Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

SUPPORTING INFORMATION

2-Nitroallyl carbonate–based green bifunctional reagents for catalytic asymmetric annulation reactions

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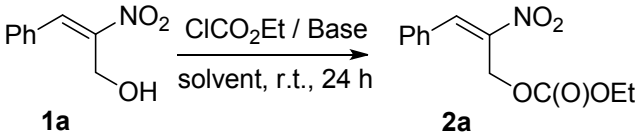
Contents

1. General information.

HRMS (high-resolution mass spectrometry) spectra were measured using electrospray ionization (ESI) and a time-of-flight (TOF) mass analyzer. The measurements were taken in the positive ion mode (interface capillary voltage 4500 V) in the mass range from m/z = 50 Da tom/z = 3000 Da; external or internal calibration was done with an electrospray calibrant solution. NMR spectra were recorded on a 300 MHz spectrometer. The chemical shifts of ^{1}H, ^{13}C were measured relative to Me_4Si, $CDCl_3$ respectively. HPLC analyses were performed on an HPLC system equipped with chiral stationary phase columns (*AD-H*, *OD-H*, *OJ-H, IB-H*), detection at 220 or 254 nm. Optical rotations were measured on a Jasco P-2000 digital polarimeter with a sodium lamp and reported as follows; $[\alpha]^{T^{\circ}C}_{D}$ (c = g/100 mL, solvent). Silica gel (0.060−0.200 mm) was used for column chromatography. All reagents and solvents were purified and dried according to common methods.

2. Synthesis of nitroallylic carbonates 2a-e.

2a. Optimization of the reaction conditions.



1a 2a

Entry[a]	Solvent	Base	Yield, %
1	THF	Et_3N	< 20% [b]
2	DCM	Et_3N	< 20% [b]
3	THF	DABCO	25
4	DCM	DABCO	35
5	THF	DMAP	60
6	DCM	DMAP	93
7	THF	DBU	40
8	DCM	DBU	37

[a]All reactions were carried out **1a** (100 mg, 0.56 mmol), base (0.61 mmol, 1.1 equiv.) and ethyl chloroformate (66.8 mg, 0.61 mmol, 1.1 equiv) in the corresponding solvent (0.5 mL) at r.t. [b] ^{1}H NMR data.

2b. Preparation of nitroallylic carbonates 2a-e. General procedure and characterization data.

General procedure. To solution of nitroallylic alcohol **1a-e** [1–3] (6.8 mmol) in DCM (4.0 mL) were added DMAP (1.22 g, 10.0 mmol) and ethyl chloroformate (0.7 mL, 10.0 mmol) at 0° C. After the reaction was completed (TLC), the mixture was diluted with CH_2Cl_2 (10 mL) and washed with H_2O (3 x 5 mL). The organic phases were dried over Na_2SO_4, filtered and evaporated (10 Torr). Yellow residue was purified by flash chromatography (*n*-hexane/EtOAc 5/1 - 2/1) to afford pure products **2a-e.** Characterization data for **2a-e** are given below:

Ethyl (2-nitro-3-phenylallyl) carbonate (**2a)** Yellow solid (1.46 g, 85%). M.p. 66-68 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.52 (s, 5H), 5.30 (s, 2H), 4.29 (q, *J* = 7.1, 14.3 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): 154.5, 144.7, 140.6, 131.4, 130.8, 130.1, 129.3, 64.8, 60.6, 14.2 ppm. HRMS (ESI): m/z calcd. for $C_{12}H_{14}NO_5^+$ $[M+H]^+$: 252.0866, found 252.0859.

3-(4-Bromophenyl)-2-nitroallyl ethyl carbonate (2b). Yellow solid (2.06 g, 92%). M.p. = 68-71 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.67-7.64 (d, *J* = 8.4 Hz, 2H), 7.40-7.38 (d, *J*

= 8.4 Hz, 2H), 5.26 (s, 2H), 4.32-4.25 (q, *J* = 7.1, 14.3 Hz, 2H), 1.39-1.34 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 154.6, 145.0, 139.3, 132.7, 131.5, 129.7, 126.3, 64.4, 60.4, 14.2 ppm. HRMS (ESI): m/z calcd. for $C_{12}H_{13}BrNO_5^+$ $[M+H]^+$: 329.9972, found 329.9981.

3-(4-Fluorophenyl)-2-nitroallyl ethyl carbonate (2c). Yellow solid (1.70 g, 93%), M.p. 55-56°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.55 (m, 2H), 7.21 (t, *J* = 5.1 Hz, 2H), 5.28 (s, 2H), 4.33-4.26 (q, *J* = 7.1, 14.3 Hz, 2H), 1.43-1.32 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 166.1, 162.8, 154.4, 144. 5, 139.4, 132.5, 132.4, 127.0, 127.0, 116.8, 116.5, 64.9, 60.5, 14.2 ppm. HRMS (ESI): m/z calcd. for $C_{12}H_{13}FNO_5^+$ $[M+H]^+$: 270.0772, found 270.0779

Ethyl (2-nitro-3-(thiophen-2-yl)allyl) carbonate (2d). Yellow solid (1.57 g, 90%). M.p. 66-69 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.76-7.74 (d, *J* = 5.3 Hz, 1H), 7.57-7.56 (d, *J* = 3.6 Hz, 1H), 7.21 (m, 1H), 5.47 (s, 2H), 4.29-4.22 (q, *J* = 7.2, 14.3 Hz, 2H), 1.32 (t, *J* = 7.1, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 154.6, 141.0, 137.0, 134.4, 133.2, 128.8, 64.7, 60.6, 14.2 ppm. HRMS (ESI): m/z calcd. for $C_{10}H_{12}NO_5S^+$ $[M+H]^+$: 258.0431, found 258.0442.

Ethyl (2-nitro-5-phenylpenta-2,4-dien-1-yl) carbonate (2e). Yellow solid (1.66 g, 88%). M.p. 75-77 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.04-8.01 (d, *J* = 10.0 Hz, 1H), 7.59 (m, 2H), 7.43 (m, 3H), 7.28-7.14 (m, 2H), 5.36 (s, 2H), 4.29-4.22 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 154.8, 147.8, 143.1, 139.9, 135.1, 130.6, 129.0, 128.1, 120.1, 64.6, 59.3, 14.1 ppm. HRMS (ESI): m/z calcd. for $C_{14}H_{16}NO_5^+$ $[M+H]^+$: 278.1023, found 278.1028.

References for sections 1 and 2

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2 R. Parella, S. Jakkampudi, H. Arman and J. C. G. Zhao, Stereoselective Synthesis of 3-Oxabicyclo[3.3.1]Nonan-2-Ones via a Domino Reaction Catalyzed by Modularly Designed Organocatalysts, *Adv. Synth. Catal.*, 2019, **361**, 208–213.

3 N. Rastogi, I. N. N. Namboothiri and M. Cojocaru, α-Hydroxymethylation of conjugated nitroalkenes via the Morita-Baylis-Hillman reaction, *Tetrahedron Lett.*, 2004, **45**, 4745–4748.

3. Catalytic asymmetric [3 + 3] annulation of 2 with 3.

Model reaction between 2a and 3a. A mixture of organocatalyst **4 – 7** (0.0025 mmol, 5 mol %), **2a** (12.6 mg, 0.05 mmol) and dimedone **3a** (7.0 mg, 0.05 mmol) in DCM (0.1 mL) was stirred at ambient temperature for 5 h. The mixture was concentrated under reduced pressure (10 Torr), the residue was purified by flash chromatography (ethyl acetate) to afford **8aa** as yellow oil.

General procedure. A mixture of organocatalyst **4b** (1.22 mg, 0.0025 mmol, 5 mol %), carbonate **2** (0.05 mmol) and cyclic enol **3** (0.05 mmol) in DCM (0.1 mL) was stirred at ambient temperature for 3-5 h. The mixture was concentrated under reduced pressure (10 Torr) and the residue was purified by flash chromatography on silicagel (ethyl acetate) to afford product **8**. Characterization data for **8** are given below:

7,7-Dimethyl-3-nitro-4-phenyl-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (8aa) Yellow oil (14.4 mg, 96%). 94% *ee*, $[\alpha]_D^{20}$: +43.1 (c 0.1, $CHCl_3$). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.32 (m, 5H), 5.18 (d, *J* = 1.5 Hz, 1H), 4.77 (dt, *J* = 13.3 Hz, 1H), 4.63 (br s, 1H), 4.03 (dd, *J* = 11.9 Hz, 1., 1H), 2.62 (d, *J* = 17.2 Hz, 1H), 2.31 (t, *J* = 21.2 Hz, 2H), 2.12 (d, *J* = 15.8 Hz, 1H), 1.09 (s, 3H), 0.96 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 196.0, 169.8, 140.9, 129.1, 128.6, 127.6, 108.3, 82.7, 63.4, 50.5, 41.6, 36.3, 32.6, 29.3, 26.9 ppm. HRMS (ESI): m/z calcd. for $C_{17}H_{20}NO_4$ $[M+H]^+$: 302.1387, found 302. 1380.

3-Nitro-4-phenyl-3,4,6,7-tetrahydrocyclopenta[b]pyran-5(2H)-one (8ab) Yellow oil (12.4 mg, 96%). 65% *ee*, $[\alpha]_D^{20}$: +56.2 (c 0.1, $CHCl_3$). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.35 (m, 5H), 5.23 (d, *J* = 1.7 Hz, 1H), 4.95 (dt, *J* = 13.4 Hz, 1H), 4.48 (br s, 1H), 4.20 (dd, *J* = 13.3 Hz, 1.8 Hz, 1H), 2.70 (m, 2H), 2.41 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 202.1, 184.0, 139.3, 129.2, 128.8, 127.9, 112.8, 82.8, 65.5, 36.8, 33.6, 26.3 ppm. HRMS (ESI): m/z calcd. for $C_{14}H_{13}NO_4$ $[M+H]^+$: 260.0917, found 260.0922.

7-Methyl-3-nitro-4-phenyl-3,4-dihydropyrano[4,3-b]pyran-5(2H)-one (8ac) Yellow oil (13.5 mg, 94%). 87% *ee*, $[\alpha]_D^{20}$: +71.7 (c 0.1, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39-7.17 (m, 5H), 5.91 (s, 1H), 4.91-4.77 (m, 3H), 4.23 (d, *J* = 12.8 Hz, 1H), 2.27 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 164.7, 162.5, 139.8, 129.3, 128.7, 128.0, 99.6, 96.4, 82.4, 63.4, 37.5, 19.7 ppm. HRMS (ESI): m/z calcd. for $C_{15}H_{14}NO_5^+$ $[M+H]^+$: 288.0866, found 288.0857.

3-Nitro-4-phenyl-3,4-dihydropyrano[3,2-c]chromen-5(2H)-one (8ad) White solid (14.9 mg, 92%), M.p. 58−60 °C. 70% *ee*, $[\alpha]_D^{20}$: +98.4 (c 0.1, $CHCl_3$). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.48 – 7.31 (m, 7H), 5.42 (d, *J* = 1.2 Hz, 1H), 5.10 (dt, *J* = 13.3 Hz, 1H), 4.83 (br s, 1H), 4.37 (dd, *J* = 12.8 Hz, 1.5 Hz, 1H) ppm. **^{13}C{^{1}H}**

NMR (75 MHz, DMSO-d_6) δ 161.0, 159.8, 152.5, 139.7, 133.2, 129.3, 128.9, 128.0, 125.0, 123.1, 117.0, 114.6, 99.8, 82.4, 64.1, 28.0 ppm. HRMS (ESI): m/z calcd. for $C_{18}H_{14}NO_5^+$ $[M+H]^+$: 324.0866, found 324.0862.

1,3-Diethyl-6-nitro-5-phenyl-2-thioxo-2,3,6,7-tetrahydro-1H-pyrano[2,3-d]pyrimidin-4(5H)-one (8ae). Yellow oil (15.7 mg, 87%). 91% *ee*, $[\alpha]_D^{20}$: +78.0 (c 0.1, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43-7.24 (m, 5H), 5.08-5.04 (m, 1H), 4.96 (s, 1H), 4.78-4.43 (m, 5H), 4.38-4.33 (m, 1H), 1.36 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$) δ 175.5, 159.4, 155.3, 138.9, 129.5, 129.0, 128.6, 128.3, 127.6, 89.7, 81.8, 64.1, 44.3, 43.7, 38.6, 12.7, 11.5 ppm. HRMS (ESI): m/z calcd. for $C_{25}H_{20}N_3O_4S^+$ $[M+H]^+$: 362.1130, found 362.1123.

6-Nitro-1,3,5-triphenyl-2-thioxo-2,3,6,7-tetrahydro-1H-pyrano[2,3-d]pyrimidin-4(5H)-one (8af) White solid (18.3 mg, 80%). 91% *ee*, $[\alpha]_D^{20}$: +201.0 (c 0.1, DMSO). M.p. 57 −59 °C. Very poor soluble compound in common solvents. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.62-7.12 (m, 15H), 5.28 (s, 1H), 4.88-4.82 (m, 2H), 4.22 (m, 1H) ppm. ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6) δ 178.0, 160.4, 156.6, 140.5, 140.0, 138.6, 129.8, 129.6, 129.5, 129.3, 129.2, 128.8, 128.4, 128.0, 90.5, 82.0, 65.2, 38.0 ppm. HRMS (ESI): m/z calcd. for $C_{25}H_{20}N_3O_4S^+$ $[M+H]^+$: 458.1130, found 458.1169.

3-Nitro-4-phenyl-3,4-dihydro-2H-benzo[g]chromene-5,10-dione (8ag) White solid (15.8 mg, 95%). 99% *ee*, $[\alpha]_D^{20}$: +102.6 (c 0.1, DMSO). M.p. >230 °C. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.06 (m, 1H), 7.88 (m, 3H), 7.40 (m, 6H), 5.35 (d, *J* = 1.6 Hz, 1H), 5.00 (m, 2H), 4.22 (dt, *J* = 14.2 Hz, 1H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 182.9, 178.4, 155.3, 140.1, 135.0, 134.3, 131.7, 131.2, 129.3, 129.0, 128.0, 126.5, 126.3, 118.8, 82.1, 63.7, 37.2 ppm. HRMS (ESI): m/z calcd. for $C_{19}H_{14}NO_5^+$ $[M+H]^+$: 336.0866, found 336.0861.

2-Nitro-1-phenyl-2,3-dihydro-1H-benzo[a]pyrano[2,3-c]phenazine (8ah). Red solid (17.2 mg, 84%). 90% *ee*, $[\alpha]_D^{20}$: +92.5 (c 0.1, DMSO). M.p. >230 °C. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.91-8.89 (m, 1H), 8.18-8.08 (m, 2H), 7.92-7.75 (m, 4H), 7.58-7.53 (m, 1H), 7.40-7.25 (m, 5H), 5.75 (s, 1H), 5.35-5.26 (m, 2H), 4.03-3.96 (m, 1H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 177.9, 145.3, 140.9, 135.3, 134.6, 132.58, 132.3, 132.0, 131.6, 131.6, 131.5, 130.8, 129.4, 128.6, 127.9, 125.3, 125.1, 114.5, 103.4, 80.7, 42.7 ppm. HRMS (ESI): m/z calcd. for $C_{25}H_{18}N_3O_3^+$ $[M+H]^+$: 408.1343, found 408.1333.

4-(4-Bromophenyl)-3-nitro-3,4-dihydro-2H-benzo[g]chromene-5,10-dione (8bg) White solid (15.5 mg, 75%). M.p. >230 °C (dec.) 97% *ee*, $[\alpha]_D^{20}$: +105.1 (c 0.1, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20-8.17 (m, 1H), 8.05-8.02 (m, 1H), 7.78-7.75 (m, 2H), 7.54-7.52 (d, *J* = 8.4

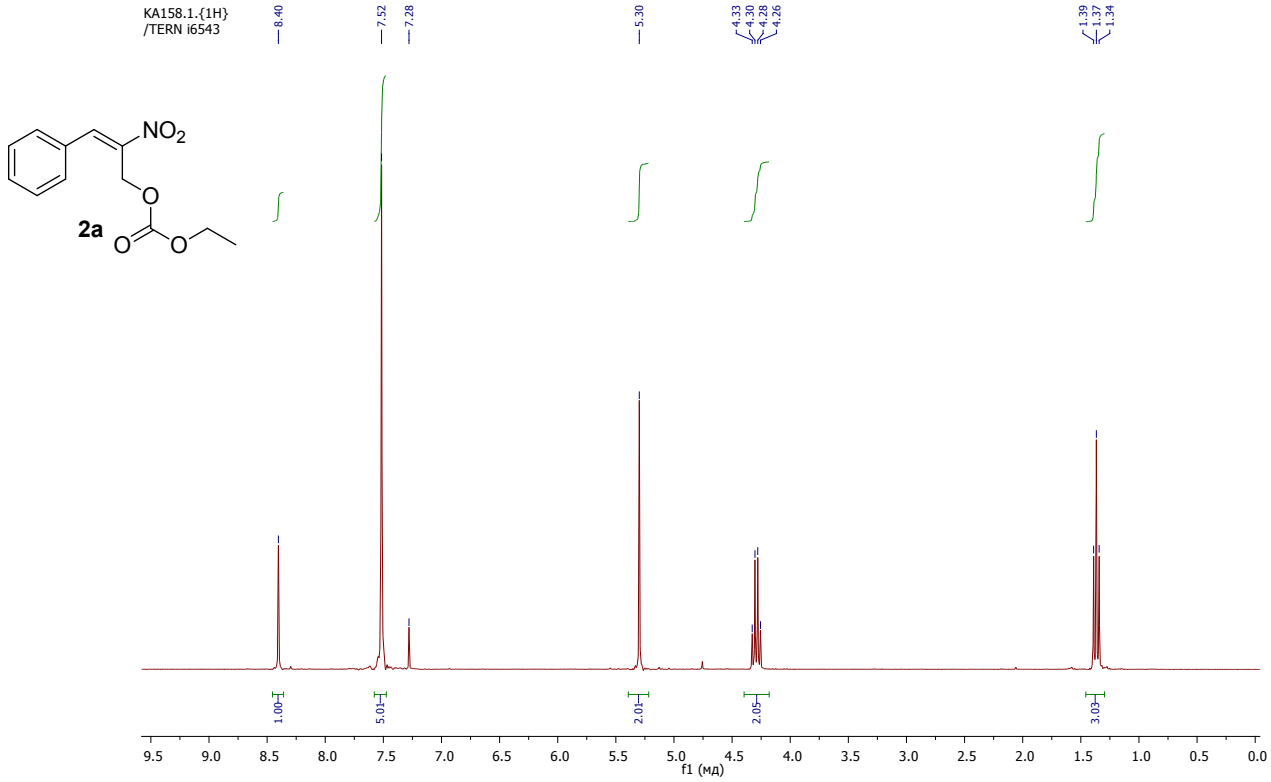
Hz, 2H), 7.20-7.17 (d, *J* = 8.4 Hz, 2H), 5.13-5.08 (m, 2H), 4.80 (s, 1H), 4.36- 4.31 (m, 1H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 182.4, 178.3, 154.4, 137.9, 134.7, 133.8, 132.7, 131.6, 130.8, 129.6, 126.8, 126.6, 122.6, 118.3, 81.6, 63.1, 37.1 ppm. HRMS (ESI): m/z calcd. for $C_{19}H_{13}BrNO_5^+$ $[M+H]^+$: 413.9932, found 413.9955.

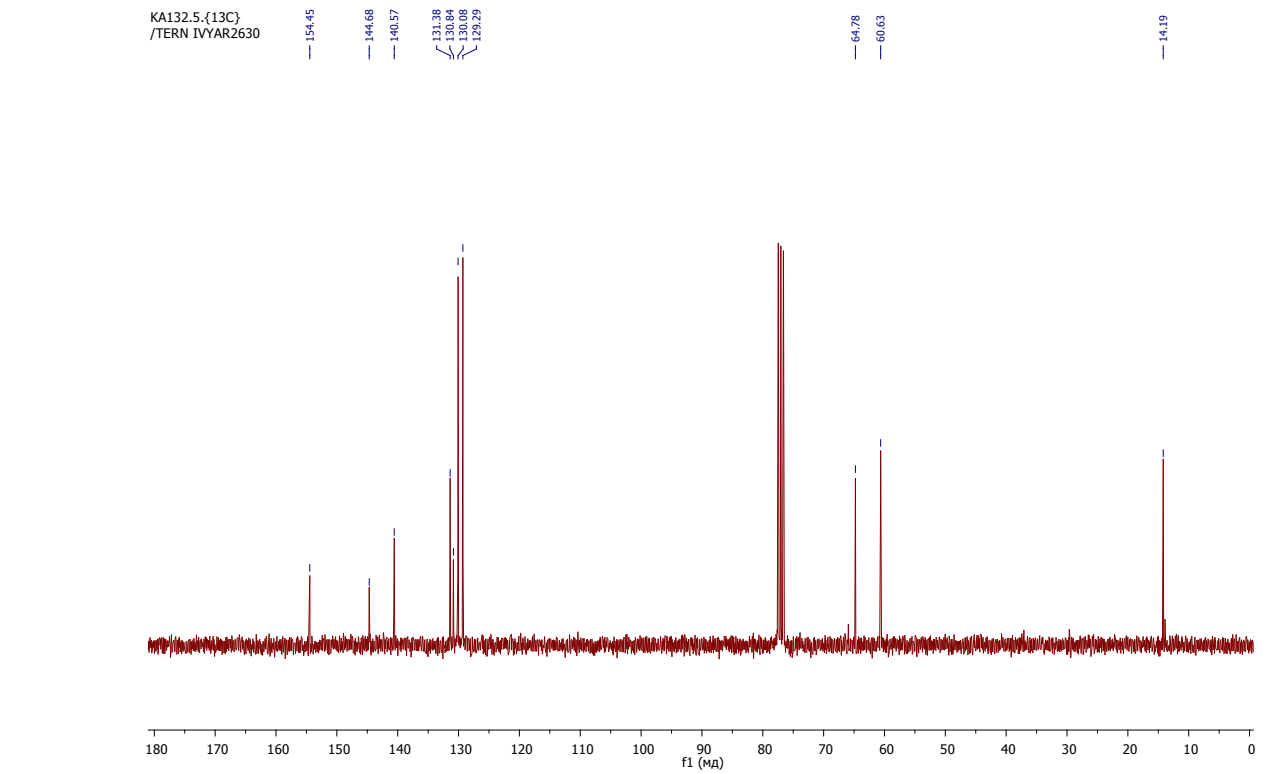
1-(4-Fluorophenyl)-2-nitro-2,3-dihydro-1H-benzo[a]pyrano[2,3-c]phenazine (8ch). Red solid (18.5 mg, 87%). 94% *ee*, $[\alpha]_D^{20}$: +101.0 (c 0.1, DMSO). M.p. >220 °C. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.91-8.89 (d, *J* = 7.6 Hz, 1H), 8.19-8.08 (dd, *J* = 25.4, 7.6 Hz, 1H), 7.91-7.14 (m, 9H), 5.74 (s, 1H), 5.35-5.27 (m, 2H), 4.04-4.00 (d, *J* = 16.6 Hz, 1H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 177.9, 145.4, 137.4, 135.4, 134.6, 132.5, 132.3, 132.0, 131.7, 131.6, 131.5, 130.9, 130.7, 125.3, 125.1, 116.2, 115.9, 114.4, 103.5, 80.6, 42.6, 38.5 ppm. HRMS (ESI): m/z calcd. for $C_{25}H_{17}FN_3O_3^+$ $[M+H]^+$: 426.1248, found 426.1241.

