Supplementary Material

Cerium(IV) ammonium nitrate for the tandem nitration and oxidative rearrangement of 2-acetyl-1-naphthol benzoylhydrazones into 1,2-diacylnaphthalenes; synthesis of benzo[*f*]phthalazines

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Email: gvarvoun@cc.uoi.gr

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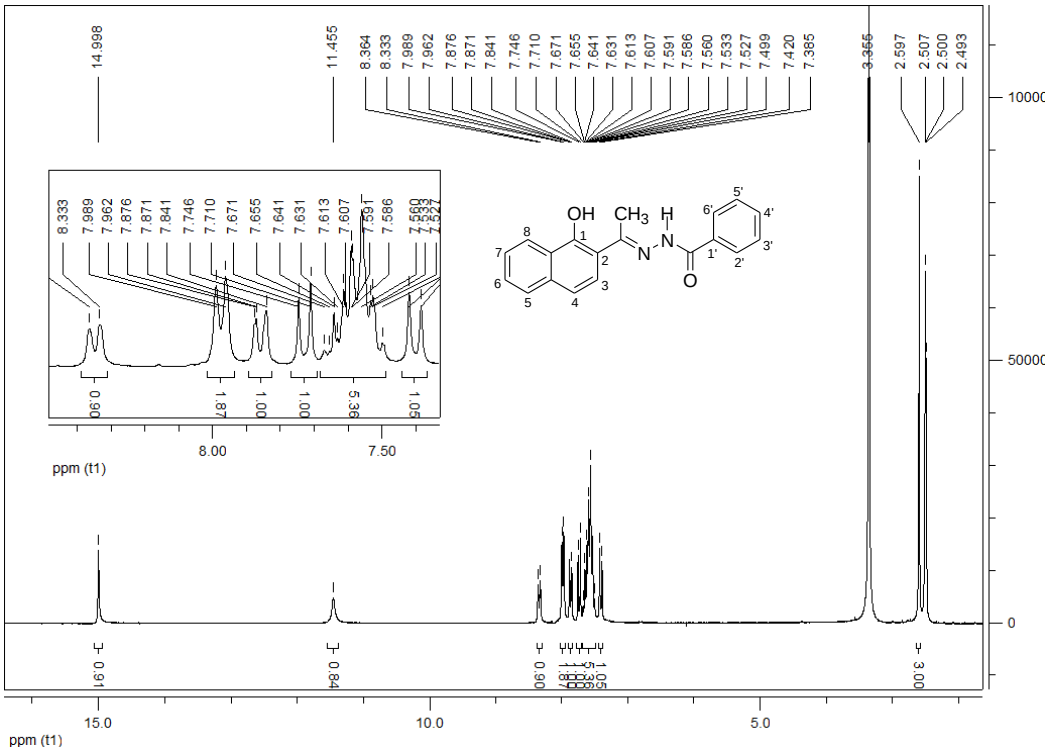
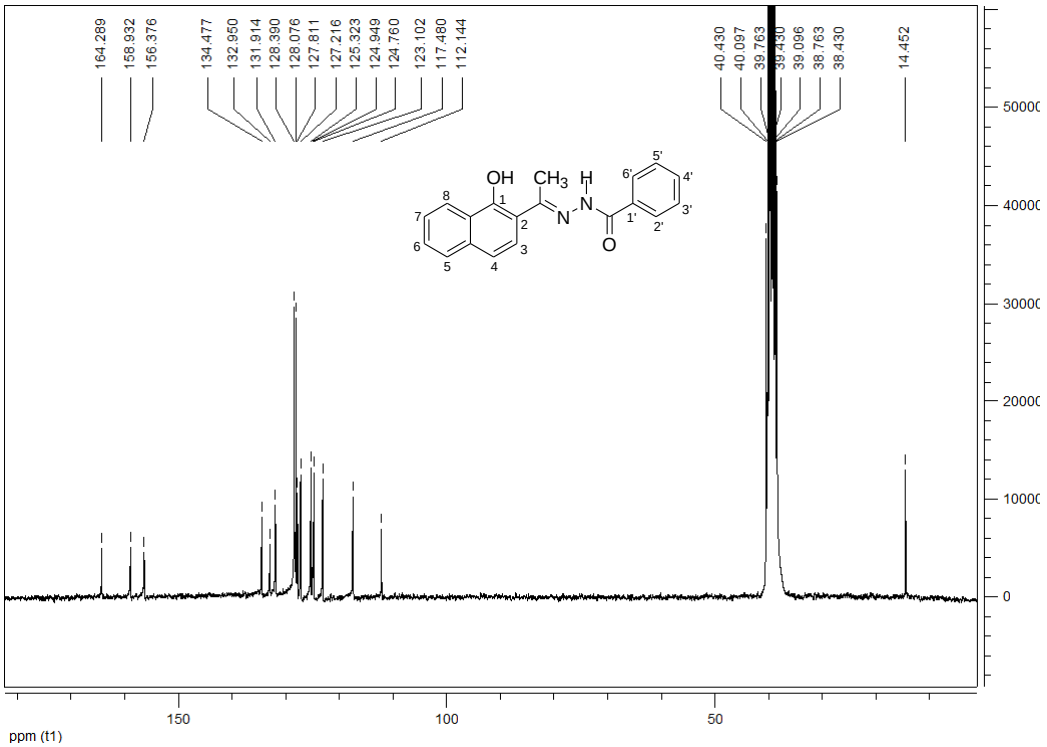
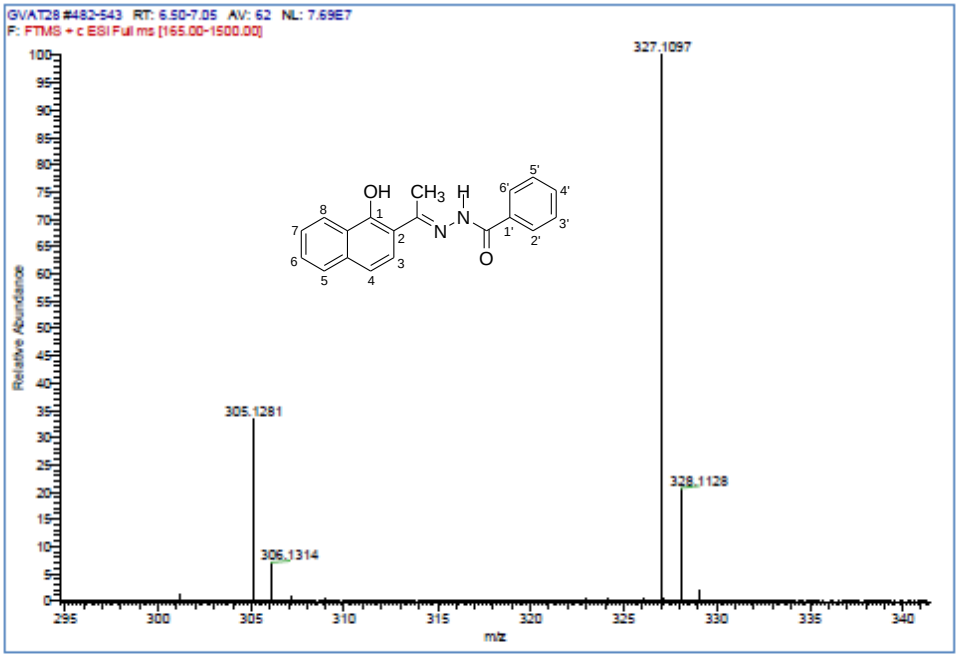
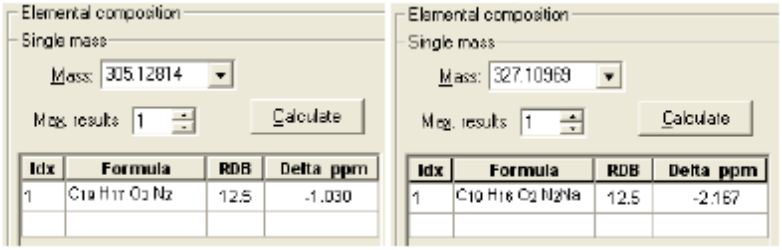


^{1}H NMR spectrum of **3a** (250 MHz, DMSO-d_6)

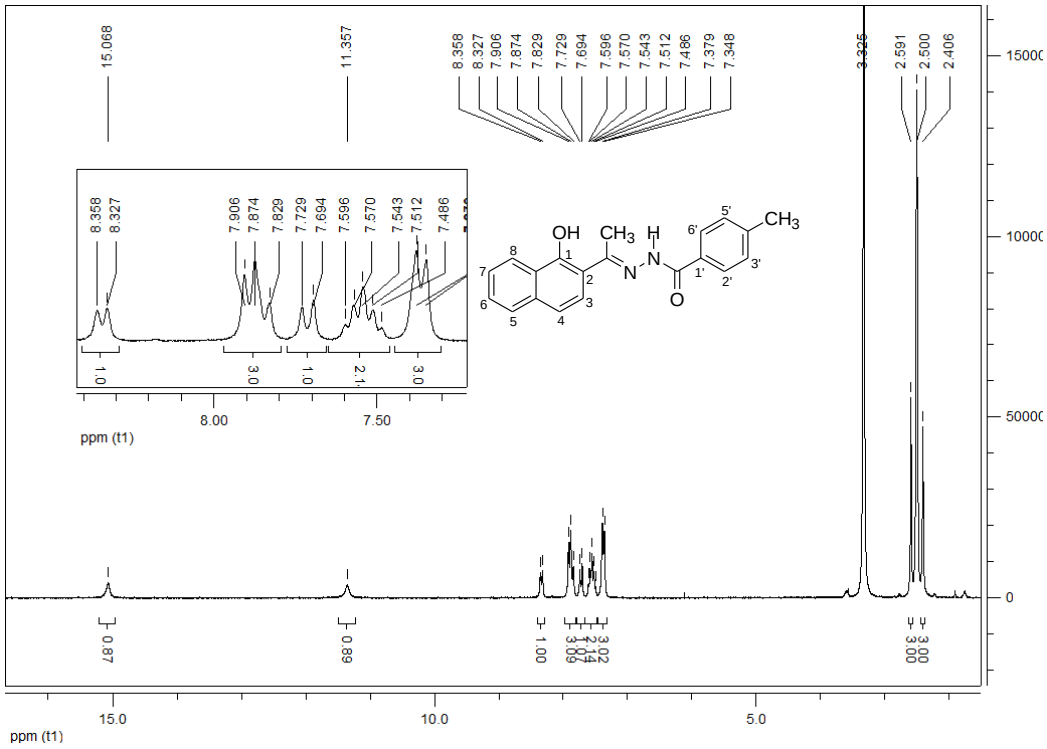


^{13}C NMR spectrum of **3a** (63 MHz, DMSO-d_6)

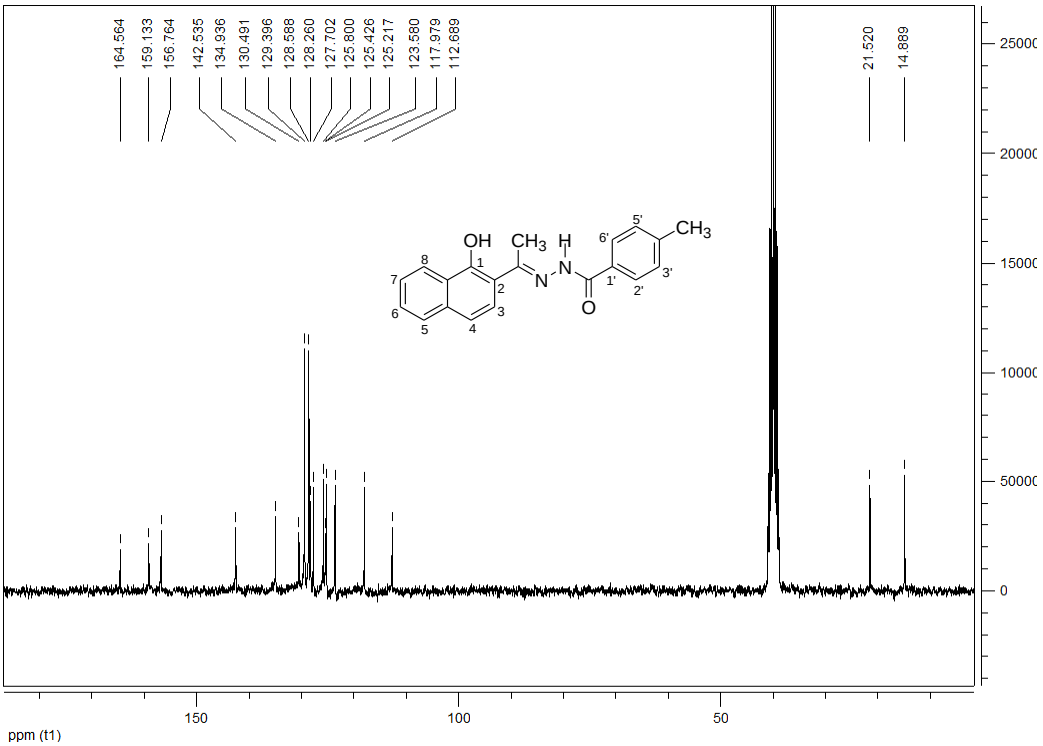




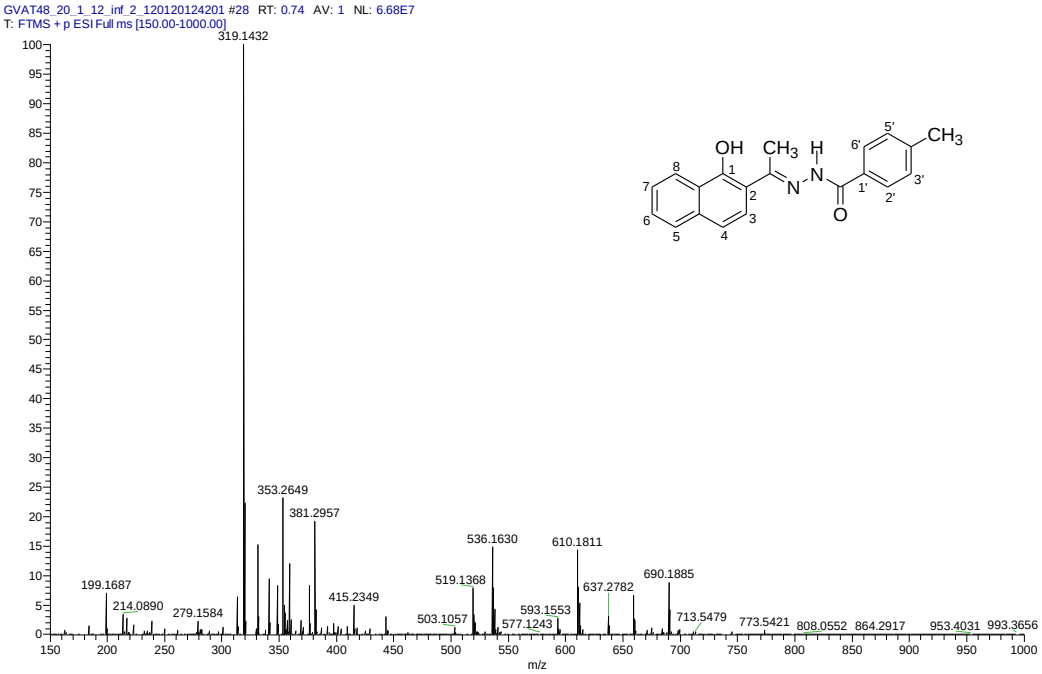
HRMS (APCI) of **3a**



^{1}H NMR spectrum of **3b** (250 MHz, DMSO-d_6)



^{13}C NMR spectrum of **3b** (63 MHz, DMSO-d_6)

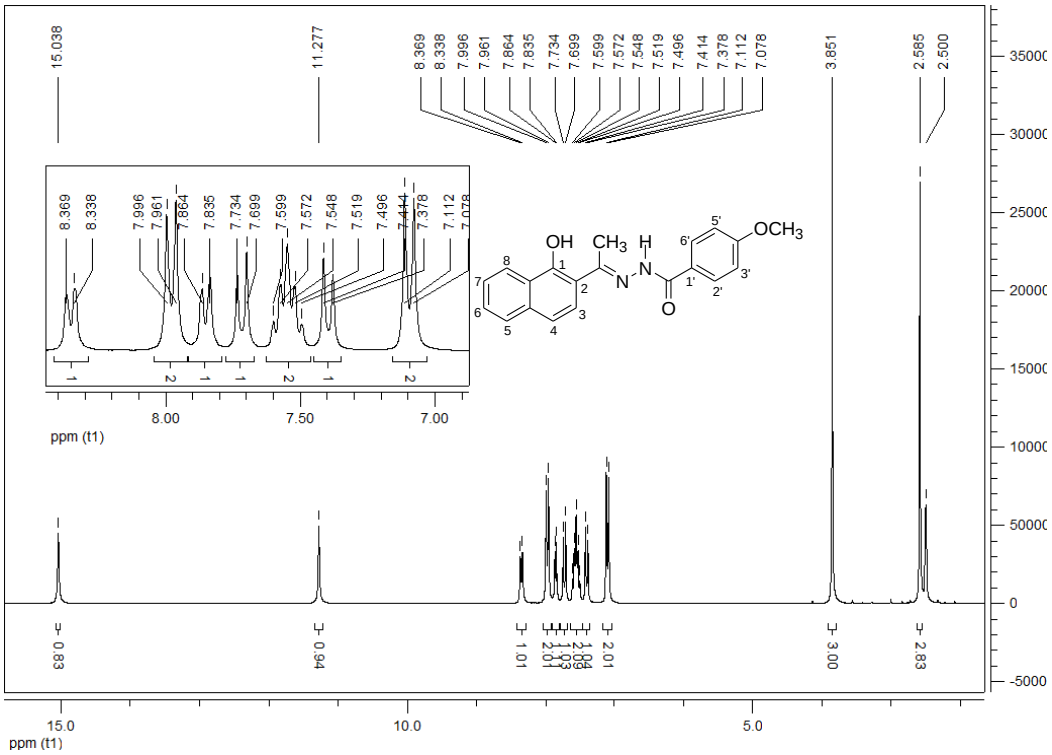


Elemental composition search on mass 319.1432

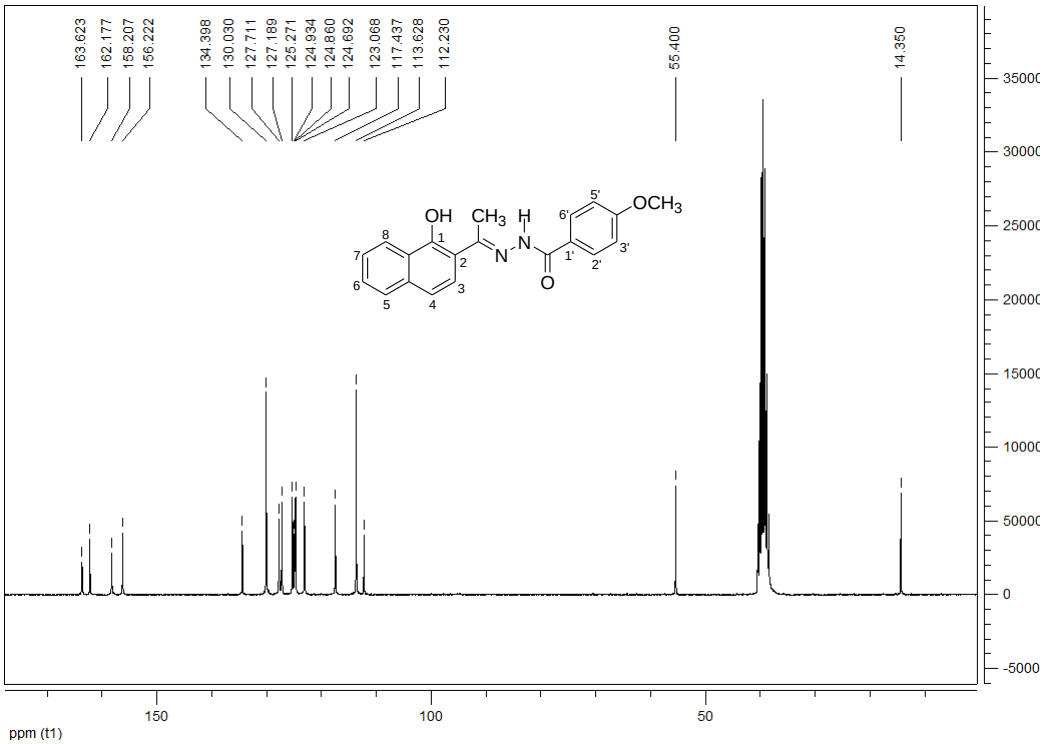
(Isotopes N-14, O-16, C-12, H-1)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
319.1432	319.1433	-0.22	0.5	C4 H19 O7 N10
	319.1428	1.37	13.0	C18 H17 O N5
	319.1441	-2.83	12.5	C20 H19 O2 N2
	319.1446	-4.42	0.0	C6 H21 O8 N7

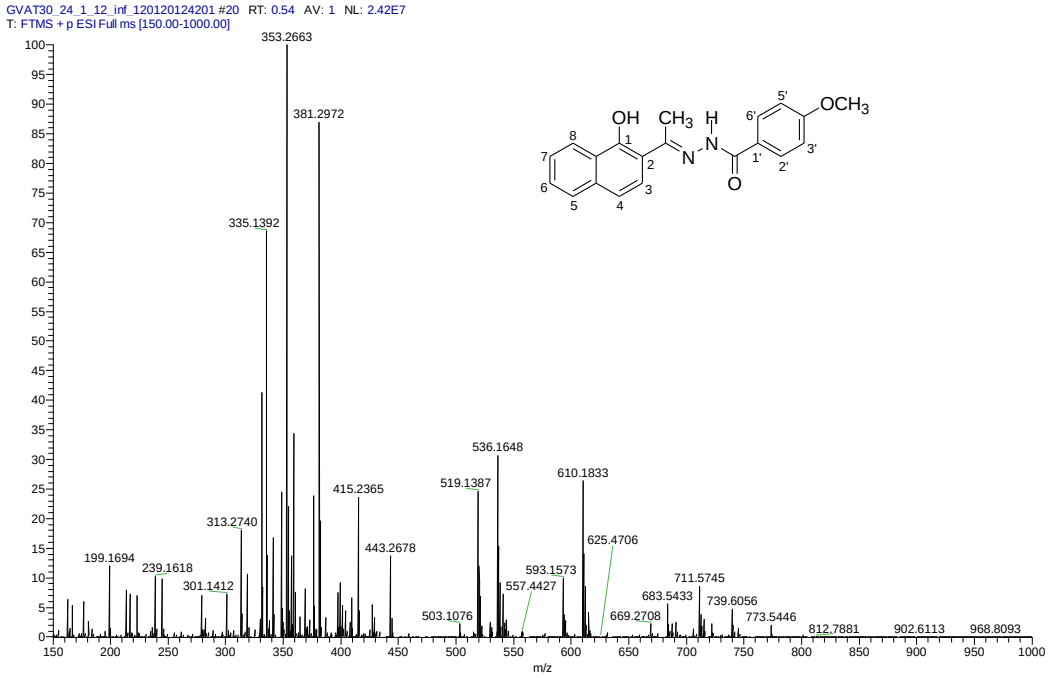
HRMS (ESI) of **3b**



^{1}H NMR spectrum of **3c** (250 MHz, DMSO-d_6)



