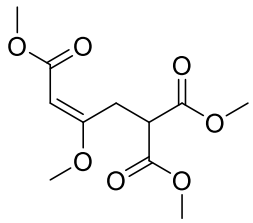
Contents

General Information

All commercially available compounds were purchased and used as received unless explicitly stated otherwise. 1,3-dimethyl-2-imidazolidinone (DMI) was dried over 4Å molecular sieves and THF was dried over sodium and benzophenone. All NMR experiments were performed on Bruker Avance III or III HD, two or four-channel NMR spectrometer operating at 400.13, 500.13 or 600.27 MHz proton frequency. The instruments were equipped with direct observe BBFO, indirect BBI or cryogenic four-channel QCI (H/C/N/F) 5 mm probes all with self-shielded z-gradient. The experiments were performed at 298 K and the temperature was calibrated using a methanol standard showing accuracy within +/- 0.2 K. The 1,1-ADEQUATE experiment was performed on a ca. 140 mM sample of **1** using 1344 and 512 increments in F2 and F1 resulting in acquisition times of 139.8 and 17 ms, respectively. The delays were set to corresponding coupling constants of 135 Hz for $^{1}J_{H,C}$ and 35 Hz $^{1}J_{C,C}$. Each increment in F1 was recorded with 16 scans resulting in a total experiment time of 3 h and 52 min. The spectra were processed with 2048 $\times$ 1024 data points using a $\pi/2$ shifted square sine-bell function in both dimensions. The NOESY spectrum was acquired with a mixing time of 3.0 s, for the HSQC-NOESY 0.85 s were used. GC-MS was performed on a Shimadzu GCMS-2020 SE equipped with a Zebron 5 MS Infernocolumn which allowed to achieve temperatures up to 350 °C. High-resolution mass spectra (HRMS) were measured as HR-ESI-ToF- MS with a Maxis 4G instrument from Bruker and HR-EI spectra were measured on a Waters Micromass AutoSpec Ultima (EI-Sector). For column chromatography silica gel Siliaflash® p60 (40–63 μm) from Silicycle was used, and TLC was performed on silica gel 60 F254 glass plates with a thickness of 0.25 mm purchased from Merck. The diffraction data were collected on a Stoe StadiVari diffractometer attached to a Ga Metaljet X-ray source at low temperature. The structure was solved with the program Superflip [1] using the charge flipping method and refined with CRYSTALS [2] using Least Squares minimisation. All carbon atoms were refined anisotropically. Molecular drawings were generated using Mercury [3].

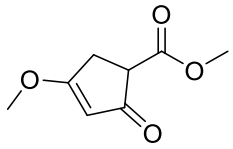
Synthetic Details

Trimethyl (*E*)-3-methoxy-3-butene-1.1.4-tricarboxylate (11)[4]:



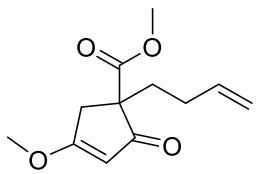
NaOMe (11.3 g, 210 mmol) was added to a stirred solution of dimethyl malonate (27.7 g, 210 mmol) in DMF (100 mL) at 20 °C. After 10 min methyl (E)-4-chloro-3-methoxy-2-butenoate (17.3 g, 105 mmol) was added dropwise over 5 min. The reaction mixture was stirred for 2 h. All the volatiles were removed under vacuum. The residue was partitioned between CH_2Cl_2 and H_2O. The aqueous layer was neutralized with HCl (32%, aq.). The organic layer was separated, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, cyclohexane/EtOAc 2:1) yielding trimethyl (*E*)-3-methoxy-3-butene-1.1.4-tricarboxylate **11** (19.9 g, 105 mmol, 73%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40 (d, $^3J_{H,H}$ = 7.7 Hz, 1H), 3.60 (s, 3H), 3.68 (s, 3H) 3.73 (s, 6H), 3.74 (d, $^3J_{H,H}$ = 7.7 Hz, 2H).

Methyl 4-methoxy-2-oxo-3-cyclopentenecarboxylate (12)[4]:



Na (157 mmol, 3.61 g) was added under an Ar atmosphere to MeOH (180 mL) over 30 min. The mixture was heated to 60 °C for 30 minutes. Trimethyl (E)-3-methoxy-3-butene-1,1,4-tricarboxylate **11** (76.6 mmol, 19.9 g) was added dropwise during 10 min. The mixture was stirred for 2 h at 60 °C then AcOH (10 mL) was added. The solvent was removed under reduced pressure and the residue was partitioned between CH_2Cl_2 and H_2O. The aqueous phase was further extracted with CH_2Cl_2 (2x). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, cyclohexane/EtOAc 1:1) yielding methyl 4-methoxy-2-oxo-3-cycloppentenecarboxylate **12** (76.6 mmol, 9.33 g, 72%) as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.78 (ddd, $^2J_{H,H}$ = 17.7 Hz, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ =1.2 Hz, 1H), 3.06 (ddd, $^2J_{H,H}$ = 17.7 Hz, $^3J_{H,H}$ = 3.1, $^4J_{H,H}$ =1.2 Hz, 1H), 3.54 (dd, $^3J_{H,H}$ = 7.6, $^3J_{H,H}$ = 3.1 Hz, 1H), 3.78 (s, 3H), 3.88 (s, 3H), 5.29 (dd, $^4J_{H,H}$ =1.2 Hz, 1H). GC-MS (EI): m/z (%) = 170.0 (100.0), 142.0 (15.7), 138.0 (25.5), 127.0 (25.3), 123.0 (32.5), 110.0 (26.2), 95.0 (31.4), 69.0 (27.2).

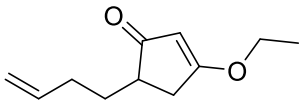
1-(But-3-enyl)-4-methoxy-2-oxo-cyclopent-3-enecarboxylic acid methyl ester (14)[5]:



Methyl 4-methoxy-2-oxo-3-cyclopentenecarboxylate **12** (58.8 mmol, 10.0 g) in DMF (50 mL) was added dropwise to a suspension of KH (61.2 mmol, 2.45 g) in DMF (350 mL). The mixture was stirred for 10 min and 4-bromo-1-butene (68.2 mmol, 9.49 g) was added dropwise. The reaction mixture was stirred at room temperature for 3 h then quenched by addition of saturated aqueous NH_4Cl. The mixture was extracted with diethyl ether (3x) and washed with brine. The solvent was removed under reduced pressure. The residue was purified by column

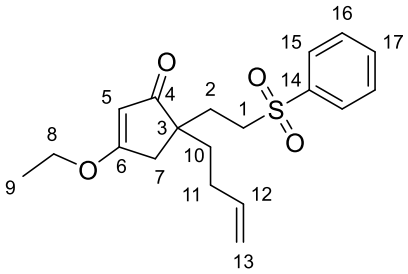
chromatography (cyclohexane/EtOAC 1:1) yielding 1-but-3-enyl-4-methoxy-2-oxo-cyclopent-3-enecarboxylic acid methyl ester **14** (40.7 mmol, 9.13 g, 69%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85 (ddd, $^2J_{H,H}$ = 13.2, $^3J_{H,H}$ = 10.0, $^3J_{H,\ H}$ = 6.0 Hz, 1H), 2.05 - 1.95(m, 2H), 2.16 (ddd, $^2J_{H,H}$ = 13.2, $^3J_{H,H}$ = 10.1, $^3J_{H,H}$ =6.1 Hz, 1H), 2.54 (dd, $^2J_{H,H}$ = 17.8, $^4J_{H,H}$ = 1.1 Hz, 1H), 3.24 (dd, $^2J_{H,H}$ = 17.8, $^4J_{H,H}$ = 1.2 Hz, 1H), 3.72 (s, 3H), 3.88 (s, 3H), 4.94 - 5.04 (m, 2H), 5.26 (dd, $^4J_{H,H}$ = 1.1 Hz, 1H), 5.78 (ddt, $^3J_{H,H}$ = 16.8, $^3J_{H,H}$ = 10.1, $^3J_{H,H}$ = 6.4 Hz, 1H). GC-MS (EI): *m/z* (%) = 126.0 (51.1), 98.0 (100.0), 80.0 (12.8), 69.0 (55.5).

5-(But-3-enyl)-3-ethoxycyclopent-2-enone (8)[5]**:**



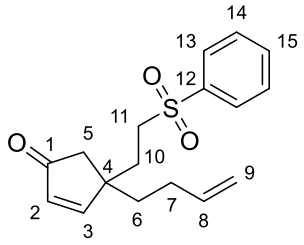
The β-ketoester **14** (40.7 mmol, 9.13 g) was dissolved in EtOH (100 mL) and KOH (48.8 mmol, 2.74 g) was added. The reaction mixture was heated to reflux for 16 h. After cooling to room temperature the solution was diluted with saturated aqueous NH_4Cl and concentrated under reduced pressure. The residue was portioned between EtOAc and H_2O. The aqueous layer was further extracted with EtOAc (3x) The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, EtOAc/cyclohexane, 4:1) to yield 5-But-3-enyl-3-ethoxy-cyclopent-2-enone **8** (31.8 mmol, 5.74 g, 86%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C):*δ* = 5.81 (ddt, $^3J_{H,H}$ = 17.0, $^3J_{H,H}$ = 10.2, $^3J_{H,H}$ = 6.6 Hz, 1H), 5.24 (t, $^4J_{H,H}$ = 1.1 Hz, 1H), 5.07 – 4.94 (m, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.75 (ddd, $^2J_{H,H}$ = 17.6, $^3J_{H,H}$ = 7.3, $^4J_{H,H}$ = 1.1 Hz, 1H), 2.48 (m, 1H), 2.30 (ddd, $^2J_{H,H}$ = 17.6, $^3J_{H,H}$ = 2.9, $^4J_{H,H}$ = 1.1 Hz, 1H), 2.22 – 2.06 (m, 2H), 1.97 (m, 1H), 1.50 – 1.39 (m, 1H), 1.41 (t, *J* = 7.1 Hz, 3H). GC-MS (EI): *m/z* (%) = 126.0 (51.1), 98.0 (100.0), 80.0 (12.8), 69.0 (55.5).

