Supporting Information for:

Visible-Light Induced Enhancement in Multi-catalytic Activity of Sulfated Carbon dots for Aerobic Carbon-Carbon Bond Formation**

Daisy Sarma, Biju Majumdar, and Tridib K. Sarma*

Discipline of Chemistry, School of Basic Sciences
Indian Institute of Technology Indore
Simrol, Khandwa Road, Indore 453552 (India)

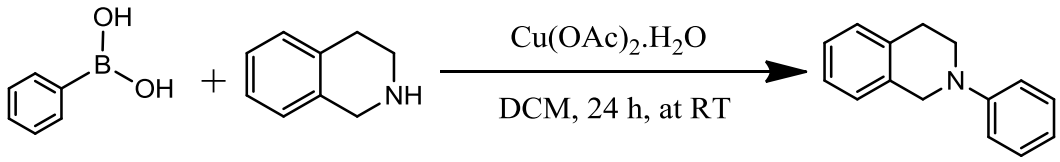
E-mail: tridib@iiti.ac.in

Instrumentation: The powder XRD measurements were carried out by using a Bruker D8 Advance X-ray diffractometer with CuKα source (wavelength= 0.154 nm). TEM images were obtained by using a JEOL JEM- 2100 microscope operated at 200 kV FTIR spectra were recorded with KBr pellets by using a Bruker Tensor 27 instrument. UV-visible measurements were performed using a Varian Cary 100 Bio spectrophotometer. Emission spectra were taken in a fluoromax-4p fluorimeter from HoribaYovin (model: FM-100). The samples were excited at different excitation wavelength ranging from 310 to 520 nm. X-ray photoelectron spectra (XPS) were recorded using an ESCA instrument, VSW of UK make. EPR measurements were carried out using a JEOL spectrometer (Model: JES-FA200). ^{1}H and ^{13}C NMR spectra were recorded with Bruker Advance (III) 400 MHz or 100 MHz spectrometers, respectively. Data for ^{1}H NMR spectra are reported as chemical shift (δ ppm), multiplicity (s=singlet, d = doublet, t = triplet, m = multiplet), coupling constant (*J* Hz) and integration and assignment data for ^{13}C NMR spectra are reported as a chemical shift. High resolutions mass spectral analyses (HRMS) were carried out using ESI-TOF-MS.

Materials: Glucose, oleic acid, oleum, catalase, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and all other chemicals were purchased from Sigma–Aldrich, India or Merck, India and used without further purification. We used Millipore water (ultrapure level) throughout the experiments.

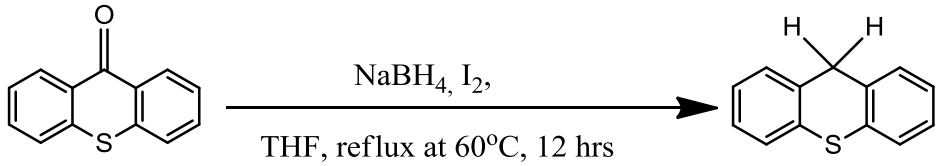
Experimental Section

Synthesis of N-phenyl-tetrahydroisoquiniline:



Phenyl boronic acid (0.368g, 2 mmol) and $Cu(OAc)_2.H_2O$ (20 mg, 0.1 mmol) in DCM (10 mL) were taken in a flask and the mixture was stirred for 5 minutes at room temperature. To this stirring suspension was added 1,2,3,4 tetrahyroisoquinoline (0.072 g, 99.□□□L, 1 mmol) and stirred under O_2 atmosphere for 24 h. The mixture was extracted with water and DCM. The product was purified using silica gel column chromatography (using 2% ethylacetate/ hexane).

Synthesis of Thioxanthene:



In the typical synthesis of thioxanthene, 5 mmol of thioxanthenone was dissolved in 40 ml of dry THF and added into it 1.2 equivalent of $NaBH_4$ and 6 mmol of I_2 at 0 °C. After bringing to room temperature, the reaction mixture was refluxed for 12 h at 60 °C.The reaction mixture was quenched with brine and extracted with ethyl acetate. The organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude residue was purified using column chromatography on silica gel (eluting with 2% ethylacetate/ hexane) to provide thioxanthene with 92% yield.

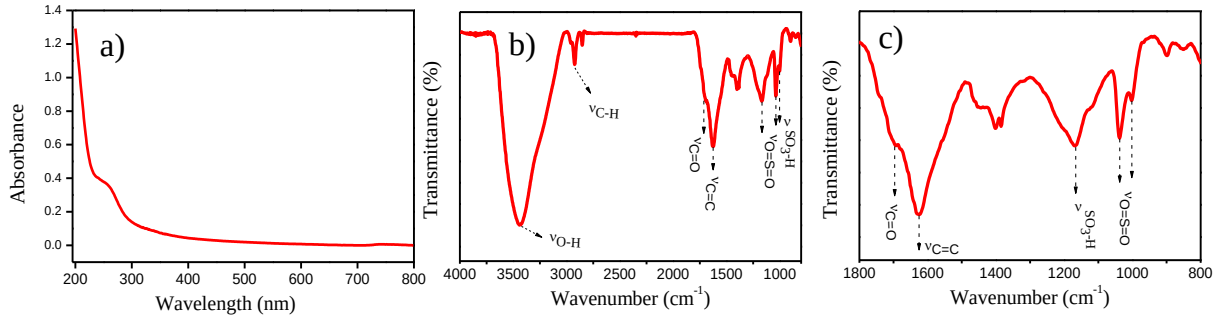


Figure S1: Characterization of s-CD

(a) UV-visible spectra of s-CDs in water; the band at 278 nm signifies π -π* transition.

(b) Full scan FTIR spectrum recorded using KBr which shows the presence of –OH, C=O, C=C, -SO_3H functionalities on s-CD surface.

(c) Magnified FTIR spectrum of s-CDs, shows peaks at 1703 cm^{-1} (C=O), 1627 cm^{-1} (C=C). Peaks at 1038 cm^{-1} and 1002 cm^{-1} are attributed to the O=S=O stretching vibrations in -SO_3H groups and peak at 1166 cm^{-1} for -SO_3H stretching.

Table S1: Elemental analysis of s-CDs

Element	C	H	O	S	Adsorbed H_2O
Wt % in s-CD	50.2	4.64	33.6	2.3	9.26
Atom ratio	4.2	4.64	2.1	0.0718	0.514

Table S2: Performance of various catalysts for the model coupling reaction[a]

Entry	Catalyst	Time (h)	3ab [b]Yield (%)	3a [b]Yield (%)
1	[c]CH_3COOH (hν)/(Δ)	12	12/7	Trace
2	[c]H_2SO_4(conc) (hν)/(Δ)	12	68/62	Trace
3	[c]Benzoic acid (hν)/(Δ)	12	16/14	Trace
4	[c]PTSA (hν)/(Δ)	12	64/69	Trace
5	[d]CD (hν)	3	20	26
6	[c]PCA (hν)	3	15	23
7	[d]s-CD (hν)	3	91	Trace
8	[d]s-CD (Δ)	10	36	20
9	[d]GO (Δ)	10	39	32
10	[d]s- GO (hν)/(Δ)	10	38/42	22/24
11	[e]s- GO (hν)/(Δ)	10	43/48	29/26

[a]Unless otherwise specified, all the reactions were carried out with 2-methoxy xanthene (0.5 mmol) and Cyclohexanone (3 mmol) as the model substrates; using 34 W blue LED lamp (hν = 425 nm) at 25 °C under O_2 environment; Δ= Reaction performed without visible-light illumination at 70 °C; [b]Isolated yield; [c]catalyst (7 mol%), [d]catalyst (5.0 mg); [e]catalyst (30 mg).

Table S3: Diasteriomeric coupling product yield

Product	Diasteriometric Ratio
3hc	2.9:1
3ia	0.92:1
3ib	1.3:1
3ic	1:1
3jb	1:1
6b	1:0.92

Leaching experiment:

The model coupling reaction of xanthene and cyclohexanone was carried out under visible light illumination under optimal reaction conditions. The reaction was stopped after 90 min (approx. 50% conversion) and the s-CD catalyst were removed from the reaction mixture by centrifugation. The reaction was further continued with the supernatant for 10 h under visible light irradiation.

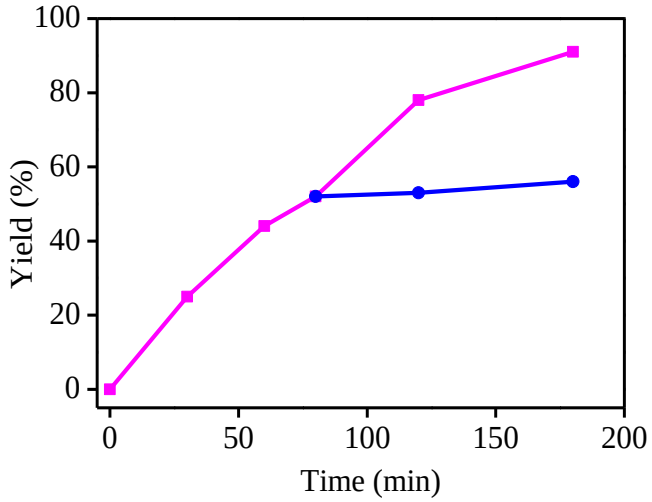


Figure S2: Reaction profile for the model coupling reaction under visible light irradiation (red) and after the s-CDs were removed by centrifugation from the reaction mixture (blue).

Recyclability studies of s-CDs:

To study the recyclability of s-CDs, the model photocatalytic reaction was performed in cycles of reactions under standard photocatalytic reaction conditions. After the completion of the 1st cycle of the reaction, the organic products were extracted using ethyl acetate, while the s-CDs were separated out by centrifugation. The 2nd cycle of the photocatalytic reaction was carried out using the recovered s-CDs as catalyst. The same s-CDs could be reused for at least for four runs with excellent yields. The s-CDs showed efficient recyclability as a photocatalyst and 76% of the desired coupling product could be obtained even after the fourth cycle.

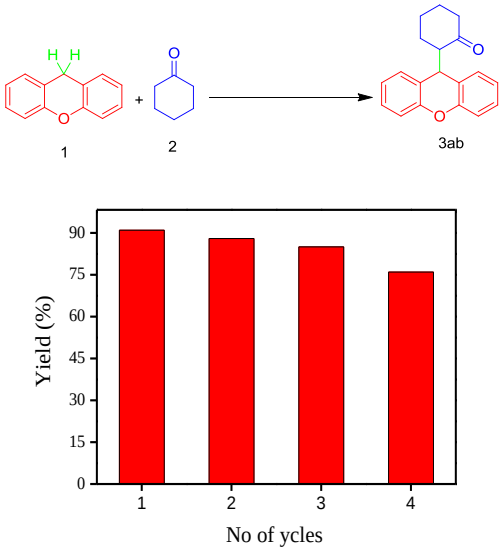


Figure S3: Recyclability test for monitoring the efficiency of s-CDs as a photocatalyst for the coupling reaction in a cycle of reactions.

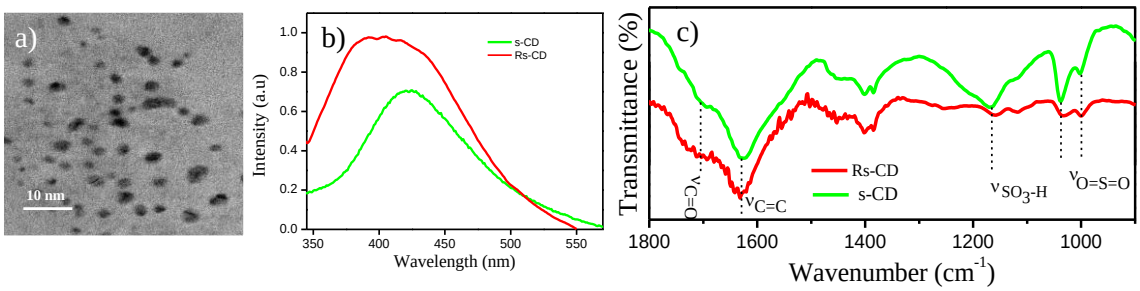


Figure S4: Characterization of recovered s-CD.

(a) The recovered s-CDs after the fourth cycle were analysed to determine the relationship between the catalytic reactivity and surface functionalities. TEM study revealed that there is no pronounced morphological change.

(b) Normalized fluorescence emission spectra of the pristine of recovered s-CDs. From the emission spectra of the recovered s-CDs, a minor blue shift in the emission peak as well as an enhancement in the fluorescence intensity was observed as compared to the pristine ones.

(c) FTIR spectra of s-CDs and recovered s-CDs after fourth cycle of reactions where the band at 1038 cm^{-1} associated with O=S=O and the band at 1166 cm^{-1} corresponding to -SO_3H groups are reduced significantly.

Table S4: Elemental analysis of Recycled s-CDs

Catalyst	Carbon	Hydrogen	Oxygen	Sulphur	Adsorbed H_2O
Wt % in Recycled s-CD	52.3	3.7	32.6	2.12	9.28
Atom ratio	4.36	3.7	2.04	0.066	0.515

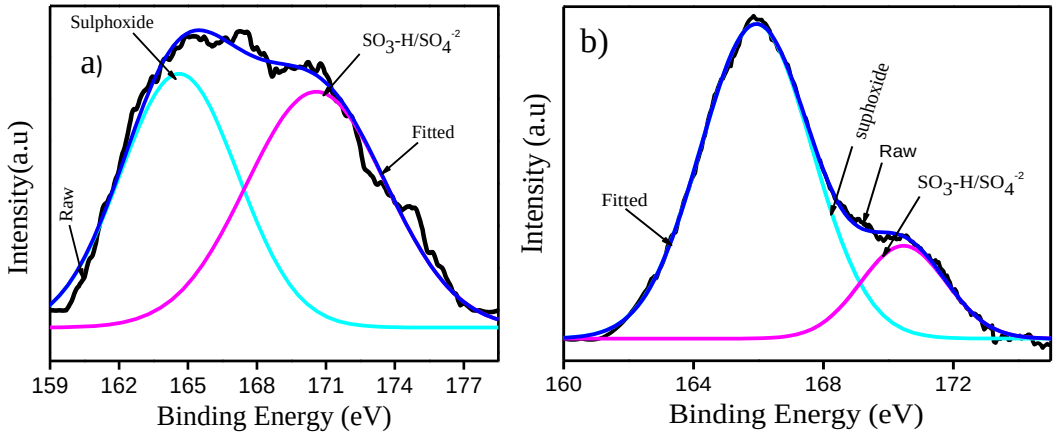


Figure S5: Comparative XPS analysis of s-CD and recovered s-CD

(a) The high resolution XPS spectra of S2p region revealed the peaks at 164.7 eV for sulfoxide and 169.7 eV for sulphonic acid and sulphate.

(b) The S2p core level XPS spectra show that the amount of SO_3-H functionality (169.7 eV) is reduced in the recovered s-CDs as compared to the pristine ones.

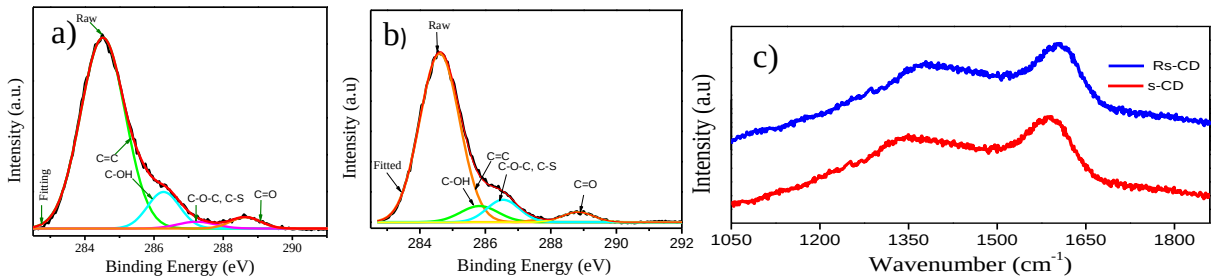


Figure S6: Comparative studies of s-CD and recovered s-CD.

(a) The C 1s region of s-CD is deconvoluted into C=C (284.5 eV), C-C (285.7), C-OH (286.3 eV), -C-O-C, C-S (287.2 eV), and -COOH (288.6 eV) bonds suggesting the presence of hydroxyl, carbonyl, and carboxylic acid groups on s-CD surface.

(b) C 1s core XPS spectra of the recovered s-CDs revealed that there was no significant change in the graphitic content as well as the oxygen functionalities such as in carboxylic group.

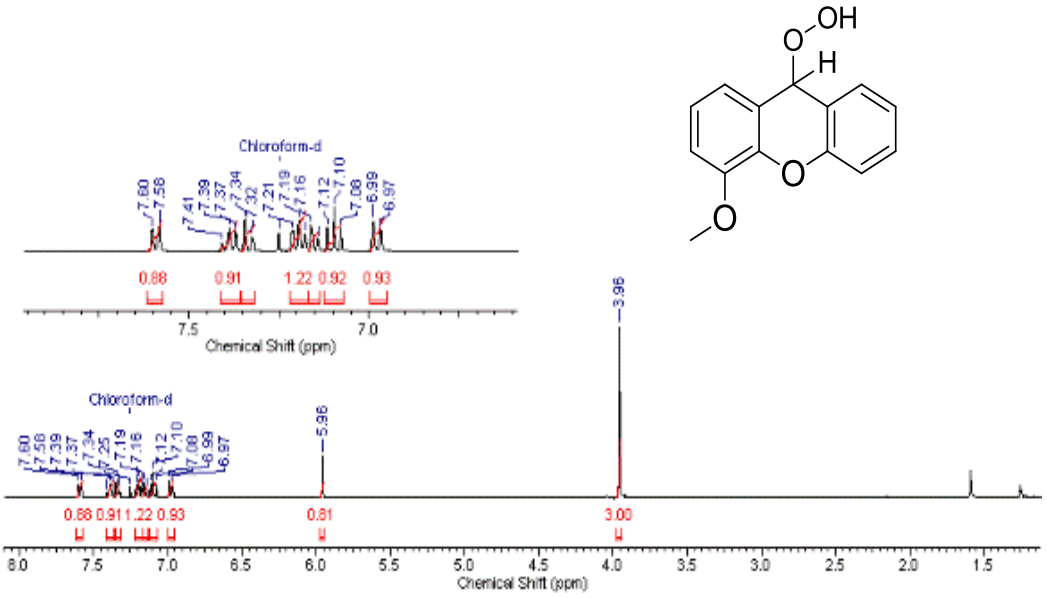
(c) The s-CD exhibited two broad peaks at D band 1346.3 cm^{-1} which attributed to the presence of sp^3 defect in graphitic plane and G band at 1586.2 cm^{-1} owing to the in plane vibration of sp^2 carbons. The intensity ratio of D and G bands (I_D/I_G=0.93) in pristine s-CD did not change appreciably after the coupling reaction. This revealed that the graphitic pool of s-CD was not affected by the reaction.

Table S5: Elemental analysis of s-CDs obtained after thermal treatment at 200° C

Catalyst	Carbon	Hydrogen	Oxygen	Sulphur	Adsorbed H_2O
Wt % in s-CD	53.6	3.9	31.2	0.93	10.37
Atom ratio	4.46	3.9	1.95	0.015	0.576

Characterization data for hydroperoxy intermediate:

9-Hydroperoxy-4-methoxy-9H-xanthene: Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.6 (d, *J* = 8.7, 1H), 7.41-7.37 (t, *J* = 8.28,1H),7.34-7.32 (d, *J* = 7.28,1H), 7.19-7.17 (t, *J* = 7.52 Hz, 1H), 7.16-7.14 (d, *J* = 8.28 Hz, 1H),7.09-7.07 (t, *J* = 7.8 Hz, 1H), 6.98-6.96 (d, *J* = 8 Hz,1H), 5.95 (s,1H), 3.95 (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.5, 147.9, 142.5, 131.3, 129.9, 122.9, 122.9, 122.4, 119.8, 119.0, 116.9, 112.0, 80.3, 56.3; Mass: 244.07, HRMS (ESI): calcd for [$C_{14}H_{12}O_4^+$ + Na^+] 267.0612, found 267.0623.



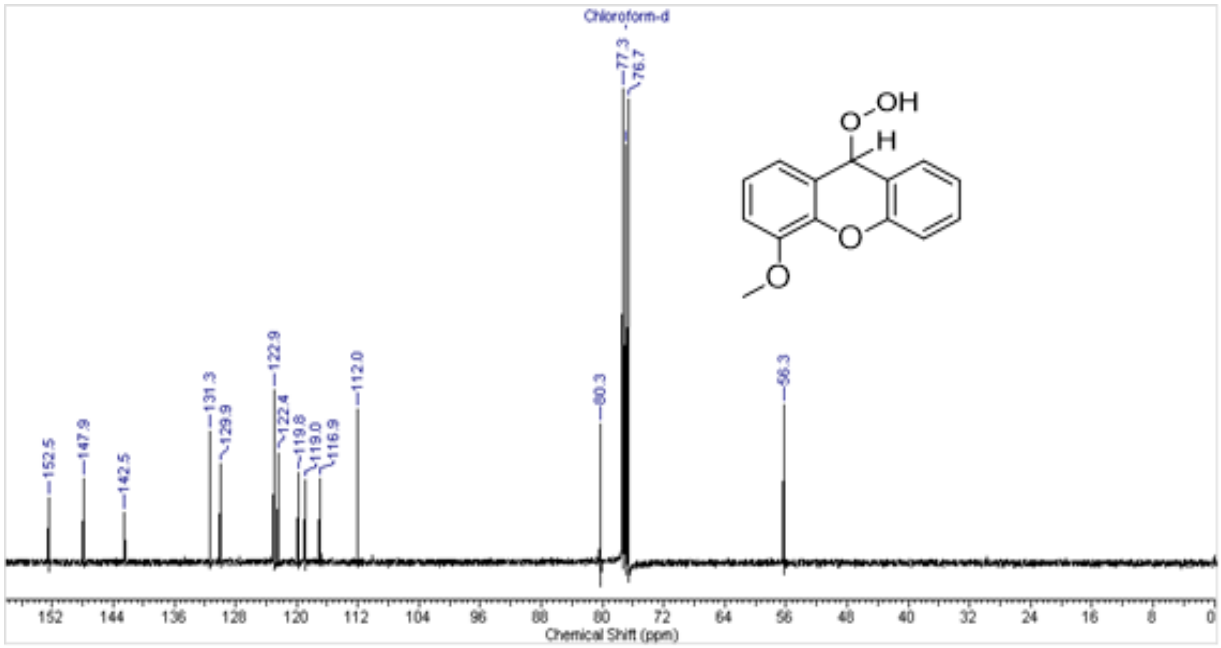


Figure S7: ^{1}H and ^{13}C NMR spectra for hydroperoxy intermediate.

Detection of hydrogen peroxide in the catalytic reactions

To detect H_2O_2 during the catalytic reaction, a modified iodometric method was employed. After 15 minutes of the reaction between 2-methoxyhydroperoxide intermediate with cyclohexanone under thermal condition (at 50°C), an equal volume of water and dichloromethane was added to extract the formed coupling product. The aqueous layer was acidified with H_2SO_4 to pH ≈ 2 and 1 mL of a 10% solution of KI and three drops of 3% solution of ammonium molybdate were added. In the presence of hydrogen peroxide I^- is oxidised to I_2, $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$, and with an excess of iodide ions, the tri-iodide ion is formed according to the reaction I_2 (aq.) + $I^- \rightarrow I^{3-}$.The formation of I^{3-} could be monitored by UV-Visible spectroscopy at wavelength 353 nm.

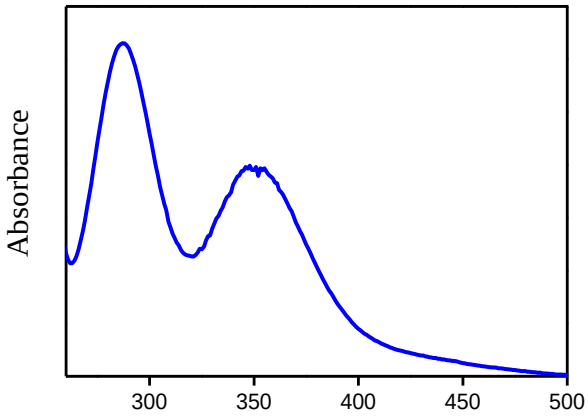


Figure S8: UV/Visible absorption spectra of the tri-iodide formed by H_2O_2 oxidation.

Radial Scavenging Analysis: To explore the involvement of various free radicals during the photocatalytic reaction, known radical scavengers were added in the reaction medium and the model photocatalytic C-C coupling reaction was studied in presence of visible-light under standard reaction conditions. Whereas Butylated hydroxytoluene (BHT) was used as a scaverger for studying the involvement of radicals in the mechanism, ascorbic acid (AA) was

used as a superoxide radical scavenger, *tert*-butyl alcohol (TBA) as ˙OH radical scavenger, EDTA as hole (h^+) scavenger and $CuCl_2$ as electron scavenger.[2]

Table S6: Control experiments of photocatalytic Cross dehydrogenative coupling of xanthene and cyclohexanone with the addition of various radical scavengers

Entry	Scavenger	Yield (%)
1	BHT	20
2	*p*-benzoquinone	17
3	TBA	85
4	EDTA	89
5	$CuCl_2$	10

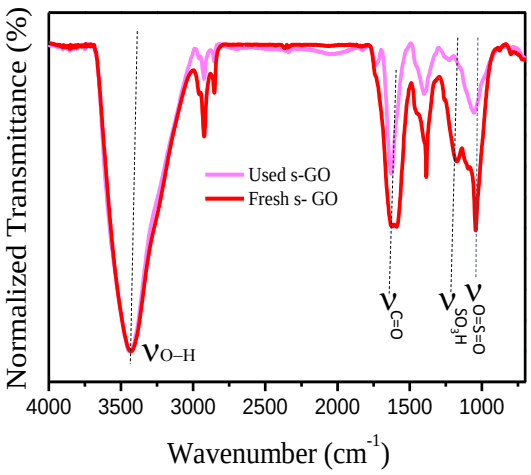


Figure S9: Normalized FTIR spectra of fresh s-GO (red) and s-GO after one cycle of reaction (pink).

