Electronic Supplementary Material (ESI) for Green Chemistry.

Carbazole-Fused Coumarin Based Oxime Esters (OXEs): Efficient Photoinitiators for Sunlight Driven Free Radical Photopolymerization

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Experimental Section

Chemicals and Materials

The monomers, trimethylolpropane triacrylate (TMPTA) and Ebecryl605 (bisphenol an epoxy diacrylate oligomer diluted with 25% of tripropyleneglycol diacrylate) were both purchased from Allnex (Ivry sur Seine, France) for free radical photopolymerization (FRP). The storage inhibitor was not removed from the monomer prior to the photopolymerization experiments. The commercial photoinitiator, diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide (TPO), was purchased from Sartomer-Lambson (United Kingdom). *N-tert*-butyl-α-phenylnitrone (PBN) was obtained from TCI Europe (Paris, France) and was used as the free radical trapping agent. The colloidal silica suspension (LUDOX AS 30, 30 wt % suspension in H_2O) used to determine the impulse response function of the fluorimeter was obtained from Sigma-Aldrich.

TMPTA is a trifunctional actrylate monomer widely used in industry. There is no evidence of induction of gene mutations in bacteria or mammalian cells. And it also did not induce comets in bone marrow or liver of mice. [1]

About Ebecryl 605 monomer, its green attributes are low/zero VOC, reducing energy consumption, lower carbon foot print, solvent free and tin free. These details are provided on the website of allnex. [2]

1. D. Kirkland and P. Fowler, Mutat Res Genet Toxicol Environ Mutagen, 2018, 828, 36-45.

2. https://allnex.com/en/product/9f749bcf-c895-4fd5-a32c-465707a3aa2d/ebecryl-605.

Synthesis of OXEs

Synthetic procedures used to access to the different structures OXE-0-OXE-17, are depicted in detail in the section of **General Informations** in end of supporting information (SI).

UV-Visible Absorption Properties

UV-Visible absorption spectra of OXEs dissolved in acetonitrile (2×10^{-5} M) were obtained with a JASCO V730 spectrometer (1 cm optical path length), and Lambert-Beer's Law (See equation (S1)) was used to calculate molar absorption coefficient of each photoinitiator. Steady-state photolysis of OXEs dissolved in acetonitrile (2×10^{-5} M) was also performed on a JASCO V730 spectrometer, under irradiation with a 405 nm LED (110 mW.cm^{-2}).

$$A = \varepsilon \times C \times L \qquad \text{equation (S1)}$$

In equation (S1), A is the absorbance of each compound in acetonitrile, C is the concentration of each compound in acetonitrile, L is the optical path length and controlled at 1 cm, ε is the molar extinction coefficient.

Fluorescence Spectra and Fluorescence Lifetime

Fluorescence spectra of OXEs (concentration in the range of 2×10^{-5} M in methyl alcohol used as the solvent) were investigated on a JASCO FP-750 spectrofluorometer and excitation wavelength was around 350 nm. Fluorescence excited-state lifetime were determined with a HORIBA PPD-850 detector.

Singlet excited-state energies (E_{S1} in kcal/mol) of OXEs were calculated from the intersection of the normalized fluorescence emission spectra and the normalized UV-visible absorption spectra and E_{S1} was calculated by equation (S2). Enthalpies of the cleavage process of the N-O bond ($\Delta H_{Cleavage}$) from OXEs were calculated by equation (S3) and equation (S4), based on the energies of the singlet or triplet excited states (E_{S1} or E_{T1}) and the dissociation energies of the N-O bond (BDE).

$$E_{S1} = {}^{1240}/_{WL} \times 23.06 \frac{kcal}{mol} \qquad \text{equation (S2)}$$

$$\Delta H_{Cleavage_{S1}} = BED_{(N-O)} - E_{S1} \quad \text{equation (S3)}$$

$$\Delta H_{Cleavage_{T1}} = BED_{(N-O)} - E_{T1} \quad \text{equation (S4)}$$

In equation (S2), WL is the x-coordinate of the intersection without unit of the normalized fluorescence emission spectra and the normalized UV-visible absorption spectra.

Free Radical Photopolymerization

First, the different OXEs and the monomer (TMPTA) were mixed in a glass bottle and stirred overnight away from light. The concentration of OXEs in all formulations was controlled to be 2×10^{-5} mol.g^{-1} in TMPTA, which corresponds to a weight percentage in the range of 0.61 wt% to 0.97 wt% in TMPTA depending on their different molecular masses of OXEs. Concentration of the commercial photoinitiator TPO was controlled at 2×10^{-5} mol.g^{-1} (0.7 wt%) in TMPTA.

In order to reduce or avoid oxygen inhibition, drops of the homogenous formulations were deposited in a mold to prepare thick sample (1.4 mm) or the laminate between two transparent polypropylene films for thin sample preparation (~25 μm). Subsequently, the kinetics of radical photopolymerization of TMPTA samples when exposed to a 405 nm LED (110 mW.cm^{-2}) at room temperature for 600 s was investigated by real-time Fourier transformed infrared (RT-FTIR) spectroscopy (JASCO FTIR-4100). The acrylate characteristic peak area of TMPTA for thin sample was selected from 1589 to 1665 cm^{-1} and that of TMPTA for thick sample was in the near-infrared range at ~6160 cm^{-1}. The photopolymerization of each formulation can be repeated for three times. The acrylate function conversion (FC) of TMPTA for a given time *t* was calculated by equation (S5):

$$FC(t) = {}^{(A_0 - A_t)}\!/_{A_0} \times 100\% \quad \text{equation (S5)}$$

Where A_0 and A_t are the peak area at $t = 0$ s and at any t respectively. The final acrylate conversion was determined by the shape of the conversion curves, which is reached

either after a plateau is reached (rate practically zero even under illumination) or after a certain illumination period.

Electron Spin Resonance Spin Trapping (ESR-ST)

ESR-ST experiments were performed with a X-band spectrometer (Bruker EMX plus). N_2 saturated solution of PBN in *tert*-butylbenzene was selected as the free radical trapping agent, and the concentration of PI dissolved in PBN solution was adjusted to 2×10^{-5} M. During ESR-ST experiments, PBN solvent containing PI was irradiated upon 405 nm LED (110 $mW\cdot cm^{-2}$) at room temperature, inside the cavity of the ESR apparatus. Then, ESR spectrum was recorded after irradiation of 405 nm LED. ESR spectra calculations were performed by WINSIM software.

Direct Laser Write (DLW)

The homogeneous formulation was deposited into a homemade glass tank (2 mm thickness). Then, a laser diode (spot size around 50 μm, 405 nm, and 110 mW) was used as the light source for a spatial irradiation controlled by a computer program to manufacture specific 3D patterns. After DLW process, these 3D patterns were cleaned by acetone to remove the uncured monomer. Finally, a scanning electron microscope (SEM) was used to observe the surface of the printed 3D patterns.

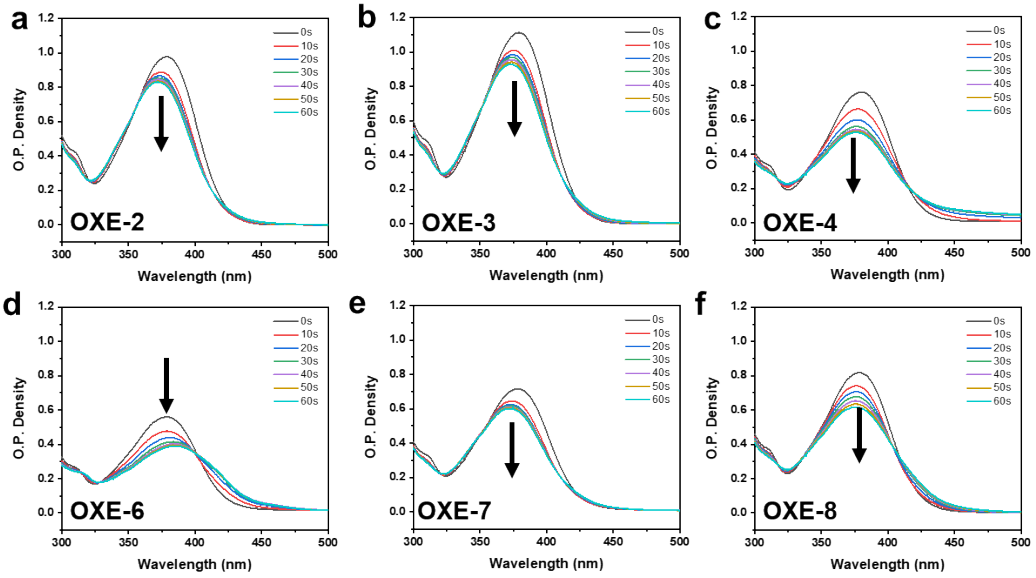


Figure S1. Steady-state photolysis of OXEs in acetonitrile upon the irradiation of 405 nm LED. (a) OXE-2, (b) OXE-3, (c) OXE-4, (d) OXE-6, (e) OXE-7 and (f) OXE-8.

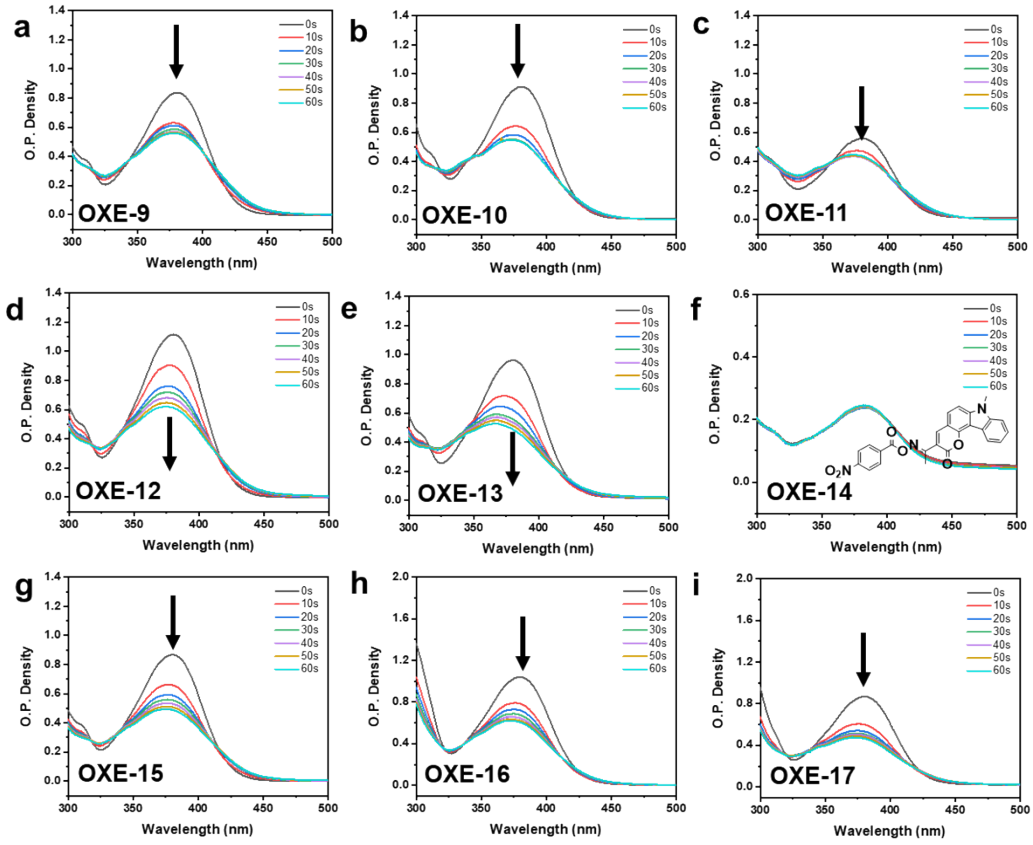


Figure S2. Steady-state photolysis of OXEs in acetonitrile upon the irradiation of 405 nm LED. (a) OXE-9, (b) OXE-10, (c) OXE-11, (d) OXE-12, (e) OXE-13 and (f) OXE-14, (g) OXE-15, (h) OXE-16, (i) OXE-17.

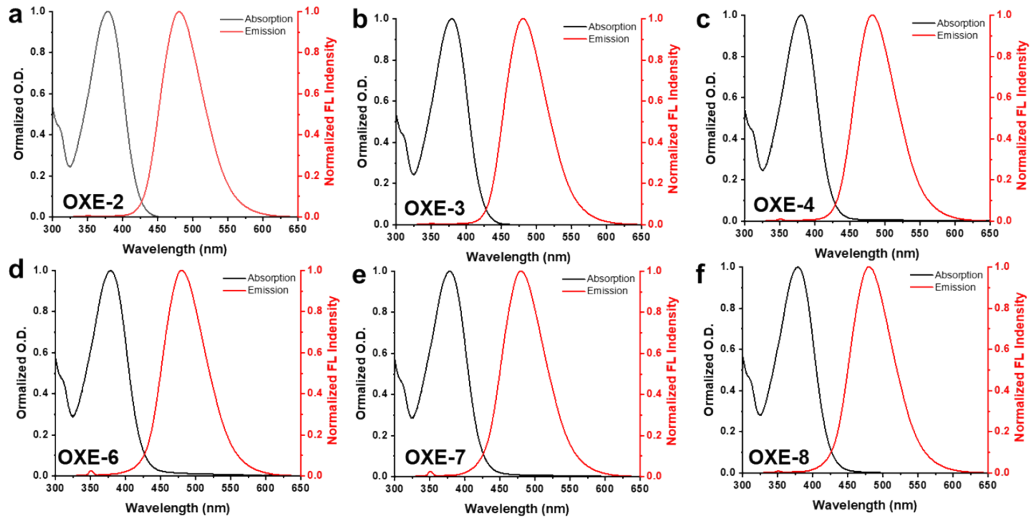


Figure S3. Singlet-state energy determination of (a) OXE-2, (b) OXE-3, (c) OXE-4, (d) OXE-6, (e) OXE-7, (f) OXE-8.

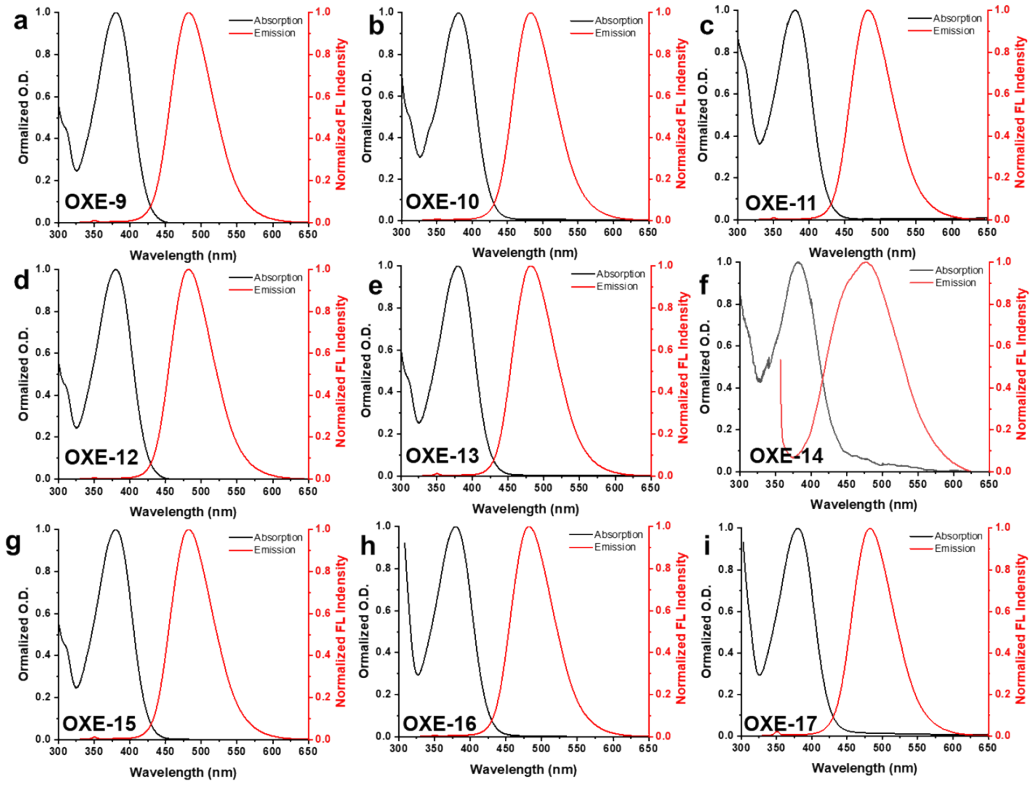


Figure S4. Singlet-state energy determination of (a) OXE-9, (b) OXE-10, (c) OXE-11, (d) OXE-12, (e) OXE-13 and (f) OXE-14, (g) OXE-15, (h) OXE-16, (i) OXE-17.

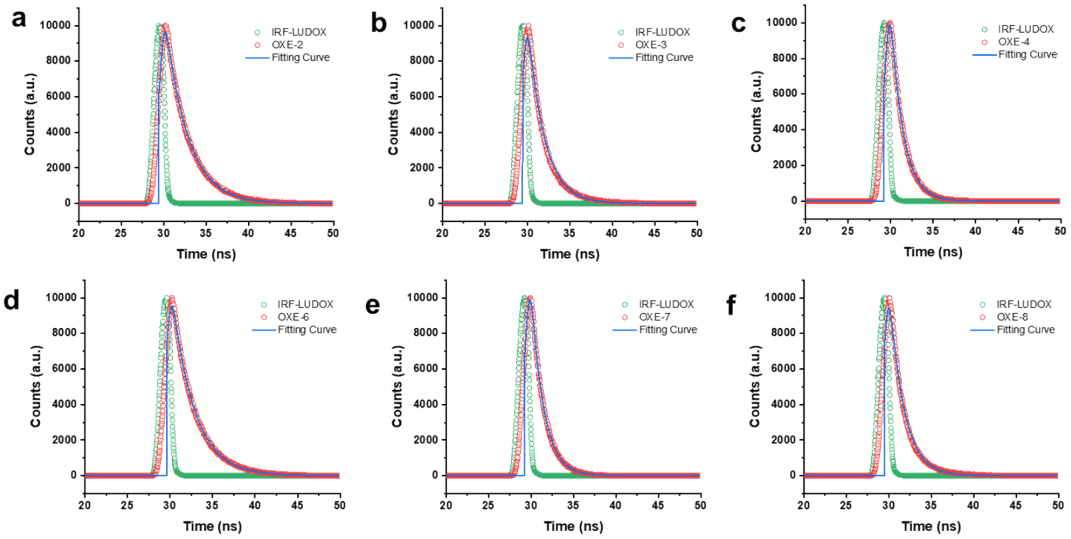


Figure S5. Fluorescence decay curve of (a) OXE-2, (b) OXE-3, (c) OXE-4, (d) OXE-6, (e) OXE-7, (f) OXE-8.

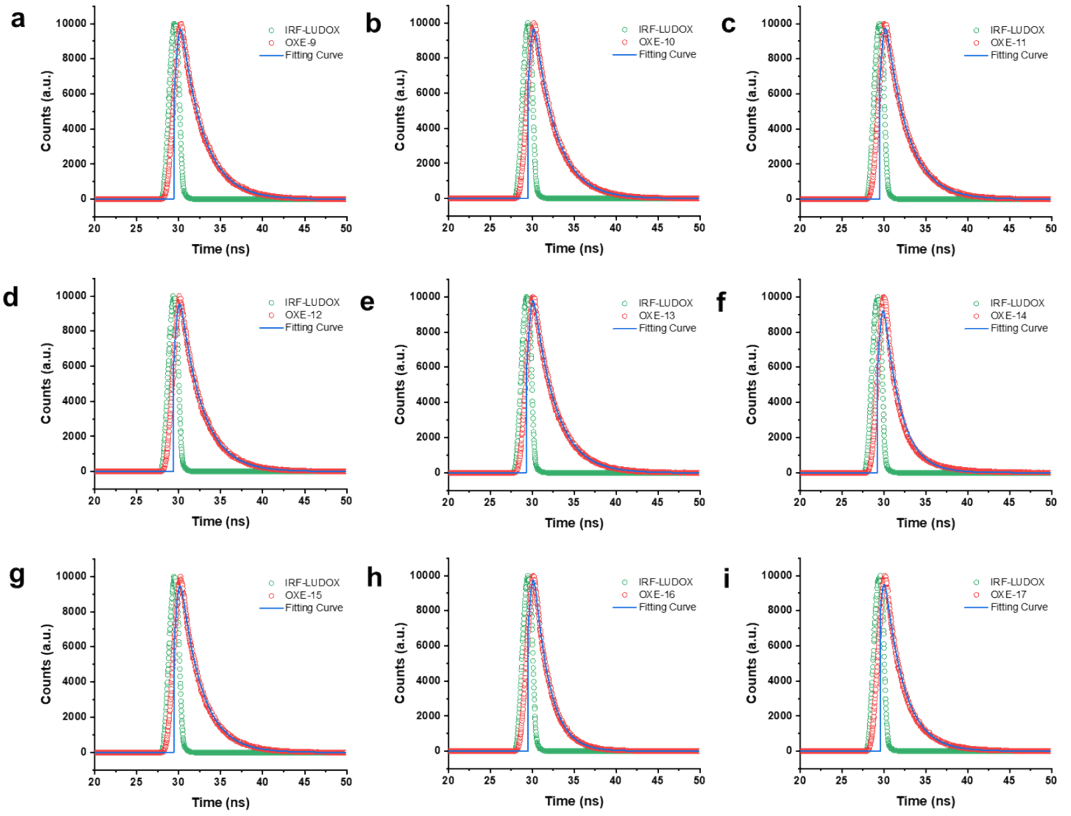


Figure S6. Fluorescence decay curve of (a) OXE-9, (b) OXE-10, (c) OXE-11, (d) OXE-12, (e) OXE-13 and (f) OXE-14, (g) OXE-15, (h) OXE-16, (i) OXE-17.

