Supplementary Information for

First Enantioselective Synthesis of Gingesulfonic Acids and Unequivocal Determination of their Absolute Stereochemistry.

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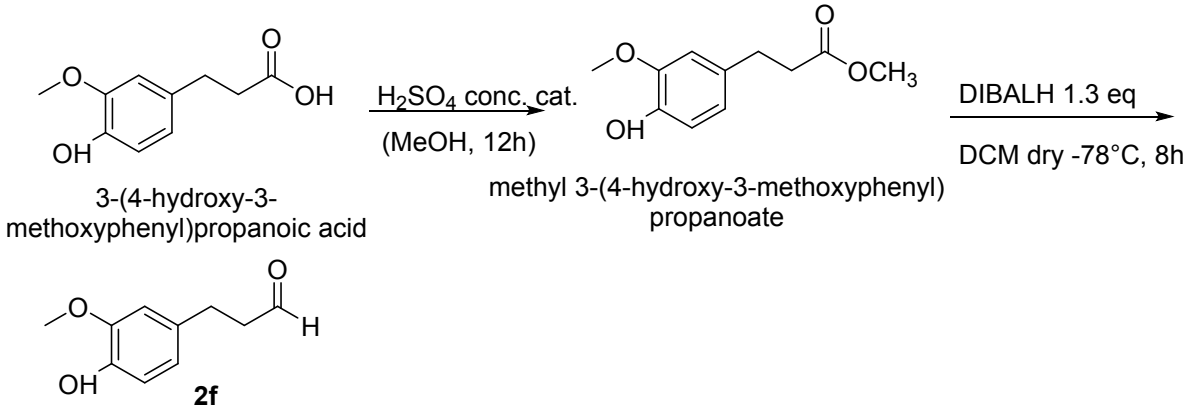
MATERIALS AND METHODS

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvent signals for ^{1}H and ^{13}C NMR (^{1}H NMR: 7.26 ppm for $CDCl_3$, 3.31 ppm for MeOD, ^{13}C NMR: 77.1 ppm for $CDCl_3$, 49.8 ppm for MeOD). Coupling constants (J) are reported in Hz. Multiplicities are reported as follows: s, singlet, d, doublet, dd, doublets of doublets, t triplet, dt, doublets of triplets, q, quartet, m, multiplet, c, complex, and br, broad. The enantiomeric excesses of the products were determined by chiral stationary phase HPLC (Daicel Chiralpak AD-H, AS), using a UV detector operating at 254 nm and 210 nm. Tetrahydrofuran was freshly distilled over sodium benzophenone prior to use according to standard procedure. All other reagents and solvents were used as purchased from Aldrich unless otherwise specified. Reactions were checked for completion by TLC (EM Science, silica gel 60 F254). Flash chromatography was performed using silica gel 60 (0.040-0.063 mm, 230-400 mesh).

The samples for the HPLC analysis were prepared by methylation of sulfonic acids. In a test tube equipped with a magnetic stirring bar, to a solution of the sulfonic acid (0.1 mmol, 1 eq.) in MeOH trimethylsilyl diazomethane (1.0 mmol, 10 eq., 2M solution in hexanes) was added at 0°C in one portion. The mixture evolves gas and gradually loses colour. The reaction was stirred for 2 hours at room temperature, then the solvent was removed under reduced pressure and in high vacuum. The methylated sulfonic acids obtained were purified by column chromatography (petroleum ether:ethyl acetate 8:2). The ^{1}H NMR for these compounds presents a new peak for the new methyl group around 3.5-4 ppm.

Preparation of aldehyde 2f



Methyl 3-(4-hydroxy-3-methoxyphenyl)propanoate[1]

In a 100 ml round-bottomed flask equipped with a magnetic stirring bar, hydroferulic acid (1 g, 5.1 mmol) was dissolved in 30 ml of methanol. 1.5% of solvent volume of H_2SO_4 was added, and the solution was left stirring at room temperature overnight. The solvent was removed under reduced

[1] Snyder, S. A.; Kontes, F. *J. Am. Chem. Soc.* **2009**, *131*, 1745.

pressure, and the residue was dissolved in 25 ml of DCM. Water (25 ml) was added, and the organic phase was extracted with DCM (3x15ml). The organic phases were combined and dried over $MgSO_4$, and the solvent was removed *in vacuo*.

Dark yellow oil (1.05 g mg, 98%); ^{1}H NMR ($CDCl_3$ 400 MHz) δ 6.82 (d, *J* = 8 Hz, 1 H), 6.70 -6.66 (m, 2 H), 5.75 (br. s, 1 H), 3.84 (s, 3 H), 3.66 (s, 3 H), 2.87 (t, *J* = 8 Hz, 2 H), 2.60 (t, *J* = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$,101MHz): δ 173.5, 146.5, 144.0, 132.1, 120.5, 114.5, 111.0, 55.6, 51.4, 35.9, 30.4.

3-(4-hydroxy-3-methoxyphenyl)propanal (2f)[2]

In strictly anhydrous conditions, in a 50 ml round-bottomed flask equipped with a magnetic stirring bar methyl-hydroferulate (200 mg, 1.00 mmol) was dissolved in dry DCM, and the temperature was brought to -78°C by means of a dry ice/acetone bath. DIBALH (1.2ml, 1.2 mmol) was added dropwise. The mixture was left stirring at -78°C for 8 h. Water (15ml) and HCl 10% (15ml) were added, and the organic layer was extracted with DCM (3x10ml). The organic fractions were combined, dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude was used on the next step without further purification.

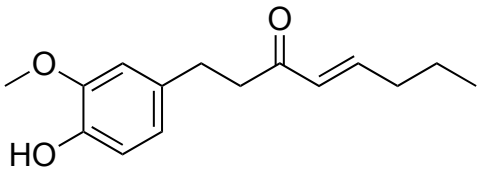
Pale yellow oil (160 mg, 91% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 6.83 (d, *J* = 8 Hz, 1H), 6.72 – 6.65 (m, 2H), 5.61 (s, 1H), 3.86 (s, 3H), 2.89 (t, *J* = 7 Hz, 2H), 2.74 (t, *J* = 7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.96, 146.62, 144.15, 132.31, 120.87, 114.54, 111.08, 55.96, 45.69, 27.91.

General procedure for the synthesis of α,β-unsaturated ketones 3a-g

In a 10 mL round-bottomed flask under magnetic stirring, one of aldehydes **2a-g** 9 mmol (3 eq.) was added to DIMCARB (5.5 eq.) at room temperature. Vanillyl acetone (**1**) 3 mmol (1 eq.) was added in a single portion. The solution was left stirring at room temperature for 48 h, then quenched with a 6N solution of HCl (10 mL) and extracted with DCM (3 x 15mL). The aqueous layer was taken to pH 7 by addition of 2N NaOH and then extracted again with DCM (3 x 15mL). The organic phases were combined, dried over anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude was purified by flash column chromatography using a mixture of hexane : ethylacetate : acetic acid (8 :2: 0.5).

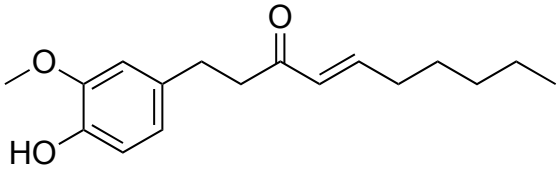
(*E*)-1-(4-hydroxy-3-methoxyphenyl)oct-4-en-3-one (3a).[3]

[2] Hattori, H.; Mitsunaga, T.; Clive, D. L. J. *Tetrahedron Lett.* **2019**, *60*, 1989.
[3] Kikuzaki, H.; Kawasaki, Y.; Nakatani, N. *ACS Symposium Series*, **1994**, *547*, 237.



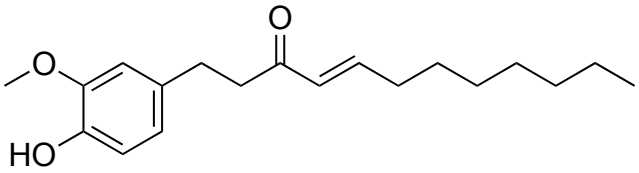
Pale yellow oil (380 mg, 51%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.85 – 6.78 (m, 2H), 6.71 – 6.67 (m, 2H), 6.09 (d, *J* = 16 Hz, 1H), 3.86 (s, 3H), 2.85 (h, *J* = 7.4 Hz, 4H), 2.20 – 2.15 (m, 2H), 1.52 – 1.43 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 147.8, 146.51, 143.9, 133.3, 130.5, 120.9, 114.4, 111.2, 55.9, 42.1, 34.6, 29.9, 21.5, 13.8. HRMS $C_{15}H_{20}O_3$ requires *m/z* 248.1412 (E^+), found *m/z* 248.1415 (M^+); ESI *m/z* 248 (M^+).

(*E*)-1-(4-hydroxy-3-methoxyphenyl)dec-4-en-3-one (3b)[4]



Yellow oil (455 mg 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 – 6.78 (m, 2H), 6.71 – 6.67 (m, 2H), 6.09 (d, *J* = 16 Hz, 1H), 3.87 (s, 3H), 2.89– 2.81 (m, 4H), 2.19 (td, *J* = 8, 1 Hz, 2H), 1.44 – 1.42 (m, 2H), 1.31 – 1.27 (m, 4H), 0.89 (t, *J* = 7 Hz, 3H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 148.0, 146.51, 143.9, 133.4, 130.4, 120.9, 114.4, 111.2, 55.9, 42.11, 32.6, 31.5, 30.0, 27.9, 22.6, 14.1. HRMS $C_{17}H_{24}O_3$ requires *m/z* 276.1725 (E^+), found *m/z* 276.1727 (M^+); ESI *m/z* 276 (M^+).

(*E*)-1-(4-hydroxy-3-methoxyphenyl)dodec-4-en-3-one (3c)[5]



Pale yellow oil (525 mg, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 – 6.78 (m, 2H), 6.71 – 6.67 (m, 2H), 6.09 (d, *J* = 16 Hz, 1H), 5.50 (bs, 1H), 3.87 (s, 3H), 2.89 – 2.81 (m, 4H), 2.19 (td, *J* = 8, 1 Hz, 2H), 1.47 – 1.40 (m, 2H), 1.28 (m, 8H), 0.88 (t, *J* = 7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 148.0, 146.5, 143.9, 133.4, 130.4, 120.9, 114.4, 111.2, 56.0, 42.1, 32.6, 31.9, 30.0, 29.3, 29.2, 28.2, 22.76, 14.2 HRMS $C_{19}H_{28}O_3$ requires *m/z* 304.2038 (E^+), found *m/z* 304.2041 (M^+); ESI *m/z* 304 (M^+).

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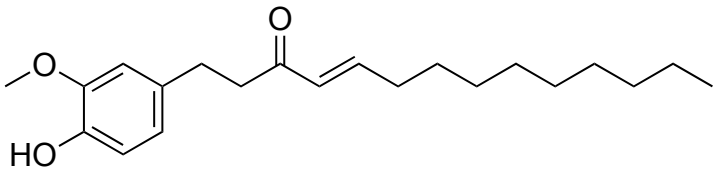
[4] Mase, N.; Kitagawa, N.; Takabe, K. *Synlett* **2010**, 93.

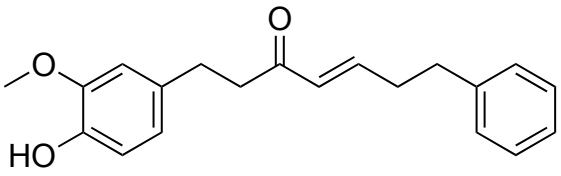
[5] Jolad, S. D.; Lantz, R. C.; Chen, G. J.; Bates, R. B.; Timmermann, B. N. *Phytochemistry* **2005**, *66*, 1614.

(*E*)-1-(4-hydroxy-3-methoxyphenyl)tetradec-4-en-3-one (3d).[5]



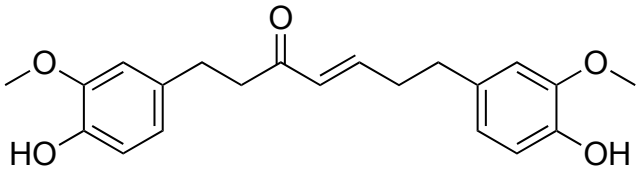
Yellow oil; (545 mg, 55%);^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 – 6.78 (m, 2H), 6.71 – 6.67 (m, 2H), 6.09 (d, *J* = 16 Hz, 1H), 3.87 (s, 3H), 2.89 – 2.81 (m, 4H), 2.19 (td, *J* = 8, 1 Hz, 2H), 1.45 – 1.40 (m, 2H), 1.28 (m, 10H), 0.88 (t, *J* = 7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 148.1, 146.5, 143.9, 133.4, 130.4, 120.9, 114.4, 111.2, 56.0, 42.1, 32.6, 32.0, 30.0, 29.6, 29.5, 29.4, 29.3, 28.2, 22.8, 14.2. HRMS $C_{21}H_{32}O_3$ requires *m/z* 332.2351 (E^+), found *m/z* 332.2347 (M^+); ESI *m/z* 332 (M^+).

(*E*)-1-(4-hydroxy-3-methoxyphenyl)-7-phenylhept-4-en-3-one (3e).



Bright orange oil (540 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 15, 7.2 Hz, 3H), 7.19 (dd, *J* = 19, 7Hz, 3H), 6.91 – 6.77 (m, 2H), 6.77 – 6.61 (m, 2H), 6.11 (d, *J* = 16 Hz, 1H), 3.87 (s, 3H), 2.90 – 2.79 (m, 4H), 2.81 – 2.73 (m, 2H), 2.53 (dd, *J* = 15, 7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 146.6, 146.5, 143.9, 140.8, 133.3, 130.9, 128.6, 128.4, 126.4, 120.9, 114.4, 111.2, 55.9, 42.2, 34.5, 34.3, 29.9. HRMS $C_{20}H_{22}O_3$ requires *m/z* 310.1569 (E^+), found *m/z* 310.1565 (M^+); ESI *m/z* 310 (M^+).

(*E*)-1,7-bis(4-hydroxy-3-methoxyphenyl)hept-4-en-3-one (3f).[6]



Bright orange oil; 747 mg 70% ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 – 6.81 (m, 3H), 6.70 – 6.63 (m, 5H), 6.10 (d, *J* = 16 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 2.88 – 2.79 (m, 4H), 2.69 (t, *J* = 7 Hz, 4H), 2.49 (dd, *J* = 14, 7 Hz, 2H); ^{13}C NMR ($CDCl_3$,101MHz): δ = 207.3, 146.6, 146.6, 146.5, 144.1, 144.0, 132.7, 130.8,

[6] Endo, K.; Kanno, E.; Oshima, Y. *Phytochemistry*, **1990**, *29*, 797.

121.1, 121.0, 120.9, 114.5, 114.4, 111.2, 111.0, 56.0, 42.3, 34.6, 34.3, 31.1, 30.0 ppm. HRMS $C_{21}H_{24}O_5$ requires *m/z* 356.1654 (E^+), found *m/z* 356.1659 (M^+); ESI *m/z* 356 (M^+).

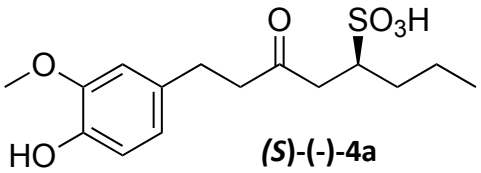
General procedure for the synthesis of racemic sulfonic acids

In a 5 ml microwave vial to a solution of the α,β-unsaturated ketone (0.20 mmol, 1 eq.) in ethanol:water 1:1 (1 mL), $NaHSO_3$ (0.44 mmol, 2.2 eq. 4.8M solution) was added. The mixture was heated at 140°C for 45 minutes in a microwave reactor (power: 160W). The mixture was allowed to cool before the solvent was removed under vacuum. The crude product was then dissolved in H_2O (3 mL), passed through a plug of freshly activated acidic ion exchange resin (2.2g) and then washed with deionized water for three consecutive times (3 x 3 mL). Finally, the pure sulfonic acids were obtained by drying the aqueous solution first under reduced pressure and finally in high vacuum.

General procedure for the synthesis of enantio-enriched sulfonic acids 4a-f (Table 2)

In a test tube equipped with a magnetic stirring bar a solution of the α,β-unsaturated ketone (0.1 mmol, 1 eq.) in a 3:1 mixture of MeOH:Toluene (1.0 mL) was added, and the temperature was kept at 0°C by means of an ice bath. To this solution were sequentially added catalyst **5** or *epi*-**5** (0.01 mmol, 0.1 eq.) and a freshly prepared solution of sodium bisulfite (0.48 M) in water (0.12 mmol, 1.2 eq.). The reaction was left stirring at 0 °C for 48 hours. The solvent was then evaporated under reduced pressure, the crude mixture was filtered off over a celite pad using 10mL of a 3:1 mixture of MeOH:Toluene, and then the solvent removed *in vacuo*. The crude product was then dissolved in H_2O (3 mL), passed through a plug of freshly activated acidic ion exchange resin (2.2g) and then washed with deionized water for three consecutive times (3 x 3 mL). Finally, the pure sulfonic acids were obtained by drying the aqueous solution first under reduced pressure and then in high vacuum.

(-) and (+)- 8-(4-hydroxy-3-methoxyphenyl)-6-oxooctane-4-sulfonic acid (4a)

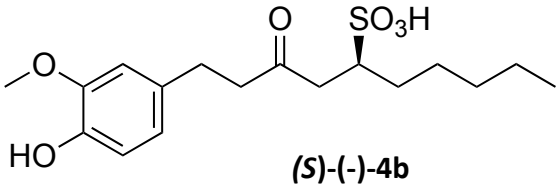


***(S)*-(-)-4a**

Dark red oil; yield: racemic mixture 32 mg 98%, (*S*)-enriched 31 mg, 93%, (*R*)-enriched 31 mg, 94%; ^{1}H NMR (400 MHz, MeOD) δ 6.78 (d, *J* = 1 Hz, 1H), 6.68 (d, *J* = 8 Hz, 1H), 6.61 (dd, *J* = 8, 1 Hz, 1H), 3.82 (s, 3H), 3.02 (dd, *J* = 17, 6 Hz, 1H), 2.82 – 2.77 (m, 4H), 2.52 (dd, *J* = 17, 6 Hz, 1H), 1.89 – 1.84

(m, 1H), 1.41 – 1.35 (m, 4H), 0.89 (t, *J* = 7 Hz, 3H); ^{13}C NMR (101 MHz, MeOD) δ 210.2, 161,1, 148.8, 145.7, 133.9, 121.7, 116.07, 113.1, 56.8, 56.3, 45.9, 44.5, 34.0, 30.3, 21.3, 14.3 $[\alpha]_D^{20}$: (*S*)-enriched, -4.7; (*R*)-enriched, +5.0 [c = 0.03, CH_3OH]; HRMS $C_{15}H_{22}O_6S$ requires *m/z* 330.1137 (E^+), found *m/z* 330.1141 (M^+); ESI m/z 330 (M^+).

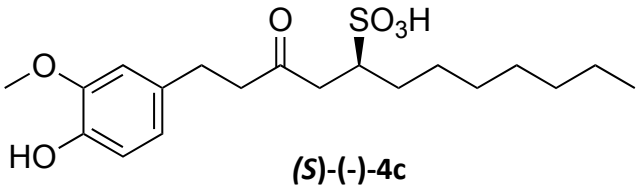
(-) and (+)- 1-(4-hydroxy-3-methoxyphenyl)-3-oxodecane-5-sulfonic acid (4b)



***(S)*-(-)-4b**

Dark green oil; yield: racemic mixture 35mg 98%, (*S*)-enriched 34mg 94%, (*R*)-enriched 33mg 92%;^{1}H NMR (400 MHz, MeOD) δ 6.78 (d, *J* = 1 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.61 (dd, *J* = 8, 2 Hz, 1H), 3.82 (s, 1H), 3.03 (dd, *J* = 17, 6 Hz, 1H), 2.84 – 2.77 (m, 1H), 2.52 (dd, *J* = 17, 6 Hz, 1H), 1.92 – 1.86 (m, 1H), 1.44 (dt, *J* = 13, 6 Hz, 1H), 1.33– 1.28 (m, 8H), 0.89 (t, *J* = 7 Hz, 1H); ^{13}C NMR (101 MHz, MeOD) δ 210.2, 148.8, 145.7, 133.9, 121.67, 116.1, 113.1, 57.1, 56.3, 45.9, 44.5, 32.9, 31.8, 30.4, 27.8, 23.5, 14.4. $[\alpha]_D^{20}$: (*S*)-enriched, -4.3: (*R*)-enriched, +4.0 [c = 0.03, CH_3OH]; HRMS $C_{17}H_{26}O_6S$ requires *m/z* 358.1450 (E^+), found *m/z* 358.1447 (M^+); ESI *m/z* 358 (M^+).

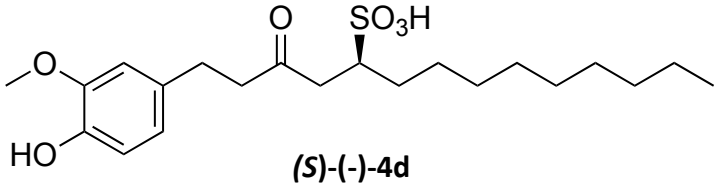
(-) and (+)- 1-(4-hydroxy-3-methoxyphenyl)-3-oxododecane-5-sulfonic acid (4c)



***(S)*-(-)-4c**

Brown oil; yield: racemic 38mg mixture 98%, (*S*)-enriched 35mg 91%, (*R*)-enriched 35mg 91%; ^{1}H NMR (400 MHz, MeOD) δ 6.78 (d, *J* = 1 Hz, 1H), 6.68 (d, *J* = 8 Hz, 1H), 6.61 (dd, *J* = 8, 1 Hz, 1H), 3.82 (s, 3H), 3.03 (dd, *J* = 17, 6 Hz, 1H), 2.84 – 2.77 (m, 4H), 2.52 (dd, *J* = 17, 6 Hz, 1H), 1.92 – 1.86 (m, 1H), 1.44 (dt, *J* = 13, 8 Hz, 1H), 1.36 – 1.28 (m, 12H), 0.89 (t, *J* = 7 Hz, 3H); ^{13}C NMR (101 MHz, MeOD) δ 210.3, 148.8, 145.7, 133.9, 121.7, 116.1, 113.1, 57.1, 56.3, 45.9, 44.5, 32.9, 31.9, 30.6, 30.4, 30.2, 28.1, 23.7, 14.4. $[\alpha]_D^{20}$: (*S*)-enriched, -4.9; (*R*)-enriched, +6.7 [c = 0.03, CH_3OH]. HRMS $C_{19}H_{30}O_6S$ requires *m/z* 386.1763 (E^+), found *m/z* 386.1759 (M^+); ESI *m/z* 386 (M^+).

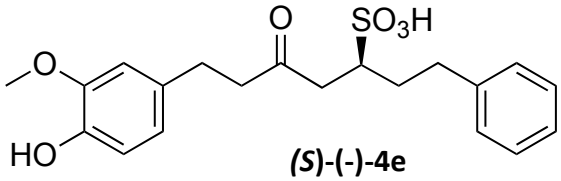
(-) and (+)- 1-(4-hydroxy-3-methoxyphenyl)-3-oxotetradecane-5-sulfonic acid (4d)



***(S)*-(-)-4d**

Brown oil; yield: racemic mixture 41mg 98%, (*S*)-enriched 39mg 94%, (*R*)-enriched 39mg 95%; ^{1}H NMR (400 MHz, MeOD) δ 6.78 (d, *J* = 1 Hz, 1H), 6.67 (d, *J* = 8 Hz, 1H), 6.61 (dd, *J* = 8, 1 Hz, 1H), 3.82 (s, 3H), 3.03 (dd, *J* = 17, 6 Hz, 1H), 2.84 – 2.77 (m, 4H), 2.53 (dd, *J* = 17, 6 Hz, 1H), 1.92 – 1.87 (m, 1H), 1.43 – 1.39 (m, 1H), 1.36 – 1.28 (m, 16H), 0.89 (t, *J* = 7 Hz, 3H); ^{13}C NMR (101 MHz, MeOD) δ 209.1, 148.9, 145.7, 133.9, 121.7, 116.1, 113.1 , 57.1, 56.3, 45.9, 44.6, 33.1 (s), 31.8, 30.7, 30.7 , 30.5, 30.4 , 30.3, 28.1, 23.7, 14.4. $[\alpha]_D^{20}$: (*S*)-enriched, -5.5; (*R*)-enriched, +4.8 [c = 0.03, CH_3OH]. HRMS $C_{21}H_{34}O_6S$ requires *m/z* 414.2076 (E^+), found *m/z* 414.2071 (M^+); ESI *m/z* 414 (M^+).

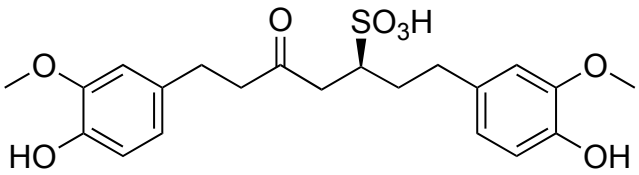
(-) and (+)- 7-(4-hydroxy-3-methoxyphenyl)-5-oxo-1-phenylheptane-3-sulfonic acid (4e)



***(S)*-(-)-4e**

Purple oil; yield: racemic mixture 38 mg 98%, (*S*)-enriched 36mg 92%, (*R*)-enriched 37 mg 95%; ^{1}H NMR (400 MHz, MeOD) δ 7.23 (t, *J* = 7 Hz, 2H), 7.14 (dd, *J* = 15, 7 Hz, 3H), 6.77 (s, 1H), 6.67 (d, *J* = 8 Hz, 1H), 6.61 (d, *J* = 8 Hz, 1H), 3.80 (s, 3H), 3.42 – 3.33 (m, 1H), 3.07 (dd, *J* = 17, 6 Hz, 1H), 2.82 – 2.73 (m, 1H), 2.73 – 2.66 (m, 1H), 2.60 (dd, *J* = 17, 7 Hz, 1H), 2.24 – 2.12 (m, 1H), 1.80 – 1.69 (m, 1H); ^{13}C NMR (101 MHz, MeOD) δ 210.4, 148.8, 145.7, 143.1, 133.9, 126.9, 121.7, 116.1, 113.1, 56.7, 56.3, 34.4, 33.9, 30.3, 30.2. $[\alpha]_D^{20}$: (*S*)-enriched, -3.1; (*R*)-enriched, +2.5 [c = 0.03, CH_3OH]. HRMS $C_{20}H_{24}O_6S$ requires *m/z* 392.1294 (E^+), found *m/z* 392.1299 (M^+); ESI i 392 (M^+).

(-) and (+)- 1,7-bis(4-hydroxy-3-methoxyphenyl)-5-oxoheptane-3-sulfonic acid (4f)

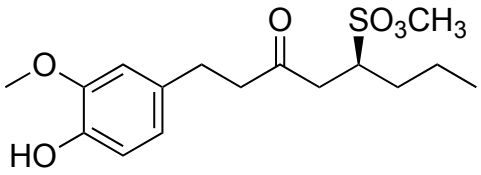


Blue oil (mg; yield): racemic mixture 43mg 98%, (*S*)-enriched 41mg 93%, (*R*)-enriched 39mg 90%; ^{1}H NMR (400 MHz, MeOD) δ 6.76 (s, 2H), 6.68 (dd, *J* = 8, 3 Hz, 2H), 6.61 – 6.58 (m, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 3.41-3.34 (m, 1H), 3.05 (dd, *J* = 17, 6 Hz, 1H), 2.82 – 2.72 (m, 4H), 2.61 (t, *J* = 8 Hz, 2H), 2.58 (dd, *J* = 18, 7 Hz, 1H), 2.18 (dt, *J* = 13, 8 Hz, 1H), 1.72 (td, *J* = 15, 7 Hz, 1H); ^{13}C NMR (101 MHz, MeOD) δ 210.2, 148.8, 148.8, 145.6, 145.5, 134.5, 133.9, 121.8, 121.6, 116.1, 116.0, 113.1, 112.9, 56.3, 56.2, 45.8, 44.6, 33.9, 33.8, 30.4, 30.3. $[\alpha]_D^{20}$: (*S*)-enriched, -3.1; (*R*)-enriched, +2.5 [c = 0.03, CH_3OH]. HRMS $C_{21}H_{26}O_8S$ requires *m/z* 438.1348 (E^+), found *m/z* 438.1352 (M^+); ESI *m/z* 438 (M^+).

Procedure for the preparation of sulfonate methyl esters of 4a-f

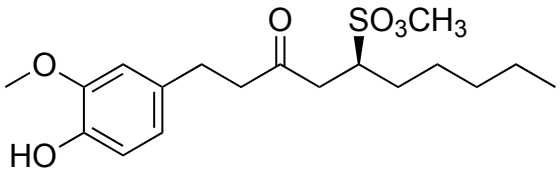
0.1 mmol of 3-oxo-1,3-diphenylpropane-1-sulfonic acid (**4a-f**) were dissolved in 1ml of MeOH and then 0.5 mmol (0.25 ml) of trimethylsilyl diazomethane was added. The reaction was stirred for 2 hours then the solvent was removed under reduced pressure and in high vacuum. The methylated sulfonic acids (***Me*-4a–f**) obtained were purified by column chromatography.

Methyl 8-(4-hydroxy-3-methylphenyl)-6-oxooctane-4-sulfonate (*Me*-4a)



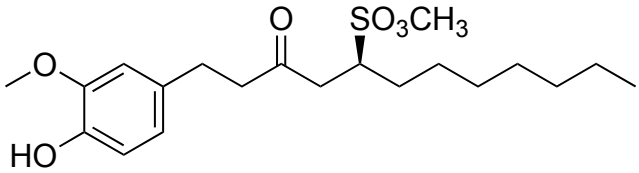
Pale yellow oil (10 mg, 30%) ^{1}H NMR (400 MHz, MeOD) δ 6.77 (d, *J* = 1 Hz, 1H), 6.69 (d, *J* = 8 Hz, 1H), 6.61 (dd, *J* = 8, 2 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.03 (dd, *J* = 18, 6 Hz, 1H), 2.79 (s, 4H), 2.68 (dd, *J* = 18, 6 Hz, 1H), 1.87 – 1.81 (m, 1H), 1.59 – 1.47 (m, 1H), 1.38 – 1.34 (m, 3H), 0.90 (t, *J* = 7 Hz, 3H). ^{13}C NMR (101 MHz, MeOD) δ 207.9, 148.8, 145.8, 133.6, 121.7, 116.1, 113.1, 56.6, 56.3, 55.8, 45.5, 42.9, 32.7, 30.3, 20.7, 14.0. HRMS $C_{16}H_{24}O_6S$ requires *m/z* 344.1294 (E^+), found *m/z* 344.1299 (M^+); ESI *m/z* 344 (M^+).

