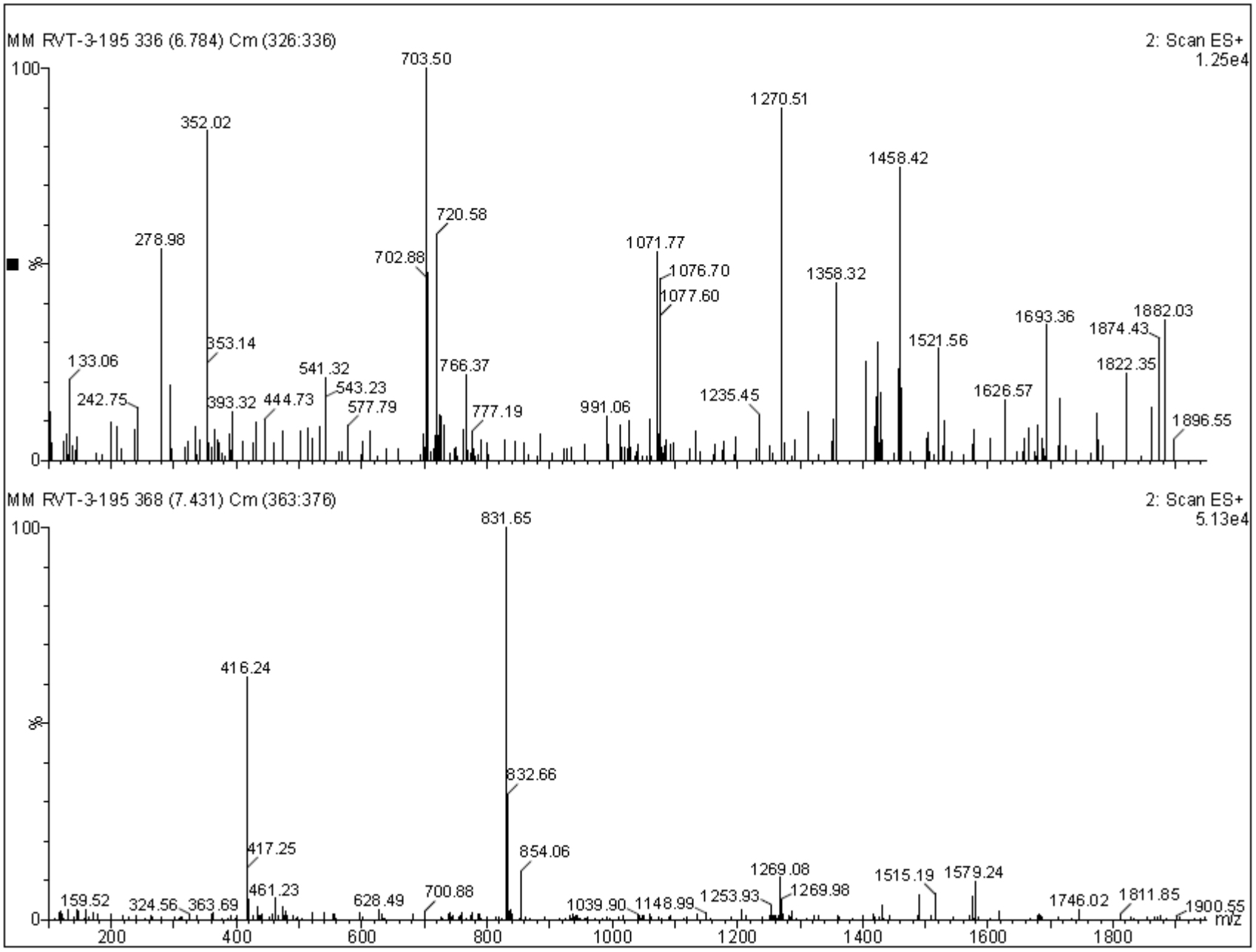


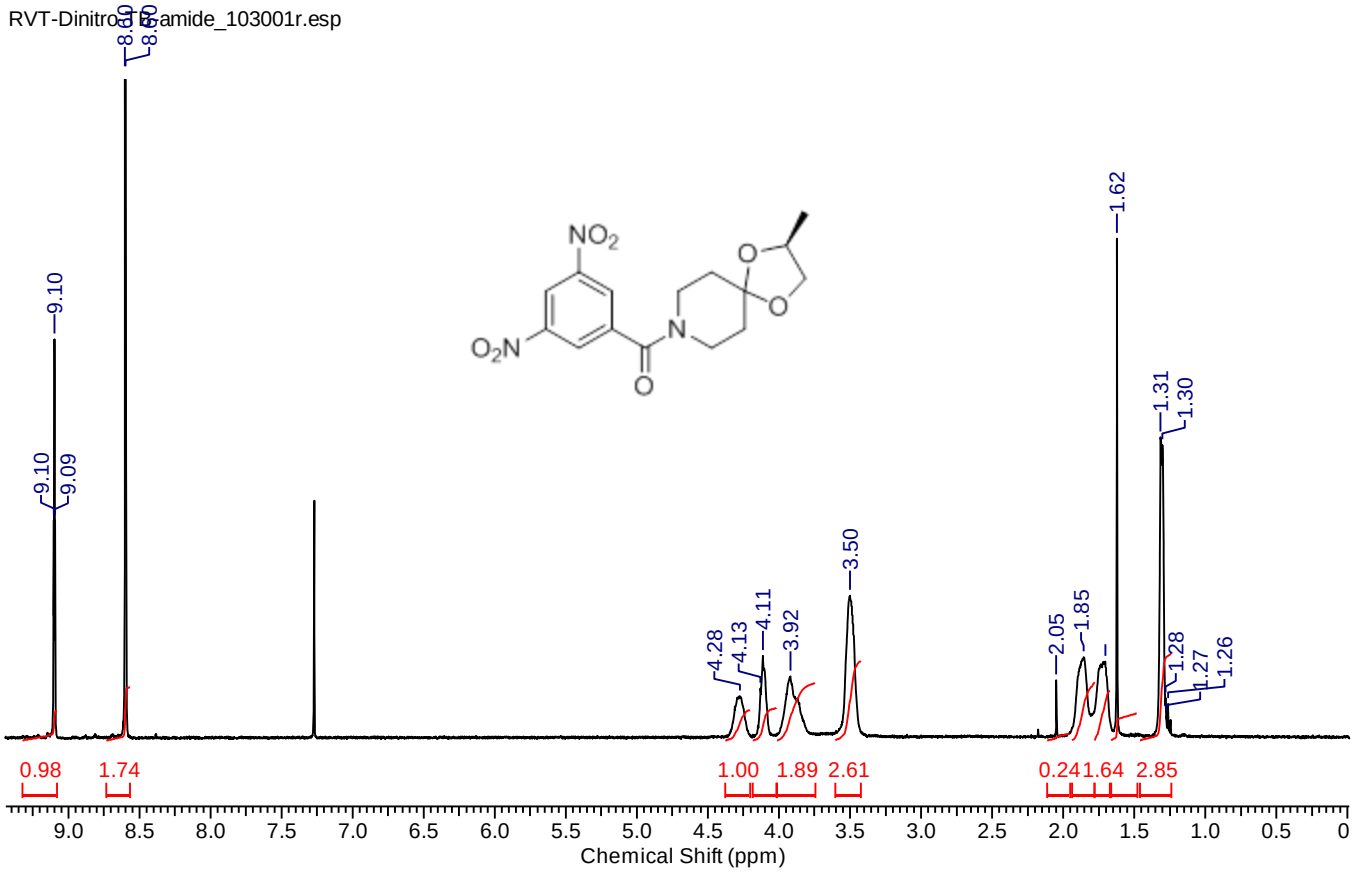
Trapping of the in situ generated nitroso intermediate of **11** by Sodium triacetoxy borohydride (Na $BH(OAc)_3$) in THF using 1,3-Cyclohexadiene to afford **46** under inert atmosphere

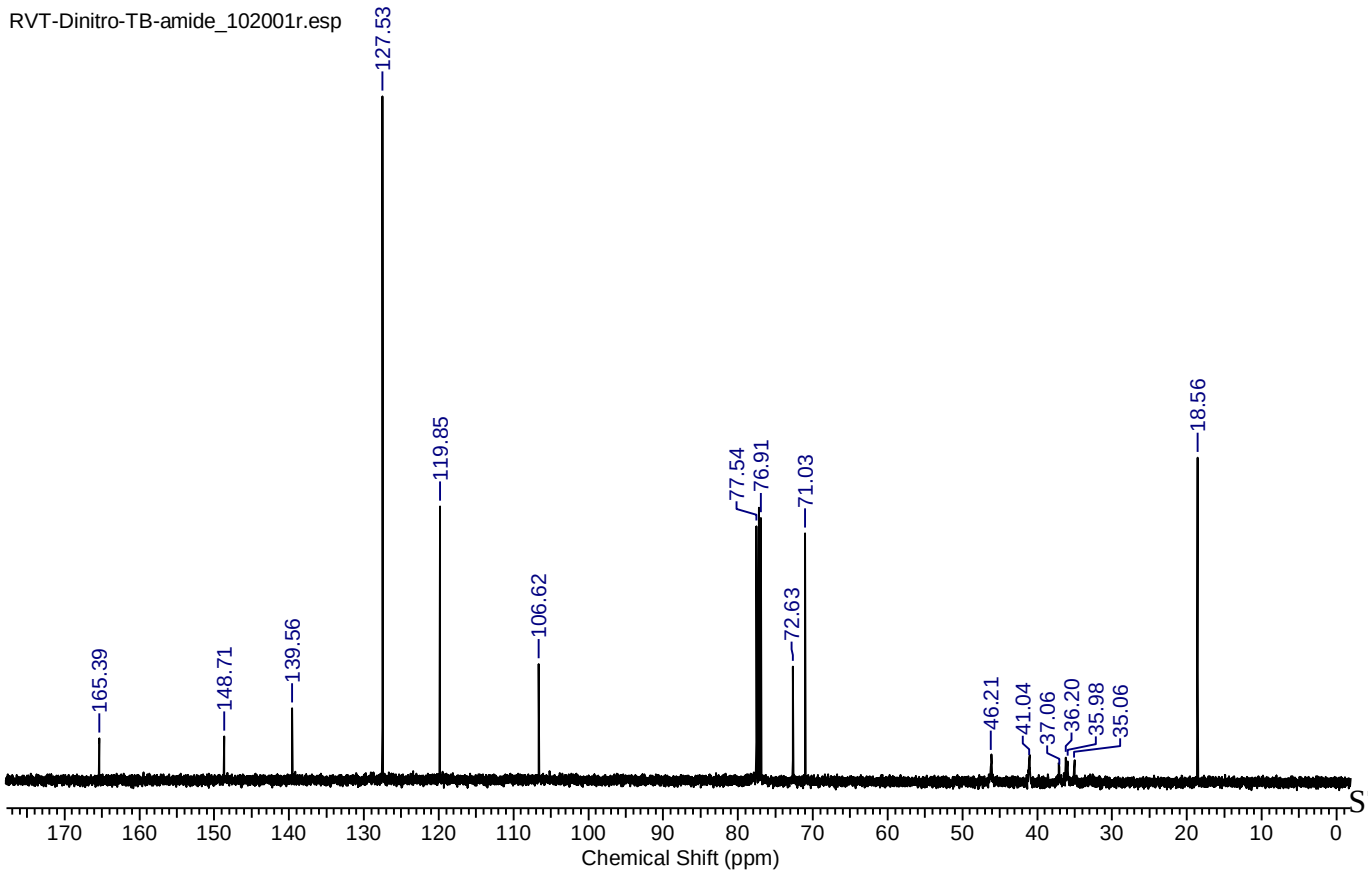


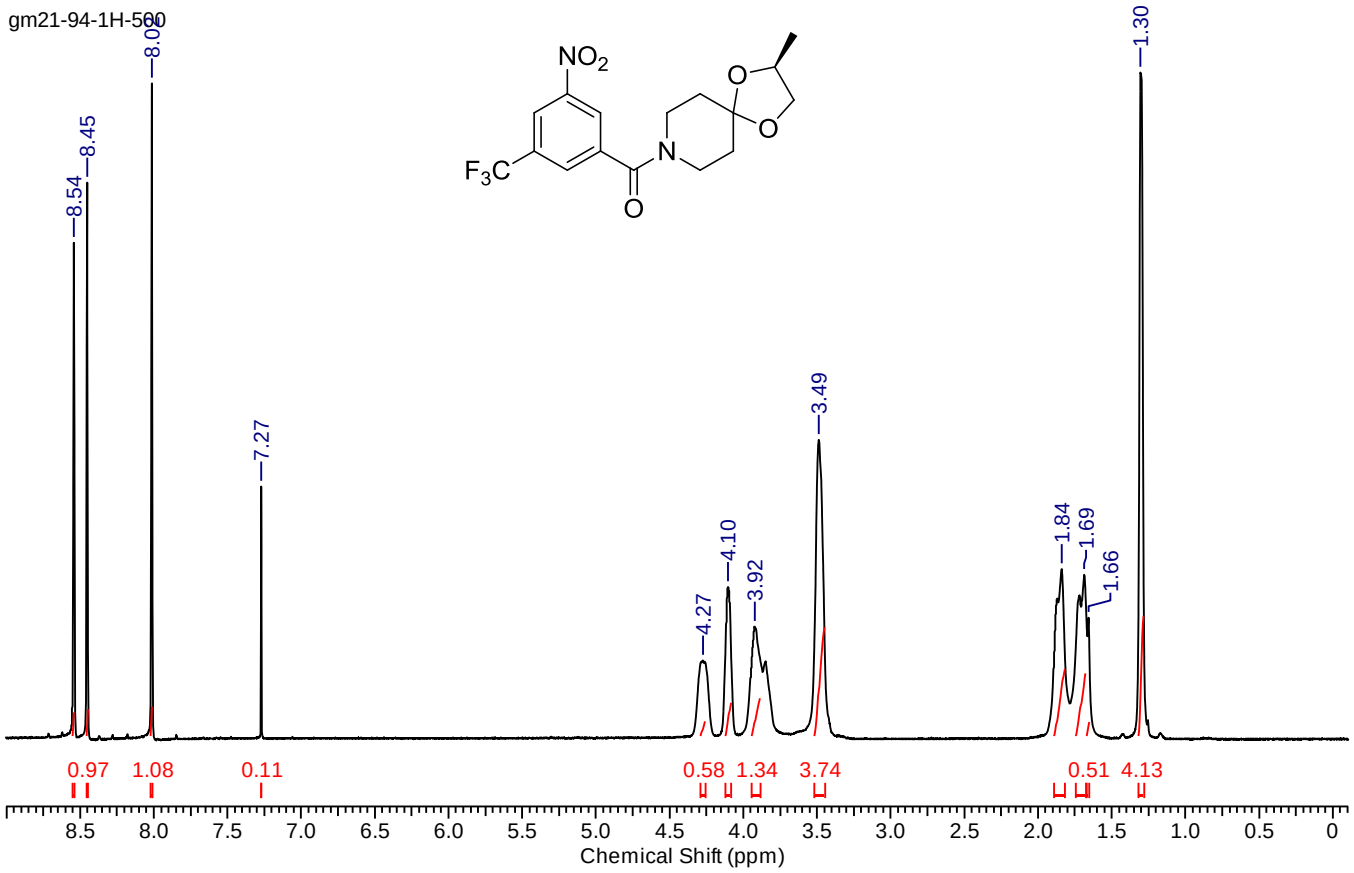
Exact Mass: 415.17434
Molecular Weight: 415.43970

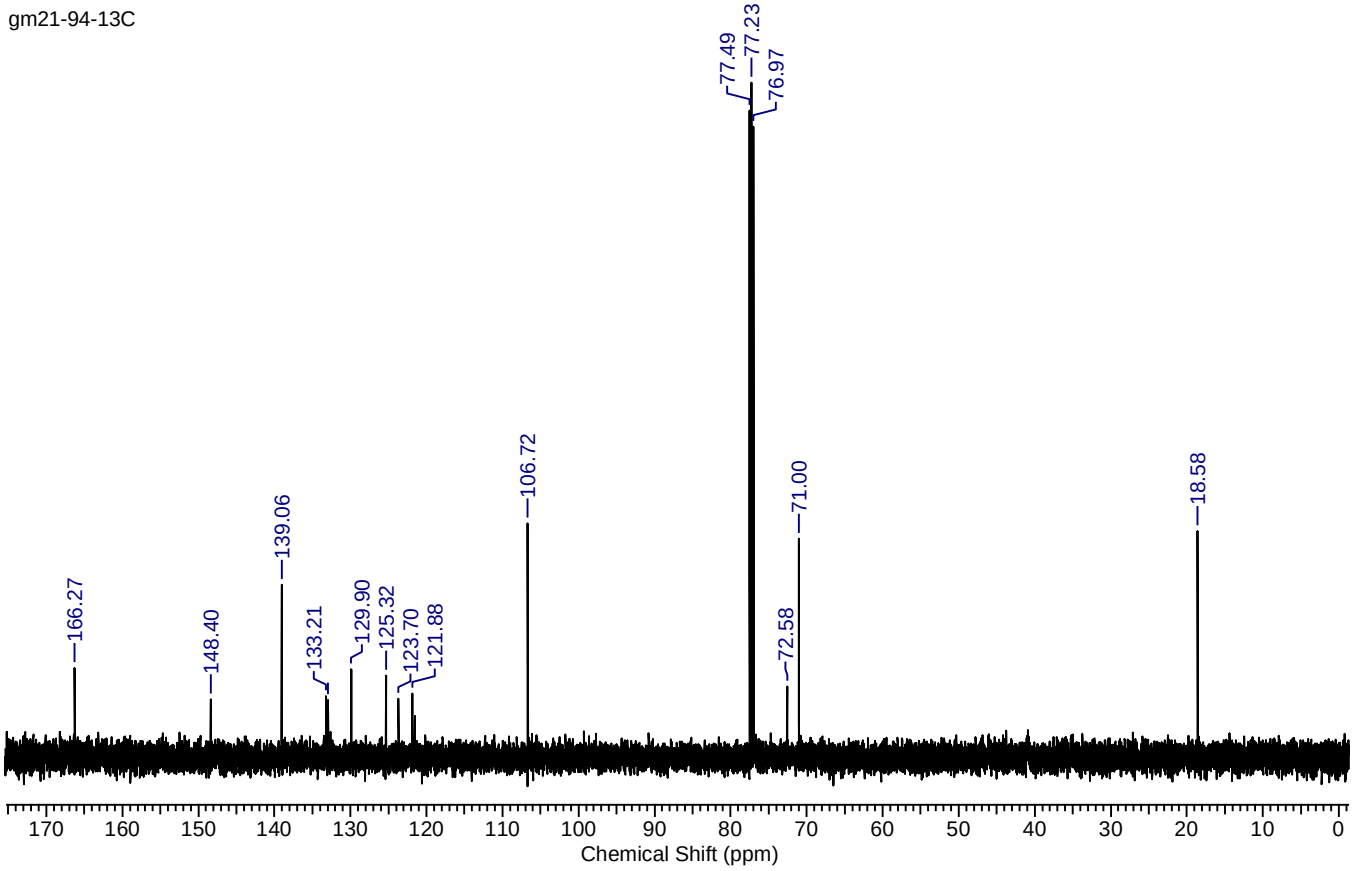

MM RVT-3-195
3: Diode Array
Range: 2.179e+2
AU
1.5e+2
1.0e+2
5.0e+1
0.0
0.60
6.70
7.50
2.00
4.00
6.00
8.00
10.00
12.00
14.00
MM RVT-3-195
2: Scan ES+
TIC
6.72e5
%
0
0.52
0.63
0.79
1.31
1.82
2.60
3.07
3.67
3.94
4.62
5.55
6.20
6.44
6.78
6.84
7.43
8.14
8.42
8.70
9.39
10.34
10.78
11.71
12.64
13.45
13.53
13.89
14.62
14.94
MM RVT-3-195
1: Scan ES-
TIC
5.23e6
%
2
0.62
1.26
2.01
2.29
3.62
3.99
4.27
4.96
5.48
6.41
6.75
7.04
8.17
8.71
9.02
9.26
10.39
11.58
12.19
12.59
13.38
13.82
14.89
Time

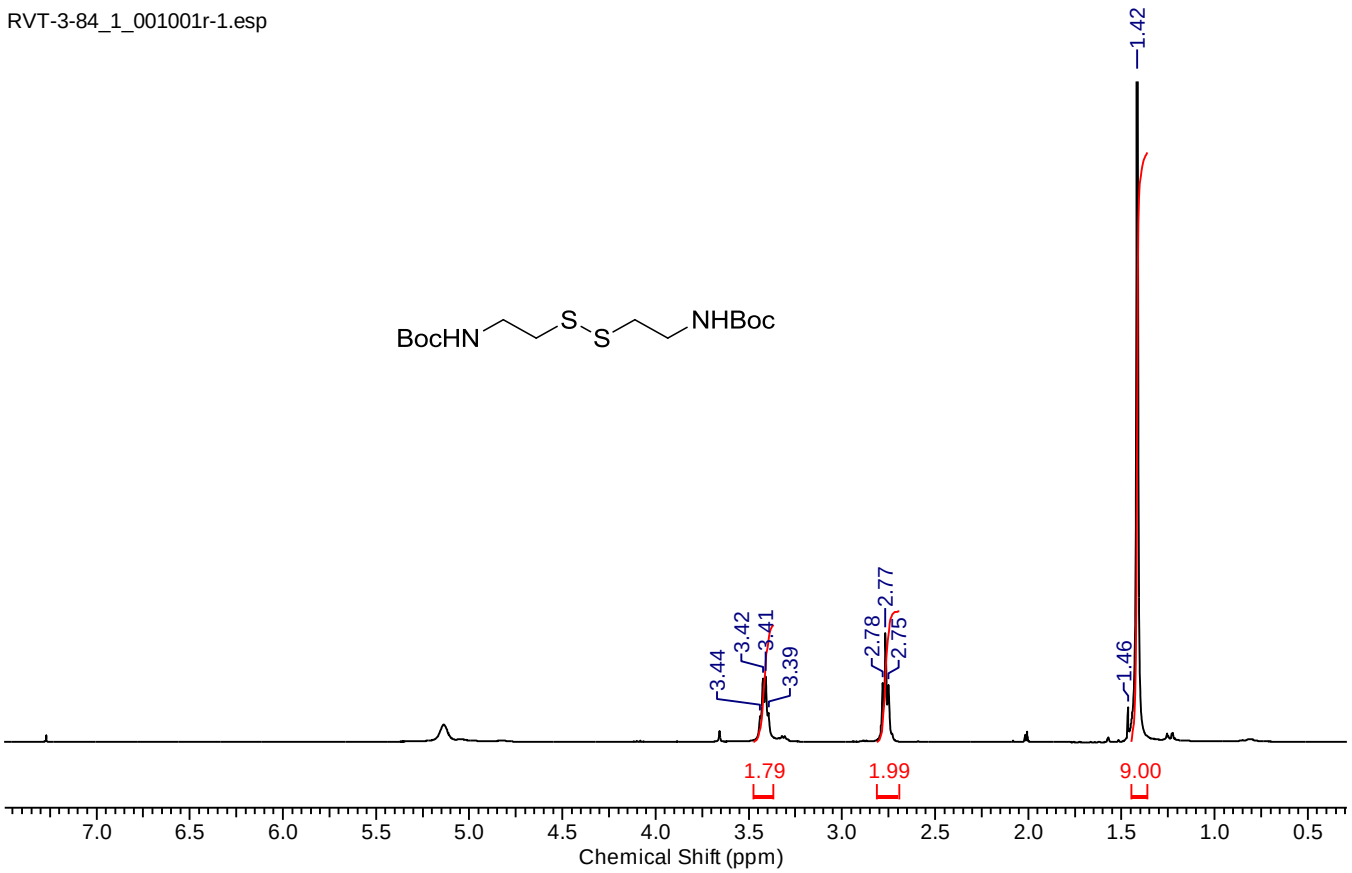

MM RVT-3-195 336 (6.784) Cm (326:336)
2: Scan ES+
1.25e4
100
%
0
703.50
1270.51
352.02
1458.42
720.58
278.98
1071.77
702.88
1076.70
1077.60
1358.32
1693.36
1882.03
1874.43
1521.56
353.14
133.06
541.32
766.37
1822.35
543.23
1626.57
242.75
393.32
444.73
577.79
777.19
991.06
1235.45
1896.55
MM RVT-3-195 368 (7.431) Cm (363:376)
2: Scan ES+
5.13e4
100
%
0
831.65
416.24
832.66
417.25
854.06
1269.08
1515.19
1579.24
159.52
324.56
363.69
461.23
628.49
700.88
1039.90
1148.99
1253.93
1269.98
1746.02
1811.85
1900.55
200
400
600
800
1000
1200
1400
1600
1800
m/z