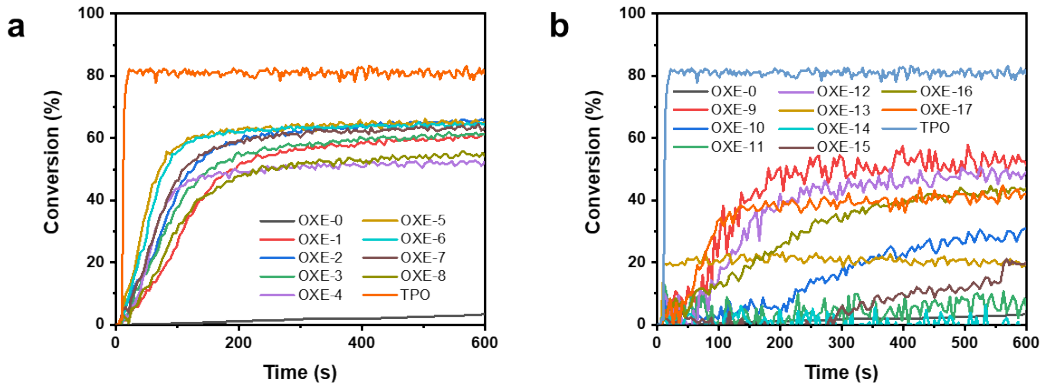


Figure S7. Photopolymerization profiles of TMPTA (1.4 mm) upon exposure to a 405 nm LED in the presence of different OXEs (2×10^{-5} mol.g^{-1} in TMPTA) and the benchmark photoinitiator TPO. The irradiation starts at t = 10 s.

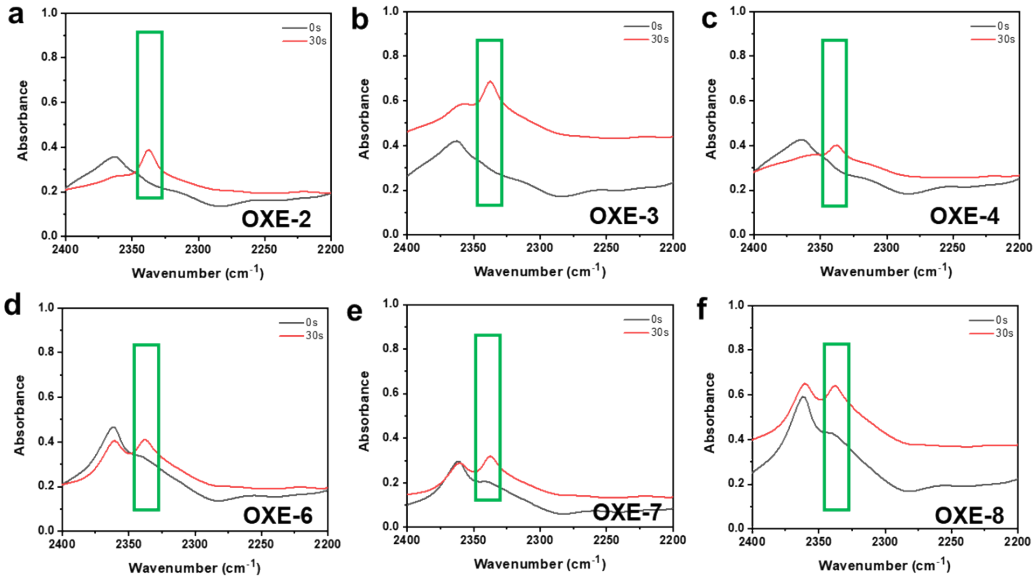


Figure S8. Infrared spectra of OXEs in TMPTA at t = 10 and 30 s. (a) OXE-2, (b) OXE-3, (c) OXE-4, (d) OXE-6, (e) OXE-7, (f) OXE-8.

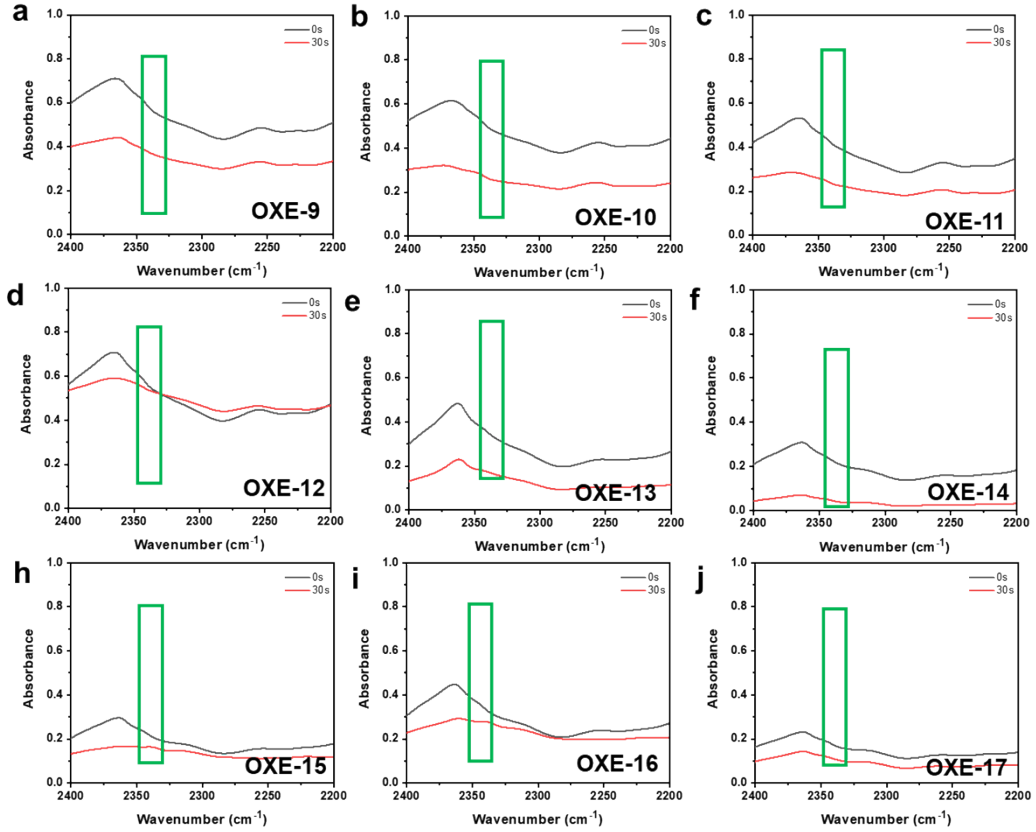


Figure S9. Infrared spectra of OXEs in TMPTA at t = 10 and 30 s. (a) OXE-9, (b) OXE-10, (c) OXE-11, (d) OXE-12, (e) OXE-13 and (f) OXE-14, (g) OXE-15, (h) OXE-16, (i) OXE-17.

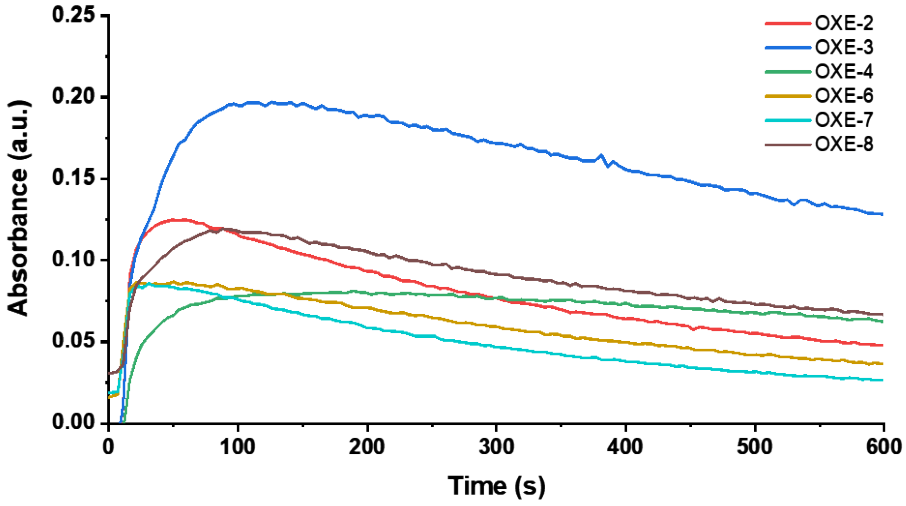


Figure S10. The absorption intensity of CO_2 obtained from the different OXE/TMPTA systems respectively.

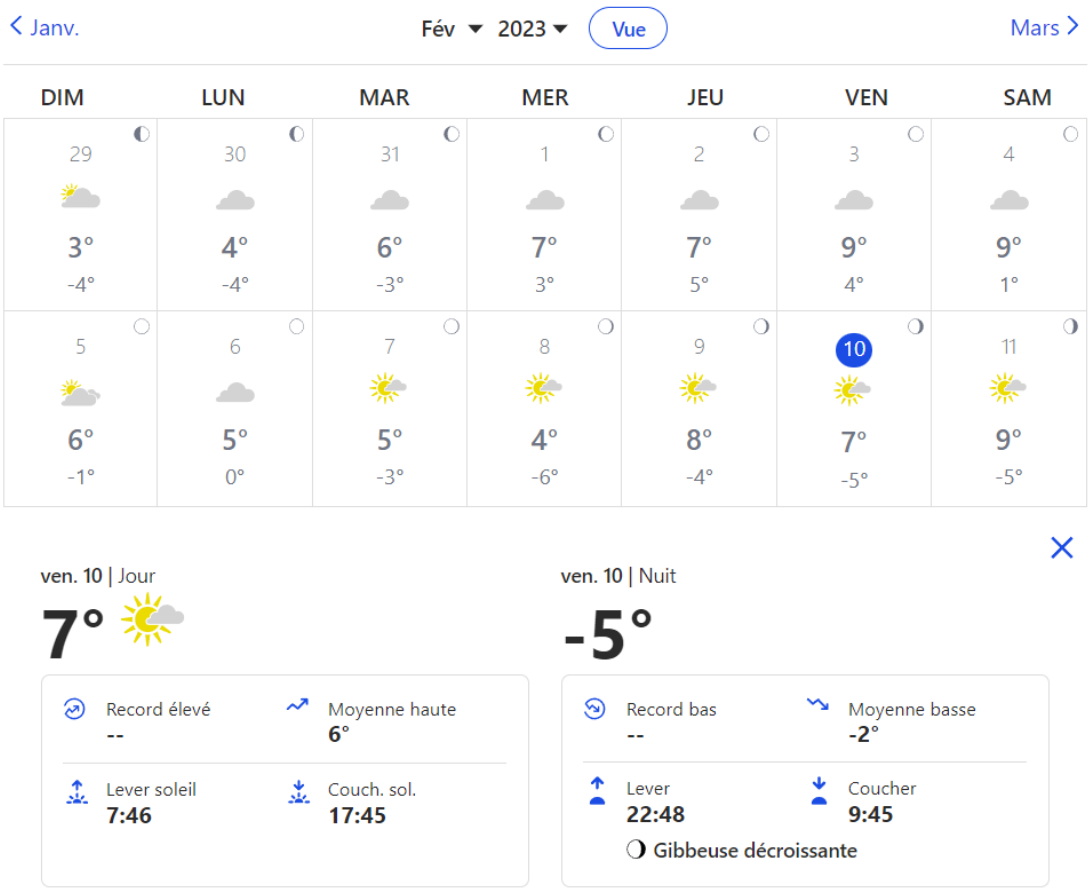
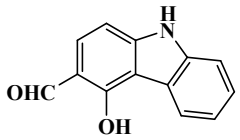


Figure S11. The weather report of February 10th 2023 in Mulhouse, France.

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).

Synthesis of 4-hydroxy-9*H*-carbazole-3-carbaldehyde



Chemical Formula: $C_{13}H_9NO_2$
Molecular Weight: 211,2200

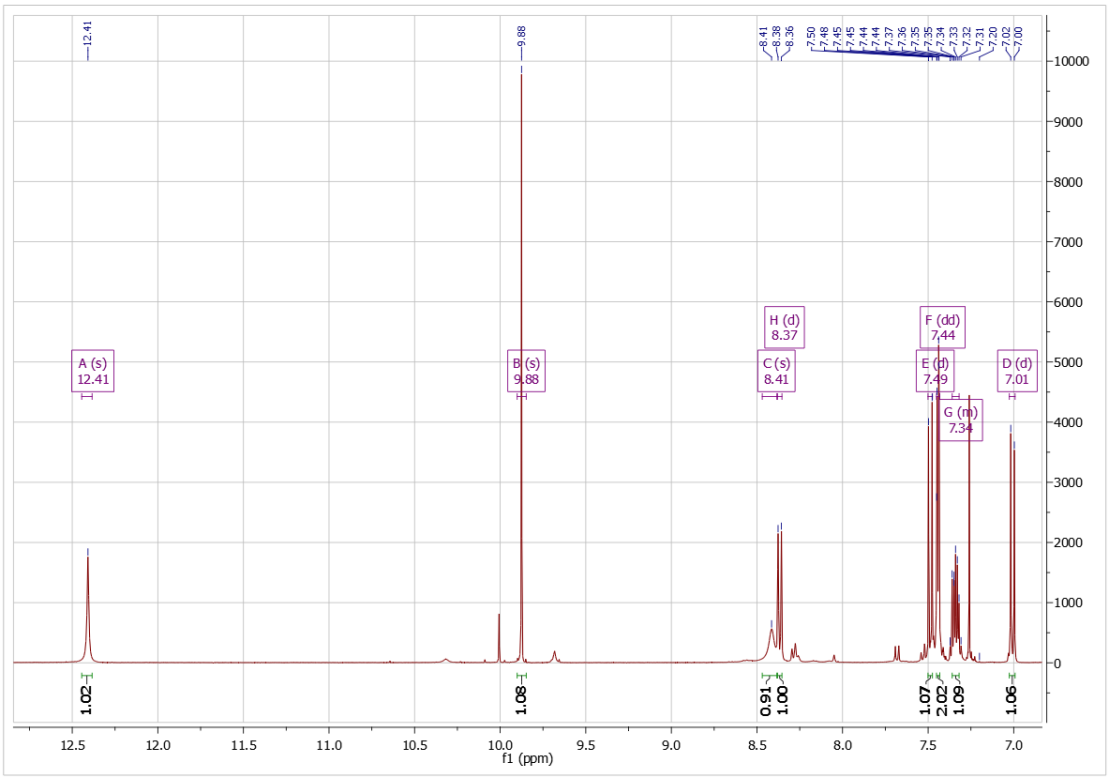
Freshly distilled phosphorous oxychloride (6.1 mL, 65.50 mmol, M = 153.12 g/mol, d = 1.64 g/mL) was added dropwise with stirring to DMF (30.6 mL, 394.63 mmol, M = 73.10 g/mol, d = 0.944 g/mL) in a flask protected from moisture and for a temperature kept between 0-5°C. 4-Hydroxy carbazole (10 g, 54.58 mmol, M = 183.21 g/mol) dissolved in dry DMF (61 mL) was then slowly added to the previous solution at 0-5°C under constant stirring. Temperature of the reaction mixture was kept at 35 °C for 2 h and the solution was then poured onto crushed ice. pH of the above solution was adjusted to pH = 7-8 with an aqueous 1% sodium hydroxide solution. The resulting precipitate was filtered off and dissolved in chloroform. The organic phase was washed with water several times, dried with $MgSO_4$, and the solvent removed under reduced pressure. The pure solid product (8.02 g, 69.56%) could be obtained by purification on column chromatography (SiO_2) using pentane/EtOAc 7:3 as the eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.41 (s, 1H), 9.88 (s, 1H), 8.41 (s, 1H), 8.37 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.44 (dd, *J* = 4.6, 0.9 Hz, 2H), 7.36 – 7.32 (m, 1H), 7.01 (d, *J* = 8.4 Hz, 1H).

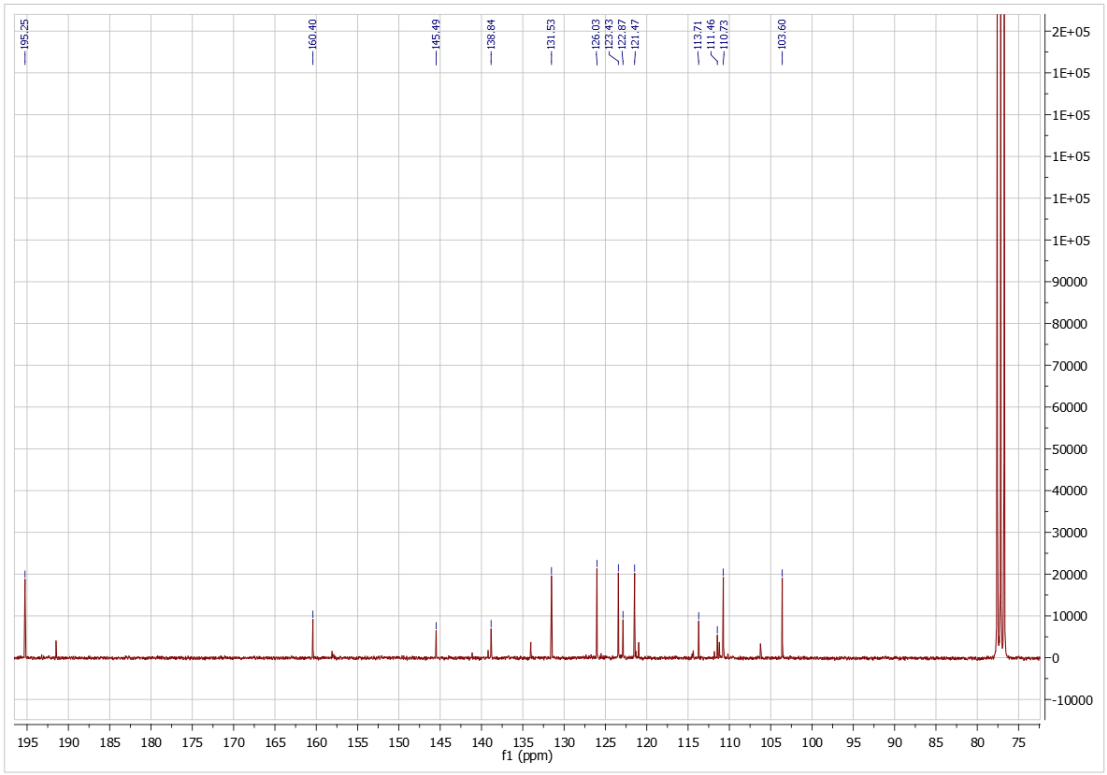
^{13}C NMR (75 MHz, $CDCl_3$) δ 195.25 (s), 160.40 (s), 145.49 (s), 138.84 (s), 131.53 (s), 126.03 (s), 123.43 (s), 122.87 (s), 121.47 (s), 113.71 (s), 111.46 (s), 110.73 (s), 103.60 (s).

Analyses are consistent with those previously reported in the literature [Construction of Highly Functionalized Xanthones via Rh-Catalyzed Cascade C–H Activation/O-Annulation, Sagar D. Nale, Debabrata Maiti, Yong Rok Lee, Org. Lett. 2021, 23, 7, 2465–2470].

