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New 4-azatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-3,5-diones *via* the cycloaddition of *N*-phenylmaleimide and cyclohepta-1,3,5-trienes

Gulnara N. Kadikova, Ekaterina S. Meshcheryakova and Leonard M. Khalilov

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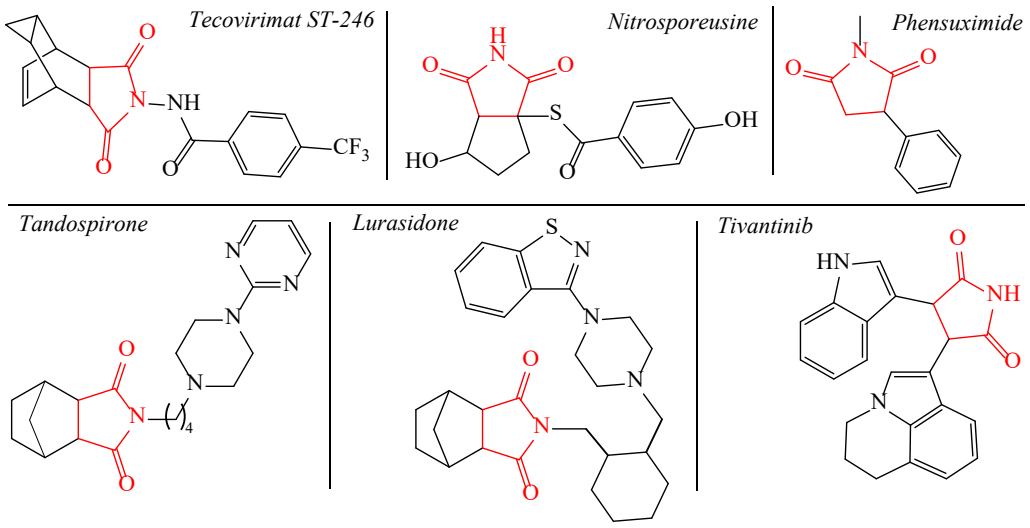
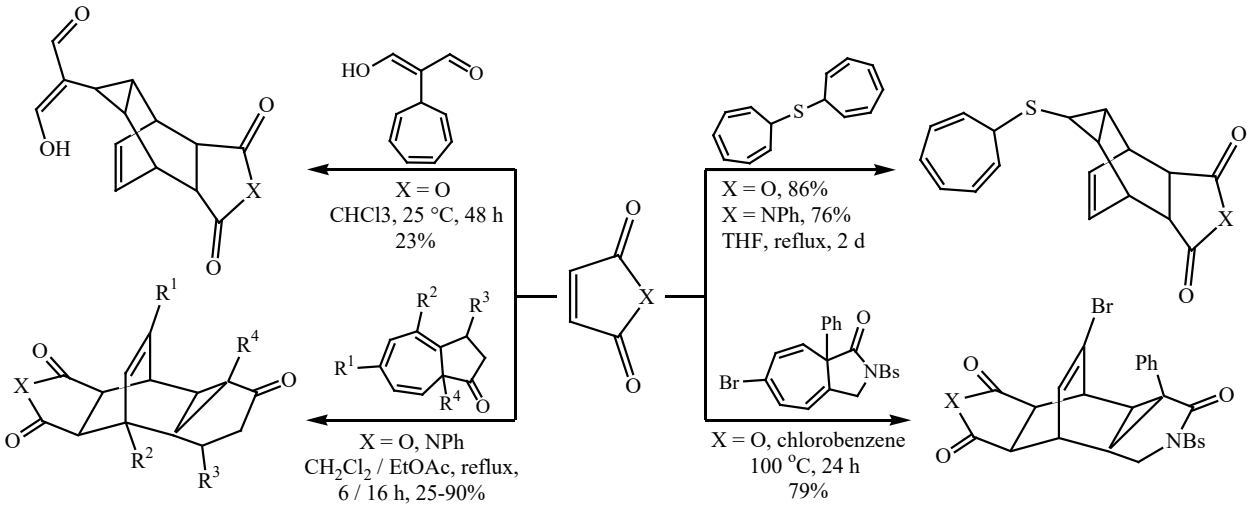


Figure S1 Drug compounds containing succinimide moiety.



Scheme S1 Previous reactions of maleic compounds and cyclohepta-1,3,5-trienes (see Refs. 6-11 of the main text).

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, $2\theta_{макс.}$ 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-, ethoxy- 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 N-phenylmaleimide to 1,3,5-cycloheptatrienes **1a-f** (general procedure)*

A solution of 1,3,5-cycloheptatriene **1a-f** (2 mmol) and *N*-phenylmaleimide (2 mmol) in *p*-xylene (2 ml) was refluxed for 3 h. The solvent was evaporated under reduced pressure, and the residue was recrystallized from a mixture of dichloromethane and petroleum ether (10:1) to afford the target products **2a-f**.

9-Ethyl-4-phenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2a): Yield 95% (0.557 g), white solid, m.p. = 158-159 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.47 (m, 2H), 7.35-7.40 (m, 1H), 7.16-7.20 (m, 2H), 5.91 (dd, 2H, *J* = 4.7 Hz, *J* = 3.5 Hz), 3.51-3.55 (m, 2H), 3.10-3.13 (m, 2H), 1.21-1.28 (m, 2H), 0.91-0.95 (m, 5H), 0.55-0.61 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.7 (2C), 131.9, 129.1 (2C), 128.7 (2C), 128.5, 126.5 (2C), 45.2 (2C), 34.0 (2C), 24.4, 19.8, 17.5 (2C), 13.4 ppm. MS (EI, 70 eV) (%) = 293 $[M]^+$ (13), 264 (1), 251 (< 1), 222 (1), 173 (9), 146 (6), 117 (28), 91 (100), 77 (8), 65 (6), 41 (4). Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.69; H, 6.47; N, 4.68.

4,9-Diphenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2b): Yield 97% (0.662 g), white solid, m.p. = 270-271 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.54 (m, 3H), 7.17-7.34 (m, 5H), 7.07 (d, *J* = 7.3 Hz, 2H), 6.02-6.13 (m, 2H), 3.67-3.77 (m, 2H), 3.19-3.27 (m, 2H), 1.73-1.79 (m, 1H), 1.52-1.60 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.4 (2C), 140.9, 131.9, 129.1 (2C), 128.7, 128.6 (2C), 128.4 (2C), 126.5 (2C), 126.4 (2C), 126.0, 45.0 (2C), 34.1 (2C), 22.3, 21.4 (2C) ppm. MS (EI, 70 eV) (%) = 341 $[M]^+$ (66), 312 (2), 281 (10), 222 (12), 207 (27), 194 (46), 168 (100), 129 (27), 115 (63), 91 (57), 77 (23), 65 (16), 51 (11). Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.92; H, 5.61; N, 4.10. Found: C, 80.84; H, 5.54; N, 4.01.

9-Allyl-4-phenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2c): Yield 93% (0.567 g), white solid, m.p. = 155-156 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.47 (m, 2H), 7.35-7.40 (m, 1H), 7.16-7.20 (m, 2H), 5.91-5.95 (m, 2H), 5.77-5.86 (m, 1H), 4.97-5.07 (m, 2H), 3.53-3.57 (m, 2H), 3.11-3.13 (m, 2H), 1.99 (t, *J* = 6.7 Hz, 2H), 1.01 (dd, 2H, *J* = 4.7 Hz, *J* = 2.4 Hz), 0.68-0.73 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.6 (2C), 137.0, 131.9, 129.1 (2C), 128.7 (2C), 128.6, 126.5 (2C), 115.0, 45.1 (2C), 35.0, 33.8 (2C), 17.4 (2C), 17.0 ppm. MS (EI, 70 eV) (%) = 305 $[M]^+$ (7), 264 (1), 173 (4), 158 (2), 129 (8), 117 (22), 91 (100), 77 (7), 54 (7), 41 (2). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.53; H, 6.16; N, 4.51.

9-Ethoxy-4-phenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2d): Yield 89% (0.550 g), white solid, m.p. = 140-141 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41-7.46 (m, 2H), 7.35-7.39 (m, 1H), 7.14-7.18 (m, 2H), 5.92 (t, 2H, *J* = 4 Hz), 3.58-3.63 (m, 2H), 3.48 (q, 2H, *J* = 7.1 Hz), 3.12-3.14 (m, 2H), 2.85-2.87 (m, 1H), 1.39-1.42 (m, 2H), 1.17 (t, 3H, *J* = 7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.3 (2C), 131.8, 129.1 (2C), 128.7 (2C), 128.6, 126.5 (2C), 66.0, 57.6, 44.6 (2C), 32.3 (2C), 17.2 (2C), 15.1 ppm. MS (EI, 70 eV) (%) = 309 $[M]^+$ (24), 280 (6), 252 (7), 222 (11), 173 (31), 161 (9), 133 (59), 116 (35), 105 (100), 91 (58), 77 (78), 65 (15), 55 (24). Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.65; H, 6.13; N, 4.45.

9-(2-Oxopropyl)-4-phenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2e): Yield 92% (0.591 g), white solid, m.p. = 174-175 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.50 (m, 3H), 7.11-7.22 (m, 2H), 5.90-6.00 (m, 2H), 3.52-3.61 (m, 2H), 3.07-3.14 (m, 2H), 2.32 (d, *J* = 7.1 Hz, 2H), 2.13 (s, 3H), 0.99-1.07 (m, 2H), 0.88-0.98 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.7, 177.4 (2C), 131.8, 129.1 (2C), 128.7 (2C), 128.6, 126.5 (2C), 45.4, 44.9 (2C), 33.6 (2C), 29.7, 17.5 (2C), 13.1 ppm. MS (EI, 70 eV) (%) = 321 $[M]^+$ (16), 278 (25), 174 (16), 147 (17), 131 (24), 105 (81), 91 (74), 77 (24), 43 (100). Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.63; H, 5.85; N, 4.31.

3,5-Dioxo-4-phenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-9-carbonitrile (2f): Yield 87% (0.505 g), white solid, m.p. = 205-206 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.48 (m, 2H), 7.37-7.42 (m, 1H), 7.13-7.19 (m, 2H), 5.95 (dd, *J* = 4.5 Hz, *J* = 3.6 Hz, 2H), 3.63-3.69 (m, 2H), 3.15-3.18 (m, 2H), 1.90 (dd, *J* = 5.1 Hz, *J* = 2.7 Hz, 2H), 1.21 (t, *J* = 3.3 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.20 (2C), 131.52, 129.18 (2C), 128.85, 128.23 (2C), 126.39 (2C), 119.93, 44.01 (2C), 32.62 (2C), 18.87 (2C), 3.08 ppm. MS (EI, 70 eV) (%) = 290 $[M]^+$ (37), 262 (2), 207 (1), 173 (9), 143 (100), 129 (8), 116 (48), 90 (17), 77 (14), 51 (7), 41 (1). Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.32; H, 4.76; N, 9.57.

Crystal data for 2a

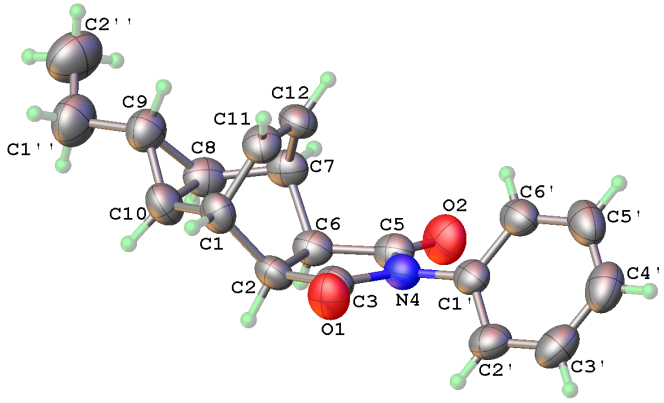


Figure S2. Geometry of molecule **2a**.

