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Access to 2,4,6-triazatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodecenes by the hetero-Diels–Alder reaction between cycloheptatrienes and azodicarboxylic acid imide

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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, S3]. 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-, acyl- and cyclohexanone-substituted 1,3,5-cycloheptatrienes were prepared as described [S4, S5]. Commercially available azodicarboxylic acid *N*-phenylimide (Aldrich) was used.

*[4+2]-Cycloaddition of azodicarboxylic acid N-phenylimide **1** to 1,3,5-cycloheptatrienes **2a-f** (general procedure).* To a stirred solution of the 1,3,5-cycloheptatriene **2a-f** (1 mmol) in 5 mL of dry chloroform azodicarboxylic acid *N*-phenylimide **1** (1 mmol) was added at 0 ºC in small

portions over a period of 5 min. After stirring at 0 ºC for an additional 10 min, the mixture was warmed up to room temperature and stirred for 30 min. The solvent was evaporated under reduced pressure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 1:1 as eluent) afforded products **3a-f**.

(1*R,7*S**,8*R**,9-*exo*,10*S**)-9-Ethyl-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3a)**: Yield 96% (0.305 g), white solid, m.p. = 175-176 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.48 (m, 4H), 7.34-7.39 (m, 1H), 6.12-6.15 (m, 2H), 5.19-5.23 (m, 2H), 1.39-1.42 (m, 2H), 1.27-1.35 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.60-0.66 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.67 (2C), 131.44, 129.08 (2C), 128.19, 126.03 (2C), 125.54 (2C), 53.59 (2C), 24.05, 23.61, 13.37, 13.32 (2C) ppm. HRMS (ESI-TOF): calcd for $C_{17}H_{17}N_3O_2Na$ [M + Na]$^+$ 318.1218, found 318.1204.

(1*R,7*S**,8*R**,9-*exo*,10*S**)-4,9-Diphenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3b)**: Yield 93% (0.340 g), white solid, m.p. = 190-191 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.52 (m, 4H), 7.36-7.42 (m, 1H), 7.22-7.35 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 2H), 6.30 (t, *J* = 3.6 Hz, 2H), 5.34-5.40 (m, 2H), 1.98-2.04 (m, 2H), 1.78-1.82 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.72 (2C), 138.37, 131.35, 129.15 (2C), 128.62 (2C), 128.33, 126.75, 126.65 (2C), 126.07 (2C), 125.58 (2C), 53.32 (2C), 26.20, 16.65 (2C) ppm. HRMS (ESI-TOF): calcd for $C_{21}H_{17}N_3O_2Na$ [M + Na]$^+$ 366.1218, found 366.1218.

(1*R,7*S**,8*R**,9-*exo*,10*S**)-9-Allyl-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3c)**: Yield 94% (0.310 g), white solid, m.p. = 140-141 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41-7.47 (m, 4H), 7.32-7.38 (m, 1H), 6.11-6.16 (m, 2H), 5.73-5.83 (m, 1H), 5.17-5.24 (m, 2H), 4.99-5.07 (m, 2H), 2.03 (t, *J* = 6.7 Hz, 2H), 1.42-1.49 (m, 2H), 0.69-0.75 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.64 (2C), 136.11, 131.44, 129.08 (2C), 128.19, 126.05 (2C), 125.52 (2C), 115.77, 53.41 (2C), 34.06, 21.24, 13.19 (2C) ppm. HRMS (ESI-TOF): calcd for $C_{18}H_{17}N_3O_2Na$ [M + Na]$^+$ 330.1218, found 330.1236.

(1*R,7*S**,8*R**,9-*exo*,10*S**)-9-Ethoxy-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3d)**: Yield 86% (0.287 g), white solid, m.p. = 135-136 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41-7.47 (m, 4H), 7.33-7.39 (m, 1H), 6.13-6.18 (m, 2H), 5.20-5.26 (m, 2H), 3.51 (q, 2H, *J* = 7 Hz), 2.86 (s, 1H), 1.86-1.89 (m, 2H), 1.18 (t, 3H, *J* = 7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.58 (2C), 131.30, 129.11 (2C), 128.28, 126.35 (2C), 125.53 (2C), 66.53, 60.01, 51.71 (2C), 15.01, 13.46 (2C) ppm. HRMS (ESI-TOF): calcd for $C_{17}H_{17}N_3O_3Na$ [M + Na]$^+$ 334.1167, found 334.1131.

(1*R,7*S**,8*R**,9-*exo*,10*S**)-9-(2-Oxopropyl)-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]-dodec-11-ene-3,5-dione (3e)**: Yield 92% (0.318 g), white solid, m.p. = 158-159 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41-7.47 (m, 4H), 7.33-7.38 (m, 1H), 6.16-6.19 (m, 2H), 5.20-5.25 (m,

2H), 2.42 (d, *J* = 6.9 Hz, 2H), 2.12-2.15 (m, 3H), 1.43-1.49 (m, 2H), 0.95-1.01 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.48, 156.63 (2C), 131.34, 129.09 (2C), 128.26, 126.07 (2C), 125.52 (2C), 53.20 (2C), 44.28, 29.87, 16.75, 13.29 (2C) ppm. HRMS (ESI-TOF): calcd for $C_{18}H_{17}N_3O_3Na$ $[M + Na]^+$ 346.1167, found 346.1139.

(1*R,7*S**,8*R**,9-*exo*,10*S**)-9-(2-Oxocyclohexyl)-4-phenyl-2,4,6-triazatetracyclo-[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3f)**: Yield 93% (0.359 g), white solid, m.p. = 191-192 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.48 (m, 4H), 7.34-7.39 (m, 1H), 6.22-6.26 (m, 1H), 6.13-6.18 (m, 1H), 5.27 (t, *J* = 4.7 Hz, 1H), 5.22 (t, *J* = 4.7 Hz, 1H), 2.40-2.46 (m, 1H), 2.24-2.32 (m, 1H), 2.04-2.17 (m, 2H), 1.82-1.95 (m, 2H), 1.58-1.76 (m, 2H), 1.40-1.54 (m, 3H), 0.86-0.92 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.04, 156.69, 156.59, 131.37, 129.09 (2C), 128.23, 126.47, 125.73, 125.54 (2C), 53.37 (2C), 52.18, 42.00, 33.82, 27.80, 24.94, 22.10, 13.40, 11.40 ppm. HRMS (ESI-TOF): calcd for $C_{21}H_{21}N_3O_3Na$ $[M + Na]^+$ 386.1480, found 386.1457.

Crystal data for 3b

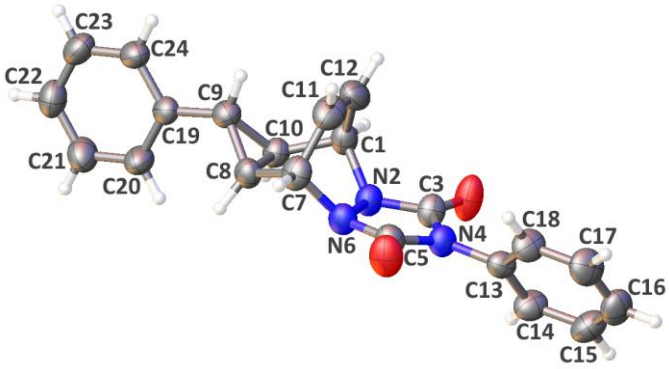


Figure S1. Geometry of molecule **3b**.

Table S1. Crystal data and structure refinement for 3b (KGN-232-22_autored).	
Identification code	KGN-232-22_autored
Empirical formula	$C_{21}H_{17}N_3O_2$
Formula weight	343.38
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	14.7894(5)
b/Å	11.5074(5)
c/Å	10.1656(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1730.06(12)
Z	4
ρ_{calc}g/cm^3	1.318
μ/mm^{-1}	0.087
F(000)	720.0
Crystal size/mm^3	0.13 × 0.04 × 0.04
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.484 to 75.198
Index ranges	-24 ≤ h ≤ 21, -19 ≤ k ≤ 19, -16 ≤ l ≤ 17
Reflections collected	23192
Independent reflections	8100 [R_{int} = 0.0293, R_{sigma} = 0.0348]
Data/restraints/parameters	8100/1/236
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.1099
Final R indexes [all data]	R_1 = 0.1050, wR_2 = 0.1352
Largest diff. peak/hole / e Å^{-3}	0.15/-0.20
Flack parameter	0.8(15)

Table S2. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 3b (KGN-232-22_autored). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O001	6039.3(13)	2185.7(15)	3241.6(18)	64.3(5)
O002	3949.7(12)	3093.5(16)	6387(2)	64.0(5)
N2	5666.5(11)	3906.2(14)	4278.0(16)	41.0(4)
N6	5003.3(11)	4197.2(15)	5256.7(18)	43.7(4)
N4	4810.5(11)	2361.8(14)	4657.7(17)	42.2(4)
C3	5571.5(14)	2745.3(18)	3983(2)	43.6(4)
C19	6854.1(13)	7740.8(17)	5368(2)	41.3(4)
C9	6652.1(13)	6501.4(18)	5678(2)	44.6(4)
C13	4440.8(12)	1219.3(17)	4512(2)	40.1(4)
C10	6404.2(13)	5707.1(16)	4559(2)	41.4(4)
C5	4527.8(13)	3198.9(18)	5558(2)	44.7(4)
C14	4204.0(16)	833(2)	3280(2)	52.6(5)
C8	5701.8(13)	6031.2(17)	5564(2)	44.5(4)
C1	6577.0(13)	4405.8(17)	4614(2)	44.8(4)
C15	3879.6(17)	-286(3)	3134(3)	61.7(6)
C20	6384.1(17)	8366(2)	4431(3)	54.9(5)
C24	7554.4(15)	8287.9(19)	6034(2)	50.8(5)
C18	4351.7(16)	513(2)	5593(2)	52.2(5)
C16	3789.3(17)	-998(2)	4210(3)	62.2(7)
C12	6800.5(17)	4002(2)	5971(3)	57.4(6)
C23	7779.7(17)	9425(2)	5755(3)	60.9(6)
C7	5402.3(16)	4954(2)	6308(2)	49.7(5)
C21	6606.6(19)	9512(2)	4161(3)	61.5(6)
C22	7306.5(17)	10040(2)	4823(3)	60.5(6)
C11	6194(2)	4295(2)	6860(3)	60.5(6)
C17	4021.4(18)	-601(2)	5435(3)	62.7(6)

Table S3. Anisotropic Displacement Parameters (Å²×10³) for 3b (KGN-232-22_autored). 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}
O001	79.6(11)	47.0(9)	66.3(11)	-13.4(8)	38.2(9)	-15.8(8)
O002	61.4(10)	59.4(10)	71.3(12)	-2.3(8)	32.5(9)	-1.7(7)
N2	45.5(8)	38.8(8)	38.8(8)	-1.2(6)	9.7(7)	-2.7(6)
N6	42.2(8)	43.7(9)	45.3(9)	-2.5(7)	10.6(7)	0.4(6)
N4	45.4(8)	39.0(8)	42.2(9)	2.7(7)	8.7(7)	-3.3(6)
C3	54.1(11)	40.1(10)	36.6(9)	2.3(7)	10.4(8)	-5.2(8)
C19	42.7(9)	39.8(9)	41.3(10)	-8.5(8)	-0.7(8)	3.6(7)
C9	45.6(10)	44.7(10)	43.5(11)	-3.3(8)	-5.2(9)	1.6(8)
C13	36.5(8)	42.4(9)	41.2(10)	7.6(8)	1.6(7)	-2.4(7)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3b (KGN-232-22_autored). 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}
C10	44.2(9)	38.9(9)	41.1(10)	-1.9(8)	1.9(8)	-0.7(7)
C5	41.2(9)	44.7(10)	48.0(11)	3.4(8)	7.0(9)	1.7(7)
C14	56.7(12)	57.9(13)	43.2(11)	8.9(10)	-4.7(10)	-6.7(10)
C8	43.3(9)	39.9(9)	50.4(12)	-5.1(9)	4.1(9)	3.2(7)
C1	40.2(9)	38.4(9)	55.8(12)	-3.2(9)	10.4(9)	-1.2(7)
C15	57.2(13)	69.2(16)	58.7(15)	-8.6(12)	-5.8(11)	-14.8(11)
C20	60.9(12)	47.3(12)	56.7(14)	-2.9(10)	-18.6(11)	-1.5(9)
C24	46.1(10)	49.6(12)	56.6(14)	-9.3(10)	-11.4(9)	4.1(9)
C18	60.7(13)	53.8(12)	42.0(11)	12.8(10)	1.0(10)	-7.4(10)
C16	54.2(12)	49.9(13)	83(2)	0.4(12)	8.2(12)	-14.0(10)
C12	52.1(12)	45.1(12)	75.0(17)	10.0(11)	-11.6(11)	2.7(9)
C23	55.1(13)	55.2(13)	72.4(17)	-14.3(12)	-8.4(12)	-9.2(10)
C7	56.0(11)	51.5(12)	41.7(11)	-7.9(9)	12.1(9)	-1.6(9)
C21	78.9(16)	47.4(13)	58.1(15)	3.1(10)	-10.5(13)	4.1(11)
C22	70.2(14)	42.3(11)	69.2(17)	-5.1(11)	5.1(12)	-4.1(10)
C11	79.9(17)	55.7(13)	46.0(13)	9.4(10)	-10.1(12)	-9.3(12)
C17	69.6(15)	54.2(14)	64.3(17)	19.3(12)	6.8(13)	-10.4(11)

Table S4. Bond Lengths for 3b (KGN-232-22_autored).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O001	C3	1.209(3)	C13	C18	1.373(3)
O002	C5	1.207(3)	C10	C8	1.504(3)
N2	N6	1.437(2)	C10	C1	1.520(3)
N2	C3	1.376(3)	C14	C15	1.383(4)
N2	C1	1.503(3)	C8	C7	1.519(3)
N6	C5	1.381(3)	C1	C12	1.492(3)
N6	C7	1.500(3)	C15	C16	1.373(4)
N4	C3	1.390(2)	C20	C21	1.386(3)
N4	C13	1.432(2)	C24	C23	1.380(3)
N4	C5	1.393(3)	C18	C17	1.382(3)
C19	C9	1.491(3)	C16	C17	1.370(4)
C19	C20	1.382(3)	C12	C11	1.317(4)
C19	C24	1.388(3)	C23	C22	1.374(4)
C9	C10	1.505(3)	C7	C11	1.504(4)
C9	C8	1.511(3)	C21	C22	1.376(4)
C13	C14	1.374(3)			

Table S5. Bond Angles for 3b (KGN-232-22_autored).							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N6	N2	C1	111.42(15)	O002	C5	N6	126.8(2)
C3	N2	N6	107.91(15)	O002	C5	N4	127.0(2)
C3	N2	C1	120.80(16)	N6	C5	N4	106.07(17)
N2	N6	C7	111.12(15)	C13	C14	C15	119.2(2)
C5	N6	N2	107.88(16)	C9	C8	C7	121.68(19)
C5	N6	C7	121.69(18)	C10	C8	C9	59.90(13)
C3	N4	C13	123.34(16)	C10	C8	C7	109.73(16)
C3	N4	C5	110.35(16)	N2	C1	C10	102.58(15)
C5	N4	C13	126.05(16)	C12	C1	N2	106.80(18)
O001	C3	N2	126.48(18)	C12	C1	C10	112.18(18)
O001	C3	N4	127.02(19)	C16	C15	C14	120.3(3)
N2	C3	N4	106.45(17)	C19	C20	C21	120.8(2)
C20	C19	C9	122.92(18)	C23	C24	C19	120.7(2)
C20	C19	C24	118.4(2)	C13	C18	C17	119.4(2)
C24	C19	C9	118.69(19)	C17	C16	C15	120.1(2)
C19	C9	C10	118.03(18)	C11	C12	C1	113.8(2)
C19	C9	C8	120.85(17)	C22	C23	C24	120.5(2)
C10	C9	C8	59.82(13)	N6	C7	C8	103.49(18)
C14	C13	N4	119.26(18)	N6	C7	C11	106.23(19)
C18	C13	N4	119.83(19)	C11	C7	C8	111.75(19)
C18	C13	C14	120.9(2)	C22	C21	C20	120.1(2)
C9	C10	C1	122.00(18)	C23	C22	C21	119.6(2)
C8	C10	C9	60.28(13)	C12	C11	C7	113.8(2)
C8	C10	C1	109.62(17)	C16	C17	C18	120.2(2)

Table S6. Torsion Angles for 3b (KGN-232-22_autored).									
A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
N2	N6	C5	O002	175.8(2)	C13	C14	C15	C16	0.5(4)
N2	N6	C5	N4	-7.7(2)	C13	C18	C17	C16	0.3(4)
N2	N6	C7	C8	61.1(2)	C10	C9	C8	C7	95.8(2)
N2	N6	C7	C11	-56.7(2)	C10	C8	C7	N6	-61.6(2)
N2	C1	C12	C11	-57.3(3)	C10	C8	C7	C11	52.3(3)
N6	N2	C3	O001	-176.6(2)	C10	C1	C12	C11	54.3(3)
N6	N2	C3	N4	5.9(2)	C5	N6	C7	C8	-170.17(17)
N6	N2	C1	C10	-64.0(2)	C5	N6	C7	C11	72.0(2)
N6	N2	C1	C12	54.2(2)	C5	N4	C3	O001	171.5(2)
N6	C7	C11	C12	56.7(3)	C5	N4	C3	N2	-11.1(2)
N4	C13	C14	C15	177.5(2)	C5	N4	C13	C14	130.5(2)
N4	C13	C18	C17	-177.9(2)	C5	N4	C13	C18	-51.4(3)
C3	N2	N6	C5	1.2(2)	C14	C13	C18	C17	0.2(3)
C3	N2	N6	C7	136.92(19)	C14	C15	C16	C17	0.0(4)