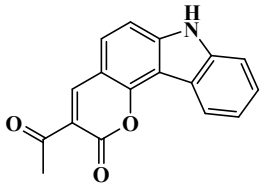
^{1}H NMR spectrum of 4-hydroxy-9*H*-carbazole-3-carbaldehyde



^{13}C NMR spectrum of 4-hydroxy-9*H*-carbazole-3-carbaldehyde



Synthesis of 3-acetylpyrano[3,2-*c*]carbazol-2(7*H*)-one



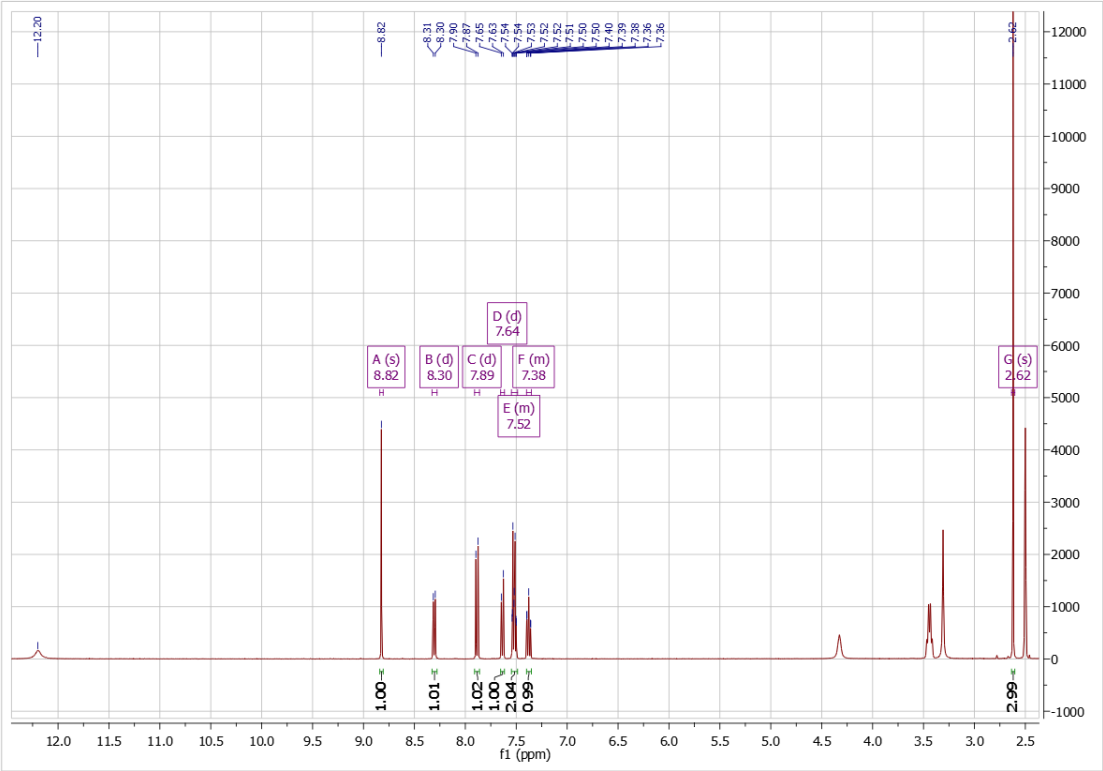
Chemical Formula: $C_{17}H_{11}NO_3$
Molecular Weight: 277,2790

4-Hydroxy-9*H*-carbazole-3-carbaldehyde (10 g, 47.34 mmol, M = 211.22 g/mol) and ethyl acetoacetate (7.19 mL, 56.81 mmol, M = 130.14 g/mol, d = 1.03 g/mL) were dissolved in 20 mL ethanol and piperidine (5.61 mL, 56.81 mmol, M = 85.15 g/mol, d = 0.862 g/mL) was added. The solution was refluxed for 2 h during which time a bright solid formed. The reaction mixture was filtered off and the crude product was recrystallized from ethanol to furnish 3-acetylpyrano[3,2-*c*]carbazole-2(7*H*)-one in pure form (11.62 g, 88.52% yield).

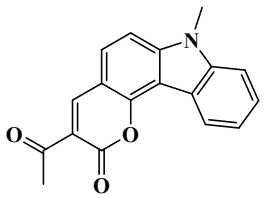
^{1}H NMR (400 MHz, DMSO) δ 12.20 (brs, 1H, NH), 8.82 (s, 1H), 8.30 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.40 – 7.35 (m, 1H), 2.62 (s, 3H).

Analyses are consistent with those previously reported in the literature [Xinyue Guo, Huanv Mao, Chunyan Bao, Decheng Wan, Ming Jin, Fused carbazole–coumarin–ketone dyes: high performance and photobleachable photoinitiators in free radical photopolymerization for deep photocuring under visible LED light irradiation, Polym. Chem., 2022, 13, 3367–3376]

^{1}H NMR spectrum of 3-acetylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 3-acetyl-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



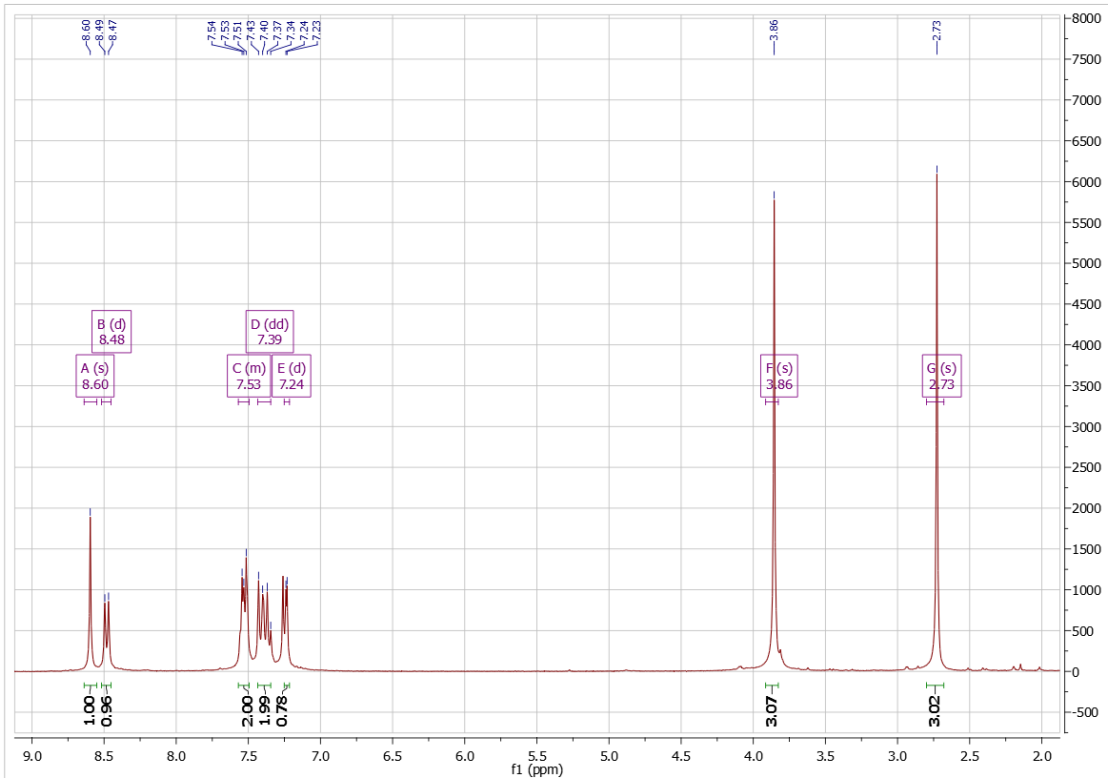
Chemical Formula: $C_{18}H_{13}NO_3$
Molecular Weight: 291,3060

3-Acetylpyrano[3,2-*c*]carbazol-2(7*H*)-one (10 g, 36.06 mmol, M = 277.28 g/mol) was dissolved in dry DMF (200 mL) in a round-bottom flask fitted with a magnetic stirrer and a condenser. Then, iodomethane (34.53 mL, 554.68 mmol, M = 141.94 g/mol, d = 2.28 g/mL) and potassium carbonate (34.86 g, 252.45 mmol, M = 138.20 g/mol) were added. The reaction was heated at 50°C for 24 h. The mixture was cooled to room temperature and then DMF was removed by rotary evaporation. After three extractions with chloroform and water and drying over $MgSO_4$, the pure solid product (10.43 g, 99.28%) could be obtained after rotary evaporation and used without any further purification.

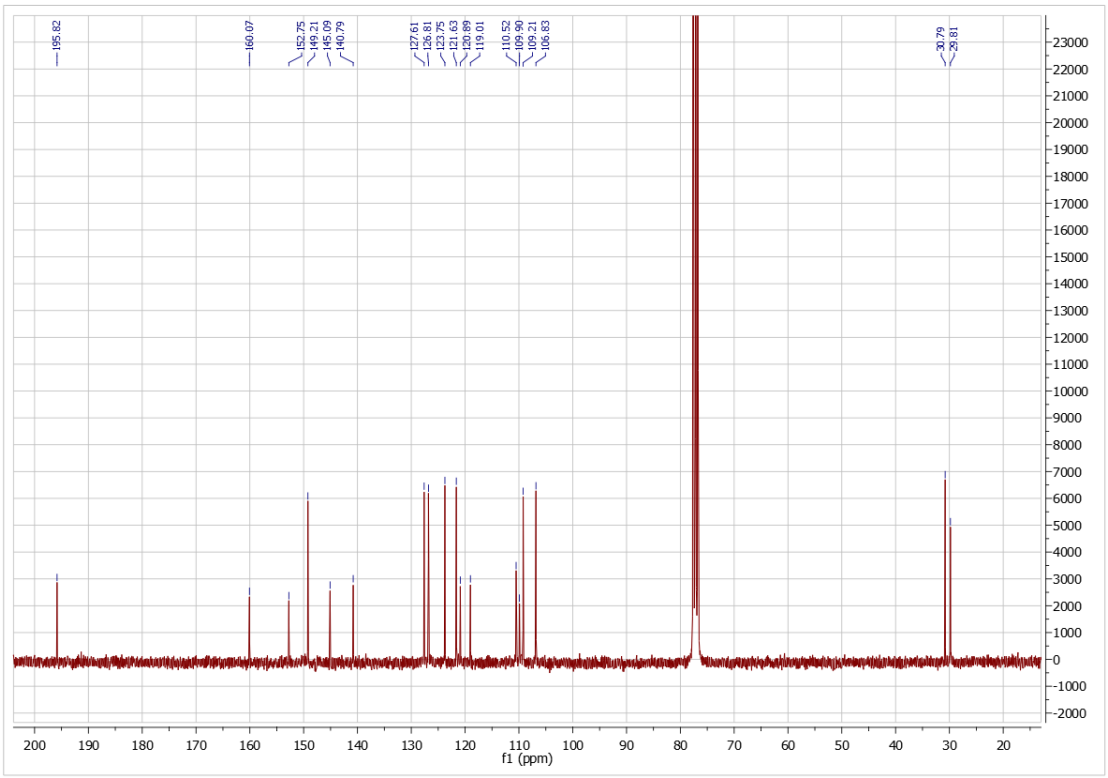
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.58 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 3.93 (s, 3H), 2.77 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 195.82 (s), 160.07 (s), 152.75 (s), 149.21 (s), 145.09 (s), 140.79 (s), 127.61 (s), 126.81 (s), 123.75 (s), 121.63 (s), 120.89 (s), 119.01 (s), 110.52 (s), 109.90 (s), 109.21 (s), 106.83 (s), 30.79 (s), 29.81 (s).

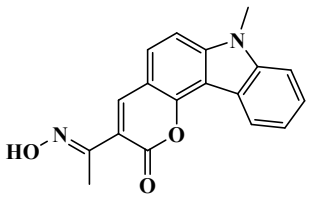
^{1}H NMR spectrum of 3-acetyl-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-acetyl-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 3-(1-(hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



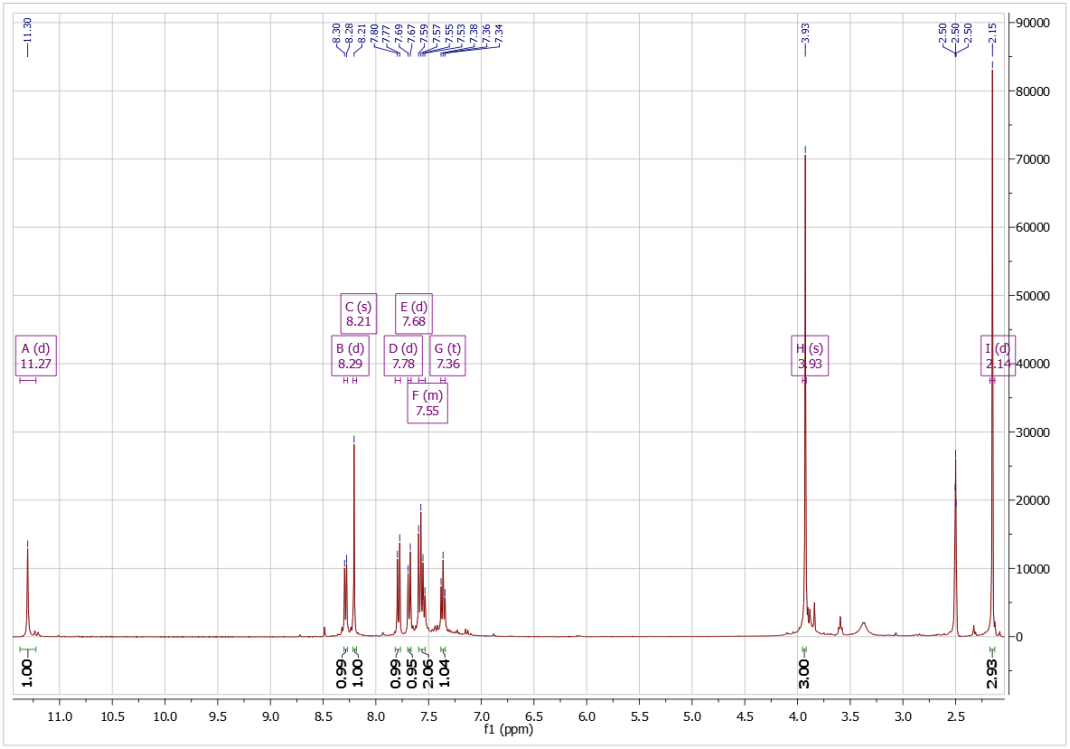
Chemical Formula: $C_{18}H_{14}N_2O_3$
Molecular Weight: 306,3210

A mixture of 3-acetyl-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (10 g, 34.33 mmol, M =291.31 g/mol), hydroxylamine hydrochloride (2.39 g, 34.33 mmol, M = 69.49 g/mol) and sodium acetate (4.67 g, 34.33 mmol, M = 136.08 g/mol) was refluxed in THF/methanol/water (400 mL/40 mL/40 mL) overnight. The solvent was evaporated under reduced pressure, and the residue was washed with water. The crude product was recrystallized from a dichloromethane/ether mixture to give the targeted product as orange needles (9.84 g, 93.58% yield).

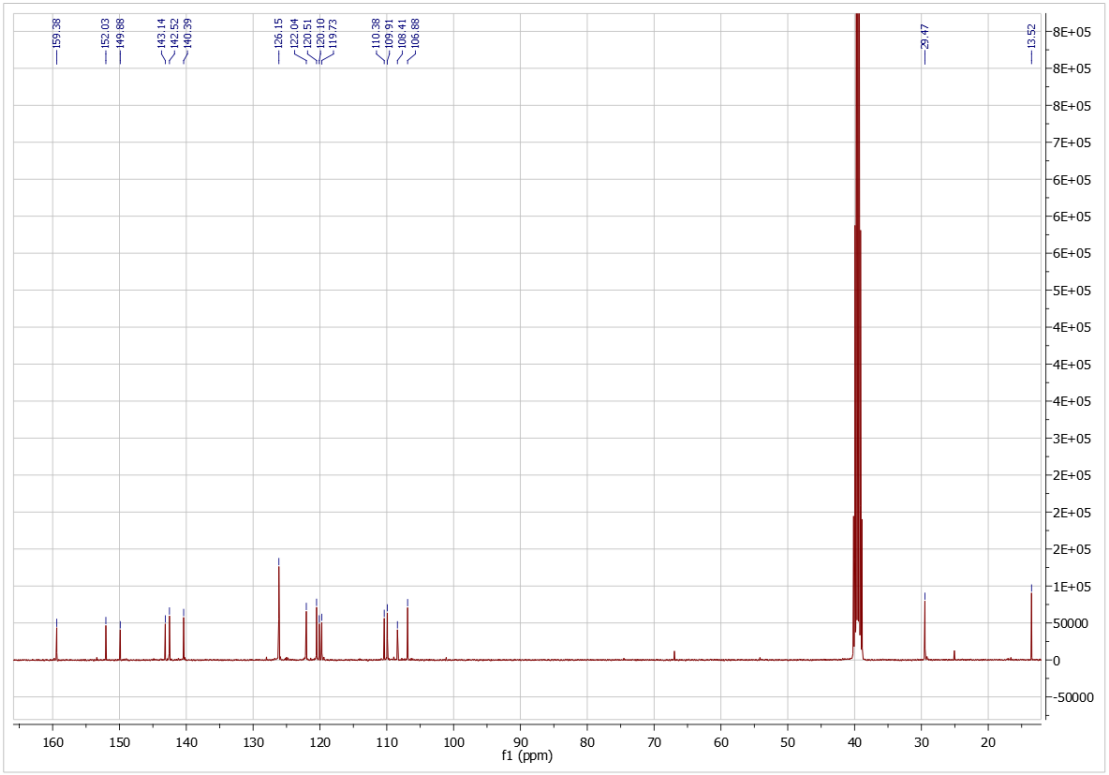
^{1}H NMR (400 MHz, DMSO) δ 11.30 (s, 1H), 8.34 (d, *J* = 7.6 Hz, 1H), 8.25 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.39 (t, *J* = 7.1 Hz, 1H), 3.99 (d, *J* = 7.8 Hz, 3H), 2.14 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 159.38 (s), 152.03 (s), 149.88 (s), 143.14 (s), 142.52 (s), 140.39 (s), 126.15 (s), 122.04 (s), 120.51 (s), 120.10 (s), 119.73 (s), 110.38 (s), 109.91 (s), 108.41 (s), 106.88 (s), 29.47 (s), 13.52 (s).

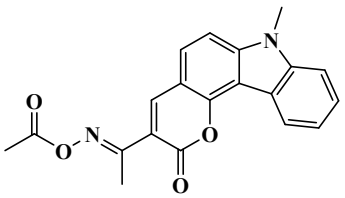
^{1}H NMR spectrum of 3-(1-(hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-(hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 3-(1-(acetoxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



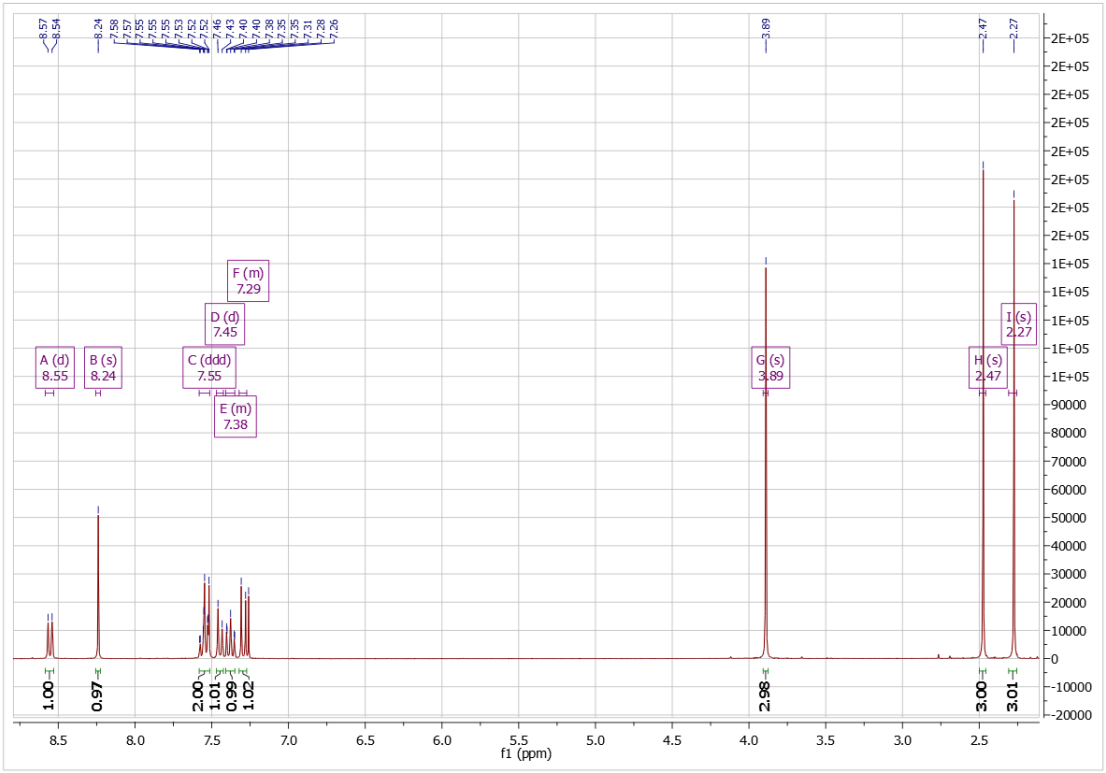
Chemical Formula: $C_{20}H_{16}N_2O_4$
Molecular Weight: 348,3580

3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, acetyl chloride (0.08 mL, 1.08 mmol, M = 78.50 g/mol, d = 1.10 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane/ether to give orange needles (0.31 g, 90.86% yield).

