Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 847–849

[4+2]-Cycloaddition of maleic anhydride to substituted cycloheptatrienes for the synthesis of novel 4-oxatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-3,5-diones

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Content:

Experimental Section

The ^{1}H, ^{13}C spectra were measured in $CDCl_3$ on a Bruker Avance-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C). The X-ray diffraction analysis were performed on an automatic four-circle diffractometer Agilent XCalibur (Gemini, Eos) (graphite monochromator, MoK_α radiation, ω-scan mode, $2\theta_{max}$. 62º) at 293 K. Collected data were processed using the program CrysAlisPro [S1]. The structures were solved by direct methods and refined using the program package SHELX [S2]. The structure was refined by a full-matrix least-square technique using anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms are generated using the proper HFIX command and refined isotropically using the riding model. Mass spectra were obtained with a Shimadzu GC–MS-QP2010 Plus spectrometer at 70 eV and a working temperature 200 °C. Elemental analyses were measured on a 1106 Carlo Erba apparatus. 7-Ethyl-, phenyl-, allyl- and acyl-substituted 1,3,5-cycloheptatrienes were prepared as described [S3]. Commercially available 2,4,6-cycloheptatriene-1-carbonitrile (Aldrich) and *p*-xylene (Aldrich) were used.

*[4+2]-Cycloaddition of maleic anhydride to 1,3,5-cycloheptatrienes **1a-e** (general procedure)*

A solution of 1,3,5-cycloheptatriene **1a-e** (2 mmol) and maleic anhydride (2 mmol) in *p*-xylene (2 ml) was refluxed for 3 hr. The solvent was evaporated under reduced pressure, and the residue was recrystallized from a mixture of petroleum ether and ethyl acetate (10:1) to afford the target products **2a-e**.

9-Ethyl-4-oxatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-3,5-dione (2a): Yield 93% (0.405 g), white solid, m.p. = 159-160 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.89-5.94 (m, 2H), 3.45-3.49 (m, 2H), 3.20-3.22 (m, 2H), 1.17-1.24 (m, 2H), 0.84-0.93 (m, 5H), 0.49-0.56 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.5 (2C), 129.3 (2C), 45.7 (2C), 33.7 (2C), 24.2, 20.3, 16.9 (2C), 13.3 ppm. MS (EI, 70 eV) (%) = 218 $[M]^+$ (1), 190 (< 1), 145 (12), 120 (24), 91 (100), 78 (15), 65 (6), 41 (3). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.42; H, 6.39.

9-Phenyl-4-oxatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-3,5-dione (2b): Yield 95% (0.505 g), white solid, m.p. = 195-196 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (dd, *J* = 9.9 Hz, *J* = 5.2 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 2H), 6.07-6.09 (m, 2H), 3.65-3.70 (m, 2H), 3.32-3.34 (m, 2H), 1.71 (t, *J* = 3.2 Hz, 1H), 1.49-1.52 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.1 (2C), 140.1, 129.2 (2C), 128.5 (2C), 126.4 (2C), 126.2, 45.5 (2C), 33.8 (2C), 22.7, 20.6 (2C) ppm. MS (EI, 70 eV) (%) = 266 $[M]^+$ (12), 238 (9), 193 (45), 167 (100), 152 (16), 129 (19), 115 (40), 91 (29), 77 (9), 65 (10), 41 (2). Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.59; H, 5.25.

9-Allyl-4-oxatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-3,5-dione (2c): Yield 89% (0.409 g), white solid, m.p. = 105-106 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.91-5.96 (m, 2H), 5.72-5.81 (m,

1H), 4.94-5.03 (m, 2H), 3.46-3.53 (m, 2H), 3.22-3.25 (m, 2H), 1.95 (t, *J* = 6.6 Hz, 2H), 0.94-0.98 (m, 2H), 0.62-0.68 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.4 (2C), 136.7, 129.4 (2C), 115.2, 45.6 (2C), 34.7, 33.5 (2C), 17.5, 16.8 (2C) ppm. MS (EI, 70 eV) (%) = 230 $[M]^+$ (< 1), 157 (3), 129 (6), 117 (13), 91 (100), 78 (12), 65 (6), 54 (10), 41 (2). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.93; H, 6.06.

3,5-Dioxo-4-oxatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-9-carbonitrile (2d): Yield 90% (0.387 g), white solid, m.p. = 176-177 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.99-6.05 (m, 2H), 3.65-3.70 (m, 2H), 3.32-3.34 (m, 2H), 1.89-1.93 (m, 2H), 1.23 (t, *J* = 3.2 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8 (2C), 128.9 (2C), 119.3, 44.6 (2C), 32.3 (2C), 18.3 (2C), 3.7 ppm. MS (EI, 70 eV) (%) = 215 $[M]^+$ (< 1), 187 (2), 169 (5), 143 (100), 116 (64), 90 (25), 77 (11), 63 (12), 51 (18). Anal. Calcd for $C_{12}H_9NO_3$: C, 66.97; H, 4.22; N, 6.51. Found: C, 66.84; H, 4.18; N, 6.43.

9-(2-Oxopropyl)-4-oxatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2e): Yield 85% (0.418 g), white solid, m.p. = 154-155 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.01-6.08 (m, 2H), 3.46-3.52 (m, 2H), 3.08-3.10 (m, 2H), 2.30 (d, *J* = 6.9 Hz, 2H), 2.11 (c, 3H), 0.96-1.00 (m, 2H), 0.80-0.86 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.3, 172.0 (2C), 130.2 (2C), 46.2 (2C), 44.8, 32.3 (2C), 29.9, 13.1 (2C), 10.2 ppm. MS (EI, 70 eV) (%) = 246 $[M]^+$ (1), 203 (12), 157 (2), 131 (13), 105 (43), 91 (37), 77 (10), 43 (100). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.17; H, 5.68.

Crystal data for 2b

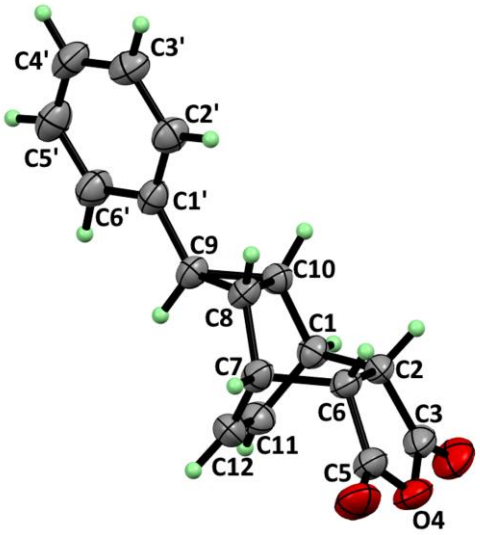


Figure S1. Geometry of molecule **2b**.

