Electronic Supplementary Material (ESI) for Green Chemistry.

Photoorganocatalytic Synthesis of Acetals from Aldehydes

Nikolaos F. Nikitas, Ierasia Triandafillidi and Christoforos G. Kokotos*

Laboratory of Organic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens,
Panepistimiopolis, Athens 15771, Greece

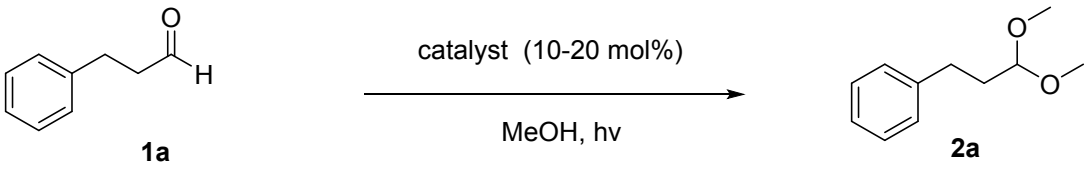
SUPPORTING INFORMATION

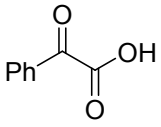
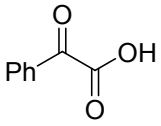
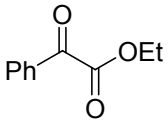
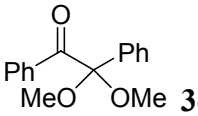
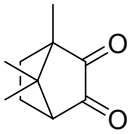
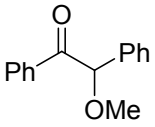
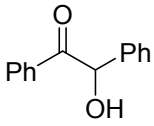
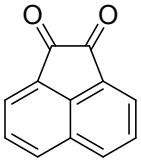
	Page
General Remarks	**S2**
Optimization of the Reaction Conditions for the Photoorganocatalytic Reaction of 3-Phenyl-propanal with Methanol	**S3**
Mechanistic Scavengers of the Reaction Conditions for the Photocatalytic Reaction of 3-Phenyl-propanal with Methanol	**S6**
Synthesis of Starting Materials	**S7**
General Procedure for the Photoorganocatalytic Synthesis of Acetals from Aldehydes	**S12**
Determination of the Quantum Yield	**S26**
Mechanistic Investigations with UV-Vis Absorption Spectra	**S28**
Fluorescence Quenching Studies	**S30**
^{13}C-NMR Mechanistic Experiments	**S36**
^{1}H-NMR Mechanistic Experiments	**S39**
^{19}F-NMR Mechanistic Experiments	**S42**
References	**S44**
NMR Spectra	**S46**

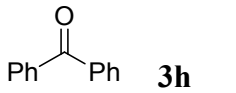
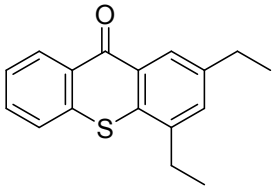
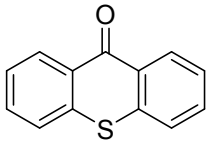
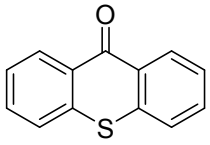
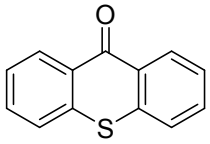
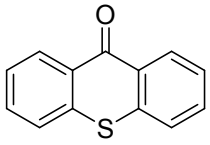
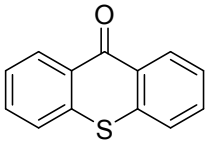
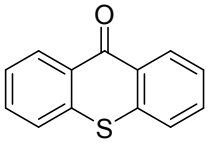
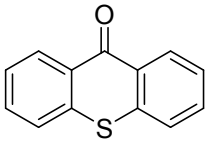
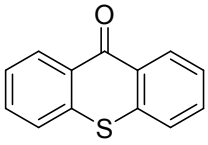
General Remarks

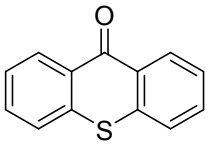
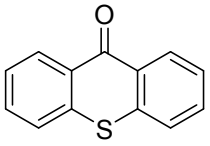
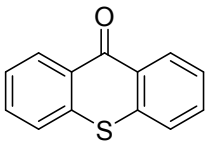
Chromatographic purification of products was accomplished using forced-flow chromatography on Merck® Kieselgel 60 F_{254} 230-400 mesh. Thin-layer chromatography (TLC) was performed on aluminum backed silica plates (0.2 mm, 60 F_{254}). Visualization of the developed chromatogram was performed by fluorescence quenching using phosphomolybdic acid, anisaldehyde or potassium permanganate stains. Mass spectra (ESI) were recorded on a Finningan® Surveyor MSQ LC-MS spectrometer. HRMS spectra were recorded on Bruker® Maxis Impact QTOF spectrometer. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on Varian® Mercury (200 MHz, 188 MHz and 50 MHz respectively), and are internally referenced to residual solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant and assignment. Data for ^{19}F NMR are reported in terms of chemical shift (δ ppm) and are internally referenced to trifluoroacetic acid. Data for ^{13}C are reported in terms of chemical shift (δ ppm). Mass spectra and conversions of the reactions were recorded on a Shimadzu® GCMS-QP2010 Plus Gas Chromatograph Mass Spectrometer utilizing a MEGA® column (MEGA-5, F.T.: 0.25μm, I.D.: 0.25mm, L: 30m, T_{max}: 350 ^{o}C, Column ID# 11475). A Varian® Cary 50 UV-Vis spectrophotometer was used as the light source for the quantum yield measurements and the UV-Vis data. A Scinco® FS-2 fluorescence spectrometer was used for the fluorescence studies.

