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Stereoselective routes to aryl substituted γ-buyrolactones and their application towards the synthesis of highly oxidised furanocembranoids

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General Methods

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under pre-dried nitrogen. NMR spectra were recorded on a Bruker Avance 300, 400, 600 and 600 Kryo spectrometers using the solvent peak as internal reference ($CDCl_3$: δ H 7.26; δ C: 77.0). Multiplicities are indicated, s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet); coupling constants (*J*) are in Hertz (Hz).

Mass spectra (MS EI and LSI) were recorded with a Finnigan MAT 95 or Varian MAT 311A. All reactions were monitored by thin–layer chromatography (TLC) using Merck silica gel plates 60 F254; visualization was accomplished with UV light and/or staining with vanillin-sulfuric acid followed by heating. Standard chromatography procedures were followed (particle size 63 – 200 mm). Solvent mixtures are understood as volume/volume. Infrared spectra were obtained using samples on a Biorad Excalibur FTS 3000 FT IR spectrometer equipped with a universal ATR sampling accessory (Specac Golden Gate Diamond Single Reflection ATR system); wave numbers v ~ are reported in cm^{-1}.

THF was distilled from sodium/benzophenone. Methanol was purchased at absolute quality and stored over molecular sieves. Solvents for column-chromatography (EtOAc, hexanes) were technical grade and distilled prior to use.

The bromoaryl derivatives, furan and thiophene were used as purchased or distilled prior to use. The Otera stannoxane catalysts were prepared according to a literature procedure.[1] Cyclopropane (+)- and (-)-**6** were prepared as described before[2]. Other chemicals (1M $ClTi(OPr^i)_3$ in hexane (Sigma-Aldrich), 1.6M n-BuLi in hexane (ACROS Organics), 2M allylmagnesium bromide/THF (Sigma-Aldrich), BF_3-OEt_2 (Merck), liquid Br_2 (99%, Fluka), tris(dimethylamino)methane (ACROS Organics)) were used as purchased from the supplier provided without further purification.

General Procedure A: Preparation of Aryltitanium Nucleophiles[3-4]

From five-membered heterocyles. As representative procedure, to a THF (26 mL) solution of furan (1.5 mL, 8.04 mmol) at –78 °C, *n*-BuLi (5.27 mL, 8.44 mmol) was added slowly. The mixture was stirred for 2 h at this temperature, and the resulting solution was treated with a solution of chlorotriisopropoxytitanium in hexane (8.84 mL, mmol, 1.1 eq) dropwise over 5 min and stirred further for 30 min.

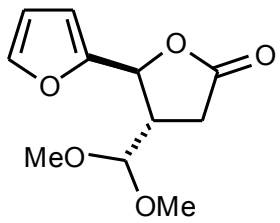
From bromophenyl derivatives. As representative procedure, to a solution of 4-methoxyphenyllithium was prepared by slow addition of *n*-butyllithium in hexane (1.6 M, 5.27 mL, 8.44 mmol, 1.05 eq) to 4-bromoanisole (1.0 mL, 8.04 mmol, 1 eq) in THF (mL) under a nitrogen atmosphere and was stirred for 2h at –78 °C. Chlorotriisopropoxytitanium in hexane (1 M, 8.84 mL, 8.84 mmol, 1.1 eq) was added dropwise over 5 min at –78 °C under nitrogen. After completion of the addition, the mixture was stirred further for 30 min.

General Procedure B: Addition of Aryltitanium Nucleophiles to Cyclopropanecarbaldehyde, 6.

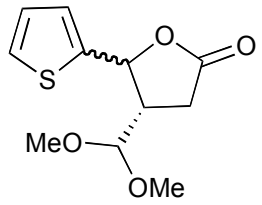
Under a nitrogen atmosphere, a solution of cyclopropylcarbaldehyde (+)-**6** (500 mg, 2.01 mmol, 1 equiv) in anhydrous THF (20 ml) was added via canula to a flame-dried three-necked flask and was cooled to -78 °C. $BF_3{\cdot}OEt_2$ (0.28 mL, 2.21 mmol, 1.1 equiv) was added via syringe and after stirring for 30 min., the aryltitanium nucleophile solution (8.04 mmol, 4 equiv) was added slowly resulting to a color change (typically yellow-orange to reddish-orange). After stirring for 16 h at -78 °C, saturated $NaHCO_3$ (45 ml) was added and the mixture was allowed to warm to room temperature. The layers were separated and the aqueous layer was extracted three times with ethyl acetate (45x2 ml). The combined organic layers were washed with brine (45 ml), H_2O (45 ml), dried (Na_2SO_4) and concentrated *in vacuo* to give the arylcarbinol cyclopropane **10** which was used for the next step without further purification.

General Procedure C: Synthesis of γ-Aryllactone Methyl Acetals 9a-g

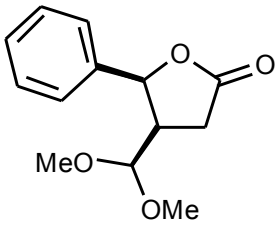
A round–bottomed flask, equipped with Dean–Stark trap was charged with arylcyclopropyl carbinol **10** (1 equiv) followed by methanol (2 mL per mmol) and Sn–catalyst **11c** (10 mol%). The mixture was gently refluxed for 12h. Afterwhich, the crude mixture was evaporated and purified by chromatography on silica gel (ethyl acetate-hexanes 1:2) to yield the protected aryllactone aldehyde, **9**.



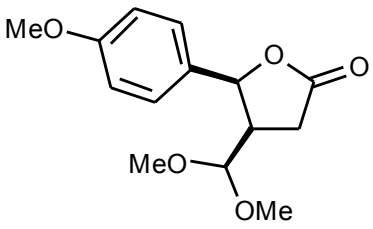
(2S,3S)-3-Dimethoxymethyl-3,4-dihydro-2H-[2,2']bifuranyl-5-one (**9a**). According to general procedure C, 182 mg (40%, 86:14 *trans-cis* ratio). *Trans-Diastereomer:* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.25 (m, 2H), 5.40 (d, *J* = 4.6 Hz, 1H), 4.35 (d, *J* = 5.7 Hz, 1H), 3.38 (s, 3H), 3.34 (s, 3H), 3.10 (m, 1H), 2.83 (dd, *J* = 17.9, 9.4 Hz, 1H), 2.61 (dd, *J* = 17.9, 5.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.9, 151.0, 143.6, 110.5, 109.2, 104.3, 74.9, 55.4, 54.5, 42.2, 30.1. HR-EIMS ($C_{11}H_{14}O_5$): calcd.: 226.0841, found: 226.08422. IR**:** $\tilde{\nu}$ 2937, 1738, 1734, 1591, 1445, 1372, 1253, 1172, 1067, 748, 632, 537, 497 cm^{-1}.



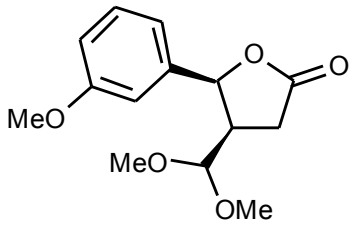
(*4S,5R*)- and (*4S,5S*)-4-Dimethoxymethyl-5-thiophen-2-yl-dihydro-furan-2-one (**9b**). According to general procedure C, 185 mg (38%, 55:45 *cis-trans* ratio). *Cis*-Diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 2.5 Hz, 1H), 7.03 (m, 2H), 5.84 (d, *J* = 7.7 Hz, 2H), 3.93 (d, *J* = 7.3 Hz, 2H), 3.59 (m, 1H), 3.25 (s, 3H), 3.21 (s, 3H), 2.73 (dd, *J* = 23.5, 13.4 Hz, 1H), 2.56 (dd, *J* = 17.6, 8.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 141.9, 126.9, 126.2, 125.9, 104.3, 78.3, 54.9, 54.8, 52.7, 43.2, 29.1. HR-EIMS ($C_{11}H_{14}O_4S$): calcd.: 242.0613 found: 242.06144 IR $\tilde{\nu}$ 2940, 2834, 1782, 1732, 1441, 1169, 1062, 953, 712, 632, 540, 495 cm^{-1}. *Trans-diastereomer:* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 2.5 Hz, 1H), 7 (m, 2H), 5.65 (d, *J* = 5.1 Hz, 1H), 4.39 (d, *J* = 5.4 Hz, 1H), 3.41 (s, 3H), 3.37 (s, 3H), 3.14 (m, 2H), 2.91 (dd, *J* = 11.1, 5.8 Hz, 1H), 2.77 (dd, *J* = 19.3, 7.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 138.2, 127.0, 126.1, 125.8, 105.1, 78.0, 55.2, 54.9, 46.6, 29.9.



(*4R,5S*)-4-Dimethoxymethyl-5-phenyl-dihydro-furan-2-one (**9c**). According to general procedure C, 214 mg (45%, >99% *cis*). Mp 86-89°C, $[\alpha]_{20}^{D}$ -17 (*c* 0.12, MeOH). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (m, 5H), 5.60 (d, *J* = 7.7 Hz, 1H), 3.63 (d, *J* = 6.1 Hz, 1H), 3.35 (m, 1H), 3.12 (s, 3H), 3.10 (s, 3H), 2.71 (dd, *J* = 17.7, 7.6 Hz, 1H), 2.58 (dd, *J* = 17.7, 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 135.7, 128.7, 125.8, 103.9, 81.9, 55.1, 52.9, 43.0, 29.7. HR-EIMS ($C_{13}H_{16}O_4$): calcd.: 236.1049, found: 236.10469. IR $\tilde{\nu}$ 3008, 2936, 2879, 2836, 1747, 1606, 1500, 1454, 1379, 1306, 1222, 1166, 1118, 1051, 972, 879, 737, 688, 562, 510, 429 cm^{-1}.

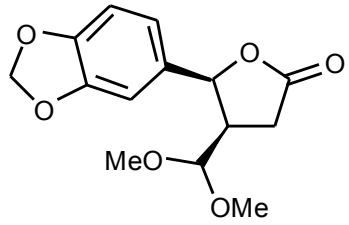


(*4R,5S*)- and and (*4S,5S*)-4-Dimethoxymethyl-5-(4-methoxy-phenyl)-dihydro-furan-2-one (**9d**). According to general procedure C, 203 mg (38%, 82:18 *cis-trans* ratio). *Cis*-Diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 1H), 5.58 (d, *J* = 7.7 Hz, 1H), 3.82 (s, 3H), 3.40 (d, *J* = 6.1 Hz, 1H), 3.17 (s, 3H), 3.13 (s, 3H), 3.08 (m, 1H), 2.70 (dd, *J* = 16.8, 7.4 Hz, 1H), 2.57 (dd, *J* = 17.7, 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 159.7, 127.6, 113.8, 103.8, 81.5, 55.5, 54.9, 52.9, 43.2, 29.5. HR-EIMS ($C_{14}H_{18}O_5$): calcd.: 266.1154, found: 266. 11558. IR**:** ν = 2962, 2836, 1779, 1613, 1515, 1462, 1254, 1176, 1020, 797, 632, 537, 497 cm^{-1}.

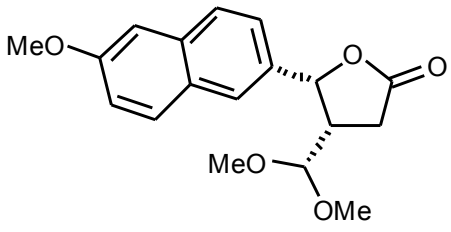


(*4R,5S*)- and and (*4S,5S*)-4-Dimethoxymethyl-5-(3-methoxy-phenyl)-dihydro-furan-2-one (**9e**). According to general procedure C, 214 mg (40%, 74:26 *cis-trans* ratio). *Cis*-

Diasteromer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 1H), 6.85 (m, 3H), 5.57 (d, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 3.68 (d, *J* = 5.8 Hz, 1H), 3.15 (s, 3H), 3.14 (s, 3H), 3.07 (m, 1H), 2.72 (dd, *J* = 17.6, 7.4 Hz, 1H), 2.57 (dd, *J* = 17.6, 8.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 159.9, 137.6, 129.6, 118.6, 113.6, 111.7, 103.3, 81.4, 55.3, 55.0, 53.3, 43.4, 29.6. HR-EIMS ($C_{14}H_{18}O_5$): calcd.: 266.1154, found: 266. 11558. IR**:** $\tilde{\nu}$ 2938, 2836, 1776, 1603, 1458, 1260, 1159, 1056, 879, 776, 696, 449 cm^{-1}. *Trans-Diastereomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 1H), 6.87 (m, 3H), 5.41 (d, *J* = 4.4 Hz, 1H), 4.29 (d, *J* = 4.5 Hz, 1H), 3.57 (s, 3H), 3.39 (s, 3H), 3.36 (s, 3H), 3.09 (m, 1H), 2.41 (dd, *J* = 16.6, 6.3 Hz, 1H), 2.28 (dd, *J* = 16.6, 6.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.42, 160.06, 143.94, 129.33, 118.88, 113.34, 111.07, 106.27, 74.03, 56.97, 55.89, 55.09, 51.64, 44.27, 30.83.



(*4R,5S*)- and and (*4S,5S*)-5-Benzo[1,3]dioxol-5-yl-4-dimethoxymethyl-dihydro-furan-2-one (**9f**). According to general procedure C, 186 mg (33%, 76:24 *cis-trans* ratio). *Cis-Diastereomer*: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.74 (m, 3H), 5.93 (s, 1H), 5.47 (d, *J* = 7.6 Hz, 1H), 3.67 (d, *J* = 6.1 Hz, 1H), 3.14 (s, 1H), 3.11 (s, 1H), 3.00 (m, 1H), 2.64 (dd, *J* = 18.1, 7.4 Hz, 1H), 2.51 (dd, *J* = 16.8, 9.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 148.0, 147.6, 129.6, 119.6, 108.2, 106.7, 103.6, 101.3, 81.4, 54.9, 53.4, 43.3, 29.5. HR-EIMS ($C_{14}H_{16}O_6$): calcd.: 280.0947, found: 280.09519. IR**:** $\tilde{\nu}$ 2936, 1776, 1612, 1492, 1445, 1243, 1177, 1036, 930, 632, 539, 495 cm^{-1}. *Trans-Diastereomer:* ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.69 (m, 3H), 5.92 (s, 1H), 5.27 (d, *J* = 4.9 Hz, 1H), 4.31 (d, *J* = 5.1 Hz, 1H), 3.34 (s, 3H), 3.28 (s, 3H), 2.98 (m, 1H), 2.63 (m, 1H), 2.51 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.0, 148.2, 147.7, 133.3, 119.3, 108.3, 106.1, 104.8, 101.3, 81.8, 65.4, 54.7, 53.4, 46.4, 29.9.



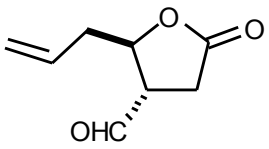
(*4S,5R*)-4-Dimethoxymethyl-5-(6-methoxy-naphthalen-2-yl)-dihydro-furan-2-one (**9g**). According to general procedure C, 235 mg (37%, 92:8 *cis-trans* ratio).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (m, 6H), 5.75 (d, *J* = 7.6 Hz, 1H), 3.93 (s, 3H), 3.66 (d, *J* = 6.1 Hz, 1H), 3.17 (m, 1H), 3.12 (s, 3H), 3.09 (s, 3H), 2.78 (dd, *J* = 17.7, 7.7 Hz, 1H), 2.63 (dd, *J* = 17.6, 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 158.2, 134.3, 130.8, 129.5, 128.4, 127.0, 125.1, 124.3, 119.5, 105.7, 103.7, 81.6, 55.3, 54.9, 53.4, 43.4, 29.7. HR-EIMS ($C_{18}H_{20}O_5$): calcd.: 316.1311, found: 316.13092. IR**:** $\tilde{\nu}$ 2999, 2929, 2837, 1772, 1609, 1487, 1458, 1384, 1302, 1265, 1182, 1119, 1054, 983, 859, 783, 704, 474 cm^{-1}.

Synthesis of trans-allyllactone 9h[2]. To a THF (26 mL) solution of allymagnesium bromide in THF (4.02 mL, 2M, 4.02 mmol, 1 eq) at –78 °C, chlorotriisopropoxytitanium in hexane

(8.84 mL, 1 M, 8.84 mmol, 1.1 eq) was added dropwise over 5 min under nitrogen atmosphere. After completion of the addition, the mixture was stirred further for 30 min.