Methyl 1-(4-hydroxy-3-methoxyphenyl)-3-oxodecane-5-sulfonate (*Me*-4b)



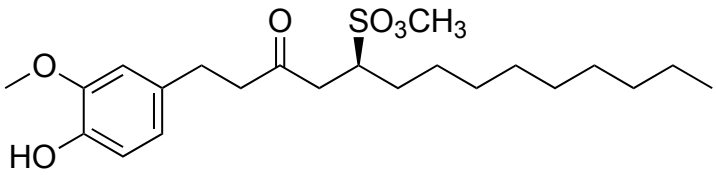
Pale yellow oil (13 mg, 36%) ^{1}H NMR (400 MHz, MeOD) δ 6.77 (d, *J* = 1 Hz, 1H), 6.69 (d, *J* = 8 Hz, 1H), 6.62 (dd, *J* = 8, 1 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 4H), 3.04 (dd, *J* = 18, 6 Hz, 1H), 2.80 (s, 4H), 2.69 (dd, *J* = 18, 6 Hz, 1H), 1.89 – 1.82 (m, 1H), 1.61 – 1.49 (m, 1H), 1.41 – 1.22 (m, 8H), 0.89 (t, *J* = 7 Hz, 4H); ^{13}C NMR (101 MHz, MeOD) δ 207.9, 148.8, 145.8, 133.6, 121.7, 116.1, 113.1, 56.6, 56.3, 55.9, 45.5, 42.9, 32.5, 30.6, 30.3, 27.1, 23.3, 14.30. HRMS $C_{18}H_{28}O_6S$ requires *m/z* 372.1607 (E^+), found *m/z* 372.1610 (M^+); ESI *m/z* 372 (M^+).

Methyl 1-(4-hydroxy-3-methoxyphenyl)-3-oxododecane-5-sulfonate (*Me*-4c)



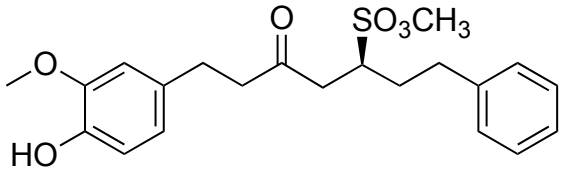
Pale yellow oil (13 mg, 32%) ^{1}H NMR (400 MHz, MeOD) δ 6.77 (s, 1H), 6.69 (d, *J* = 8 Hz, 1H), 6.61 (dd, *J* = 8, 1 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.04 (dd, *J* = 18, 6 Hz, 1H), 2.79 (s, 4H), 2.69 (dd, *J* = 18, 6 Hz, 1H), 1.89 – 1.84 (m, 1H), 1.55 – 1.53 (m, 1H), 1.35 – 1.27 (m, 12H), 0.89 (t, *J* = 7 Hz, 3H). ^{13}C NMR (101 MHz, MeOD) δ 207.8, 148.8, 145.8, 133.6, 121.7, 116.1, 113.1, 56.6, 56.3, 55.9, 45.5, 42.9, 32.8, 30.6, 30.3, 30.0, 27.4, 23.6, 14.4. HRMS $C_{20}H_{32}O_6S$ requires *m/z* 400.1920 (E^+), found *m/z* 400.1916 (M^+); ESI *m/z* 400 (M^+).

Methyl 1-(4-hydroxy-3-methoxyphenyl)-3-oxotetradecane-5-sulfonate (*Me*-4d)



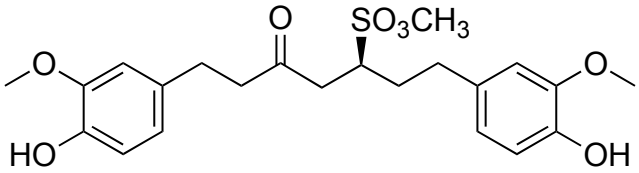
Pale yellow oil (12 mg, 28%) ^{1}H NMR (400 MHz, MeOD) δ 6.77 (s, 1H), 6.69 (d, *J* = 8 Hz, 1H), 6.61 (dd, *J* = 8, 1 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.04 (dd, *J* = 18, 6 Hz, 1H), 2.79 (s, 4H), 2.69 (dd, *J* = 18, 6 Hz, 1H), 1.87 (td, *J* = 14, 6 Hz, 1H), 1.56 – 1.52 (m, 1H), 1.33 – 1.28 (m, 15H), 0.89 (t, *J* = 7 Hz, 3H). ^{13}C NMR (101 MHz, MeOD) δ 207.8, 148.8, 145.8, 133.6, 121.7, 116.1, 113.1, 56.6, 56.3, 55.9, 45.5, 42.9, 33.0, 30.6, 30.5, 30.4, 30.3, 30.31, 27.4, 23.7, 14.5. HRMS $C_{22}H_{36}O_6S$ requires *m/z* 428.2233 (E^+), found *m/z* 428.229 (M^+); ESI *m/z* 428 (M^+).

Methyl 7-(4-hydroxy-3-methoxyphenyl)-5-oxo-1-phenylheptane-3-sulfonate (*Me*-4e)



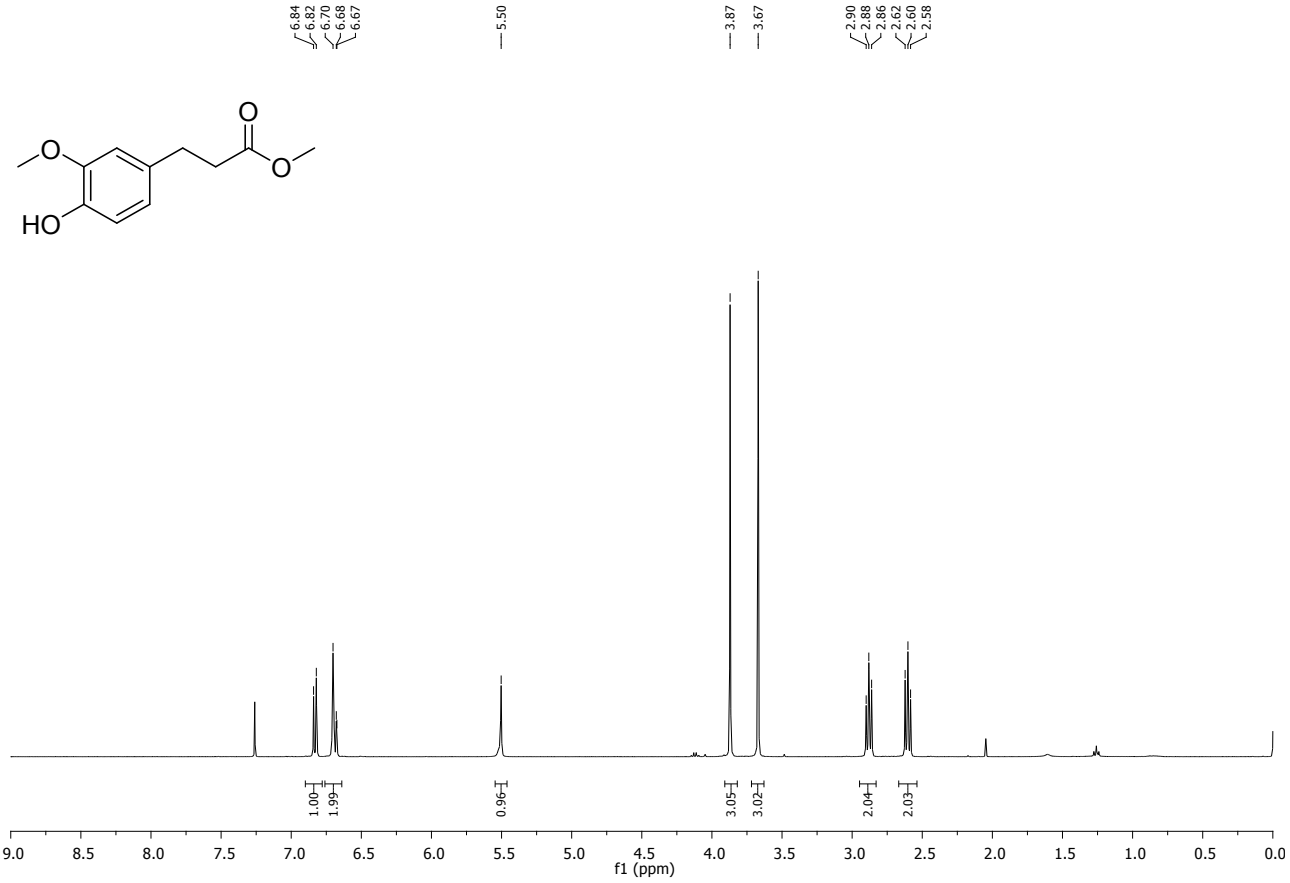
Pale yellow oil (15 mg, 36%) ^{1}H NMR (400 MHz, MeOD) δ 7.26 (t, *J* = 7 Hz, 2H), 7.16 (dd, *J* = 15, 7 Hz, 3H), 6.78 (d, *J* = 9 Hz, 1H), 6.69 (d, *J* = 8 Hz, 1H), 6.62 (d, *J* = 8 Hz, 1H), 3.85 – 3.76 (m, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.07 (dd, *J* = 18, 6 Hz, 1H), 2.77 (t, *J* = 3 Hz, 4H), 2.76 – 2.59 (m, 3H), 2.16 (ddd, *J* = 15, 10, 6 Hz, 1H), 1.86 (dt, *J* = 14, 7 Hz, 1H). ^{13}C NMR (101 MHz, MeOD) δ 207.7, 148.8, 145.8, 141.9, 133.7, 129.6, 129.5, 127.3, 121.7, 116.1, 113.1, 56.7, 56.3, 55.3, 45.4, 42.84, 33.4, 32.5, 30.3. HRMS $C_{21}H_{26}O_6S$ requires *m/z* 406.1450 (E^+), found *m/z* 406.1454 (M^+); ESI *m/z* 406 (M^+).

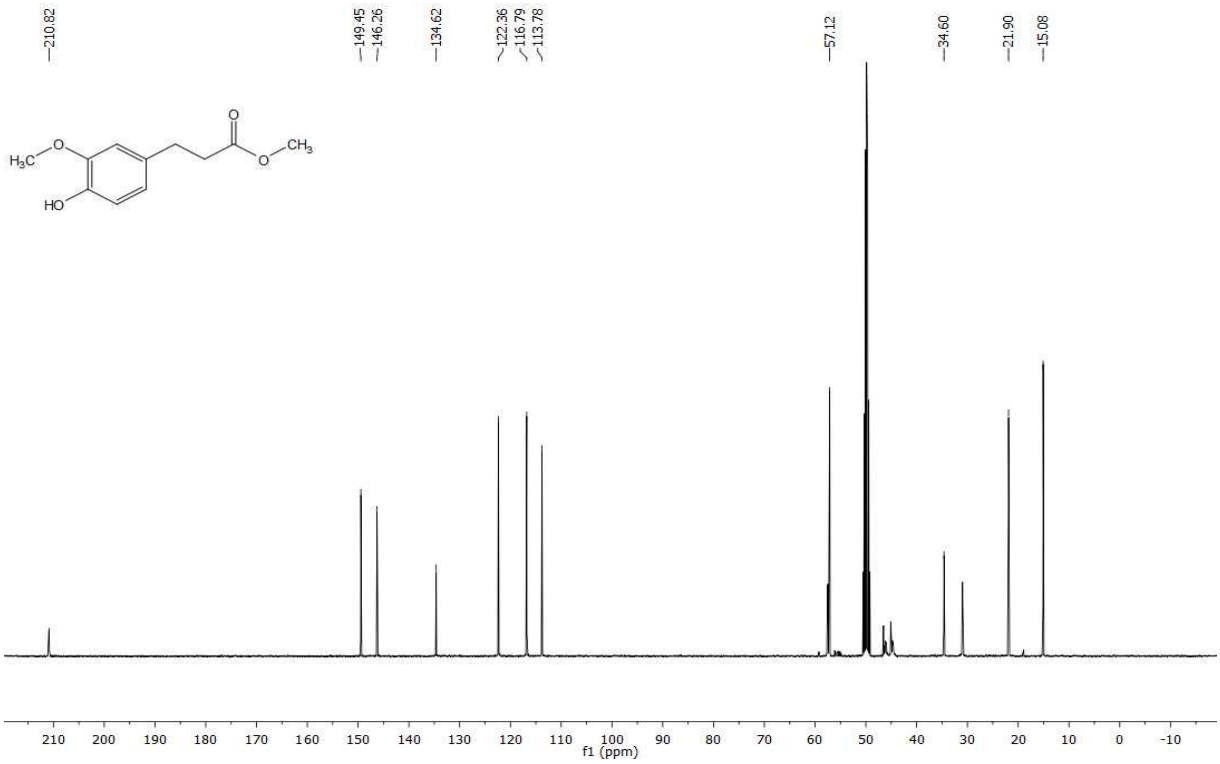
Methyl 1,7-bis(4-hydroxy-3-methoxyphenyl)-5-oxoheptane-3-sulfonate (*Me*-4f)



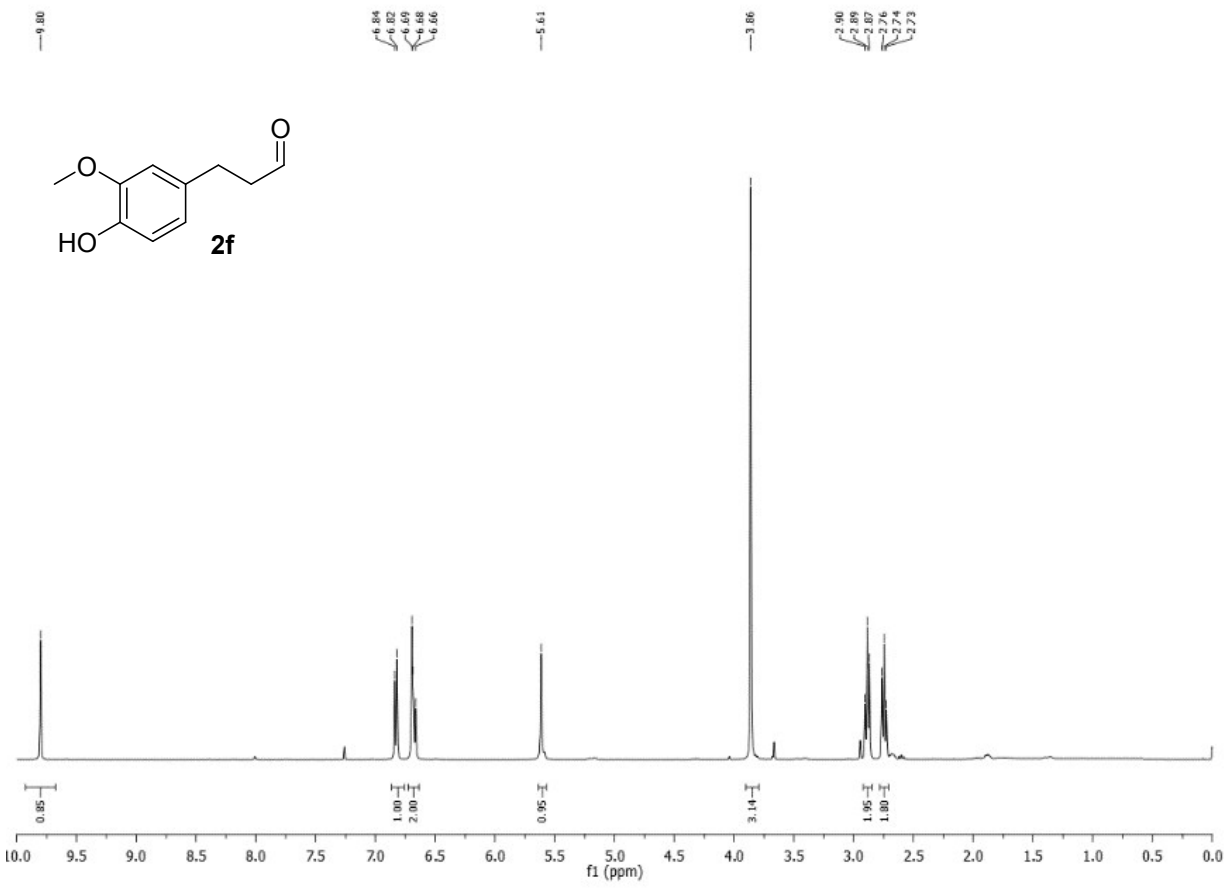
Pale yellow oil (17.1 mg, 51% yield) ^{1}H NMR (400 MHz, MeOD) δ 6.73 (dd, *J* = 13, 12 Hz, 2H), 6.68 (dd, *J* = 12, 4 Hz, 2H), 6.61 (dd, *J* = 13, 8 Hz, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.73 (s, 3H), 3.07 (dd, *J* = 19, 6 Hz, 1H), 2.78 (s, 4H), 2.73 (d, *J* = 5 Hz, 1H), 2.70 – 2.53 (m, 2H), 2.18 – 2.13 (m, 1H), 1.85 (td, *J* = 14, 8 Hz, 1H). ^{13}C NMR (101 MHz, MeOD) δ 207.8, 148.9, 148.8, 145.9, 145.8, 133.7, 133.2, 121.9, 121.7, 116.3, 116.2, 113.2, 113.1, 56.7, 56.3, 55.08, 54.8, 45.5, 42.8, 33.0, 32.5, 30.3. HRMS $C_{22}H_{28}O_8S$ requires *m/z* 452.1505 (E^+), found *m/z* 452.1509 (M^+); ESI *m/z* 452 (M^+).

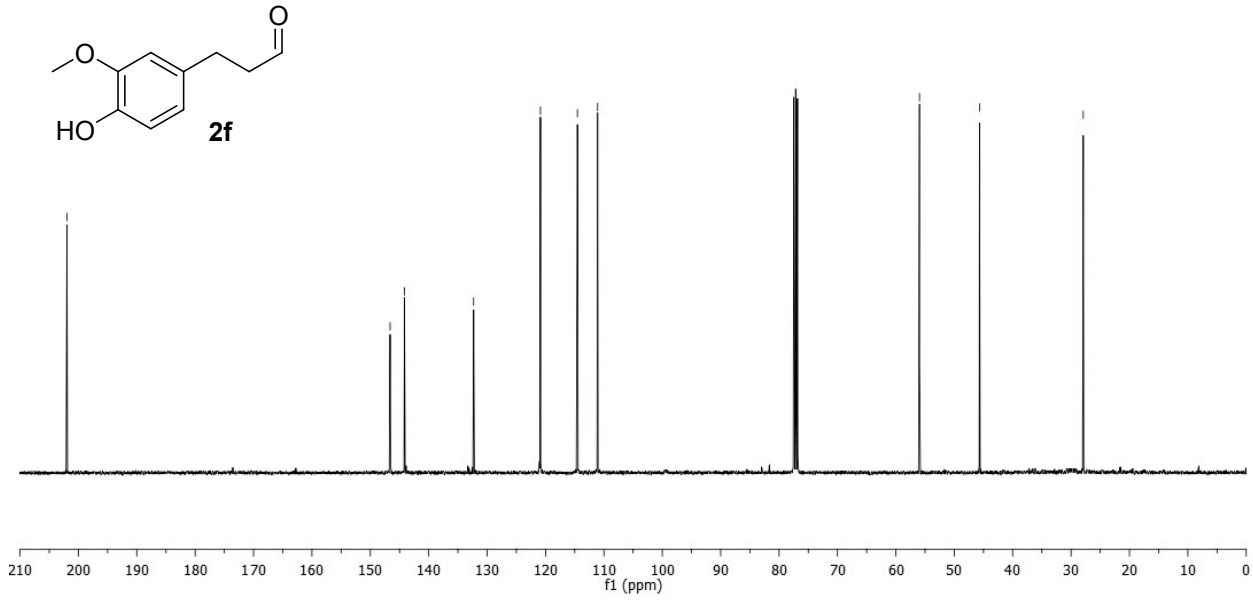
Methyl 3-(4-hydroxy-3-methoxyphenyl)propanoate



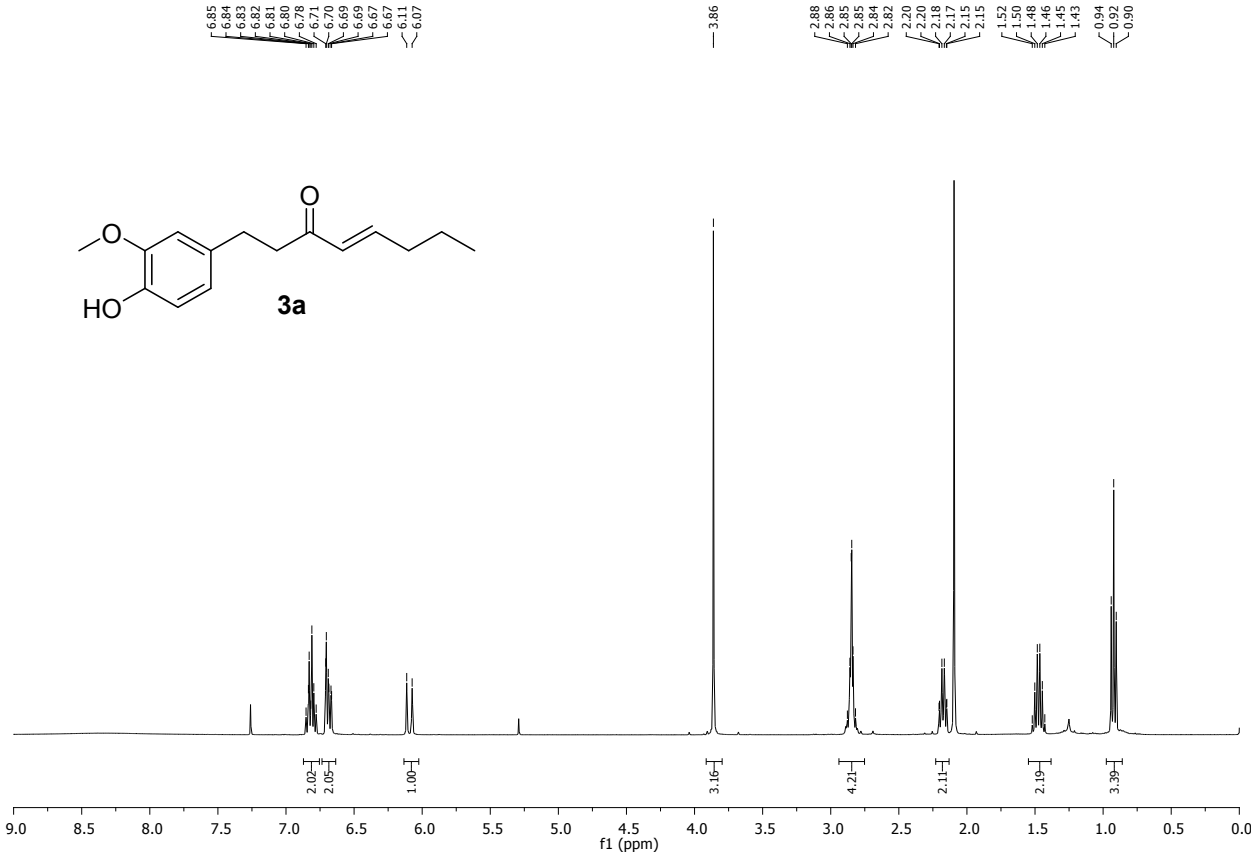


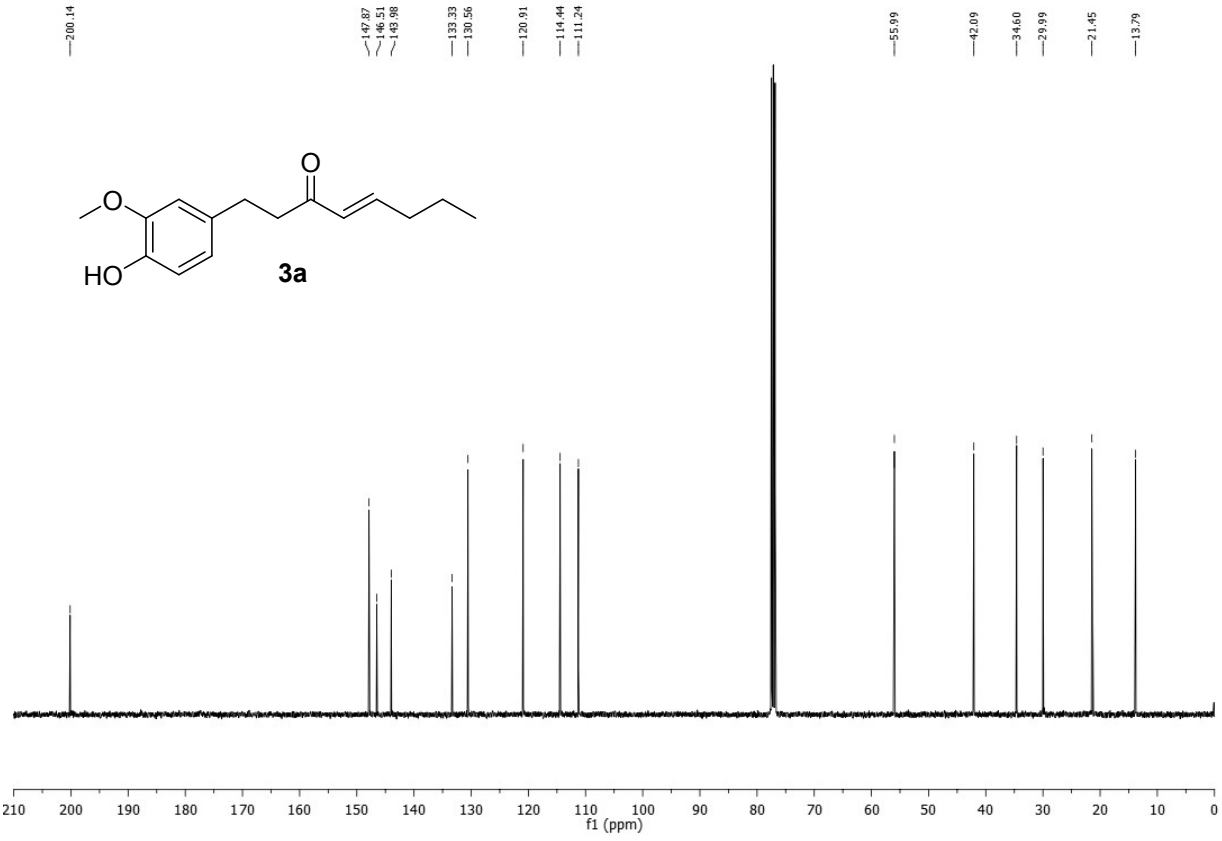
3-(4-hydroxy-3-methoxyphenyl)propanal (2f)



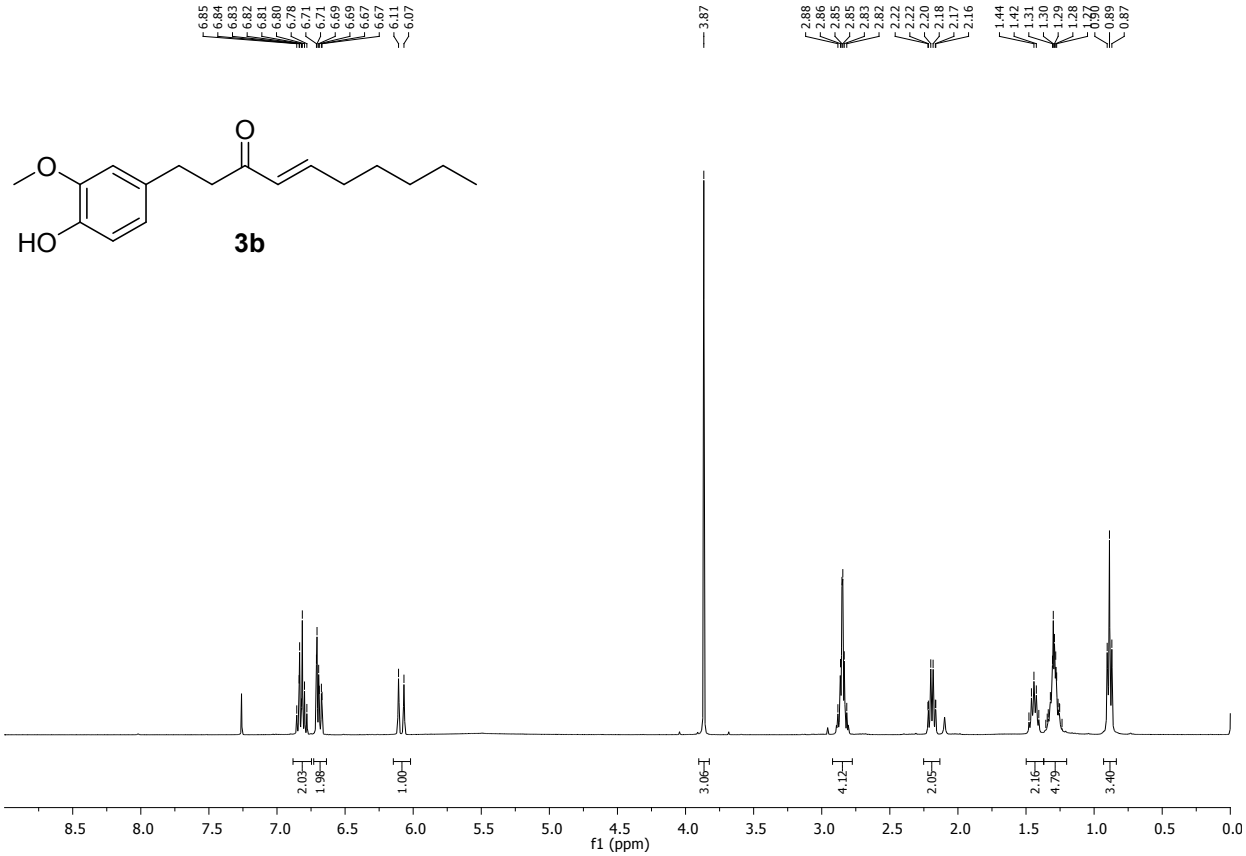


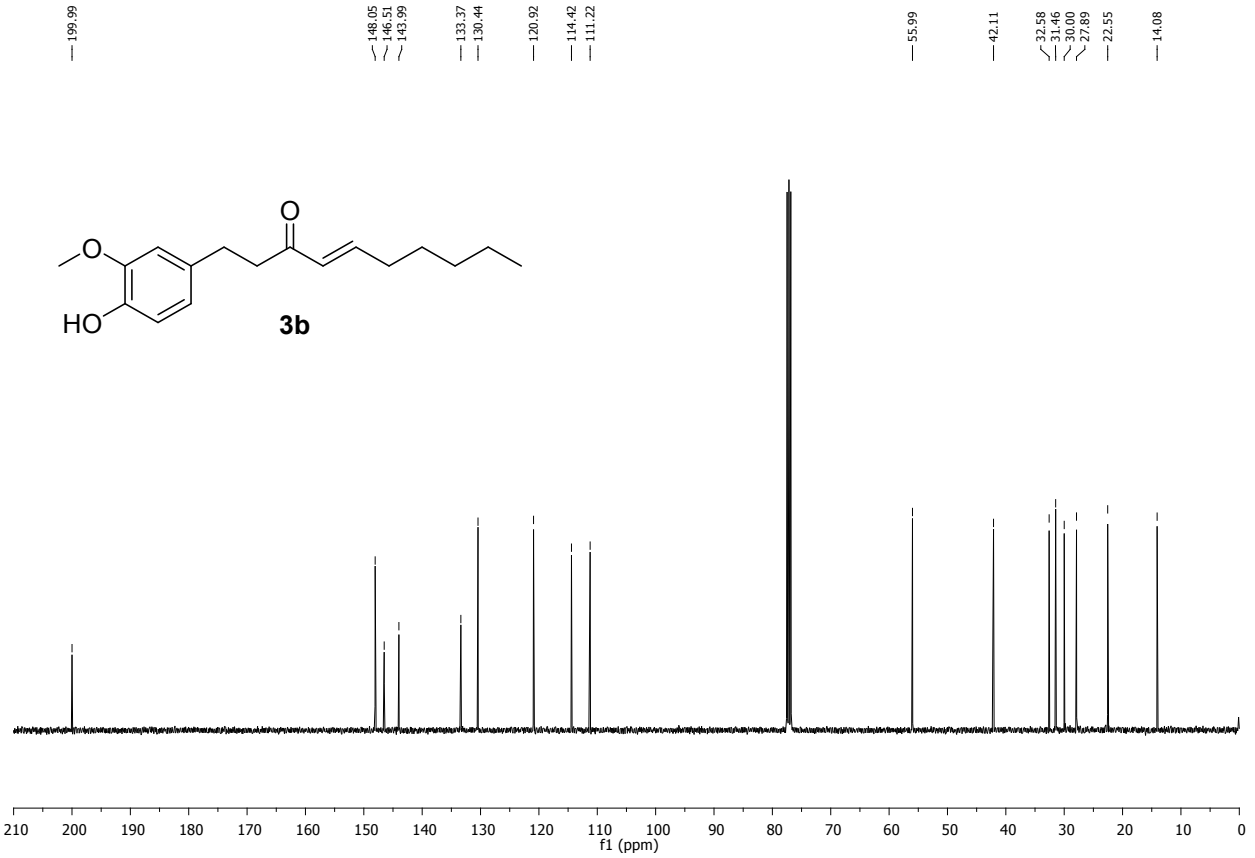
(*E*)-1-(4-hydroxy-3-methoxyphenyl)oct-4-en-3-one (3a)