^{13}C NMR spectrum of **3c** (63 MHz, DMSO-d_6)

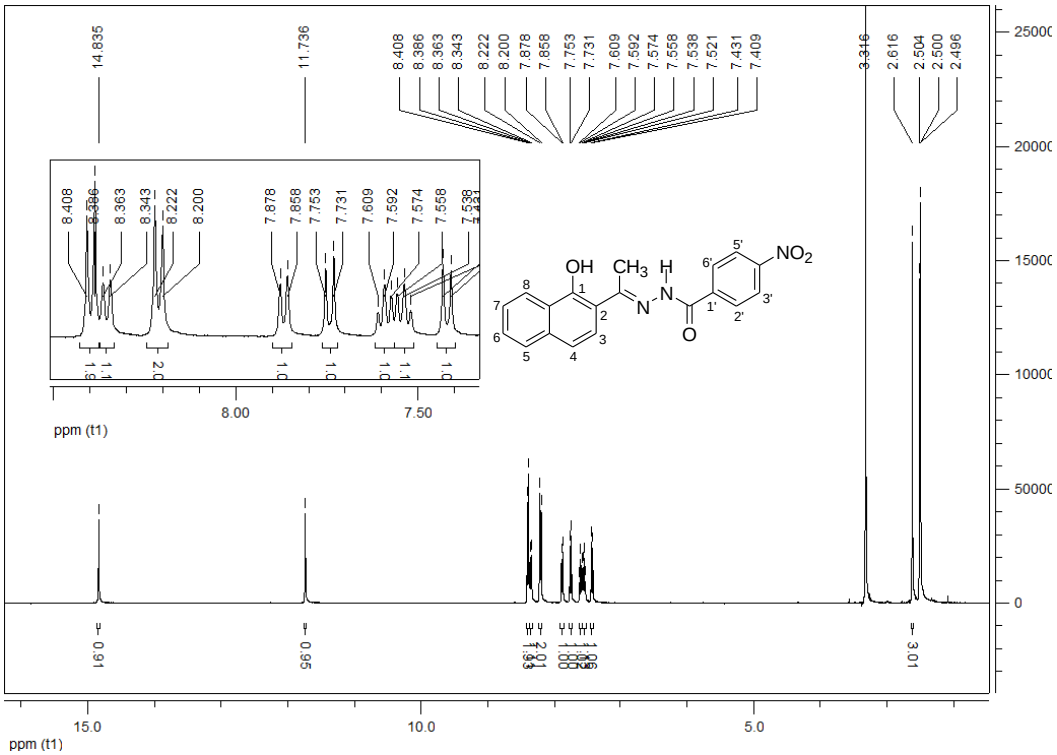


Elemental composition search on mass 335.1392

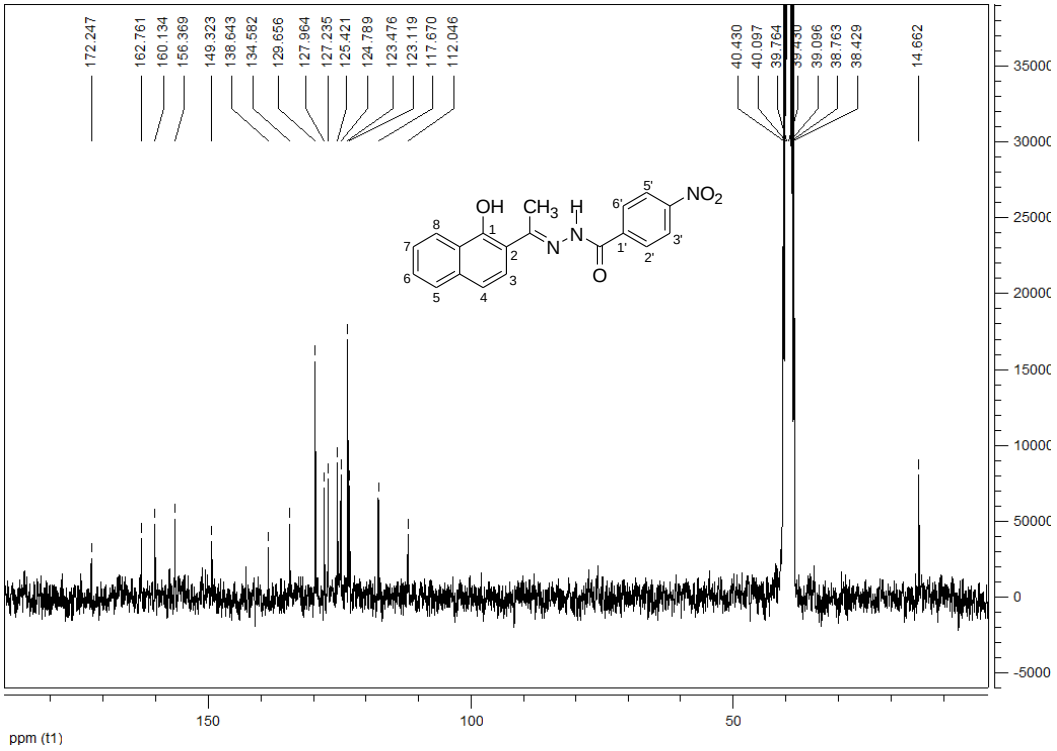
(Isotopes N-14, O-16, C-12, H-1)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
335.1392	335.1390	0.54	12.5	C20 H19 O3 N2
335.1395		-0.97	0.0	C6 H21 O9 N7
335.1382		3.03	0.5	C4 H19 O8 N10
335.1377		4.55	13.0	C18 H17 O2 N5
335.1409		-4.98	-0.5	C8 H23 O10 N4

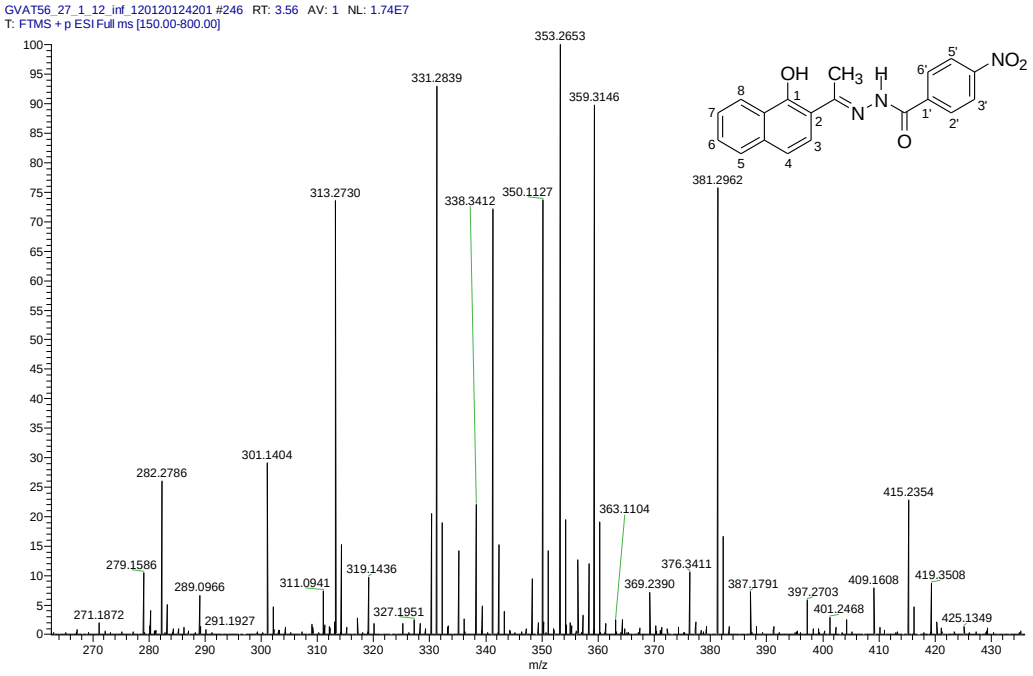
HRMS (ESI) of **3c**



^{1}H NMR spectrum of **3d** (400 MHz, DMSO-d_6)



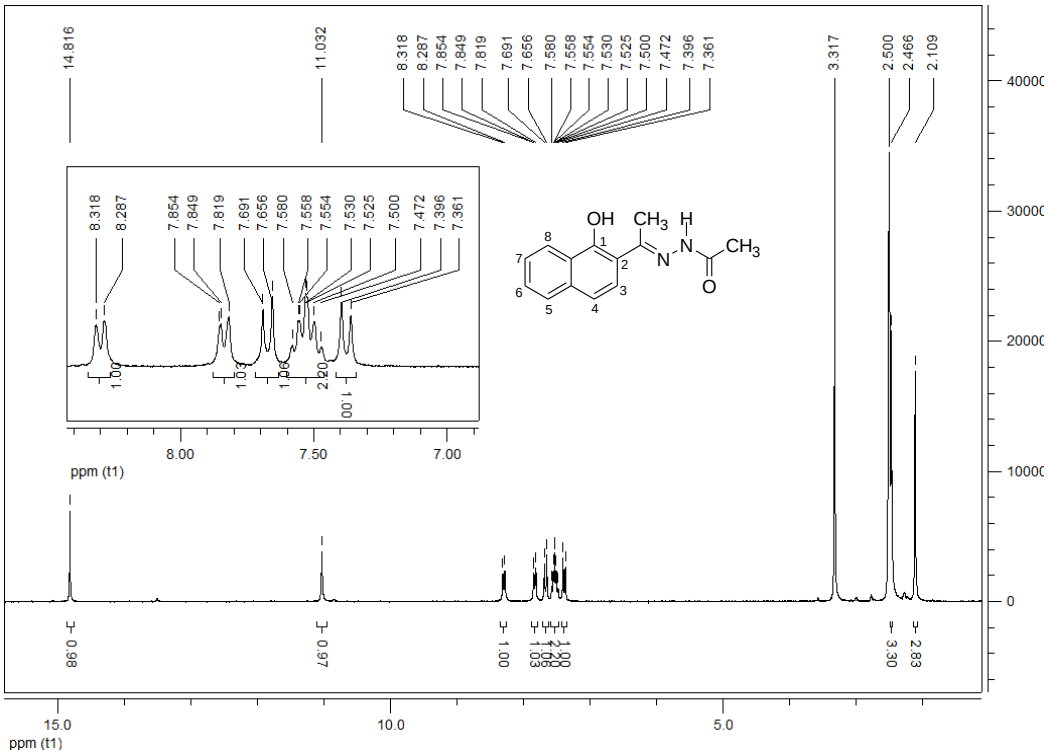
^{13}C NMR spectrum of **3d** (100.6 MHz, DMSO-d_6)



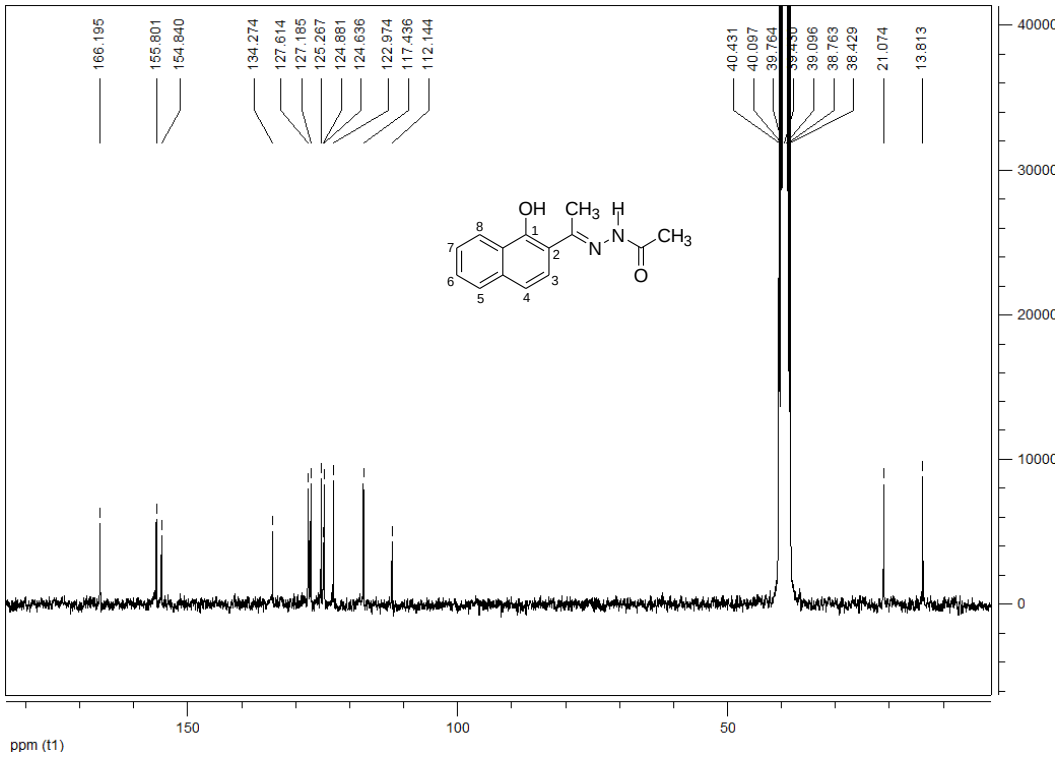
Elemental composition search on mass 350.1127
(Isotopes N-14, O-16, C-12, H-1)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
350.1127	350.1122	1.46	14.0	C17 H14 O3 N6
350.1135		-2.38	13.5	C19 H16 O4 N3
350.1140		-3.83	1.0	C5 H18 O10 N8

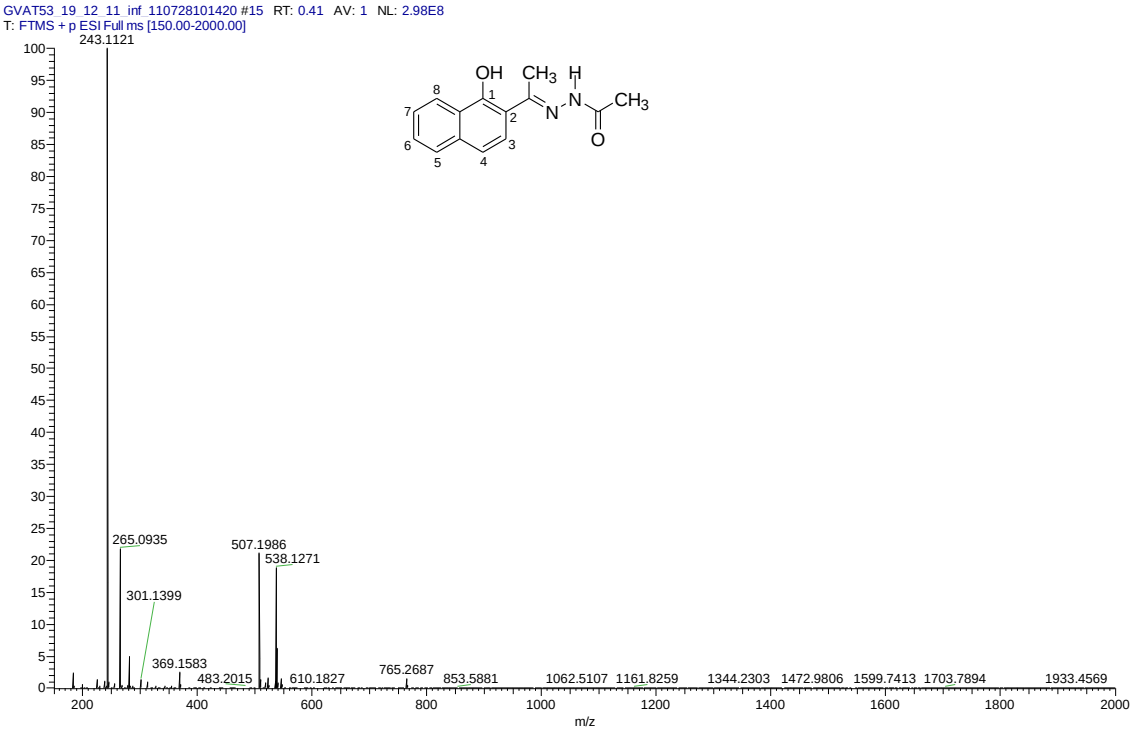
HRMS (ESI) of **3d**



^{1}H NMR spectrum of **3e** (250 MHz, DMSO-d_6)



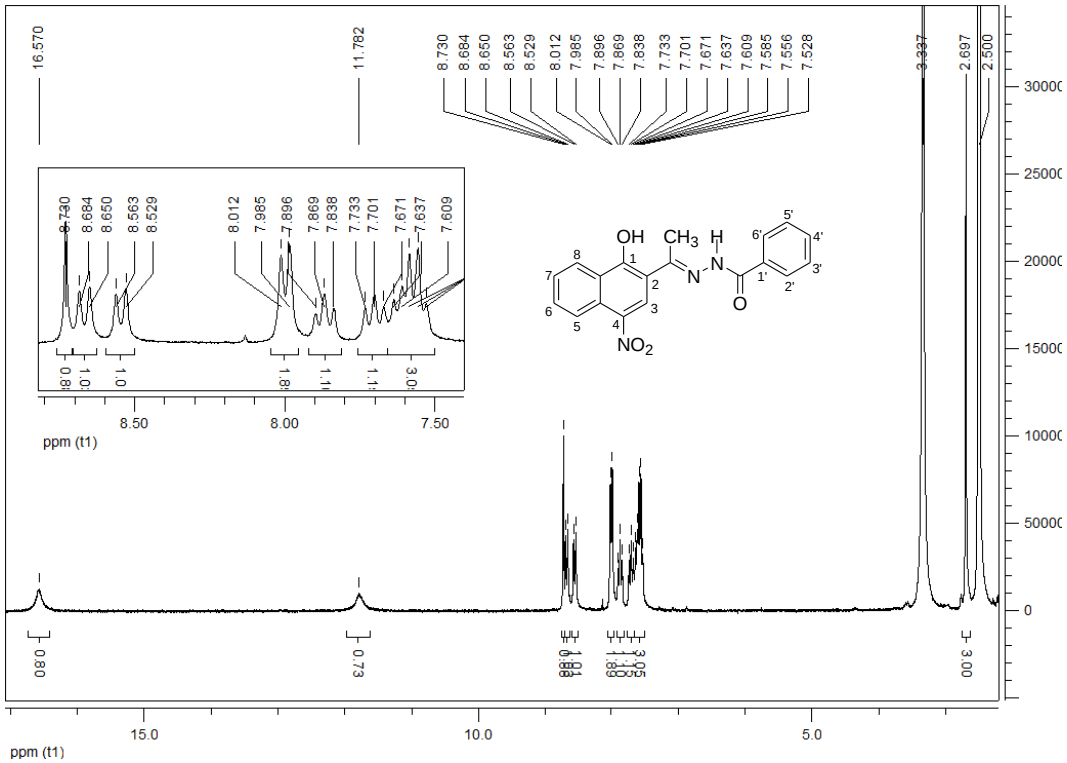
^{13}C NMR spectrum of **3e** (63 MHz, DMSO-d_6)



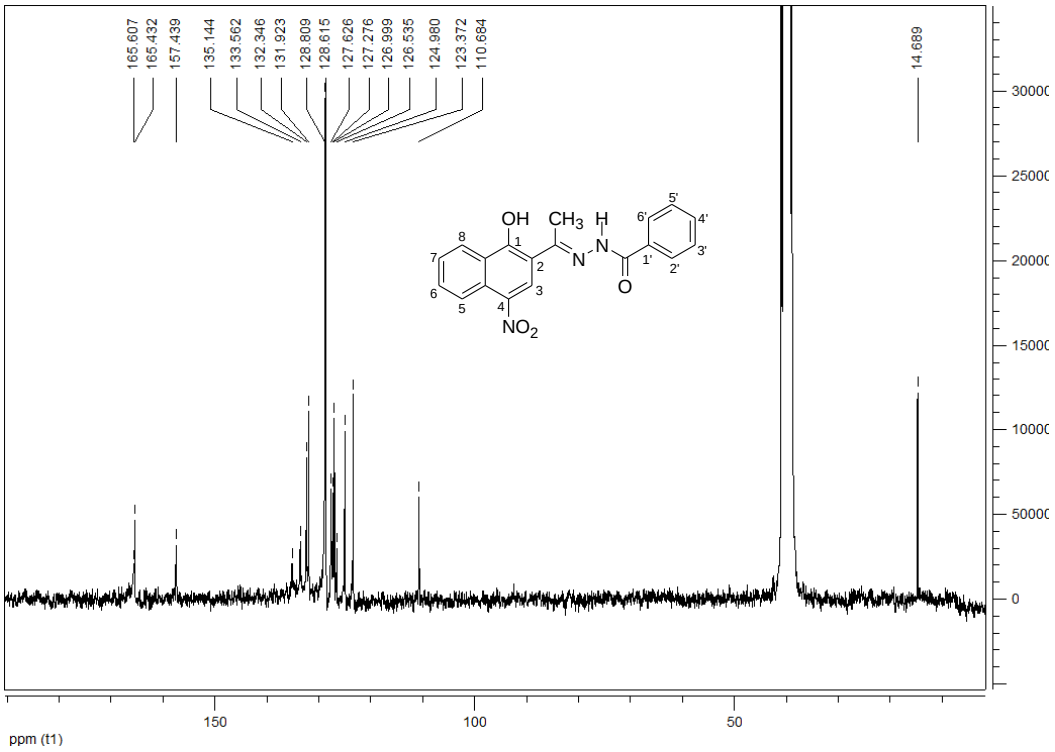
Elemental composition search on mass 243.1121
(Isotopes O-16, C-12, H-1, N-14)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
243.1121	243.1115	2.63	9.0	C12 H13 O N5
	243.1128	-2.90	8.5	C14 H15 O2 N2

