Supporting Information

for

Iodobenzene Catalysed Synthesis of Spirofurans & Benzopyrans by Oxidative Cyclisation of Vinylogous esters

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SI-1. Experimental Procedures

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I. General Procedures

Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Bruker DRX400 spectrometer operating at 400 MHz for proton and 100 MHz for carbon nuclei or a Varian DRX 300 spectrometer operating at 300 MHz for proton and 75 MHz for carbon. Infrared spectra (ν_{max}) were recorded on a Perkin-Elmer RXI FTIR Spectrometer. Low-resolution mass spectrometry (ESI) was performed on a Micromass Platform QMS spectrometer. Electrospray high-resolution mass spectra (ESI-HRMS) were recorded on a Bruker BioApex 47e FTMS fitted with an Analytical electrospray source using NaI for accurate mass calibration. Electron impact high-resolution mass spectra (EI-HRMS) were recorded on a ThermoQuest MAT95XP using electron ionization (70 eV), and memplying PerFluoroKerosene (PFK) as a reference sample. Flash column chromatography was performed on silica gel (Davisil LC60A, 40-63 μm silica media) using compressed air or nitrogen. Thin layer chromatography (TLC) was performed using aluminum-backed plates coated with 0.2 mm silica (Merck, DC-Platten, Kieselgel; 60 F_{254} plates). Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable stain followed by heating.

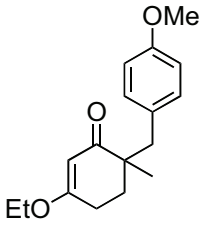
Starting materials and reagents were purchased from Sigma-Aldrich and were used as supplied or, in case of some liquids, distilled. Hexafluoroisopropanol was supplied by Oakwood chemicals. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Unless stated otherwise all reactions were conducted in flame dried glassware under an inert atmosphere (N_2). Vinylogous ester **3a** was prepared using the procedure reported below and was characterized by comparison to the literature.[1]

[1] M. Fagnoni, P. Schmoldt, T. Kirschberg, J. Mattay *Tetrahedron* 1998, **54**, 6427

II. Synthesis of Vinylogous esters

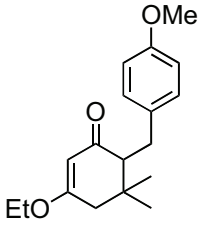
General procedure: A magnetically stirred solution of HMDS (2.29 mL, 11.0 mmol) or DIPA (11.0 mmol) in THF (10 mL) was cooled to -78 °C and treated dropwise with *n*-BuLi (6.87 mL, 11.0 mmol).[2] The solution was stirred at the same temperature for 30 min. The enol ether (1.40 g, 10.0 mmol) was then added dropwise at -78 °C and the reaction mixture was stirred for a further 30 min. After 30 min, HMPA (1.91 mL, 11.0 mmol) followed by 4-methoxybenzyl bromide (1.4 mL, 10.0 mmol) were added successively to the mixture. The cooling bath was removed and the resulting mixture was allowed to warm to room temperature over night, then diluted with Et_2O (20 mL) and sat. NH_4Cl (20 mL). The combined organic extracts were washed with H_2O (20 mL), sat. $NaHCO_3$ (20 mL) and brine (20 mL), then dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification *via* column chromatography afforded the products as oils.

3-Ethoxy-6-(4-methoxybenzyl)-6-methylcyclohex-2-enone (1b) R_f 0.5 (3:7, v/v EtOAc:hexane); IR



ν_{max} 2931, 1648, 1608, 1190; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.05 ($d_{AA'XX'}$, J = 8.4 Hz, 2H), 6.80 ($d_{AA'XX'}$, J = 8.4 Hz, 2H), 5.29 (s, 1H), 3.88 (q, J = 7.0 Hz, 2H), 3.78 (s, 3H), 2.95 (d, J = 13.5 Hz, 1H), 2.64 (d, J = 13.5 Hz, 1H), 2.41 (t, J = 6.3 Hz, 2H), 1.83 – 1.79 (m, 1H), 1.61 (m, 1H), 1.35 (t, J = 7.0 Hz, 3H), 1.06 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.63, 175.79, 158.13, 131.55, 129.88, 113.33, 101.62, 64.14, 55.18, 44.47, 41.96, 30.88, 26.13, 22.66, 14.15; ESI-HRMS Found $(M+H)^+$ 275.1648, $C_{17}H_{22}O_3$ requires $(M+H)^+$ 275.1647.

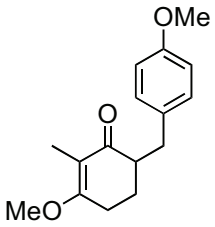
3-Ethoxy-6-(4-methoxybenzyl)-5,5-dimethylcyclohex-2-enone (1c) R_f 0.4 (1:9, v/v EtOAc:hexane);



IR ν_{max} 3068, 3029, 2959, 2934, 2873, 1654, 1616, 1585, 1377, 1358, 1178, 1154; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.13 ($d_{AA'XX'}$, J = 6.8 Hz, 2H), 6.79 ($d_{AA'XX'}$, J = 6.8 Hz, 2H), 5.28 (s, 1H), 3.88 (m, 2H), 3.77 (s, 3H), 2.92 (dd, J = 14.0 Hz, 8.0 Hz, 1H), 2.68 (dd, J = 14.0 Hz, 1.0 Hz, 1H), 2.32 – 2.29 (m, 3H), 1.36 (t J = 7.2 Hz, 3H), 1.11 (s, 3H), 1.02 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 200.95, 173.91, 157.72, 133.77, 129.85, 113.67, 101.00, 64.07, 59.39, 55.21, 42.67, 35.74, 30.99, 29.02, 23.66, 14.13; ESI-HRMS Found $(M+H)^+$ 289.1794, $C_{18}H_{24}O_3$ requires $(M+H)^+$ 289.1798.

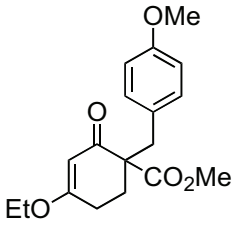
[2] HMDS was used for 1st alkylation while DIPA was used for the 2nd alkylation.

3-Methoxy-6-(4-methoxybenzyl)-2-methylcyclohex-2-enone (1d) R_f 0.4 (3:7, v/v EtOAc:hexane);

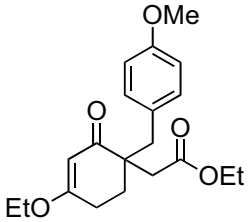


IR ν_{max} 2943, 2861, 1611, 1511, 1242; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16 ($d_{AA'XX'}$, J = 8.6 Hz, 2H), 6.81 ($d_{AA'XX'}$, J = 8.6 Hz, 2H), 3.71 (s, 2 X 3H), 3.27 (dd, J = 13.4 Hz, 3.6 Hz, 1H), 2.58 (dtd, J = 13.4 Hz, 5.1 Hz, 1.2 Hz, 1H), 2.45-2.32 (m, 3H), 1.93 (ddd, J = 13.2 Hz, 8.4 Hz, 5.0 Hz, 1H), 1.70 (s, 3H), 1.57 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.64, 170.78, 157.92, 132.22, 130.06, 114.18, 113.73, 55.19 54.96, 46.41, 35.02, 24.96, 23.69, 7.62; ESI-HRMS Found $(M)^+$ 260.1408, $C_{16}H_{20}O_3$ requires $(M)^+$ 260.1407.

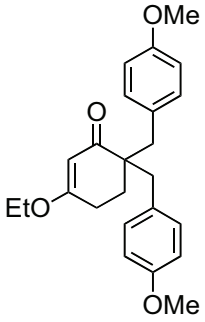
Methyl 4-ethoxy-1-(4-methoxybenzyl)-2-oxocyclohex-3-enecarboxylate (1e) R_f (3:7, v/v EtOAc:hexane); IR ν_{max} 2981, 2949, 2836, 1727, 1654, 1602, 1512, 1245, 1177; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.04 ($d_{AA'XX'}$, J = 8.4 Hz, 2H), 6.77 ($d_{AA'XX'}$, J = 8.4 Hz, 2H), 5.38 (s, 1H), 3.88 (q, J = 7.2 Hz, 2H), 3.77 (s, 3H), 3.69 (s, 3H), 3.19 (q, J = 14.0 Hz, 2H), 2.61 (m, 1H), 2.28 (m, 2H), 1.78 (m, 1H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.7, 177.06, 171.68, 158.41, 131.44, 128.59, 113.91, 102.69, 64.39, 57.00, 55.14, 52.42, 39.25, 28.06, 26.58, 14.07; ESI-HRMS Found $(M)^+$ 318.1483, $C_{18}H_{22}O_5$ requires $(M)^+$ 318.1467.



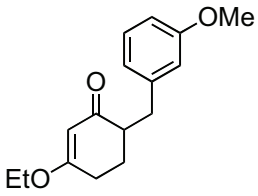
Ethyl 2-(4-ethoxy-1-(4-methoxybenzyl)-2-oxocyclohex-3-en-1-yl)acetate (1f) R_f 0.3 (3:7, v/v EtOAc:hexane); IR ν_{max} 2981, 2937, 1732, 1651, 1609, 1512, 1248, 1192; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.10-7.05 (m, 2H), 6.83-6.80 (m, 2H), 5.38 (s, 1H), 4.06 (m, 2H), 3.93 (m, 2H), 3.78 (s, 3H), 2.96 (d, J = 14.0 Hz, 1H), 2.86 (d, J = 16.0 Hz, 1H), 2.68 (d, J = 14.0 Hz, 1H), 2.61 (m, 1H), 2.42 – 2.39 (m, 2H), 2.15 (d, J = 16.0 Hz, 1H), 1.79 (m, 1H), 1.36 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 200.57, 175.58, 171.62, 158.43, 131.55, 130.11, 113.59, 102.29, 64.25, 60.26, 55.25, 47.22, 39.93, 34.76, 28.19, 26.02, 14.17, 14.4; ESI-HRMS Found $(M+H)^+$ 347.1845, $C_{20}H_{26}O_5$ requires $(M+H)^+$ 347.1853.



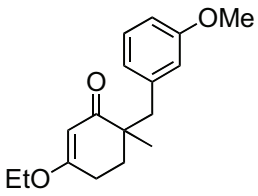
3-Ethoxy-6,6-bis(4-methoxybenzyl)cyclohex-2-enone (1g) R_f 0.4 (3:7, v/v EtOAc:hexane); IR ν_{max} 2982, 2935, 1645, 1609, 1511, 1248, 1195, 1178; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.02 ($d_{AA'XX'}$, J = 8.8 Hz, 4H), 6.76 ($d_{AA'XX'}$, J = 8.8 Hz, 4H), 5.28 (s, 1H), 3.88 (q, J = 7.2 Hz, 2H), 3.81 (s, 6H), 3.29 (dd, J = 13.5 Hz, 1.2 Hz, 2H), 2.51 – 2.34 (m, 4H), 1.94 – 1.89 (m, 2H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 202.5, 176.0, 158.1, 131.9, 129.7, 113.3, 103.0, 64.2, 55.1, 49.4, 45.8, 26.9, 26.2, 14.1; ESI-HRMS Found $(M+H)^+$ 381.2058, $C_{24}H_{28}O_4$ requires $(M+H)^+$ 381.2060.



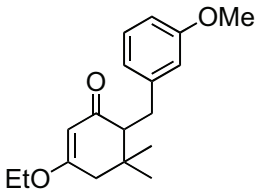
3-Ethoxy-6-(3-methoxybenzyl)cyclohex-2-enone (1h) R_f 0.3 (3:7, v/v EtOAc:hexane); IR ν_{max} 3050, 2981, 2940, 1651, 1609, 1257, 1191; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.19 (t, J = 7.2 Hz, 1H), 6.78 – 6.74 (m, 3H), 5.36 (s, 1H), 3.89 (m, 2H), 3.79 (s, 3H), 3.35 (d, J = 10.0 Hz, 1H), 2.47 – 2.42 (m, 2H), 2.37 – 2.35 (m, 2H), 1.92 (m, 1H), 1.62 (m, 1H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 200.37, 177.04, 159.68, 141.88, 129.31, 121.62, 115.91, 111.39, 102.25, 64.26, 55.16, 47.04, 35.75, 28.25, 25.59, 14.14; ESI-HRMS Found $(M+H)^+$ 261.1484, $C_{16}H_{20}O_3$ requires $(M+H)^+$ 261.1491.



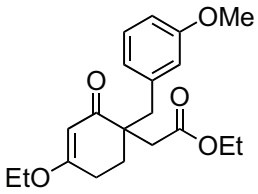
3-Ethoxy-6-(3-methoxybenzyl)-6-methylcyclohex-2-enone (1i) R_f 0.5 (3:7, v/v EtOAc:hexane); IR ν_{max} 2930, 1648, 1609, 1190; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.17 (t, J = 7.6 Hz, 1H), 6.77 – 6.70 (m, 3H), 5.29 (s, 1H), 3.88 (q, J = 7.2 Hz, 2H), 3.78 (s, 3H), 2.95 (d, J = 13.5 Hz, 1H), 2.64 (d, J = 13.5 Hz, 1H), 2.42 – 2.39 (m, 2H), 1.88 – 1.81 (m, 1H), 1.66 – 1.61 (m, 1H), 1.35 (t, J = 7.2 Hz, 3H), 1.09 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.45, 175.80, 159.24, 139.55, 128.78, 123.17, 116.58, 111.45, 101.58, 64.17, 55.14, 44.39, 42.91, 31.32, 26.14, 22.78, 14.16; ESI-HRMS Found $(M+H)^+$ 275.1639, $C_{17}H_{22}O_3$ requires $(M+H)^+$ 275.1647.



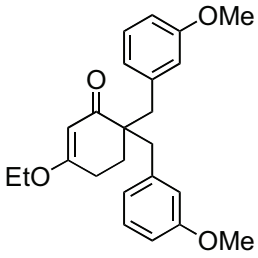
3-Ethoxy-6-(3-methoxybenzyl)-5,5-dimethylcyclohex-2-enone (1j) R_f 0.5 (3:7, v/v EtOAc:hexane); IR ν_{max} 3070, 3049, 2960, 2936, 1652, 1615, 1261, 1218; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16 (t, J = 7.6 Hz, 1H), 6.83 – 6.80 (m, 2H), 6.70 (dd, J = 7.6 Hz, 2.0 Hz, 1H), 5.30 (s, 1H), 3.88 (m, 2H), 3.78 (s, 3H), 3.05 (dd, J = 14.0 Hz, 8.0 Hz, 1H), 2.67 (dd, J = 14.0 Hz, 4.0 Hz, 1H), 2.38 (dd, J = 7.6 Hz, 4.0 Hz, 1H), 2.31 (d, J = 9.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H), 1.11 (s, 3H), 1.01 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 200.57, 173.91, 159.48, 143.65, 129.10, 121.34, 114.76, 111.07, 101.03, 64.07, 59.02, 55.09, 43.00, 35.92, 31.59, 29.06, 23.22, 14.12; ESI-HRMS Found $(M+H)^+$289.1797, $C_{18}H_{24}O_3$ requires $(M+H)^+$ 289.1804.



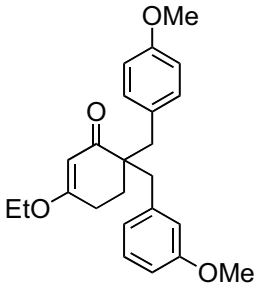
Ethyl 2-(4-ethoxy-1-(3-methoxybenzyl)-2-oxocyclohex-3-en-1-yl)acetate (1k) R_f 0.3 (3:7, v/v EtOAc:hexane); IR ν_{max} 2980, 2936, 1734, 1654, 1648, 1609, 1191, 1173; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.0 Hz, 1H), 6.79 – 6.71 (m, 3H), 5.39 (s, 1H), 4.08 (m, 2H), 3.93 (m, 2H), 3.79 (s, 3H), 3.01 (d, *J* = 13.2 Hz, 1H), 2.88 (d, *J* = 16.0 Hz, 1H), 2.71 (d, *J* = 13.2 Hz, 1H), 2.61 (m, 1H), 2.43 – 2.38 (m, 1H), 2.25 (m, 1H), 2.19 (d, *J* = 16.0 Hz, 1H), 1.83 – 1.79 (m, 1H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.28, 175.59, 171.64, 159.35, 138.21, 129.04, 123.05, 116.64, 111.73, 101.74, 64.24, 55.14, 46.52, 40.73, 39.92, 30.60, 27.66, 25.99, 14.15, 13.66; ESI-HRMS Found $(M+H)^+$ 347.1853, $C_{20}H_{26}O_5$ requires $(M+H)^+$ 347.1858.



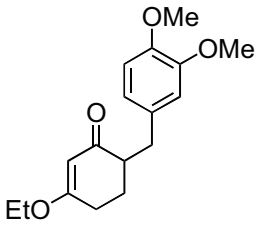
3-Ethoxy-6,6-bis(3-methoxybenzyl)cyclohex-2-enone (1l) R_f 0.4 (3:7, v/v EtOAc:hexane); IR ν_{max}2934, 1646, 1607, 1262, 1195; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 8.0 Hz, 2H), 6.76 – 6.68 (m, 6H), 5.32 (s, 1H), 3.84 (q, *J* = 7.2 Hz, 2H), 3.75 (s, 6H), 3.20 (d, *J* = 13.2 Hz, 2H), 2.52 (d, *J* = 13.2 Hz, 2H), 2.38 (t, *J* = 6.4 Hz, 2H), 1.74 (t, *J* = 6.4 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.98, 175.92, 159.22, 139.20, 128.81, 123.35, 116.60, 111.73, 102.76, 64.14, 55.12, 49.35, 41.94, 30.88, 27.05, 26.16, 14.10; ESI-HRMS Found $(M+H)^+$ 381.2056, $C_{24}H_{28}O_4$ requires $(M+H)^+$ 381.2066.



3-Ethoxy-6-(3-methoxybenzyl)-6-(4-methoxybenzyl)cyclohex-2-enone (1m) R_f 0.4 (3:7, v/v EtOAc:hexane); IR ν_{max} 2981, 2936, 1645, 1608, 1511, 1250, 1195; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 8.0 Hz, 1H), 7.03 ($d_{AA'XX'}$, *J* = 8.8 Hz, 2H), 6.77 ($d_{AA'XX'}$, *J* = 8.8 Hz, 2H), 6.72 – 6.68 (m, 3H), 5.31 (s, 1H), 3.83 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 3.20 (d, *J* = 13.6 Hz, 1H), 3.16 (d, *J* = 13.6 Hz, 1H), 2.51 (d, *J* = 8.0 Hz, 1H), 2.48 (d, *J* = 8.0 Hz, 1H), 2.38 (t, *J* = 6.4 Hz, 2H), 1.73 (t, *J* = 6.4 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 202.12, 175.89, 159.23, 158.16, 139.35, 131.80, 129.53, 128.78, 123.35, 116.59, 113.37, 111.70, 102.81, 64.11, 55.16, 55.12, 49.43, 41.83, 41.14, 27.02, 26.16, 14.10; ESI-HRMS Found $(M+H)^+$ 381.2060, $C_{24}H_{28}O_4$ requires $(M+H)^+$ 381.2066.



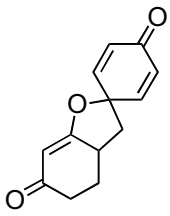
6-(3,4-Dimethoxybenzyl)-3-ethoxycyclohex-2-enone (1n) R_f 0.5 (3:1, v/v EtOAc:hexane); IR ν_{max} 2963, 1648, 1606, 1516, 1190; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.78 (d, *J* = 8.0 Hz, 1H), 6.73 – 6.70 (m, 2H), 5.36 (s, 1H), 3.89 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.28 (dd, *J* = 13.2 Hz, 3.6 Hz, 1H), 2.49 – 2.38 (m, 4H), 1.94 (m, 1H), 1.61 (m, 1H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 200.63, 177.11, 148.87, 147.40, 132.65, 121.15, 112.35, 111.11, 102.21, 64.25, 55.83, 47.18, 35.28, 28.11, 25.46, 14.15, 14.10; ESI-HRMS Found $(M+H)^+$ 291.1588; $C_{17}H_{22}O_4$ requires $(M+H)^+$ 291.1596.



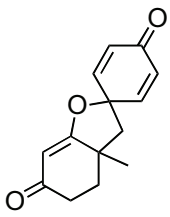
III. Oxidative Cyclisations

General procedure: A solution of vinylogous ester **3** (0.5 mmol) and iodobenzene (20 mg, 0.1 mmol) in 9:1 HFIP/TFA (5 mL) was cooled to 0 °C under air atmosphere. *m*-CPBA (1.5 equiv.) was then added in one portion and the reaction mixture was stirred over 4 hours and allowed to warm to room temperature. After completion of the reaction (as indicated by TLC), the solvent was removed under reduced pressure and the crude material subjected to column chromatography to afford the pure product.

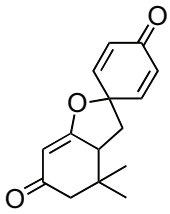
4,5-Dihydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-4',6(3aH)-dione (2a) R_f 0.4 (3:1, v/v EtOAc:hexane); IR ν_{max} 3050, 2930, 2871, 1672, 1623, 1178; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.90 (dd, *J* = 10.4 Hz, 3.2 Hz, 1H), 6.77 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H), 6.30 (dd, *J* = 10.0 Hz, 2.0 Hz, 1H), 6.90 (dd, *J* = 10.4 Hz, 2.0 Hz, 1H), 5.52 (s, 1H), 3.30 (m, 1H), 2.51 – 2.30 (m, 4H), 2.01 (t, *J* = 12.8 Hz, 1H), 1.77 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 198.37, 184.20, 180.12, 146.37, 143.71, 129.90, 128.74, 102.08, 83.37, 40.74, 39.86, 36.01, 27.87; ESI-HRMS Found $(M+H)^+$ 217.0863, $C_{13}H_{12}O_3$ requires $(M+H)^+$ 217.0865.



3a-Methyl-4,5-dihydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-4',6(3aH)-dione (2b) R_f 0.2 (3:1, v/v EtOAc:hexane); IR ν_{max}2922, 2852, 1672, 1637, 1625, 1190; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 10.8 Hz, 3.6 Hz, 1H), 6.67 (dd, *J* = 10.0 Hz, 3.6 Hz, 1H), 6.26 – 6.22 (m, 2H), 5.46 (s, 1H), 2.47 (m, 2H), 2.28 (d, *J* = 13.6 Hz, 1H), 2.19 (d, *J* = 13.6 Hz, 1H), 2.14 (m, 1H), 1.97 (td, *J* = 12.8 Hz, 5.6 Hz, 1H), 1.55 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 197.96, 184.14, 184.0, 147.88, 145.51, 128.52, 128.09, 102.07, 83.22, 48.15, 42.90, 35.39, 32.81, 25.18; ESI-HRMS Found $(M+H)^+$ 231.1013, $C_{14}H_{14}O_3$ requires $(M+H)^+$231.1016.

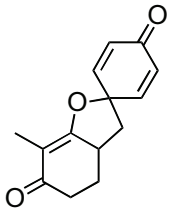


4,4-Dimethyl-4,5-dihydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-4',6(3aH)-dione (2c)



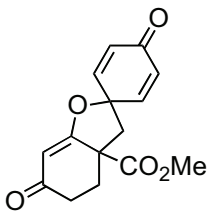
R_f 0.3 (3:1, v/v EtOAc:hexane); IR ν_{max} 3048, 2962, 2932, 1675, 1628, 1181; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.90 (dd, *J* = 10.0 Hz, 2.8 Hz, 1H), 6.77 (dd, *J* = 10.0 Hz, 2.8 Hz, 1H), 6.30 (dd, *J* = 10.0 Hz, 2.0 Hz, 1H), 6.24 (dd, *J* = 10.0 Hz, 2.0 Hz, 1H), 5.53 (s, 1H), 3.26 (m, 1H), 2.29 (d, *J* = 2.0 Hz, 2H), 2.23 (m, 2H), 2.11 (t, *J* = 12.8 Hz, 1H), 1.14 (s, 3H), 0.99 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 198.01, 184.17, 178.04, 146.41, 143.81, 129.83, 128.72, 101.34, 82.76, 51.98, 50.24, 35.64, 35.03, 29.43, 19.74, 14.15 (1 extra signal); ESI-HRMS Found $(M+H)^+$ 245.1170, $C_{15}H_{17}O_3$ requires $(M+H)^+$ 245.1178.

