Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Complex Chromene Derivatives through a Silver-Catalysed Cascade Reaction of Simple *o*-Alkynylsalicylaldehydes and Alkenes

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1. General

1 H NMR spectra were recorded on a Bruker AV-400 (400 MHz) or Bruker DPX-300 (300 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift, multiplicity: (s) = singlet, (d) = doublet, (t) = triplet, (tt)= triplet of triplets, (m) = multiplet, (bs) = broad singlet, (dd) = doublet of doublets, (ddd)= doublet doublet of doublets, (app t) = apparent triplet, (app td)= apparent triplet of doublets; coupling constants (*J* in Hz), integration and assignment. ^{13}C NMR spectra were recorded on a Bruker Bruker AV-400 (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ = 76.95 ppm). Bidimensional NMR experiments (COSY, HSQC, HMBC and NOESY) were recorded on a Bruker AV-400 (400 MHz). High-resolution mass spectrometry was carried out on a Micromass AutoSpec device employing electronic impact fragmentation methods (EI) or electrospray ionization methods (ESI). Melting points have been measured in a Gallenkamp device and have not been corrected.

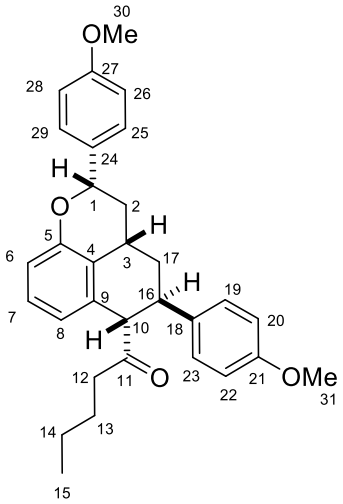
All reactions were conducted in dried glassware under an inert atmosphere of argon when required. Solvents were dried and deoxygenated with a PureSolv® column system before use. Technical grade starting materials were purified before use. Purification of the final products was performed by column chromatography carried out employing silica gel 60 (230-240 mesh, Aldrich) as the stationary phase.

2. Experimental procedures and characterization data

Synthesis of compounds 4a-m

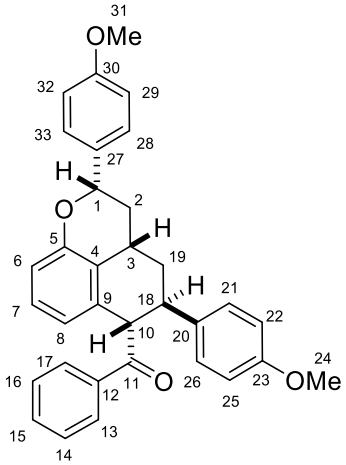
Silver triflate (0.01 mmol) and diphenylphosphate (0.01 mmol) are added to a solution of the corresponding *ortho*-alkynylsalicylaldehyde derivative **1** (0.1 mmol) and styrene derivative **2** (0.25 mmol) in THF (1 mL) at 0 ºC. The mixture is allowed to warm to room temperature and then stirred for 12 hours. After this time the crude of the reaction is diluted in diethyl ether (1 mL) and filtered over a pad of silica gel. The solvents are evaporated and the residue is purified by column chromatography in silica gel using a mixture of hexane / ethyl acetate (10:1) as eluent.

1-[(2*S,3a*S**,5*R**,6*S**)-2,5-Bis(4-methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl]pentan-1-one (4a)**



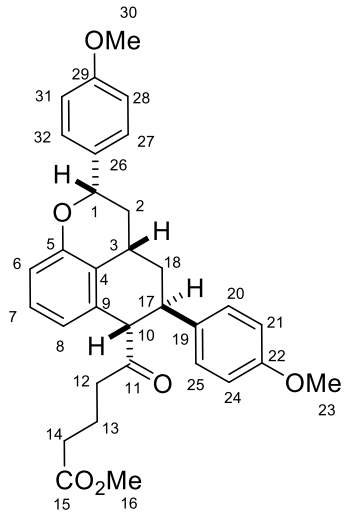
White solid; R_f: 0.30 (hexanes/ethyl acetate 5:1), Melting point: 82-85 ºC; Isolated yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.24 (d, J = 8.9 Hz, 2H, $H_{25,29}$), 7.05 (d, J = 8.7 Hz, 2H, $H_{19,23}$), 7.04 (t, J = 8.3, 1H, H_7), 6.83 (d, J = 8.9 Hz, 2H, $H_{26,28}$), 6.76 (d, J = 8.7 Hz, 1H, $H_{20,22}$), 6.82 (dd, J = 8.3, 1.3 Hz, 1H, H_6), 6.57 (dd, J = 8.3, 1.3 Hz, 1H, H_8), 5.10 (dd, J = 11.3, 2.6 Hz, 1H, H_1), 4.24 (d, J = 2.5 Hz, 1H, H_{10}), 3.83 (s, 3H, H_{30}), 3.82 (s, 3H, H_{31}), 3.42 - 3.39 (m, 1H, H_{16}), 2.77 (tt, J = 11.0, 5.2 Hz, 1H, H_3), 2.57 (t, J = 7.3 Hz, 2H, H_{12}), 2.10-1.79 (m, 4H, $H_{2,17}$), 1.68-1.50 (m, 2H, H_{13}), 1.32 (sextuplet, J = 7.3 Hz, 2H, H_{14}), 0.91 (t, J = 7.3 Hz, 3H, H_{15}). ^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm): 211.3, 159.4, 158.2, 154.4, 136.6, 133.9, 133.9, 128.3, 127.5, 127.4, 123.3, 120.3, 114.7, 113.9, 113.9, 78.3, 77.2, 55.33, 55.3, 42.6, 39.0, 36.7, 33.4, 28.0, 26.0, 22.3, 13.9. HMRS: calculated for $C_{31}H_{34}O_4$ $[M]^+$ 470.2452 found 470.2466.

[(2*S,3a*S**,5*R**,6*S**)-2,5-Bis(4-methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl](phenyl)methanone (4b)**



White solid; R_f: 0.46 (hexanes/ethyl acetate 5:1); Melting point: 133-135 ºC, Yield: 69%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.00 (d, *J* = 7.3 Hz, 2H, $H_{13,17}$), 7.58 (t, *J* = 7.3 Hz, 1H, H_{15}), 7.46 (t, *J* = 7.3 Hz, 2H, $H_{14,16}$), 7.34 (d, *J* = 8.7 Hz, 2H, $H_{21,26}$), 7.20 (d, *J* = 8.7 Hz, 2H, $H_{28,33}$), 7.10 (t, *J* = 7.8 Hz, 1H, H_7), 6.92 (d, *J* = 8.7 Hz, 2H, $H_{22,25}$), 6.88 (d, *J* = 8.7, 2H, $H_{29,32}$), 6.82(d, *J* = 7.8 Hz, 1H, H_6), 6.60 (d, *J* = 7.8 Hz, 1H, H_8), 5.19-5.17 (m, 1H, H_{10}), 5.12 (dd, *J* = 10.8, 3.2 Hz, 1H, H_1), 3.82 (s, 6H, $H_{24,31}$), 3.52-3.50 (m, 1H, H_{18}), 2.80 (tt, *J* = 11.3, 4.7 Hz, 1H, H_3), 2.11 – 1.81 (m, 4H, $H_{2,19}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm)= 200.7, 159.4, 158.4, 154.2, 136.3, 136.2, 134.2, 134.0, 133.2, 128.8, 128.8, 128.7, 128.5, 127.5, 127.4, 123.8, 121.0, 114.7, 114.0, 113.9, 78.3, 55.3, 55.3, 49.7, 39.8, 36.7, 33.0, 27.9. HMRS: calculated for $C_{33}H_{30}O_4$ $[M]^+$ 490.2139 found 490.2146.

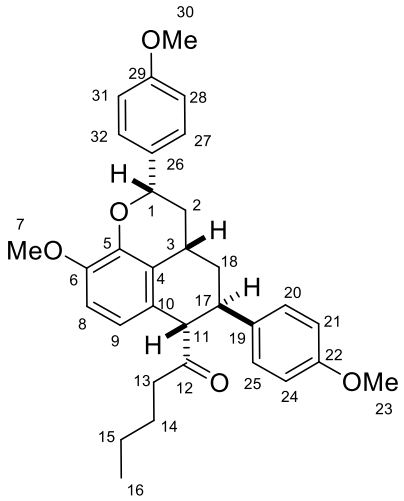
Methyl 5-[(2*S,3a*S**,5*R**,6*S**)-2,5-bis(4-methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl]-5-oxopentanoate (4c)**



White solid; R_f: 0.40 (hexanes/ethyl acetate 5:1); Melting point: 96-98 ºC; Isolated yield: 72%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.34 (d, *J* = 8.7 Hz, 2H, $H_{27,32}$), 7.19 - 7.10 (m, 1H, H_7), 7.14 (d, *J* = 8.7 Hz, 2H, $H_{20,25}$), 6.93 (d, *J* = 8.7 Hz, 2H, $H_{28,31}$), 6.86 (d, *J* = 8.7 Hz, 2H, $H_{21,24}$), 6.84 – 6.79 (m, 1H, H_6), 6.67 (d, *J* = 7.5 Hz, 1H, H_8), 5.10 (dd, *J* = 11.4, 2.6 Hz, 1H, H_1), 4.21 (d, *J* = 2.6 Hz, 1H,

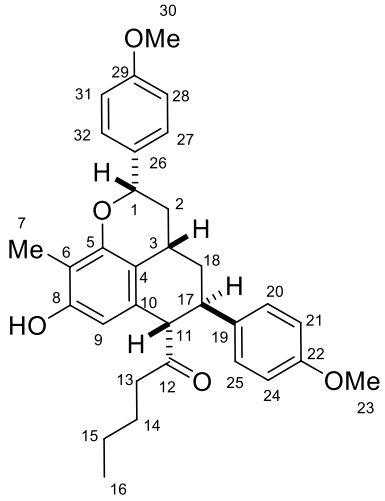
H_{10}), 3.83 (s, 3H, H_{23}), 3.82 (s, 3H, H_{30}), 3.68 (s, 3H, H_{16}), 3.45 – 3.34 (m, 1H, H_{17}), 2.89 – 2.68 (m, 1H, H_3), 2.65 (t, *J* = 7.0 Hz, 2H, H_{12}), 2.34 (app td, *J* = 7.2, 2.2 Hz, 2H, H_{18}), 2.10 – 1.79 (m, 6H, $H_{2,13,14}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 210.4, 173.6, 159.4, 158.3, 154.4, 136.5, 133.8, 133.7, 128.3, 128.3, 127.5, 127.4, 126.5, 123.2, 120.3, 114.8, 113.9, 113.7, 78.3, 55.4, 55.3, 55.3, 51.6, 41.6, 39.0, 36.7, 33.4, 32.9, 28.0, 19.0. HMRS: calculated for $C_{32}H_{34}O_6$ $[M]^+$ 514.2650 found 514.2346.

1-[(2*S,3a*S**,5*R**,6*S**)-9-Methoxy-2,5-bis(4-methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl]pentan-1-one (4d)**



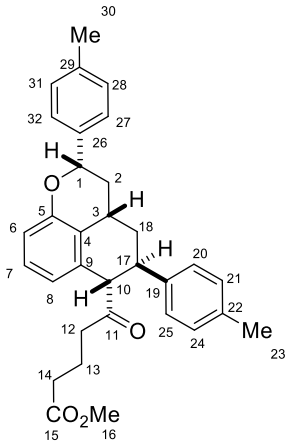
White solid; R_f: 0.27 (hexanes/ethyl acetate 5:1); Melting point: 88-90ºC; Isolated yield: 58%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.35 (d, *J* = 8.7 Hz, 2H, $H_{20,25}$), 7.15 (d, *J* = 8.7 Hz, 2H, $H_{27,32}$), 6.90 (d, *J* = 8.7 Hz, 2H, $H_{21,24}$), 6.85 (d, *J* = 8.7 Hz, 2H, $H_{28,31}$), 6.82 (d, *J* = 8.3 Hz, 1H, H_9), 6.61 (d, *J* = 8.3 Hz, 1H, H_8), 5.13 (dd, *J* = 11.5, 2.7 Hz, 1H, H_1), 4.18 (d, *J* = 2.6 Hz, 1H, H_{11}), 3.86 (s, 3H, H_{23}), 3.82 (s, 3H, H_7), 3.81 (s, 3H, H_{30}), 3.31 - 3.34 (m, 1H, H_{17}), 2.76 (tt, *J* = 12.8, 5.9 Hz, 1H, H_3), 2.54 (t, *J* = 7.3 Hz, 2H, H_{13}), 2.16 – 1.77 (m, 4H, $H_{2,18}$), 1.62 – 1.28 (m, 4H, $H_{14,15}$), 0.90 (t, *J* = 7.3 Hz, 3H, H_{16}). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 211.8, 159.3, 158.2, 146.9, 143.6, 136.7, 134.0, 128.4, 127.4, 125.5, 123.9, 119.5, 113.8, 110.4, 56.0, 55.3, 54.9, 42.5, 39.0, 37.0, 33.4, 28.2, 26.0, 22.3, 13.9. HMRS: calculated for $C_{32}H_{36}O_5$ $[M]^+$ 500.2557 found 500.2570.

1-[(2*S,3a*S**,5*R**,6*S**)-8-Hydroxy-2,5-bis(4-methoxyphenyl)-9-methyl-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl]pentan-1-one (4e)**



White solid; Rf: 0.15 (hexanes/ethyl acetate 5:1); Melting point: 91-93ºC; Isolated yield: 66%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.34 (d, J = 8.7 Hz, 2H, $H_{27,32}$), 7.15 (d, J = 8.7 Hz, 2H, $H_{20,25}$), 6.93 (d, J = 8.7 Hz, 2H, $H_{28,31}$), 6.86 (d, J = 8.7 Hz, 2H, $H_{21,24}$), 6.15 (s, 1H, H_9), 5.17 (s, 1H, OH), 5.12 (dd, J = 11.4, 2.3 Hz, 1H, H_1), 4.14 (d, J = 2.5 Hz, 1H, H_{11}), 3.84 (s, 3H, H_{30}), 3.81 (s, 3H, H_{23}), 3.36 – 3.32 (m, 1H, H_{17}), 2.81 – 2.61 (m, 1H, H_3), 2.61 – 2.49 (m, 2H, H_{13}), 2.11 (s, 3H, H_7), 2.06 – 1.64 (m, 4H, $H_{2,18}$), 1.65 – 1.47 (m, 2H, H_{14}), 1.31 (sextuplet, J = 7.3 Hz, 2H, H_{15}), 0.91 (t, J = 7.3 Hz, 3H, H_{16}). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 211.9, 159.1, 158.2, 153.1, 152.9, 136.7, 134.5, 130.8, 128.4, 127.0, 115.6, 113.8, 113.8, 110.0, 106.8, 78.3, 55.3, 42.4, 39.1, 37.2, 33.6, 27.6, 26.0, 22.3, 13.9, 8.2. HMRS: calculated for $C_{32}H_{36}O_6$ $[M]^+$ 500.2557 found 500.2565.

