

Supplementary Material**Visible light-promoted C-C bond formation from hydroxyaryls in water**Dafne Saporito,^a Sergio A. Rodriguez^b and María T. Baumgartner^{*a}^aINFIQC- Dpto. Química Orgánica, Fac. Ciencias Químicas, UNC, Ciudad Universitaria. Córdoba (5000), Argentina.^bCONICET, Instituto de Ciencias Químicas, FAYA, UNSE, Av. Belgrano Sur 1912, Santiago del Estero (4200), Argentina.^{*}Corresponding author. Email: tere@fcq.unc.edu.ar*Table of contents*

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Materials and Methods

^1H and ^{13}C NMR spectra were recorded with a 400 MHz (^1H : 400.16 MHz and ^{13}C : 100.63 MHz) nuclear magnetic resonance spectrometer, using chloroform, acetone and DMSO deuterated. Chemical shifts of ^1H NMR and ^{13}C NMR were recorded in parts per million (ppm, δ) relative to the residual solvent peak as an internal standard [CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm and $\delta_{\text{C}} = 77.16$ ppm, CD_3COCD_3 : $\delta_{\text{H}} = 2.05$ ppm and $\delta_{\text{C}} = 29.84$ ppm and DMSO-d_6 : $\delta_{\text{H}} = 2.50$ ppm and $\delta_{\text{C}} = 39.52$ ppm]. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet and m=multiplet). Gas chromatographic analyses were performed on a GC with a flame-ionization detector, using HP-5 columns (30m x 0.32mm x 0.25 μm or 10m x 0.53mm x 2.65 μm). The GC/MS analyses were carried out on a GC-MS QP 5050 spectrometer employing a Vf-5 ms 30m x 0.25mm x 0.25 μm column and electronic impact ionization (70 eV). High-resolution mass spectra were recorded by TOF using electron impact ionization (EI) or the electrospray ionization (ESI, APCI) method. Irradiation was conducted in a reactor equipped with two 400-W lamps emitting at a maximum of 350 nm (Philips Model HPT, water-refrigerated) or with UV-LEDs (LED Lustrous color Xnes lamp, $\lambda = 400 \pm 20$ nm, 9.4 V, 1050 mA). Column chromatography was performed on silica gel (70–270 mesh). Potentiometric titration of halide ions was performed in a pH meter using an Ag/Ag^+ electrode. Potassium tert-butoxide, 5-bromouracil, 4-hydroxycoumarin and 9-phenanthrol were commercially available (Sigma-Aldrich, Buenos Aires, Argentina) and used as received.

Substrate synthesis

1-iodo-2-naphthol (2b)^[1,2] was prepared from reaction of 2-naphthol, iodide and H_2O_2 in ethanol.

N-(2-iodophenyl)acetamide (4)^[3]

O-iodoaniline (1.57 g, 7.16 mmol) was dissolved in 10 ml of anhydrous tetrahydrofuran under N_2 atmosphere. The mixture was cooled to 0–5 °C using an ice bath. Acetyl chloride (1.76 gr, 22.42 mmol) was added dropwise over 30 minutes. Then the ice bath was removed and the mixture was allowed to stir overnight at room temperature. A brown - violet precipitate was formed. The solvent was removed. The crude was dissolved with ethyl acetate and washed with solution of 5% sodium bicarbonate (three replicates), then with saturated sodium chloride and finally with bidistilled water. The crystals obtained were distilled at reduced pressure in a K \ddot{u} gelrohr equip. Yield: 73%. Mp: 109–110 °C. ^1H NMR (CDCl_3 , 400MHz): δ 8.21 (1H, d, $J = 8.4$ Hz), 7.78 (1H, d, $J = 7.8$ Hz), 7.35 (1H, t, $J = 8.5, 7.1$ Hz), 6.85 (1H, t, $J = 7.8, 7.1$ Hz), 2.24 (3H, s). MS (m/e, %): 63 (14), 65 (30), 91 (16), 92 (47), 134 (100), 219 (51), 261 (10).

2-iodo-N-methylbenzamide (10a)^[4,5]

2-iodobenzoic acid was converted to 2-iodobenzyl chloride by heating with excess PCl_5 at 80 °C for 2 h. The 2-iodobenzyl chloride (3.15 g, 11.15 mmol) was dissolved in dry benzene (30 mL) under N_2 . The resulting solution was cooled in an ice bath and then was added a solution of methylamine (2.02 equiv.) in benzene (10 mL) with slight agitation. The precipitate formed was filtered and washed with dilute HCl (3x50 mL), saturated sodium bicarbonate solution (3x50 mL), distilled water (3x50 mL) and finally with ethyl ether (2x25 mL). The crystalline powder obtained was purified by recrystallization with ethanol.

Mp: 145–146 °C. ^1H NMR (CDCl_3 , 400MHz): δ 7.80 (1H, d), 7.19 (3H, m), 6.10 (1H, s), 3.00 (3H, d).

2-iodobenzamide (10b)^[4,6]

It was reacted o-iodobenzoic acid (2.5127 g, 0.01 mol) with thionyl chloride (3.65 mL, 0.05 mol) at reflux for one hour, controlling the temperature between 90-95 °C in an oil bath. After the reaction, the reflux is removed and the excess of Cl₂SO is evaporated placing a hose bubbling on a beaker with water, with flow of N₂. The product is left at room temperature and then was add dropwise 2 mL of NH₄OH. The solid obtained is filtered and washed with bidistilled water to remove residual base and take to dryness. The product obtained is purified by recrystallization with ethanol.

Yield: 22%. Mp: 184-186 °C. ¹H NMR (CDCl₃, 400MHz): δ 7.95 (1H, m), 7.53 (1H, m), 7.44(1H, m), 7.17 (1H, m). MS (m/e, %): 247 (100), 231 (82), 203 (31), 120 (12), 102 (11), 77 (12), 76 (37), 74 (10), 65 (11), 51 (11), 50 (20).

