Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Supporting Information

Diels-Alder cycloaddition of o-quinonedimethides and alkylidène-5H-furan-2-ones: New and rapid access to lambertellol cores and arthrinone derivatives.

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General Experimental Methods.

All reactions sensitive to oxygen and moisture were carried out in oven-dried glassware under a slight positive pressure of argon unless otherwise noted.

^{1}H NMR and ^{13}C NMR spectra were recorded on a AC300, AC400 or AC500 using the deuterated solvent as internal deuterium lock. Chemical shift data are given in units δ relative to residual protic solvents where δ (chloroform) = 7.26 ppm and δ (benzene) = 7.16 ppm. The multiplicity of a signal is indicated as: br - broad, s - singlet, d - doublet, t - triplet, q - quartet, m - multiplet, dd - doublet of doublets, dt - doublet of triplets, etc. Coupling constants (J) are quoted in Hz and recorded to the nearest 0.1 Hz. ^{13}C NMR Spectra were recorded on a AC300, AC400 or AC500 spectrometer using the deuterated solvents as internal deuterium lock. Chemical shift data are given in units δ relative to residual protic solvents where δ (chloroform) = 77.16 ppm, δ (benzene) = 128.06 ppm and δ (acetonitrile) = 1.32 ppm. NMR Spectra were assigned using information ascertained from DEPT, HMQC and NOE experiments.

Reagents and solventss were commercial grades and were used as supplied. Benzene was distilled from calcium hydride and stored over molecular sieves 4 Å. Commercially available C_6D_6 was used without further purification.

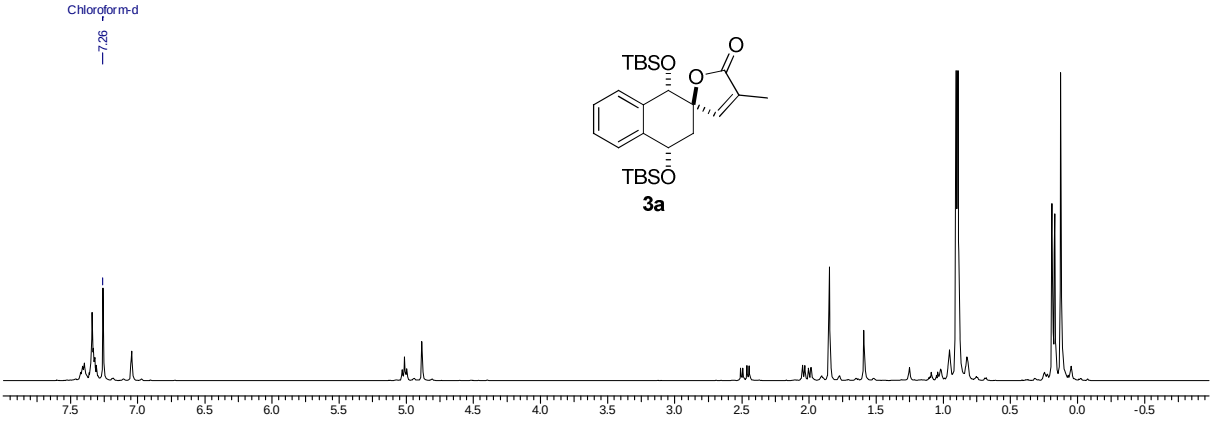
Mass spectra (MS) were performed with a triple quadrupole system with a pneumatically assisted electrospray interface. High resolution mass spectra (HRMS) have been performed using a mass spectrometer equipped with a pneumatically assisted atmospheric pressure ionization. The sample was ionized in positive mode electrospray in the following conditions: electrospray voltage (ISV): 5500 V; orifice voltage (OR): 70 V; nebulising gas flow pressure (air): 0.6 psi. The mass spectrum was obtained using a time of flight analyzer (TOF). The measure was realized in triplicate. The sample was dissolved in methanol (500 μL) then diluted (dilution factor 4/10000) in a methanolic solution of ammonium acetate (3 mM). The sample solution was infused in the ionization source at a 5 μL/min flow rate.

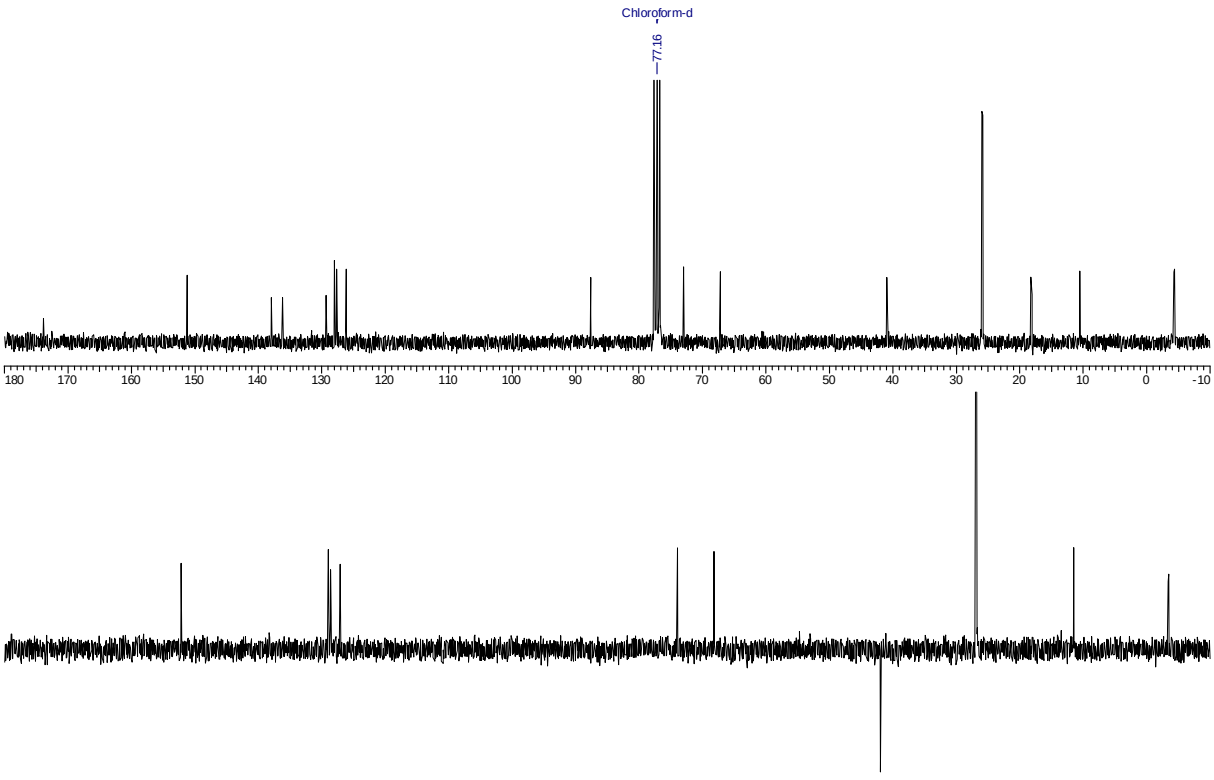
Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F254. Flash column chromatography was performed on Merck Kieselgel 60 (230–400 mesh).

Infrared spectra were recorded on a Bruker VERTEX70 Fourier transform infrared spectrometer equipped with a single reflection diamond ATR Bruker A222 accessory. The measurements were done for pure samples. For each individual spectrum, about 30 scans were averaged at 4 cm^{-1} resolution. The diamond crystal without sample served as reference. All the system was purged with dry air. The identification of peaks was done with the standard method proposed in OPUS 6.0 software.

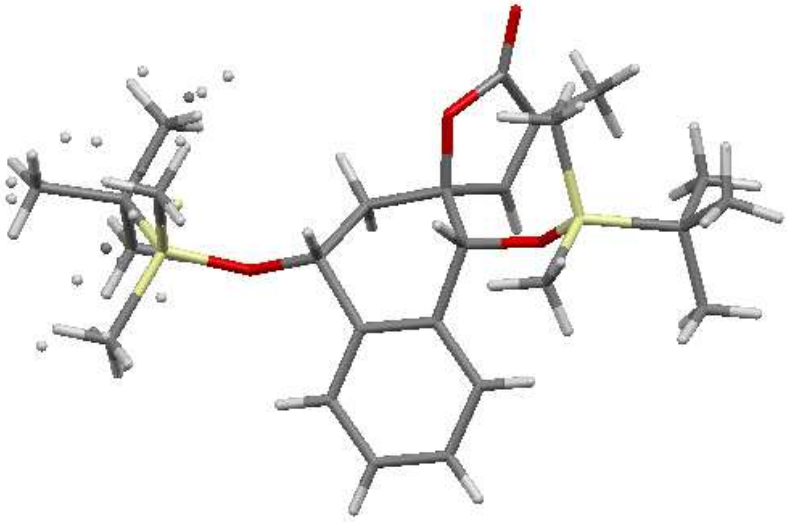
Melting point were performed with Buchï Melting Point B-540

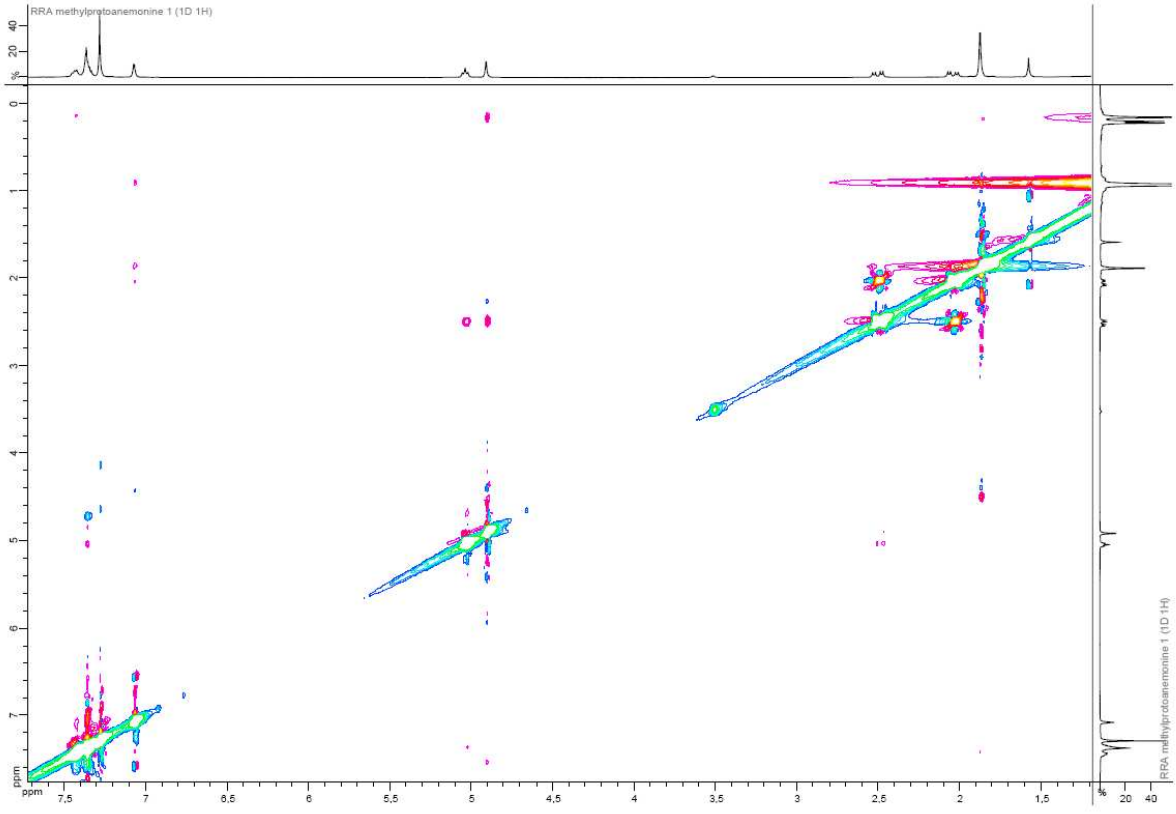
(1'*S*,2*R*,4'*S*)- and (1'*R*,2*S*,4'*R*)-1',4'-bis(tert-butyldimethylsilyloxy)-3-methyl-3',4'-dihydro-1'*H*,5*H*-spiro[furan-2,2'-naphthalen]-5-one (3a). In a oven-dried Schlenk tube, *trans*-1,2-bis(*tert*-butyldimethylsilyloxy)-1,2-benzocyclobutene **1** (460 mg, 1.26 mmol) and butenolide **2a** (166 mg, 1.51 mmol, 1.2 equiv) were dissolved in benzene-D6 (3.2 mL). The solution was degassed for 10 min at -80°C three times. The mixture was then heated at 50°C. The reaction was followed by ^{1}H NMR and after disappearance of **1** (4 hours), the solvents was removed under vacuum. The crude product was purified by flash chromatography (9:1 petroleum ether:ether) to give **3a** (524 mg) in 87% yield . **Mp** = 160 °C; **^{1}H NMR** (300MHz, $CDCl_3$) δ 7.43-7.40 (1H, m, CH_{Ar}), 7.37-7.31 (3H, m, 3 x CH_{Ar}), 7.05 (1H, br q, J = 1.5 Hz, CH), 5.01 (1H, t, J = 5.1 Hz, CH), 4.89 (1H, s, CH), 2.48 (1H, dd, J = 13.8 Hz and 5.1 Hz, CH_2), 2.02 (1H, dd, J = 13.8 Hz and 5.1 Hz, CH_2), 1.85 (3H, br d, J = 1.5 Hz, CH_3), 0.90 (9H, s, 3 x CH_3), 0.89 (9H, s, 3 x CH_3), 0.19 (3H, s, CH_3), 0.17 (3H, s, CH_3), 0.13 (6H, s, 2 x CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.8 (C), 151.2 (CH), 137.9 (C), 136.2 (C), 129.3 (C), 128.0$_2$ (CH), 127.9$_8$ (CH), 127.6 (CH), 126.2 (CH), 87.6 (C), 73.0 (CH), 67.2 (CH), 40.9 (CH_2), 25.9 (3 x CH_3), 25.8 (3 x CH_3), 18.2 (C), 18.1 (C), 10.5 (CH_3), -4.3$_0$ (C), -4.3$_4$ (C), -4.4$_0$ (C), -4.4$_3$ (C); **IR** (ν_{max}): 2955, 2928, 2886, 2856, 1749, 1472, 1460, 1253, 1187, 1127, 1071, 1027, 1010 cm^{-1}; **MS**: *m/z* (ESI+) 497 $(M + Na)^+$; **HRMS** found 475.2693 $[M + H]^+$, $C_{26}H_{43}O_4Si_2$ requires 475.2694.