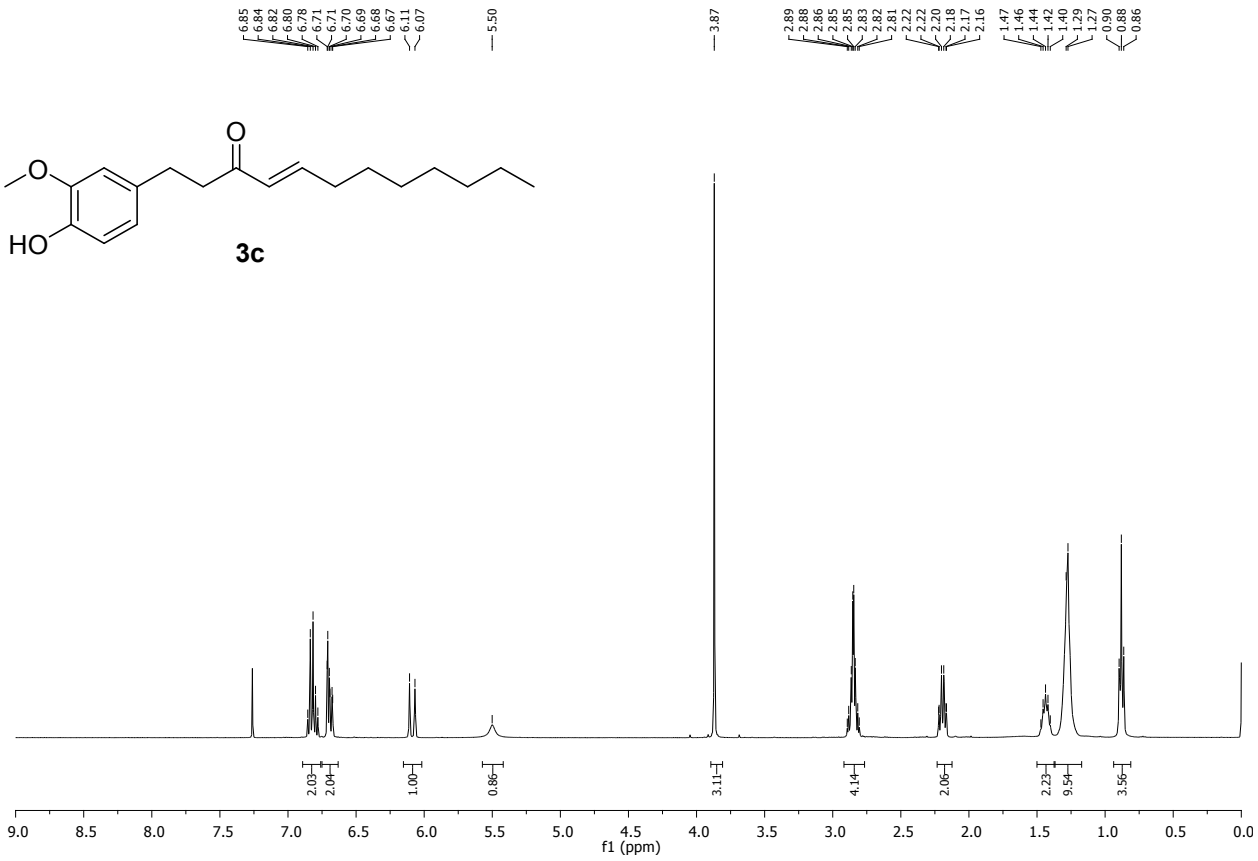


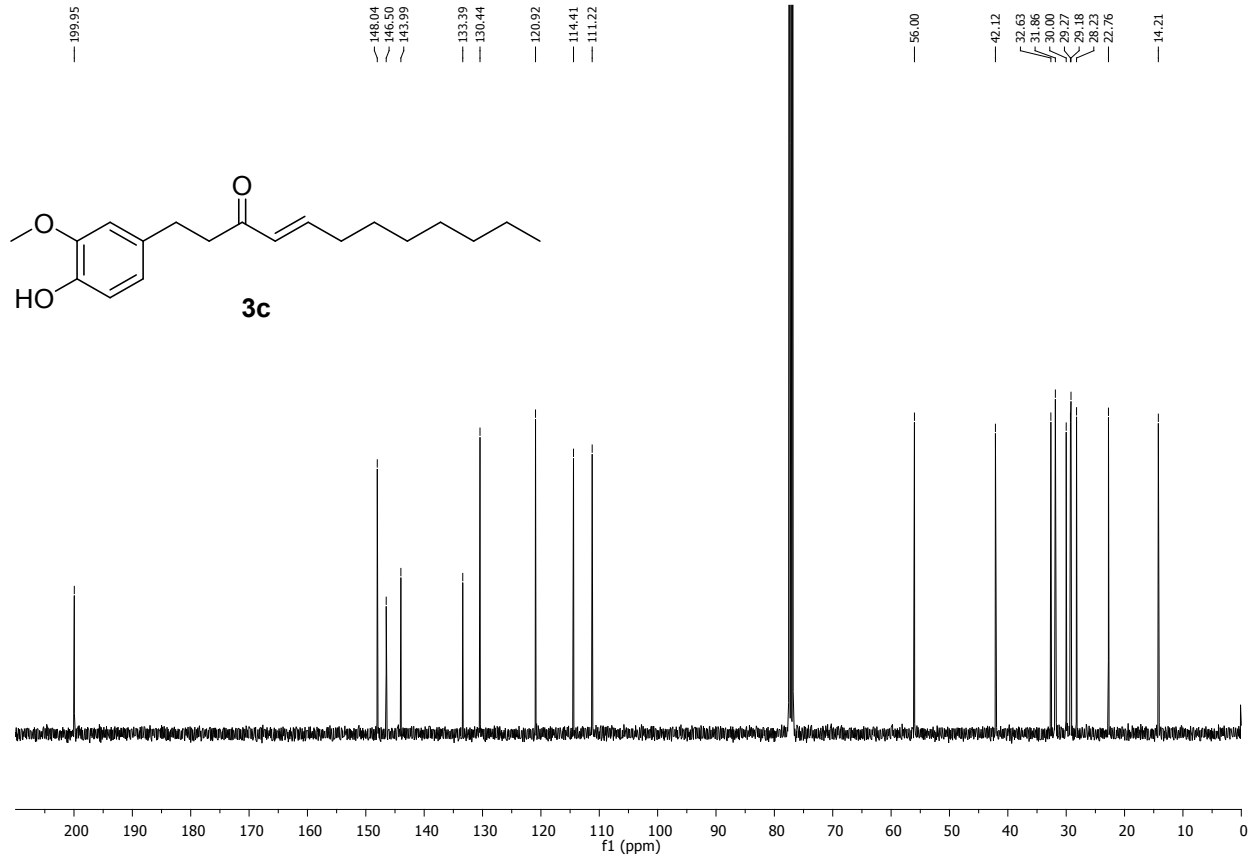
(*E*)-1-(4-hydroxy-3-methoxyphenyl)dec-4-en-3-one (3b)



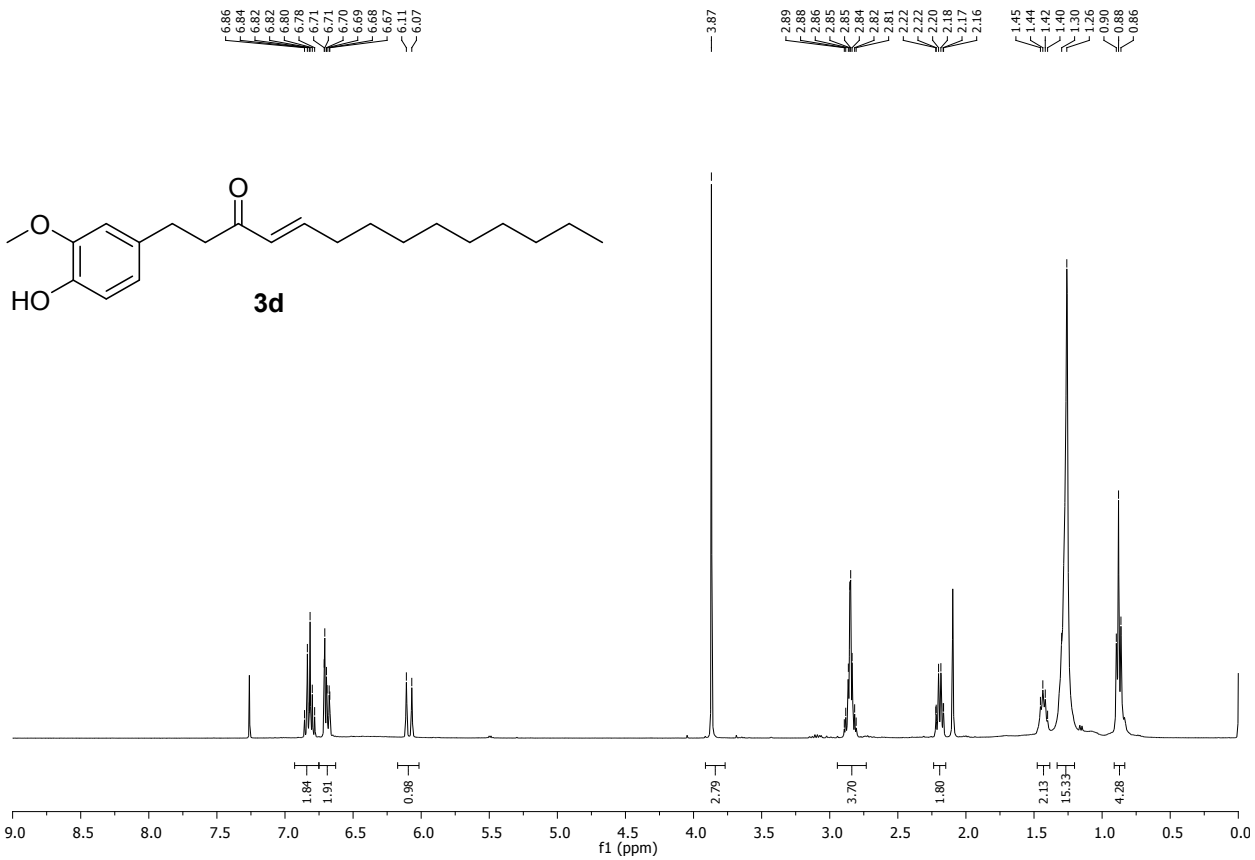


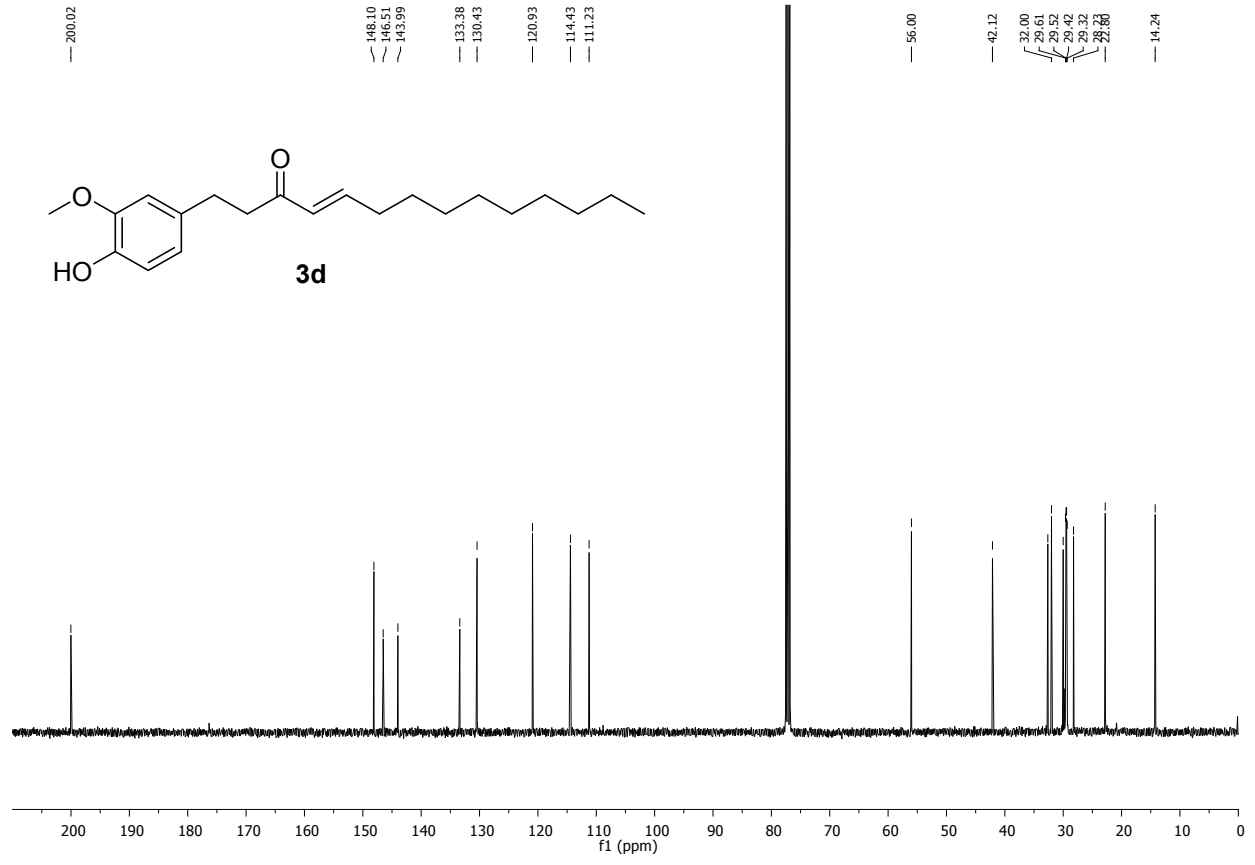
(*E*)-1-(4-hydroxy-3-methoxyphenyl)dodec-4-en-3-one (3c)



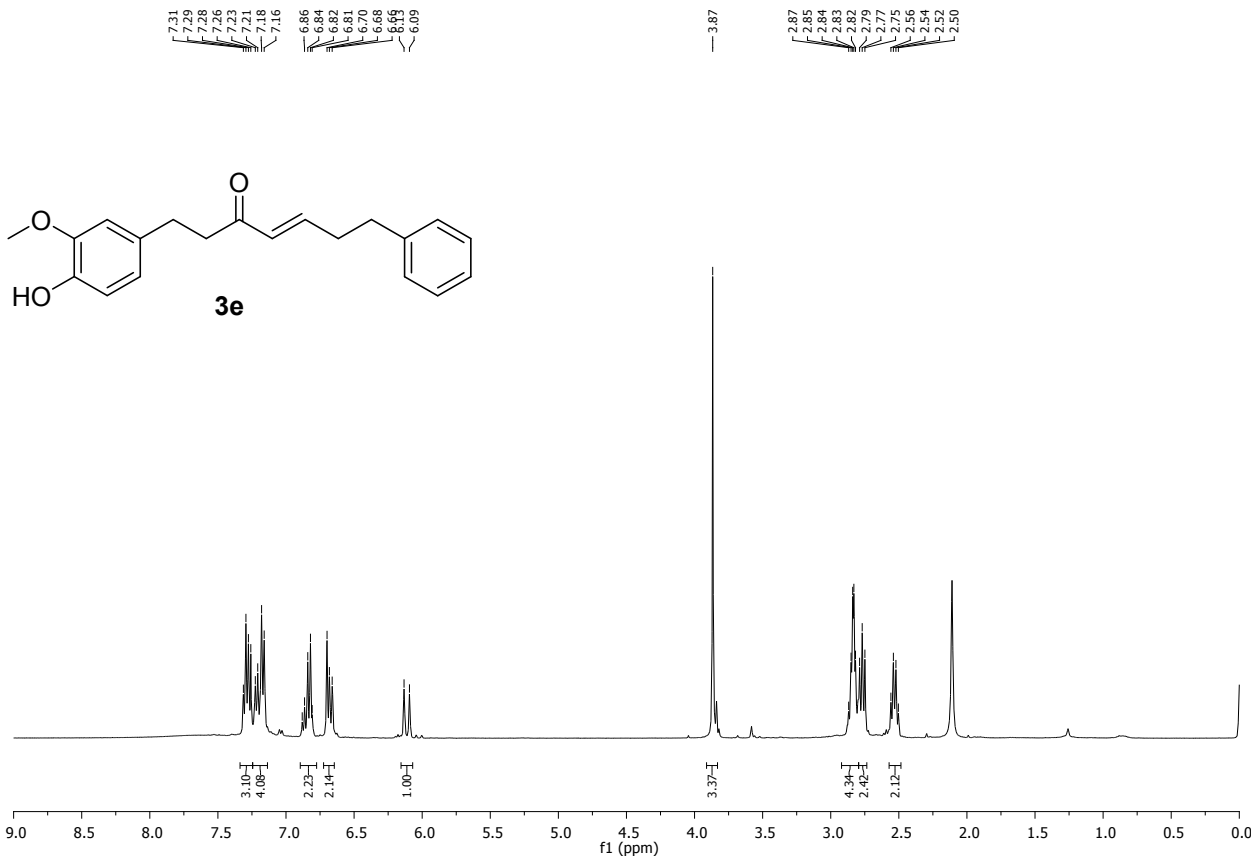


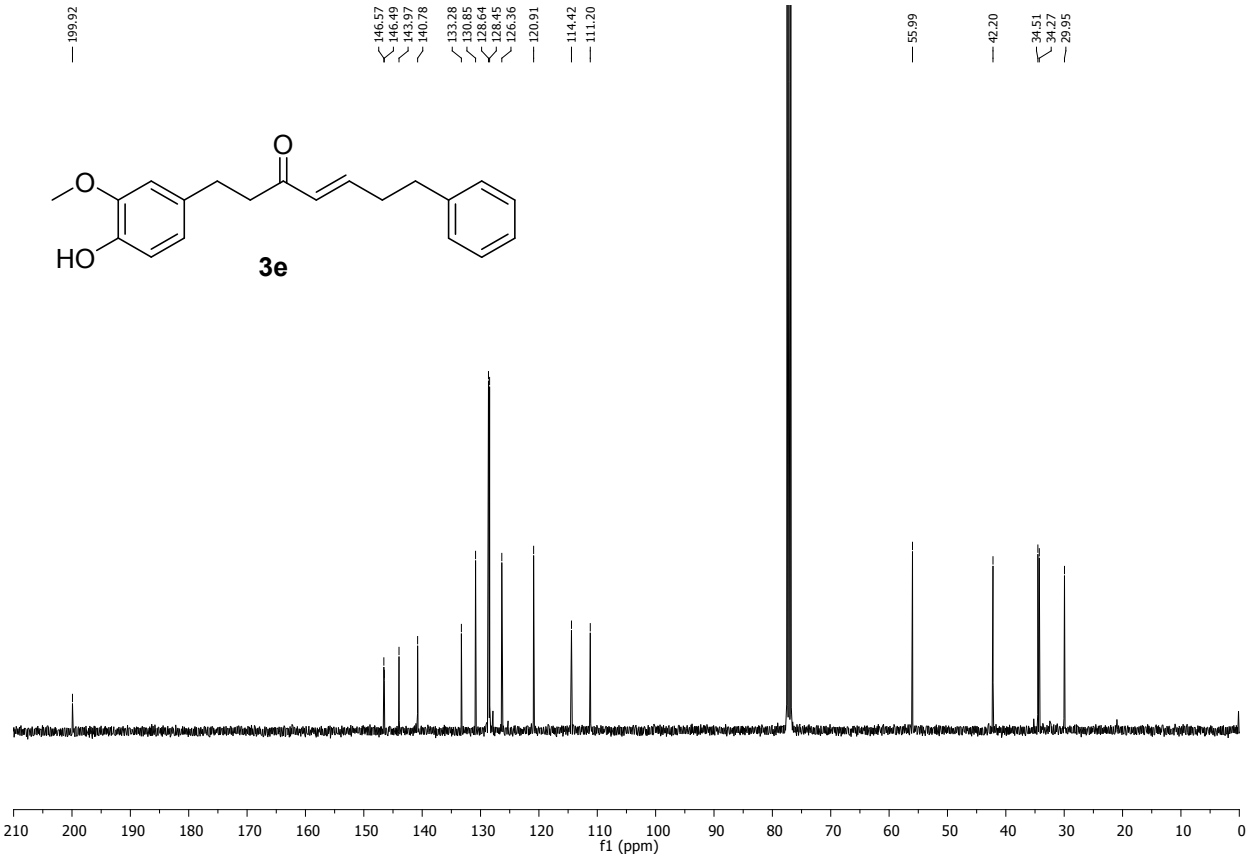
(*E*)-1-(4-hydroxy-3-methoxyphenyl)tetradec-4-en-3-one (3d)





(*E*)-1-(4-hydroxy-3-methoxyphenyl)-7-phenylhept-4-en-3-one (3e)





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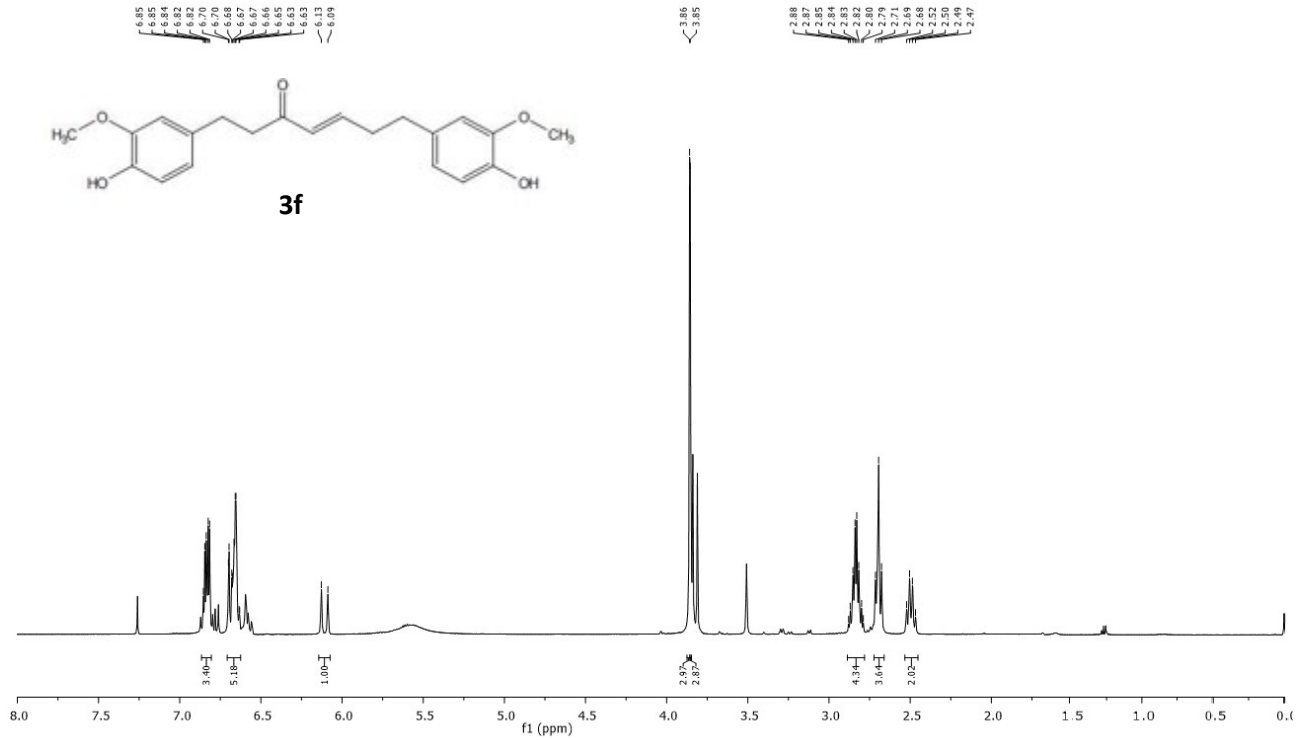
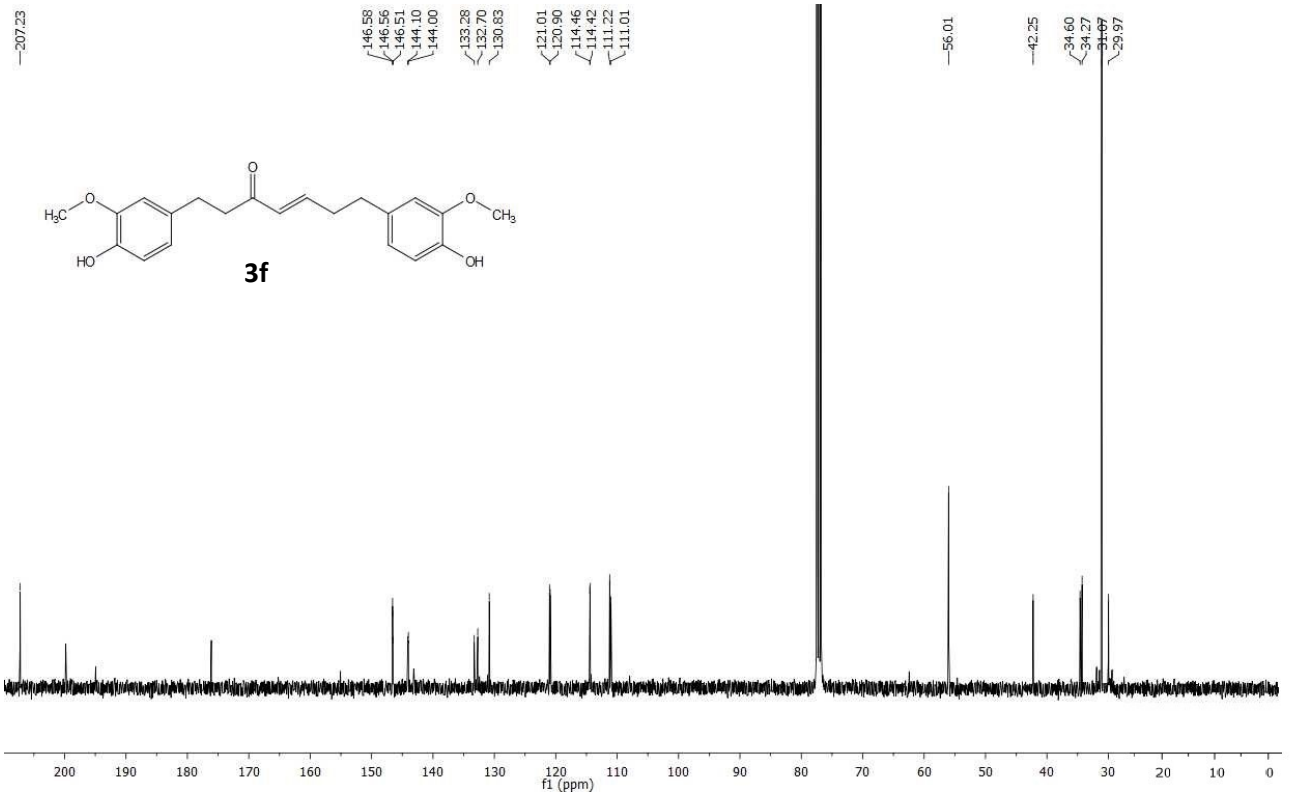
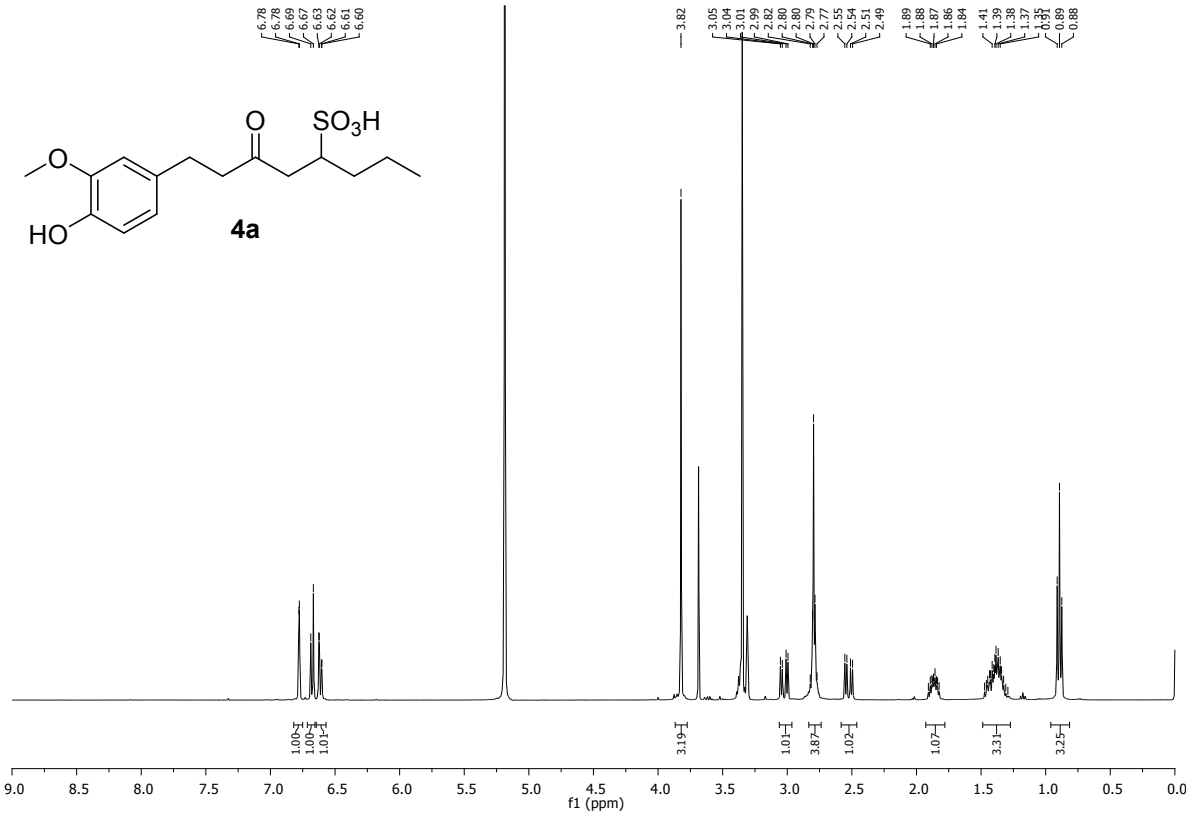
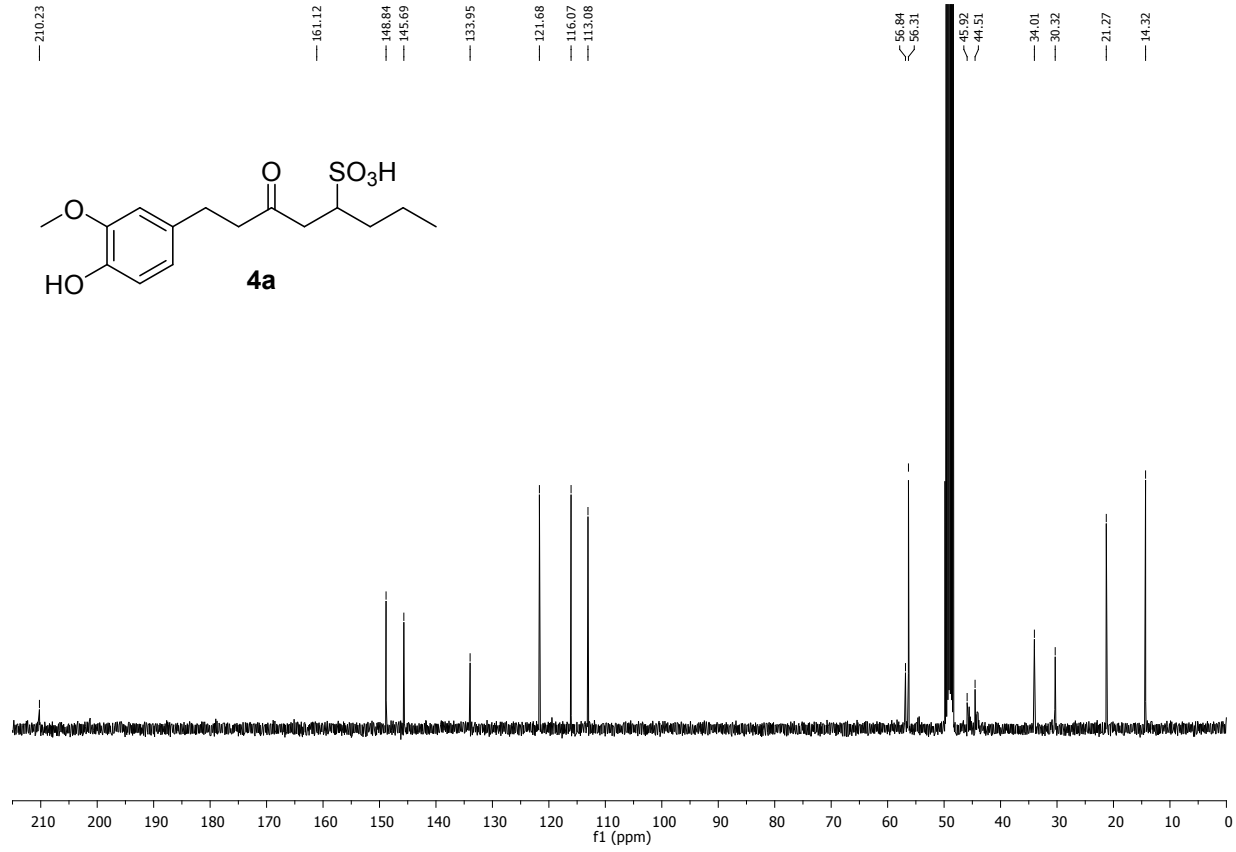
(*E*)-1,7-bis(4-hydroxy-3-methoxyphenyl)hept-4-en-3-one (3f)