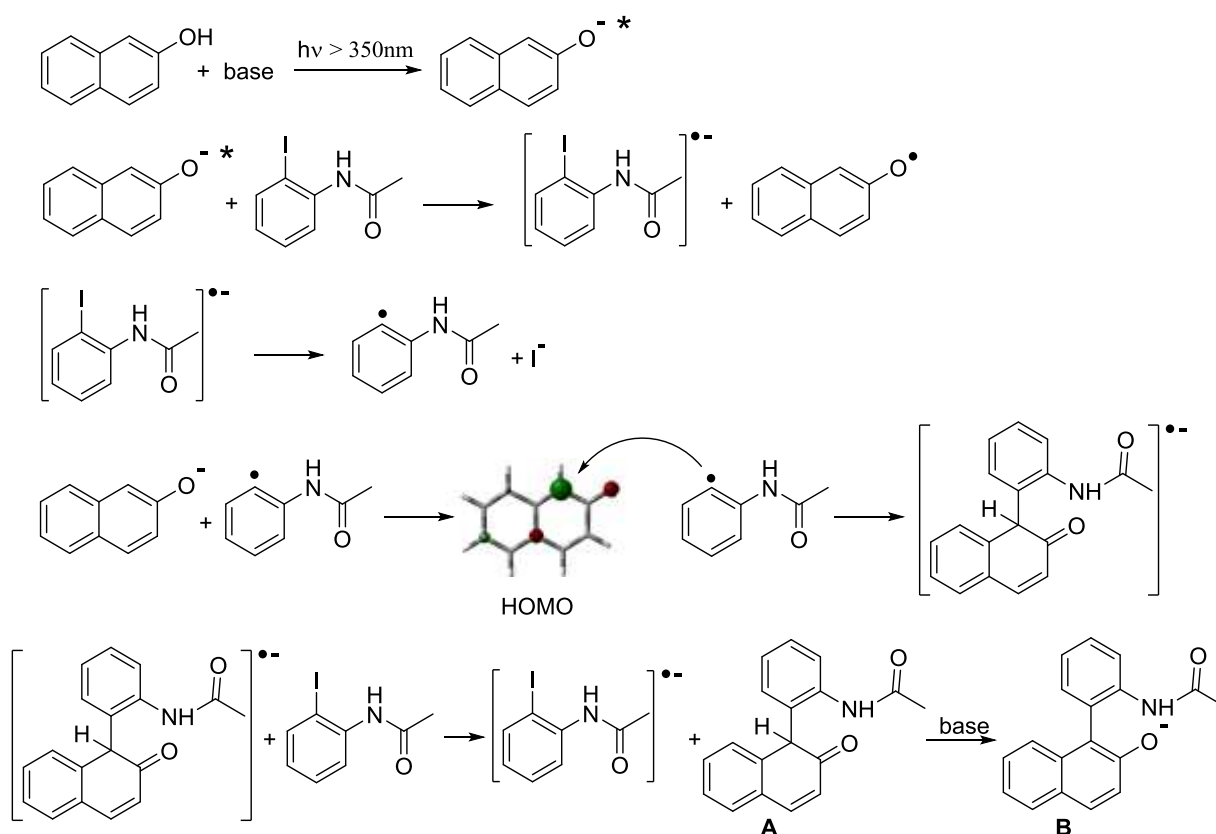
Table S1. Photoinduced reactions of the anion of 1 and 4 in water ^A

Entry	Ratio 1/4	4/mM	5 %
1	5:1	20	59
2	3:1	22	55
3	2:1	22	41
4	3:1	30	43
5	3:1	61	31
6 ^B	3:1	22	< 5

^A KO^tBu, N₂, 3 h, isolated yield

^B Reaction was carried out in the dark

Reaction mechanism of 1 and 4



In the initiation step, the 2-naphthoxide anion was generated by the acid-base reaction from 2-naphthol. The photophysical properties of the 2-naphthoxide anion are known (Soumillion, J. Ph.; Vandereecken, P.; Van Der Auweraer, M.; De Schryver, F. C.; Schanck, A. *J. Am. Chem. Soc.* **1989**, *111*, 2217- 2225. Legros, B.; Vandereecken, P.; Soumillion, J. Ph. *J. Phys. Chem.* **1991**, *95*, 4752-4761) and their photoexcitation occurs under the reaction conditions. The fluorescent excited state of the 2-naphthoxide ion is quenched by aromatic halides as electron acceptors according to an electron-transfer mechanism (Arguello, J.E.; Peñeñory, A.B. *J. Org. Chem.* **2003**, *68*, 2362-2368).

In the propagation step, 2-naphthoxide ions react with the aromatic radical and the substitution product is obtained exclusively at the C₁ position. Different approaches may explain the regiochemistry of coupling reactions, considering that it is generally governed by thermodynamic control and the predominant reaction product is generated by the most stable radical anion. Or according to the frontier orbital (FO) theory,^[7] the preferred site of coupling is that corresponding to bond formation at the atom bearing the largest orbital coefficient in the highest occupied molecular orbital (HOMO) of the anion (Pierini, A. B.; Baumgartner, M. T.; Rossi, R. A. *J. Org. Chem.* **1991**, *56*, 580-586).

The radical anions of substitution product transfer their odd electron to the substrate to continue the propagation cycle to give the aryl radical and product **A**. Under the basic reaction conditions, the latter yield the more stable enol tautomer **B**.

Figure S1. UV-VIS spectra of: 2-naphthol (**1**), 4-hydroxycoumarin (**8**), phenantrol (**12**) at pH 13.

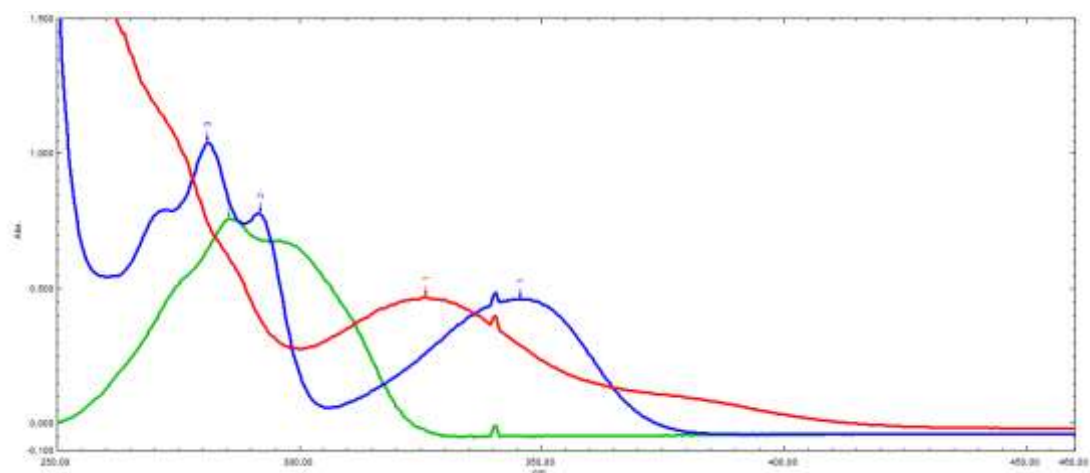


Figure S2. S1 and the emission spectrum of the Philips lamp.