7-Methyl-4,5-dihydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-4',6(3aH)-dione (2d)



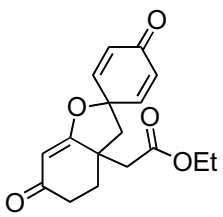
R_f 0.2 (3:1, v/v EtOAc:hexane); IR ν_{max} 2926, 1671, 1627, 1217; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.92 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H), 6.79 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H), 6.32 (dd *J* = 10.0 Hz, 2.8 Hz, 1H), 6.23 (dd, *J* = 10.0 Hz, 2.8 Hz , 1H), 3.29 (m, 1H), 2.55 (m, 1H), 2.40 (m, 2H), 2.29 (m, 1H), 2.00 (t, *J* = 12.8 Hz, 1H), 1.75 (m, 1H), 1.70 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 198.09, 184.42, 174.68, 147.07, 144.37, 129.65, 128.47, 109.37, 82.64, 41.41, 39.62, 36.01, 27.69, 7.31; EI-HRMS Found $(M)^+$ 230.0942 $C_{14}H_{14}O_3$ requires $(M)^+$ 230.0943.

Methyl 4',6-dioxo-3a,4,5,6-tetrahydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-3a-carboxylate (2e)



R_f 0.3 (3:1, v/v EtOAc:hexane); IR ν_{max} 2956, 1733, 1673, 1633, 1187; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.77 (dd, *J* = 10.8 Hz, 3.2 Hz, 1H), 6.71 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H), 6.28 (dd *J* = 10.0 Hz, 2.0 Hz, 1H), 6.21 (dd, *J* = 10.8 Hz, 2.0 Hz , 1H), 5.65 (s, 1H), 3.87 (s, 3H), 2.88 (d, *J* = 14.0 Hz 1H), 2.65 (m, 1H), 2.45 (m, 1H), 2.35 (dd, *J* = 13.6 Hz, 4.8 Hz, 1H), 2.27 (d, *J* = 14.0 Hz, 1H), 2.04 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 197.34, 183.93, 175.76, 171.95, 146.54, 143.87, 129.40, 128.76, 104.33, 82.81, 54.24, 53.68, 44.97, 33.53; EI-HRMS Found $(M)^+$ 274.0831, $C_{14}H_{14}O_3$ requires $(M)^+$ 274.0841.

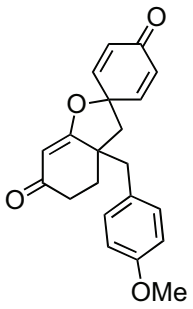
Ethyl 2-(4',6-dioxo-3a,4,5,6-tetrahydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]dien]-3a-yl)acetate (2f)



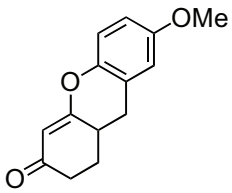
R_f 0.3 (3:1, v/v EtOAc:hexane); IR ν_{max} 2981, 2942, 1728, 1673, 1645, 1629, 1184; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.06 (dd, *J* = 10.0, 3.2 Hz, 1H), 6.66 (dd, *J* = 10.0, 3.2 Hz, 1H), 6.28 – 6.23 (m, 2H), 5.53 (s, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.89 (dd, *J* = 15.6, 1.6 Hz, 1H), 2.84 (d, *J* = 14.0 Hz, 1H), 2.67 (dd, *J* = 15.6, 1.6 Hz, 1H), 2.53 (m, 3H), 2.11 (dd, *J* = 14.0, 1.2 Hz, 1H), 1.90 (m, 1H), 1.27 (t, *J* = 14.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 197.88, 184.05, 181.83, 169.45, 147.43,

144.97, 128.81, 128.27, 103.09, 83.34, 61.34, 45.26, 44.23, 39.32, 32.58, 32.08, 14.17; ESI-HRMS Found $(M+H)^+$ 303.1227, $C_{17}H_{18}O_5$ requires $(M+H)^+$ 303.1232.

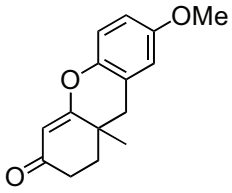
3a-(4-Methoxybenzyl)-4,5-dihydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-4',6(3aH)-dione (2g) R_f 0.3 (1:1, v/v EtOAc:hexane); IR ν_{max} 3044, 2935, 2871, 1671, 1643, 1624, 1180; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.08 ($d_{AA'XX'}$, J = 8.8 Hz, 2H), 6.90 ($d_{AA'XX'}$, J = 8.8 Hz, 2H), 6.65 ($d_{AA'XX'}$, J = 10.4 Hz, 2H), 6.23 – 6.17 (m, 2H), 5.60 (s, 1H), 3.80 (s, 3H), 3.00 (s, 2H), 2.63 (m, 1H), 2.53 (d, J = 14.4 Hz, 1H), 2.47 (m, 1H), 2.30 (dd , J = 13.2 Hz, 5.2 Hz, 1H), 1.85 (d, J = 14.4 Hz, 1H), 1.80 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ197.81, 184.16, 183.68, 159.13, 148.07, 145.37, 131.36, 128.61, 127.61, 127.35, 114.25, 103.11, 83.29, 60.35, 55.31, 47.76, 43.30, 40.75, 32.89, 32.55, 21.01, 14.16; EI-HRMS Found $(M)^+$ 336.1356, $C_{21}H_{20}O_4$ requires $(M)^+$ 336.1362.



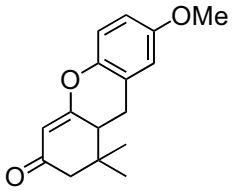
7-Methoxy-9,9a-dihydro-1H-xanthen-3(2H)-one (3h) R_f 0.5 (1:1, v/v EtOAc:hexane); IR ν_{max} 3017, 2941, 1648, 1607, 1221, 1201; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.96 (d, J = 9.2 Hz, 1H), 6.77 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 6.66 (brd, J = 2.4 Hz, 1H), 5.77 (s, 1H), 3.80 (s, 3H), 2.87 (dd, J = 15.2 Hz, 5.6 Hz, 1H), 2.78 (m, 1H), 2.61- 2.51 (m, 2H), 2.45 – 2.41 (m, 1H), 2.36 – 2.32 (m, 1H), 1.85 – 1.81 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.09, 175.81, 155.66, 144.73, 122.18, 116.76, 114.02, 113.28, 106.10, 55.61, 38.20, 36.11, 33.17, 32.89; ESI-HRMS Found $(M+H)^+$ 231.1013, $C_{14}H_{14}O_3$ requires $(M+H)^+$ 231.1016.



7-Methoxy-9a-methyl-9,9a-dihydro-1H-xanthen-3(2H)-one (3i) R_f 0.4 (1:1, v/v EtOAc:hexane); IR ν_{max} 2925, 2853, 1654, 1648, 1630, 1602, 1214, 1198; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.94 (d, J = 8.8 Hz, 1H), 6.77 (dd, J = 8.8 Hz, 2.8 Hz, 1H), 6.64 (d, J = 2.8 Hz, 1H), 5.64 (s, 1H), 3.79 (s, 3H), 2.75 (d, J = 15.6 Hz, 1H), 2.66 – 2.57 (m, 2H), 2.47 (dt, J = 15.6 Hz, 3.6 Hz, 1H), 2.04 (m, 2H), 1.18 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.07, 176.79, 155.66, 144.34, 122.14, 116.77, 114.05, 113.29, 106.07, 55.62, 38.05, 36.21, 33.70, 32.99, 21.24; ESI-HRMS Found $(M+H)^+$ 245.1171, $C_{15}H_{16}O_3$ requires $(M+H)^+$ 245.1172.

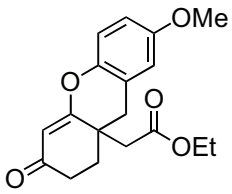


7-Methoxy-1,1-dimethyl-9,9a-dihydro-1H-xanthen-3(2H)-one (3j) R_f 0.5 (1:1, v/v EtOAc:hexane);



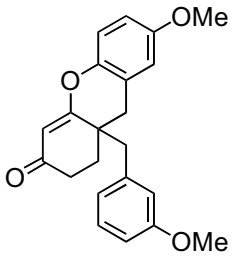
IR ν_{max} 3066, 2963, 2876, 1720, 1654, 1630, 1605, 1209; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.8 Hz, 1H), 6.76 (dd, *J* = 8.8 Hz, 3.2 Hz, 1H), 6.69 (d, *J* = 3.2 Hz, 1H), 5.80 (s, 1H), 3.78 (s, 3H), 2.84 (d, *J* = 10.8 Hz, 1H), 2.67 (m, 2H), 2.43 (d, *J* = 15.6 Hz, 1H), 2.29 (d, *J* = 15.6 Hz, 1H), 1.23 (s, 3H), 1.07 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.09, 172.72, 155.62, 144.74, 124.04, 116.96, 113.32, 113.30, 106.25, 55.61, 52.70, 43.19, 36.17, 28.33, 23.38, 20.61; ESI-HRMS Found $(M+H)^+$ 259.1327, $C_{16}H_{18}O_3$ requires $(M+H)^+$ 259.1329.

Ethyl 2-(7-methoxy-3-oxo-2,3,9,9a-tetrahydro-1H-xanthen-9a-yl)acetate (3k) R_f 0.5 (1:1, v/v EtOAc:hexane);



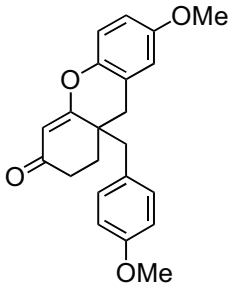
IR ν_{max} 2940,2837, 1728, 1656, 1632, 1201; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 9.2 Hz, 1H), 6.78 (dd, *J* = 9.2, 3.2 Hz, 1H), 6.66 (d, *J* = 3.2 Hz, 1H), 5.69 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 3.21 (d, *J* = 16.0 Hz, 1H), 2.46 - 2.64 (m, 6H), 1.93 (td, *J* = 10.0, 1.2 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 198.33, 174.26, 169.70, 155.88, 144.25, 121.57, 116.76, 114.07, 113.75, 106.93, 60.81, 55.65, 35.78, 35.48, 34.26, 33.68, 32.47, 14.14; ESI-HRMS Found $(M+H)^+$ 317.1380, $C_{18}H_{20}O_5$ requires $(M+H)^+$ 317.1384.

7-Methoxy-9a-(3-methoxybenzyl)-9,9a-dihydro-1H-xanthen-3(2H)-one (3l) R_f 0.6 (1:1, v/v EtOAc:hexane);



IR ν_{max} 2983, 2836, 1654, 1630, 1602, 1208, 1195; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.84 – 6.79 (m, 2H), 6.66 (d, *J* = 2.8 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.52 – 6.51 (m, 1H), 5.77 (s, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 2.81 (d, *J* = 13.6 Hz, 1H), 2.69 – 2.65 (m, 3H), 2.50 (m, 2H), 2.17 (m ,1H), 1.74 (td, *J* = 10.0 Hz, 4.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 198.66, 176.13, 159.49, 155.85, 144.67, 136.76, 129.28, 122.65, 121.83, 116.94, 116.33, 114.08, 113.40, 112.23, 107.08, 55.70, 55.10, 36.92, 36.76, 33.94, 33.64, 31.50; ESI-HRMS Found $(M+H)^+$ 351.1589, $C_{22}H_{22}O_4$ requires $(M+H)^+$ 351.1591.

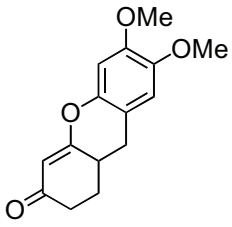
7-Methoxy-9a-(4-methoxybenzyl)-9,9a-dihydro-1H-xanthen-3(2H)-one (3m) R_f 0.3 (1:1, v/v EtOAc:hexane);



IR ν_{max} 3032, 2936, 1718, 1651, 1631, 1610, 1512, 1196; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.8 Hz, 1H), 6.89 ($d_{AA'XX'}$, *J* = 8.8 Hz, 2H), 6.82 (m, 3H), 6.65 (d, *J* = 2.8 Hz, 1H), 5.77 (s, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 2.78 (d, *J* = 14.4 Hz, 1H), 2.67 – 2.61 (m, 3H), 2.51 – 2.40 (m, 2H), 2.15 – 2.05 (m, 1H), 1.75 – 1.65 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.28, 176.88, 158.68, 155.86, 144.62, 131.23, 127.03, 121.83, 116.89, 114.16, 113.72,

113.18, 106.87, 55.69, 55.16, 36.84, 35.97, 33.67, 33.47, 31.29; ESI-HRMS Found $(M+H)^+$ 351.1582, $C_{22}H_{22}O_4$ requires $(M+H)^+$ 351.1591.

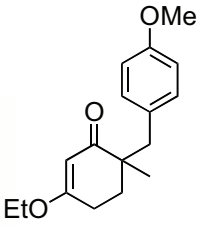
6,7-Dimethoxy-9,9a-dihydro-1H-xanthen-3(2H)-one (3n) R_f 0.4 (3:1, v/v EtOAc:hexane); IR ν_{max}

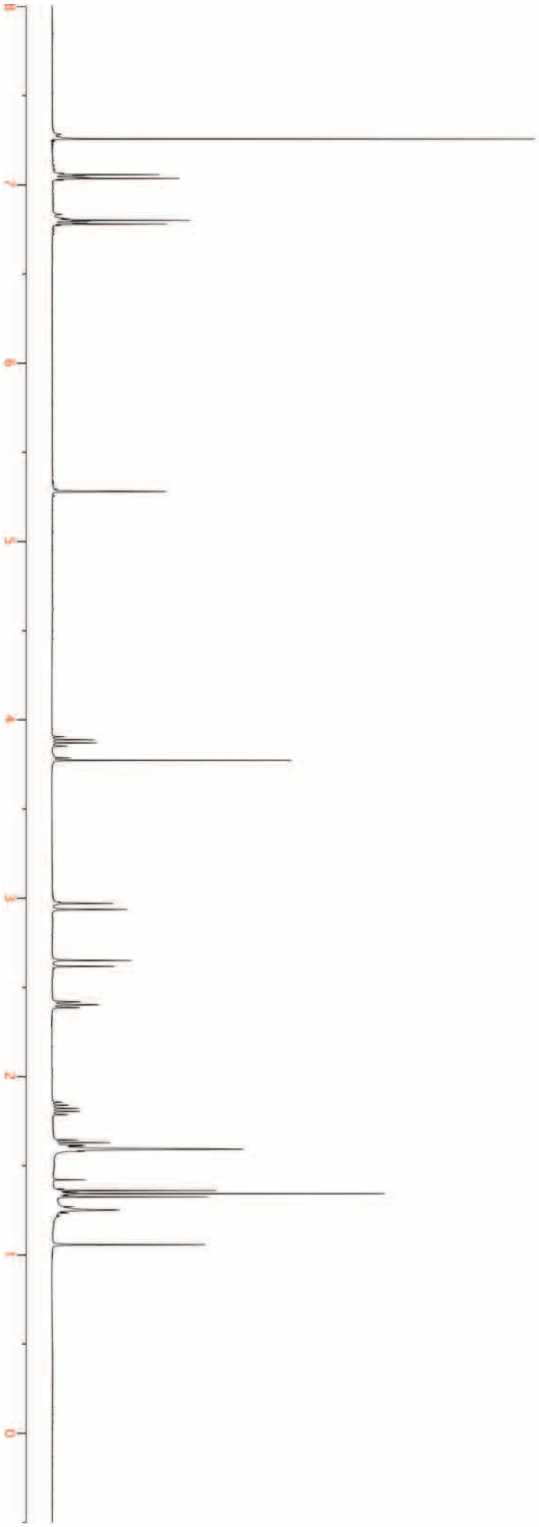


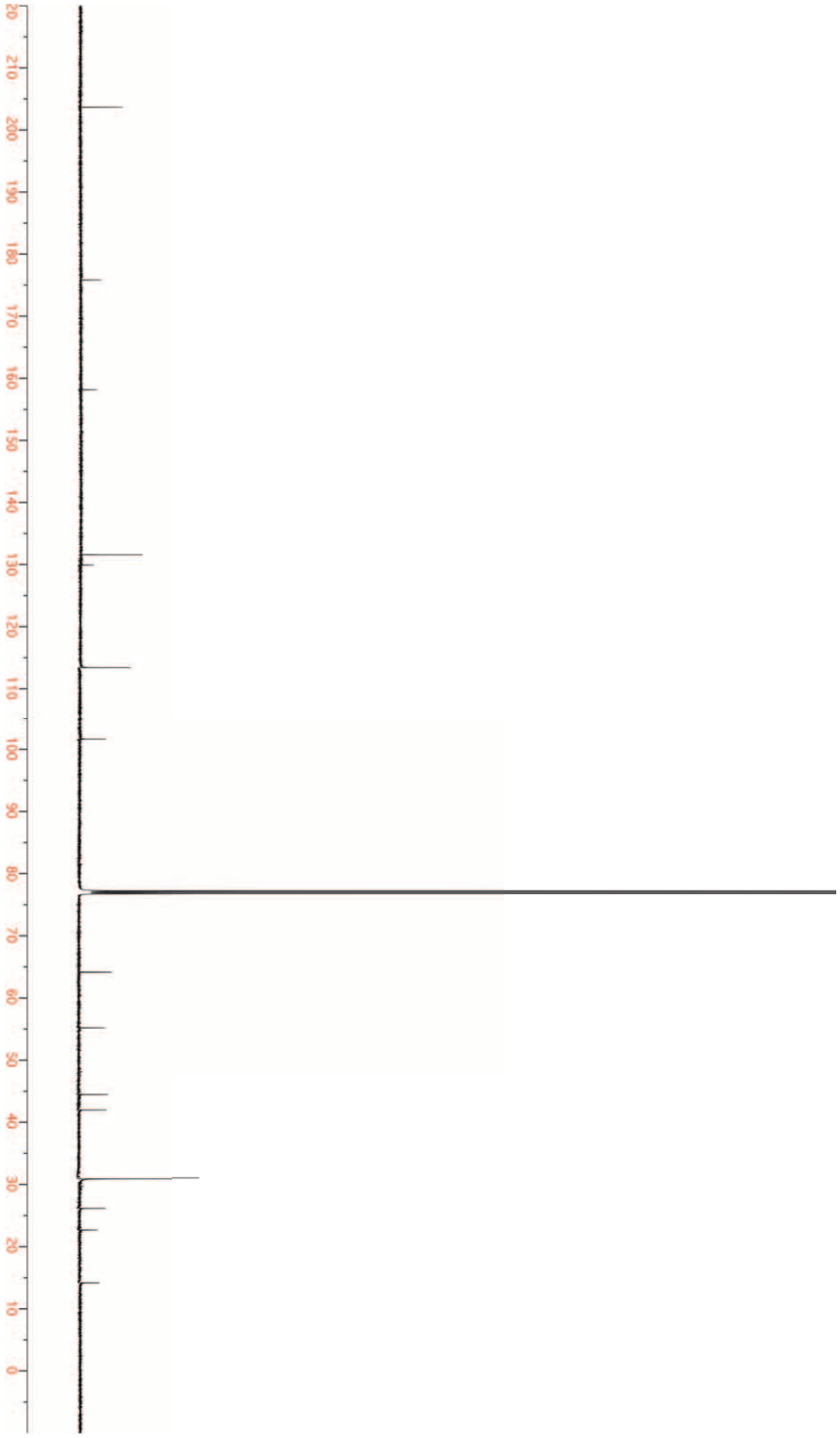
3002, 2939, 1636, 1606, 1515, 1216, 1192; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.60 (s, 1H), 6.59 (s, 1H), 5.74 (s, 1H), 3.84 (s, 2 X 3H), 2.82 (d, *J* = 14.0 Hz, 1H), 2.75 (m, 1H), 2.53 – 2.49 (m, 2H), 2.42 – 2.39 (m , 1H), 2.35 – 2.28 (m, 1H), 1.80 – 1.75 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.16, 173.70, 148.87, 145.22, 144.53, 112.73, 110.85, 107.17, 100.89, 56.39, 56.07, 36.72, 33.01,29.27, 28.83; ESI-HRMS Found $(M+H)^+$ 261.1123; $C_{15}H_{16}O_4$ requires $(M+H)^+$ 261.1121.

