Cationic iron porphyrins combined with sodium dodecyl sulphate for micellar catalysis of cyclopropanation reactions

Supporting information

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Contents:

General remarks

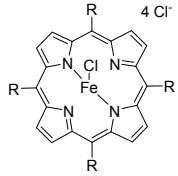
Iron(III) meso-tetra(N-methyl-4-pyridyl)porphyrin pentachloride (Fe(Cl)-TMe4PyP, **C3**), iron(III) meso-tetra(4-sulfonatophenyl)porphyrin pentachloride (Fe(Cl)-TSPP, **C5**), iron(III) chloride mesoporphyrin IX (Fe(Cl)-MPIX, **C6**), dihydrogen meso-tetra(N-methyl-2-pyridyl)porphyrin tetrachloride (H_2-TMe2PyP) and dihydrogen meso-tetra(N-methyl-3-pyridyl)porphyrin tetrachloride (H_2-TMe3PyP) were obtained from Frontier Scientific. Iron(III) chloride tetraphenylporphyrin (Fe(Cl)-TPP, **C4**) was obtained from Sigma Aldrich. Ethyl diazoacetate was obtained from Sigma Aldrich (lotnumber STBD3196V) as a solution containing 14.1 wt% dichloromethane according to the Certificate of Analysis. No purification was performed prior to use, however the amounts used were corrected for the presence of dichloromethane. All other chemicals were obtained from Sigma Aldrich, Acros Organics or TCI Europe and used without further purification, unless stated otherwise.

Column chromatography was performed using silica gel 60 Å (Merck, 200-400 mesh) or by automated column chromatography on a Grace Reveleris using standard silica cartridges.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Mercury Plus 400 (400 and 100 MHz respectively) or an Agilent MR 400 (400 and 100 MHz respectively). Chemical shifts (δ) are denoted in ppm using residual solvent peaks as internal standard (δ_C = 77.2 and δ_H = 7.26 for $CDCl_3$, δ_C = 39.5 and δ_H = 2.50 for DMSO-d6, δ_C = 49.0 and δ_H = 3.31 for CD_3OD, δ_H = 4.79 for D_2O).
UV/Vis absorption spectra were recorded on a Jasco V-660 spectrophotometer in 1 cm path length quartz cuvettes.
Mass spectra (HRMS) were recorded on a Thermo Fisher Scientific Orbitrap XL.
UPLC-TOF was performed on a Waters Acquity Xevo G2 TOF with Acquity HSS T3 1.8 µm column using a gradient of water/acetonitrile (0.3 ml min^{-1}) with 0.1% formic acid (FA) or 0.1% ammonia: 95/5 to 20/80 in 20 min, hold 20/80 for 5 min, 20/80 to 95/5 in 1 min, hold 95/5 for 4 min.
HPLC analysis was performed on a Shimadzu 20AD system using a Chiracel-OBH column (100% n-heptane, 0.5 ml min^{-1}).

Room temperature is defined as 20-25°C.

General procedure for the metalation of porphyrins



C1: R = 

C2: R = 

Procedure adapted from literature.[1]
To a three necked amber-glass round-bottom flask under nitrogen atmosphere was added dihydrogen meso-tetra(N-methyl-2-pyridyl)porphyrin tetrachloride (H_2-TMe2PyP) or dihydrogen meso-tetra(N-methyl-3-pyridyl)porphyrin tetrachloride (H_2-TMe3PyP) (100 mg, 147 µmol) and 60 ml double distilled water. The pH was adjusted to 2 with 1M HCl and iron(II)dichloride tetrahydrate (40 eq, 885 mg, 5.9 mmol) was added. The mixture was heated to reflux and stirred overnight, progress of the reaction was followed by TLC (SiO_2, MeCN/sat. aq. KNO_3/H_2O 8:1:1) where disappearance of the fluorescence of the starting material at 365 nm was observed. After 16 hours the mixture was cooled to room temperature and filtered over a sintered glass filter P4. The iron(III) porphyrin was precipitated by adding a saturated aqueous NH_4PF_6 solution (2 ml). The suspension was centrifuged (15 min, 4000 rpm, 5°C), the liquid was decanted and the remaining solid was dried overnight under nitrogen gas flow. The precipitate was washed with diethyl ether (5 × 5 mL), centrifuging (15 min, 4000 rpm, 5°C) and decanting the liquid between every wash step. After the last wash the solid was dried on air and subsequently dissolved in a minimal amount of acetone. The metalloporphyrin was precipitated by addition of a saturated solution of methyl-tri-octylammonium chloride in acetone (2 ml). The suspension was centrifuged (15 min, 4000 rpm, 5°C) and afterwards the liquid was decanted. The solid was washed with acetone (5 × 10 mL), centrifuging

(10 min, 4000 rpm, 5°C) and decanting the liquid between every wash step. The whole precipitation procedure (with PF_6^- and with Cl^-) was repeated once more. The solid was dried under nitrogen gas flow overnight and dissolved in a minimal amount of double distilled water (6 ml). The solution was filtered through a 0.45 µm syringe filter into an amber-glass vial and a 10 µl aliquot was withdrawn for yield and purity determination by UV/Vis spectroscopy. The solution was lyophilized to obtain the iron(III) porphyrin as a brown solid.

Fe(Cl)-TMe2PyP (**C1**): 65.0 mg (63%). UV/vis (0.01M HCl in H_2O): λ_{max} at 395 nm (Soret band), in accordance with literature data.

UPLC-TOF (ESI^+, 0.1% formic acid in MeCN/H_2O):

calcd for $C_{44}H_{36}N_8Fe^{2+}$ $[M^{4+}\text{-}Cl^-\text{+}3e^-]^{2+}$ 366.12, found 364.63

calcd for $C_{44}H_{36}N_8Fe^{3+}$ $[M^{4+}\text{-}Cl^-\text{+}2e^-]^{3+}$ 244.08, found 244.10

calcd for $C_{43}H_{33}N_8Fe^{3+}$ $[M^{4+}\text{-}Cl^-\text{-}Me\text{+}2e^-]^{3+}$ 239.07 , found 239.09

calcd for $C_{44}H_{36}N_8Fe^{4+}$ $[M^{4+}\text{-}Cl^-\text{+}e^-]^{4+}$ 183.06, found 183.08

No unmetallated porphyrin was detected in UV or mass.

All spectra can be found in SI3.

Fe(Cl)-TMe3PyP (**C2**): 99.3 mg (88%). UV/vis (0.01M HCl in H_2O): λ_{max} at 397 nm (Soret band), in accordance with literature data.

UPLC-TOF (ESI^+, 0.1% formic acid in MeCN/H_2O):

calcd for $C_{44}H_{36}N_8Fe^{2+}$ $[M^{4+}\text{-}Cl^-\text{+}3e^-]^{2+}$ 366.12, found 364.61

calcd for $C_{44}H_{36}N_8Fe^{3+}$ $[M^{4+}\text{-}Cl^-\text{+}2e^-]^{3+}$ 244.08, found 243.41

calcd for $C_{44}H_{36}N_8Fe^{4+}$ $[M^{4+}\text{-}Cl^-\text{+}e^-]^{4+}$ 183.06, found 183.06

No unmetallated porphyrin was detected in UV or mass.

All spectra can be found in SI4.

Preparation of metalloporphyrin stock solutions

Extinction coefficients ε have been reported for **C1**, **C2** and **C3**:

- 128824 M^{-1} cm^{-1} at 395 nm in 0.01M HCl in H_2O for **C1** and **C2**[1]
- 100000 M^{-1} cm^{-1} at 398 nm in 0.01M HCl in H_2O for **C3**[2]

Stock solutions of **C1**, **C2** and **C3** were prepared by dissolving an amount of solid metalloporphyrin in double distilled water and vortexing for 10 minutes.

A 5 µl aliquot of this solution was diluted in 995 µl of the appropriate solvent (100x dilution). This was diluted further, typically to 2000-5000x dilution to obtain an absorbance below 1 AU.

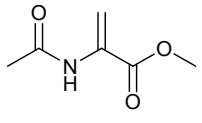
The absorbance was measured at the specified wavelength, this value was subsequently used to calculate the concentration of the sample used the Lambert-Beer law:

$$c = \frac{A}{\varepsilon \times l} \times d$$

Where A is the absorbance, ε is the extinction coefficient at the specified wavelength, l is the path length and d is the dilution factor.

Stock solution of 75 µM porphyrin in water were prepared.

Synthesis of methyl 2-acetamidoacrylate (1g)

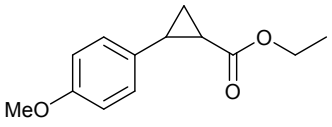


Procedure adapted from literature.[3]

To a three necked round-bottom flask with Dean-Stark trap under nitrogen atmosphere was added 8.7 g (7.7 ml, 77 mmol, 1 eq) methyl pyruvate, 5.0 g (85 mmol, 1.1 eq) acetamide, 13 mg (77 µmol, 0.001 eq) *p*-toluenesulfonic acid, 10 mg (77 µmol, 0.001 eq) 4-methoxyphenol and 150 ml toluene. The mixture was heated to reflux for 24 hours while monitoring the amount of water collected. After 24 hours, the mixture was cooled to room temperature

and subsequently concentrated *in vacuo*. The obtained yellow oil was redissolved in 120 ml dichloromethane and transferred to a separatory funnel. The organic phase was washed with 60 ml saturated aqueous sodium bicarbonate solution, followed by 2x60 ml demineralized water. The organic phase was dried over magnesium sulphate and concentrated *in vacuo*. The obtained yellow oil was coated on Celite 545 and purified by automated column chromatography (40 g SiO_2, pet. Ether 40-65/Et_2O, 0 to 40% in 30 min).
3.6 g (25 mmol, 33%) product was obtained as a white crystalline solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 6.60 (s, 1H), 5.88 (d, *J* = 1.4 Hz, 1H), 3.85 (s, 3H), 2.13 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 164.6, 130.8, 108.7, 53.0, 24.6. HRMS calcd for $C_6H_{10}NO_3$ $[M+H]^+$ 144.06552, found 144.06539. HRMS calcd for $C_6H_9NO_3Na$ $[M+Na]^+$ 166.04746, found 166.04735.
All spectra can be found in SI5.

Synthesis of ethyl 2-(4-methoxyphenyl)cyclopropane-1-carboxylate (3a)



Procedure adapted from literature.[1,4]
To a round bottom flask was added iron(III) chloride tetraphenylporphyrin (Fe(Cl)-TPP, 14 mg, 26 µmol), 2-ethoxy-2-oxoethanominium chloride (560 mg, 4.1 mmol), double distilled water (10 ml), glacial acetic acid (18 µL, 31 µmol) and 4-vinylanisole (269 µL, 2.0 mmol). The solution was stirred and heated to 40°C. Sodium nitrite (332 mg, 5.0 mmol) at once. The reaction was followed by TLC using heptane/ethyl acetate 95:5 as mobile phase. The solution was stirred overnight and the reaction quenched by addition of 10 ml double distilled water when 4-vinylanisole was not observed anymore by TLC. The solution was extracted with dichloromethane (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over magnesium sulphate. After evaporation of the solvent, the product was purified by column chromatography (SiO_2, heptane/ethyl acetate 95:5). The product was obtained as a red solid. After additional recrystallization from absolute ethanol the product was obtained as a white solid (157 mg, 0.7 mmol, 36% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J=8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 2.48 (ddd, J= 10.0, 6.5, 4.2 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.55 (dt, J = 9.5, 4.9 Hz, 1H), 1.32 – 1.22 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.6, 158.3, 132.1, 127.4, 113.9, 60.6, 55.3, 25.6, 23.9, 16.7, 14.3. Enantiomeric excess was analyzed by HPLC analysis (Chiralcel-OBH, n-heptane 100%, 0.5 ml/min. Retention times: 46.5 (*trans*) and 61.4 min (*trans*). A racemic mixture of *trans*-**2** was obtained, no *cis*-**2** was observed.
All spectra can be found in SI6.

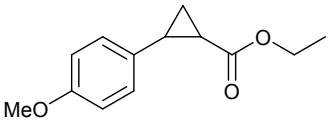
Representative procedure for the cyclopropanation via micellar catalysis

To a 20 ml glass vial with stirring bar was added catalyst (0.75 µmol, see Note 1), sodium dodecyl sulphate (0.2 mmol, 58 mg) and double distilled water (10 mL). The solution was stirred at room temperature until all the sodium dodecyl sulphate was dissolved. 4-vinylanisole (75 µmol, 10.1 µL) was added and the mixture was stirred for 15 min at room temperature. Ethyl 2-diazoacetate (2 eq, 150 µmol, 18 µL) was added and the reaction was stirred at room temperature for 1 hour. The reaction was followed by TLC using heptane/ethyl acetate 95:5 as the mobile phase. The solution was extracted with ethyl acetate (4x10 mL, see Note 2) and the combined organic phases were washed with brine (10 mL). The organic phase was dried over magnesium sulphate and the solvent was evaporated. The crude was dissolved in 1 ml 20 mM hexamethyldisiloxane (HMDSO) in $CDCl_3$ for determination of the yield by ^{1}H-NMR.
The product was purified by flash column chromatography (SiO_2, heptane/ethyl acetate = 99:1). Racemic mixtures were obtained in every case.

Results with **C1-C3** can be found in the main article Tables 1 and 2, additional data on catalysis with **C3** can be found in Table SI2. Results obtained with **C4-C6** can be found in Table SI1.
Spectra of the isolated products can be found in SI7, representative spectra for micellar catalysis can be found in SI8.

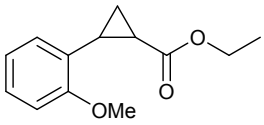
Note 1: **C1**-**C3** were added as 10 mL of a 75 µM stock solution in double distilled water, the described addition of 10 mL double distilled water was then omitted. **C4**-**C6** were added as solid.
Note 2: Solid sodium chloride or brine can be added to accelerate separation of both layers.

Characterization of compounds obtained from micellar catalysis



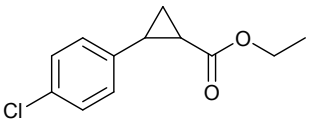
Ethyl 2-(4-methoxyphenyl)cyclopropane-1-carboxylate (3a)
98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 2.48 (ddd, J = 10.3, 6.6, 4.4 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.55 (dt, J = 9.6, 4.9 Hz, 1H), 1.35 – 1.20 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 158.3, 132.1, 127.4, 113.9, 60.6, 55.3, 25.6, 23.9, 16.7, 14.3.

NMR data in agreement with those reported in the literature.[1,5]



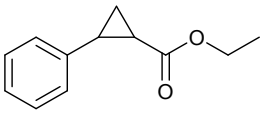
Ethyl 2-(2-methoxyphenyl)cyclopropane-1-carboxylate (3b)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 2H), 6.95 – 6.82 (m, 2H), 4.20 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 2.76 (ddd, J = 9.2, 6.8, 4.5 Hz, 1H), 1.87 (dt, J = 9.4, 4.9 Hz, 1H), 1.57 (dt, J = 9.4, 4.7 Hz, 1H), 1.35 – 1.27 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 158.2, 128.3, 127.4, 125.8, 120.3, 110.3, 60.4, 55.4, 22.7, 21.1, 15.7, 14.2.

NMR data in agreement with those reported in the literature.[4]



Ethyl 2-(4-chlorophenyl)cyclopropane-1-carboxylate (3c)
15 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 2.48 (ddd, J = 9.8, 6.4, 4.4 Hz, 1H), 1.85 (dt, J = 9.0, 4.9 Hz, 1H), 1.59 (dt, J = 9.5, 5.0 Hz, 1H), 1.34 – 1.14 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 138.6, 132.1, 128.5, 127.5, 60.7, 25.4, 24.1, 16.9, 14.2.

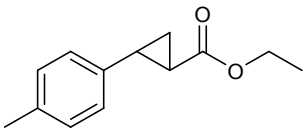
NMR data in agreement with those reported in the literature.[6]



Ethyl 2-(phenyl)cyclopropane-1-carboxylate (3d)

8% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.00 (m, 5H), 4.17 (q, J = 7.1 Hz, 2H), 2.51 (ddd, J = 10.2, 6.3, 4.3 Hz, 1H), 1.90 (dt, J = 9.3, 4.7 Hz, 1H), 1.59 (dt, J = 9.7, 4.9 Hz, 1H), 1.34 – 1.25 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 140.1, 128.5, 126.5, 126.2, 60.7, 26.2, 24.2, 17.1, 14.3.

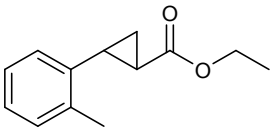
NMR data in agreement with those reported in the literature.[1,5]



Ethyl 2-(*p*-tolyl)cyclopropane-1-carboxylate (3e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.46 (ddd, *J* = 9.6, 6.5, 4.2 Hz, 1H), 2.29 (s, 3H), 1.84 (dt, *J* = 8.4, 4.7 Hz, 1H), 1.59 – 1.48 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 137.1, 136.1, 129.1, 126.1, 60.6, 25.9, 24.0, 21.0, 16.9, 14.3.

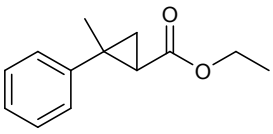
NMR data in agreement with those reported in the literature.[5]



Ethyl 2-(*o*-tolyl)cyclopropane-1-carboxylate (3f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.08 (m, 3H), 7.02 – 6.94 (m, 1H), 4.18 (d, *J* = 7.1 Hz, 2H), 2.50 (ddd, *J* = 9.1, 6.8, 4.5 Hz, 1H), 2.37 (s, 3H), 1.79-1.75 (m, 1H), 1.58-1.53 (m, 1H), 1.31-1.26 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $cdcl_3$) δ 173.9, 138.0, 137.9, 129.8, 126.7, 125.9, 60.6, 24.6, 22.3, 19.5, 15.3, 14.3.

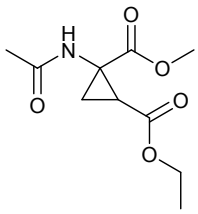
NMR data in agreement with those reported in the literature.[5]



Ethyl 2-methyl 2-phenylcyclopropane-1-carboxylate (3g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.12 (m, 6H, cis- and trans-isomer), 4.16 (q, *J* = 7.1 Hz, 2H, trans-isomer), 3.80 (m, cis-isomer), 1.93 (dd, *J* = 8.3, 6.0 Hz, 1H, trans-isomer), 1.87 (dd, *J* = 7.8, 5.4 Hz, cis-isomer), 1.74 (m, cis-isomer), 1.49 (s, 3H, trans-isomer), 1.44-1.36 (m, 3H, cis- and trans-isomer), 1.27 (t, *J* = 7.1 Hz, 3H, trans-isomer), 1.11 (dd, *J* = 7.7, 4.6 Hz, cis-isomer), 0.91 (t, *J* = 7.1 Hz, cis-isomer). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2 (trans-isomer), 145.9 (trans-isomer), 128.8 (cis-isomer), 128.4 (trans-isomer), 128.1 (cis-isomer), 127.3 (trans-isomer), 126.6 (cis-isomer), 126.4 (trans-isomer), 60.5 (trans-isomer), 30.6 (trans-isomer), 28.5 (cis-isomer), 27.9 (trans-isomer), 20.8 (trans-isomer), 19.9 (trans-isomer), 14.4 (trans-isomer).