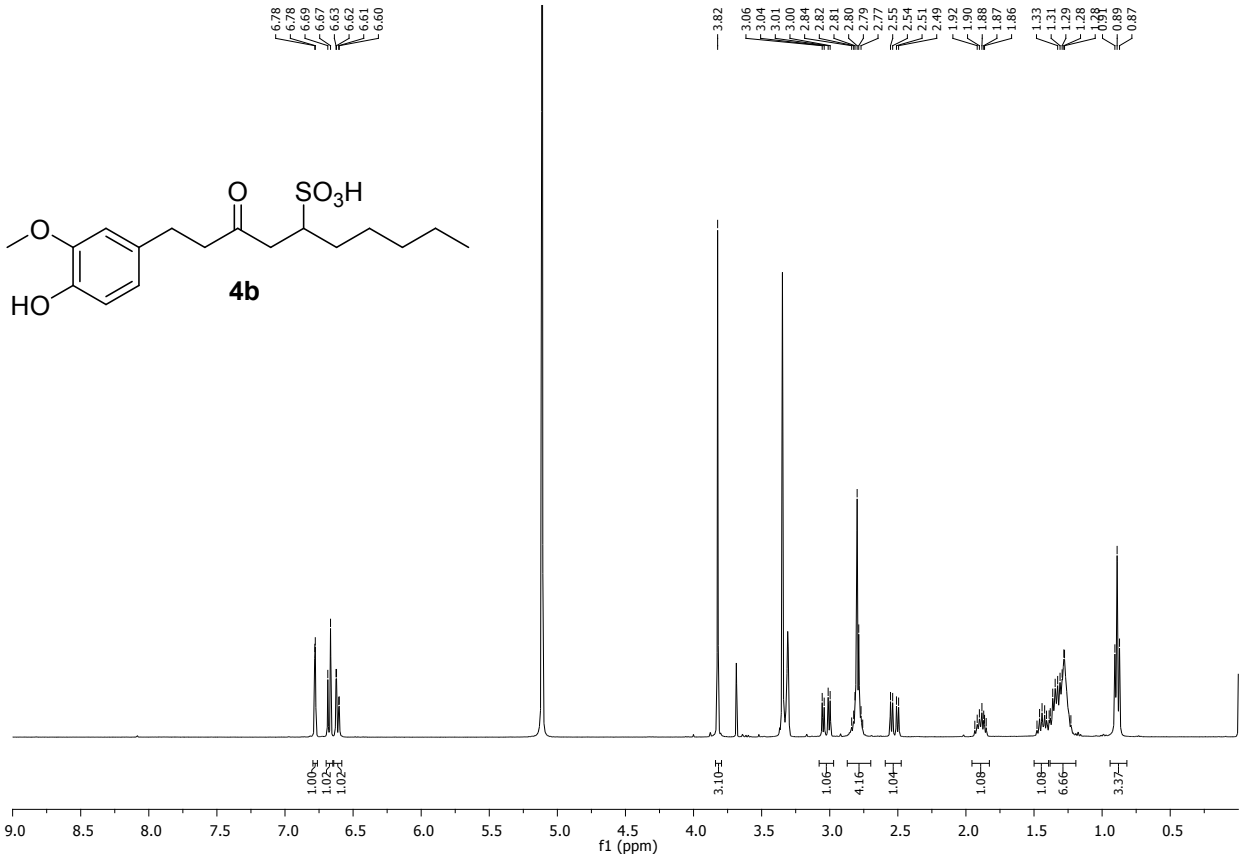


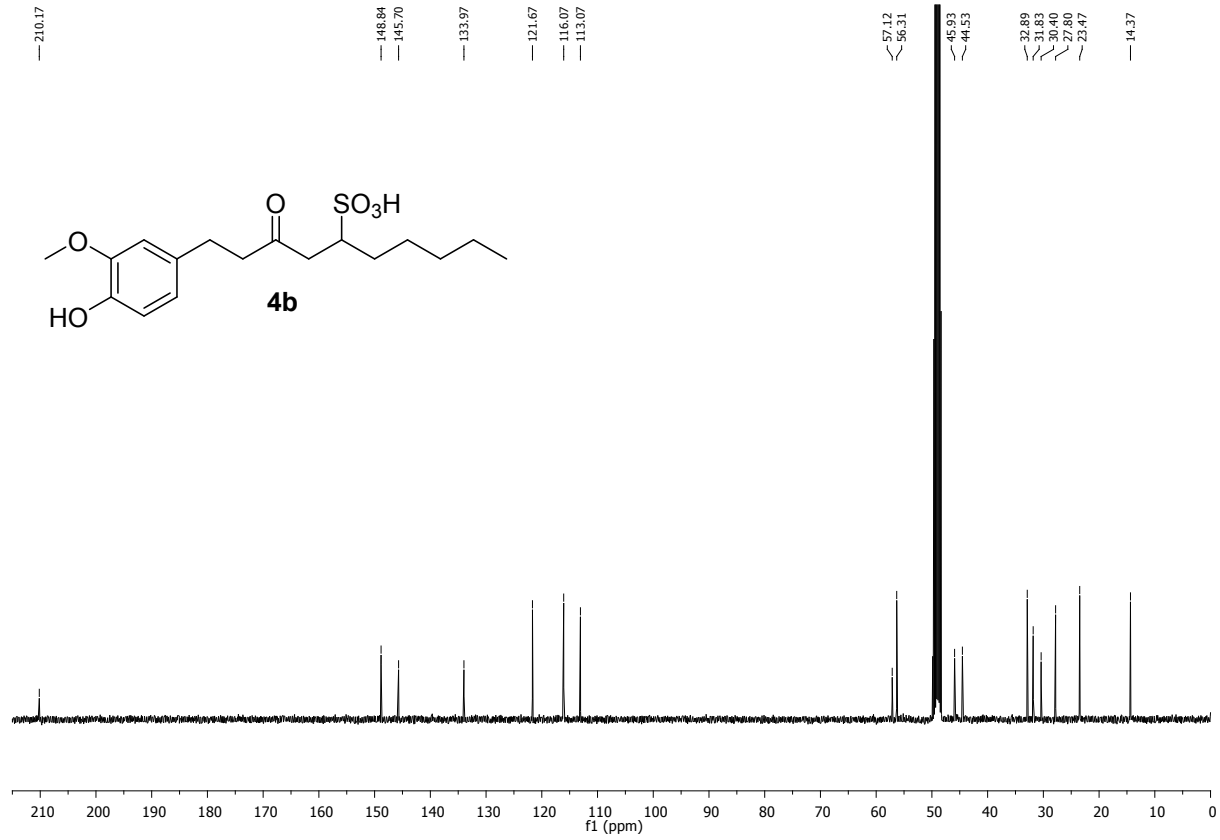
8-(4-hydroxy-3-methoxyphenyl)-6-oxooctane-4-sulfonic acid (4a)



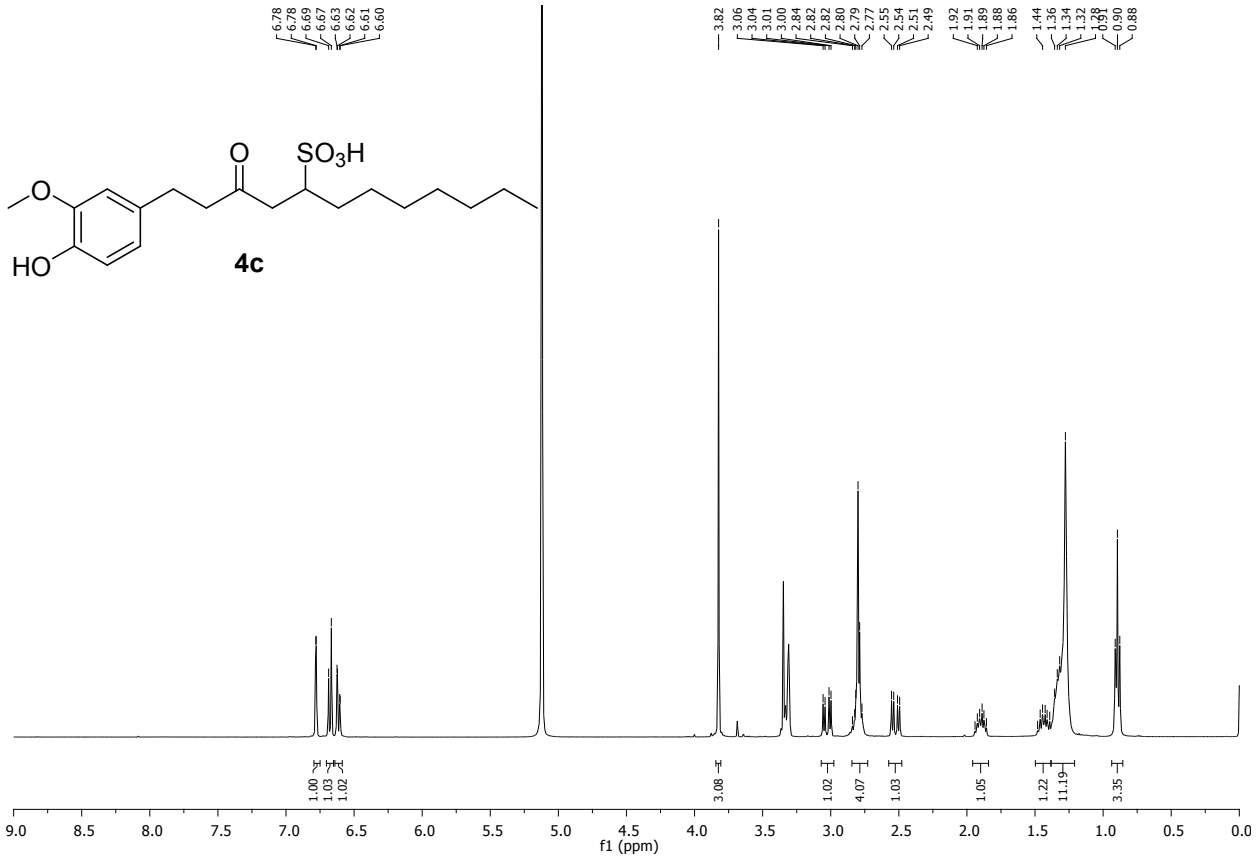


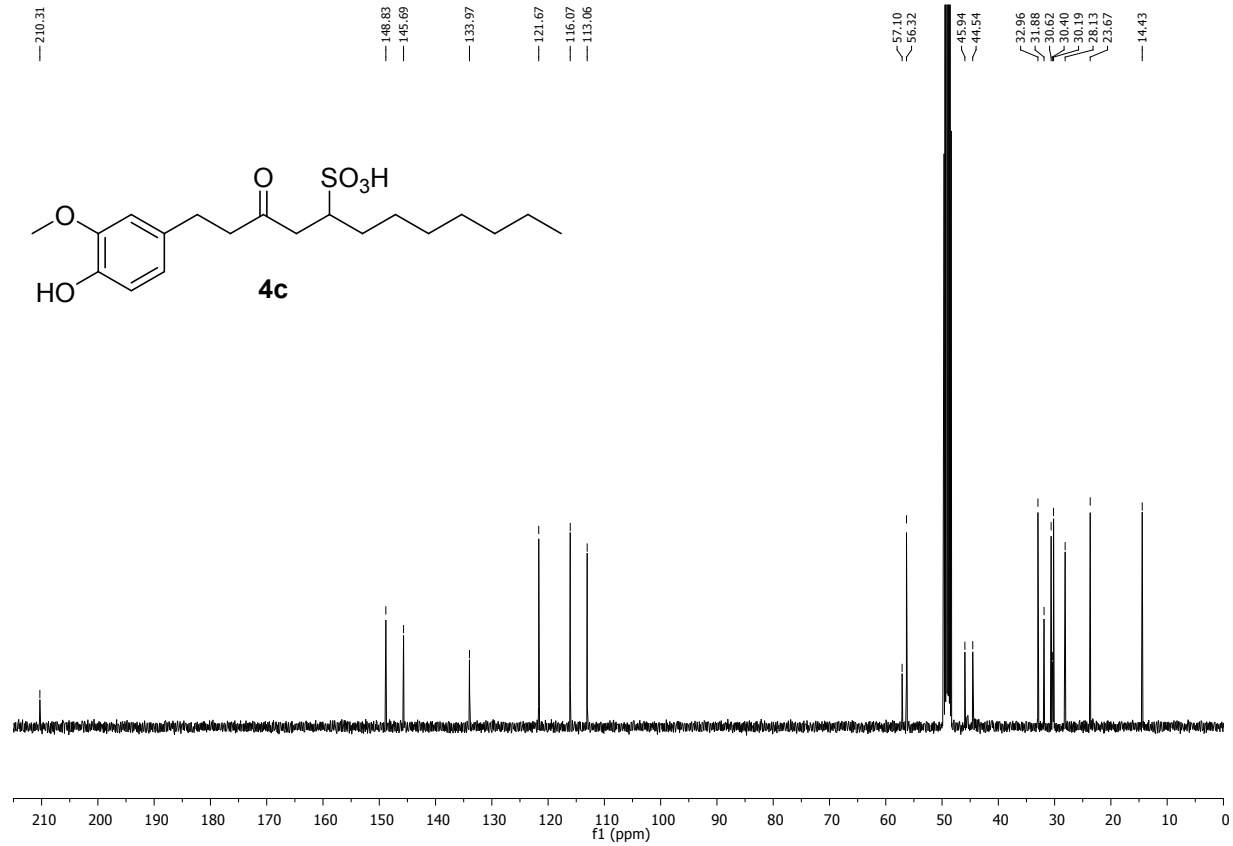
1-(4-hydroxy-3-methoxyphenyl)-3-oxodecane-5-sulfonic acid (4b)



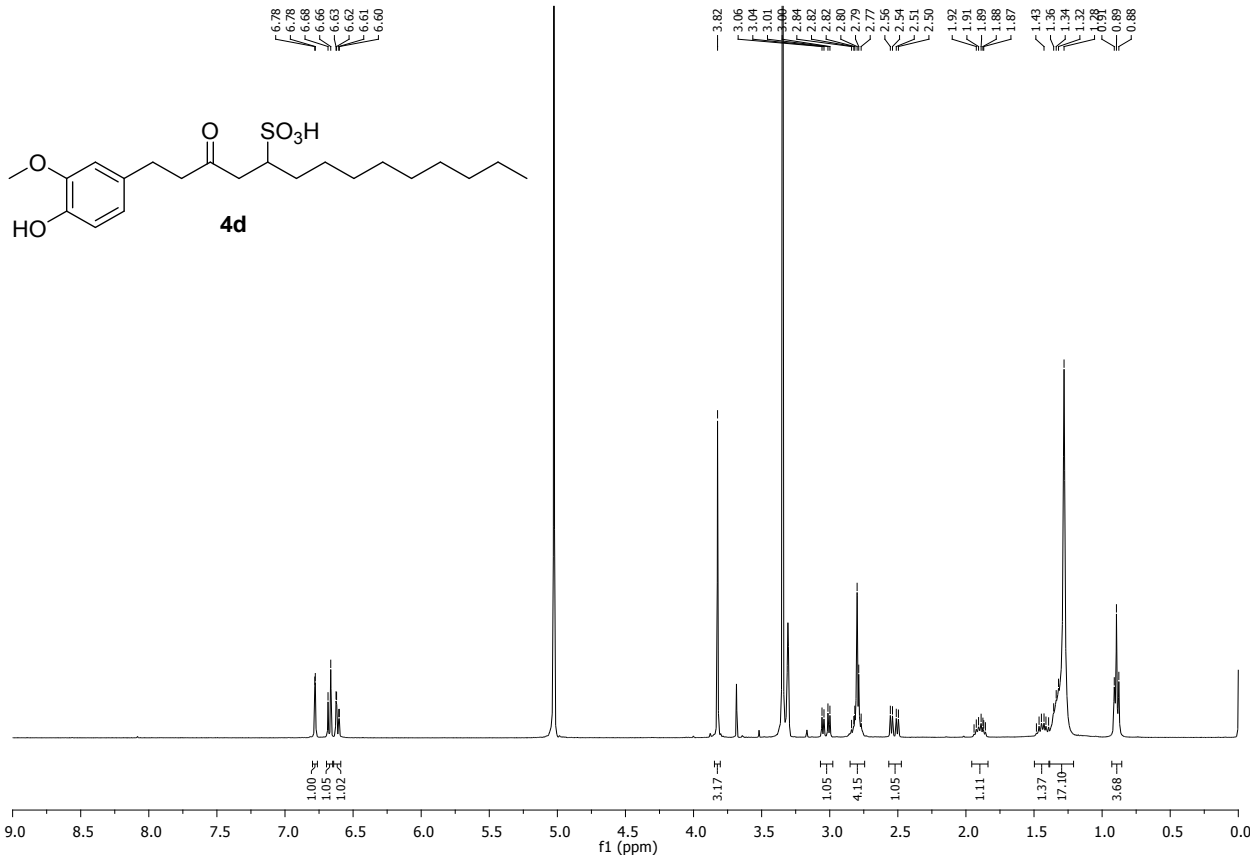


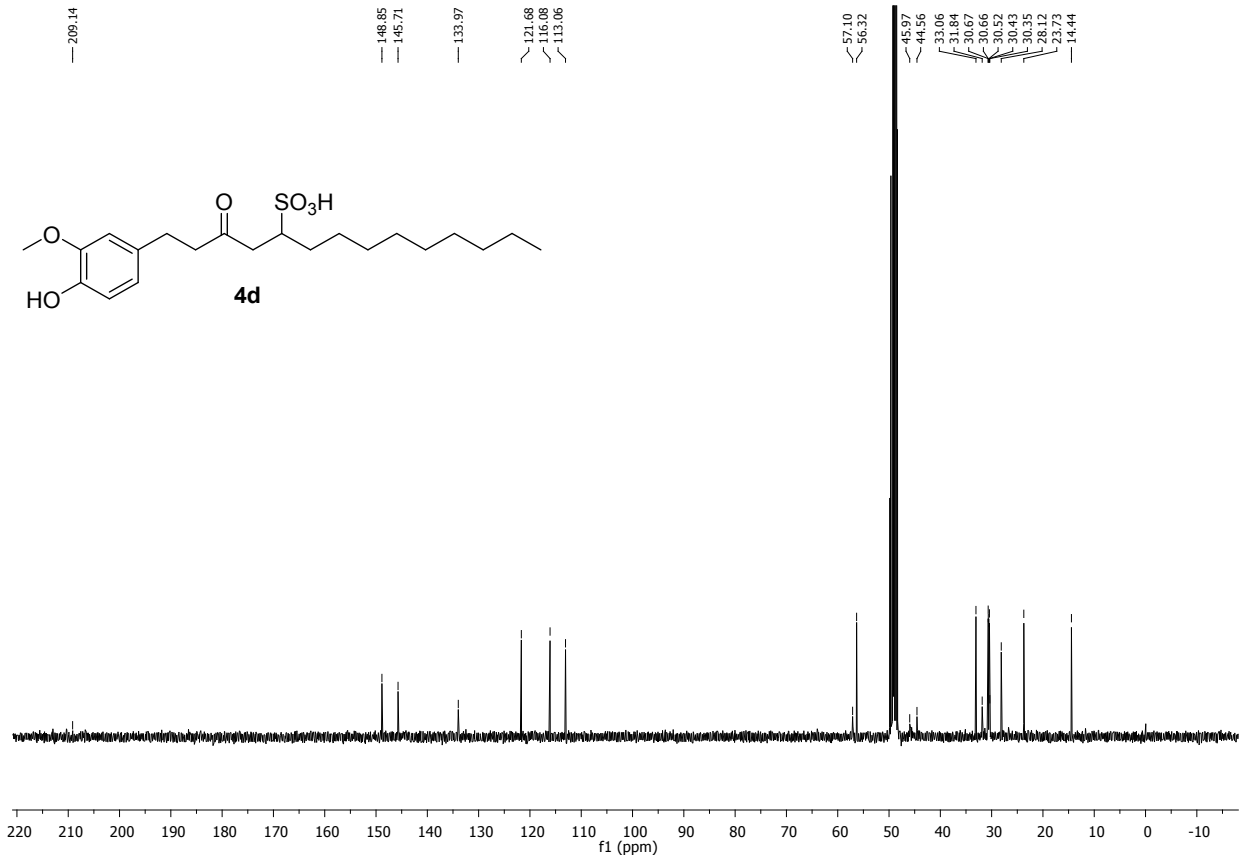
1-(4-hydroxy-3-methoxyphenyl)-3-oxododecane-5-sulfonic acid (4c)



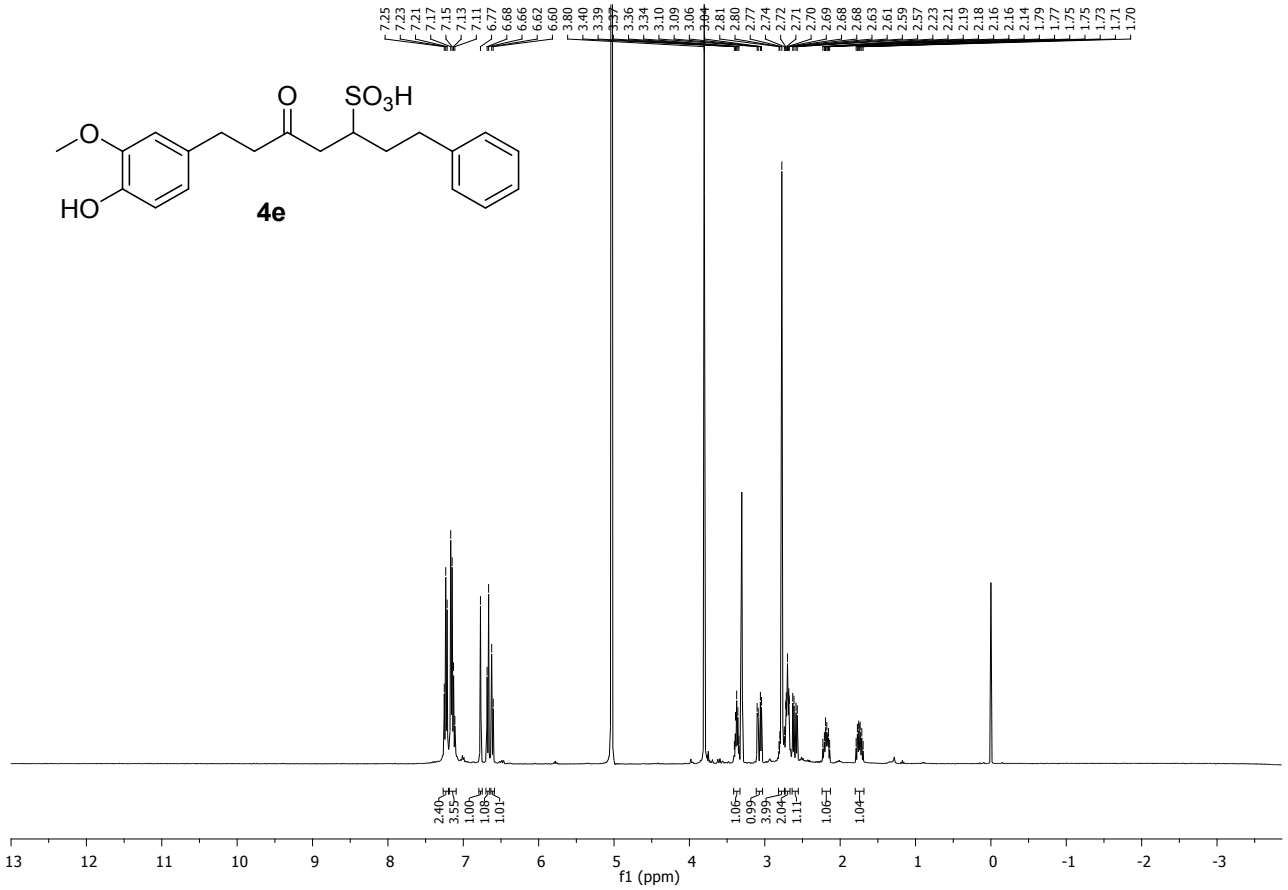


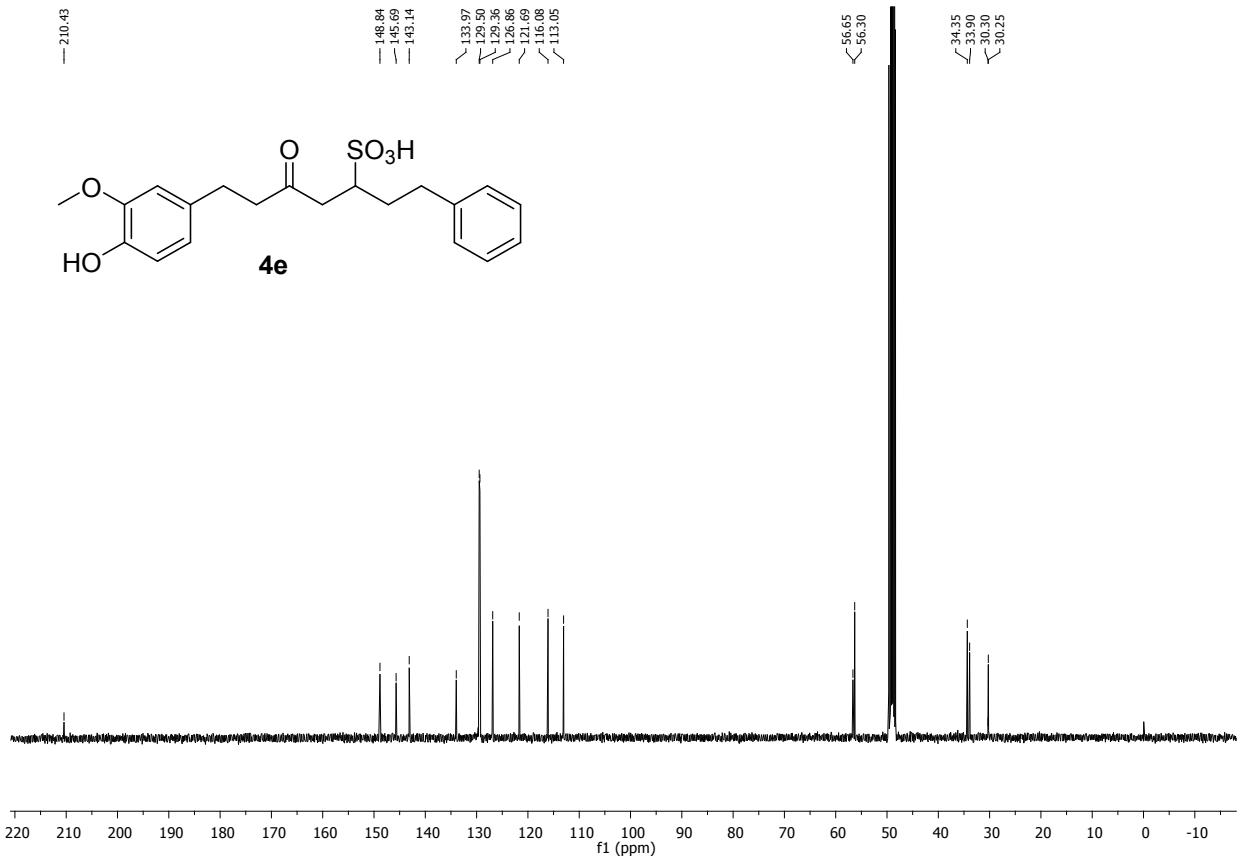
1-(4-hydroxy-3-methoxyphenyl)-3-oxotetradecane-5-sulfonic acid (4d)