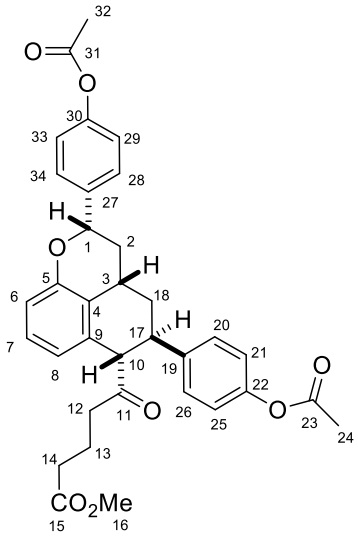
Methyl 5-[(2*S,3a*S**,5*R**,6*S**)-2,5-bis(4-methylphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl]-5-oxopentanoate (4f)**



White solid*;* R_f: 0.33 (hexanes/ethyl acetate 8:1)*;* Melting point: 82-85 ºC*;* Isolated yield: 44%. ^{1}H RMN (300 MHz, $CDCl_3$) δ (ppm) 7.35 – 7.09 (m, 9H, $H_{7,20,21,24,25,27,28,31,32}$), 6.83 (d, *J* = 7.9 Hz, 1H, H_6), 6.67 (d, *J* = 7.5 Hz, 1H, H_8), 5.11 (dd, *J* = 11.4, 2.2 Hz, 1H, H_1), 4.23 (d, *J* = 2.0 Hz, 1H, H_{10}), 3.68 (s, 3H, H_{16}), 3.47 – 3.34 (m, 1H, H_{17}), 2.87 – 2.76 (m, 1H, H_3), 2.67 – 2.63 (m, 2H, H_{12}),

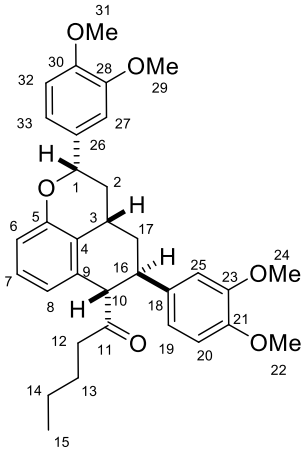
2.37, 2.36 (2 s, 6H, $H_{23,30}$), 2.32 (td, *J* = 7.3, 1.6 Hz, 2H, H_{18}), 2.11 – 1.81 (m, 6H, $H_{2,13,14}$). ^{13}C RMN (75 MHz, $CDCl_3$) δ (ppm) 210.5, 173.7, 154.5, 141.6, 138.9, 137.8, 136.36, 133.8, 129.4, 129.3, 127.6, 127.4, 126.1, 123.4, 120.4, 115.0, 78.5, 55.3, 51.7, 41.7, 39.6, 36.9, 33.5, 33.1, 28.0, 21.3, 21.1, 19.1. HMRS: calculated for $C_{32}H_{35}O_4$ $[M+1]^+$ 483.2529 found 483.2527.

[(2*S,3a*S**,5*R**,6*S**)-6-(5-methoxy-5-oxopentanoyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromene-2,5-diyl]bis(4,1-phenylene) diacetate (4g)**



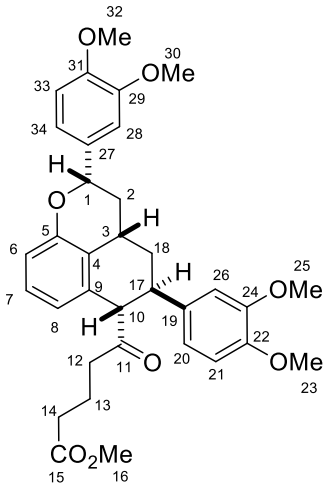
Yellow solid*;* R_f: 0.29 (hexanes/ethyl acetate 2:1)*;* Melting point: 99-102 ºC*;* Isolated yield: 67%. ^{1}H RMN (300 MHz, $CDCl_3$) δ (ppm) 7.41 (d, *J* = 8.5 Hz, 2H, $H_{28,34}$), 7.20 (d, *J* = 8.5 Hz, 2H, $H_{20,26}$), 7.14 – 7.06 (m, 3H, $H_{7,29,33}$), 7.01 (d, *J* = 8.5 Hz, 2H, $H_{21,25}$), 6.81 (d, *J* = 8.0 Hz, 1H, H_6), 6.67 (d, *J* = 7.6 Hz, 1H, H_8), 5.14 (dd, *J* = 11.4, 2.0 Hz, 1H, H_1), 4.20 (s, 1H, H_{10}), 3.66 (s, 3H, H_{16}), 3.44 (m, 1H, H_{17}), 2.78 – 2.72 (m, 1H, H_3), 2.67 – 2.63 (m, 2H, H_{12}), 2.36 – 2.25 (m, 2H, H_{18}), 231 (s, 6H, $H_{24,32}$), 2.00 – 1.80 (m, 6H, $H_{2,13,14}$). ^{13}C RMN (75 MHz, $CDCl_3$) δ (ppm) 210.2, 173.7, 169.7, 169.6, 154.3, 150.4, 149.4, 141.9, 139.4, 133.4, 128.5, 127.8, 127.2, 123.2, 121.8, 120.6, 115.0, 78.0, 55.1, 51.7, 41.6, 39.3, 36.8, 33.1, 33.0, 27.8, 21.3, 19.1. HMRS: calculated for $C_{34}H_{35}O_8$ $[M+1]^+$ 571.2326 found 571.2326.

1-[(2*S,3a*S**,5*R**,6*S**)- 2,5-Bis(3,4-dimethoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl]pentan-1-one (4h)**



White solid*;* R_f: 0.10 (hexanes/ethyl acetate 5:1)*;* Melting point: 62-64 ºC*;* Isolated yield: 63%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.15 (t, *J* = 7.8 Hz, 1H, H_7), 7.03 – 6.46 (m, 8H, $H_{6,8,19,20,25,27,32,33}$), 5.10 (dd, *J* = 11.2, 2.7 Hz, 1H, H_1), 4.26 (d, *J* = 2.5 Hz, 1H, H_{10}), 3.91 (s, 3H, H_{22}), 3.89 (s, 3H, H_{24}), 3.88 (s, 3H, H_{29}), 3.84 (s, 3H, H_{31}), 3.41 – 3.37 (m, 1H, H_{16}), 2.78 (tt, *J* = 10.9, 5.2 Hz, 1H, H_3), 2.60 (t, *J* = 7.3 Hz, 2H, H_{12}), 2.14 – 1.81 (m, 4H, $H_{2,17}$), 1.73 – 1.49 (m, 2H, H_{13}), 1.32 (sextuplet, *J* = 7.4 Hz, 2H, H_{14}), 0.91 (t, *J* = 7.4 Hz, 3H, H_{15}). ^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm) = 211.3, 154.3, 149.1, 148.8, 148.8, 147.7, 137.0, 134.3, 133.9, 127.5, 125.0, 123.1, 120.3, 119.0, 118.6, 116.1, 114.8, 111.1, 111.0, 111.0, 109.1, 78.6, 56.0, 55.9, 55.9, 55.3, 42.7, 39.3, 36.7, 33.3, 28.1, 26.0, 22.3, 13.9. HMRS: calculated for $C_{33}H_{38}O_6$ $[M]^+$ 530.2663 found 530.2679.

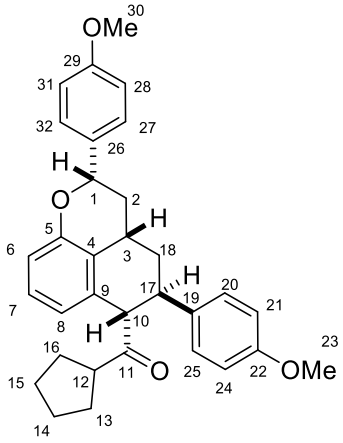
Methyl 5-[(2*S,3a*S**,5*R**,6*S**)-2,5-bis(3,4-dimethoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl)-5-oxopentanoate (4i)**



Yellow solid*;* R_f: 0.36 (hexanes/ethyl acetate 1:1)*;* Melting point: 72-75 ºC*;* Isolated yield: 85%. ^{1}H RMN (300 MHz, $CDCl_3$) δ (ppm) 7.12 (t, *J* = 7.8 Hz, 1H, H_7), 7.01 – 6.59 (m, 8H, $H_{6,8,20,21,26,28,33,34}$), 5.08 (dd, *J* = 11.3, 2.3 Hz, 1H, H_1), 4.21 (d, *J* = 2.1 Hz, 1H, H_{10}), 3.89 (s, 3H, H_{23}), 3.87 (s, 3H, H_{25}), 3.85 (s, 3H, H_{30}), 3.81 (s, 3H, H_{32}), 3.65 (s, 3H, H_{16}), 3.43 – 3.32 (m, 1H, H_{17}),

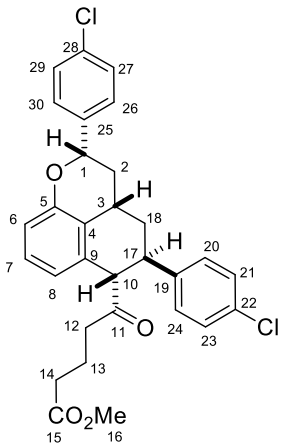
2.82 – 2.69 (m, 1H, H_3), 2.67 – 2.63 (m, 2H, H_{12}), 2.36 – 2.26 (m, 2H, H_{18}), 2.03 – 1.83 (m, 6H, $H_{2,13,14}$). ^{13}C RMN (75 MHz, $CDCl_3$) δ (ppm) 210.5, 173.7, 154.4, 149.2, 149.0, 148.9, 147.8, 137.0, 134.4, 133.7, 127.7, 123.2, 120.4, 119.1, 118.6, 115.0, 111.3, 111.1, 109.3, 78.7, 56.1, 56.0, 55.5, 51.7, 41.7, 39.4, 36.8, 33.4, 33.0, 28.2, 19.1. HMRS: calculated for $C_{34}H_{39}O_8$ $[M+1]^+$ 571.2639 found 575.2622

[(2*S,3a*S**,5*R*,6*S**)-2,5-Bis(4-methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl](cyclopentyl)methanone (4j)**



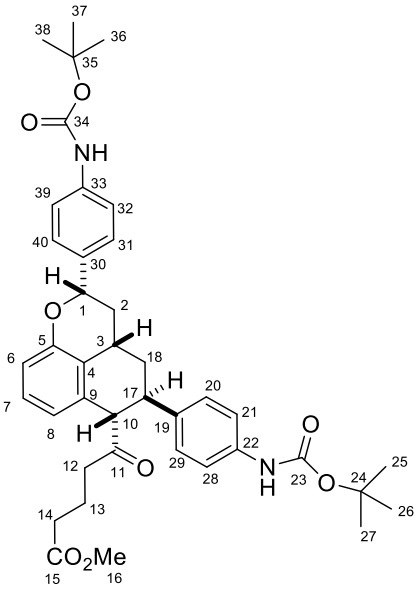
White solid*;* R_f: 0.46 (hexanes/ethyl acetate 5:1)*;* Melting point: 89-92 ºC*;* Isolated yield: 46%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.34 (d, *J* = 8.7 Hz, 2H, $H_{27,32}$), 7.17 (d, *J* = 8.7 Hz, 2H, $H_{20,25}$), 7.20 - 7.08 (m, 1H, H_7), 6.93 (d, *J* = 8.7 Hz, 2H, $H_{22,24}$), 6.86 (d, *J*= 8.7 Hz, 2H, $H_{28,31}$), 6.88 – 6.75 (m, 1H, H_6), 6.63 (d, *J* = 7.5 Hz, 1H, H_8), 5.10 (dd, *J* = 11.5, 2.5 Hz, 1H, H_1), 4.33 (d, *J* = 2.8 Hz, 1H, H_{10}), 3.83 (s, 3H, H_{30}), 3.82 (s, 3H, H_{23}), 3.41 - 3.35 (m, 1H, H_{17}), 3.10 (quintuplet, *J* = 7.8 Hz, 1H, H_{12}), 2.79 (tt, *J* = 10.7, 5.7 Hz, 1H, H_3), 2.13 – 1.40 (m, 12H, $H_{2,13,14,15,16,18}$). ^{13}C NMR (75 MHz, CDCl3) δ (ppm) = 213.4, 159.4, 158.2, 154.3, 136.8, 134.3, 133.9, 128.40, 127.4, 123.5, 120.2, 114.6, 113.9, 113.9, 78.2, 55.3, 55.3, 54.9, 51.4, 38.9, 36.8, 33.4, 30.0, 29.0, 28.1, 26.0, 26.0. HMRS: calculated for $C_{32}H_{34}O_4$ $[M]^+$ 482.2452 found 482.2457.

Methyl 5-[(2*S,3a*S**,5*R**,6*S**)-2,5-bis(4-chlorophenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl]-5-oxopentanoate (4k)**



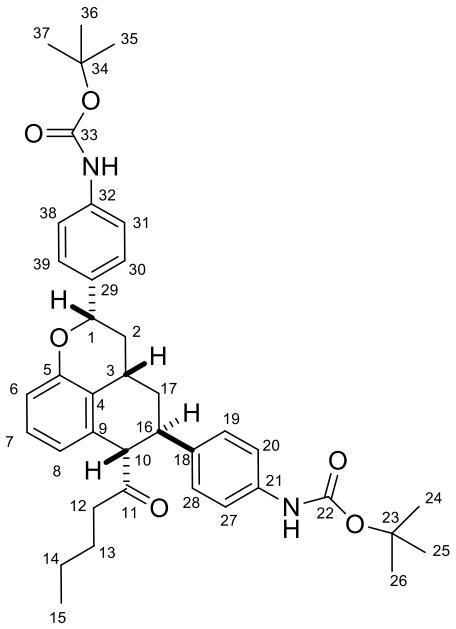
Yellow solid; R_f: 0.27 (hexanes/ethyl acetate 2:1); Melting point: 93-96 ºC; Isolated yield: 40%. ^{1}H RMN (300 MHz, $CDCl_3$) δ (ppm) 7.44 – 7.10 (m, 9H, $H_{7,20,21,23,24,26,27,29,30}$), 6.84 (d, *J* = 8.0 Hz, 1H, H_6), 6.69 (d, *J* = 7.5 Hz, 1H, H_8), 5.12 (dd, *J* = 11.6, 2.4 Hz, 1H, H_1), 4.18 (d, *J* = 2.1 Hz, 1H, H_{10}), 3.68 (s, 3H, H_{16}), 3.48 – 3.40 (m, 1H, H_{17}), 2.76 – 2.67 (m, 1H, H_3), 2.65 (t, *J* = 7.2 Hz, 2H, H_{12}), 2.39 – 2.28 (m, 2H, H_{18}), 2.17 – 1.76 (m, 6H, $H_{2,13,14}$). ^{13}C RMN (75 MHz, $CDCl_3$) δ (ppm) 209.9, 173.5, 154.1, 142.7, 140.1, 133.7, 133.3, 132.5, 128.7, 127.8, 127.3, 122.8, 120.5, 115.0, 77.7, 54.9, 51.6, 41.6, 39.2, 36.7, 33.1, 32.8, 27.8, 18.9. HMRS: calculated for $C_{30}H_{29}Cl_2O_4$ $[M+1]^+$ 523.1437 found 523.1435

