A green and effective route leading to antiradical agents with 3-arylmethyl 4-hydroxyquinolin-2(1*H*)-one moiety

Inese Mieriņa, Agnese Stikute, Māra Jure

Institute of Technology of Organic Chemistry, Faculty of Materials Science and Applied Chemistry, Riga Technical University

P.Valdena Str. 3/7, Riga, Latvia, LV 1048

e-mail: inese.mierina@rtu.lv

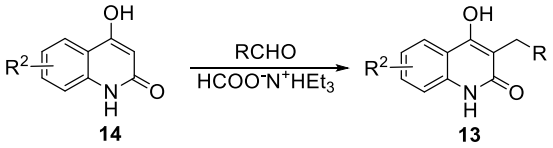
Table of contents

1. GENERAL

NMR spectra were recorded on Bruker Avance 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) or Bruker Avance 500 (^{1}H: 500 MHz; ^{13}C: 126 MHz) spectrometer. The spectra were calibrated with respect to the peak of residual solvent (chloroform, ^{1}H: δ = 7.26 ppm; ^{13}C: δ = 77.0 ppm; DMSO, ^{1}H: δ = 2.50 ppm; ^{13}C: δ = 39.5 ppm). IR spectra were recorded by Perkin Elmer spectrometer (model: Spectrum BX, FT-IS system) for solid sample in KBr disc. The melting points were measured by Stuart SMP10 apparatus and are uncorrected. The UV/Vis absorbance measurements were done with Camspec M501 Single Beam Scanning UV/Visible spectrophotometer. All commercially available reagents were used without additional purification.

2. SYNTHESIS OF TARGET COMPOUNDS

General procedure for the synthesis of 3-arylmethyl-4-hydroxyquinolin-2(1H)-ones with triethylammonium formate

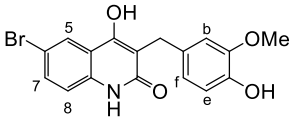


14 **13**

4-Hydroxyquinolin-2(1*H*)-one (1.3 mmol, 1 eq.) and the desired aldehyde (1.3 mmol, 1 eq.) was heated in triethylammonium formate at 140°C. When the reaction was completed (monitored by TLC) the reaction mixture was poured in ice, the precipitants were filtered, air-dried and crystalized from EtOH.

The triethylammonium formate was prepared right before the reaction as follows: formic acid (1.3 mL, 1.6 g, 24.5 mmol) was added drop-wise to triethylamine (2 mL, 1.45 g, 14.4 mmol) at 0°C (ice bath).

6-Bromo-4-hydroxy-3-(4-hydroxy-3-methoxybenzyl)quinolin-2(1H)-one 12a



The compound was obtained from 6-bromoquinolin-2(1*H*)-one **13a** and vanillin **16a** according to the general procedure (reaction time 5 h) as a white solid (83%) with mp 240-242°C.

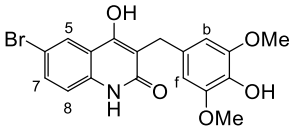
IR (KBr) υ (cm^{-1}): 3215, 1640, 1595.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ (ppm): 11.49 (1H, s, OH), 10.47 (1H, s, NH), 8.61 (1H, s, OH), 8.04 (1H, s, H-5), 7.61 (1H, d, *J* = 8.7 Hz, H-7), 7.22 (1H, d, *J* = 8.7 Hz, H-8), 6.88 (1H, s, H-b), 6.58-6.61 (2H, m, H-e,f), 3.82 (2H, s, CH_2), 3.70 (3H, s, OCH_3).

^{13}C NMR (75.5 MHz, DMSO-*d*$_6$) δ (ppm): 163.3, 156.2, 147.2, 144.5, 136.5, 132.5, 131.3, 124.9, 120.3, 117.1, 115.1, 112.9, 112.5, 55.6, 28.0.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{17}H_{14}BrNO_4]^+$ 376.0179; found 376.0173.

6-Bromo-4-hydroxy-3-(4-hydroxy-3,5-dimethoxybenzyl)quinolin-2(1H)-one 12b



The compound was obtained from 6-bromoquinolin-2(1*H*)-one **13a** and syringaldehyde **16b** according to the general procedure (reaction time 5 h) as a pale pink solid (78%) with mp 267-269°C.

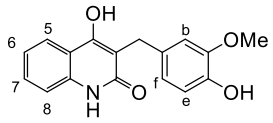
IR (KBr) υ (cm^{-1}): 3225-2950, 1640, 1600.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ (ppm): 11.50 (1H, s, OH), 10.49 (1H, brs, NH), 8.05 (1H, d, *J* = 2.0 Hz, H-5), 8.03 (1H, s, OH), 7.61 (1H, dd, *J* = 8.7 Hz, *J* = 2.0 Hz, H-7), 7.22 (1H, d, *J* = 8.7 Hz, H-8), 6.55 (2H, s, H-b,f), 3.83 (2H, s, CH_2), 3.67 (6H, s, 2×OCH_3).

^{13}C NMR (75.5 MHz, DMSO-*d*$_6$) δ (ppm): 163.2, 156.4, 147.8, 136.5, 133.8, 132.6, 130.6, 124.9, 117.1, 112.8, 112.4, 106.1, 56.0, 28.5.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{18}H_{16}BrNO_5]^+$ 406.0285; found 406.0260.

4-Hydroxy-3-(4-hydroxy-3-methoxybenzyl)quinolin-2(1H)-one 12c



The compound was obtained from quinolin-2(1*H*)-one **13b** and vanillin **16a** according to the general procedure (reaction time 6 h) as a white solid (56%) with mp 215-217°C.

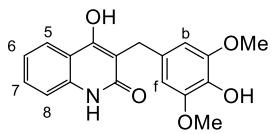
IR (KBr) υ (cm^{-1}): 3530, 3050, 1630, 1605.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ (ppm): 11.36 (1H, s, OH), 10.27 (1H, s, NH), 8.62 (1H, s, OH), 7.91 (1H, dd, *J* = 8.4 Hz, *J* = 1.4 Hz, H-5/8), 7.45 (1H, td, *J* 8.4 = Hz, *J* = 1.4 Hz, H-6/7), 7.27 (1H, dd, *J* = 8.4 Hz, *J* = 1.4 Hz, H-5/8), 7.16 (1H, td, *J* = 8.4 Hz, *J* = 1.4 Hz, H-6/7), 6.91 (1H, s, H-b), 6.62-6.65 (2H, m, H-e,f), 3.84 (2H, s, CH_2), 3.70 (3H, s, OCH_3).

^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ (ppm): 163.6, 157.5, 147.2, 144.5, 137.6, 131.7, 130.0, 122.7, 121.1, 120.4, 115.4, 115.2, 115.0, 113.0, 111.4, 55.6, 28.0.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{17}H_{15}NO_4]^+$ 298.1074; found 298.1057.

4-Hydroxy-3-(4-hydroxy-3,5-dimethoxybenzyl)quinolin-2(1H)-one 12d



The compound was obtained from quinolin-2(1*H*)-one **13b** and syringaldehyde **16b** according to the general procedure (reaction time 6.25 h) as a white solid (71%) with mp 252-254°C.

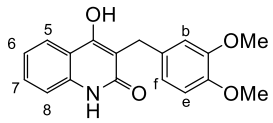
IR (KBr) υ (cm^{-1}): 3490, 3090-3000, 1645, 1600.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ (ppm): 11.35 (1H, s, OH), 10.25 (1H, s, NH), 8.01 (1H, s, OH), 7.91 (1H, d, *J* = 7.8 Hz, H-5/8), 7.45 (1H, t, *J* = 7.8 Hz, H-6/7), 7.26 (1H, d, *J* = 7.8 Hz, H-5/8), 7.14 (1H, t, *J* = 7.8 Hz, H-6/7), 6.57 (1H, s, H-b,f), 3.82 (2H, s, CH_2), 3.67 (6H, s, 2×OCH_3).

^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ (ppm): 163.5, 157.4, 147.8, 137.5, 133.7, 130.9, 129.9, 122.7, 121.0, 115.3, 114.9, 111.3, 106.1, 55.9, 28.4.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{18}H_{17}NO_5]^+$ 328.1179; found 328.1105.

3-(3,4-Dimethoxybenzyl)-4-hydroxyquinolin-2(1H)-one 12e



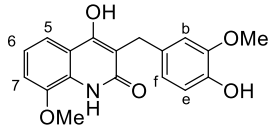
The compound was obtained from quinolin-2(1*H*)-one **13b** and veratralaldehyde **16c** according to the general procedure (reaction time 5.5 h) as a white solid (57%).

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ (ppm): 11.37 (1H, s, OH), 10.78-9.86 (1H, brs, NH), 7.91 (1H, d, *J* = 7.6 Hz, H-5/8), 7.45 (1H, t, *J* = 7.6 Hz, H-6/7), 7.27 (1H, d, *J* = 7.6 Hz, H-5/8), 7.15 (1H, t, *J* = 7.6 Hz, H6/7), 6.95 (1H, s, H-b), 6.79 (1H, d, *J* = 7.6 Hz, H-e), 6.74 (1H, d, *J* = 7.6 Hz, H-f), 3.86 (2H, s, CH_2), 3.69 (3H, s, OCH_3), 3.67 (3H, s, OCH_3).

^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ (ppm): 163.6, 157.5, 148.4, 147.0, 137.6, 133.5, 130.0, 122.7, 121.1, 120.0, 115.4, 115.0, 112.7, 111.9, 111.2, 55.6, 55.4, 28.0.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{18}H_{18}NO_4]^+$ 312.1230; found 312.1237.

4-Hydroxy-3-(4-hydroxy-3-methoxybenzyl)-8-methoxyquinolin-2(1H)-one 12f



The compound was obtained from 8-methoxyquinolin-2(1*H*)-one **13c** and vanillin **16a** according to the general procedure (reaction time 6.5 h) as a white solid (62%) with mp 242-244°C.

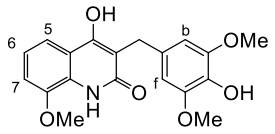
IR (KBr) υ (cm^{-1}): 3510, 3080-3000, 1635, 1605.

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ (ppm): 10.20-10.33 (2H, m, NH, OH), 8.60 (1H, s, OH), 7.51 (1H, t, *J* 9.0 Hz, H-6), 7.09-7.12 (2H, m, H-5,7), 6.90 (1H, s, H-b), 6.59-6.64 (2H, m, H-e,f), 3.88 (3H, s, OCH_3), 3.83 (2H, s, CH_2), 3.70 (3H, s, OCH_3).

^{13}C NMR (75.5 MHz, DMSO-*d*$_6$) δ (ppm): 163.0, 157.5, 147.1, 145.5, 144.5, 131.6, 127.5, 120.9, 120.2, 115.8, 115.0, 114.4, 112.9, 111.8, 110.5, 56.1, 55.5, 27.9.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{18}H_{17}NO_5]^+$ 328.1179; found 328.1177.

4-Hydroxy-3-(4-hydroxy-3,5-dimethoxybenzyl)-8-methoxyquinolin-2(1H)-one 12g



The compound was obtained from 8-methoxyquinolin-2(1*H*)-one **13c** and syringaldehyde **16b** according to the general procedure (reaction time 6.75 h) as a white solid (67%) with mp 252-254°C.

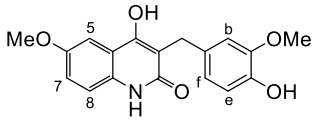
IR (KBr) υ (cm^{-1}): 3540, 3220, 1635, 1605.

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ (ppm): 10.21-10.39 (2H, m, NH, OH), 8.02 (1H, s, OH), 7.51 (1H, t, *J* = 8.8 Hz, H-6), 7.08-7.13 (2H, m, H-5,7), 6.58 (2H, s, H-b,f), 3.88 (3H, s, OCH_3), 3.83 (2H, s, CH_2), 3.67 (6H, s, 2×OCH_3).

^{13}C NMR (75.5 MHz, DMSO-*d*$_6$) δ (ppm): 163.0, 157.6, 147.7, 145.5, 133.7, 130.8, 127.5, 121.0, 115.9, 114.4, 111.7, 110.5, 106.1, 56.0, 28.4.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{19}H_{19}NO_6]^+$ 358.1285; found 358.1276.

4-Hydroxy-3-(4-hydroxy-3-methoxybenzyl)-6-methoxyquinolin-2(1H)-one 12h



The compound was obtained from 6-methoxyquinolin-2(1*H*)-one **13d** and vanillin **16a** according to the general procedure (reaction time 4 h) as a yellow solid (78%) with mp 212-213°C.

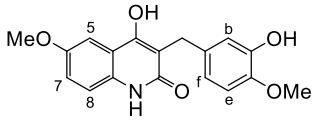
IR (KBr) υ (cm^{-1}): 3465, 3070-3000, 1645, 1600.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ (ppm): 11.23 (1H, s, OH), 10.18 (1H, s, NH), 8.59 (1H, s, OH), 7.40 (1H, d, *J* = 2.5 Hz, H-5), 7.20 (1H, d, *J* = 8.9 Hz, H-8), 7.11 (1H, dd, *J* = 8.9 Hz, *J* = 2.5 Hz, H-7), 6.89 (1H, s, H-b), 6.59-6.64 (2H, m, H-e,f), 3.81 (2H, s, CH_2), 3.78 (3H, s, OCH_3), 3.70 (3H, s, OCH_3).

^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ (ppm): 163.0, 156.9, 153.8, 147.1, 144.5, 132.0, 131.7, 120.3, 119.0, 116.3, 115.7, 115.1, 113.0, 111.8, 104.4, 55.6, 55.4, 28.1.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{18}H_{18}O_5]^+$ 328.1179; found 328.1176.

4-Hydroxy-3-(3-hydroxy-4-methoxybenzyl)-6-methoxyquinolin-2(1H)-one 12i



The compound was obtained from 6-methoxyquinolin-2(1*H*)-one **13d** and isovanillin **16d** according to the general procedure (reaction time 5.5 h) as a white solid (70%) with mp 210-213°C.

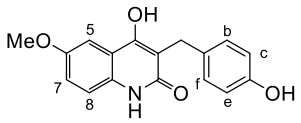
IR (KBr) υ (cm^{-1}): 2975, 1650, 1600.

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ (ppm): 11.24 (1H, s, OH), 10.22 (1H, s, NH), 8.70 (1H, s, OH), 7.41 (1H, d, *J* = 2.0 Hz, H-5), 7.21 (1H, d, *J* = 8.9 Hz, H-8), 7.11 (1H, dd, *J* = 8.9 Hz, *J* 2.0 Hz, H-7), 6.75 (1H, d, *J* = 8.1 Hz, H-e), 6.69 (1H, s, H-b), 6.64 (1H, d, *J* = 8.1 Hz, H-f), 3.75-3.82 (5H, m, OCH_3, CH_2), 3.68 (3H, s, OCH_3).

^{13}C NMR (75.5 MHz, DMSO-*d*$_6$) δ (ppm): 163.0, 157.0, 153.8, 146.1, 145.7, 133.6, 132.1, 119.0, 118.9, 116.3, 115.8, 112.2, 111.6, 104.4, 55.8, 55.4, 28.0.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{18}H_{18}O_5]^+$ 328.1179; found 328.1194.

4-Hydroxy-3-(4-hydroxybenzyl)-6-methoxyquinolin-2(1H)-one 12j



The compound was obtained from 6-methoxyquinolin-2(1*H*)-one **13d** and 4-hydroxybenzaldehyde **16e** according to the general procedure (reaction time 5.7 h) as a white solid (80%) with mp 267-269°C.

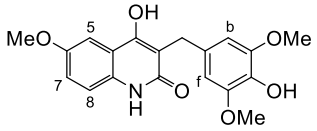
IR (KBr) υ (cm^{-1}): 3090, 1640, 1600.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ (ppm): 11.22 (1H, s, OH), 10.18 (1H, s, NH), 9.04 (1H, s, OH), 7.41 (1H, s, H-5), 7.21 (1H, d, *J* = 8.5 Hz, H-8), 7.09 (1H, d, *J* = 8.5 Hz, H-7), 7.05 (2H, d, *J* = 7.4 Hz, H-b,f), 6.61 (2H, d, *J* = 7.4 Hz, H-c,e), 3.62-3.94 (5H, m, OCH_3, CH_2).

^{13}C NMR (75.5 MHz, DMSO-*d*$_6$) δ (ppm): 163.0, 156.9, 155.2, 153.8, 132.0, 130.9, 129.1, 119.0, 116.3, 115.7, 114.8, 111.8, 104.4, 55.4, 27.7.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{17}H_{15}O_4]^+$ 298.1074; found 298.1081.

4-Hydroxy-3-(4-hydroxy-3,5-dimethoxybenzyl)-6-methoxyquinolin-2(1H)-one 12k



The compound was obtained from 6-methoxyquinolin-2(1*H*)-one **13d** and syringaldehyde **16b** according to the general procedure (reaction time 4.5 h) as a white solid (82%) with mp 244-246°C.

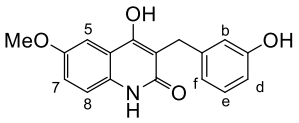
IR (KBr) υ (cm^{-1}): 3285-3000, 1640, 1605.

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ (ppm): 11.26 (1H, s, OH), 10.21 (1H, s, NH), 8.03 (1H, s, OH), 7.41 (1H, d, *J* = 2.6 Hz, H-5), 7.20 (1H, d, *J* = 8.9 Hz, H-8), 7.11 (1H, dd, *J* = 8.9 Hz, *J* = 2.6 Hz, H-7), 6.57 (2H, s, H-b,f), 3.81 (2H, s, CH_2), 3.78 (3H, s, OCH_3), 3.70 (6H, s, 2×OCH_3).

^{13}C NMR (75.5 MHz, DMSO-*d*$_6$) δ (ppm): 163.2, 157.2, 153.9, 147.7, 133.7, 132.1, 131.0, 119.1, 116.5, 115.9, 111.8, 106.2, 104.5, 56.0, 55.5, 28.5.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{19}H_{19}NO_6]^+$ 358.1285; found 358.1281.

4-Hydroxy-3-(3-hydroxybenzyl)-6-methoxyquinolin-2(1H)-one 12l



The compound was obtained from 6-methoxyquinolin-2(1*H*)-one **13d** and 3-hydroxybenzaldehyde **16f** according to the general procedure (reaction time 6.5 h) as a white solid (60%) with mp 224-225°C.

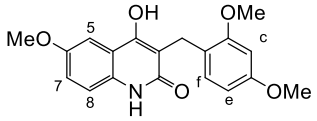
IR (KBr) υ (cm^{-1}): 3050, 1645, 1600.

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ (ppm): 11.26 (1H, s, OH), 10.25 (1H, s, NH), 9.11 (1H, s, OH), 7.42 (1H, d, *J* = 2.6 Hz, H-5), 7.22 (1H, d, *J* = 8.9 Hz, H-8), 7.12 (1H, dd, *J* = 8.9 Hz, *J* = 2.6 Hz, H-7), 7.00 (1H, t, *J* = 7.9 Hz, H-e), 6.69 (1H, d, *J* = 7.9 Hz, H-d), 6.64 (1H, s, H-b), 6.51 (1H, dd, *J* = 7.9 Hz, *J* = 1.6 Hz, H-f), 3.85 (2H, s, CH_2), 3.79 (3H, s, OCH_3).

^{13}C NMR (75.5 MHz, DMSO-*d*$_6$) δ (ppm): 163.0, 157.3, 157.1, 153.8, 142.2, 132.1, 128.8, 119.1, 116.3, 115.8, 115.1, 112.4, 111.1, 104.4, 55.5, 28.5.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{17}H_{15}O_4]^+$ 298.1074; found 298.1099.

3-(2,4-Dimethoxybenzyl)-4-hydroxy-6-methoxyquinolin-2(1H)-one 12m



The compound was obtained from 6-methoxyquinolin-2(1*H*)-one **13d** and 2,4-dimethoxybenzaldehyde **16g** according to the general procedure (reaction time 6 h) as a white solid (84%) with mp 222-224°C.

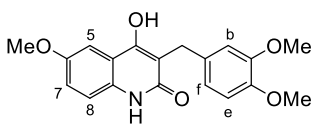
IR (KBr) υ (cm^{-1}): 3395, 1660, 1610.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ (ppm): 11.24 (1H, s, OH), 9.94-10.11 (1H, brs, NH), 7.38 (1H, d, *J* = 2.6 Hz, H=5), 7.23 (1H, d, *J* = 8.9 Hz, H-8), 7.13 (1H, dd, *J* = 8.9 Hz, *J* = 2.6 Hz, H-7), 6.62 (1H, d, *J* = 8.3 Hz, H-f), 6.54 (1H, d, *J* = 2.2 Hz, H-c), 6.34 (1H, dd, *J* = 8.3 Hz, *J* = 2.2 Hz, H-e), 3.83 (3H, s, OCH_3), 3.79 (3H, s, OCH_3), 3.75 (2H, s, CH_2), 3.69 (3H, s, OCH_3).

^{13}C NMR (75.5 MHz, DMSO-*d*$_6$) δ (ppm): 163.0, 158.7, 157.8, 153.8, 132.1, 127.6, 119.9, 119.1, 116.3, 115.6, 109.5, 104.3, 104.1, 98.1, 55.4, 55.3, 55.1, 22.3.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{19}H_{19}NO_5]^+$ 342.1336; found 342.1309.

3-(3,4-Dimethoxybenzyl)-4-hydroxy-6-methoxyquinolin-2(1H)-one 12n



The compound was obtained from 6-methoxyquinolin-2(1*H*)-one **13d** and veratralaldehyde **16c** according to the general procedure (reaction time 5.5 h) as a white solid (72%) with mp 210-211°C.

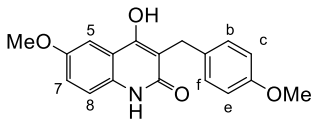
IR (KBr) υ (cm^{-1}): 3130, 1640, 1610.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ (ppm): 11.24 (1H, s, OH), 10.11-10.34 (1H, brs, NH), 7.41 (1H, d, *J* = 2.7 Hz, H-5), 7.21 (1H, d, *J* = 8.9 Hz, H-8), 7.11 (1H, dd, *J* = 8.9 Hz, *J* = 2.7 Hz, H-7), 6.94 (1H, d, *J* = 1.4 Hz, H-b), 6.79 (1H, d, *J* = 8.3 Hz, H-e), 6.74 (1H, dd, *J* = 8.3 Hz, *J* = 1.4 Hz, H-f), 3.85 (2H, s, CH_2), 3.78 (3H, s, OCH_3), 3.69 (3H, s, OCH_3), 3.67 (3H, s, OCH_3).

^{13}C NMR (75.5 MHz, DMSO-*d*$_6$) δ (ppm): 163.1, 157.1, 153.8, 148.4, 147.0, 133.5, 132.0, 120.0, 119.0, 116.3, 115.7, 112.8, 111.9, 111.6, 104.4, 55.6, 55.4, 28.1.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{19}H_{19}NO_5]^+$ 342.1336; found 342.1337.

4-Hydroxy-6-methoxy-3-(4-methoxybenzyl)quinolin-2(1H)-one 12o



The compound was obtained from 6-methoxyquinolin-2(1*H*)-one **13d** and anisaldehyde **16h** according to the general procedure (reaction time 6 h) as a white solid (76%) with mp 221-222°C.

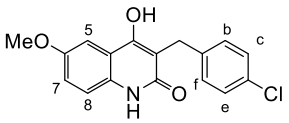
IR (KBr) υ (cm^{-1}): 3365, 1650, 1610.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ (ppm): 11.23 (1H, s, OH), 10.23 (1H, s, NH), 7.41 (1H, d, *J* = 2.5 Hz, H-5), 7.21 (1H, d, *J* = 8.9 Hz, H-8), 7.17 (2H, d, *J* = 8.6 Hz, H-b,f), 7.11 (1H, dd, *J* = 8.9 Hz, *J* = 2.5 Hz, H-7), 6.78 (2H, d, *J* = 8.6 Hz, H-c,e), 3.84 (2H, s, CH_2), 3.78 (3H, s, OCH_3), 3.68 (3H, s, OCH_3).

^{13}C NMR (75.5 MHz, DMSO-*d*$_6$) δ (ppm): 163.0, 157.3, 157.0, 153.8, 132.8, 132.0, 129.2, 119.0, 116.3, 115.7, 113.4, 111.7, 104.3, 55.5, 55.0, 27.8.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{18}H_{16}NO_4]^+$ 312.1230; found 312.1230.

3-(4-Chlorobenzyl)-4-hydroxy-6-methoxyquinolin-2(1H)-one 12p



The compound was obtained from 6-methoxyquinolin-2(1*H*)-one **13d** and 4-chlorobenzaldehyde **16i** according to the general procedure (reaction time 5.5 h) as a white solid (84%) with mp 267-268°C.

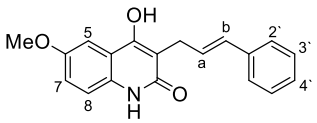
IR (KBr) υ (cm^{-1}): 3140-3040, 1645, 1605.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ (ppm): 11.28 (1H, s, OH), 10.36 (1H, brs, NH), 7.42 (1H, d, *J* = 2.8 Hz, H-5), 7.26-7.28 (4H, m, H-b,c,e,f), 7.22 (1H, d, *J* = 8.9 Hz, H-8), 7.12 (1H, dd, *J* = 8.9 Hz, *J* = 2.8 Hz, H-7), 3.90 (2H, s, CH_2), 3.78 (3H, s, OCH_3).

^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm): 162.8, 157.4, 153.8, 140.0, 132.1, 130.1, 128.1, 119.2, 116.4, 115.6, 110.8, 104.4, 55.4, 28.3.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{17}H_{13}ClNO_3]^+$ 316.0735; found 316.0757.

3-Cinnamyl-4-hydroxy-6-methoxyquinolin-2(1H)-one 12r



The compound was obtained from 6-methoxyquinolin-2(1*H*)-one **13d** and cinnamaldehyde **16k** according to the general procedure (reaction time 6 h) as a light green solid (69%) with mp 212-213°C.

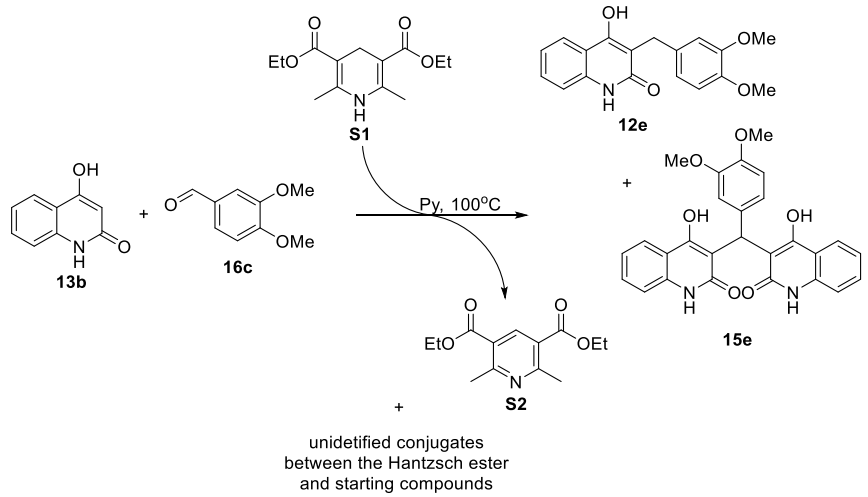
IR (KBr) υ (cm^{-1}):3425-2825, 1650.

^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 11.25 (1H, s, OH), 10.20 (1H, brs, NH), 7.40 (1H, s, H-5), 7.33 (2H, d, *J* = 7.6 Hz, 2×H-2`), 7.27 (3H, t, *J* = 7.6 Hz, 2×H-3`), 7.21 (1H, d, *J* = 8.8 Hz, H-8), 7.17 (1H, t, *J* = 7.6 Hz, H-4`), 7.11 (1H, *J* = 8.8 Hz, H-7), 6.38 (1H, d, *J* = 16.6 Hz, H-b), 6.31 (1H, dt, *J* = 16.6 Hz, *J* = 4.7 Hz, H-a), 3.79 (3H, s, OCH_3), 3.48 (2H, d, *J* = 4.7 Hz, CH_2).

^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm): 162.9, 157.1, 153.8, 137.3, 132.0, 129.2, 128.5, 128.1, 126.8, 125.7, 119.0, 116.3, 115.8, 109.6, 104.3, 55.4, 26.3.

HRMS *m/z*: $[M+H]^+$ calcd for $[C_{19}H_{18}NO_3]^+$ 308.1281; found 308.1280.

Synthesis of 3-(3,4-dimethoxybenzyl)-4-hydroxyquinolin-2(1H)-one 12e with the Hantzsch ester as the hydride source



Procedure A

4-Hydroxyquinolin-2(1*H*)-one **13b** (50 mg, 0.31 mmol, 1 eq.), veratraldehyde **16c** (50 mg, 0.31 mmol, 1 eq.) and the Hantzsch ester (78 mg, 0.33 mmol, 1.1 eq.) was heated in pyridine (1 mL) under argon at 100°C for 2 h. The reaction mixture was evaporated; the solid residue was suspended in ethanol, poured in ice, filtered and purified on silica (Hex:EtOAc (3:1) → EtOAc (100%) → EtOAc:MeOH (50:1)). The product was

obtained as were obtained as white solid (32 mg, 33%). Besides the product **12e**, the pyridine derivative **S2** was isolated.

Procedure B

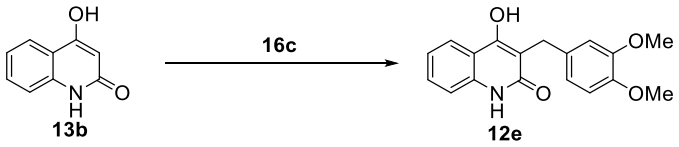
4-Hydroxyquinolin-2(1*H*)-one **13b** (50 mg, 0.31 mmol, 1 eq.), veratraldehyde **16c** (50 mg, 0.31 mmol, 1 eq.) and the Hantzsch ester (78 mg, 0.33 mmol, 1.1 eq.) was heated in pyridine (1 mL) under air at 100°C for 2 h. The reaction mixture was evaporated; the solid residue was suspended in ethanol, poured in ice, filtered and purified on silica (Hex:EtOAc (3:1) → EtOAc (100%) → EtOAc:MeOH (50:1)). The product was obtained as were obtained as white solid (24 mg, 25%). Besides the product **12e**, the pyridine derivative **S2**, *bis*-4-hydroxyquinolin-2(1*H*)-one **15e** and some unidentified impurities were isolated.

Procedure C

4-Hydroxyquinolin-2(1*H*)-one **14b** (50 mg, 0.31 mmol, 1 eq.), veratraldehyde **17c** (50 mg, 0.31 mmol, 1 eq.) and the Hantzsch ester (78 mg, 0.33 mmol, 1.1 eq.) was heated in pyridine (1 mL) under argon at 100°C for 2 h. The reaction mixture was evaporated; the solid residue was dissolved in EtOAc (25 mL), washed with 10% hydrochloric acid (4×10 mL) and brine (4×10 mL). The organic phase was dried over Na_2SO_4, filtered and evaporated. Crystallization of the solid residue from ethanol lead to the product as white solid (30 mg, 31%).

Table 1

Comparison of various reaction conditions



Procedure	Atmosphere	Isolation of the products	Products in the ^{1}H NMR spectrum of the crude product
B*	Air	1. evaporate till dry residue 2. suspend in ethanol, pour in ice and filter	Product **12e** Corresponding *bis*-4-hydroxyquinolin-2(1*H*)-one **15** Unreacted starting compounds Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate Unidentified conjugates with the Hantzsch ester
A*	Ar	1. evaporate till dry residue 2. suspend in ethanol, pour in ice and filter	Product **12e** Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate
C	Ar	1. evaporate till dry residue 2. dissolve in EtOAc, wash with 10% HCl/H_2O and brine, dry over Na_2SO_4 and evaporate	Product **12e** Unreacted aldehyde **16c**
**	air	Pour in ice and filter	Product **12e**

*Spectroscopically pure compound **13e** was obtained via purification on silica. **The product was synthesized under the following conditions provided in this paper

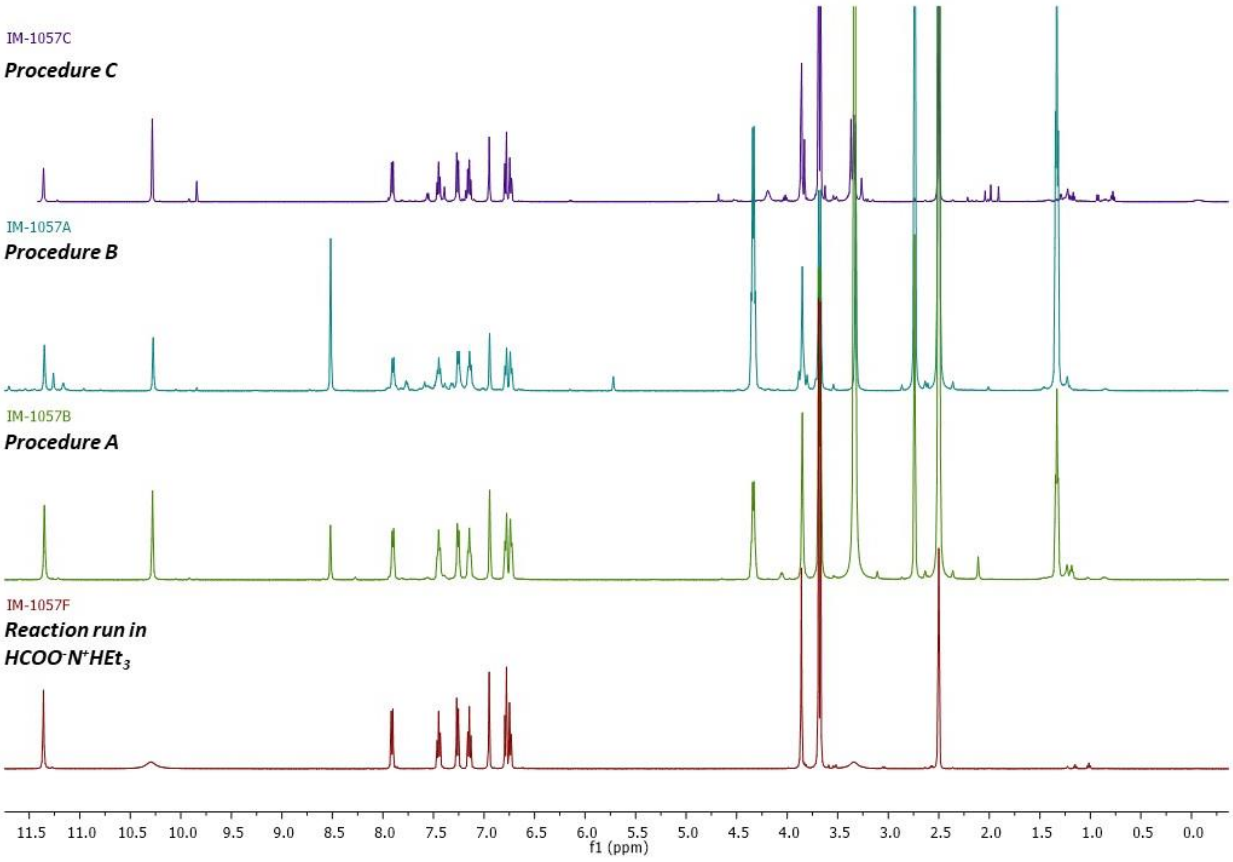


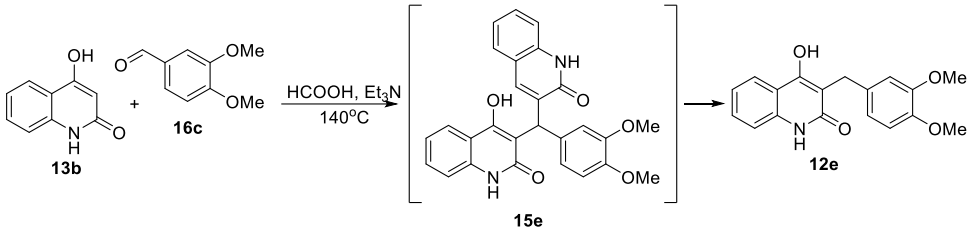
Fig. S1. Comparison of the ^{1}H NMR spectra (500 MHz, DMSO-d_6) of technical product obtained by different methods

3. COMPARISON OF THE PRICES FOR TRIETHYLAMMONIUM FORMATE AND THE HANTZSCH ESTER

Supplier	The Hantzsch ester		Formic acid		Triethylamine		Price per 1 mol *in situ* generated triethylammonium formate, Eur	Ratio of prices: $HCOO^-N^+HEt_3$: Hantzsch ester
	Eur / package	Eur / mol	Eur / package	Eur / mol	Eur / package	Eur / mol		
Acros	67.70 / 1 g	16 925	38.00 / 1 L	1.4	24.60 / 100 mL	4.66	6.06	1 : 2 793
Merck	1320 / 50 g	66 667	90.70 / 1 L	3.42	253.00 / 2.5 L	1.41	4.83	1: 13 803
Fluorochem	40.37 / 100 g	102	59.37 / 1 kg	2.73	20.19 / 1 L	0.28	3.01	1 : 34

4. NMR STUDIES OF THE REACTION BETWEEN THE ALDEHYDE AND THE 4-HYDROXYQUINOLIN-2(1*H*)-ONE

Experiment no 1:



4-Hydroxyquinolin-2(1*H*)-one **13b** (190 mg, 1.2 mmol, 1 eq.), veratraldehyde **16c** (200 mg, 1.2 mmol) was heated in the mixture of formic acid (1.2 mL) and triethyl amine (1.8 mL) at 140°C. The ^{1}H NMR spectra was registered after regular time intervals: the reaction mixture (~0.1 mL) was dissolved in DMSO-d_6 (~0.5 mL) and the spectra was recorded immediately.

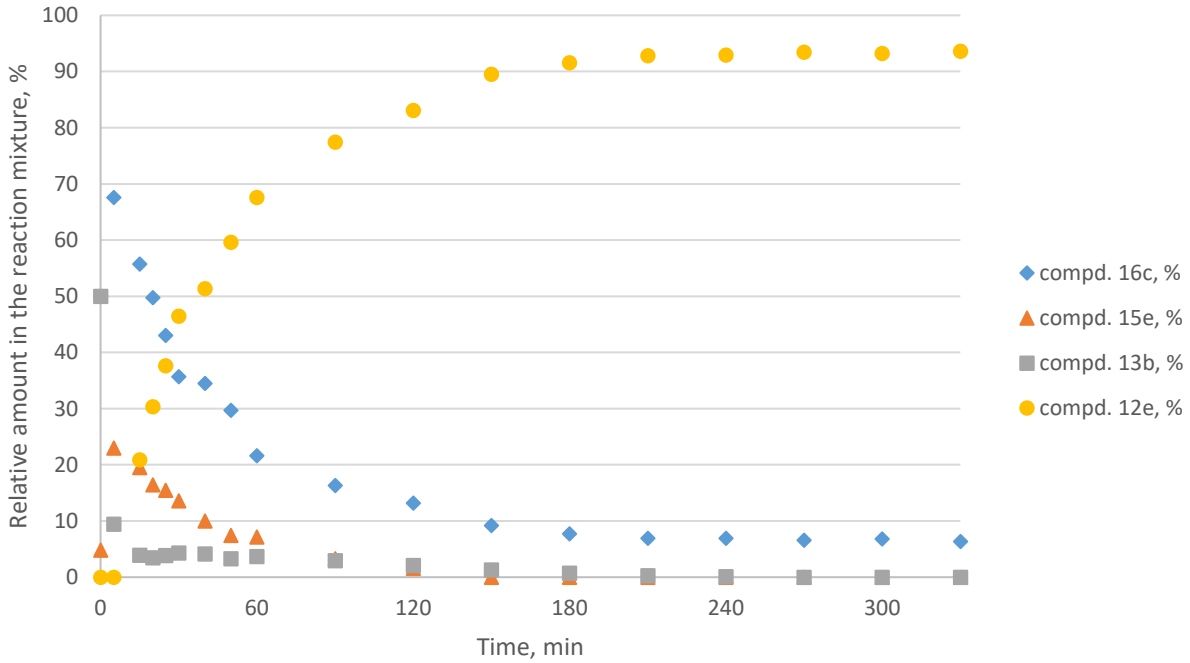


Fig. S2. Relative ratio of the starting compounds **13b** and **16c**, the intermediate **15e** and the product **12e** in the reaction mixture

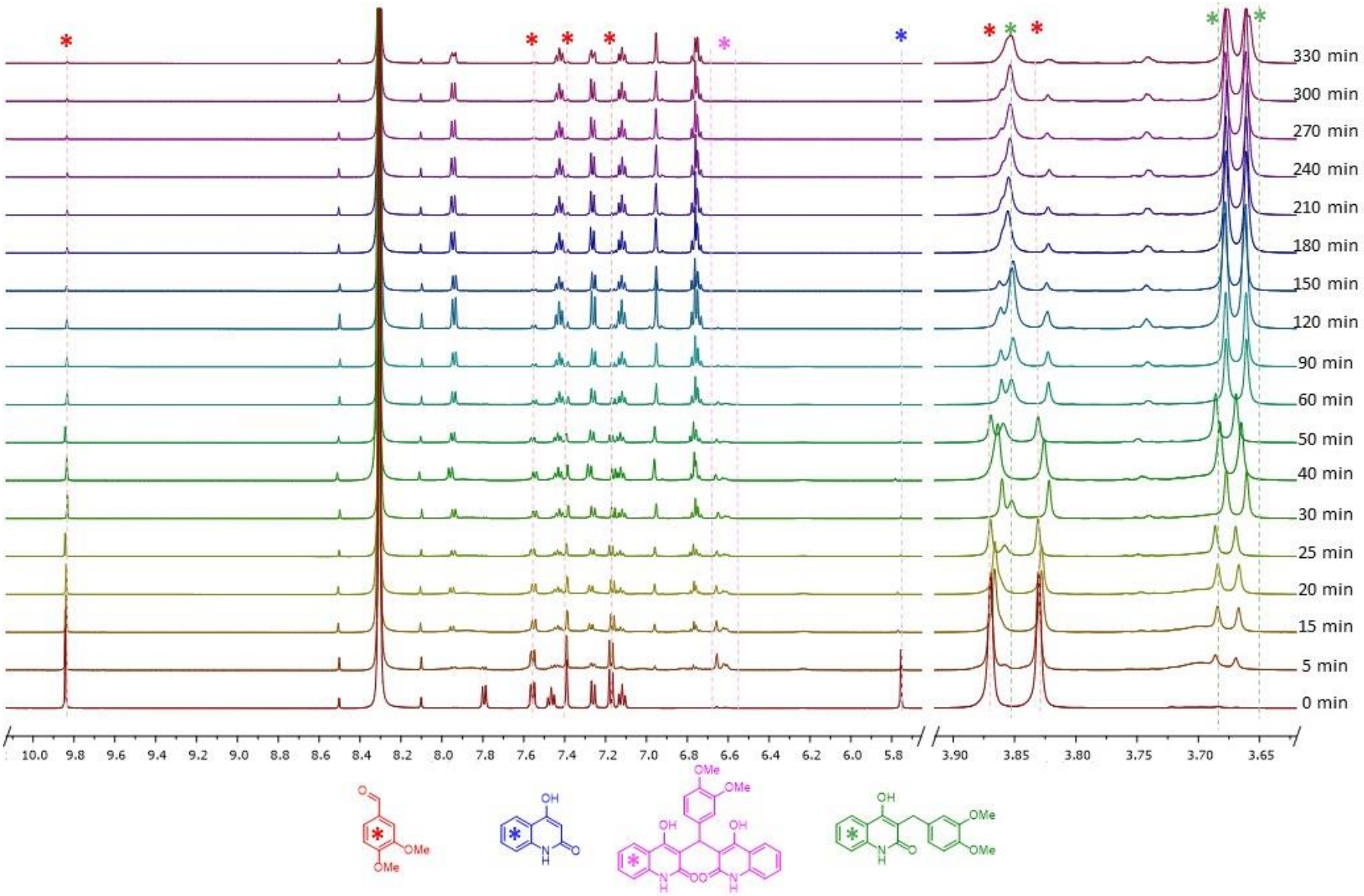
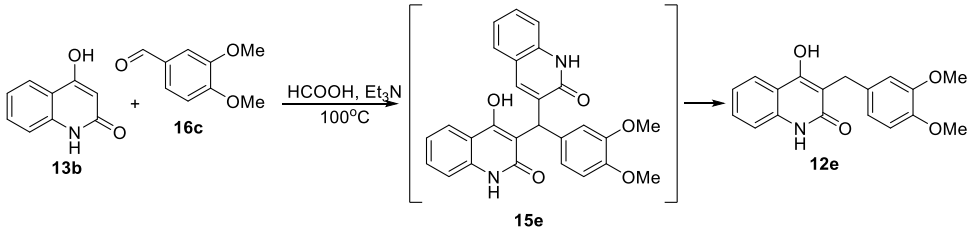


Fig. S3. ^{1}H-NMR spectrum (500 MHz, DMSO-d_6) registered for the reaction mixture

Experiment no 2:



4-Hydroxyquinolin-2(1*H*)-one **13b** (190 mg, 1.2 mmol, 1 eq.), veratraldehyde **16c** (200 mg, 1.2 mmol) and diphenylmethane (198 mg, 1.18 mmol; internal standard) was heated in the mixture of formic acid (1.2 mL) and triethyl amine (1.8 mL) at 100°C. The ^{1}H NMR spectra was registered after regular time intervals: the reaction mixture (~0.1 mL) was dissolved in DMSO-d_6 (~0.5 mL) and the spectra was recorded immediately. Parameters for ^{1}H NMR spectrum: 64 scans, relaxation delay – 10 s.

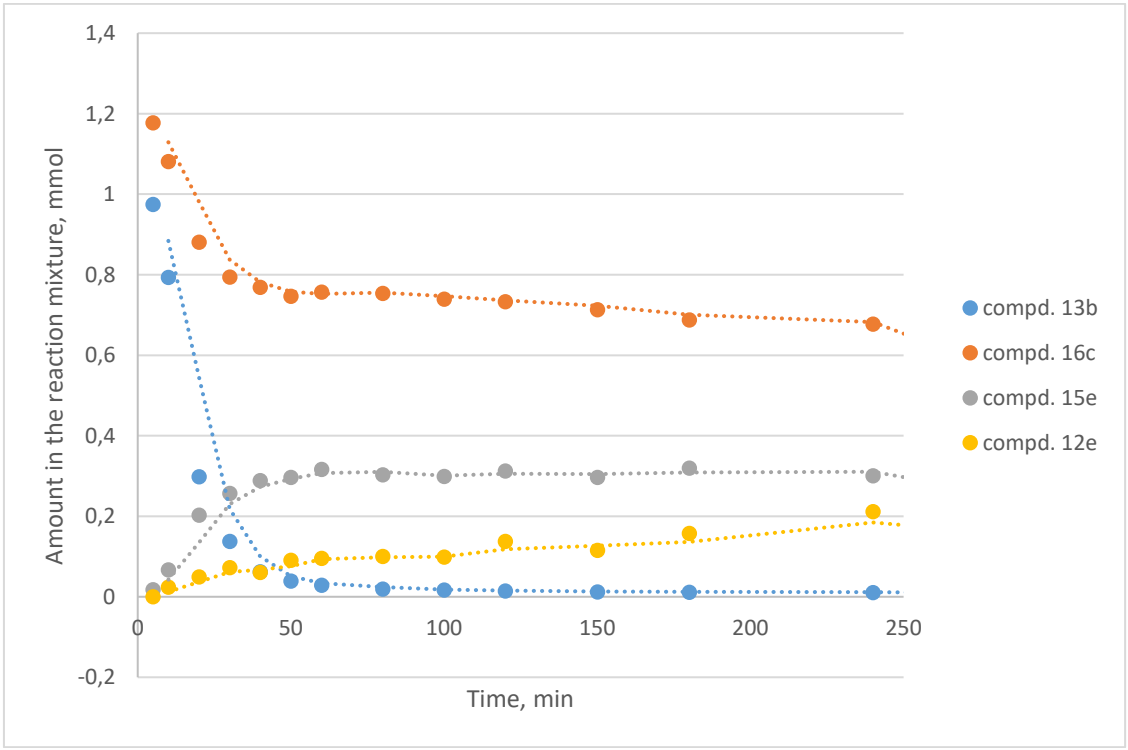


Fig. S4. Amount of the starting compounds **13b** and **16c**, the intermediate **15e** and the product **12e** in the reaction mixture

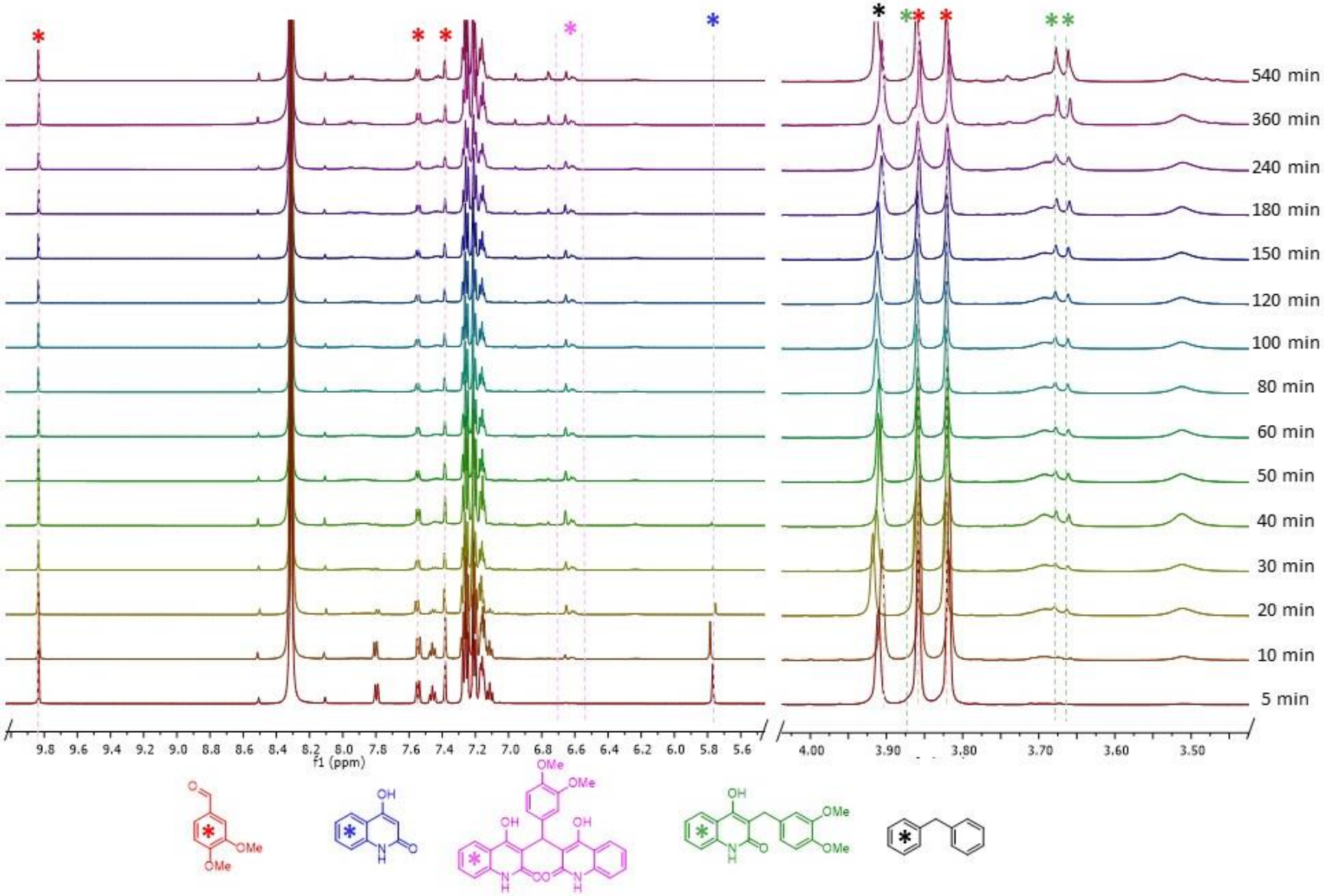
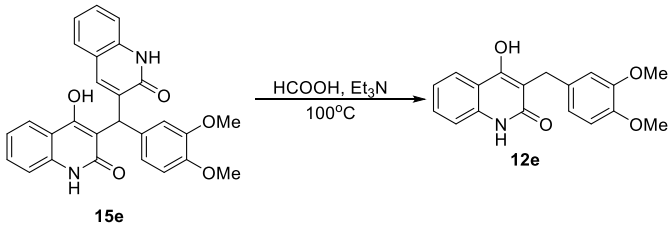


Fig S5. ^{1}H-NMR spectra (500 MHz, DMSO-d_6) registered for the reaction mixture

Experiment no 3:



bis-4-Hydroxyquinolin-2(1*H*)-one **15e** (20 mg, 0.04 mmol, 1 eq.) and diphenylmethane (17.17 mg, 0.10 mmol; internal standard) was heated in the mixture of formic acid (0.6 mL) and triethyl amine (0.9 mL) at 120°C. The ^{1}H NMR spectra was registered after regular time intervals: the reaction mixture (~0.1 mL) was dissolved in DMSO-d_6 (~0.5 mL) and the spectra was recorded immediately. Parameters for ^{1}H NMR spectrum: 64 scans, relaxation delay – 10 s.

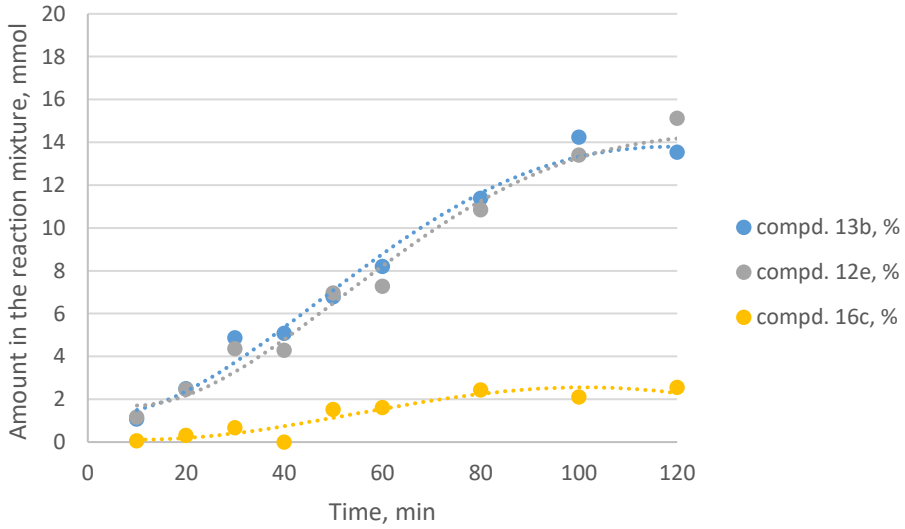


Fig. S6. Amount of the starting compounds **13b, 16c**, and **12e** in the reaction mixture

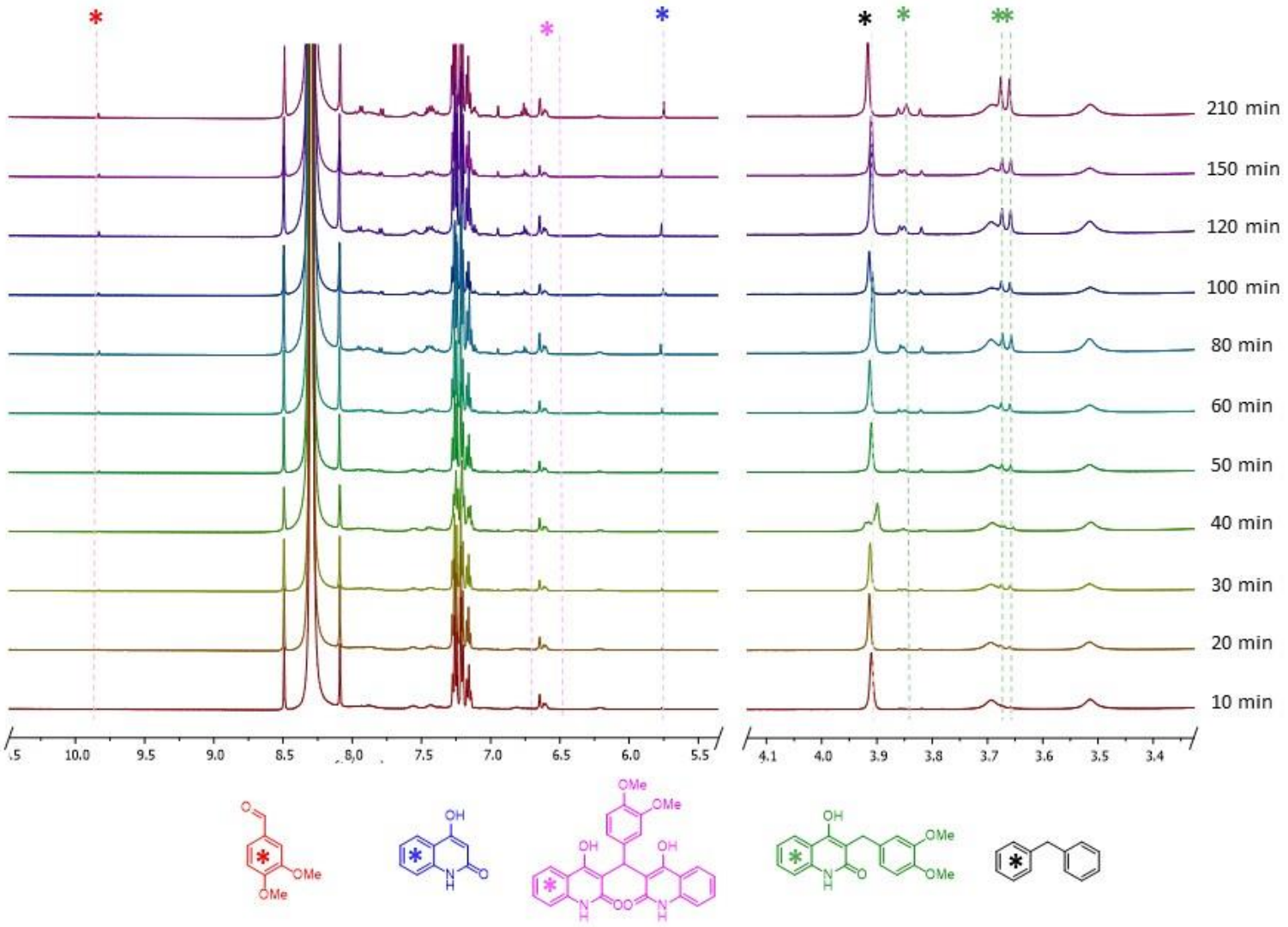


Fig. S7. ^{1}H-NMR spectra (500 MHz, DMSO-d_6) registered for the reaction mixture

5. ANTIRADICAL ACTIVITY

The compounds **12** were tested for their antiradical activity against DPPH and GO radicals according to the protocol described previously[1] and the antiradical activity (inhibition of free radical when the ratio free radical:antioxidant is 1:1) and IC_{50} (concentration which inhibits 50% of the free radical) were calculated. The reaction time for DPPH test was 30 min, for GO test – 2 h.

6. ANTIRADICAL ACTIVITY (KINETIC STUDIES)

The compound **12c**,**e** (0.033 mmol) was dissolved the acetone, *t*-BuOH, MeOH, MeCN, EtOAc, DMF, DMSO, *i*-PrOH, CF_3CH_2OH, THF, EtOH (5 mL, volumetric flask) leading to the solution with concentration 6521 μM. The DPPH (2.2 mg, 5.6 μmol) was dissolved in the required solvent (50 mL, volumetric flask) leading to the solution with concentration ~112 μM.

The compound **12c**,**e** (0.033 mmol) and acetic acid (100 eq), phenol (100 eq.), pyridine (100 eq.), malonic acid (50 eq.), TFA (100 eq.), aniline (100 eq.) or Et_3N (100 eq.) was dissolved in 96% ethanol (5 mL, volumetric flask) leading to solution with concentration 6521 μM (for compound **12c**,**e**).

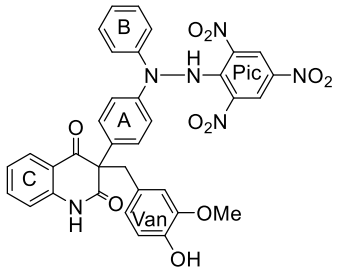
Later the corresponding antioxidant solution (1.5 mL) and DPPH solution (1.5 mL) was mixed in cuvette and absorption of the solution was immediately measured and then each 5 s. The experiment was realized for 3 min. The measurement was done at the absorption maximum (λ = 515 nm). Each experiment was repeated triple. The experiments was done at room temperature (19°C, without additional temperature control for the cuvette) at the same day. For the kinetic curves see Supporting information.

The mathematical processing of the data was done with MS Office software. The reaction rates were characterized with the slope of the trendlines.

7. ISOLATION OF THE REACTION PRODUCTS BETWEEN COMPOUND 12c,e AND DPPH

The compound **12c**,**e** (0.16 mmol) and DPPH (63 mg, 0.16 mmol) was stirred in EtOH (10 mL) at room temperature overnight. The reaction mixture was evaporated and the products were isolated on silica (Hex:EtOAc (100:1 → 0:1) → EtOAc:MeOH (40:1).

3-(4-Hydroxy-3-methoxybenzyl)-3-{4-[1-phenyl-2-(2,4,6-trinitrophenyl)hydrazinyl]phenyl}quinoline-2,4(1*H*,3*H*)-dione 18a



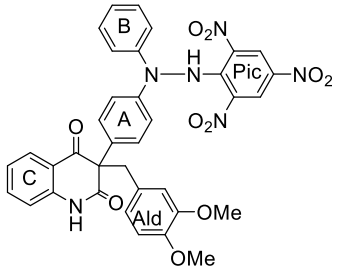
[1] Mieriņa I, Jure M, Zēberga S, Makareviciene V, Zicāne D, Tetere Z, Rāviņa I. Eur. J. Lipid Sci. Technol. 2017; 119: 1700172.

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 10.09 (1H, s, NH), 9.21 (1H, s, Pic), 8.49 (1H, s, Pic), 8.13 (1H, s, NH), 7.91 (1H, d, *J* = 7.6 Hz, H-C), 7.47 (1H, t, *J* = 7.5 Hz H from B or C), 7.40 (2H, d, *J* = 8.1 Hz, H from A or B), 7.34 (2H, t, *J* = 8.1 Hz, H from A or B), 7.21 (1H, t, *J* = 7.0 Hz, H from C or B), 7.13-7.01 (6H, m, H from A, B or C), 6.78-6.71 (2H, m, Van), 6.65 (1H, d, *J* = 6.7 Hz, Van), 5.41 (s, 1H, OH), 3.89 (1H, d, *J* = 12.5 Hz, H from CH_2), 3.69 (3H, s, OCH_3), 3.64 (1H, d, *J* = 12.5 Hz, H from CH_2).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 195.1, 172.3, 146.1, 145.9, 145.5, 144.6, 142.0, 140.3, 136.8, 136.6, 135.7, 129.9, 129.8, 128.3, 128.0, 126.6, 126.4, 125.2, 124.0, 123.6, 121.5, 121.4, 120.3, 120.2, 119.5, 116.1, 114.2, 113.4, 55.9, 42.2, 29.9.

HRMS *m/z*: $[M+NH_4]^+$ calcd for $[C_{35}H_{30}N_7O_{10}]^+$ 708.2049; found 708.2026.

3-(3,4-Dimethoxybenzyl)-3-{4-[1-phenyl-2-(2,4,6-trinitrophenyl)hydrazinyl]phenyl}quinoline-2,4(1*H*,3*H*)-dione 18b



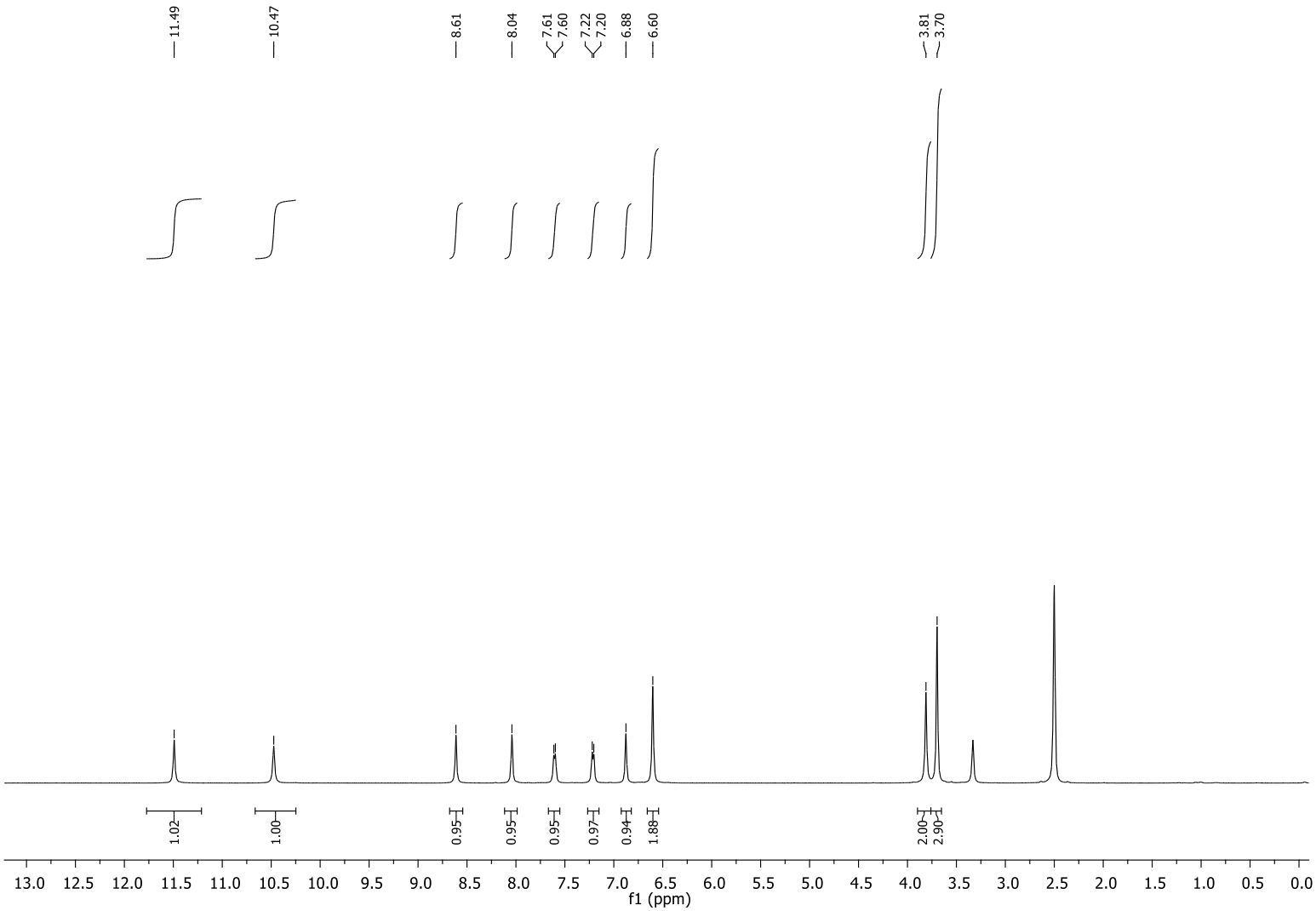
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 10.10 (1H, s, NH), 9.19 (1H, s, Pic), 8.91 (1H, s, NH), 8.48 (1H, s, Pic), 7.90 (1H, d, *J* = 7.6 Hz, H-C), 7.46 (1H, t, *J* = 7.5 Hz H from B or C), 7.38 (2H, d, *J* = 8.0 Hz, H from A or B), 7.33 (2H, t, *J* = 8.1 Hz, H from B), 7.20 (1H, t, *J* = 7.0 Hz, H from C or B), 7.12-7.04 (3H, m, H from A, B or C), 7.02 (2H, d, *J* = 8,8 Hz, H from A or B), 6.80-6.75 (2H, m, H from C or Ald), 6.73 (1H, d, *J* = 8.3 Hz, H from C or Ald), 6.51 (1H, d, *J* = 8.3 Hz, H from Ald), 3.91 (1H, d, *J* = 12.2 Hz, H from CH_2), 3.69 (3H, s, OCH_3), 3.66 (3H, s, OCH_3), 3.65 (1H, d, *J* = 12.2 Hz, H from CH_2).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 195.0, 172.9, 148.4, 147.87, 145.88, 145.84, 145.41, 145.39, 142.0, 140.3, 136.8, 136.6, 135.6, 129.9, 128.7, 128.2, 126.6, 126.4, 125.2, 124.0, 122.7, 121.5, 121.4, 120.1, 120.1, 119.4, 116.3, 113.7, 110.9, 66.8, 55.8, 42.1.

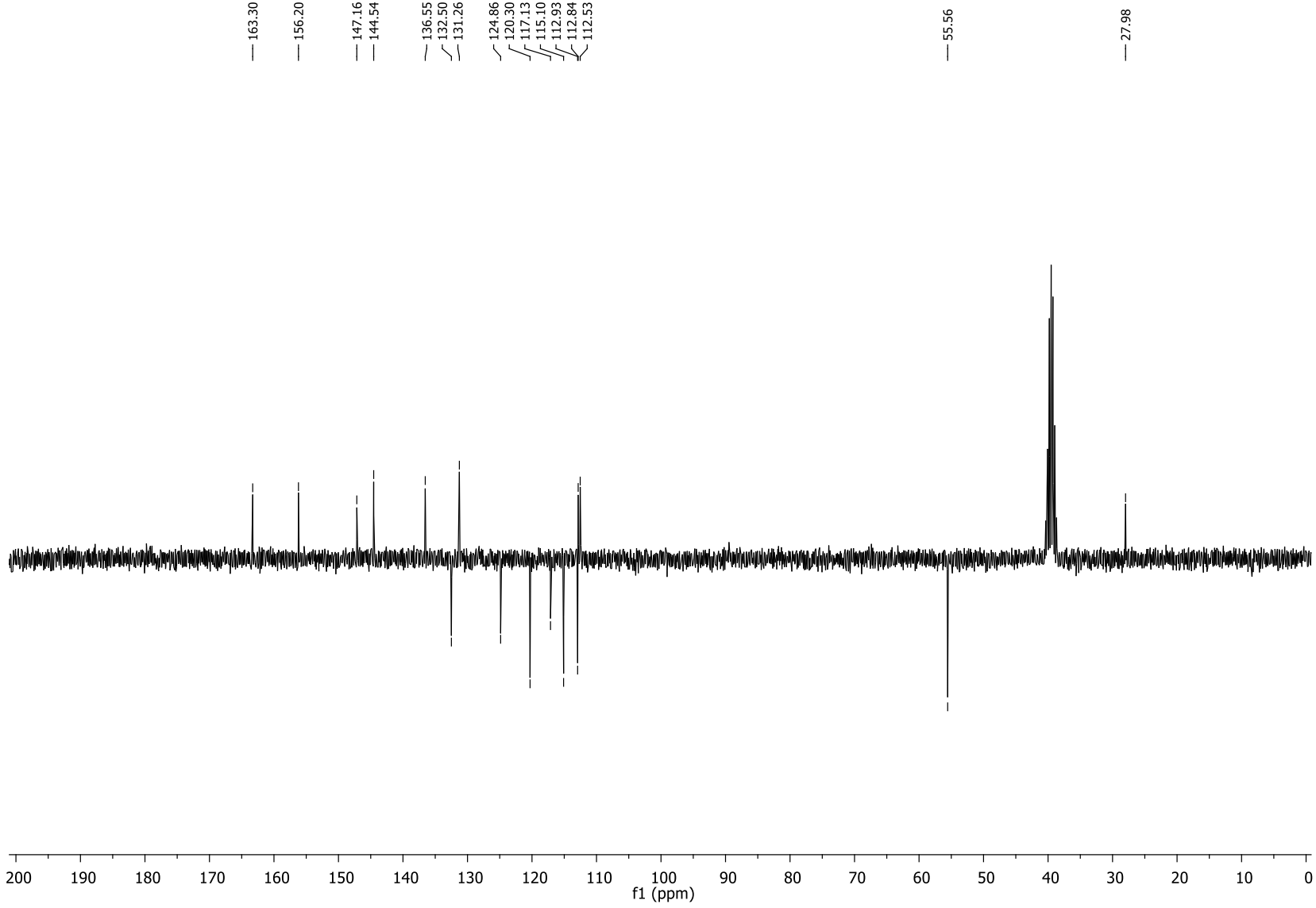
HRMS *m/z*: $[M+NH_4]^+$ calcd for $[C_{356}H_{32}N_7O_{10}]^+$ 722.2205; found 722.2200.