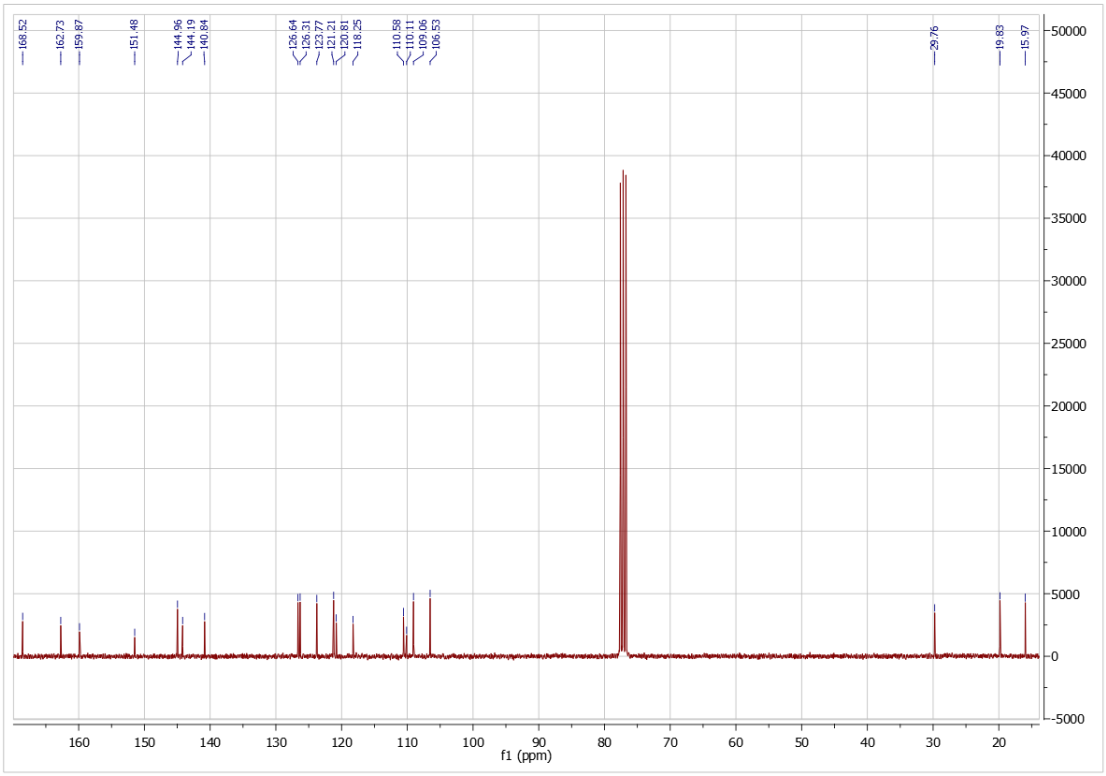
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.7 Hz, 1H), 8.24 (s, 1H), 7.55 (ddd, *J* = 8.7, 5.0, 1.5 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.32 – 7.27 (m, 1H), 3.89 (s, 3H), 2.47 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.52 (s), 162.73 (s), 159.87 (s), 151.48 (s), 144.96 (s), 144.19 (s), 140.84 (s), 126.64 (s), 126.31 (s), 123.77 (s), 121.21 (s), 120.81 (s), 118.25 (s), 110.58 (s), 110.11 (s), 109.06 (s), 106.53 (s), 29.76 (s), 19.83 (s), 15.97 (s).

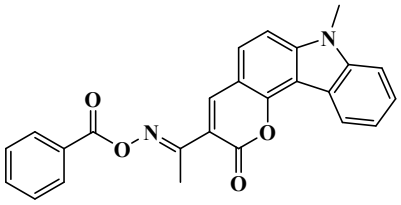
^{1}H NMR spectrum of 3-(1-(acetoxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-(acetoxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one


168.52
162.73
159.87
151.48
144.96
144.19
140.84
126.64
126.31
123.77
121.21
120.81
118.25
110.58
110.11
109.06
105.53
29.76
19.83
15.97
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

Synthesis of 3-(1-((benzoyloxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



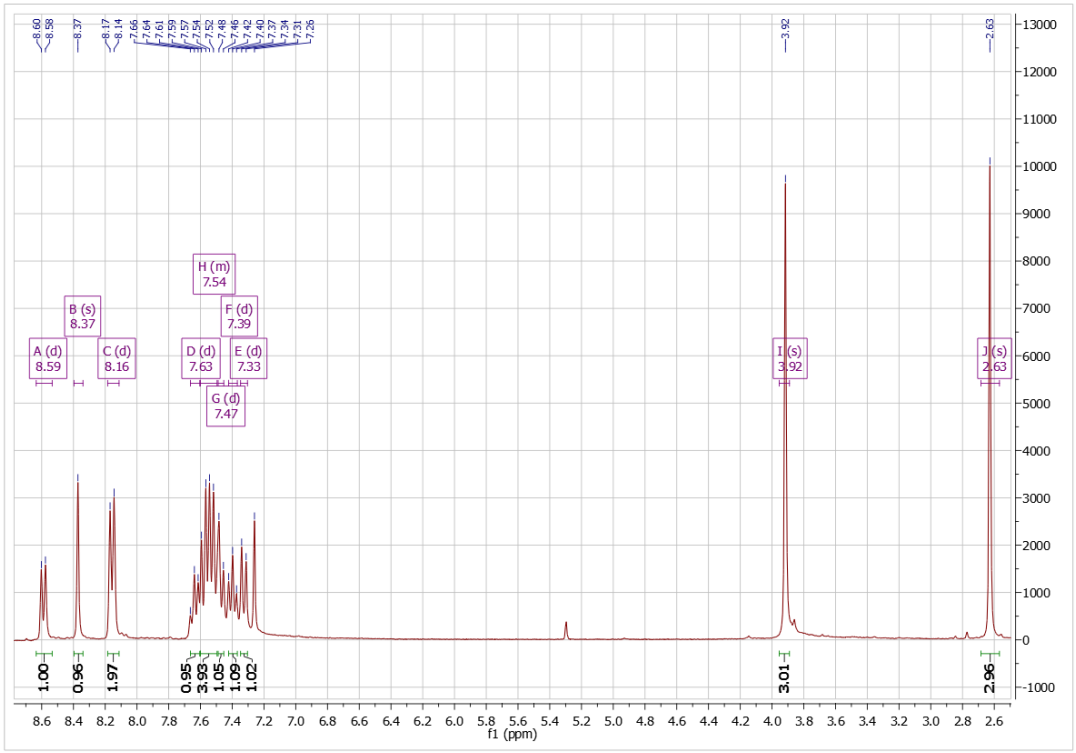
Chemical Formula: $C_{25}H_{18}N_2O_4$
Molecular Weight: 410,4290

3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, benzoyl chloride (0.13 mL, 1.08 mmol, M = 160.87 g/mol, d = 1.21 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane/ether to give orange needles (0.33 g, 82.10% yield).

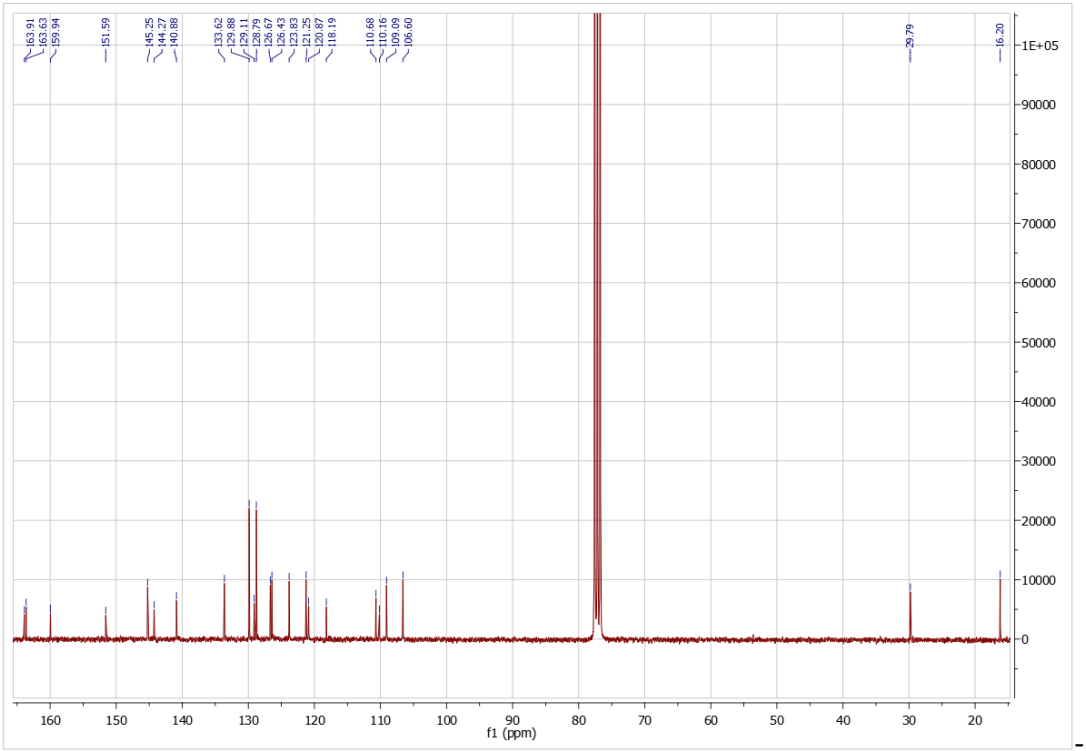
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.8 Hz, 1H), 8.37 (s, 1H), 8.16 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.0 Hz, 1H), 7.60 – 7.50 (m, 4H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 3.92 (s, 3H), 2.63 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.91 (s), 163.63 (s), 159.94 (s), 151.59 (s), 145.25 (s), 144.27 (s), 140.88 (s), 133.62 (s), 129.88 (s), 129.11 (s), 128.79 (s), 126.67 (s), 126.43 (s), 123.83 (s), 121.25 (s), 120.87 (s), 118.19 (s), 110.68 (s), 110.16 (s), 109.09 (s), 106.60 (s), 29.79 (s), 16.20 (s).

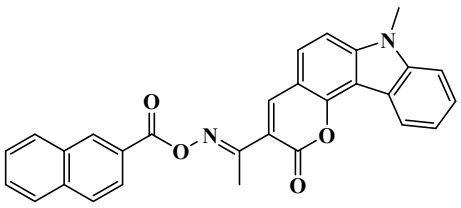
^{1}H NMR spectrum of 3-(1-((benzoyloxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-((benzoyloxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 3-(1-(((2-naphthoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



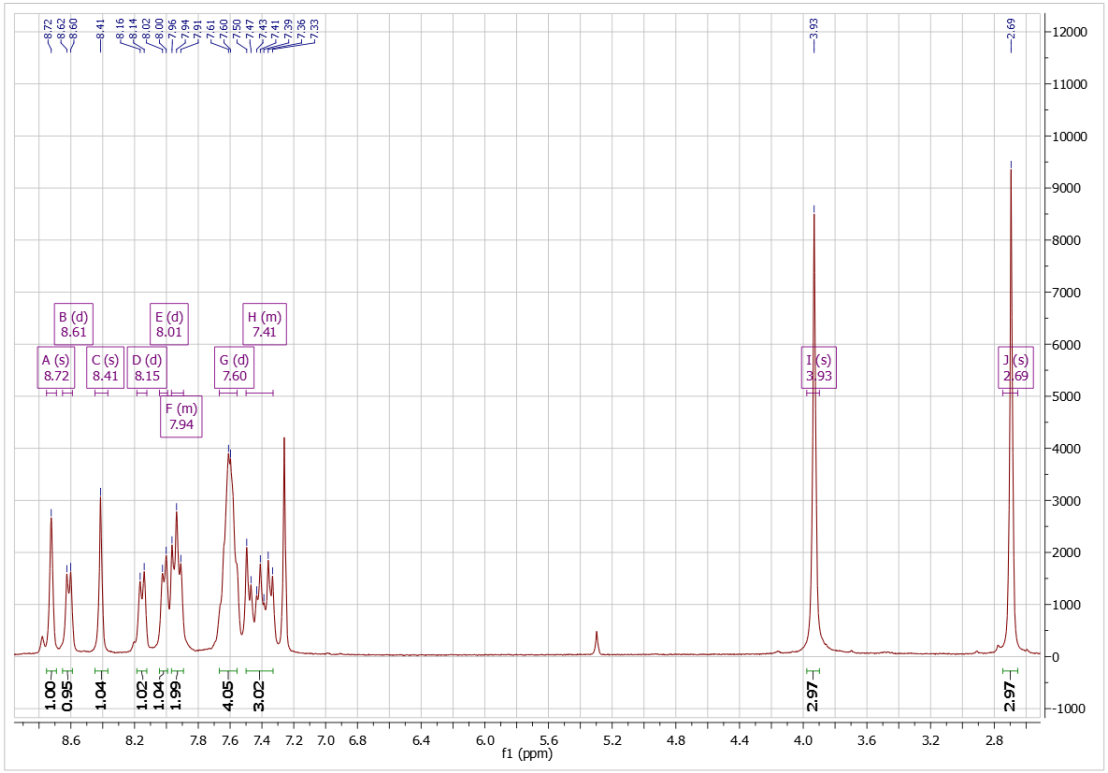
Chemical Formula: $C_{29}H_{20}N_2O_4$
Molecular Weight: 460,4890

3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane (50 mL). Then, 2-naphthoyl chloride (0.21 g, 1.08 mmol, M = 190.63 g/mol) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane/ether to give orange needles (0.42 g, 93.13% yield).

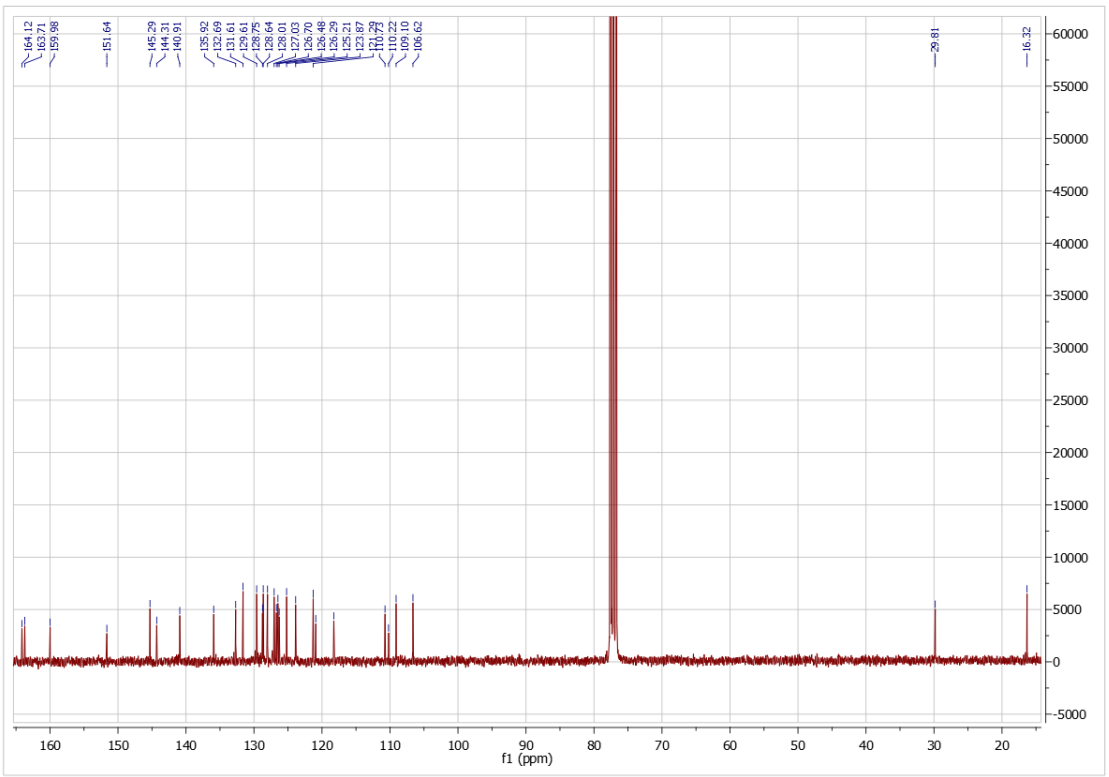
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.61 (d, *J* = 7.1 Hz, 1H), 8.41 (s, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 7.0 Hz, 1H), 7.97 – 7.89 (m, 2H), 7.60 (d, *J* = 3.8 Hz, 4H), 7.50 – 7.33 (m, 3H), 3.93 (s, 3H), 2.69 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.12 (s), 163.71 (s), 159.98 (s), 151.64 (s), 145.29 (s), 144.31 (s), 140.91 (s), 135.92 (s), 132.69 (s), 131.61 (s), 129.61 (s), 128.75 (s), 128.64 (s), 128.01 (s), 127.03 (s), 126.70 (s), 126.48 (s), 126.29 (s), 125.21 (s), 123.87 (s), 121.29 (s), 120.91 (s), 118.26 (s), 110.73 (s), 110.22 (s), 109.10 (s), 106.62 (s), 29.81 (s), 16.32 (s).

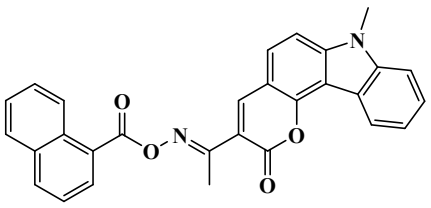
^{1}H NMR spectrum of 3-(1-(((2-naphthoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-(((2-naphthoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 3-(1-(((1-naphthoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



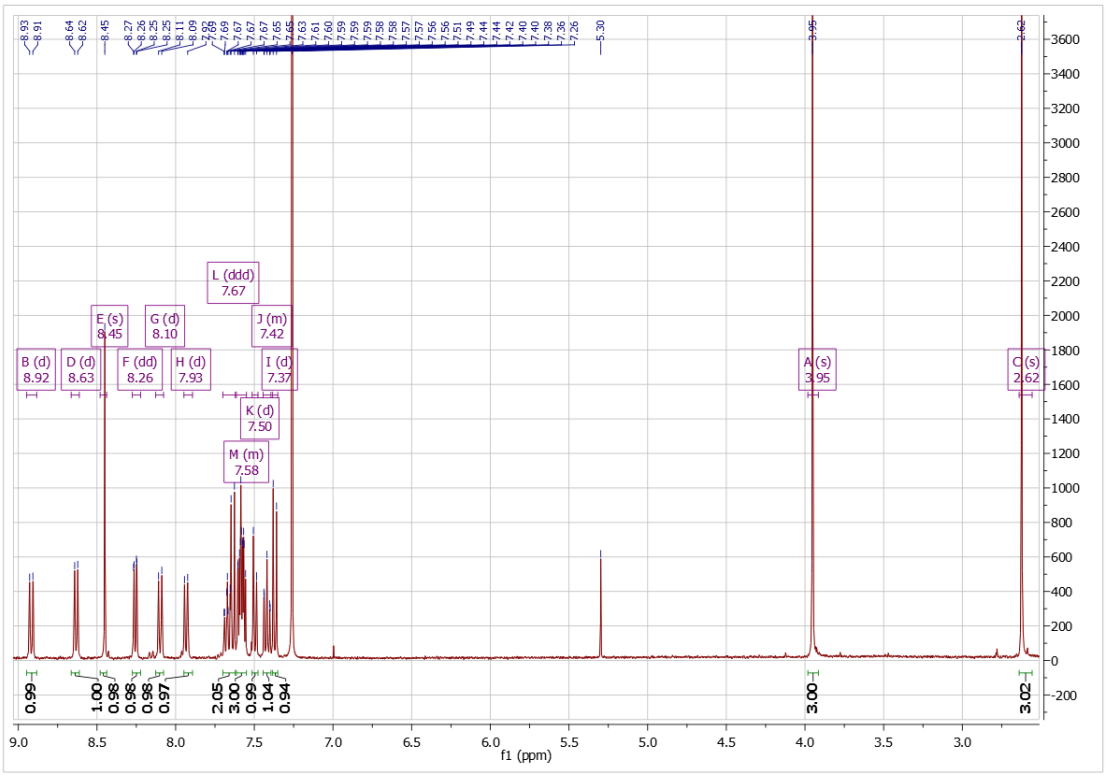
Chemical Formula: $C_{29}H_{20}N_2O_4$
Molecular Weight: 460,4890

3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, 1-naphthoyl chloride (0.16 mL, 1.08 mmol, M = 190.63 g/mol, d = 1.26 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane/ether to give orange needles (0.29 g, 64.30% yield).