5-(But-3-enyl)-3-ethoxy-5-(2-(phenylsulfonyl)ethyl)cyclopent-2-enone (16)[6]**:**



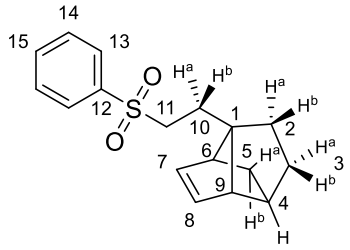
To a solution of diisopropylamine (47.7 mmol, 6.74 mL) in 32 mL dry THF was added at 0 °C a solution of *n*-BuLi in hexane (1.6 M, 38.2 mmol, 23.8 mL). After 30 minutes the solution was cooled to -78 °C and a solution of the cyclopentenone **8**(31.8 mmol, 5.73 g) in 32 mL dry THF was added drop wise. The solution was stirred for 30 min at -78 °C and then warmed up to 0°C. After addition of 22 mL of dry 1,3-dimethyl-2-imidazolidinone (DMI) the solution turned red. Then a solution of phenyl vinyl sulfone (38.2 mmol, 6.42 g) in THF (80 mL) was added dropwise. After complete addition the solution was allowed to reach room temperature. After 1 h the reaction was quenched by the addition of NH_4Cl and the aqueous phase was extracted with EtOAc (3x). The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography (SiO2, EtOAc/cyclohexane, 4:1) to yield **16** (20.2 mmol, 7.03 g, 74%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C):*δ* = 7.89 – 7.83 (m, 2H, H-16), 7.70–7.62 (m, 1H, H-17), 7.60–7.54 (m, 2H, H-15), 5.71 (ddt, $^3J_{H,H}$ = 16.8, $^3J_{H,H}$ = 10.2, $^3J_{H,H}$ = 6.5 Hz, 1H, H-12), 5.19 (t, $^4J_{H,H}$ = 1.1 Hz, 1H, H-5), 5.02–4.83 (m, 2H, H-13), 4.03 (q, $^3J_{H,H}$ = 7.1 Hz, 2H, H-8), 3.18 – 2.90 (m, 2H, H-1), 2.56 (dd, $^2J_{H,H}$ = 18.1, $^4J_{H,H}$ = 1.1 Hz, 1H, H-7), 2.36 (dd, $^2J_{H,H}$ = 18.1, $^4J_{H,H}$ = 1.1 Hz, 1H, H-7), 2.01 – 1.81 (m, 4H, H-2, H-11), 1.64 – 1.45 (m, 2H, H-10), 1.41 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, H-9). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 207.80 (C-4), 187.99 (C-6), 138.95 (C-14), 137.63 (C-12), 133.96 (C 17), 129.49 (C-15), 128.18 (C-16), 115.28 (C-13), 104.07 (C-5), 68.07 (C-8), 51.96 (C-1), 49.19 (C-3), 39.57 (C-7), 35.40 (C-10), 29.57 (C-2), 28.45 (C-11), 14.24 (C-9). HRMS (ESI, +): *m/z* calcd. for $C_{19}H_{24}O_4S$ $[M+H]^+$ 349.1468; found: 349.1468.

4-(But-3-en-1-yl)-4-(2-(phenylsulfonyl)ethyl)cyclopent-2-enone (17):



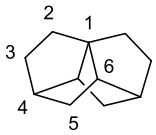
Cyclopentenone **16** (8.61 mmol, 3.00 g) was dissolved in toluene (50 mL) and DIBAL-H (1 M in hexane, 9.47 mmol, 9.47 mL) was added dropwise while cooling with a water bath. After complete addition of the reagent the reaction stirred for 1 h at room temperature. The solution was quenched with 2 M aq. HCl (30 mL) and stirred for 20 min at room temperature. The aqueous phase was extracted with DCM (2x) and the combined organic phase was washed with water (2x) and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, EtOAc/cyclohexane 1:1) yielding cyclopentenone **17** (7.41 mmol, 2.26 g, 86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.91 – 7.88 (m, 2H, H-14), 7.71 – 7.67 (m, 1H, H-15), 7.62 – 7.57 (m, 2H, H-13), 7.32 (d, $^3J_{H,H}$ = 5.7 Hz, 1H, H-2), 6.13 (d, $^3J_{H,H}$ = 5.7 Hz, 1H, H-3), 5.72 (ddt, $^3J_{H,H}$ = 16.8, $^3J_{H,H}$ = 10.2, $^3J_{H,H}$ = 6.5 Hz, 1H, H-8), 5.01 – 4.95 (m, 2H, H-9), 3.01 – 2.86 (m, 2H, H-11), 2.25 (d, $^2J_{H,H}$ = 18.8 Hz, 1H, H-5), 2.07 (d, $^2J_{H,H}$ = 18.8 Hz, 1H, H-5), 2.07 – 1.87 (m, 4H, H-10, H-7), 1.68 – 1.54 (m, 2H, H-6). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 207.77 (C-1), 168.94 (C-2), 138.92 (C-12), 137.29 (C8), 134.33 (C-3), 134.16 (C-15), 129.62 (C-13), 128.10 (C-14), 115.65 (C-9), 52.32 (C-11), 47.34 (C-4), 44.83 (C-5), 37.98 (C-6), 30.58 (C-10), 28.81 (C-7).

1-(2-(phenylsulfonyl)ethyl)tricyclo[4.3.0.0^{4,9}]non-7-en (6):



Cyclopentenone **17** (7.56 mmol, 2.30 g) was dissolved in MeOH (70 mL) and $CeCl_3 \cdot 7H_2O$ (9.07 mmol, 3.38 g) was added. The reaction mixture was cooled to 0 °C and $NaBH_4$ was slowly added. The mixture was stirred for 1 h. Upon completion, the mixture was quenched with saturated aqueous NH_4Cl and extracted with DCM (3x). The organic phase was washed with water (1x), brine (1x) and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude product was passed through a silica plug (*t*BME) and the solvent was removed. The oil was dissolved in toluene (600 mL) and a catalytic amount of *p*-TsOH was added. The solution was heated to reflux under *Dean-Stark* conditions for 32h. After cooling to room temperature the solution was washed with saturated aqueous Na_2CO_3 (1x), water (1x) and brine (1x). The solvent was removed under reduced pressure and the crude product was purified by column-chromatography (SiO_2, EtOAc/cyclohexane, 1:2) to yield **6** (5.38 mmol, 1.55 g, 71%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ = 7.90-7.87 (m, 2H, H-14), 7.66-7.63 (m, 1H, H-15), 7.58-7.54 (m, 2H, H-13), 5.98-5.96 (m, 1H, H-7), 5.72-5.70 (m, 1H, H-8), 2.99-2.88 (m, 2H, H-11), 2.30-2.28 (m, 1H, H-9), 2.16-2.14 (m, 1H, H-6), 1.87-1.81 (m, 1H, H$^{a\text{ or }b}$-10), 1.71-1.65 (m, 3H, H$^{a\text{ or }b}$-10, H-4, H^a-2), 1.62-1.55 (m 1H, H^b-3), 1.36-1.24 (m, 3H, H^b-5, H^a-2, H^b-2), 0.91 (ddd, $^2J_{H,H}$ = 11.4, $^3J_{H,H}$ = 6.3, $^4J_{H,H}$ = 2.3 Hz, 1H, H^b-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 139.27 (C-12), 136.92 (C-7), 133.65 (C-15), 129.34 (C-13), 129.26 (C-8), 128.18 (C-14), 67.83 (C-1), 55.97 (C-9), 54.63 (C-11), 49.30 (C-6), 35.40 (C-4), 34.14 (C-5), 32.89 (C-3), 27.11 (C-2), 23.69 (C-10).

Tetracyclo[5.2.2.0^{1,6}.0^{4,9}]undecane (1):