Table S1. Crystal data and structure refinement for 2a.	
Identification code	2a
Empirical formula	$C_{19}H_{19}NO_2$
Formula weight	293.35
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.9614(11)
b/Å	6.3031(4)
c/Å	12.6364(8)
α/°	90
β/°	102.019(5)
γ/°	90
Volume/Å^3	1555.04(17)
Z	4
ρ_{calc}g/cm^3	1.253
μ/mm^{-1}	0.081
F(000)	624.0
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.172 to 75.824
Index ranges	$-33 \leq h \leq 33$, $-10 \leq k \leq 10$, $-20 \leq l \leq 21$
Reflections collected	38495
Independent reflections	7962 [R_{int} = 0.0526, R_{sigma} = 0.0465]
Data/restraints/parameters	7962/0/200
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0802, wR_2 = 0.1715
Final R indexes [all data]	R_1 = 0.1619, wR_2 = 0.2144
Largest diff. peak/hole / e Å^{-3}	0.33/-0.31

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

Atom	*x*	*y*	*z*	U(eq)
O1	7712.9(6)	225.4(18)	5759.8(10)	62.9(3)
O2	8755.5(6)	6382(2)	5148.4(11)	70.8(4)
N4	8343.2(6)	3241.9(19)	5675.8(10)	46.8(3)
C3	7850.5(7)	1731(2)	5255.8(12)	47.2(3)
C1'	8750.3(7)	3137(2)	6746.5(12)	47.1(3)
C5	8368.0(7)	4907(2)	4956.2(13)	51.0(4)
C6	7838.0(7)	4514(2)	3945.5(12)	48.7(3)
C2	7524.0(8)	2356(2)	4117.8(12)	47.8(3)
C11	6617.2(7)	4178(3)	4768.1(12)	52.5(4)
C7	7263.3(8)	6213(2)	3760.5(13)	52.2(4)
C12	6893.3(8)	6044(3)	4674.2(12)	53.0(4)
C1	6735.5(8)	2556(2)	3964.8(12)	50.7(4)
C2'	9147.2(8)	1364(3)	7063.4(14)	57.6(4)
C6'	8741.3(8)	4800(3)	7456.5(14)	57.4(4)
C8	6793.1(9)	5543(3)	2699.1(13)	56.9(4)
C9	6033.6(9)	5287(3)	2561.8(14)	62.5(4)
C10	6491.5(10)	3400(3)	2816.2(13)	60.6(4)
C3'	9536.5(9)	1263(4)	8098.0(16)	69.2(5)
C5'	9133.9(9)	4665(4)	8496.5(16)	70.6(5)
C4'	9528.0(9)	2904(4)	8806.6(16)	73.8(6)
C1"	5589.6(12)	5521(4)	1446.2(17)	84.9(6)
C2"	5367.8(14)	7738(5)	1185(2)	102.7(8)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2a. 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}
O1	70.7(7)	45.4(6)	71.3(7)	5.3(5)	12.2(6)	-15.5(5)
O2	62.4(7)	59.5(8)	90.8(9)	4.4(6)	16.8(6)	-25.0(6)
N4	43.9(6)	41.9(6)	56.7(7)	-3.7(5)	15.5(5)	-6.2(5)
C3	48.3(7)	37.4(7)	58.5(8)	-6.5(6)	17.3(6)	-4.2(6)
C1'	36.3(6)	51.4(8)	56.7(8)	-5.0(6)	16.5(5)	-5.5(6)
C5	45.1(7)	46.0(8)	66.7(9)	-0.3(7)	22.9(6)	-6.5(6)
C6	49.6(8)	46.2(8)	55.7(8)	-0.3(6)	23.4(6)	-4.8(6)
C2	55.9(8)	38.3(7)	52.7(8)	-9.1(6)	18.9(6)	-4.1(6)
C11	46.3(7)	64.0(10)	51.2(8)	-1.7(7)	19.3(6)	-5.2(7)
C7	54.8(8)	38.0(7)	67.4(9)	2.7(6)	21.1(7)	-5.6(6)
C12	52.8(8)	52.4(9)	56.3(8)	-13.4(7)	17.4(6)	0.9(7)
C1	54.0(8)	43.2(8)	54.8(8)	-4.1(6)	10.8(6)	-13.2(6)
C2'	47.1(8)	60.4(10)	68.9(10)	-1.5(8)	20.2(7)	4.9(7)
C6'	46.6(8)	57.0(10)	71.6(10)	-11.9(8)	19.1(7)	-5.4(7)

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2a. 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}**
C8	63.6(10)	61.2(10)	50.2(8)	4.8(7)	21.6(7)	2.3(8)
C9	60.5(10)	70.0(12)	55.9(9)	2.2(8)	9.7(7)	0.2(8)
C10	71.4(11)	58.9(10)	49.5(8)	-9.2(7)	8.5(7)	-3.2(8)
C3'	44.2(8)	84.7(14)	78.6(12)	10.1(10)	12.4(8)	5.8(8)
C5'	59.3(10)	84.7(14)	70.0(11)	-24.4(10)	18.8(8)	-20.6(10)
C4'	50.0(9)	104.5(17)	65.6(11)	-1.2(11)	9.1(8)	-13.9(10)
C1"	82.2(14)	101.9(18)	64.9(12)	9.0(11)	2.2(10)	4.4(13)
C2"	95.6(17)	114(2)	95.4(17)	21.8(15)	13.2(13)	24.5(16)

Table S4. Bond Lengths for 2a.						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
O1	C3	1.2063(18)		C11	C1	1.494(2)
O2	C5	1.2013(18)		C7	C12	1.498(2)
N4	C3	1.3921(18)		C7	C8	1.528(2)
N4	C1'	1.4274(19)		C1	C10	1.527(2)
N4	C5	1.396(2)		C2'	C3'	1.376(2)
C3	C2	1.502(2)		C6'	C5'	1.385(2)
C1'	C2'	1.380(2)		C8	C9	1.498(2)
C1'	C6'	1.382(2)		C8	C10	1.499(3)
C5	C6	1.500(2)		C9	C10	1.494(3)
C6	C2	1.532(2)		C9	C1"	1.508(2)
C6	C7	1.551(2)		C3'	C4'	1.371(3)
C2	C1	1.550(2)		C5'	C4'	1.369(3)
C11	C12	1.315(2)		C1"	C2"	1.482(3)

Table S5. Bond Angles for 2a.								
Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
C3	N4	C1'	123.18(12)		C8	C7	C6	103.97(13)
C3	N4	C5	112.58(13)		C11	C12	C7	114.59(13)
C5	N4	C1'	124.17(12)		C11	C1	C2	105.74(11)
O1	C3	N4	123.88(14)		C11	C1	C10	110.09(14)
O1	C3	C2	127.62(14)		C10	C1	C2	105.16(13)
N4	C3	C2	108.48(12)		C3'	C2'	C1'	119.32(17)
C2'	C1'	N4	119.45(14)		C1'	C6'	C5'	119.20(17)
C2'	C1'	C6'	120.65(15)		C9	C8	C7	123.60(14)
C6'	C1'	N4	119.90(14)		C9	C8	C10	59.79(12)
O2	C5	N4	123.97(15)		C10	C8	C7	110.40(13)
O2	C5	C6	127.62(15)		C8	C9	C1"	118.77(16)
N4	C5	C6	108.41(12)		C10	C9	C8	60.12(12)

Table S5. Bond Angles for 2a.								
Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
C5	C6	C2	105.23(12)		C10	C9	C1"	119.55(17)
C5	C6	C7	112.50(13)		C8	C10	C1	110.63(13)
C2	C6	C7	108.83(11)		C9	C10	C1	122.78(14)
C3	C2	C6	105.06(12)		C9	C10	C8	60.09(12)
C3	C2	C1	111.56(12)		C4'	C3'	C2'	120.28(19)
C6	C2	C1	110.15(12)		C4'	C5'	C6'	119.94(18)
C12	C11	C1	114.98(13)		C5'	C4'	C3'	120.61(18)
C12	C7	C6	107.62(12)		C2"	C1"	C9	113.0(2)
C12	C7	C8	110.22(13)					

Table S6. Torsion Angles for 2a.										
A	**B**	**C**	**D**	**Angle/°**		**A**	**B**	**C**	**D**	**Angle/°**
O1	C3	C2	C6	173.52(15)		C6	C7	C12	C11	-58.99(18)
O1	C3	C2	C1	54.2(2)		C6	C7	C8	C9	128.96(16)
O2	C5	C6	C2	176.94(16)		C6	C7	C8	C10	62.38(16)
O2	C5	C6	C7	-64.7(2)		C2	C6	C7	C12	52.27(16)
N4	C3	C2	C6	-4.69(15)		C2	C6	C7	C8	-64.64(15)
N4	C3	C2	C1	−124.02(13)		C2	C1	C10	C8	-61.97(16)
N4	C1'	C2'	C3'	−179.67(14)		C2	C1	C10	C9	−128.94(16)
N4	C1'	C6'	C5'	179.34(14)		C11	C1	C10	C8	51.50(18)
N4	C5	C6	C2	-3.32(15)		C11	C1	C10	C9	-15.5(2)
N4	C5	C6	C7	115.03(13)		C7	C6	C2	C3	−116.02(13)
C3	N4	C1'	C2'	57.19(19)		C7	C6	C2	C1	4.25(16)
C3	N4	C1'	C6'	−122.48(16)		C7	C8	C9	C10	-95.59(17)
C3	N4	C5	O2	−179.84(15)		C7	C8	C9	C1"	154.94(18)
C3	N4	C5	C6	0.41(16)		C7	C8	C10	C1	1.01(19)
C3	C2	C1	C11	58.15(15)		C7	C8	C10	C9	117.82(15)
C3	C2	C1	C10	174.64(12)		C12	C11	C1	C2	57.86(17)
C1'	N4	C3	O1	1.5(2)		C12	C11	C1	C10	-55.24(18)
C1'	N4	C3	C2	179.76(12)		C12	C7	C8	C9	13.9(2)
C1'	N4	C5	O2	3.2(2)		C12	C7	C8	C10	-52.70(18)
C1'	N4	C5	C6	−176.52(12)		C1	C11	C12	C7	1.3(2)
C1'	C2'	C3'	C4'	0.2(3)		C2'	C1'	C6'	C5'	-0.3(2)
C1'	C6'	C5'	C4'	0.5(3)		C2'	C3'	C4'	C5'	-0.1(3)
C5	N4	C3	O1	−175.50(15)		C6'	C1'	C2'	C3'	0.0(2)
C5	N4	C3	C2	2.79(16)		C6'	C5'	C4'	C3'	-0.3(3)
C5	N4	C1'	C2'	-		C8	C7	C12	C11	53.76(19)

Table S6. Torsion Angles for 2a.										
A	B	C	D	Angle/°		A	B	C	D	Angle/°
				126.19(16)						
C5	N4	C1'	C6'	54.1(2)		C8	C9	C10	C1	96.49(17)
C5	C6	C2	C3	4.76(14)		C8	C9	C1"	C2"	-88.9(3)
C5	C6	C2	C1	125.03(12)		C9	C8	C10	C1	-116.80(16)
C5	C6	C7	C12	-63.95(15)		C10	C8	C9	C1"	-109.5(2)
C5	C6	C7	C8	179.14(12)		C10	C9	C1"	C2"	-158.9(2)
C6	C2	C1	C11	-58.12(15)		C1"	C9	C10	C1	-155.32(18)
C6	C2	C1	C10	58.37(15)		C1"	C9	C10	C8	108.20(19)

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2a.				
Atom	*x*	*y*	*z*	U(eq)
H6	8055.06	4452.61	3318.27	58
H2	7638.25	1315.98	3606.43	57
H11	6366.89	3889.82	5295.17	63
H7	7448.02	7641.11	3710.11	63
H12	6861.53	7168.92	5137.5	64
H1	6521.37	1195.09	4070	61
H2'	9151.53	249.26	6582.77	69
H6'	8475.04	5995.02	7238.79	69
H8	6965.6	5785.74	2037.74	68
H9	5836.09	5819.31	3158.44	75
H10	6489.62	2390.33	2225.59	73
H3'	9806.38	75.49	8317.33	83
H5'	9129.75	5768.21	8983.55	85
H4'	9792.38	2821.6	9504.38	89
H1'A	5841.71	5022.37	916.13	102
H1'B	5187.49	4630.39	1392.61	102
H2'A	5137.08	7826.76	439.79	154
H2'B	5761.13	8651.8	1308.47	154
H2'C	5061.52	8171.25	1638.02	154

Experimental

A suitable crystal of $C_{19}H_{19}NO_2$ **2a** 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 2a

Crystal Data for **2a** $C_{19}H_{19}NO_2$ (M =293.35 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 19.9614(11) Å, b = 6.3031(4) Å, c = 12.6364(8) Å, β = 102.019(5)°, V = 1555.04(17) Å^3, Z = 4, T = 293(2) K, μ(Mo Kα) = 0.081 mm^{-1}, *Dcalc* = 1.253 g/cm^3, 38495 reflections measured (4.172° ≤ 2Θ ≤ 75.824°), 7962 unique (R_{int} = 0.0526, R_{sigma} = 0.0465) which were used in all calculations. The final R_1 was 0.0802 (I > 2σ(I)) and wR_2 was 0.2144 (all data).