Table S1. Crystal data and structure refinement for 2b.	
Identification code	**2b**
Empirical formula	$C_{17}H_{14}O_3$
Formula weight	266.28
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.7039(15)
b/Å	6.2945(5)
c/Å	16.394(2)
α/°	90
β/°	114.320(14)
γ/°	90
Volume/Å^3	1288.7(3)
Z	4
ρ_{calc}g/cm^3	1.372
μ/mm^{-1}	0.094
F(000)	560.0
Crystal size/mm^3	0.3 × 0.15 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.454 to 75.494
Index ranges	$-23 \leq h \leq 22$, $-10 \leq k \leq 9$, $-28 \leq l \leq 20$
Reflections collected	17148
Independent reflections	6440 [R_{int} = 0.0803, R_{sigma} = 0.1081]
Data/restraints/parameters	6440/0/237
Goodness-of-fit on F^2	0.959
Final R indexes [I>=2σ (I)]	R_1 = 0.0660, wR_2 = 0.1266
Final R indexes [all data]	R_1 = 0.1692, wR_2 = 0.1678
Largest diff. peak/hole / e Å^{-3}	0.19/-0.25

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2b. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O4	6750.4(9)	2548.1(16)	7020.8(8)	49.3(3)
O1	8495.2(10)	2335.6(19)	7900.3(9)	60.4(3)
O2	5154.4(9)	3047(2)	5887.3(10)	60.5(4)
C2	7916.9(11)	3814(2)	6401.8(10)	33.6(3)
C10	8518.6(10)	3526(2)	5211.6(10)	33.5(3)
C8	7387.6(10)	3778(2)	4524.5(10)	33.8(3)
C1	8538.3(10)	2329(2)	6026.6(10)	34.6(3)
C6	6763.9(10)	4062(2)	5704.5(10)	33.0(3)
C1'	8589.2(10)	3174(2)	3660.0(10)	36.2(3)
C9	8170.2(10)	2462(2)	4312.2(11)	36.3(3)
C2'	8456.0(11)	5207(3)	3304.2(12)	42.8(4)
C7	6599.8(10)	2767(2)	4851.1(11)	36.2(3)
C11	7908.3(12)	302(2)	5750.4(12)	41.6(4)
C3'	8828.0(11)	5742(3)	2667.6(12)	45.0(4)
C12	6917.1(12)	527(2)	5151.9(12)	42.5(4)
C4'	9347.6(12)	4262(3)	2374.2(12)	46.6(4)
C3	7816.8(13)	2860(2)	7195.3(11)	42.2(4)
C5	6098.5(13)	3219(2)	6160.6(12)	42.0(4)
C6'	9128.1(12)	1709(3)	3361.0(13)	46.4(4)
C5'	9502.1(14)	2247(3)	2730.1(13)	50.9(4)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O4	65.2(7)	49.9(6)	45.3(8)	9.1(5)	35.5(6)	-2.2(5)
O1	78.9(8)	64.1(8)	34.9(8)	13.3(5)	20.0(6)	3.8(6)
O2	51.1(6)	79.0(8)	64.4(10)	0.5(7)	36.9(7)	-11.2(5)
C2	42.4(7)	31.6(6)	27.3(8)	-0.2(5)	15.1(6)	-4.9(5)
C10	33.0(6)	37.5(7)	31.9(8)	-1.0(5)	15.3(6)	-3.0(5)
C8	34.8(6)	40.2(7)	29.2(8)	2.4(5)	15.9(6)	1.1(5)
C1	35.2(6)	36.9(7)	30.3(8)	1.7(5)	12.1(6)	1.6(5)
C6	39.0(6)	32.3(7)	32.4(8)	3.2(5)	19.6(6)	1.0(5)
C1'	32.5(6)	47.6(8)	30.5(8)	-3.0(6)	14.8(6)	0.1(5)
C9	39.1(7)	40.2(8)	35.4(9)	-2.8(6)	21.1(6)	-0.3(5)
C2'	41.4(7)	47.3(8)	45.6(11)	0.2(7)	24.0(7)	4.0(6)
C7	32.0(6)	46.7(8)	31.2(8)	0.0(6)	14.3(6)	-2.7(5)
C11	54.4(8)	31.1(7)	44.4(10)	3.3(6)	25.6(7)	2.3(6)
C3'	40.2(7)	56.3(9)	39.4(10)	8.5(7)	17.2(7)	1.3(6)
C12	51.5(8)	37.0(7)	44.2(10)	-8.3(6)	25.0(7)	-12.3(6)
C4'	39.6(7)	72.2(11)	32.5(10)	3.2(7)	19.2(7)	-0.8(7)

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2b. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C3	61.0(9)	35.0(7)	34.2(9)	1.9(6)	23.2(8)	-1.2(6)
C5	51.6(8)	41.2(8)	43.4(10)	0.4(6)	29.9(8)	-3.1(6)
C6'	52.0(9)	49.3(9)	47.5(11)	0.0(7)	30.1(8)	5.1(7)
C5'	51.6(9)	63.4(10)	48.5(12)	-3.5(8)	31.5(8)	5.9(7)

Table S4. Bond Lengths for 2b.					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O4	C3	1.3827(19)	C1	C11	1.502(2)
O4	C5	1.388(2)	C6	C7	1.553(2)
O1	C3	1.1934(19)	C6	C5	1.495(2)
O2	C5	1.1869(18)	C1'	C9	1.476(2)
C2	C1	1.552(2)	C1'	C2'	1.387(2)
C2	C6	1.5297(19)	C1'	C6'	1.391(2)
C2	C3	1.489(2)	C2'	C3'	1.379(2)
C10	C8	1.5027(19)	C7	C12	1.498(2)
C10	C1	1.524(2)	C11	C12	1.315(2)
C10	C9	1.507(2)	C3'	C4'	1.374(2)
C8	C9	1.505(2)	C4'	C5'	1.376(2)
C8	C7	1.528(2)	C6'	C5'	1.373(3)

Table S5. Bond Angles for 2b.							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C3	O4	C5	110.49(12)	C8	C9	C10	59.86(9)
C6	C2	C1	109.39(12)	C1'	C9	C10	120.86(12)
C3	C2	C1	111.50(12)	C1'	C9	C8	121.81(13)
C3	C2	C6	104.81(12)	C3'	C2'	C1'	121.19(15)
C8	C10	C1	110.48(11)	C8	C7	C6	103.66(11)
C8	C10	C9	60.01(9)	C12	C7	C8	110.87(11)
C9	C10	C1	121.49(12)	C12	C7	C6	106.43(13)
C10	C8	C9	60.13(9)	C12	C11	C1	114.99(12)
C10	C8	C7	110.66(12)	C4'	C3'	C2'	120.38(16)
C9	C8	C7	121.71(12)	C11	C12	C7	114.66(12)
C10	C1	C2	103.62(11)	C3'	C4'	C5'	119.22(17)
C11	C1	C2	106.85(11)	O4	C3	C2	110.26(13)
C11	C1	C10	110.79(12)	O1	C3	O4	119.76(16)
C2	C6	C7	109.95(11)	O1	C3	C2	129.96(15)
C5	C6	C2	104.19(12)	O4	C5	C6	110.26(12)
C5	C6	C7	111.86(11)	O2	C5	O4	120.07(15)
C2'	C1'	C9	124.16(13)	O2	C5	C6	129.67(16)
C2'	C1'	C6'	117.43(16)	C5'	C6'	C1'	121.28(16)
C6'	C1'	C9	118.39(14)	C6'	C5'	C4'	120.48(16)