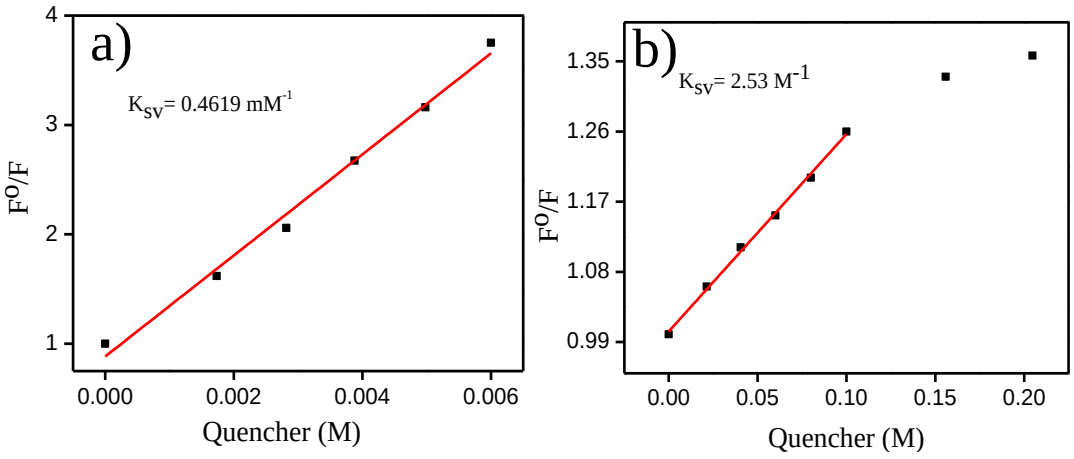


Figure S10: Stern–Volmer plots for the quenching of luminescence quantum yields (454 nm excitation) of the s-CDs.

(a) Electron acceptor 2,4-dinitrotoluene (DNT, 0.9 V vs NHE) in toluene were added to the s-CD aqueous solution. The emission intensity of s-CD at 424 nm was efficiently quenched. The Stern- Volmer quenching constants ($K_{sv} = \tau_F{}^{\circ}k_q$) were calculated from the linear regression and found to be 0.4619 mM^{-1}.

(b) Electron donor N, N-diethylaniline (DEA, 0.88 V vs NHE) in methanol were added to the aqueous s-CD solution and the calculated Stern-Volmer quenching constants were found to be 2.53 M^{-1}.

Photocurrent response measurements:

Commercial indium tin oxide (ITO) was used as the substrate for electrode build-up, and cleaned by sonication sequentially for 20 min each in acetone, 10% KOH in ethanol and doubly deionized water. Photo-electrochemical experiments were performed in a conventional three-electrode cell (Pyrex window) with a platinum wire as the auxiliary electrode and an $Hg/HgCl_2$ (saturated KCl) as the reference electrode. The working electrodes were ITO/s-CDs, with the glass side facing the incident light. They were prepared by spreading aqueous slurries over ITO glass substrates. Lithium perchlorate ($LiClO_4$) in acetonitrile was used as a electrolyte in cells. A 34 W blue LED light was used as light source and positioned 4 cm away from the photo-electrochemical cell. The photocurrent signal was recorded with a CHI 660C workstation (CH Instruments, Chenhua, Shanghai, China) connected to a personal computer. All electrochemical experiments were carried out at room temperature.

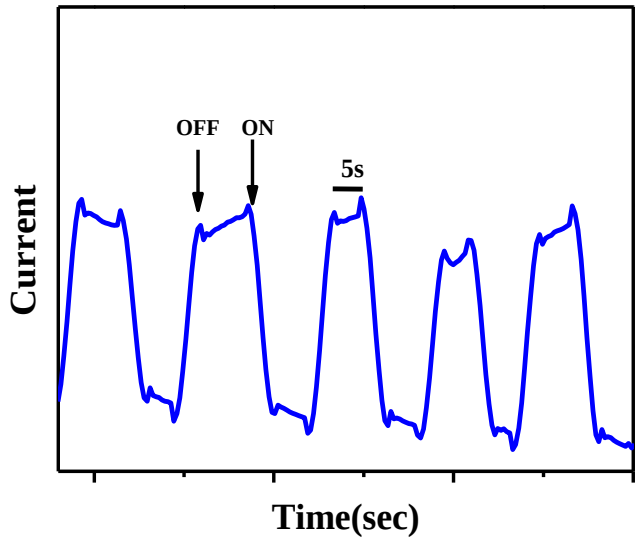


Figure S11: Transient photocurrent response of s-CDs under visible light.

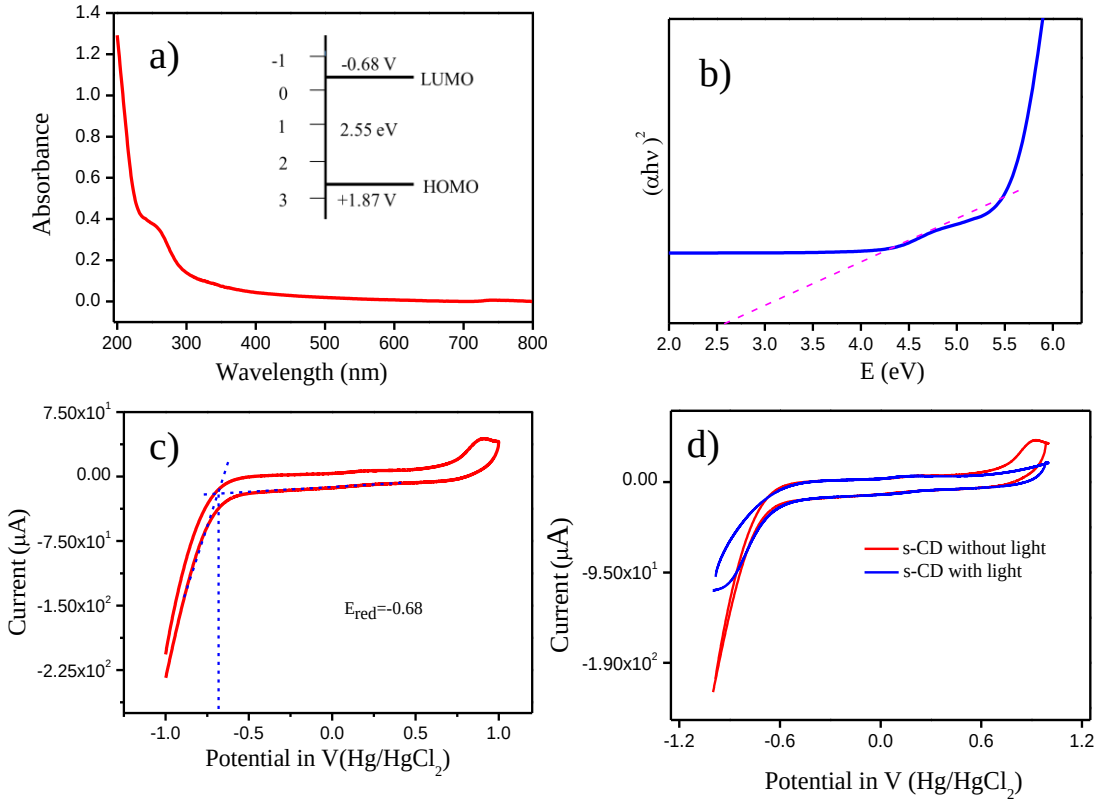


Figure S12: (a) Band gap of s-CD obtained from UV-Visible spectrum and calculated using Kubelka–Munk theory; (b) Reduction potential of s-CD measured by cyclic voltammetry; (c) HOMO/LUMO band positions of s-CD; (d) Cyclic voltamograms of the s-CDs/ITO electrode in acetonitrile using lithium perchlorate ($LiClO_4$) as an electrolyte under visible light irradiation or without light irradiation.

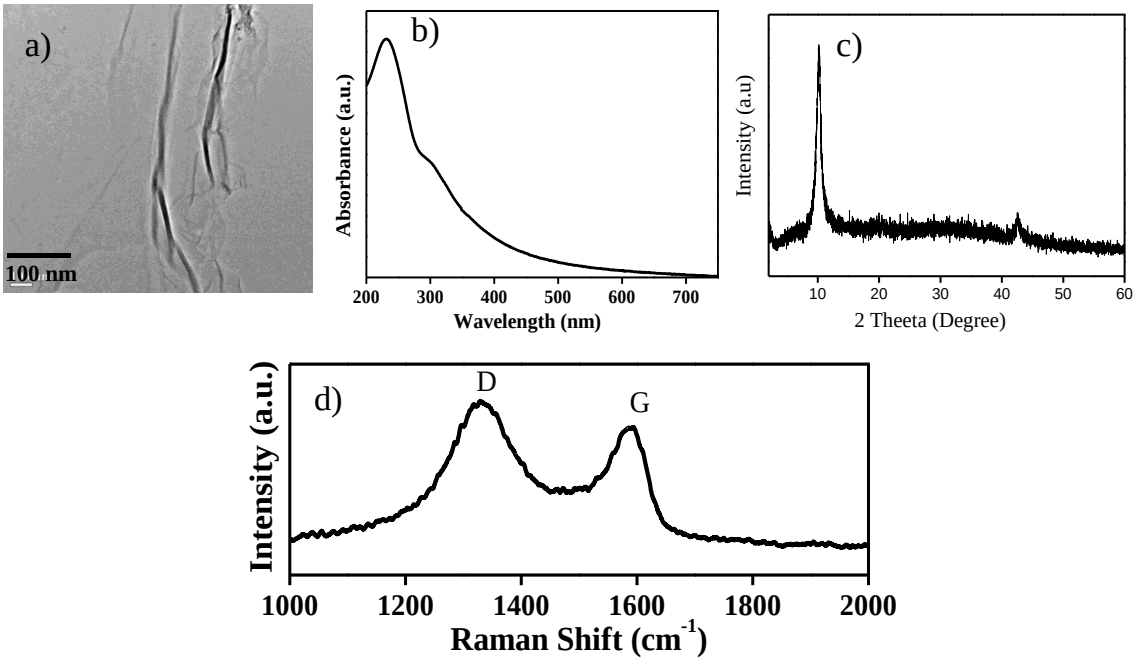


Figure S13: Characterization of graphene oxide (GO).

(a) The transmission electron microscopy (TEM) analysis indicated a layered structure of GO.

(b) UV-visible study showed two absorption peaks, a maximum at 230 nm corresponding to π−π* transitions of aromatic C−C bonds and a shoulder at 305 nm attributed to n−π* transitions of C-O bonds.

(c) The X-ray diffraction (XRD) pattern showed a characteristic peak at 2θ value of 10.2° with d spacing of 0.865 nm.

(d) Raman spectra of GO showing the D and G band of graphitic carbon.

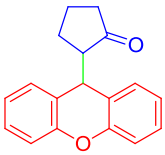
Table S7: Elemental analysis of s-GO

Catalyst	Carbon	Hydrogen	Oxygen	Sulphur	Adsorbed H_2O
Wt % in s-GO	48.32	2.49	37.1	2.24	9.85
Atom ratio	4.03	2.49	2.31	0.07	0.547

References:

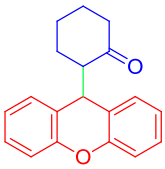
1. B.S. Chaput, A. Sud, A. Pinter, S. Dehn, P. Schulze, M. Klussmann, *Angew. Chem. Int. Ed*. **2013**, *52*, 13228-13232; *Angew. Chem*. **2013**, *125*, 13470-13474.
2. Y. Zhang, M. Park, H. Y. Kim, B. Ding, S. J. Park, *Sci. Rep*. **2017**, *7*, 45086.

^{1}H and ^{13}C NMR spectra:



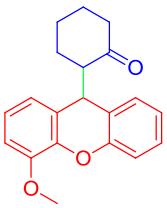
3aa

2-(9H-xanthen-9-yl)cyclopentanone: colourless solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ *ppm* 7.29-7.22 (m, 3H), 7.15-7.10 (m, 4H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.79 (d, *J* = 2.7 Hz, 1H), 2.47 (td, *J* = 9.7 Hz, *J* = 2.2 Hz, 1H), 2.27 (dd, *J* = 18.5 Hz, *J* = 7.4 Hz, 1H), 1.84-1.76 (m, 2H), 1.69-1.63 (m, 1H), 1.61-1.51 (m, 1H), 1.44 (ddd, *J* = 23.3 Hz, *J* = 11.3 Hz, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ *ppm* 199.4, 153.1, 152.5, 129.2, 128.2, 127.8, 124.5, 123.7, 123.5, 121.9; 116.4, 116.3, 59.9, 39.3, 38.0, 24.0, 20.4 HR-MS (ESI positive) m/z: calcd. For $C_{18}H_{16}O_2Na^+$, $[M+Na]^+$: 287.135551; found: 315.135314.



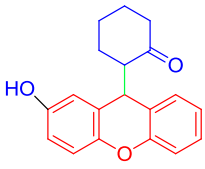
3ab

2-(9H-xanthen-9-yl)cyclohexanone: colourless solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ *ppm* 7.42 (dd, *J* = 7.52 Hz, 1H), 7.23-7.17 (m, 3H), 7.07-7.0 (m, 4H), 4.93 (s, 1H), 2.52-2.39 (m, 2H), 2.27-2.19 (m, 1H), 1.94-1.91 (m, 1H), 1.77-1.69 (m, 2H), 1.48-1.40 (m, 2H), 1.14-1.04 (m, 1H), 1.55-1.41 (m, 2H), 1.15 (ddd, *J* = 25.6 Hz, *J* = 12.8 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ *ppm* 210.8, 153.3, 153.0, 130.5, 128.8, 127.8, 127.7, 125.6, 123.5, 123.2, 122.9, 116.3, 116.1, 60.7, 42.1, 36.7, 26.7, 24.8, 23.1; HR-MS (EI) m/z: calcd. for $C_{19}H_{18}O_2Na^+$ $[M+Na]^+$: 301.130678; found: 301.130632.



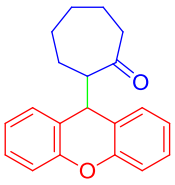
3ac

9-(2,4-dimethoxyphenyl)-4-methoxy-9H-xanthene: White solid, ^{1}H NMR (400 MHz) δ *ppm* 7.20 (d, J= 8.4 Hz, 1H), 7.13 (dt, J=8.4 Hz, 1H), 7.08 (d, J= 7.64 Hz, 1H), 6.91 (dt, J= 7.6 Hz, 1H), 6.85 (t, J= 7.64 Hz, 1H), 6.82 (d, J= 8.4 Hz, 1H), 6.75 (d, J= 7.64 Hz, 1H), 6.70 (d, J= 7.64 Hz, 1H), 6.43 (s, 1H), 6.32 (dd, J= 8.4 Hz, 1H), 5.69 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ *ppm* 210.1, 153.2, 152.9, 147.9, 147.8, 142.8, 142.6, 130.4, 128.7, 127.7, 127.6, 126.6, 125.6, 123.9, 123.7, 123.4. 123.2, 122.8, 122.7, 122.2, 120.4, 116.7, 116.7, 116.6, 110.2, 110.0, 60.5, 56.2, 56.1, 42.13, 42.09, 36.8, 36.7, 29.7, 29.7, 27.8, 27.5, 26.7, 26.6, 24.74, 24.72; HR-MS (EI) m/z: calcd. for $C_{20}H_{20}O_2Na^+$ $[M+Na]^+$: 301.150668; found: 301.150652.



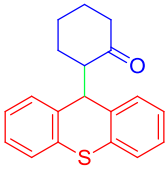
3ad

2-(2-hydroxy-9H-xanthen-9-yl)cyclohexanone: Yellow solid, ^{1}H NMR (400 MHz) δ *ppm* 7.42 (dd, *J* = 7.52 Hz, 1H), 7.23-7.17 (m, 3H), 7.07-7.0 (m, 2H), 6.99-6.92 (m,3H), 4.93 (s, 1H), 2.52-2.39 (m, 2H), 2.27-2.19 (m, 1H), 1.94-1.91 (m, 1H), 1.77-1.69 (m, 2H), 1.48-1.40 (m, 2H), 1.14-1.04 (m, 1H), 1.55-1.41 (m, 2H), 1.15 (ddd, *J* = 25.6 Hz, *J* = 12.8 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ ppm* 210.8, 153.3, 153.0, 130.5, 128.8, 127.8, 127.7, 125.6, 123.5, 123.2, 122.9, 116.3, 116.1, 60.7, 42.1, 36.7, 26.7, 24.8, 23.1; HR-MS (EI) m/z: calcd. for $C_{19}H_{18}O_3Na^+$ $[M+Na]^+$: 317.120568; found: 317.120343.



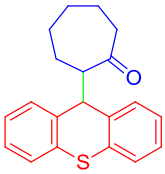
3ae

2-(9H-xanthen-9-yl)cycloheptanone: colourless solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ *ppm* 7.26-7.20 (m, 3H), 7.10-7.04 (m, 4H), 7.01 (t, *J* = 7.3 Hz, 1H), 4.64 (d, *J* = 3.9 Hz, 1H), 2.5 (d, *J* = 11.4 Hz, 1H), 2.36-2.32 (m, *J* = 12.4 Hz,1H), 2.16-2.06 (m, 1H), 1.74-1.72 (br m, 3H), 1.38-1.12 (m, 4H), 1.05-0.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ *ppm* 216.4, 153.2, 153.0, 129.1, 128.7, 128.1, 127.9, 124.5, 123.6, 123.1, 121.9, 116.6, 116.3, 62.4, 44.7, 42.1, 29.9, 28.5, 25.1, 24.8. HR-MS (ESI positive) m/z: calcd. For $C_{20}H_{20}NaO_2$ $[M+Na]^+$: 315.135551; found: 315.135314.



3ba

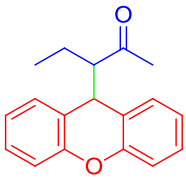
2-(9H-thioxanthen-9-yl)cyclohexanone: Light yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ *ppm* 7.63 (dd, *J* = 7.56 Hz, *J* = 1.68 Hz, 1H), 7.42-7.36 (m, 2H), 7.24-7.10 (m, 6H), 4.69 (d, *J* = 9.52 Hz, 1H), 3.14-3.07 (m, 1H), 2.35-2.30 (m, 1H), 2.22-2.14 (m, 1H), 2.01-1.94 (m, 1H), 1.76-1.69 (m, 1H), 1.63-1.50 (m, 3H), 1.40-1.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ *ppm* 212.1, 141.9, 138.6, 136.6, 133.7, 132.7, 130.9, 130.2, 127.2, 126.6, 126.4, 126.2, 50.4, 47.3, 43.2, 33.9, 29.8, 28.9, 25.3; HR-MS (ESI positive) m/z: calcd. For $C_{19}H_{18}NaOS$ $[M+Na]^+$: 317.095651; found: 315.09311.



3bb

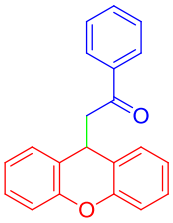
2-(9H-thioxanthen-9-yl)cycloheptanone: White soild, ^{1}H NMR (400 MHz, $CDCl_3$): δ *ppm* 7.42-7.36 (m, 1H), 7.28-7.27 (m, 1H), 7.24-7.10 (m, 5H), 4.50 (d, *J* = 10.2 Hz, 1H), 2.31-2.23 (m, 1H), 2.10-2.04 (m, 1H), 2.16-2.06 (m, 1H), 1.76-1.66 (br m, 3H), 1.50-1.44 (m, 1H), 1.38-1.34 (m, 1H), 1.24 (br s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ *ppm* 214.5, 136.9, 135.8, 133.4, 132.6, 130.5, 130.3, 127.3 (t), 127.0, 126.7, 126.45, 126.41, 126.1, 50.9, 50.0, 43.7, 29.7, 28.4, 27.8, 23.6; HR-MS (ESI positive) m/z: calcd. For $C_{20}H_{20}NaOS$ $[M+Na]^+$: 332.115851; found: 332.114113.



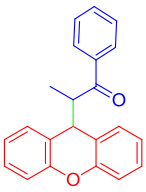
3ca

3-(9H-xanthen-9-yl)pentan-2-one: Brown oil, ^1H NMR (400 MHz, $CDCl_3$): δ *ppm* 7.27-7.21 (m, 2H), 7.15-7.02 (m, 6H), 4.08 (d, *J* = 8.5 Hz, 1H), 2.69 (t, *J=10.8* 1H), 1.76 (s, 3H), 1.62-1.55 (m, 1H), 1.39-1.33 (m,1H), 0.73 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ *ppm* 212.2, 153.2, 129.6, 128.8, 128.1, 127.9, 124.7, 124.1, 123.5, 123.1, 116.7, 61.0, 42.8, 33.4, 22.9, 12.0; HR-MS (EI) m/z: calcd. for $C_{18}H_{18}O_2$ $[M+Na]^+$: 289.120678; found: 266.120632.



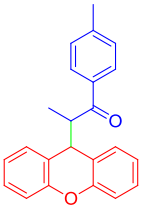
3cb

1-phenyl-2-(9H-xanthen-9-yl)ethanone: White solid, ^1H NMR (400 MHz, $CDCl_3$): δ *ppm* 7.79 (d, *J* = 5.4 Hz, 2H), 7.48 (t, *J* = 8.04 Hz, 1H), 7.37-7.30 (m, 4H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.1 (d, *J* = 6.84 Hz, 2H), 7.02 (t, *J* = 5.6 Hz, 2H), 4.85 (t, *J* = 4.4 Hz, 1H), 3.34 (d, *J* = 5.1 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ *ppm* 197.2, 152.3, 129.5, 128.8, 128.5, 128.1, 127.9, 126.3, 125.5, 123.5, 116.6, 57.1, 43.3; HR-MS (ESI positive) m/z: calcd. for $C_{21}H_{16}NaO_2$ $[M+Na]^+$: 323.104136; found: 323.104250.



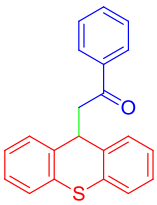
3cc

1-phenyl-2-(9H-xanthen-9-yl)propan-1-one: Pale yellow oil, ^{1}H NMR (400 MHz, CDCl3): *δ ppm* 7.67 (d, *J* = 7.28 Hz, 2H), 7.41 (t, *J* = 7.52 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.19 (td, *J* = 8.5 Hz, *J* =1.5 Hz, 1H), 7.11(d, *J* = 7.5 Hz, 1H), 7.09-6.96 (m, 5H), 6.85(td, *J* = 7.5 Hz, *J* =2.0 Hz,1H), 4.32 (d, *J* = 7.7 Hz, 1H), 3.64-3.57 (m, 1H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ ppm* 203.4 , 153.4, 153.1, 137.1, 129.9, 129.0, 128.6, 128.2, 127.9 , 125.2, 123.6 , 116.58, 116.62, 68.4, 48.6, 42.8, 29.8, 14.6 HRMS (ESI positive) m/z: calcd. for $C_{22}H_{18}NaO_2$ $[M+Na]^+$: 337.119729; found: 337.119576.



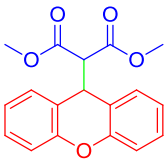
3cd

1-(p-tolyl)-2-(9H-xanthen-9-yl)propan-1-one: Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): *δ ppm* 7.66 (d, *J* = 7.7 Hz, *J* =1.4 Hz, 2H), 7.26 (t, *J* = 9.0 Hz, 1H), 7.19-7.03 (m, 8H), 6.92 (td, *J* = 6.4 Hz, *J* =1.5 Hz, 1H), 4.40 (d, *J* = 7.6 Hz, 1H), 3.68-3.61 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ ppm* 202.1 , 173.5, 165.4, 159.4, 157.3, 151.5, 130.8, 129.5, 128.1, 127.5, 125.1 , 123.0, 123.3 , 116.7, 104.9, 98.8, 55.6, 55.3, 36.4, 31.0 HRMS (ESI positive) m/z: calcd. for $C_{23}H_{20}NaO_2$ $[M+Na]^+$: 351.139789; found: 333.139578.



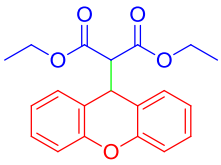
3da

1-phenyl-2-(9H-thioxanthen-9-yl)ethanone: Colourless oil,^{1}H NMR (400 MHz, $CDCl_3$): *δ ppm* 7.80 (d, *J* = 5.3 Hz, 2H), 7.49 (t, *J* = 8.01 Hz, 1H), 7.36-7.32 (m, 4H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.1 (d, *J* = 6.84 Hz, 2H), 7.03 (t, *J* = 5.6 Hz, 2H), 4.86 (t, *J* = 4.4 Hz, 1H), 3.34 (d, *J* = 5.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ ppm* 198.1, 152.2, 129.4, 128.6, 128.4, 128.2, 127.7, 126.3, 125.5, 123.5, 116.5, 57.1, 43.3; HRMS (ESI positive) m/z: calcd. for $C_{21}H_{16}NaOS$ $[M+Na]^+$: 339.073724; found: 339.070572.



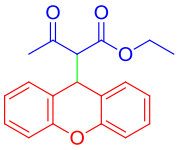
3ea

dimethyl 2-(9H-xanthen-9-yl)malonate: Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): *δ ppm* 7.30 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2H), 7.25 (td, *J* =8.1 Hz, *J* = 1.7 Hz, 2H), 7.15 (dd, *J* = 8.2 Hz, *J* = 1.1 Hz, 2H), 7.05 (td, *J* = 7.4 Hz, *J* = 1.2 Hz, 2H), 4.82 (d, *J* = 9.0 Hz, 1H), 3.6 (d, *J* = 9.0 Hz, 1H), 3.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ ppm* 167.6, 152.7, 129.1, 128.9, 123.4, 122.7, 116.9, 60.0, 52.5, 39.9; HR-MS (ESI positive) m/z: calcd. for $C_{18}H_{16}NaO_5$ $[M+Na]^+$: 335.088992; found: 335.088817.



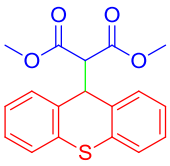
3eb

diethyl 2-(9H-xanthen-9-yl)malonate: Brown oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ *ppm* 7.32 (dd, *J* = 7.6 Hz, *J* = 1.5 Hz, 2H), 7.26-7.22 (m, 2H), 7.14 (dd, *J* = 8.2 Hz, *J* = 1.04 Hz, 2H), 7.05 (td, *J* = 7.4 Hz, *J* = 1.2 Hz, 2H), 4.81 (d, *J* = 8.9 Hz, 1H), 4.06-3.94 (m, 2H), 3.59 (d, *J* = 8.9 Hz, 1H), 1.08 (t, *J* =7.2 Hz, 6H); ^{13}C NMR (100 MHz, CDCl3): δ *ppm* 167.5 , 153.2, 129.0, 128.5, 123.4, 122.9, 116.7, 61.6, 60.3, 39.7, 13.5; HR-MS (ESI positive) m/z: calcd. for $C_{20}H_{20}NaO_5$ $[M+Na]^+$: 363.117982; found: 335.117812.



