Stereochemical dominance in hierarchically formed helicates

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ABSTRACT: The competition of different chiral ligands in the control of stereochemistry of hierarchically formed helical coordination compounds is investigated. It is found that sterically demanding chiral units can dominate the chiral induction of the helix even if they are present as a minor species. Hereby the relative strength of stereoinduction of different chiral units can be evaluated.

Experimental Procedures

1. Materials and methods

2,3- Dihydroxybenzoic acid was acquired from FluoroChem (Hadfield, Glossop/UK). Thionyl chloride was obtained from Acros (Schwerte/ Germany). All solvents were used without further purification. THF-d_8 was purchased from Sigma Aldrich (Taufkirchen / Germany). NMR spectra were obtained with an Inova 400 spectrometer (Varian Inc.) and a VNMRS 600 spectrometer (Varian Inc.). ESI-MS measurements were metered at a Finnigan SSQ 7000 (Waltham, MA/USA). CD spectra were preserved with a Lakewood 62Ds. The concentration for CD measurements was $1 * 10^{-3}$ mol L^{-1}. It was measured in an 1mm thick cuvette.

2. General procedure for ligand synthesis

2,3-Dihydroxybenzoic acid (1 eq.) was suspended in thionyl chloride (30 eq.) and refluxed for three hours. A change from suspension to a clear solution indicated a full conversion to the acid chloride. Afterwards the remained thionyl chloride was removed under reduced pressure. The remaining residue (2,3 dioxosulfinylbenzoyl chloride) was diluted in chloroform. A solution of the corresponding alcohol (5 eq.) and triethylamine (5 eq.) in chloroform was prepared and added to the solution of the 2,3 dioxosulfinylbenzoyl chloride. The received reaction mixture was refluxed for 24 hours, washed with a saturated $NaHCO_3$ solution and afterwards dried over $MgSO_4$. Purification of the target ester was achieved via column chromatography. The chromatography conditions of each compound were described in the analytic data.

3. General procedure for helicates $Li[Li_3(L)_6Ti_2]$

The catechol ligand (3 eq.), $TiO(acac)_2$ (1eq.) and $LiCO_3$ (1 eq.) were dissolved in methanol and strongly stirred for 24 hours. Afterwards the solvent was removed under reduced pressure and the pure complex was obtained as an orange solid.

4. Procedure for mixed helicates $Li[Li_3(L^X)_n(L^Y)_mTi_2]$

Catechol ligand X (n eq.), Catecholigand Y (m eq.) (m + n = 6), $TiO(acac)_2$ (2 eq.) and $LiCO_3$ (2 eq.) were dissolved in methanol and strongly stirred for 24 hours. Afterwards the solvent was removed under reduced pressure and the complex was obtained as an orange solid.

Results and Discussion

5. Analytical data

L^{1S}-H_2[1]
The ligand was synthesized according to the general procedure. Column chromatography (pentane / ethyl acetate 20 : 1) afforded the product as a colourless oil (51 %, 597 mg, 2.31 mmol).

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.47 – 7.42 (m, 3H), 7.40 – 7.35 (m, 2H), 7.33 – 7.28 (m, 1H), 7.02 (dd, J = 7.9, 1.6 Hz, 1H), 6.78 (t, J = 7.9 Hz, 1H), 6.15 (q, J = 6.6 Hz, 1H), 1.66 (d, J = 6.6 Hz, 3H). ppm.
^{13}C NMR (400 MHz, Chloroform-d): δ = 169.7, 149.1, 145.2, 141.1, 128.8, 128.3, 126.0, 120.7, 112.0, 119.2, 112.8, 73.9, 22.4 ppm.
MS (negative ESI-MS, MeOH): m/z (%) = 257.08072 (72, [M-H$^+$], $C_{15}H_{13}O_4^-$, calc. 257.08193).

L^{1R}-H_2 [2]
The ligand was synthesized according to the general procedure. Column chromatography (pentane / ethyl acetate 20 : 1) afforded the product as a colourless oil (46 %, 438 mg, 4.54 mmol).

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.46 – 7.39 (m, 3H), 7.40 – 7.33 (m, 2H), 7.32 – 7.26 (m, 1H), 7.01 (dd, J = 8.0, 1.6 Hz, 1H), 6.76 (t, J = 8.0 Hz, 1H), 6.14 (q, J = 6.6 Hz, 1H), 1.66 (d, J = 6.6 Hz, 3H) ppm.

^{13}C NMR (100 MHz, Chloroform-d): δ = 169.7, 149.1, 145.2, 141.1, 128.8, 128.3, 126.0, 120.7, 112.0, 119.2, 112.8, 73.9, 22.4 ppm.
MS (negative ESI-MS, MeOH): m/z (%) = 257.08057 (100, [M-H$^+$], $C_{15}H_{13}O_4^-$, calc. 257.08193).

L^{2}-H_2[3]
The ligand was synthesized according to the general procedure. Column chromatography (pentane / ethyl acetate 2:1) afforded the product as a colourless solid (77 %, 855 mg, 3.50 mmol).

^{1}H NMR (600 MHz, Chloroform-d): δ = 10.88 (s, 1H), 7.45 – 7.36 (m, 6H), 7.11 (dd, J = 8.0, 1.5 Hz, 1H), 6.79 (t, J = 8.0 Hz, 1H), 5.63 (s, 1H), 5.39 (s, 2H) ppm.
^{13}C NMR (151 MHz, Chloroform-d): δ = 170.3, 149.1, 145.2, 135.3, 128.9, 128.7, 128.4, 120.8, 120.0, 119.4, 112.6, 67.3 ppm.
MS (negative ESI-MS, MeOH): m/z (%) = 243.06616 (100, [M-H$^+$], $C_{14}H_{11}O_4^-$, calc. 243.06616).

$L^{3(-)}$-H_2[4]
The ligand was synthesized according to the general procedure. Column chromatography (DCM / pentane 3:1) afforded the product as a colourless oil (68 %, 850 mg, 3.10 mmol).

^{1}H NMR (400 MHz, Chloroform-*d*): δ = 10.94 (s, 1H), 7.35 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.10 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.79 (t, *J* = 8.0 Hz, 1H), 5.71 – 5.66 (m, 1H), 5.63 (s, 1H), 4.72 (d, *J* = 1.5 Hz, 2H), 2.46 – 2.43 (m, 1H), 2.38 – 2.34 (m, 1H), 2.31 – 2.27 (m, 1H), 2.21 (td, *J* = 5.6, 1.5 Hz, 1H), 2.15 – 2.11 (m, 1H), 1.31 (s, 3H), 1.23 (d, *J* = 8.7 Hz, 1H), 0.87 (s, 3H) ppm.
^{13}C NMR (151 MHz, Chloroform-d): δ = 170.4, 149.0, 145.2, 142.4, 122.9, 120.7, 119.8, 119.3, 112.8, 68.2, 43.8, 40.8, 38.3, 31.7, 31.5, 26.3, 21.3 ppm.
MS (negative ESI-MS, MeOH): m/z (%) = 287.12720 (10, [M-H$^+$], $C_{17}H_{19}O_4^-$, calc. 287.12888).

$L^{4(-)}$-H_2[4]
The ligand was synthesized according to the general procedure. Column chromatography (pentane / ethyl acetate 10:1) afforded the product as a colourless oil (62 %, 823 mg, 2.81 mmol).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 11.12 (s, 1H), 7.37 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.10 (dd, *J* = 8.0, 0.9 Hz, 1H), 6.79 (t, *J* = 8.0 Hz, 1H), 5.66 (s, 1H), 4.96 (td, *J* = 10.9, 4.4 Hz, 1H), 2.13 – 2.10 (m, 1H), 1.96 – 1.90 (m, 1H), 1.77 – 1.72 (m, 2H), 1.60 – 1.57 (m, 2H), 1.17 – 1.10 (m, 2H), 0.93 (dd, *J* = 10.0, 7.0 Hz, 7H), 0.79 (d, *J* = 7.0 Hz, 3H) ppm.
^{13}C NMR (151 MHz, Chloroform-d): δ = 170.1, 149.1, 145.2, 120.7, 119.7, 119.2, 113.1, 76.0, 47.3, 40.9, 34.3, 31.6, 26.7, 23.8, 22.1, 20.8, 16.7 ppm.
MS (positive ESI-MS, MeOH): m/z (%) = 315.15820 (100, [M+Na$^+$], $C_{17}H_{24}O_4Na^+$, calc. 315.15668).

$L^{5(-)}$-H_2[4]
The ligand was synthesized according to the general procedure. Column chromatography (pentane / ethyl acetate 20:1) afforded the product as a colourless solid (59 %, 784 mg, 2.70 mmol).

^{1}H NMR (600 MHz, Methanol-d_4): δ = 7.39 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.04 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.79 (t, *J* = 8.0 Hz, 1H), 5.19 (ddd, *J* = 10.0, 3.5, 2.2 Hz, 1H), 2.54 – 2.49(m, 1H), 2.15 (ddd, *J* = 13.4, 10.0, 4.5 Hz, 1H), 1.91 – 1.85 (m, 1H), 1.77 (t, *J* = 4.5 Hz, 1H), 1.52 – 1.47 (m, 1H), 1.39 – 1.35 (m, 1H), 1.18 (dd, *J* = 14.0, 3.5 Hz, 1H), 1.02 (s, 3H), 0.97 (d, *J* = 10.0 Hz, 6H) ppm.
^{13}C NMR (151 MHz, Methanol-d_4): δ = 172.1, 151.4, 147.2, 121.7, 121.0, 120.1, 114.3, 82.5, 50.2, 46.3, 37.8, 28.9, 28.3, 20.1, 19.2, 13.9 ppm.
MS (negative ESI-MS, MeOH): m/z (%) = 289.14253 (40, [M-H$^+$], $C_{17}H_{22}O_4^-$, calc. 289.14453).

$Li[Li_3L^{1S}{}_6Ti_2]$[1]
^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.22 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.92 – 6.88 (m, 2H), 6.80 – 6.72 (m, 3H), 6.68 – 6.59 (m, 2H), 4.46 (q, *J* = 6.6 Hz, 1H), 1.07 (d, *J* = 6.6 Hz, 3H) ppm.
MS (negative ESI-MS, MeOH): m/z (%) = 1653.37715 (100, [M_D-Li$^+$], $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calcd. 1653.38581).

$Li[Li_3L^{1R}{}_6Ti_2]$[2]
^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.22 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.93 – 6.88 (m, 2H), 6.80 – 6.70 (m, 3H), 6.68 – 6.59 (m, 2H), 4.47 (q, *J* = 6.6 Hz, 1H), 1.07 (d, *J* = 6.6 Hz, 3H) ppm.
MS (negative ESI-MS, MeOH): m/z (%) = 1653.37255 (100, [M_D-Li$^+$], $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calcd. 1653.38581).

$Li[Li_3L^2{}_6Ti_2]$[3]
^{1}H NMR (400 MHz, Methanol-d4): δ = 7.26 – 7.15 (m, 6H), 6.63 (dd, J = 7.8, 1.6 Hz, 1H), 6.51 (t, J = 7.8 Hz, 1H), 4.56 (d, J = 12.7 Hz, 1H), 4.06 (d, J = 12.7 Hz, 1H).
MS (negative ESI-MS, MeOH): m/z (%) = 1569.27952 (100, [M_D-Li$^+$], $C_{84}H_{60}Li_3O_{24}Ti_2^-$, calcd. 1569.29191).

$Li[Li_3L^{3(-)}{}_6Ti_2]$[4]
^{1}H NMR (400 MHz, THF-d_8): (dimer) δ = 7.04 (dd, J = 7.3, 2.5 Hz, 1H), 6.46 – 6.38 (m, 2H), 5.40 – 5.34 (m, 1H), 4.00 (d, J = 13.0 Hz, 1H), 3.27 (d, J = 13.0 Hz, 1H), 2.41 – 2.34 (m, 1H), 2.28 – 2.15 (m, 2H), 2.10 – 2.01 (m, 2H), 1.28 (m, 3H), 1.15 (d, J = 8.6 Hz, 1H), 0.81 (d, J = 5.3 Hz, 3H) ppm.
MS (negative ESI-MS, MeOH): m/z (%) = 1833.65804 (100, [M_D-Li$^+$], $C_{102}H_{108}Li_3O_{24}Ti_2^-$, calcd. 1833.66751).

$Li[Li_3L^{4(-)}{}_6Ti_2]$[4]
^{1}H NMR (400 MHz, THF-d_8): (dimer) δ = 7.04 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.47 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.41 (t, *J* = 8.0 Hz, 1H), 3.89 – 3.80 (m, 1H), 1.59 – 1.37 (m, 4H), 1.31 – 1.17 (m, 1H), 1.08 (t, *J* = 10.8 Hz, 1H), 0.95 – 0.89 (m, 1H), 0.85 (d, *J* = 6.5 Hz, 3H), 0.82 – 0.72 (m, 2H), 0.64 (d, *J* = 6.5 Hz, 3H), 0.25 (d, *J* = 6.5 Hz, 3H) ppm.
MS (negative ESI-MS, MeOH): m/z (%) = 1857.84788 (100, [M_D-Li$^+$], $C_{102}H_{132}Li_3O_{24}Ti_2^-$, calcd. 1857.85531).

$Li[Li_3L^{5(-)}{}_6Ti_2]^{[4]}$

^{1}H NMR (400 MHz, THF-d_8): (dimer) δ = 7.04 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.43 (t, *J* = 8.0 Hz, 1H), 6.36 (dd, *J* = 8.0, 1.7 Hz, 1H), 3.69 – 3.63 (m, 1H), 2.03 – 1.93 (m, 2H), 1.64 – 1.55 (m, 1H), 1.43 – 1.37 (m, 1H), 1.30 – 1.20 (m, 1H), 0.98 – 0.92 (m, 1H), 0.88 (s, 3H), 0.81 (s, 3H), 0.73 (s, 3H), 0.69 – 0.64 (m, 1H) ppm.

MS (negative ESI-MS, MeOH): m/z (%) = 1846.75165 (100, $[M_D\text{-}Li^+]$, $C_{102}H_{120}Li_3O_{24}Ti_2^-$, calcd. 1846.76141).

$Li[Li_3L^2{}_XL^{1S}{}_{(6-X)}Ti_2]$

$Li[Li_3L^2{}_6L^{1S}{}_0Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1569.27952 (100, $[M_D\text{-}Li^+]$, $C_{84}H_{60}Li_3O_{24}Ti_2^-$, calc. 1569.29191).

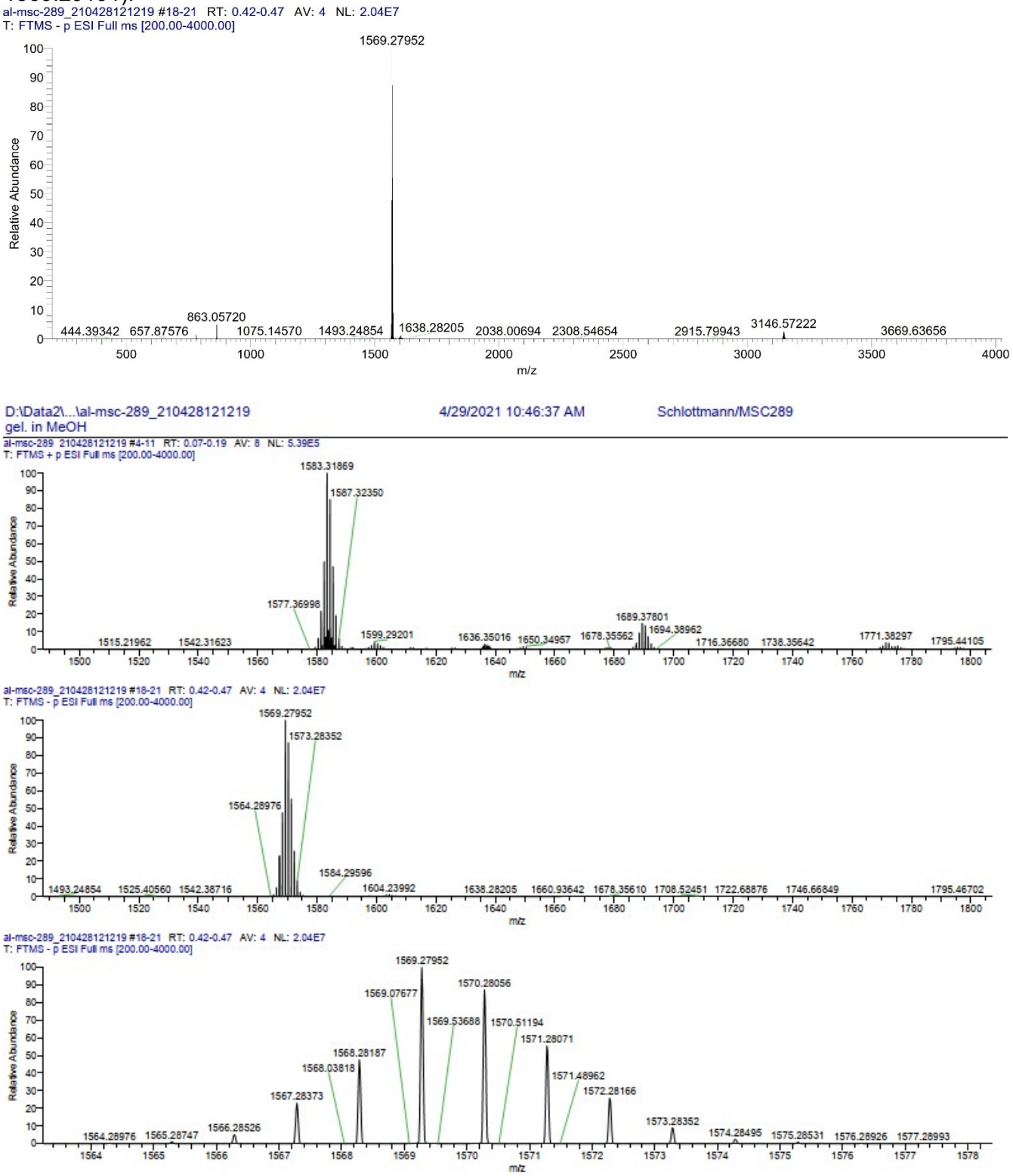


Figure 1: ESI mass spectrum of $Li[Li_3L^2{}_6L^{1S}{}_0Ti_2]$.

$Li[Li_3L^2{}_5L^{1S}{}_1Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1583.30461 (83, $[M_D\text{-}Li^+]$, $C_{85}H_{62}Li_3O_{24}Ti_2^-$, calc. 1583.30756).

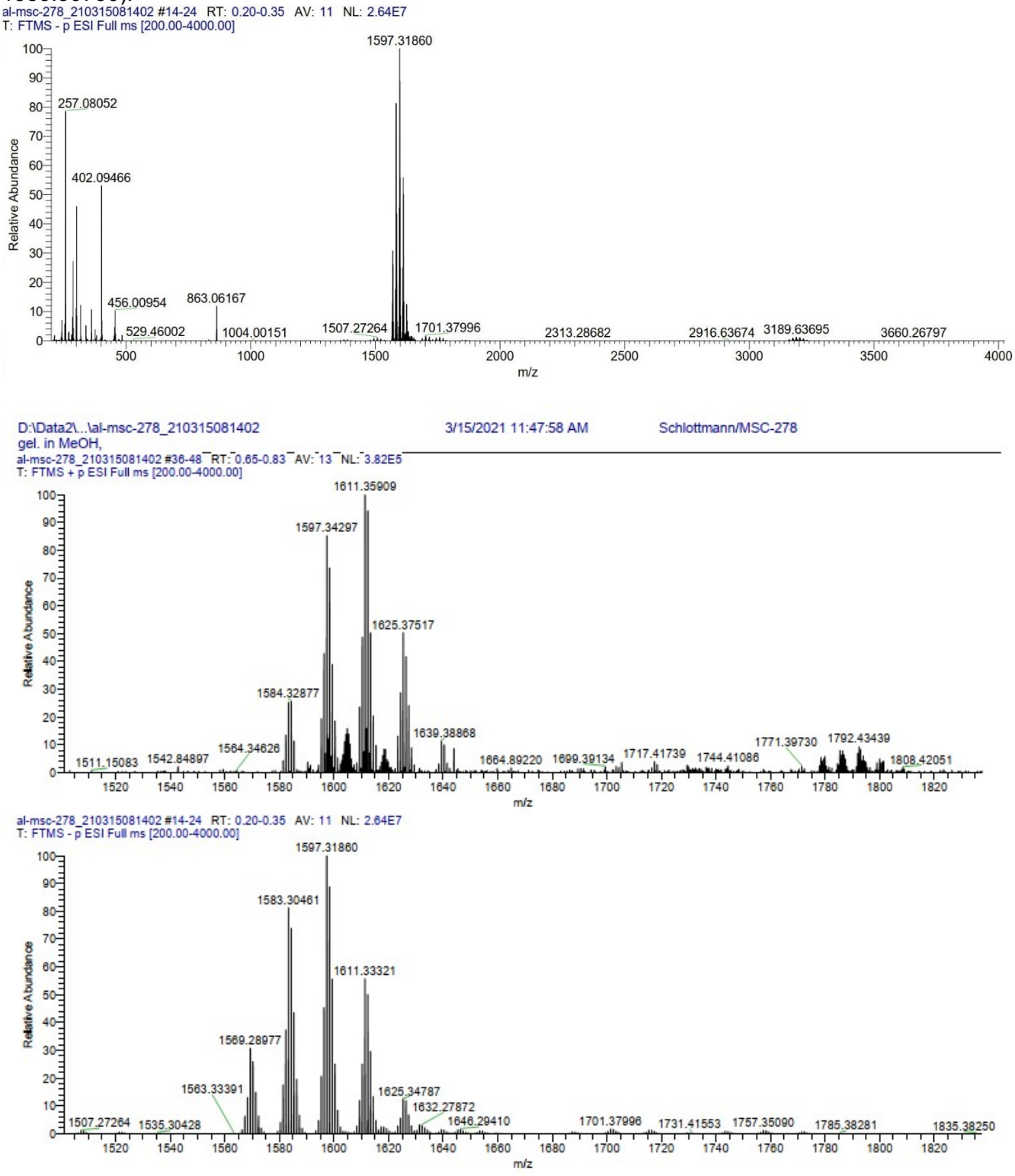


Figure 2: ESI mass spectrum of $Li[Li_3L^2{}_5L^{1S}{}_1Ti_2]$.

$Li[Li_3L^2{}_4L^{1S}{}_2Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1597.30430 (98, $[M_D\text{-}Li^+]$, $C_{86}H_{64}Li_3O_{24}Ti_2^-$, calc. 1597.32321).

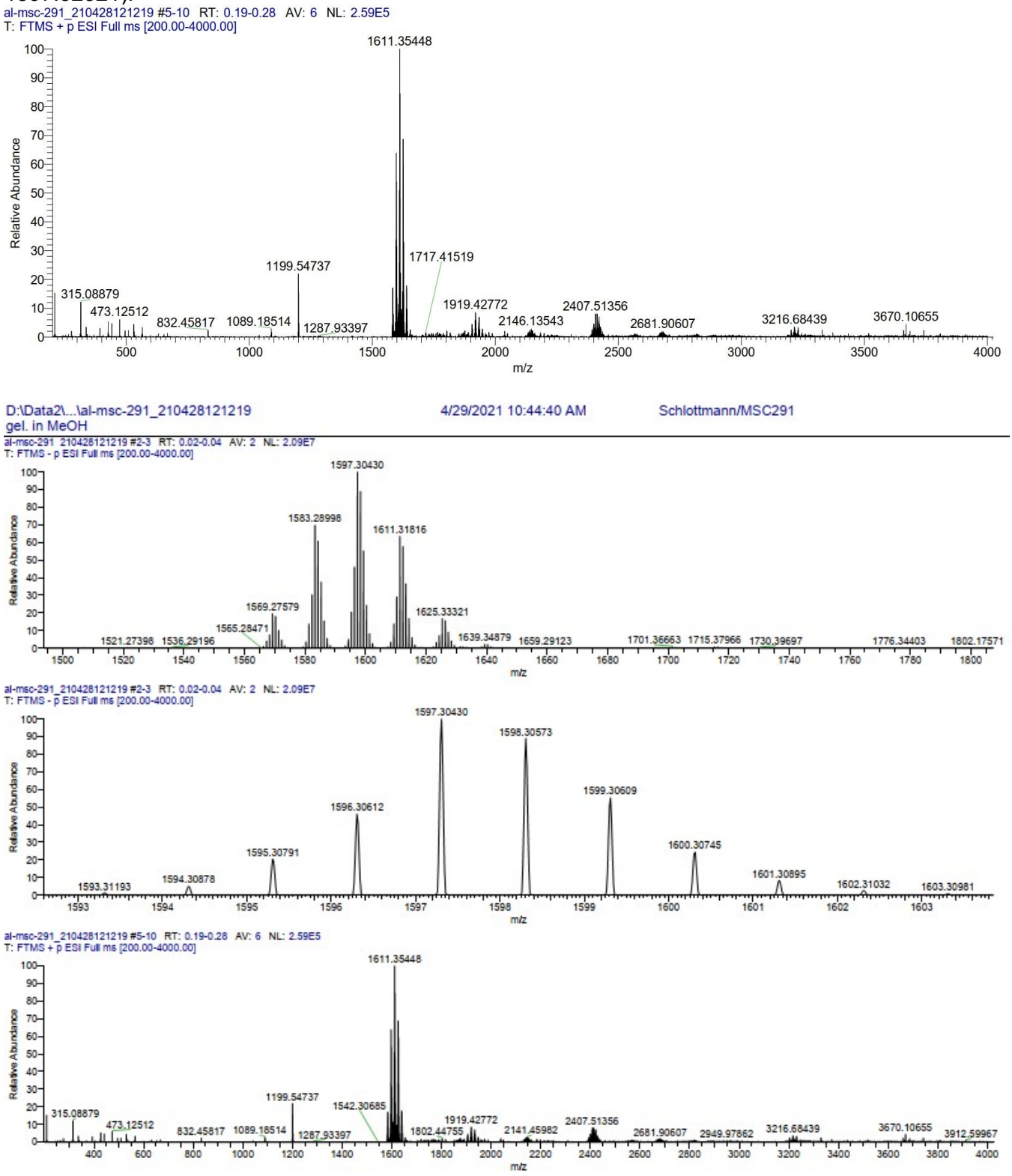


Figure 3: ESI mass spectrum of $Li[Li_3L^2{}_4L^{1S}{}_2Ti_2]$.

$Li[Li_3L^2{}_3L^{1S}{}_3Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1611.32531 (100, $[M_D\text{-}Li^+]$, $C_{87}H_{66}Li_3O_{24}Ti_2^-$, calc. 1611.33886).

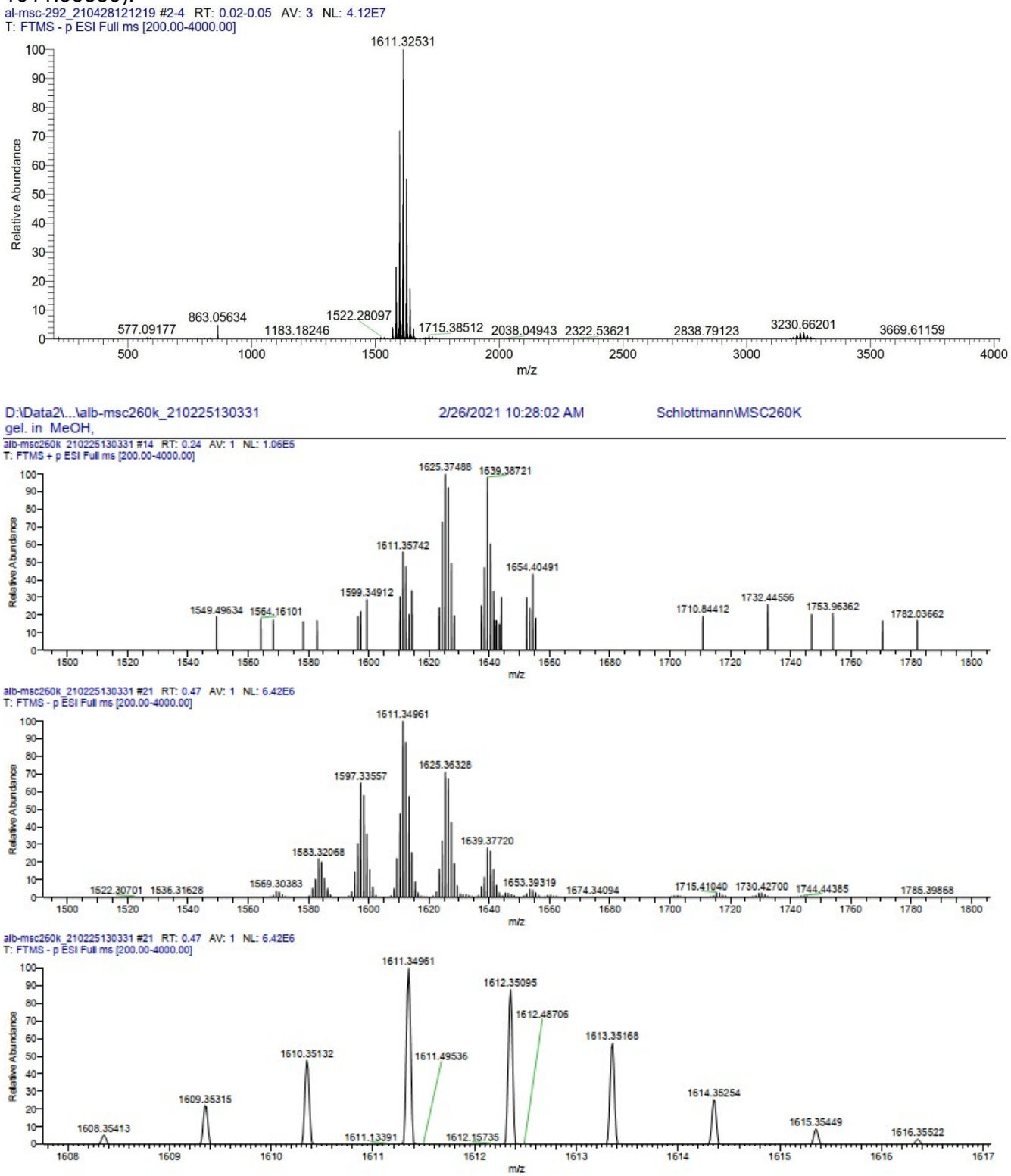


Figure 4: ESI mass spectrum of $Li[Li_3L^2{}_3L^{1S}{}_3Ti_2]$

$Li[Li_3L^2{}_2L^{1S}{}_4Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1625.33654 (85, [M_D-Li^+], $C_{88}H_{68}Li_3O_{24}Ti_2^-$, calc. 1625.35451).