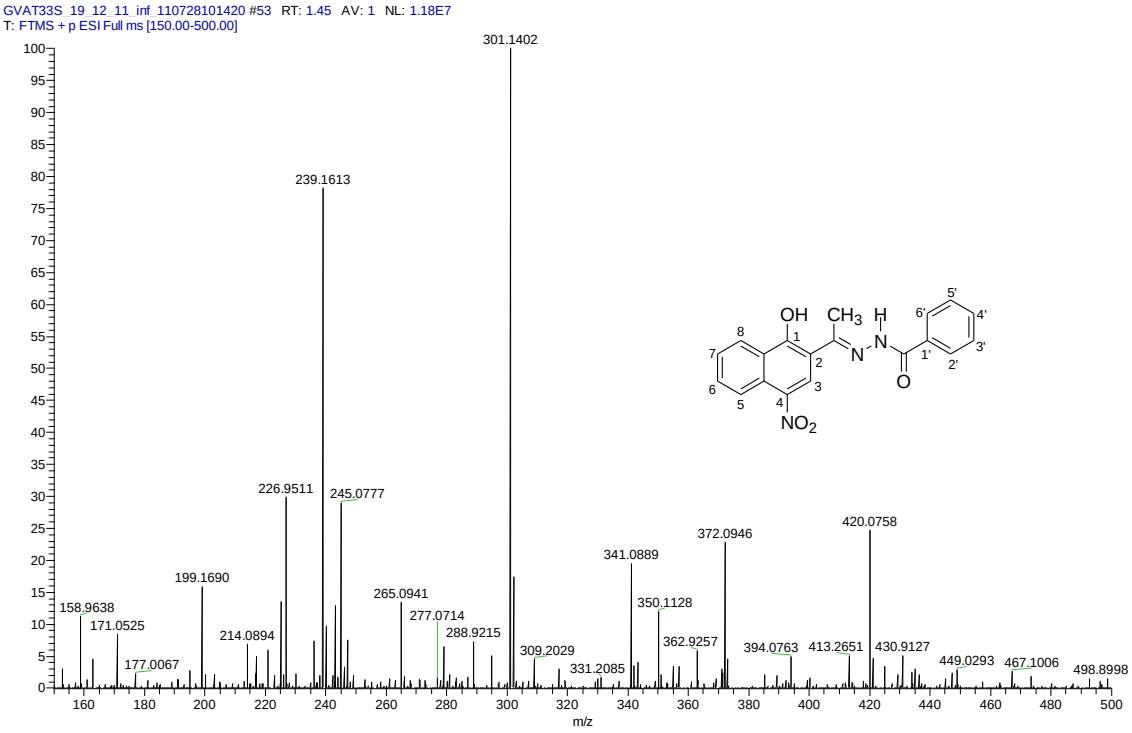
HRMS (ESI) of **3e**



^{1}H NMR spectrum of **4a** (250 MHz, DMSO-d_6)



^{13}C NMR spectrum of **4a** (63 MHz, DMSO-d_6)



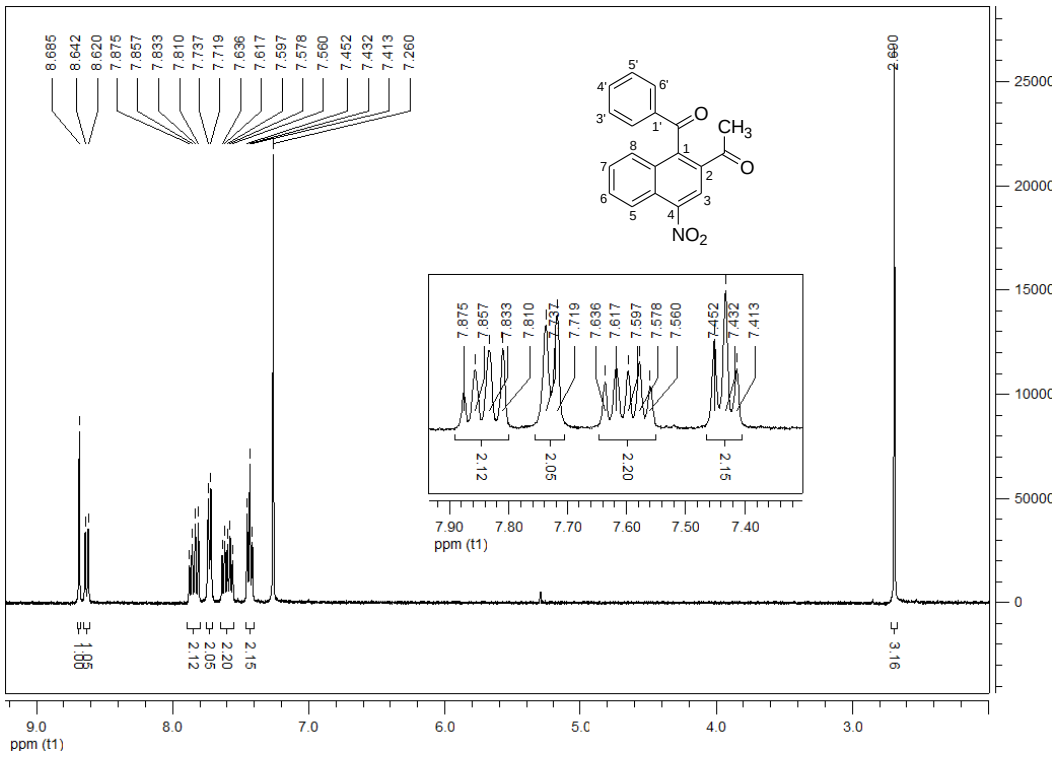
Elemental composition search on mass 350.1128
(Isotopes N-14, O-16, C-12, H-1)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
350.1128	350.1122	1.74	14.0	C17 H14 O3 N6
	350.1135	-2.09	13.5	C19 H16 O4 N3
	350.1140	-3.54	1.0	C5 H18 O10 N8

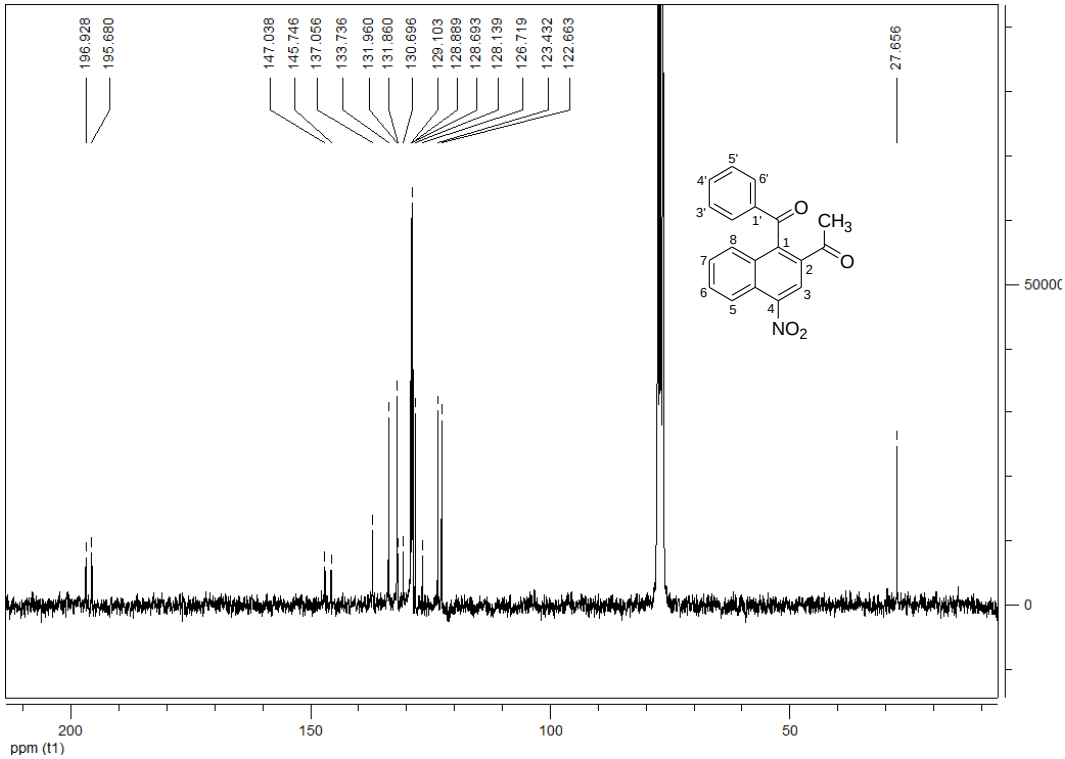
Elemental composition search on mass 372.0947
(Isotopes N-14, O-16, C-12, H-1, Na-23)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
372.0941	1.52	14.0		C17 H13 O3 N6 Na
372.0941	1.53	1.0		C5 H16 O4 N10 Na4
372.0955	-2.07	0.5		C7 H18 O5 N7 Na4
372.0955	-2.09	13.5		C19 H15 O4 N3 Na
372.0939	2.26	12.5		C16 H14 O6 N5
372.0939	2.27	-0.5		C4 H17 O7 N9 Na3
372.0957	-2.71	-0.5		C4 H18 O13 N7

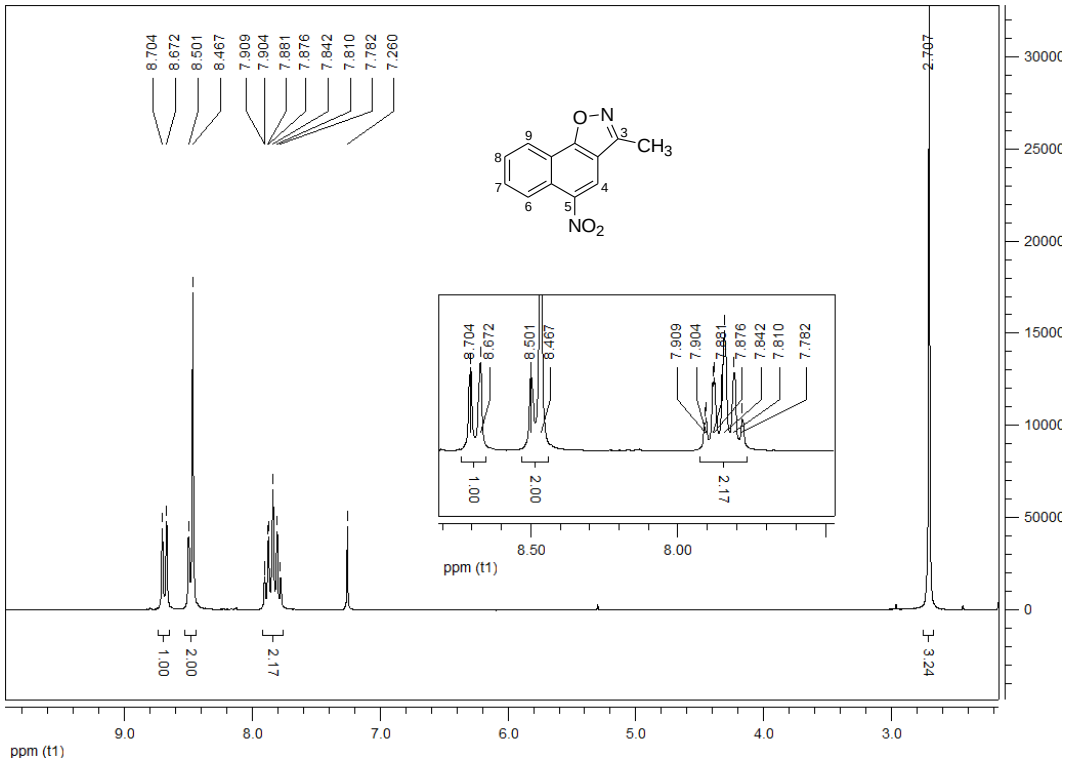
HRMS (ESI) of **4a**



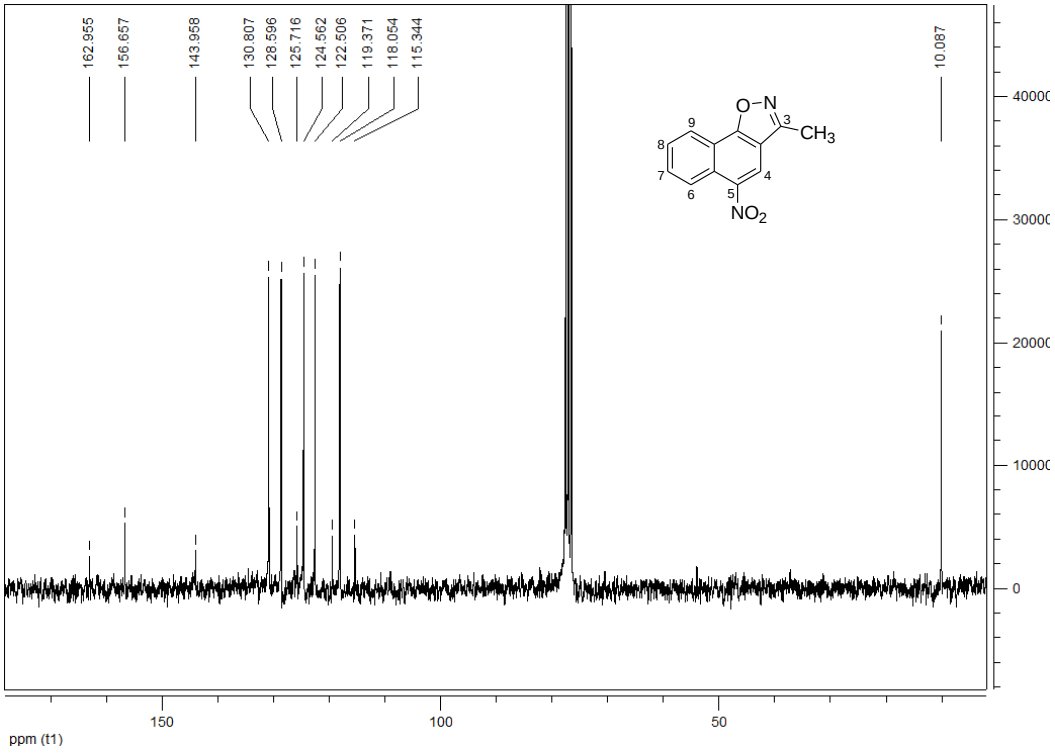
^{1}H NMR spectrum of **5a** (400 MHz, $CDCl_3$)



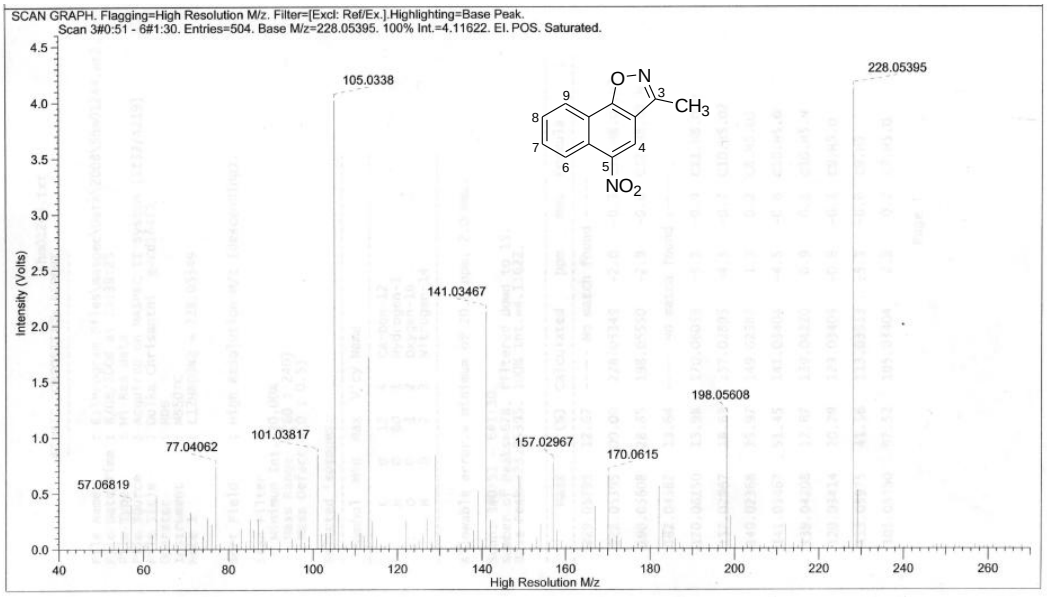
^{13}C NMR spectrum of **5a** (100.6 MHz, $CDCl_3$)



^{1}H NMR spectrum of **6** (250 MHz, $CDCl_3$)



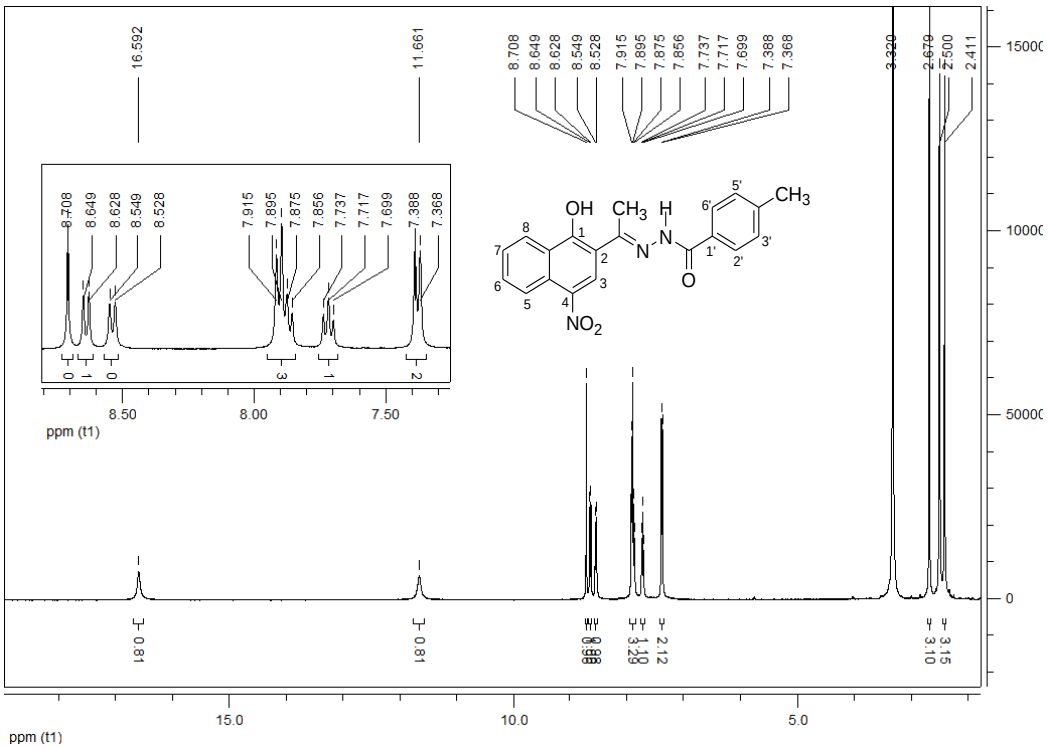
^{13}C NMR spectrum of **6** (63 MHz, $CDCl_3$)



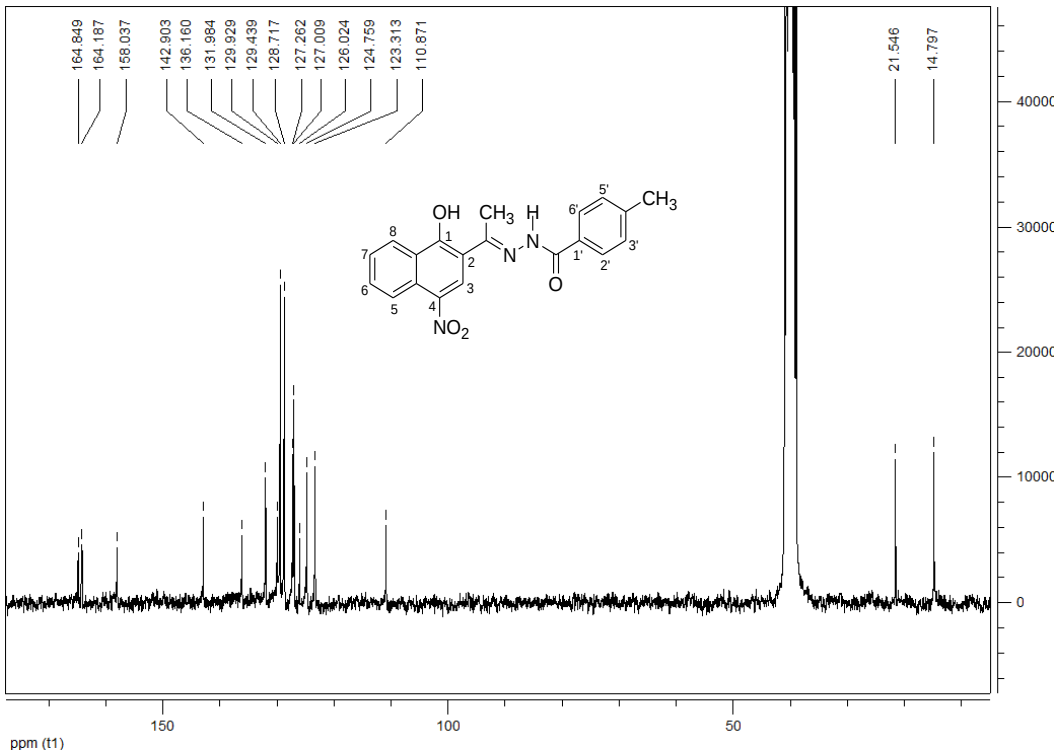
Scan: 3#0:51 - 6#1:30.
Number of Peaks=678, filtered down to 15.
Base Peak=228.05395, 100% Int.=4.11622.