Under a nitrogen atmosphere, a solution of cyclopropylcarbaldehyde (-)-**6** (500 mg, 2.01 mmol, 1 equiv) in anhydrous THF (20 ml) was added via canula to a flame-dried three-necked flask and was cooled to -78 °C. $BF_3{\cdot}OEt_2$ (0.28 mL, 2.21 mmol, 1.1 equiv) was added via syringe and after stirring for 30 min., the allyltitanium nucleophile solution (8.04 mmol, 4 equiv) was added slowly resulting to a color change (orange-red). After stirring for 16 h at -78 °C, saturated $NaHCO_3$ (45 ml) was added and the mixture was allowed to warm to room temperature. The layers were separated and the aqueous layer was extracted three times with ethyl acetate (45x2 ml). The combined organic layers were washed with brine (45 ml), H_2O (45 ml), dried (Na_2SO_4) and concentrated *in vacuo* to give the allylcarbinol cyclopropane **13** which was used for the next step without further purification.

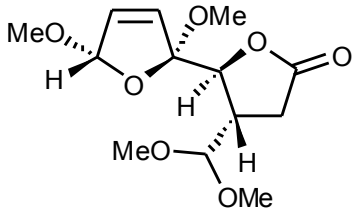
Crude alcohol **13** (1.0 equiv) was dissolved in MeOH (10 ml/mmol) and cooled to 0 °C. $Ba(OH)_2{\cdot}8H_2O$ (0.55 equiv) was added in small portions over 1 h. After 1 h stirring at 0 °C, DCM (10 ml/mmol) and H_2O (10 ml/mmol) were added and the layers were separated. The aqueous layer was again extracted with DCM (3x10 ml/mmol). The combined organic layers were dried (Na_2SO_4), filtered and concentrated *in vacuo*. Chromatography on silica gel (hexanes:ethylacetate 1:1) afforded the corresponding lactone aldehyde **9h** as a very light yellow oil.

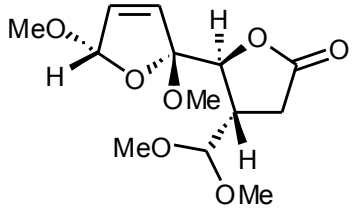


(2R,3S)-2-Allyl-5-oxo-tetrahydro-furan-3-carbaldehyde (**9h**). 90 mg (29%, 94:6 *trans-cis* ratio).^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 7.9 Hz, 1.1 Hz, 1H), 7.33 (td, *J* = 7.6 Hz, 1.3 Hz, 1H), 7.10 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.07- 6.97 (m, 1H), 5.60 (d, *J* = 4.7 Hz, 1H), 4.48 (d, *J* = 4.4 Hz, 1H), 2.45 (tt, *J* = 11.3 Hz, 3.5 Hz, 1H), 2.08 – 1.91 (m, 1H), 1.84 – 1.54 (m, 3H), 1.49 – 0.97 (m, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 211.0, 139.4, 139.0, 129.3, 127.9, 127.6, 99.3, 80.1, 45.4, 28.9, 26.6, 24.7, 24.5, 24.0.

Synthesis of compound 14a-c from 9a[5].

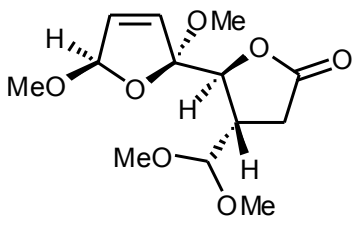
A solution of **9a** (40 mg, 0.388, 1 equiv) in a mixture of MeOH (0.1 mL) and diethyl ether (70 μL) was stirred and cooled to -40°C. Liquid bromine (7.1 μL, 0.1429 mmol, 1.03) in dry MeOH (0.1 mL) was added dropwise over 5 min. After addition, stirring was continued for an additional 10 min. The mixture was saturated with ammonia gas to pH 8, allowed to warm to room temperature, diluted with ether and evaporated. The residue (2:1:1 mixture of three stereoisomers) was purified by flash chromatography (silica, 1:1 EtOAc–hexanes) to afford a mixture of **14a** and **14b** (19 mg) and pure **14c** (19 mg).





(2S,3S,2'R,5'S)-3-Dimethoxymethyl-2',5'-dimethoxy-3,4,2',5'-tetrahydro-2H-[2,2']bifuranyl-5-one (**14a**) and (2S,3S,2'S,5'S)-3-Dimethoxymethyl-2',5'-dimethoxy-3,4,2',5'-tetrahydro-2H-[2,2']bifuranyl-5-one (**14b**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.13 (d, *J* = 2.8 Hz, 1H), 6.09 (d, *J* = 0.9 Hz, 1H), 6.07 (d, *J* = 0.8

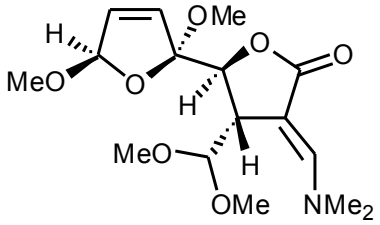
Hz, 1H), 5.81 (s, 1H), 5.48 (s, 1H), 4.40 (d, *J* = 2.0 Hz, 1H), 4.26 (d, *J* = 5.5 Hz, 1H), 4.23 (d, *J* = 1.5 Hz, 1H), 3.51 (s, 2H), 3.46 (s, 1H), 3.40 (s, 3H), 3.38 (d, *J* = 1.0 Hz, 3H), 3.19 (s, 1H), 3.12 (s, 1H), 3.03 – 2.94 (m, 1H), 2.72 (ddd, *J* = 17.9, 10.0, 5.7 Hz, 1H), 2.40 (dt, *J* = 18.0, 2.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.6, 132.7, 132.4, 132.1, 130.9, 113.4, 112.4, 108.5, 107.4, 105.5, 105.3, 83.7, 83.4, 56.5, 55.5, 55.3, 54.9, 54.6, 53.9, 50.7, 50.1, 37.9, 30.0. HR-LSIMS ($C_{13}H_{20}O_7$ + H): calcd.: 289.1287, found: 289.13010. IR**:** $\tilde{\nu}$ 2944, 2838, 1769, 1632, 1444, 1373, 1188, 1118, 1075, 1017, 972, 829, 697, 625 cm^{-1}.



(2S,3S,2'S,5'R)-3-Dimethoxymethyl-2',5'-dimethoxy-3,4,2',5'-tetrahydro-2H-[2,2']bifuranyl-5-one (**14c**).^{1}H NMR (300 MHz, $CDCl_3$) δ 6.18 (dd, *J* = 5.9, 0.9 Hz, 1H), 5.87 (dd, *J* = 5.9, 1.3 Hz, 1H), 5.76 (s, 1H), 4.49 (d, *J* = 2.1 Hz, 1H), 4.27 (d, *J* = 5.6 Hz, 1H), 3.45 (s, 3H), 3.39 (s, 6H), 3.16 (s, 3H), 3.00 (m, 1H), 2.67 (dd, *J* = 18.0, 10.0 Hz, 1H), 2.43 (dd, *J* = 18.0, 2.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) d 176.7, 133.7, 129.9, 114.2, 109.3, 104.6, 80.7, 56.5, 54.9, 54.4, 50.0, 38.0, 29.5. HR-LSIMS ($C_{13}H_{20}O_7$ + H): calcd.: 289.1287, found: 289.13010.IR**:** $\tilde{\nu}$ 2942, 2835, 1780, 1632, 1450, 1374, 1247, 1193, 1117, 1076, 1016, 981, 834, 631, 536, 497 cm^{-1}.

Synthesis of compound 15[6].

A mixture of 7 mg **14c** (0.0243 mmol, 1 eq) and 5.9 μL (0.0340 mmol, 1.4 eq) of tris-(dimethylamino)methane was heated under nitrogen with stirring at 70 °C for 48 h. The crude product was dried under vacuum for 2 h and filtered on silica gel with 2:1 hexanes-ethyl acetate to give 7 mg (81%) of **15**.

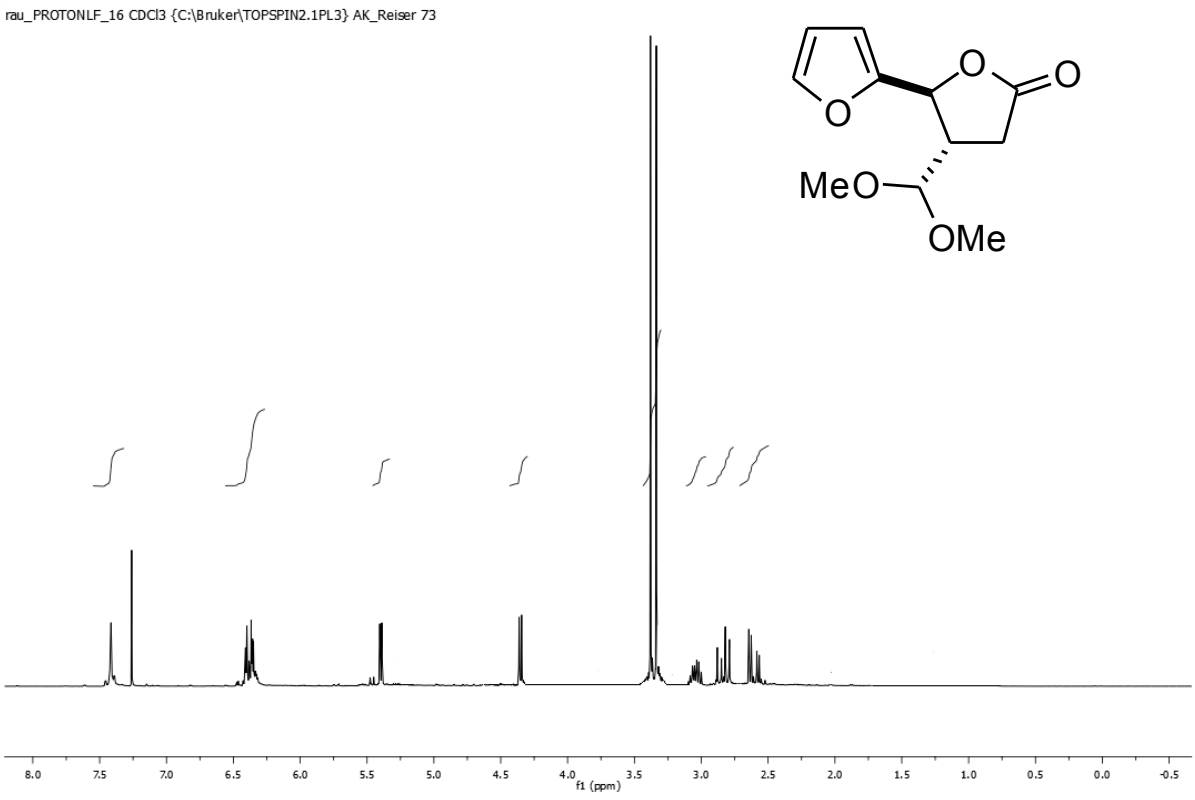


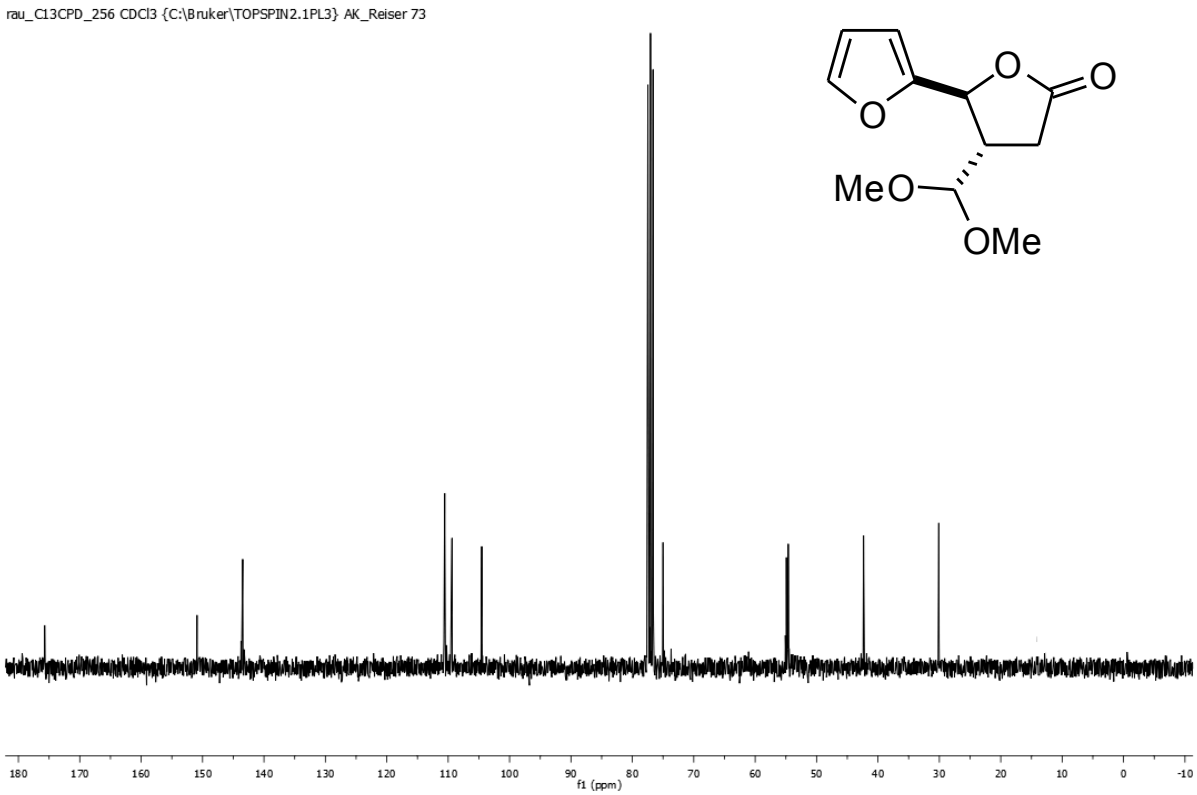
(2S,3S,2'S,5'R)-3-Dimethoxymethyl-4-dimethylaminomethy-lene-2',5'-dimethoxy-3,4,2',5'-tetrahydro-2H-[2,2']bifuranyl-5-one (**15**). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, *J* = 0.8 Hz, 1H), 6.07 (dd, *J* = 5.9, 0.8 Hz, 1H), 5.88 (dd, *J* = 5.9, 1.2 Hz, 1H), 5.76 (s, 1H), 4.49 (s, 1H), 4.15 (d, *J* = 6.7 Hz, 1H), 3.75 (d, *J* = 6.7 Hz, 1H), 3.44 (s, 3H), 3.41 (s, 3H), 3.41 (s, 3H), 3.15 (s, 3H), 3.04 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.0, 147.9, 132.5, 130.5, 114.8, 109.1, 107.2, 88.1, 79.0, 57.2, 56.3, 53.9, 50.0, 41.9, 29.7. HR-EIMS ($C_{16}H_{25}NO_7$): calcd.: 343.1631, found: 343.16316. IR**:** $\tilde{\nu}$ 2923, 2851, 1722, 1616, 1444, 1375, 1193, 1119, 1015, 771, 697, 6222, 575, 437 cm^{-1}.