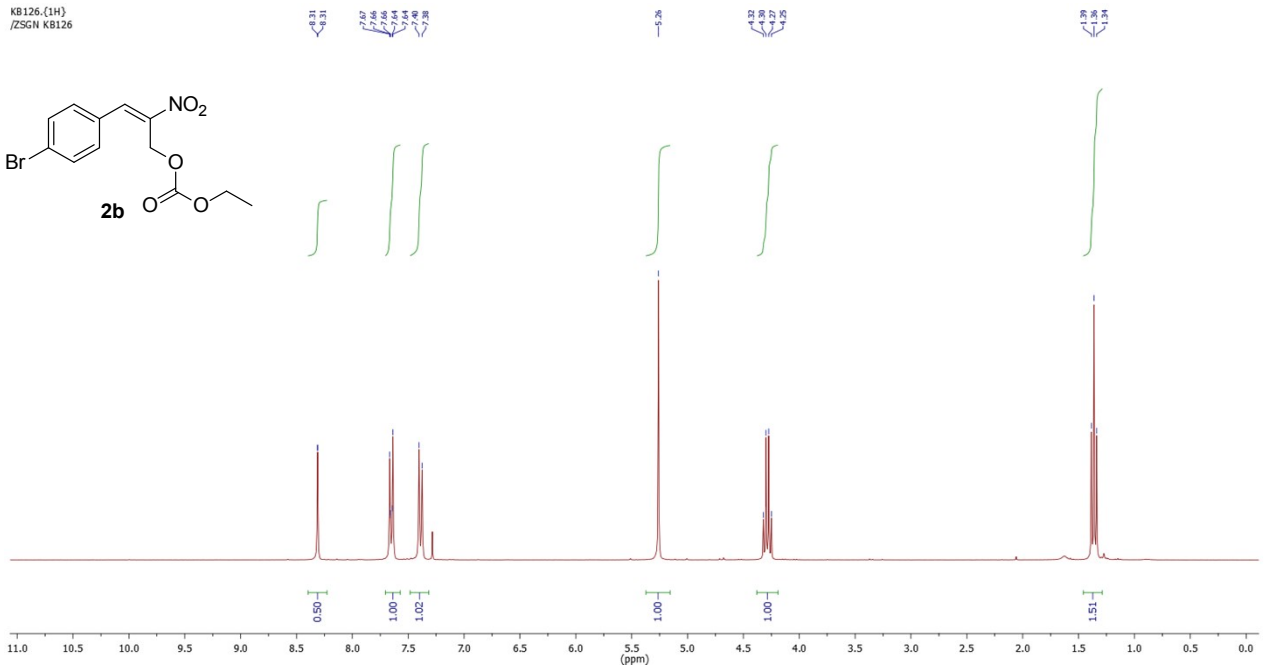
3-Nitro-4-(thiophen-2-yl)-3,4-dihydro-2H-benzo[g]chromene-5,10-dione (8dg). White solid (15.7 mg, 91%). M.p. 177-180 °C. 92% *ee*, $[\alpha]_D^{20}$: +79.8 (c 0.1, DMSO). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.05 (m, 1H), 7.94 (m, 1H), 7.86 (m, 1H), 7.51 (m, 1H), 7.17 (m, 1H), 6.99 (m, 1H), 5.44 (s, 1H), 5.08 (m, 1H), 5.00 (m, 2H), 4.22 (m, 1H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 182.7, 178.4, 154.4, 142.4, 135.1, 134.4, 131.6, 131.1, 128.1, 127.8, 126.8, 126.6, 126.4, 119.3, 81.5, 64.2, 32.2 ppm. HRMS (ESI): m/z calcd. for $C_{17}H_{12}NO_5S^+$ $[M+H]^+$: 342.0431, found 342.0452.

3-Nitro-4-styryl-3,4-dihydro-2H-benzo[g]chromene-5,10-dione. (8eg) White solid (16.2 mg, 90%). 99% *ee*, $[\alpha]_D^{20}$: +113.6 (c 0.1, DMSO). M.p. >230 °C (dec.) **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.05-7.86 (m, 5H), 7.44-7.24 (m, 6H), 6.71-6.45 (m, 2H), 5.46 (s, 1H), 5.12-5.07 (m, 1H), 4.54-4.50 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 182.9, 178.5, 154.6, 136.7, 135.0, 134.4, 134.3, 131.8, 131.1, 129.0, 128.3, 127.8, 126.9, 126.4, 126.4, 118.9, 79.5, 64.1, 34.7 ppm. HRMS (ESI): m/z calcd. for $C_{21}H_{16}NO_5^+$ $[M+H]^+$: 362.1018, found 362.1028.

5. NMR pictures for compounds 2 and 8.



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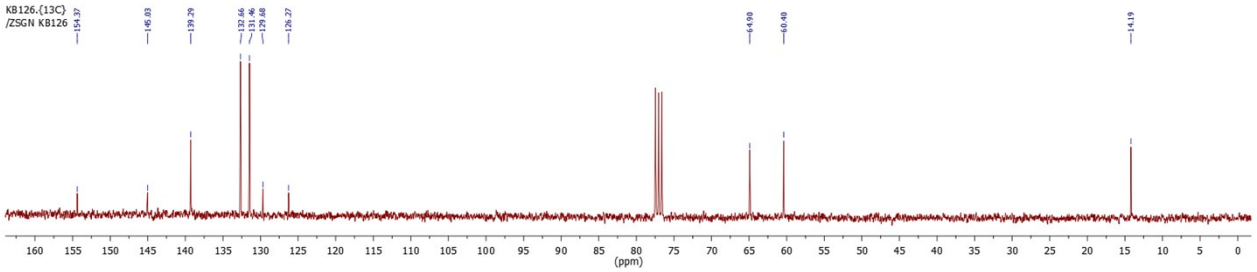
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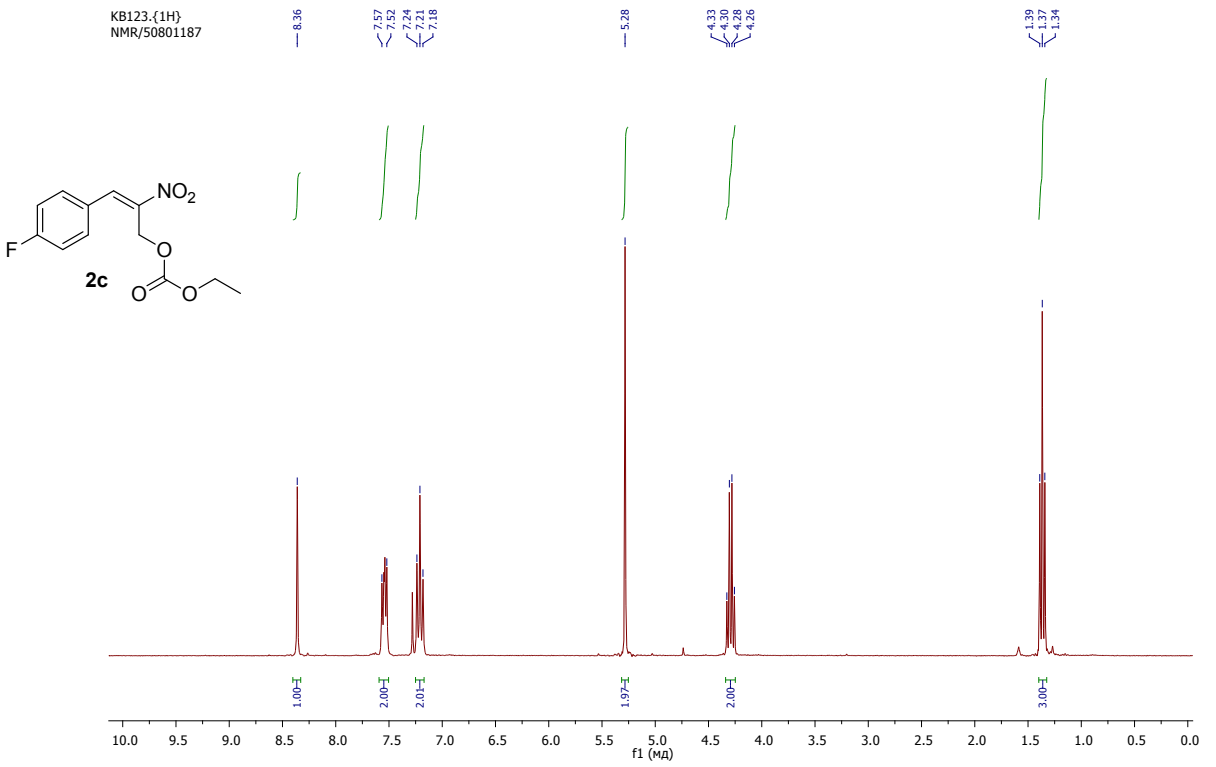
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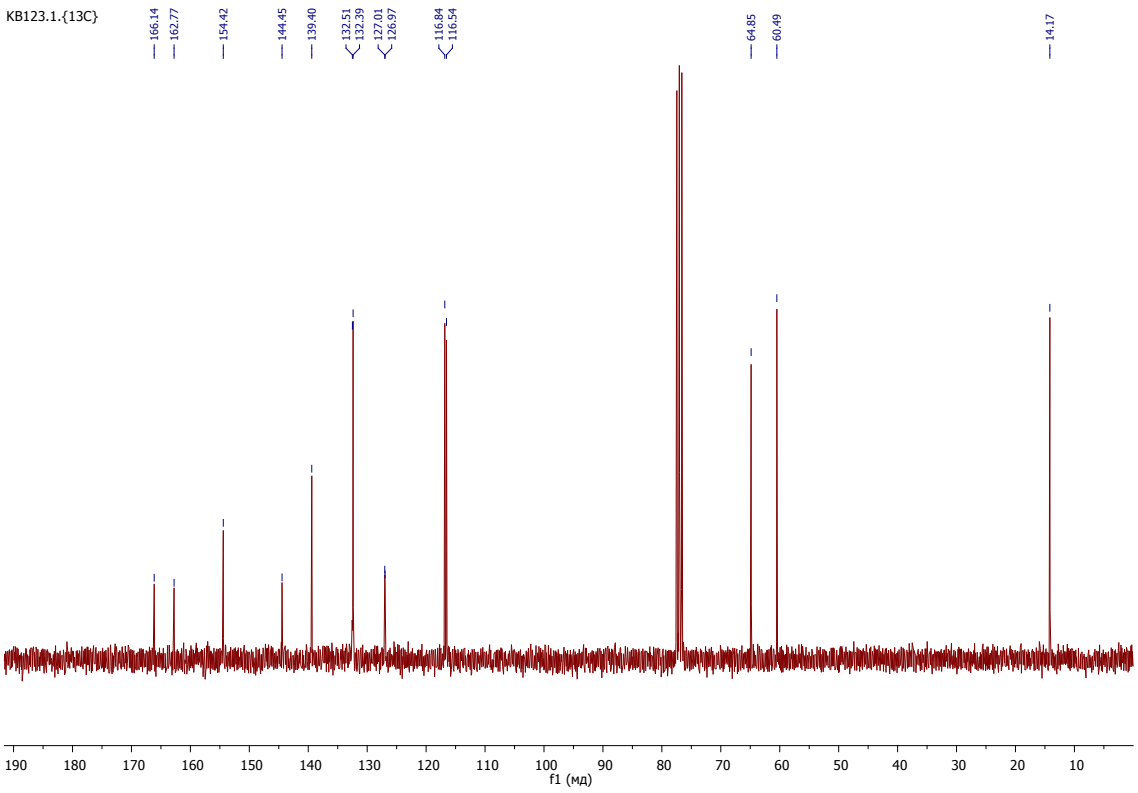
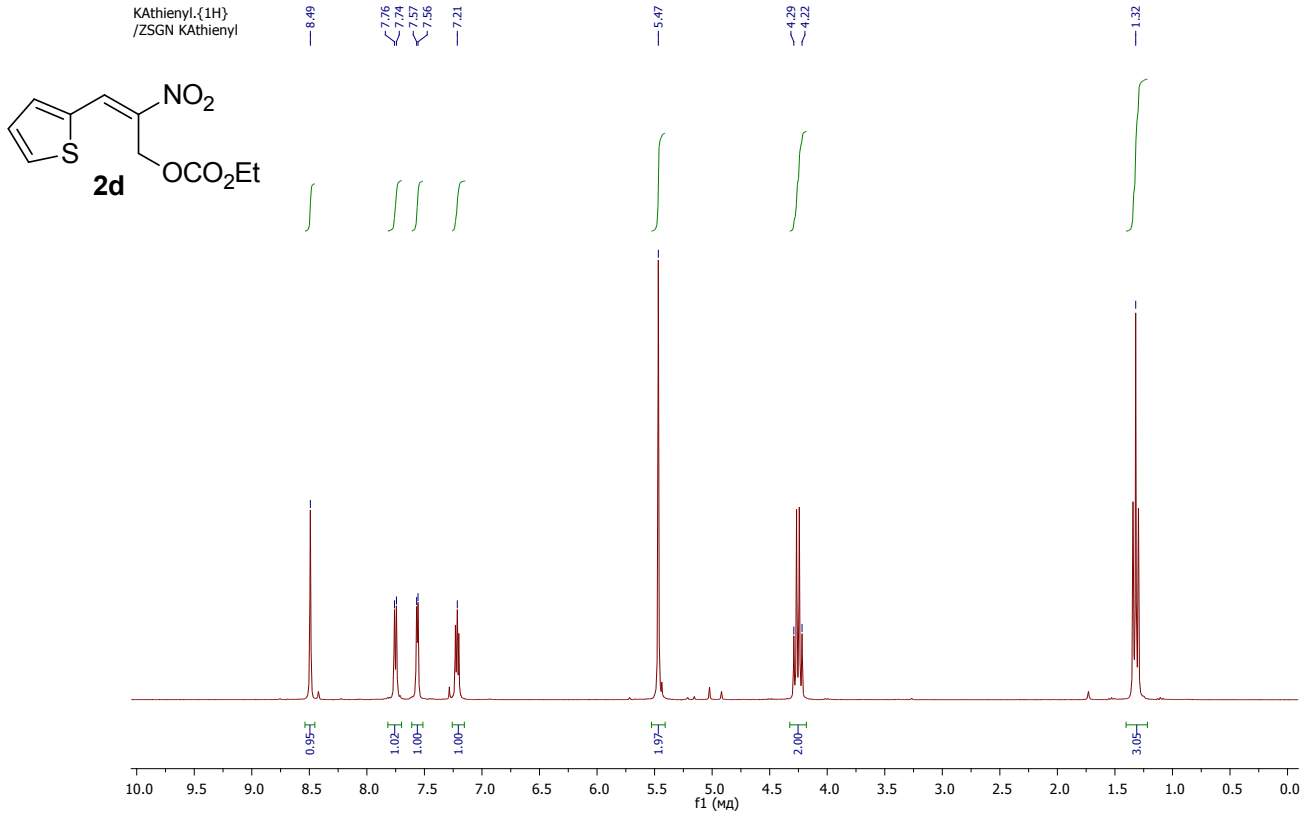
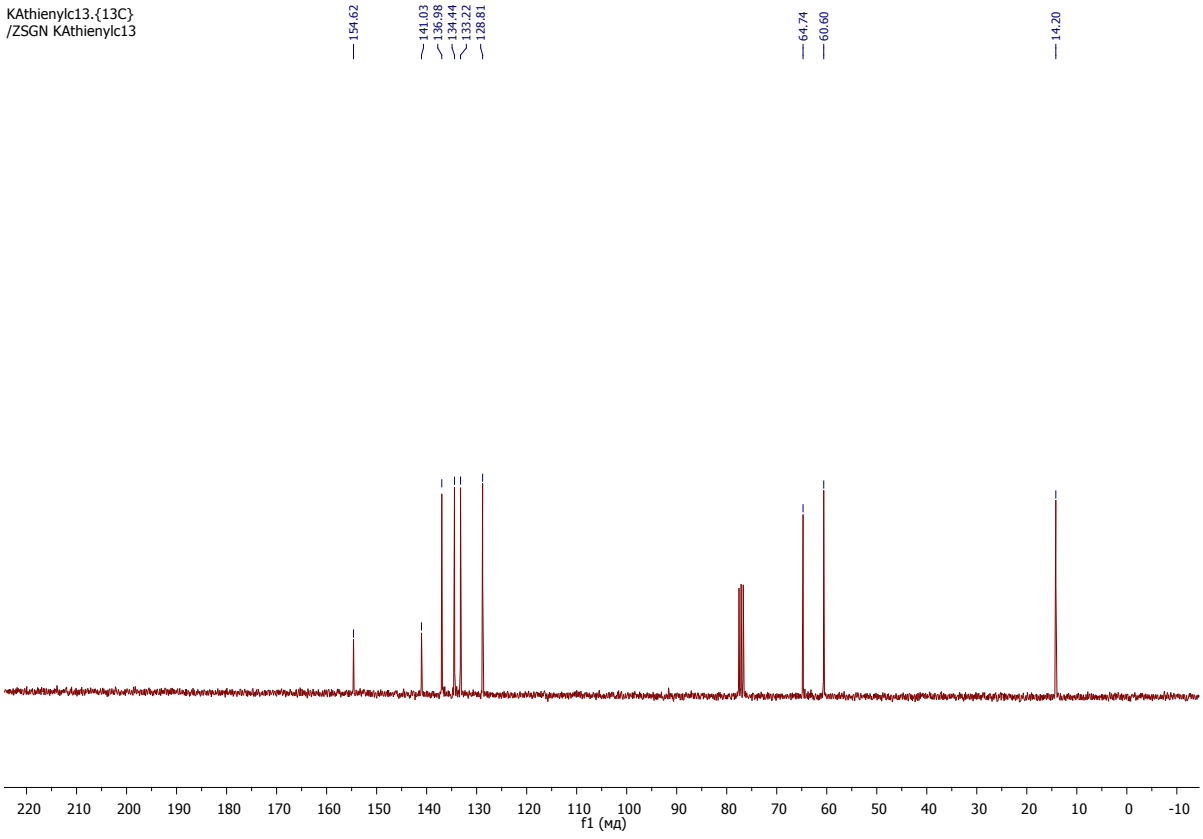
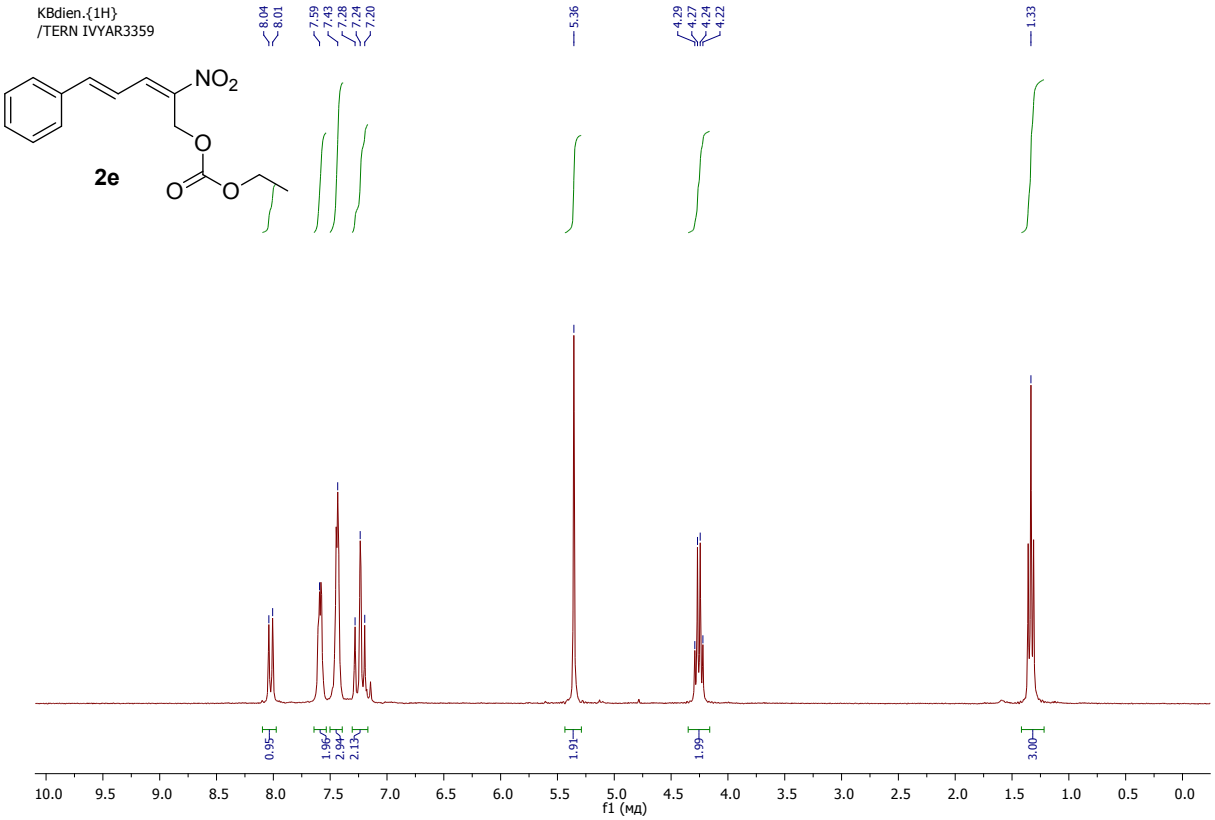
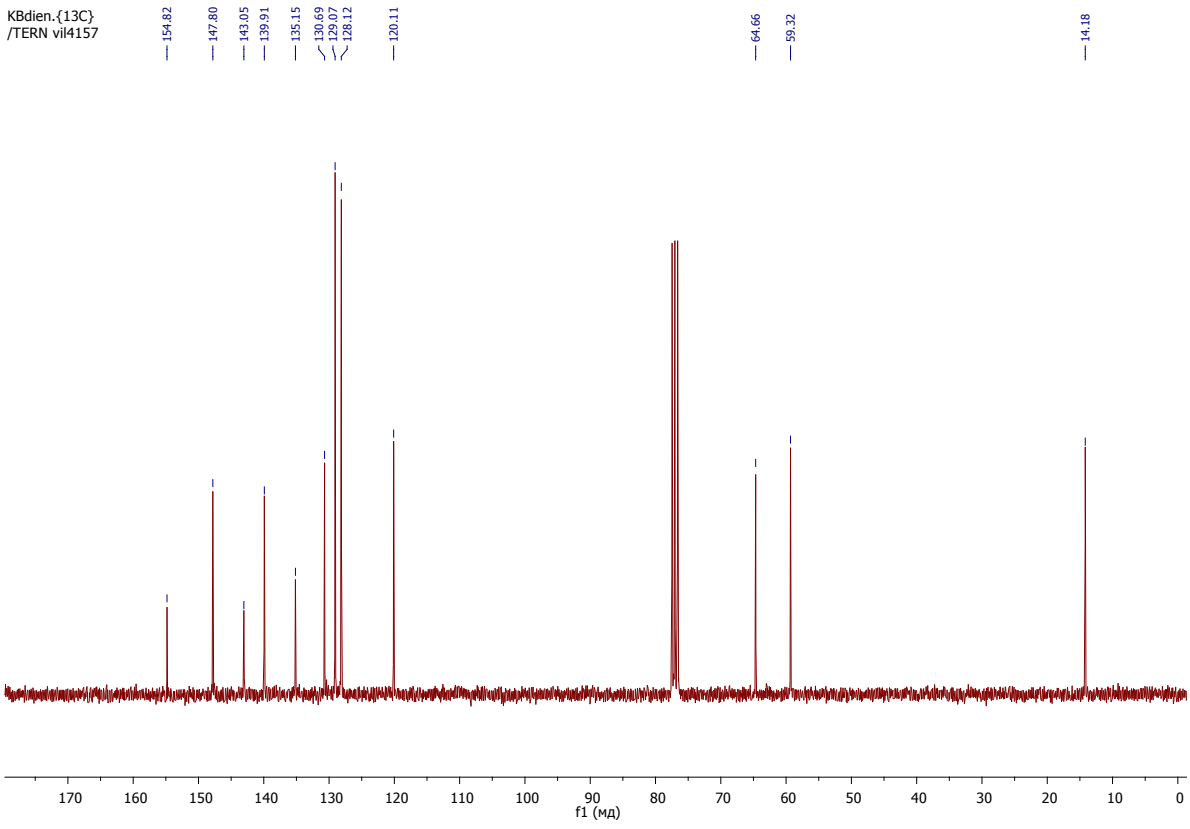
7.57
7.52
7.24
7.21
7.18
5.28
4.33
4.30
4.28
4.26
1.39
1.37
1.34
NO2
F
O
O
O
2c
1.00
2.00
2.01
1.97
2.00
3.00
f1 (мд)