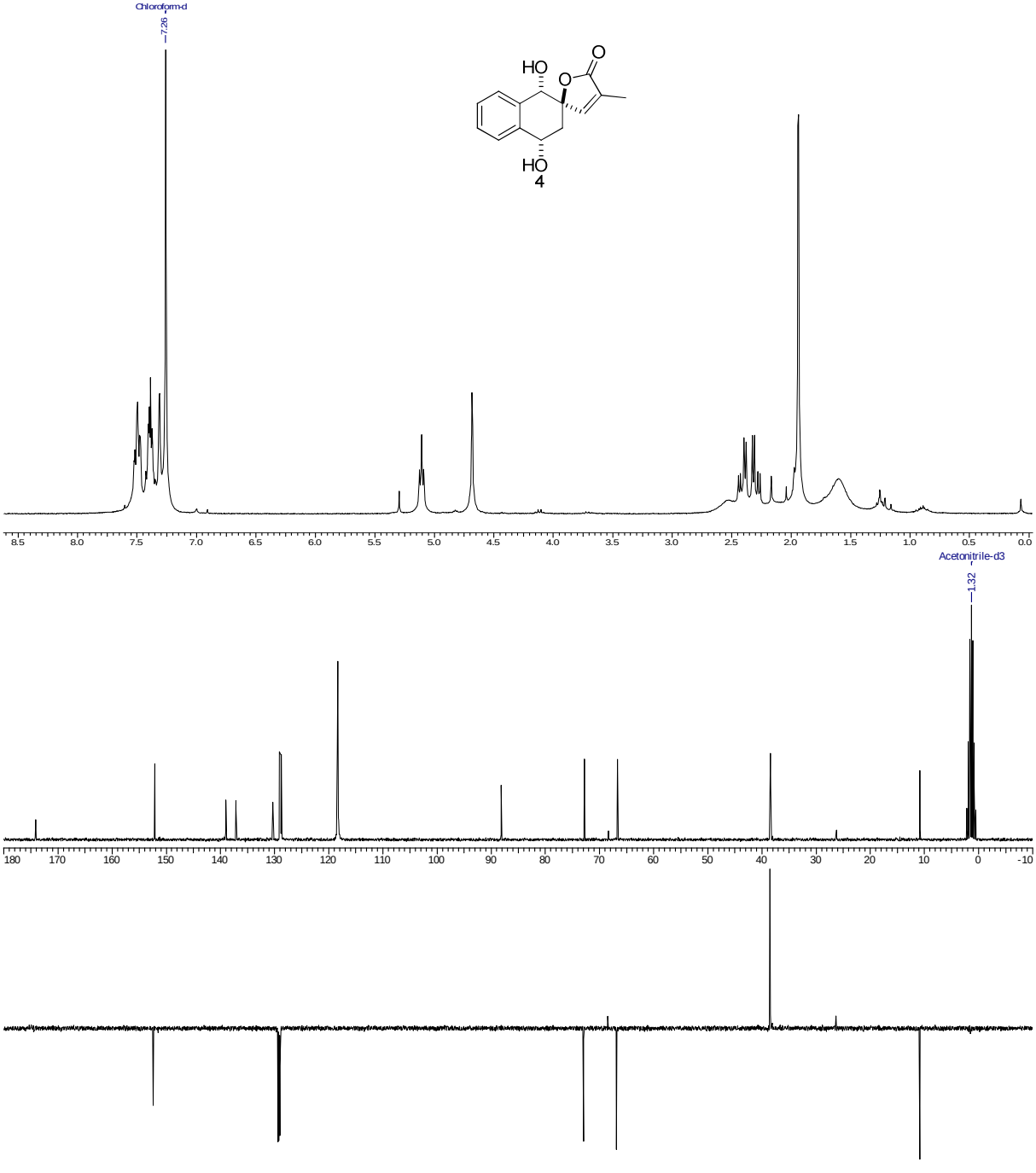


X-Ray Analysis

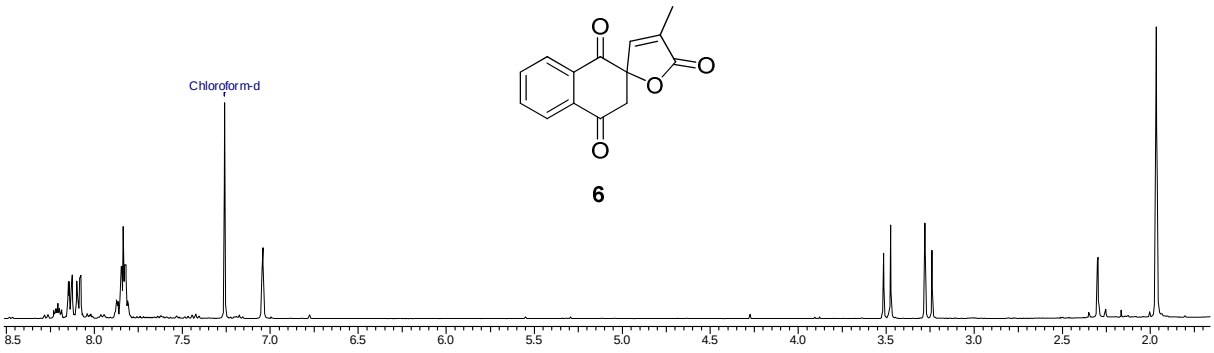


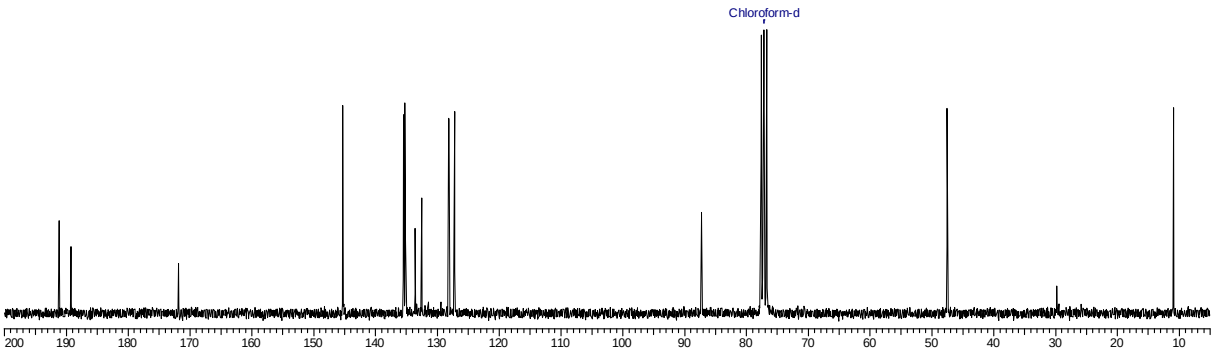


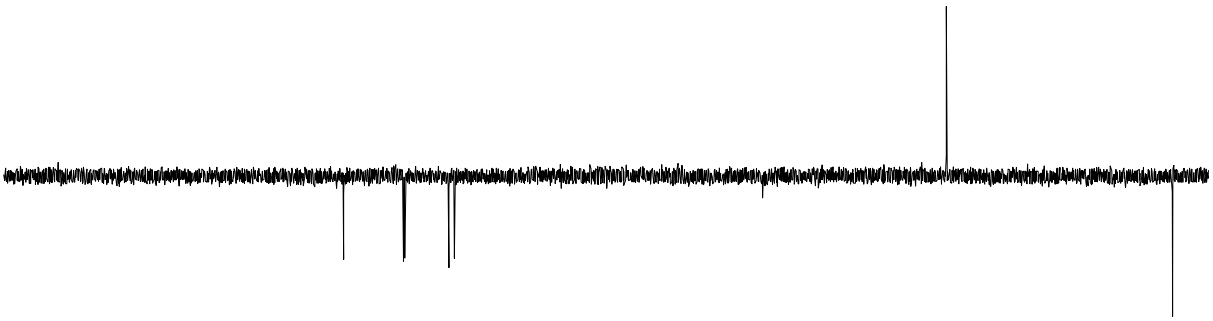
(1'*S*,2*R*,4'*S*)- and (1'*R*,2*S*,4'*R*)-1',4'-dihydroxy-4-methyl-3',4'-dihydro-1'*H*,5*H*-spiro[furan-2,2'-naphthalen]-5-one (4). In an oven dry flask, **3a** (150 mg, 0.32 mmol, 1 equiv) was dissolved in THF (8 mL). At 0°C, TBAF solution (0.790 mL, 0.79 mmol, 1M in THF, 2.5 equiv) was added dropwise. After completion of the reaction, the mixture was quenched with aqueous saturated $NaHCO_3$ solution. The aqueous layer was extracted with EtOAc. The combined organic phases were then concentrated and the crude product was purified by flash chromatography (2:8 petroleum ether:ethyl acetate) to give the diol **4** (74 mg) in quantitative yield. **^{1}H NMR** (300MHz, $CDCl_3$) δ 7.57-7.46 (2H, m, CH_{Ar}), 7.43-7.35 (2H, m, CH_{Ar}), 7.32 (1H, br q, J = 1.5 Hz, CH), 5.11 (1H, t, J = 5.5 Hz, CH), 4.68 (1H, s, CH), 2.53 (1H, bs, OH), 2.41 (1H, dd, J = 14.0 and 5.5 Hz, CH_2), 2.30 (1H, dd, J = 14.0 and 5.5 Hz, CH_2), 1.94 (3H, d, J = 1.5 Hz, CH_3); **^{13}C NMR** (75 MHz, CD_3CN) δ 174.2 (C), 152.1 (CH), 139.0 (C), 137.7 (C), 130.3 (C), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 88.1 (C), 72.8 (CH), 66.7 (CH), 38.4 (CH_2), 10.8 (CH_3); **IR** (ν_{max}): 3293, 2954, 2926, 2904, 2868, 1748, 1142, 1065, 1044, 1024, 1000, 973 cm^{-1}; **MS**: *m/z* (ESI+) 269 $(M + Na)^+$; **HRMS** found 247.0966 $[M + H]^+$, $C_{14}H_{15}O_4$ requires 247.0965.



(±)-Deoxylambertellol C, (±)-4-methyl-1'*H*,5*H*-spiro[furan-2,2'-naphthalene]-1',4',5(3'*H*)-trione (6). To a solution of diol **4** (29 mg, 0.123 mmol) in CH_2Cl_2 (1.5 mL), under argon, at 0 °C, was added Dess-Martin periodinane (157 mg, 0.371 mmol, 3 equiv). The reaction mixture was stirred at room temperature and monitored by TLC. After disappearance of the starting material, the mixture was poured into (1/1) mixture of saturated aqueous solution of $Na_2S_2O_3$and saturated aqueous solution of $NaHCO_3$ (20 mL) and shaken vigorously for 5 min. The aqueous layer was extracted with DCM. The combined organic layers were washed with a saturated aqueous $NaHCO_3$ solution, saturated aqueous NaCl, dried over Na_2SO_4, and concentrated under vacuum to give the crude product **5** (28 mg) in quantitative yield. **Mp** = 225 °C; **^{1}H NMR** (300MHz, $CDCl_3$) δ 8.16–8.13 (1H, m, CH_{Ar}), 8.11–8.08 (1H, m, CH_{Ar}), 7.88-7.80 (2H, m, CH_{Ar}), 7.04 (1H, br q, J = 1.5 Hz, CH), 3.50 (1H, d, J = 16.2 Hz, CH_2), 3.26 (1H, d, J = 16.2 Hz, CH_2), 1.97 (3H, br d, J = 1.5 Hz , CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 191.2 (C), 189.3 (C), 171.8 (C), 145.2 (CH), 135.5 (CH), 135.3 (CH), 135.1 (C), 133.6 (C), 132.6 (C), 128.2 (CH), 127.2 (CH), 87.3 (C), 47.6 (CH_2), 11.0 (CH_3); **HRMS** found 243.0646 $[M + H]^+$, $C_{14}H_{11}O_4$ requires 243.0652.







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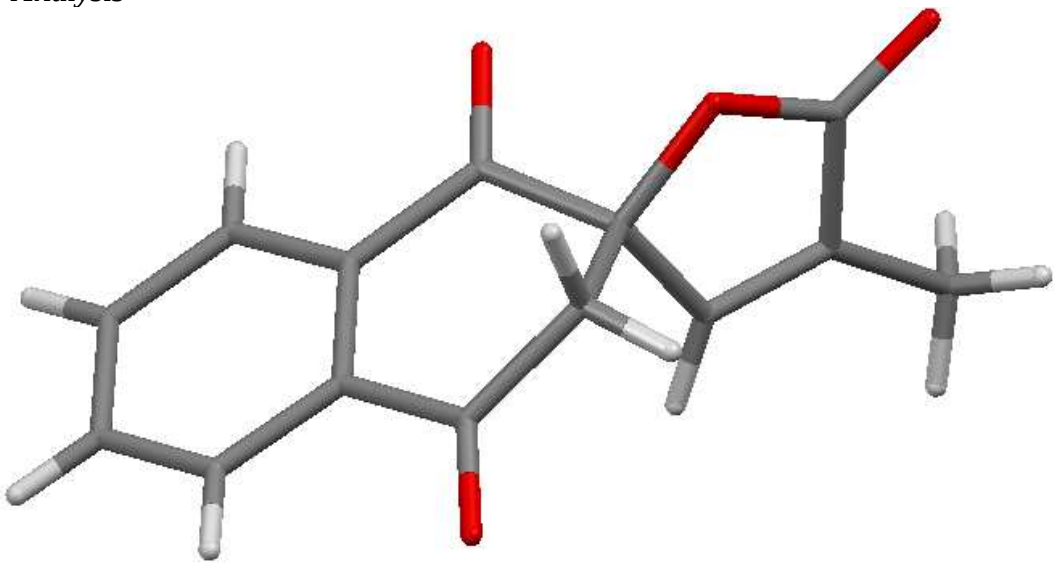
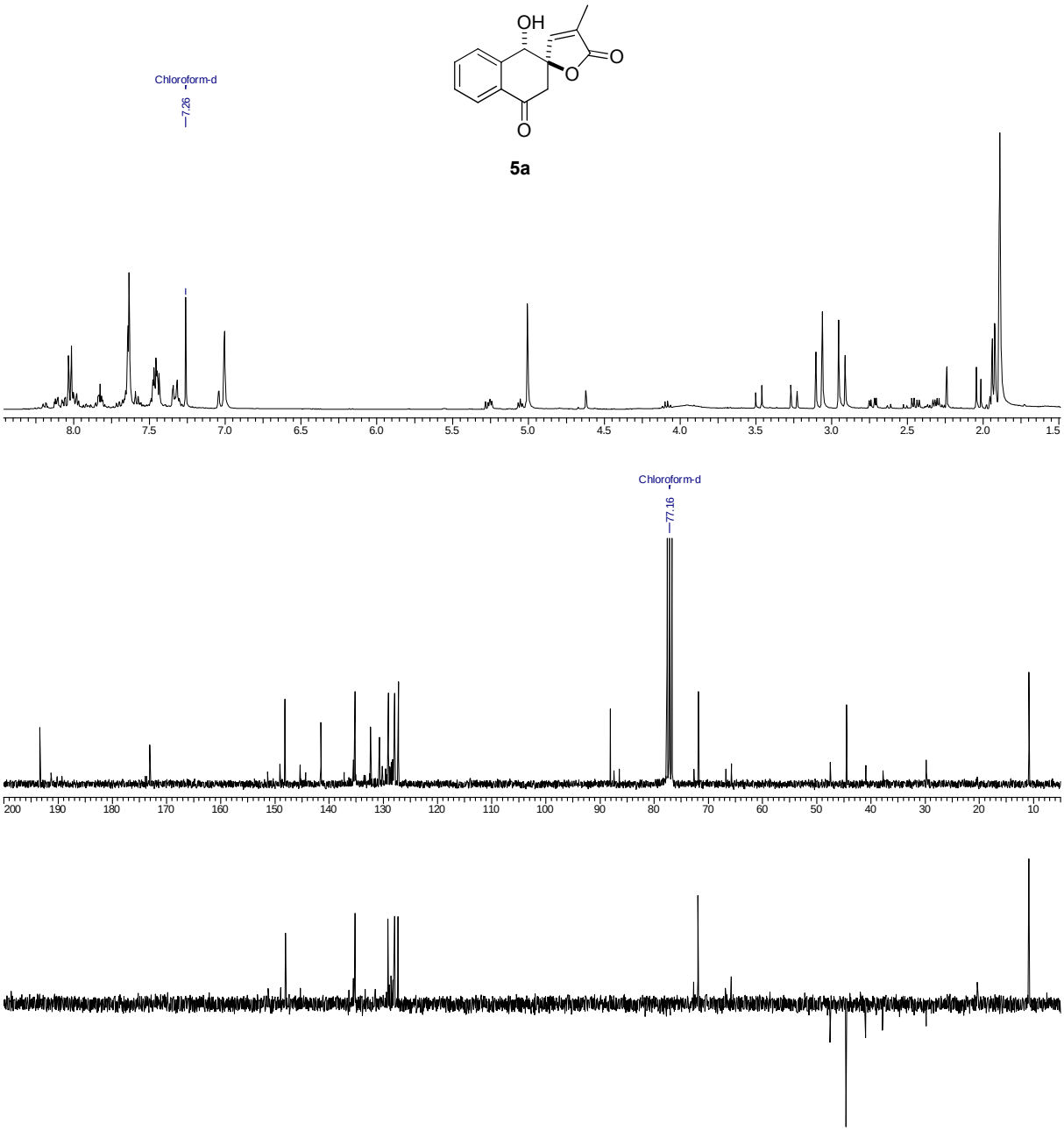
X-Ray Analysis



(±)-Deoxylambertellol B, (1'*S*,2*R*)- and (1'*R*,2*S*)-1'-hydroxy-4-methyl-1'H,5H-spiro[furan-2,2'-naphthalene]-4',5(3'H)-dione (5a).To a solution of diol **4** (35 mg, 0149 mmol,) in CH_2Cl_2 (2 mL), under argon, at 0 °C, was added Dess-Martin periodinane (63 mg, 0.149 mmol, 1 equiv). The reaction mixture was stirred at room temperature and monitored by TLC. After disappearance of the starting material, the mixture was poured into a (1/1) saturated aqueous solution of $Na_2S_2O_3$/$NaHCO_3$ (10 mL) and shaken vigorously for 5 min. The aqueous layer was extracted with DCM. The combined organic layers were washed with a saturated aqueous $NaHCO_3$ solution, saturated aqueous NaCl, dried over Na_2SO_4, and concentrated under vacuum to give a 1/0.2/0.2/0.2 mixture of **5a**/**5b**/**6** and **4** (33 mg) respectively. **^{1}H NMR** of **5a** (400MHz, $CDCl_3$) δ 8.04 (1H, d, J = 7.8 Hz, CH_{Ar}), 7.68-7.64 (1H, m, CH_{Ar}), 7.50-7.45 (1H, m, CH_{Ar}), 7.35-7.31 (1H, m, CH_{Ar}), 7.00 (1H, br s, CH), 5.03 (1H, br s, CH), 3.75 (1H, m, OH), 3.08 (1H, d, J = 17.1 Hz, CH_2), 2.95 (1H, d, J = 17.1 Hz, CH_2), 1.90 (3H, br s, CH_3); **^{13}C NMR** (75 MHz, C_6D_6) δ 193.2 (C), 173.0 (C), 147.0 (CH), 141.4 (C), 135.2 (CH), 132.4 (C), 130.7 (C), 129.1 (CH), 127.9 (CH), 127.2 (CH), 88.0 (C), 71.9 (CH), 44.6 (CH_2), 10.8 (CH_3).



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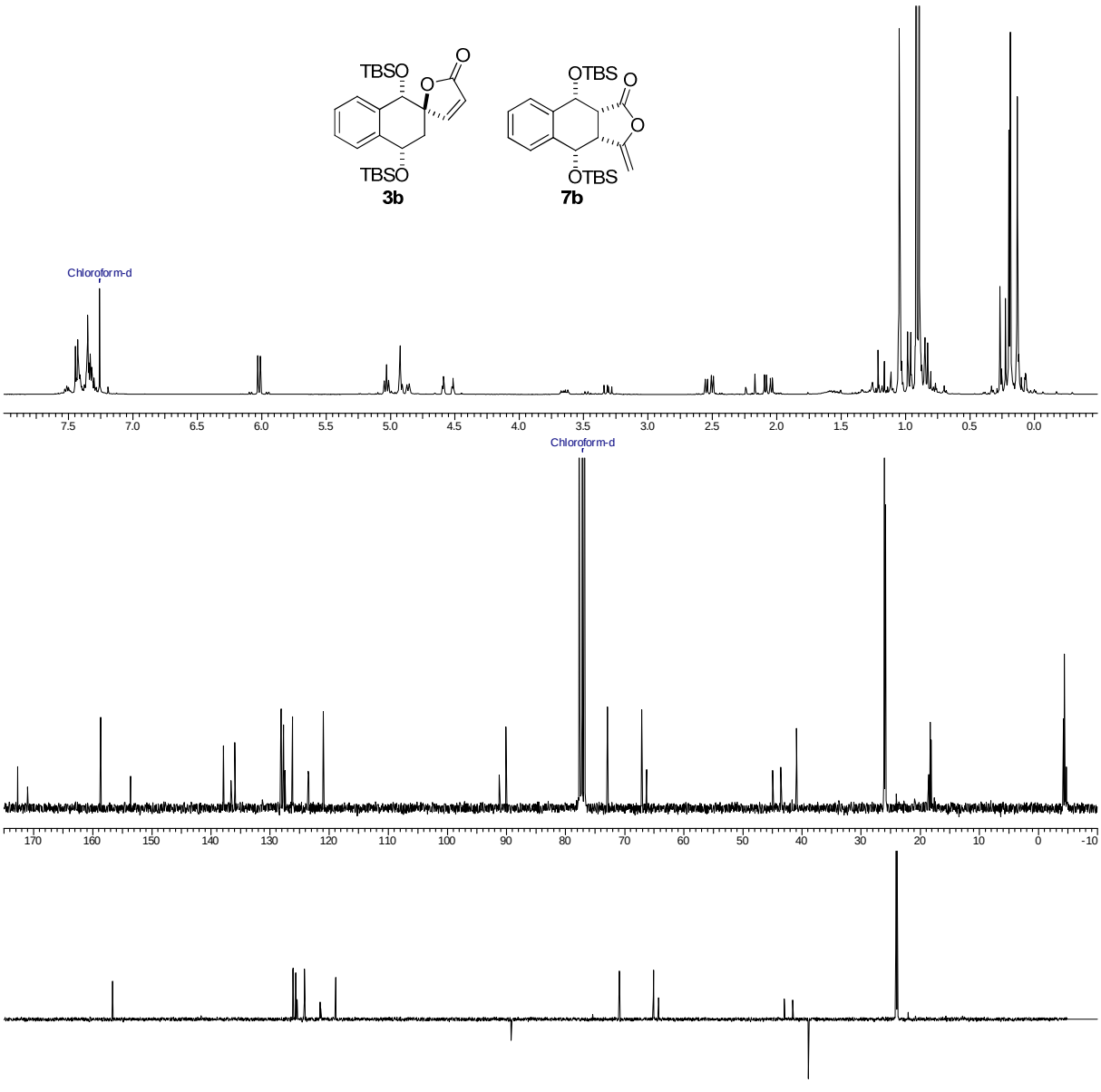
General procedure for cycloaddition

In a oven-dried Schlenk tube, *trans*-1,2-bis(*tert*-butyldimethylsilyloxy)-1,2-benzocyclobutene **1** (50 mg, 0.137 mmol) and butenolide **2** (0.164 mmol, 1.2 equiv) were dissolved in benzene-D6 (350µl). The solution was degassed for 10 min at -80°C three times. The mixture was then heated at 50°C. The reaction was followed by ^{1}H NMR and after disappearance of **1** (4-5 hours), the solvents was removed under vacuum. The crude product was purified by flash chromatography.

(1'*S*,2*R*,4'*S*)- and (1'*R*,2*S*,4'*R*)-1',4'-bis(*tert*-butyldimethylsilyloxy)-3',4'-dihydro-1'*H*,5*H*-spiro[furan-2,2'-naphthalen]-5-one (3b). **^{1}H NMR** (300MHz, $CDCl_3$) δ 7.45-7.30 (5H, m, CH and 4x CH_{Ar}), 6.02 (1H, d, J = 5.7 Hz, CH), 5.03 (1H, t, J = 5.1 Hz, CH), 4.93 (1H, s, CH), 2.52 (1H, dd, J = 13.9 and 5.1 Hz, CH_2), 2.06 (1H, dd, J = 13.9 and 5.1 Hz, CH_2), 0.92 (9H, s, 3 x CH_3), 0.90 (9H, s, 3 x CH_3), 0.19 (6H, s, 2 x CH_3), 0.13 (6H, s, 2 x CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.6 (C), 158.6 (CH), 137.8 (C), 135.9 (C), 128.1 (CH), 128.(CH), 127.6 (CH), 126.2 (CH), 120.9 (CH), 90.0 (C), 72.9 (CH), 67.1 (CH), 40.9 (CH_2), 26.0 (3 x CH_3), 25.9 (3 x CH_3), 18.3 (C), 18.1 (C), -4.2 (CH_3), -4.4 (3 x CH_3).

