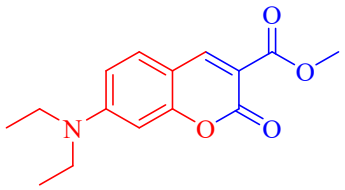
Synthesis of the different coumarins

General informations

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. ^{1}H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 or a Bruker Avance 300 spectrometer of the Spectropole: ^{1}H (400 MHz), ^{1}H (300 MHz), ^{13}C (100 MHz), and ^{13}C (75 MHz). All ^{1}H chemical shifts were referenced to the solvent peak $CDCl_3$ (7.26 ppm), DMSO-d_6 (2.49 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak $CDCl_3$ (77.0 ppm). All photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis.

*Synthesis of methyl 7-(diethylamino)-2-oxo-2H-chromene-3-carboxylate (**3**)*



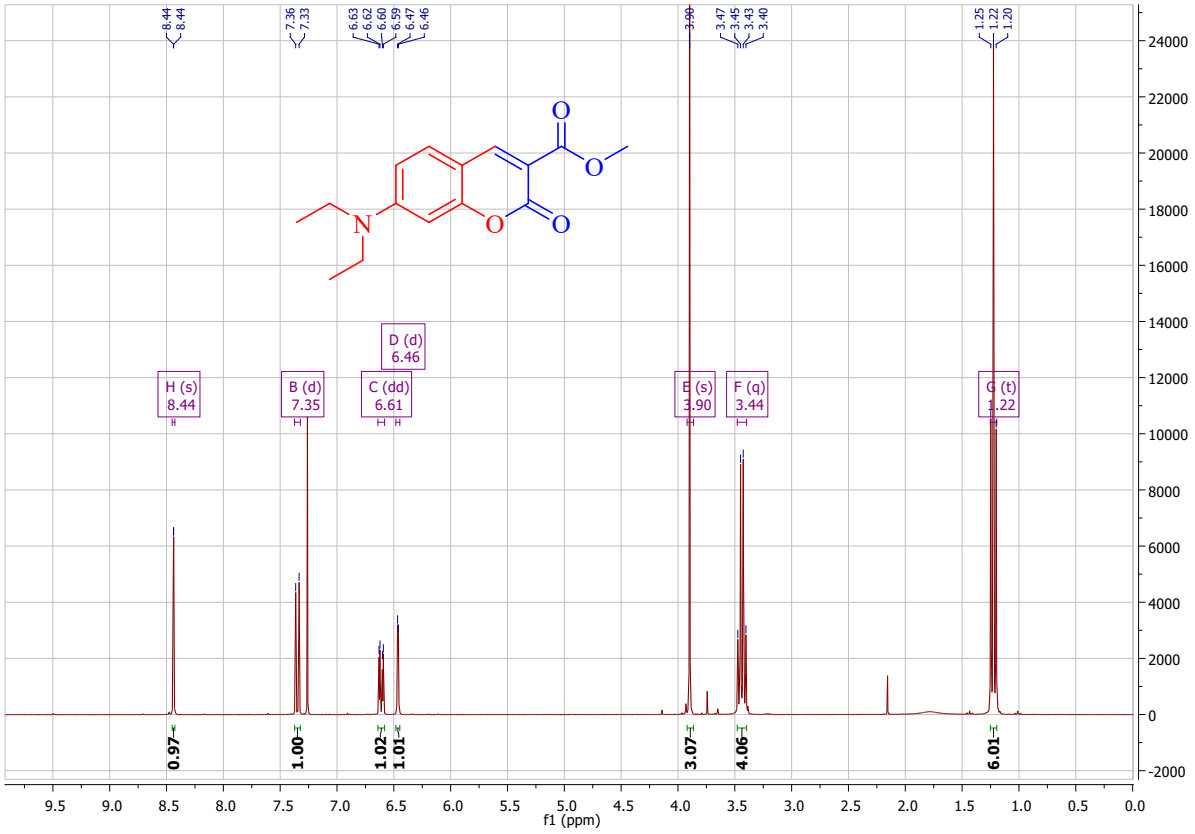
Chemical Formula: $C_{15}H_{17}NO_4$
Molecular Weight: 275,30

4-(Diethylamino)-2-hydroxybenzaldehyde (3.60 g, 18.6 mmol, M = 193.25 g/mol) and dimethyl malonate (2.18 mL, 19 mmol) were suspended in methanol (50 mL) and a few drops of piperidine were added. The solution was refluxed overnight. After cooling, the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2) using chloroform as the eluent. The product was isolated as an oil in 84% yield.

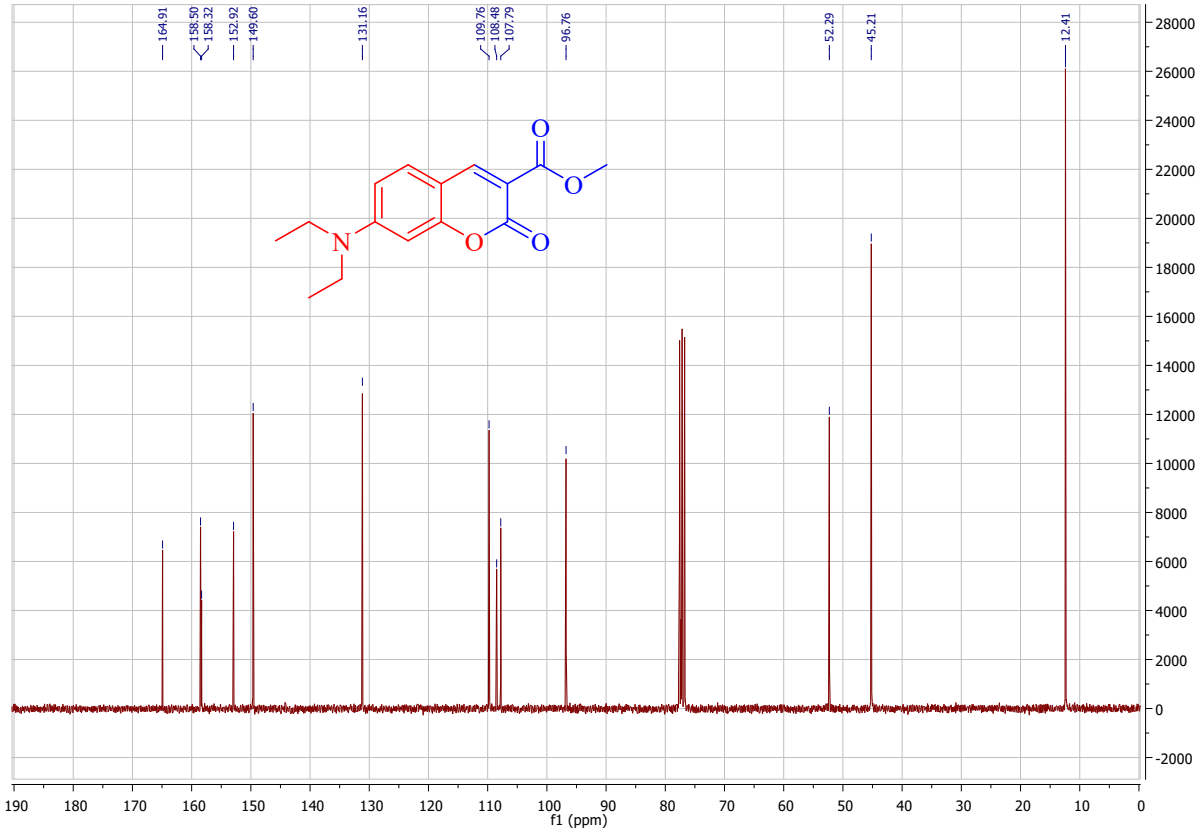
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.36 (d, J = 8.9 Hz, 1H), 6.64 (dd, J = 8.9, 2.4 Hz, 1H), 6.49 (d, J = 2.3 Hz, 1H), 3.91 (s, 3H), 3.45 (q, J = 7.1 Hz, 4H), 1.23 (t, J = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.85, 158.44, 158.26, 152.86, 149.54, 131.10, 109.71, 108.42, 107.73, 96.70, 52.23, 45.15, 12.35

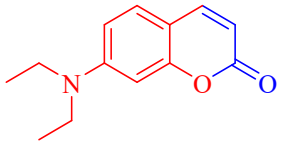
*[1]H NMR spectrum of methyl 7-(diethylamino)-2-oxo-2H-chromene-3-carboxylate (**3**)*



^{13}C NMR spectrum of m*ethyl 7-(diethylamino)-2-oxo-2H-chromene-3-carboxylate (**3**)*



*Synthesis of 7-(diethylamino)-2H-chromen-2-one (**4**)*



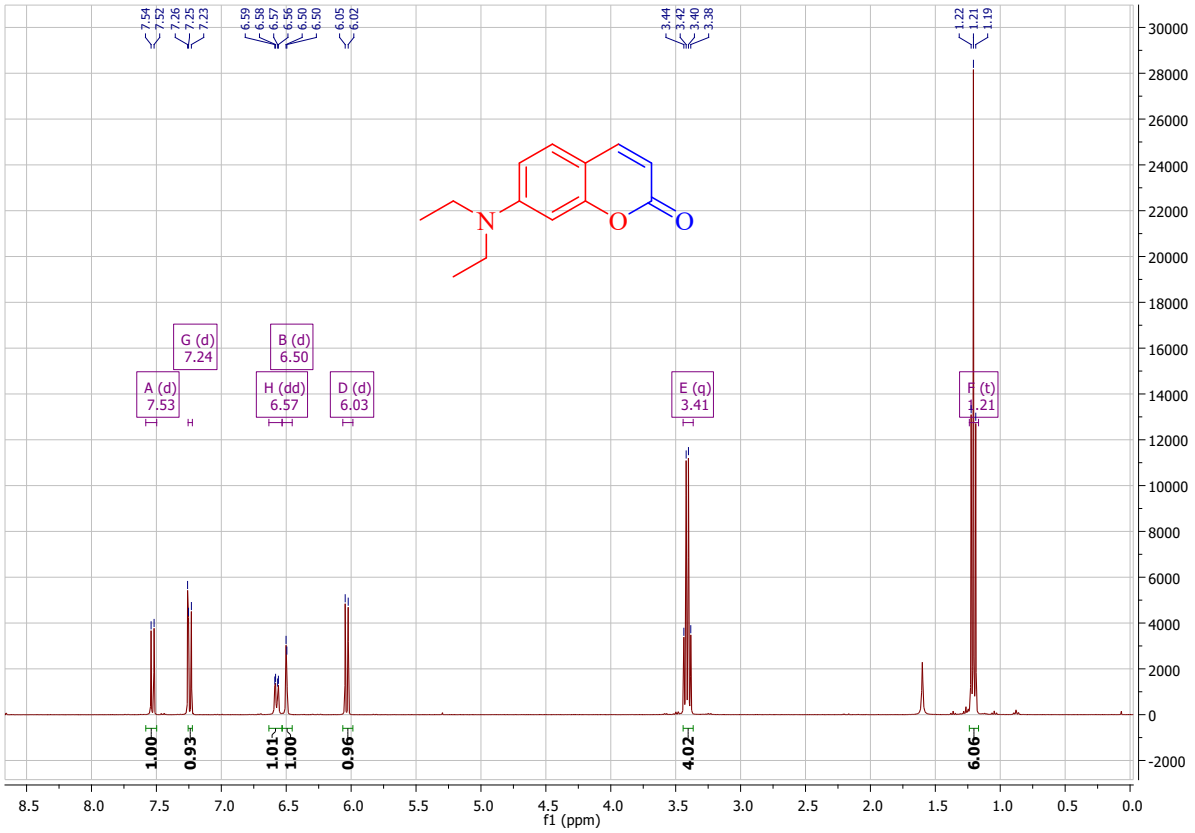
Chemical Formula: $C_{13}H_{15}NO_2$
Molecular Weight: 217,27

Dimethyl malonate (**2.64 g**, 20 mmol, M = 132.11 g/mol) and piperidine (**1 mL**, 10 mmol, M = 85.15 g/mol) were mixed and added to the solution of 4-(diethylamino)salicylaldehyde (**1.93 g**, 10 mmol, M = 193.24 g/mol) dissolved in absolute ethanol (30 mL). After stirring and heating to reflux for 6 hours, the solvent was removed by rotate evaporating. Then, concentrated aqueous HCl (20 mL) and acetic acid (20 mL) were added for hydrolysis and stirred thoroughly for another 6 hours. After the mixture cooled down to room temperature, ice water (100 mL) were poured into the solution and then 40% NaOH solution was added dropwise to adjust pH to ~5. Then, a pale precipitate formed immediately. After stirring for another 30 min, the solid was filtered off, washed with water and then recrystallized with toluene, dried under reduced pressure to give the targeted compound in 75% yield.

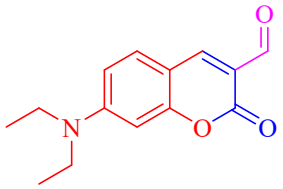
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 9.3 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 6.57 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 6.03 (d, *J* = 9.3 Hz, 1H), 3.41 (q, *J* = 7.1 Hz, 4H), 1.21 (t, *J* = 7.1 Hz, 6H).