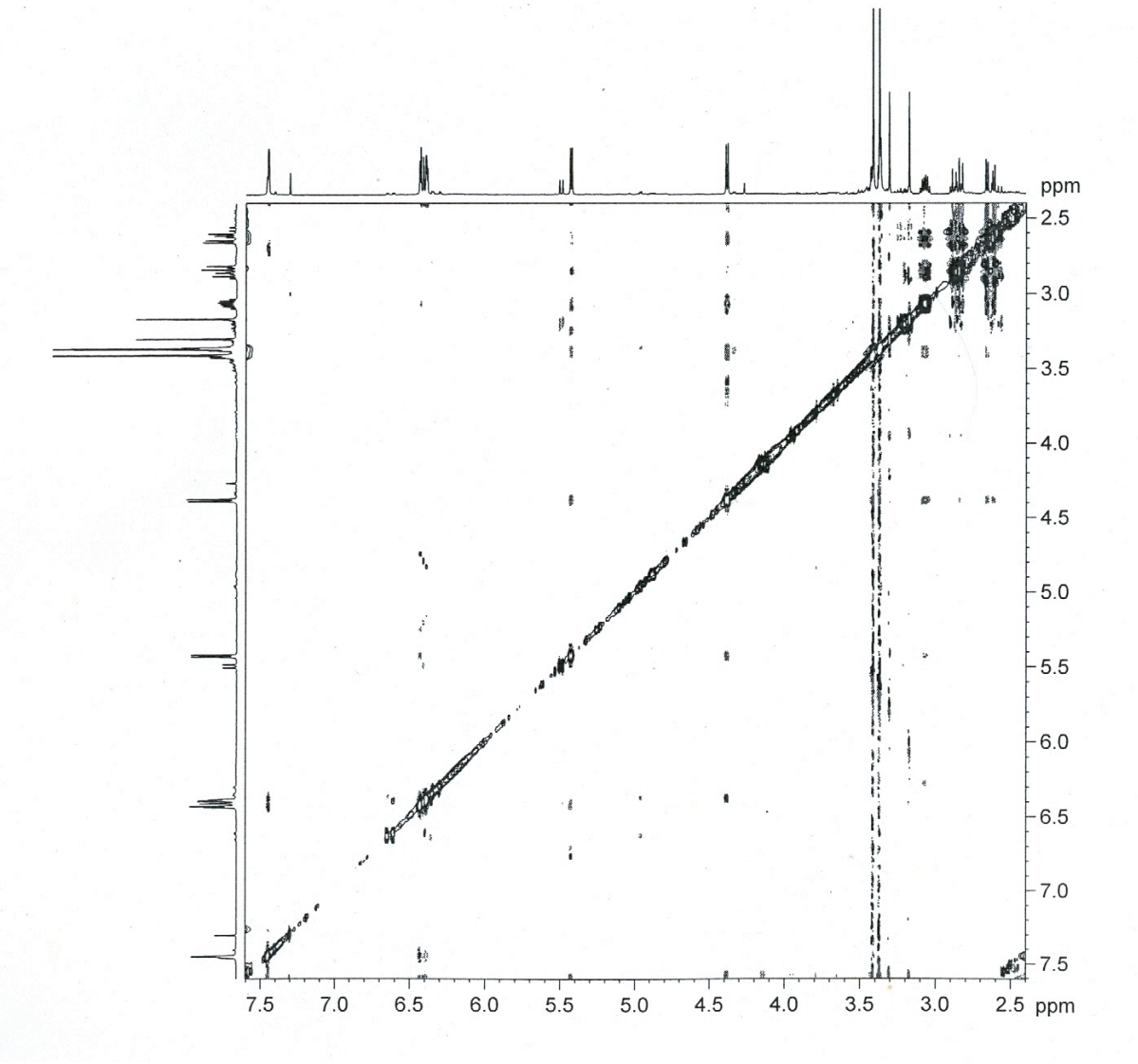
References

1. A. Orita, K. Sakamoto, Y. Hamada, A. Mitsutome and J. Otera, *Tetrahedron*, 1999, **55**, 2899.
2. (a) R. Bandichhor, B. Nosse, S. Sörgel, C. Böhm, M. Seitz and O. Reiser, *Chem. Eur. J.* 2003, **9**, 260; (b) C. Böhm and O. Reiser, *Org. Lett.*, 2001, **3**, 1315.
3. M. D. Rausch and H. B. Gordon, *J. Organomet. Chem*. 1974, **74**, 85.
4. B. Weidmann, L. Widler, A. G. Olivero, C. D. Maycock and D. Seebach, *Helv. Chim. Acta* 1981, **64**, 357.
5. W. Du and Y. Hu, *Carbohydrate Res.* 2006, **341**, 725.
6. H. H. Wasserman, J. L. Ives, *J. Org. Chem.* 1978, **43**, 3