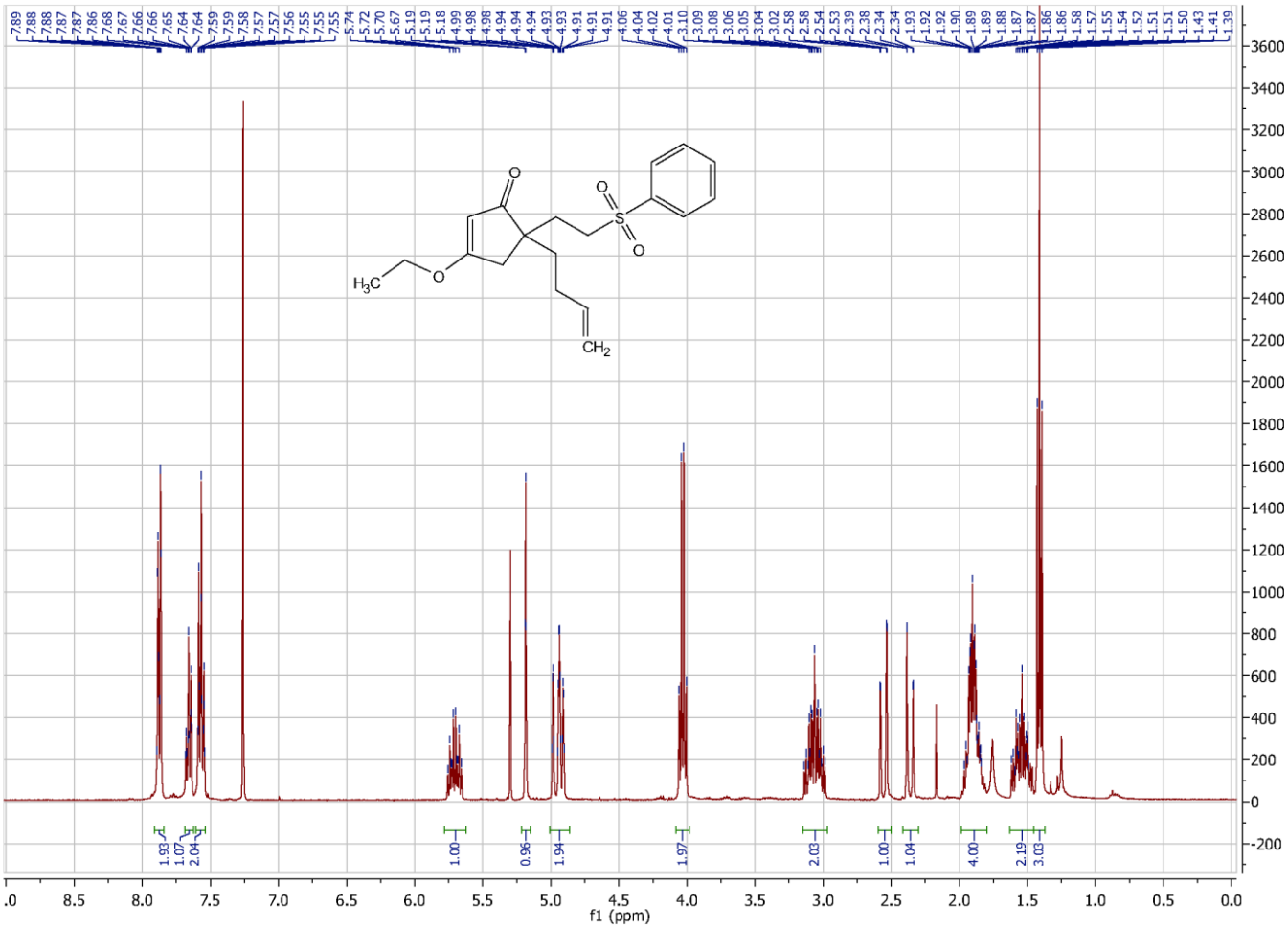


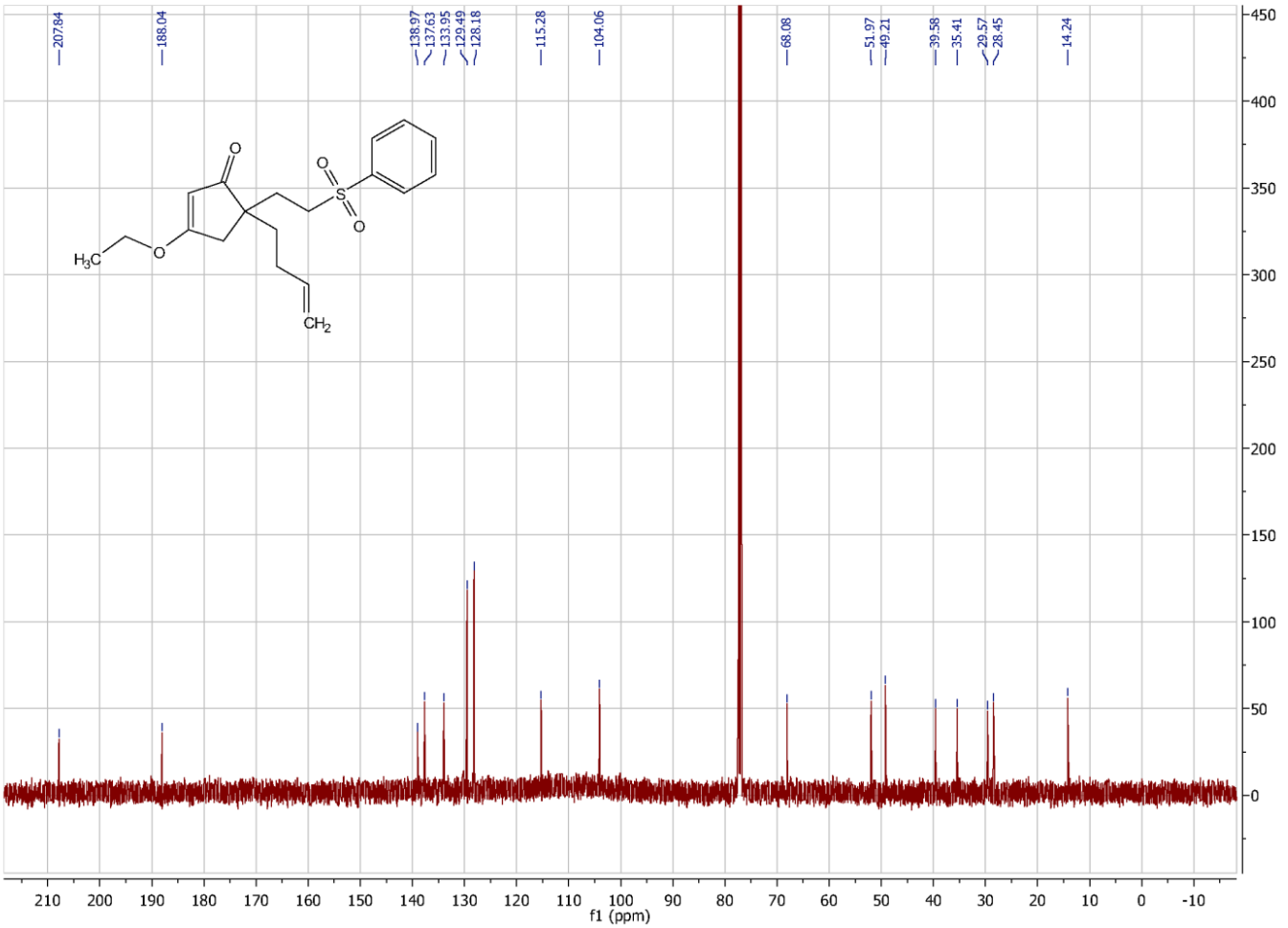
According to the literature known procedure[7], a freshly prepared solution of LDMAN (0.5 M in THF, 20.0 mmol) was cooled to -78 °C and added dropwise to a stirring solution of sulfone **6** (5.38 mmol, 1.55 g) in THF at -78 °C. After complete addition the reaction mixture was stirred for 20 min and quenched by the addition of 1 M aq. HCl. The mixture was allowed to warm up to room temperature and the organic layer was diluted with pentane and washed consecutively with 1 M aqueous HCl (2x), 32% aq. NaOH (2x) and brine (1x). The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2, pentane) to yield **1** (0.135 mmol, 21.0 mg, 3%) as a colorless solid.

To an oven-dried 50 mL Schlenk filled with argon a 0.1 M solution of SmI_2 in THF (2.58 mmol, 25.8 mL, 10.0 eq) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (20.6 mmol, 2.50 mL, 80.0 eq.) were added. Under stirring a solution of **6** (74.4 mg, 0.258 mmol, 1.00 eq) in THF (1 mL) was added. The mixture was stirred for 2 h at 80°C. The mixture was cooled to 0°C and quenched with water (20 mL). The solution was extracted with pentane (3x) and the organic phase was washed with 2 M auqueous HCl (3x), 1 M aqueous NaOH (3x) and water (2x). The solvent was removed by distillation with a Vigreux column. The crude mixture was passed through a silica plug (pentane). The solvent was removed by distillation with a Vigreux column and the remaining pentane was allowed to evaporate at room temperature yielding **1** (0.258 mmol, 10.7 mg, 28%) as a colorless solid. ^{1}H NMR (600 MHz, C_6D_6 25°C): δ = 1.80 (m_c, 1H, H-4), 1.61 (m_c, 1H, H^a-3), 1.56 (m_c, 1H, H^a-2), 1.51 (m_c, 1H, H^b-2), 1.46 (m_c, 1H, H^b-5), 1.44 (m_c, 1H, H-6), 1.38 (m_c, 1H, H^b-3), 1.10 (m_c, 1H, H^a-5). ^{13}C NMR (151 MHz, C_6D_6): δ = 57.11 (C-1), 50.97 (C-6), 42.28 (C-4), 32.62 (C-3), 29.96 (C-5). 25.60 (C-2). GC-MS (EI, 70 eV): *m/z* (%) = 148.2 (54), 120.2 (41), 119.2 (100), 106.2 (22), 105.1 (24), 93.1 (20.22), 92.1 (47), 91.1 (67), 80.1 (33), 79.1 (87), 77.1 (35). HRMS (EI, +): *m/z* calcd. for $C_{11}H_{16}$ $[M]^+$ 148.1252; found: 148.1249. Melting point: 49°C

Spectra

^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) and ^{13}C-NMR ($CDCl_3$, 126 MHz, 298 K) of **16**.





HR-ESI spectra of **16**.

Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	Lorenzo Delarue Bizzini	Instrument / Ser#	maXis 4G 21243
Comment	LDB25, ca. 10 ug/ml MeOH		

Acquisition Parameter

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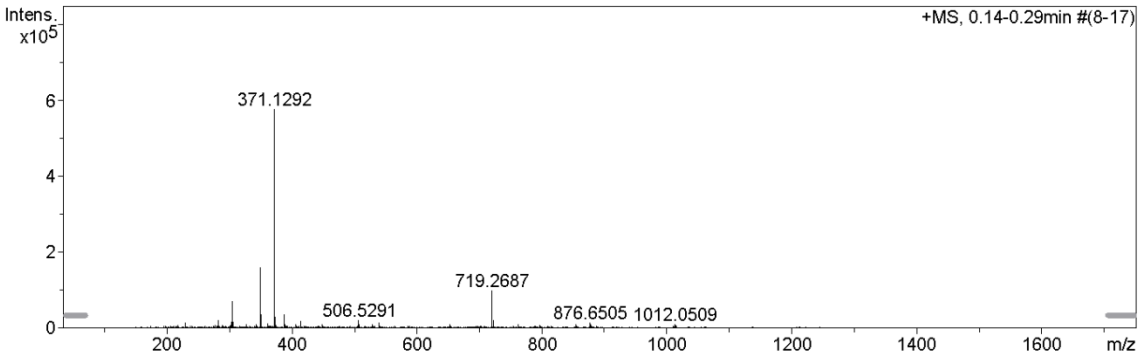

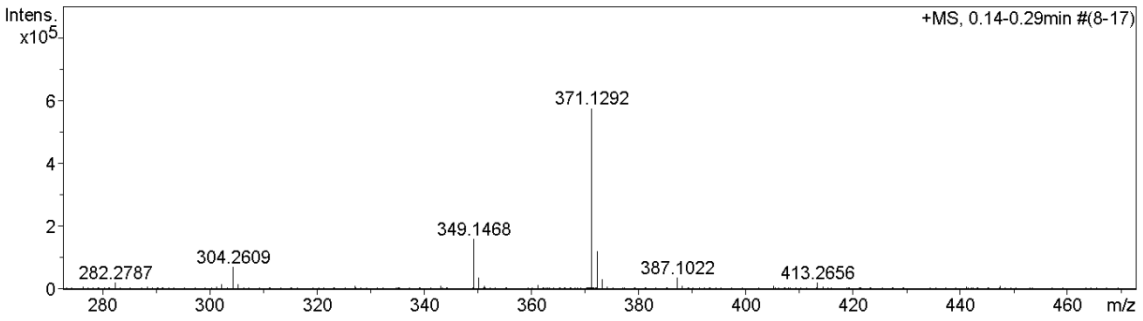

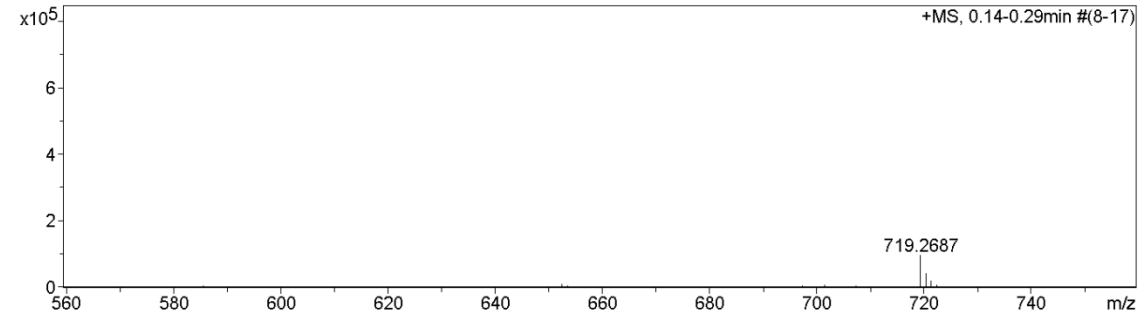

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	z
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371.1292	1	C 19 H 24 Na O 4 S	100.00	371.1288	-0.5	-1.2	14.2	7.5	even	
387.1022	1	C 19 H 24 K O 4 S	100.00	387.1027	0.4	1.2	11.2	7.5	even	
697.2856	1	C 38 H 49 O 8 S 2	100.00	697.2863	0.8	1.1	98.4	14.5	even	
719.2687	1	C 38 H 48 Na O 8 S 2	100.00	719.2683	-0.4	-0.6	5.5	14.5	even	

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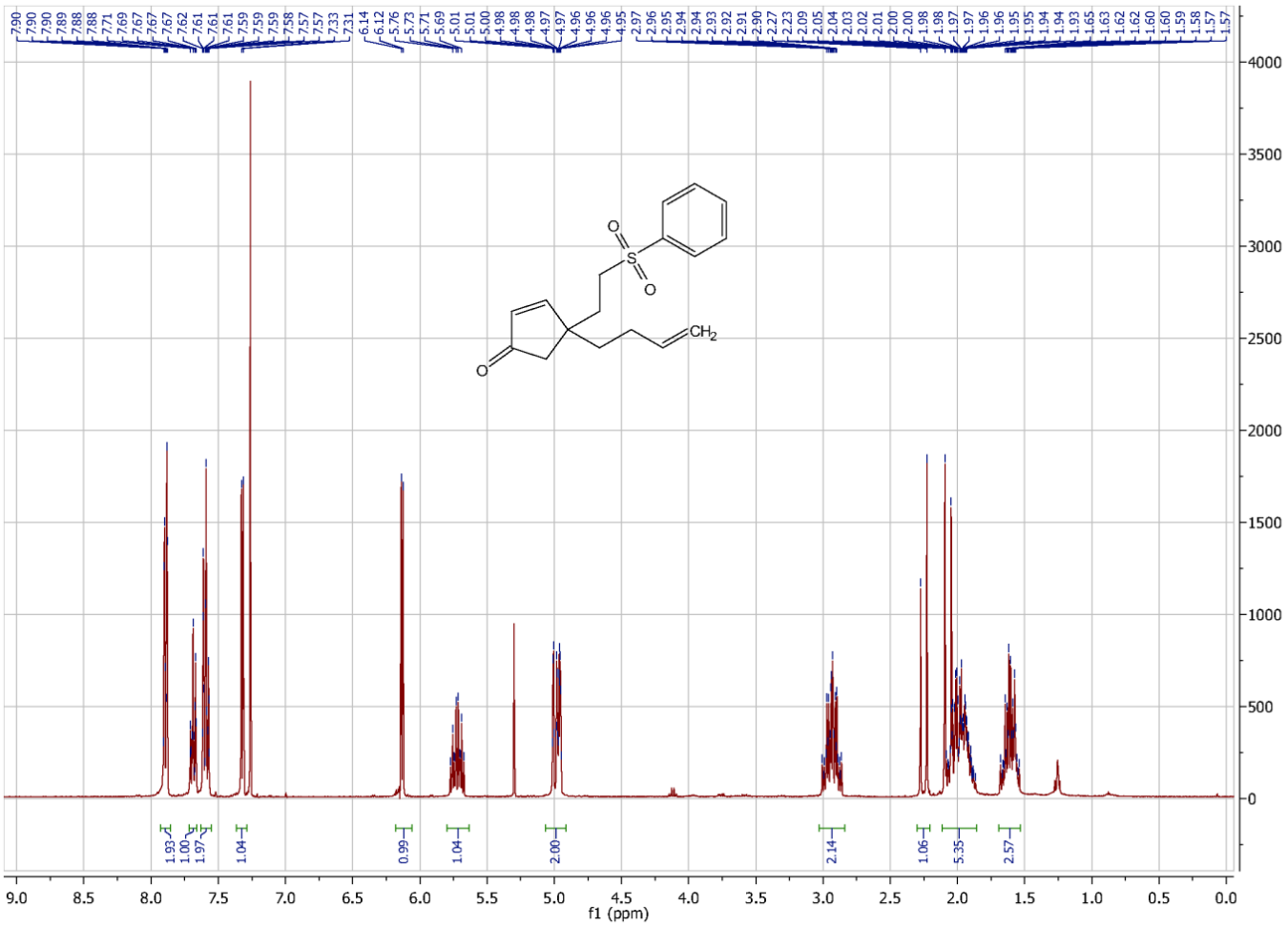
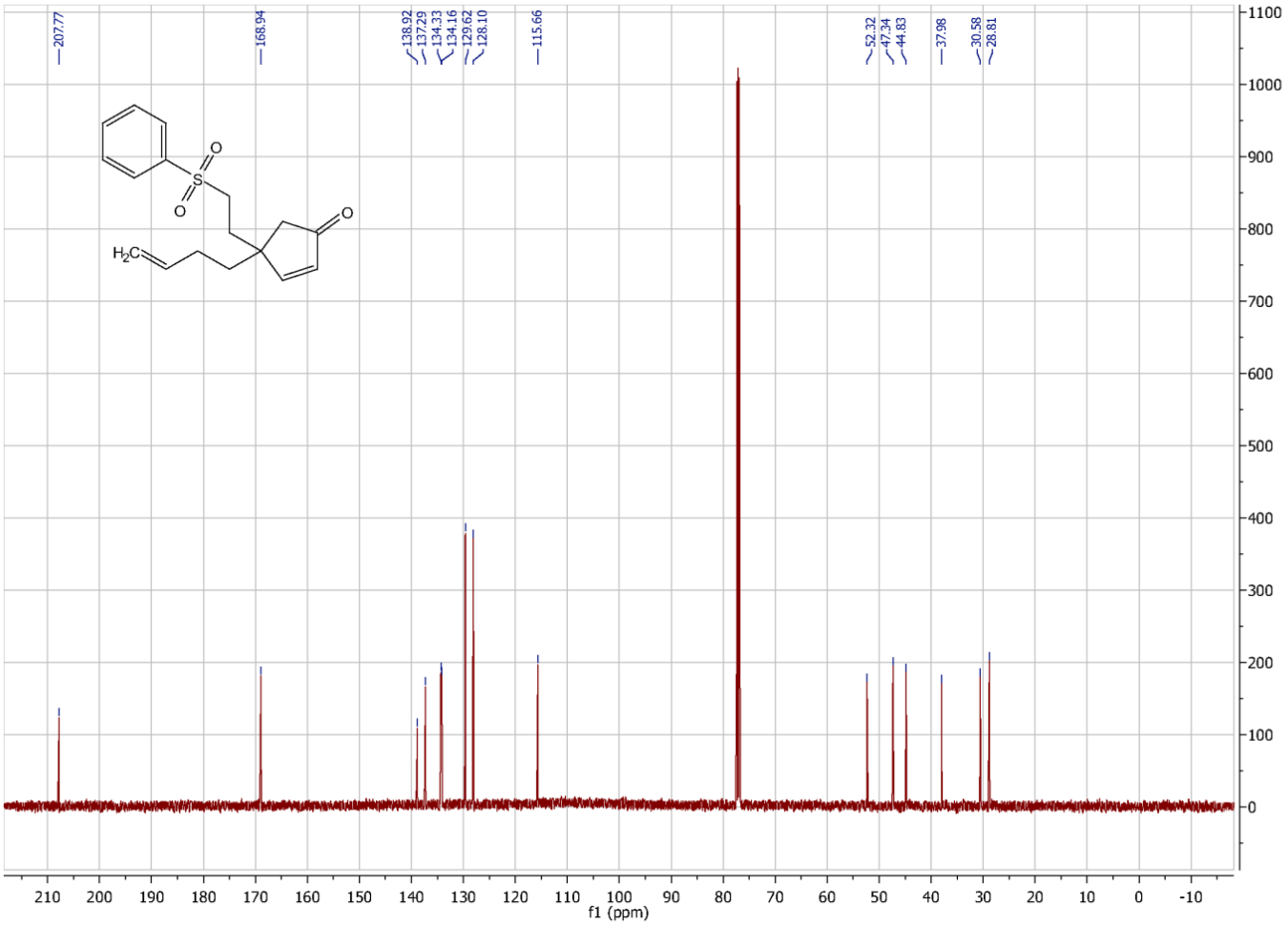
^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) and ^{13}C-NMR ($CDCl_3$, 126 MHz, 298 K) of **17**.