NMR data in agreement with those reported in the literature.[5]

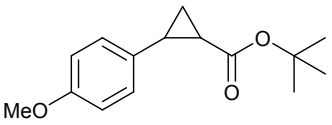


2-ethyl 1-methyl 1-acetamidocyclopropane-1,2-dicarboxylate (3j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (s, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.73 (s, 3H), 2.73 (dd, J = 9.2, 7.4 Hz, 1H), 2.00 (s, 3H), 1.88 (dd, J = 9.2, 5.1 Hz, 1H), 1.67 (dd, J = 7.3, 5.2 Hz, 1H), 1.29 – 1.25 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 170.4, 169.1, 61.4, 53.1, 39.6, 28.6, 22.9, 21.6, 14.1.

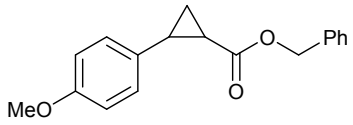
NMR data in agreement with those reported in the literature.[7]



tert-Butyl 2-(4-methoxyphenyl)cyclopropane-1-carboxylate (3k)

80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 2.40 (ddd, J = 9.0, 6.4, 4.1 Hz, 1H), 1.75 (ddd, J = 8.1, 5.3, 4.2 Hz, 1H), 1.51 – 1.45 (m, 10H), 1.21 – 1.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 158.2, 132.5, 130.1, 127.2, 113.9, 55.3, 28.2, 28.0, 25.2, 24.9, 16.7.

NMR data in agreement with those reported in the literature.[8]



Benzyl 2-(4-methoxyphenyl)cyclopropane-1-carboxylate (3l)

97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 5H), 7.03 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 5.16 (s, 2H), 3.78 (s, 3H), 2.53 (ddd, J = 9.1, 6.6, 4.2 Hz, 1H), 1.89 (ddd, J = 8.1, 5.2, 4.1 Hz, 1H), 1.60 (dt, J = 9.4, 4.6 Hz, 1H), 1.28 (ddd, J = 8.0, 6.5, 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 158.3, 136.0, 131.9, 130.3, 128.6, 128.2, 128.2, 127.4, 113.9, 66.5, 55.3, 25.9, 23.8, 16.9.

NMR data in agreement with those reported in the literature.[9]

Published ^{1}H-NMR data of compounds **3h** and **3i** was used as reference for catalysis.[10,11]

References

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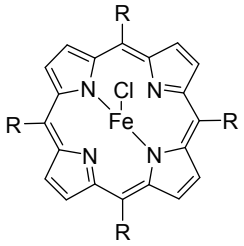
Table SI1: Micelle accelerated catalytic cyclopropanation with neutral and anionic iron porphyrin catalysts

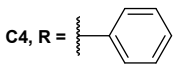
Reaction conditions unless stated otherwise: 75 µmol **1a** (final concentration 7.5 mM), 2 eq **2a**, 10 mL H_2O, room temperature. All reactions were performed *in duplo*. Room temperature (RT) is defined as 20-25°C.

Entry	Catalyst	Surfactant	Time (h)	**3a** (%)
1	-	10 mM SDS	40	-
2	1 mol% **C4**	-	1.5	29±3
3	1 mol% **C4**	10 mM SDS	1.5	33±2
4	10 mol% **C4**	10 mM SDS	1.5	32±1
5	1 mol% **C4**	20 mM SDS	1.5	<5
6	1 mol% **C4**	20 mM DTAB	1.5	54±4
7[a]	1 mol% **C4**	13 mM TPGS-1000	1	9±2
8	1 mol% **C4**	20 mM TPGS-1000	1	17±14
9	1 mol% **C5**	-	1	<5
10	1 mol% **C5**	10 mM SDS	2	15±1
11	1 mol% **C5**	20 mM DTAB	1	18±2
12[b]	1 mol% **C5**	-	1	<5[c]
13[b]	1 mol% **C5**	20 mM DTAB	1	<5[c]
14	1 mol% **C6**	-	2	5±2
15	1 mol% **C6**	20 mM SDS	2	5±1

a) 13 mM is approximately 2% wt/v. b) 75 µmol **1c** was used c) Product **3c** was formed



C4, R =



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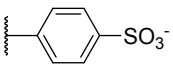
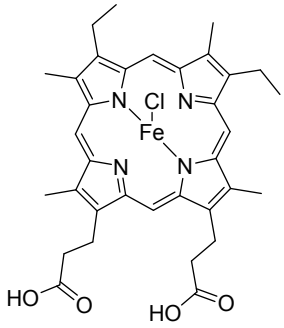
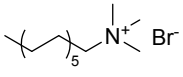
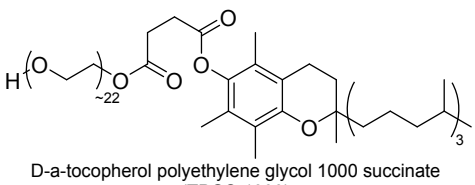




C6



dodecyltrimethylammonium bromide (DTAB)



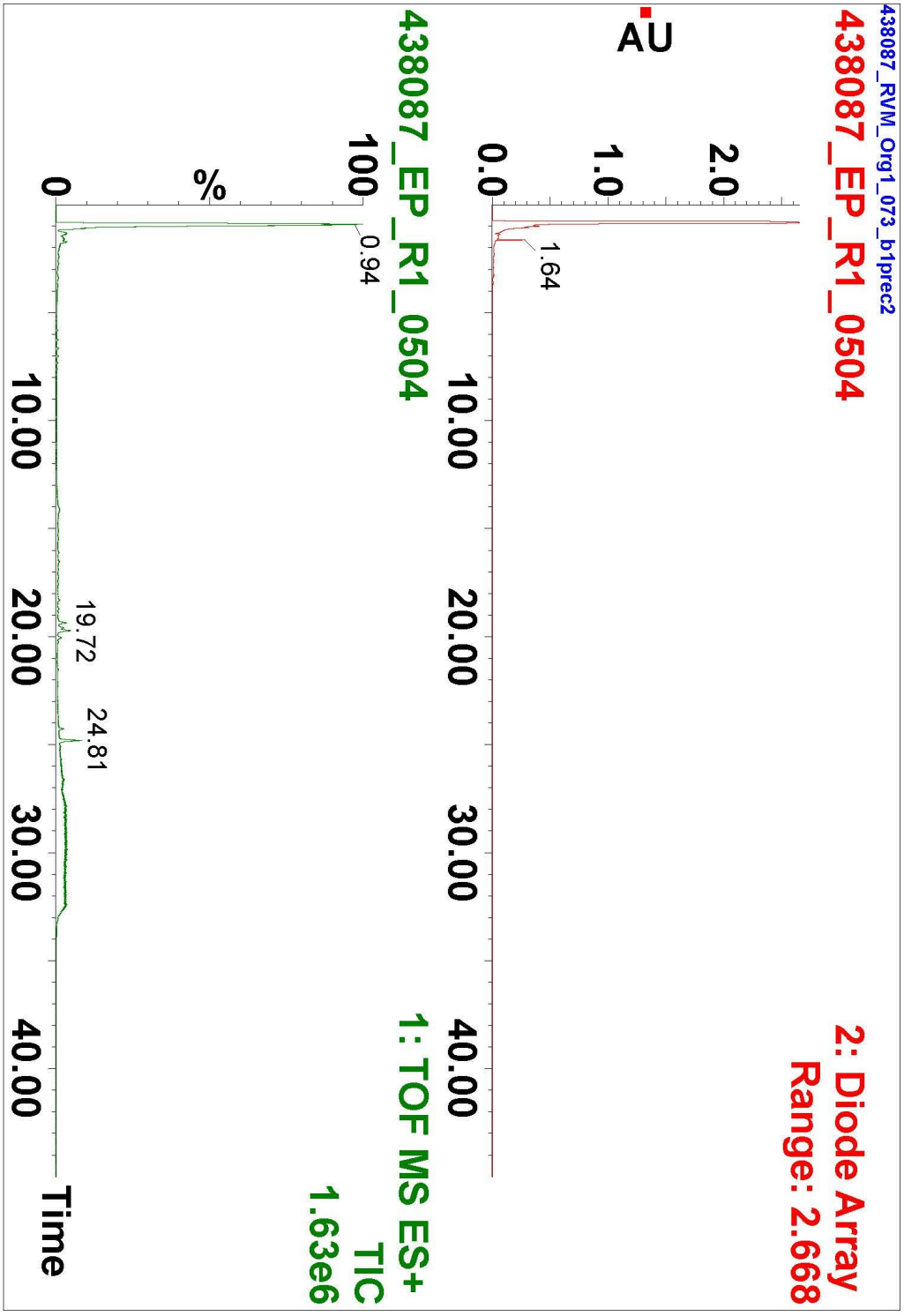
D-a-tocopherol polyethylene glycol 1000 succinate (TPGS-1000)

Table SI2: Additional data for the micelle accelerated catalytic cyclopropanation with C3 as catalyst
Reaction conditions: 75 µmol **1a** (final concentration 7.5 mM), 2 eq **2a**, 10 mL H_2O, **C3** as catalyst. All reactions were performed *in duplo*. Room temperature (RT) is defined as 20-25°C.

Entry	% **C3**	Surfactant	Temperature (°C)	Time (h)	**3a** (%)
1	1	-	RT	1	13±2
2	1	1 mM SDeS	RT	1	41±0
3	1	20 mM SDeS	RT	1	32±5
4	1	20 mM STS	RT	1	17±1
5	1	5 mM SDS	RT	1	23±3
6	1	10 mM SDS	RT	1	60±7
7	1	15 mM SDS	RT	1	92±3
8	1	20 mM SDS	RT	1	98±2
9	1	25 mM SDS	RT	1	81±7
10	2	10 mM SDS	RT	1	31±5
11	20	10 mM SDS	RT	1	-
12	0.5	10 mM SDS	RT	1	62±6
13	0.5	20 mM SDS	RT	1	59±11
14	0.1	10 mM SDS	RT	1.5	8±1