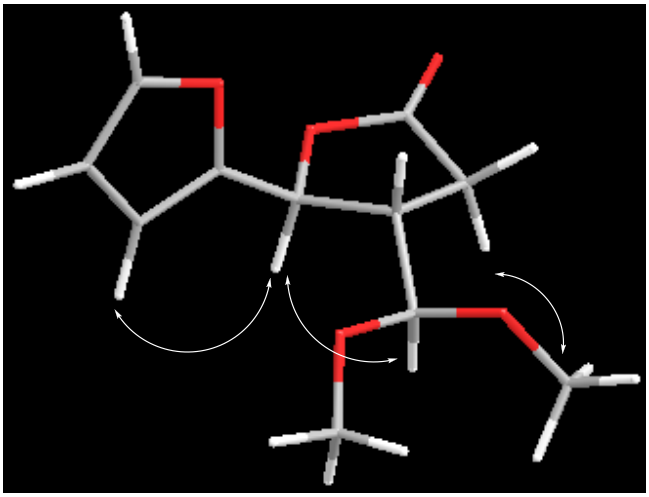
^{1}H and ^{13}C NMR Spectra of 9a





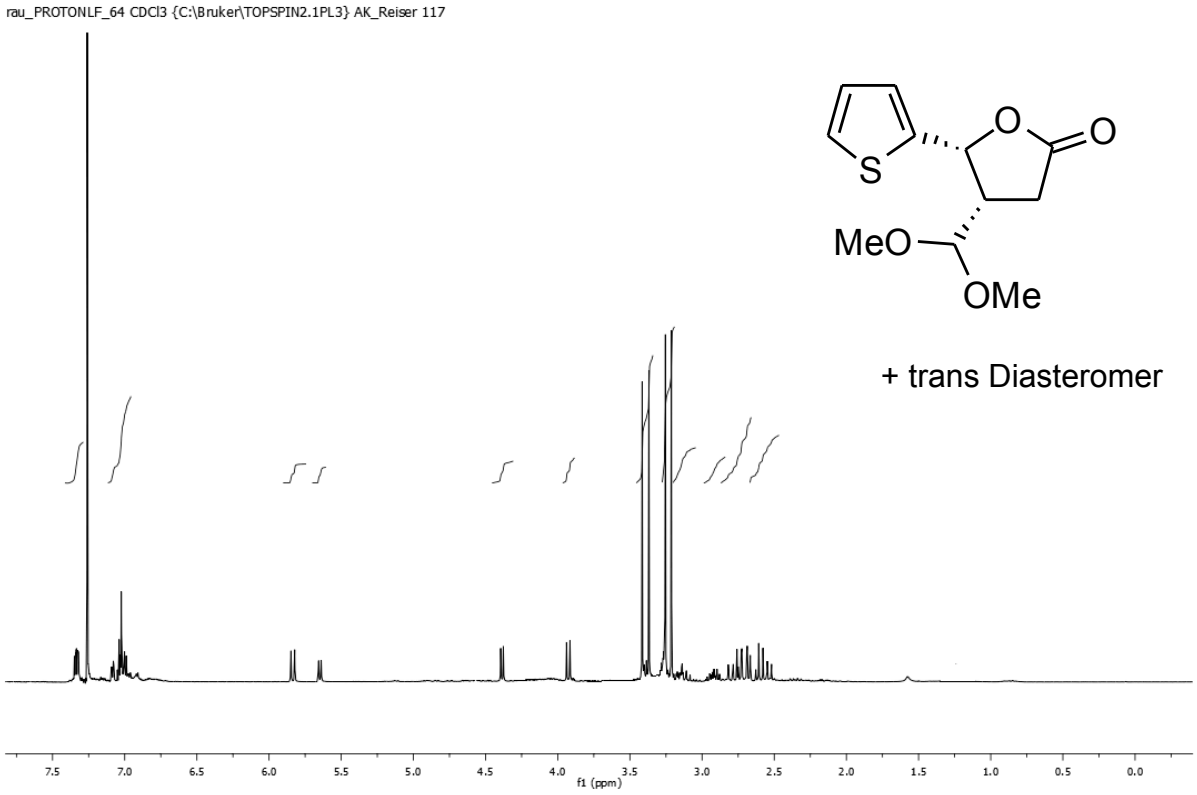


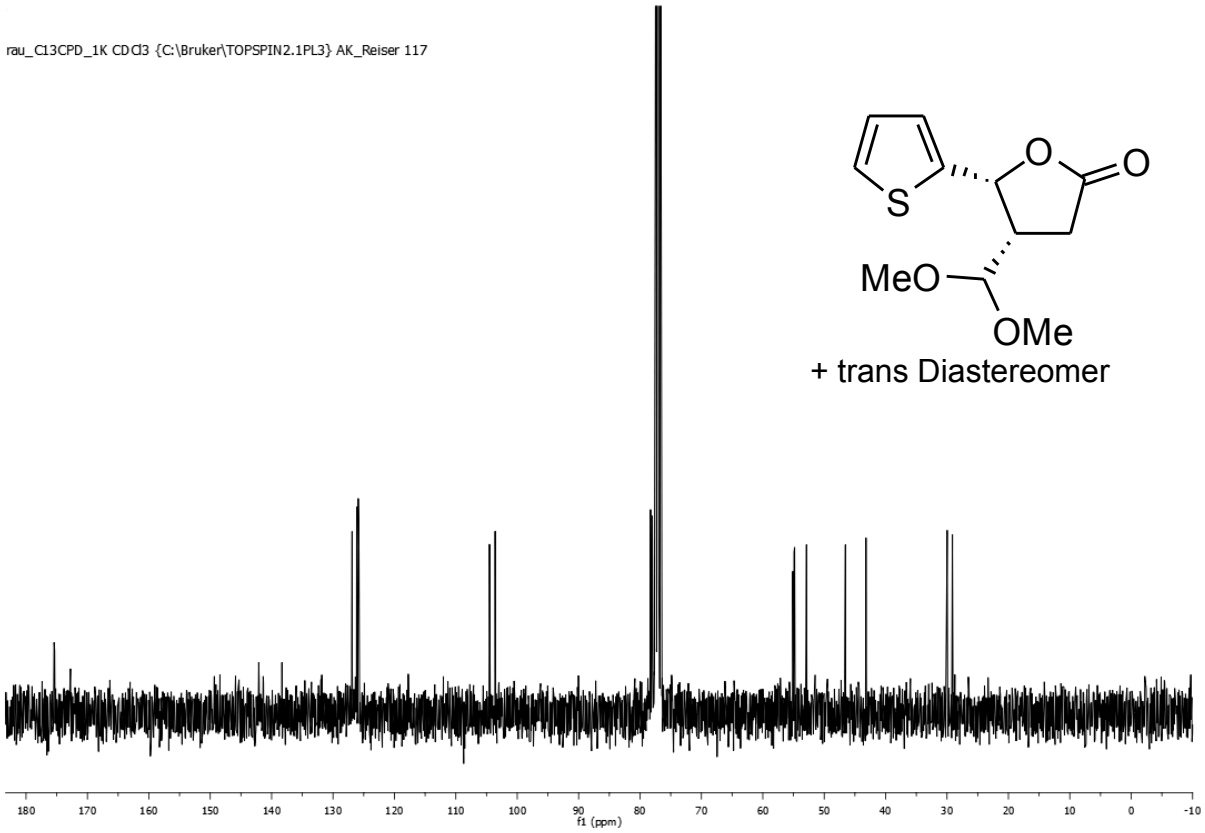
2D NOESY spectrum of lactone 9a



Key NOESY correlations in 9a

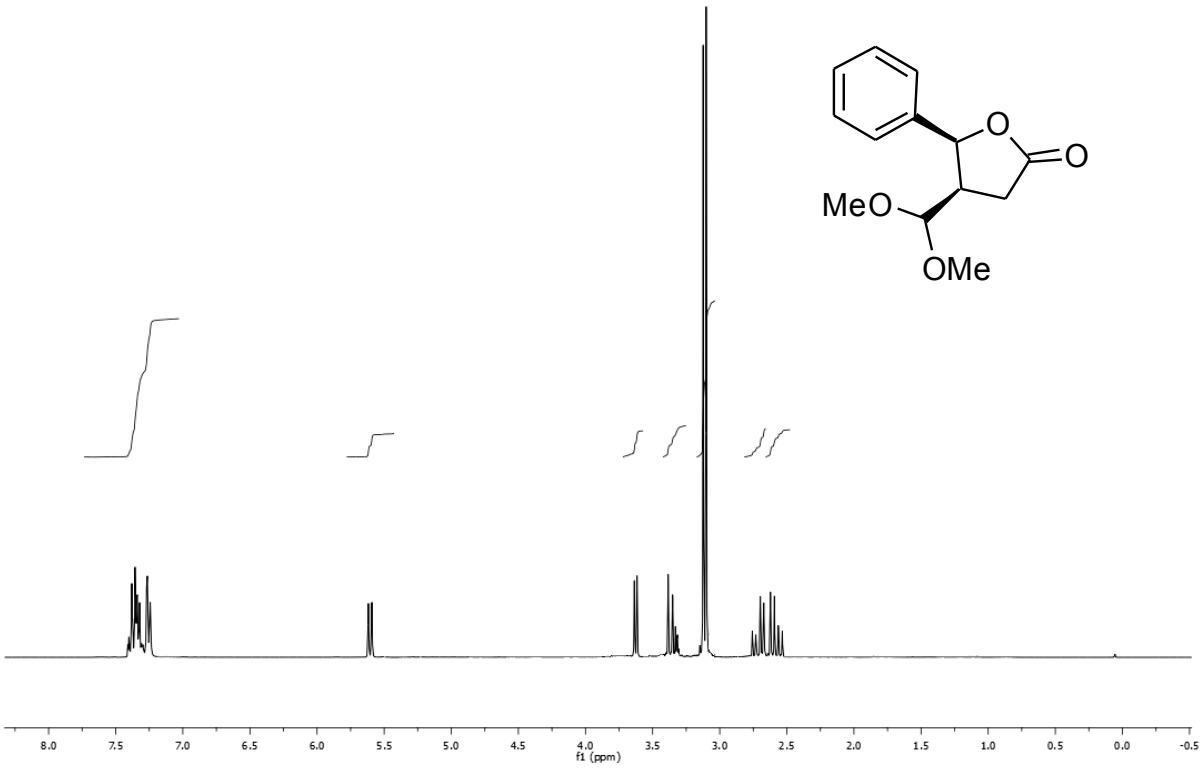
^{1}H and ^{13}C NMR Spectra of 9b



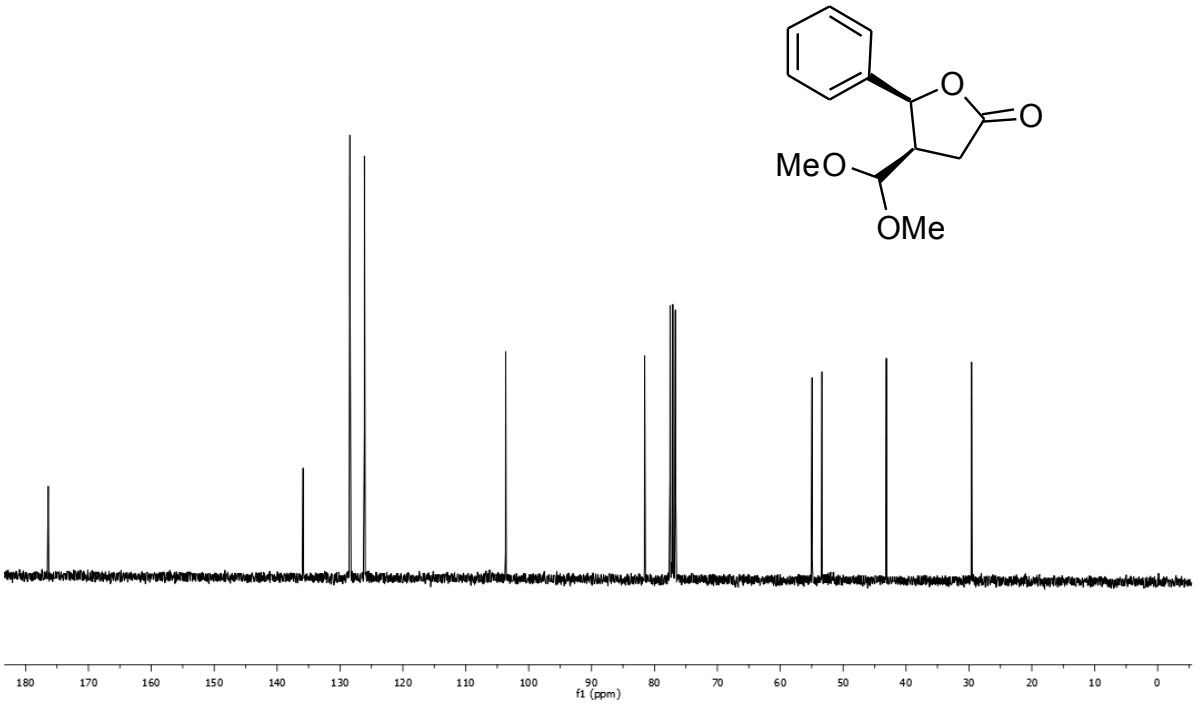


^{1}H and ^{13}C NMR Spectra of 9c

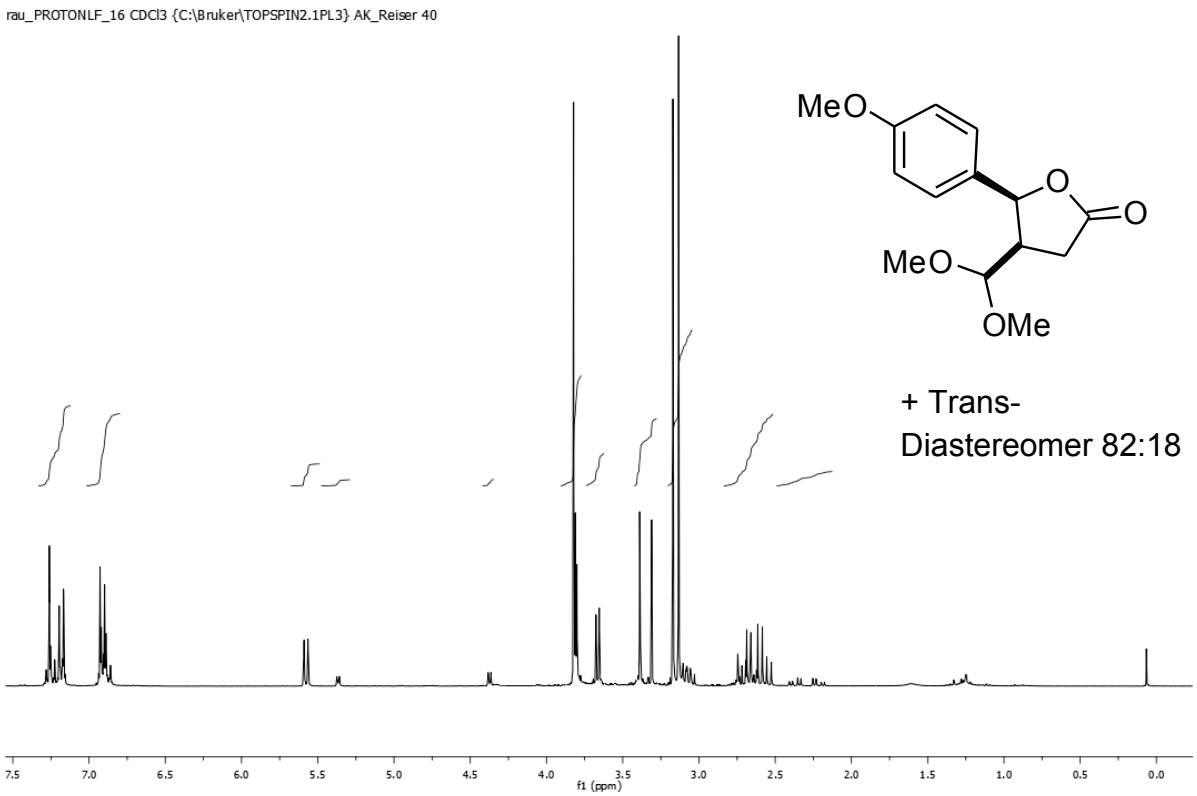
rau_PROTONLF_16 CDCl3 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 75



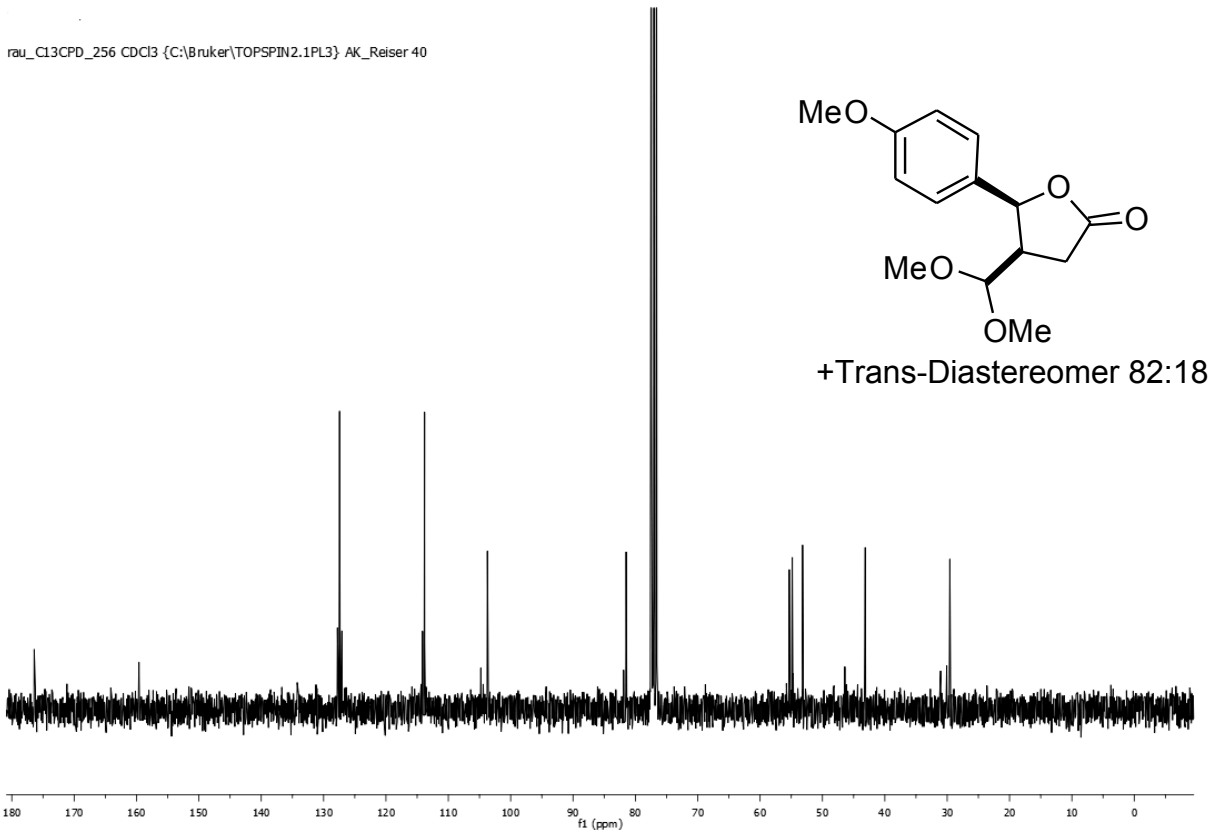
rau_C13CPD_256 CDCl3 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 75