HR-ESI spectra of **17**.

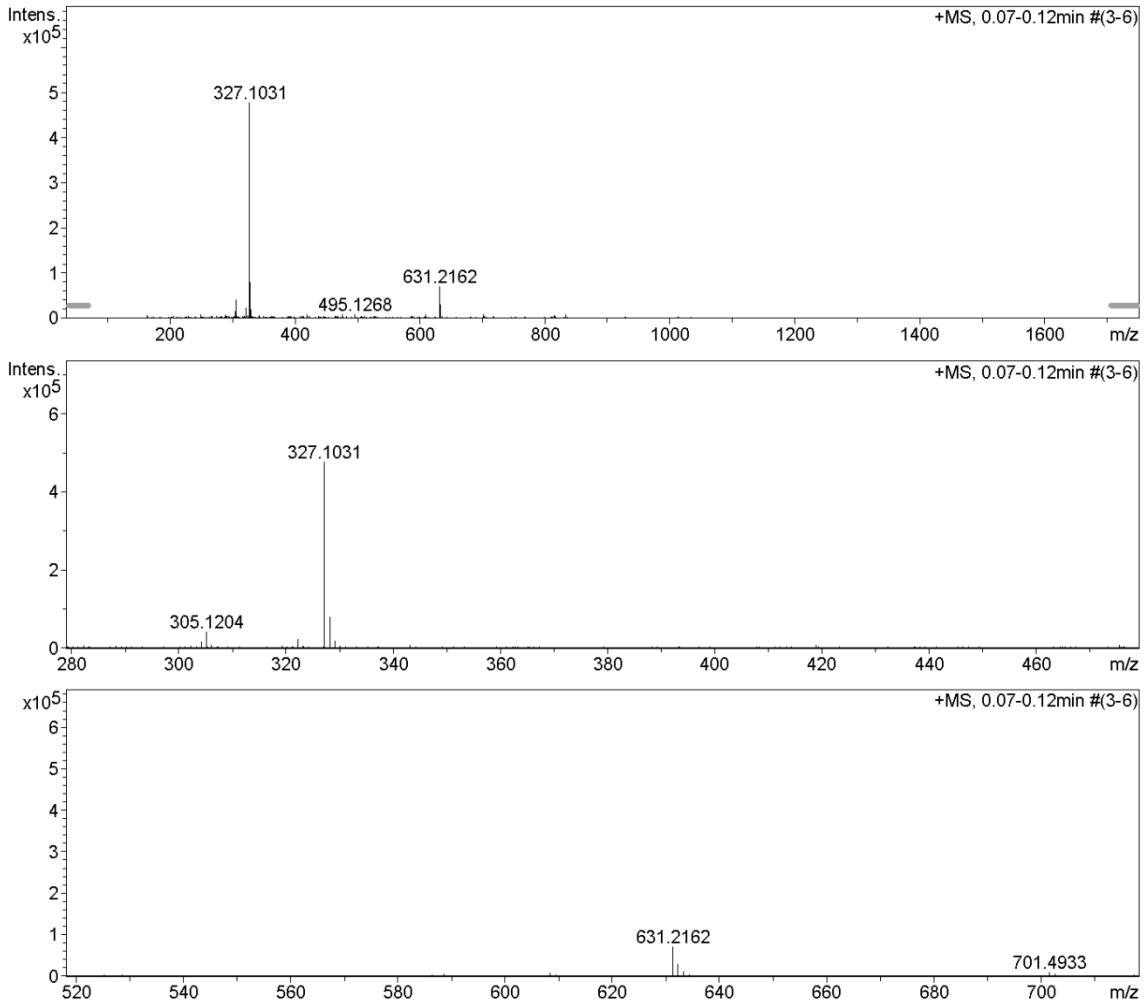
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	E:\acq data for data analysis\LDB26 001.d	Acquisition Date	16.05.2017 09:16:21
Method	hn Direct_Infusion_pos mode_75-1700 mid 4eV.m	Operator	hn
Sample Name	Lorenzo Delarue Bizzini	Instrument / Ser#	maXis 4G 21243
Comment	LDB26, ca. 10 ug/ml MeOH		