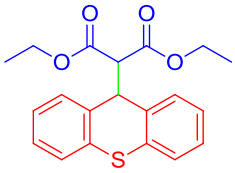
3ec

ethyl 3-oxo-2-(9H-xanthen-9-yl)butanoate: Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ *ppm* 7.33 (dd, *J* = 7.7 Hz, *J* =1.4 Hz, 1H), 7.27-7.24 (m, 3H), 7.14 (ddd, *J* = 8.5 Hz, *J* = 4.1 Hz, *J* = 1.3 Hz, 2H), 7.04 (m, 2H), 4.85 (d, *J* = 9.2 Hz, 1H), 4.03-3.94 (m, 2H), 3.79 (d, *J* = 9.2 Hz, 1H), 1.90 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3): δ *ppm* 201.8 , 167.4, 153.4, 153.3, 129.7, 129.3, 128.49, 128.47, 123.6 (t), 123.5 123.4, 123.3 , 116.9, 116.7, 63.9, 60.3, 39.5, 32.9, 13.9; HRMS (ESI positive) m/z: calcd. for C19H18NaO4 $[M+Na]^+$: 333.109729; found: 333.109576.



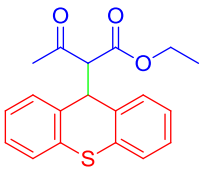
3fa

dimethyl 2-(9H-thioxanthen-9-yl)malonate: Light yellow solid,^{1}H NMR (400 MHz, $CDCl_3$): δ *ppm* 7.44-7.42 (m, 2H), 7.40-7.38 (m, 2H), 7.20-7.19 (m, 4H), 4.91 (d, *J* = 9.04 Hz, 1H), 4.2 (d, *J* = 9.04 Hz, 1H), 3.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 167.7, 153.2, 134.3, 133.5, 130.0, 127.3, 126.5, 52.4, 51.4, 48.7; HR-MS (ESI positive) m/z: calcd. for $C_{18}H_{16}NaO_4S$ $[M+Na]^+$: 351.078972; found: 351.078816.



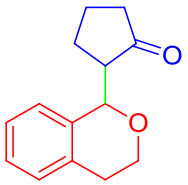
3fb

diethyl 2-(9H-thioxanthen-9-yl)malonate: Light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): *δ ppm* 7.44-7.41 (m, 4H), 7.20-7.18 (m, 4H), 4.82 (d, *J* = 8.9 Hz, 1H), 4.91 (d, *J* = 8.8 Hz , 1H), 4.16 (d, *J* = 8.9 Hz, 1H), 3.99-3.87 (m, 4H) 1.03 (t, J= 5.84, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): *δ ppm* 167.5, 153.4, 134.5, 133.6, 130.2, 127.2, 126.5, 61.3, 51.5, 48.7, 13.8; HR-MS (ESI positive) m/z: calcd. For $C_{20}H_{20}NaO_4S$ $[M+Na]^+$: 379.097282; found: 363.097132.



3fc

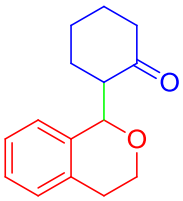
methyl 3-oxo-2-(9H-thioxanthen-9-yl)butanoate: White solid, ^{1}H NMR (400 MHz, $CDCl_3$): *δ ppm* 7.43-7.40 (m, 3H), 7.34 (m, 1H), 7.20-7.18 (m, 4H), 4.93 (d, *J* = 11.0 Hz, 1H), 4.46 (d, *J* = 10.76 Hz, 1H), 3.97-3.88 (m, 2H), 1.82 (s, 3H), 1.05 (t, *J* = 7.01 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3): *δ ppm* 201.9, 167.4, 134.7, 134.4, 133.9, 133.44, 133.39, 130.6, 130.2, 127.3, 127.2, 127.1, 126.8, 126.6, 61.4, 57.5, 48.4, 31.2, 13.9; HRMS (ESI positive) m/z: calcd. for $C_{18}H_{16}NaO_3S$ $[M+Na]^+$: 335.068572; found: 333.0684576.



3ga

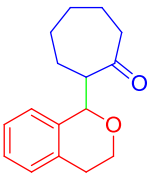
2-(isochroman-1-yl)cyclopentanone: Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): *δ ppm* 7.34-7.20 (m, 4H), 4.35 (d, *J*= 7.6,1H), 3.75 (m, 2H), 2.77-2.70 (m, 3H), 2.10-1.85 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ ppm* 211.8, 137.1, 136.3, 127.5, 125.8, 125.7, 125.5, 77.5, 62.6,

54.7, 38.9, 28.6, 21.2, 14.1, HRMS (EI) m/z calcd for $C_{14}H_{16}O_2$ $[M+Na]^+$ 239.09380, found 231.09326.



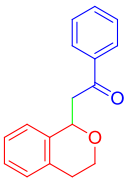
3gb

2-(isochroman-1-yl)cyclohexanone: Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ *ppm* 7.23-7.14 (m, 3H), 7.13-7.09 (m, 1H), 7.01 (d, J=7.0 Hz, 1H), 5.48 (s, 1H), 4.16 (dd, J=11.0, 5.4 Hz, 1H), 3.75 (t, J=11.3 Hz, 1H), 3.05-2.97 (m, 1H), 2.75 (dd, J=11.1, 5.6 Hz, 1H), 2.62-2.53 (m, 2H), 2.3-2.30 (m, 1H), 1.99 (dd, J=8.2, 4.8 Hz, 1H), 1.89-1.82 (m, 1H), 1.76 (ddd, J=32.4, 20.4, 12.8 Hz, 2H), 1.64 (d, J=7.1 Hz, 1H), 1.54 (t, J=12.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ *ppm* 210.8, 136.6, 135.5, 128.9, 126.3, 126.2, 123.9, 73.7, 64.3, 55.7, 42.0,29.3, 26.1, 25.2, 24.5 HRMS (EI) m/z calcd for $C_{15}H_{18}NaO_2$ $[M+Na]^+$ 253.1180, found 253.1163.



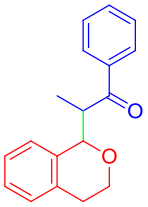
3gc

2-(isochroman-1-yl)cycloheptanone: Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ *ppm* 7.33 (m, 2H), 7.23 (m, 2H), 4.4 (d, J=10.9, 1H), 3.75-3.65 (m, 2H), 3.05 (m, 1H), 2.71 (m, 2H), 2.52-2.4 (m, 2H), 1.66-141.0 (m, 8H), ^{13}C NMR (100 MHz, $CDCl_3$): δ *ppm* 214.6, 137.1, 136.3, 127.6, 125.8, 125.7,125.5, 78.0, 62.6, 54.6, 42.4, 29.5, 28.6, 26.7,24.2,22.7; HRMS (EI) m/z calcd for $C_{15}H_{18}NaO_2$ $[M+Na]^+$ 253.1180, found 253.1163.



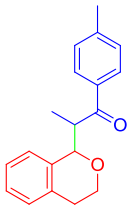
3ha

2-(isochroman-1-yl)-1-phenylethanone: Pale yellow,^{1}H NMR ($CDCl_3$, 300 MHz) *δ ppm* 8.04 (d, *J*=7.17 Hz, 2H), 7.60-7.45 (m, 3H), 7.26-7.13 (m, 4H), 5.54 (d, *J*=8.7 Hz, 1H), 4.16-4.09 (m, 1H), 3.86-3.78 (m, 1H), 3.67-3.59 (m, 1H), 3.36-3.30 (m 1H), 3.08-2.98 (m, 1H), 2.76-2.69 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ ppm* 198.1, 137.5, 137.1, 134.0, 133.1, 129.0, 128.5, 128.3, 126.5, 126.2, 124.5, 72.6,63.4, 45.4, 28.8; HRMS (EI) m/z calcd for $C_{17}H_{16}NaO_2$ $[M+Na]^+$ 275.0923, found 275.0912.



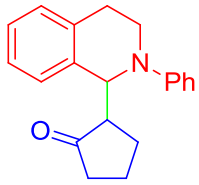
3hb

2-(isochroman-1-yl)-1-phenylpropan-1-one: Yellow solid,^{1}H NMR ($CDCl_3$, 300 MHz) *δ ppm* 7.99-7.91 (m, 2H), 7.58-7.40 (m, 3H), 7.25-7.01 (m, 4H), 5.28-5.21 (m, 1H), 4.13-4.0 (m, 2H), 3.68-3.53 (m, 1H), 3.06-2.95 (m, 1H), 2.65-2.54 (m, 1H), 1.20-1.06 (m, 3H); ^{13}C NMR ($CDCl_3$,75 MHz) *δ ppm* 201.8, 177.2, 136.6, 135.8, 135.0, 132.7 (two peaks), 129.1, 128.7, 128.6, 128.5, 128.3, 126.6, 126.5, 126.3, 125.8, 124.5, 77.4, 76.6, 63.9, 63.3, 47.2, 46.7, 29.6, 28.8,13.6, 9.7; HRMS (EI) m/z calcd for $C_{18}H_{18}NaO_2$ $[M+Na]^+$ 289.11760, found 289.11742.



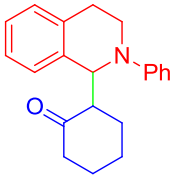
3hc

2-(isochroman-1-yl)-1-(p-tolyl)propan-1-one: Light yellow solid, Diastereomeric ratio 2.9: 1, ^{1}H NMR (400 MHz) *δ ppm* 7.87 (d, *J*= 8.4 Hz , 2H), 7.26 (d, J= 8.4 Hz, 2H), 7.16-7.08 (m, 4H), 5.26 (d, *J*= 3.8, 1H), 4.12-4.06 (m, 1H), 4.00-3.91 (m, 1H), 3.61-3.55 (m, 1H), 3.02-2.94 (m, 1H), 2.60-2.53 (m, 1H), 2.39 (s, 3H), 1.07 (d, *J*= , 3H); ^{13}C NMR ($CDCl_3$,100 MHz) *δ ppm* 201.5, 143.5, 143.4, 136.4, 135.1, 134.3, 129.4,129.2, 128.6, 126.6, 126.4, 124.6, 72.1, 70.4, 65.3, 64.0, 46.8, 34.3, 31.9, 29.5, 29.4, 29.3, 29.2, 28.9, 25.0, 22.7, 21.6, 14.2, 10.2; HRMS (EI) m/z calcd for $C_{19}H_{20}NaO_2$ $[M+Na]^+$ 303.1380, found 303.1382.



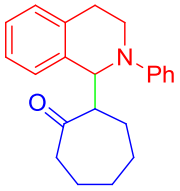
3ia

2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclopentanone: Dark brown soild, Diastereomeric ratio 6.92:1, ^{1}H NMR (400 MHz) δ ppm 7.29-7.15 (m, 4H), 7.11-7.07 (m, 1H), 7.02 (d, J= 8. Hz, 2H), 6.92 (d, J= 7.6 Hz, 1H), 6.77 (t, J= 7.64 Hz, 1H), 5.58 (s, 1H), 3.57-3.46 (m, 2H), 3.04-2.89 (m, 2H), 2.74-2.69 (m, 1H), 2.30-2.23 (m, 1H), 2.08-2.02 (m, 2H), 1.85-1.75 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 202.9, 153.4, 153.1, 143.7, 134.6, 129.9, 129.3, 129.0, 128.3, 128.1, 127.8, 125.3, 123.4, 123.0, 116.52, 116.48, 48.5, 42.7, 32.0, 31.0, 29.8, 21.6, 14.6; HRMS (EI) m/z calcd for $C_{20}H_{21}NNaO$ $[M+Na]^+$ 314.1462, found 314.1451.



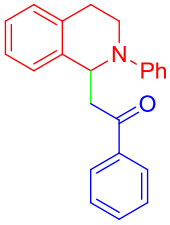
3ib

2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexanone: Yellow oil diastereomeric ratio = 1.3 : 1; Isolated major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ *ppm* 7.23 (dd, *J* = 12.8, 7.1 Hz, 3H), 7.19 – 7.10 (m, 4H), 6.93 (d, *J* = 8.1 Hz, 2H), 5.63 (d, *J* = 4.5 Hz, 1H), 3.82 – 3.67 (m,1H), 3.64 – 3.47 (m, 2H), 2.93 – 2.85 (m, 2H), 2.47 (t, *J* = 9.9 Hz, 2H), 2.30 (ddd, *J* = 25.7, 15.3, 9.7 Hz, 2H), 1.86 (d, *J* = 6.3 Hz, 2H), 1.68 – 1.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ *ppm*, 214.5, 149.3, 140.3, 135.9, 134.6, 129.3, 128.7, 127.9, 125.8, 118.1, 116.4, 114.9, 112.3, 59.3, 56.5, 54.9, 54.0, 42.6, 41.4, 32.8, 30.2, 28.7, 27.7, 27.0, 25.7, 23.8; HRMS (EI) m/z calcd for $C_{21}H_{23}NNaO_2$ $[M+Na]^+$ 328.1680, found 267.1676.



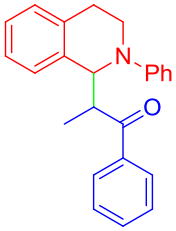
3ic

2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cycloheptanone: Light brown solid, Diastereomeric ratio 1:1, ^{1}H NMR (400 MHz) *δ ppm* 7.21 (d, J= 8.36 Hz, 1H), 7.20 (d, J = 9.16 Hz, 1 H), 7.11-7.02 (m, 4H), 6.90 (d, J= 8.4 Hz, 2H), 6.68 (t, J= 7.64 Hz, 1H), 5.41 (d, J= 8.4, 1H), 3.55 (t, J= 6.12 Hz, 2H), 3.06-2.97 (m, 2H), 2.87-2.80 (m, 1H), 2.43-2.35 (m, 1H), 2.25-2.19 (m, 1H), 2.11-2.06 (m, 1H), 1.87-1.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ *ppm*, 215.4, 149.8, 138.7, 134.3, 129.2, 128.3, 127.1, 126.7, 126.2, 117.0, 113.3, 70.3, 65.1, 63.4, 59.5, 57.9, 44.3, 43.0, 31.9, 29.6, 29.4, 29.0, 28.2, 27.2, 24.8, 23.5, 22.6, 14.0; HR-MS (ESI positive) m/z: calcd. for $C_{22}H_{25}NNaO$ [M+Na]+: 342.181672; found: 342.181517.



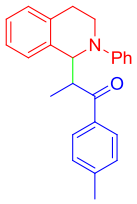
3ja

1-phenyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone: Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$): *δ ppm* 7.84 (d, *J* = 7.0 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.0 Hz, 3H), 7.14-7.10 (m, 3H), 6.96 (d, *J* = 8 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 5.67 (t, *J* =5.4 Hz, 1H), 3.64-3.54 (m, 3H), 3.41 (dd, *J* = 16.7, 7.0 Hz, 1H), 3.13-3.07 (m, 1H), 2.93 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ ppm* 198.6, 148.7, 138.5, 137.2, 134.5, 133.1, 129.3, 128.5, 128.3, 128.1, 127.1, 126.8, 126.2, 117.9, 114.3, 55.0, 45.3, 42.1, 27.6; HR-MS m/z: calcd for $C_{23}H_{21}NNaO[M+Na]^{+}$: 350.1515; found: 350.1511.



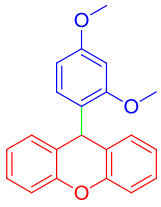
3jb

1-phenyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-1-one: Light yellow oil, Diastereomeric ratio 1:1, ^{1}H NMR (400 MHz) δ *ppm* 7.63 (d, J= 7.64 Hz, 2H), 7.41 (t, J=7.64 Hz, 1H), 7.28 (t, J=7.6 Hz, 2H), 7.20 (t, J= 8.4 Hz, 2H), 7.03 (t, J= 6.88 Hz, 2H), 6.99 (d, J= 9.16 Hz, 2H), 6.88 (t, J= 6.88 Hz, 1H), 6.84 (t, J= 7.64 Hz, 1H), 6.68 (t, J= 7.64 Hz, 1H), 5.39 (d, J= 9.16 Hz, 1H), 3.99-3.94 (m, 1H), 3.63-3.59 (m, 2H), 3.05-2.99 (m, 1H), 2.92-2.87 (m, 1H), 1.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ *ppm*, 204.5, 137.5, 134.4, 132.9, 129.2, 128.1, 127.3, 126.9, 126.0, 113.4, 70.3, 65.2, 63.4, 48.3, 34.2, 31.9, 29.7, 24.9, 22.7, 16.6, 14.1; HR-MS (ESI positive) m/z: calcd. for $C_{24}H_{23}NNaO$ $[M+Na]^{+}$: 364.168792; found: 364.168681.



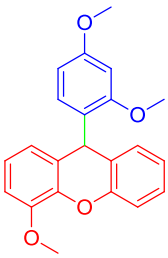
3jc

2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-(p-tolyl)propan-1-one: Brown solid, Diastereomeric ratio 1:1, ^{1}H NMR (400 MHz) δ *ppm* 7.44 (d, J= 8.4 Hz, 2H), 7.11-7.07 (m, 3H), 6.98 (d, J=8.4 Hz, 2H), 6.93-6.85 (m, 4H), 6.77 (t, J= 8.4 Hz, 1H), 6.73 (t, J= 6.88 Hz, 1H), 6.56 (t, J= 7.64 Hz, 1H), 5.29 (d, J= 9.16 Hz, 1H), 3.87-3.79 (m, 1H), 3.50 (t, J = 6.08 Hz, 2H), 2.95-2.88 (m, 1H), 2.81-2.74 (m, 1H), 2.18 (s, 3H), 1.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ *ppm* 205.6, 137.6, 134.6, 133.1, 130.2, 128.1, 127.4, 126.5, 126.3, 114.1, 71.3, 65.2, 63.6, 48.2, 34.3, 31.7, 29.5, 24.7, 22.5, 16.7, 13.3 14.1; HR-MS (ESI positive) m/z: calcd. for $C_{25}H_{25}NNaO$ $[M+Na]^+$: 378.178982; found: 378.178817.



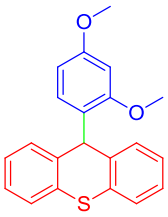
6a

9-(2,4-dimethoxyphenyl)-9H-xanthene: White solid, ^{1}H NMR ($CDCl_3$, 400 MHz) *δ ppm* 7.20 (td, *J* = 8.2 Hz, *J* = 1.4 Hz, 2H), 7.12-7.08 (m, 4H), 6.97 (td, *J* = 7.7 Hz, *J* = 1.3 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 5.72 (s, 1H), 3.84 (s, 3H), 3.75(s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ *ppm* 159.3, 157.1, 151.5, 130.7, 129.3, 128.1, 127.6, 125.1, 123.0, 116.2, 104.8, 98.7, 55.6, 55.2, 36.4; HRMS: calcd for $C_{21}H_{18}NaO_3$ $[M+Na]^+$ 341.1153, found: 341.1141.



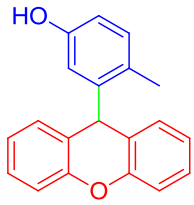
6b

9-(2,4-dimethoxyphenyl)-4-methoxy-9H-xanthene: white solid, Diastereomeric ratio 1:1.3, ^{1}H NMR (400 MHz) δ *ppm* 7.20 (d, J= 8.4 Hz, 1H), 7.13 (dt, J=8.4 Hz, 1H), 7.08 (d, J= 7.64 Hz, 1H), 6.91 (dt, J= 7.6 Hz, 1H), 6.85 (t, J= 7.64 Hz, 1H), 6.82 (d, J= 8.4 Hz, 1H), 6.75 (d, J= 7.64 Hz, 1H), 6.70 (d, J= 7.64 Hz, 1H), 6.43 (s, 1H), 6.32 (dd, J= 8.4 Hz, 1H), 5.69 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ *ppm*, 160.3, 159.7, 159.3, 158.4, 157.0, 151.2, 149.6, 147.7, 141.0, 137.5, 132.9, 130.6, 130.1, 129.5, 129.3, 128.4, 128.0, 127.3, 126.6, 126.5, 126.4. 126.3, 125.9, 124.9, 123.2, 122.5, 122.2, 121.1, 119.6, 116.5, 116.1, 110.3, 109.7, 104.8, 104.0, 103.7, 100.2, 98.8, 98.7, 59.5, 56.2, 55.2, 45.6, 36.2, 31.9, 29.6, 22.6, 14.1; $C_{22}H_{20}NaO_3$ $[M+Na]^+$ 371.1288, found: 317.1280.



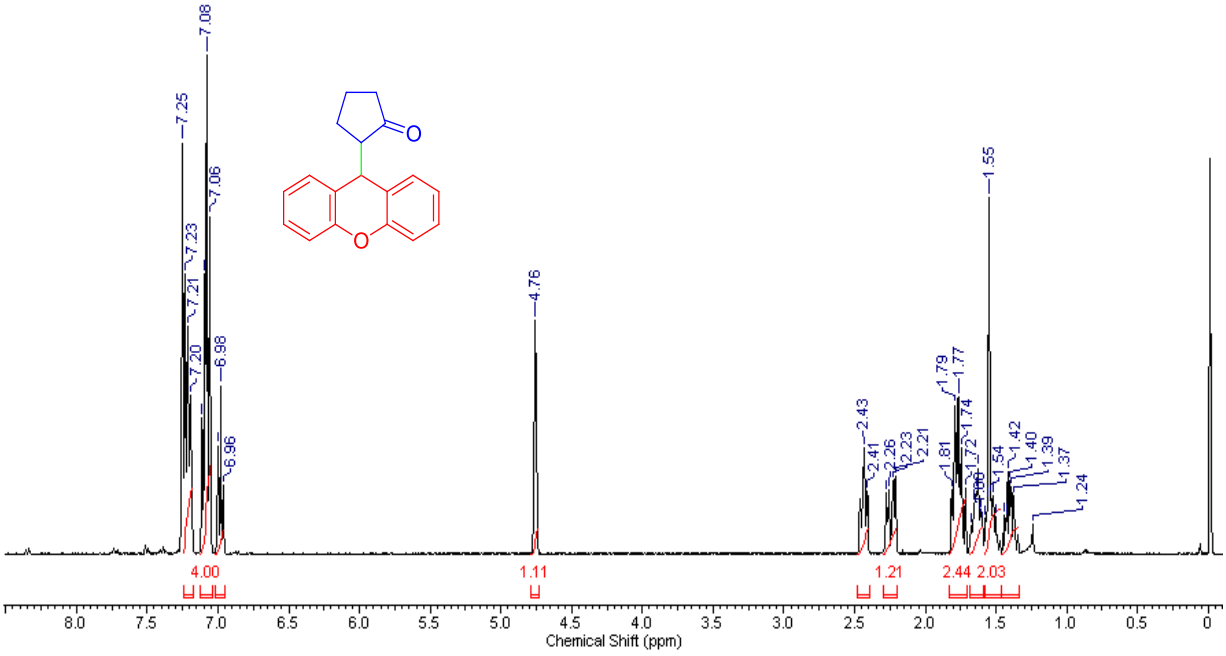
6c

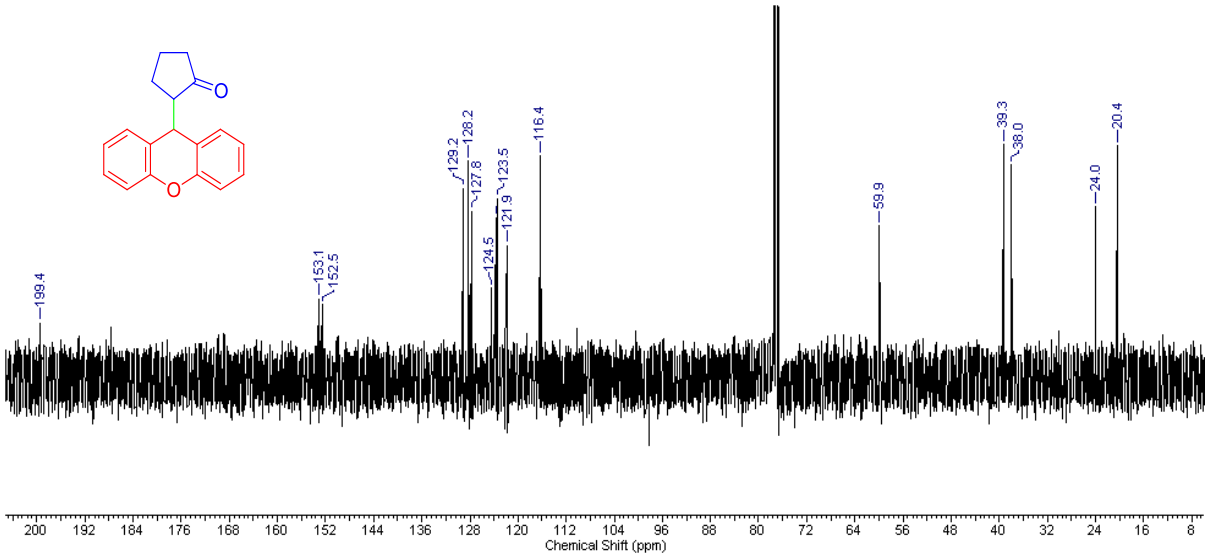
9-(2,4-dimethoxyphenyl)-9H-thioxanthene: Light yellow solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.39-7.34 (m, 4H), 7.16-7.14 (m, 4H), 6.98 (d, *J* = 8.28 Hz, 1H), 6.46 (s, 1H), 6.34 (d, *J* = 8.5 Hz, 1H), 5.64 (s, 1H), 3.84 (s, 3H), 3.73(s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.7, 157.5, 137.6, 133.0, 130.2, 130.1, 129.9, 129.6, 126.9, 126.7, 126.5, 126.4, 126.0, 124.6, 122.3, 106.2, 104.0, 98.8, 55.3, 45.7, 29.8. HRMS: calcd for $C_{21}H_{18}O_2S$ $[M+Na]^+$ 357.0972, found: 357.0969.