^{1}H and ^{13}C NMR Spectra of 9d

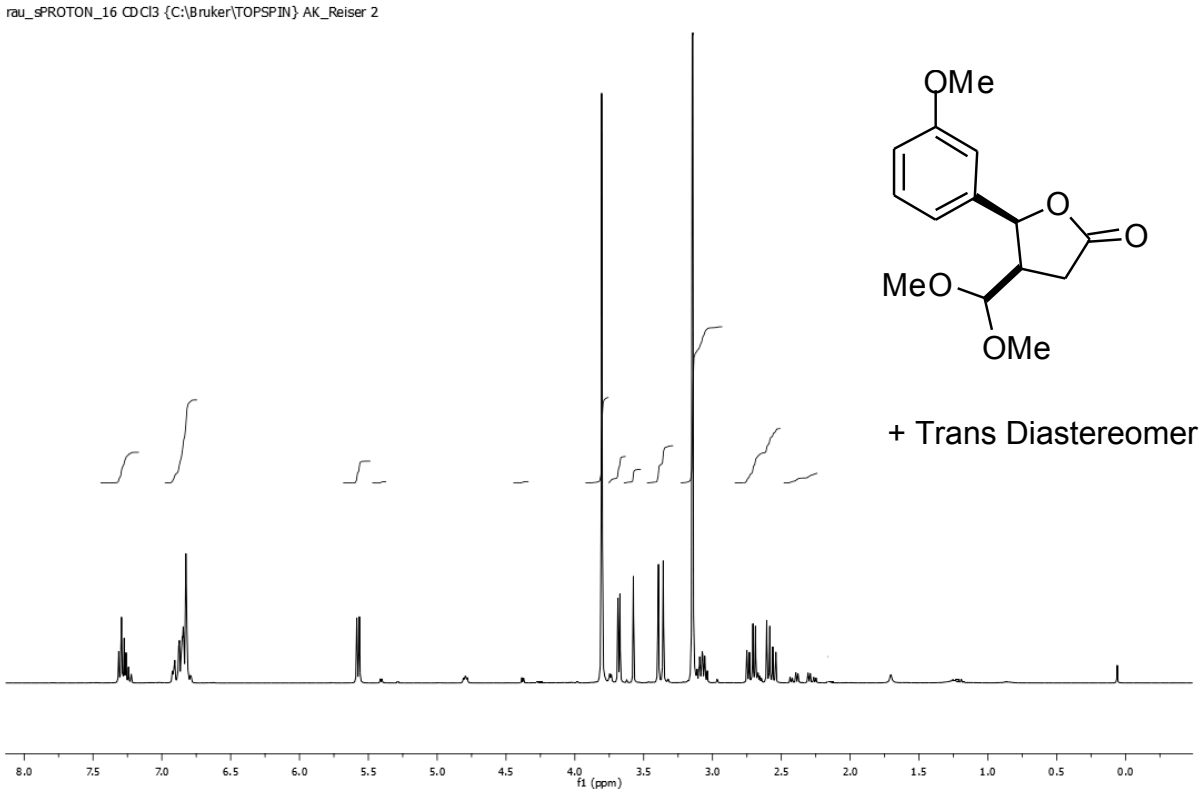


+ Trans-Diastereomer 82:18

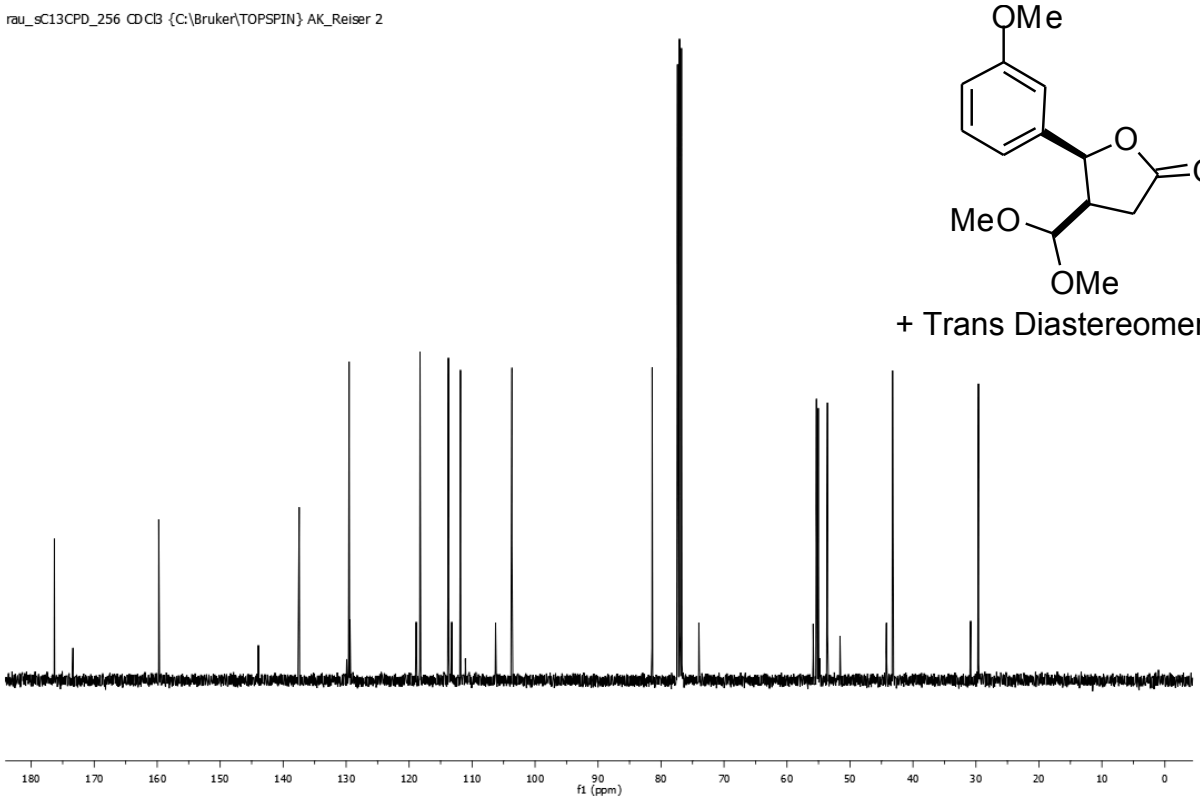


+Trans-Diastereomer 82:18

^{1}H and ^{13}C NMR Spectra of 9e

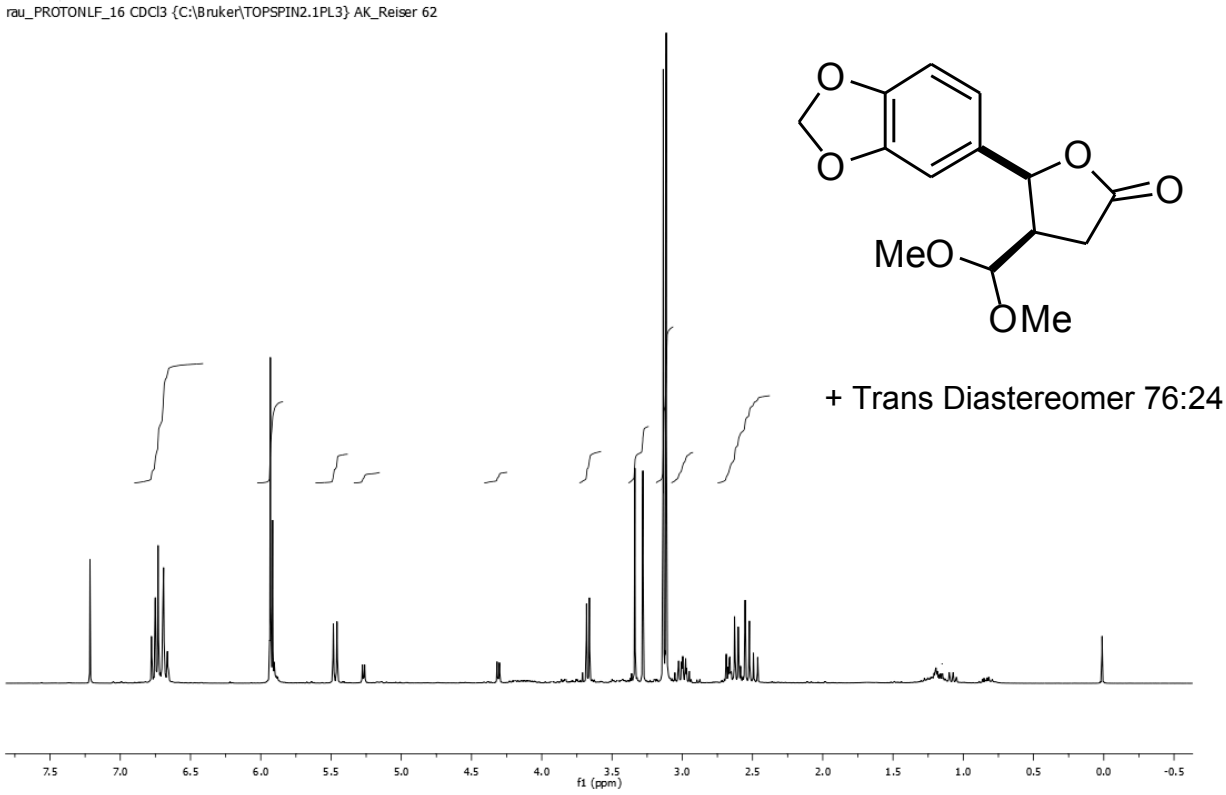


+ Trans Diastereomer 74:26



+ Trans Diastereomer 74:26

^{1}H and ^{13}C NMR Spectra of 9f



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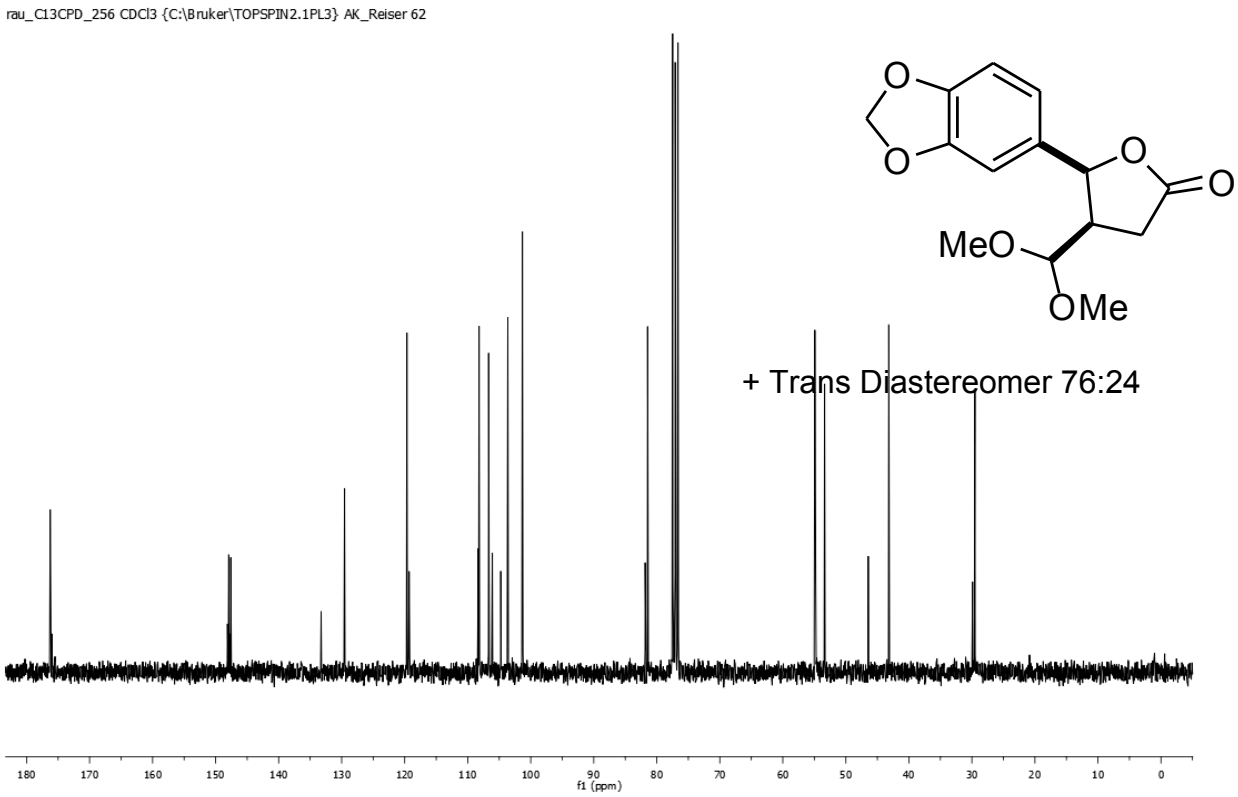

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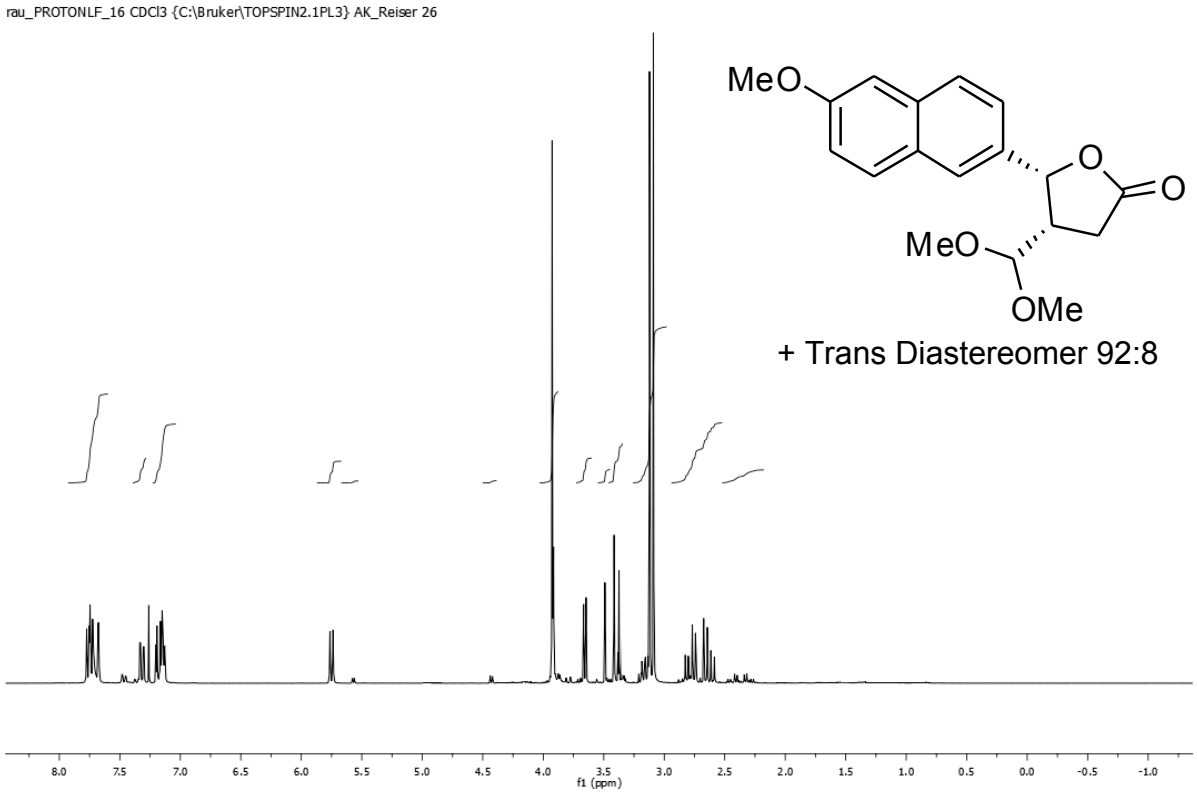
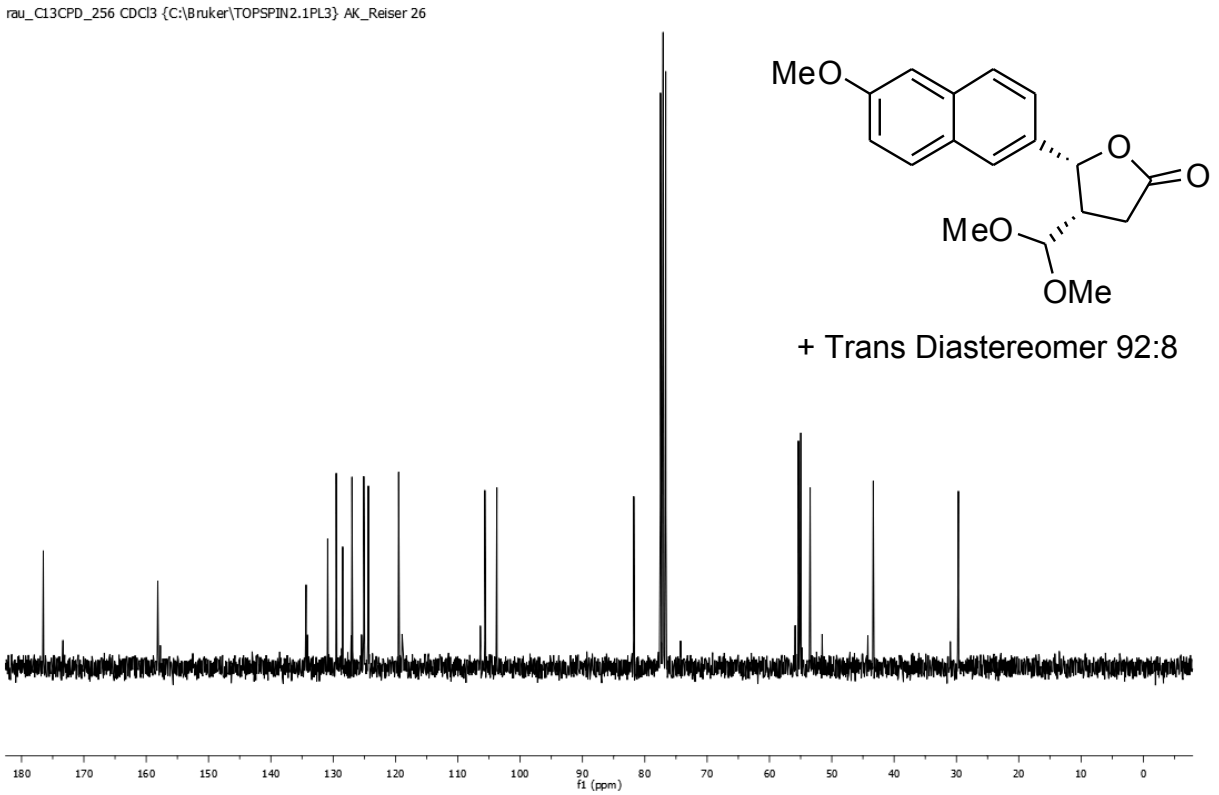
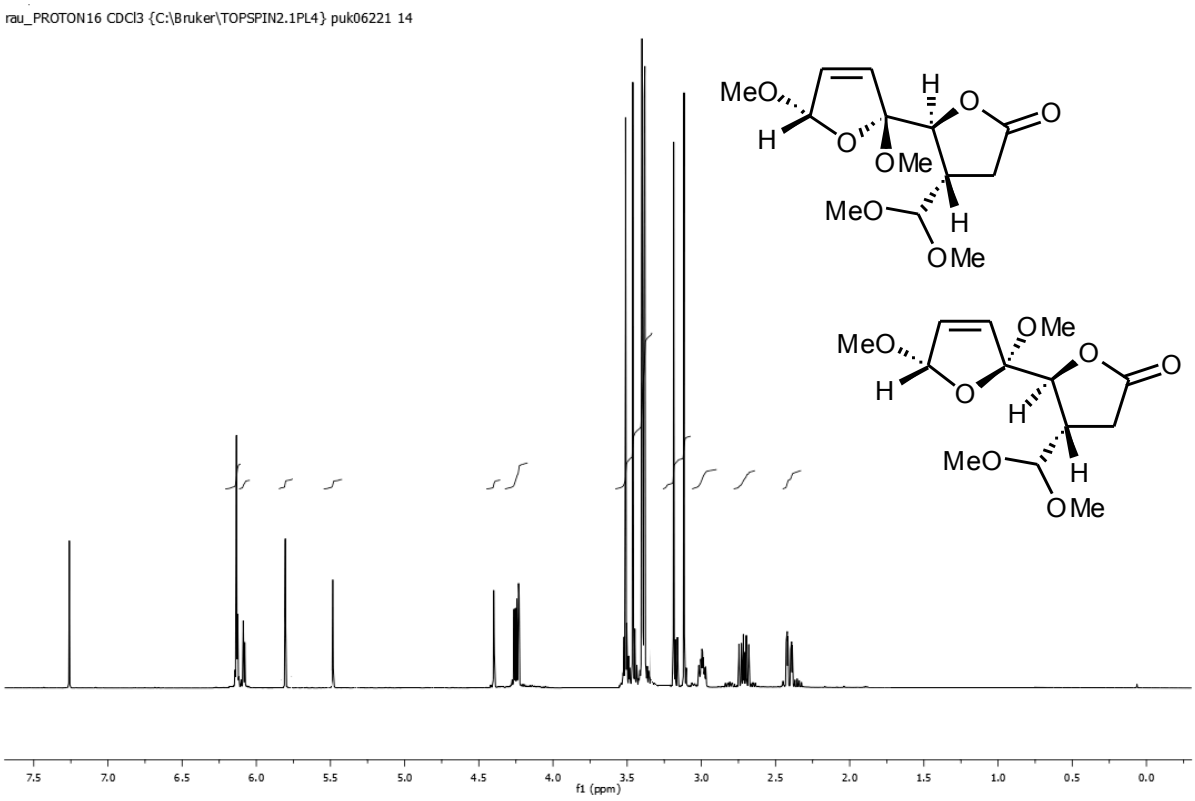
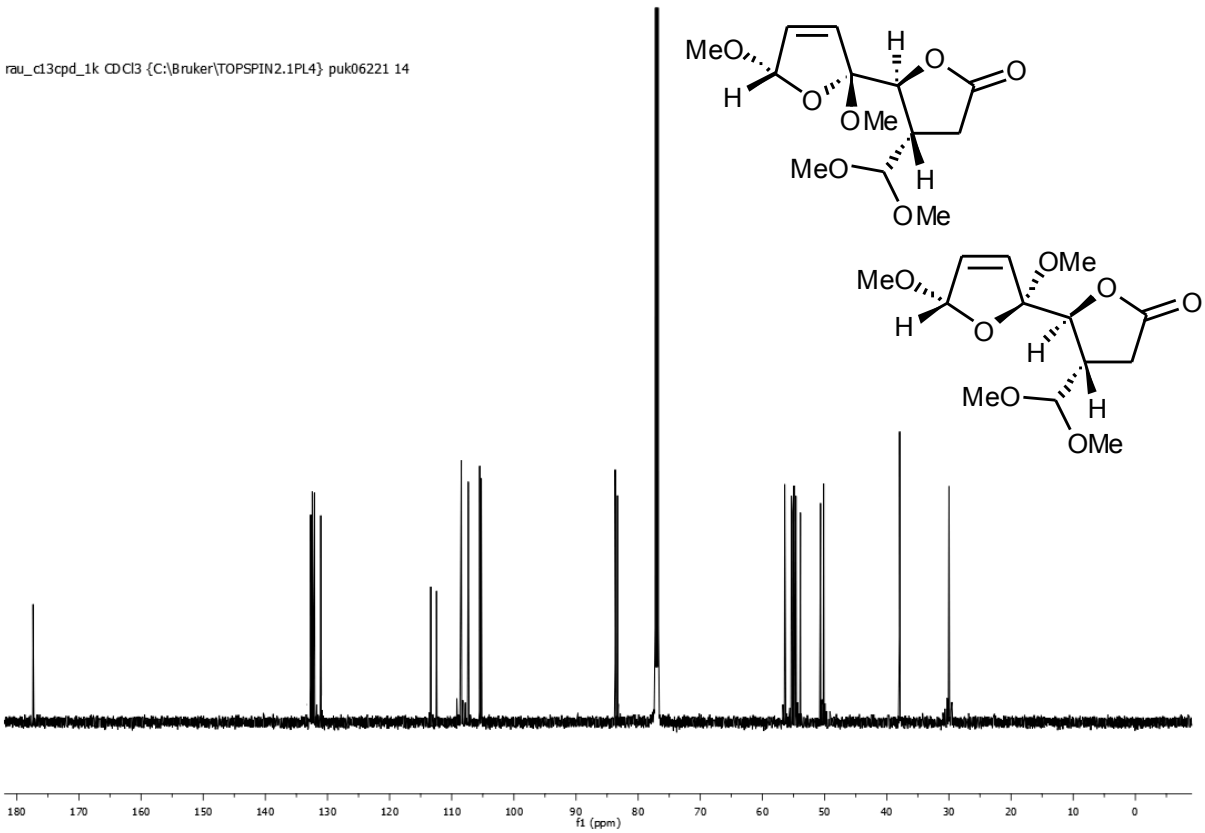
^{1}H and ^{13}C NMR Spectra of 9g