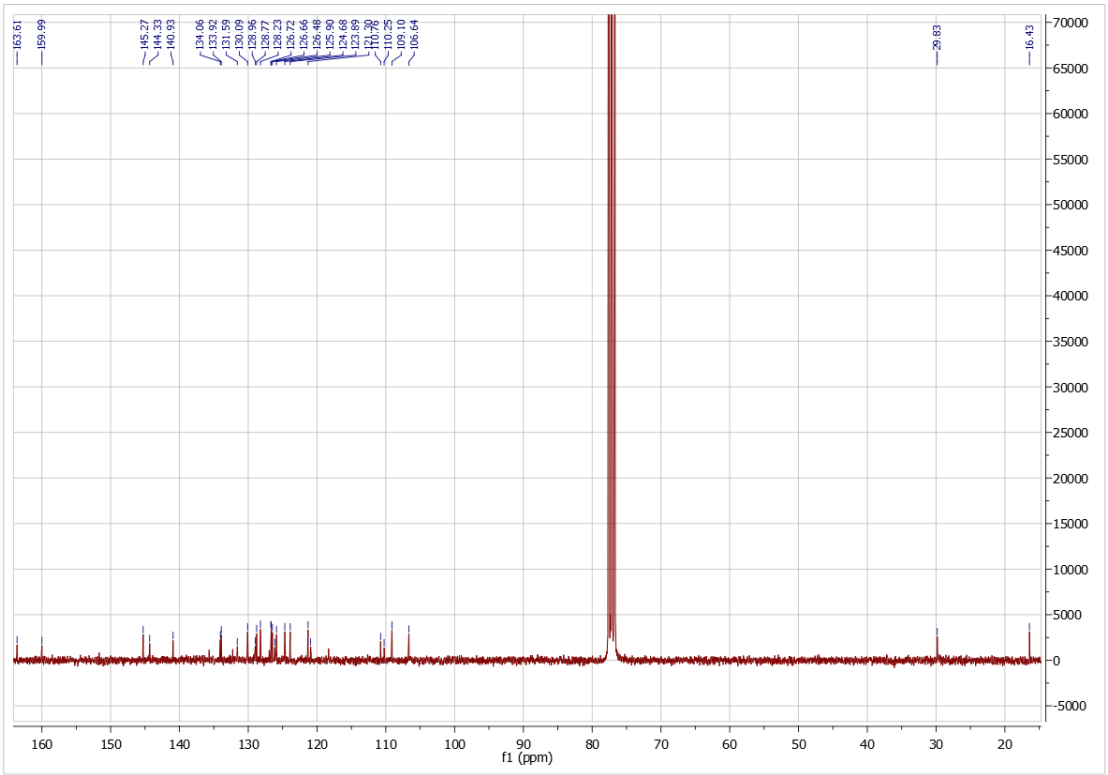
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 8.3 Hz, 1H), 8.63 (d, *J* = 7.8 Hz, 1H), 8.45 (s, 1H), 8.26 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.67 (ddd, *J* = 16.3, 8.9, 5.0 Hz, 2H), 7.61 – 7.55 (m, 3H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 3.95 (s, 3H), 2.62 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.61 (s), 159.99 (s), 145.27 (s), 144.33 (s), 140.93 (s), 134.06 (s), 133.99 (s), 131.59 (s), 130.09 (s), 128.96 (s), 128.77 (s), 128.23 (s), 126.72 (s), 126.66 (s), 126.48 (s), 125.90 (s), 124.68 (s), 123.89 (s), 121.30 (s), 120.93 (s), 110.76 (s), 110.25 (s), 109.10 (s), 106.64 (s), 29.83 (s), 16.43 (s).

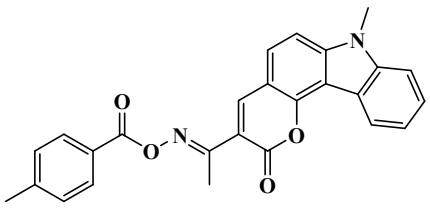
^{1}H NMR spectrum of 3-(1-(((1-naphthoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-(((1-naphthoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 7-methyl-3-(1-(((4-methylbenzoyl)oxy)imino)ethyl)pyrano[3,2-*c*]carbazol-2(7*H*)-one



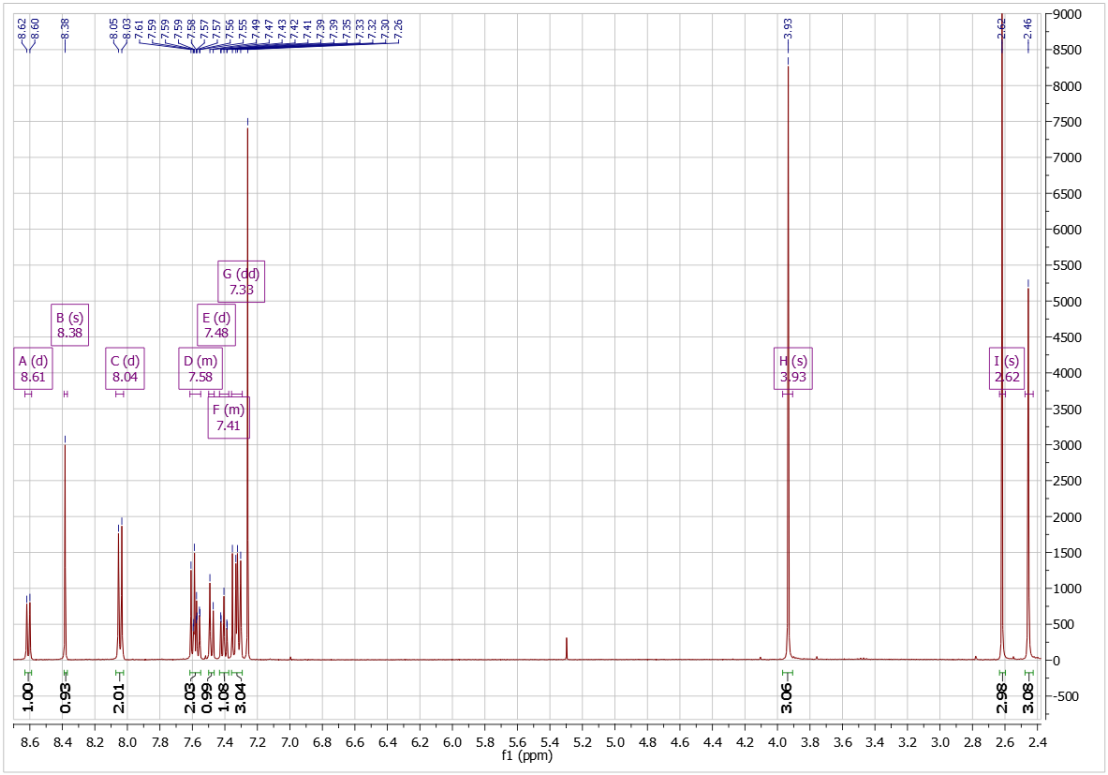
Chemical Formula: $C_{26}H_{20}N_2O_4$
Molecular Weight: 424,4560

3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, 4-methylbenzoyl chloride (0.14 mL, 1.08 mmol, M = 154.59 g/mol, d = 1.17 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane/ether to give orange needles (0.36 g, 86.60% yield).

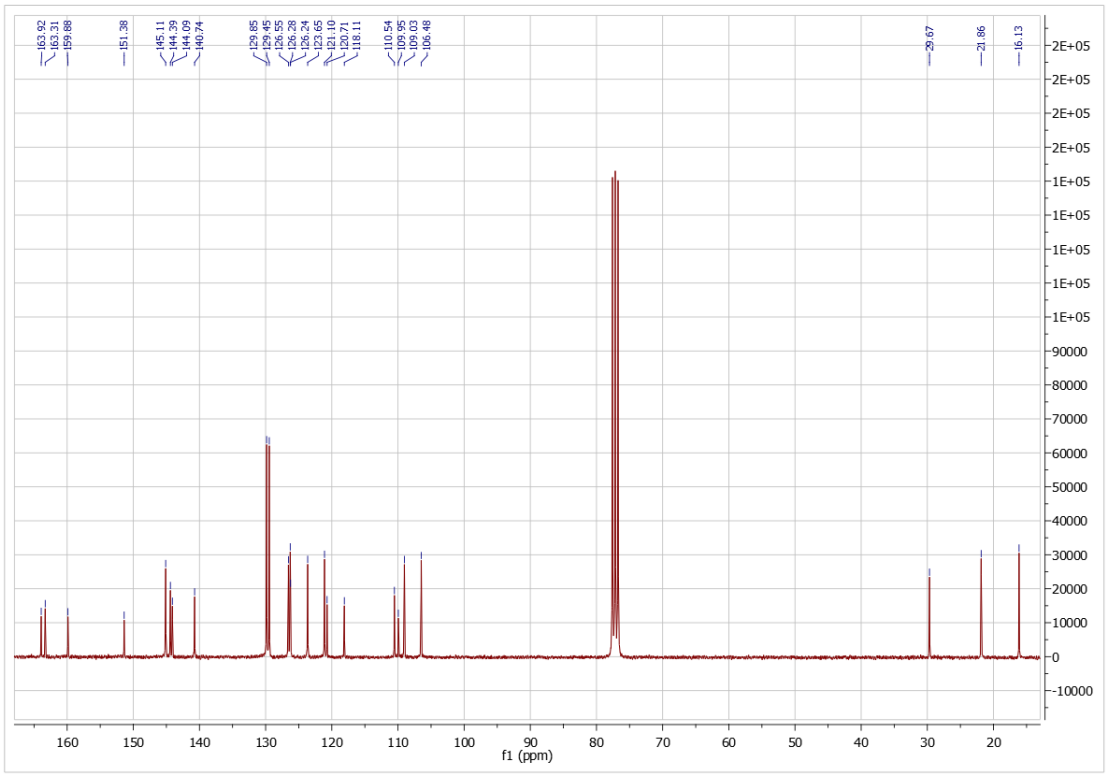
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 7.7 Hz, 1H), 8.38 (s, 1H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.33 (dd, *J* = 12.2, 8.3 Hz, 3H), 3.93 (s, 3H), 2.62 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.92 (s), 163.31 (s), 159.88 (s), 151.38 (s), 145.11 (s), 144.39 (s), 144.09 (s), 140.74 (s), 129.85 (s), 129.45 (s), 126.55 (s), 126.28 (s), 126.24 (s), 123.65 (s), 121.10 (s), 120.71 (s), 118.11 (s), 110.54 (s), 109.95 (s), 109.03 (s), 106.48 (s), 29.67 (s), 21.86 (s), 16.13 (s).

^{1}H NMR spectrum of 7-methyl-3-(1-(((4-methylbenzoyl)oxy)imino)ethyl)pyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 7-methyl-3-(1-(((4-methylbenzoyl)oxy)imino)ethyl)pyrano[3,2-*c*]carbazol-2(7*H*)-one


163.92
163.31
159.88
151.38
145.11
144.39
144.09
140.74
129.85
129.45
126.55
126.28
126.24
123.65
121.10
120.71
118.11
110.54
109.95
109.03
106.48
29.67
21.86
16.13
2E+05
2E+05
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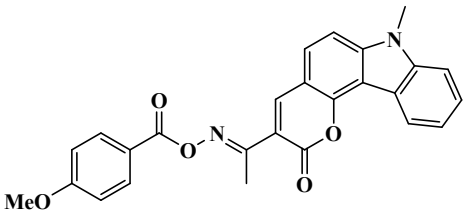
1E+05
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

Synthesis of 3-(1-(((4-methoxybenzoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



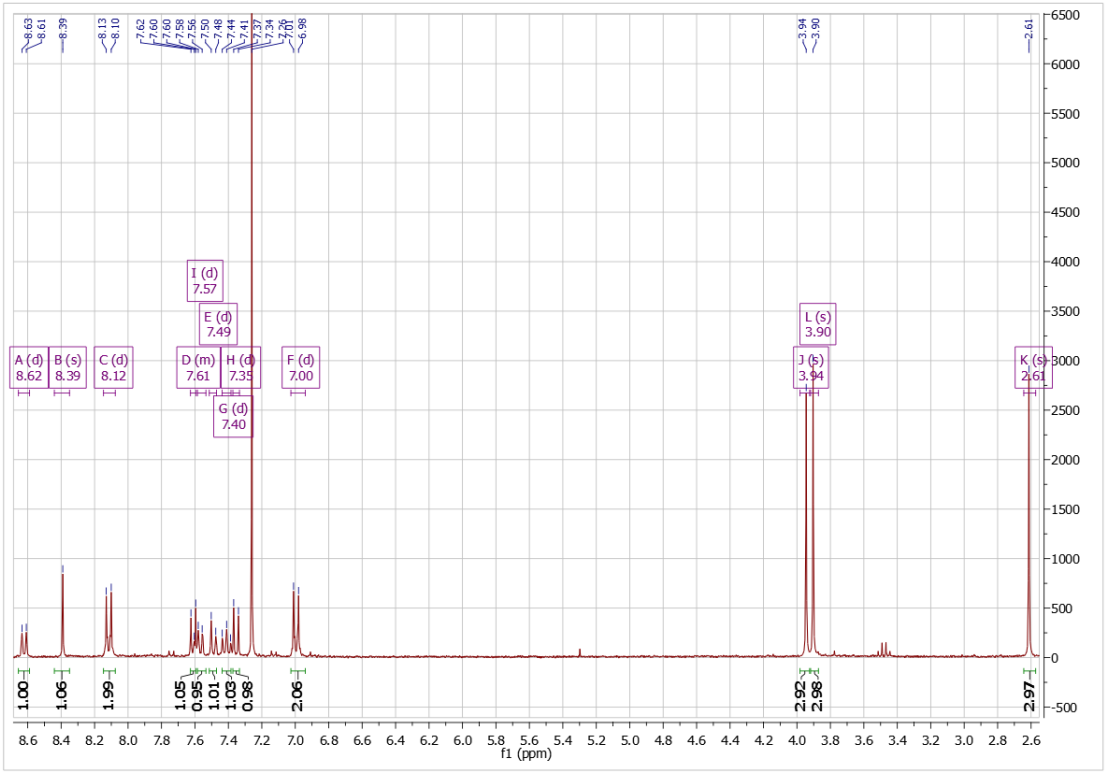
Chemical Formula: $C_{26}H_{20}N_2O_5$
Molecular Weight: 440,4550

3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, 4-methoxybenzoyl chloride (0.15 mL, 1.08 mmol, M = 170.59 g/mol, d = 1.26 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane/ether to give orange needles (0.37 g, 85.77% yield).

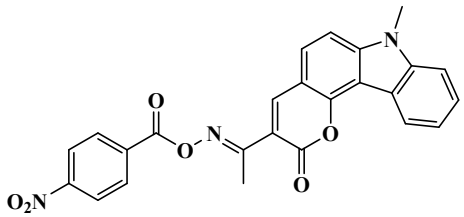
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (d, *J* = 7.8 Hz, 1H), 8.39 (s, 1H), 8.12 (d, *J* = 8.9 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.57 (d, *J* = 7.0 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 2.61 (s, 3H).

HRMS (ESI MS) m/z: theor: 441.1445 found: 441.1441 ($[M+H]^+$ detected)

^{1}H NMR spectrum of 3-(1-(((4-methoxybenzoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 7-methyl-3-(1-(((4-nitrobenzoyl)oxy)imino)ethyl)pyrano[3,2-*c*]carbazol-2(7*H*)-one

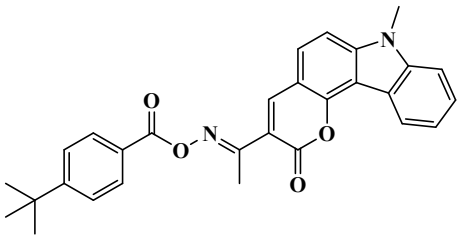


Chemical Formula: $C_{25}H_{17}N_3O_6$
Molecular Weight: 455,4260

3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, 4-nitrobenzoyl chloride (0.22 g, 1.08 mmol, M = 185.56 g/mol) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane/ether to give orange needles (0.36 g, 80.71% yield).

HRMS (ESI MS) m/z: theor: 456.1190 found: 456.1190 ($[M+H]^+$ detected)

Synthesis of 3-(1-(((4-(*tert*-butyl)benzoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Chemical Formula: $C_{29}H_{26}N_2O_4$
Molecular Weight: 466,5370

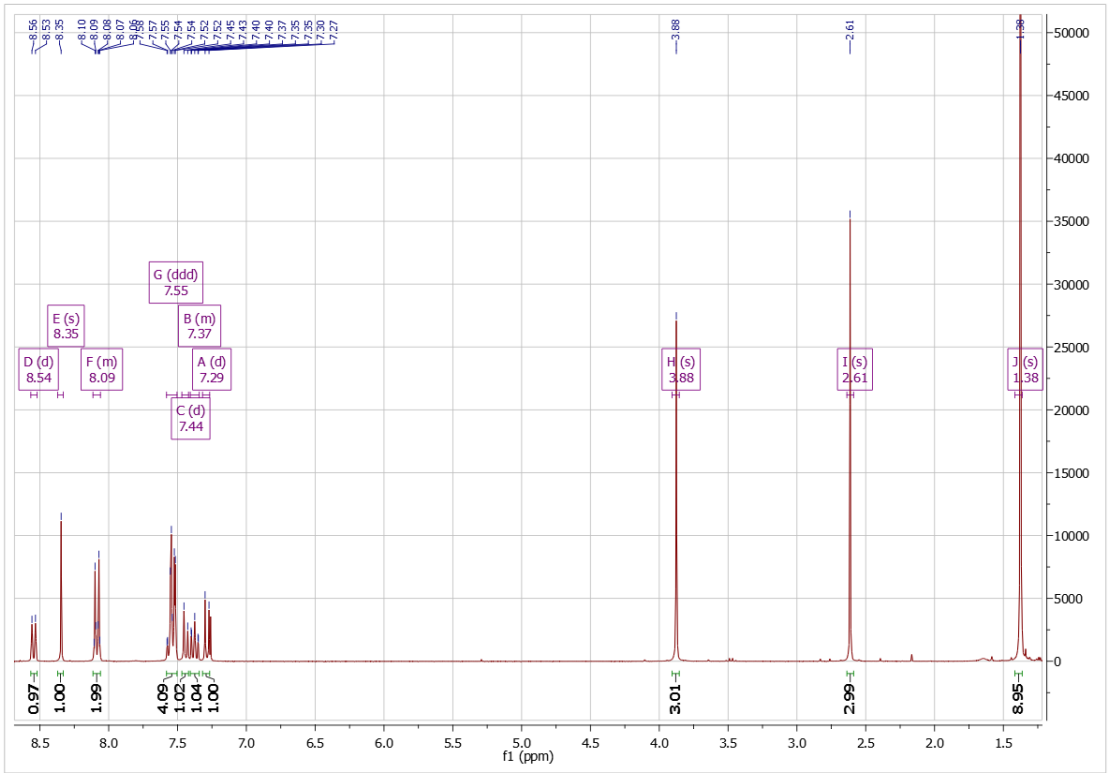
3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, 4-(*tert*-butyl)benzoyl chloride (0.23 mL, 1.08 mmol, M = 196.67 g/mol, d = 1.01 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane/ether to give orange needles (0.41 g, 89.73% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.7 Hz, 1H), 8.35 (s, 1H), 8.11 – 8.06 (m, 2H), 7.55 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 4H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 3.88 (s, 3H), 2.61 (s, 3H), 1.38 (s, 9H).

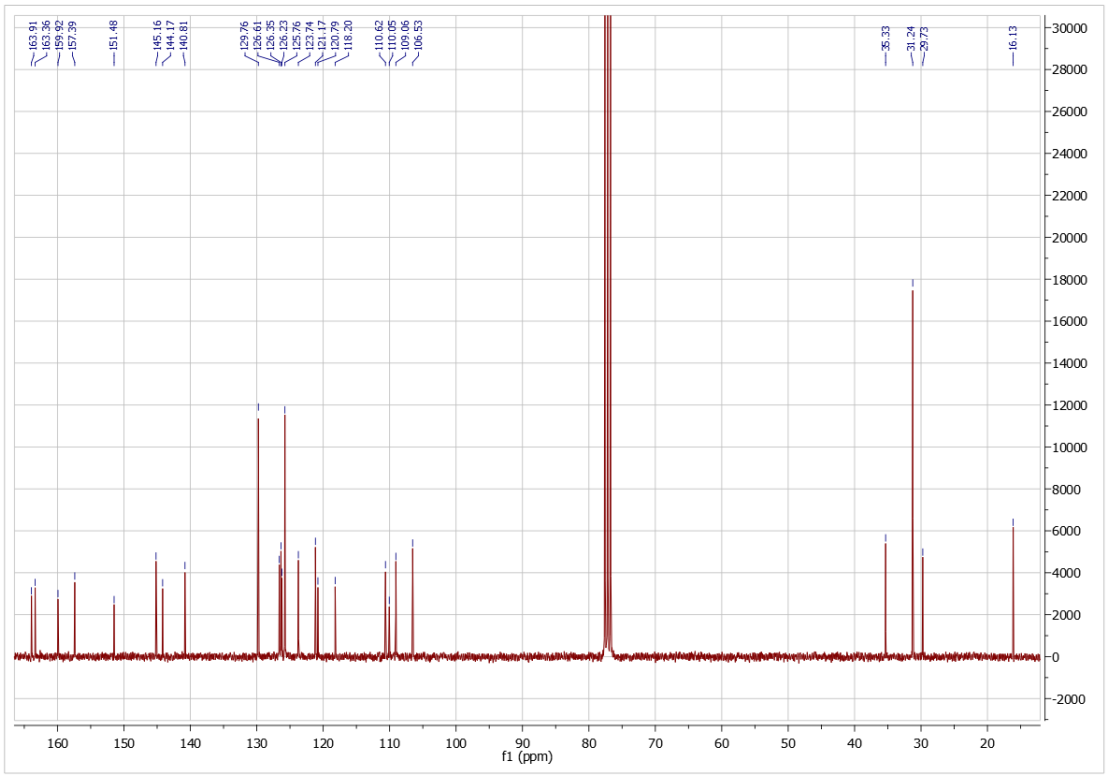
^{13}C NMR (75 MHz, $CDCl_3$) δ 163.91 (s), 163.36 (s), 159.92 (s), 157.39 (s), 151.48 (s), 145.16 (s), 144.17 (s), 140.81 (s), 129.76 (s), 126.61 (s), 126.35 (s), 126.23 (s), 125.76 (s), 123.74 (s), 121.17 (s), 120.79 (s), 118.20 (s), 110.62 (s), 110.05 (s), 109.06 (s), 106.53 (s), 35.33 (s), 31.24 (s), 29.73 (s), 16.13 (s).