IV ^{1}H NMR & ^{13}C NMR of new compounds

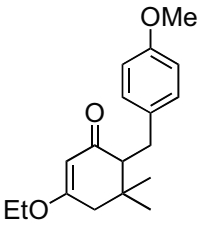
3-Ethoxy-6-(4-methoxybenzyl)-6-methylcyclohex-2-enone (1b)

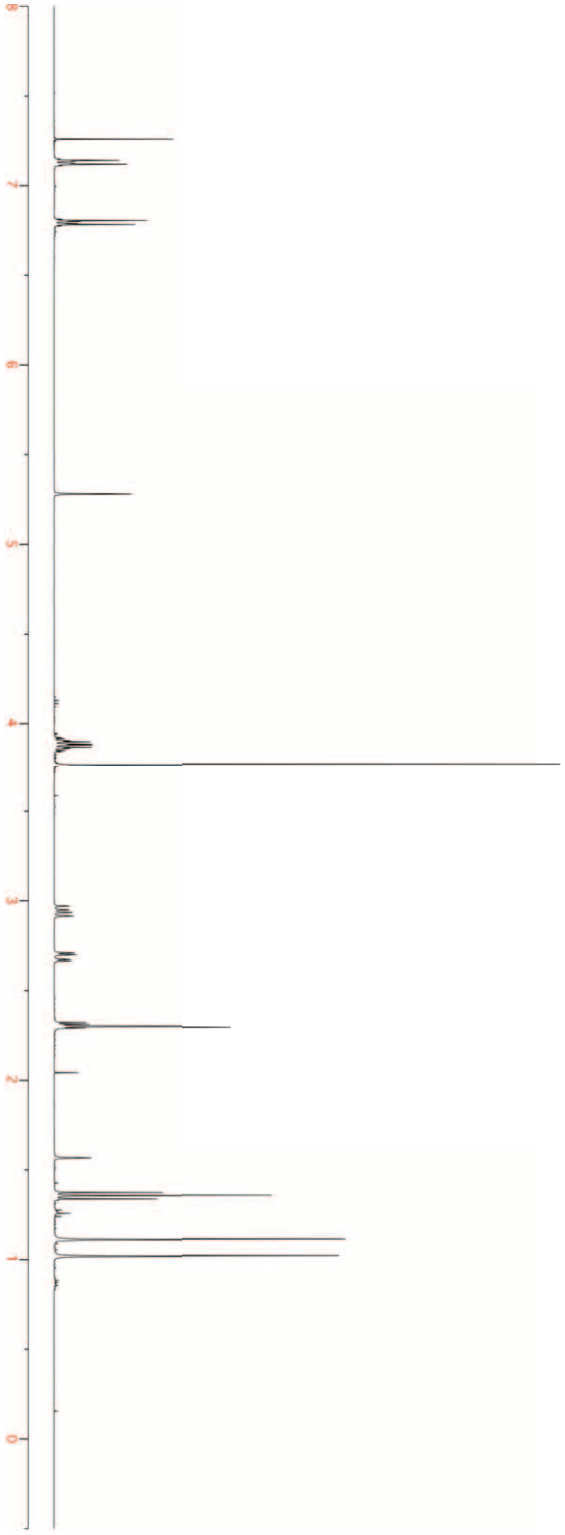


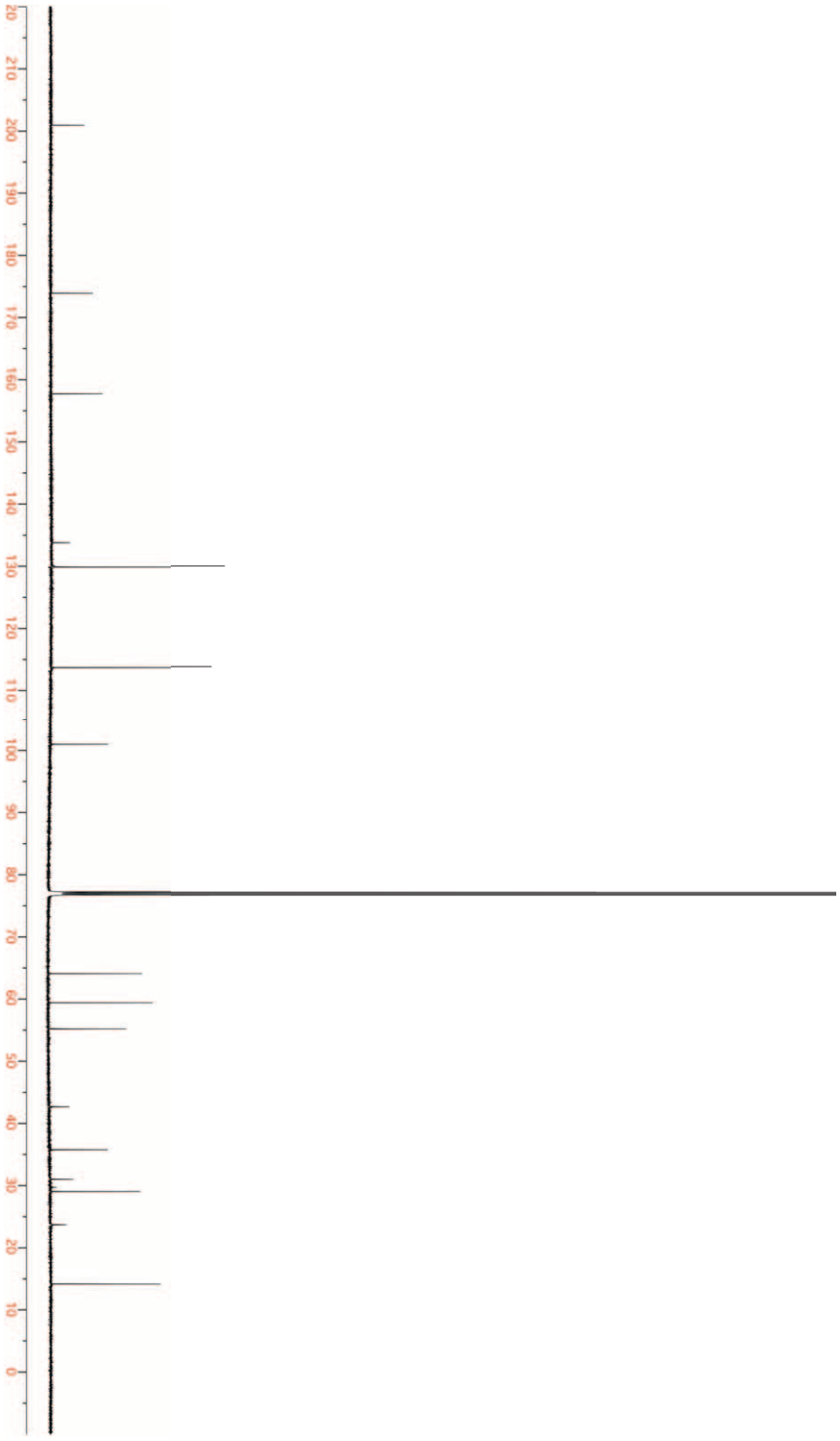




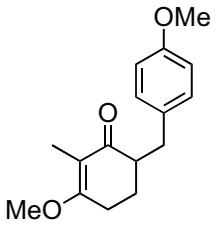
3-Ethoxy-6-(4-methoxybenzyl)-5,5-dimethylcyclohex-2-enone (1c)

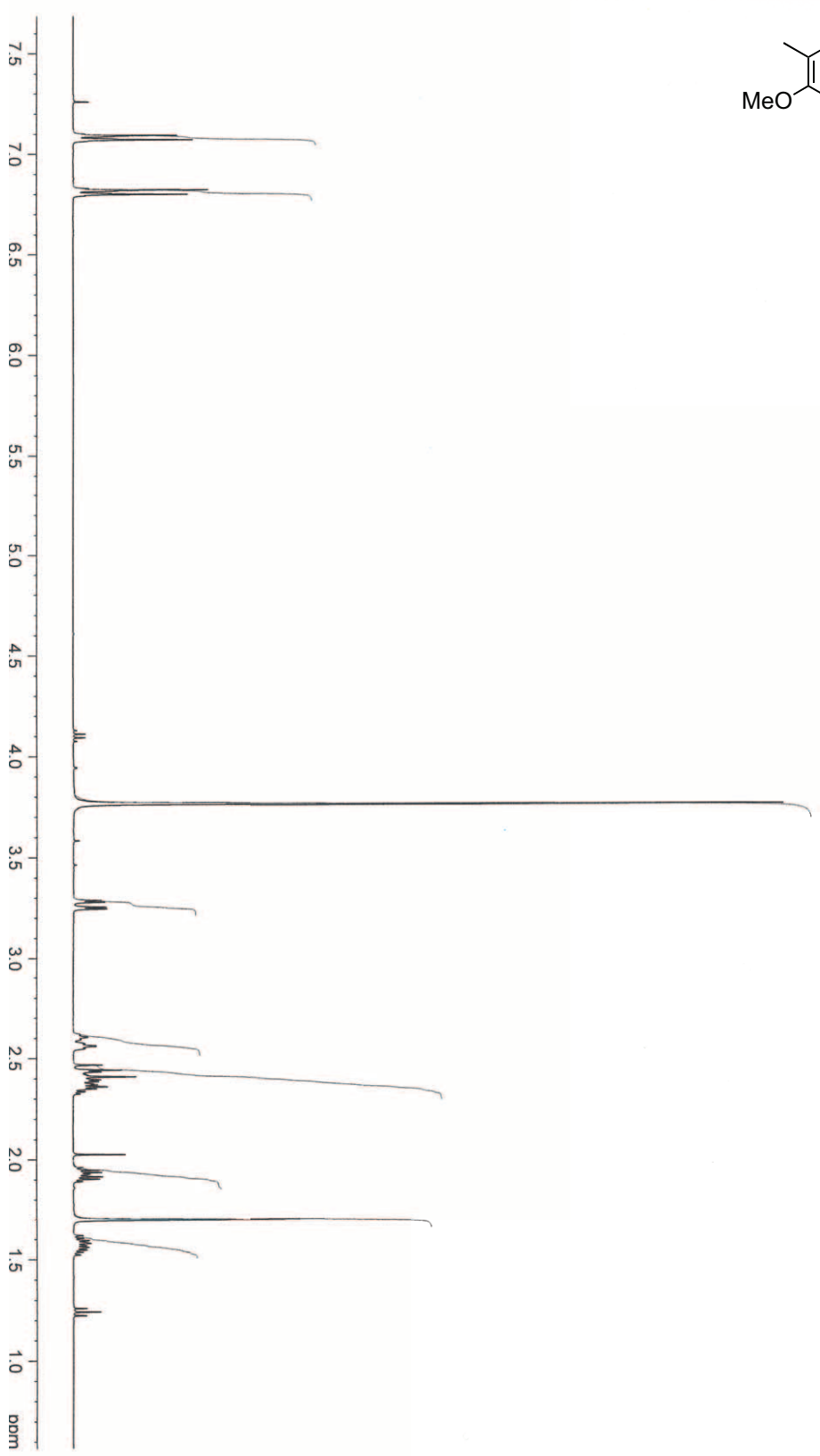


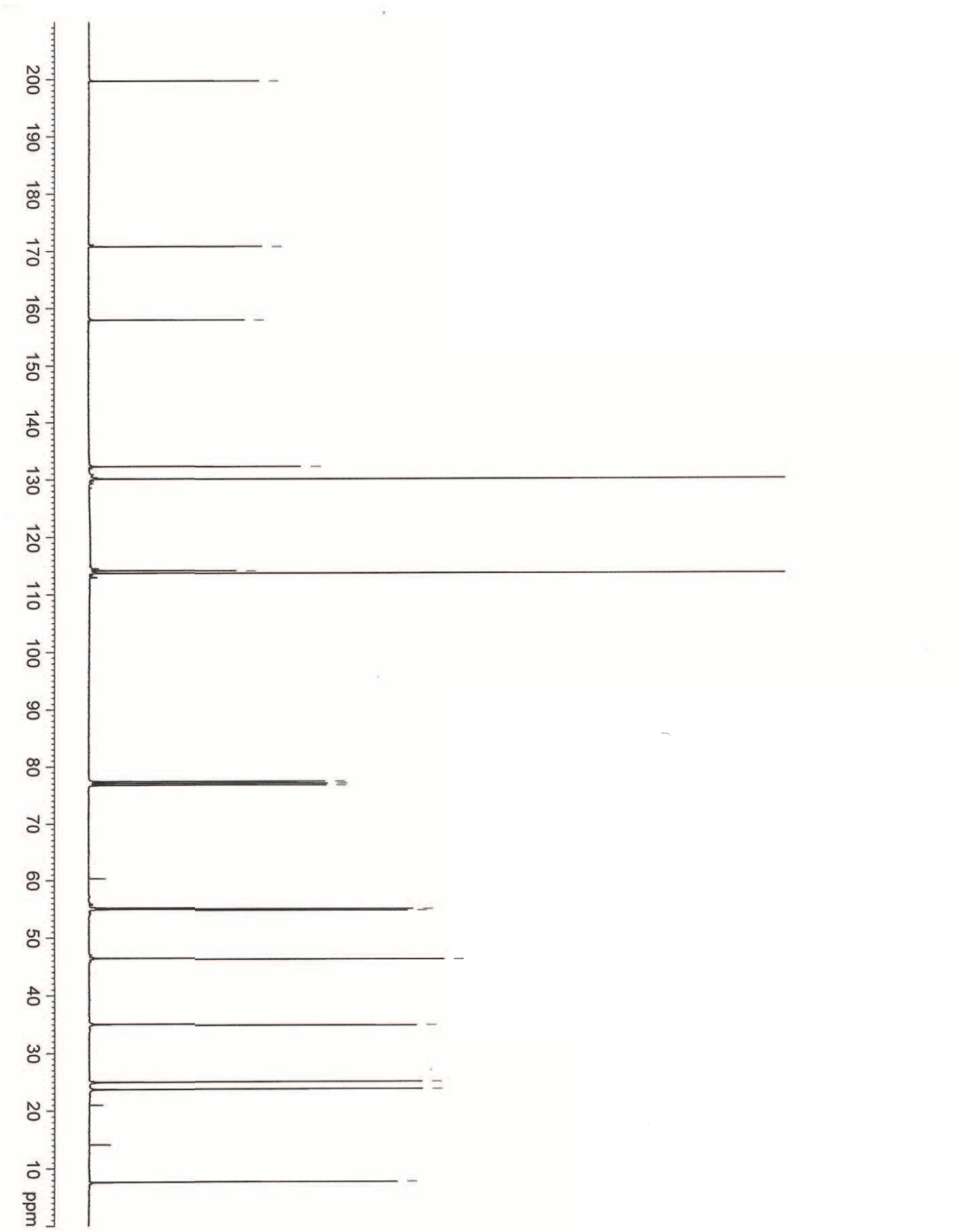




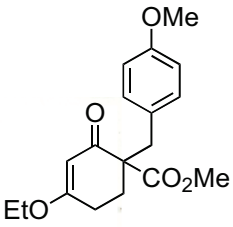
3-Methoxy-6-(4-methoxybenzyl)-2-methylcyclohex-2-enone (1d)

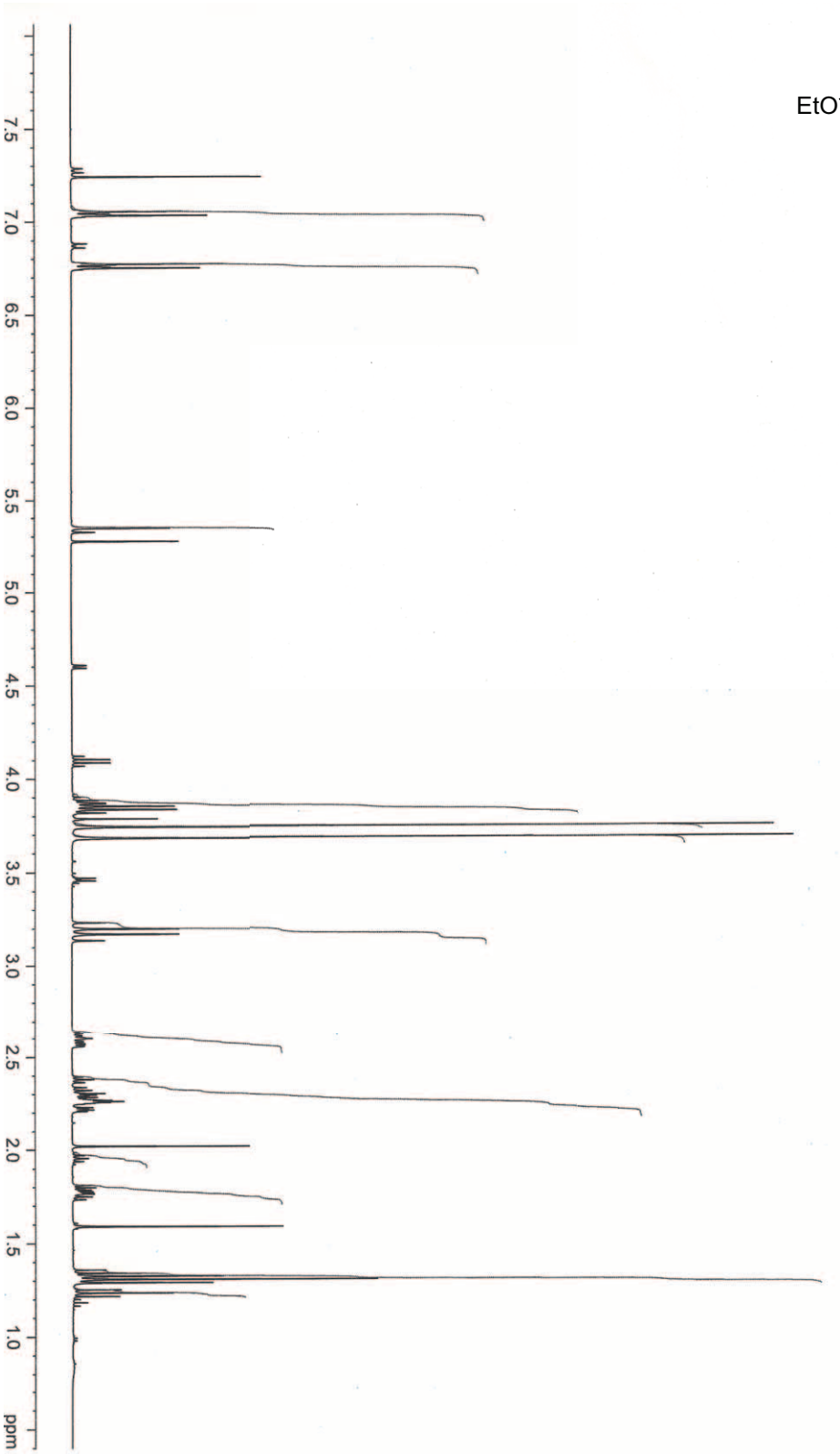


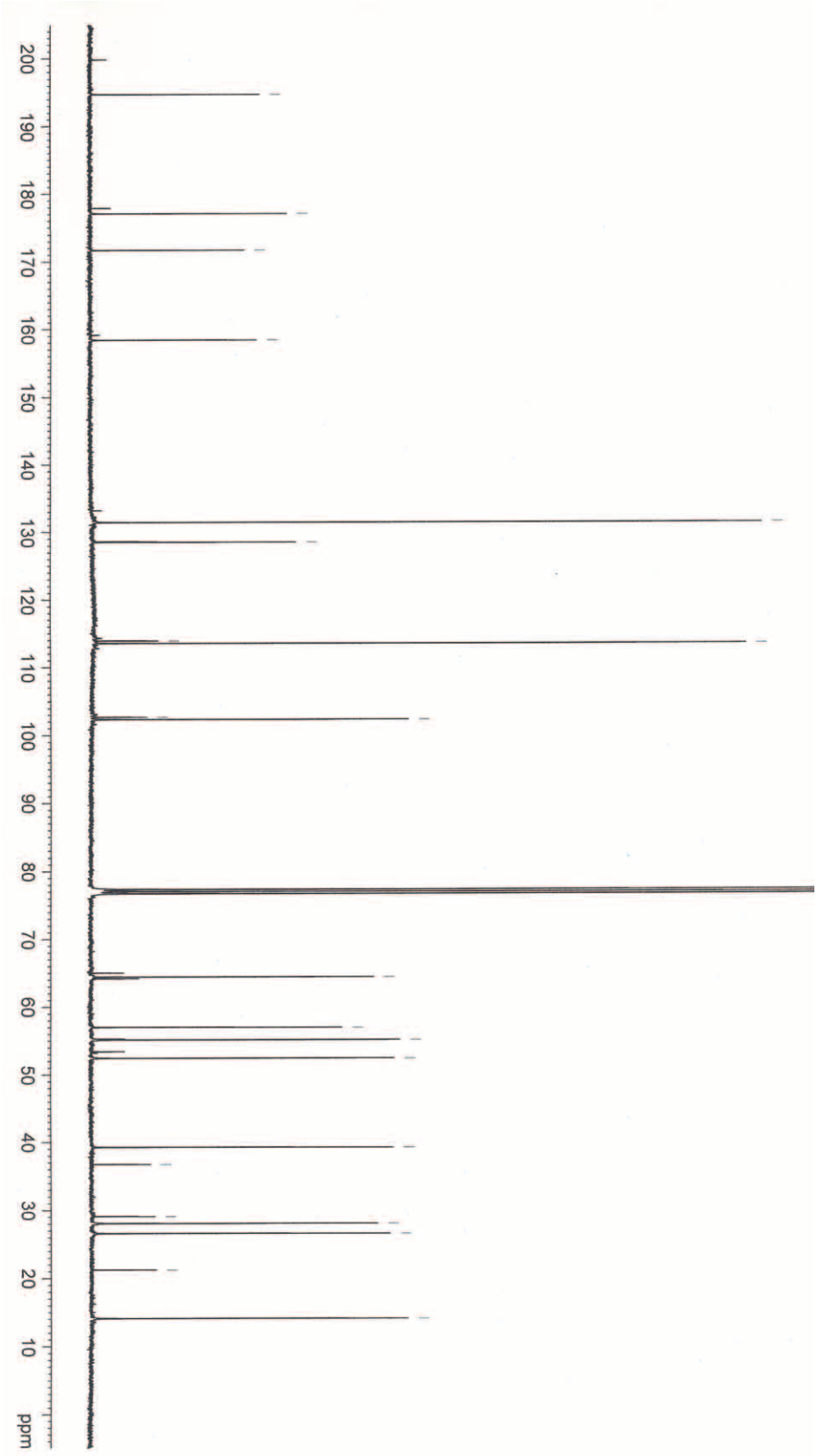




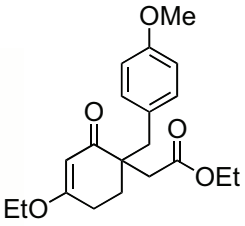
Methyl 4-ethoxy-1-(4-methoxybenzyl)-2-oxocyclohex-3-enecarboxylate (1e)

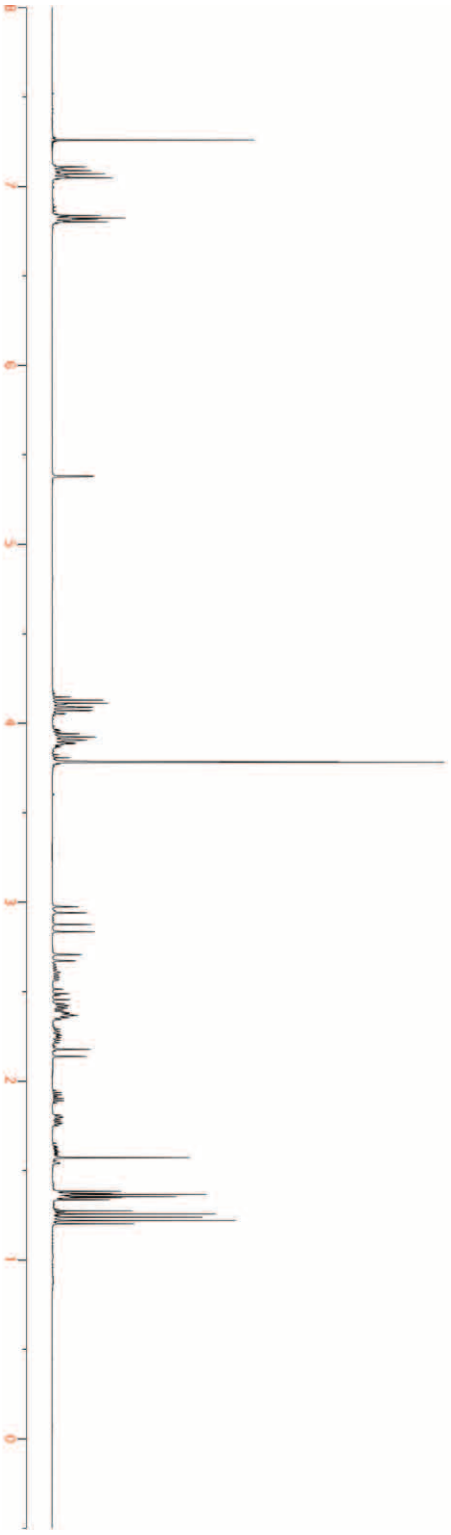


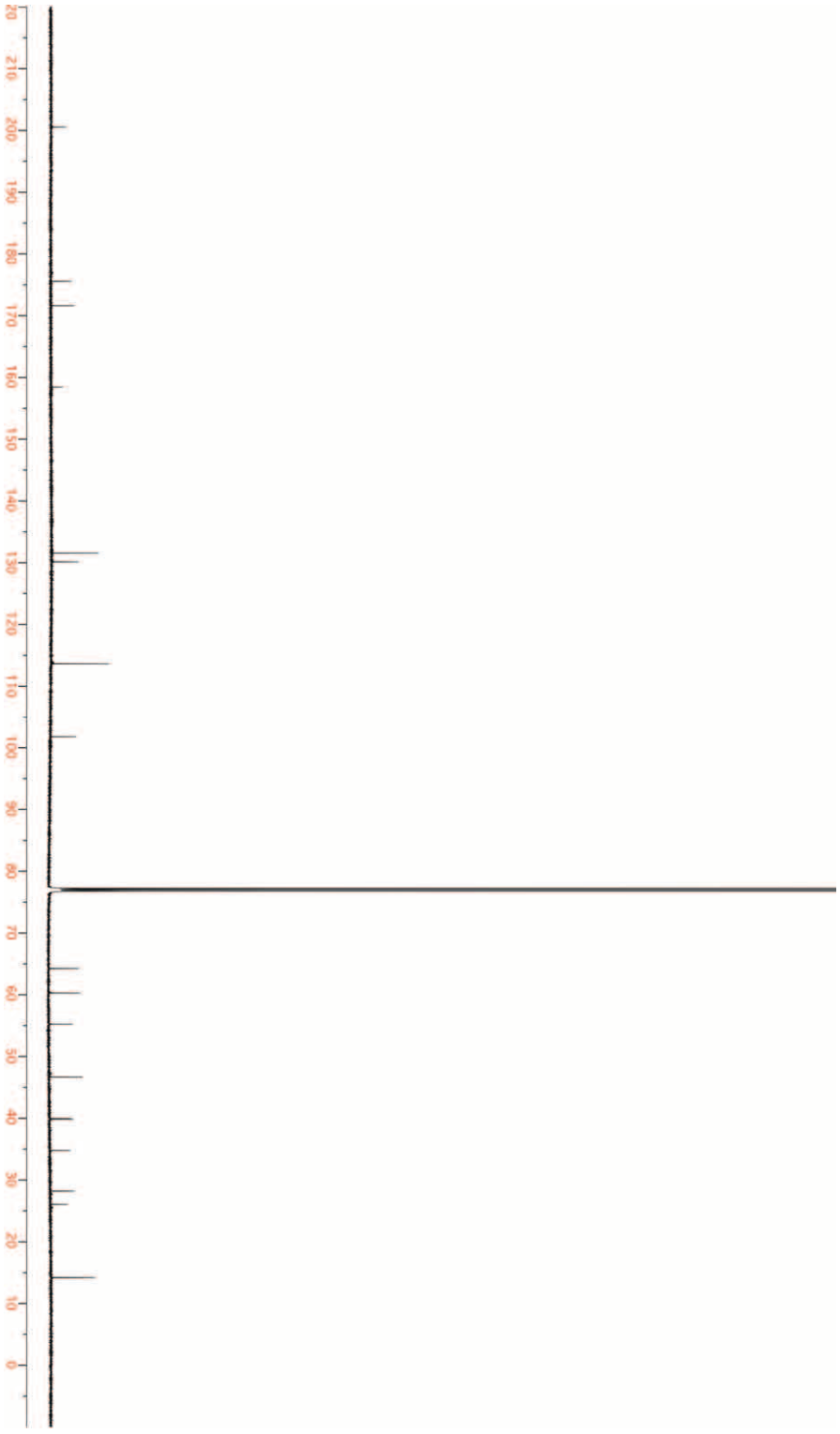




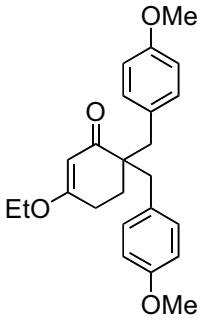
Ethyl 2-(4-ethoxy-1-(4-methoxybenzyl)-2-oxocyclohex-3-en-1-yl)acetate (1f)