Methyl 5-{(2*S,3a*S**,5*R**,6*S**)-2,5-bis[4-(*tert*-butoxycarbonylamino)phenyl]-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl}-5-oxopentanoate (4l)**



Yellow solid*;* R_f: 0.28 (hexanes/ethyl acetate 3:1)*;* Melting point: 89-92 ºC*;* Isolated yield: 82%. ^{1}H RMN (300 MHz, $CDCl_3$) δ (ppm) 7.43 – 7.07 (m, 9H, $H_{7,20,21,28,29,31,32,39,40}$), 6.81 (d, *J* = 8.0 Hz, 1H, H_6), 6.66 (d, *J* = 7.5 Hz, 1H, H_8), 6.57 (s, 2H, NH), 5.07 (d, *J* = 10.3 Hz, 1H, H_1), 4.20 (s, 1H, H_{10}), 3.67 (s, 3H, H_{16}), 3.41 – 3.38 (s, 1H, H_{17}), 2.80 – 2.68 (m, 1H, H_3), 2.63 (t, *J* = 6.8 Hz, 2H, H_{12}), 2.39 – 2.26 (m, 2H, H_{18}), 2.00 – 1.70 (m, 6H, $H_{2,13,14}$), 1.53 (s, 18H, $H_{25,26,27,36,37,38}$). ^{13}C RMN (75 MHz, $CDCl_3$) δ (ppm) 210.4, 173.6, 154.3, 152.8, 152.7, 138.9, 138.1, 136.9, 136.2, 133.6, 127.8, 127.5, 126.7, 123.2, 120.3, 118.8, 118.6, 114.8, 80.6, 78.1, 55.1, 51.6, 41.5, 39.1, 36.6, 33.3, 32.9, 28.3, 27.9, 18.9. HMRS: calculated for $C_{40}H_{49}N_2O_8$ $[M+1]^+$ 685.3483 found 685.3474

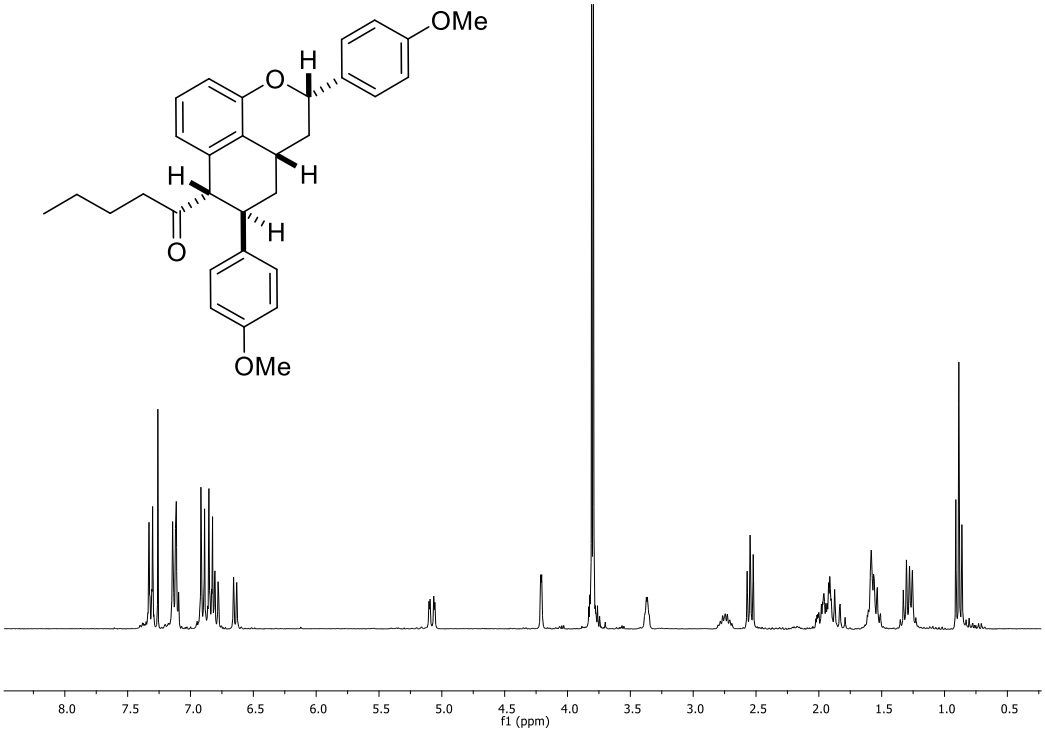
di-tert-butyl [((2*S,3a*S**,5*R**,6*S**)-6-pentanoyl-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromene-2,5-diyl)bis(4,1-phenylene)]dicarbamate (4m)**



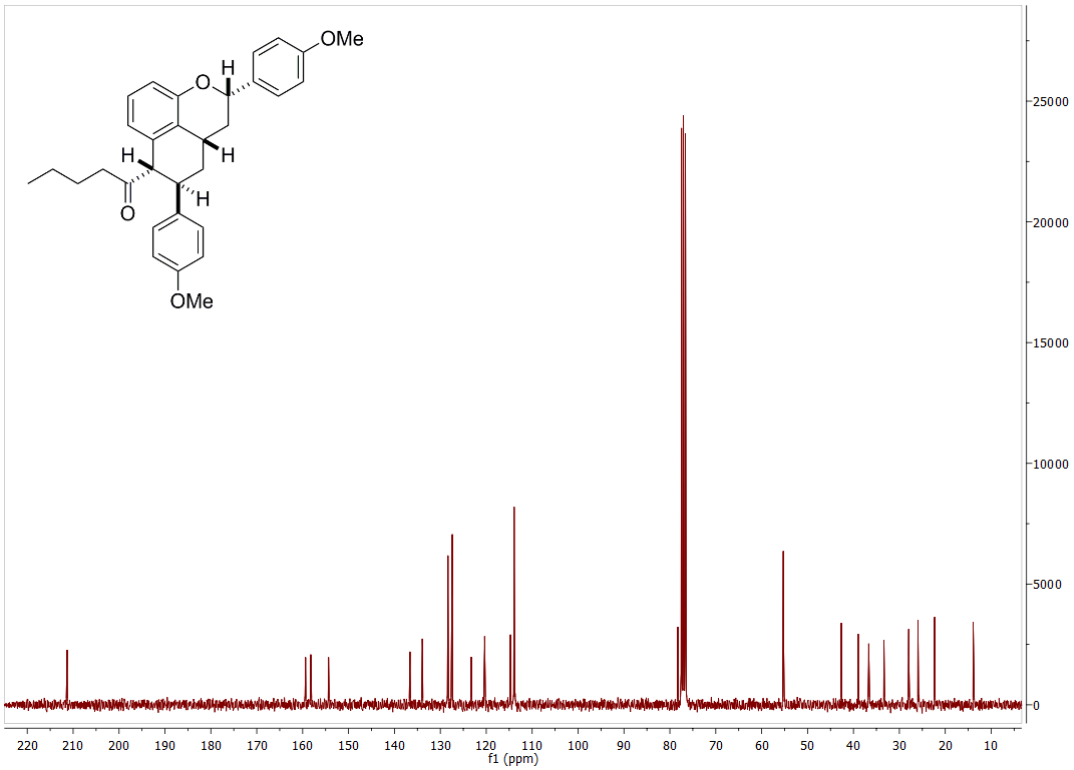
Yellow solid*;* Rf: 0.30 (hexanes/ethyl acetate 3:1)*;* Melting point: 200-202 ºC*;* Yield: 75% ^{1}H RMN (300 MHz, $CDCl_3$) δ (ppm) 7.55 – 7.01 (m, 9H, $H_{7,19,20,27,28,30,31,38,39}$), 6.81 (d, *J* = 8.1 Hz, 1H, H_6), 6.66 (d, *J* = 7.7 Hz, 1H, H_8), 6.55 (s, 2H, NH), 5.08 (d, *J* = 11.2 Hz, 1H, H_1), 4.23 (s, 1H, H_{10}), 3.39 (bs, 1H, H_{16}), 2.83 – 2.66 (m, 1H, H_3), 2.61 – 2.52 (m, 2H, H_{12}), 2.07 – 1.72 (m, 4H, $H_{2,17}$), 1.68 – 1.13 (m, 22H, $H_{13,14,24,25,26,36,37,38}$), 0.90 (t, *J* = 7.2 Hz, 3H, H_{15}). ^{13}C RMN (75 MHz, $CDCl_3$) δ (ppm) 211.4, 154.4, 153.0, 152.9, 139.2, 138.2, 137.0, 136.4, 134.0, 128.0, 127.6, 126.9, 123.4, 120.5, 119.0, 118.7, 114.8, 80.7, 78.3, 55.2, 42.7, 39.2, 36.8, 33.4, 28.5, 28.0, 26.0, 22.4, 14.0. HMRS: calculated for $C_{39}H_{49}N_2O_6$ $[M+1]^+$ 641.3585 found 641.3586

3. NMR spectra

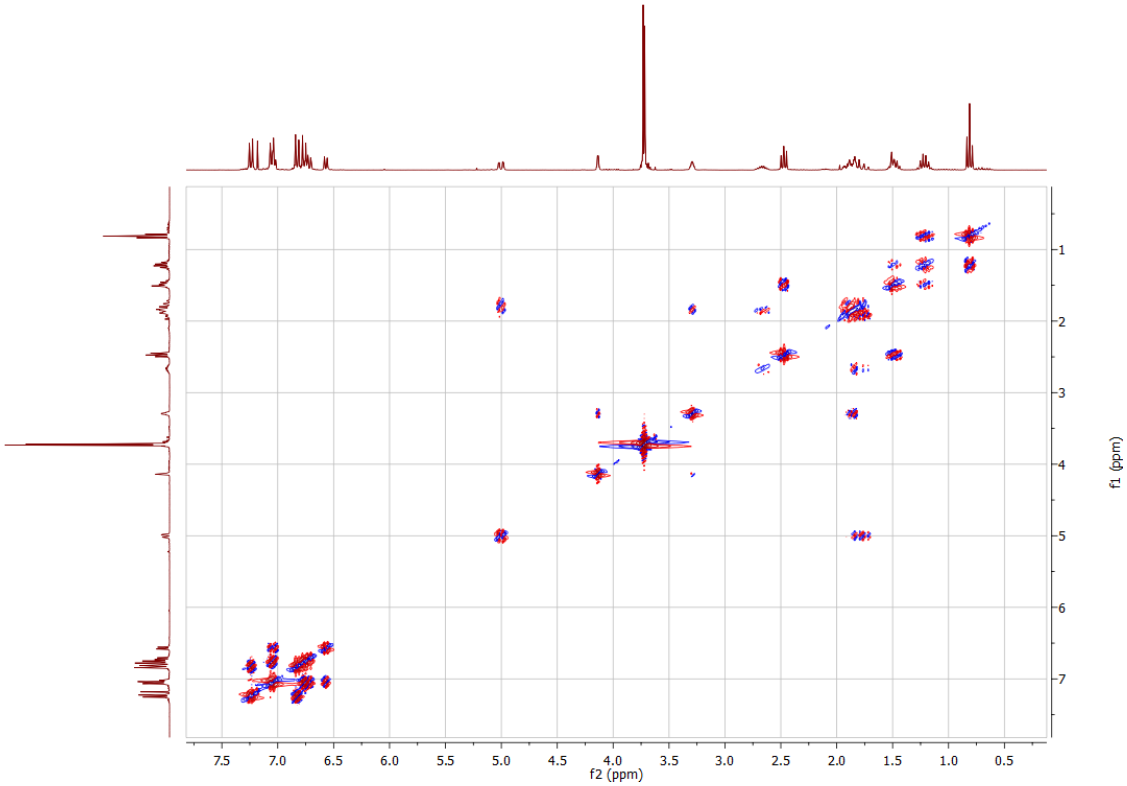
1-[(2*S,3a*S**,5*R**,6*S**)-2,5-Bis(4-methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl]pentan-1-one (4a)**