Table S6. Torsion Angles for 3b (KGN-232-22_autored).									
A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C3	N2	C1	C10	167.83(17)	C8	C9	C10	C1	-95.7(2)
C3	N2	C1	C12	-74.0(2)	C8	C10	C1	N2	61.2(2)
C3	N4	C13	C14	-55.8(3)	C8	C10	C1	C12	-53.1(2)
C3	N4	C13	C18	122.3(2)	C8	C7	C11	C12	-55.5(3)
C3	N4	C5	O002	-171.8(2)	C1	N2	N6	C5	−133.66(18)
C3	N4	C5	N6	11.8(2)	C1	N2	N6	C7	2.1(2)
C19	C9	C10	C8	-111.2(2)	C1	N2	C3	O001	-46.9(3)
C19	C9	C10	C1	153.05(18)	C1	N2	C3	N4	135.70(19)
C19	C9	C8	C10	106.6(2)	C1	C10	C8	C9	116.37(19)
C19	C9	C8	C7	−157.61(19)	C1	C10	C8	C7	0.5(2)
C19	C20	C21	C22	0.4(4)	C1	C12	C11	C7	1.0(3)
C19	C24	C23	C22	0.8(4)	C15	C16	C17	C18	-0.4(4)
C9	C19	C20	C21	-178.9(2)	C20	C19	C9	C10	38.1(3)
C9	C19	C24	C23	178.4(2)	C20	C19	C9	C8	-31.7(3)
C9	C10	C8	C7	-115.9(2)	C20	C19	C24	C23	-0.6(3)
C9	C10	C1	N2	127.75(19)	C20	C21	C22	C23	-0.2(4)
C9	C10	C1	C12	13.5(3)	C24	C19	C9	C10	-140.8(2)
C9	C8	C7	N6	-127.7(2)	C24	C19	C9	C8	149.4(2)
C9	C8	C7	C11	-13.9(3)	C24	C19	C20	C21	0.0(4)
C13	N4	C3	O001	-3.1(3)	C24	C23	C22	C21	-0.4(4)
C13	N4	C3	N2	174.34(18)	C18	C13	C14	C15	-0.6(3)
C13	N4	C5	O002	2.6(4)	C7	N6	C5	O002	45.7(3)
C13	N4	C5	N6	−173.84(18)	C7	N6	C5	N4	−137.85(19)

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3b (KGN-232-22_autored).				
Atom	***x***	***y***	***z***	**U(eq)**
H9	7024.34	6152.46	6371.38	53
H10	6348.28	6059.43	3685.36	50
H14	4261.19	1318.87	2553.97	63
H8	5229.04	6575.78	5287.38	53
H1	7039.33	4168.03	3977.62	54
H15	3721.84	-558.24	2304.08	74
H20	5912.66	8014.42	3974.91	66
H24	7874.88	7883.78	6674.66	61
H18	4512.18	782.2	6423.02	63
H16	3570.41	-1750.15	4107.16	75
H12	7320.17	3582.4	6169.69	69
H23	8255.15	9777.97	6201.31	73

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3b (KGN-232-22_autored).				
Atom	***x***	***y***	***z***	**U(eq)**
H7	4958.01	5141.47	6991.41	60
H21	6282.57	9924.88	3530.83	74
H22	7458.23	10807.57	4641.61	73
H11	6250.76	4110.94	7747.14	73
H17	3956.32	-1083.75	6162.57	75

Experimental

A suitable crystal of $C_{21}H_{17}N_3O_2$ **3b** (KGN-232-22_autored) was selected and performed on a Xcalibur, Eos diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [S6], the structure was solved with the SHELXT [S2] structure solution program using Intrinsic Phasing and refined with the SHELXL [S3] refinement package using Least Squares minimisation.

Crystal structure determination of 3b (KGN-232-22_autored)

Crystal Data for **3b** $C_{21}H_{17}N_3O_2$ (*M* =343.38 g/mol): orthorhombic, space group $Pna2_1$ (no. 33), *a* = 14.7894(5) Å, *b* = 11.5074(5) Å, *c* = 10.1656(4) Å, *V* = 1730.06(12) Å^3, *Z* = 4, *T* = 293(2) K, μ(Mo Kα) = 0.087 mm^{-1}, *Dcalc* = 1.318 g/cm^3, 23192 reflections measured (4.484° ≤ 2Θ ≤ 75.198°), 8100 unique (R_{int} = 0.0293, R_{sigma} = 0.0348) which were used in all calculations. The final R_1 was 0.0542 (I > 2σ(I)) and wR_2 was 0.1352 (all data).

CCDC 2431659 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Crystal data for 3c

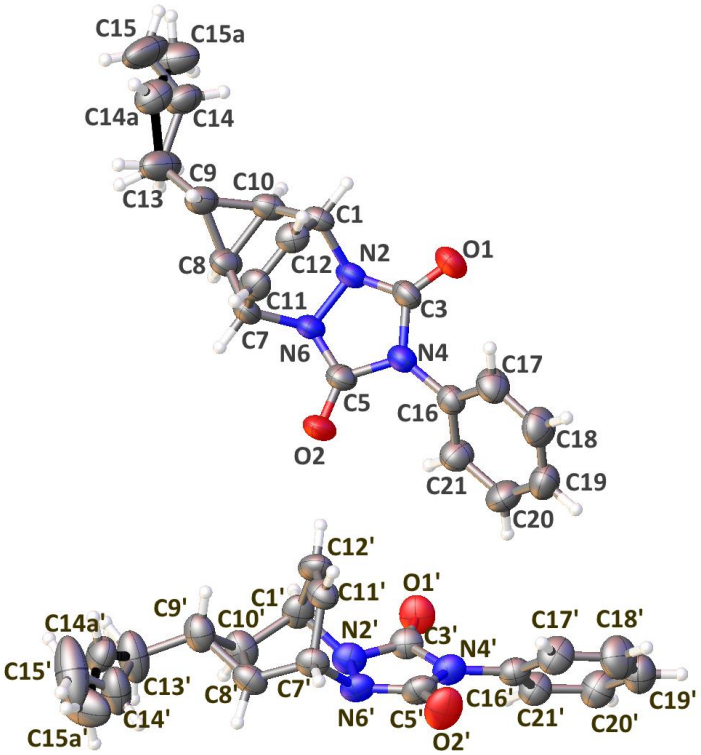


Figure S2. Geometry of molecule **3c**.

Table S8. Crystal data and structure refinement for 3c (KGN-235-12_autored).	
Identification code	KGN-235-12_autored
Empirical formula	$C_{18}H_{17}N_3O_2$
Formula weight	307.34
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	17.8836(8)
b/Å	7.2303(3)
c/Å	24.2750(9)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	3138.8(2)
Z	8
$\rho_{calc}g/cm^3$	1.301
μ/mm^{-1}	0.087
F(000)	1296.0
Crystal size/mm^3	0.30 × 0.08 × 0.06
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.556 to 75.45
Index ranges	$-30 \leq h \leq 29$, $-11 \leq k \leq 12$, $-41 \leq l \leq 40$

Reflections collected	42300
Independent reflections	15275 [R_{int} = 0.0420, R_{sigma} = 0.0543]
Data/restraints/parameters	15275/1/453
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0668, wR_2 = 0.1361
Final R indexes [all data]	R_1 = 0.1485, wR_2 = 0.1745
Largest diff. peak/hole / e $Å^{-3}$	0.18/-0.18
Flack parameter	-0.3(5)

Table S9. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 3c (KGN-235-12_autored). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2'	-7311(2)	-2427(3)	-4718.5(15)	59.3(9)
O2	-4520.8(17)	-6402(4)	-6903.3(10)	68.5(7)
O1'	-7020.5(17)	-6271(4)	-3235.4(11)	72.3(8)
N6'	-6700.0(19)	-2098(4)	-3889.5(13)	47.8(7)
N4'	-7408.0(14)	-4586(4)	-4007.8(10)	46.0(6)
O1	-4796(2)	-2601(3)	-5409.1(16)	64.7(10)
N4	-4902.6(14)	-4737(3)	-6125.5(10)	45.4(5)
N6	-4105.3(14)	-3443(3)	-6709.5(10)	44.8(5)
N2'	-6604.7(14)	-3311(4)	-3423.2(10)	46.9(6)
N2	-4197.7(18)	-2246(3)	-6243.9(14)	44.2(7)
C5'	-7150.4(17)	-2979(4)	-4262.3(13)	45.2(6)
C7	-3300.6(19)	-3501(4)	-6888.4(12)	42.7(7)
C5	-4503.6(18)	-5043(4)	-6611.6(13)	46.7(7)
C3'	-7002.9(18)	-4898(5)	-3523.6(13)	50.3(7)
C20'	-9152(2)	-6101(6)	-4682.7(18)	60.8(9)
C16'	-7976.0(17)	-5768(4)	-4233.6(13)	44.8(6)
C9'	-4972(2)	-353(5)	-3306.1(15)	59.0(8)
C21'	-8612.9(19)	-4981(5)	-4453.7(15)	53.0(7)
C11	-2946(2)	-2947(6)	-5965.8(18)	54.5(8)
C3	-4648.3(18)	-3137(4)	-5869.4(13)	46.5(6)
C16	-5467.9(17)	-5912(4)	-5902.8(12)	43.9(6)
C12	-2861.5(19)	-4059(5)	-6389.7(14)	49.8(7)
C10'	-5623(2)	-1413(5)	-3081.0(15)	50.5(8)
C21	-5382(3)	-7816(5)	-5895(2)	61.7(11)
C7'	-5967(2)	-1262(5)	-4062.8(13)	51.7(7)
C1	-3478.0(19)	-1372(4)	-6072.7(13)	50.2(7)
C8	-3139(2)	-1512(5)	-7058.4(15)	48.5(8)
C19'	-9063(3)	-7994(6)	-4689(2)	68.5(12)
C10	-3251(2)	-241(4)	-6572.8(15)	53.6(8)
C1'	-5798(2)	-3386(5)	-3246.0(13)	44.9(7)
C17	-6111.1(19)	-5132(5)	-5685.0(16)	56.5(8)

Table S9. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3c (KGN-235-12_autored). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C8'	-5729(2)	-137(5)	-3565.1(15)	57.4(8)
C11'	-5364.0(19)	-3970(5)	-3745.7(14)	50.8(7)
C12'	-5459(3)	-2853(6)	-4172.5(18)	56.5(9)
C9	-2491(2)	-432(5)	-6836.0(15)	56.9(8)
C20	-5931(3)	-8913(5)	-5663.6(19)	70.2(11)
C13	-2212(3)	1190(6)	-7177(2)	81.3(19)
C13'	-4676(3)	1270(6)	-2969(2)	82.1(19)
C18	-6657(2)	-6264(6)	-5456(2)	65.0(10)
C17'	-7873(3)	-7665(5)	-4240(3)	63.7(12)
C19	-6567(3)	-8131(6)	-5449(2)	64.1(10)
C18'	-8429(3)	-8760(5)	-4465(2)	77.4(12)
C14A	-1557(7)	669(13)	-7557(4)	67(2)
C15A	-1659(8)	760(20)	-8063(6)	94(4)
C2	-4031(6)	711(13)	-2592(4)	59.7(19)
C4	-4154(8)	840(20)	-2069(6)	93(5)
C15'	-3767(10)	864(19)	-2244(10)	132(8)
C14'	-4416(8)	595(13)	-2388(5)	78(3)
C14	-1957(6)	540(12)	-7748(5)	65(2)
C15	-1254(8)	898(18)	-7911(8)	104(5)

Table S10. Anisotropic Displacement Parameters (Å^2×10^3) for 3c (KGN-235-12_autored). The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2'	73(2)	58.1(16)	46.9(19)	17.5(10)	-17.9(19)	1.6(11)
O2	85.4(18)	68.8(15)	51.4(14)	-27.3(12)	10.0(12)	-14.6(13)
O1'	85.8(19)	76.6(18)	54.5(15)	34.6(13)	-13.7(13)	-16.0(14)
N6'	54.9(18)	49.2(13)	39.2(16)	11.6(12)	-6.4(13)	8.7(13)
N4'	46.5(13)	50.3(13)	41.0(12)	12.2(10)	-2.5(10)	5.2(10)
O1	81(3)	63.0(17)	50(2)	-22.2(11)	27(2)	-13.5(12)
N4	47.7(13)	48.1(13)	40.5(12)	-10.1(10)	2.6(10)	0.8(10)
N6	50.6(14)	51.9(14)	32.0(11)	-9.5(10)	1.9(10)	3.3(11)
N2'	49.2(14)	59.5(15)	32.1(11)	12.7(10)	0.8(10)	3.8(11)
N2	48.5(16)	44.8(12)	39.4(15)	-11.5(11)	9.8(12)	0.9(11)
C5'	45.5(16)	48.2(15)	41.9(15)	9.7(13)	-5.6(12)	10.0(13)
C7	51.2(17)	45.2(14)	31.7(15)	-7.3(11)	4.3(12)	6.3(12)
C5	50.6(15)	52.4(16)	37.3(14)	-11.9(11)	-2.8(12)	0.3(13)
C3'	49.9(16)	64.6(19)	36.4(14)	14.2(13)	2.5(12)	0.6(14)
C20'	55(2)	63(2)	64(2)	10.7(18)	-9.4(17)	0.8(17)
C16'	44.3(15)	48.7(15)	41.5(14)	6.0(12)	2.1(12)	4.7(12)

Table S10. Anisotropic Displacement Parameters ($Å^2×10^3$) for 3c (KGN-235-12_autored). 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}
C9'	69(2)	54.8(19)	53.3(18)	2.8(14)	-16.2(17)	-3.6(16)
C21'	50.6(17)	47.3(16)	61(2)	5.6(14)	-2.7(15)	6.0(13)
C11	54(2)	71(2)	39.2(19)	2.8(18)	-6.2(15)	-7.3(18)
C3	51.4(17)	43.6(15)	44.6(16)	-8.6(13)	8.9(13)	4.1(14)
C16	44.6(15)	45.8(15)	41.4(14)	-4.6(11)	-4.4(12)	0.3(12)
C12	50.1(17)	51.2(17)	48.1(16)	6.9(14)	0.8(14)	5.5(13)
C10'	65(2)	51.0(17)	35.3(15)	-1.2(12)	-5.3(15)	11.6(15)
C21	61(3)	49.7(18)	74(3)	-9.3(19)	-1(2)	6.5(17)
C7'	61.6(19)	55.4(18)	38.1(14)	15.4(12)	-7.4(13)	-6.4(14)
C1	62.2(19)	49.8(16)	38.6(14)	-15.3(12)	10.9(14)	-10.1(14)
C8	62(2)	49.1(16)	34.8(15)	-0.1(12)	7.5(14)	7.1(14)
C19'	75(3)	64(2)	67(3)	3(2)	-9(2)	-10(2)
C10	66(2)	40.5(15)	54.0(18)	-7.5(13)	15.5(16)	1.1(14)
C1'	51.2(18)	51.6(16)	31.9(15)	9.2(12)	-3.6(13)	7.2(13)
C17	56.0(19)	48.6(17)	65(2)	-1.4(15)	7.0(16)	4.9(14)
C8'	74(2)	47.1(16)	51.5(18)	6.1(14)	-15.1(17)	4.5(15)
C11'	48.9(17)	54.2(17)	49.2(17)	-7.1(14)	-3.6(13)	6.9(14)
C12'	57(2)	78(2)	34.9(18)	-1.6(17)	7.8(15)	-7.9(18)
C9	66(2)	50.7(17)	53.4(18)	-3.5(14)	18.4(16)	-3.4(15)
C20	78(3)	43.9(17)	88(3)	1.4(17)	1(2)	-5.0(17)
C13	106(4)	52(2)	86(3)	-2.4(19)	47(3)	-3(2)
C13'	107(4)	54(2)	85(3)	4(2)	-45(3)	-9(2)
C18	51(2)	74(2)	71(3)	-2(2)	12.6(18)	-4.0(18)
C17'	59(3)	55(2)	77(3)	11.4(19)	-6(2)	11.7(16)
C19	64(3)	63(2)	66(3)	-1(2)	2(2)	-17(2)
C18'	91(3)	47.5(19)	93(3)	4(2)	-7(3)	4(2)
C14A	60(5)	64(5)	77(6)	9(4)	9(5)	3(4)
C15A	79(8)	129(11)	75(7)	6(7)	22(7)	14(8)
C2	48(4)	66(5)	65(5)	0(4)	-6(4)	-10(4)
C4	85(9)	137(11)	57(5)	-9(6)	-23(6)	33(8)
C15'	129(14)	61(6)	210(20)	-13(9)	-109(15)	10(8)
C14'	100(8)	63(5)	72(6)	5(4)	-32(6)	-23(5)
C14	65(5)	66(5)	64(5)	8(4)	22(5)	-7(4)
C15	103(10)	74(6)	134(14)	3(7)	72(10)	-13(8)