Table S6. Torsion Angles for 2b.									
A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C2	C1	C11	C12	58.13(18)	C9	C10	C8	C7	115.54(13)
C2	C6	C7	C8	-61.38(13)	C9	C10	C1	C2	−129.57(12)
C2	C6	C7	C12	55.61(14)	C9	C10	C1	C11	-15.30(17)
C2	C6	C5	O4	0.13(15)	C9	C8	C7	C6	129.01(14)
C2	C6	C5	O2	−178.77(16)	C9	C8	C7	C12	15.18(19)
C10	C8	C9	C1'	−109.74(15)	C9	C1'	C2'	C3'	−177.14(14)
C10	C8	C7	C6	62.14(14)	C9	C1'	C6'	C5'	177.54(15)
C10	C8	C7	C12	-51.70(16)	C2'	C1'	C9	C10	-60.23(19)
C10	C1	C11	C12	-54.09(18)	C2'	C1'	C9	C8	11.3(2)
C8	C10	C1	C2	-62.96(14)	C2'	C1'	C6'	C5'	-0.8(2)
C8	C10	C1	C11	51.31(15)	C2'	C3'	C4'	C5'	-0.7(2)
C8	C10	C9	C1'	111.30(15)	C7	C8	C9	C10	-97.09(15)
C8	C7	C12	C11	53.58(19)	C7	C8	C9	C1'	153.17(14)
C1	C2	C6	C7	-0.50(15)	C7	C6	C5	O4	118.85(13)
C1	C2	C6	C5	119.52(12)	C7	C6	C5	O2	-60.0(2)
C1	C2	C3	O4	−118.12(13)	C3'	C4'	C5'	C6'	1.0(3)
C1	C2	C3	O1	60.3(2)	C3	O4	C5	O2	178.96(14)
C1	C10	C8	C9	−115.36(13)	C3	O4	C5	C6	-0.06(16)
C1	C10	C8	C7	0.18(16)	C3	C2	C1	C10	177.93(11)
C1	C10	C9	C8	96.90(13)	C3	C2	C1	C11	60.87(15)
C1	C10	C9	C1'	−151.81(13)	C3	C2	C6	C7	−120.17(12)
C1	C11	C12	C7	0.3(2)	C3	C2	C6	C5	-0.14(14)
C6	C2	C1	C10	62.47(13)	C5	O4	C3	O1	−178.62(14)
C6	C2	C1	C11	-54.59(15)	C5	O4	C3	C2	-0.04(16)
C6	C2	C3	O4	0.12(15)	C5	C6	C7	C8	−176.62(11)
C6	C2	C3	O1	178.51(16)	C5	C6	C7	C12	-59.63(15)
C6	C7	C12	C11	-58.49(17)	C6'	C1'	C9	C10	121.57(15)
C1'	C2'	C3'	C4'	-0.4(2)	C6'	C1'	C9	C8	−166.95(14)
C1'	C6'	C5'	C4'	-0.2(3)	C6'	C1'	C2'	C3'	1.1(2)

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2b.				
Atom	***x***	***y***	***z***	**U(eq)**
H10	9015(11)	4710(20)	5331(11)	36(4)
H8	7149(11)	5120(20)	4206(11)	36(4)
H1	9282(11)	2120(20)	6478(11)	36(4)
H2'	8095(13)	6250(30)	3498(13)	53(5)
H6	6565(11)	5460(20)	5552(11)	36(4)
H7	5865(12)	2880(20)	4403(12)	39(4)
H2	8301(11)	5130(20)	6598(11)	40(4)
H9	8068(12)	890(30)	4307(13)	49(4)
H6'	9219(13)	280(30)	3647(14)	65(6)
H3'	8721(14)	7160(30)	2414(14)	58(5)
H12	6406(13)	-620(30)	4901(13)	53(5)
H11	8252(13)	-1060(30)	6011(13)	57(5)
H4'	9599(14)	4660(30)	1934(15)	67(6)
H5'	9858(16)	1160(30)	2541(16)	77(6)

Experimental

A suitable crystal of $C_{17}H_{14}O_3$ **2b** was selected and performed on a Xcalibur, Eos diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [S4], the structure was solved with the SHELXT [S2(*a*)] structure solution program using Intrinsic Phasing and refined with the SHELXL [S2(*b*)] refinement package using Least Squares minimisation.

Crystal structure determination of 2b

Crystal Data for **2b** $C_{17}H_{14}O_3$ (M =266.28 g mol^{-1}): monoclinic, space group $P2_1/n$ (no. 14), a = 13.7039(15) Å, b = 6.2945(5) Å, c = 16.394(2) Å, β = 114.320(14)°, V = 1288.7(3) Å^3, Z = 4, T = 293(2) K, μ(MoKα) = 0.094 mm^{-1}, D_{calc} = 1.372 g cm^{-3}, 17148 reflections measured (5.454° ≤ 2Θ ≤ 75.494°), 6440 unique (R_{int} = 0.0803, R_{sigma} = 0.1081) which were used in all calculations. The final R_1 was 0.0660 (I > 2σ(I)) and wR_2 was 0.1678 (all data).