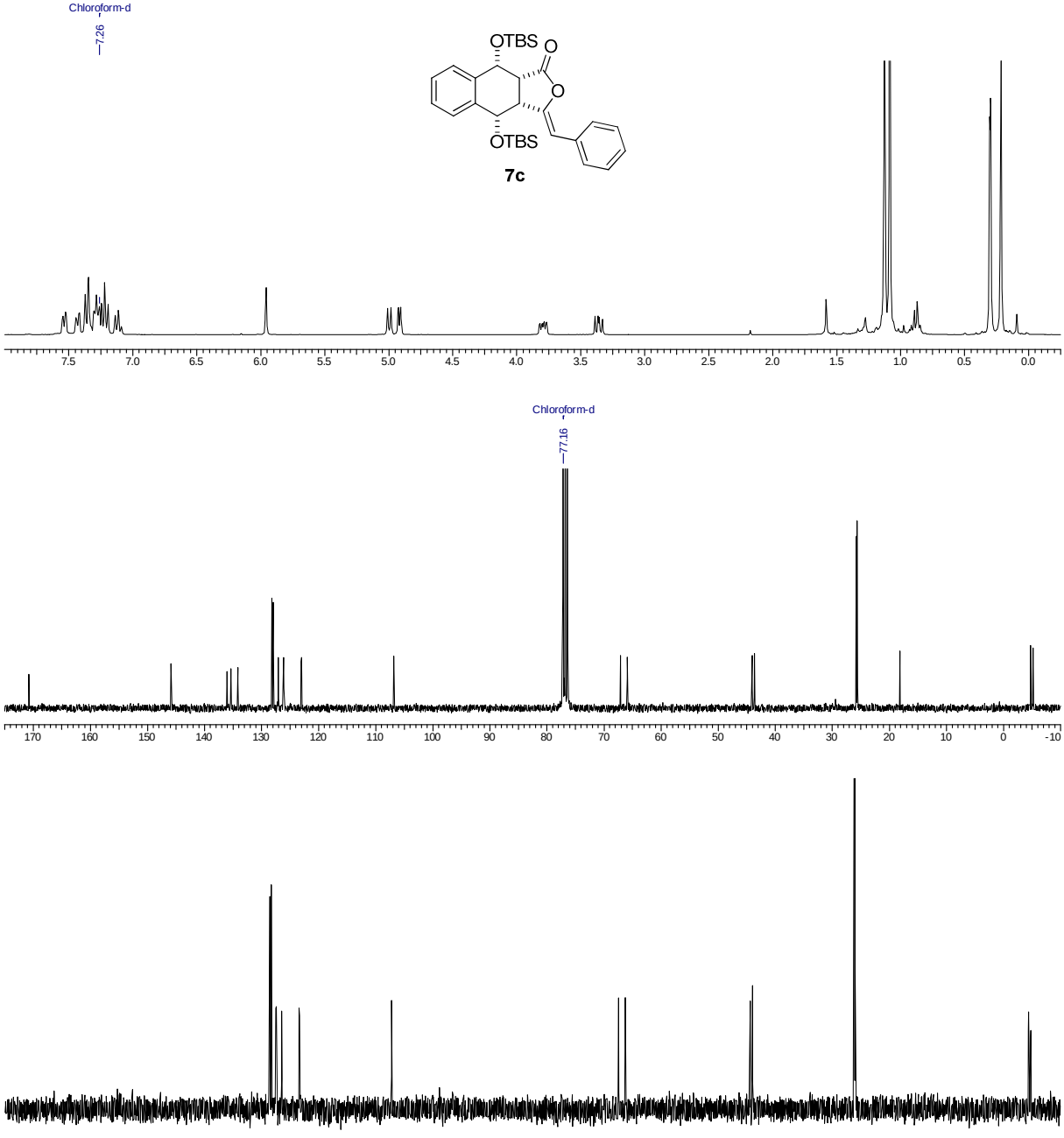
(3a*S*,4*S*,9*R*,9a*R*)- and (3a*R*,4*R*,9*S*,9a*S*)-4,9-bis(tert-butyldimethylsilyloxy)-3-methylene-3a,4,9,9a-tetrahydronaphtho[2,3-c]furan-1(3*H*)-one (7b). **^{1}H NMR** (300MHz, $CDCl_3$) δ 7.53-7.30 (4H, m, CH_{Ar}), 4.92 (1H, d, J = 7.5 Hz, CH), 4.86 (1H, d, J = 5.1 Hz, CH), 4.59 (1H, t, J = 2.0 Hz, CH_2), 4.52 (1H, t, J = 2.0 Hz, CH_2), 3.68-3.62 (1H, m, CH), 3.31 (1H, dd, J = 10,2 and 7.5 Hz, CH), 1.05 (18H, br s, 9 x CH_3), 0.27 (3H, s, CH_3), 0.23 (3H, s, CH_3), 0.20 (6H, s, 2 x CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.0 (C), 153.6 (C), 136.5 (C), 135.8 (C), 127.4_2 (CH), 127.3_8 (CH), 123.5 (CH), 123.4 (CH), 91.2 (CH_2), 67.1 (CH), 66.2 (CH), 44.9 (CH), 43.5 (CH), 26.1 (3 x CH_3), 26.0 (3 x CH_3), 18.6 (C), 18.5 (C), -4.4 (CH_3), -4.5 (CH_3), -4.8 (CH_3), -4.9 (CH_3).



(3a*S*,4*S*,9*R*,9a*R*,*Z*)- and (3a*R*,4*R*,9*S*,9a*S*,*Z*)-4,9-Bis-(*tert*-butyl-dimethyl-silanyloxy)-3-[1-phenyl-meth-(*Z*)-ylidene]-3a,4,4a,8a,9,9a-hexahydro-3*H*-naphtho[2,3-*c*]furan-1-one (7c).

Solvents used for column of chromatography: 95:5 (petroleum ether:diethyl ether)

Mp = 180 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55-7.51 (1H, m, CH_{Ar}), 7.43-7.40 (1H, m, CH_{Ar}), 7.36-7.32 (2H, m, CH_{Ar}), 7.30-7.26 (2H, m, CH_{Ar}), 7.24-7.19 (2H, m, CH_{Ar}), 7.13-7.08 (1H, m, CH_{Ar}), 5.94 (1H, br d, J = 1.4 Hz, CH), 4.98 (1H, d, J = 7.3 Hz, CH), 4.90 (1H, d, J = 5.4 Hz, CH), 3.79 (1H, ddd, J = 10.2 and 5.4 and 1.4 Hz, CH), 3.35 (1H, dd, J = 10.2 and 7.3 Hz, CH), 1.12 (9H, s, 3 x CH_3), 1.08 (9H, s, 3 x CH_3), 0.30 (3H, br s, CH_3), 0.29 (3H, br s, CH_3), 0.21 (6H, br s, 2 x CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.1 (C), 146.3 (C), 136.4 (C), 135.7 (C), 134.5 (C), 128.6 (2 x CH), 128.3 (2 x CH), 127.6 (CH), 127.4 (CH), 126.5 (CH), 123.5 (CH), 123.3 (CH), 107.2 (CH), 67.5 (CH), 66.3 (CH), 44.4 (CH), 44.0 (CH), 26.2 (3 x CH_3), 26.0 (3 x CH_3), 18.5 (2 x C), -4.3 (CH_3), -4.4 (CH_3), -4.7 (CH_3), -4.8 (CH_3); **IR** (ν_{max}): 2950, 2928, 2885, 2856, 1810, 1675, 1651, 1471, 1462, 1339, 1252, 1121, 1072, 1019 cm^{-1}; **MS**: *m/z* (ESI+) 559 $(M + Na)^+$, **HRMS** found 537.2851 $[M + H]^+$, $C_{31}H_{45}O_4Si_2$ requires 537.2851.



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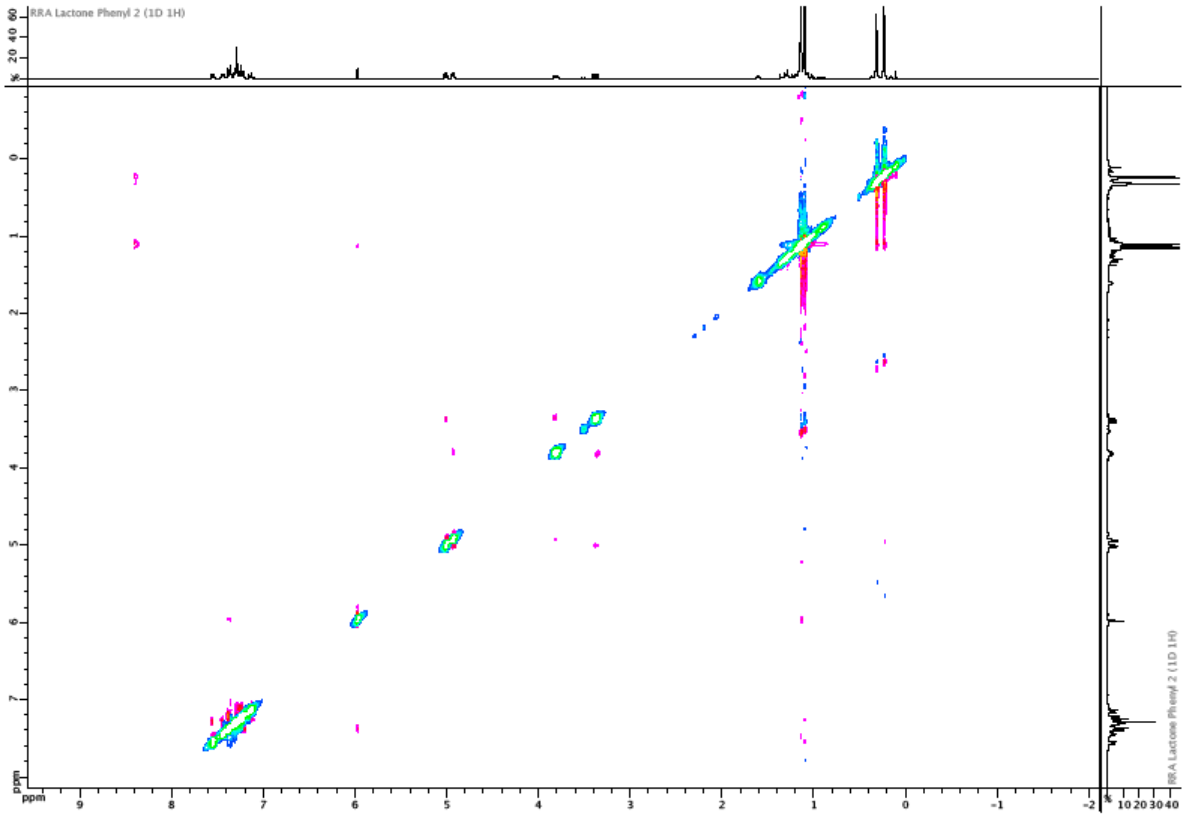
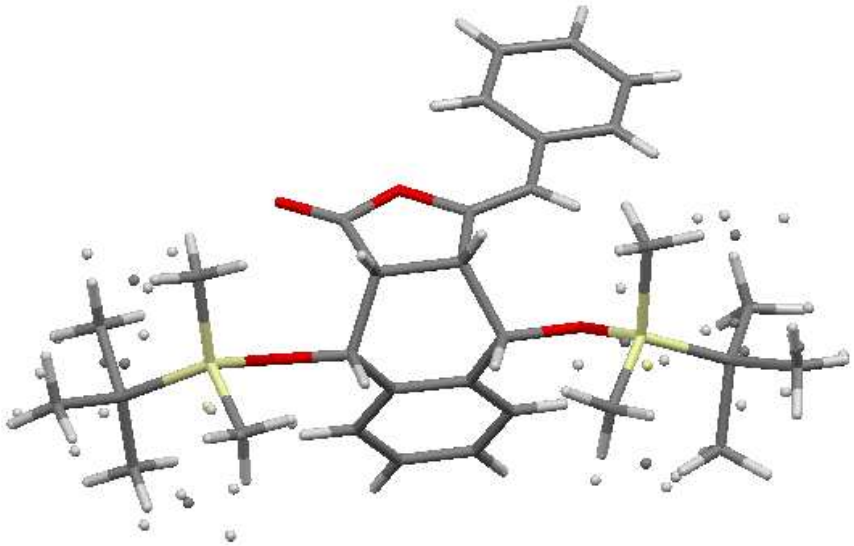


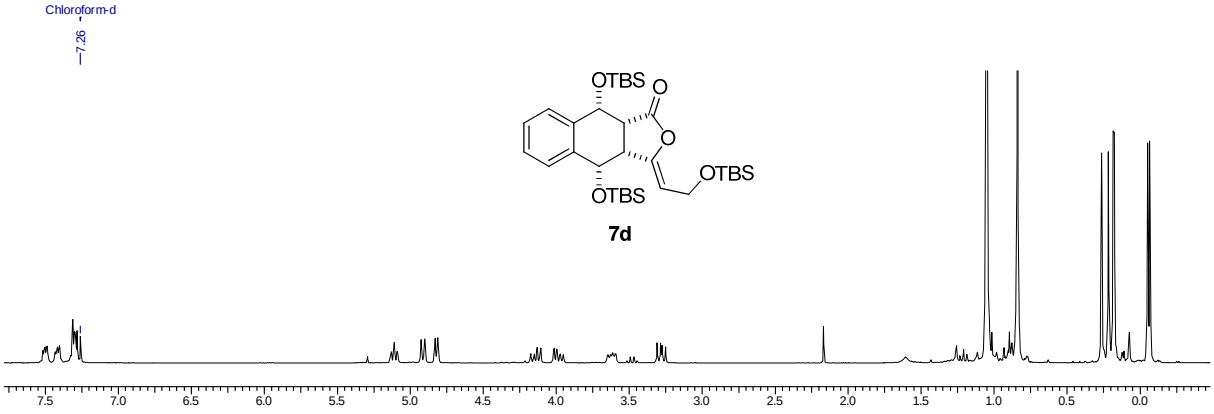
X-Ray Analysis

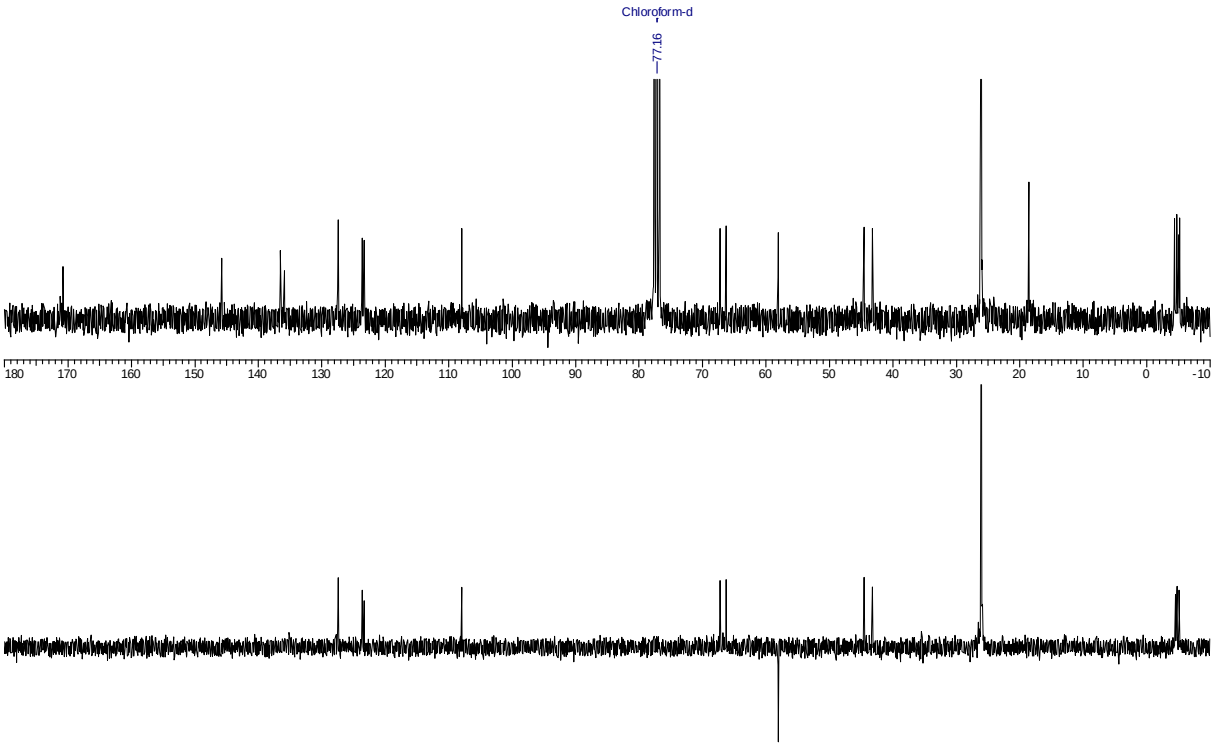


(3a*S*,4*S*,9*R*,9a*R*,*Z*)- and (3a*R*,4*R*,9*S*,9a*S*,*Z*)-4,9-Bis-(*tert*-butyl-dimethyl-silanyloxy)-3-[2-(*tert*-butyl-dimethyl-silanyloxy)-eth-(*Z*)-ylidene]-3a,4,9,9a-tetrahydro-3*H*-naphtho[2,3-*c*]furan-1-on (7d).

Solvents used for column of chromatography: 95:5 (petroleum ether:diethyl ether)

Mp = 87 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.52-7.49 (1H, m, CH_{Ar}), 7.43-7.41 (1H, m, CH_{Ar}), 7.33-7.28 (2H, m, 2 x CH_{Ar}), 5.14-5.09 (1H, m, CH), 4.92 (1H, d, J = 7.3 Hz, CH), 4.82 (1H, d, J = 5.5 Hz, CH), 4.14 (1H, br dd, J = 13.0 and 7.0 Hz, CH_2), 3.98 (1H, br dd, J = 13.0 and 6.0 Hz, CH_2), 3.65-3.59 (1H, m, CH), 3.28 (1H, dd, J = 10.3 and 7.3 Hz), 1.05 (18H, s, 6 x CH_3), 0.84 (9H, s, 3 x CH_3), 0.26 (3H, s, CH_3), 0.22 (3H, s, CH_3), 0.18 (3H, br s, CH_3), 0.17 (3H, br s, CH_3), -0.05 (3H, s, CH_3), -0,07 (3H, s, CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.8 (C), 145.8 (C), 136.5 (C), 135.8 (C), 127.4_3 (CH), 127.3_8 (CH), 123.6 (CH), 123.3 (CH), 107.9 (CH), 67.2 (CH), 66.2 (CH), 58.0 (CH_2), 44.5 (CH), 43.2 (CH), 26.1 (3 x CH_3), 26.0_3 (3 x CH_3), 26.0_1 (3 x CH_3), 18.5 (2 x C), 18.4 (C), -4.4 (CH_3), -4.5 (CH_3), -4.8 (CH_3), -4.9 (CH_3), -5.1 (CH_3), -5.2 (CH_3); **IR** (ν_{max}): 2955, 2928, 2885, 2857, 1789, 1700, 1471, 1461, 1253, 1188, 1122, 1106, 1069, 1024, 1005 cm^{-1}; **MS**: *m/z* (ESI+) 627 $(M + Na)^+$; **HRMS** found 622.3775 $[M + NH_4]^+$, $C_{32}H_{60}NO_5Si_3$ requires 622.3774.