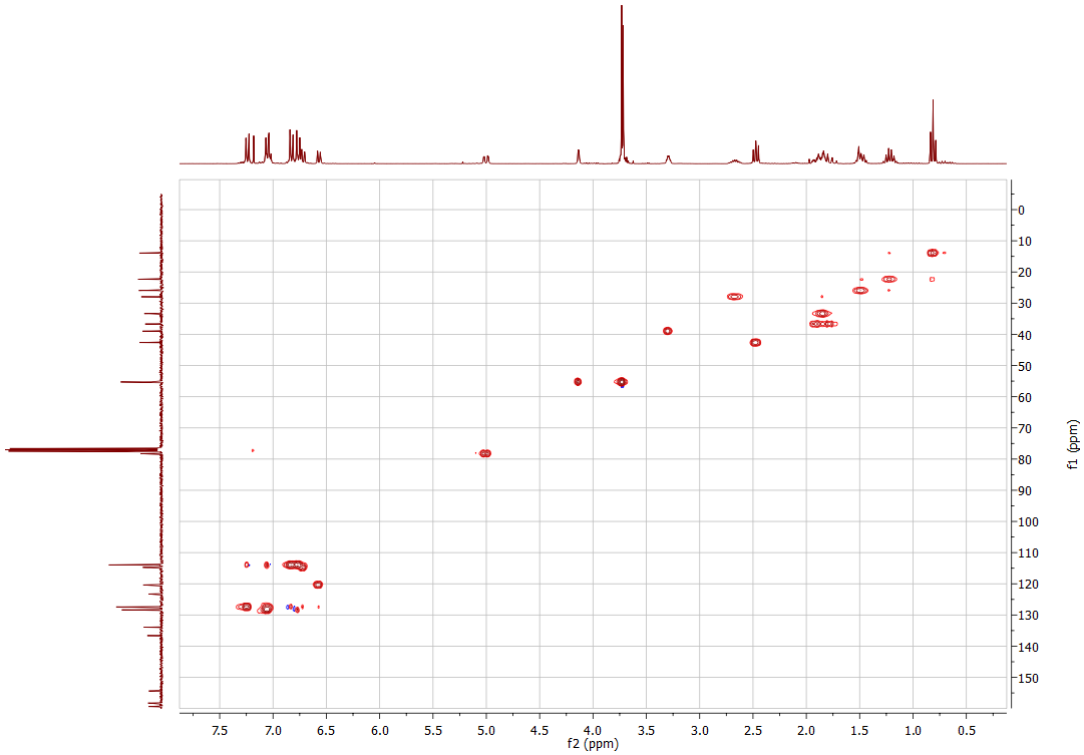
^{1}H-NMR



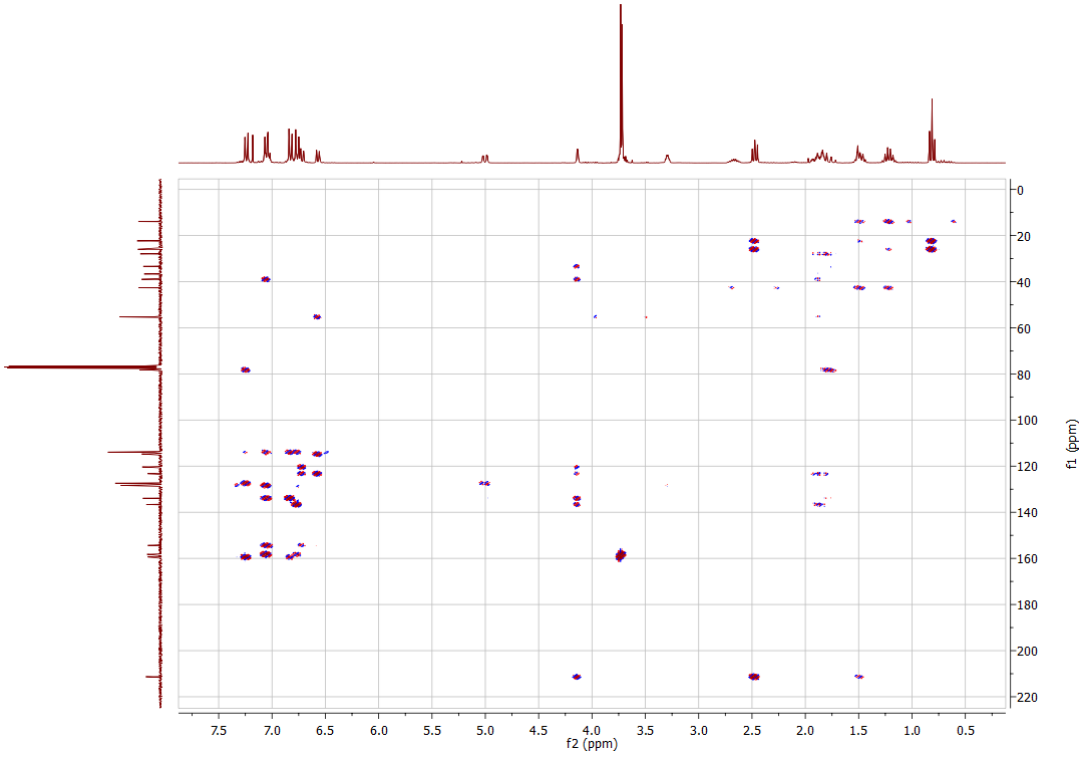
^{13}C-NMR



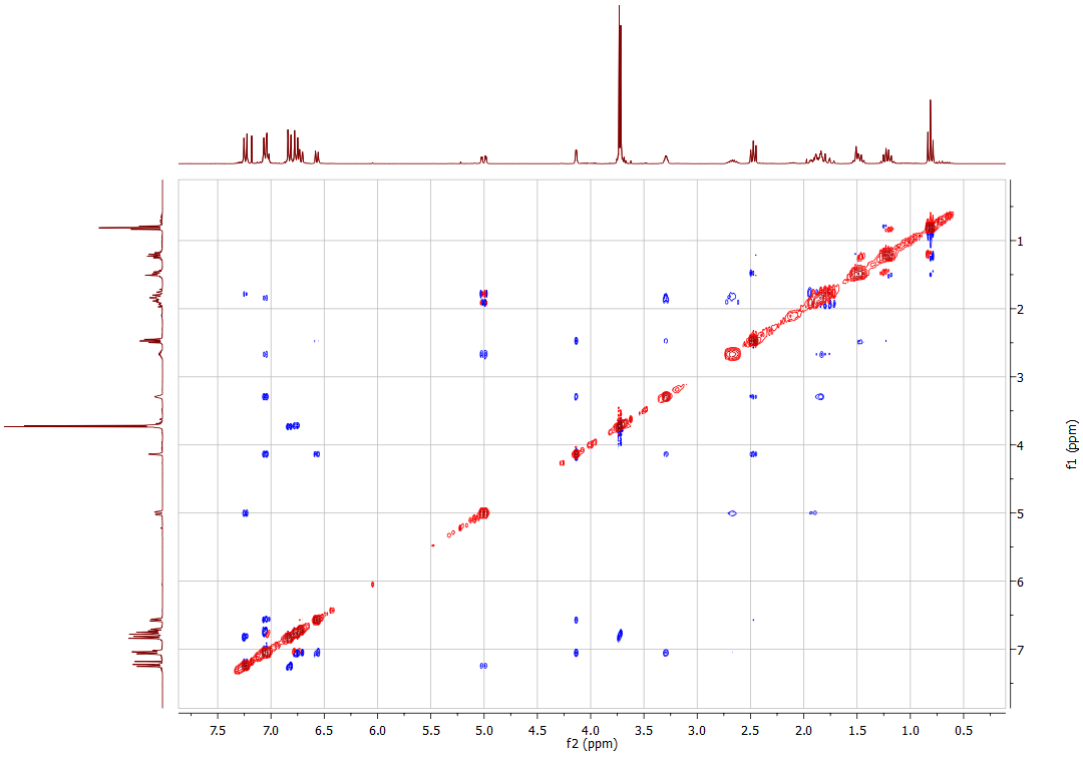
COSY-NMR



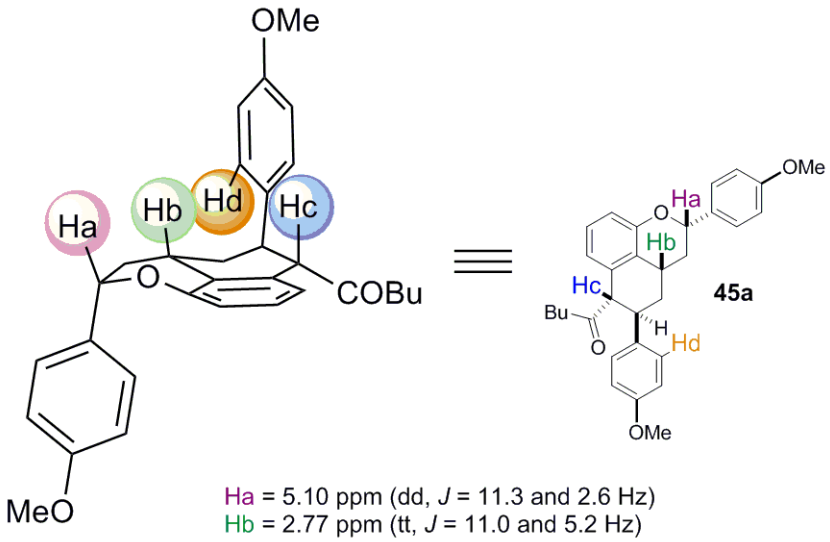
HSQC-NMR



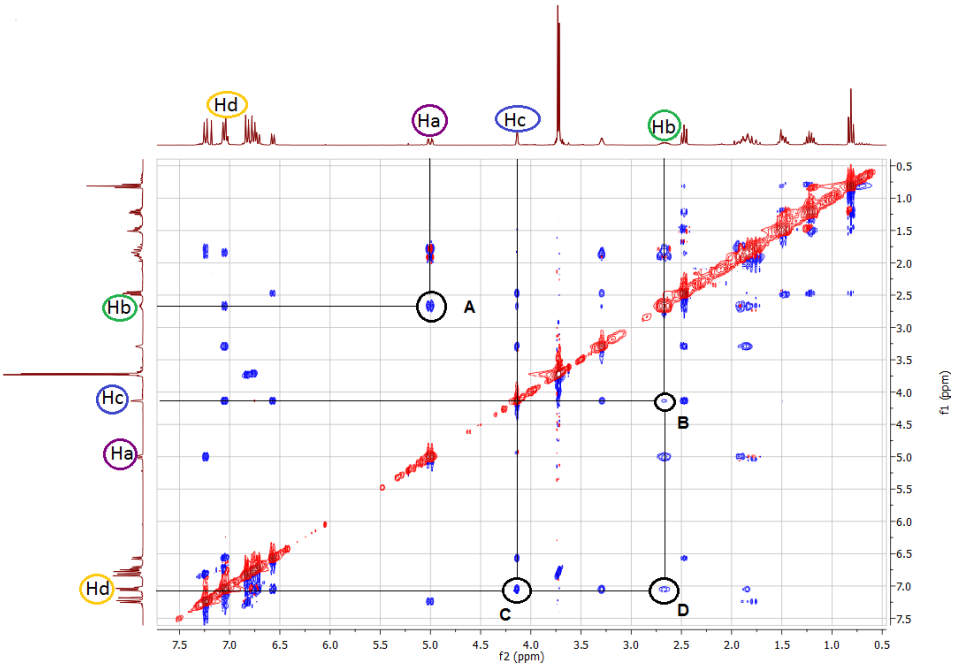
HMBC-NMR



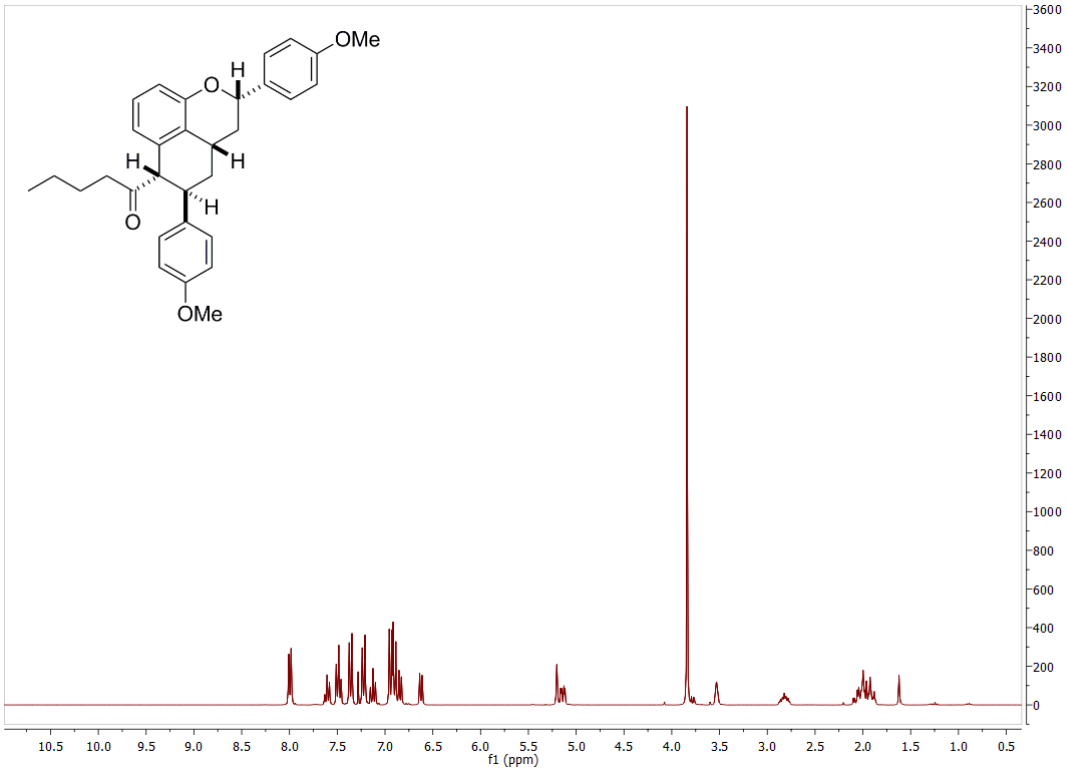
NOESY-NMR



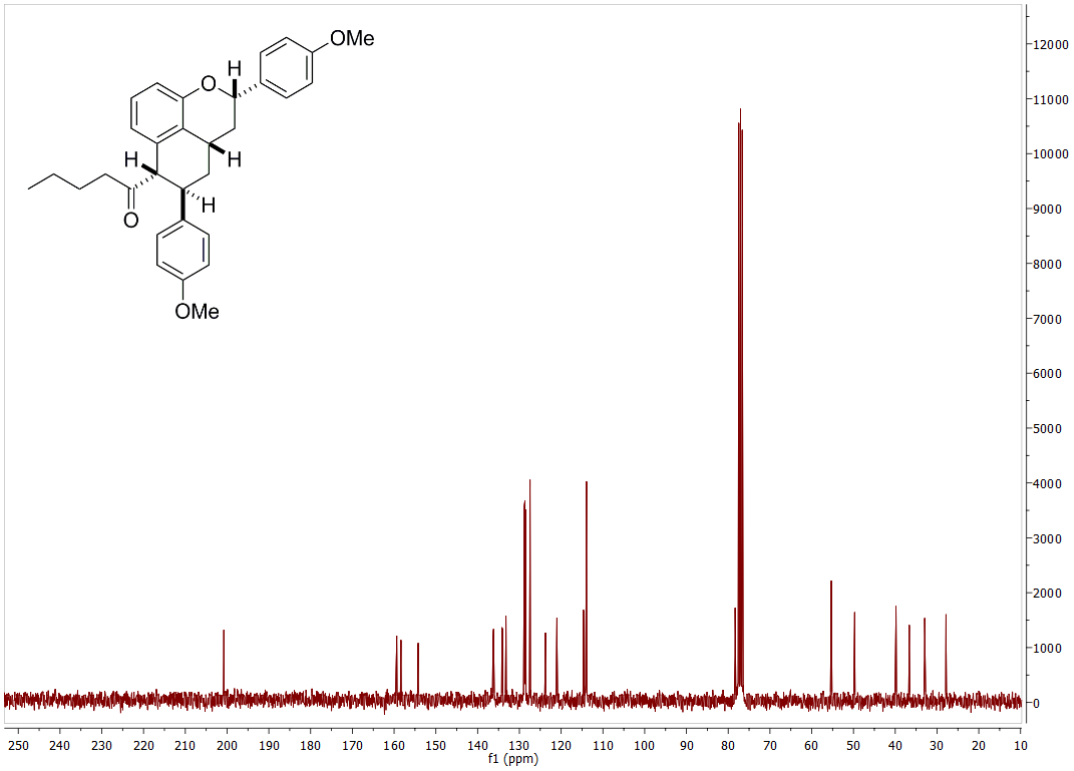
Ha = 5.10 ppm (dd, *J* = 11.3 and 2.6 Hz)
Hb = 2.77 ppm (tt, *J* = 11.0 and 5.2 Hz)
Hc = 4.24 ppm (d, *J* = 2.5 Hz)
Hd = 7.15 ppm (d, *J* = 8.7 Hz)



[(2*S,3a*S**,5*R**,6*S**)-2,5-Bis(4-methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl](phenyl)methanone (4b)**