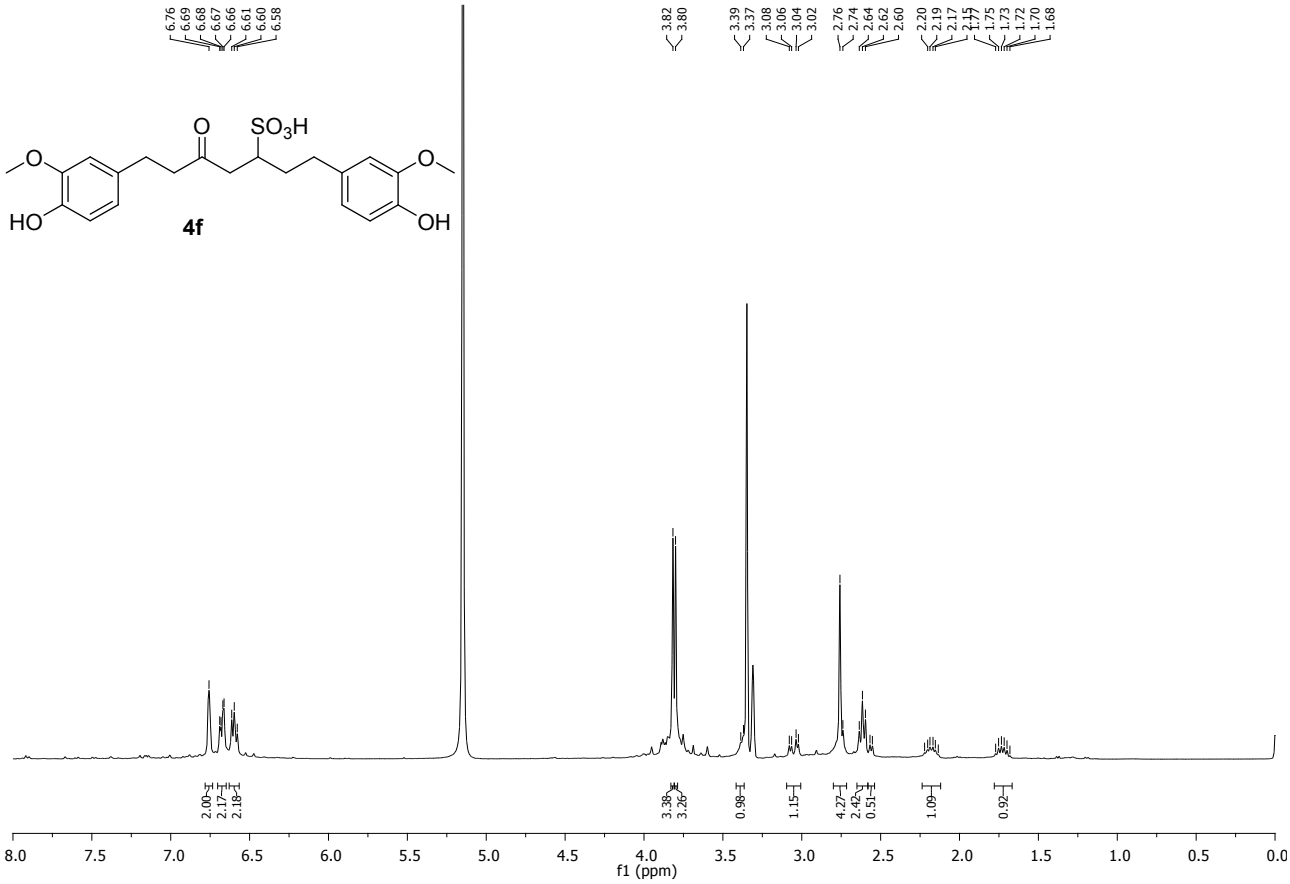


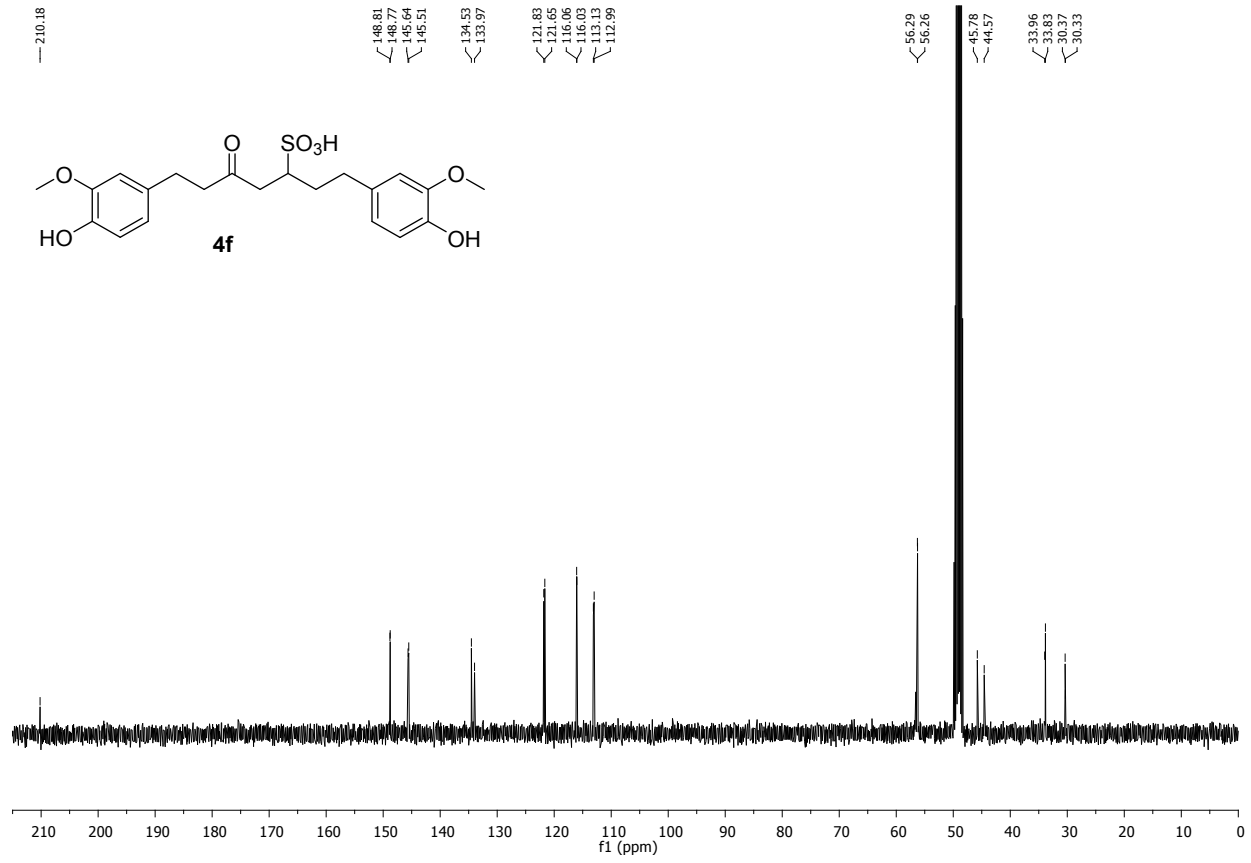
7-(4-hydroxy-3-methoxyphenyl)-5-oxo-1-phenylheptane-3-sulfonic acid (4e)



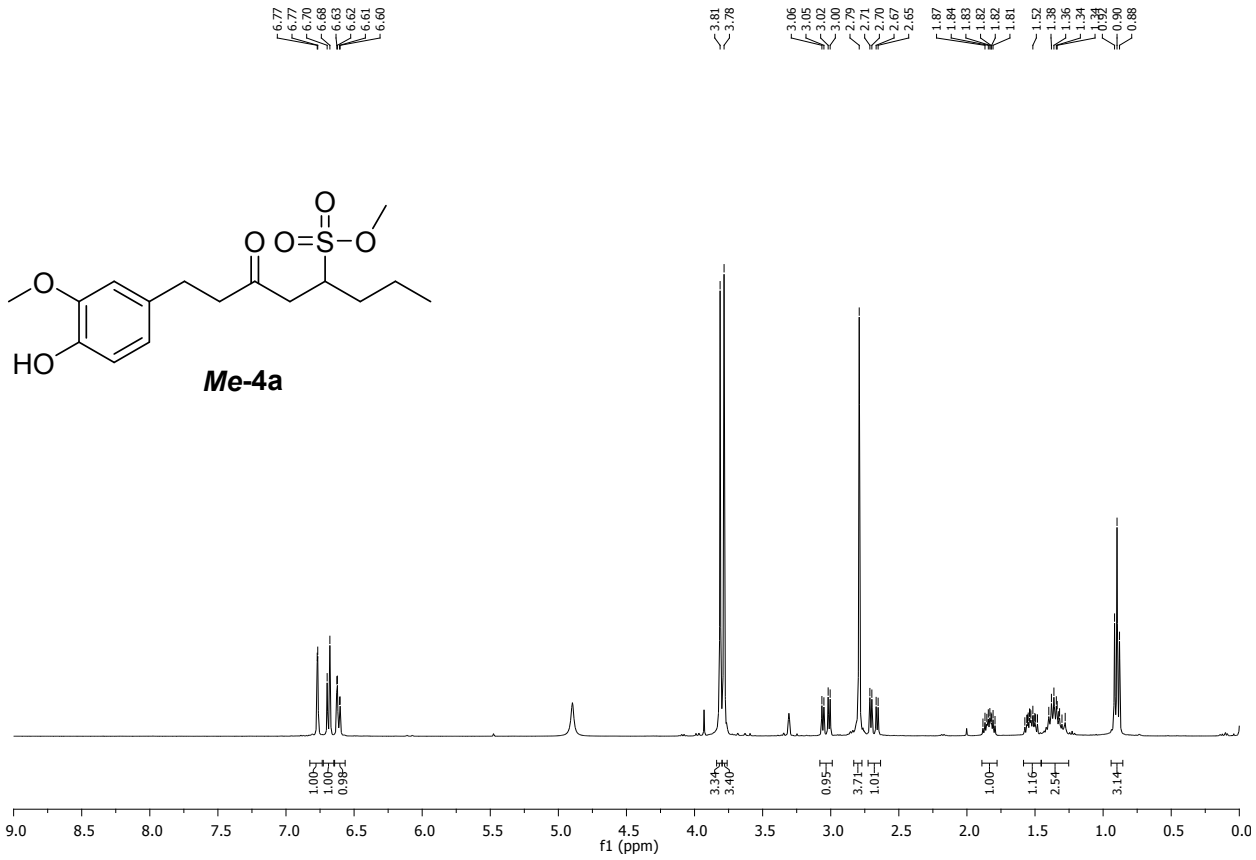


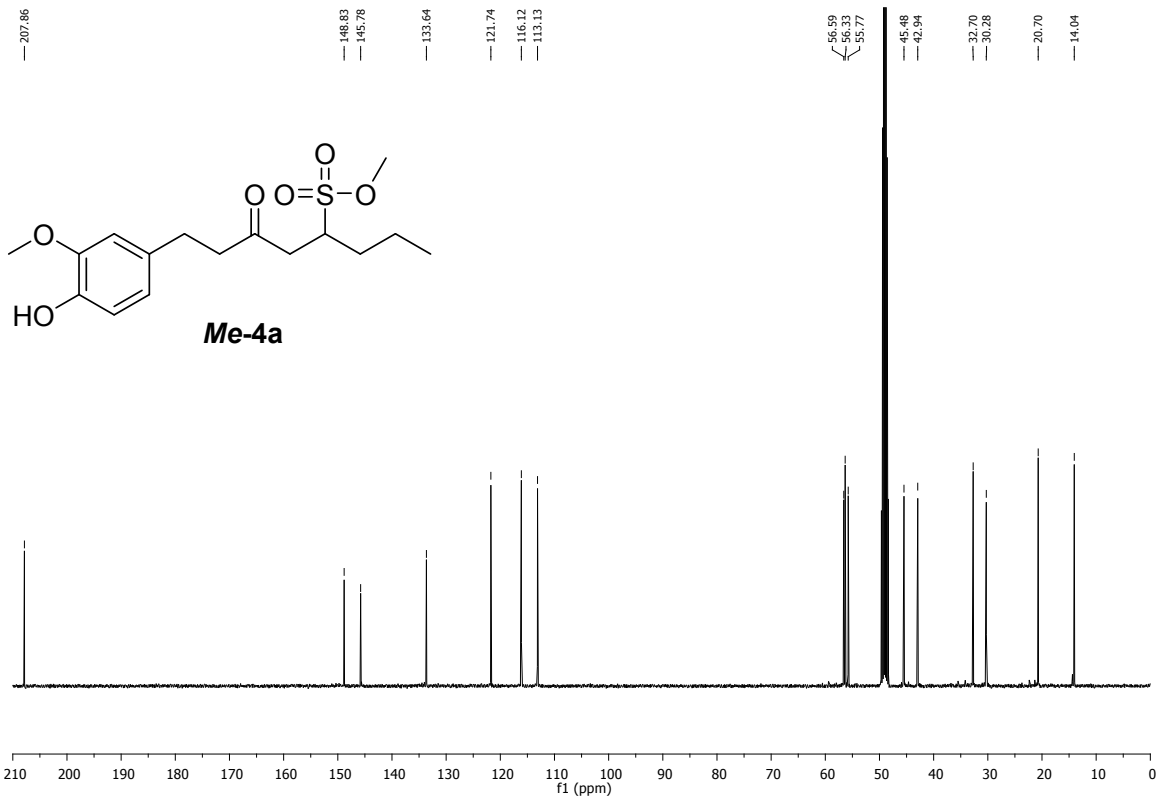
1,7-bis(4-hydroxy-3-methoxyphenyl)-5-oxoheptane-3-sulfonic acid (4f)



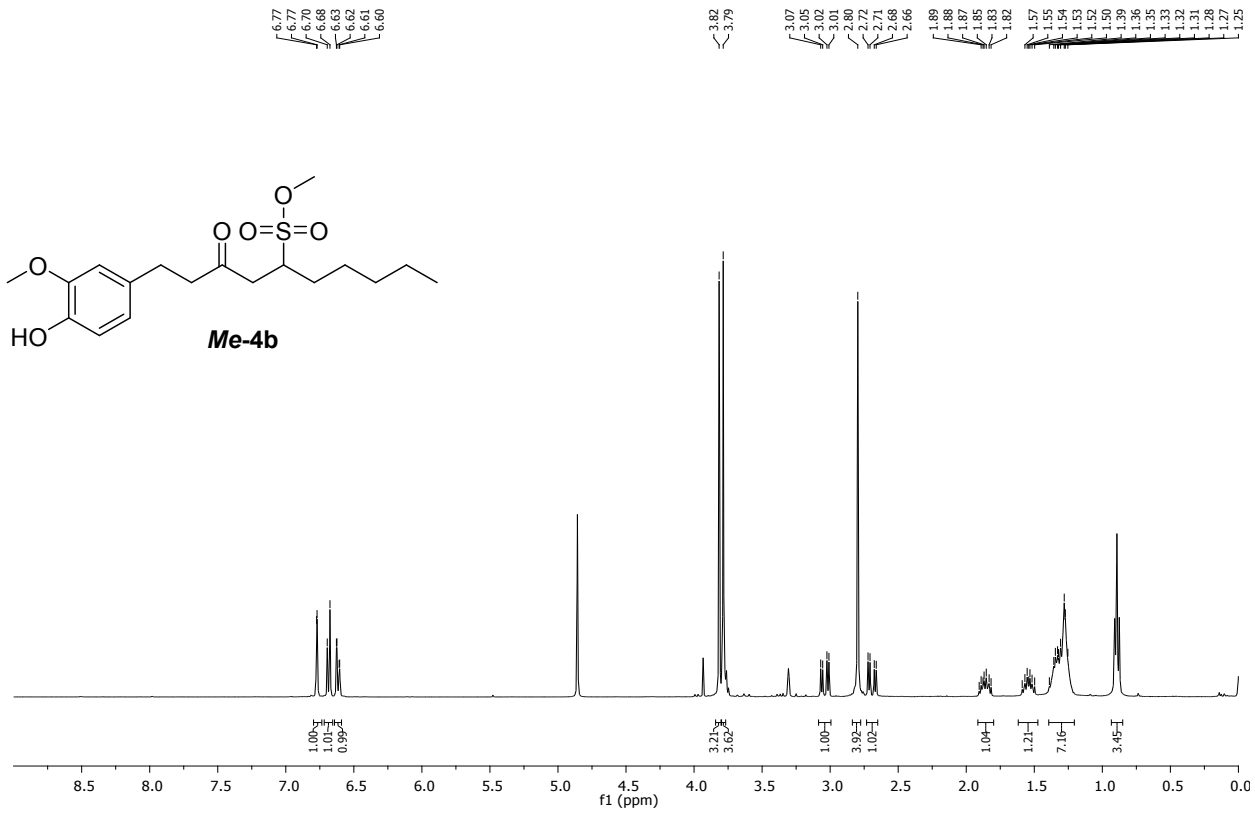


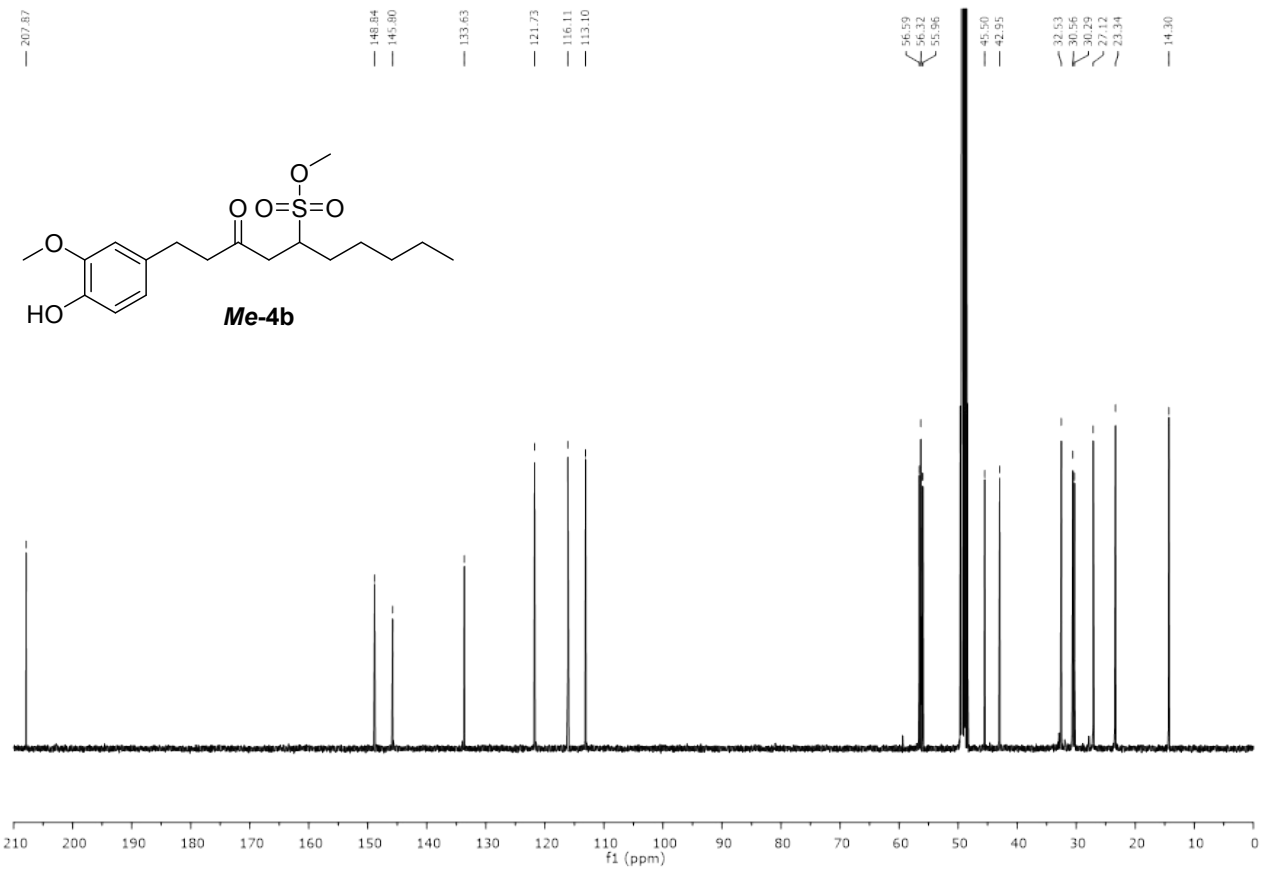
Methyl 8-(4-hydroxy-3methylphenyl)-6-oxooctane-4-sulfonate (*Me*-4a)



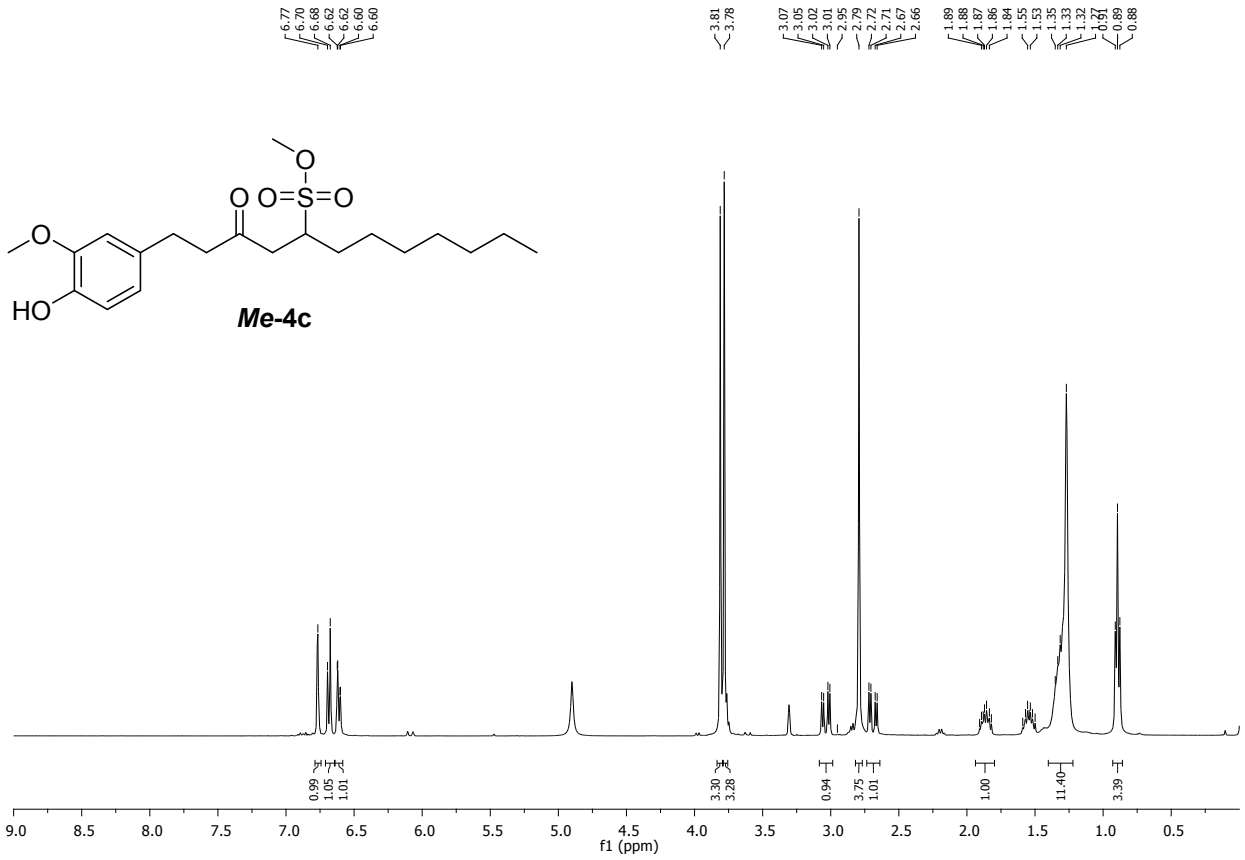


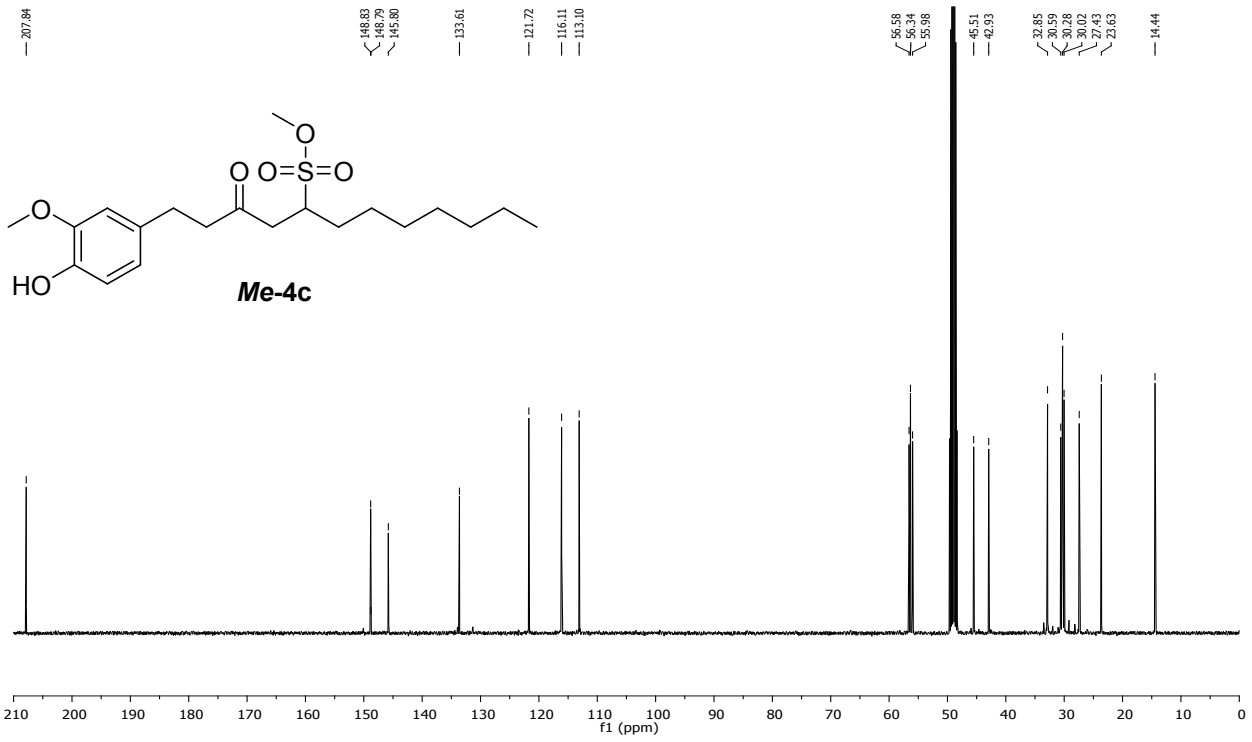
Methyl 1-(4-hydroxy-3-methoxyphenyl)-3-oxodecane-5-sulfonate (*Me*-4b)