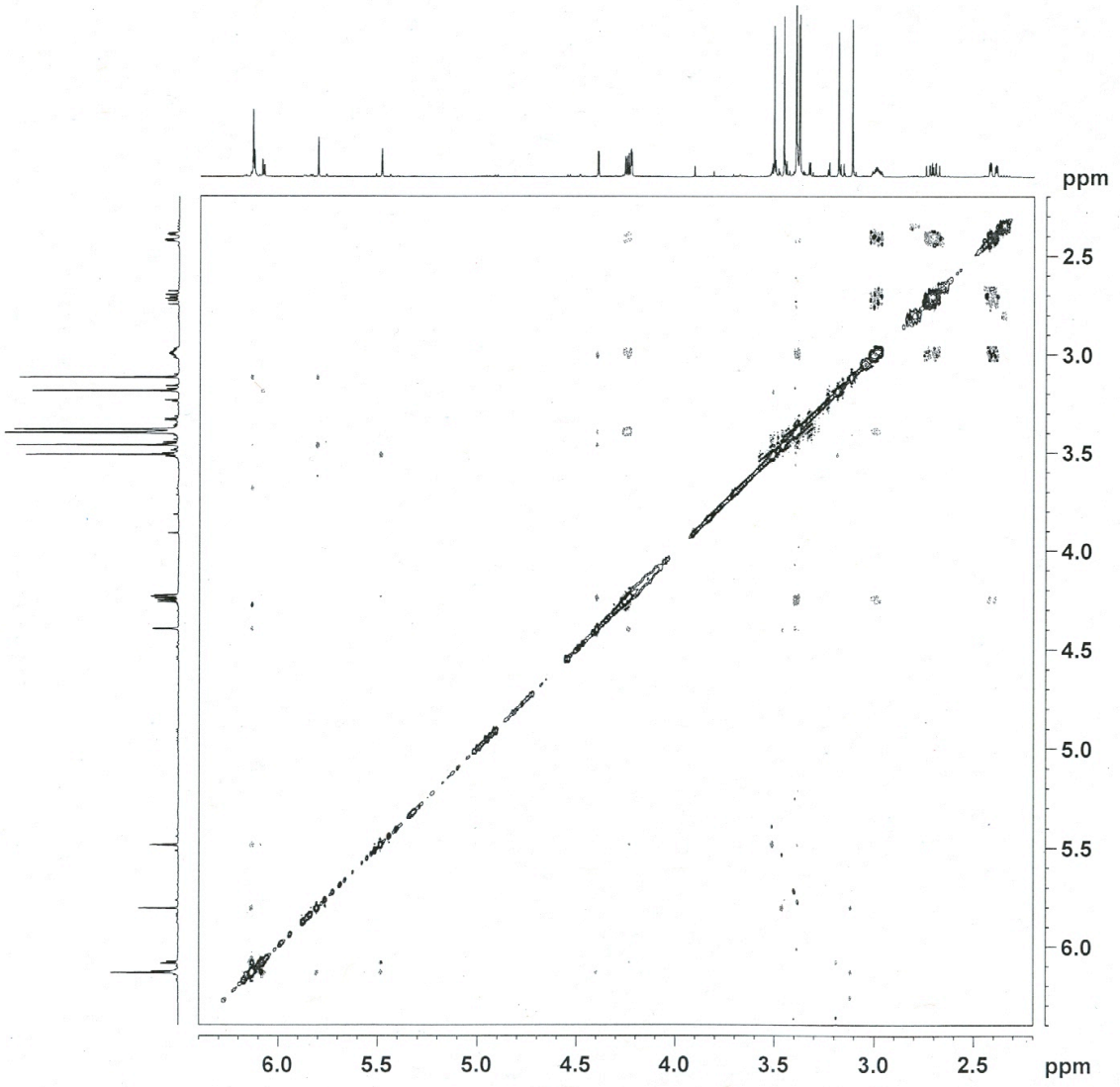




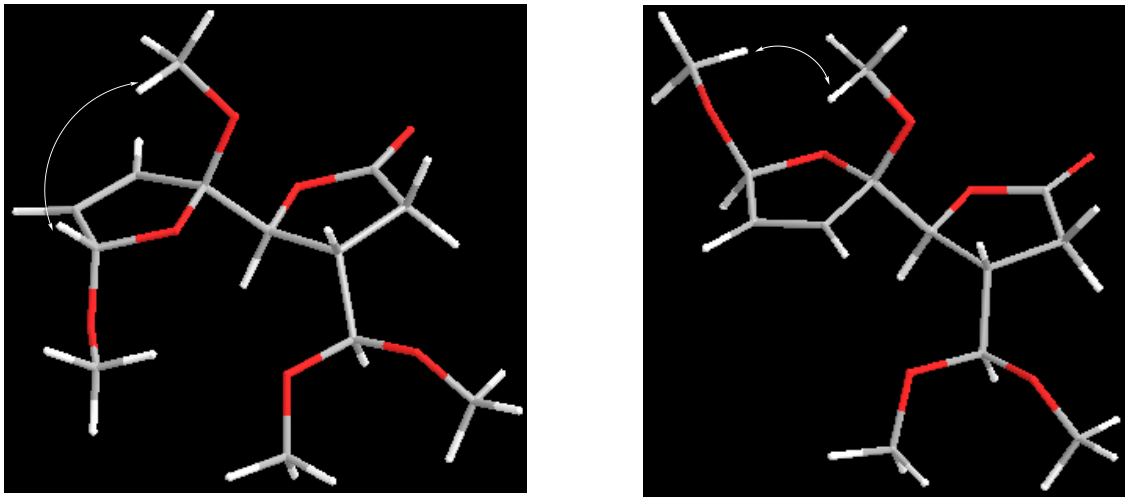
^{1}H and ^{13}C NMR Spectra of 14a & 14b