Optimization of the Reaction Conditions for the Photocatalytic Reaction of 3-Phenyl-propanal with Methanol



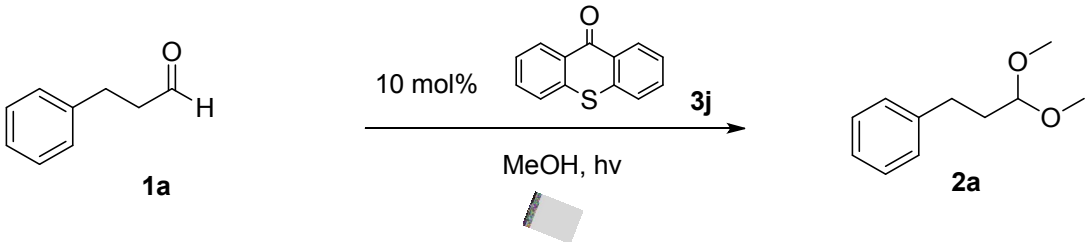
Entry	Catalyst	Catalyst Loading (mol%)	Time (h)	Yield (%)[a]
1	 **3a**	20	18	100
2[b]	 **3a**	20	18	90
3	 **3b**	20	18	33
4	 **3c**	20	18	28
5	 **3d**	20	18	13
6	 **3e**	20	18	22
7	 **3f**	20	18	17
8	 **3g**	20	18	18

9	 **3h**	20	18	0
10	 **3i**	20	18	90
11	 **3j**	20	18	95
12	 **3j**	10	18	95
13	 **3j**	5	18	75
14	 **3j**	2	18	62
15	-	-	18	5
16[b]	 **3j**	10	18	5
17[c]	 **3j**	10	18	5
18	 **3j**	10	1.5	95
19[d]	 **3j**	10	1.5	65

20[e]	 **3j**	10	1.5	34
21[f]	 **3j**	10	1.5	55
22[g]	 **3j**	10	1.5	61

[a] Isolated yield
[b] Reaction was kept in the dark
[c] Reaction was kept under household bulb irradiation and the reaction tube was covered with foil
[d] Reaction took place in methanol-acetonitrile mixture (1:1)
[e] Reaction took place in methanol-dichloromethane (1:1)
[f] Reaction took place in methanol-benzene (1:1)
[g] Reaction took place in methanol-tetrahydrofuran (1:1)

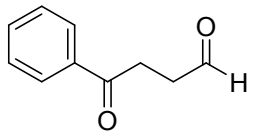
Mechanistic Scavengers of the Reaction Conditions for the Photocatalytic Reaction of 3-Phenyl-propanal with Methanol



Entry	Quencher (equiv.)	Notes	Yield (%)
1	BHT (1.0)	Radical Scavenger	0
2	TEMPO (1.0)	Radical Scavenger	0
3	NaN_3 (1.0)	Singlet Oxygen Scavenger	0
4	DABCO (1.0)	Singlet Oxygen Scavenger	24
5	Benzoquinone (1.0)	Superoxide Radical Anion Scavenger	24
6	$NaNO_2$ (1.0)	Cut-off Filter 400 nm	0
7	Ar atmosphere	-	40

Synthesis of Starting Materials

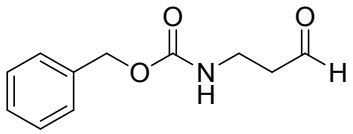
Synthesis of 4-oxo-4-phenylbutanal (1u)[1]



To an ice cold solution of 4-oxo-4-phenylbutanoic acid (1.0 equiv., 356 mg, 2.00 mmol) in dry THF (8 mL), a solution of $LiAlH_4$ 1M in dry THF (4.0 equiv., 8.0 mL, 8.00 mmol) was added dropwise. After warming at r.t., the reaction mixture was stirred for 2 h. The reaction mixture was quenched slowly with water (3 mL) at 0 ^oC. The solvent was removed and the reaction mixture was extracted with AcOEt (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude diol was used without further purification in the next step.

A flame-dried 50 mL flask was charged with oxalyl chloride (2.4 equiv., 0.4 mL, 4.80 mmol) in dry CH_2Cl_2 (3 mL). The solution was cooled at -78 °C and a solution of DMSO (2.2 equiv., 0.3 mL, 4.40 mmol) in dry CH_2Cl_2 (3 mL) was added slowly. After stirring for 30 min, a solution of the mixture in dry CH_2Cl_2 (3 mL) was added and the reaction mixture was stirred for 30 min. Triethylamine (10.0 equiv., 2.7 mL, 20.00 mmol) was added and the mixture was left warming at r.t.. The mixture was treated with ice and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography on silica gel (Pet. Ether/AcOEt 8:2), to yield the desired ketoaldehyde **1u**; Yellow oil; 72% yield; ^1H NMR (200 MHz, $CDCl_3$) δ: 9.78 (1H, s, CHO), 7.90-7.85 (2H, m, ArH), 7.51-7.32 (3H, m, ArH), 3.25-3.18 (2H, m, CH_2), 2.84-2.77 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 201.0, 198.0, 136.5, 133.5, 128.8, 128.2, 37.7, 31.2; MS 163 $[M+H]^+$.

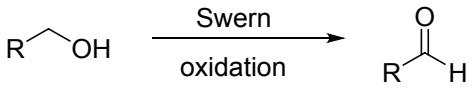
Synthesis of benzyl (3-oxopropyl)carbamate (1v)[2]



To an ice cold solution of 3-hydroxypropylamine (1.0 equiv., 600 mg, 8.00 mmol) in 1M aqueous NaOH (1.1 equiv., 8.8 mL, 8.80 mmol), benzyl chloroformate (1.1 equiv., 0.84 mL, 8.80 mmol) was added dropwise. After warming at r.t., the reaction mixture was stirred for 1 h and CH_2Cl_2 (6 mL) was added and the reaction mixture was stirred for 3 h. The reaction mixture was acidified with aqueous HCl 1M and the aqueous layer was extracted with $CHCl_3$ (3 x 10 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude material was used without further purification in next step.

A flame-dried 50 mL flask was charged with PCC (2.0 equiv., 1.07 g, 5.00 mmol) in dry CH_2Cl_2 (15 mL). The solution was cooled at 0 °C and benzyl(3-hydroxypropyl)carbamate (1.0 equiv., 522 mg, 2.50 mmol) was added slowly. After stirring for 2 h, silica gel (100 mg) was added to the reaction mixture to quench the reaction. The mixture was then vacuum filtered through Celite and silica gel and washed with diethyl ether. The solvent was removed *in vacuo* and the crude mixture was purified by column chromatography on silica gel (Pet. Ether/AcOEt 1:1), to yield the corresponding benzyl (3-oxopropyl)carbamate; Colorless oil; 68% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.73 (1H, s, CHO), 7.35-7.30 (5H, m, ArH), 5.32 (1H, br s, NH), 5.05 (2H, s, OCH_2), 3.48-3.39 (2H, m, NCH_2), 2.67 (2H, t, J = 6.0 Hz, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 201.3, 165.4, 136.5, 128.7, 128.3, 128.2, 66.9, 44.2, 34.6; MS 208 $[M+H]^+$.