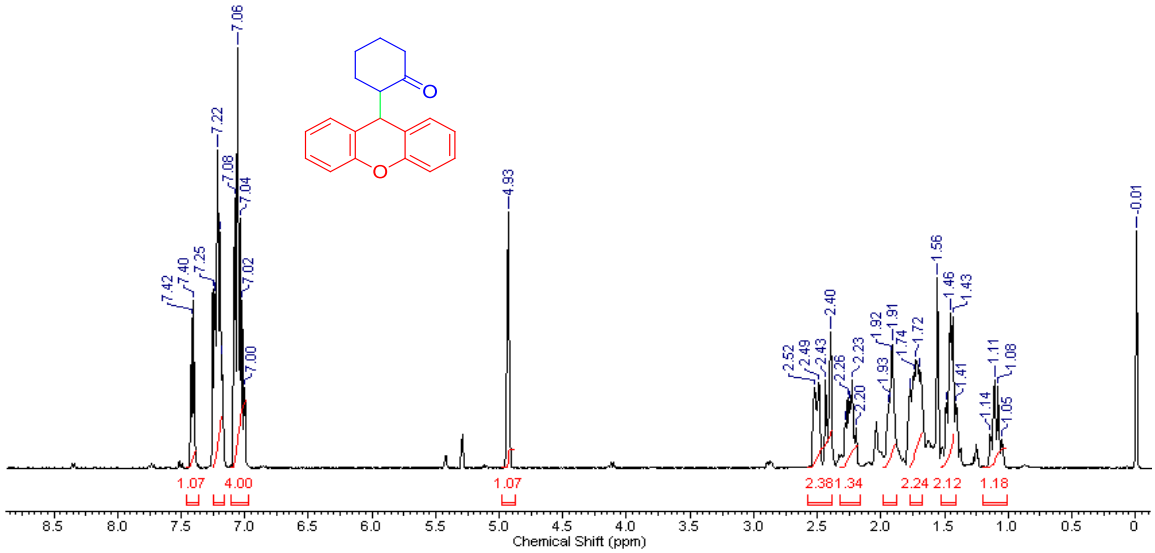


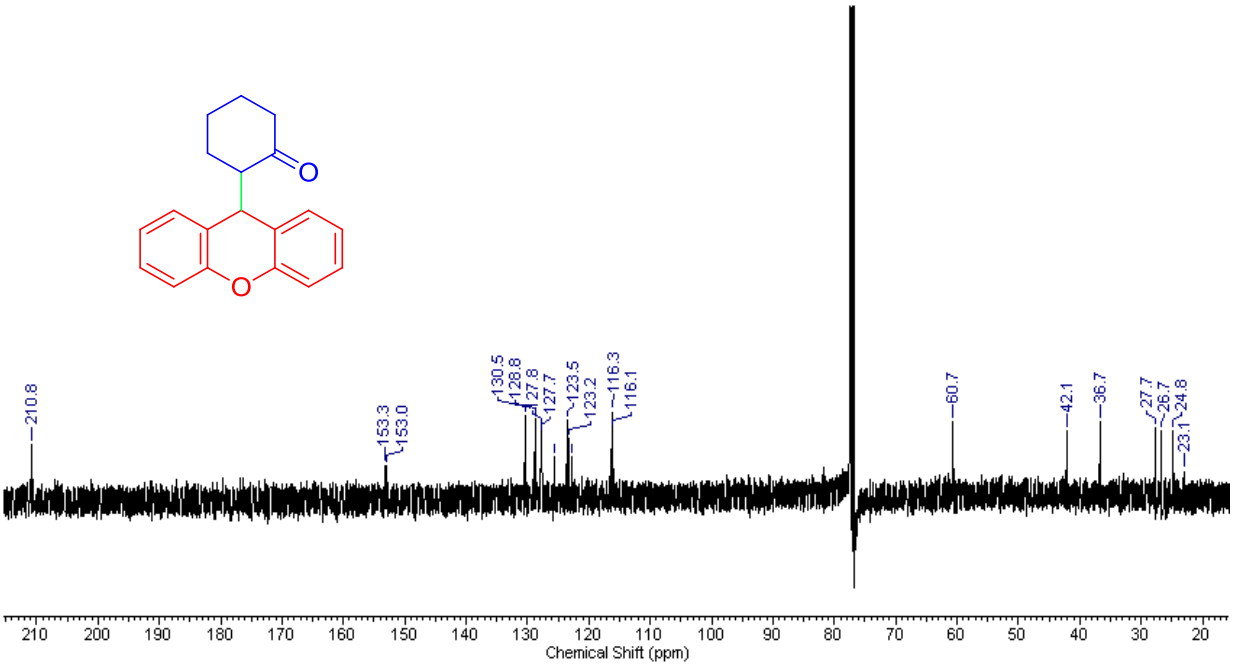
6d

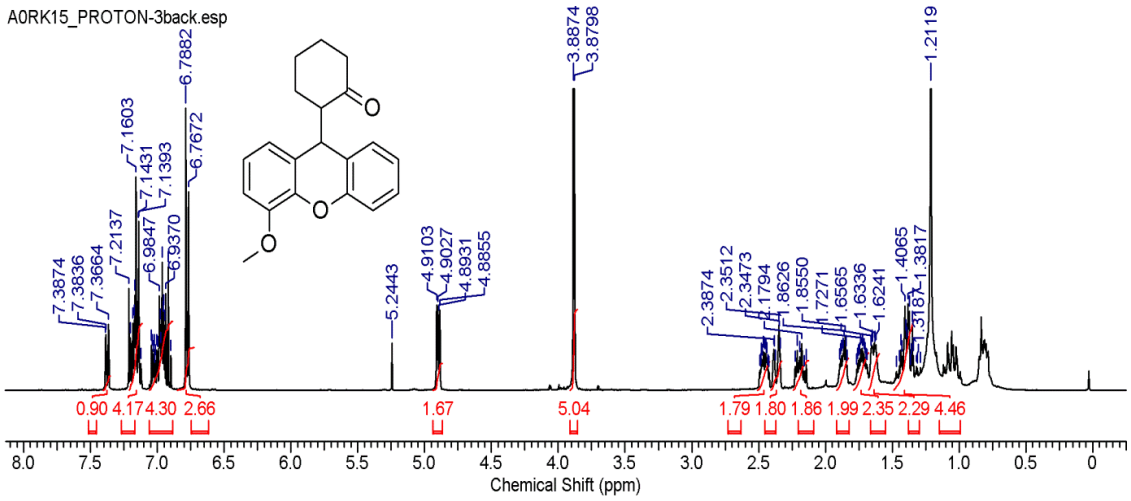
4-methyl-3-(9H-xanthen-9-yl)phenol: Light yellow solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):11.71(s,1H), 7.48-7.35 (m, 4H), 7.19-7.04 (m, 3H), 7.02-6.97 (m, 2H),6.89-6.84 (m, 1H), 6.73(dd, *J*= 6.6Hz , *J*=2.0 Hz, 1H), 5.28 (s, 1H), 4.90 (s, 1H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 161.8, 155.8, 149.0, 142.6, 138.7, 133.3, 132.5, 130.1, 128.3, 126.5, 122.7, 122.3, 120.0, 119.2, 118.5, 117.7, 117.3, 115.1, 29.8, 20.5. HRMS: calcd for $C_{20}H_{16}NaO_2$ $[M+Na]^+$ 311.1067, found: 311.1064.

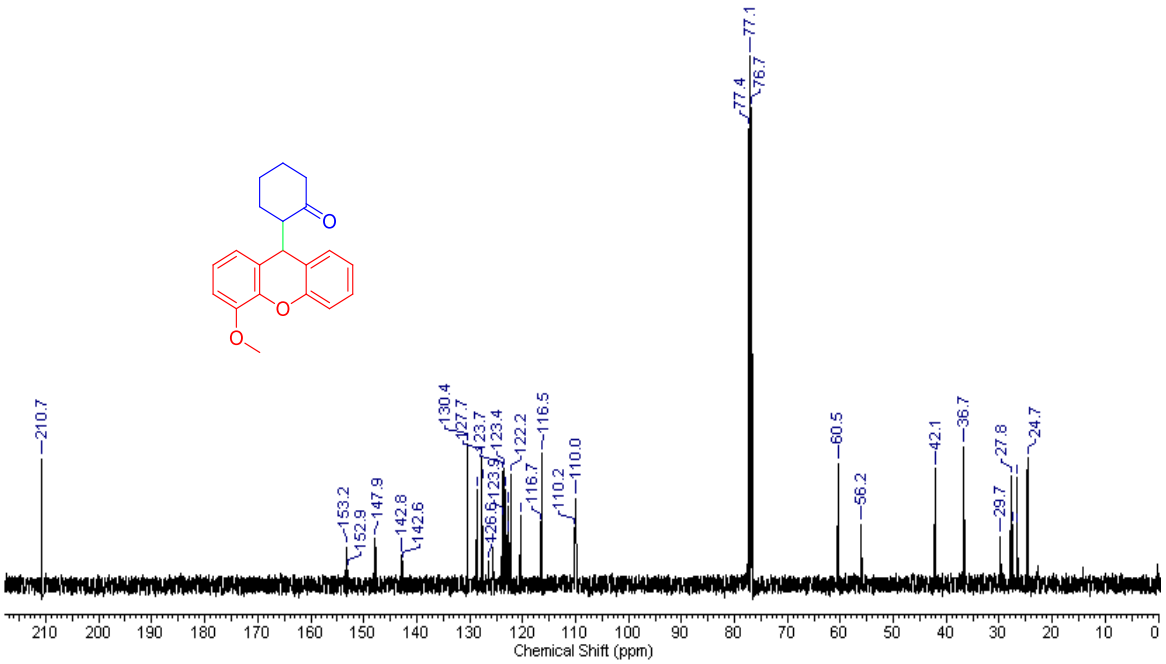


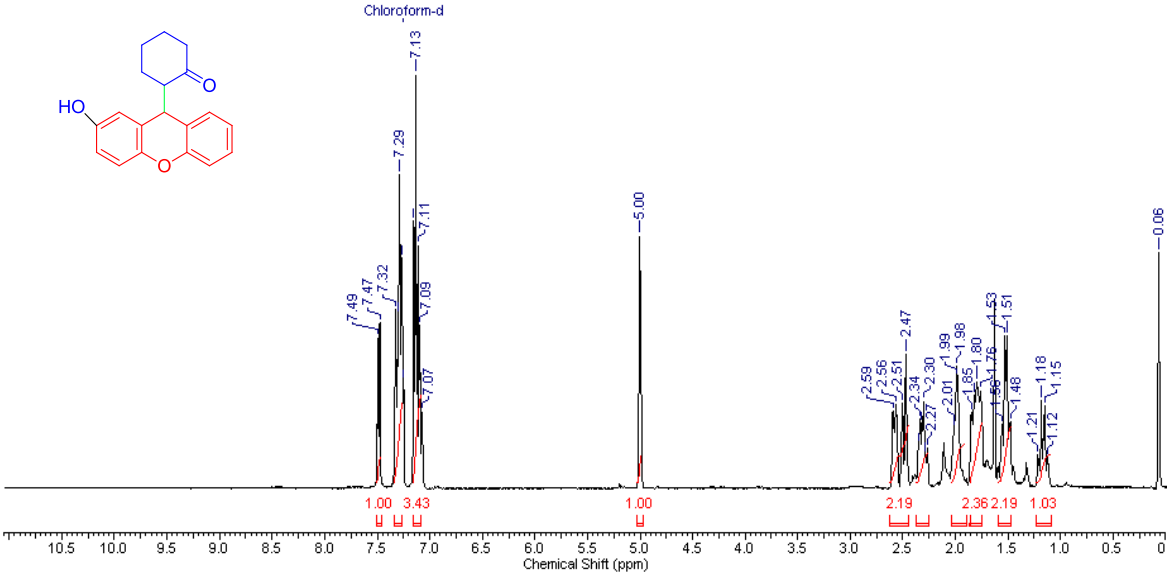

O
O
199.4
153.1
152.5
129.2
128.2
127.8
124.5
123.5
121.9
116.4
59.9
39.3
38.0
24.0
20.4
Chemical Shift (ppm)

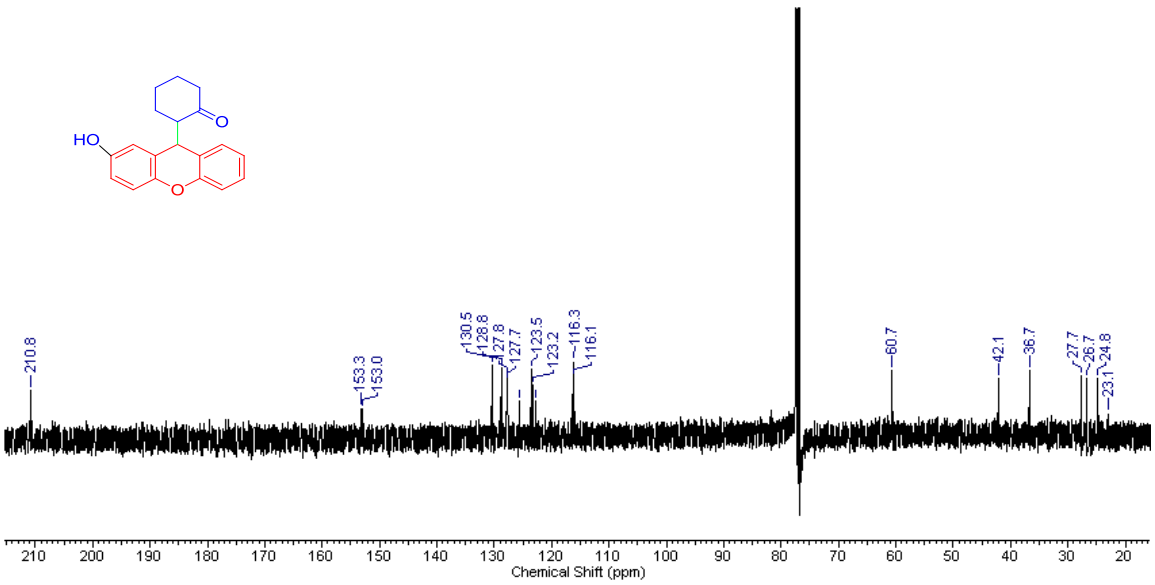

O
O
7.42
7.40
7.25
7.22
7.08
7.06
7.04
7.02
7.00
4.93
2.52
2.49
2.43
2.40
2.26
2.23
2.20
1.93
1.92
1.91
1.74
1.72
1.56
1.46
1.43
1.41
1.14
1.11
1.08
1.05
0.01
1.07
4.00
1.07
2.38
1.34
2.24
2.12
1.18
Chemical Shift (ppm)

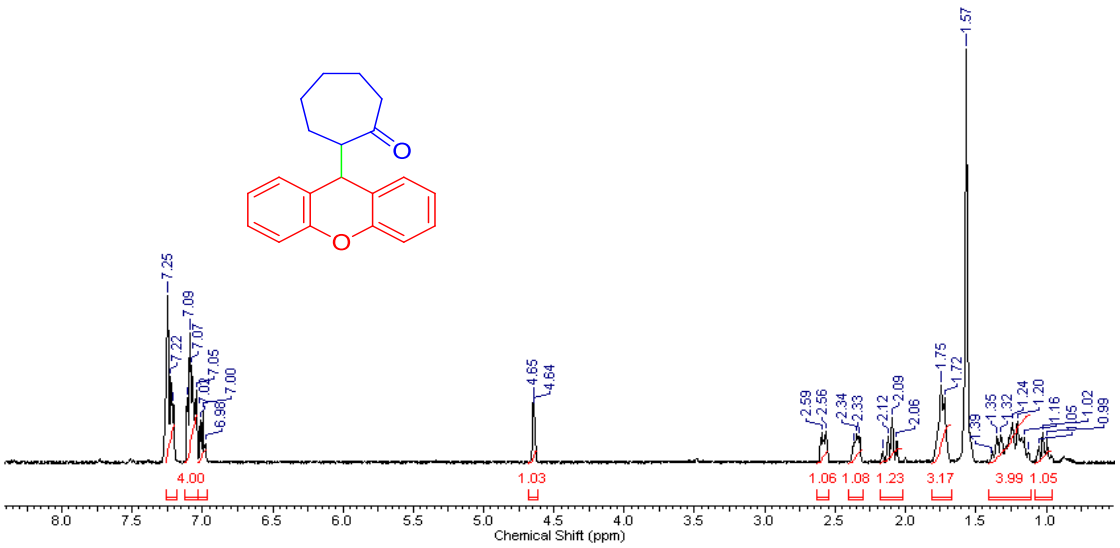

210.8
153.3
153.0
130.5
128.8
127.8
127.7
123.5
123.2
116.3
116.1
60.7
42.1
36.7
27.7
26.7
24.8
23.1
Chemical Shift (ppm)

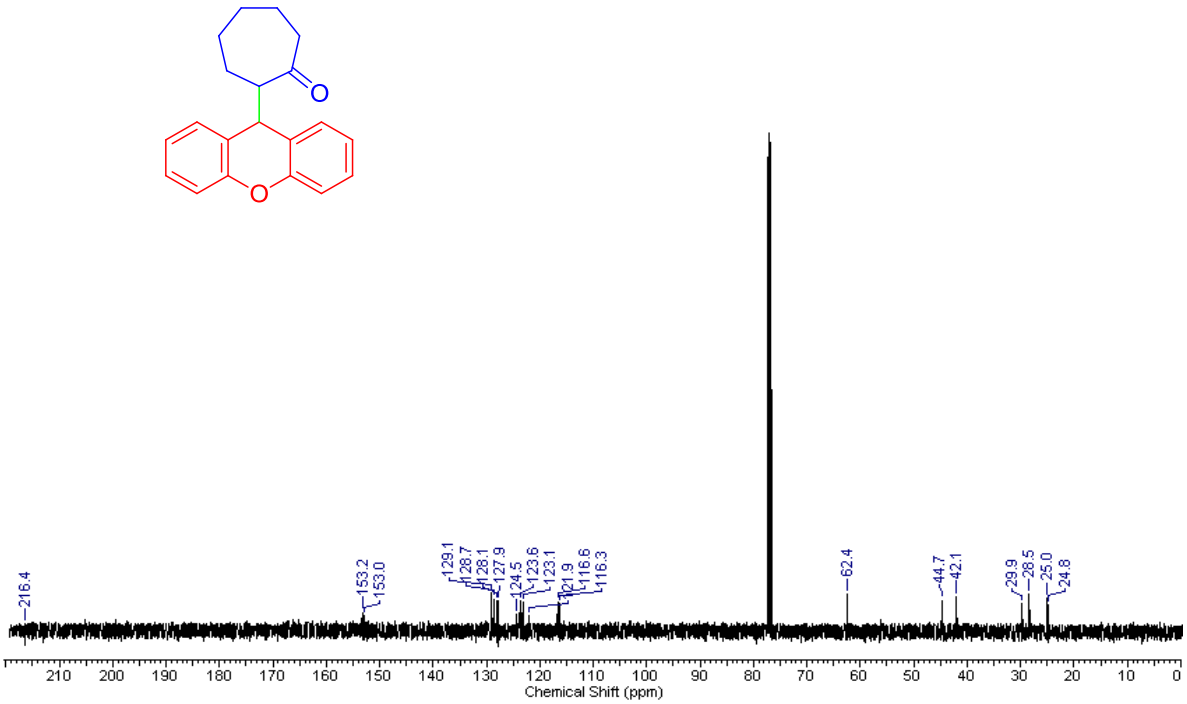

A0RK15_PROTON-3back.esp
7.7882
7.6672
7.1603
7.1431
7.1393
7.2137
6.9847
6.9370
7.3874
7.3836
7.3664
5.2443
4.9103
4.9027
4.8931
4.8855
3.8874
3.8798
1.2119
2.3874
2.3512
2.3473
1.8626
1.8550
1.7271
1.6565
1.6336
1.6241
1.4065
1.3817
0.90 4.17 4.30 2.66
1.67
5.04
1.79 1.80 1.86 1.99 2.35 2.29 4.46
Chemical Shift (ppm)

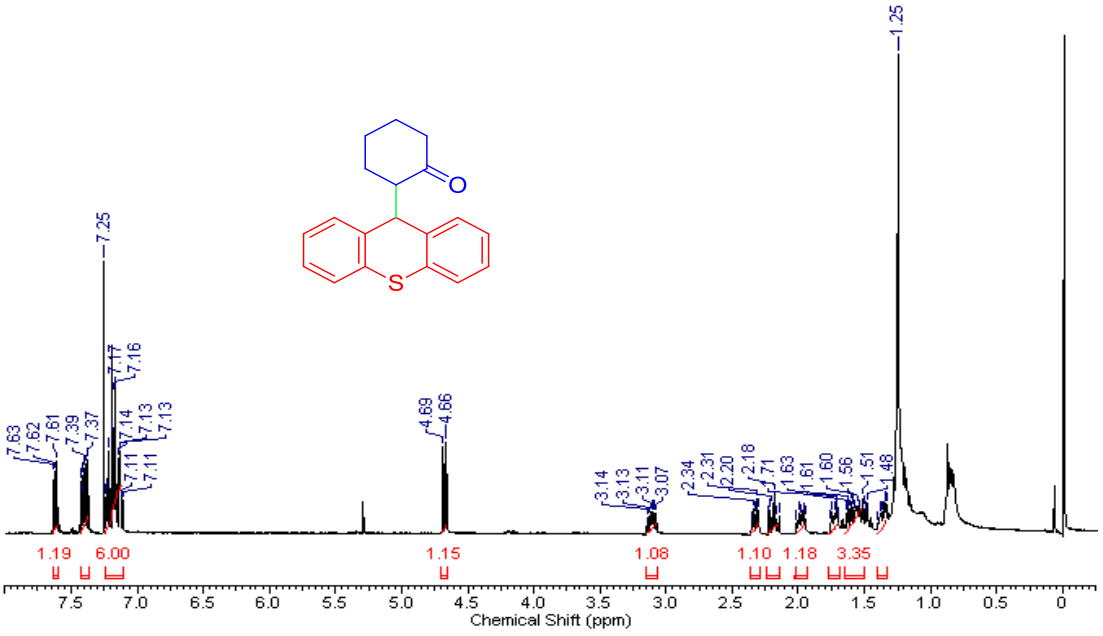

O
O
O
210.7
153.2
152.9
147.9
142.8
142.6
130.4
127.7
123.7
123.4
123.9
122.2
116.7
116.5
110.2
110.0
77.4
77.1
76.7
60.5
56.2
42.1
36.7
29.7
27.8
24.7
Chemical Shift (ppm)

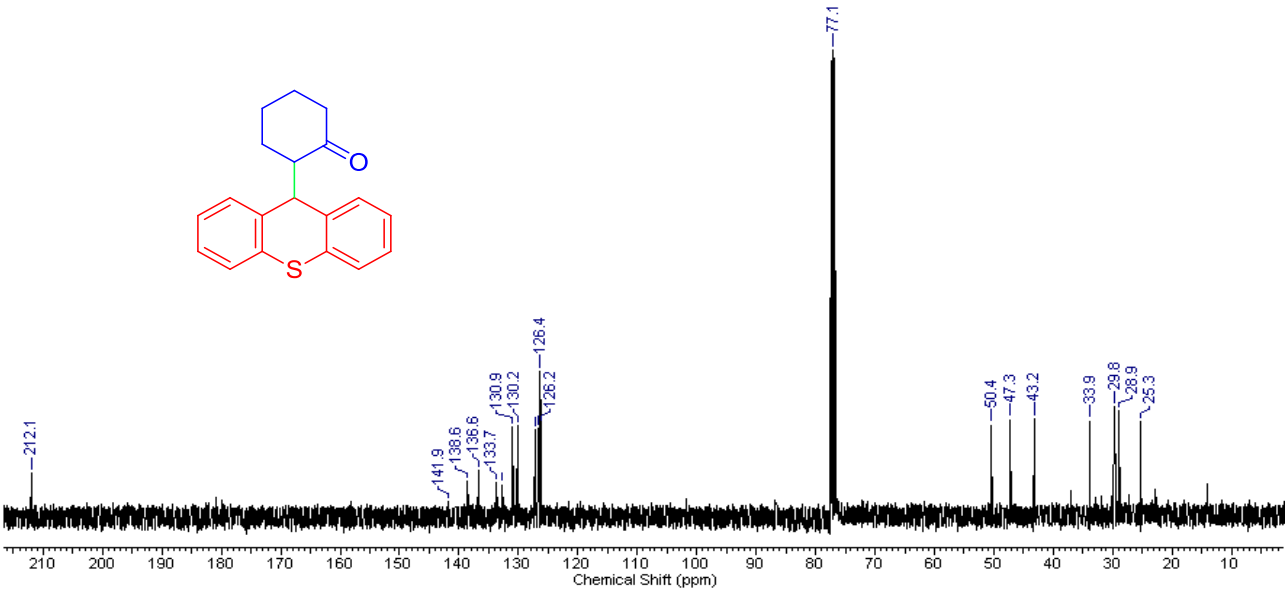

HO
O
O
Chloroform-d
7.49
7.47
7.32
7.29
7.13
7.11
7.09
7.07
5.00
2.59
2.56
2.51
2.47
2.34
2.30
2.27
2.01
1.99
1.98
1.80
1.76
1.53
1.51
1.48
1.21
1.18
1.15
1.12
0.06
1.00
3.43
1.00
2.19
2.36
2.19
1.03
Chemical Shift (ppm)

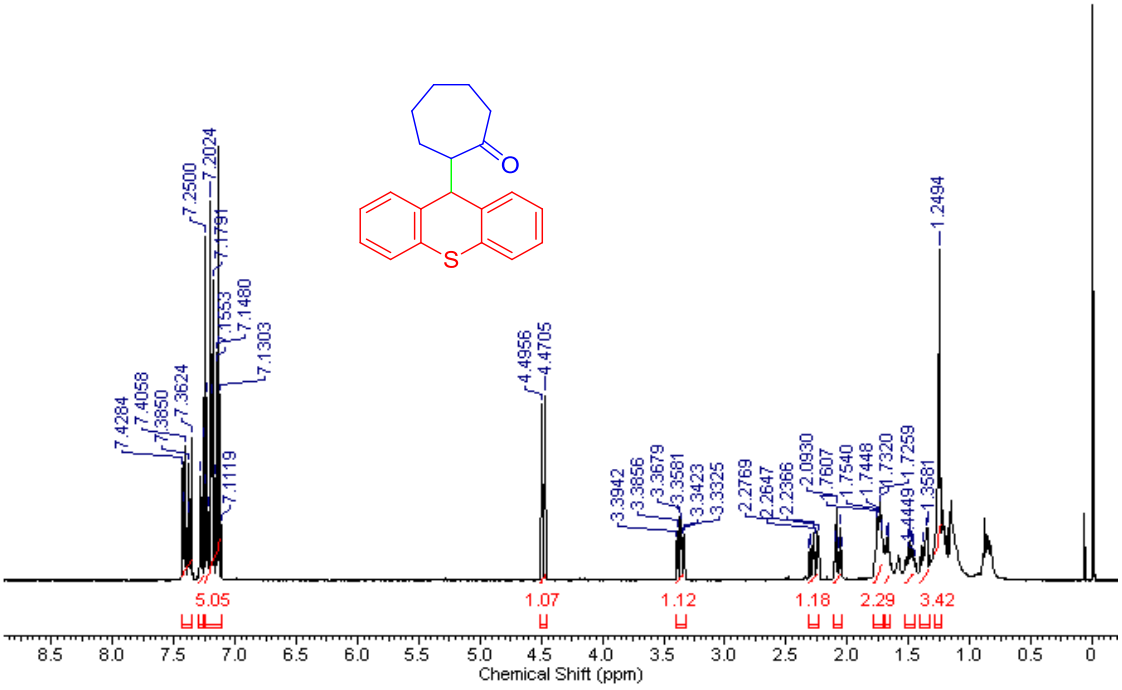

HO
O
O
210.8
153.3
153.0
130.5
128.8
127.8
127.7
123.5
123.2
116.3
116.1
60.7
42.1
36.7
27.7
26.7
24.8
23.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
Chemical Shift (ppm)