Analyses were consistent with those previously reported in the literature [Tailored Coumarin Dyes for Photoredox Catalysis: Calculation, Synthesis, and Electronic Properties, Andrea Gualandi, Artur Nenov, Marianna Marchini, Giacomo Rodeghiero, Irene Conti, Ettore Paltanin, Matteo Balletti, Paola Ceroni, Marco Garavelli, Pier Giorgio Cozzi, ChemCatChem 2021, 13, 981–989]

*[1]H NMR spectrum of 7-(diethylamino)-2H-chromen-2-one (**4**)*



*Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde (**5**)*



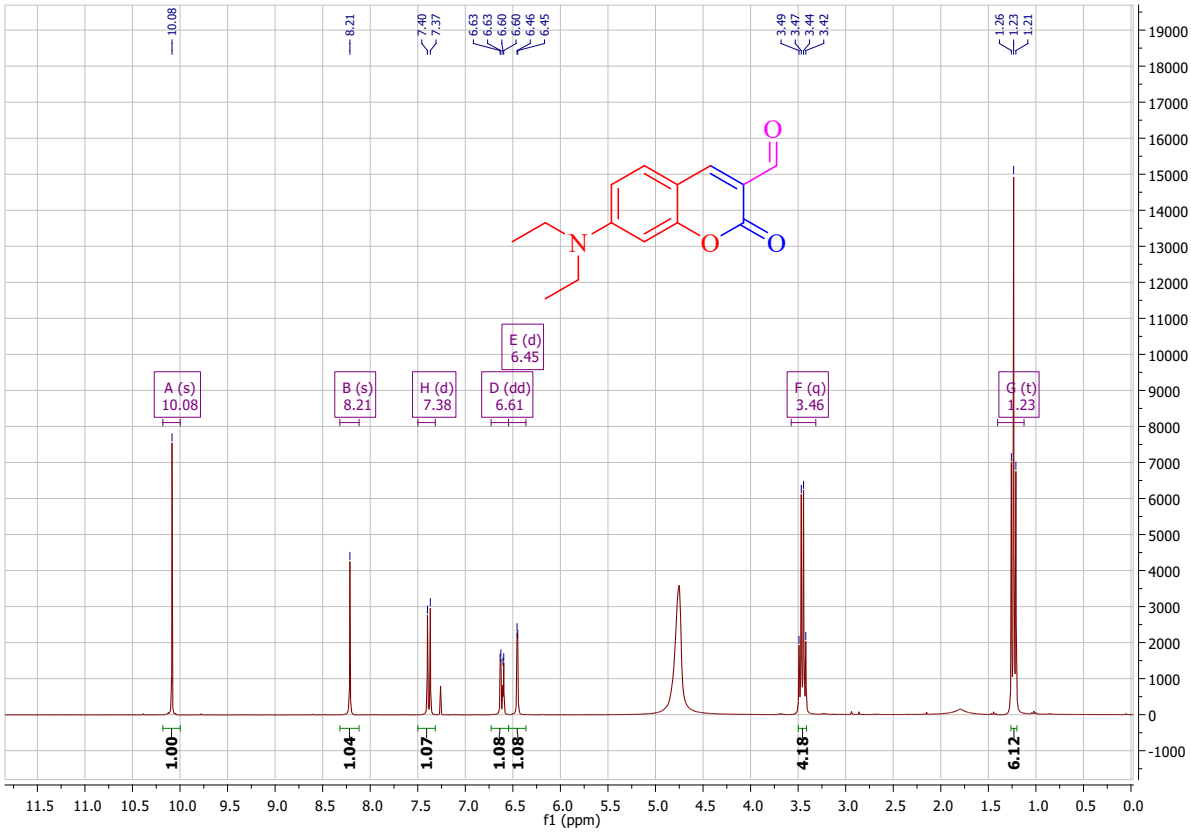
Chemical Formula: $C_{14}H_{15}NO_3$
Molecular Weight: 245,28

Phosphorus oxychloride $POCl_3$ (**20 mL)** was added dropwise to dry DMF (20 mL) at 0°C under Argon and stirred during 30 minutes at 50°C. Then, 7-(diethylamino)-2*H*-chromen-2-one (**15.0 g**, 69.1 mmol, M = 217.27 g/mol) in DMF (100 mL) was added to the mixture and the solution was stirred to 60°C overnight. After, the mixture was poured onto ice/water (500 mL), a solution of aq. NaOH 20% was added. The resulting precipitate was filtered off, washed with water and dried under vacuum (89% yield).

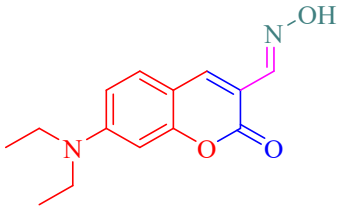
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.21 (s, 1H), 7.38 (d, J = 9.0 Hz, 1H), 6.61 (dd, J = 9.0, 2.5 Hz, 1H), 6.45 (d, J = 2.3 Hz, 1H), 3.46 (q, J = 7.1 Hz, 4H), 1.23 (t, J = 7.1 Hz, 6H)

Analyses were consistent with those previously reported in the literature [Detection of Biothiols with a Fast-Responsive and Water-Soluble Pyrazolone-Based Fluorogenic Probe, Kévin Renault, Pierre-Yves Renard, Cyrille Sabot, Eur. J. Org. Chem. 2018, 6494–6498]

*[1]H NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde (**5**)*



*Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde oxime (**OXE-A**)*



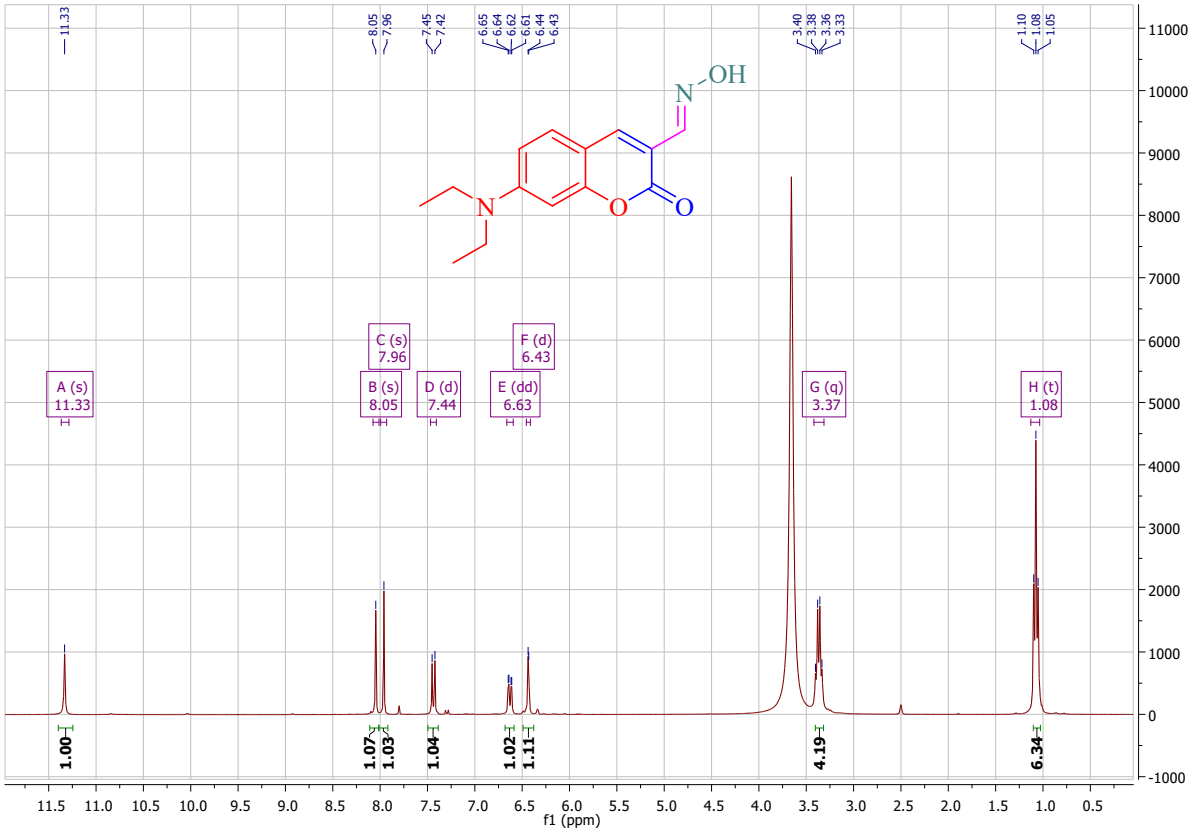
Chemical Formula: $C_{14}H_{15}NO_3$
Molecular Weight: 245,28

A mixture of 7-(diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde (**4.90 g**, 20.0 mmol, M = 245.28 g/mol), hydroxylamine hydrochloride (**2.08 g**, 30.0 mmol, M = 69.49 g/mol) and anhydrous sodium acetate (**2.48 g**, 30.0 mmol, M = 82.03 g/mol) was refluxed in ethanol (200 mL) under N_2 atmosphere overnight. The solvent was evaporated under reduced pressure, and the residue was washed with water. The raw product was recrystallized from ethanol to give orange needles (92% yield).

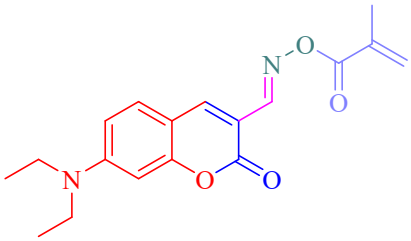
^{1}H NMR (300 MHz, DMSO) δ 11.33 (s, 1H), 8.05 (s, 1H), 7.96 (s, 1H), 7.44 (d, J = 8.9 Hz, 1H), 6.63 (dd, J = 8.9, 2.2 Hz, 1H), 6.43 (d, J = 2.0 Hz, 1H), 3.37 (q, J = 6.8 Hz, 4H), 1.08 (t, J = 7.0 Hz, 6H).

Analyses were consistent with those previously reported in the literature [Polymerizable Oxime Esters: An Efficient Photoinitiator with Low Migration Ability for 3D Printing to Fabricate Luminescent Devices, Wanwan Qiu, Junzhe Zhu, Kurt Dietliker, Zhiquan Li, ChemPhotoChem 2020, 4, 5296–5303]

*[1]H NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde oxime (**OXE-A**)*



*Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-methacryloyl oxime (**OXE-B**)*



Chemical Formula: $C_{18}H_{20}N_2O_4$
Molecular Weight: 328,37

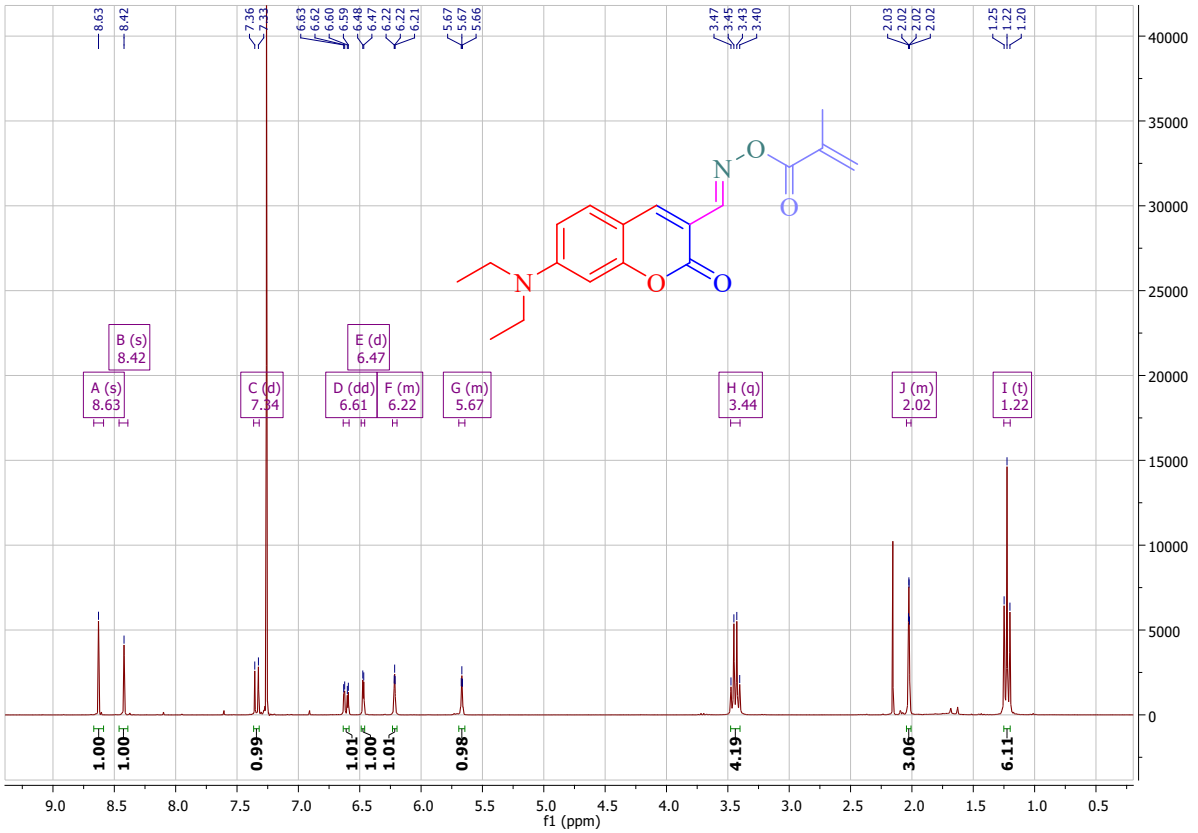
7-(Diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde oxime (**1.30 g**, 5.0 mmol, M = 260.29 g/mol) and triethylamine (**3.00 mL**, 22.0 mmol, M = 101.19 g/mol, d = 0.726) were dissolved in anhydrous dichloromethane (100 mL). Then, methacryloyl chloride (**0.63 g**, 6.0 mmol, M = 104.53 g/mol) dissolved in dichloromethane (50 mL) was added dropwise over a period of 1h. The flask was then stirred at room temperature for 1h under N_2 atmosphere. The solution was subsequently washed with 2M HCl, sat. $NaHCO_3$, and sat. NaCl aqueous solutions and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was purified chromatographically (SiO_2, DCM) to furnish the targeted product (51% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.42 (s, 1H), 7.34 (d, *J* = 9.0 Hz, 1H), 6.61 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.47 (d, *J* = 2.4 Hz, 1H), 6.23 – 6.20 (m, 1H), 5.69 – 5.64 (m, 1H), 3.44 (q, *J* = 7.1 Hz, 4H), 2.04 – 2.01 (m, 3H), 1.22 (t, *J* = 7.1 Hz, 6H).