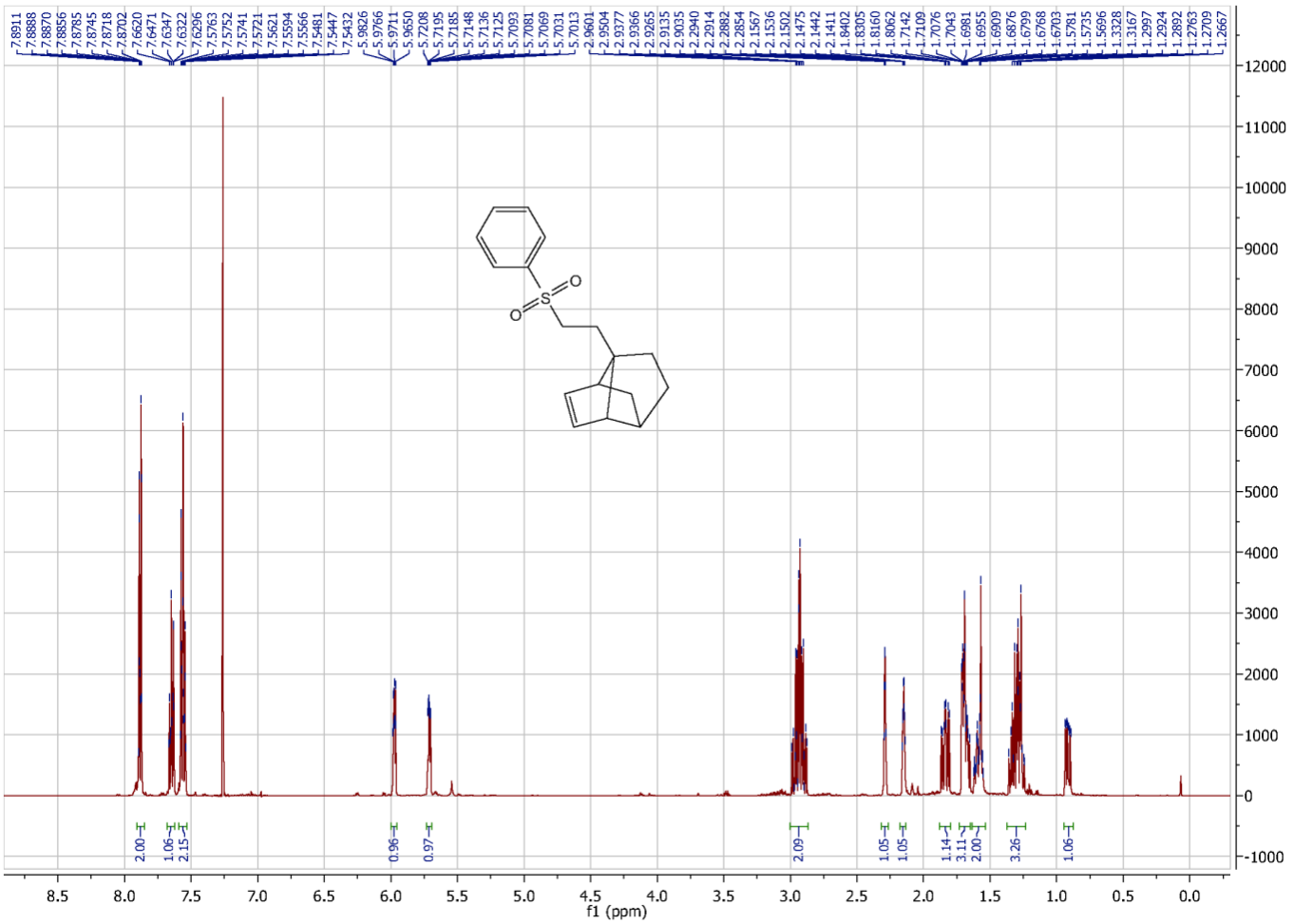
Acquisition Parameter

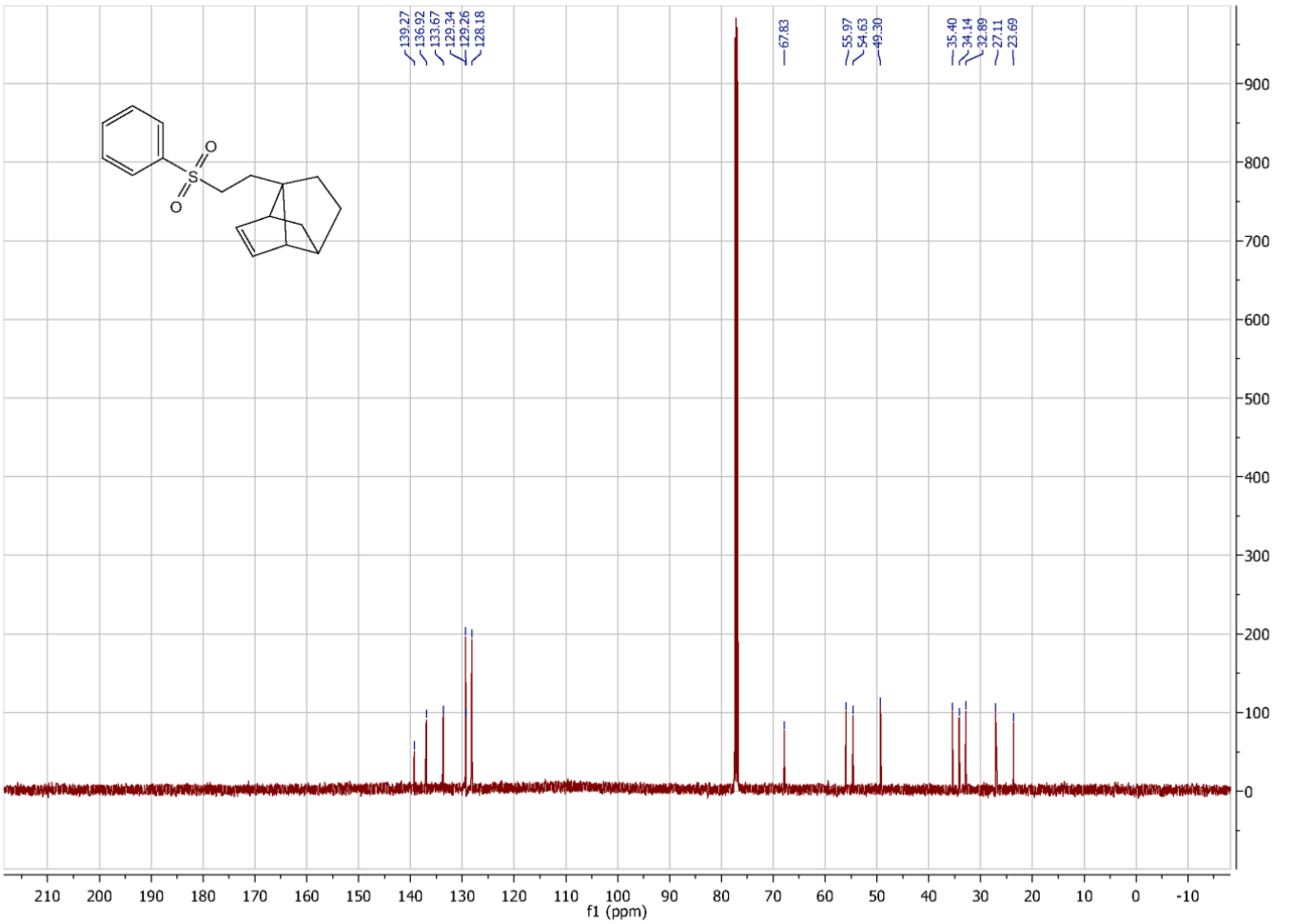
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1700 m/z	Collision Energy	8.0 eV	Set Ion Energy (MS only)	4.0 eV



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	z
305.1204	1	C 17 H 21 O 3 S	100.00	305.1206	0.2	0.7	8.0	7.5	even	1+
322.1469	1	C 17 H 24 N O 3 S	100.00	322.1471	0.2	0.7	14.8	6.5	even	
327.1031	1	C 17 H 20 Na O 3 S	100.00	327.1025	-0.5	-1.6	20.2	7.5	even	
631.2162	1	C 34 H 40 Na O 6 S 2	100.00	631.2159	-0.3	-0.5	10.7	14.5	even	

^{1}H-NMR ($CDCl_3$, 500 MHz, 298 K) and ^{13}C-NMR ($CDCl_3$, 126 MHz, 298 K) of **6**.





HR-ESI spectra of **6**.

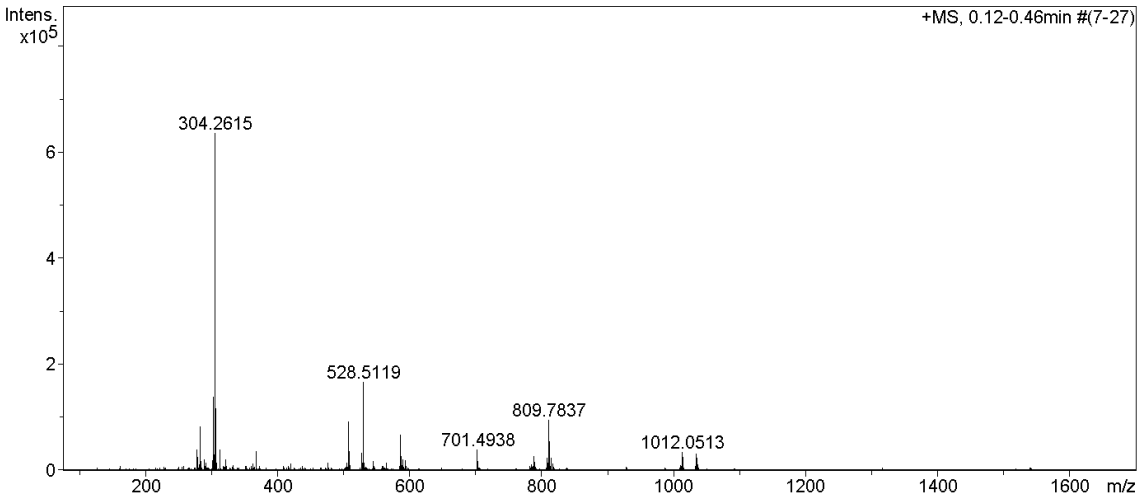
Mass Spectrum SmartFormula Report

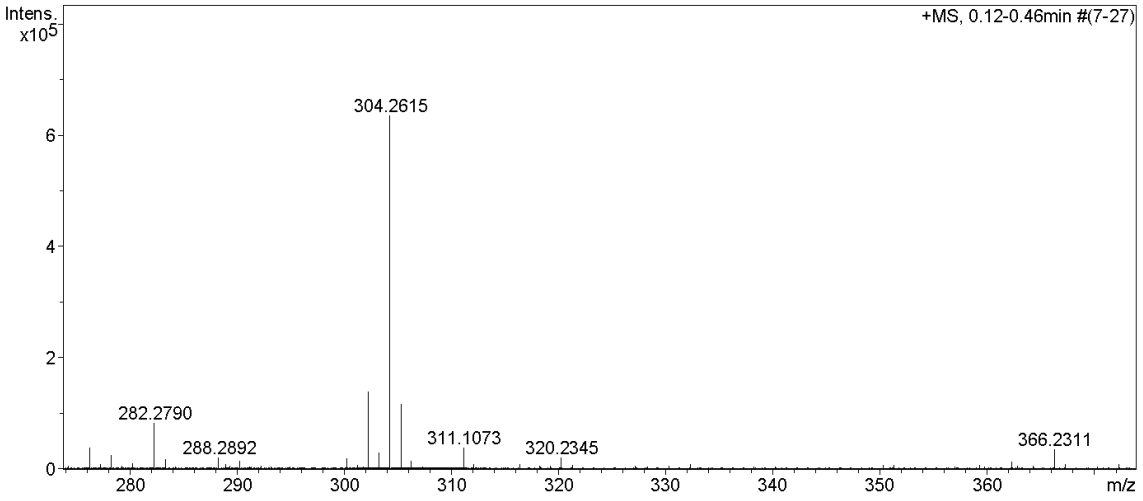
Analysis Info

Analysis Name	E:\acq data for data analysis\LDB27 001.d	Acquisition Date	06.06.2017 15:09:45
Method	hn Direct_Infusion_pos mode_75-1700 mid 4eV.m	Operator	hn
Sample Name	Lorenzo Delarue Bizzini	Instrument / Ser#	maXis 4G 21243
Comment	LDB27, ca. 10 ug/ml MeOH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1700 m/z	Collision Energy	8.0 eV	Set Ion Energy (MS only)	4.0 eV





Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	z
311.1073	1	C 17 H 20 Na O 2 S	100.00	311.1076	0.3	0.9	14.0	7.5	even	1+