Table S11. Bond Lengths for 3c (KGN-235-12_autored).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2'	C5'	1.212(5)	C11	C12	1.315(6)
O2	C5	1.212(4)	C11	C1	1.506(5)
O1'	C3'	1.215(4)	C16	C21	1.386(5)

Table S11. Bond Lengths for 3c (KGN-235-12_autored).					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
N6'	N2'	1.442(4)	C16	C17	1.386(5)
N6'	C5'	1.369(5)	C10'	C1'	1.514(5)
N6'	C7'	1.503(5)	C10'	C8'	1.506(5)
N4'	C5'	1.394(4)	C21	C20	1.381(7)
N4'	C3'	1.399(4)	C7'	C8'	1.518(5)
N4'	C16'	1.436(4)	C7'	C12'	1.490(6)
O1	C3	1.212(5)	C1	C10	1.519(5)
N4	C5	1.397(4)	C8	C10	1.508(5)
N4	C3	1.390(4)	C8	C9	1.498(5)
N4	C16	1.427(4)	C19'	C18'	1.373(7)
N6	N2	1.433(4)	C10	C9	1.507(5)
N6	C7	1.504(4)	C1'	C11'	1.501(5)
N6	C5	1.379(4)	C17	C18	1.389(5)
N2'	C3'	1.373(4)	C11'	C12'	1.324(6)
N2'	C1'	1.506(4)	C9	C13	1.520(5)
N2	C3	1.375(5)	C20	C19	1.373(6)
N2	C1	1.493(4)	C13	C14A	1.538(11)
C7	C12	1.498(5)	C13	C14	1.533(11)
C7	C8	1.524(5)	C13'	C2	1.527(11)
C20'	C21'	1.376(5)	C13'	C14'	1.562(12)
C20'	C19'	1.378(6)	C18	C19	1.359(6)
C16'	C21'	1.381(4)	C17'	C18'	1.383(7)
C16'	C17'	1.384(5)	C14A	C15A	1.242(18)
C9'	C10'	1.497(6)	C2	C4	1.292(17)
C9'	C8'	1.500(5)	C15'	C14'	1.23(2)
C9'	C13'	1.526(5)	C14	C15	1.343(15)

Table S12. Bond Angles for 3c (KGN-235-12_autored).							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N2'	N6'	C7'	111.2(3)	C17	C16	N4	119.4(3)
C5'	N6'	N2'	107.8(3)	C11	C12	C7	114.0(3)
C5'	N6'	C7'	121.0(3)	C9'	C10'	C1'	123.1(3)
C5'	N4'	C3'	109.6(3)	C9'	C10'	C8'	59.9(2)
C5'	N4'	C16'	124.1(2)	C8'	C10'	C1'	110.2(3)
C3'	N4'	C16'	126.2(3)	C20	C21	C16	119.8(4)
C5	N4	C16	126.0(2)	N6'	C7'	C8'	103.8(3)
C3	N4	C5	110.0(3)	C12'	C7'	N6'	105.7(3)
C3	N4	C16	123.9(2)	C12'	C7'	C8'	112.6(3)
N2	N6	C7	110.8(2)	N2	C1	C11	105.8(3)
C5	N6	N2	108.1(2)	N2	C1	C10	103.7(3)
C5	N6	C7	121.3(2)	C11	C1	C10	112.1(3)

Table S12. Bond Angles for 3c (KGN-235-12_autored).							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N6'	N2'	C1'	111.1(2)	C10	C8	C7	109.8(3)
C3'	N2'	N6'	107.9(3)	C9	C8	C7	122.8(3)
C3'	N2'	C1'	121.1(3)	C9	C8	C10	60.2(2)
N6	N2	C1	112.1(3)	C18'	C19'	C20'	119.5(4)
C3	N2	N6	107.8(2)	C8	C10	C1	109.4(3)
C3	N2	C1	121.3(3)	C9	C10	C1	122.0(3)
O2'	C5'	N6'	126.2(3)	C9	C10	C8	59.6(2)
O2'	C5'	N4'	127.0(3)	N2'	C1'	C10'	103.9(3)
N6'	C5'	N4'	106.8(3)	C11'	C1'	N2'	106.0(3)
N6	C7	C8	103.5(2)	C11'	C1'	C10'	111.8(3)
C12	C7	N6	106.0(3)	C16	C17	C18	119.7(3)
C12	C7	C8	111.9(3)	C9'	C8'	C10'	59.7(2)
O2	C5	N4	127.5(3)	C9'	C8'	C7'	122.1(3)
O2	C5	N6	126.4(3)	C10'	C8'	C7'	109.1(3)
N6	C5	N4	106.1(2)	C12'	C11'	C1'	113.2(3)
O1'	C3'	N4'	127.0(3)	C11'	C12'	C7'	114.1(4)
O1'	C3'	N2'	126.5(3)	C8	C9	C10	60.3(2)
N2'	C3'	N4'	106.4(3)	C8	C9	C13	117.4(4)
C21'	C20'	C19'	120.5(4)	C10	C9	C13	117.2(3)
C21'	C16'	N4'	119.1(3)	C19	C20	C21	120.5(4)
C21'	C16'	C17'	120.9(4)	C9	C13	C14A	112.8(4)
C17'	C16'	N4'	120.0(3)	C9	C13	C14	110.7(4)
C10'	C9'	C8'	60.3(2)	C9'	C13'	C2	112.3(5)
C10'	C9'	C13'	117.9(4)	C9'	C13'	C14'	110.3(4)
C8'	C9'	C13'	117.2(3)	C19	C18	C17	120.5(4)
C20'	C21'	C16'	119.4(3)	C18'	C17'	C16'	118.4(4)
C12	C11	C1	113.6(3)	C18	C19	C20	120.1(4)
O1	C3	N4	127.4(3)	C19'	C18'	C17'	121.2(4)
O1	C3	N2	125.9(3)	C15A	C14A	C13	117.9(13)
N2	C3	N4	106.6(2)	C4	C2	C13'	116.2(11)
C21	C16	N4	121.2(3)	C15'	C14'	C13'	119.3(18)
C21	C16	C17	119.4(3)	C15	C14	C13	119.0(13)

Table S13. Torsion Angles for 3c (KGN-235-12_autored).									
A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
N6'	N2'	C3'	O1'	175.7(3)	C9'	C13'	C2	C4	-115.4(12)
N6'	N2'	C3'	N4'	-6.9(3)	C9'	C13'	C14'	C15'	122.0(12)
N6'	N2'	C1'	C10'	61.9(3)	C21'	C20'	C19'	C18'	-0.1(7)
N6'	N2'	C1'	C11'	-56.0(3)	C21'	C16'	C17'	C18'	-1.1(7)
N6'	C7'	C8'	C9'	127.5(3)	C11	C1	C10	C8	52.3(4)
N6'	C7'	C8'	C10'	61.8(4)	C11	C1	C10	C9	-13.3(4)

Table S13. Torsion Angles for 3c (KGN-235-12_autored).									
A	B	C	D	Angle/°	A	B	C	D	Angle/°
N6'	C7'	C12'	C11'	-58.2(4)	C3	N4	C5	O2	171.2(3)
N4'	C16'	C21'	C20'	178.5(3)	C3	N4	C5	N6	-11.5(3)
N4'	C16'	C17'	C18'	-179.6(4)	C3	N4	C16	C21	-134.3(4)
N4	C16	C21	C20	178.3(4)	C3	N4	C16	C17	45.0(4)
N4	C16	C17	C18	-178.6(3)	C3	N2	C1	C11	73.0(4)
N6	N2	C3	O1	173.6(4)	C3	N2	C1	C10	-168.9(3)
N6	N2	C3	N4	-7.1(4)	C16	N4	C5	O2	-6.3(5)
N6	N2	C1	C11	-56.2(4)	C16	N4	C5	N6	171.1(3)
N6	N2	C1	C10	61.9(3)	C16	N4	C3	O1	8.4(6)
N6	C7	C12	C11	-58.0(4)	C16	N4	C3	N2	-170.8(3)
N6	C7	C8	C10	60.6(3)	C16	C21	C20	C19	1.2(8)
N6	C7	C8	C9	127.3(3)	C16	C17	C18	C19	-0.6(6)
N2'	N6'	C5'	O2'	-174.8(3)	C12	C7	C8	C10	-53.1(4)
N2'	N6'	C5'	N4'	7.3(3)	C12	C7	C8	C9	13.5(5)
N2'	N6'	C7'	C8'	-62.5(3)	C12	C11	C1	N2	56.5(4)
N2'	N6'	C7'	C12'	56.2(4)	C12	C11	C1	C10	-55.8(4)
N2'	C1'	C11'	C12'	57.4(4)	C10'	C9'	C8'	C7'	-94.7(3)
N2	N6	C7	C12	55.3(3)	C10'	C9'	C13'	C2	93.9(6)
N2	N6	C7	C8	-62.7(3)	C10'	C9'	C13'	C14'	59.5(8)
N2	N6	C5	O2	-175.8(3)	C10'	C1'	C11'	C12'	-55.2(4)
N2	N6	C5	N4	6.7(3)	C21	C16	C17	C18	0.8(6)
N2	C1	C10	C8	-61.3(3)	C21	C20	C19	C18	-1.0(7)
N2	C1	C10	C9	-126.9(3)	C7'	N6'	N2'	C3'	-135.0(3)
C5'	N6'	N2'	C3'	-0.2(4)	C7'	N6'	N2'	C1'	0.0(4)
C5'	N6'	N2'	C1'	134.8(3)	C7'	N6'	C5'	O2'	-45.4(5)
C5'	N6'	C7'	C8'	169.5(3)	C7'	N6'	C5'	N4'	136.8(3)
C5'	N6'	C7'	C12'	-71.8(4)	C1	N2	C3	O1	42.5(5)
C5'	N4'	C3'	O1'	-170.9(3)	C1	N2	C3	N4	-138.2(3)
C5'	N4'	C3'	N2'	11.8(3)	C1	C11	C12	C7	1.0(5)
C5'	N4'	C16'	C21'	-44.7(4)	C1	C10	C9	C8	95.0(3)
C5'	N4'	C16'	C17'	133.8(4)	C1	C10	C9	C13	-157.4(4)
C7	N6	N2	C3	-135.0(3)	C8	C7	C12	C11	54.2(4)
C7	N6	N2	C1	0.9(4)	C8	C10	C9	C13	107.6(4)
C7	N6	C5	O2	-46.2(5)	C8	C9	C13	C14A	-94.6(7)
C7	N6	C5	N4	136.3(3)	C8	C9	C13	C14	-59.7(7)
C7	C8	C10	C1	0.7(4)	C19'	C20'	C21'	C16'	0.6(6)
C7	C8	C10	C9	117.2(3)	C10	C8	C9	C13	-107.2(4)
C7	C8	C9	C10	-95.5(4)	C10	C9	C13	C14A	-163.4(6)
C7	C8	C9	C13	157.3(3)	C10	C9	C13	C14	-128.5(6)
C5	N4	C3	O1	-169.1(4)	C1'	N2'	C3'	O1'	46.2(5)
C5	N4	C3	N2	11.6(4)	C1'	N2'	C3'	N4'	-136.5(3)
C5	N4	C16	C21	42.8(5)	C1'	C10'	C8'	C9'	-117.4(3)
C5	N4	C16	C17	-137.8(3)	C1'	C10'	C8'	C7'	-0.7(4)

Table S13. Torsion Angles for 3c (KGN-235-12_autored).									
A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C5	N6	N2	C3	0.2(4)	C1'	C11'	C12'	C7'	0.5(5)
C5	N6	N2	C1	136.2(3)	C17	C16	C21	C20	-1.1(7)
C5	N6	C7	C12	-73.1(3)	C17	C18	C19	C20	0.7(7)
C5	N6	C7	C8	168.9(3)	C8'	C9'	C10'	C1'	95.6(4)
C3'	N4'	C5'	O2'	170.3(4)	C8'	C9'	C13'	C2	162.9(5)
C3'	N4'	C5'	N6'	-11.9(3)	C8'	C9'	C13'	C14'	128.6(7)
C3'	N4'	C16'	C21'	138.9(3)	C8'	C10'	C1'	N2'	-60.6(3)
C3'	N4'	C16'	C17'	-42.6(5)	C8'	C10'	C1'	C11'	53.2(4)
C3'	N2'	C1'	C10'	-169.9(3)	C8'	C7'	C12'	C11'	54.5(5)
C3'	N2'	C1'	C11'	72.1(3)	C12'	C7'	C8'	C9'	13.6(5)
C20'	C19'	C18'	C17'	-1.1(8)	C12'	C7'	C8'	C10'	-52.1(4)
C16'	N4'	C5'	O2'	-6.6(5)	C9	C8	C10	C1	-116.5(4)
C16'	N4'	C5'	N6'	171.2(3)	C9	C13	C14A	C15A	115.3(12)
C16'	N4'	C3'	O1'	5.9(5)	C9	C13	C14	C15	-123.0(10)
C16'	N4'	C3'	N2'	-171.4(3)	C13'	C9'	C10'	C1'	-157.3(3)
C16'	C17'	C18'	C19'	1.7(8)	C13'	C9'	C10'	C8'	107.1(4)
C9'	C10'	C1'	N2'	-127.1(3)	C13'	C9'	C8'	C10'	-108.2(4)
C9'	C10'	C1'	C11'	-13.3(5)	C13'	C9'	C8'	C7'	157.1(4)
C9'	C10'	C8'	C7'	116.7(4)	C17'	C16'	C21'	C20'	0.0(6)

Table S14. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3c (KGN-235-12_autored).				
Atom	***x***	***y***	***z***	**U(eq)**
H7	-3224.92	-4364.26	-7194.67	51
H20'	-9579.7	-5576.98	-4834.56	73
H9'	-4601.77	-1062.71	-3515.5	71
H21'	-8677.1	-3704.68	-4447.29	64
H11	-2701.06	-3116.41	-5631.75	65
H12	-2556.22	-5100.26	-6380.83	60
H10'	-5825.13	-993.02	-2727.21	61
H21	-4955.96	-8354.21	-6045.96	74
H7'	-6025.49	-480.45	-4389.74	62
H1	-3541.66	-592.26	-5745.77	60
H8	-3345.9	-1103.44	-7411.78	58
H19'	-9428.32	-8746.31	-4843.25	82
H10	-3523.24	913.66	-6639.17	64
H1'	-5725.29	-4245.6	-2938.49	54
H17	-6177.34	-3856.89	-5692.01	68
H8'	-5994.29	1026.83	-3497.85	69
H11'	-5058.92	-5011.48	-3754.7	61
H12'	-5228.31	-3045.42	-4511.12	68
H9	-2114.38	-1127.64	-6628.79	68

Table S14. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 3c (KGN-235-12_autored).				
Atom	***x***	***y***	***z***	**U(eq)**
H20	-5868.48	-10189.12	-5652.65	84
H13E	-2053.1	2171.98	-6930.97	98
H13F	-2620.27	1661	-7399.15	98
H13G	-1797.02	1779.58	-6988.47	98
H13H	-2608.61	2094.57	-7216.78	98
H13A	-5078.95	1772.79	-2747.21	99
H13B	-4507.14	2235.11	-3217.19	99
H13C	-5065.58	2193.47	-2927.58	99
H13D	-4258.69	1837.8	-3160.24	99
H18	-7086.07	-5740.58	-5306.97	78
H17'	-7439.42	-8190.55	-4097.82	76
H19	-6937.51	-8879.75	-5299.13	77
H18'	-8373.5	-10039.06	-4463.32	93
H14A	-1098.58	298.03	-7413.23	80
H15C	-2120.8	1131.78	-8199.74	113
H15D	-1274.64	452.62	-8303.71	113
H2	-3575.49	301.03	-2730.81	72
H4A	-4615.08	1252.52	-1941.86	112
H4B	-3781.39	516.09	-1819.45	112
H15A	-3436.02	1463.98	-2479.58	158
H15B	-3606.01	467.46	-1899.46	158
H14'	-4749.52	-4.79	-2154.72	94
H14	-2284.3	-93.19	-7978.36	78
H15E	-930.04	1532.07	-7677.99	124
H15F	-1091.46	512.7	-8255.91	124

Table S15. Atomic Occupancy for 3c (KGN-235-12_autored).					
Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C13	0.997(16)	H13E	0.5	H13F	0.5
H13G	0.5	H13H	0.5	C13'	0.993(15)
H13A	0.5	H13B	0.5	H13C	0.5
H13D	0.5	C14A	0.5	H14A	0.5
C15A	0.5	H15C	0.5	H15D	0.5
C2	0.5	H2	0.5	C4	0.5
H4A	0.5	H4B	0.5	C15'	0.5
H15A	0.5	H15B	0.5	C14'	0.5
H14'	0.5	C14	0.5	H14	0.5
C15	0.5	H15E	0.5	H15F	0.5

Experimental

A suitable crystal of $C_{18}H_{17}N_3O_2$ **3c** (KGN-235-12_autored) was selected and performed on a Xcalibur, Eos diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [S6], the structure was solved with the SHELXT [S2] structure solution program using Intrinsic Phasing and refined with the SHELXL [S3] refinement package using Least Squares minimisation.