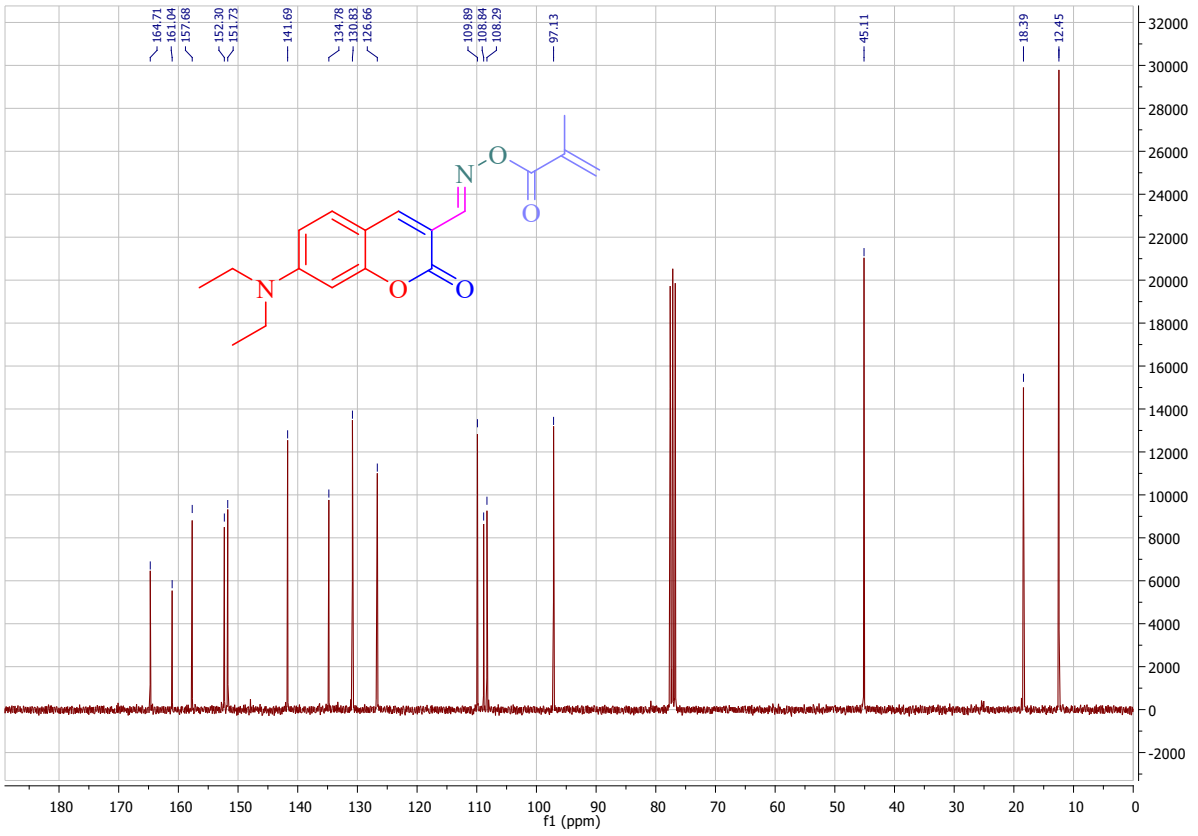
^{13}C NMR (75 MHz, $CDCl_3$) δ 164.71, 161.04, 157.68, 152.30, 151.73, 141.69, 134.78, 130.83, 126.66, 109.89, 108.84, 108.29, 97.13, 45.11, 18.39, 12.45.

HRMS (ESI MS) m/z: theor: 328.1423 found: 328.1420 ($M^{+\cdot}$ detected)

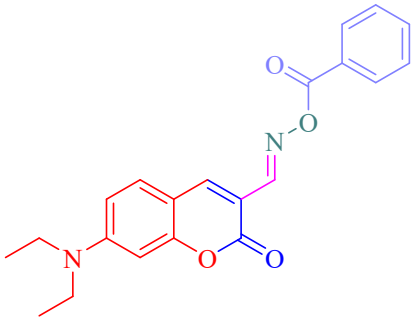
*[1]H NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-methacryloyl oxime (**OXE-B**)*



*[13]C NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-methacryloyl oxime (**OXE-B**)*



*Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-benzoyl oxime (**OXE-C**)*



Chemical Formula: $C_{21}H_{20}N_2O_4$
Molecular Weight: 364,40

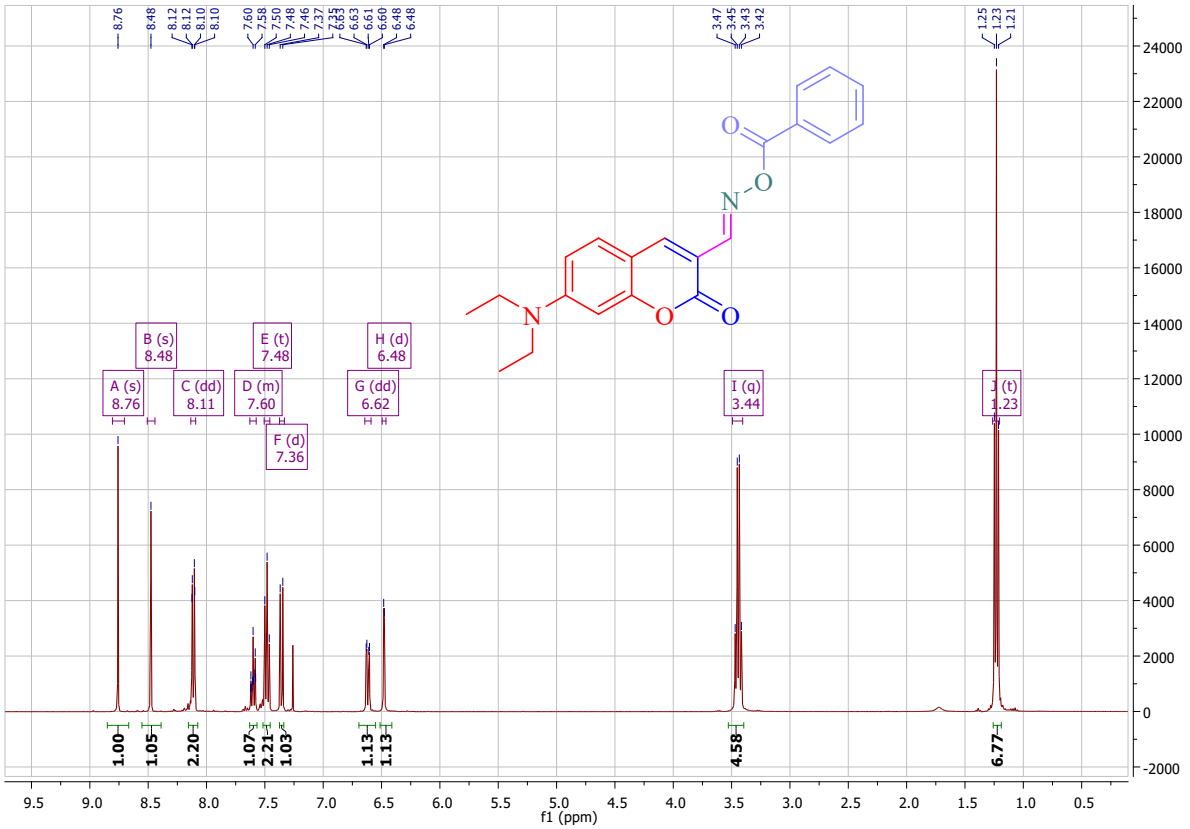
7-(Diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde oxime (**1.30 g**, 5.0 mmol, M = 260.29 g/mol) and triethylamine (**3.00 mL**, 22.0 mmol, M = 101.19 g/mol, d = 0.726) were dissolved in anhydrous dichloromethane (100 mL). Then, benzoyl chloride (0.84 g, **0.69 mL**, 6.0 mmol, M = 140.57 g/mol, d = 1.211) dissolved in dichloromethane (50 mL) was added dropwise over a period of 1h. The flask was then stirred at room temperature for 1h under N_2 atmosphere. The solution was subsequently washed with 2M HCl, sat. $NaHCO_3$, and sat. NaCl aqueous solutions and dried over $MgSO_4$. After evaporation of the volatiles, the resulting solid was purified by recrystallization in Et_2O (91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.48 (s, 1H), 8.11 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.9 Hz, 1H), 6.62 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.48 (d, *J* = 2.4 Hz, 1H), 3.44 (q, *J* = 7.1 Hz, 4H), 1.23 (t, *J* = 7.1 Hz, 6H).

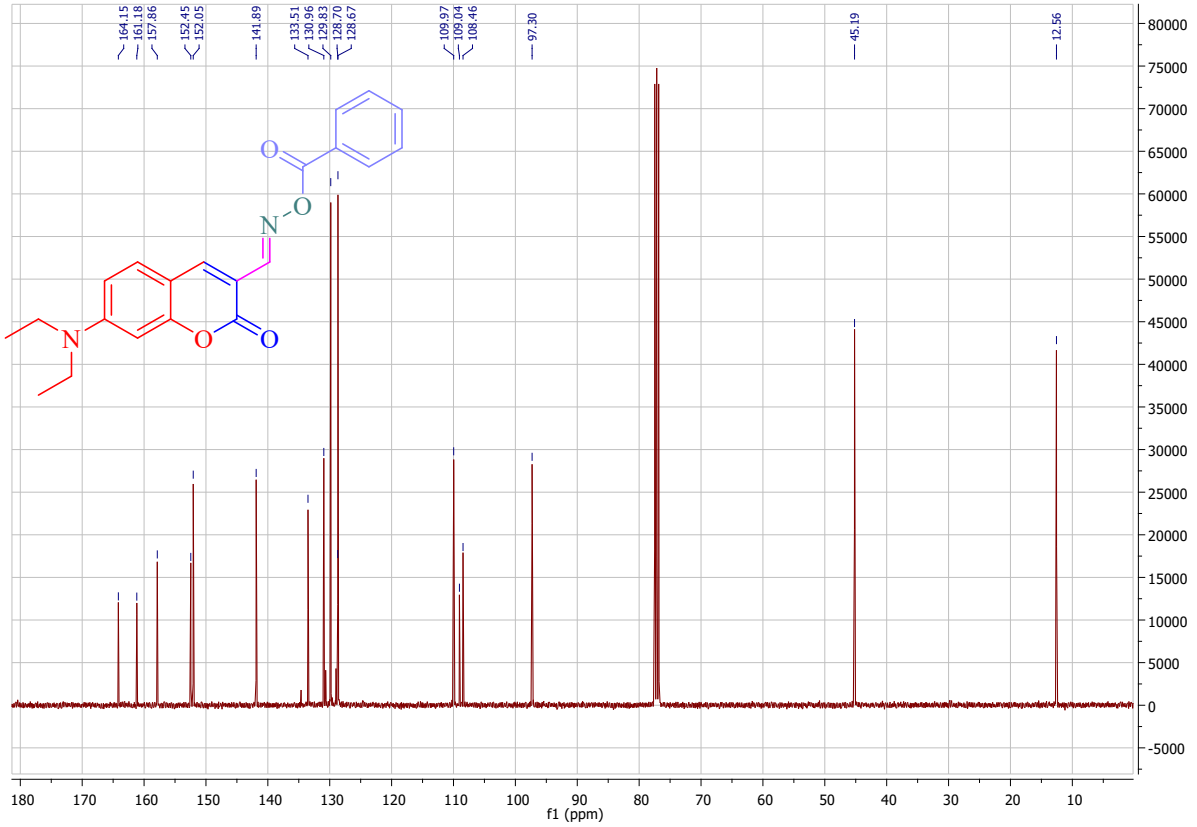
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.15, 161.18, 157.86, 152.45, 152.05, 141.89, 133.51, 130.96, 129.83, 128.70, 128.67, 109.97, 109.04, 108.46, 97.30, 45.19, 12.56.