HRMS (ESI MS) m/z: theor: 467.1965 found: 467.1967 ($[M+H]^+$ detected)

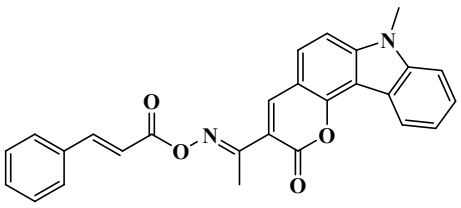
^{1}H NMR spectrum of 3-(1-(((4-(*tert*-butyl)benzoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-(((4-(*tert*-butyl)benzoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 3-(1-((cinnamoyloxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



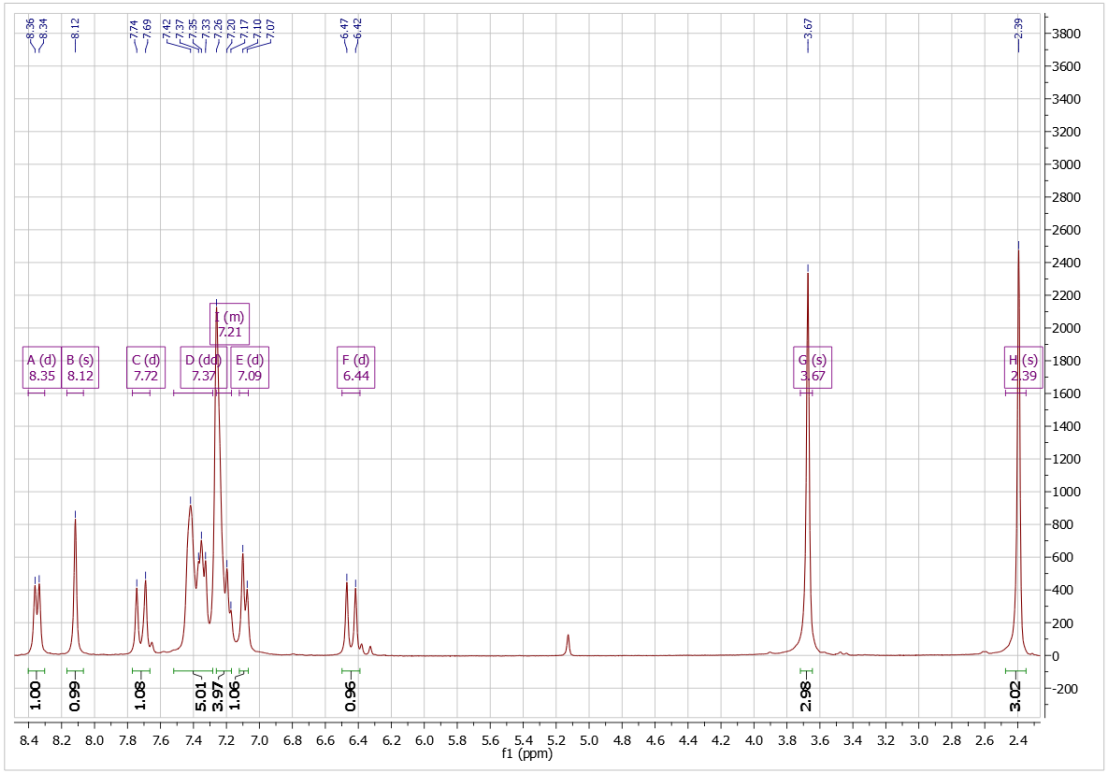
Chemical Formula: $C_{27}H_{20}N_2O_4$
Molecular Weight: 436,4670

3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, cinnamoyl chloride (0.18 g, 1.08 mmol, M = 166.60 g/mol) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane /ether to give orange needles (0.38 g, 88.90% yield).

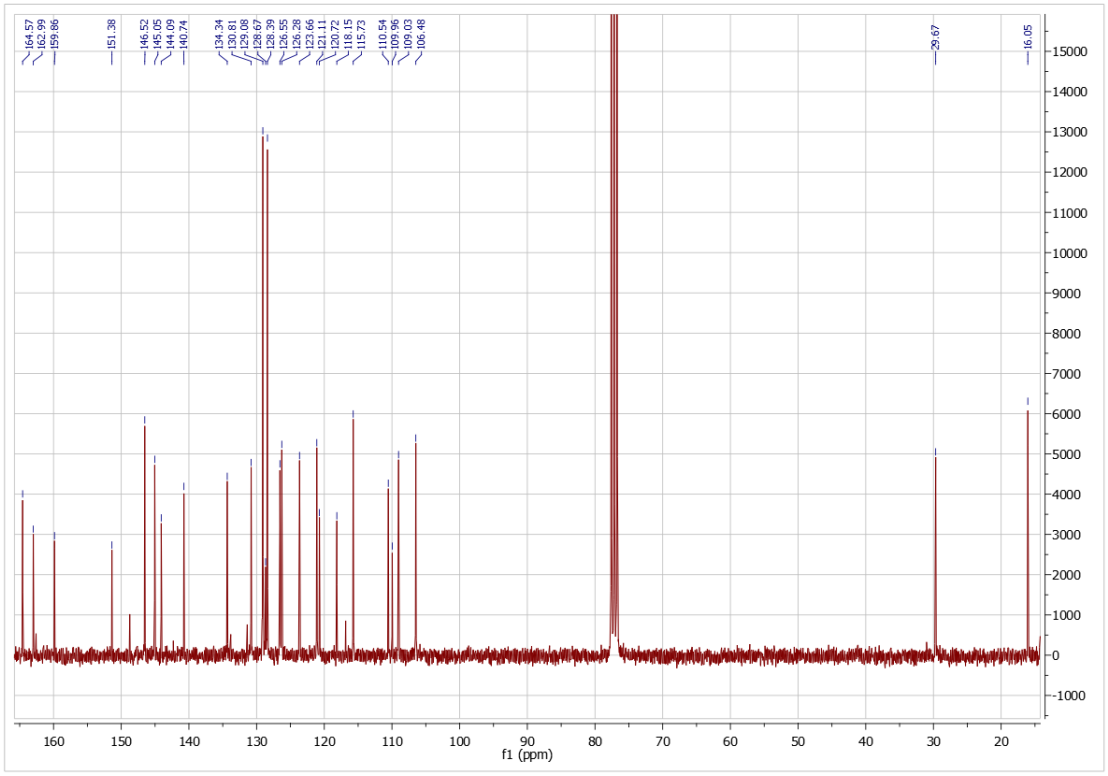
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.6 Hz, 1H), 8.12 (s, 1H), 7.72 (d, *J* = 16.0 Hz, 1H), 7.37 (dd, *J* = 16.3, 11.0 Hz, 5H), 7.26 – 7.17 (m, 4H), 7.09 (d, *J* = 7.9 Hz, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 3.67 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.57 (s), 162.99 (s), 159.86 (s), 151.38 (s), 146.52 (s), 145.05 (s), 144.09 (s), 140.74 (s), 134.34 (s), 130.81 (s), 129.08 (s), 128.67 (s), 128.39 (s), 126.55 (s), 126.28 (s), 123.66 (s), 121.11 (s), 120.72 (s), 118.15 (s), 115.73 (s), 110.54 (s), 109.96 (s), 109.03 (s), 106.48 (s), 29.67 (s), 16.05 (s).

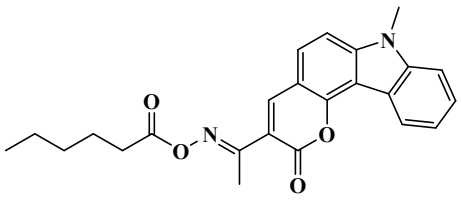
^{1}H NMR spectrum of 3-(1-((cinnamoyloxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-((cinnamoyloxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one


164.57
162.99
159.86
151.38
146.52
145.05
144.09
140.74
134.34
130.81
129.08
128.67
128.39
126.55
126.28
123.66
121.11
120.72
118.15
115.73
110.54
109.96
109.03
106.48
29.67
16.05
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

Synthesis of 3-(1-((hexanoyloxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



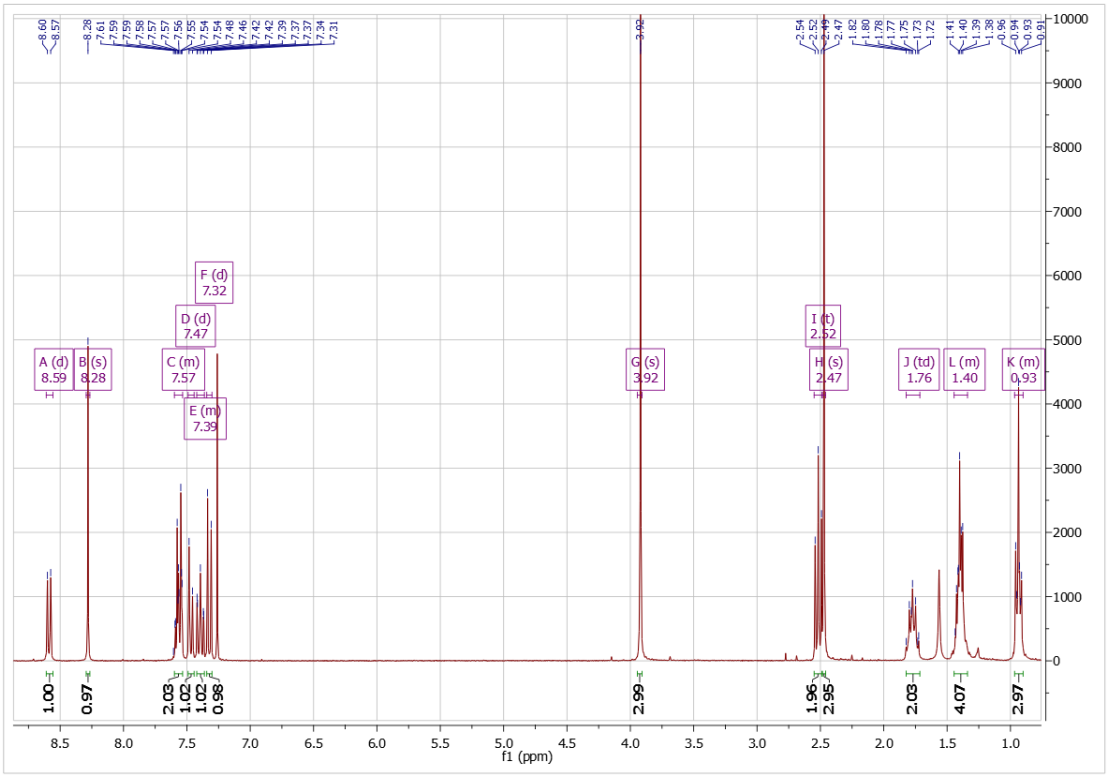
Chemical Formula: $C_{24}H_{24}N_2O_4$
Molecular Weight: 404,4660

3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, hexanoyl chloride (0.15 mL, 1.08 mmol, M = 134.60 g/mol, d = 0.963 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane /ether to give orange needles (0.28 g, 70.69% yield).

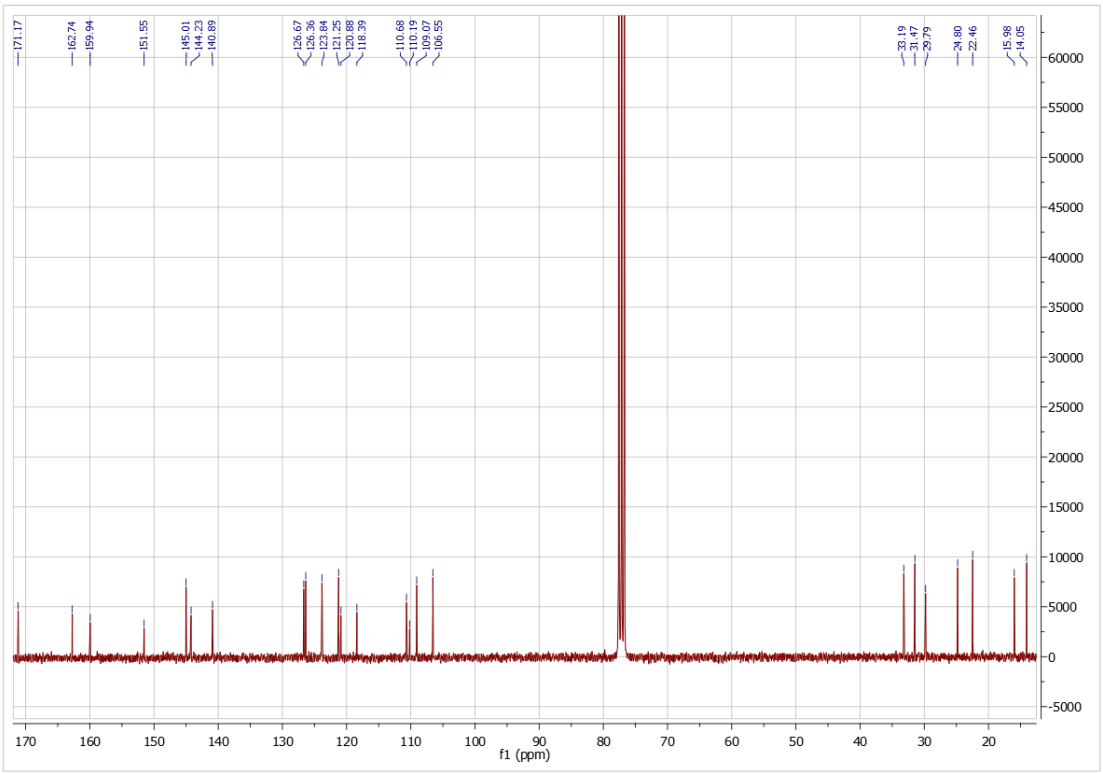
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.7 Hz, 1H), 8.28 (s, 1H), 7.60 – 7.53 (m, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 3.92 (s, 3H), 2.52 (t, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.76 (td, *J* = 7.4, 3.6 Hz, 2H), 1.44 – 1.34 (m, 4H), 0.97 – 0.90 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.17 (s), 162.74 (s), 159.94 (s), 151.55 (s), 145.01 (s), 144.23 (s), 140.89 (s), 126.67 (s), 126.36 (s), 123.84 (s), 121.25 (s), 120.88 (s), 118.39 (s), 110.68 (s), 110.19 (s), 109.07 (s), 106.55 (s), 33.19 (s), 31.47 (s), 29.79 (s), 24.80 (s), 22.46 (s), 15.98 (s), 14.05 (s).

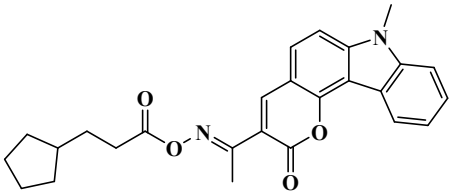
^{1}H NMR spectrum of 3-(1-((hexanoyloxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-((hexanoyloxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one


171.17
162.74
159.94
151.55
145.01
144.23
140.89
126.67
126.36
123.84
121.25
120.88
118.39
110.68
110.19
109.07
106.55
33.19
31.47
29.79
24.80
22.46
15.98
14.05
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

Synthesis of 3-(1-(((3-cyclopentylpropanoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Chemical Formula: $C_{26}H_{26}N_2O_4$
Molecular Weight: 430,5040

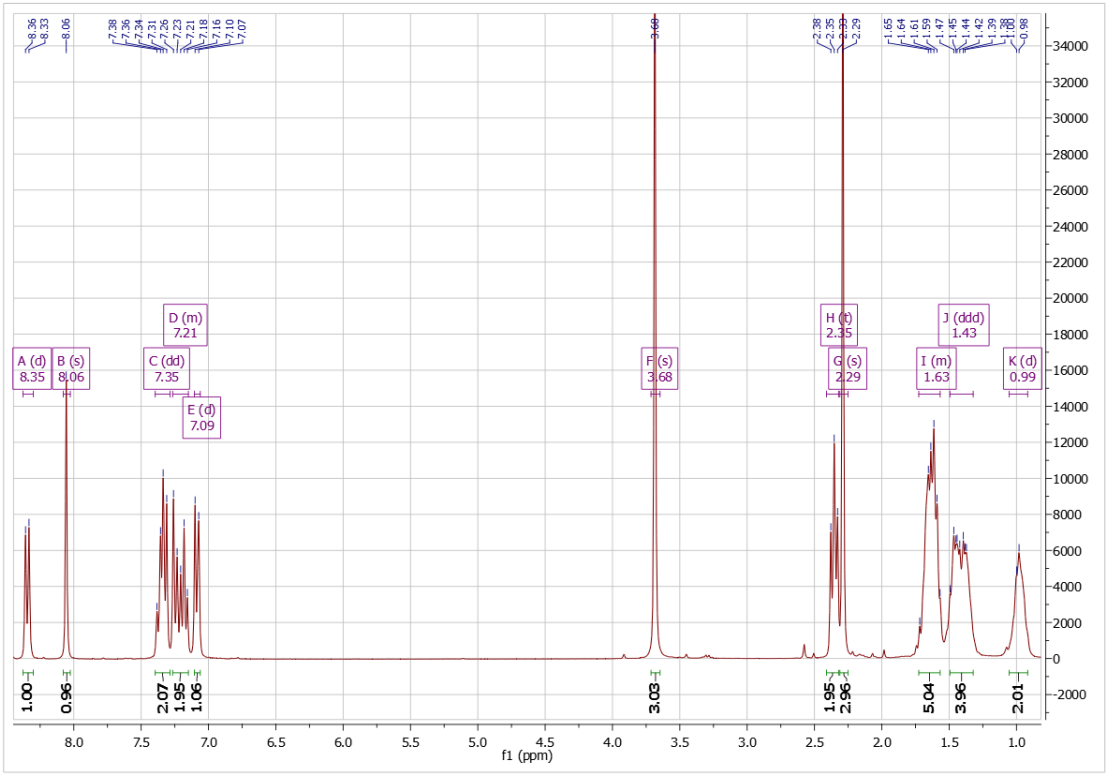
3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, 3-cyclopentylpropanoyl chloride (0.17 mL, 1.08 mmol, M = 170.59 g/mol, d = 1.05 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane /Ether to give orange needles (0.30 g, 71.15% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.8 Hz, 1H), 8.06 (s, 1H), 7.35 (dd, *J* = 13.8, 7.9 Hz, 2H), 7.27 – 7.15 (m, 2H), 7.09 (d, *J* = 8.2 Hz, 1H), 3.68 (s, 3H), 2.35 (t, *J* = 7.5 Hz, 2H), 2.29 (s, 3H), 1.73 – 1.57 (m, 5H), 1.43 (ddd, *J* = 20.9, 9.9, 5.4 Hz, 4H), 0.99 (d, *J* = 5.5 Hz, 2H).