Crystal data for 2e

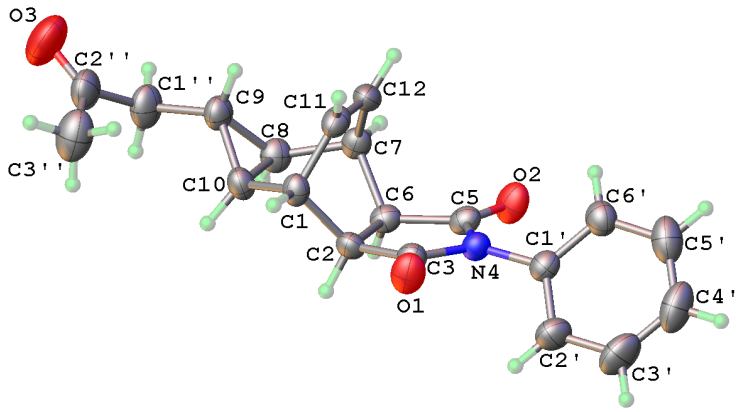


Figure S3. Geometry of molecule **2e.**

Table S8. Crystal data and structure refinement for 2e.	
Identification code	**2e**
Empirical formula	$C_{20}H_{19}NO_3$
Formula weight	321.36
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.7312(6)
b/Å	6.4502(2)
c/Å	17.9286(8)
α/°	90
β/°	109.229(5)
γ/°	90
Volume/Å^3	1608.52(12)
Z	4
ρ_{calc}g/cm^3	1.327
μ/mm^{-1}	0.089
F(000)	680.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.36 to 75.358
Index ranges	$-24 \leq h \leq 24$, $-10 \leq k \leq 5$, $-29 \leq l \leq 29$
Reflections collected	39823
Independent reflections	8177 [R_{int} = 0.0507, R_{sigma} = 0.0535]
Data/restraints/parameters	8177/0/218
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0629, wR_2 = 0.1508
Final R indexes [all data]	R_1 = 0.1376, wR_2 = 0.1828
Largest diff. peak/hole / e Å^{-3}	0.28/-0.20

Table S9. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2e. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	6936.3(7)	-1643.6(15)	7109.3(6)	49.7(3)
O1	6742.8(8)	4124.7(15)	5608.4(7)	49.8(3)
N4	7064.1(7)	1130.7(15)	6344.3(6)	32.5(2)
C2	5940.1(9)	3431.8(18)	6572.9(7)	33.2(2)
C6	5971.2(9)	1448.3(19)	7049.8(7)	33.0(2)
C5	6695.4(8)	77.6(19)	6861.7(7)	34.2(2)
C11	4562.8(9)	1981(2)	5541.3(7)	37.2(3)
C12	4591.2(9)	247(2)	5941.0(8)	38.1(3)
C1'	7874.2(8)	445.7(19)	6135.7(7)	34.8(2)
C8	4356.1(10)	2149(2)	7067.5(8)	38.9(3)
O3	1161.2(10)	5150(3)	6222.6(12)	100.4(6)
C7	4948.1(9)	493.2(19)	6818.0(8)	36.0(3)
C9	3421.4(10)	2987(2)	6519.0(8)	40.1(3)
C1	4896.7(9)	3869.0(18)	6036.7(7)	33.8(2)
C10	4338.7(9)	4123.1(19)	6617.3(8)	37.4(3)
C3	6608.1(9)	3030.7(18)	6108.7(7)	34.4(2)
C6'	7895.6(11)	-1518(2)	5838.3(9)	44.7(3)
C5'	8700.6(13)	-2137(3)	5661.2(10)	59.1(4)
C2''	2005.4(11)	5383(3)	6348.8(10)	54.1(4)
C2'	8642.0(10)	1787(2)	6254.8(9)	47.9(3)
C1''	2710.1(12)	3883(3)	6876.8(11)	54.4(4)
C4'	9465.7(13)	-821(3)	5773.0(12)	66.3(5)
C3'	9437.2(12)	1136(3)	6066.6(12)	64.5(5)
C3''	2379.2(16)	7161(3)	6011.0(13)	74.1(6)

Table S10. Anisotropic Displacement Parameters (Å^2×10^3) for 2e. 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}
O2	45.3(5)	44.3(6)	61.5(6)	23.4(5)	20.3(5)	11.5(4)
O1	51.9(6)	41.9(5)	64.1(7)	18.3(5)	30.6(5)	4.2(4)
N4	29.6(4)	30.5(5)	37.5(5)	2.7(4)	11.1(4)	-0.4(4)
C2	34.5(5)	25.5(5)	40.2(6)	-2.6(4)	13.1(5)	-3.4(4)
C6	32.0(5)	35.3(6)	30.2(5)	2.8(4)	8.2(4)	-1.5(4)
C5	29.1(5)	35.3(6)	35.3(6)	6.1(5)	6.4(4)	-1.0(4)
C11	29.9(5)	48.7(8)	32.6(5)	-3.5(5)	9.6(4)	4.6(5)
C12	31.3(5)	33.4(6)	48.9(7)	-10.9(5)	12.3(5)	-2.3(4)
C1'	30.6(5)	39.0(7)	34.5(6)	4.0(5)	10.1(4)	1.8(5)
C8	42.0(6)	41.4(7)	37.9(6)	3.5(5)	19.3(5)	2.4(5)
O3	48.2(8)	94.5(11)	163.0(17)	11.4(11)	40.7(9)	9.5(7)
C7	35.4(6)	30.1(6)	45.4(7)	7.6(5)	17.2(5)	0.1(4)

C9	38.7(6)	40.6(7)	47.4(7)	0.4(5)	22.8(5)	3.8(5)
C1	36.6(6)	29.4(6)	38.8(6)	5.7(4)	16.8(5)	4.6(4)
C10	41.3(6)	30.3(6)	45.2(7)	-2.3(5)	20.7(5)	2.3(5)
C3	32.6(5)	28.6(6)	42.4(6)	2.7(5)	12.7(5)	-2.3(4)
C6'	45.5(7)	40.1(7)	48.1(7)	1.5(6)	14.8(6)	5.5(5)
C5'	69.9(11)	56.5(10)	57.8(9)	6.2(7)	30.2(8)	23.1(8)
C2"	46.2(8)	56.8(9)	68.2(10)	-5.2(7)	30.8(7)	9.5(7)
C2'	38.5(7)	51.5(9)	55.8(8)	-1.6(6)	18.5(6)	-7.2(6)
C1"	54.4(9)	56.5(9)	66.9(10)	7.8(7)	39.9(8)	9.6(7)
C4'	53.9(9)	86.0(13)	69.7(11)	19.7(10)	34.9(9)	25.8(9)
C3'	39.7(8)	84.7(13)	75.0(12)	12.2(9)	26.8(8)	-2.3(8)
C3"	69.9(12)	74.8(13)	88.5(14)	25.4(10)	40.8(11)	20.7(10)

Table S11. Bond Lengths for 2e.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C5	1.2049(15)	C1'	C2'	1.3837(18)
O1	C3	1.2080(15)	C8	C7	1.5358(17)
N4	C5	1.3960(15)	C8	C9	1.5044(19)
N4	C1'	1.4329(15)	C8	C10	1.5032(18)
N4	C3	1.3945(15)	O3	C2"	1.198(2)
C2	C6	1.5311(16)	C9	C10	1.4959(18)
C2	C1	1.5469(18)	C9	C1"	1.5121(18)
C2	C3	1.5057(17)	C1	C10	1.5328(17)
C6	C5	1.5069(17)	C6'	C5'	1.384(2)
C6	C7	1.5527(17)	C5'	C4'	1.372(3)
C11	C12	1.3213(19)	C2"	C1"	1.504(2)
C11	C1	1.4921(18)	C2"	C3"	1.485(2)
C12	C7	1.4931(19)	C2'	C3'	1.387(2)
C1'	C6'	1.3785(19)	C4'	C3'	1.374(3)

Table S12. Bond Angles for 2e.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	N4	C1'	124.27(10)	C8	C7	C6	103.90(10)
C3	N4	C5	112.01(10)	C8	C9	C1"	118.23(12)
C3	N4	C1'	123.47(10)	C10	C9	C8	60.13(9)
C6	C2	C1	109.89(10)	C10	C9	C1"	119.21(12)
C3	C2	C6	105.09(9)	C11	C1	C2	106.64(9)
C3	C2	C1	112.60(10)	C11	C1	C10	110.24(10)
C2	C6	C7	109.53(10)	C10	C1	C2	104.05(10)
C5	C6	C2	104.98(9)	C8	C10	C1	110.86(10)
C5	C6	C7	113.81(10)	C9	C10	C8	60.22(9)
O2	C5	N4	124.15(12)	C9	C10	C1	122.23(11)

O2	C5	C6	127.04(11)	O1	C3	N4	123.90(11)
N4	C5	C6	108.80(10)	O1	C3	C2	127.38(11)
C12	C11	C1	115.00(11)	N4	C3	C2	108.72(10)
C11	C12	C7	114.74(11)	C1'	C6'	C5'	118.97(15)
C6'	C1'	N4	120.76(11)	C4'	C5'	C6'	120.87(16)
C6'	C1'	C2'	120.83(12)	O3	C2"	C1"	119.77(17)
C2'	C1'	N4	118.40(12)	O3	C2"	C3"	121.43(18)
C9	C8	C7	123.00(11)	C3"	C2"	C1"	118.79(15)
C10	C8	C7	110.09(10)	C1'	C2'	C3'	119.09(15)
C10	C8	C9	59.65(9)	C2"	C1"	C9	114.21(13)
C12	C7	C6	107.34(9)	C5'	C4'	C3'	119.81(15)
C12	C7	C8	110.11(10)	C4'	C3'	C2'	120.42(16)

Table S13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2e.

Atom	*x*	*y*	*z*	U(eq)
H2	6179.56	4601.5	6932.95	40
H6	6198.02	1778.08	7614.89	40
H11	4350.47	2021.15	4992.21	45
H12	4403.63	-1026.18	5695.36	46
H8	4466.17	2285.86	7634.99	47
H7	4948.86	-828.65	7087.72	43
H9	3143.97	2239.68	6019.45	48
H1	4855.73	5112.72	5713.23	41
H10	4440.96	5415.67	6921.04	45
H6'	7377.08	-2412.66	5758.03	54
H5'	8723.22	-3461.73	5463.71	71
H2'	8624.93	3107.38	6458.29	57
H1'A	2355.31	2754.52	7008.77	65
H1'B	3062.95	4586.25	7364.52	65
H4'	10002.13	-1252.65	5650.26	80
H3'	9954.66	2030.25	6139.76	77
H3'A	2663.38	6660.01	5634.39	111
H3'B	2855.47	7884.81	6426.77	111
H3'C	1860.41	8086.64	5753.34	111