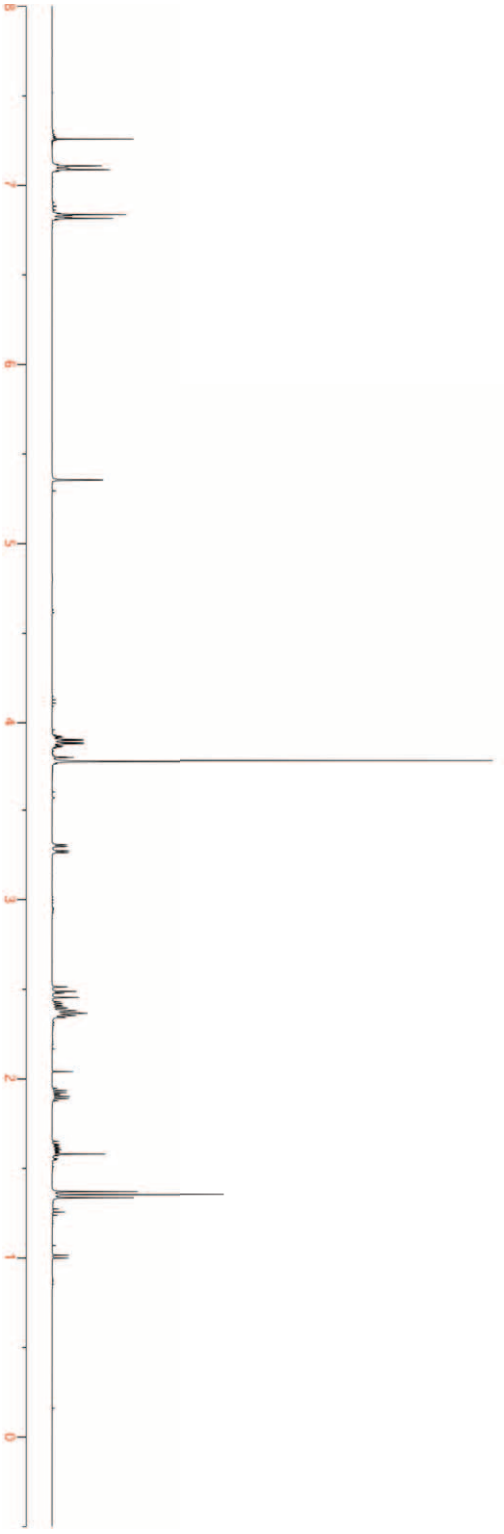


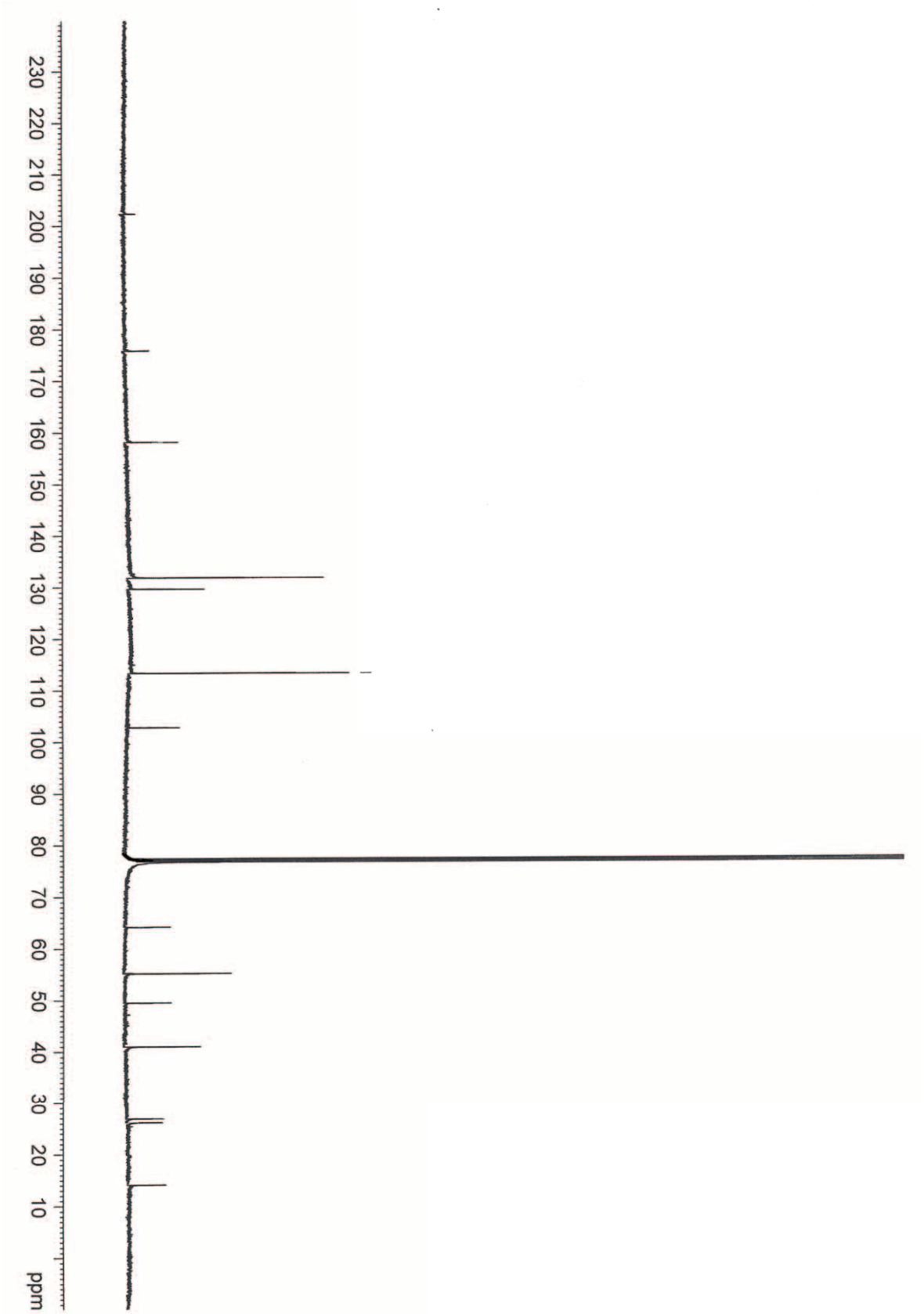




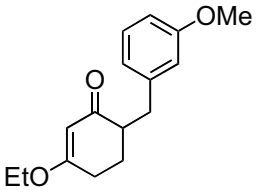
3-Ethoxy-6,6-bis(4-methoxybenzyl)cyclohex-2-enone (1g)

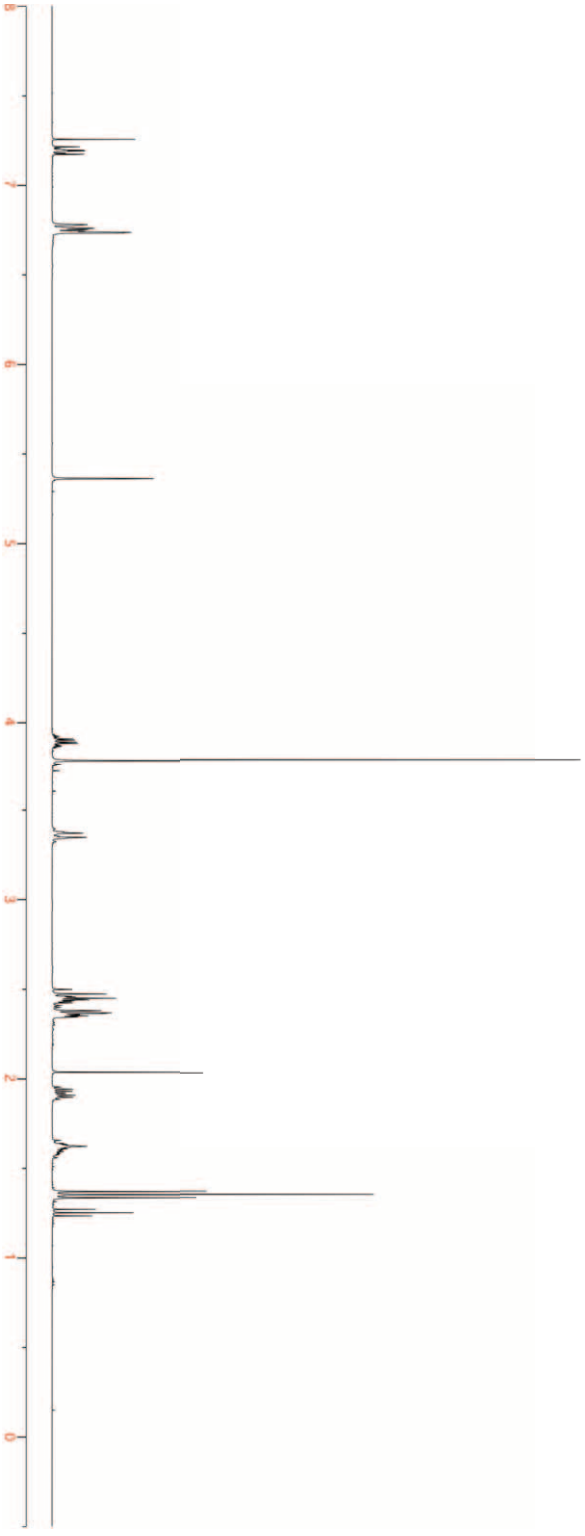


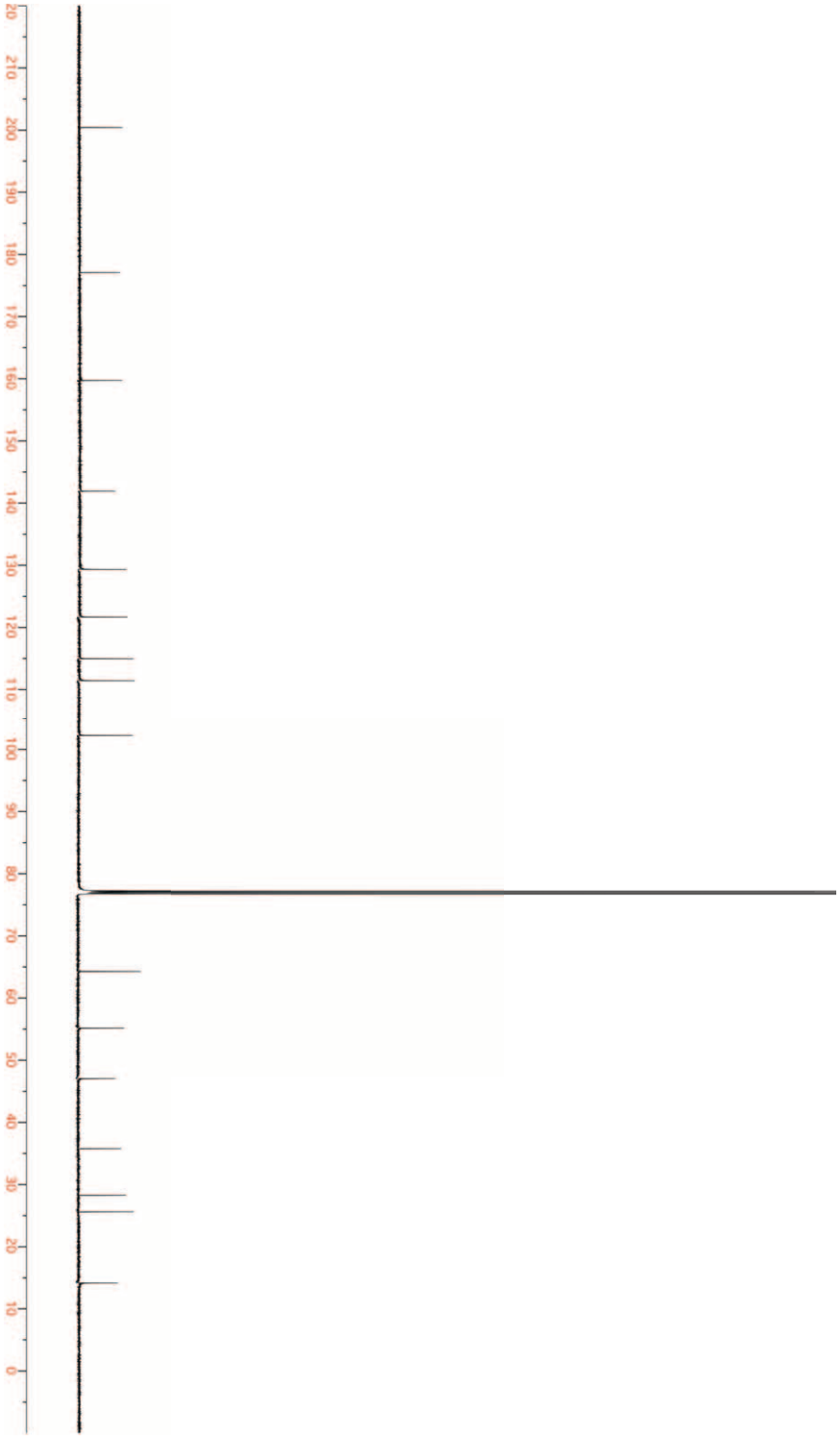




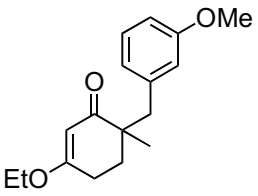
3-Ethoxy-6-(3-methoxybenzyl)cyclohex-2-enone (1h)

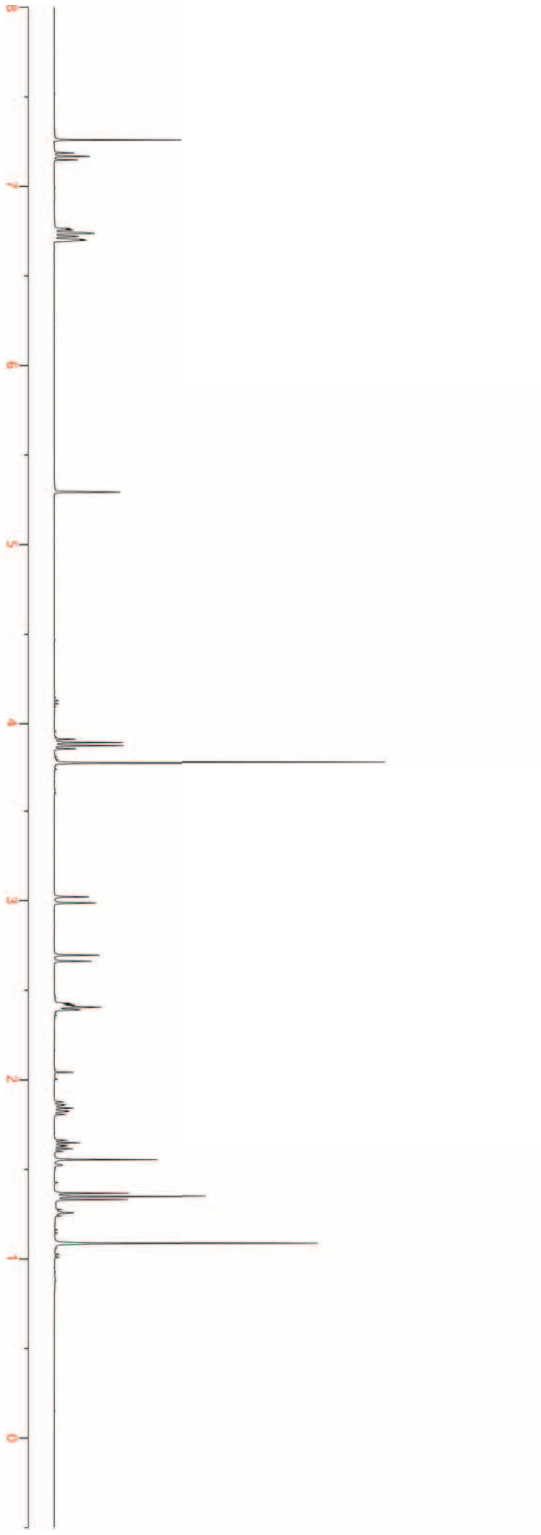


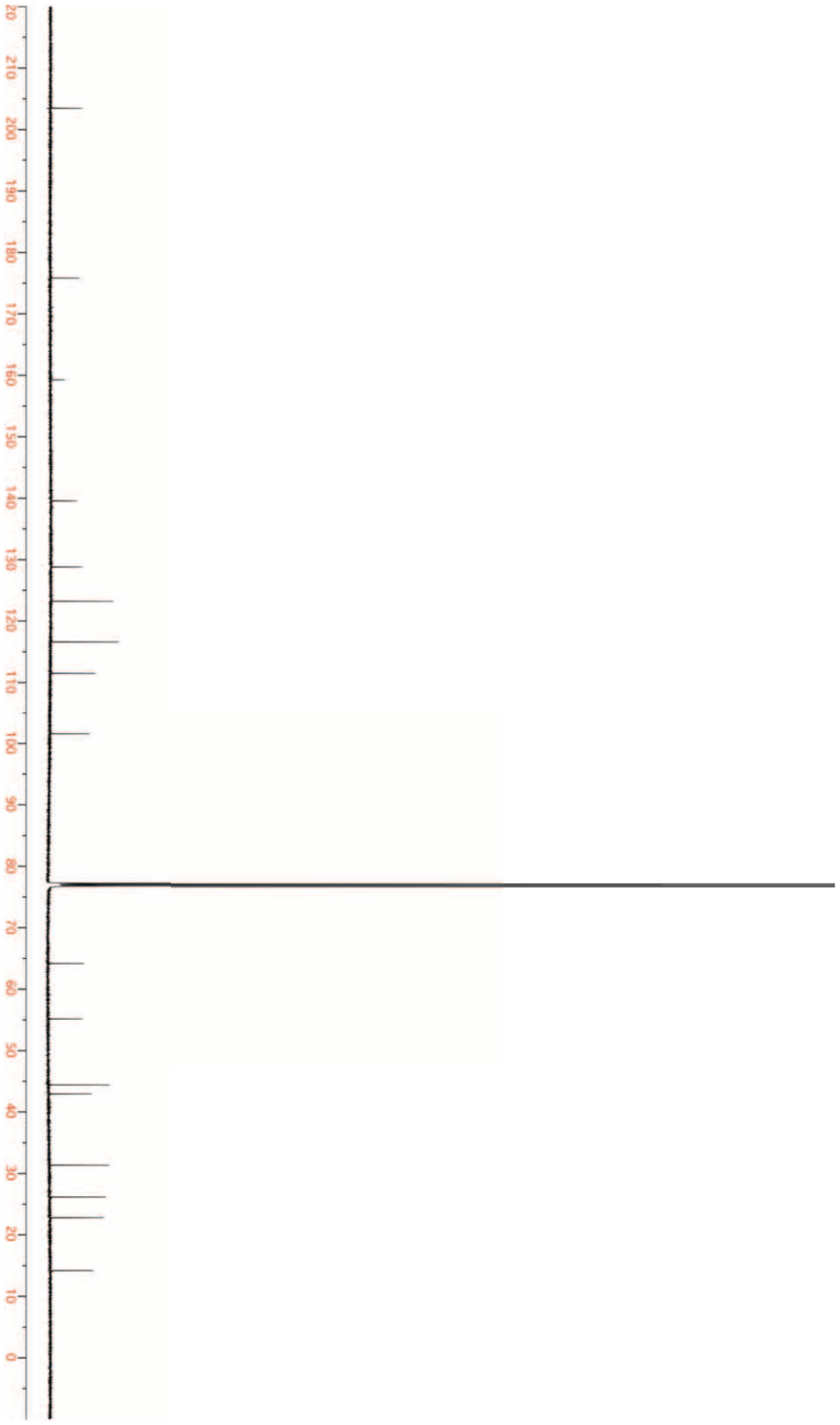




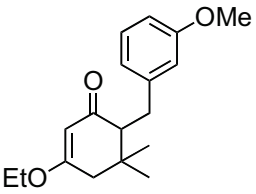
3-Ethoxy-6-(3-methoxybenzyl)-6-methylcyclohex-2-enone (1i)