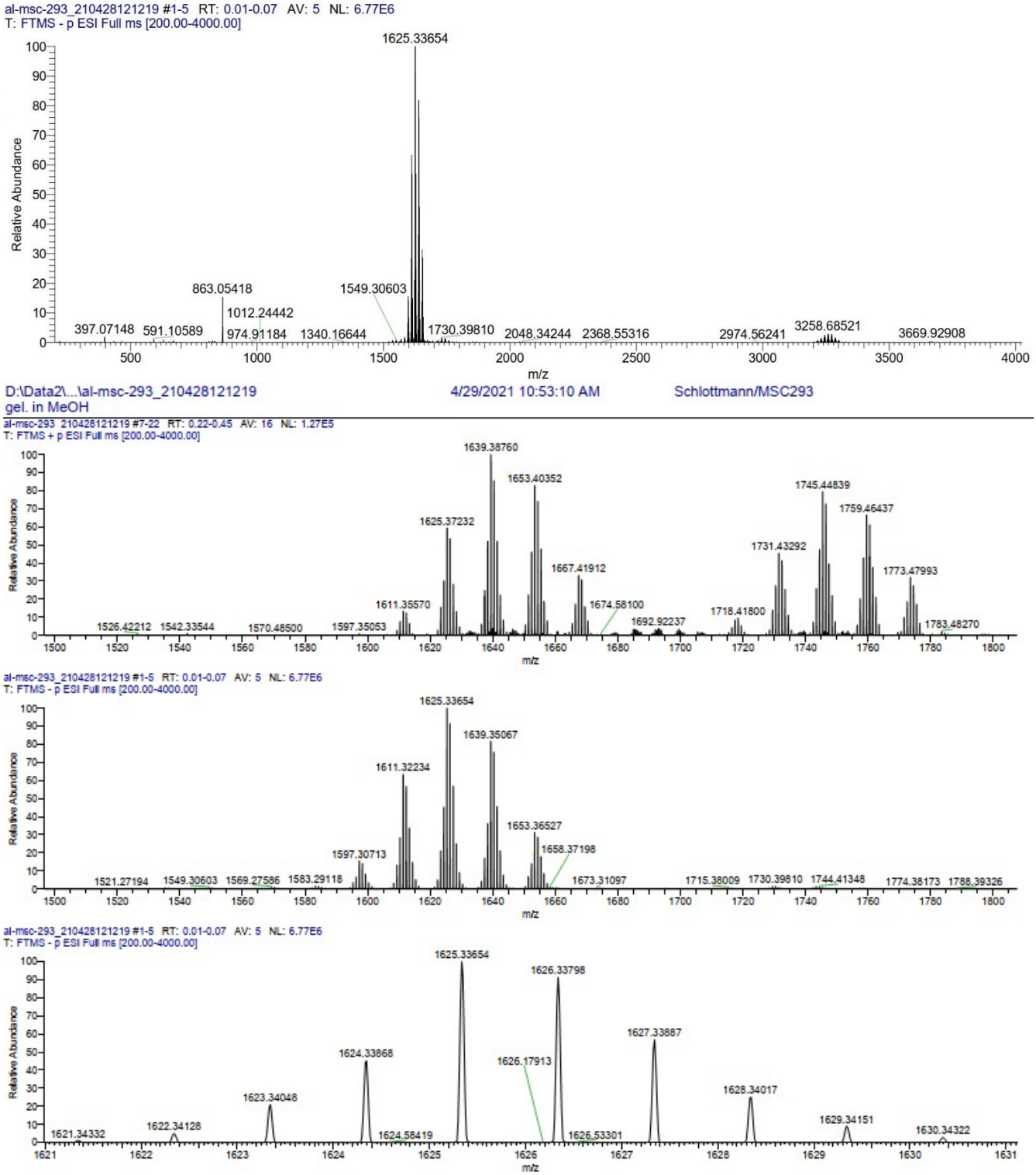


Figure 5: ESI mass spectrum of $Li[Li_3L^2{}_2L^{1S}{}_4Ti_2]$.

$Li[Li_3L^2{}_1L^{1S}{}_5Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1639.35440 (85, $[M_D\text{-}Li^+]$, $C_{89}H_{70}Li_3O_{24}Ti_2^-$, calc. 1639.37016).

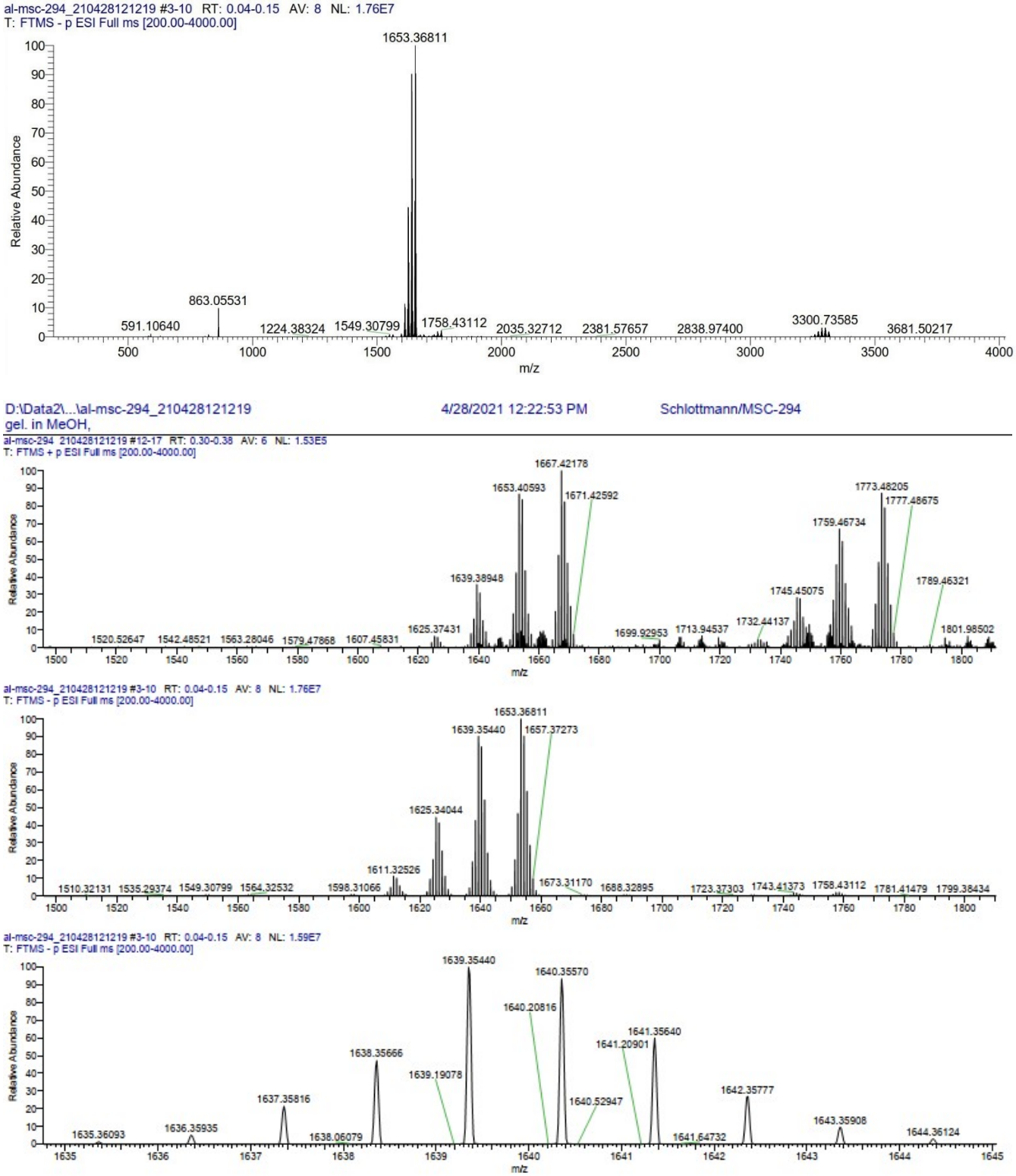


Figure 6: ESI mass spectrum of $Li[Li_3L^2{}_1L^{1S}{}_5Ti_2]$.

$Li[Li_3L^2{}_0L^{1S}{}_6Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1653.37715 (100, $[M_D\text{-}Li^+]$, $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calc. 1653.38581).

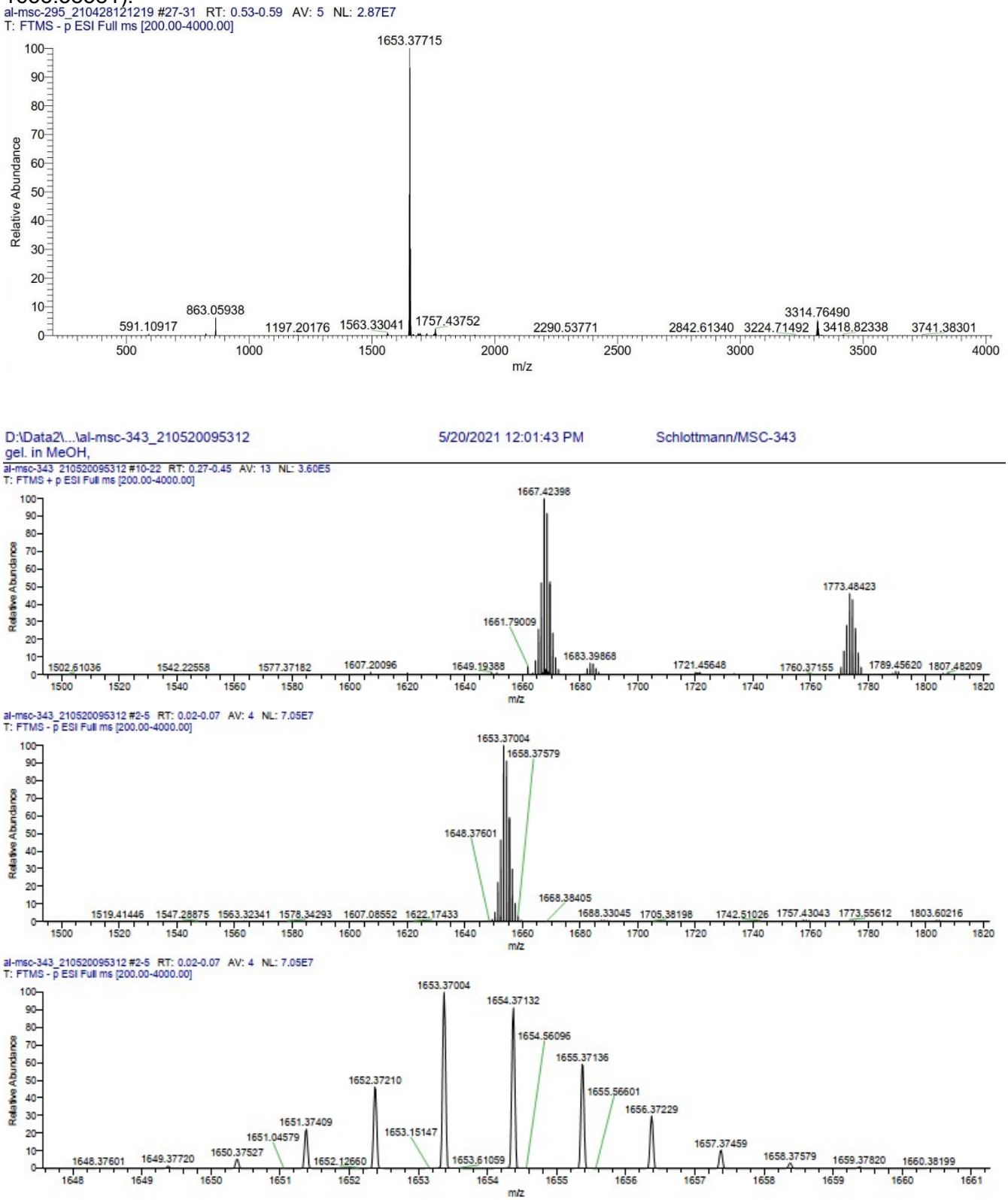


Figure 7: ESI mass spectrum of $Li[Li_3L^2{}_0L^{1S}{}_6Ti_2]$.

$Li[Li_3L^{3(-)}{}_XL^{5(-)}{}_{(6-X)}Ti_2]$

$Li[Li_3L^{3(-)}{}_6L^{5(-)}{}_0Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1833.65804 (100, $[M_D\text{-}Li^+]$, $C_{102}H_{108}Li_3O_{24}Ti_2^-$, calc. 1833.66751).

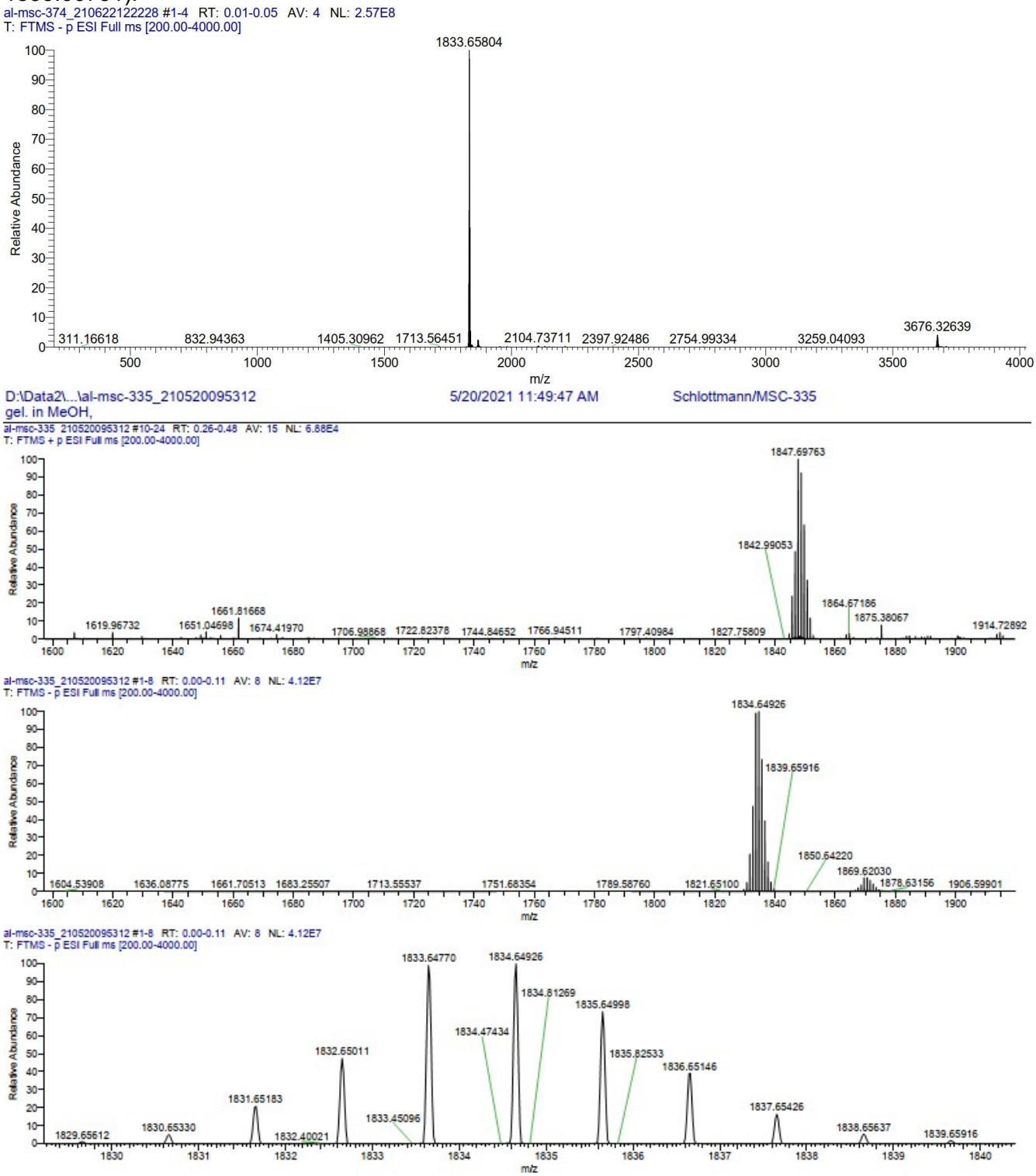


Figure 8: ESI mass spectrum of $Li[Li_3L^{3(-)}{}_6L^{5(-)}{}_0Ti_2]$.

$Li[Li_3L^{3(-)}{}_5L^{5(-)}{}_1Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1835.66780 (100, $[M_D\text{-}Li^+]$, $C_{102}H_{110}Li_3O_{24}Ti_2^-$, calc. 1835.68316).

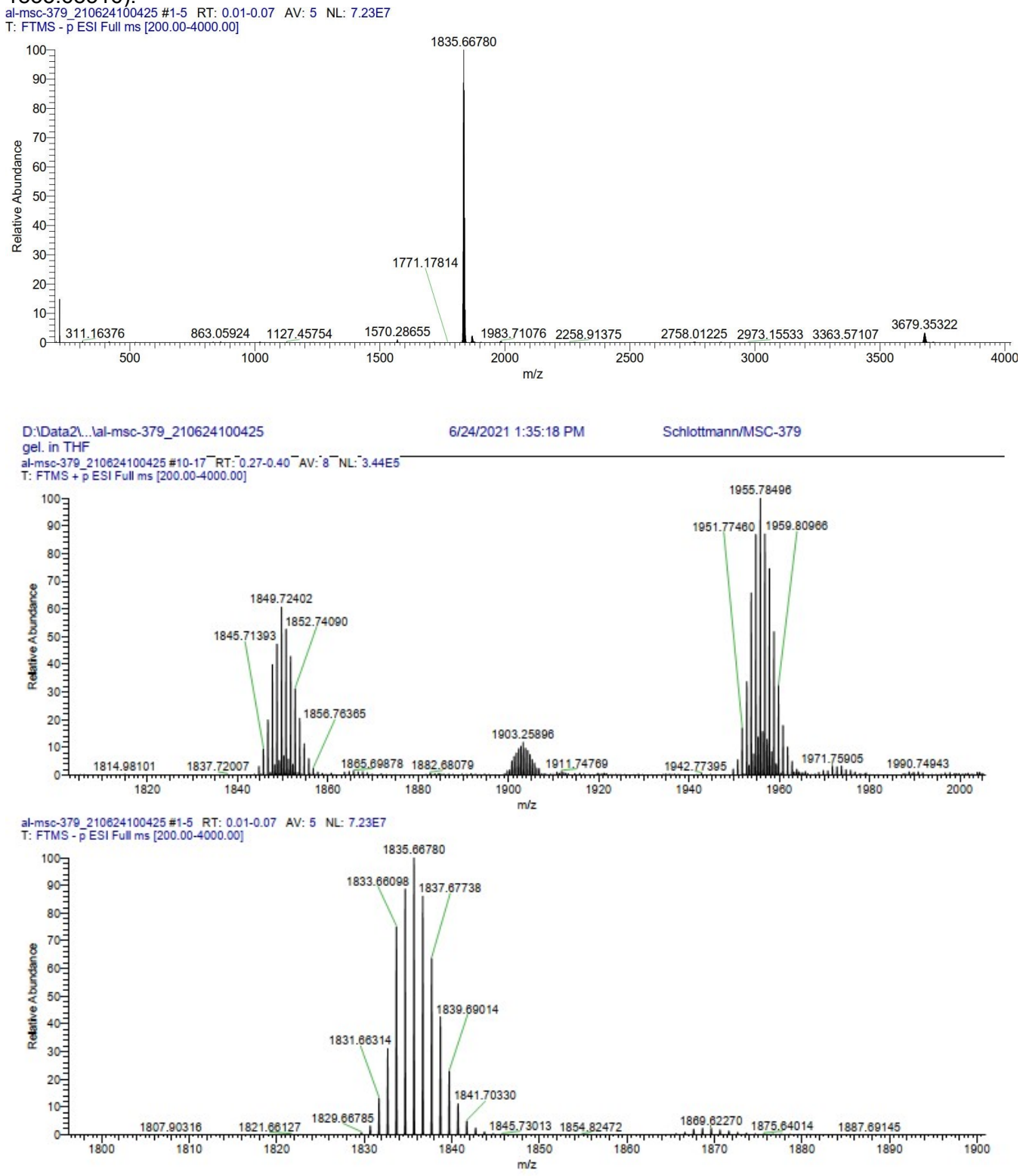


Figure 9: ESI mass spectrum of $Li[Li_3L^{3(-)}{}_5L^{5(-)}{}_1Ti_2]$.

$Li[Li_3L^{3(-)}{}_4L^{5(-)}{}_2Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1837.69110 (100, $[M_D\text{-}Li^+]$, $C_{102}H_{112}Li_3O_{24}Ti_2^-$, calc. 1837.69881).

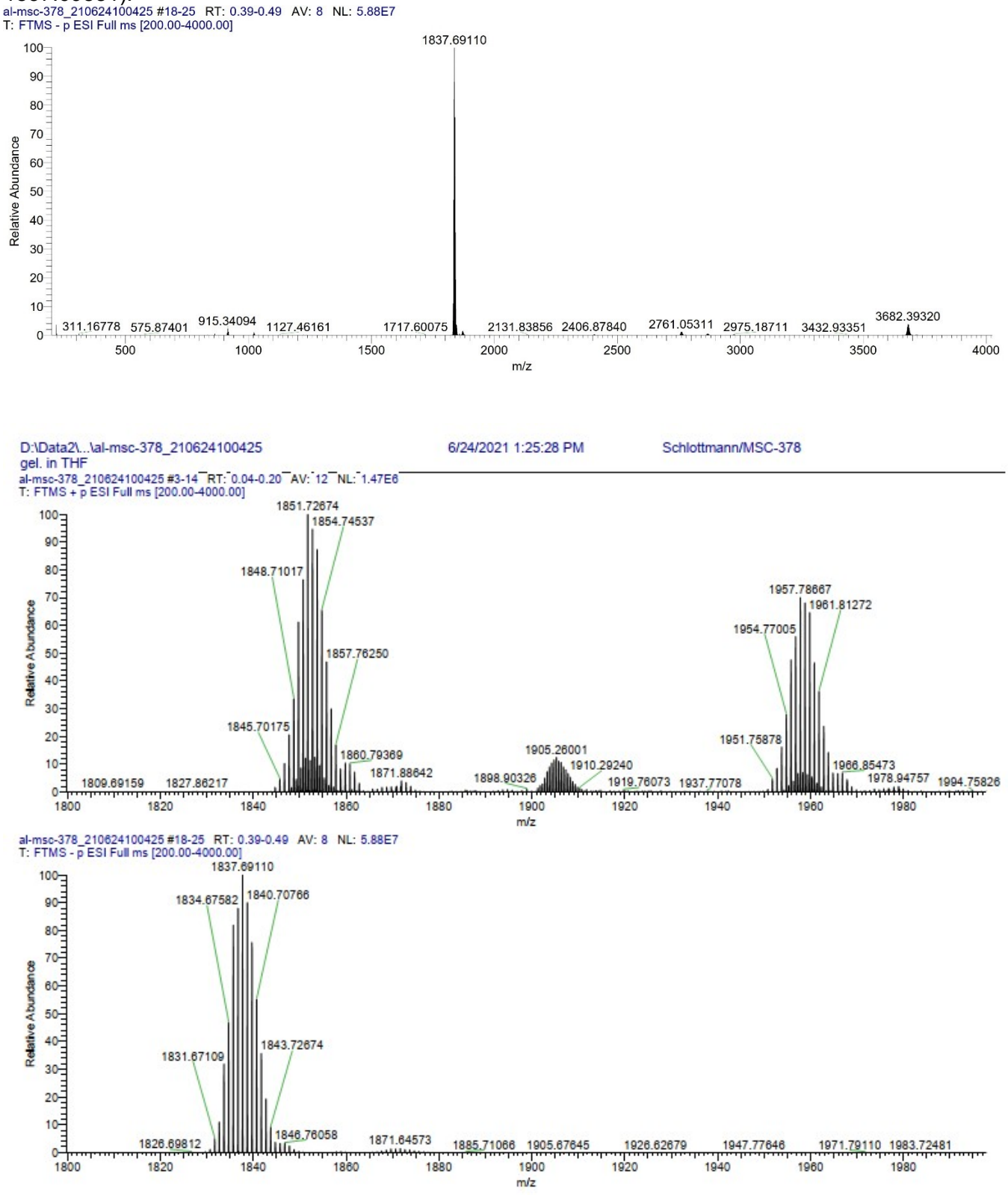


Figure 10: ESI mass spectrum of $Li[Li_3L^{3(-)}{}_4L^{5(-)}{}_2Ti_2]$.

$Li[Li_3L^{3(-)}{}_3L^{5(-)}{}_3Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1839.69744 (100, $[M_D\text{-}Li^+]$, $C_{102}H_{114}Li_3O_{24}Ti_2^-$, calc. 1839.71446).

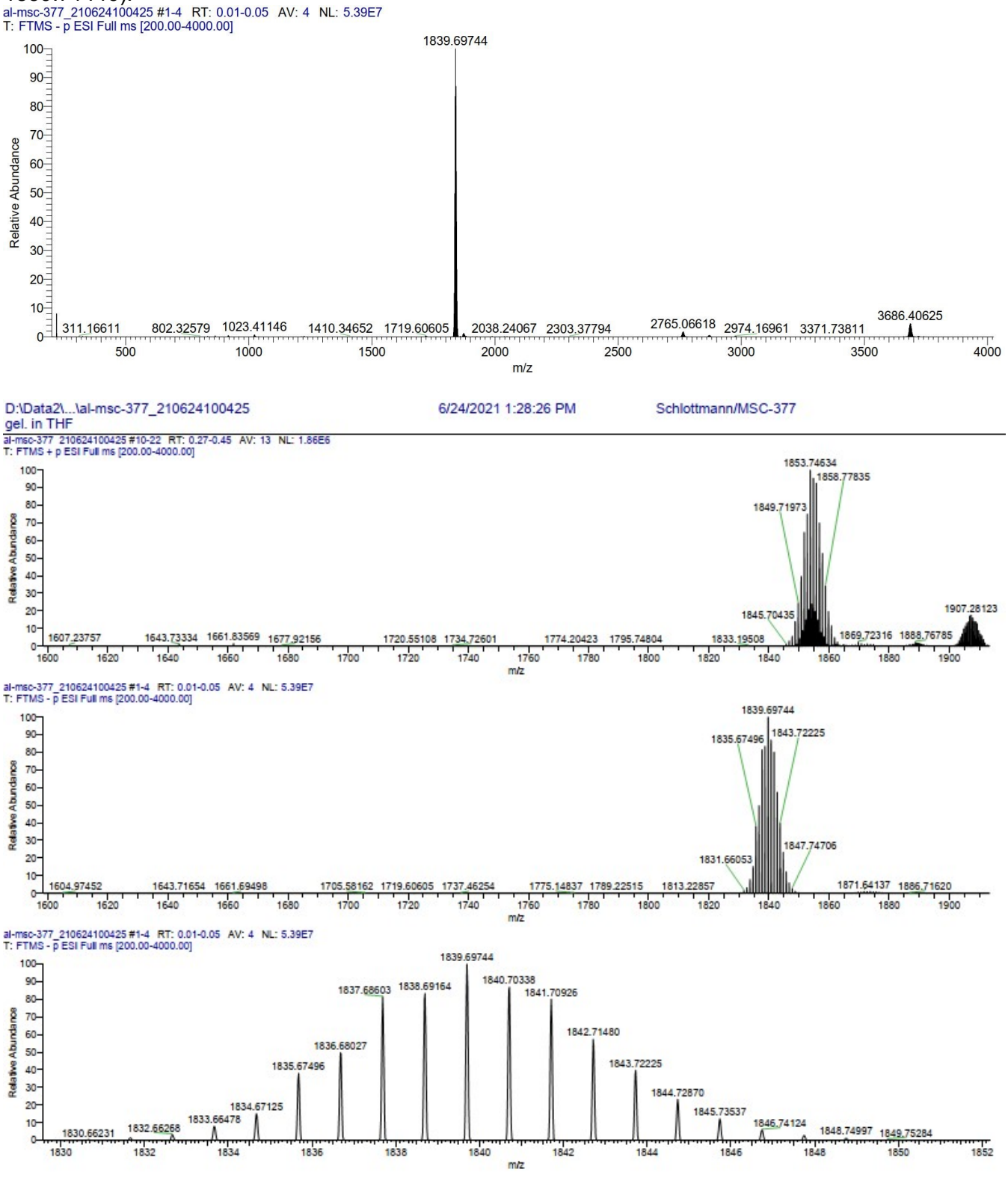


Figure 11: ESI mass spectrum of $Li[Li_3L^{3(-)}{}_3L^{5(-)}{}_3Ti_2]$.

$Li[Li_3L^{3(-)}{}_2L^{5(-)}{}_4Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1843.73601 (100, $[M_D\text{-}Li^+]$, $C_{102}H_{116}Li_3O_{24}Ti_2^-$, calc. 1841.73011).