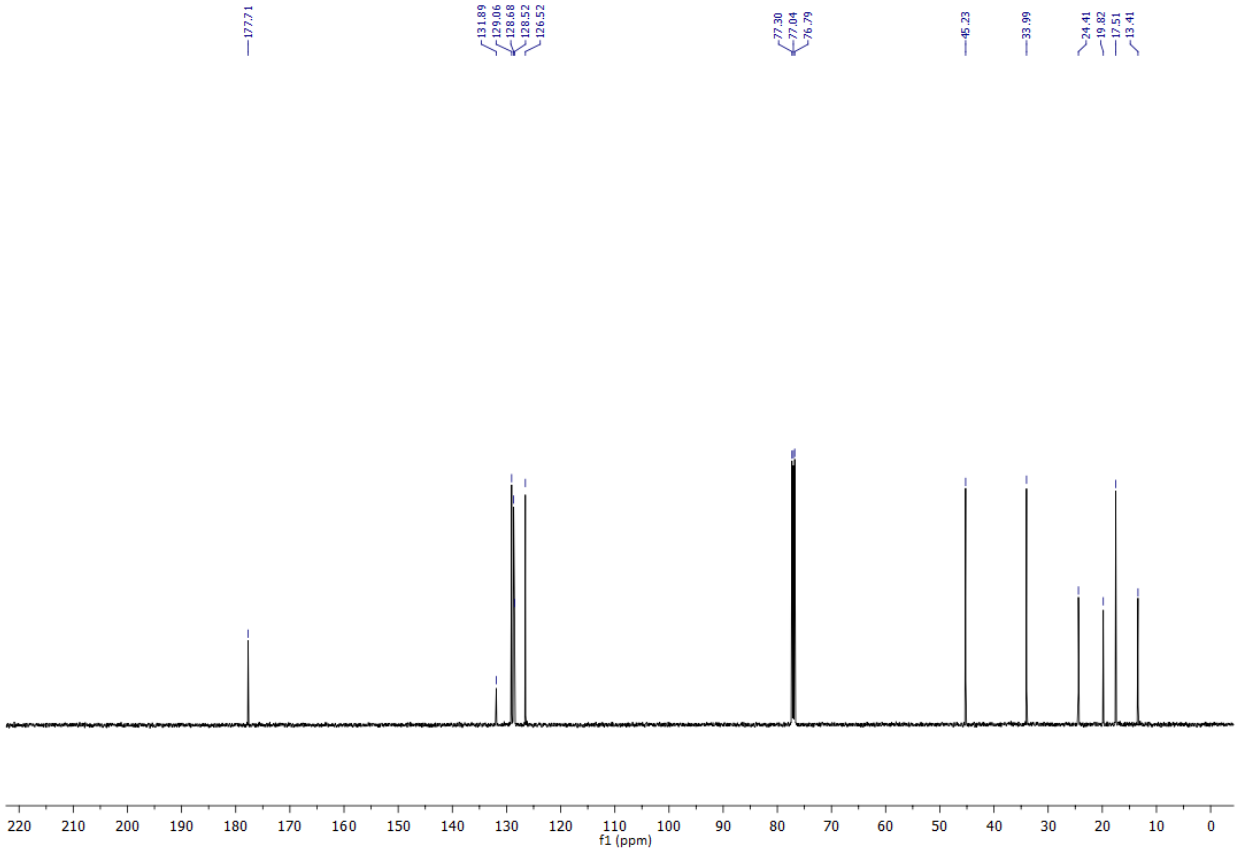
Experimental

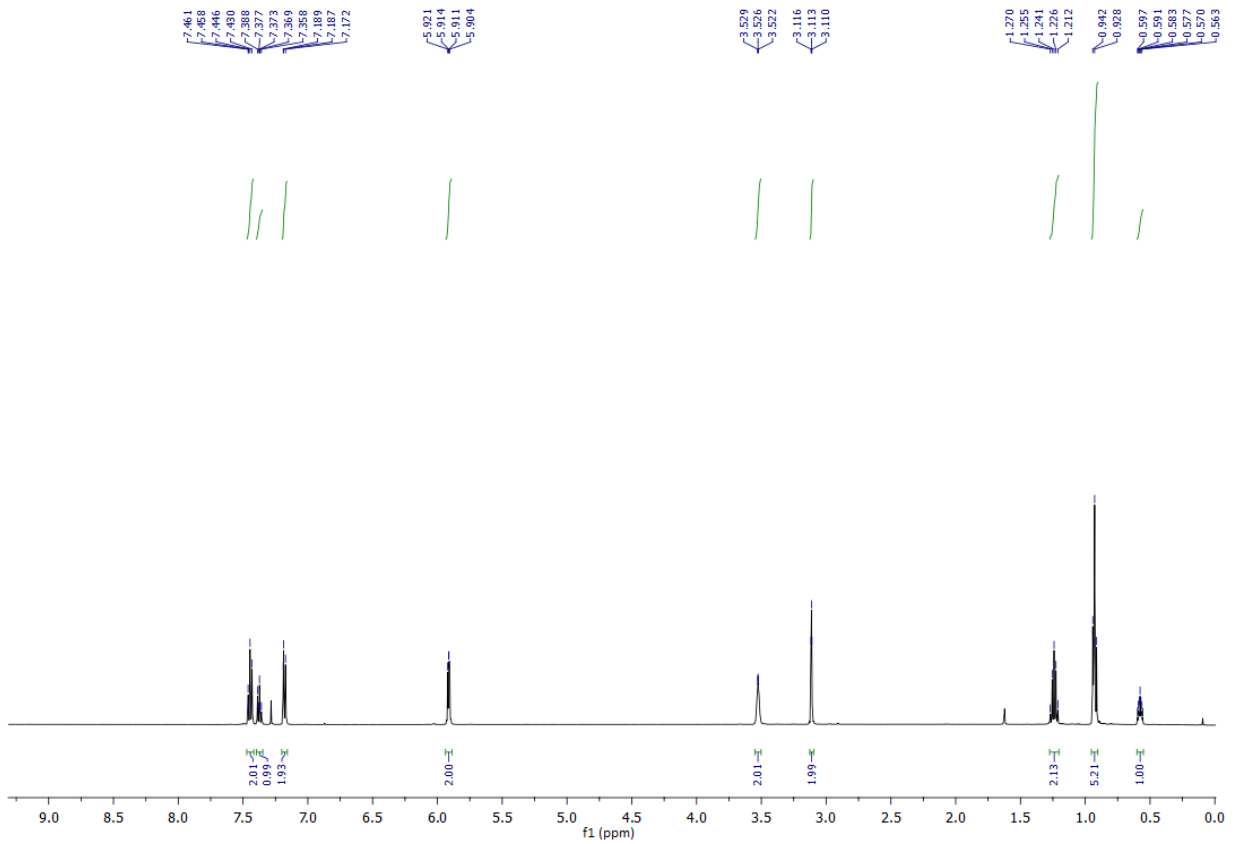
A suitable crystal of $C_{20}H_{19}NO_3$ **2e** was selected and performed on a Xcalibur, Eos diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [S4], the structure was solved with the SHELXT [S2(*a*)] structure solution program using Intrinsic Phasing and refined with the SHELXL [S2(*b*)] refinement package using Least Squares minimisation.

Crystal structure determination of 2e

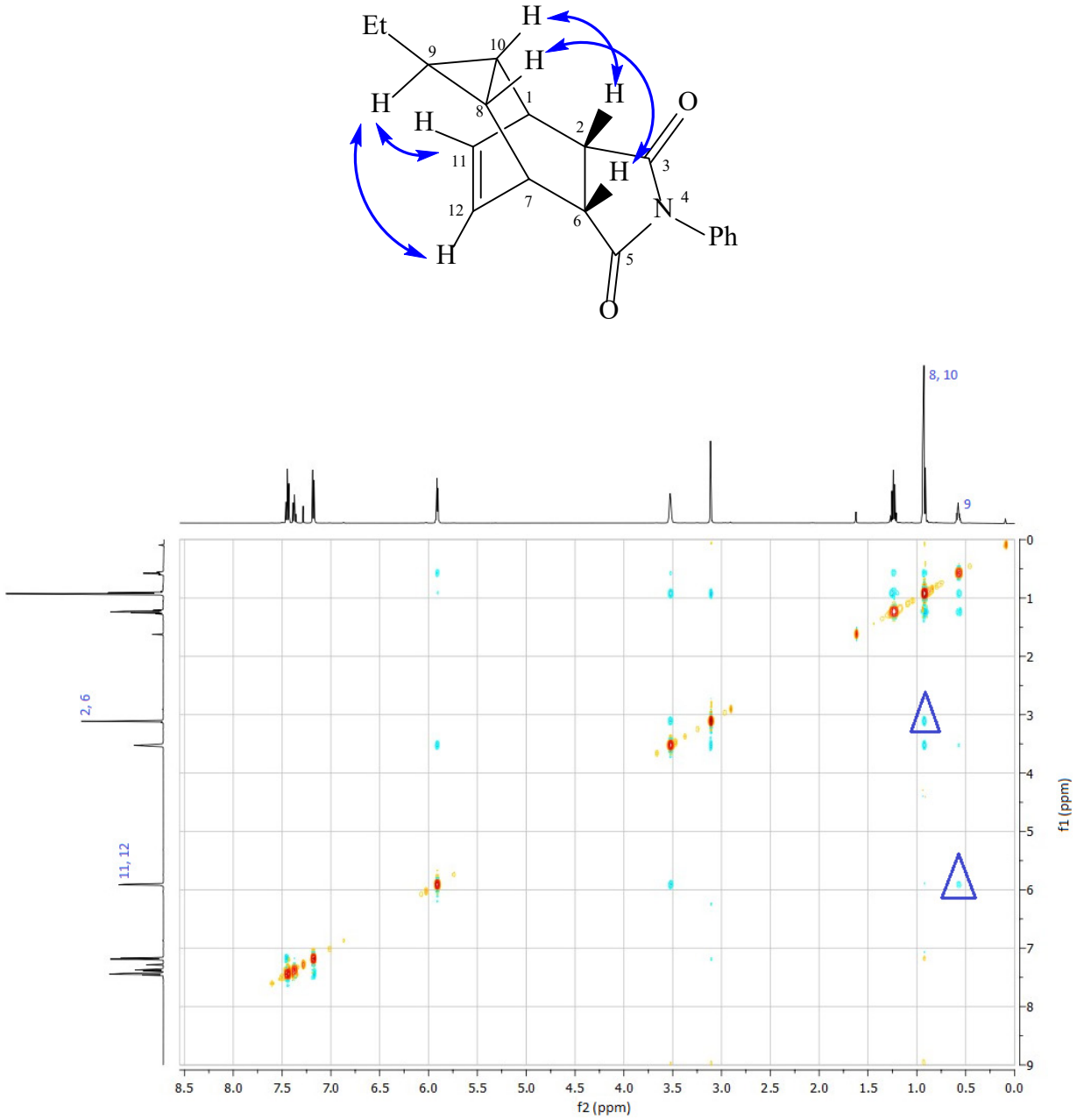
Crystal Data for **2e** $C_{20}H_{19}NO_3$ (M =321.36 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 14.7312(6) Å, b = 6.4502(2) Å, c = 17.9286(8) Å, β = 109.229(5)°, V = 1608.52(12) Å^3, Z = 4, T = 293(2) K, μ(MoKα) = 0.089 mm^{-1}, $Dcalc$ = 1.327 g/cm^3, 39823 reflections measured (4.36° ≤ 2Θ ≤ 75.358°), 8177 unique (R_{int} = 0.0507, R_{sigma} = 0.0535) which were used in all calculations. The final R_1 was 0.0629 (I > 2σ(I)) and wR_2 was 0.1828 (all data).