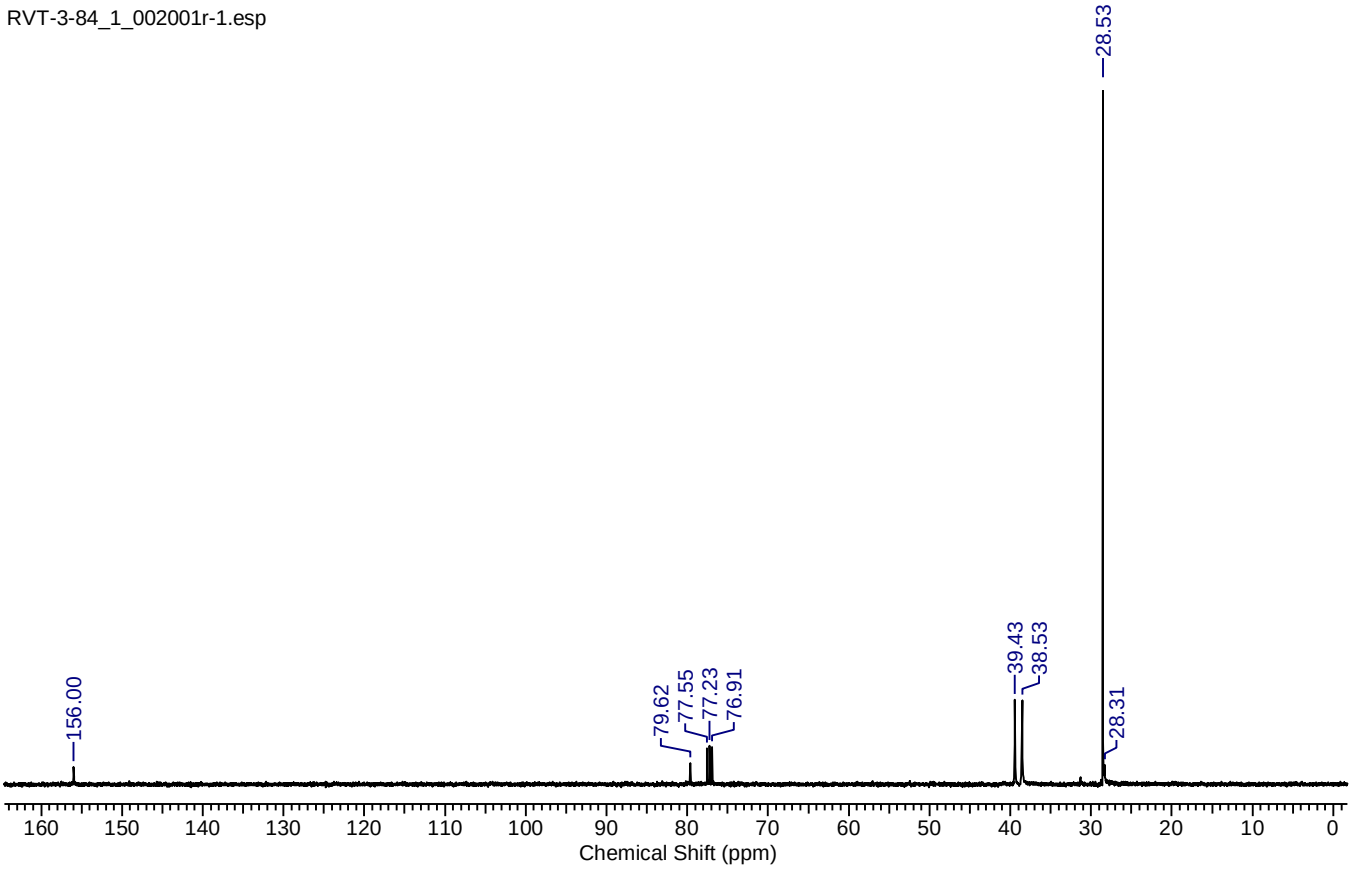

RVT-Dinitro-TB-amide_103001r.esp
8.80
8.80
9.10
9.10
9.09
1.62
1.31
1.30
3.50
4.28
4.13
4.11
3.92
2.05
1.85
1.28
1.27
1.26
0.98
1.74
1.00
1.89
2.61
0.24
1.64
2.85
Chemical Shift (ppm)


RVT-Dinitro-TB-amide_102001r.esp
127.53
119.85
106.62
77.54
76.91
71.03
72.63
18.56
165.39
148.71
139.56
46.21
41.04
37.06
36.20
35.98
35.06
Chemical Shift (ppm)

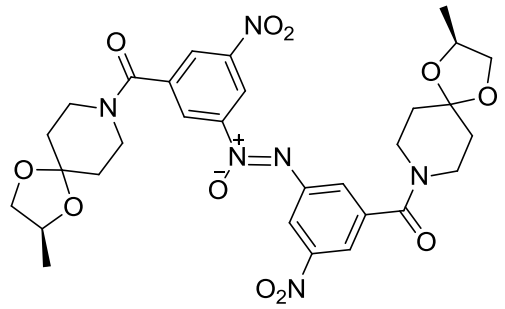

gm21-94-1H-500
NO2
F3C
O
N
O
O
O
8.54
8.45
8.02
7.27
4.27
4.10
3.92
3.49
1.84
1.69
1.66
1.30
0.97
1.08
0.11
0.58
1.34
3.74
0.51
4.13
Chemical Shift (ppm)


gm21-94-13C
77.49
77.23
76.97
166.27
148.40
139.06
133.21
129.90
125.32
123.70
121.88
106.72
72.58
71.00
18.58
Chemical Shift (ppm)

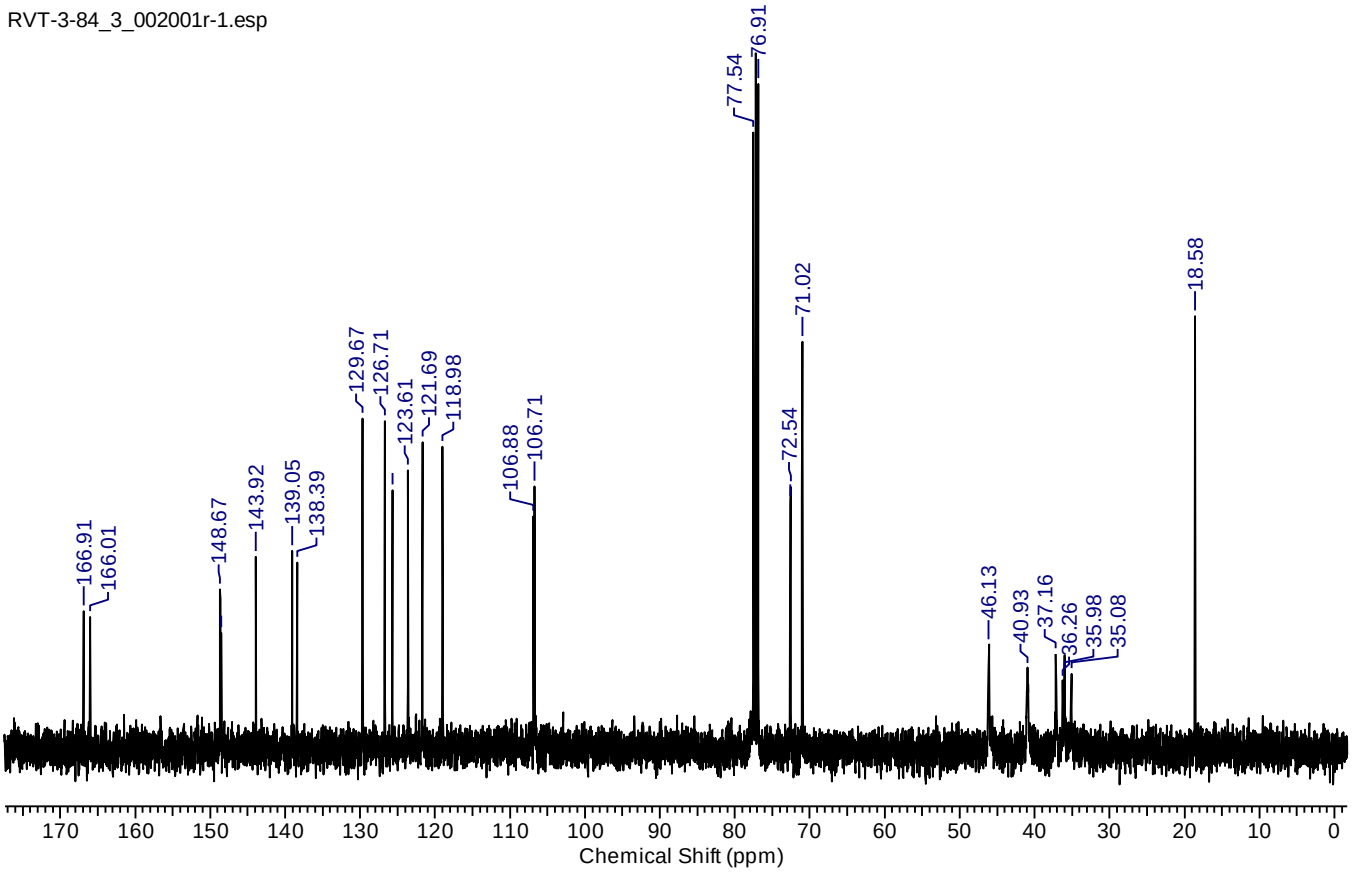

RVT-3-84_1_001001r-1.esp
BocHN
S
S
NHBoc
1.42
3.44
3.42
3.41
3.39
2.78
2.77
2.75
1.46
1.79
1.99
9.00
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


RVT-3-84_1_002001r-1.esp
28.53
156.00
79.62
77.55
77.23
76.91
39.43
38.53
28.31
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