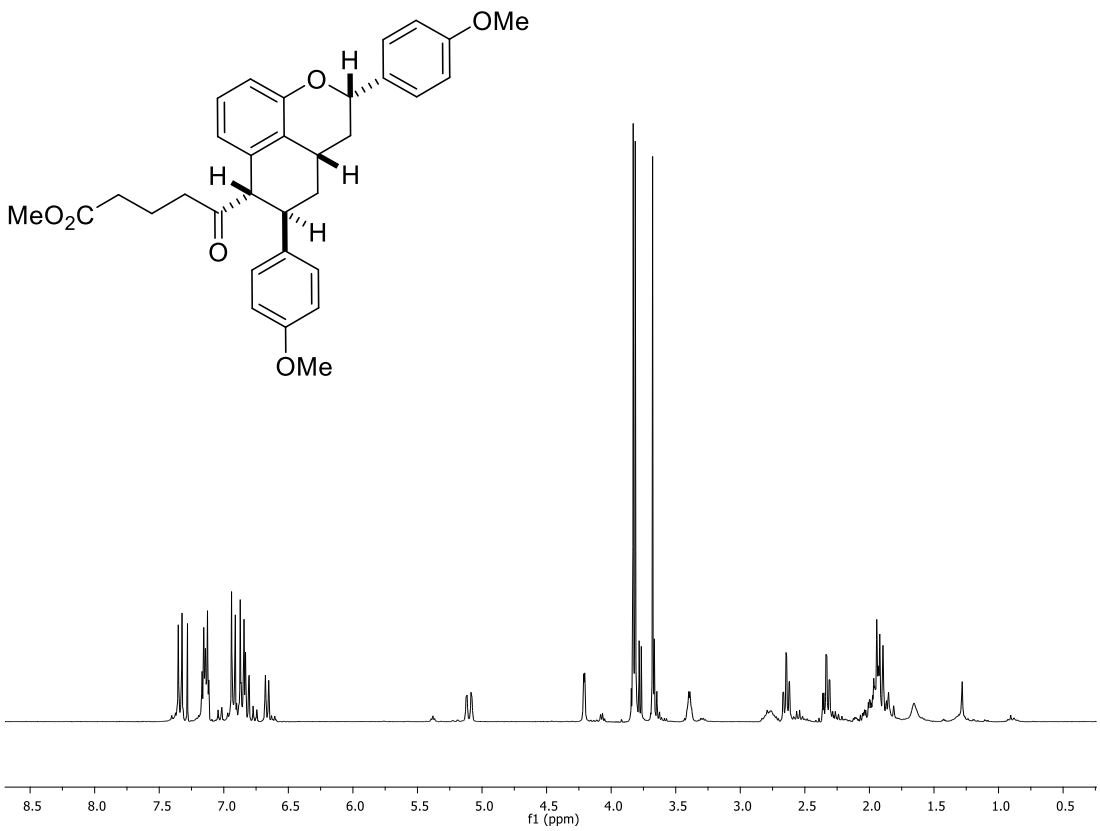


^{1}H-NMR

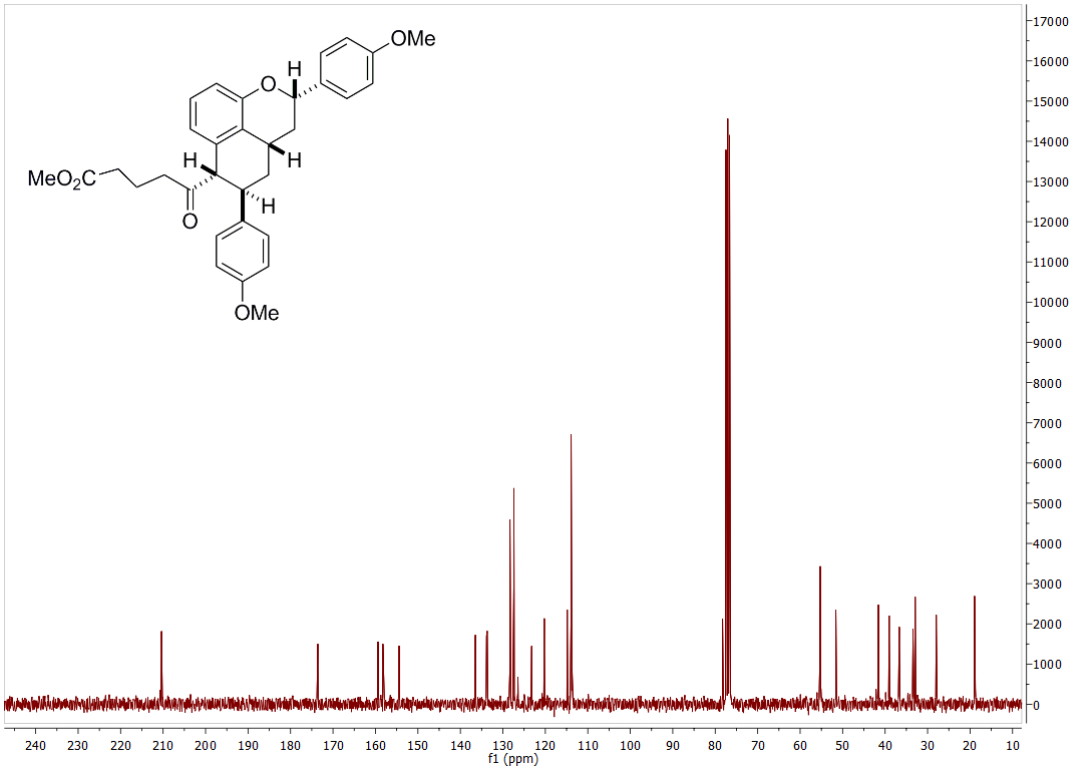


^{13}C-NMR

Methyl 5-[(2*S,3a*S**,5*R**,6*S**)-2,5-bis(4-methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl]-5-oxopentanoate (4c)**

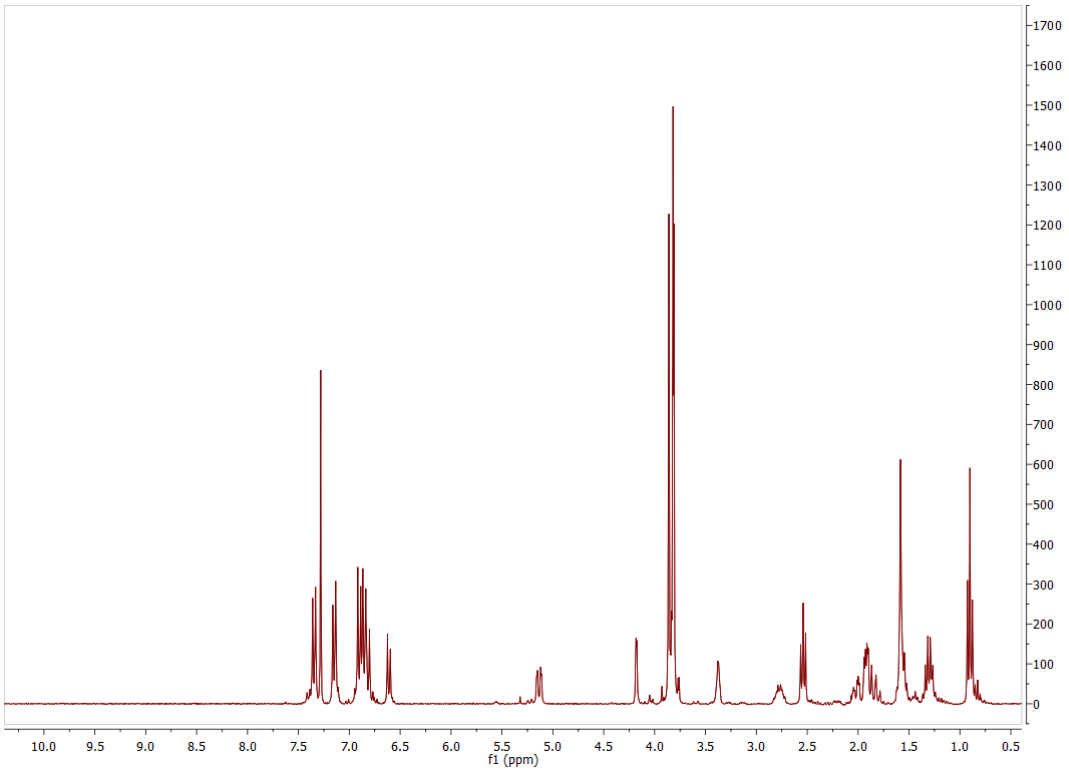


^{1}H-NMR

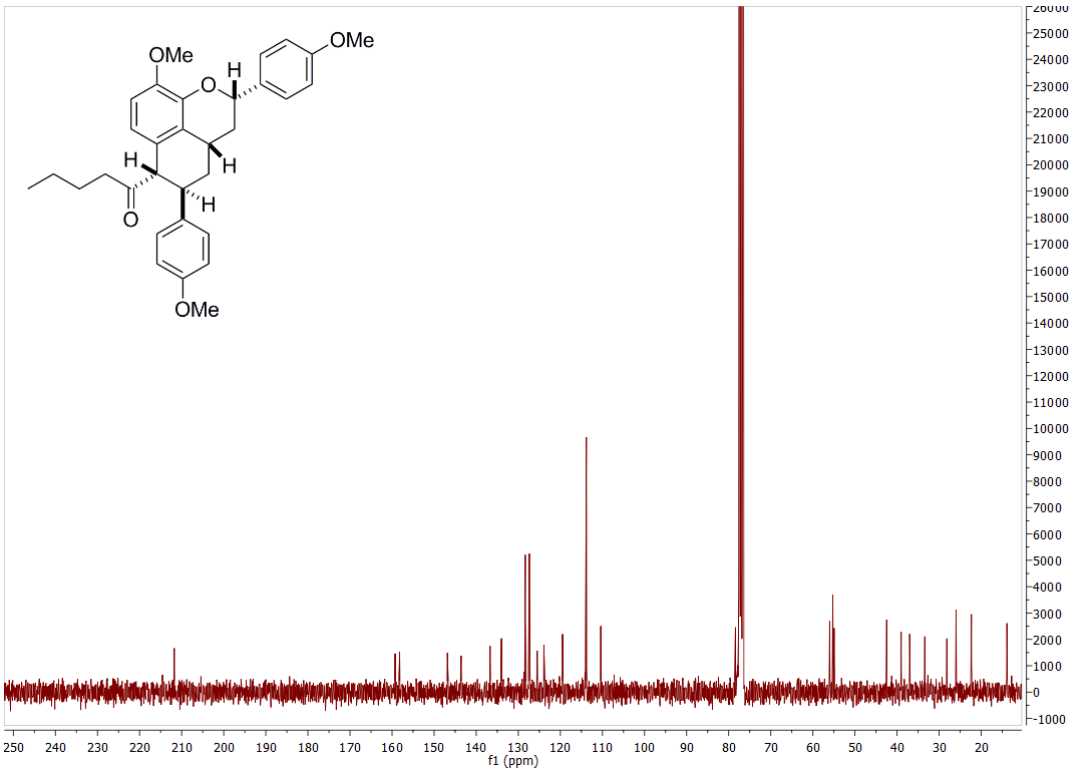


^{13}C-NMR

1-[(2*S,3a*S**,5*R**,6*S**)-9-Methoxy-2,5-bis(4-methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl]pentan-1-one (4d)**

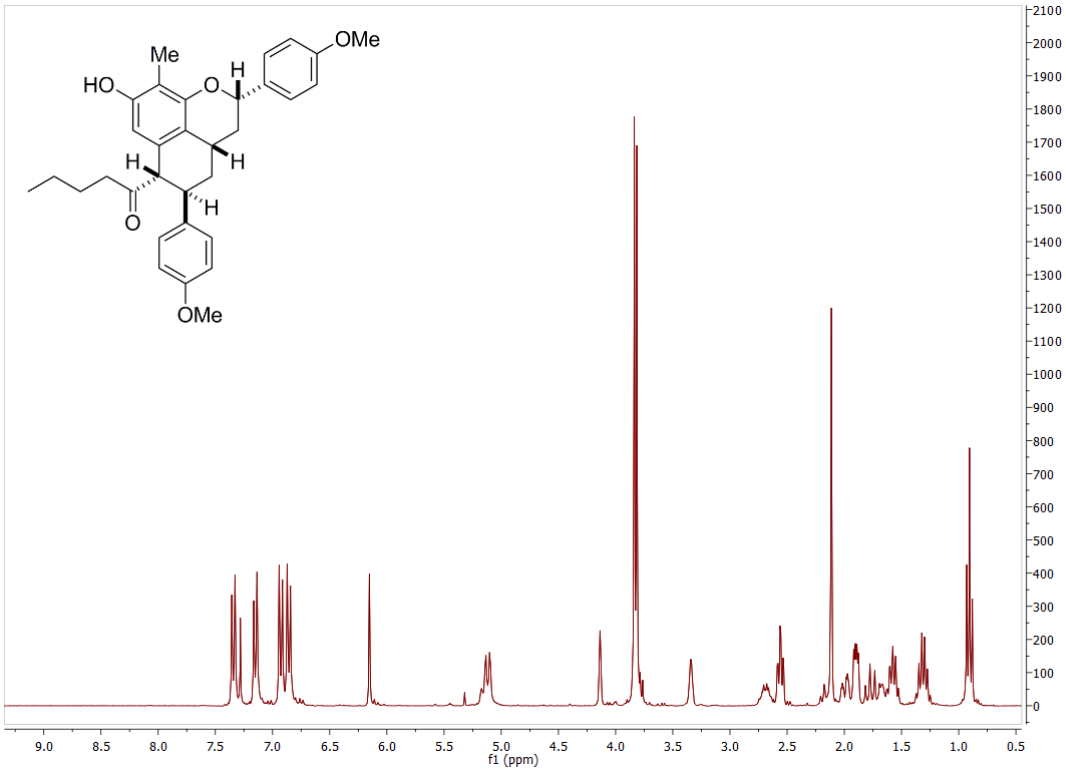


^{1}H-NMR

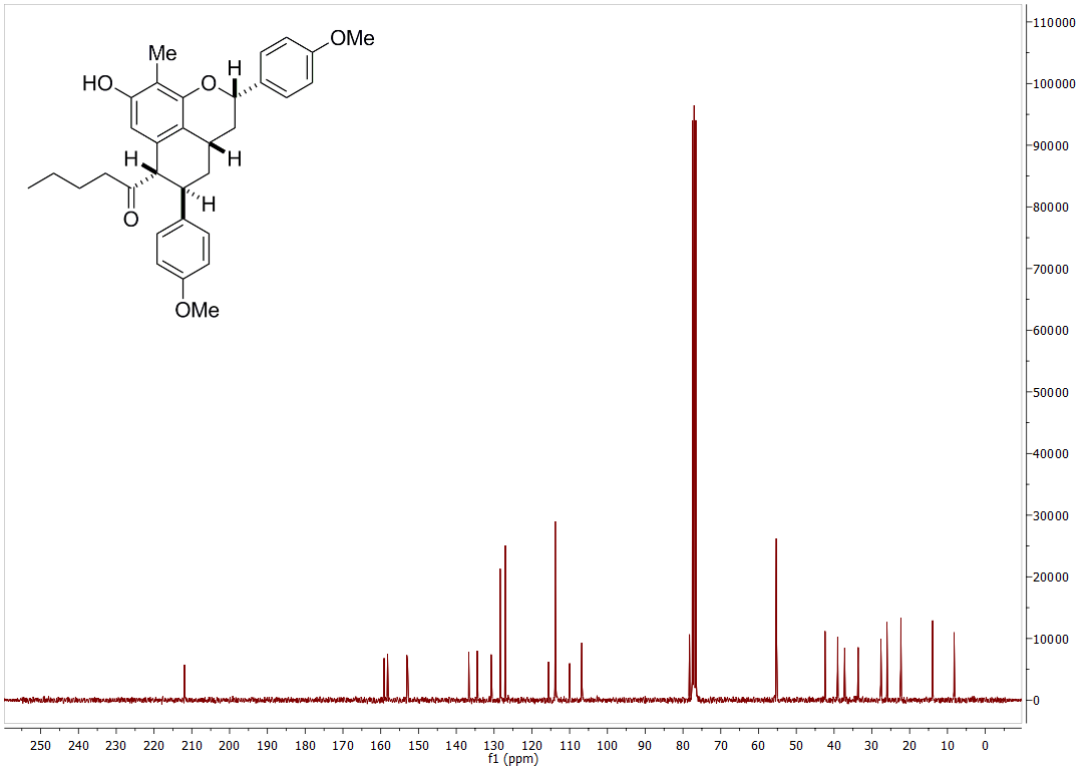


^{13}C-NMR

1-[(2*S,3a*S**,5*R**,6*S**)-8-Hydroxy-2,5-bis(4-methoxyphenyl)-9-methyl-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl]pentan-1-one (4e)**