Mass	(%)	Calculated	ppm	mmu	Formula
229.05795	12.67	----- No match found -----			
228.05395	100.00	228.05349	-2.0	-0.5	C12.H8.O3.N2
198.05608	28.85	198.05550	-2.9	-0.6	C12.H8.O2.N
182.04582	13.64	----- No match found -----			
170.06150	15.98	170.06059	-5.3	-0.9	C11.H8.O.N
157.02967	18.69	157.02895	-4.5	-0.7	C10.H5.O2
149.02368	15.97	149.02387	1.3	0.2	C8.H5.O3
141.03467	51.45	141.03404	-4.5	-0.6	C10.H5.O
139.04208	12.67	139.04220	0.9	0.1	C10.H5.N
129.03414	20.29	129.03404	-0.8	-0.1	C9.H5.O
113.03975	41.56	113.03913	-5.5	-0.6	C9.H5
105.03380	97.52	105.03404	2.2	0.2	C7.H5.O

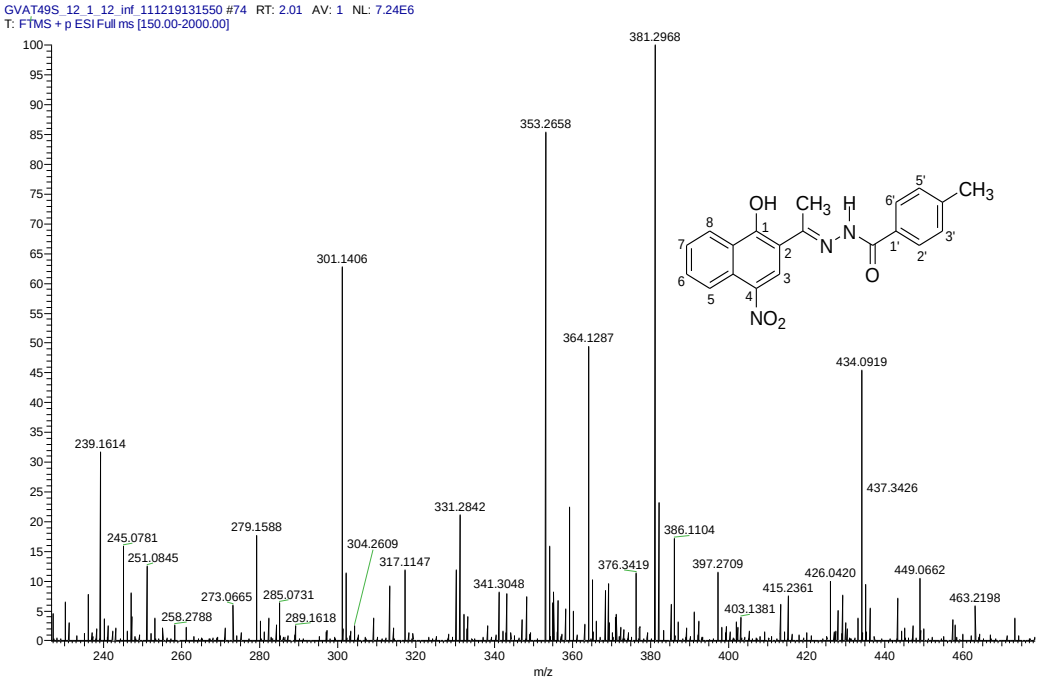
HRMS (ESI) of **6**



^{1}H NMR spectrum of **4b** (250 MHz, DMSO-d_6)



^{13}C NMR spectrum of **4b** (DMSO-d_6, 63 MHz)



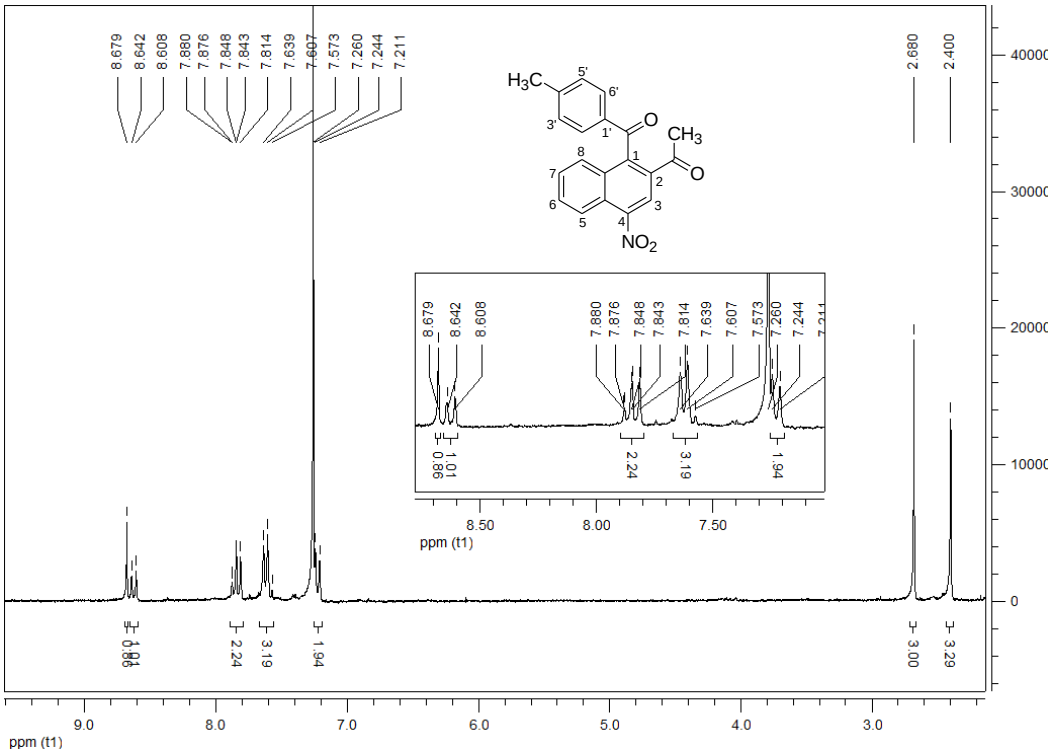
Elemental composition search on mass 364.1287
(Isotopes N-14, O-16, C-12, H-1)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
364.1287	364.1292	-1.33	13.5	C20 H18 O4 N3
364.1278	2.36	14.0		C18 H16 O3 N6
364.1297	-2.72	1.0		C6 H20 O10 N8
364.1305	-5.00	18.5		C21 H14 N7

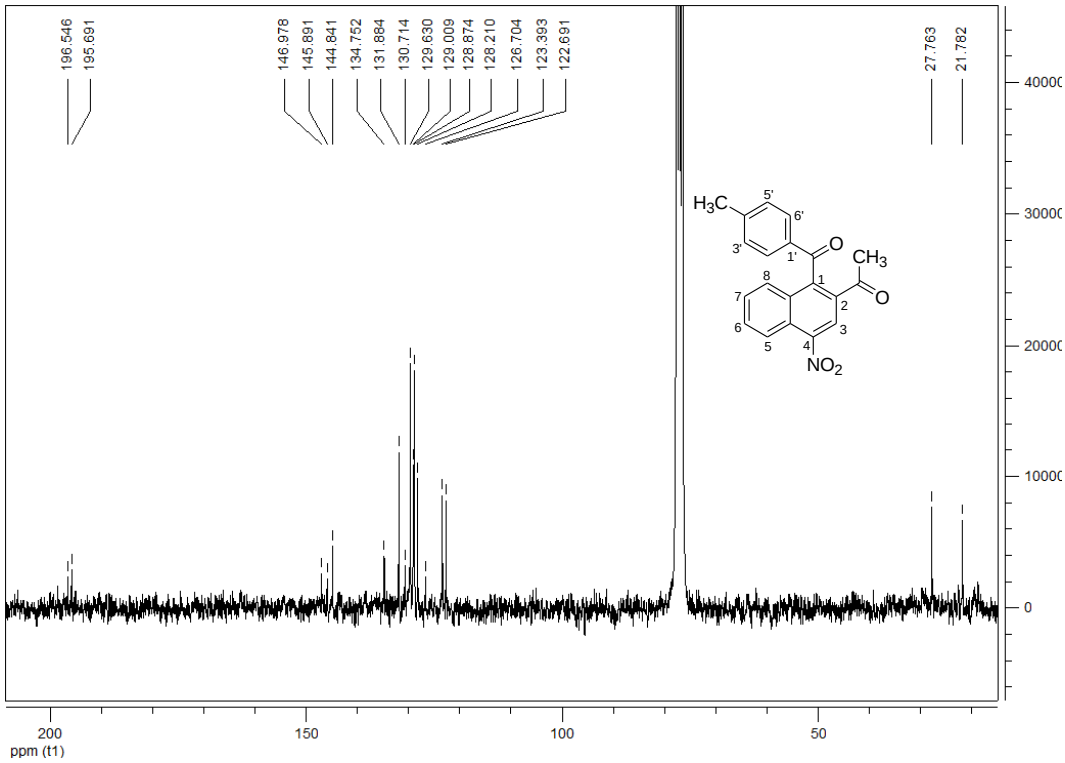
Elemental composition search on mass 386.1104
(Isotopes N-14, O-16, C-12, H-1, Na-23)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
386.1104	386.1103	0.16	11.5	C21 H19 O2 N Na3
386.1098	1.59	14.0		C18 H15 O3 N6 Na
386.1098	1.61	1.0		C6 H18 O4 N10 Na4
386.1111	-1.87	0.5		C8 H20 O5 N7 Na4
386.1111	-1.88	13.5		C20 H17 O4 N3 Na
386.1095	2.31	12.5		C17 H16 O6 N5

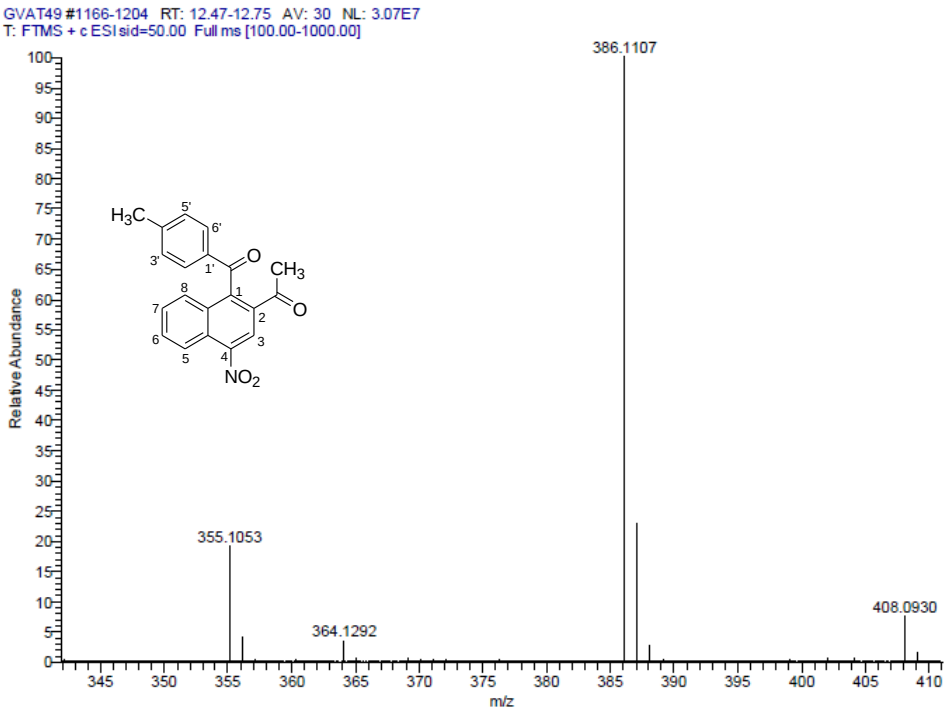
HRMS (ESI) of **4b**



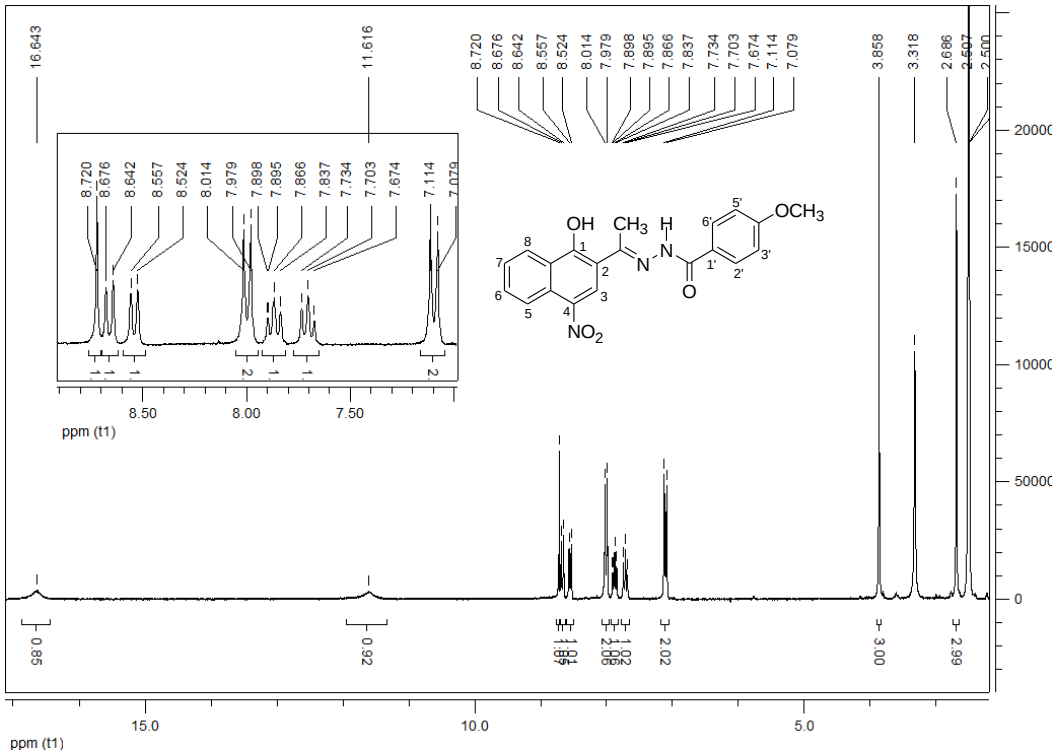
^{1}H NMR spectrum of **5b** (250 MHz, $CDCl_3$)



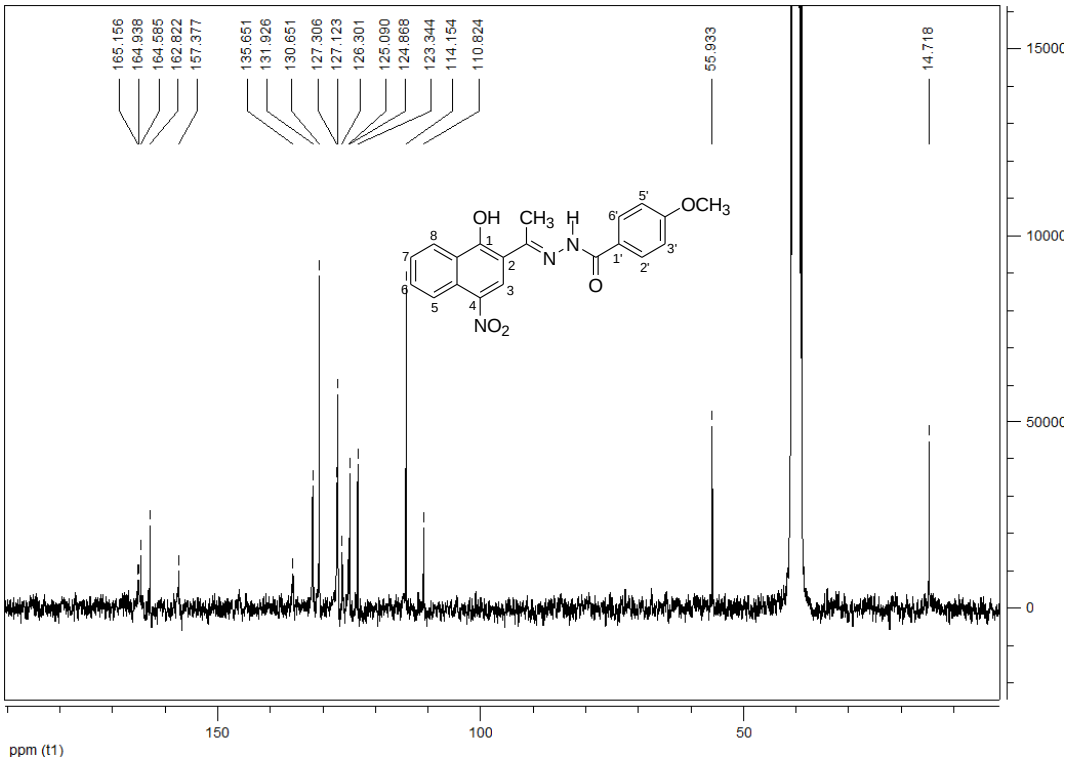
^{13}C NMR spectrum of **5b** (63 MHz, $CDCl_3$)



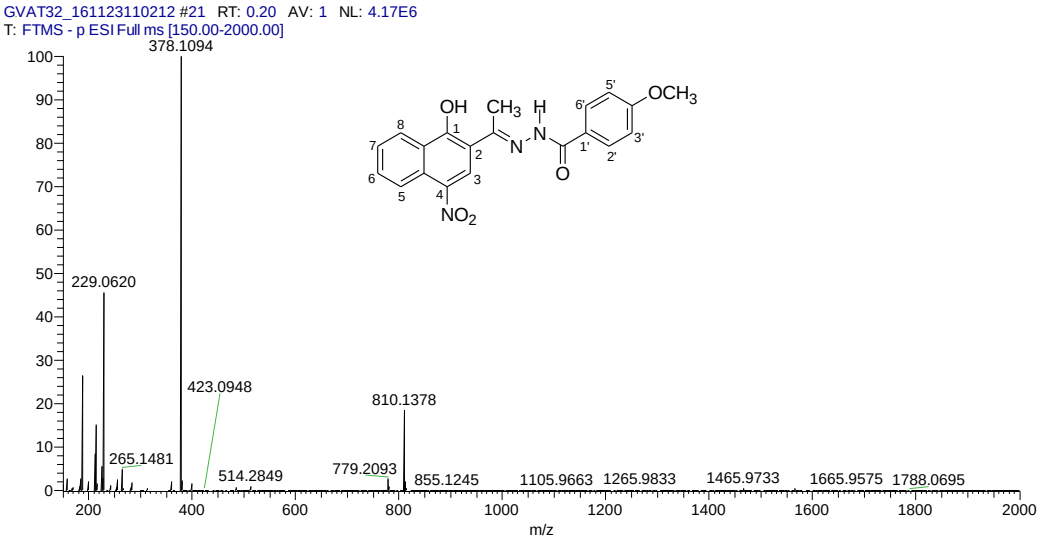
HRMS (ESI) of **5b**



^{1}H NMR spectrum of **4c** (250 MHz, DMSO-d_6)



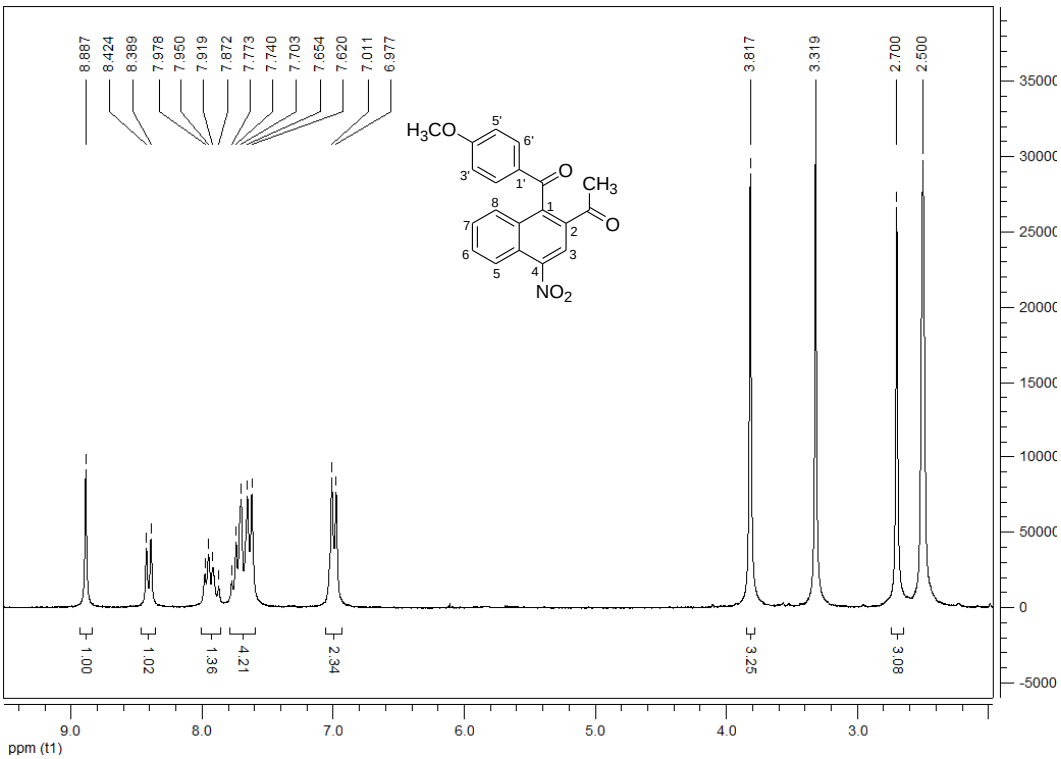
^{13}C NMR spectrum of **4c** (63 MHz, DMSO-d_6)



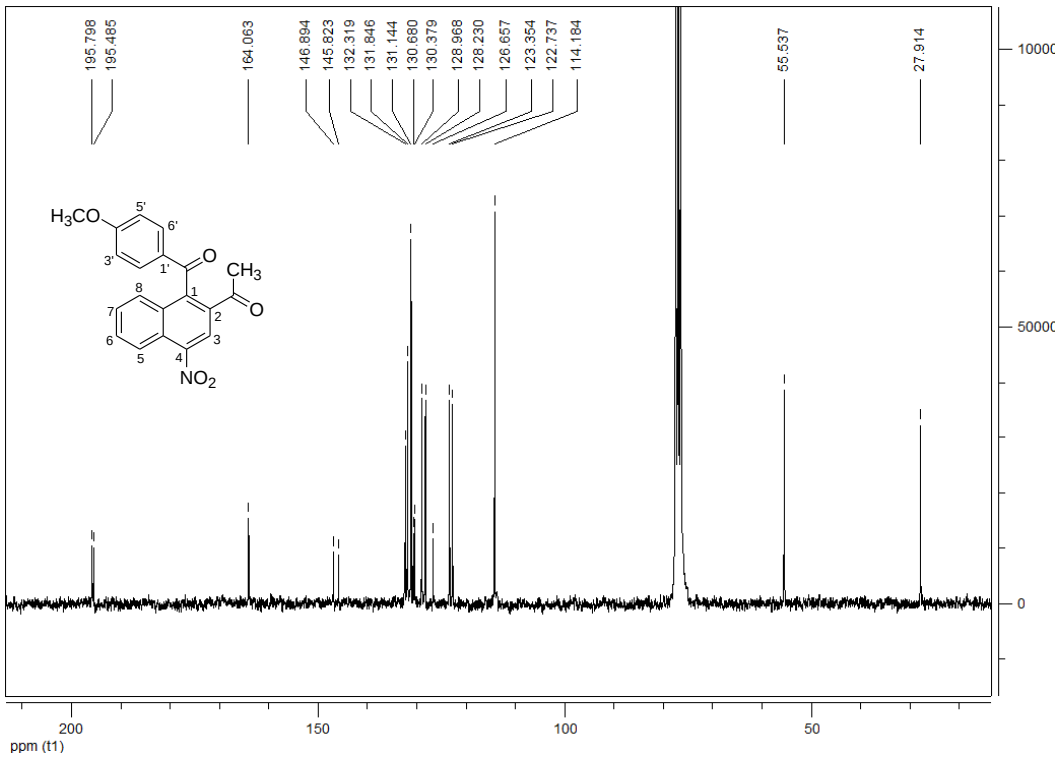
Elemental composition search on mass 378.1094
(Isotopes N-14, C-12, H-1, O-16)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
378.1094	378.1095	-0.27	14.5	C20 H16 O5 N3