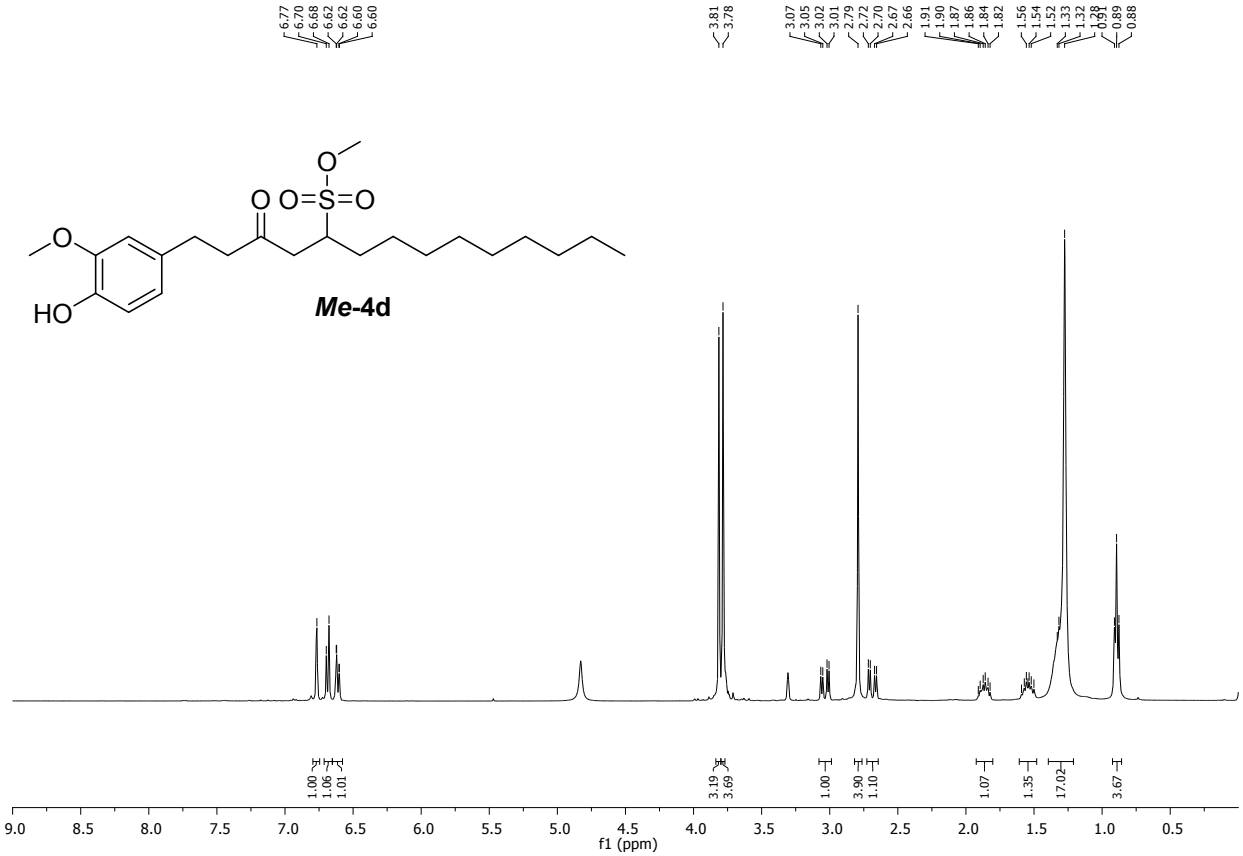


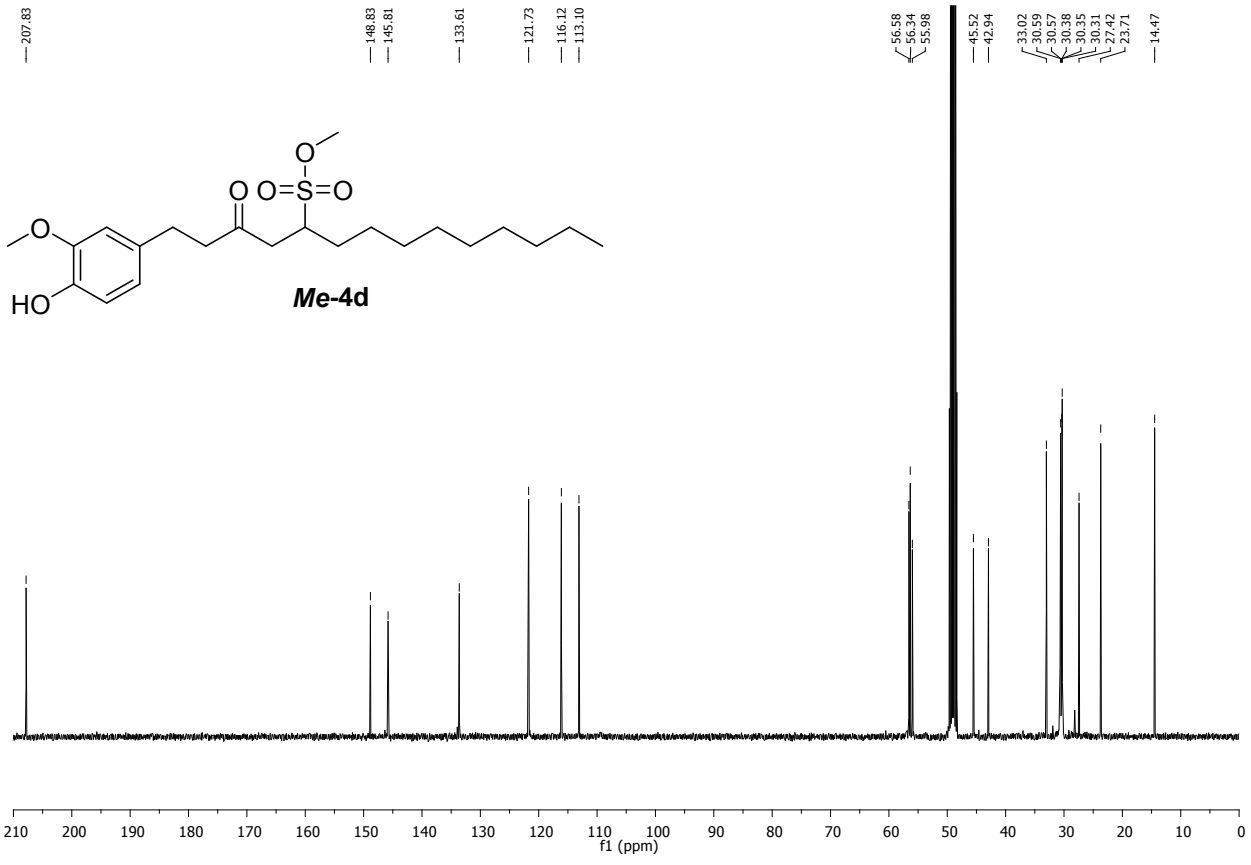
Methyl 1-(4-hydroxy-3-methoxyphenyl)-3-oxododecane-5-sulfonate (*Me*-4c)



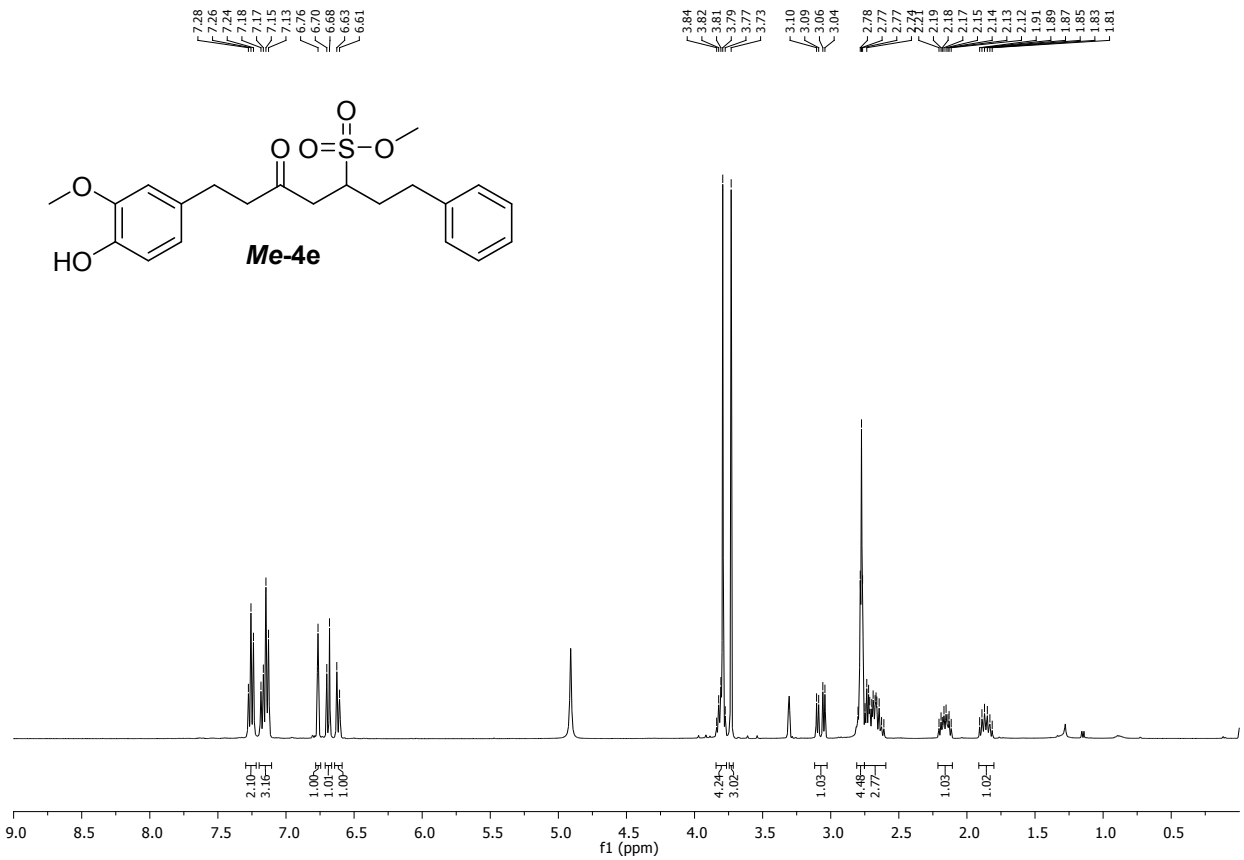


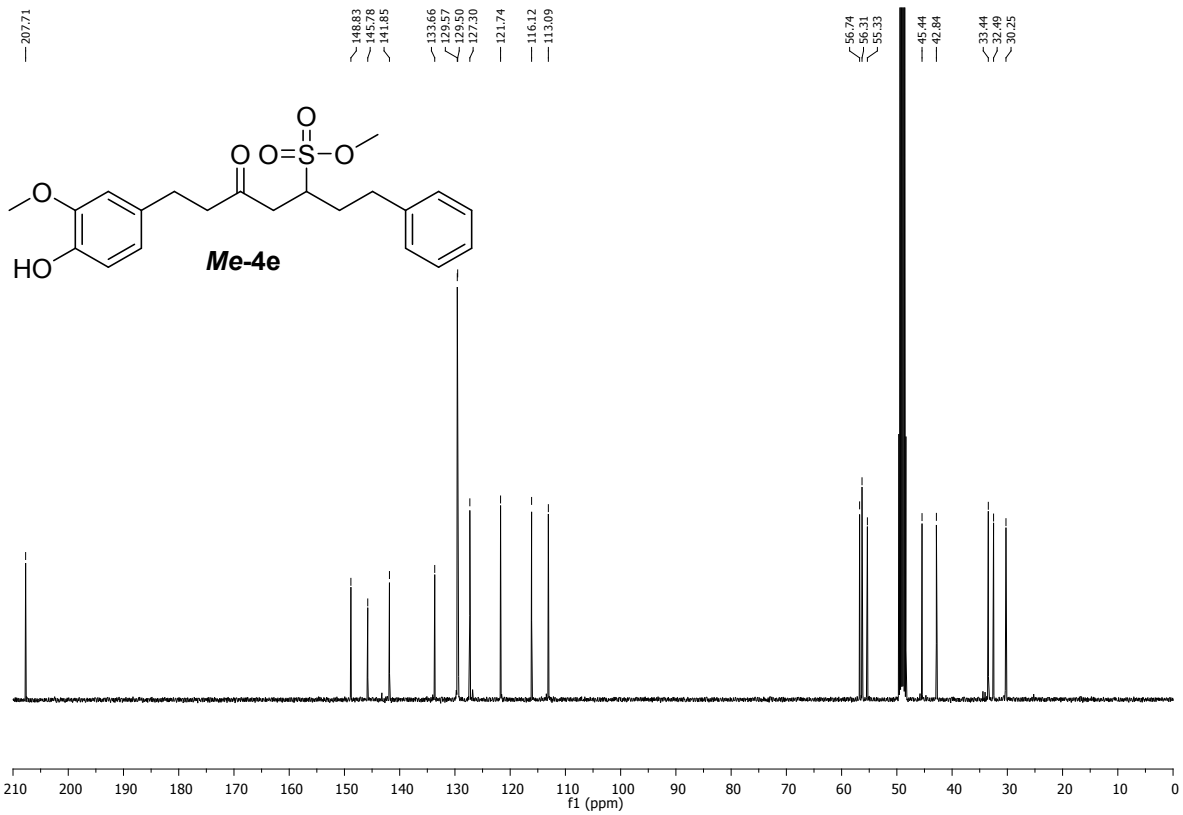
Methyl 1-(4-hydroxy-3-methoxyphenyl)-3-oxotetradecane-5-sulfonate (*Me*-4d)



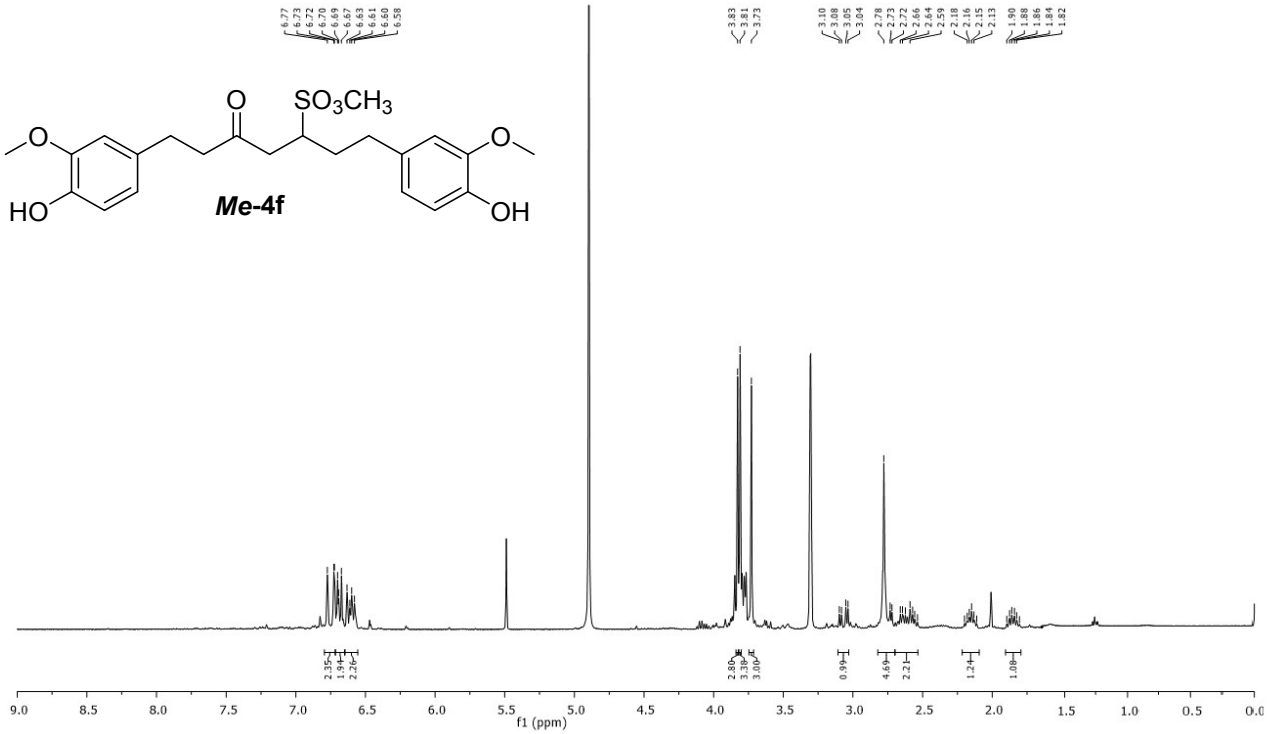


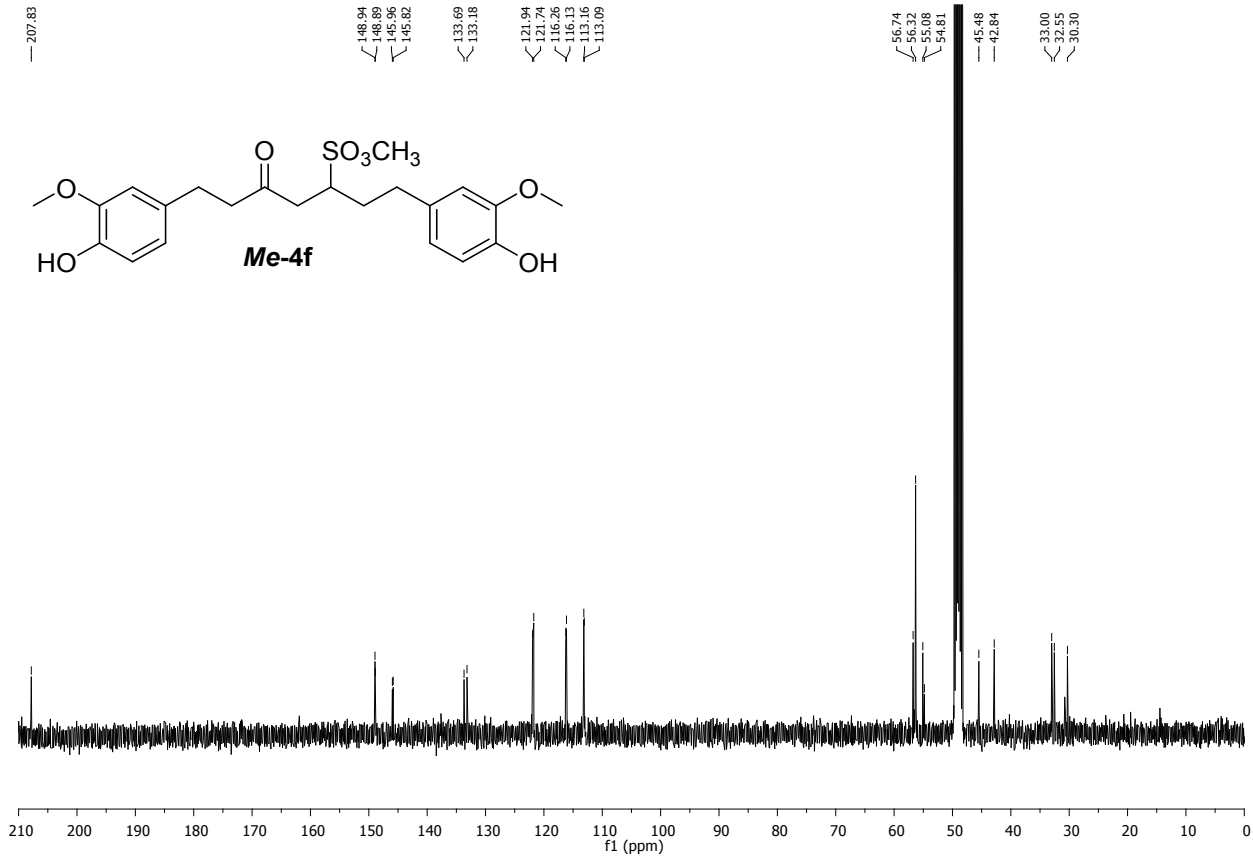
Methyl 7-(4-hydroxy-3-methoxyphenyl)-5-oxo-1-phenylheptane-3-sulfonate (*Me*-4e)



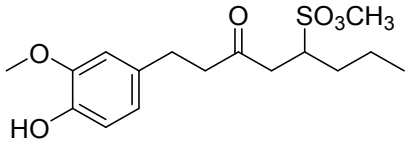


Methyl 1,7-bis(4-hydroxy-3-methoxyphenyl)-5-oxoheptane-3-sulfonate (*Me*-4f)





***Me*-4a racemic**

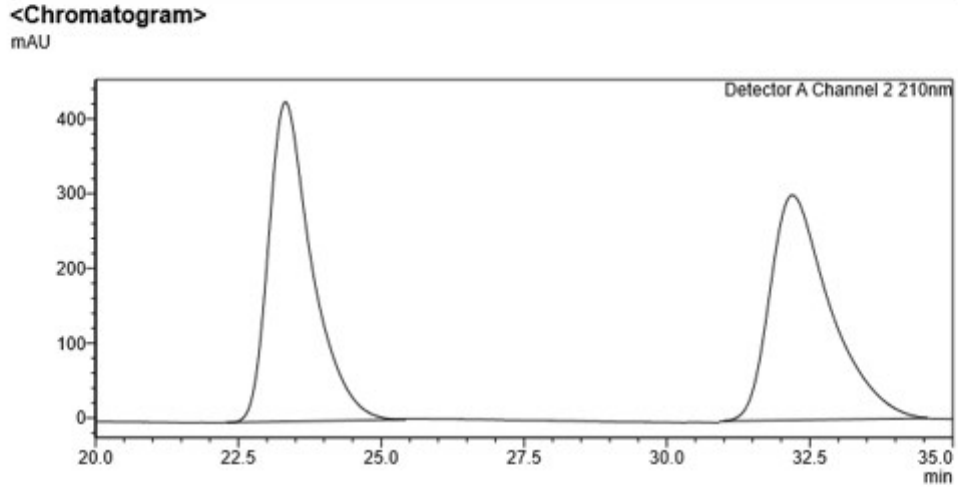


SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: GB 112.2-AD-B10%-1ml-60min		
Sample ID	: GB 112.2-AD-B10%-1ml-60min		
Data Filename	: GB 112.2-AD-B10%-1ml-60min001.lcd		
Method Filename	: AD-B10%-1ml-60min.lcm		
Batch Filename	:		
Vial #	: 1-12	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 16/01/2020 11:21:49	Acquired by	: System Administrator
Date Processed	: 16/01/2020 12:21:50	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 210nm

Peak#	Ret. Time	Area	Height	Conc.
1	23.402	41969	0	50.431
2	32.345	41251	912	49.569
Total		83220	912	

***Me*-(*S*)-4a**

Software Version	: 6.3.1.0504	Date	: 13/11/2018 11:57:41
Operator	: manager	Sample Name	: LGN 68-A
Sample Number	:	Study	:
AutoSampler	: SER200	Rack/Vial	: 0/1
Instrument Name	: PerkinElmer LC	Channel	: A
Instrument Serial #	: None	A/D mV Range	: 1000
Delay Time	: 0.00 min	End Time	: 45.00 min
Sampling Rate	: 2.2727 pts/s		
Sample Volume	: 1.000000 ul		
Sample Amount	: 1.0000	Area Reject	: 0.000000
Data Acquisition Time	: 18/04/2012 14:54:35	Dilution Factor	: 1.00
		Cycle	: 1

Raw Data File : C:\TOTALCHROM DATA\Results\Gaia\LGN 68-ALGN 68-A.ad.B15%.1ml.A.001.raw
Result File : C:\TOTALCHROM DATA\Results\Gaia\LGN 68-ALGN 68-A.ad.B15%.1ml.A.001.rst [Editing in Progress]
Inst Method : C:\TOTALCHROM DATA\Methods\B15%-1mL-45min from C:\TOTALCHROM DATA\Results\Gaia\LGN 68-ALGN 68-A.ad.B15%.1ml.A.001.raw
Proc Method : C:\TOTALCHROM DATA\Methods\B15%-1mL-45min from C:\TOTALCHROM DATA\Results\Gaia\LGN 68-ALGN 68-A.ad.B15%.1ml.A.001.rst [Editing in Progress]
Calib Method : C:\TOTALCHROM DATA\Methods\B15%-1mL-45min from C:\TOTALCHROM DATA\Results\Gaia\LGN 68-ALGN 68-A.ad.B15%.1ml.A.001.rst [Editing in Progress]
Report Format File: C:\PenExe\TcWS\Ver6.3.1\Config\User\manager\Default.rpt
Sequence File : C:\TOTALCHROM DATA\Sequences\blank 18-04-.ad.B15%.1ml.-..seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Raw Amount	Adjusted Amount
1		23.452	6075904.82	121448.45	8.44	8.44			*MM	6.0759	6.0759
2		33.807	65940303.36	768910.15	91.56	91.56			*MM	65.9403	65.9403
			72016208.17	890358.60	100.00	100.00				72.0162	72.0162

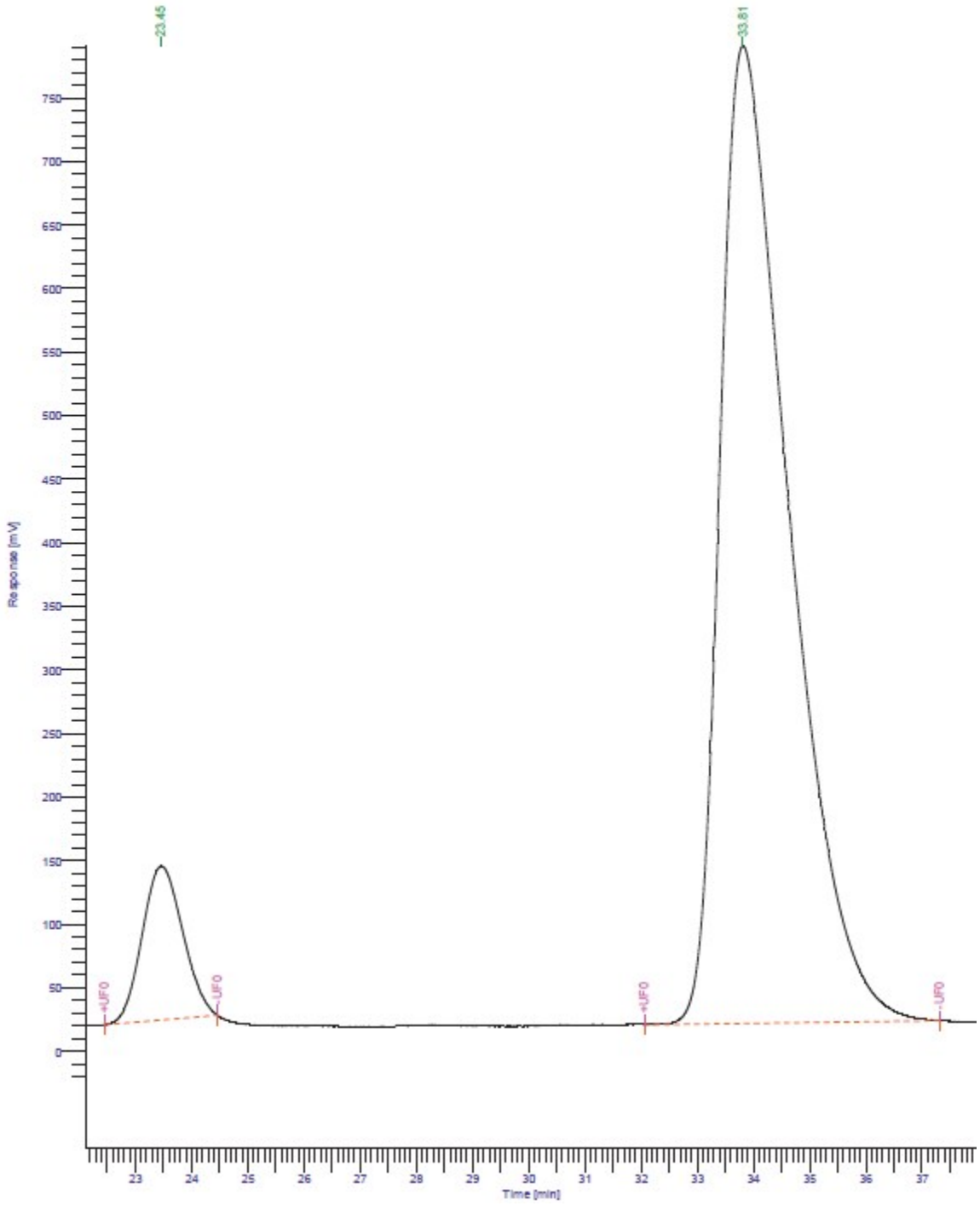
Missing Component Report

Component	Expected Retention (Calibration File)

All components were found

Chromatogram

Sample Name : LGN 68-A Sample #: Page 1 of 1
FileName : C:\TOTALCHROM DATA\Results\Gala\LGN 68-ALGN 68-A.ad.B15%.1ml.A.001.raw
Date : 13/11/2018 11:59:27
Method : Time of Injection: 18/04/2012 14:54:35
Start Time : 22.12 min End Time : 37.96 min Low Point : -24.30 mAU High Point : 790.88 mAU
Plot Offset: -24.30 mAU Plot Scale: 815.2 mAU



***Me*-(*R*)-4a**

Software Version	: 6.3.1.0504	Date	: 14/11/2018 12:36:28
Operator	: manager	Sample Name	: LGN 69-A
Sample Number	:	Study	:
AutoSampler	: SER200	Rack/Vial	: 0/1
Instrument Name	: PerkinElmer LC	Channel	: A
Instrument Serial #	: None	A/D mV Range	: 1000
Delay Time	: 0.00 min	End Time	: 45.00 min
Sampling Rate	: 2.2727 pts/s		
Sample Volume	: 1.000000 ul		
Sample Amount	: 1.0000	Area Reject	: 0.000000
Data Acquisition Time	: 20/04/2012 19:55:49	Dilution Factor	: 1.00
		Cycle	: 1

Raw Data File : C:\TOTALCHROM DATA\Results\Gaia\LGN 69-ALGN 69-A.ad.B15%.1ml.A.001-20120420-195557.raw
Result File : C:\TOTALCHROM DATA\Results\Gaia\LGN 69-ALGN 69-A.ad.B15%.1ml.A.001-20120420-204135.rst [Editing in Progress]
Inst Method : C:\TOTALCHROM DATA\Methods\B15%-1mL-45min from C:\TOTALCHROM DATA\Results\Gaia\LGN 69-ALGN 69-A.ad.B15%.1ml.A.001-20120420-195557.raw
Proc Method : C:\TOTALCHROM DATA\Methods\B15%-1mL-45min from C:\TOTALCHROM DATA\Results\Gaia\LGN 69-ALGN 69-A.ad.B15%.1ml.A.001-20120420-204135.rst [Editing in Progress]
Calib Method : C:\TOTALCHROM DATA\Methods\B15%-1mL-45min from C:\TOTALCHROM DATA\Results\Gaia\LGN 69-ALGN 69-A.ad.B15%.1ml.A.001-20120420-204135.rst [Editing in Progress]
Report Format File: C:\PenExe\TcWS\Ver6.3.1\Config\User\manager\Default.rpt
Sequence File : C:\TOTALCHROM DATA\Sequences\LGN 68-F-.ad.B15%.1ml.-..seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Raw Amount	Adjusted Amount
1		22.154	6443238.65	128995.43	9.84	9.84			*MM	6.4432	6.4432
2		31.841	59027717.07	696921.14	90.16	90.16			*MM	59.0277	59.0277
			65470955.73	825916.56	100.00	100.00				65.4710	65.4710

Missing Component Report

Component	Expected Retention (Calibration File)