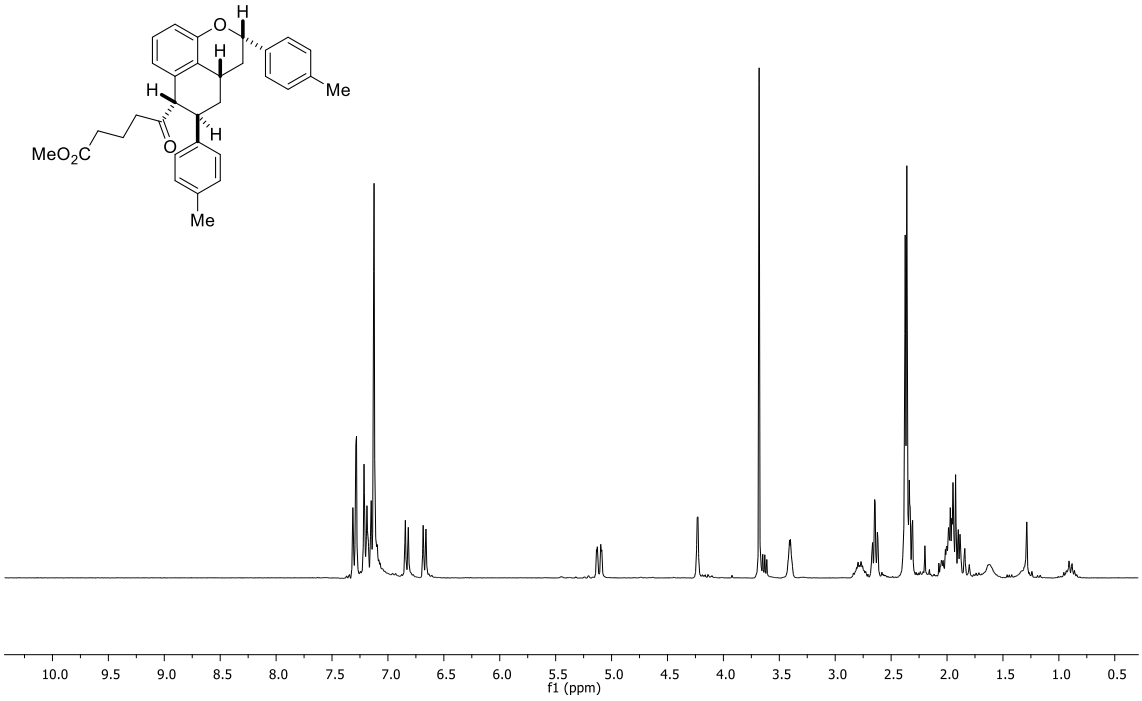


^{1}H-NMR

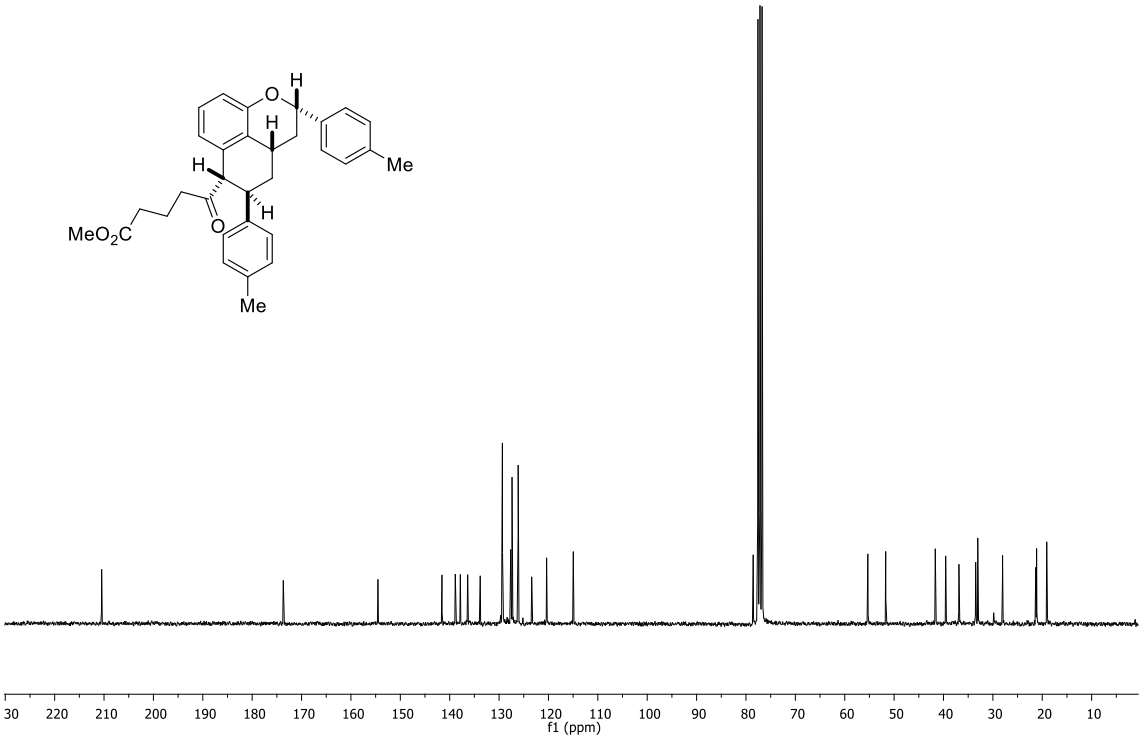


^{13}C-NMR

Methyl 5-[(2S*,3aS*,5R*,6S*)-2,5-bis(4-methylphenyl-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl]-5-oxopentanoate (4f)

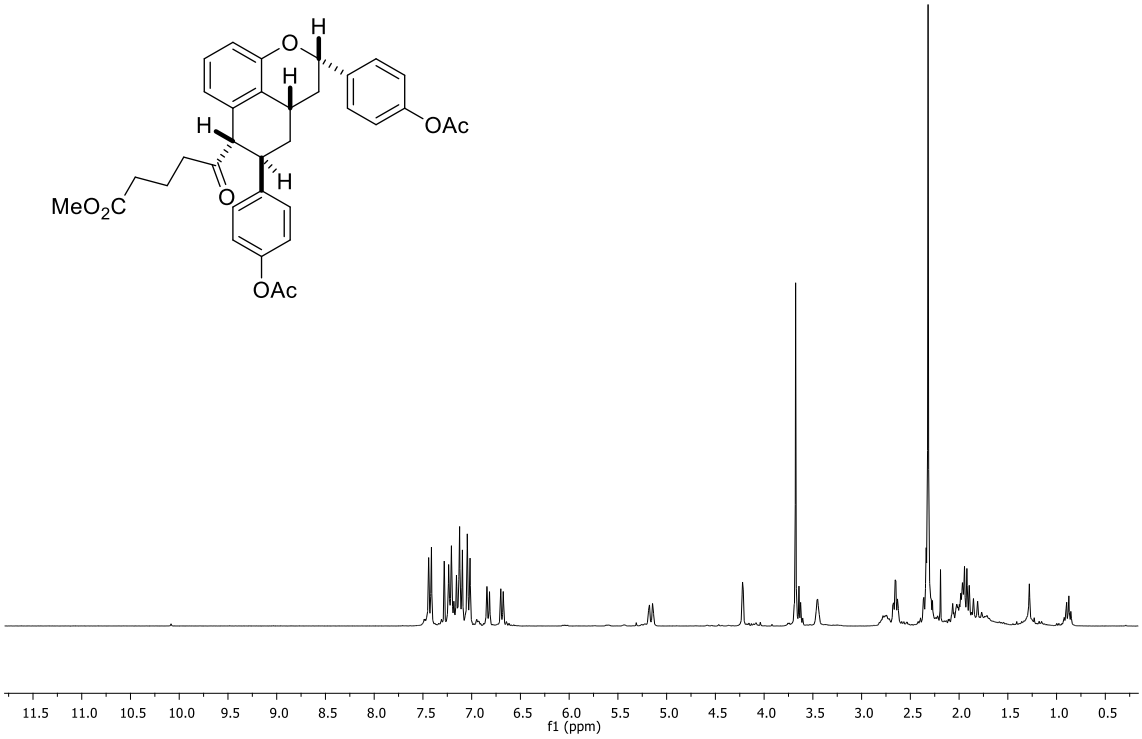


^{1}H-NMR

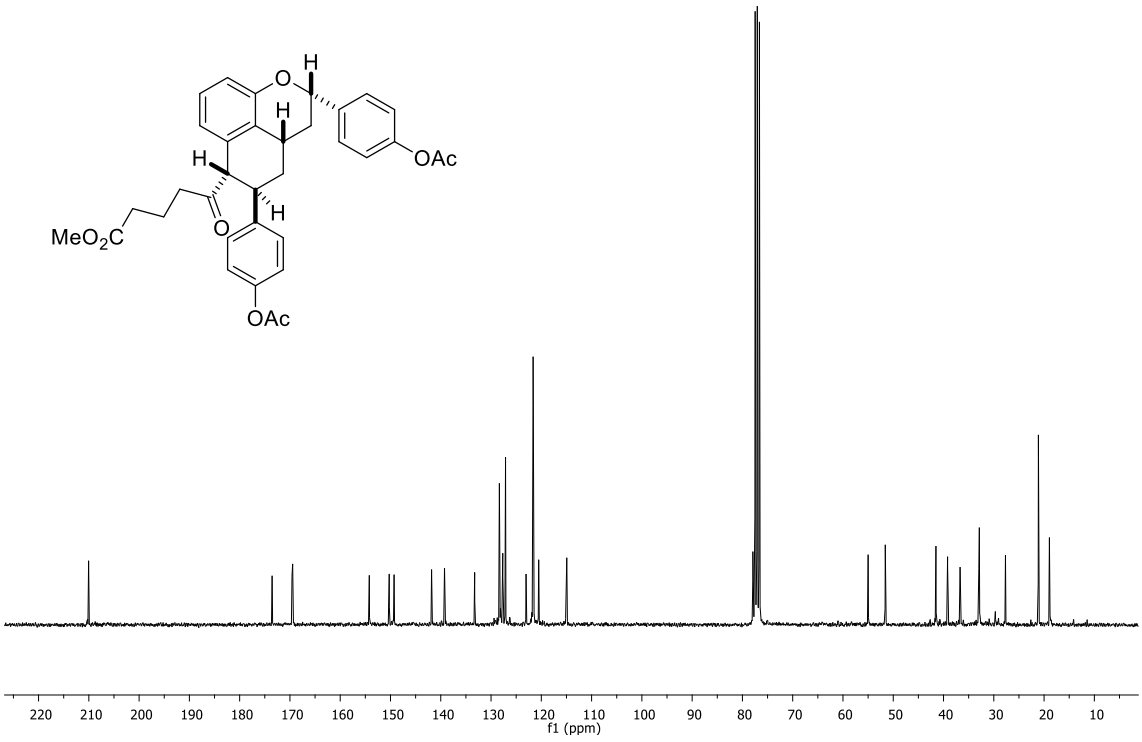


^{13}C-NMR

(2*S,3a*S**,5*R**,6*S**)-6-(5-Methoxy-5-oxopentanoyl)-2,3,3a,4,5,6-hexahydrobenzo[de]chromene-2,5-diyl)bis(4,1-phenylene) diacetate (4g)**

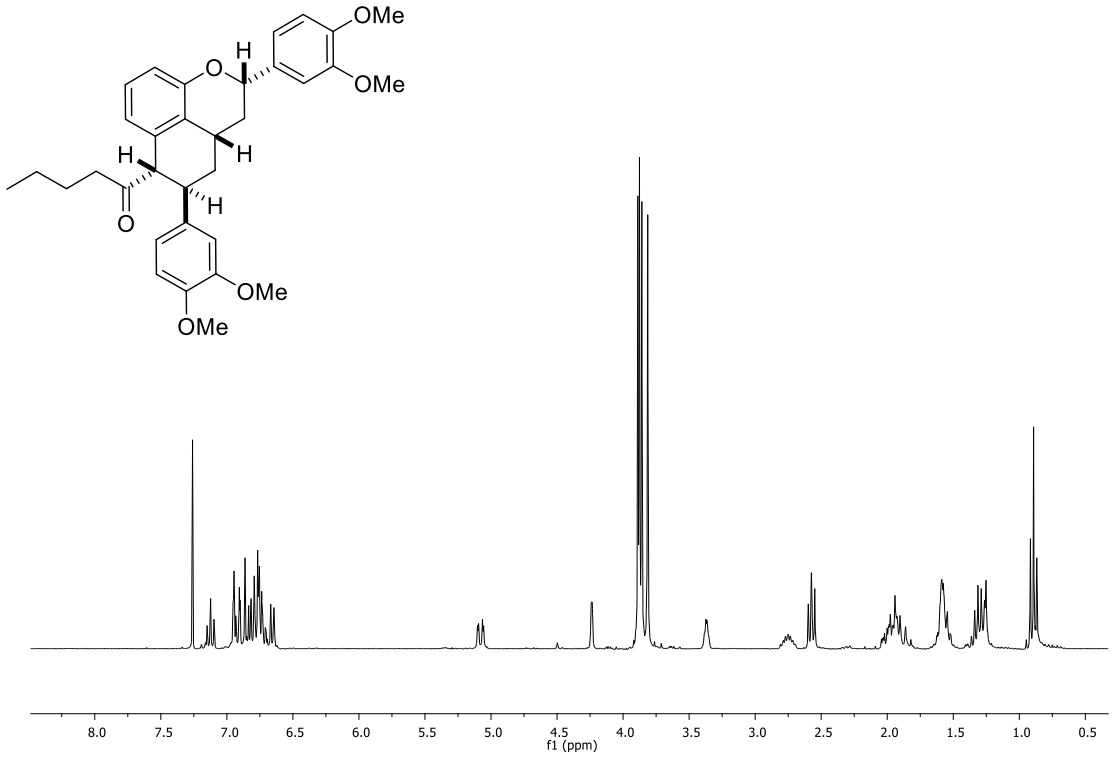


^{1}H-NMR

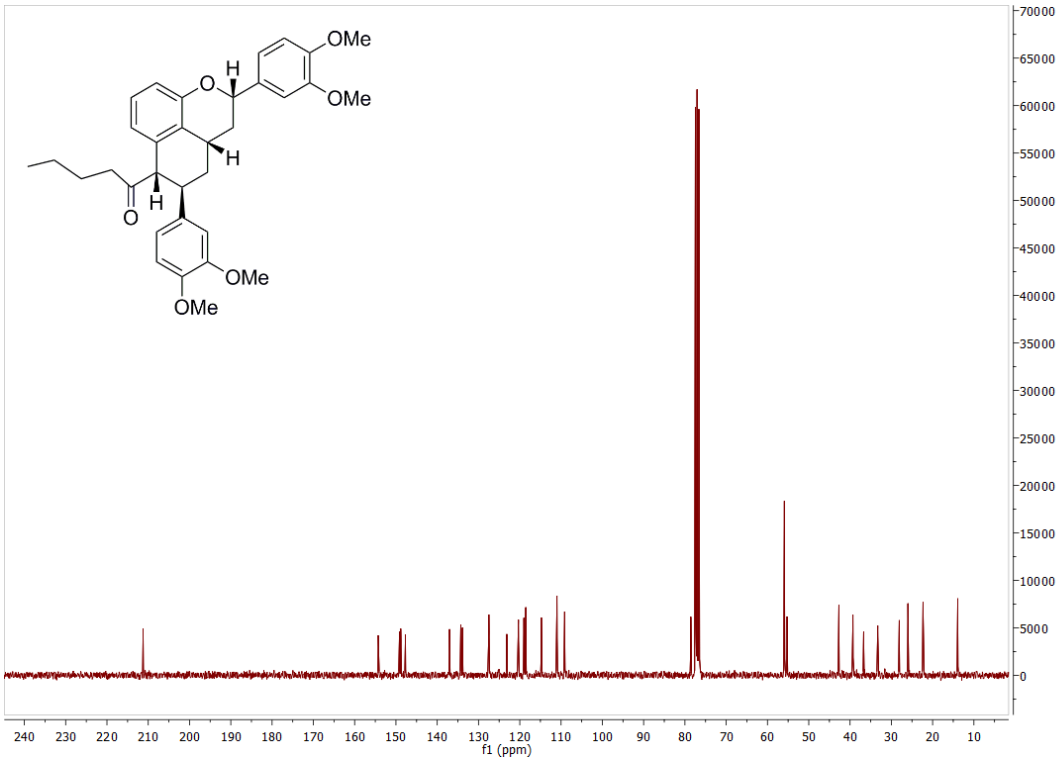


^{13}C-NMR

1-[(2*S,3a*S**,5*R**,6*S**)-2,5-Bis(3,4-dimethoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[de]chromen-6-yl]pentan-1-one (4h)**