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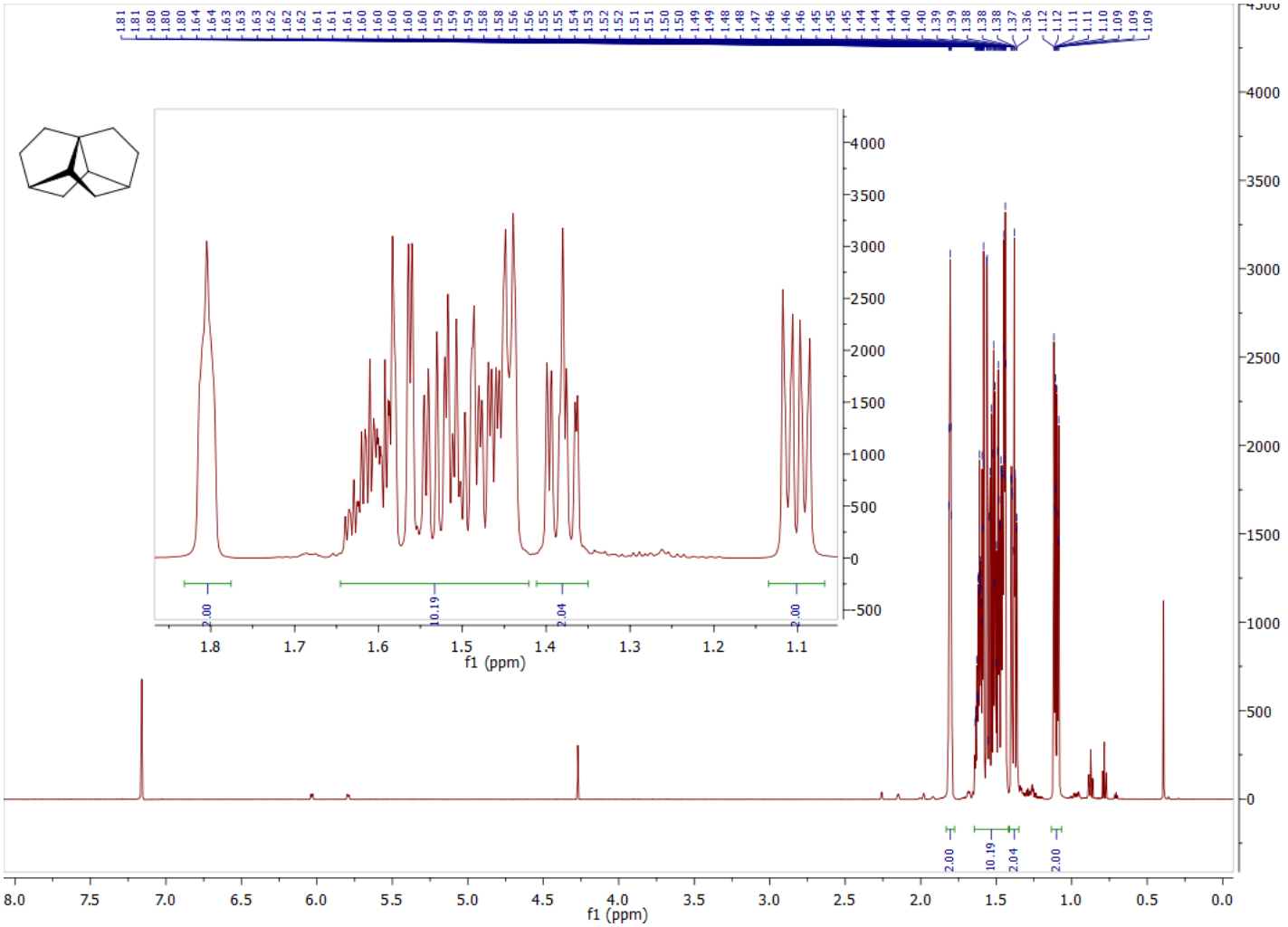
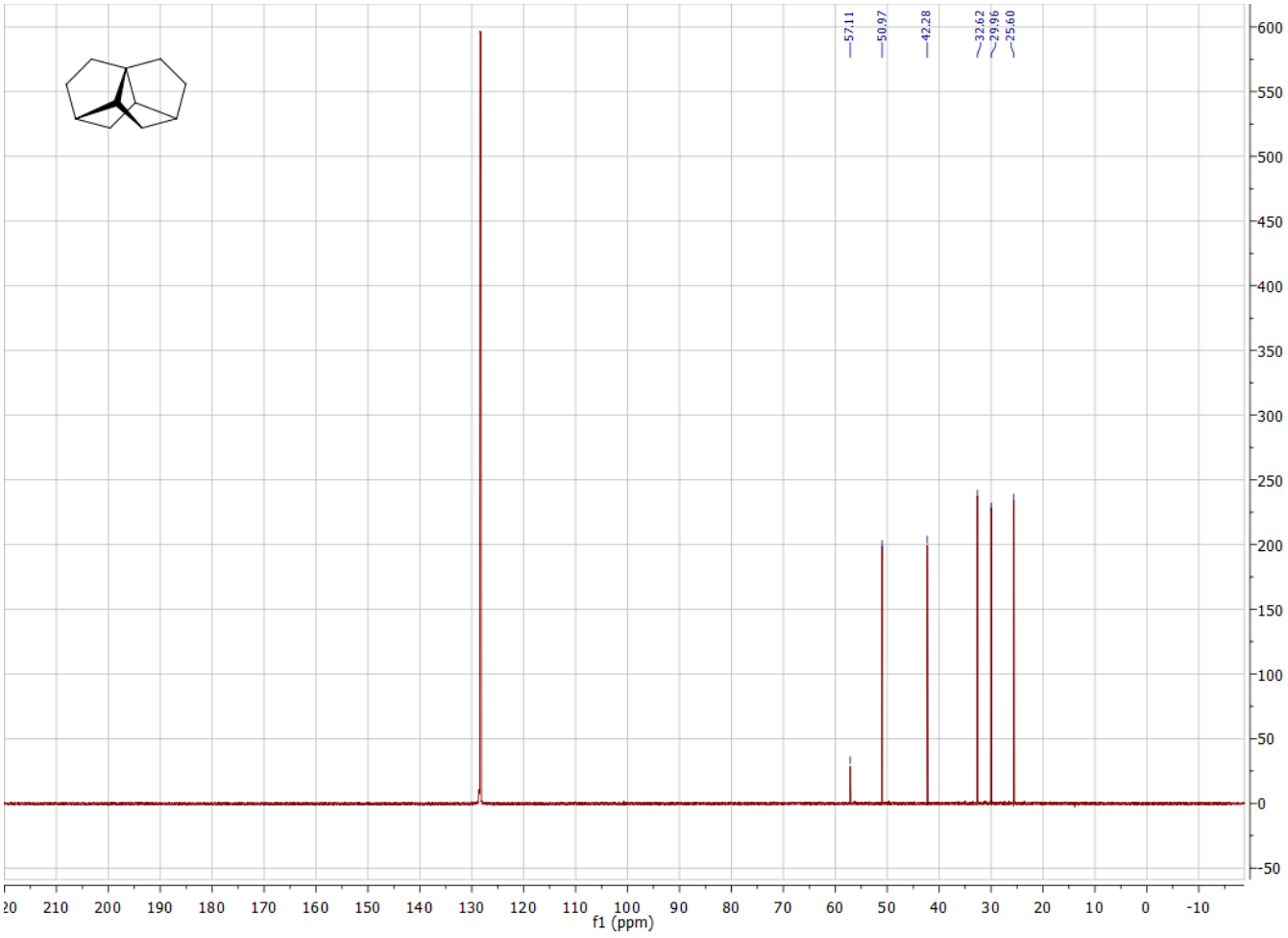
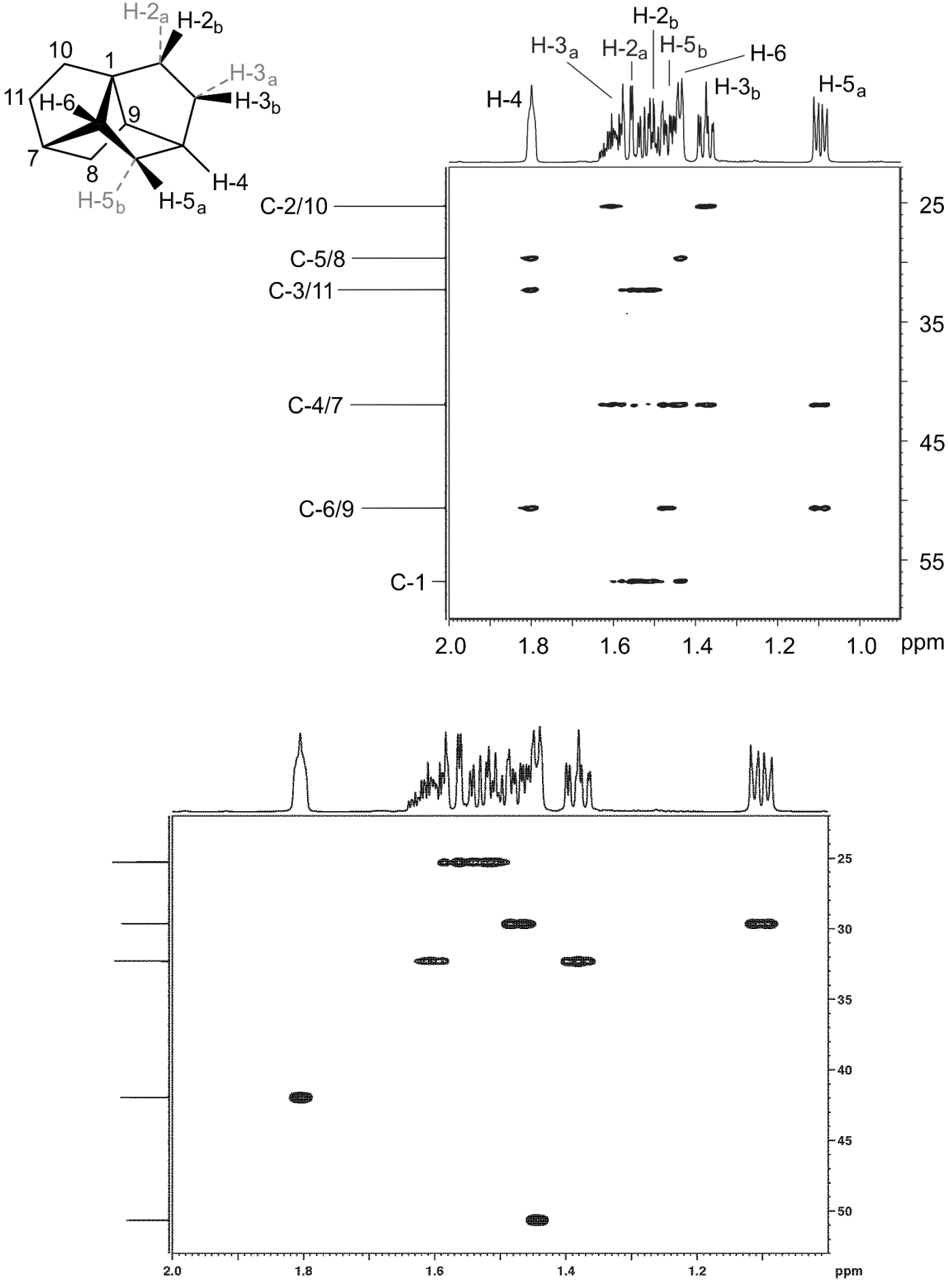
^{1}H-NMR (C_6D_6, 600 MHz, 298 K) and ^{13}C-NMR (C_6D_6, 151 MHz, 298 K) of **1**.