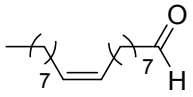
General Synthesis of Aldehydes 1x-z and 1ac



A flame dry round-bottom flask was charged with a solution of oxalyl chloride (2M) (1.2 equiv., 0.60 mL, 1.20 mmol) in dry CH_2Cl_2 (1.5 mL) under argon atmosphere at -78 ^{o}C. Dimethylsulfoxide (1.1 equiv., 86 mg, 1.10 mmol) in dry CH_2Cl_2 (1.5 mL) was added

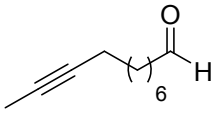
dropwise and the reaction mixture was left for 30 min. The alcohol (1.0 equiv., 1.00 mmol) was dissolved in dry CH_2Cl_2 (1.5 mL) and was added in the reaction mixture. After 30 min, triethylamine (5.0 equiv., 0.45 mL, 5.00 mmol) was added and the reaction mixture was stirred at -78 ^oC for 15 min. The reaction was extracted with with CH_2Cl_2 (3 x 5 mL) and ice-water (1o mL). The combined organic layers were washed with brine (2 x 5 mL) and dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude mixture was purified by column chromatography eluting with petroleum ether:ethyl acetate (9:1-8:2).

(*Z*)-Hex-3-enal (1x)[3]



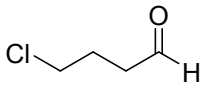
Colorless oil; 88% yield; ^1H NMR (200 MHz, $CDCl_3$) δ: 9.74 (1H, s, CHO), 5.32-5.30 (2H, m, 2 x =CH), 2.39 (2H, t, *J* = 7.3 Hz, C*H*$_2$CHO), 2.05-1.85 (3H, m, CH_2 and C*H*H), 1.67-1.50 (3H, m, CH_2 and CH*H*), 1.33-1.16 (20H, m, 10 x CH_2), 0.86 (3H, t, *J* = 6.4 Hz, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 202.8, 129.9, 129.6, 43.9, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 29.0, 28.9, 27.2, 27.1, 22.6, 22.0, 14.1; MS 267 $[M+H]^+$.

Hex-4-ynal (1y)[3]



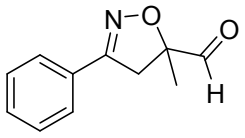
Colorless oil; 82% yield; ^1H NMR (200 MHz, $CDCl_3$) δ: 9.70 (1H, s, CHO), 2.36 (2H, t, *J* = 7.3 Hz, C*H*$_2$CHO), 2.10-1.96 (2H, m, CH_2), 1.71 (3H, s, CH_3), 1.67-1.46 (2H, m, CH_2), 1.45-1.10 (8H, m, 4 x CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 202.6, 79.0, 75.3, 43.7, 28.9, 28.8, 28.7, 28.5, 21.9, 18.5, 3.3; MS 167 $[M+H]^+$.

4-Chlorobutanal (1z)[4]



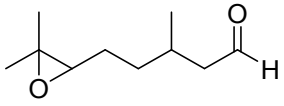
Colorless liquid with low b.p.; 90% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.78 (1H, s, CHO), 3.56 (2H, t, *J* = 6.3 Hz, CH_2CCl), 2.60 (2H, t, *J* = 7.3 Hz, C*H*$_2$CHO), 2.22-2.00 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 202.1, 45.3, 42.1, 26.0; MS 107 $[M+H]^+$.

5-Methyl-3-phenyl-4,5-dihydroisoxazole-5-carbaldehyde (1ac)



Pale yellow viscous oil; 87% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.65 (1H, s, CHO), 7.65-7.61 (2H, m, ArH), 7.39-7.36 (3H, m, ArH), 3.67 (1H, t, *J* = 17.0 Hz, C*H*H), 3.07 (1H, t, *J* = 17.0 Hz, CH*H*), 1.55 (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 198.9, 156.7, 137.2, 130.3, 128.6, 126.6, 88.9, 41.1, 19.7; HRMS exact mass calculated for $[M+H]^+$ ($C_{11}H_{12}NO_2^+$) requires *m/z* 190.0863, found *m/z* 190.0860.

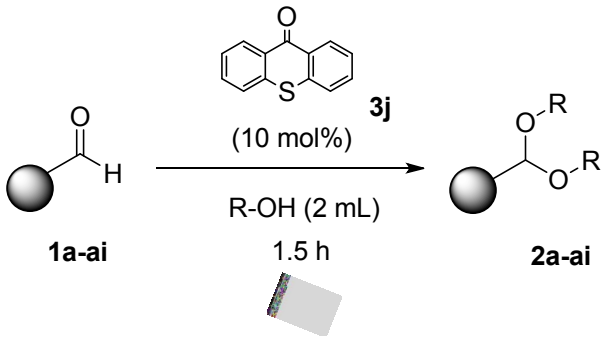
Synthesis of 5-(3,3-dimethyloxiran-2-yl)-3-methylpentanal (1aa)[5]



To a solution of (±)-citronellal (1.0 equiv., 154 mg, 1.00 mmol) in CH_2Cl_2 (5 mL), 3-chloroperbenzoic acid (1.5 equiv., 258 mg, 1.50 mmol) was added slowly. After warming at r.t., the reaction mixture was stirred for 2 h. The reaction mixture was filtered over Celite and washed with CH_2Cl_2 (2 x 5 mL). The filtrate was washed with sat. K_2CO_3 (1 x 10 mL), dried over Na_2SO_4 and the solvent was removed *in vacuo*. The aldehyde was used for the photochemical reaction without further purification; Colorless oil; 78% yield;

Mixture of diastereoisomers; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.68 (0.5H, s, CHO), 9.67 (0.5H, s, CHO), 2.61 (1H, t, J = 5.8 Hz, OCH), 2.43-1.86 (5H, m, 2 x CH_2 and CH), 1.48-1.36 (2H m, CH_2), 1.22 (3H, s, CH_3), 1.18 (3H, m, CH_3), 0.91 (1.5H, d, J = 6.5 Hz, CH_3), 0.88 (1.5H, d, J = 6.5 Hz, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 202.8, 202.3, 64.0, 63.9, 58.1, 50.8, 50.6, 33.3, 27.7, 27.5, 26.2, 25.5, 25.2, 19.7, 19.6, 18.5, 18.4; MS 171 $[M+H]^+$.