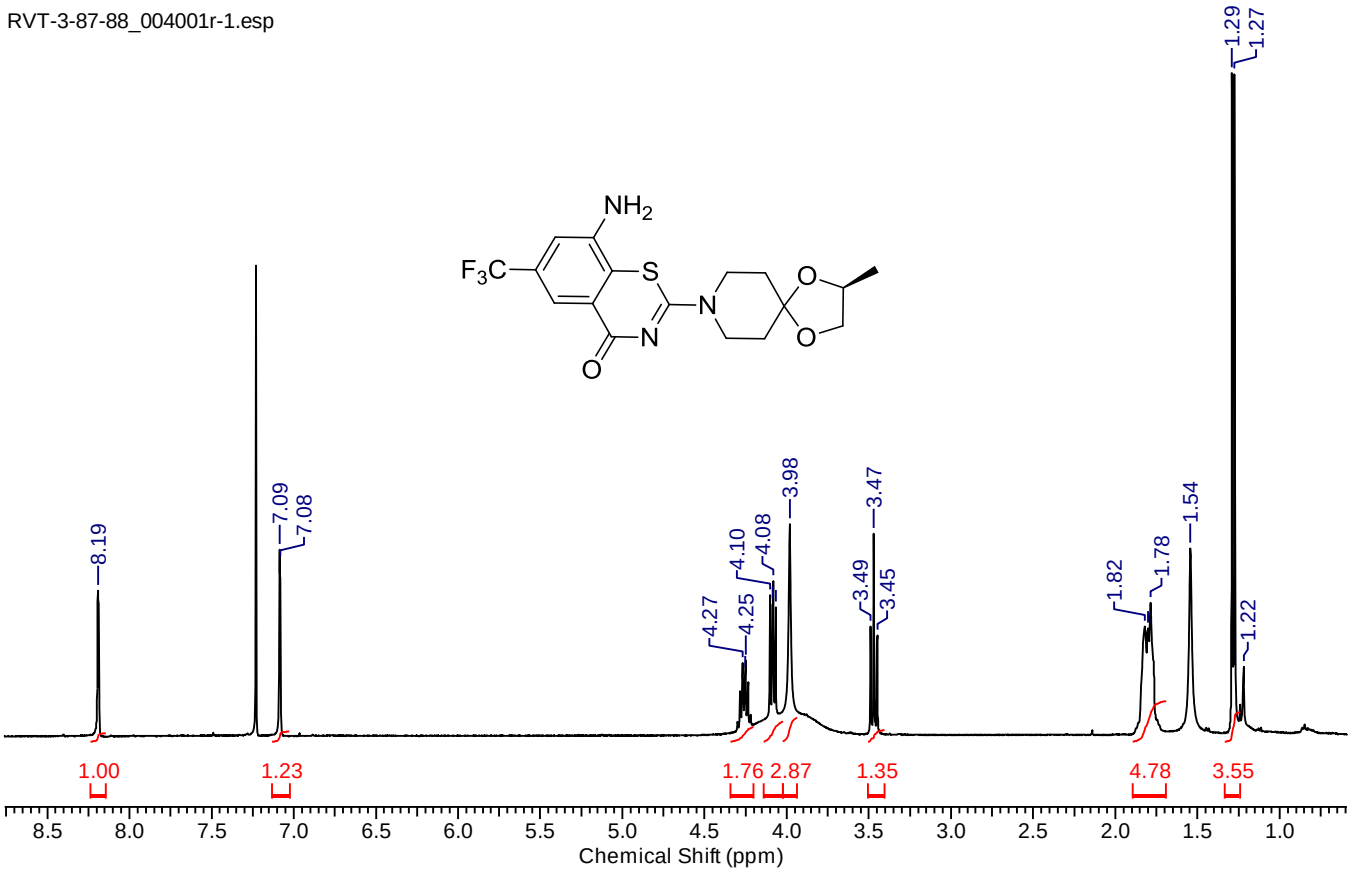
RVT-3-84_3_001001r-1.esp



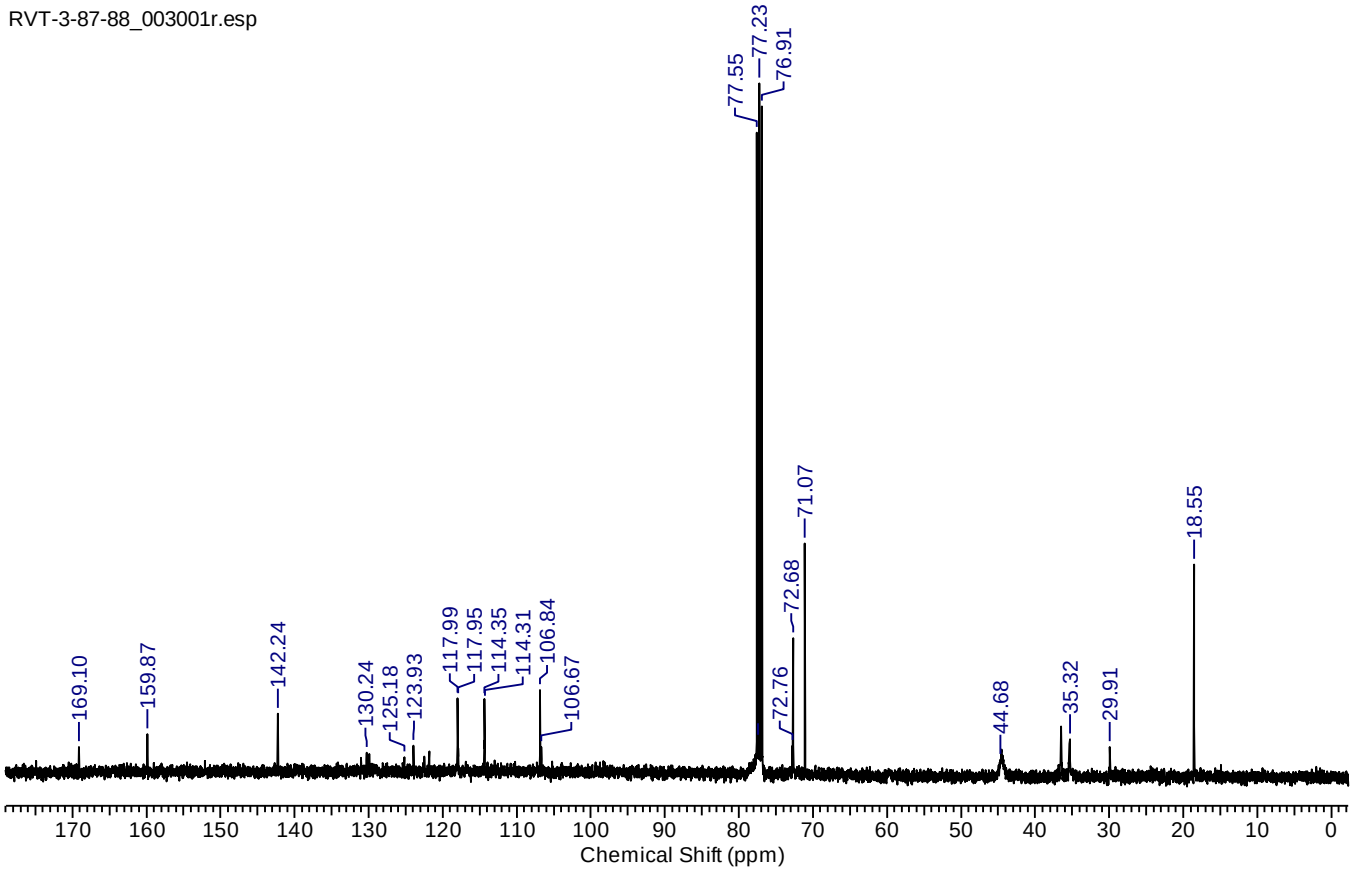
RVT-3-84_3_002001r-1.esp

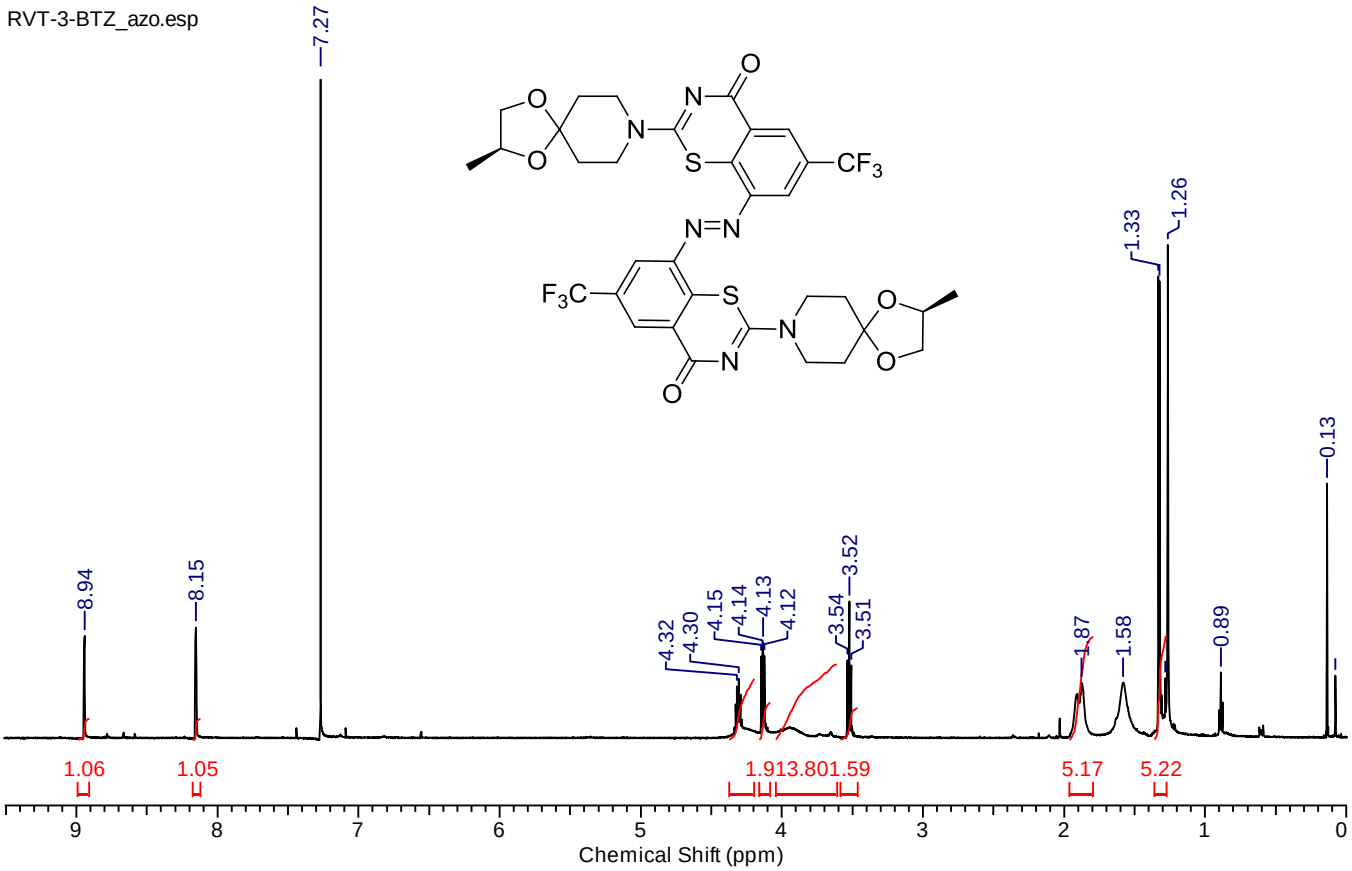


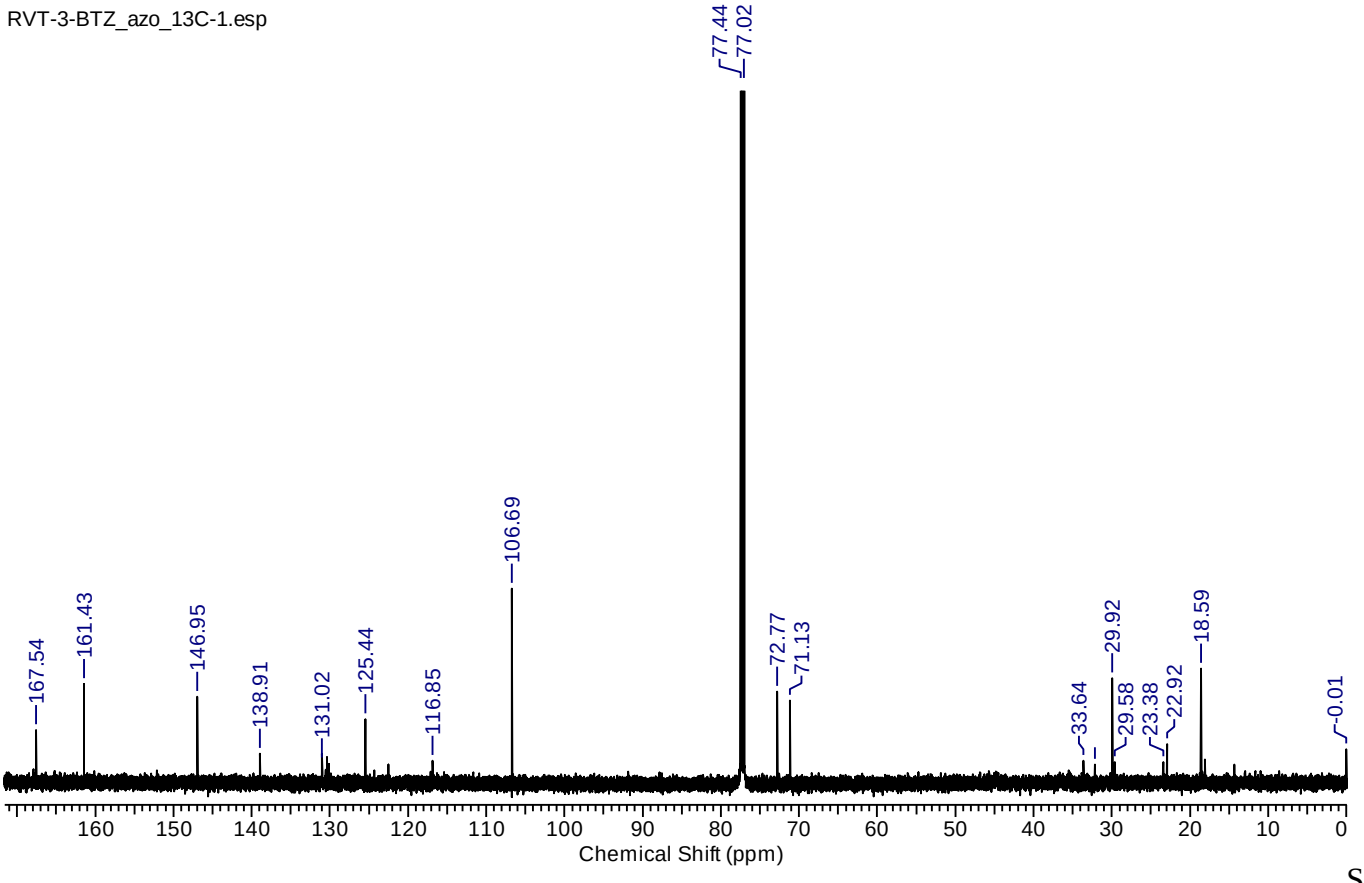
RVT-3-87-88_004001r-1.esp



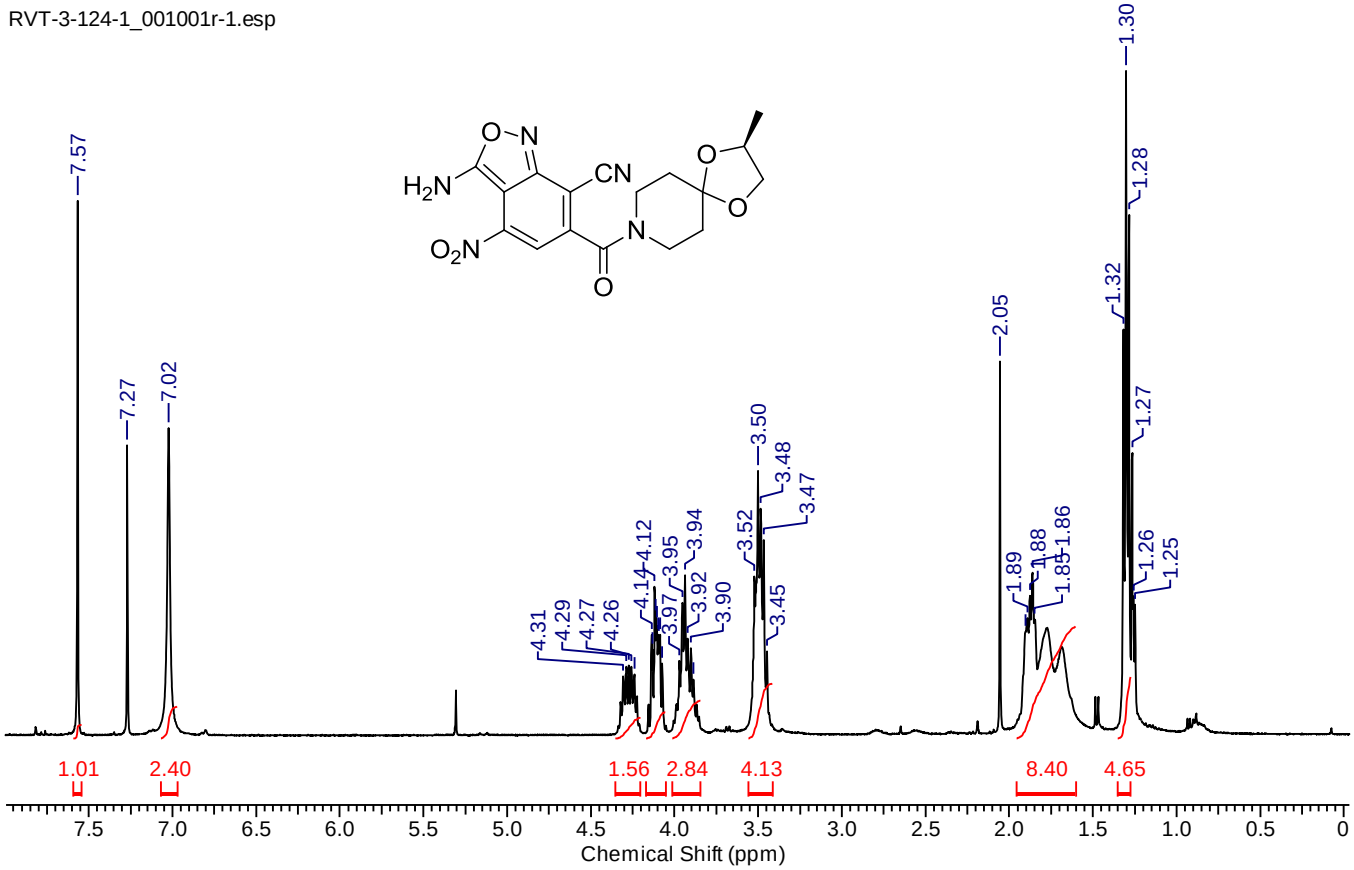
RVT-3-87-88_003001r.esp



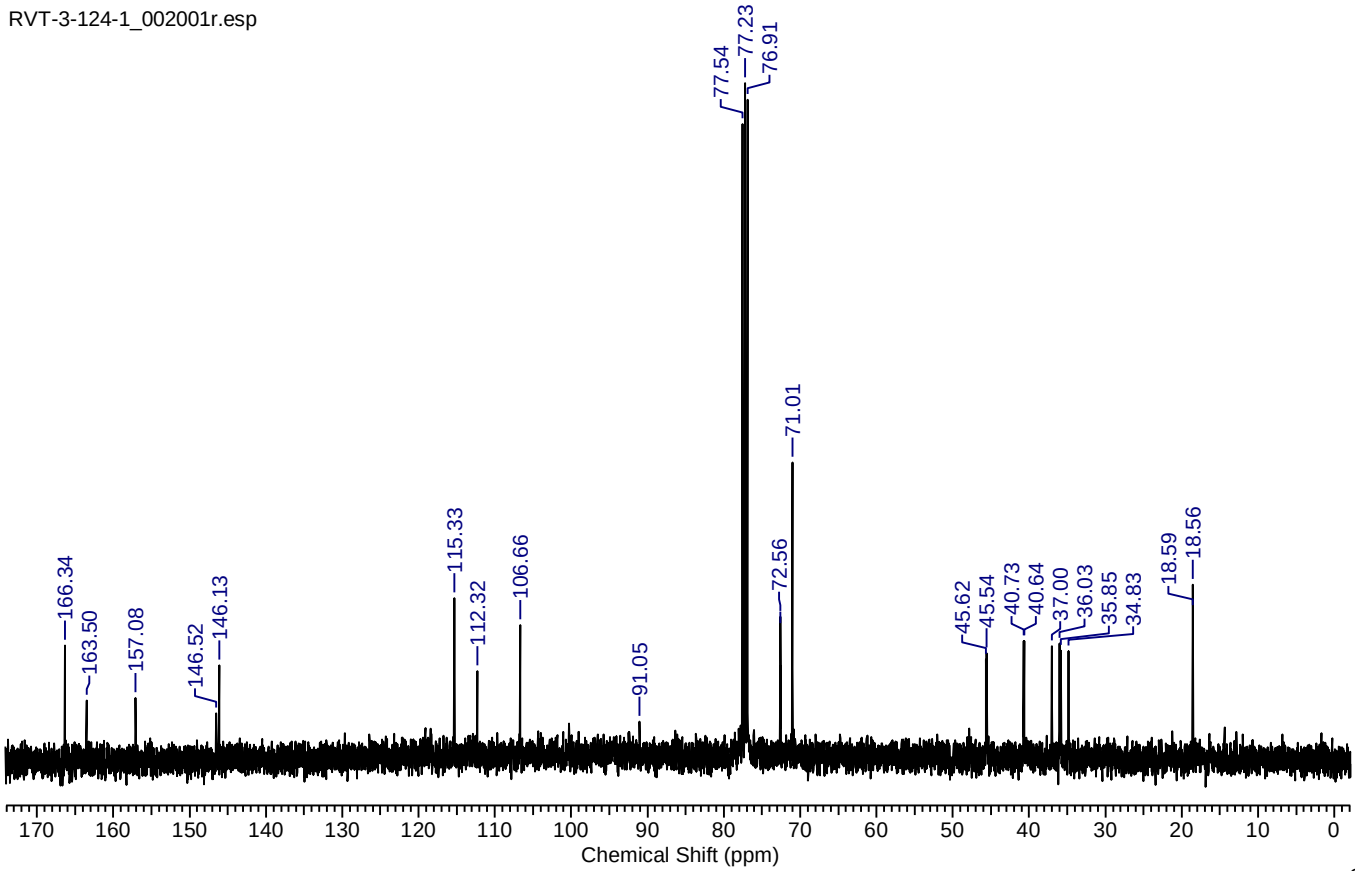

RVT-3-BTZ_azo.esp
7.27
8.94
8.15
4.32
4.30
4.15
4.14
4.13
4.12
3.54
3.52
3.51
1.87
1.58
1.33
1.26
0.89
0.13
1.06
1.05
1.91
3.80
1.59
5.17
5.22
Chemical Shift (ppm)

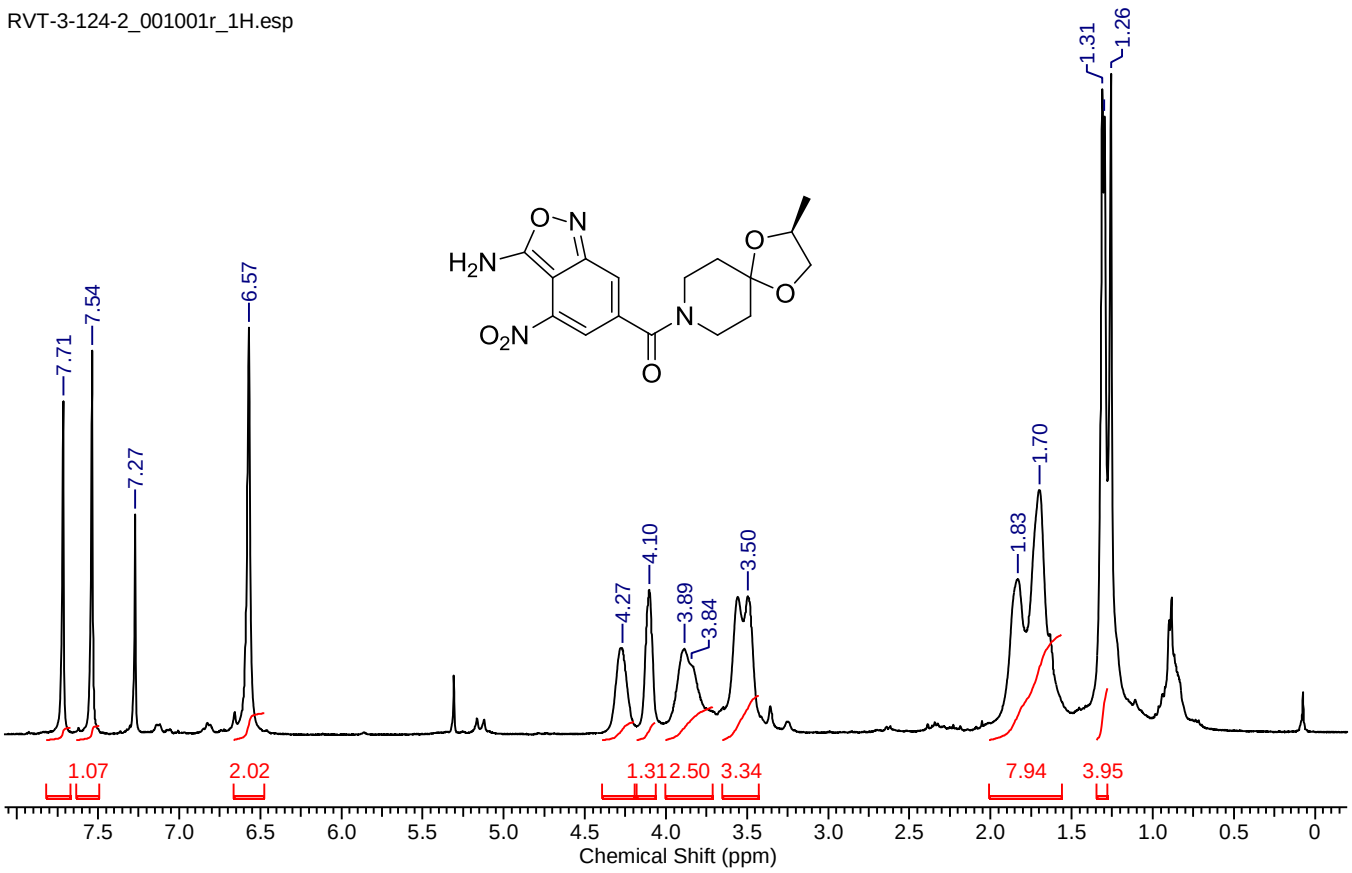

RVT-3-BTZ_azo_13C-1.esp
77.44
77.02
167.54
161.43
146.95
138.91
131.02
125.44
116.85
106.69
72.77
71.13
33.64
29.92
29.58
23.38
22.92
18.59
0.01
Chemical Shift (ppm)