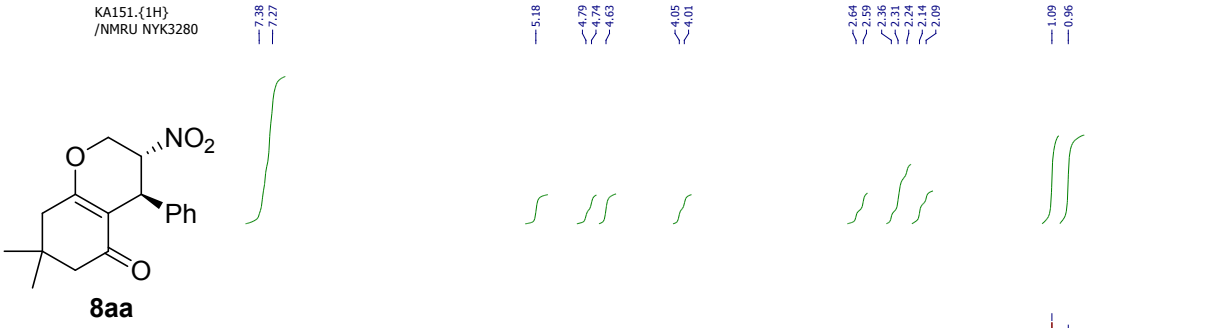

KB123.1.{13C}
166.14
162.77
154.42
144.45
139.40
132.51
132.39
127.01
126.97
116.84
116.54
64.85
60.49
14.17
f1 (мд)


KAthienyl.{1H}
/ZSGN KAthienyl
8.49
7.76
7.74
7.57
7.56
7.21
5.47
4.29
4.22
1.32
NO2
S
OCO2Et
2d
0.95
1.02
1.00
1.00
1.97
2.00
3.05
f1 (мд)

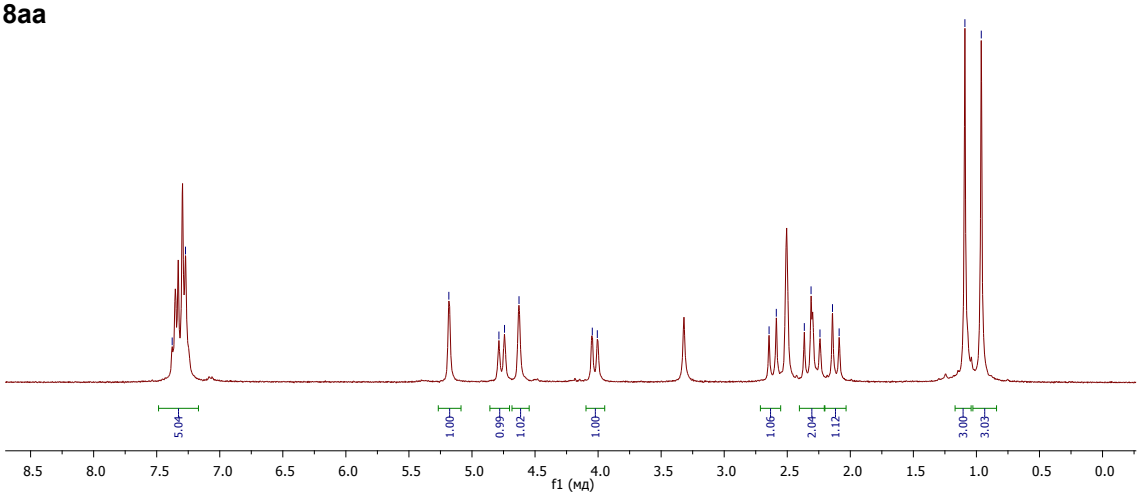

KAthienylc13.{13C}
/ZSGN KAthienylc13
154.62
141.03
136.98
134.44
133.22
128.81
64.74
60.60
14.20
f1 (мд)

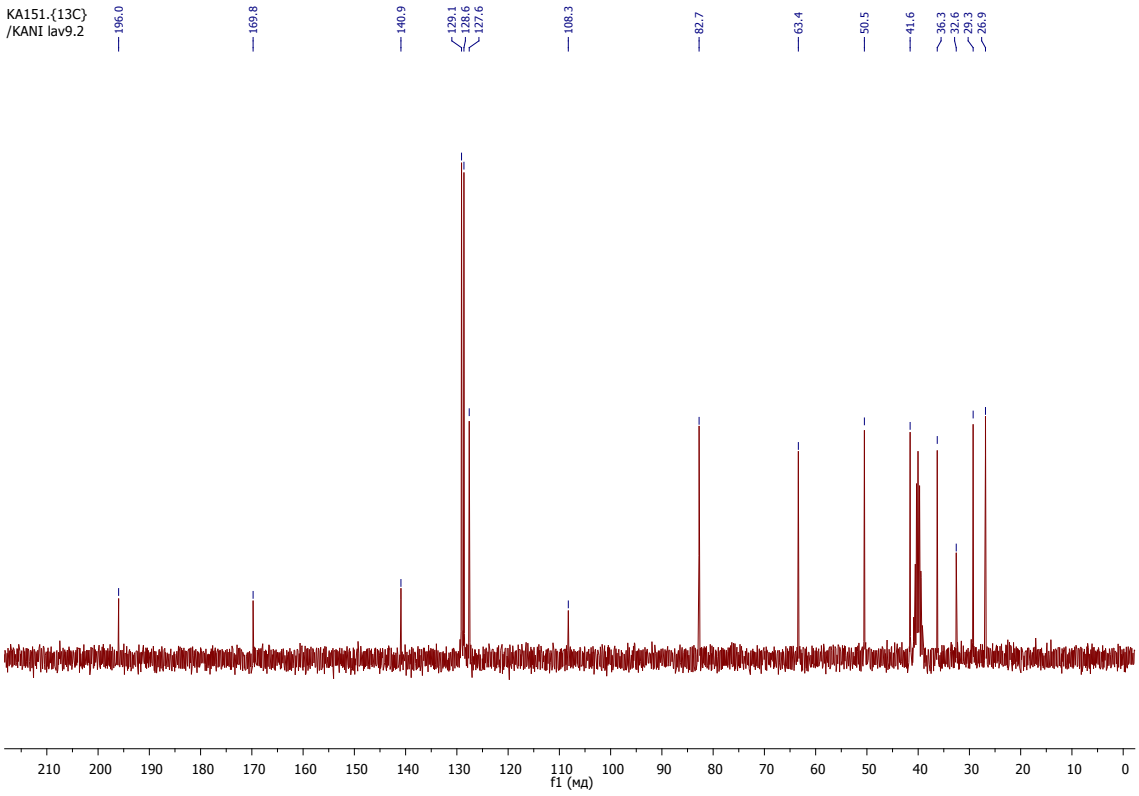

KBdien.{1H}
/TERN IVYAR3359
8.04
8.01
7.59
7.43
7.28
7.24
7.20
5.36
4.29
4.27
4.24
4.22
1.33
NO2
O
O
O
2e
0.95
1.96
2.94
2.13
1.91
1.99
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (мд)

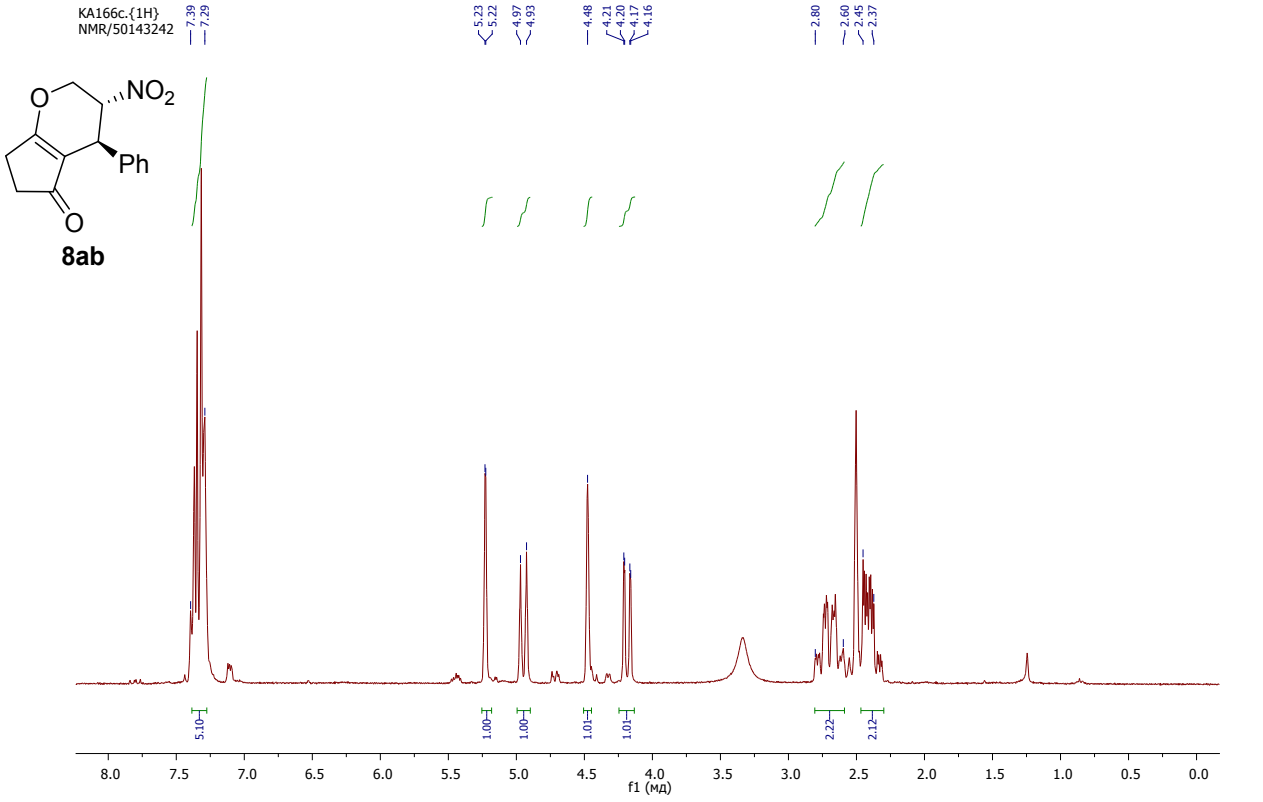

KBdien.{13C}
/TERN vil4157
154.82
147.80
143.05
139.91
135.15
130.69
129.07
128.12
120.11
64.66
59.32
14.18
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