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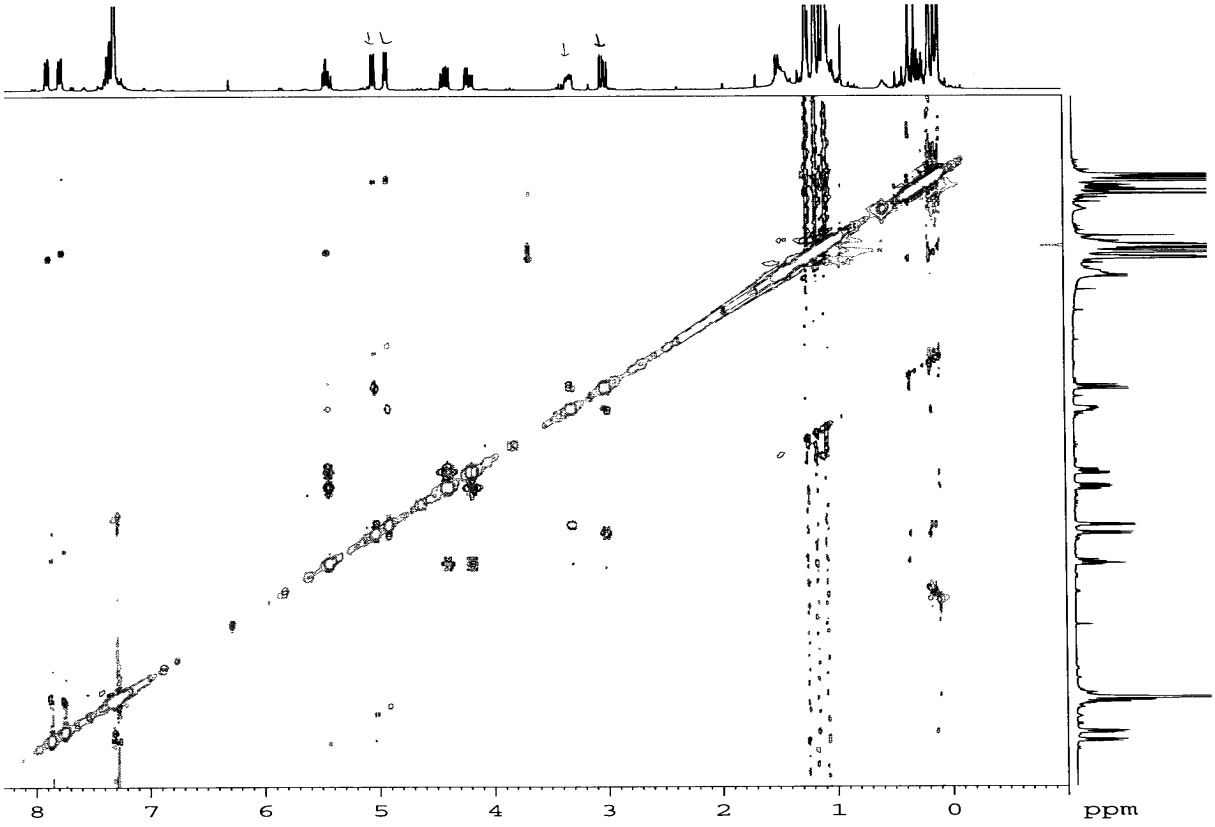
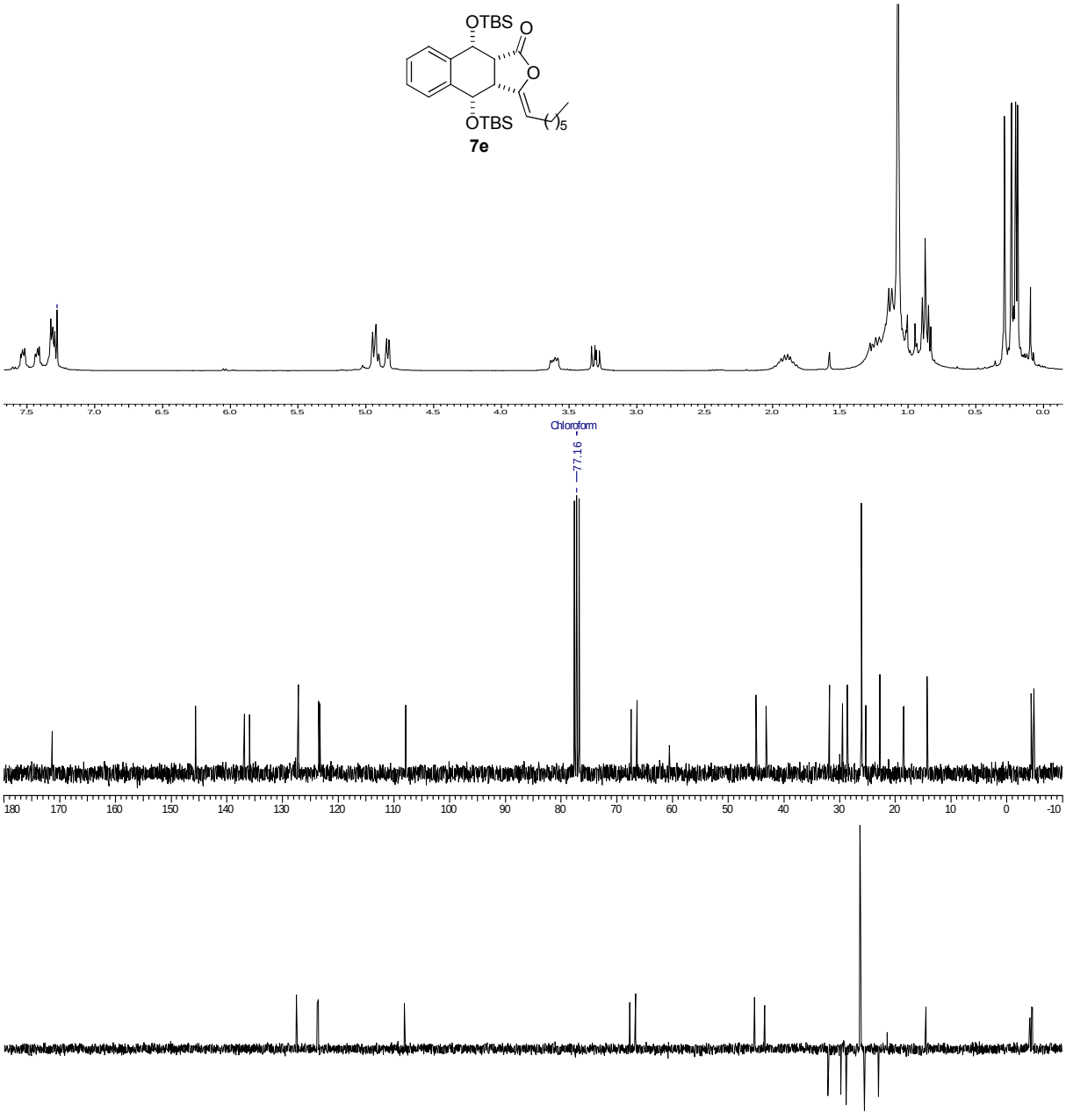


(3a*S*,4*S*,9*R*,9a*R*,*Z*)- and (3a*R*,4*R*,9*S*,9a*S*,*Z*)-4,9-Bis(*tert*-butyldimethylsilyloxy)-3-heptylidene-3a,4,9,9a-tetrahydronaphtho[2,3-c]furan-1(3*H*)-one (7e).

Solvents used for column of chromatography: 99:1 (petroleum ether:diethyl ether)

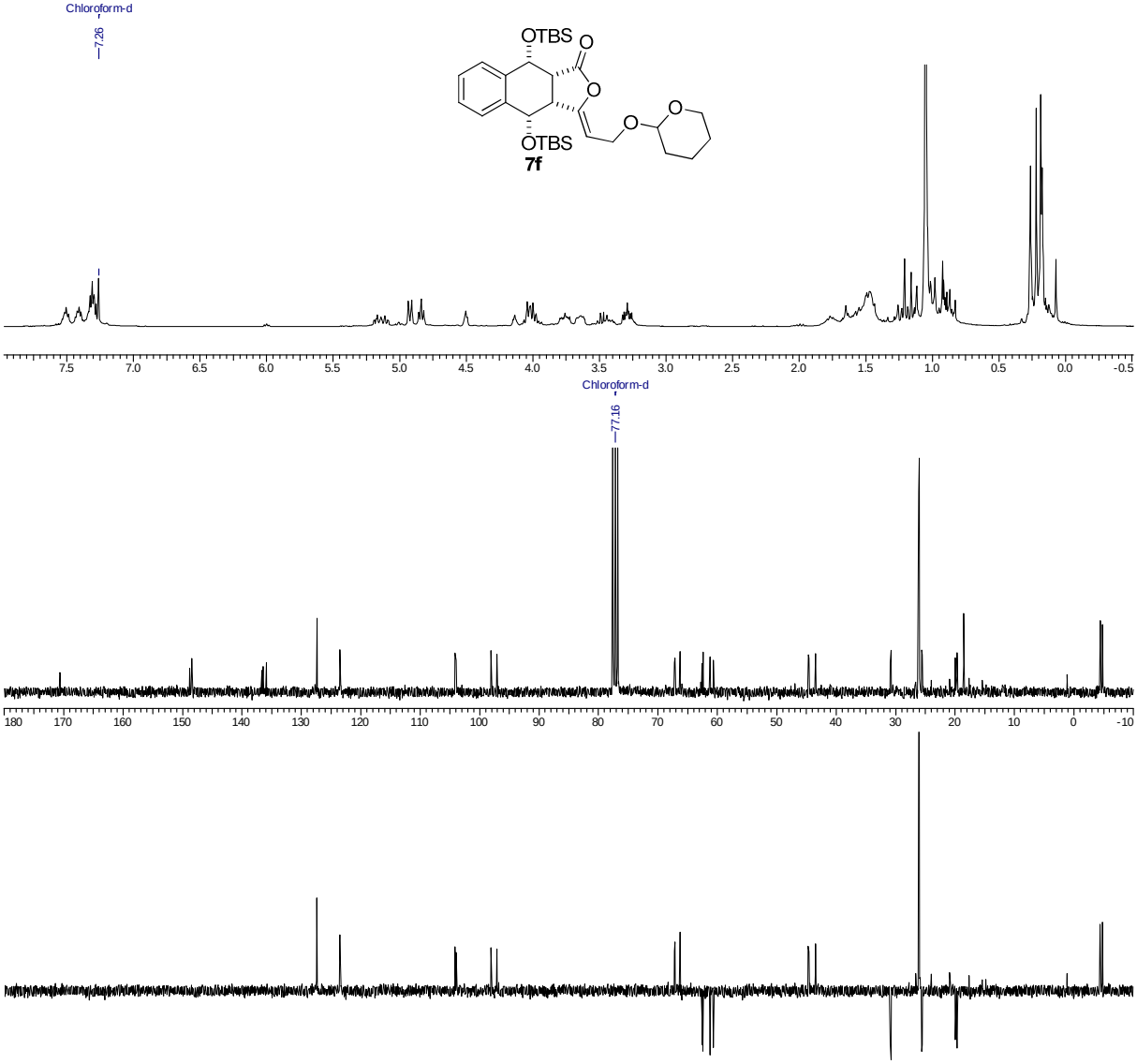
Mp = 68 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53-7.50 (1H, m, $CH_{Ar.}$), 7.42-7.39 (1H, m, $CH_{Ar.}$), 7.31-7.26 (2H, m, 2 x $CH_{Ar.}$), 4.93-4.88 (2H, m, 2 x CH), 4.82 (1H, d, *J* = 5.3 Hz, CH), 3.60 (1H, br ddd, *J* = 10.3 and 5.3 and 1.2 Hz, CH), 3,29 (1H, dd, *J* = 10.3 and 7.4 Hz, CH), 1.98-1.78 (2H, m, CH_2), 1.26 – 0.98 (8H, m, 4 x CH_2), 1.05 (18H, s, 9 x CH_3) 0.85 (3H, t, *J* = 6.9 Hz, CH_3), 0.27 (3H, s, CH_3), 0.22 (3H, s, CH_3), 0.19 (3H, s, CH_3), 0.17 (3H, s, CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.3 (C), 145.6 (C), 136.8 (C), 135.9 (C), 127.2_2 (CH), 127.1_8 (CH), 123.5 (CH), 123.3 (CH), 107.8 (CH), 67.4 (CH), 66.3 (CH), 45.0 (CH), 43.2 (CH), 31.8 (CH_2), 29.5 (CH_2), 28.6 (CH_2), 26.1 (3 x CH_3), 26.0 (3 x CH_3), 25.3 (CH_2), 22.7 (CH_2), 18.6 (C), 18.5 (C), 14.3 (CH_3), -4.4 (CH_3), -4.5 (CH_3), -4.8 (CH_3), -4.9 (CH_3); **IR** (ν_{max}): 2954, 2926, 2855, 1781, 1699, 1471, 1461, 1254, 1172, 1126, 1071, 1027 cm^{-1}; **MS**: *m/z* (ESI+) 567 $(M + Na)^+$; **HRMS** found 545.3483 $[M + H]^+$, $C_{31}H_{53}O_4Si_2$ requires 545.3477.



(3a*S*,4*S*,9*R*,9a*R*,*Z*)- and (3a*R*,4*R*,9*S*,9a*S*,*Z*)-4,9-Bis-(*tert*-butyl-dimethyl-silanyloxy)-3-[2-(tetrahydro-pyran-2-yloxy)-eth-(*Z*)-ylidene]-3a,4,9,9a-tetrahydro-3*H*-naphtho[2,3-*c*]furan-1-one (7f).

Solvents used for column of chromatography: 8:2 (petroleum ether:diethyl ether)

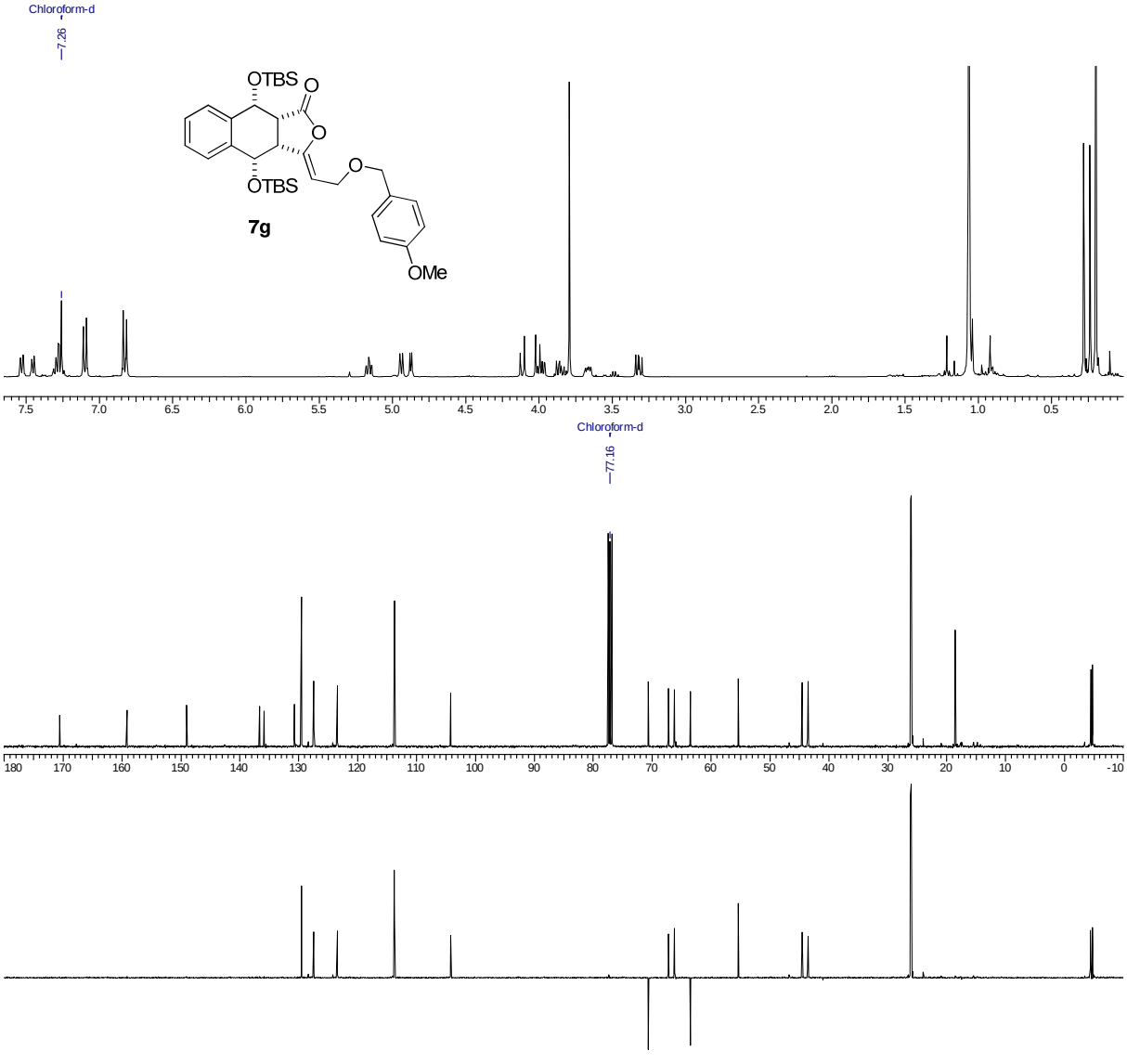
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.47 (2H, m, 2 x CH_{Ar}), 7.43-7.28 (2H, m, 2 x CH_{Ar}), 7.34-7.28 (4H, m, 4 x CH_{Ar}), 5.19-5.08 (2H, m), 4.92 (2H, d, J = 7.4 Hz, 2 x CH), 4.84 (2H, m, 2 x CH), 4.50 (1H, m, CH), 4.13 (1H, m, CH), 4.07-3.95 (4H, m, 2 x CH_2), 3.79-3.72 (2H, m, 2 x CH_2), 3.68-3.61 (2H, m, 2 x CH), 3.47-3.38 (2H, m, 2 x CH_2) 3.32-3.26 (4H, m, 2 x CH and 2 x CH_2), 1.81-1.43 (12H, m, 6 x CH_2), 1.05 (18H, s, 6 x CH_3), 0.26 (6H, s, 2 x CH_3), 0.22 (6H, s, 2 x CH_3), 0.18 (6H, s, 2 x CH_3), 0.17 (6H, br s, 2 x CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.7 (C), 170.6 (C), 148.8 (C), 148.4 (C), 136.6 (C), 136.4 (C), 135.9 (C), 135.8 (C), 127.4 (4 x CH), 123.5 (2 x CH), 123.4 (CH), 123.3 (CH), 104.1 (CH), 103.9 (CH), 98.1 (CH), 97.1 (CH), 67.2 (CH), 67.1 (CH), 66.3 (CH), 66.2 (CH), 62.6 (CH_2), 62.4 (CH_2), 61.2 (CH_2), 60.6 (CH_2), 44.7 (CH), 44.6 (CH), 43.5 (CH), 43.4 (CH), 30.9 (CH_2), 30.7 (CH_2), 26.12 (9 x CH_3), 26.0 (9 x CH_3), 25.6 (CH_2), 25.5 (CH_2), 19.9 (CH_2), 19.7 (CH_2),18.5 (4 x C), -4.4 (2 x CH_3), -4.5 (CH3), -4.8 (2 x CH_3), -4.9 (CH_3); **IR** (ν_{max}): 2931, 2886, 2858, 1804, 1699, 1472, 1460, 1378, 1340, 1325, 1257, 1183, 1123, 1095, 1073, 1045, 1024, 947 cm^{-1}; **MS**: *m/z* (ESI+) 597 (M + Na)$^{+}$; **HRMS** found 592.3490 [M + NH_4]$^{+}$, $C_{31}H_{54}NO_6Si_2$ requires 592.3484.



(3a*S*,4*S*,9*R*,9a*R*,*Z*)- and (3a*R*,4*R*,9*S*,9a*S*,*Z*)-4,9-Bis-(*tert*-butyl-dimethyl-silanyloxy)-3-[2-(4-methoxy-benzyloxy)-eth-(*Z*)-ylidene]-3a,4,9,9a-tetrahydro-3*H*-naphtho[2,3-c]furan-1-one (7g).

Solvents used for column of chromatography: 8:2 (petroleum ether:diethyl ether)

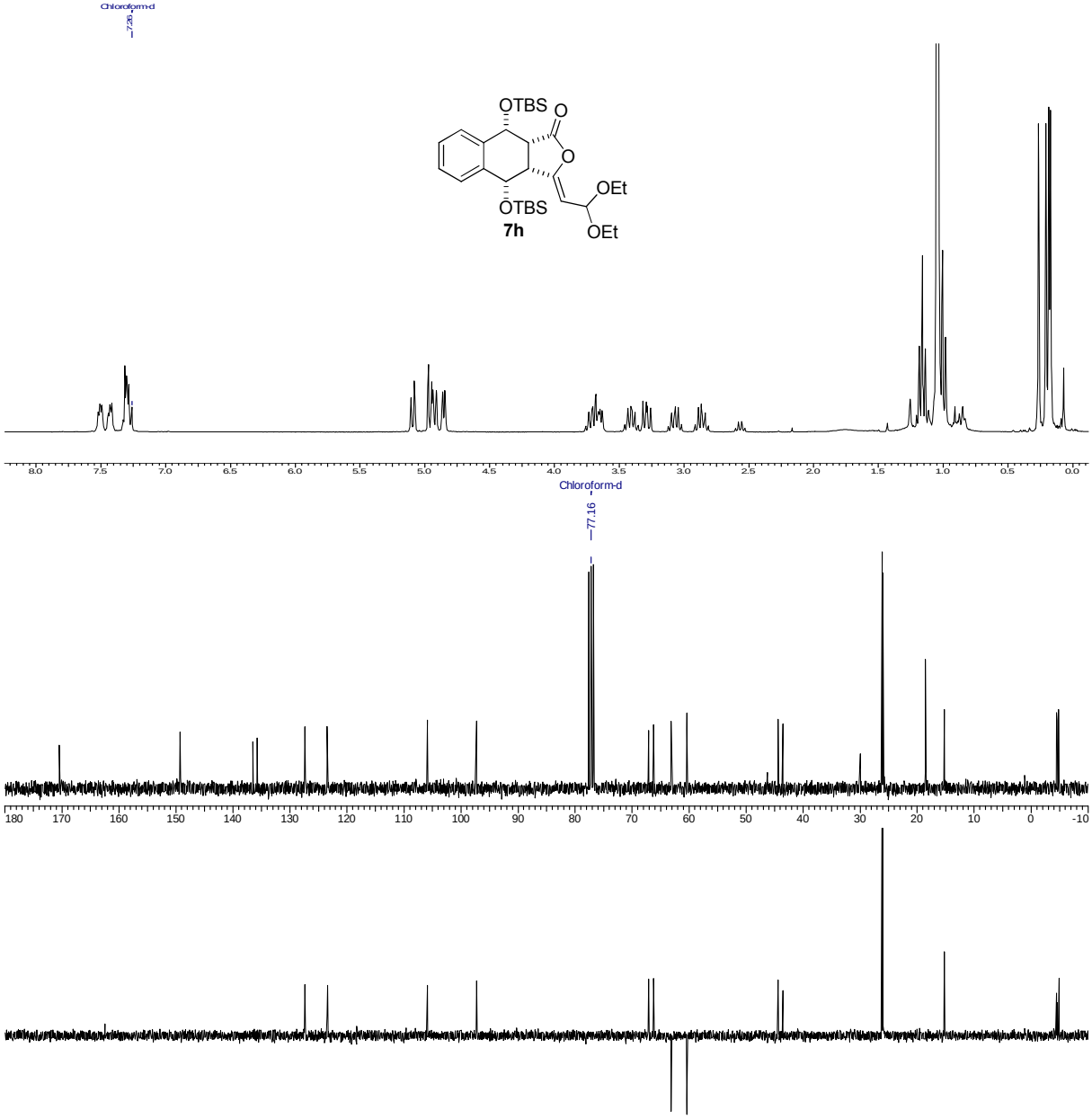
^{1}H **NMR** (400 MHz, $CDCl_3$) δ 7.53 (1H, br d, J = 7.3 Hz, CH_{Ar}), 7.45 (1H, br d, J = 7.0 Hz CH_{Ar}), 7.31-7.24 (2H, m, 2 x CH_{Ar}), 7.10 (2H, d, J = 8.6 Hz, 2 x CH), 6.83 (2H, d, J = 8.6 Hz, 2 x CH), 5.16 (1H, m, CH), 4.94 (1H, d, J = 7.5 Hz, CH), 4.88 (1H, d, J = 5.3 Hz, CH), 4.12 (1H, d, J = 11.3 Hz, CH_2), 4.00 (1H, d, J = 11.3 Hz, CH_2), 4.01-3.96 (1H, br dd, J = 12.6 and 7.0 Hz, 1 x CH_2), 3.88-3.82 (1H, br dd, J = 12.6 and 7.8 Hz, 1 x CH_2), 3.79 (3H, s, CH_3), 3.69-3.64 (1H, m, CH), 3.32 (1H, dd, J = 10.3 and 7.5 Hz, CH), 1.06 (18H, br s, 6 x CH_3), 0.28 (3H, s, CH_3), 0.24 (3H, s, CH_3), 0.20 (6H, m, 2 x CH_3); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 170.6 (C), 159.2 (C), 149.0 (C), 136.7 (C), 135.9 (C), 130.7 (C), 129.5 (2 x CH), 127.5 (CH), 127.4 (CH), 123.5 (CH), 123.4 (CH), 113.8 (2 x CH), 104.2 (CH), 70.6 (CH_2), 67.3 (CH), 66.2 (CH), 63.5 (CH_2), 55.4 (CH_3), 44.6 (CH), 43.6 (CH), 26.2 (3 x CH_3), 26.0 (3 x CH_3), 18.6 (2 x C), -4.4 (CH_3), -4.5 (CH_3), -4.7 (CH_3), -4.9 (CH_3); **IR** (ν_{max}): 2953, 2928, 2884, 2855, 1803, 1692, 1512, 1471, 1462, 1250, 1190, 1124, 1067, 1027, 1009 cm^{-1}; **MS**: *m/z* (ESI+) 633 (M + Na)$^+$; **HRMS** found 628.3478 [M + NH_4]$^+$, $C_{34}H_{54}NO_6Si_2$ requires 628.3484.