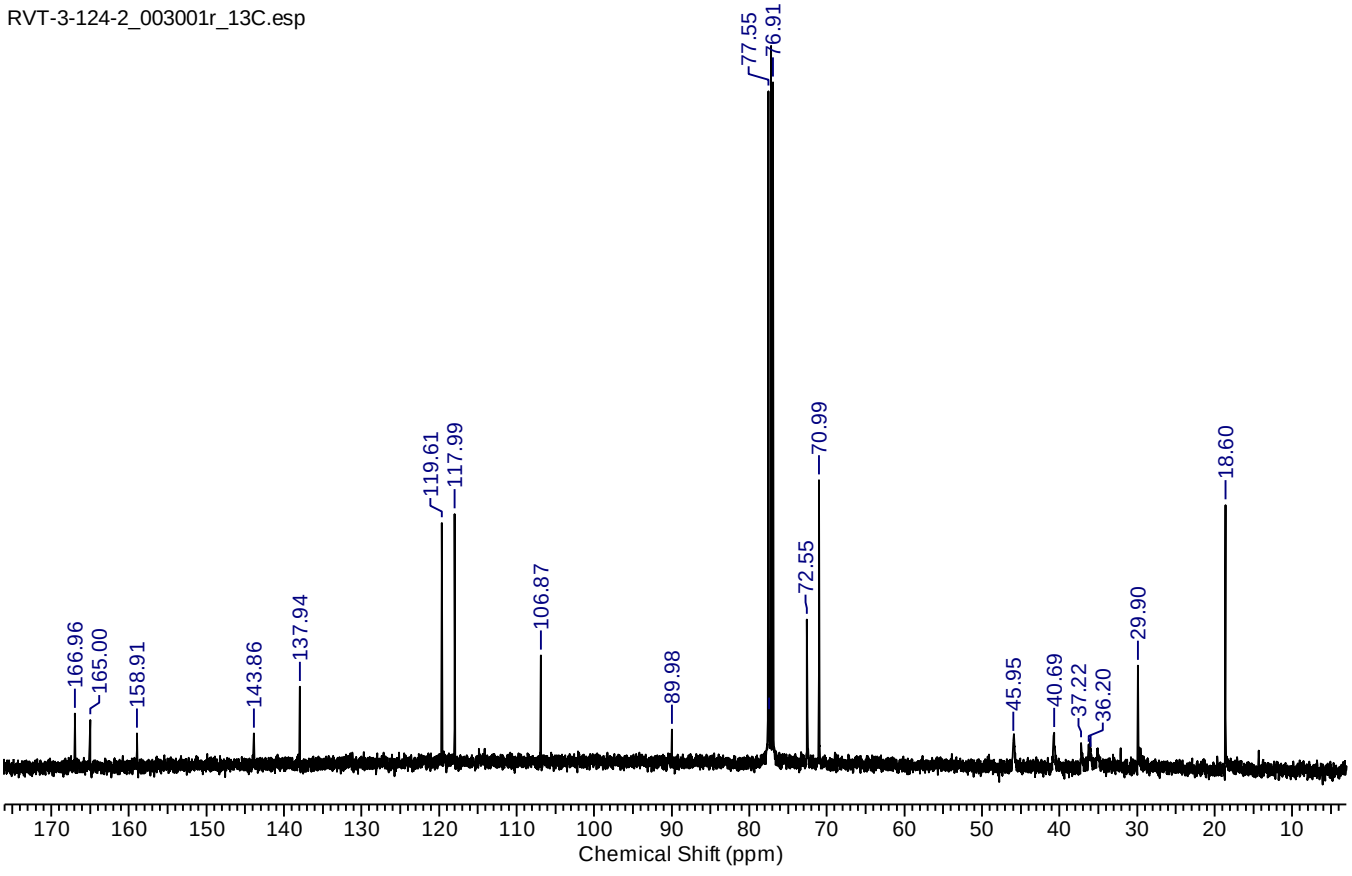
RVT-3-124-1_001001r-1.esp

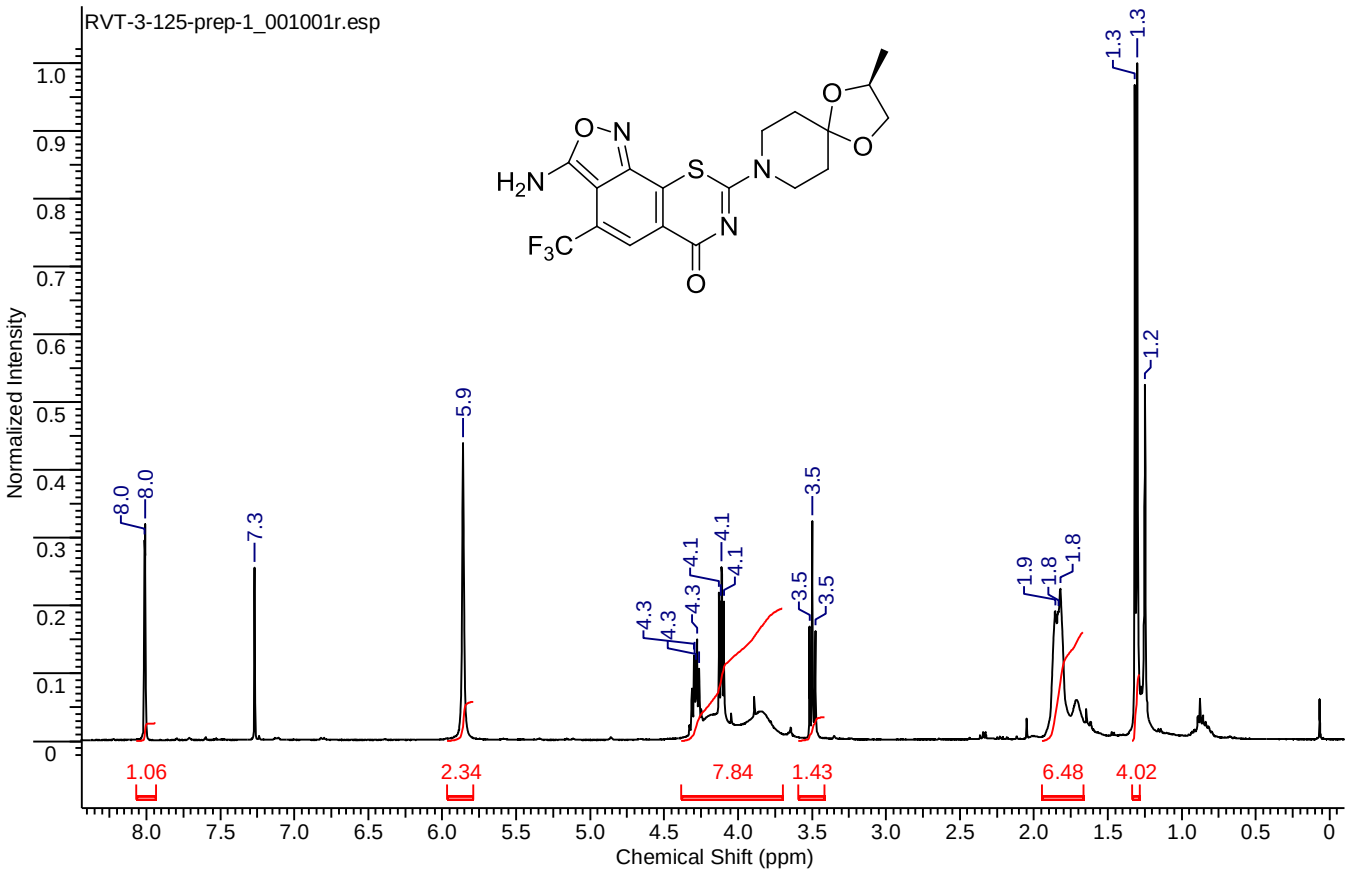


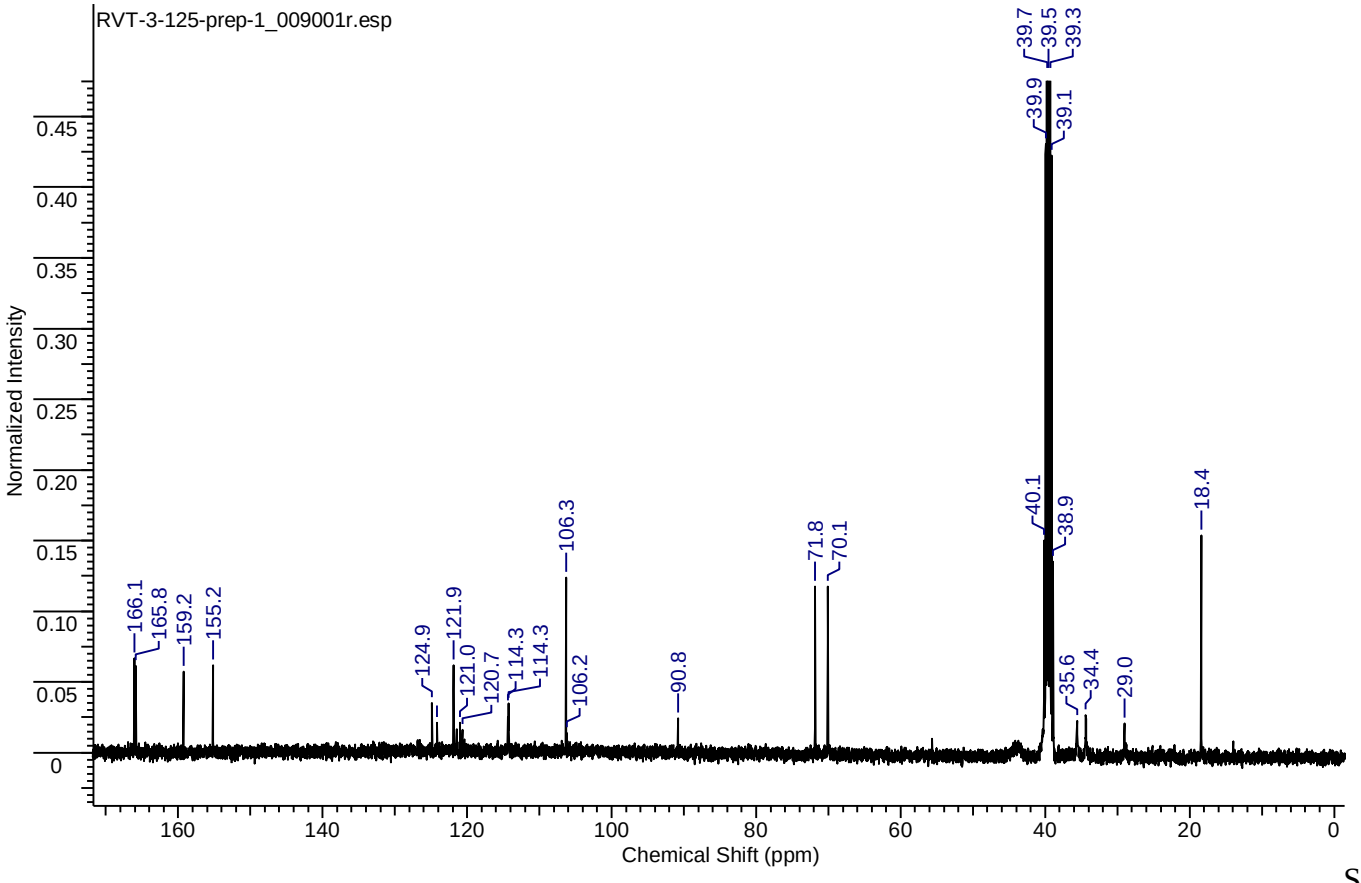
RVT-3-124-1_002001r.esp

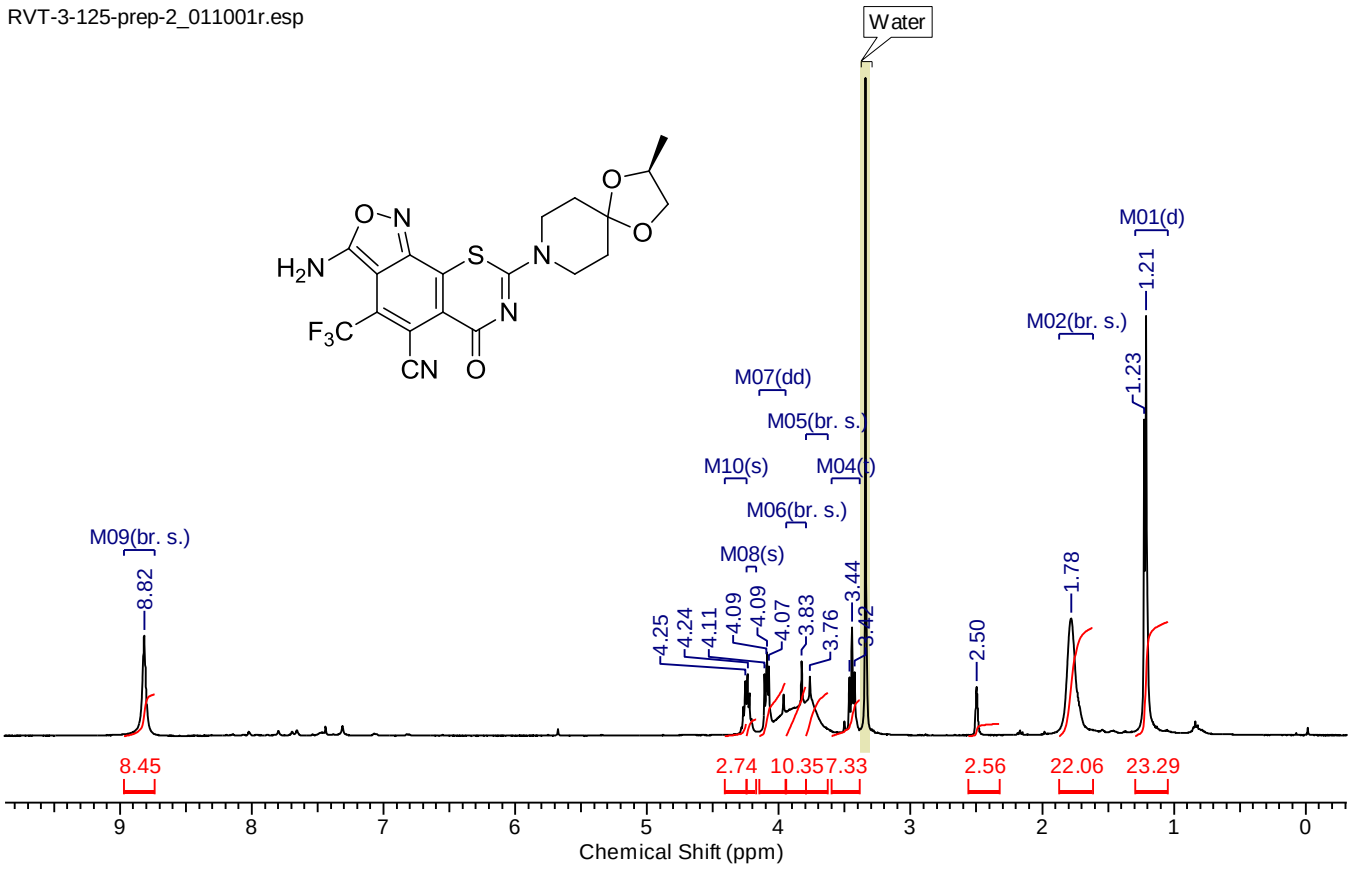


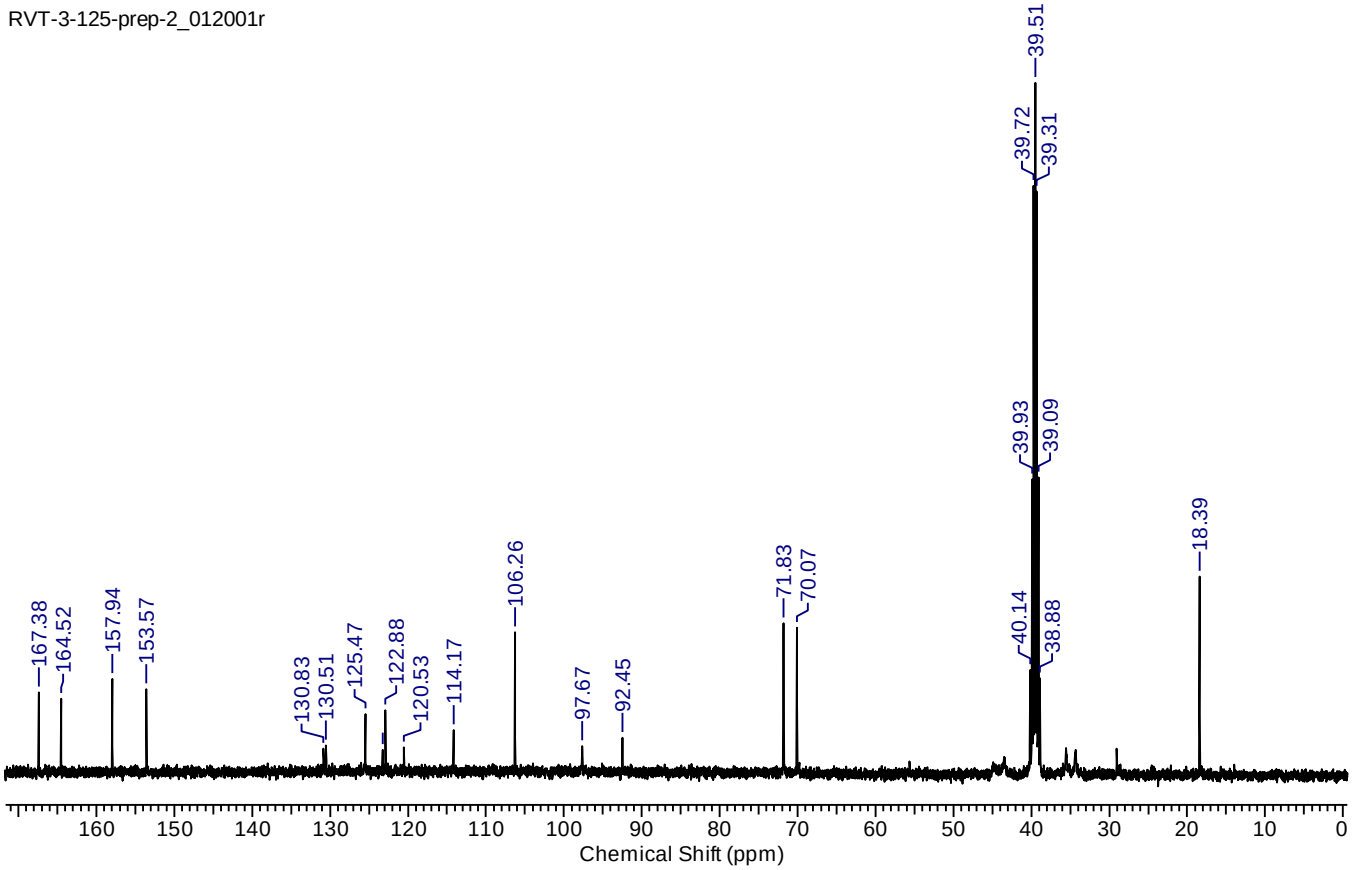

RVT-3-124-2_001001r_1H.esp
7.71
7.54
7.27
6.57
4.27
4.10
3.89
3.84
3.50
1.83
1.70
1.31
1.26
1.07
2.02
1.31
2.50
3.34
7.94
3.95
Chemical Shift (ppm)

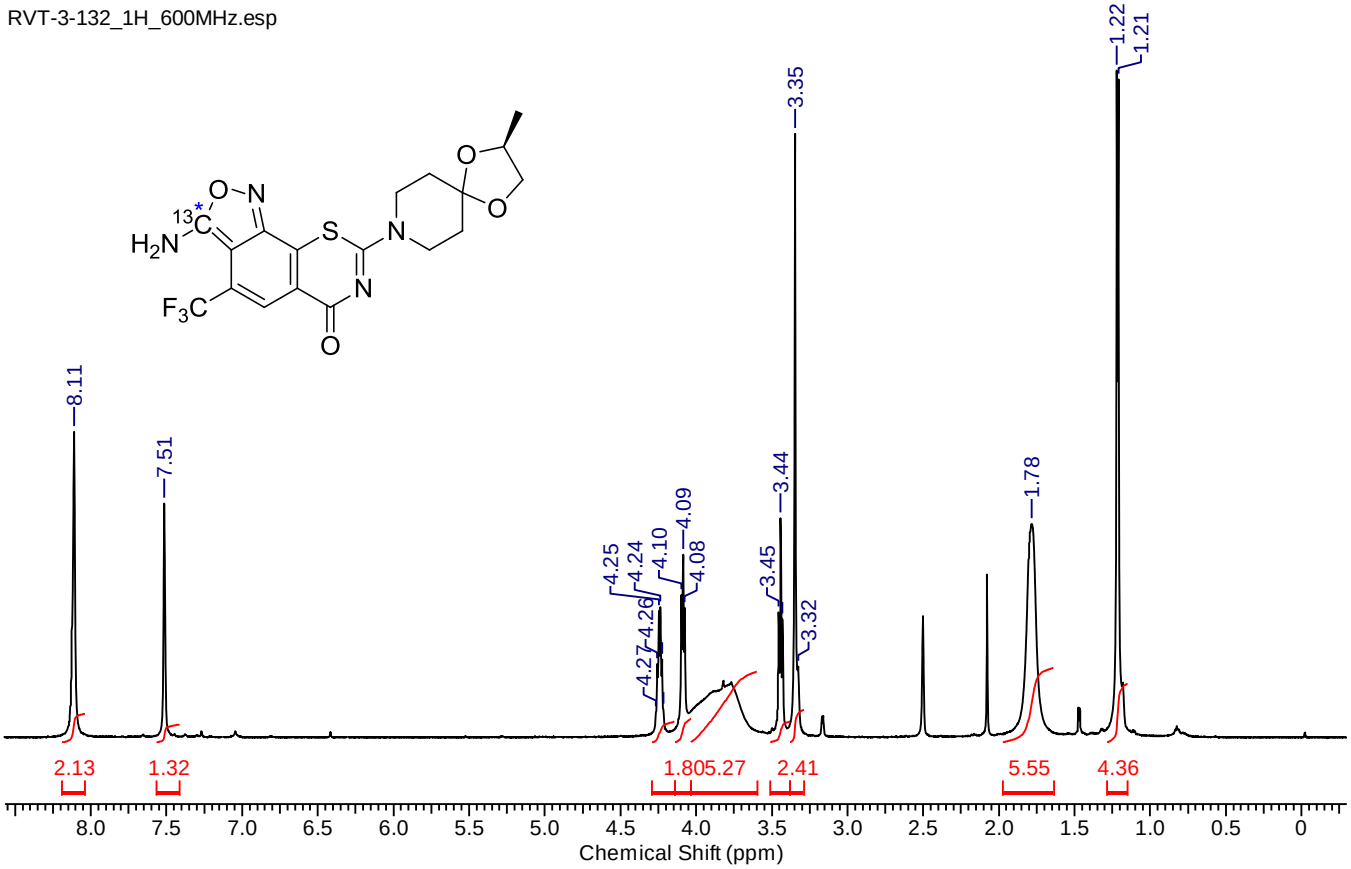

RVT-3-124-2_003001r_13C.esp
77.55
76.91
119.61
117.99
106.87
89.98
72.55
70.99
45.95
40.69
37.22
36.20
29.90
18.60
166.96
165.00
158.91
143.86
137.94
Chemical Shift (ppm)

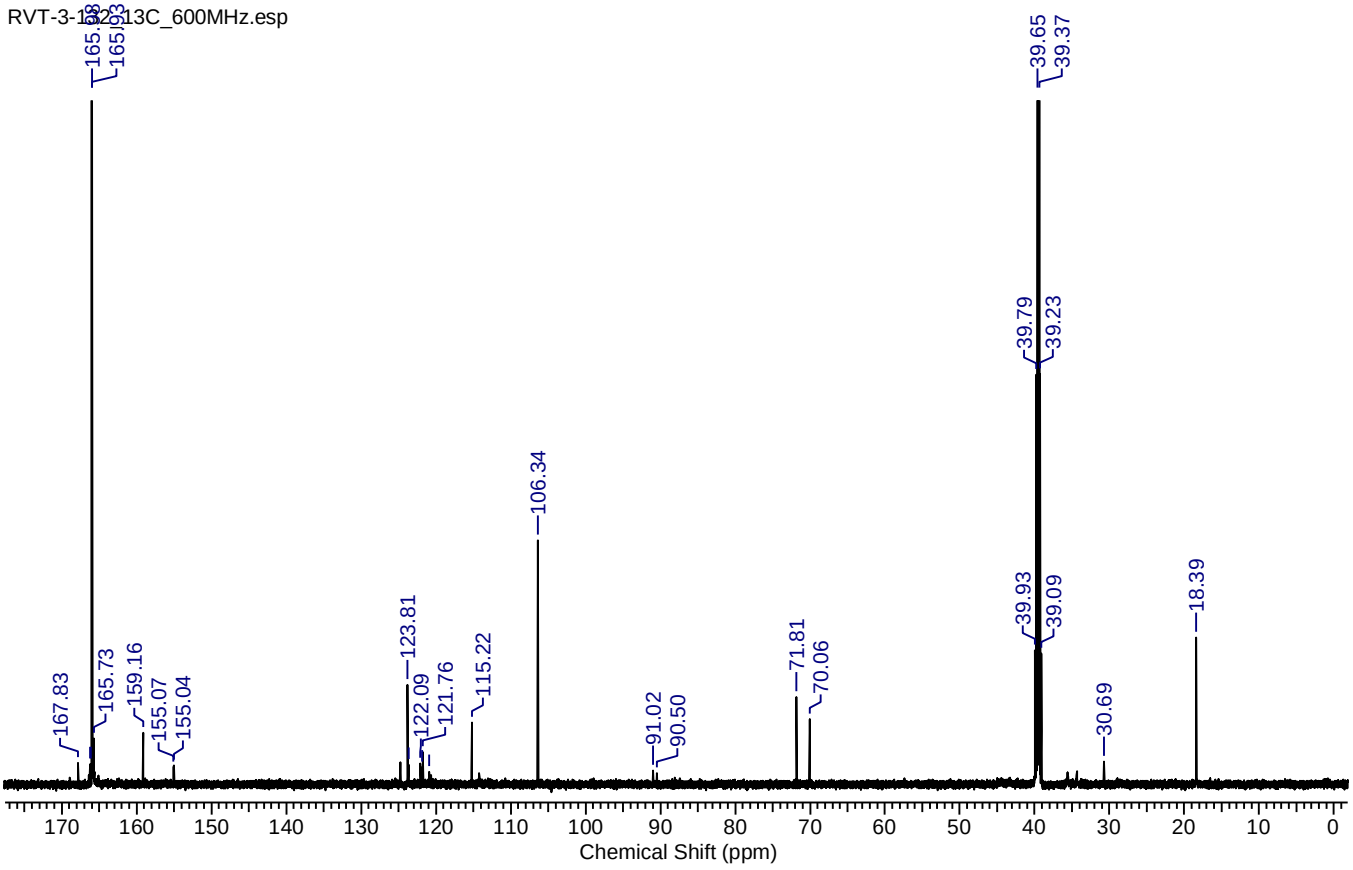

RVT-3-125-prep-1_001001r.esp
Normalized Intensity
Chemical Shift (ppm)
8.0
8.0
7.3
5.9
4.3
4.3
4.1
4.1
4.1
3.5
3.5
3.5
1.9
1.8
1.8
1.3
1.3
1.2
1.06
2.34
7.84
1.43
6.48
4.02

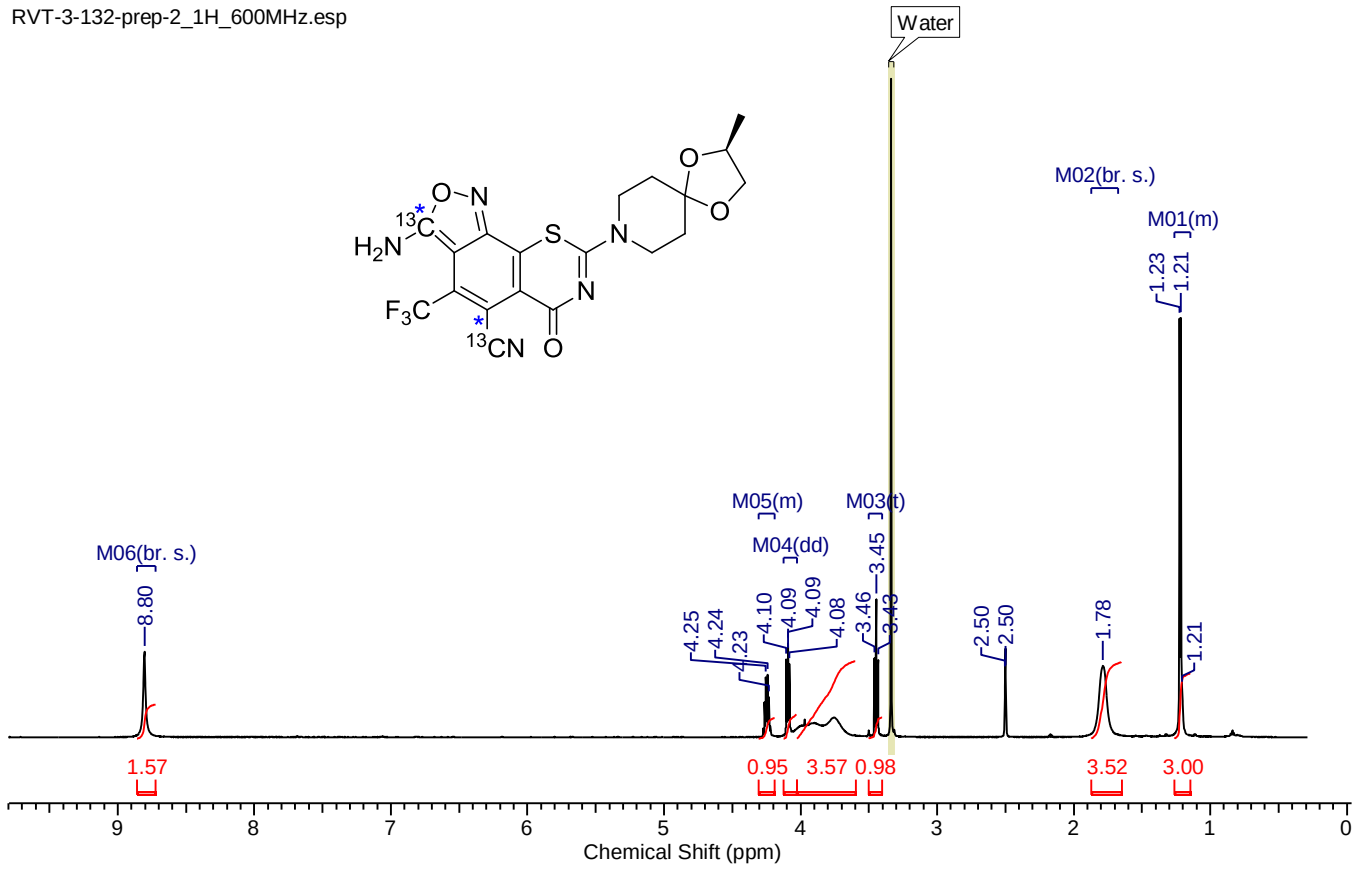

RVT-3-125-prep-1_009001r.esp
Normalized Intensity
Chemical Shift (ppm)
166.1
165.8
159.2
155.2
124.9
121.9
121.0
120.7
114.3
114.3
106.3
106.2
90.8
71.8
70.1
39.7
39.5
39.3
39.9
39.1
40.1
38.9
35.6
34.4
29.0
18.4