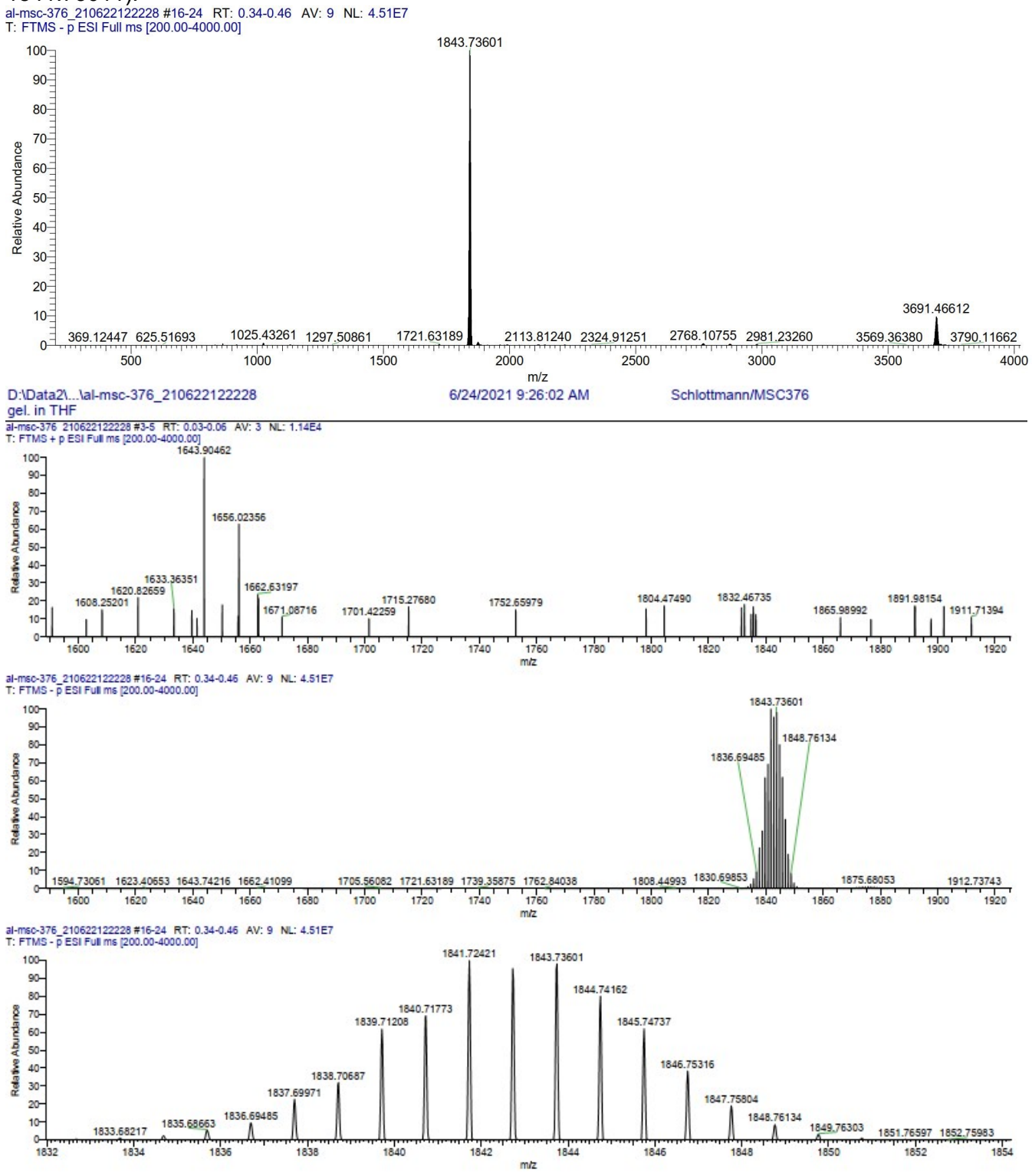


Figure 12: ESI mass spectrum of $Li[Li_3L^{3(-)}{}_2L^{5(-)}{}_4Ti_2]$.

$Li[Li_3L^{3(-)}{}_1L^{5(-)}{}_5Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1843.73251 (100, $[M_D\text{-}Li^+]$, $C_{102}H_{118}Li_3O_{24}Ti_2^-$, calc. 1843.74576).

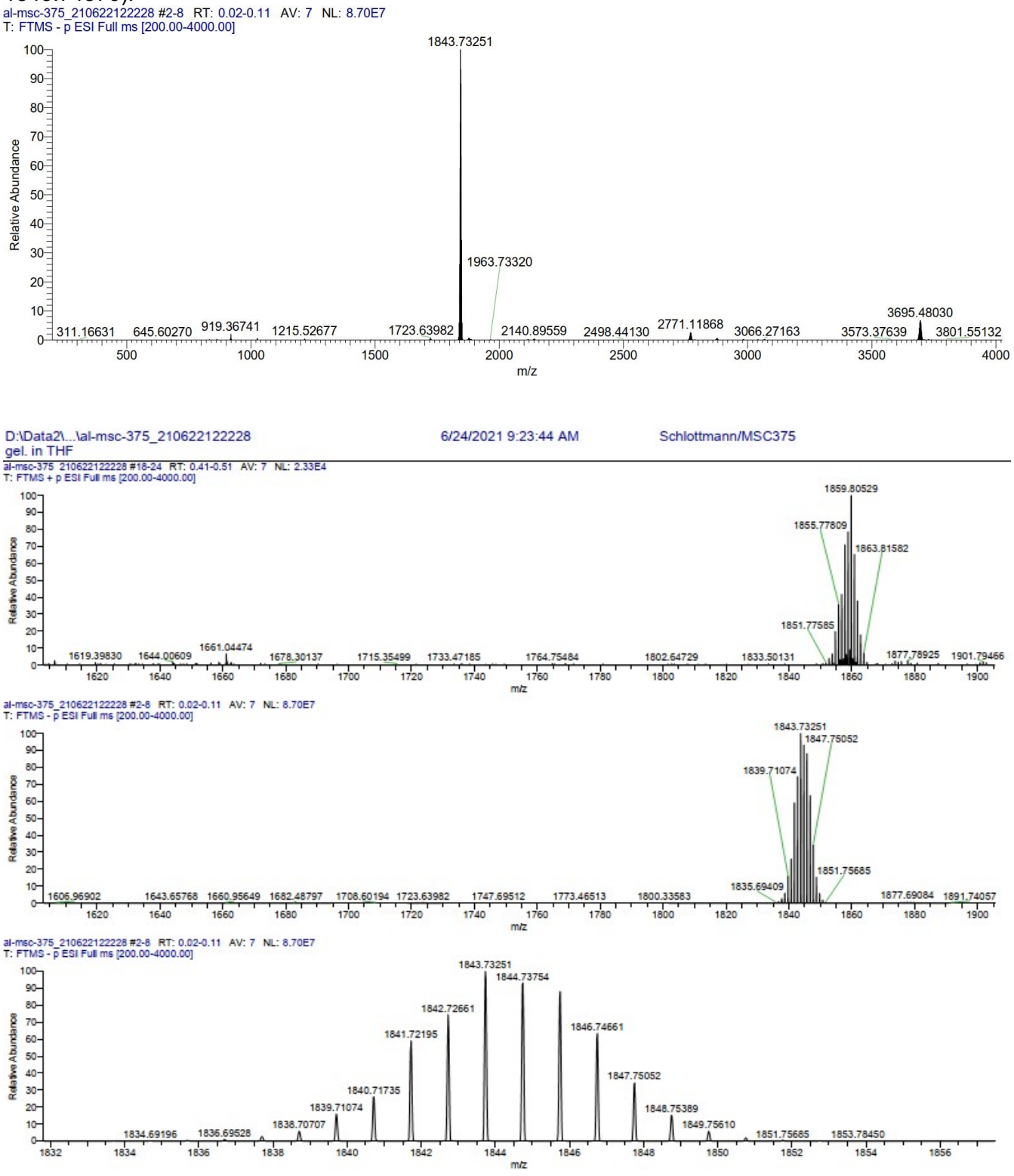


Figure 13: ESI mass spectrum of $Li[Li_3L^{3(-)}{}_1L^{5(-)}{}_5Ti_2]$.

$Li[Li_3L^{3(-)}{}_0L^{5(-)}{}_6Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1845.75165 (100, $[M_D\text{-}Li^+]$, $C_{102}H_{120}Li_3O_{24}Ti_2^-$, calc. 1845.76141).

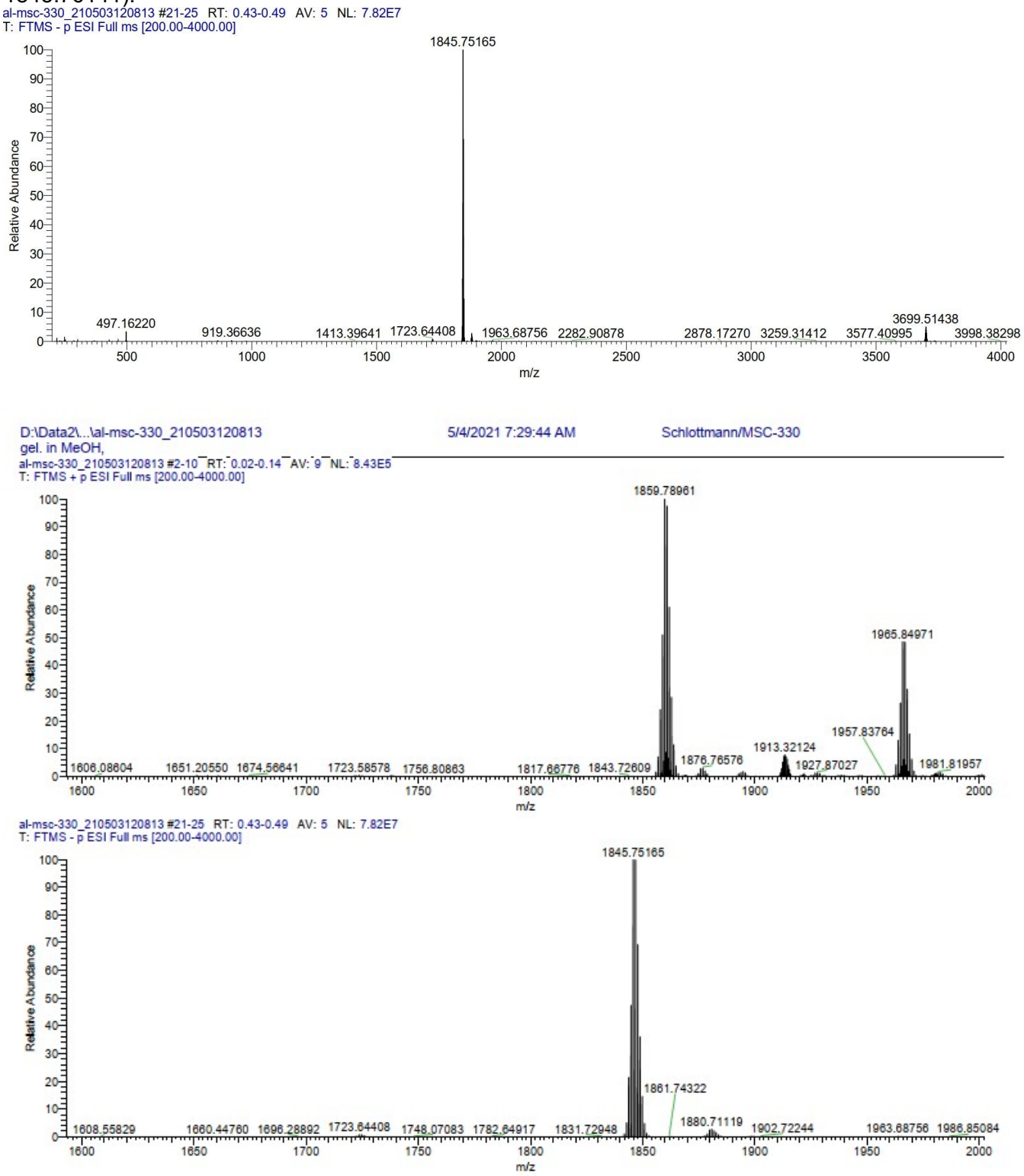
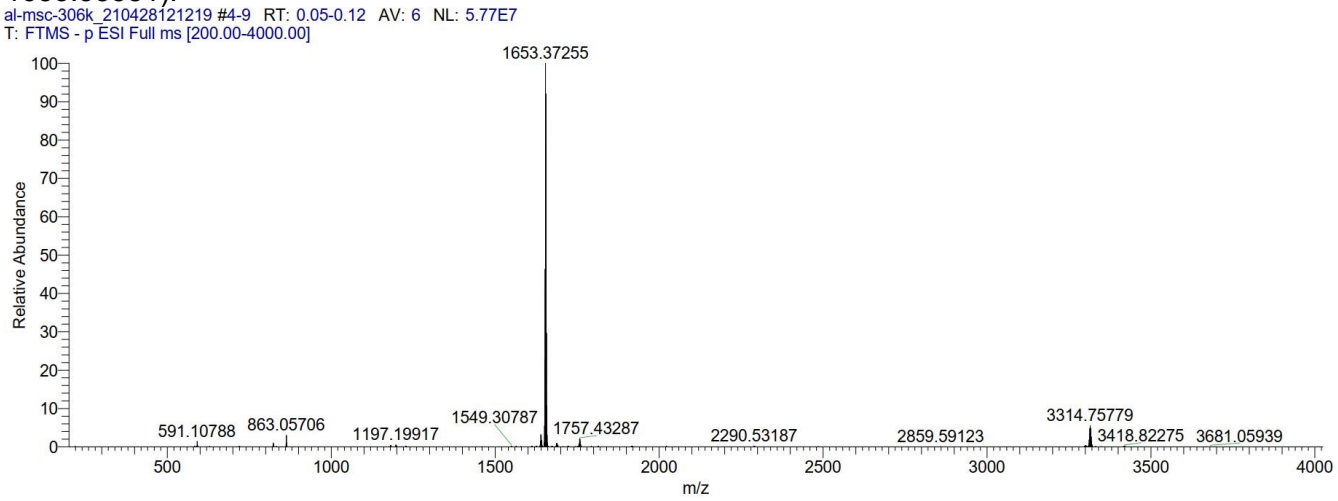


Figure 14: ESI mass spectrum of $Li[Li_3L^{3(-)}{}_0L^{5(-)}{}_6Ti_2]$.

$Li[Li_3L^{1R}_XL^{5(-)}_{(6-X)}Ti_2]$

$Li[Li_3L^{1R}_6L^{5(-)}_0Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1653.37255 (100, $[M_D\text{-}Li^+]$, $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calc. 1653.38581).



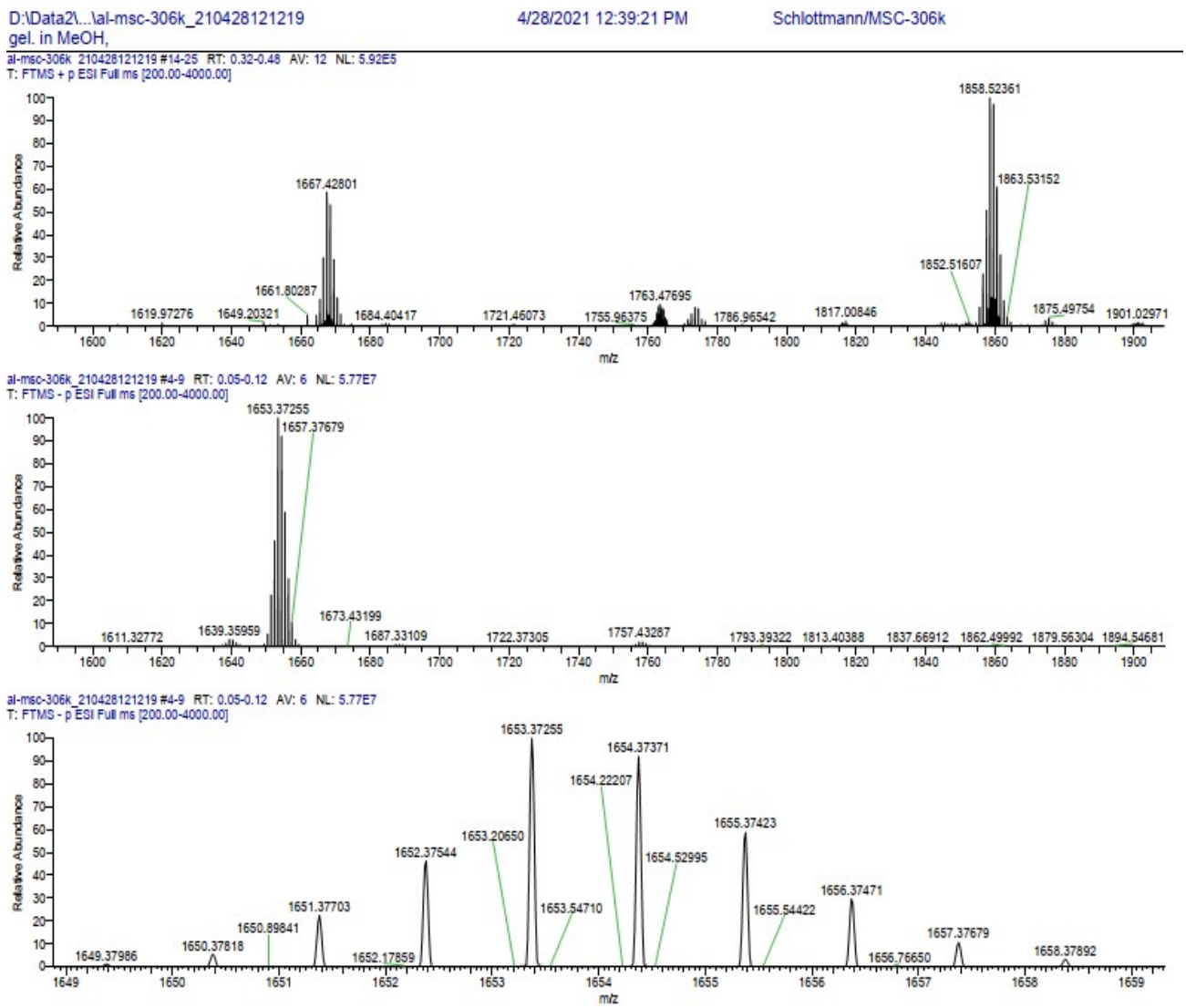
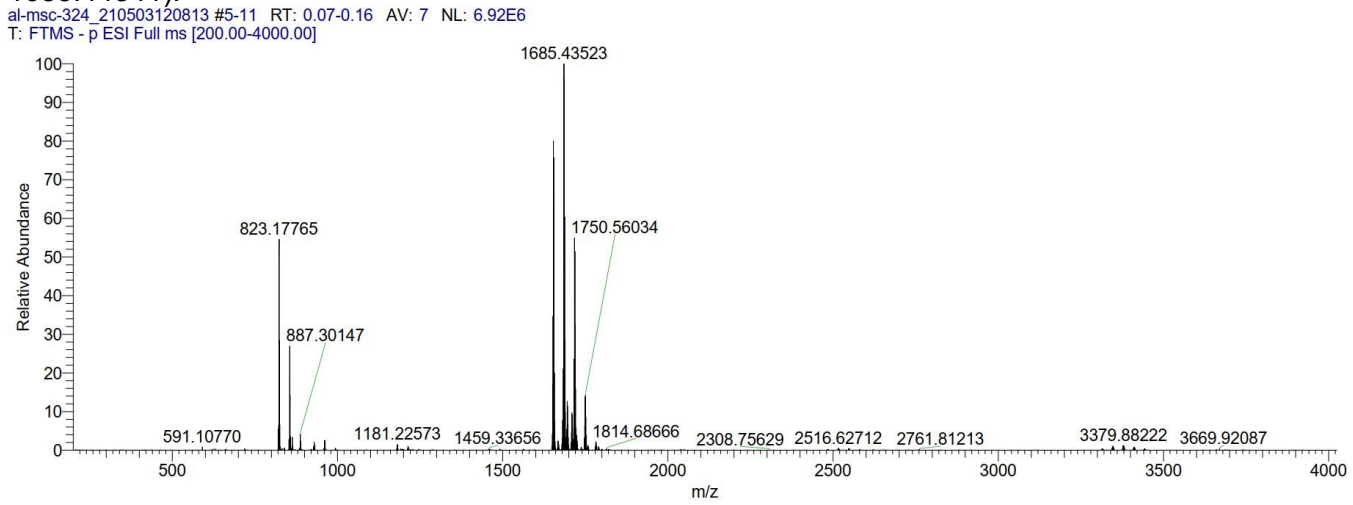


Figure 15: ESI mass spectrum of $Li[Li_3L^{1R}{}_6L^{5(-)}{}_0Ti_2]$.
$Li[Li_3L^{1R}{}_5L^{5(-)}{}_1Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1685.43523 (100, $[M_D\text{-}Li^+]$, $C_{92}H_{80}Li_3O_{24}Ti_2^-$, calc. 1685.44841).



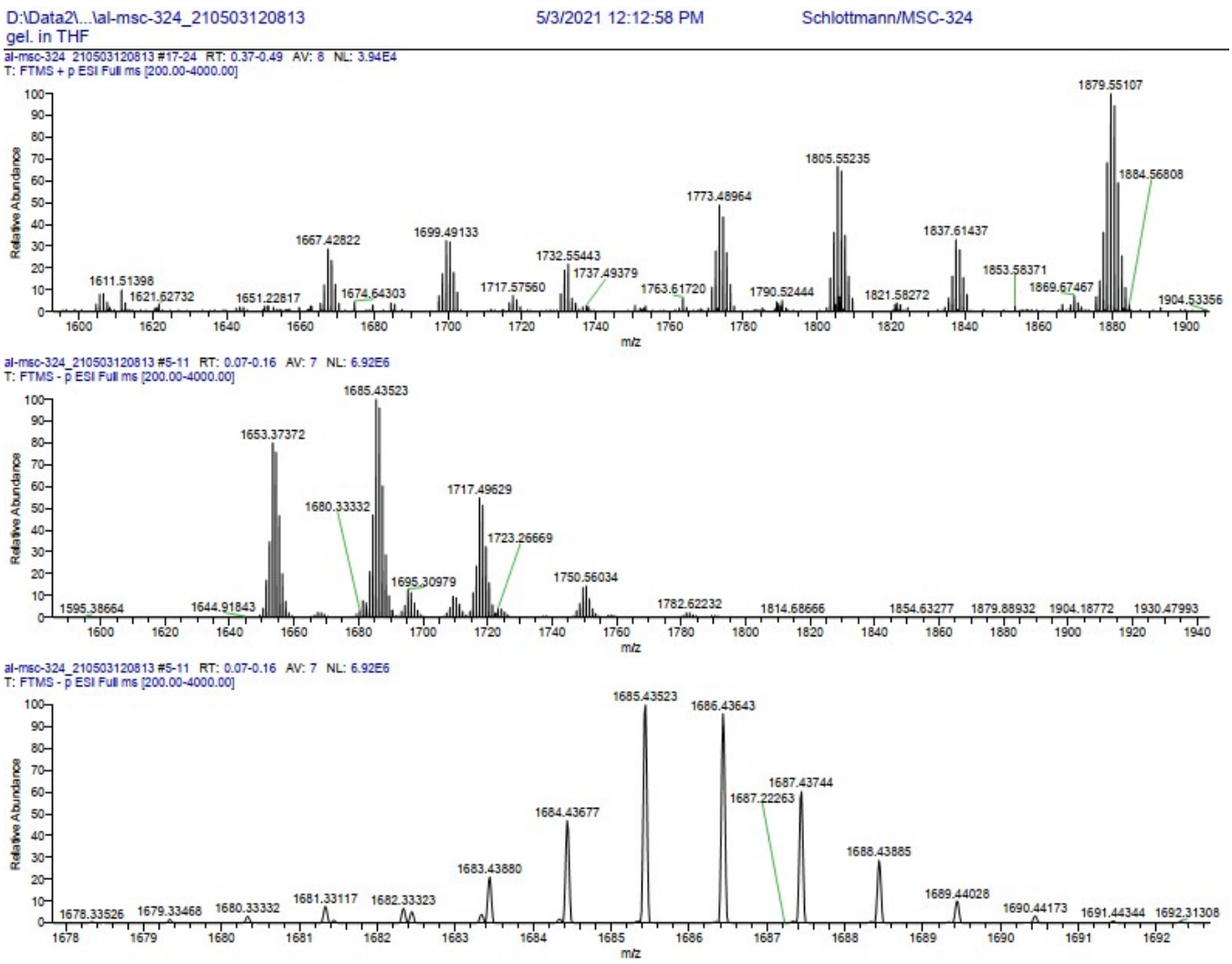
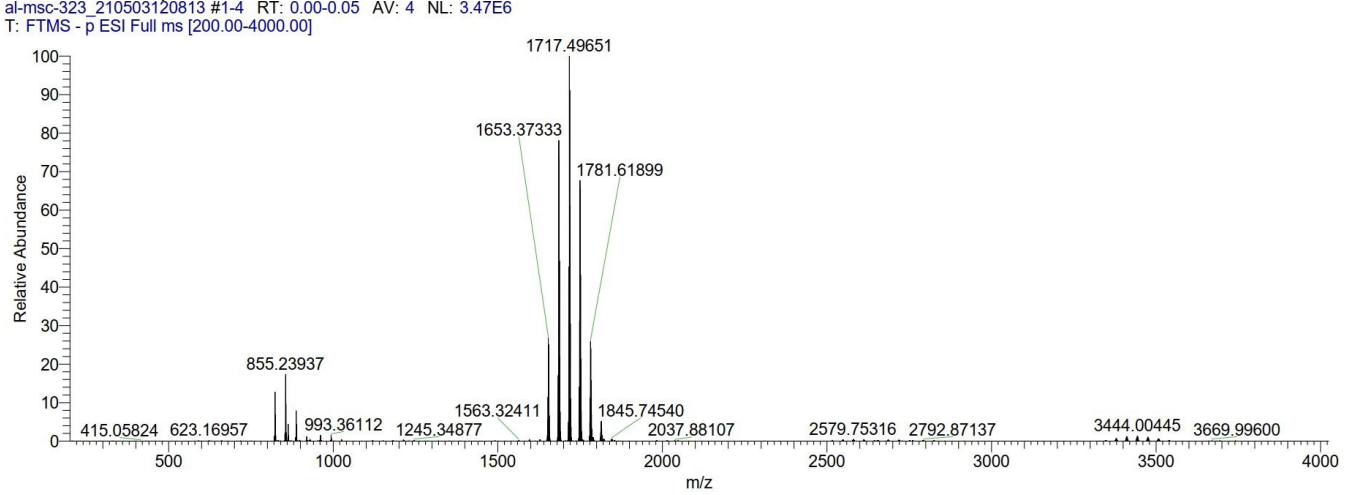


Figure 16: ESI mass spectrum of $Li[Li_3L^{1R}{}_5L^{5(-)}{}_1Ti_2]$.

$Li[Li_3L^{1R}{}_4L^{5(-)}{}_2Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1717.49651 (100, $[M_D\text{-}Li^+]$, $C_{94}H_{88}Li_3O_{24}Ti_2^-$, calc. 1717.51101).



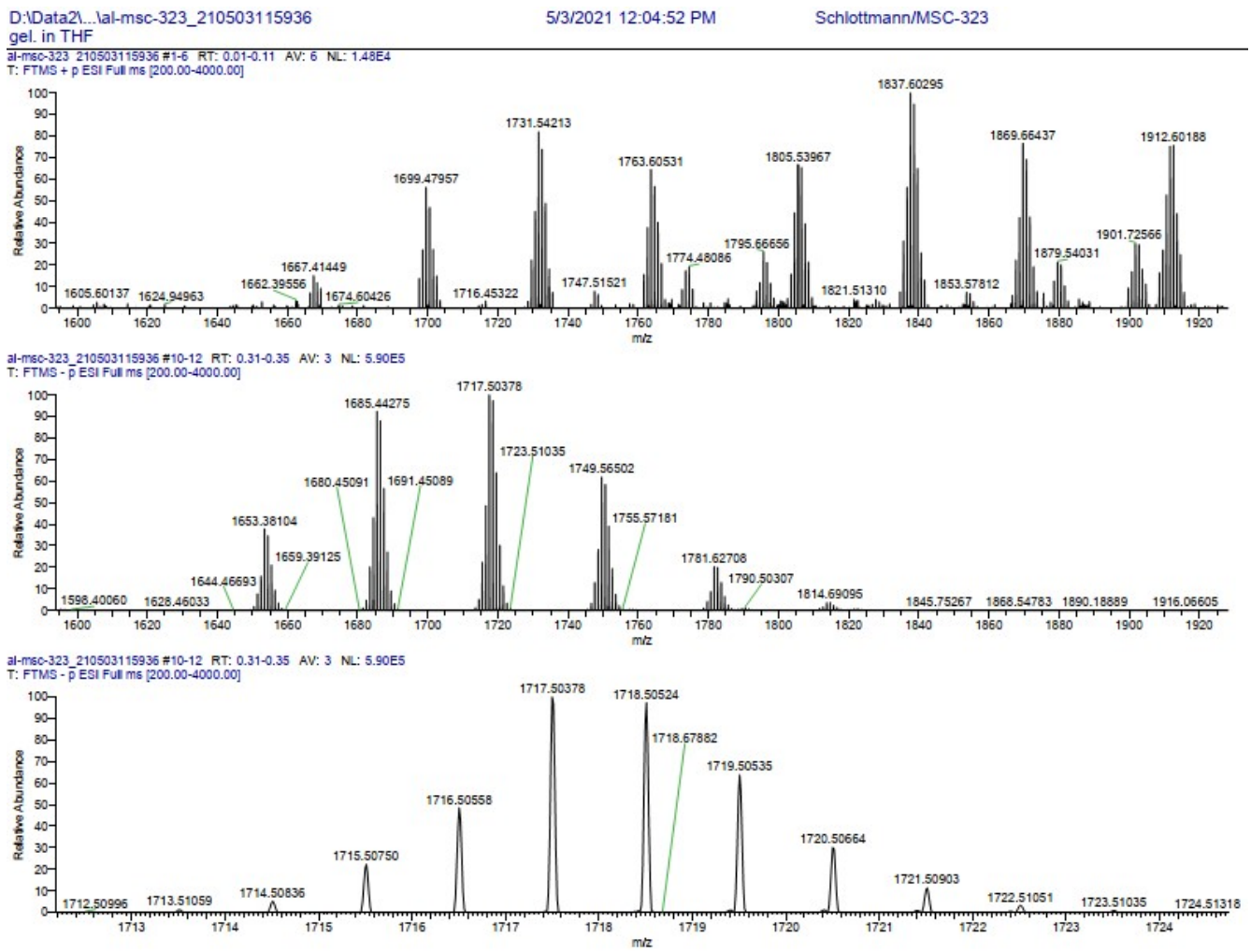
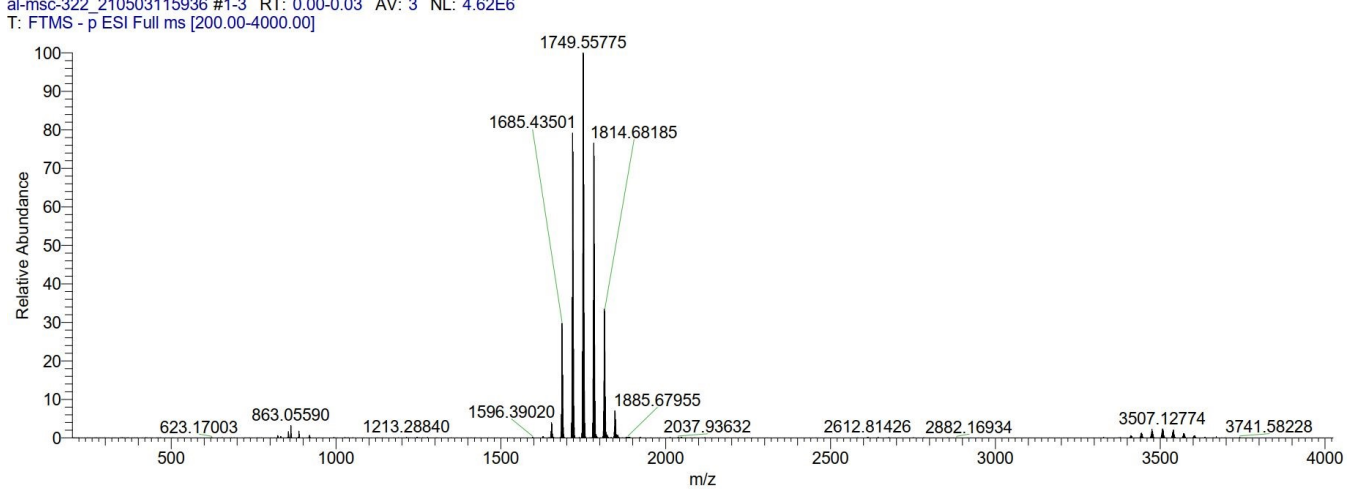


Figure 17: ESI mass spectrum of $Li[Li_3L^{1R}{}_4L^{5(-)}{}_2Ti_2]$.