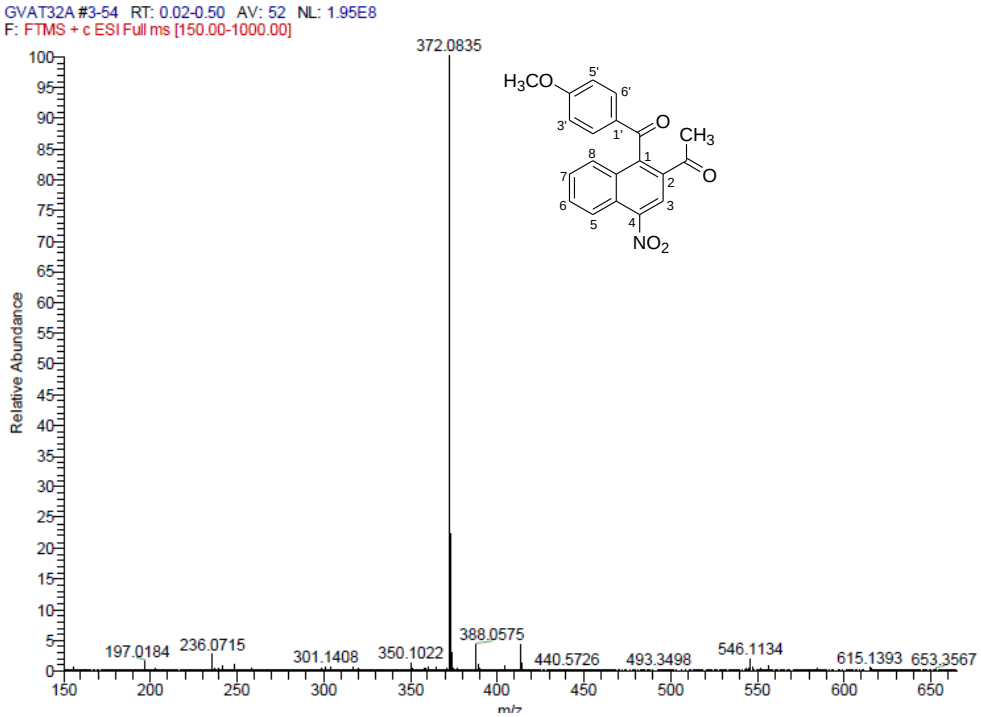
HRMS (ESI) of **4c**

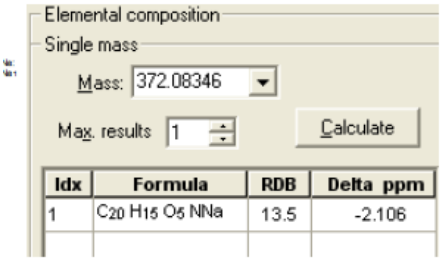


^{1}H NMR spectrum of **5c** (250 MHz, DMSO-d_6)



^{13}C NMR spectrum of **5c** (63 MHz, DMSO-d_6)




Elemental composition

Single mass

Mass: 372.08346

Max. results 1

Calculate

Idx	Formula	RDB	Delta ppm
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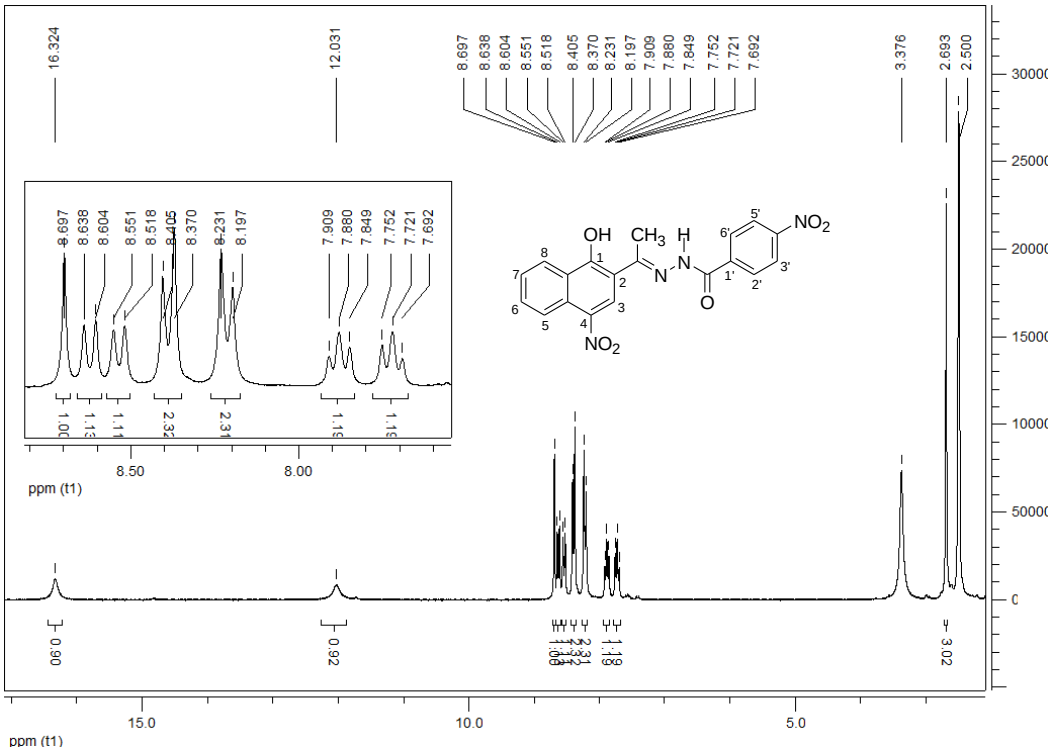
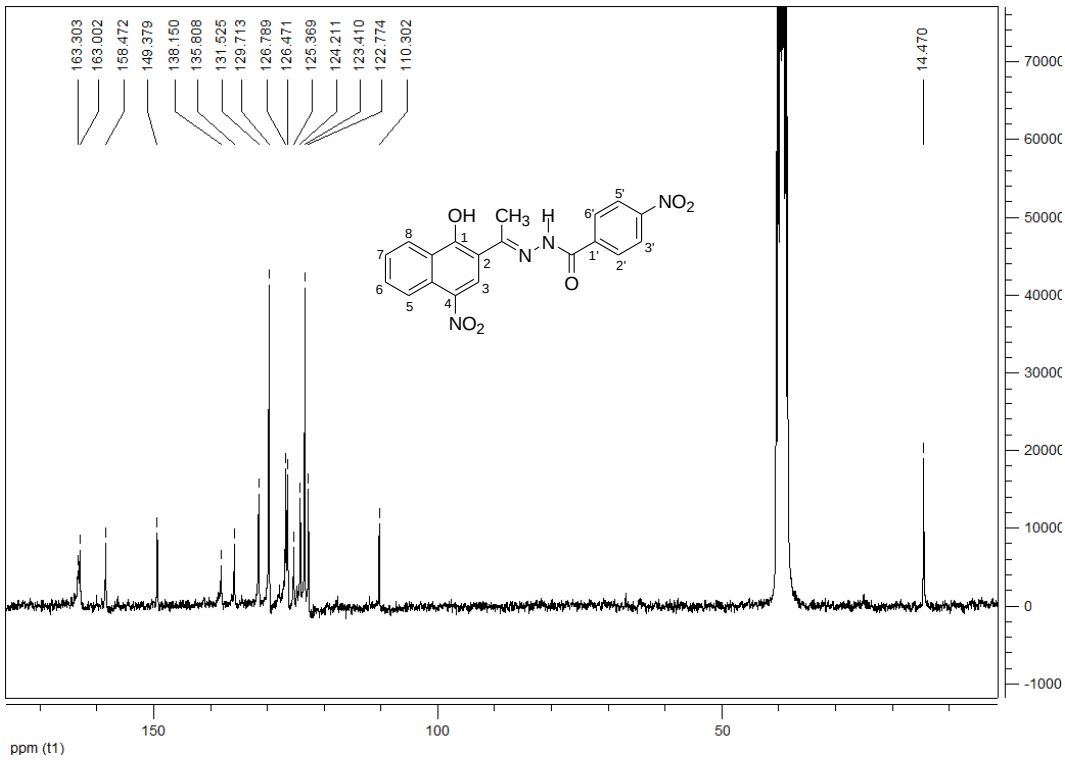
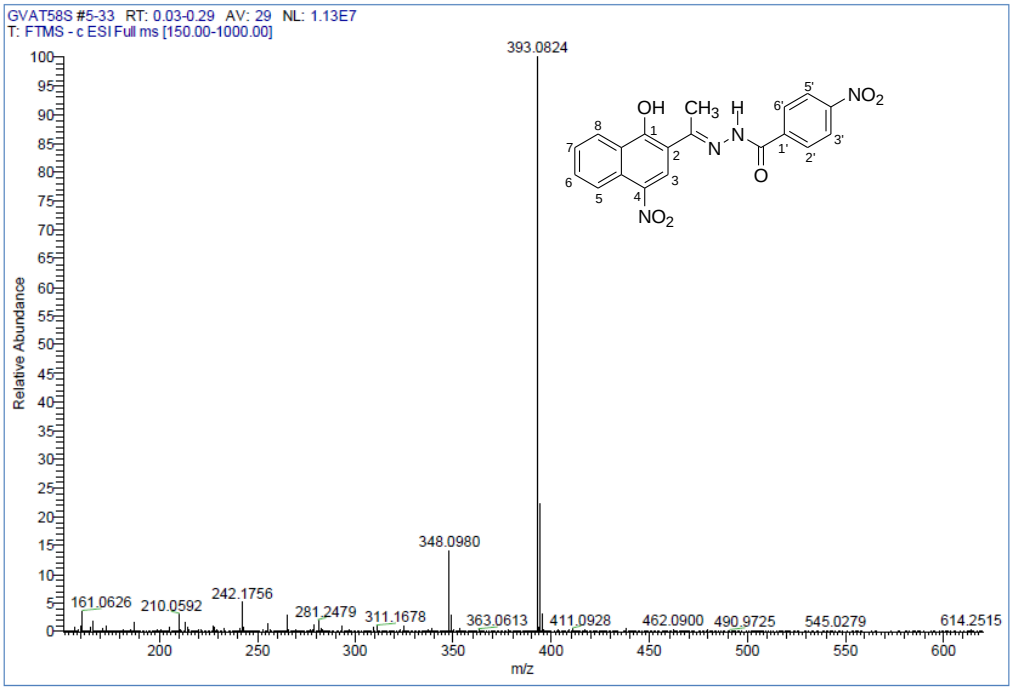
HRMS (APCI) of **5c**

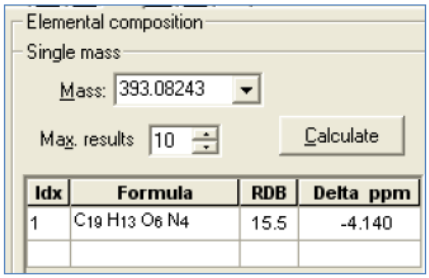


^{1}H NMR spectrum of **4d** (250 MHz, DMSO-d_6)

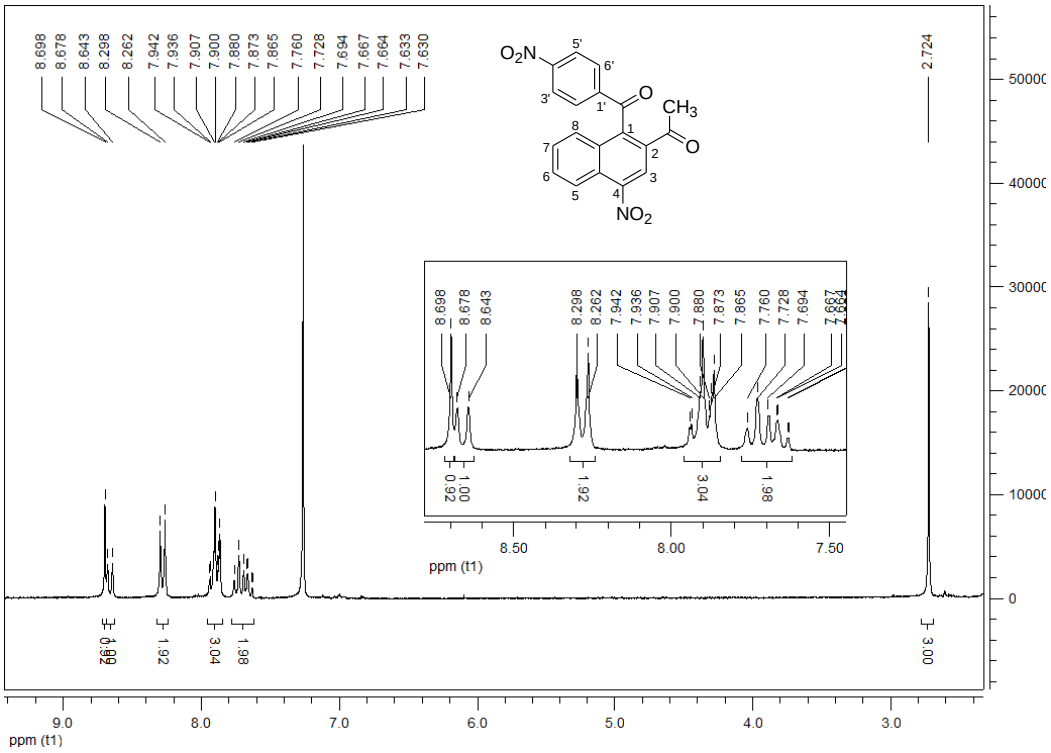


^{13}C NMR spectrum of **4d** (63 MHz, DMSO-d_6)

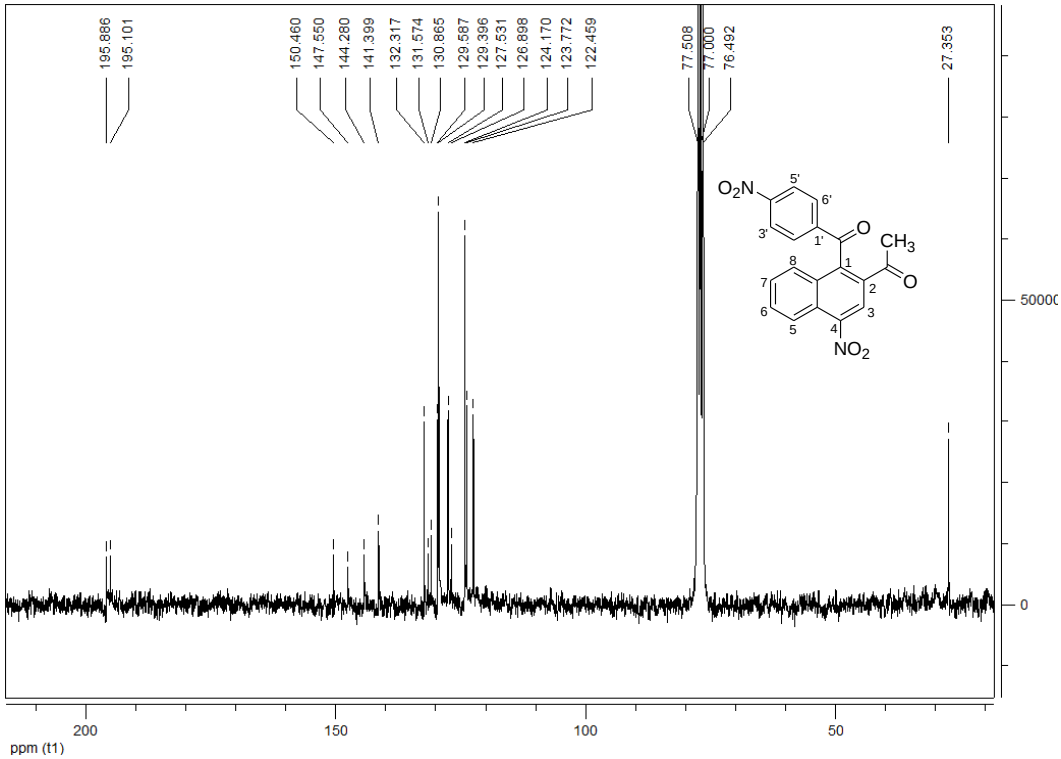




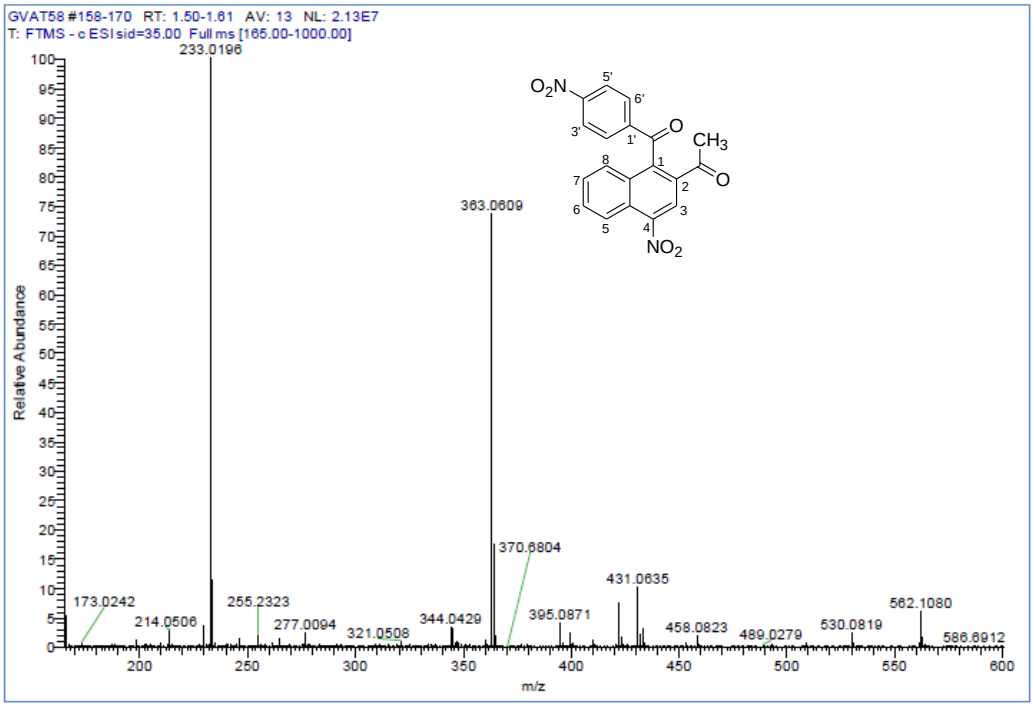
HRMS (APCI) of **4d**

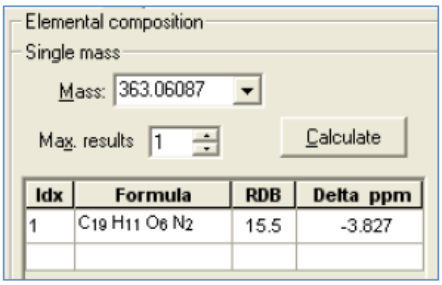


^{1}H NMR spectrum of **5d** (250 MHz, $CDCl_3$)

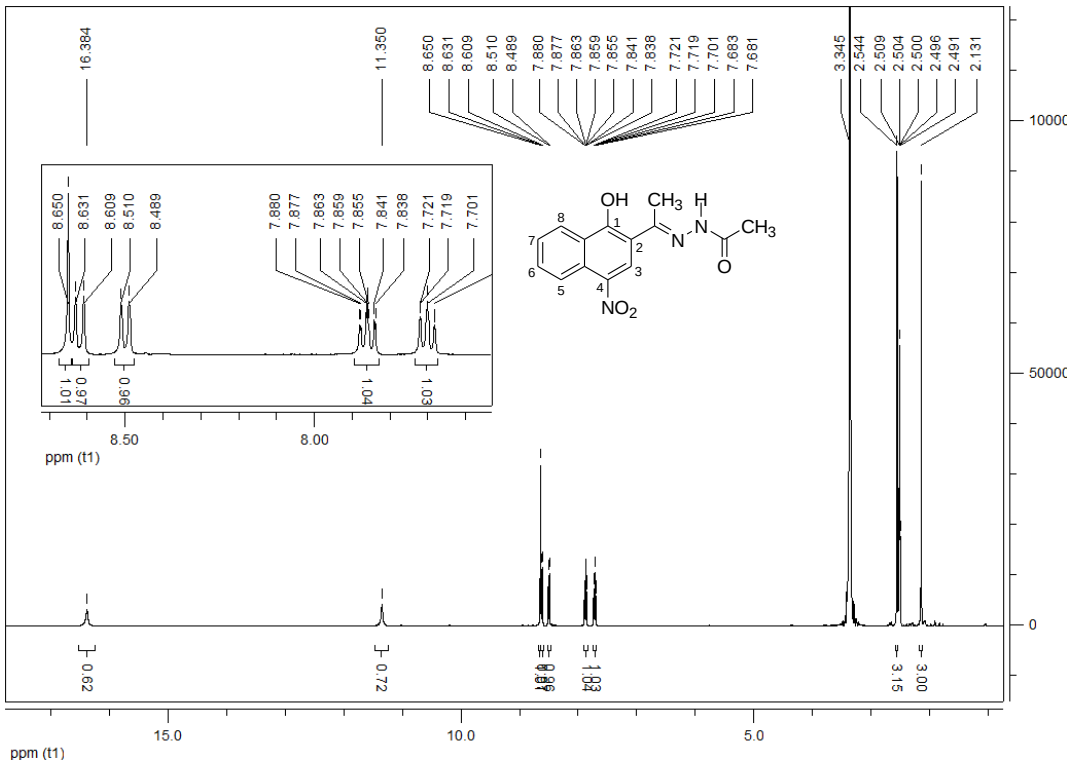


^{13}C NMR spectrum of **5d** (63 MHz, $CDCl_3$)