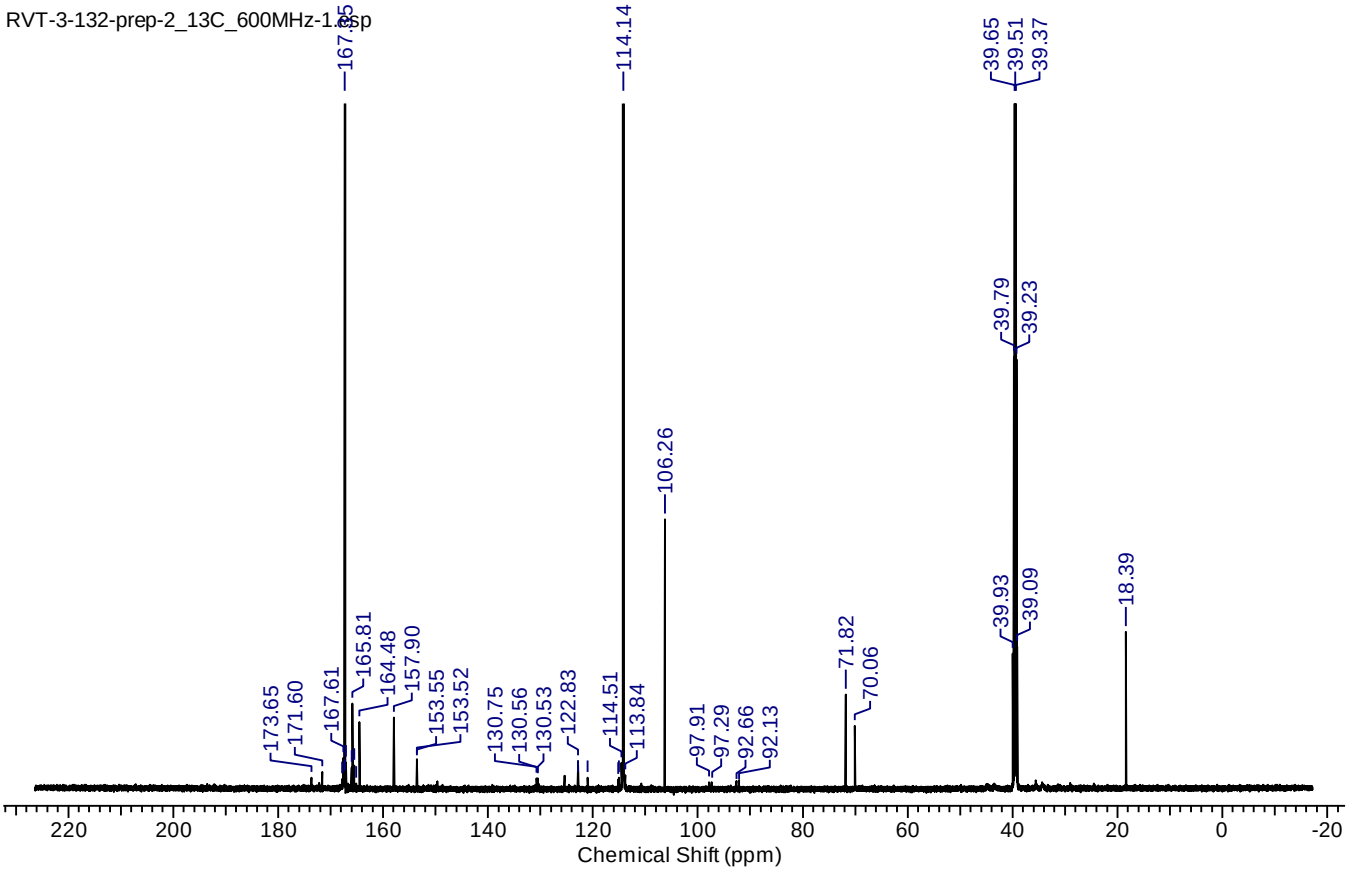

RVT-3-125-prep-2_011001r.esp
Water
M01(d)
1.21
M02(br. s.)
1.23
M07(dd)
M05(br. s.)
M10(s)
M04(t)
M06(br. s.)
M08(s)
M09(br. s.)
8.82
4.25
4.24
4.11
4.09
4.09
4.07
3.83
3.76
3.44
3.42
2.50
1.78
8.45
2.74
10.35
7.33
2.56
22.06
23.29
Chemical Shift (ppm)


RVT-3-125-prep-2_012001r
39.51
39.72
39.31
39.93
39.09
18.39
167.38
164.52
157.94
153.57
130.83
130.51
125.47
122.88
120.53
114.17
106.26
97.67
92.45
71.83
70.07
40.14
38.88
Chemical Shift (ppm)


RVT-3-132_1H_600MHz.esp
8.11
7.51
4.25
4.24
4.26
4.27
4.10
4.09
4.08
3.45
3.44
3.35
3.32
1.78
1.22
1.21
2.13
1.32
1.80
5.27
2.41
5.55
4.36
Chemical Shift (ppm)

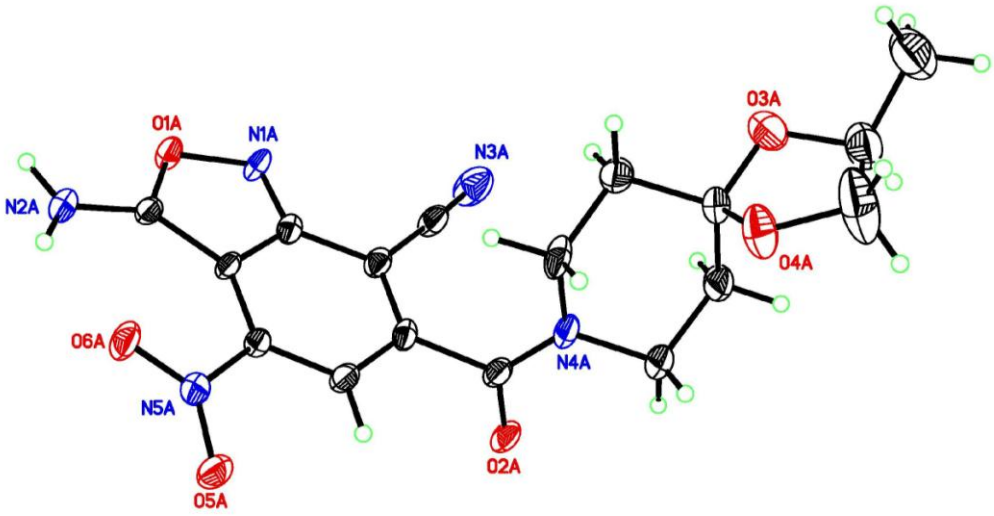

RVT-3-132_13C_600MHz.esp
165.73
165.23
167.83
165.73
159.16
155.07
155.04
123.81
122.09
121.76
115.22
106.34
91.02
90.50
71.81
70.06
39.65
39.37
39.79
39.23
39.93
39.09
30.69
18.39
Chemical Shift (ppm)


RVT-3-132-prep-2_1H_600MHz.esp
Water
M02(br. s.)
M01(m)
M05(m)
M03(t)
M04(dd)
M06(br. s.)
1.57
0.95
3.57
0.98
3.52
3.00
Chemical Shift (ppm)


RVT-3-132-prep-2_13C_600MHz-1.esp
Chemical Shift (ppm)

X-ray Structure Report

for compound **32 (nd1236)**.



DISCUSSION

The compound crystallizes as dark red plate-like crystals. There are four molecules of the compound in the primitive, acentric, monoclinic space group $P2_1$. There are two crystallographically independent molecules in the asymmetric unit. They are chemically identical and differ only in minor variations of derived parameters (predominantly torsion angles). The two molecules are the same enantiomer, and the structure depicted is the correct absolute configuration. This was determined by the known handedness at C15, and by comparison of Friedel pairs of reflections. The Flack *x* parameter was refined to 0.1(2) and the Bayesian statistical analysis of Friedel reflections yielded a Hooft *y* parameter of 0.09(10). Values of zero indicate the correct enantiomorph of the space group and hence the correct absolute configuration of the molecule. A value of one indicates the inverted absolute stereochemistry. These analyses are in agreement with the known chirality at C16. Though the structural information indicates a pseudo center of symmetry, this does not exist since the crystal is enantiopure.

Formally the compound is:
(*S*)-3-amino-6-(2-methyl-1,4-dioxa-8-azaspiro[4.5]decane-8-carbonyl)-4-nitrobenzo[c]isoxazole-7-carbonitrile (see Figures).

The fused 5, 6-bicyclic ring systems demonstrate a high level of conjugation with bond distances appropriate for aromatic contacts through out (see Table of Bond Distances). The tautomerism is depicted in the appended ChemDraw diagram. However, the formal single bonds depicted in this scheme exhibit aromatic character rather than single bond/double bond character. For example the C1-C6 contacts are 1.428(3) and 1.426(3) Å, respectively. An ideal aromatic C-C distance is 1.39 Å and a true single bond is closer to 1.54 Å.

Surprisingly the *exo*-cyclic primary amines (N2A/B) have shorter than expected N-C distances of 1.311(3) and 1.326(3) Å, respectively which are indicative of a multiple bond. However, the hydrogen atoms associated with these amines were reliably located from a difference Fourier map and were refined freely. In each case, one hydrogen forms a good intermolecular H-bond to the carbonyl oxygen, O2, of a neighboring molecule related by translation along the *b*-axis. The other forms a bifurcated H-bond to the nitro oxygen O6 of the other molecule of the pair related by the crystallographic screw axis and an intramolecular H-bond to O6 (see Table of Hydrogen Bonds for details). The packing motif is a linear, one-dimensional chain of H-bond molecules that are parallel to the crystallographic *b*-axis.

The high degree of conjugation within the structure leads to bond distances that vary from ideal bond parameters. These deviations are not exceptionally different, just notably different from ideal.

CRYSTAL SUMMARY

Crystal data for $C_{17}H_{17}N_5O_6$; M_r = 387.36; Monoclinic; space group $P2_1$; a = 10.7900(4) Å; b = 10.1646(4) Å; c = 16.7717(7) Å; α = 90°; β = 105.078(2)°; γ = 90°; V = 1776.13(12) $Å^3$; Z = 4; T = 120(2) K; λ(Cu-Kα) = 1.54184 Å; μ(Cu-Kα) = 0.952 mm^{-1}; d_{calc} = 1.449g.cm^{-3}; 34618

reflections collected; 6265 unique (R_{int} = 0.0279); giving R_1 = 0.0354, wR_2 = 0.0943 for 5863 data with [I>2σ(I)] and R_1 = 0.0378, wR_2 = 0.0961 for all 6265 data. Residual electron density ($e^-.Å^{-3}$) max/min: 0.254/-0.204.

An arbitrary sphere of data were collected on a dark red plate-like crystal, having approximate dimensions of 0.14 × 0.10 × 0.04 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.5°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

REFERENCES

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H. D. Flack, *Acta Cryst.*, **1983**, *A39*, 876.

Table 1. Crystal data and structure refinement for nd1236.

Identification code	nd1236
Empirical formula	$C_{17}H_{17}N_5O_6$
Formula weight	387.36
Temperature	120(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 10.7900(4) Å α = 90°
	b = 10.1646(4) Å β = 105.078(2)°
	c = 16.7717(7) Å γ = 90°
Volume	1776.13(12) $Å^3$
Z	4
Density (calculated)	1.449 $g.cm^{-3}$
Absorption coefficient (μ)	0.952 mm^{-1}
F(000)	808
Crystal color, habit	dark red, plate
Crystal size	0.14 × 0.10 × 0.04 mm^3
θ range for data collection	2.73 to 71.33°
Index ranges	$-13 \le h \le 13$, $-12 \le k \le 11$, $-20 \le l \le 20$
Reflections collected	34618
Independent reflections	6265 [R_{int} = 0.0279]
Completeness to θ = 71.33°	99.6 %
Absorption correction	Numerical
Max. and min. transmission	1.0000 and 0.8920
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6265 / 1 / 523
Goodness-of-fit on F^2	1.038
Final R indices [I>2σ(I)]	R_1 = 0.0354, wR_2 = 0.0943
R indices (all data)	R_1 = 0.0378, wR_2 = 0.0961
Absolute structure parameter	0.1(2)
Largest diff. peak and hole	0.254 and -0.204 $e^-.Å^{-3}$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for nd1236. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1A)	-0.04420(16)	0.31699(17)	0.15774(10)	0.023(1)
O(2A)	0.00386(17)	0.96806(18)	0.11833(10)	0.026(1)
O(3A)	0.25351(17)	1.0037(2)	0.49191(11)	0.039(1)
O(4A)	0.38900(16)	1.0358(3)	0.41171(12)	0.040(1)
O(5A)	0.25220(17)	0.6030(2)	-0.01749(11)	0.030(1)
O(6A)	0.24724(17)	0.40574(18)	0.03054(11)	0.027(1)
N(1A)	-0.07749(18)	0.4369(2)	0.19251(12)	0.023(1)
N(2A)	0.0749(2)	0.2347(2)	0.07730(13)	0.025(1)
N(3A)	-0.1297(2)	0.7390(3)	0.28954(16)	0.042(1)
N(4A)	0.1556(2)	0.9294(2)	0.23809(12)	0.025(1)
N(5A)	0.21586(19)	0.5225(2)	0.02556(12)	0.022(1)
C(1A)	-0.0113(2)	0.5263(3)	0.16452(14)	0.019(1)
C(2A)	-0.0074(2)	0.6637(3)	0.18458(14)	0.021(1)
C(3A)	0.0647(2)	0.7468(2)	0.14896(14)	0.019(1)
C(4A)	0.1323(2)	0.6975(3)	0.09352(14)	0.021(1)
C(5A)	0.1322(2)	0.5663(2)	0.07738(13)	0.018(1)
C(6A)	0.0635(2)	0.4762(2)	0.11244(14)	0.018(1)
C(7A)	0.0383(2)	0.3387(2)	0.11148(14)	0.020(1)
C(8A)	-0.0758(2)	0.7083(3)	0.24212(15)	0.026(1)
C(9A)	0.0724(2)	0.8920(3)	0.16803(14)	0.022(1)
C(10A)	0.2520(2)	0.8425(3)	0.29165(16)	0.030(1)
C(11A)	0.2447(3)	0.8522(3)	0.38049(15)	0.034(1)
C(12A)	0.2623(2)	0.9945(3)	0.40943(15)	0.026(1)
C(13A)	0.1634(3)	1.0825(3)	0.35264(15)	0.031(1)
C(14A)	0.1679(3)	1.0677(3)	0.26297(16)	0.033(1)
C(15A)	0.3326(2)	1.1147(3)	0.52779(15)	0.043(1)
C(16A)	0.4297(3)	1.1253(5)	0.4786(2)	0.072(1)
C(17A)	0.3858(4)	1.0914(4)	0.6181(2)	0.067(1)
O(1B)	0.45637(16)	0.74916(17)	0.15512(10)	0.024(1)
O(2B)	0.50146(16)	0.09677(18)	0.11572(10)	0.025(1)
O(3B)	0.74971(16)	0.0804(2)	0.48907(10)	0.035(1)
O(4B)	0.88944(16)	0.0393(2)	0.41063(11)	0.036(1)
O(5B)	0.75858(18)	0.4662(2)	-0.01724(11)	0.031(1)
O(6B)	0.75217(17)	0.66203(17)	0.03141(11)	0.026(1)
N(1B)	0.42213(19)	0.6285(2)	0.18855(12)	0.025(1)
N(2B)	0.5795(2)	0.8329(2)	0.07737(13)	0.022(1)
N(3B)	0.3579(3)	0.3235(3)	0.27749(16)	0.043(1)
N(4B)	0.65687(19)	0.1394(2)	0.23426(12)	0.023(1)
N(5B)	0.72027(19)	0.5451(2)	0.02583(12)	0.021(1)
C(1B)	0.4895(2)	0.5399(3)	0.16039(14)	0.021(1)
C(2B)	0.4906(2)	0.4019(3)	0.17843(13)	0.020(1)

C(3B)	0.5645(2)	0.3195(2)	0.14471(14)	0.020(1)
C(4B)	0.6354(2)	0.3683(3)	0.09141(14)	0.020(1)
C(5B)	0.6372(2)	0.5005(2)	0.07572(13)	0.019(1)
C(6B)	0.5655(2)	0.5927(3)	0.11003(14)	0.019(1)
C(7B)	0.5402(2)	0.7272(3)	0.11003(14)	0.021(1)
C(8B)	0.4172(2)	0.3557(3)	0.23324(16)	0.028(1)
C(9B)	0.5726(2)	0.1734(2)	0.16405(13)	0.019(1)
C(10B)	0.7562(2)	0.2265(3)	0.28417(15)	0.030(1)
C(11B)	0.7493(3)	0.2230(3)	0.37344(15)	0.032(1)
C(12B)	0.7623(2)	0.0850(3)	0.40703(15)	0.030(1)
C(13B)	0.6631(2)	-0.0052(3)	0.35262(15)	0.029(1)
C(14B)	0.6669(3)	0.0016(3)	0.26261(15)	0.027(1)
C(15B)	0.8718(2)	0.0453(2)	0.54353(13)	0.034(1)
C(16B)	0.9316(3)	-0.0317(4)	0.48631(17)	0.041(1)
C(17B)	0.8486(3)	-0.0272(4)	0.61576(17)	0.050(1)
H(2AA)	0.046(3)	0.157(3)	0.0885(16)	0.023(7)
H(2AB)	0.139(3)	0.242(3)	0.0496(18)	0.036(8)
H(4A)	0.1779	0.7562	0.0674	0.025
H(10A)	0.3389	0.8681	0.2881	0.036
H(10B)	0.2366	0.7504	0.2724	0.036
H(11A)	0.3124	0.7968	0.4161	0.040
H(11B)	0.1604	0.8194	0.3850	0.040
H(13A)	0.1802	1.1754	0.3699	0.037
H(13B)	0.0766	1.0592	0.3575	0.037
H(14A)	0.0972	1.1190	0.2269	0.040
H(14B)	0.2501	1.1030	0.2564	0.040
H(15A)	0.2787	1.1961	0.5195	0.052
H(16A)	0.4328	1.2161	0.4580	0.086
H(16B)	0.5161	1.1013	0.5129	0.086
H(17D)	0.4396	1.0123	0.6266	0.101
H(17E)	0.3152	1.0793	0.6442	0.101
H(17F)	0.4377	1.1673	0.6430	0.101
H(2BA)	0.556(3)	0.907(4)	0.095(2)	0.046(10)
H(2BB)	0.627(3)	0.827(3)	0.0492(17)	0.022(7)
H(4B)	0.6821	0.3093	0.0662	0.024
H(10C)	0.7426	0.3175	0.2628	0.036
H(10D)	0.8421	0.1970	0.2806	0.036
H(11C)	0.8186	0.2783	0.4074	0.038
H(11D)	0.6661	0.2602	0.3771	0.038
H(13C)	0.5765	0.0202	0.3569	0.035
H(13D)	0.6793	-0.0968	0.3726	0.035
H(14C)	0.7482	-0.0369	0.2566	0.032
H(14D)	0.5950	-0.0501	0.2281	0.032
H(15B)	0.9232	0.1265	0.5628	0.040
H(16C)	1.0264	-0.0320	0.5062	0.049
H(16D)	0.9002	-0.1236	0.4802	0.049

H(17A)	0.7885	-0.0997	0.5961	0.075
H(17B)	0.8122	0.0330	0.6493	0.075
H(17C)	0.9300	-0.0627	0.6493	0.075

Table 3. Anisotropic displacement parameters ($Å^2$) for nd1236.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1A)	0.0260(8)	0.0140(9)	0.0295(9)	-0.0021(7)	0.0097(6)	-0.0025(7)
O(2A)	0.0330(9)	0.0123(9)	0.0306(9)	0.0036(7)	0.0046(7)	0.0033(8)
O(3A)	0.0446(11)	0.0447(13)	0.0272(9)	-0.0016(8)	0.0064(8)	-0.0056(9)
O(4A)	0.0304(9)	0.0473(13)	0.0417(10)	-0.0184(10)	0.0068(8)	-0.0102(10)
O(5A)	0.0449(11)	0.0183(10)	0.0353(9)	0.0018(8)	0.0234(8)	-0.0030(9)
O(6A)	0.0341(9)	0.0134(10)	0.0354(9)	-0.0016(8)	0.0142(7)	0.0039(8)
N(1A)	0.0267(10)	0.0103(11)	0.0324(10)	0.0007(8)	0.0098(8)	-0.0002(8)
N(2A)	0.0344(11)	0.0144(12)	0.0287(10)	-0.0009(9)	0.0097(9)	-0.0012(9)
N(3A)	0.0528(13)	0.0273(14)	0.0558(13)	0.0032(11)	0.0324(11)	0.0062(11)
N(4A)	0.0325(10)	0.0122(11)	0.0275(10)	-0.0027(8)	0.0045(8)	-0.0021(8)
N(5A)	0.0263(9)	0.0178(12)	0.0218(9)	-0.0016(8)	0.0077(7)	-0.0033(9)
C(1A)	0.0198(10)	0.0150(12)	0.0210(10)	-0.0016(9)	0.0045(8)	0.0006(9)
C(2A)	0.0226(10)	0.0146(13)	0.0236(10)	0.0010(9)	0.0029(8)	0.0025(9)
C(3A)	0.0202(10)	0.0134(12)	0.0218(10)	-0.0027(9)	0.0023(8)	0.0007(9)
C(4A)	0.0236(11)	0.0147(12)	0.0221(10)	0.0024(9)	0.0037(8)	-0.0017(9)
C(5A)	0.0205(10)	0.0139(13)	0.0185(10)	-0.0003(9)	0.0042(8)	0.0002(9)
C(6A)	0.0226(10)	0.0103(12)	0.0199(10)	0.0016(9)	0.0020(8)	-0.0008(9)
C(7A)	0.0230(10)	0.0139(12)	0.0188(10)	0.0013(9)	0.0006(8)	-0.0019(9)
C(8A)	0.0317(11)	0.0149(13)	0.0335(11)	0.0028(9)	0.0111(9)	0.0024(10)
C(9A)	0.0272(11)	0.0140(13)	0.0258(11)	0.0016(10)	0.0102(9)	0.0001(10)
C(10A)	0.0307(12)	0.0139(12)	0.0386(13)	-0.0061(11)	-0.0030(10)	0.0035(10)
C(11A)	0.0412(13)	0.0227(14)	0.0283(12)	0.0023(10)	-0.0064(10)	-0.0003(11)
C(12A)	0.0299(11)	0.0225(13)	0.0249(11)	-0.0058(10)	0.0039(9)	-0.0051(10)
C(13A)	0.0417(13)	0.0193(15)	0.0285(12)	-0.0033(10)	0.0027(10)	0.0047(11)
C(14A)	0.0513(15)	0.0163(15)	0.0280(13)	-0.0012(10)	0.0035(11)	-0.0025(12)
C(15A)	0.0507(13)	0.0364(15)	0.0370(12)	-0.0092(11)	0.0015(10)	0.0051(11)
C(16A)	0.0547(19)	0.096(3)	0.069(2)	-0.049(2)	0.0225(17)	-0.034(2)
C(17A)	0.087(3)	0.059(2)	0.0405(16)	-0.0071(16)	-0.0105(16)	0.009(2)
O(1B)	0.0312(9)	0.0115(9)	0.0302(9)	-0.0016(7)	0.0110(7)	0.0027(7)
O(2B)	0.0314(8)	0.0147(9)	0.0274(8)	-0.0006(7)	0.0023(6)	-0.0001(8)
O(3B)	0.0378(10)	0.0405(12)	0.0241(8)	0.0047(8)	0.0054(7)	0.0023(8)
O(4B)	0.0303(9)	0.0438(12)	0.0351(9)	0.0124(9)	0.0083(7)	0.0088(9)
O(5B)	0.0417(10)	0.0187(10)	0.0362(9)	-0.0017(8)	0.0187(8)	0.0039(8)
O(6B)	0.0330(9)	0.0128(10)	0.0328(9)	0.0029(8)	0.0117(7)	0.0000(7)
N(1B)	0.0292(10)	0.0166(12)	0.0310(10)	0.0034(8)	0.0102(8)	0.0010(9)
N(2B)	0.0325(11)	0.0084(11)	0.0253(10)	0.0000(8)	0.0090(9)	0.0039(9)
N(3B)	0.0574(14)	0.0263(14)	0.0560(14)	-0.0030(11)	0.0365(12)	-0.0120(11)
N(4B)	0.0288(9)	0.0126(11)	0.0247(9)	0.0013(8)	0.0046(7)	-0.0018(8)
N(5B)	0.0252(9)	0.0118(10)	0.0253(9)	0.0009(8)	0.0051(7)	0.0010(9)
C(1B)	0.0222(11)	0.0153(12)	0.0221(10)	-0.0022(9)	0.0020(8)	0.0018(10)