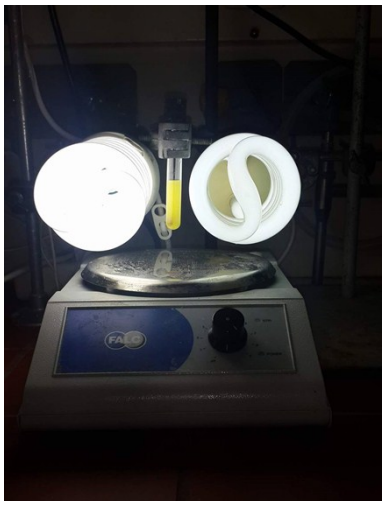
General Procedure for the Photoorganocatalytic Synthesis of Acetals



In a glass vial with a screw cap containing thioxanthene-9-one **3j** (10.6 mg, 0.05 mmol) in alcohol (2 mL), aldehyde (0.50 mmol) was added. The vial was sealed with a screw cap and left stirring under household bulb irradiation (2 x 80W household lamps, see photos below) for 1.5 h. The desired product was isolated either by solvent evaporation, distillation or after purification by column chromatography.

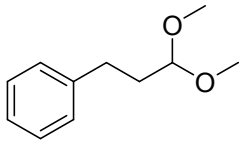
A

B



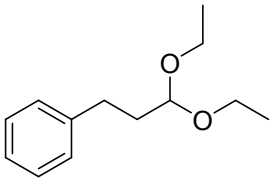
Scheme. **A**: 2 x 80W fluorescent household lamps utilized for the photocatalytic reaction. Bulbs are placed symmetrically 3 cm away from the reaction tube. **B**: Beginning of the reaction.

(3,3-Dimethoxypropyl)benzene (2a)[6]



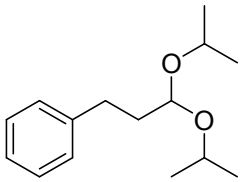
Colorless oil; 95% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.33-7.18 (5H, m, ArH), 4.37 (1H, t, J = 5.8 Hz, OCH), 3.33 (6H, s, 2 x OCH_3), 2.68 (2H, t, J = 7.6 Hz, CH_2), 1.98-1.87 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 141.8, 128.4, 125.9, 103.7, 52.8, 34.0, 30.8; MS (ESI) m/z 181 $[M+H]^+$.

(3,3-Diethoxypropyl)benzene (2b)[7]



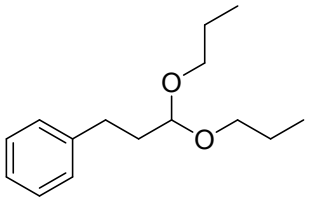
Colorless oil; 97% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.31-7.17 (5H, m, ArH), 4.48 (1H, t, J = 5.8 Hz, OCH), 3.77-3.41 (4H, m, 2 x OCH_2), 2.69 (2H, t, J = 7.8 Hz, $PhCH_2$), 1.99-1.88 (2H, m, CH_2), 1.21 (6H, t, J = 7.0 Hz, 2 x CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 141.9, 128.6, 128.5, 126.0, 102.3, 61.2, 35.2, 31.2, 15.6; MS (ESI) m/z 209 $[M+H]^+$.

(3,3-Diisopropoxypropyl)benzene (2c)[8]



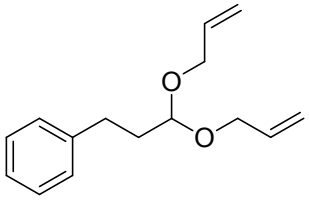
Colorless oil; 60% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.32-7.17 (5H, m, ArH), 4.56 (1H, t, J = 6.0 Hz, OCH), 3.86 (2H, sept, J = 6.0 Hz, 2 x OCH), 2.70 (2H, t, J = 6.0 Hz, $PhCH_2$), 1.97-1.87 (2H, m, CH_2), 1.20 (6H, d, J = 6.0 Hz, 2 x CH_3), 1.14 (6H, d, J = 6.0 Hz, 2 x CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 142.2, 128.6, 128.5, 125.9, 99.9, 67.9, 37.1, 31.3, 23.6, 22.8; MS (ESI) m/z 237 $[M+H]^+$.

(3,3-Dipropoxypropyl)benzene (2d)



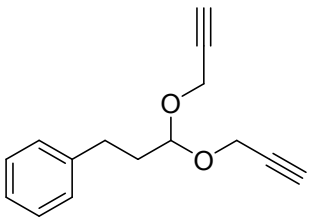
Colorless oil; 93% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.32-7.17 (5H, m, ArH), 4.49 (1H, t, J = 6.0 Hz, OCH), 3.62-3.51 (2H, m, OCH_2), 3.44-3.33 (2H, m, OCH_2), 2.70 (2H, t, J = 6.0 Hz, $PhCH_2$), 2.01-1.90 (2H, m, CH_2), 1.66-1.56 (4H, m, 2 x CH_2), 0.95 (6H, t, J = 8.0 Hz, 2 x CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 141.8, 128.3, 128.2, 125.7, 102.3, 67.2, 35.0, 31.0, 23.1, 10.7; HRMS exact mass calculated for $[M+Na]^+$ ($C_{15}H_{24}O_2Na^+$) requires *m/z* 259.1668, found *m/z* 259.1664.

(3,3-Bis(allyloxy)propyl)benzene (2e)



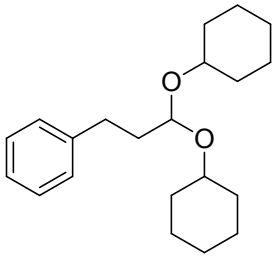
Colorless oil; 70% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.34-7.20 (5H, m, ArH), 6.05-5.85 (2H, m, 2 x =CH), 5.37-5.15 (4H, m, 2 x =CH_2), 4.63 (1H, t, J = 6.0 Hz, OCH), 4.19-3.96 (4H, m, 2 x OCH_2), 2.73 (2H, t, J = 8.0 Hz, $PhCH_2$), 2.06-1.95 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 141.8, 131.9, 128.6, 126.1, 116.9, 101.7, 66.5, 35.2, 31.2; HRMS exact mass calculated for $[M+Na]^+$ ($C_{15}H_{20}O_2Na^+$) requires *m/z* 255.1355, found *m/z* 255.1350.