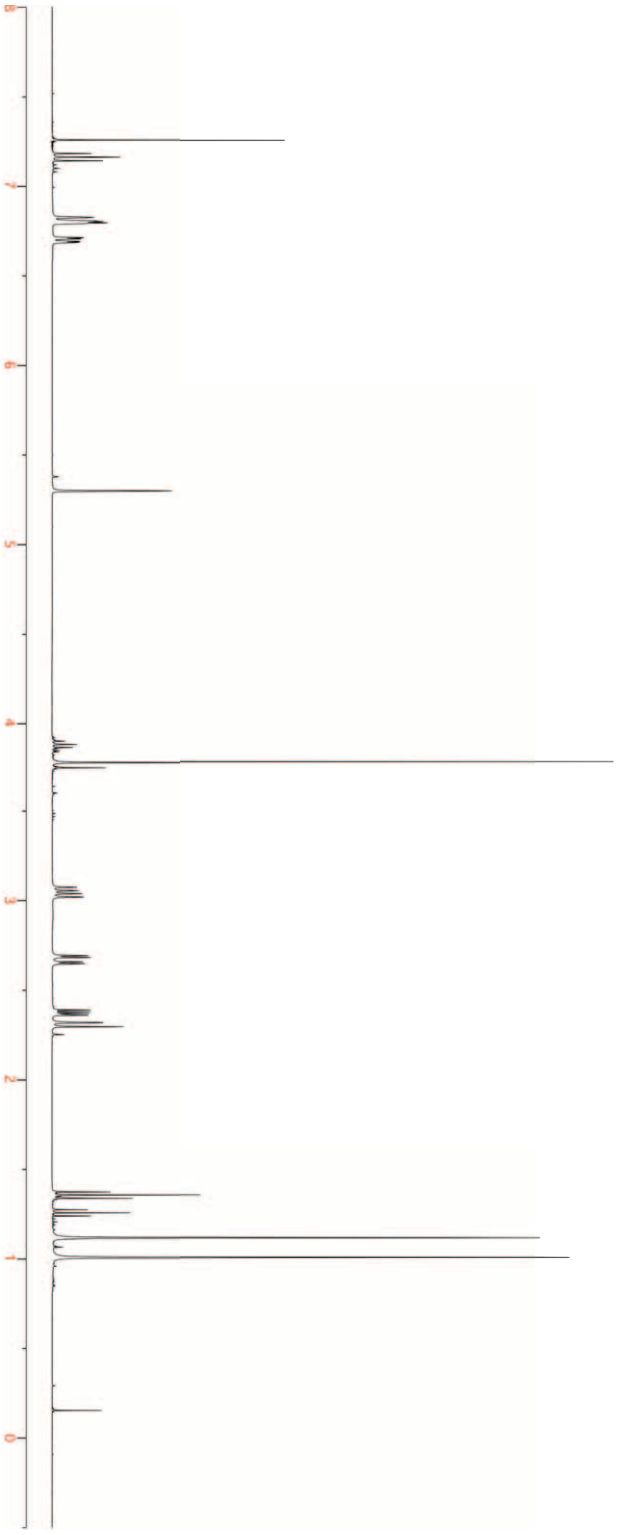


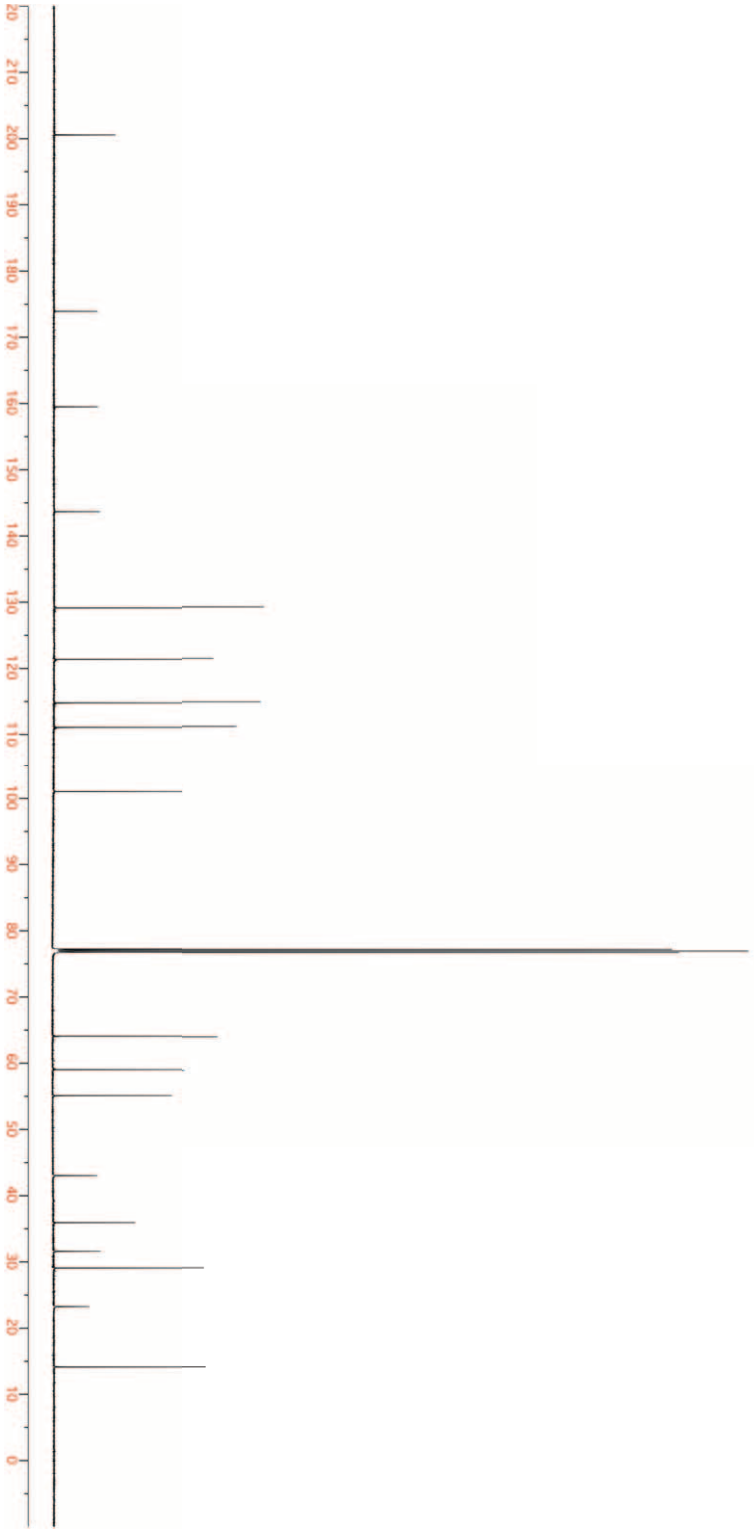




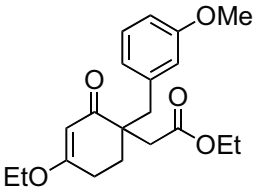
3-Ethoxy-6-(3-methoxybenzyl)-5,5-dimethylcyclohex-2-enone (1j)

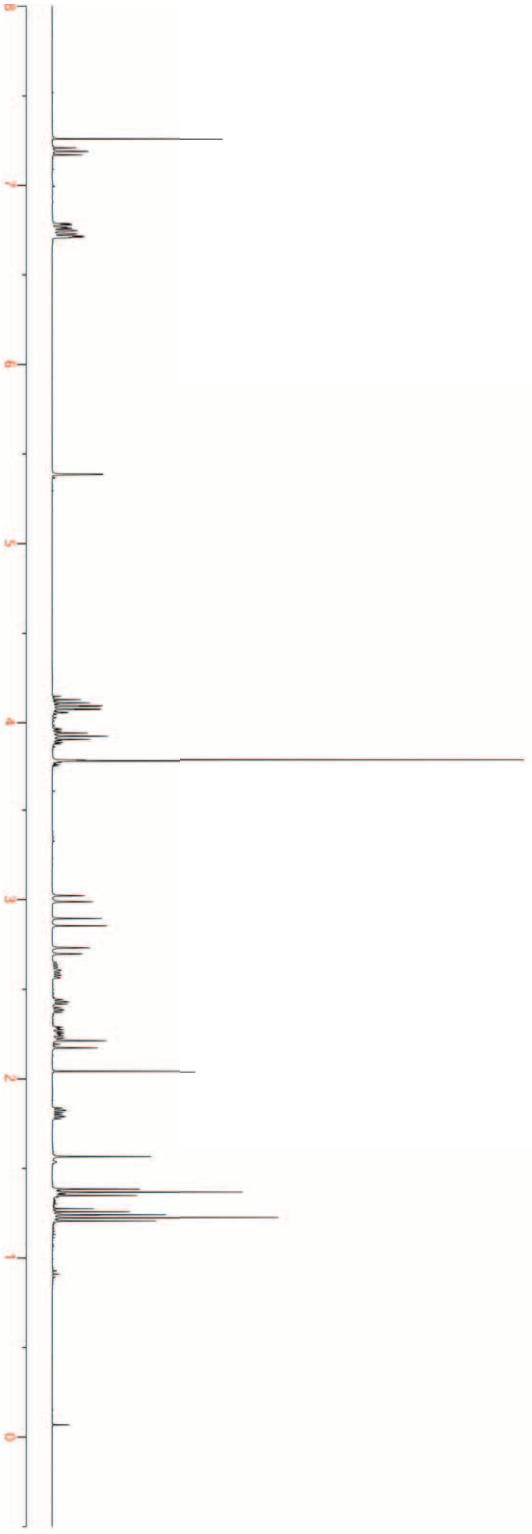


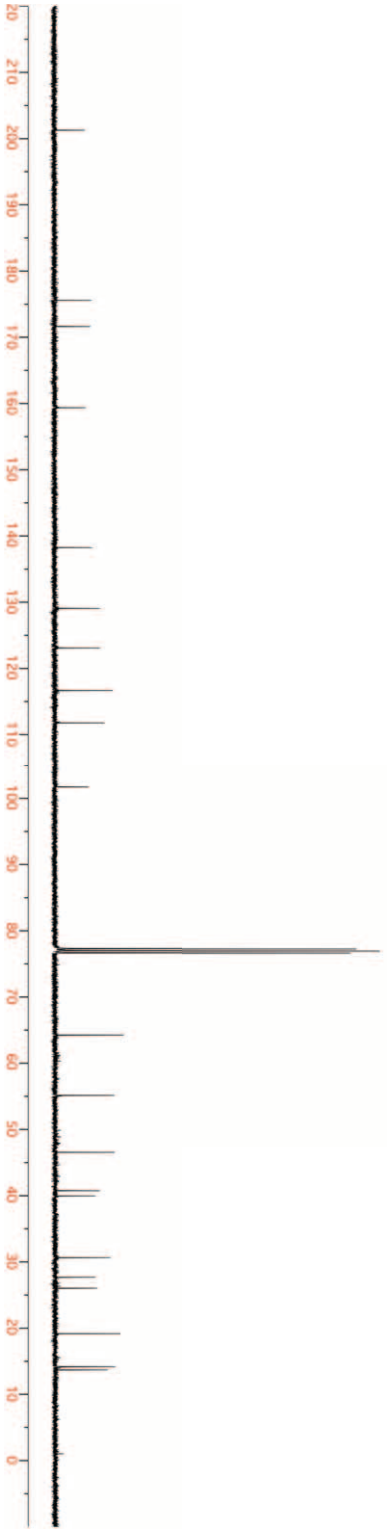




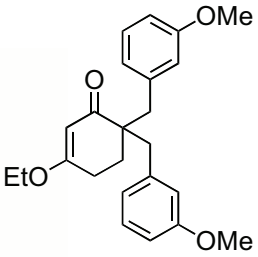
Ethyl 2-(4-ethoxy-1-(3-methoxybenzyl)-2-oxocyclohex-3-en-1-yl)acetate (1k)

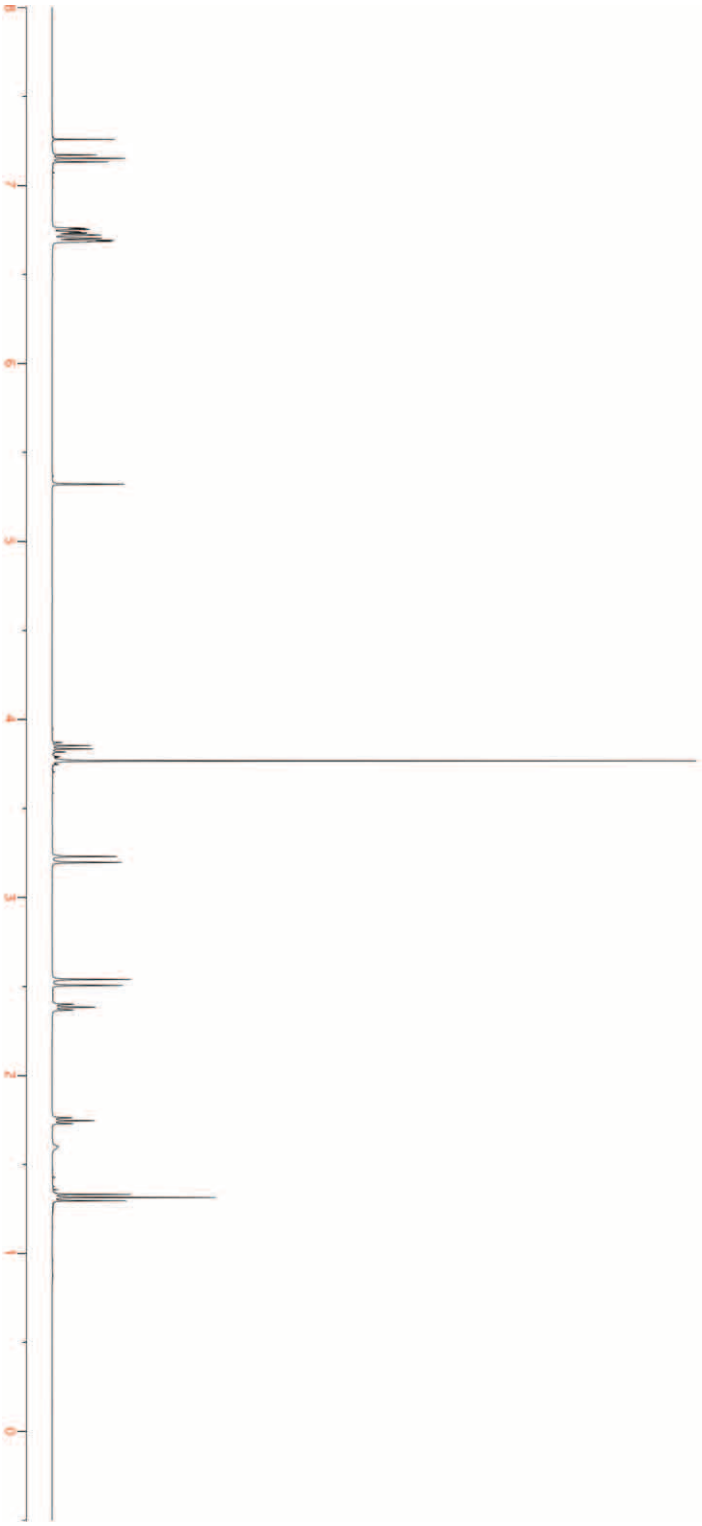


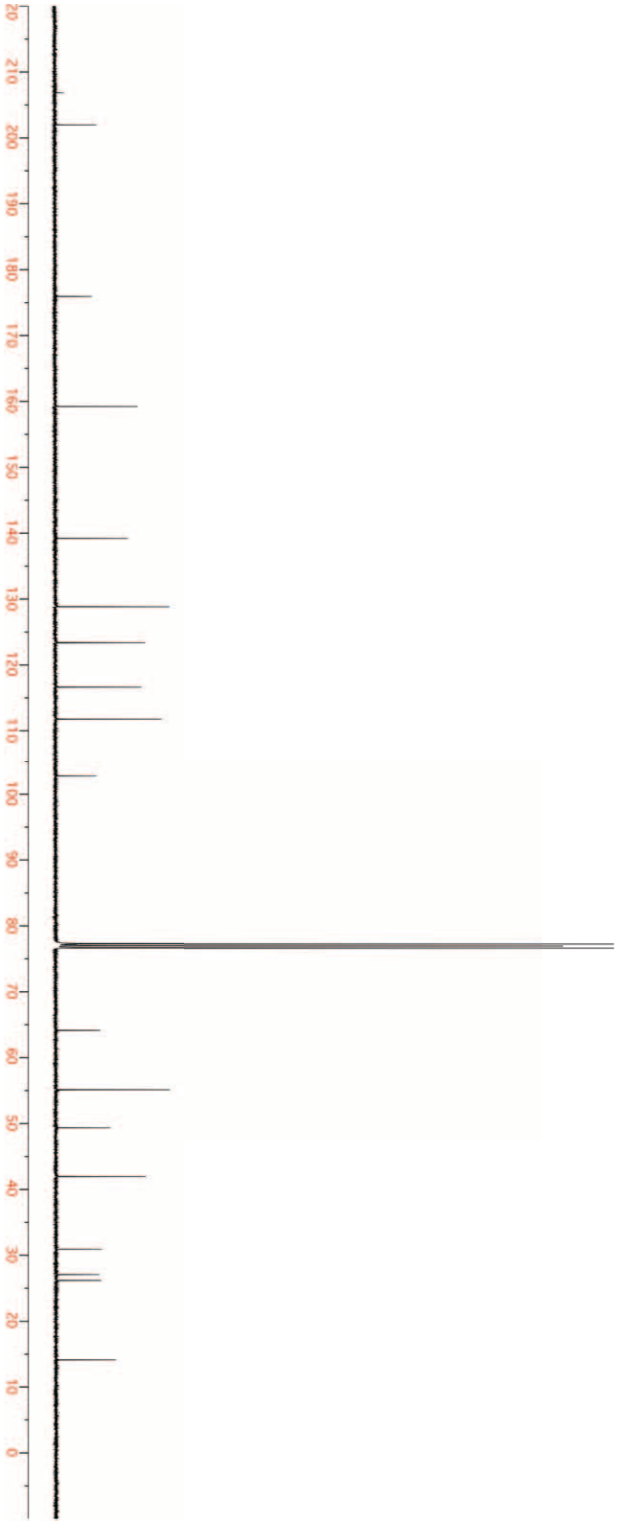




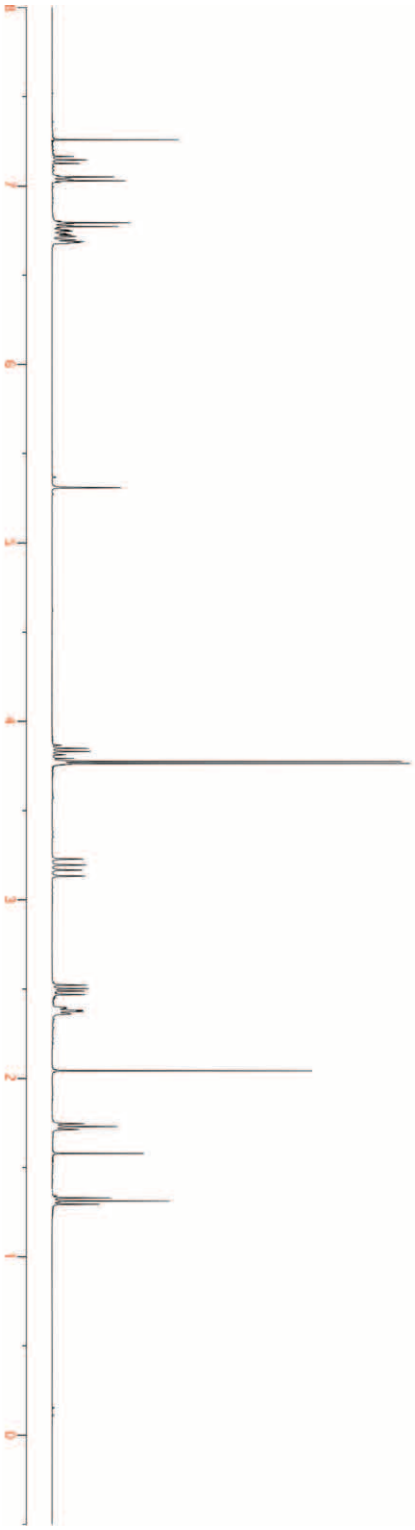
3-Ethoxy-6,6-bis(3-methoxybenzyl)cyclohex-2-enone (1l)

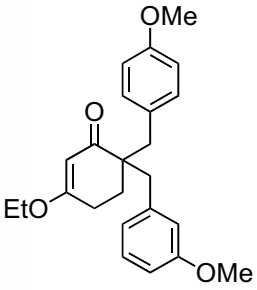


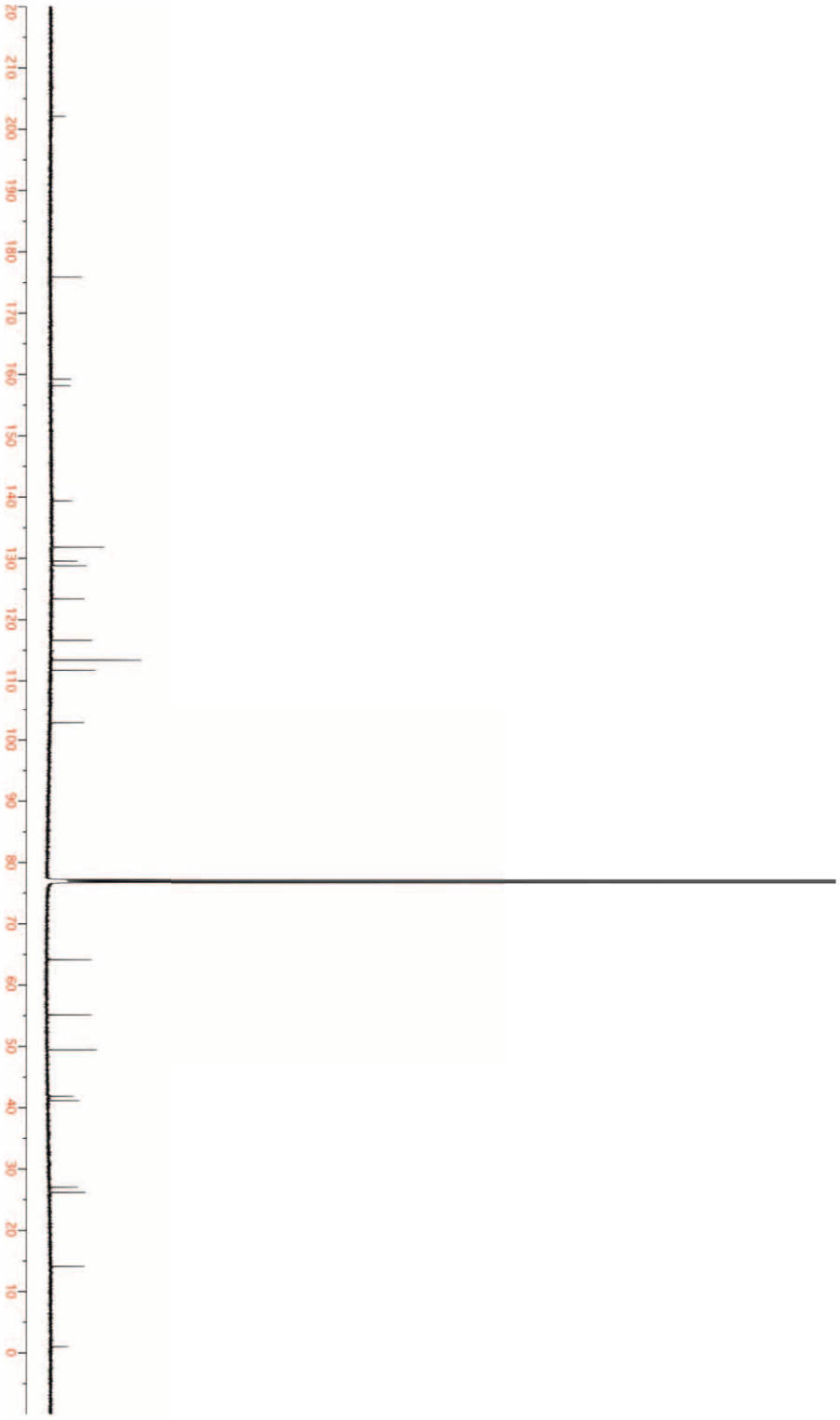




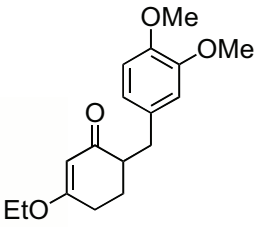
3-Ethoxy-6-(3-methoxybenzyl)-6-(4-methoxybenzyl)cyclohex-2-enone (1m)