C(2B)	0.0221(10)	0.0147(12)	0.0224(10)	0.0009(9)	0.0057(8)	-0.0009(9)
C(3B)	0.0228(11)	0.0132(13)	0.0213(10)	-0.0029(10)	-0.0005(8)	-0.0006(9)
C(4B)	0.0207(10)	0.0145(13)	0.0226(10)	-0.0017(9)	0.0032(8)	0.0011(9)
C(5B)	0.0216(10)	0.0137(13)	0.0204(11)	-0.0009(9)	0.0028(8)	0.0011(9)
C(6B)	0.0206(10)	0.0159(12)	0.0199(10)	0.0031(9)	0.0030(8)	-0.0029(10)
C(7B)	0.0230(11)	0.0154(12)	0.0238(11)	-0.0021(10)	0.0045(8)	0.0026(10)
C(8B)	0.0335(12)	0.0128(13)	0.0398(13)	-0.0019(10)	0.0125(10)	-0.0012(10)
C(9B)	0.0209(10)	0.0124(13)	0.0248(11)	0.0016(9)	0.0081(8)	0.0000(9)
C(10B)	0.0292(11)	0.0271(15)	0.0293(12)	0.0048(11)	-0.0003(9)	-0.0079(11)
C(11B)	0.0354(12)	0.0251(14)	0.0304(12)	-0.0009(11)	0.0004(10)	-0.0042(11)
C(12B)	0.0300(12)	0.0331(15)	0.0262(11)	0.0004(11)	0.0068(9)	0.0008(11)
C(13B)	0.0337(12)	0.0244(15)	0.0285(12)	0.0094(10)	0.0082(10)	0.0002(11)
C(14B)	0.0408(13)	0.0113(13)	0.0279(12)	0.0043(9)	0.0081(10)	0.0036(10)
C(15B)	0.0379(11)	0.0263(12)	0.0295(10)	0.0032(9)	-0.0040(8)	-0.0028(9)
C(16B)	0.0360(13)	0.0440(16)	0.0385(13)	0.0191(12)	0.0009(10)	0.0109(12)
C(17B)	0.0706(19)	0.0430(18)	0.0320(13)	0.0061(13)	0.0064(12)	0.0004(15)

Table 4. Bond lengths [Å] for nd1236.

atom-atom	distance	atom-atom	distance
O(1A)-C(7A)	1.343(3)	O(1A)-N(1A)	1.437(3)
O(2A)-C(9A)	1.232(3)	O(3A)-C(12A)	1.414(3)
O(3A)-C(15A)	1.448(3)	O(4A)-C(12A)	1.421(3)
O(4A)-C(16A)	1.422(4)	O(5A)-N(5A)	1.221(3)
O(6A)-N(5A)	1.231(3)	N(1A)-C(1A)	1.315(3)
N(2A)-C(7A)	1.311(3)	N(3A)-C(8A)	1.144(3)
N(4A)-C(9A)	1.335(3)	N(4A)-C(14A)	1.463(3)
N(4A)-C(10A)	1.477(3)	N(5A)-C(5A)	1.475(3)
C(1A)-C(6A)	1.428(3)	C(1A)-C(2A)	1.435(3)
C(2A)-C(3A)	1.384(3)	C(2A)-C(8A)	1.432(3)
C(3A)-C(4A)	1.414(3)	C(3A)-C(9A)	1.508(4)
C(4A)-C(5A)	1.360(3)	C(4A)-H(4A)	0.9500
C(5A)-C(6A)	1.401(3)	C(6A)-C(7A)	1.423(3)
C(10A)-C(11A)	1.516(4)	C(11A)-C(12A)	1.522(4)
C(12A)-C(13A)	1.523(4)	C(13A)-C(14A)	1.525(3)
C(15A)-C(17A)	1.493(4)	C(15A)-C(16A)	1.497(4)
O(1B)-C(7B)	1.340(3)	O(1B)-N(1B)	1.437(3)
O(2B)-C(9B)	1.236(3)	O(3B)-C(12B)	1.418(3)
O(3B)-C(15B)	1.439(3)	O(4B)-C(16B)	1.428(3)
O(4B)-C(12B)	1.435(3)	O(5B)-N(5B)	1.221(3)
O(6B)-N(5B)	1.234(3)	N(1B)-C(1B)	1.319(3)
N(2B)-C(7B)	1.326(3)	N(3B)-C(8B)	1.146(3)
N(4B)-C(9B)	1.333(3)	N(4B)-C(10B)	1.472(3)
N(4B)-C(14B)	1.474(3)	N(5B)-C(5B)	1.449(3)
C(1B)-C(6B)	1.426(3)	C(1B)-C(2B)	1.434(4)
C(2B)-C(3B)	1.376(3)	C(2B)-C(8B)	1.439(3)
C(3B)-C(4B)	1.409(3)	C(3B)-C(9B)	1.518(3)
C(4B)-C(5B)	1.370(3)	C(4B)-H(4B)	0.9500
C(5B)-C(6B)	1.429(3)	C(6B)-C(7B)	1.394(4)
C(10B)-C(11B)	1.519(3)	C(11B)-C(12B)	1.504(4)
C(12B)-C(13B)	1.520(4)	C(13B)-C(14B)	1.522(3)
C(15B)-C(17B)	1.494(4)	C(15B)-C(16B)	1.508(4)
N(2A)-H(2AA)	0.89(3)	N(2A)-H(2AB)	0.93(3)
C(10A)-H(10A)	0.9900	C(10A)-H(10B)	0.9900
C(11A)-H(11A)	0.9900	C(11A)-H(11B)	0.9900
C(13A)-H(13A)	0.9900	C(13A)-H(13B)	0.9900
C(14A)-H(14A)	0.9900	C(14A)-H(14B)	0.9900
C(15A)-H(15A)	1.0000	C(16A)-H(16A)	0.9900
C(16A)-H(16B)	0.9900	C(17A)-H(17D)	0.9800
C(17A)-H(17E)	0.9800	C(17A)-H(17F)	0.9800
N(2B)-H(2BA)	0.88(4)	N(2B)-H(2BB)	0.78(3)
C(10B)-H(10C)	0.9900	C(10B)-H(10D)	0.9900

C(11B)-H(11C)	0.9900	C(11B)-H(11D)	0.9900
C(13B)-H(13C)	0.9900	C(13B)-H(13D)	0.9900
C(14B)-H(14C)	0.9900	C(14B)-H(14D)	0.9900
C(15B)-H(15B)	1.0000	C(16B)-H(16C)	0.9900
C(16B)-H(16D)	0.9900	C(17B)-H(17A)	0.9800
C(17B)-H(17B)	0.9800	C(17B)-H(17C)	0.9800

Symmetry transformations used to generate equivalent atoms:

Table 5. Bond angles [°] for nd1236.

atom-atom-atom	angle	atom-atom-atom	angle
C(7A)-O(1A)-N(1A)	111.64(18)	C(12A)-O(3A)-C(15A)	106.0(2)
C(12A)-O(4A)-C(16A)	107.9(2)	C(1A)-N(1A)-O(1A)	102.97(17)
C(9A)-N(4A)-C(14A)	121.0(2)	C(9A)-N(4A)-C(10A)	124.8(2)
C(14A)-N(4A)-C(10A)	113.8(2)	O(5A)-N(5A)-O(6A)	124.1(2)
O(5A)-N(5A)-C(5A)	119.1(2)	O(6A)-N(5A)-C(5A)	116.8(2)
N(1A)-C(1A)-C(6A)	114.7(2)	N(1A)-C(1A)-C(2A)	125.0(2)
C(6A)-C(1A)-C(2A)	120.3(2)	C(3A)-C(2A)-C(8A)	122.9(2)
C(3A)-C(2A)-C(1A)	118.6(2)	C(8A)-C(2A)-C(1A)	118.5(2)
C(2A)-C(3A)-C(4A)	120.7(2)	C(2A)-C(3A)-C(9A)	120.8(2)
C(4A)-C(3A)-C(9A)	118.5(2)	C(5A)-C(4A)-C(3A)	120.3(2)
C(4A)-C(5A)-C(6A)	122.0(2)	C(4A)-C(5A)-N(5A)	116.4(2)
C(6A)-C(5A)-N(5A)	121.5(2)	C(5A)-C(6A)-C(7A)	139.3(2)
C(5A)-C(6A)-C(1A)	117.9(2)	C(7A)-C(6A)-C(1A)	102.8(2)
N(2A)-C(7A)-O(1A)	116.1(2)	N(2A)-C(7A)-C(6A)	135.9(2)
O(1A)-C(7A)-C(6A)	107.9(2)	N(3A)-C(8A)-C(2A)	177.2(3)
O(2A)-C(9A)-N(4A)	124.4(3)	O(2A)-C(9A)-C(3A)	118.7(2)
N(4A)-C(9A)-C(3A)	116.9(2)	N(4A)-C(10A)-C(11A)	110.5(2)
C(10A)-C(11A)-C(12A)	109.9(2)	O(3A)-C(12A)-O(4A)	105.26(18)
O(3A)-C(12A)-C(11A)	109.9(2)	O(4A)-C(12A)-C(11A)	109.2(2)
O(3A)-C(12A)-C(13A)	111.0(2)	O(4A)-C(12A)-C(13A)	110.9(2)
C(11A)-C(12A)-C(13A)	110.5(2)	C(12A)-C(13A)-C(14A)	111.2(2)
N(4A)-C(14A)-C(13A)	110.7(2)	O(3A)-C(15A)-C(17A)	109.1(3)
O(3A)-C(15A)-C(16A)	104.4(2)	C(17A)-C(15A)-C(16A)	115.5(3)
O(4A)-C(16A)-C(15A)	105.8(3)	C(7B)-O(1B)-N(1B)	110.95(18)
C(12B)-O(3B)-C(15B)	108.73(17)	C(16B)-O(4B)-C(12B)	106.34(19)
C(1B)-N(1B)-O(1B)	102.80(18)	C(9B)-N(4B)-C(10B)	125.1(2)
C(9B)-N(4B)-C(14B)	120.5(2)	C(10B)-N(4B)-C(14B)	114.0(2)
O(5B)-N(5B)-O(6B)	123.1(2)	O(5B)-N(5B)-C(5B)	119.4(2)
O(6B)-N(5B)-C(5B)	117.4(2)	N(1B)-C(1B)-C(6B)	114.2(2)
N(1B)-C(1B)-C(2B)	124.5(2)	C(6B)-C(1B)-C(2B)	121.2(2)
C(3B)-C(2B)-C(1B)	118.8(2)	C(3B)-C(2B)-C(8B)	122.5(2)
C(1B)-C(2B)-C(8B)	118.6(2)	C(2B)-C(3B)-C(4B)	121.0(2)
C(2B)-C(3B)-C(9B)	121.0(2)	C(4B)-C(3B)-C(9B)	118.0(2)
C(5B)-C(4B)-C(3B)	120.3(2)	C(4B)-C(5B)-C(6B)	122.0(2)
C(4B)-C(5B)-N(5B)	117.4(2)	C(6B)-C(5B)-N(5B)	120.5(2)
C(7B)-C(6B)-C(1B)	103.1(2)	C(7B)-C(6B)-C(5B)	140.4(2)
C(1B)-C(6B)-C(5B)	116.5(2)	N(2B)-C(7B)-O(1B)	115.7(2)
N(2B)-C(7B)-C(6B)	135.4(2)	O(1B)-C(7B)-C(6B)	108.9(2)
N(3B)-C(8B)-C(2B)	177.5(3)	O(2B)-C(9B)-N(4B)	125.5(2)
O(2B)-C(9B)-C(3B)	119.0(2)	N(4B)-C(9B)-C(3B)	115.5(2)
N(4B)-C(10B)-C(11B)	109.3(2)	C(12B)-C(11B)-C(10B)	111.5(2)
O(3B)-C(12B)-O(4B)	106.28(19)	O(3B)-C(12B)-C(11B)	111.8(2)

O(4B)-C(12B)-C(11B)	108.2(2)	O(3B)-C(12B)-C(13B)	109.4(2)
O(4B)-C(12B)-C(13B)	110.2(2)	C(11B)-C(12B)-C(13B)	110.8(2)
C(12B)-C(13B)-C(14B)	111.8(2)	N(4B)-C(14B)-C(13B)	110.1(2)
O(3B)-C(15B)-C(17B)	108.6(2)	O(3B)-C(15B)-C(16B)	101.39(18)
C(17B)-C(15B)-C(16B)	116.7(2)	O(4B)-C(16B)-C(15B)	102.3(2)
C(7A)-N(2A)-H(2AA)	117.7(18)	C(7A)-N(2A)-H(2AB)	120(2)
H(2AA)-N(2A)-H(2AB)	122(3)	C(5A)-C(4A)-H(4A)	119.9
C(3A)-C(4A)-H(4A)	119.9	N(4A)-C(10A)-H(10A)	109.5
C(11A)-C(10A)-H(10A)	109.5	N(4A)-C(10A)-H(10B)	109.5
C(11A)-C(10A)-H(10B)	109.5	H(10A)-C(10A)-H(10B)	108.1
C(10A)-C(11A)-H(11A)	109.7	C(12A)-C(11A)-H(11A)	109.7
C(10A)-C(11A)-H(11B)	109.7	C(12A)-C(11A)-H(11B)	109.7
H(11A)-C(11A)-H(11B)	108.2	C(12A)-C(13A)-H(13A)	109.4
C(14A)-C(13A)-H(13A)	109.4	C(12A)-C(13A)-H(13B)	109.4
C(14A)-C(13A)-H(13B)	109.4	H(13A)-C(13A)-H(13B)	108.0
N(4A)-C(14A)-H(14A)	109.5	C(13A)-C(14A)-H(14A)	109.5
N(4A)-C(14A)-H(14B)	109.5	C(13A)-C(14A)-H(14B)	109.5
H(14A)-C(14A)-H(14B)	108.1	O(3A)-C(15A)-H(15A)	109.2
C(17A)-C(15A)-H(15A)	109.2	C(16A)-C(15A)-H(15A)	109.2
O(4A)-C(16A)-H(16A)	110.6	C(15A)-C(16A)-H(16A)	110.6
O(4A)-C(16A)-H(16B)	110.6	C(15A)-C(16A)-H(16B)	110.6
H(16A)-C(16A)-H(16B)	108.7	C(15A)-C(17A)-H(17D)	109.5
C(15A)-C(17A)-H(17E)	109.5	H(17D)-C(17A)-H(17E)	109.5
C(15A)-C(17A)-H(17F)	109.5	H(17D)-C(17A)-H(17F)	109.5
H(17E)-C(17A)-H(17F)	109.5	C(7B)-N(2B)-H(2BA)	114(2)
C(7B)-N(2B)-H(2BB)	121(2)	H(2BA)-N(2B)-H(2BB)	125(3)
C(5B)-C(4B)-H(4B)	119.9	C(3B)-C(4B)-H(4B)	119.9
N(4B)-C(10B)-H(10C)	109.8	C(11B)-C(10B)-H(10C)	109.8
N(4B)-C(10B)-H(10D)	109.8	C(11B)-C(10B)-H(10D)	109.8
H(10C)-C(10B)-H(10D)	108.3	C(12B)-C(11B)-H(11C)	109.3
C(10B)-C(11B)-H(11C)	109.3	C(12B)-C(11B)-H(11D)	109.3
C(10B)-C(11B)-H(11D)	109.3	H(11C)-C(11B)-H(11D)	108.0
C(12B)-C(13B)-H(13C)	109.3	C(14B)-C(13B)-H(13C)	109.3
C(12B)-C(13B)-H(13D)	109.3	C(14B)-C(13B)-H(13D)	109.3
H(13C)-C(13B)-H(13D)	107.9	N(4B)-C(14B)-H(14C)	109.6
C(13B)-C(14B)-H(14C)	109.6	N(4B)-C(14B)-H(14D)	109.6
C(13B)-C(14B)-H(14D)	109.6	H(14C)-C(14B)-H(14D)	108.1
O(3B)-C(15B)-H(15B)	109.9	C(17B)-C(15B)-H(15B)	109.9
C(16B)-C(15B)-H(15B)	109.9	O(4B)-C(16B)-H(16C)	111.3
C(15B)-C(16B)-H(16C)	111.3	O(4B)-C(16B)-H(16D)	111.3
C(15B)-C(16B)-H(16D)	111.3	H(16C)-C(16B)-H(16D)	109.2
C(15B)-C(17B)-H(17A)	109.5	C(15B)-C(17B)-H(17B)	109.5
H(17A)-C(17B)-H(17B)	109.5	C(15B)-C(17B)-H(17C)	109.5
H(17A)-C(17B)-H(17C)	109.5	H(17B)-C(17B)-H(17C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [°] for nd1236.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(7A)-O(1A)-N(1A)-C(1A)	-0.1(2)	O(1A)-N(1A)-C(1A)-C(6A)	0.7(2)
O(1A)-N(1A)-C(1A)-C(2A)	-177.4(2)	N(1A)-C(1A)-C(2A)-C(3A)	-178.7(2)
C(6A)-C(1A)-C(2A)-C(3A)	3.4(3)	N(1A)-C(1A)-C(2A)-C(8A)	2.8(4)
C(6A)-C(1A)-C(2A)-C(8A)	-175.2(2)	C(8A)-C(2A)-C(3A)-C(4A)	178.9(2)
C(1A)-C(2A)-C(3A)-C(4A)	0.5(3)	C(8A)-C(2A)-C(3A)-C(9A)	-1.4(4)
C(1A)-C(2A)-C(3A)-C(9A)	-179.8(2)	C(2A)-C(3A)-C(4A)-C(5A)	-3.1(3)
C(9A)-C(3A)-C(4A)-C(5A)	177.2(2)	C(3A)-C(4A)-C(5A)-C(6A)	1.8(4)
C(3A)-C(4A)-C(5A)-N(5A)	-173.97(18)	O(5A)-N(5A)-C(5A)-C(4A)	-19.5(3)
O(6A)-N(5A)-C(5A)-C(4A)	158.7(2)	O(5A)-N(5A)-C(5A)-C(6A)	164.7(2)
O(6A)-N(5A)-C(5A)-C(6A)	-17.1(3)	C(4A)-C(5A)-C(6A)-C(7A)	179.4(3)
N(5A)-C(5A)-C(6A)-C(7A)	-5.0(4)	C(4A)-C(5A)-C(6A)-C(1A)	2.0(3)
N(5A)-C(5A)-C(6A)-C(1A)	177.53(18)	N(1A)-C(1A)-C(6A)-C(5A)	177.3(2)
C(2A)-C(1A)-C(6A)-C(5A)	-4.5(3)	N(1A)-C(1A)-C(6A)-C(7A)	-1.0(3)
C(2A)-C(1A)-C(6A)-C(7A)	177.1(2)	N(1A)-O(1A)-C(7A)-N(2A)	179.72(19)
N(1A)-O(1A)-C(7A)-C(6A)	-0.6(2)	C(5A)-C(6A)-C(7A)-N(2A)	2.8(5)
C(1A)-C(6A)-C(7A)-N(2A)	-179.5(3)	C(5A)-C(6A)-C(7A)-O(1A)	-176.8(3)
C(1A)-C(6A)-C(7A)-O(1A)	0.9(2)	C(3A)-C(2A)-C(8A)-N(3A)	-150(6)
C(1A)-C(2A)-C(8A)-N(3A)	28(6)	C(14A)-N(4A)-C(9A)-O(2A)	2.4(4)
C(10A)-N(4A)-C(9A)-O(2A)	-170.1(2)	C(14A)-N(4A)-C(9A)-C(3A)	-178.5(2)
C(10A)-N(4A)-C(9A)-C(3A)	8.9(3)	C(2A)-C(3A)-C(9A)-O(2A)	-99.4(3)
C(4A)-C(3A)-C(9A)-O(2A)	80.3(3)	C(2A)-C(3A)-C(9A)-N(4A)	81.5(3)
C(4A)-C(3A)-C(9A)-N(4A)	-98.8(3)	C(9A)-N(4A)-C(10A)-C(11A)	-129.4(2)
C(14A)-N(4A)-C(10A)-C(11A)	57.5(3)	N(4A)-C(10A)-C(11A)-C(12A)	-56.7(3)
C(15A)-O(3A)-C(12A)-O(4A)	33.5(3)	C(15A)-O(3A)-C(12A)-C(11A)	151.0(2)
C(15A)-O(3A)-C(12A)-C(13A)	-86.5(2)	C(16A)-O(4A)-C(12A)-O(3A)	-28.1(4)
C(16A)-O(4A)-C(12A)-C(11A)	-146.0(3)	C(16A)-O(4A)-C(12A)-C(13A)	92.0(3)
C(10A)-C(11A)-C(12A)-O(3A)	179.10(19)	C(10A)-C(11A)-C(12A)-O(4A)	-65.9(3)
C(10A)-C(11A)-C(12A)-C(13A)	56.3(3)	O(3A)-C(12A)-C(13A)-C(14A)	-177.1(2)
O(4A)-C(12A)-C(13A)-C(14A)	66.3(3)	C(11A)-C(12A)-C(13A)-C(14A)	-54.9(3)
C(9A)-N(4A)-C(14A)-C(13A)	131.2(2)	C(10A)-N(4A)-C(14A)-C(13A)	-55.5(3)
C(12A)-C(13A)-C(14A)-N(4A)	53.6(3)	C(12A)-O(3A)-C(15A)-C(17A)	-149.9(3)
C(12A)-O(3A)-C(15A)-C(16A)	-25.9(3)	C(12A)-O(4A)-C(16A)-C(15A)	11.6(4)
O(3A)-C(15A)-C(16A)-O(4A)	8.7(4)	C(17A)-C(15A)-C(16A)-O(4A)	128.5(3)
C(7B)-O(1B)-N(1B)-C(1B)	-0.1(2)	O(1B)-N(1B)-C(1B)-C(6B)	-0.5(2)
O(1B)-N(1B)-C(1B)-C(2B)	178.6(2)	N(1B)-C(1B)-C(2B)-C(3B)	179.6(2)
C(6B)-C(1B)-C(2B)-C(3B)	-1.4(3)	N(1B)-C(1B)-C(2B)-C(8B)	-2.3(4)
C(6B)-C(1B)-C(2B)-C(8B)	176.7(2)	C(1B)-C(2B)-C(3B)-C(4B)	-1.8(3)
C(8B)-C(2B)-C(3B)-C(4B)	-179.8(2)	C(1B)-C(2B)-C(3B)-C(9B)	178.0(2)
C(8B)-C(2B)-C(3B)-C(9B)	0.0(4)	C(2B)-C(3B)-C(4B)-C(5B)	3.5(3)
C(9B)-C(3B)-C(4B)-C(5B)	-176.3(2)	C(3B)-C(4B)-C(5B)-C(6B)	-2.0(3)
C(3B)-C(4B)-C(5B)-N(5B)	175.06(19)	O(5B)-N(5B)-C(5B)-C(4B)	18.7(3)
O(6B)-N(5B)-C(5B)-C(4B)	-159.0(2)	O(5B)-N(5B)-C(5B)-C(6B)	-164.2(2)