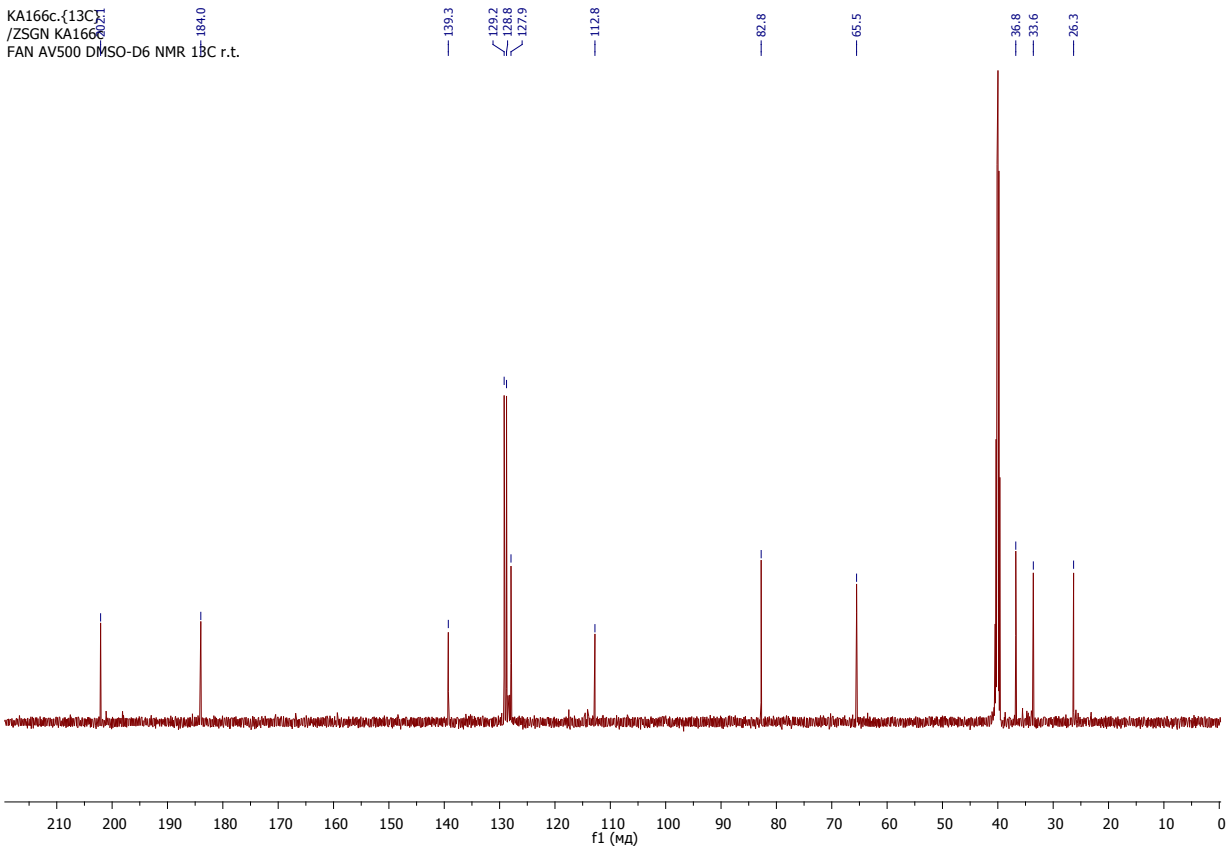

KA151.{1H}
/NMRU NYK3280
7.38
7.27
5.18
4.79
4.74
4.63
4.05
4.01
2.64
2.59
2.36
2.31
2.24
2.14
2.09
1.09
0.96
NO2
O
Ph
O

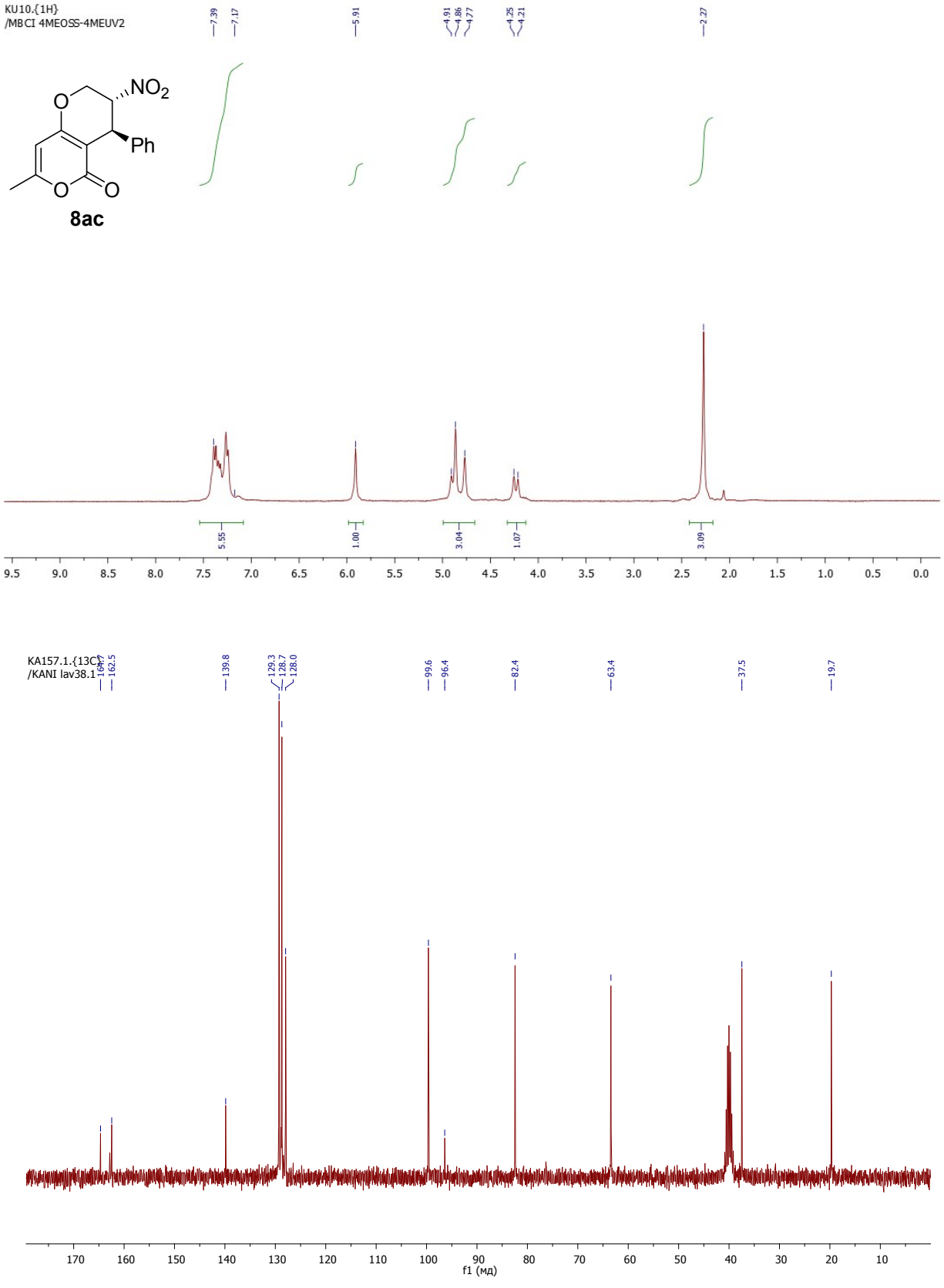
8aa

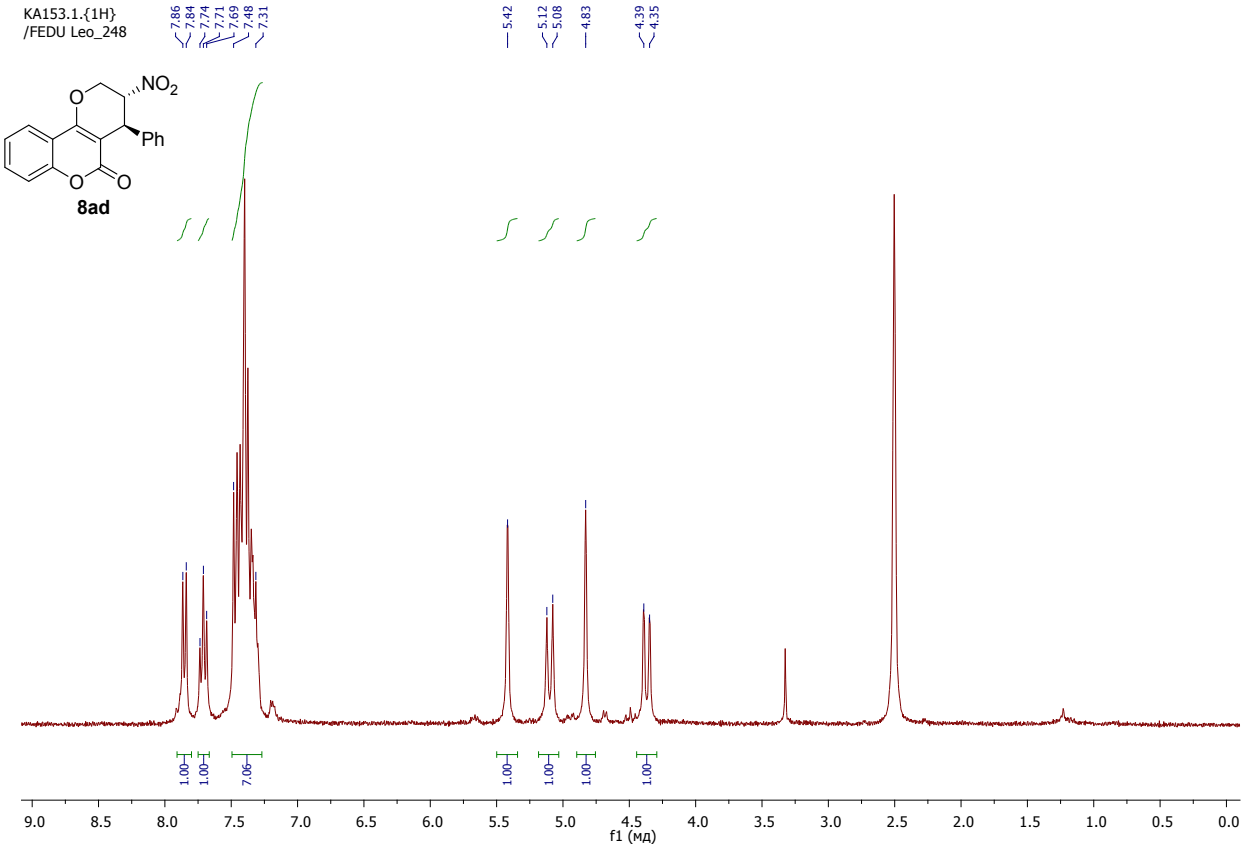

5.04
1.00
0.99
1.02
1.00
1.06
2.04
1.12
3.00
3.03
f1 (мд)

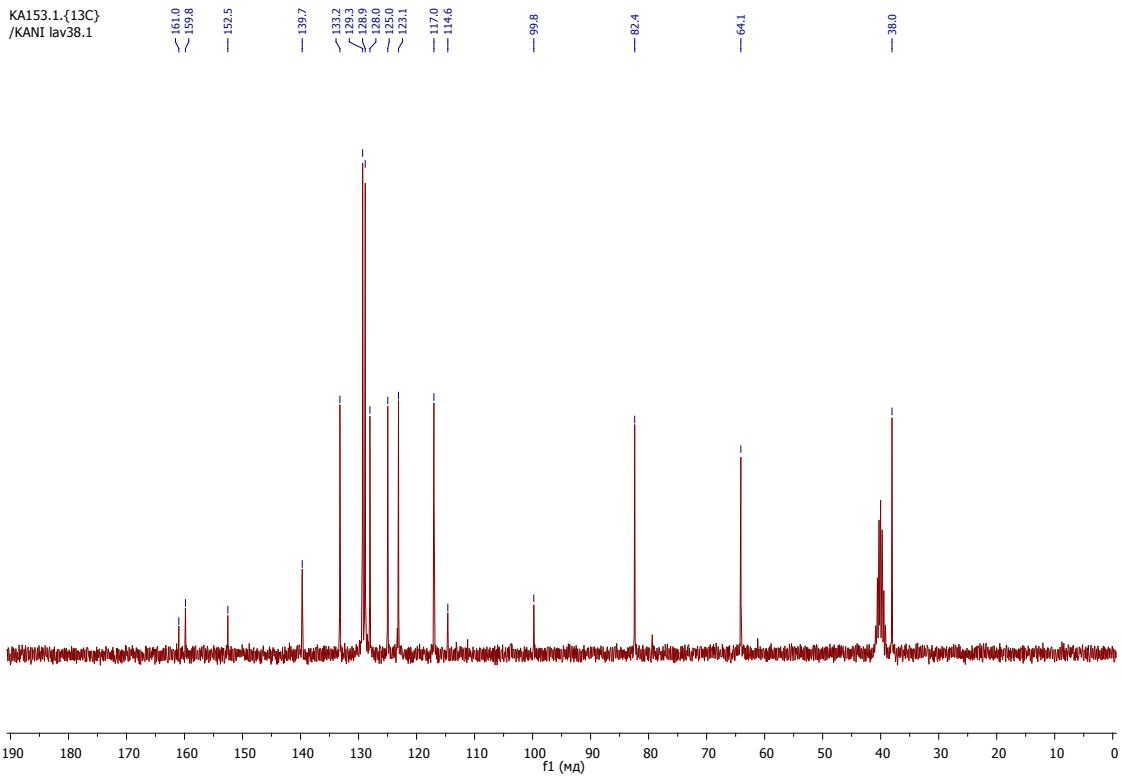

KA151.{13C}
/KANI lav9.2
196.0
169.8
140.9
129.1
128.6
127.6
108.3
82.7
63.4
50.5
41.6
36.3
32.6
29.3
26.9
f1 (мд)

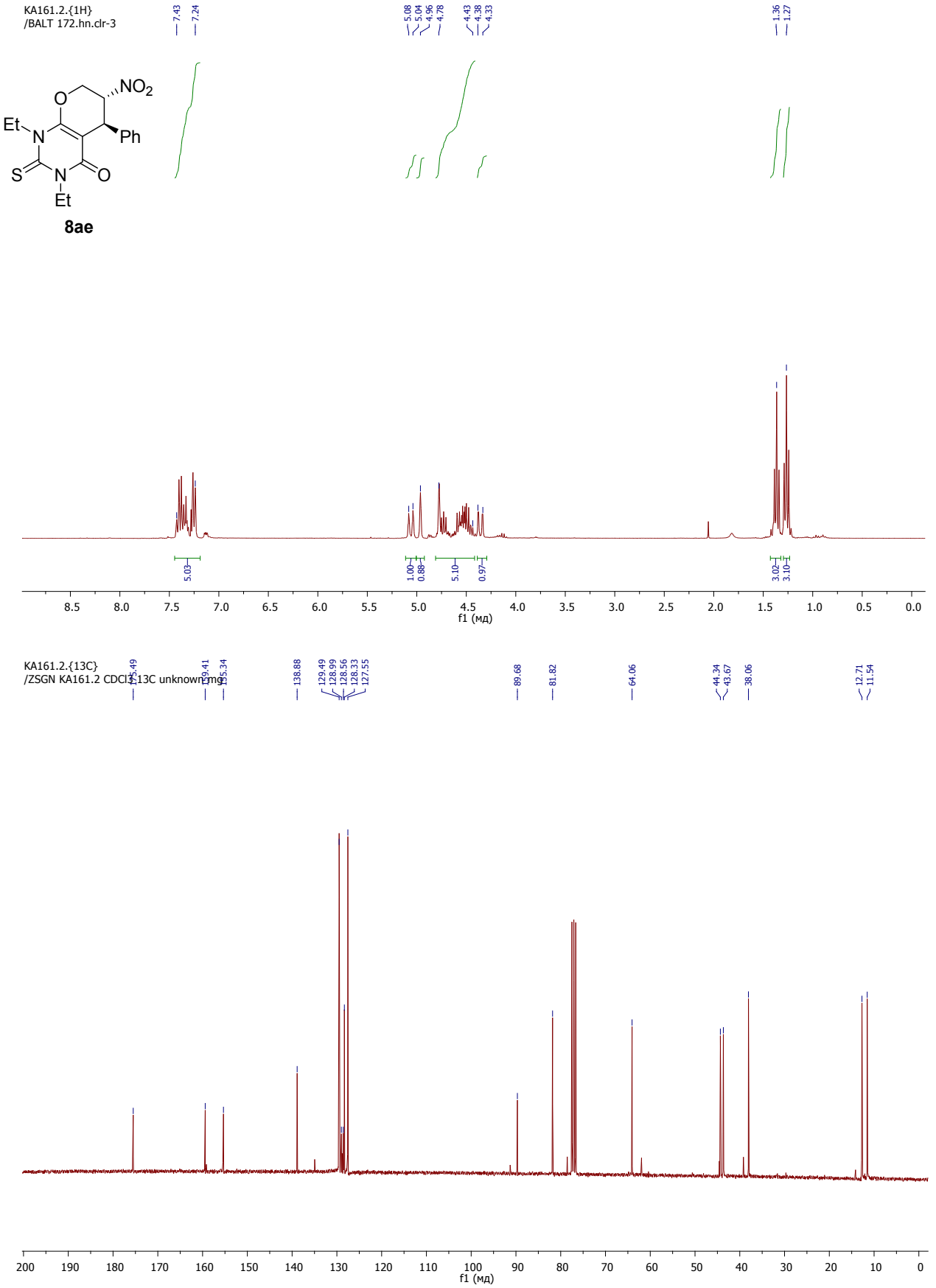

KA166c.{1H}
NMR/50143242
7.39
7.29
5.23
5.22
4.97
4.93
4.48
4.21
4.20
4.17
4.16
2.80
2.60
2.45
2.37
O
NO2
Ph
O
8ab
5.10
1.00
1.00
1.01
1.01
2.22
2.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (мд)


KA166c.{13C}
/ZSGN KA166c
FAN AV500 DMSO-D6 NMR 13C r.t.
184.0
139.3
129.2
128.8
127.9
112.8
82.8
65.5
36.8
33.6
26.3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

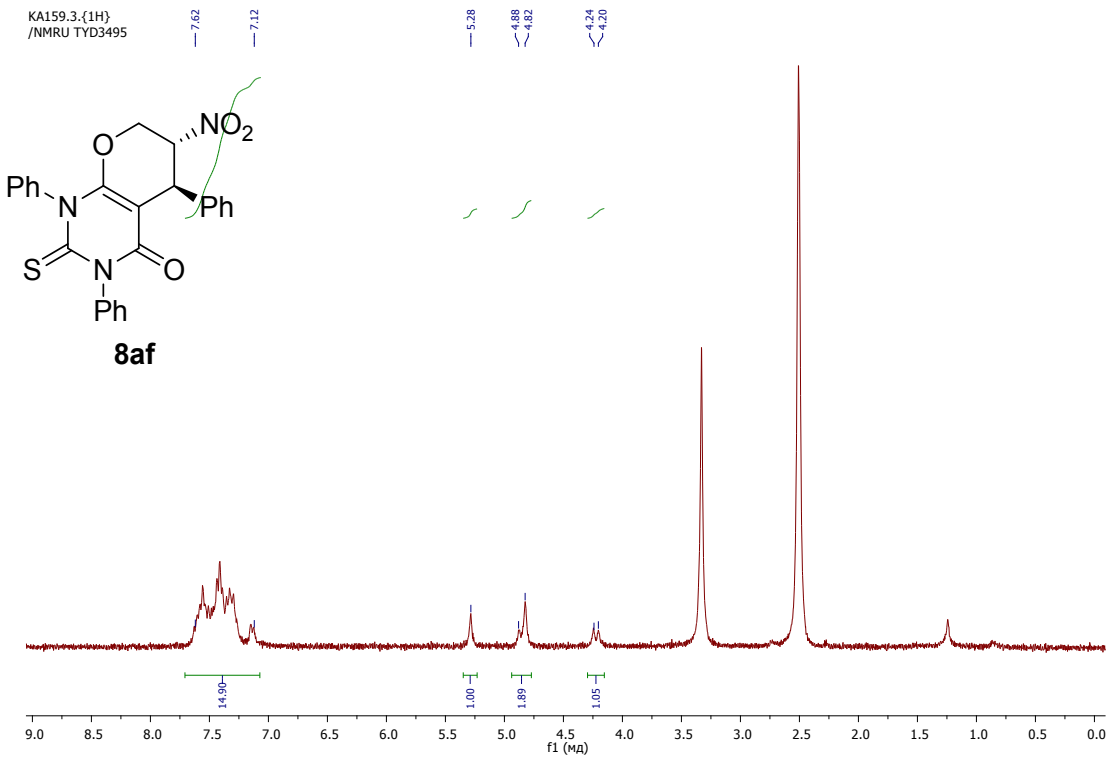

KU10.{1H}
/MBCI 4MEOSS-4MEUV2
7.39
7.17
5.91
4.91
4.86
4.77
4.25
4.21
2.27
NO2
Ph
O
O
O
8ac
5.55
1.00
3.04
1.07
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
KA157.1.{13C}
/KANI lav38.1
164.7
162.5
139.8
129.3
128.7
128.0
99.6
96.4
82.4
63.4
37.5
19.7
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (мд)


KA153.1.{1H}
/FEDU Leo_248
7.86
7.84
7.74
7.71
7.69
7.48
7.31
5.42
5.12
5.08
4.83
4.39
4.35
NO2
Ph
O
O
O
8ad
1.00
1.00
7.06
1.00
1.00
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (мд)

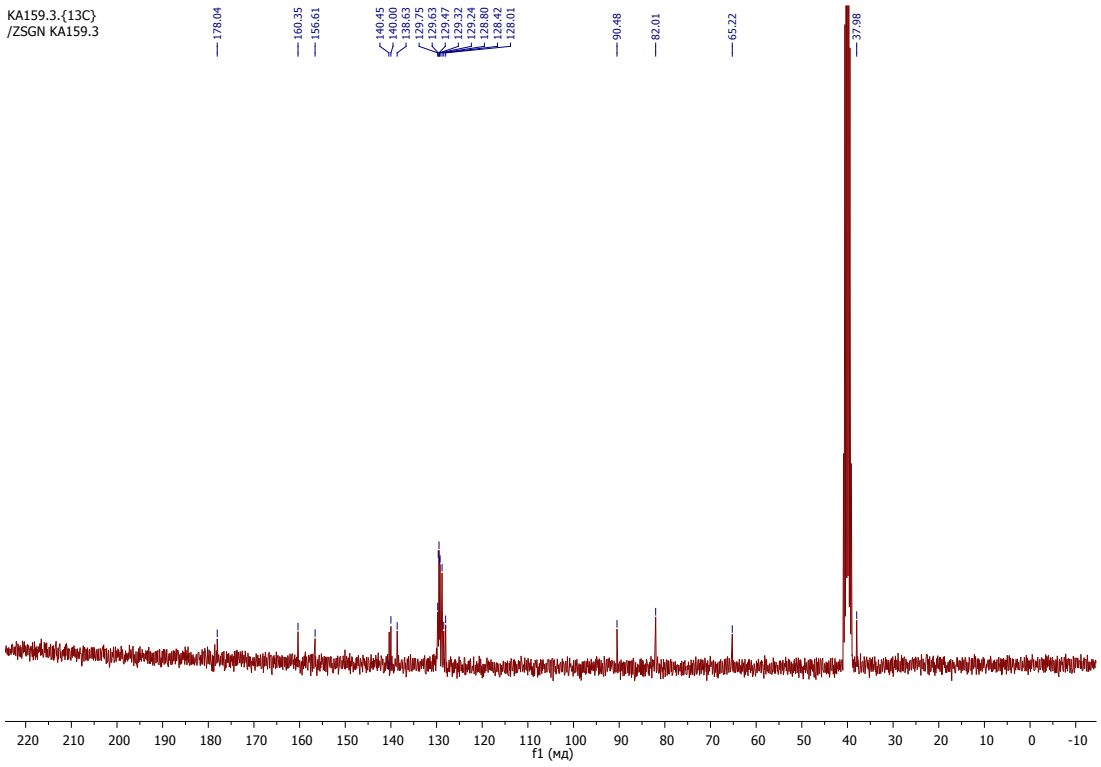

KA153.1.{13C}
/KANI lav38.1
161.0
159.8
152.5
139.7
133.2
129.3
128.9
128.0
125.0
123.1
117.0
114.6
99.8
82.4
64.1
38.0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

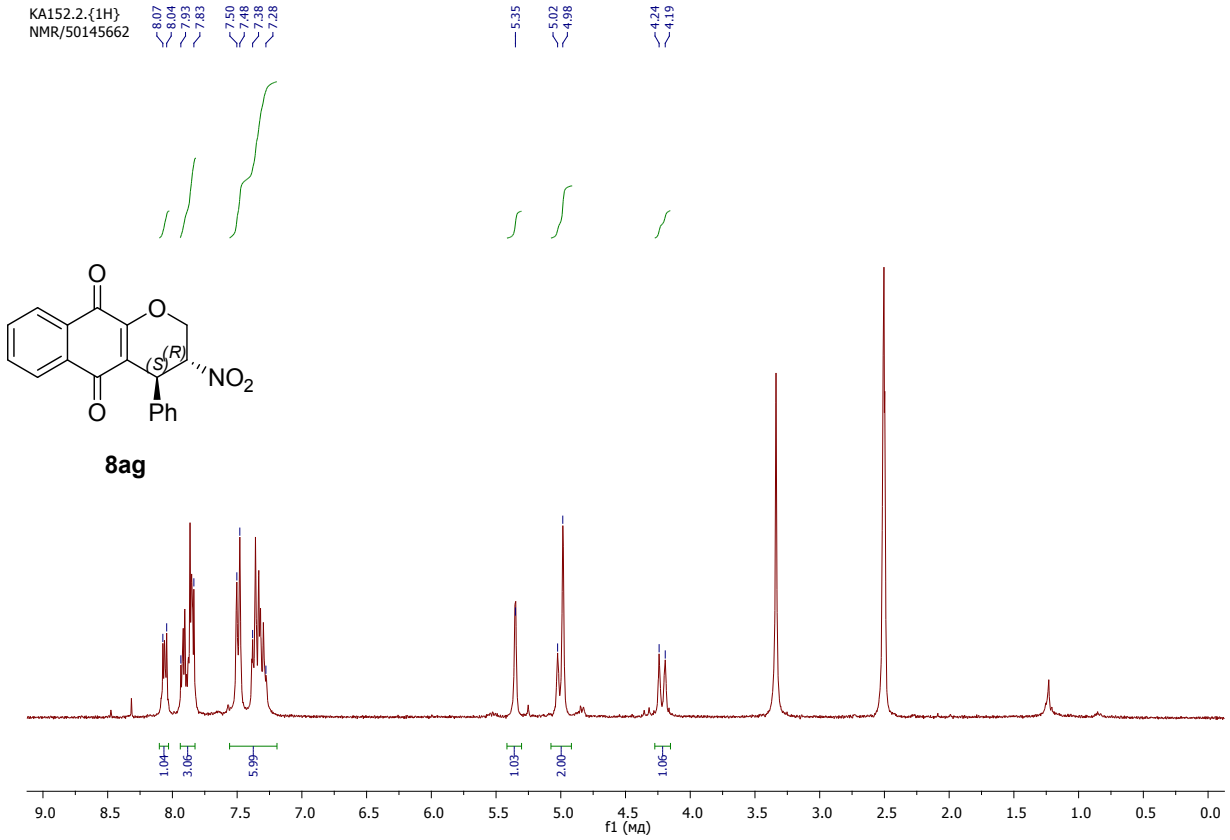

KA161.2.{1H}
/BALT 172.hn.clr-3
7.43
7.24
5.08
5.04
4.96
4.78
4.43
4.38
4.33
1.36
1.27
NO2
Et
N
O
Ph
S
N
O
Et
5.03
1.00
0.88
5.10
0.97
3.02
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (мд)
KA161.2.{13C}
/ZSGN KA161.2 CDCl3 13C unknown 1mg
75.49
69.41
65.34
138.88
129.49
128.99
128.56
128.33
127.55
89.68
81.82
64.06
44.34
43.67
38.06
12.71
11.94
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