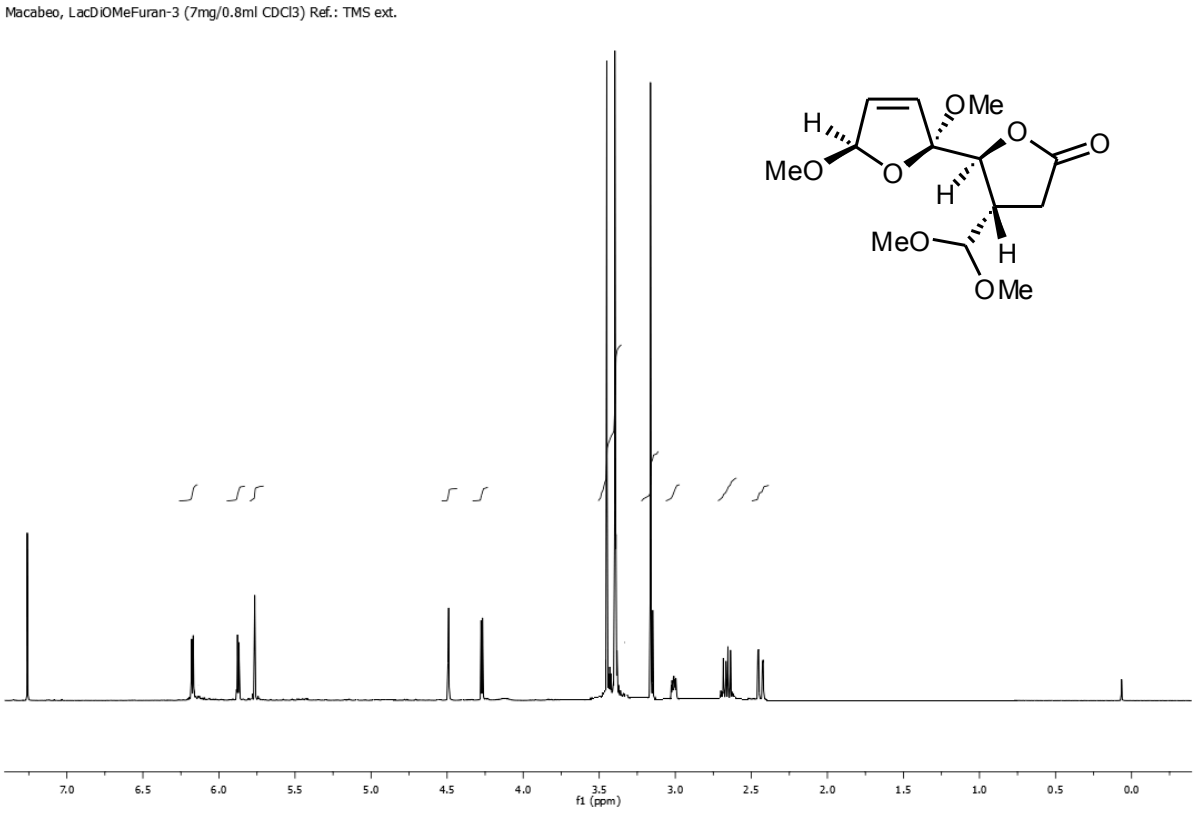


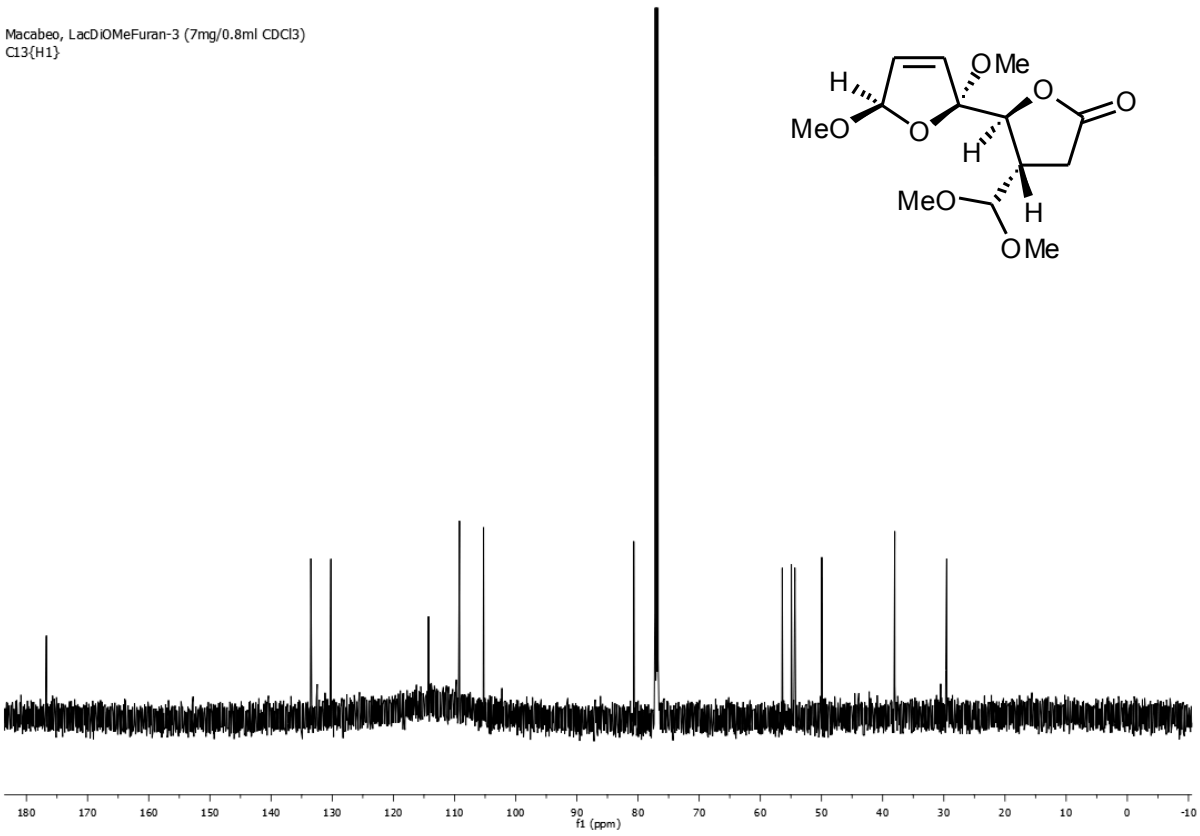
2D NOESY spectrum of 14a and 14b

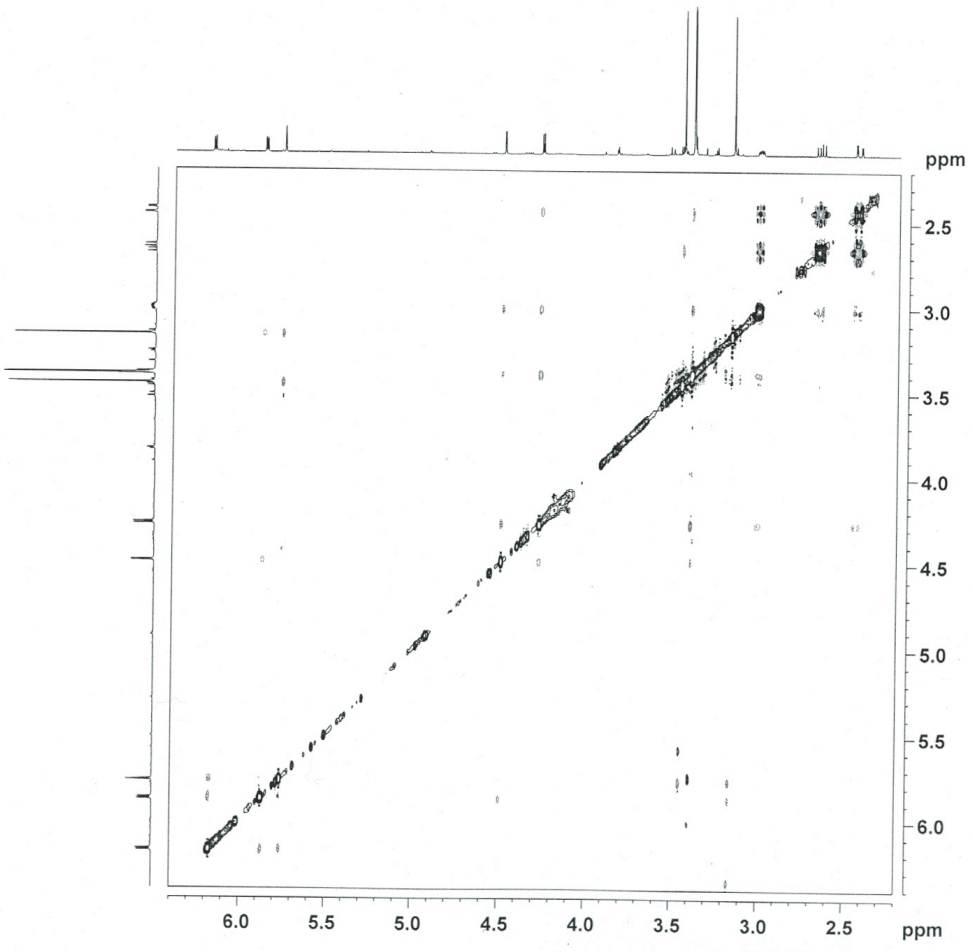


Key NOESY correlations in 14a and 14b

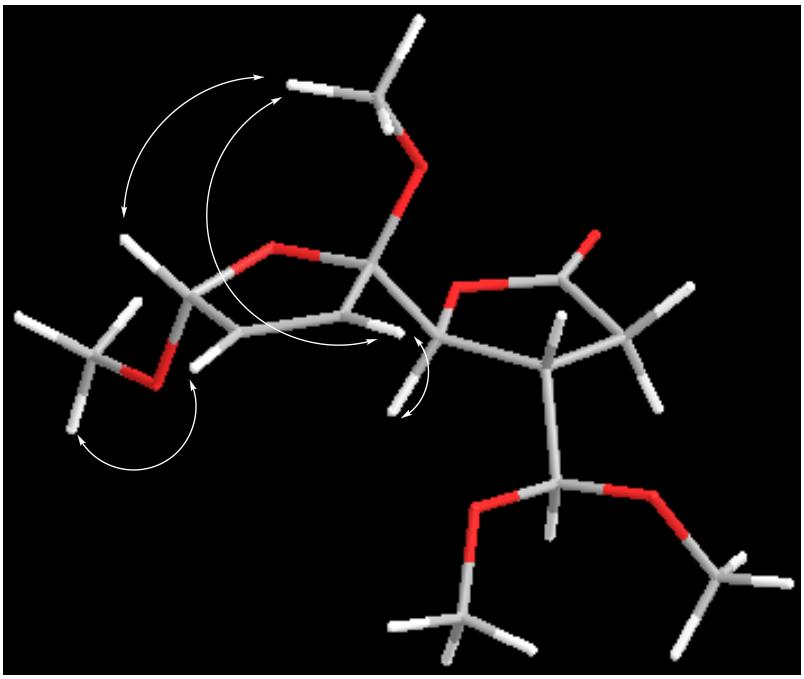
^{1}H and ^{13}C NMR Spectra of 14c





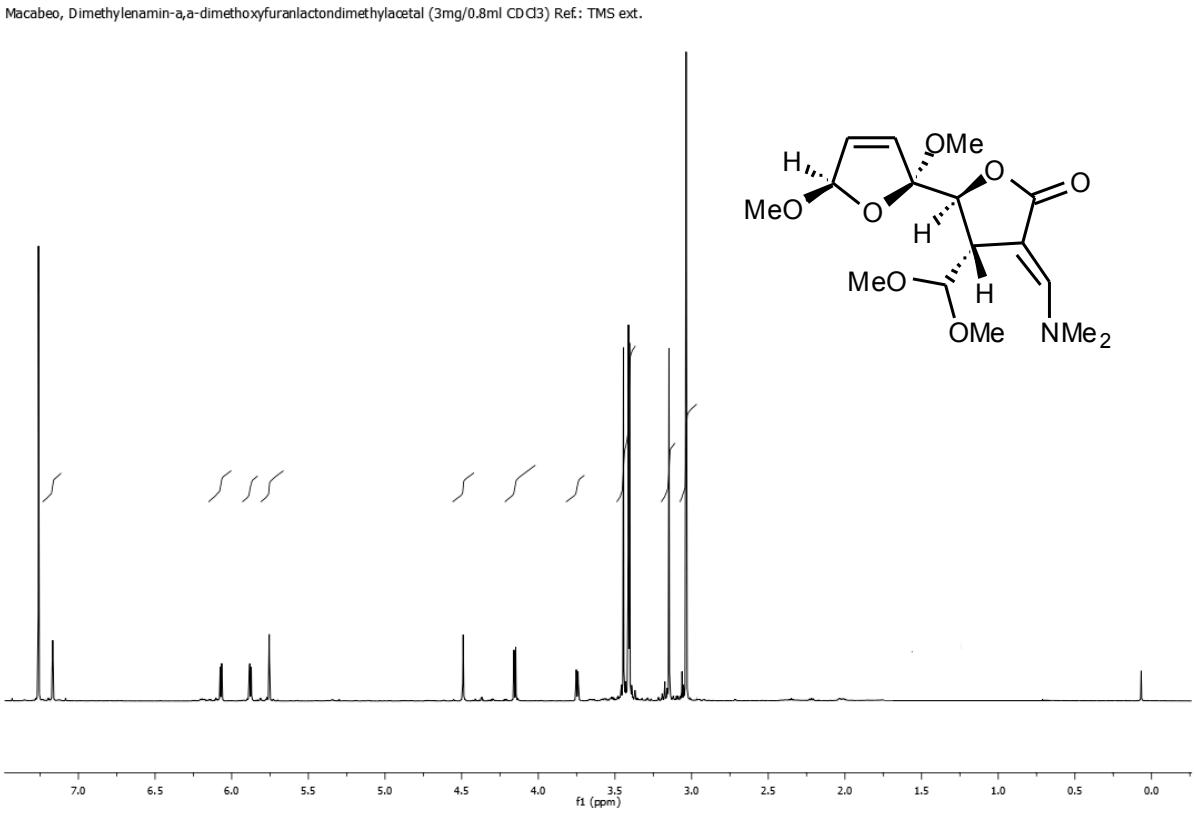


2D NOESY spectrum of 14c



Key NOESY correlations in 14c

^{1}H and ^{13}C NMR Spectra of 15



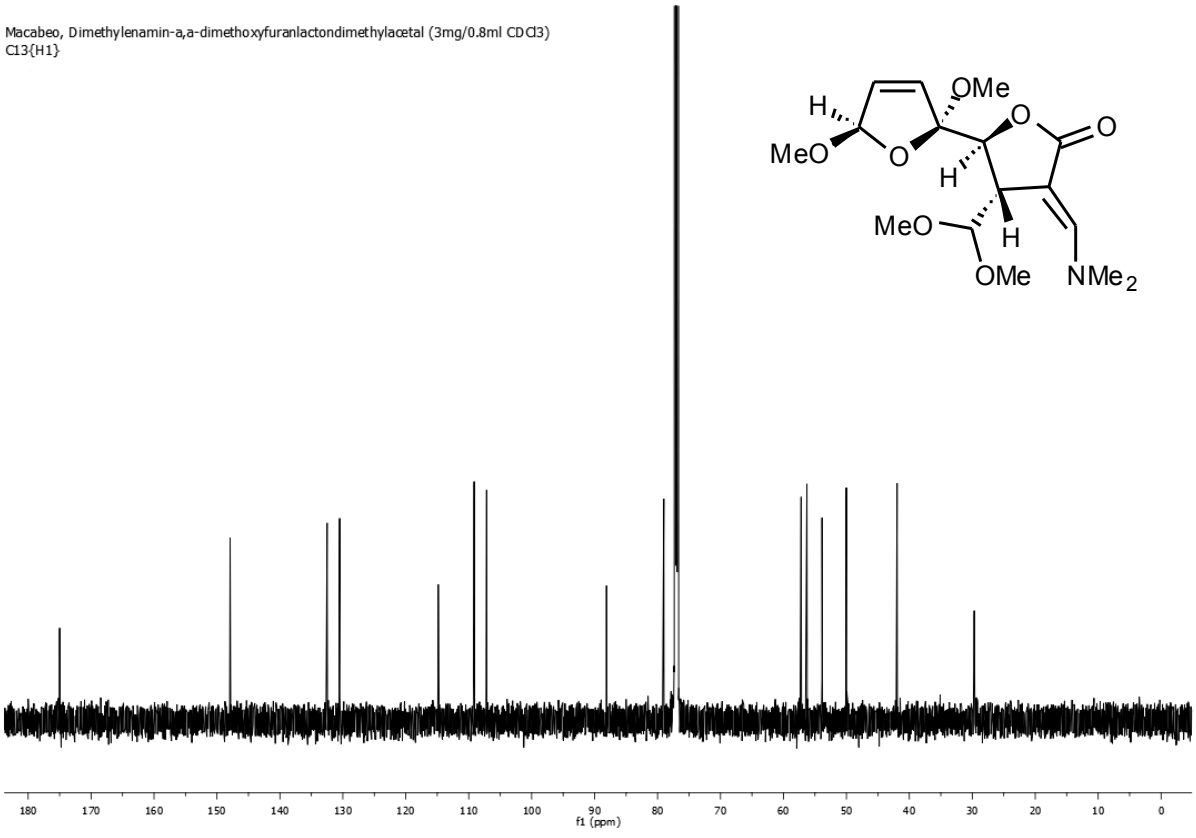
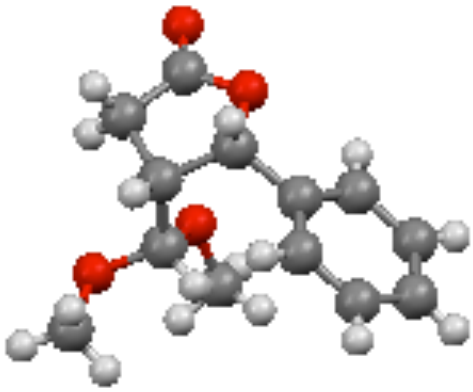


Table 1. Crystal data and structure refinement for lactone 9c.



Crystal Data ;

Empirical formula ;$C_{13}H_{16}O_4$
Formula weight ;236.26

Crystal size ;0.467 x 0.148 x 0.050 mm

Crystal description;needle

Crystal colour;colourless

Crystal system;Orthorhombic

Space group ;P 21 21 21

Unit cell dimensions ;a = 5.9224(2) A alpha = 90 deg.
;b = 11.4859(4) A beta = 90 deg.
;c = 17.6998(5) A gamma = 90 deg.

Volume ;1204.01(7) A^3
Z, Calculated density ;4, 1.303 Mg/m^3
Absorption coefficient ;0.796 mm^-1
F(000) ;504

Data Collection ;

Measurement device type ;Goniometer Xcalibur, detector: Ruby (Gemini ultra Mo)
Measuremnet method ;\w scans
Temperature ;123 K
Wavelength ;1.54184 A
Monochromator ; graphite
Theta range for data collection ;4.59 to 66.57 deg.
Index ranges ;-6<=h<=7, -10<=k<=13, -20<=l<=20
Reflections collected / unique ;5996 / 2090 [R(int) = 0.0182]
Reflections greater I>2\s(I);2043
Absorption correction ;Semi-empirical from equivalents
Max. and min. transmission ;0.962 and 0.784

Refinement ;

Refinement method ;Full-matrix least-squares on F^2
Hydrogen treatment ;:
Data / restraints / parameters ;2090 / 0 / 156

Goodness-of-fit on F^2 ;1.074
Final R indices [I>2sigma(I)] ;R1 = 0.0292, wR2 = 0.0746
R indices (all data) ;R1 = 0.0296, wR2 = 0.0749
Absolute structure parameter ;0.07(15)

Largest diff. peak and hole ;0.104 and -0.181 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for i142.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

;x ;y ;z ;U(eq)

O(1);2241(2);2951(1);1836(1);26(1)
O(2);-632(2);2633(1);1052(1);35(1)
O(3);1689(2);5504(1);1482(1);28(1)
O(4);3986(2);6092(1);521(1);36(1)
C(1);1235(2);3014(1);1151(1);27(1)
C(2);2790(2);3581(1);594(1);30(1)
C(3);4540(2);4200(1);1083(1);26(1)
C(4);4509(2);3440(1);1803(1);24(1)
C(5);5037(2);4043(1);2541(1);24(1)
C(6);7183(2);4506(1);2647(1);29(1)
C(7);7713(2);5095(1);3311(1);31(1)
C(8);6110(3);5202(1);3876(1);34(1)
C(9);3986(3);4724(1);3779(1);38(1)
C(10);3449(2);4150(1);3109(1);30(1)
C(11);3905(2);5472(1);1212(1);26(1)
C(12);1124(3);6603(1);1813(1);37(1)
C(13);6090(3);6650(1);388(1);45(1)

Table 3. Bond lengths [A] and angles [deg] for i142.

O(1)-C(1);1.3531(15)
O(1)-C(4);1.4568(15)
O(2)-C(1);1.2020(15)
O(3)-C(11);1.3972(15)
O(3)-C(12);1.4310(17)
O(4)-C(11);1.4162(16)
O(4)-C(13);1.421(2)
C(1)-C(2);1.4981(17)
C(2)-C(3);1.5270(17)
C(3)-C(4);1.5454(18)
C(3)-C(11);1.5263(19)
C(4)-C(5);1.5106(18)
C(5)-C(6);1.3906(17)
C(5)-C(10);1.3830(17)
C(6)-C(7);1.3907(19)
C(7)-C(8);1.385(2)
C(8)-C(9);1.384(2)
C(9)-C(10);1.3923(19)
C(2)-H(2A);0.9900

C(2)-H(2B);0.9900
C(3)-H(3);1.0000
C(4)-H(4);1.0000
C(6)-H(6);0.9500
C(7)-H(7);0.9500
C(8)-H(8);0.9500
C(9)-H(9);0.9500
C(10)-H(10);0.9500
C(11)-H(11);1.0000
C(12)-H(12A);0.9800
C(12)-H(12B);0.9800
C(12)-H(12C);0.9800
C(13)-H(13A);0.9800
C(13)-H(13B);0.9800
C(13)-H(13C);0.9800

C(1)-O(1)-C(4);110.51(9)
C(11)-O(3)-C(12);112.52(11)
C(11)-O(4)-C(13);113.52(11)
O(1)-C(1)-O(2);121.06(11)
O(1)-C(1)-C(2);110.01(10)
O(2)-C(1)-C(2);128.92(11)
C(1)-C(2)-C(3);104.26(10)
C(2)-C(3)-C(4);101.35(10)
C(2)-C(3)-C(11);111.32(10)
C(4)-C(3)-C(11);114.54(10)
O(1)-C(4)-C(3);105.13(9)
O(1)-C(4)-C(5);109.51(10)
C(3)-C(4)-C(5);116.79(10)
C(4)-C(5)-C(6);118.82(11)
C(4)-C(5)-C(10);121.91(11)
C(6)-C(5)-C(10);119.27(11)
C(5)-C(6)-C(7);120.46(11)
C(6)-C(7)-C(8);119.90(12)
C(7)-C(8)-C(9);119.86(12)
C(8)-C(9)-C(10);120.12(14)
C(5)-C(10)-C(9);120.38(12)
O(3)-C(11)-O(4);108.31(10)
O(3)-C(11)-C(3);107.91(10)
O(4)-C(11)-C(3);110.13(10)
C(1)-C(2)-H(2A);111.00
C(1)-C(2)-H(2B);111.00
C(3)-C(2)-H(2A);111.00
C(3)-C(2)-H(2B);111.00
H(2A)-C(2)-H(2B);109.00
C(2)-C(3)-H(3);110.00
C(4)-C(3)-H(3);110.00
C(11)-C(3)-H(3);110.00
O(1)-C(4)-H(4);108.00
C(3)-C(4)-H(4);108.00
C(5)-C(4)-H(4);108.00
C(5)-C(6)-H(6);120.00
C(7)-C(6)-H(6);120.00
C(6)-C(7)-H(7);120.00

C(8)-C(7)-H(7);120.00
C(7)-C(8)-H(8);120.00
C(9)-C(8)-H(8);120.00
C(8)-C(9)-H(9);120.00
C(10)-C(9)-H(9);120.00
C(5)-C(10)-H(10);120.00
C(9)-C(10)-H(10);120.00
O(3)-C(11)-H(11);110.00
O(4)-C(11)-H(11);110.00
C(3)-C(11)-H(11);110.00
O(3)-C(12)-H(12A);109.00
O(3)-C(12)-H(12B);109.00
O(3)-C(12)-H(12C);109.00
H(12A)-C(12)-H(12B);109.00
H(12A)-C(12)-H(12C);110.00
H(12B)-C(12)-H(12C);109.00
O(4)-C(13)-H(13A);109.00
O(4)-C(13)-H(13B);109.00
O(4)-C(13)-H(13C);109.00
H(13A)-C(13)-H(13B);109.00
H(13A)-C(13)-H(13C);109.00
H(13B)-C(13)-H(13C);109.00

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for i142.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

;U11 ;U22 ;U33 ;U23 ;U13 ;U12

O(1);27(1);27(1);23(1);-1(1);-1(1);-3(1)
O(2);28(1);40(1);35(1);-10(1);-4(1);-1(1)
O(3);29(1);24(1);32(1);-3(1);1(1);2(1)
O(4);42(1);37(1);28(1);11(1);-2(1);-5(1)
C(1);29(1);25(1);25(1);-7(1);-1(1);6(1)
C(2);37(1);30(1);23(1);-4(1);0(1);2(1)
C(3);26(1);30(1);21(1);0(1);3(1);1(1)
C(4);22(1);24(1);25(1);0(1);1(1);1(1)
C(5);28(1);21(1);23(1);3(1);-2(1);4(1)
C(6);27(1);29(1);30(1);0(1);1(1);2(1)
C(7);29(1);28(1);37(1);-1(1);-6(1);-2(1)
C(8);41(1);33(1);27(1);-4(1);-4(1);-3(1)
C(9);40(1);45(1);28(1);-7(1);6(1);-7(1)
C(10);28(1);35(1);28(1);-2(1);3(1);-5(1)
C(11);29(1);28(1);23(1);4(1);-1(1);-2(1)
C(12);43(1);26(1);41(1);-5(1);1(1);5(1)
C(13);55(1);40(1);39(1);8(1);9(1);-11(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for i142.

;x ;y ;z ;U(eq)

H(2A);1962;4144;273;36
H(2B);3515;2992;265;36
H(3);6058;4153;838;31
H(4);5607;2787;1734;29
H(6);8294;4420;2265;34
H(7);9173;5423;3376;38
H(8);6468;5604;4330;40
H(9);2892;4786;4169;45
H(10);1983;3829;3043;36
H(11);4952;5835;1587;32
H(12A);2044;6727;2266;55
H(12B);-478;6607;1952;55
H(12C);1418;7227;1448;55
H(13A);6027;7073;-93;67
H(13B);6403;7199;799;67
H(13C);7291;6064;366;67

Table 6. Torsion angles [deg] for i142.