HRMS (ESI MS) m/z: theor: 364.1423 found: 364.1422 ($M^{+\cdot}$ detected)

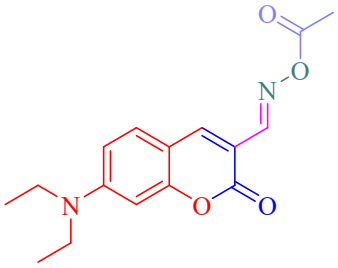
*[1]H NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-benzoyl oxime (**OXE-C**)*



*[13]C NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-benzoyl oxime (**OXE-C**)*



*Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-acetyl oxime (**OXE-D**)*



Chemical Formula: $C_{16}H_{18}N_2O_4$
Molecular Weight: 302,33

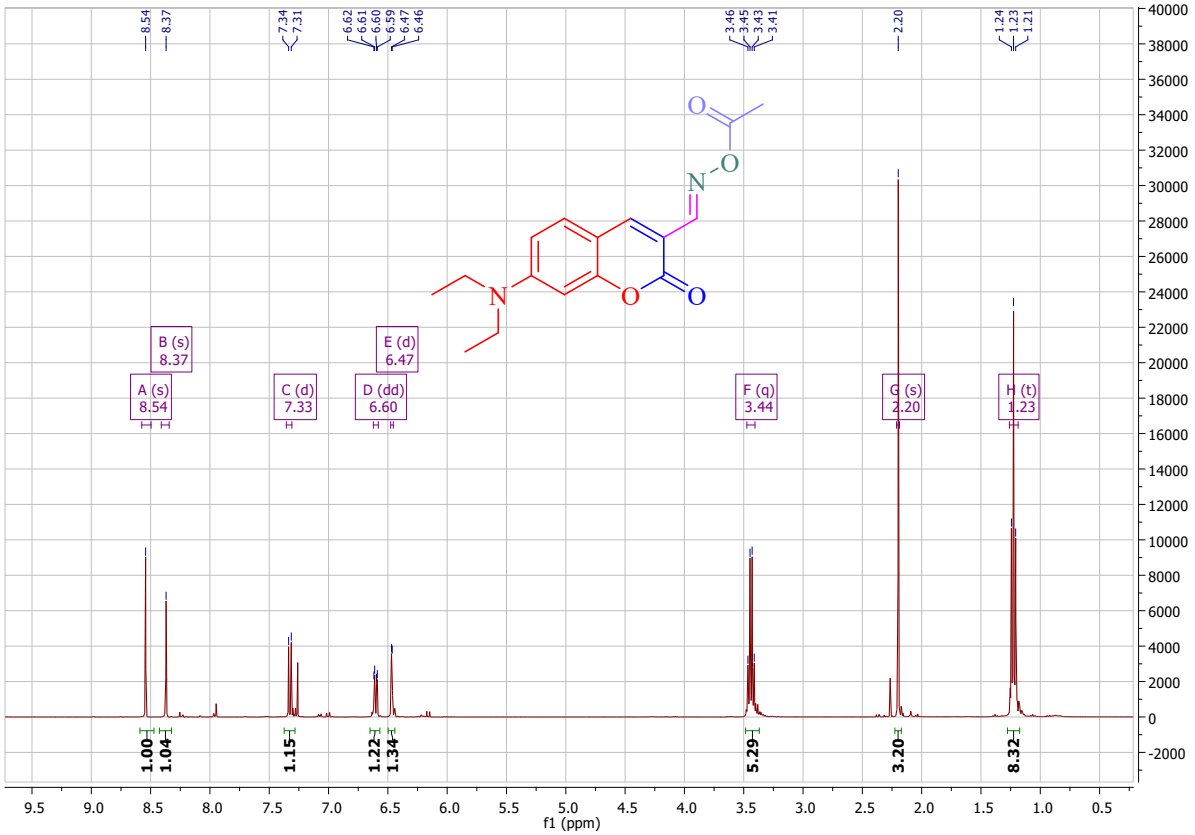
7-(Diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde oxime (**1.04 g**, 4.0 mmol, M = 260.29 g/mol) and triethylamine (**3.00 mL**, 22.0 mmol, M = 101.19 g/mol, d = 0.726) were dissolved in anhydrous dichloromethane (100 mL). Then, acetic anhydride (400 mg, **380 µL**, 4.0 mmol, M = 102.09 g/mol, d = 1.08) dissolved in dichloromethane (50 mL) was added dropwise over a period of 1h. The flask was then stirred at room temperature for 1h under N_2 atmosphere. The solution was subsequently washed with 2M HCl, sat. $NaHCO_3$, and sat. NaCl aqueous solutions and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was purified chromatographically (SiO_2, DCM) to furnish the targeted product (87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.37 (s, 1H), 7.33 (d, *J* = 8.9 Hz, 1H), 6.60 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.47 (d, *J* = 2.5 Hz, 1H), 3.44 (q, *J* = 7.1 Hz, 4H), 2.20 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H).

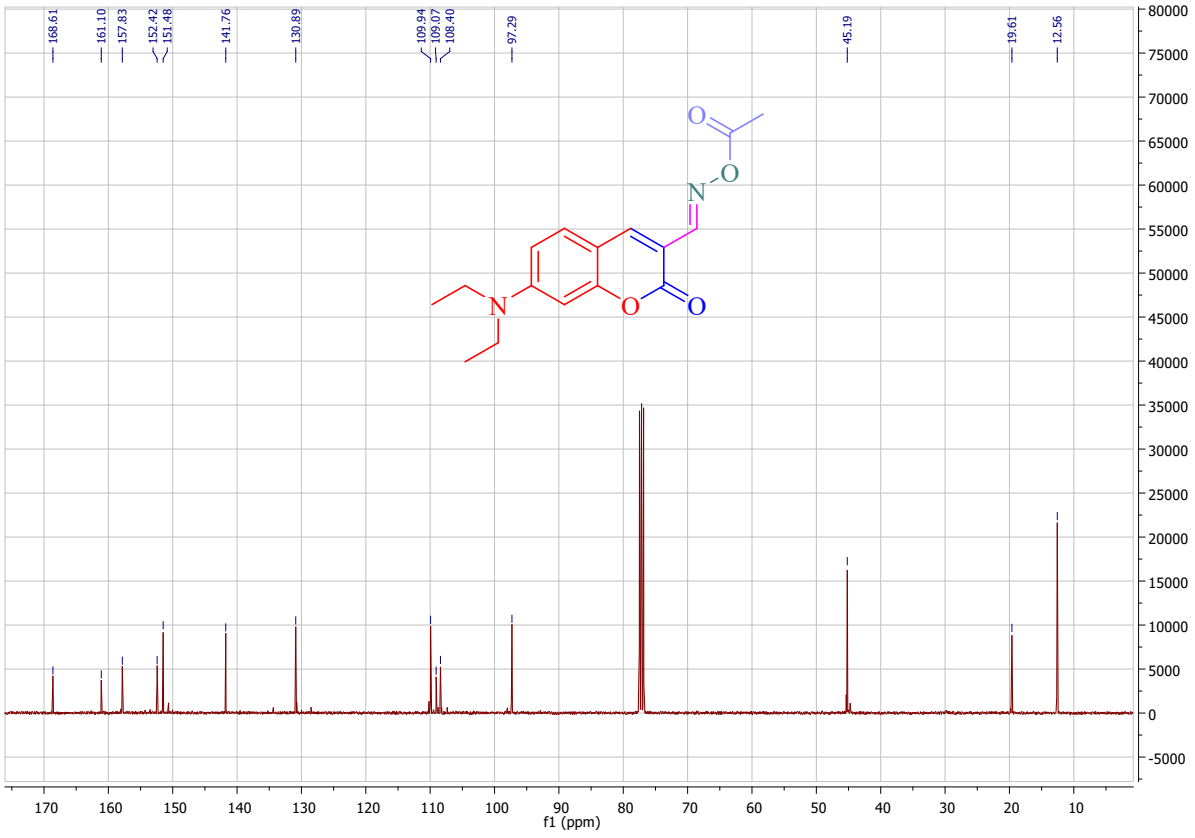
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.61, 161.10, 157.83, 152.42, 151.48, 141.76, 130.89, 109.94, 109.07, 108.40, 97.29, 45.19, 19.61, 12.56.

HRMS (ESI MS) m/z: theor: 302.1267 found: 302.1261 ($M^{+\cdot}$ detected).

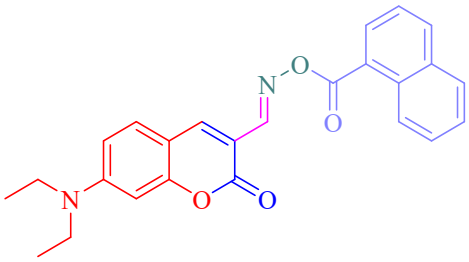
*[1]H NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-acetyl oxime (**OXE-D**)*



*[13]C NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-acetyl oxime (**OXE-D**)*



*Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(1-naphthoyl) oxime (**OXE-E**)*



Chemical Formula: $C_{25}H_{22}N_2O_4$
Molecular Weight: 414,46

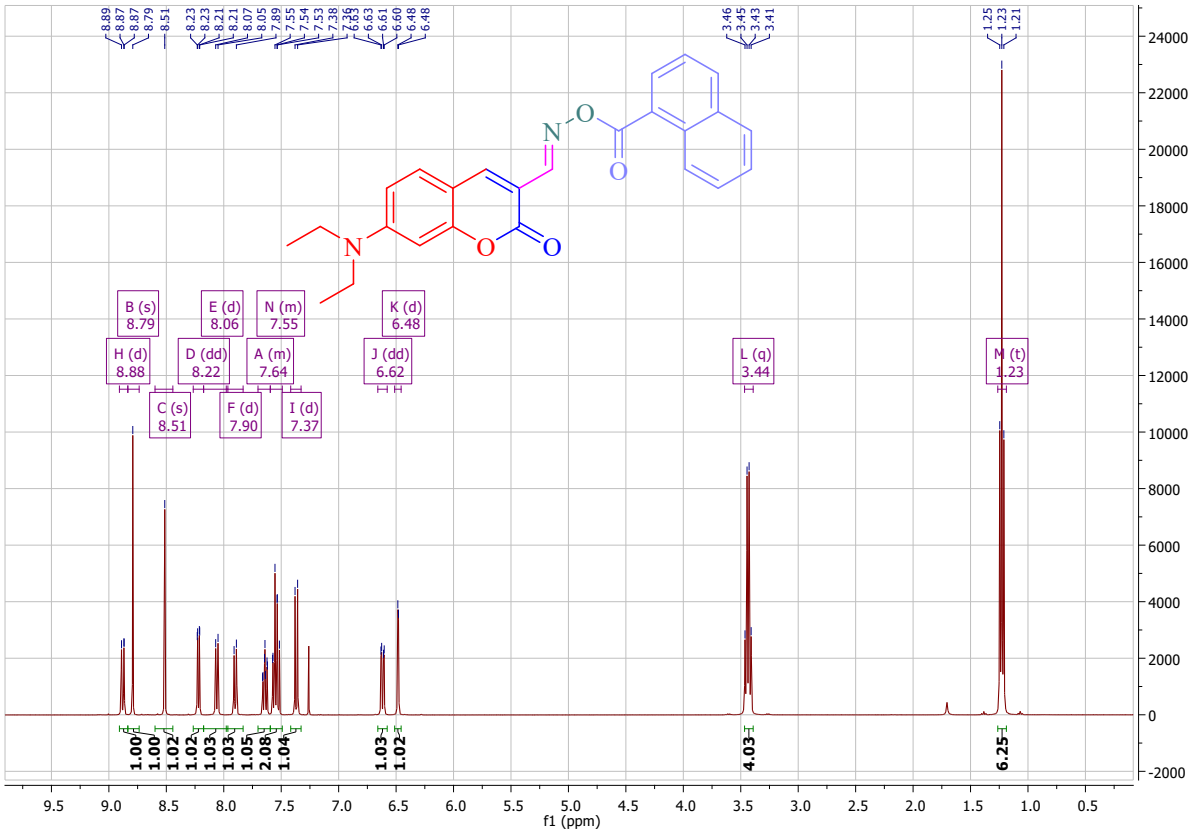
7-(Diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde oxime (**1.30 g**, 5.0 mmol, M = 260.29 g/mol) and triethylamine (**3.00 mL**, 22.0 mmol, M = 101.19 g/mol, d = 0.726) were dissolved in anhydrous dichloromethane (100 mL). Then, 1-naphthoyl chloride (1.14 g, 6.0 mmol, M = 190.63 g/mol) dissolved in dichloromethane (50 mL) was added dropwise over a period of 1h. The flask was then stirred at room temperature for 1h under N_2 atmosphere. The solution was subsequently washed with 2M HCl, sat. $NaHCO_3$, and sat. NaCl aqueous solutions and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was purified chromatographically (SiO_2, DCM) to furnish the targeted product (74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 9.0 Hz, 1H), 8.79 (s, 1H), 8.51 (s, 1H), 8.22 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.59 (m, 1H), 7.59 – 7.49 (m, 2H), 7.37 (d, *J* = 8.9 Hz, 1H), 6.62 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.48 (d, *J* = 2.3 Hz, 1H), 3.44 (q, *J* = 7.1 Hz, 4H), 1.23 (t, *J* = 7.1 Hz, 6H).