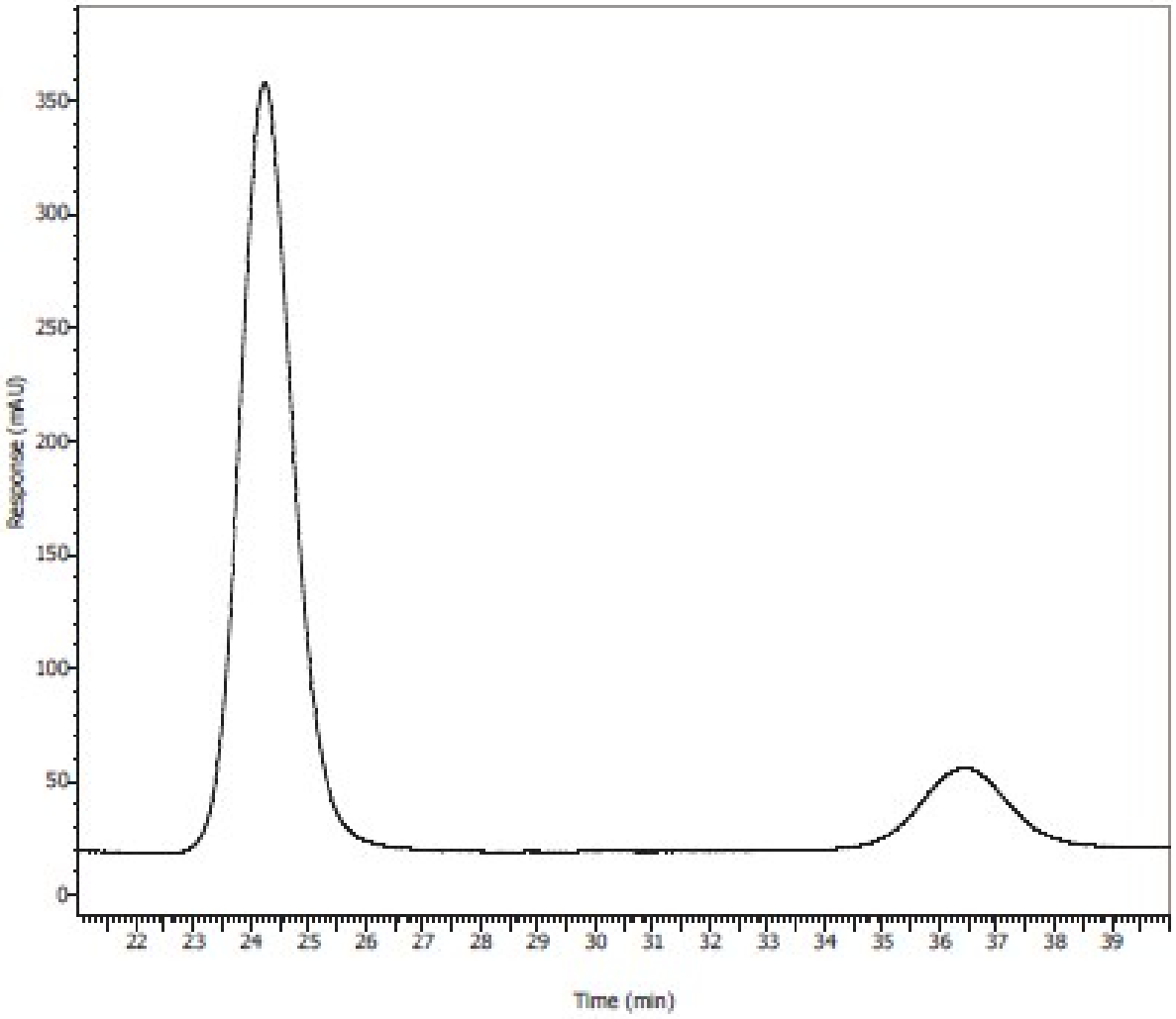
All components were found

Chromatogram

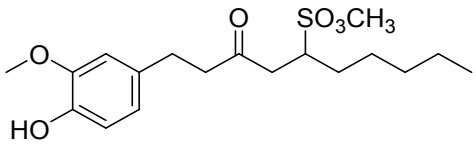
Software Version : 6.3.1.0504
Sample Name : LGN 54 cat. 10
Data Aoquisition Time : 04/03/2012 12:03:57

Date : 27/02/2019 16:20:32
Sample Number :

Raw Data File : C:\TOTALCHROM DATA\Results\Gala\LGN 54 cat. 10\LGN 54 cat. 10.ad.B10%.1ml.A.001.raw



***Me*-4b racemic**



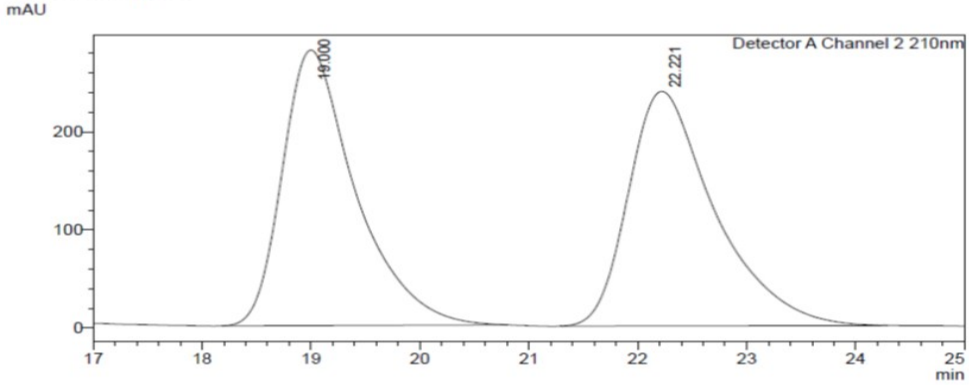
13/12/2018 10:53:11 Page 1 / 1

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: GB 113 6-gingersulfonic_racem_15%		
Sample ID	: GB 113 6-gingersulfonic_racem		
Data Filename	: GB 113 6-gingersulfonic_racem_15%.lcd		
Method Filename	: AD-B15%-1ml-60min.lcm		
Batch Filename	:		
Vial #	: 1-7	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 06/12/2018 12:33:44	Acquired by	: System Administrator
Date Processed	: 06/12/2018 13:33:46	Processed by	: System Administrator

<Chromatogram>



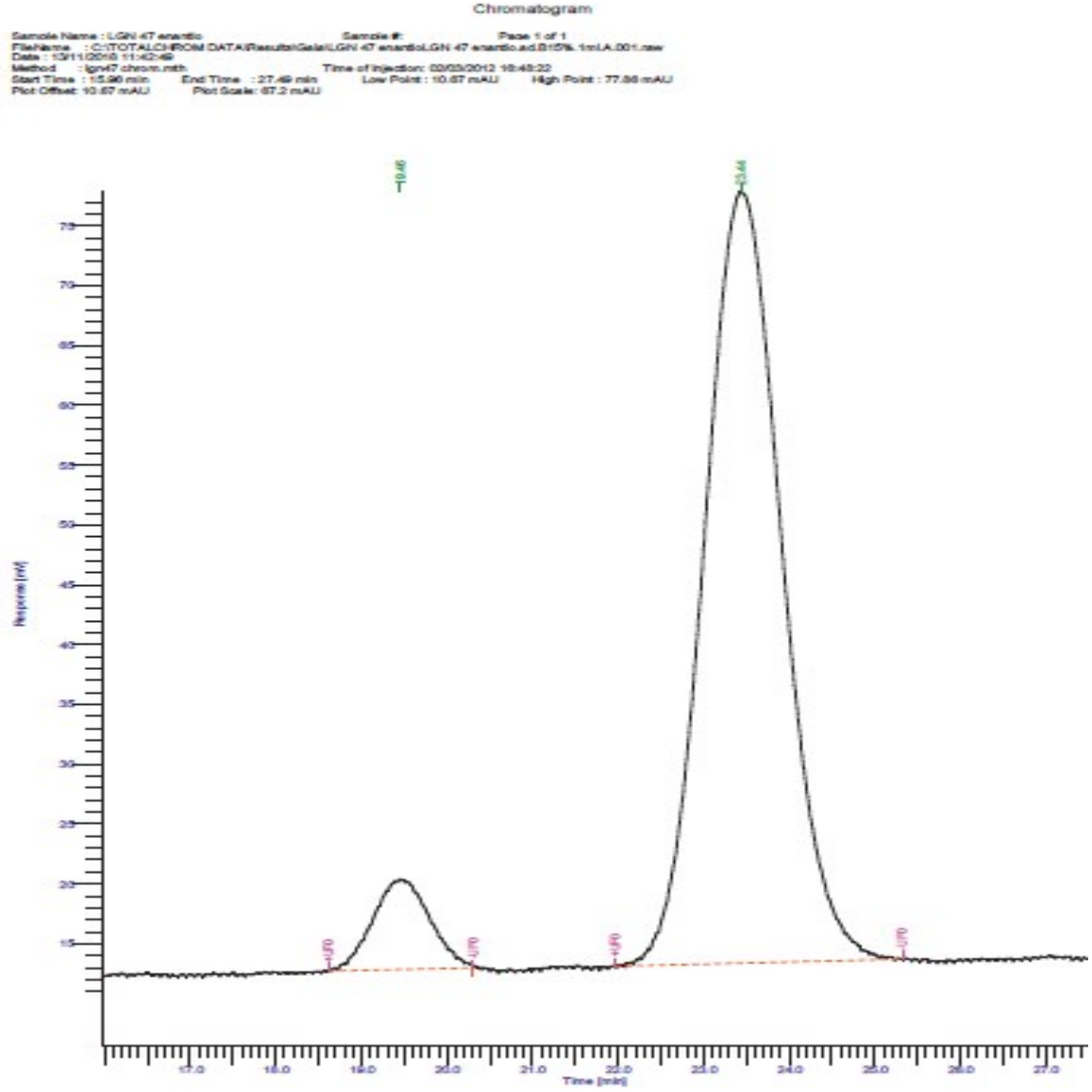
<Peak Table>

Detector A Channel 2 210nm

Peak#	Ret. Time	Area	Height	Conc.
1	19.000	13140761	280765	49.945
2	22.221	13169920	239075	50.055
Total		26310681	519840	

C:\LabSolutions\Data\Grazia\GB 113 6-gingersulfonic_racem_15%.lcd

***Me*-(*S*)-4b**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Raw Amount	Adjusted Amount
1		19.455	348928.97	7565.54	7.93	7.93			*MM	0.3489	0.3489
2		23.437	4049025.40	64468.10	92.07	92.07			*MM	4.0490	4.0490
			4397954.37	72033.63	100.00	100.00				4.3980	4.3980

Missing Component Report

Component	Expected Retention (Calibration File)

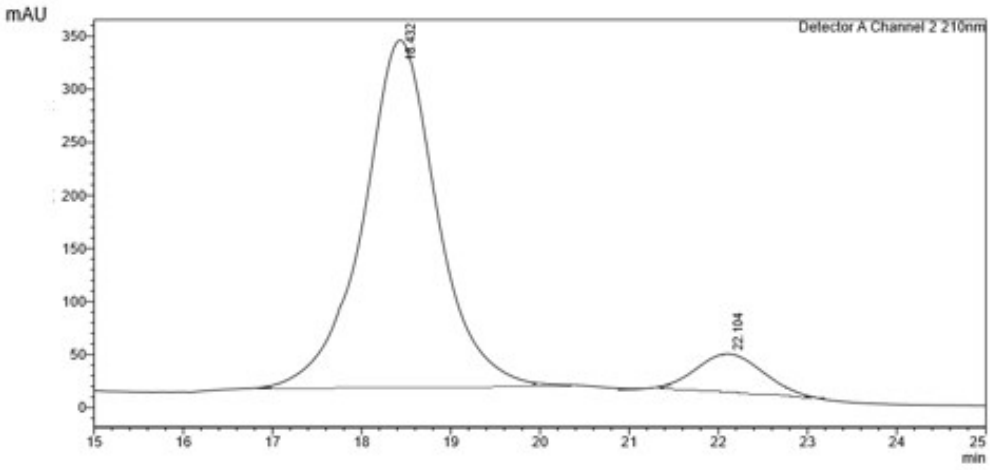
***Me*-(*R*)-4b**

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: GB 293-AD-B17%-1ml-60min		
Sample ID	: GB 293-AD-B17%-1ml-60min		
Data Filename	: GB 293-AD-B17%-1ml-60min001.lcd		
Method Filename	: AD-B17%-1ml-60min.lcm		
Batch Filename	:		
Vial #	: 1-13	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 16/01/2020 14:09:24	Acquired by	: System Administrator
Date Processed	: 16/01/2020 14:39:29	Processed by	: System Administrator

<Chromatogram>

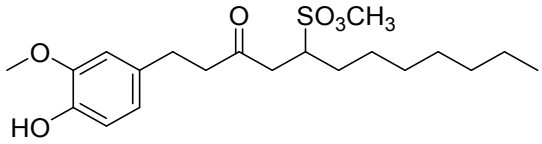


<Peak Table>

Detector A Channel 2 210nm

Peak#	Ret. Time	Area	Height	Conc.
1	18.432	22729218	335309	95.322
2	22.104	1115494	27347	4.678
Total		23844712	362655	

***Me*-4c racemic**

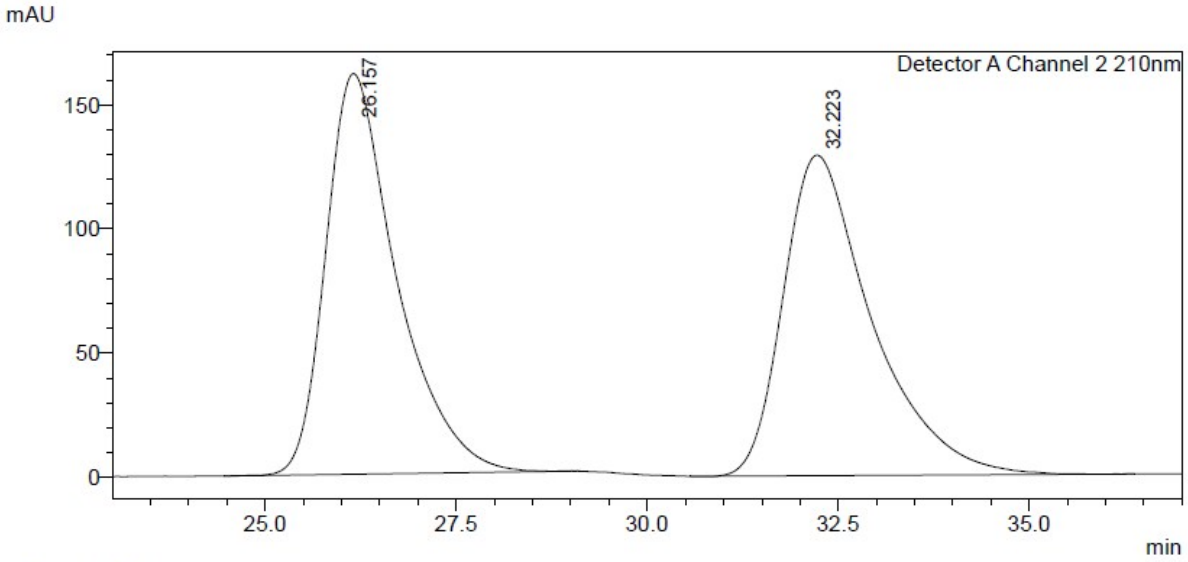


SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: GB 114 8-gingersulfonic_racem		
Sample ID	: GB 114 8-gingersulfonic_racem		
Data Filename	: GB 114 8-gingersulfonic_racem.lcd		
Method Filename	: AD-B10%-1ml-60min.lcm		
Batch Filename	:		
Vial #	: 1-8	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 06/12/2018 14:06:03	Acquired by	: System Administrator
Date Processed	: 06/12/2018 15:06:04	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 210nm

Peak#	Ret. Time	Area	Height	Conc.
1	26.157	10388789	161228	49.966
2	32.223	10403066	128978	50.034
Total		20791855	290206	

***Me*-(*S*)-4c**

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Raw Amount	Adjusted Amount
1		25.755	1820782.27	30814.29	12.18	12.18			*MM	1.8208	1.8208
2		32.340	13128792.58	189144.91	87.82	87.82			*MM	13.1288	13.1288
			14949574.86	219959.21	100.00	100.00				14.9496	14.9496

Missing Component Report

Component	Expected Retention (Calibration File)

All components were found

Chromatogram

Sample Name : LGN 121 Sample # : Page 1 of 1

FileName : C:\TOTALCHROM DATA\Results\Gela\LGN 121.ad\S10%.1ml.A.001.rsw

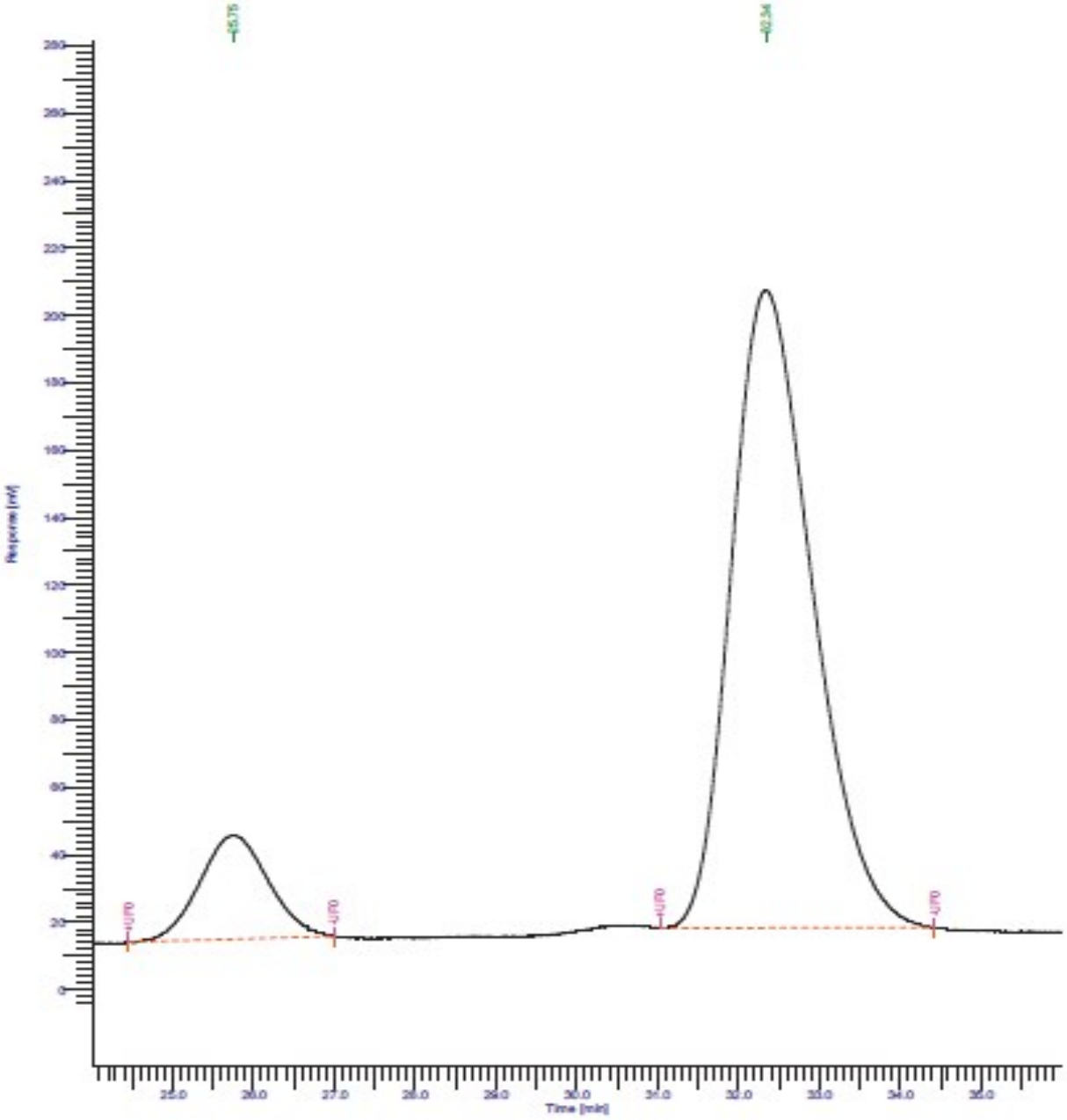
Data : 13/11/2012 15:49:58

Method :

Time of Injection: 06/09/2012 16:05:24

Start Time : 24.00 min End Time : 36.00 min Low Point : -4.79 mAU High Point : 201.21 mAU

Plot Offset: -4.79 mAU Plot Scale: 206.0 mAU



***Me*-(*R*)-4c**

Software Version	: 6.3.1.0504	Date	: 13/11/2018 12:20:14
Operator	: manager	Sample Name	: LGN 122
Sample Number	:	Study	:
AutoSampler	: SER200	Rack/Vial	: 0/1
Instrument Name	: PerkinElmer LC	Channel	: A
Instrument Serial #	: None	A/D mV Range	: 1000
Delay Time	: 0.00 min	End Time	: 40.00 min
Sampling Rate	: 2.2727 pts/s		
Sample Volume	: 1.000000 ul	Area Reject	: 0.000000
Sample Amount	: 1.0000	Dilution Factor	: 1.00
Data Acquisition Time	: 08/09/2012 16:49:36	Cycle	: 1

Raw Data File : C:\TOTALCHROM DATA\Results\Gaia\LGN 122.ad.B10%.1ml.A.001.raw
Result File : C:\TOTALCHROM DATA\Results\Gaia\LGN 122.ad.B10%.1ml.A.001.rst [Editing in Progress]
Inst Method : C:\TOTALCHROM DATA\Methods\B10%-1mL-40min from C:\TOTALCHROM DATA\Results\Gaia\LGN 122.ad.B10%.1ml.A.001.raw
Proc Method : C:\TOTALCHROM DATA\Methods\B10%-1mL-40min from C:\TOTALCHROM DATA\Results\Gaia\LGN 122.ad.B10%.1ml.A.001.rst [Editing in Progress]
Calib Method : C:\TOTALCHROM DATA\Methods\B10%-1mL-40min from C:\TOTALCHROM DATA\Results\Gaia\LGN 122.ad.B10%.1ml.A.001.rst [Editing in Progress]
Report Format File: C:\PenExe\TcWS\Ver6.3.1\Config\User\manager\Default.rpt
Sequence File : C:\TOTALCHROM DATA\Sequences\LGN 121.ad.B10%.1ml.-..seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Raw Amount	Adjusted Amount
1		25.549	9786584.33	176371.20	87.89	87.89			*MM	9.7866	9.7866
2		32.362	1348742.01	20085.96	12.11	12.11			*MM	1.3487	1.3487
			11135326.34	196457.16	100.00	100.00				11.1353	11.1353

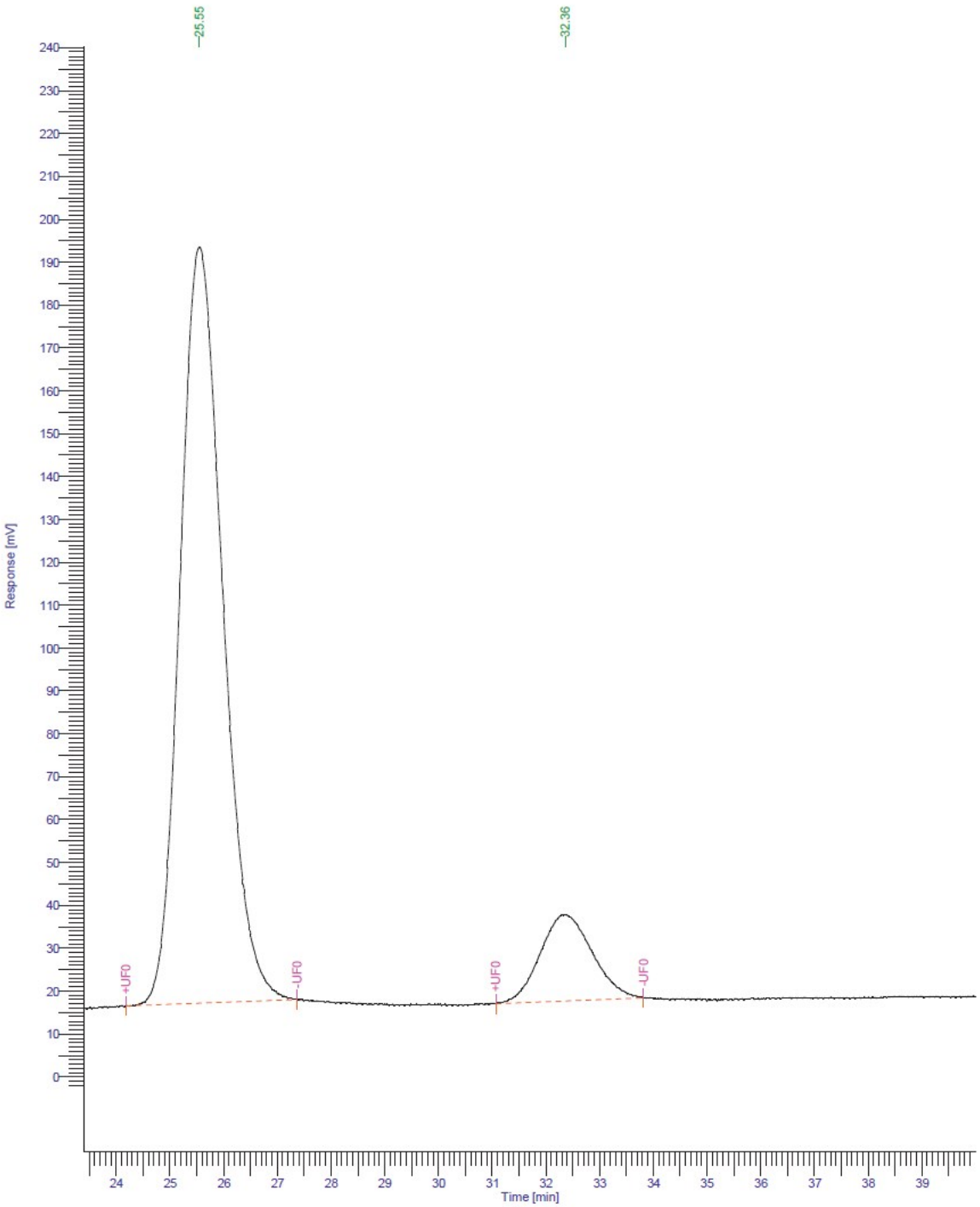
Missing Component Report

Component	Expected Retention (Calibration File)

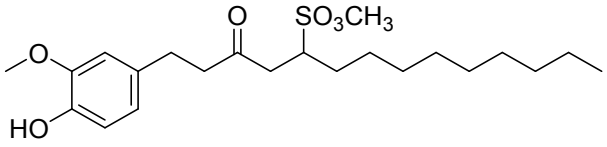
All components were found

Chromatogram

Sample Name : LGN 122 Sample #: Page 1 of 1
FileName : C:\TOTALCHROM DATA\Results\Gaia\LGN 122.ad.B10%.1ml.A.001.raw
Date : 13/11/2018 12:21:38
Method : Time of Injection: 08/09/2012 16:49:36
Start Time : 23.40 min End Time : 40.00 min Low Point : -2.10 mAU High Point : 240.24 mAU
Plot Offset: -2.10 mAU Plot Scale: 242.3 mAU



Methylated-4d racemic



Software Version	: 6.3.1.0504	Date	: 14/11/2018 11:27:54
Operator	: manager	Sample Name	: LGN.111
Sample Number	:	Study	:
AutoSampler	: SER200	Rack/Vial	: 0/1
Instrument Name	: PerkinElmer LC	Channel	: A
Instrument Serial #	: None	A/D mV Range	: 1000
Delay Time	: 0.00 min	End Time	: 59.99 min
Sampling Rate	: 2.2727 pts/s		
Sample Volume	: 1.000000 ul		
Sample Amount	: 1.0000	Area Reject	: 0.000000
Data Acquisition Time	: 04/09/2012 13:04:53	Dilution Factor	: 1.00
		Cycle	: 1

Raw Data File : C:\TOTALCHROM DATA\Results\Gaia\LGN.111.AD.B10%.1ml.A.001.raw
Result File : C:\TOTALCHROM DATA\Results\Gaia\LGN.111.AD.B10%.1ml.A.001.rst [Editing in Progress]
Inst Method : C:\TOTALCHROM DATA\Methods\B10%-1mL-60min from C:\TOTALCHROM DATA\Results\Gaia\LGN.111.AD.B10%.1ml.A.001.raw
Proc Method : C:\TOTALCHROM DATA\Methods\B10%-1mL-60min from C:\TOTALCHROM DATA\Results\Gaia\LGN.111.AD.B10%.1ml.A.001.rst [Editing in Progress]
Calib Method : C:\TOTALCHROM DATA\Methods\B10%-1mL-60min from C:\TOTALCHROM DATA\Results\Gaia\LGN.111.AD.B10%.1ml.A.001.rst [Editing in Progress]
Report Format File: C:\PenExe\TcWS\Ver6.3.1\Config\User\manager\Default.rpt
Sequence File : C:\TOTALCHROM DATA\Sequences\blank.AD.B10%.1ml.-..seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Raw Amount	Adjusted Amount
1		20.753	6656356.48	153820.71	49.78	49.78			*MM	6.6564	6.6564
2		25.381	6714565.01	120431.57	50.22	50.22			*MM	6.7146	6.7146
			13370921.48	274252.28	100.00	100.00				13.3709	13.3709

Missing Component Report

Component	Expected Retention (Calibration File)

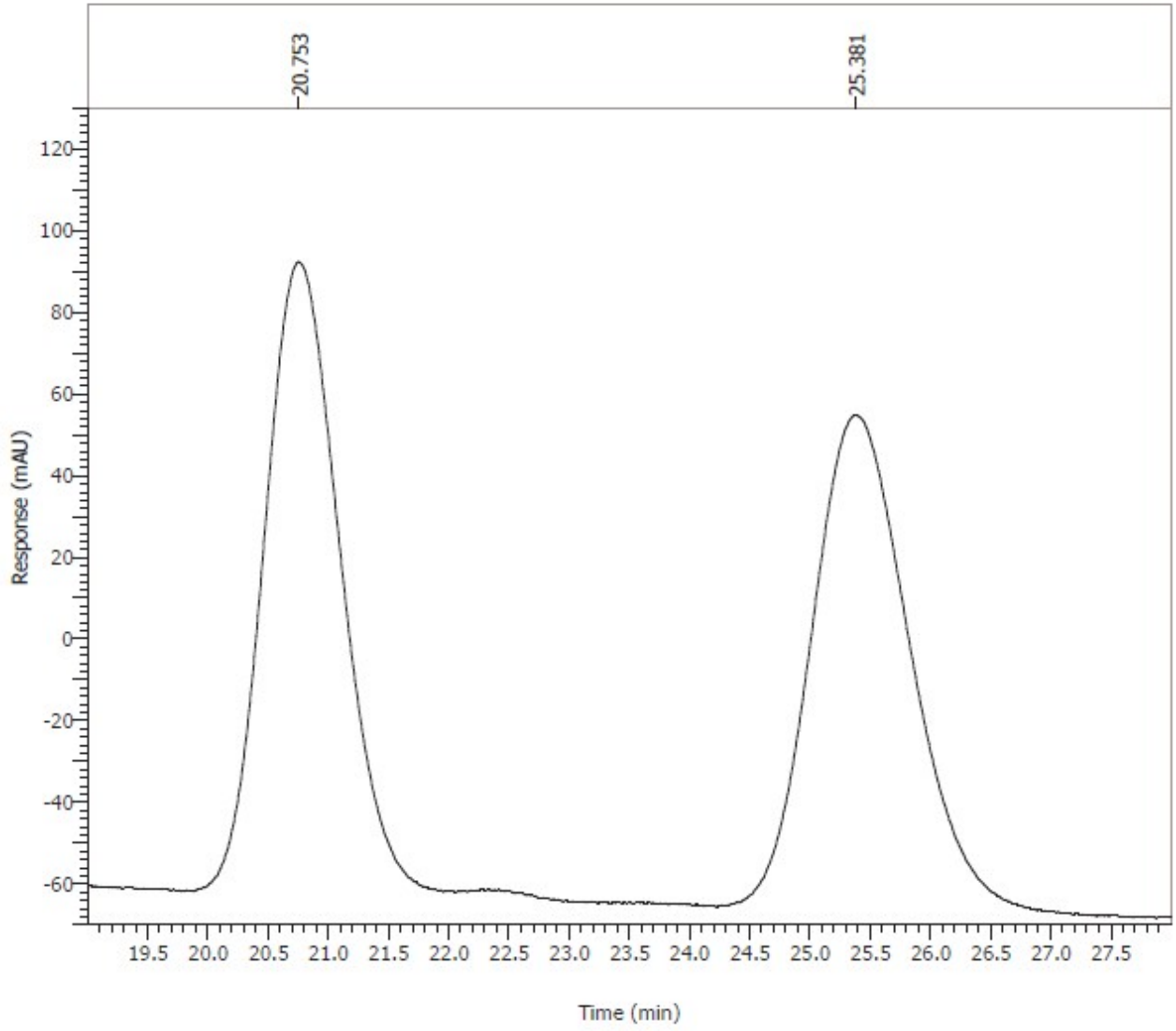
All components were found

Chromatogram

Software Version : 6.3.1.0504
Sample Name : LGN.111
Data Acquisition Time : 04/09/2012 13:04:53