$Li[Li_3L^{1R}{}_3L^{5(-)}{}_3Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1749.55775 (100, $[M_D\text{-}Li^+]$, $C_{96}H_{96}Li_3O_{24}Ti_2^-$, calc. 1749.57361).



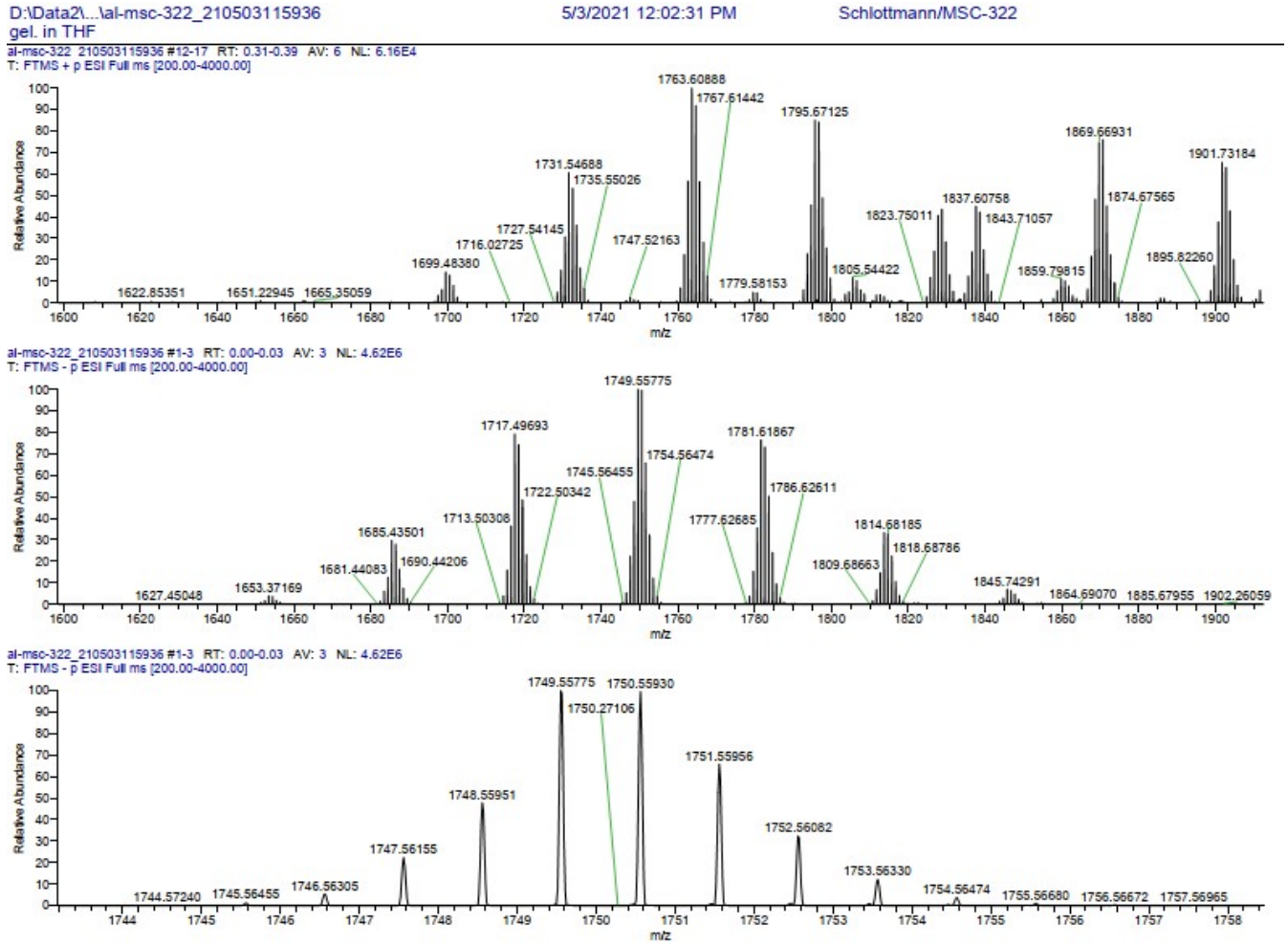
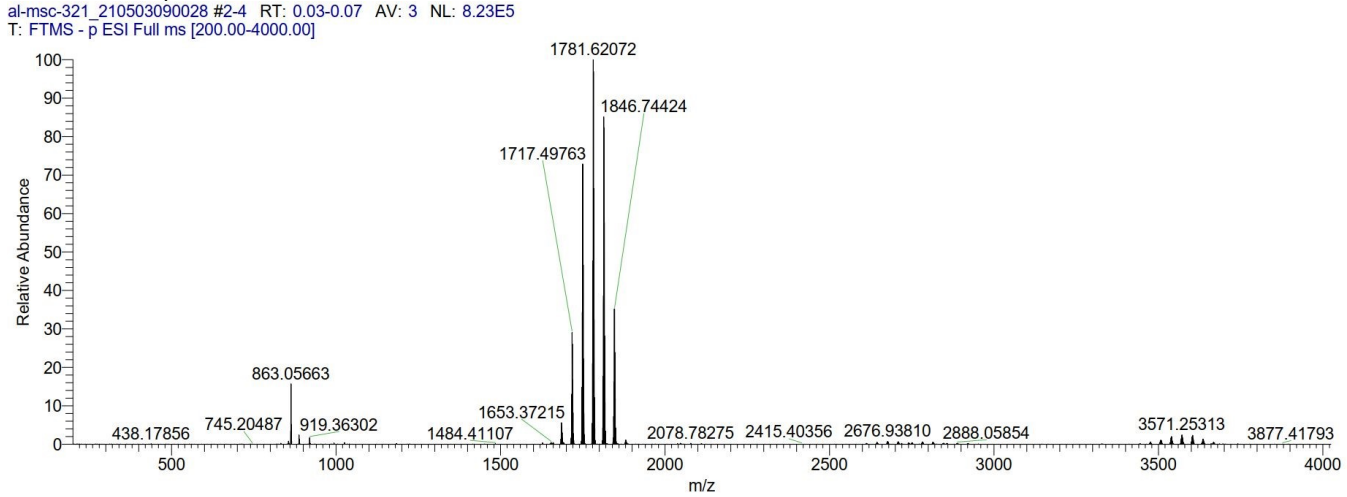


Figure 18: ESI mass spectrum of $Li[Li_3L^{1R}{}_3L^{5(-)}{}_3Ti_2]$.

$Li[Li_3L^{1R}{}_2L^{5(-)}{}_4Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1781.62072 (100, $[M_D\text{-}Li^+]$, $C_{98}H_{104}Li_3O_{24}Ti_2^-$, calc. 1781.63621).



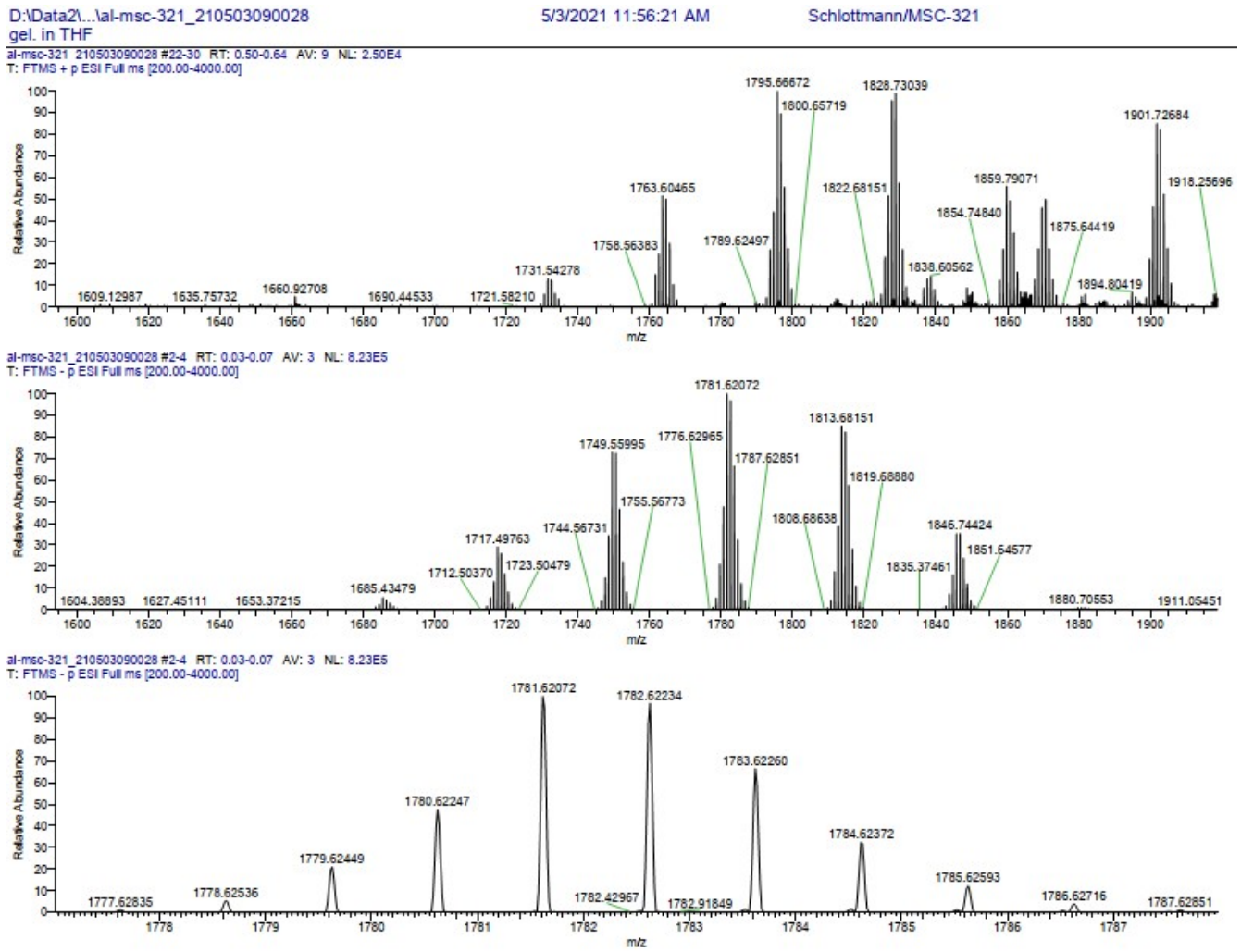
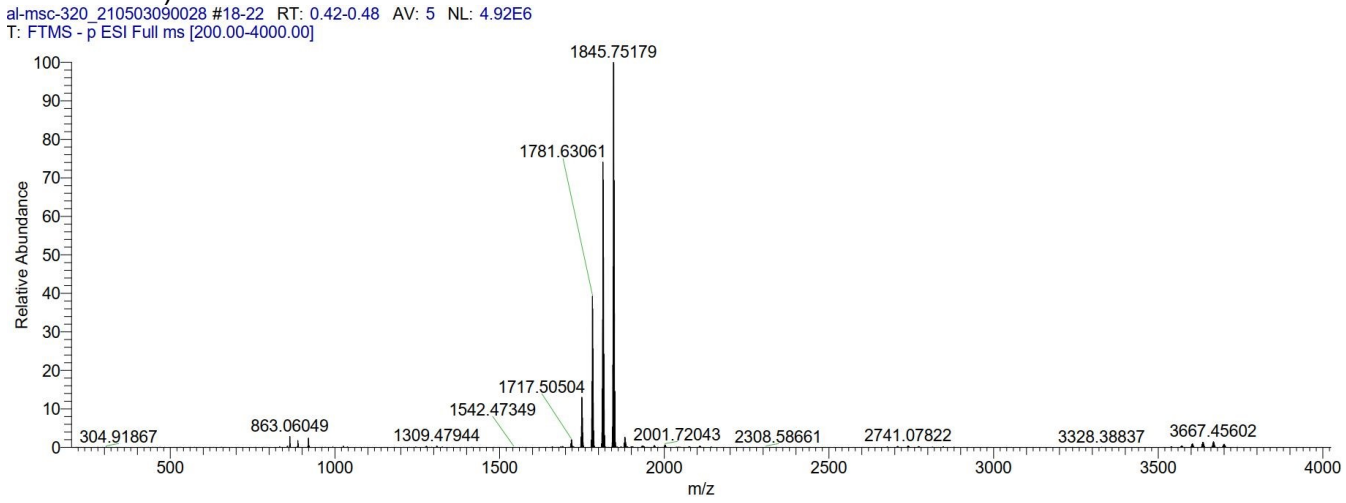


Figure 19: ESI mass spectrum of $Li[Li_3L^{1R}{}_2L^{5(-)}{}_4Ti_2]$.

$Li[Li_3L^{1R}{}_1L^{5(-)}{}_5Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1813.69221 (80, $[M_D\text{-}Li^+]$, $C_{100}H_{112}Li_3O_{24}Ti_2^-$, calc. 1813.69881).



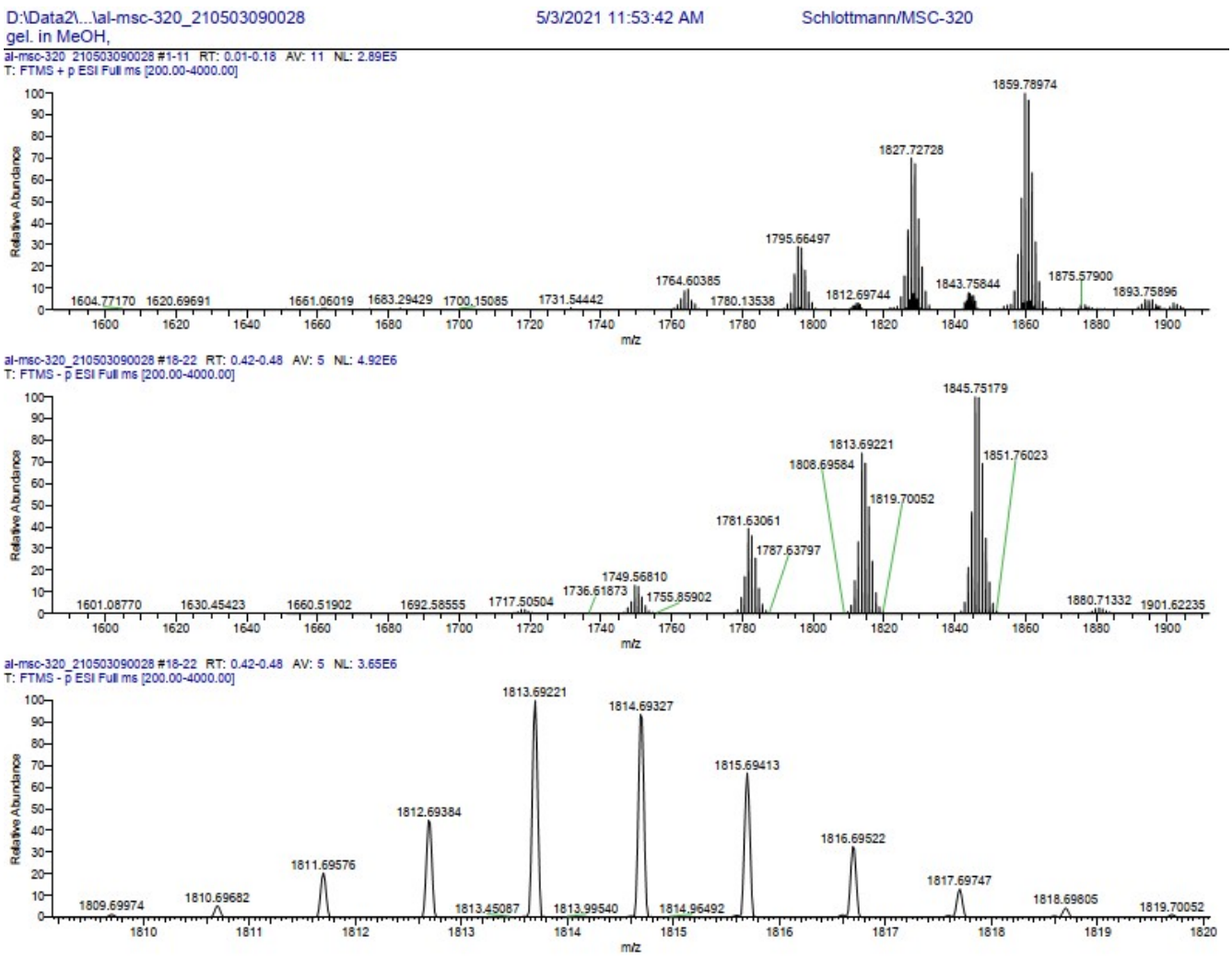


Figure 20: ESI mass spectrum of $Li[Li_3L^{1R}{}_1L^{5(-)}{}_5Ti_2]$.

$Li[Li_3L^{1R}{}_0L^{5(-)}{}_6Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1845.75165 (80, $[M_D\text{-}Li^+]$, $C_{102}H_{120}Li_3O_{24}Ti_2^-$, calc. 1845.76142).

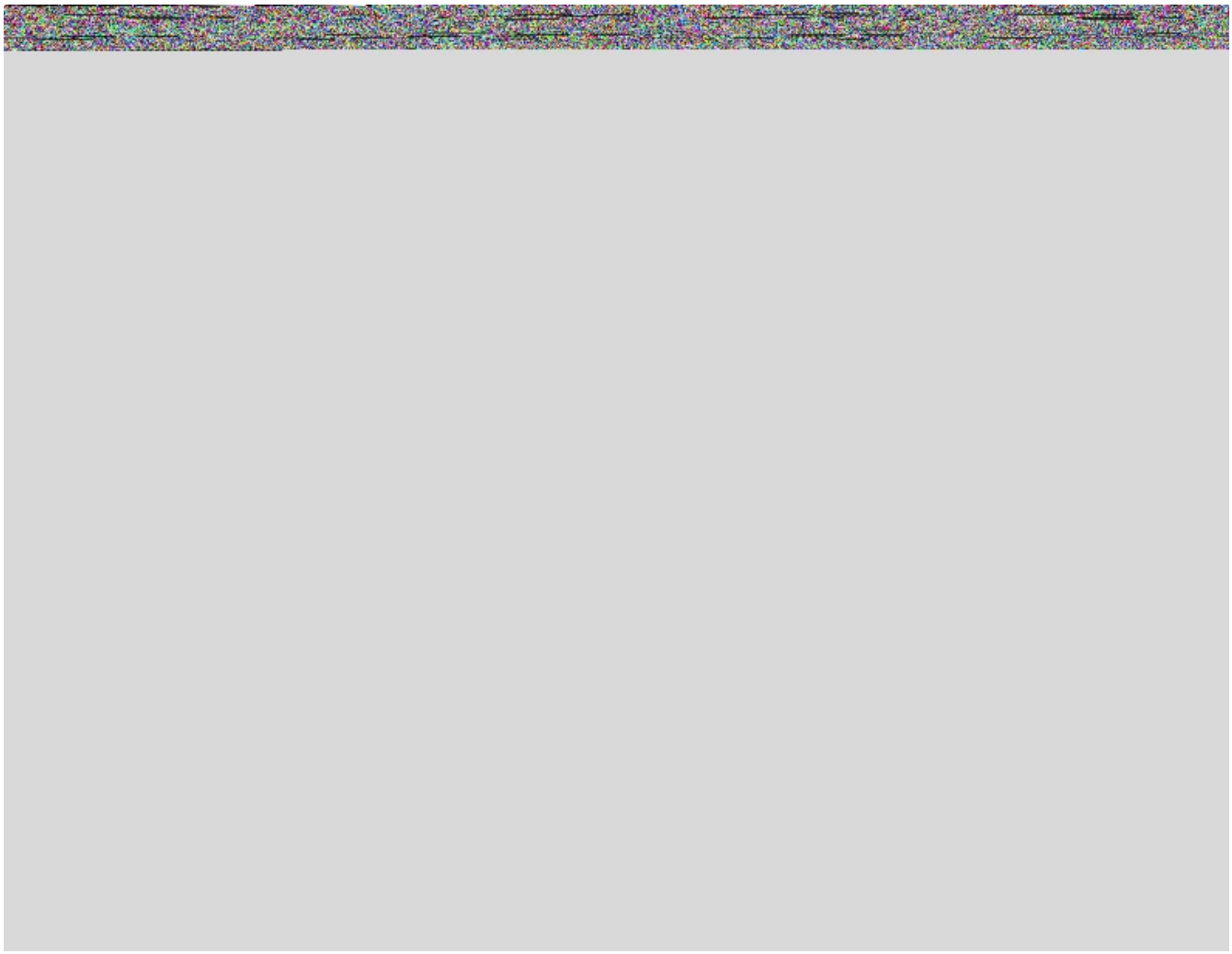


Figure 21: ESI mass spectrum of $Li[Li_3L^{1R}{}_0L^{5(-)}{}_6Ti_2]$.

$Li[Li_3L^{1R}{}_XL^{1S}{}_{(6-X)}Ti_2]$

$Li[Li_3L^{1R}{}_6L^{1S}{}_0Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1653.37255 (100, $[M_D\text{-}Li^+]$, $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calc. 1653.38581).

Figure 22: ESI mass spectrum of $Li[Li_3L^{1R}{}_6L^{1S}{}_0Ti_2]$.

$Li[Li_3L^{1R}{}_5L^{1S}{}_1Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1653.37739 (100, $[M_D\text{-}Li^+]$, $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calc. 1653.38581).

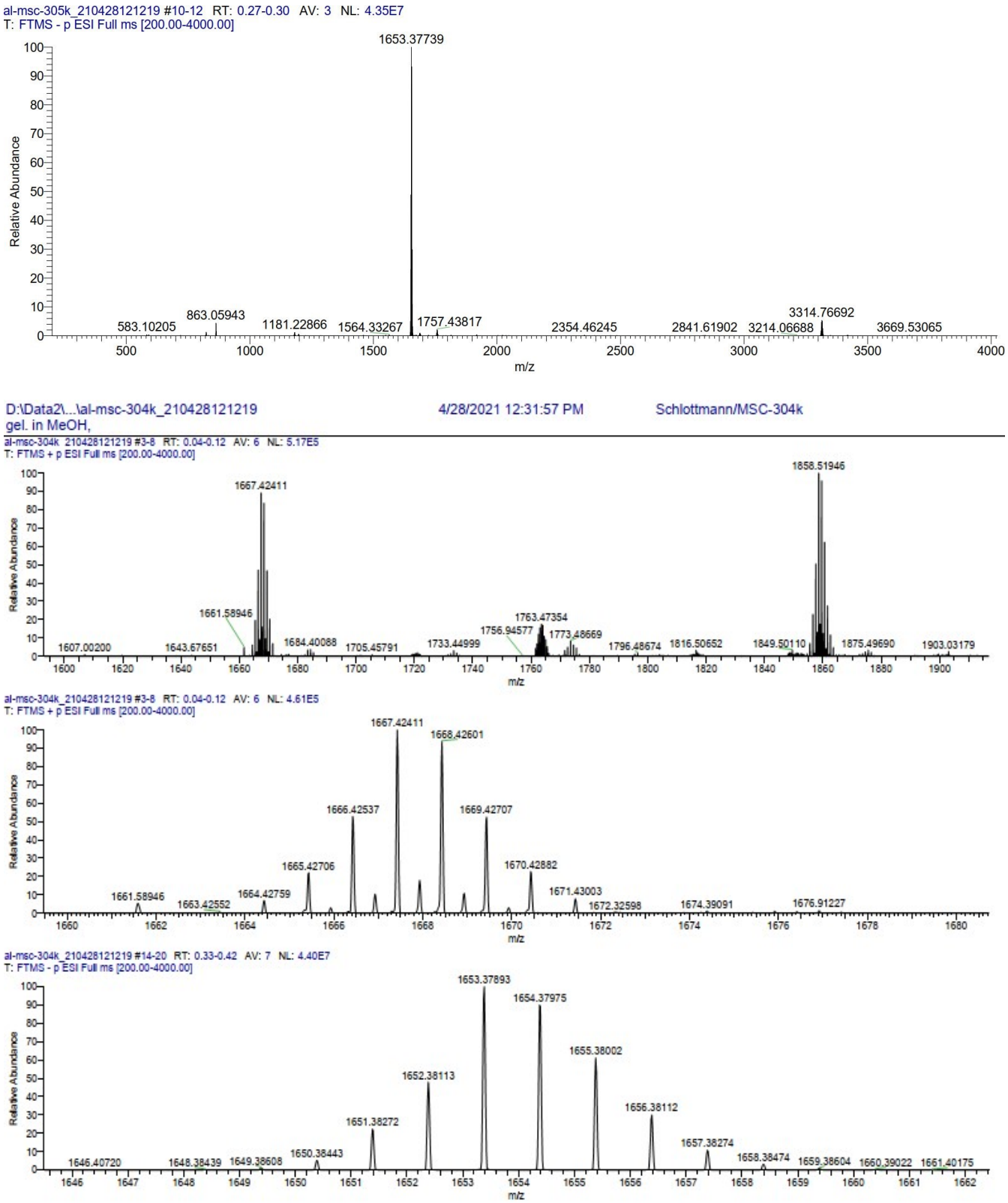


Figure 23: ESI mass spectrum of $Li[Li_3L^{1R}{}_5L^{1S}{}_1Ti_2]$.

$Li[Li_3L^{1R}{}_4L^{1S}{}_2Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1653.37893 (100, $[M_D\text{-}Li^+]$, $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calc. 1653.38581).

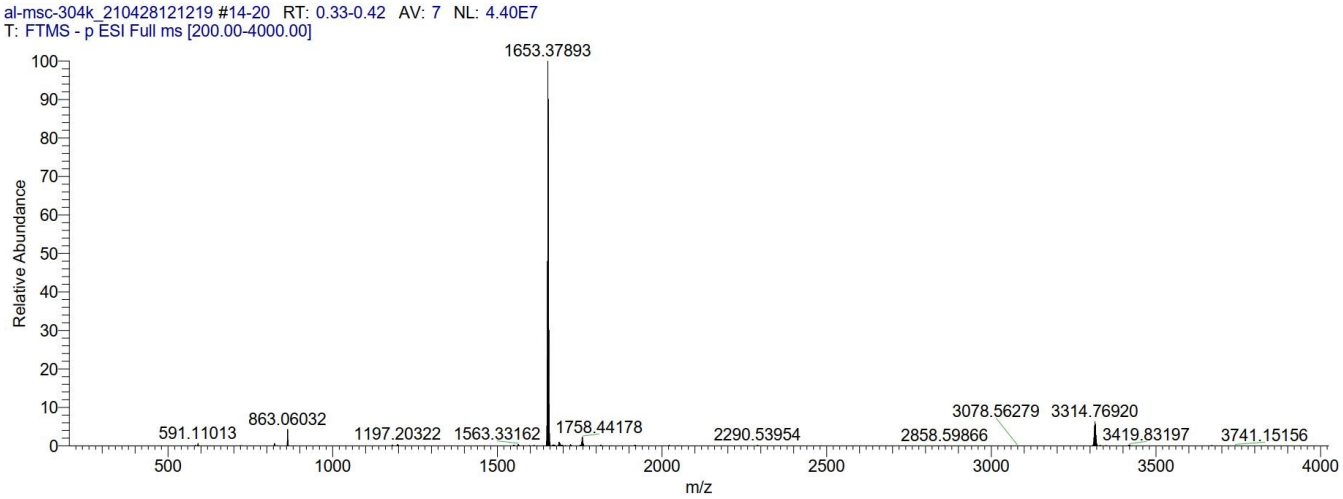


Figure 24: ESI mass spectrum of $Li[Li_3L^{1R}{}_4L^{1S}{}_2Ti_2]$.

$Li[Li_3L^{1R}{}_3L^{1S}{}_3Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1653.37194 (100, $[M_D\text{-}Li^+]$, $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calc. 1653.38581).

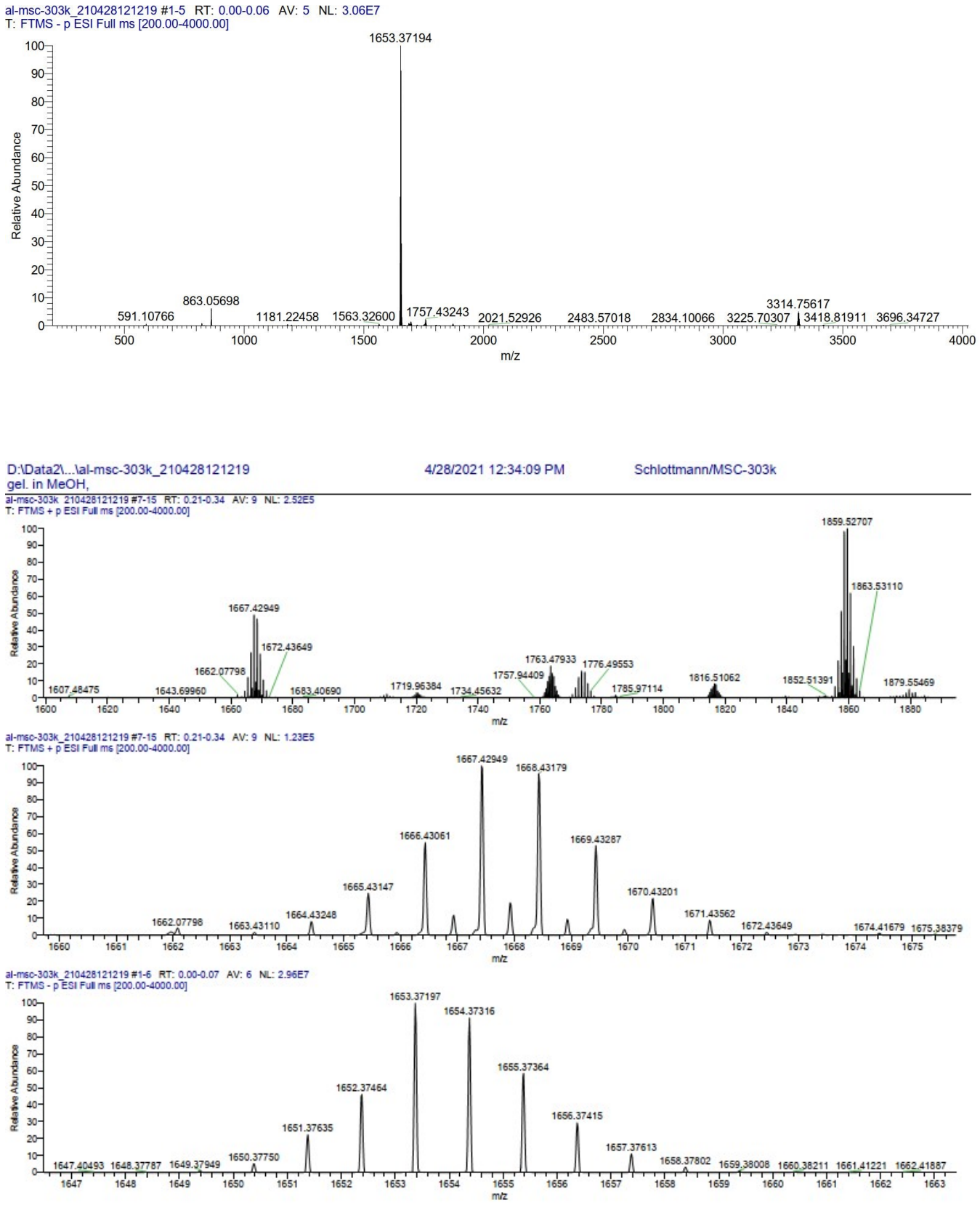


Figure 25: ESI mass spectrum of $Li[Li_3L^{1R}{}_3L^{1S}{}_3Ti_2]$.