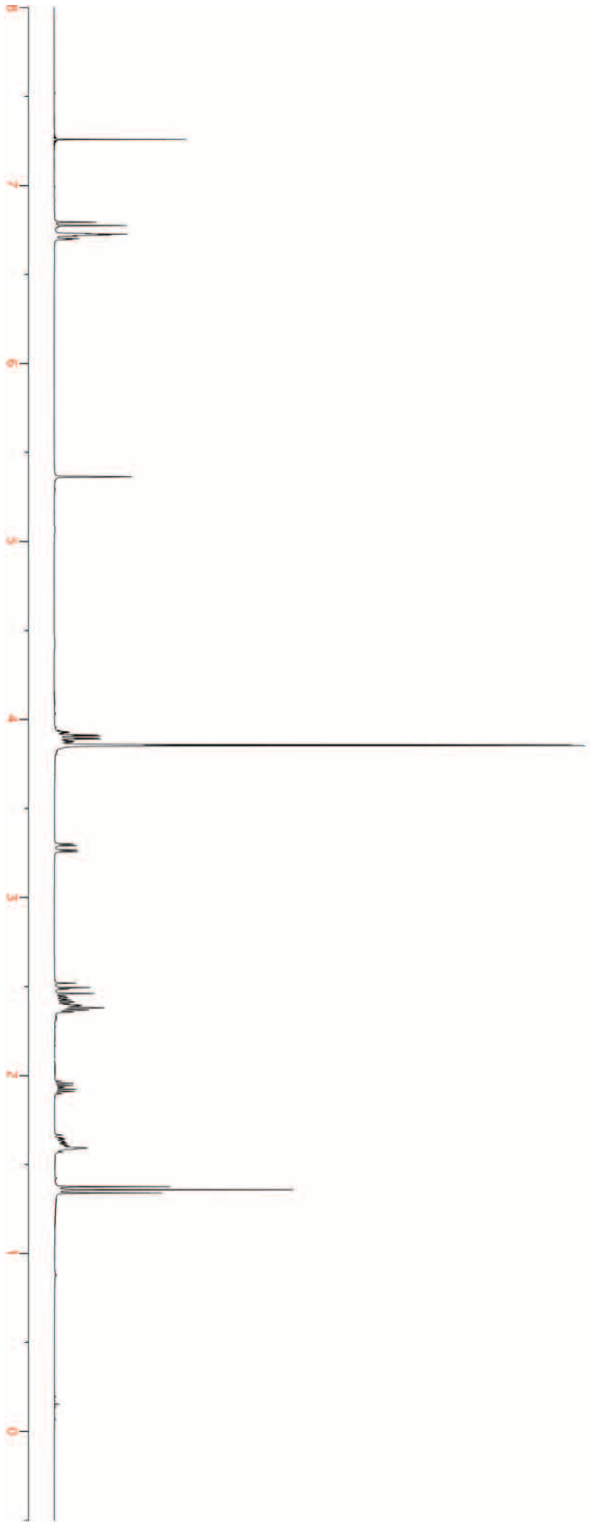


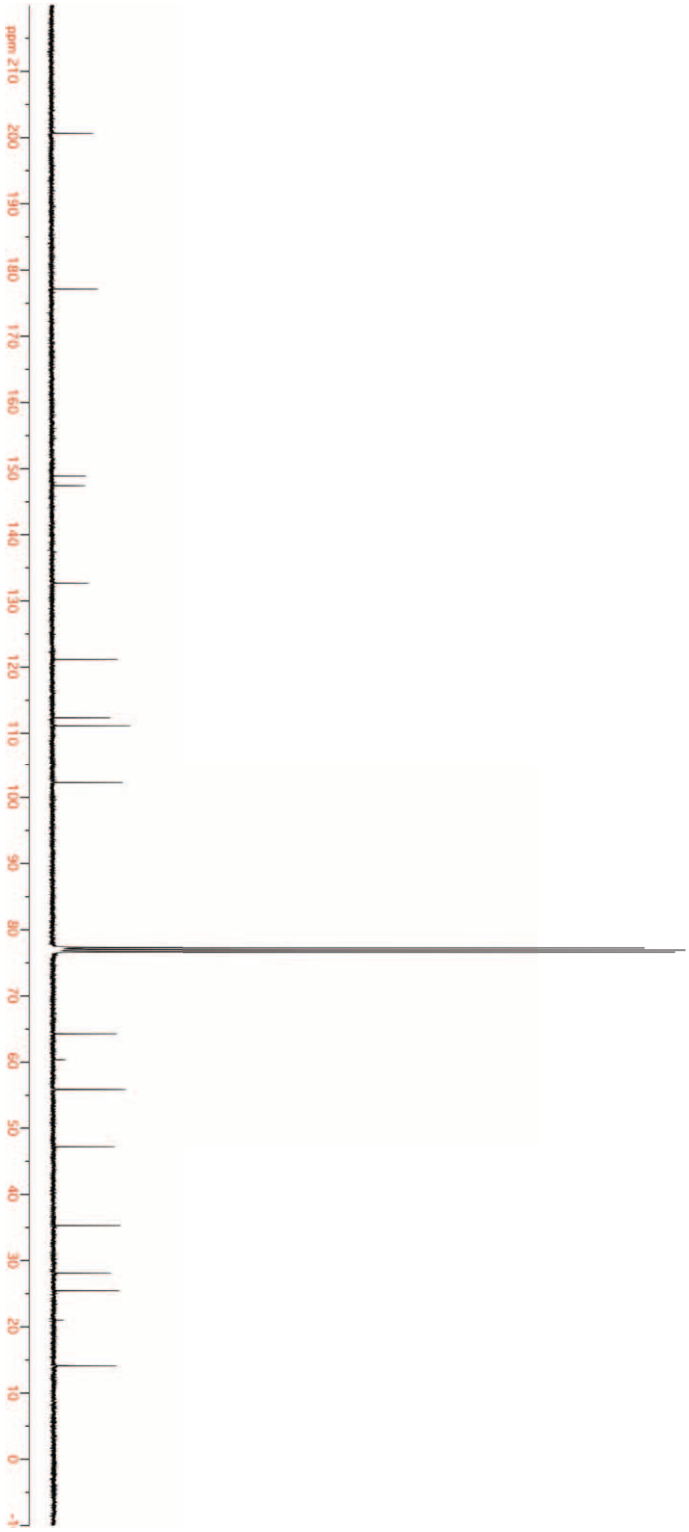




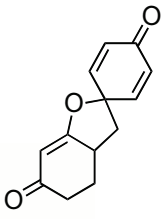
6-(3,4-Dimethoxybenzyl)-3-ethoxycyclohex-2-enone (1n)

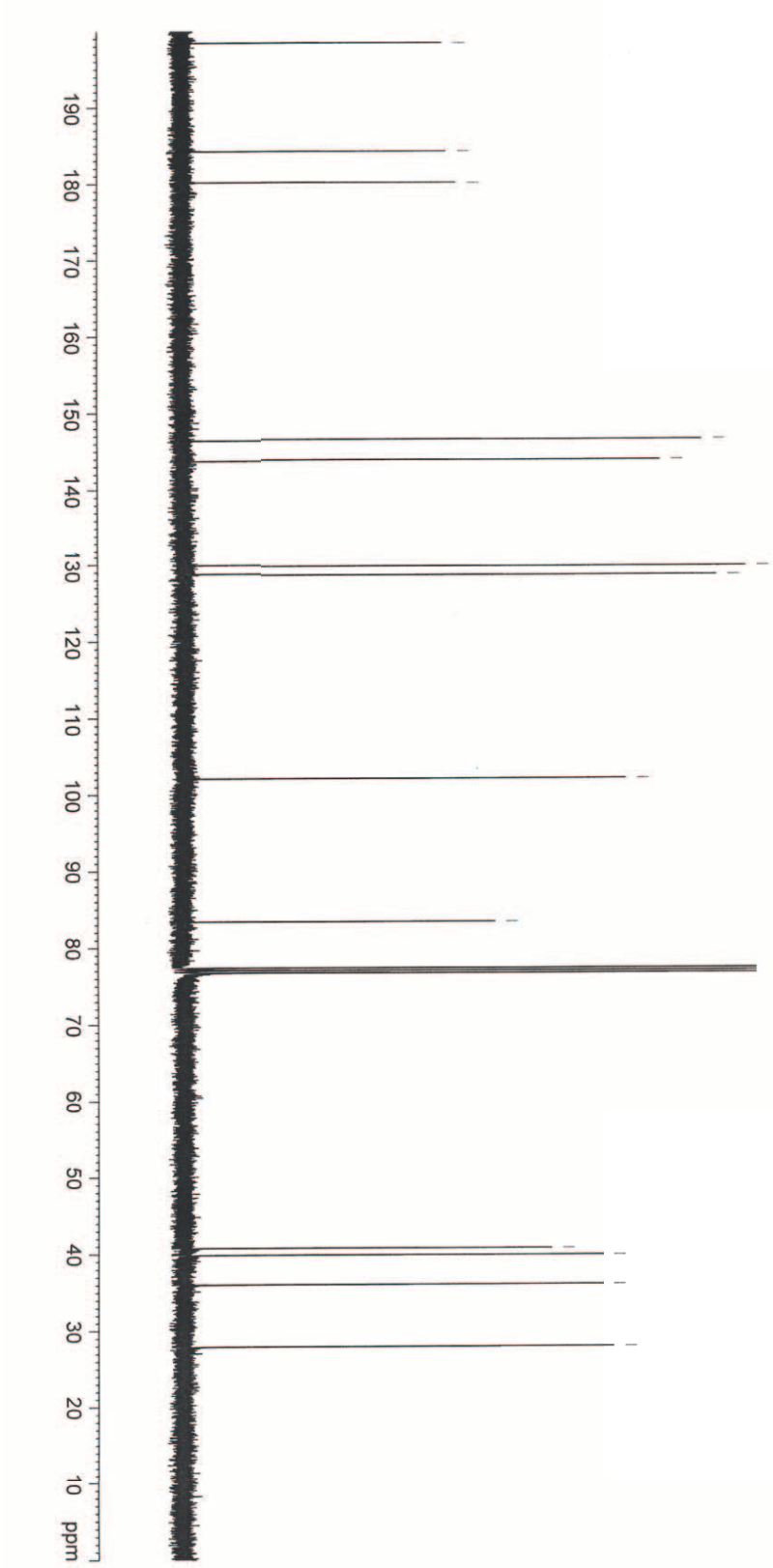




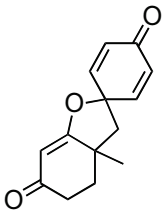


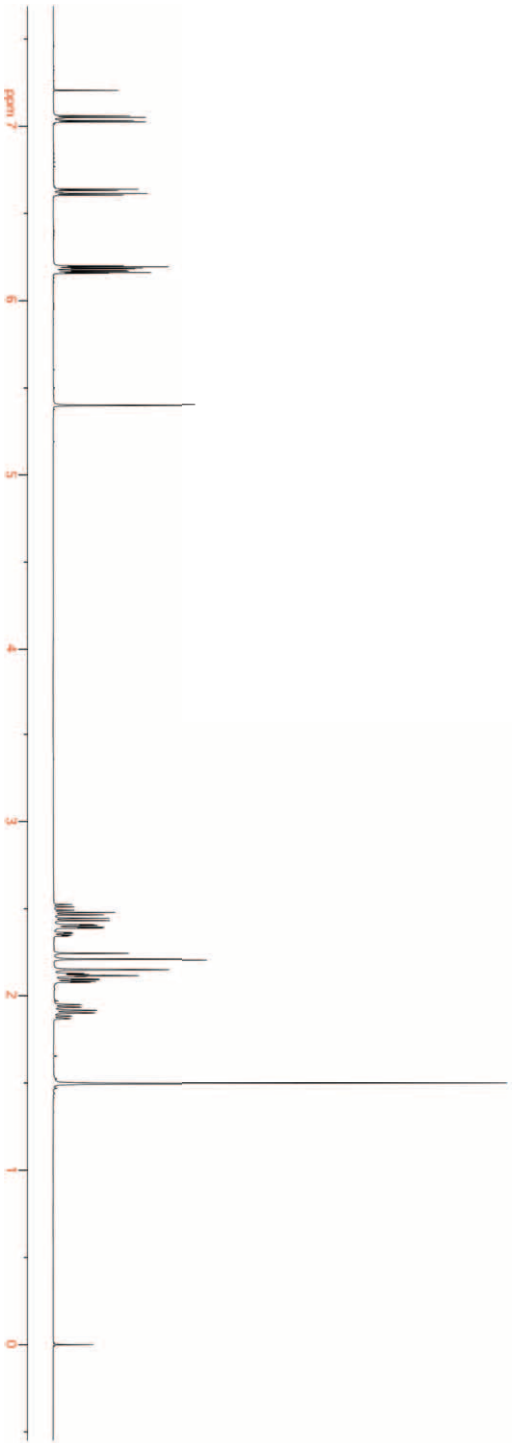
4,5-Dihydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-4',6(3aH)-dione (2a)

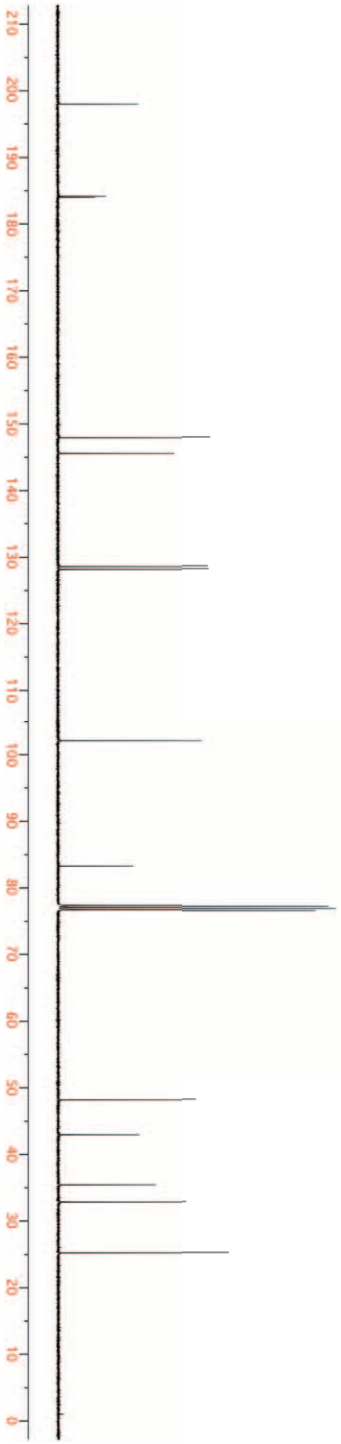




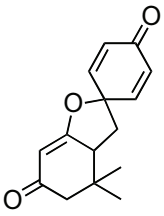
3a-Methyl-4,5-dihydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-4',6(3aH)-dione (2b)

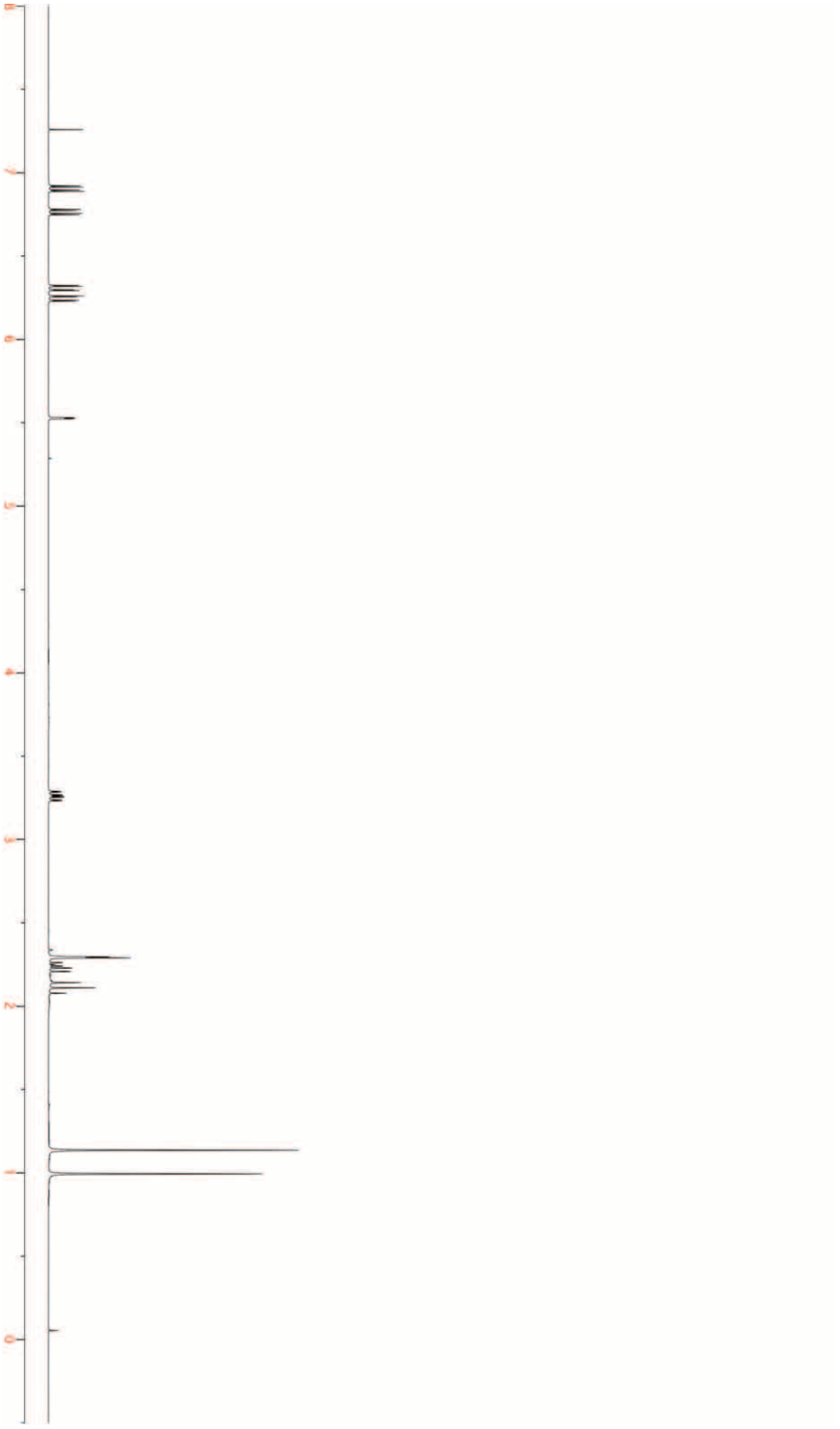


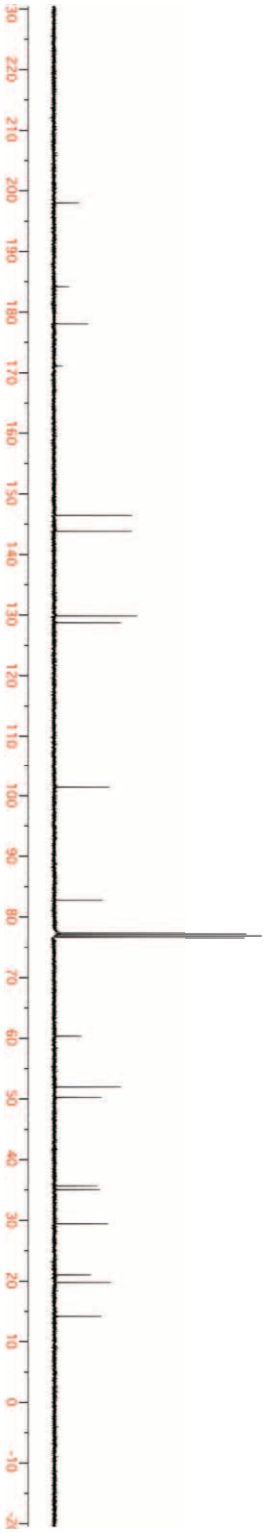




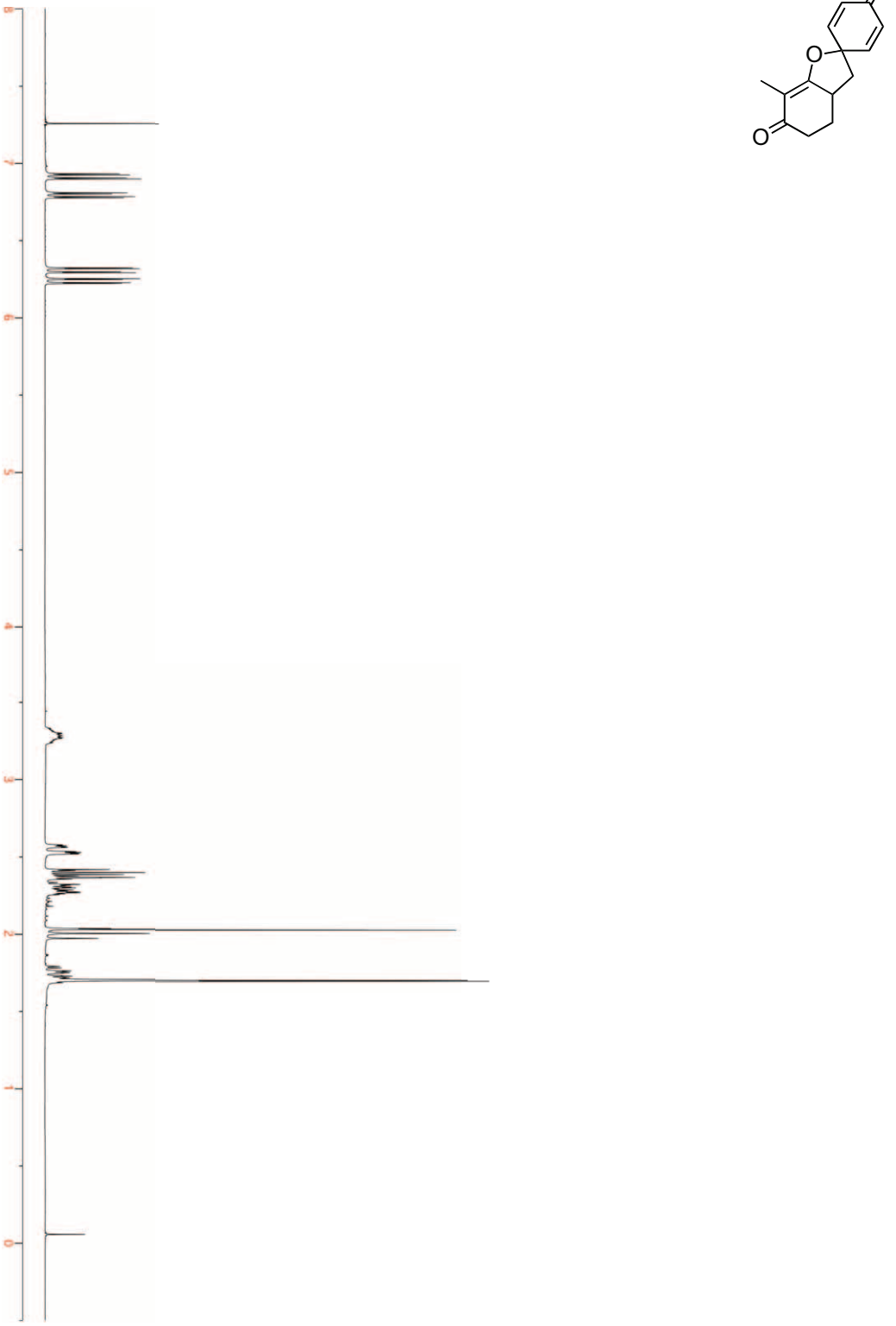
4,4-Dimethyl-4,5-dihydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-4',6(3aH)-dione (2c)