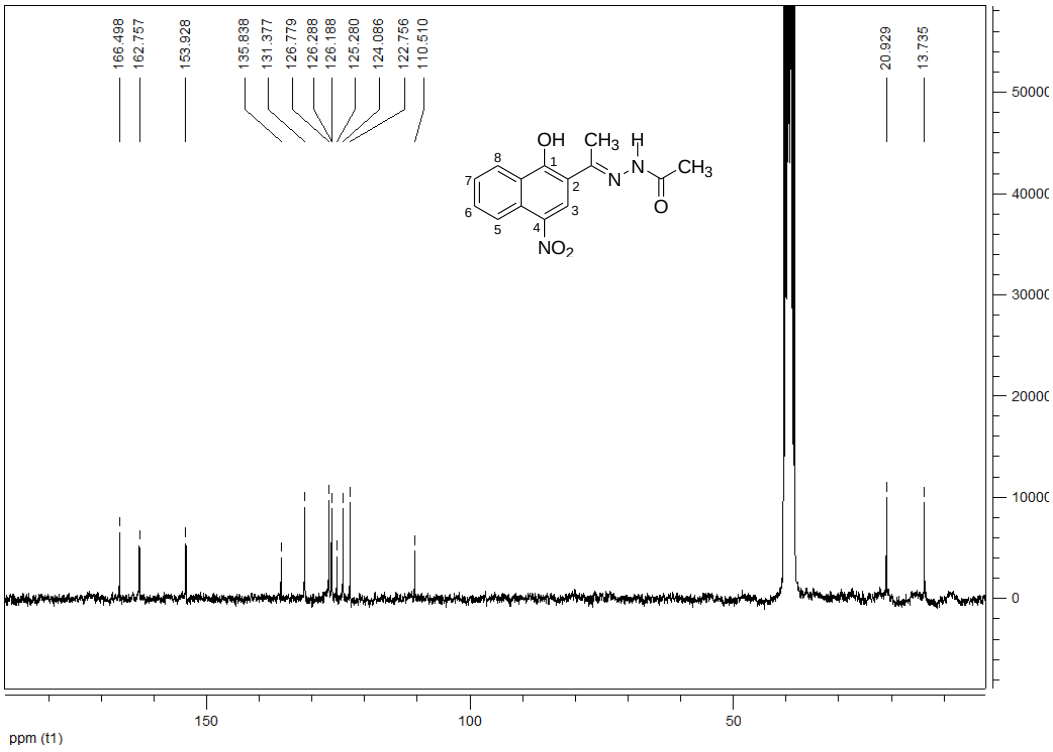




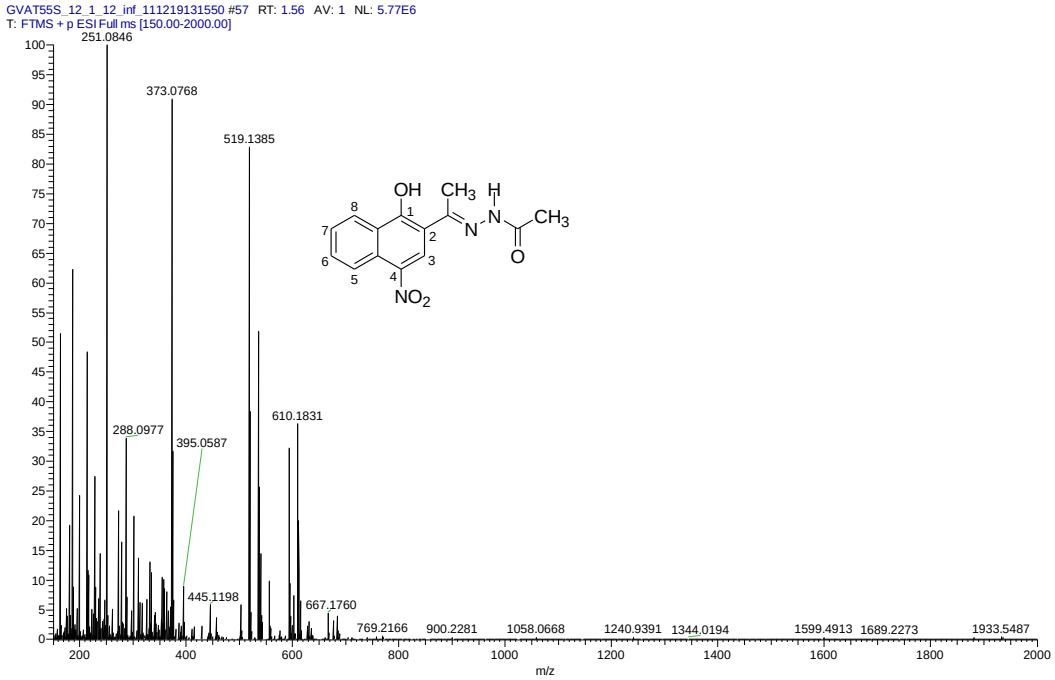
HRMS (APCI) of **5d**



^{1}H NMR spectrum of **4e** (400 MHz, DMSO-d_6)



^{13}C NMR spectrum of **4e** (100.6 MHz, DMSO-d_6)

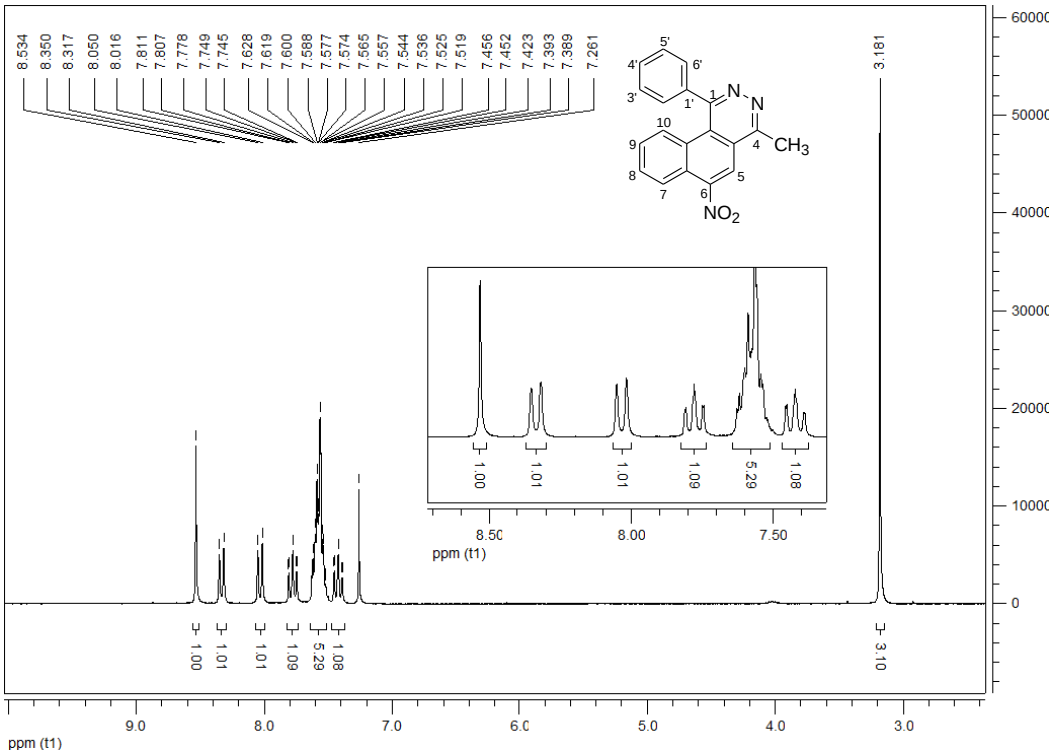


Elemental composition search on mass 288.0977

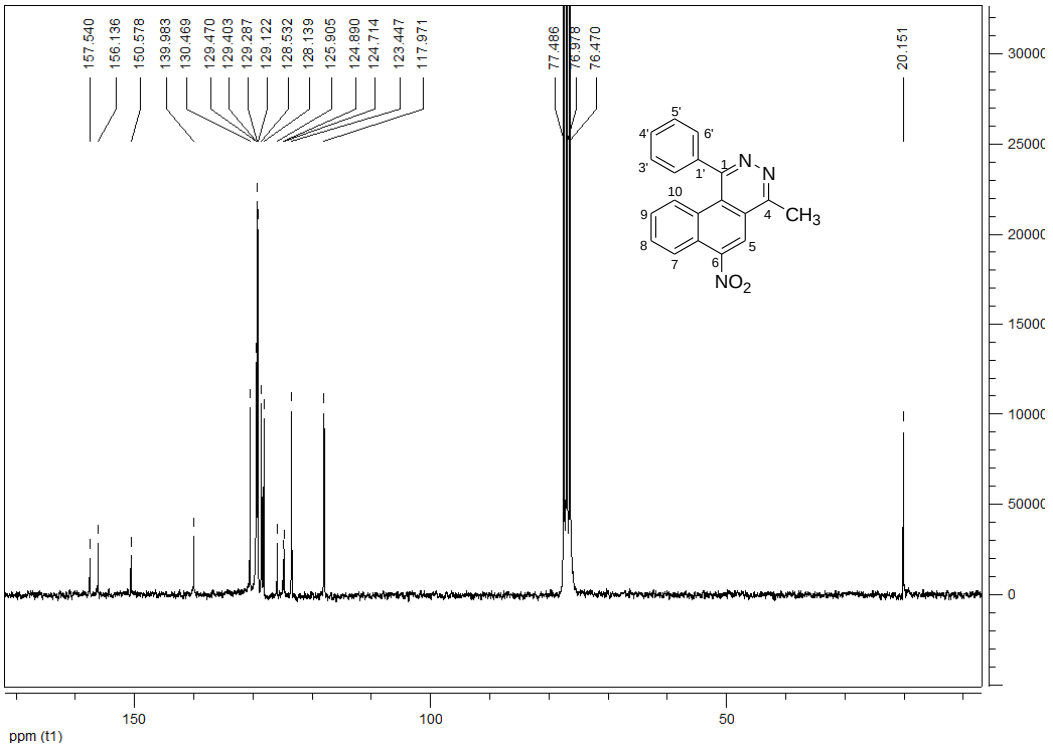
(Isotopes N-14, O-16, C-12, H-1)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
288.0977	288.0979	-0.63	9.5	C14 H14 O4 N3
288.0965		4.03	10.0	C12 H12 O3 N6

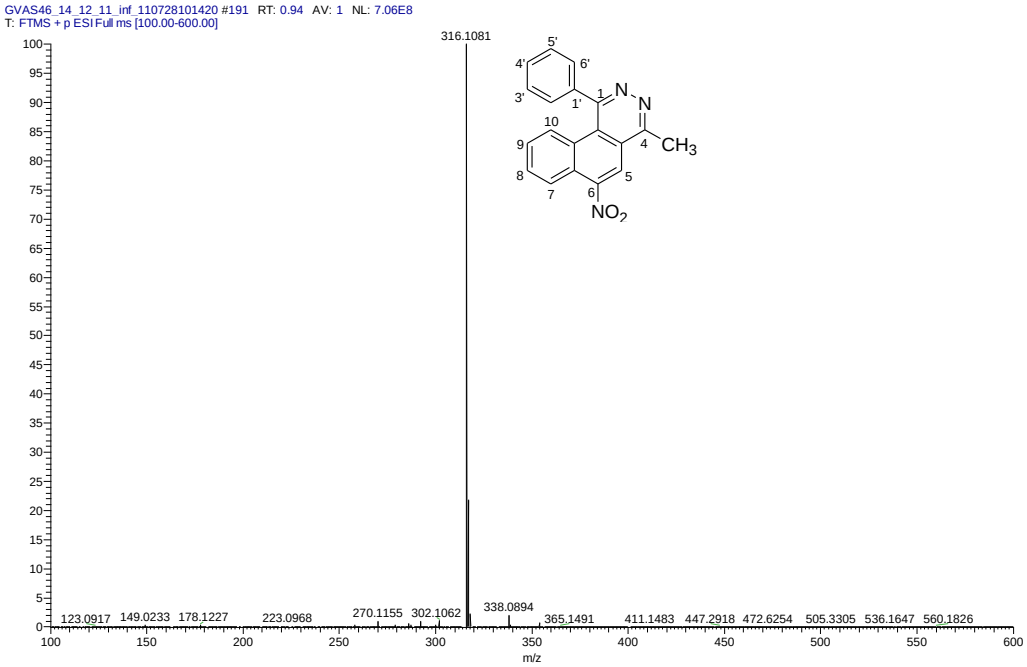
HRMS (ESI) of **4e**



^{1}H NMR spectrum of **7a** (250 MHz, $CDCl_3$)



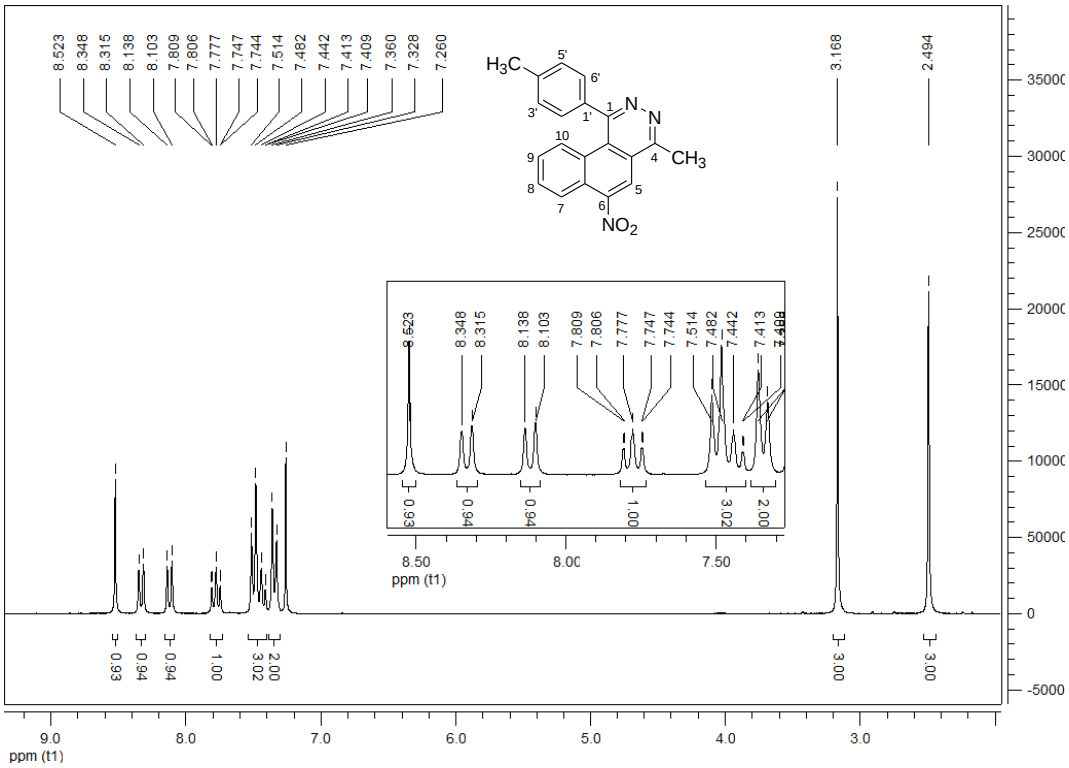
^{13}C NMR spectrum of **7a** (63 MHz, $CDCl_3$)



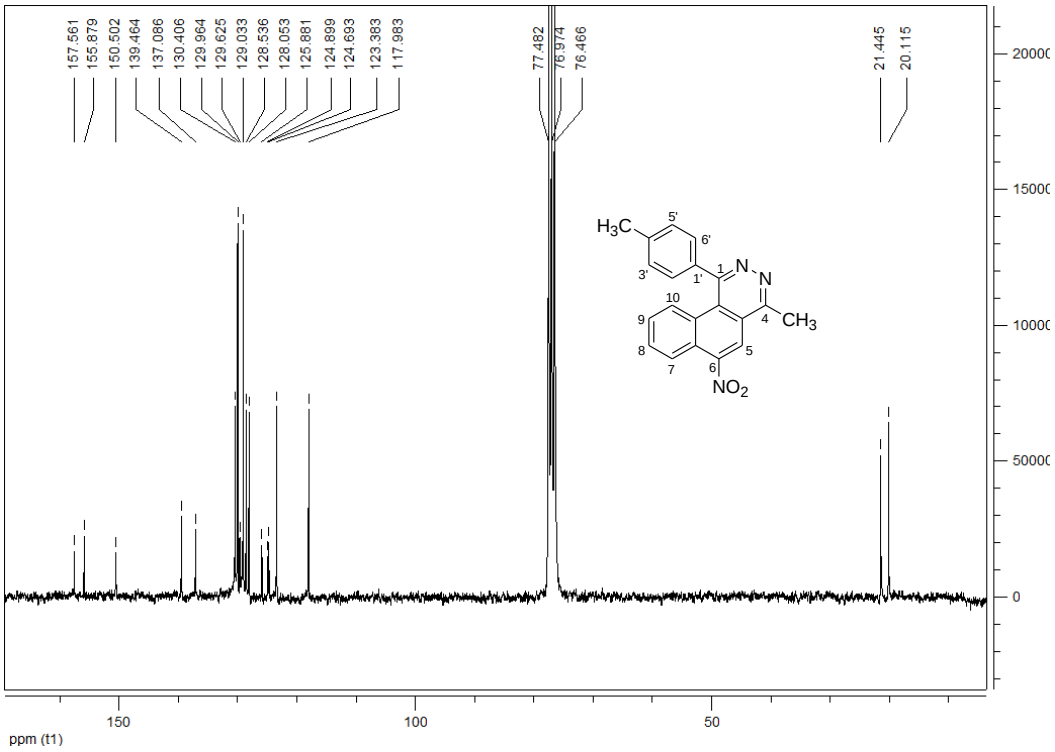
<u>Elemental composition search on mass 316.1081</u>
(Isotopes O-16, C-12, H-1, N-14)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
316.1081	316.1081	0.15	14.5	C19 H14 O2 N3
316.1086		-1.46	2.0	C5 H16 O8 N8
316.1094		-4.10	14.0	C21 H16 O3
316.1067		4.40	15.0	C17 H12 O N6

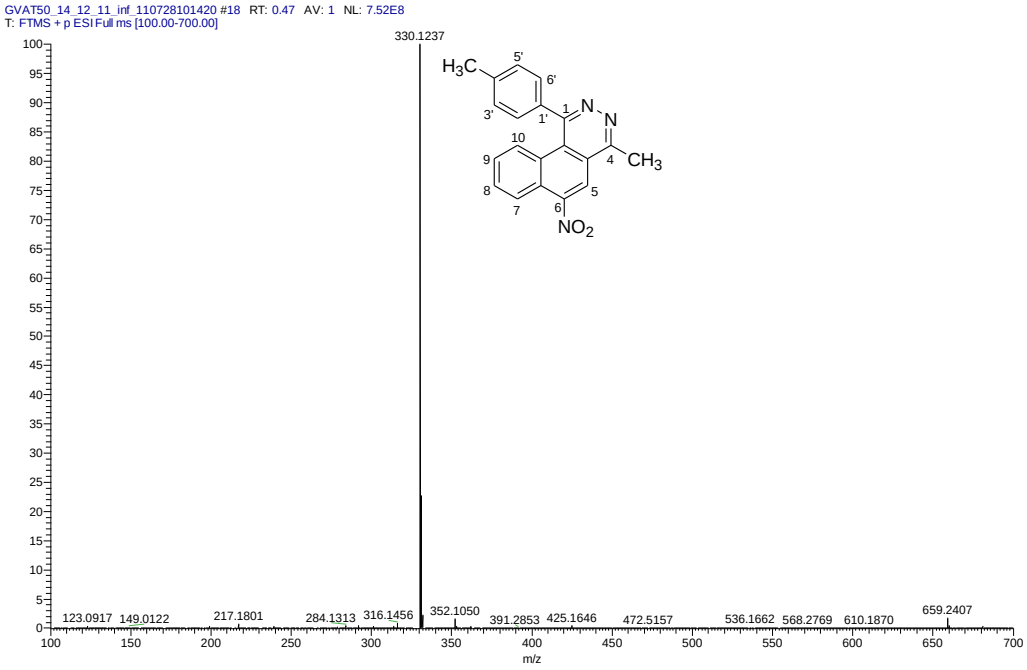
HRMS (ESI) of **7a**



^{1}H NMR spectrum of **7b** (250 MHz, $CDCl_3$)



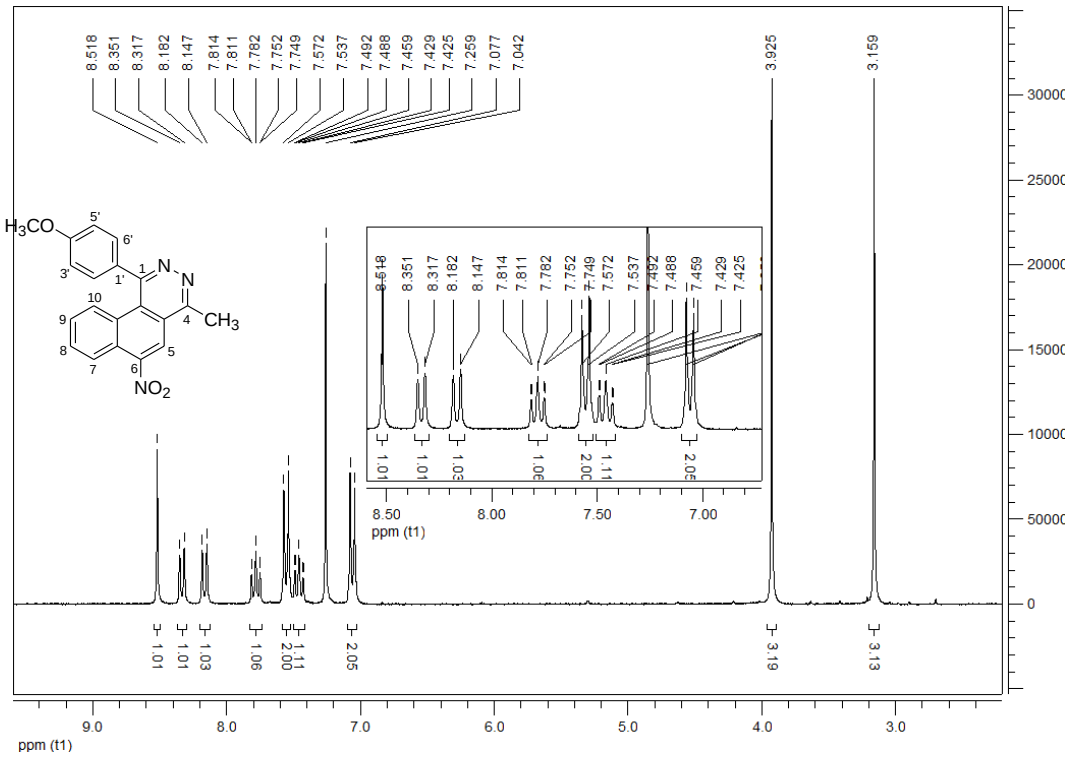
^{13}C NMR spectrum of **7b** (63 MHz, $CDCl_3$)