Date : 11/03/2019 17:02:36
Sample Number :

Raw Data File : C:\TOTALCHROM DATA\Results\Gaia\LGN.111.AD.B10%.1ml.A.001.raw



***Me*-(*S*)-4d**

Software Version	: 6.3.1.0504	Date	: 13/11/2018 12:05:25
Operator	: manager	Sample Name	: LGN 119
Sample Number	:	Study	:
AutoSampler	: SER200	Rack/Vial	: 0/1
Instrument Name	: PerkinElmer LC	Channel	: B
Instrument Serial #	: None	A/D mV Range	: 1000
Delay Time	: 0.00 min	End Time	: 40.00 min
Sampling Rate	: 2.2727 pts/s		
Sample Volume	: 1.000000 ul		
Sample Amount	: 1.0000	Area Reject	: 0.000000
Data Acquisition Time	: 06/09/2012 11:14:48	Dilution Factor	: 1.00
		Cycle	: 1

Raw Data File : C:\TOTALCHROM DATA\Results\Gaia\LGN 119.ad.B10%.1ml.B.001.raw
Result File : C:\TOTALCHROM DATA\Results\Gaia\LGN 119.ad.B10%.1ml.B.001.rst [Editing in Progress]
Inst Method : C:\TOTALCHROM DATA\Methods\B10%-1mL-40min from C:\TOTALCHROM DATA\Results\Gaia\LGN 119.ad.B10%.1ml.B.001.raw
Proc Method : C:\TOTALCHROM DATA\Methods\B10%-1mL-40min from C:\TOTALCHROM DATA\Results\Gaia\LGN 119.ad.B10%.1ml.B.001.rst [Editing in Progress]
Calib Method : C:\TOTALCHROM DATA\Methods\B10%-1mL-40min from C:\TOTALCHROM DATA\Results\Gaia\LGN 119.ad.B10%.1ml.B.001.rst [Editing in Progress]
Report Format File: C:\PenExe\TcWS\Ver6.3.1\Config\User\manager\Default.rpt
Sequence File : C:\TOTALCHROM DATA\Sequences\bianco.ad.B10%.1ml.-..seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Raw Amount	Adjusted Amount
1		21.655	594263.70	12863.86	10.31	10.31			*MM	0.5943	0.5943
2		26.349	5169091.24	83324.11	89.69	89.69			*MM	5.1691	5.1691
			5763354.94	96187.98	100.00	100.00				5.7634	5.7634

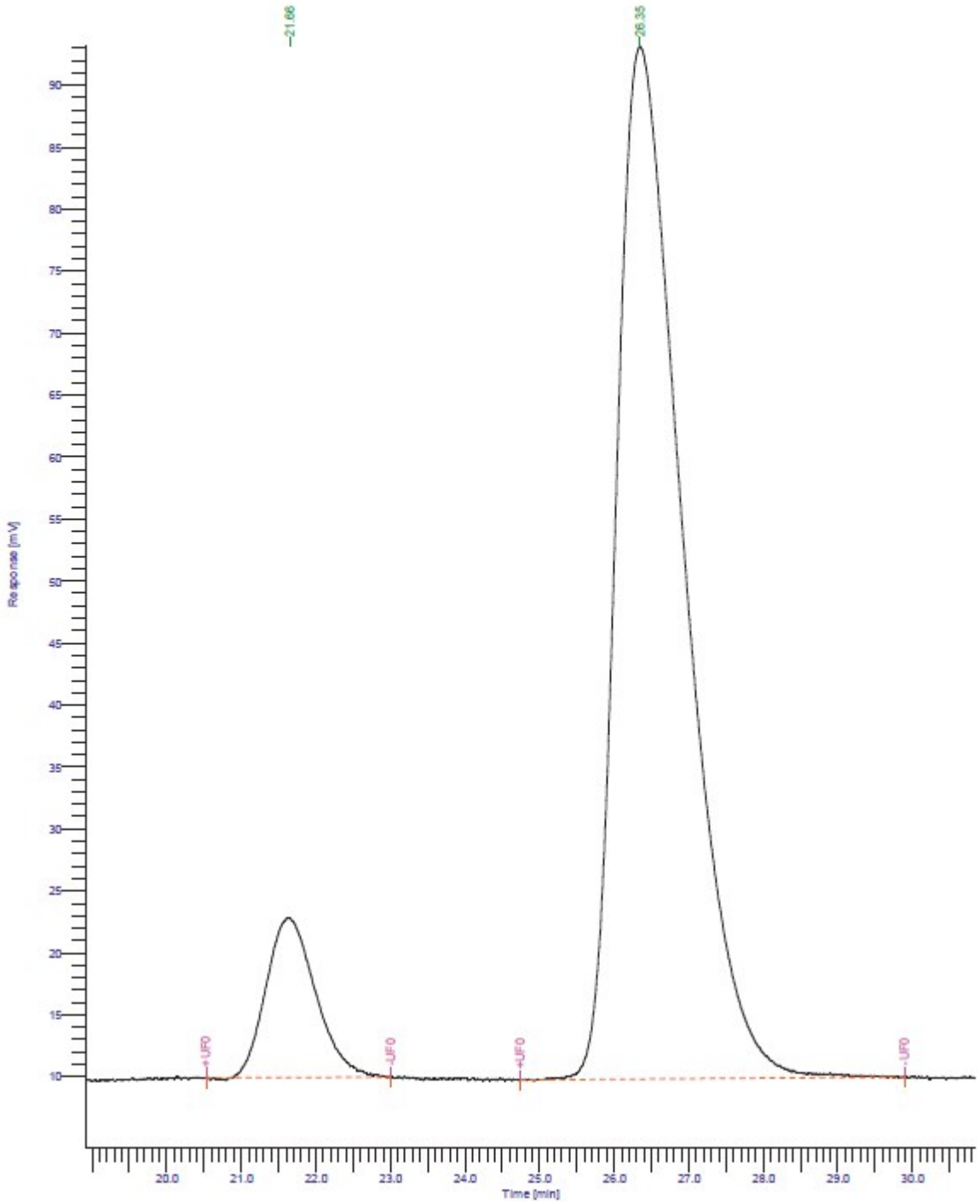
Missing Component Report

Component	Expected Retention (Calibration File)

All components were found

Chromatogram

Sample Name : LGN 119 Sample #: Page 1 of 1
FileName : C:\TOTALCHROM DATA\Results\Gala\LGN 119.ad.B10%.1ml.B.001.raw
Date : 13/11/2018 12:07:58
Method : Time of Injection: 06/09/2012 11:14:48
Start Time : 18.92 min End Time : 30.84 min Low Point : 9.59 mAU High Point : 93.15 mAU
Plot Offset: 9.59 mAU Plot Scale: 83.6 mAU



***Me*-(R)-4d**

Software Version	: 6.3.1.0504	Date	: 13/11/2018 12:10:09
Operator	: manager	Sample Name	: LGN 120
Sample Number	:	Study	:
AutoSampler	: SER200	Rack/Vial	: 0/1
Instrument Name	: PerkinElmer LC	Channel	: A
Instrument Serial #	: None	A/D mV Range	: 1000
Delay Time	: 0.00 min	End Time	: 40.00 min
Sampling Rate	: 2.2727 pts/s		
Sample Volume	: 1.000000 ul		
Sample Amount	: 1.0000	Area Reject	: 0.000000
Data Acquisition Time	: 06/09/2012 12:46:35	Dilution Factor	: 1.00
		Cycle	: 1

Raw Data File : C:\TOTALCHROM DATA\Results\Gaia\LGN 120.ad.B10%.1ml.A.001.raw
Result File : C:\TOTALCHROM DATA\Results\Gaia\LGN 120.ad.B10%.1ml.A.001.rst [Editing in Progress]
Inst Method : C:\TOTALCHROM DATA\Methods\B10%-1mL-40min from C:\TOTALCHROM DATA\Results\Gaia\LGN 120.ad.B10%.1ml.A.001.raw
Proc Method : C:\TOTALCHROM DATA\Methods\B10%-1mL-40min from C:\TOTALCHROM DATA\Results\Gaia\LGN 120.ad.B10%.1ml.A.001.rst [Editing in Progress]
Calib Method : C:\TOTALCHROM DATA\Methods\B10%-1mL-40min from C:\TOTALCHROM DATA\Results\Gaia\LGN 120.ad.B10%.1ml.A.001.rst [Editing in Progress]
Report Format File: C:\PenExe\TcWS\Ver6.3.1\Config\User\manager\Default.rpt
Sequence File : C:\TOTALCHROM DATA\Sequences\bianco.ad.B10%.1ml.-..seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Raw Amount	Adjusted Amount
1		21.017	25869945.69	544972.85	86.05	86.05			*MM	25.8699	25.8699
2		26.063	4194420.75	75753.99	13.95	13.95			*MM	4.1944	4.1944
			30064366.44	620726.84	100.00	100.00				30.0644	30.0644

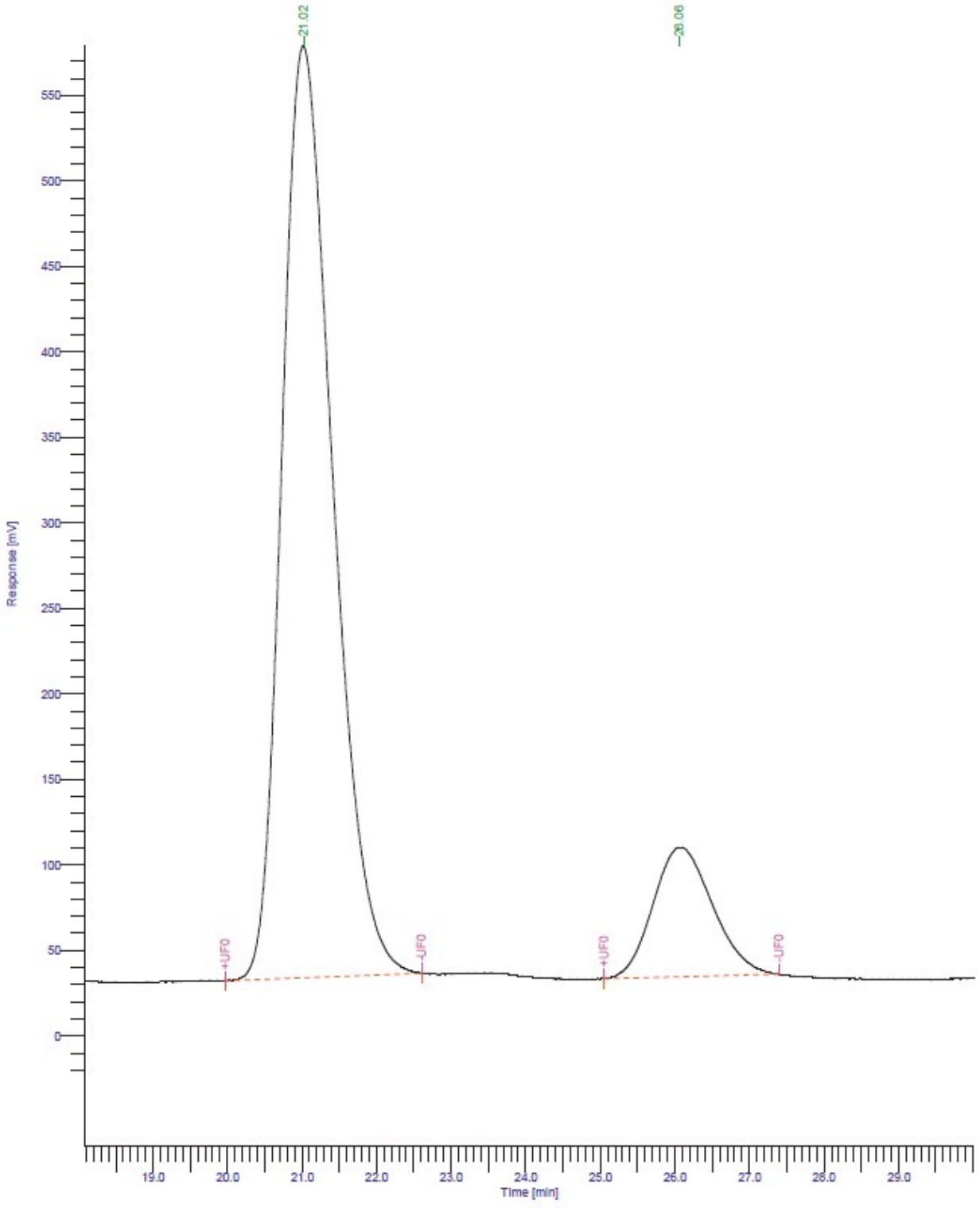
Missing Component Report

Component	Expected Retention (Calibration File)

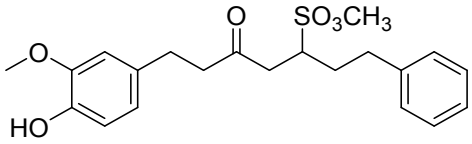
All components were found

Chromatogram

Sample Name : LGN 120 Sample #: Page 1 of 1
FileName : C:\TOTALCHROM DATA\Results\Gala\LGN 120.ad.B10%.1ml.A.001.raw
Date : 13/11/2018 12:10:56
Method : Time of Injection: 06/09/2012 12:46:35
Start Time : 18.09 min End Time : 30.01 min Low Point : -26.61 mAU High Point : 579.01 mAU
Plot Offset: -26.61 mAU Plot Scale: 605.6 mAU



***Me*-4e racemic**

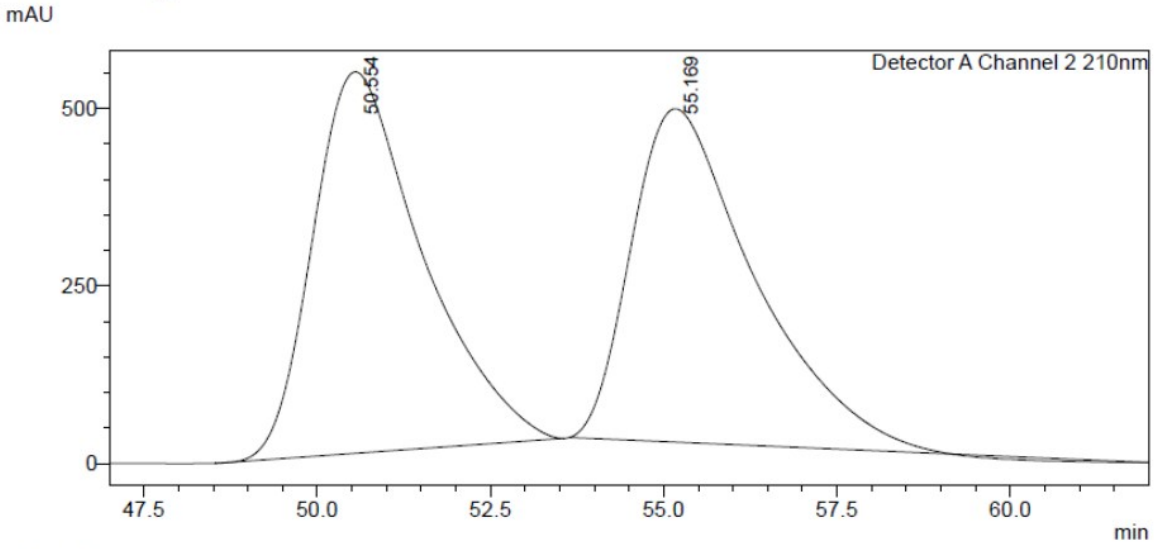


SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: GB 116 benzyl-gingersulfonic_racem_AD_20%_0.5		
Sample ID	: GB 116 ben-gingersulfonic_racem		
Data Filename	: GB 116 benzyl-gingersulfonic_racem_AD_20%_0.5.lcd		
Method Filename	: AD-B20%-0.50ml-90min.lcm		
Batch Filename	:		
Vial #	: 1-9	Sample Type	: Unknown
Injection Volume	: 15 uL		
Date Acquired	: 13/12/2018 13:42:02	Acquired by	: System Administrator
Date Processed	: 13/12/2018 15:12:03	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 210nm

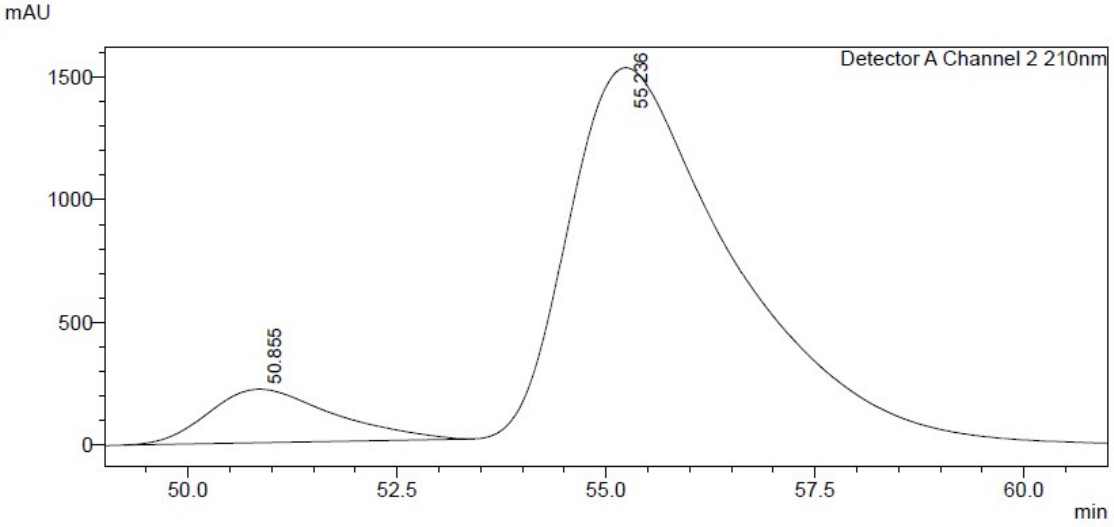
Peak#	Ret. Time	Area	Height	Conc.
1	50.554	59032335	536802	50.551
2	55.169	57746544	469164	49.449
Total		116778879	1005967	

***Me*-(*S*)-4e**

<Sample Information>

Sample Name	: GB 153_benzylginger sulf_soos_AD-B20%-0.5ml		
Sample ID	: GB 153_benzylginger sulf_soos		
Data Filename	: GB 153_benzylginger sulf_soos_AD-B20%-0.5ml.lcd		
Method Filename	: AD-B20%-0.50ml-90min.lcm		
Batch Filename	:		
Vial #	: 1-14	Sample Type	: Unknown
Injection Volume	: 15 uL		
Date Acquired	: 04/02/2019 11:55:36	Acquired by	: System Administrator
Date Processed	: 04/02/2019 13:25:38	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 210nm

Peak#	Ret. Time	Area	Height	Conc.
1	50.855	22558886	217989	9.858
2	55.236	206283268	1515863	90.142
Total		228842155	1733852	

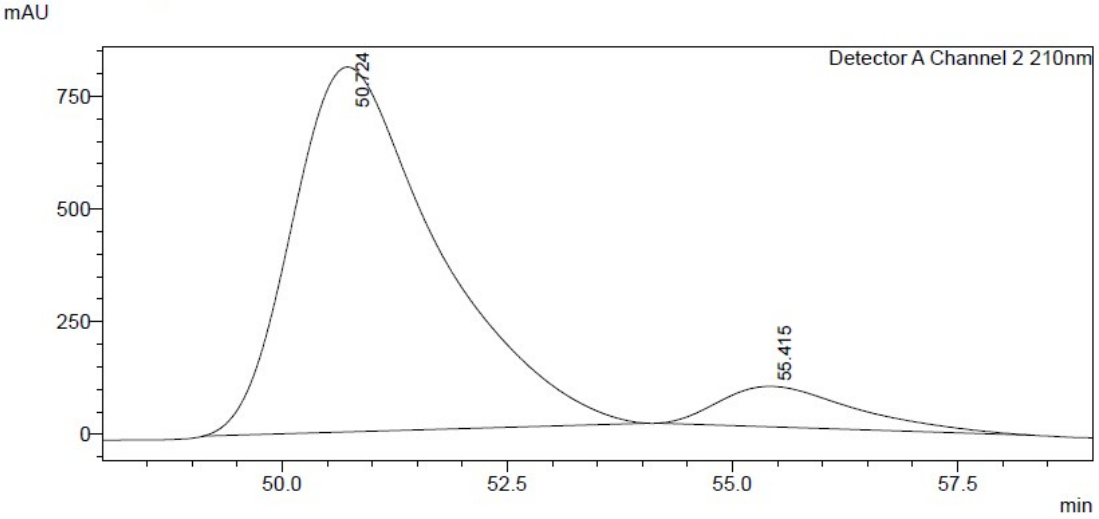
***Me*-(*R*)-4e**

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: GB 154_benzylginger sulf_antisoos_AD-B20%-0.5ml		
Sample ID	: GB 154_benzylginger sulf_antiso		
Data Filename	: GB 154_benzylginger sulf_antisoos_AD-B20%-0.5mll.lcd		
Method Filename	: AD-B20%-0.50ml-90min.lcm		
Batch Filename	:		
Vial #	: 1-13	Sample Type	: Unknown
Injection Volume	: 15 uL		
Date Acquired	: 04/02/2019 10:20:38	Acquired by	: System Administrator
Date Processed	: 04/02/2019 11:50:39	Processed by	: System Administrator

<Chromatogram>

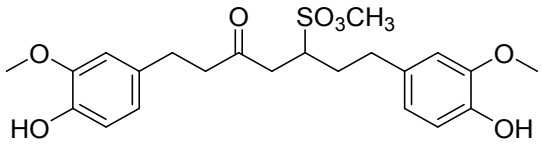


<Peak Table>

Detector A Channel 2 210nm

Peak#	Ret. Time	Area	Height	Conc.
1	50.724	91276117	808735	90.622
2	55.415	9445638	89619	9.378
Total		100721755	898354	

***Me*-4f Racemic**

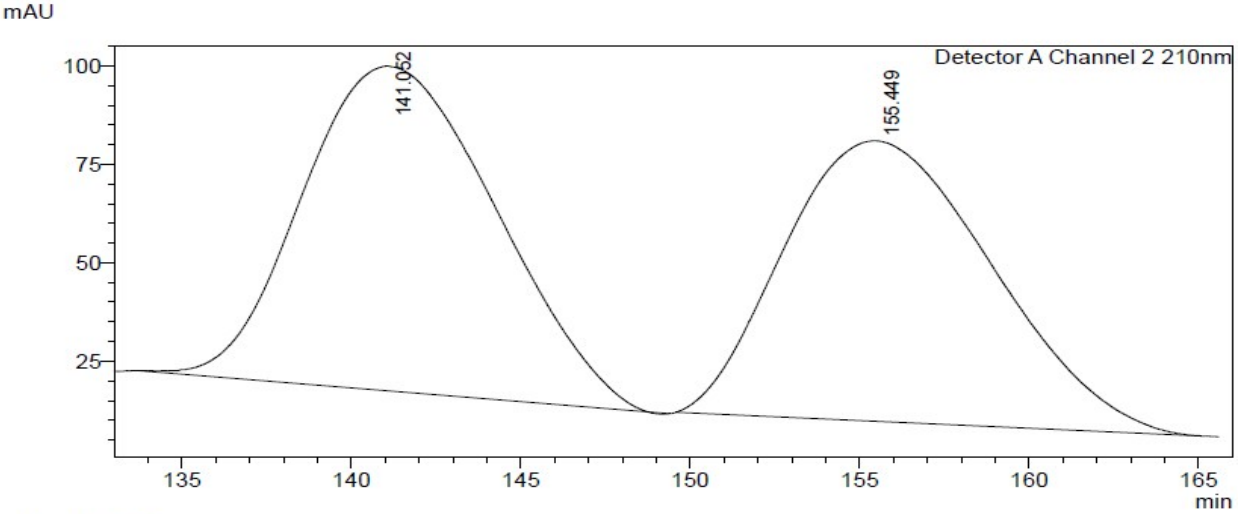


SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: GB 163_shogaolo_rac_AS-B25%-0.5ml-25C-180min		
Sample ID	: GB 163_shogaolo_rac_AS-B25%-0.5		
Data Filename	: GB 163_shogaolo_rac_AS-B25%-0.5ml-25C-180min.lcd		
Method Filename	: AS-B25%-0.5ml-25C-180min.lcm		
Batch Filename	:		
Vial #	: 1-12	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 13/02/2019 11:56:29	Acquired by	: System Administrator
Date Processed	: 13/02/2019 14:42:05	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 210nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	141.052	32715840	82455	0.000	51.885
2	155.449	30338301	71241	0.000	48.115
Total		63054141	153696		100.000

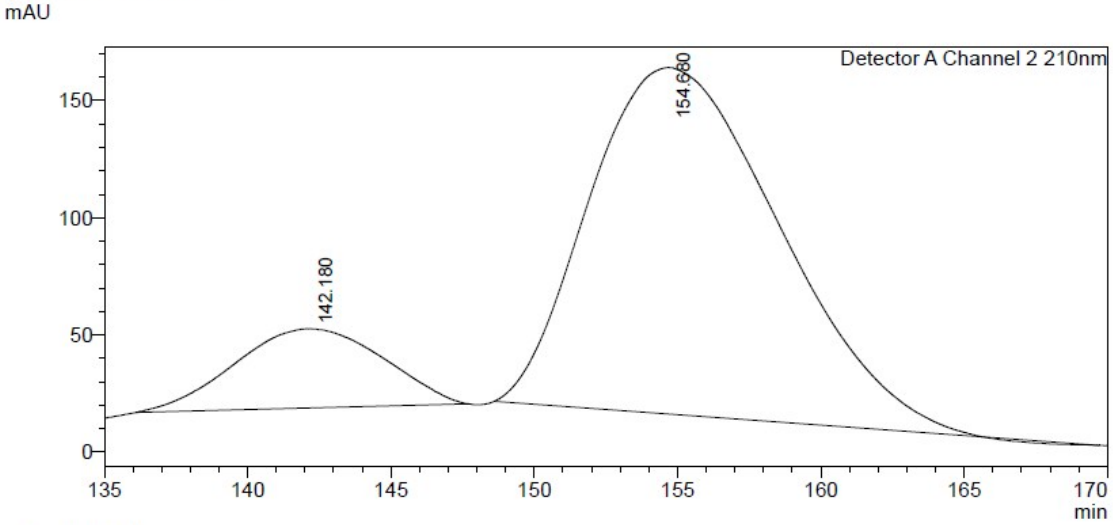
***Me*-(*S*)-4f**

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: GB 155_shogaolo_soos_AS-B25-0.5ml		
Sample ID	: GB 155_shogaolo_soos_AS-B25-0.5		
Data Filename	: GB 155_shogaolo_soos_AS-B25-0.5ml.lcd		
Method Filename	: AS-B25%-0.5ml-25C-180min.lcm		
Batch Filename	:		
Vial #	: 1-15	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 11/02/2019 09:26:49	Acquired by	: System Administrator
Date Processed	: 11/02/2019 12:26:51	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 210nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	142.180	12126797	33789	0.000	15.105
2	154.680	68154912	147828	0.000	84.895
Total		80281709	181617		100.000

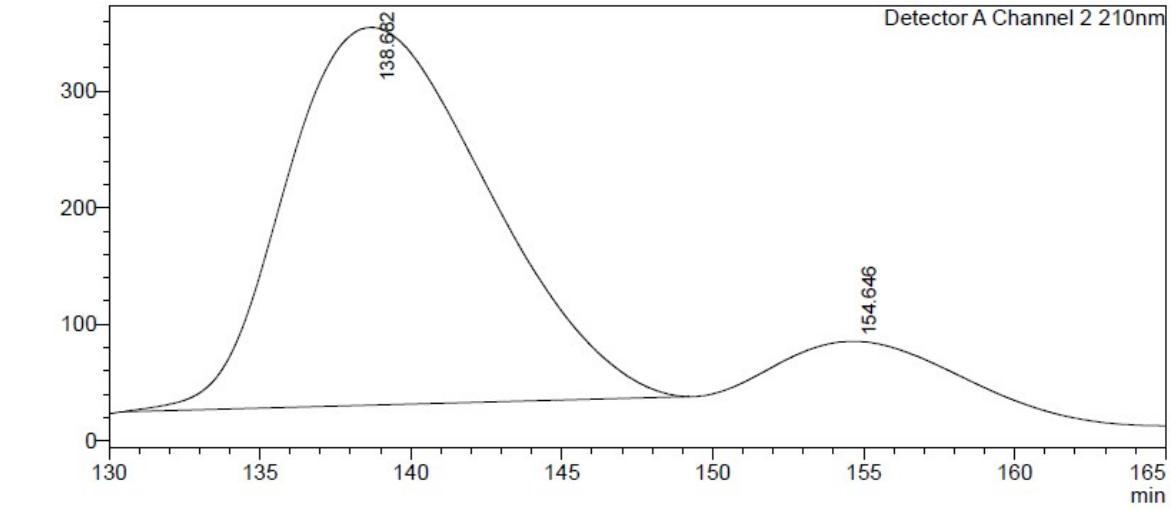
***Me*-(*R*)-4f**

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: GB 156_shogaolo_antisoos_AS-B25%-0.5ml-25C-180min		
Sample ID	: GB 156_shogaolo_antisoos_AS-B25		
Data Filename	: GB 156_shogaolo_antisoos_AS-B25%-0.5ml-25C-180min.lcd		
Method Filename	: AS-B25%-0.5ml-25C-180min.lcm		
Batch Filename	:		
Vial #	: 1-14	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 12/02/2019 12:08:58	Acquired by	: System Administrator
Date Processed	: 12/02/2019 14:57:57	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 210nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	138.682	150376459	324019	0.000	87.264
2	154.646	21947367	55242	0.000	12.736
Total		172323826	379261		100.000