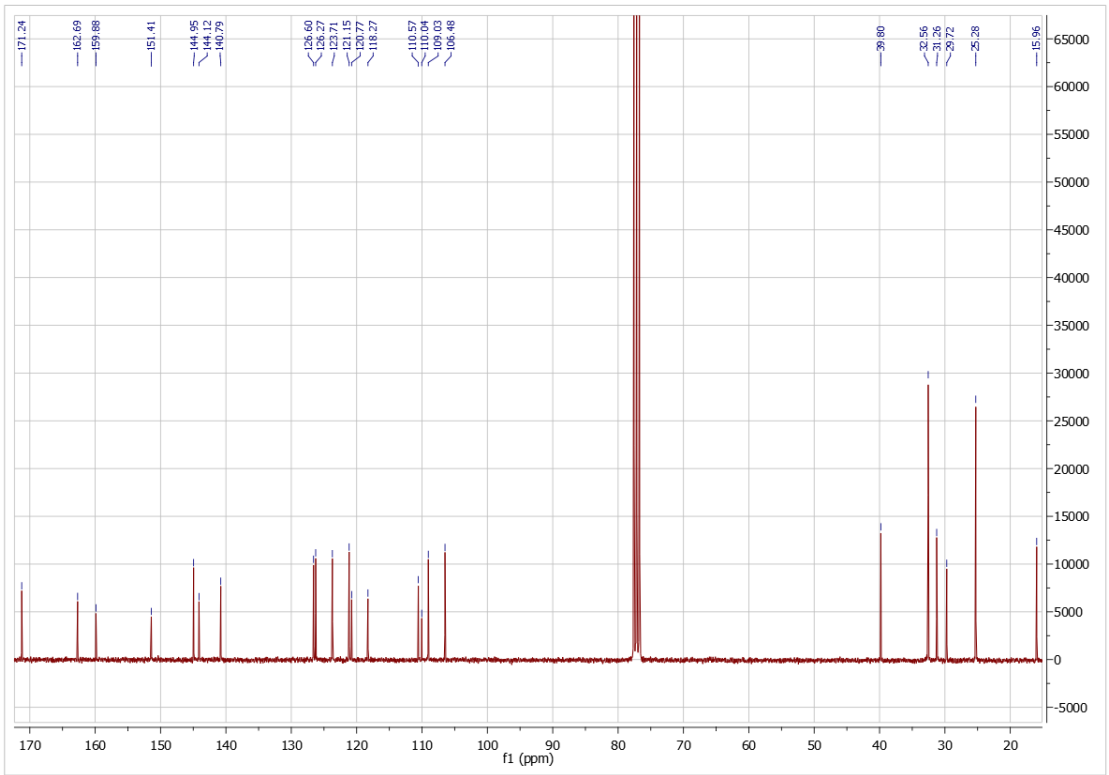
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.24 (s), 162.69 (s), 159.88 (s), 151.41 (s), 144.95 (s), 144.12 (s), 140.79 (s), 126.60 (s), 126.27 (s), 123.71 (s), 121.15 (s), 120.77 (s), 118.27 (s), 110.57 (s), 110.04 (s), 109.03 (s), 106.48 (s), 39.80 (s), 32.56 (s), 31.26 (s), 29.72 (s), 25.28 (s), 15.96 (s).

HRMS (ESI MS) m/z: theor: 431.1965 found: 431.1964 ($[M+H]^+$ detected)

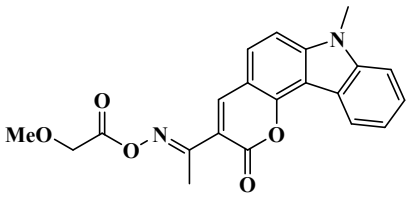
^{1}H NMR spectrum of 3-(1-(((3-cyclopentylpropanoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-(((3-cyclopentylpropanoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 3-(1-((2-methoxyacetoxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Chemical Formula: $C_{21}H_{18}N_2O_5$
Molecular Weight: 378,3840

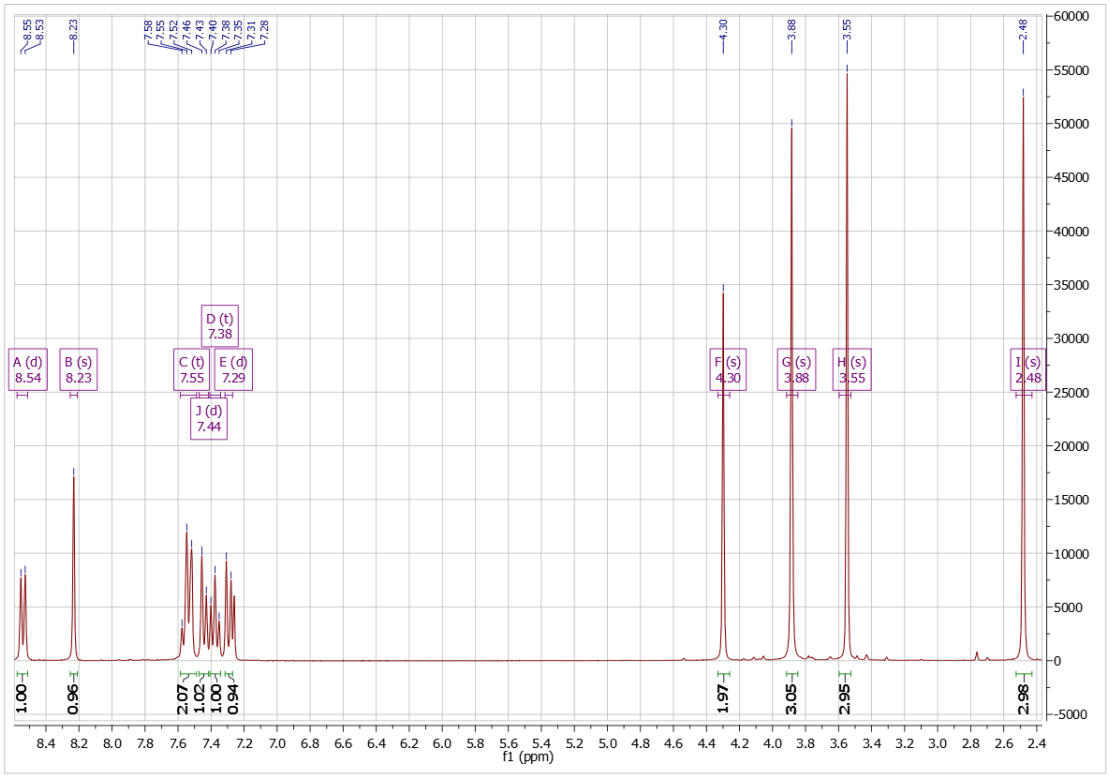
3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, 2-methoxyacetyl chloride (0.10 mL, 1.08 mmol, M = 108.52 g/mol, d = 1.19 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane/ether to give orange needles (0.35 g, 94.45% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.8 Hz, 1H), 8.23 (s, 1H), 7.55 (t, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 4.30 (s, 2H), 3.88 (s, 3H), 3.55 (s, 3H), 2.48 (s, 3H).

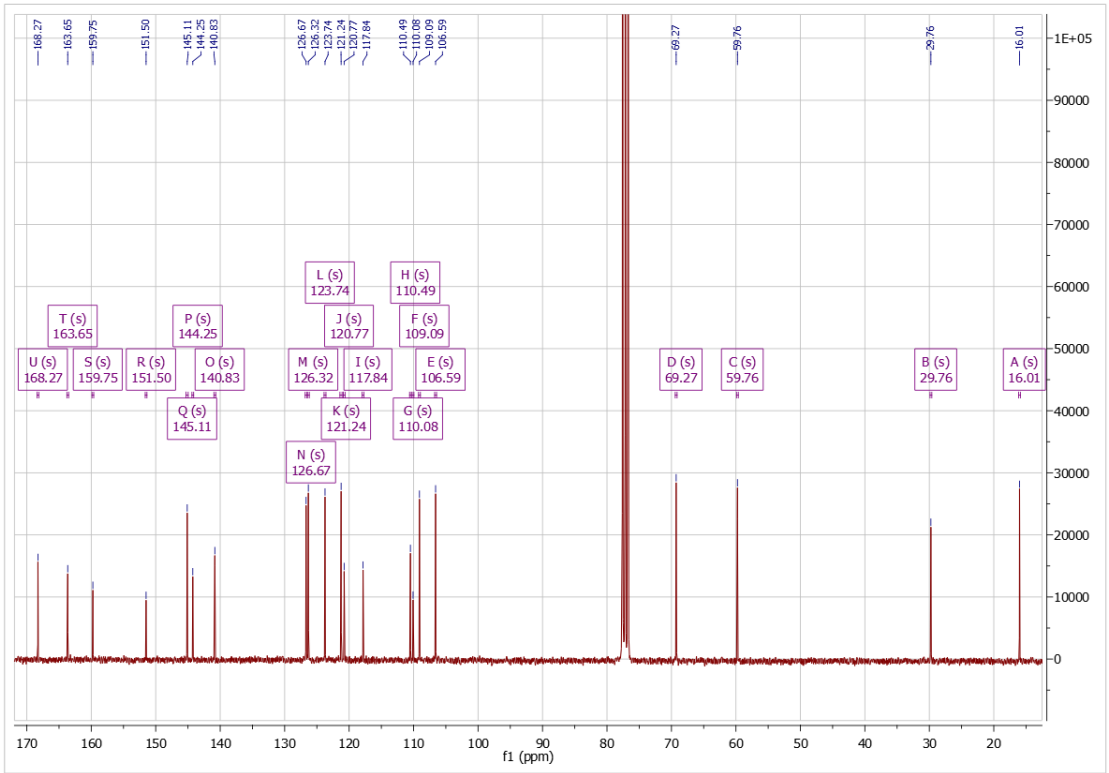
^{13}C NMR (75 MHz, $CDCl_3$) δ 168.27 (s), 163.65 (s), 159.75 (s), 151.50 (s), 145.11 (s), 144.25 (s), 140.83 (s), 126.67 (s), 126.32 (s), 123.74 (s), 121.24 (s), 120.77 (s), 117.84 (s), 110.49 (s), 110.08 (s), 109.09 (s), 106.59 (s), 69.27 (s), 59.76 (s), 29.76 (s), 16.01 (s).

HRMS (ESI MS) m/z: theor: 379.1288 found: 379.1288 ($[M+H]^+$ detected)

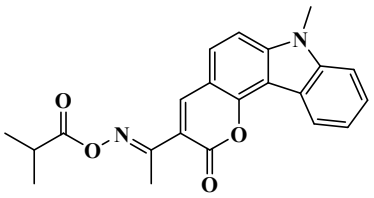
^{1}H NMR spectrum of 3-(1-((2-methoxyacetoxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-((2-methoxyacetoxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 3-(1-((isobutyryloxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



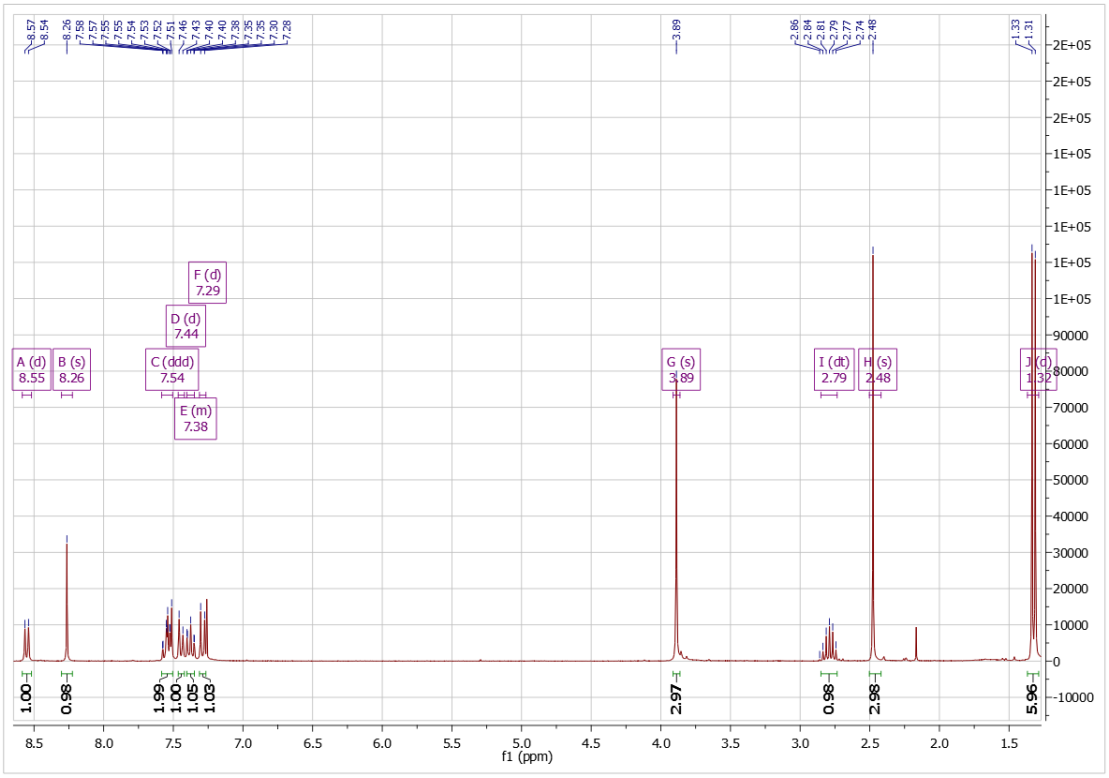
Chemical Formula: $C_{22}H_{20}N_2O_4$
Molecular Weight: 376,4120

3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, isobutyryl chloride (0.12 mL, 1.08 mmol, M = 106.55 g/mol, d = 1.02 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane/ether to give orange needles (0.29 g, 78.67% yield).

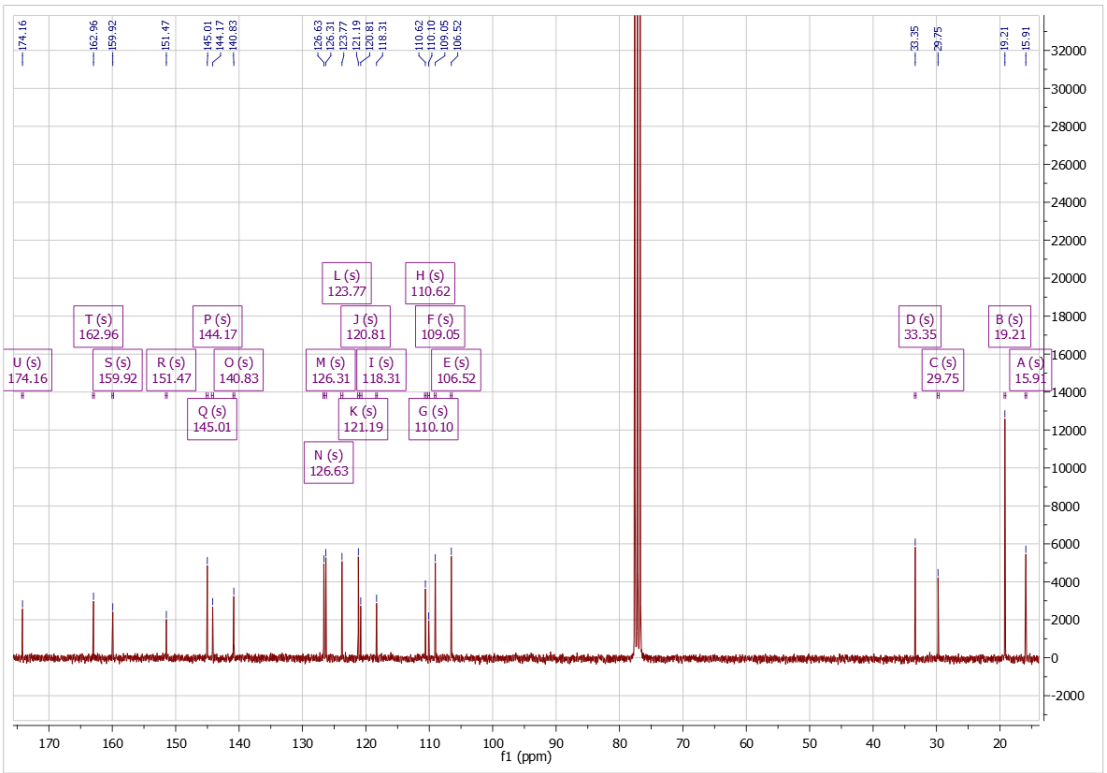
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.7 Hz, 1H), 8.26 (s, 1H), 7.54 (ddd, *J* = 10.2, 6.3, 2.1 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 3H), 2.79 (dt, *J* = 14.0, 7.0 Hz, 1H), 2.48 (s, 3H), 1.32 (d, *J* = 7.0 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.16 (s), 162.96 (s), 159.92 (s), 151.47 (s), 145.01 (s), 144.17 (s), 140.83 (s), 126.63 (s), 126.31 (s), 123.77 (s), 121.19 (s), 120.81 (s), 118.31 (s), 110.62 (s), 110.10 (s), 109.05 (s), 106.52 (s), 33.35 (s), 29.75 (s), 19.21 (s), 15.91 (s).

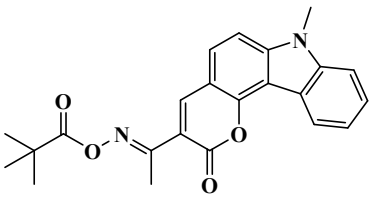
^{1}H NMR spectrum of 3-(1-((isobutyryloxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-((isobutyryloxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 7-methyl-3-(1-((pivaloyloxy)imino)ethyl)pyrano[3,2-*c*]carbazol-2(7*H*)-one



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

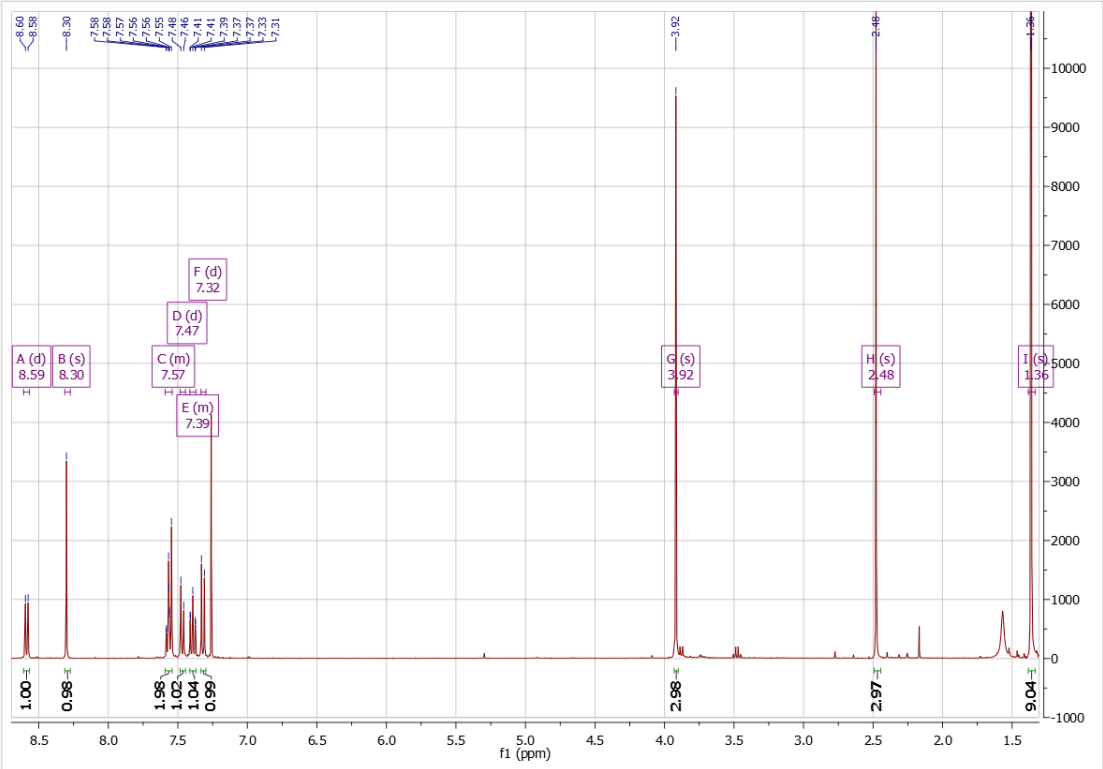
3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, pivaloyl chloride (0.13 mL, 1.08 mmol, M = 120.58 g/mol, d = 0.979 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane/ether to give orange needles (0.34 g, 88.92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.8 Hz, 1H), 8.30 (s, 1H), 7.59 – 7.54 (m, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 3.92 (s, 3H), 2.48 (s, 3H), 1.36 (s, 9H).