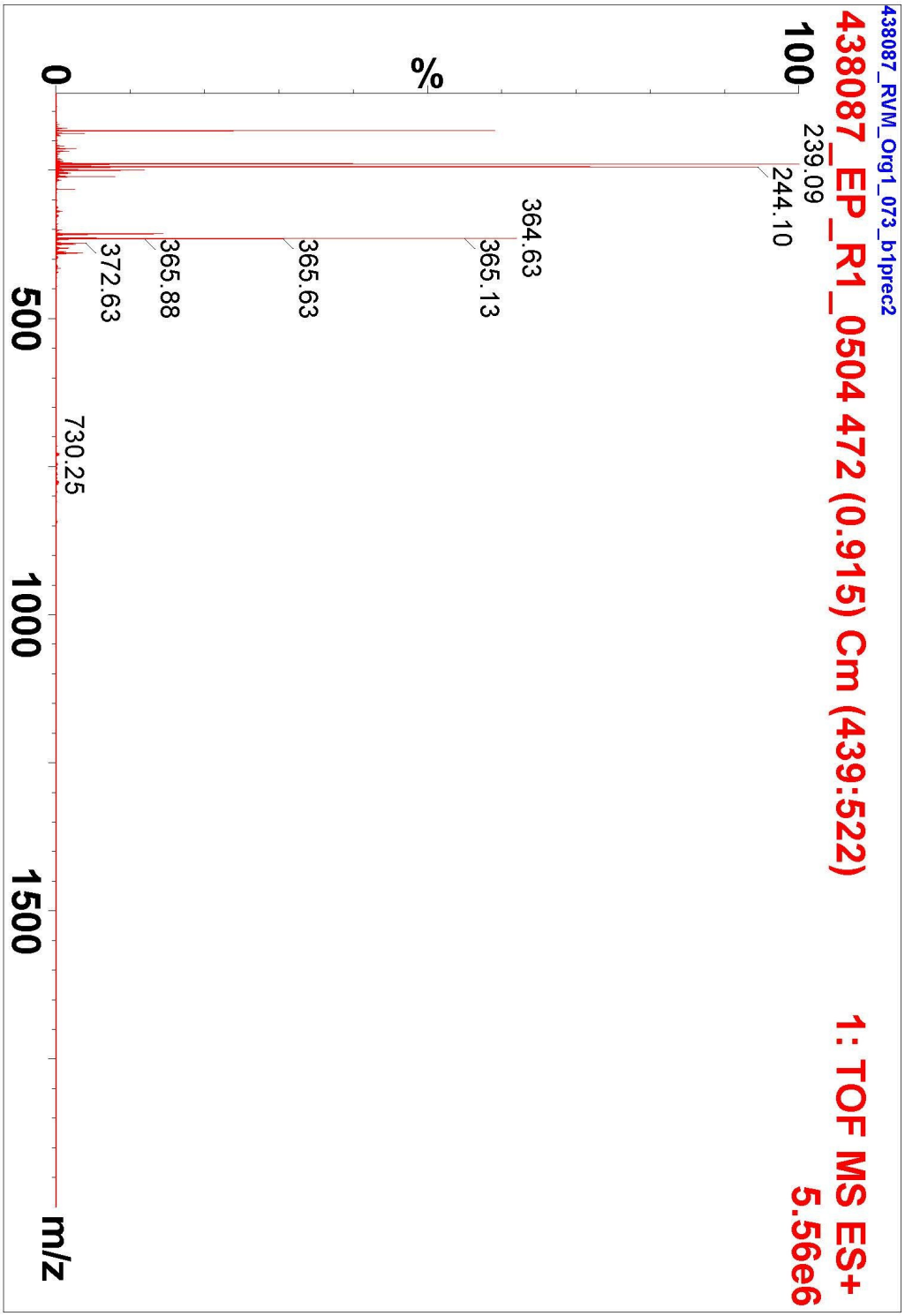
SI3: Characterization of C1

UPLC-TOF



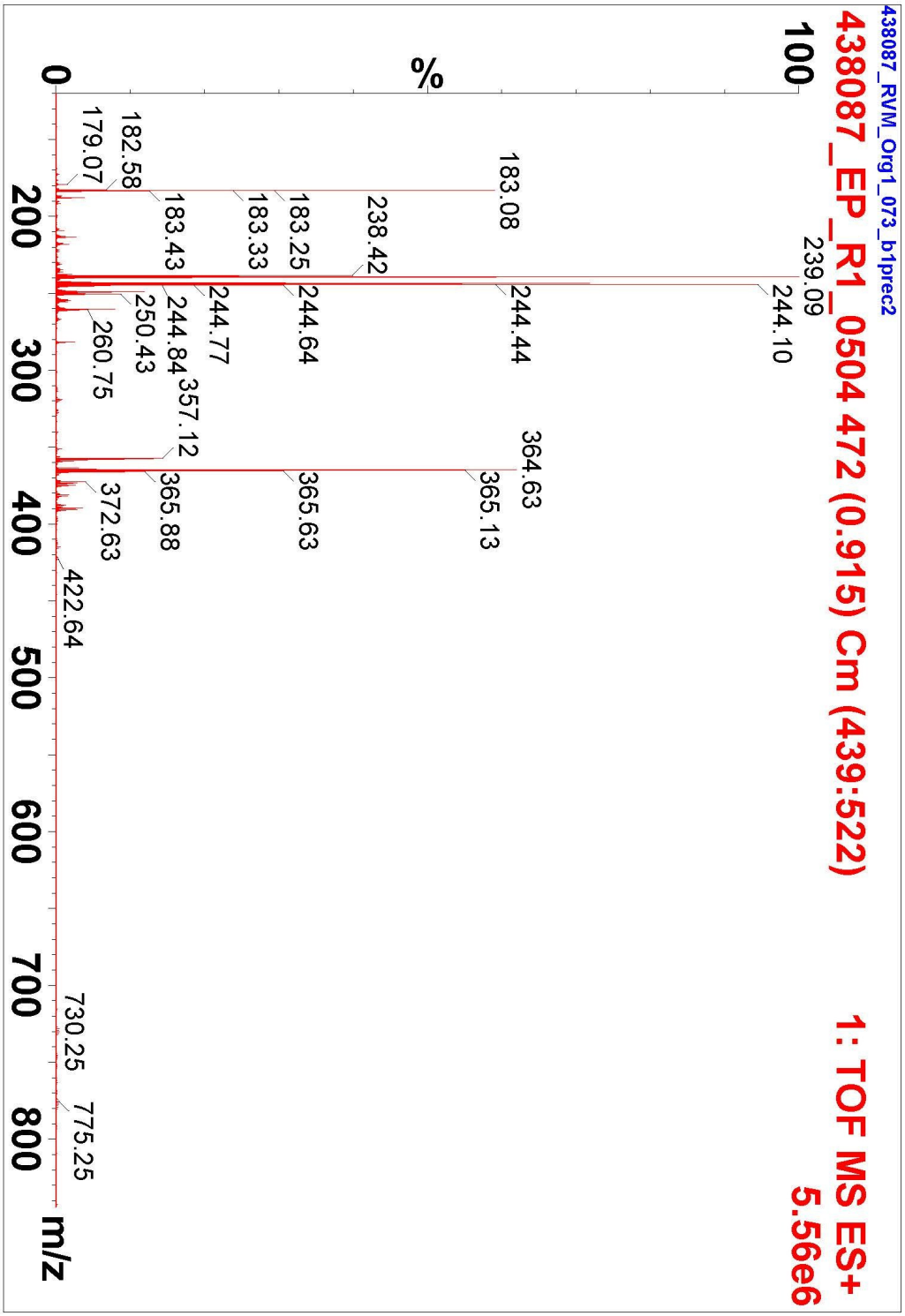
SI3: Characterization of C1

UPLC-TOF



SI3: Characterization of C1

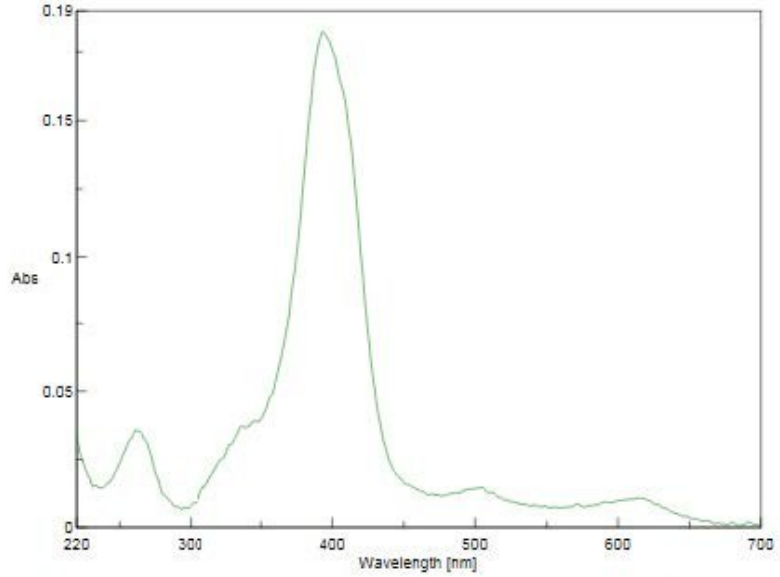
UPLC-TOF



SI3: Characterization of C1

UV/Vis spectroscopy

0.01M aqueous HCl, 25°C, 1.40 µM



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SI4: Characterization of C2

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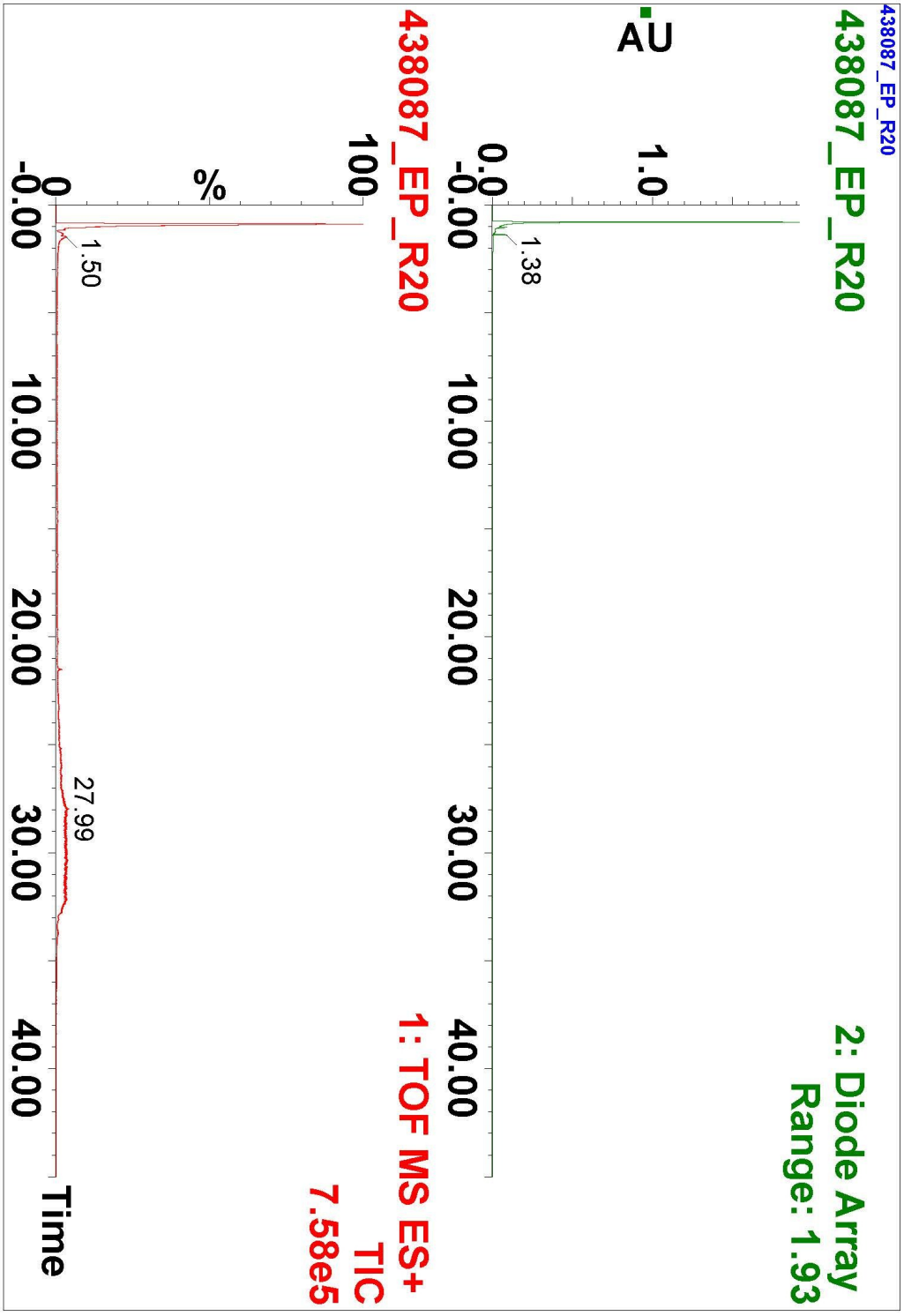
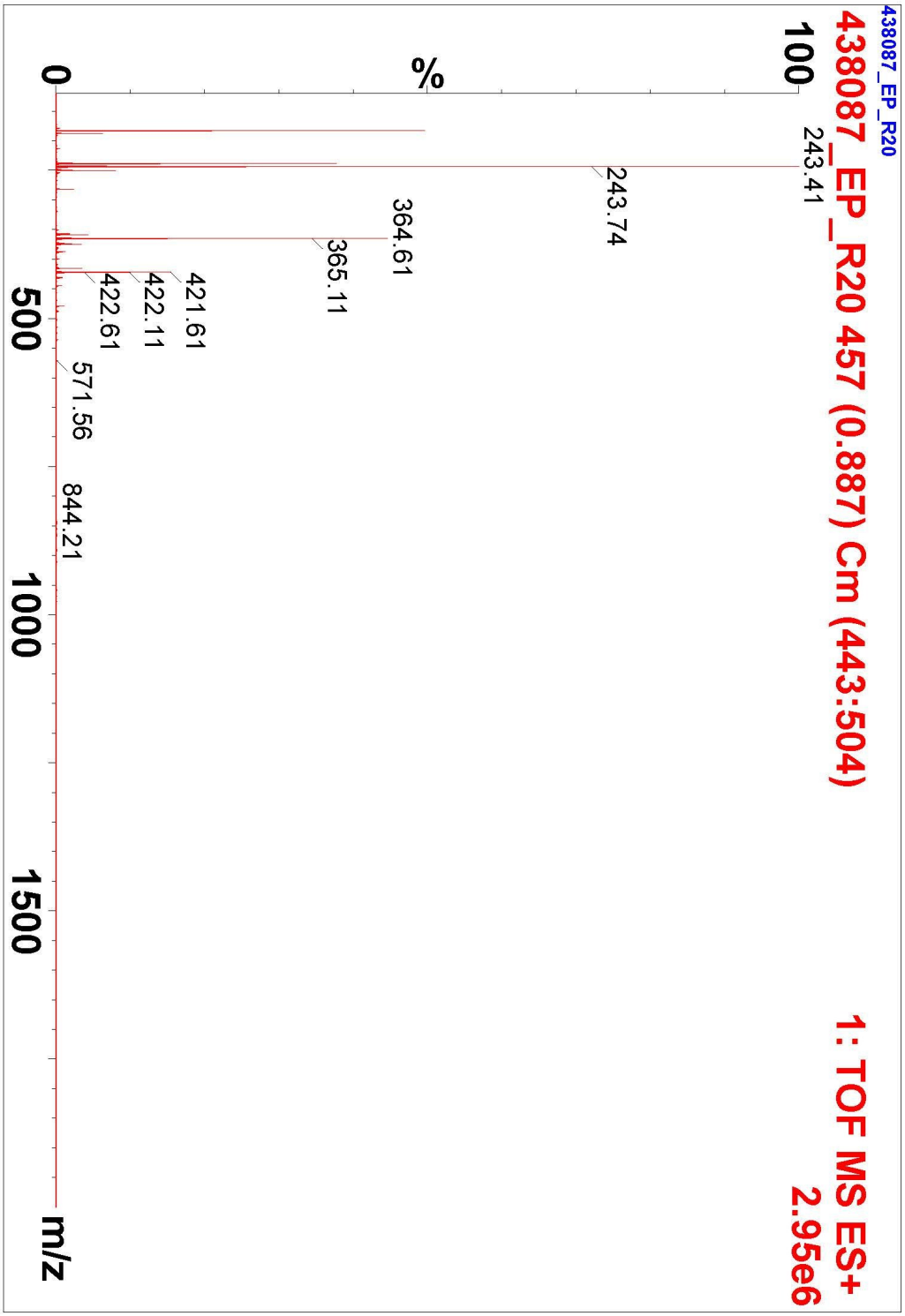


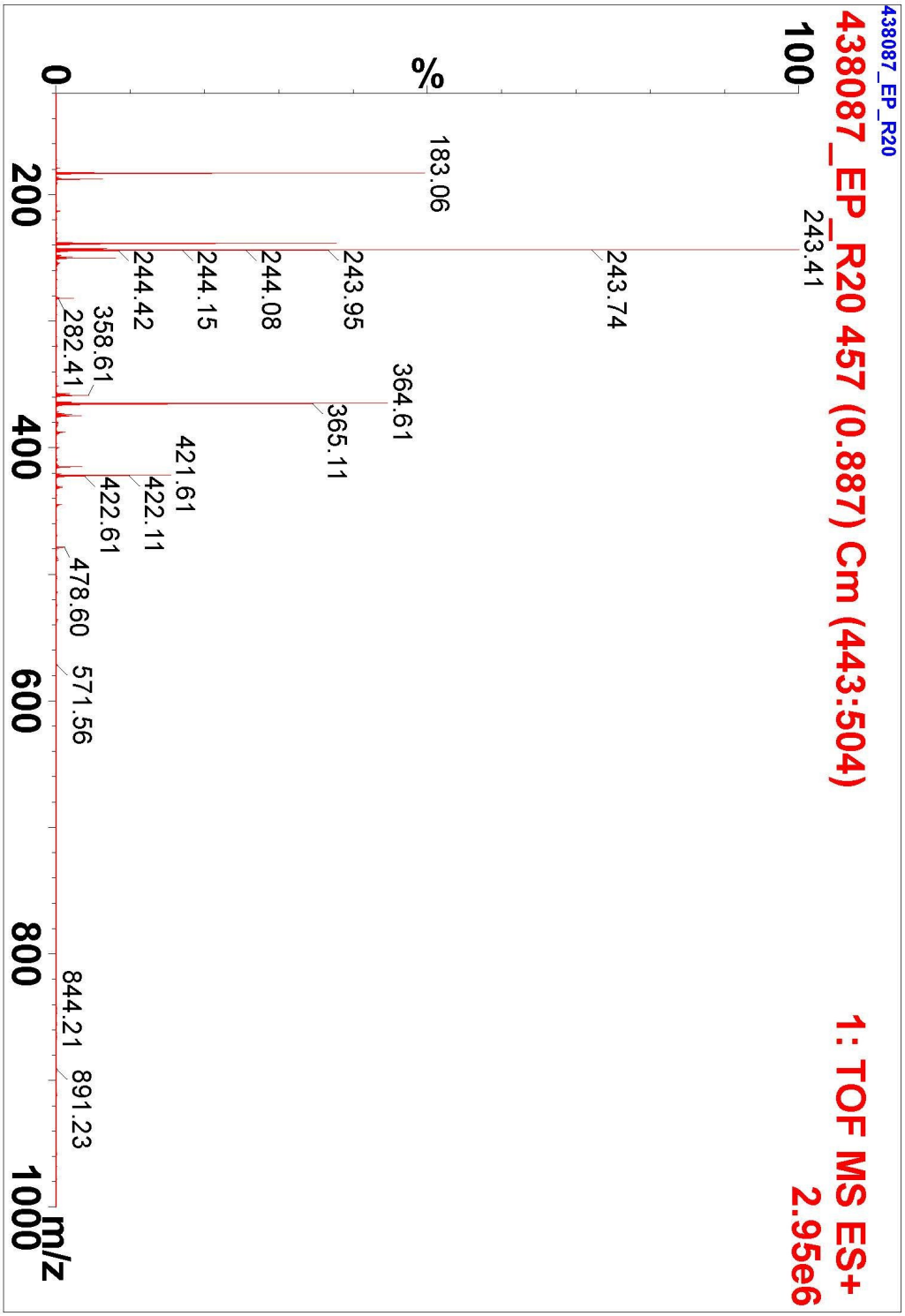
SI4: Characterization of C2

UPLC-TOF



SI4: Characterization of C2

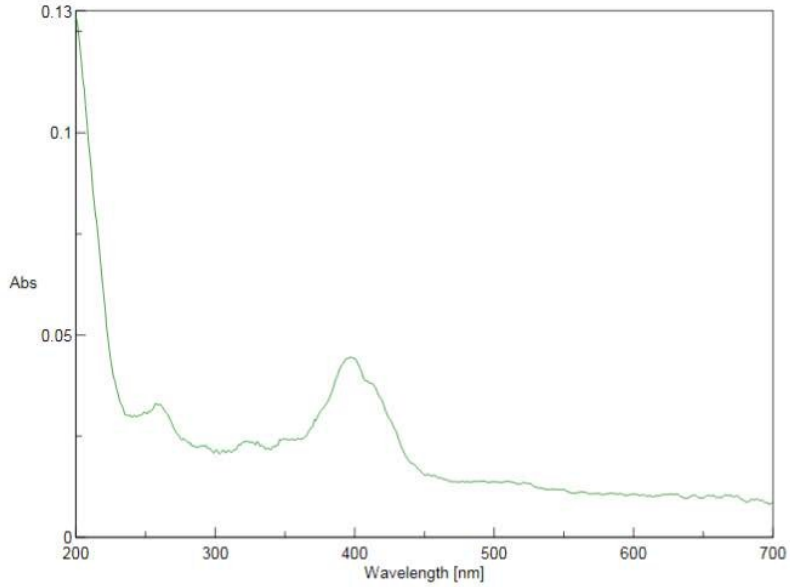
UPLC-TOF



SI4: Characterization of C2

UV/Vis spectroscopy

0.01M aqueous HCl, 25°C, 0.35 µM



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SI5: Characterization of 1j

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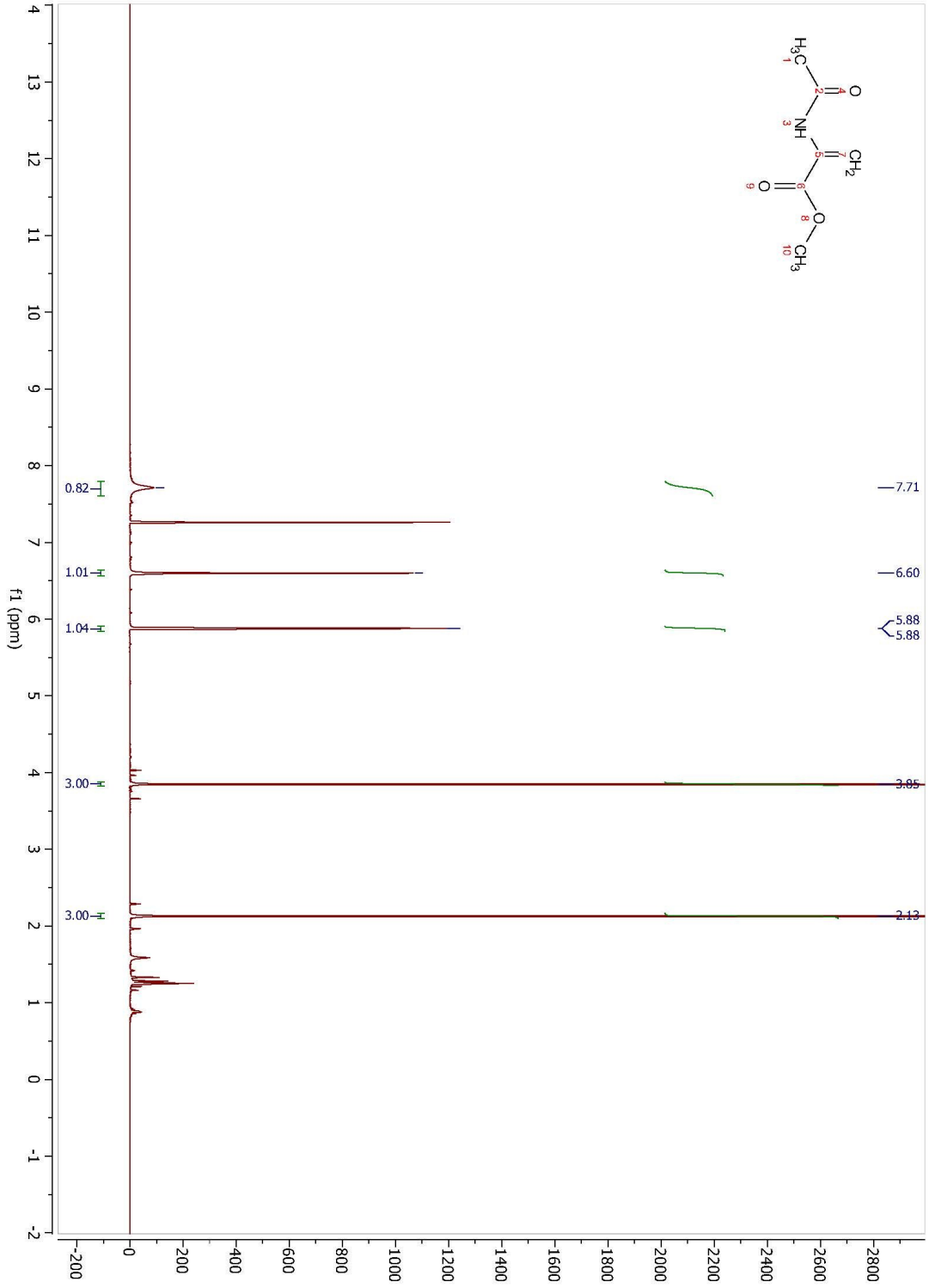