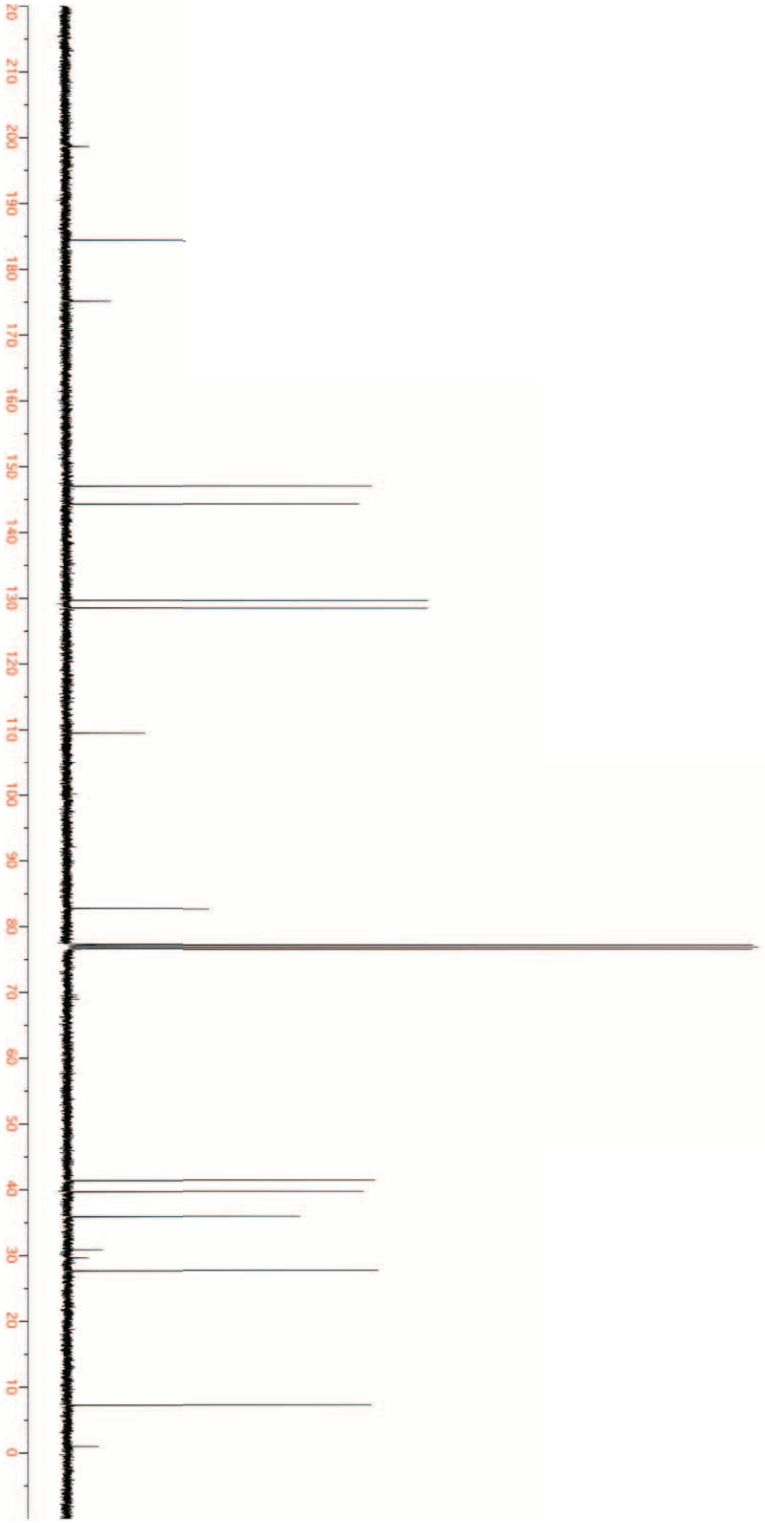






7-Methyl-4,5-dihydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-4',6(3aH)-dione (2d)

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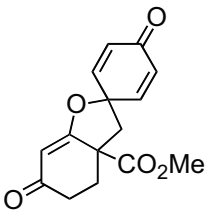
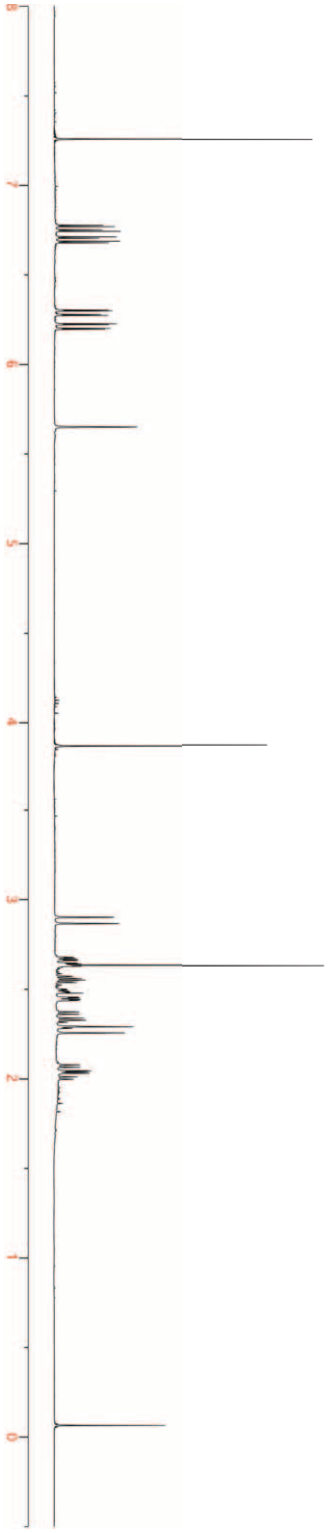
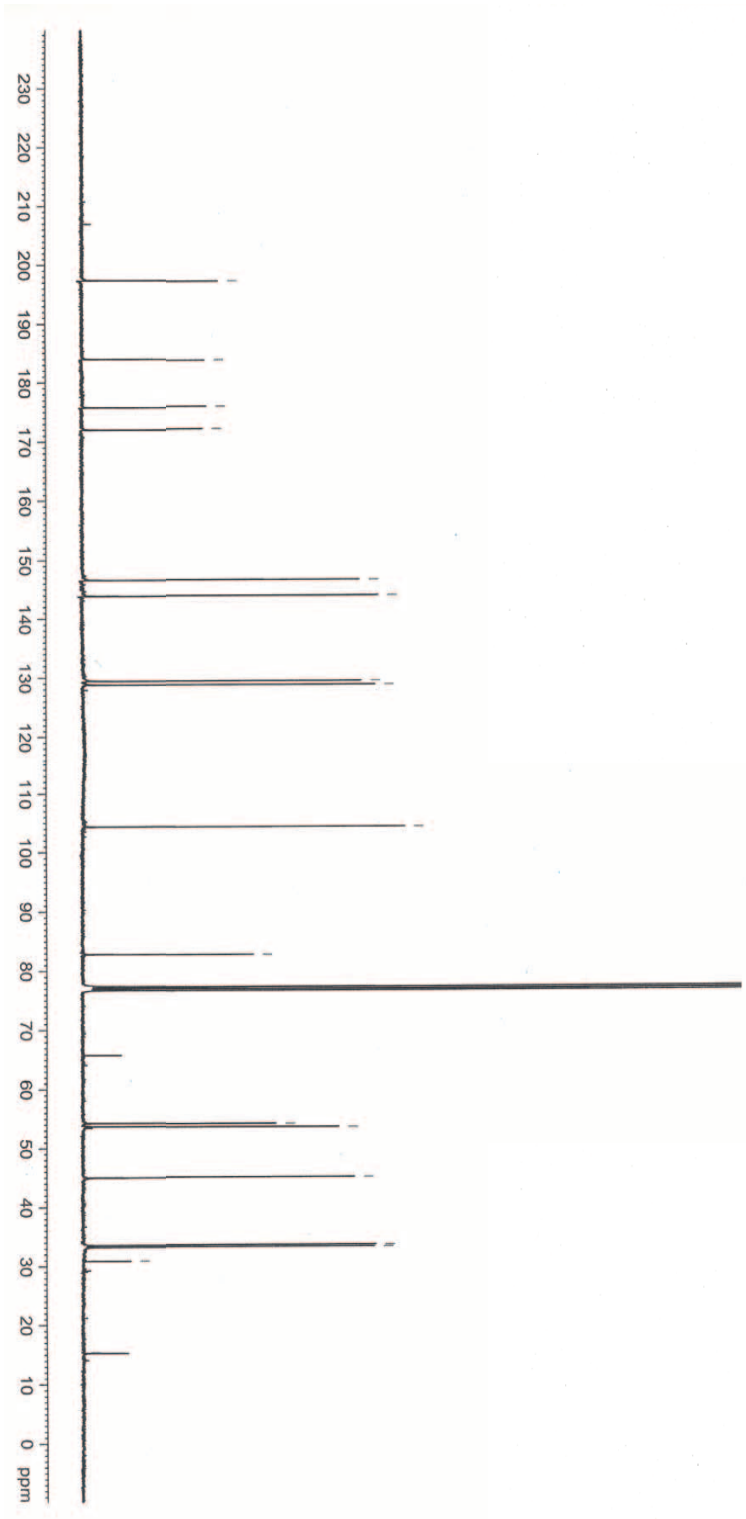
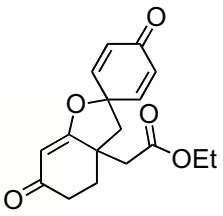
Methyl 4',6-dioxo-3a,4,5,6-tetrahydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-3a-carboxylate (2e)

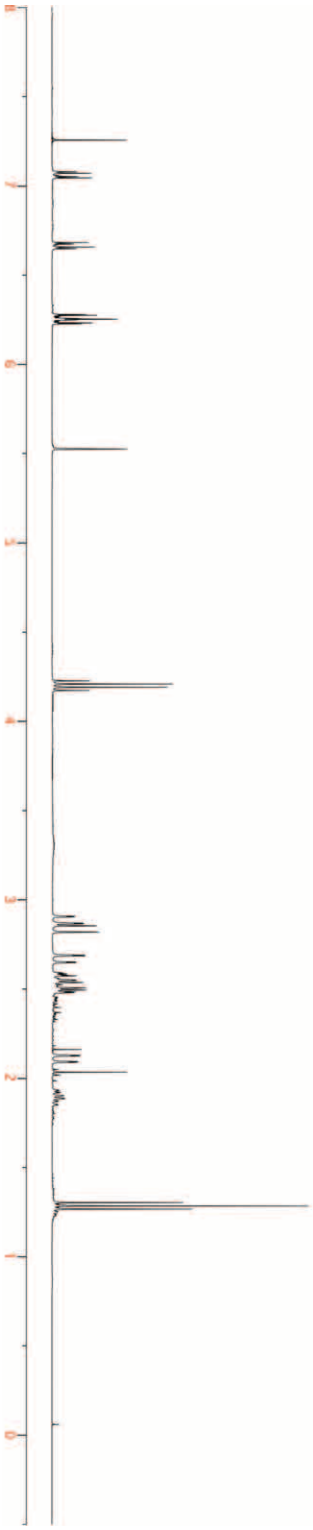


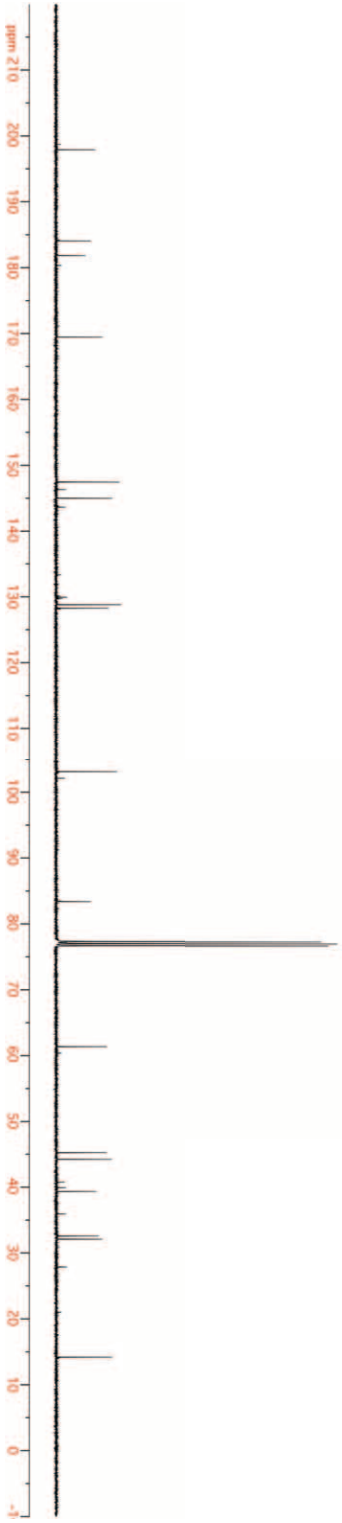




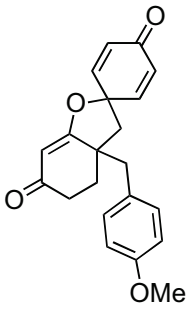
Ethyl 2-(4',6-dioxo-3a,4,5,6-tetrahydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]dien]-3a-yl)acetate (2f)

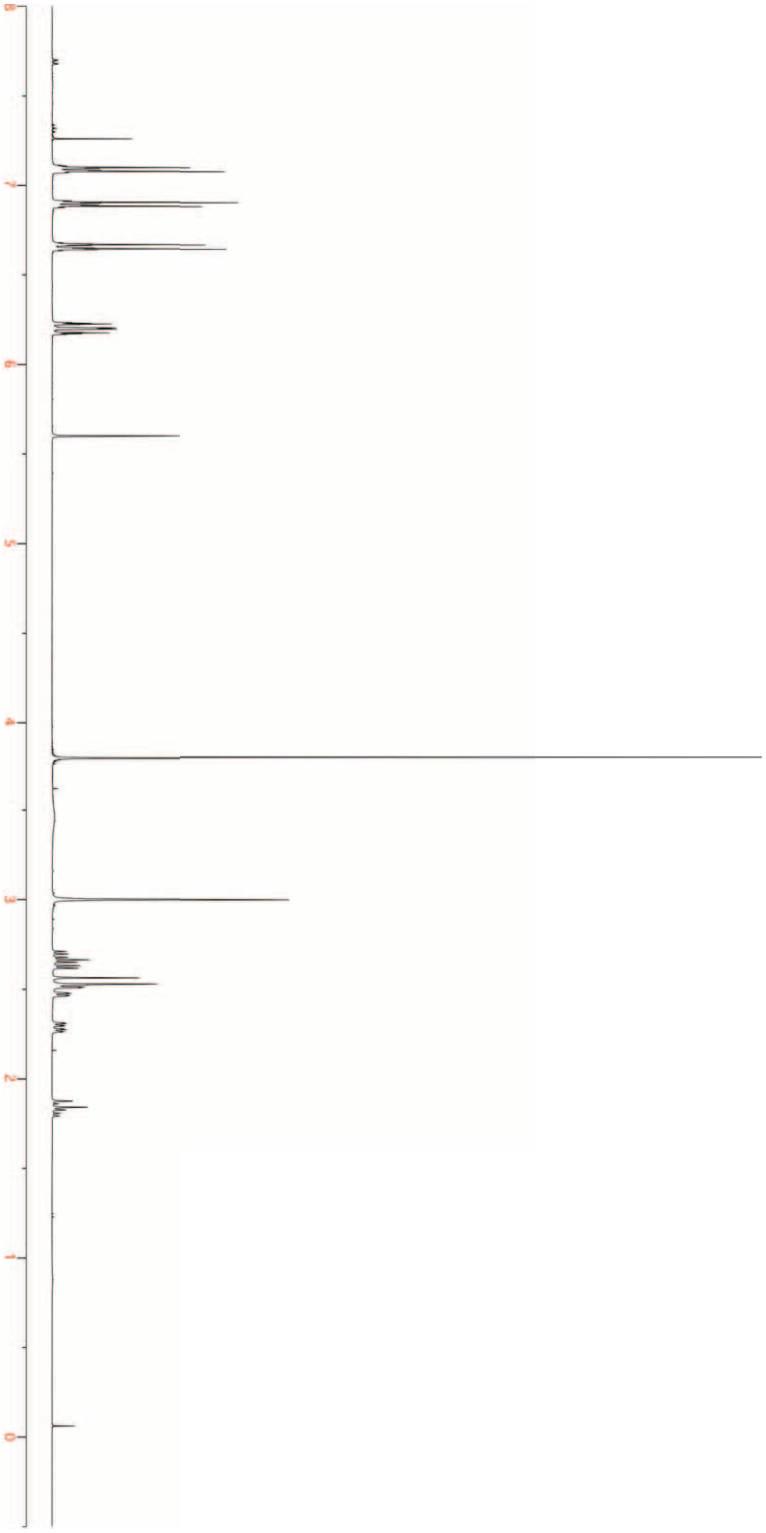


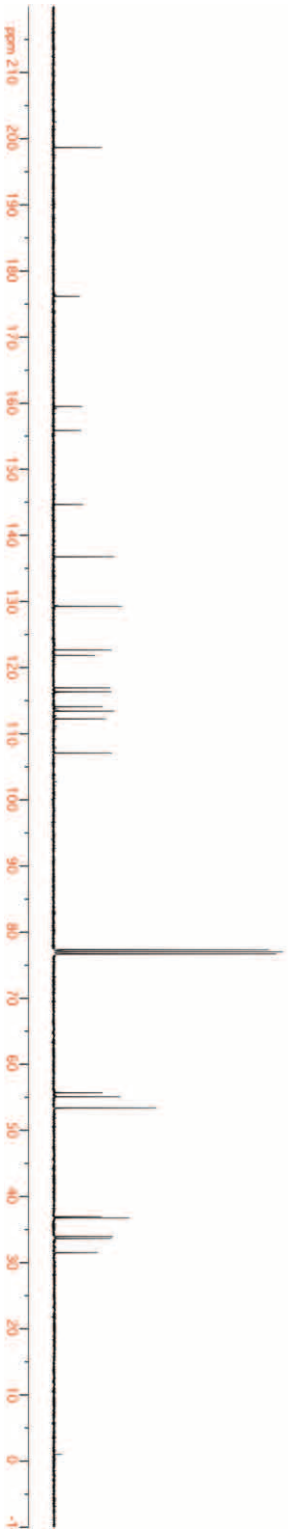




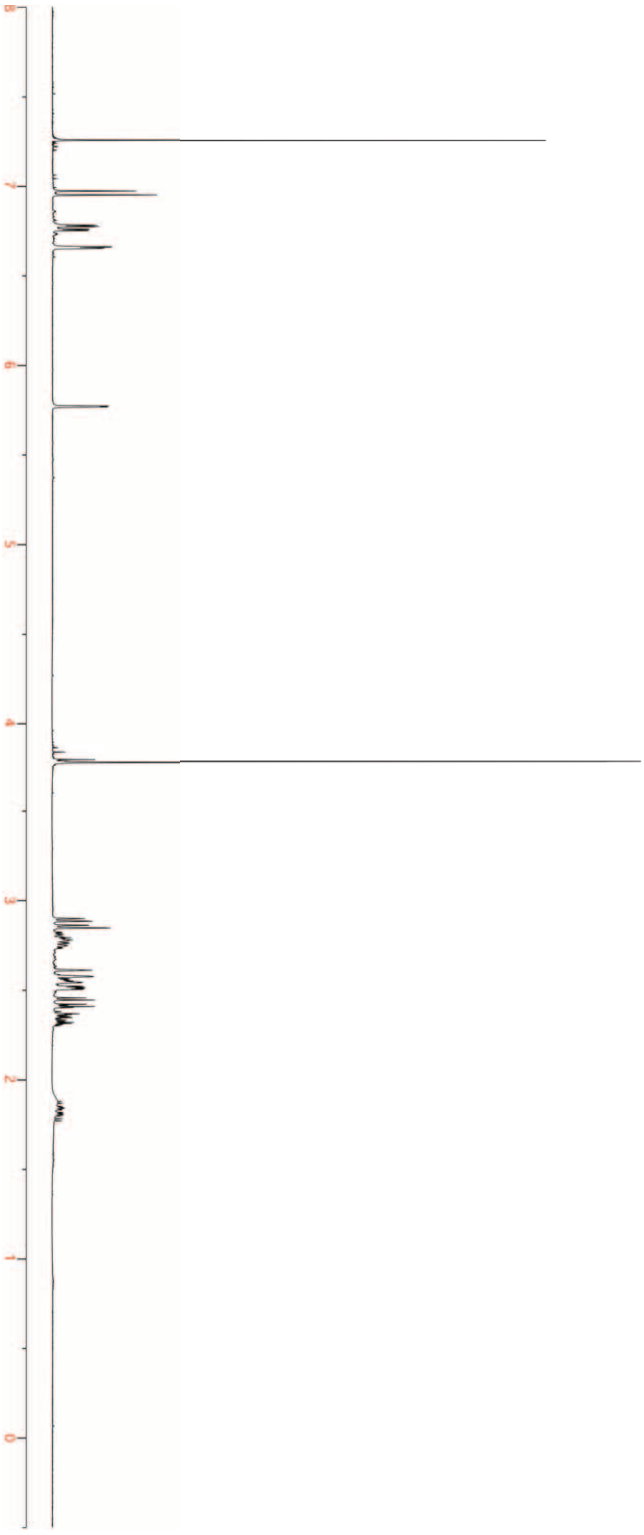
3a-(4-Methoxybenzyl)-4,5-dihydro-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-4',6(3aH)-dione (2g)

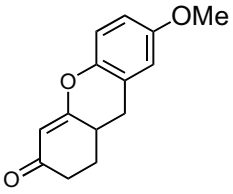


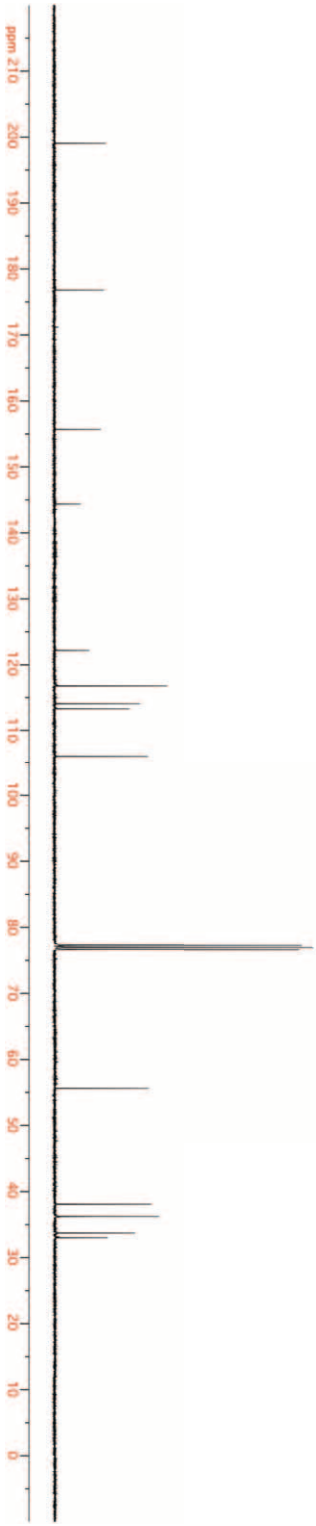




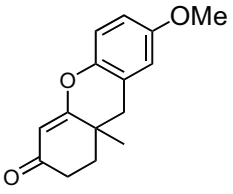
7-Methoxy-9,9a-dihydro-1H-xanthen-3(2H)-one (3h)