1,1 adequate and HSQC (C_6D_6, 298 K) of **1**.



NOESY (C_6D_6 298 K) of **1**.

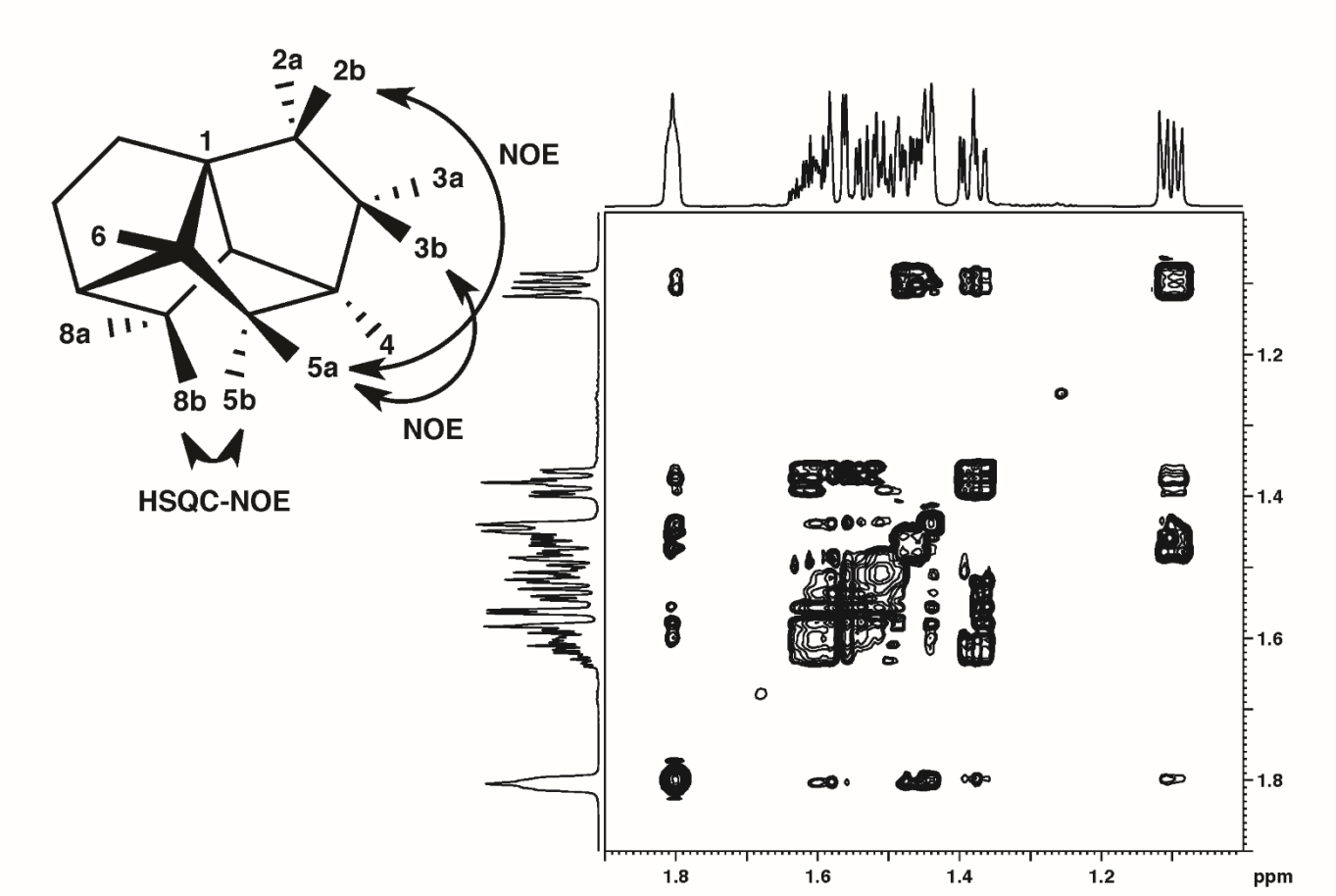
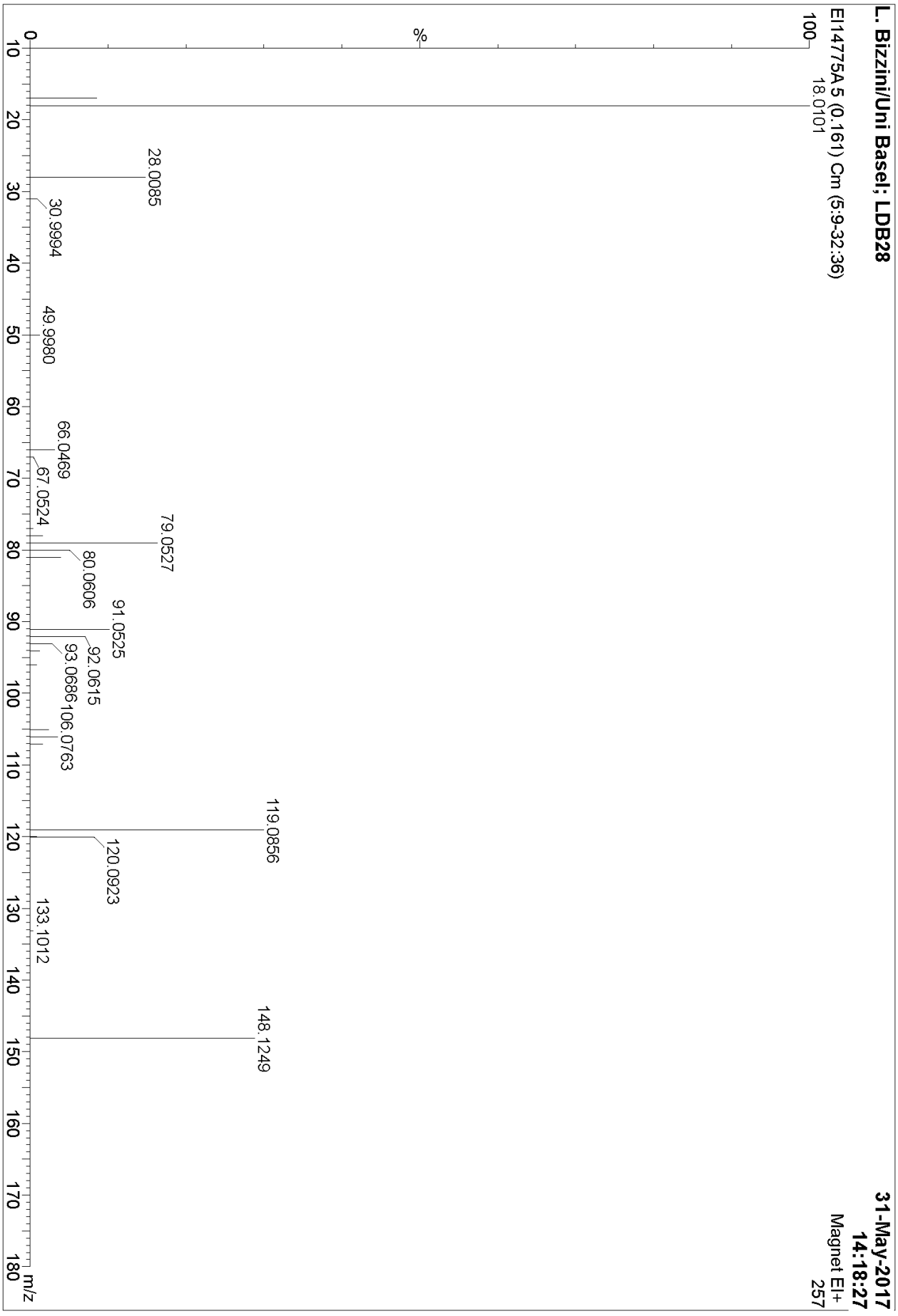


Figure S1: 2D-NOESY NMR of **1.**

HR-EI spectra of **1**.



X-Ray Cristallography Data

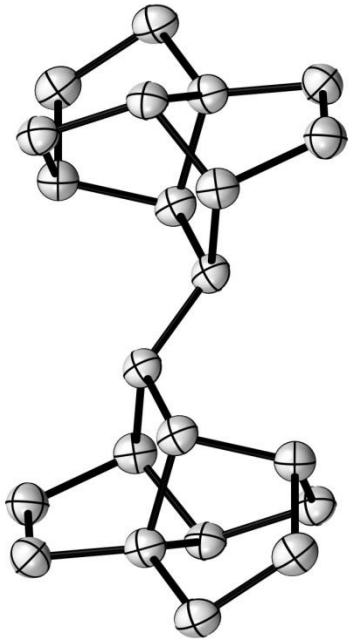


Fig. 1: Molecular structure of **18**, the ellipsoids represent the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1: Crystal data and structure refinement for **18**.

Empirical formula	$C_{22}H_{30}$
Formula weight	294.48
Temperature/K	123
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.8515(4)
b/Å	11.0768(8)
c/Å	12.6463(9)
α/°	90
β/°	99.386(5)
γ/°	90
Volume/Å^3	808.71(10)
Z	2
ρ_{calc}g/cm^3	1.209
μ/mm^{-1}	0.315
F(000)	324
Crystal size/mm^3	0.06 × 0.19 × 0.25
Radiation	GaKα (λ = 1.34143)
Θ range for data collection/°	4.644 to 57.411
Index ranges	$-7 \leq h \leq 6$ $-13 \leq k \leq 12$ $-9 \leq l \leq 15$
Reflections collected	5526
Independent reflections	1626 [R_{int} = 0.078]
Observed reflections	1507 [I > 2σ(I)]
Parameters	100
Goodness-of-fit on F^2	1.074
Final R indexes [I≥2σ(I)]	R_1 = 0.0836, wR_2 = 0.0982
Final R indexes [all data]	R_1 = 0.0851, wR_2 = 0.0997
Largest diff. peak/hole / e Å-3	*0.35/–0.26*
CCDC number	*1556107*

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