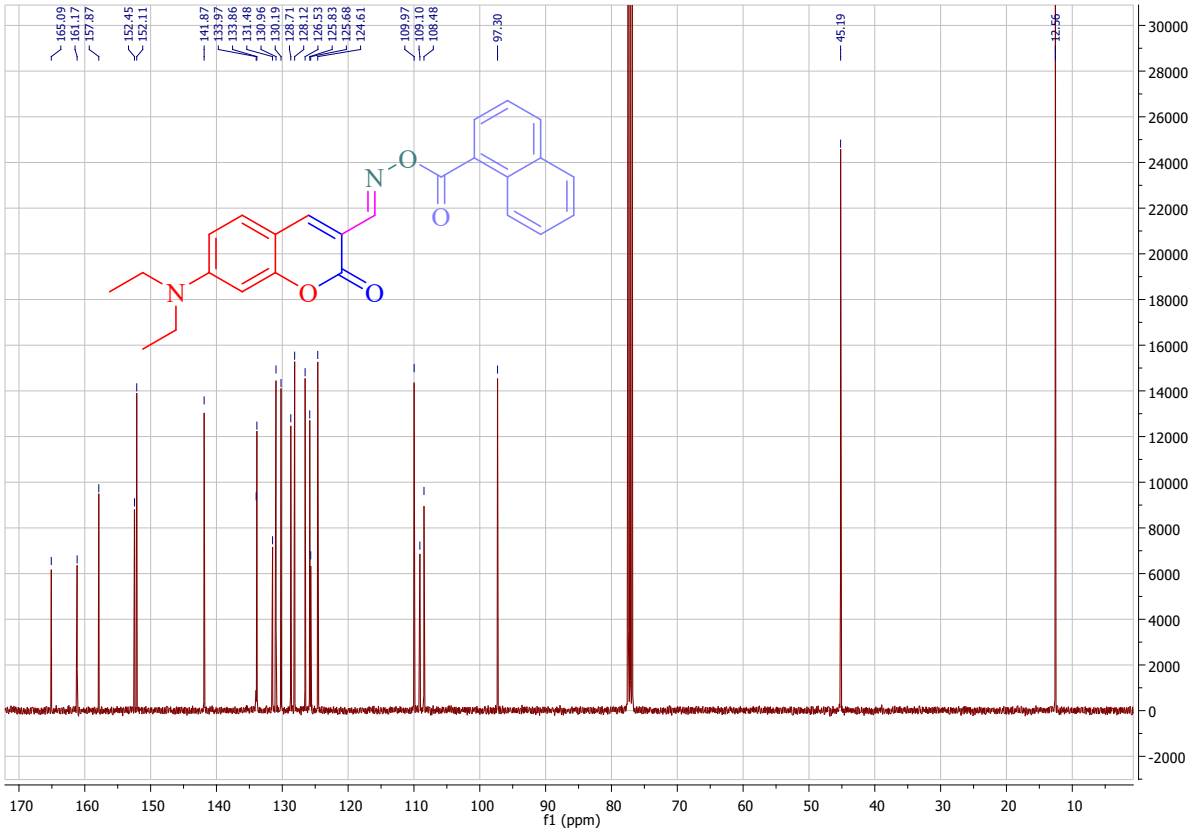
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.09, 161.17, 157.87, 152.45, 152.11, 141.87, 133.97, 133.86, 131.48, 130.96, 130.19, 128.71, 128.12, 126.53, 125.83, 125.68, 124.61, 109.97, 109.10, 108.48, 97.30, 45.19, 12.56.

HRMS (ESI MS) m/z: theor: 414.1580 found: 414.1582 ($M^{+\cdot}$ detected)

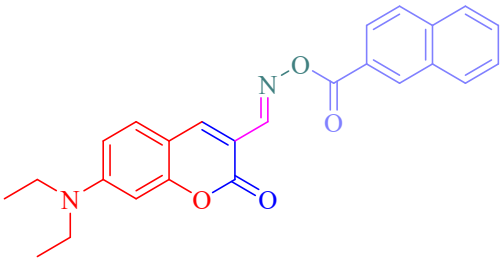
*[1]H NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(1-naphthoyl) oxime (**OXE-E**)*



*[13]C NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(1-naphthoyl) oxime (**OXE-E**)*



Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(2-naphthoyl) oxime ***(OXE-F)***



Chemical Formula: $C_{25}H_{22}N_2O_4$
Molecular Weight: 414,46

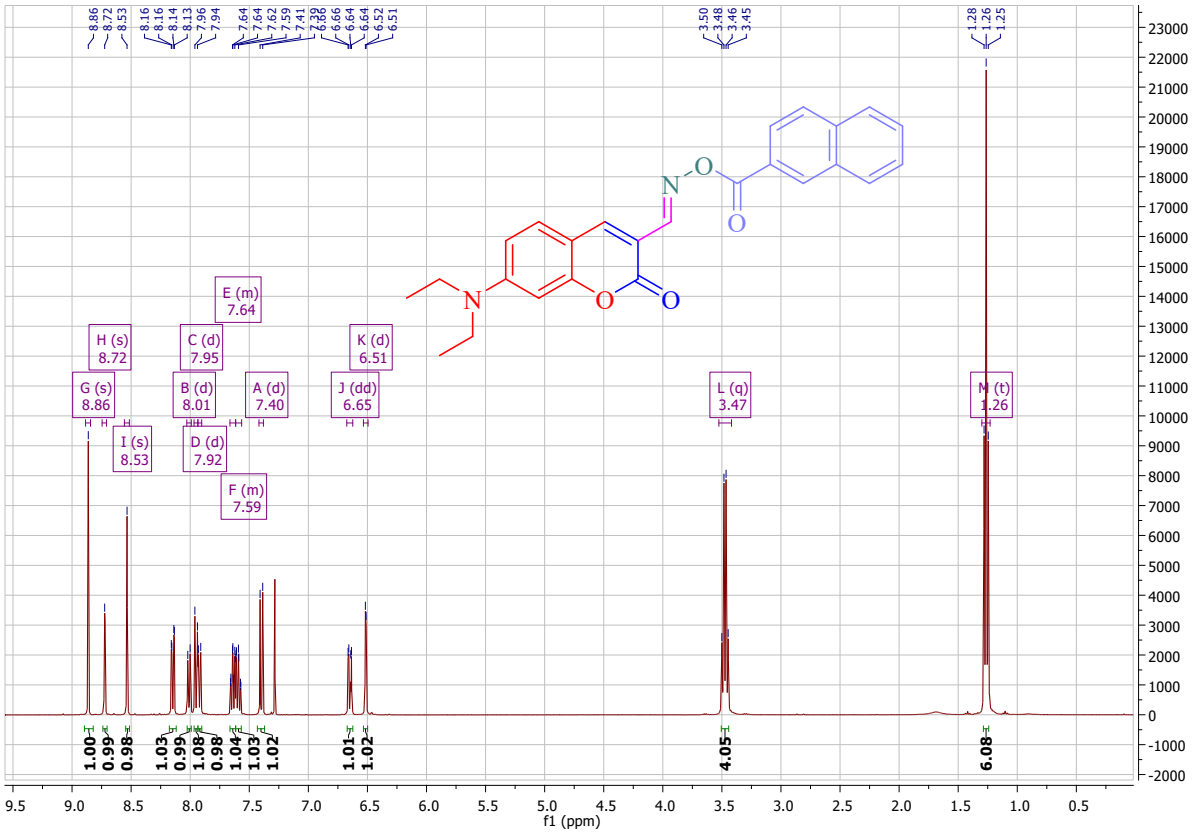
7-(Diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde oxime (**1.30 g**, 5.0 mmol, M = 260.29 g/mol) and triethylamine (**3.00 mL**, 22.0 mmol, M = 101.19 g/mol, d = 726 mg/mL) were dissolved in anhydrous dichloromethane (100 mL). Then, 2-naphthoyl chloride (**1.14 g**, 6.0 mmol, M = 190.63 g/mol) dissolved in dichloromethane (50 mL) was added dropwise over a period of 1h. The flask was then stirred at room temperature for 1h under N_2 atmosphere. The solution was subsequently washed with 2M HCl, sat. $NaHCO_3$, and sat. NaCl aqueous solutions and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was purified chromatographically (SiO_2, DCM) to furnish the targeted product (82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.70 (s, 1H), 8.52 (s, 1H), 8.13 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.59 – 7.54 (m, 1H), 7.38 (d, *J* = 8.9 Hz, 1H), 6.63 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 3.45 (q, *J* = 7.2 Hz, 4H), 1.24 (t, *J* = 7.1 Hz, 6H).

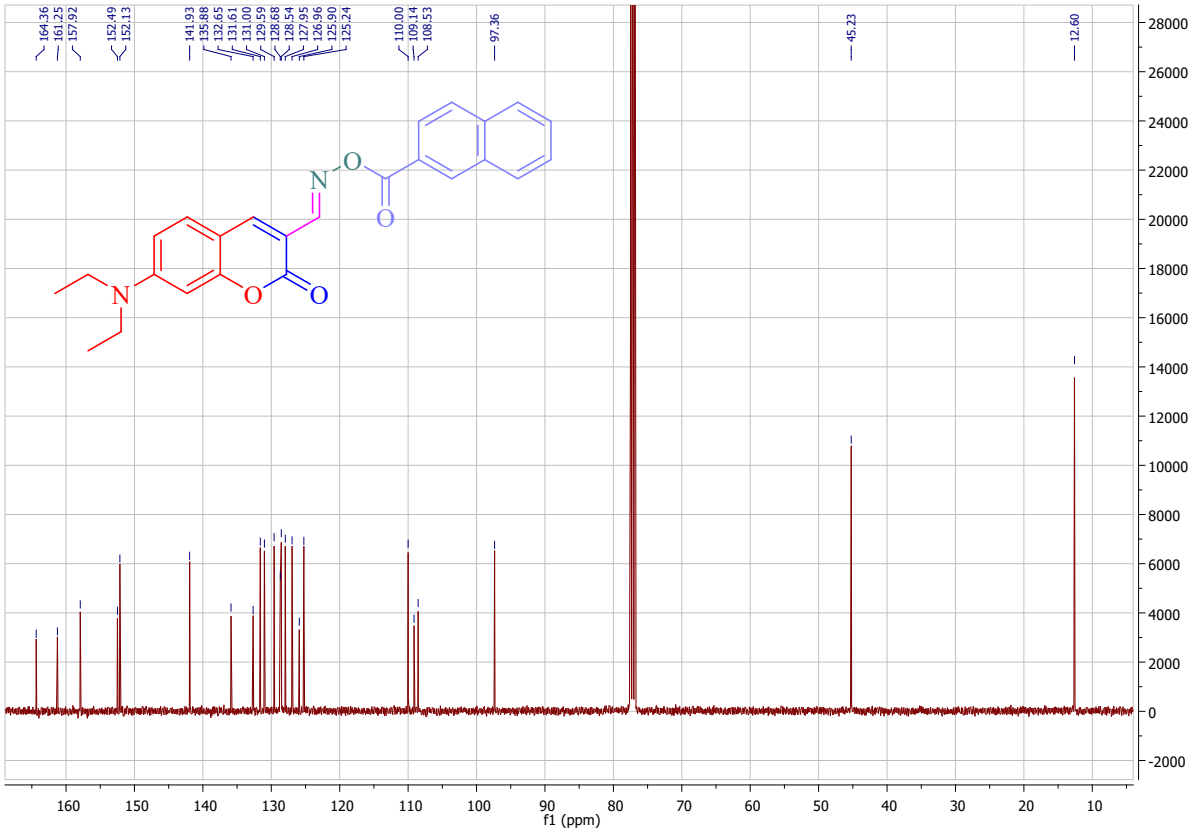
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.36, 161.25, 157.92, 152.49, 152.13, 141.93, 135.88, 132.65, 131.61, 131.00, 129.59, 128.68, 128.54, 127.95, 126.96, 125.90, 125.24, 110.00, 109.14, 108.53, 97.36, 45.23, 12.60.