8ae

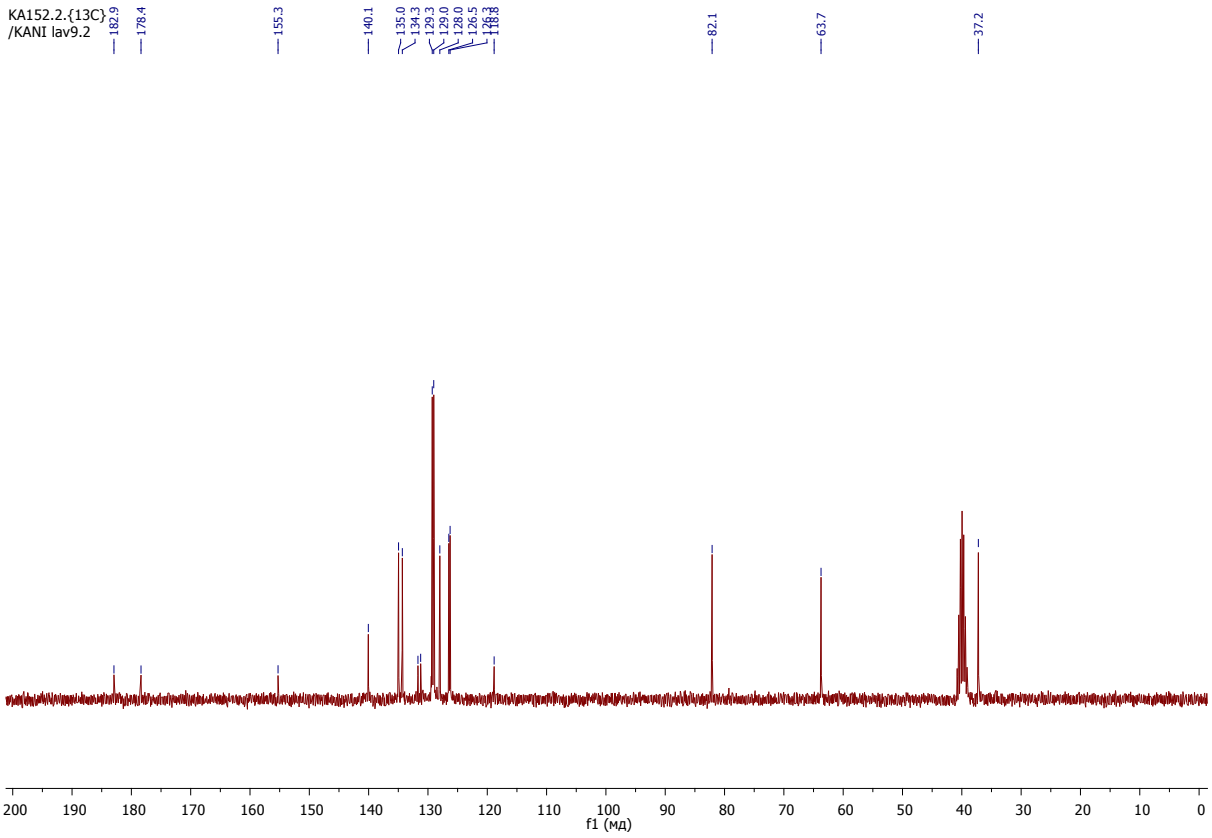

KA159.3.{1H}
/NMRU TYD3495
7.62
7.12
5.28
4.88
4.82
4.24
4.20
NO2
O
Ph
N
Ph
S
N
O
Ph
14.90
1.00
1.89
1.05
f1 (мд)

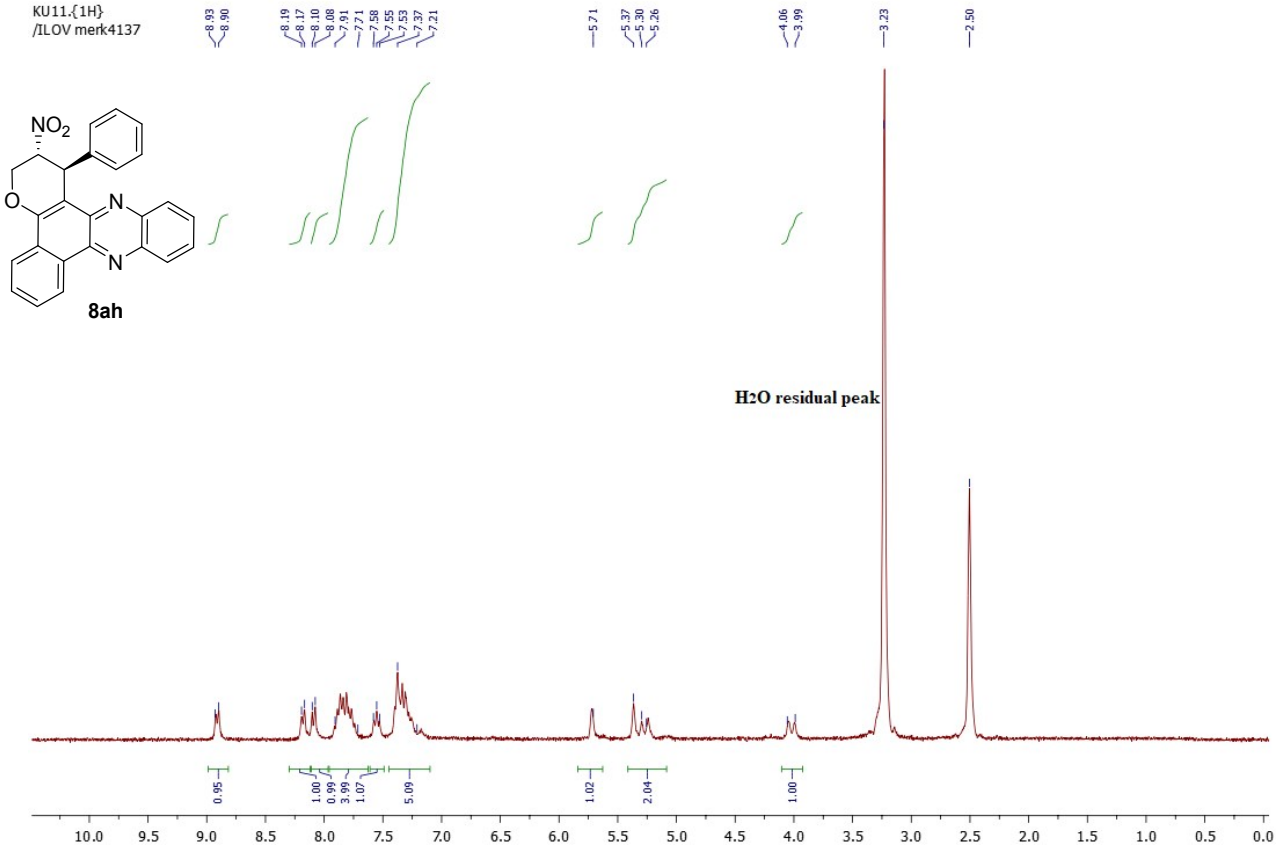
8af

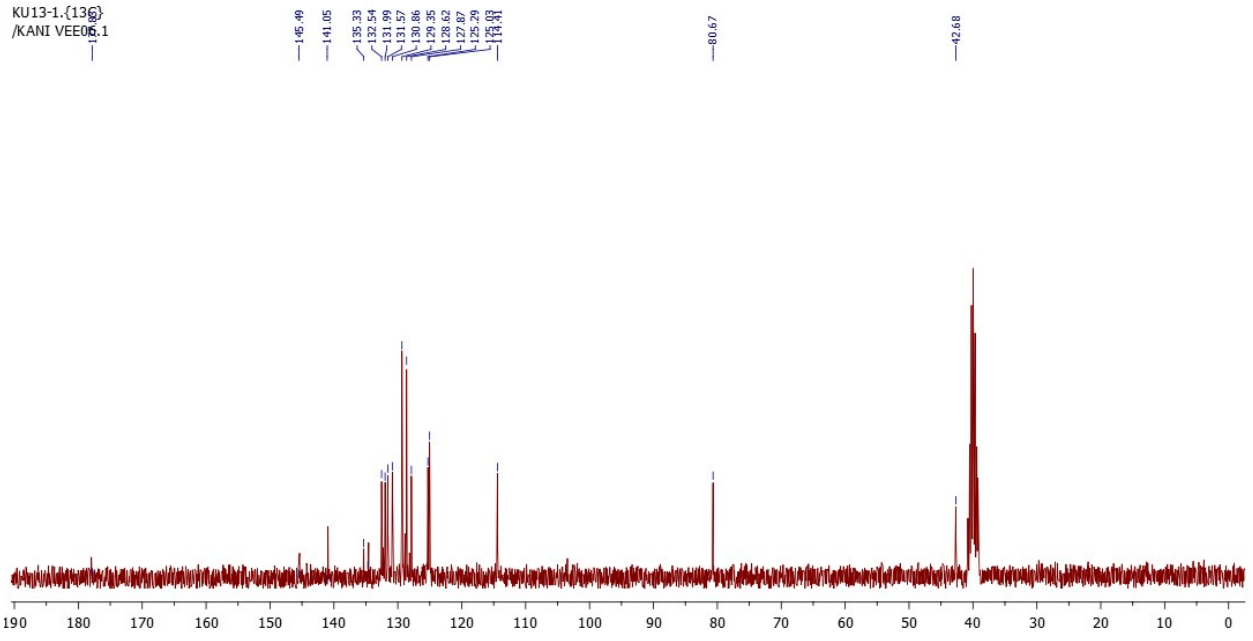

KA159.3.{13C}
/ZSGN KA159.3
178.04
160.35
156.61
140.45
140.00
138.63
129.75
129.63
129.47
129.32
129.24
128.80
128.42
128.01
90.48
82.01
65.22
37.98
f1 (мд)

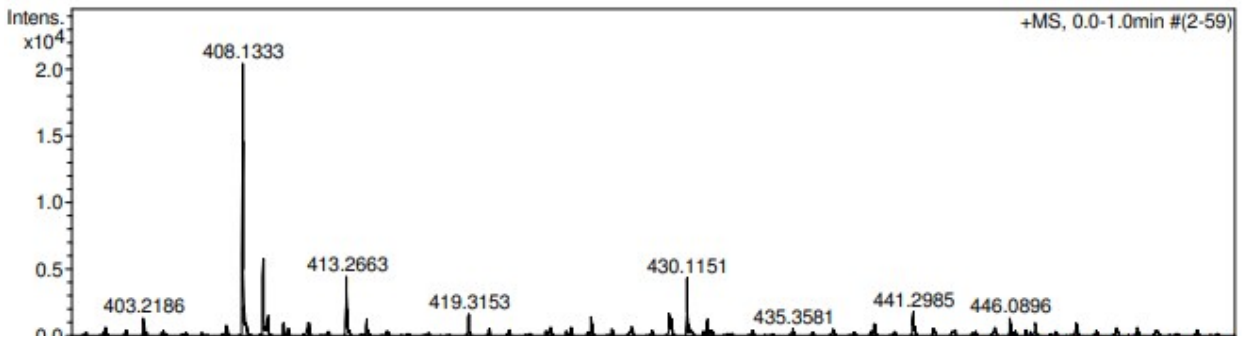

KA152.2.{1H}
NMR/50145662
8.07
8.04
7.93
7.83
7.50
7.48
7.38
7.28
5.35
5.02
4.98
4.24
4.19
O
O
O
O
(S)
(R)
NO2
Ph
1.04
3.06
5.99
1.03
2.00
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (мд)

8ag

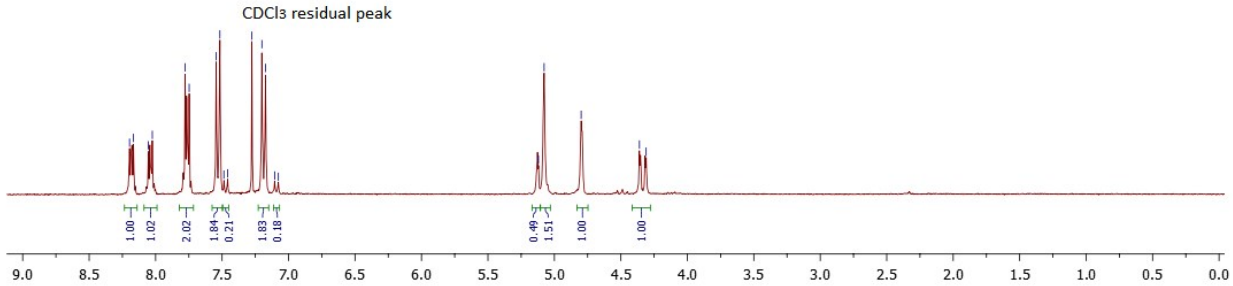

KA152.2.{13C}
/KANI lav9.2
182.9
178.4
155.3
140.1
135.0
134.3
129.3
129.0
128.0
126.5
82.1
63.7
37.2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)


KU11.{1H}
/ILOV merk4137
8.93
8.90
8.19
8.17
8.10
8.08
7.91
7.71
7.58
7.55
7.53
7.37
7.21
5.71
5.37
5.30
5.26
4.06
3.99
3.23
2.50
NO2
O
N
N
8ah
H2O residual peak
0.95
1.00
0.99
3.99
1.07
5.09
1.02
2.04
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

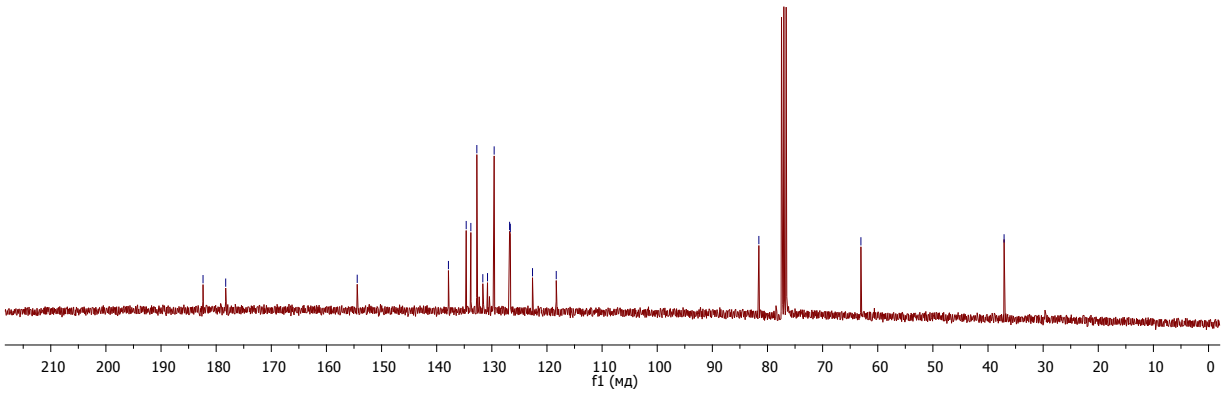

KU13-1.{13C}
/KANI VEE06.1
145.49
141.05
135.33
132.54
131.99
131.57
130.86
129.35
128.62
127.87
125.29
125.03
114.41
80.67
42.68
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

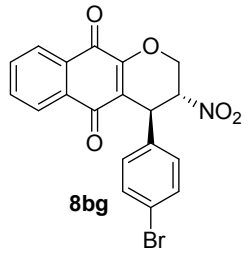

Intens.
x10^4
2.0
1.5
1.0
0.5
+MS, 0.0-1.0min #(2-59)
408.1333
413.2663
430.1151
403.2186
419.3153
435.3581
441.2985
446.0896


KA182.23.{1H}
8.20
8.17
8.05
8.02
7.78
7.75
7.54
7.52
7.49
7.46
7.28
7.20
7.17
7.10
7.08
5.12
5.08
4.80
4.36
4.31

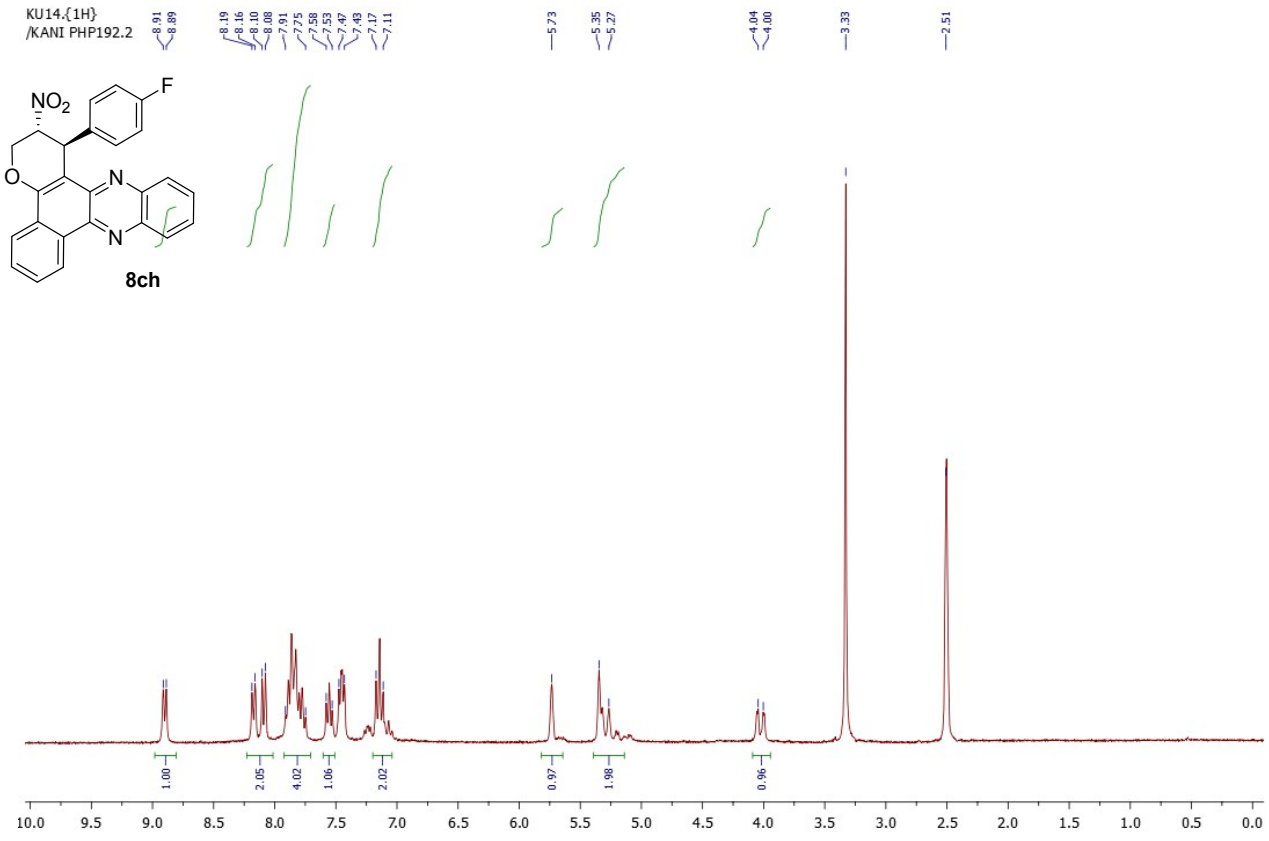

CDCl3 residual peak
1.00
1.02
2.02
1.84
0.21
1.83
0.18
0.49
1.51
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

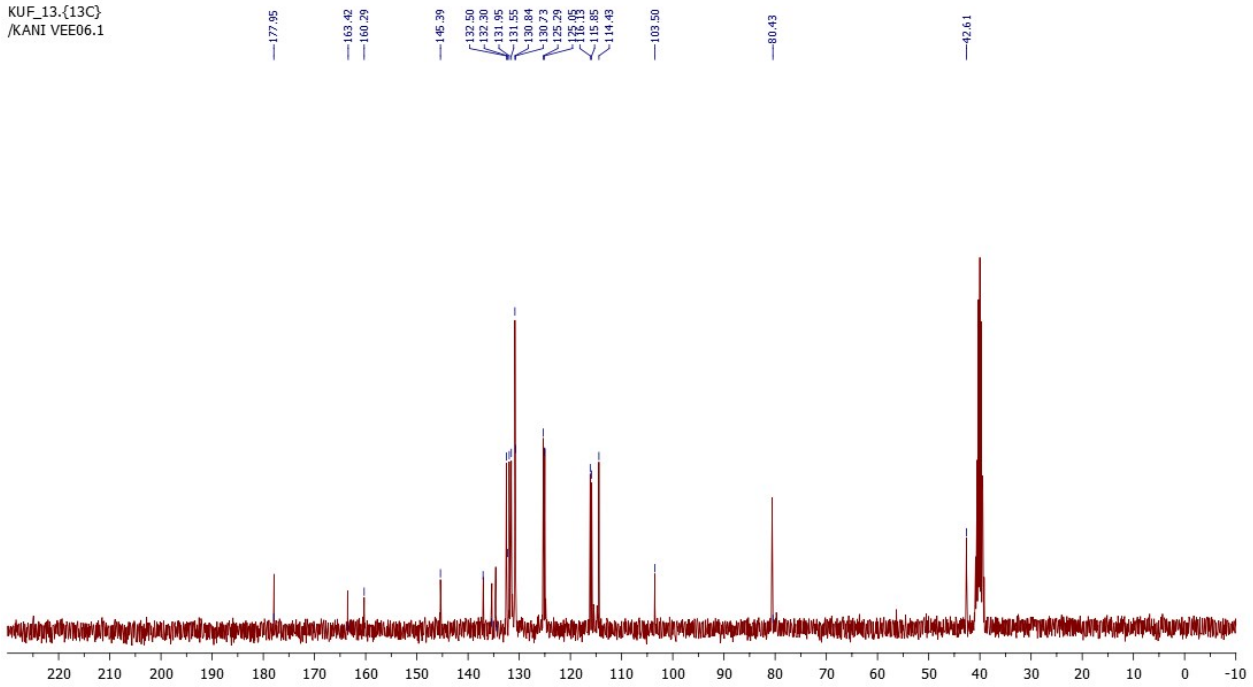

KA182.{13C}
/ZSGN KA182 CDCl3 13C unknown mg
192.38
189.27
154.42
137.87
134.65
133.80
132.72
131.63
130.78
129.58
126.78
126.64
122.62
118.32
81.57
63.05
37.09