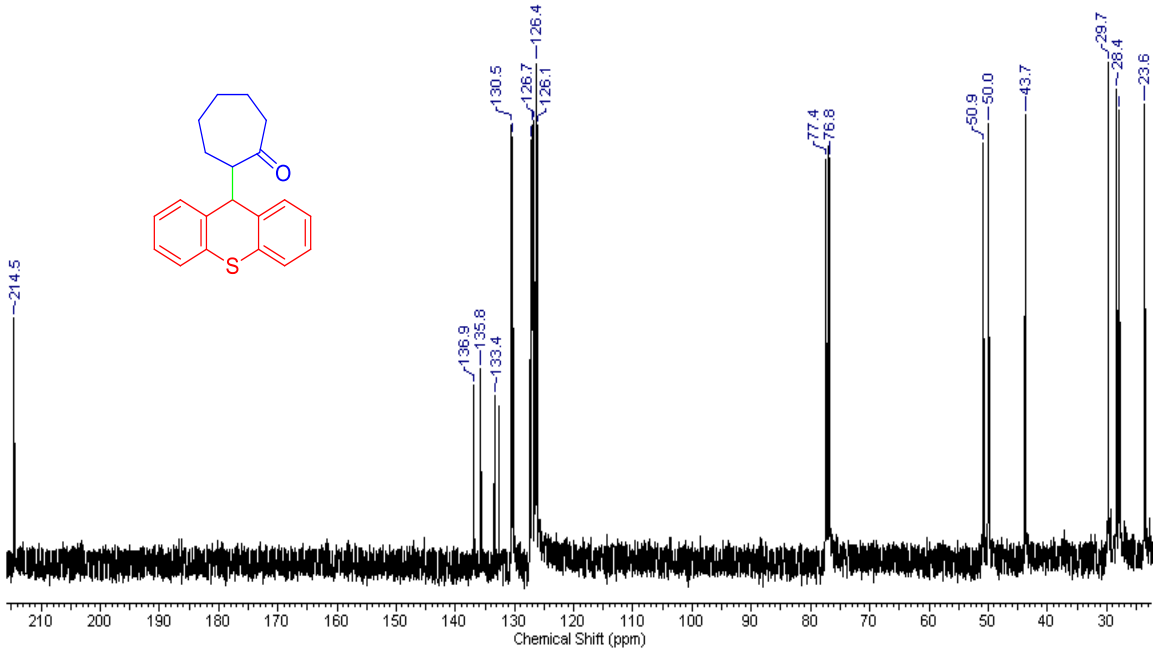

O
O
7.25
7.22
7.09
7.07
7.05
7.03
7.00
6.98
4.65
4.64
2.59
2.56
2.34
2.33
2.12
2.09
2.06
1.75
1.72
1.57
1.39
1.35
1.32
1.24
1.20
1.16
1.05
1.02
0.99
4.00
1.03
1.06
1.08
1.23
3.17
3.99
1.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
Chemical Shift (ppm)

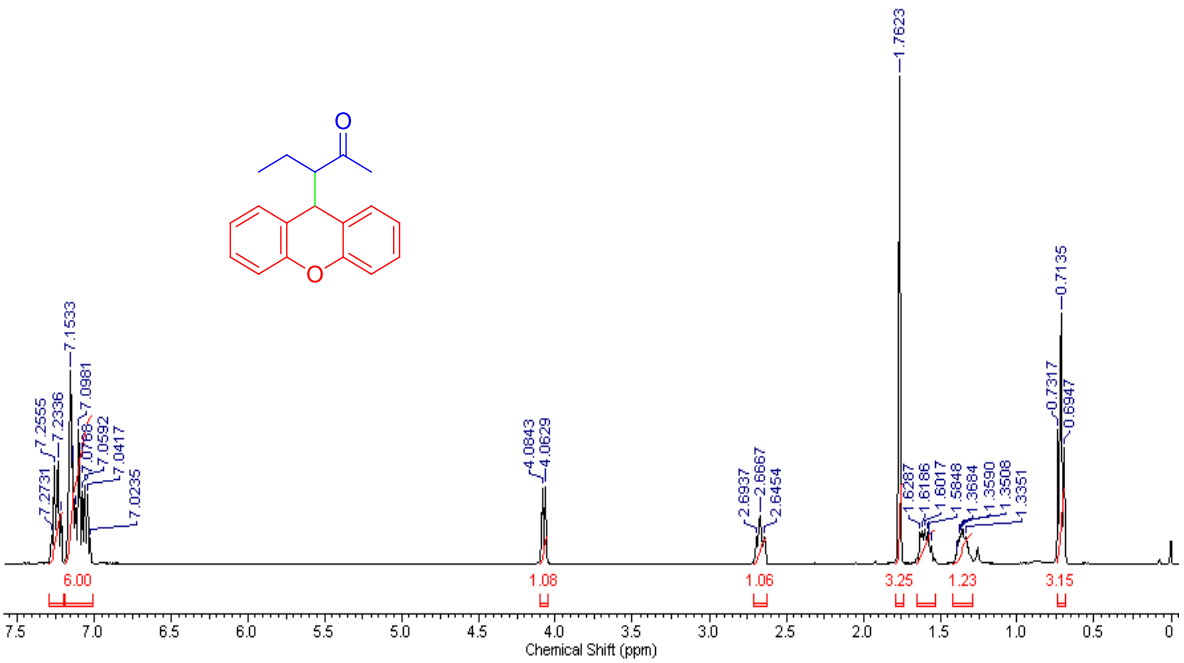

O
O
216.4
153.2
153.0
129.1
128.7
128.1
127.9
124.5
123.6
123.1
121.9
116.6
116.3
62.4
44.7
42.1
29.9
28.5
25.0
24.8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

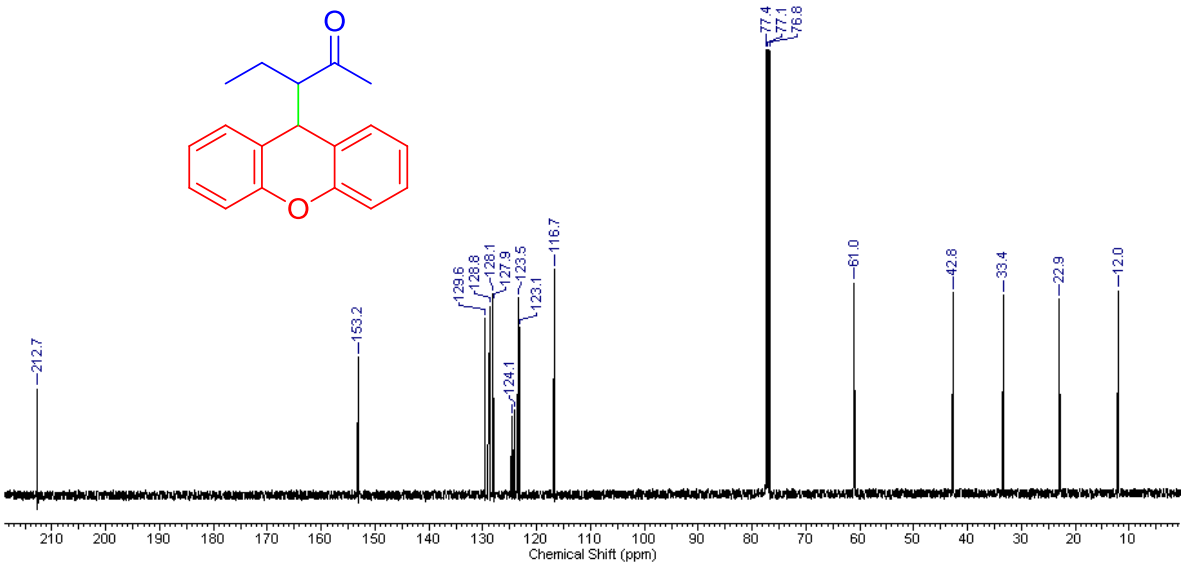

O
S
7.63
7.62
7.61
7.39
7.37
7.25
7.17
7.16
7.14
7.13
7.13
7.11
7.11
4.69
4.66
3.14
3.13
3.11
3.07
2.34
2.31
2.20
2.18
1.71
1.63
1.61
1.60
1.56
1.51
1.48
1.25
1.19
6.00
1.15
1.08
1.10
1.18
3.35
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

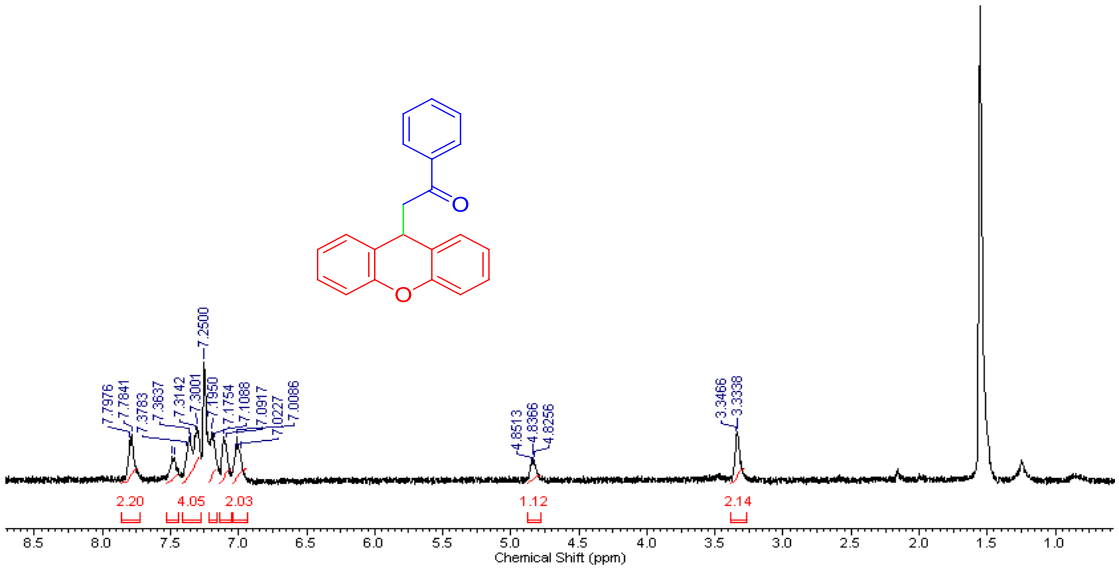

O
S
212.1
141.9
138.6
136.6
133.7
130.9
130.2
126.4
126.2
77.1
50.4
47.3
43.2
33.9
29.8
28.9
25.3
Chemical Shift (ppm)

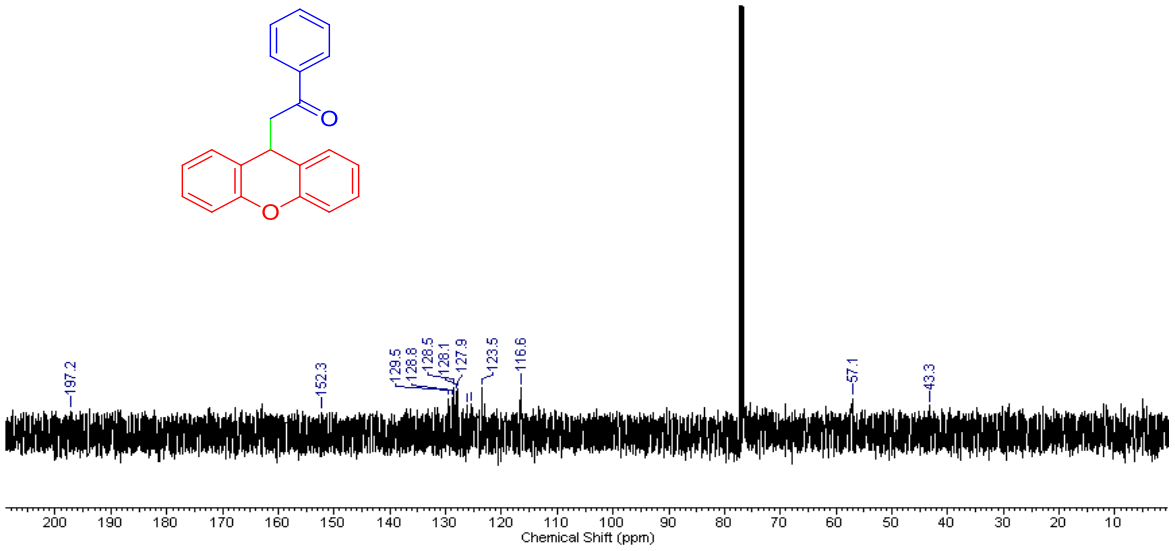

O
S
7.4284
7.4058
7.3850
7.3624
7.2500
7.2024
7.1791
7.1553
7.1480
7.1303
7.1119
4.4956
4.4705
3.3942
3.3856
3.3679
3.3581
3.3423
3.3325
2.2769
2.2647
2.2366
2.0930
1.7607
1.7540
1.7448
1.7320
1.7259
1.4449
1.3581
1.2494
5.05
1.07
1.12
1.18
2.29
3.42
Chemical Shift (ppm)

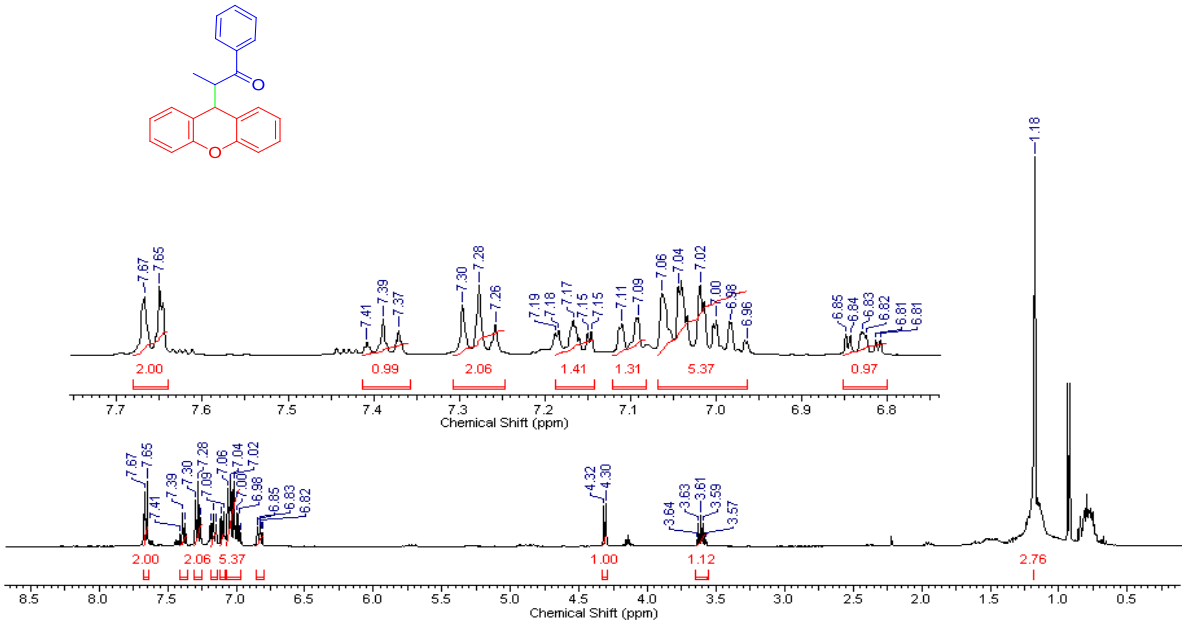

O
S
214.5
136.9
135.8
133.4
130.5
126.7
126.4
126.1
77.4
76.8
50.9
50.0
43.7
29.7
28.4
23.6
Chemical Shift (ppm)

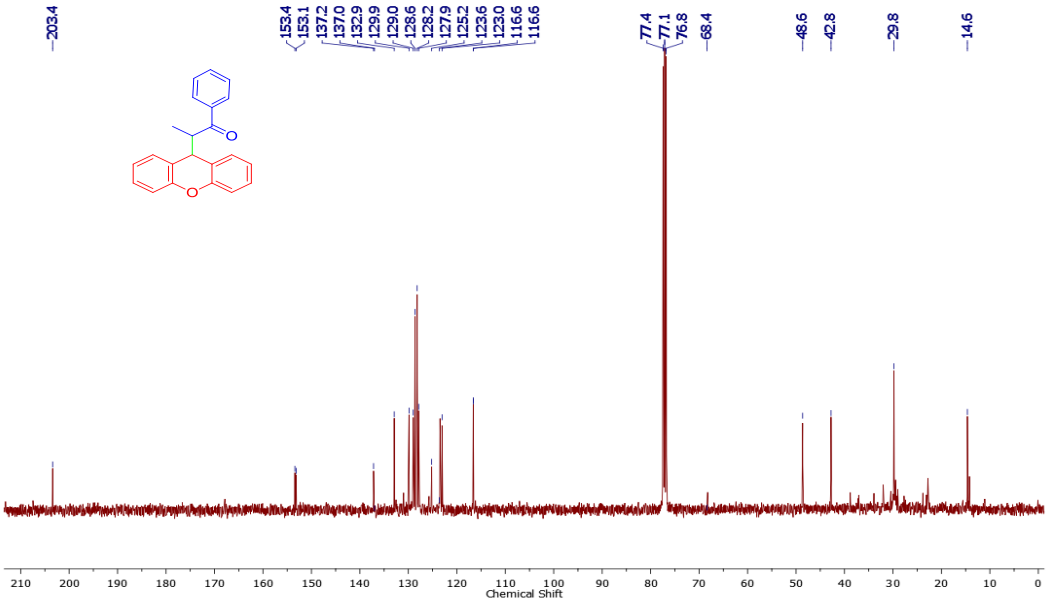

O
O
7.2731
7.2555
7.2336
7.1533
7.0981
7.0768
7.0592
7.0417
7.0235
4.0843
4.0629
2.6937
2.6667
2.6454
1.7623
1.6287
1.6186
1.6017
1.5848
1.3684
1.3590
1.3508
1.3351
0.7317
0.7135
0.6947
6.00
1.08
1.06
3.25
1.23
3.15
Chemical Shift (ppm)

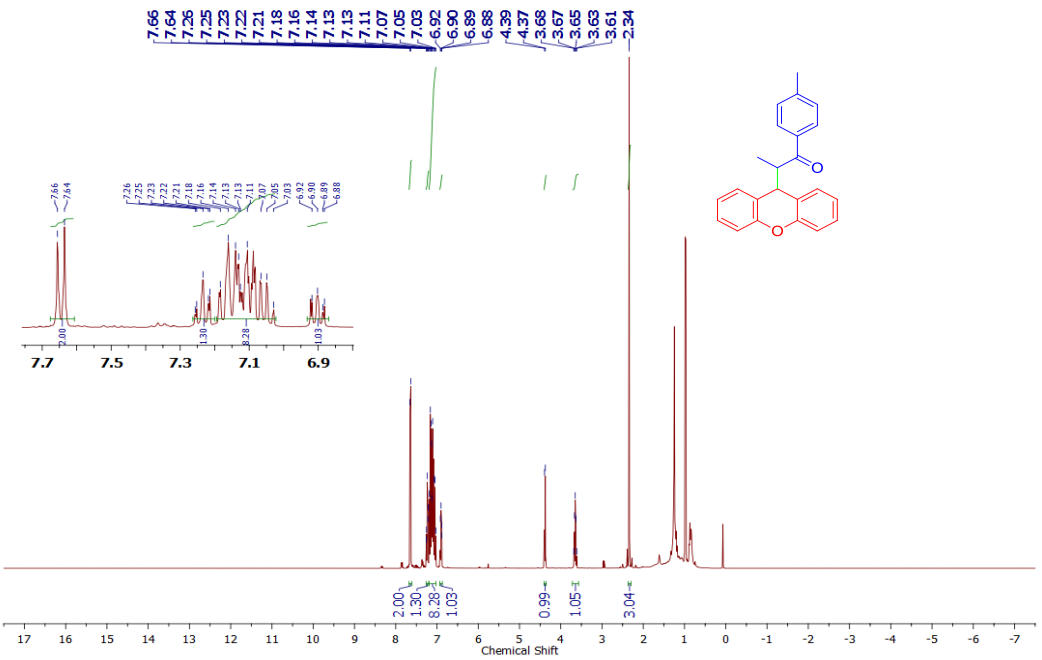

O
O
77.4
77.1
76.8
212.7
153.2
129.6
128.8
128.1
127.9
123.5
123.1
116.7
124.1
61.0
42.8
33.4
22.9
12.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Chemical Shift (ppm)

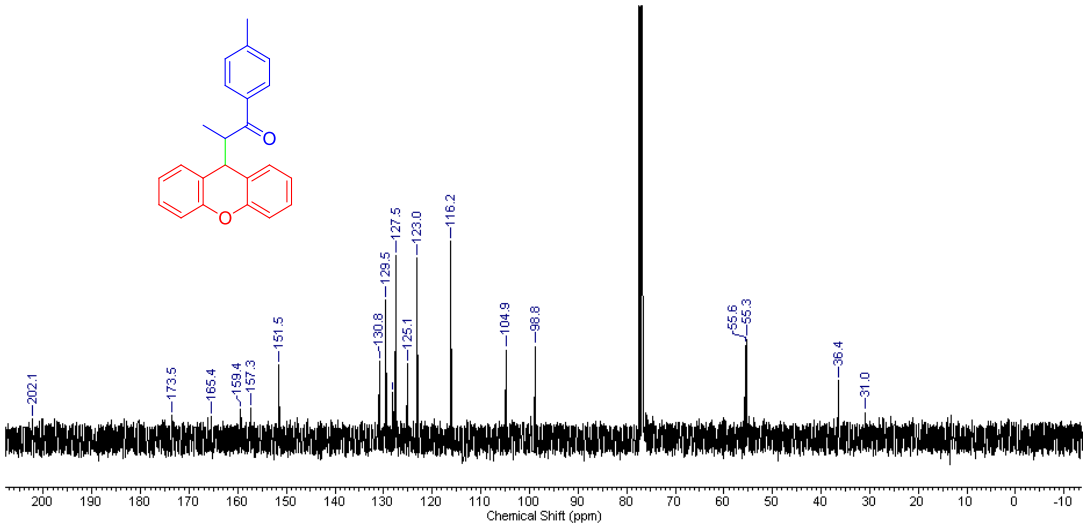

O
O
7.7976
7.7841
7.3783
7.3637
7.3142
7.3001
7.2500
7.1950
7.1754
7.1088
7.0917
7.0227
7.0066
4.8513
4.8366
4.8256
3.3466
3.3338
2.20
4.05
2.03
1.12
2.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
Chemical Shift (ppm)

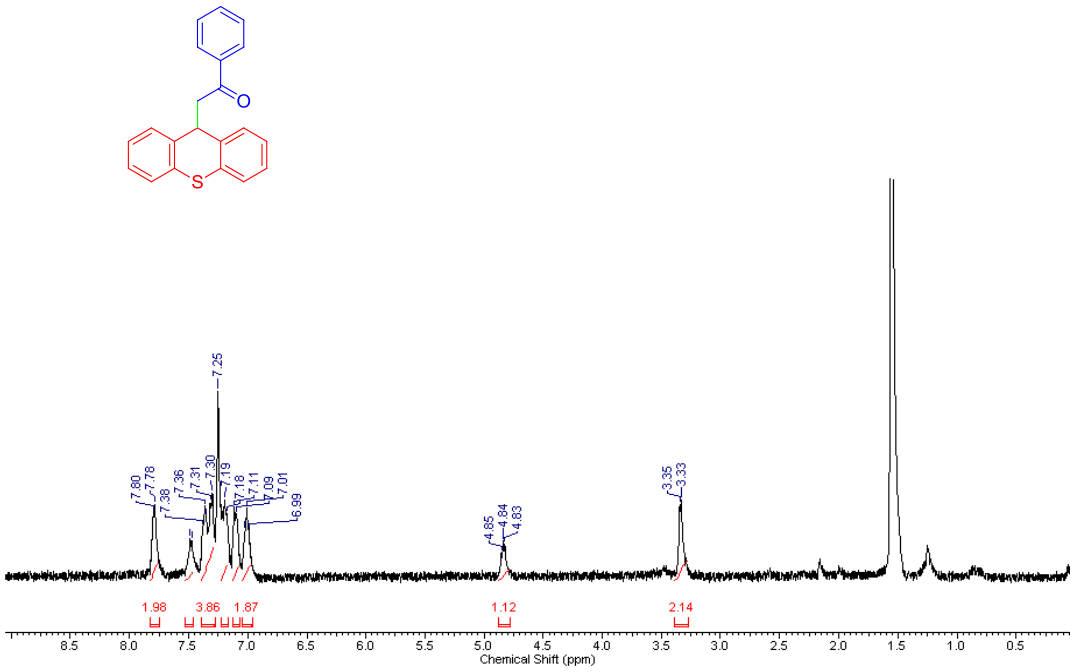

O
O
197.2
152.3
129.5
128.8
128.5
128.1
127.9
123.5
116.6
57.1
43.3
Chemical Shift (ppm)