$Li[Li_3L^{1R}{}_2L^{1S}{}_4Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1653.37965 (100, $[M_D\text{-}Li^+]$, $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calc. 1653.38581).

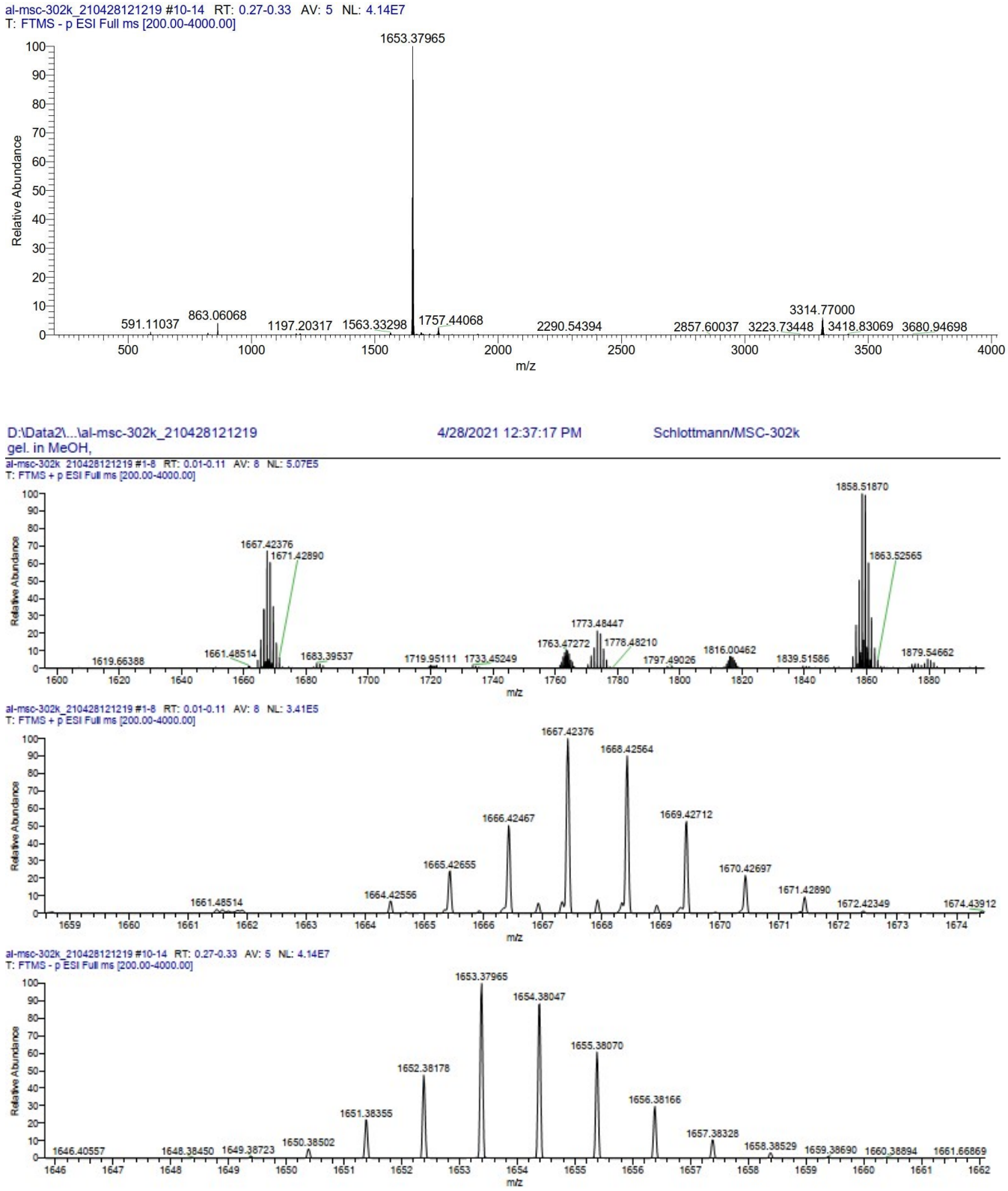


Figure 26: ESI mass spectrum of $Li[Li_3L^{1R}{}_2L^{1S}{}_4Ti_2]$.

$Li[Li_3L^{1R}{}_1L^{1S}{}_5Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1653.37994 (100, $[M_D\text{-}Li^+]$, $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calc. 1653.38581).

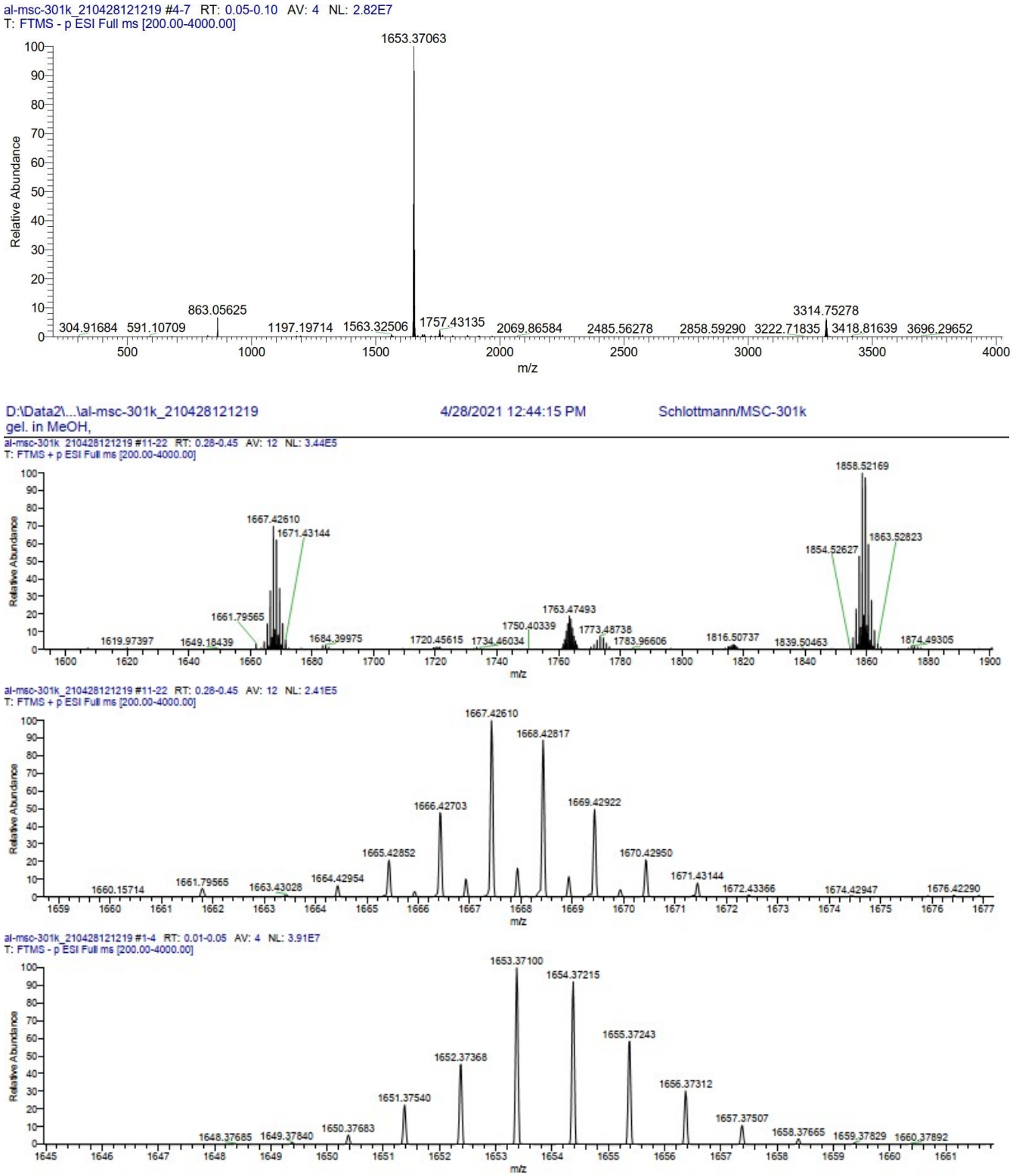


Figure 27: ESI mass spectrum of $Li[Li_3L^{1R}{}_1L^{1S}{}_5Ti_2]$.

$Li[Li_3L^{1R}{}_0L^{1S}{}_6Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1653.37715 (100, $[M_D\text{-}Li^+]$, $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calc. 1653.38581).

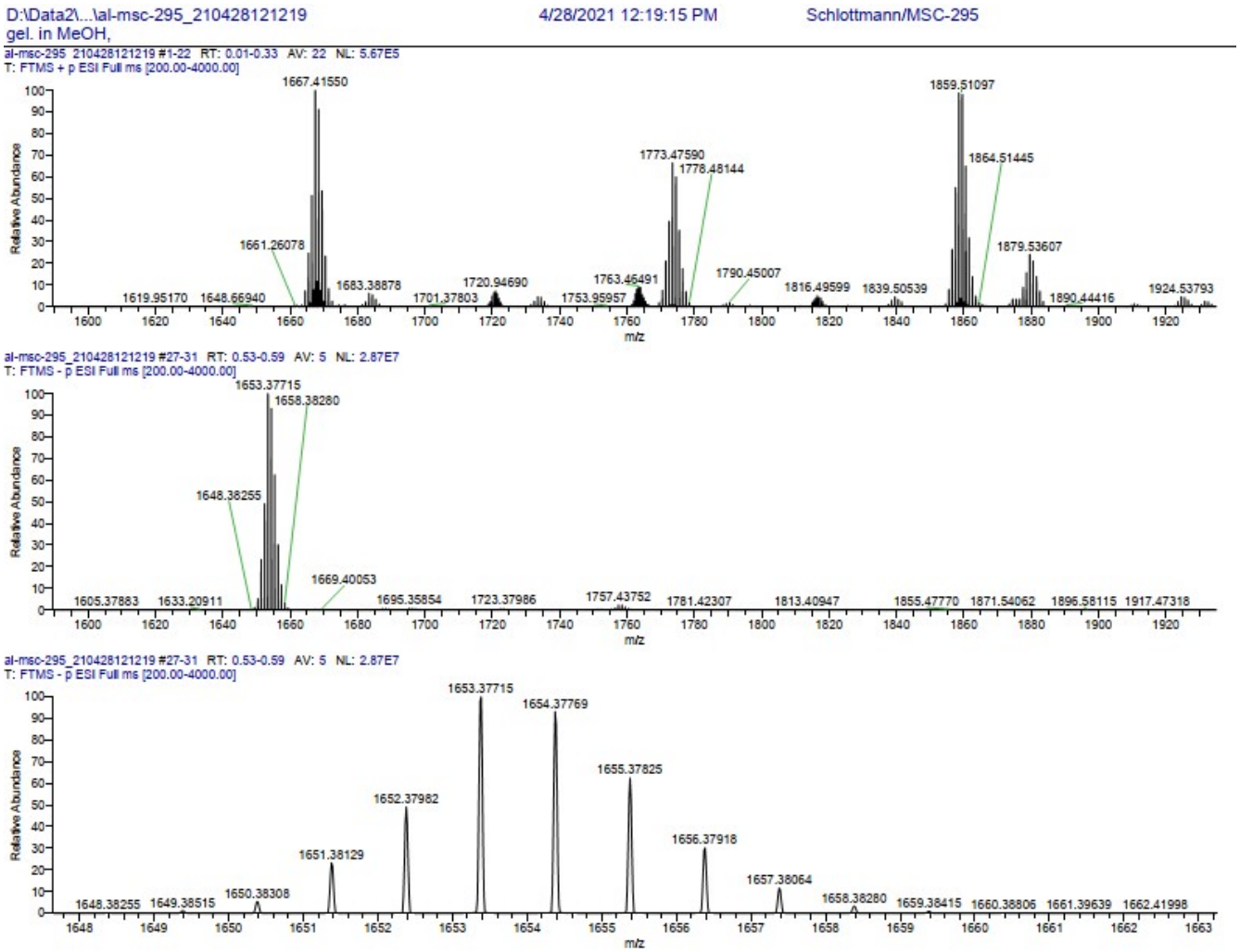


Figure 28: ESI mass spectrum of $Li[Li_3L^{1R}{}_0L^{1S}{}_6Ti_2]$.

$Li[Li_3L^{1S}{}_XL^{4(-)}{}_{(6-X)}Ti_2]$

$Li[Li_3L^{1S}{}_6L^{4(-)}{}_0Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1653.37715 (100, $[M_D\text{-}Li^+]$, $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calc. 1653.38581).

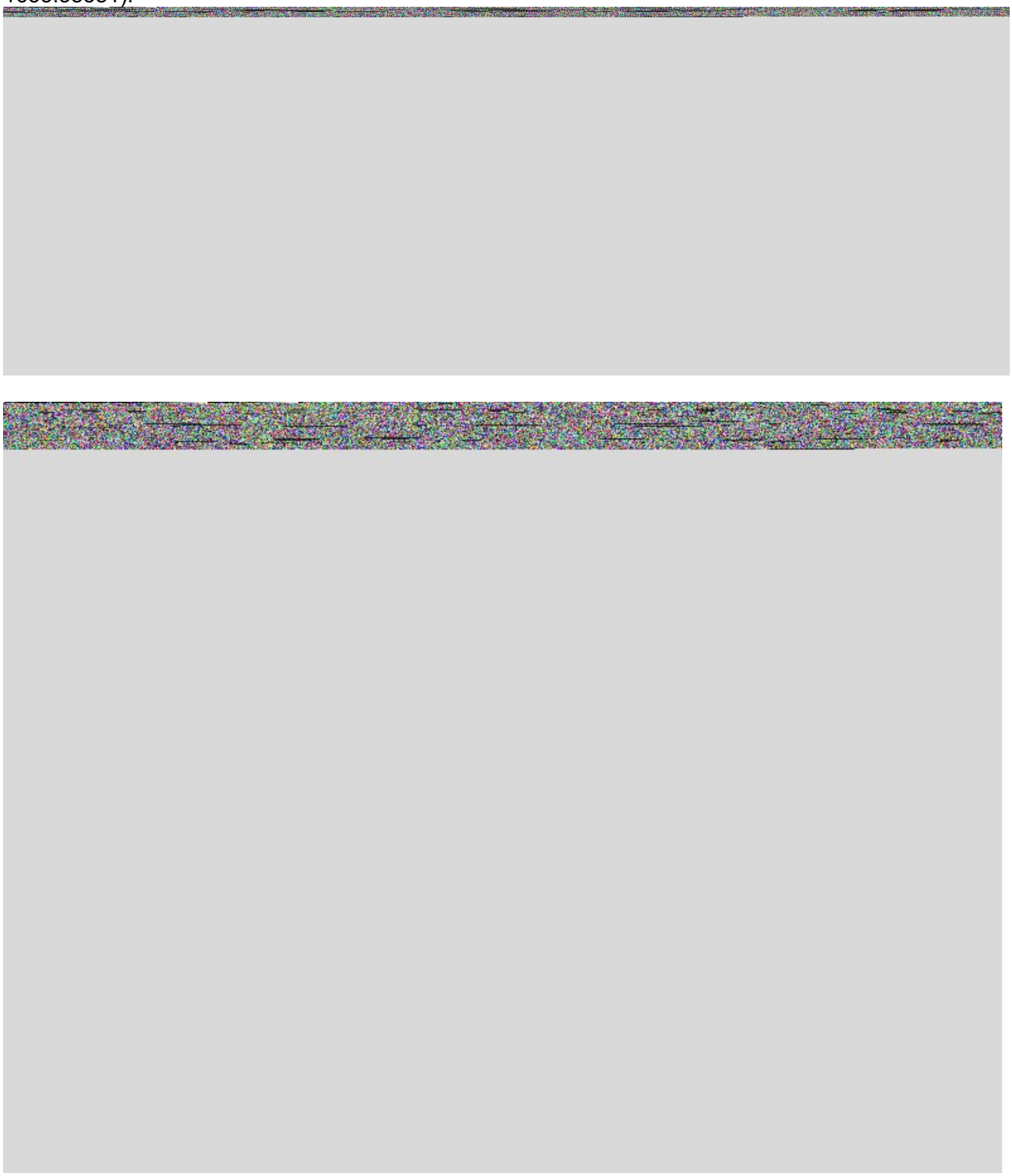


Figure 29: ESI mass spectrum of $Li[Li_3L^{1S}{}_6L^{4(-)}{}_0Ti_2]$.

$Li[Li_3L^{1S}{}_5L^{4(-)}{}_1Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1687.44485 (58, $[M_D\text{-}Li^+]$, $C_{92}H_{82}Li_3O_{24}Ti_2^-$, calc. 1687.46406).

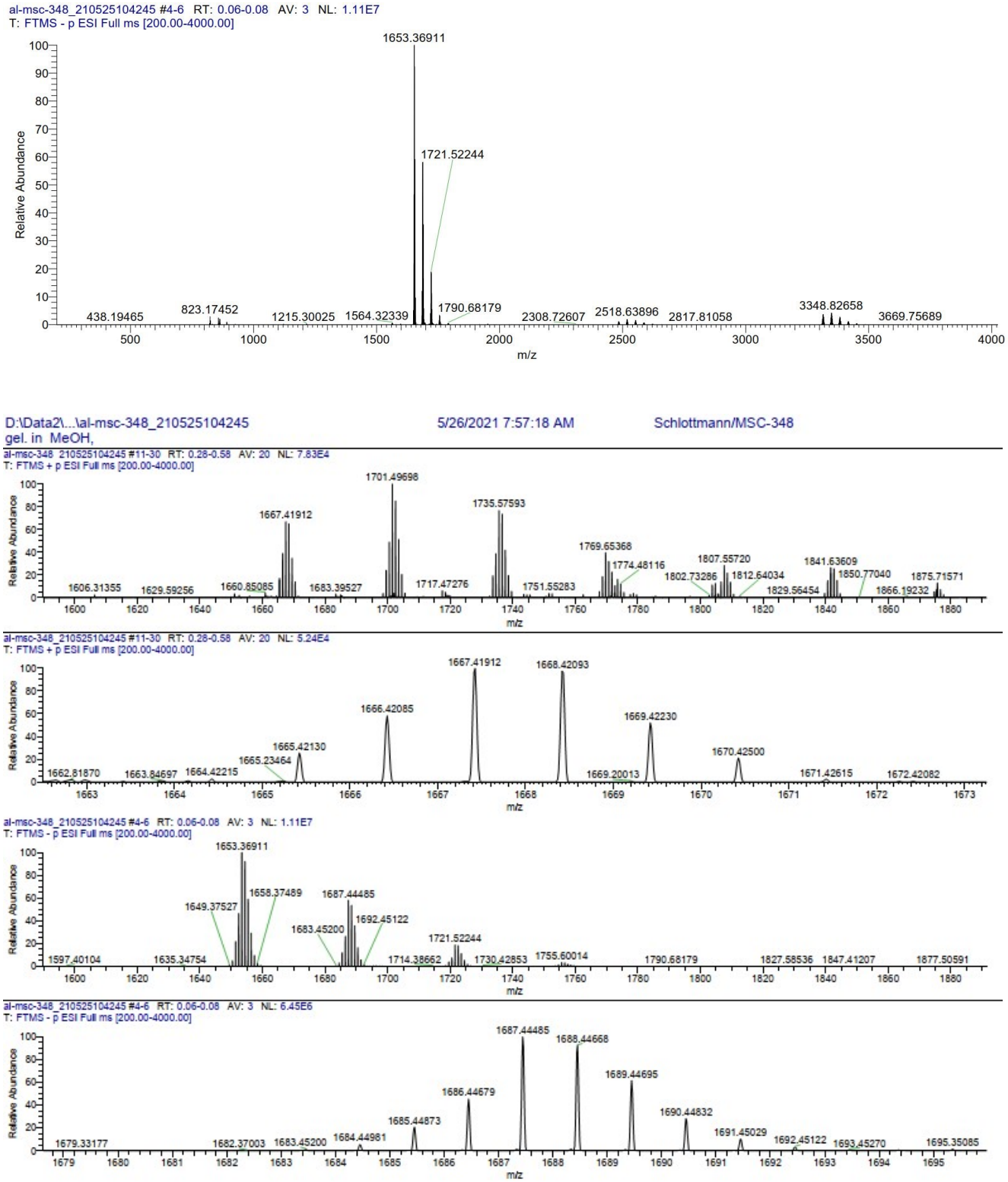


Figure 30: ESI mass spectrum of $Li[Li_3L^{1S}{}_5L^{4(-)}{}_1Ti_2]$.

$Li[Li_3L^{1S}{}_4L^{4(-)}{}_2Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1721.53055 (60, $[M_D\text{-}Li^+]$, $C_{94}H_{92}Li_3O_{24}Ti_2^-$, calc. 1721.54231).

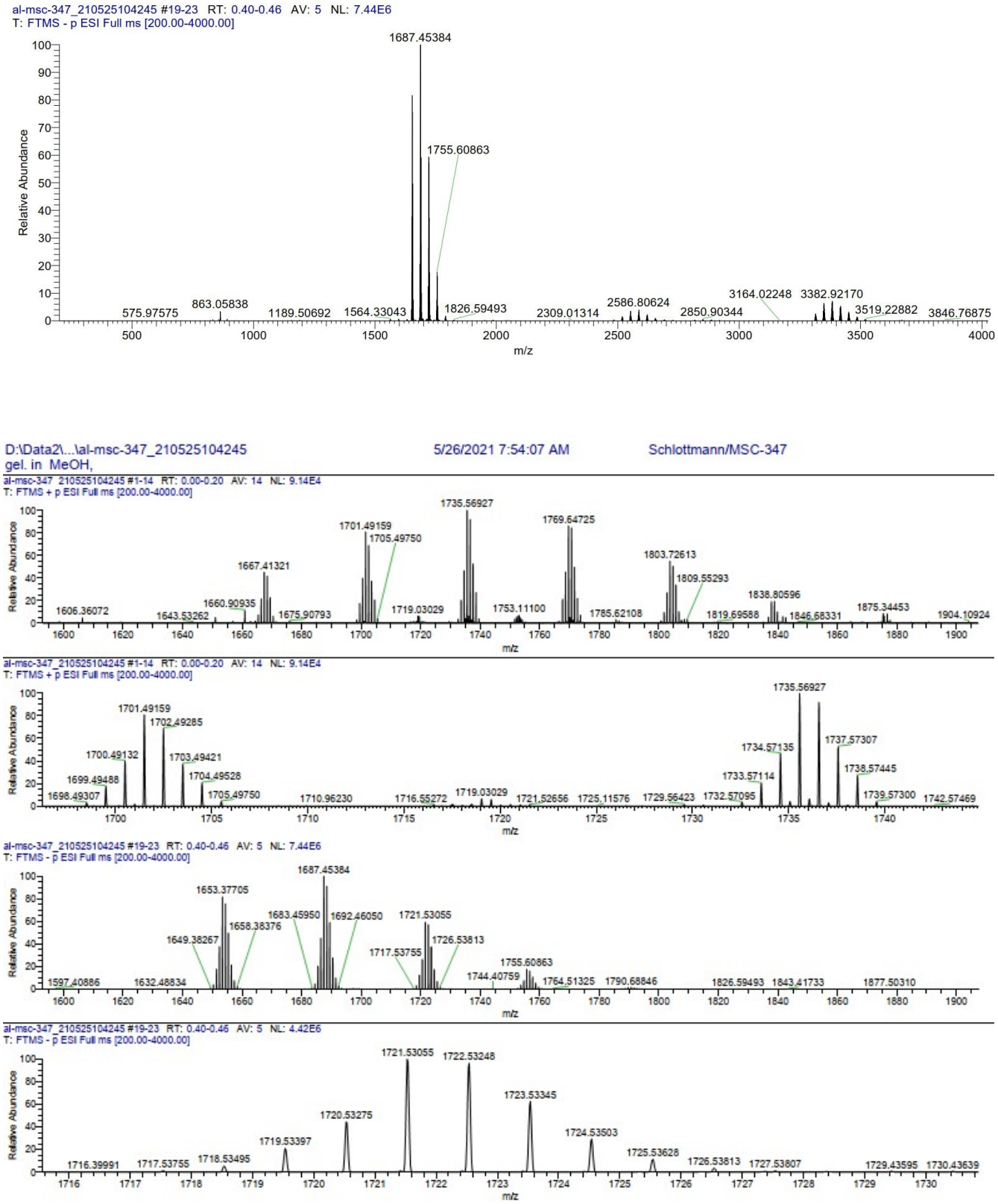


Figure 31: ESI mass spectrum of $Li[Li_3L^{1S}{}_4L^{4(-)}{}_2Ti_2]$.

$Li[Li_3L^{1S}{}_3L^{4(-)}{}_3Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1755.61304 (100, $[M_D\text{-}Li^+]$, $C_{96}H_{102}Li_3O_{24}Ti_2^-$, calc. 1755.62056).

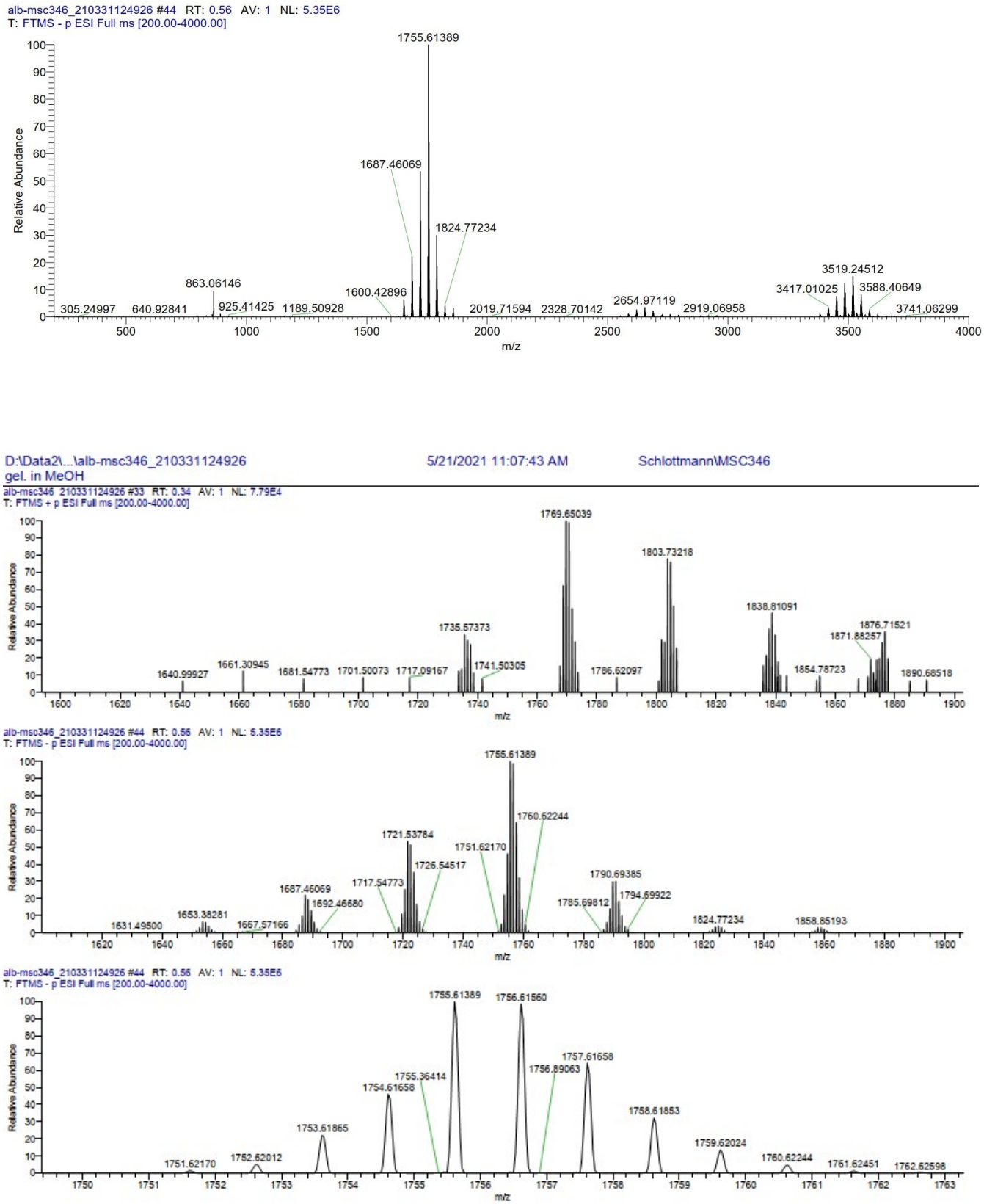


Figure 32: ESI mass spectrum of $Li[Li_3L^{1S}{}_3L^{4(-)}{}_3Ti_2]$.

$Li[Li_3L^{1S}{}_2L^{4(-)}{}_4Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1789,69189 (40, $[M_D\text{-}Li^+]$, $C_{98}H_{112}Li_3O_{24}Ti_2^-$, calc. 1789.69881).