Refinement model description

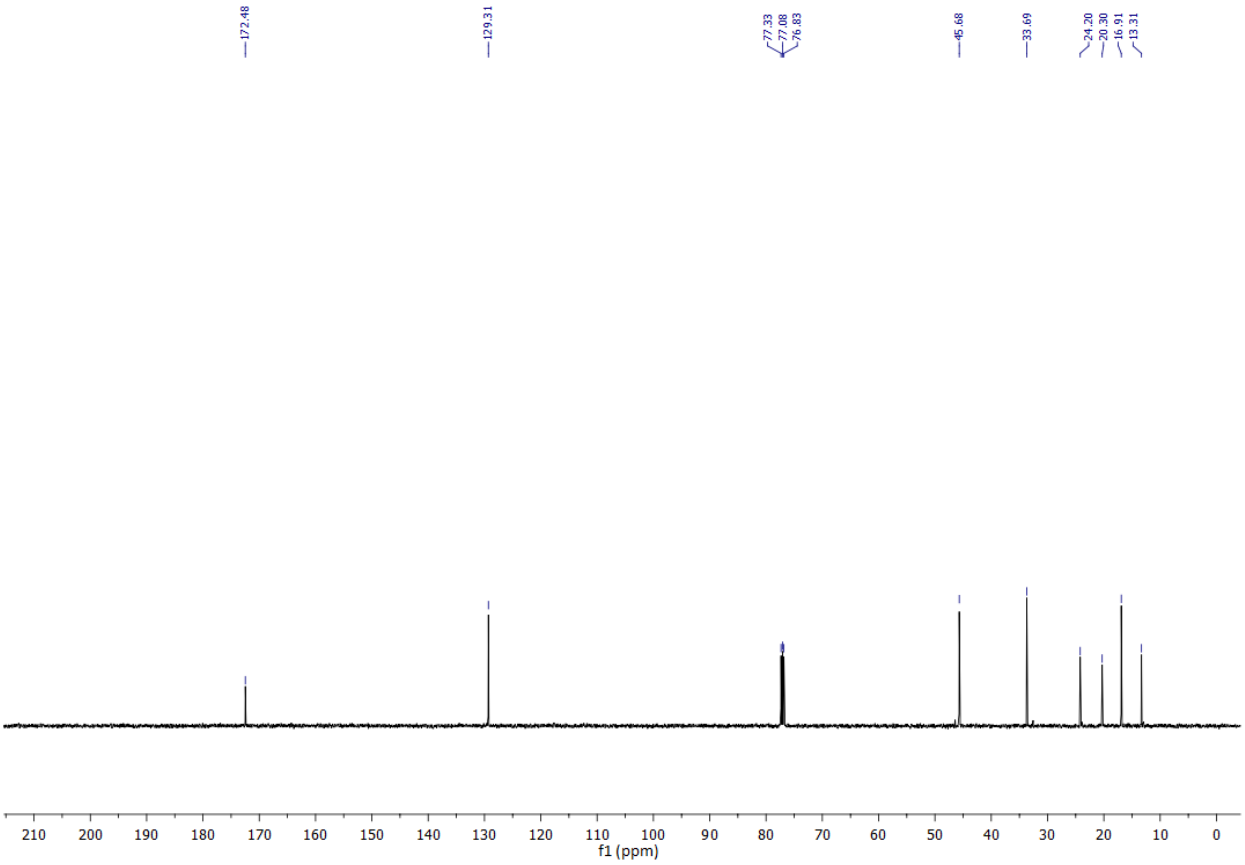
Number of restraints - 0, number of constraints - unknown.

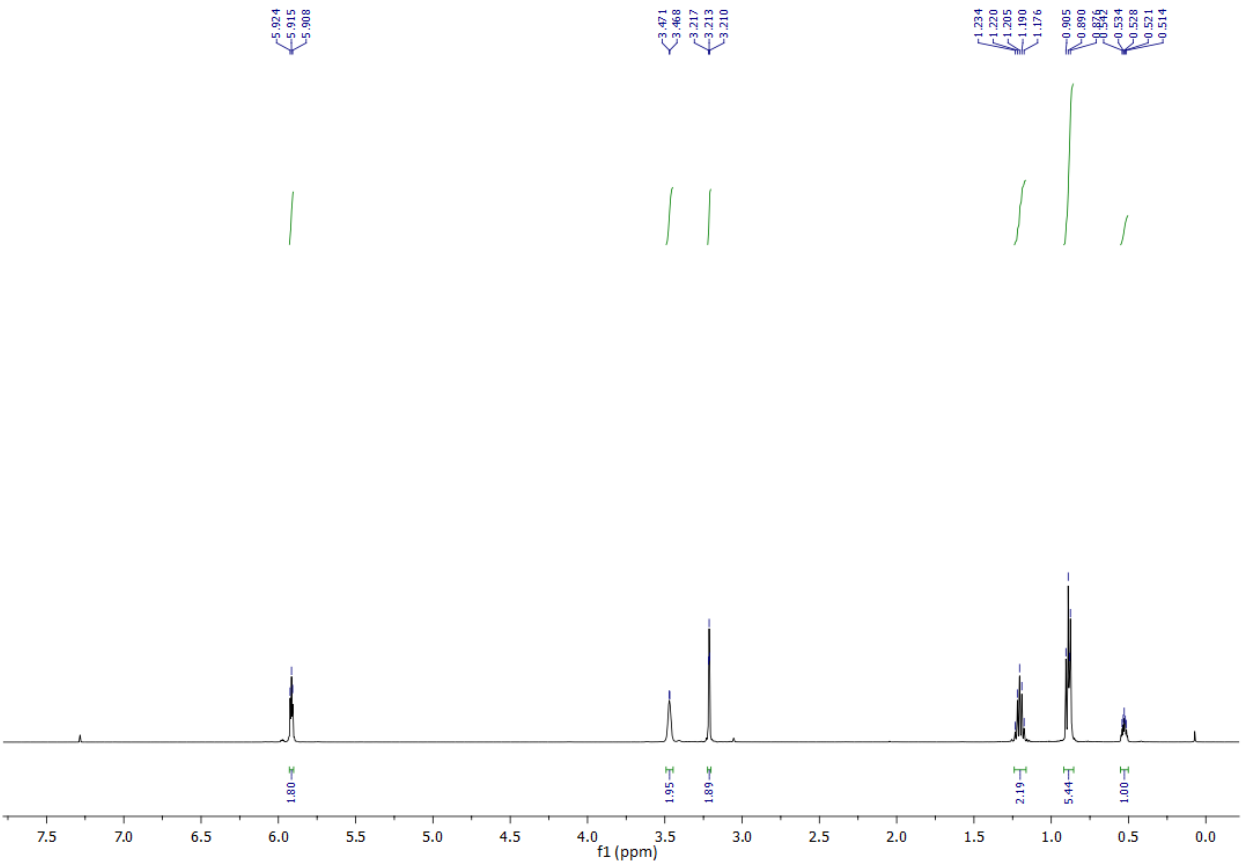
Details:

N/A

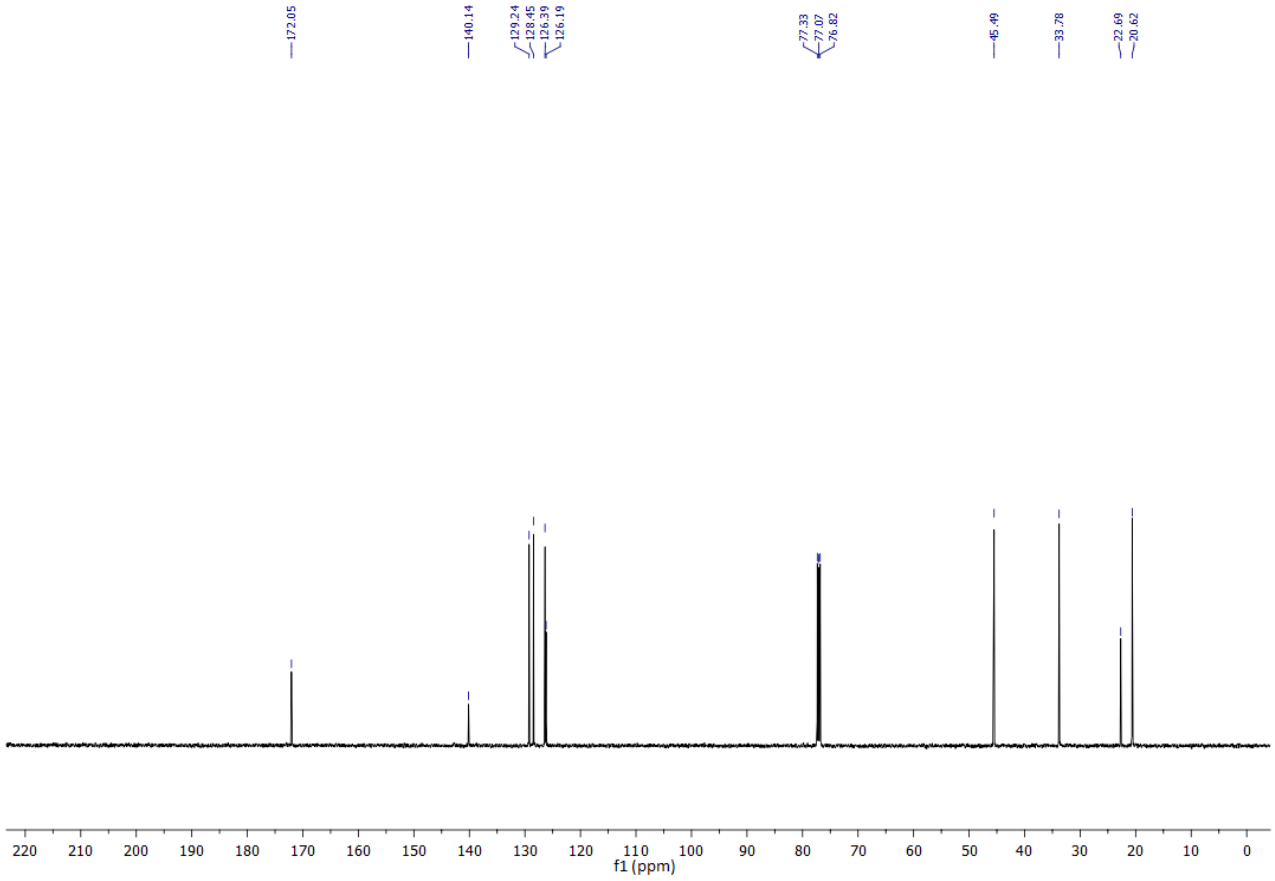
This report has been created with Olex2, compiled on 2020.11.12 svn.r5f609507 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

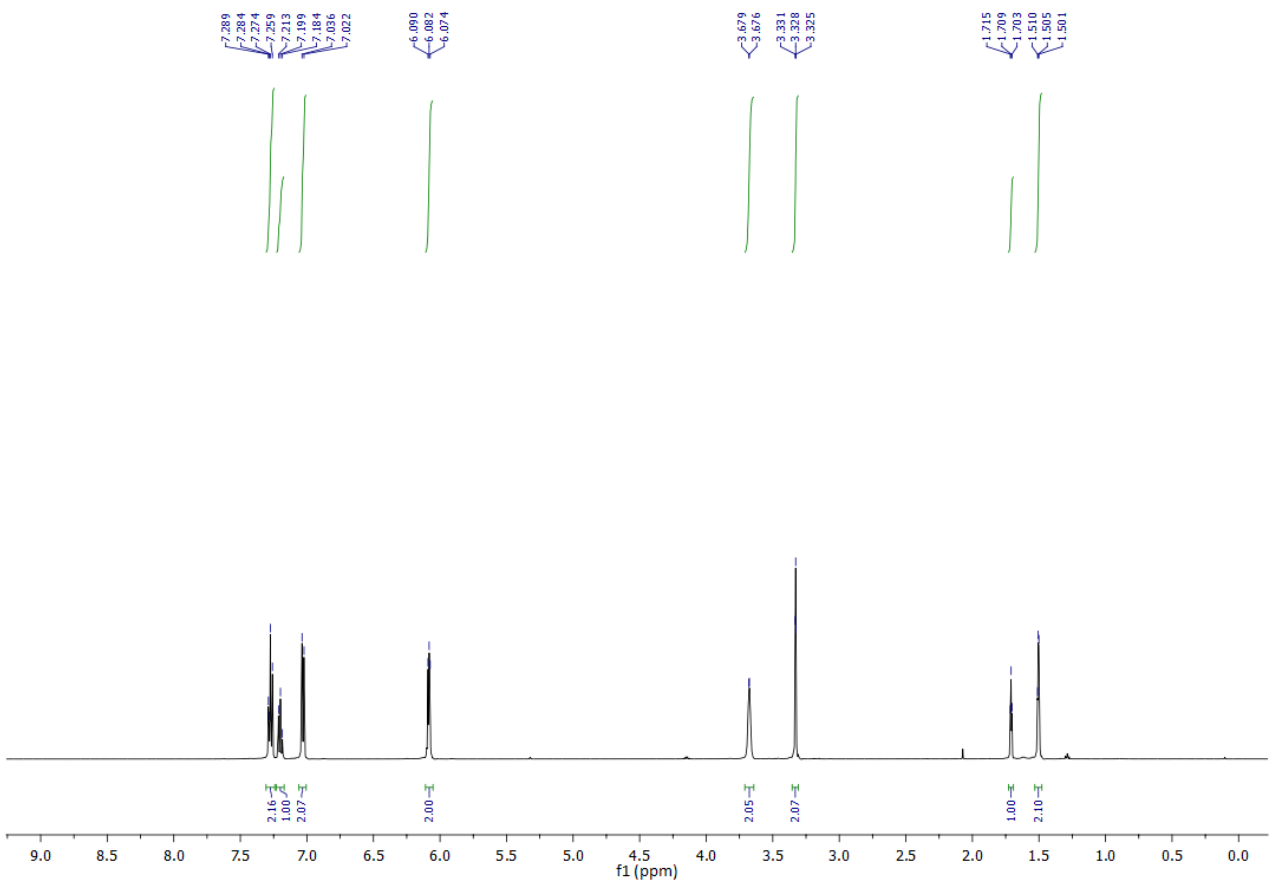
9-Ethyl-4-oxatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2a):