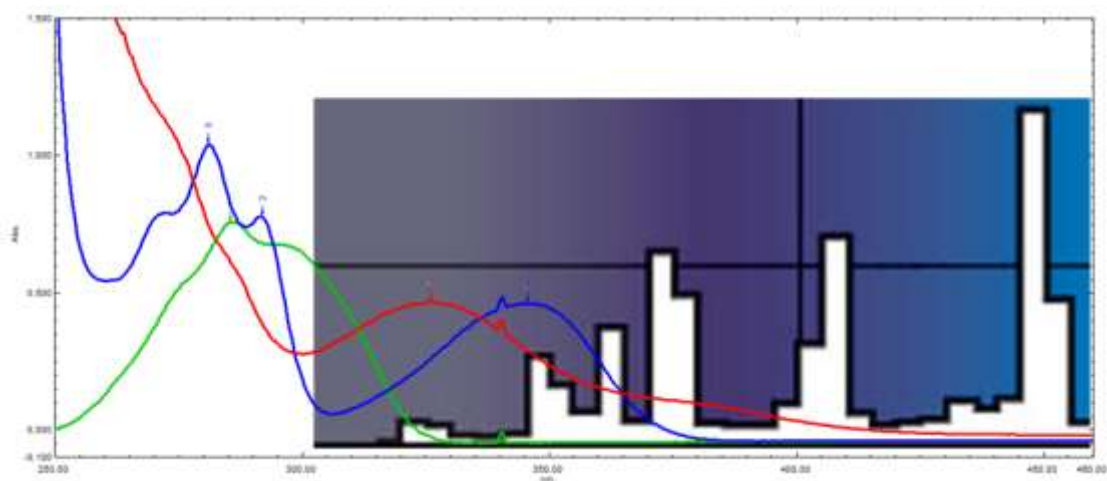


Figure S3: UV-VIS spectra of: 2-naphthol (1) at pH 8 and pH 13

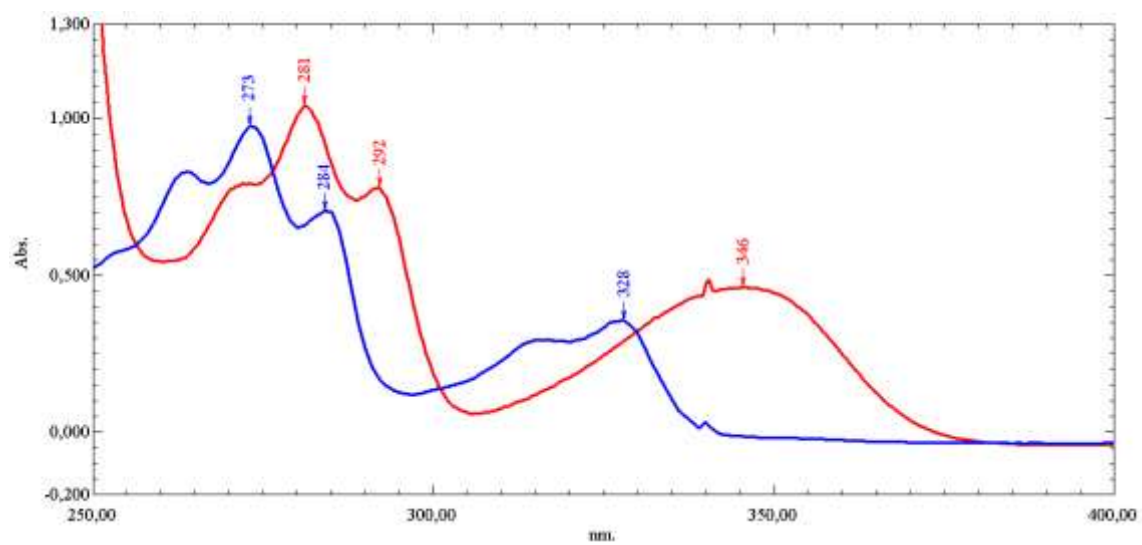
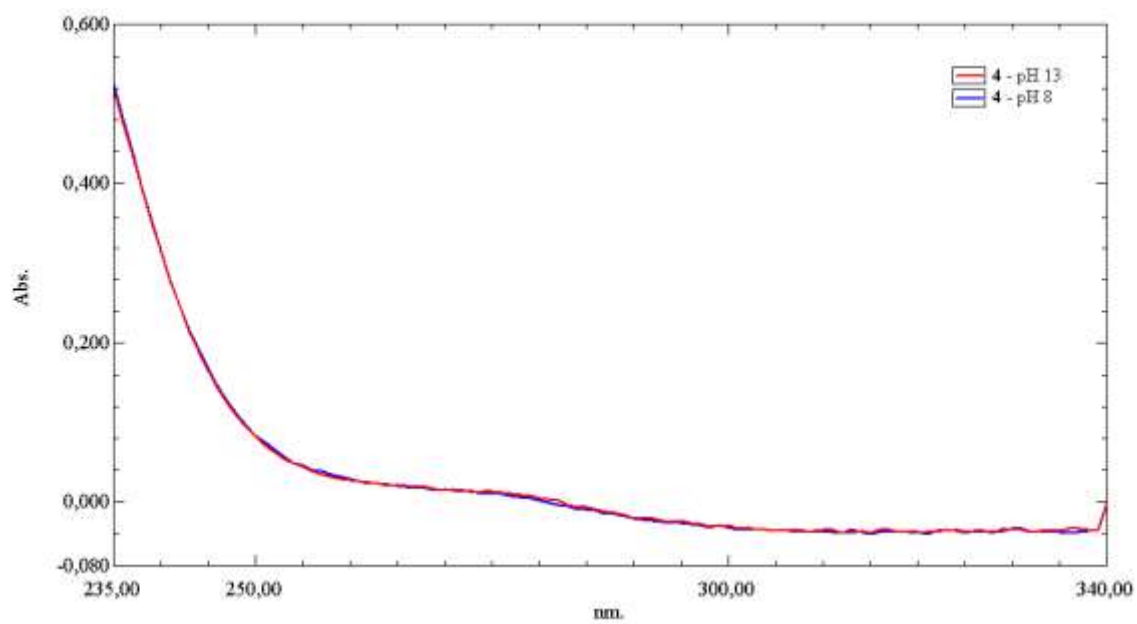