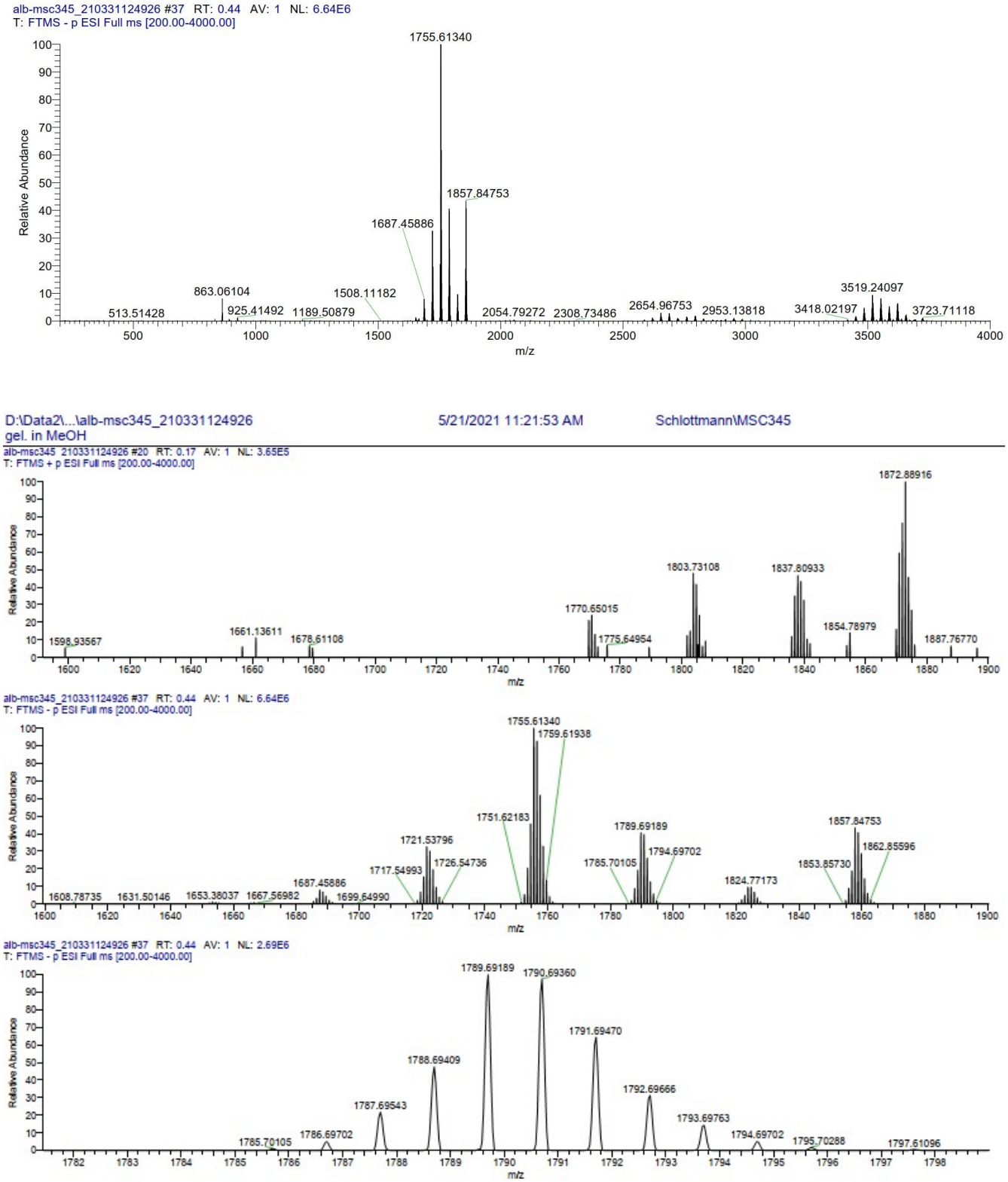


Figure 33: ESI mass spectrum of $Li[Li_3L^{1S}{}_2L^{4(-)}{}_4Ti_2]$.

$Li[Li_3L^{1S}{}_1L^{4(-)}{}_5Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1824.77454 (40, $[M_D\text{-}Li^+]$, $C_{100}H_{122}Li_3O_{24}Ti_2^-$, calc. 1823.77706).

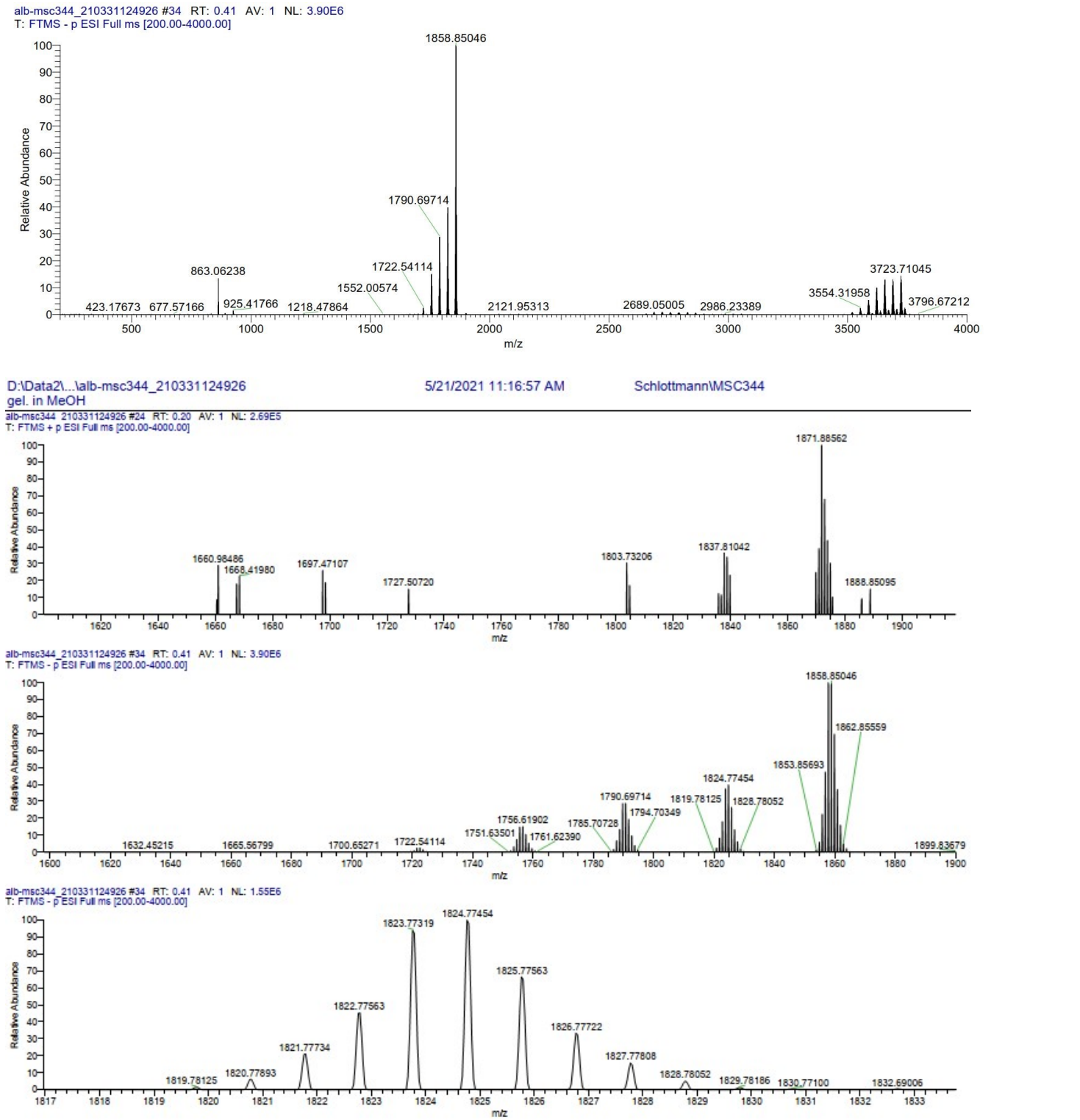


Figure 34: ESI mass spectrum of $Li[Li_3L^{1S}{}_1L^{4(-)}{}_5Ti_2]$.

$Li[Li_3L^{1S}{}_0L^{4(-)}{}_6Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1857.84788 (100, $[M_D\text{-}Li^+]$, $C_{102}H_{132}Li_3O_{24}Ti_2^-$, calc. 1857.85531).

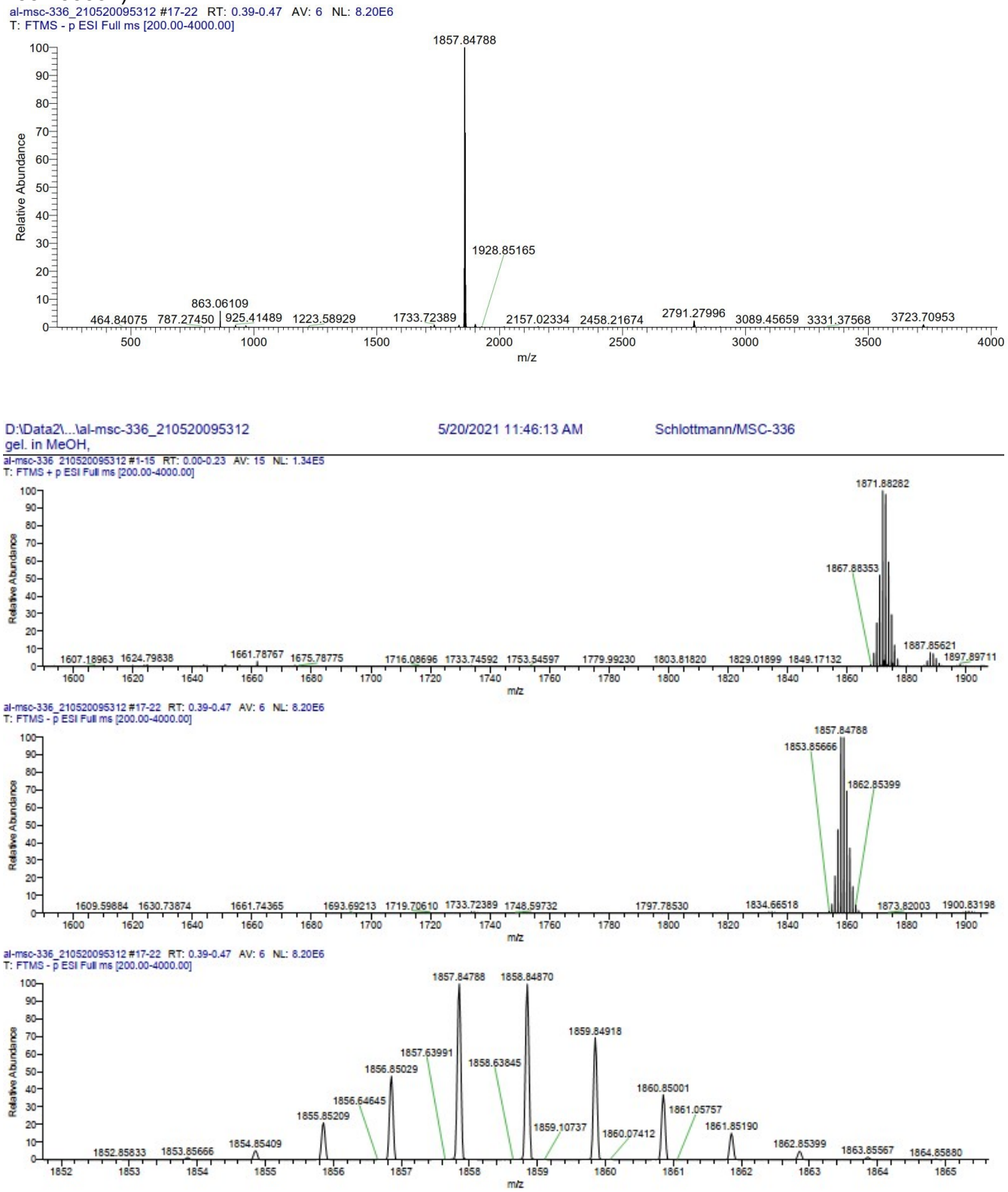


Figure 35: ESI mass spectrum of $Li[Li_3L^{1S}{}_0L^{4(-)}{}_6Ti_2]$.

$Li[Li_3L^{1S}{}_xL^{3(-)}{}_{(6-X)}Ti_2]$

$Li[Li_3L^{1S}_6L^{3(-)}_0Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1653.37715 (40, $[M_D\text{-}Li^+]$, $C_{90}H_{72}Li_3O_{24}Ti_2^-$, calc. 1653.38581).

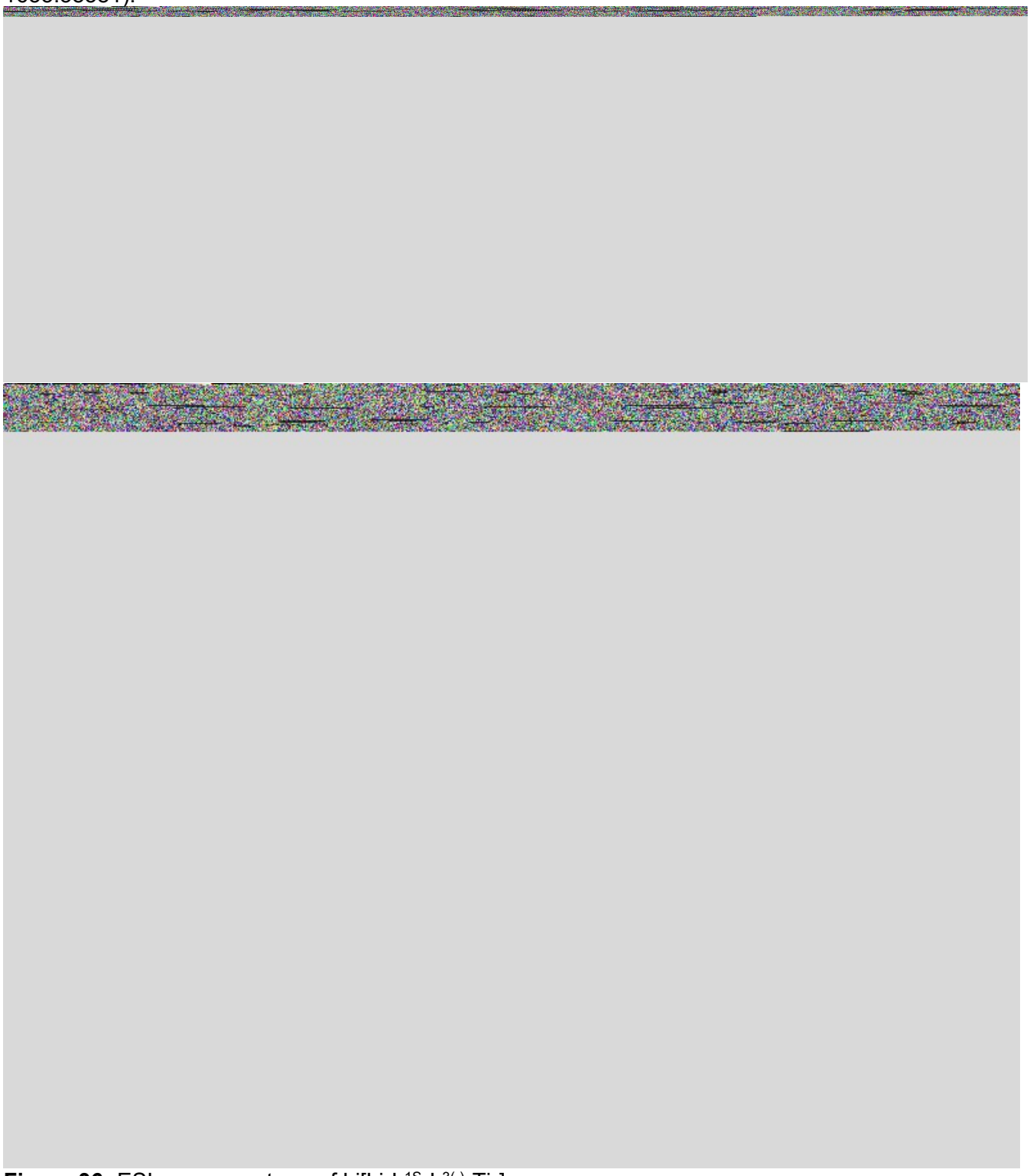


Figure 36*:* ESI mass spectrum of $Li[Li_3L^{1S}_6L^{3(-)}_0Ti_2]$.

$Li[Li_3L^{1S}_5L^{3(-)}_1Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1683.42603 (40, [M_D-Li^+], $C_{92}H_{78}Li_3O_{24}Ti_2^-$, calc. 1683.43276).

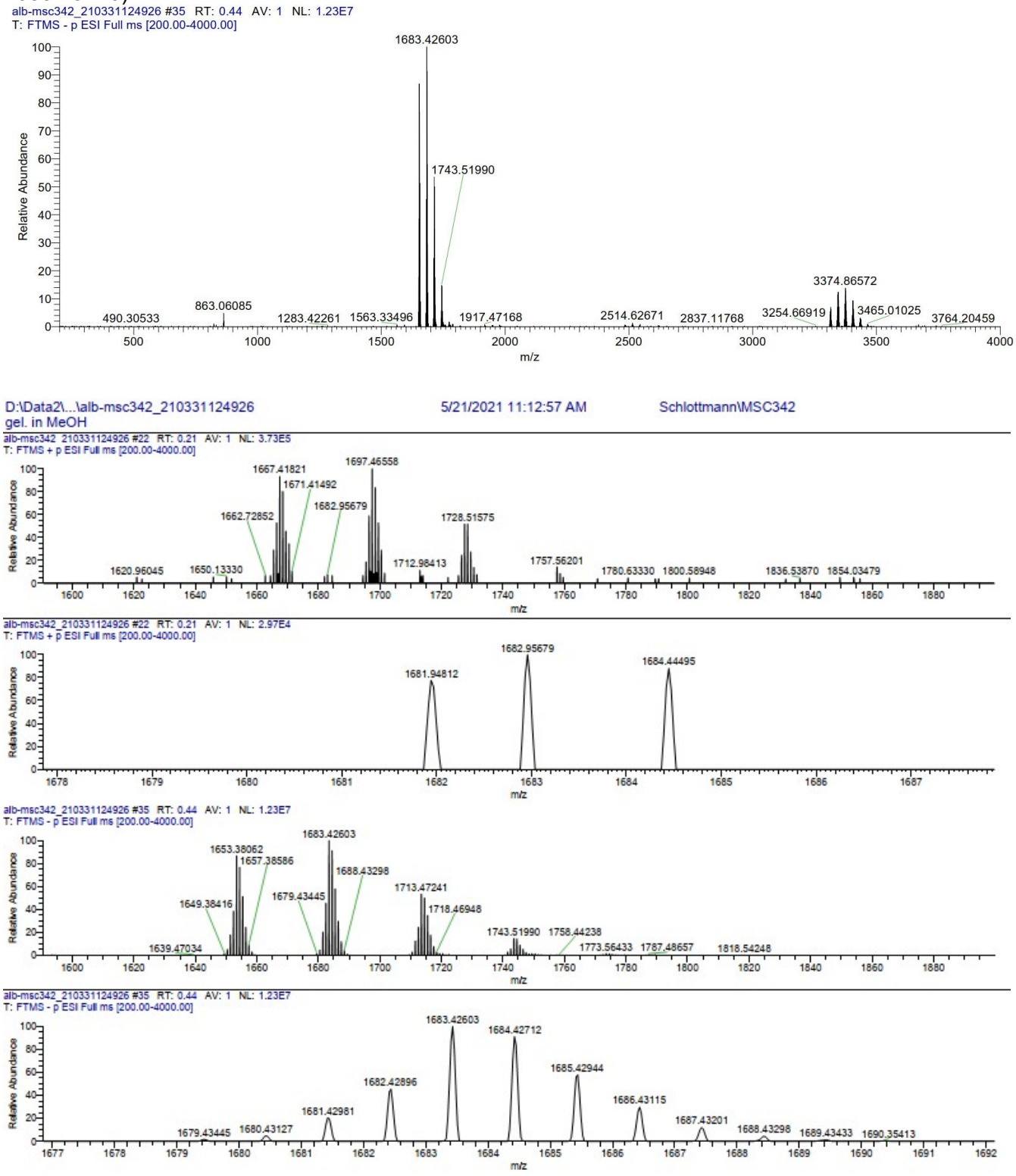


Figure 37: ESI mass spectrum of $Li[Li_3L^{1S}{}_5L^{3(-)}{}_1Ti_2]$.

$Li[Li_3L^{1S}{}_4L^{3(-)}{}_2Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1713.46318 (100, [M_D-Li^+], $C_{94}H_{84}Li_3O_{24}Ti_2^-$, calc. 1713.47971).

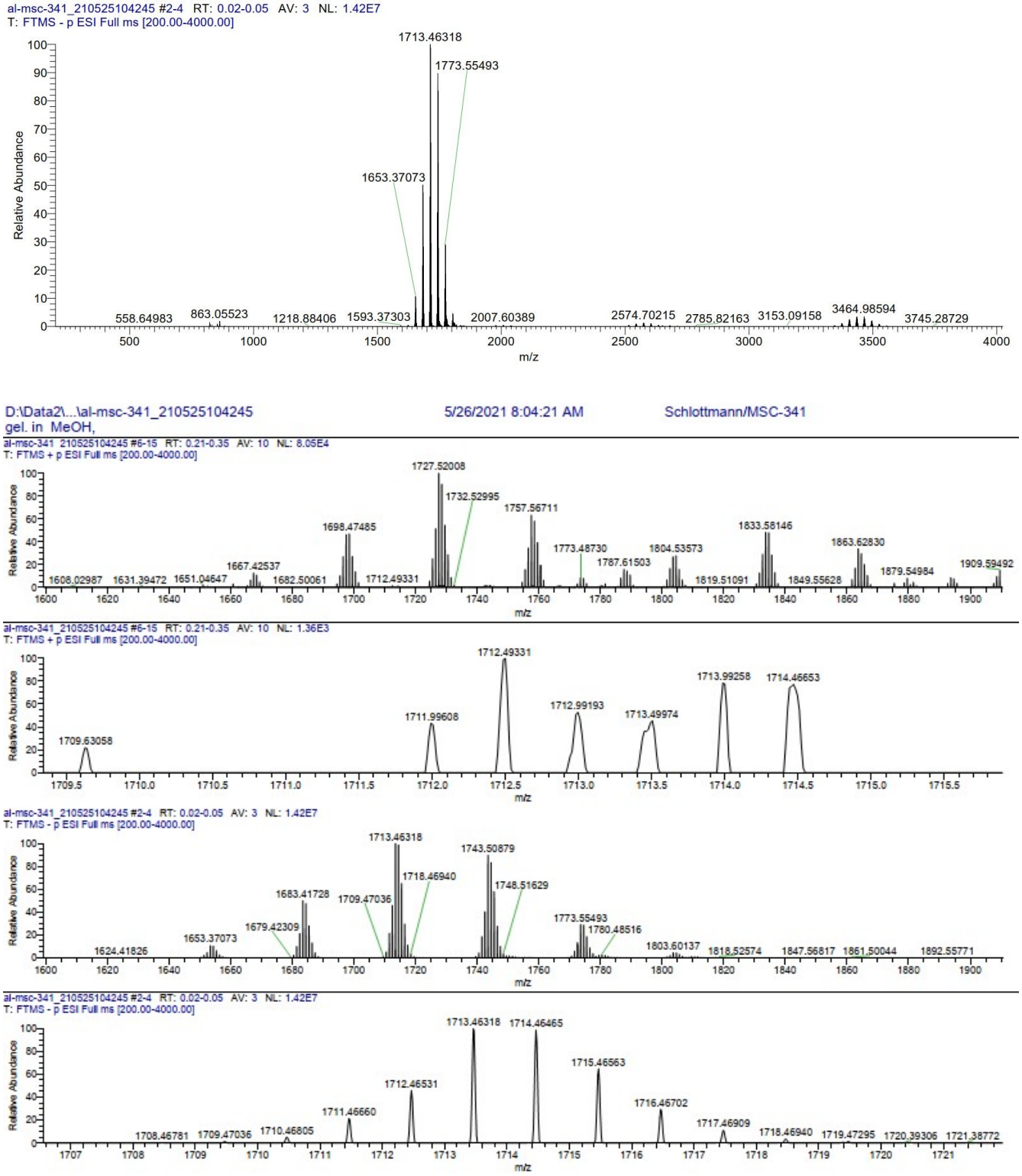


Figure 38: ESI mass spectrum of $Li[Li_3L^{1S}{}_4L^{3(-)}{}_2Ti_2]$.

$Li[Li_3L^{1S}{}_3L^{3(-)}{}_3Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1743.51755 (100, [M_D-Li^+], $C_{96}H_{90}Li_3O_{24}Ti_2^-$, calc. 1743.52666).

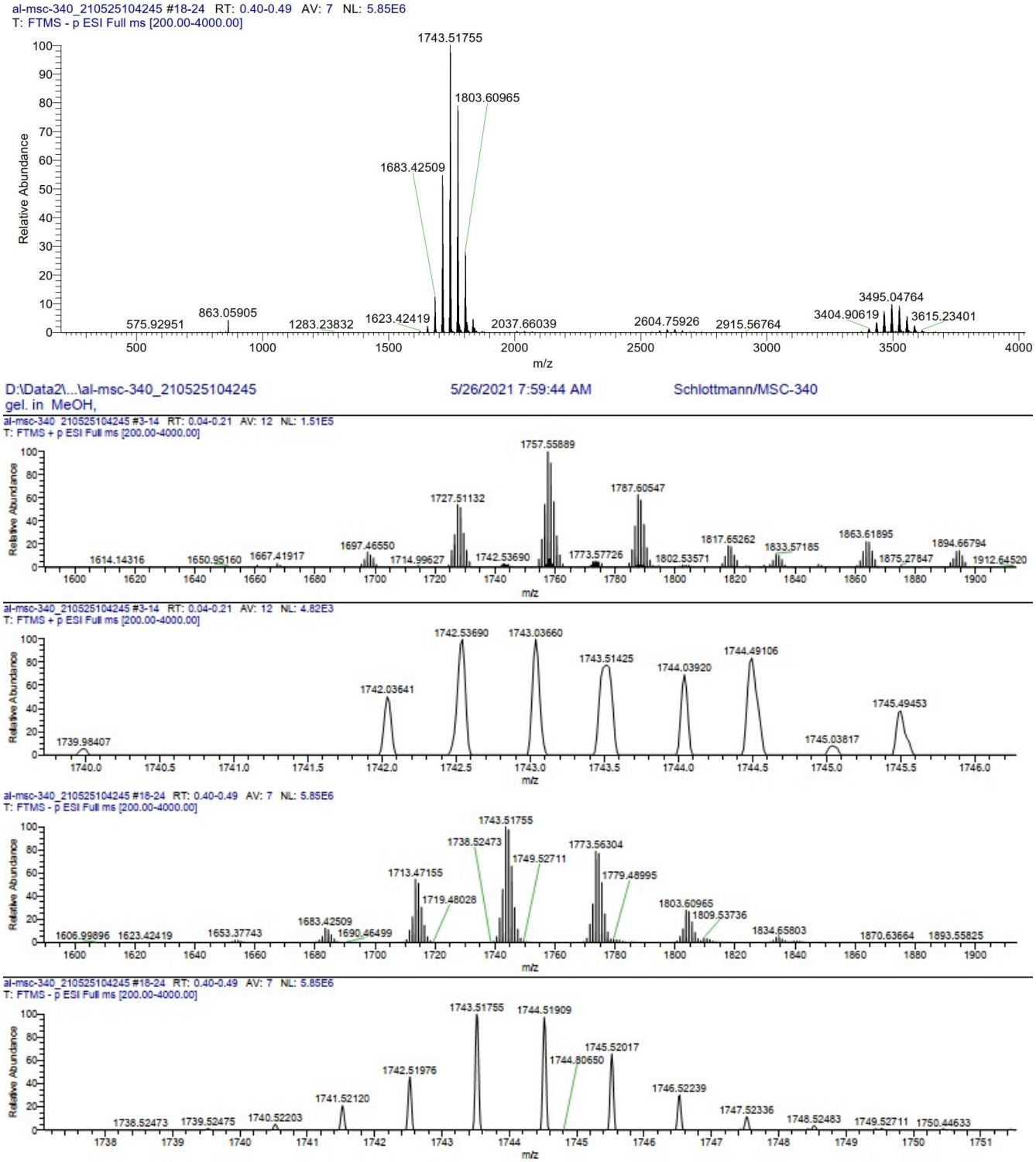


Figure 39: ESI mass spectrum of $Li[Li_3L^{1S}{}_3L^{3(-)}{}_3Ti_2]$.

$Li[Li_3L^{1S}{}_2L^{3(-)}{}_4Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1773.55572 (100, [M_D-Li^+], $C_{98}H_{96}Li_3O_{24}Ti_2^-$, calc. 1773.57361).

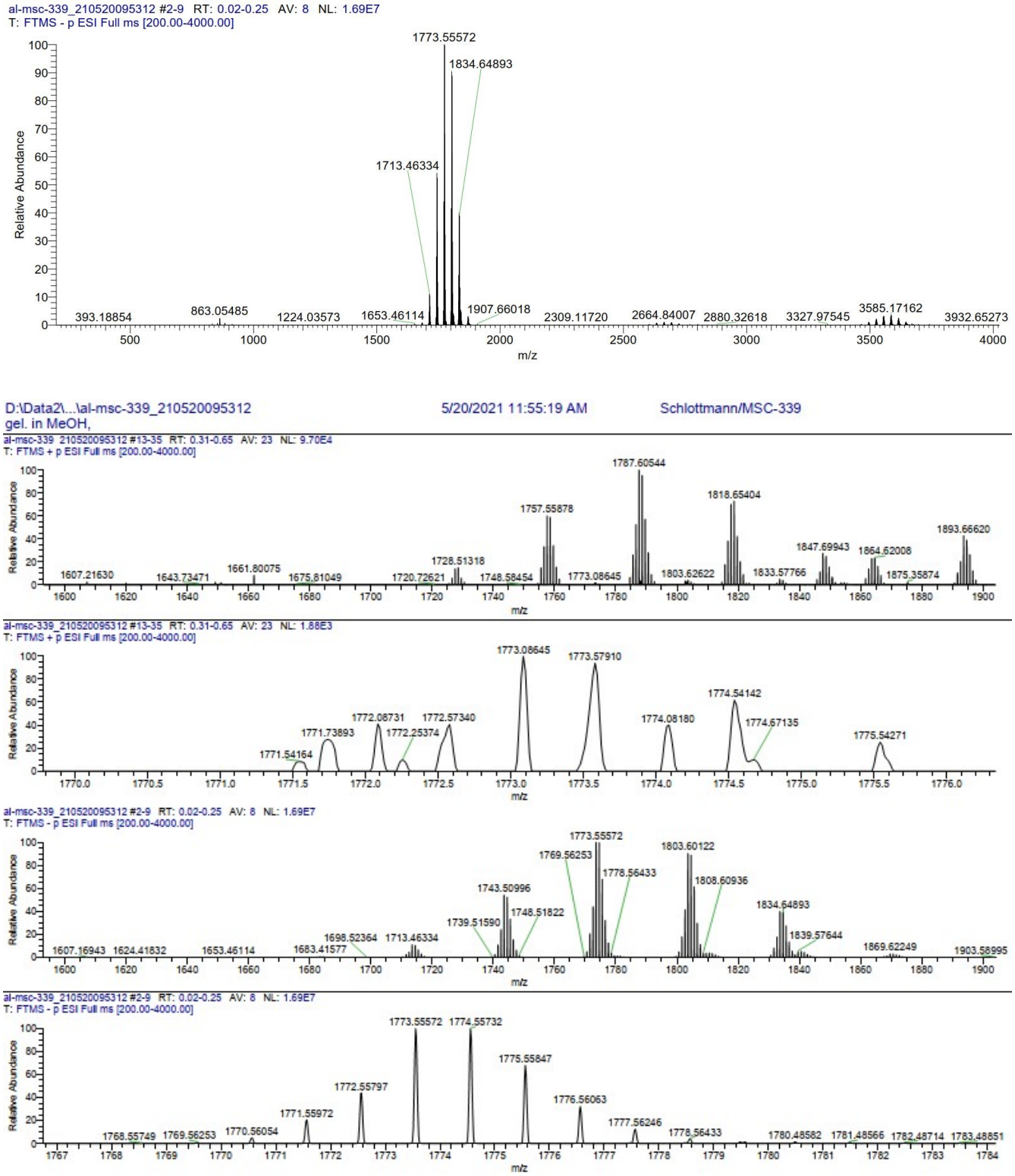


Figure 40: ESI mass spectrum of $Li[Li_3L^{1S}{}_2L^{3(-)}{}_4Ti_2]$

$Li[Li_3L^{1S}{}_1L^{3(-)}{}_5Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1804.61160 (95, [M_D-Li^+], $C_{100}H_{102}Li_3O_{24}Ti_2^-$, calc. 1803.62056).