Crystal structure determination of 3c (KGN-235-12_autored)

Crystal Data for $C_{18}H_{17}N_3O_2$ (M =307.34 g/mol): orthorhombic, space group $Pna2_1$ (no. 33), a = 17.8836(8) Å, b = 7.2303(3) Å, c = 24.2750(9) Å, V = 3138.8(2) Å^3, Z = 8, T = 293(2) K, μ(Mo Kα) = 0.087 mm^{-1}, *Dcalc* = 1.301 g/cm^3, 42300 reflections measured (4.556° ≤ 2Θ ≤ 75.45°), 15275 unique (R_{int} = 0.0420, R_{sigma} = 0.0543) which were used in all calculations. The final R_1 was 0.0668 (I > 2σ(I)) and wR_2 was 0.1745 (all data).

Crystal data for 3f

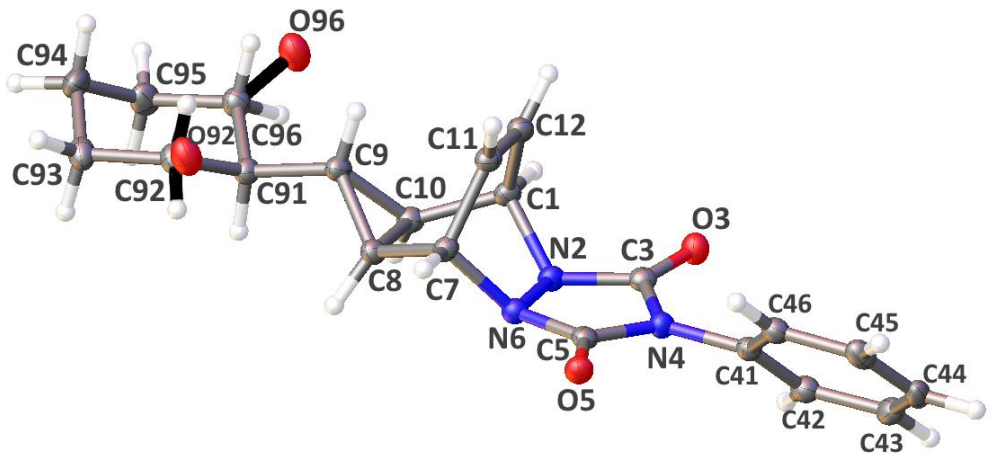


Figure S3. Geometry of molecule **3f**.

Table S16. Crystal data and structure refinement for 3f (KGN-237-29).		
Identification code	kgn-237-29	
Empirical formula	$C_{21}H_{21}N_3O_3$	
Formula weight	363.41	
Temperature	99.99(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 20.98934(19) Å	α= 90°
	b = 6.21764(5) Å	β= 90°
	c = 13.50582(13) Å	γ = 90°
Volume	1762.57(3) $Å^3$	
Z	4	
Density (calculated)	1.369 g/cm^3	
Absorption coefficient	0.756 mm^{-1}	
F(000)	768	
Crystal size	0.7 x 0.5 x 0.44 mm^3	
Theta range for data collection	4.213 to 80.620°	
Index ranges	-26<=h<=26, -7<=k<=7, -17<=l<=16	
Reflections collected	23596	
Independent reflections	3592 [R(int) = 0.0335]	
Observed reflections	3580	
Completeness to theta = 67.684°	100.0%	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.313	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3592/2/249	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R_1 = 0.0305, wR_2 = 0.0785	

R indices (all data)	R_1 = 0.0306, wR_2 = 0.0786
Absolute structure parameter	-0.34(8)
Extinction coefficient	0.0031(3)
Largest diff. peak and hole	0.192 and -0.173 e.Å^{-3}

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 3f (KGN-237-29). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O(3)	4938(1)	6275(2)	6847(1)	21(1)
O(5)	4936(1)	-130(2)	5163(1)	22(1)
O(92)	2168(4)	8922(16)	4339(9)	31(1)
O(96)	2152(1)	2847(3)	2864(2)	31(1)
N(2)	4146(1)	4377(3)	6025(1)	18(1)
N(4)	5103(1)	2851(3)	6185(1)	18(1)
N(6)	4137(1)	2302(3)	5554(1)	18(1)
C(1)	3838(1)	6069(3)	5382(1)	18(1)
C(3)	4756(1)	4715(3)	6390(1)	17(1)
C(5)	4751(1)	1489(3)	5573(2)	18(1)
C(7)	3795(1)	2379(3)	4573(1)	19(1)
C(8)	3122(1)	3104(3)	4847(2)	19(1)
C(9)	2817(1)	4990(3)	4339(2)	19(1)
C(10)	3146(1)	5325(3)	5320(2)	18(1)
C(11)	4165(1)	5962(3)	4388(2)	18(1)
C(12)	4140(1)	4031(3)	3959(2)	19(1)
C(41)	5746(1)	2456(3)	6487(1)	18(1)
C(42)	5904(1)	431(3)	6855(2)	21(1)
C(43)	6532(1)	36(3)	7135(2)	24(1)
C(44)	6987(1)	1651(4)	7060(2)	25(1)
C(45)	6821(1)	3654(3)	6697(2)	24(1)
C(46)	6197(1)	4075(3)	6397(2)	21(1)
C(91)	2096(1)	5097(3)	4315(2)	19(1)
C(92)	1857(1)	7429(3)	4275(2)	24(1)
C(93)	1132(1)	7592(3)	4160(2)	25(1)
C(94)	898(1)	6282(4)	3278(2)	31(1)
C(95)	1106(1)	3931(4)	3363(2)	28(1)
C(96)	1824(1)	3809(3)	3451(2)	22(1)

Table S18. Bond lengths [Å] for 3f (KGN-237-29).

O(3)-C(3)	1.211(2)	C(41)-C(42)	1.394(3)
O(5)-C(5)	1.212(2)	C(41)-C(46)	1.387(3)
O(92)-C(92)	1.138(10)	C(42)-H(42)	0.9500
O(96)-C(96)	1.208(3)	C(42)-C(43)	1.392(3)
N(2)-N(6)	1.439(2)	C(43)-H(43)	0.9500
N(2)-C(1)	1.510(2)	C(43)-C(44)	1.389(3)
N(2)-C(3)	1.389(2)	C(44)-H(44)	0.9500
N(4)-C(3)	1.396(2)	C(44)-C(45)	1.383(3)
N(4)-C(5)	1.395(2)	C(45)-H(45)	0.9500

N(4)-C(41)	1.433(2)	C(45)-C(46)	1.395(3)
N(6)-C(5)	1.385(2)	C(46)-H(46)	0.9500
N(6)-C(7)	1.507(2)	C(91)-H(91)	1.0000
C(1)-H(1)	1.0000	C(91)-C(92)	1.536(3)
C(1)-C(10)	1.527(2)	C(91)-C(96)	1.526(3)
C(1)-C(11)	1.510(3)	C(92)-H(92A)	0.9900
C(7)-H(7)	1.0000	C(92)-H(92B)	0.9900
C(7)-C(8)	1.528(3)	C(92)-C(93)	1.531(3)
C(7)-C(12)	1.505(3)	C(93)-H(93A)	0.9900
C(8)-H(8)	1.0000	C(93)-H(93B)	0.9900
C(8)-C(9)	1.502(3)	C(93)-C(94)	1.524(3)
C(8)-C(10)	1.522(3)	C(94)-H(94A)	0.9900
C(9)-H(9)	1.0000	C(94)-H(94B)	0.9900
C(9)-C(10)	1.508(3)	C(94)-C(95)	1.530(3)
C(9)-C(91)	1.515(2)	C(95)-H(95A)	0.9900
C(10)-H(10)	1.0000	C(95)-H(95B)	0.9900
C(11)-H(11)	0.9500	C(95)-C(96)	1.515(3)
C(11)-C(12)	1.334(3)	C(96)-H(96A)	0.9900
C(12)-H(12)	0.9500	C(96)-H(96B)	0.9900

Table S19. Bond angles [°] for 3f (KGN-237-29).			
N(6)-N(2)-C(1)	111.37(14)	C(43)-C(42)-C(41)	118.78(18)
C(3)-N(2)-N(6)	107.76(14)	C(43)-C(42)-H(42)	120.6
C(3)-N(2)-C(1)	119.60(15)	C(42)-C(43)-H(43)	119.9
C(3)-N(4)-C(41)	125.21(16)	C(44)-C(43)-C(42)	120.22(19)
C(5)-N(4)-C(3)	110.31(15)	C(44)-C(43)-H(43)	119.9
C(5)-N(4)-C(41)	124.29(16)	C(43)-C(44)-H(44)	119.9
N(2)-N(6)-C(7)	111.51(14)	C(45)-C(44)-C(43)	120.22(17)
C(5)-N(6)-N(2)	107.87(14)	C(45)-C(44)-H(44)	119.9
C(5)-N(6)-C(7)	118.09(16)	C(44)-C(45)-H(45)	119.7
N(2)-C(1)-H(1)	111.6	C(44)-C(45)-C(46)	120.55(19)
N(2)-C(1)-C(10)	103.16(15)	C(46)-C(45)-H(45)	119.7
N(2)-C(1)-C(11)	106.61(15)	C(41)-C(46)-C(45)	118.59(19)
C(10)-C(1)-H(1)	111.6	C(41)-C(46)-H(46)	120.7
C(11)-C(1)-H(1)	111.6	C(45)-C(46)-H(46)	120.7
C(11)-C(1)-C(10)	111.80(16)	C(9)-C(91)-H(91)	107.7
O(3)-C(3)-N(2)	126.37(17)	C(9)-C(91)-C(92)	111.70(16)
O(3)-C(3)-N(4)	127.02(17)	C(9)-C(91)-C(96)	111.54(16)
N(2)-C(3)-N(4)	106.49(15)	C(92)-C(91)-H(91)	107.7
O(5)-C(5)-N(4)	127.24(17)	C(96)-C(91)-H(91)	107.7
O(5)-C(5)-N(6)	126.36(18)	C(96)-C(91)-C(92)	110.24(17)
N(6)-C(5)-N(4)	106.35(16)	O(92)-C(92)-C(91)	125.4(5)
N(6)-C(7)-H(7)	111.5	O(92)-C(92)-C(93)	121.6(5)
N(6)-C(7)-C(8)	103.67(15)	C(91)-C(92)-H(92A)	109.0
C(8)-C(7)-H(7)	111.5	C(91)-C(92)-H(92B)	109.0
C(12)-C(7)-N(6)	106.08(14)	H(92A)-C(92)-H(92B)	107.8
C(12)-C(7)-H(7)	111.5	C(93)-C(92)-C(91)	113.05(17)
C(12)-C(7)-C(8)	112.10(16)	C(93)-C(92)-H(92A)	109.0
C(7)-C(8)-H(8)	117.4	C(93)-C(92)-H(92B)	109.0

C(9)-C(8)-C(7)	120.89(17)	C(92)-C(93)-H(93A)	109.4
C(9)-C(8)-H(8)	117.4	C(92)-C(93)-H(93B)	109.4
C(9)-C(8)-C(10)	59.84(12)	H(93A)-C(93)-H(93B)	108.0
C(10)-C(8)-C(7)	109.83(15)	C(94)-C(93)-C(92)	111.31(18)
C(10)-C(8)-H(8)	117.4	C(94)-C(93)-H(93A)	109.4
C(8)-C(9)-H(9)	116.2	C(94)-C(93)-H(93B)	109.4
C(8)-C(9)-C(10)	60.75(13)	C(93)-C(94)-H(94A)	109.4
C(8)-C(9)-C(91)	118.01(16)	C(93)-C(94)-H(94B)	109.4
C(10)-C(9)-H(9)	116.2	C(93)-C(94)-C(95)	111.10(18)
C(10)-C(9)-C(91)	117.97(16)	H(94A)-C(94)-H(94B)	108.0
C(91)-C(9)-H(9)	116.2	C(95)-C(94)-H(94A)	109.4
C(1)-C(10)-H(10)	117.4	C(95)-C(94)-H(94B)	109.4
C(8)-C(10)-C(1)	109.18(15)	C(94)-C(95)-H(95A)	109.7
C(8)-C(10)-H(10)	117.4	C(94)-C(95)-H(95B)	109.7
C(9)-C(10)-C(1)	121.63(17)	H(95A)-C(95)-H(95B)	108.2
C(9)-C(10)-C(8)	59.41(13)	C(96)-C(95)-C(94)	109.70(18)
C(9)-C(10)-H(10)	117.4	C(96)-C(95)-H(95A)	109.7
C(1)-C(11)-H(11)	123.0	C(96)-C(95)-H(95B)	109.7
C(12)-C(11)-C(1)	114.03(17)	O(96)-C(96)-C(91)	123.23(18)
C(12)-C(11)-H(11)	123.0	O(96)-C(96)-C(95)	122.7(2)
C(7)-C(12)-H(12)	123.4	C(91)-C(96)-H(96A)	108.8
C(11)-C(12)-C(7)	113.25(18)	C(91)-C(96)-H(96B)	108.8
C(11)-C(12)-H(12)	123.4	C(95)-C(96)-C(91)	113.97(17)
C(42)-C(41)-N(4)	118.78(17)	C(95)-C(96)-H(96A)	108.8
C(46)-C(41)-N(4)	119.58(17)	C(95)-C(96)-H(96B)	108.8
C(46)-C(41)-C(42)	121.63(18)	H(96A)-C(96)-H(96B)	107.7
C(41)-C(42)-H(42)	120.6		

Table S20. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 3f (KGN-237-29). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(3)	20(1)	23(1)	18(1)	-4(1)	-3(1)	0(1)
O(5)	20(1)	22(1)	24(1)	-4(1)	-2(1)	1(1)
O(92)	23(1)	34(1)	35(1)	-11(1)	0(1)	1(1)
O(96)	23(1)	34(1)	35(1)	-11(1)	0(1)	1(1)
N(2)	17(1)	19(1)	16(1)	-1(1)	-1(1)	0(1)
N(4)	16(1)	21(1)	17(1)	-2(1)	-1(1)	0(1)
N(6)	17(1)	21(1)	16(1)	-2(1)	-2(1)	-1(1)
C(1)	16(1)	20(1)	16(1)	0(1)	-2(1)	0(1)
C(3)	17(1)	22(1)	13(1)	1(1)	2(1)	-1(1)
C(5)	18(1)	19(1)	16(1)	2(1)	1(1)	-2(1)
C(7)	18(1)	23(1)	15(1)	-2(1)	-3(1)	-1(1)
C(8)	17(1)	22(1)	17(1)	0(1)	0(1)	-2(1)
C(9)	15(1)	25(1)	17(1)	0(1)	-1(1)	-1(1)
C(10)	15(1)	24(1)	16(1)	0(1)	0(1)	0(1)