SI5: Characterization of 1j

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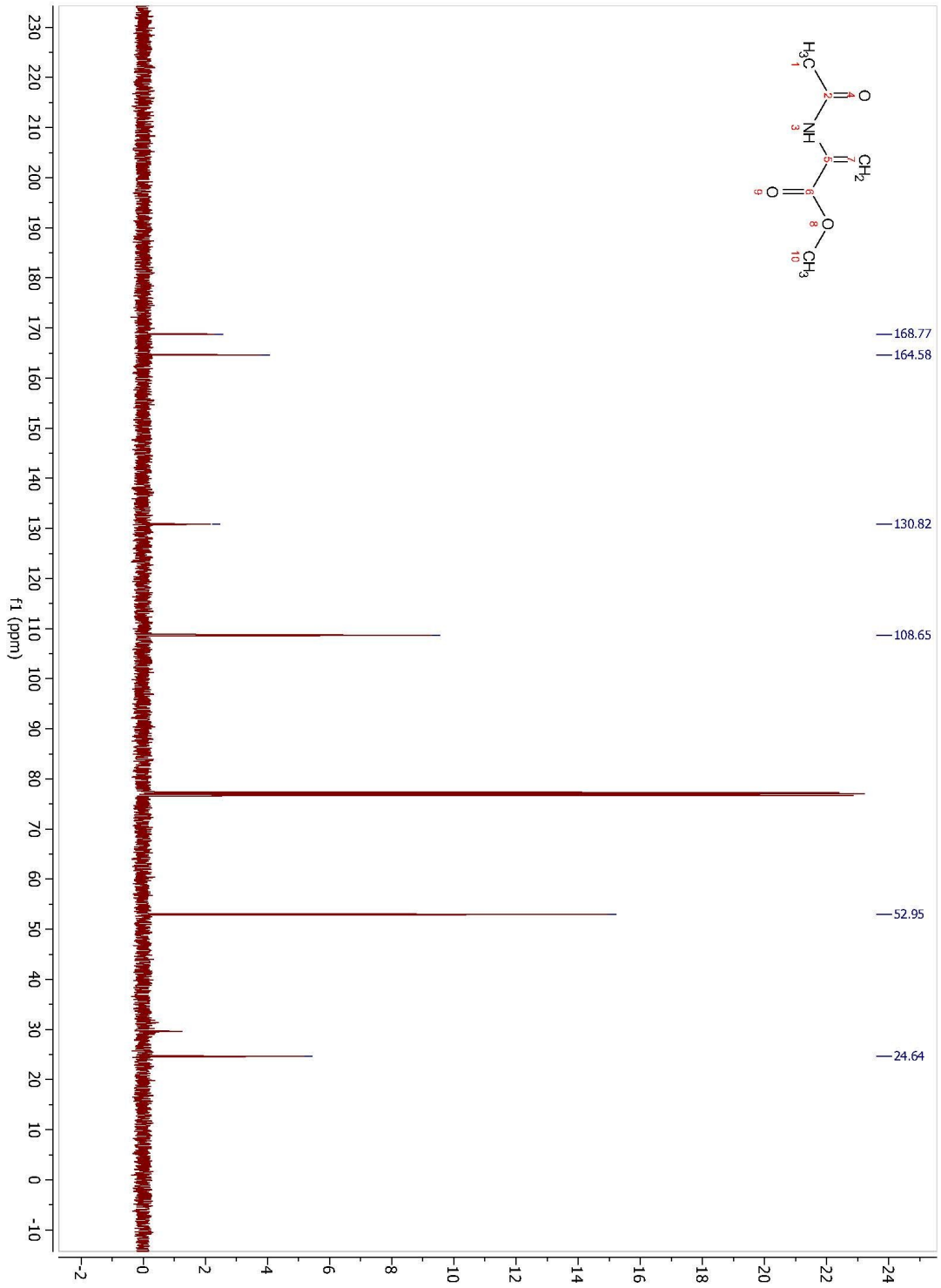

SI5: Characterization of 1j

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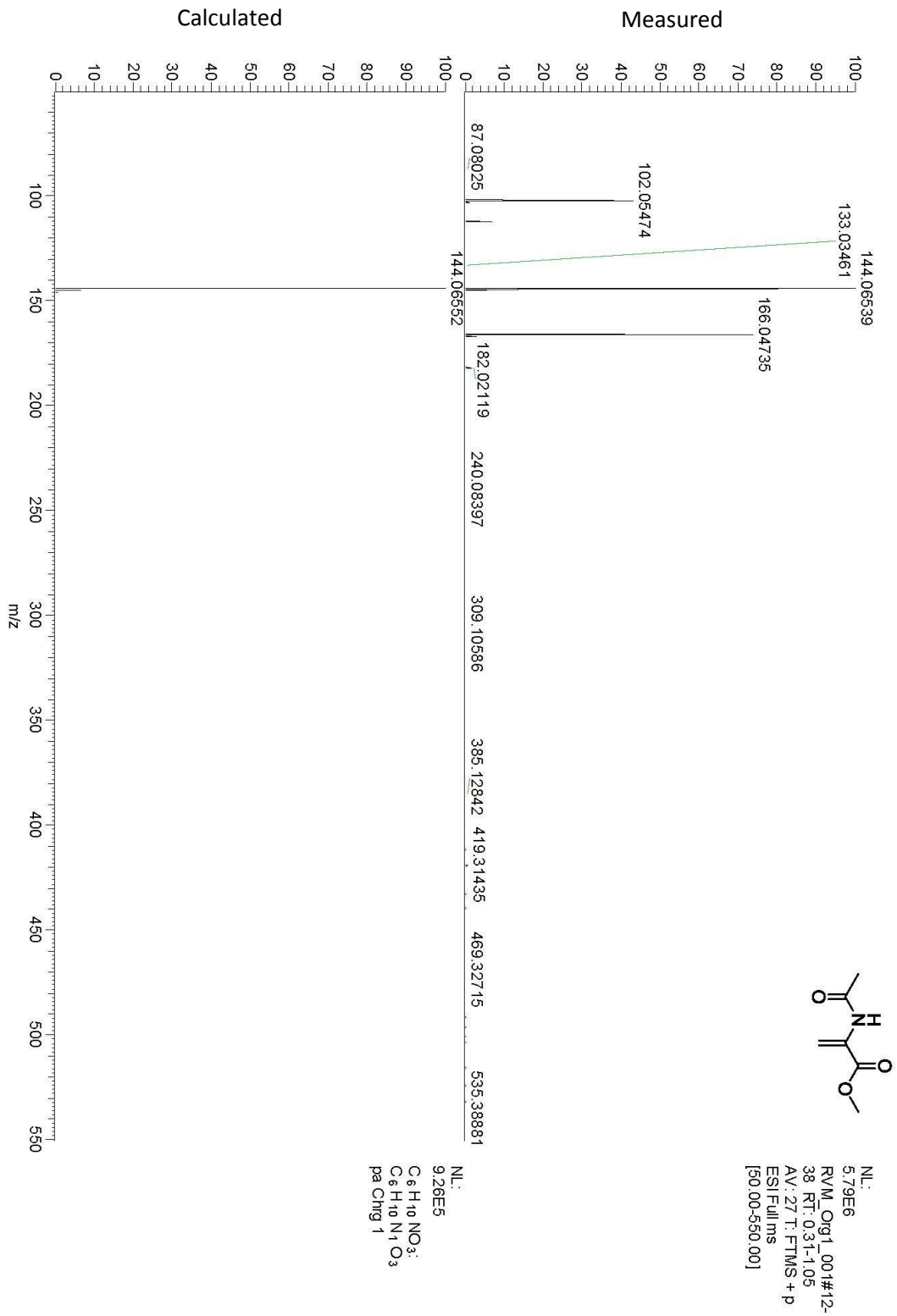
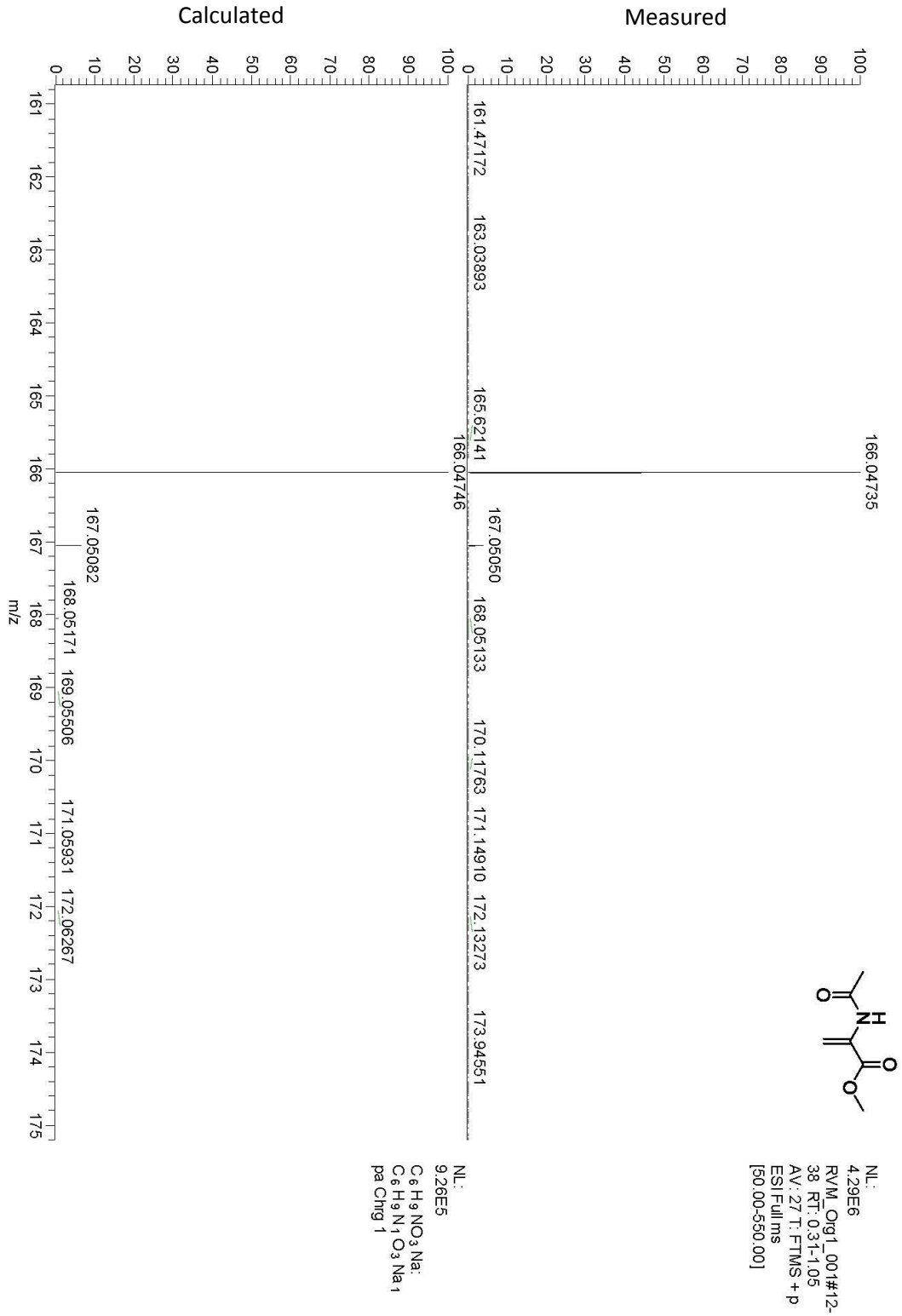


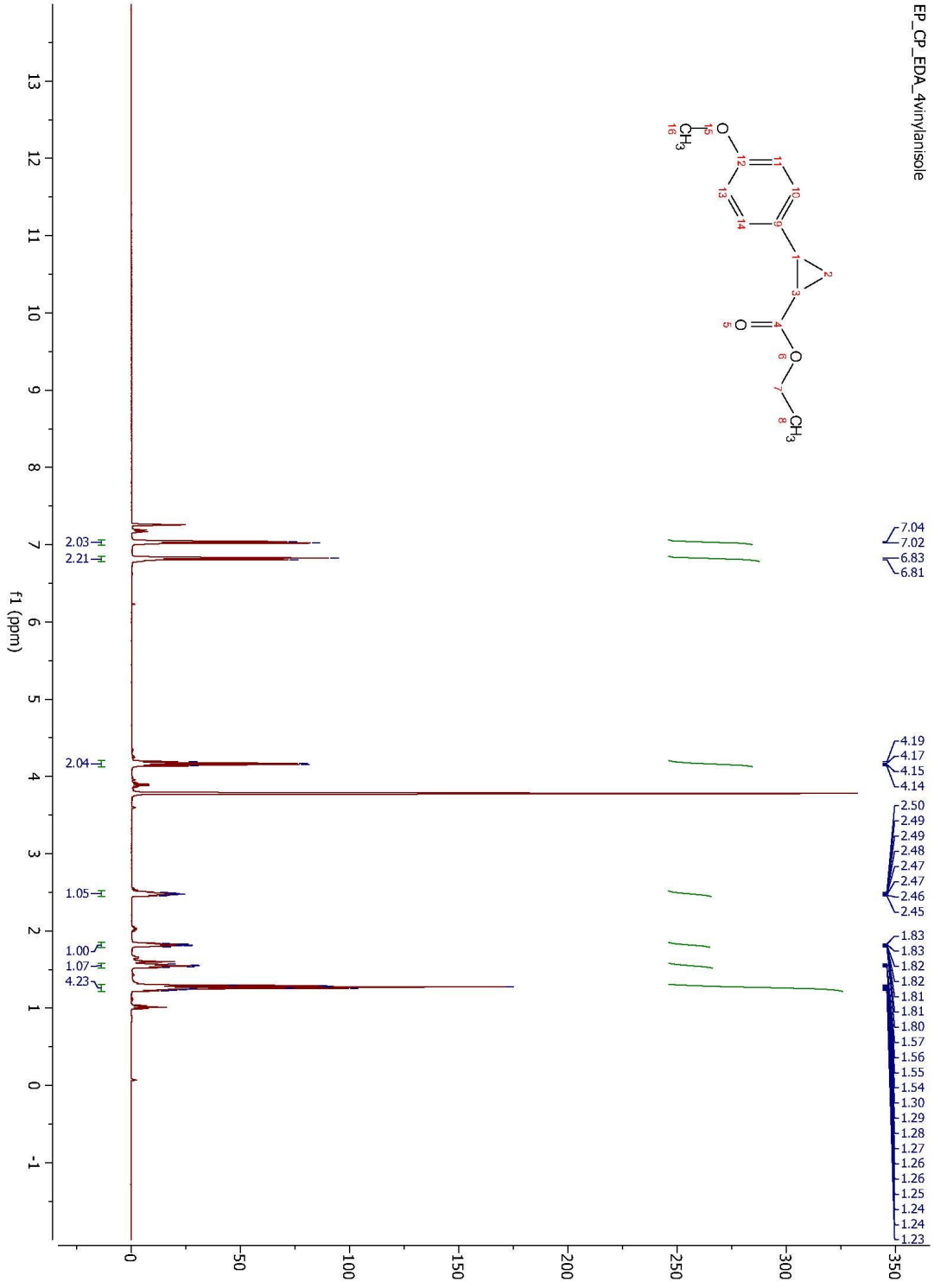
Characterization of 1j

HRMS



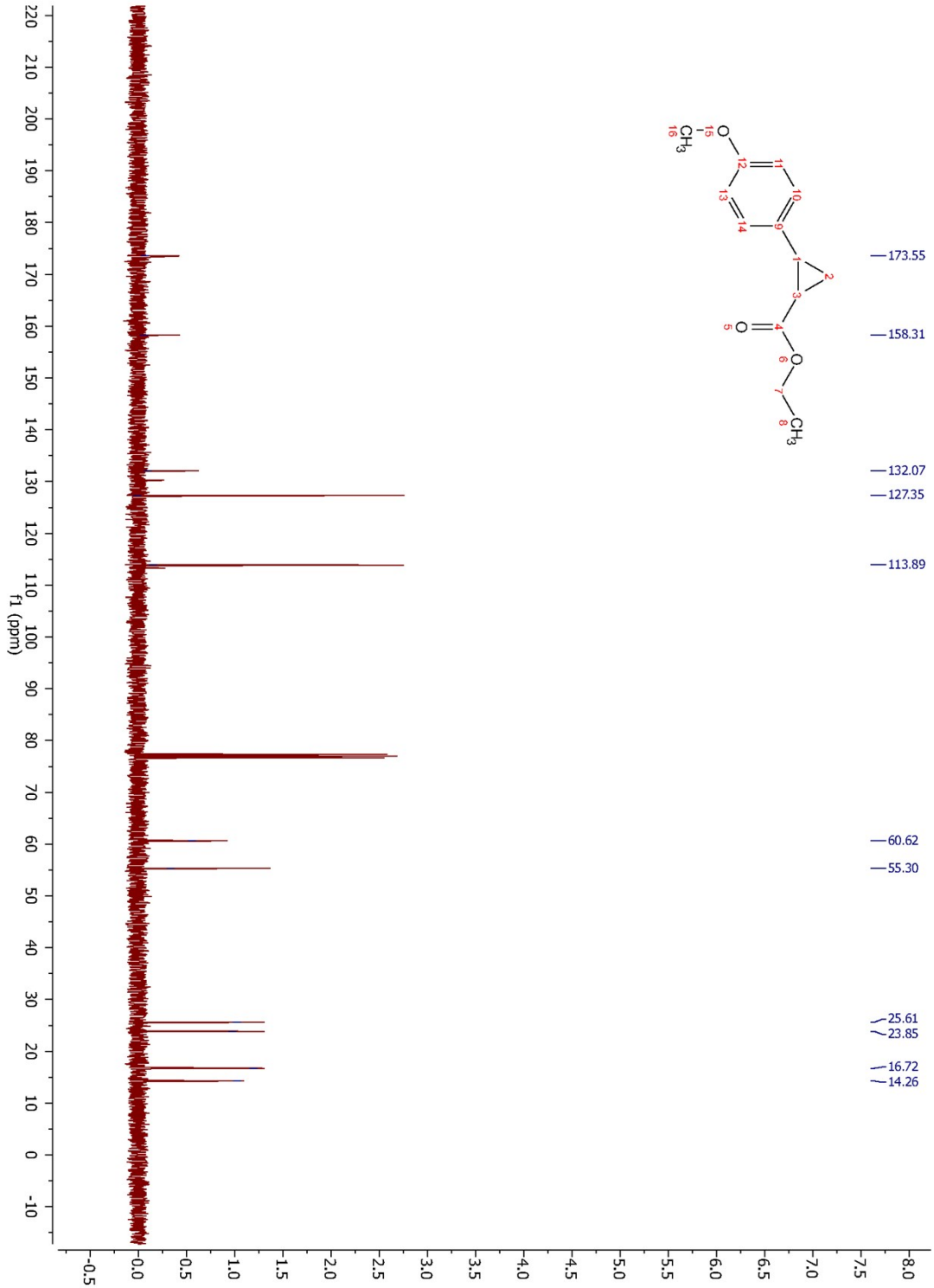
SI6: Characterization of 3a

^{1}H-NMR



SI6: Characterization of 3a

^{13}C-NMR



SI6: Characterization of 3a

From described synthesis

HPLC

SHIMADZU LabSolutions **Analysis Report**

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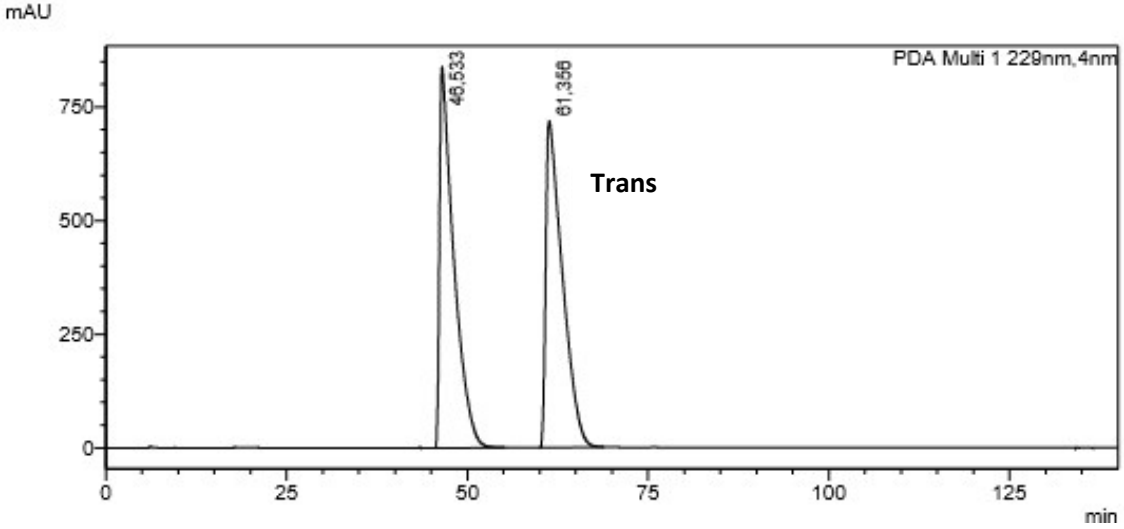