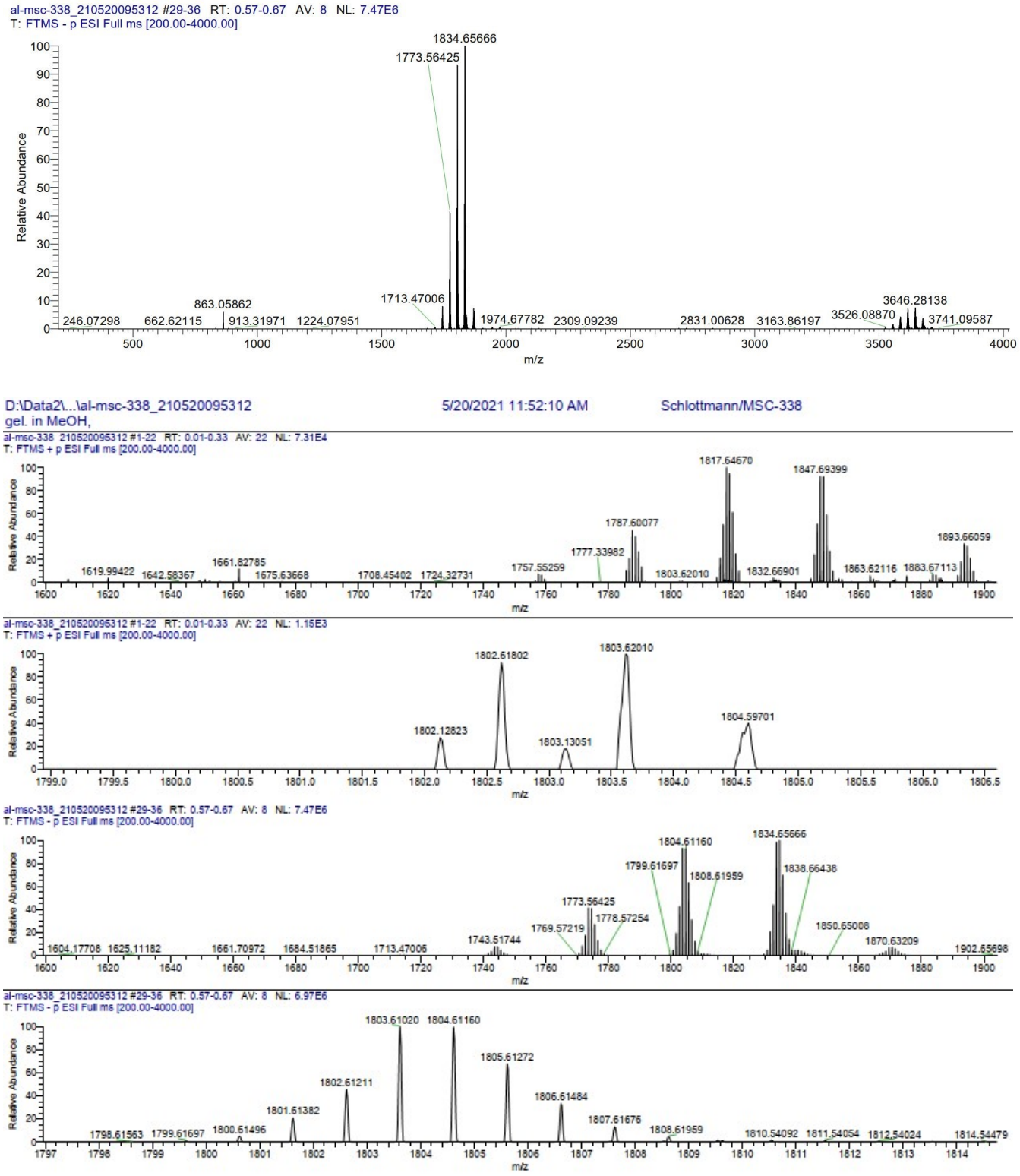


Figure 41: ESI mass spectrum of $Li[Li_3L^{1S}{}_1L^{3(-)}{}_5Ti_2]$.

$Li[Li_3L^{1S}{}_0L^{3(-)}{}_6Ti_2]$

MS (negative ESI-MS, MeOH): m/z (%) = 1834.64926 (40, $[M_D\text{-}Li^+]$, $C_{102}H_{108}Li_3O_{24}Ti_2^-$, calc. 1833.66751).

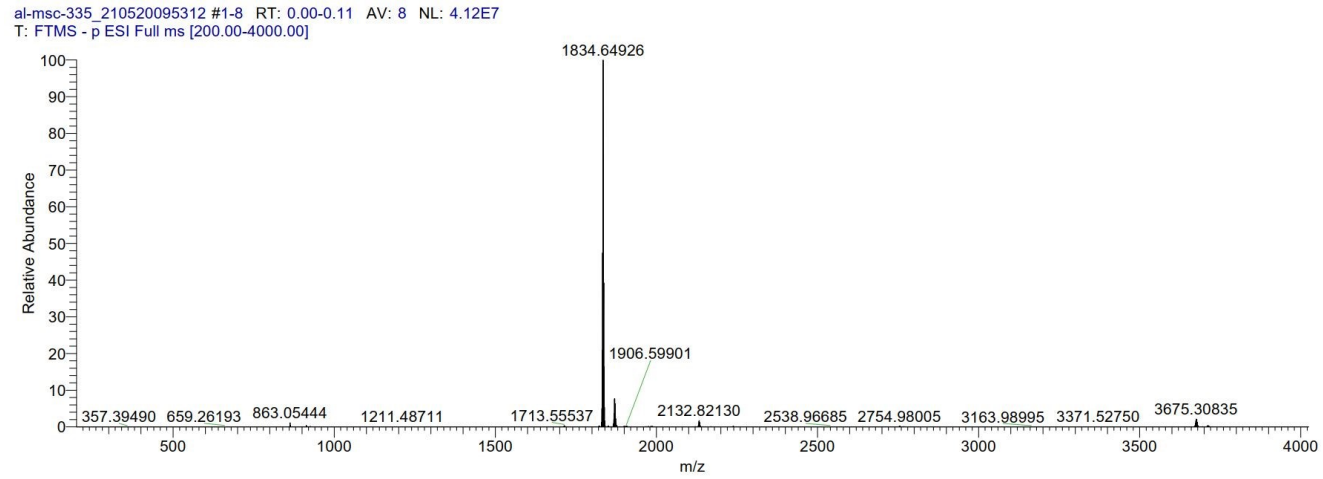


Figure 42: ESI mass spectrum of $Li[Li_3L^{1S}{}_0L^{3(-)}{}_6Ti_2]$.

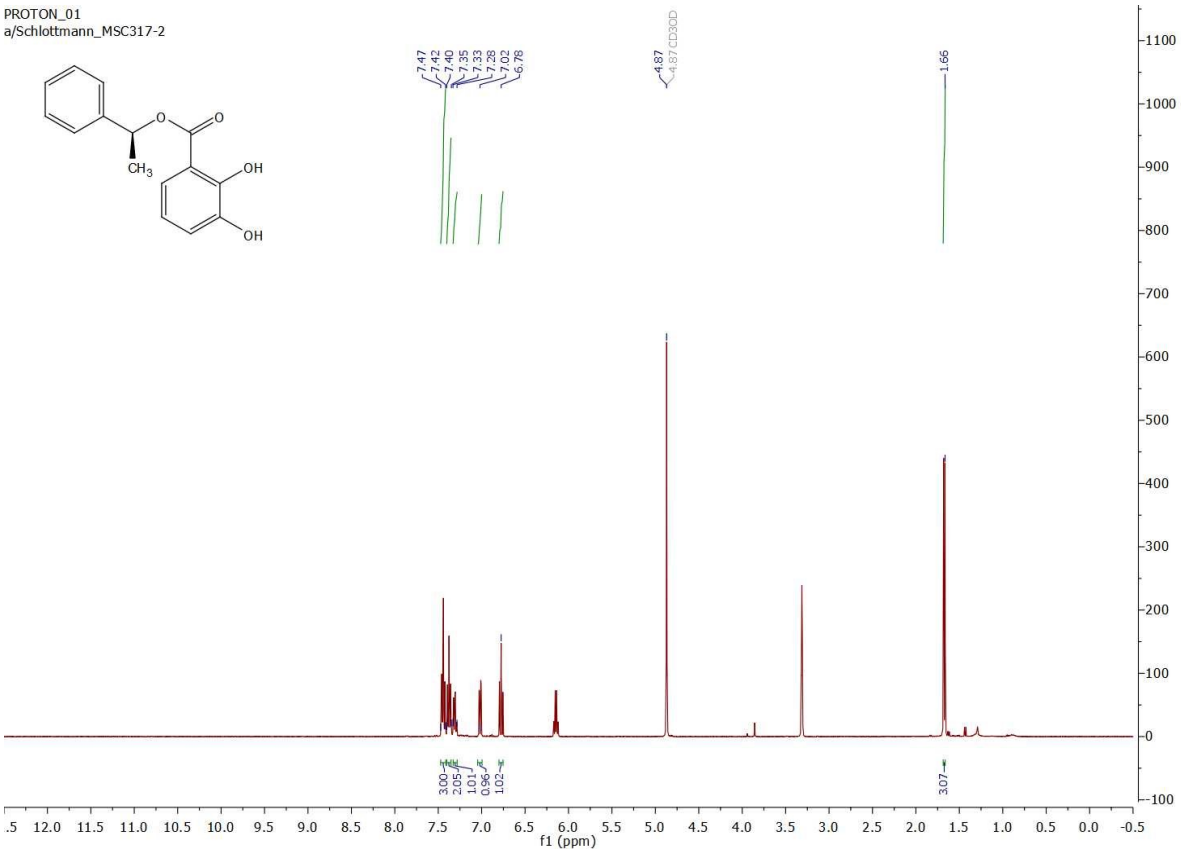


Figure 43: ^{1}H NMR Spektrum of L^{1S}-H_2 in MeOH-d_4.

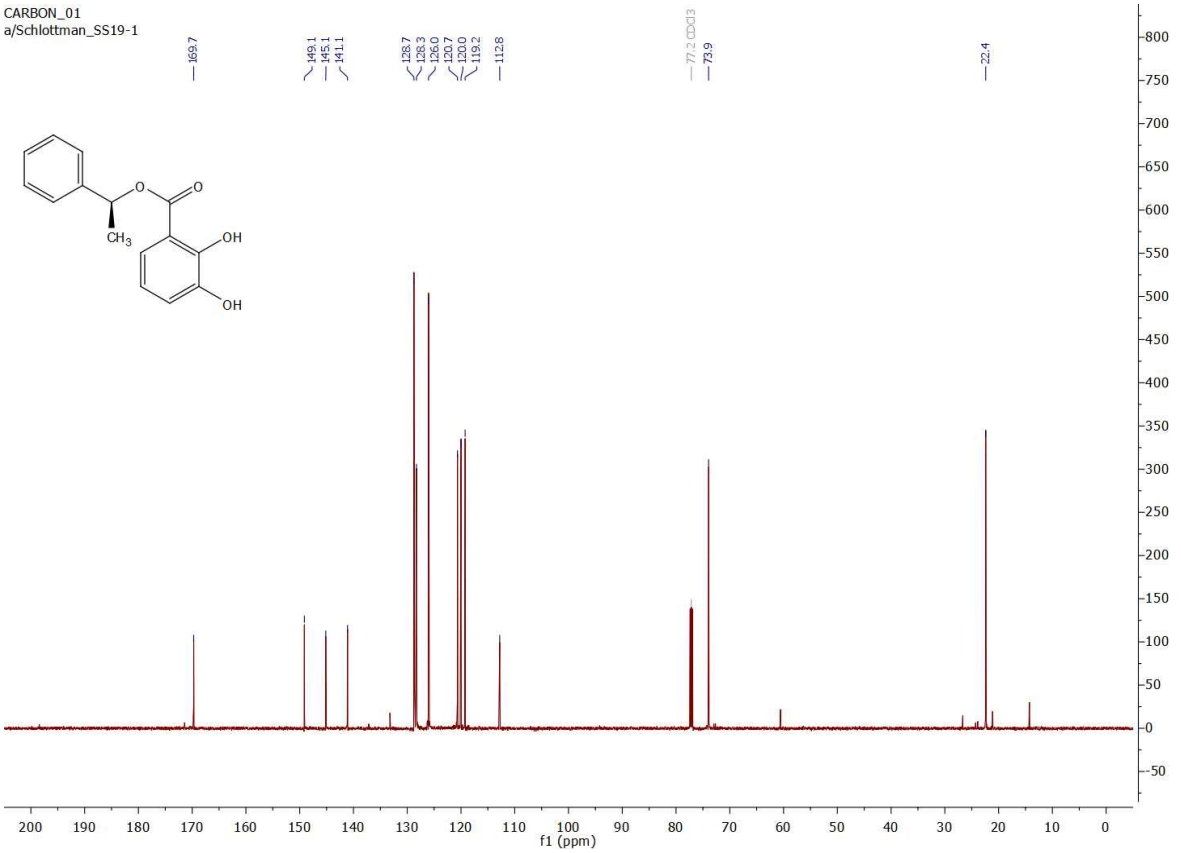


Figure 44: ^{13}C NMR Spektrum of L^{1S}-H_2 in $CDCl_3$.

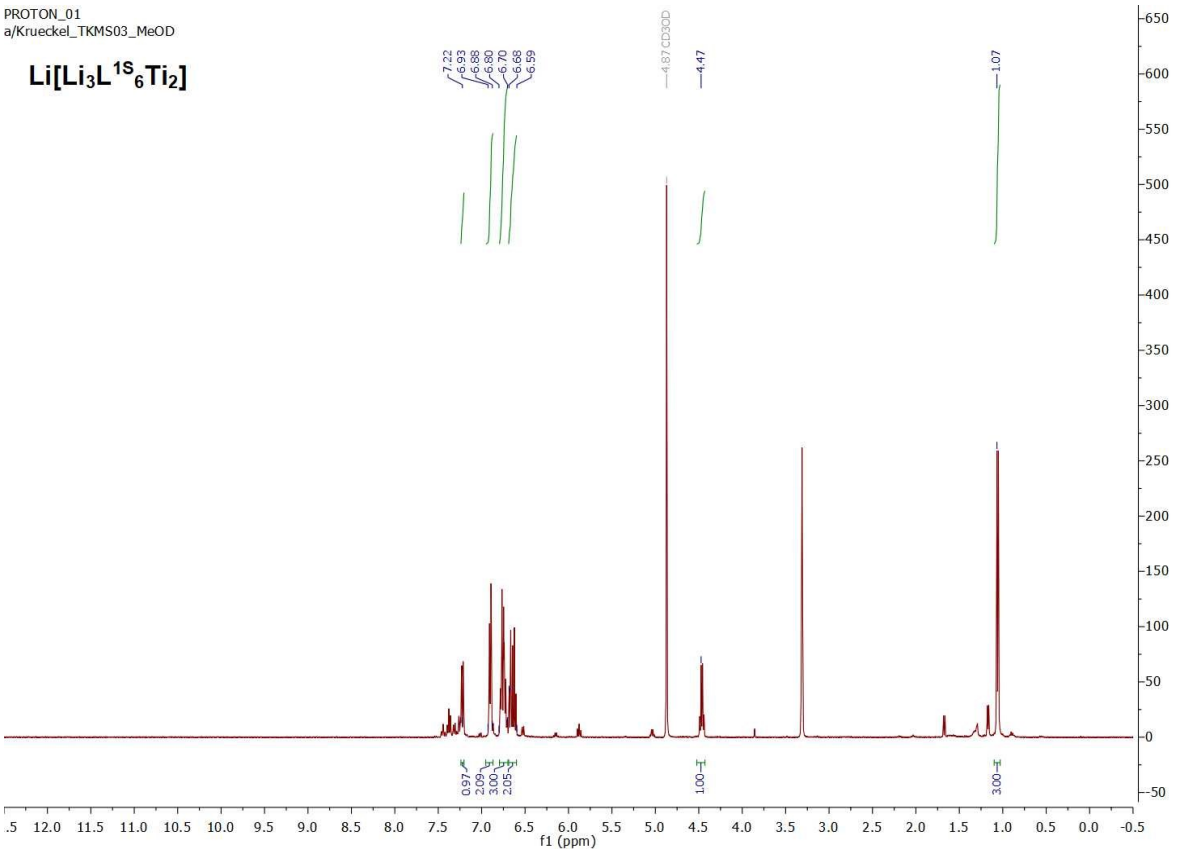


Figure 45: ^{1}H NMR Spektrum of Li[Li$_3$L$^{1S}_6$Ti$_2$] in MeOH-d_4.

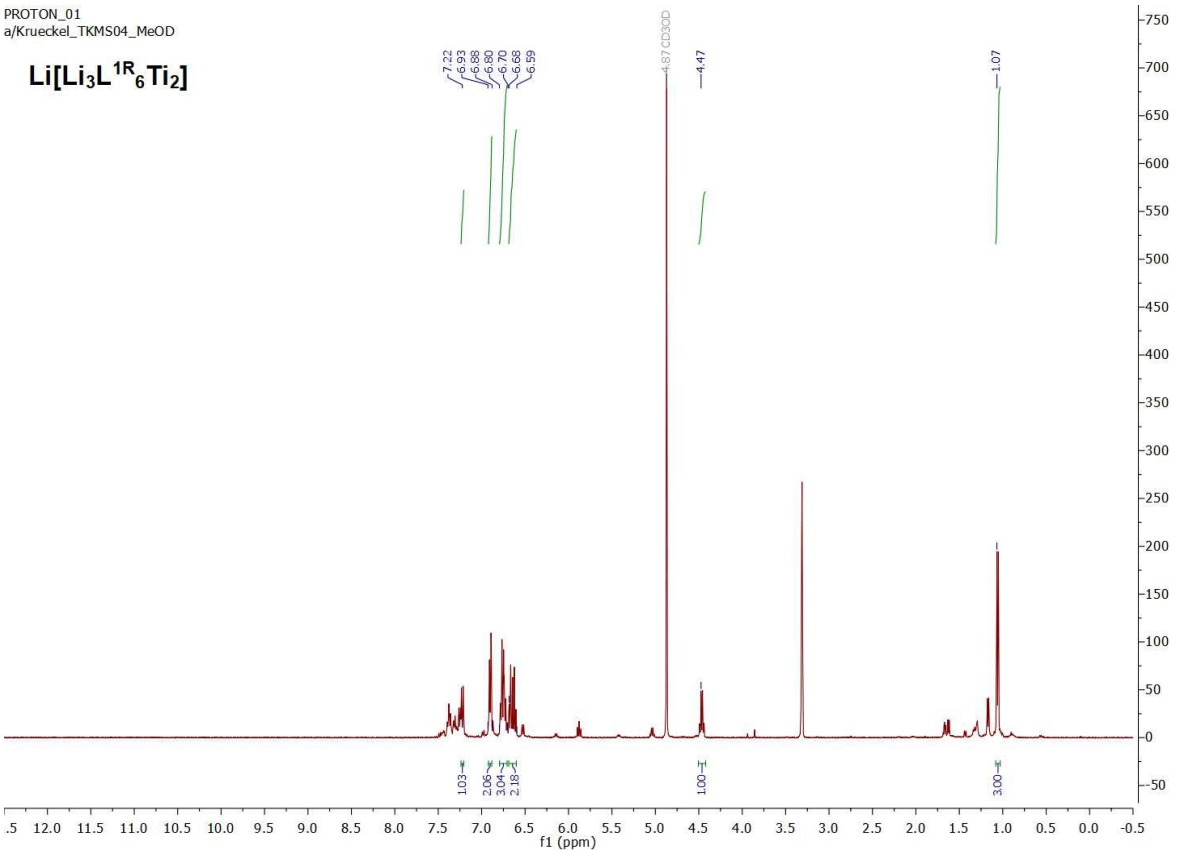


Figure 46: ^{1}H NMR Spektrum of Li[Li$_3$L$^{1S}_6$Ti$_2$] in MeOH-d_4.

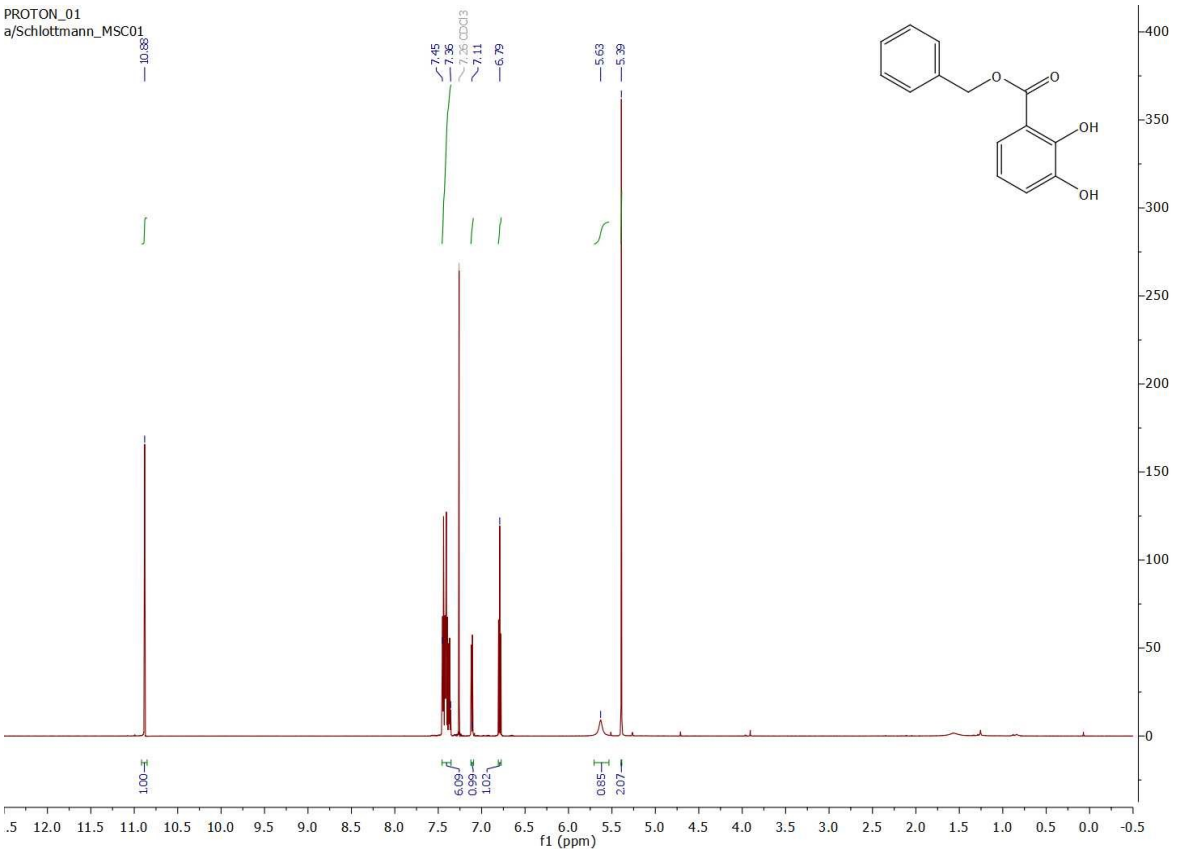


Figure 47: ^{1}H NMR Spektrum of L^{2}-H_2 in $CDCl_3$.

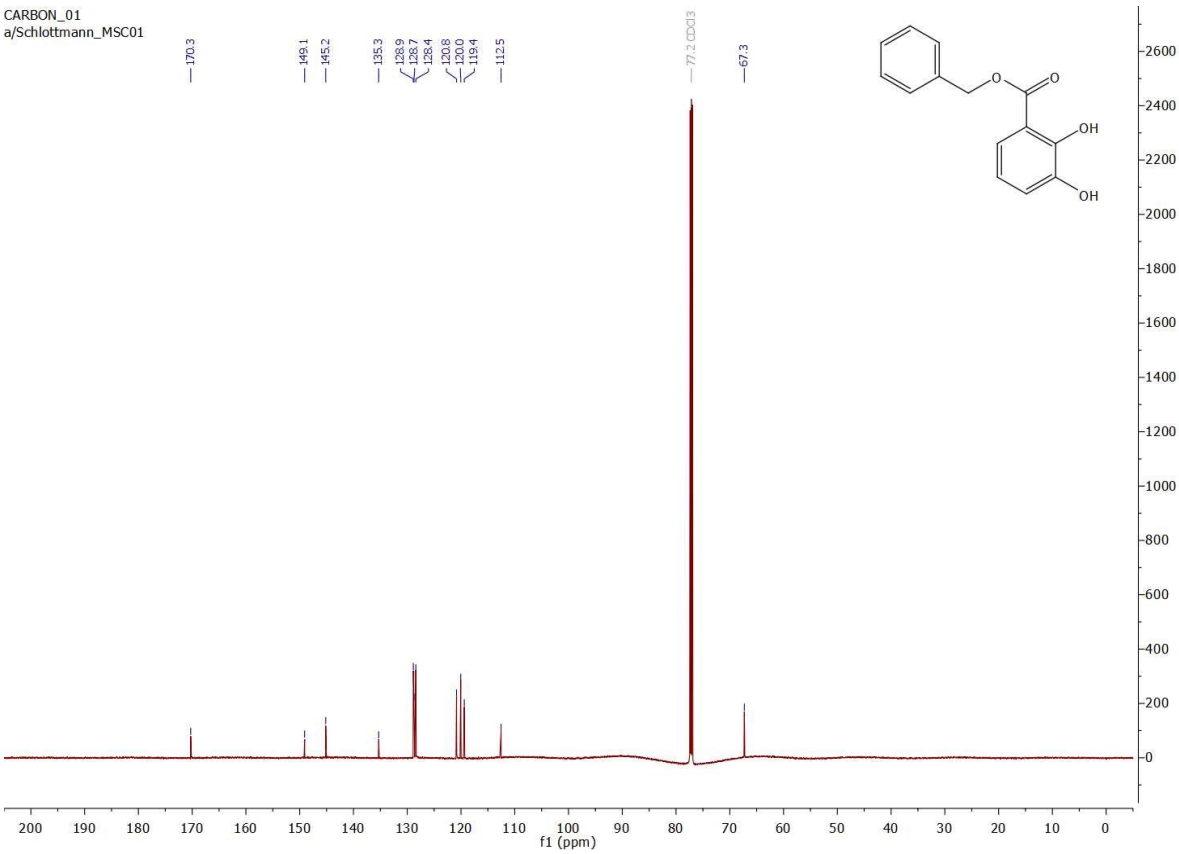


Figure 48: ^{13}C NMR Spektrum of L^{2}-H_2 in $CDCl_3$.

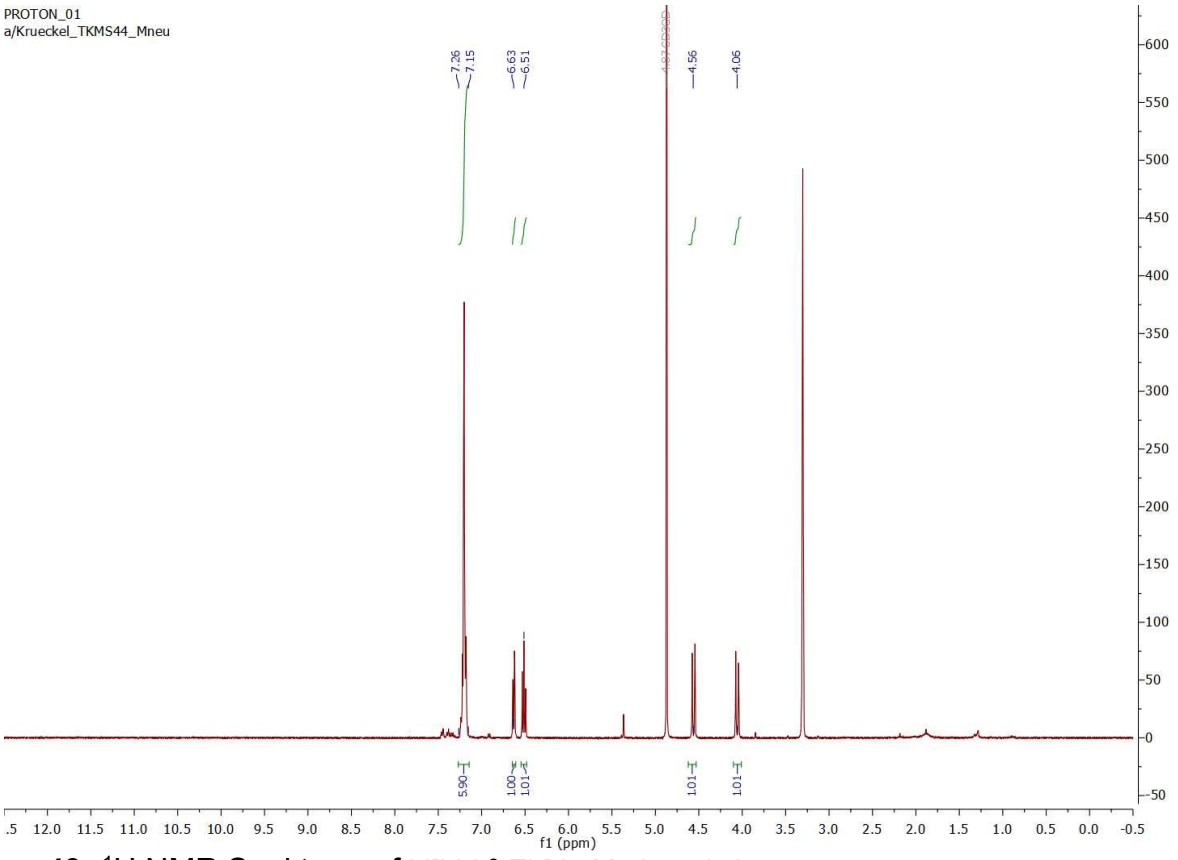


Figure 49: ^{1}H NMR Spektrum of $Li[Li_3L^2{}_6Ti_2]$ in Methanol-d_4.