8. NMR SPECTRA FOR THE NEW COMPOUNDS

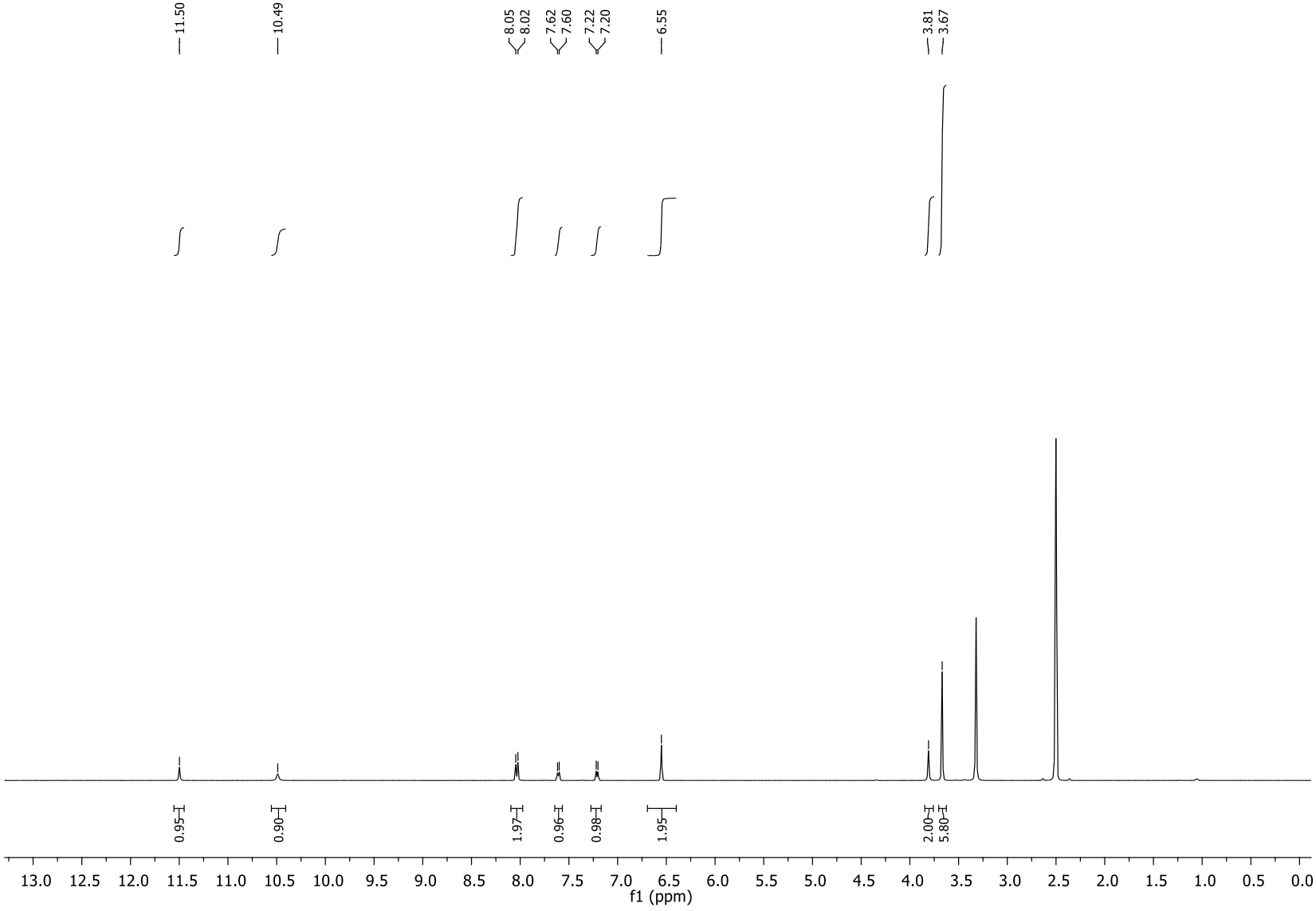
^{1}H NMR spectrum for 6-bromo-4-hydroxy-3-(4-hydroxy-3-methoxybenzyl)quinolin-2(1H)-one 12a (500 MHz, DMSO-d_6):



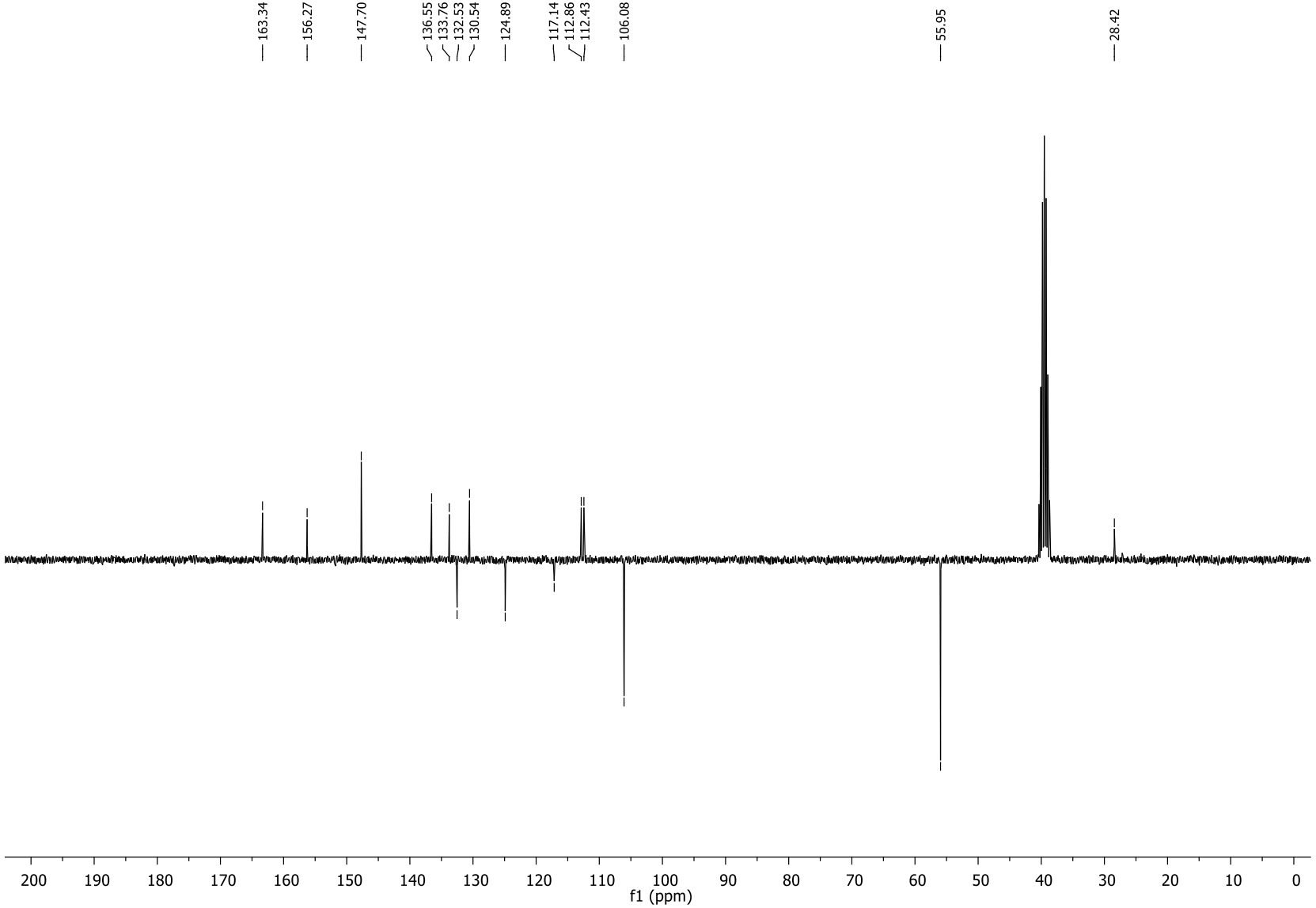
^{13}C NMR spectrum for 6-bromo-4-hydroxy-3-(4-hydroxy-3-methoxybenzyl)quinolin-2(1H)-one 12a (75 MHz, DMSO-d_6):



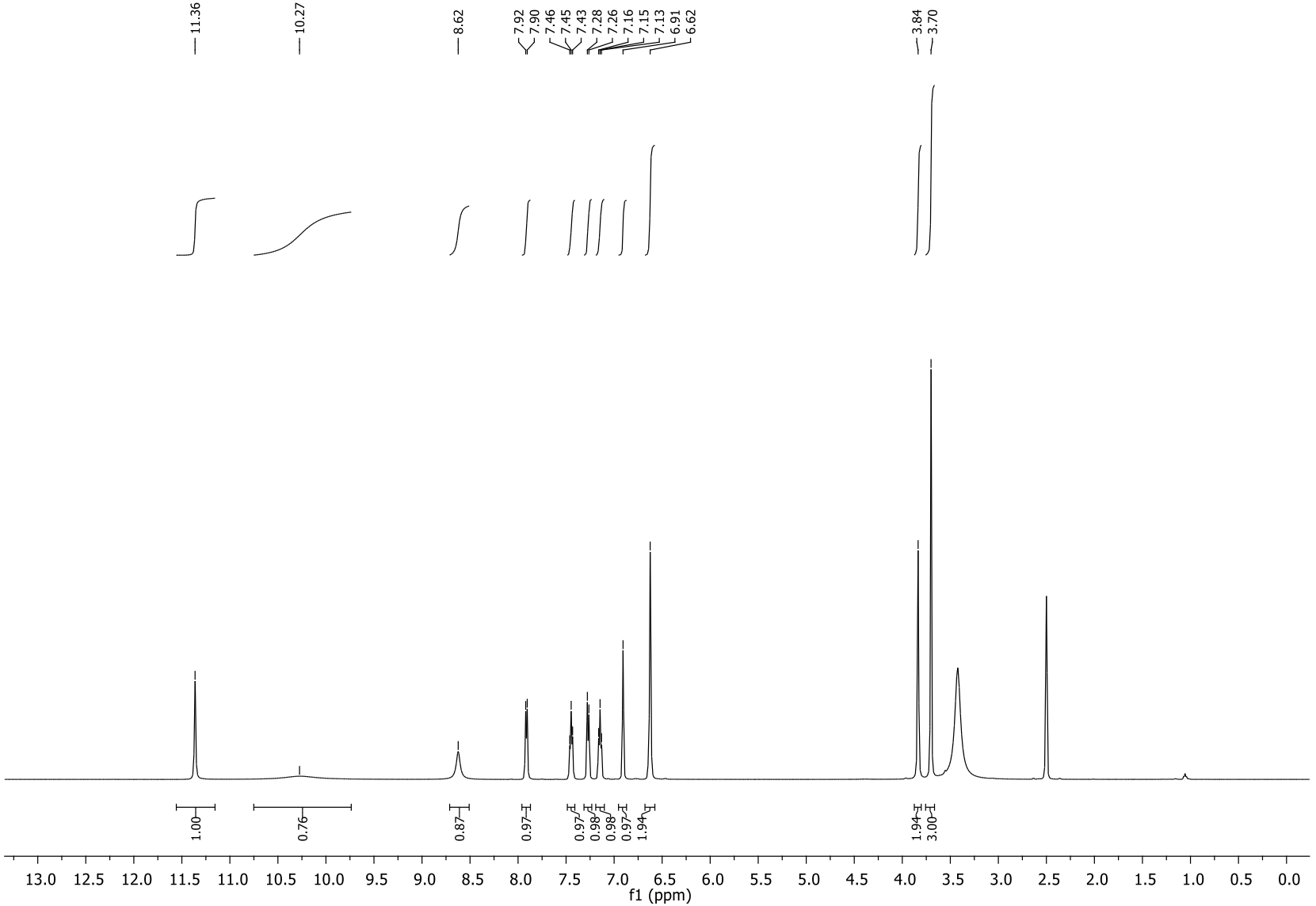
^{1}H NMR spectrum for 6-bromo-4-hydroxy-3-(4-hydroxy-3,5-dimethoxybenzyl)quinolin-2(1H)-one 12b (500 MHz, DMSO-d_6):



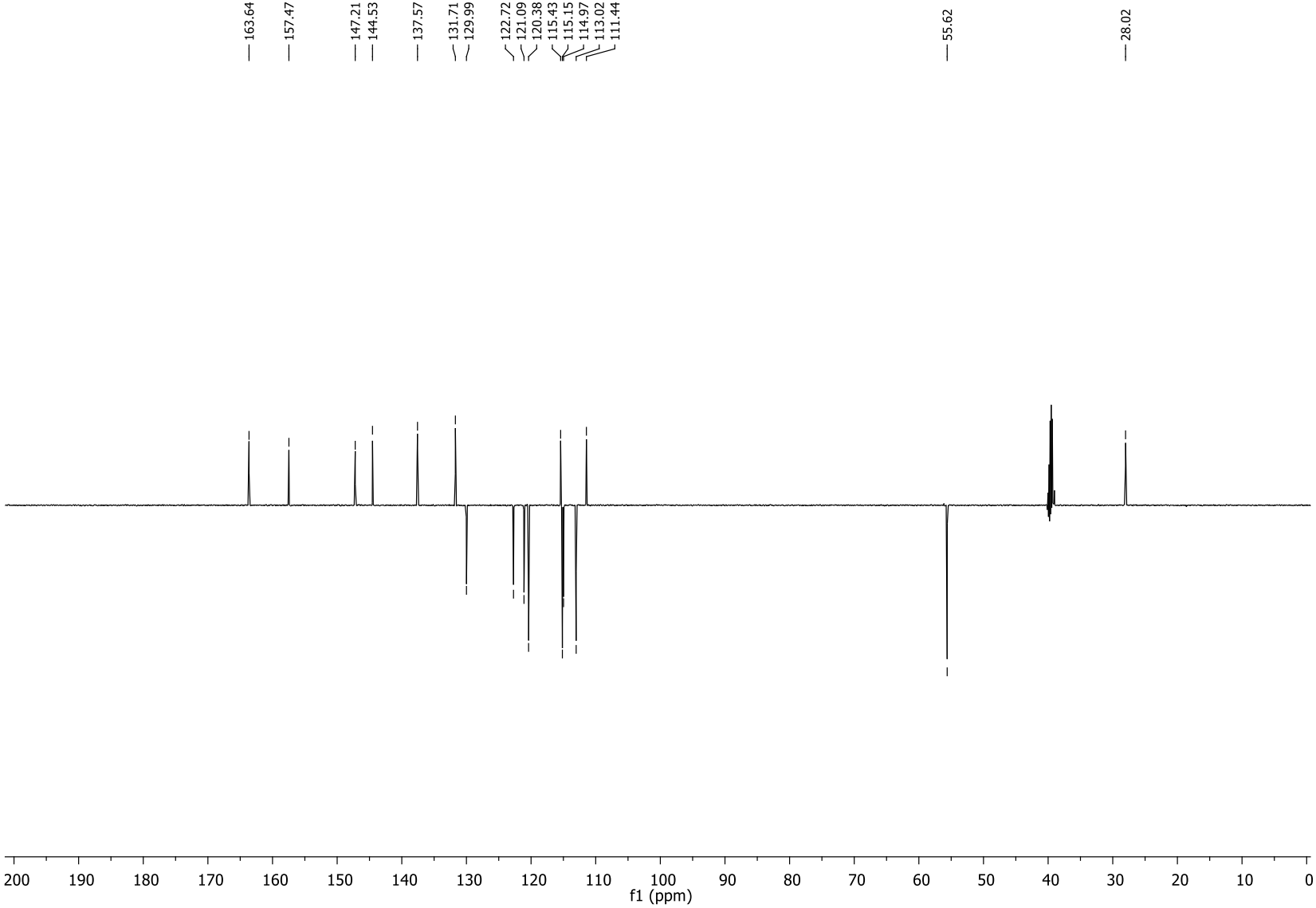
^{13}C NMR spectrum for 6-bromo-4-hydroxy-3-(4-hydroxy-3,5-dimethoxybenzyl)quinolin-2(1H)-one 12b (75 MHz, DMSO-d_6):



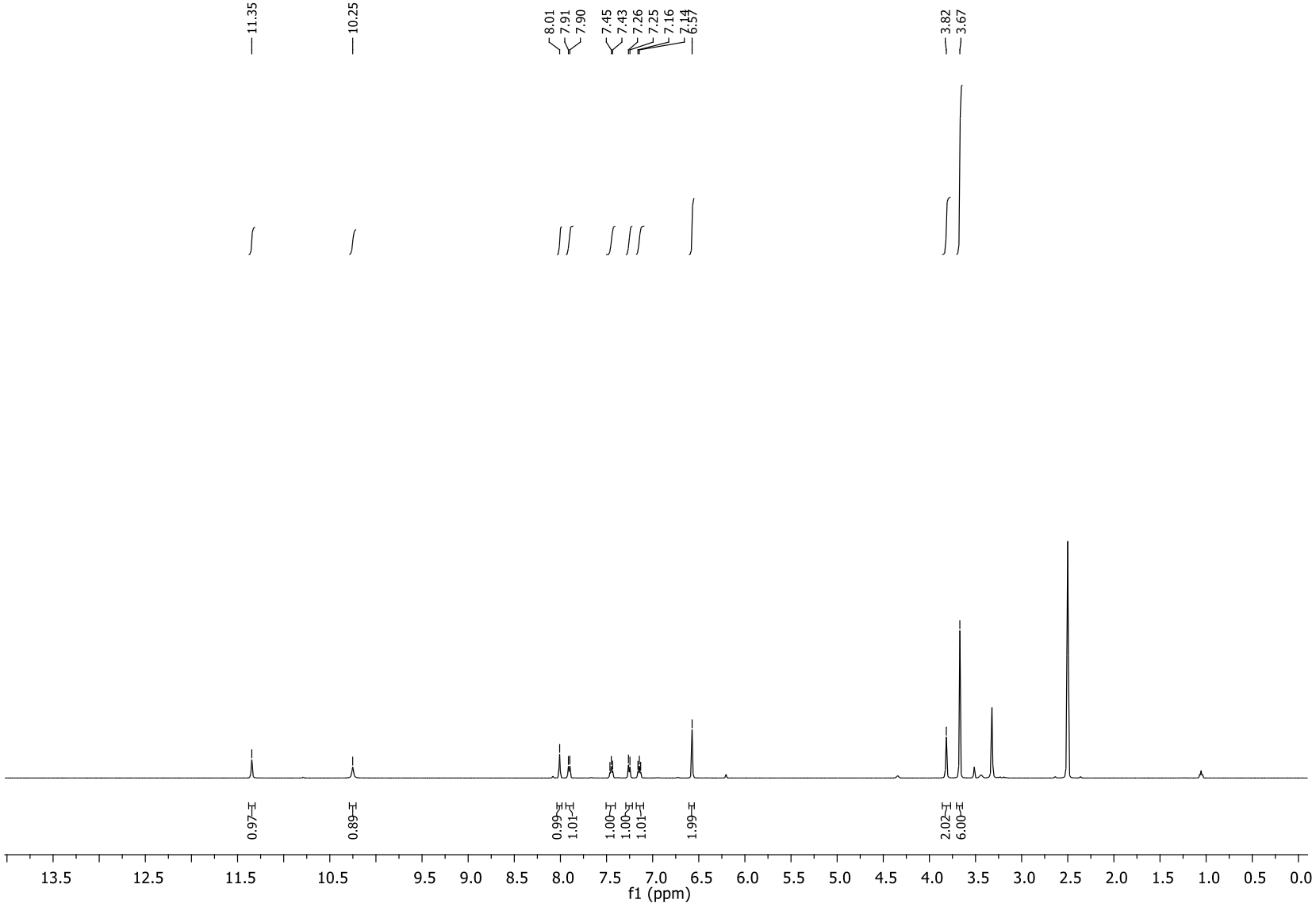
^{1}H NMR spectrum for 4-hydroxy-3-(4-hydroxy-3-methoxybenzyl)quinolin-2(1H)-one 12c (500 MHz, DMSO-d_6):



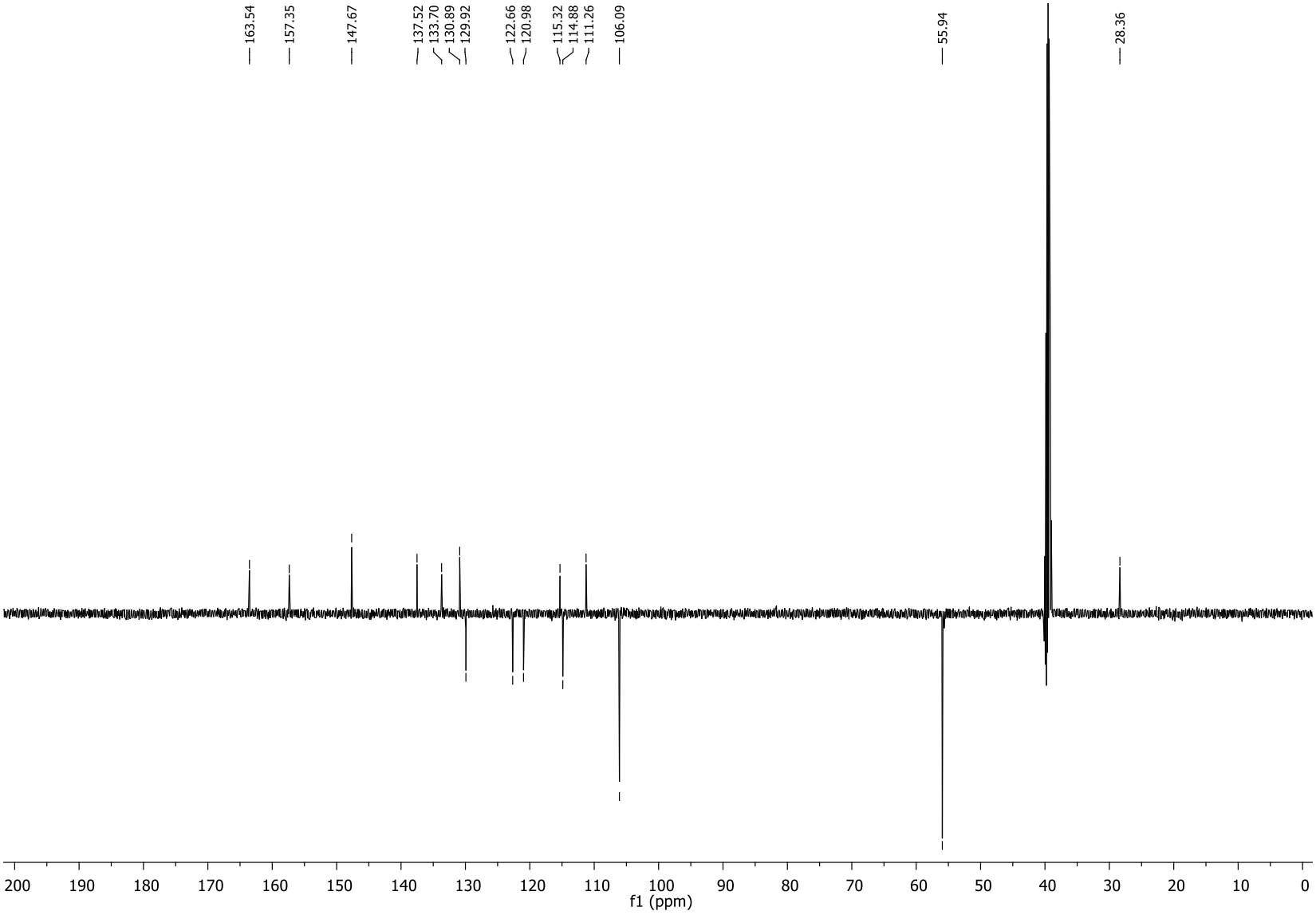
^{13}C NMR spectrum for 4-hydroxy-3-(4-hydroxy-3-methoxybenzyl)quinolin-2(1H)-one 12c (126 MHz, DMSO-d_6):



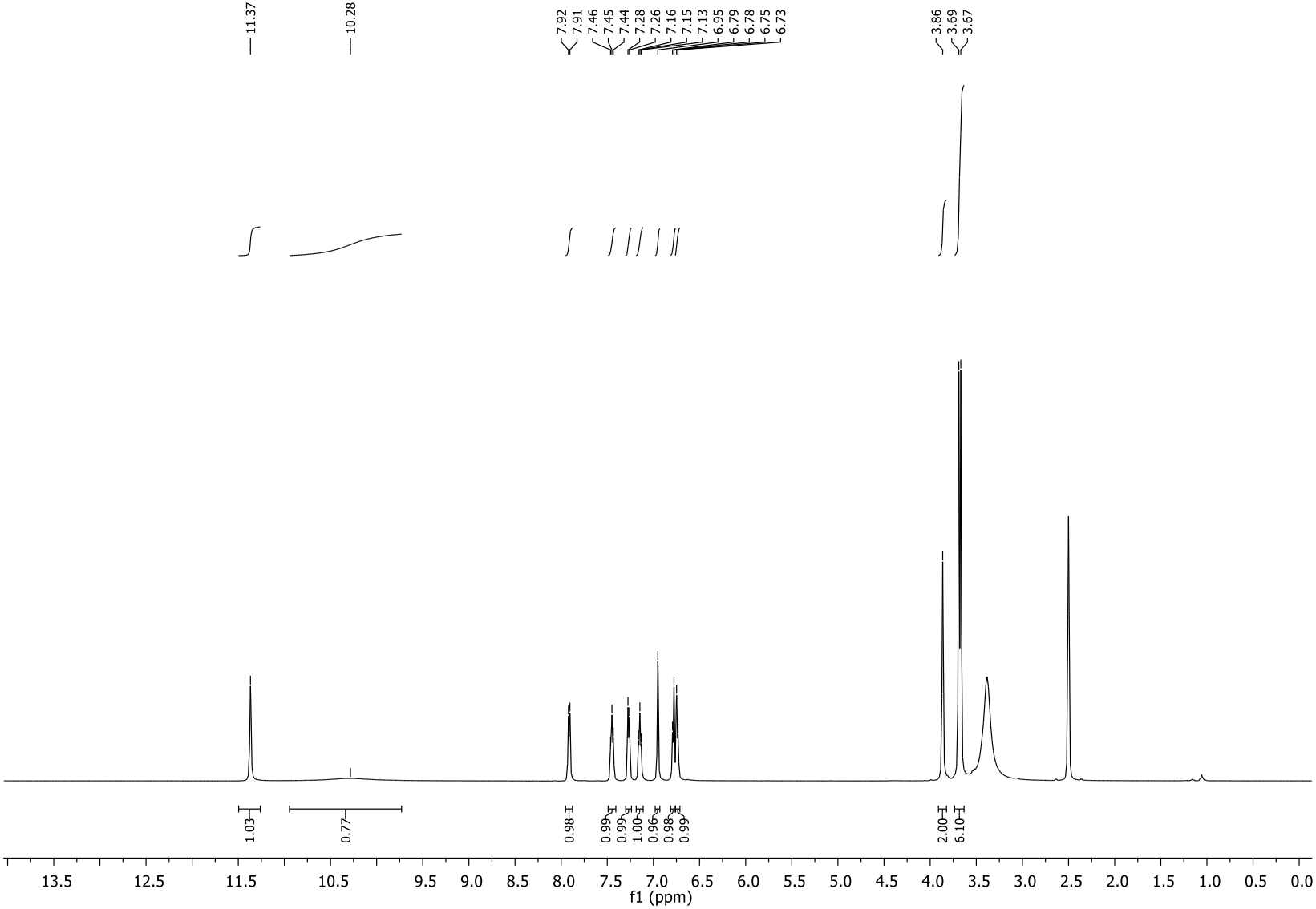
^{1}H NMR spectrum for 4-hydroxy-3-(4-hydroxy-3,5-dimethoxybenzyl)quinolin-2(1H)-one 12d (500 MHz, DMSO-d_6):



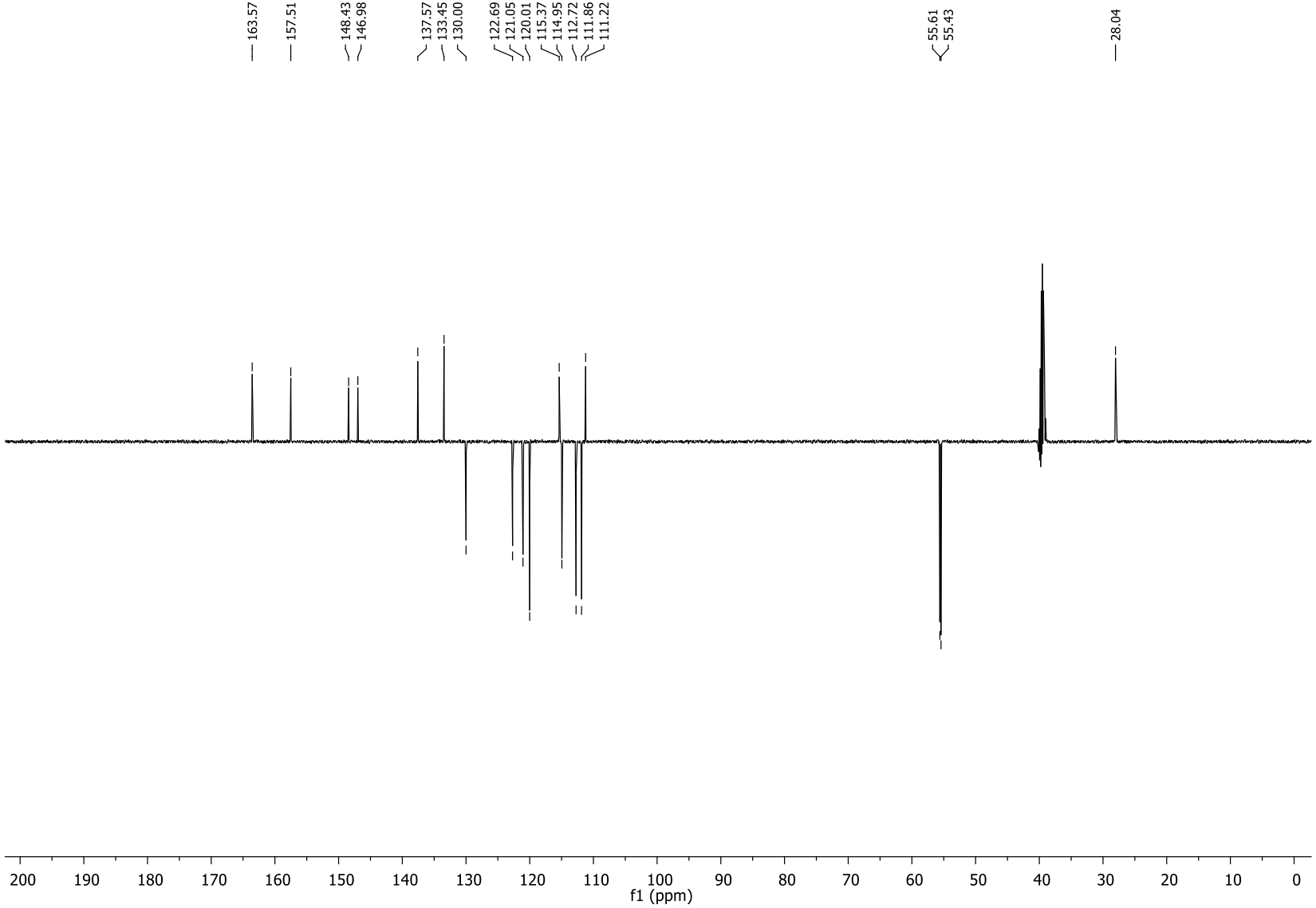
^{13}C NMR spectrum for 4-Hydroxy-3-(4-hydroxy-3,5-dimethoxybenzyl)quinolin-2(1H)-one 12d (126 MHz, DMSO-d_6):



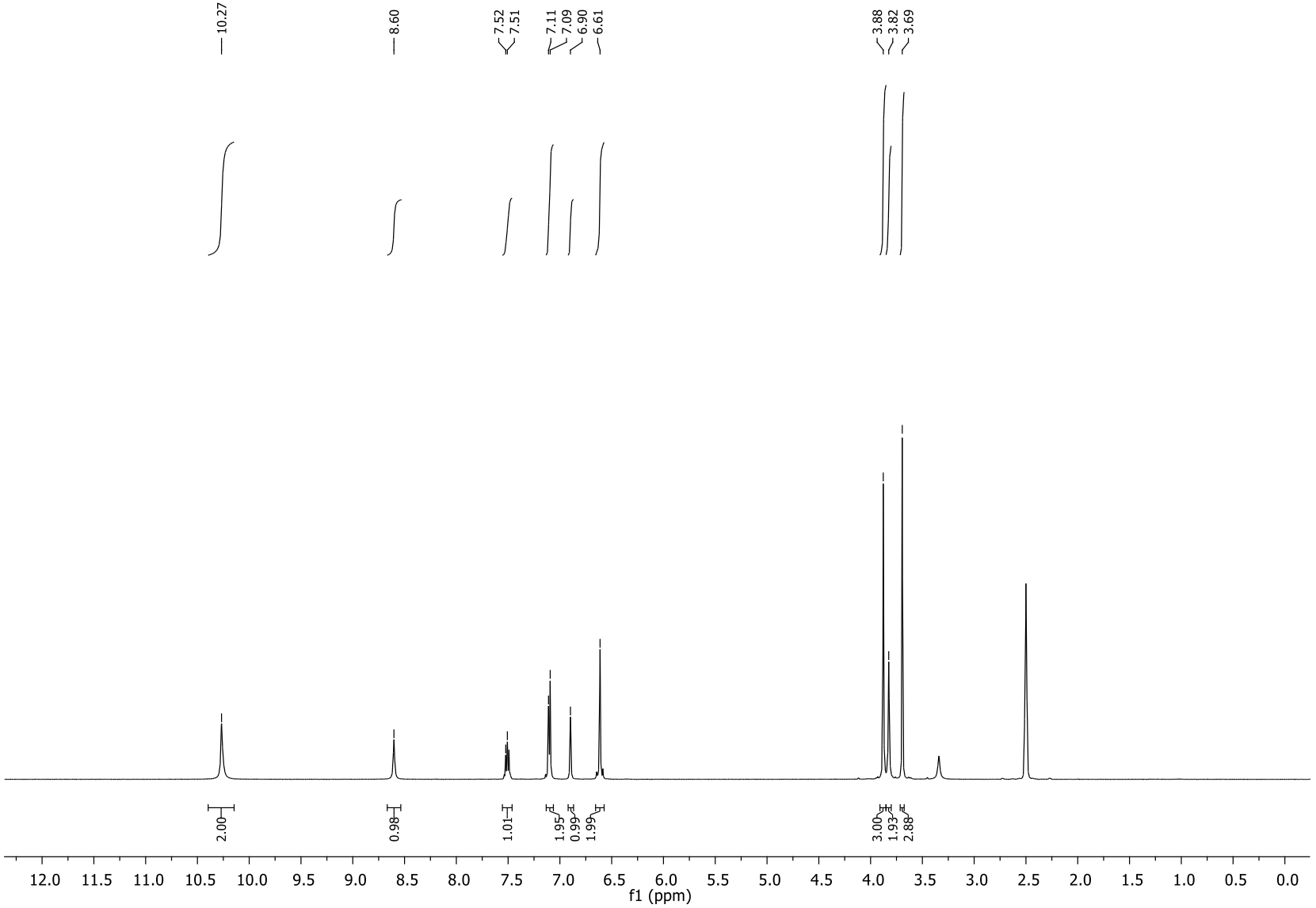
^{1}H NMR spectrum for 3-(3,4-dimethoxybenzyl)-4-hydroxyquinolin-2(1H)-one 12e (500 MHz, DMSO-d_6):



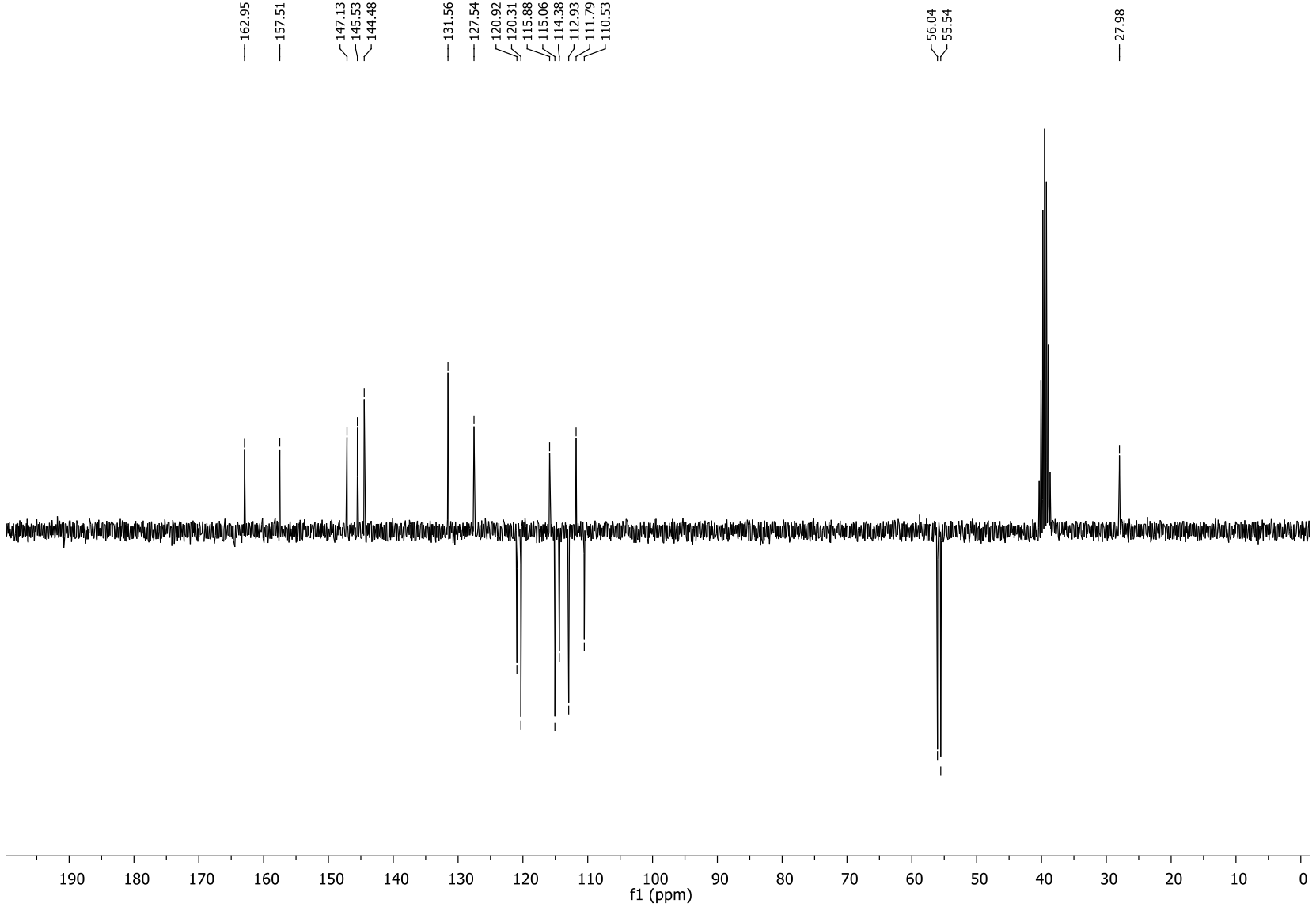
^{13}C NMR spectrum for 3-(3,4-dimethoxybenzyl)-4-hydroxyquinolin-2(1H)-one 12e (126 MHz, DMSO-d_6):



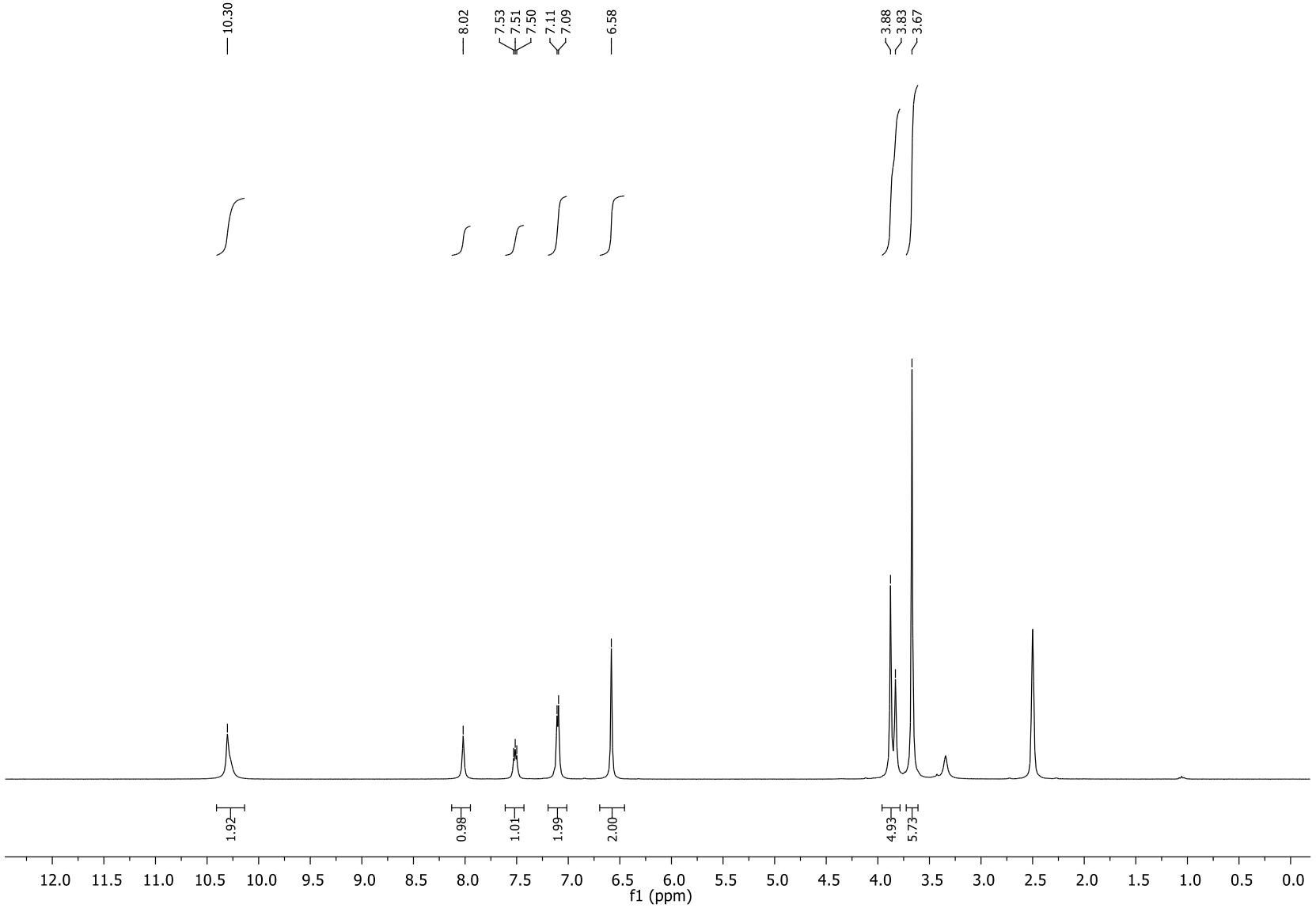
^{1}H NMR spectrum for 4-hydroxy-3-(4-hydroxy-3-methoxybenzyl)-8-methoxyquinolin-2(1H)-one 12f (300 MHz, DMSO-d_6):



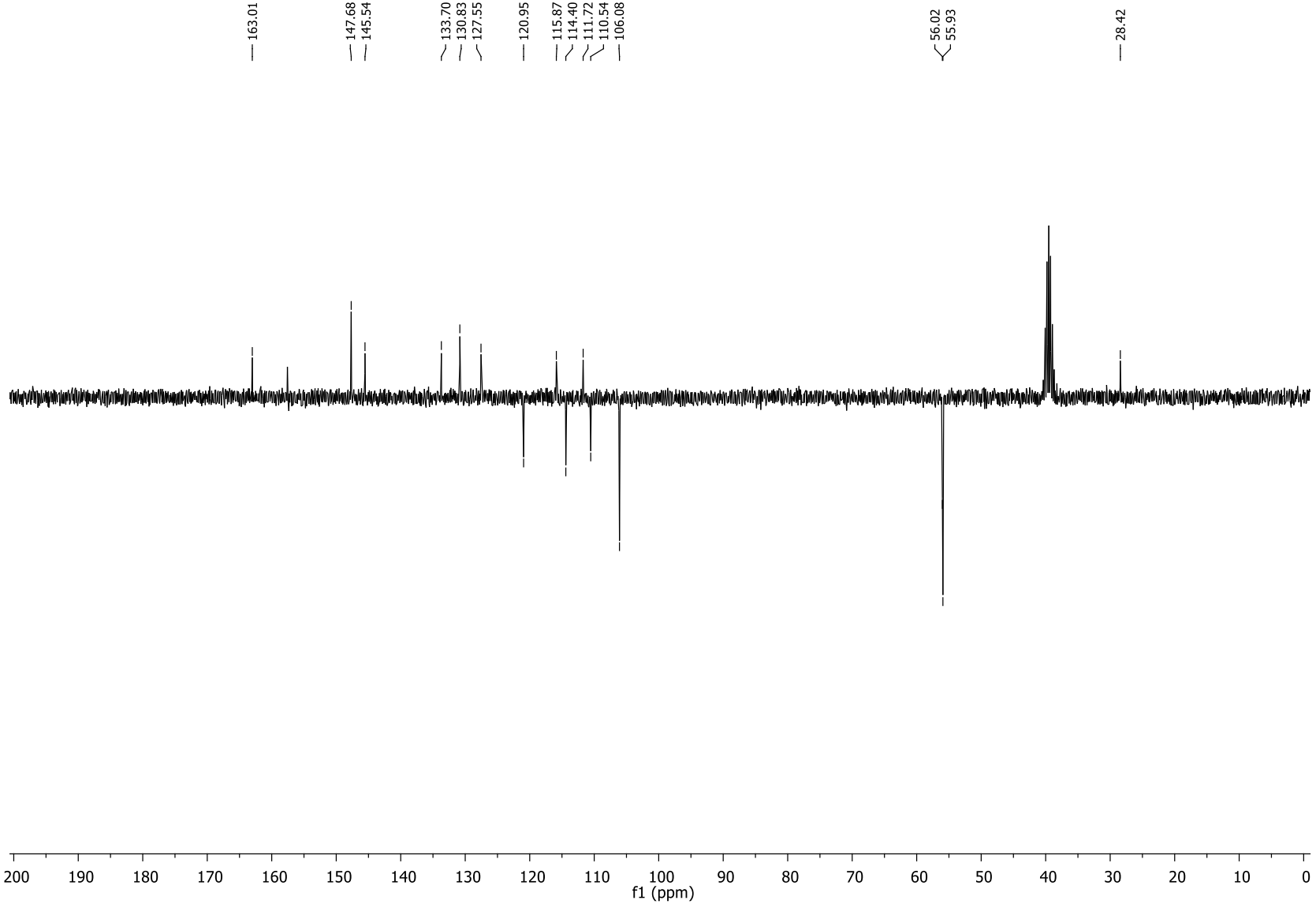
^{13}C NMR spectrum for 4-Hydroxy-3-(4-hydroxy-3-methoxybenzyl)-8-methoxyquinolin-2(1H)-one 12f (75 MHz, DMSO-d_6):



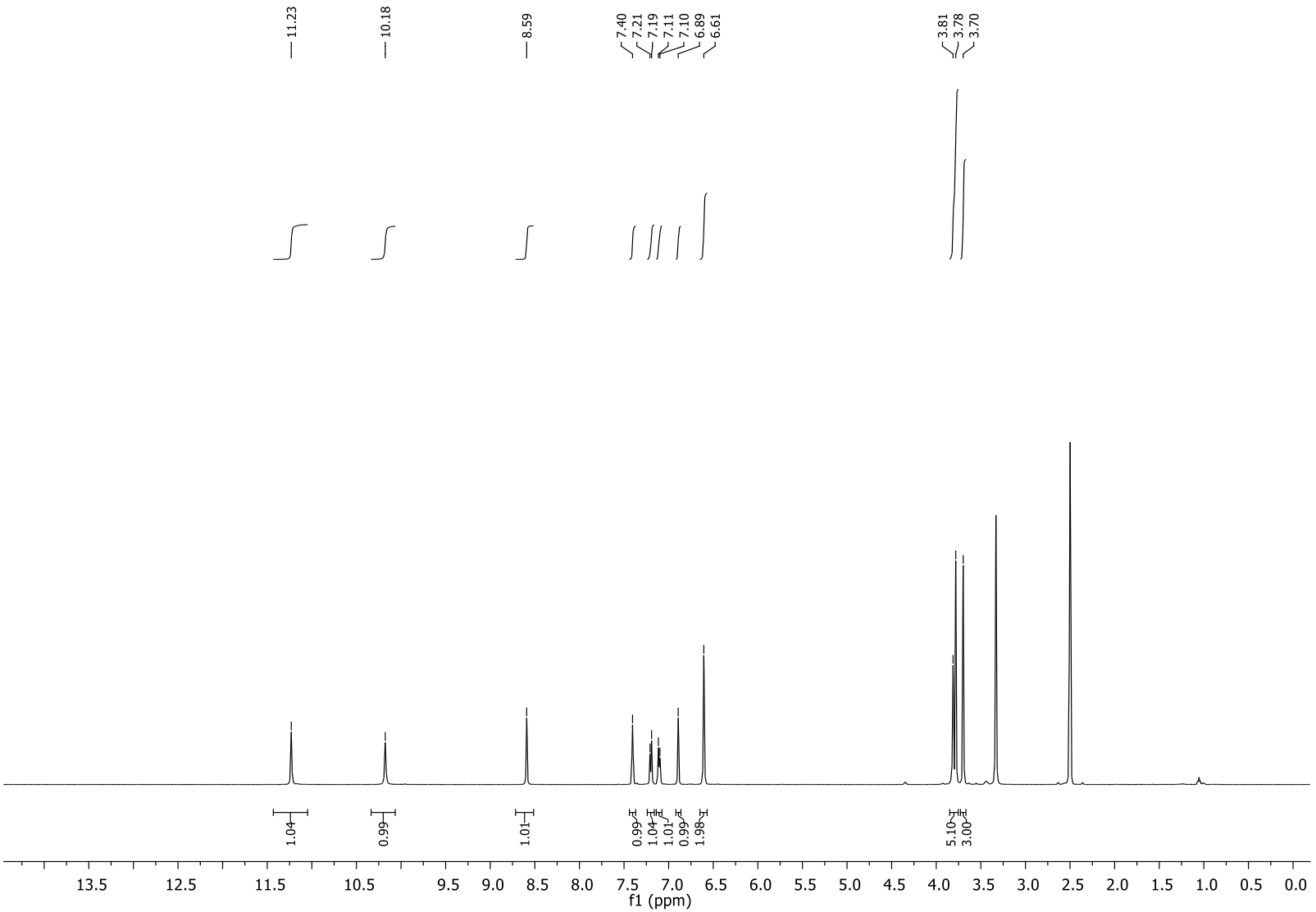
^{1}H NMR spectrum for 4-hydroxy-3-(4-hydroxy-3,5-dimethoxybenzyl)-8-methoxyquinolin-2(1H)-one 12g (300 MHz, DMSO-d_6):



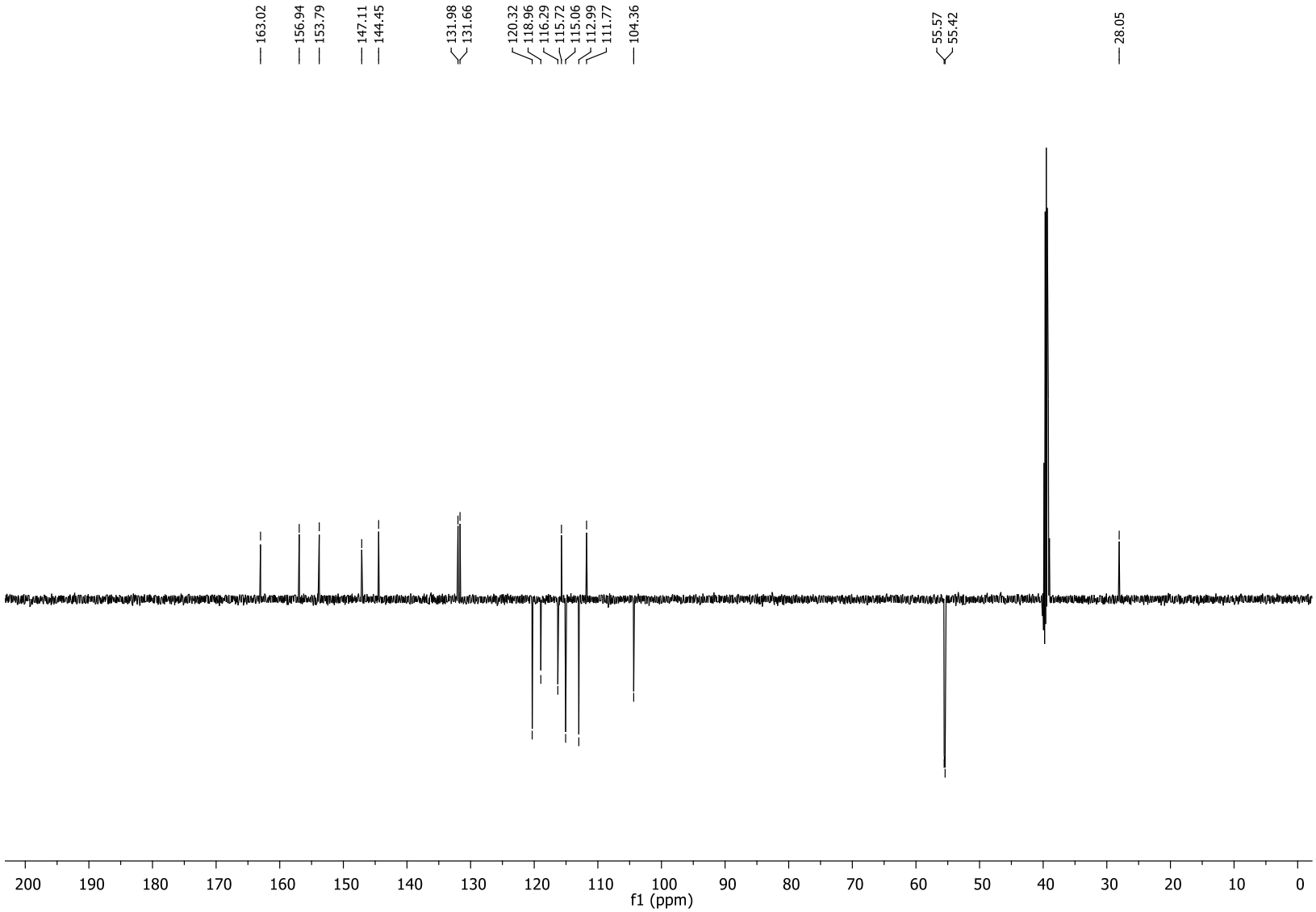
^{13}C NMR spectrum for 4-Hydroxy-3-(4-hydroxy-3,5-dimethoxybenzyl)-8-methoxyquinolin-2(1H)-one 12g (75 MHz, DMSO-d_6):



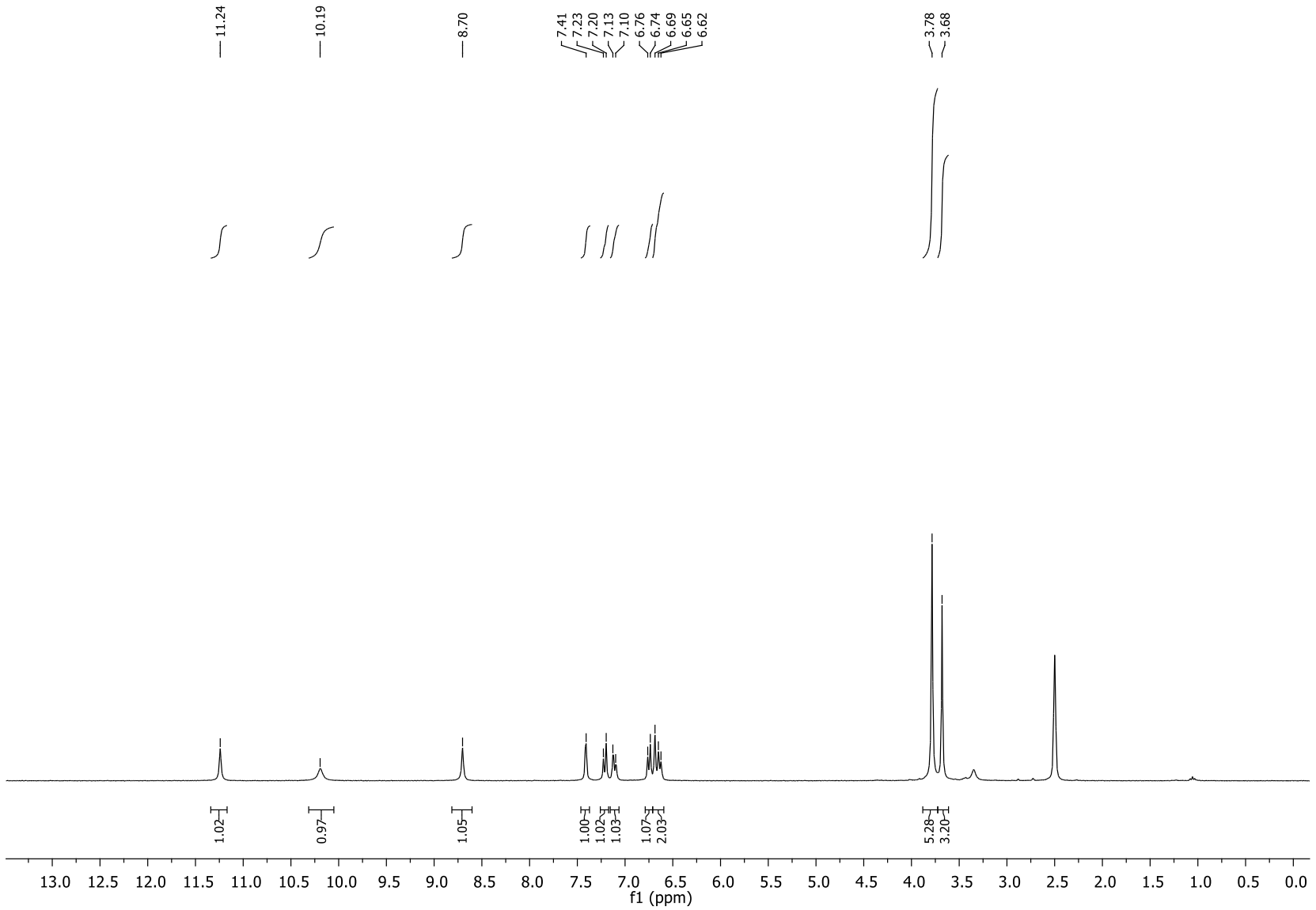
^{1}H NMR spectrum for 4-hydroxy-3-(4-hydroxy-3-methoxybenzyl)-6-methoxyquinolin-2(1H)-one 12h (500 MHz, DMSO-d_6):



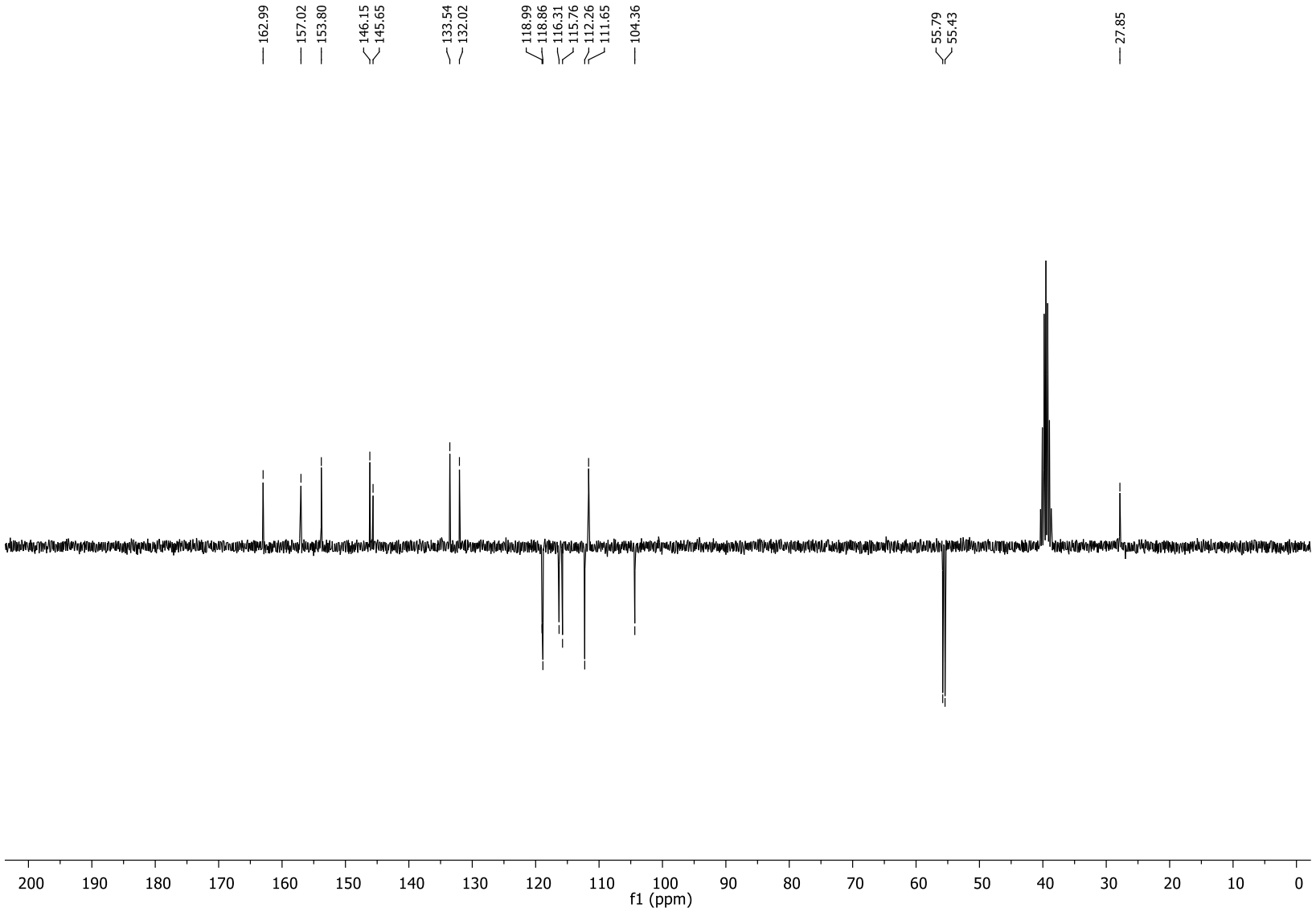
^{13}C NMR spectrum for 4-hydroxy-3-(4-hydroxy-3-methoxybenzyl)-6-methoxyquinolin-2(1H)-one 12h (126 MHz, DMSO-d_6):



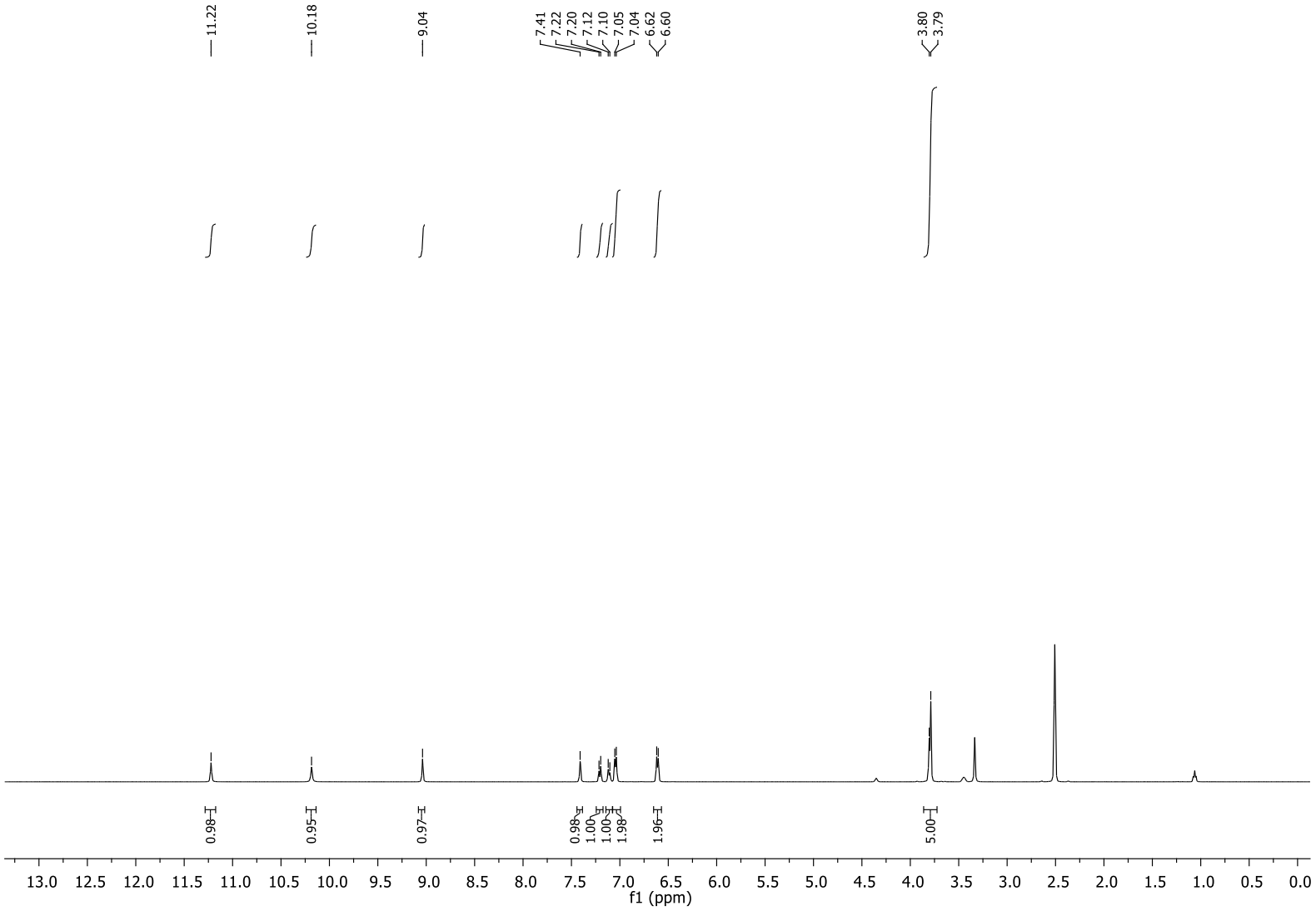
^{1}H NMR spectrum for 4-hydroxy-3-(3-hydroxy-4-methoxybenzyl)-6-methoxyquinolin-2(1H)-one 12i (300 MHz, DMSO-d_6):



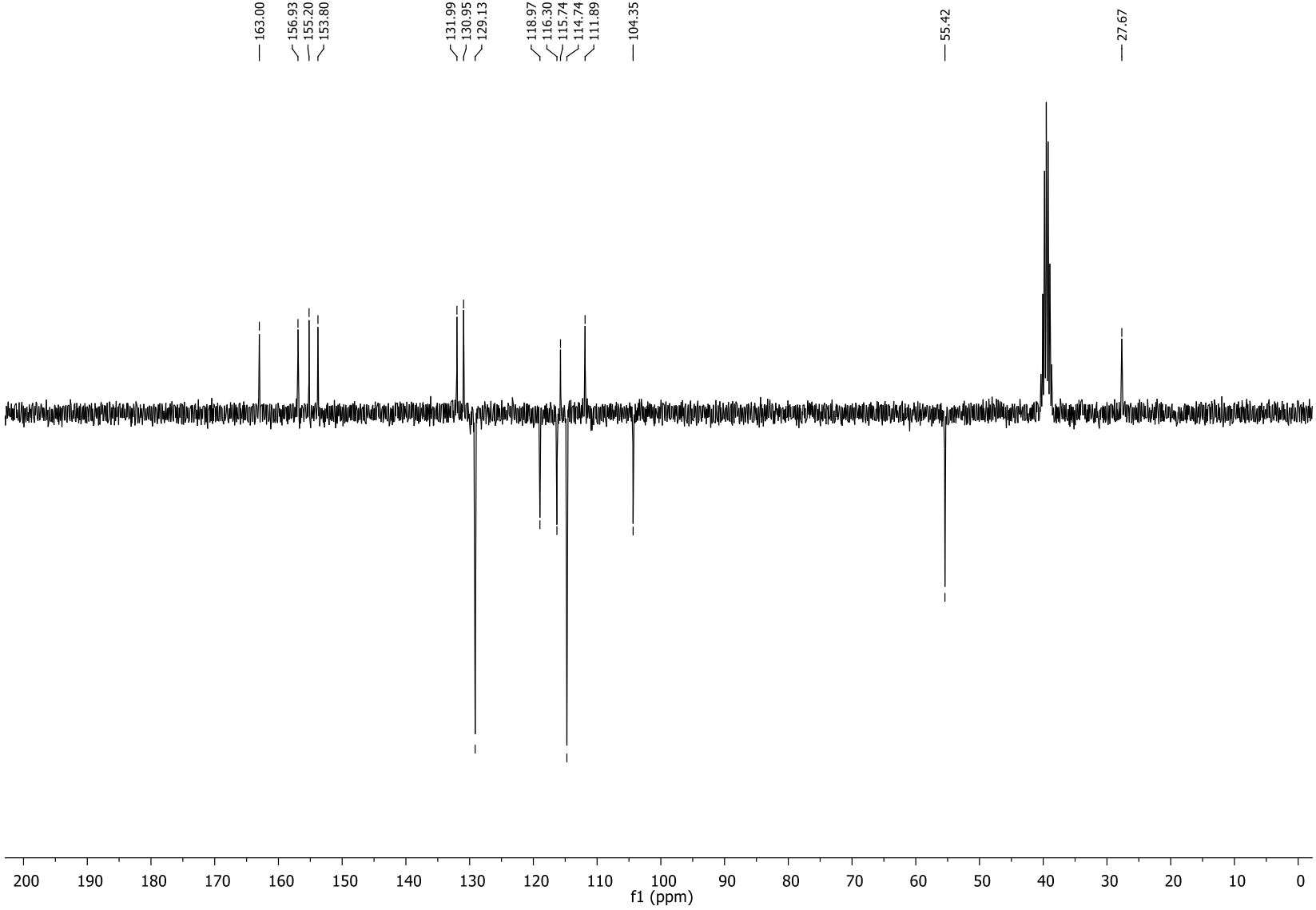
^{13}C NMR spectrum for 4-hydroxy-3-(3-hydroxy-4-methoxybenzyl)-6-methoxyquinolin-2(1H)-one 12i (75 MHz, DMSO-d_6):



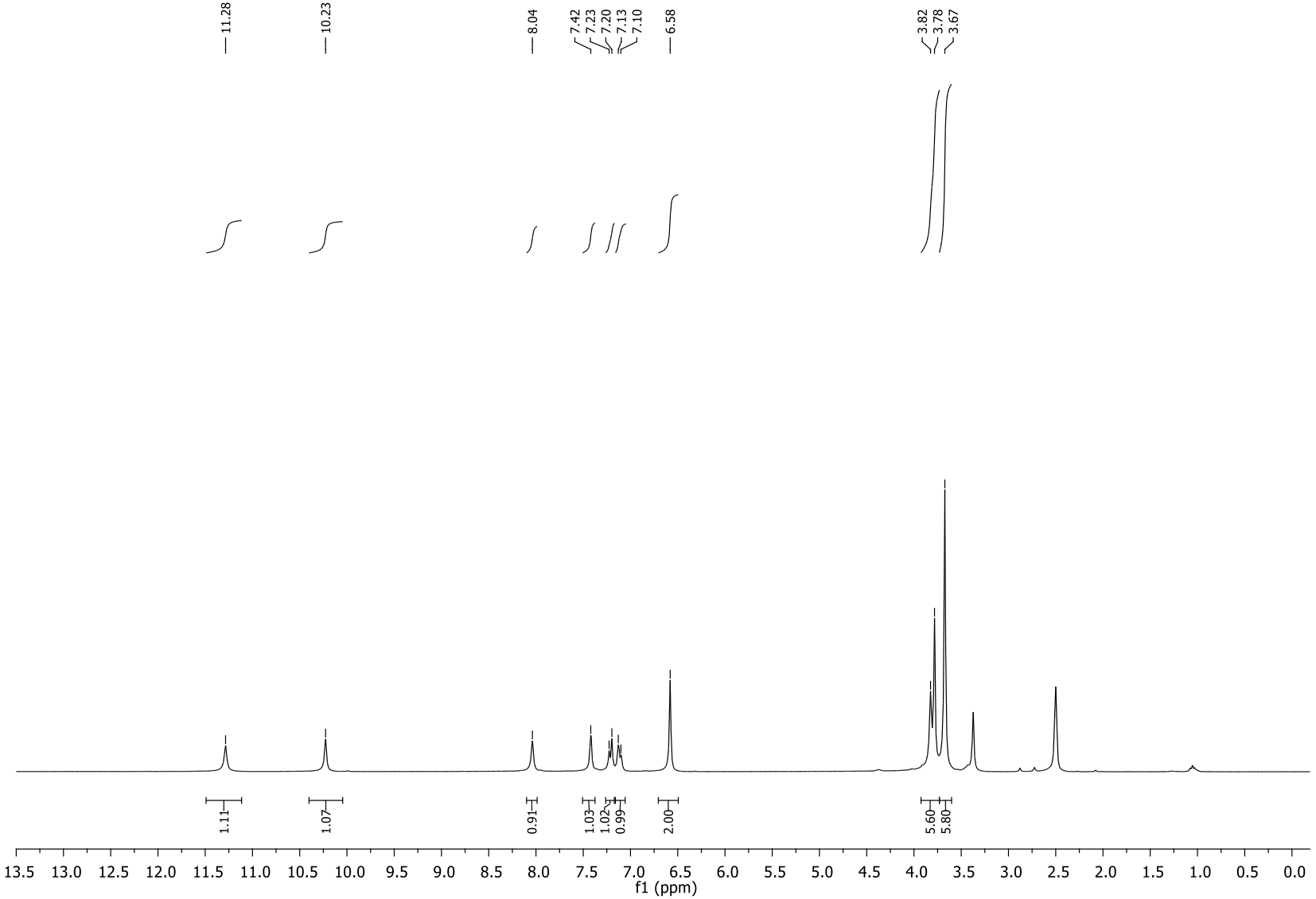
^{1}H NMR spectrum for 4-hydroxy-3-(4-hydroxybenzyl)-6-methoxyquinolin-2(1H)-one 12j (500 MHz, DMSO-d_6):



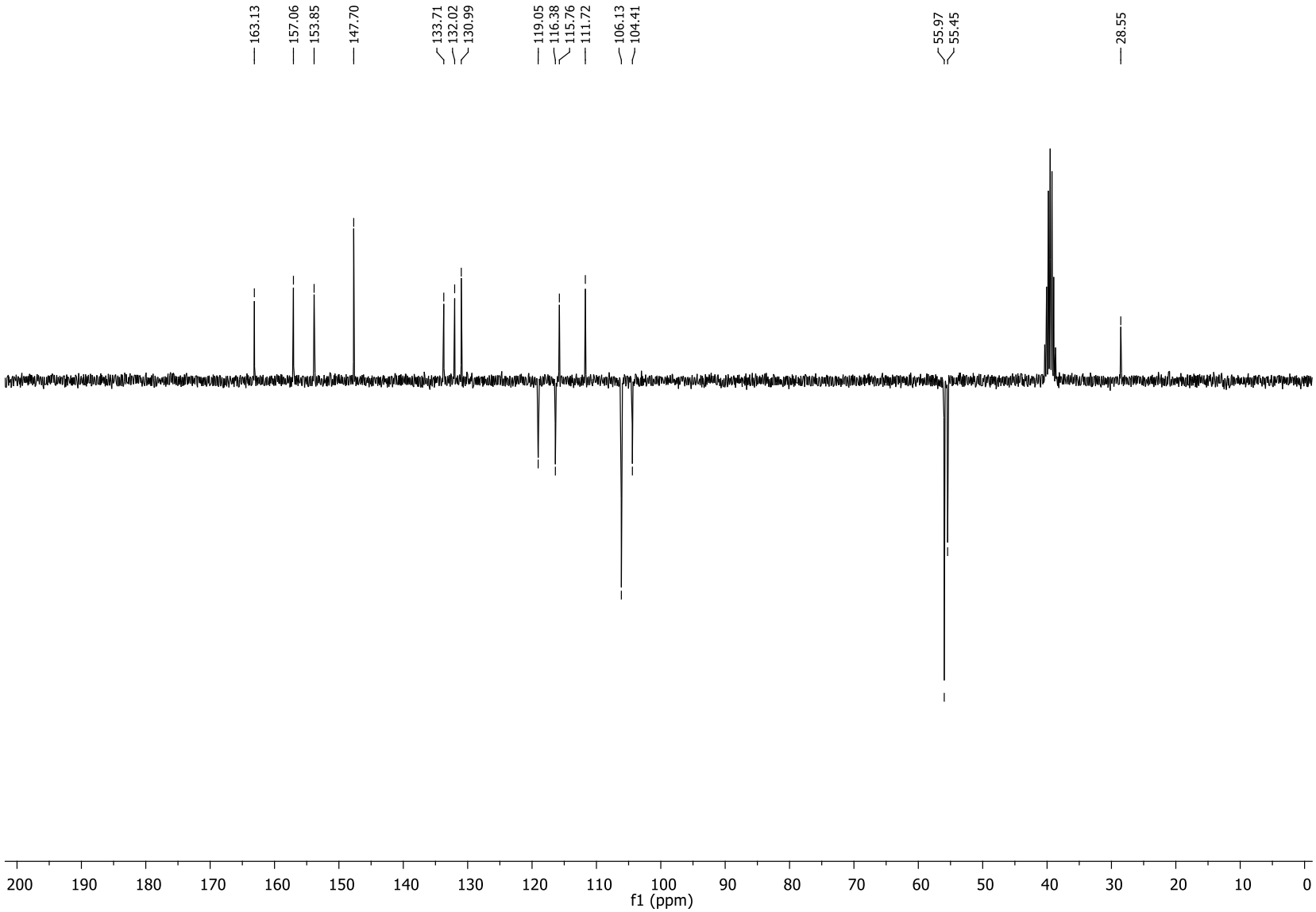
^{13}C NMR spectrum for 4-hydroxy-3-(4-hydroxybenzyl)-6-methoxyquinolin-2(1H)-one 12j (75 MHz, DMSO-d_6):



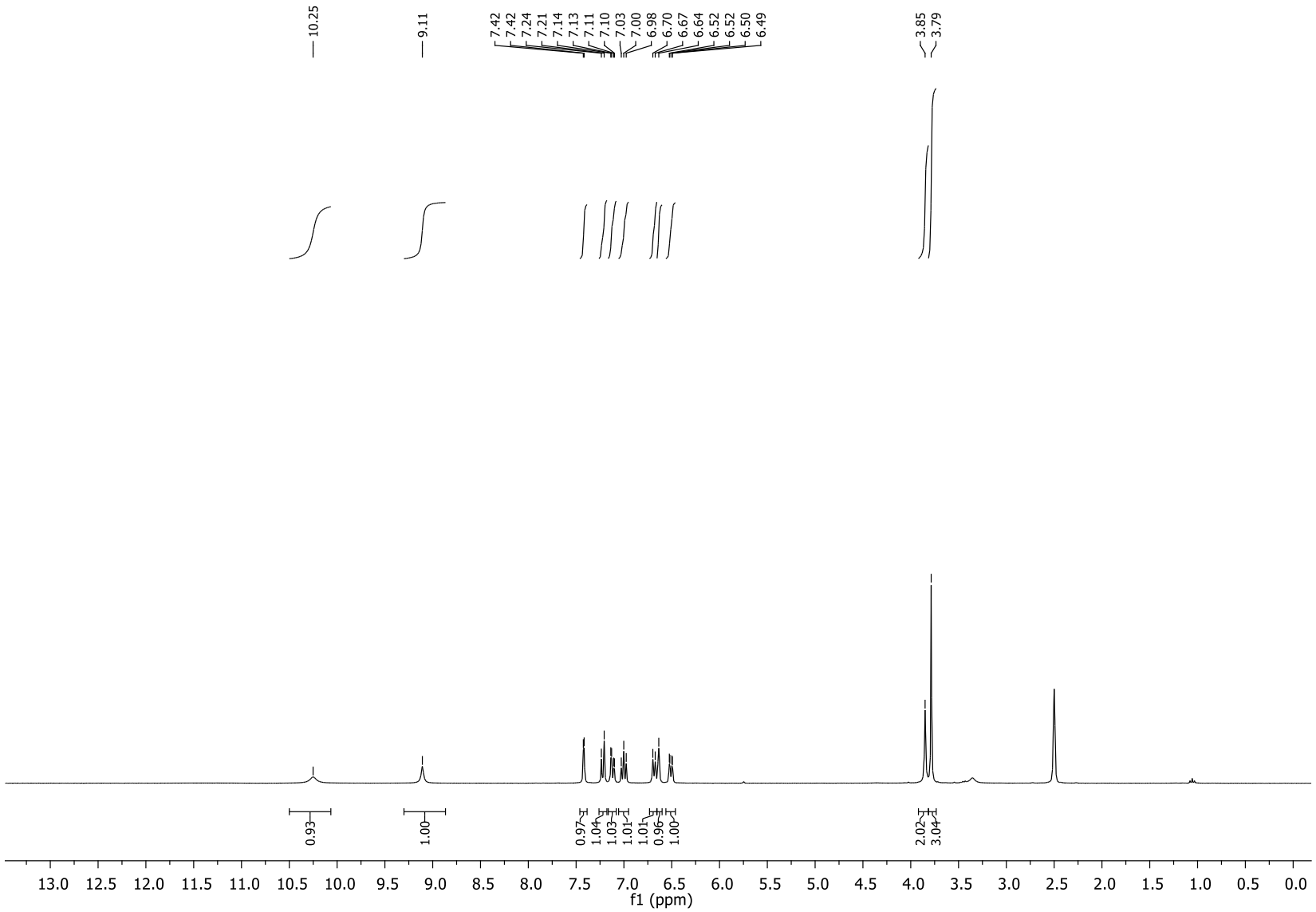
^{1}H NMR spectrum for 4-hydroxy-3-(4-hydroxy-3,5-dimethoxybenzyl)-6-methoxyquinolin-2(1H)-one 12k (300 MHz, DMSO-d_6):



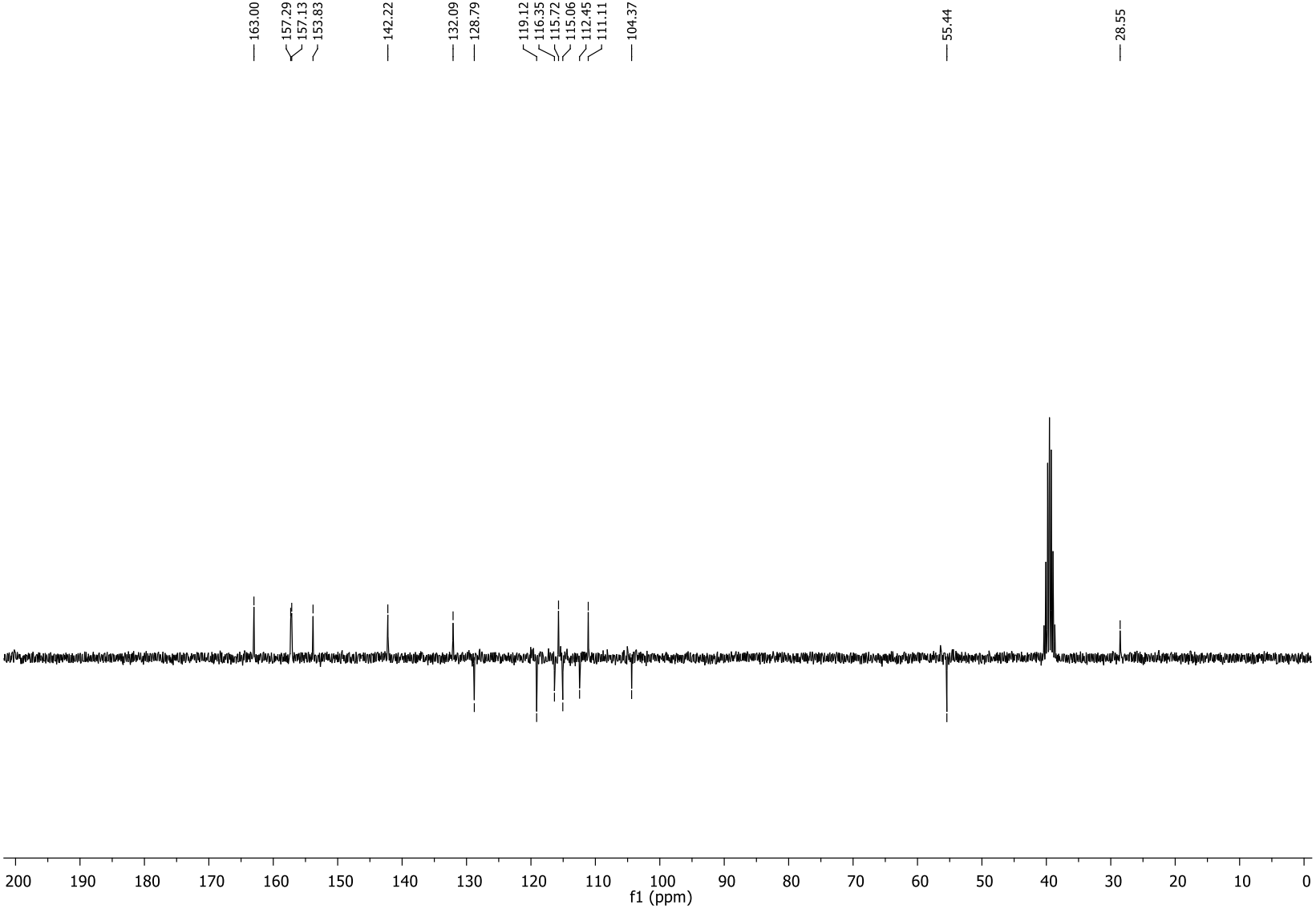
^{13}C NMR spectrum for 4-hydroxy-3-(4-hydroxy-3,5-dimethoxybenzyl)-6-methoxyquinolin-2(1H)-one 12k (75 MHz, DMSO-d_6):