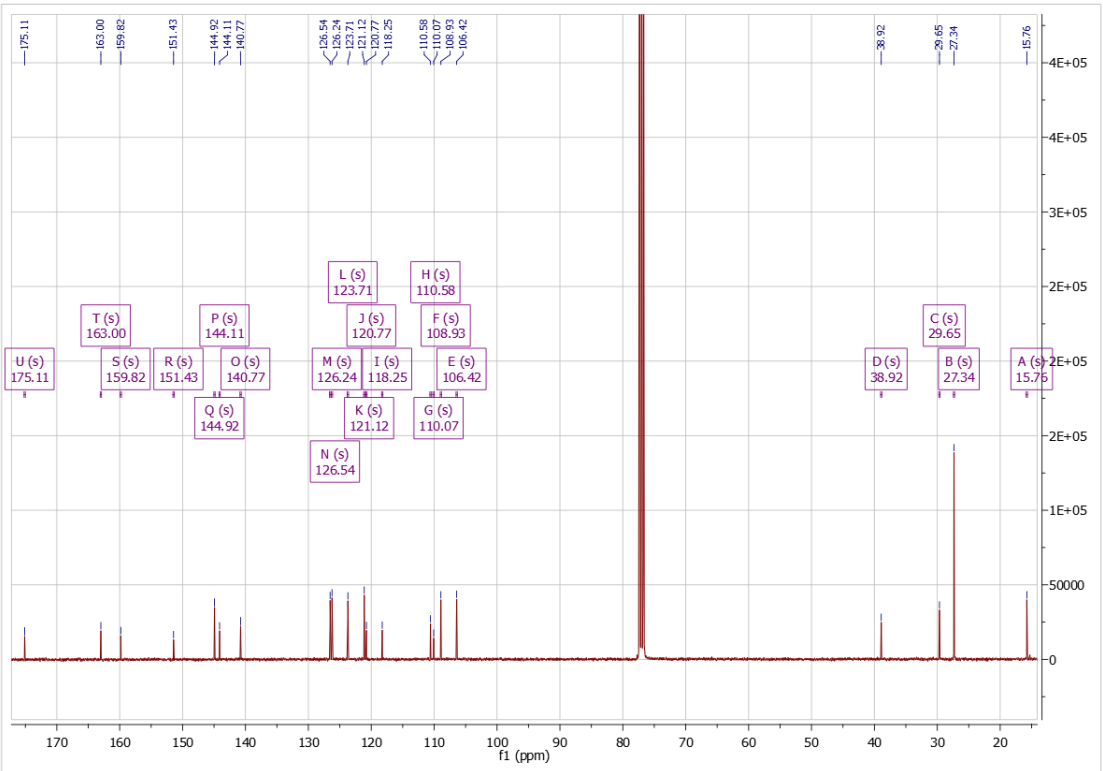
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.11 (s), 163.00 (s), 159.82 (s), 151.43 (s), 144.92 (s), 144.11 (s), 140.77 (s), 126.54 (s), 126.24 (s), 123.71 (s), 121.12 (s), 120.77 (s), 118.25 (s), 110.58 (s), 110.07 (s), 108.93 (s), 106.42 (s), 38.92 (s), 29.65 (s), 27.34 (s), 15.76 (s).

HRMS (ESI MS) m/z: theor: 391.1652 found: 391.1648 ($[M+H]^+$ detected)

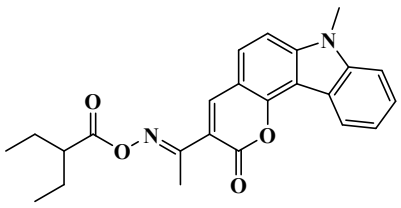
^{1}H NMR spectrum of 7-methyl-3-(1-((pivaloyloxy)imino)ethyl)pyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 7-methyl-3-(1-((pivaloyloxy)imino)ethyl)pyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 3-(1-(((2-ethylbutanoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



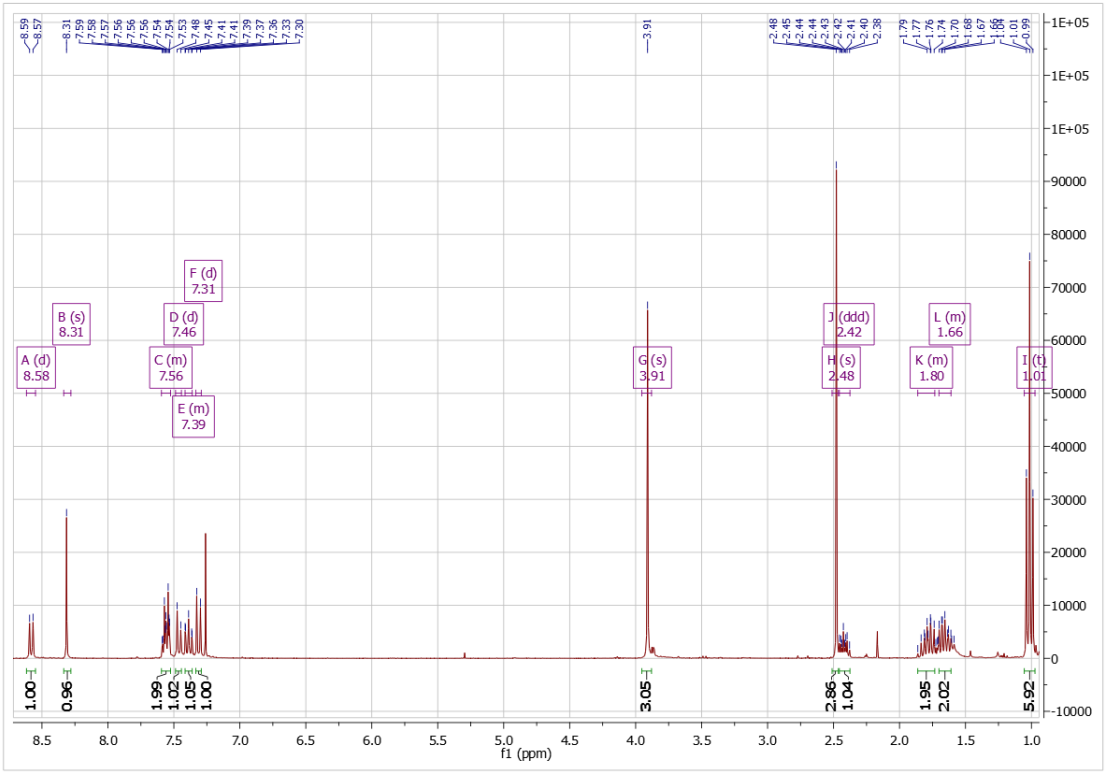
Chemical Formula: $C_{24}H_{24}N_2O_4$
Molecular Weight: 404,4660

3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, 2-ethylbutanoyl chloride (0.15 mL, 1.08 mmol, M = 134.60 g/mol, d = 0.982 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane/ether to give orange needles (0.25 g, 63.11% yield).

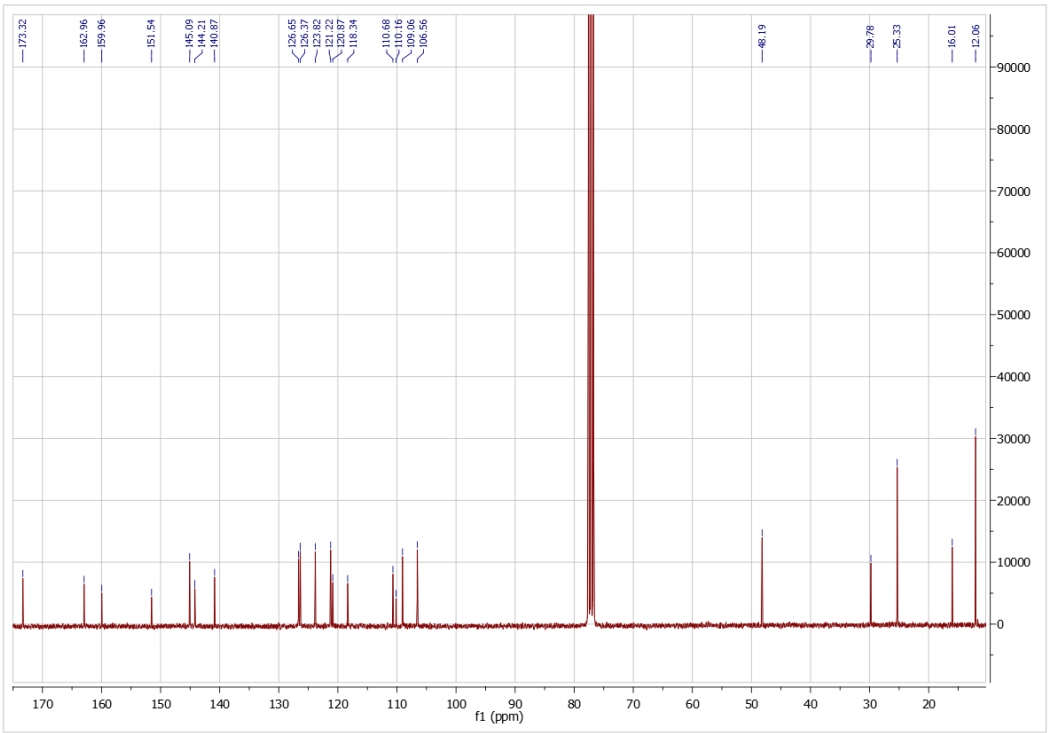
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, *J* = 7.8 Hz, 1H), 8.31 (s, 1H), 7.59 – 7.52 (m, 2H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 2.48 (s, 3H), 2.42 (ddd, *J* = 14.1, 7.1, 4.4 Hz, 1H), 1.86 – 1.73 (m, 2H), 1.70 – 1.61 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.32 (s), 162.96 (s), 159.96 (s), 151.54 (s), 145.09 (s), 144.21 (s), 140.87 (s), 126.65 (s), 126.37 (s), 123.82 (s), 121.22 (s), 120.87 (s), 118.34 (s), 110.68 (s), 110.16 (s), 109.06 (s), 106.56 (s), 48.19 (s), 29.78 (s), 25.33 (s), 16.01 (s), 12.06 (s).

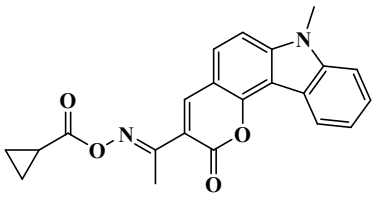
^{1}H NMR spectrum of 3-(1-(((2-ethylbutanoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-(((2-ethylbutanoyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 3-(1-(((cyclopropanecarbonyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Chemical Formula: $C_{22}H_{18}N_2O_4$
Molecular Weight: 374,3960

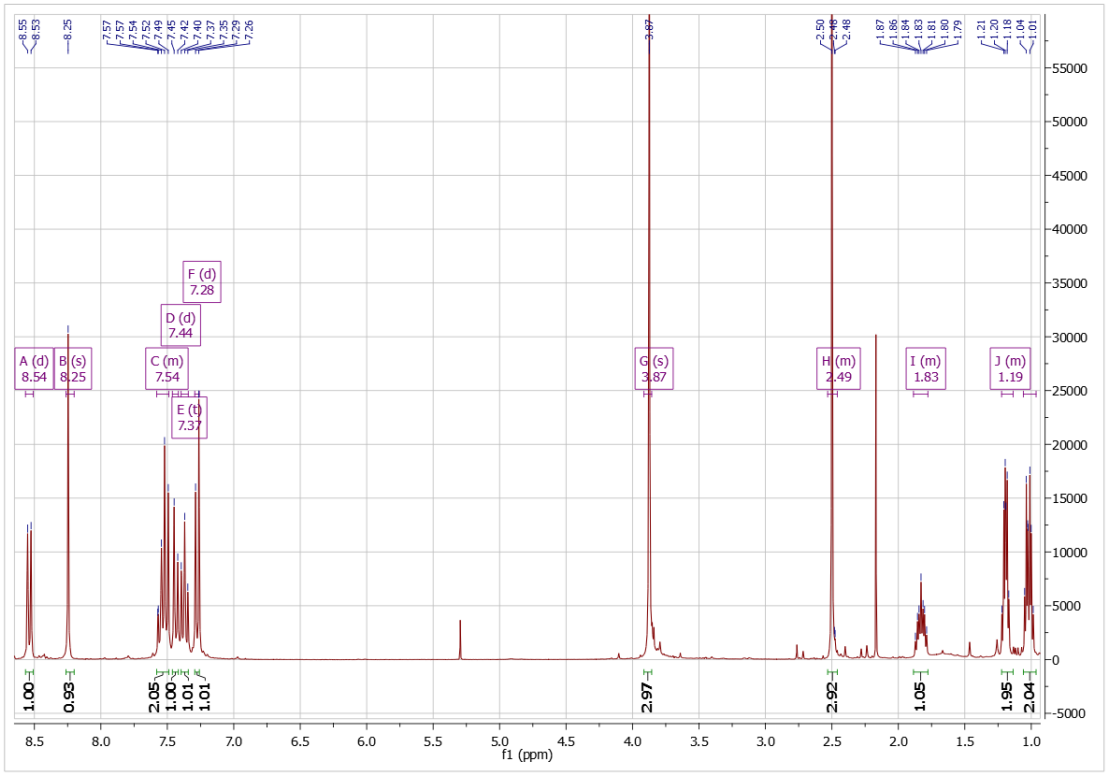
3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, cyclopropanecarbonyl chloride (0.10 mL, 1.08 mmol, M = 104.53 g/mol, d = 1.15 g/mL) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane /Ether to give orange needles (0.25 g, 68.18% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.8 Hz, 1H), 8.25 (s, 1H), 7.58 – 7.49 (m, 2H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 3.87 (s, 3H), 2.53 – 2.46 (m, 3H), 1.89 – 1.78 (m, 1H), 1.22 – 1.14 (m, 2H), 1.06 – 0.96 (m, 2H).

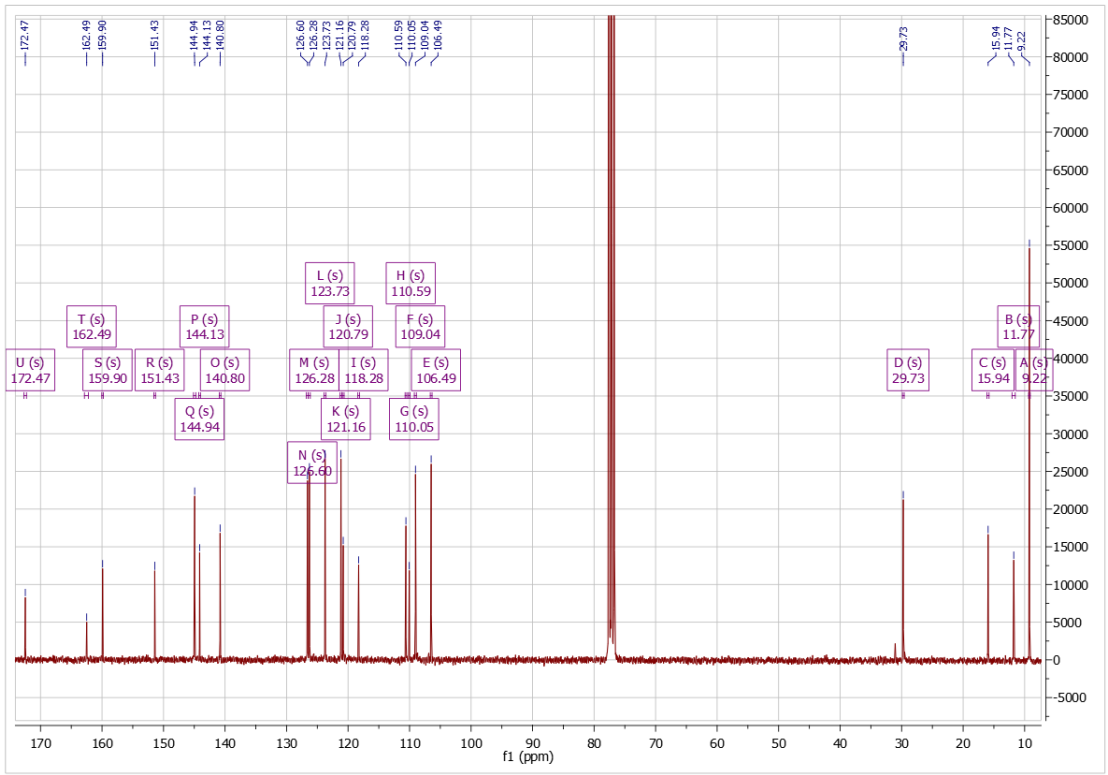
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.47 (s), 162.49 (s), 159.90 (s), 151.43 (s), 144.94 (s), 144.13 (s), 140.80 (s), 126.60 (s), 126.28 (s), 123.73 (s), 121.16 (s), 120.79 (s), 118.28 (s), 110.59 (s), 110.05 (s), 109.04 (s), 106.49 (s), 29.73 (s), 15.94 (s), 11.77 (s), 9.22 (s).

HRMS (ESI MS) m/z: theor: 375.1339 found: 375.1338 ($[M+H]^+$ detected)

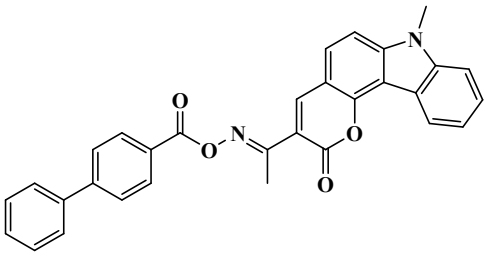
^{1}H NMR spectrum of 3-(1-(((cyclopropanecarbonyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-(((cyclopropanecarbonyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



Synthesis of 3-(1-((([1,1'-biphenyl]-4-carbonyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



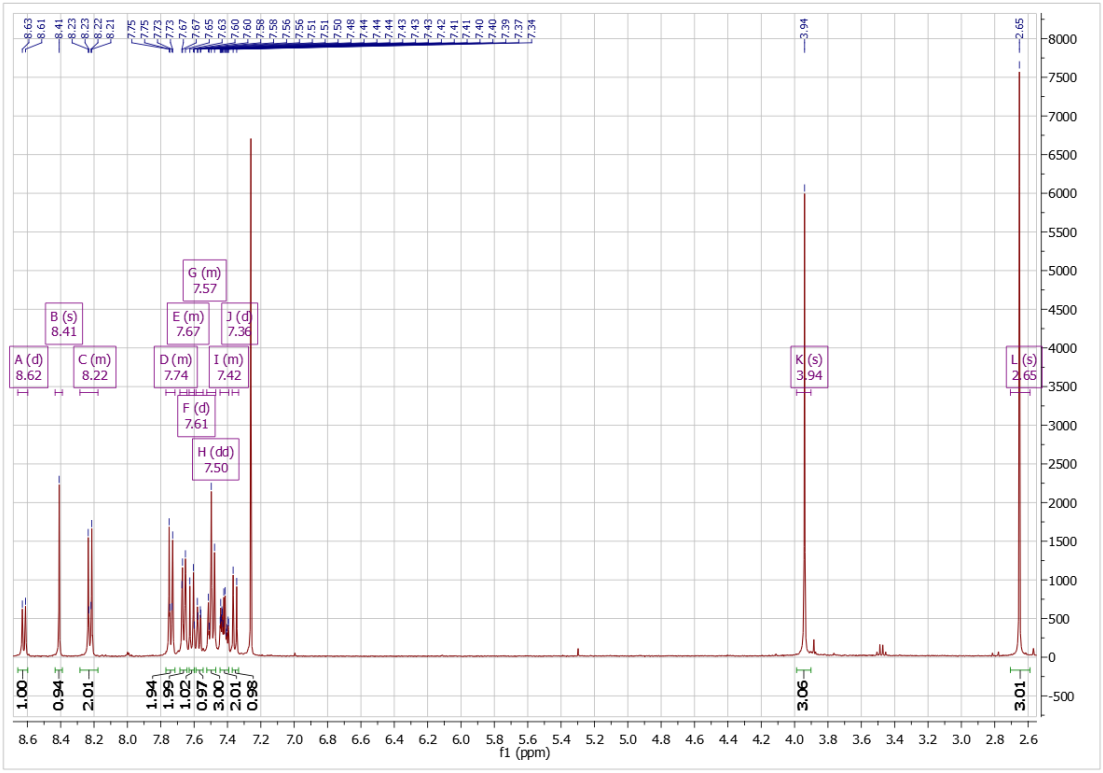
Chemical Formula: $C_{31}H_{22}N_2O_4$
Molecular Weight: 486,5270

3-(1-(Hydroxyimino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one (0.3 g, 0.98 mmol, M = 306.32 g/mol) and triethylamine (0.82 mL, 5.88 mmol, M = 101.19 g/mol, d = 0.726 g/mL) were dissolved in anhydrous dichloromethane stabilized on amylene (50 mL). Then, [1,1'-biphenyl]-4-carbonyl chloride (0.23 g, 1.08 mmol, M = 216.66 g/mol) was added directly. The flask was then stirred at room temperature overnight. The solution was subsequently washed with 6 M aq. HCl and dried over $MgSO_4$. After evaporation of the volatiles, the crude product was recrystallized from dichloromethane /Ether to give orange needles (0.36 g, 75.55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 7.6 Hz, 1H), 8.41 (s, 1H), 8.28 – 8.18 (m, 2H), 7.77 – 7.71 (m, 2H), 7.69 – 7.64 (m, 2H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.50 (dd, *J* = 10.1, 4.8 Hz, 3H), 7.44 – 7.39 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 1H), 3.94 (s, 3H), 2.65 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.81 (s), 163.59 (s), 159.93 (s), 151.51 (s), 146.37 (s), 145.25 (s), 144.21 (s), 140.82 (s), 139.97 (s), 130.38 (s), 129.13 (s), 128.45 (s), 127.72 (s), 127.43 (s), 126.51 (d, *J* = 18.0 Hz), 123.76 (s), 121.20 (s), 120.81 (s), 118.12 (s), 110.63 (s), 110.08 (s), 109.07 (s), 106.57 (s), 29.74 (s), 16.21 (s).

^{1}H NMR spectrum of 3-(1-((([1,1'-biphenyl]-4-carbonyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one



^{13}C NMR spectrum of 3-(1-((([1,1'-biphenyl]-4-carbonyl)oxy)imino)ethyl)-7-methylpyrano[3,2-*c*]carbazol-2(7*H*)-one