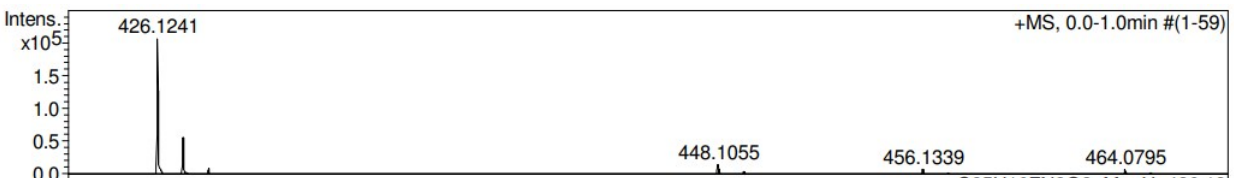

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

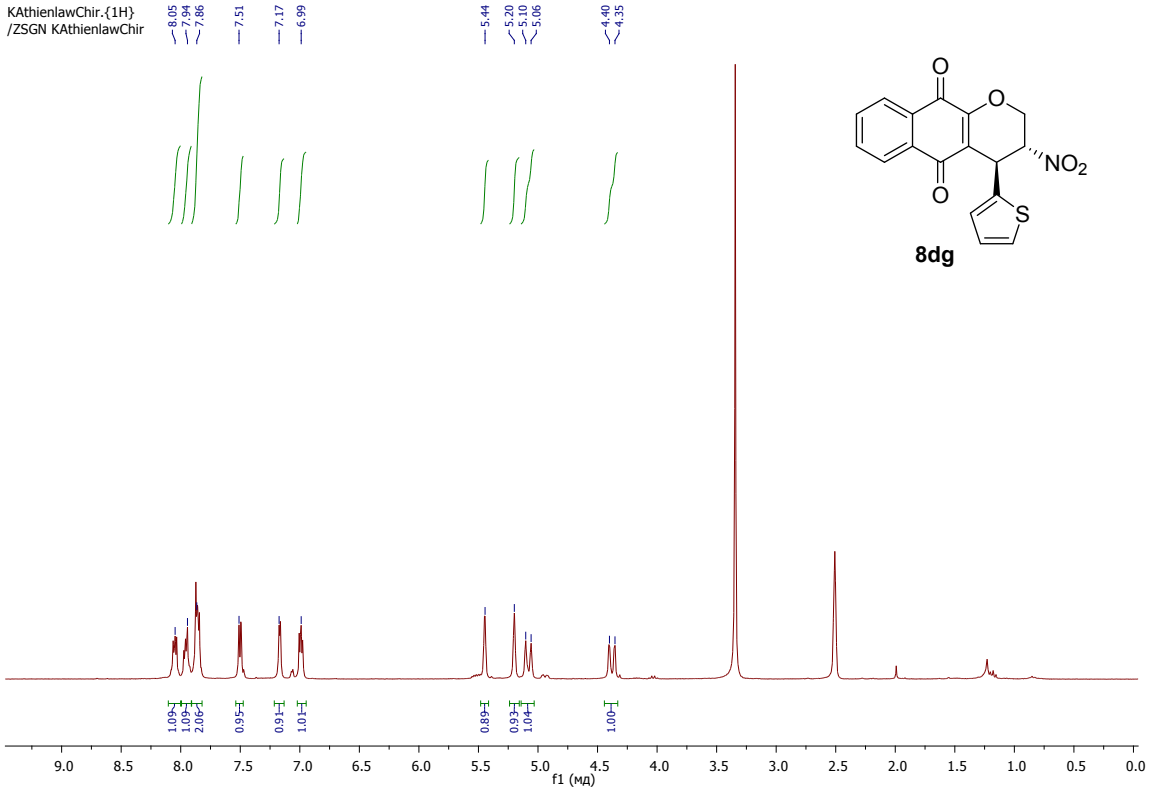

O
O
O
NO2
Br

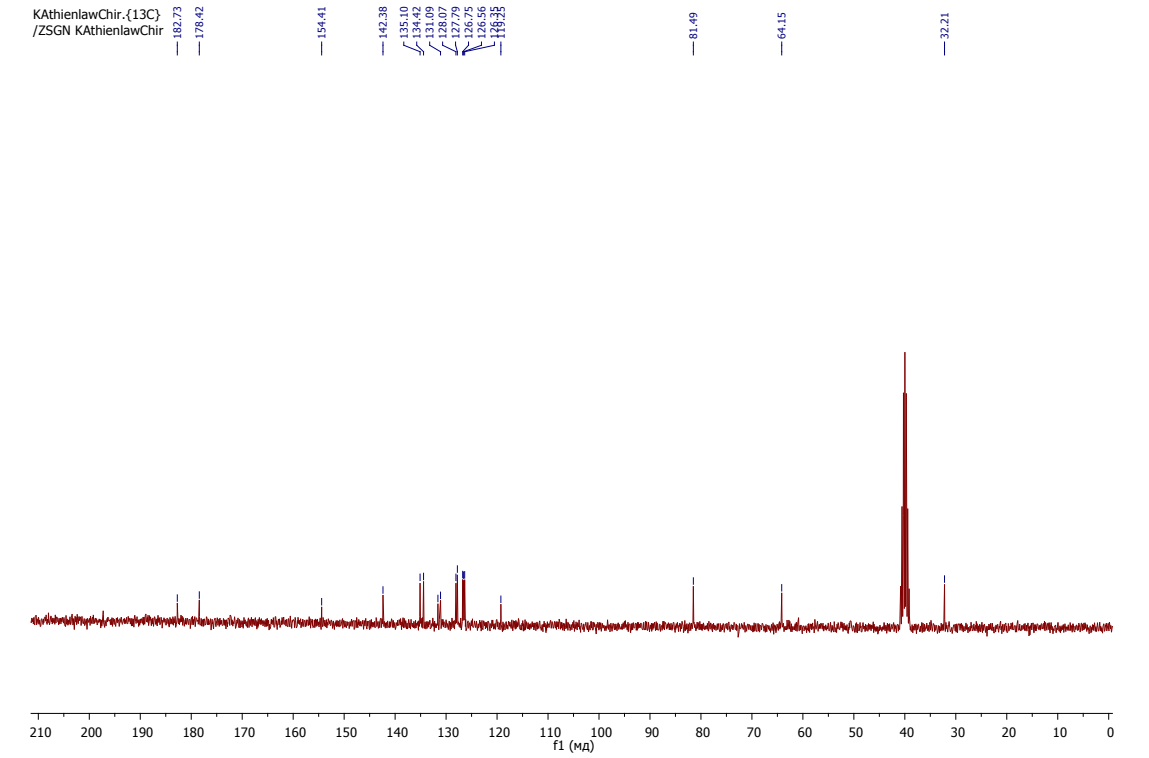
8bg

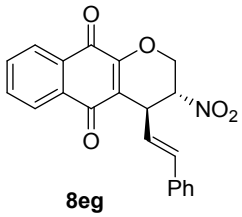

KU14.{1H}
/KANI PHP192.2
8.91
8.89
8.19
8.16
8.10
8.08
7.91
7.75
7.58
7.53
7.47
7.43
7.17
7.11
5.73
5.35
5.27
4.04
4.00
3.33
2.51
NO2
F
O
N
N
8ch
1.00
2.05
4.02
1.06
2.02
0.97
1.98
0.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


KUF_13.{13C}
/KANI VEE06.1
177.95
163.42
160.29
145.39
132.50
132.30
131.95
131.55
130.84
130.73
125.29
116.13
115.85
114.43
103.50
80.43
42.61
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

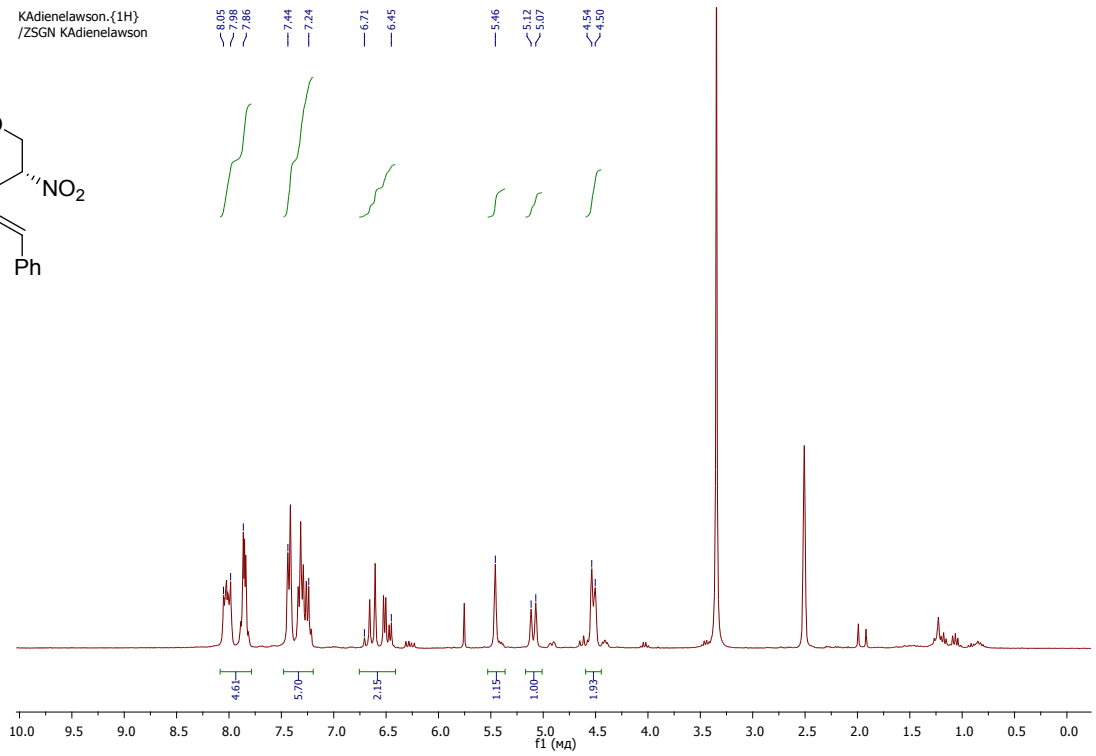

Intens.
x10^5
1.5
1.0
0.5
0.0
426.1241
+MS, 0.0-1.0min #(1-59)
448.1055
456.1339
464.0795

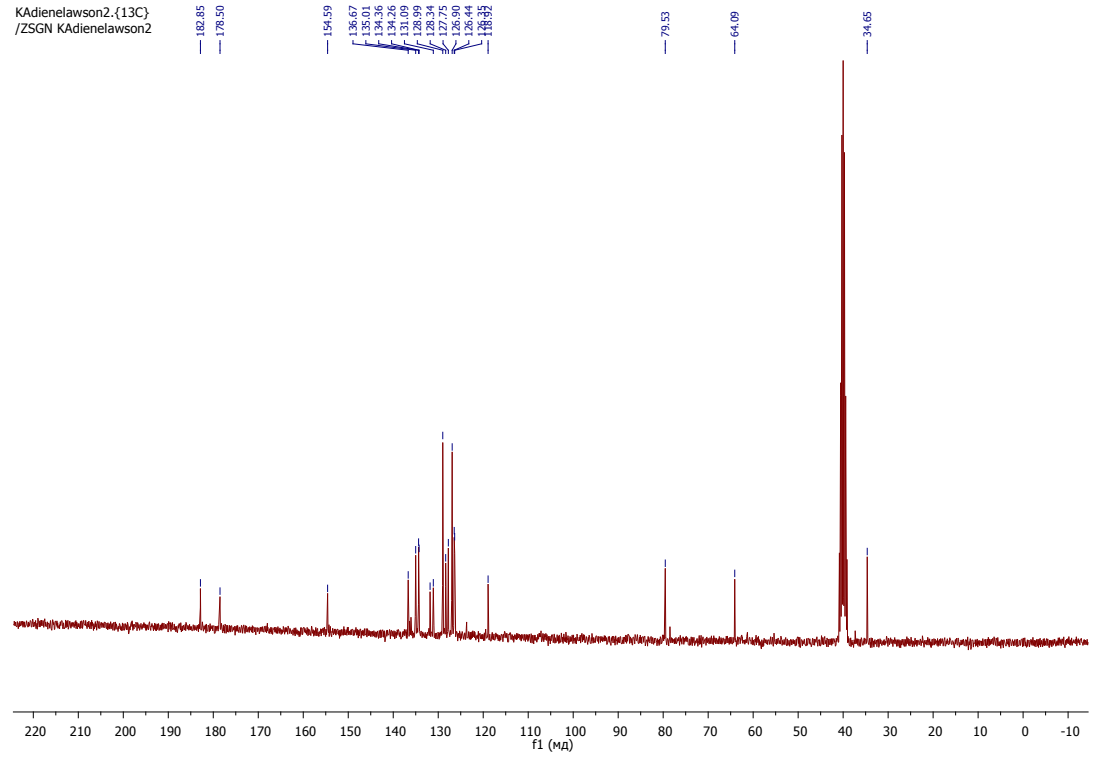

KAthienlawChir.{1H}
/ZSGN KAthienlawChir
8.05
7.94
7.86
7.51
7.17
6.99
5.44
5.20
5.10
5.06
4.40
4.35
1.09
1.09
2.06
0.95
0.91
1.01
0.89
0.93
1.04
1.00
f1 (мд)
O
O
O
NO2
S
8dg


KAthienlawChir.{13C}
/ZSGN KAthienlawChir
182.73
178.42
154.41
142.38
135.10
134.42
131.09
128.07
127.79
126.75
126.56
81.49
64.15
32.21
f1 (мд)


O
O
O
NO2
Ph

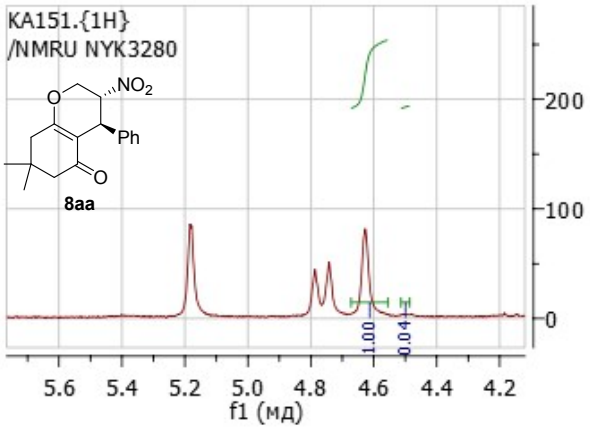
8eg


KAdienelawson.{1H}
/ZSGN KAdienelawson
8.05
7.98
7.86
7.44
7.24
6.71
6.45
5.46
5.12
5.07
4.54
4.50
4.61
5.70
2.15
1.15
1.00
1.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (мд)

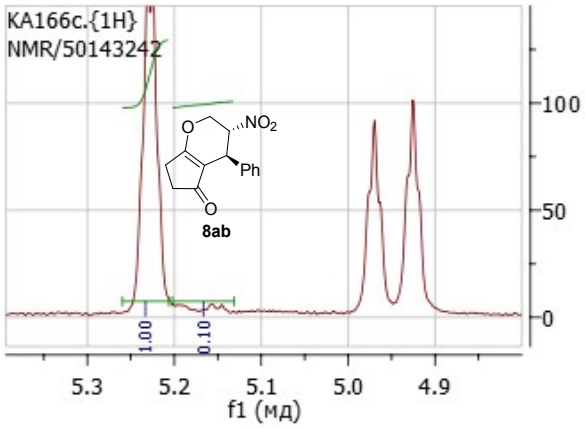

KAdienelawson2.{13C}
/ZSGN KAdienelawson2
182.85
178.50
154.59
136.67
135.01
134.36
134.26
131.09
128.99
128.34
127.75
126.00
126.44
126.35
118.92
79.53
64.09
34.65
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (мд)

Determination of *Dr* values for compounds 8 by ^{1}H NMR

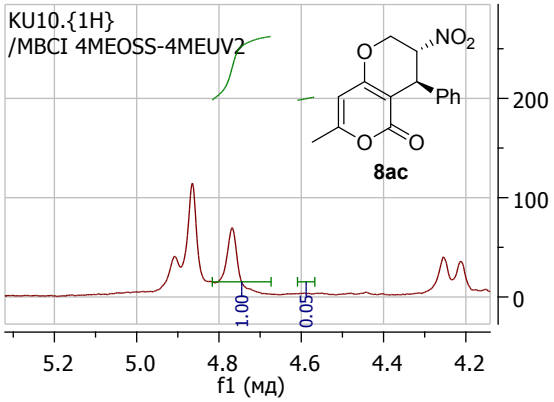
(**8aa**): *Dr* anti/syn = 25:1



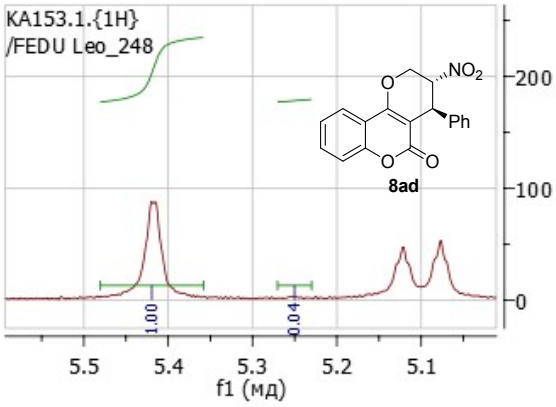
(**8ab**): *Dr* anti/syn = 10:1



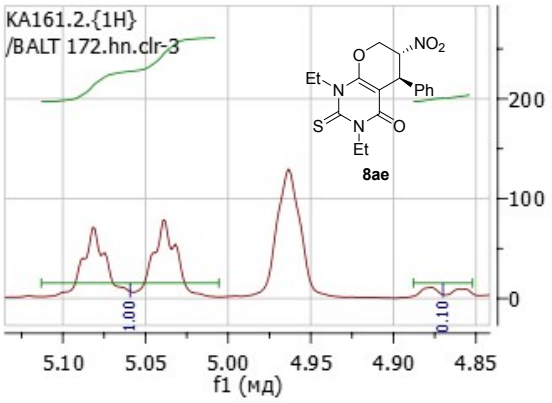
(**8ac**): *Dr* anti/syn = 20:1



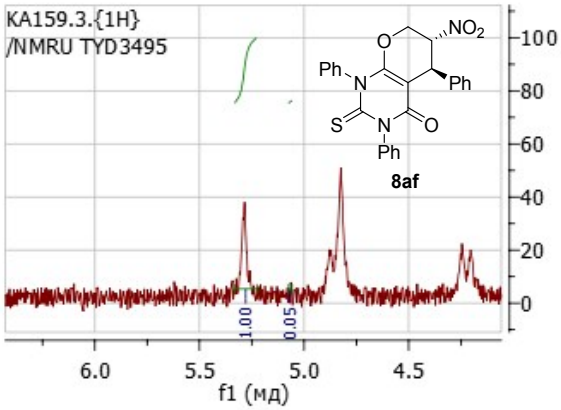
(**8ad**): *Dr* anti/syn = 25:1



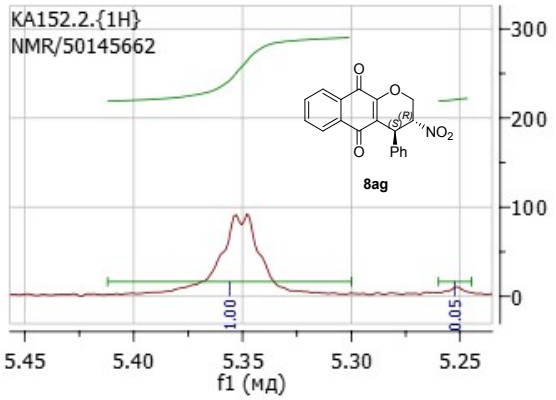
(**8ae**): *Dr* anti/syn = 10:1



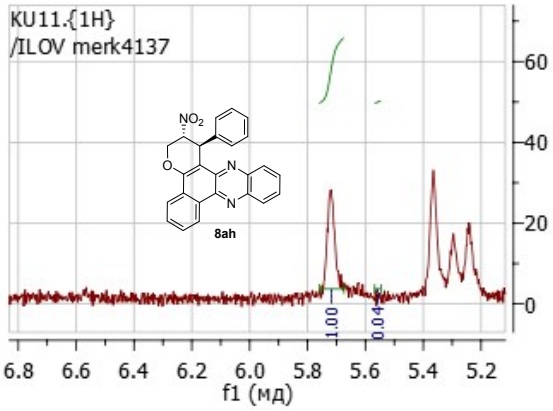
(**8af**): *Dr* anti/syn = 20:1



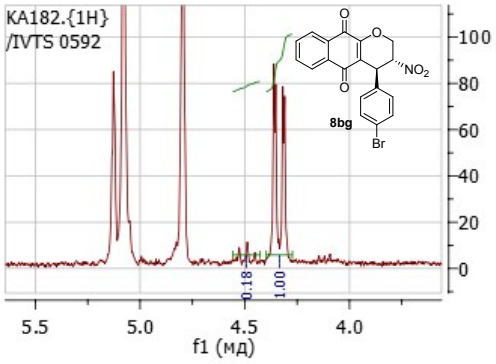
(**8ag**): *Dr* anti/syn = 20:1



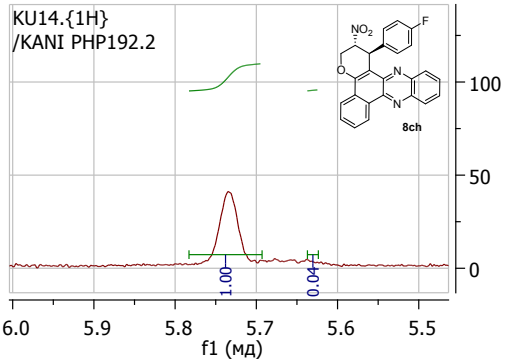
(**8ah**): *Dr* anti/syn = 25:1



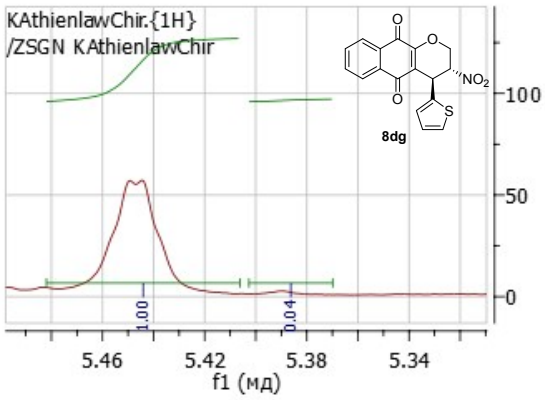
(**8bg**): *Dr* anti/syn = 5.5:1



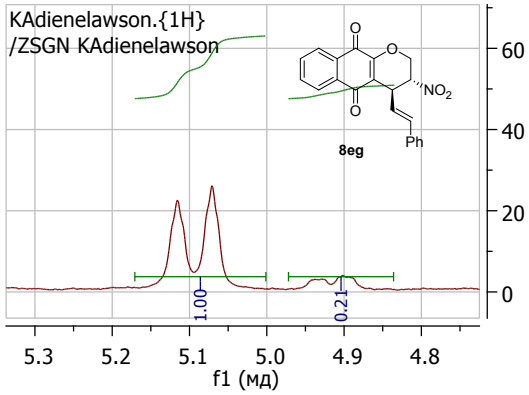
(**8ch**): *Dr* anti/syn = 25:1



(**8dg**): *Dr* anti/syn = 25:1



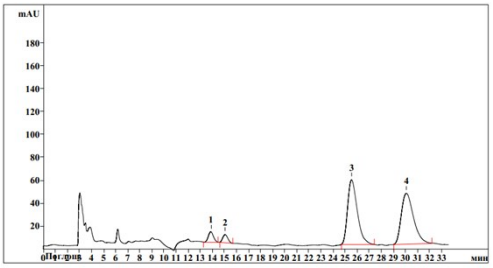
(**8eg**): *Dr* anti/syn = 5:1



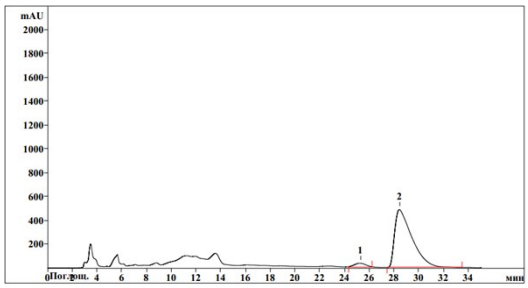
5. HPLC data for all Michael adducts 8.