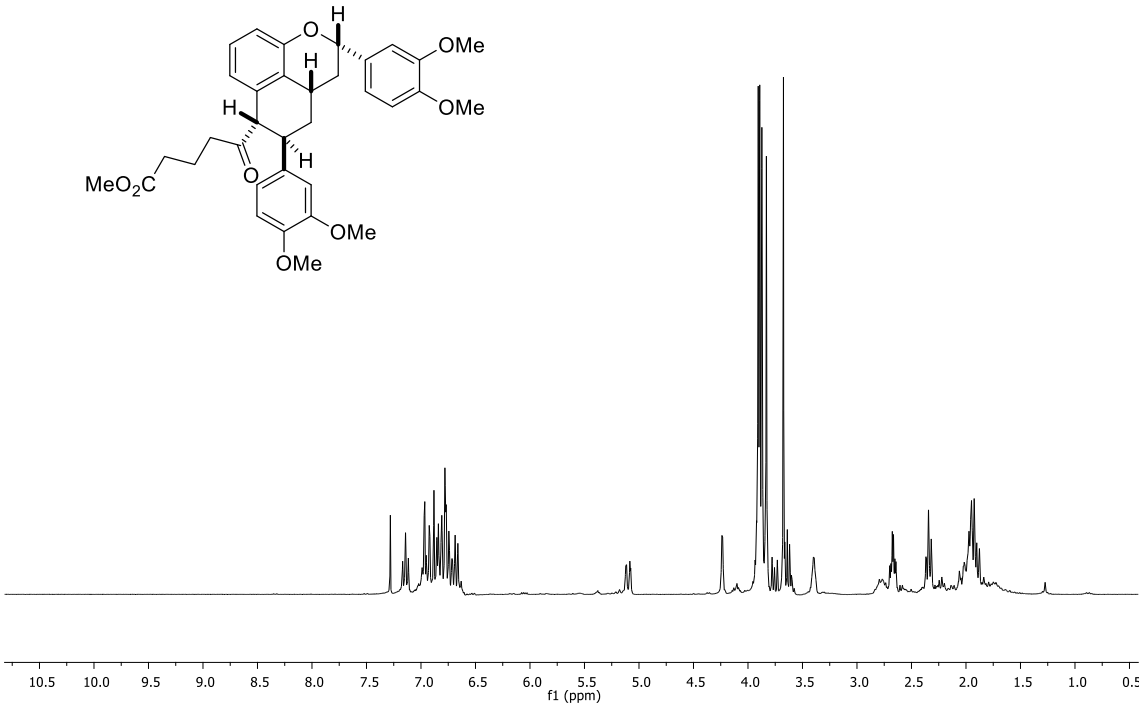


^{1}H-NMR

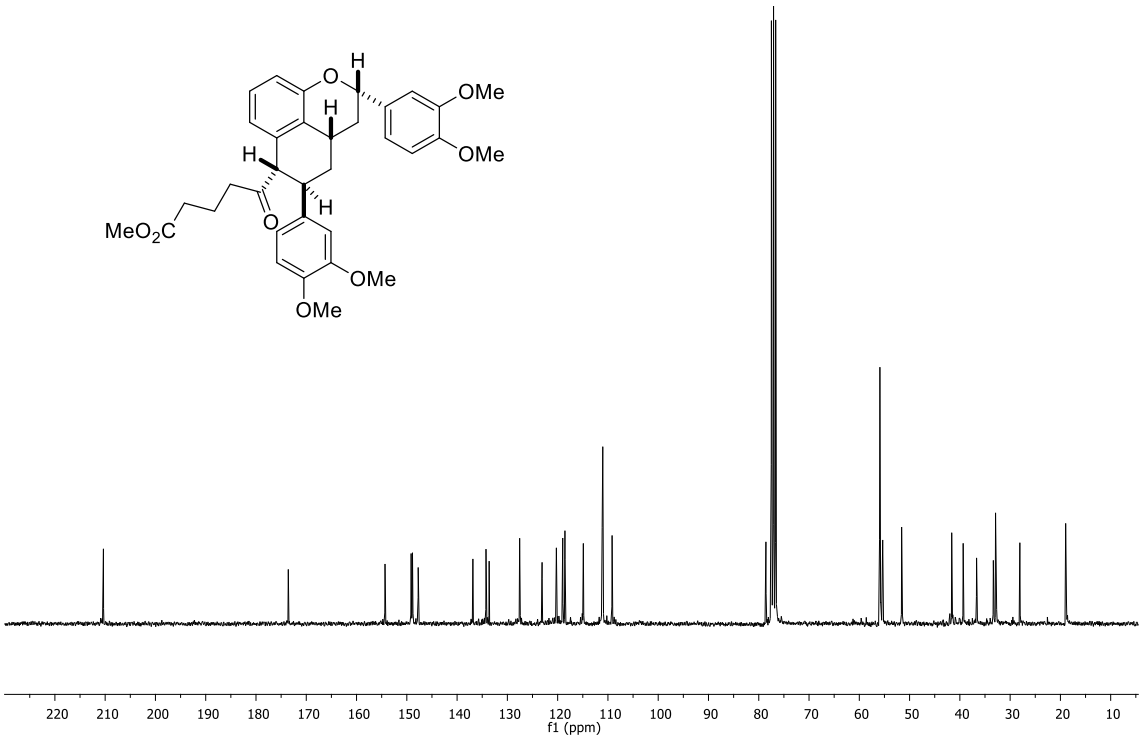


^{13}C-NMR

Methyl 5-[(2S*,3aS*,5R*,6S*)-2,5-bis(3,4-dimethoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl)-5-oxopentanoate (4i)

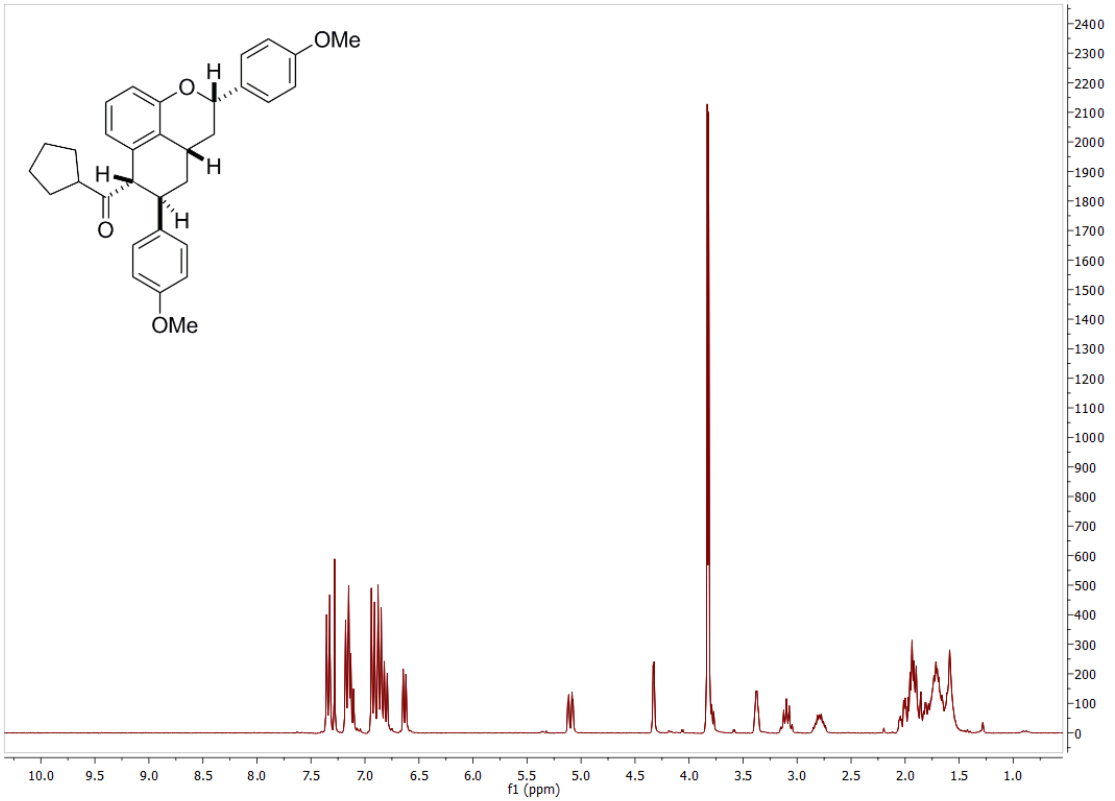


^{1}H-NMR

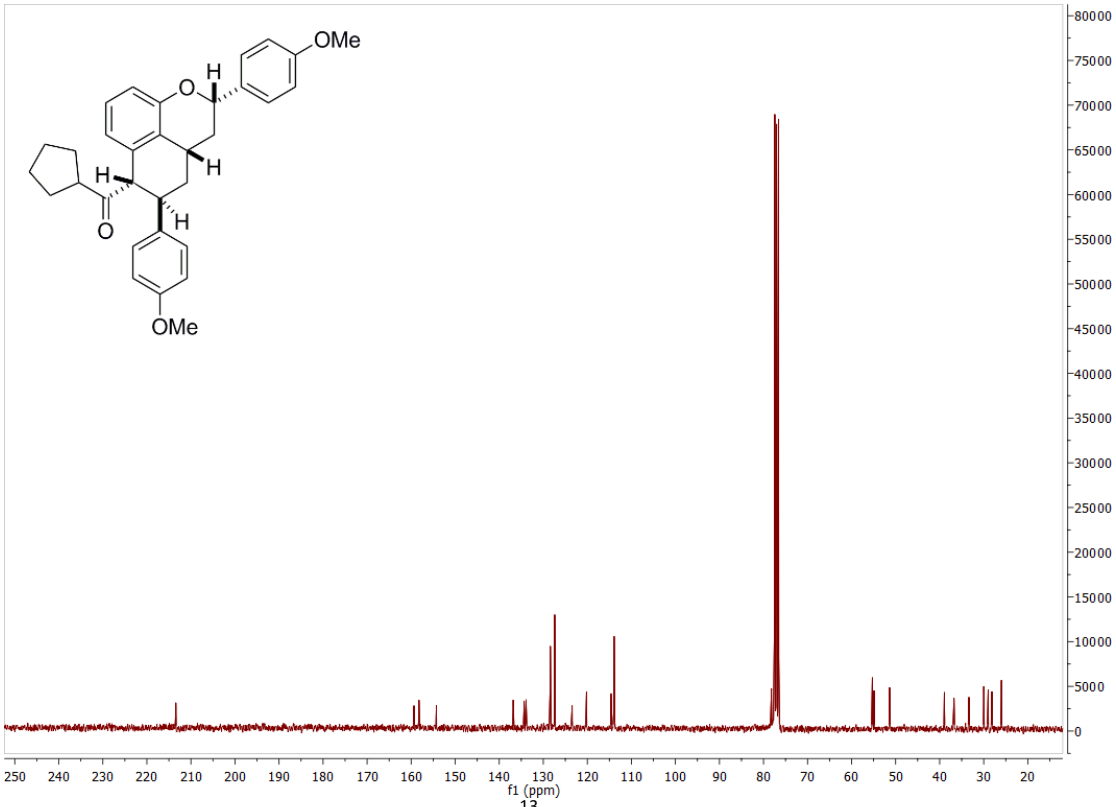


^{13}C-NMR

[(2*S,3a*S**,5*R*,6*S**)-2,5-Bis(4-methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl](cyclopentyl)methanone (4j)**