SI6: Characterization of 3a

From micellar catalysis

HPLC

SHIMADZU LabSolutions **Analysis Report**

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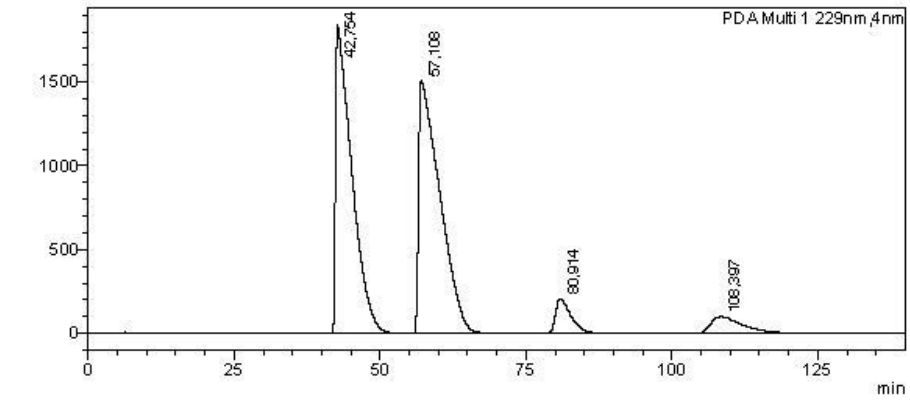

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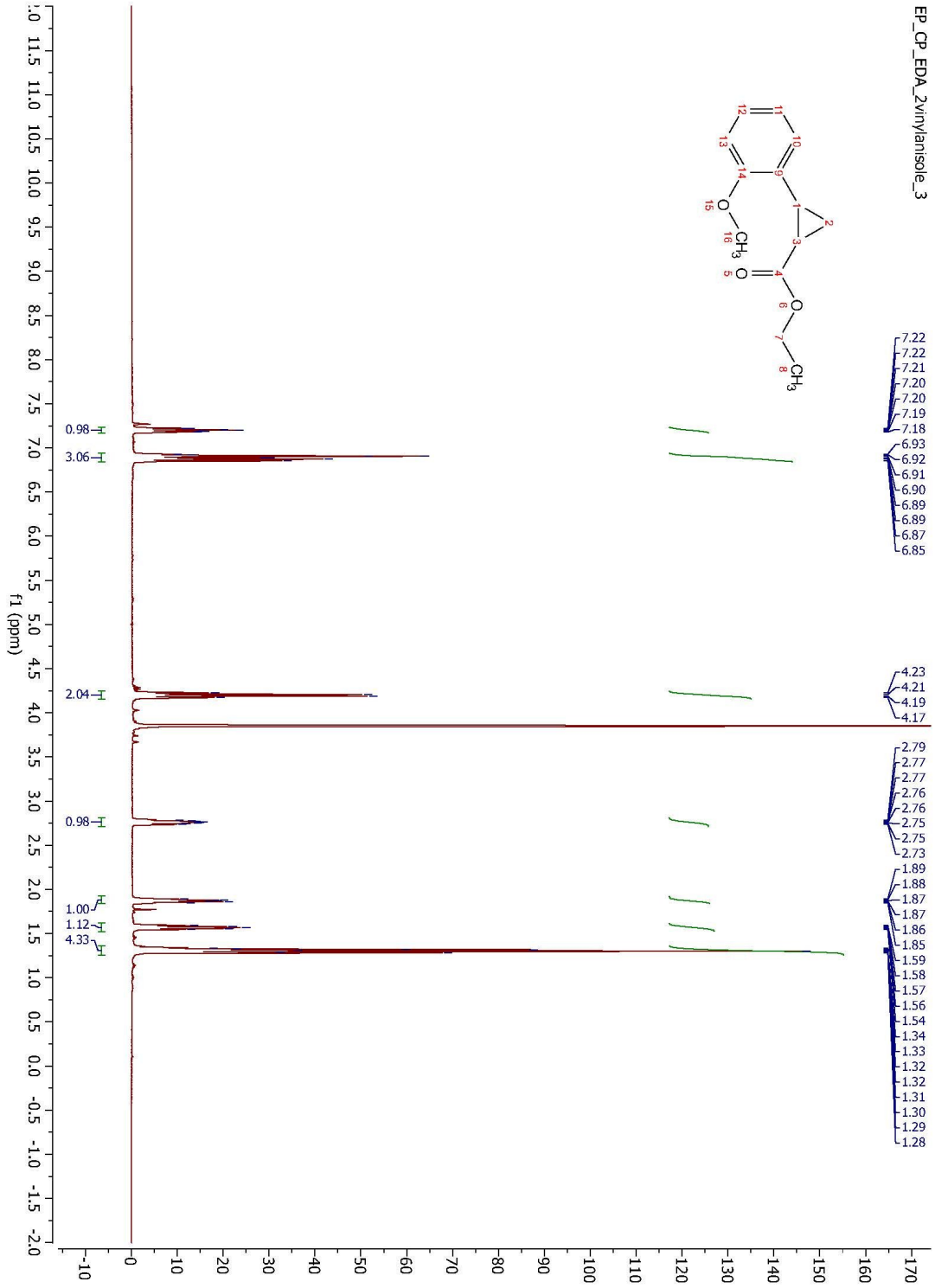
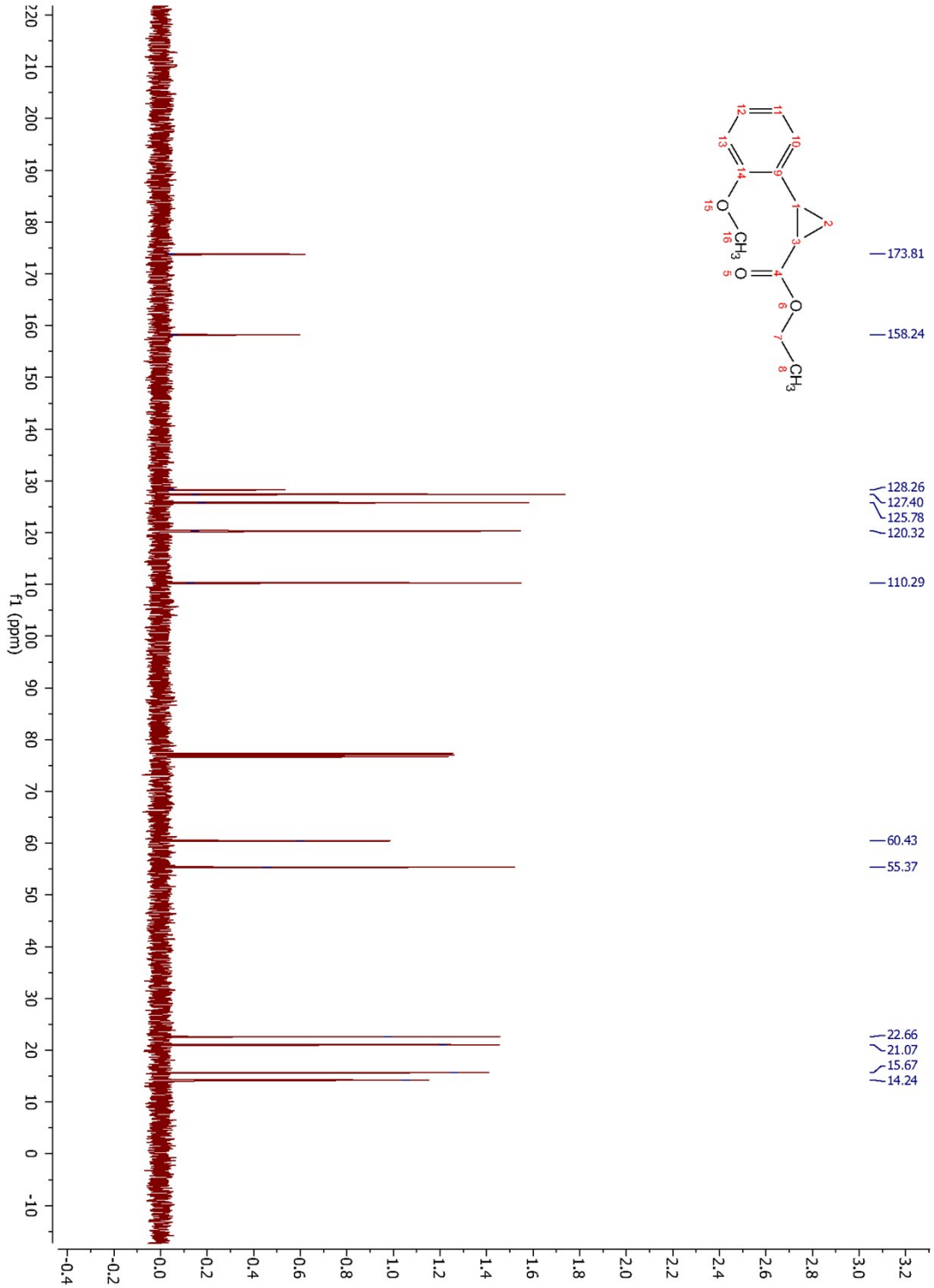
SI7: Characterization of compounds from micellar catalysis

3b, ^{1}H-NMR



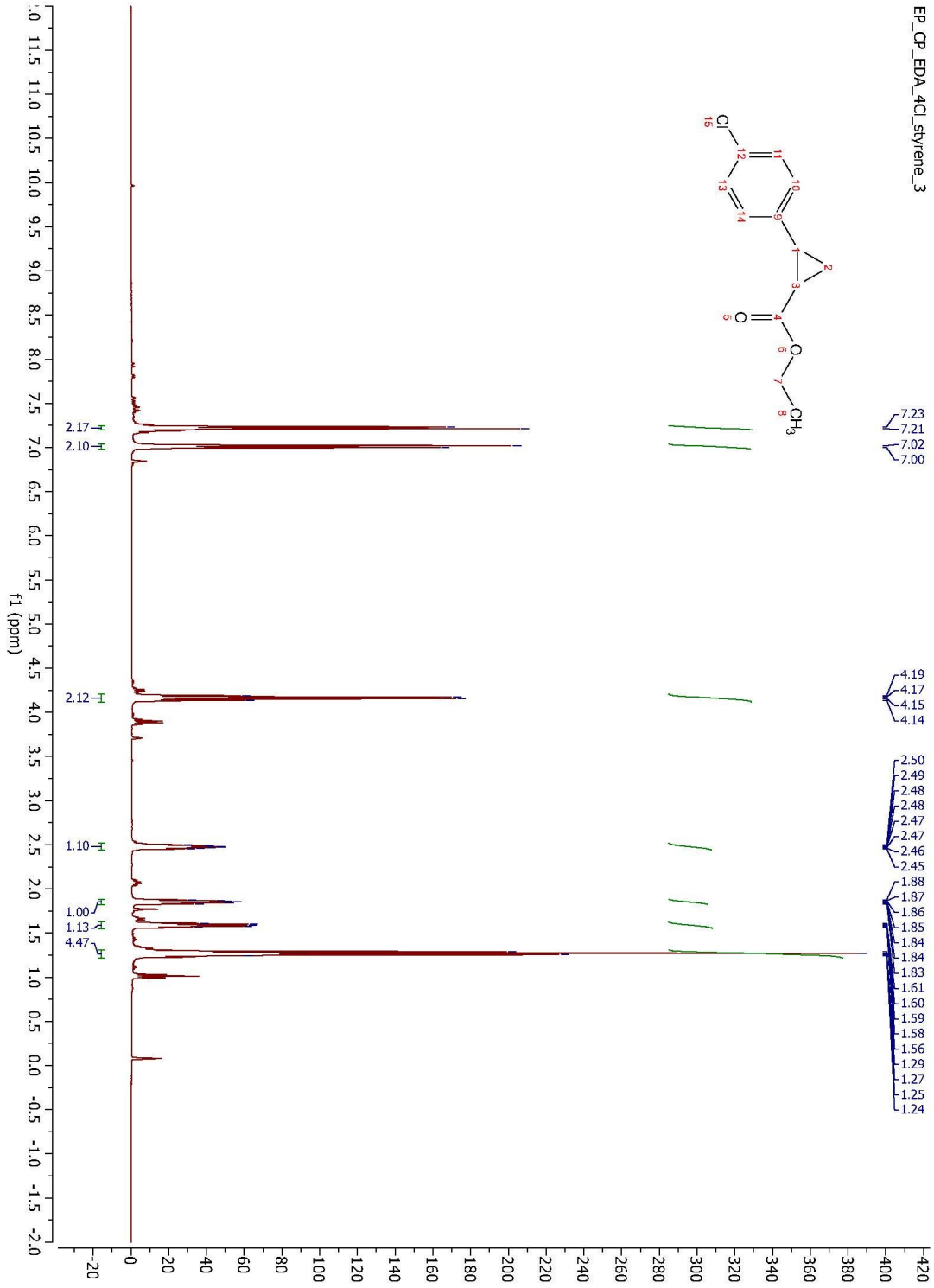
SI7: Characterization of compounds from micellar catalysis

3b, ^{13}C-NMR



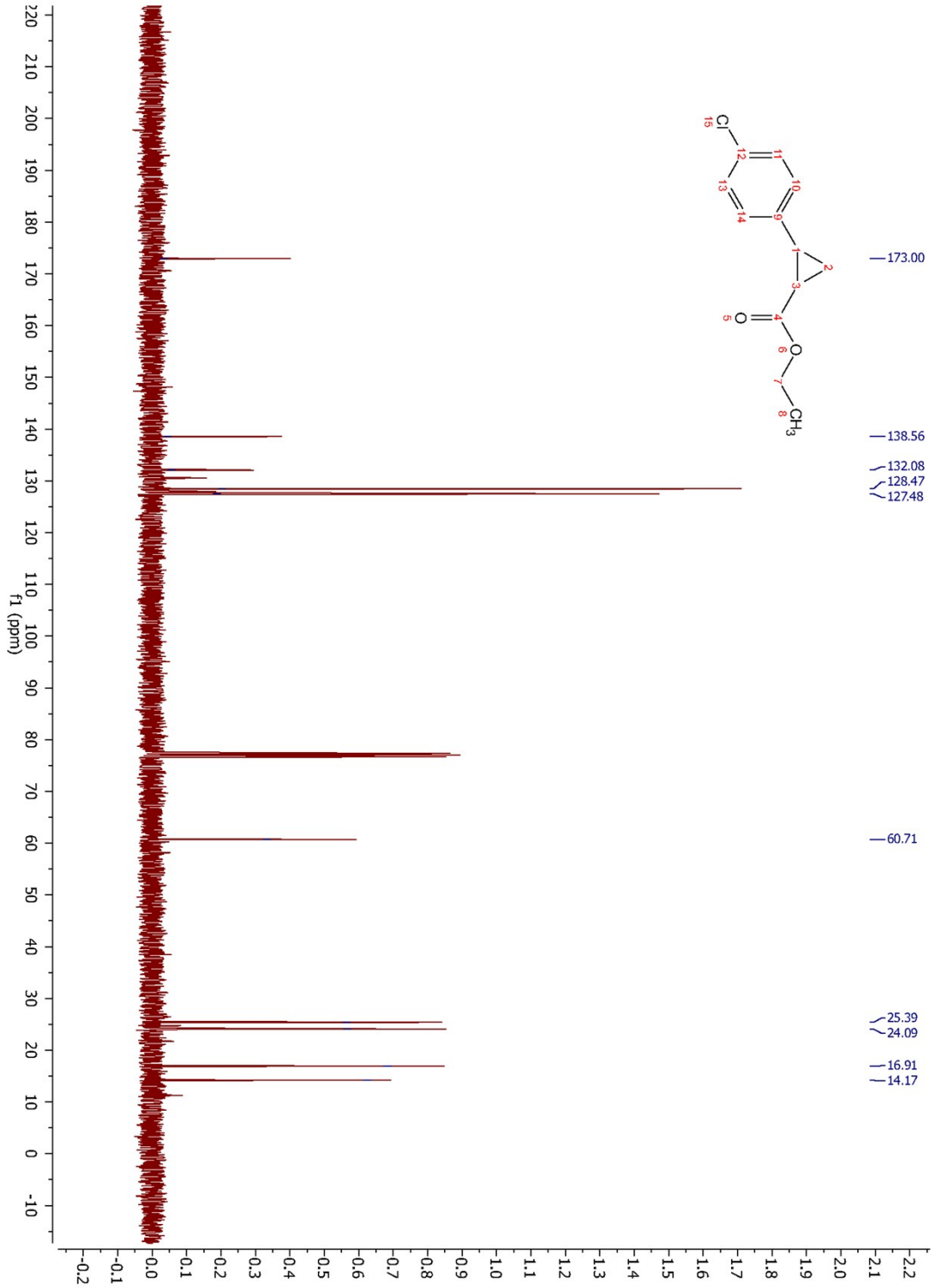
SI7: Characterization of compounds from micellar catalysis