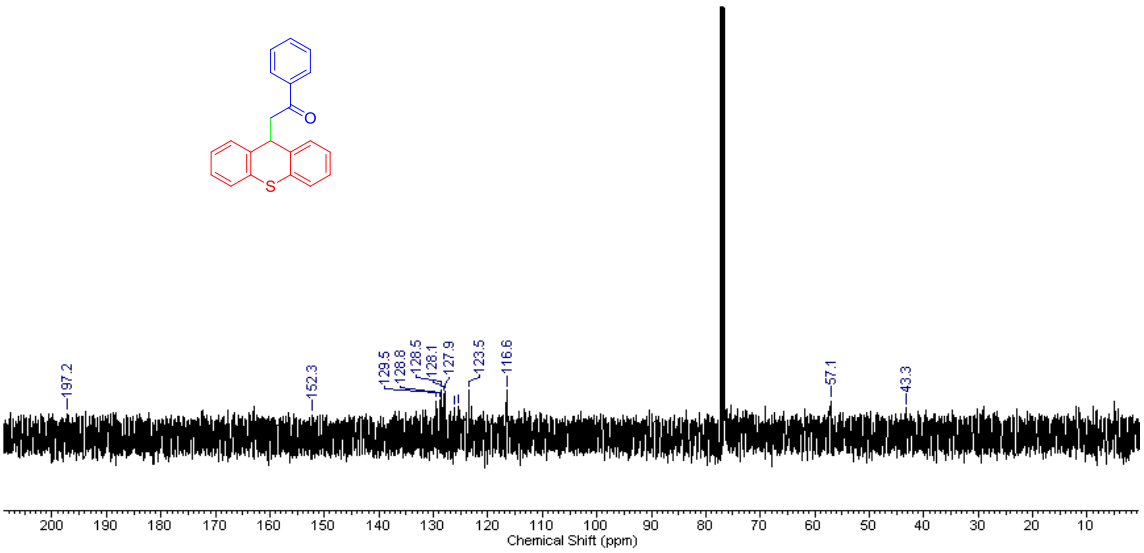

O
O
7.67
7.65
7.41
7.39
7.37
7.30
7.28
7.26
7.19
7.18
7.17
7.15
7.15
7.11
7.09
7.06
7.04
7.02
7.00
6.98
6.96
6.85
6.84
6.83
6.82
6.81
6.81
2.00
0.99
2.06
1.41
1.31
5.37
0.97
Chemical Shift (ppm)
1.18
4.32
4.30
3.64
3.63
3.61
3.59
3.57
2.00
2.06
5.37
1.00
1.12
2.76
Chemical Shift (ppm)

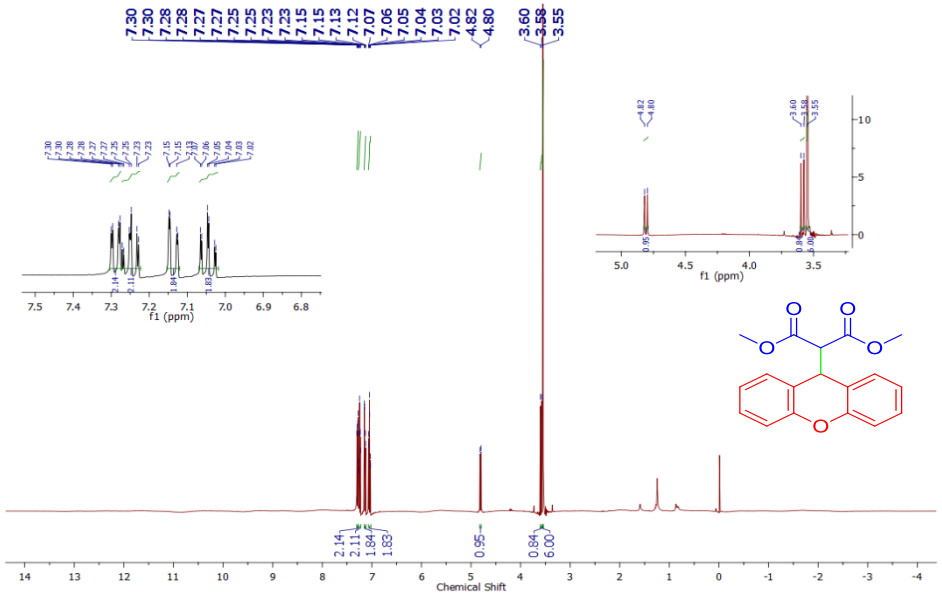

203.4
153.4
153.1
137.2
137.0
132.9
129.9
129.0
128.6
128.2
127.9
125.2
123.6
123.0
116.6
116.6
77.4
77.1
76.8
68.4
48.6
42.8
29.8
14.6
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift

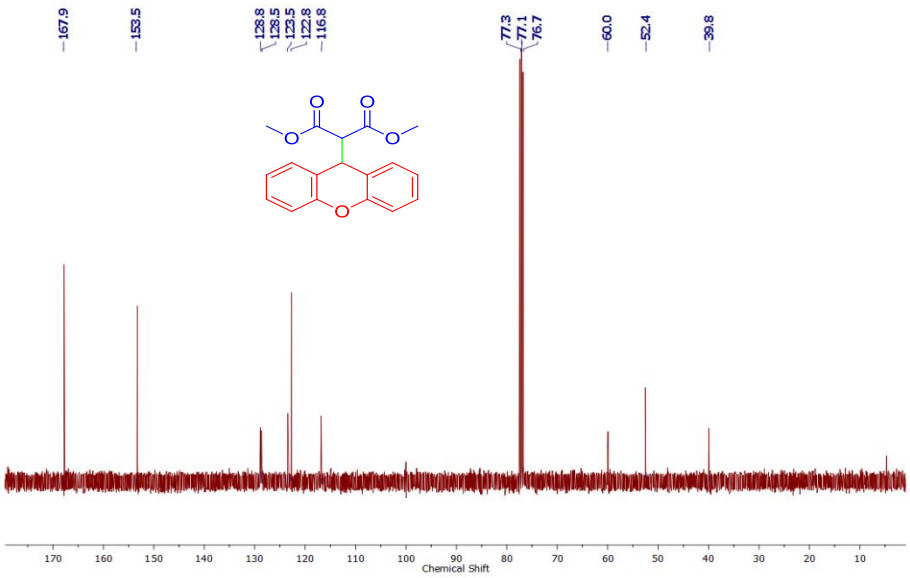

7.66
7.64
7.26
7.25
7.23
7.22
7.21
7.18
7.16
7.14
7.13
7.13
7.11
7.07
7.05
7.03
6.92
6.90
6.89
6.88
4.39
4.37
3.68
3.67
3.65
3.63
3.61
2.34
O
O
7.7
7.5
7.3
7.1
6.9
2.00
1.30
8.28
1.03
0.99
1.05
3.04
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7
Chemical Shift

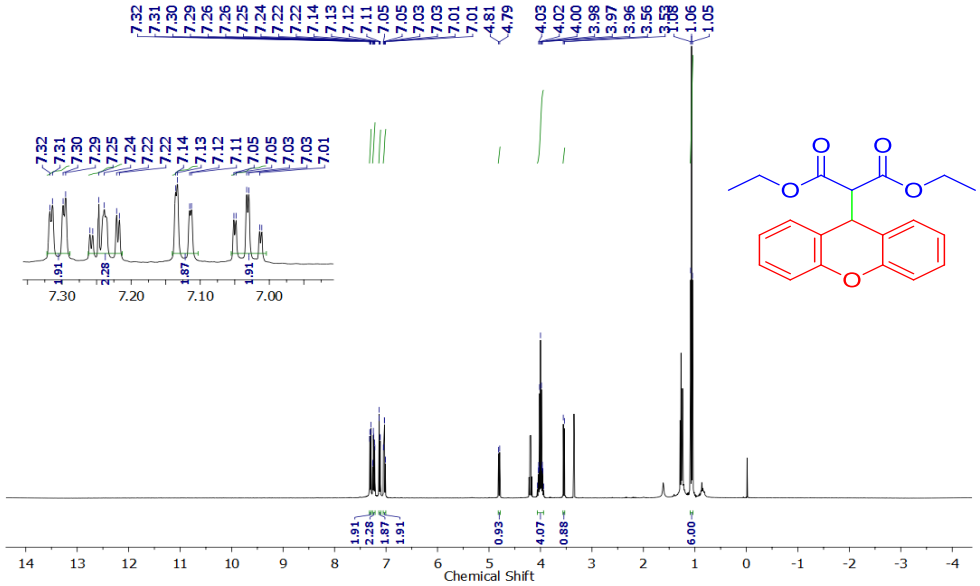

O
O
202.1
173.5
165.4
159.4
157.3
151.5
130.8
129.5
127.5
125.1
123.0
116.2
104.9
98.8
55.6
55.3
36.4
31.0
Chemical Shift (ppm)

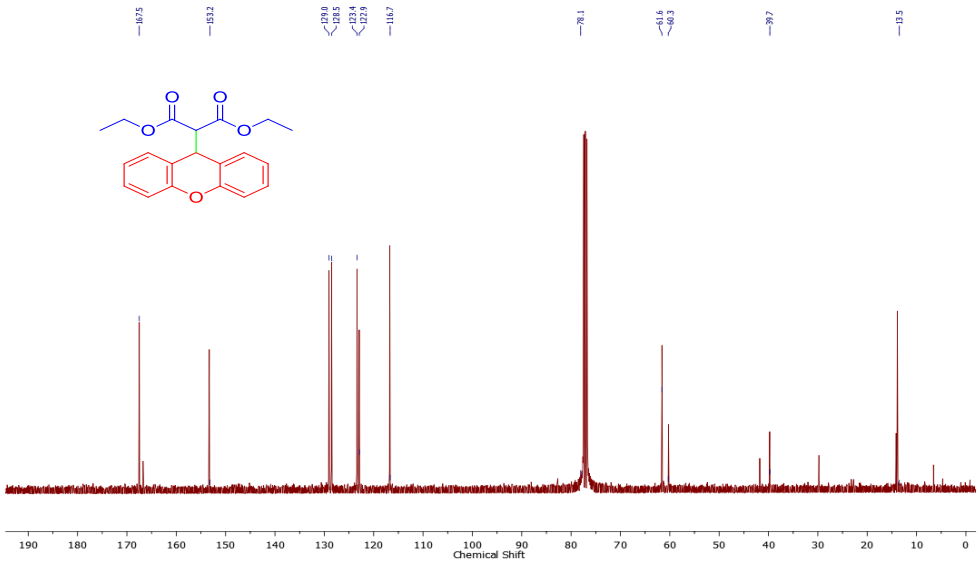

O
S
7.80
7.78
7.36
7.36
7.31
7.30
7.25
7.19
7.18
7.11
7.09
7.01
6.99
4.85
4.84
4.83
3.35
3.33
1.98
3.86
1.87
1.12
2.14
Chemical Shift (ppm)

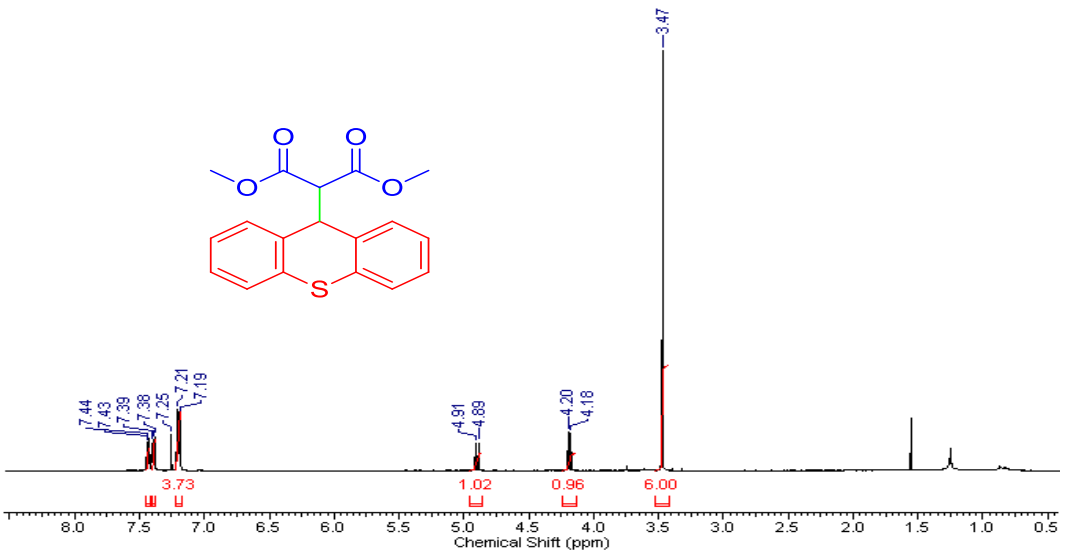

O
S
197.2
152.3
129.5
128.8
128.5
128.1
127.9
123.5
116.6
57.1
43.3
Chemical Shift (ppm)

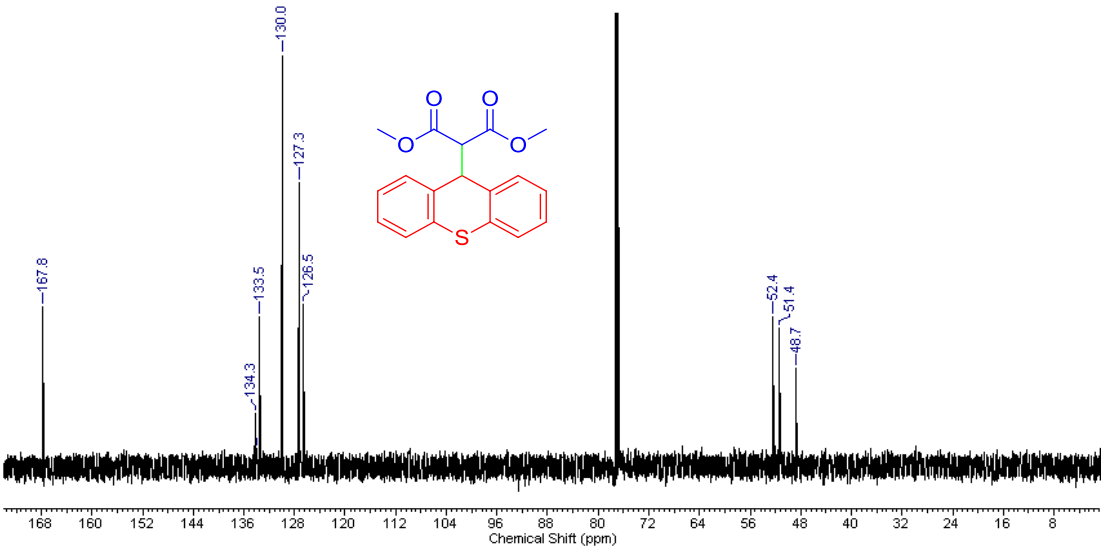

7.30
7.30
7.28
7.28
7.27
7.27
7.25
7.25
7.23
7.23
7.15
7.15
7.13
7.12
7.07
7.06
7.05
7.04
7.03
7.02
4.82
4.80
3.60
3.58
3.55
f1 (ppm)
Chemical Shift
2.14
2.11
1.84
1.83
0.95
0.84
6.00
O
O
O
O
O

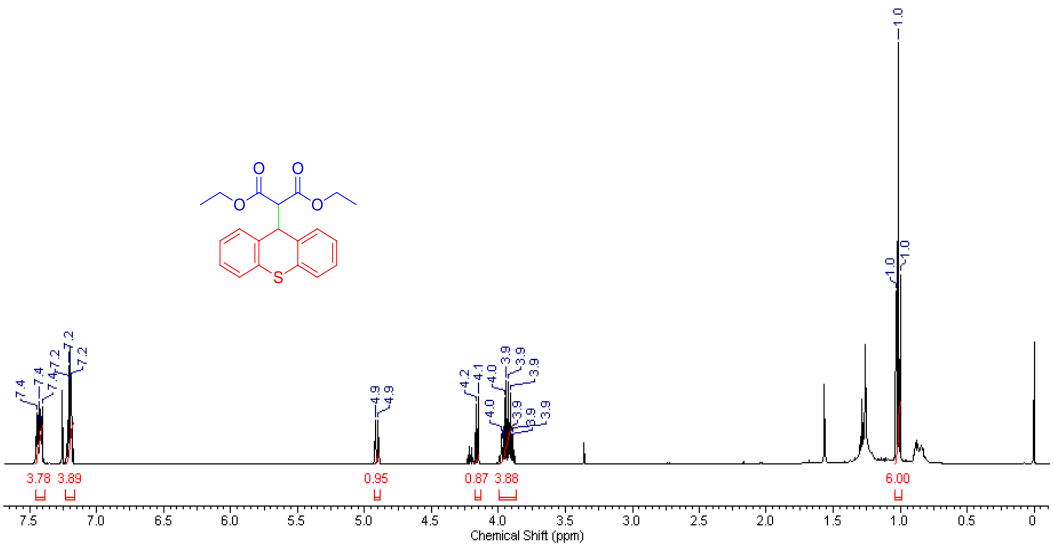

167.9
153.5
128.8
128.5
123.5
122.8
116.8
77.3
77.1
76.7
60.0
52.4
39.8
Chemical Shift

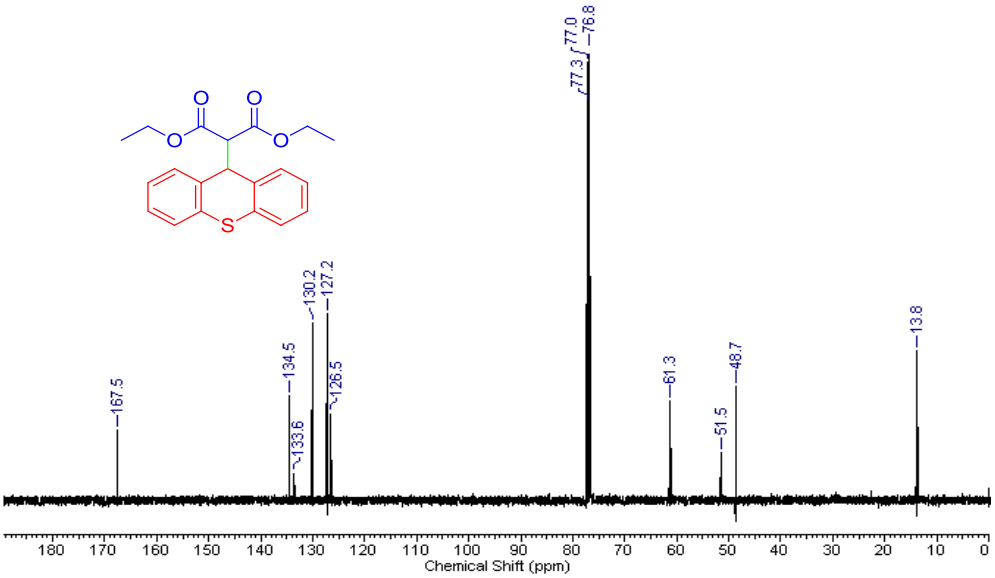

7.32
7.31
7.30
7.29
7.26
7.25
7.24
7.22
7.22
7.14
7.13
7.12
7.11
7.05
7.03
7.03
7.01
7.01
4.81
4.79
4.03
4.02
4.00
3.98
3.97
3.96
3.56
1.06
1.05
1.91
2.28
1.87
1.91
0.93
4.07
0.88
6.00
Chemical Shift

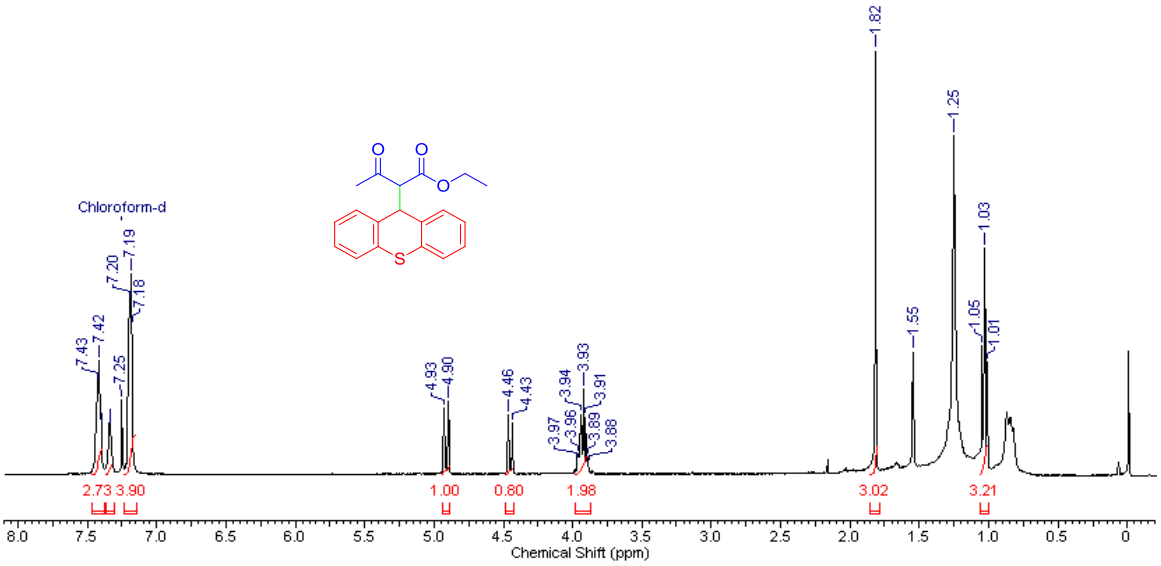

167.5
153.2
129.0
128.5
123.4
122.9
116.7
78.1
61.6
60.3
39.7
13.5
Chemical Shift

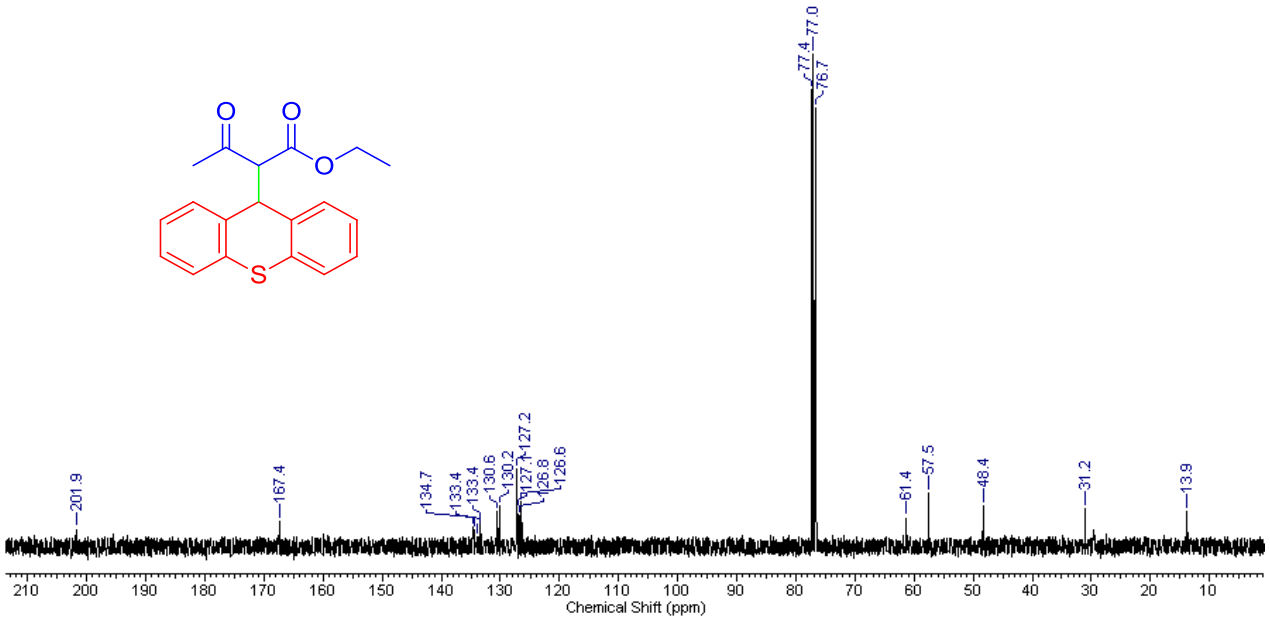

3.47
7.44
7.43
7.39
7.38
7.25
7.21
7.19
4.91
4.89
4.20
4.18
3.73
1.02
0.96
6.00
Chemical Shift (ppm)

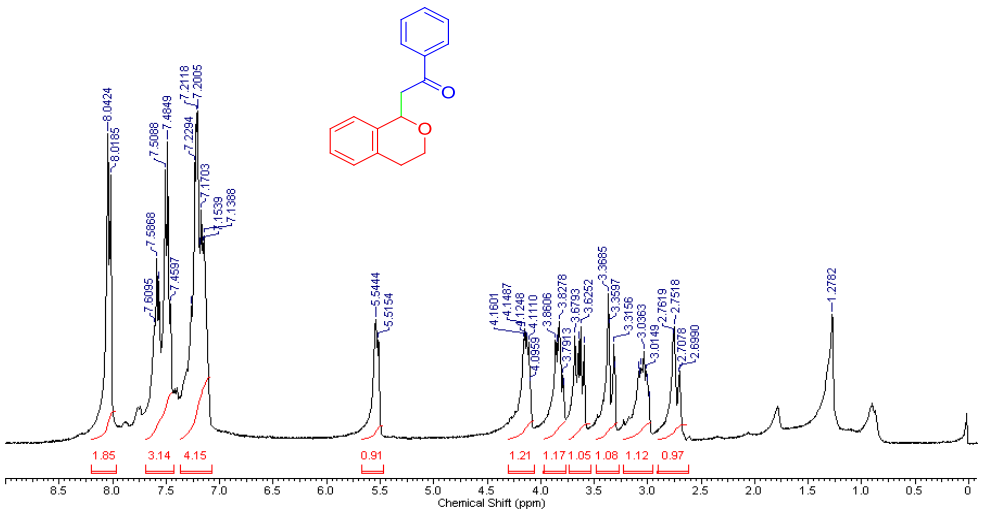

167.8
134.3
133.5
130.0
127.3
126.5
52.4
51.4
48.7
Chemical Shift (ppm)