(3,3-Bis(prop-2-yn-1-yloxy)propyl)benzene (2f)



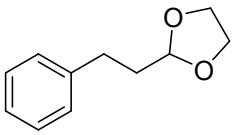
Colorless oil; 70% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.33- 7.17 (5H, m, ArH), 4.82 (1H, t, J = 6.0 Hz, OCH), 4.25 (4H, d, J = 2.4 Hz, 2 x OCH_2), 2.73 (2H, t, J = 7.0 Hz, $PhCH_2$), 2.44 (2H, t, J = 2.4 Hz, ΞCH), 2.06-1.95 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 141.4, 128.6, 126.2, 101.1, 79.9, 74.5, 53.4, 34.9, 30.8; HRMS exact mass calculated for $[M+Na]^+$ ($C_{15}H_{16}O_2Na^+$) requires *m/z* 251.1042, found *m/z* 251.1037.

((3-Phenylpropane-1,1-diyl)bis(oxy))dicyclohexane (2g)



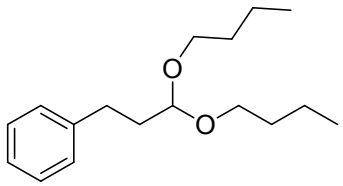
Colorless oil; 55% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.32-7.18 (5H, m, ArH), 4.66 (1H, t, J = 6.0 Hz, OCH), 3.58-3.45 (2H, m, 2 x OCH), 2.69 (2H, t, J = 8.0 Hz, $PhCH_2$), 1.98-1.67 (10H, m, 5 x CH_2), 1.54-1.24 (12H, m, 6 x CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 142.2, 128.6, 128.5, 125.9, 99.4, 73.8, 37.3, 33.8, 33.0, 31.4, 26.1, 24.6, 24.5; HRMS exact mass calculated for $[M+Na]^+$ ($C_{21}H_{32}O_2Na^+$) requires *m/z* 339.2294, found *m/z* 339.2301.

2-Phenethyl-1,3-dioxolane (2h)[7]



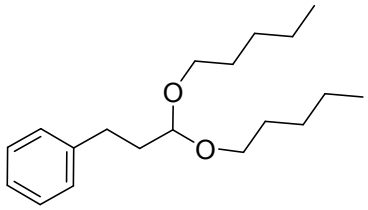
Colorless oil; 65% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.32-7.19 (5H, m, ArH), 4.89 (1H, t, J = 6.0 Hz, OCH), 4.04-3.83 (4H, m, 2 x OCH_2), 2.75 (2H, t, J = 7.0 Hz, $PhCH_2$), 2.04-1.93 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 141.7, 128.6, 128.5, 126.1, 104.0, 65.1, 35.7, 30.3; MS (ESI) m/z 179 $[M+H]^+$.

(3,3-Dibutoxypropyl)benzene (2i)[9]



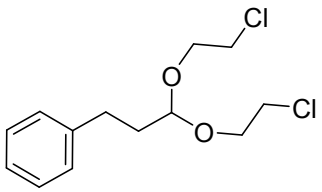
Colorless oil; 85% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.32-7.14 (5H, m, ArH), 4.49 (1H, t, J = 6.0 Hz, OCH), 3.63-3.55 (2H, m, OCH_2), 3.48-3.37 (2H, m, OCH_2), 2.69 (2H, t, J = 6.0 Hz, $PhCH_2$), 2.05-1.90 (2H, m, CH_2), 1.62-1.35 (8H, m, 4 x CH_2), 0.94 (6H, t, J = 7.0 Hz, 2 x CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 142.0, 128.6, 128.5, 126.0, 102.5, 65.4, 35.2, 32.2, 31.3, 19.7, 14.2; MS (ESI) m/z 265 $[M+H]^+$.

(3,3-Bis(pentyloxy)propyl)benzene (2j)



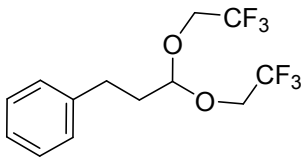
Colorless oil; 60% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.29-7.18 (5H, m, ArH), 4.48 (1H, t, J = 6.0 Hz, OCH), 3.64-3.56 (2H, m, OCH_2), 3.47-3.36 (2H, m, OCH_2), 2.69 (2H, t, J = 7.0 Hz, $PhCH_2$), 2.00-1.89 (2H, m, CH_2), 1.59 (4H, m, 2 x CH_2), 1.35 (8H, m, 4 x CH_2), 0.91 (6H, t, J = 6.0 Hz, 2 x CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 142.0, 128.6, 128.5, 126.0, 102.5, 65.8, 35.2, 31.3, 29.8, 28.7, 22.8, 14.3; HRMS exact mass calculated for $[M+Na]^+$ ($C_{19}H_{32}O_2Na^+$) requires *m/z* 315.2294, found *m/z* 315.2304.

(3,3-Bis(2-chloroethoxy)propyl)benzene (2k)



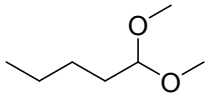
Yellow oil; 87% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.29-7.16 (5H, m, ArH), 4.64 (1H, t, J = 6.0 Hz, OCH), 3.93-3.73 (4H, m, 2 x OCH_2), 3.65 (4H, t, J = 6.0 Hz, 2 x CH_2Cl), 2.73 (2H, t, J = 6.0 Hz, $PhCH_2$), 2.05-1.94 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 141.4, 128.6, 128.6, 126.2, 102.5, 65.5, 43.5, 34.6, 31.0; HRMS exact mass calculated for $[M+H]^+$ ($C_{13}H_{19}Cl_2O_2^+$) requires *m/z* 271.0263, found *m/z* 271.0259.