HRMS (ESI MS) m/z: theor: 414.1580 found: 414.1586 ($M^{+\cdot}$ detected)

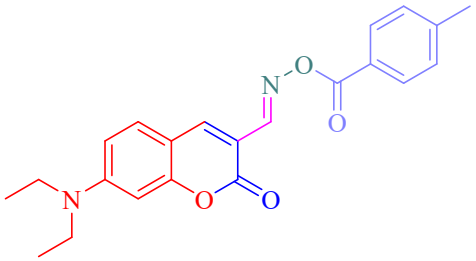
*[1]H NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(2-naphthoyl) oxime (**OXE-F**)*



*[13]C NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(2-naphthoyl) oxime (**OXE-F**)*



Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(4-methylbenzoyl) oxime ***(OXE-G)***



Chemical Formula: $C_{22}H_{22}N_2O_4$
Molecular Weight: 378,43

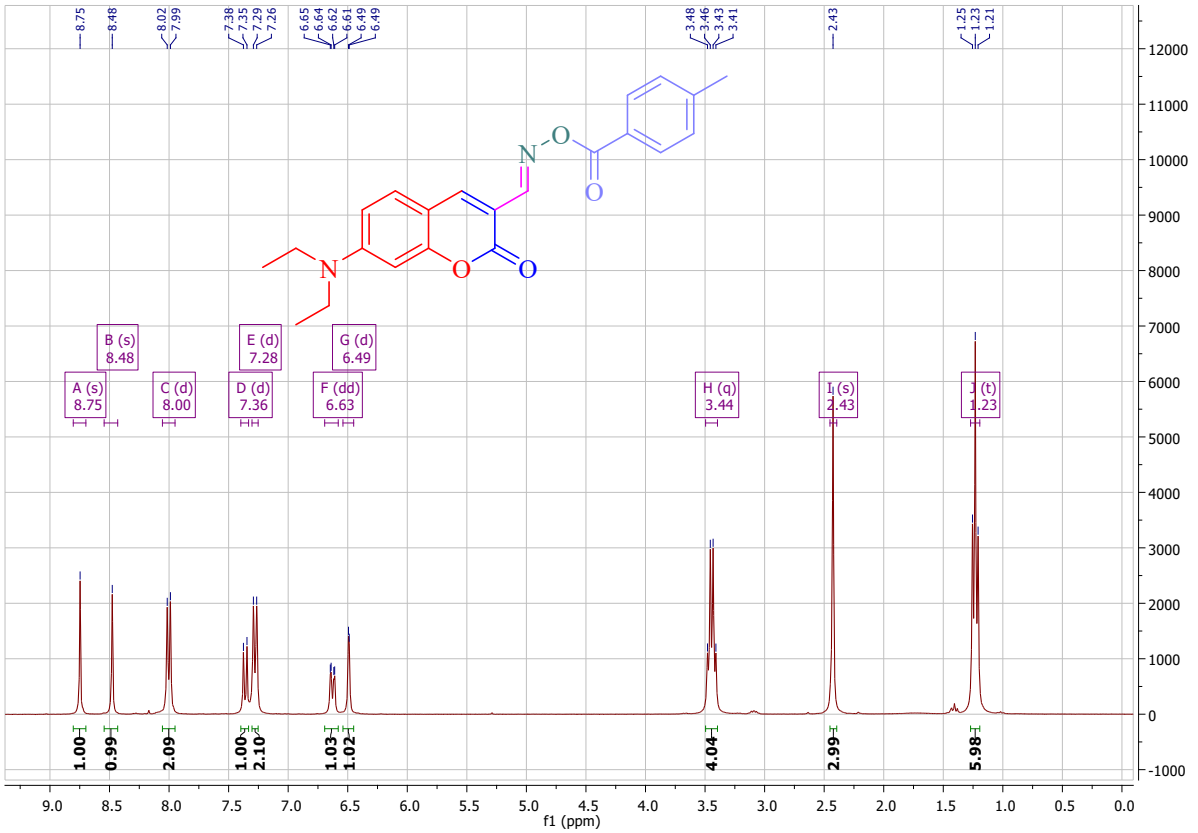
7-(Diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde oxime (**1.60 g**, 6.15 mmol, M = 260.29 g/mol) was added in anhydrous dichloromethane. Then, triethylamine (3.73 g, **5.14 mL**, 36.88 mmol, M = 101.19 g/mol, d = 0.726) was added to obtain a clear solution. Then, 4-methylbenzoyl chloride (1.43 g, **1.22 mL**, 9.22 mmol, M = 154.59 g/mol, d = 1.17) was added. The flask was then stirred at room temperature overnight under N_2 atmosphere. The solution was washed with diluted HCl, dried over $MgSO_4$ and the solvent removed under reduced pressure. After evaporation of the volatiles, the resulting solid was purified by recrystallization in Et_2O (82% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.48 (s, 1H), 8.00 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.9 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.63 (dd, *J* = 8.9, 2.1 Hz, 1H), 6.49 (d, *J* = 1.8 Hz, 1H), 3.44 (q, *J* = 7.0 Hz, 4H), 2.43 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H).

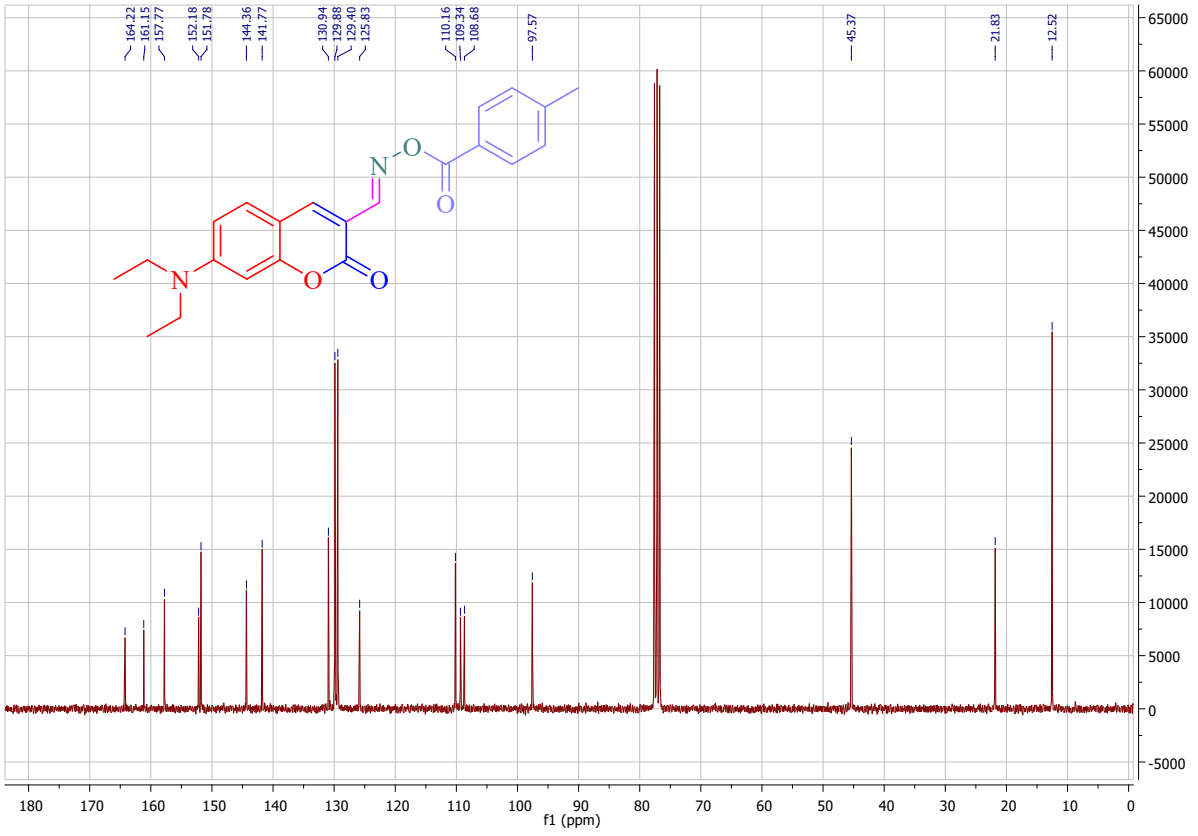
^{13}C NMR (75 MHz, $CDCl_3$) δ 164.22, 161.15, 157.77, 152.18, 151.78, 144.36, 141.77, 130.94, 129.88, 129.40, 125.83, 110.16, 109.34, 108.68, 97.57, 45.37, 21.83, 12.52.

HRMS (ESI MS) m/z: theor: 378.1580 found: 378.4275 ($M^{+\cdot}$ detected)

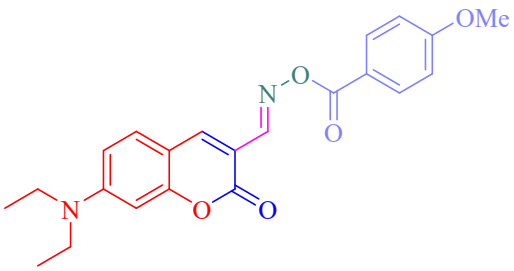
*[1]H NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(4-methylbenzoyl) oxime (**OXE-G**)*



*[13]C NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(4-methylbenzoyl) oxime (**OXE-G**)*



*Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(4-methoxybenzoyl) oxime (**OXE-H**)*



Chemical Formula: $C_{22}H_{22}N_2O_5$
Molecular Weight: 394,43

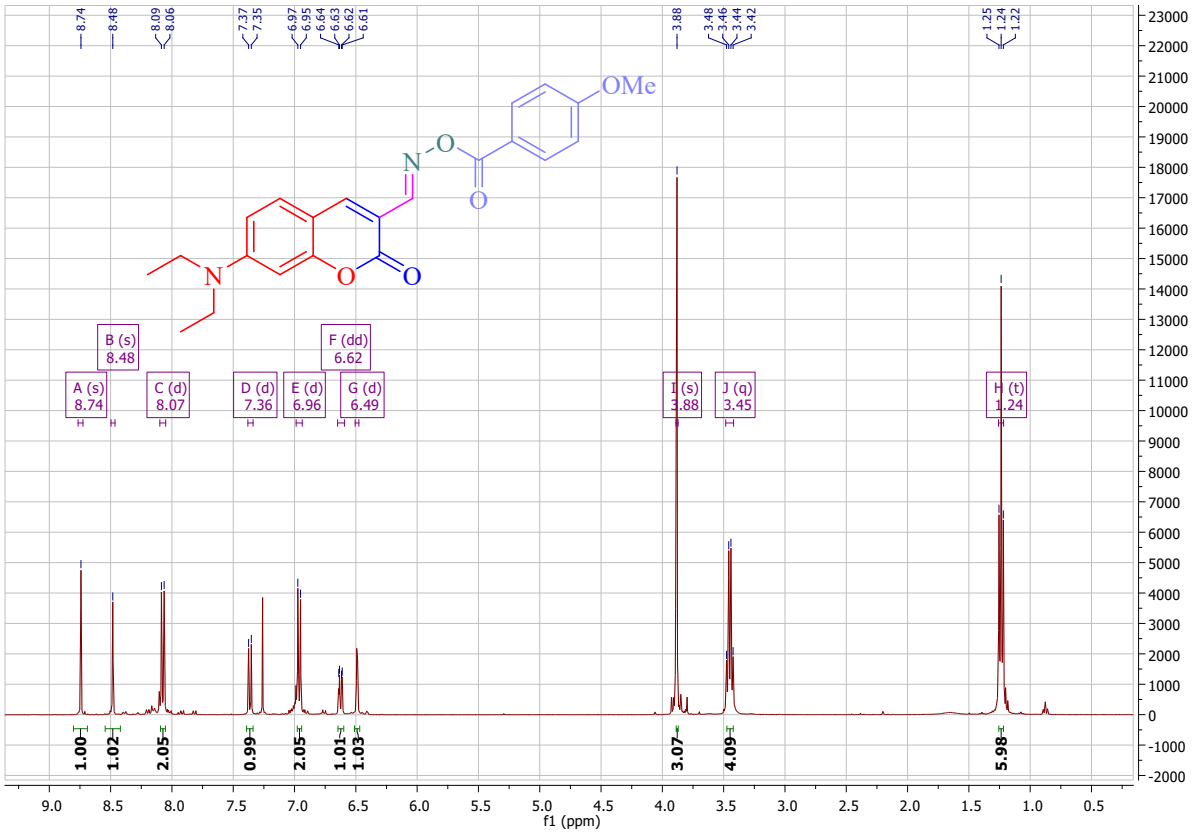
7-(Diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde oxime (**2.00 g**, 7.68 mmol, M = 260.29 g/mol) was added in anhydrous dichloromethane. Then, triethylamine (4.67 g, **6.43 mL**, 46.10 mmol, M = 101.19 g/mol, d = 0.726) was added to obtain a clear solution. Then, 4-methoxybenzoyl chloride (**1.97 g**, 11.53 mmol, M = 170.59 g/mol) was added. The flask was then stirred at room temperature overnight under N_2 atmosphere. The solution was washed with diluted HCl, dried over $MgSO_4$ and the solvent removed under reduced pressure. After evaporation of the volatiles, the resulting solid was purified by recrystallization in Et_2O (91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.48 (s, 1H), 8.07 (d, *J* = 8.9 Hz, 2H), 7.36 (d, *J* = 8.9 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.62 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.49 (d, *J* = 2.3 Hz, 1H), 3.88 (s, 3H), 3.45 (q, *J* = 7.1 Hz, 4H), 1.24 (t, *J* = 7.1 Hz, 6H).