C(4)-O(1)-C(1)-O(2);178.35(12)
C(4)-O(1)-C(1)-C(2);-0.75(13)
C(1)-O(1)-C(4)-C(5);145.08(10)
C(1)-O(1)-C(4)-C(3);18.85(12)
C(12)-O(3)-C(11)-O(4);-76.69(12)
C(12)-O(3)-C(11)-C(3);164.10(10)
C(13)-O(4)-C(11)-C(3);-93.59(12)
C(13)-O(4)-C(11)-O(3);148.61(11)
O(1)-C(1)-C(2)-C(3);-17.81(13)
O(2)-C(1)-C(2)-C(3);163.19(13)
C(1)-C(2)-C(3)-C(11);-94.90(12)
C(1)-C(2)-C(3)-C(4);27.31(12)
C(2)-C(3)-C(11)-O(4);-65.80(13)
C(2)-C(3)-C(11)-O(3);52.24(13)
C(2)-C(3)-C(4)-C(5);-149.76(10)
C(4)-C(3)-C(11)-O(3);-62.00(13)
C(2)-C(3)-C(4)-O(1);-28.15(11)
C(11)-C(3)-C(4)-C(5);-29.80(15)
C(4)-C(3)-C(11)-O(4);179.97(9)
C(11)-C(3)-C(4)-O(1);91.80(11)
O(1)-C(4)-C(5)-C(10);-4.28(16)
C(3)-C(4)-C(5)-C(6);-64.86(15)
C(3)-C(4)-C(5)-C(10);115.00(13)
O(1)-C(4)-C(5)-C(6);175.86(11)
C(4)-C(5)-C(6)-C(7);178.31(12)
C(10)-C(5)-C(6)-C(7);-1.56(19)
C(4)-C(5)-C(10)-C(9);-179.27(12)
C(6)-C(5)-C(10)-C(9);0.6(2)

C(5)-C(6)-C(7)-C(8);1.3(2)
C(6)-C(7)-C(8)-C(9);0.0(2)
C(7)-C(8)-C(9)-C(10);-1.0(2)
C(8)-C(9)-C(10)-C(5);0.7(2)

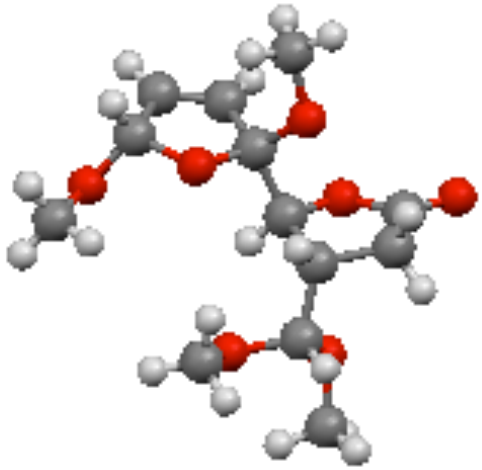
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen-bonds for i142 [A and deg.].

D-H...A;d(D-H);d(H...A);d(D...A);<(DHA)

C(2)-H(2A)...O(4); 0.9900; 2.5800; 2.9732(17); 104.00
C(2)-H(2B)...O(2)#1; 0.9900; 2.4900; 3.3609(16); 147.00
C(4)-H(4)...O(2)#2; 1.0000; 2.5400; 3.3030(15); 133.00
C(10)-H(10)...O(1); 0.9500; 2.3700; 2.7370(15); 103.00

Table 1. Crystal data and structure refinement for compound 14a.



Crystal Data ;

Empirical formula ;$C_{13}H_{20}O_7$
Formula weight ;288.29

Crystal size ;0.2359 x 0.1897 x 0.1102 mm

Crystal description ;plate

Crystal colour ;colourless

Crystal system;Monoclinic

Space group ;P 21

Unit cell dimensions ;a = 7.8226(2) A alpha = 90 deg.
;b = 10.0497(2) A beta = 102.925(2) deg.
;c = 9.1628(2) A gamma = 90 deg.

Volume ;702.08(3) A^3

Z, Calculated density ;2, 1.364 Mg/m^3

Absorption coefficient ;0.943 mm^-1

F(000) ;308

Data Collection ;

Measurement device type ;Goniometer Xcalibur, detector: Ruby (Gemini ultra Mo)
Measuremnet method ;\w scans
Temperature ;123 K
Wavelength ;1.54184 A
Monochromator ; graphite
Theta range for data collection ;4.95 to 66.79 deg.
Index ranges ;-9<=h<=8, -11<=k<=11, -10<=l<=10
Reflections collected / unique ;6700 / 2377 [R(int) = 0.0245]
Reflections greater I>2\s(I);2308
Absorption correction ;Analytical
Max. and min. transmission ;0.916 and 0.864

Refinement ;

Refinement method ;Full-matrix least-squares on F^2
Hydrogen treatment ;:

Data / restraints / parameters ;2377 / 1 / 181
Goodness-of-fit on F^2 ;1.080
Final R indices [I>2sigma(I)] ;R1 = 0.0282, wR2 = 0.0739
R indices (all data) ;R1 = 0.0289, wR2 = 0.0742
Absolute structure parameter ;0.06(15)
Largest diff. peak and hole ;0.238 and -0.150 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for j031.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

;x ;y ;z ;U(eq)

O(1);9253(2);9784(1);372(1);35(1)
O(2);8220(2);9260(1);2375(1);26(1)
O(3);8670(2);6642(1);5202(1);27(1)
O(4);4803(2);8009(1);636(1);30(1)
O(5);4570(2);6380(1);2296(1);31(1)
O(6);10664(2);7422(1);3865(1);27(1)
O(7);6893(2);6896(1);6922(1);31(1)
C(1);8697(2);8946(2);1083(2);26(1)
C(2);8421(2);7487(2);748(2);26(1)
C(3);7430(2);6983(2);1892(2);24(1)
C(4);7738(2);8081(2);3092(2);24(1)
C(5);9212(2);7761(2);4455(2);24(1)
C(6);9544(2);8840(2);5627(2);25(1)
C(7);9214(2);8397(2);6881(2);27(1)
C(8);8607(2);6978(2);6716(2);27(1)
C(9);5486(2);6787(2);1210(2);26(1)
C(10);3062(3);7903(2);-267(2);44(1)
C(11);4699(3);4992(2);2590(2);37(1)
C(12);12262(2);7196(2);4950(2);31(1)
C(13);6325(3);5556(2);7003(2);39(1)

Table 3. Bond lengths [A] and angles [deg] for j031.

O(1)-C(1);1.204(2)
O(2)-C(1);1.355(2)
O(2)-C(4);1.4454(19)
O(3)-C(5);1.430(2)
O(3)-C(8);1.4394(19)
O(4)-C(9);1.395(2)
O(4)-C(10);1.430(3)
O(5)-C(9);1.411(2)
O(5)-C(11);1.420(2)
O(6)-C(5);1.405(2)
O(6)-C(12);1.430(2)
O(7)-C(8);1.397(2)
O(7)-C(13);1.426(2)
C(1)-C(2);1.504(2)
C(2)-C(3);1.523(2)
C(3)-C(4);1.538(2)

C(3)-C(9);1.522(2)
C(4)-C(5);1.532(2)
C(5)-C(6);1.507(2)
C(6)-C(7);1.311(2)
C(7)-C(8);1.500(2)
C(2)-H(2A);0.9900
C(2)-H(2B);0.9900
C(3)-H(3);1.0000
C(4)-H(4);1.0000
C(6)-H(6);0.9500
C(7)-H(7);0.9500
C(8)-H(8);1.0000
C(9)-H(9);1.0000
C(10)-H(10A);0.9800
C(10)-H(10B);0.9800
C(10)-H(10C);0.9800
C(11)-H(11A);0.9800
C(11)-H(11B);0.9800
C(11)-H(11C);0.9800
C(12)-H(12A);0.9800
C(12)-H(12B);0.9800
C(12)-H(12C);0.9800
C(13)-H(13A);0.9800
C(13)-H(13B);0.9800
C(13)-H(13C);0.9800

C(1)-O(2)-C(4);110.93(12)
C(5)-O(3)-C(8);110.80(12)
C(9)-O(4)-C(10);112.80(13)
C(9)-O(5)-C(11);113.15(14)
C(5)-O(6)-C(12);115.31(12)
C(8)-O(7)-C(13);112.46(14)
O(1)-C(1)-O(2);120.89(15)
O(1)-C(1)-C(2);128.60(15)
O(2)-C(1)-C(2);110.51(14)
C(1)-C(2)-C(3);104.79(13)
C(2)-C(3)-C(4);103.37(13)
C(2)-C(3)-C(9);112.08(13)
C(4)-C(3)-C(9);111.63(13)
O(2)-C(4)-C(3);106.15(12)
O(2)-C(4)-C(5);108.46(12)
C(3)-C(4)-C(5);113.66(13)
O(3)-C(5)-O(6);110.18(12)
O(3)-C(5)-C(4);107.77(12)
O(3)-C(5)-C(6);104.28(12)
O(6)-C(5)-C(4);105.29(12)
O(6)-C(5)-C(6);115.06(13)
C(4)-C(5)-C(6);114.11(13)
C(5)-C(6)-C(7);110.15(14)
C(6)-C(7)-C(8);110.77(14)
O(3)-C(8)-O(7);110.90(13)
O(3)-C(8)-C(7);103.98(13)
O(7)-C(8)-C(7);109.49(13)
O(4)-C(9)-O(5);108.03(13)

O(4)-C(9)-C(3);107.73(13)
O(5)-C(9)-C(3);111.50(12)
C(1)-C(2)-H(2A);111.00
C(1)-C(2)-H(2B);111.00
C(3)-C(2)-H(2A);111.00
C(3)-C(2)-H(2B);111.00
H(2A)-C(2)-H(2B);109.00
C(2)-C(3)-H(3);110.00
C(4)-C(3)-H(3);110.00
C(9)-C(3)-H(3);110.00
O(2)-C(4)-H(4);109.00
C(3)-C(4)-H(4);109.00
C(5)-C(4)-H(4);110.00
C(5)-C(6)-H(6);125.00
C(7)-C(6)-H(6);125.00
C(6)-C(7)-H(7);125.00
C(8)-C(7)-H(7);125.00
O(3)-C(8)-H(8);111.00
O(7)-C(8)-H(8);111.00
C(7)-C(8)-H(8);111.00
O(4)-C(9)-H(9);110.00
O(5)-C(9)-H(9);110.00
C(3)-C(9)-H(9);110.00
O(4)-C(10)-H(10A);109.00
O(4)-C(10)-H(10B);110.00
O(4)-C(10)-H(10C);109.00
H(10A)-C(10)-H(10B);109.00
H(10A)-C(10)-H(10C);109.00
H(10B)-C(10)-H(10C);109.00
O(5)-C(11)-H(11A);109.00
O(5)-C(11)-H(11B);109.00
O(5)-C(11)-H(11C);109.00
H(11A)-C(11)-H(11B);109.00
H(11A)-C(11)-H(11C);109.00
H(11B)-C(11)-H(11C);109.00
O(6)-C(12)-H(12A);109.00
O(6)-C(12)-H(12B);109.00
O(6)-C(12)-H(12C);109.00
H(12A)-C(12)-H(12B);109.00
H(12A)-C(12)-H(12C);109.00
H(12B)-C(12)-H(12C);109.00
O(7)-C(13)-H(13A);109.00
O(7)-C(13)-H(13B);109.00
O(7)-C(13)-H(13C);110.00
H(13A)-C(13)-H(13B);109.00
H(13A)-C(13)-H(13C);110.00
H(13B)-C(13)-H(13C);109.00

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for j031.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

;U11 ;U22 ;U33 ;U23 ;U13 ;U12

O(1);44(1);34(1);28(1);2(1);12(1);-9(1)
O(2);34(1);23(1);22(1);0(1);9(1);0(1)
O(3);37(1);22(1);24(1);-1(1);12(1);-1(1)
O(4);25(1);31(1);34(1);3(1);4(1);-1(1)
O(5);32(1);33(1);33(1);-1(1);15(1);-6(1)
O(6);25(1);33(1);25(1);-1(1);10(1);2(1)
O(7);31(1);34(1);31(1);-1(1);12(1);-1(1)
C(1);24(1);30(1);23(1);-1(1);5(1);-2(1)
C(2);26(1);29(1);26(1);-3(1);11(1);-2(1)
C(3);26(1);24(1);24(1);-2(1);9(1);0(1)
C(4);26(1);22(1);25(1);0(1);11(1);0(1)
C(5);27(1);22(1);25(1);0(1);11(1);1(1)
C(6);25(1);22(1);27(1);0(1);6(1);0(1)
C(7);28(1);28(1);24(1);-4(1);7(1);1(1)
C(8);31(1);30(1);23(1);1(1);11(1);1(1)
C(9);28(1);27(1);25(1);-2(1);10(1);-3(1)
C(10);28(1);49(1);51(1);6(1);4(1);-1(1)
C(11);40(1);34(1);38(1);4(1);14(1);-8(1)
C(12);28(1);33(1);33(1);-3(1);7(1);1(1)
C(13);40(1);38(1);43(1);1(1);14(1);-10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for j031.

;x ;y ;z ;U(eq)

H(2A);9559;7021;861;31
H(2B);7725;7349;-285;31
H(3);7958;6128;2338;29
H(4);6625;8250;3427;28
H(6);9937;9714;5479;30
H(7);9341;8906;7773;32
H(8);9411;6392;7446;33
H(9);5329;6114;387;31
H(10A);2283;7541;337;52
H(10B);3064;7310;-1115;52
H(10C);2645;8786;-640;52
H(11A);5933;4749;2961;44
H(11B);4217;4501;1665;44
H(11C);4036;4768;3346;44
H(12A);12094;6470;5617;37
H(12B);12595;8008;5538;37
H(12C);13193;6957;4438;37
H(13A);7097;5106;7849;47
H(13B);6370;5091;6072;47
H(13C);5120;5549;7143;47

Table 6. Torsion angles [deg] for j031.

C(4)-O(2)-C(1)-O(1);-175.12(15)
C(4)-O(2)-C(1)-C(2);4.87(17)
C(1)-O(2)-C(4)-C(5);106.11(14)
C(1)-O(2)-C(4)-C(3);-16.39(16)
C(5)-O(3)-C(8)-O(7);115.81(14)
C(8)-O(3)-C(5)-C(6);1.53(16)
C(8)-O(3)-C(5)-C(4);-120.08(13)
C(5)-O(3)-C(8)-C(7);-1.78(16)
C(8)-O(3)-C(5)-O(6);125.53(13)
C(10)-O(4)-C(9)-C(3);169.57(13)
C(10)-O(4)-C(9)-O(5);-69.85(16)
C(11)-O(5)-C(9)-O(4);159.69(14)
C(11)-O(5)-C(9)-C(3);-82.12(17)
C(12)-O(6)-C(5)-O(3);-69.43(16)
C(12)-O(6)-C(5)-C(6);48.08(18)
C(12)-O(6)-C(5)-C(4);174.63(13)
C(13)-O(7)-C(8)-C(7);-171.21(13)
C(13)-O(7)-C(8)-O(3);74.61(16)
O(1)-C(1)-C(2)-C(3);-171.28(17)
O(2)-C(1)-C(2)-C(3);8.73(17)
C(1)-C(2)-C(3)-C(9);102.81(15)
C(1)-C(2)-C(3)-C(4);-17.54(16)
C(4)-C(3)-C(9)-O(5);-61.85(17)
C(2)-C(3)-C(4)-O(2);20.65(15)
C(2)-C(3)-C(4)-C(5);-98.49(15)
C(9)-C(3)-C(4)-O(2);-100.01(14)
C(2)-C(3)-C(9)-O(5);-177.27(13)
C(4)-C(3)-C(9)-O(4);56.52(16)
C(2)-C(3)-C(9)-O(4);-58.90(16)
C(9)-C(3)-C(4)-C(5);140.86(14)
C(3)-C(4)-C(5)-C(6);179.10(13)
C(3)-C(4)-C(5)-O(6);51.98(16)
O(2)-C(4)-C(5)-C(6);61.30(17)
O(2)-C(4)-C(5)-O(3);176.59(11)
O(2)-C(4)-C(5)-O(6);-65.82(15)
C(3)-C(4)-C(5)-O(3);-65.61(16)
O(6)-C(5)-C(6)-C(7);-121.42(15)
C(4)-C(5)-C(6)-C(7);116.68(16)
O(3)-C(5)-C(6)-C(7);-0.63(18)
C(5)-C(6)-C(7)-C(8);-0.47(19)
C(6)-C(7)-C(8)-O(3);1.38(18)
C(6)-C(7)-C(8)-O(7);-117.19(15)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen-bonds for j031 [A and deg.].

D-H...A;d(D-H);d(H...A);d(D...A);<(DHA)

C(2)-H(2B)...O(7)#1; 0.9900; 2.5400; 3.492(2); 162.00
C(4)-H(4)...O(5); 1.0000; 2.5400; 2.965(2); 105.00
C(6)-H(6)...O(3)#2; 0.9500; 2.3700; 3.307(2); 167.00
C(7)-H(7)...O(1)#3; 0.9500; 2.5600; 3.483(2); 165.00
C(12)-H(12C)...O(5)#4; 0.9800; 2.5100; 3.437(2); 158.00