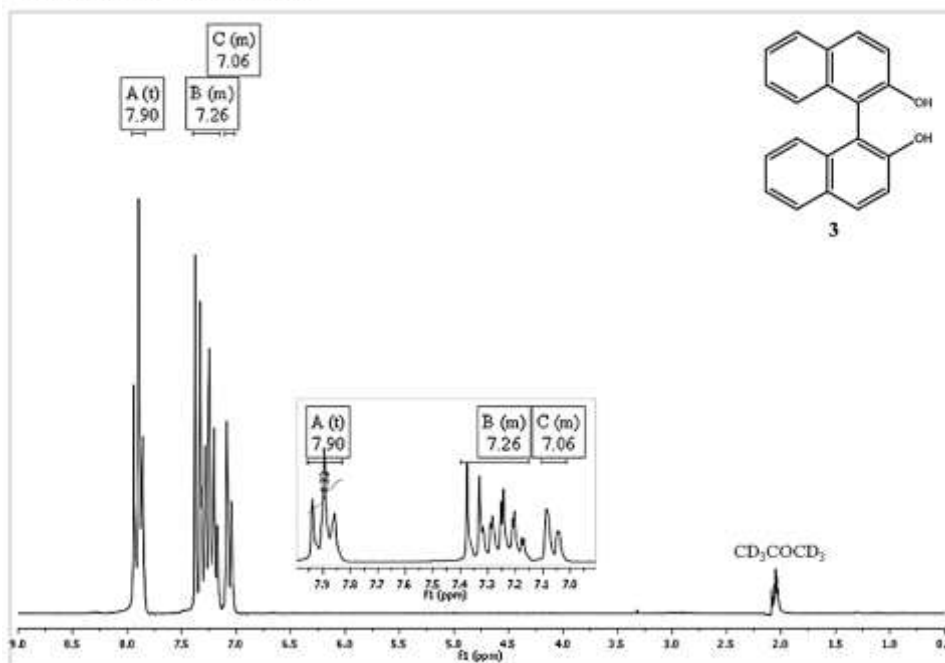
Figure S4: UV-VIS spectra of: 4 pH 8 and pH 13



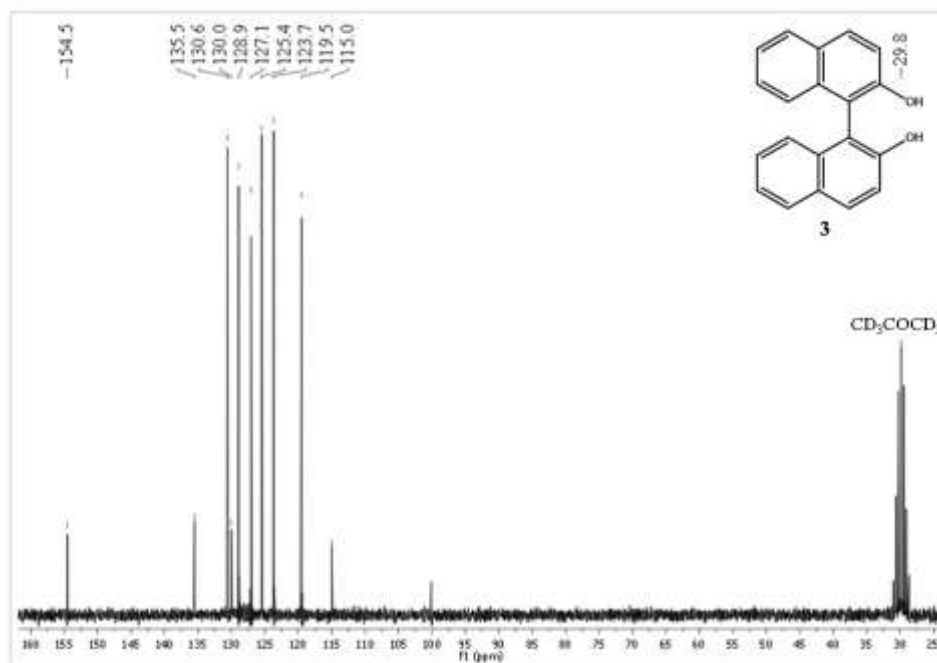
Compounds characterization

BINOL (3).

^1H NMR (400 MHz, CD_3COCD_3)

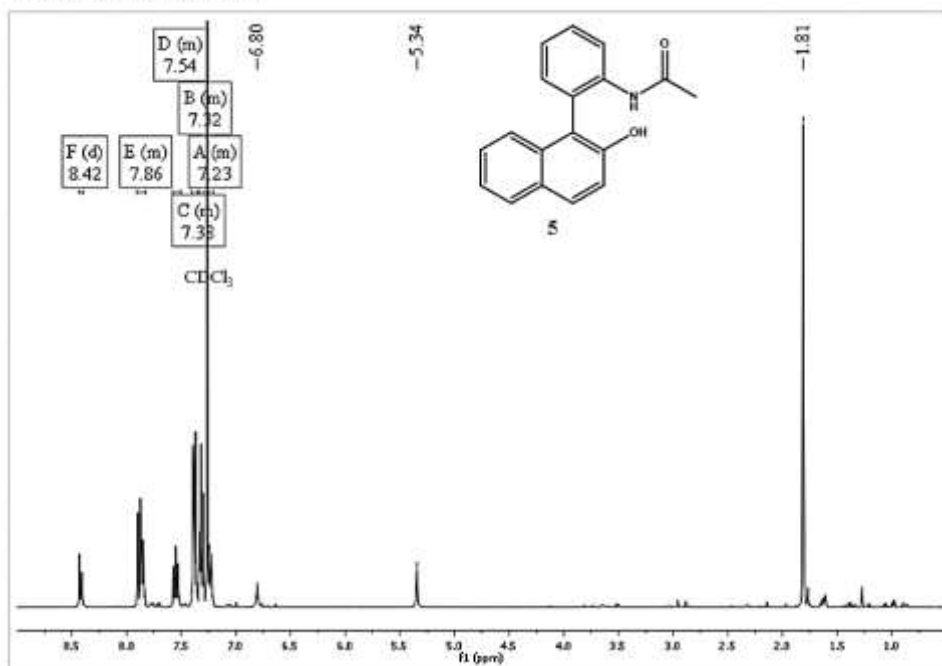


^{13}C NMR (101 MHz, CD_3COCD_3)