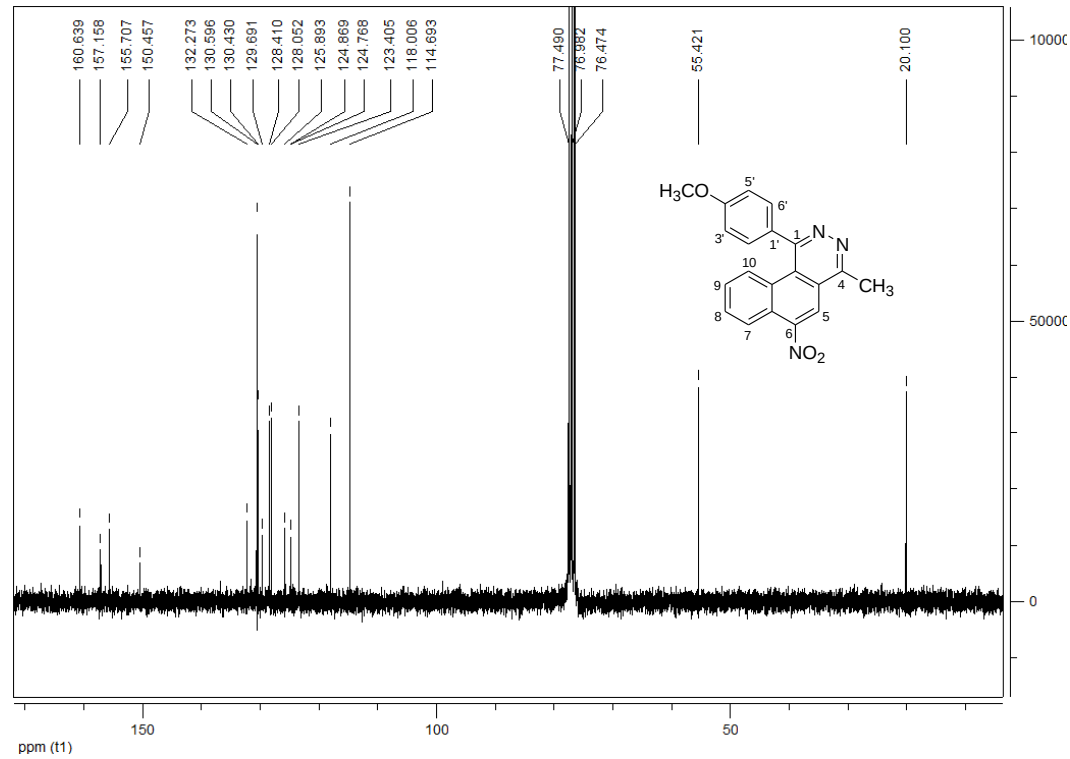
Elemental composition search on mass 330.1237
(Isotopes O-16, C-12, H-1, N-14)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
330.1237	330.1237	-0.01	14.5	C20 H16 O2 N3
	330.1242	-1.55	2.0	C6 H18 O8 N8
	330.1224	4.06	15.0	C18 H14 O N6
	330.1250	-4.08	14.0	C22 H18 O3

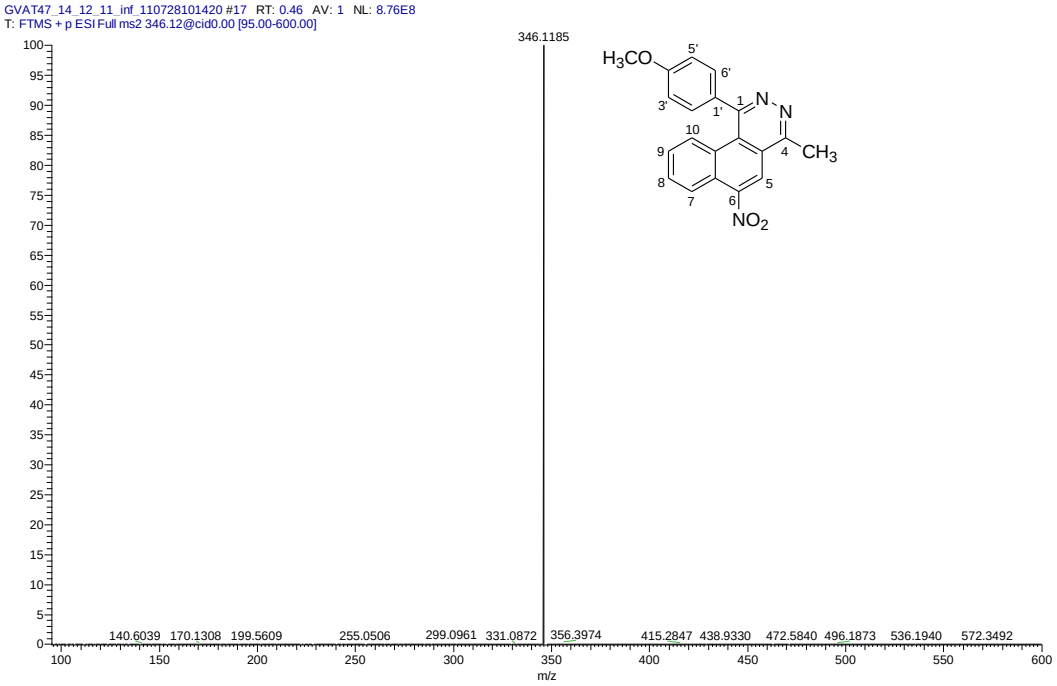
HRMS (ESI) of **7b**



^{1}H NMR spectrum of **7c** (250 MHz, $CDCl_3$)



^{13}C NMR spectrum of **7c** (63 MHz, $CDCl_3$)

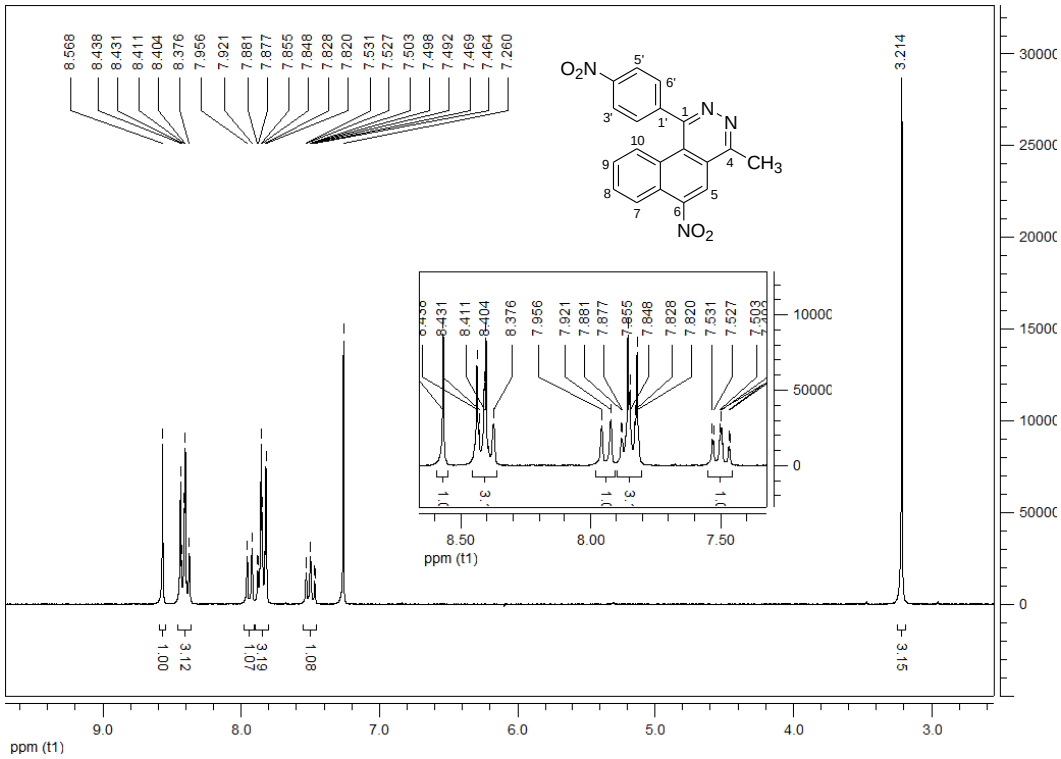


Elemental composition search on mass 346.1185

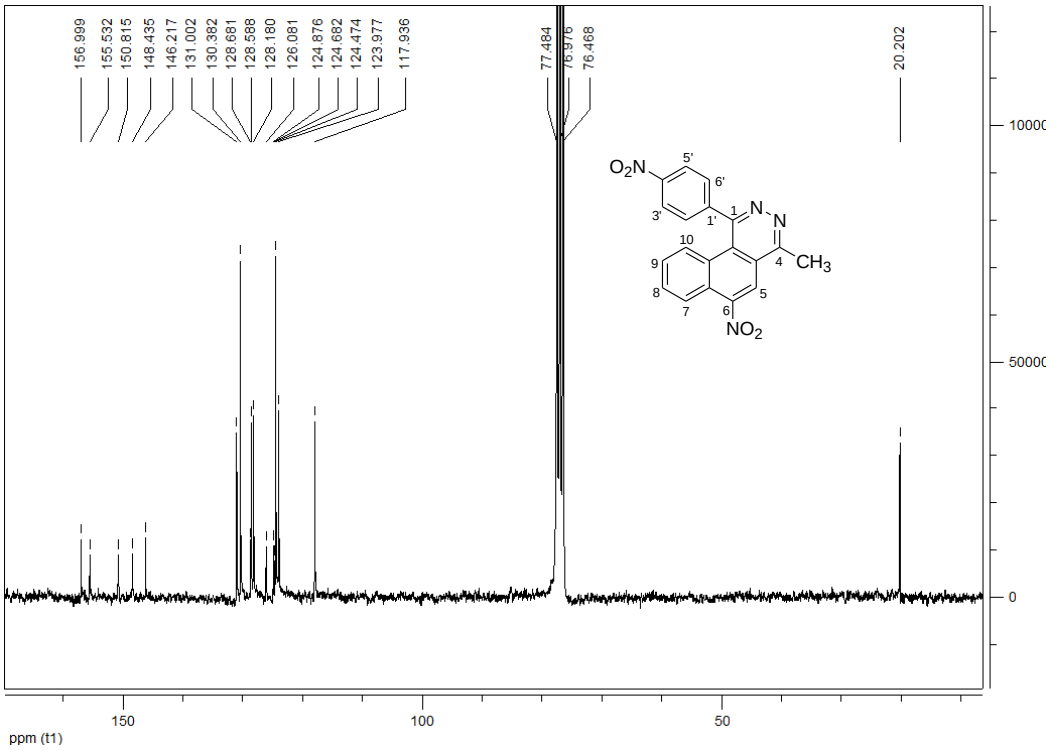
(Isotopes O-16, C-12, H-1, N-14)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
346.1185	346.1186	-0.34	14.5	C20 H16 O3 N3
	346.1191	-1.81	2.0	C6 H18 O9 N8
	346.1173	3.54	15.0	C18 H14 O2 N6
	346.1200	-4.22	14.0	C22 H18 O4

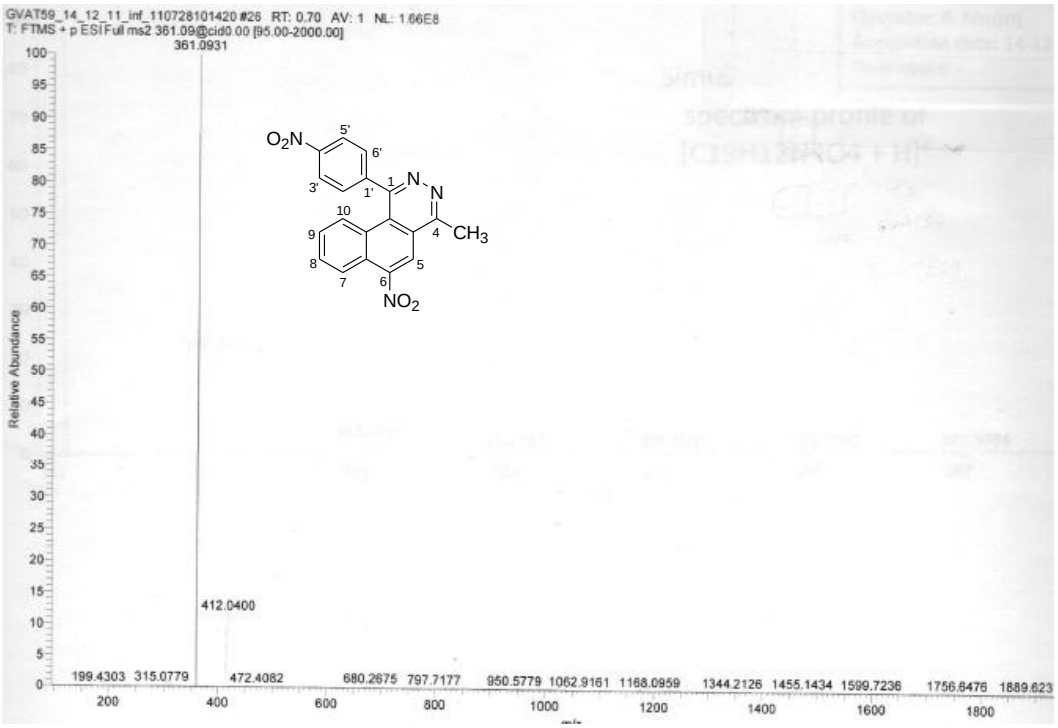
HRMS (ESI) of **7c**



^{1}H NMR spectrum of **7d** (250 MHz, $CDCl_3$)



^{13}C NMR spectrum of **7d** (63 MHz, $CDCl_3$)



Elemental composition search on mass 361.0931
(Isotopes O-16, C-12, H-1, N-14)

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
361.0931	361.0931	-0.09	15.5	C19 H13 O4 N4
	361.0936	-1.49	3.0	C5 H15 O10 N9
	361.0918	3.62	10.5	C18 H17 O8
	361.0918	3.63	16.0	C17 H11 O3 N7
	361.0945	-3.79	20.5	C20 H9 N8
	361.0945	-3.81	15.0	C21 H15 O5 N

HRMS (ESI) of **7d**

X-Ray Crystallography Information

X-ray diffraction experiments

Crystal structures were determined on a Bruker SMART 6000 diffractometer at 100(2)K using CuKα radiation (λ = 1.54178 Å). Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using least-squares minimization on F2. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance.

Crystal data for 5a. $C_{19}H_{13}NO_4$ (M = 319.30 g/mol), monoclinic, space group P21/c (no. 14), a = 9.2487(4)Å, b = 34.4391(13)Å, c = 9.2838(4)Å, β = 92.429(3), V = 2954.4(2)Å3, Z = 8, μ(CuKα) = 0.841 mm-1, F(000) = 1328, Dcalc = 1.436 g/cm^3, 28245 reflections measured (5.132 ≤ 2Θ ≤ 133.19), 5109 unique (Rint = 0.1306, Rsigma = 0.0807) which were used in all calculations. The final R1 was 0.0600 (I > 2σ(I)) and wR2 was 0.1363 (all data), data/parameters: 5109/435, largest difference peak and hole: 0.23 and -0.23 e Å−3.

Crystal data for 6. $C_{12}H_8N_2O_3$ (M = 228.20 g/mol), monoclinic, space group P21/n (no. 14), a = 13.9799(16)Å, b = 3.7383(4)Å, c = 18.894(2)Å, β = 99.269(4), V = 974.52(18)Å3, Z = 4, μ(CuKα) = 0.961 mm-1, F(000) = 472, Dcalc = 1.555 g/cm^3, 6561 reflections measured (7.33 ≤ 2Θ ≤ 109.494), 1194 unique (Rint = 0.0915, Rsigma = 0.0632) which were used in all calculations. The final R1 was 0.0488 (I > 2σ(I)) and wR2 was 0.1195 (all data), data/parameters: 1194/155, largest difference peak and hole: 0.20 and −0.22 e Å−3.

CCDC 1519801-1519802 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst*. **2009**, *42*, 339–341.
2. Sheldrick, G.M. *Acta Cryst*. **2008**, *A64*, 112–122.
3. Sheldrick, G.M. *Acta Cryst*. **2015**, *C71*, 3–8.

X-ray data collection and structure refinement

Crystallographic data for 5a

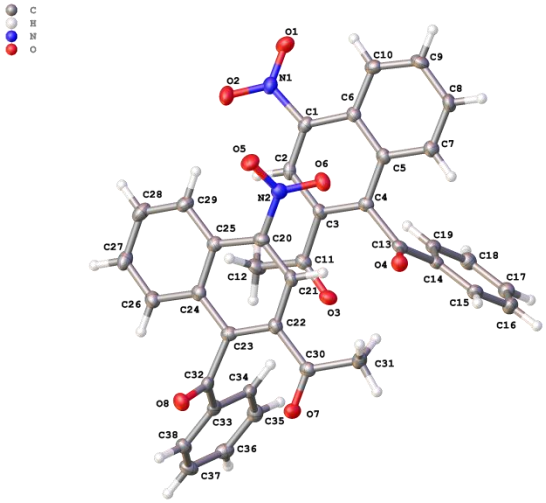


Table 1. Crystal data and structure refinement for **5a**

Identification code	CCDC 1519801
Empirical formula	$C_{13.82}H_{9.45}N_{0.73}O_{2.91}$
Formula weight	232.22
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.2487(4)
b/Å	34.4391(13)
c/Å	9.2838(4)
α/°	90
β/°	92.429(3)
γ/°	90
Volume/Å^3	2954.4(2)
Z	11
ρ_{calc}g/cm^3	1.436
μ/mm^{-1}	0.841
F(000)	1328.0
Crystal size/mm^3	0.45 × 0.15 × 0.08
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.132 to 133.19
Index ranges	-11 ≤ h ≤ 11, -40 ≤ k ≤ 40, -11 ≤ l ≤ 11
Reflections collected	28245
Independent reflections	5109 [R_{int} = 0.1306, R_{sigma} = 0.0807]
Data/restraints/parameters	5109/0/435
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0600, wR_2 = 0.1227
Final R indexes [all data]	R_1 = 0.0974, wR_2 = 0.1363
Largest diff. peak/hole / e Å^{-3}	0.23/-0.23

Table 2. Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for **5a.** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
C1	9910(3)	664.0(8)	1650(3)	18.9(7)
C2	9050(3)	915.2(8)	2344(3)	17.7(6)
C3	8210(3)	1192.5(9)	1580(3)	18.4(6)
C4	8214(3)	1195.3(8)	86(3)	17.6(6)
C5	9123(3)	936.7(9)	-657(3)	19.0(7)
C6	10036(3)	666.3(8)	115(3)	17.8(6)
C7	9159(3)	947.4(9)	-2186(3)	22.0(7)
C8	10068(3)	712.5(9)	-2911(3)	23.9(7)
C9	10963(3)	448.2(9)	-2144(3)	24.8(7)
C10	10950(3)	420.7(9)	-677(3)	21.6(7)

C11	7367(3)	1491.3(9)	2366(3)	20.3(7)
C12	7595(4)	1517.3(10)	3976(3)	26.8(7)
C13	7236(3)	1462.3(9)	-840(3)	19.3(7)
C14	7855(3)	1838.5(9)	-1317(3)	17.9(6)
C15	7138(3)	2044.8(9)	-2434(3)	20.9(7)
C16	7713(4)	2388.0(9)	-2918(3)	25.8(7)
C17	8992(3)	2531.4(9)	-2283(3)	23.5(7)
C18	9704(4)	2331.1(9)	-1182(3)	23.2(7)
C19	9140(3)	1981.1(9)	-704(3)	19.7(7)
C20	5099(3)	627.2(8)	1906(3)	19.2(7)
C21	4269(3)	883.3(9)	1136(3)	19.9(7)
C22	3386(3)	1150.2(9)	1840(3)	19.1(6)
C23	3366(3)	1146.8(8)	3336(3)	19.0(6)
C24	4298(3)	892.3(9)	4156(3)	19.2(7)
C25	5211(3)	622.9(8)	3444(3)	18.9(6)
C26	4390(4)	906.1(9)	5695(3)	22.7(7)
C27	5334(4)	675.7(9)	6463(3)	25.7(7)
C28	6246(4)	417.0(9)	5756(3)	27.0(7)
C29	6186(3)	391.1(9)	4281(3)	22.9(7)
C30	2474(3)	1437.4(9)	1014(3)	19.6(7)
C31	2607(3)	1462.3(10)	-599(3)	25.2(7)
C32	2370(3)	1401.9(9)	4189(3)	19.6(7)
C33	2895(3)	1791.1(9)	4677(3)	19.3(7)
C34	4082(3)	1964.8(9)	4058(3)	19.6(7)
C35	4563(4)	2323.5(9)	4536(3)	23.9(7)
C36	3889(3)	2509.8(9)	5651(3)	23.4(7)
C37	2717(4)	2335.9(10)	6276(3)	25.1(7)
C38	2215(3)	1979.7(9)	5793(3)	21.3(7)
N1	10762(3)	396.5(7)	2592(3)	21.7(6)
N2	5893(3)	339.6(7)	1080(3)	20.9(6)
O1	11937(2)	280.7(7)	2204(2)	28.8(5)
O2	10254(3)	306.7(6)	3749(2)	30.0(6)
O3	6550(2)	1708.5(6)	1701(2)	24.8(5)
O4	6060(2)	1346.3(6)	-1273(2)	22.6(5)
O5	5967(2)	4.7(6)	1542(2)	28.1(5)
O6	6433(2)	445.7(6)	-39(2)	25.4(5)
O7	1656(2)	1652.1(6)	1644(2)	24.4(5)
O8	1232(2)	1265.5(6)	4569(2)	24.0(5)