3c, ^{1}H-NMR



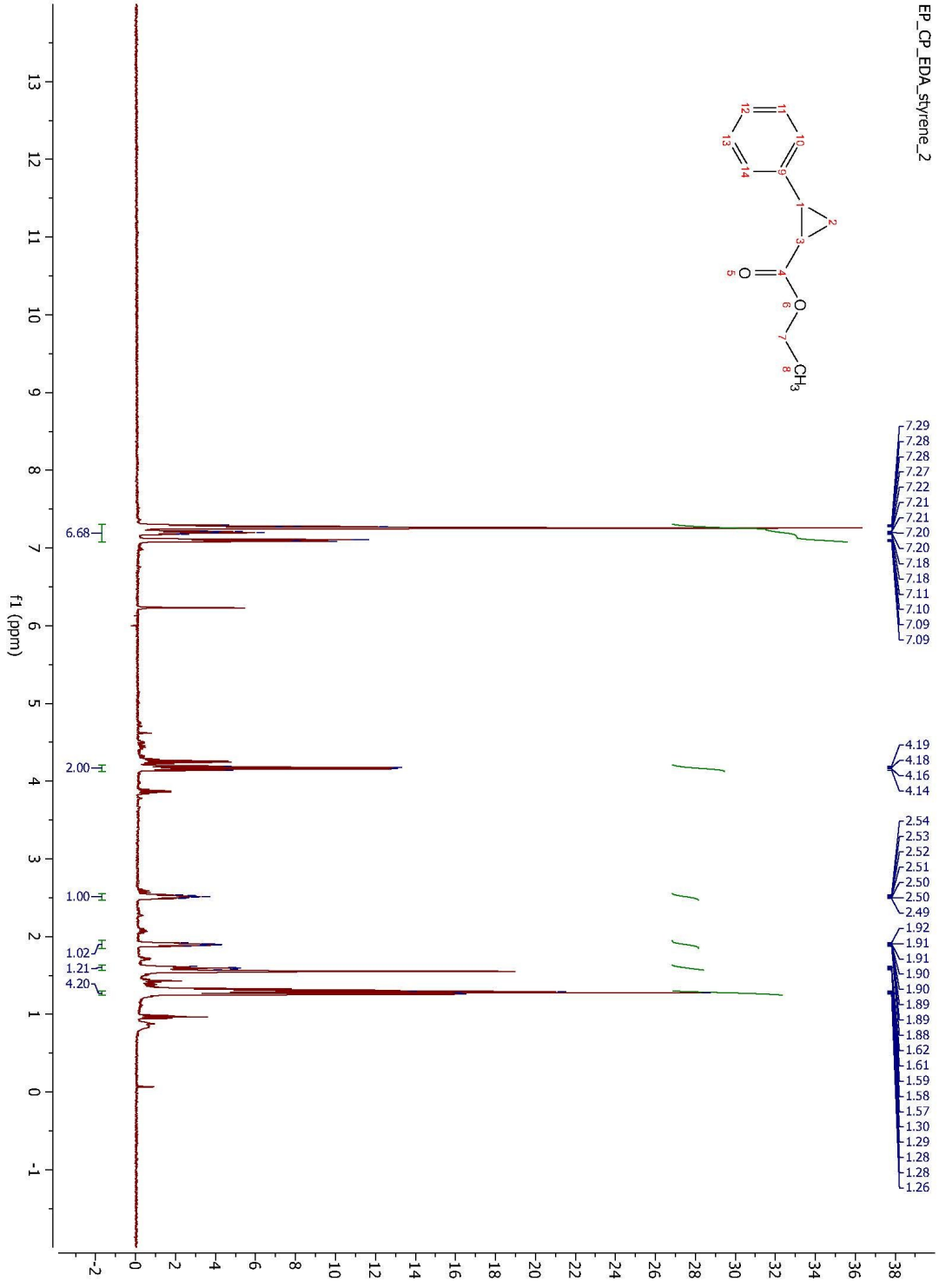
SI7: Characterization of compounds from micellar catalysis

3c, ^{13}C-NMR



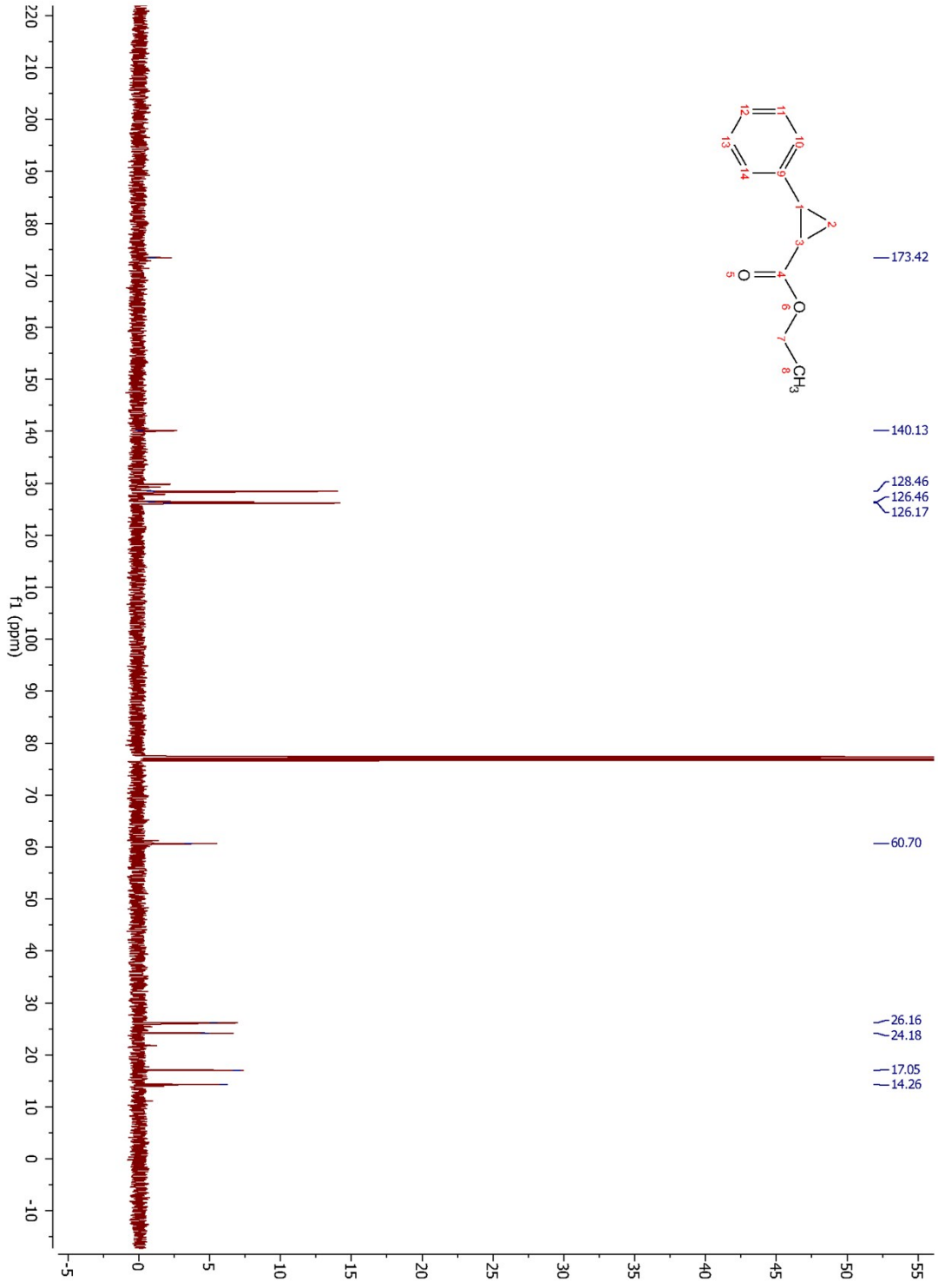
SI7: Characterization of compounds from micellar catalysis

3d, ^{1}H-NMR



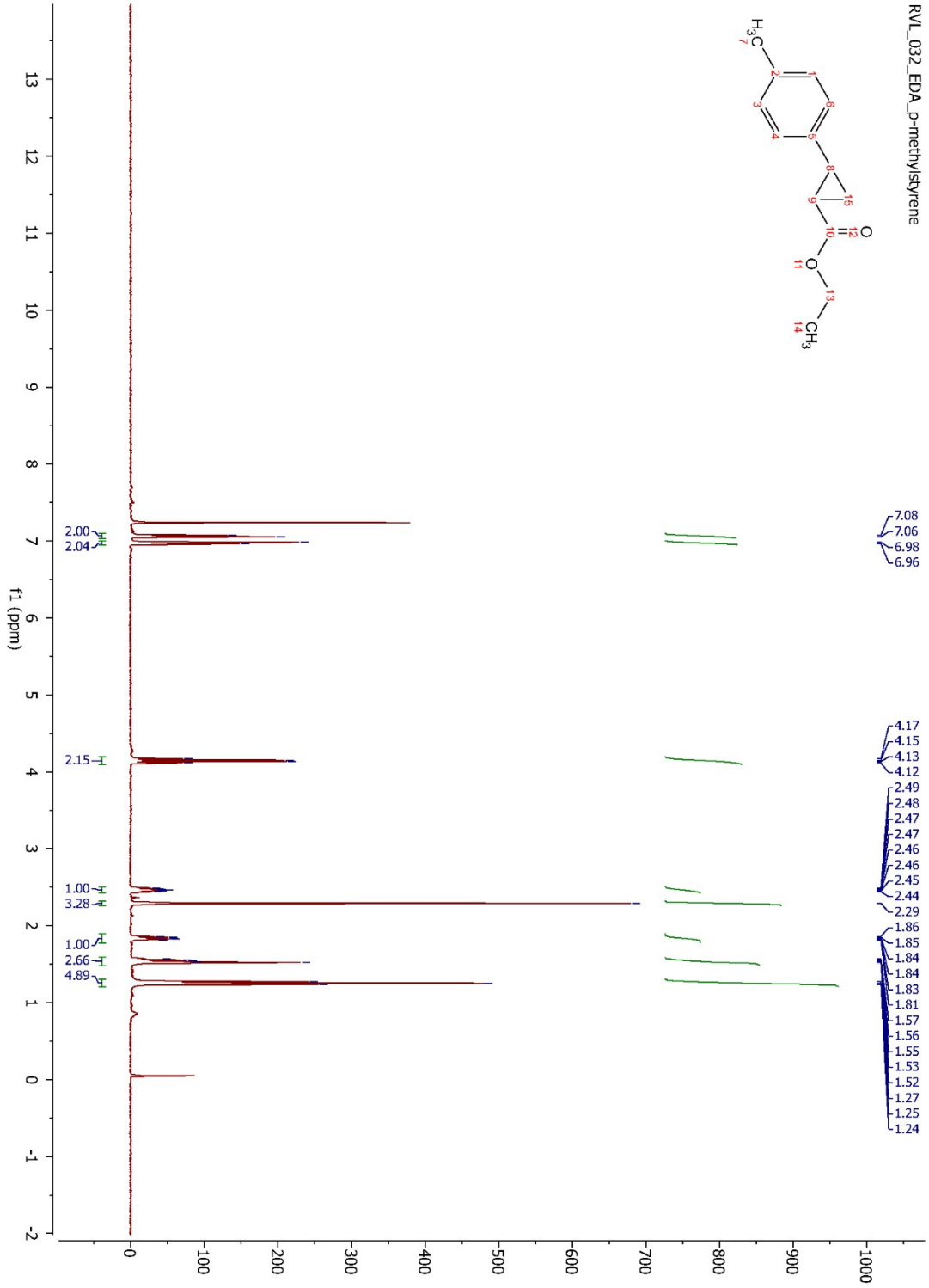
SI7: Characterization of compounds from micellar catalysis

3d, ^{13}C-NMR



SI7: Characterization of compounds from micellar catalysis

3e, ^{1}H-NMR



SI7: Characterization of compounds from micellar catalysis

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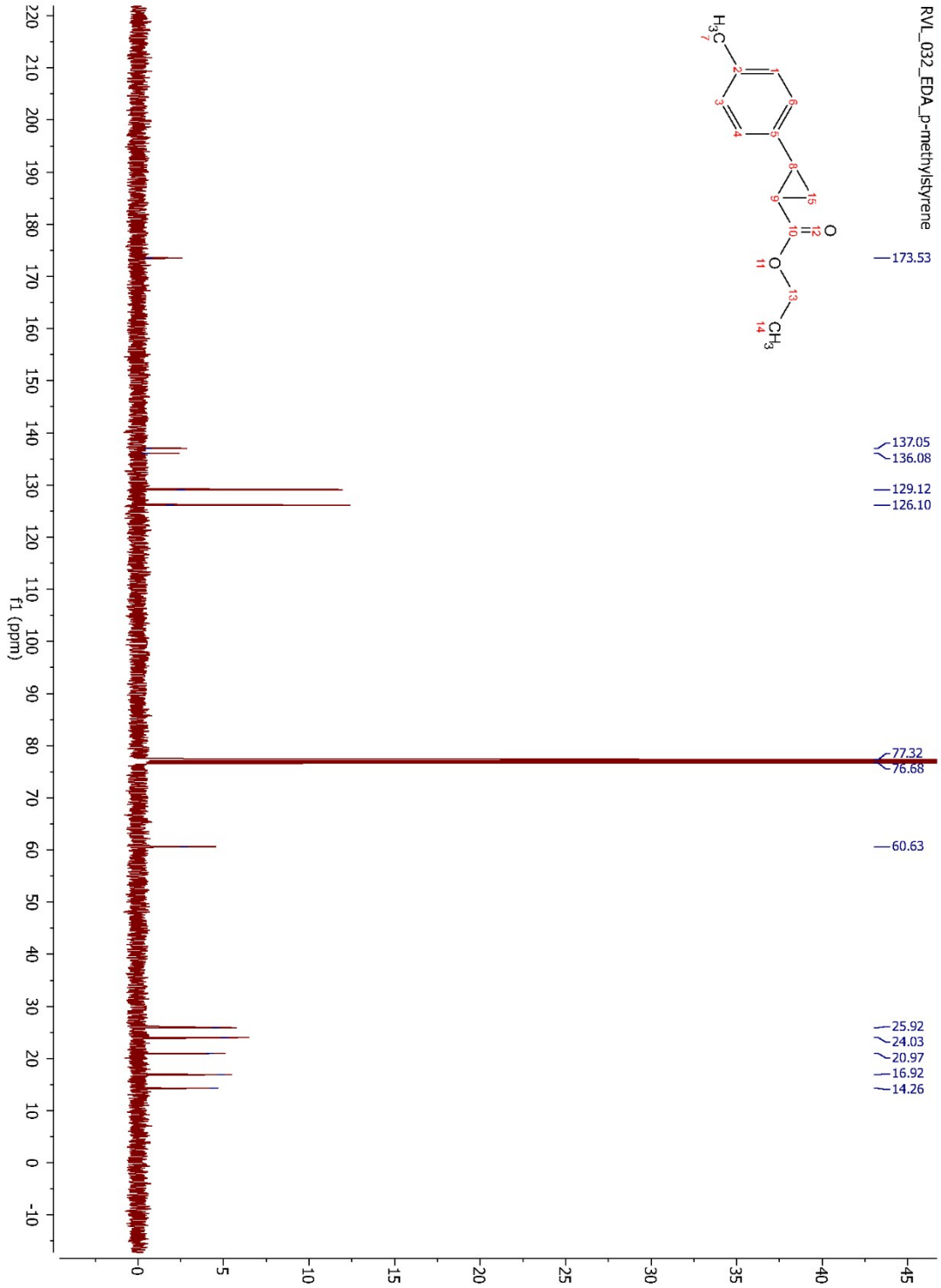
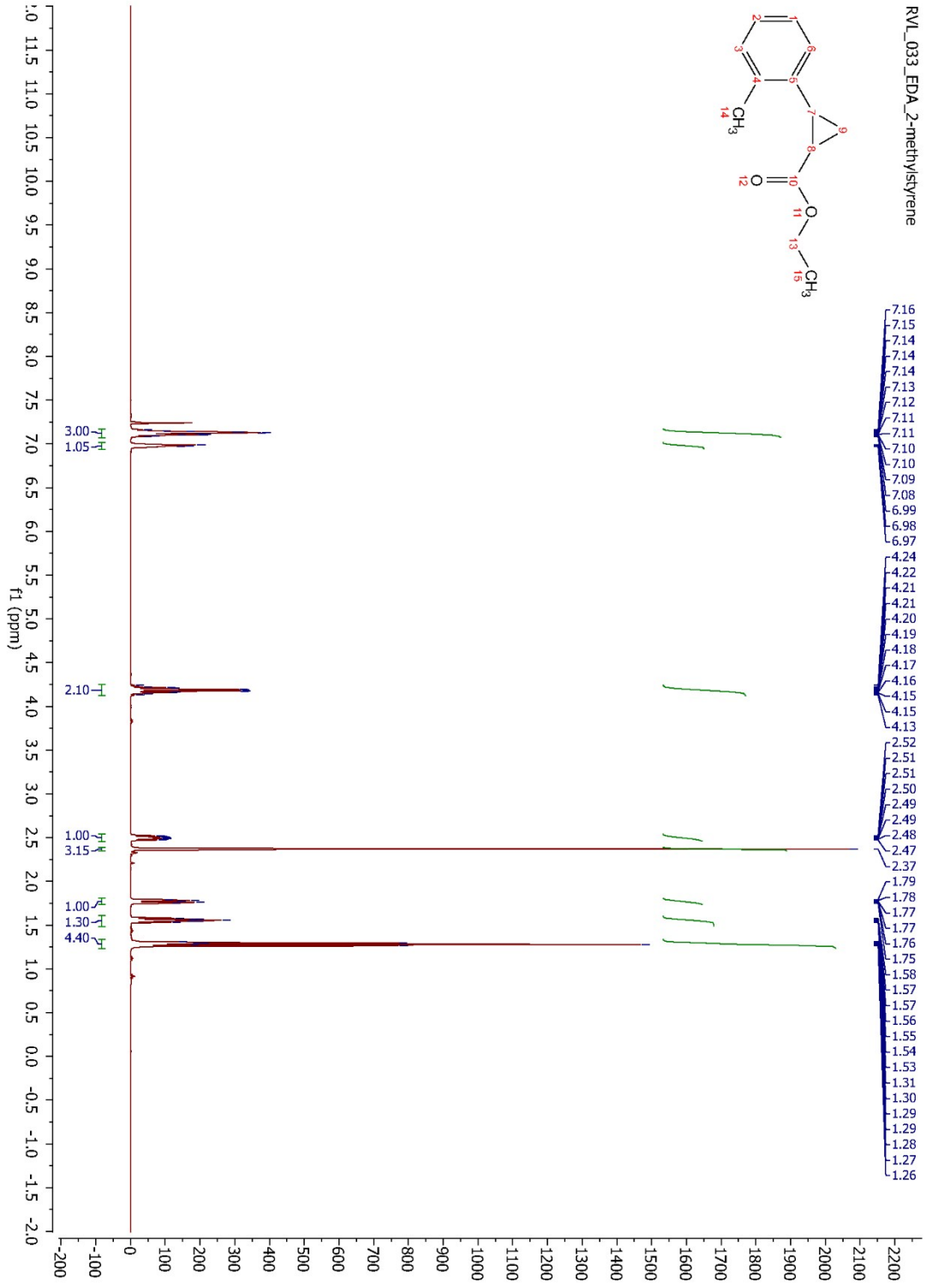