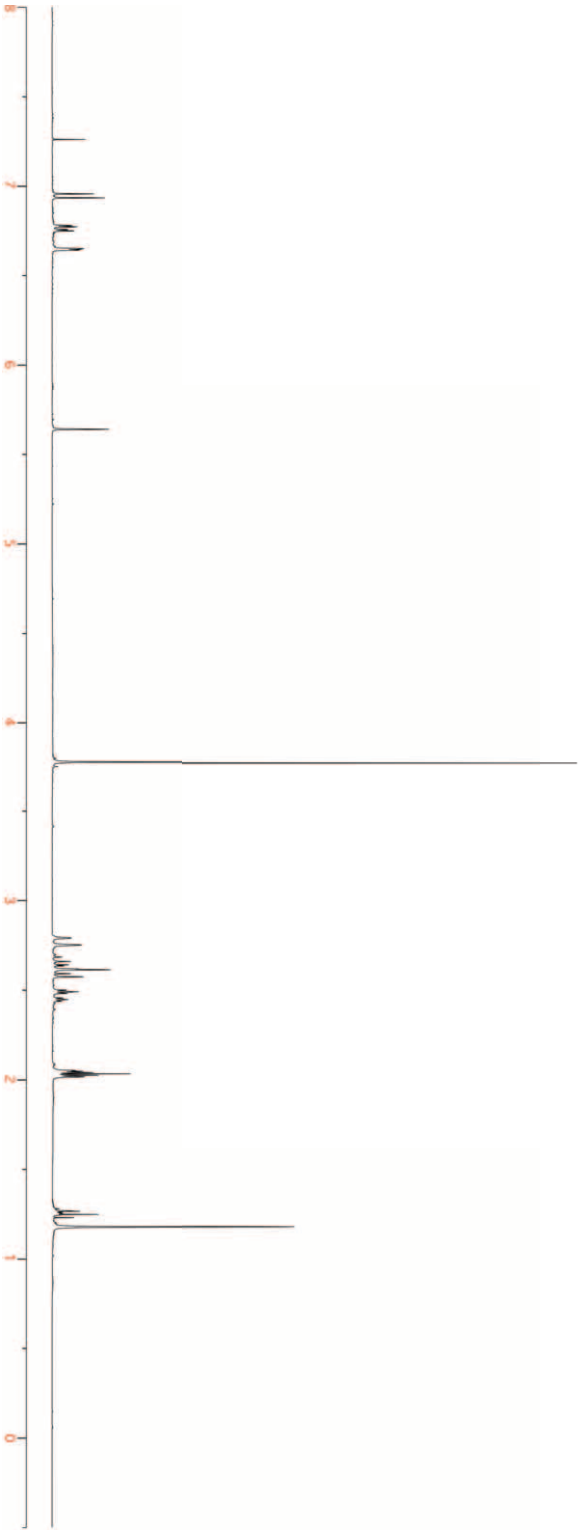


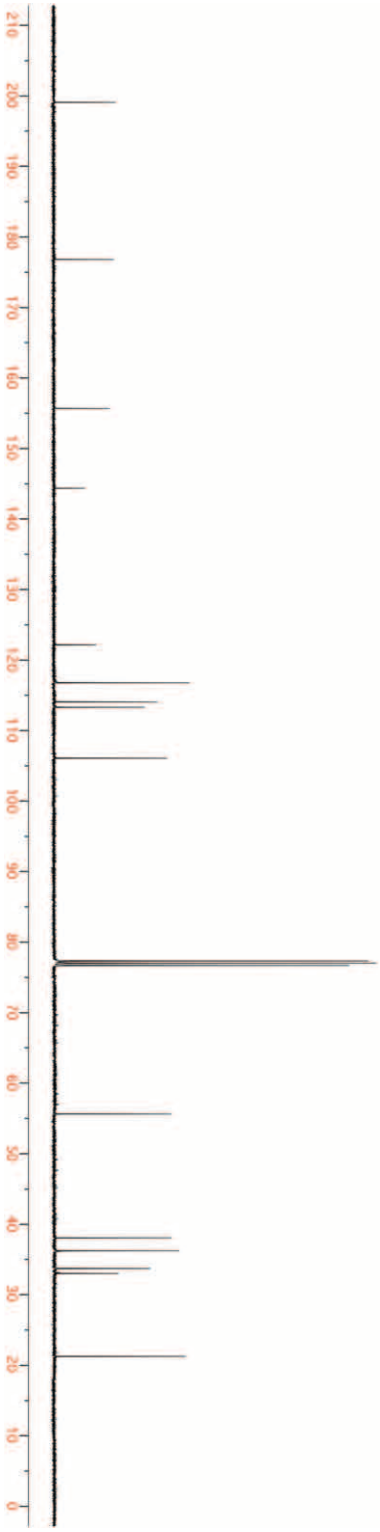




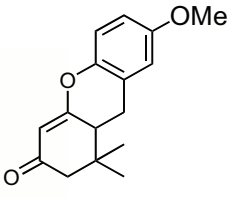
7-Methoxy-9a-methyl-9,9a-dihydro-1H-xanthen-3(2H)-one (3i)

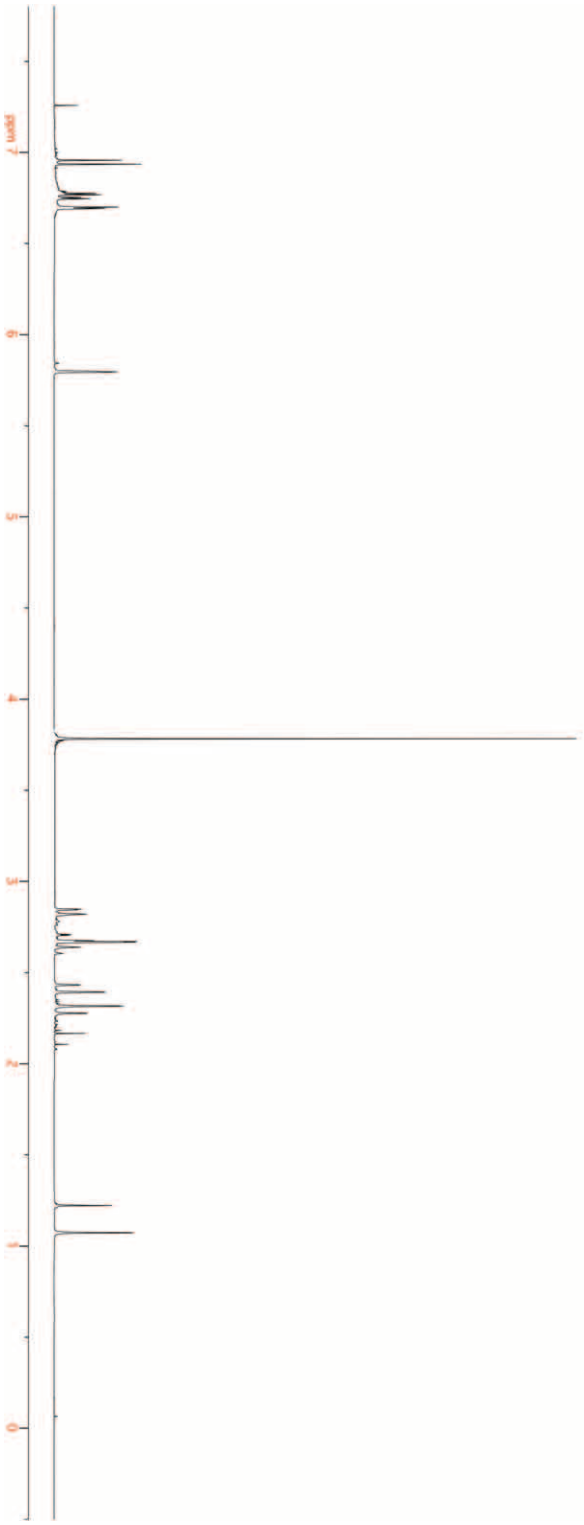


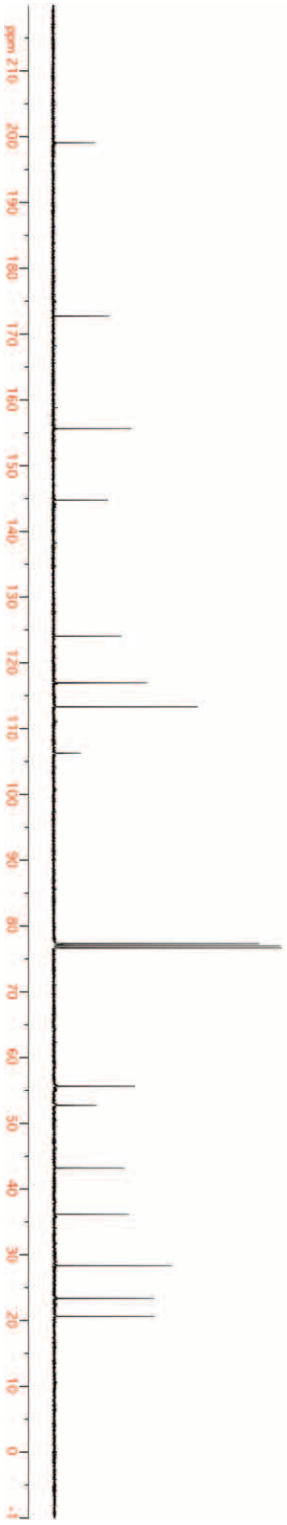




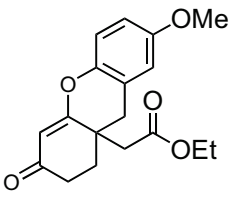
7-Methoxy-1,1-dimethyl-9,9a-dihydro-1H-xanthen-3(2H)-one (3j)

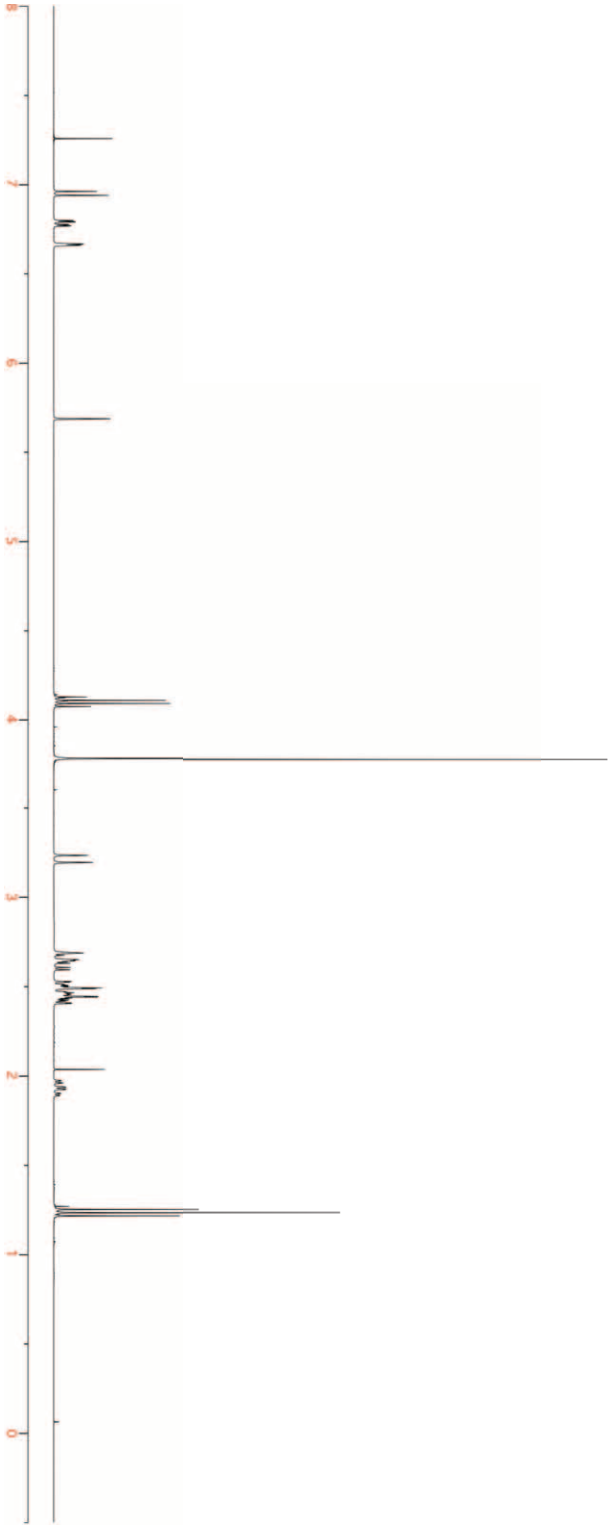


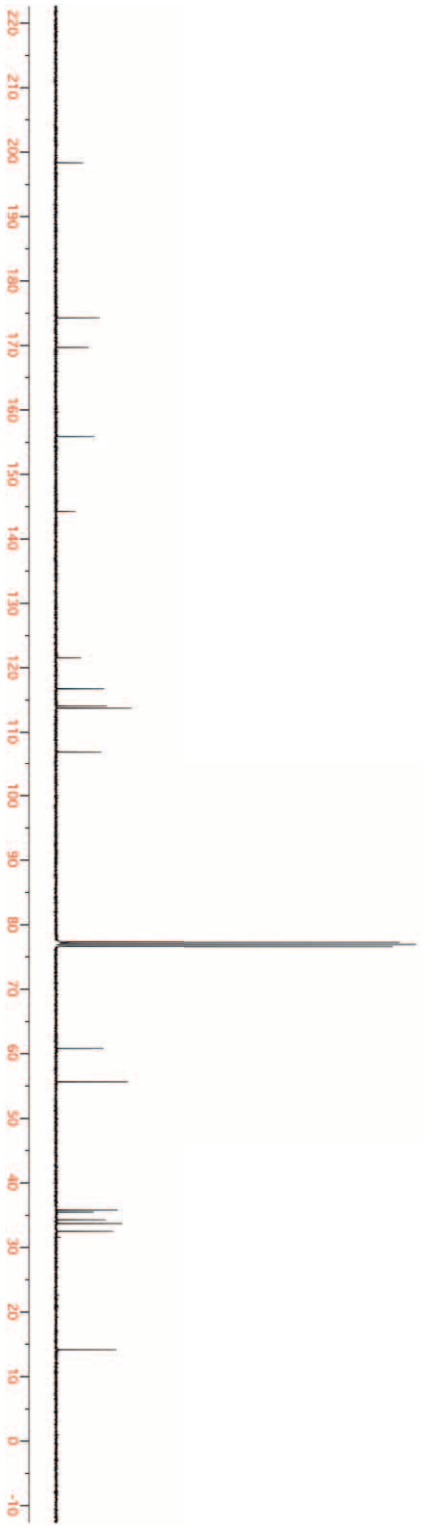




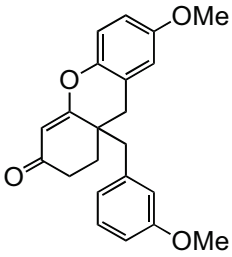
Ethyl 2-(7-methoxy-3-oxo-2,3,9,9a-tetrahydro-1H-xanthen-9a-yl)acetate (3k)

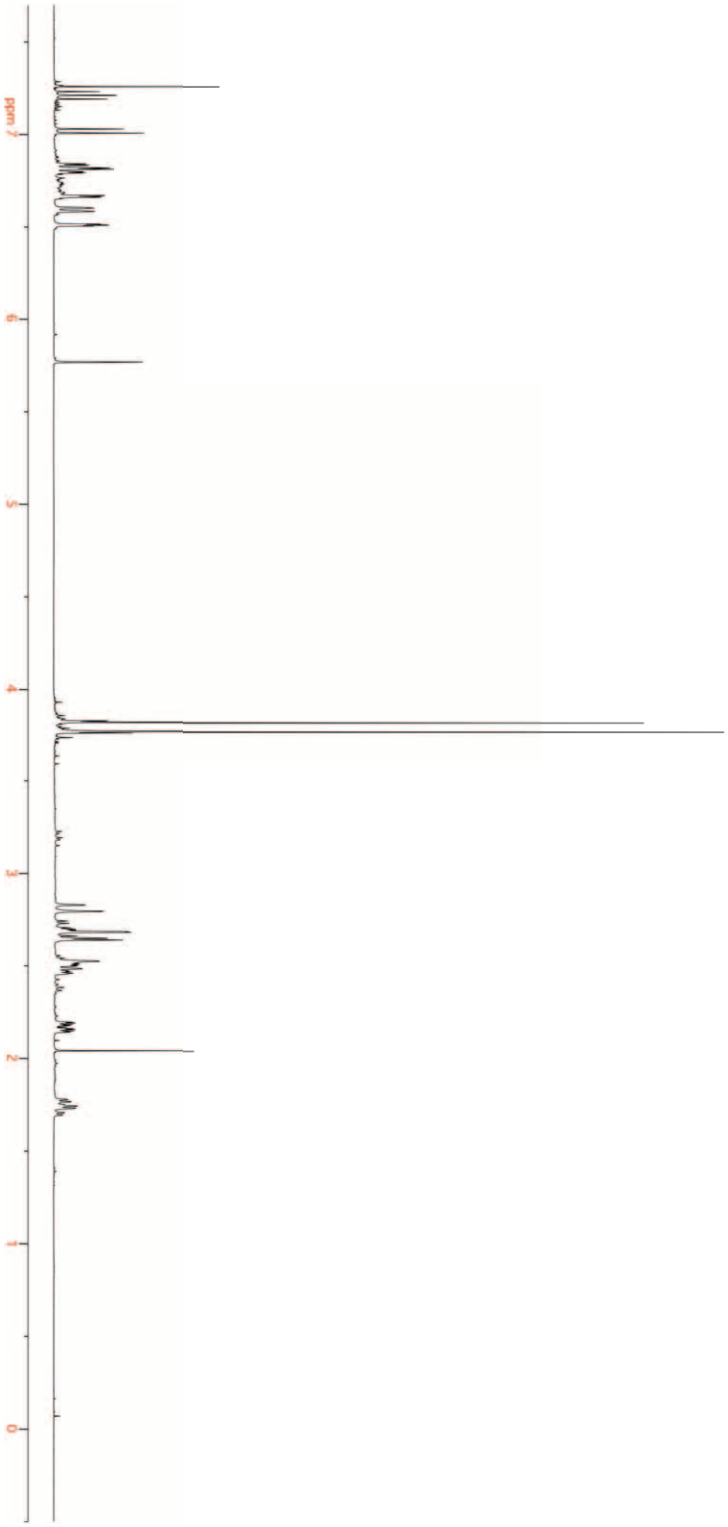


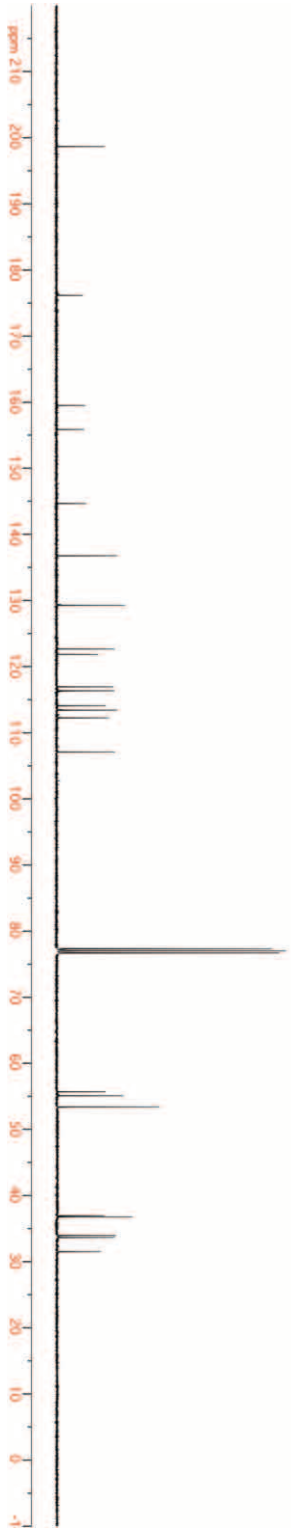




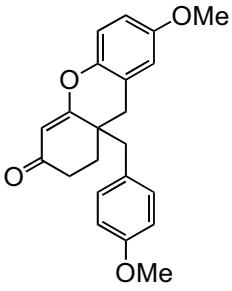
7-Methoxy-9a-(3-methoxybenzyl)-9,9a-dihydro-1H-xanthen-3(2H)-one (3l)

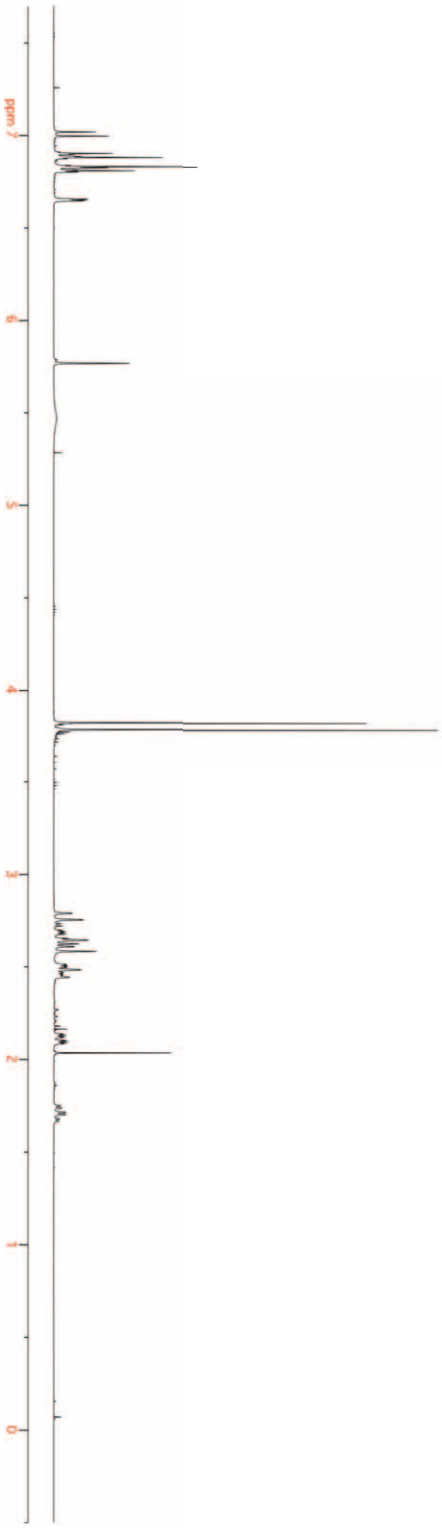


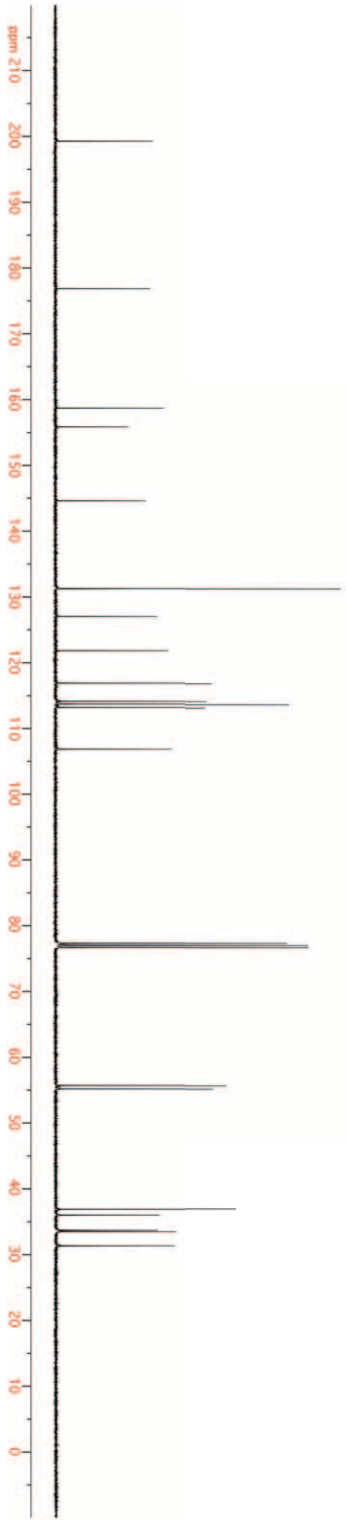




7-Methoxy-9a-(4-methoxybenzyl)-9,9a-dihydro-1H-xanthen-3(2H)-one (3m)



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6,7-Dimethoxy-9,9a-dihydro-1H-xanthen-3(2H)-one (3n)