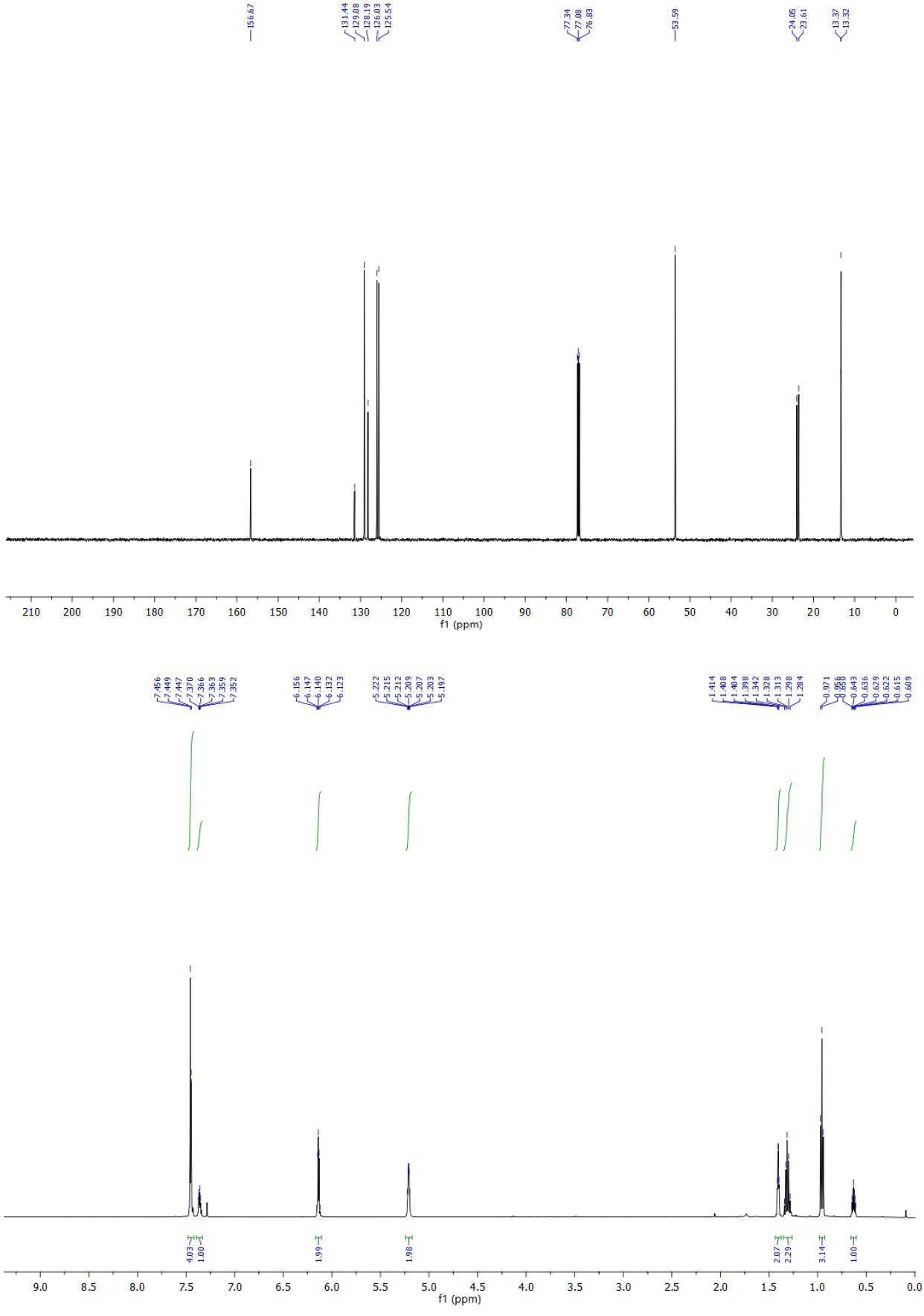
C(11)	16(1)	22(1)	18(1)	2(1)	-1(1)	-2(1)
C(12)	16(1)	26(1)	15(1)	-1(1)	-1(1)	0(1)
C(41)	16(1)	23(1)	15(1)	-2(1)	0(1)	1(1)
C(42)	21(1)	24(1)	18(1)	0(1)	1(1)	0(1)
C(43)	27(1)	27(1)	19(1)	0(1)	-1(1)	7(1)
C(44)	17(1)	39(1)	18(1)	-7(1)	-4(1)	7(1)
C(45)	19(1)	32(1)	20(1)	-8(1)	1(1)	-4(1)
C(46)	20(1)	25(1)	17(1)	-2(1)	2(1)	-1(1)
C(91)	15(1)	22(1)	18(1)	1(1)	-1(1)	-1(1)
C(92)	21(1)	24(1)	26(1)	0(1)	3(1)	-1(1)
C(93)	20(1)	26(1)	30(1)	4(1)	3(1)	4(1)
C(94)	21(1)	49(1)	24(1)	5(1)	-4(1)	9(1)
C(95)	18(1)	41(1)	25(1)	-8(1)	-4(1)	-1(1)
C(96)	19(1)	26(1)	23(1)	-2(1)	-1(1)	0(1)

Table S21. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 3f (KGN-237-29).

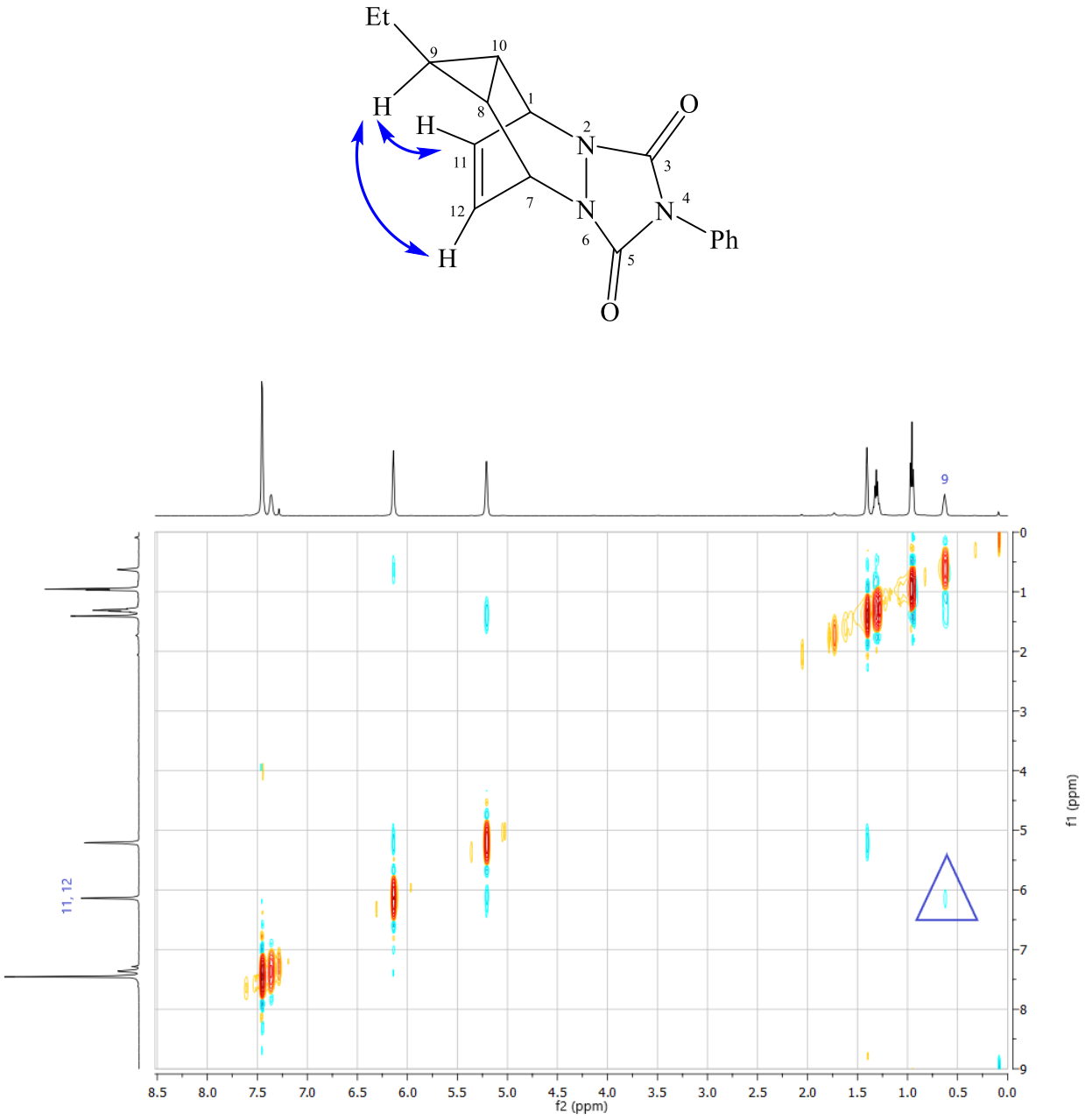
Atom	***x***	***y***	***z***	**U(eq)**
H(1)	3873	7533	5683	21
H(7)	3793	940	4242	22
H(8)	2833	2013	5154	22
H(9)	3044	5559	3742	23
H(10)	2870	5578	5912	22
H(11)	4371	7163	4094	22
H(12)	4321	3729	3330	23
H(42)	5590	-660	6914	25
H(43)	6650	-1342	7377	29
H(44)	7414	1378	7258	30
H(45)	7134	4753	6652	28
H(46)	6084	5441	6136	25
H(91)	1934	4438	4941	22
H(92A)	1986	8179	4889	28
H(92B)	2062	8173	3711	28
H(93A)	925	7062	4772	30
H(93B)	1011	9118	4069	30
H(94A)	1071	6905	2660	38
H(94B)	428	6357	3245	38
H(95A)	906	3268	3954	33
H(95B)	964	3124	2771	33
H(96A)	2016	4344	2828	27
H(96B)	1950	2284	3529	27

Table S22. Torsion angles [°] for 3f (KGN-237-29).			
O(92)-C(92)-C(93)-C(94)	128.2(7)	C(7)-C(8)-C(10)-C(9)	114.93(18)
N(2)-N(6)-C(5)-O(5)	-172.65(19)	C(8)-C(7)-C(12)-C(11)	55.5(2)
N(2)-N(6)-C(5)-N(4)	9.7(2)	C(8)-C(9)-C(10)-C(1)	94.83(19)
N(2)-N(6)-C(7)-C(8)	-60.43(18)	C(8)-C(9)-C(91)-C(92)	151.25(18)
N(2)-N(6)-C(7)-C(12)	57.82(19)	C(8)-C(9)-C(91)-C(96)	-84.9(2)
N(2)-C(1)-C(10)-C(8)	-60.60(19)	C(9)-C(8)-C(10)-C(1)	-116.06(18)
N(2)-C(1)-C(10)-C(9)	-125.86(18)	C(9)-C(91)-C(92)-O(92)	-6.3(8)
N(2)-C(1)-C(11)-C(12)	57.0(2)	C(9)-C(91)-C(92)-C(93)	175.10(17)
N(4)-C(41)-C(42)-C(43)	179.01(18)	C(9)-C(91)-C(96)-O(96)	-0.4(3)
N(4)-C(41)-C(46)-C(45)	179.93(18)	C(9)-C(91)-C(96)-C(95)	-177.63(17)
N(6)-N(2)-C(1)-C(10)	64.43(18)	C(10)-C(1)-C(11)-C(12)	-55.0(2)
N(6)-N(2)-C(1)-C(11)	-53.46(18)	C(10)-C(8)-C(9)-C(91)	-108.11(19)
N(6)-N(2)-C(3)-O(3)	-178.65(18)	C(10)-C(9)-C(91)-C(92)	81.4(2)
N(6)-N(2)-C(3)-N(4)	-2.5(2)	C(10)-C(9)-C(91)-C(96)	-154.76(18)
N(6)-C(7)-C(8)-C(9)	127.54(18)	C(11)-C(1)-C(10)-C(8)	53.6(2)
N(6)-C(7)-C(8)-C(10)	61.53(19)	C(11)-C(1)-C(10)-C(9)	-11.7(3)
N(6)-C(7)-C(12)-C(11)	-57.0(2)	C(12)-C(7)-C(8)-C(9)	13.5(2)
C(1)-N(2)-N(6)-C(5)	128.50(16)	C(12)-C(7)-C(8)-C(10)	-52.5(2)
C(1)-N(2)-N(6)-C(7)	-2.7(2)	C(41)-N(4)-C(3)-O(3)	0.1(3)
C(1)-N(2)-C(3)-O(3)	52.9(3)	C(41)-N(4)-C(3)-N(2)	-176.02(17)
C(1)-N(2)-C(3)-N(4)	-130.99(17)	C(41)-N(4)-C(5)-O(5)	-4.5(3)
C(1)-C(11)-C(12)-C(7)	-0.7(2)	C(41)-N(4)-C(5)-N(6)	173.15(17)
C(3)-N(2)-N(6)-C(5)	-4.5(2)	C(41)-C(42)-C(43)-C(44)	1.0(3)
C(3)-N(2)-N(6)-C(7)	-135.72(16)	C(42)-C(41)-C(46)-C(45)	-0.9(3)
C(3)-N(2)-C(1)-C(10)	-168.78(16)	C(42)-C(43)-C(44)-C(45)	-0.7(3)
C(3)-N(2)-C(1)-C(11)	73.3(2)	C(43)-C(44)-C(45)-C(46)	-0.4(3)
C(3)-N(4)-C(5)-O(5)	170.75(19)	C(44)-C(45)-C(46)-C(41)	1.2(3)
C(3)-N(4)-C(5)-N(6)	-11.6(2)	C(46)-C(41)-C(42)-C(43)	-0.2(3)
C(3)-N(4)-C(41)-C(42)	137.2(2)	C(91)-C(9)-C(10)-C(1)	-156.99(17)
C(3)-N(4)-C(41)-C(46)	-43.6(3)	C(91)-C(9)-C(10)-C(8)	108.18(19)
C(5)-N(4)-C(3)-O(3)	-175.12(19)	C(91)-C(92)-C(93)-C(94)	-53.2(3)
C(5)-N(4)-C(3)-N(2)	8.8(2)	C(92)-C(91)-C(96)-O(96)	124.2(2)
C(5)-N(4)-C(41)-C(42)	-48.2(3)	C(92)-C(91)-C(96)-C(95)	-52.9(2)
C(5)-N(4)-C(41)-C(46)	131.0(2)	C(92)-C(93)-C(94)-C(95)	56.1(2)
C(5)-N(6)-C(7)-C(8)	173.83(16)	C(93)-C(94)-C(95)-C(96)	-57.1(2)
C(5)-N(6)-C(7)-C(12)	-67.9(2)	C(94)-C(95)-C(96)-O(96)	-120.7(2)
C(7)-N(6)-C(5)-O(5)	-45.2(3)	C(94)-C(95)-C(96)-C(91)	56.5(2)
C(7)-N(6)-C(5)-N(4)	137.18(16)	C(96)-C(91)-C(92)-O(92)	-130.9(7)
C(7)-C(8)-C(9)-C(10)	-96.30(19)	C(96)-C(91)-C(92)-C(93)	50.5(2)
C(7)-C(8)-C(9)-C(91)	155.59(17)		
C(7)-C(8)-C(10)-C(1)	-1.1(2)		

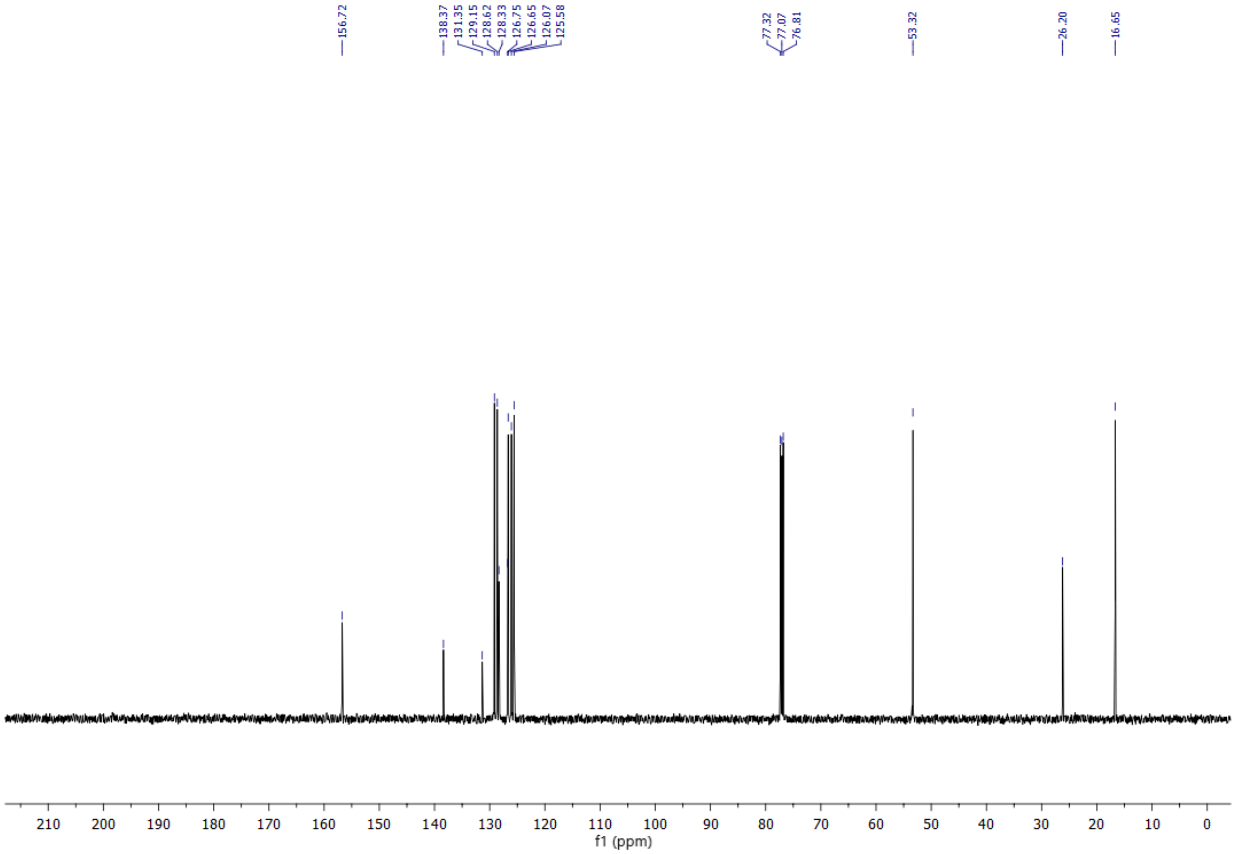
(1*R,7*S**,8*R**,9-*exo*,10*S**)-9-Ethyl-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3a)**:

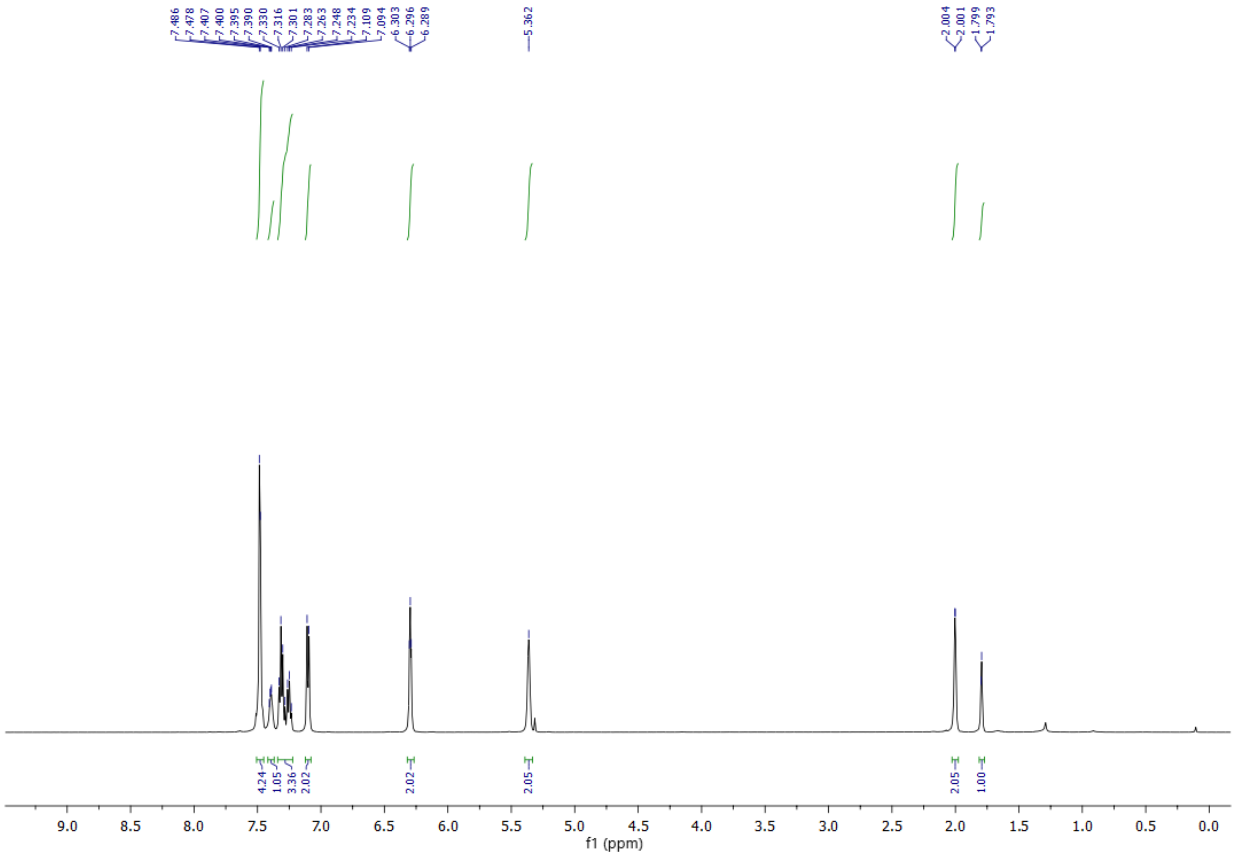


NOESY (9↔11, 9↔12) correlations for (1*R,7*S**,8*R**,9-*exo*,10*S**)-9-ethyl-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3a)**:

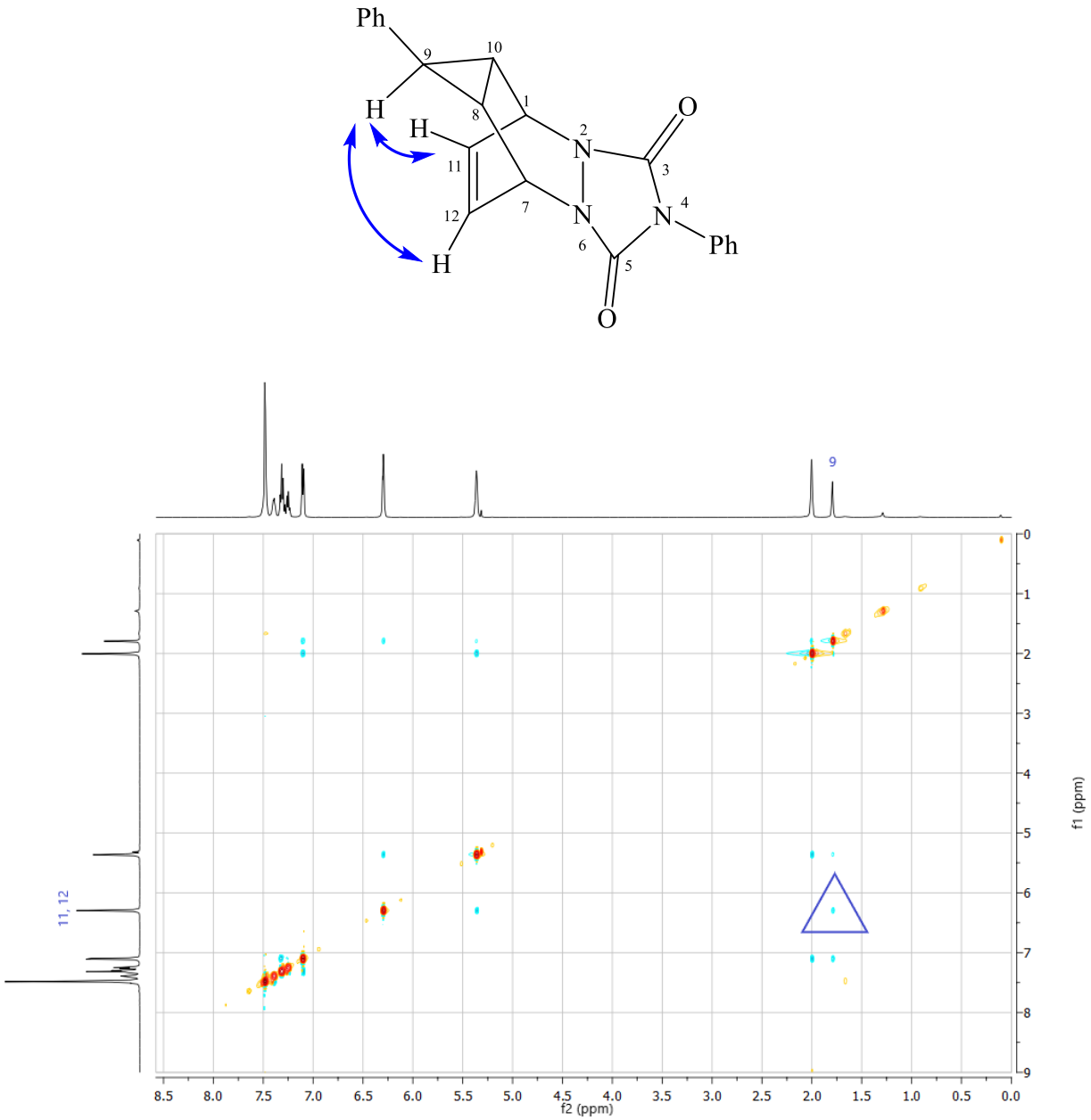


(1*R,7*S**,8*R**,9-*exo*,10*S**)-4,9-Diphenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3b)**:

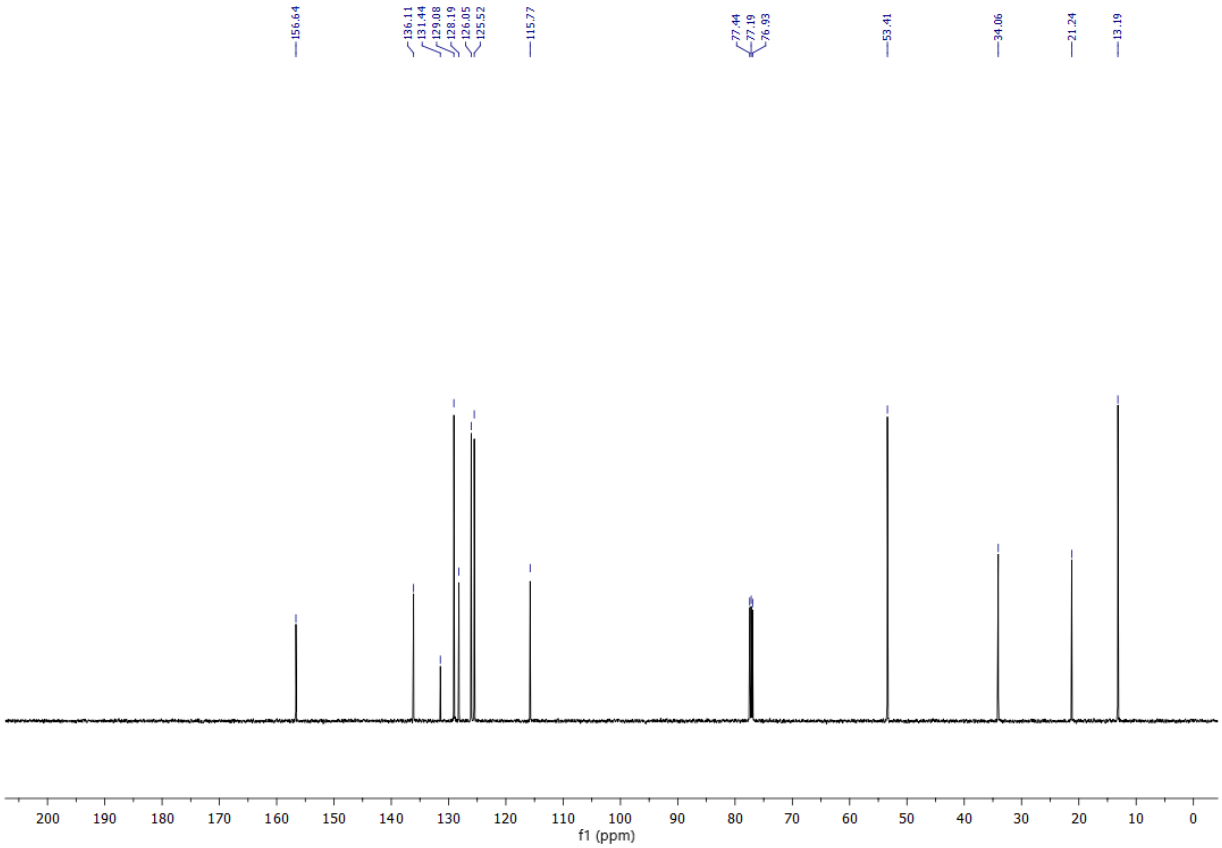


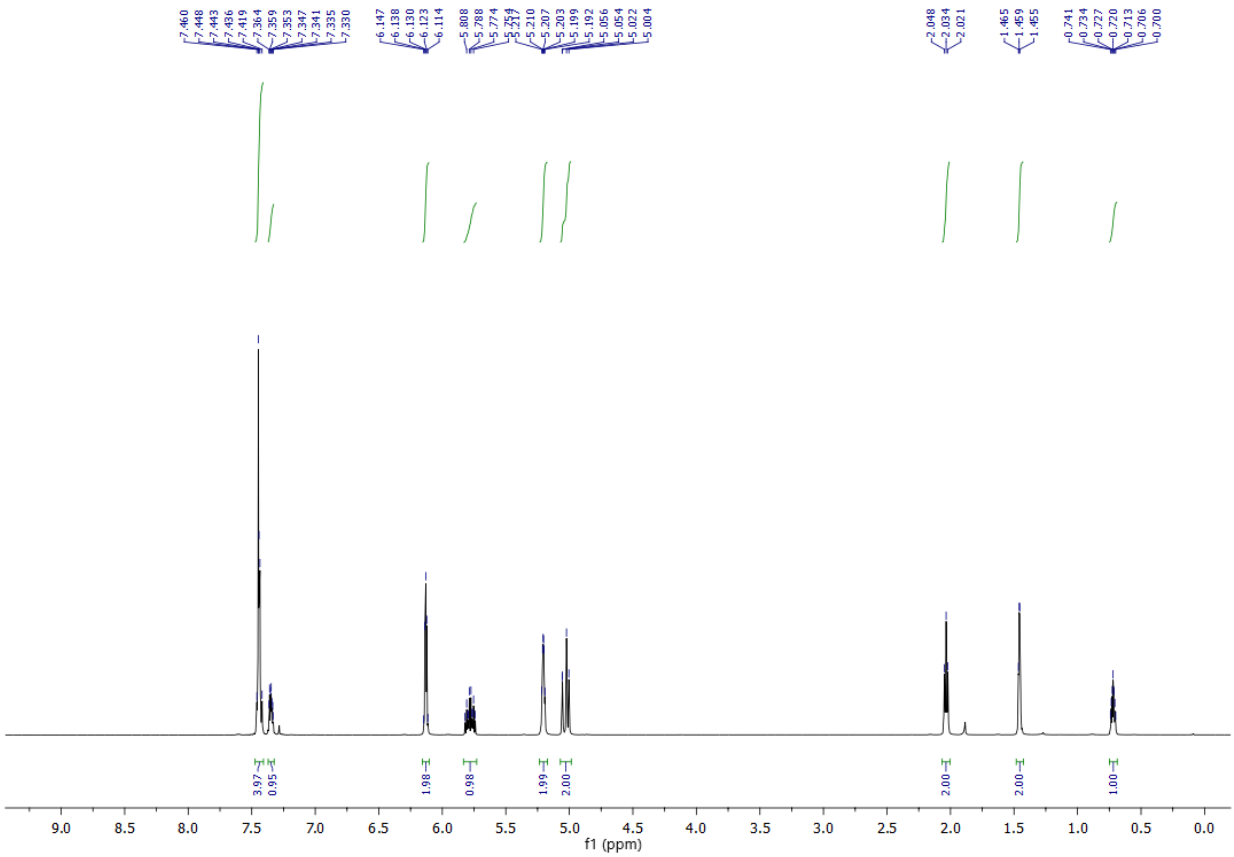


NOESY (9↔11, 9↔12) correlations for (1*R,7*S**,8*R**,9-*exo*,10*S**)-4,9-diphenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3b)**:

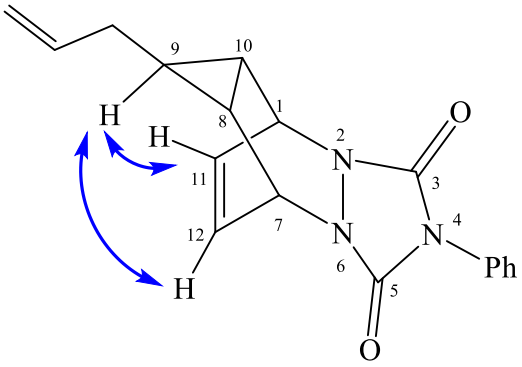


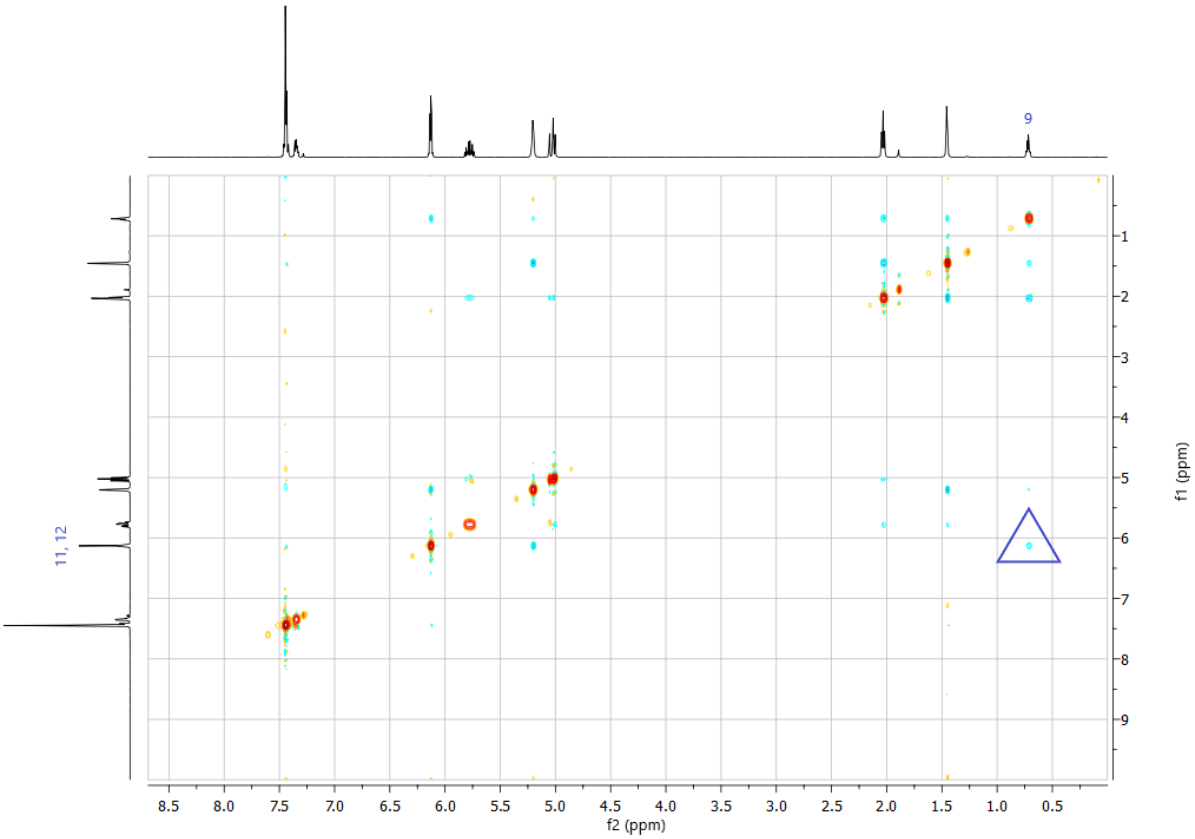
(1*R,7*S**,8*R**,9-*exo*,10*S**)-9-Allyl-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3c)**:



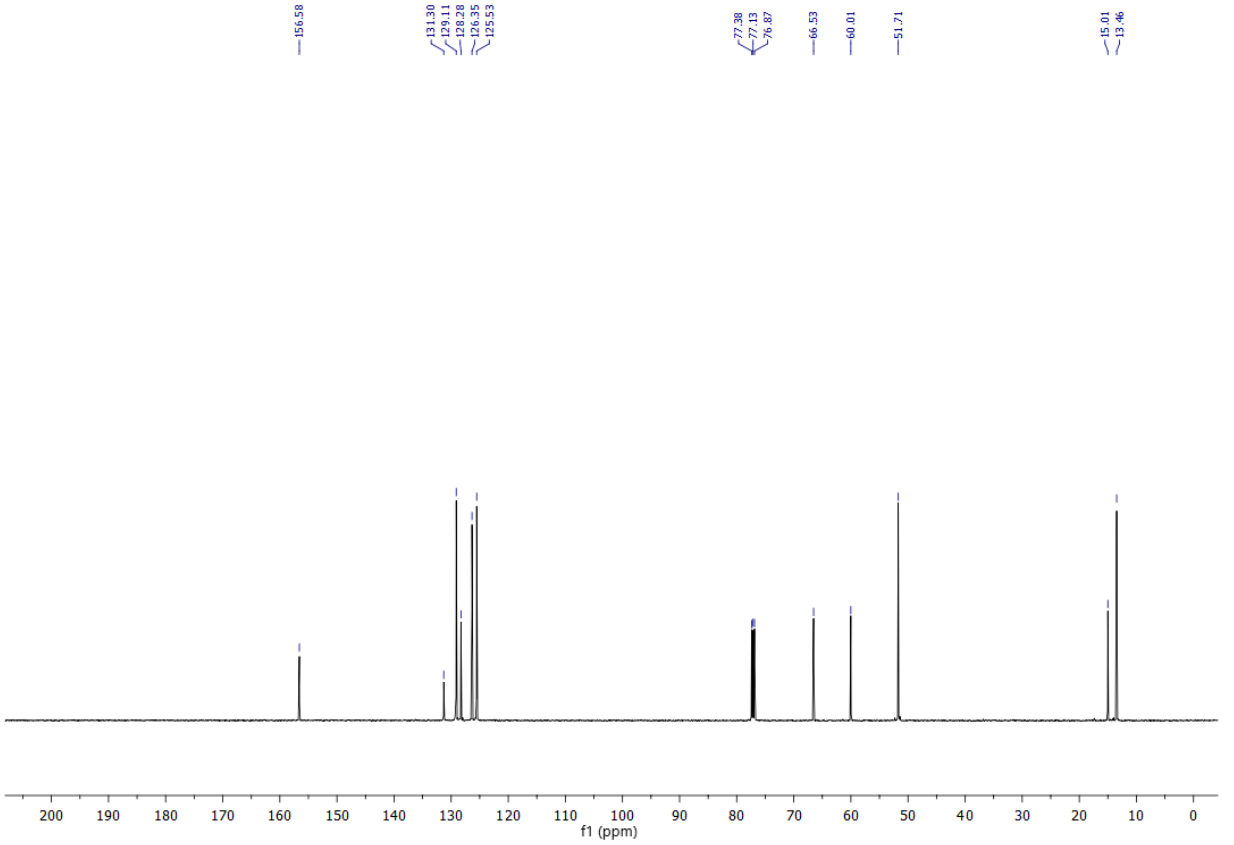


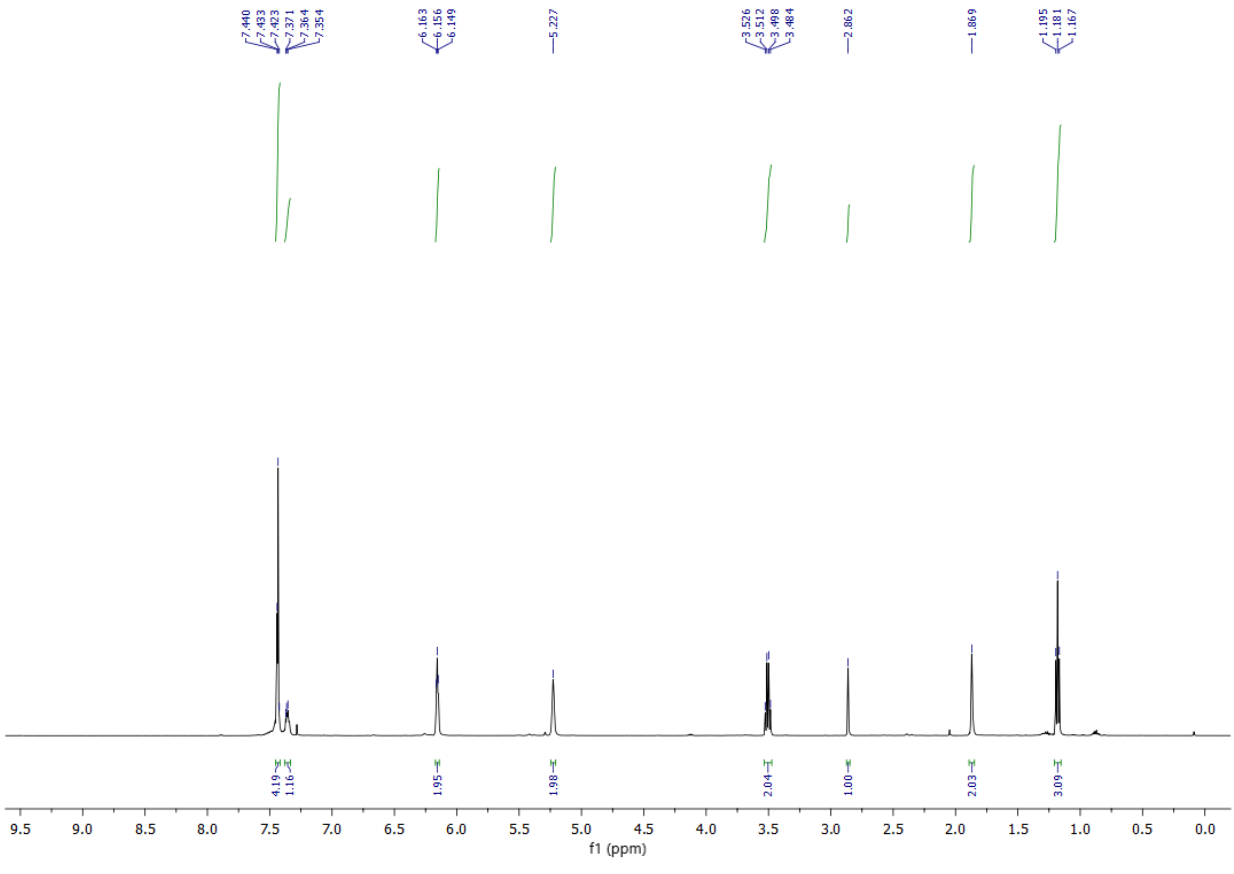
NOESY (9↔11, 9↔12) correlations for (1*R,7*S**,8*R**,9-*exo*,10*S**)-9-allyl-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3c)**:



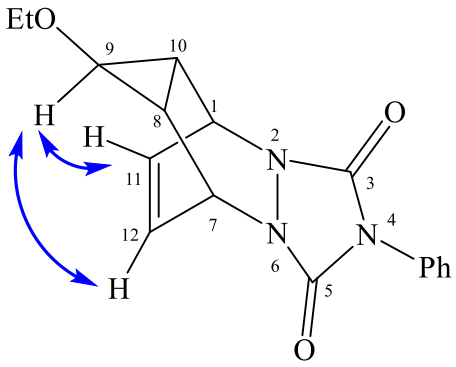


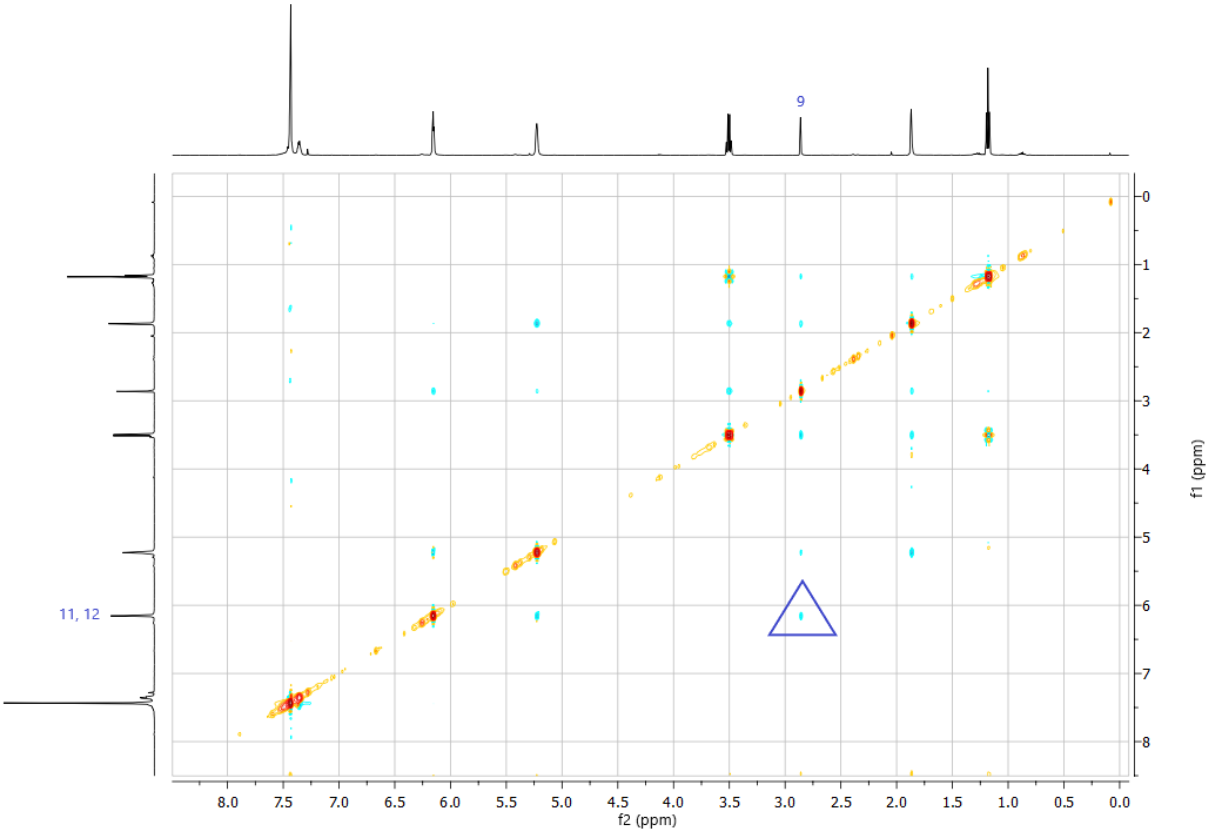
(1*R,7*S**,8*R**,9-*exo*,10*S**)-9-Ethoxy-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3d)**:



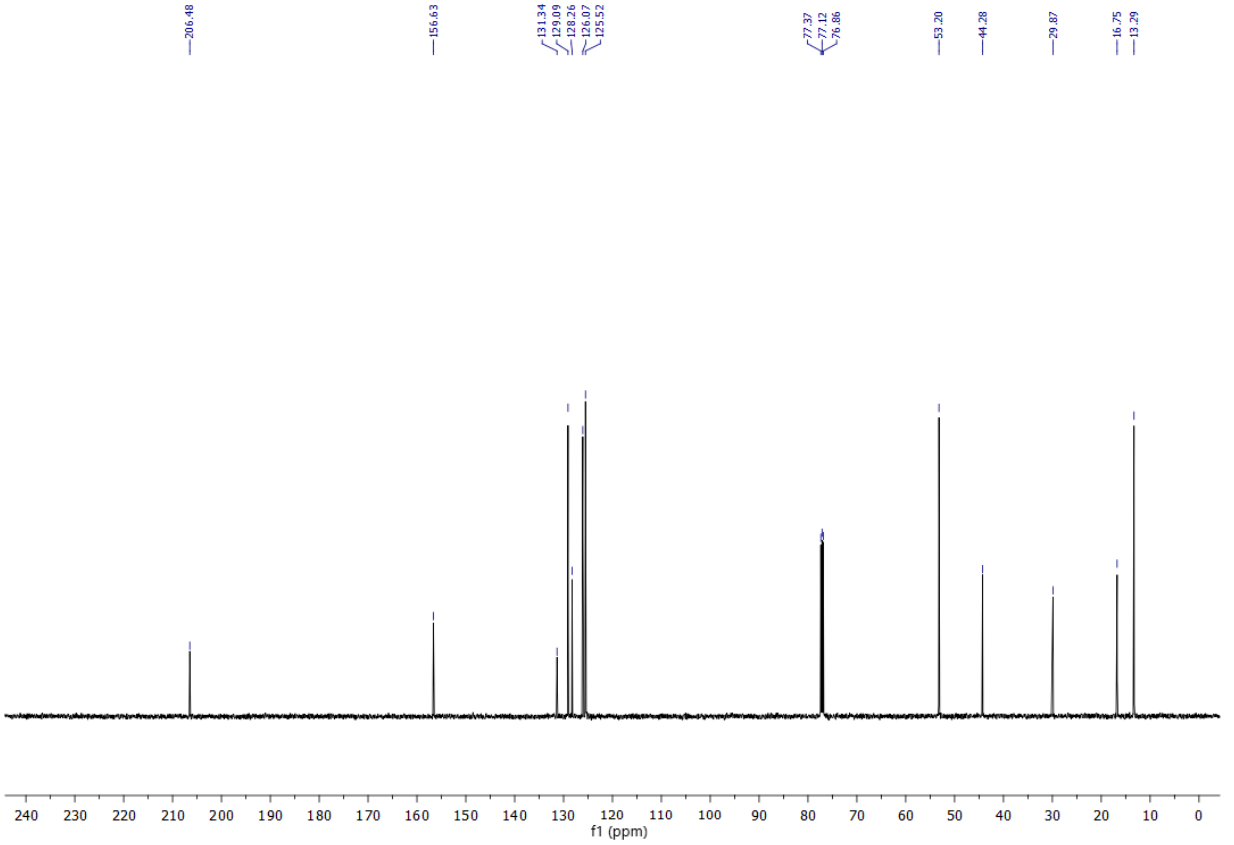


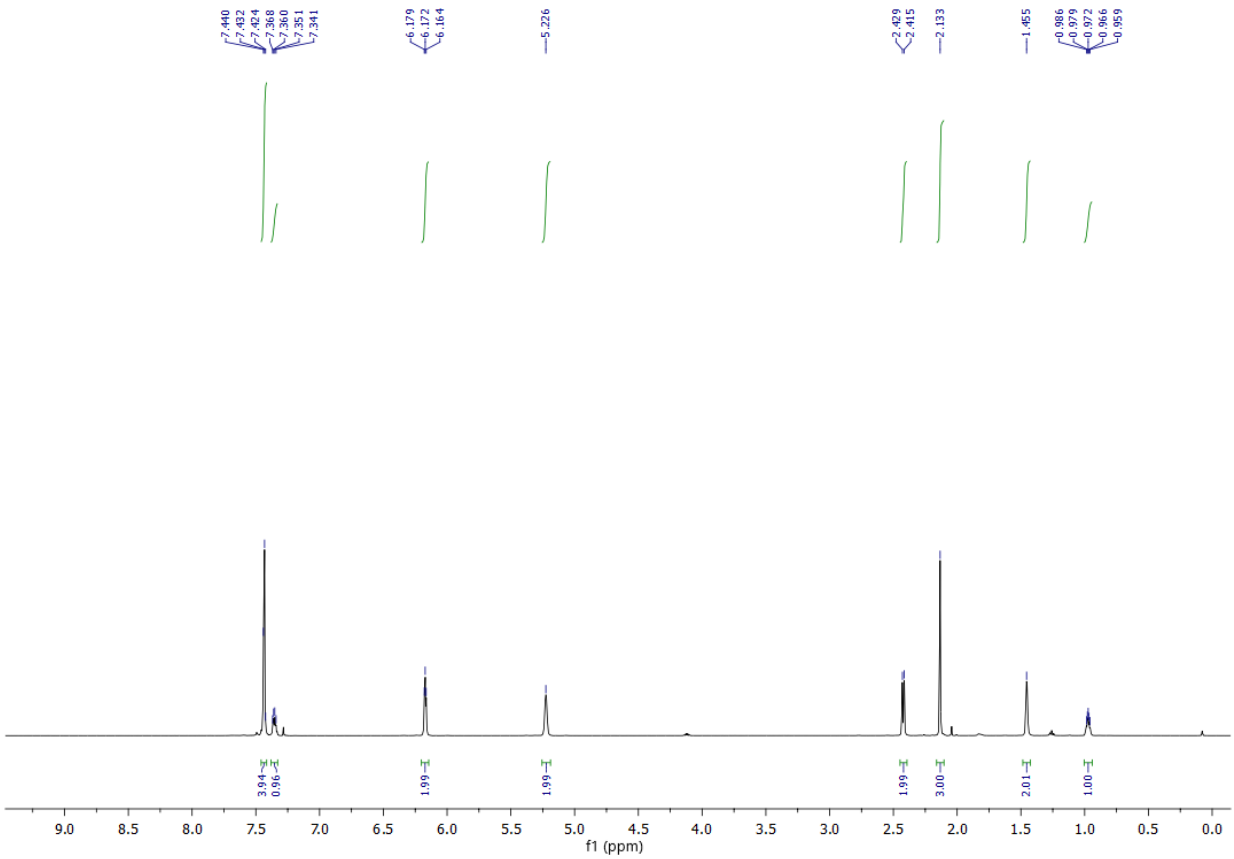
NOESY (9↔11, 9↔12) correlations for (1*R,7*S**,8*R**,9-*exo*,10*S**)-9-ethoxy-4-phenyl-2,4,6-triazatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-3,5-dione (3d)**:



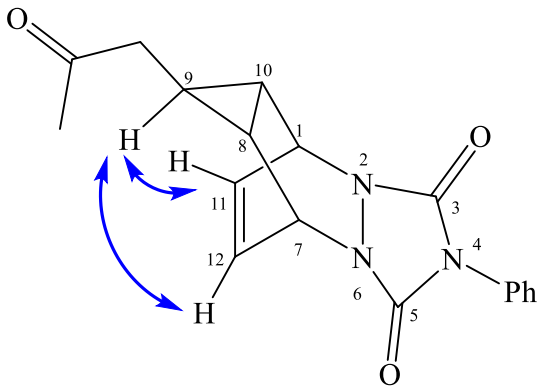


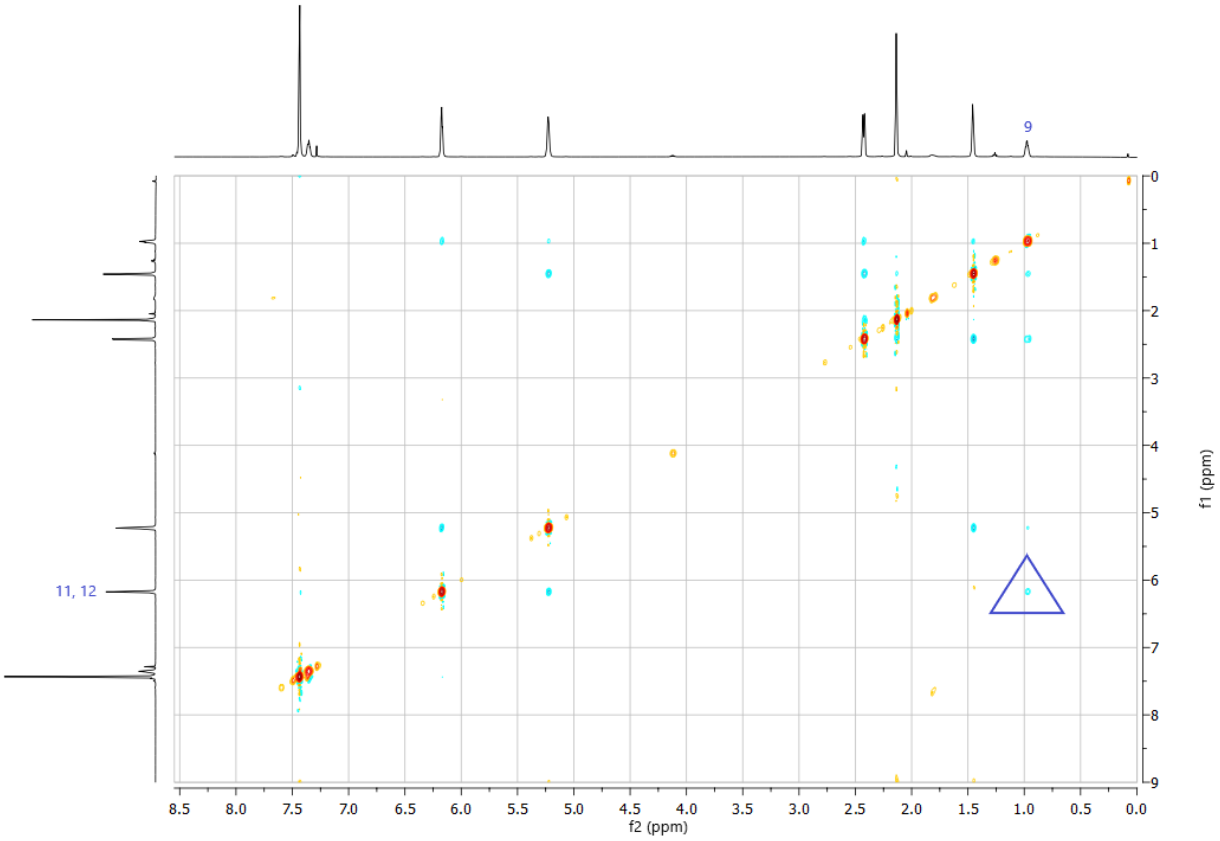
(1*R,7*S**,8*R**,9-*exo*,10*S**)-9-(2-Oxopropyl)-4-phenyl-2,4,6-triazatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-3,5-dione (3e)**:



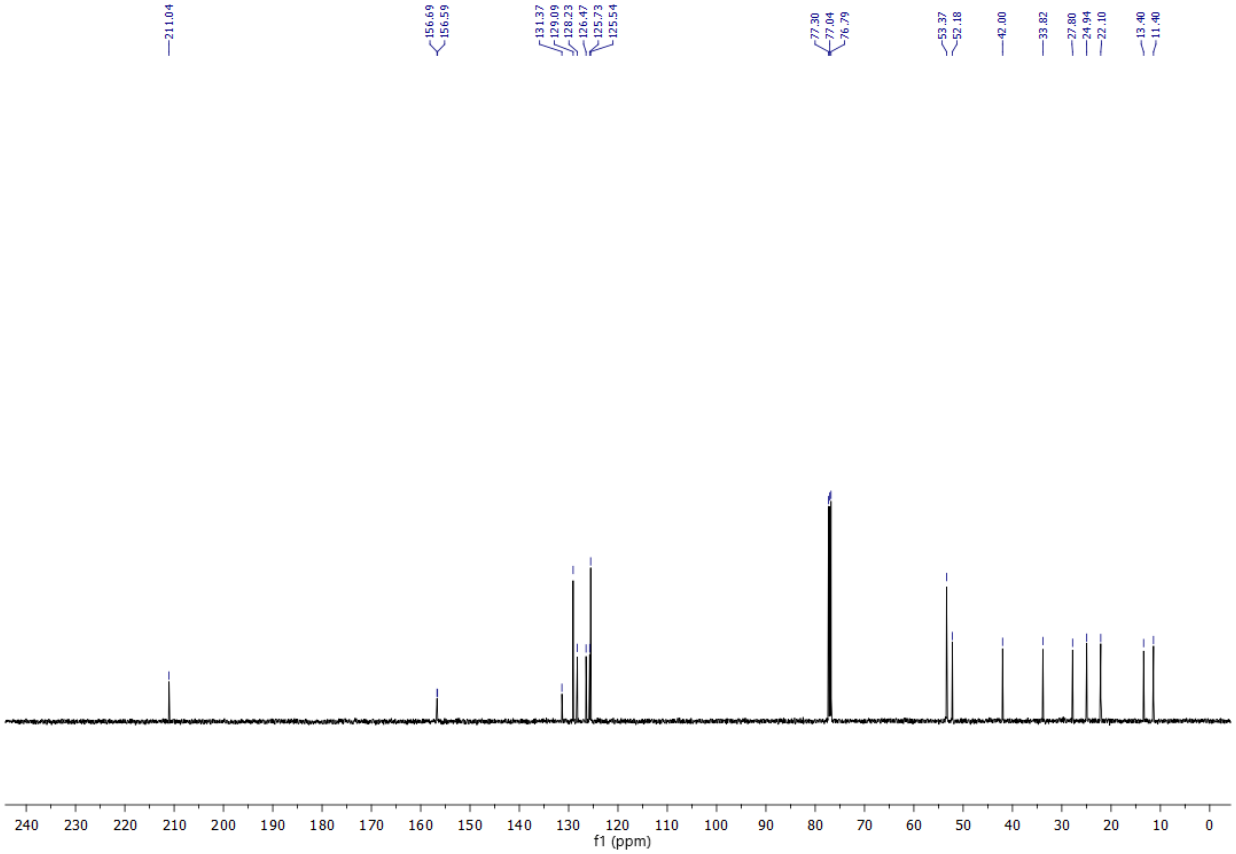


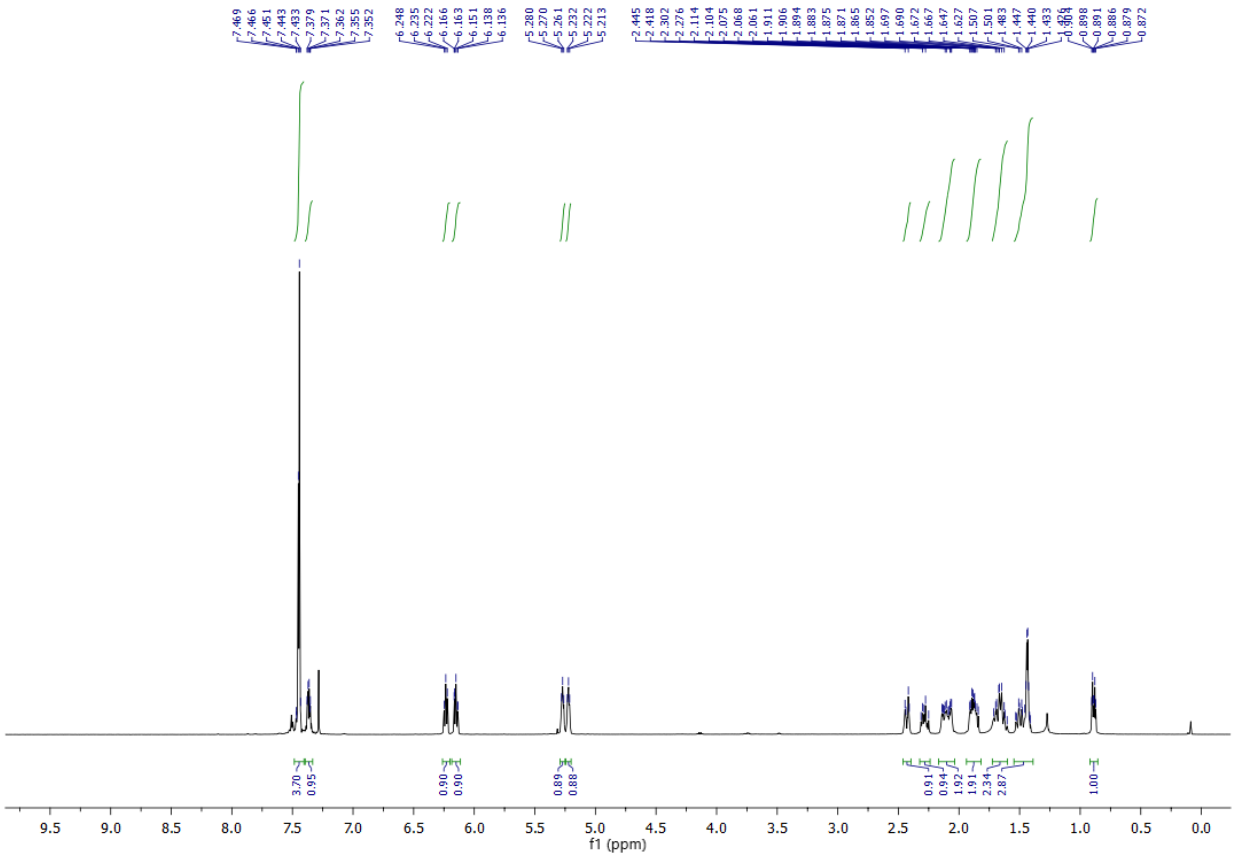
NOESY (9↔11, 9↔12) correlations for (1*R,7*S**,8*R**,9-*exo*,10*S**)-9-(2-oxopropyl)-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3e)**:



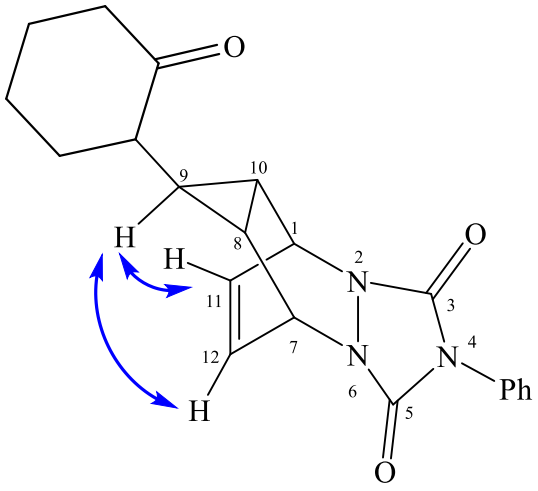


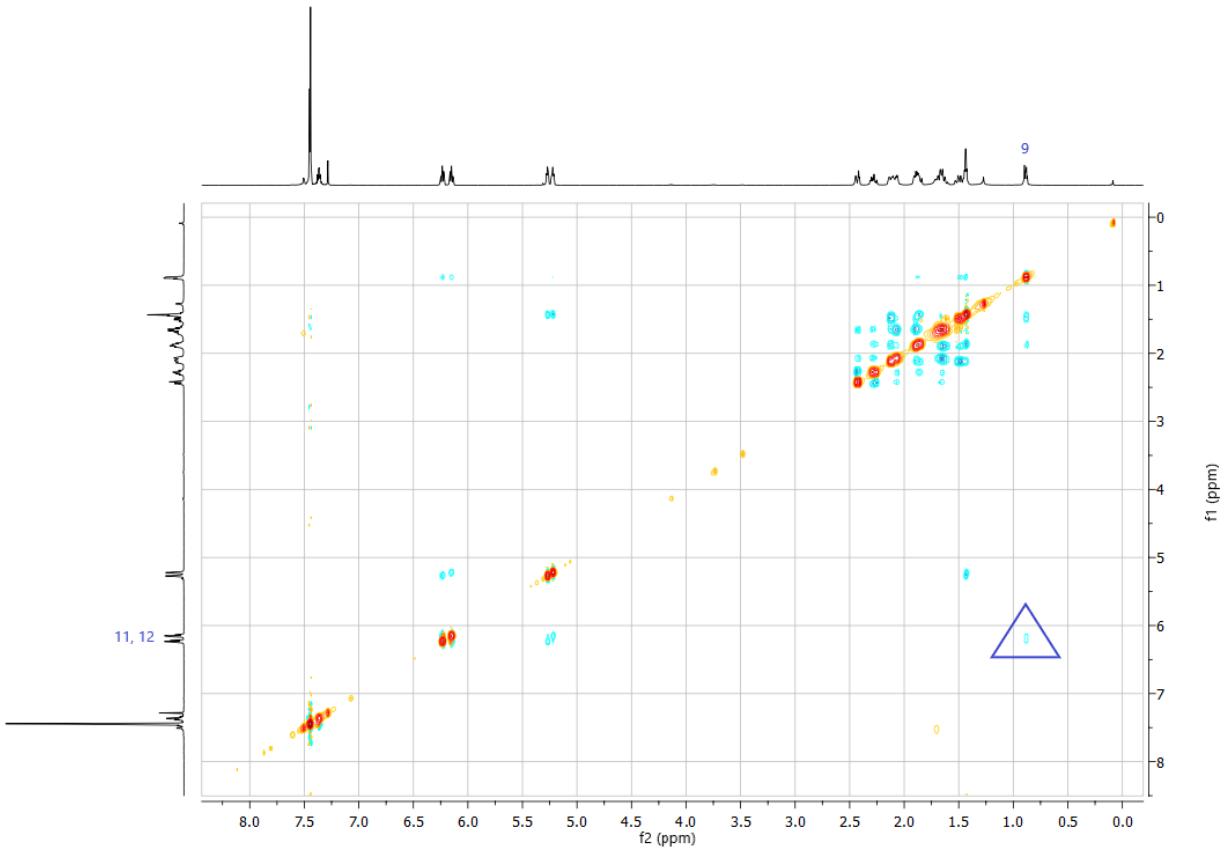
(1*R,7*S**,8*R**,9-*exo*,10*S**)-9-(2-Oxocyclohexyl)-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3f)**:





NOESY (9↔11, 9↔12) correlations for (1*R,7*S**,8*R**,9-*exo*,10*S**)-9-(2-oxocyclohexyl)-4-phenyl-2,4,6-triazatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodec-11-ene-3,5-dione (3f)**:





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