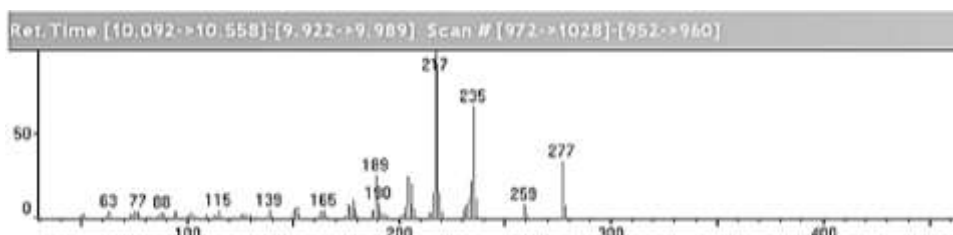
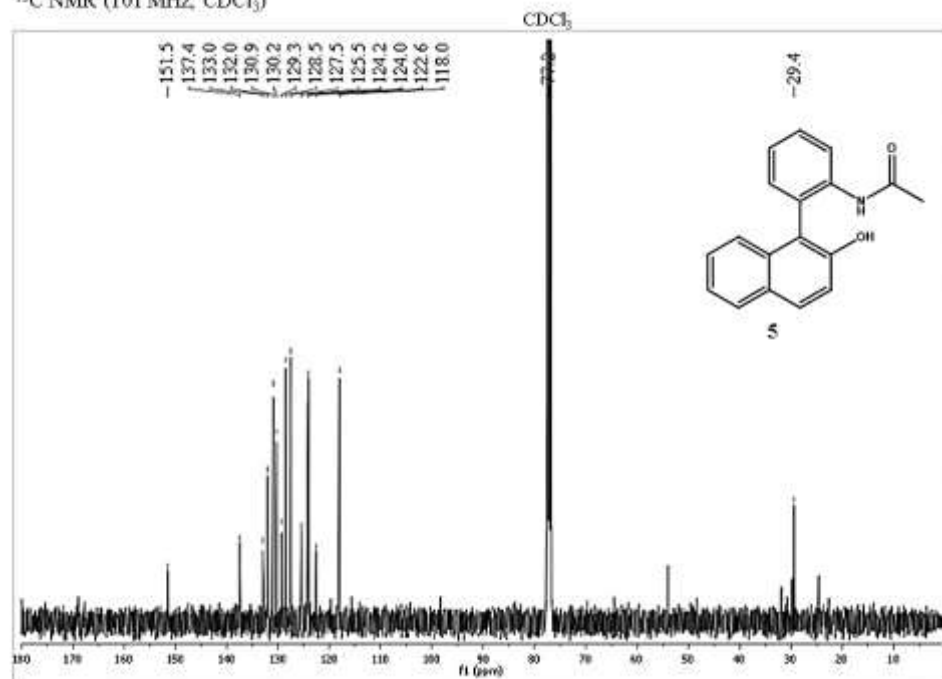


N-(2-(2-hydroxynaphthalen-1-yl)phenyl)acetamide (5).

¹H NMR (400 MHz, CDCl₃)

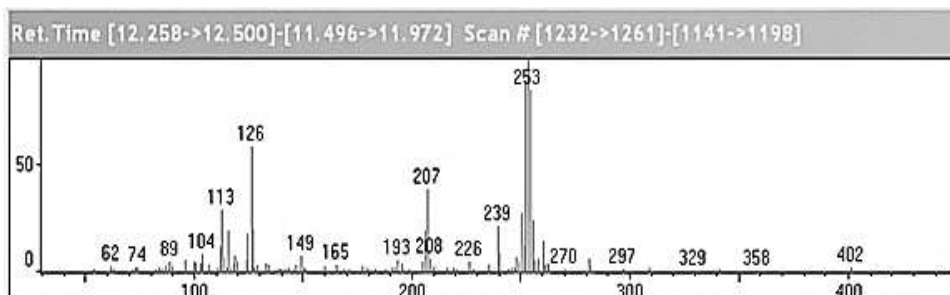
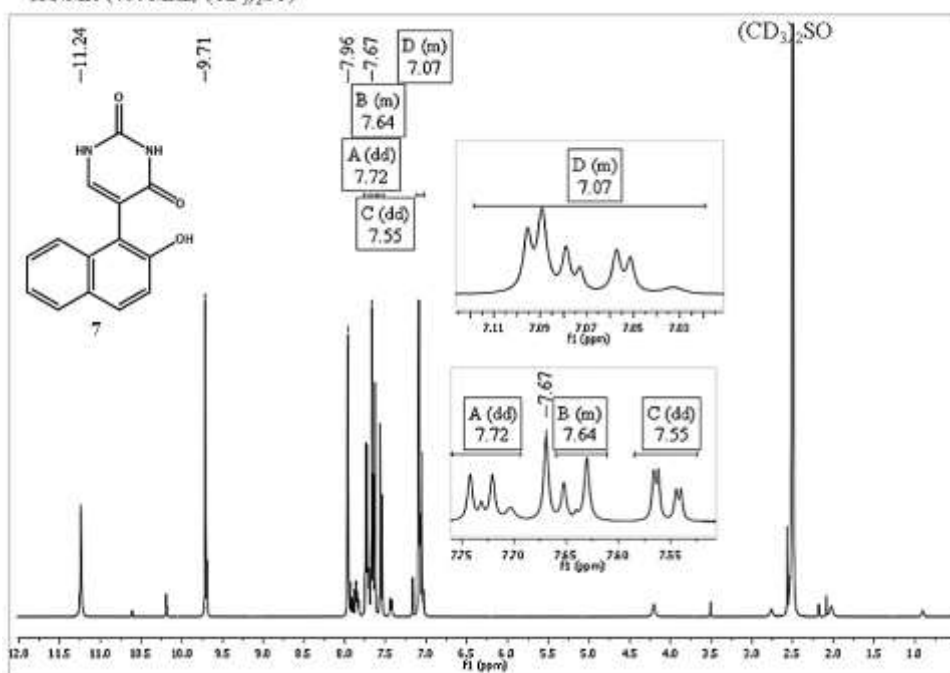


¹³C NMR (101 MHz, CDCl₃)

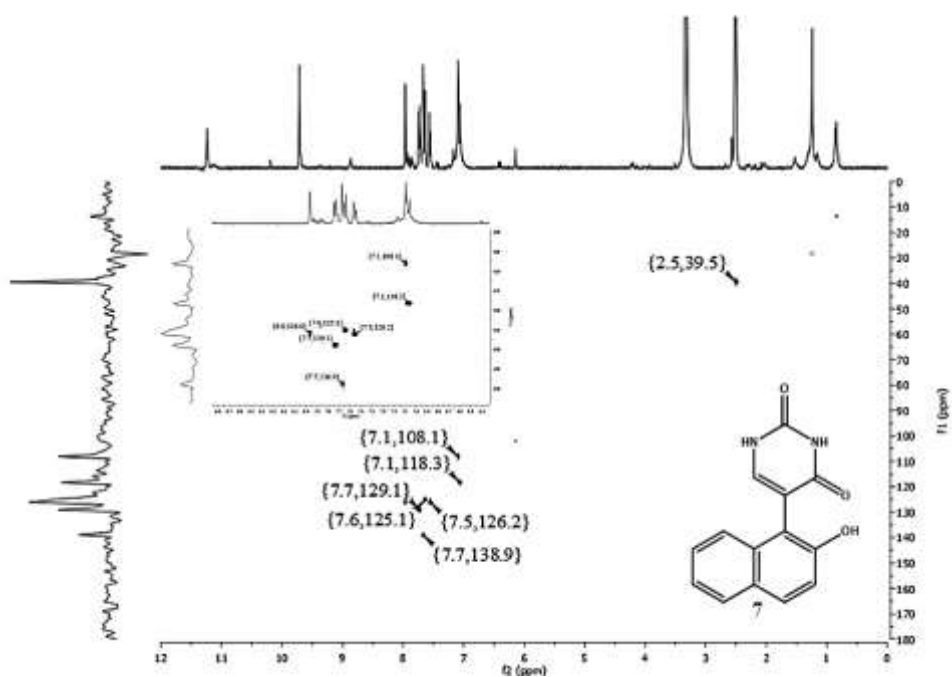


1-(5-uracil)-2-naphthol (7).