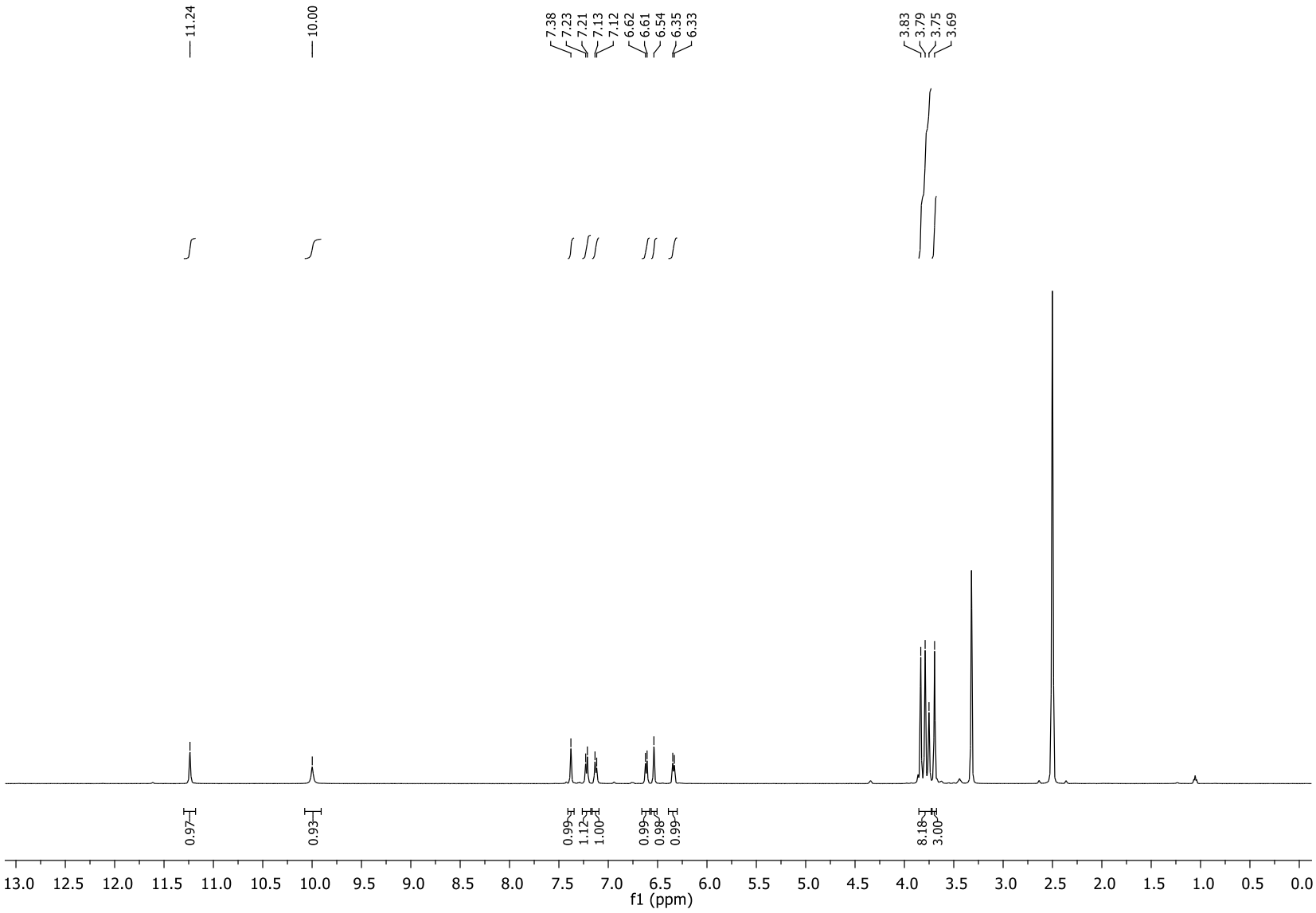
^{1}H NMR spectrum for 4-hydroxy-3-(3-hydroxybenzyl)-6-methoxyquinolin-2(1H)-one 12l (300 MHz, DMSO-d_6):



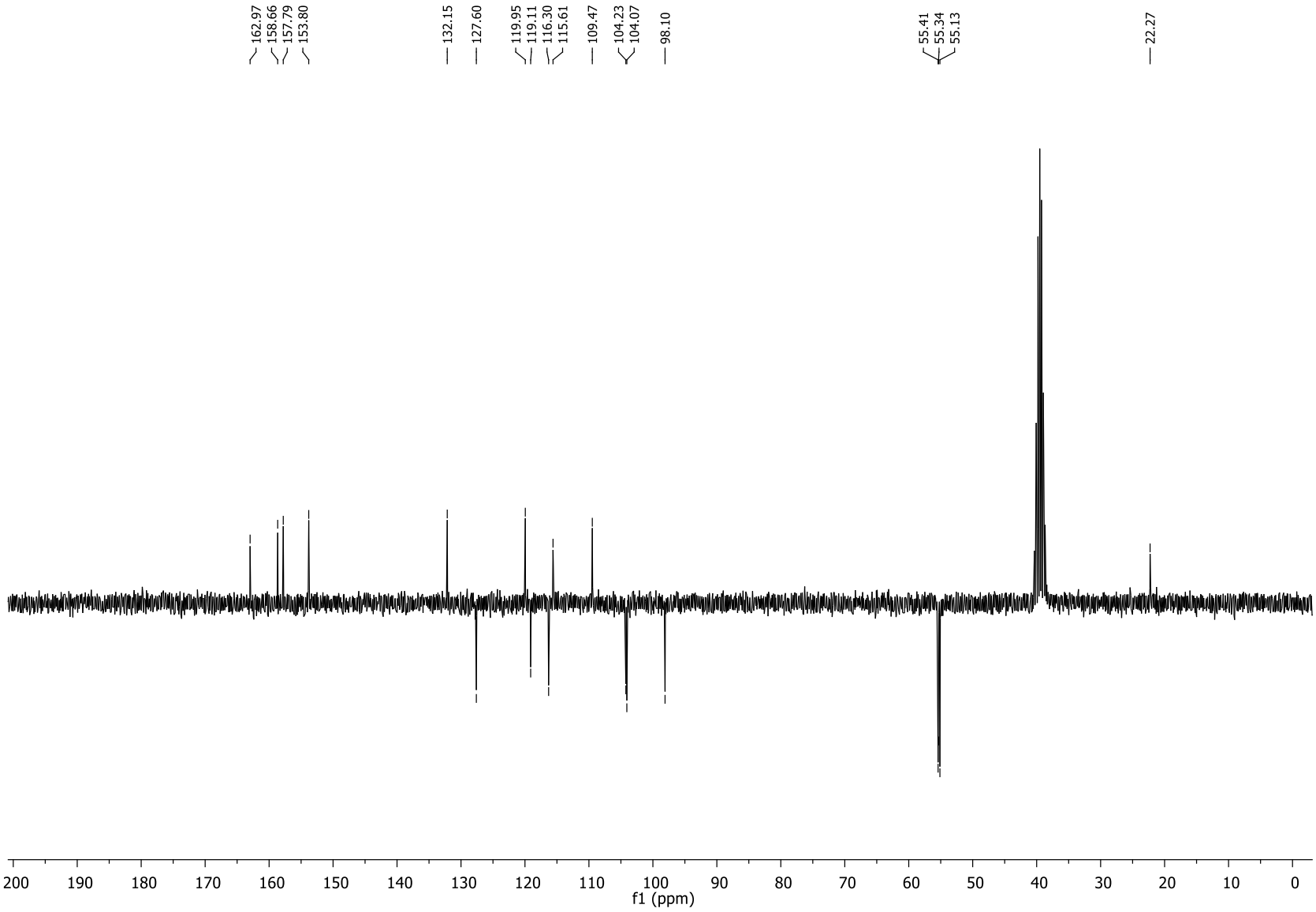
^{13}C NMR spectrum for 4-hydroxy-3-(3-hydroxybenzyl)-6-methoxyquinolin-2(1H)-one 12l (75 MHz, DMSO-d_6):



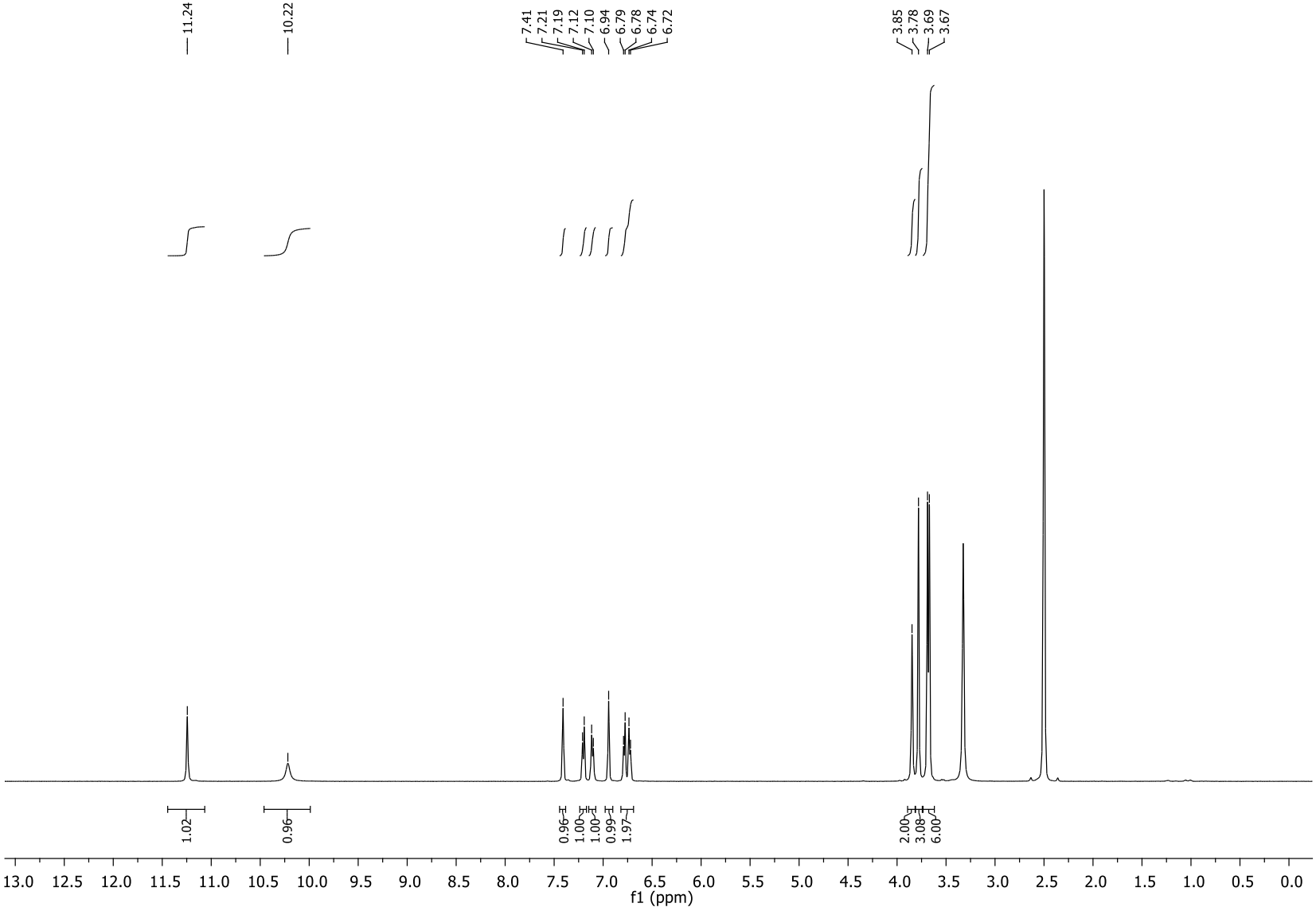
^{1}H NMR spectrum for 3-(2,4-dimethoxybenzyl)-4-hydroxy-6-methoxyquinolin-2(1H)-one 12m (500 MHz, DMSO-d_6):



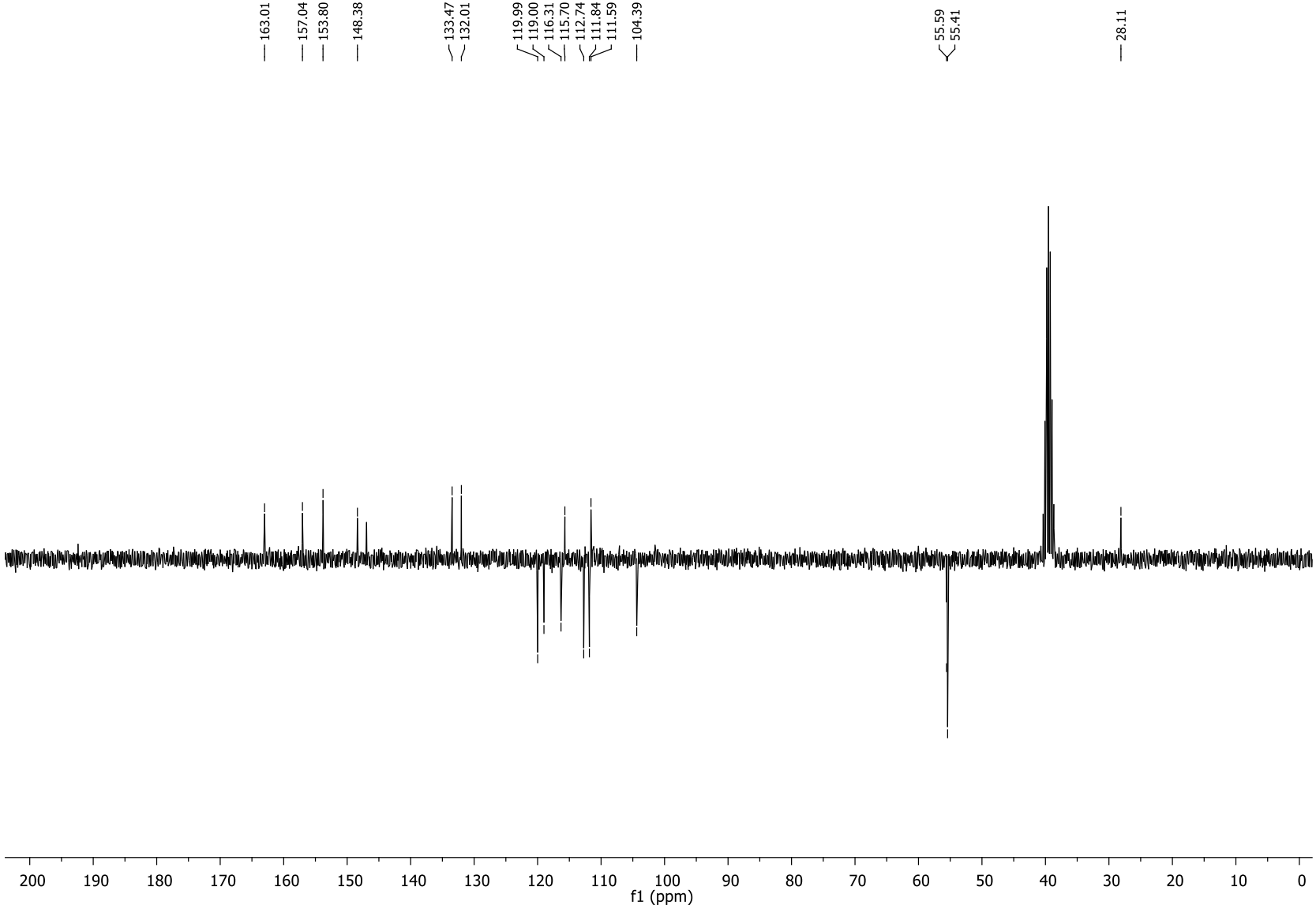
^{13}C NMR spectrum for 3-(2,4-dimethoxybenzyl)-4-hydroxy-6-methoxyquinolin-2(1H)-one 12m (75 MHz, DMSO-d_6):



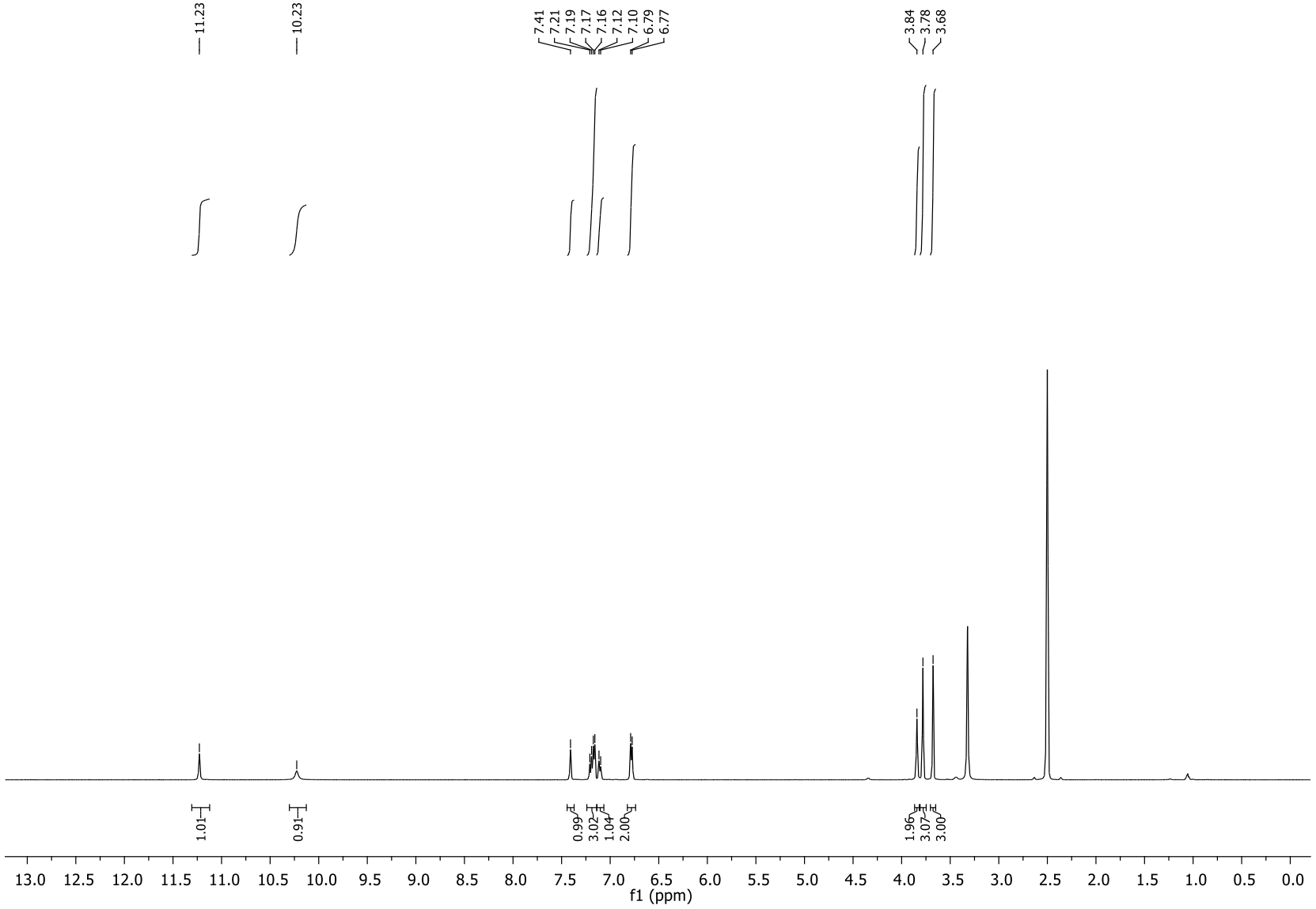
^{1}H NMR spectrum for 3-(3,4-dimethoxybenzyl)-4-hydroxy-6-methoxyquinolin-2(1H)-one 12n (500 MHz, DMSO-d_6):



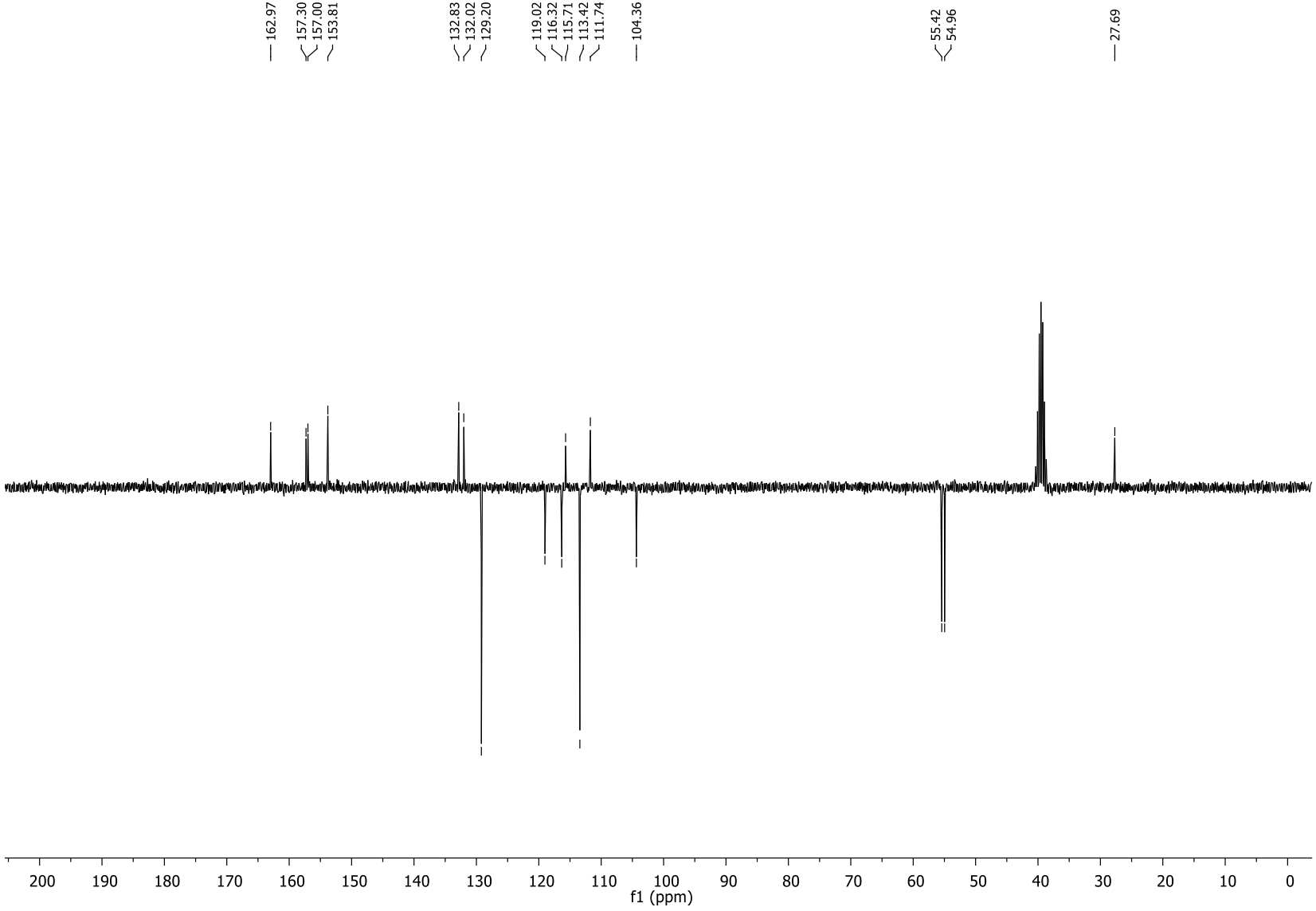
^{13}C NMR spectrum for 3-(3,4-dimethoxybenzyl)-4-hydroxy-6-methoxyquinolin-2(1H)-one 12n (75 MHz, DMSO-d_6):



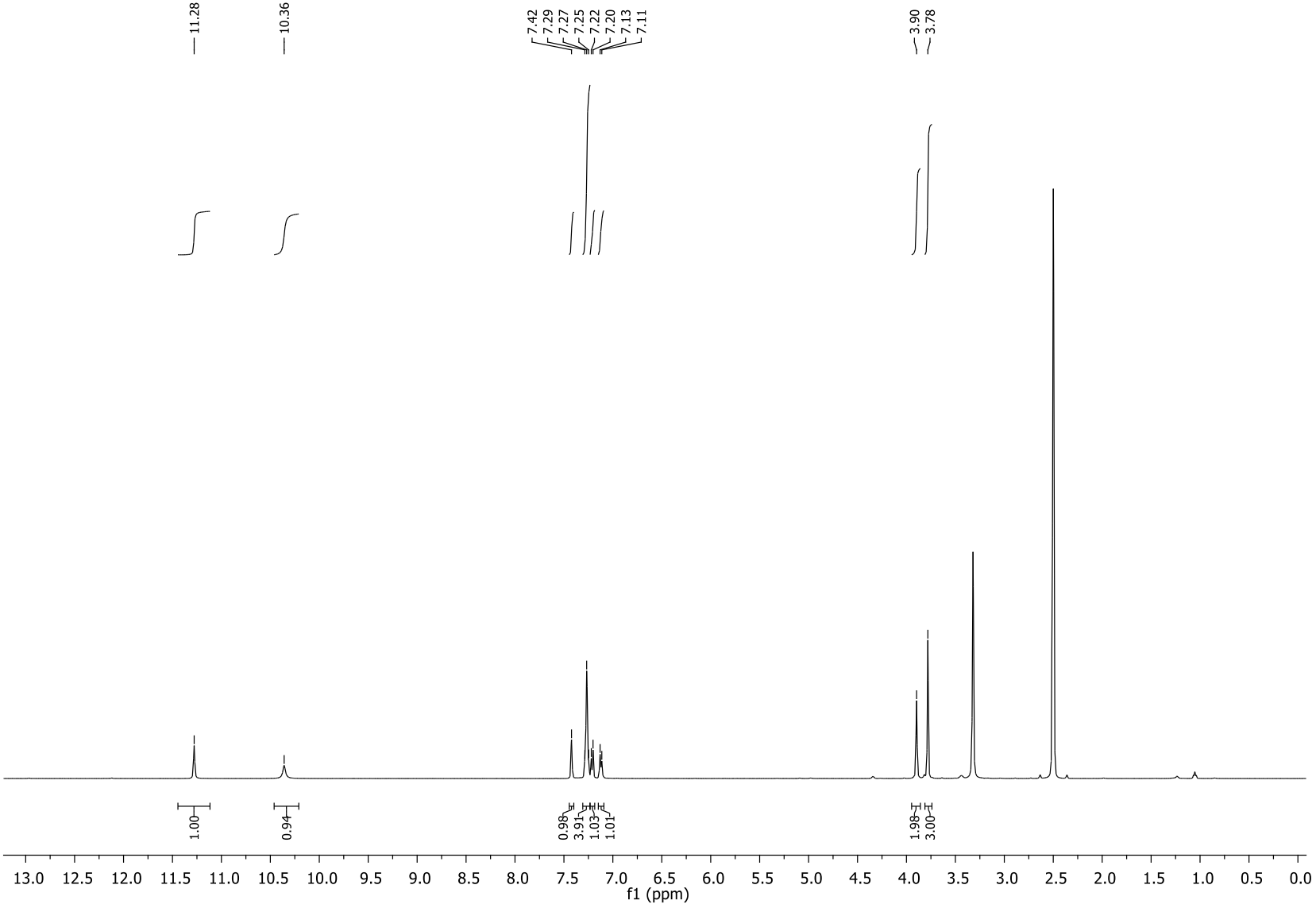
^{1}H NMR spectrum for 4-hydroxy-6-methoxy-3-(4-methoxybenzyl)quinolin-2(1H)-one 12o (500 MHz, DMSO-d_6):



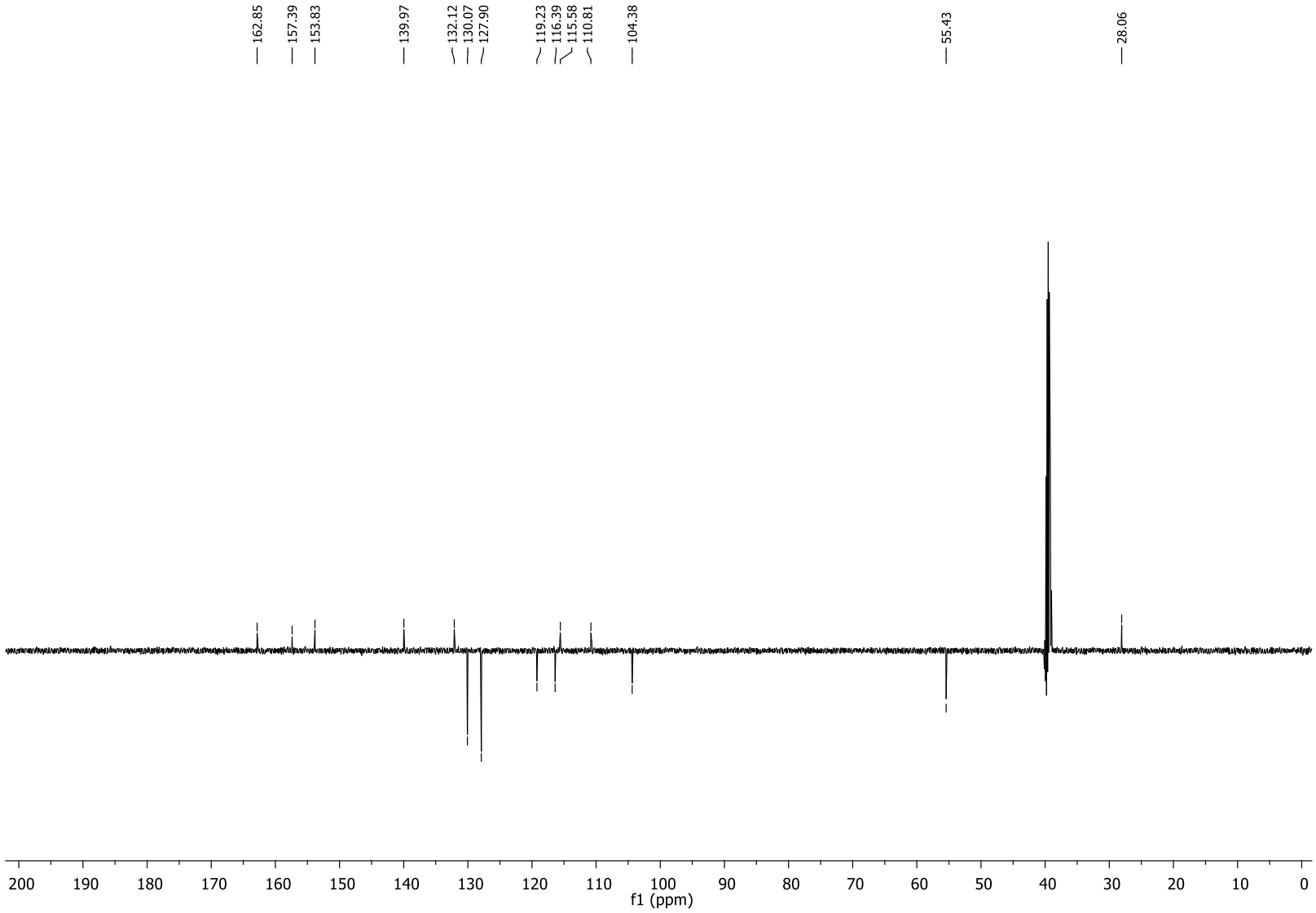
^{13}C NMR spectrum for 4-hydroxy-6-methoxy-3-(4-methoxybenzyl)quinolin-2(1H)-one 12o (75 MHz, DMSO-d_6):



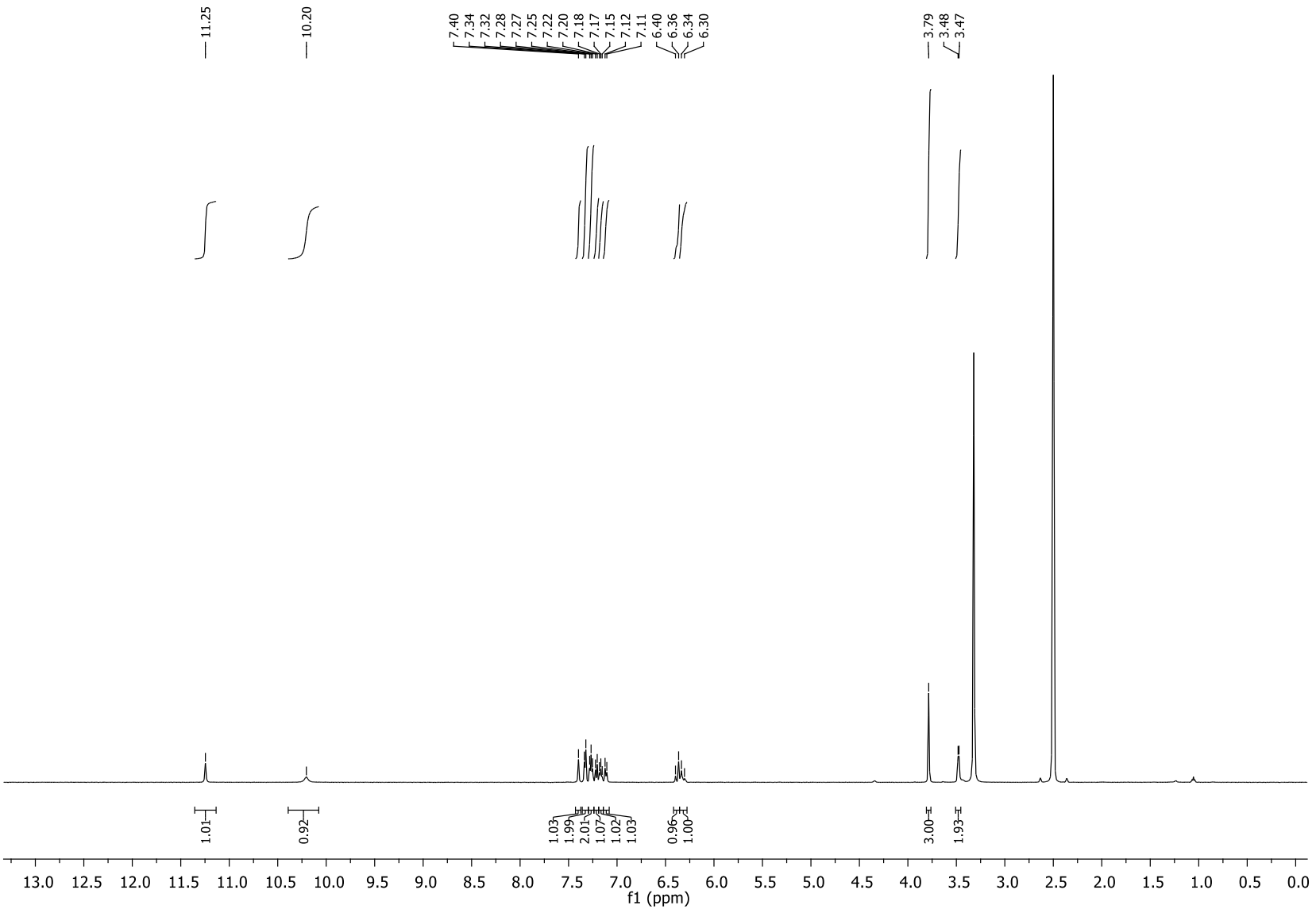
^{1}H NMR spectrum for 3-(4-chlorobenzyl)-4-hydroxy-6-methoxyquinolin-2(1H)-one 12p (500 MHz, DMSO-d_6):



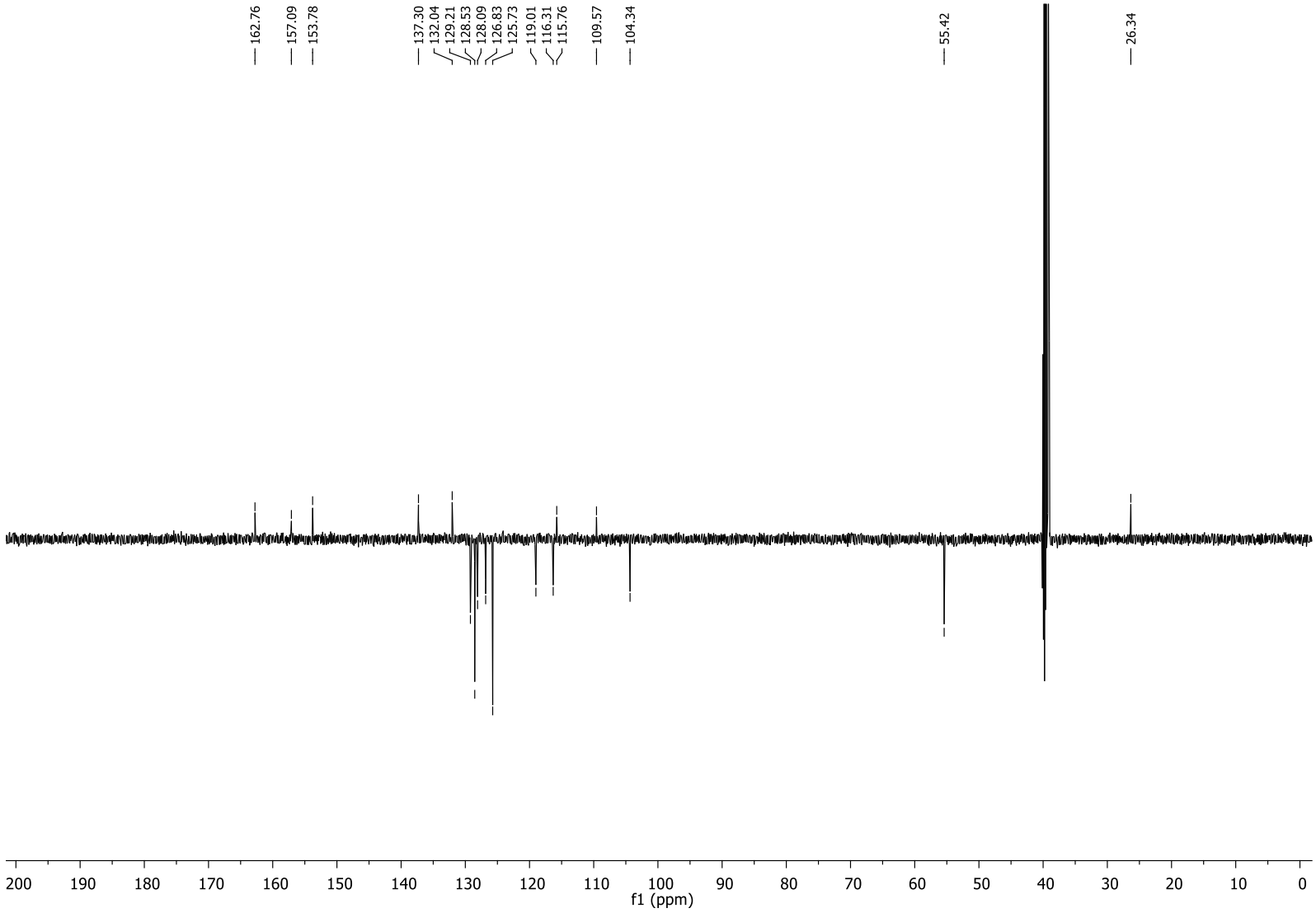
^{13}C NMR spectrum for 3-(4-chlorobenzyl)-4-hydroxy-6-methoxyquinolin-2(1H)-one 12p (126 MHz, DMSO-d_6):



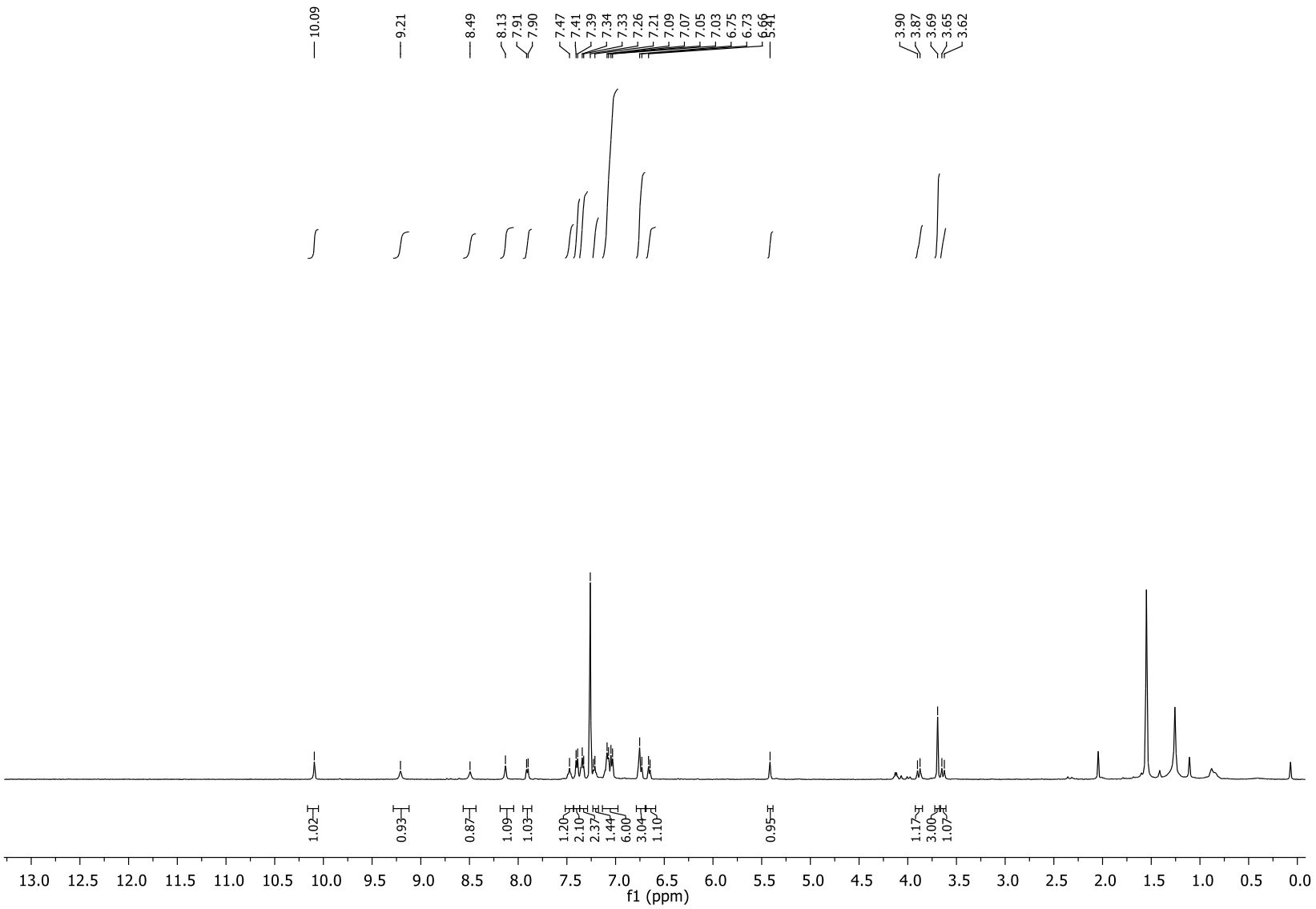
^{1}H NMR spectrum for 3-cinnamyl-4-hydroxy-6-methoxyquinolin-2(1H)-one 12r (500 MHz, DMSO-d_6):



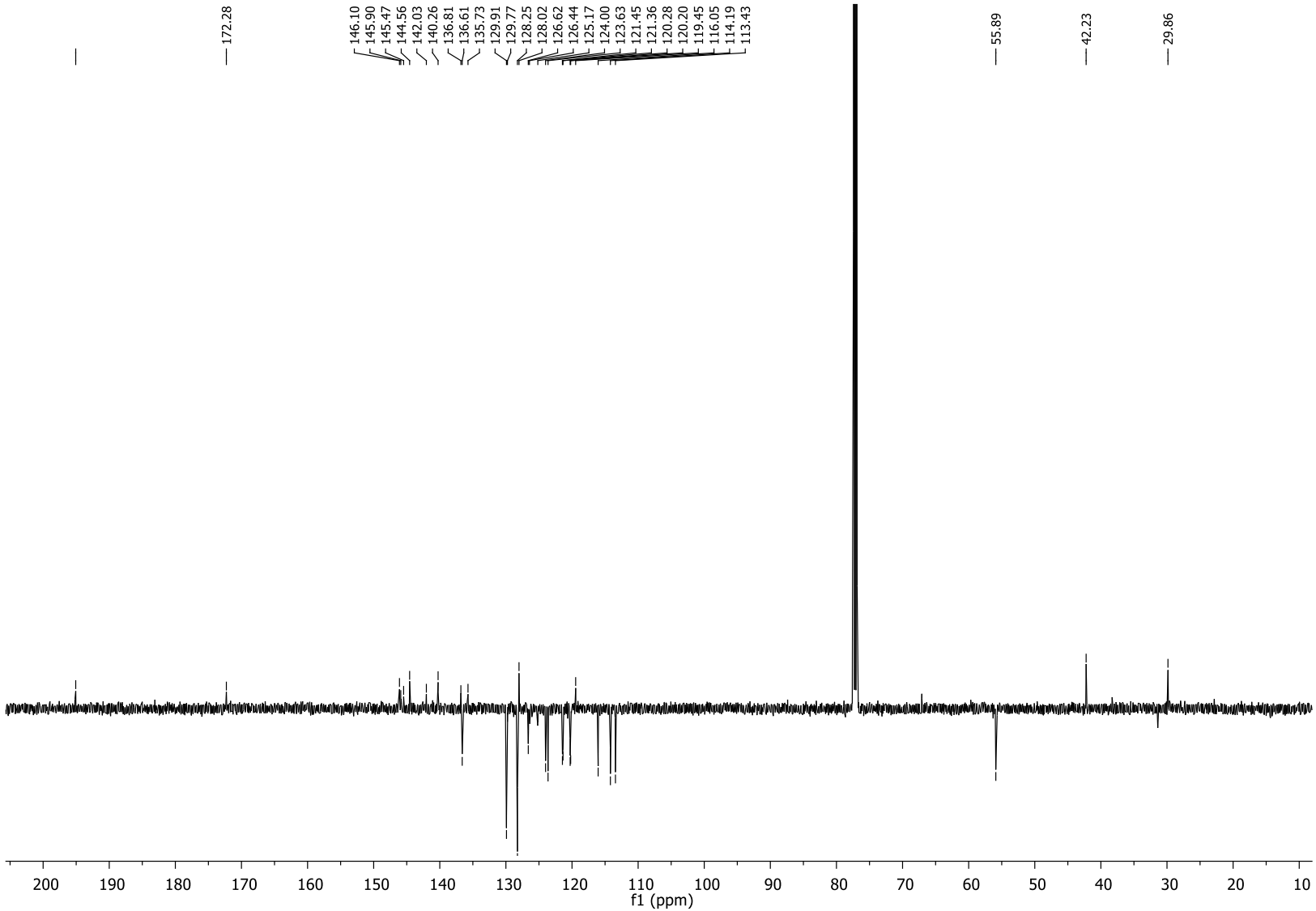
^{13}C NMR spectrum for 3-cinnamyl-4-hydroxy-6-methoxyquinolin-2(1H)-one 12r (126 MHz, DMSO-d_6):



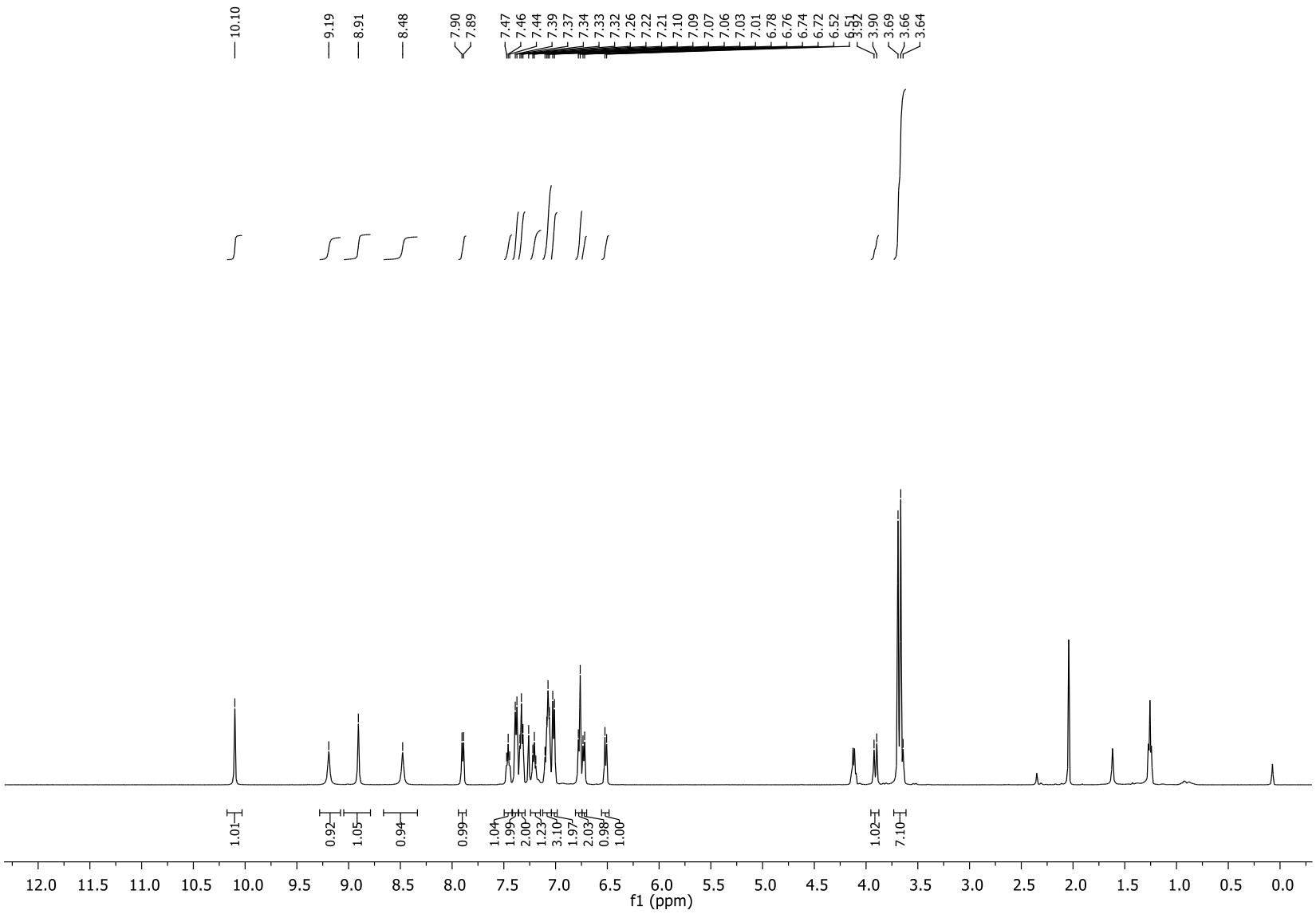
^{1}H NMR spectrum for 3-(4-hydroxy-3-methoxybenzyl)-3-{4-[1-phenyl-2-(2,4,6-trinitrophenyl)hydrazinyl]phenyl}quinoline-2,4(1H,3H)-dione 18a (500 MHz, $CDCl_3$):



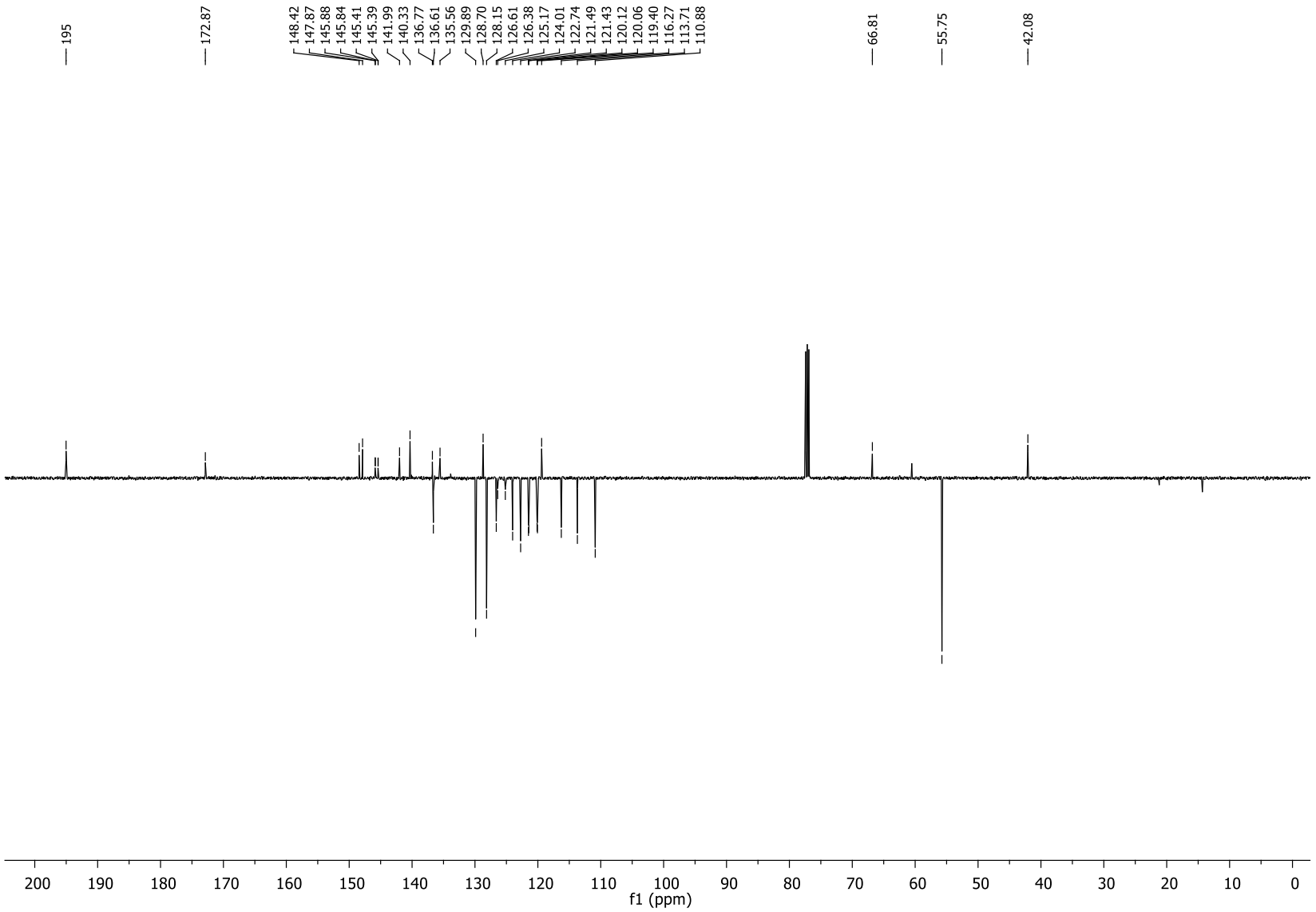
^{13}C NMR spectrum for 3-(4-hydroxy-3-methoxybenzyl)-3-{4-[1-phenyl-2-(2,4,6-trinitrophenyl)hydrazinyl]phenyl}quinoline-2,4(1H,3H)-dione 18a (126 MHz, $CDCl_3$):



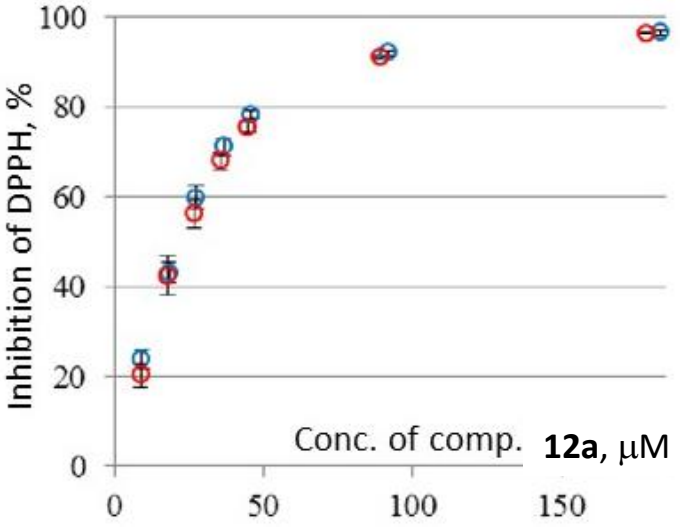
^{1}H NMR spectrum for 3-(3,4-dimethoxybenzyl)-3-{4-[1-phenyl-2-(2,4,6-trinitrophenyl)hydrazinyl]phenyl}quinoline-2,4(1H,3H)-dione 18b (500 MHz, $CDCl_3$):

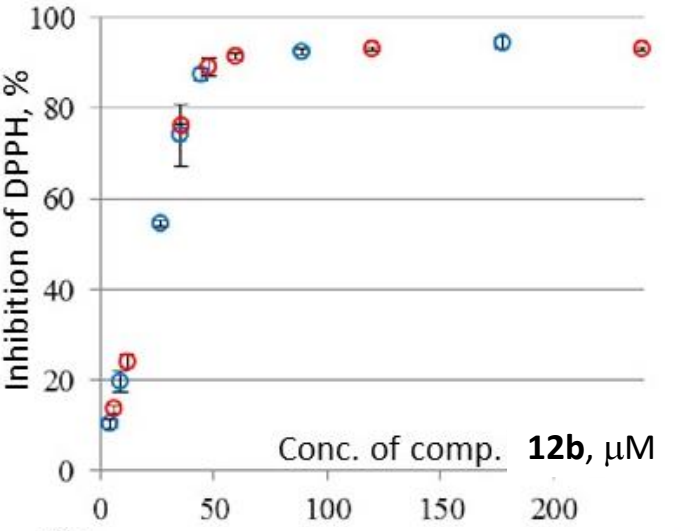


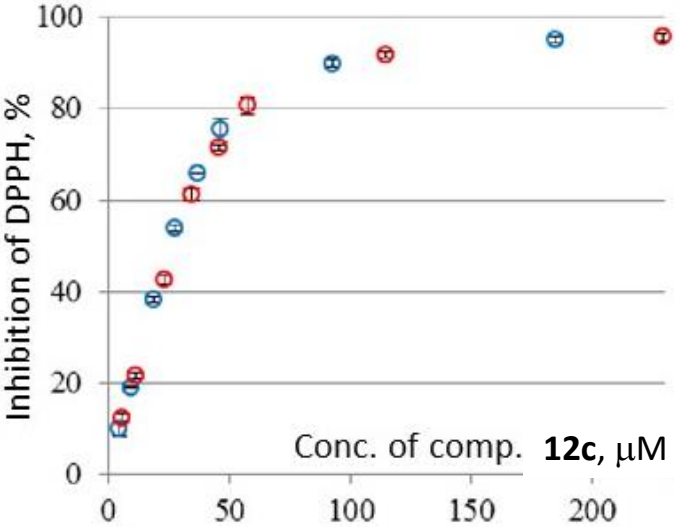
^{13}C NMR spectrum for 3-(3,4-dimethoxybenzyl)-3-{4-[1-phenyl-2-(2,4,6-trinitrophenyl)hydrazinyl]phenyl}quinoline-2,4(1H,3H)-dione 18b (126 MHz, $CDCl_3$):



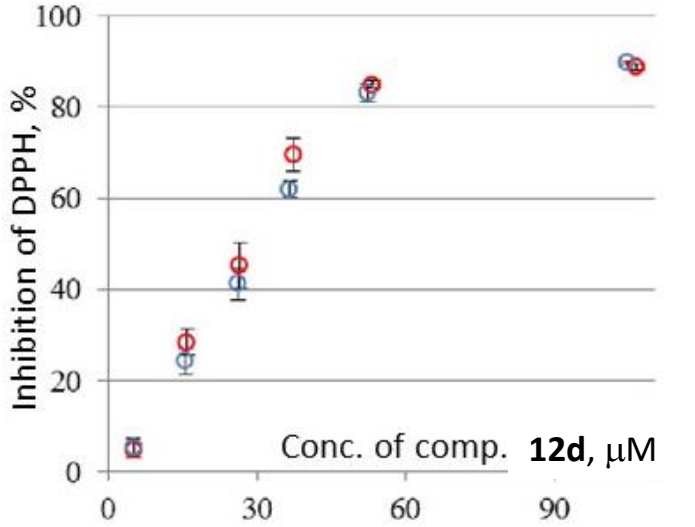
9. INHIBITION OF DPPH DEPENDING ON THE CONCENTRATION OF THE COMPOUND 12[2]

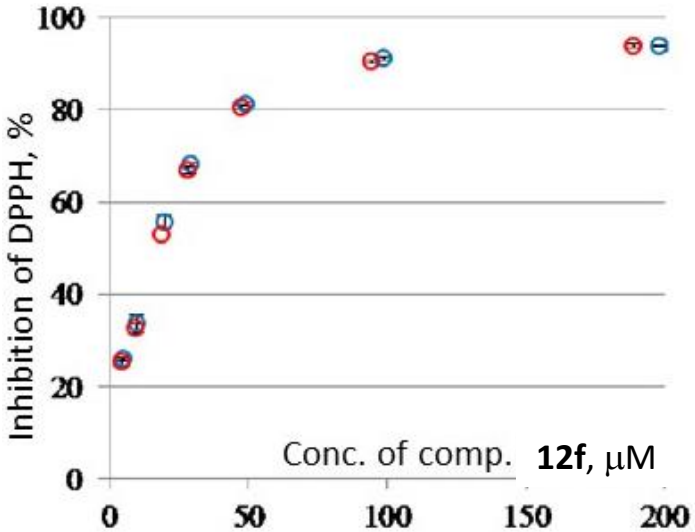


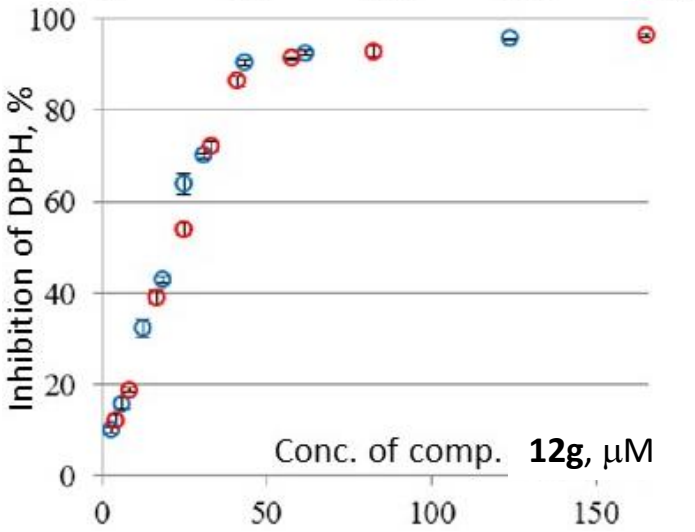


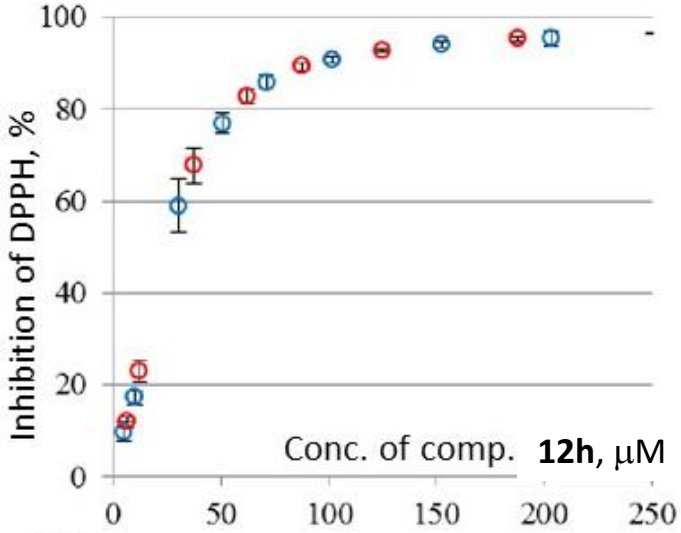


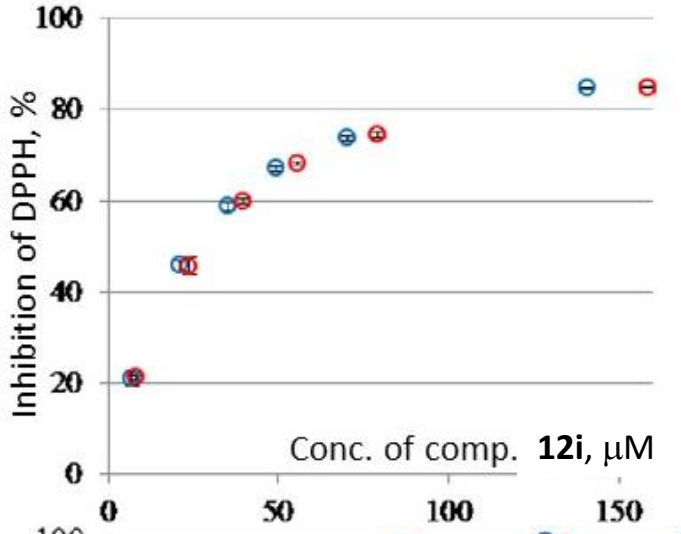
[2] Points in red and blue corresponds to results of two parallel independent experiments

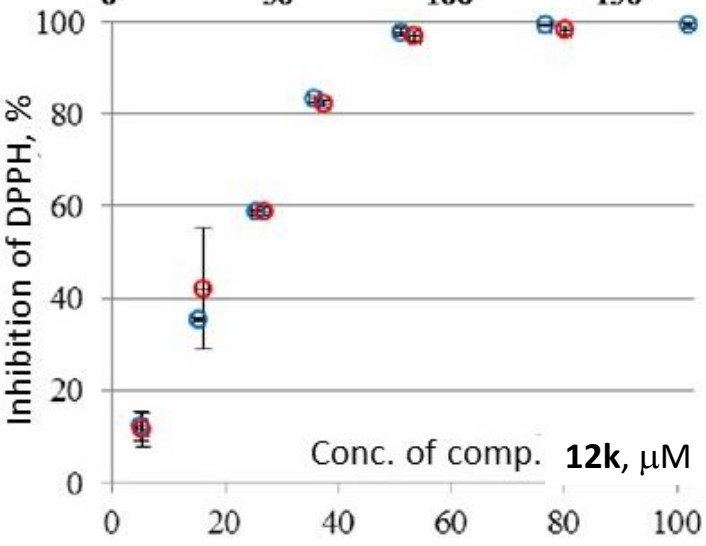

Inhibition of DPPH, %
100
80
60
40
20
0
0
30
60
90
Conc. of comp. 12d, μM


Inhibition of DPPH, %
100
80
60
40
20
0
0
50
100
150
200
Conc. of comp. 12f, μM

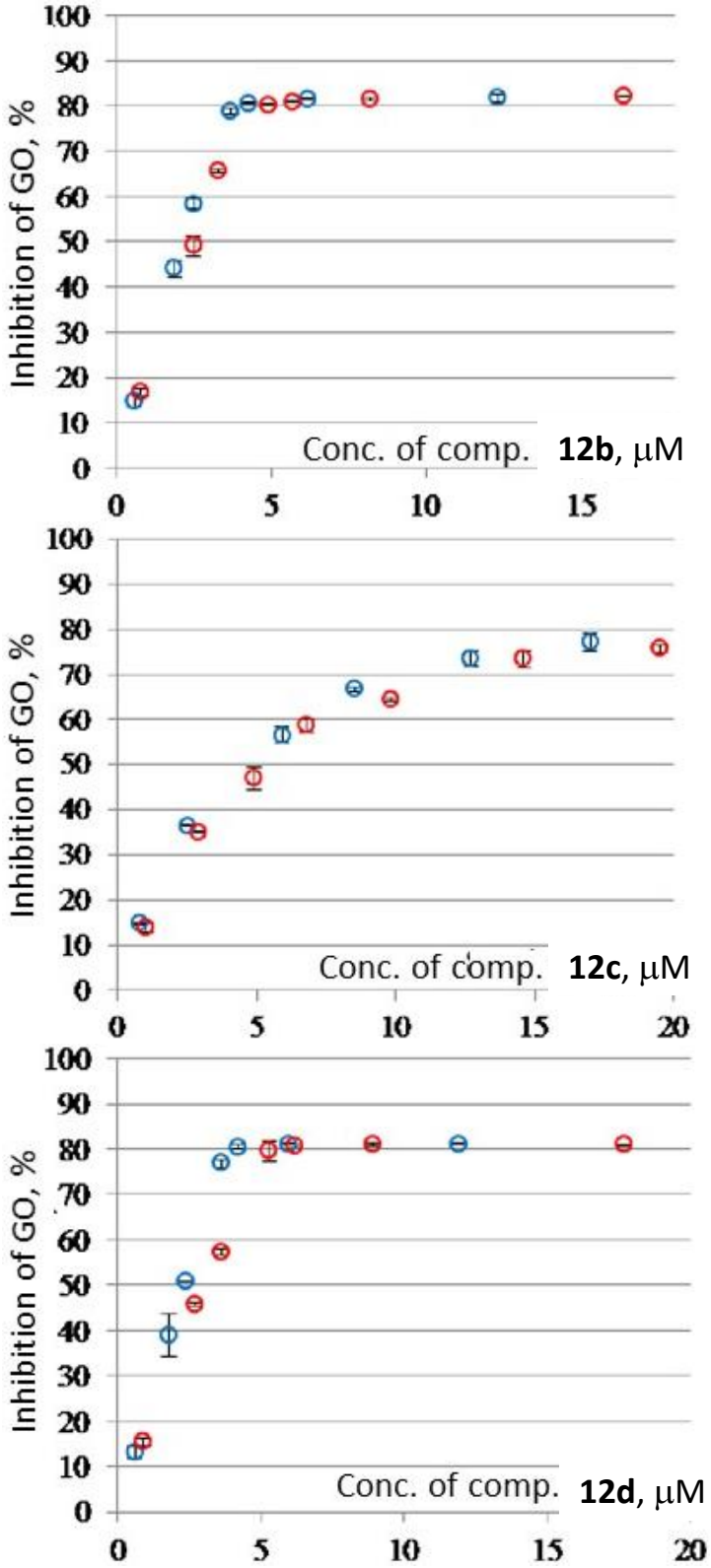

Inhibition of DPPH, %
100
80
60
40
20
0
0
50
100
150
Conc. of comp. 12g, μM


Inhibition of DPPH, %
Conc. of comp. 12h, μM

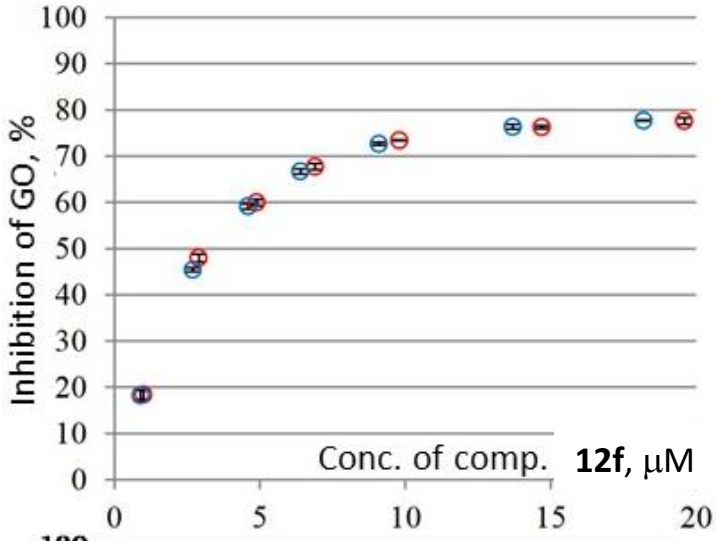

Inhibition of DPPH, %
Conc. of comp. 12i, μM


Inhibition of DPPH, %
Conc. of comp. 12k, μM

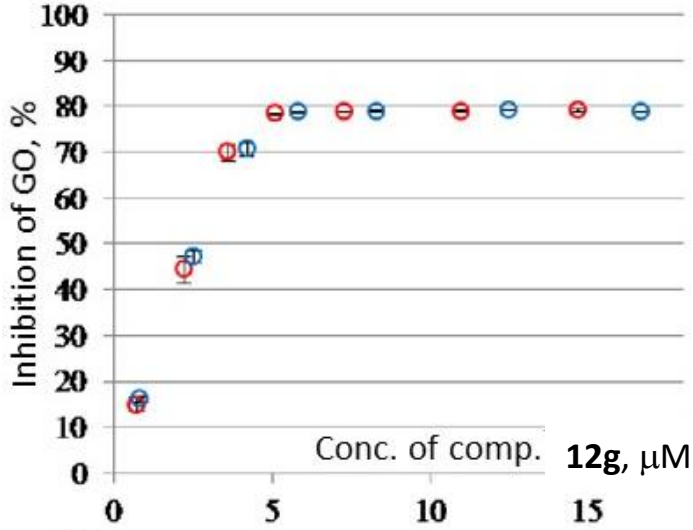
10.INHIBITION OF GO DEPENDING ON THE CONCENTRATION OF THE COMPOUND 12[3]



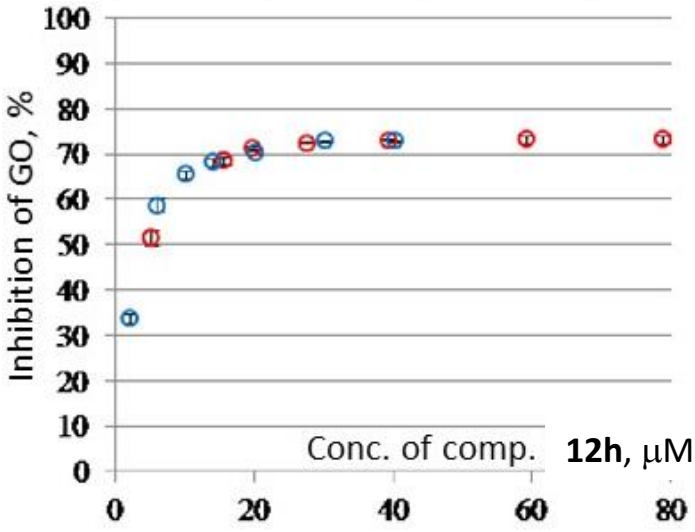
[3] [3] Points in red and blue corresponds to results of two parallel independent experiments



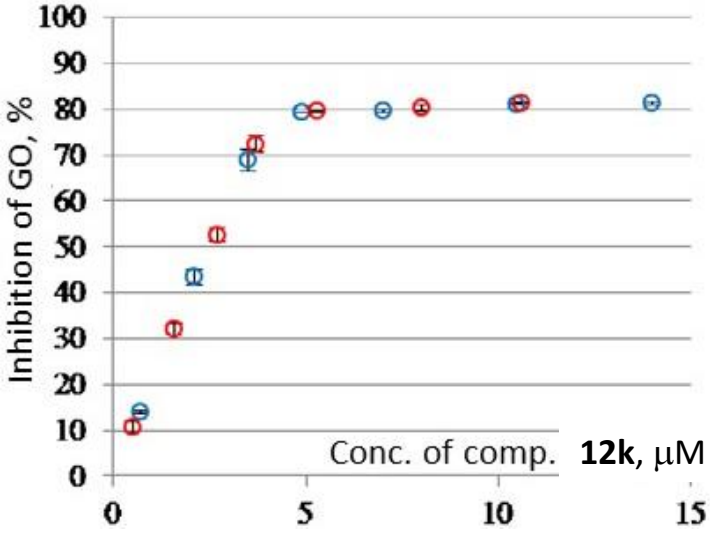
12f, μM



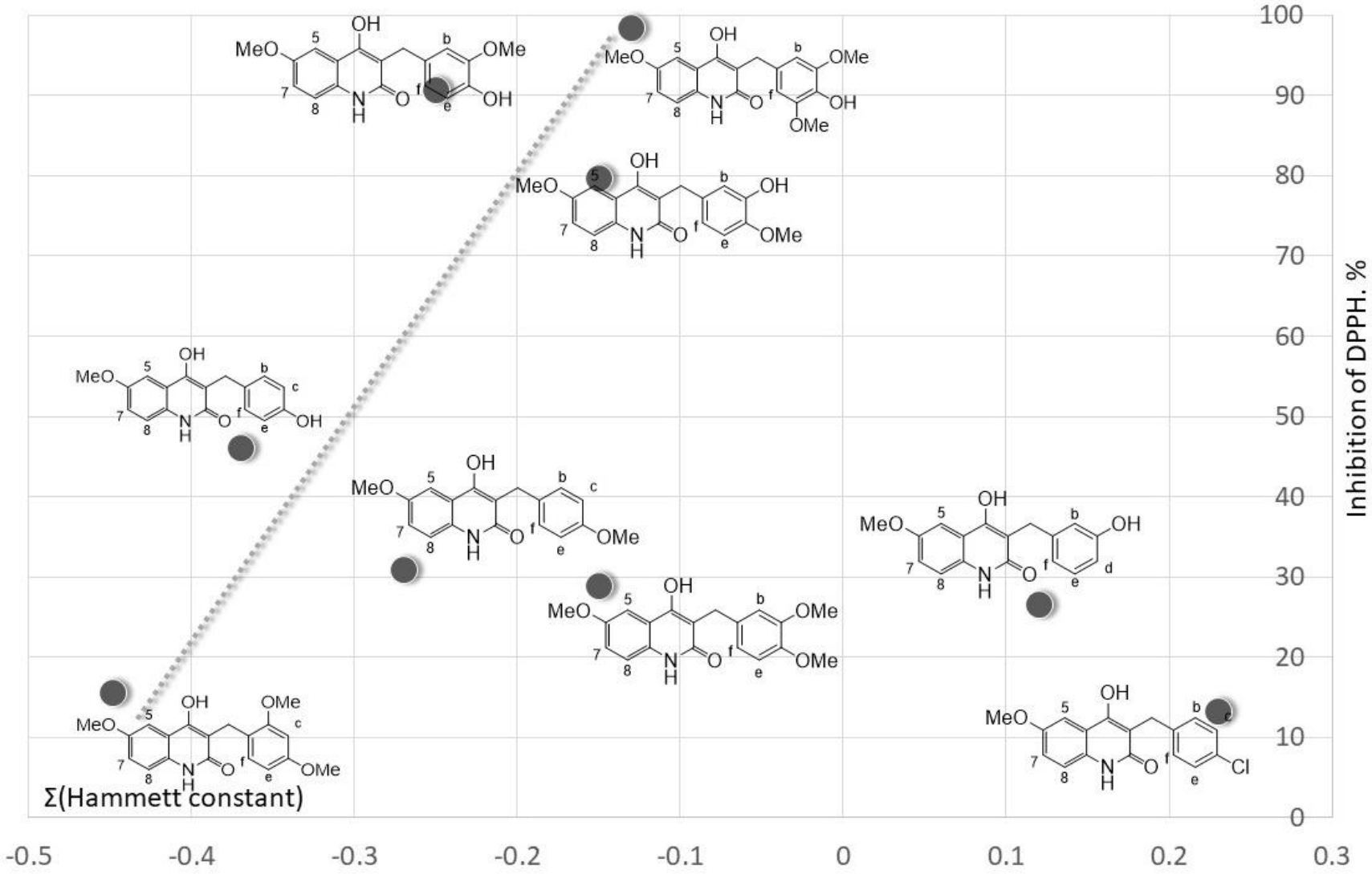
12g, μM



12h, μM

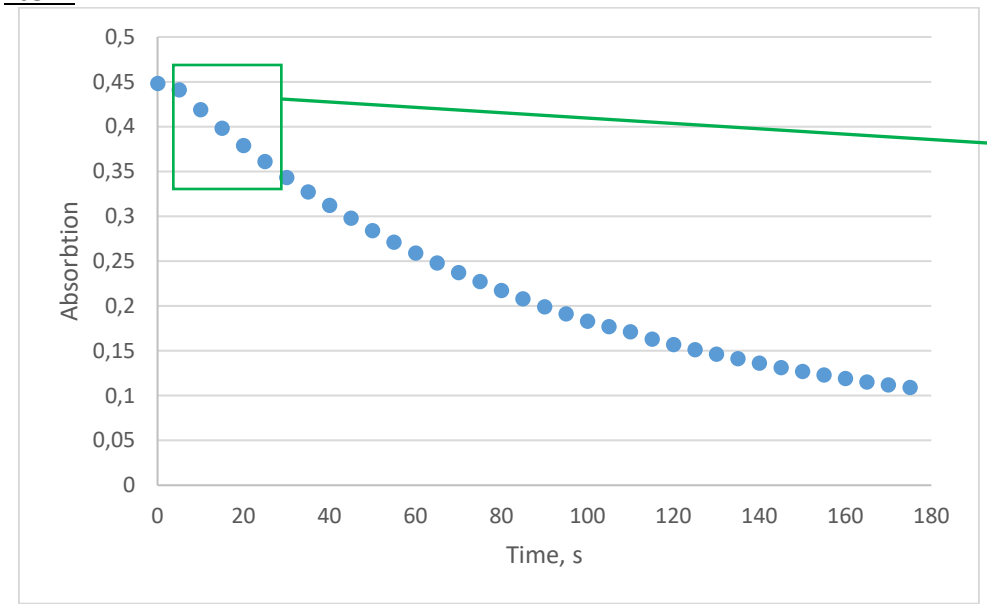

Inhibition of GO, %
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
Conc. of comp. 12k, μM

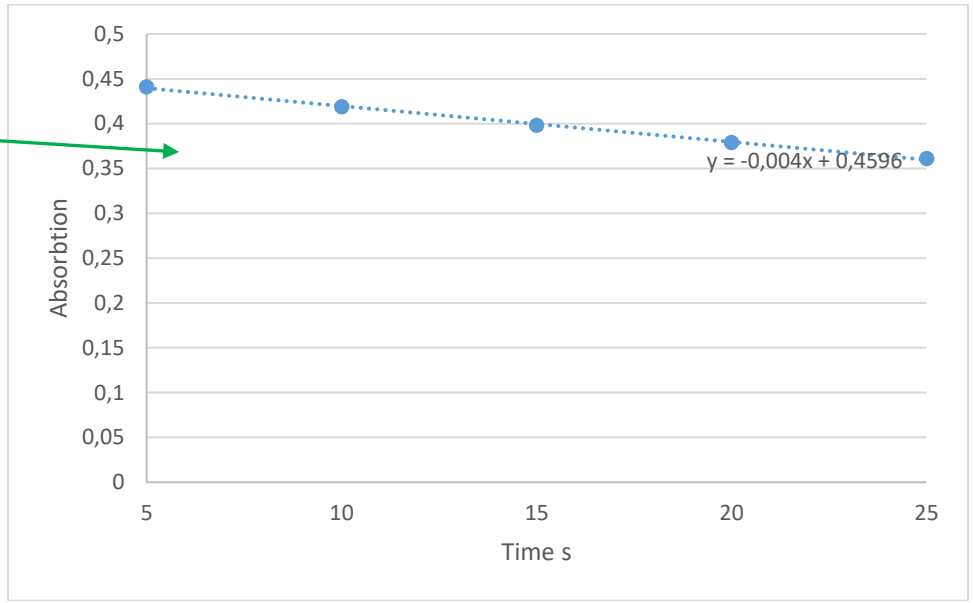
11. CORRELATION BETWEEN THE INHIBITION OF DPPH AND SUBSTITUENT ELECTRONIC EFFECTS