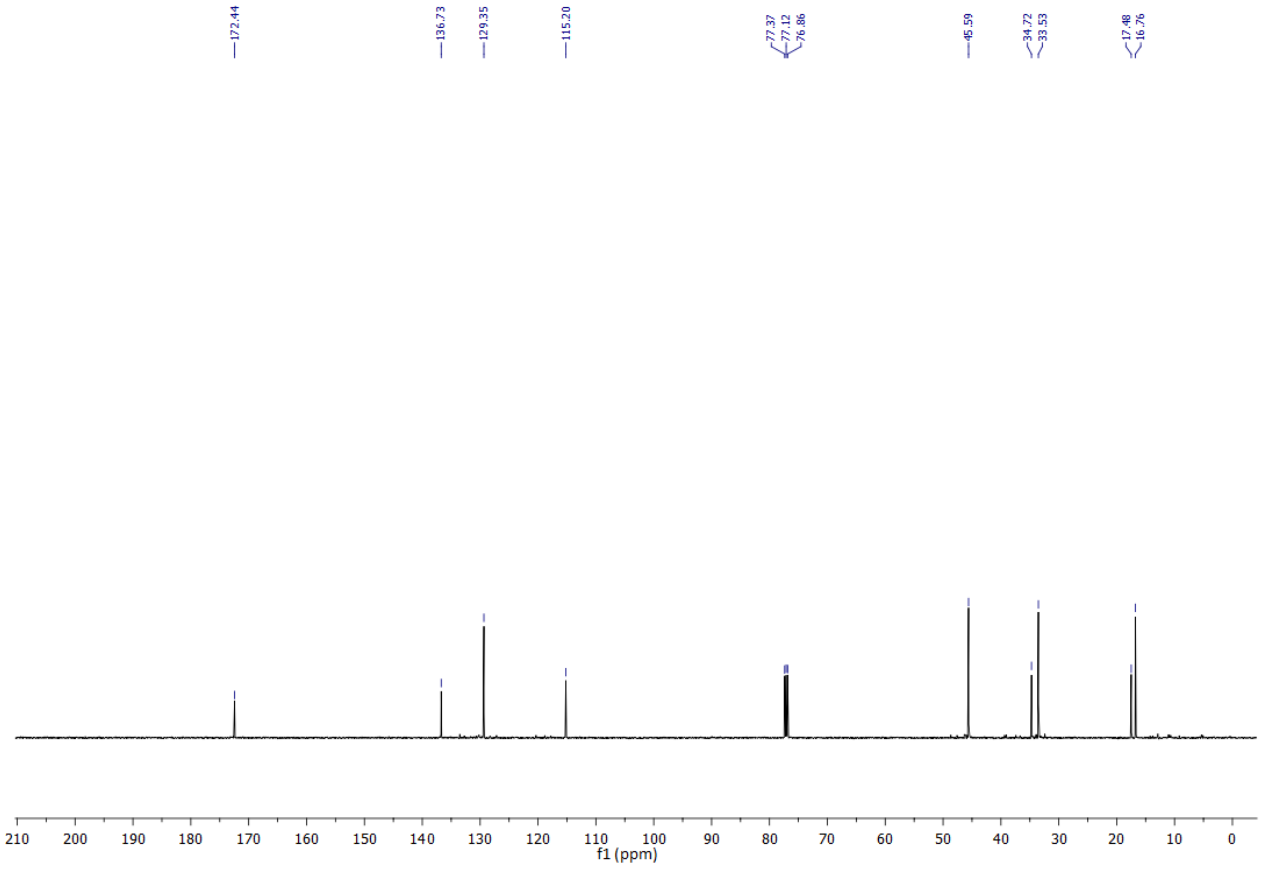


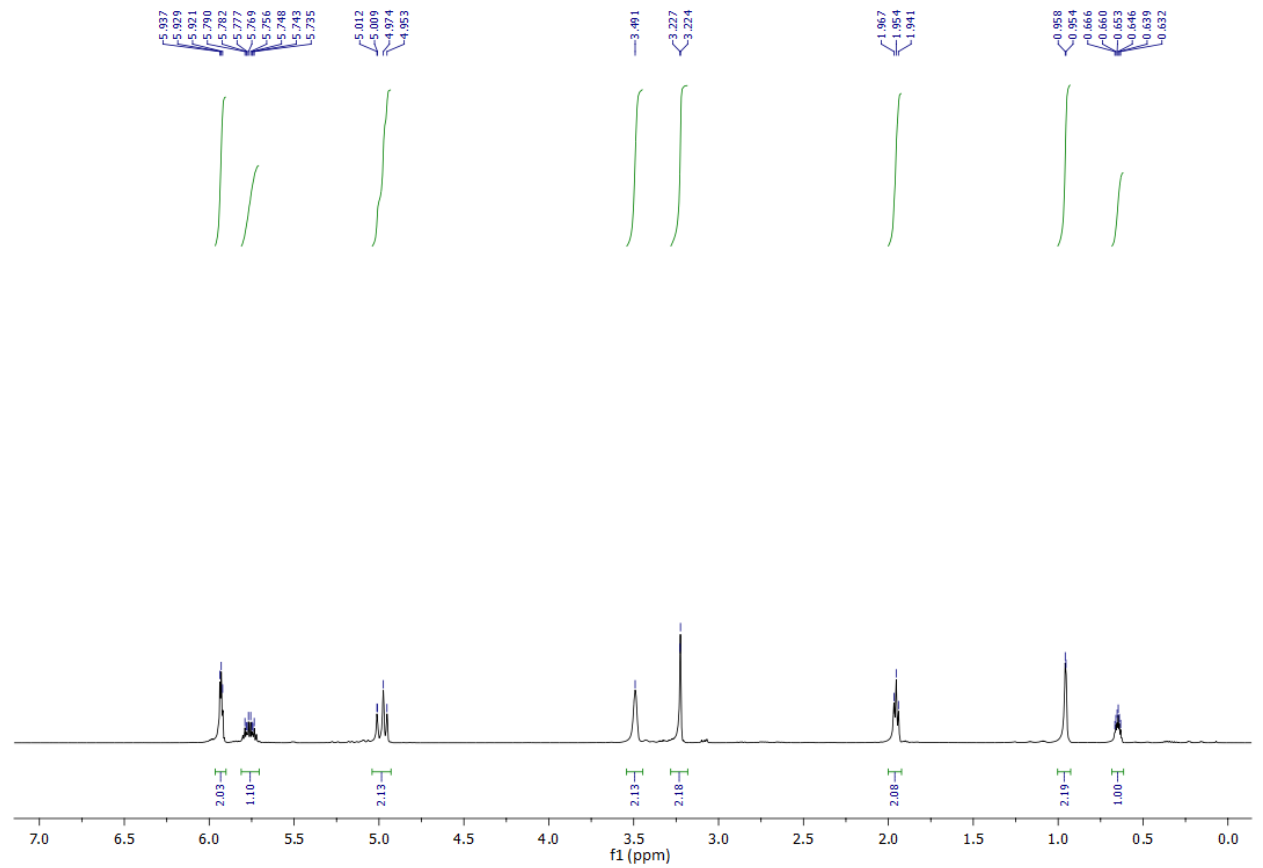
9-Phenyl-4-oxatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2b):