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

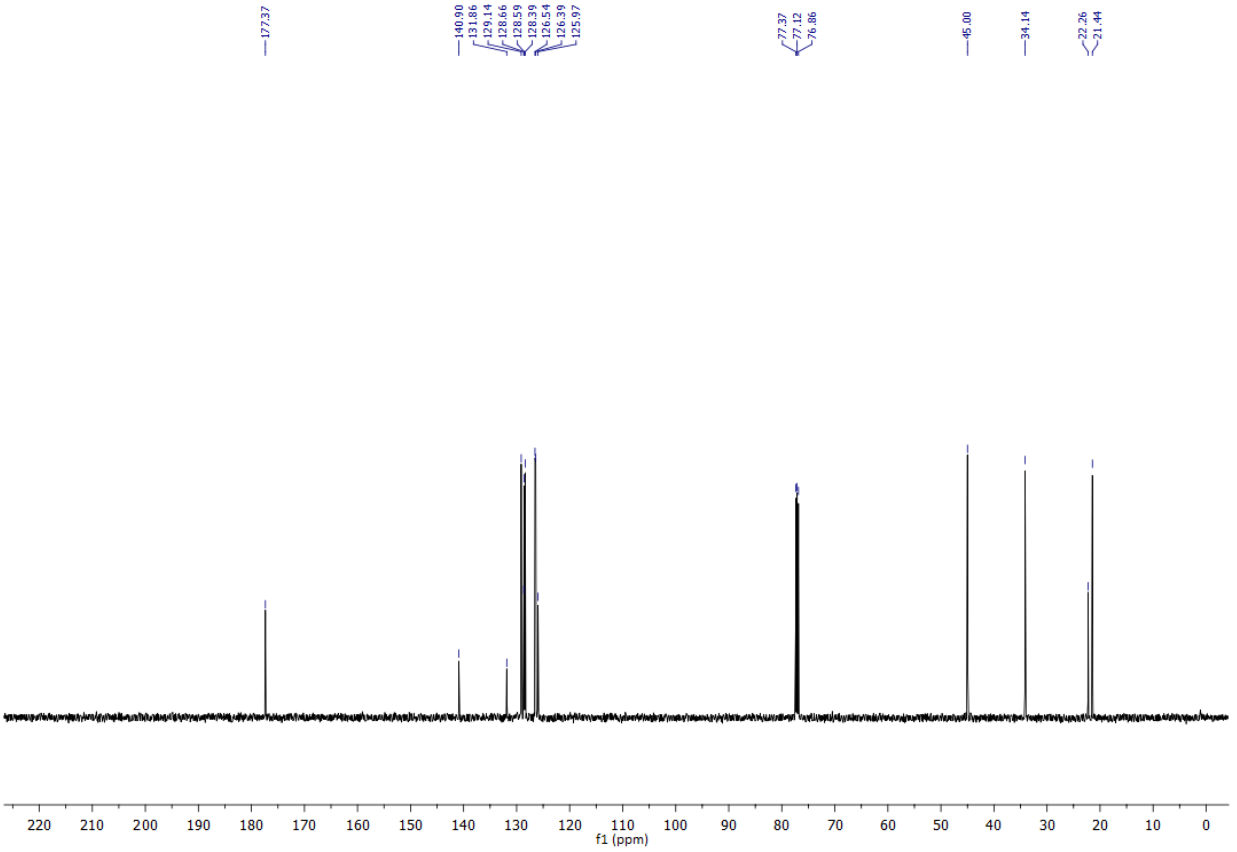


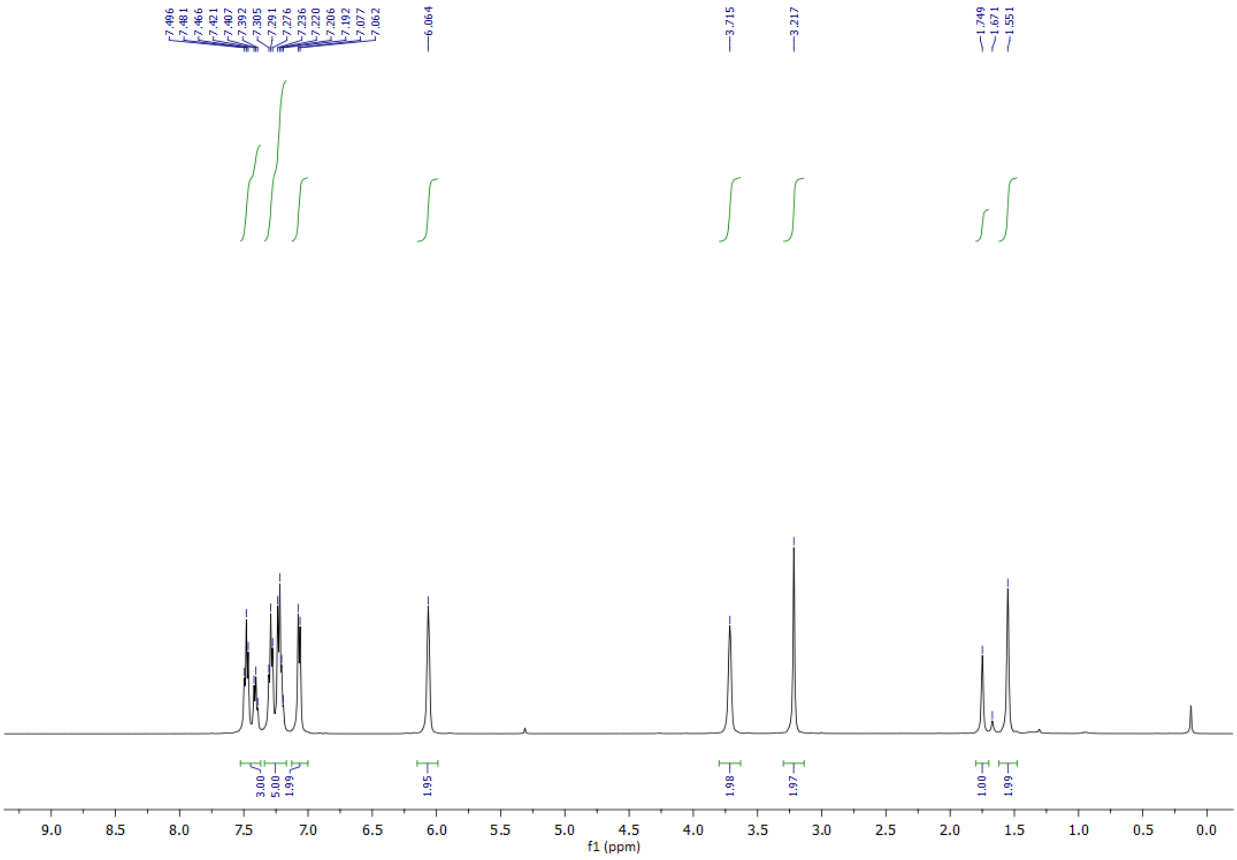


Key NOESY (↔) correlations for 9-ethyl-4-phenyl-4-azatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-3,5-dione (2a):

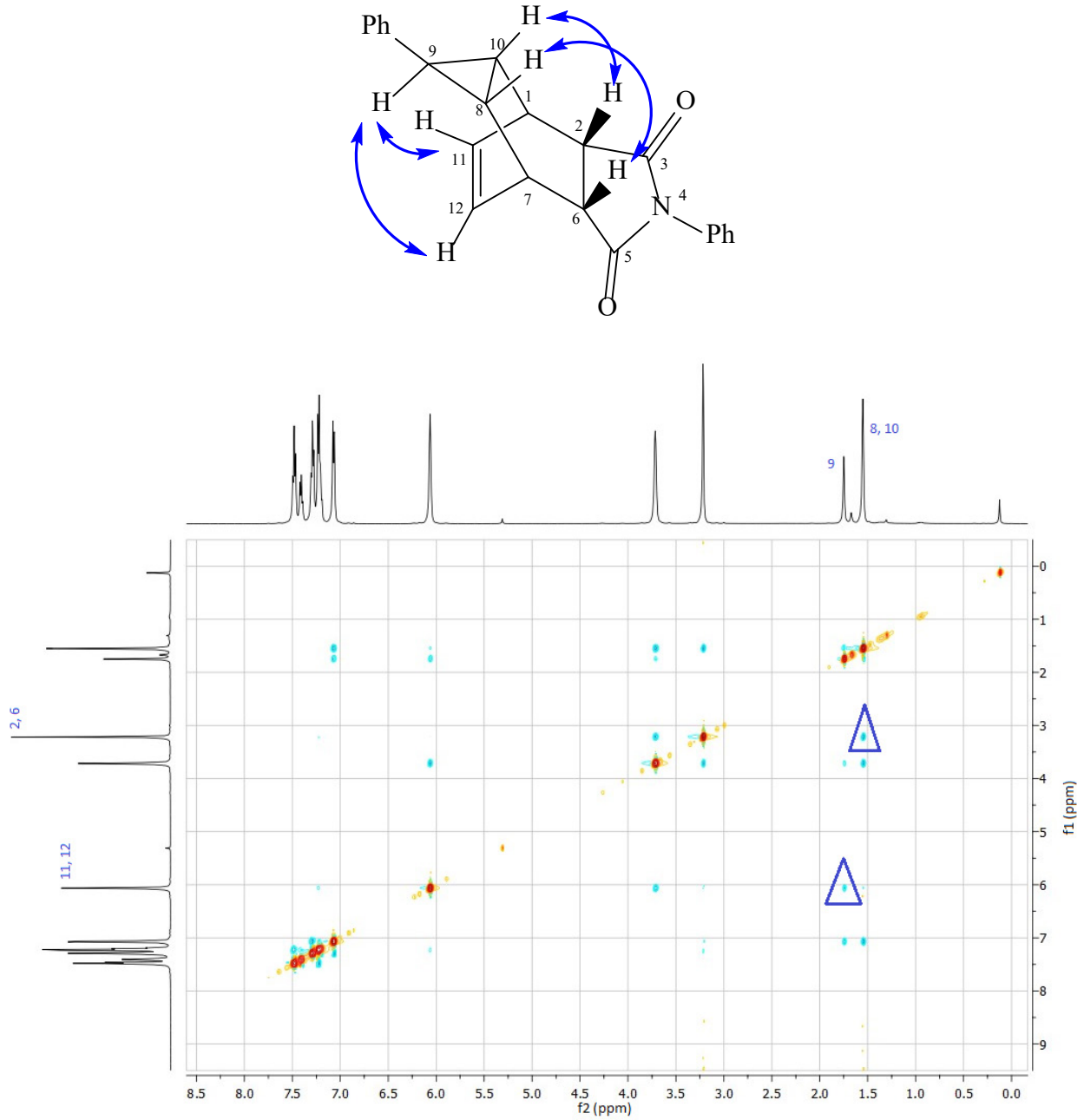


4,9-Diphenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2b):

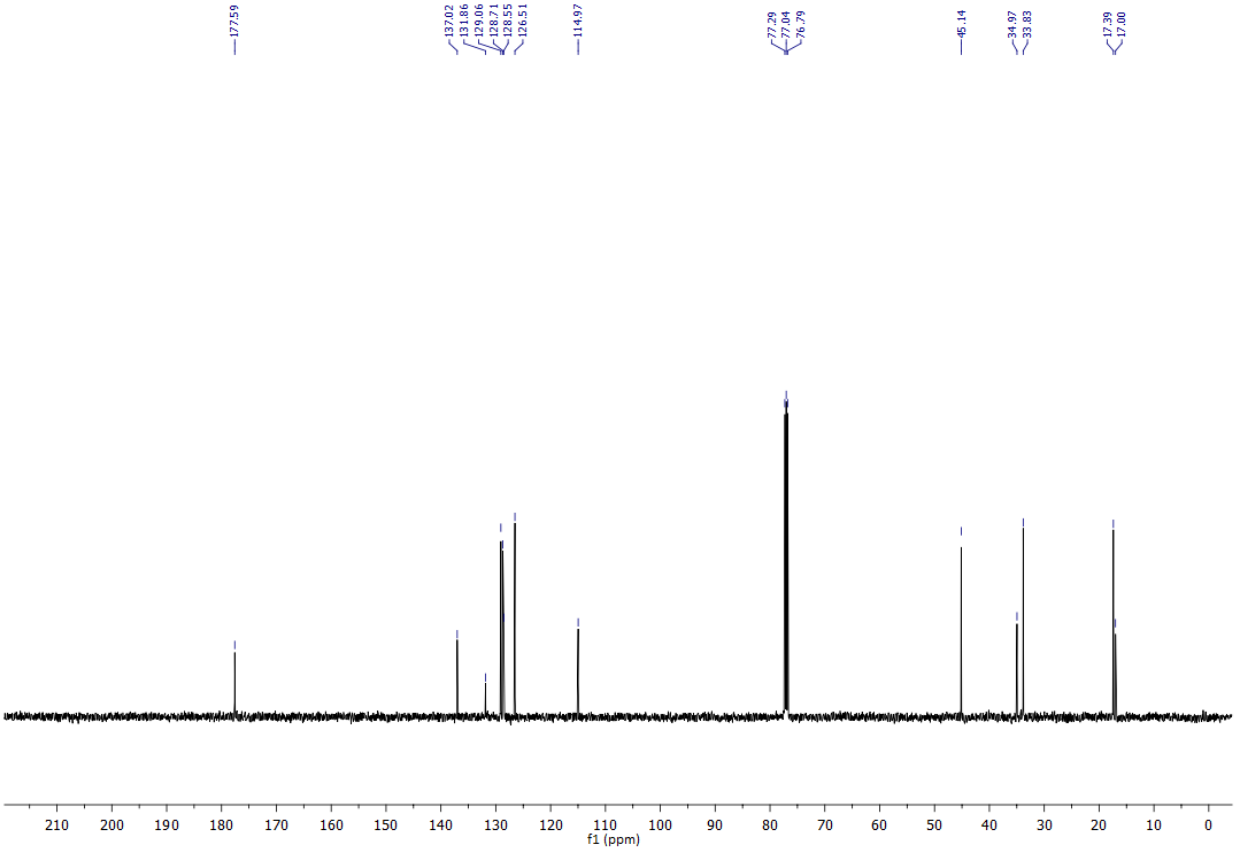


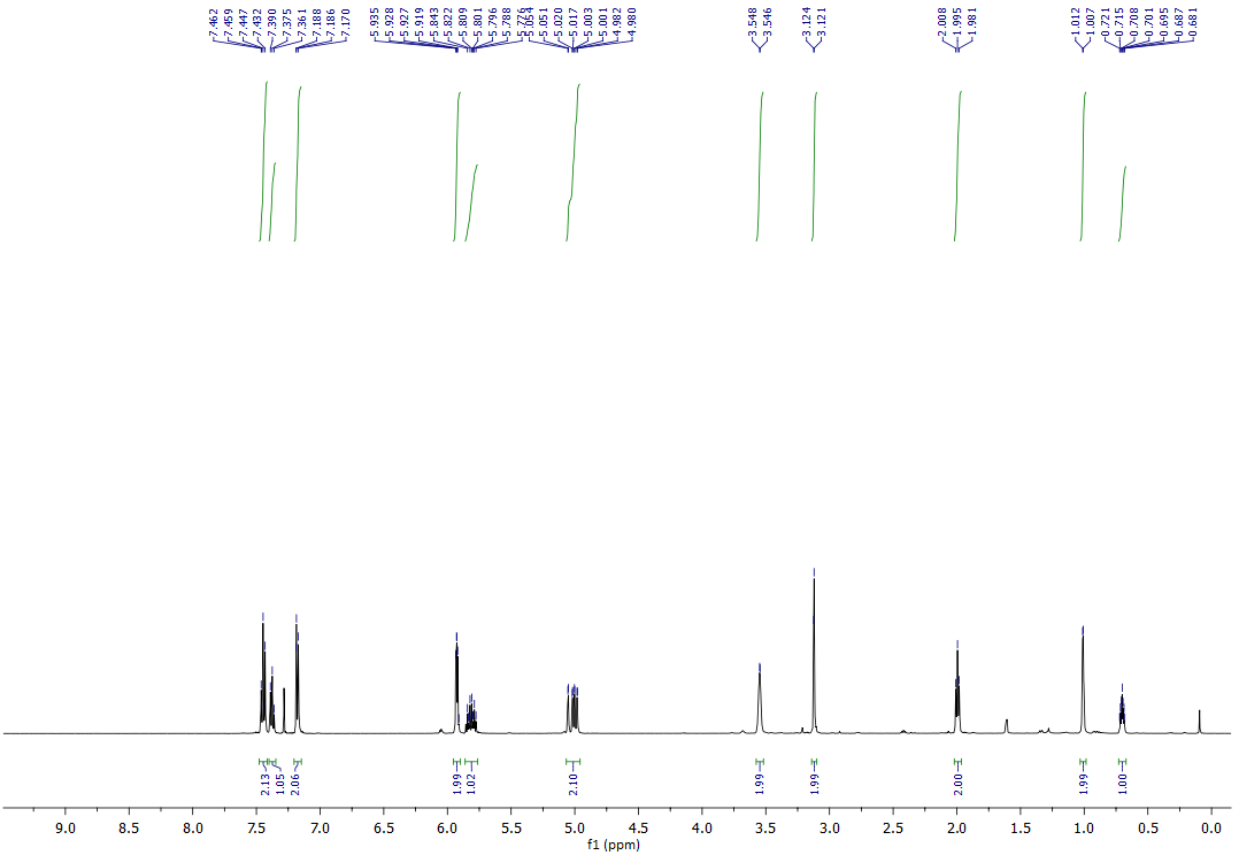


Key NOESY (↔) correlations for 4,9-diphenyl-4-azatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-3,5-dione (2b):