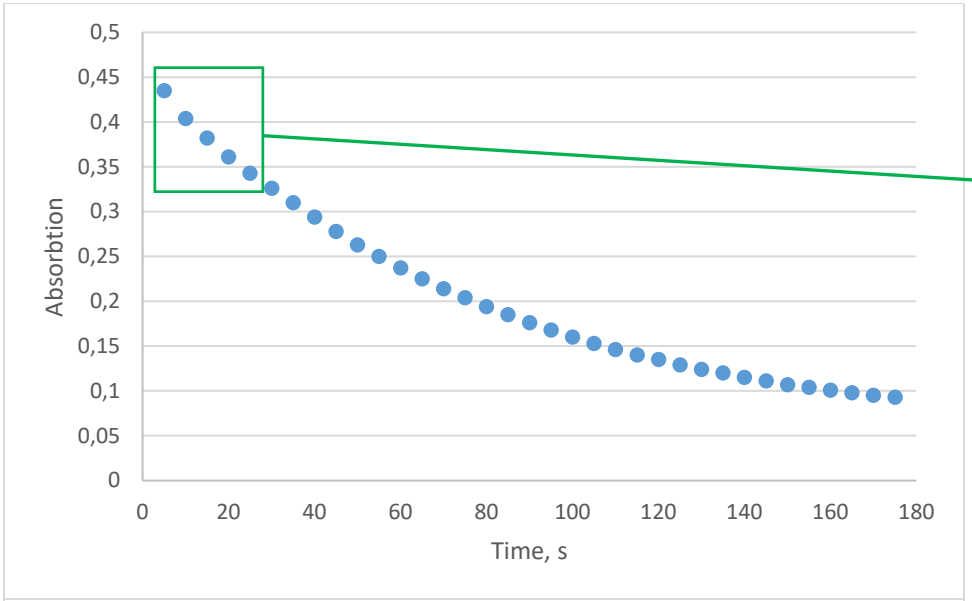


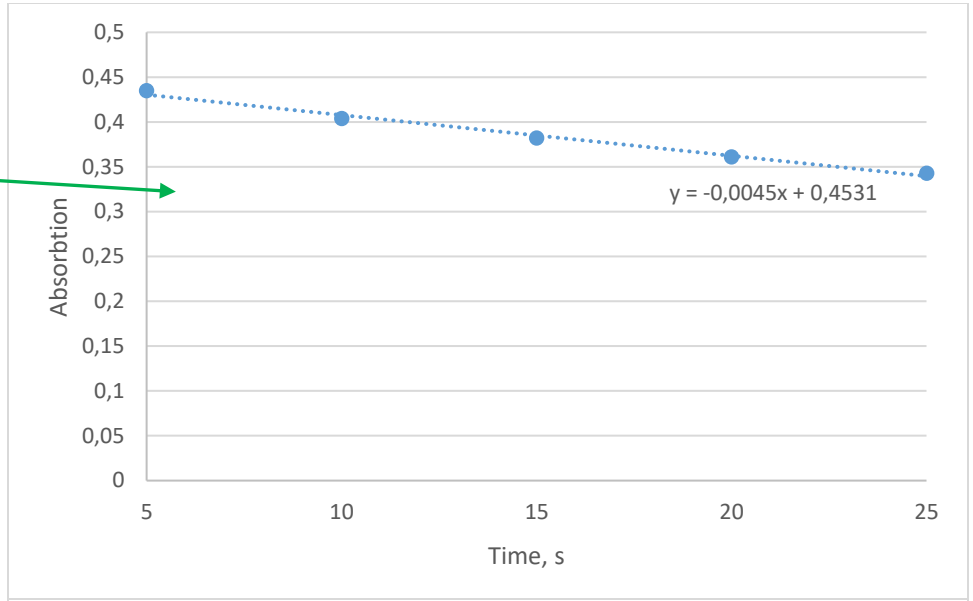
12.KINETIC CURVES FOR THE REACTION BETWEEN DPPH AND COMPOUND 12c (IN VARIOUS SOLVENTS)

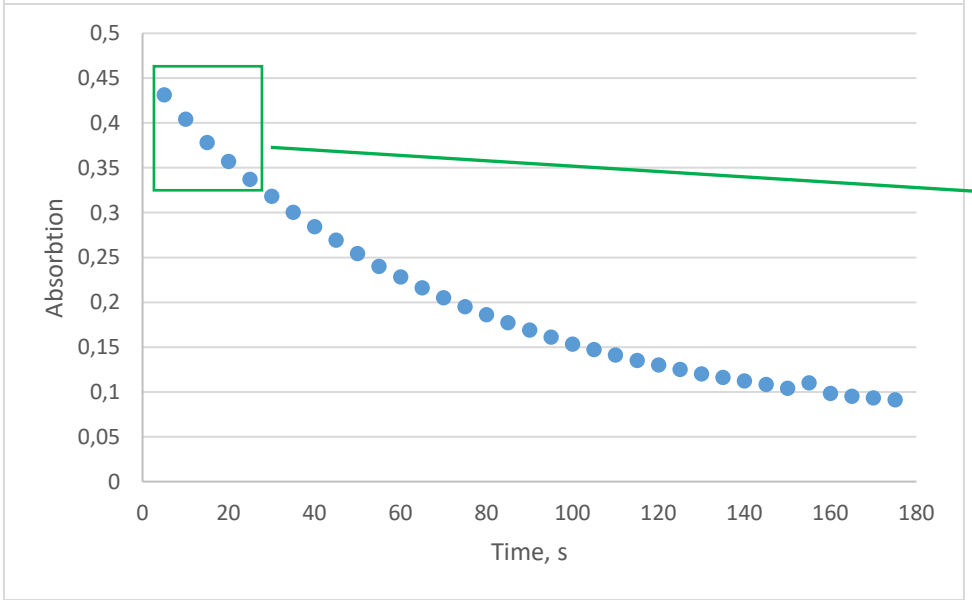
EtOH:

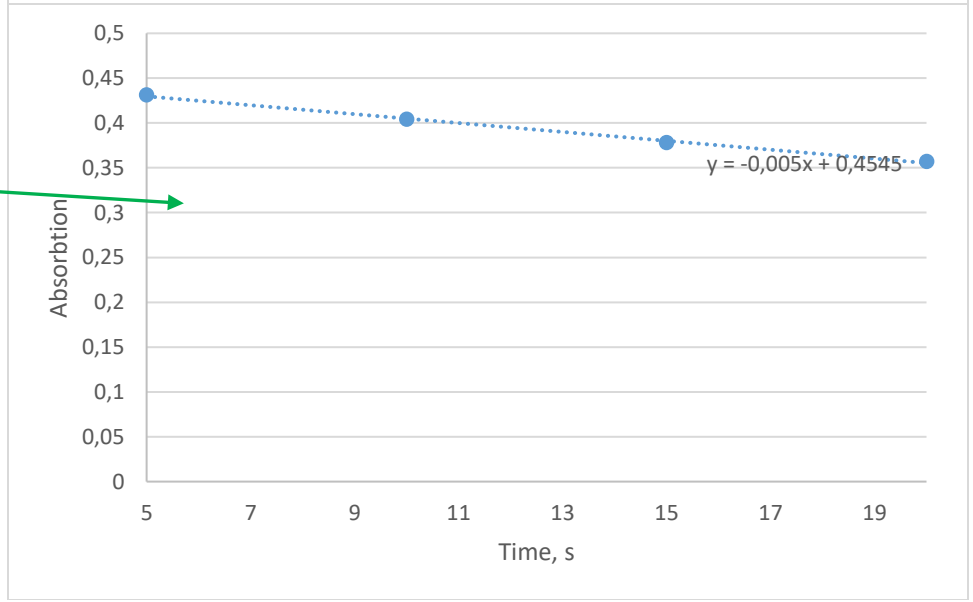




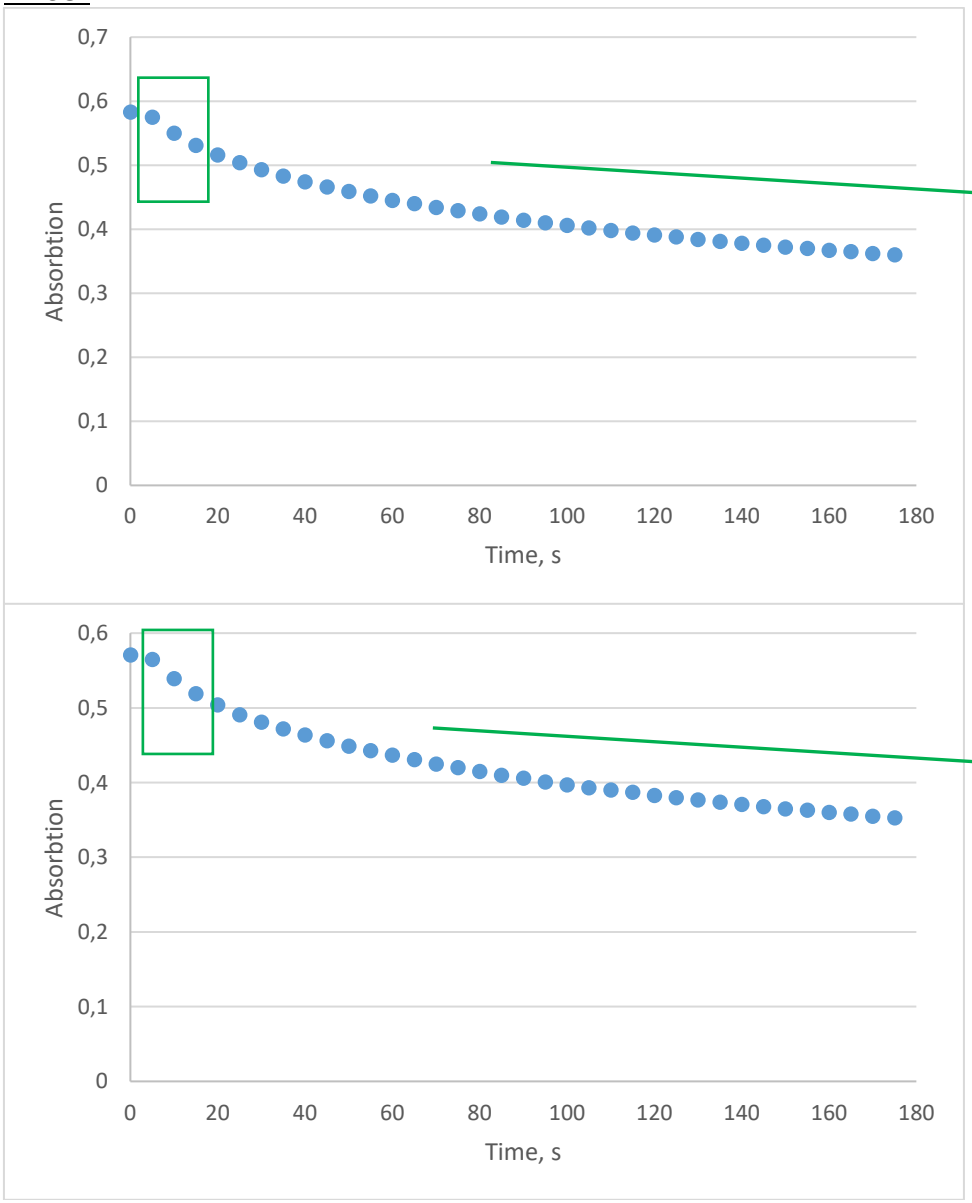

Absorbtion
Time, s

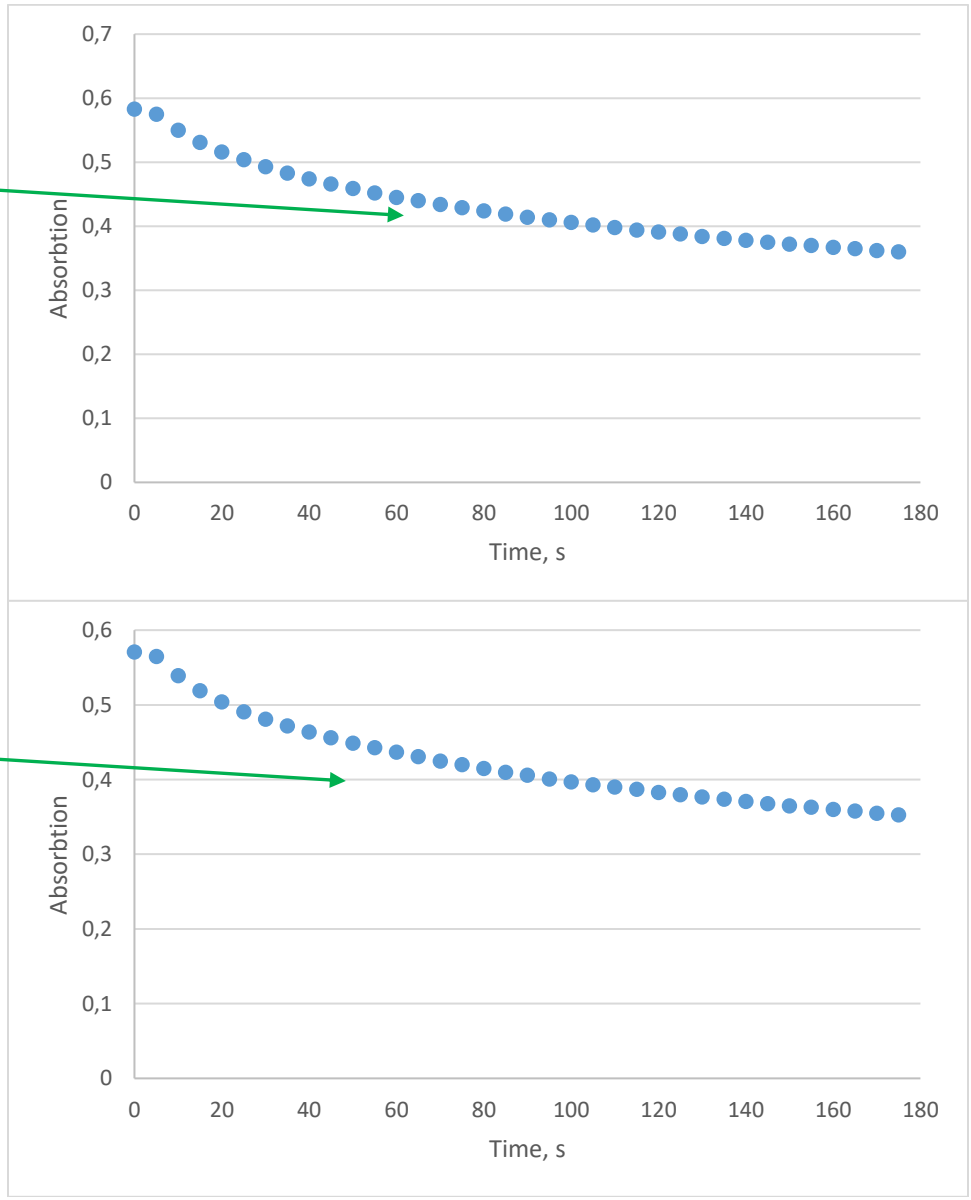

y = -0,0045x + 0,4531
Absorbtion
Time, s


Absorbtion
Time, s


y = -0,005x + 0,4545
Absorbtion
Time, s

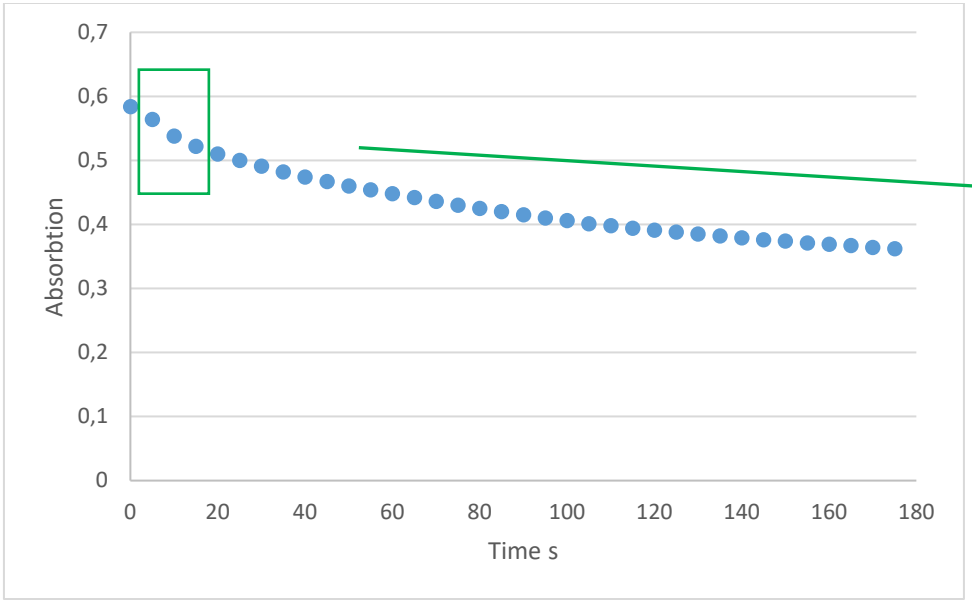
DMSO:

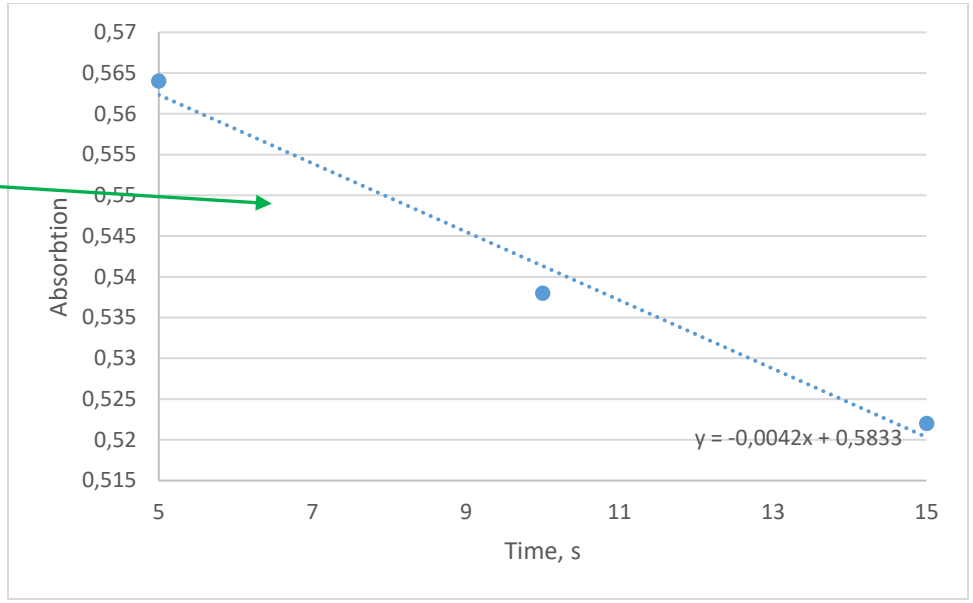

0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0 20 40 60 80 100 120 140 160 180
Time, s


0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0 20 40 60 80 100 120 140 160 180
Time, s

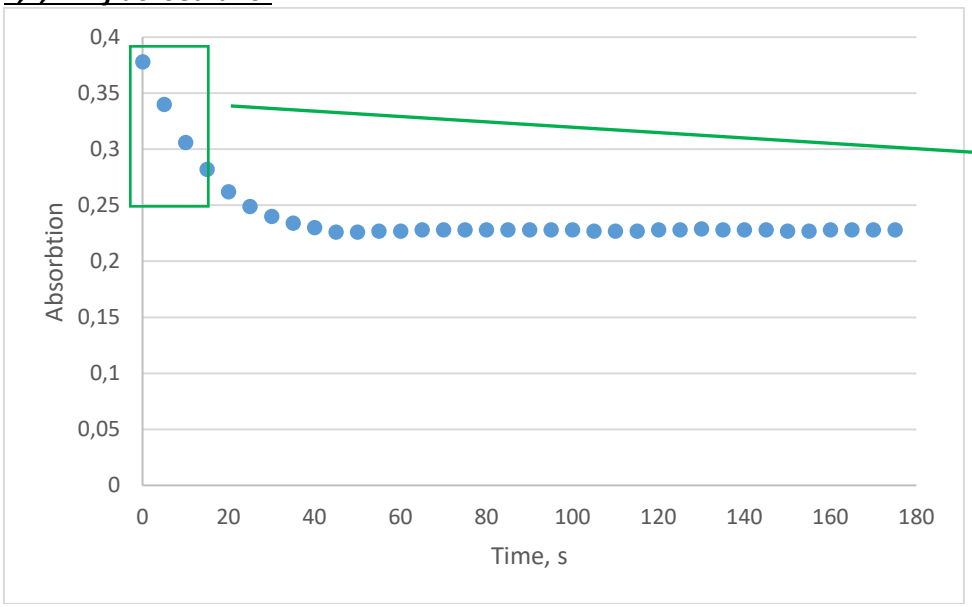
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0 20 40 60 80 100 120 140 160 180
Time, s

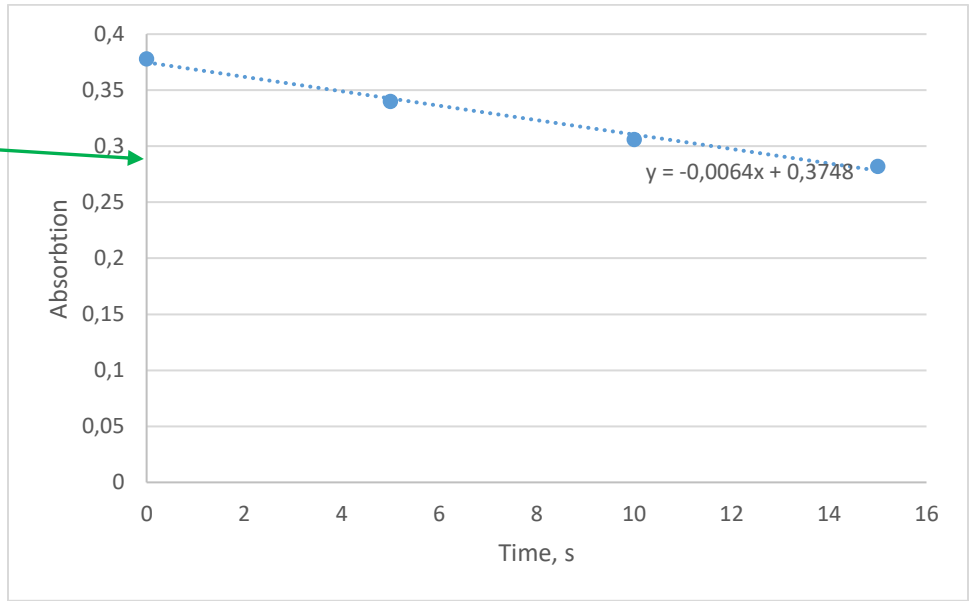
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0 20 40 60 80 100 120 140 160 180
Time, s

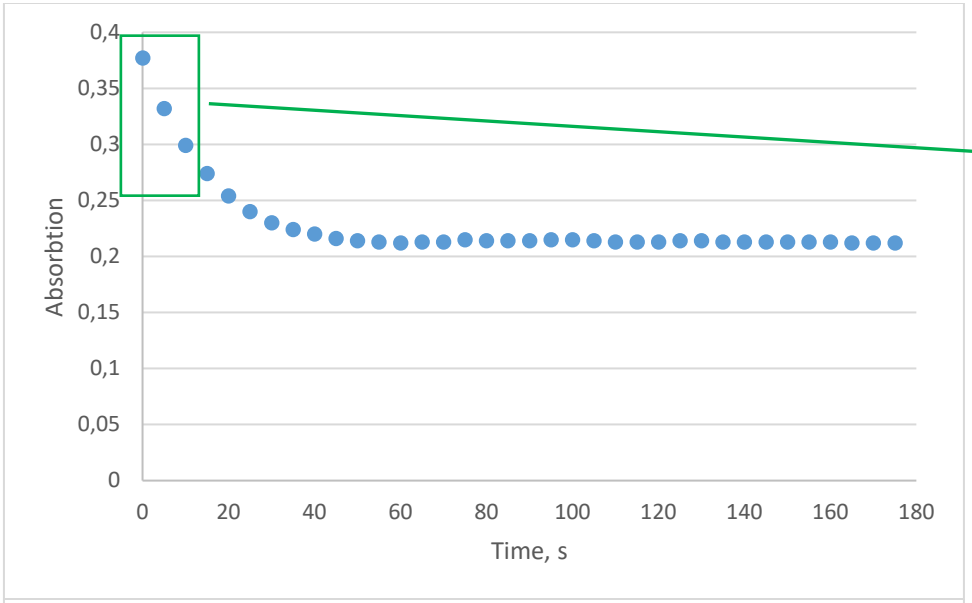


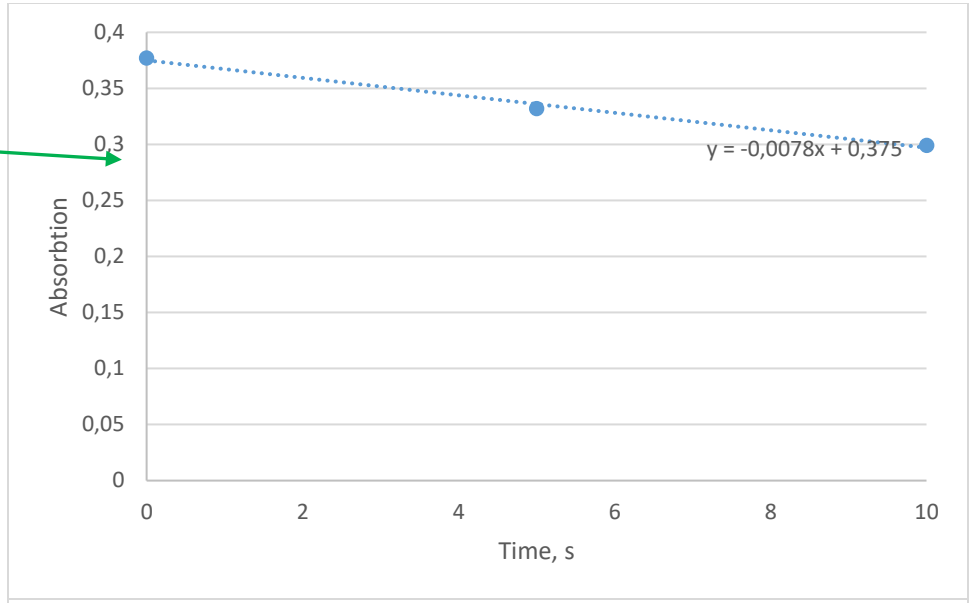


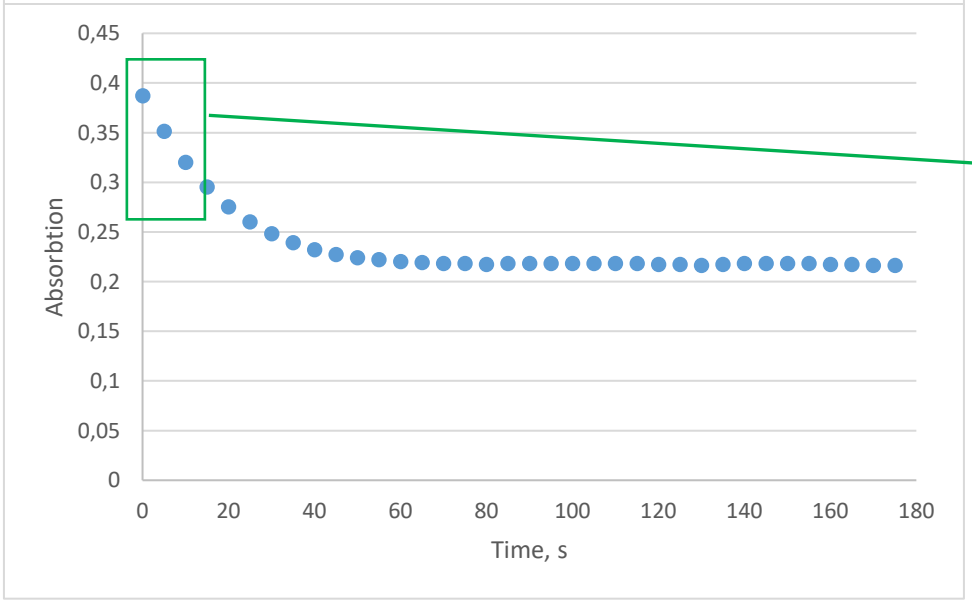
2,2,2-Trifluoroethanol

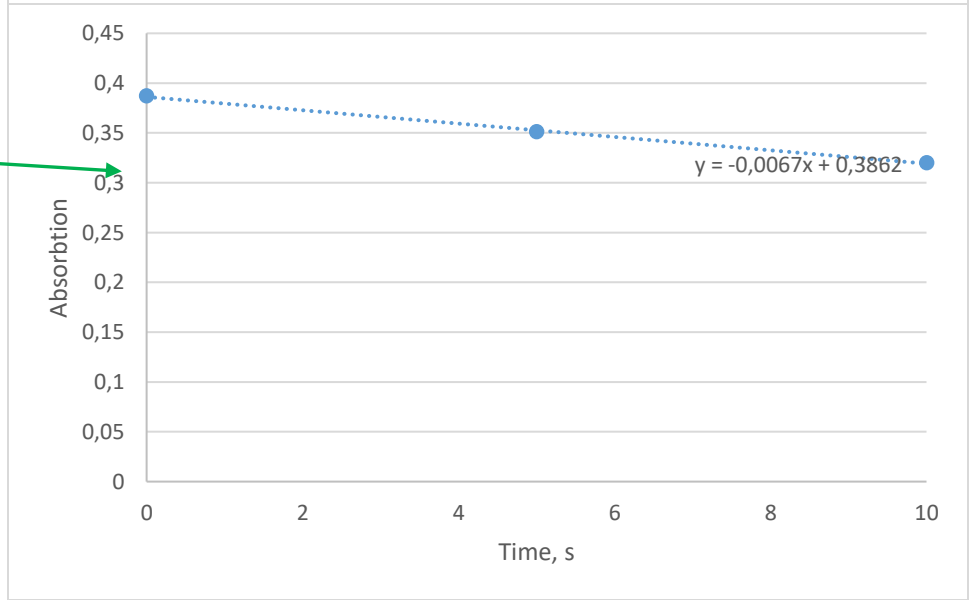




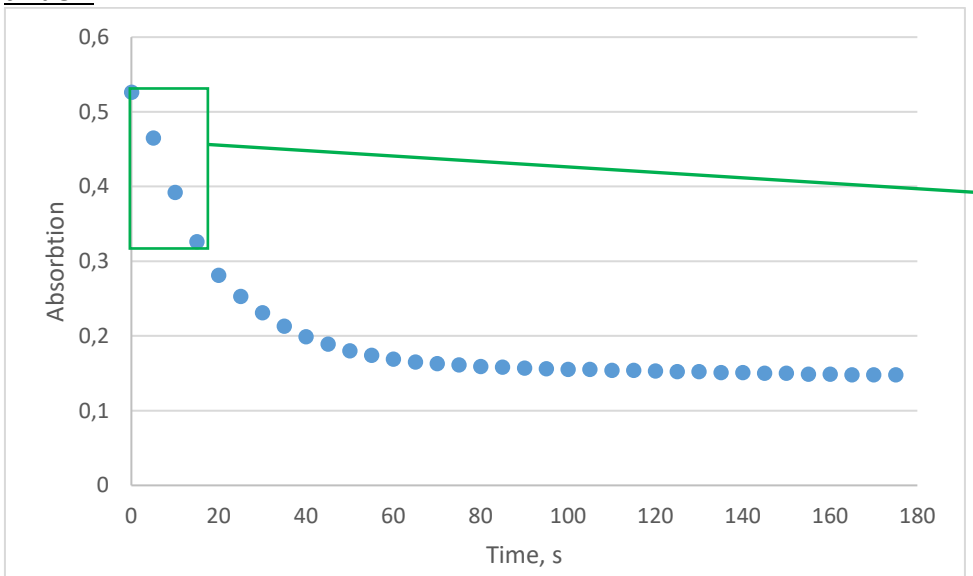

0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

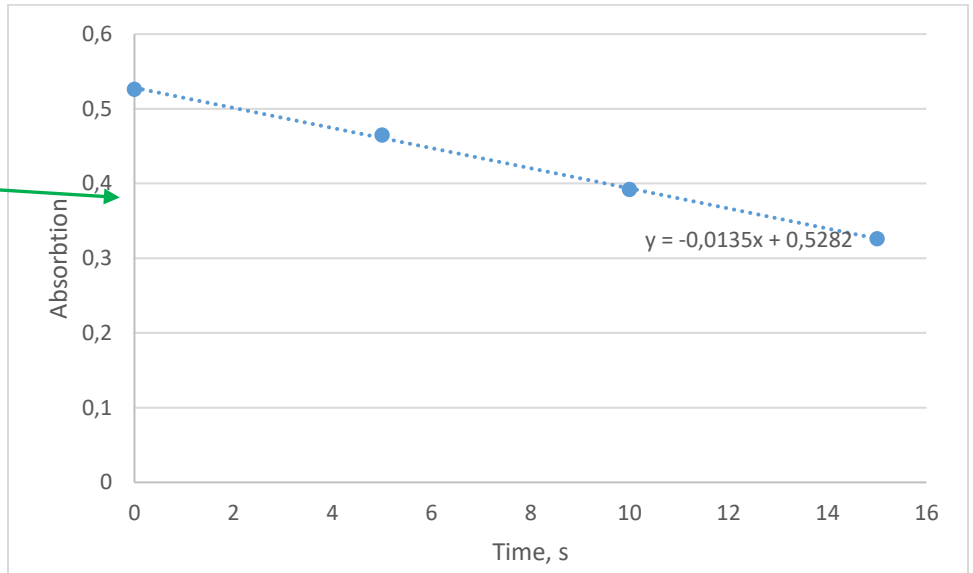

0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,0078x + 0,375
0
2
4
6
8
10
Time, s

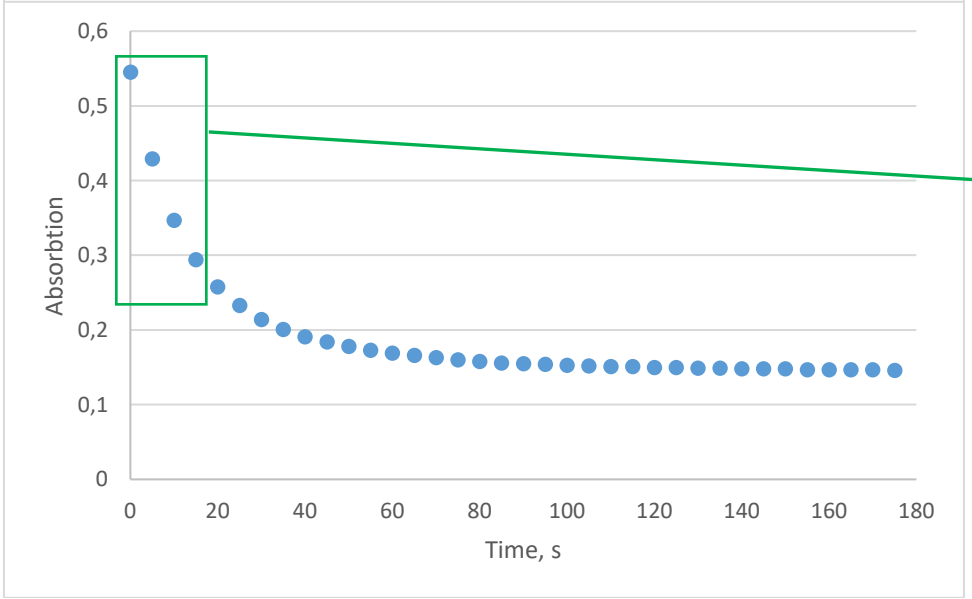

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

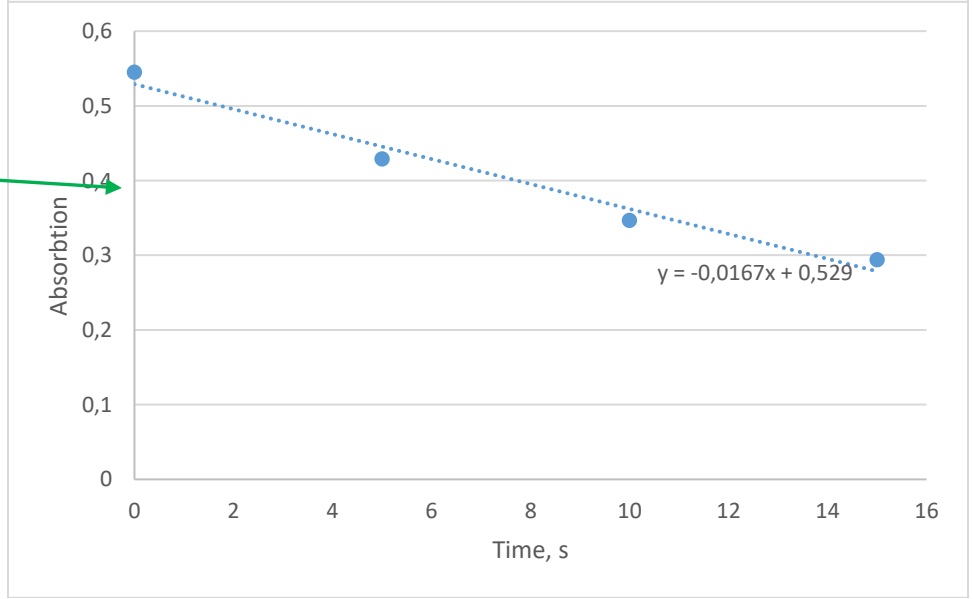

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,0067x + 0,3862
0
2
4
6
8
10
Time, s

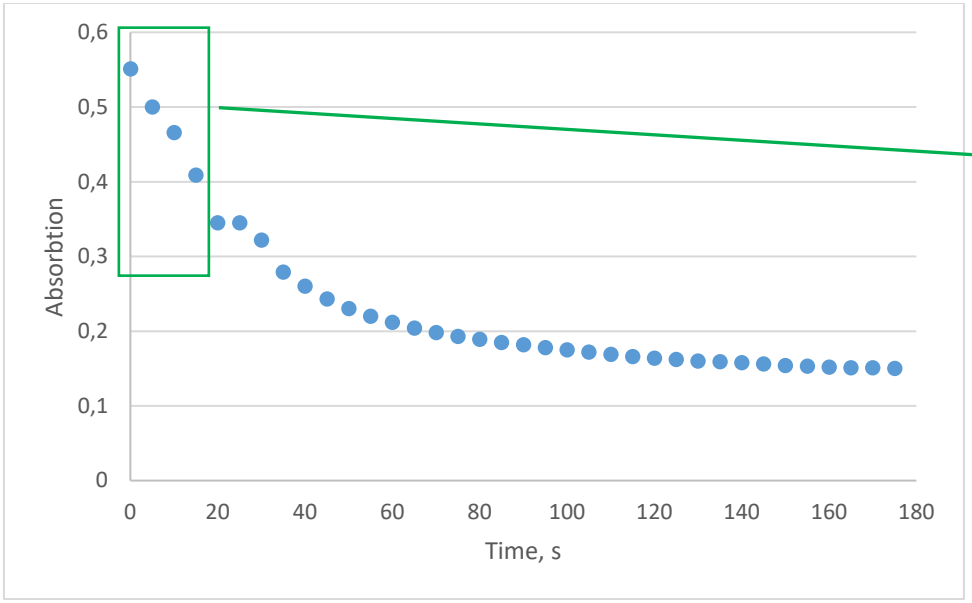
t-BuOH

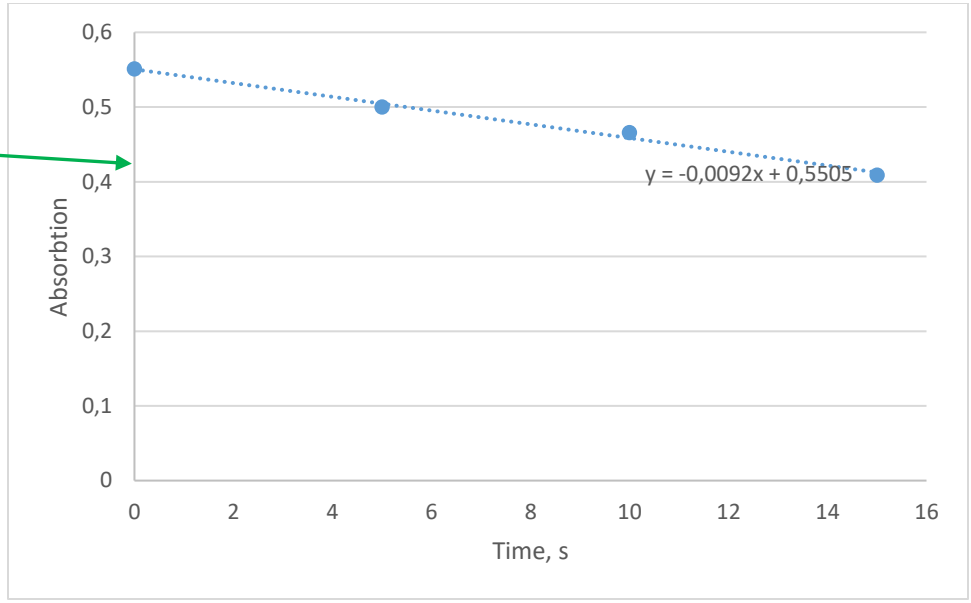

0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
y = -0,0135x + 0,5282
0
2
4
6
8
10
12
14
16
Time, s

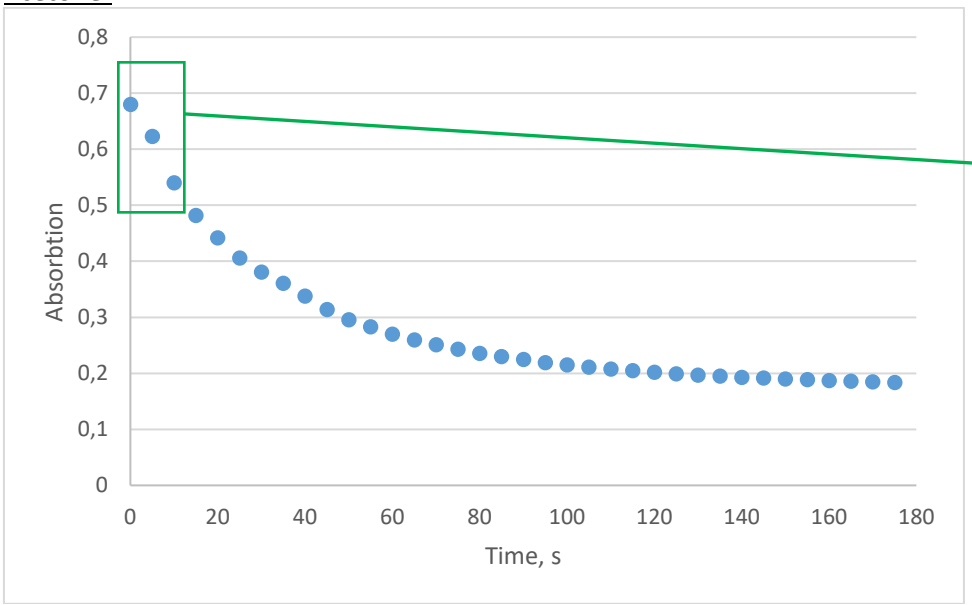

0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

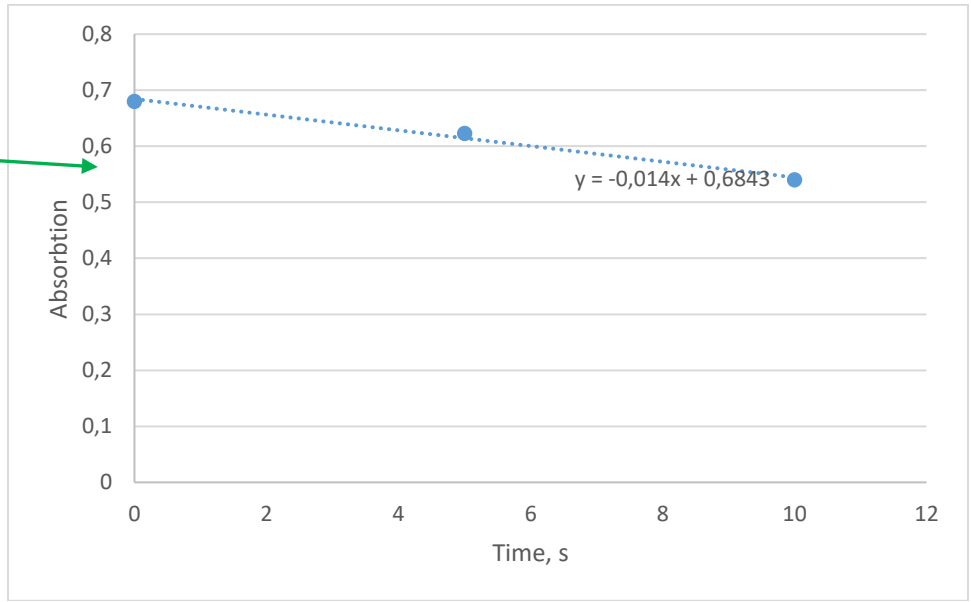

0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
y = -0,0167x + 0,529
0
2
4
6
8
10
12
14
16
Time, s

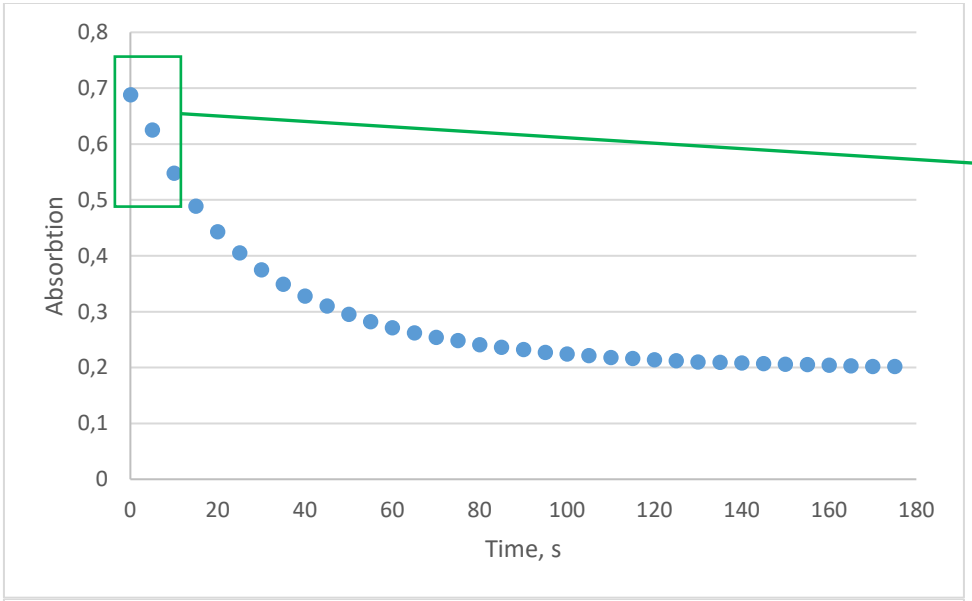

0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

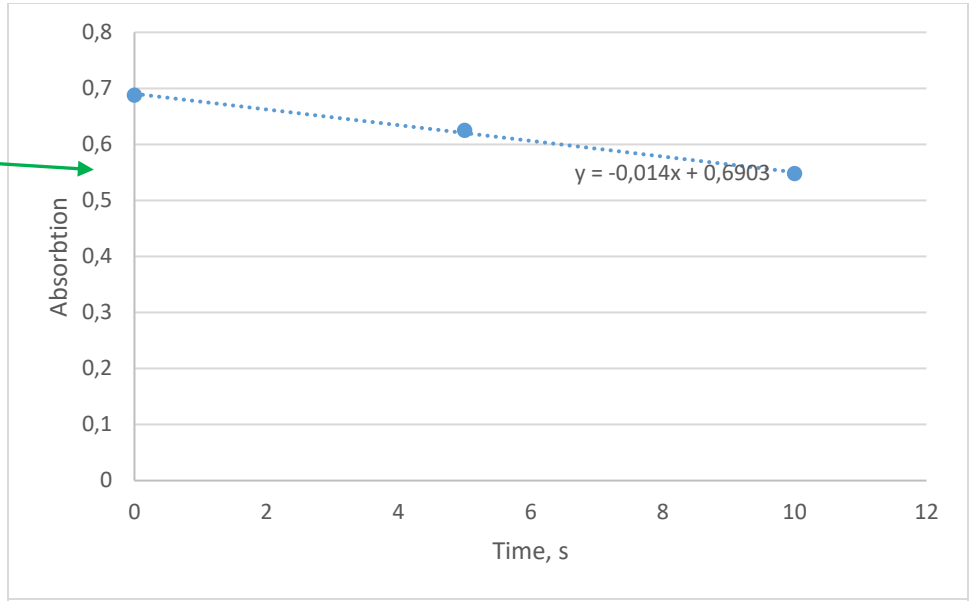

0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
y = -0,0092x + 0,5505
0
2
4
6
8
10
12
14
16
Time, s

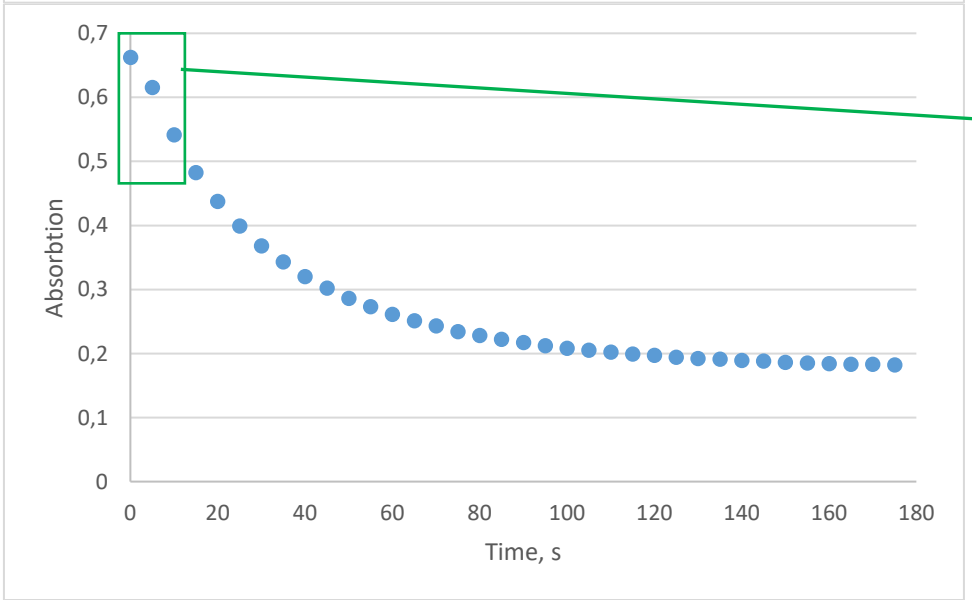
Acetone:

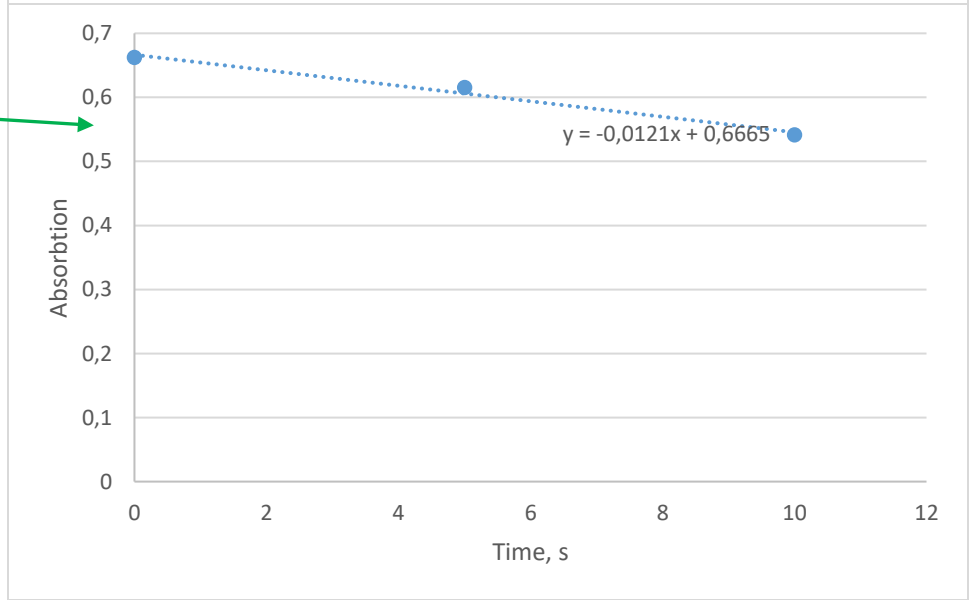

0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
y = -0,014x + 0,6843
0
2
4
6
8
10
12
Time, s

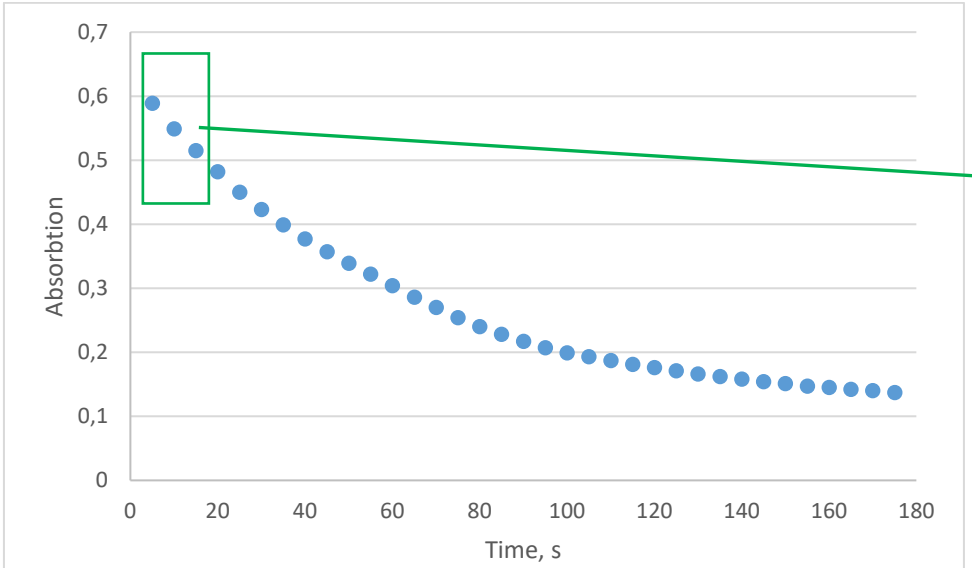

0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

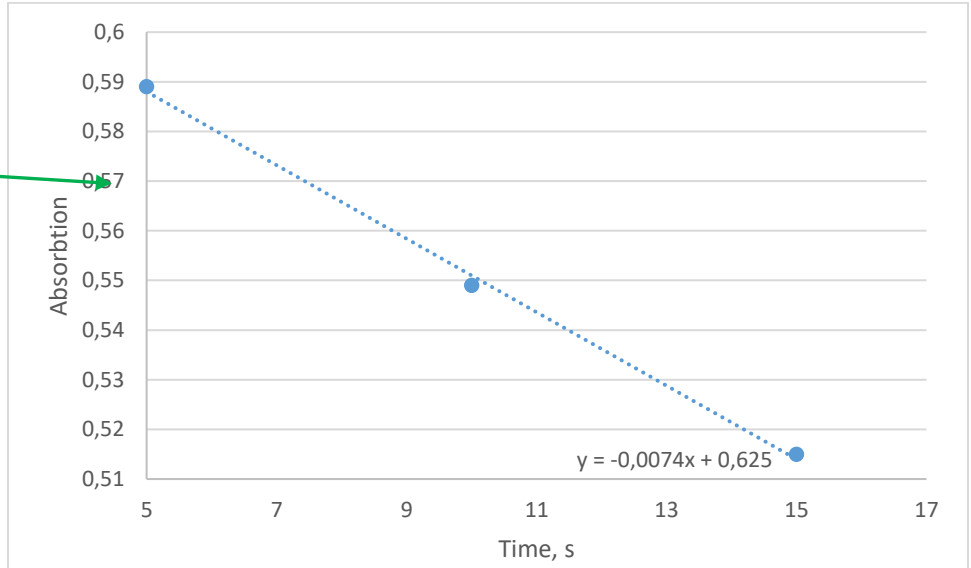

0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
y = -0,014x + 0,6903
0
2
4
6
8
10
12
Time, s

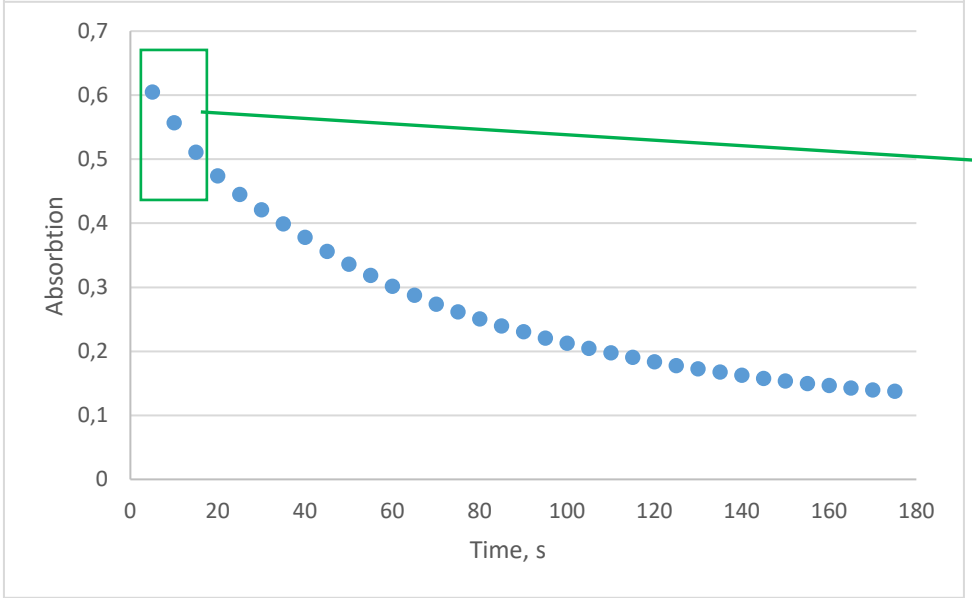

0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

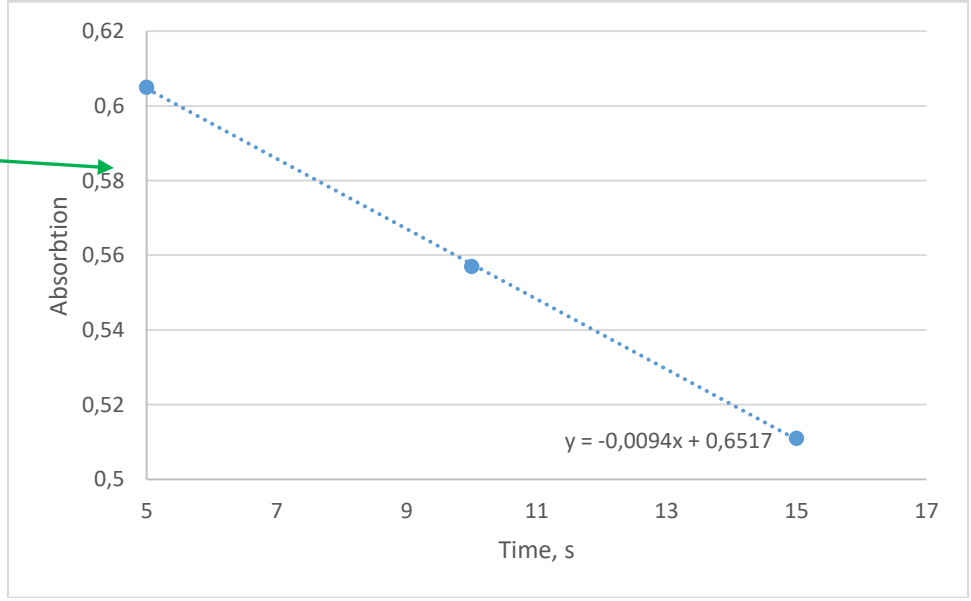

0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
y = -0,0121x + 0,6665
0
2
4
6
8
10
12
Time, s

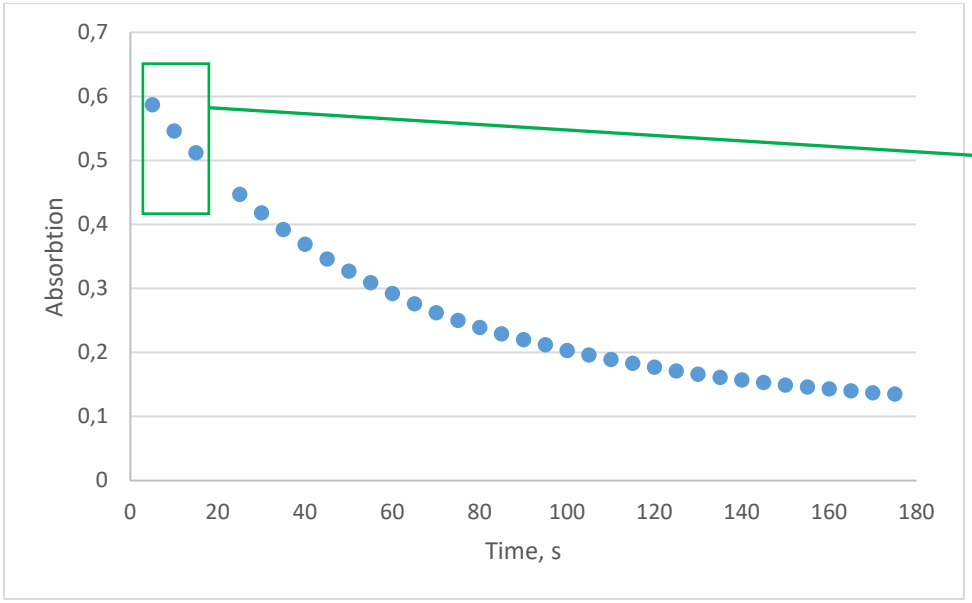
i-PrOH:

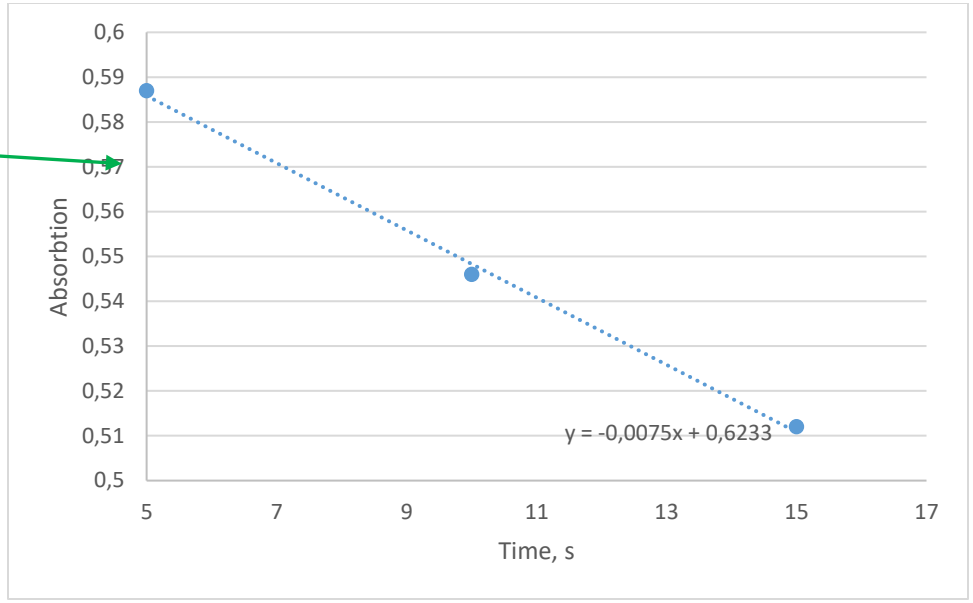

0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,6
0,59
0,58
0,57
0,56
0,55
0,54
0,53
0,52
0,51
Absorbtion
y = -0,0074x + 0,625
5
7
9
11
13
15
17
Time, s

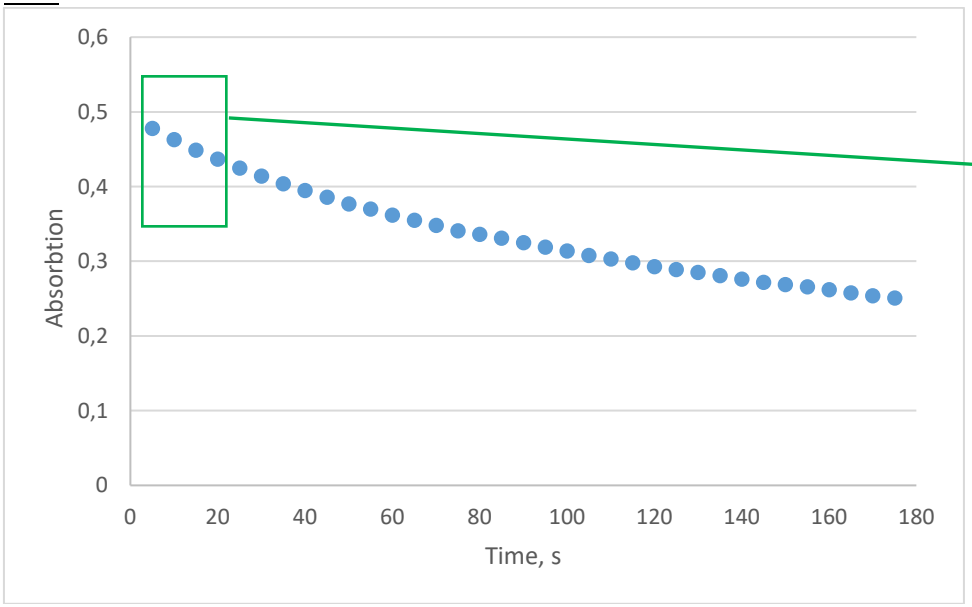

0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

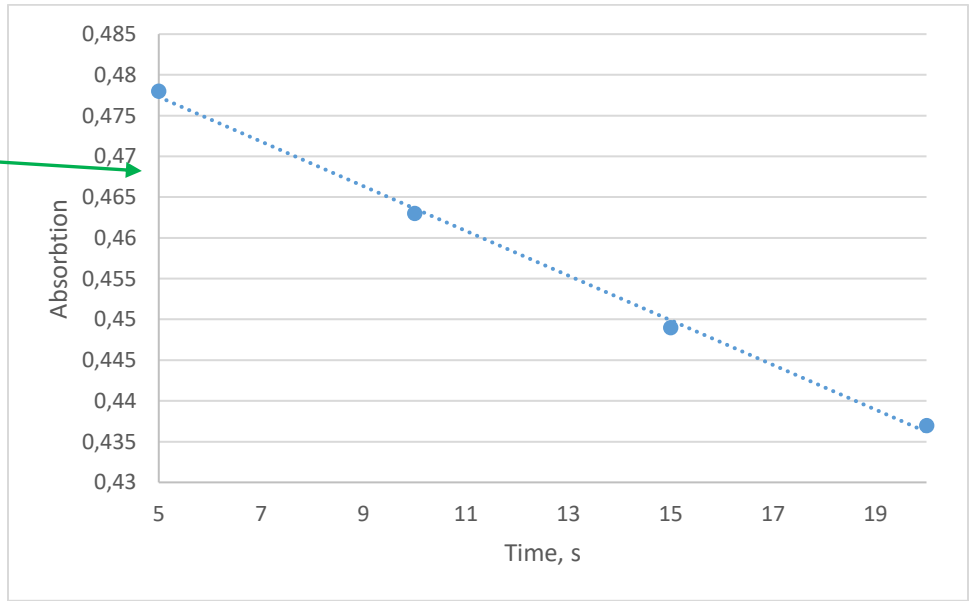

0,62
0,6
0,58
0,56
0,54
0,52
0,5
Absorbtion
y = -0,0094x + 0,6517
5
7
9
11
13
15
17
Time, s

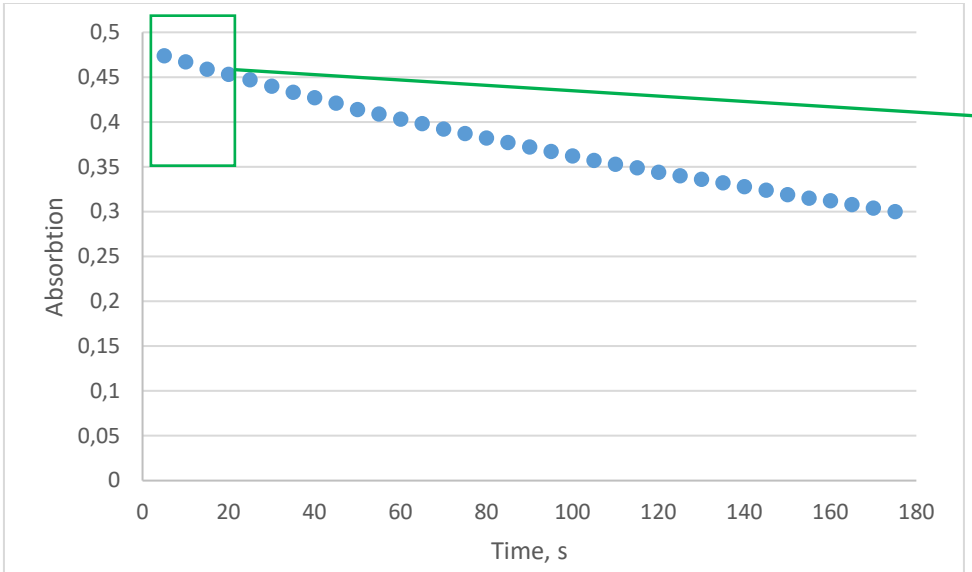

Absorbtion
Time, s

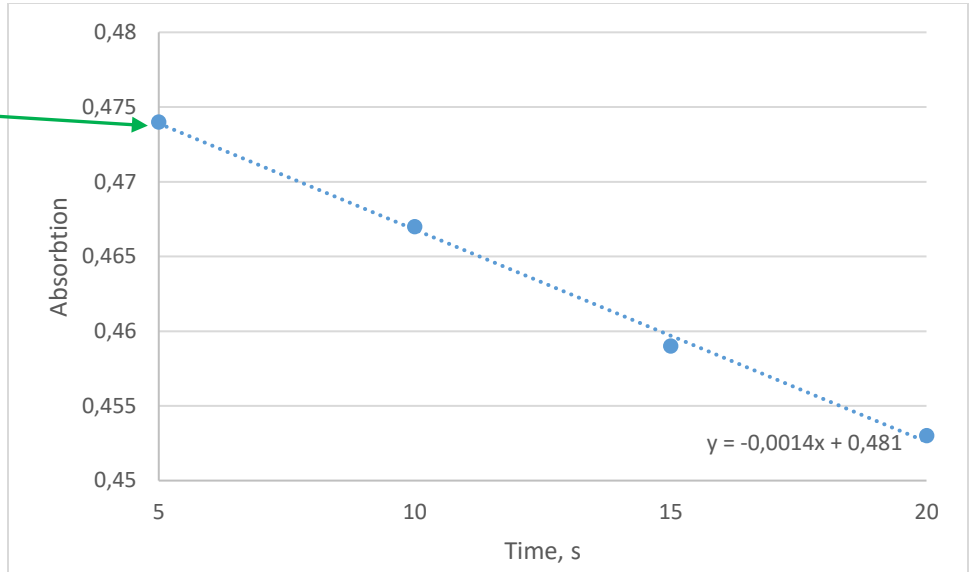

Absorbtion
Time, s
y = -0,0075x + 0,6233

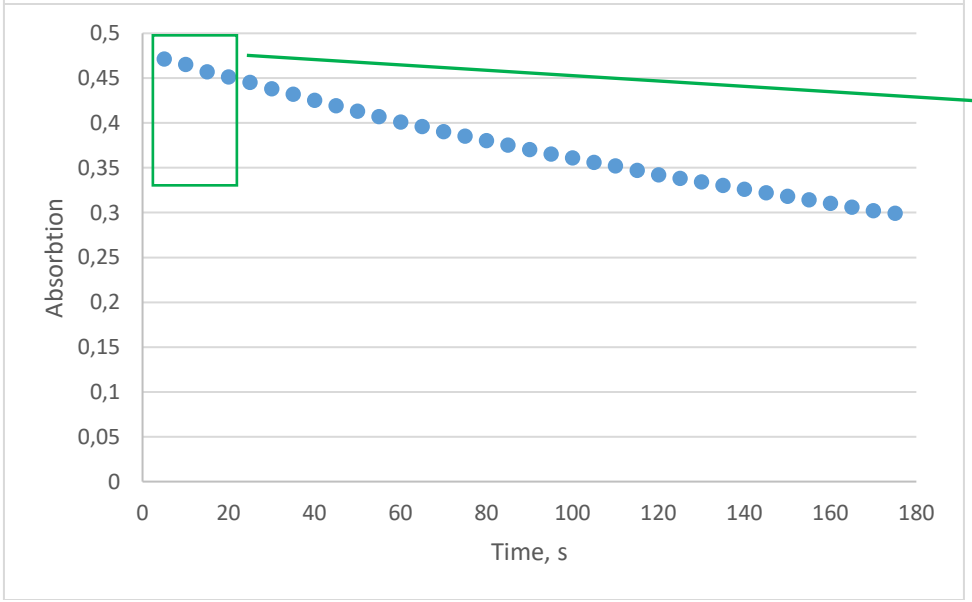
THF:

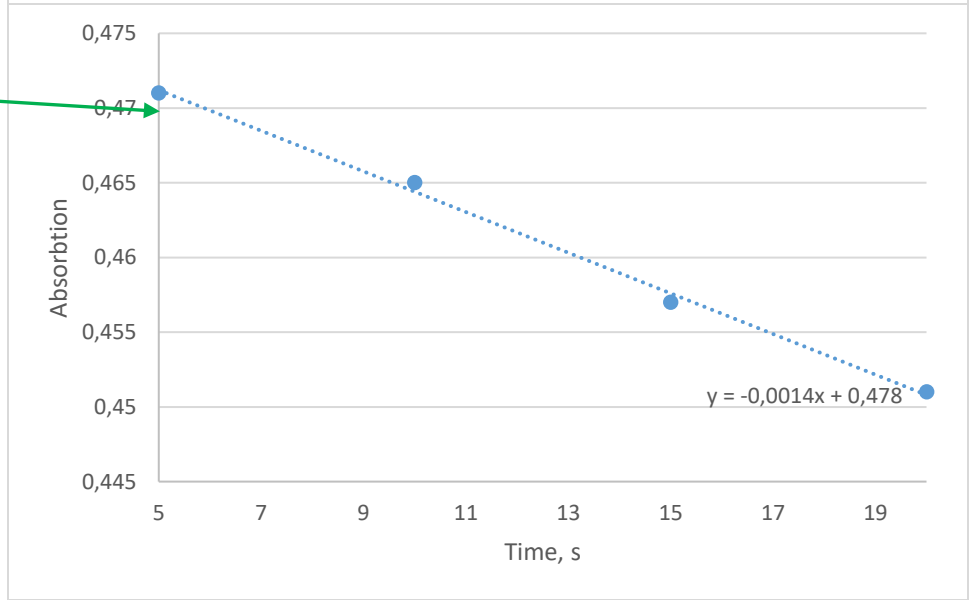

Absorbtion
Time, s


Absorbtion
Time, s

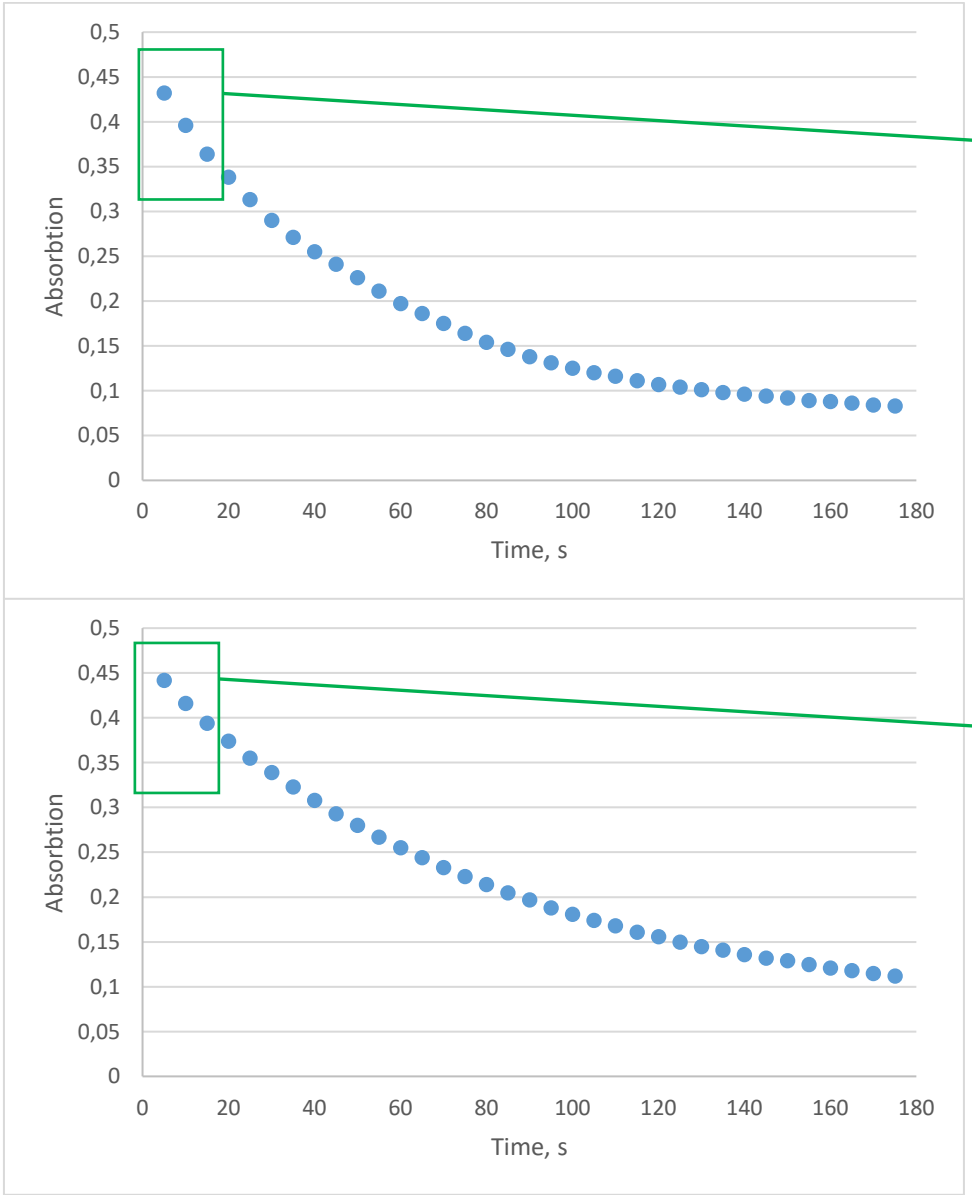

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

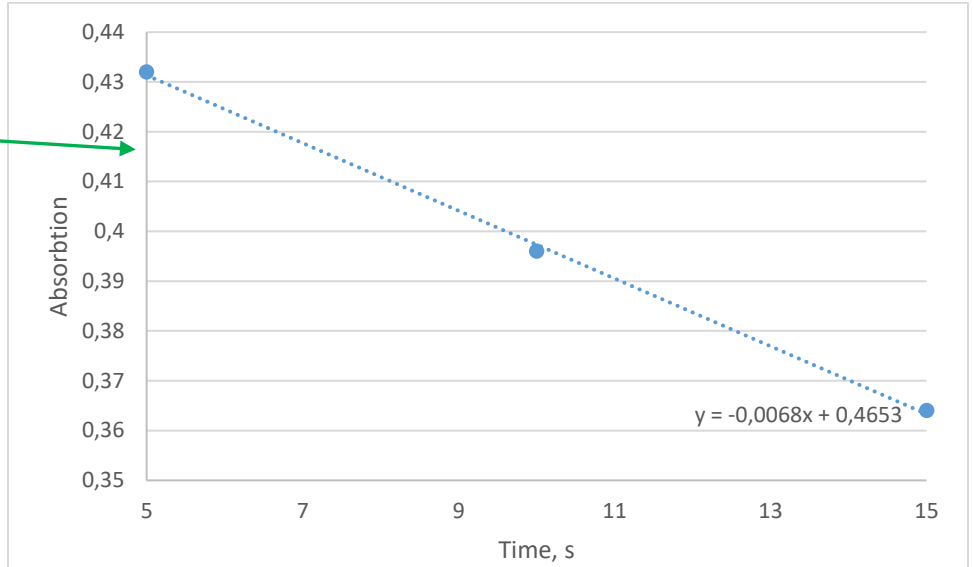

0,48
0,475
0,47
0,465
0,46
0,455
0,45
Absorbtion
y = -0,0014x + 0,481
5
10
15
20
Time, s