(3a*S*,4*S*,9*R*,9a*R*,*Z*)- and (3a*R*,4*R*,9*S*,9a*S*,*Z*)-4,9-Bis-(*tert*-butyl-dimethyl-silanyloxy)-3-[2,2-diethoxy-eth-(*Z*)-ylidene]-3a,4,9,9a-tetrahydro-3*H*-naphtho[2,3-*c*]furan-1-one (7h).

Solvents used for column of chromatography: 85:15 (petroleum ether:diethyl ether)

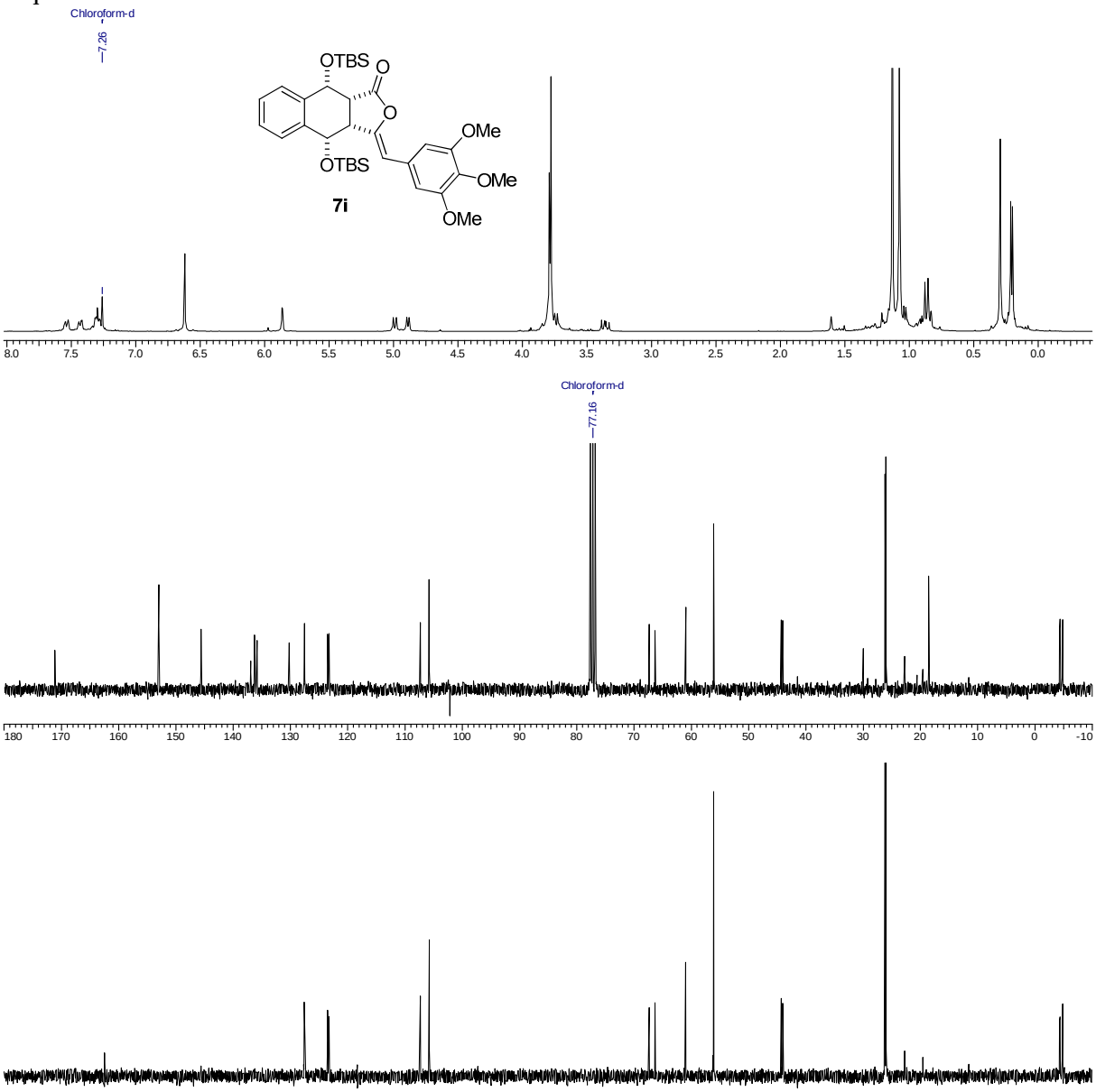
Mp = 128 °C; **^{1}H NMR** (300MHz, $CDCl_3$) δ 7.52-7.49 (1H, m, CH_{Ar}), 7.44-7.41 (1H, m, CH_{Ar}), 7.33-7.28 (2H, m, 2 x CH_{Ar}), 5.09 (1H, br d, *J* = 7.7 Hz, CH), 4.96 (1H, d, *J* = 7.7, CH), 4.93 (1H, d, *J* = 7.6 Hz, CH), 4.85 (1H, d, *J* = 5.5 Hz, CH), 3.76-3.63 (2H, m, CH and C*H*$_2$), 3.46-3.35 (1H, m, C*H*$_2$), 3.29 (1H, dd, *J* = 10.2 and 7.6 Hz, C*H*$_2$), 3.12-3.02 (1H, m, C*H*$_2$), 2.91-2.81 (1H, m, C*H*$_2$), 1.16 (3H, t, *J* = 7.1 Hz, CH_3), 1.05 (9H, s, 3 x CH_3), 1.04 (9H, s, 3 x CH_3), 1.03 (3H, t, *J* = 7.1 Hz, CH_3), 0.26 (3H, s, CH_3), 0.21 (3H, s, CH_3), 0.18 (3H, s, CH_3), 0.17 (3H, s, CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.4 (C), 149.2 (C), 136.5 (C), 135.7 (C), 127.4 (CH), 127.3 (CH), 123.5 (CH), 123.4 (CH), 105.9 (CH), 97.3 (CH), 67.1 (CH), 66.2 (CH), 63.1 (CH_2), 60.3 (CH_2), 44.4 (CH), 43.5 (CH), 26.1 (3 x CH_3), 26.0 (3 x CH_3), 18.5 (2 x C), 15.2$_3$ (CH_3), 15.2$_1$ (CH_3), -4.4 (CH_3), -4.5 (CH_3), -4.8 (CH_3), -4.9 (CH_3); **IR** (ν_{max}): 2955, 2931, 2897, 2858, 1797, 1705, 1473, 1464, 1339, 1255, 1192, 1114, 1071, 1018, 1008 cm^{-1}; **MS**: *m/z* (ESI+) 585 $(M + Na)^+$; **HRMS** found 585.3035 $[M + Na]^+$, $C_{30}H_{50}O_6Si_2Na$ requires 585.3038.



(3a*S*,4*S*,9*R*,9a*R*,*Z*)- and (3a*R*,4*R*,9*S*,9a*S*,*Z*)-4,9-Bis-(*tert*-butyl-dimethyl-silanyloxy)-3-[1-(3,4,5-trimethoxy-phenyl)-meth-(*Z*)-ylidene]-3a,4,9,9a-tetrahydro-3*H*-naphtho[2,3-*c*]furan-1-one (7i).

Solvents used for column of chromatography: 7:3 (petroleum ether:diethyl ether)

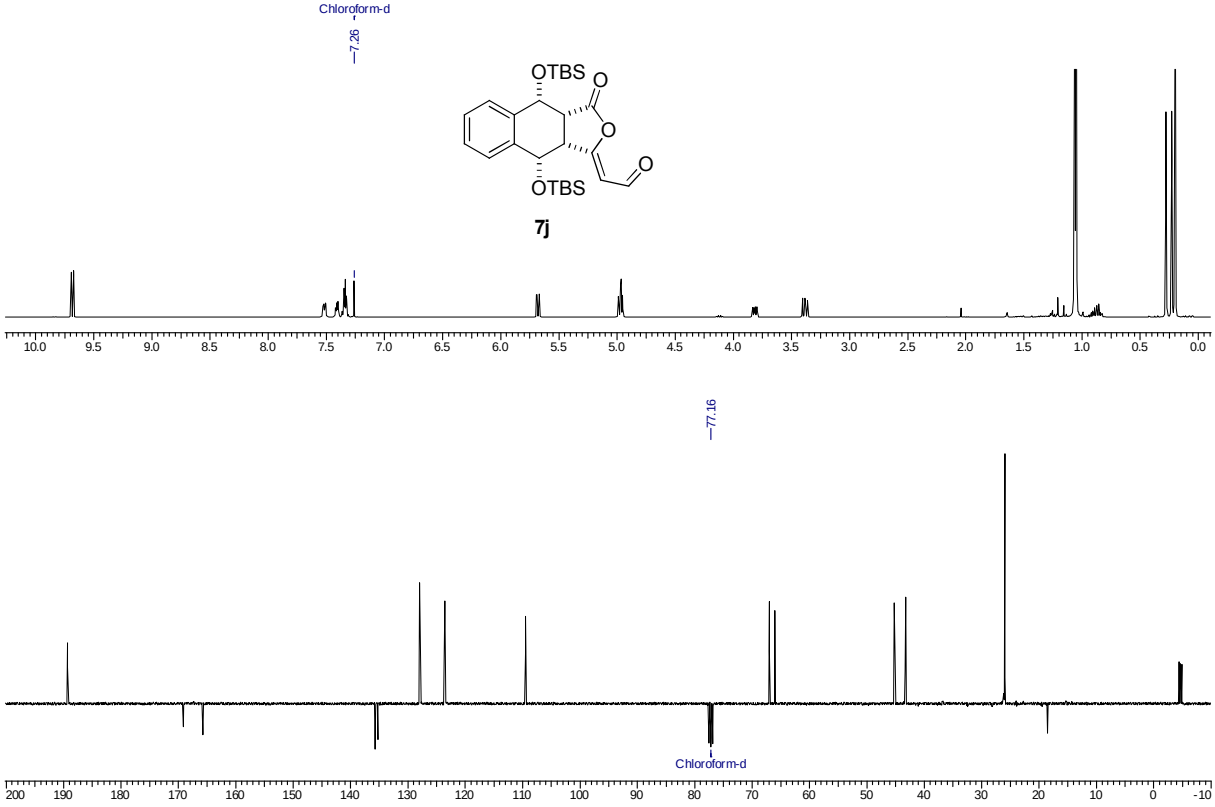
Mp = 178 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55-7.52 (1H, m, CH_{Ar}), 7.44-7.41 (1H, m, CH_{Ar}), 7.34-7.28 (2H, m, 2 x CH_{Ar}), 6.62 (2H, s, 2 x CH_{Ar}), 5.86 (1H, br s, CH), 4.99 (1H, d, J = 7.0 Hz, CH), 4.89 (1H, d, J = 5.6 Hz, CH), 3.79 (3H, s, CH_3), 3.78 (6H, s, 2 x CH_3), 3.78-3.73 (1H, m, CH), 3.36 (1H, dd, J = 10.3 Hz and 7.0 Hz, CH), 1.13 (9H, s, 3 x CH_3), 1.08 (9H, s, 3 x CH_3), 0.30 (6H, s, 2 x CH_3), 0.21 (3H, s, CH_3), 0.20 (3H, s, CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.1 (C), 153.0 (2 x C), 145.6 (C), 136.9 (C), 136.3 (C), 135.8 (C), 130.2 (C), 127.6 (CH), 127.5 (CH), 123.5 (CH), 123.3 (CH), 107.3 (CH), 105.8 (2 x CH), 67.3 (CH), 66.3 (CH), 60.9 (CH_3), 56.1 (2 x CH_3), 44.3 (CH), 44.0 (CH), 26.2 (3 x CH_3), 26.0 (3 x CH_3), 18.5 (2 x C), -4.3 (CH_3), -4.4 (CH_3), -4.7 (CH_3), -4.8 (CH_3); **IR** (ν_{max}): 2954, 2932, 2895, 2886, 2856, 1801, 1684, 1580, 1507, 1469, 1453, 1419, 1331, 1249, 1119, 1074, 1024, 1004 cm^{-1}; **MS**: *m/z* (ESI+) 649 $(M + Na)^+$;**HRMS** found 627.3168 $[M + H]^+$, $C_{34}H_{51}O_7Si_2$ requires 627.3168.



(3a*S*,4*S*,9*R*,9a*R*,*Z*)- and (3a*R*,4*R*,9*S*,9a*S*,*Z*)-[4,9-Bis-(*tert*-butyl-dimethyl-silanyloxy)-3-oxo-3a,4,9,9a-tetrahydro-3*H*-naphtho[2,3-*c*]furan-(1*Z*)-ylidene]-acetaldehyde (7j).

Solvents used for column of chromatography: 6:4 (petroleum ether:diethyl ether)

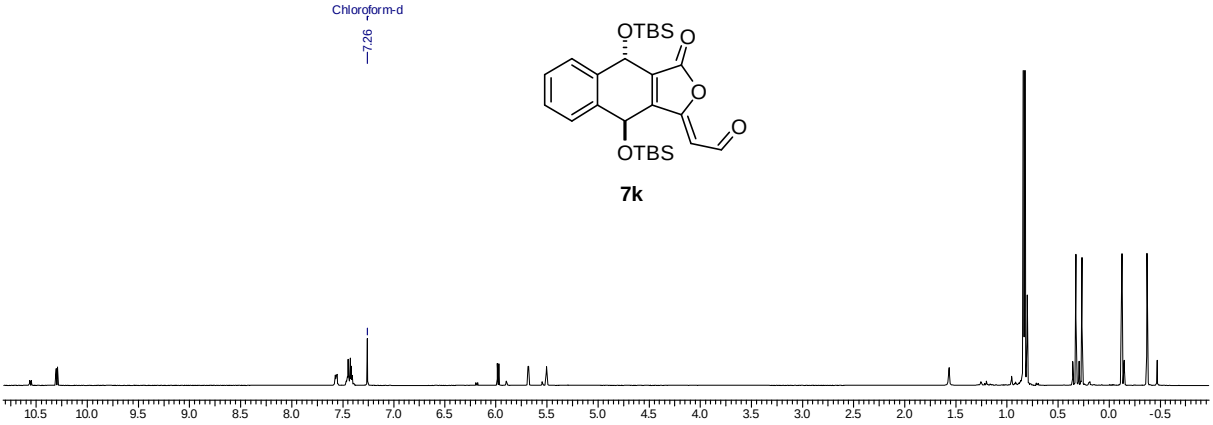
Mp = 151 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.68 (1H, d, *J* = 7.9 Hz, CH), 7.53-7.50 (1H, m, $CH_{Ar.}$), 7.43-7.39 (1H, m, $CH_{Ar.}$), 7.37-7.32 (2H, m, 2 x $CH_{Ar.}$), 5.68 (1H, dd, *J* = 7.9 and 1.5 Hz, CH), 4.99-4.95 (2H, m, 2 x CH), 3.81 (1H, br ddd, *J* = 10.0 and 5.7 and 1.5 Hz, CH), 3.38 (1H, dd, *J* = 10.0 and 7.6 Hz, CH), 1.06 (9H, s, 3 x CH_3), 1.05 (9H, s, 3 x CH_3), 0.28 (3H, s, CH_3), 0.23 (3H, s, CH_3), 0.20 (6H, s, 2 x CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 189.3 (CH), 169.1 (C), 165.7 (C), 135.7 (C), 135.2 (C), 127.9 (2 x CH), 123.5$_3$ (CH), 123.5 (CH), 109.4 (CH), 67.0 (CH), 66.0 (CH), 45.2 (CH), 43.3 (CH), 26.1 (3 x CH_3), 25.9 (3 x CH_3), 18.5 (2 x C), -4.4 (CH_3), -4.6 (CH_3), -4.7 (CH_3), -4.9 (CH_3); **IR** (ν_{max}): 2954, 2930, 2886, 2857, 1823, 1665, 1650, 1254, 1128, 1096, 1070, 1005 cm^{-1}; **MS**: *m/z* (ESI+) 511 $(M + Na)^+$;**HRMS** found 489.2489 $[M + H]^+$, $C_{26}H_{41}O_5Si_2$ requires 489.2487.



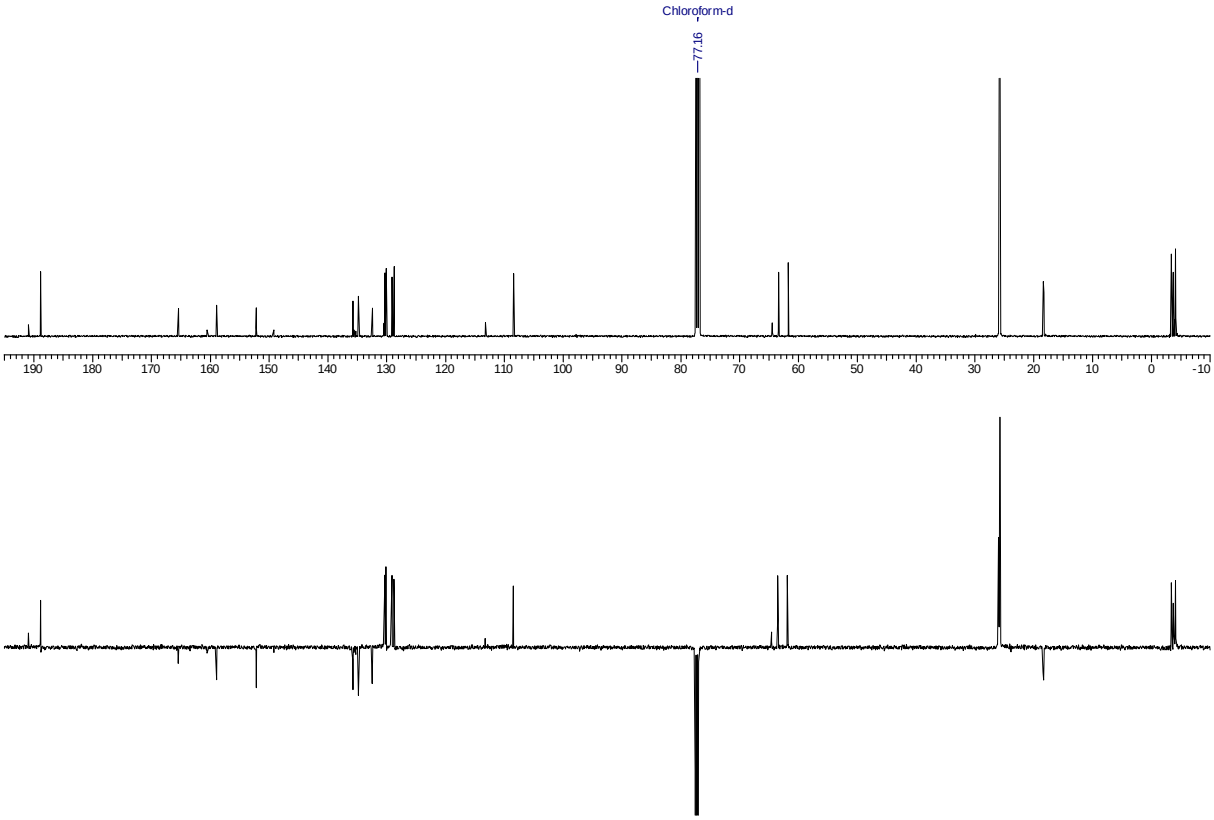
(*Z*)-2-((4*S*,9*S*)- and (*Z*)-2-((4*R*,9*R*)-4,9-bis(*tert*-butyldimethylsilyloxy)-3-oxonaphtho[2,3-*c*]furan-1(3*H*,4*H*,9*H*)-ylidene)acetaldehyde (7k).