O(6B)-N(5B)-C(5B)-C(6B)	18.1(3)	N(1B)-C(1B)-C(6B)-C(7B)	0.8(3)
C(2B)-C(1B)-C(6B)-C(7B)	-178.3(2)	N(1B)-C(1B)-C(6B)-C(5B)	-178.07(19)
C(2B)-C(1B)-C(6B)-C(5B)	2.9(3)	C(4B)-C(5B)-C(6B)-C(7B)	-179.4(3)
N(5B)-C(5B)-C(6B)-C(7B)	3.7(4)	C(4B)-C(5B)-C(6B)-C(1B)	-1.2(3)
N(5B)-C(5B)-C(6B)-C(1B)	-178.11(18)	N(1B)-O(1B)-C(7B)-N(2B)	-178.99(19)
N(1B)-O(1B)-C(7B)-C(6B)	0.6(2)	C(1B)-C(6B)-C(7B)-N(2B)	178.7(3)
C(5B)-C(6B)-C(7B)-N(2B)	-3.0(5)	C(1B)-C(6B)-C(7B)-O(1B)	-0.8(2)
C(5B)-C(6B)-C(7B)-O(1B)	177.6(3)	C(3B)-C(2B)-C(8B)-N(3B)	170(7)
C(1B)-C(2B)-C(8B)-N(3B)	-8(7)	C(10B)-N(4B)-C(9B)-O(2B)	168.9(2)
C(14B)-N(4B)-C(9B)-O(2B)	-3.3(3)	C(10B)-N(4B)-C(9B)-C(3B)	-12.1(3)
C(14B)-N(4B)-C(9B)-C(3B)	175.7(2)	C(2B)-C(3B)-C(9B)-O(2B)	95.8(3)
C(4B)-C(3B)-C(9B)-O(2B)	-84.4(3)	C(2B)-C(3B)-C(9B)-N(4B)	-83.2(3)
C(4B)-C(3B)-C(9B)-N(4B)	96.6(2)	C(9B)-N(4B)-C(10B)-C(11B)	129.3(2)
C(14B)-N(4B)-C(10B)-C(11B)	-58.0(3)	N(4B)-C(10B)-C(11B)-C(12B)	56.4(3)
C(15B)-O(3B)-C(12B)-O(4B)	5.8(3)	C(15B)-O(3B)-C(12B)-C(11B)	-112.1(2)
C(15B)-O(3B)-C(12B)-C(13B)	124.8(2)	C(16B)-O(4B)-C(12B)-O(3B)	19.3(3)
C(16B)-O(4B)-C(12B)-C(11B)	139.5(2)	C(16B)-O(4B)-C(12B)-C(13B)	-99.2(3)
C(10B)-C(11B)-C(12B)-O(3B)	-177.17(19)	C(10B)-C(11B)-C(12B)-O(4B)	66.1(3)
C(10B)-C(11B)-C(12B)-C(13B)	-54.9(3)	O(3B)-C(12B)-C(13B)-C(14B)	176.8(2)
O(4B)-C(12B)-C(13B)-C(14B)	-66.7(3)	C(11B)-C(12B)-C(13B)-C(14B)	53.1(3)
C(9B)-N(4B)-C(14B)-C(13B)	-130.5(2)	C(10B)-N(4B)-C(14B)-C(13B)	56.5(3)
C(12B)-C(13B)-C(14B)-N(4B)	-52.9(3)	C(12B)-O(3B)-C(15B)-C(17B)	-150.3(2)
C(12B)-O(3B)-C(15B)-C(16B)	-26.8(3)	C(12B)-O(4B)-C(16B)-C(15B)	-35.4(3)
O(3B)-C(15B)-C(16B)-O(4B)	37.6(2)	C(17B)-C(15B)-C(16B)-O(4B)	155.3(2)

Symmetry transformations used to generate equivalent atoms:

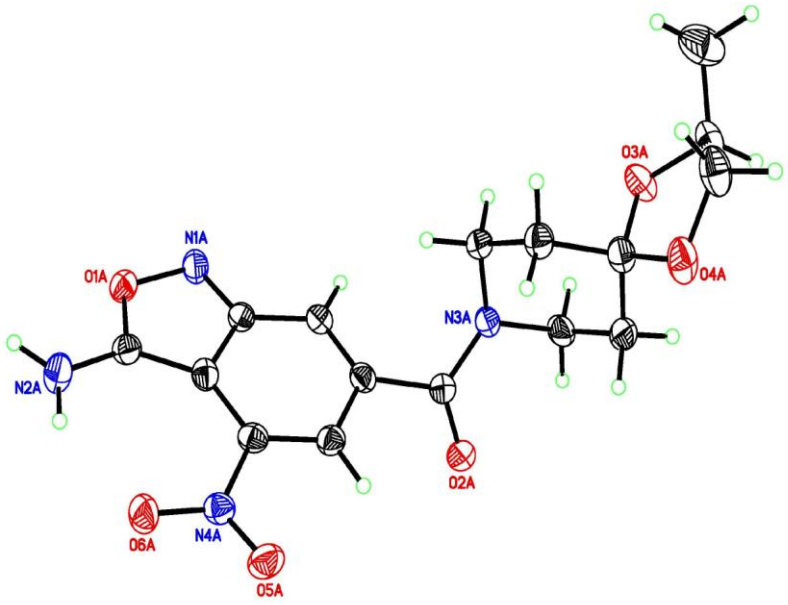
Table 7. Hydrogen bonds for nd1236 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2A)-H(2AA)...O(2A)#1	0.89(3)	2.06(3)	2.946(3)	173(2)
N(2A)-H(2AB)...O(6A)	0.93(3)	2.10(3)	2.803(3)	131(3)
N(2A)-H(2AB)...O(6B)#2	0.93(3)	2.18(3)	3.020(3)	151(3)
N(2B)-H(2BA)...O(2B)#3	0.88(4)	2.07(4)	2.932(3)	169(3)
N(2B)-H(2BB)...O(6A)#4	0.78(3)	2.29(3)	3.013(3)	155(3)
N(2B)-H(2BB)...O(6B)	0.78(3)	2.22(3)	2.798(3)	131(3)

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z #2 -x+1,y-1/2,-z #3 x,y+1,z #4 -x+1,y+1/2,-z

X-ray Structure Report

for compound **31 (nd1237)**



DISCUSSION

The compound crystallizes as dark red blocks. There are two crystallographically independent molecules of the compound in the asymmetric unit of the primitive, acentric, monoclinic space group $P2_1$. The correct enantiomer of the compound and enantiomorph of the space group were determined by comparison of the known handedness of the molecule and by comparison of intensities of Friedel pairs of reflections. The measurement of intensity differences agreed with the known configuration. The Flack *x* parameter is 0.06(17) and the Hooft *y* parameter, based on Bayesian statistical analysis of the reflections is 0.10(5). Values of zero are indicative of the correct configuration.

The structure of the molecules is analogous to compound **32**. Although there are two crystallographically independent molecules in the asymmetric unit, they are chemically identical. The connectivity and variation of bond distances is also similar. The tautomer is depicted in the appended ChemDraw Figure. Examination of the structure reveals one difference compared with ND1236. The benzo-isoxazol ring systems of the two independent molecules form a π-π stacking interaction (ring – ring distance = 3.31Å). presumably lack of steric interference allows this favorable interaction.

The amino hydrogens (N2) on both molecules were located from a difference Fourier map and included in refined positions. As with the cyano analog, one hydrogen forms an intramolecular H-bond with a nitro oxygen. The remaining amino hydrogen forms an H-bond to the carbonyl oxygen, O2, of an adjacent molecule related by translation along the *b*-axis. Unlike the cyano adduct, this H-bond is to the same molecular species, and not to the other molecule in the asymmetric unit. The resulting motif is a pair of one-dimensional chains of each molecule that are oriented parallel to the b-axis with additional stacking from the weak π-π interactions (see Figures).

The bond distances and angles within the molecules exhibit the same variations as observed with the cyano-analog.

CRYSTAL SUMMARY

Crystal data for $C_{16}H_{18}N_4O_6$; M_r = 362.34; Monoclinic; space group $P2_1$; *a* = 9.66900(10) Å; *b* = 8.06660(10) Å; *c* = 20.7830(3) Å; α = 90°; β = 90.6040(10)°; γ = 90°; V = 1620.90(4) $Å^3$; Z = 4; T = 120(2) K; λ(Cu-Kα) = 1.54184 Å; μ(Cu-Kα) = 0.979 mm^{-1}; d_{calc} = 1.485g.cm^{-3}; 25993 reflections collected; 5760 unique (R_{int} = 0.0221); giving R_1 = 0.0393, wR_2 = 0.1100 for 5559 data with [I>2σ(I)] and R_1 = 0.0406, wR_2 = 0.1116 for all 5760 data. Residual electron density (e^-.$Å^{-3}$) max/min: 0.384/-0.250.

An arbitrary sphere of data were collected on a dark red block-like crystal, having approximate dimensions of 0.08 × 0.08 × 0.06 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.5°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement

parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

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Table 1. Crystal data and structure refinement for nd1237.

Identification code	nd1237
Empirical formula	$C_{16}H_{18}N_4O_6$
Formula weight	362.34
Temperature	120(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 9.66900(10) Å α = 90°
	b = 8.06660(10) Å β = 90.6040(10)°
	c = 20.7830(3) Å γ = 90°
Volume	1620.90(4) $Å^3$
Z	4
Density (calculated)	1.485 $g.cm^{-3}$
Absorption coefficient (μ)	0.979 mm^{-1}
F(000)	760
Crystal color, habit	dark red, block
Crystal size	0.08 × 0.08 × 0.06 mm^3
θ range for data collection	2.13 to 71.36°
Index ranges	$-11 \le h \le 11$, $-9 \le k \le 9$, $-25 \le l \le 22$
Reflections collected	25993
Independent reflections	5760 [R_{int} = 0.0221]
Completeness to θ = 71.36°	96.9 %
Absorption correction	Numerical
Max. and min. transmission	0.9907 and 0.9247
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5760 / 1 / 487
Goodness-of-fit on F^2	1.051
Final R indices [I>2σ(I)]	R_1 = 0.0393, wR_2 = 0.1100
R indices (all data)	R_1 = 0.0406, wR_2 = 0.1116
Absolute structure parameter	0.06(17)
Largest diff. peak and hole	0.384 and -0.250 $e^-.Å^{-3}$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for nd1237. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1A)	0.97602(15)	0.5268(2)	0.76550(8)	0.029(1)
O(2A)	0.29114(16)	0.5648(2)	0.80606(9)	0.036(1)
O(3A)	0.20879(19)	-0.0409(2)	0.92124(8)	0.034(1)
O(4A)	0.16671(18)	0.1301(3)	1.00691(8)	0.037(1)
O(5A)	0.63721(17)	0.9346(2)	0.92257(8)	0.033(1)
O(6A)	0.84021(16)	0.9394(2)	0.88079(9)	0.035(1)
N(1A)	0.86081(19)	0.4216(3)	0.75275(10)	0.029(1)
N(2A)	1.0425(2)	0.7537(3)	0.82162(10)	0.032(1)
N(3A)	0.34478(18)	0.3042(3)	0.83781(9)	0.027(1)
N(4A)	0.72547(19)	0.8760(3)	0.88854(9)	0.025(1)
C(1A)	0.7601(2)	0.4898(3)	0.78547(10)	0.024(1)
C(2A)	0.6223(2)	0.4267(3)	0.78907(11)	0.026(1)
C(3A)	0.5277(2)	0.5122(3)	0.82438(10)	0.024(1)
C(4A)	0.5633(2)	0.6636(3)	0.85619(10)	0.025(1)
C(5A)	0.6958(2)	0.7213(3)	0.85441(10)	0.024(1)
C(6A)	0.7996(2)	0.6375(3)	0.81934(10)	0.024(1)
C(7A)	0.9410(2)	0.6521(3)	0.80473(10)	0.026(1)
C(8A)	0.3772(2)	0.4627(3)	0.82342(10)	0.026(1)
C(9A)	0.1994(2)	0.2503(3)	0.83338(12)	0.031(1)
C(10A)	0.1364(2)	0.2398(3)	0.89993(13)	0.032(1)
C(11A)	0.2213(2)	0.1268(3)	0.94347(11)	0.029(1)
C(12A)	0.3737(2)	0.1766(3)	0.94379(11)	0.029(1)
C(13A)	0.4303(2)	0.1906(3)	0.87595(10)	0.026(1)
C(14A)	0.1519(2)	-0.1386(3)	0.97223(11)	0.032(1)
C(15A)	0.1784(3)	-0.0347(4)	1.03042(12)	0.038(1)
C(16A)	0.2189(4)	-0.3053(5)	0.97198(14)	0.052(1)
O(1B)	0.50694(15)	0.9211(2)	0.73712(8)	0.027(1)
O(2B)	1.19168(16)	0.8864(2)	0.69740(9)	0.035(1)
O(3B)	1.26680(16)	1.4994(2)	0.58171(8)	0.030(1)
O(4B)	1.31372(18)	1.3331(3)	0.49589(9)	0.038(1)
O(5B)	0.84579(16)	0.5173(3)	0.57779(8)	0.033(1)
O(6B)	0.63786(18)	0.5228(3)	0.61325(9)	0.042(1)
N(1B)	0.62214(18)	1.0261(3)	0.74966(9)	0.028(1)
N(2B)	0.44125(19)	0.6911(3)	0.68293(10)	0.029(1)
N(3B)	1.13701(18)	1.1455(3)	0.66329(9)	0.026(1)
N(4B)	0.75521(19)	0.5790(3)	0.60944(9)	0.028(1)
C(1B)	0.7226(2)	0.9581(3)	0.71585(10)	0.023(1)
C(2B)	0.8599(2)	1.0216(3)	0.71263(10)	0.025(1)
C(3B)	0.9554(2)	0.9378(3)	0.67790(11)	0.025(1)
C(4B)	0.9193(2)	0.7883(3)	0.64454(10)	0.025(1)
C(5B)	0.7865(2)	0.7302(3)	0.64634(10)	0.024(1)

C(6B)	0.6824(2)	0.8123(3)	0.68187(10)	0.022(1)
C(7B)	0.5420(2)	0.7959(3)	0.69744(10)	0.025(1)
C(8B)	1.1055(2)	0.9884(3)	0.67891(10)	0.025(1)
C(9B)	1.2799(2)	1.2046(3)	0.66965(11)	0.029(1)
C(10B)	1.3460(2)	1.2248(3)	0.60380(12)	0.030(1)
C(11B)	1.2588(2)	1.3330(3)	0.55959(11)	0.026(1)
C(12B)	1.1090(2)	1.2730(3)	0.55696(11)	0.027(1)
C(13B)	1.0489(2)	1.2569(3)	0.62438(10)	0.026(1)
C(14B)	1.2579(3)	1.6020(3)	0.52438(11)	0.036(1)
C(15B)	1.3403(3)	1.5016(4)	0.47750(14)	0.047(1)
C(16B)	1.3156(3)	1.7706(4)	0.53673(14)	0.043(1)
H(2NA)	1.129(4)	0.733(6)	0.8100(19)	0.073(12)
H(2NB)	1.016(2)	0.839(4)	0.8446(11)	0.018(6)
H(2A)	0.5970	0.3273	0.7674	0.031
H(4A)	0.4947	0.7241	0.8786	0.030
H(9A)	0.1943	0.1403	0.8123	0.038
H(9B)	0.1461	0.3299	0.8067	0.038
H(10A)	0.0407	0.1968	0.8963	0.039
H(10B)	0.1322	0.3521	0.9191	0.039
H(12A)	0.3844	0.2845	0.9660	0.035
H(12B)	0.4280	0.0930	0.9681	0.035
H(13A)	0.5267	0.2319	0.8778	0.032
H(13B)	0.4308	0.0799	0.8554	0.032
H(14A)	0.0499	-0.1513	0.9653	0.039
H(15A)	0.1090	-0.0568	1.0640	0.046
H(15B)	0.2719	-0.0557	1.0484	0.046
H(16A)	0.2059	-0.3568	0.9296	0.078
H(16B)	0.1767	-0.3754	1.0049	0.078
H(16C)	0.3180	-0.2933	0.9812	0.078
H(2NC)	0.356(3)	0.711(4)	0.6948(13)	0.035(7)
H(2ND)	0.456(3)	0.613(4)	0.6525(13)	0.031(7)
H(2B)	0.8843	1.1211	0.7344	0.030
H(4B)	0.9876	0.7296	0.6212	0.030
H(9C)	1.3344	1.1246	0.6956	0.034
H(9D)	1.2809	1.3124	0.6924	0.034
H(10C)	1.4388	1.2751	0.6092	0.036
H(10D)	1.3578	1.1143	0.5839	0.036
H(12C)	1.1048	1.1640	0.5351	0.032
H(12D)	1.0525	1.3522	0.5315	0.032
H(13C)	1.0444	1.3674	0.6450	0.031
H(13D)	0.9538	1.2116	0.6216	0.031
H(14B)	1.1596	1.6106	0.5093	0.043
H(15C)	1.3090	1.5226	0.4327	0.056
H(15D)	1.4401	1.5278	0.4812	0.056
H(16D)	1.2684	1.8207	0.5734	0.065
H(16E)	1.3015	1.8401	0.4985	0.065

H(16F)	1.4148	1.7620	0.5463	0.065

Table 3. Anisotropic displacement parameters ($Å^2$) for nd1237.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1A)	0.0239(7)	0.0291(9)	0.0325(8)	-0.0027(7)	0.0045(6)	0.0013(6)
O(2A)	0.0242(7)	0.0286(10)	0.0542(11)	0.0056(8)	0.0008(7)	0.0024(6)
O(3A)	0.0493(10)	0.0244(10)	0.0274(8)	-0.0008(7)	0.0089(7)	-0.0080(7)
O(4A)	0.0435(9)	0.0376(11)	0.0311(9)	-0.0118(8)	0.0155(7)	-0.0124(8)
O(5A)	0.0318(8)	0.0311(10)	0.0366(9)	-0.0078(8)	0.0028(7)	0.0055(7)
O(6A)	0.0273(8)	0.0318(9)	0.0460(10)	-0.0122(8)	0.0032(7)	-0.0065(7)
N(1A)	0.0251(9)	0.0298(11)	0.0327(10)	-0.0011(8)	0.0037(7)	-0.0044(8)
N(2A)	0.0233(9)	0.0391(13)	0.0346(11)	-0.0059(10)	0.0019(8)	-0.0028(8)
N(3A)	0.0219(8)	0.0251(11)	0.0332(10)	0.0069(8)	0.0009(7)	-0.0017(7)
N(4A)	0.0261(9)	0.0233(10)	0.0259(9)	-0.0027(8)	-0.0031(7)	0.0008(7)
C(1A)	0.0237(9)	0.0237(12)	0.0250(10)	0.0038(9)	0.0009(8)	0.0006(8)
C(2A)	0.0257(10)	0.0222(12)	0.0308(11)	0.0030(9)	0.0006(8)	-0.0016(8)
C(3A)	0.0245(10)	0.0226(12)	0.0259(10)	0.0051(9)	0.0001(8)	-0.0019(8)
C(4A)	0.0242(9)	0.0249(12)	0.0247(10)	0.0028(8)	0.0005(8)	0.0022(8)
C(5A)	0.0273(10)	0.0225(12)	0.0235(10)	0.0037(9)	-0.0024(8)	0.0018(8)
C(6A)	0.0230(9)	0.0265(12)	0.0224(10)	0.0050(9)	-0.0018(8)	-0.0019(8)
C(7A)	0.0256(10)	0.0248(12)	0.0269(10)	0.0009(9)	0.0000(8)	0.0018(9)
C(8A)	0.0239(10)	0.0241(13)	0.0286(11)	-0.0001(9)	0.0019(8)	-0.0005(9)
C(9A)	0.0248(10)	0.0253(13)	0.0438(13)	0.0046(10)	-0.0048(9)	-0.0055(9)
C(10A)	0.0231(9)	0.0240(12)	0.0504(14)	-0.0063(10)	0.0042(9)	-0.0042(8)
C(11A)	0.0327(11)	0.0249(12)	0.0289(11)	-0.0076(10)	0.0091(9)	-0.0061(9)
C(12A)	0.0286(10)	0.0310(13)	0.0276(11)	0.0006(10)	0.0034(9)	-0.0014(9)
C(13A)	0.0230(9)	0.0257(12)	0.0307(11)	0.0055(9)	0.0030(8)	0.0019(8)
C(14A)	0.0317(11)	0.0343(12)	0.0315(11)	0.0079(9)	0.0004(9)	-0.0097(10)
C(15A)	0.0426(13)	0.0437(16)	0.0290(12)	-0.0059(11)	0.0046(10)	-0.0174(11)
C(16A)	0.077(2)	0.0425(18)	0.0373(14)	0.0080(12)	-0.0014(14)	0.0039(15)
O(1B)	0.0216(7)	0.0261(9)	0.0324(8)	-0.0045(7)	0.0032(6)	0.0005(6)
O(2B)	0.0236(7)	0.0257(10)	0.0564(11)	0.0085(8)	0.0025(7)	0.0015(6)
O(3B)	0.0346(8)	0.0201(9)	0.0359(8)	-0.0002(7)	0.0008(7)	-0.0046(6)
O(4B)	0.0376(9)	0.0400(11)	0.0363(9)	-0.0005(8)	0.0153(7)	-0.0070(8)
O(5B)	0.0315(8)	0.0322(10)	0.0356(8)	-0.0092(8)	0.0016(7)	0.0050(7)
O(6B)	0.0315(8)	0.0379(11)	0.0572(11)	-0.0205(9)	0.0106(8)	-0.0114(8)
N(1B)	0.0221(8)	0.0250(11)	0.0365(10)	-0.0044(9)	0.0056(7)	-0.0019(7)
N(2B)	0.0217(9)	0.0314(12)	0.0333(10)	-0.0029(9)	-0.0003(8)	-0.0017(8)
N(3B)	0.0196(8)	0.0264(11)	0.0313(9)	0.0032(8)	0.0007(7)	-0.0032(7)
N(4B)	0.0263(9)	0.0276(11)	0.0297(10)	-0.0013(8)	0.0015(8)	0.0017(8)
C(1B)	0.0245(9)	0.0218(12)	0.0242(10)	0.0024(9)	0.0026(8)	0.0000(9)
C(2B)	0.0256(10)	0.0211(11)	0.0279(11)	0.0013(9)	0.0034(8)	-0.0023(9)
C(3B)	0.0233(9)	0.0231(12)	0.0279(10)	0.0049(9)	0.0012(8)	-0.0021(9)
C(4B)	0.0253(10)	0.0232(12)	0.0263(10)	-0.0001(9)	0.0041(8)	0.0029(9)

C(5B)	0.0273(10)	0.0212(11)	0.0223(10)	0.0023(9)	-0.0004(8)	-0.0018(8)
C(6B)	0.0238(10)	0.0201(11)	0.0222(9)	0.0045(8)	-0.0001(8)	0.0004(8)
C(7B)	0.0269(10)	0.0265(13)	0.0219(10)	0.0037(9)	-0.0003(8)	0.0045(9)
C(8B)	0.0224(9)	0.0256(12)	0.0265(10)	0.0004(9)	0.0052(8)	0.0016(9)
C(9B)	0.0230(10)	0.0278(13)	0.0350(12)	0.0038(10)	-0.0030(9)	-0.0040(9)
C(10B)	0.0215(9)	0.0253(12)	0.0437(13)	-0.0007(10)	0.0041(9)	-0.0029(9)
C(11B)	0.0252(10)	0.0244(12)	0.0293(11)	-0.0017(9)	0.0057(9)	-0.0025(9)
C(12B)	0.0237(10)	0.0279(12)	0.0286(11)	-0.0012(9)	0.0013(8)	-0.0042(9)
C(13B)	0.0212(9)	0.0282(12)	0.0282(11)	0.0046(9)	0.0031(8)	0.0013(8)
C(14B)	0.0355(12)	0.0360(13)	0.0355(12)	0.0091(10)	-0.0016(10)	-0.0042(10)
C(15B)	0.0552(16)	0.0420(17)	0.0436(14)	0.0080(13)	0.0156(13)	-0.0093(13)
C(16B)	0.0587(16)	0.0281(14)	0.0422(14)	0.0048(11)	-0.0008(12)	-0.0044(12)

Table 4. Bond lengths [Å] for nd1237.