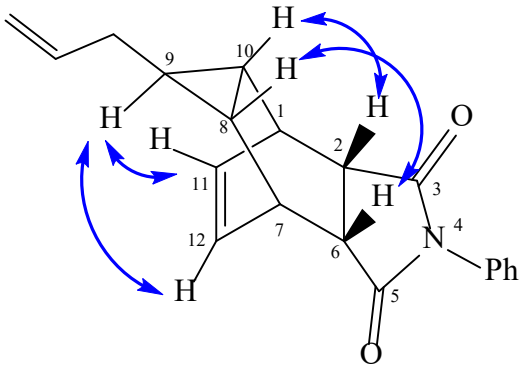


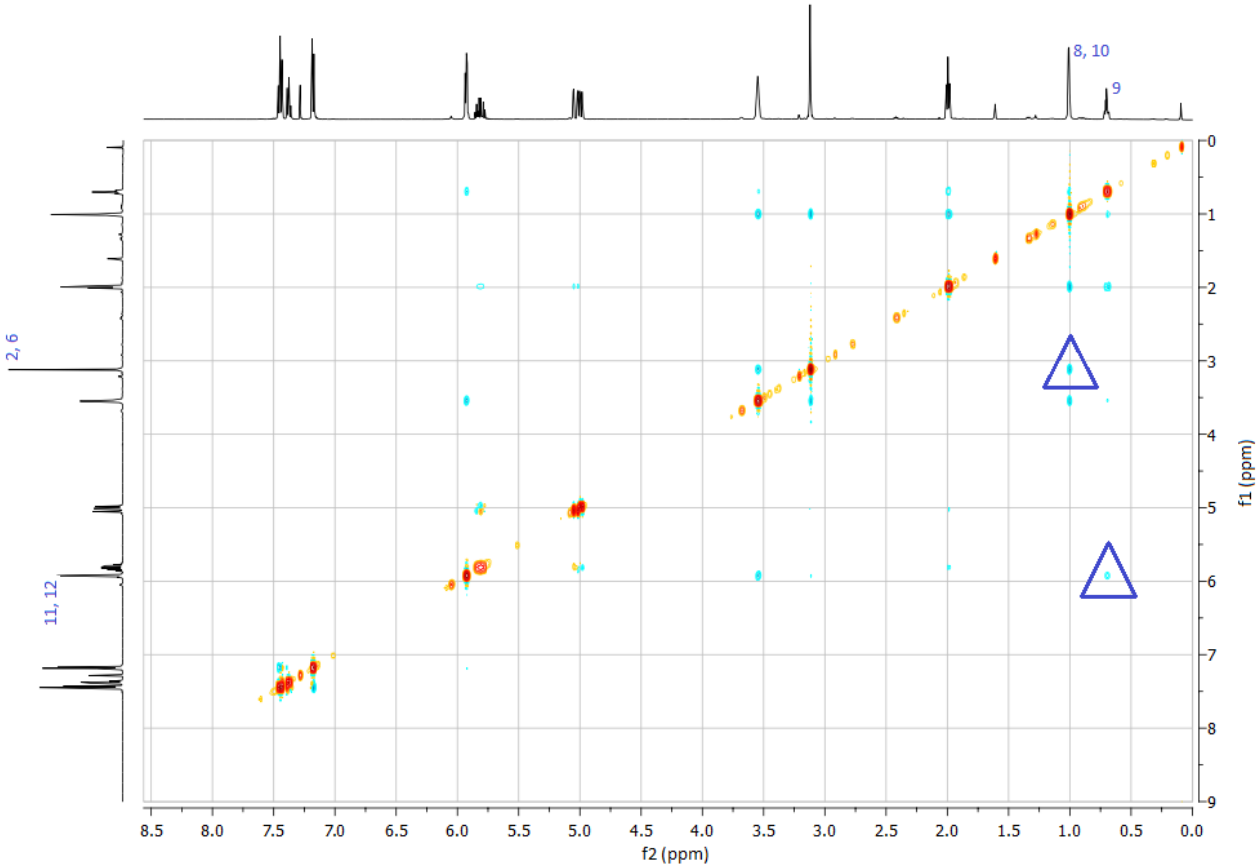
9-Allyl-4-phenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2c):



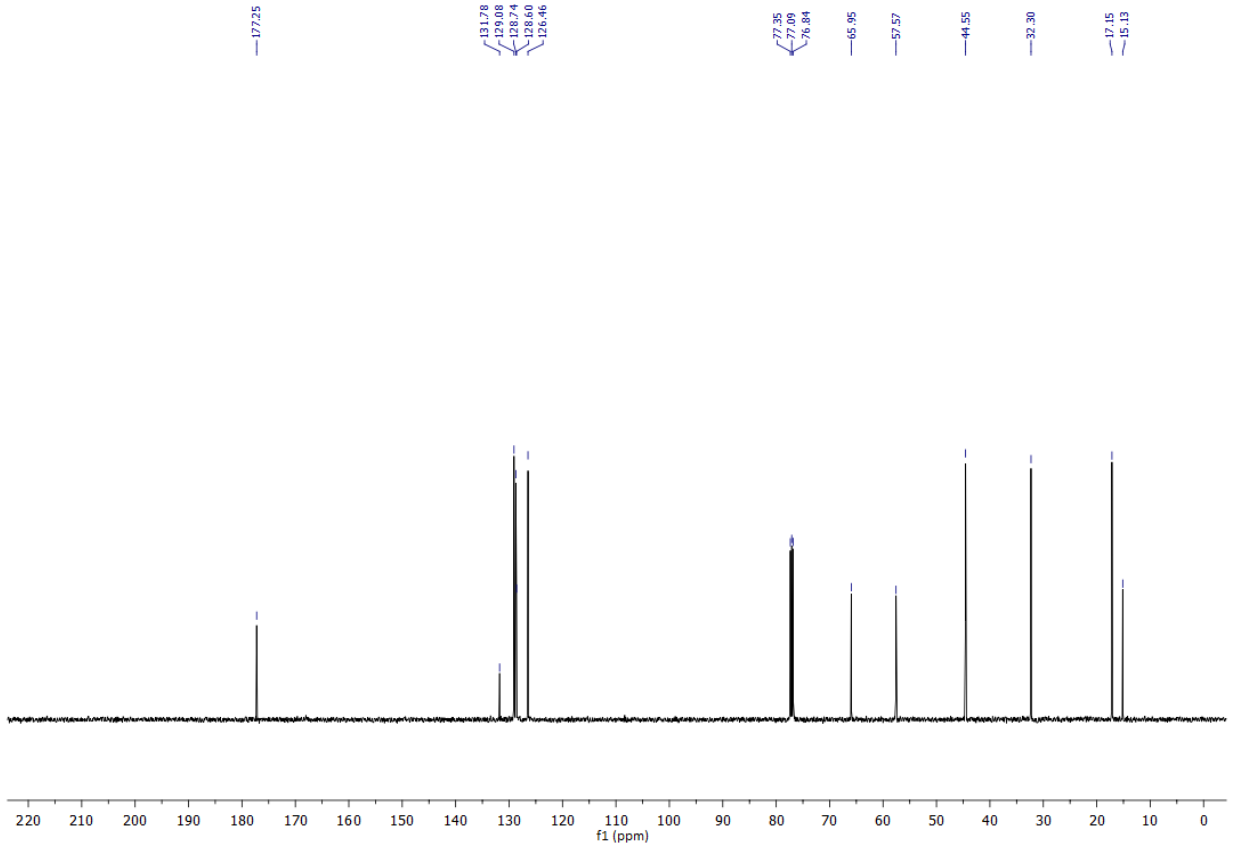


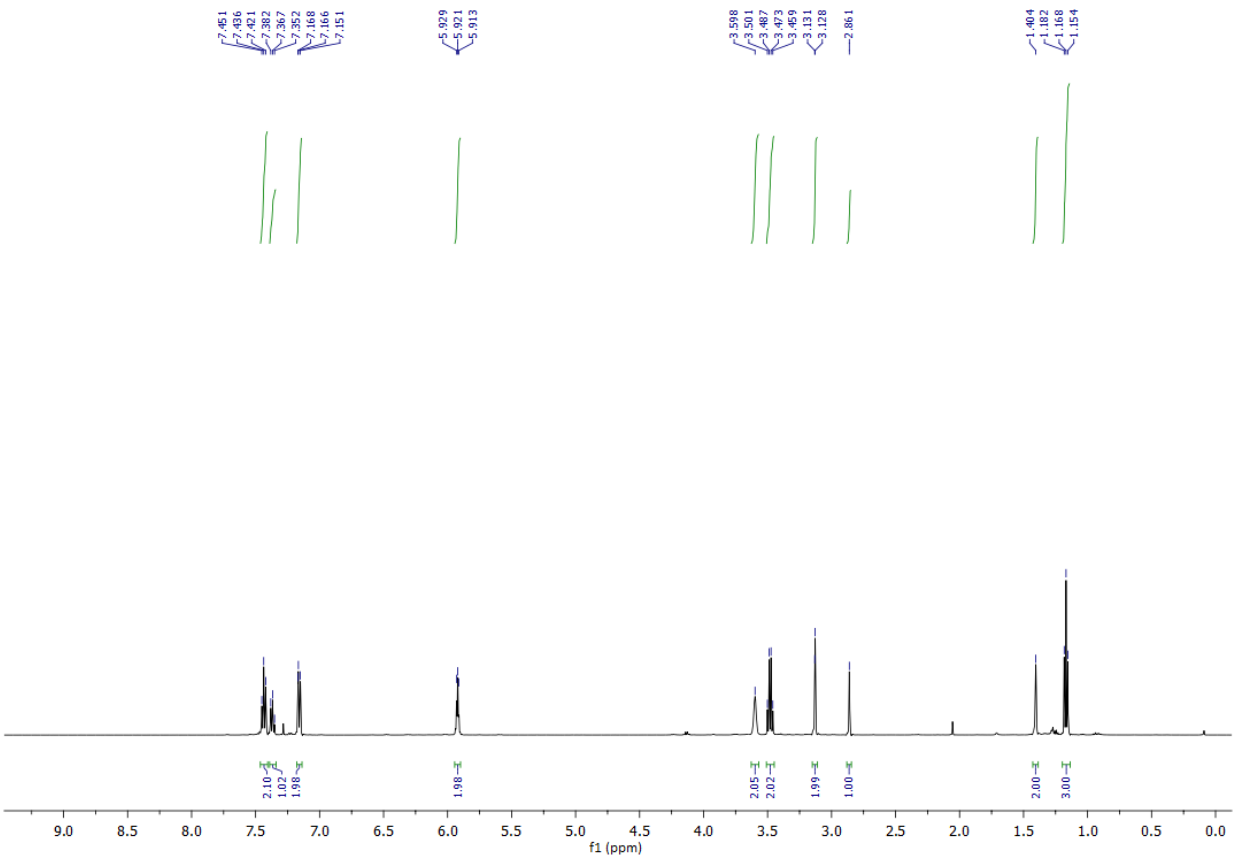
Key NOESY (↔) correlations for 9-allyl-4-phenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2c):