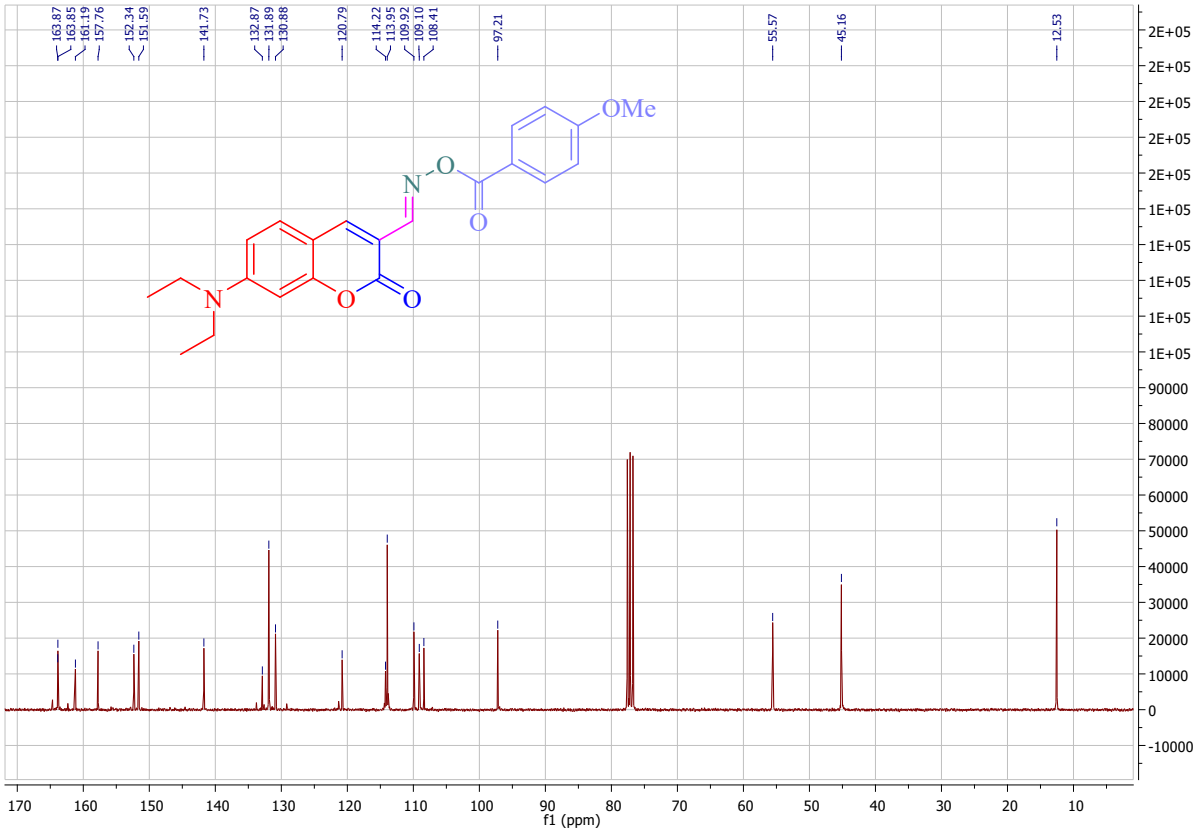
^{13}C NMR (75 MHz, $CDCl_3$) δ 163.87, 163.85, 161.19, 157.76, 152.34, 151.59, 141.73, 132.87, 131.89, 130.88, 120.79, 114.22, 113.95, 109.92, 109.10, 108.41, 97.21, 55.57, 45.16, 12.53.

HRMS (ESI MS) m/z: theor: 394.1529 found: 394.1533 ($M^{+\cdot}$ detected)

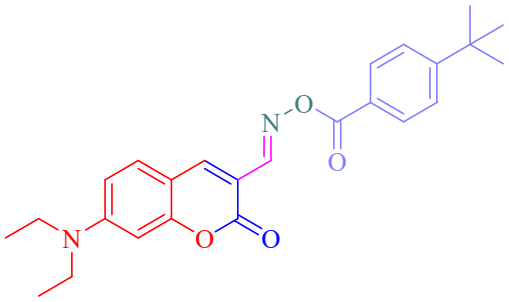
*^{1}H NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(4-methoxybenzoyl) oxime (**OXE-H**)*



*^{13}C NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(4-methoxybenzoyl) oxime (**OXE-H**)*



*Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(4-(tert-butyl)benzoyl) oxime (**OXE-I**)*



Chemical Formula: $C_{25}H_{28}N_2O_4$
Molecular Weight: 420,51

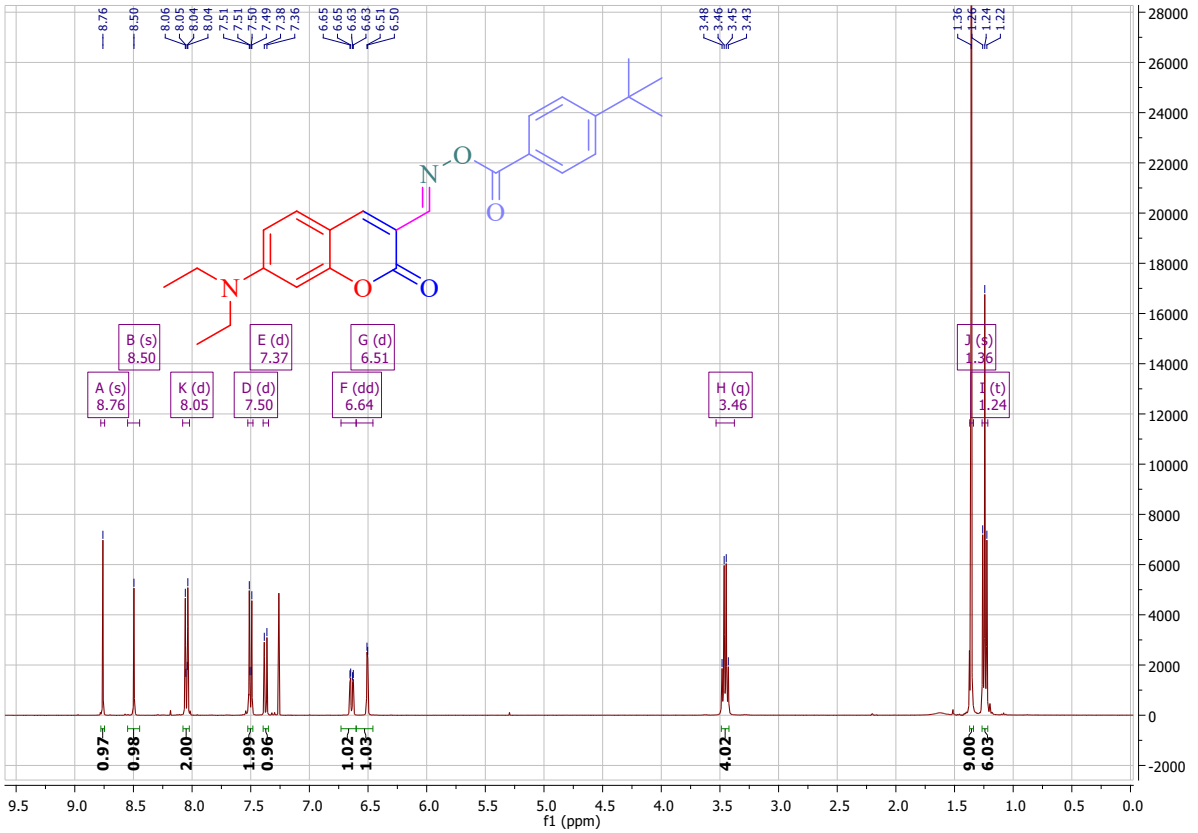
7-(Diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde oxime (**2.00 g**, 7.68 mmol, M = 260.29 g/mol) was added in anhydrous dichloromethane. Then, triethylamine (4.67 g, **6.43 mL**, 46.10 mmol, M = 101.19 g/mol, d = 0.726) was added to obtain a clear solution. Then, 4-(*tert*-butyl)benzoyl chloride (2.27 g, **2.27 mL**, 11.53 mmol, M = 196.67 g/mol, d = 1.00 g/mL) was added. The flask was then stirred at room temperature overnight under N_2 atmosphere. The solution was washed with diluted HCl, dried over $MgSO_4$ and the solvent removed under reduced pressure. After evaporation of the volatiles, the resulting solid was purified by recrystallization in Et_2O (64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.50 (s, 1H), 8.05 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.9 Hz, 1H), 6.64 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.51 (d, *J* = 2.3 Hz, 1H), 3.46 (q, *J* = 7.1 Hz, 4H), 1.36 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 6H).

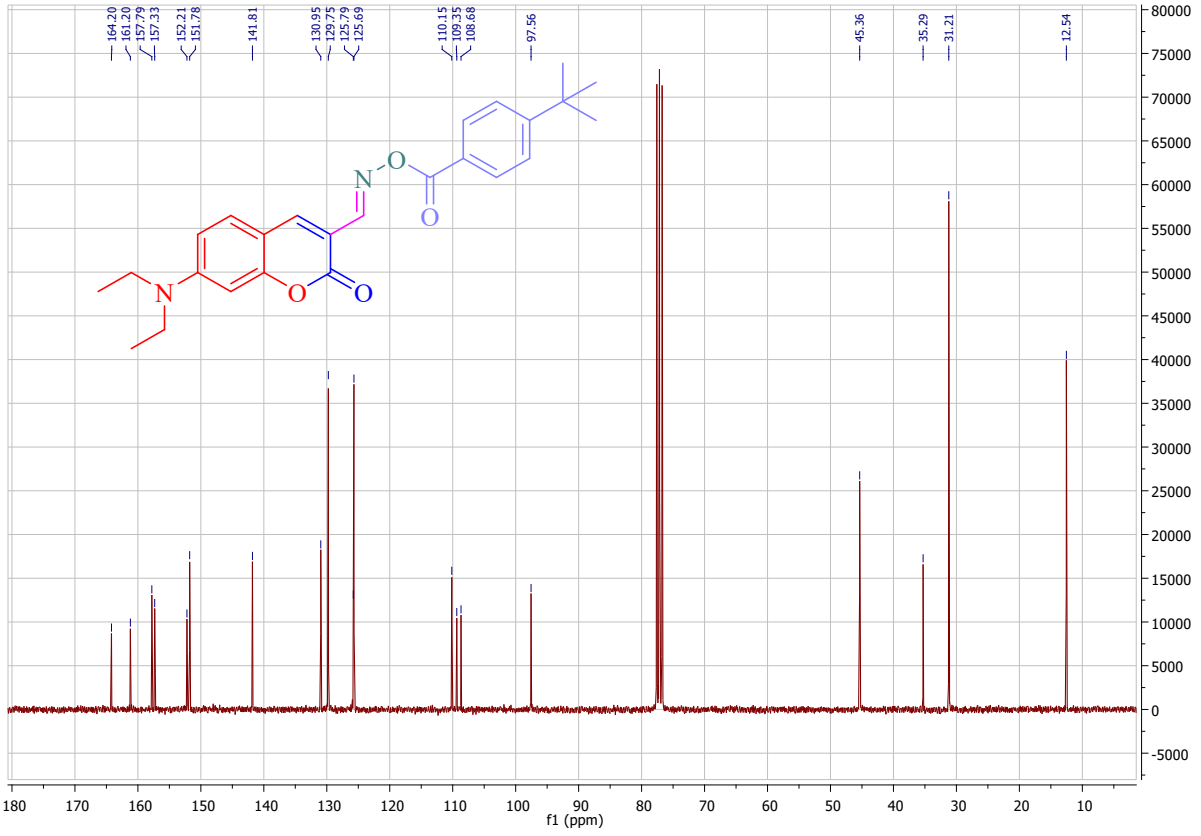
^{13}C NMR (75 MHz, $CDCl_3$) δ 164.20, 161.20, 157.79, 157.33, 152.21, 151.78, 141.81, 130.95, 129.75, 125.79, 125.69, 110.15, 109.35, 108.68, 97.56, 45.36, 35.29, 31.21, 12.54.