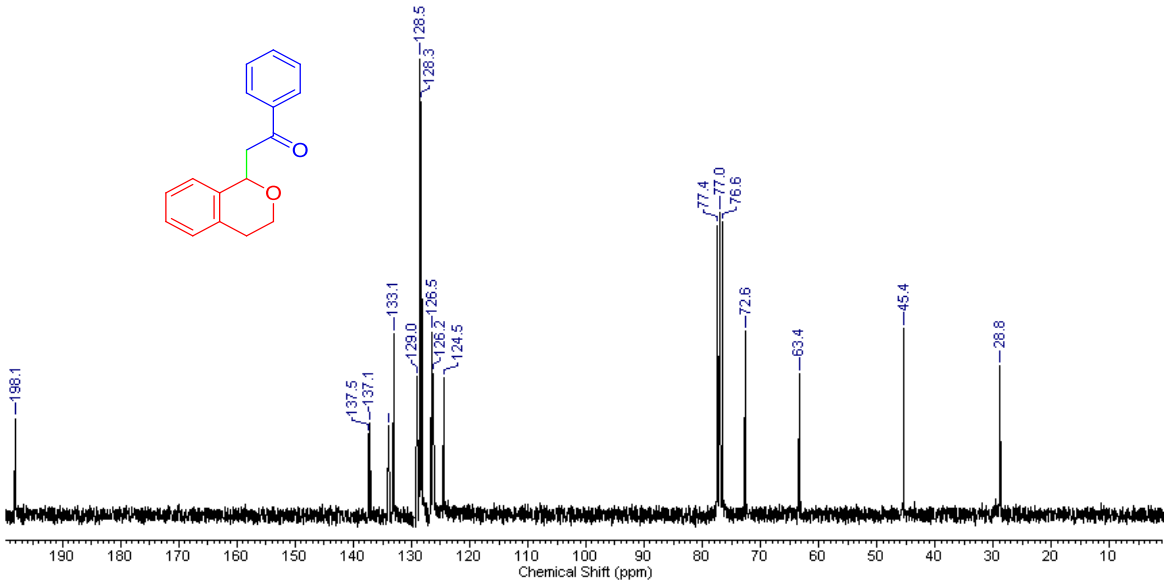

7.4
7.4
7.4
7.2
7.2
7.2
4.9
4.9
4.2
4.1
4.0
4.0
3.9
3.9
3.9
3.9
3.9
3.9
1.0
1.0
1.0
3.78
3.89
0.95
0.87
3.88
6.00
Chemical Shift (ppm)

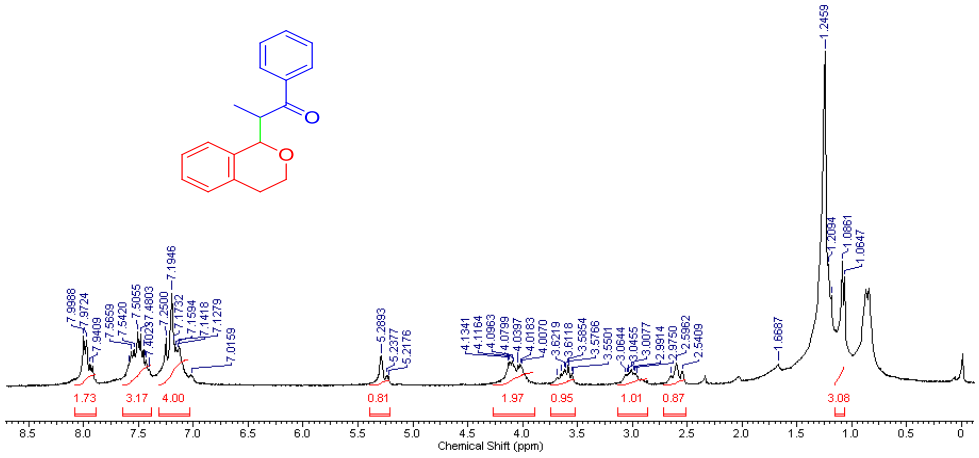

O
O
O
O
S
167.5
134.5
133.6
130.2
127.2
126.5
77.3
77.0
76.8
61.3
51.5
48.7
13.8
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

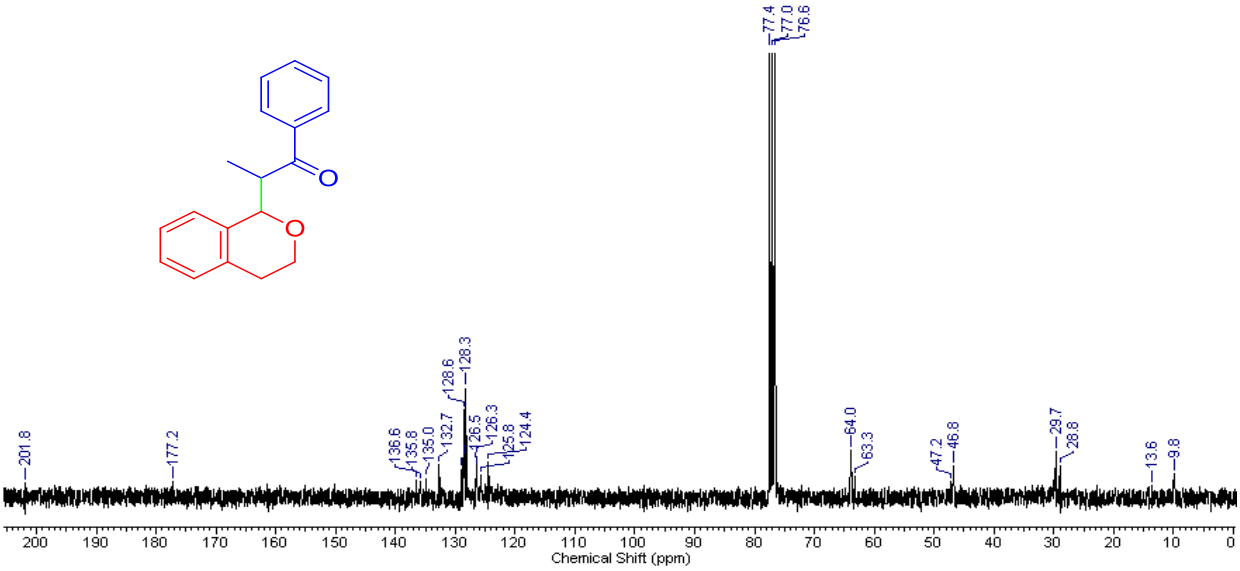

Chloroform-d
O
O
O
S
7.43
7.42
7.25
7.20
7.19
7.18
4.93
4.90
4.46
4.43
3.97
3.96
3.94
3.93
3.91
3.89
3.88
1.82
1.55
1.25
1.05
1.03
1.01
2.73
3.90
1.00
0.80
1.98
3.02
3.21
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

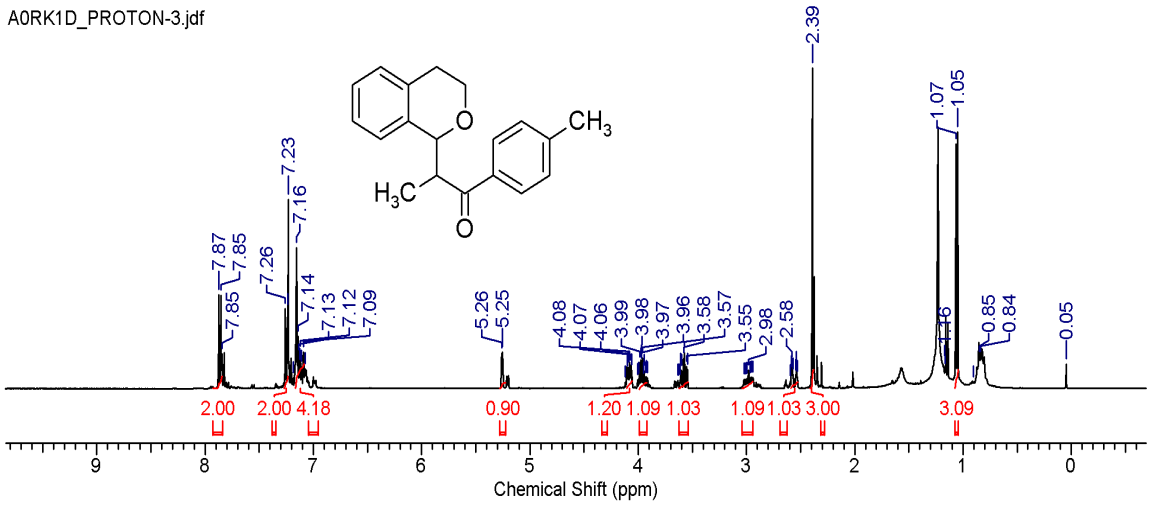

O
O
O
S
201.9
167.4
134.7
133.4
133.4
130.6
130.2
127.7
127.2
126.8
126.6
77.4
77.0
76.7
61.4
57.5
48.4
31.2
13.9
Chemical Shift (ppm)

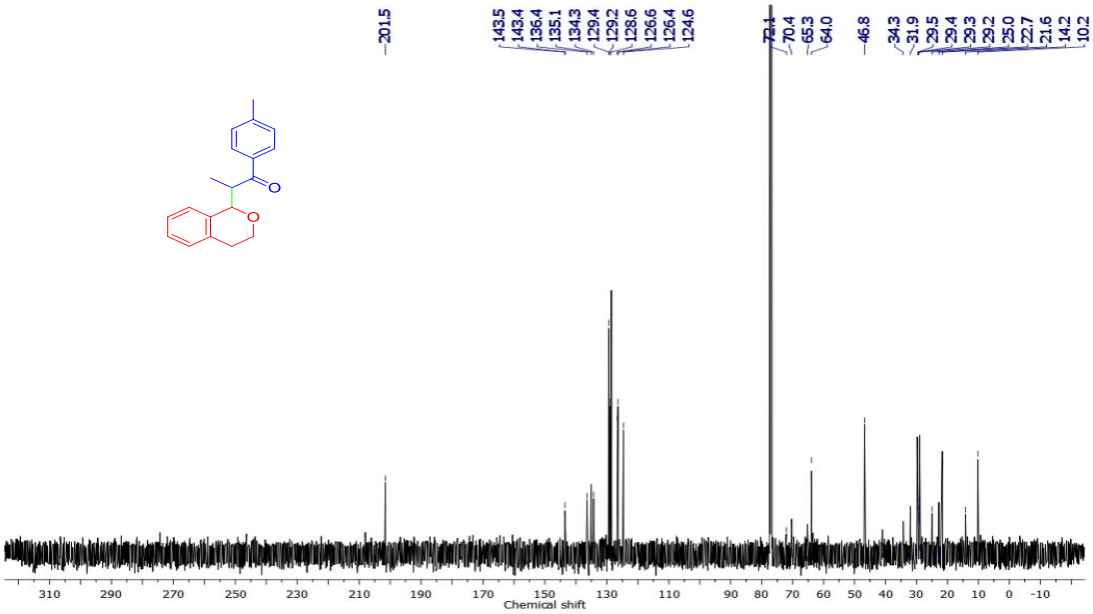

O
O
8.0424
8.0185
7.5088
7.4849
7.2118
7.2005
7.2294
7.1703
7.1539
7.1388
7.5868
7.6095
7.4597
5.5444
5.5154
4.1601
4.1487
4.1248
4.1110
4.0959
3.8606
3.8278
3.7793
3.6793
3.6252
3.3685
3.3597
3.3156
3.0363
3.0149
2.7619
2.7518
2.7078
2.6890
1.2782
1.85
3.14
4.15
0.91
1.21
1.17
1.05
1.08
1.12
0.97
Chemical Shift (ppm)


198.1
137.5
137.1
133.1
129.0
128.5
128.3
126.5
126.2
124.5
77.4
77.0
76.6
72.6
63.4
45.4
28.8
Chemical Shift (ppm)

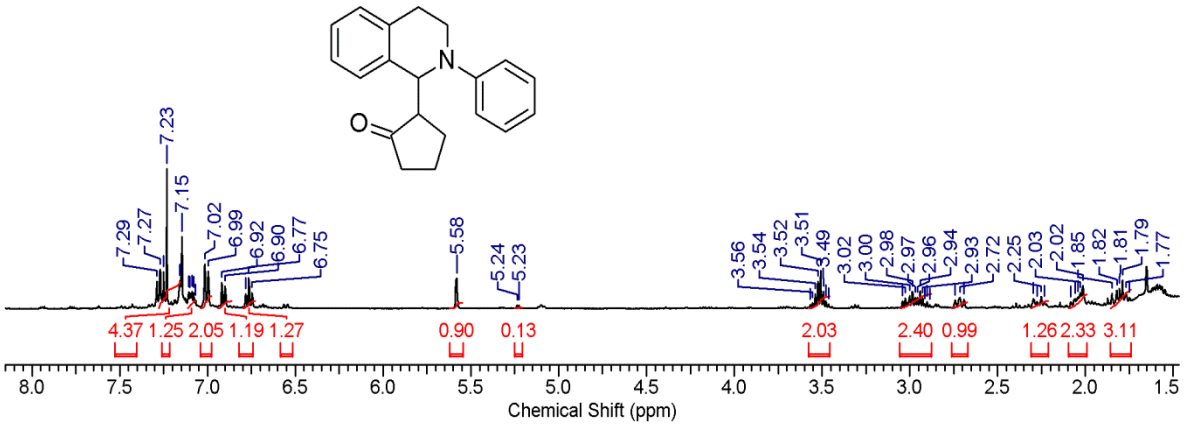

1.2459
1.2094
1.0861
1.0647
7.9988
7.9724
7.9409
7.5659
7.5420
7.5055
7.4803
7.4237
7.2500
7.1946
7.1732
7.1394
7.1118
7.1279
7.0159
5.2893
5.2377
5.2176
4.1341
4.1164
4.0963
4.0799
4.0397
4.0183
4.0070
3.6219
3.6018
3.5784
3.5766
3.5501
3.0644
3.0455
3.0077
2.9914
2.9750
2.5962
2.5409
1.6687
1.73
3.17
4.00
0.81
1.97
0.95
1.01
0.87
3.08
Chemical Shift (ppm)

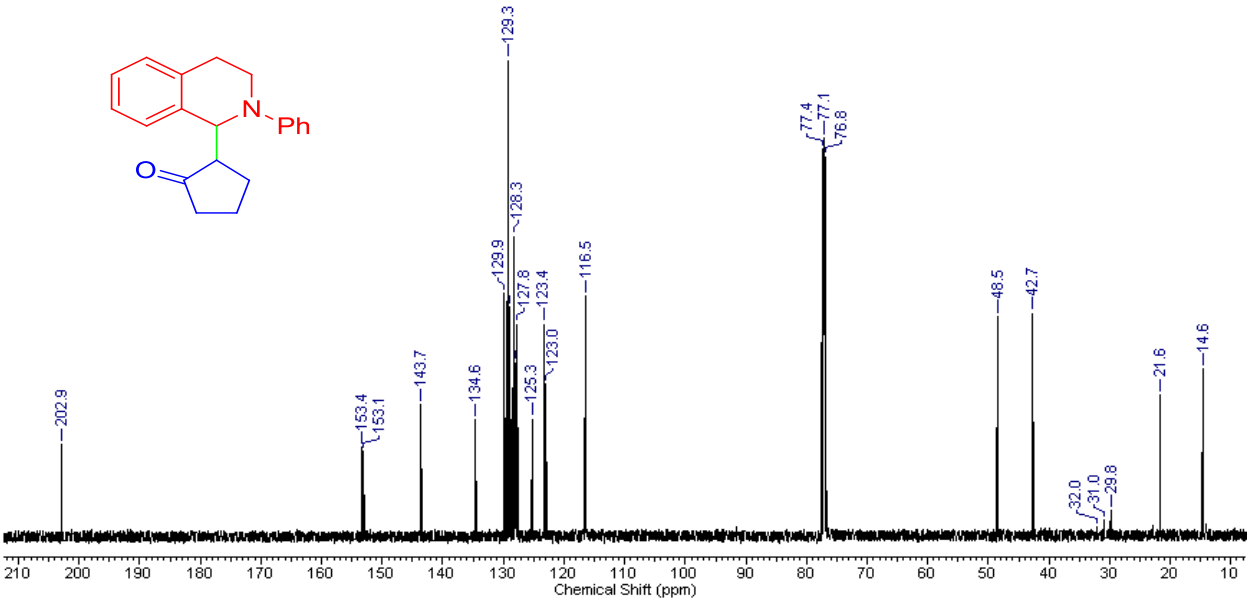

O
O
77.4
77.0
76.6
201.8
177.2
136.6
135.8
135.0
132.7
128.6
128.3
126.5
126.3
125.8
124.4
64.0
63.3
47.2
46.8
29.7
28.8
13.6
9.8
Chemical Shift (ppm)

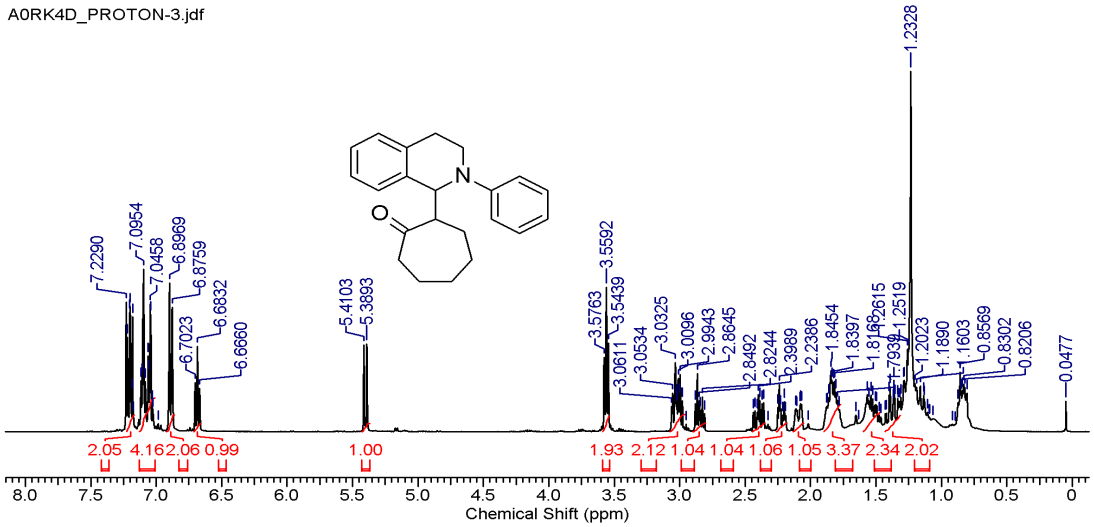

A0RK1D_PROTON-3.jdf
O
CH3
H3C
O
2.39
1.07
1.05
7.87
7.85
7.85
7.26
7.23
7.16
7.14
7.13
7.12
7.09
5.26
5.25
4.08
4.07
4.06
3.99
3.98
3.97
3.96
3.58
3.57
3.55
2.98
2.58
1.16
0.85
0.84
0.05
2.00
2.00
4.18
0.90
1.20
1.09
1.03
1.09
1.03
3.00
3.09
Chemical Shift (ppm)

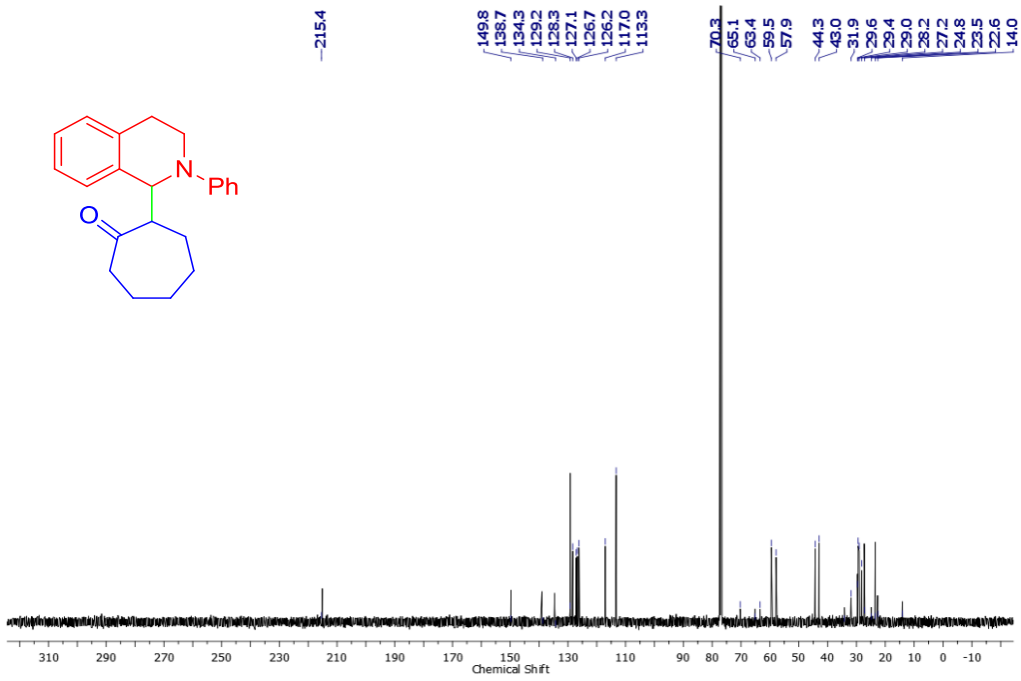


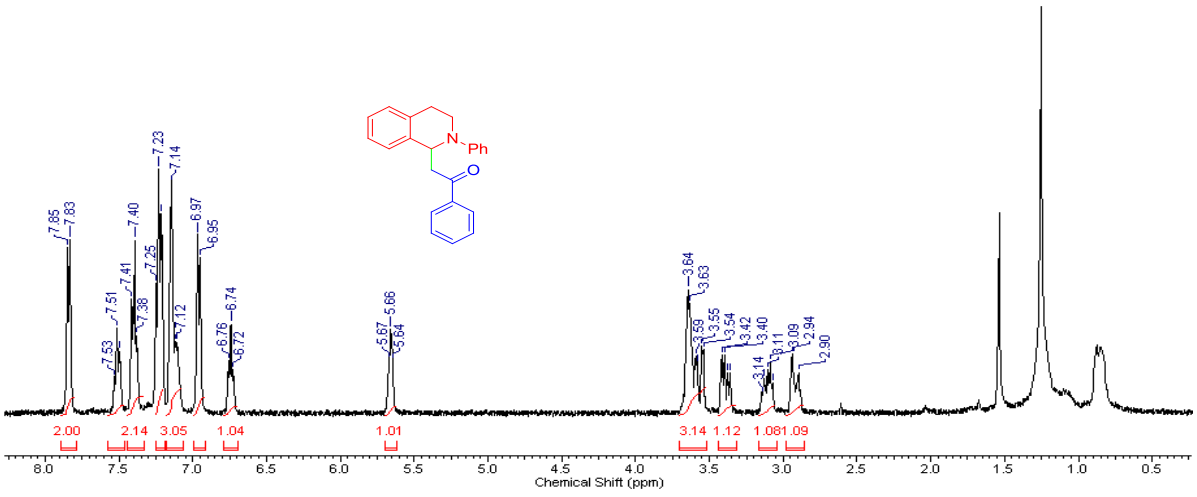
AORK6D_PROTON-3.jdf

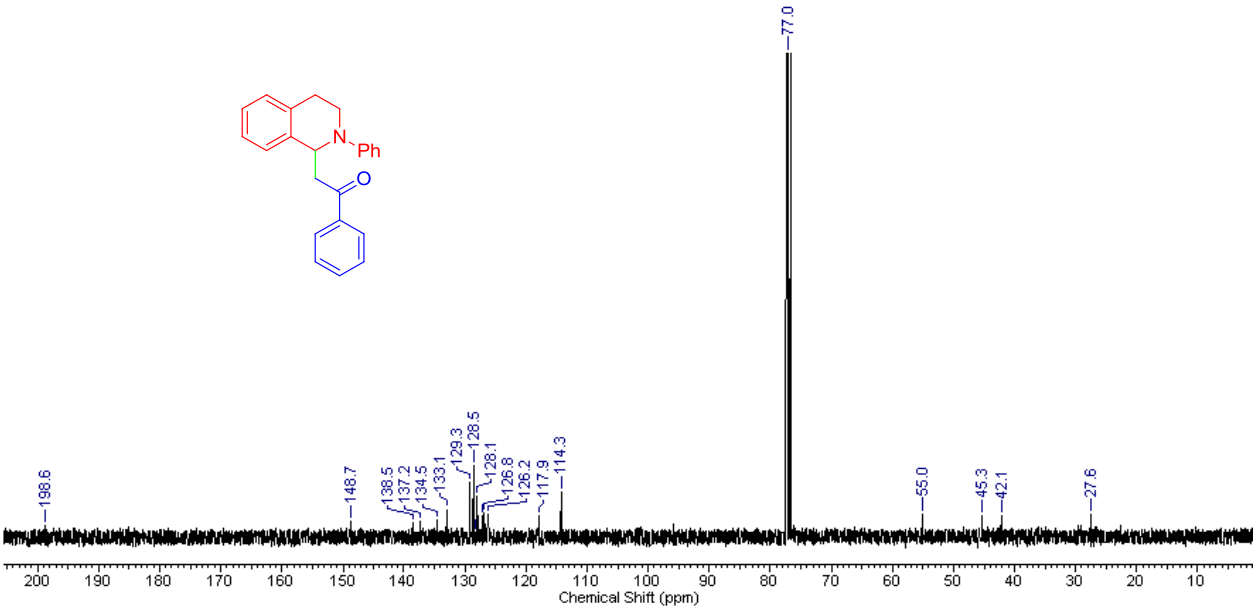


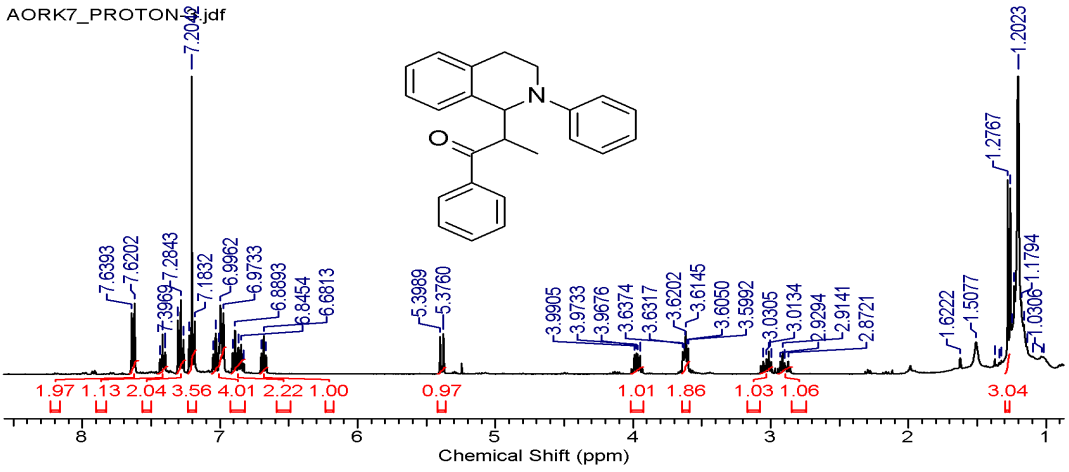

N
Ph
O
202.9
153.4
153.1
143.7
134.6
129.9
129.3
128.3
127.8
125.3
123.4
123.0
116.5
77.4
77.1
76.8
48.5
42.7
32.0
31.0
29.8
21.6
14.6
Chemical Shift (ppm)