(3,3-Bis(2,2,2-trifluoroethoxy)propyl)benzene (2l)



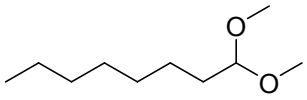
Colorless oil; 20% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.34-7.16 (5H, m, ArH), 4.75 (1H, t, J = 6.0 Hz, OCH), 3.90 (4H, q, J = 7.0 Hz, 2 x CH_2CF_3), 2.71 (2H, t, J = 6.0 Hz, $PhCH_2$), 1.98 (2H, q, J = 6.0 Hz, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 140.2, 128.6, 128.3, 126.3, 123.7 (q, J = 277.6 Hz), 102.3, 62.0 (q, J = 277.6 Hz), 33.8, 30.4; ^{19}F (188 MHz, $CDCl_3$): δ -32.2 (t, J = 8.5 Hz); HRMS exact mass calculated for $[M+H]^+$ ($C_{13}H_{17}F_6O_2^+$) requires *m/z* 317.0971, found *m/z* 317.0977.

1,1-Dimethoxypentane (2m)



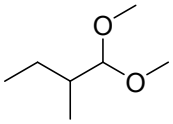
Colorless oil; 89% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.34 (1H, t, J = 6.0 Hz, OCH), 3.30 (6H, s, 2 x OCH_3), 1.63-1.53 (2H, m, CH_2), 1.34-1.21 (4H, m, 2 x CH_2), 0.89 (3H, t, J = 6.0 Hz, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 104.7, 52.7, 32.3, 26.9, 22.7, 14.2; HRMS exact mass calculated for $[M+H]^+$ ($C_7H_{17}O_2^+$) requires *m/z* 133.1223, found *m/z* 133.1228.

1,1-Dimethoxyoctane (2n)[6]



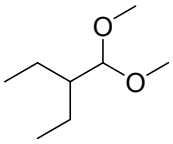
Colorless oil; 75% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.34 (1H, t, J = 6.0 Hz, OCH), 3.29 (6H, s, 2 x OCH_3), 1.58-1.52 (2H, m, CH_2), 1.27 (10H, m, 5 x CH_2), 0.86 (3H, t, J = 6.0 Hz, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 104.7, 52.7, 32.6, 31.9, 29.6, 29.4, 24.8, 22.8, 14.2; MS (ESI) m/z 175 $[M+H]^+$.

1,1-Dimethoxy-2-methylbutane (2o)[10]



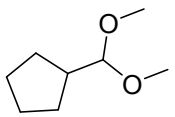
Colorless oil; 82% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.02 (1H, d, J = 6.6 Hz, OCH), 3.34 (6H, s, 2 x OCH_3), 1.72-1.45 (2H, m, CH_2), 1.15-1.07 (1H, m, CH), 0.92-0.85 (6H, m, 2 x CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 108.9, 54.1, 53.9, 37.3, 24.9, 14.0, 11.5; MS (ESI) m/z 133 $[M+H]^+$.

3-(Dimethoxymethyl)pentane (2p)



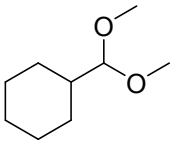
Colorless oil; 78% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.15 (1H, d, J = 5.9 Hz, OCH), 3.33 (6H, s, 2 x OCH_3), 1.53-1.24 (5H, m, 2 x CH_2 and CH), 0.86 (6H, t, J = 7.2 Hz, 2 x CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 107.4, 54.1, 42.9, 20.8, 11.1; HRMS exact mass calculated for $[M+H]^+$ ($C_8H_{19}O_2^+$) requires *m/z* 147.1380, found *m/z* 147.1385.

(Dimethoxymethyl)cyclopentane (2q)[10]



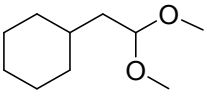
Colorless oil; 75% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.08 (1H, d, J = 7.9 Hz, OCH), 3.31 (6H, s, 2 x OCH_3), 1.74-1.28 (9H, m, 4 x CH_2 and CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 108.5, 53.0, 41.8, 28.4, 25.8; MS (ESI) m/z 145 $[M+H]^+$.

(Dimethoxymethyl)cyclohexane (2r)[11]



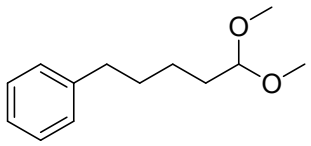
Colorless oil; 75% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.97 (1H, d, J = 7.1 Hz, OCH), 3.31 (6H, s, 2 x OCH_3), 1.77-1.59 (6H, m, 5 x C*H*H and CH), 1.25-0.92 (5H, m, 5 x CH*H*); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 108.7, 53.7, 40.2, 28.2, 26.5, 25.9; MS (ESI) m/z 84 $[M+H]^+$.

(2,2-Dimethoxyethyl)cyclohexane (2s)[12]



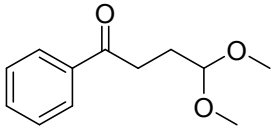
Colorless oil; 70% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.64 (1H, t, J = 5.8 Hz, OCH), 3.28 (6H, s, 2 x OCH_3), 1.73-1.65 (5H, m, 2 x CH_2 and CH), 1.48-1.39 (2H, m, CH_2), 1.27-1.16 (4H, m, 2 x CH_2), 0.98-0.87 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 102.8, 52.5, 40.1, 33.9, 33.7, 26.7, 26.4; MS (ESI) m/z 173 $[M+H]^+$.

(5,5-Dimethoxypentyl)benzene (2t)[13]



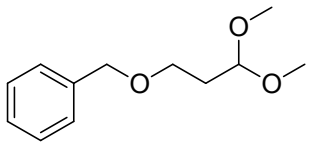
Colorless oil, 92% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.32-7.16 (5H, m, ArH), 4.37 (1H, t, J = 5.6 Hz, OCH), 3.32 (6H, s, 2 x OCH_3), 2.63 (2H, t, J = 7.2 Hz, $PhCH_2$), 1.74-1.58 (4H, m, 2 x CH_2), 1.48-1.36 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 142.7, 128.6, 128.5, 125.8, 104.6, 52.8, 36.1, 32.6, 31.5, 24.5; MS (ESI) m/z 209 $[M+H]^+$.

4,4-Dimethoxy-1-phenylbutan-1-one (2u)[14]



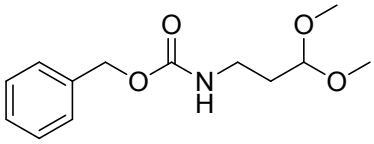
Yellow oil, 92% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.97-7.93 (2H, m, ArH), 7.55-7.38 (3H, m, ArH), 4.46 (1H, t, J = 5.5 Hz, OCH), 3.32 (6H, s, 2 x OCH_3), 3.04 (2H, t, J = 7.3 Hz, $COCH_2$), 2.09-1.99 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 199.7, 137.1, 133.2, 128.8, 128.2, 104.1, 53.5, 33.5, 27.1; MS (ESI) m/z 209 $[M+H]^+$.