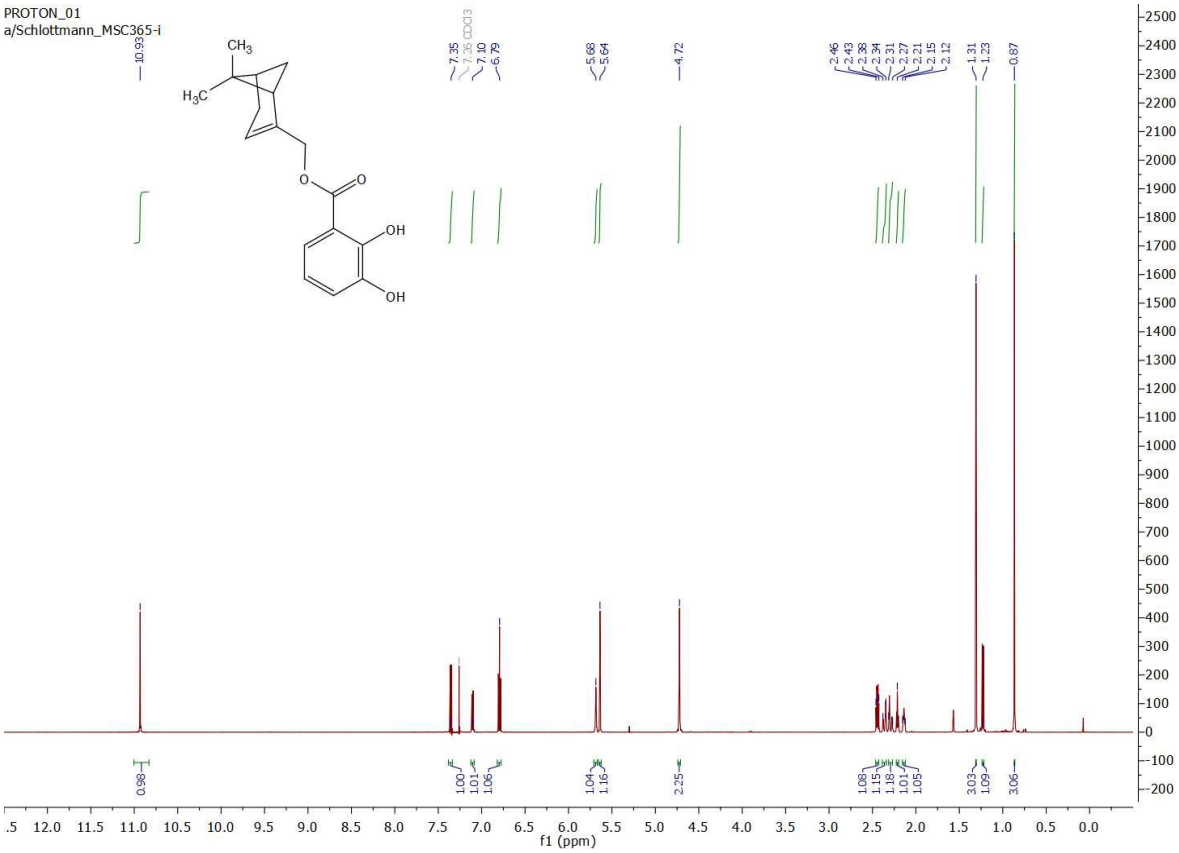


Figure 50: ^{1}H NMR Spektrum of $L^{3(-)}$-H_2 in $CDCl_3$.

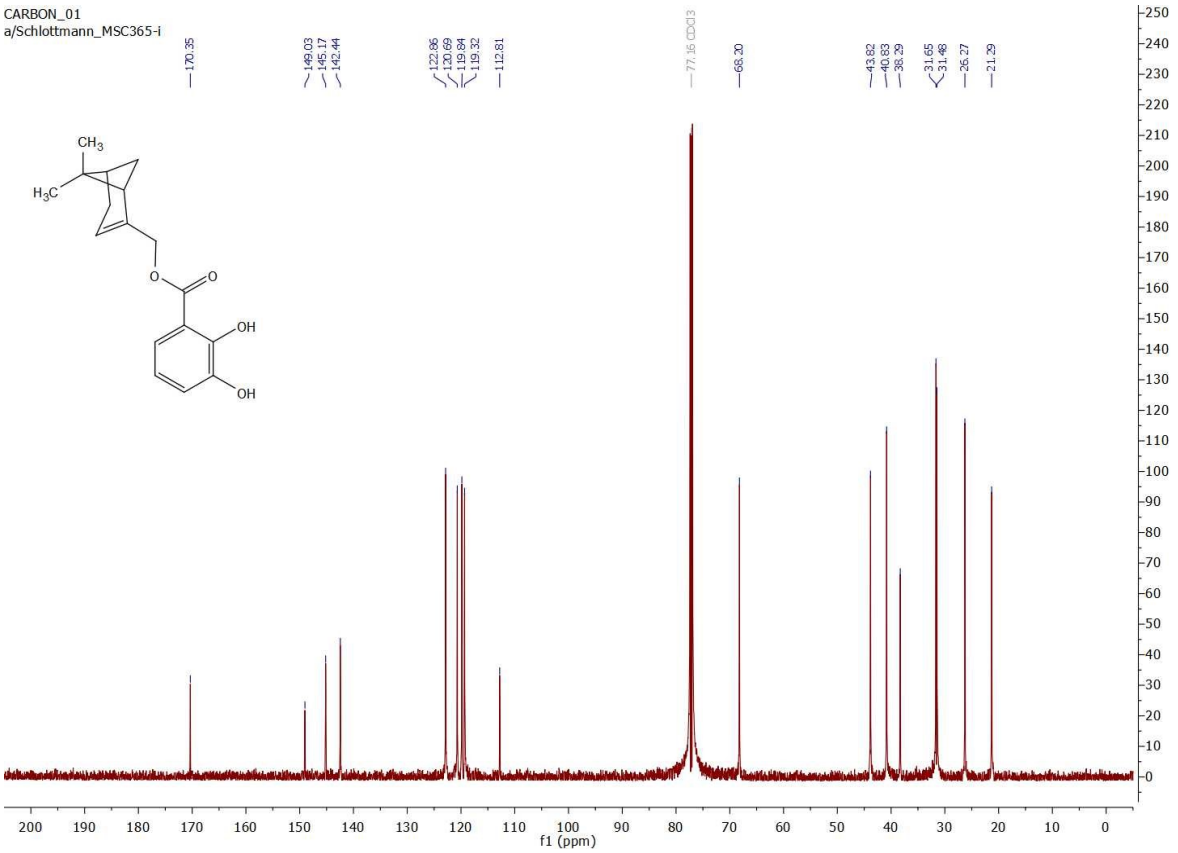


Figure 51: ^{13}C NMR Spektrum of $L^{3(-)}$-H_2 in $CDCl_3$.

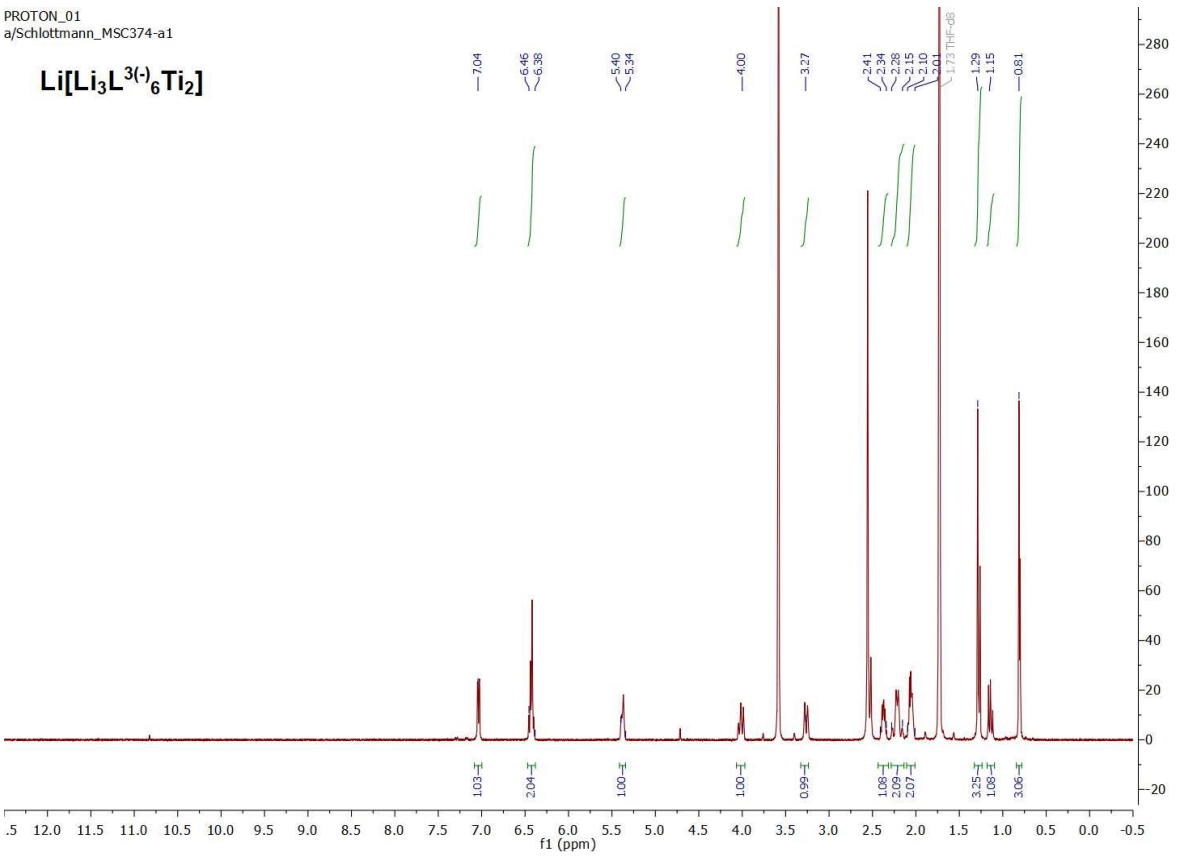


Figure 52: ^{1}H NMR Spektrum of $Li[Li_3L^{3(-)}{}_6Ti_2]$ in THF-d_8.

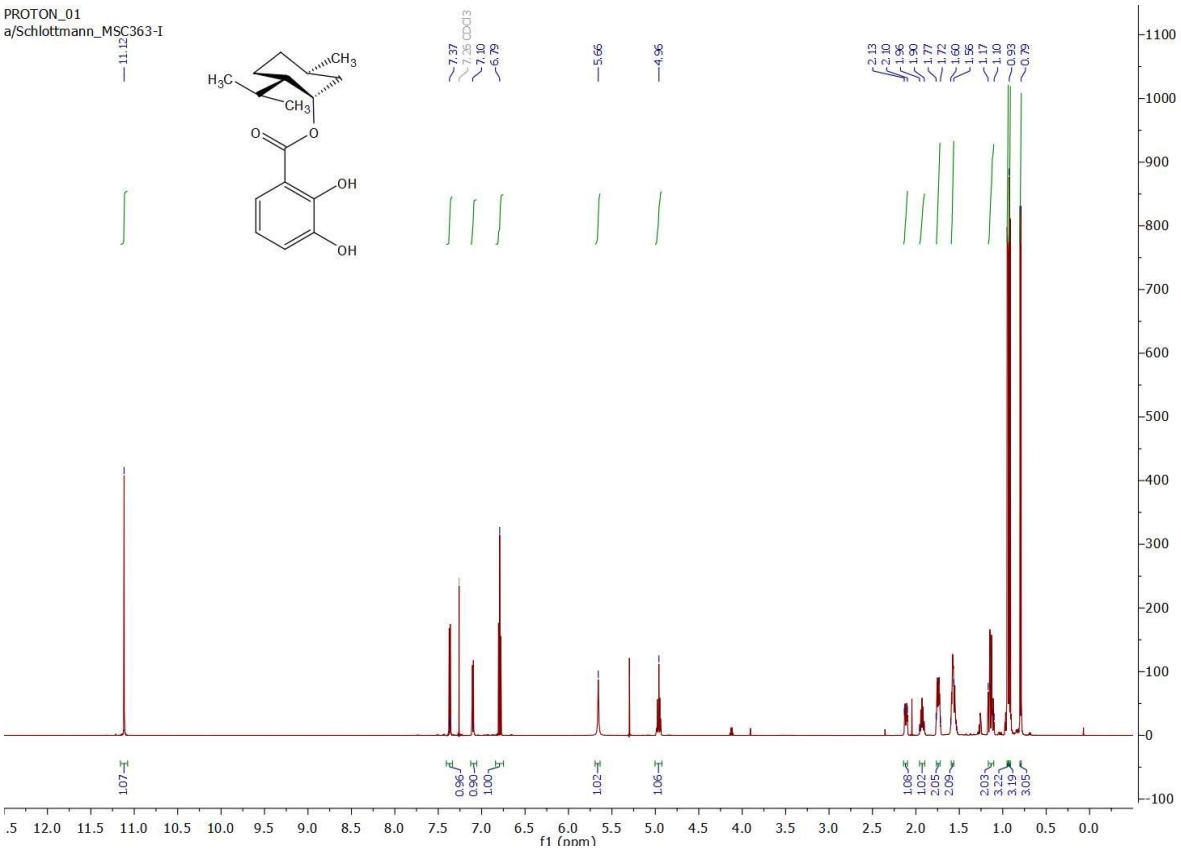


Figure 53: ^{1}H NMR Spektrum of $L^{4(-)}$-H_2 in $CDCl_3$.

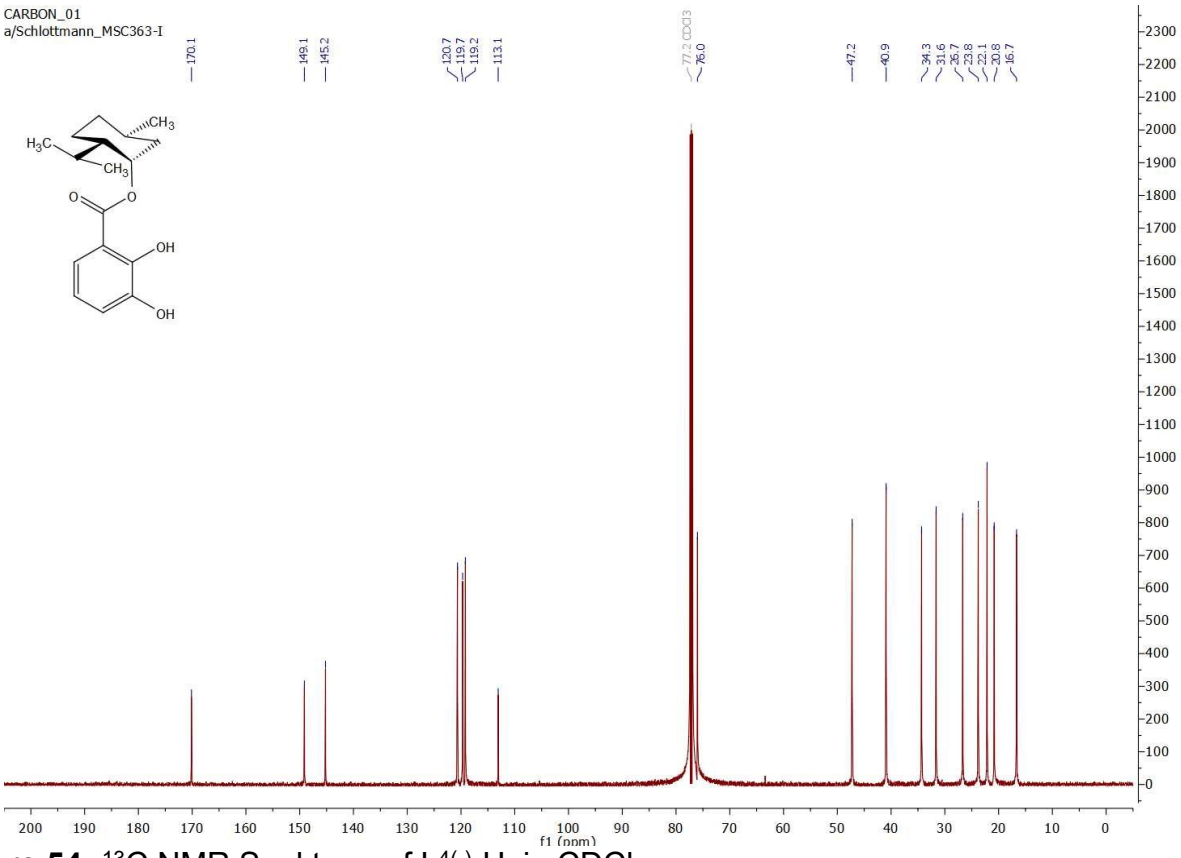


Figure 54: ^{13}C NMR Spektrum of $L^{4(-)}$-H_2 in $CDCl_3$.

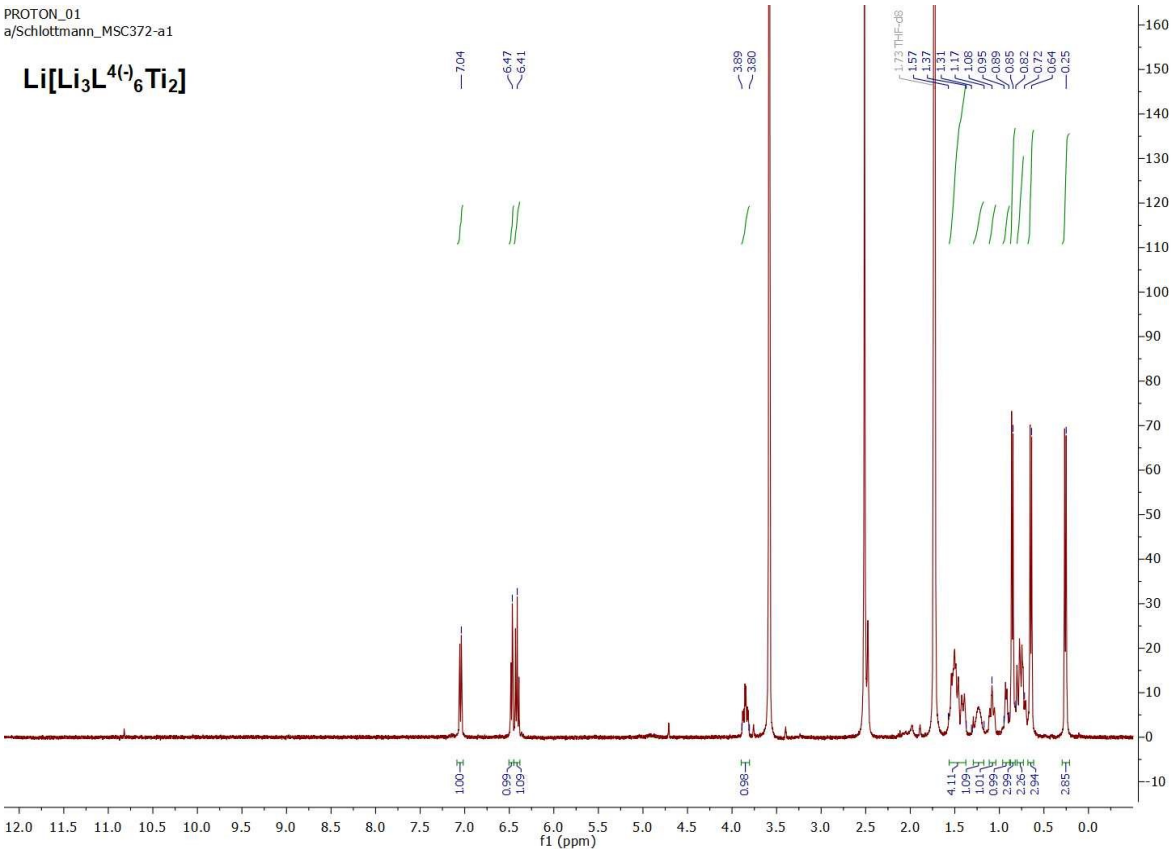


Figure 55: ^{1}H NMR Spektrum of $Li[Li_3L^{4(-)}{}_6Ti_2]$ in THF-d_8.

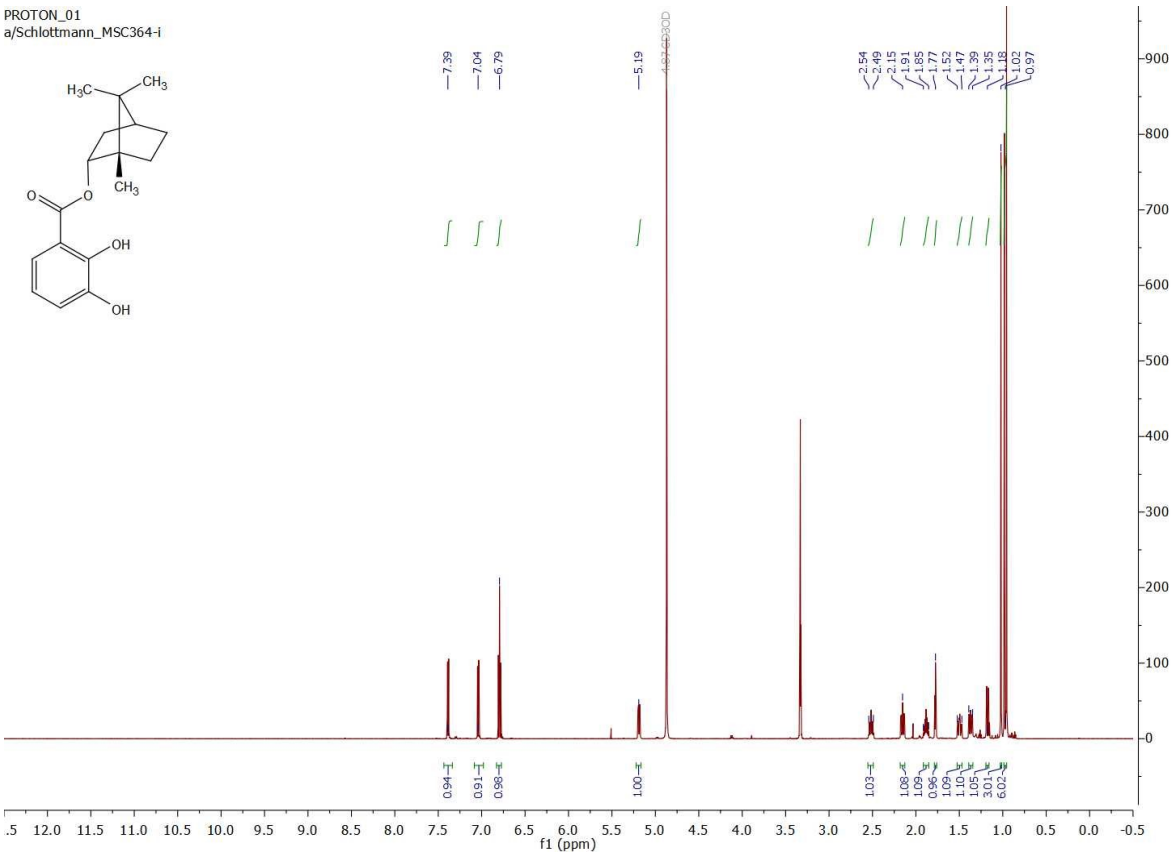


Figure 56: ^{1}H NMR Spektrum of $L^{5(-)}$-H_2 in $CDCl_3$.

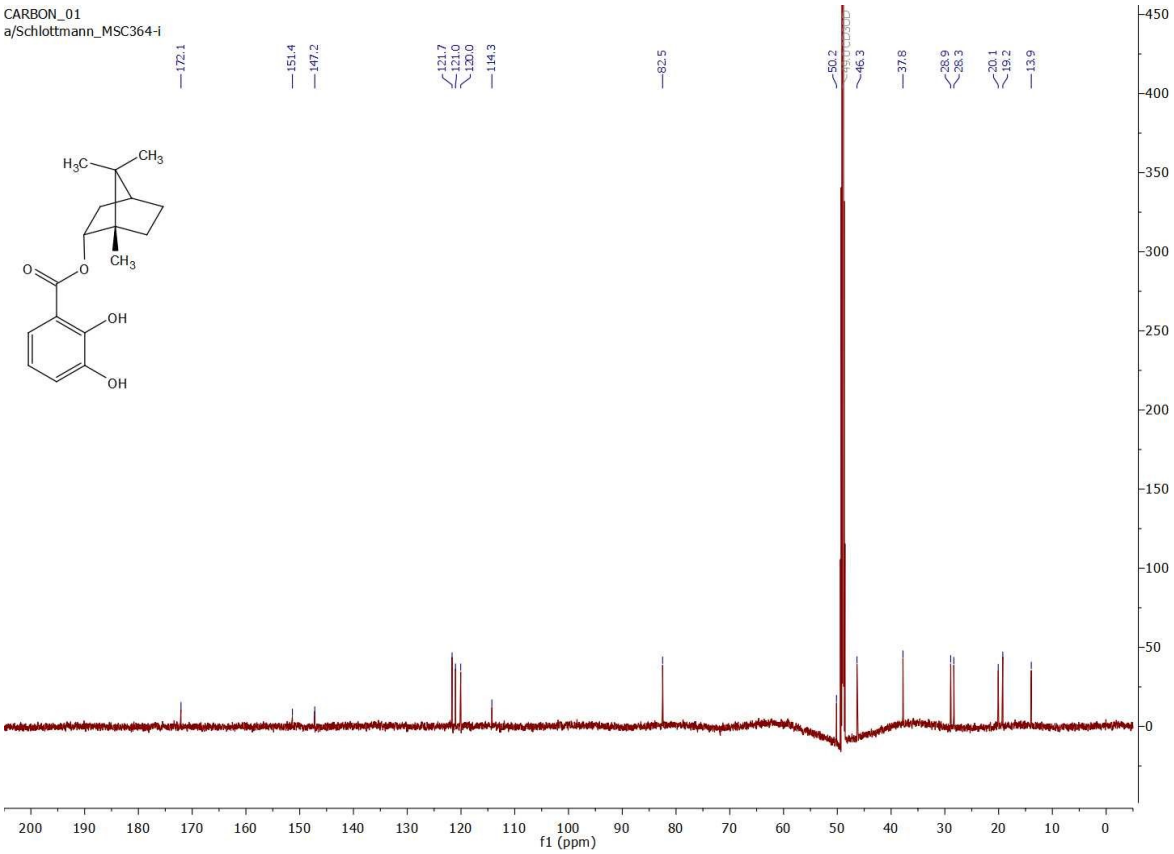


Figure 57: ^{13}C NMR Spektrum of $L^{5(-)}$-H_2 in $CDCl_3$.

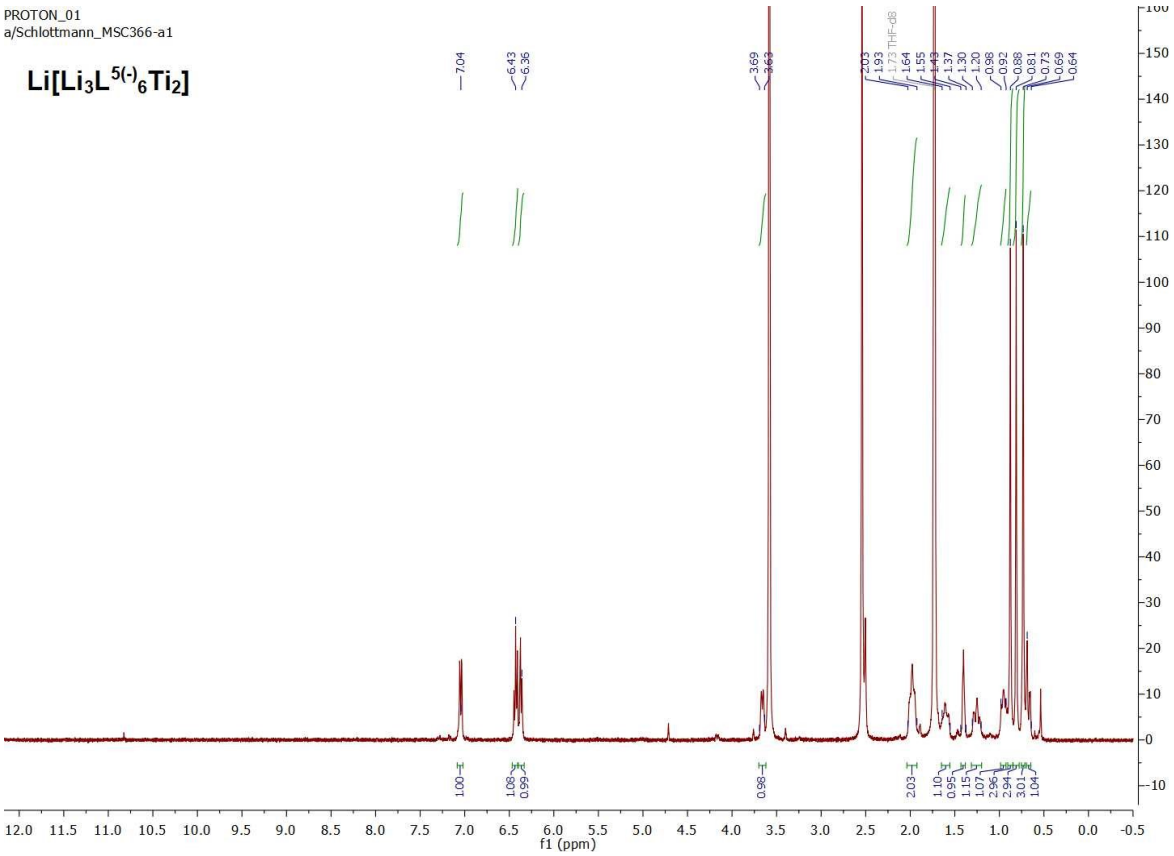


Figure 58: ^{1}H NMR Spektrum of $Li[Li_3L^{5(-)}{}_6Ti_2]$ in THF-d_8.

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