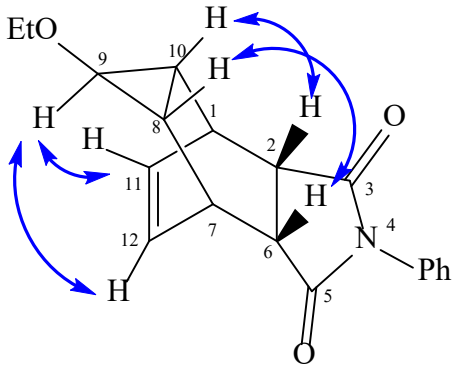


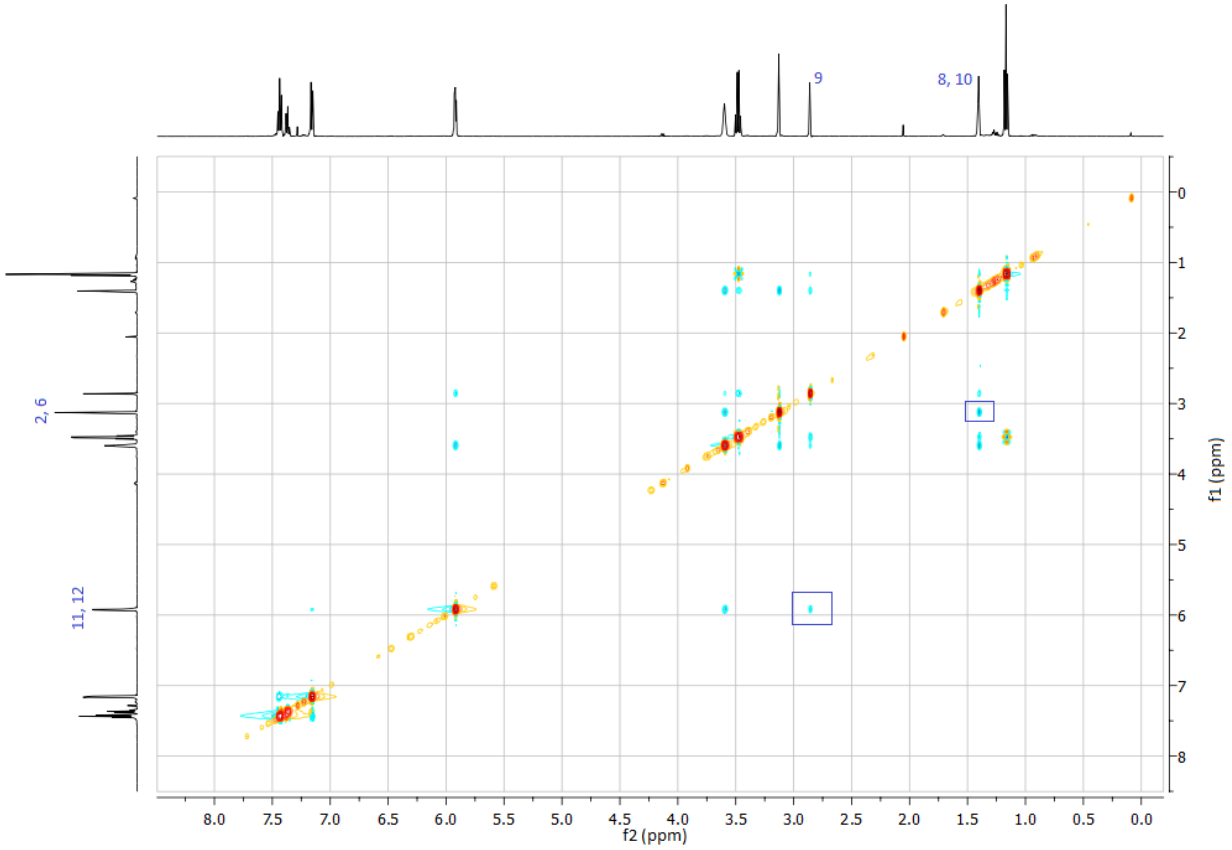
9-Ethoxy-4-phenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2d):



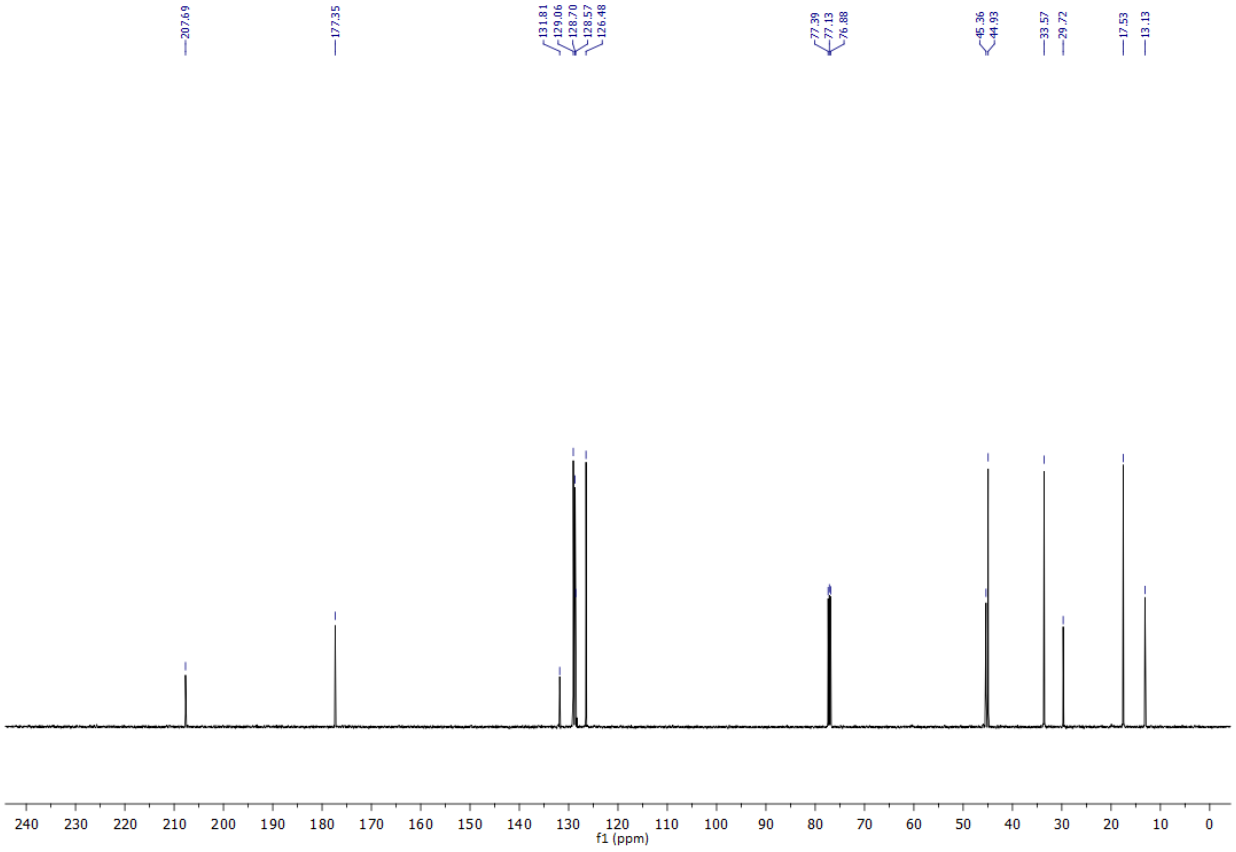


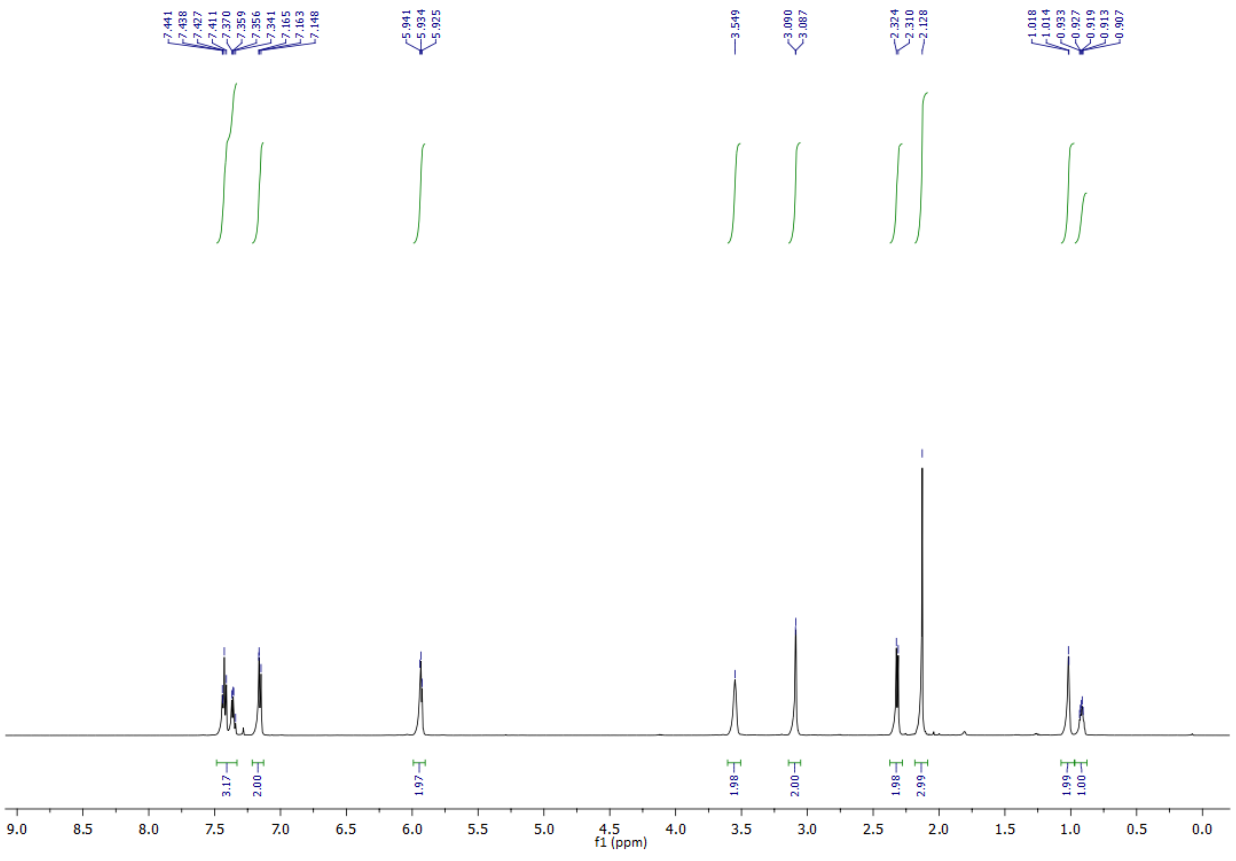
Key NOESY (↔) correlations for 9-ethoxy-4-phenyl-4-azatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-3,5-dione (2d):



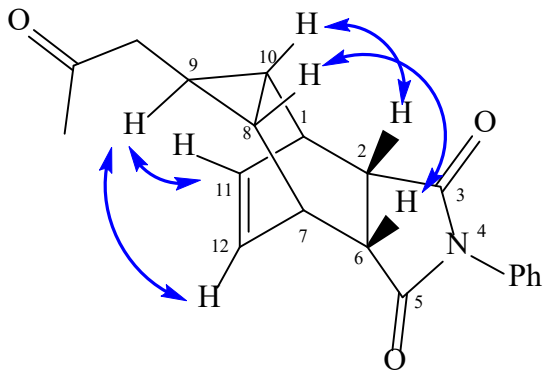


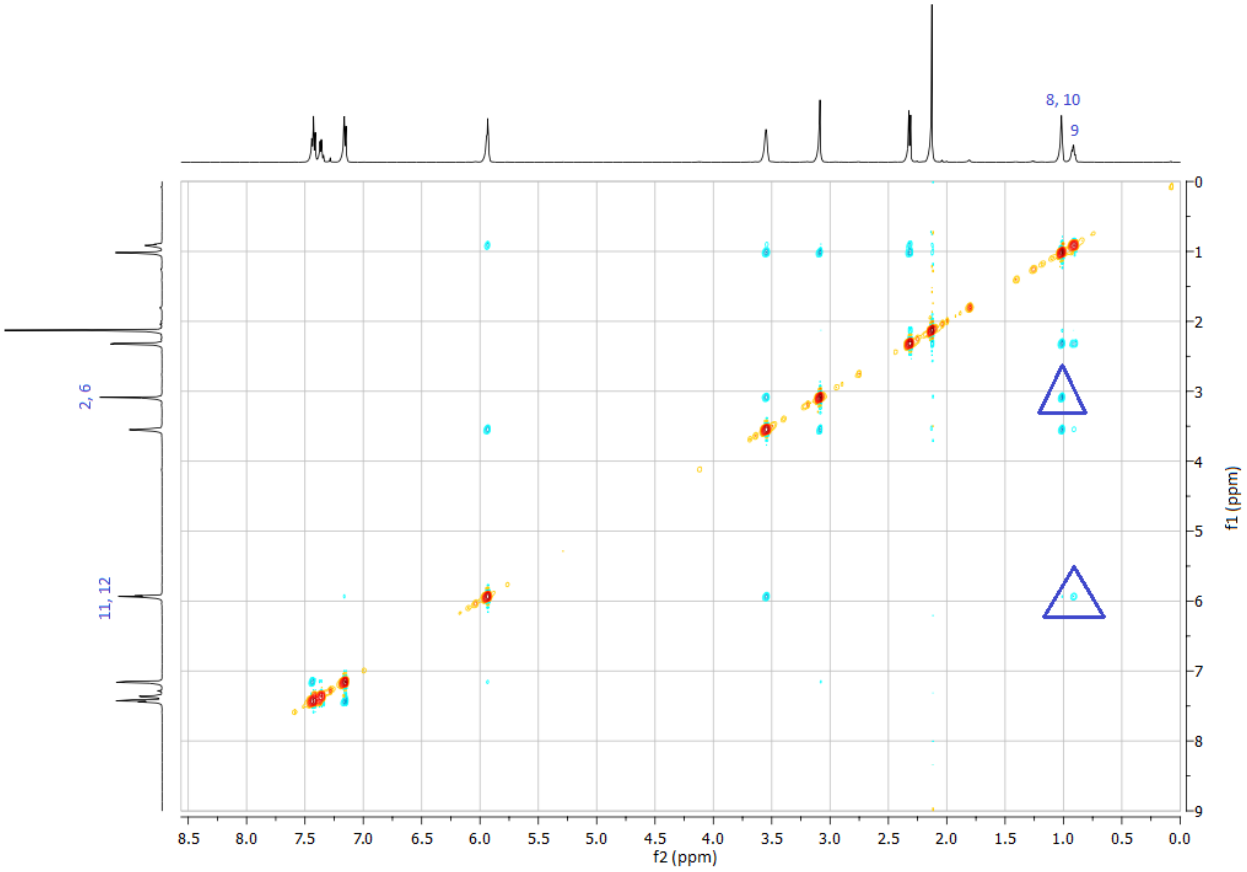
9-(2-Oxopropyl)-4-phenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2e):