Table 3. Anisotropic displacement parameters ($Å^2×10^3$) for EV14. 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}
C1	19.8(16)	16.3(15)	20.5(16)	2.7(12)	-2.8(13)	-2.9(12)
C2	19.9(16)	19.3(16)	13.6(14)	0.5(11)	-1.1(13)	-7.8(12)
C3	18.6(16)	21.7(16)	15.0(15)	-2.8(12)	1.7(13)	-2.1(12)
C4	13.8(15)	17.7(15)	21.3(16)	-0.7(12)	1.5(13)	-1.5(12)
C5	18.6(16)	19.4(16)	19.3(15)	-0.2(12)	3.0(13)	-3.0(12)
C6	19.1(15)	16.4(15)	18.2(15)	-1.1(12)	2.6(13)	-2.0(12)
C7	23.3(17)	23.0(17)	19.6(16)	-0.9(13)	1.4(14)	0.3(13)
C8	29.1(18)	27.9(18)	15.0(15)	0.7(13)	5.0(14)	0.0(14)
C9	23.9(17)	22.9(17)	28.1(17)	-5.2(14)	8.4(15)	4.1(13)
C10	19.7(16)	17.9(16)	27.4(17)	1.6(13)	2.7(14)	1.5(12)
C11	18.8(16)	21.2(16)	21.2(16)	-3.2(13)	3.1(14)	-1.4(13)
C12	26.7(18)	31.3(19)	22.4(16)	-7.1(14)	2.0(15)	5.5(14)
C13	17.6(17)	22.7(17)	17.9(15)	-4.6(12)	3.3(14)	3.2(12)
C14	17.7(15)	18.6(15)	17.5(15)	-0.9(12)	3.4(13)	3.1(12)
C15	16.1(16)	26.8(17)	19.7(15)	-0.3(13)	-0.7(13)	3.0(13)
C16	24.2(18)	29.5(19)	23.9(17)	7.1(14)	2.1(15)	5.4(14)
C17	24.3(17)	21.3(17)	25.2(17)	0.0(13)	4.0(14)	0.0(13)
C18	22.1(17)	26.4(17)	21.2(16)	-2.4(13)	1.2(14)	-1.6(13)
C19	20.0(17)	21.9(17)	17.1(15)	-1.6(12)	1.0(13)	4.3(12)
C20	18.1(16)	16.5(15)	23.2(16)	-1.7(12)	2.4(14)	0.6(12)
C21	22.0(17)	21.7(16)	16.3(15)	0.1(12)	5.0(13)	-3.1(12)
C22	19.1(16)	20.3(16)	17.9(15)	-0.4(12)	2.4(13)	-1.9(12)
C23	17.7(15)	16.3(15)	22.9(16)	-1.1(12)	0.3(13)	-0.9(12)
C24	18.2(16)	18.7(16)	20.8(16)	0.8(12)	2.2(13)	-2.6(12)
C25	19.3(16)	16.0(15)	21.3(16)	-0.2(12)	0.0(14)	-2.0(12)
C26	27.7(18)	20.3(16)	20.5(16)	-1.0(12)	3.8(14)	-1.0(13)
C27	37(2)	21.0(17)	18.3(16)	1.1(13)	-4.6(15)	-2.4(14)
C28	31.5(19)	20.8(17)	27.8(18)	4.6(13)	-8.5(15)	0.3(14)
C29	24.6(17)	18.9(16)	25.0(17)	0.8(13)	-2.0(14)	2.9(13)
C30	17.3(16)	18.5(16)	23.2(16)	-1.0(12)	2.6(14)	-1.3(12)
C31	22.3(17)	30.8(18)	22.6(17)	7.6(14)	1.5(14)	3.7(14)
C32	19.9(17)	22.7(17)	15.9(15)	5.0(12)	-1.1(14)	1.1(13)
C33	20.7(16)	22.1(16)	14.8(15)	1.2(12)	-3.5(13)	1.6(12)
C34	22.8(17)	18.7(16)	17.5(15)	2.3(12)	2.1(14)	4.2(12)
C35	23.2(17)	26.4(17)	22.1(17)	1.8(13)	0.2(14)	-1.6(13)
C36	22.5(17)	20.9(16)	26.2(17)	-3.9(13)	-5.4(14)	2.4(13)
C37	24.2(18)	28.7(18)	22.5(17)	-7.6(14)	0.9(14)	5.4(14)
C38	17.1(15)	26.9(17)	20.0(16)	-0.5(13)	2.5(13)	1.8(13)
N1	25.5(15)	19.7(14)	20.0(14)	2.5(11)	1.0(12)	-2.0(11)
N2	20.1(14)	21.6(15)	20.8(14)	-1.4(11)	-1.1(12)	-0.4(11)
O1	23.6(12)	29.5(13)	33.3(13)	7.8(10)	0.1(11)	5(1)

O2	45.0(15)	26.3(13)	19.1(12)	3.6(9)	4.6(11)	4.9(11)
O3	25.2(12)	24.4(12)	25.0(12)	-3.7(9)	4.4(10)	5.3(10)
O4	19.5(12)	25.5(12)	22.7(12)	0.8(9)	0.4(10)	-0.4(9)
O5	35.6(13)	18.0(12)	30.7(12)	2.1(10)	2.8(11)	4.7(10)
O6	29.3(13)	25.6(12)	21.8(12)	-1.2(9)	6.6(10)	-3.1(10)
O7	25.3(12)	26.7(12)	21.0(11)	-0.7(9)	-0.9(10)	6.9(10)
O8	21.2(12)	28.1(12)	23.1(12)	0.8(9)	4.3(10)	-2.4(9)

Table 4. Bond lengths for **5a**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.357(4)	C20	N2	1.468(4)
C1	C6	1.434(4)	C21	C22	1.408(4)
C1	N1	1.475(4)	C22	C23	1.390(4)
C2	C3	1.404(4)	C22	C30	1.491(4)
C3	C4	1.387(4)	C23	C24	1.426(4)
C3	C11	1.499(4)	C23	C32	1.519(4)
C4	C5	1.423(4)	C24	C25	1.435(4)
C4	C13	1.528(4)	C24	C26	1.428(4)
C5	C6	1.429(4)	C25	C29	1.412(4)
C5	C7	1.422(4)	C26	C27	1.359(5)
C6	C10	1.423(4)	C27	C28	1.408(5)
C7	C8	1.365(4)	C28	C29	1.371(4)
C8	C9	1.403(5)	C30	C31	1.511(4)
C9	C10	1.366(5)	C30	O7	1.224(4)
C11	C12	1.503(4)	C32	C33	1.490(4)
C11	O3	1.213(4)	C32	O8	1.219(4)
C13	C14	1.491(4)	C33	C34	1.395(4)
C13	O4	1.212(4)	C33	C38	1.395(4)
C14	C15	1.400(4)	C34	C35	1.380(4)
C14	C19	1.385(4)	C35	C36	1.388(4)
C15	C16	1.379(4)	C36	C37	1.387(5)
C16	C17	1.390(5)	C37	C38	1.380(4)
C17	C18	1.377(5)	N1	O1	1.226(3)
C18	C19	1.393(4)	N1	O2	1.230(3)
C20	C21	1.354(4)	N2	O5	1.232(3)
C20	C25	1.427(4)	N2	O6	1.228(3)

Table 5. Bond angles for **5a**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	C1	C6	122.8(3)	C20	C21	C22	120.5(3)
C2	C1	N1	115.2(3)	C21	C22	C30	121.4(3)
C6	C1	N1	121.9(3)	C23	C22	C21	119.4(3)
C1	C2	C3	121.1(3)	C23	C22	C30	119.2(3)
C2	C3	C11	120.6(3)	C22	C23	C24	120.3(3)
C4	C3	C2	119.0(3)	C22	C23	C32	123.4(3)
C4	C3	C11	120.4(3)	C24	C23	C32	116.3(3)
C3	C4	C5	120.5(3)	C23	C24	C25	120.4(3)
C3	C4	C13	122.7(3)	C23	C24	C26	121.5(3)
C5	C4	C13	116.9(3)	C26	C24	C25	118.1(3)
C4	C5	C6	120.9(3)	C20	C25	C24	115.8(3)
C7	C5	C4	120.4(3)	C29	C25	C20	125.0(3)
C7	C5	C6	118.7(3)	C29	C25	C24	119.1(3)
C5	C6	C1	115.5(3)	C27	C26	C24	121.0(3)
C10	C6	C1	125.8(3)	C26	C27	C28	120.6(3)
C10	C6	C5	118.6(3)	C29	C28	C27	120.4(3)
C8	C7	C5	121.2(3)	C28	C29	C25	120.7(3)
C7	C8	C9	119.8(3)	C22	C30	C31	118.6(3)
C10	C9	C8	121.4(3)	O7	C30	C22	120.2(3)
C9	C10	C6	120.3(3)	O7	C30	C31	121.1(3)
C3	C11	C12	118.1(3)	C33	C32	C23	118.8(3)
O3	C11	C3	120.1(3)	O8	C32	C23	118.6(3)
O3	C11	C12	121.8(3)	O8	C32	C33	122.2(3)
C14	C13	C4	117.7(3)	C34	C33	C32	120.9(3)
O4	C13	C4	119.3(3)	C38	C33	C32	119.6(3)
O4	C13	C14	122.6(3)	C38	C33	C34	119.6(3)
C15	C14	C13	119.0(3)	C35	C34	C33	120.0(3)
C19	C14	C13	121.3(3)	C34	C35	C36	120.3(3)
C19	C14	C15	119.7(3)	C37	C36	C35	119.7(3)
C16	C15	C14	120.0(3)	C38	C37	C36	120.4(3)
C15	C16	C17	119.9(3)	C37	C38	C33	119.9(3)
C18	C17	C16	120.6(3)	O1	N1	C1	119.1(2)
C17	C18	C19	119.7(3)	O1	N1	O2	123.4(3)
C14	C19	C18	120.1(3)	O2	N1	C1	117.5(3)
C21	C20	C25	123.4(3)	O5	N2	C20	118.1(2)
C21	C20	N2	116.6(3)	O6	N2	C20	118.2(2)
C25	C20	N2	119.9(3)	O6	N2	O5	123.7(3)

Table 6. Torsion angles for **5a**

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C1	C2	C3	C4	3.1(4)	C21	C20	N2	O5	-140.2(3)
C1	C2	C3	C11	-174.5(3)	C21	C20	N2	O6	39.2(4)
C1	C6	C10	C9	179.3(3)	C21	C22	C23	C24	4.0(4)
C2	C1	C6	C5	-3.7(4)	C21	C22	C23	C32	-175.3(3)
C2	C1	C6	C10	177.8(3)	C21	C22	C30	C31	-5.3(4)
C2	C1	N1	O1	-150.0(3)	C21	C22	C30	O7	176.0(3)
C2	C1	N1	O2	28.7(4)	C22	C23	C24	C25	-3.3(4)
C2	C3	C4	C5	-3.8(4)	C22	C23	C24	C26	174.5(3)
C2	C3	C4	C13	174.6(3)	C22	C23	C32	C33	-91.0(4)
C2	C3	C11	C12	7.6(4)	C22	C23	C32	O8	96.1(4)
C2	C3	C11	O3	-173.8(3)	C23	C22	C30	C31	174.6(3)
C3	C4	C5	C6	0.7(4)	C23	C22	C30	O7	-4.1(4)
C3	C4	C5	C7	-178.2(3)	C23	C24	C25	C20	-0.8(4)
C3	C4	C13	C14	95.4(3)	C23	C24	C25	C29	176.2(3)
C3	C4	C13	O4	-91.9(4)	C23	C24	C26	C27	-176.7(3)
C4	C3	C11	C12	-169.9(3)	C23	C32	C33	C34	17.3(4)
C4	C3	C11	O3	8.7(4)	C23	C32	C33	C38	-161.1(3)
C4	C5	C6	C1	2.9(4)	C24	C23	C32	C33	89.6(3)
C4	C5	C6	C10	-178.5(3)	C24	C23	C32	O8	-83.2(4)
C4	C5	C7	C8	177.3(3)	C24	C25	C29	C28	1.1(5)
C4	C13	C14	C15	164.6(3)	C24	C26	C27	C28	0.0(5)
C4	C13	C14	C19	-13.7(4)	C25	C20	C21	C22	-3.9(5)
C5	C4	C13	C14	-86.2(3)	C25	C20	N2	O5	39.0(4)
C5	C4	C13	O4	86.5(3)	C25	C20	N2	O6	-141.6(3)
C5	C6	C10	C9	0.9(4)	C25	C24	C26	C27	1.1(5)
C5	C7	C8	C9	1.6(5)	C26	C24	C25	C20	-178.7(3)
C6	C1	C2	C3	0.8(5)	C26	C24	C25	C29	-1.6(4)
C6	C1	N1	O1	27.5(4)	C26	C27	C28	C29	-0.6(5)
C6	C1	N1	O2	-153.7(3)	C27	C28	C29	C25	0.1(5)
C6	C5	C7	C8	-1.7(5)	C30	C22	C23	C24	-175.9(3)
C7	C5	C6	C1	-178.2(3)	C30	C22	C23	C32	4.8(4)
C7	C5	C6	C10	0.4(4)	C32	C23	C24	C25	176.1(3)
C7	C8	C9	C10	-0.2(5)	C32	C23	C24	C26	-6.1(4)
C8	C9	C10	C6	-1.0(5)	C32	C33	C34	C35	-179.3(3)
C11	C3	C4	C5	173.8(3)	C32	C33	C38	C37	178.4(3)
C11	C3	C4	C13	-7.9(4)	C33	C34	C35	C36	1.3(5)
C13	C4	C5	C6	-177.7(3)	C34	C33	C38	C37	0.0(5)
C13	C4	C5	C7	3.4(4)	C34	C35	C36	C37	-0.8(5)
C13	C14	C15	C16	-178.3(3)	C35	C36	C37	C38	-0.2(5)
C13	C14	C19	C18	179.2(3)	C36	C37	C38	C33	0.6(5)
C14	C15	C16	C17	-0.9(5)	C38	C33	C34	C35	-1.0(5)
C15	C14	C19	C18	0.9(4)	N1	C1	C2	C3	178.3(3)

C15	C16	C17	C18	0.7(5)	N1	C1 C6 C5	178.9(3)
C16	C17	C18	C19	0.2(5)	N1	C1 C6 C10	0.4(5)
C17	C18	C19	C14	-1.1(4)	N2	C20 C21 C22	175.2(3)
C19	C14	C15	C16	0.1(4)	N2	C20 C25 C24	-174.7(3)
C20	C21	C22	C23	-0.5(5)	N2	C20 C25 C29	8.5(5)
C20	C21	C22	C30	179.4(3)	O4	C13 C14 C15	-7.8(4)
C20	C25	C29	C28	177.8(3)	O4	C13 C14 C19	173.8(3)
C21	C20	C25	C24	4.5(4)	O8	C32 C33 C34	-170.2(3)
C21	C20	C25	C29	-172.4(3)	O8	C32 C33 C38	11.5(4)

Table 7. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for **5a**

Atom	*x*	*y*	*z*	U(eq)
H2	9015	903	3364	21
H7	8538	1121	-2713	26
H8	10096	728	-3931	29
H9	11590	285	-2656	30
H10	11554	237	-184	26
H12A	7110	1750	4328	40
H12B	8633	1533	4226	40
H12C	7189	1286	4423	40
H15	6257	1948	-2857	25
H16	7234	2526	-3684	31
H17	9379	2769	-2611	28
H18	10576	2431	-750	28
H19	9637	1840	44	24
H21	4282	883	114	24
H26	3782	1079	6189	27
H27	5379	689	7486	31
H28	6908	259	6304	32
H29	6806	215	3817	27
H31A	2004	1676	-982	38
H31B	2283	1218	-1045	38
H31C	3619	1510	-817	38
H34	4560	1836	3308	24
H35	5358	2444	4099	29
H36	4230	2755	5985	28
H37	2258	2463	7041	30
H38	1406	1863	6219	26

Crystallographic data for 6

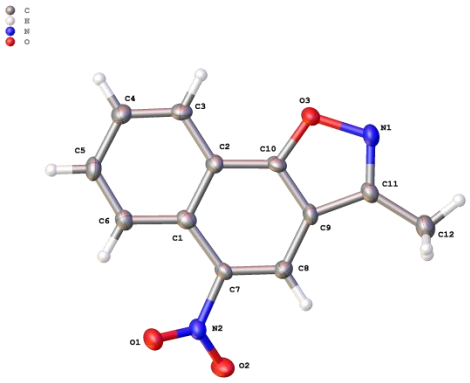


Table 1. Crystal data and structure refinement for **6**

Identification code	CCDC 1519802
Empirical formula	$C_{12}H_8N_2O_3$
Formula weight	228.20
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.9799(16)
b/Å	3.7383(4)
c/Å	18.894(2)
α/	90
β/	99.269(4)
γ/	90
Volume/Å^3	974.52(18)
Z	4
ρ_{calc}g/cm^3	1.555
μ/mm^{-1}	0.961
F(000)	472.0
Crystal size/mm^3	0.5 × 0.3 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.33 to 109.494
Index ranges	-14 ≤ h ≤ 14, -3 ≤ k ≤ 3, -20 ≤ l ≤ 20
Reflections collected	6561
Independent reflections	1194 [R_{int} = 0.0915, R_{sigma} = 0.0632]
Data/restraints/parameters	1194/0/155
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0488, wR_2 = 0.1094
Final R indexes [all data]	R_1 = 0.0769, wR_2 = 0.1195
Largest diff. peak/hole / e Å^{-3}	0.20/-0.22

Table 2. Fractional atomic coordinates ($\times10^4$) and equivalent isotropic displacement parameters ($Å^2\times10^3$) for 6. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
C1	5291(2)	3442(10)	8458.9(17)	22(1)
C2	5927(2)	4613(10)	7987.3(17)	21.1(9)
C3	6860(2)	5912(10)	8258.2(18)	23(1)
C4	7166(2)	6072(10)	8981.1(18)	26.4(10)
C5	6546(2)	4937(11)	9451.0(18)	26.2(10)
C6	5636(2)	3650(10)	9203.0(17)	22.2(10)
C7	4330(2)	2257(10)	8136.0(17)	19.1(9)
C8	4009(2)	2141(10)	7416.7(17)	22.5(9)
C9	4658(2)	3174(10)	6959.4(17)	21(1)
C10	5567(2)	4408(10)	7242.1(17)	20.8(9)
C11	4635(2)	3413(10)	6195.3(17)	23.5(10)
C12	3831(2)	2378(11)	5611.9(17)	30.7(10)
N1	5446(2)	4686(9)	6044.0(14)	27.8(9)
N2	3633(2)	1159(9)	8587.7(15)	24.4(8)
O1	3903.9(16)	-602(7)	9130.4(13)	30.5(7)
O2	2772.3(17)	1996(8)	8393.6(12)	34.5(8)
O3	6062.9(15)	5326(7)	6719.2(11)	27.2(7)

Table 3. Anisotropic displacement parameters ($Å^2\times10^3$) for **6**. 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}
C1	21(2)	24(3)	23(2)	0.8(18)	6.9(16)	3.8(17)
C2	17.1(19)	27(3)	19(2)	2.9(18)	2.2(15)	4.0(17)
C3	16.2(19)	27(3)	27(2)	0.1(18)	7.0(16)	0.3(17)
C4	19(2)	35(3)	25(2)	0(2)	2.7(16)	1.2(18)
C5	26(2)	33(3)	18(2)	-0.2(19)	-1.4(17)	5.5(19)
C6	25(2)	24(3)	18(2)	0.5(17)	4.2(16)	1.4(17)
C7	18.3(19)	22(3)	18(2)	5.4(17)	5.7(16)	2.2(17)
C8	17.9(19)	30(3)	20(2)	0.1(18)	1.7(16)	0.0(18)
C9	24(2)	27(3)	11.7(19)	2.0(17)	2.5(16)	4.3(18)
C10	14.9(19)	27(3)	22(2)	2.9(18)	7.5(16)	2.4(17)
C11	25(2)	28(3)	18(2)	2.5(18)	5.6(16)	2.1(19)
C12	32(2)	39(3)	21(2)	-0.1(19)	4.5(17)	1(2)
N1	28.6(18)	41(3)	13.6(16)	0.4(15)	2.4(13)	-0.5(16)
N2	21.6(18)	34(2)	17.8(18)	1.3(16)	2.5(14)	3.1(15)
O1	27.9(14)	42(2)	21.4(15)	7.6(14)	4.2(11)	0.2(13)
O2	18.8(14)	55(2)	30.7(15)	11.3(14)	5.6(11)	3.7(13)
O3	20.7(13)	42.6(19)	19.3(14)	2.6(13)	6.2(11)	-2.6(12)

Table 4. Bond Lengths for **6**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.425(5)	C8	C9	1.404(5)
C1	C6	1.413(4)	C9	C10	1.376(5)
C1	C7	1.453(5)	C9	C11	1.442(4)
C2	C3	1.408(5)	C10	O3	1.340(4)
C2	C10	1.419(4)	C11	C12	1.493(4)
C3	C4	1.365(4)	C11	N1	1.303(4)
C4	C5	1.403(5)	N1	O3	1.440(3)
C5	C6	1.369(5)	N2	O1	1.226(3)
C7	C8	1.362(4)	N2	O2	1.240(3)
C7	N2	1.454(4)			

Table 5. Bond angles for **6**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	C1	C7	117.3(3)	C8	C9	C11	136.1(3)
C6	C1	C2	117.2(3)	C10	C9	C8	120.1(3)
C6	C1	C7	125.4(3)	C10	C9	C11	103.8(3)
C3	C2	C1	120.8(3)	C9	C10	C2	124.1(3)
C3	C2	C10	122.6(3)	O3	C10	C2	125.1(3)
C10	C2	C1	116.5(3)	O3	C10	C9	110.8(3)
C4	C3	C2	120.1(3)	C9	C11	C12	128.0(3)
C3	C4	C5	119.6(3)	N1	C11	C9	111.2(3)
C6	C5	C4	121.6(3)	N1	C11	C12	120.7(3)
C5	C6	C1	120.6(3)	C11	N1	O3	106.5(2)
C1	C7	N2	120.1(3)	O1	N2	C7	119.8(3)
C8	C7	C1	124.2(3)	O1	N2	O2	122.5(3)
C8	C7	N2	115.7(3)	O2	N2	C7	117.7(3)
C7	C8	C9	117.7(3)	C10	O3	N1	107.7(2)

Table 6 Torsion angles for EV15

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C1	C2	C3	C4	-0.1(6)	C7	C1	C2	C10	-1.8(5)
C1	C2	C10	C9	0.1(5)	C7	C1	C6	C5	-177.5(4)
C1	C2	C10	O3	-178.8(3)	C7	C8	C9	C10	-2.9(5)
C1	C7	C8	C9	1.2(6)	C7	C8	C9	C11	179.0(4)
C1	C7	N2	O1	-39.8(5)	C8	C7	N2	O1	141.3(3)
C1	C7	N2	O2	141.8(3)	C8	C7	N2	O2	-37.1(5)
C2	C1	C6	C5	0.1(5)	C8	C9	C10	C2	2.3(6)

C2	C1	C7	C8	1.2(6)	C8	C9	C10	O3	-178.6(3)
C2	C1	C7	N2	-177.6(3)	C8	C9	C11	C12	-2.8(7)
C2	C3	C4	C5	-0.1(5)	C8	C9	C11	N1	177.8(4)
C2	C10	O3	N1	179.4(3)	C9	C10	O3	N1	0.3(4)
C3	C2	C10	C9	-179.6(4)	C9	C11	N1	O3	0.6(4)
C3	C2	C10	O3	1.5(6)	C10	C2	C3	C4	179.6(4)
C3	C4	C5	C6	0.3(6)	C10	C9	C11	C12	178.9(4)
C4	C5	C6	C1	-0.3(6)	C10	C9	C11	N1	-0.4(4)
C6	C1	C2	C3	0.1(5)	C11	C9	C10	C2	-179.0(3)
C6	C1	C2	C10	-179.6(3)	C11	C9	C10	O3	0.0(4)
C6	C1	C7	C8	178.8(4)	C11	N1	O3	C10	-0.6(4)
C6	C1	C7	N2	0.0(6)	C12	C11	N1	O3	-178.8(3)
C7	C1	C2	C3	177.9(3)	N2	C7	C8	C9	-179.9(3)

Table 7. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for **6**

Atom	*x*	*y*	*z*	U(eq)
H3	7276	6679	7937	28
H4	7795	6946	9165	32
H5	6762	5065	9954	31
H6	5234	2890	9534	27
H8	3369	1387	7231	27
H12A	4009	2986	5146	46
H12B	3240	3671	5673	46
H12C	3716	-203	5634	46