0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

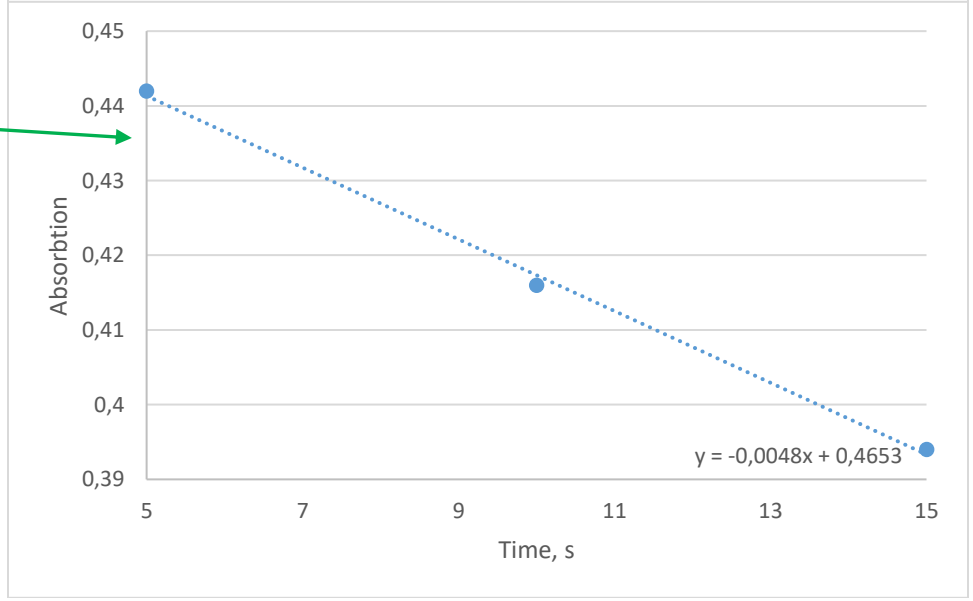

0,475
0,47
0,465
0,46
0,455
0,45
0,445
Absorbtion
y = -0,0014x + 0,478
5
7
9
11
13
15
17
19
Time, s

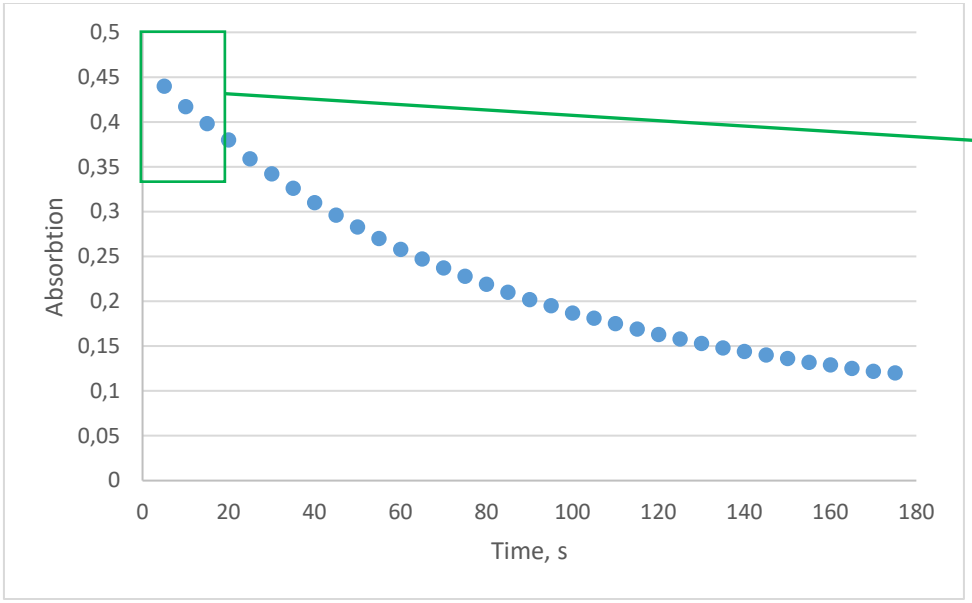
MeOH

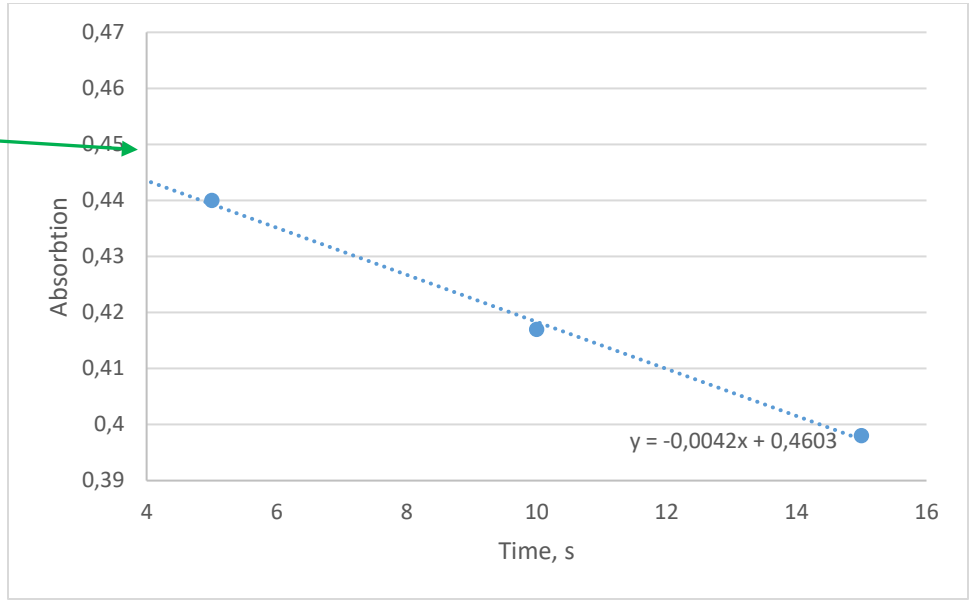

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,44
0,43
0,42
0,41
0,4
0,39
0,38
0,37
0,36
0,35
Absorbtion
y = -0,0068x + 0,4653
5
7
9
11
13
15
Time, s

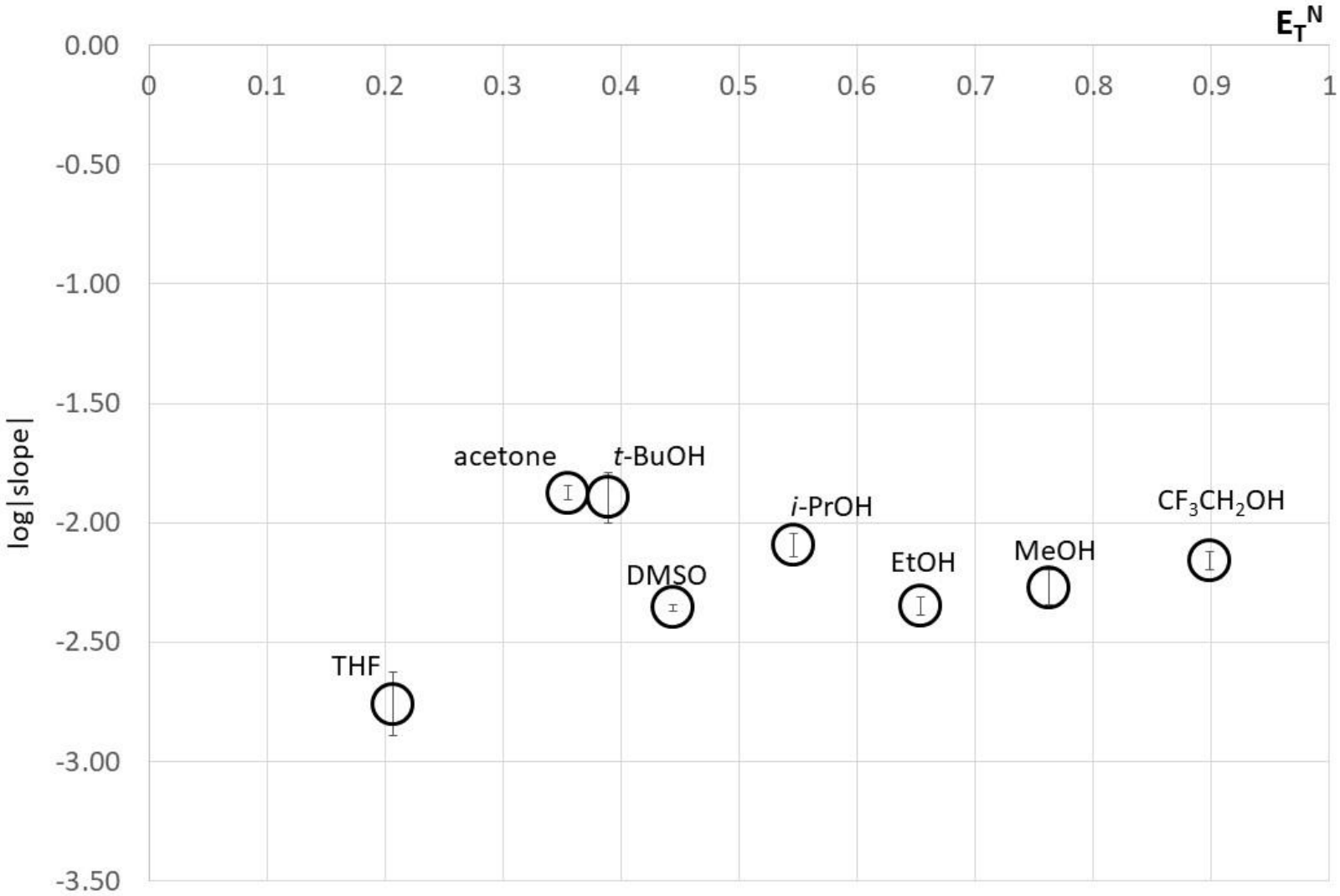
0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

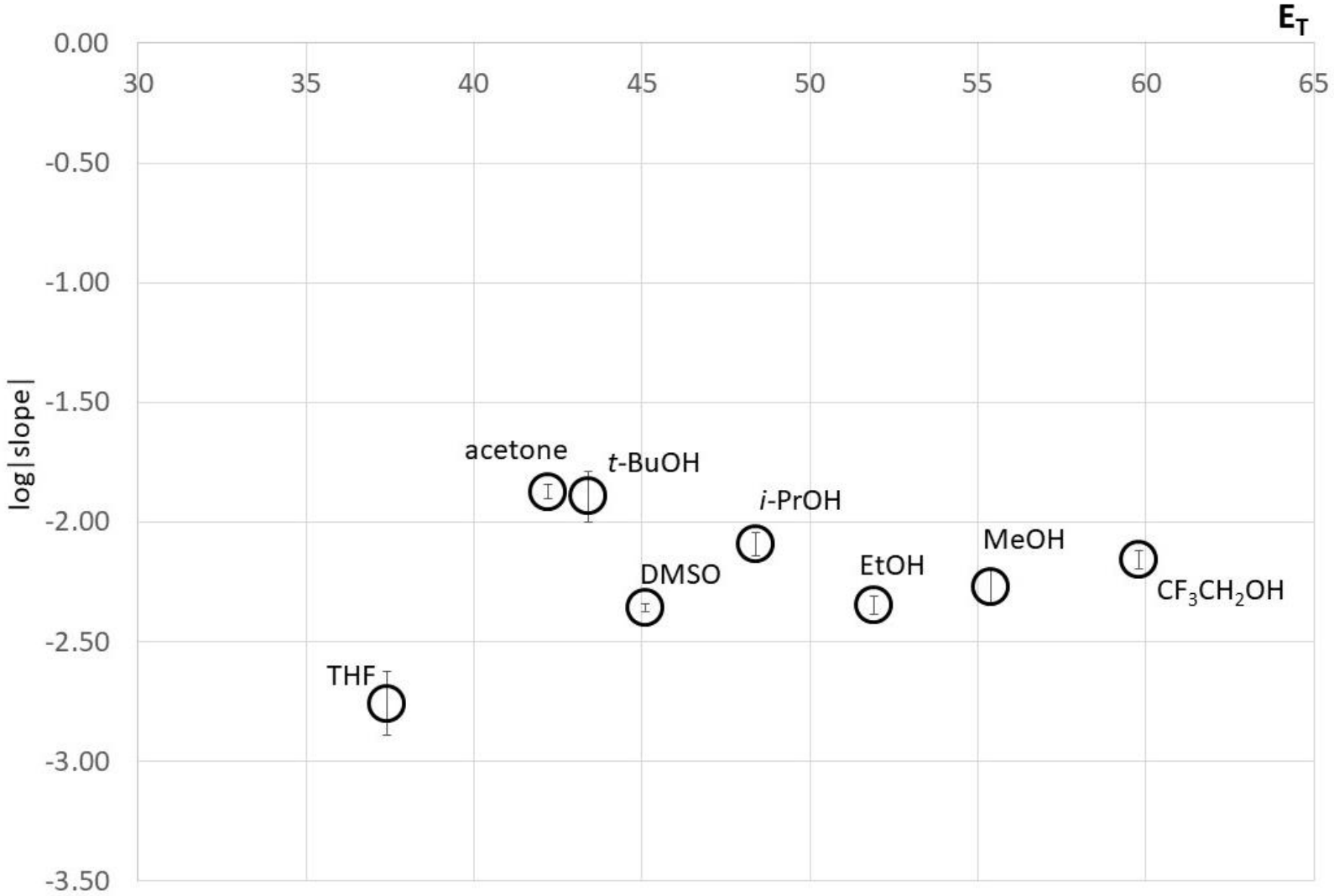

0,45
0,44
0,43
0,42
0,41
0,4
0,39
Absorbtion
y = -0,0048x + 0,4653
5
7
9
11
13
15
Time, s

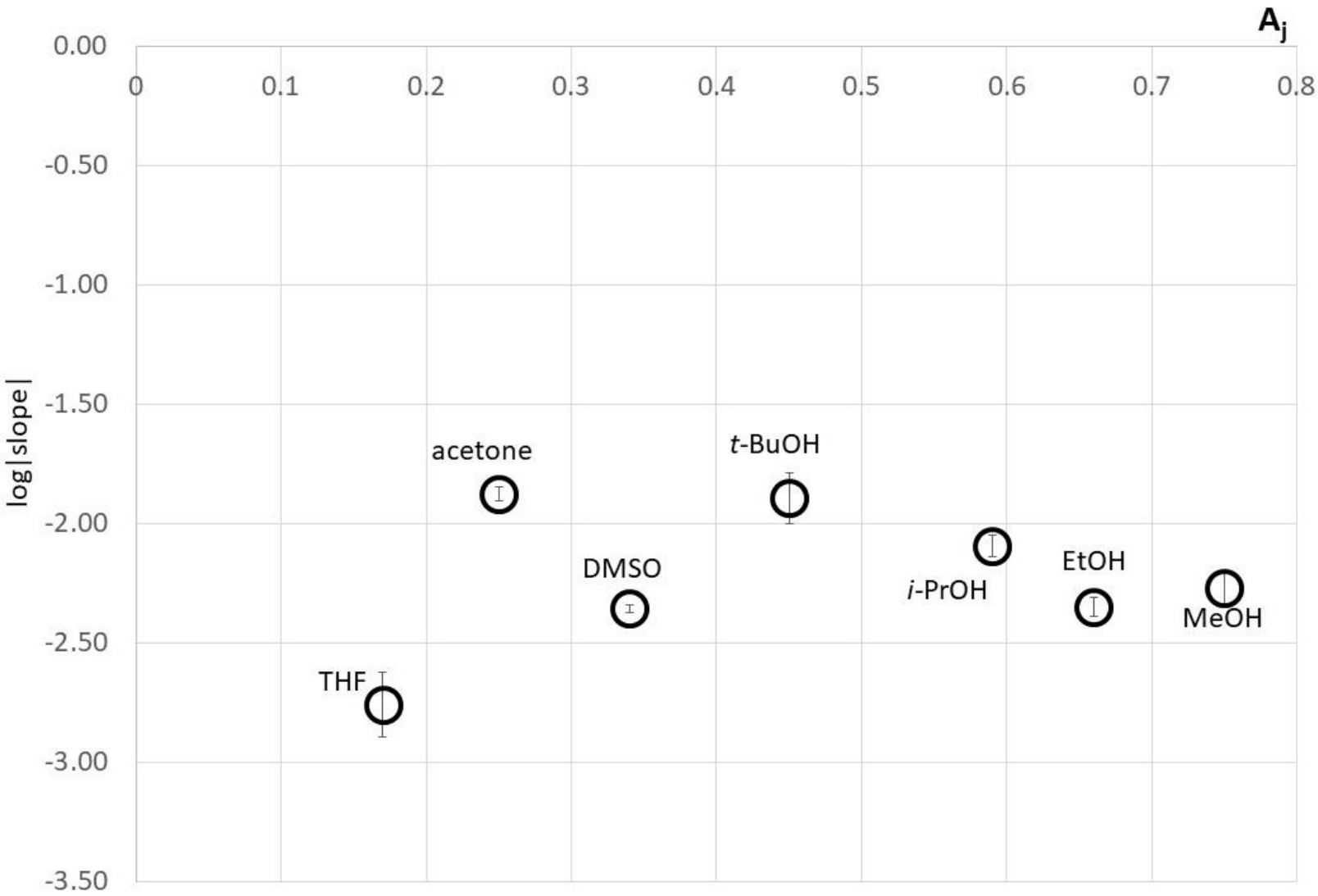

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

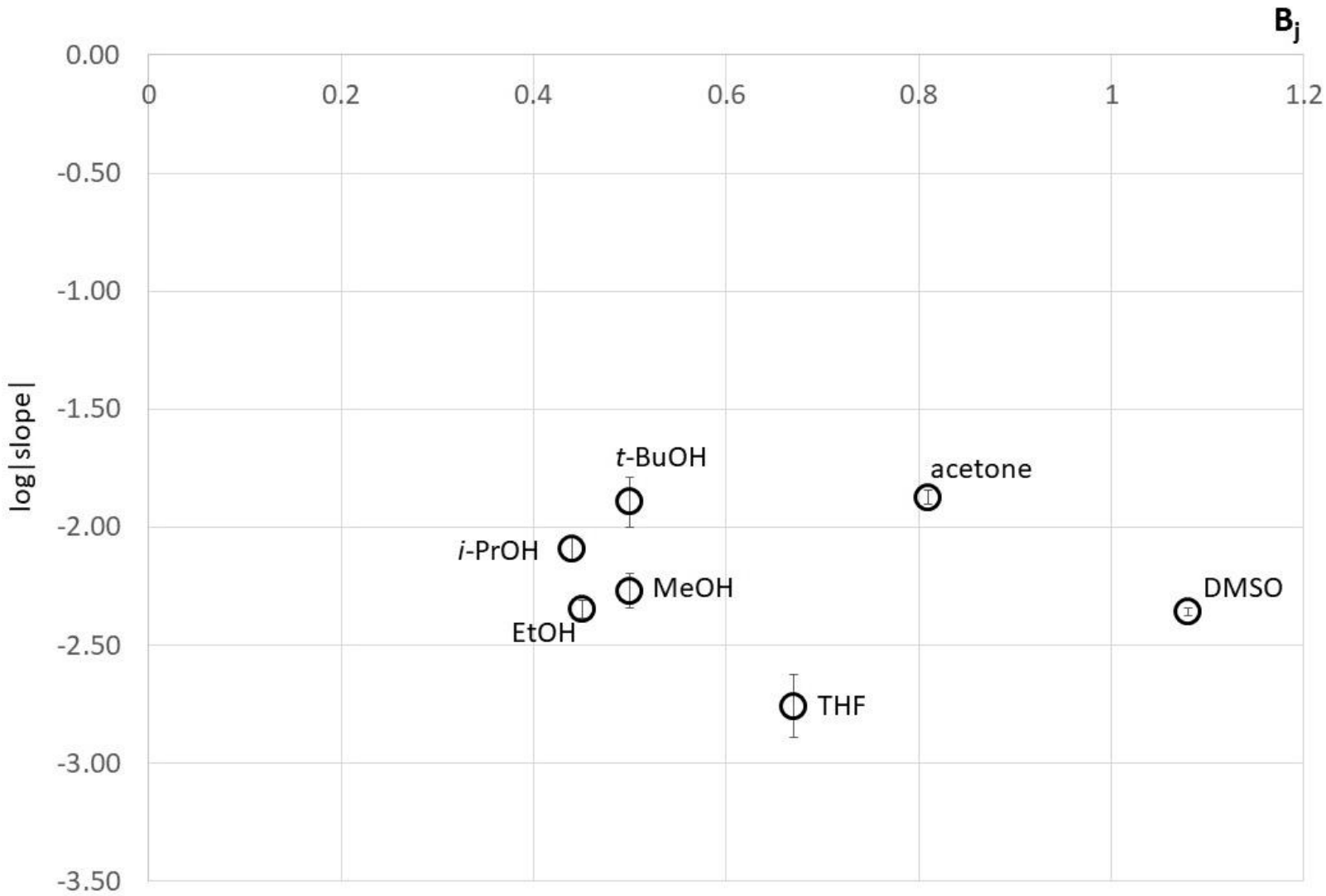

0,47
0,46
0,45
0,44
0,43
0,42
0,41
0,4
0,39
Absorbtion
4
6
8
10
12
14
16
Time, s
y = -0,0042x + 0,4603

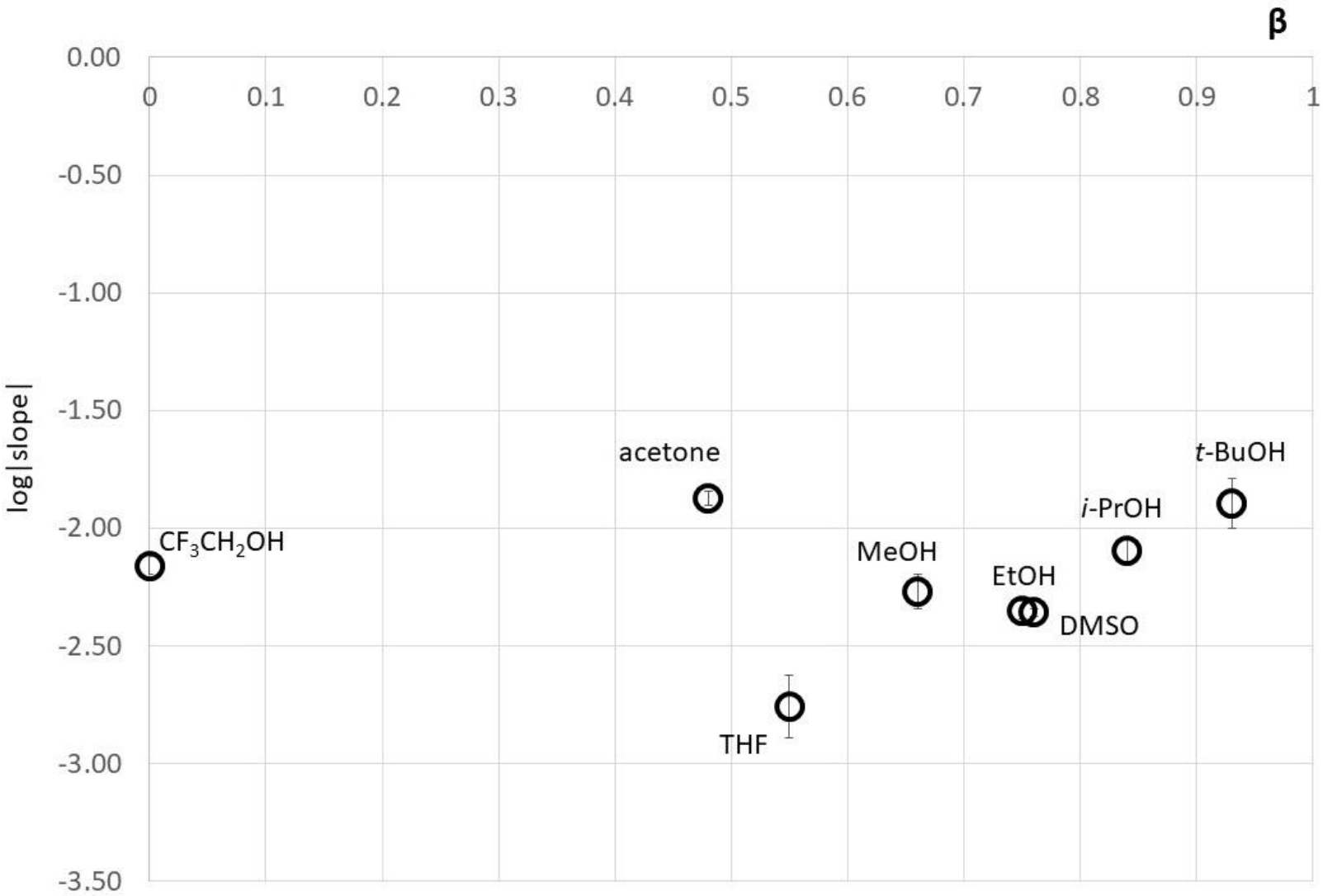
13.CORRELATION BETWEEN REACTION (12c + DPPH) RATE (CHARACTERIZED WITH LOG|SLOPE|) AND VARIOUS SOLVENT PARAMETERS

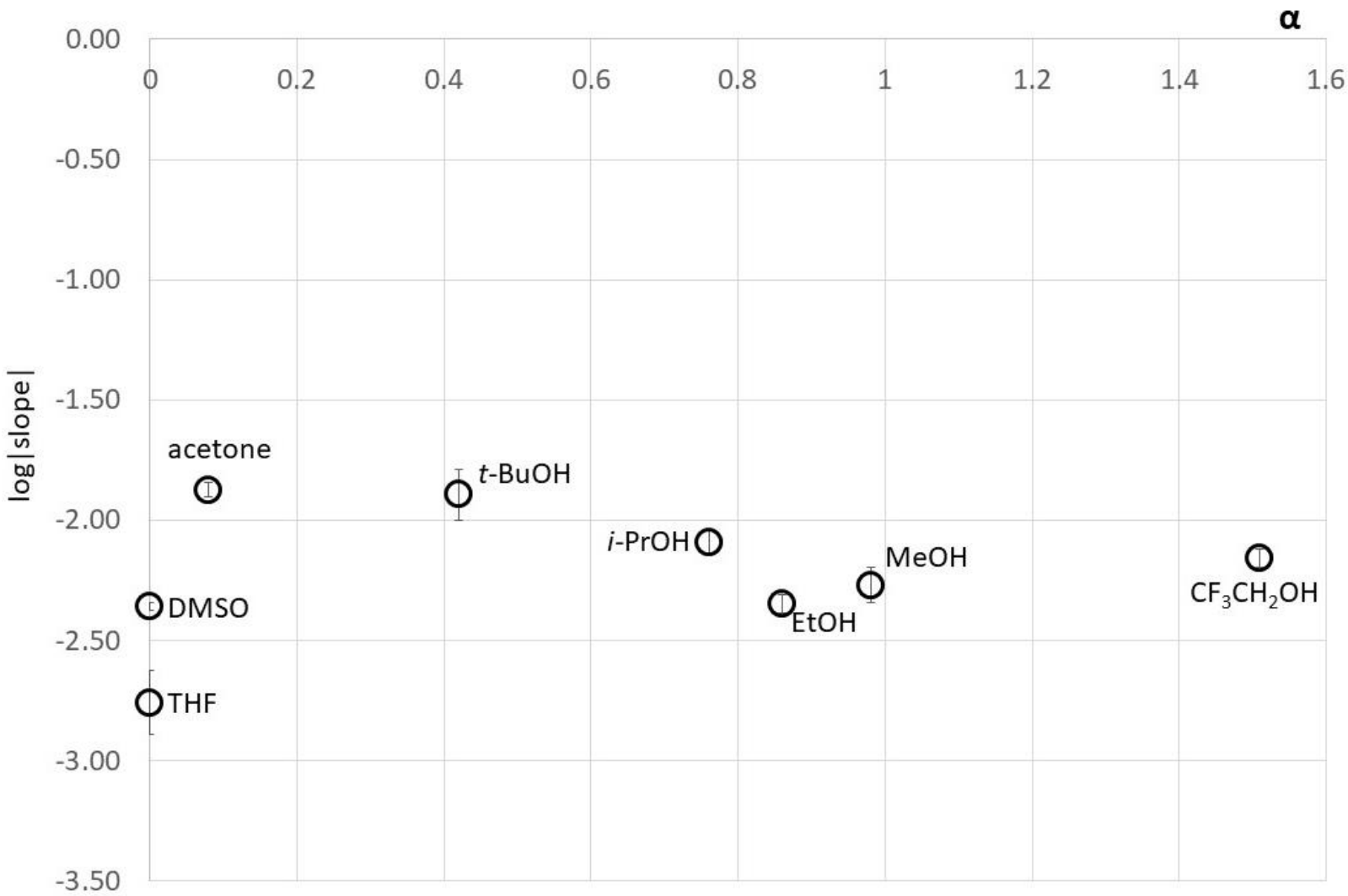



E_T
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
log|slope|
30
35
40
45
50
55
60
65
acetone
t-BuOH
i-PrOH
DMSO
EtOH
MeOH
CF_3CH_2OH
THF


A_j
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
log|slope|
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
acetone
t-BuOH
DMSO
i-PrOH
EtOH
MeOH
THF

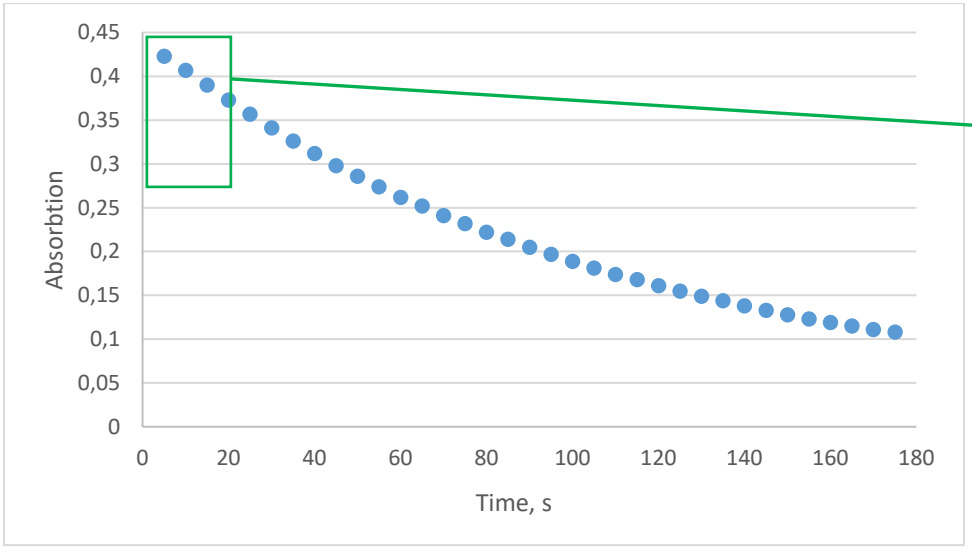

B_j
0.00
0
0.2
0.4
0.6
0.8
1
1.2
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
log|slope|
t-BuOH
acetone
i-PrOH
MeOH
DMSO
EtOH
THF

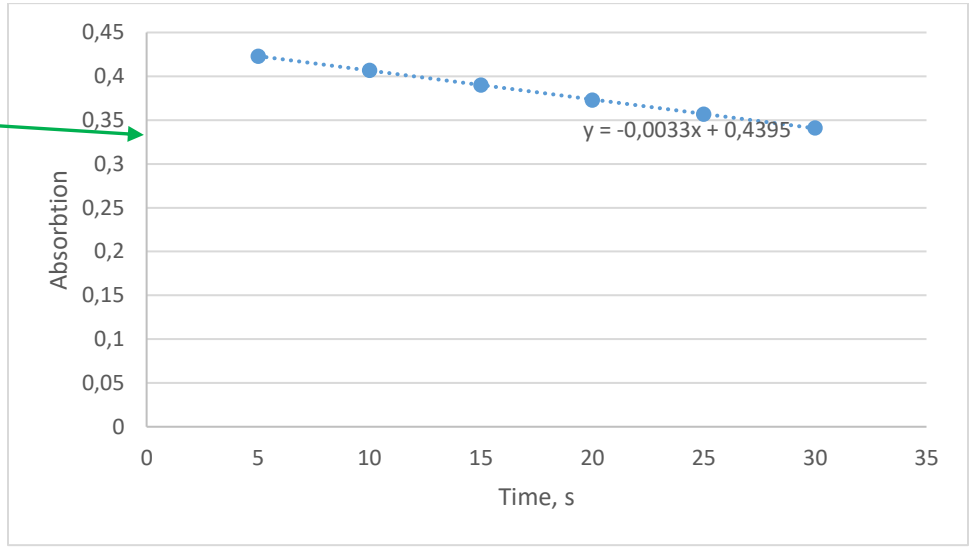

β
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
log|slope|
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
CF3CH2OH
acetone
THF
MeOH
EtOH
DMSO
i-PrOH
t-BuOH

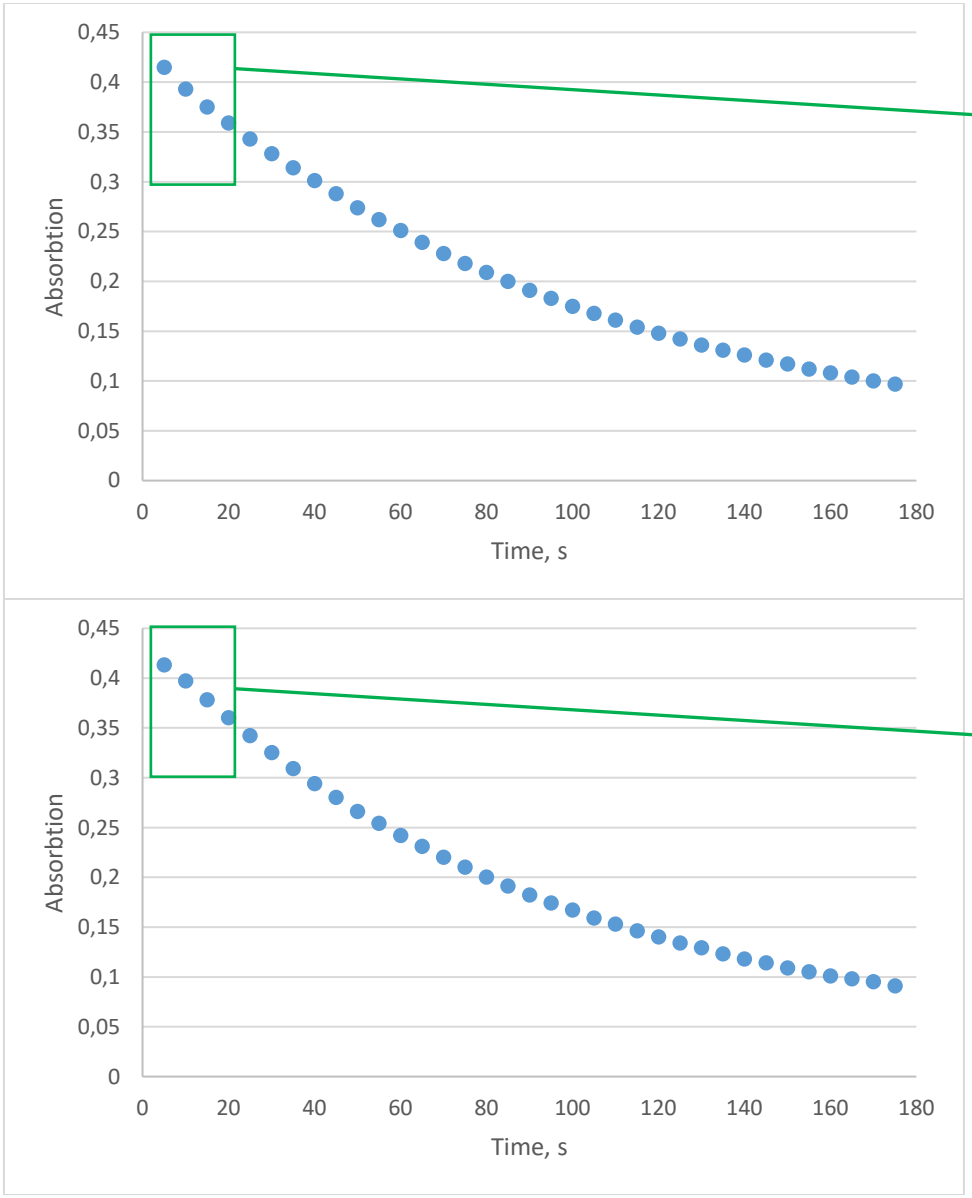

α
0.00
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
log|slope|
acetone
t-BuOH
i-PrOH
MeOH
DMSO
EtOH
CF3CH2OH
THF

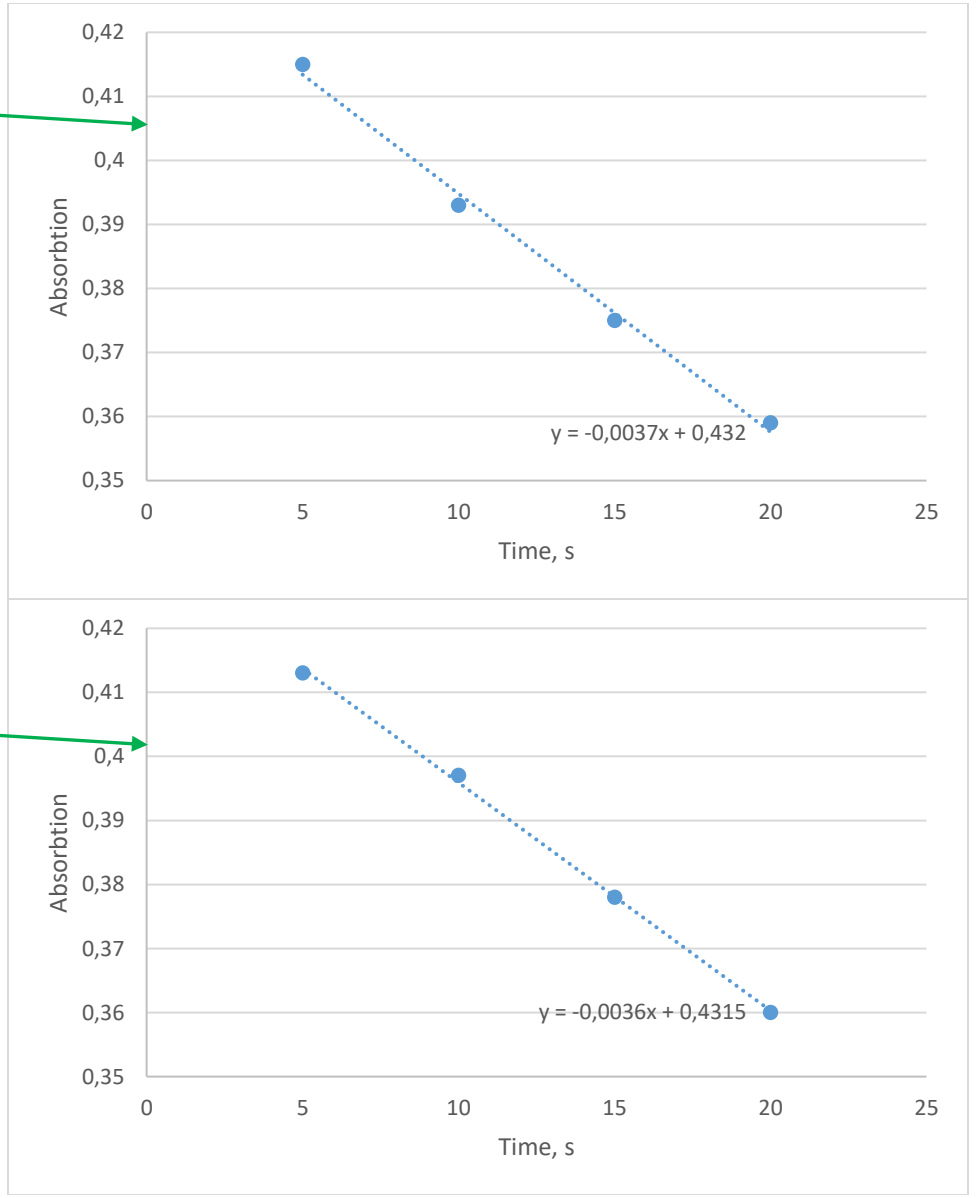
14.KINETIC CURVES FOR THE REACTION BETWEEN DPPH AND COMPOUND 12c IN EtOH (IN PRESENCE OF VARIOUS ADDITIVES)

AcOH





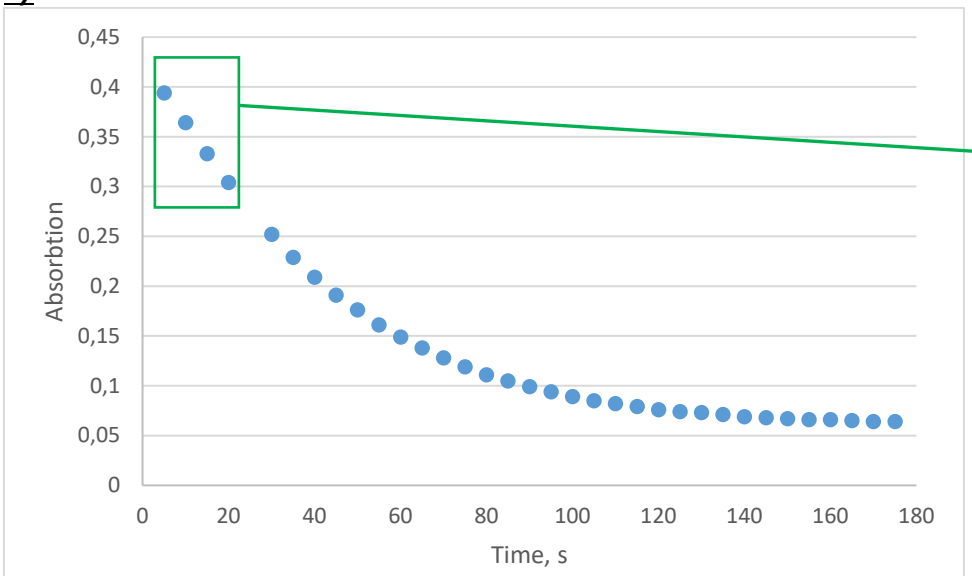

Absorbtion
Time, s
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
20
40
60
80
100
120
140
160
180

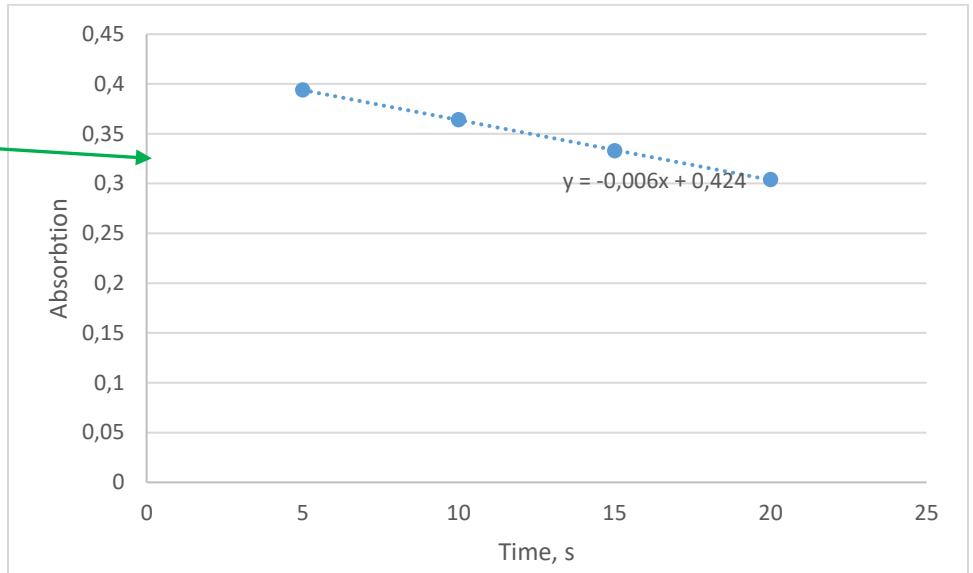

Absorbtion
Time, s
y = -0,0037x + 0,432
0,42
0,41
0,4
0,39
0,38
0,37
0,36
0,35
0
5
10
15
20
25

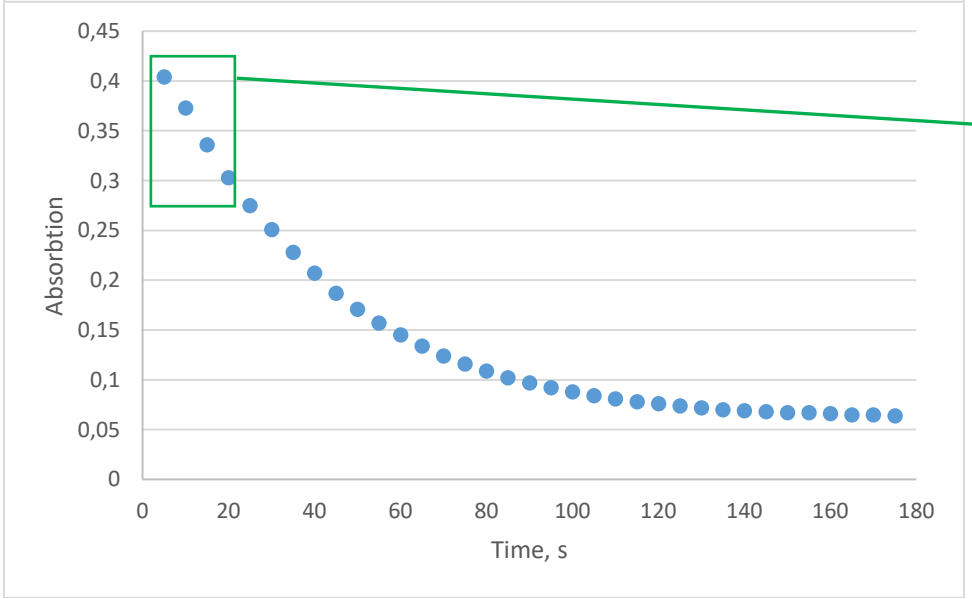
Absorbtion
Time, s
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
20
40
60
80
100
120
140
160
180

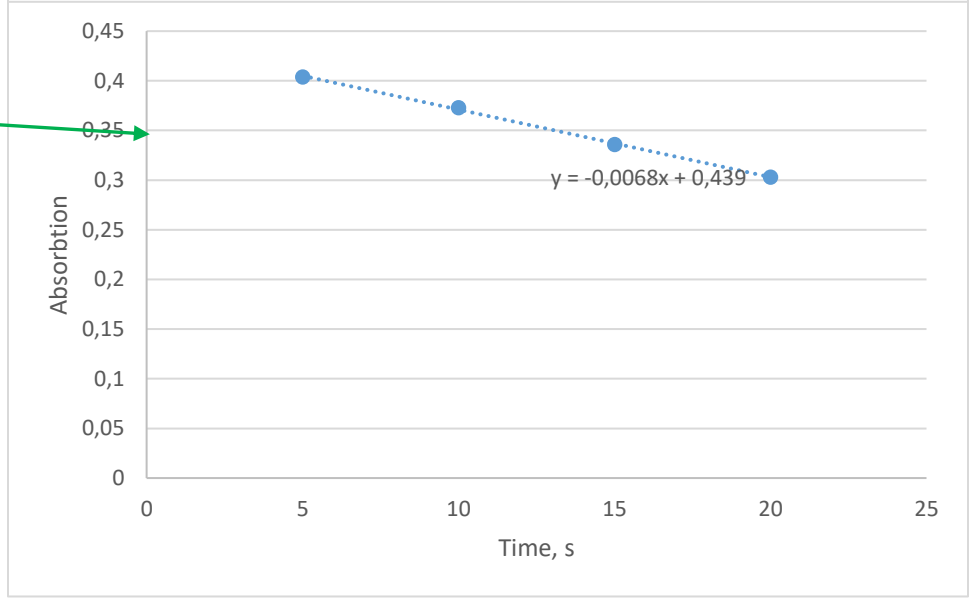
Absorbtion
Time, s
y = -0,0036x + 0,4315
0,42
0,41
0,4
0,39
0,38
0,37
0,36
0,35
0
5
10
15
20
25

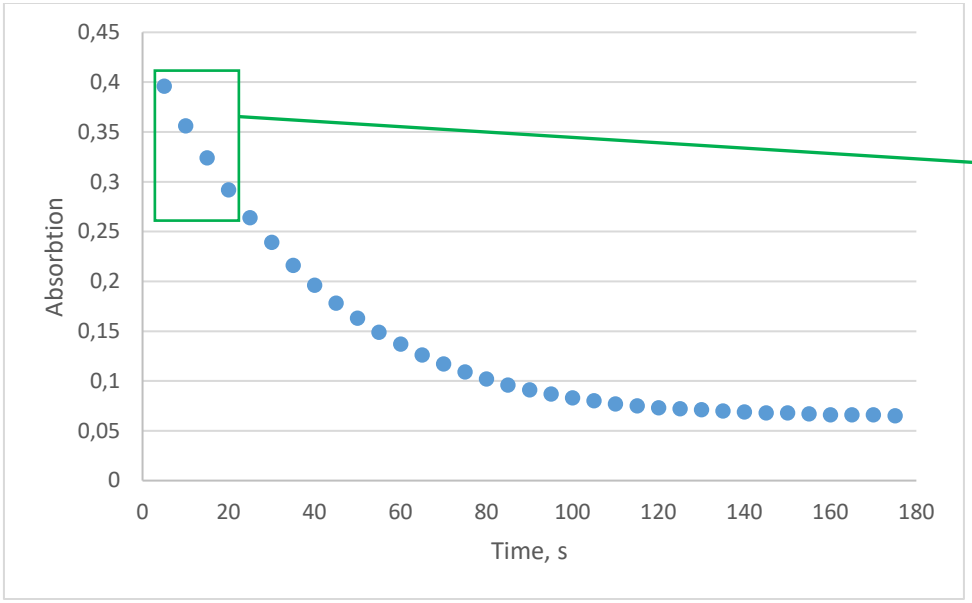
Py

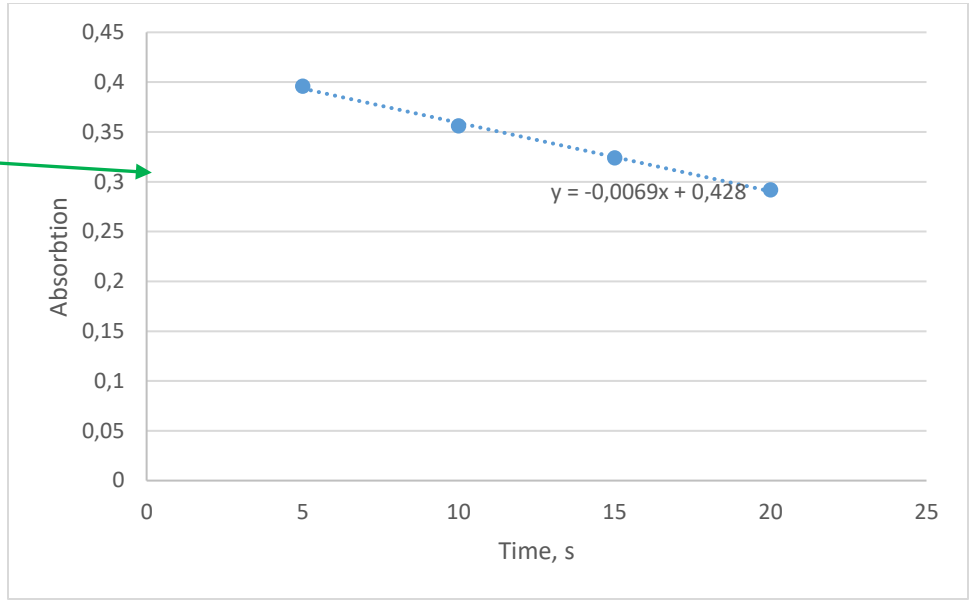

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,006x + 0,424
0
5
10
15
20
25
Time, s

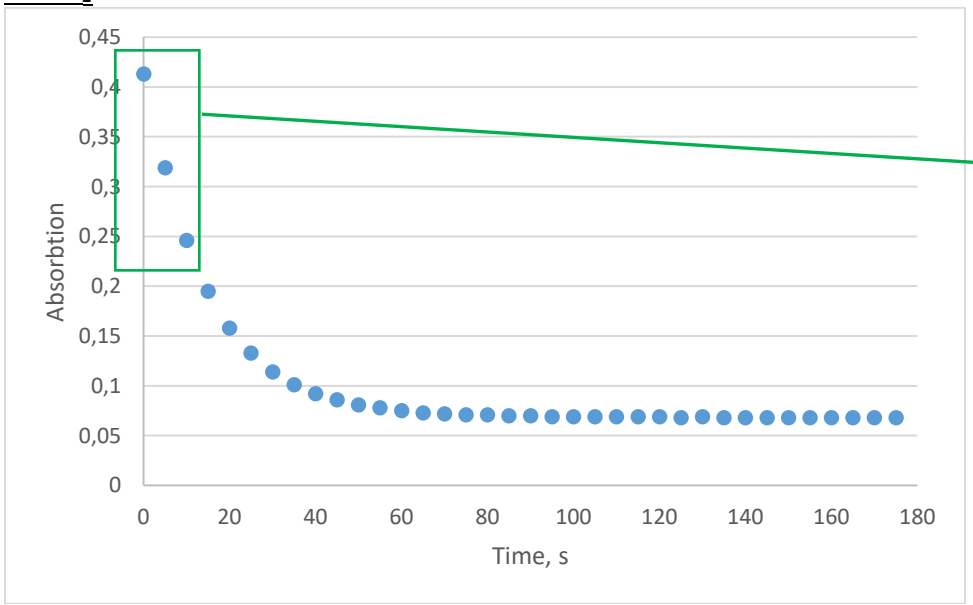

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

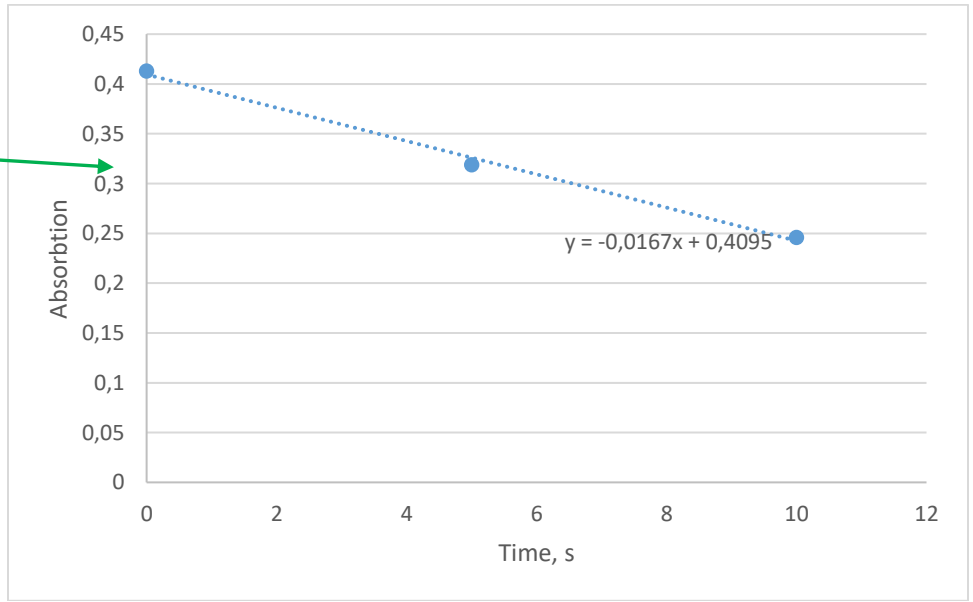

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,0068x + 0,439
0
5
10
15
20
25
Time, s

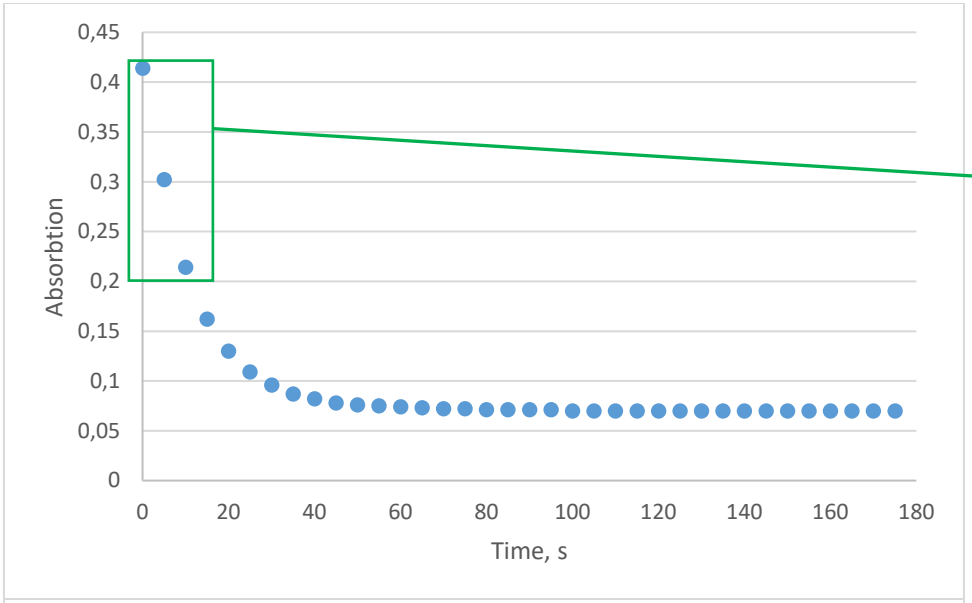

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

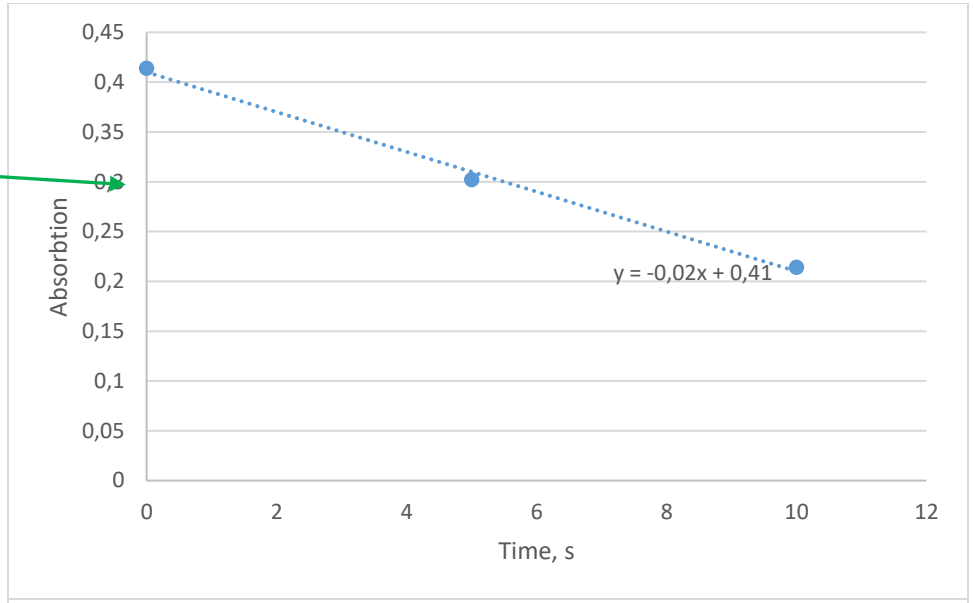

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,0069x + 0,428
0
5
10
15
20
25
Time, s

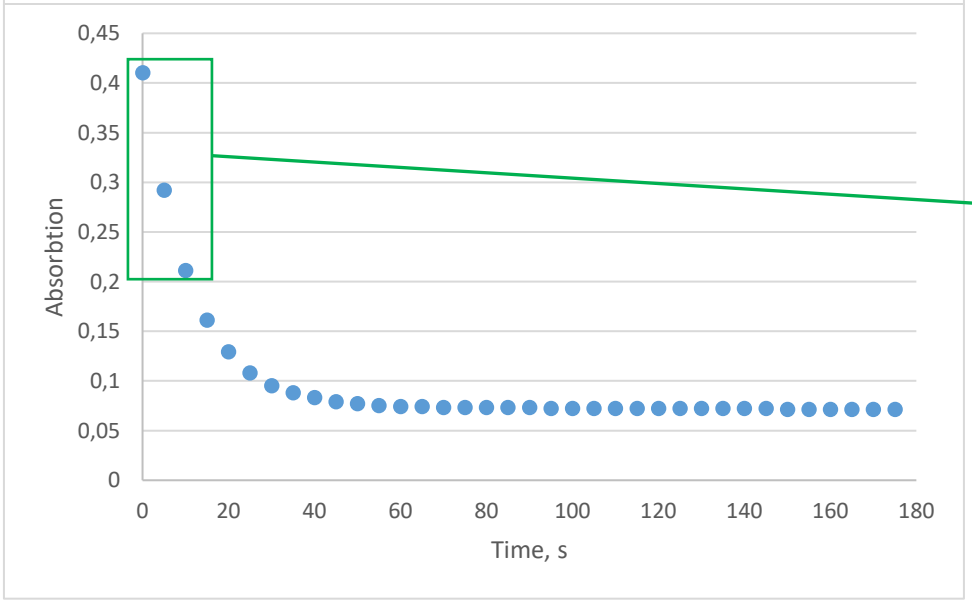
Ph-NH$_2$

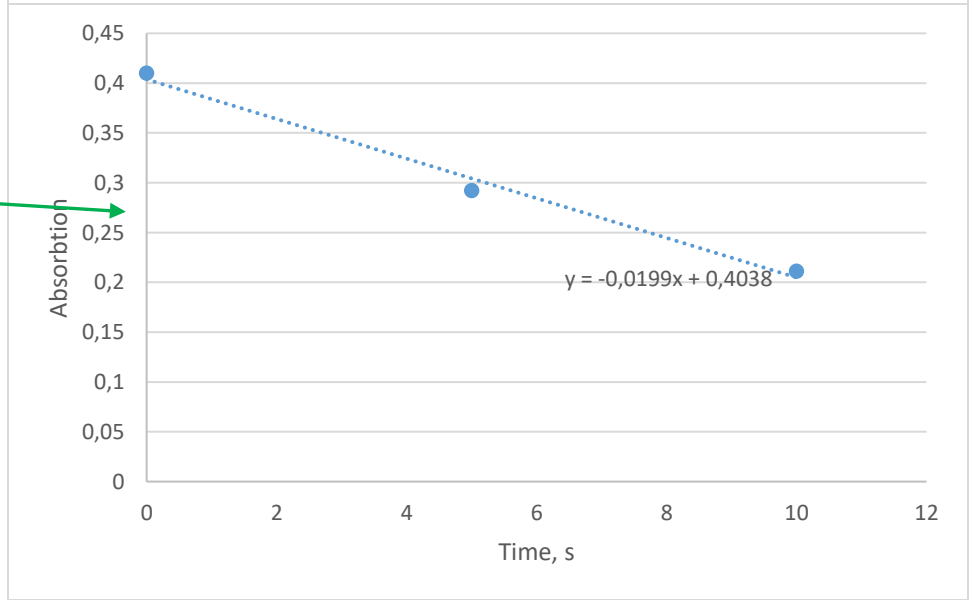

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,0167x + 0,4095
0
2
4
6
8
10
12
Time, s

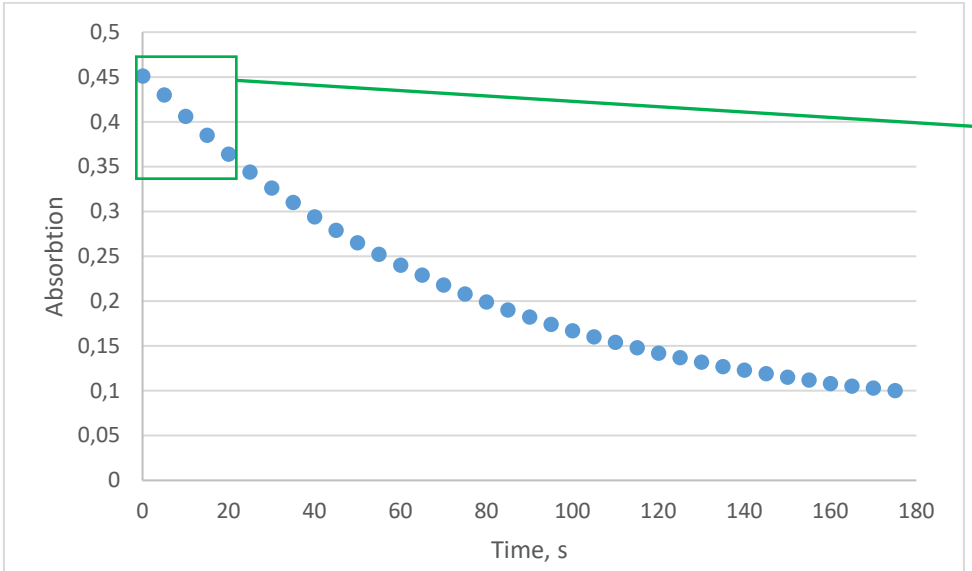

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

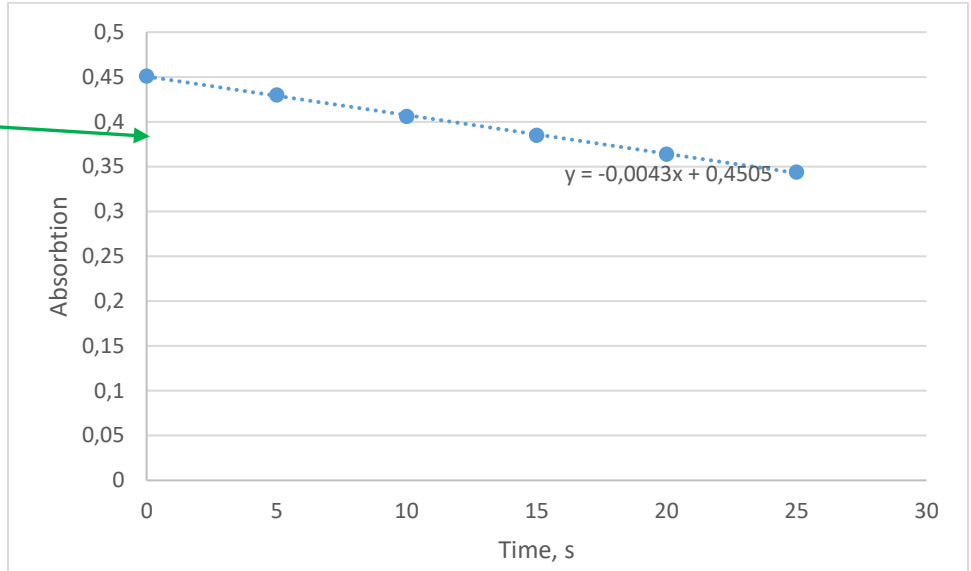

0,45
0,4
0,35
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,02x + 0,41
0
2
4
6
8
10
12
Time, s

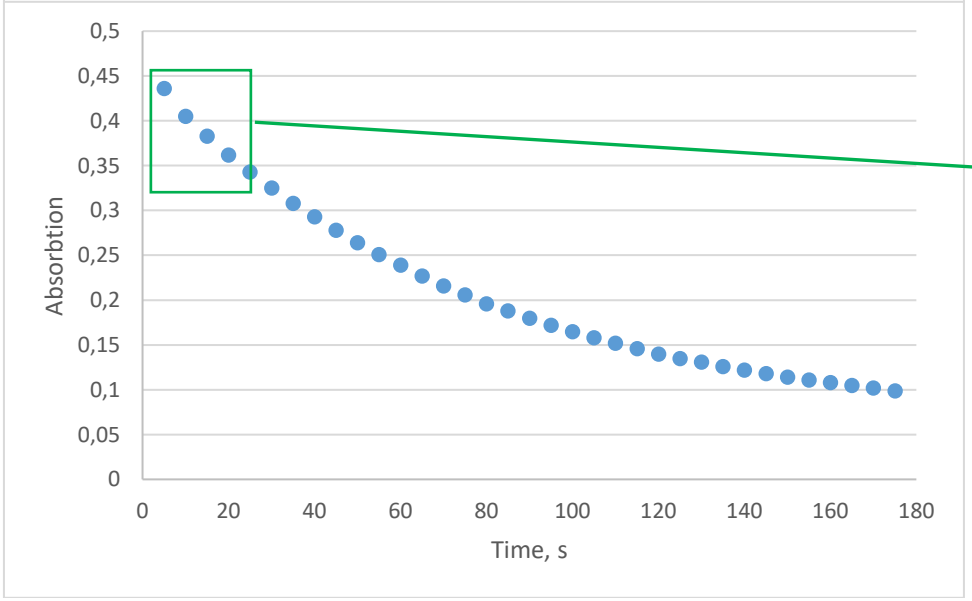

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

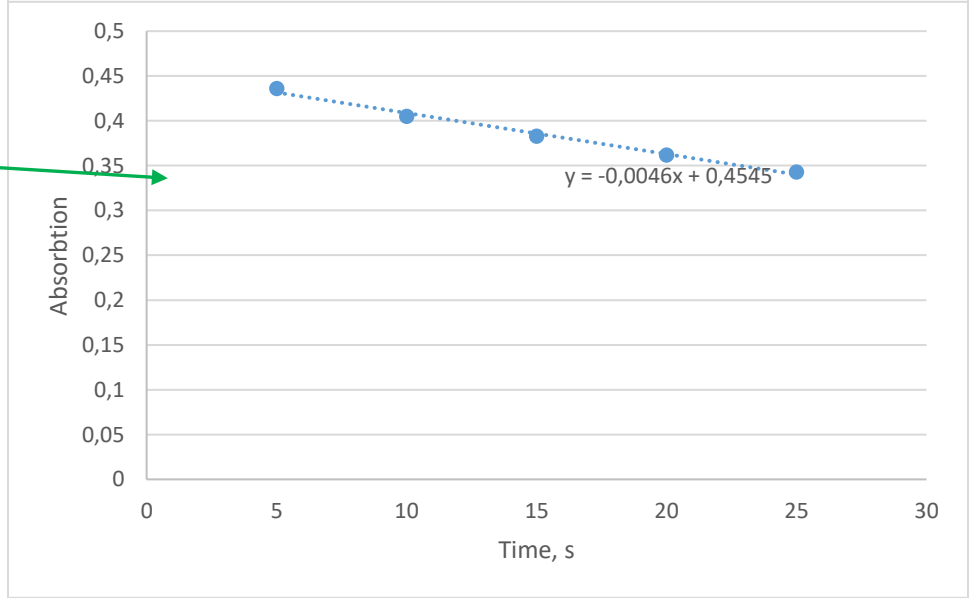

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,0199x + 0,4038
0
2
4
6
8
10
12
Time, s

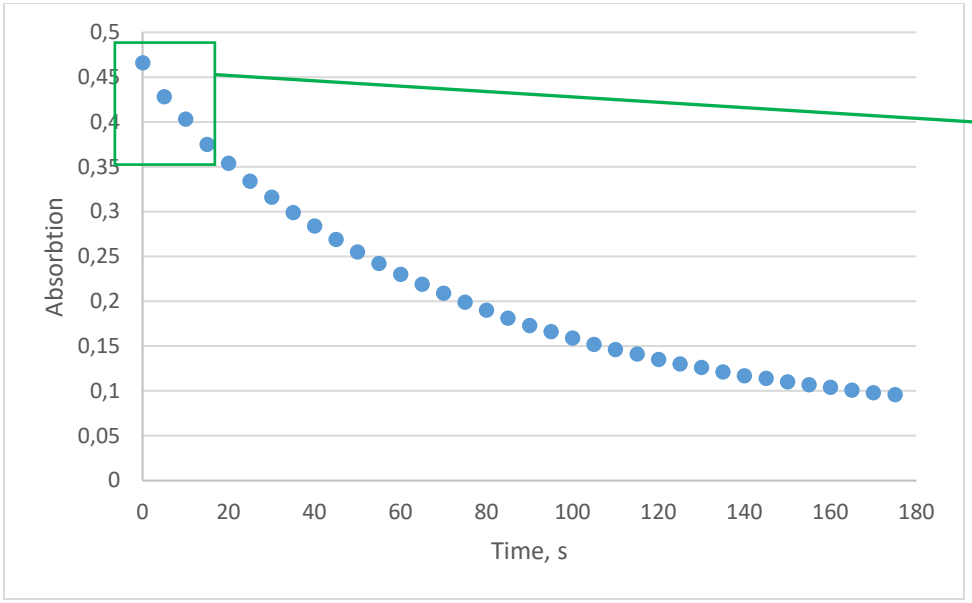
TFA:

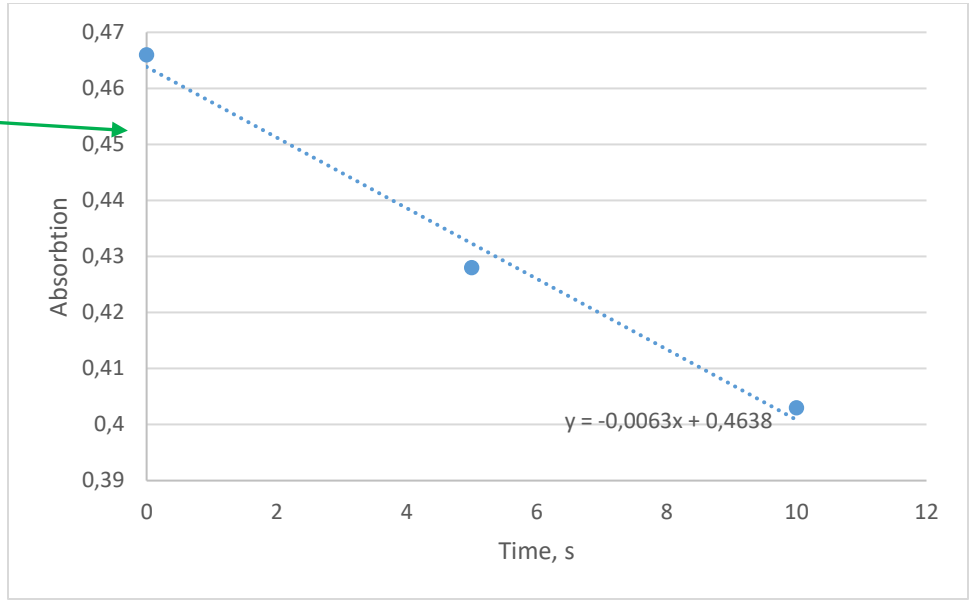

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,0043x + 0,4505
0
5
10
15
20
25
30
Time, s

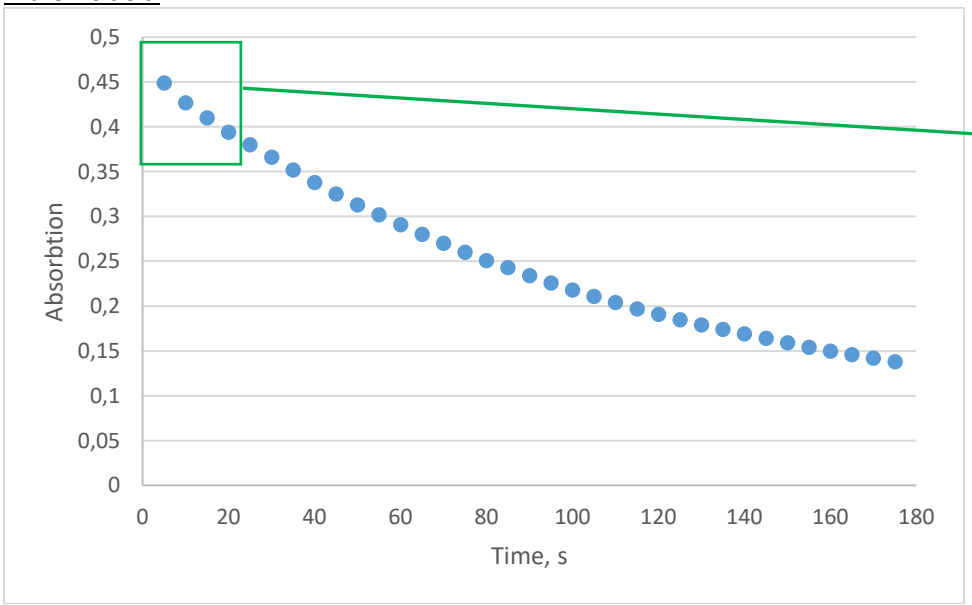

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

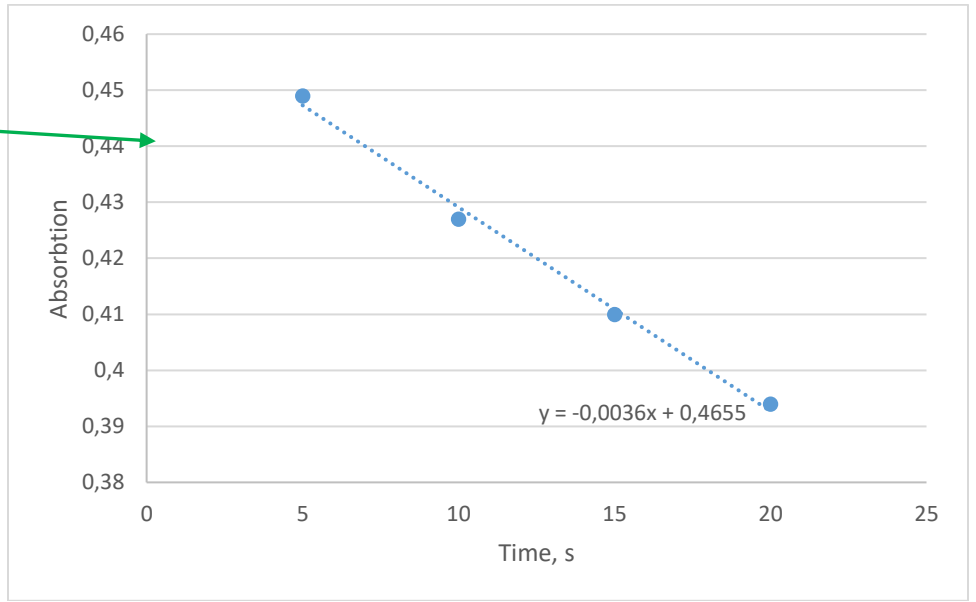

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,0046x + 0,4545
0
5
10
15
20
25
30
Time, s