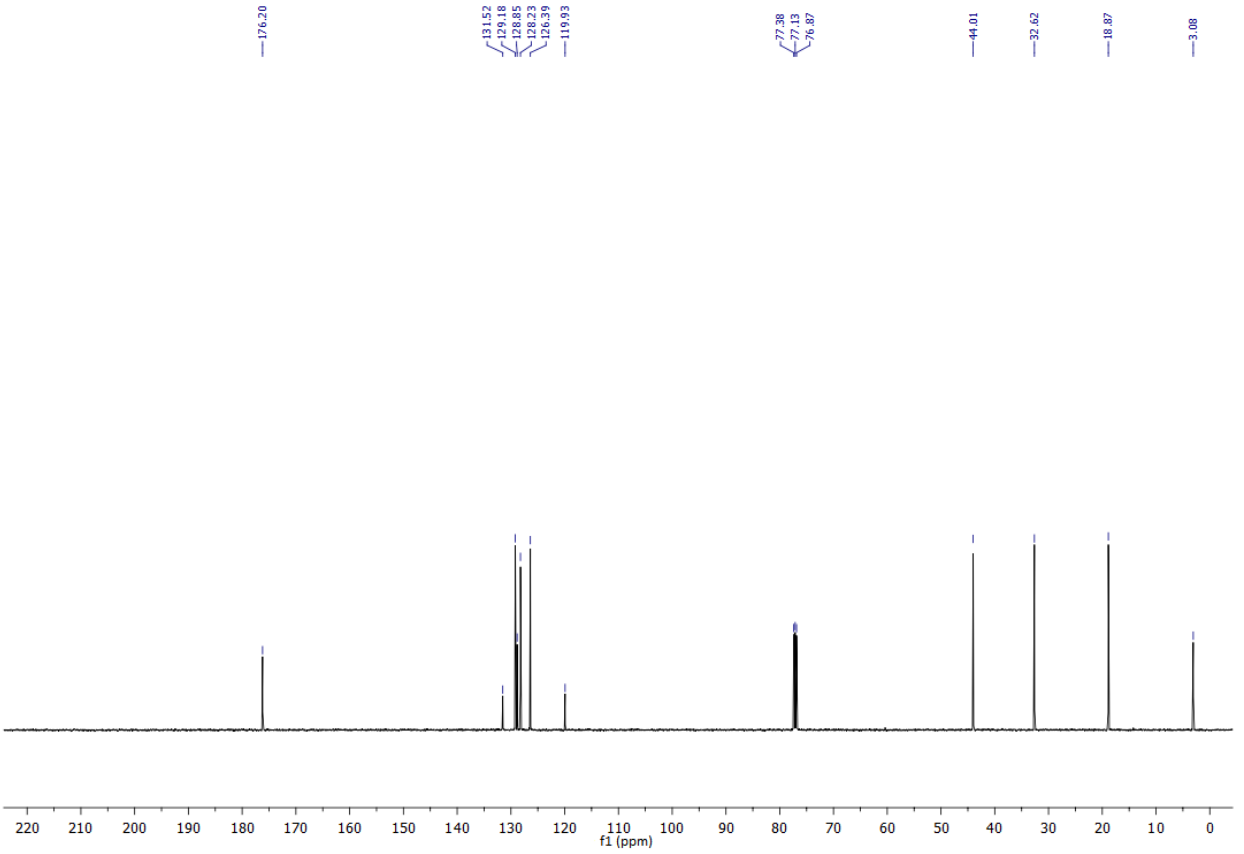


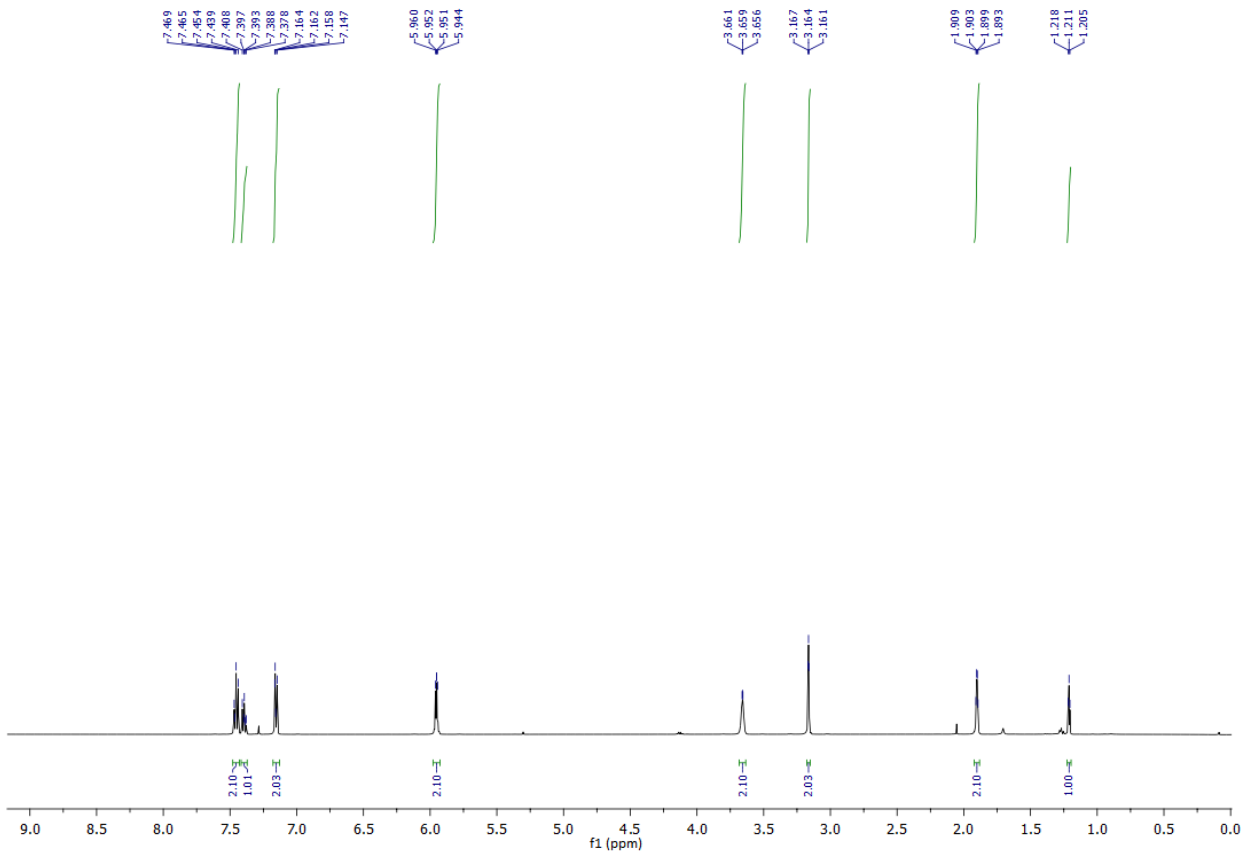
Key NOESY (↔) correlations for 9-(2-oxopropyl)-4-phenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (2e):



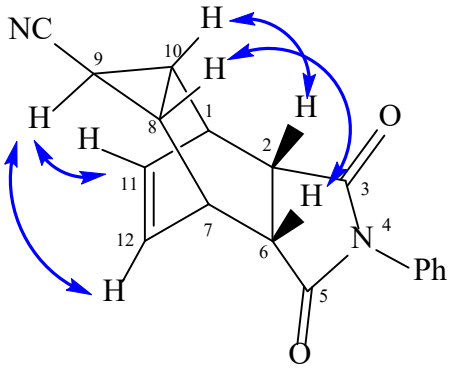


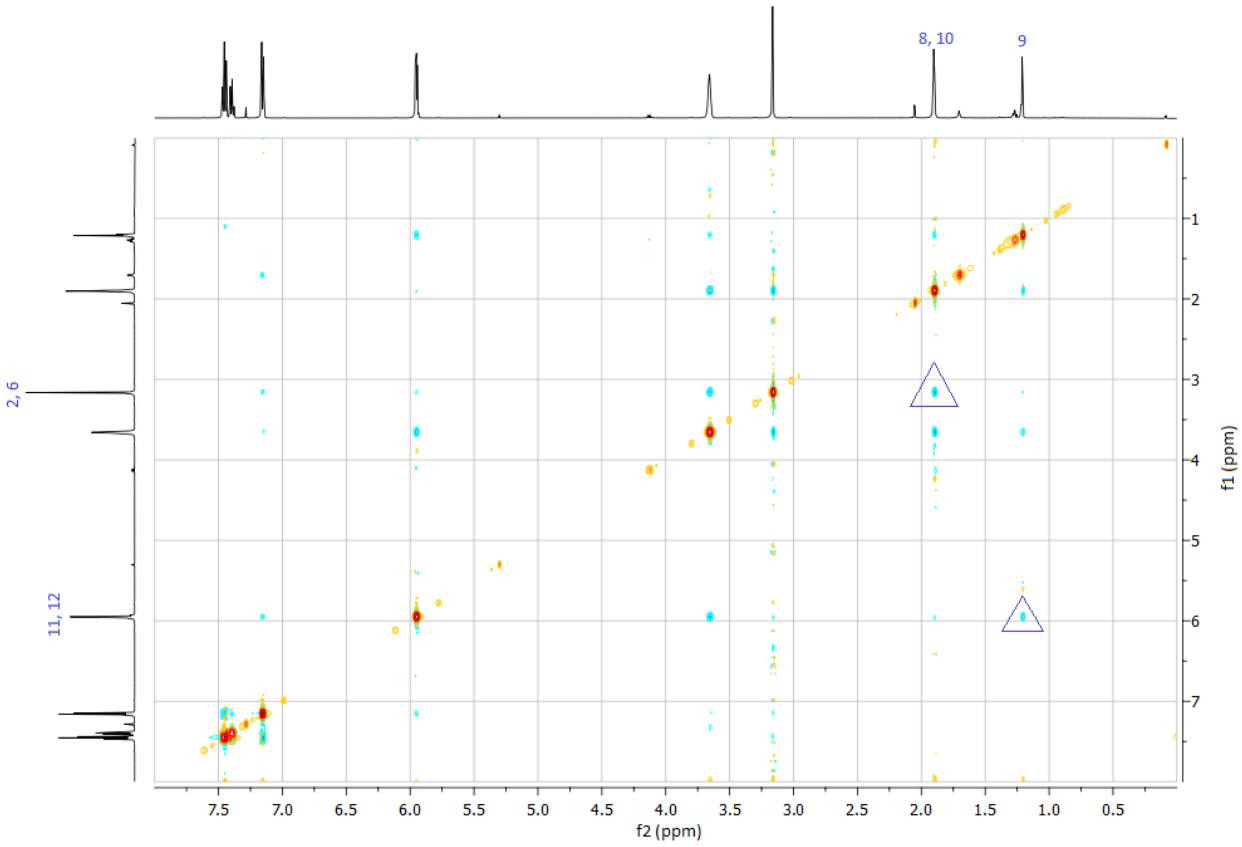
3,5-Dioxo-4-phenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-9-carbonitrile (2f):





Key NOESY (↔) correlations for 3,5-dioxo-4-phenyl-4-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-9-carbonitrile (2f):





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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.

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