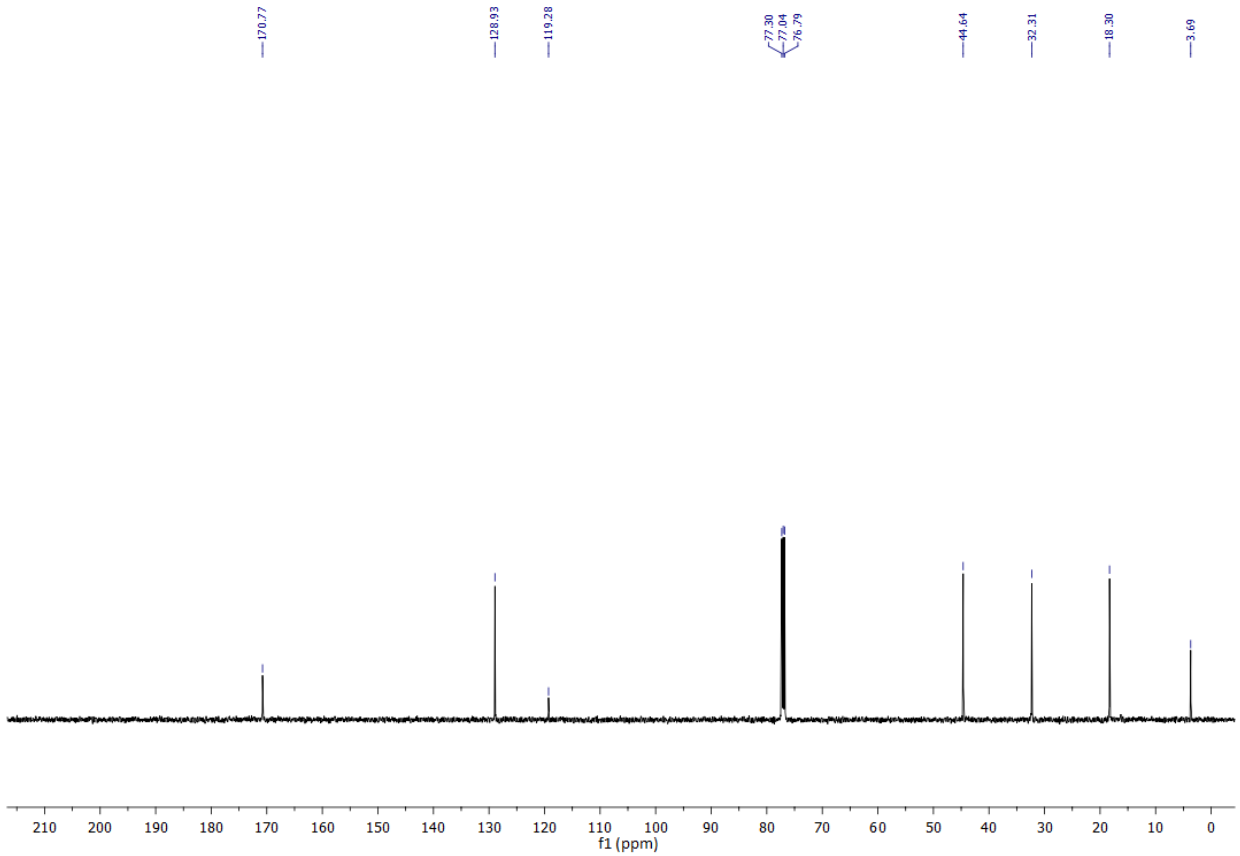


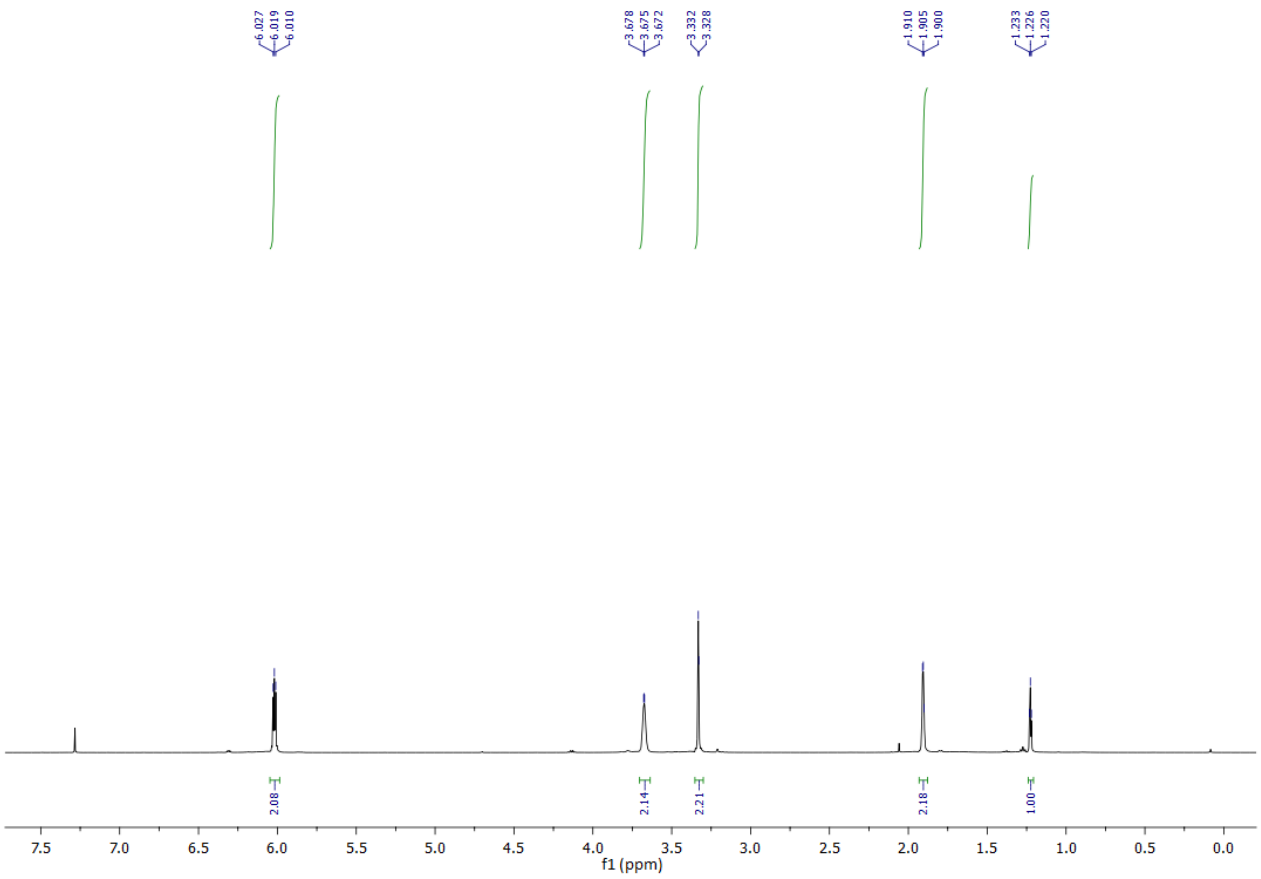
9-Allyl-4-oxatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2c):