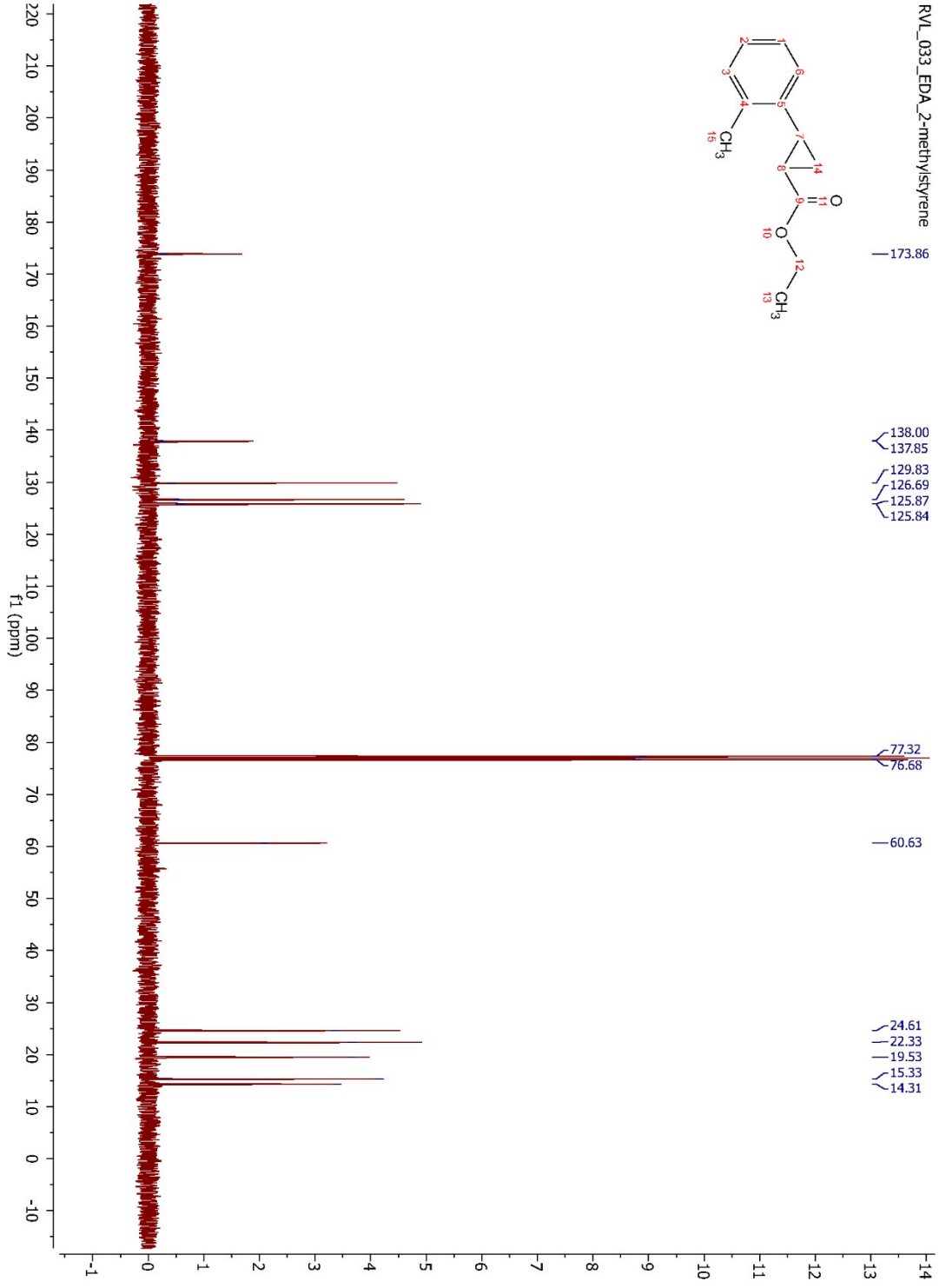
SI7: Characterization of compounds from micellar catalysis

3f, ^{1}H-NMR



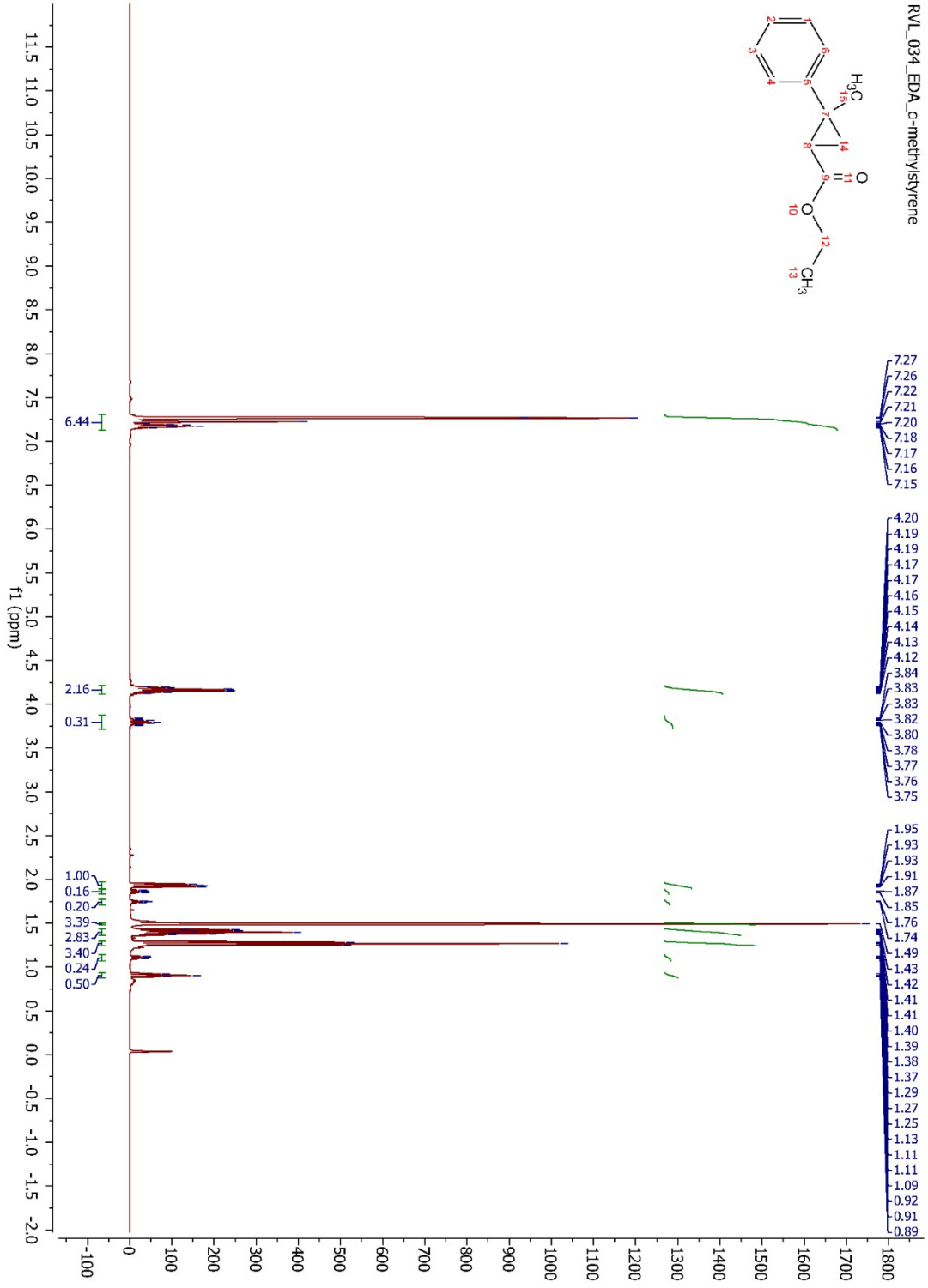
SI7: Characterization of compounds from micellar catalysis

3f, ^{13}C-NMR



SI7: Characterization of compounds from micellar catalysis

3g, ^{1}H-NMR



SI7: Characterization of compounds from micellar catalysis

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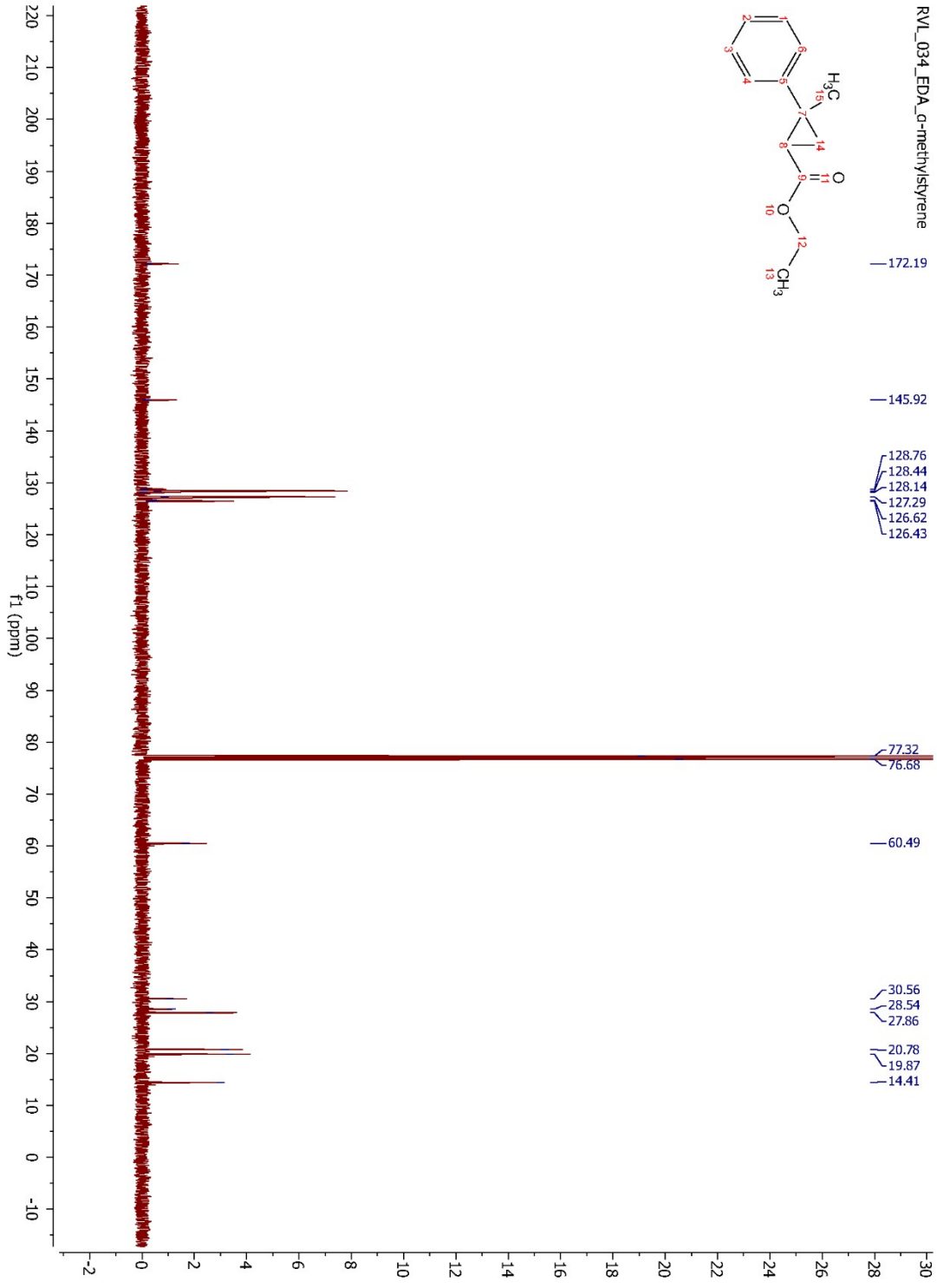
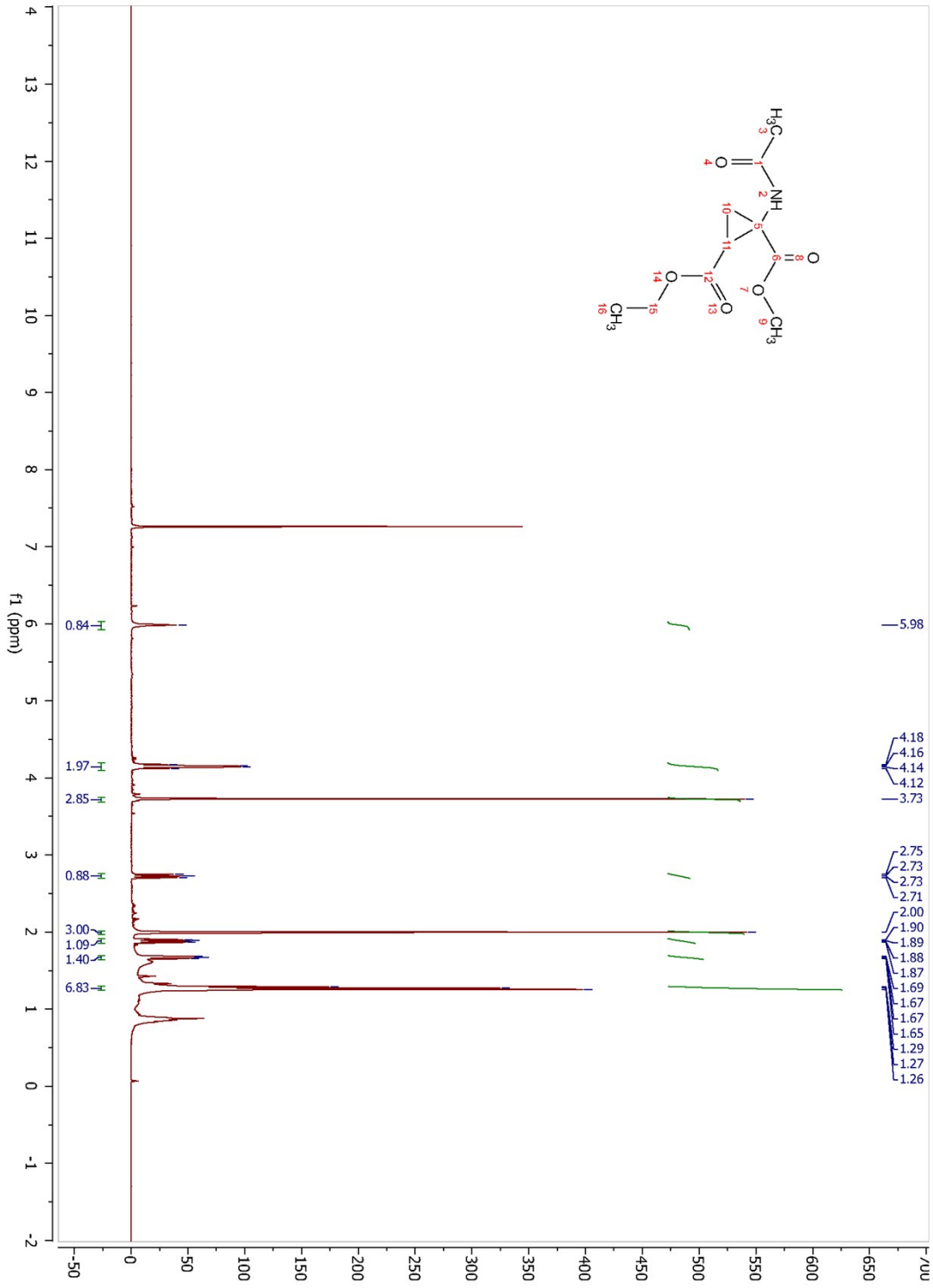


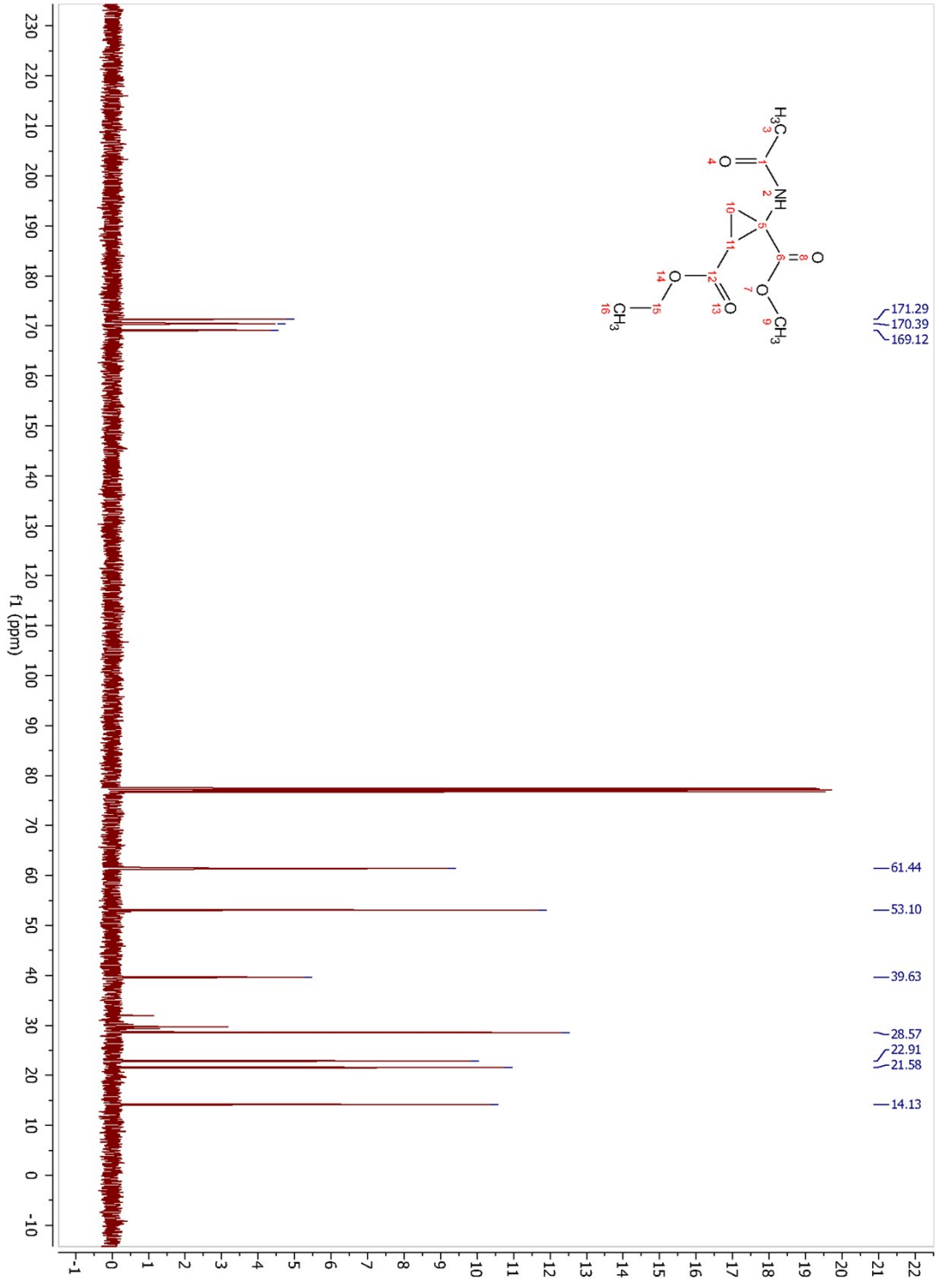
SI7: Characterization of compounds from micellar catalysis