*Solvents used for column of chromatography of **3o**: 10:0 to 8:2 (petroleum ether:diethyl ether)*

Mp = 126-129 °C**; ^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.30 (1H, d, J = 7.8 Hz, CH), 7.59-7.55 (1H, m, $CH_{Ar.}$), 7.47-7.39 (3H, m, $CH_{Ar.}$), 5.98 (1H, d, J = 7.8 Hz, CH), 5.68 (1H, br s, CH), 5.51 (1H, br s, CH), 0.84 (9H, s, 3 x CH_3), 0.82 (9H, s, 3 x CH_3), 0.32 (3H, s, CH_3), 0.26 (3H, s, CH_3), -0.12 (3H, s, CH_3), -0.37 (3H, s, CH_3), **^{13}C NMR** (125 MHz, $CDCl_3$) δ 188.8. (CH), 165.4 (C), 159.0 (C), 152.2 (C), 135.8 (C), 134.8 (C), 132.5 (C), 130.3 (CH), 130.1 (CH), 129.1 (CH), 128.8 (CH), 108.4 (CH), 63.4 (CH), 61.7 (CH), 25.9 (3 x CH_3), 25.7 (3 x CH_3), 18.4 (C), 18.3 (C), -3.4 (CH_3), -3.7 (CH_3), -4.1$_2$ (CH_3), -4.1$_4$ (CH_3); **IR** (ν_{max}): 2953, 2930, 2886, 2858, 1802, 1667, 1649, 1252, 1130, 1085, 1063, 1022, 1005, 951 cm^{-1}; **MS**: *m/z* (ESI+) 509 $(M + Na)^+$;**HRMS** found 487.2330 $[M + H]^+$, $C_{26}H_{39}O_5Si_2$ requires 487.2331.



7k



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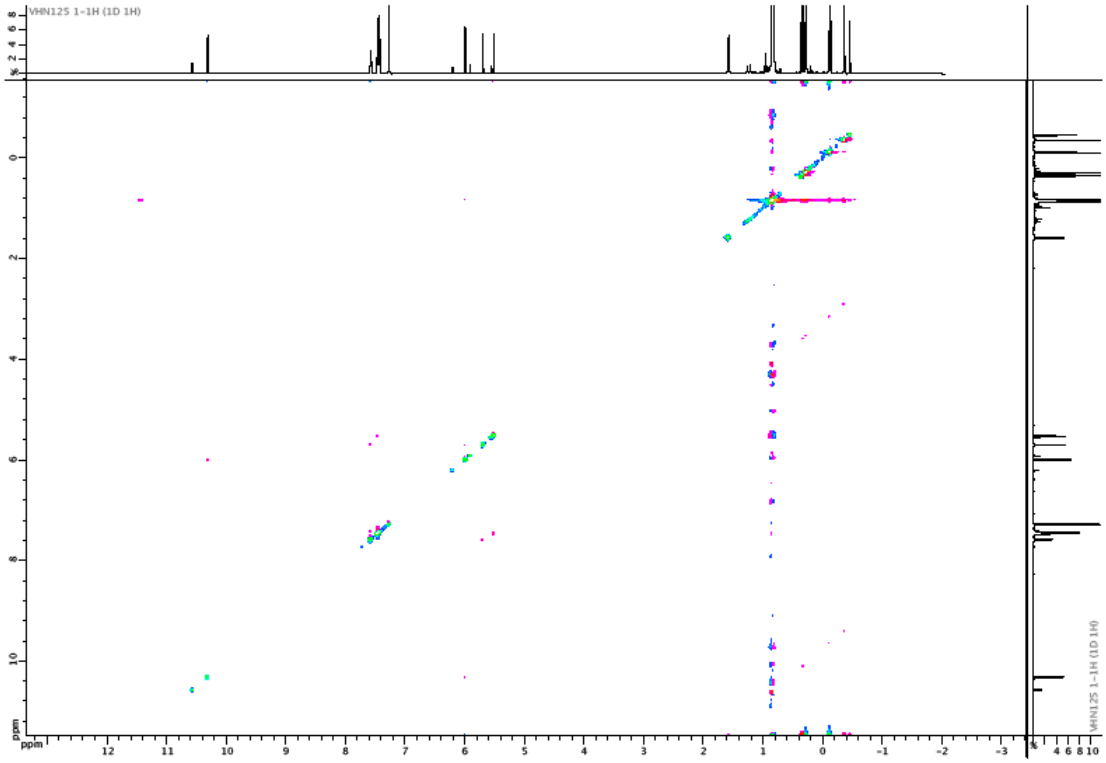
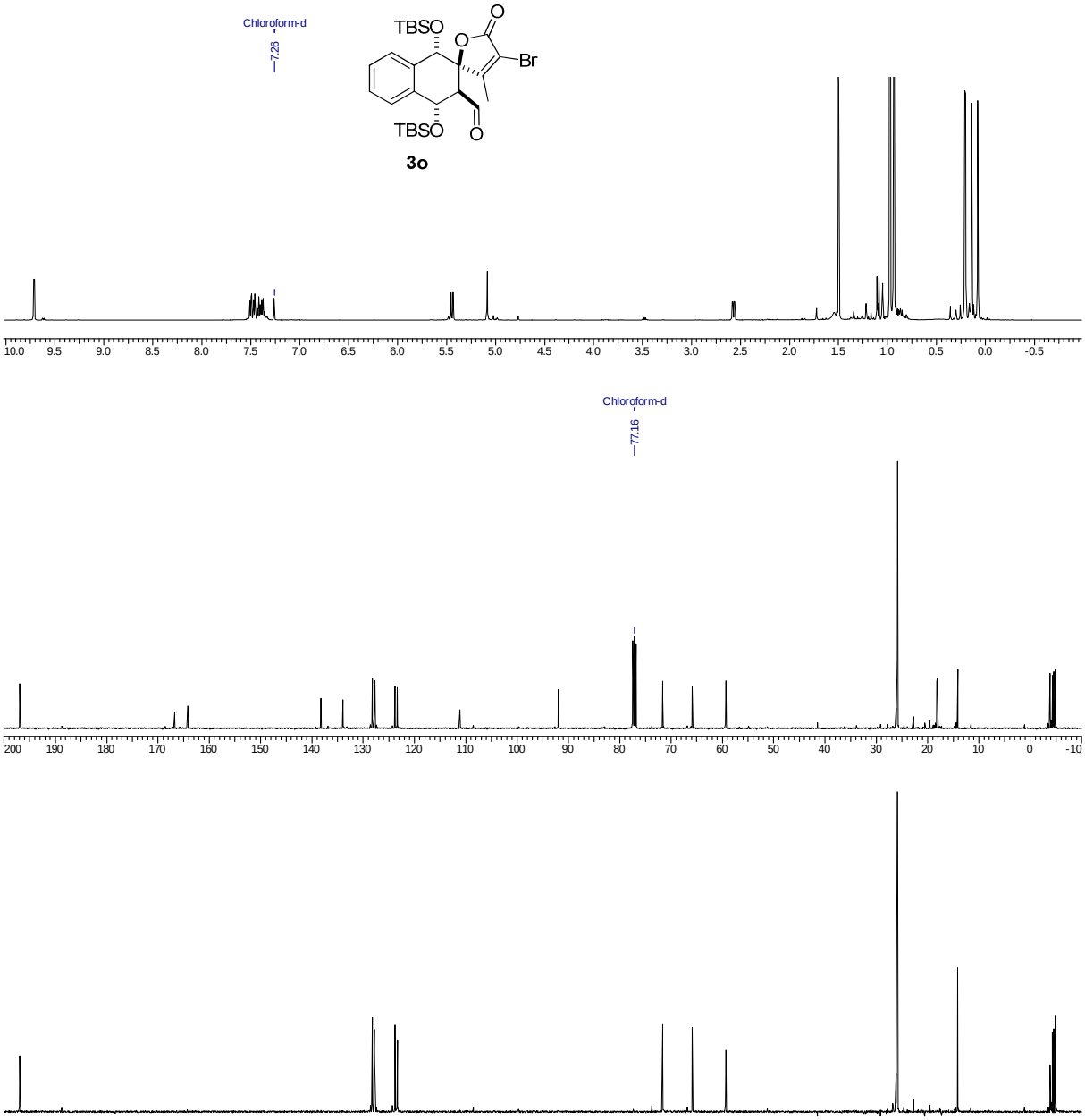
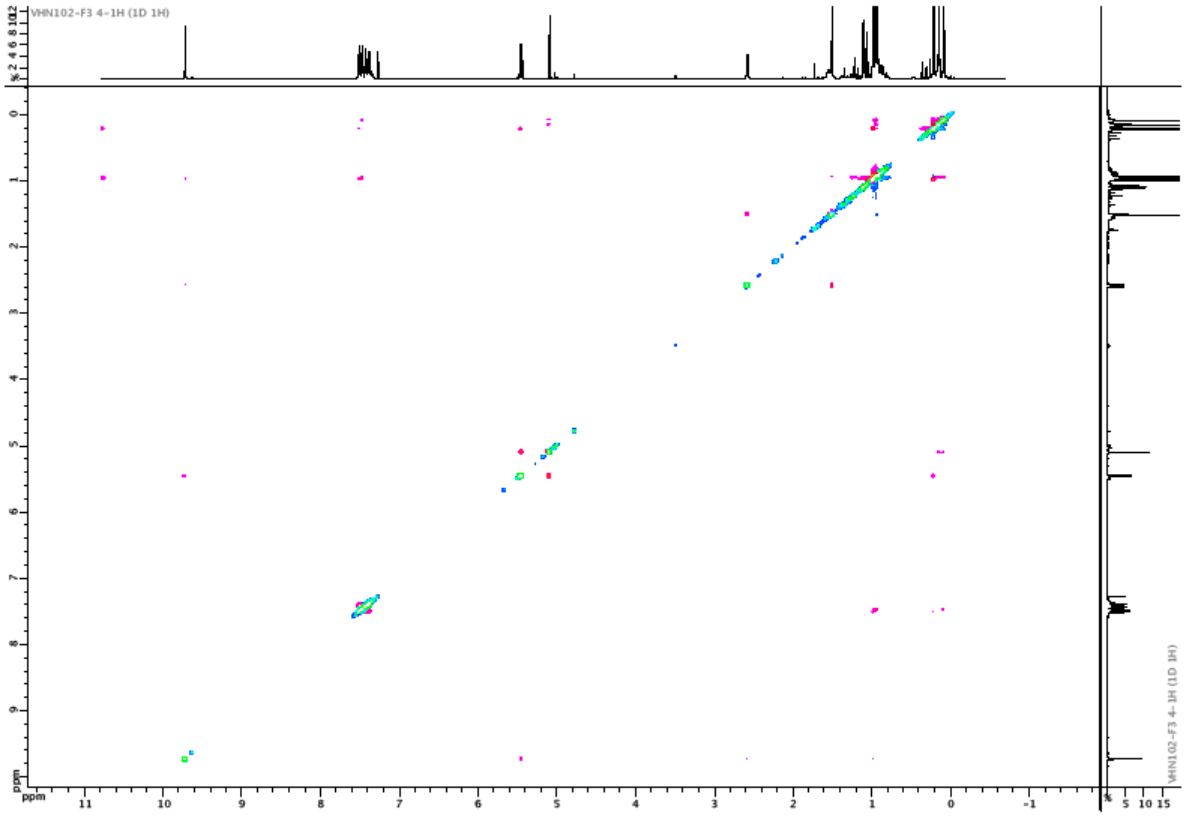


*Solvents used for column of chromatography of **3o**: 10:0 to 9:1 (petroleum ether:diethyl ether)*

(1'*S*,2*R*,3'*S*,4'*S*)- and (1'*R*,2*S*,3'*R*,4'*R*)-4-bromo-1',4'-bis(*tert*-butyldimethylsilyloxy)-3-methyl-5-oxo-3',4'-dihydro-1'*H*,5*H*-spiro[furan-2,2'-naphthalene]-3'-carbaldehyde (3o). **Mp** = 67°C; **^{1}H NMR** (500MHz, $CDCl_3$) δ 9.71 (1H, d, *J* = 3.8 Hz, CH), 7.50–7.34 (4H, m, 4 x CH_{Ar}), 5.44 (1H, d, *J* = 10.1 Hz, CH), 5.08 (1H, s, CH), 2.57 (1H, dd, *J* = 10.1 and 3.8 Hz, CH), 1.50 (3H, s, CH_3), 0.98 (9H, s, 3 x CH_3), 0.93 (9H, s, 3 x CH_3), 0.21 (3H, s, CH_3), 0.20 (3H, s, CH_3), 0.14 (3H, s, CH_3), 0.08 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.0 (CH), 166.8 (C), 164.2 (C), 138.3 (C), 134.0 (C), 128.2 (CH), 127.8 (CH), 123.8 (CH), 123.3 (CH), 111.2 (C), 92.0 (C), 71.7 (CH), 65.9 (CH), 59.4 (CH), 25.9 (6 x CH_3), 18.2 (C), 18.1 (C), 14.1 (CH_3), -3.9 (CH_3), -4.3 (CH_3), -4.6 (CH_3), -4.9 (CH_3); **IR** (ν_{max}): 2954, 2930, 2886, 2857, 1777, 1729, 1472, 1462, 1256, 1178, 1132, 1071, 1004 cm^{-1}; **MS**: *m/z* (ESI+) 605 (M + Na)$^+$;**HRMS** found 598.2020 $[M + NH_4]^+$, $C_{27}H_{45}N\,O_5BrSi_2$ requires 598.2014.

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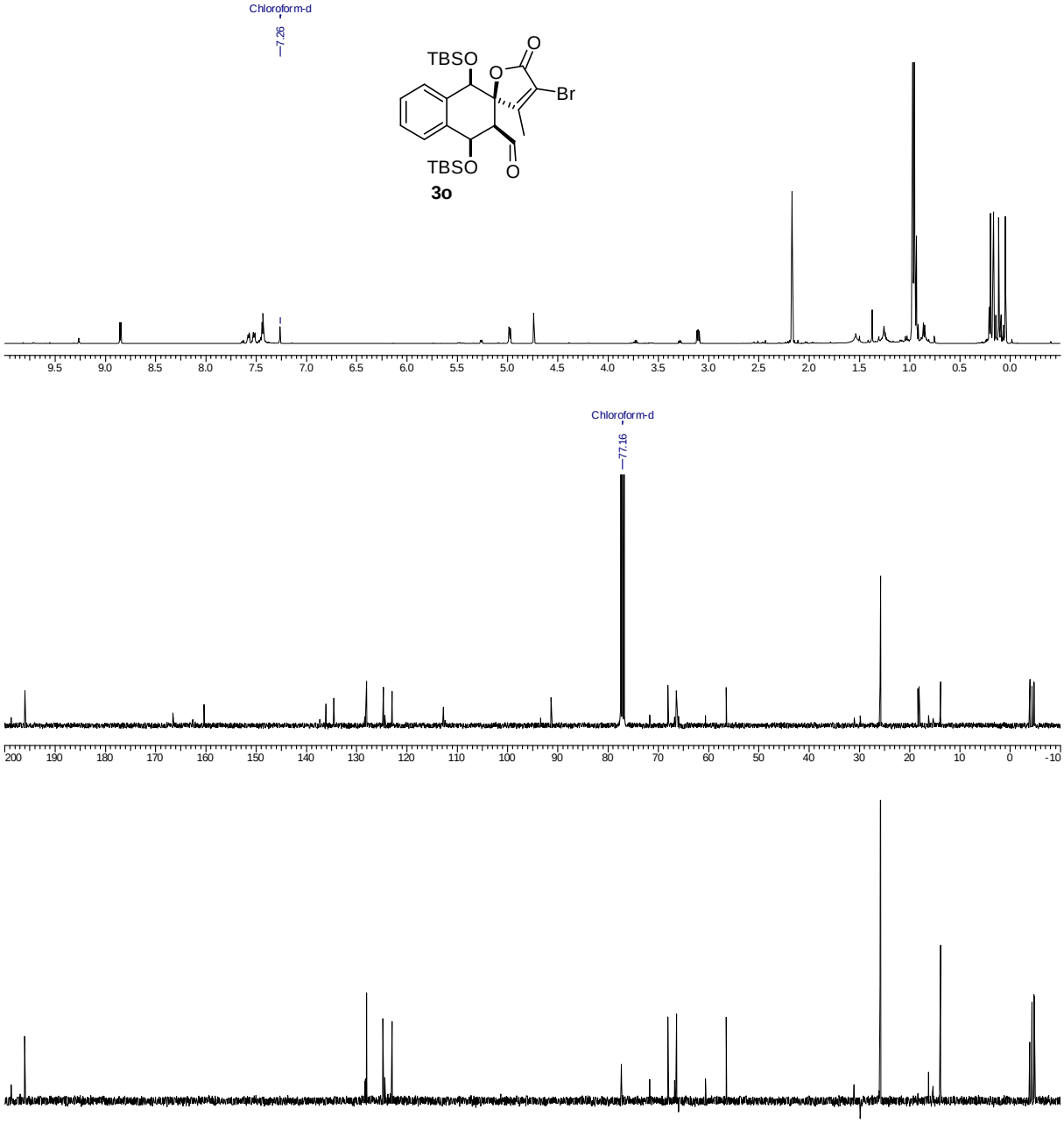
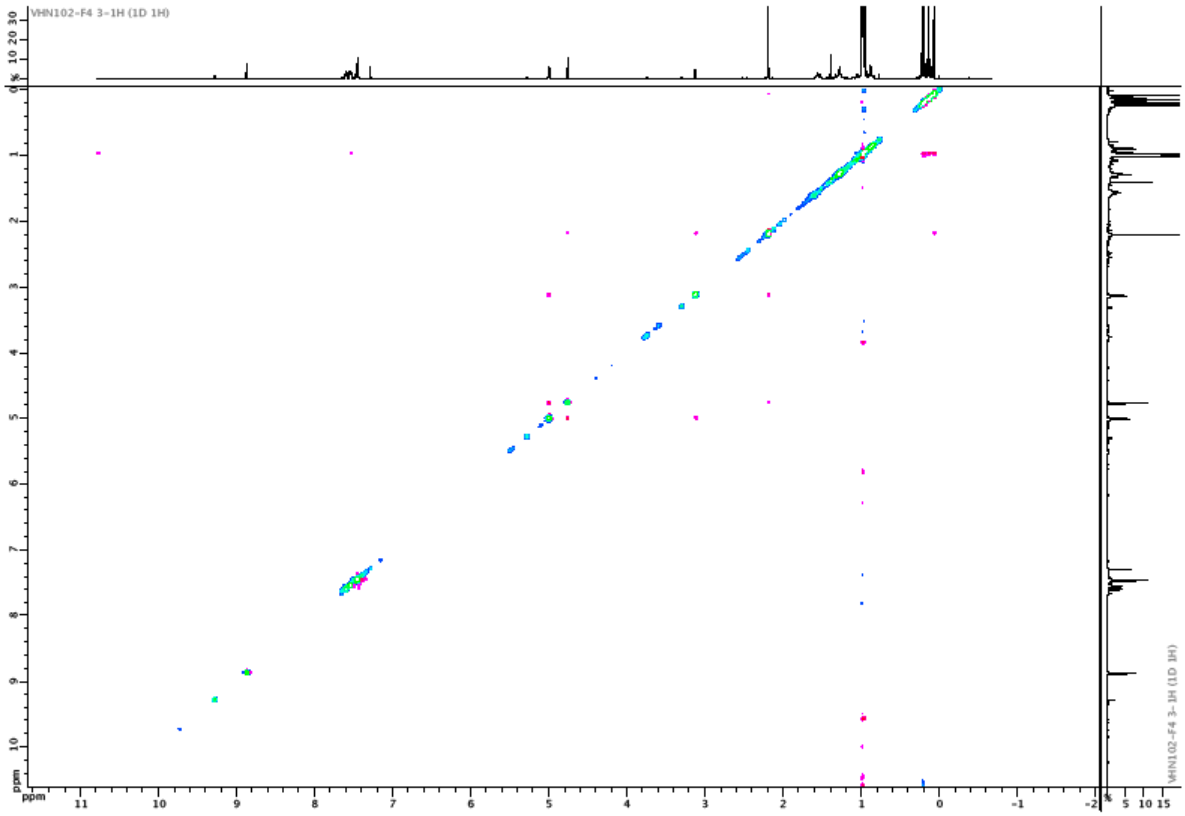
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
VHN102-F3 4-1H (1D 1H)

(1'*R*,2*R*,3'*S*,4'*R*)- and (1'*S*,2*S*,3'*R*,4'*S*)-4-bromo-1',4'-bis(tert-butyldimethylsilyloxy)-3-methyl-5-oxo-3',4'-dihydro-1'H,5H-spiro[furan-2,2'-naphthalene]-3'-carbaldehyde (3o). Mp = 230 °C**; ^{1}H NMR** (500MHz, $CDCl_3$) δ 8.84 (1H, d, *J* = 4.5 Hz, CH), 7.59-7.56 (1H, m, CH_{Ar}), 7.53-7.50 (1H, m, CH_{Ar}), 7.46-7.41 (2H, m, 2 x CH_{Ar}), 4.98 (1H, d, *J* = 7.0 Hz, CH), 4.74 (1H, s, CH), 3.10 (1H, dd, *J* = 7.0 and 4.5 Hz, CH), 2.17 (3H, s, CH_3), 0.97 (9H, s, 3 x CH_3), 0.96 (3H, s, CH_3), 0.20 (3H, s, CH_3), 0.17 (3H, s, CH_3), 0.11 (3H, s, CH_3), 0.05 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.1 (CH), 166.6 (C), 160.4 (C), 136.1 (C), 134.6 (C), 128.0_9 (CH), 128.0_6 (CH), 124.8 (CH), 123.0 (CH), 112.8 (C), 91.3 (C), 68.1 (CH), 66.4 (CH), 56.5 (CH), 25.9 (3 x CH_3), 25.8 (3 x CH_3), 18.4 (C), 18.1 (C), 13.9 (CH_3), -3.9 (CH_3), -4.3 (CH_3), -4.7 (CH_3), -4.8 (CH_3); **IR** (ν_{max}): 2953, 2929, 2886, 2856, 1758, 1729, 1471, 1461, 1253, 1186, 1124, 1069, 1025, 1004, 991 cm^{-1}; **MS**: *m/z* (ESI+) 605 $(M + Na)^+$; **HRMS** found 598.2020 $[M + NH_4]^+$, $C_{27}H_{45}N\,O_5BrSi_2$ requires 598.2014.