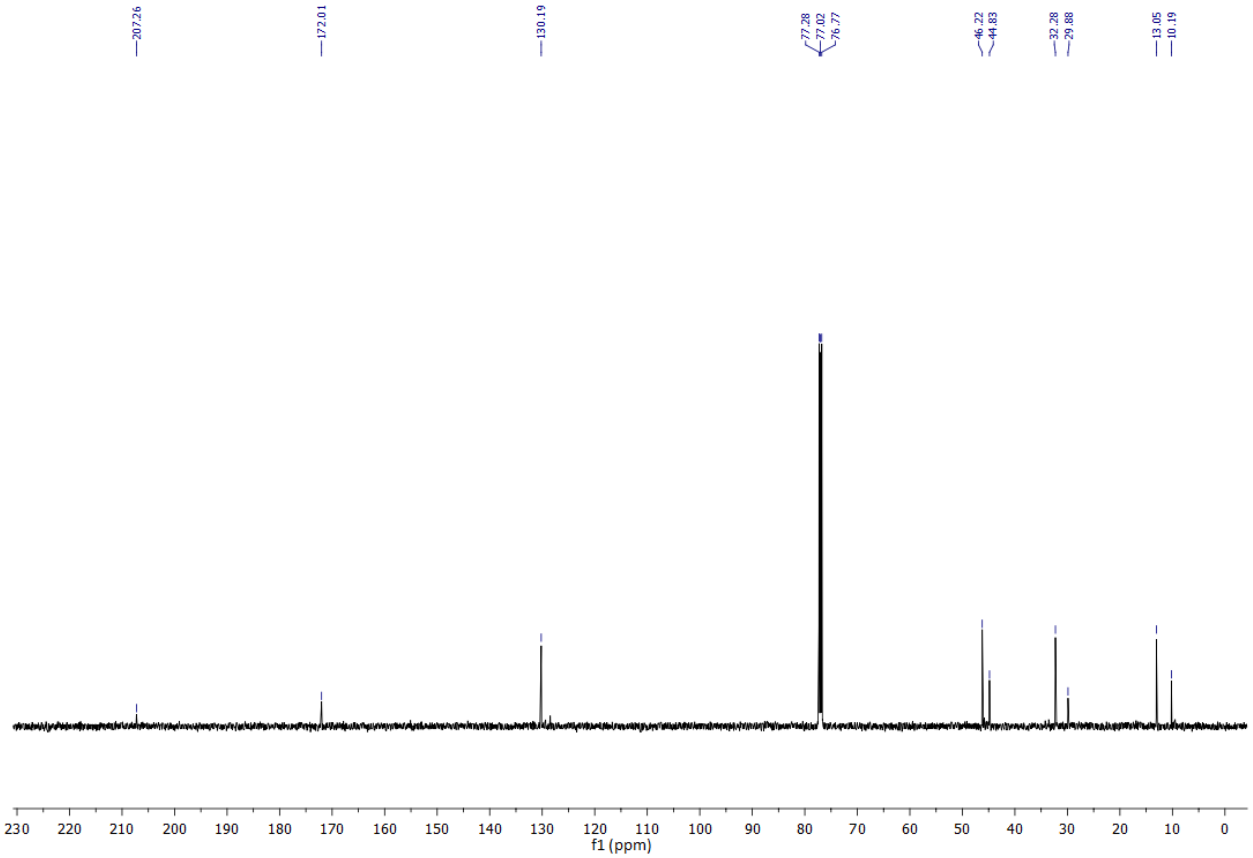


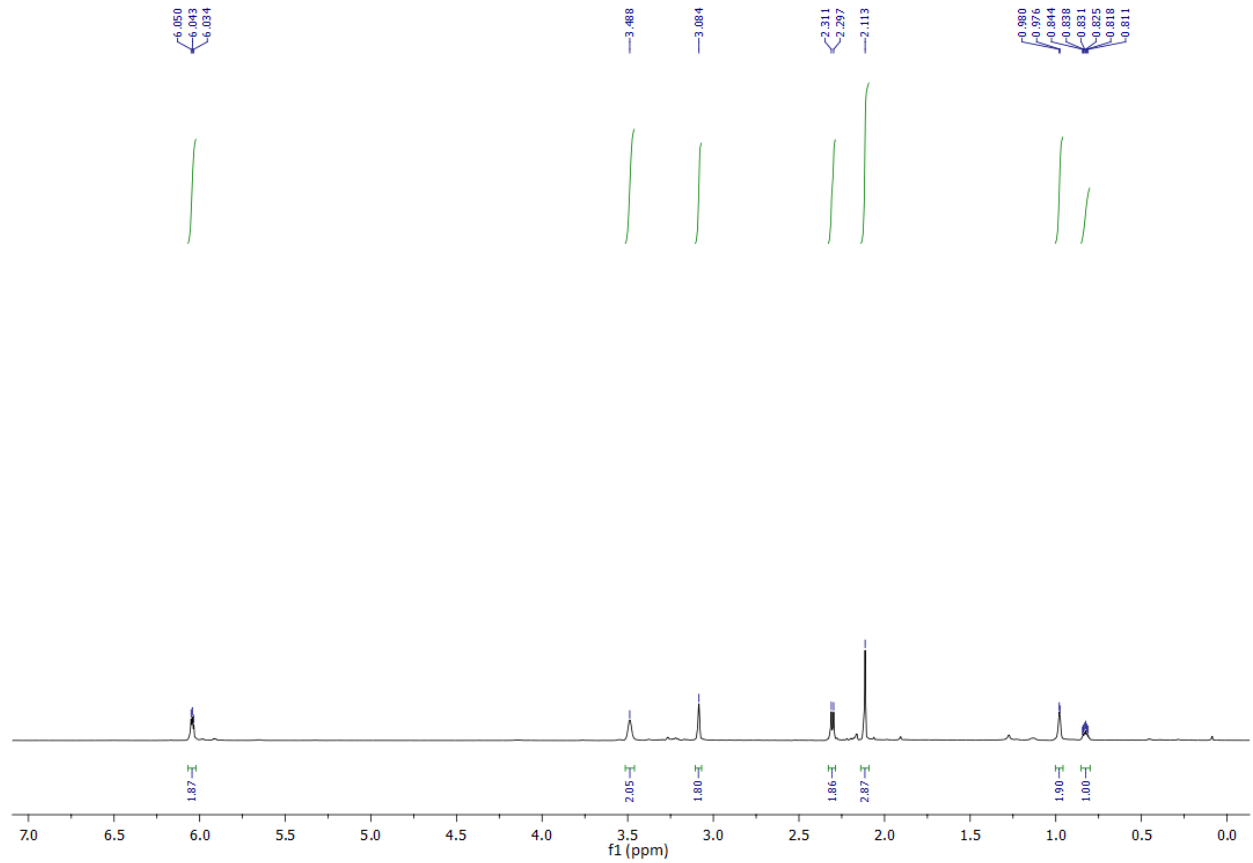
3,5-Dioxo-4-oxatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-9-carbonitrile (2d):





9-(2-Oxopropyl)-4-oxatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2e):





References

S1. CrysAlisPRO, Oxford Diffraction, Agilent Technologies UK Ltd, Yarnton, England.

S2. (*a*) G. M. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3; (*b*) G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71,** 3.

S3. K. Conrow, *J. Am. Chem. Soc.*, 1961, **83**, 2343.

S4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.