7,7-Dimethyl-3-nitro-4-phenyl-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (8aa):

94% *ee* [HPLC *Chiralpak OD-H*, *n-hexane/*^{i}*PrOH* 90:10, 1 mL min^{-1}, 254 nm, t_{major}= 30.1 min, t_{minor} = 25.5 min].



Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %	Конц.
1	13.88	9.08	263.50	3.92	263.5
2	15.08	7.06	205.00	3.05	205
3	25.54	56.39	3141.52	46.71	3142
4	30.08	44.34	3115.75	46.33	3116
4	33.58	116.87	6725.78	100.00	6726

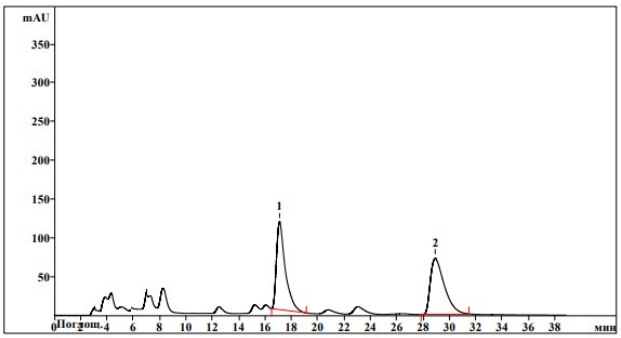


РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %	Конц.
1	25.27	28.99	1741.03	3.54	1741
2	28.46	485.80	47494.56	96.46	4.749e+004
2	35.12	514.79	49235.58	100.00	4.924e+004

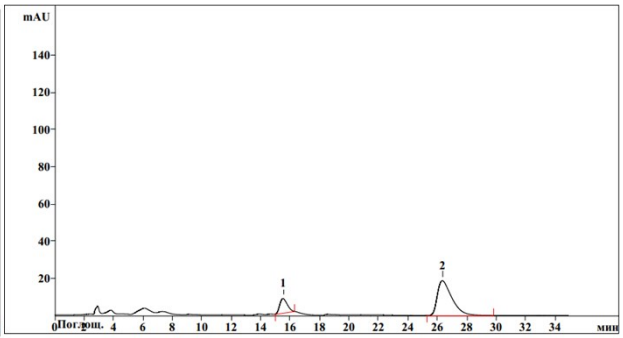
3-Nitro-4-phenyl-3,4,6,7-tetrahydrocyclopenta[b]pyran-5(2H)-one (8ab):

65% *ee* [HPLC *Chiralpak AD-H*, *n-hexane/*^{i}*PrOH* 90:10, 1 mL min^{-1}, 254 nm, t_{minor}= 17.1 min, t_{major} = 28.9 min].



РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %	Конц.
1	17.11	113.54	5309.65	50.00	5310
2	28.93	71.87	5308.85	50.00	5309
2	38.88	185.41	10618.50	100.00	1.062e+004

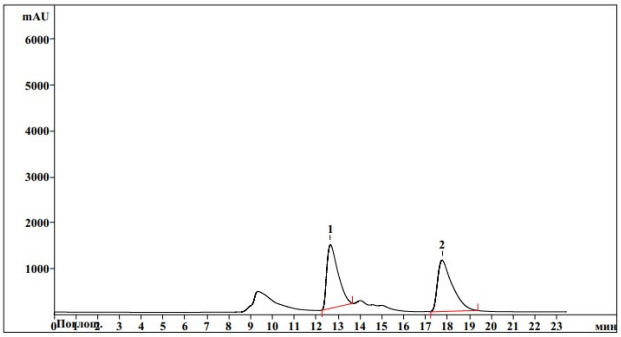


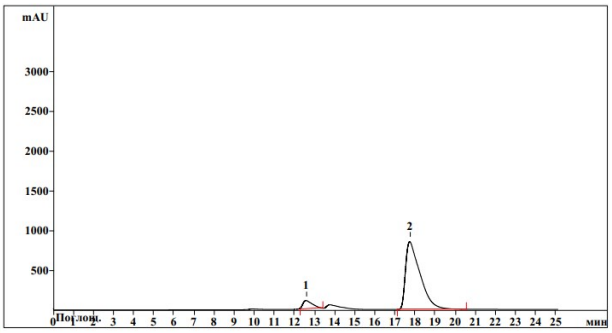
РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %	Конц.
1	15.51	7.73	272.43	17.68	272.4
2	26.35	18.66	1268.90	82.32	1269
2	34.93	26.39	1541.33	100.00	1541

7-Methyl-3-nitro-4-phenyl-3,4-dihydropyrano[4,3-b]pyran-5(2H)-one (8ac):

86% *ee* [HPLC *Chiralpak AD-H*, *n-hexane/ⁱPrOH* 70:30, 1 mL min^{-1}, 220 nm, t_{major}= 17.8 min, t_{minor} = 12.7 min].



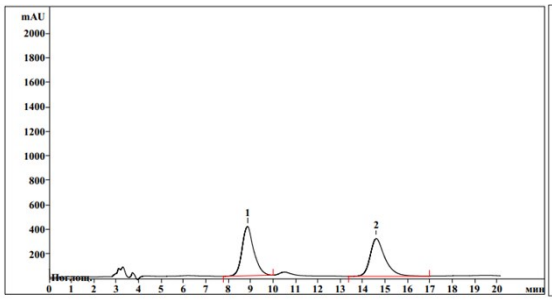


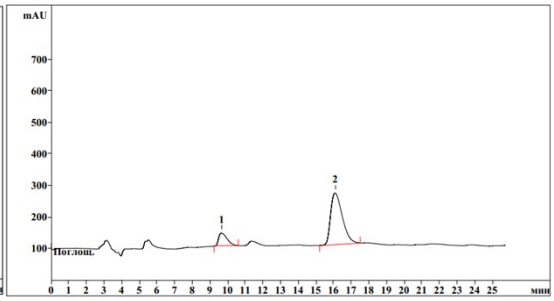
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	12.66	1381.91	49342.74	48.62
2	17.76	1114.78	52145.54	51.38
2	23.46	2496.68	101488.28	100.00

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	12.58	98.33	3183.49	6.90
2	17.74	852.16	42951.56	93.10
2	25.12	950.49	46135.05	100.00

3-Nitro-4-phenyl-3,4-dihydropyrano[3,2-c]chromen-5(2H)-one (8ad):

70% *ee* [HPLC *Chiralpak AD-H*, *n-hexane/ⁱPrOH* 70:30, 1 mL min^{-1}, 254 nm, t_{major}= 14.6 min, t_{minor} = 8.9 min].



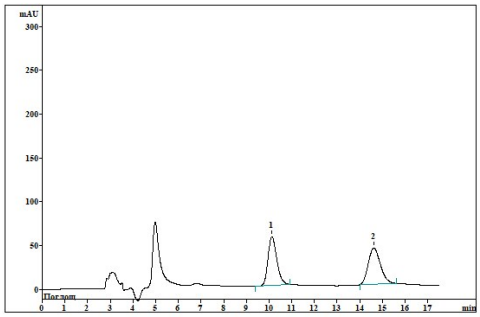


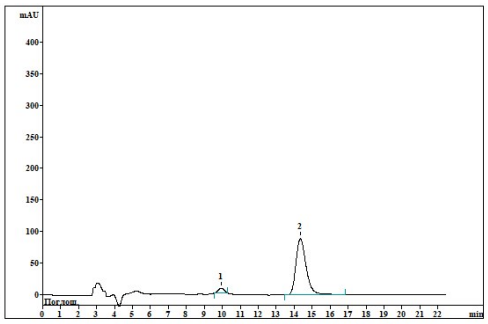
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	8.861	401.17	14736.18	50.90
2	14.61	306.60	14212.91	49.10
2	34.47	707.77	28949.09	100.00

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	9.659	40.80	1366.50	15.40
2	16.09	163.32	7505.00	84.60
2	25.76	204.11	8871.50	100.00

1,3-Diethyl-6-nitro-5-phenyl-2-thioxo-2,3,6,7-tetrahydro-1H-pyrano[2,3-d]pyrimidin-4(5H)-one (8ae):

91% *ee* [HPLC *Chiralpak IB-H*, *n-hexane/DCM* 60:40, 0.7 mL min^{-1}, 220 nm, t_{minor}= 10.1 min, t_{major} = 14.6 min].





РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Response normalization
Стандарт: No

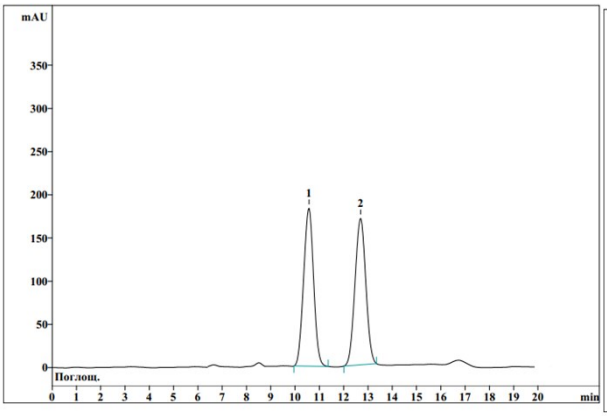
Пик	Время min	Площадь mAU*sec	Площадь %
1	10.13	1504.68	49.51
2	14.62	1534.67	50.49
2	17.52	3039.35	100.00

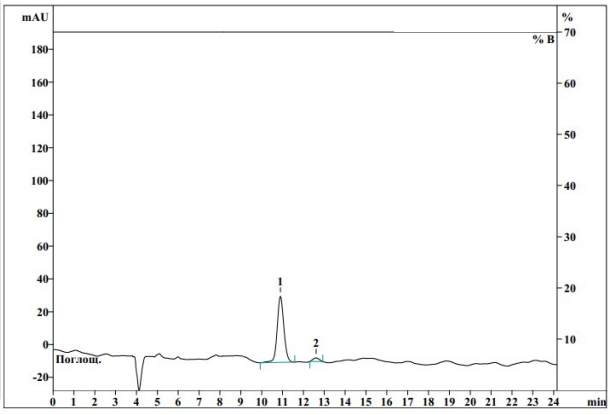
РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Response normalization
Стандарт: No

Пик	Время min	Площадь mAU*sec	Площадь %
1	9.955	171.81	4.65
2	14.35	3520.29	95.35
2	22.48	3692.10	100.00

6-Nitro-1,3,5-triphenyl-2-thioxo-2,3,6,7-tetrahydro-1H-pyrano[2,3-d]pyrimidin-4(5H)-one (8af):

91% *ee* [HPLC *Chiralpak IB-H*, *n-hexane/DCM* 70:30, 0.6 mL min^{-1}, 220 nm, t_{major} = 10.6 min, t_{minor} = 12.7 min.]





РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Response normalization
Стандарт: No

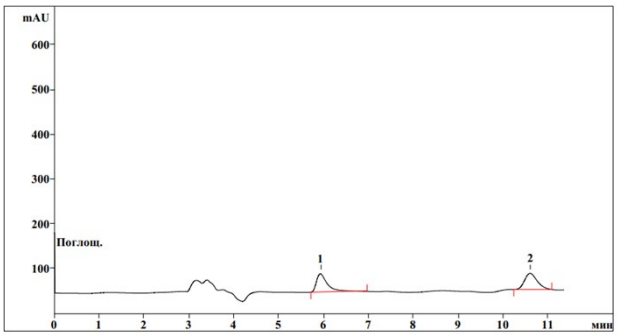
Пик	Время min	Площадь mAU*sec	Площадь %	Компонент
1	10.56	5231.42	49.93	
2	12.69	5246.72	50.07	
2	23.25	10478.14	100.00	

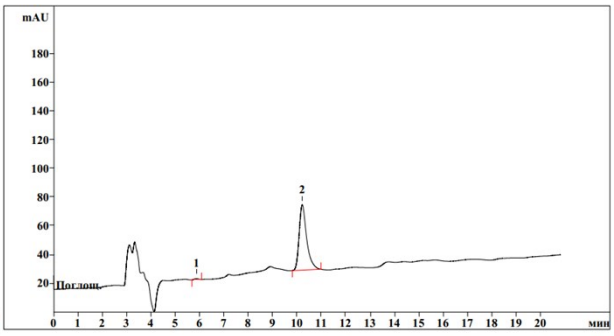
РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Response normalization
Стандарт: No

Пик	Время min	Площадь mAU*sec	Площадь %	Компонент
1	10.92	891.70	95.14	
2	12.64	45.55	4.86	
2	24.16	937.25	100.00	

3-Nitro-4-phenyl-3,4-dihydro-2H-benzo[g]chromene-5,10-dione (8ag):

99% *ee* [HPLC *Chiralpak OJ-H*, *n-hexane/*^{i}*PrOH* 70:30, 1 mL min^{-1}, 220 nm, t_{major}= 10.6 min, t_{minor} = 5.9 min].



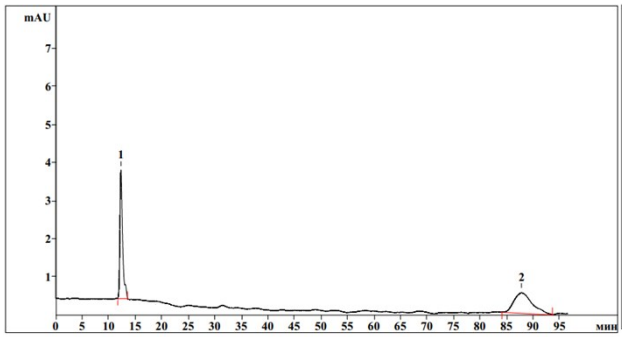


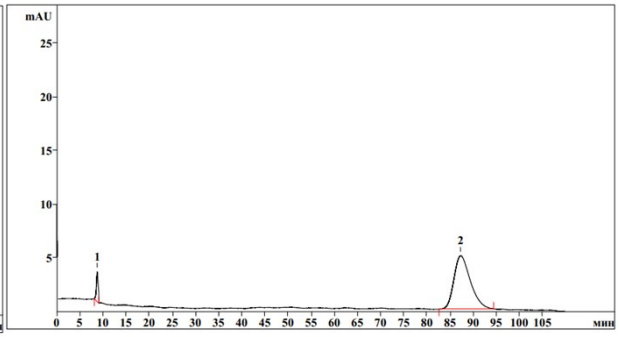
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	5.935	40.89	718.16	50.26
2	10.61	36.29	710.80	49.74
2	24.73	77.18	1428.96	100.00

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	5.875	0.76	8.69	0.88
2	10.22	45.56	979.38	99.12
2	20.83	46.33	988.06	100.00

2-Nitro-1-phenyl-2,3-dihydro-1H-benzo[a]pyrano[2,3-c]phenazine (8ah):

90% *ee* [HPLC *Chiralpak AD-H*, *n-hexane/*^{i}*PrOH* 70:30, 1 mL min^{-1}, 220 nm, t_{major}= 12.3 min, t_{minor} = 87.9 min].





РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

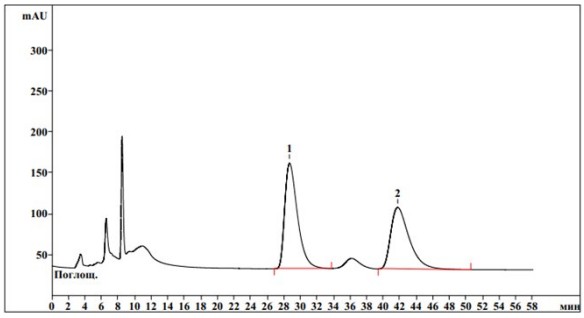
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	12.33	3.37	118.91	48.60
2	87.89	0.53	125.77	51.40
2	96.53	3.91	244.68	100.00

РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	8.822	2.79	77.39	5.90
2	87.33	4.98	1233.16	94.10
2	109.8	7.76	1310.54	100.00

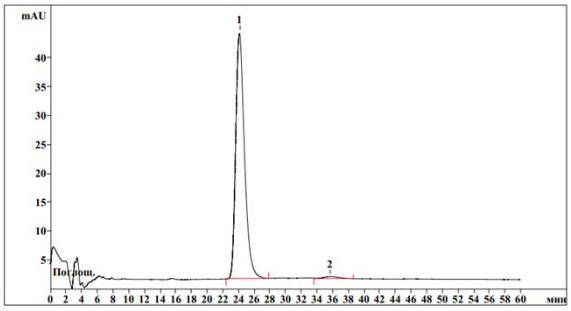
4-(4-bromophenyl)-3-nitro-3,4-dihydro-2H-benzo[g]chromene-5,10-dione (8bg):

97% *ee* [HPLC *Chiralpak OD-H*, *n-hexane/*^{i}*PrOH* 70:30, 1 mL min^{-1}, 220 nm, t_{major}= 28.7 min, t_{minor} = 41.8 min].



РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	28.71	129.11	13858.94	54.12
2	41.76	75.58	11748.92	45.88
2	58.11	204.69	25607.86	100.00

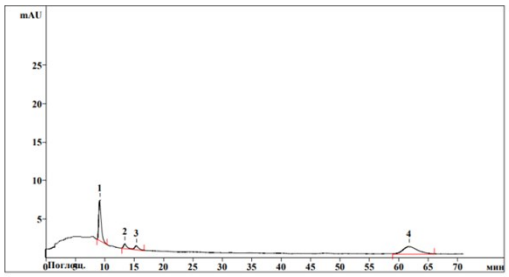


РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	24.12	42.51	3322.27	98.60
2	35.75	0.35	47.04	1.40
2	59.98	42.86	3369.32	100.00

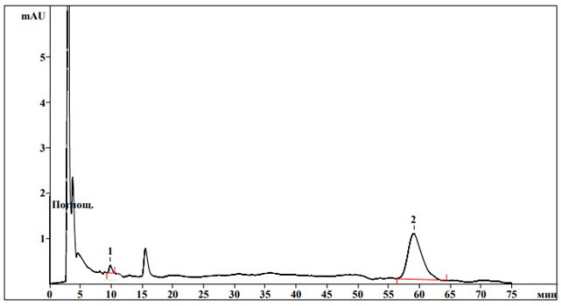
1-(4-Fluorophenyl)-2-nitro-2,3-dihydro-1H-benzo[a]pyrano[2,3-c]phenazine (8ch):

94% *ee* [HPLC *Chiralpak AD-H*, *n-hexane/*^{i}*PrOH* 70:30, 1 mL min^{-1}, 220 nm, t_{major}= 61.7 min, t_{minor} = 9.2 min].



РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	9.18	5.25	154.39	44.03
2	13.45	0.54	21.85	6.23
3	15.4	0.48	20.53	5.86
4	61.74	0.93	153.89	43.89
4	70.97	7.21	350.67	100.00

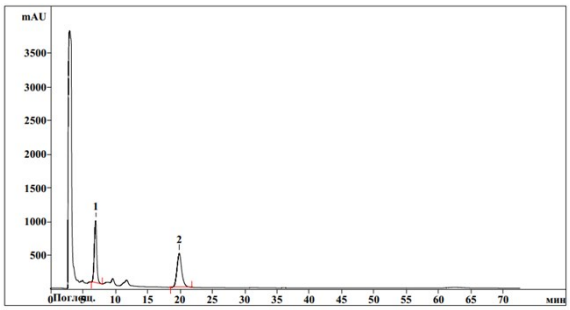


РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	9.429	0.16	5.17	3.12
2	59.07	1.00	160.77	96.88

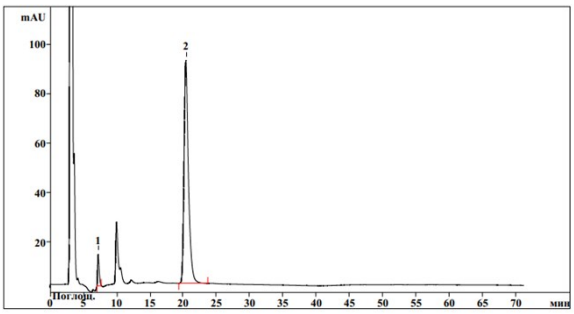
3-Nitro-4-(thiophen-2-yl)-3,4-dihydro-2H-benzo[g]chromene-5,10-dione (8dg):

91% *ee* [HPLC *Chiralpak AD-H*, *n-hexane/*^{i}*PrOH* 80:20, 1 mL min^{-1}, 220 nm, t_{major}= 20.4 min, t_{minor} = 7.0 min].



РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	6.982	921.72	24036.73	48.21
2	19.91	504.12	25821.96	51.79
2	72.58	1425.84	49858.68	100.00

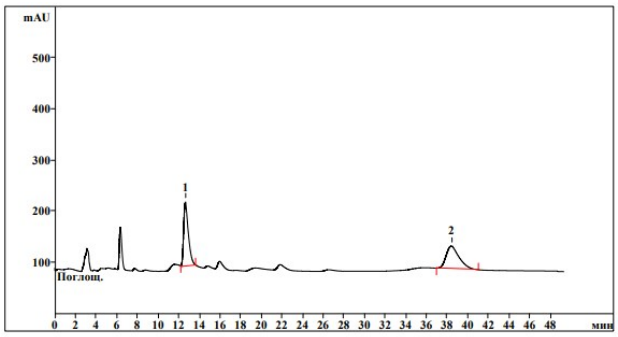


РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	7.243	12.55	203.56	4.71
2	20.41	89.75	4114.67	95.29
2	71.16	102.30	4318.23	100.00

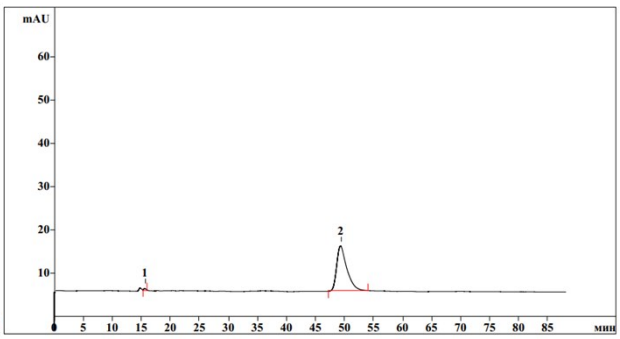
3-Nitro-4-styryl-3,4-dihydro-2H-benzo[g]chromene-5,10-dione (8eg):

99% *ee* [HPLC *Chiralpak AD-H*, *n-hexane/*^{i}*PrOH* 80:20, 1 mL min^{-1}, 220 nm, t_{major}= 38.4 min, t_{minor} = 12.7 min].



РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	12.65	122.85	3859.79	49.86
2	38.41	44.16	3881.05	50.14
2	49.31	167.02	7740.84	100.00



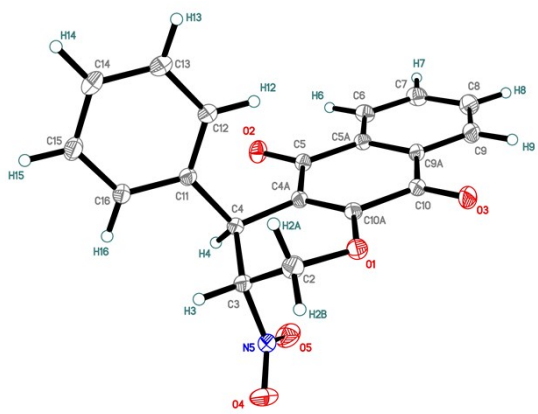
РЕЗУЛЬТАТЫ РАСЧЕТА
Метод расчета: Заказной
Стандарт: Нет

Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	15.6	0.31	6.84	0.54
2	49.33	10.40	1269.40	99.46
2	88.15	10.72	1276.24	100.00

6. X-ray crystallographic data and refinement details for product 8ag.

X-ray diffraction data were collected at 100K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless φ- and ω-scan technique), using Mo K_α-radiation (0.71073 Å). The intensity data were integrated by the SAINT program[1] and were corrected for absorption and decay using SADABS.[2] The structure was solved by direct methods using SHELXT[3] and refined on F^2 using SHELXL-2018.[4] Positions of all atoms were found from the electron density difference map. Atoms were refined with individual anisotropic (non-H atoms) and isotropic (H-atoms) displacement parameters. Four reflections (0 1 1, 1 3 $\bar{1}$, $\bar{1}$ 2 $\bar{1}$, 1 1 0) were affected by the beam stop, therefore they were omitted from the refinement. Aspherical scattering factors[5] were applied at the final steps of the refinement. The absolute structure parameter was determined by using 2637 quotients [(I+)-(I-)]/[(I+)+(I-)].[6] The SHELXTL program suite[1] was used for molecular graphics.

1. Bruker. APEX-III. *Bruker AXS Inc.*, Madison, Wisconsin, USA, 2018.
2. Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Cryst.* **2015**, 48, 3–10. https://doi.org/10.1107/S1600576714022985
3. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, A71, 3-8. https://doi.org/10.1107/S2053273314026370
4. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, C71, 3-8. https://doi.org/10.1107/S2053229614024218
5. Lübben, J.; Wandtke, C.M.; Hübschle, Ch.B.; Ruf, M.; Sheldrick, G.M.; Dittrich, B. Aspherical scattering factors for SHELXL – model, implementation and application. *Acta Cryst.* 2019, **A75**, 50-62. https://doi.org/10.1107/S2053273318013840
6. Parsons, S.; Flack, H.D.; Wagner, T. Use of intensity quotients and differences in absolute structure refinement. *Acta Cryst.* 2013, **B69**, 249-259. https://doi.org/10.1107/S2052519213010014



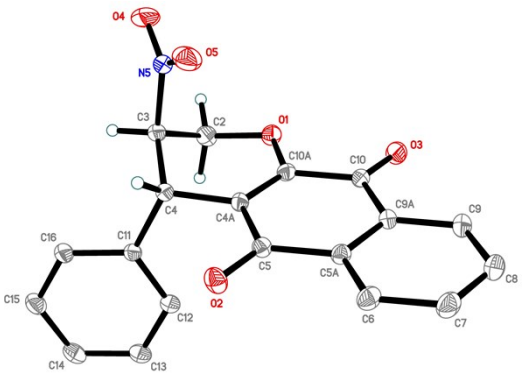


Table 1. Crystal data and structure refinement for KA152-3.

Identification code	KA152-3	
Empirical formula	C19 H13 N O5	
Formula weight	335.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4_3$	
Unit cell dimensions	a = 12.42180(14) Å	α= 90°.
	b = 12.42180(14) Å	β= 90°.
	c = 9.8189(2) Å	γ = 90°.
Volume	1515.07(5) $Å^3$	
Z	4	
Density (calculated)	1.470 g/cm^3	
Absorption coefficient	0.108 mm^{-1}	
F(000)	696	
Crystal size	0.33 x 0.21 x 0.08 mm^3	
Theta range for data collection	2.644 to 33.419°.	
Index ranges	-19<=h<=19, -19<=k<=19, -15<=l<=15	
Reflections collected	59697	
Independent reflections	5899 [R(int) = 0.0289]	
Observed reflections	5688	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8499 and 0.7971	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5899 / 1 / 281	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0205, wR2 = 0.0526	
R indices (all data)	R1 = 0.0222, wR2 = 0.0541	
Absolute structure parameter	-0.03(13)	
Largest diff. peak and hole	0.173 and -0.111 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for KA152-3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	346(1)	7133(1)	3337(1)	18(1)
O(2)	3563(1)	6570(1)	5806(1)	20(1)
O(3)	-364(1)	8310(1)	5372(1)	23(1)
O(4)	245(1)	4384(1)	2272(1)	41(1)
O(5)	945(1)	4637(1)	4271(1)	30(1)
N(5)	865(1)	4841(1)	3059(1)	24(1)
C(2)	807(1)	6674(1)	2128(1)	20(1)
C(3)	1544(1)	5737(1)	2453(1)	18(1)
C(4)	2453(1)	6088(1)	3399(1)	14(1)
C(4A)	1998(1)	6788(1)	4511(1)	14(1)
C(5)	2652(1)	6949(1)	5741(1)	14(1)
C(5A)	2182(1)	7566(1)	6894(1)	14(1)
C(6)	2766(1)	7675(1)	8101(1)	18(1)
C(7)	2324(1)	8235(1)	9193(1)	22(1)
C(8)	1310(1)	8701(1)	9082(1)	23(1)
C(9)	724(1)	8594(1)	7884(1)	21(1)
C(9A)	1156(1)	8018(1)	6790(1)	15(1)
C(10)	517(1)	7895(1)	5527(1)	16(1)
C(10A)	1008(1)	7238(1)	4414(1)	14(1)
C(11)	3319(1)	6643(1)	2551(1)	14(1)
C(12)	3528(1)	7740(1)	2668(1)	16(1)
C(13)	4318(1)	8224(1)	1866(1)	18(1)
C(14)	4891(1)	7618(1)	921(1)	21(1)
C(15)	4684(1)	6519(1)	797(1)	21(1)
C(16)	3905(1)	6036(1)	1614(1)	18(1)

Table 3. Bond lengths [Å] and angles [°] for KA152-3.

O(1)-C(10A)	1.3466(10)
O(1)-C(2)	1.4361(11)
O(2)-C(5)	1.2272(10)
O(3)-C(10)	1.2194(10)
O(4)-N(5)	1.2291(12)
O(5)-N(5)	1.2210(13)
N(5)-C(3)	1.5182(12)
C(2)-C(3)	1.5151(13)
C(2)-H(2A)	1.051(16)
C(2)-H(2B)	0.996(17)
C(3)-C(4)	1.5260(12)
C(3)-H(3)	1.012(16)
C(4)-C(4A)	1.5053(11)
C(4)-C(11)	1.5251(11)
C(4)-H(4)	1.000(15)
C(4A)-C(10A)	1.3540(11)
C(4A)-C(5)	1.4693(11)
C(5)-C(5A)	1.4869(11)
C(5A)-C(6)	1.3950(11)
C(5A)-C(9A)	1.3975(11)
C(6)-C(7)	1.3908(12)
C(6)-H(6)	0.993(16)
C(7)-C(8)	1.3900(14)
C(7)-H(7)	1.043(17)
C(8)-C(9)	1.3894(14)
C(8)-H(8)	0.98(2)
C(9)-C(9A)	1.3981(12)
C(9)-H(9)	1.017(15)
C(9A)-C(10)	1.4803(12)
C(10)-C(10A)	1.4945(11)
C(11)-C(12)	1.3919(11)
C(11)-C(16)	1.3949(11)
C(12)-C(13)	1.3958(12)
C(12)-H(12)	0.980(15)
C(13)-C(14)	1.3902(13)
C(13)-H(13)	0.979(15)
C(14)-C(15)	1.3947(14)
C(14)-H(14)	1.017(17)

C(15)-C(16)	1.3928(12)
C(15)-H(15)	0.980(17)
C(16)-H(16)	0.962(14)

C(10A)-O(1)-C(2)	116.35(6)
O(5)-N(5)-O(4)	124.64(9)
O(5)-N(5)-C(3)	119.26(8)
O(4)-N(5)-C(3)	116.08(9)
O(1)-C(2)-C(3)	111.81(7)
O(1)-C(2)-H(2A)	108.1(9)
C(3)-C(2)-H(2A)	107.8(9)
O(1)-C(2)-H(2B)	108.2(10)
C(3)-C(2)-H(2B)	109.1(10)
H(2A)-C(2)-H(2B)	111.9(14)
C(2)-C(3)-N(5)	108.07(7)
C(2)-C(3)-C(4)	110.84(7)
N(5)-C(3)-C(4)	112.49(7)
C(2)-C(3)-H(3)	108.5(9)
N(5)-C(3)-H(3)	102.9(8)
C(4)-C(3)-H(3)	113.6(8)
C(4A)-C(4)-C(11)	113.62(6)
C(4A)-C(4)-C(3)	109.19(7)
C(11)-C(4)-C(3)	108.57(7)
C(4A)-C(4)-H(4)	110.2(9)
C(11)-C(4)-H(4)	106.9(8)
C(3)-C(4)-H(4)	108.2(8)
C(10A)-C(4A)-C(5)	120.27(7)
C(10A)-C(4A)-C(4)	121.88(7)
C(5)-C(4A)-C(4)	117.83(7)
O(2)-C(5)-C(4A)	120.04(7)
O(2)-C(5)-C(5A)	121.33(7)
C(4A)-C(5)-C(5A)	118.63(7)
C(6)-C(5A)-C(9A)	119.82(7)
C(6)-C(5A)-C(5)	119.55(7)
C(9A)-C(5A)-C(5)	120.61(7)
C(7)-C(6)-C(5A)	119.91(8)
C(7)-C(6)-H(6)	120.1(10)
C(5A)-C(6)-H(6)	120.0(10)
C(8)-C(7)-C(6)	120.30(8)
C(8)-C(7)-H(7)	120.5(9)

C(6)-C(7)-H(7)	119.2(9)
C(9)-C(8)-C(7)	120.13(8)
C(9)-C(8)-H(8)	118.3(11)
C(7)-C(8)-H(8)	121.6(11)
C(8)-C(9)-C(9A)	119.87(9)
C(8)-C(9)-H(9)	121.3(9)
C(9A)-C(9)-H(9)	118.8(9)
C(5A)-C(9A)-C(9)	119.95(8)
C(5A)-C(9A)-C(10)	120.64(7)
C(9)-C(9A)-C(10)	119.40(7)
O(3)-C(10)-C(9A)	122.83(8)
O(3)-C(10)-C(10A)	120.44(8)
C(9A)-C(10)-C(10A)	116.73(7)
O(1)-C(10A)-C(4A)	124.78(7)
O(1)-C(10A)-C(10)	112.19(7)
C(4A)-C(10A)-C(10)	123.02(7)
C(12)-C(11)-C(16)	119.12(7)
C(12)-C(11)-C(4)	121.89(7)
C(16)-C(11)-C(4)	118.97(7)
C(11)-C(12)-C(13)	120.41(8)
C(11)-C(12)-H(12)	119.2(9)
C(13)-C(12)-H(12)	120.3(9)
C(14)-C(13)-C(12)	120.24(8)
C(14)-C(13)-H(13)	121.4(9)
C(12)-C(13)-H(13)	118.4(9)
C(13)-C(14)-C(15)	119.61(8)
C(13)-C(14)-H(14)	119.7(9)
C(15)-C(14)-H(14)	120.6(9)
C(16)-C(15)-C(14)	119.96(8)
C(16)-C(15)-H(15)	120.8(10)
C(14)-C(15)-H(15)	119.2(10)
C(15)-C(16)-C(11)	120.65(8)
C(15)-C(16)-H(16)	118.2(9)
C(11)-C(16)-H(16)	121.1(9)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for KA152-3. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	16(1)	21(1)	17(1)	-3(1)	-4(1)	1(1)
O(2)	15(1)	26(1)	19(1)	0(1)	-2(1)	5(1)
O(3)	14(1)	24(1)	32(1)	-9(1)	-2(1)	4(1)
O(4)	31(1)	43(1)	50(1)	-22(1)	9(1)	-21(1)
O(5)	26(1)	24(1)	42(1)	7(1)	6(1)	-3(1)
N(5)	17(1)	19(1)	35(1)	-9(1)	8(1)	-4(1)
C(2)	18(1)	28(1)	15(1)	-4(1)	-2(1)	-1(1)
C(3)	15(1)	20(1)	19(1)	-6(1)	3(1)	-5(1)
C(4)	14(1)	15(1)	15(1)	-2(1)	1(1)	-1(1)
C(4A)	13(1)	14(1)	13(1)	-1(1)	0(1)	0(1)
C(5)	14(1)	16(1)	13(1)	0(1)	0(1)	0(1)
C(5A)	16(1)	15(1)	12(1)	-1(1)	0(1)	-1(1)
C(6)	22(1)	19(1)	14(1)	-1(1)	-2(1)	-2(1)
C(7)	27(1)	23(1)	14(1)	-3(1)	-1(1)	-4(1)
C(8)	26(1)	28(1)	17(1)	-7(1)	4(1)	-3(1)
C(9)	19(1)	25(1)	20(1)	-7(1)	4(1)	-1(1)
C(9A)	14(1)	16(1)	16(1)	-3(1)	2(1)	-1(1)
C(10)	13(1)	15(1)	18(1)	-4(1)	0(1)	0(1)
C(10A)	13(1)	15(1)	15(1)	-2(1)	-1(1)	-1(1)
C(11)	13(1)	16(1)	14(1)	-2(1)	0(1)	-1(1)
C(12)	15(1)	16(1)	16(1)	1(1)	0(1)	-1(1)
C(13)	16(1)	19(1)	20(1)	4(1)	-1(1)	-2(1)
C(14)	16(1)	27(1)	19(1)	4(1)	2(1)	-2(1)
C(15)	17(1)	27(1)	20(1)	-2(1)	5(1)	-2(1)
C(16)	16(1)	21(1)	18(1)	-4(1)	3(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for KA152-3.

	x	y	z	U(eq)
H(2A)	1270(13)	7271(13)	1646(18)	32(4)
H(2B)	209(13)	6416(13)	1536(19)	38(4)
H(3)	1805(12)	5414(12)	1566(17)	26(3)
H(4)	2789(12)	5429(12)	3799(16)	26(4)
H(6)	3488(13)	7340(12)	8186(18)	33(4)
H(7)	2764(13)	8303(13)	10094(18)	32(4)
H(8)	985(14)	9099(14)	9840(20)	44(4)
H(9)	-12(12)	8941(12)	7775(16)	29(4)
H(12)	3131(12)	8164(12)	3345(16)	27(3)
H(13)	4451(12)	8996(12)	1980(16)	30(4)
H(14)	5472(13)	7976(12)	349(18)	34(4)
H(15)	5115(13)	6090(13)	161(18)	35(4)
H(16)	3787(11)	5274(11)	1518(15)	21(3)

Table 6. Torsion angles [°] for KA152-3.

C(10A)-O(1)-C(2)-C(3)	41.23(10)
O(1)-C(2)-C(3)-N(5)	65.21(9)
O(1)-C(2)-C(3)-C(4)	-58.48(9)
O(5)-N(5)-C(3)-C(2)	-108.50(9)
O(4)-N(5)-C(3)-C(2)	69.93(10)
O(5)-N(5)-C(3)-C(4)	14.19(11)
O(4)-N(5)-C(3)-C(4)	-167.38(8)
C(2)-C(3)-C(4)-C(4A)	44.08(9)
N(5)-C(3)-C(4)-C(4A)	-77.03(8)
C(2)-C(3)-C(4)-C(11)	-80.27(8)
N(5)-C(3)-C(4)-C(11)	158.61(7)
C(11)-C(4)-C(4A)-C(10A)	105.17(9)
C(3)-C(4)-C(4A)-C(10A)	-16.17(10)
C(11)-C(4)-C(4A)-C(5)	-76.43(9)
C(3)-C(4)-C(4A)-C(5)	162.23(7)
C(10A)-C(4A)-C(5)-O(2)	-177.55(8)
C(4)-C(4A)-C(5)-O(2)	4.03(11)
C(10A)-C(4A)-C(5)-C(5A)	3.12(11)
C(4)-C(4A)-C(5)-C(5A)	-175.30(7)
O(2)-C(5)-C(5A)-C(6)	-3.01(12)
C(4A)-C(5)-C(5A)-C(6)	176.30(7)
O(2)-C(5)-C(5A)-C(9A)	178.22(8)
C(4A)-C(5)-C(5A)-C(9A)	-2.46(11)
C(9A)-C(5A)-C(6)-C(7)	-0.09(12)
C(5)-C(5A)-C(6)-C(7)	-178.86(8)
C(5A)-C(6)-C(7)-C(8)	-1.05(14)
C(6)-C(7)-C(8)-C(9)	1.16(15)
C(7)-C(8)-C(9)-C(9A)	-0.13(15)
C(6)-C(5A)-C(9A)-C(9)	1.11(12)
C(5)-C(5A)-C(9A)-C(9)	179.87(8)
C(6)-C(5A)-C(9A)-C(10)	-179.00(8)
C(5)-C(5A)-C(9A)-C(10)	-0.24(12)
C(8)-C(9)-C(9A)-C(5A)	-1.00(13)
C(8)-C(9)-C(9A)-C(10)	179.11(8)
C(5A)-C(9A)-C(10)-O(3)	-177.11(8)
C(9)-C(9A)-C(10)-O(3)	2.78(13)
C(5A)-C(9A)-C(10)-C(10A)	2.24(11)
C(9)-C(9A)-C(10)-C(10A)	-177.87(8)

C(2)-O(1)-C(10A)-C(4A)	-11.56(12)
C(2)-O(1)-C(10A)-C(10)	169.76(7)
C(5)-C(4A)-C(10A)-O(1)	-179.63(7)
C(4)-C(4A)-C(10A)-O(1)	-1.27(12)
C(5)-C(4A)-C(10A)-C(10)	-1.09(12)
C(4)-C(4A)-C(10A)-C(10)	177.27(7)
O(3)-C(10)-C(10A)-O(1)	-3.53(11)
C(9A)-C(10)-C(10A)-O(1)	177.10(7)
O(3)-C(10)-C(10A)-C(4A)	177.77(8)
C(9A)-C(10)-C(10A)-C(4A)	-1.60(11)
C(4A)-C(4)-C(11)-C(12)	-9.77(11)
C(3)-C(4)-C(11)-C(12)	111.92(8)
C(4A)-C(4)-C(11)-C(16)	171.32(7)
C(3)-C(4)-C(11)-C(16)	-66.99(10)
C(16)-C(11)-C(12)-C(13)	-0.42(12)
C(4)-C(11)-C(12)-C(13)	-179.33(8)
C(11)-C(12)-C(13)-C(14)	1.21(13)
C(12)-C(13)-C(14)-C(15)	-1.09(13)
C(13)-C(14)-C(15)-C(16)	0.19(14)
C(14)-C(15)-C(16)-C(11)	0.61(14)
C(12)-C(11)-C(16)-C(15)	-0.49(13)
C(4)-C(11)-C(16)-C(15)	178.45(8)