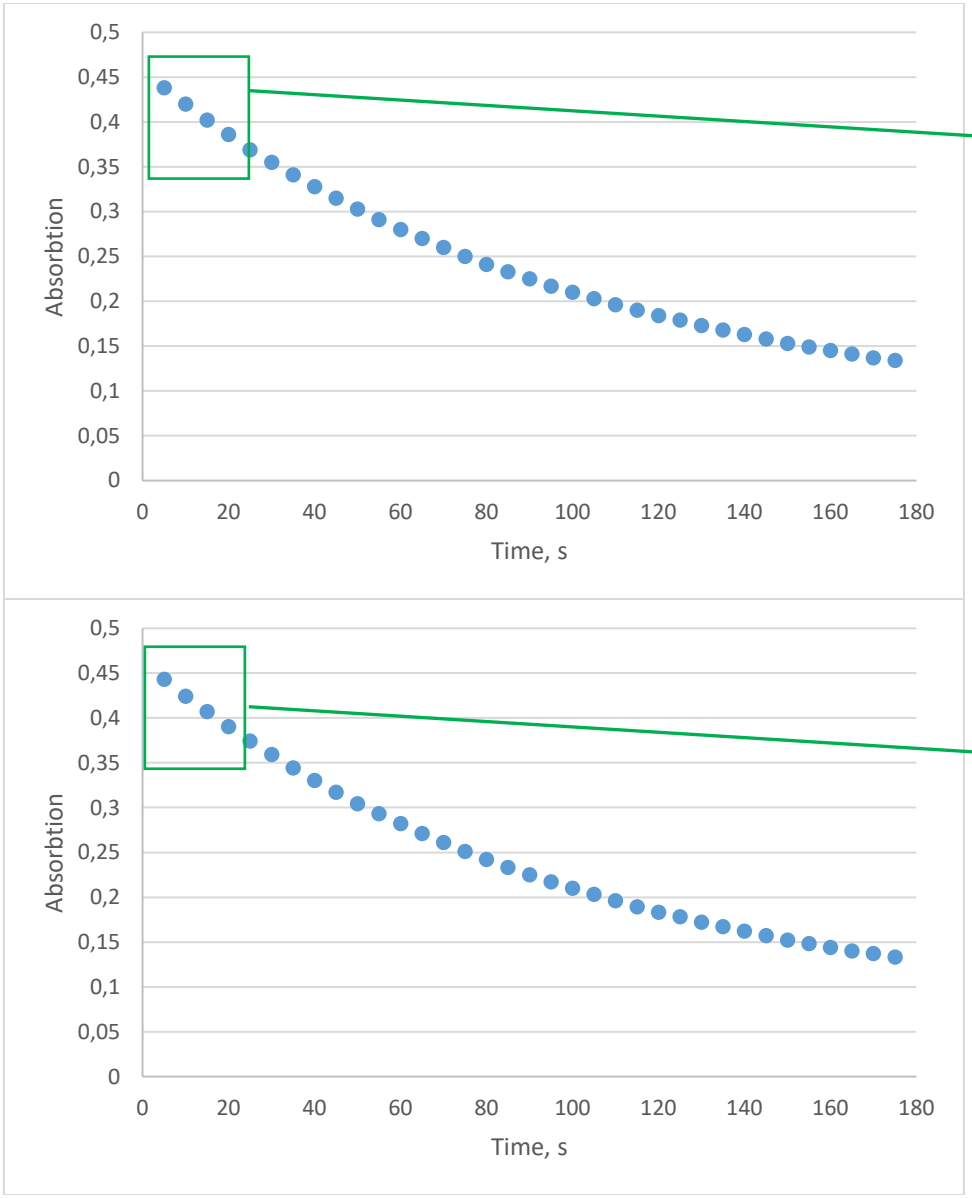


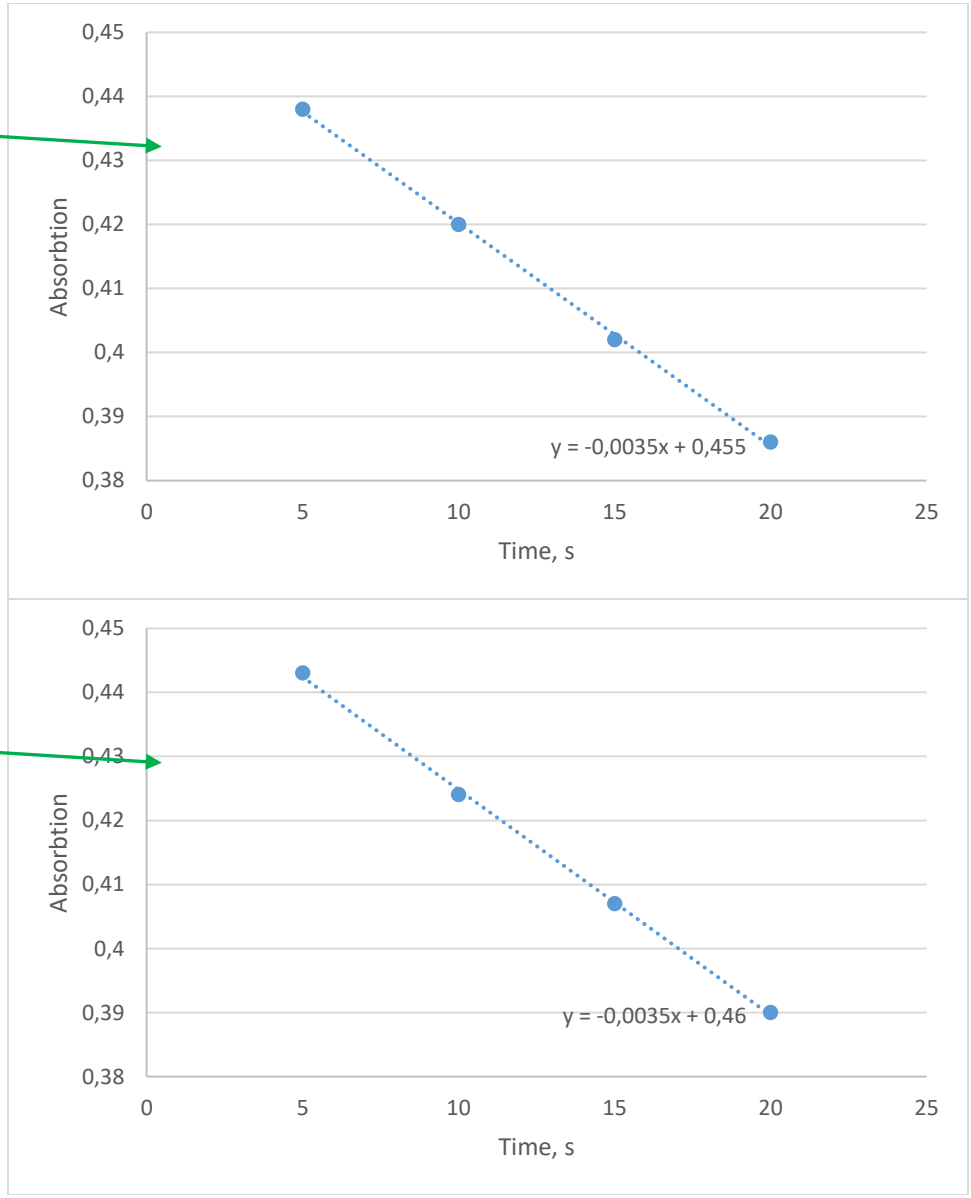


Malonic acid





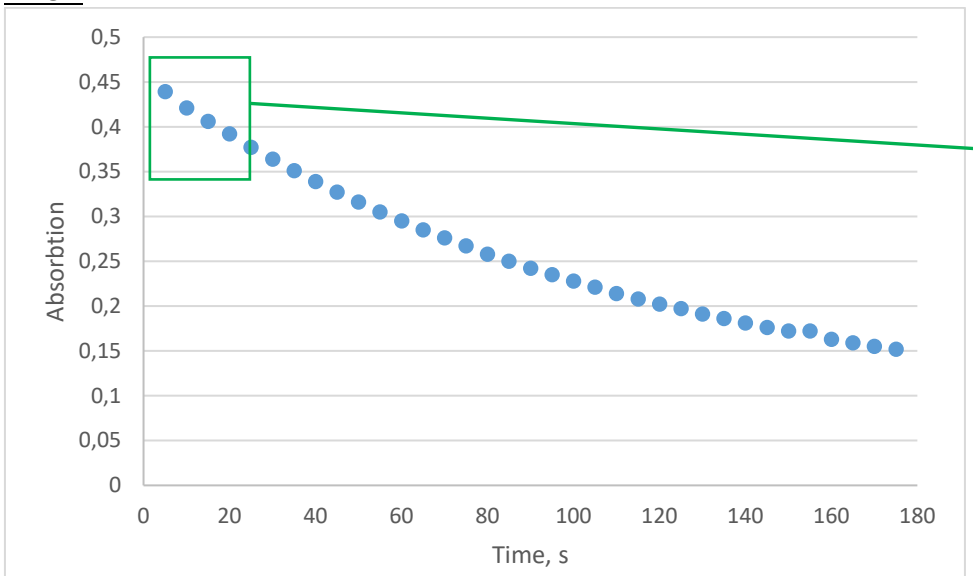

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

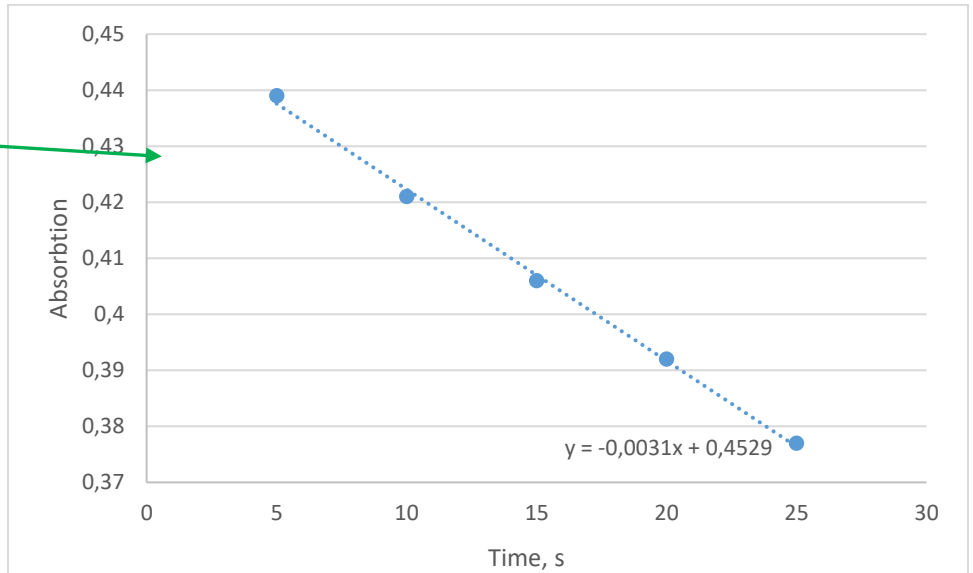

0,45
0,44
0,43
0,42
0,41
0,4
0,39
0,38
Absorbtion
y = -0,0035x + 0,455
0
5
10
15
20
25
Time, s

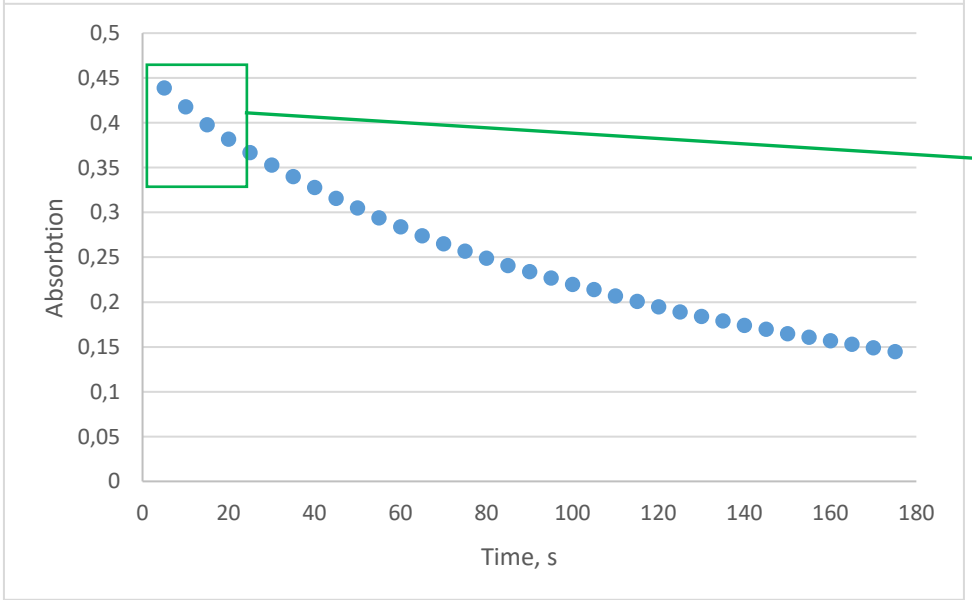
0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

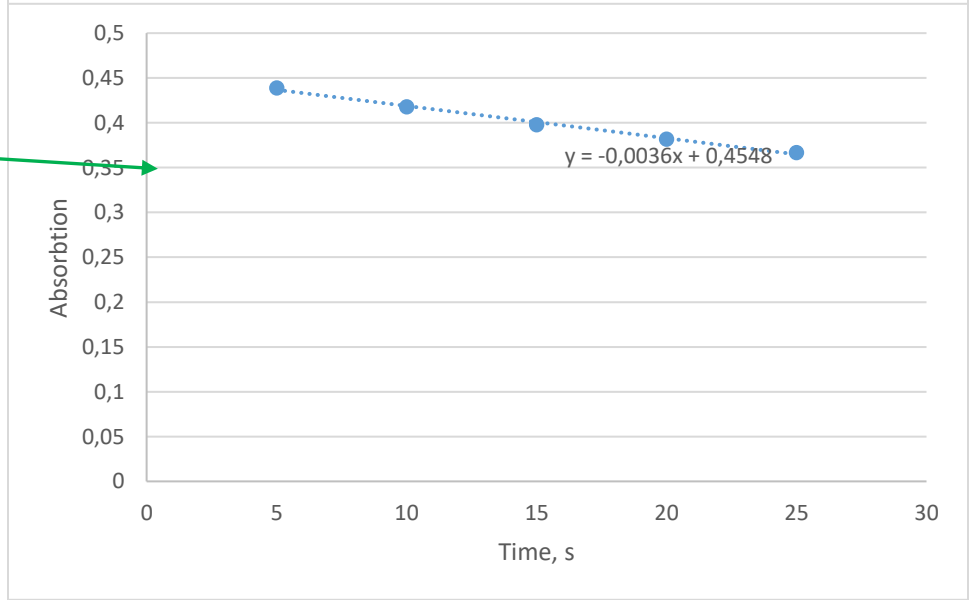
0,45
0,44
0,43
0,42
0,41
0,4
0,39
0,38
Absorbtion
y = -0,0035x + 0,46
0
5
10
15
20
25
Time, s

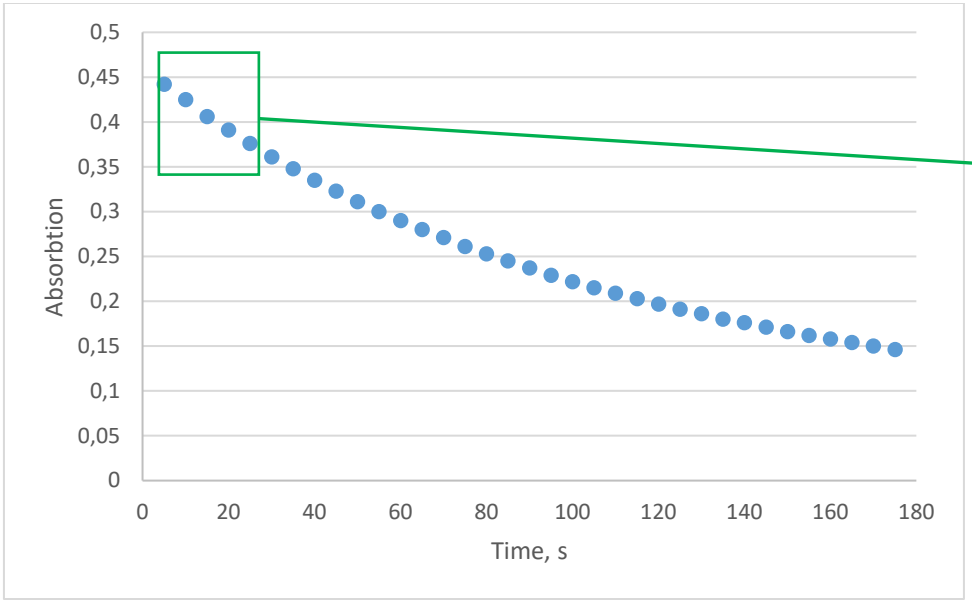
Ph-OH

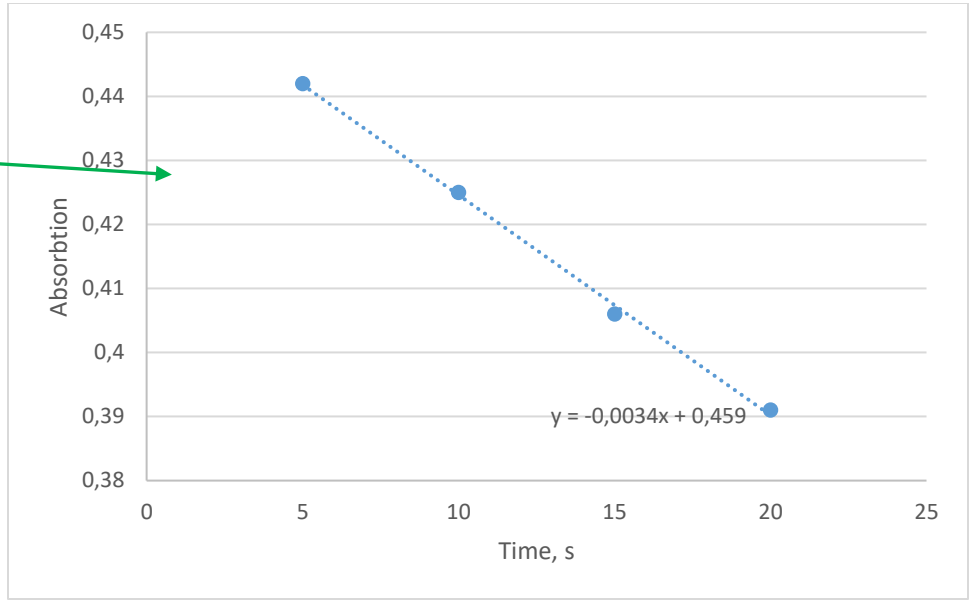

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,45
0,44
0,43
0,42
0,41
0,4
0,39
0,38
0,37
Absorbtion
y = -0,0031x + 0,4529
0
5
10
15
20
25
30
Time, s


0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

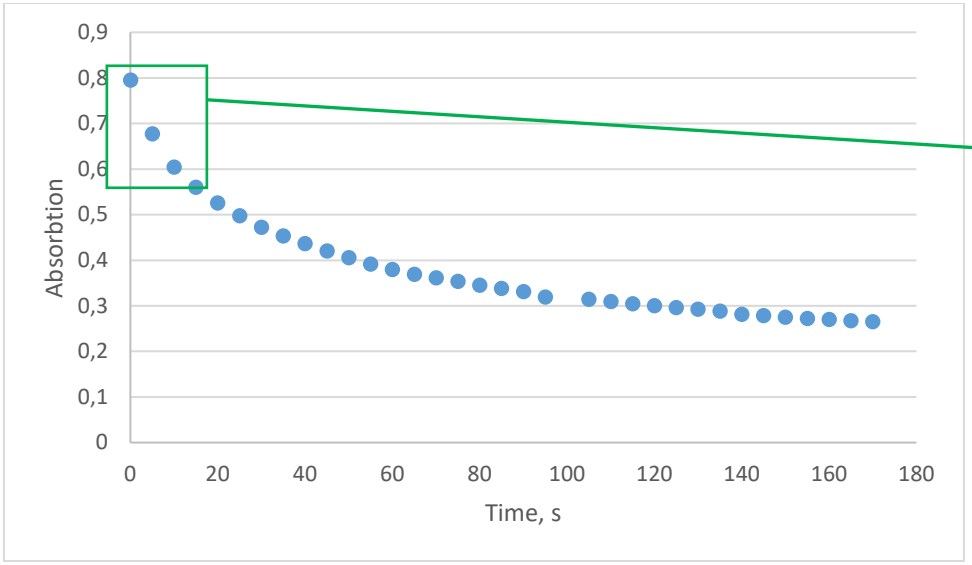

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,0036x + 0,4548
0
5
10
15
20
25
30
Time, s

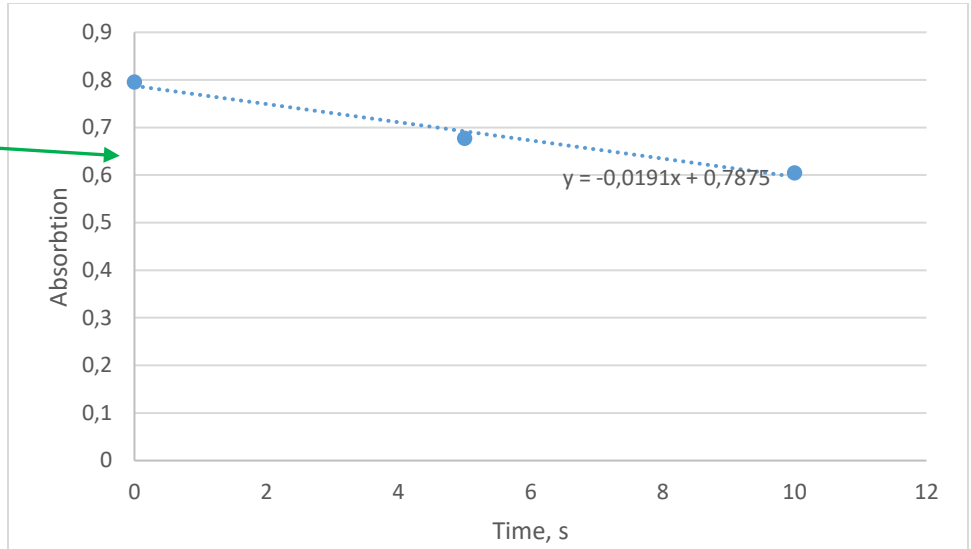

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

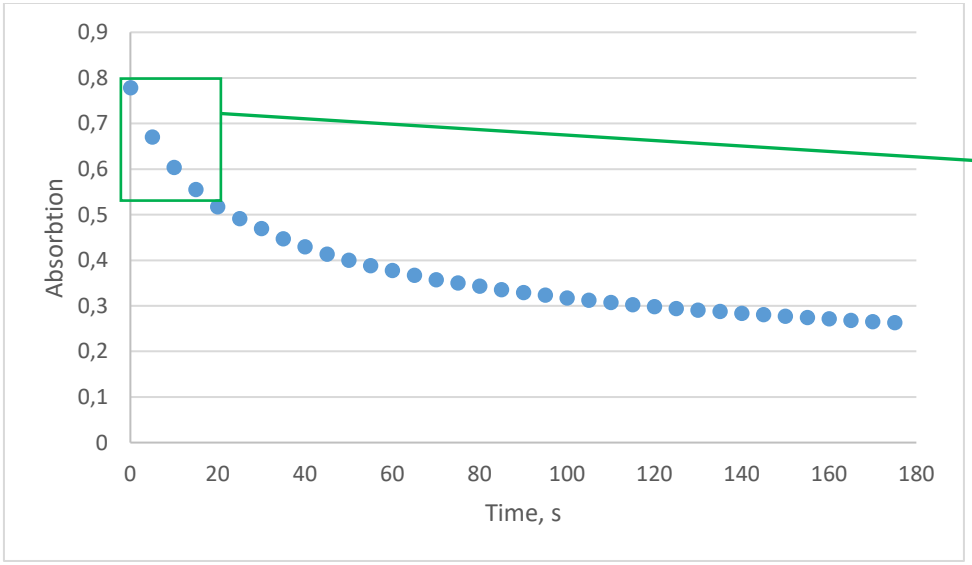

0,45
0,44
0,43
0,42
0,41
0,4
0,39
0,38
Absorbtion
y = -0,0034x + 0,459
0
5
10
15
20
25
Time, s

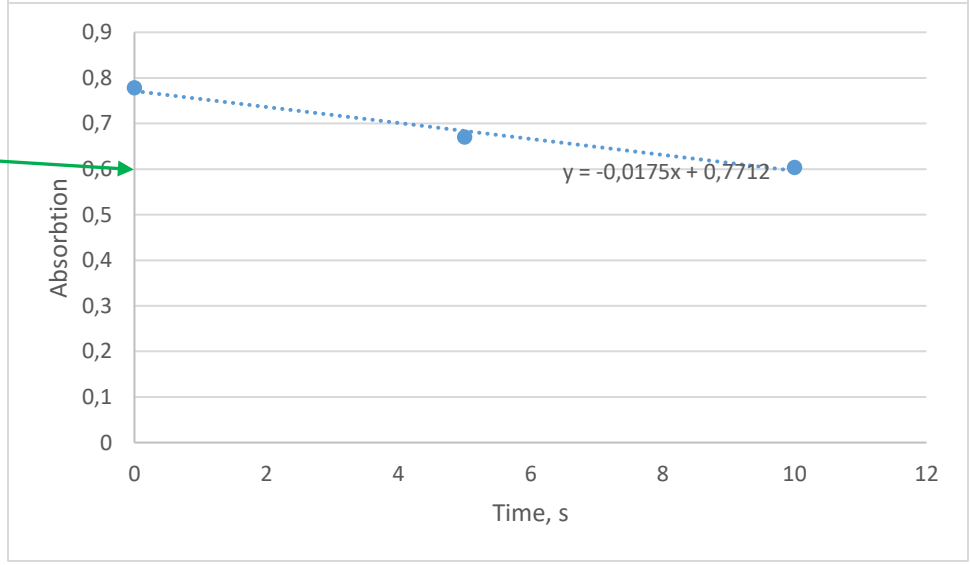
15.KINETIC CURVES FOR THE REACTION BETWEEN DPPH AND COMPOUND 12e (IN VARIOUS SOLVENTS)

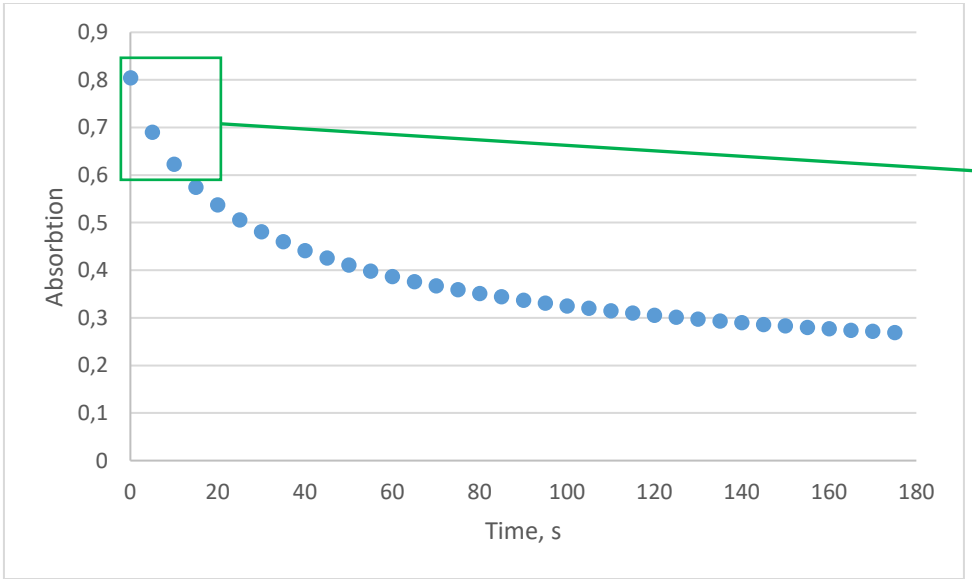
Acetone

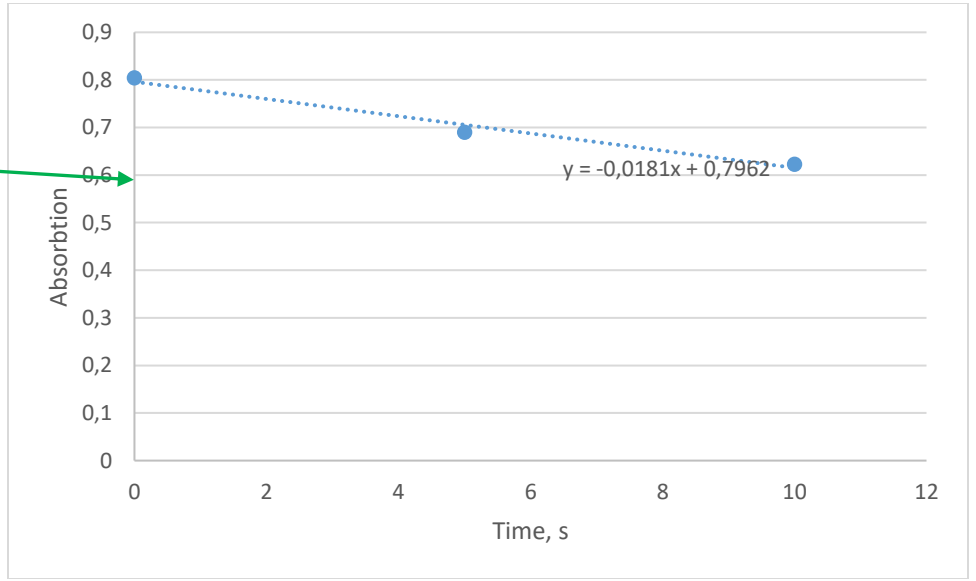




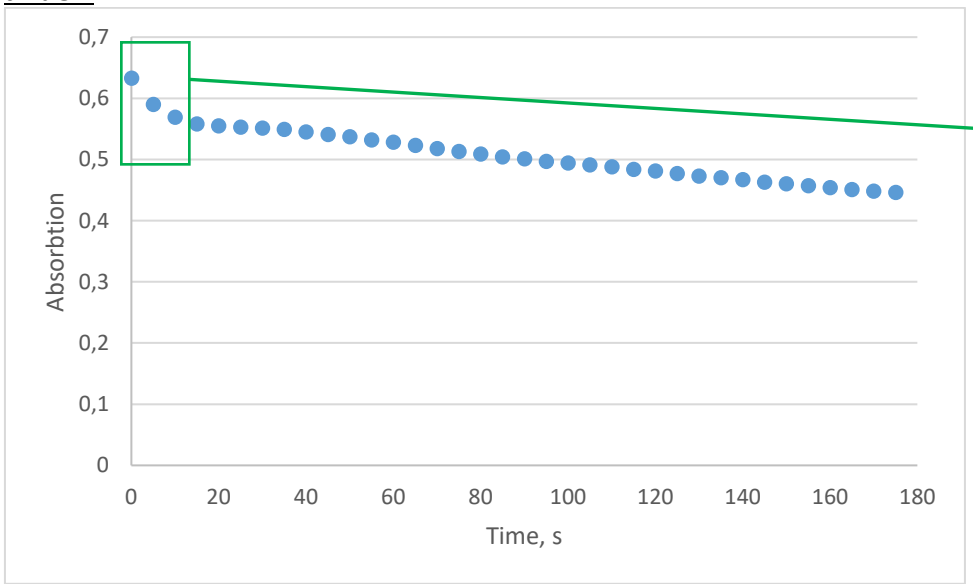


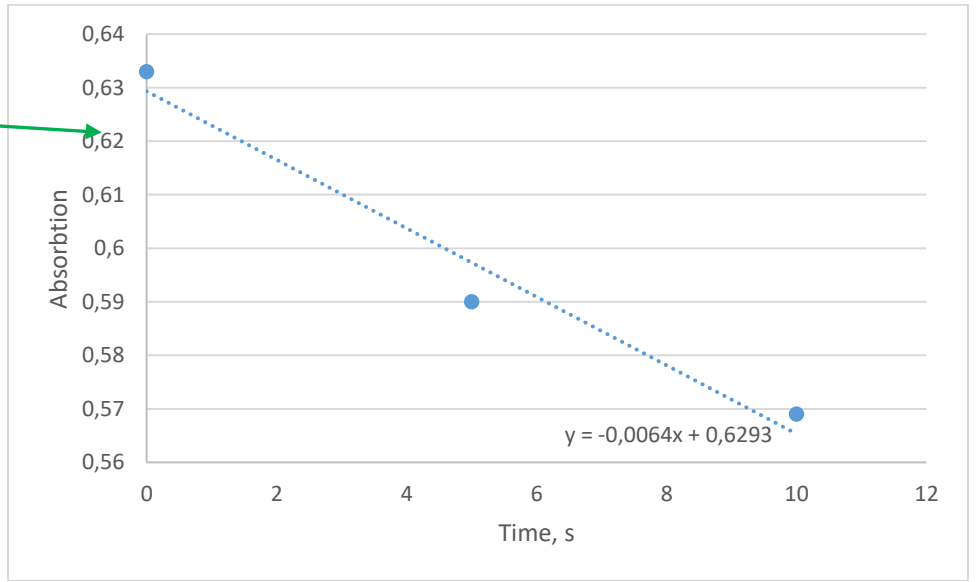


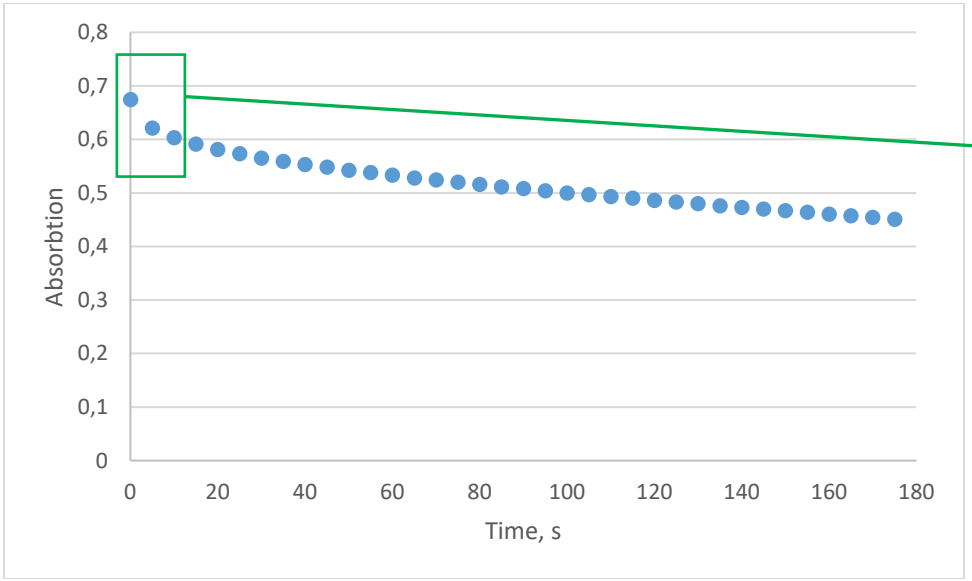

Absorbtion
Time, s
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
0
20
40
60
80
100
120
140
160
180

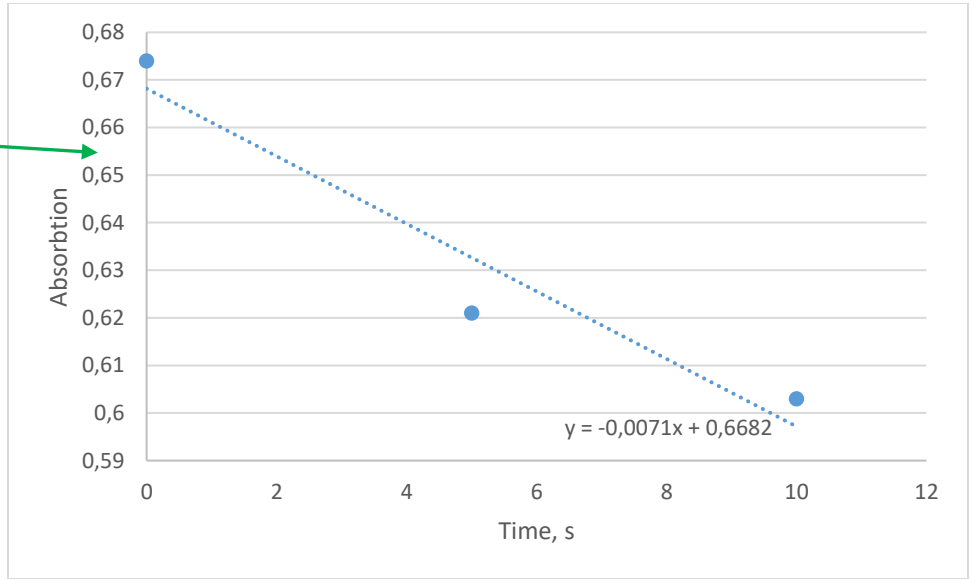

y = -0,0181x + 0,7962
Absorbtion
Time, s
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
0
2
4
6
8
10
12

t-BuOH

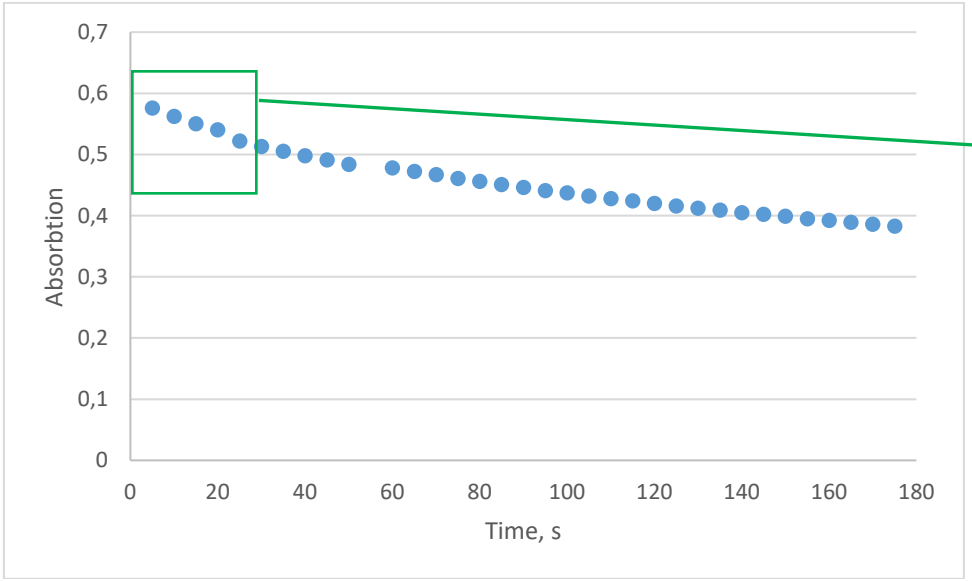

Absorbtion
Time, s
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
0
20
40
60
80
100
120
140
160
180

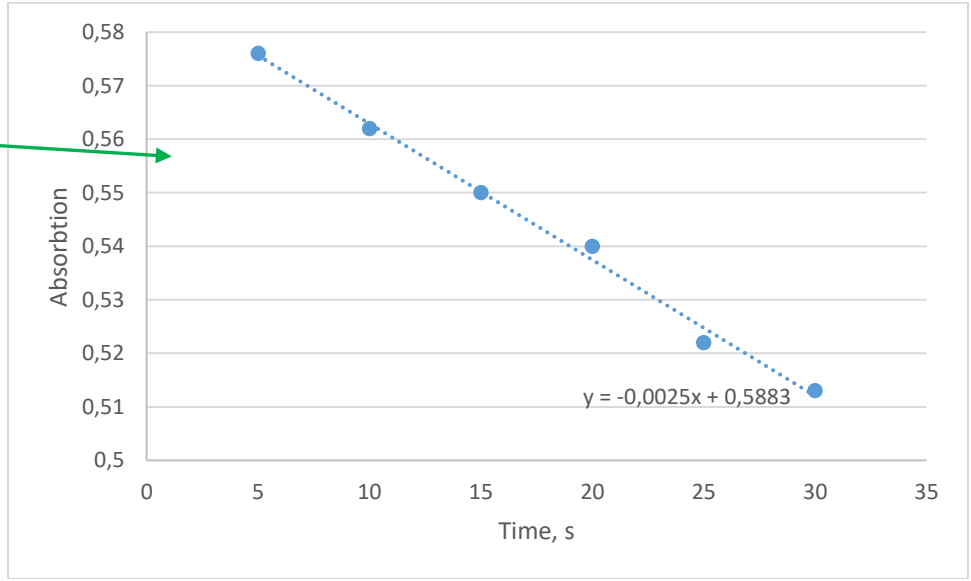

y = -0,0064x + 0,6293
Absorbtion
Time, s
0,64
0,63
0,62
0,61
0,6
0,59
0,58
0,57
0,56
0
2
4
6
8
10
12

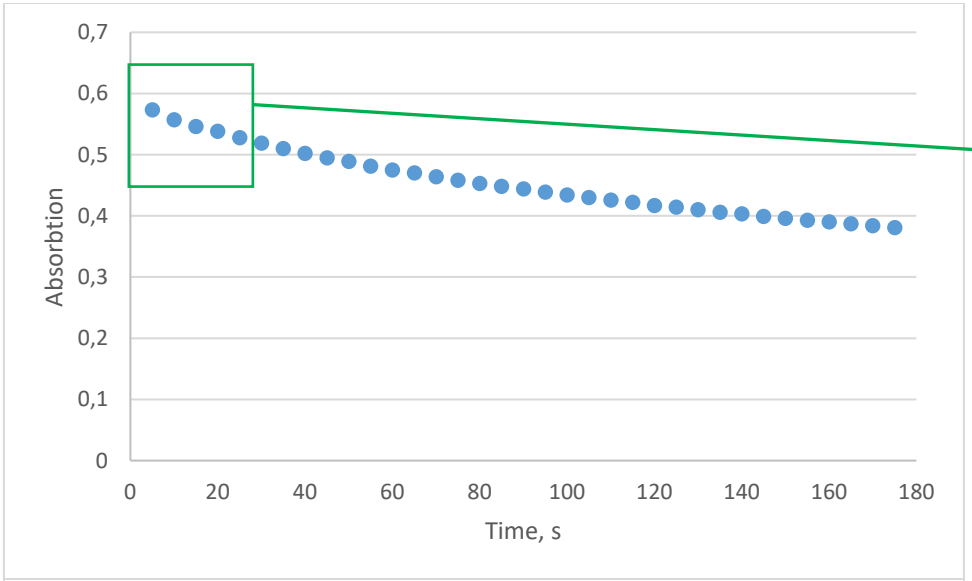

0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

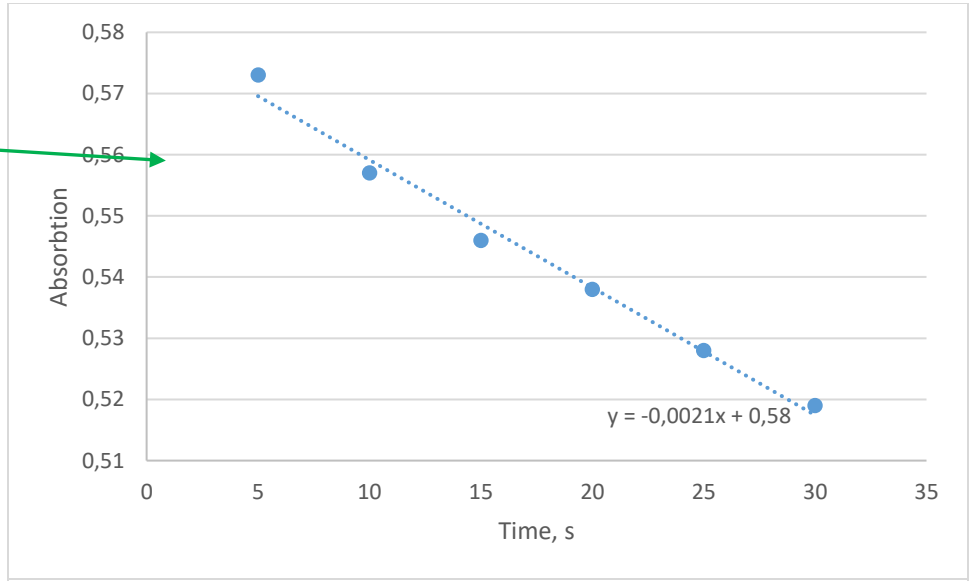

0,68
0,67
0,66
0,65
0,64
0,63
0,62
0,61
0,6
0,59
Absorbtion
y = -0,0071x + 0,6682
0
2
4
6
8
10
12
Time, s

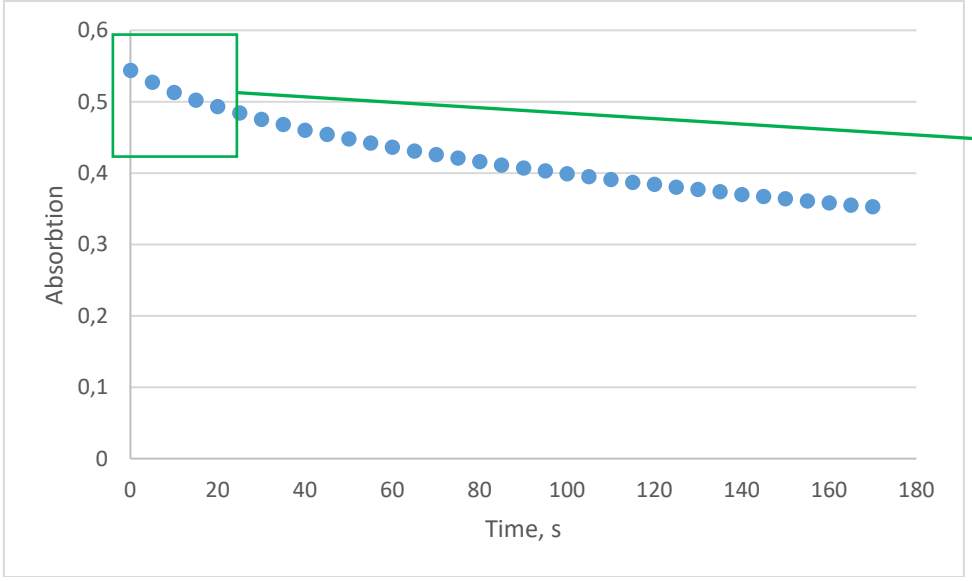
MeOH

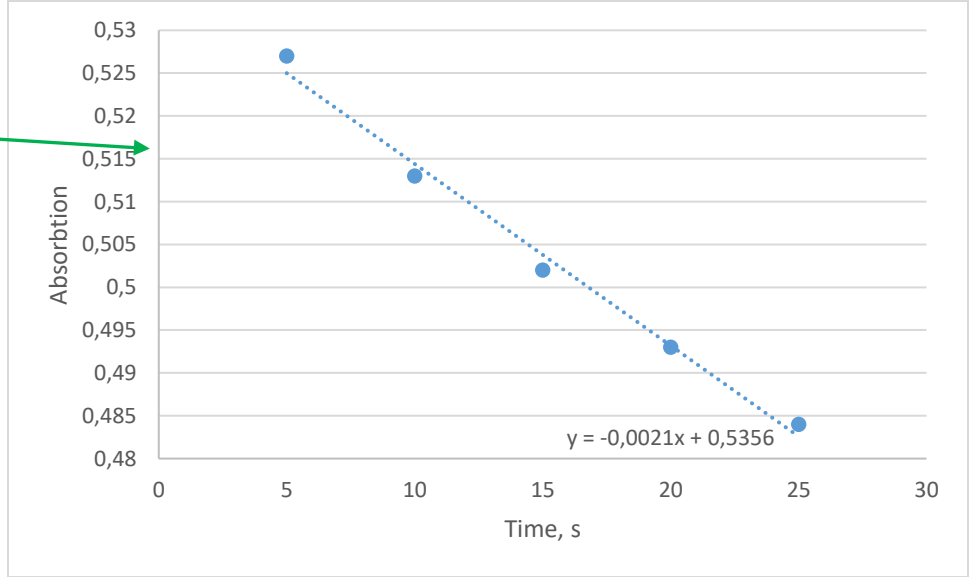

0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,58
0,57
0,56
0,55
0,54
0,53
0,52
0,51
0,5
Absorbtion
y = -0,0025x + 0,5883
0
5
10
15
20
25
30
35
Time, s

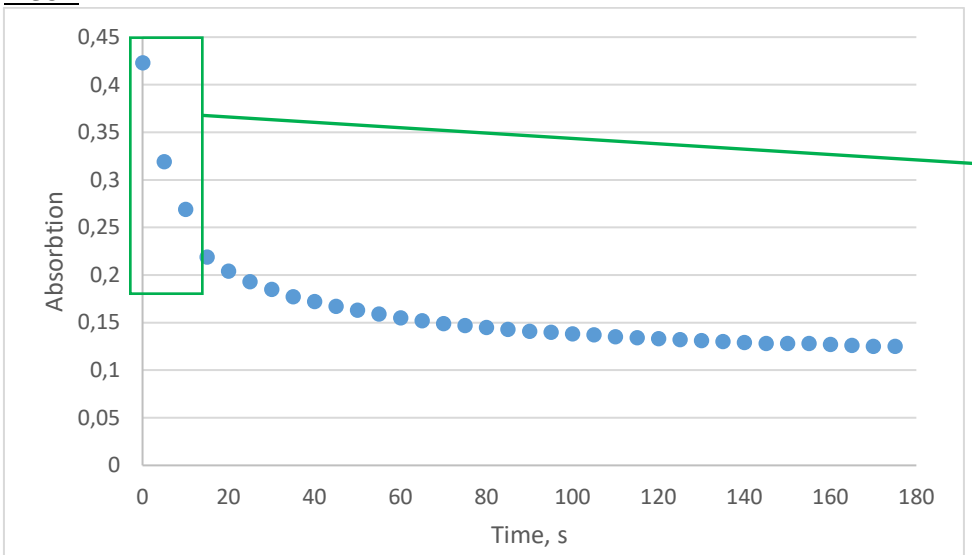

0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

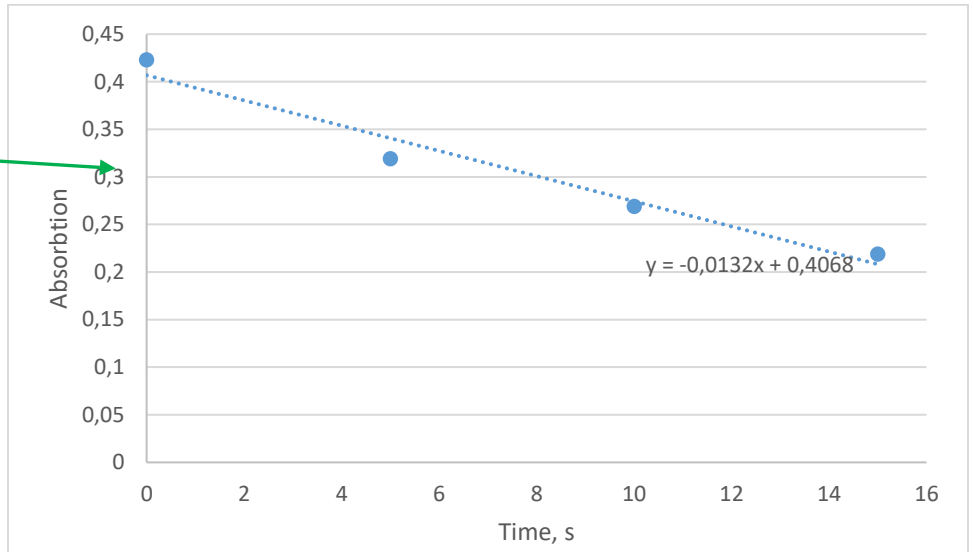

0,58
0,57
0,56
0,55
0,54
0,53
0,52
0,51
Absorbtion
y = -0,0021x + 0,58
0
5
10
15
20
25
30
35
Time, s

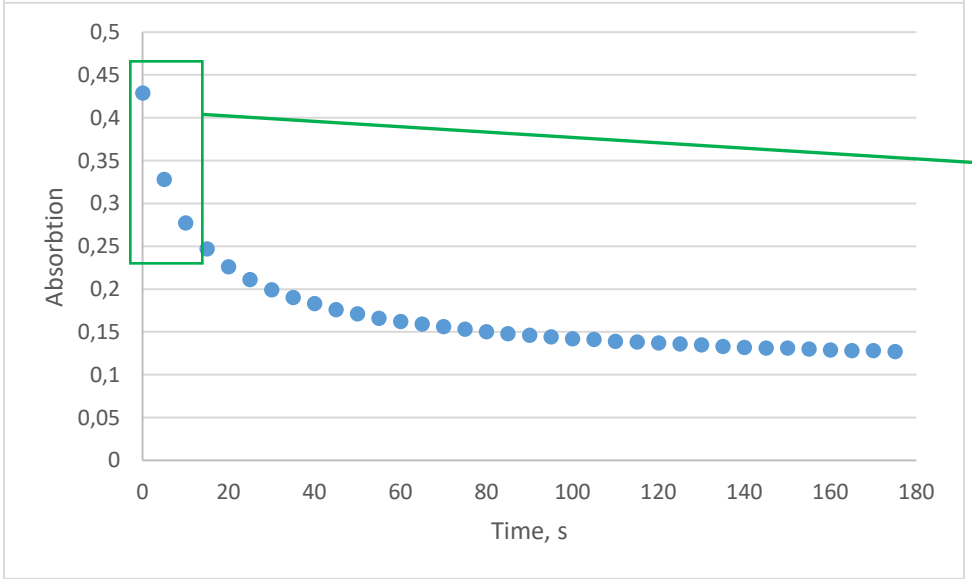

0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

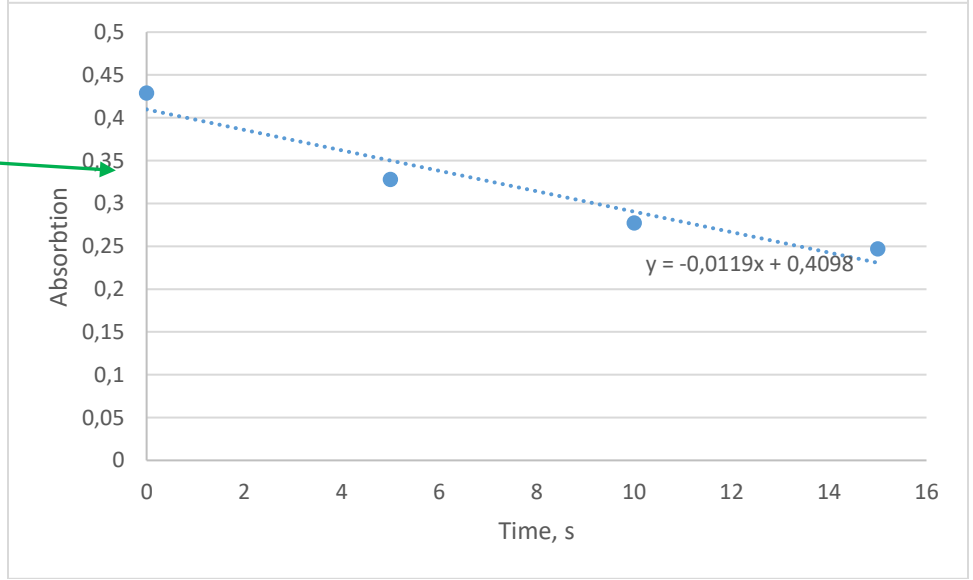

0,53
0,525
0,52
0,515
0,51
0,505
0,5
0,495
0,49
0,485
0,48
Absorbtion
y = -0,0021x + 0,5356
0
5
10
15
20
25
30
Time, s

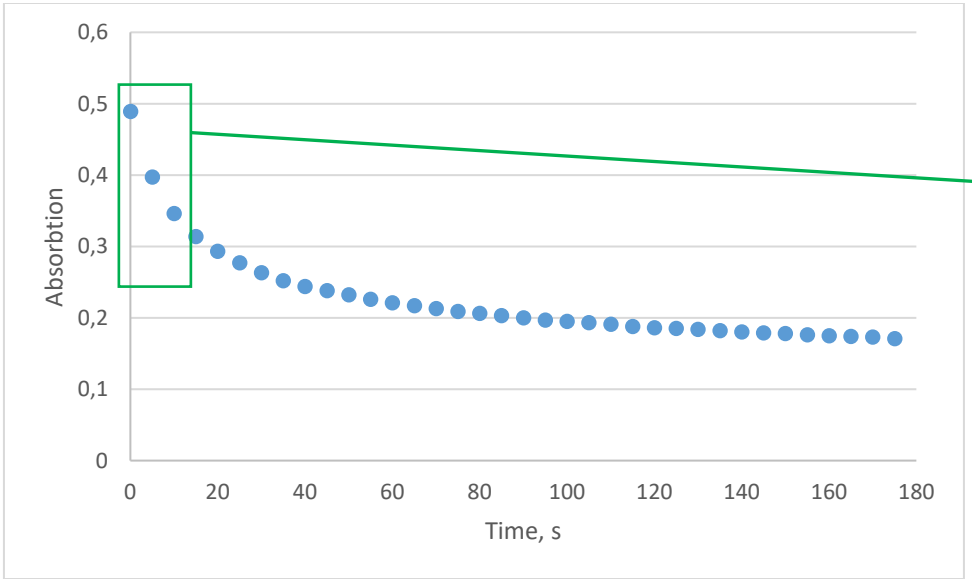
MeCN

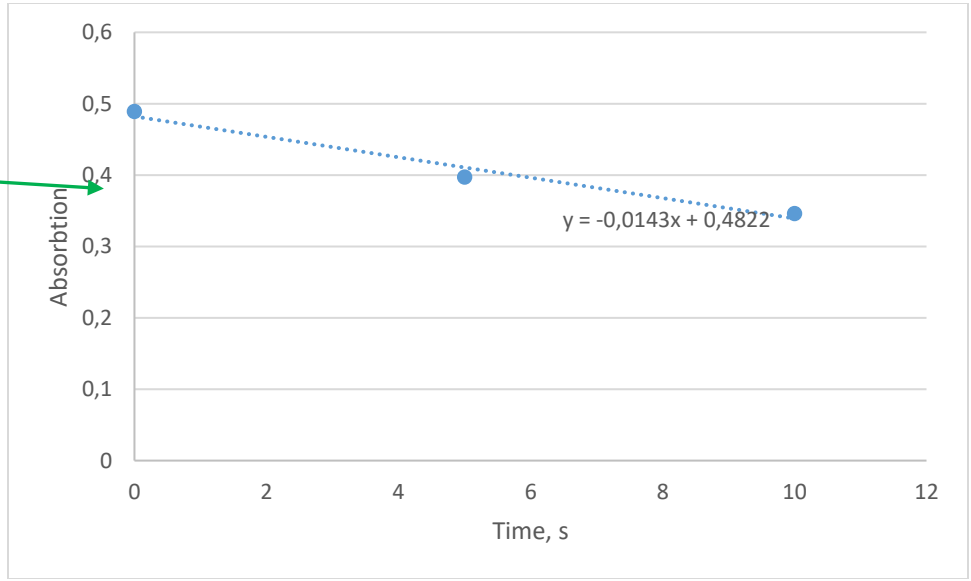

Absorbtion
Time, s
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
20
40
60
80
100
120
140
160
180


Absorbtion
Time, s
y = -0,0132x + 0,4068
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
2
4
6
8
10
12
14
16

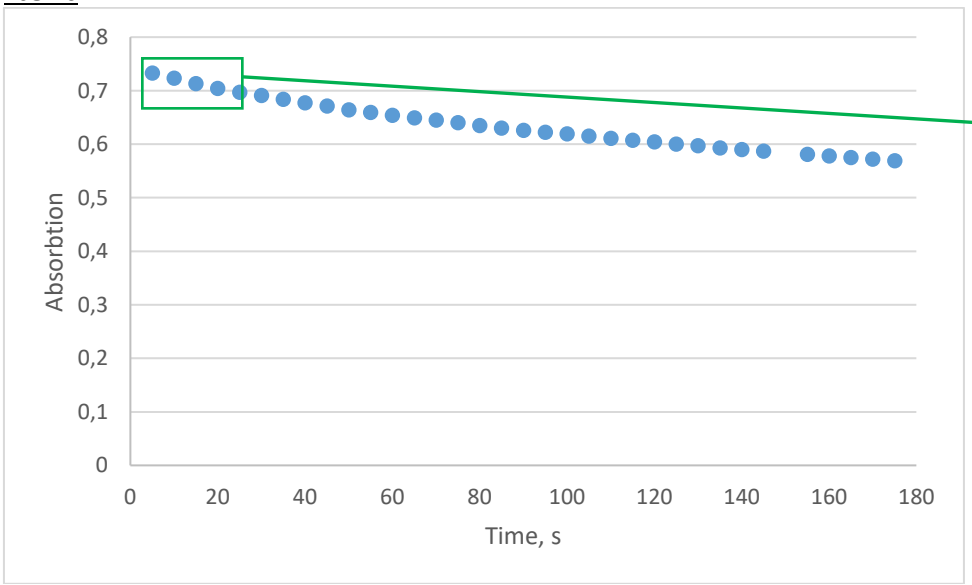

Absorbtion
Time, s
0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
20
40
60
80
100
120
140
160
180

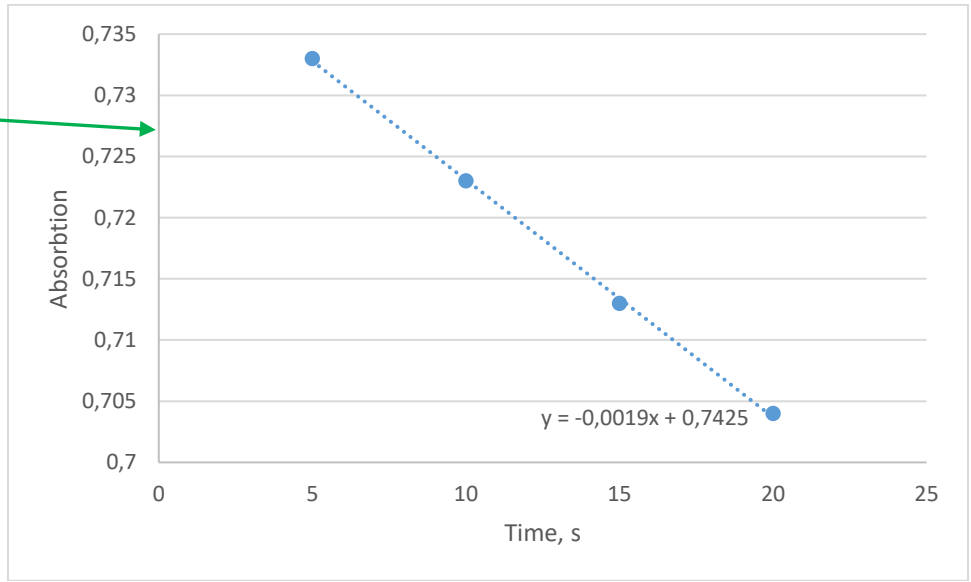

Absorbtion
Time, s
y = -0,0119x + 0,4098
0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
2
4
6
8
10
12
14
16

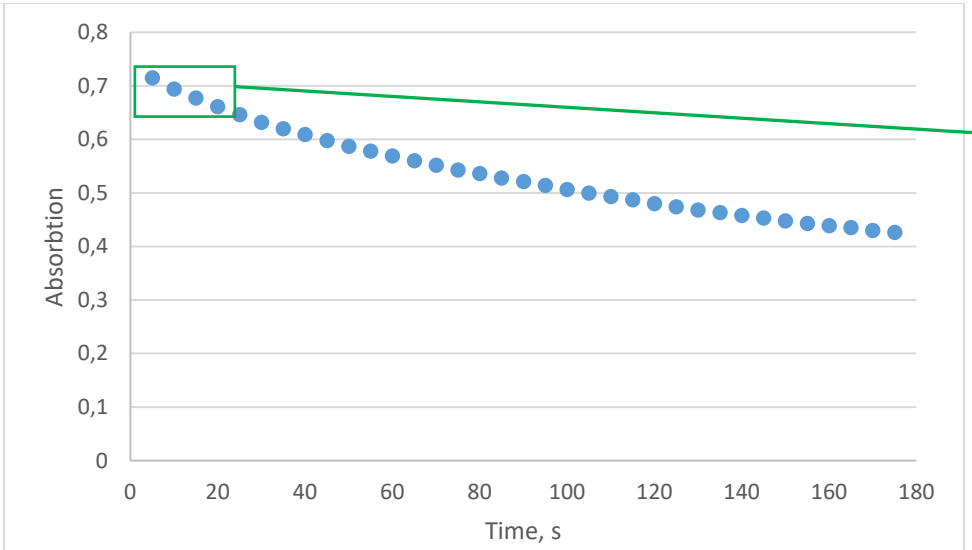

0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

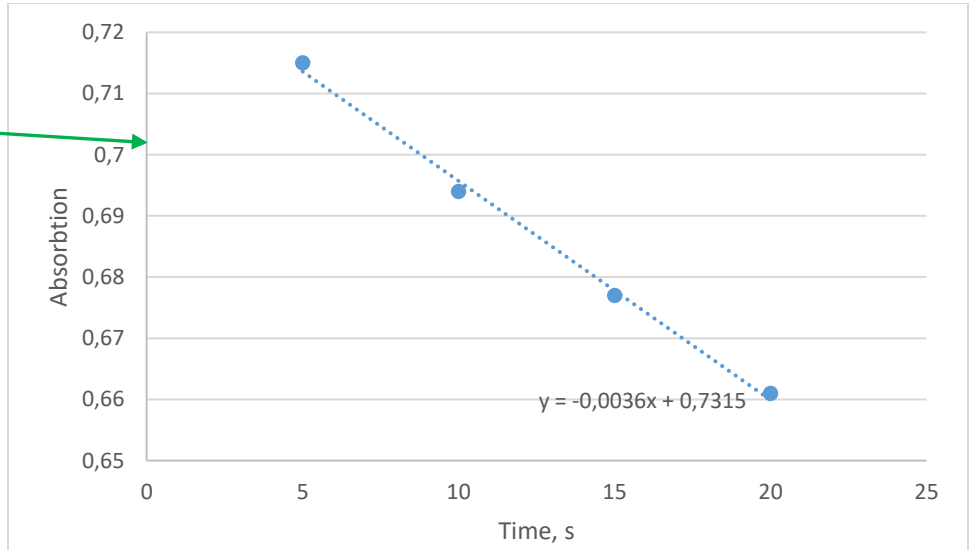

0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
y = -0,0143x + 0,4822
0
2
4
6
8
10
12
Time, s

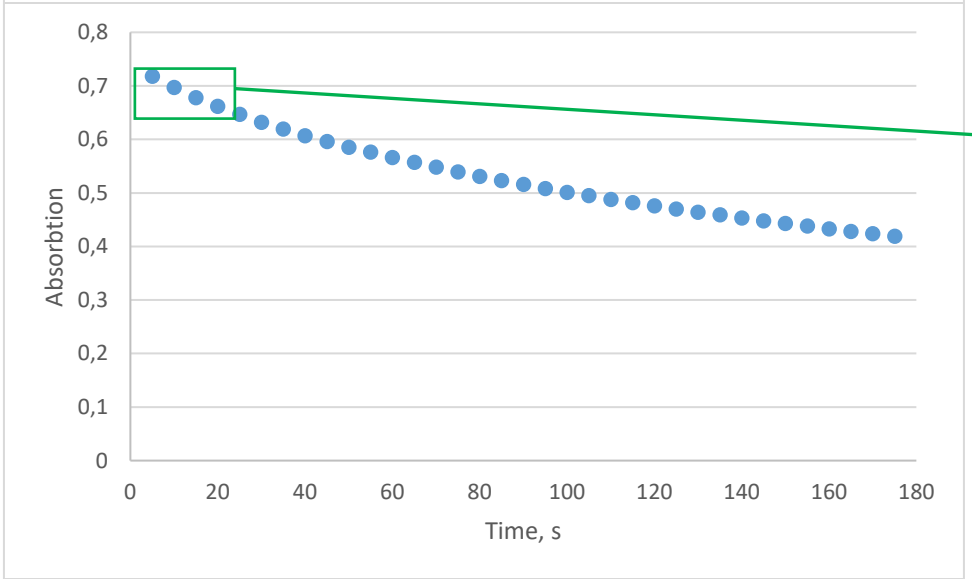
EtOAc

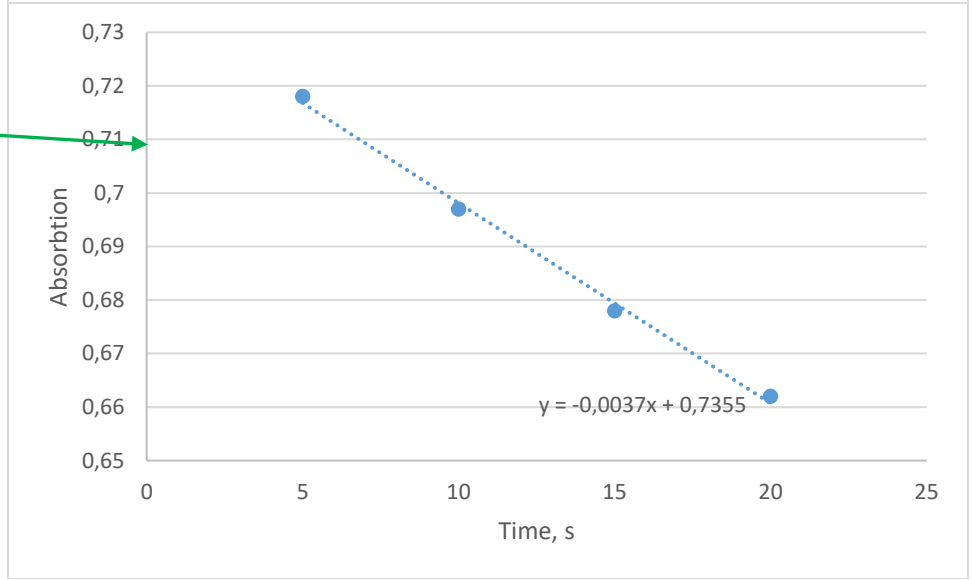

0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,735
0,73
0,725
0,72
0,715
0,71
0,705
0,7
Absorbtion
y = -0,0019x + 0,7425
0
5
10
15
20
25
Time, s

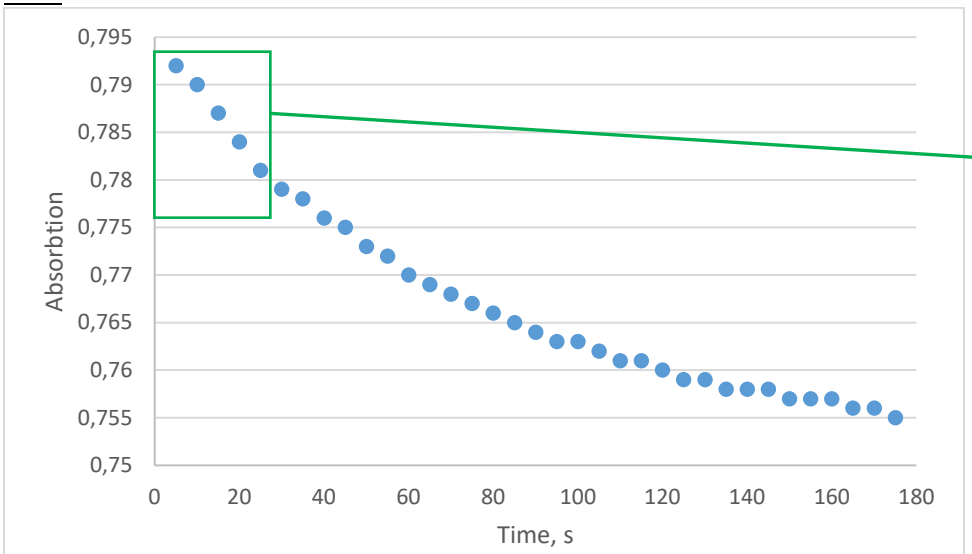

0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

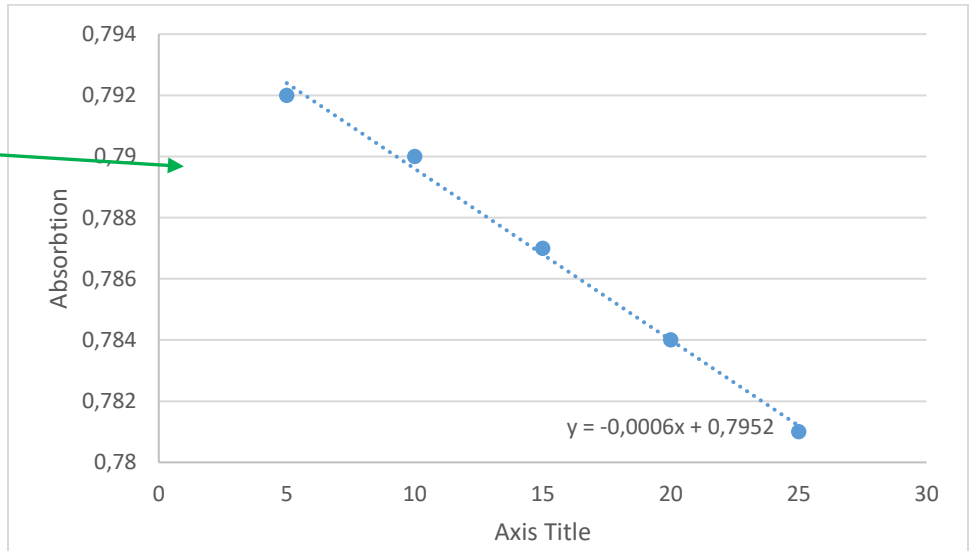

0,72
0,71
0,7
0,69
0,68
0,67
0,66
0,65
Absorbtion
y = -0,0036x + 0,7315
0
5
10
15
20
25
Time, s

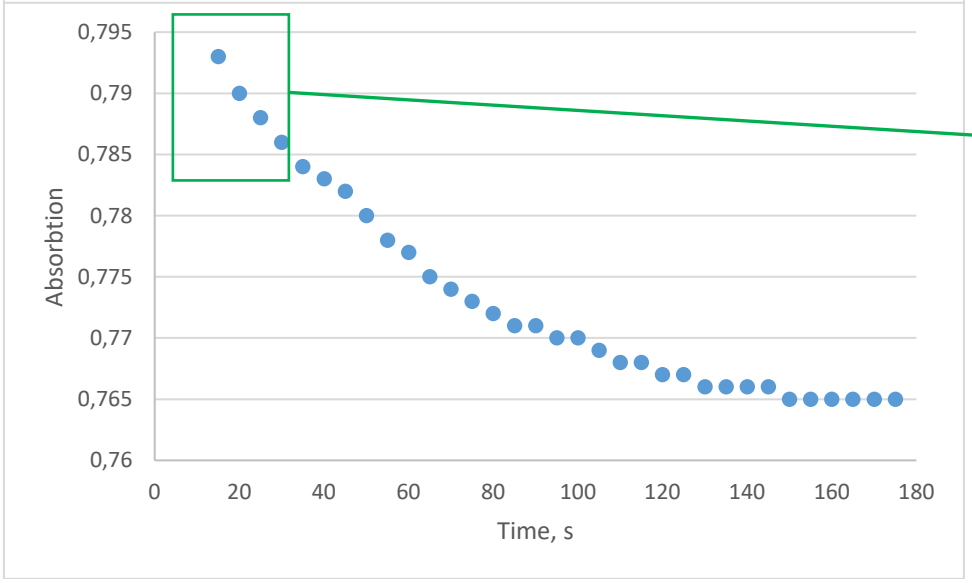

0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

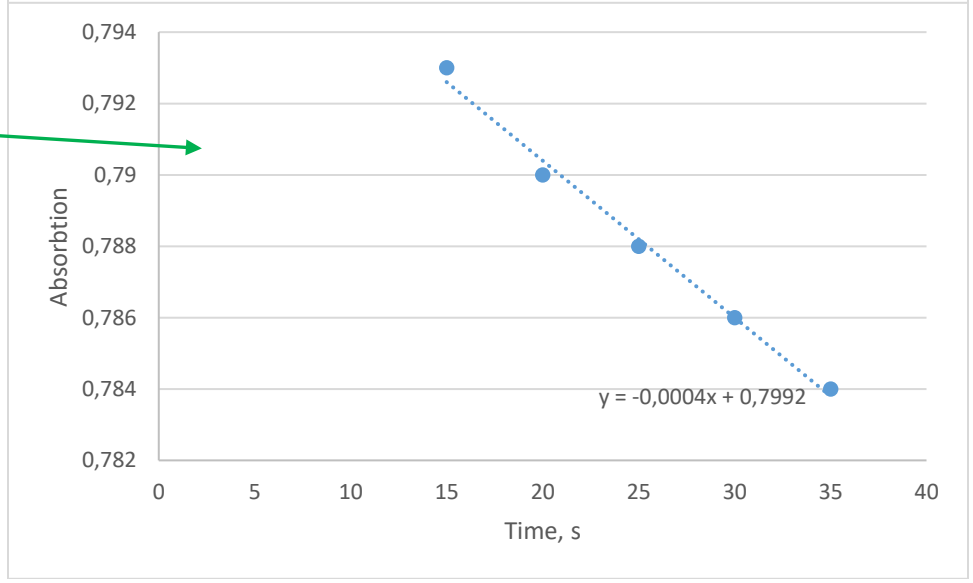

0,73
0,72
0,71
0,7
0,69
0,68
0,67
0,66
0,65
Absorbtion
y = -0,0037x + 0,7355
0
5
10
15
20
25
Time, s

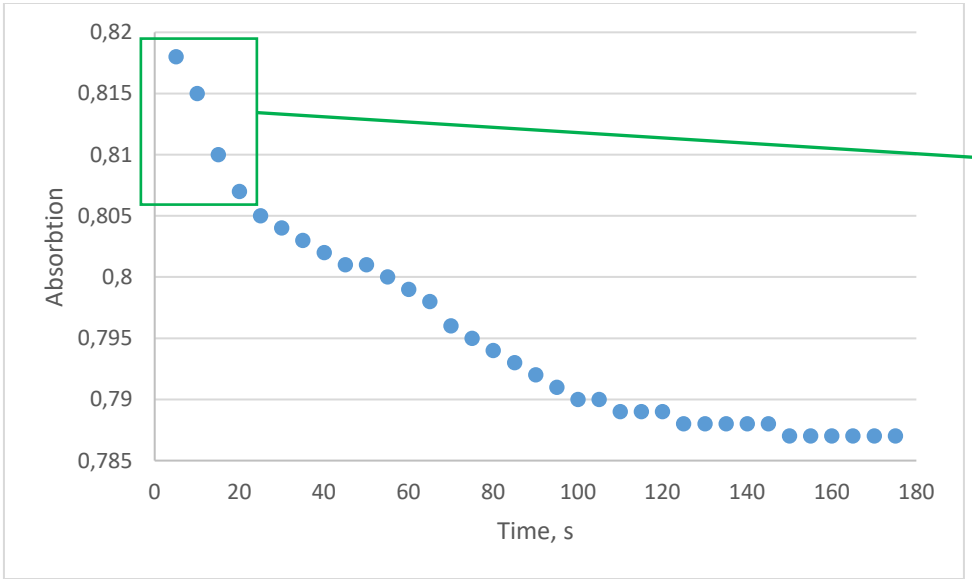
DMF

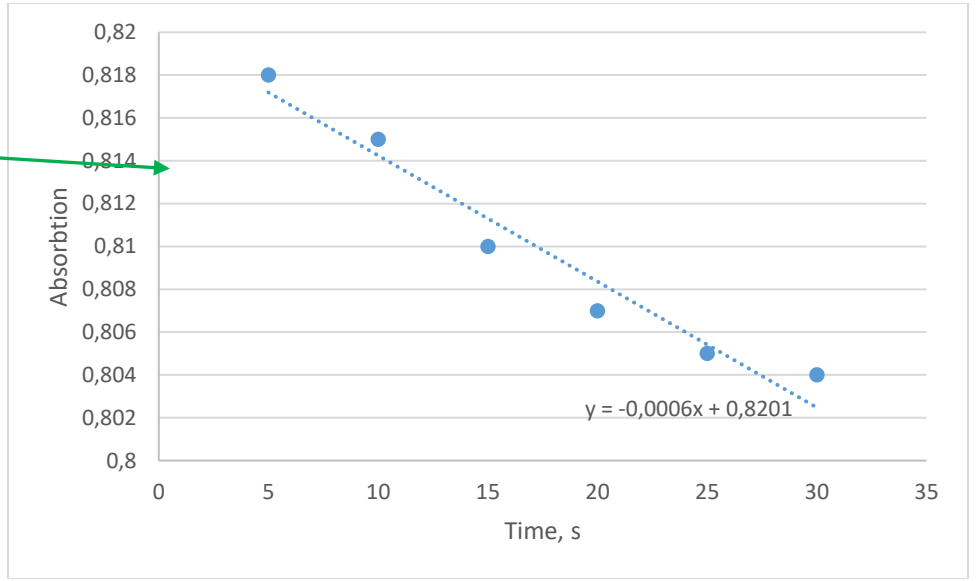

0,795
0,79
0,785
0,78
0,775
0,77
0,765
0,76
0,755
0,75
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,794
0,792
0,79
0,788
0,786
0,784
0,782
0,78
Absorbtion
y = -0,0006x + 0,7952
0
5
10
15
20
25
30
Axis Title