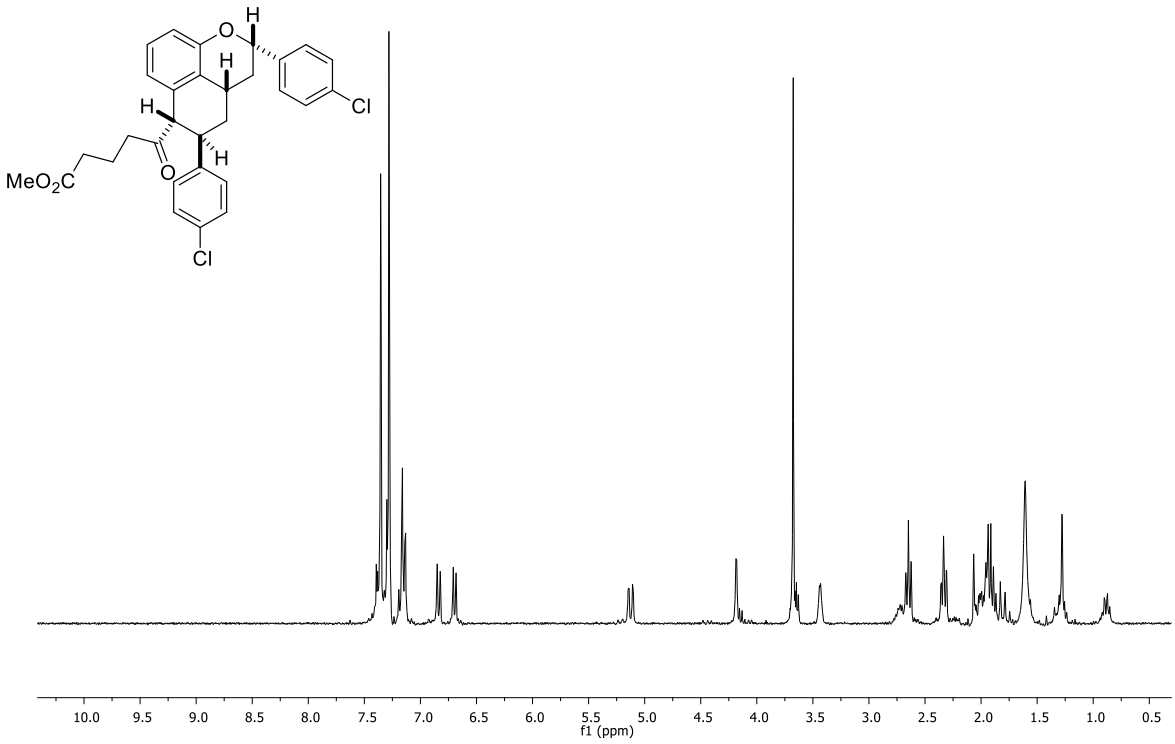


^{1}H-NMR

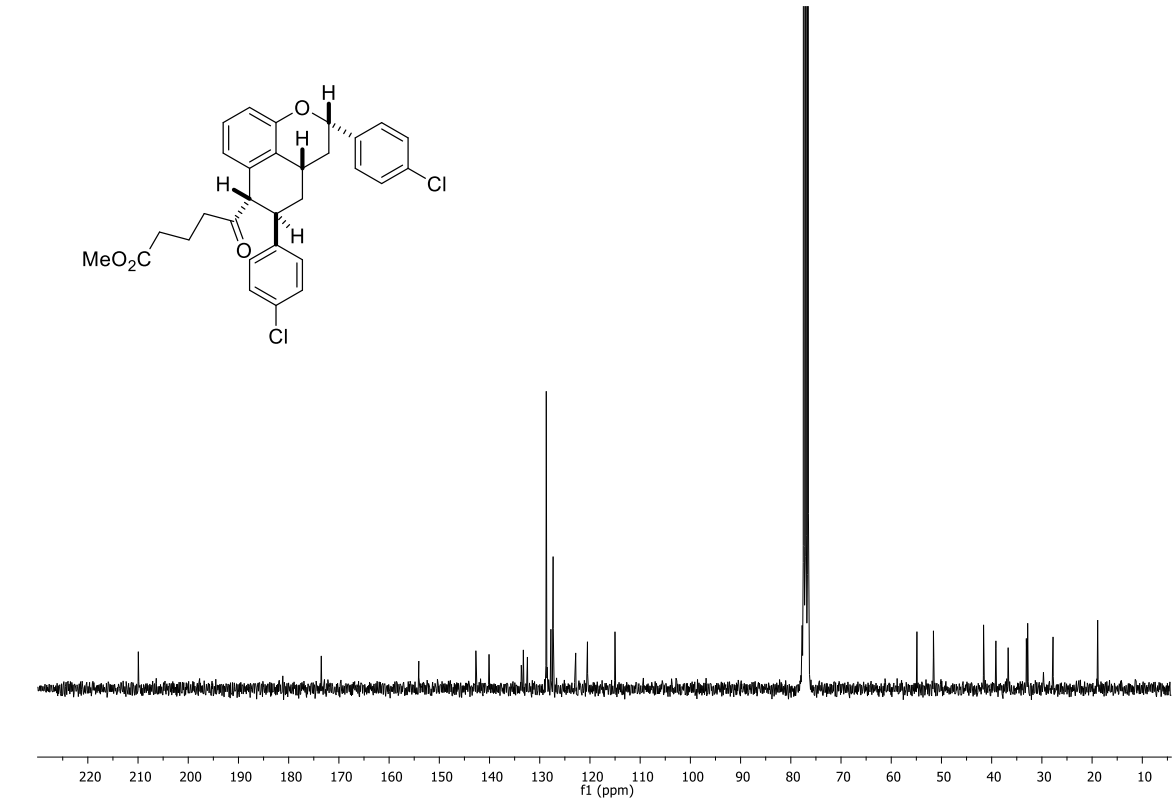


^{13}C-NMR

Methyl 5-[(2S*,3aS*,5R*,6S*)-2,5-bis(4-chlorophenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl)-5-oxopentanoate (4k)

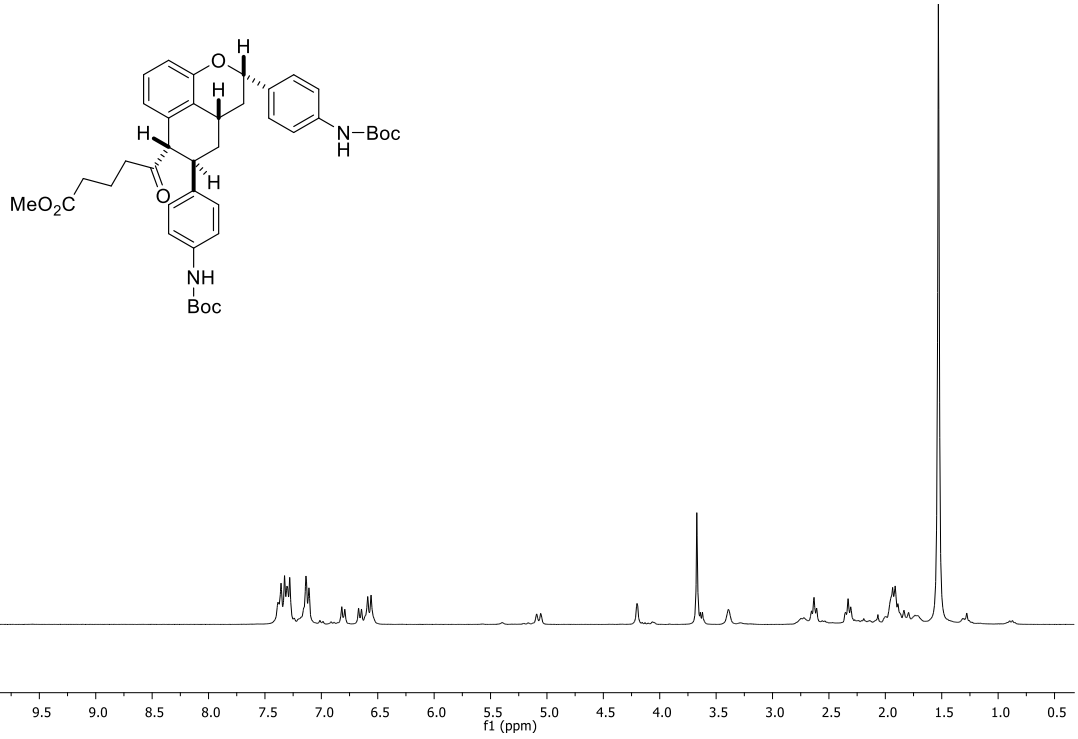


^{1}H-NMR

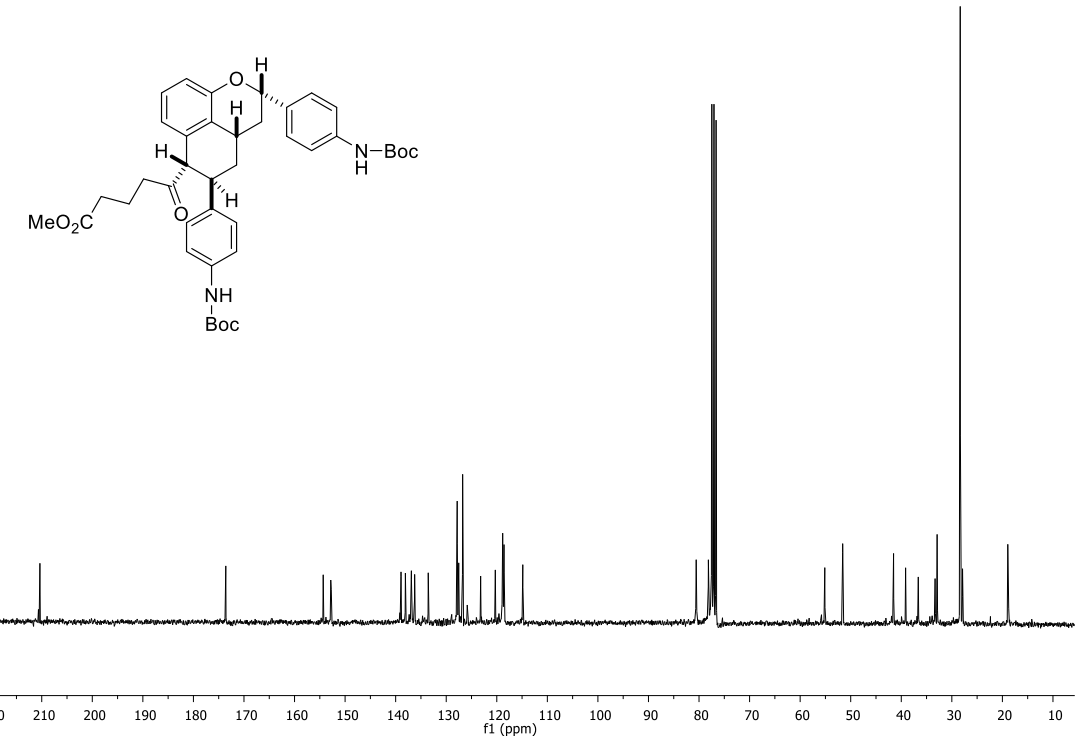


^{13}C-NMR

Methyl 5-[(2S*,3aS*,5R*,6S*)-2,5-bis(4-((tert-butoxycarbonyl)amino)phenyl)-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromen-6-yl)-5-oxopentanoate (4l)

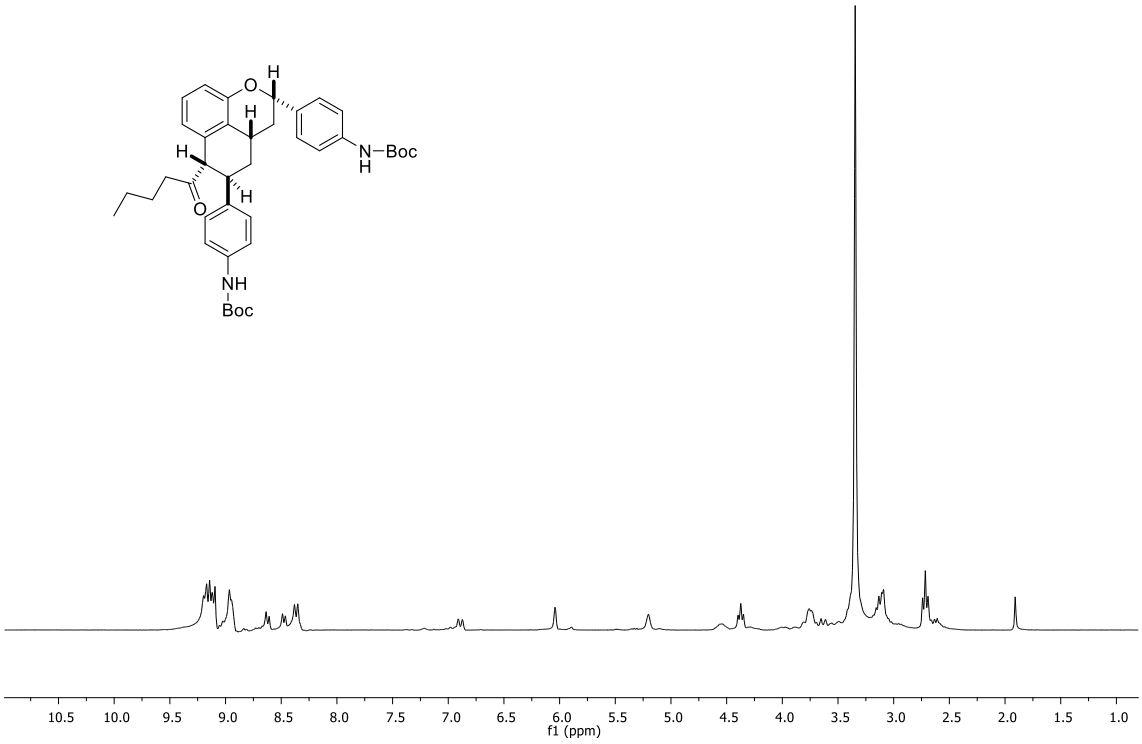


^{1}H-NMR

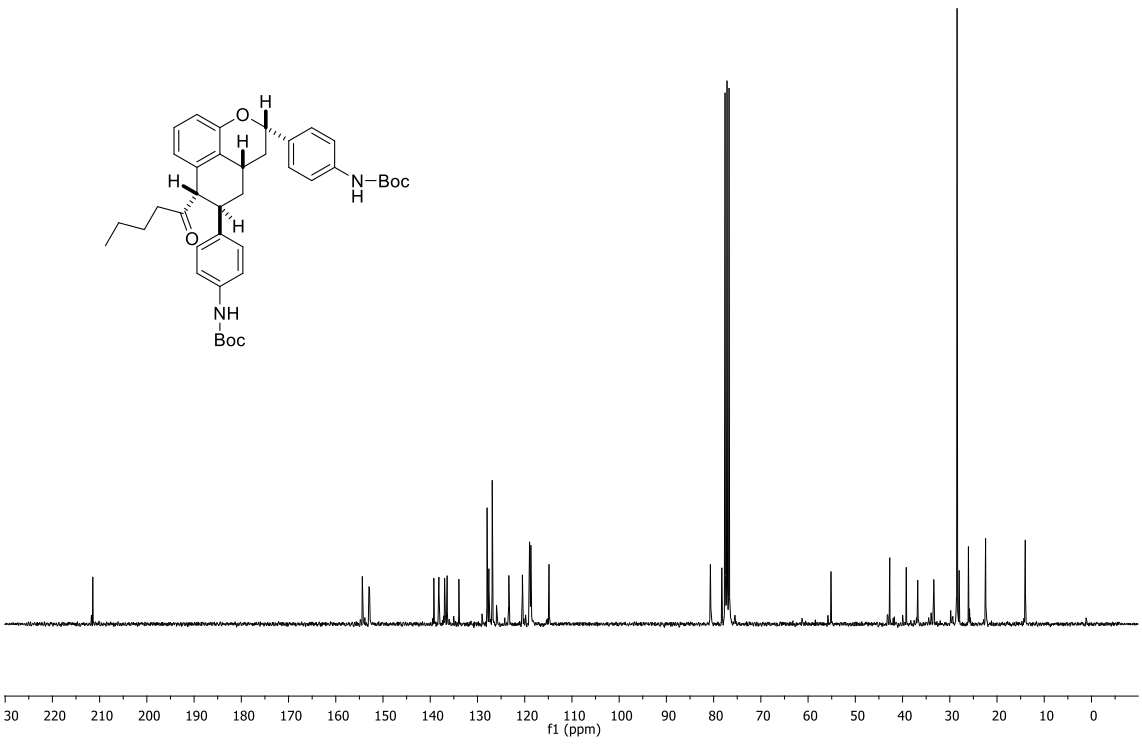


^{13}C-NMR

Di-*tert*-butyl [((2S*,3aS*,5R*,6S*)-6-pentanoyl-2,3,3a,4,5,6-hexahydrobenzo[*de*]chromene-2,5-diyl)bis(4,1-phenylene)]dicarbamate (4m)



^{1}H-NMR



^{13}C-NMR