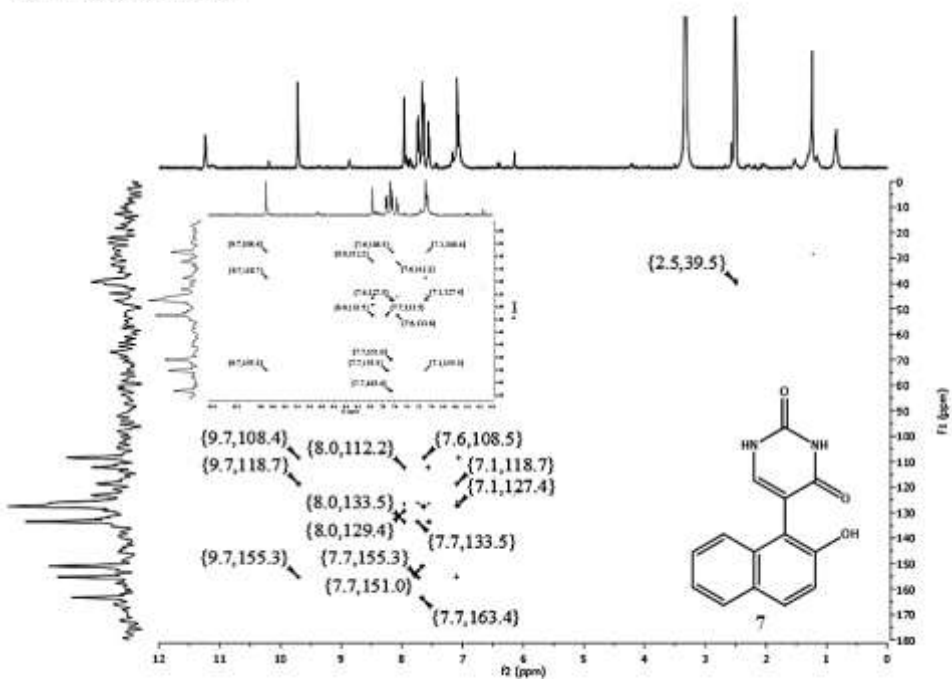
¹H NMR (400 MHz, (CD₃)₂SO)



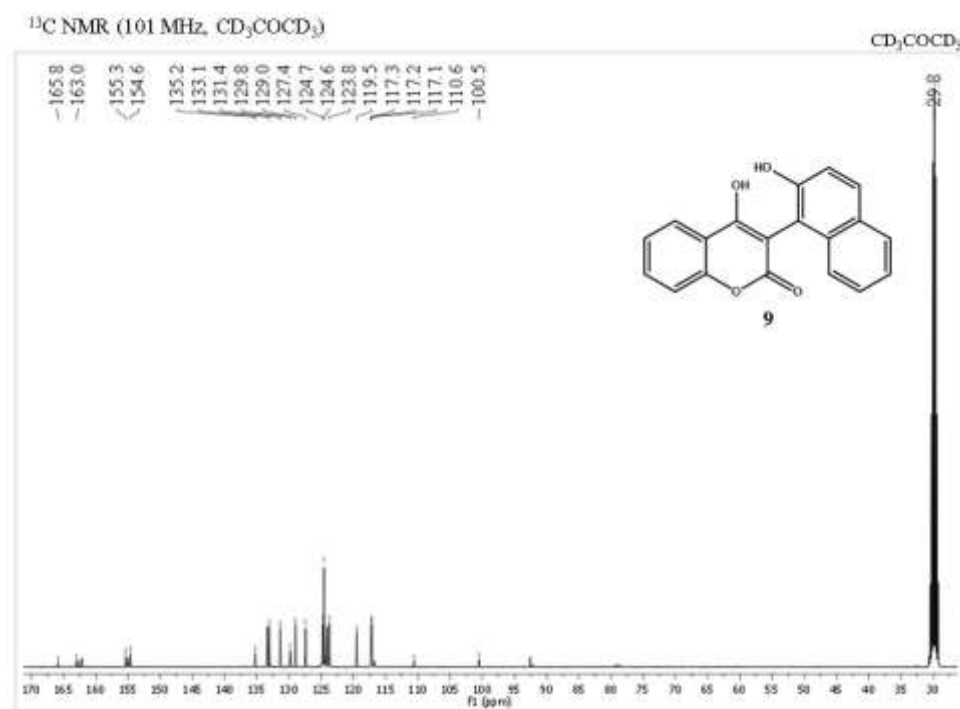
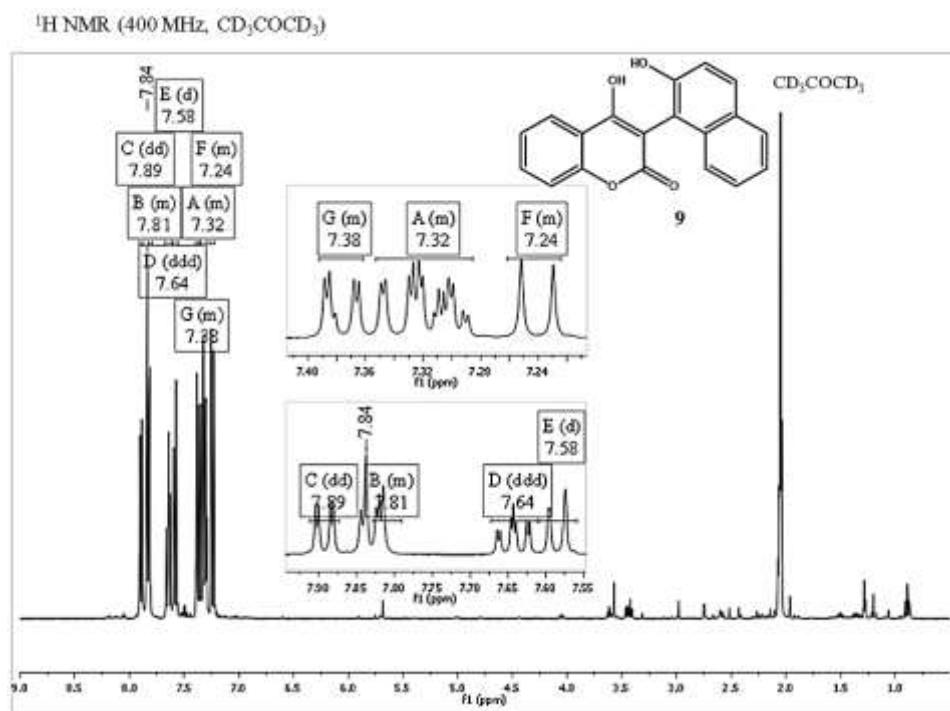
HSQC-NMR ((CD₃)₂SO)



HMBC-NMR ((CD₃)₂SO)



4-hydroxy-3-(2-hydroxynaphthalen-1-yl)-2H-chromen-2-one (**9**).