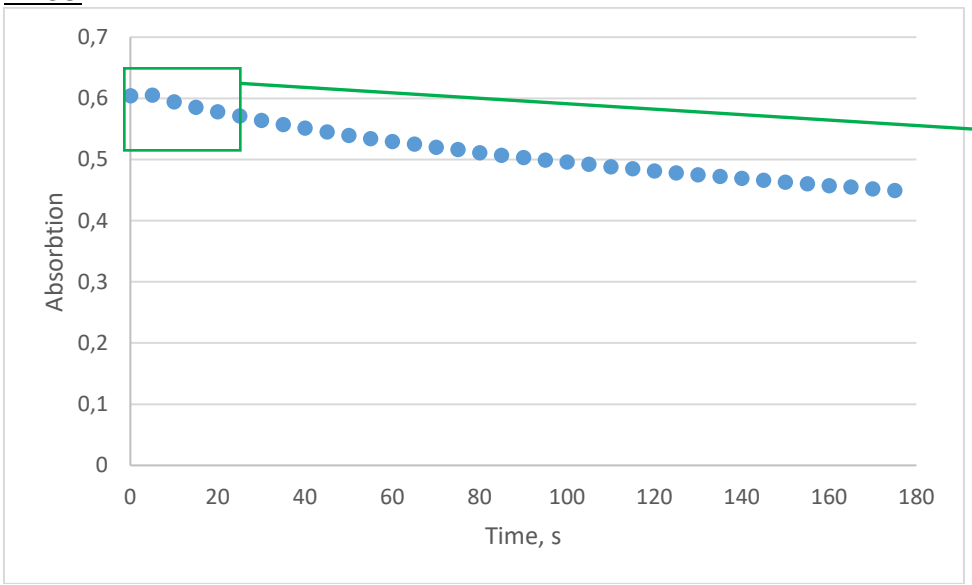

0,795
0,79
0,785
0,78
0,775
0,77
0,765
0,76
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

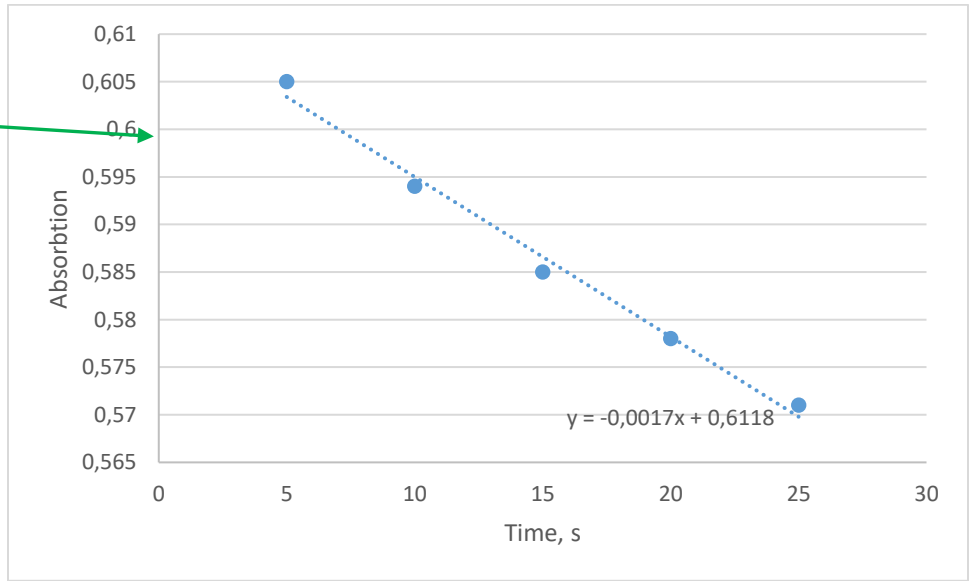

0,794
0,792
0,79
0,788
0,786
0,784
0,782
Absorbtion
y = -0,0004x + 0,7992
0
5
10
15
20
25
30
35
40
Time, s

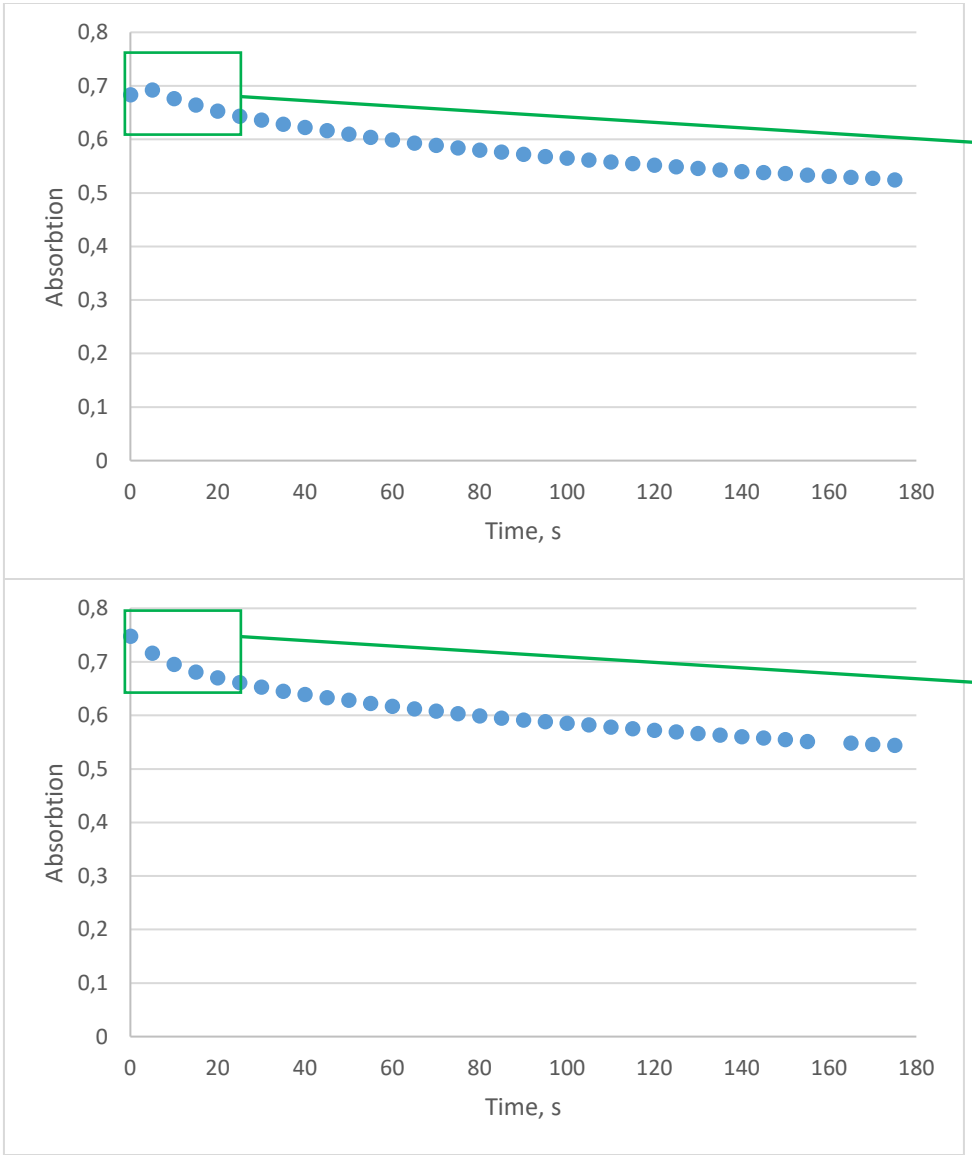

0,82
0,815
0,81
0,805
0,8
0,795
0,79
0,785
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

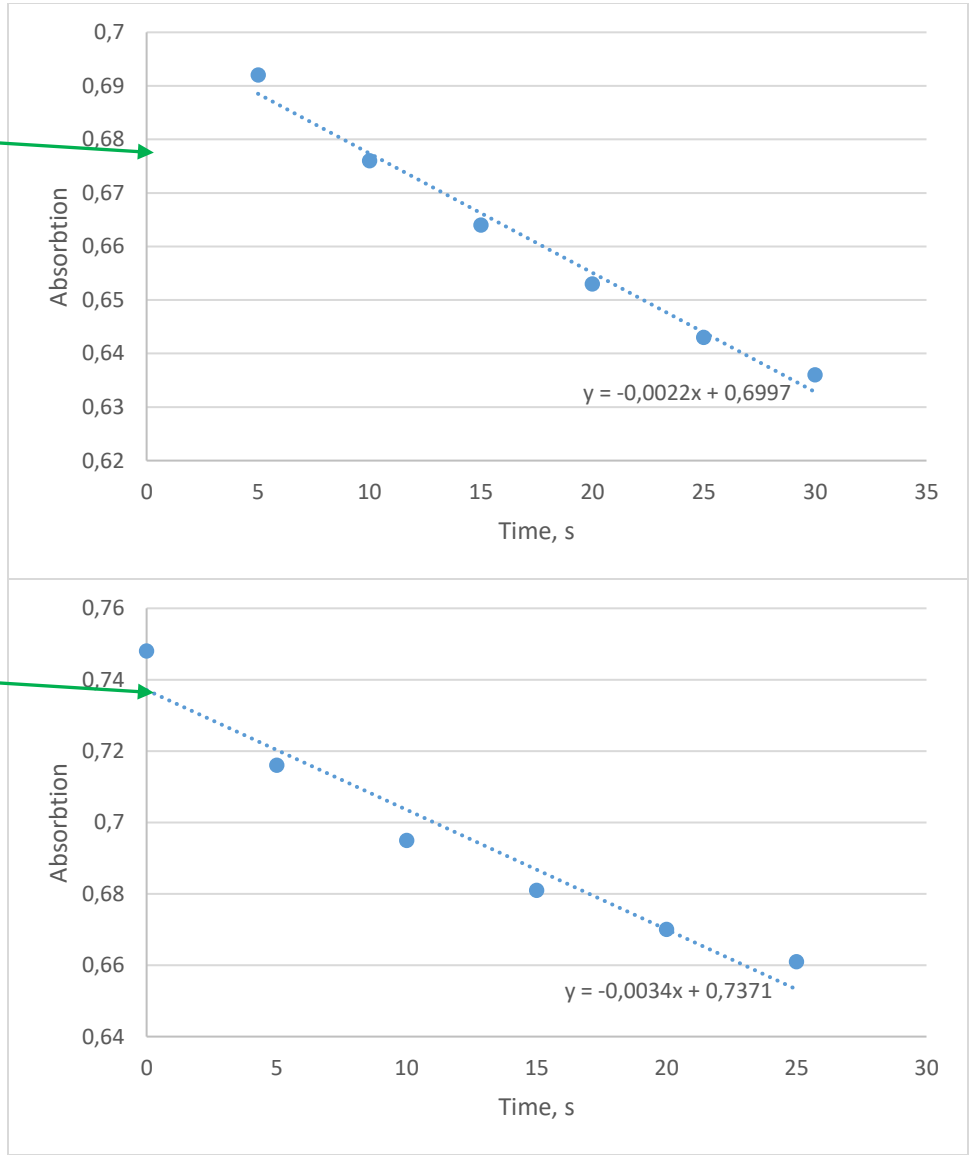

0,82
0,818
0,816
0,814
0,812
0,81
0,808
0,806
0,804
0,802
0,8
Absorbtion
y = -0,0006x + 0,8201
0
5
10
15
20
25
30
35
Time, s

DMSO


0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,61
0,605
0,6
0,595
0,59
0,585
0,58
0,575
0,57
0,565
Absorbtion
y = -0,0017x + 0,6118
0
5
10
15
20
25
30
Time, s

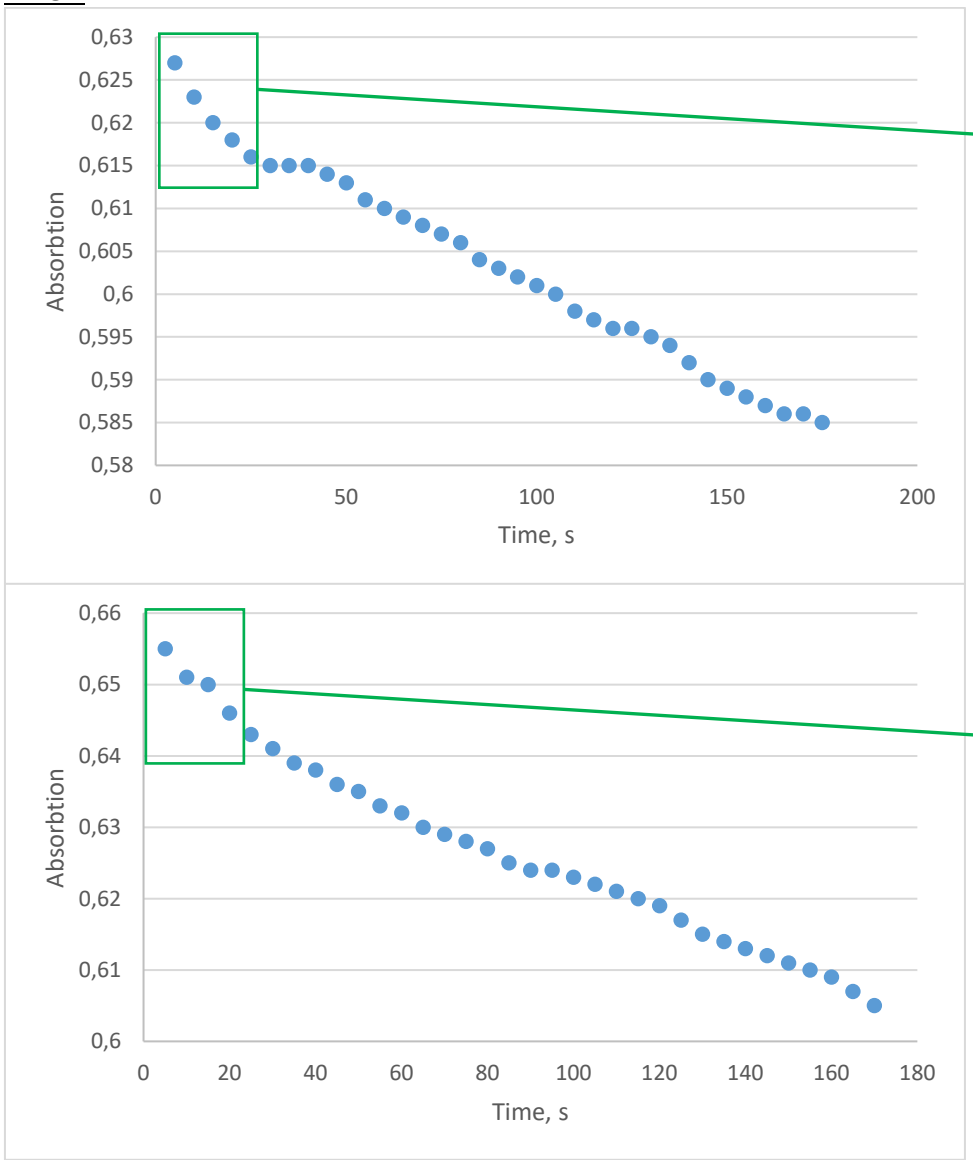

Absorbtion
Time, s

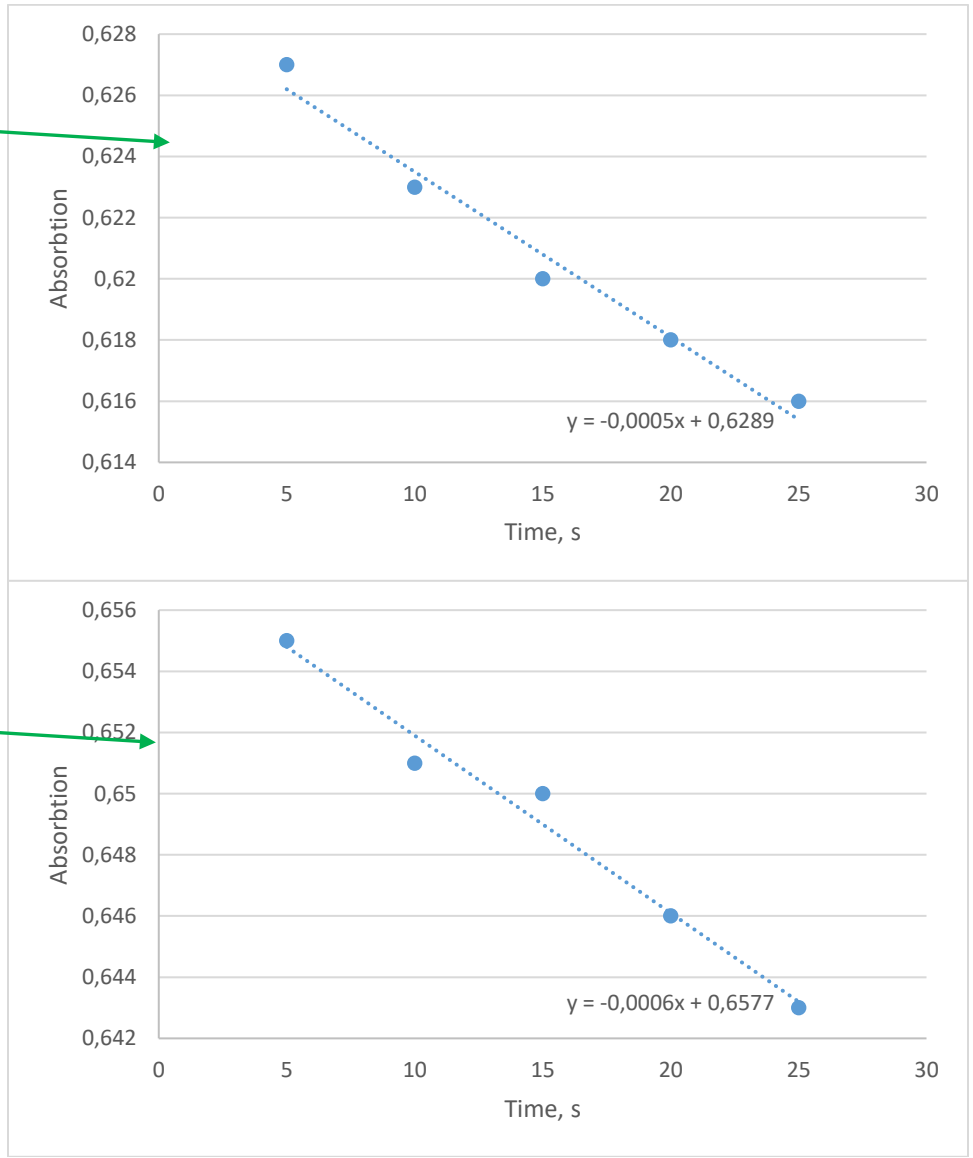

Absorbtion
Time, s
y = -0,0022x + 0,6997

Absorbtion
Time, s

Absorbtion
Time, s
y = -0,0034x + 0,7371

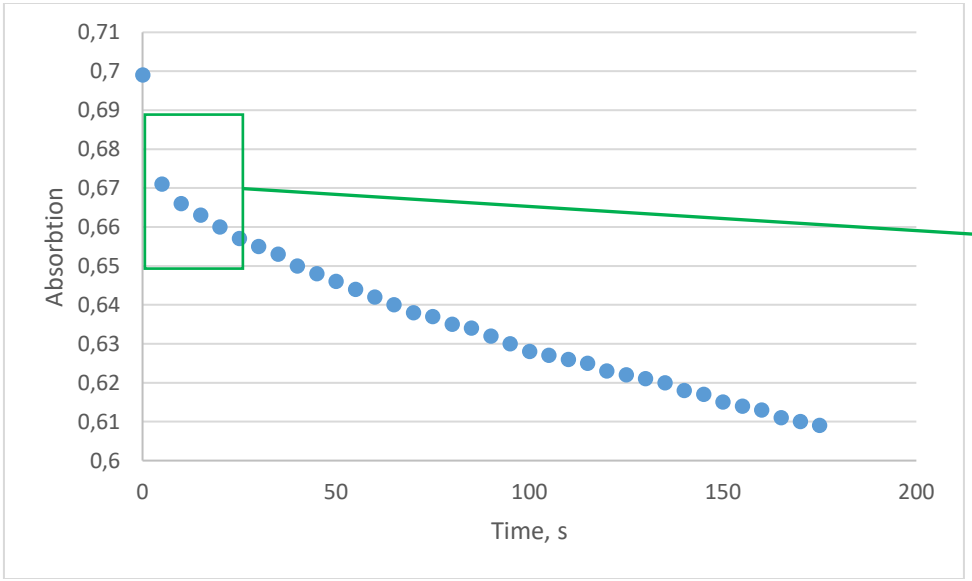
i-PrOH

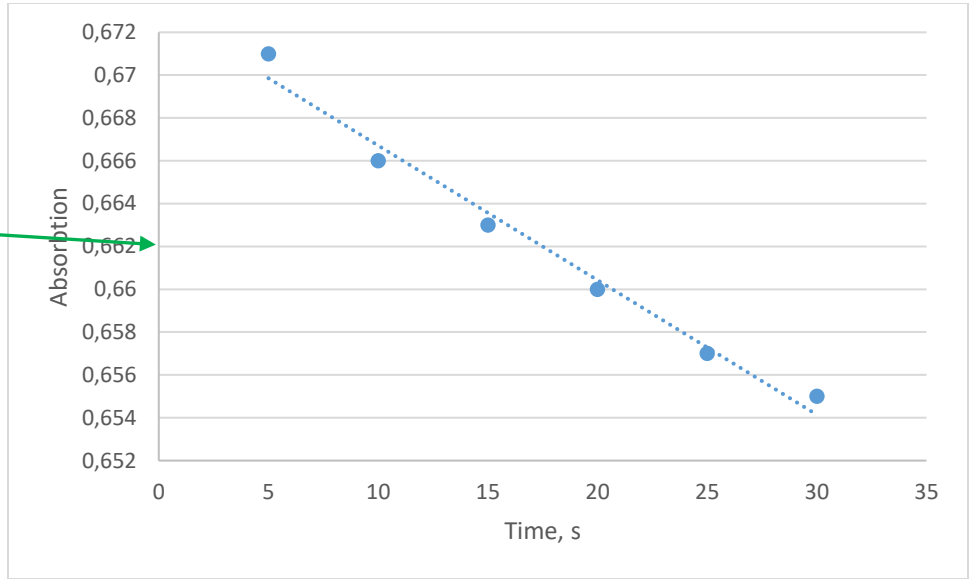

0,63
0,625
0,62
0,615
0,61
0,605
0,6
0,595
0,59
0,585
0,58
Absorbtion
0
50
100
150
200
Time, s


0,628
0,626
0,624
0,622
0,62
0,618
0,616
0,614
Absorbtion
y = -0,0005x + 0,6289
0
5
10
15
20
25
30
Time, s

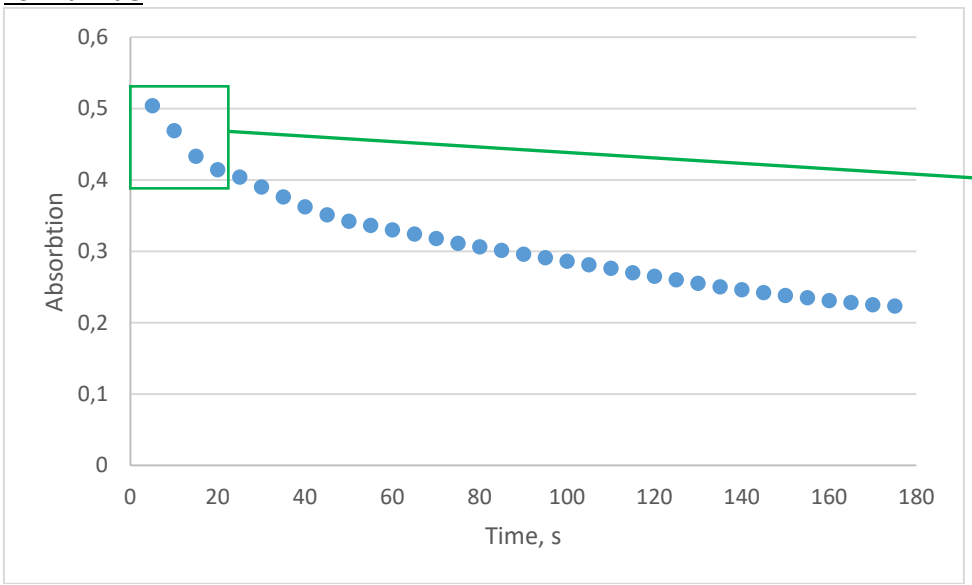
0,66
0,65
0,64
0,63
0,62
0,61
0,6
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

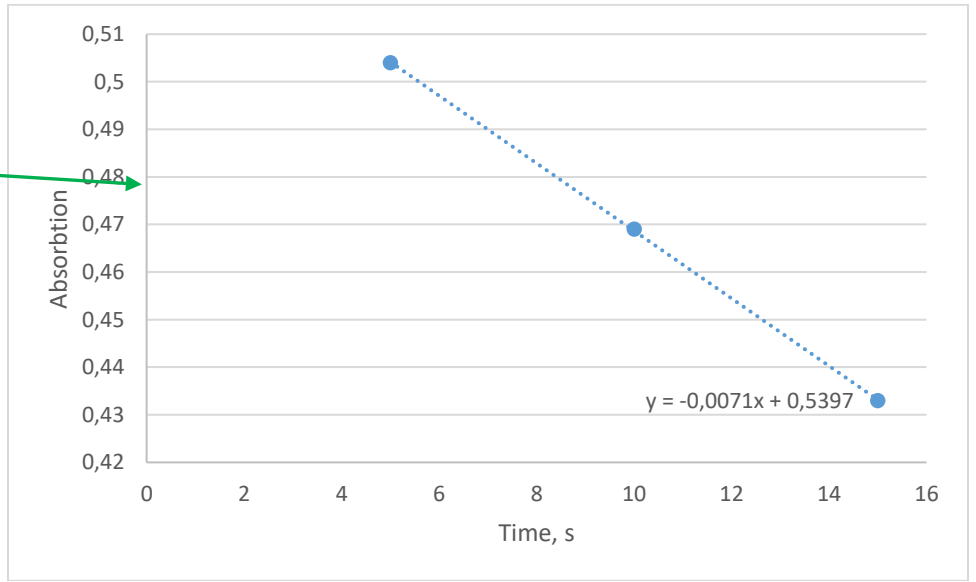
0,656
0,654
0,652
0,65
0,648
0,646
0,644
0,642
Absorbtion
y = -0,0006x + 0,6577
0
5
10
15
20
25
30
Time, s

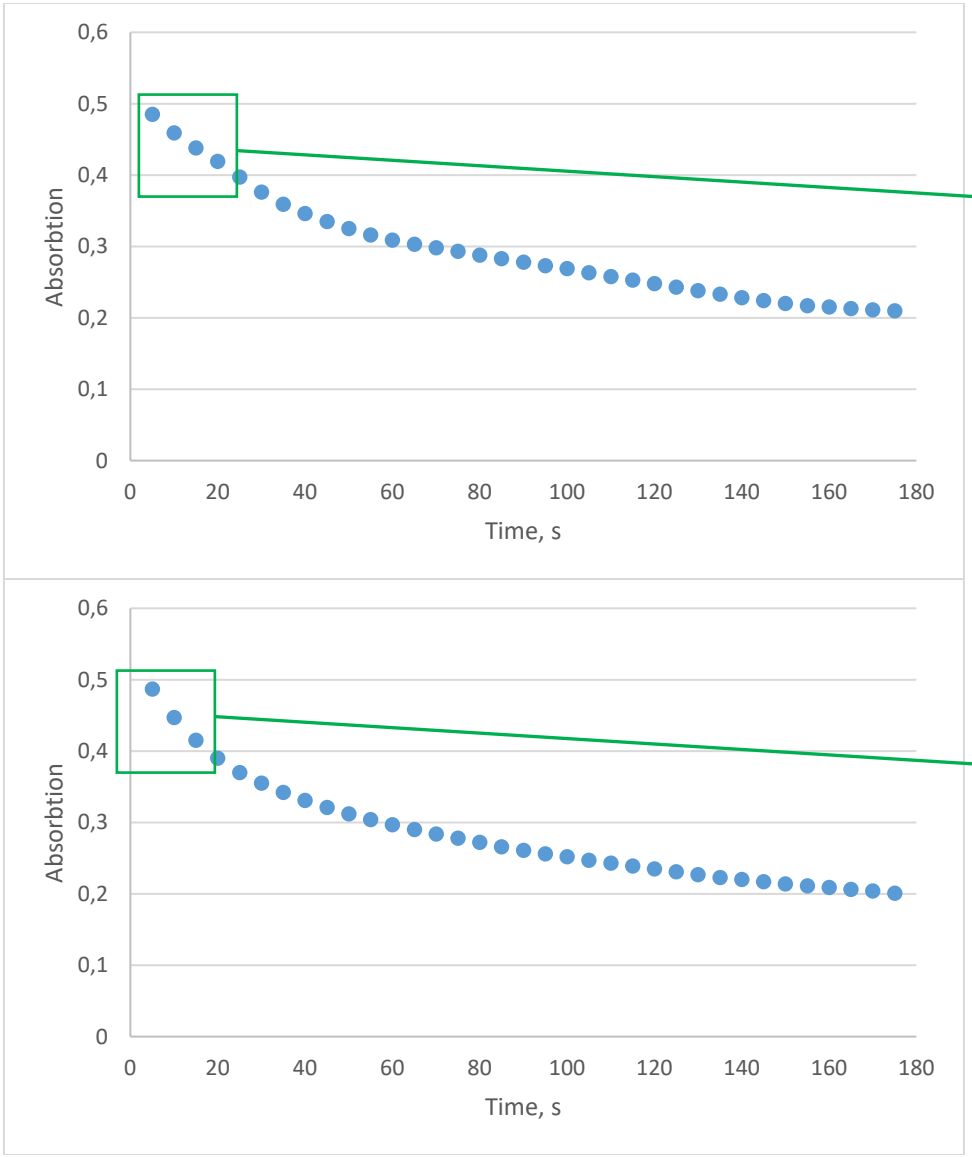

0,71
0,7
0,69
0,68
0,67
0,66
0,65
0,64
0,63
0,62
0,61
0,6
Absorbtion
0
50
100
150
200
Time, s

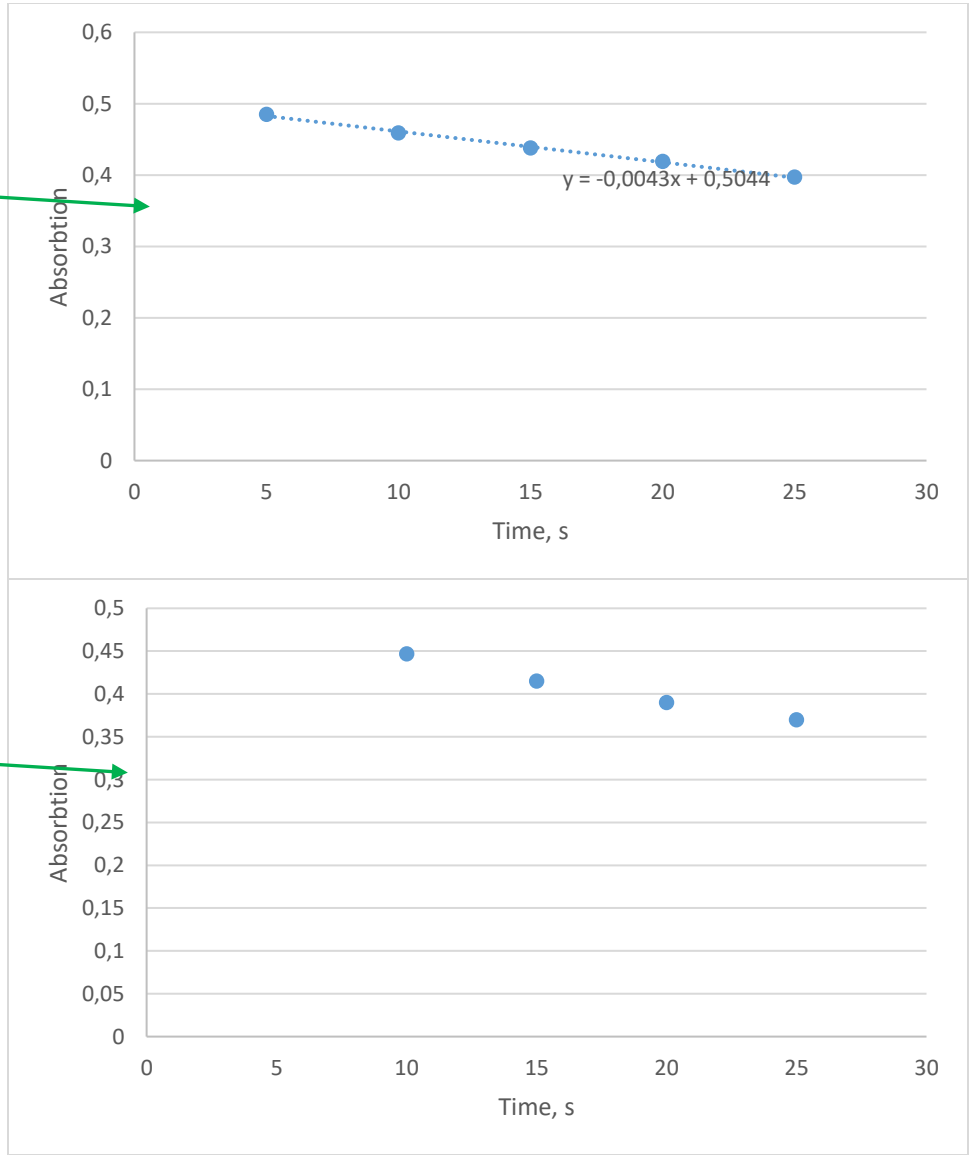

0,672
0,67
0,668
0,666
0,664
0,662
0,66
0,658
0,656
0,654
0,652
Absorbtion
0
5
10
15
20
25
30
35
Time, s

Formamide


0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,51
0,5
0,49
0,48
0,47
0,46
0,45
0,44
0,43
0,42
Absorbtion
y = -0,0071x + 0,5397
0
2
4
6
8
10
12
14
16
Time, s

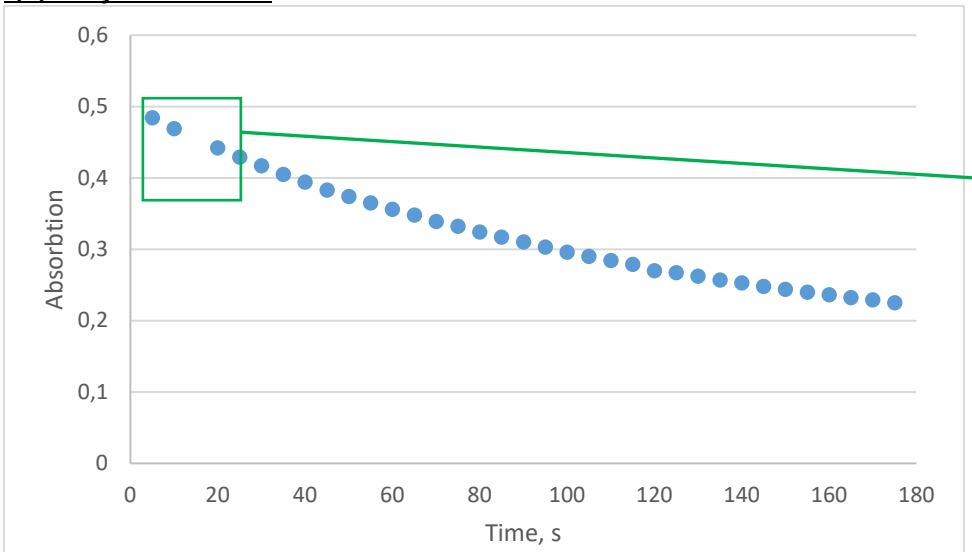

Absorbtion
Time, s
0,6
0,5
0,4
0,3
0,2
0,1
0
0 20 40 60 80 100 120 140 160 180

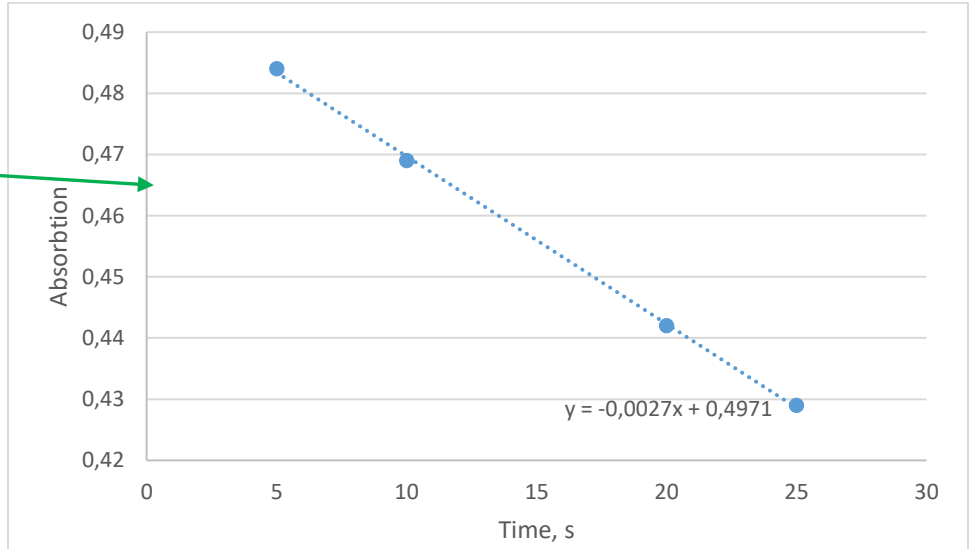

y = -0,0043x + 0,5044
Absorbtion
Time, s
0,6
0,5
0,4
0,3
0,2
0,1
0
0 5 10 15 20 25 30

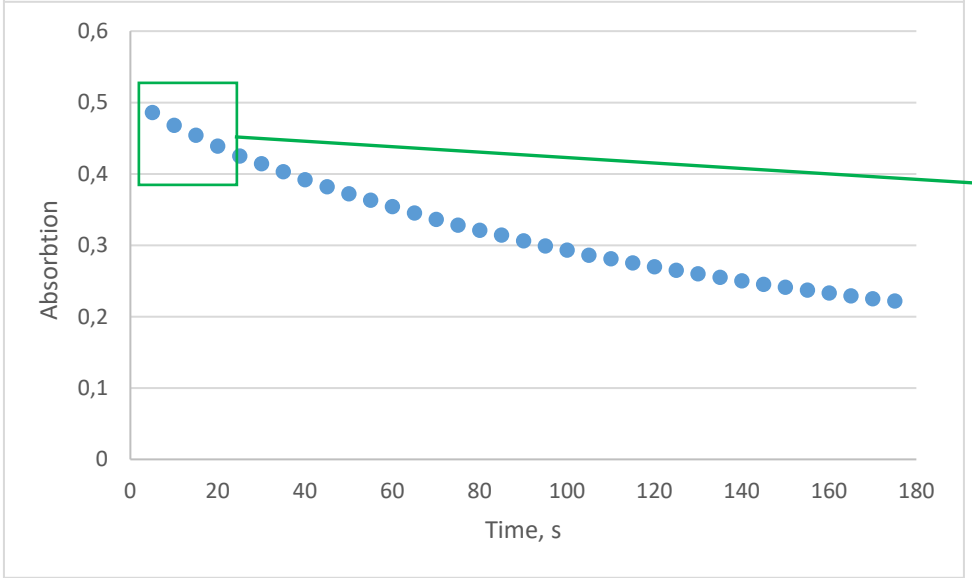
Absorbtion
Time, s
0,6
0,5
0,4
0,3
0,2
0,1
0
0 20 40 60 80 100 120 140 160 180

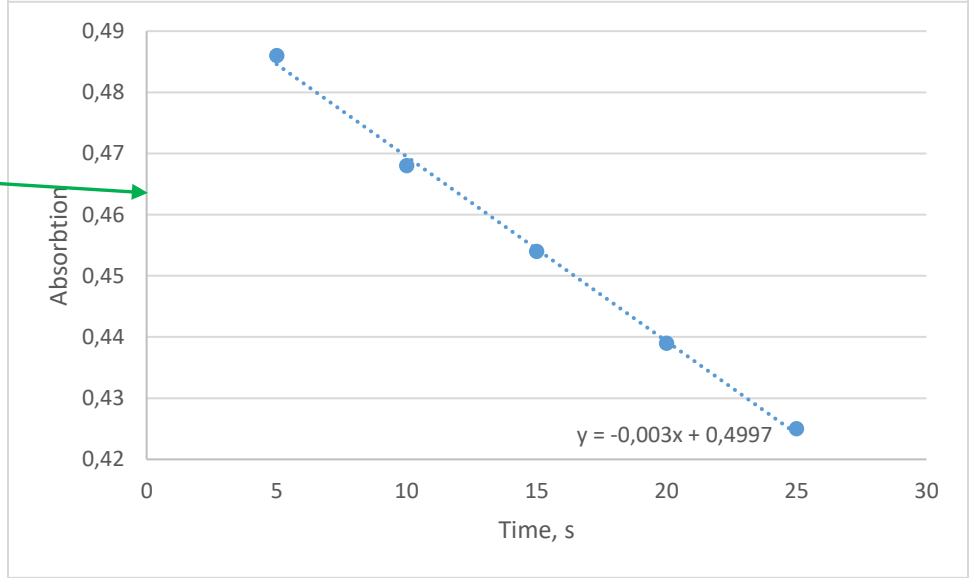
Absorbtion
Time, s
0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0 5 10 15 20 25 30

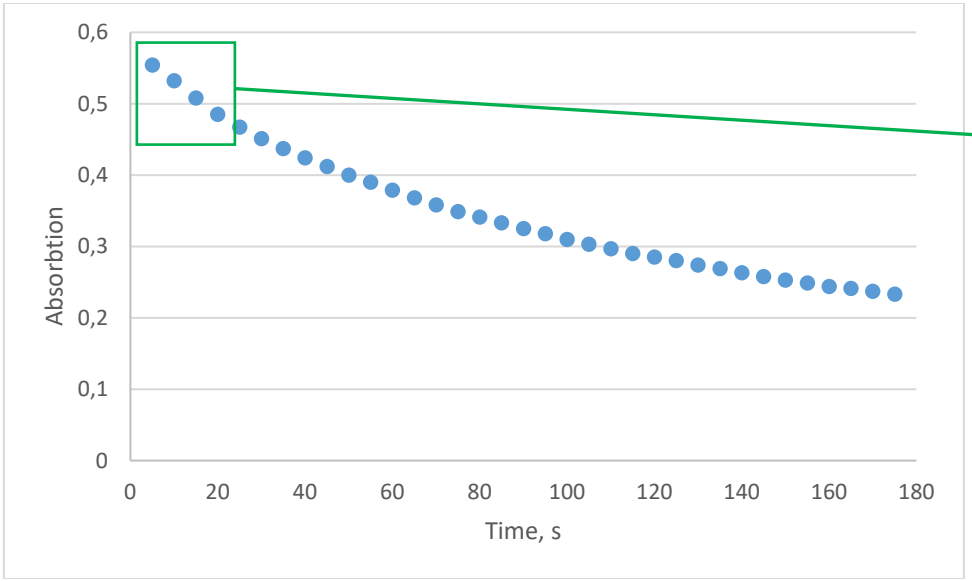
2,2,2-Trifluoroethanol

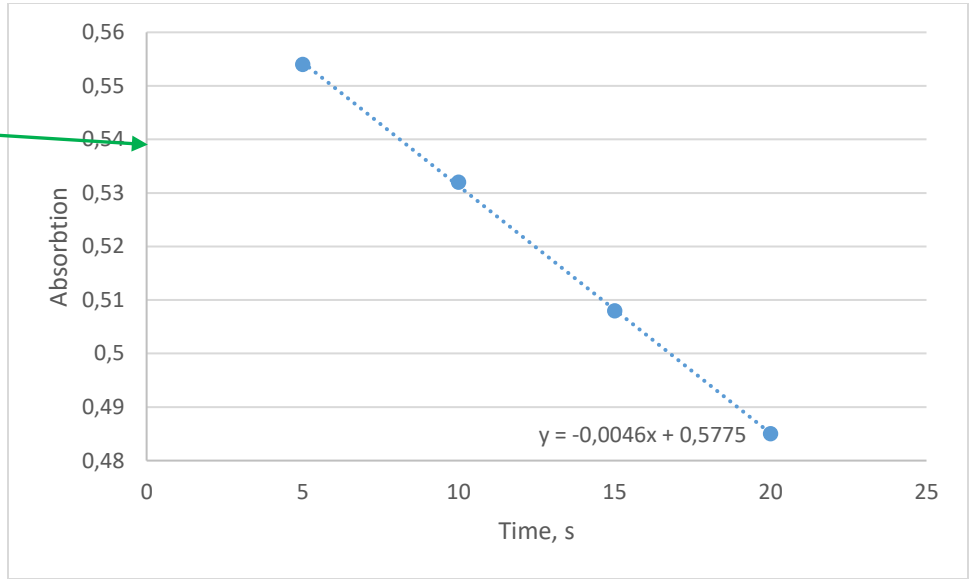




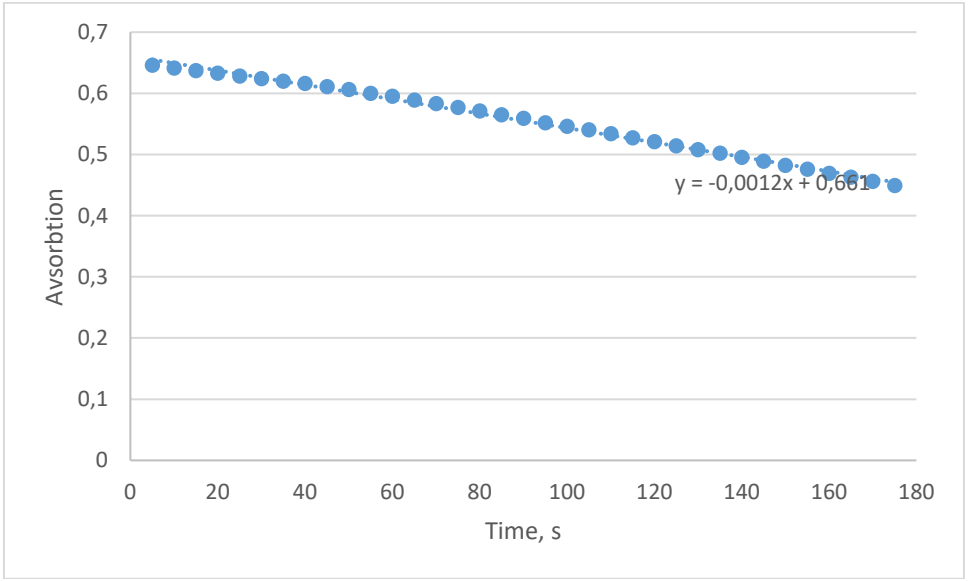


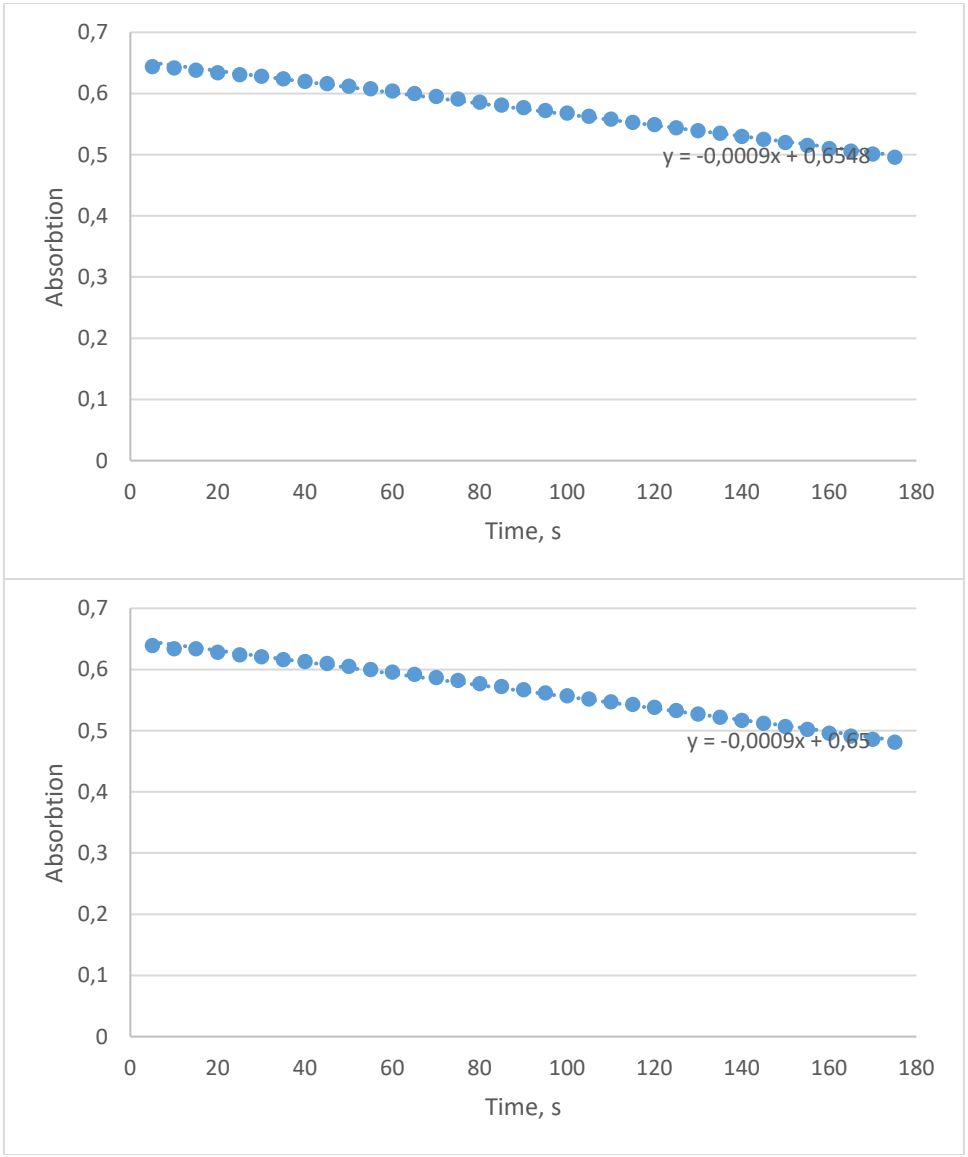



0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

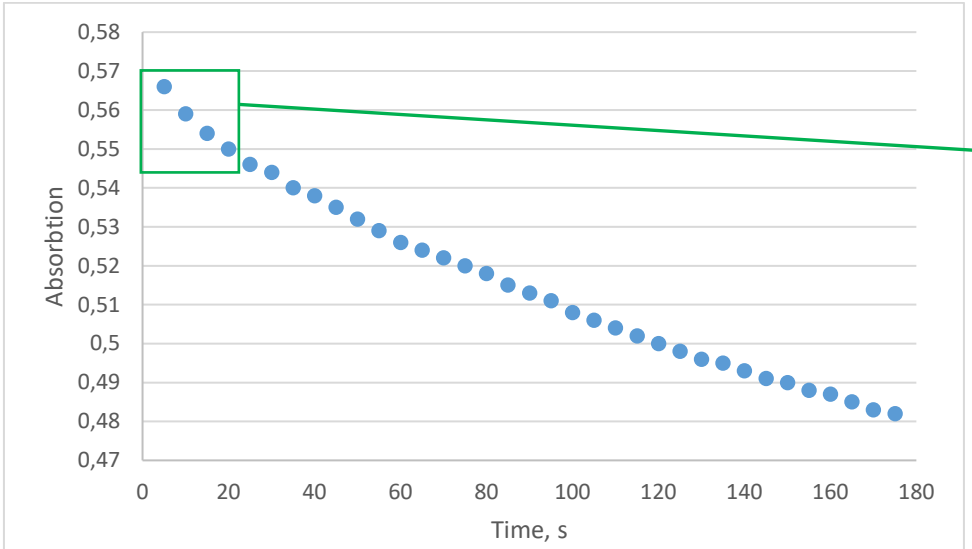

0,56
0,55
0,54
0,53
0,52
0,51
0,5
0,49
0,48
Absorbtion
y = -0,0046x + 0,5775
0
5
10
15
20
25
Time, s

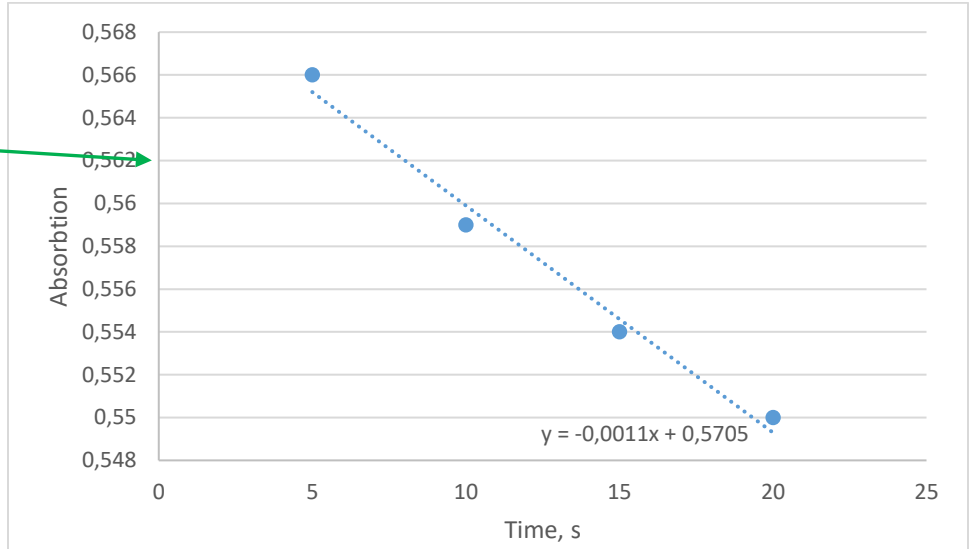
THF

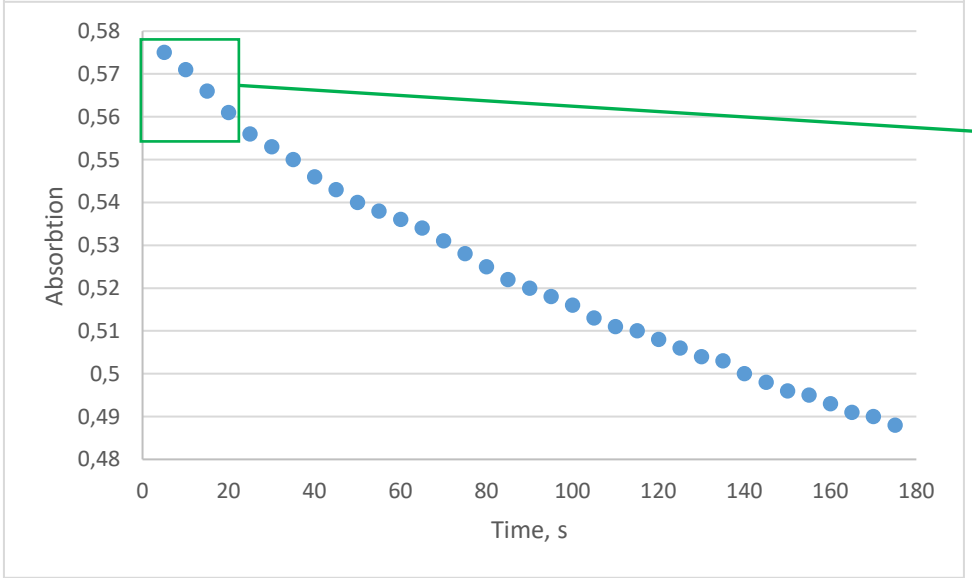

0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Avsorbtion
y = -0,0012x + 0,661
0
20
40
60
80
100
120
140
160
180
Time, s

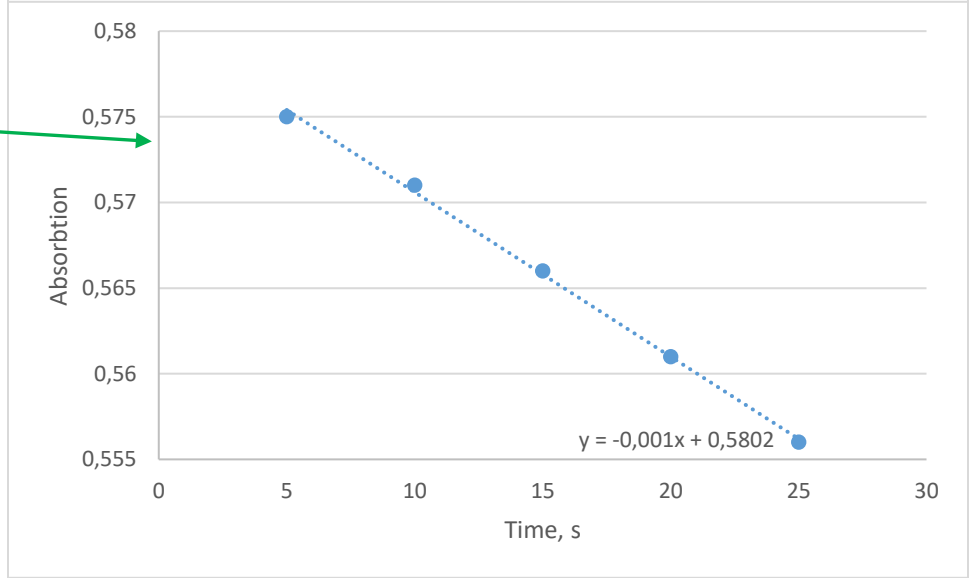

0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
y = -0,0009x + 0,6548
0
20
40
60
80
100
120
140
160
180
Time, s
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Absorbtion
y = -0,0009x + 0,65
0
20
40
60
80
100
120
140
160
180
Time, s

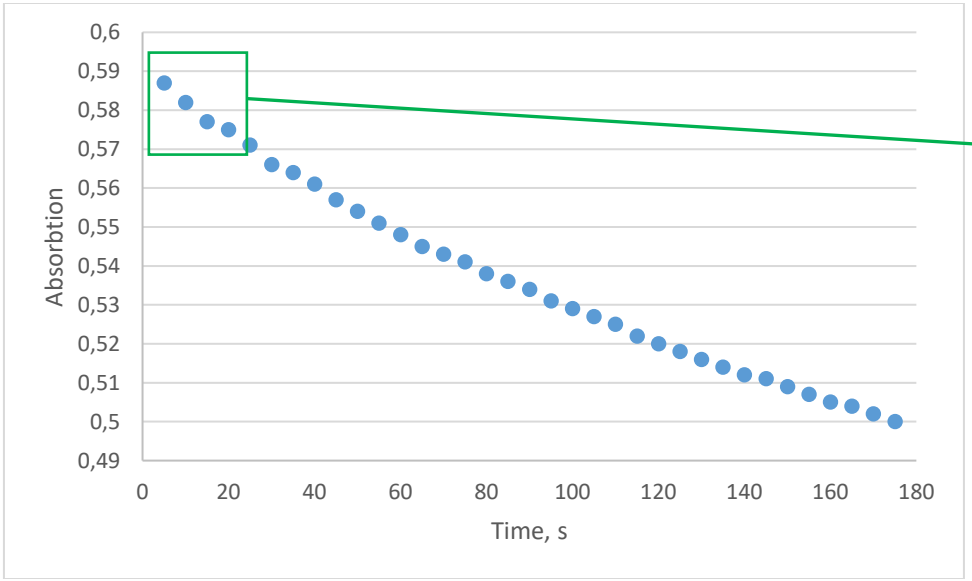
EtOH

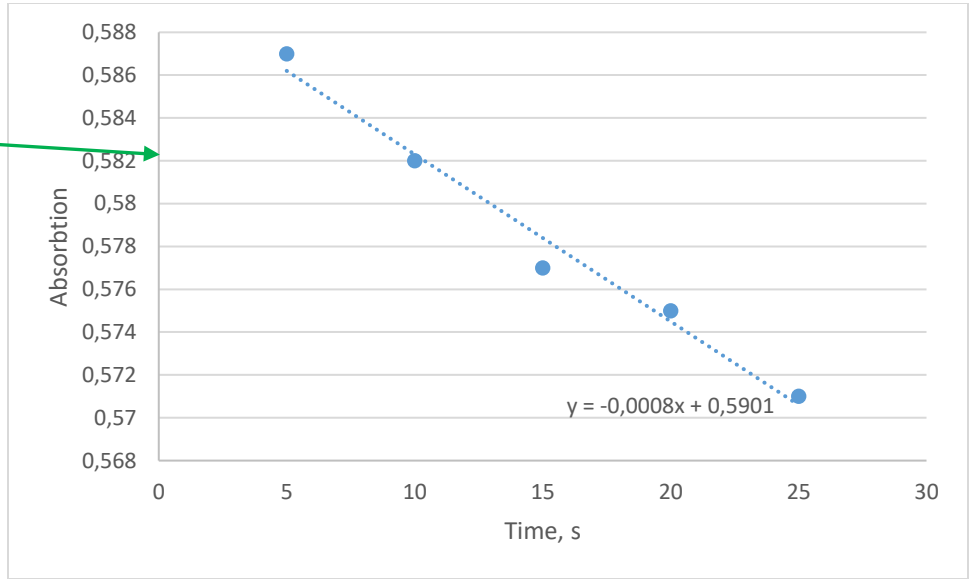

0,58
0,57
0,56
0,55
0,54
0,53
0,52
0,51
0,5
0,49
0,48
0,47
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,568
0,566
0,564
0,562
0,56
0,558
0,556
0,554
0,552
0,55
0,548
Absorbtion
y = -0,0011x + 0,5705
0
5
10
15
20
25
Time, s

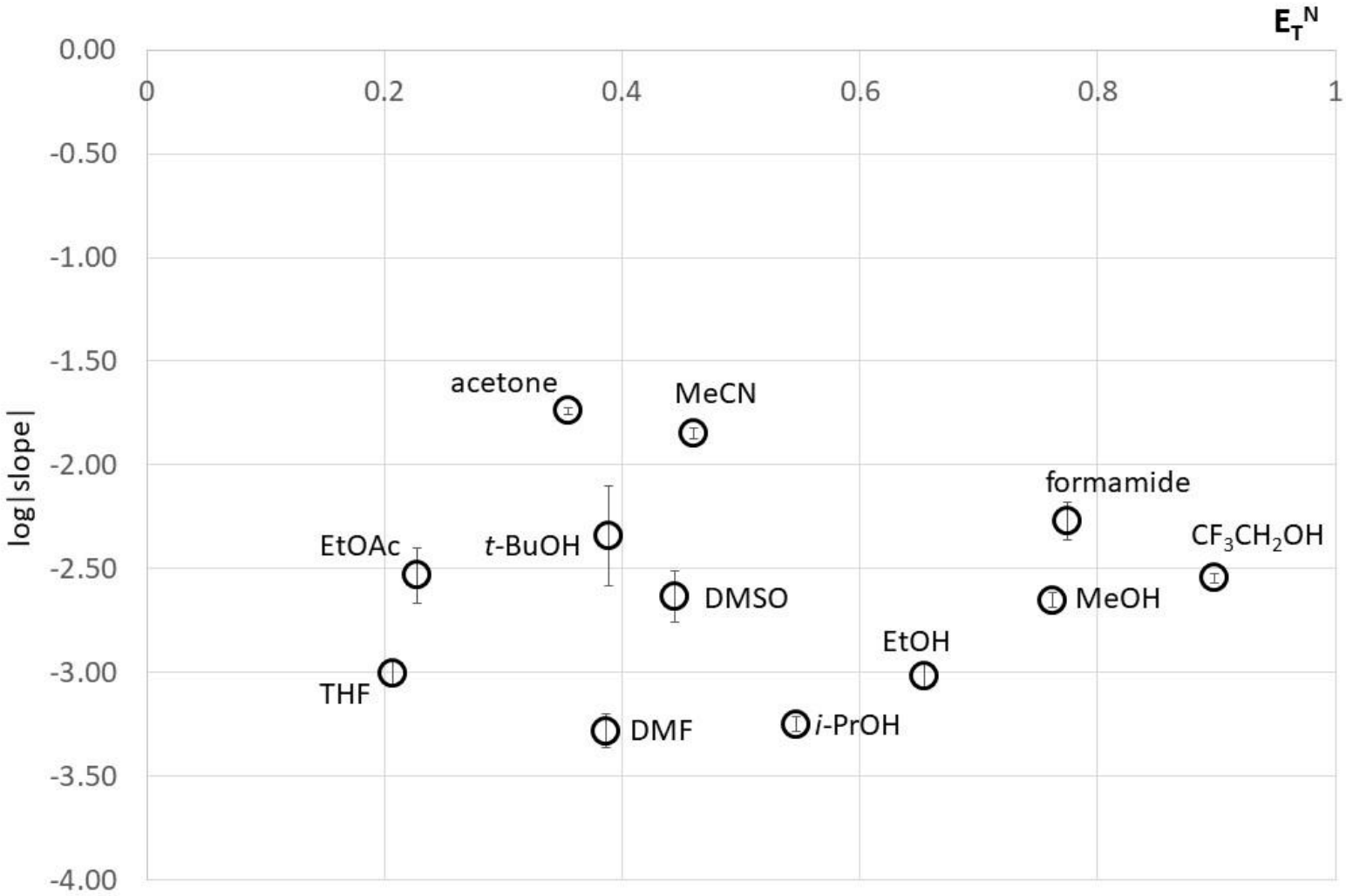

0,58
0,57
0,56
0,55
0,54
0,53
0,52
0,51
0,5
0,49
0,48
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

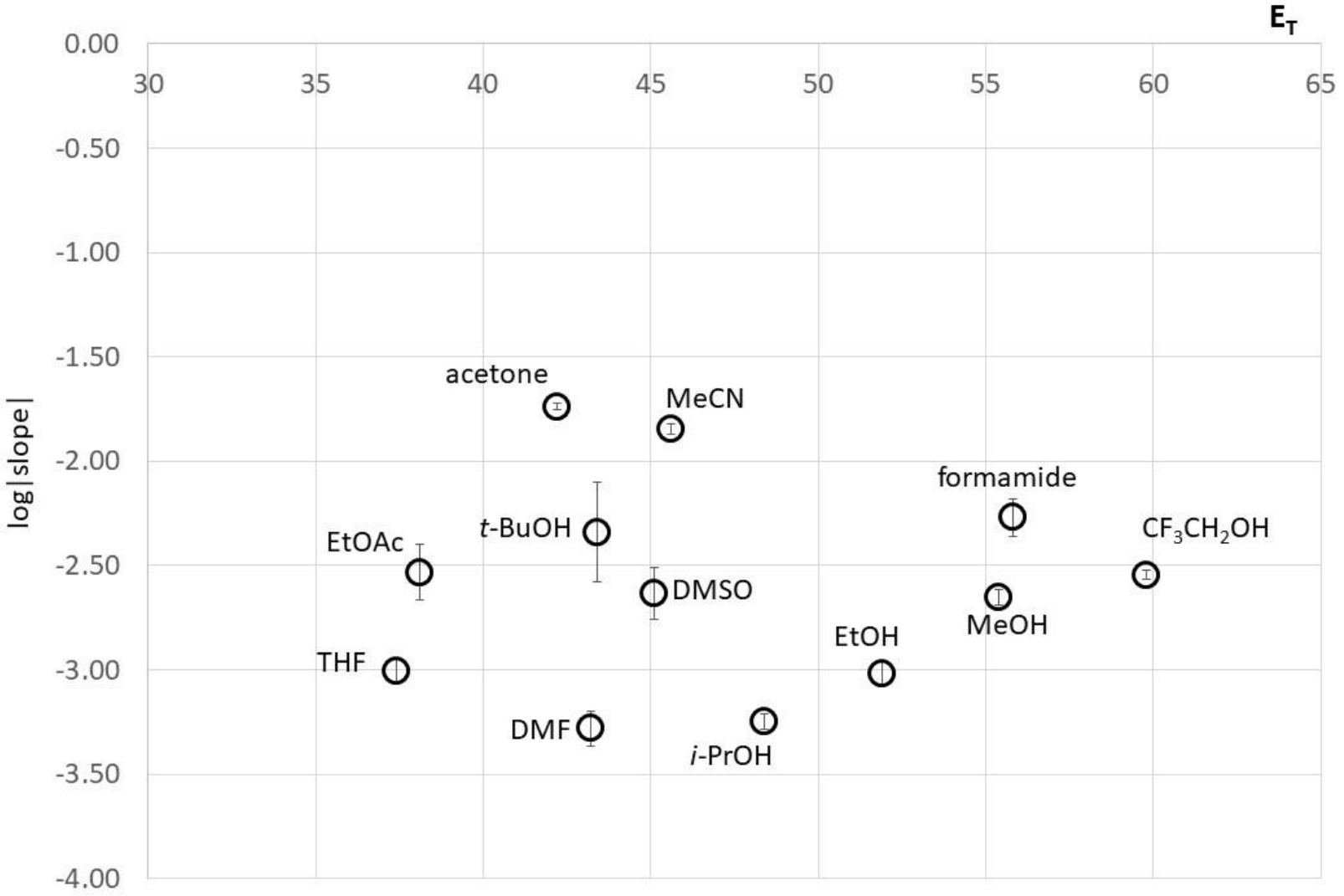

0,58
0,575
0,57
0,565
0,56
0,555
Absorbtion
y = -0,001x + 0,5802
0
5
10
15
20
25
30
Time, s

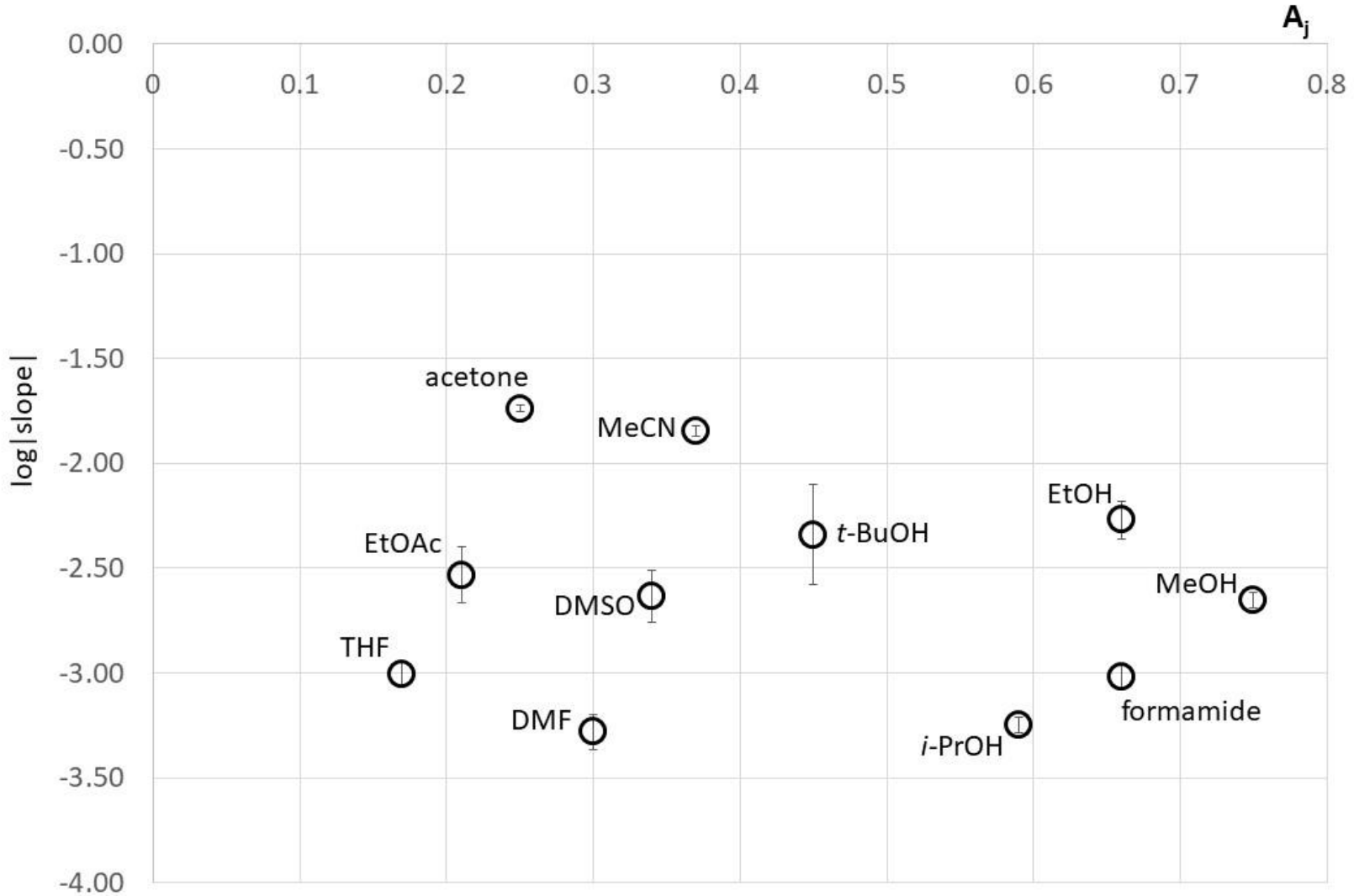

0,6
0,59
0,58
0,57
0,56
0,55
0,54
0,53
0,52
0,51
0,5
0,49
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

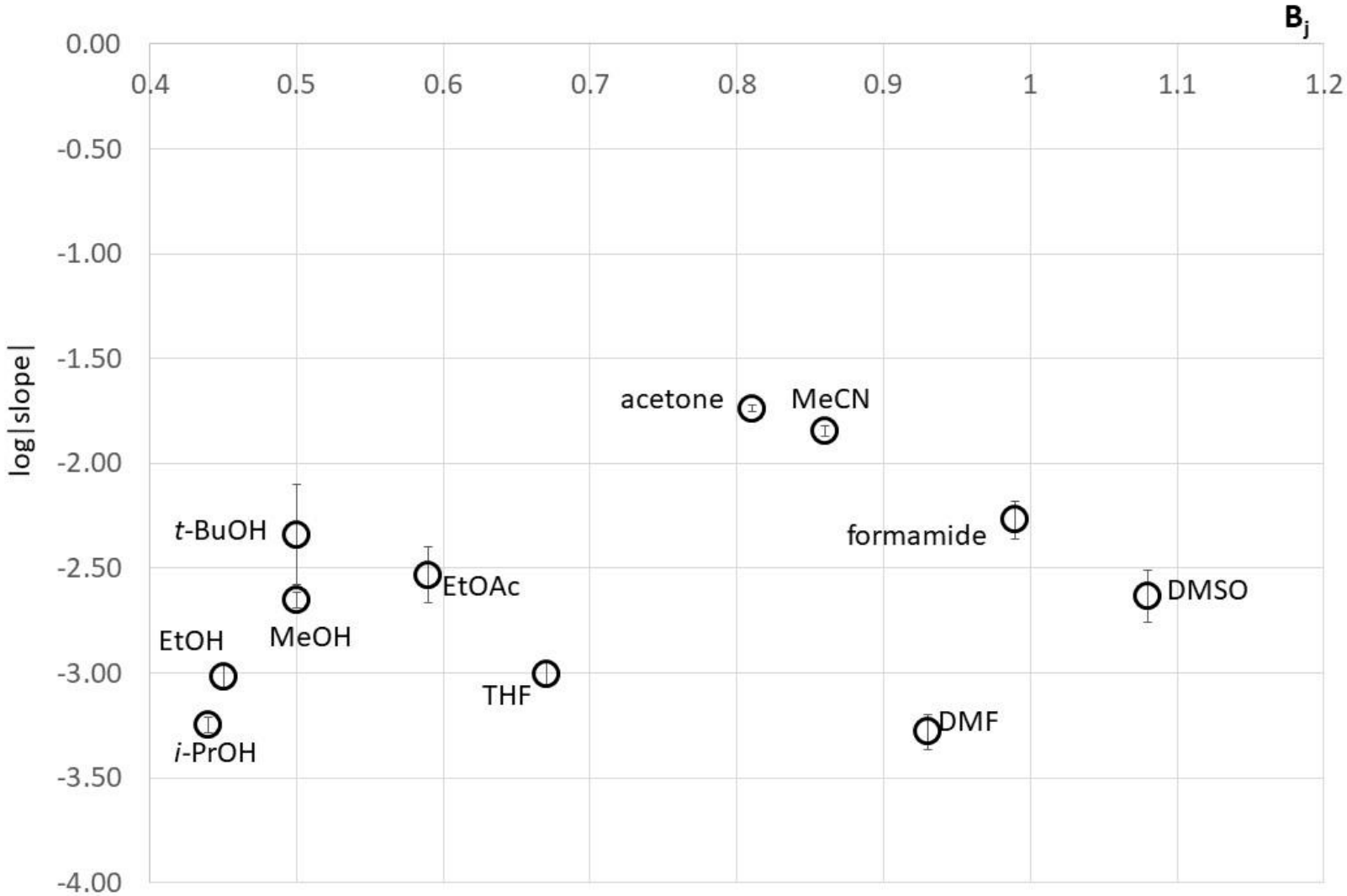

0,588
0,586
0,584
0,582
0,58
0,578
0,576
0,574
0,572
0,57
0,568
Absorbtion
0
5
10
15
20
25
30
Time, s
y = -0,0008x + 0,5901

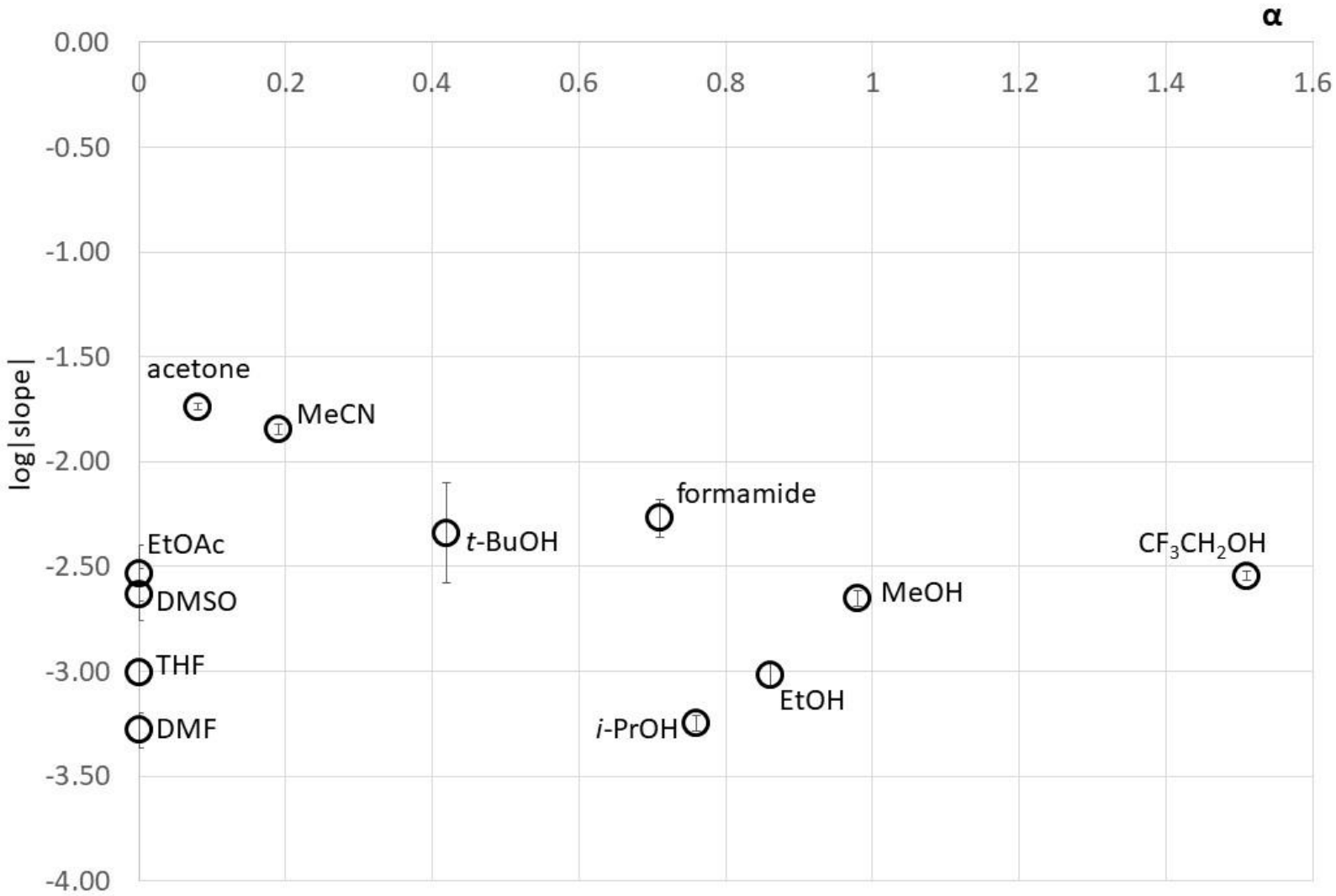
16.CORRELATION BETWEEN REACTION (12e + DPPH) RATE (CHARACTERIZED WITH LOG|SLOPE|) AND VARIOUS SOLVENT PARAMETERS