((3,3-Dimethoxypropoxy)methyl)benzene (2v)[15]



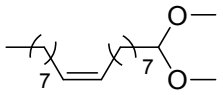
Colorless oil, 87% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.35-7.26 (5H, m, ArH), 4.57 (1H, t, J = 5.8 Hz, OCH), 4.51 (2H, s, OCH_2Ph), 3.55 (2H, t, J = 6.2 Hz, OCH_2), 3.33 (6H, s, 2 x OCH_3), 1.92 (2H, q, J = 6.0 Hz, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.6, 128.5, 127.8, 127.8, 102.4, 73.2, 66.4, 53.3, 33.3; MS (ESI) m/z 211 $[M+H]^+$.

Benzyl (3,3-dimethoxypropyl)carbamate (2w)[16]



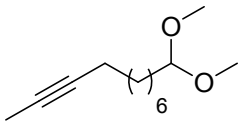
Colorless oil, 89% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.35-726 (5H, m, ArH), 5.28 (1H, br s, NH), 5.07 (2H, s, OCH_2Ph), 4.40 (1H, t, J = 5.4 Hz, OCH), 3.30 (6H, s, 2 x OCH_3), 3.29-3.21 (2H, m, NCH_2), 1.80 (2H, q, J = 6.2 Hz, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 156.6, 136.8, 128.7, 128.3, 128.2, 103.8, 66.7, 53.4, 37.2, 32.6; MS (ESI) m/z 254 $[M+H]^+$.

(*Z*)-1,1-Dimethoxyhex-3-ene (2x)[17]



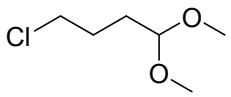
Colorless oil; 72% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 5.39-5.24 (2H, m, 2 x =CH), 4.33 (1H, t, J = 5.7 Hz, OCH), 3.28 (6H, s, 2 x OCH_3), 2.00-1.95 (4H, m, 2 x CH_2), 1.58-1.52 (2H, m, CH_2), 1.27-1.24 (22H, m, 11 x CH_2), 0.85 (3H, t, J = 6.4 Hz, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 129.9, 129.7, 104.5, 52.4, 32.4, 31.9, 29.7, 29.5, 29.4, 29.3, 29.2, 27.1, 24.6, 22.7, 14.1; HRMS exact mass calculated for $[M+H]^+$ ($C_{20}H_{41}O_2^+$) requires *m/z* 313.3101, found *m/z* 313.3105.

6,6-Dimethoxyhex-2-yne (2y)



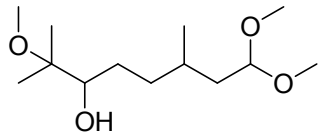
Colorless oil; 95% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.31 (1H, t, J = 5.6 Hz, OCH), 3.25 (6H, s, 2 x OCH_3), 2.07-2.02 (2H, m, CH_2), 1.72 (3H, s, CH_3), 1.55-1.26 (12H, m, 6 x CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 104.4, 79.2, 75.2, 52.4, 32.4, 29.3, 29.0, 28.9, 28.7, 24.5, 18.6, 3.4; HRMS exact mass calculated for $[M+H]^+$ ($C_{13}H_{25}O_2^+$) requires *m/z* 213.1849, found *m/z* 213.1854.

4-Chloro-1,1-dimethoxybutane (2z)[18]



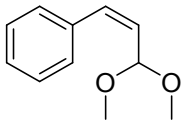
Colorless liquid with low b.p.; 33% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.37 (1H, t, J = 5.3 Hz, OCH), 3.55 (2H, t, J = 6.3 Hz, CH_2Cl), 3.31 (6H, s, 2 x OCH_3), 1.89-1.66 (4H, m, 2 x CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 103.8, 52.8, 44.8, 29.8, 27.7; MS (ESI) m/z 153 $[M+H]^+$.

2,8,8-Trimethoxy-2-methyloctan-3-ol (2aa)



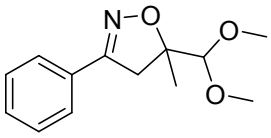
Reaction time 18 h. Colorless oil; 74% yield; Mixture of diastereoisomers; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.46-4.41 (1H, m, OCH), 3.37-3.33 (1H, m, C*H*OH), 3.27 (6H, s, 2 x OCH_3), 3.18 (3H, s, OCH_3), 2.46 (1H, br s, OH), 1.71-1.21 (7H, m, 3 x CH_2 and CH), 1.08 (3H, s, CH_3), 1.05 (3H, s, CH_3), 0.90-0.84 (3H, m, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 103.1, 103.0, 77.5, 76.8, 52.7, 52.6, 52.3, 52.2, 48.9, 39.6, 39.2, 34.6, 34.3, 29.2, 29.0, 28.5, 28.4, 20.7, 19.9, 19.6, 18.7; HRMS exact mass calculated for $[M+H]^+$ ($C_{13}H_{29}O_4^+$) requires *m/z* 249.2060, found *m/z* 249.2066. In order to characterize the product of the selective opening of the epoxide, a test reaction for the formation of the acetal under acidic conditions took place: In a solution of **1aa** (51 g, 0.30 mmol) in absolute MeOH (1 mL), trifluoroacetic acid (0.03 mL, 0.45 mmol) was added and the reaction mixture was left stirring for 5 h. Based on literature, the epoxide was opened selectively and the methoxy group ends up at the most substituted carbon. This product was characterized by ^{1}H-NMR and ^{13}C-NMR, and the spectra were identical with those obtained for the compound utilizing our method. Moreover, literature on similar aliphatic compounds was employed,[19] in order to specify the differences between the two possible regioisomers.