HRMS (ESI MS) m/z: theor: 420.2049 found: 420.2046 ($M^{+\cdot}$ detected)

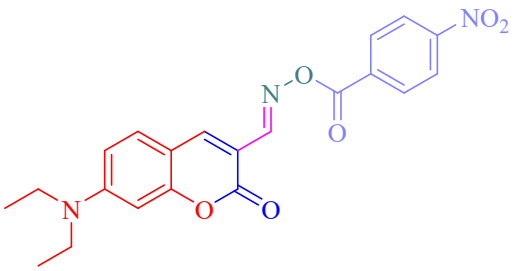
*[1]H NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(4-(tert-butyl)benzoyl) oxime (**OXE-I**)*



*[13]C NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(4-(tert-butyl)benzoyl) oxime (**OXE-I**)*



Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(4-nitrobenzoyl) oxime ***(OXE-J)***



Chemical Formula: $C_{21}H_{19}N_3O_6$
Molecular Weight: 409,40

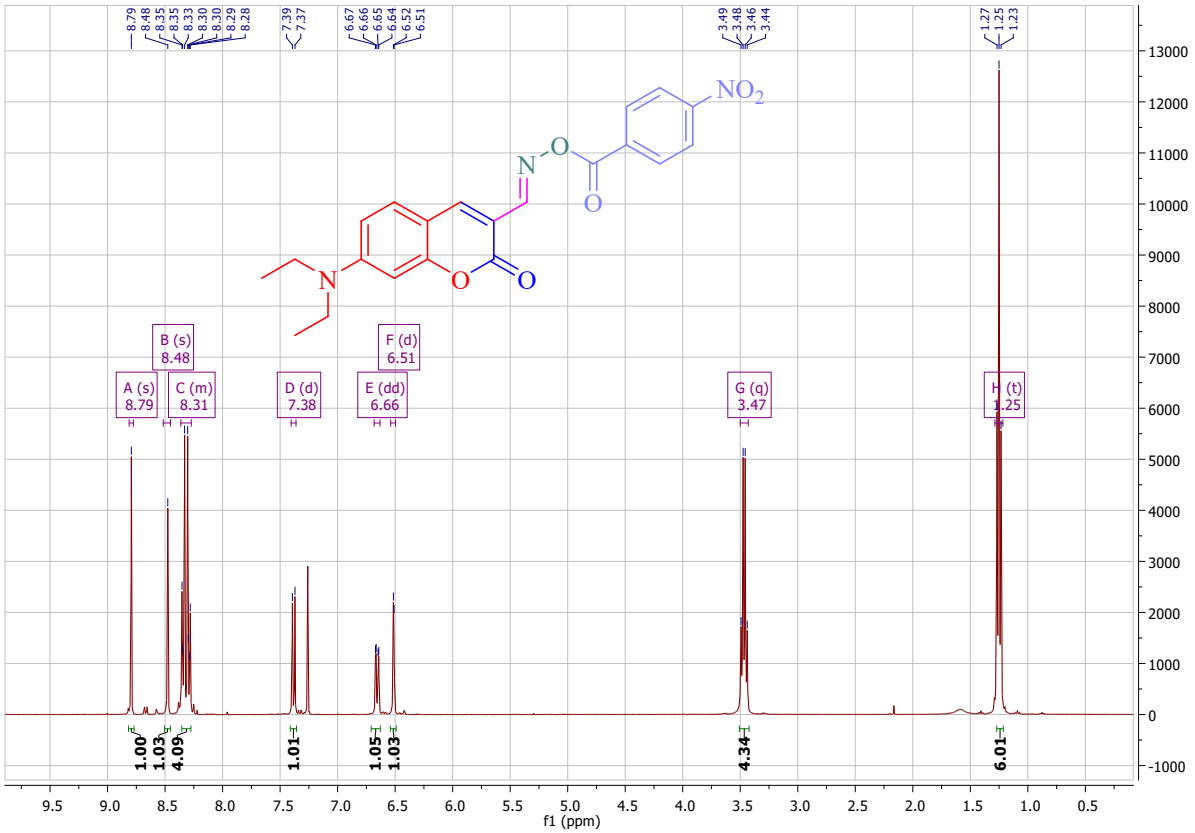
7-(Diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde oxime (**1.70 g**, 6.53 mmol, M = 260.29 g/mol) was added in anhydrous dichloromethane. Then, triethylamine (3.97 g, **5.46 mL**, 39.19 mmol, M = 101.19 g/mol, d = 0.726) was added to obtain a clear solution. Then, 4-nitrobenzoyl chloride (**1.82 g**, 9.80 mmol, M = 185.56 g/mol) was added. The flask was then stirred at room temperature overnight under N_2 atmosphere. The solution was washed with diluted HCl, dried over $MgSO_4$ and the solvent removed under reduced pressure. After evaporation of the volatiles, the resulting solid was purified by recrystallization in Et_2O (74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.48 (s, 1H), 8.36 – 8.27 (m, 4H), 7.38 (d, *J* = 8.9 Hz, 1H), 6.66 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.51 (d, *J* = 2.3 Hz, 1H), 3.47 (q, *J* = 7.1 Hz, 4H), 1.25 (t, *J* = 7.1 Hz, 6H).

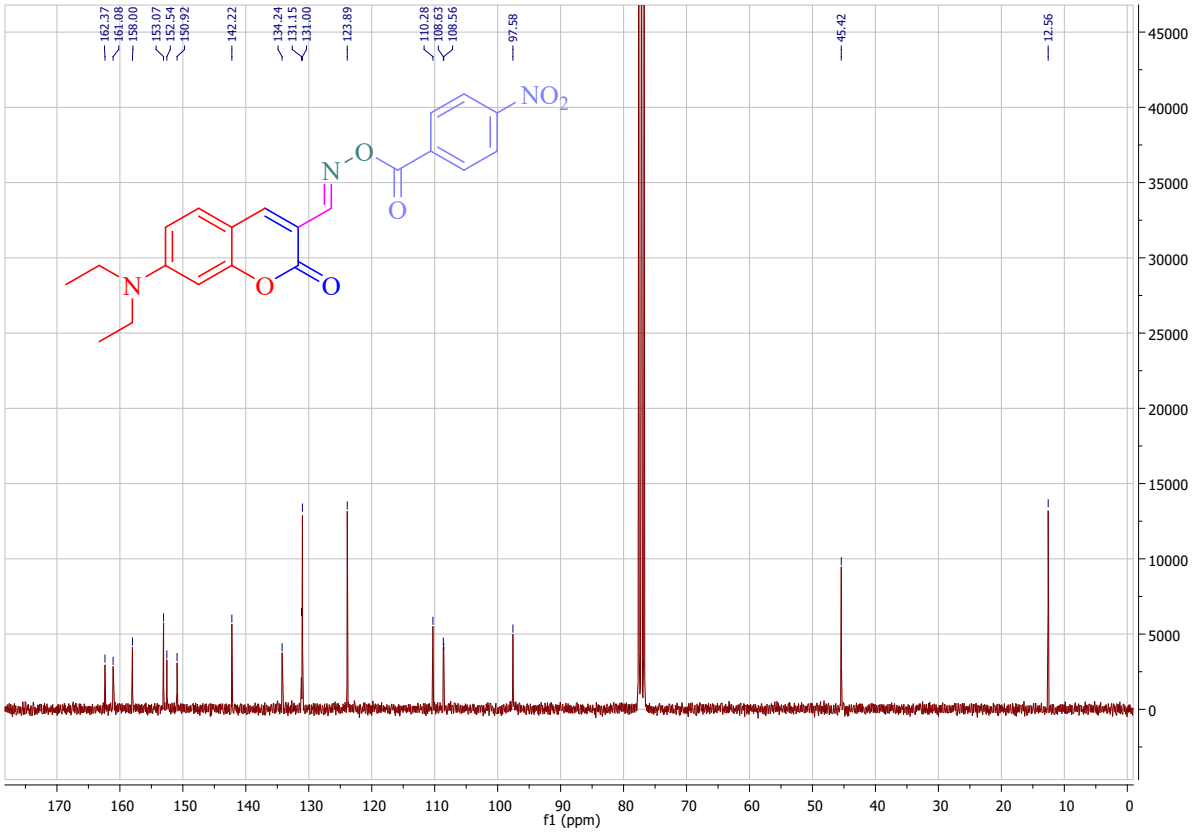
^{13}C NMR (75 MHz, $CDCl_3$) δ 162.37, 161.08, 158.00, 153.07, 152.54, 150.92, 142.22, 134.24, 131.15, 131.00, 123.89, 110.28, 108.63, 108.56, 97.58, 45.42, 12.56.

HRMS (ESI MS) m/z: theor: 409.1274 found: 409.1271 ($M^{+\cdot}$ detected)

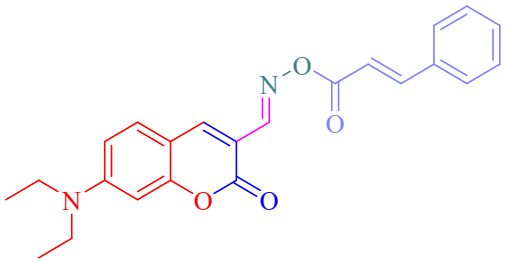
*[1]H NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(4-nitrobenzoyl) oxime (**OXE-J**)*



*[13]C NMR spectrum 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-(4-nitrobenzoyl) oxime (**OXE-J**)*



*Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-cinnamoyl oxime (**OXE-K**)*



Chemical Formula: $C_{23}H_{22}N_2O_4$
Molecular Weight: 390,4390

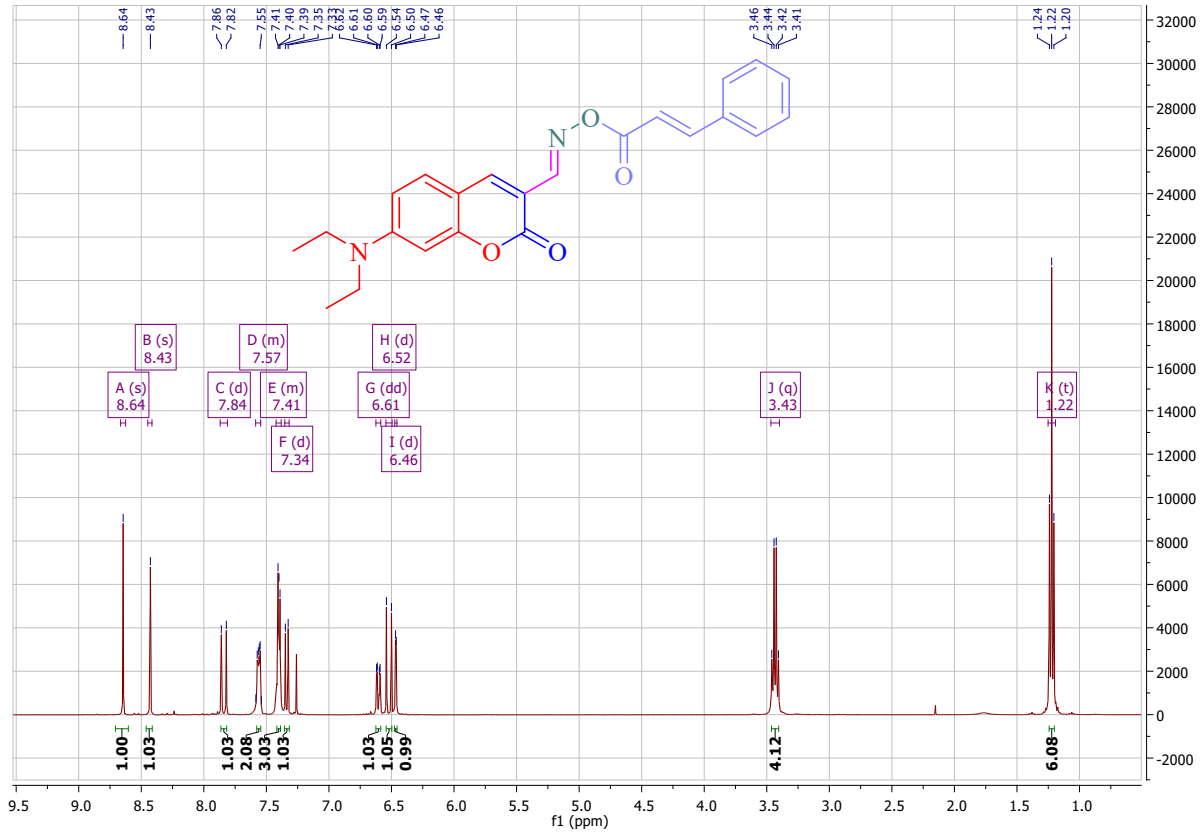
7-(Diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde oxime (**1.30 g**, 5.0 mmol, M = 260.29 g/mol) and triethylamine (**3.00 mL**, 22.0 mmol, M = 101.19 g/mol, d = 0.726) were dissolved in anhydrous dichloromethane (100 mL). Then, cinnamoyl chloride (**1.00 g**, 6.0 mmol, M = 166.60 g/mol) dissolved in dichloromethane (50 mL) was added dropwise over a period of 1h. The flask was then stirred at room temperature for 1h under N_2 atmosphere. The solution was subsequently washed with 2M HCl, sat. $NaHCO_3$, and sat. NaCl aqueous solutions and dried over $MgSO_4$. After evaporation of the volatiles, the resulting solid was purified by recrystallization in Et_2O (89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.43 (s, 1H), 7.84 (d, *J* = 16.0 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.42 – 7.38 (m, 3H), 7.34 (d, *J* = 9.0 Hz, 1H), 6.61 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.46 (d, *J* = 2.3 Hz, 1H), 3.43 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.67, 161.09, 157.79, 152.37, 151.57, 146.39, 141.74, 134.32, 130.88, 130.74, 129.04, 128.34, 115.57, 109.91, 109.12, 108.41, 97.25, 45.15, 12.54.

HRMS (ESI MS) m/z: theor: 390.1580 found: 390.1582 ($M^{+\cdot}$ detected)

*[1]H NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-cinnamoyl oxime (**OXE-K**)*



*[13]C NMR spectrum of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde O-cinnamoyl oxime (**OXE-K**)*