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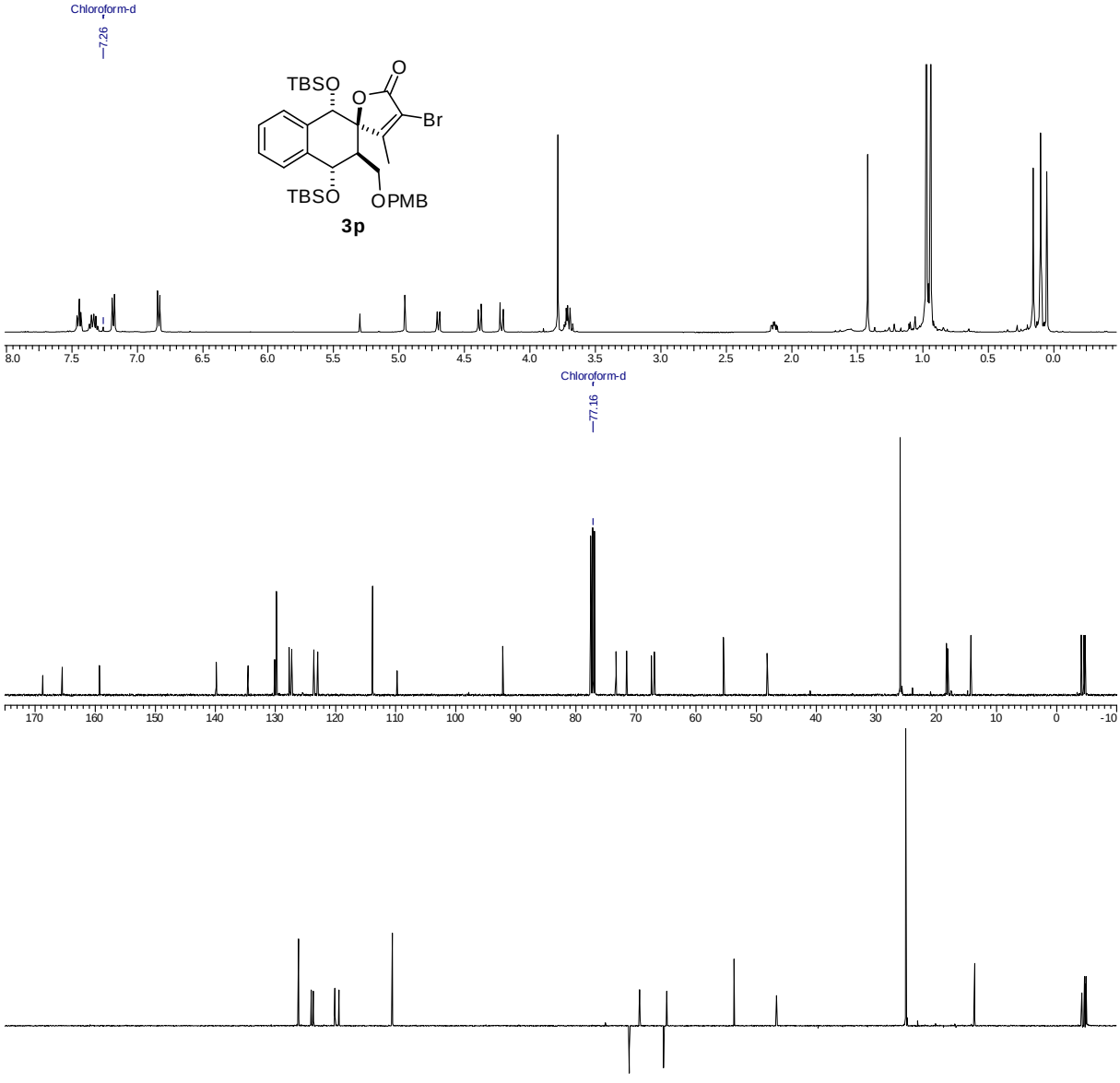
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
%
5
10
15
VHN102-F4 3-1H (1D 1H)

*Solvents used for column of chromatography of **3p**: 10:0 to 8:2 (petroleum ether:diethyl ether)*

(1'*S*,2*R*,3'*S*,4'*S*)- and (1'*R*,2*S*,3'*R*,4'*R*)-4-bromo-1',4'-bis(tert-butyldimethylsilyloxy)-3'-((4-methoxybenzyloxy)methyl)-3-methyl-3',4'-dihydro-1'H,5H-spiro[furan-2,2'-naphthalen]-5-one (3p). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.43 (2H, m, 2 x CH_{Ar}), 7.38-7.29 (2H, m, 2 x CH_{Ar}), 7.18 (2H, d, J = 8.5 Hz, 2 x CH_{Ar}), 6.84 (2H, d, J = 8.5 Hz, 2 x CH_{Ar}), 4.96 (1H, s, CH), 4.70 (1H, d, J = 10.3 Hz, CH), 4.38 (1H, d, J = 11.1 Hz, CH_2), 4.22 (1H, d, J = 11.1 Hz, CH_2), 3.78 (3H, s, CH_3), 3.75-3.67 (2H, m, CH_2), 2.13 (1H, td, J = 10.3 and 4.0 Hz, CH), 1.42 (3H, s, CH_3), 0.97 (9H, m, 3 x CH_3), 0.94 (9H, m, 3 x CH_3), 0.16 (3H, s, CH_3), 0.10 (6H, s, 2 x CH_3), 0.05 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7 (C), 165.5 (C), 159.3 (C), 139.8 (C), 134.5 (C), 130.1 (C), 129.8 (2 x CH), 127.6 (CH), 127.2 (CH), 123.6 (CH), 122.9 (CH), 113. 8 (2 x CH), 109.7 (C), 92.1 (C), 73.3 (CH_2), 71.5 (CH), 67.4 (CH_2), 66.9 (CH), 55.4 (CH_3), 48.1 (CH), 26.0 (6 x CH_3), 18.3 (C), 18.1 (C), 14.2 (CH_3), -4.1 (CH_3), -4.6 (CH_3), -4.7 (CH_3), -4.8 (CH_3); **IR** (ν_{max}): 2953, 2929, 2885, 2857, 1772, 1513, 1471, 1462, 1249, 1177, 1130, 1092, 1069, 1031, 1008 cm^{-1}; **MS**: *m/z* (ESI+) 727 (M + Na)$^{+}$;**HRMS** found 720.2752 $[M + NH_4]^{+}$, $C_{35}H_{55}NO_6BrSi_2$ requires 720.2746.



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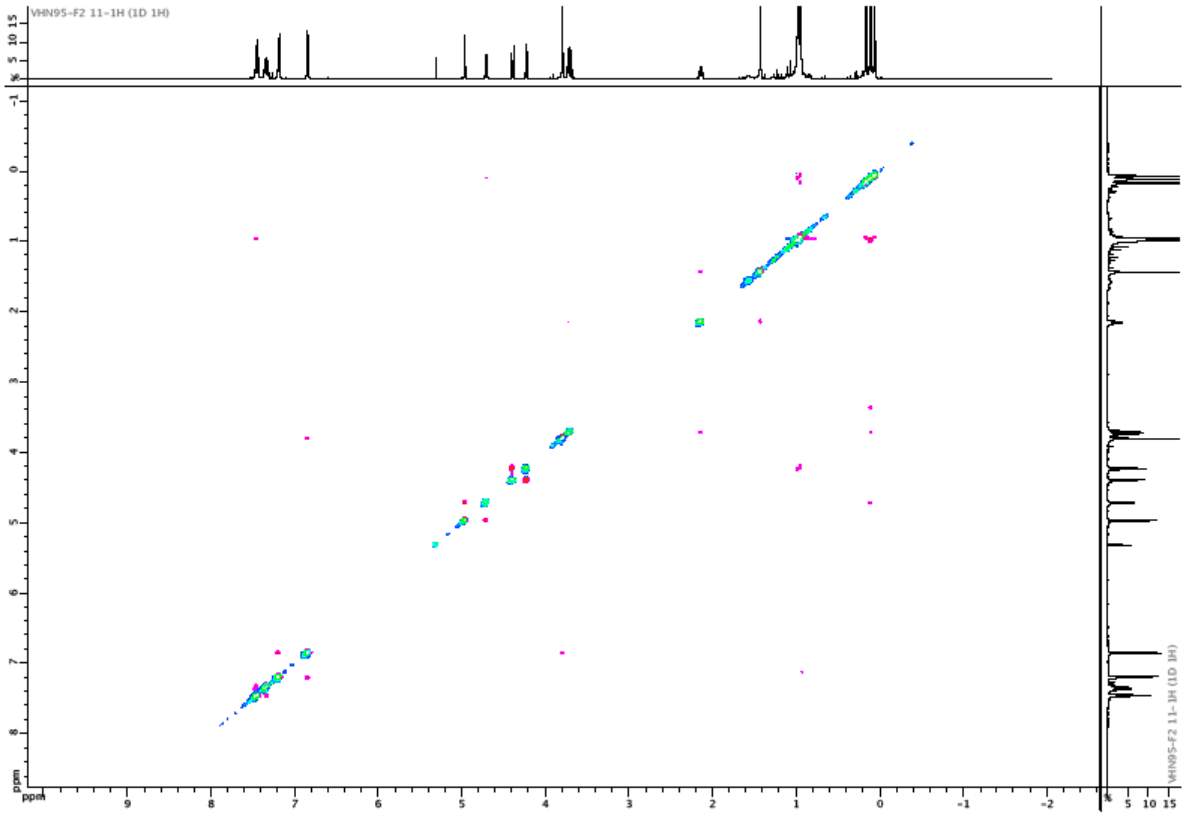
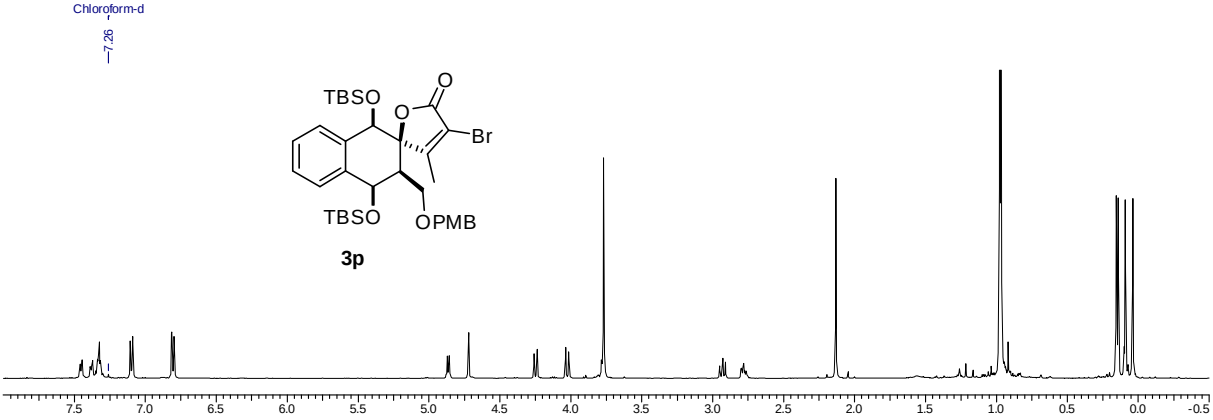
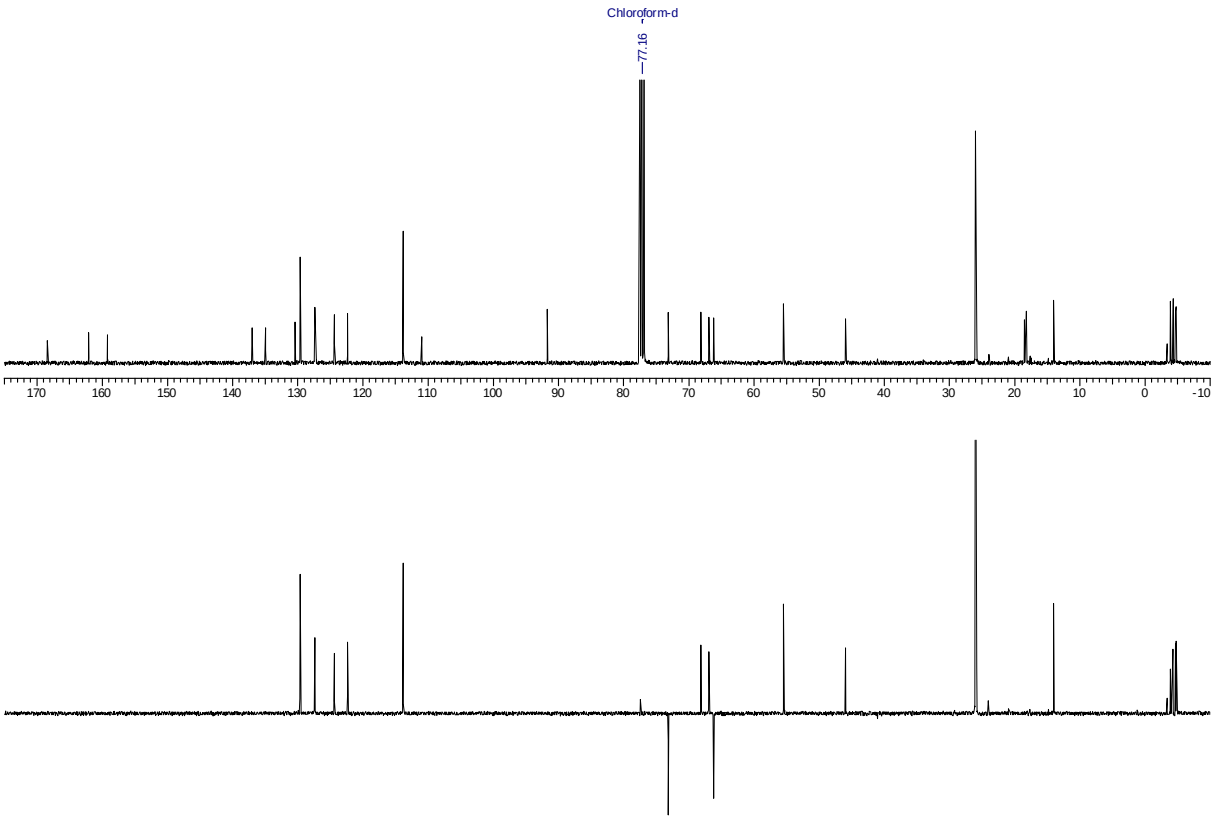


(1'*R*,2*R*,3'*S*,4'*R*)- and (1'*S*,2*S*,3'*R*,4'*S*)-4-bromo-1',4'-bis(tert-butyldimethylsilyloxy)-3'-((4-methoxybenzyloxy)methyl)-3-methyl-3',4'-dihydro-1'H,5H-spiro[furan-2,2'-naphthalen]-5-one (3p). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.44 (1H, m, CH_{Ar}), 7.40-7.31 (3H, m, 3 x CH_{Ar}), 7.10 (2H, d, J = 8.7 Hz, 2 x CH_{Ar}), 6.81 (2H, d, J = 8.7 Hz, 2 x CH_{Ar}), 4.86 (1H, d, J = 6.8 Hz, CH), 4.72 (1H, s, CH), 4.25 (1H, d, J = 11.0 Hz, CH_2), 4.03 (1H, d, J = 11.0 Hz, CH_2), 3.79-3.75 (4H, m, CH_2 and CH_3), 2.93 (1H, dd, J = 10.3 and 9.3 Hz, CH_2), 2.81-2.76 (1H, m, CH), 2.13 (3H, s, CH_3), 0.98 (9H, s, 3 x CH_3), 0.97 (9H, s, 3 x CH_3), 0.15 (3H, s, CH_3), 0.14 (3H, s, CH_3), 0.09 (3H, s, CH_3), 0.04 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4 (C), 162.1 (C), 159.2 (C), 137.0 (C), 134.9 (C), 130.4 (CH), 129.6 (2 x CH), 127.4 (2 x CH), 124.3 (CH), 122.3 (CH), 113.8 (2 x CH), 111.0 (C), 91.7 (C), 73.1 (CH_2), 68.1 (CH), 66.9 (CH), 66.1 (CH_2), 55.4 (CH), 45.9 (CH), 25.9 (6 x CH_3), 18.4 (C), 18.2 (C), 14.0 (CH_3), -3.9 (CH_3), -4.3 (CH_3), -4.7 (CH_3), -4.8 (CH_3); **IR** (ν_{max}): 2953, 2929, 2885, 2856, 1754, 1513, 1471, 1462, 1248, 1129, 1072, 1025, 1005 cm^{-1}; **MS**: *m/z* (ESI+) 727 (M + Na)$^{+}$;**HRMS** found 720.2747 [M + NH_4^{+}], $C_{35}H_{55}NO_6BrSi_2$ requires 720.2746.