atom-atom	distance	atom-atom	distance
O(1A)-C(7A)	1.345(3)	O(1A)-N(1A)	1.423(3)
O(2A)-C(8A)	1.223(3)	O(3A)-C(11A)	1.434(3)
O(3A)-C(14A)	1.435(3)	O(4A)-C(15A)	1.420(4)
O(4A)-C(11A)	1.426(3)	O(5A)-N(4A)	1.210(3)
O(6A)-N(4A)	1.234(3)	N(1A)-C(1A)	1.314(3)
N(2A)-C(7A)	1.322(3)	N(3A)-C(8A)	1.351(3)
N(3A)-C(13A)	1.462(3)	N(3A)-C(9A)	1.473(3)
N(4A)-C(5A)	1.462(3)	C(1A)-C(2A)	1.429(3)
C(1A)-C(6A)	1.434(3)	C(2A)-C(3A)	1.365(3)
C(3A)-C(4A)	1.429(3)	C(3A)-C(8A)	1.509(3)
C(4A)-C(5A)	1.364(3)	C(5A)-C(6A)	1.418(3)
C(6A)-C(7A)	1.409(3)	C(9A)-C(10A)	1.520(4)
C(10A)-C(11A)	1.520(4)	C(11A)-C(12A)	1.526(3)
C(12A)-C(13A)	1.522(3)	C(14A)-C(15A)	1.491(3)
C(14A)-C(16A)	1.493(4)	O(1B)-C(7B)	1.349(3)
O(1B)-N(1B)	1.421(2)	O(2B)-C(8B)	1.230(3)
O(3B)-C(11B)	1.420(3)	O(3B)-C(14B)	1.453(3)
O(4B)-C(11B)	1.431(3)	O(4B)-C(15B)	1.436(4)
O(5B)-N(4B)	1.208(3)	O(6B)-N(4B)	1.225(3)
N(1B)-C(1B)	1.324(3)	N(2B)-C(7B)	1.323(3)
N(3B)-C(8B)	1.344(3)	N(3B)-C(9B)	1.466(3)
N(3B)-C(13B)	1.474(3)	N(4B)-C(5B)	1.471(3)
C(1B)-C(6B)	1.424(3)	C(1B)-C(2B)	1.425(3)
C(2B)-C(3B)	1.358(3)	C(3B)-C(4B)	1.432(3)
C(3B)-C(8B)	1.507(3)	C(4B)-C(5B)	1.368(3)
C(5B)-C(6B)	1.418(3)	C(6B)-C(7B)	1.405(3)
C(9B)-C(10B)	1.525(3)	C(10B)-C(11B)	1.517(3)
C(11B)-C(12B)	1.528(3)	C(12B)-C(13B)	1.528(3)
C(14B)-C(16B)	1.491(4)	C(14B)-C(15B)	1.502(4)
N(2A)-H(2NA)	0.89(4)	N(2A)-H(2NB)	0.88(3)
C(2A)-H(2A)	0.9500	C(4A)-H(4A)	0.9500
C(9A)-H(9A)	0.9900	C(9A)-H(9B)	0.9900
C(10A)-H(10A)	0.9900	C(10A)-H(10B)	0.9900
C(12A)-H(12A)	0.9900	C(12A)-H(12B)	0.9900
C(13A)-H(13A)	0.9900	C(13A)-H(13B)	0.9900
C(14A)-H(14A)	1.0000	C(15A)-H(15A)	0.9900
C(15A)-H(15B)	0.9900	C(16A)-H(16A)	0.9800
C(16A)-H(16B)	0.9800	C(16A)-H(16C)	0.9800
N(2B)-H(2NC)	0.88(3)	N(2B)-H(2ND)	0.90(3)
C(2B)-H(2B)	0.9500	C(4B)-H(4B)	0.9500
C(9B)-H(9C)	0.9900	C(9B)-H(9D)	0.9900
C(10B)-H(10C)	0.9900	C(10B)-H(10D)	0.9900

C(12B)-H(12C)	0.9900	C(12B)-H(12D)	0.9900
C(13B)-H(13C)	0.9900	C(13B)-H(13D)	0.9900
C(14B)-H(14B)	1.0000	C(15B)-H(15C)	0.9900
C(15B)-H(15D)	0.9900	C(16B)-H(16D)	0.9800
C(16B)-H(16E)	0.9800	C(16B)-H(16F)	0.9800

Symmetry transformations used to generate equivalent atoms:

Table 5. Bond angles [°] for nd1237.

atom-atom-atom	angle	atom-atom-atom	angle
C(7A)-O(1A)-N(1A)	111.09(16)	C(11A)-O(3A)-C(14A)	108.20(18)
C(15A)-O(4A)-C(11A)	105.8(2)	C(1A)-N(1A)-O(1A)	103.72(19)
C(8A)-N(3A)-C(13A)	125.59(19)	C(8A)-N(3A)-C(9A)	119.27(19)
C(13A)-N(3A)-C(9A)	112.51(18)	O(5A)-N(4A)-O(6A)	123.7(2)
O(5A)-N(4A)-C(5A)	118.75(19)	O(6A)-N(4A)-C(5A)	117.55(19)
N(1A)-C(1A)-C(2A)	125.1(2)	N(1A)-C(1A)-C(6A)	113.98(19)
C(2A)-C(1A)-C(6A)	121.0(2)	C(3A)-C(2A)-C(1A)	118.5(2)
C(2A)-C(3A)-C(4A)	121.4(2)	C(2A)-C(3A)-C(8A)	120.7(2)
C(4A)-C(3A)-C(8A)	117.4(2)	C(5A)-C(4A)-C(3A)	120.1(2)
C(4A)-C(5A)-C(6A)	121.4(2)	C(4A)-C(5A)-N(4A)	117.2(2)
C(6A)-C(5A)-N(4A)	121.3(2)	C(7A)-C(6A)-C(5A)	139.9(2)
C(7A)-C(6A)-C(1A)	102.6(2)	C(5A)-C(6A)-C(1A)	117.50(19)
N(2A)-C(7A)-O(1A)	115.9(2)	N(2A)-C(7A)-C(6A)	135.5(2)
O(1A)-C(7A)-C(6A)	108.6(2)	O(2A)-C(8A)-N(3A)	123.0(2)
O(2A)-C(8A)-C(3A)	118.6(2)	N(3A)-C(8A)-C(3A)	118.3(2)
N(3A)-C(9A)-C(10A)	110.54(19)	C(9A)-C(10A)-C(11A)	110.84(19)
O(4A)-C(11A)-O(3A)	106.53(19)	O(4A)-C(11A)-C(10A)	109.6(2)
O(3A)-C(11A)-C(10A)	109.31(19)	O(4A)-C(11A)-C(12A)	110.97(19)
O(3A)-C(11A)-C(12A)	109.1(2)	C(10A)-C(11A)-C(12A)	111.1(2)
C(13A)-C(12A)-C(11A)	111.85(19)	N(3A)-C(13A)-C(12A)	109.96(18)
O(3A)-C(14A)-C(15A)	103.1(2)	O(3A)-C(14A)-C(16A)	108.8(2)
C(15A)-C(14A)-C(16A)	116.0(2)	O(4A)-C(15A)-C(14A)	103.58(19)
C(7B)-O(1B)-N(1B)	110.89(16)	C(11B)-O(3B)-C(14B)	105.69(18)
C(11B)-O(4B)-C(15B)	108.4(2)	C(1B)-N(1B)-O(1B)	103.53(18)
C(8B)-N(3B)-C(9B)	120.05(19)	C(8B)-N(3B)-C(13B)	125.14(19)
C(9B)-N(3B)-C(13B)	112.98(18)	O(5B)-N(4B)-O(6B)	124.1(2)
O(5B)-N(4B)-C(5B)	118.65(19)	O(6B)-N(4B)-C(5B)	117.29(19)
N(1B)-C(1B)-C(6B)	114.02(19)	N(1B)-C(1B)-C(2B)	124.4(2)
C(6B)-C(1B)-C(2B)	121.6(2)	C(3B)-C(2B)-C(1B)	119.0(2)
C(2B)-C(3B)-C(4B)	120.9(2)	C(2B)-C(3B)-C(8B)	121.2(2)
C(4B)-C(3B)-C(8B)	117.6(2)	C(5B)-C(4B)-C(3B)	119.9(2)
C(4B)-C(5B)-C(6B)	121.7(2)	C(4B)-C(5B)-N(4B)	117.2(2)
C(6B)-C(5B)-N(4B)	121.03(19)	C(7B)-C(6B)-C(5B)	140.2(2)
C(7B)-C(6B)-C(1B)	102.87(19)	C(5B)-C(6B)-C(1B)	116.87(19)
N(2B)-C(7B)-O(1B)	115.40(19)	N(2B)-C(7B)-C(6B)	135.9(2)
O(1B)-C(7B)-C(6B)	108.7(2)	O(2B)-C(8B)-N(3B)	123.5(2)
O(2B)-C(8B)-C(3B)	118.2(2)	N(3B)-C(8B)-C(3B)	118.22(19)
N(3B)-C(9B)-C(10B)	110.95(18)	C(11B)-C(10B)-C(9B)	111.67(18)
O(3B)-C(11B)-O(4B)	106.23(19)	O(3B)-C(11B)-C(10B)	108.63(18)
O(4B)-C(11B)-C(10B)	110.56(18)	O(3B)-C(11B)-C(12B)	111.06(19)
O(4B)-C(11B)-C(12B)	109.14(18)	C(10B)-C(11B)-C(12B)	111.1(2)
C(11B)-C(12B)-C(13B)	111.33(17)	N(3B)-C(13B)-C(12B)	109.36(17)

O(3B)-C(14B)-C(16B)	111.1(2)	O(3B)-C(14B)-C(15B)	101.4(2)
C(16B)-C(14B)-C(15B)	113.8(2)	O(4B)-C(15B)-C(14B)	103.9(2)
C(7A)-N(2A)-H(2NA)	120(3)	C(7A)-N(2A)-H(2NB)	114.5(16)
H(2NA)-N(2A)-H(2NB)	125(3)	C(3A)-C(2A)-H(2A)	120.7
C(1A)-C(2A)-H(2A)	120.7	C(5A)-C(4A)-H(4A)	120.0
C(3A)-C(4A)-H(4A)	120.0	N(3A)-C(9A)-H(9A)	109.5
C(10A)-C(9A)-H(9A)	109.5	N(3A)-C(9A)-H(9B)	109.5
C(10A)-C(9A)-H(9B)	109.5	H(9A)-C(9A)-H(9B)	108.1
C(9A)-C(10A)-H(10A)	109.5	C(11A)-C(10A)-H(10A)	109.5
C(9A)-C(10A)-H(10B)	109.5	C(11A)-C(10A)-H(10B)	109.5
H(10A)-C(10A)-H(10B)	108.1	C(13A)-C(12A)-H(12A)	109.2
C(11A)-C(12A)-H(12A)	109.2	C(13A)-C(12A)-H(12B)	109.2
C(11A)-C(12A)-H(12B)	109.2	H(12A)-C(12A)-H(12B)	107.9
N(3A)-C(13A)-H(13A)	109.7	C(12A)-C(13A)-H(13A)	109.7
N(3A)-C(13A)-H(13B)	109.7	C(12A)-C(13A)-H(13B)	109.7
H(13A)-C(13A)-H(13B)	108.2	O(3A)-C(14A)-H(14A)	109.6
C(15A)-C(14A)-H(14A)	109.6	C(16A)-C(14A)-H(14A)	109.6
O(4A)-C(15A)-H(15A)	111.0	C(14A)-C(15A)-H(15A)	111.0
O(4A)-C(15A)-H(15B)	111.0	C(14A)-C(15A)-H(15B)	111.0
H(15A)-C(15A)-H(15B)	109.0	C(14A)-C(16A)-H(16A)	109.5
C(14A)-C(16A)-H(16B)	109.5	H(16A)-C(16A)-H(16B)	109.5
C(14A)-C(16A)-H(16C)	109.5	H(16A)-C(16A)-H(16C)	109.5
H(16B)-C(16A)-H(16C)	109.5	C(7B)-N(2B)-H(2NC)	121(2)
C(7B)-N(2B)-H(2ND)	118.9(18)	H(2NC)-N(2B)-H(2ND)	119(3)
C(3B)-C(2B)-H(2B)	120.5	C(1B)-C(2B)-H(2B)	120.5
C(5B)-C(4B)-H(4B)	120.0	C(3B)-C(4B)-H(4B)	120.0
N(3B)-C(9B)-H(9C)	109.5	C(10B)-C(9B)-H(9C)	109.5
N(3B)-C(9B)-H(9D)	109.5	C(10B)-C(9B)-H(9D)	109.5
H(9C)-C(9B)-H(9D)	108.0	C(11B)-C(10B)-H(10C)	109.3
C(9B)-C(10B)-H(10C)	109.3	C(11B)-C(10B)-H(10D)	109.3
C(9B)-C(10B)-H(10D)	109.3	H(10C)-C(10B)-H(10D)	107.9
C(11B)-C(12B)-H(12C)	109.4	C(13B)-C(12B)-H(12C)	109.4
C(11B)-C(12B)-H(12D)	109.4	C(13B)-C(12B)-H(12D)	109.4
H(12C)-C(12B)-H(12D)	108.0	N(3B)-C(13B)-H(13C)	109.8
C(12B)-C(13B)-H(13C)	109.8	N(3B)-C(13B)-H(13D)	109.8
C(12B)-C(13B)-H(13D)	109.8	H(13C)-C(13B)-H(13D)	108.2
O(3B)-C(14B)-H(14B)	110.1	C(16B)-C(14B)-H(14B)	110.1
C(15B)-C(14B)-H(14B)	110.1	O(4B)-C(15B)-H(15C)	111.0
C(14B)-C(15B)-H(15C)	111.0	O(4B)-C(15B)-H(15D)	111.0
C(14B)-C(15B)-H(15D)	111.0	H(15C)-C(15B)-H(15D)	109.0
C(14B)-C(16B)-H(16D)	109.5	C(14B)-C(16B)-H(16E)	109.5
H(16D)-C(16B)-H(16E)	109.5	C(14B)-C(16B)-H(16F)	109.5
H(16D)-C(16B)-H(16F)	109.5	H(16E)-C(16B)-H(16F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [°] for nd1237.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(7A)-O(1A)-N(1A)-C(1A)	0.0(2)	O(1A)-N(1A)-C(1A)-C(2A)	-178.6(2)
O(1A)-N(1A)-C(1A)-C(6A)	0.8(2)	N(1A)-C(1A)-C(2A)-C(3A)	-179.1(2)
C(6A)-C(1A)-C(2A)-C(3A)	1.5(3)	C(1A)-C(2A)-C(3A)-C(4A)	1.3(3)
C(1A)-C(2A)-C(3A)-C(8A)	172.7(2)	C(2A)-C(3A)-C(4A)-C(5A)	-3.3(3)
C(8A)-C(3A)-C(4A)-C(5A)	-175.0(2)	C(3A)-C(4A)-C(5A)-C(6A)	2.5(3)
C(3A)-C(4A)-C(5A)-N(4A)	-179.37(19)	O(5A)-N(4A)-C(5A)-C(4A)	8.6(3)
O(6A)-N(4A)-C(5A)-C(4A)	-171.4(2)	O(5A)-N(4A)-C(5A)-C(6A)	-173.3(2)
O(6A)-N(4A)-C(5A)-C(6A)	6.7(3)	C(4A)-C(5A)-C(6A)-C(7A)	179.5(3)
N(4A)-C(5A)-C(6A)-C(7A)	1.4(4)	C(4A)-C(5A)-C(6A)-C(1A)	0.3(3)
N(4A)-C(5A)-C(6A)-C(1A)	-177.83(19)	N(1A)-C(1A)-C(6A)-C(7A)	-1.2(2)
C(2A)-C(1A)-C(6A)-C(7A)	178.2(2)	N(1A)-C(1A)-C(6A)-C(5A)	178.30(19)
C(2A)-C(1A)-C(6A)-C(5A)	-2.3(3)	N(1A)-O(1A)-C(7A)-N(2A)	177.4(2)
N(1A)-O(1A)-C(7A)-C(6A)	-0.8(2)	C(5A)-C(6A)-C(7A)-N(2A)	4.1(5)
C(1A)-C(6A)-C(7A)-N(2A)	-176.6(3)	C(5A)-C(6A)-C(7A)-O(1A)	-178.2(3)
C(1A)-C(6A)-C(7A)-O(1A)	1.2(2)	C(13A)-N(3A)-C(8A)-O(2A)	-160.9(2)
C(9A)-N(3A)-C(8A)-O(2A)	-0.7(3)	C(13A)-N(3A)-C(8A)-C(3A)	23.5(3)
C(9A)-N(3A)-C(8A)-C(3A)	-176.3(2)	C(2A)-C(3A)-C(8A)-O(2A)	-121.6(3)
C(4A)-C(3A)-C(8A)-O(2A)	50.2(3)	C(2A)-C(3A)-C(8A)-N(3A)	54.2(3)
C(4A)-C(3A)-C(8A)-N(3A)	-134.1(2)	C(8A)-N(3A)-C(9A)-C(10A)	-102.6(2)
C(13A)-N(3A)-C(9A)-C(10A)	60.0(3)	N(3A)-C(9A)-C(10A)-C(11A)	-55.6(3)
C(15A)-O(4A)-C(11A)-O(3A)	23.9(2)	C(15A)-O(4A)-C(11A)-C(10A)	142.1(2)
C(15A)-O(4A)-C(11A)-C(12A)	-94.7(2)	C(14A)-O(3A)-C(11A)-O(4A)	-2.2(2)
C(14A)-O(3A)-C(11A)-C(10A)	-120.65(19)	C(14A)-O(3A)-C(11A)-C(12A)	117.6(2)
C(9A)-C(10A)-C(11A)-O(4A)	175.20(19)	C(9A)-C(10A)-C(11A)-O(3A)	-68.4(2)
C(9A)-C(10A)-C(11A)-C(12A)	52.2(3)	O(4A)-C(11A)-C(12A)-C(13A)	-174.3(2)
O(3A)-C(11A)-C(12A)-C(13A)	68.6(3)	C(10A)-C(11A)-C(12A)-C(13A)	-52.1(3)
C(8A)-N(3A)-C(13A)-C(12A)	102.3(2)	C(9A)-N(3A)-C(13A)-C(12A)	-59.0(3)
C(11A)-C(12A)-C(13A)-N(3A)	54.6(3)	C(11A)-O(3A)-C(14A)-C(15A)	-19.0(2)
C(11A)-O(3A)-C(14A)-C(16A)	-142.7(2)	C(11A)-O(4A)-C(15A)-C(14A)	-35.4(2)
O(3A)-C(14A)-C(15A)-O(4A)	33.3(2)	C(16A)-C(14A)-C(15A)-O(4A)	152.1(2)
C(7B)-O(1B)-N(1B)-C(1B)	0.4(2)	O(1B)-N(1B)-C(1B)-C(6B)	-0.7(2)
O(1B)-N(1B)-C(1B)-C(2B)	179.3(2)	N(1B)-C(1B)-C(2B)-C(3B)	177.9(2)
C(6B)-C(1B)-C(2B)-C(3B)	-2.1(3)	C(1B)-C(2B)-C(3B)-C(4B)	0.4(3)
C(1B)-C(2B)-C(3B)-C(8B)	-173.0(2)	C(2B)-C(3B)-C(4B)-C(5B)	1.4(3)
C(8B)-C(3B)-C(4B)-C(5B)	175.0(2)	C(3B)-C(4B)-C(5B)-C(6B)	-1.5(3)
C(3B)-C(4B)-C(5B)-N(4B)	178.13(19)	O(5B)-N(4B)-C(5B)-C(4B)	-2.6(3)
O(6B)-N(4B)-C(5B)-C(4B)	176.9(2)	O(5B)-N(4B)-C(5B)-C(6B)	177.0(2)
O(6B)-N(4B)-C(5B)-C(6B)	-3.5(3)	C(4B)-C(5B)-C(6B)-C(7B)	-178.3(3)
N(4B)-C(5B)-C(6B)-C(7B)	2.1(4)	C(4B)-C(5B)-C(6B)-C(1B)	-0.2(3)
N(4B)-C(5B)-C(6B)-C(1B)	-179.77(19)	N(1B)-C(1B)-C(6B)-C(7B)	0.8(2)
C(2B)-C(1B)-C(6B)-C(7B)	-179.3(2)	N(1B)-C(1B)-C(6B)-C(5B)	-178.02(19)

C(2B)-C(1B)-C(6B)-C(5B)	2.0(3)	N(1B)-O(1B)-C(7B)-N(2B)	179.94(19)
N(1B)-O(1B)-C(7B)-C(6B)	0.1(2)	C(5B)-C(6B)-C(7B)-N(2B)	-2.0(5)
C(1B)-C(6B)-C(7B)-N(2B)	179.7(3)	C(5B)-C(6B)-C(7B)-O(1B)	177.8(2)
C(1B)-C(6B)-C(7B)-O(1B)	-0.4(2)	C(9B)-N(3B)-C(8B)-O(2B)	-1.8(3)
C(13B)-N(3B)-C(8B)-O(2B)	161.7(2)	C(9B)-N(3B)-C(8B)-C(3B)	174.1(2)
C(13B)-N(3B)-C(8B)-C(3B)	-22.5(3)	C(2B)-C(3B)-C(8B)-O(2B)	120.7(3)
C(4B)-C(3B)-C(8B)-O(2B)	-52.9(3)	C(2B)-C(3B)-C(8B)-N(3B)	-55.4(3)
C(4B)-C(3B)-C(8B)-N(3B)	131.0(2)	C(8B)-N(3B)-C(9B)-C(10B)	107.0(2)
C(13B)-N(3B)-C(9B)-C(10B)	-58.3(3)	N(3B)-C(9B)-C(10B)-C(11B)	53.4(3)
C(14B)-O(3B)-C(11B)-O(4B)	28.1(2)	C(14B)-O(3B)-C(11B)-C(10B)	147.10(18)
C(14B)-O(3B)-C(11B)-C(12B)	-90.4(2)	C(15B)-O(4B)-C(11B)-O(3B)	-6.2(3)
C(15B)-O(4B)-C(11B)-C(10B)	-123.9(2)	C(15B)-O(4B)-C(11B)-C(12B)	113.6(2)
C(9B)-C(10B)-C(11B)-O(3B)	71.1(2)	C(9B)-C(10B)-C(11B)-O(4B)	-172.73(18)
C(9B)-C(10B)-C(11B)-C(12B)	-51.4(3)	O(3B)-C(11B)-C(12B)-C(13B)	-67.9(2)
O(4B)-C(11B)-C(12B)-C(13B)	175.3(2)	C(10B)-C(11B)-C(12B)-C(13B)	53.2(3)
C(8B)-N(3B)-C(13B)-C(12B)	-105.0(2)	C(9B)-N(3B)-C(13B)-C(12B)	59.4(2)
C(11B)-C(12B)-C(13B)-N(3B)	-56.1(3)	C(11B)-O(3B)-C(14B)-C(16B)	-159.1(2)
C(11B)-O(3B)-C(14B)-C(15B)	-37.8(2)	C(11B)-O(4B)-C(15B)-C(14B)	-17.2(3)
O(3B)-C(14B)-C(15B)-O(4B)	33.2(3)	C(16B)-C(14B)-C(15B)-O(4B)	152.6(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for nd1237 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2A)-H(2NA)...O(2A)#1	0.89(4)	2.07(5)	2.868(3)	148(4)
N(2A)-H(2NB)...O(3A)#2	0.88(3)	2.62(2)	3.090(3)	114.5(18)
N(2A)-H(2NB)...O(6A)	0.88(3)	2.04(3)	2.763(3)	139(2)
N(2B)-H(2NC)...O(2B)#3	0.88(3)	2.13(3)	2.900(3)	146(3)
N(2B)-H(2ND)...O(3B)#4	0.90(3)	2.51(3)	3.096(3)	123(2)
N(2B)-H(2ND)...O(6B)	0.90(3)	2.08(3)	2.759(3)	131(2)

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z #2 x+1,y+1,z #3 x-1,y,z #4 x-1,y-1,z