3j, ^{1}H-NMR



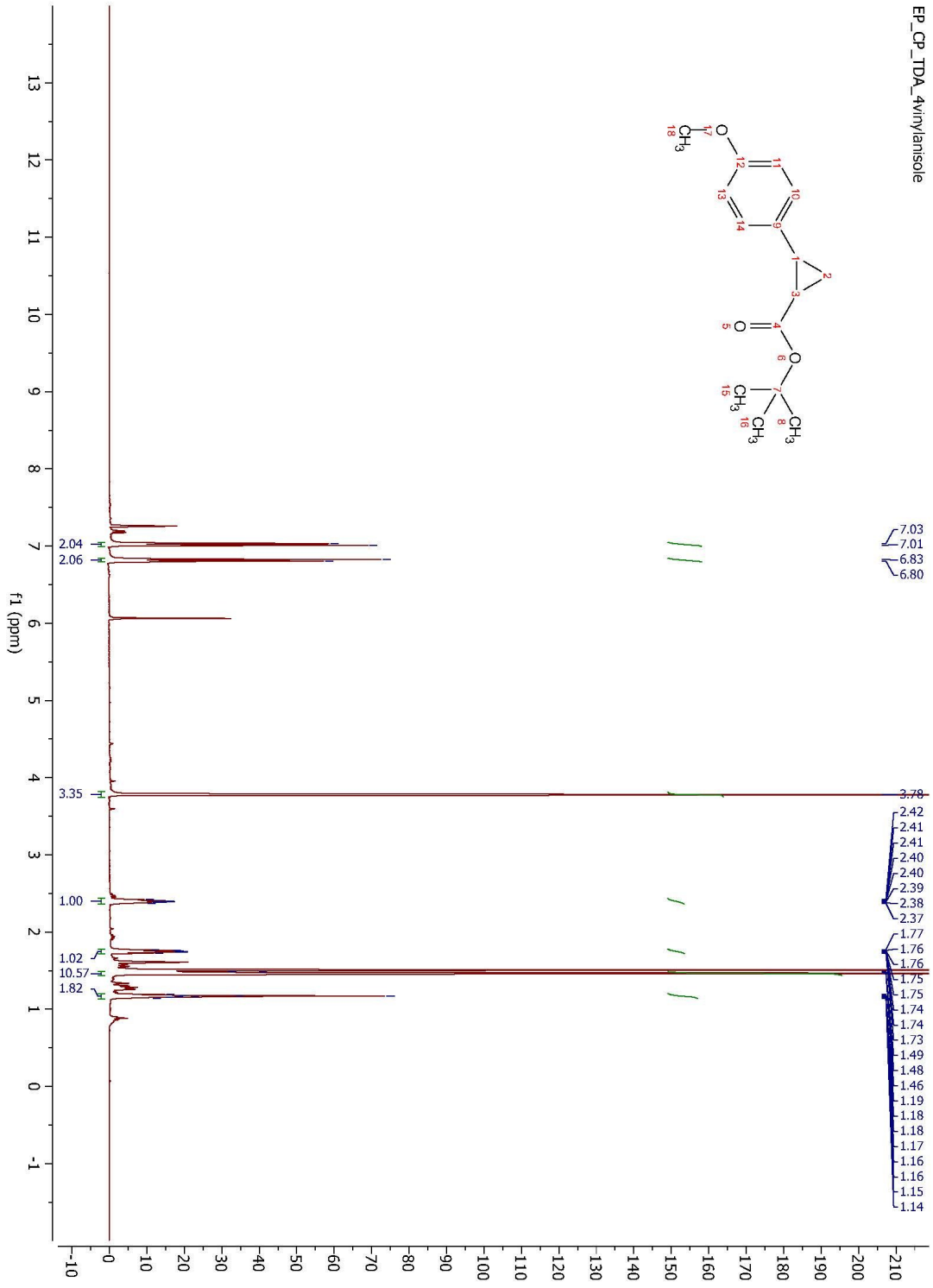
SI7: Characterization of compounds from micellar catalysis

3j, ^{13}C-NMR



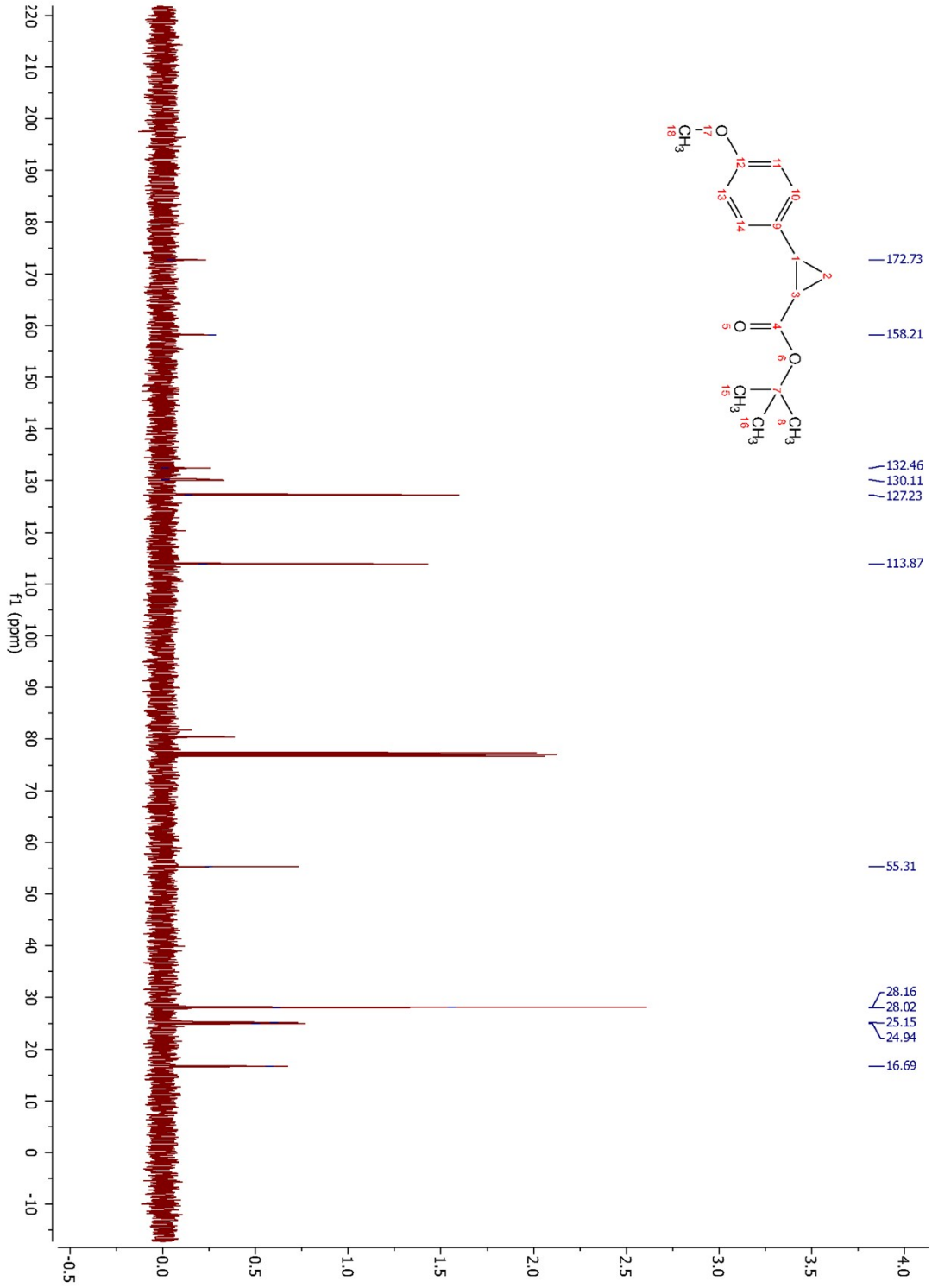
SI7: Characterization of compounds from micellar catalysis

3k, ^{1}H-NMR



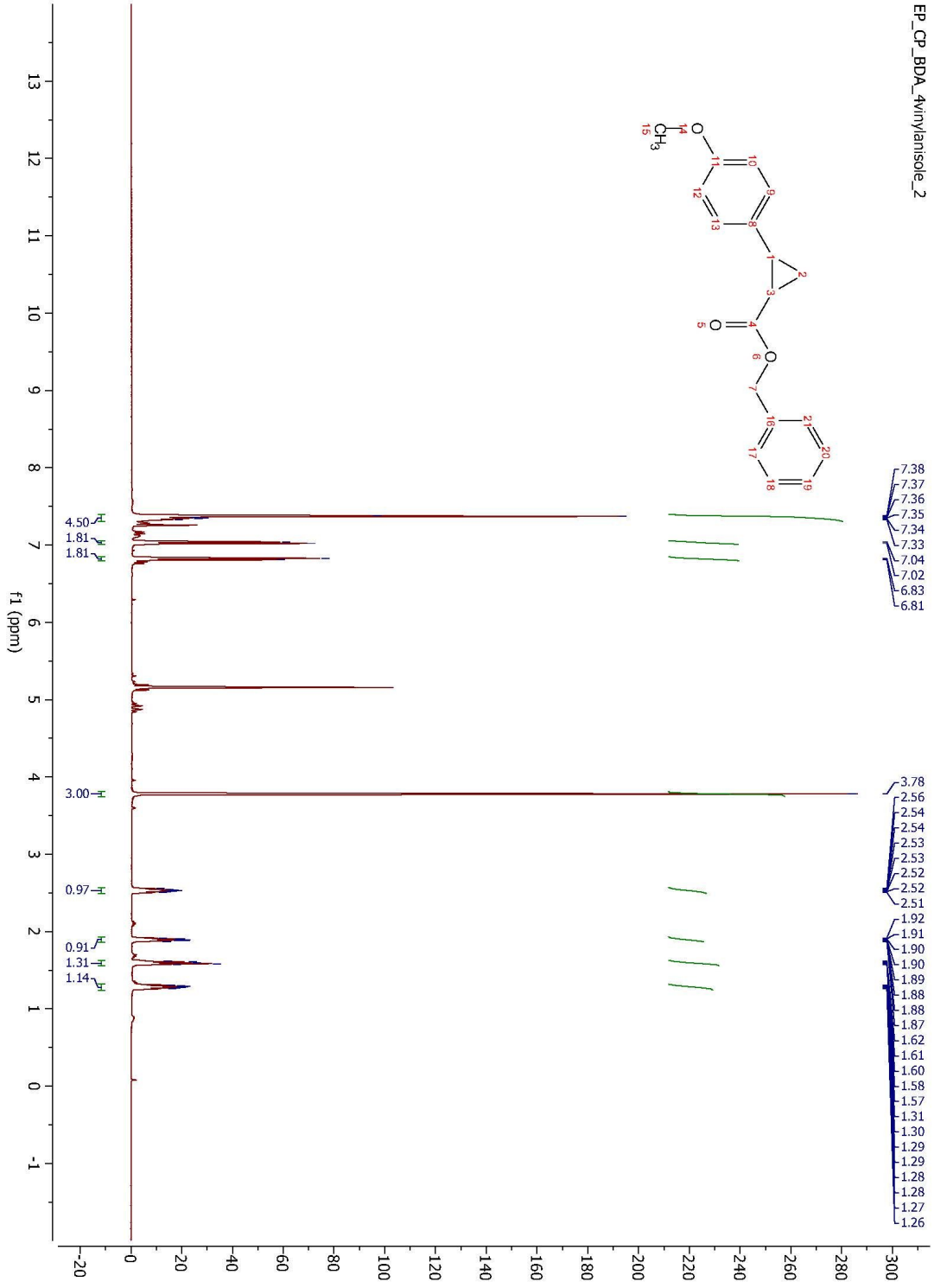
SI7: Characterization of compounds from micellar catalysis

3k, ^{13}C-NMR



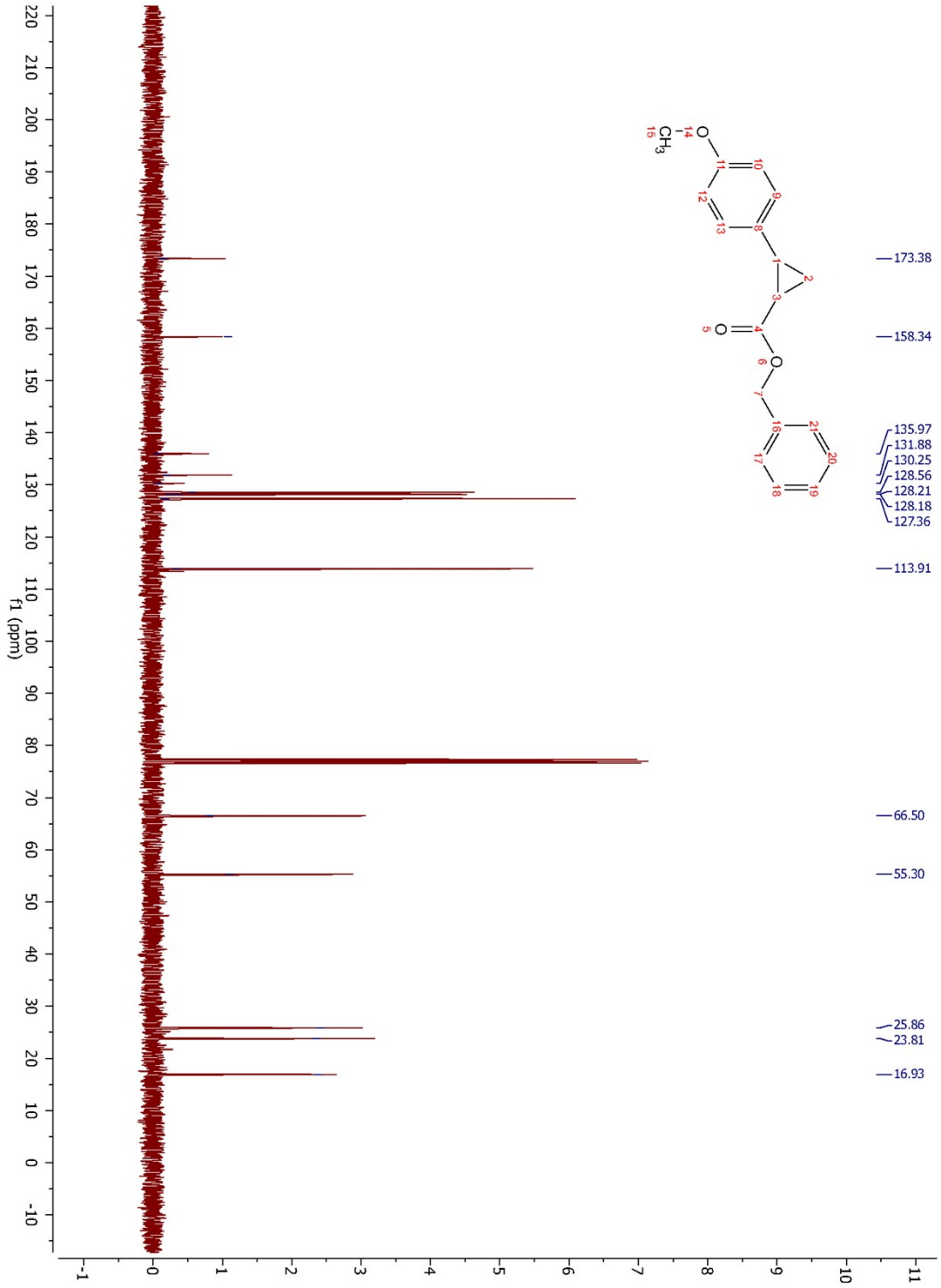
SI7: Characterization of compounds from micellar catalysis

3l, ^{1}H-NMR



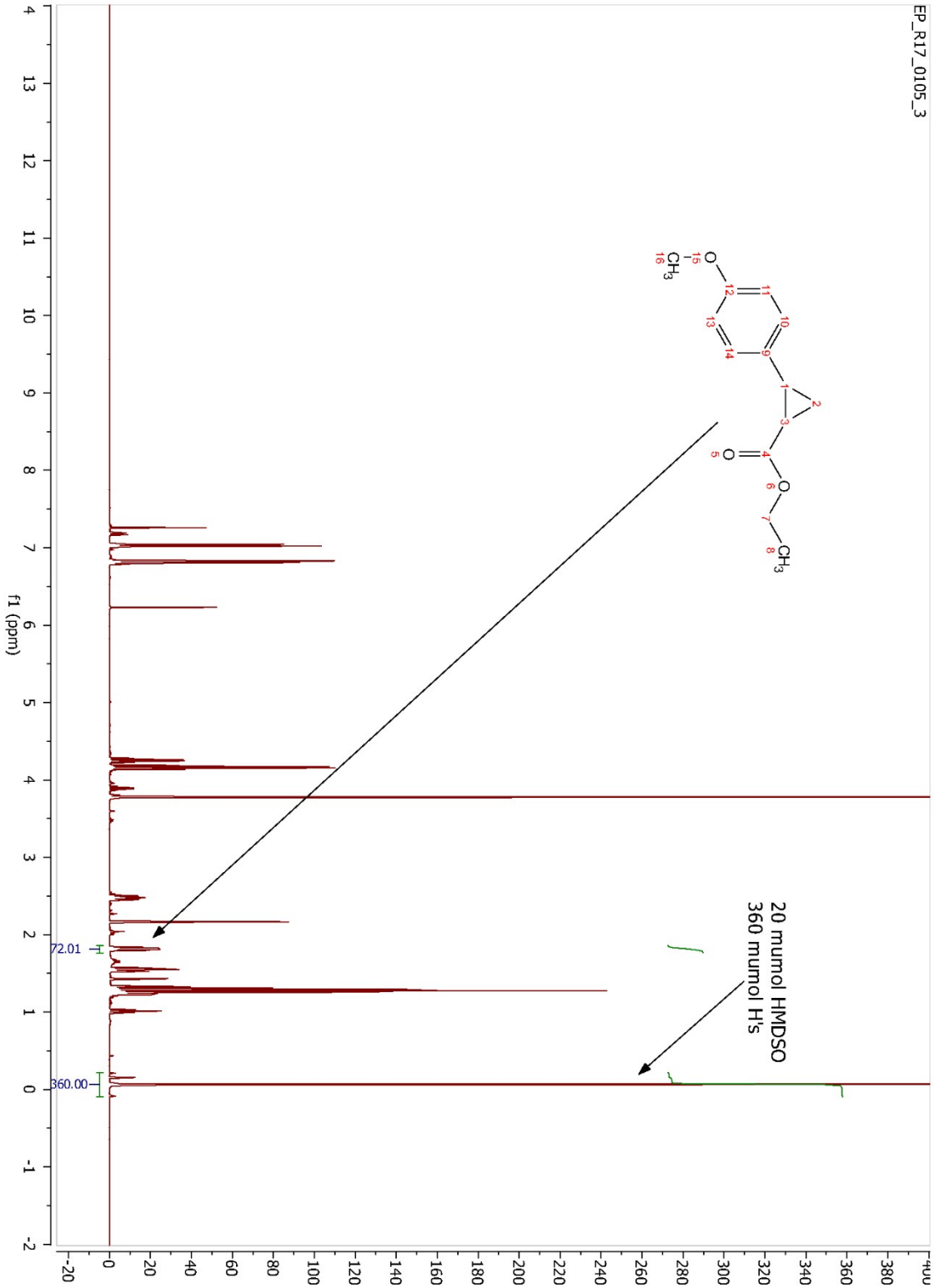
SI7: Characterization of compounds from micellar catalysis

3l, ^{13}C-NMR



SI8: Example ^{1}H-NMR spectra from micellar catalysis

20 mM SDS, 1 mol% **C3**, 75 µmol **1a** (Table 1 entry 7)



SI8: Example ^{1}H-NMR spectra from micellar catalysis

20 mM SDS, 1 mol% **C3**, 75 µmol **1i** (Table 2 entry 11)