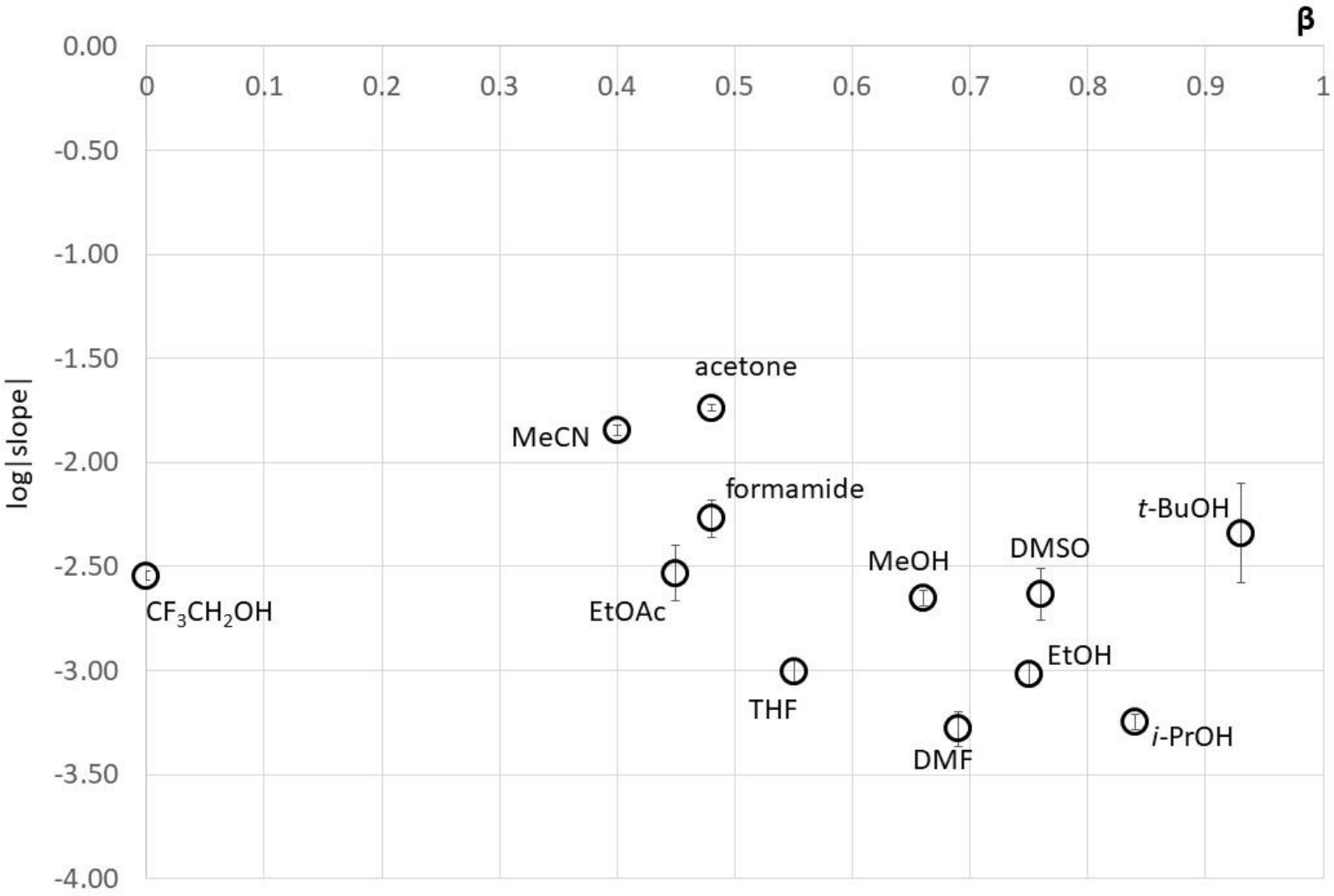



E_T
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
-4.00
30
35
40
45
50
55
60
65
log|slope|
acetone
MeCN
formamide
t-BuOH
CF3CH2OH
EtOAc
DMSO
MeOH
EtOH
THF
DMF
i-PrOH


A_j
0.00
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
-4.00
log|slope|
acetone
MeCN
EtOAc
DMSO
THF
DMF
t-BuOH
EtOH
MeOH
formamide
i-PrOH

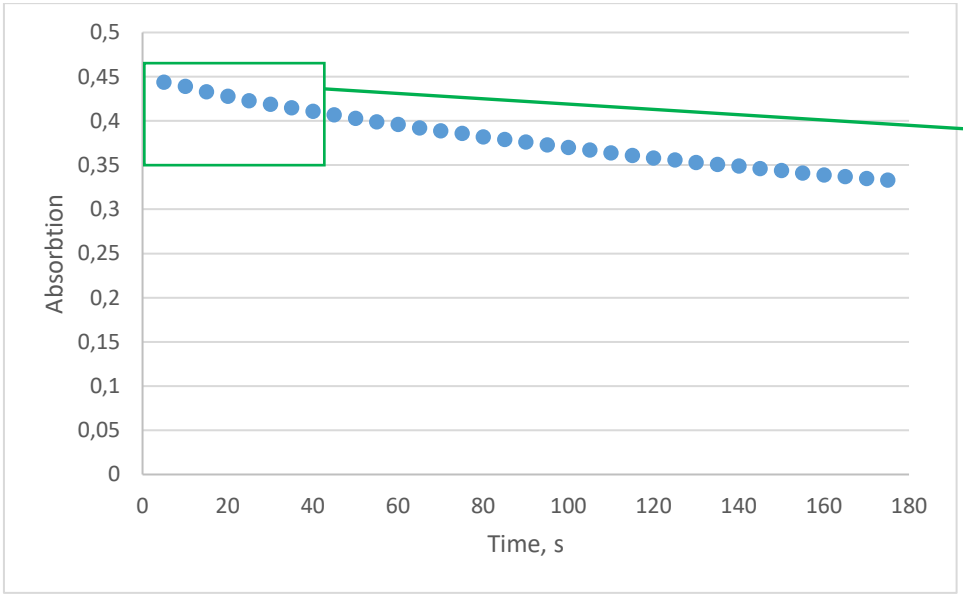

B_j
0.00
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
-4.00
log|slope|
acetone
MeCN
formamide
DMSO
t-BuOH
EtOAc
MeOH
EtOH
THF
DMF
i-PrOH

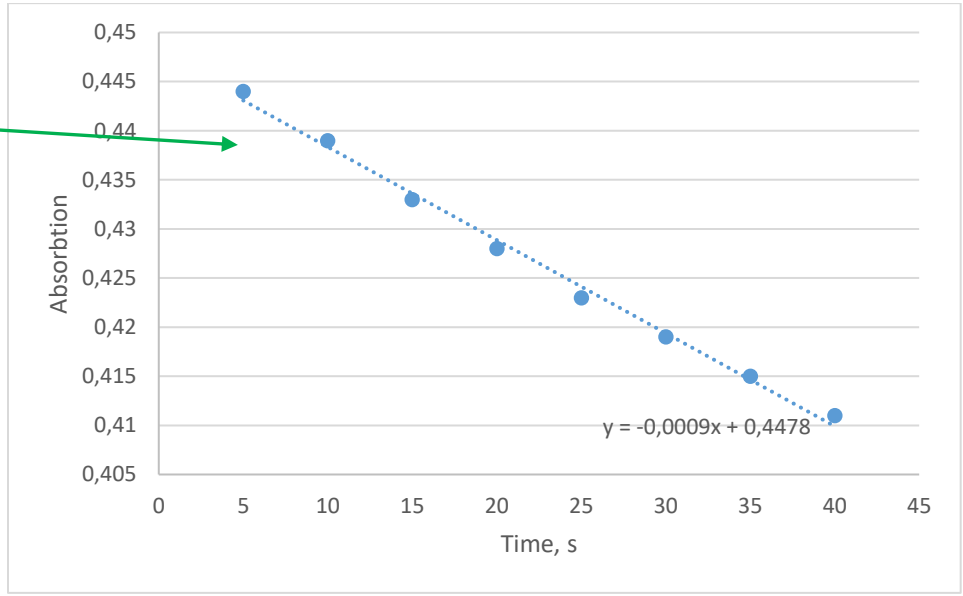

α
0.00
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
-4.00
log|slope|
acetone
MeCN
t-BuOH
formamide
EtOAc
DMSO
MeOH
CF3CH2OH
THF
EtOH
DMF
i-PrOH

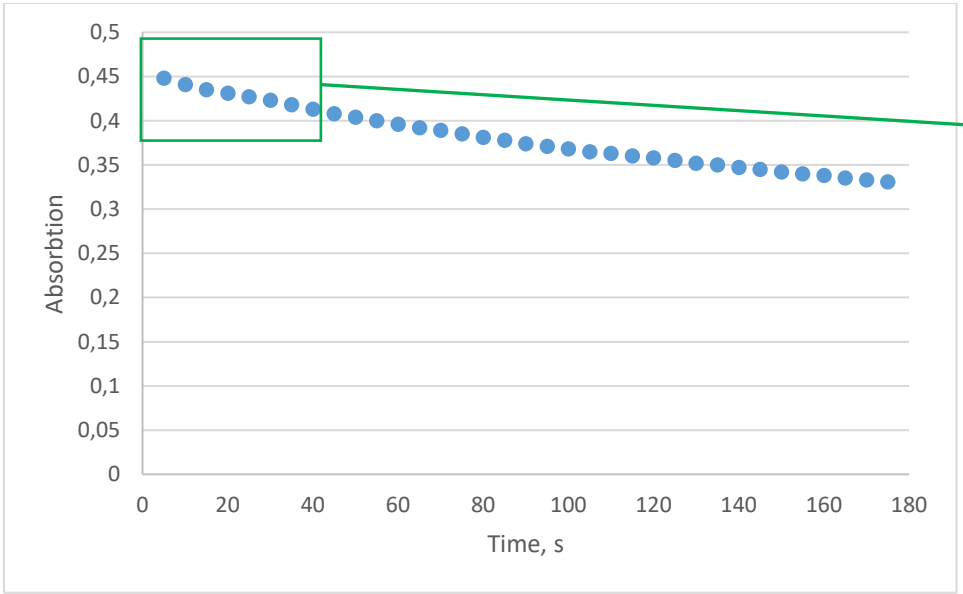

β
0.00
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
-4.00
log|slope|
acetone
MeCN
formamide
t-BuOH
DMSO
MeOH
CF3CH2OH
EtOAc
EtOH
THF
i-PrOH
DMF

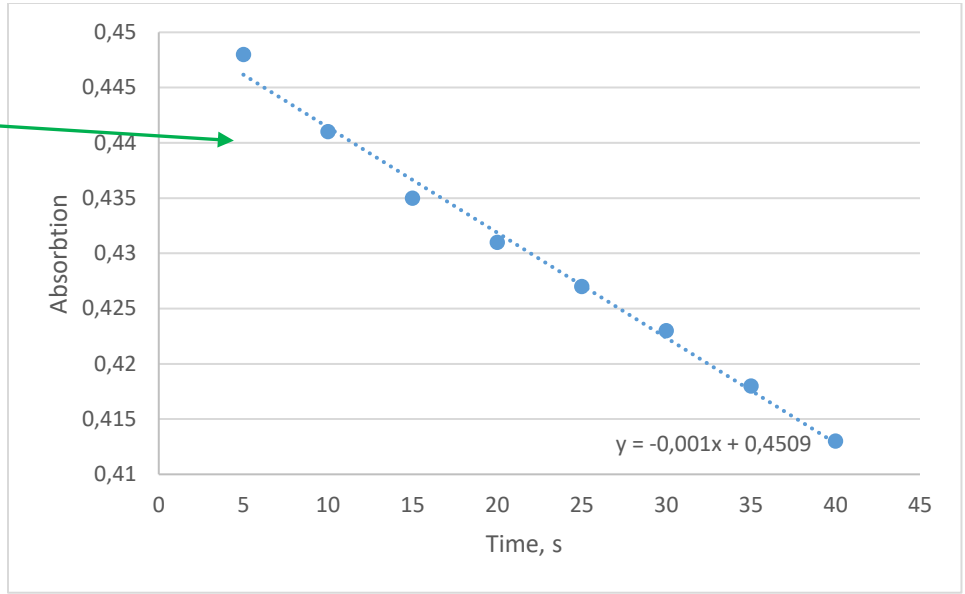
17.KINETIC CURVES FOR THE REACTION BETWEEN DPPH AND COMPOUND 12c IN EtOH (IN PRESENCE OF VARIOUS ADDITIVES)

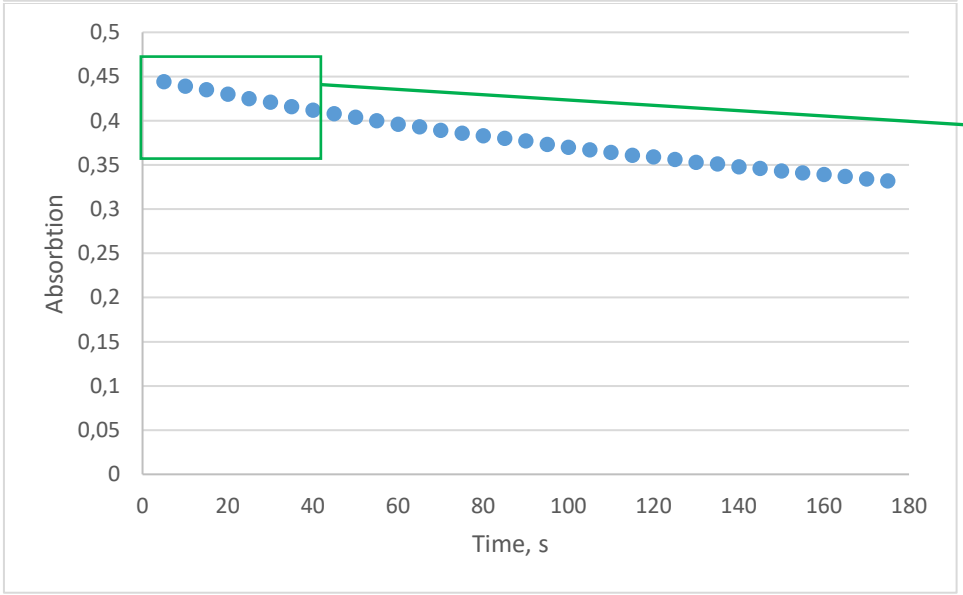
AcOH

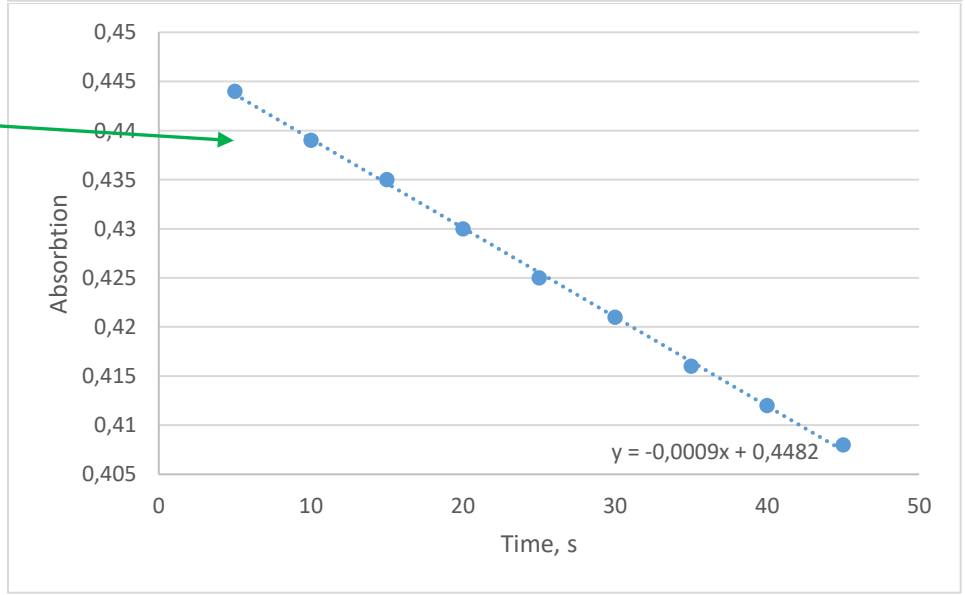




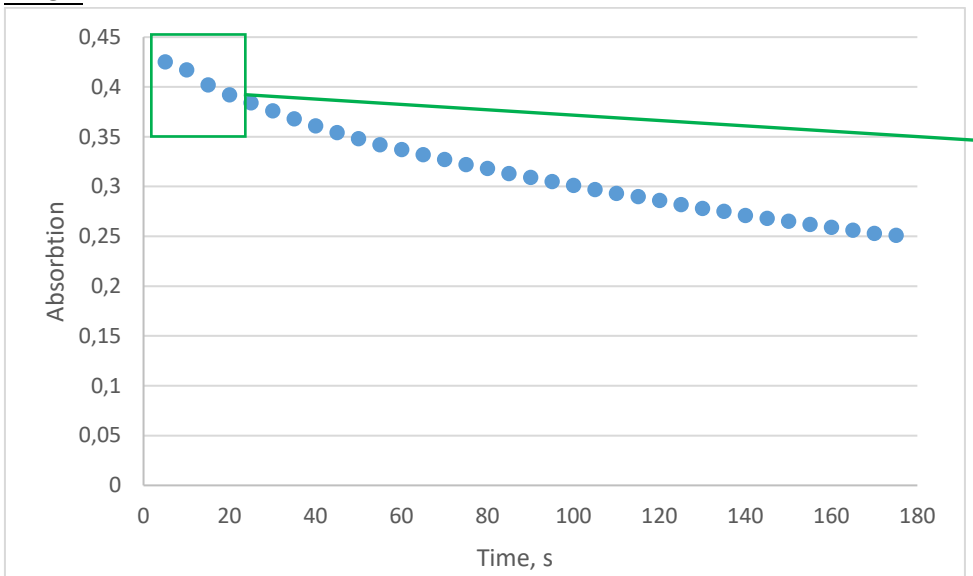

Absorbtion
Time, s

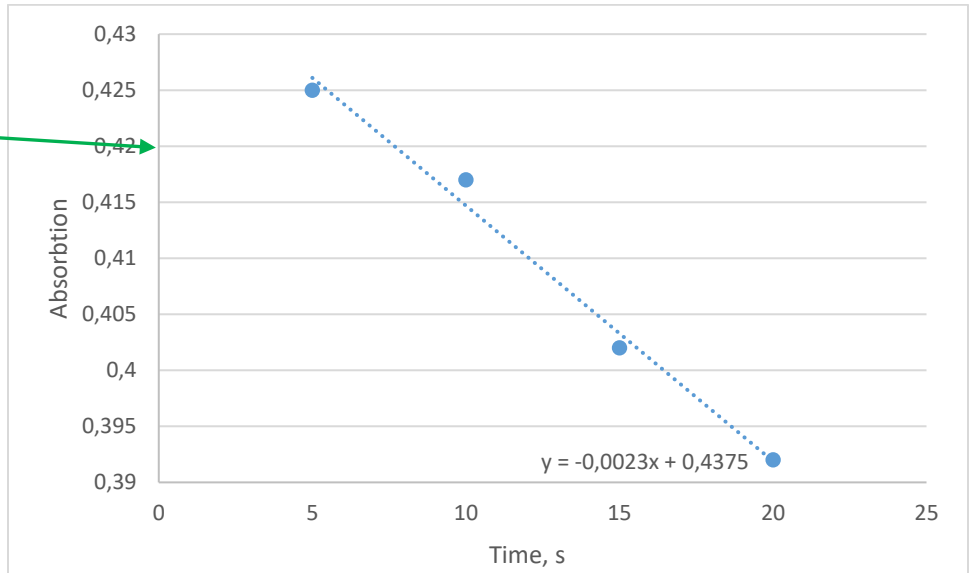

Absorbtion
Time, s
y = -0,001x + 0,4509

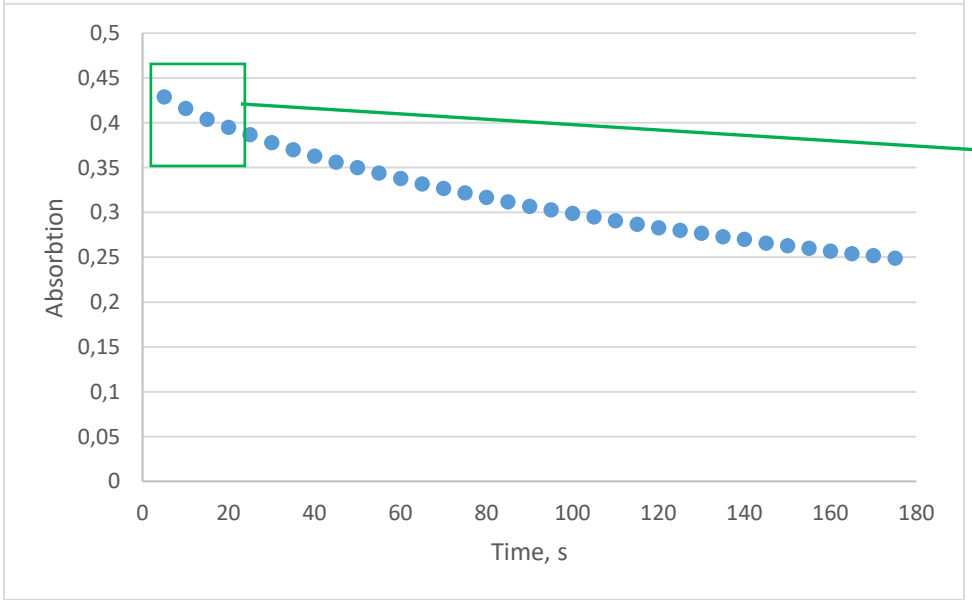

Absorbtion
Time, s

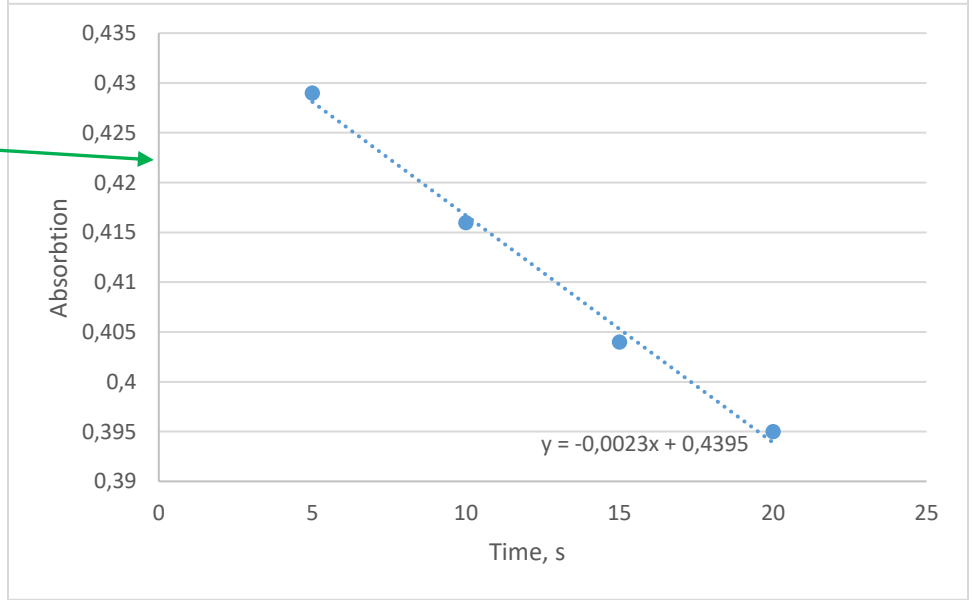

Absorbtion
Time, s
y = -0,0009x + 0,4482

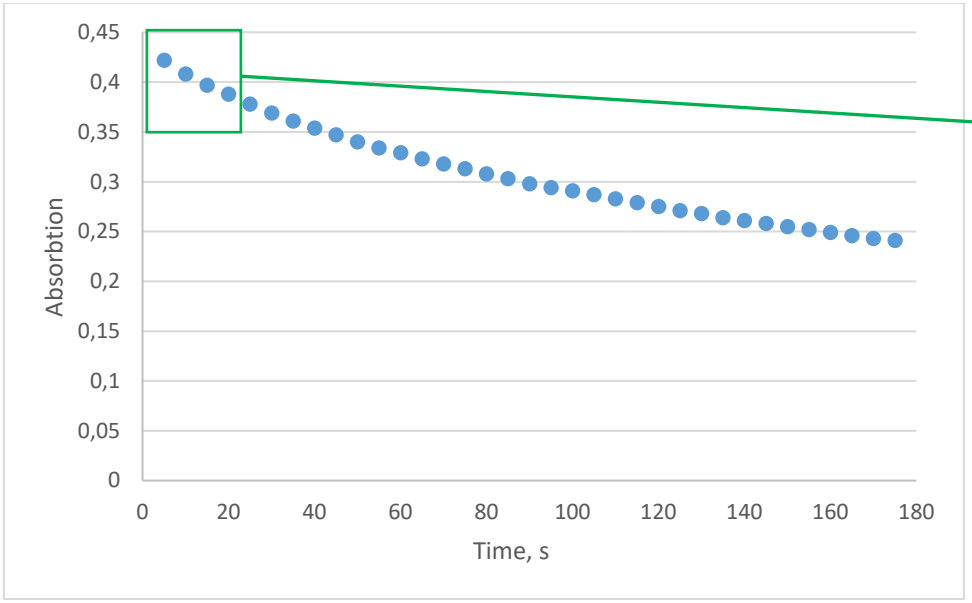
Ph-OH

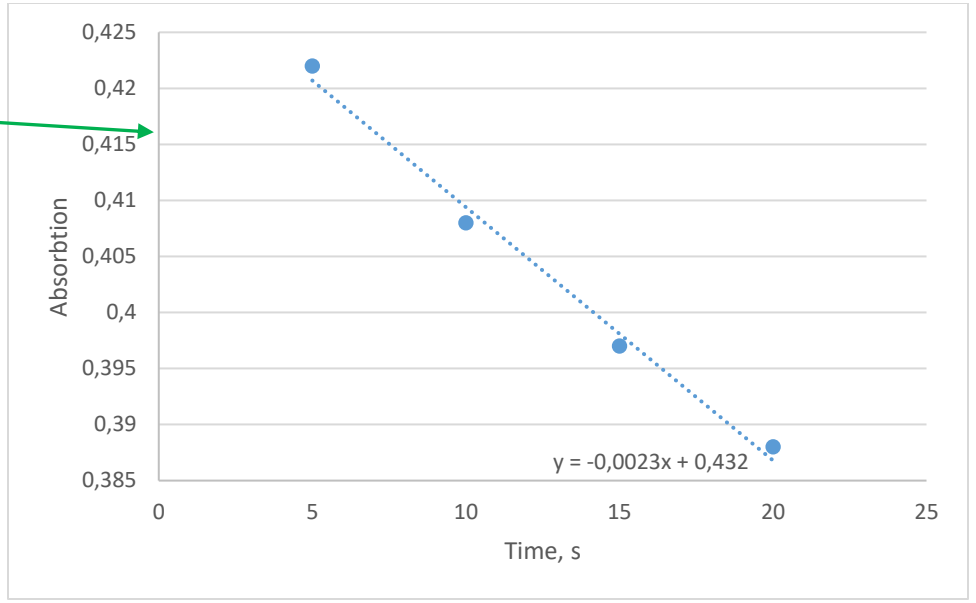

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,43
0,425
0,42
0,415
0,41
0,405
0,4
0,395
0,39
Absorbtion
y = -0,0023x + 0,4375
0
5
10
15
20
25
Time, s

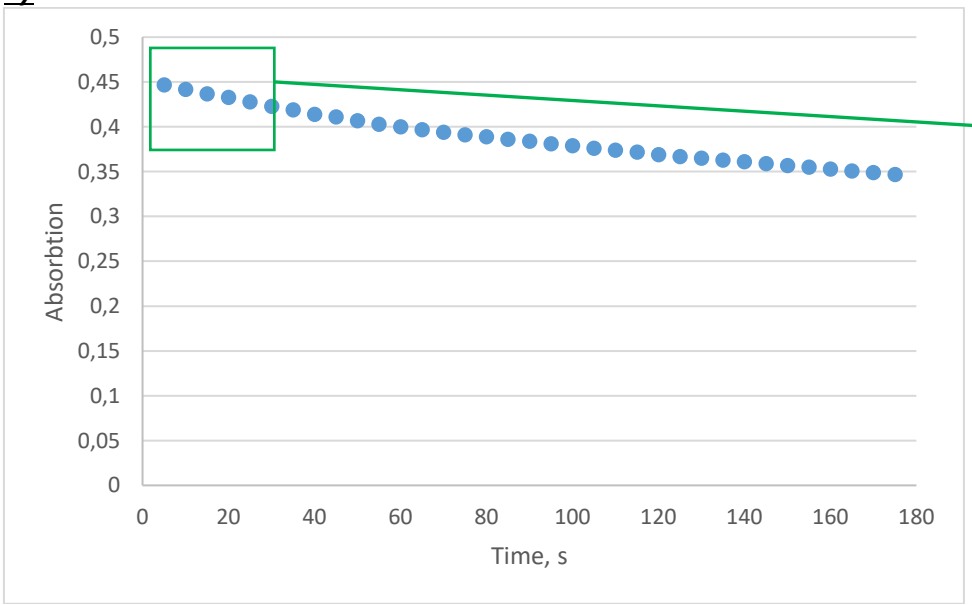

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

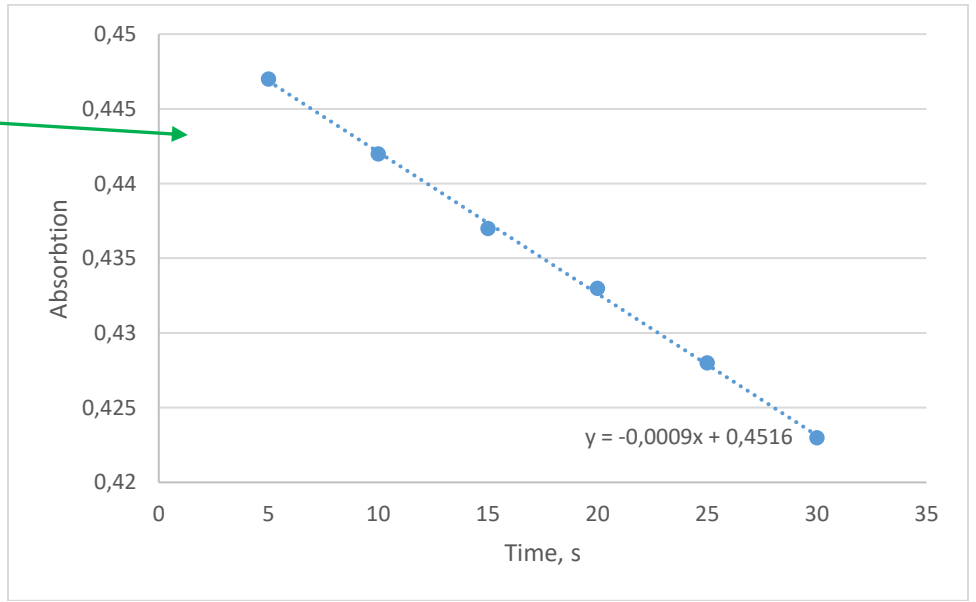

0,435
0,43
0,425
0,42
0,415
0,41
0,405
0,4
0,395
0,39
Absorbtion
y = -0,0023x + 0,4395
0
5
10
15
20
25
Time, s

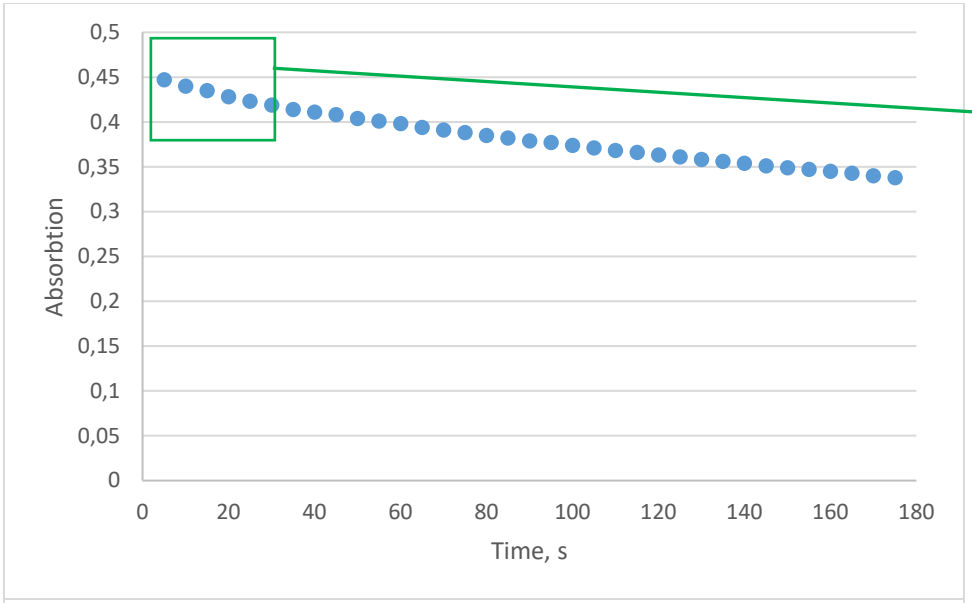

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

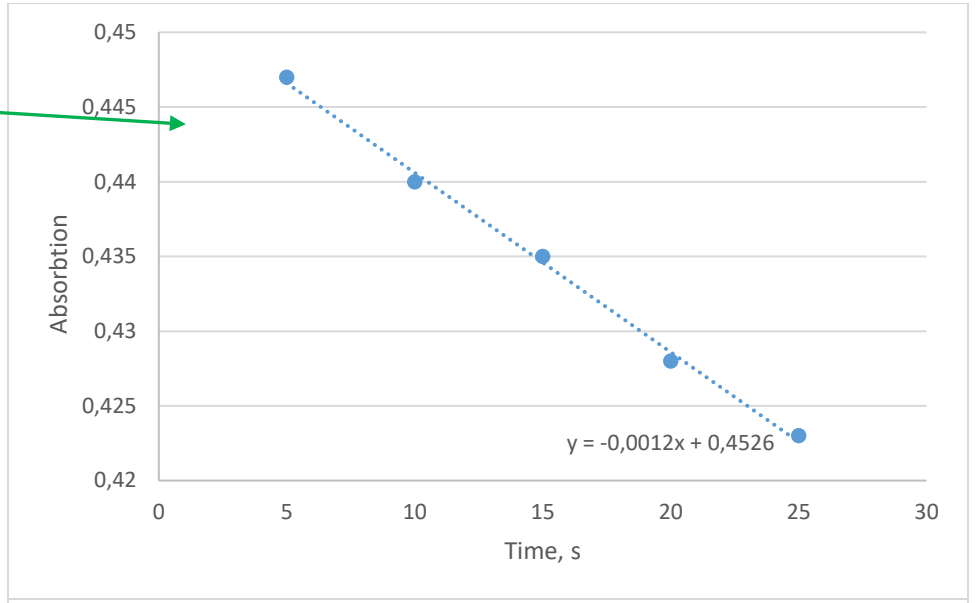

0,425
0,42
0,415
0,41
0,405
0,4
0,395
0,39
0,385
Absorbtion
y = -0,0023x + 0,432
0
5
10
15
20
25
Time, s

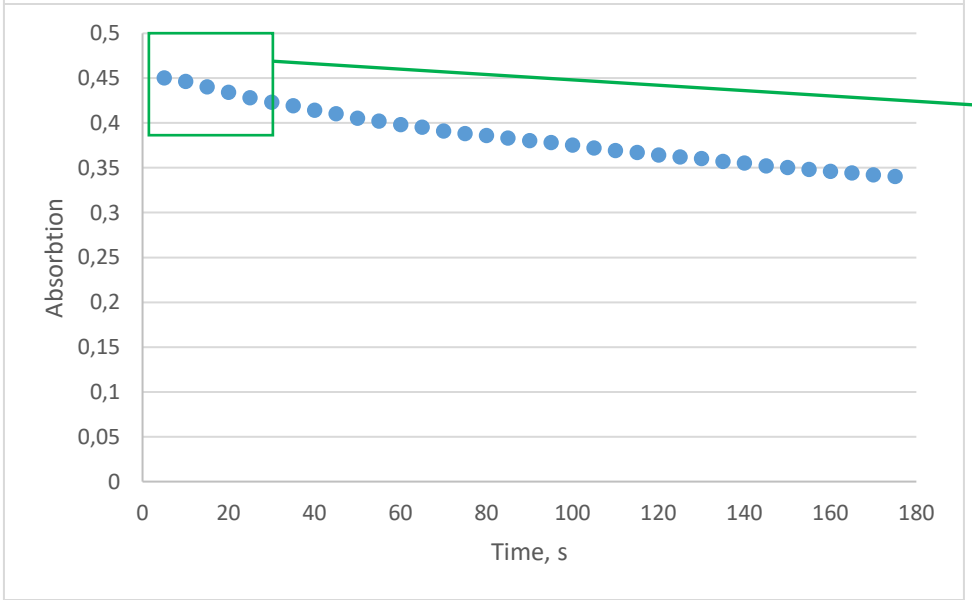
Py

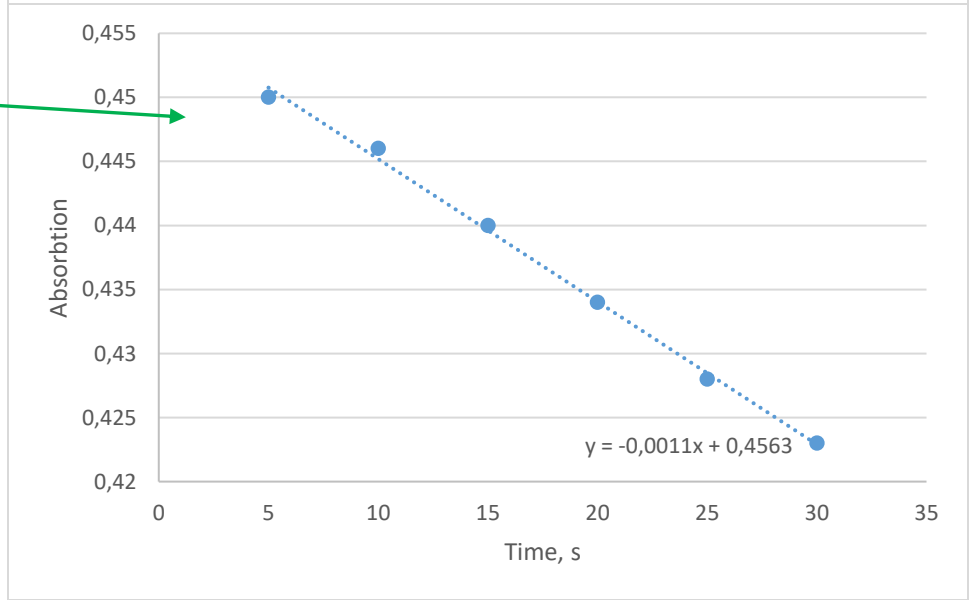

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,45
0,445
0,44
0,435
0,43
0,425
0,42
Absorbtion
y = -0,0009x + 0,4516
0
5
10
15
20
25
30
35
Time, s

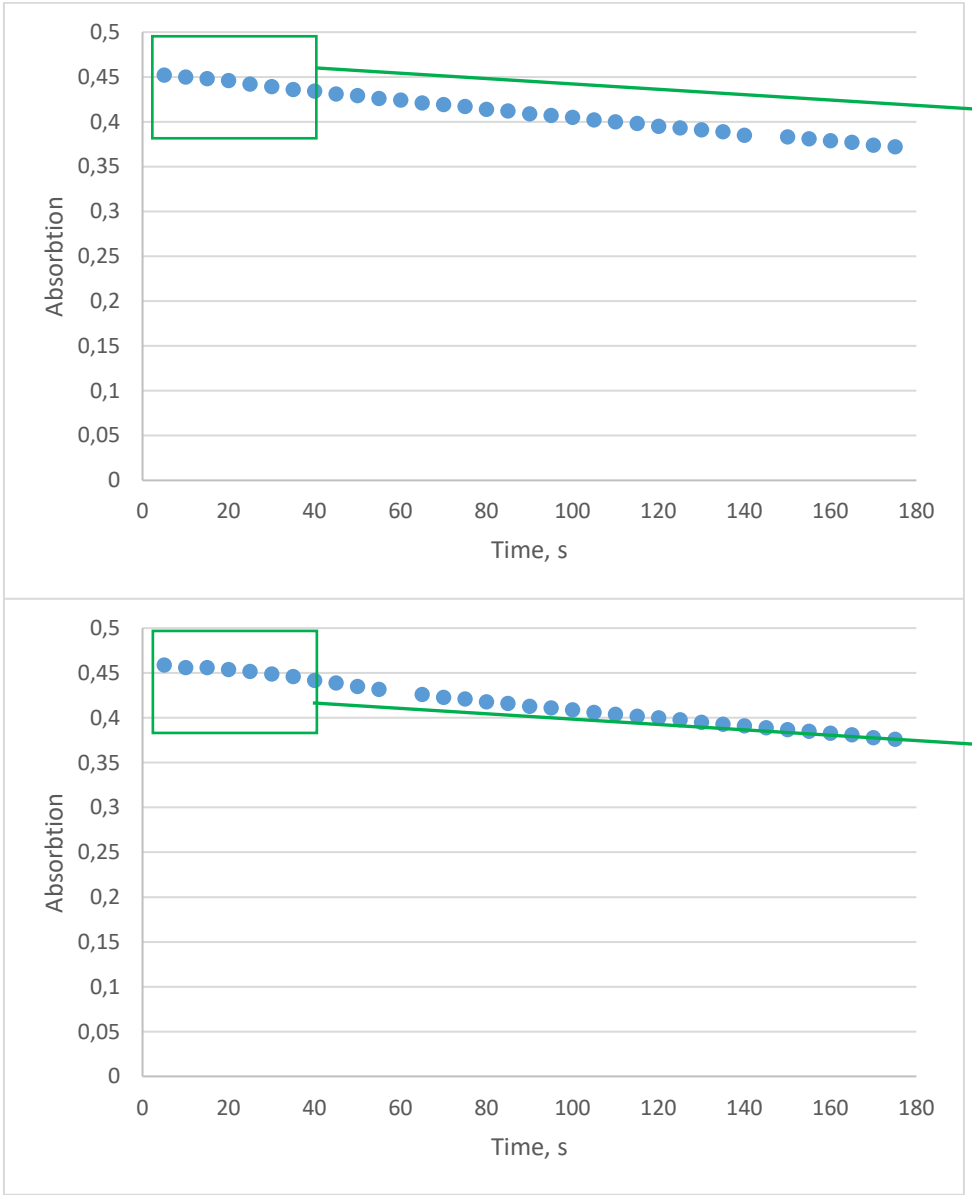

Absorbtion
Time, s
0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
20
40
60
80
100
120
140
160
180

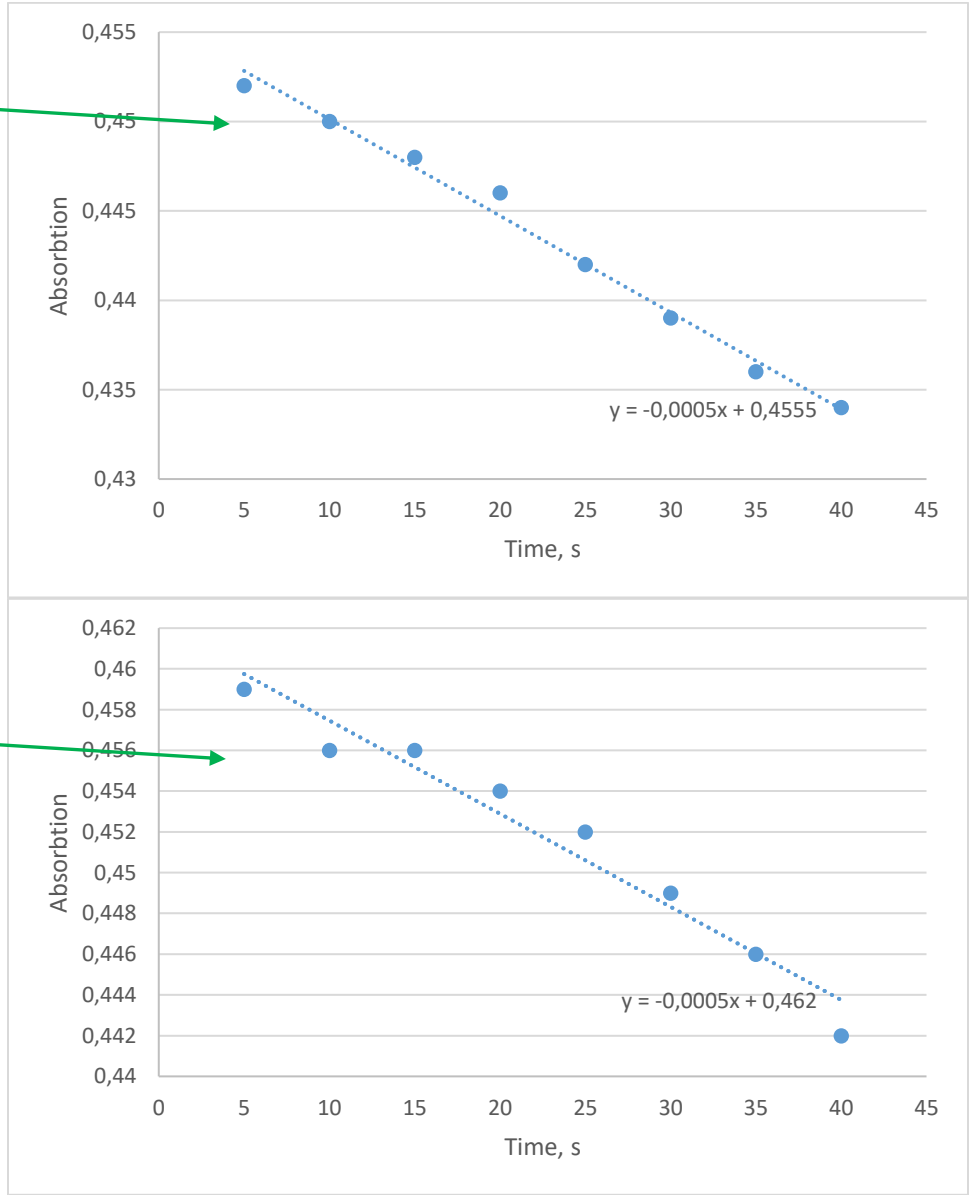

Absorbtion
Time, s
y = -0,0012x + 0,4526
0,45
0,445
0,44
0,435
0,43
0,425
0,42
0
5
10
15
20
25
30

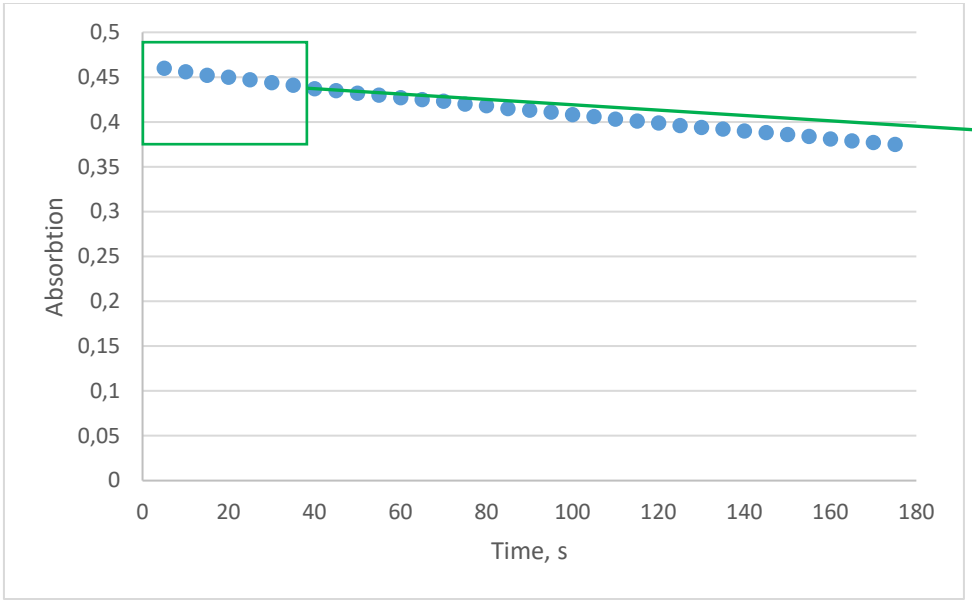

Absorbtion
Time, s
0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
20
40
60
80
100
120
140
160
180

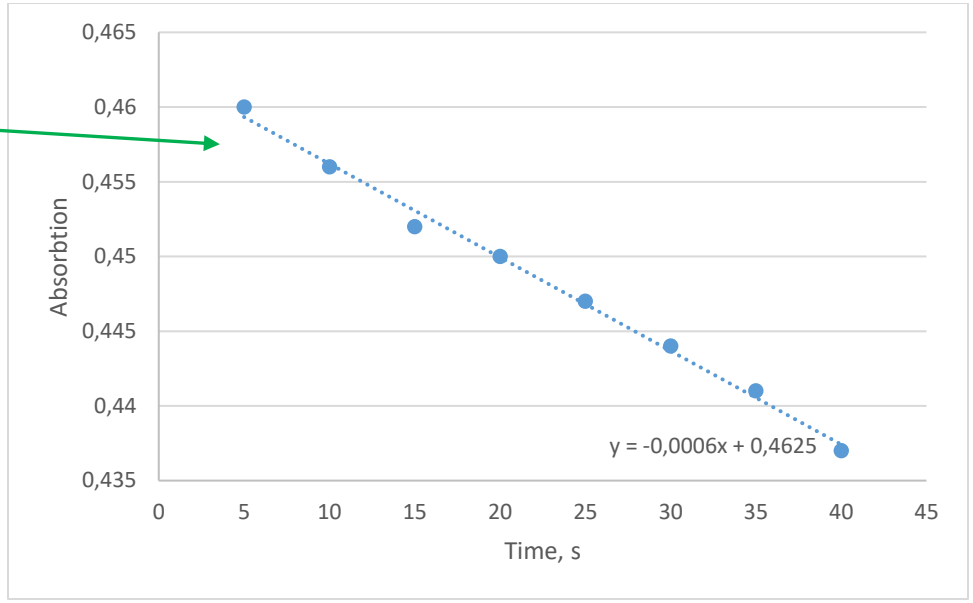

Absorbtion
Time, s
y = -0,0011x + 0,4563
0,455
0,45
0,445
0,44
0,435
0,43
0,425
0,42
0
5
10
15
20
25
30
35

Malonic acid

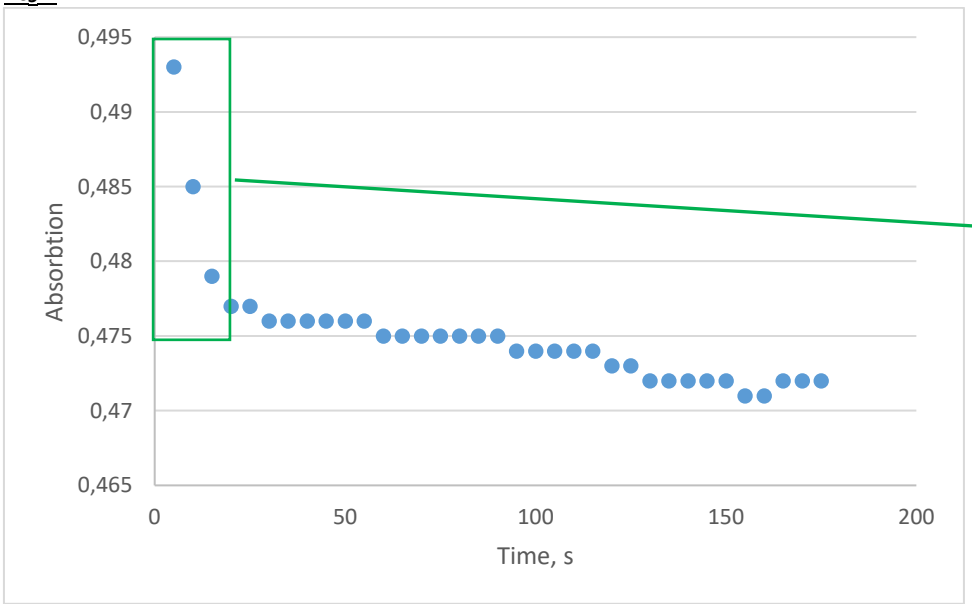


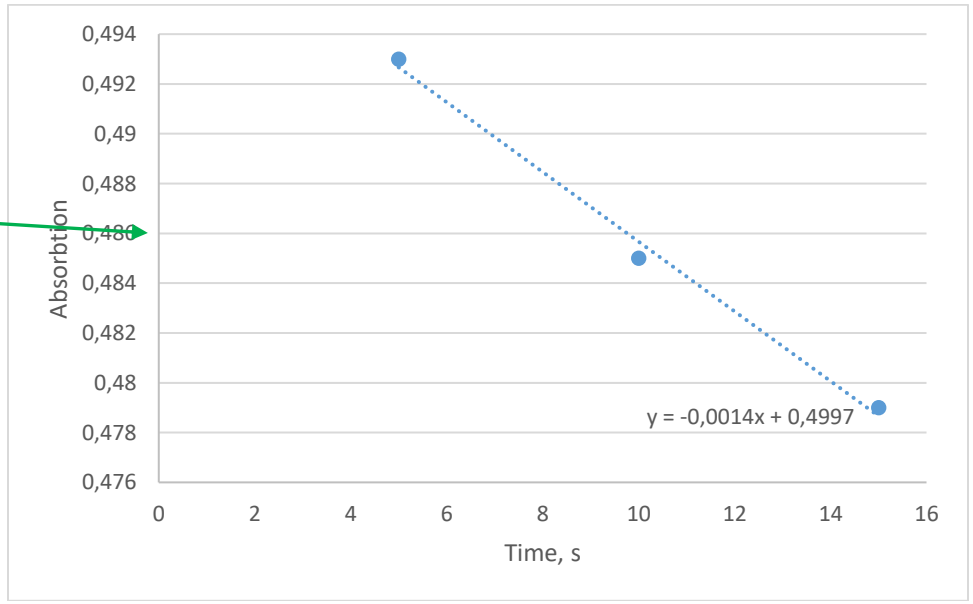


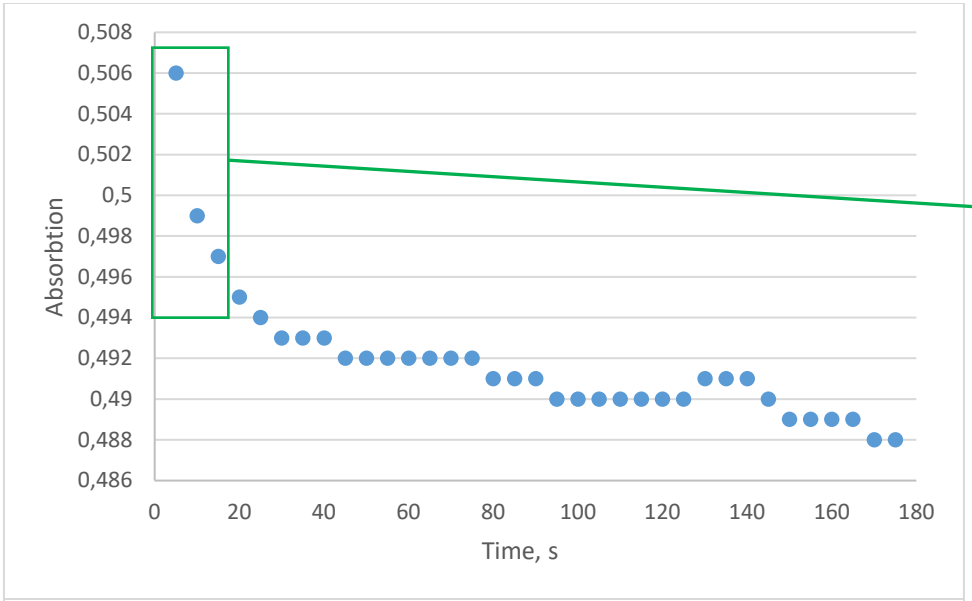

Absorbtion
Time, s

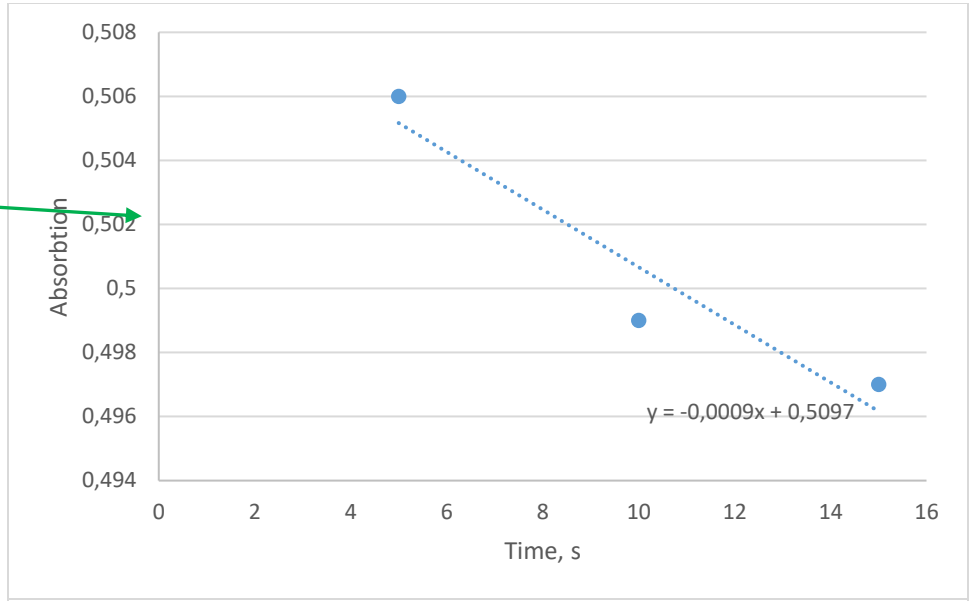

Absorbtion
Time, s
y = -0,0006x + 0,4625

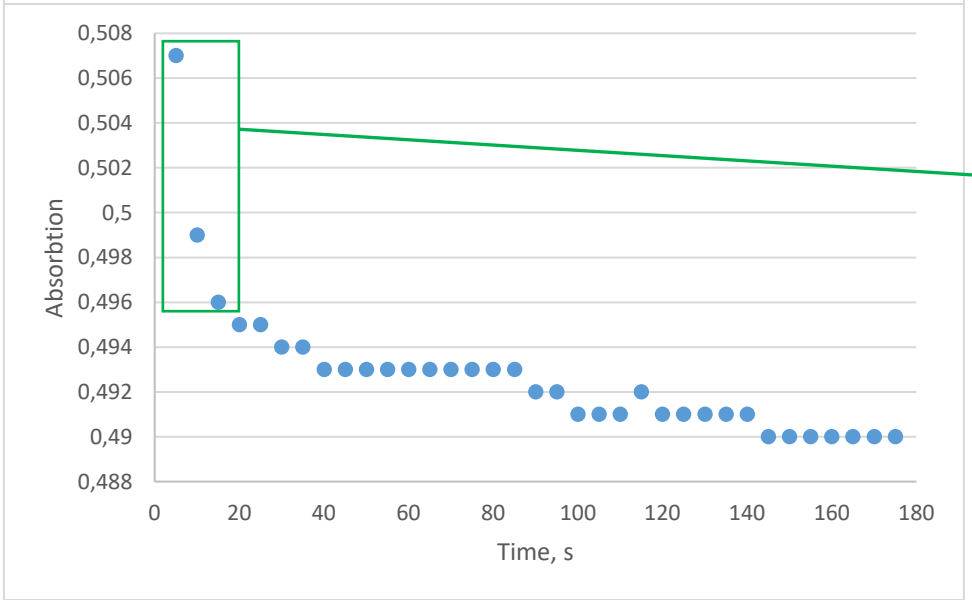
Et₃N

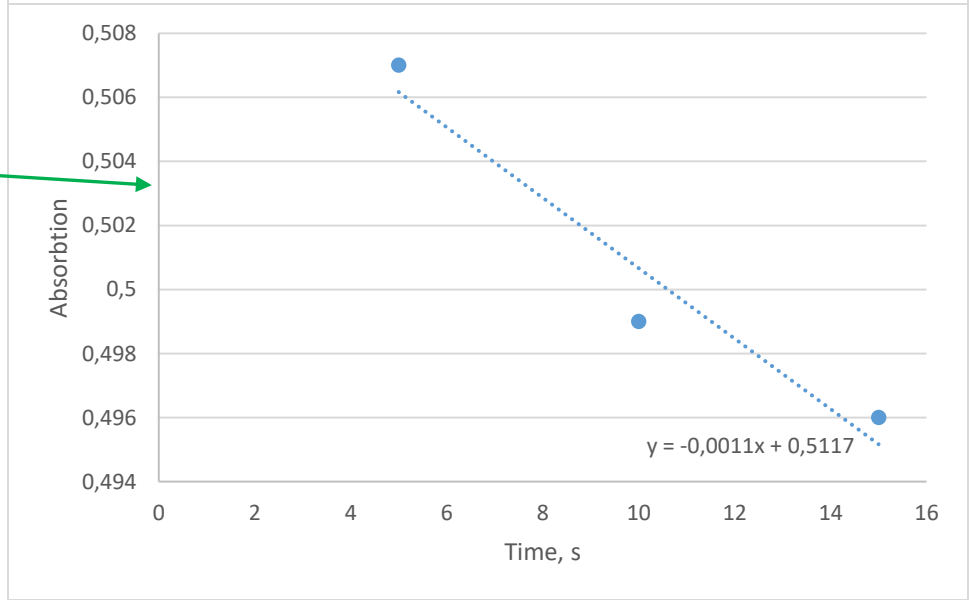

Absorbtion
Time, s


Absorbtion
Time, s
y = -0,0014x + 0,4997

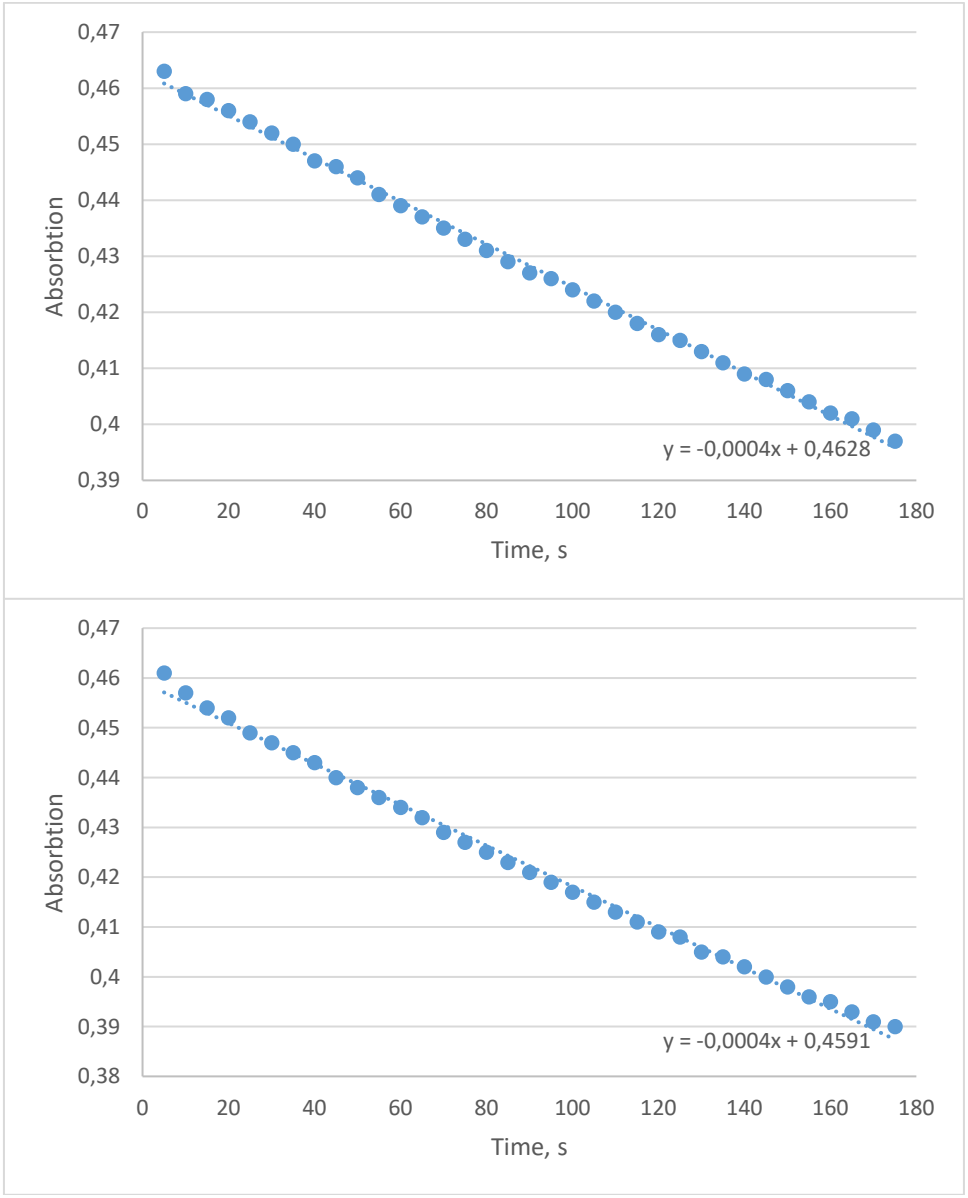

0,508
0,506
0,504
0,502
0,5
0,498
0,496
0,494
0,492
0,49
0,488
0,486
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

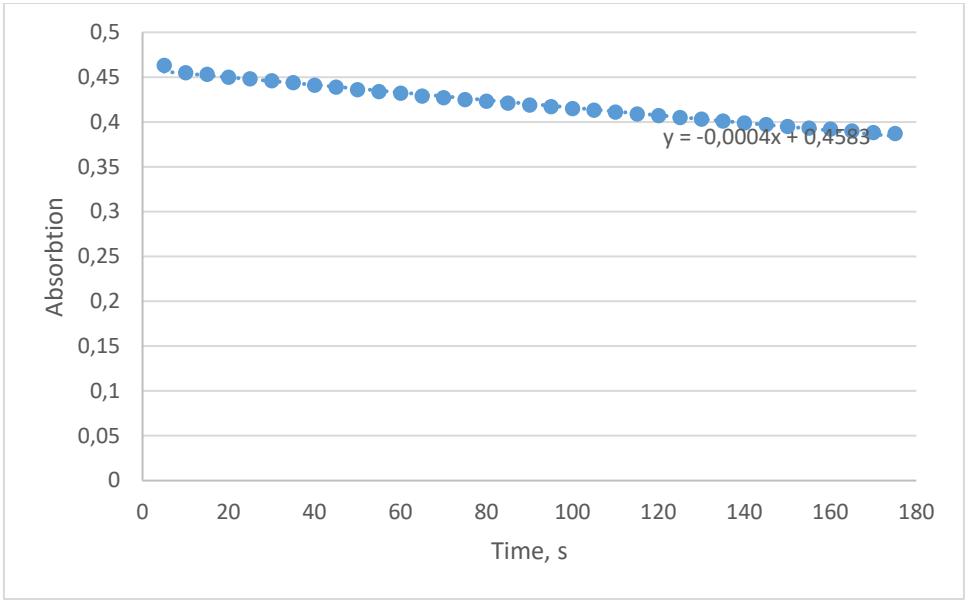

0,508
0,506
0,504
0,502
0,5
0,498
0,496
0,494
Absorbtion
y = -0,0009x + 0,5097
0
2
4
6
8
10
12
14
16
Time, s


0,508
0,506
0,504
0,502
0,5
0,498
0,496
0,494
0,492
0,49
0,488
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

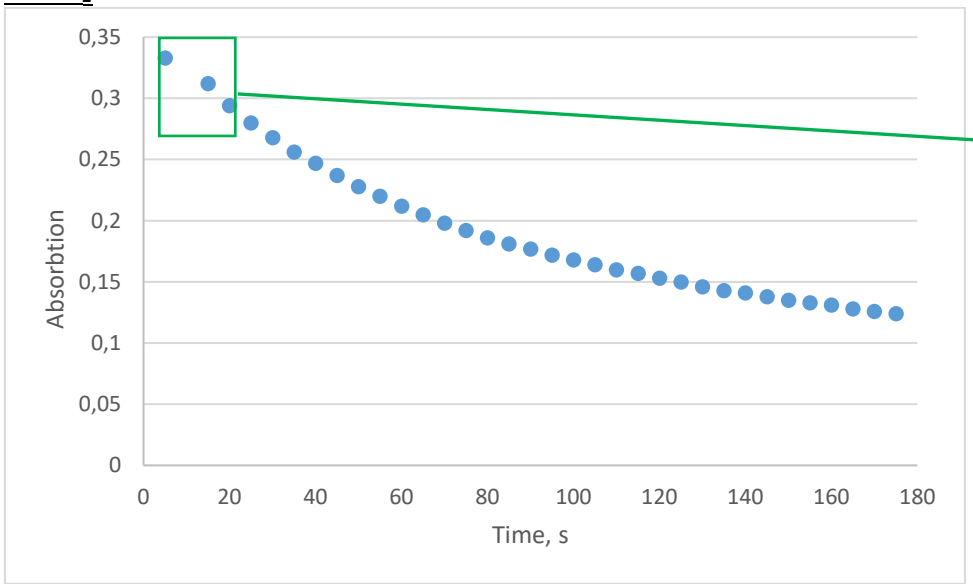

0,508
0,506
0,504
0,502
0,5
0,498
0,496
0,494
Absorbtion
y = -0,0011x + 0,5117
0
2
4
6
8
10
12
14
16
Time, s

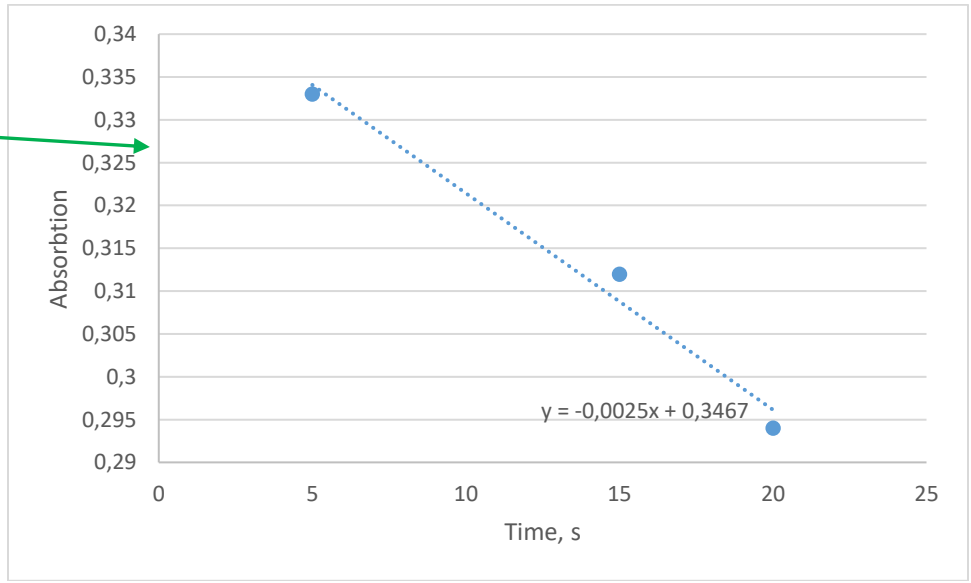
TFA:

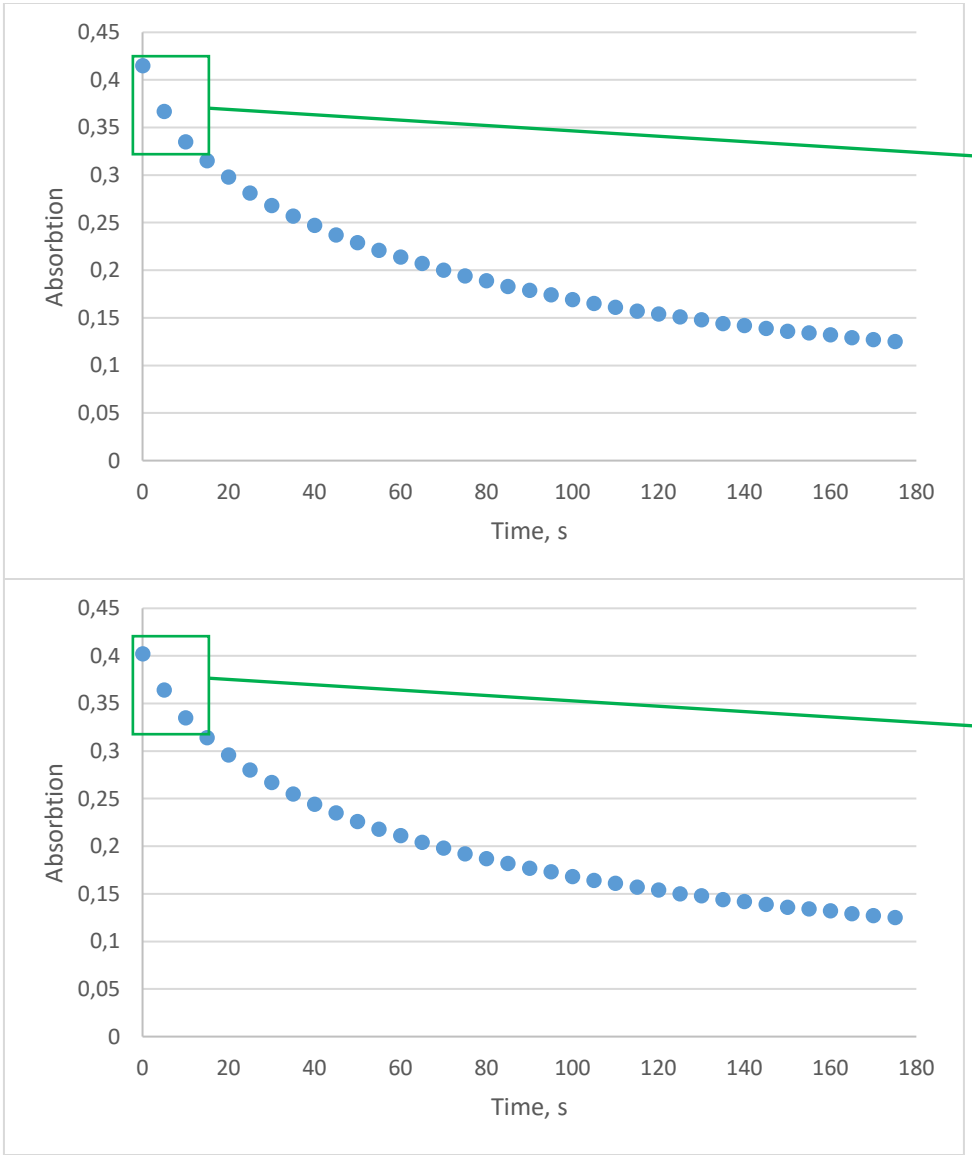

0,47
0,46
0,45
0,44
0,43
0,42
0,41
0,4
0,39
Absorbtion
y = -0,0004x + 0,4628
0
20
40
60
80
100
120
140
160
180
Time, s
0,47
0,46
0,45
0,44
0,43
0,42
0,41
0,4
0,39
0,38
Absorbtion
y = -0,0004x + 0,4591
0
20
40
60
80
100
120
140
160
180
Time, s

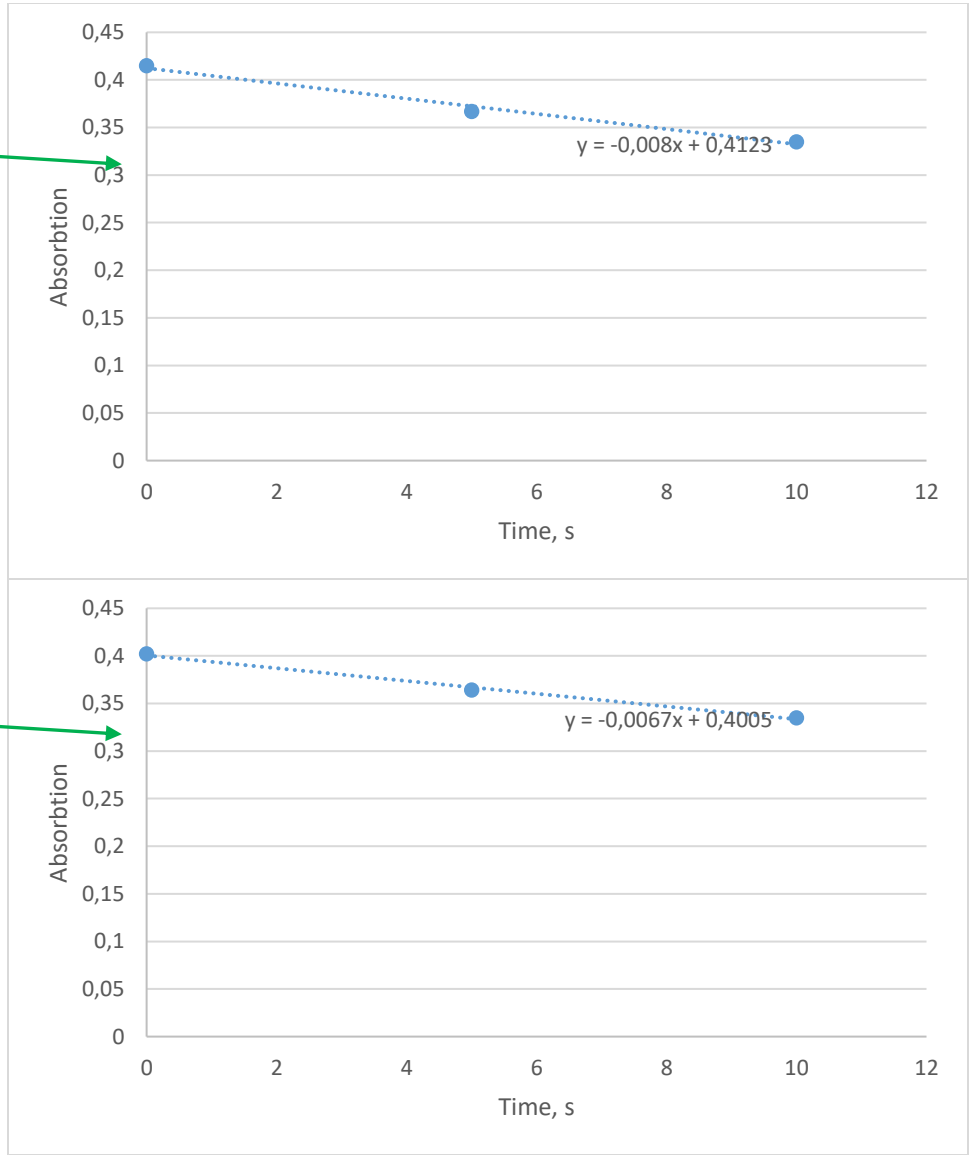

0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,0004x + 0,4583
0
20
40
60
80
100
120
140
160
180
Time, s

Ph-NH$_2$


0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,34
0,335
0,33
0,325
0,32
0,315
0,31
0,305
0,3
0,295
0,29
Absorbtion
y = -0,0025x + 0,3467
0
5
10
15
20
25
Time, s


0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s


0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,008x + 0,4123
0
2
4
6
8
10
12
Time, s

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
0
20
40
60
80
100
120
140
160
180
Time, s

0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Absorbtion
y = -0,0067x + 0,4005
0
2
4
6
8
10
12
Time, s