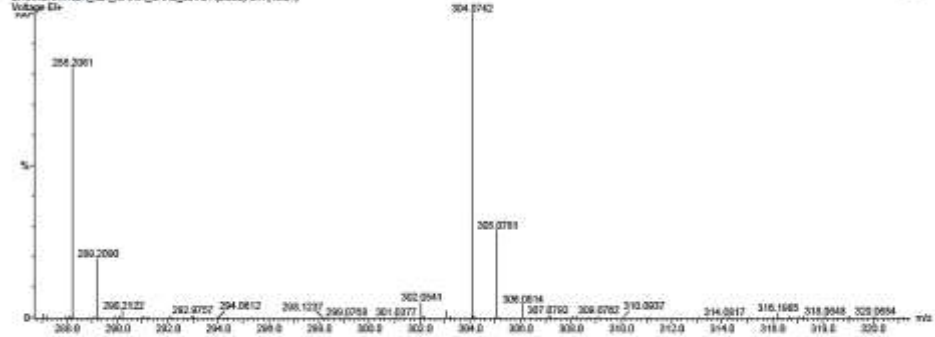


Elemental Composition Report

Multiple Mass Analysis: 16 mass(es) processed - displaying only valid results
 Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
 Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
 45 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
 Elements Used:
 12C: 17-19 13C: 0-2 H: 12-12 O: 4-4
 BAUMGARTNER_EA_MARIA_SAFI_304
 BAUMGARTNER_EA_MARIA_SAFI_304 24 (2.082) Cm (19.24)

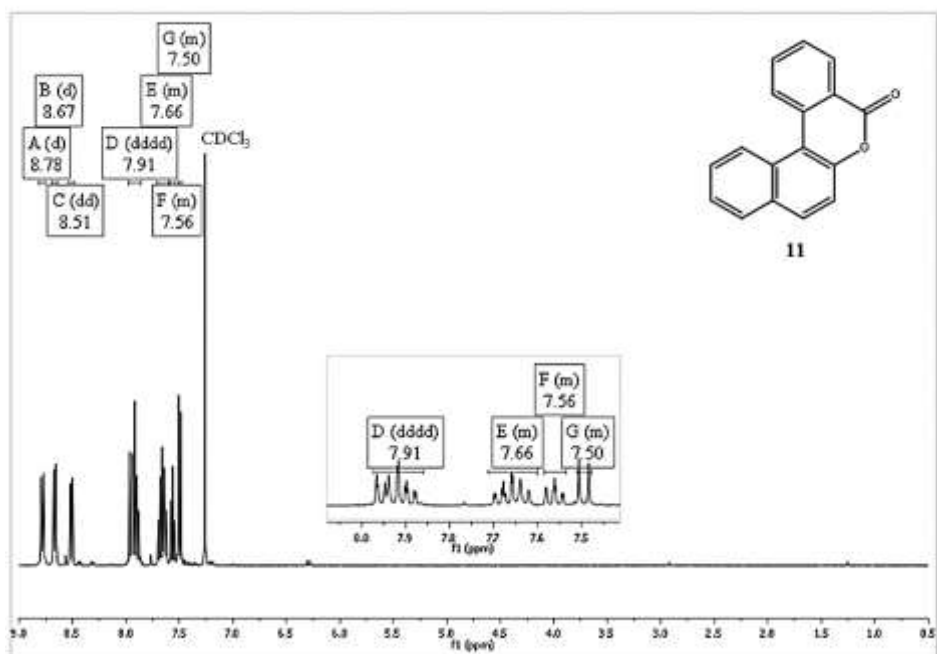
UNIDADE DE MASSA E PROTEOMICA_USC



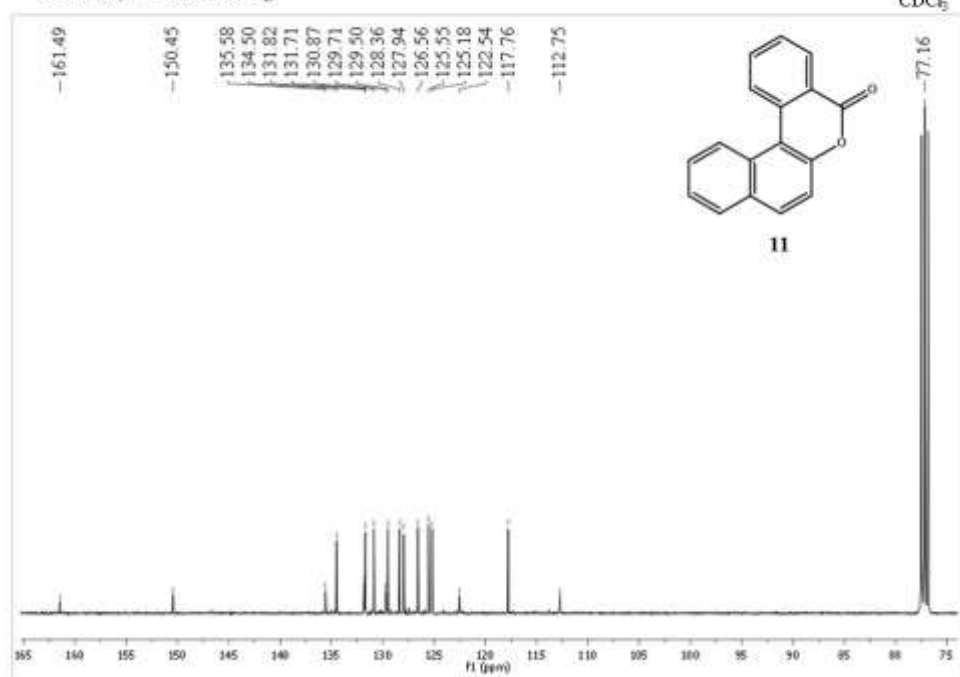
Mass	Rel.	Calc.	Mass	mDa	DBE	1-PIE	Formula
304.0742	100.00	304.07396	0.4	2.0	14.8	88.8	C12C19 H12 O6
310.0782	28.38	310.07699	1.2	0.9	14.8	0.8	C12C19 H30 O6
306.0814	9.01	306.08053	1.1	0.6	14.8	9.1	C12C17 H20C2 H12 O6

5H-dibenzo[c,f]chromen-5-one (11).