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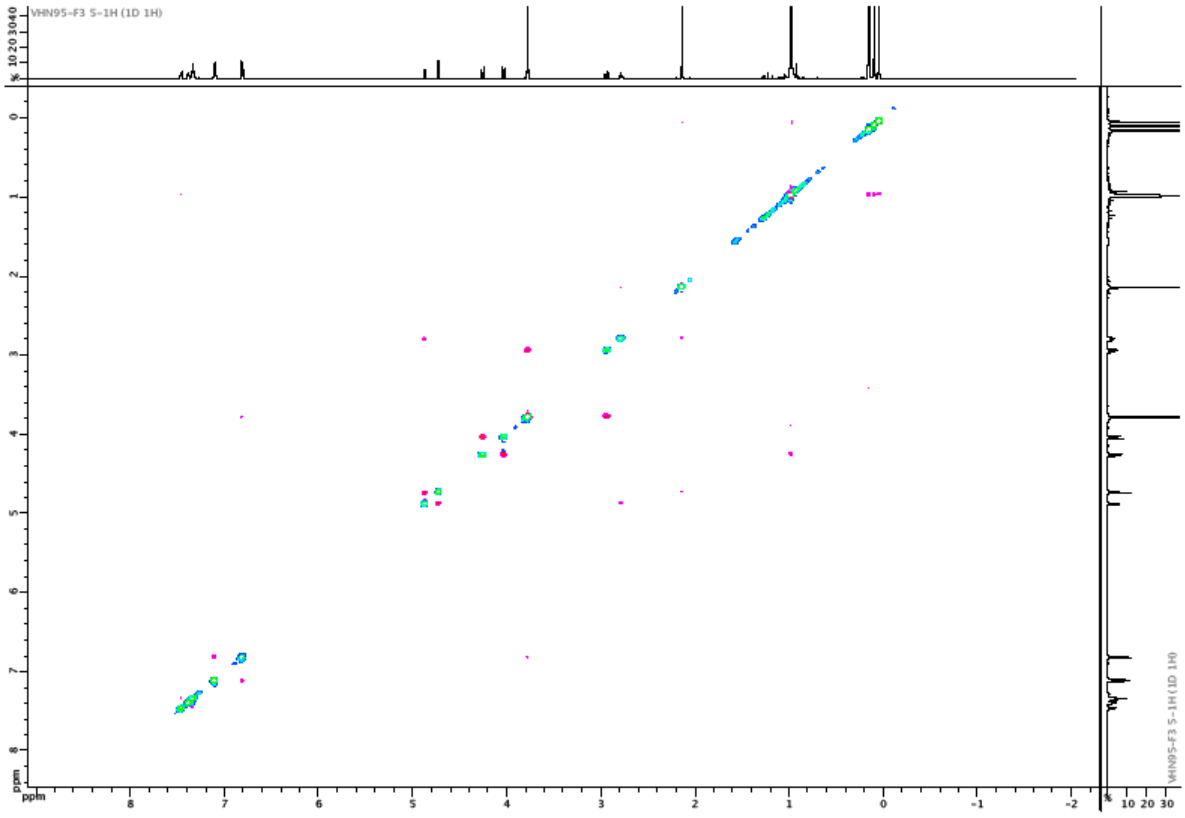
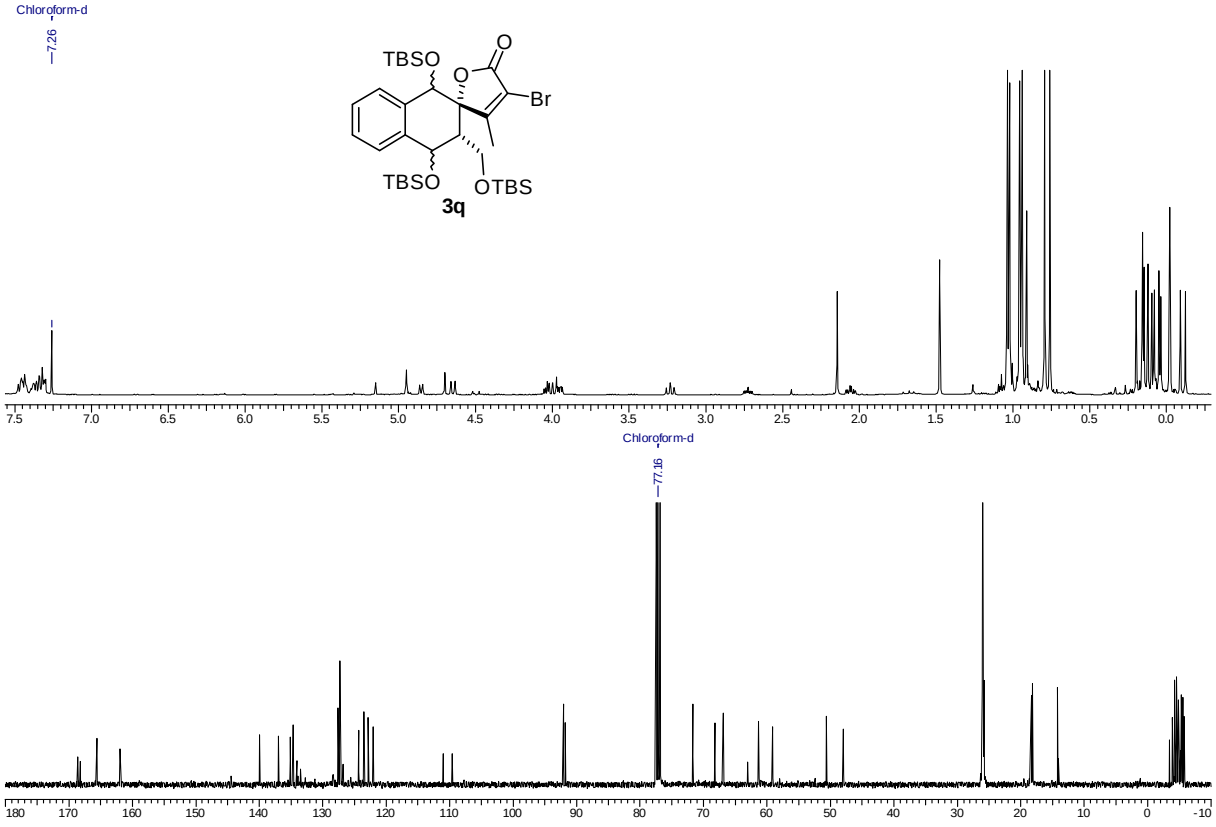


4-bromo-1',4'-bis(tert-butyldimethylsilyloxy)-3'-((tert-butyldimethylsilyloxy)methyl)-3-methyl-3',4'-dihydro-1'H,5H-spiro[furan-2,2'-naphthalen]-5-one (3q).

*Solvents used for column of chromatography of **3q**: 10:0 to 9:1 (petroleum ether:diethyl ether)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.30 (m, CH_{Ar}), 4.95 (1H, s, CH), 4.86 (1H, d, J = 7.0 Hz, CH), 4.70 (1H, s, CH), 4.65 (1H, d, J = 10.5 Hz, CH), 4.05-3.93 (3H, m, CH_2 + CH_2), 3.23 (1H, t, J = 10.3 Hz, CH_2), 2.75-2.70 (1H, m, CH), 2.14 (3H, s, CH_3), 2.06 (1H, td, J = 10.3 and 4.3 Hz, CH), 1.48 (3H, s, CH_3), 1.04 (9H, s, 3 x CH_3), 1.02 (9H, s, 3 x CH_3), 0.96 (9H, s, 3 x CH_3), 0.94 (9H, s, 3 x CH_3), 0.80 (9H, s, 3 x CH_3), 0.76 (9H, s, 3 x CH_3), 0.20 (3H, s, CH_3), 0.16 (3H, s, CH_3), 0.13 (3H, s, CH_3), 0.15 (3H, s, CH_3), 0.12 (3H, s, CH_3), 0.10 (3H, s, CH_3), 0.08 (3H, s, CH_3), 0.05 (3H, s, CH_3), 0.04 (3H, s, CH_3), -0.02 (3H, s, CH_3), -0.09 (3H, s, CH_3), -0.12 (3H, s, CH_3),**^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.6 (C), 168.2 (C), 165.6 (C), 161.9 (C), 139.9 (C), 137.0 (C), 135.1 (C), 134.7 (C), 127.6 (CH), 127.3 (2 x CH), 127.2 (CH), 124.3 (CH), 123.5 (CH), 122.8 (CH), 122.1 (CH), 111.0 (C), 109.6 (C), 92.1 (C), 91.8 (C), 71.7 (CH), 68.2 (CH), 67.0 (CH), 66.9 (CH), 61.3 (CH_2), 59.1 (CH_2), 50.6 (CH), 48.0 (CH), 26.0 (12 x CH_3), 18.5 (C), 18.4 (C), 18.3 (C), 18.2 (C), 18.1$_4$ (C), 18.1$_2$ (C), 14.2 (CH_3), 14.1 (CH_3), -3.9 (CH_3), -4.2$_6$ (CH_3), 4.2$_9$ (CH_3), -4.5$_5$ (CH_3), -4.5$_6$ (CH_3), -4.6$_1$ (CH_3), -4.8 (CH_3), -4.9 (CH_3), -5.3 (CH_3), -5.4 (CH_3), -5.6 (CH_3), 5.8 (CH_3); **IR** (ν_{max}): 2953, 2929, 2886, 2857, 1775, 1476, 1462, 1253, 1130, 1099, 1069, 1006 cm^{-1}; **MS**: *m/z* (ESI+) 721 (M + Na)$^+$; **HRMS** found 716.3022 [M + NH_4^+], $C_{33}H_{61}NO_5Si_3Br$ requires 716.3022.



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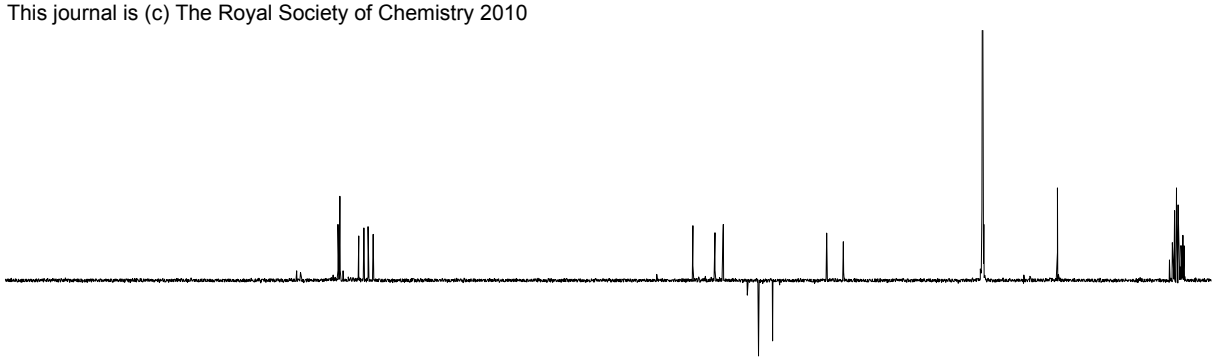
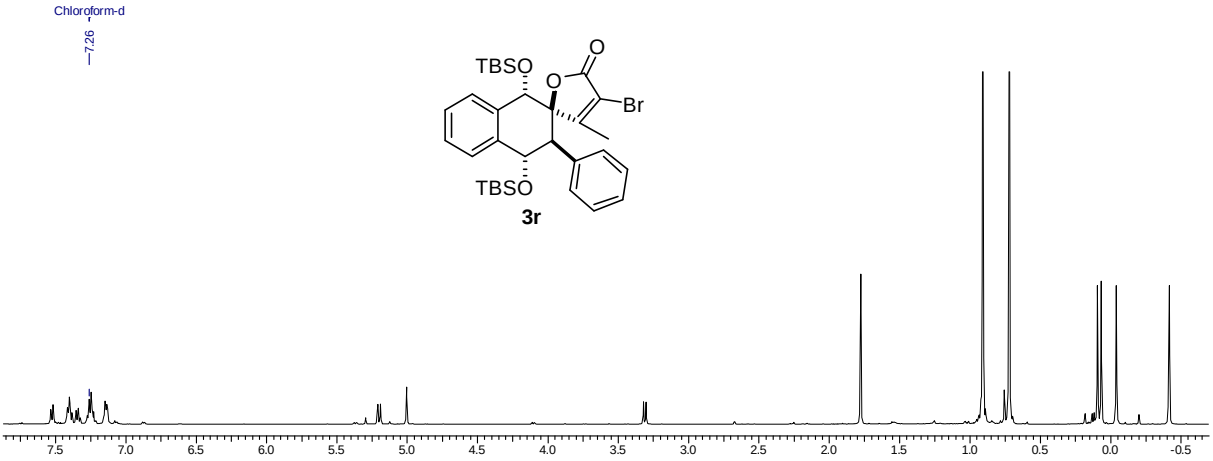
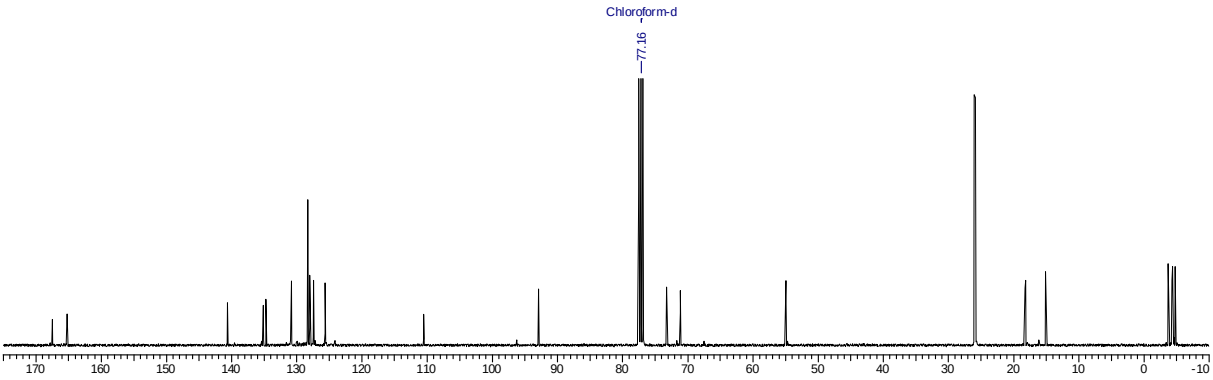
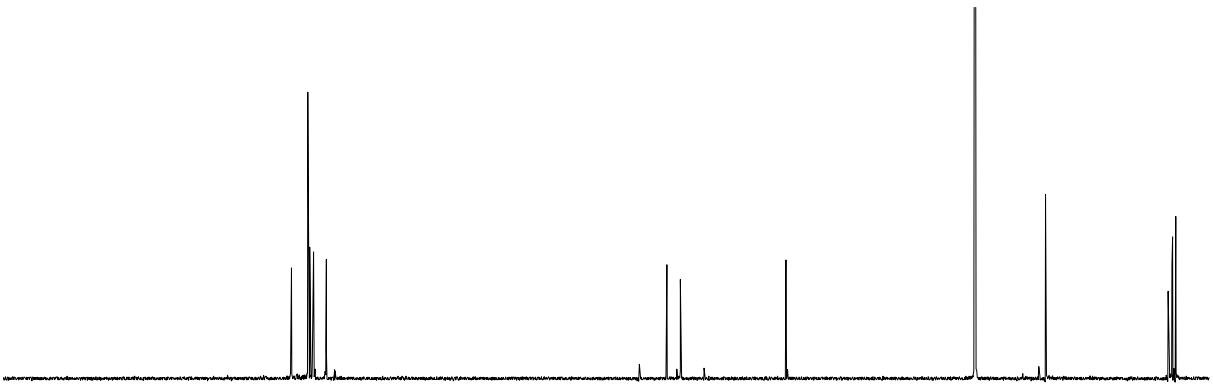


Solvents used for column of chromatography of ***3r****: 10:0 to 9:1 (petroleum ether:diethyl ether)*

(1'*S*,2*R*,3'*S*,4'*S*)- and (1'*R*,2*S*,3'*R*,4'*R*)-4-bromo-1',4'-bis(tert-butyldimethylsilyloxy)-3'-phenyl-3-methyl-3',4'-dihydro-1'H,5H-spiro[furan-2,2'-naphthalen]-5-one (3r). Mp = 151 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54-7.52 (1H, m, 1 x CH_{Ar}), 7.42-7.33 (4H, m, 4 x CH_{Ar}), 7.28-7.23 (2H, m, 2 x CH_{Ar}), 7.15-7.13 (2H, m, 2 x CH_{Ar}), 5.21 (1H, d, J = 9.5 Hz, CH), 5.01 (1H, s, CH), 3.31 (1H, d, J = 9.5 Hz, CH), 1.78 (3H, s, CH_3), 0.91 (9H, s, 3 x CH_3), 0.73 (9H, s, 3 x CH_3), 0.10 (3H, s, CH_3), 0.07 (3H, s, CH_3), -0.04 (3H, s, CH_3), -0.41 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5 (C), 165.2 (C), 140.6 (C), 135.1 (C), 134.7 (C), 130.8 (2 x CH), 128.3 (2 x CH), 128.2 (CH), 128.2 (CH), 127.4 (CH), 125.6 (CH), 125.5 (CH), 110.4 (C), 92.8 (C), 73.2 (CH), 71.1 (CH), 54.9 (CH), 26.0 (CH_3), 25.83 (CH_3), 18.3 (C), 18.1 (C), 15.1 (CH_3), -3.7 (C), -4.3 (C), -4.4 (C), -4.8 (C); **IR** (ν_{max}): 2954, 2929, 2886, 2857, 1778, 1471, 1459, 1253, 1181, 1130, 1074, 1022, 989 cm^{-1}; **MS**: *m/z* (ESI+) 721 $(M + Na)^+$; **HRMS** found 629.2112 $[M + H^+]$, $C_{32}H_{46}BrO_4Si_2$ requires 629.2113.







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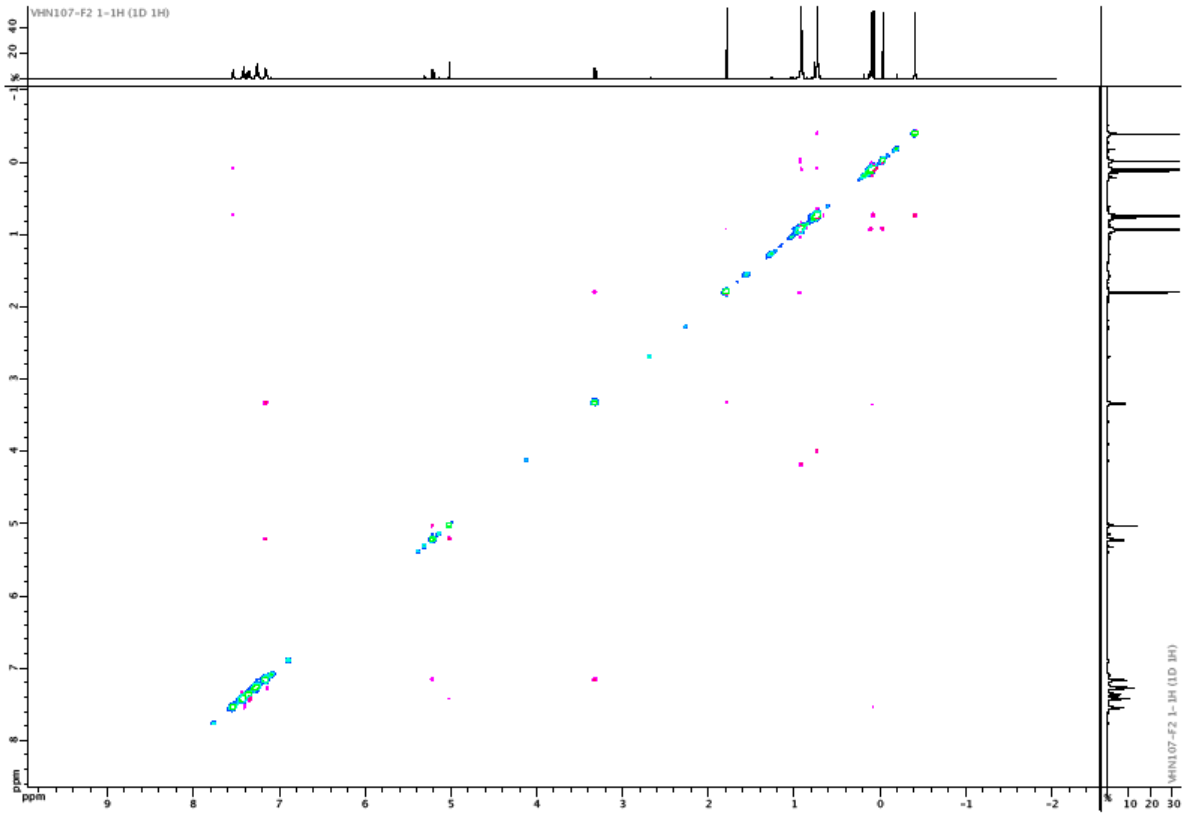

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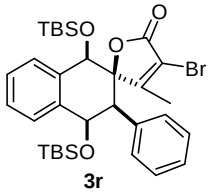
(1'*R*,2*R*,3'*S*,4'*R*)- and (1'*S*,2*S*,3'*R*,4'*S*)-4-bromo-1',4'-bis(tert-butyldimethylsilyloxy)-3'-phenyl-3-methyl-3',4'-dihydro-1'H,5H-spiro[furan-2,2'-naphthalen]-5-one (3r)

3r is in mixture with the remaining lactone 2r



3r

Carasteristic signals

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (1H, d, J = 8.5 Hz, CH), 4.97 (1H, s, CH), 3.75 (1H, d, J = 8.5 Hz, CH), 2.26 (3H, s, CH_3), 0.94 (9H, s, 3 x CH_3), 0.70 (9H, s, 3 x CH_3), 0.16 (3H, s, CH_3), 0.10 (3H, s, CH_3), 0.09 (3H, s, CH_3), -0.10 (3H, s, CH_3), **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0 (C), 160.7 (C), 138.3 (C), 135.2 (C), 132.9 (C), 131.3 (2 x CH), 128.3 (CH), 127.6 (CH), 127.3_3 (CH), 127.2_7 (2 x CH), 127.2 (CH), 124.6 (CH), 123.2 (CH), 109.9 (C), 92.9 (C), 68.9 (CH), 67.3 (CH), 52.4 (CH), 25.9 (3 x CH_3), 25.6 (3 x CH_3), 18.2 (C), 18.1 (C), 14.6 (CH_3), -3.6 (CH_3), -4.2 (CH_3), -4.6 (CH_3), -4.7 (CH_3).