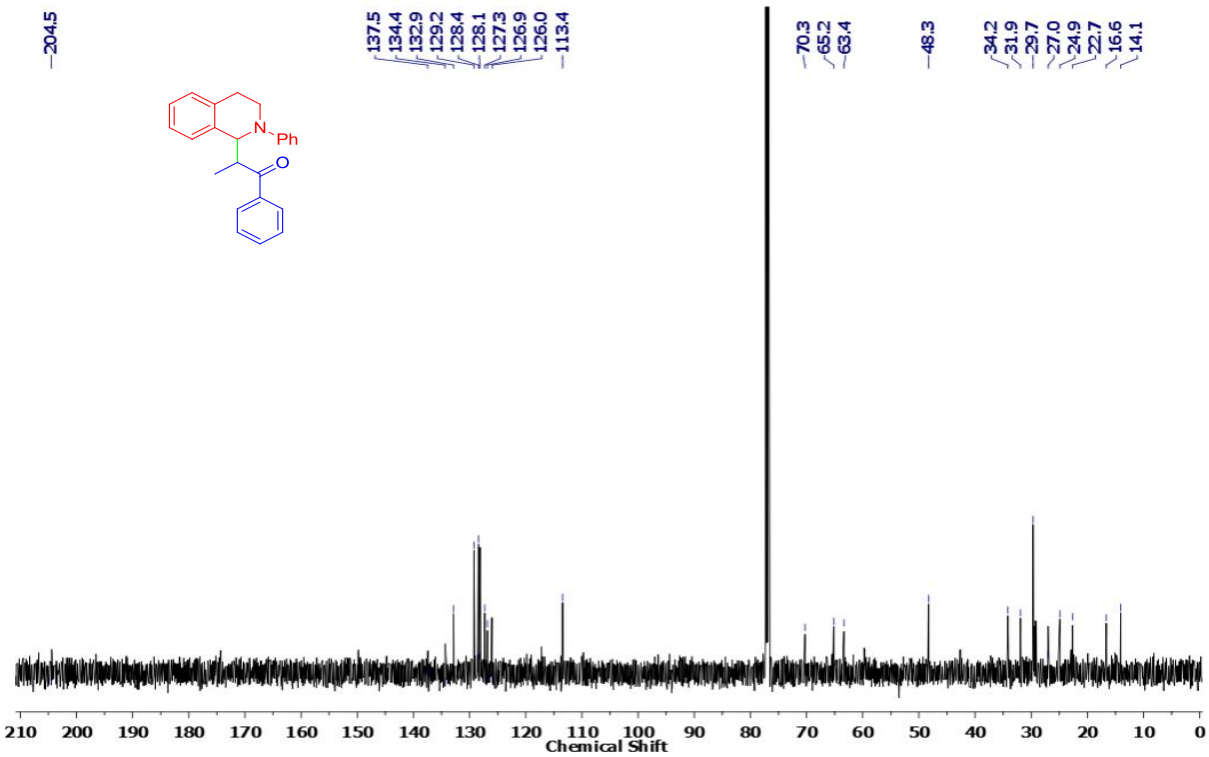

A0RK4D_PROTON-3.jdf
N
O
7.2290
7.0954
7.0458
6.8969
6.8759
6.6832
6.6660
6.7023
5.4103
5.3893
3.5763
3.5592
3.5439
3.0611
3.0534
3.0325
3.0096
2.9943
2.8645
2.8492
2.8244
2.3989
2.2386
1.8454
1.8397
1.8168
1.2615
1.2519
1.2328
1.2023
1.1890
1.1603
0.8569
0.8302
0.8206
0.0477
2.05 4.16 2.06 0.99
1.00
1.93 2.12 1.04 1.04 1.06 1.05 3.37 2.34 2.02
Chemical Shift (ppm)

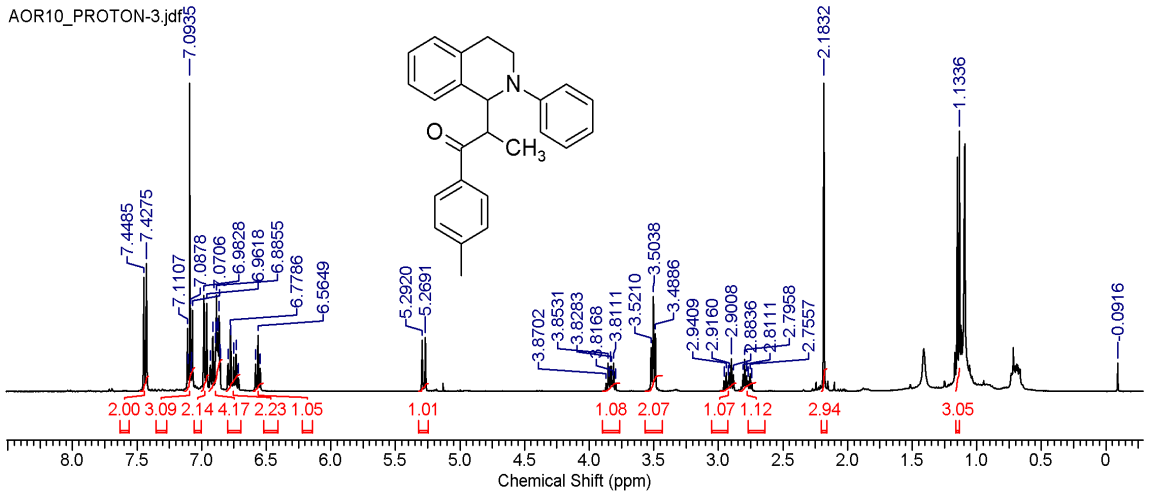

215.4
149.8
138.7
134.3
129.2
128.3
127.1
126.7
126.2
117.0
113.3
70.3
65.1
63.4
59.5
57.9
44.3
43.0
31.9
29.6
29.4
29.0
28.2
27.2
24.8
23.5
22.6
14.0
N
Ph
O
Chemical Shift

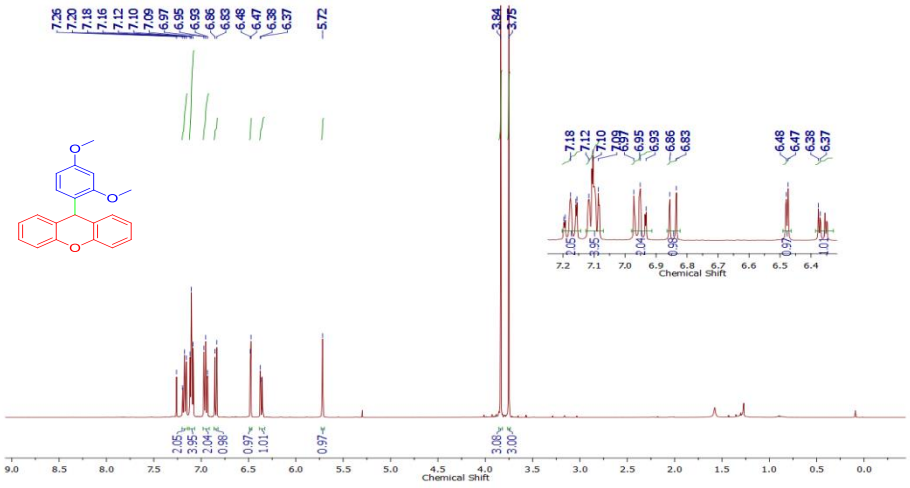

7.85
7.83
7.53
7.51
7.41
7.40
7.38
7.25
7.23
7.14
7.12
6.97
6.95
6.76
6.74
6.72
5.67
5.66
5.64
3.64
3.63
3.59
3.55
3.54
3.42
3.40
3.14
3.11
3.09
2.94
2.90
2.00
2.14
3.05
1.04
1.01
3.14
1.12
1.08
1.09
N
Ph
O
Chemical Shift (ppm)

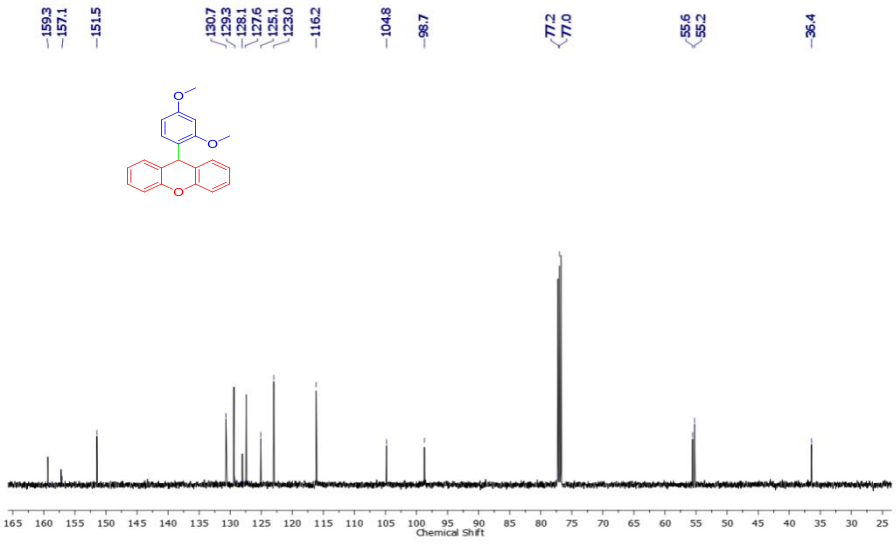

N
Ph
O
198.6
148.7
138.5
137.2
134.5
133.1
129.3
128.5
128.1
126.8
126.2
117.9
114.3
77.0
55.0
45.3
42.1
27.6
Chemical Shift (ppm)

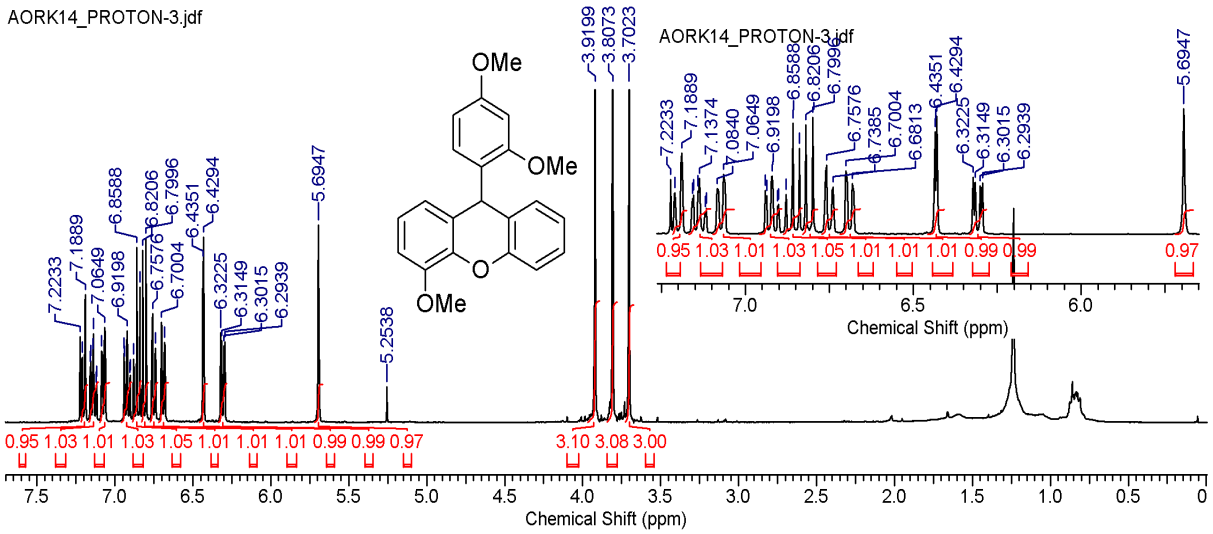

AORK7_PROTON_2.jdf
N
O
7.6393
7.6202
7.3969
7.2843
7.2042
7.1832
6.9962
6.9733
6.8893
6.8454
6.6813
5.3989
5.3760
3.9905
3.9733
3.9676
3.6374
3.6317
3.6202
3.6145
3.6050
3.5992
3.0305
3.0134
2.9294
2.9141
2.8721
1.6222
1.5077
1.2767
1.2023
1.1794
1.0306
1.97 1.13 2.04 3.56 4.01 2.22 1.00
0.97
1.01 1.86
1.03 1.06
3.04
Chemical Shift (ppm)

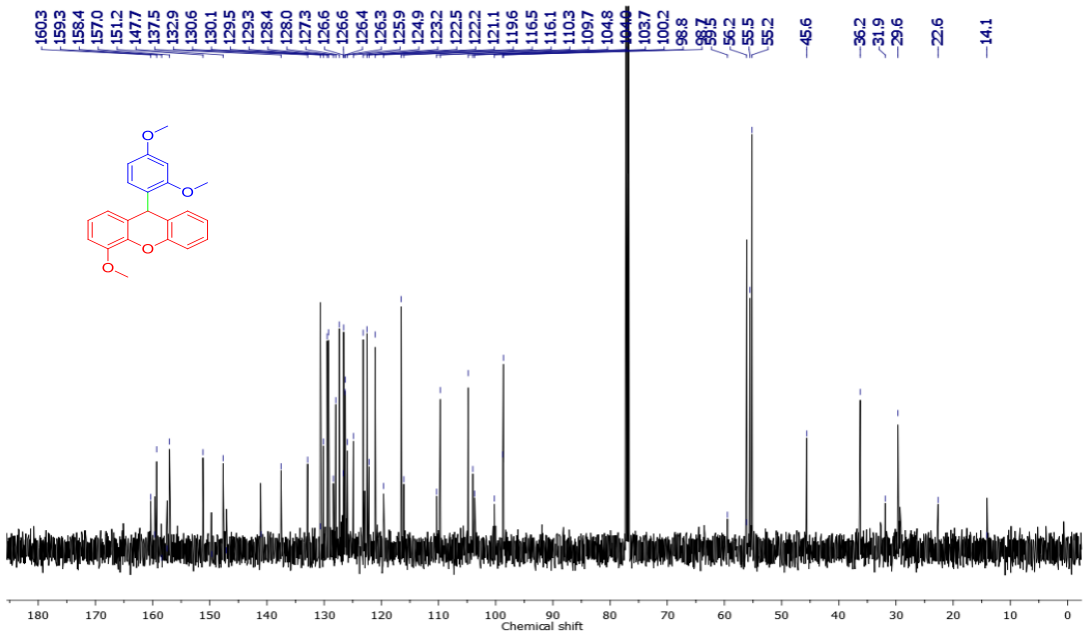

204.5
137.5
134.4
132.9
129.2
128.4
128.1
127.3
126.9
126.0
113.4
70.3
65.2
63.4
48.3
34.2
31.9
29.7
27.0
24.9
22.7
16.6
14.1
N
Ph
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift

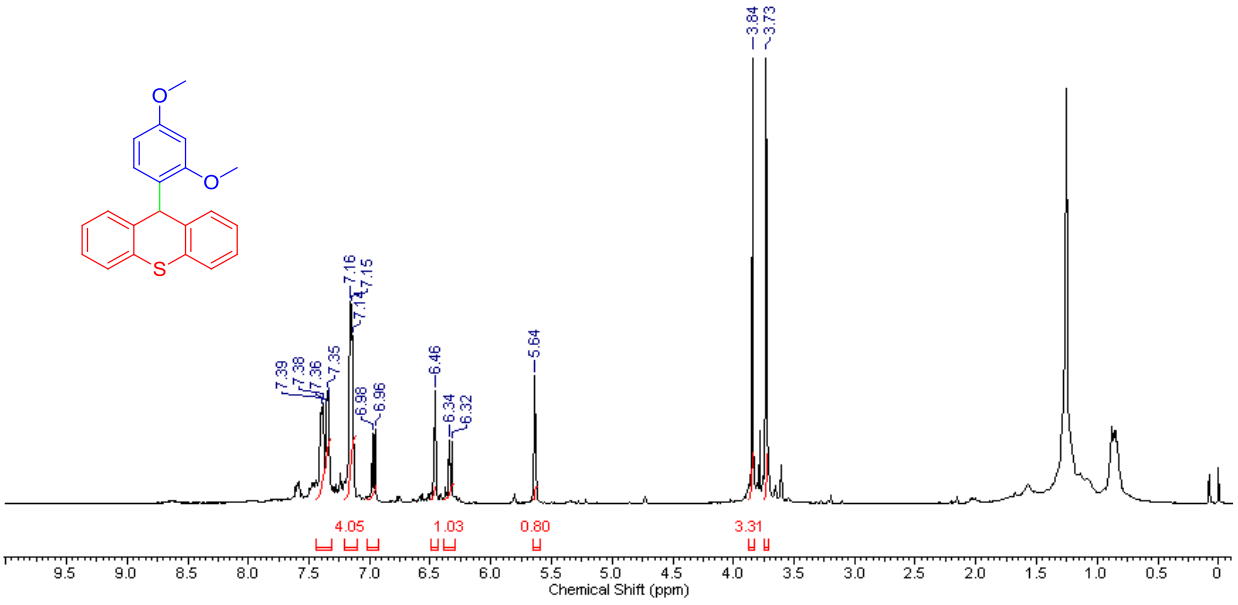

AOR10_PROTON-3.jdf
7.0935
7.4485
7.4275
7.1107
7.0878
7.0706
6.9828
6.9618
6.8855
6.7786
6.5649
5.2920
5.2691
3.8702
3.8531
3.8283
3.8168
3.8111
3.5210
3.5038
3.4886
2.9409
2.9160
2.9008
2.8836
2.8111
2.7958
2.7557
2.1832
1.1336
0.0916
N
O
CH3
2.00 3.09 2.14 4.17 2.23 1.05
1.01
1.08 2.07
1.07 1.12
2.94
3.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

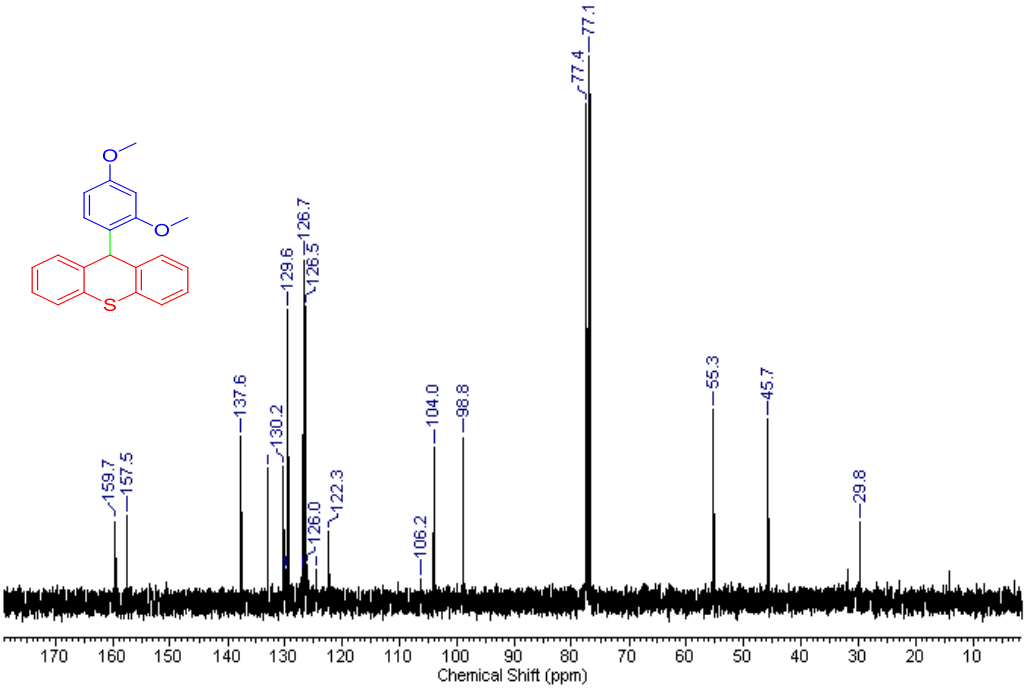

7.26
7.20
7.18
7.16
7.12
7.10
7.09
6.97
6.95
6.93
6.86
6.83
6.48
6.47
6.38
6.37
5.72
3.84
3.75
2.05
3.95
2.04
0.98
0.97
1.01
0.97
3.08
3.00
Chemical Shift

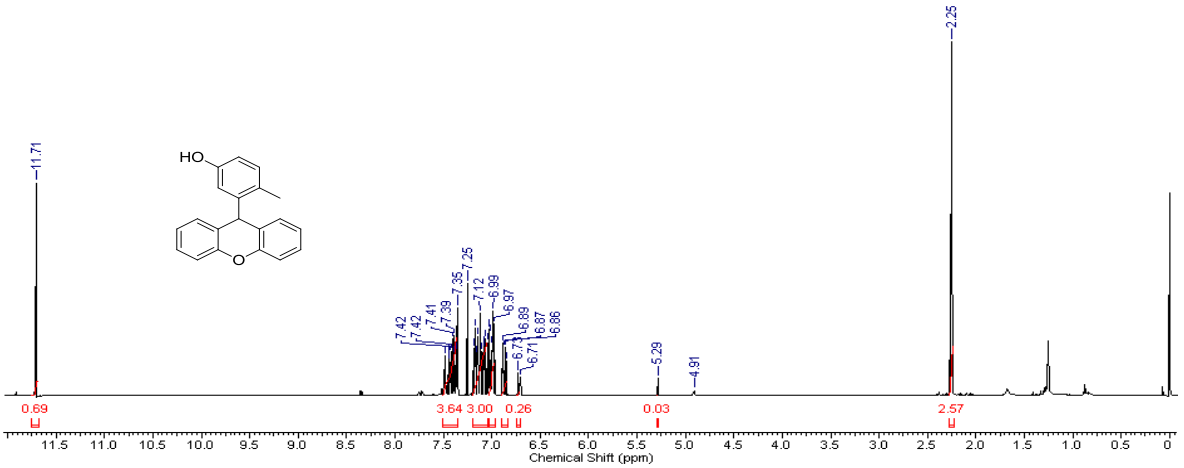

159.3
157.1
151.5
130.7
129.3
128.1
127.6
125.1
123.0
116.2
104.8
98.7
77.2
77.0
55.6
55.2
36.4
Chemical Shift

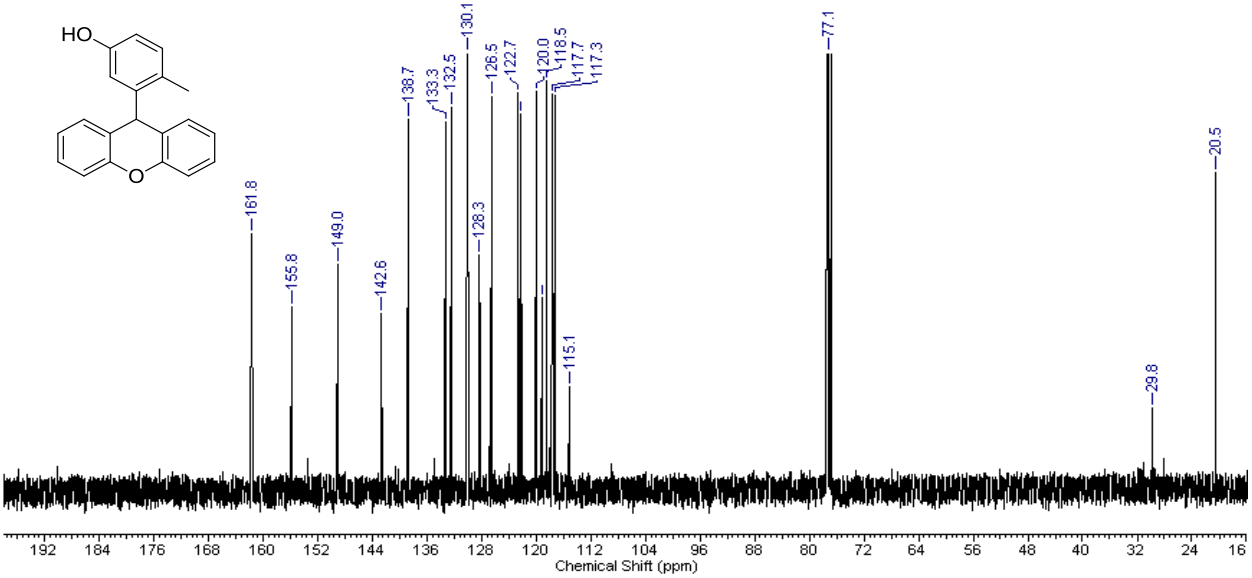

AORK14_PROTON-3.jdf
OMe
OMe
OMe
7.2233
7.1889
7.0649
6.9198
6.8588
6.8206
6.7996
6.7576
6.7004
6.4351
6.4294
6.3225
6.3149
6.3015
6.2939
5.6947
5.2538
3.9199
3.8073
3.7023
0.95 1.03 1.01 1.03 1.05 1.01 1.01 1.01 0.99 0.99 0.97
3.10 3.08 3.00
Chemical Shift (ppm)
AORK14_PROTON-3.jdf
0.95 1.03 1.01 1.03 1.05 1.01 1.01 1.01 0.99 0.99
0.97
Chemical Shift (ppm)


Chemical shift


3.84
3.73
7.39
7.38
7.36
7.35
7.16
7.15
6.98
6.96
6.46
6.34
6.32
5.64
4.05
1.03
0.80
3.31
Chemical Shift (ppm)


77.4
77.1
129.6
126.7
126.5
137.6
130.2
104.0
98.8
55.3
45.7
159.7
157.5
126.0
122.3
106.2
29.8
Chemical Shift (ppm)


HO
O
11.71
7.42
7.42
7.41
7.39
7.35
7.25
7.12
6.99
6.97
6.89
6.87
6.86
6.73
6.71
5.29
4.91
2.25
0.69
3.64
3.00
0.26
0.03
2.57
Chemical Shift (ppm)


HO
O
161.8
155.8
149.0
142.6
138.7
133.3
132.5
130.1
128.3
126.5
122.7
120.0
118.5
117.7
117.3
115.1
77.1
29.8
20.5
Chemical Shift (ppm)