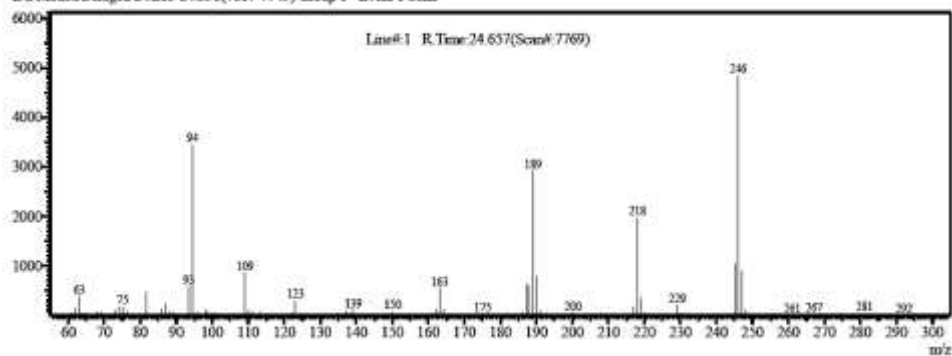
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

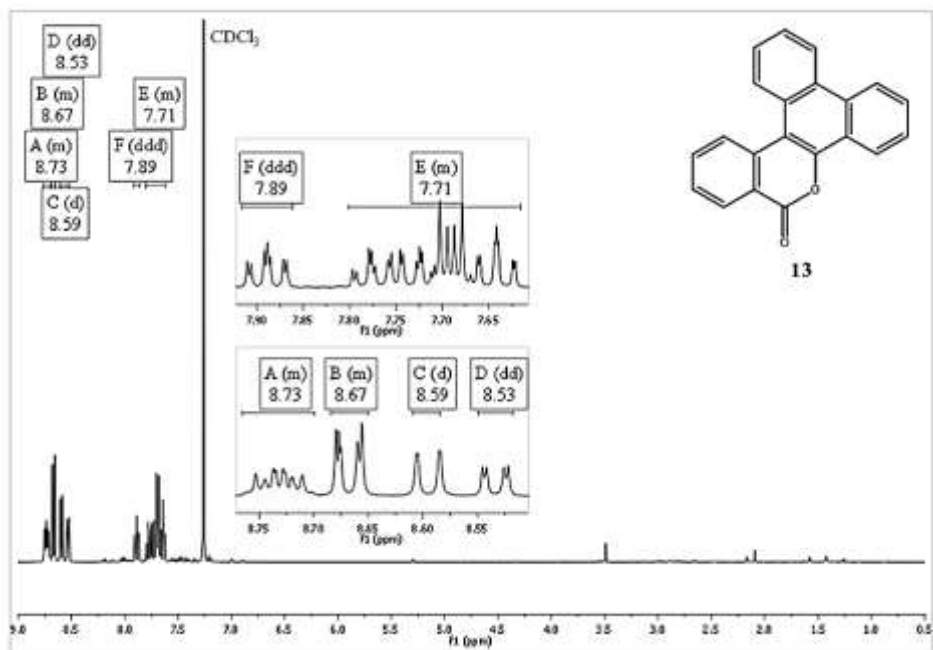


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BG Mode:Averaged 24.213-24.598(7617-7749) Group 1 - Event 1 Scan



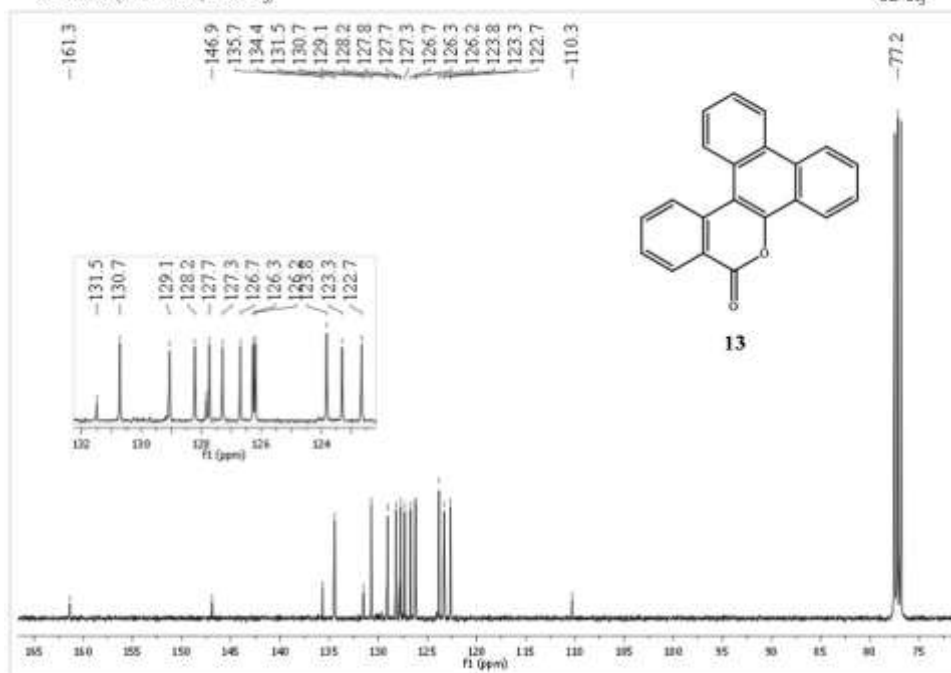
6H-tribenzo[c,f,h]chromen-6-one (**13**).

¹H NMR (400 MHz, CDCl₃)

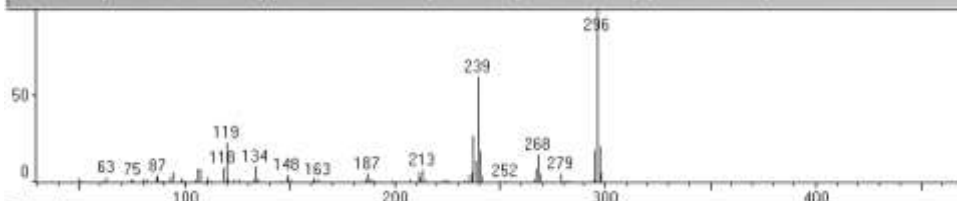


¹³C NMR (101 MHz, CDCl₃)

CDCl₃



Ret. Time [40.150->40.292]:[39.511->39.938] Scan # [4339->4356]:[4263->4314]



Reactors

400-W lamps



UV-LEDs



References

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