(*Z*)-(3,3-Dimethoxyprop-1-en-1-yl)benzene (2ab)



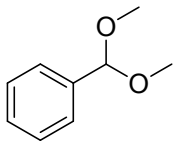
Reaction time 18 h. Colorless oil, 66% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.26-7.09 (5H, m, ArH), 6.54 (1H, d, J = 12.0 Hz, =CH), 5.60 (1H, dd, J = 12.0 and 7.3 Hz, =CH), 4.96 (1H, d, J = 7.3 Hz, OCH), 3.21 (6H, s, 2 x OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 136.0, 133.5, 129.0, 128.2, 128.0, 127.9, 99.5, 52.2; HRMS exact mass calculated for $[M+H]^+$ ($C_{11}H_{15}O_2^+$) requires *m/z* 179.1067, found *m/z* 179.1065. Upon heating or standing, isomerization occurred. Colorless oil, mixture of *Z:E* isomers 40:60; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.27-7.09 (5H, m, ArH), 6.62-6.51 (1H, m, =CH), 6.00 (0.6H, dd, J = 16.2 and 4.9 Hz, =CH), 5.60 (0.4H, dd, J = 12.0 and 7.3 Hz, =CH), 4.95 (0.4H, d, J = 7.3 Hz, OCH), 4.80 (0.6H, d, J = 4.9 Hz, OCH), 3.22-3.19 (6H, m, 2 x OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 136.0, 133.5, 131.2, 129.5, 129.0, 128.5, 128.2, 128.1, 128.0, 127.4, 126.7, 125.6, 102.8, 99.4, 52.7 52.2.

5-(Dimethoxymethyl)-5-methyl-3-phenyl-4,5-dihydroisoxazole (2ac)



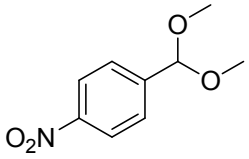
Pale yellow oil, 87% yield; Mixture of rotamers; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.70-7.61 (2H, m, ArH), 7.40-7.30 (3H, m, ArH), 4.56 (4.51) (1H, s, OCH), 3.69 (1H, d, J = 17.2 Hz, C*H*H), 3.46 (3.45) (6H, s, 2 x OCH_3), 3.01 (1H, d, J = 17.2 Hz, CH*H*), 1.57 (1.46) (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 156.9, 137.3, 130.5, 128.7, 126.5, 99.8, 99.6, 88.2, 87.9, 55.9, 41.3, 41.2, 19.8; HRMS exact mass calculated for $[M+H]^+$ ($C_{13}H_{18}NO_3^+$) requires *m/z* 236.1281, found *m/z* 236.1281.

(Dimethoxymethyl)benzene (2ad)[6]



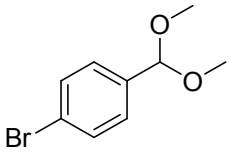
Colorless oil, 89% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.47-7.31 (5H, m, ArH), 5.40 (1H, s, OCH), 3.33 (6H, s, 2 x OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.2, 128.6, 128.4, 126.9, 103.3, 52.9; MS (ESI) m/z 153 $[M+H]^+$.

1-(Dimethoxymethyl)-4-nitrobenzene (2ae)[6]



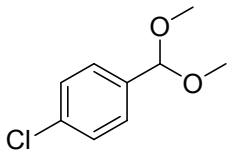
Colorless oil, 59% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.21 (2H, d, J = 7.8 Hz, ArH), 7.63 (2H, d, J = 7.8 Hz, ArH), 5.46 (1H, s, OCH), 3.32 (6H, s, 2 x OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 145.2, 128.0, 123.6, 120.8, 101.7, 52.9; MS (ESI) m/z 198 $[M+H]^+$.

1-Bromo-4-(dimethoxymethyl)benzene (2af)[6]



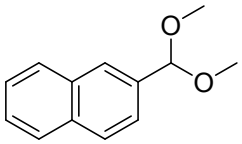
Colorless oil, 74% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.48 (2H, d, J = 8.5 Hz, ArH), 7.31 (2H, d, J = 8.5 Hz, ArH), 5.35 (1H, s, OCH), 3.29 (6H, s, 2 x OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 137.3, 131.5, 128.7, 122.7, 102.4, 52.7; MS (ESI) m/z 231 $[M+H]^+$.

1-Chloro-4-(dimethoxymethyl)benzene (2ag)[6]



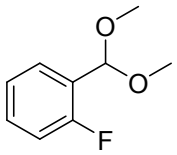
Colorless oil, 84% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.38 (2H, d, J = 8.8 Hz, ArH), 7.32 (2H, d, J = 8.8 Hz, ArH), 5.36 (1H, s, OCH), 3.30 (6H, s, 2 x OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 136.8, 134.4, 128.5, 128.3, 102.4, 52.7; MS (ESI) m/z 187 $[M+H]^+$.

2-(Dimethoxymethyl)naphthalene (2ah)[20]



Colorless oil, 90% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.96-7.84 (4H, m, ArH), 7.59-7.47 (3H, m, ArH), 5.57 (1H, s, OCH), 3.38 (6H, s, 2 x OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 135.6, 133.6, 133.2, 128.5, 128.3, 127.9, 126.4, 126.3, 126.2, 124.6, 103.3, 52.9; MS (ESI) m/z 203 $[M+H]^+$.

1-(Dimethoxymethyl)-2-fluorobenzene (2ai)[21]



Colorless oil, 93% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.60-6.99 (4H, m, ArH), 5.61 (1H, s, OCH), 3.37 (6H, s, 2 x OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 160.3 (d, J = 248.4 Hz), 130.1 (d, J = 8.3 Hz), 127.9 (d, J = 3.8 Hz), 125.2 (d, J = 12.5 Hz), 123.7 (d, J = 3.6 Hz), 115.3 (d, J = 3.6 Hz), 98.5 (d, J = 3.6 Hz), 53.4; ^{19}F (188 MHz, $CDCl_3$): δ -77.6; MS (ESI) m/z 171 $[M+H]^+$.

Determination of the Quantum Yield

Determination of the photon flux of the lamps

A 0.006M solution of potassium ferrioxalate was prepared by dissolving 120 mg of potassium ferrioxalate hydrate in 40 mL of 0.05M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 10 mg of phenanthroline and 2.25 g of sodium acetate in 250 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the lamps, 2.0 mL of the solution of potassium ferrioxalate was placed in the cuvette, UV-Vis absorbance recorded (absorbance of interest at 510 nm) and irradiated for 90 seconds at the lamps. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was allowed to rest for 1 h (complete coordination of ferrous ions to phenanthroline). The absorbance of the solution was then measured at 510 nm.

The fraction of light absorbed (f) by this solution was calculated, using this absorbance (A):

$$f = 1 - 10^{-A} = 1 - 10^{-4.9987} = 0.9999$$

In order to measure the photon flux, the mol of Fe^{2+} are required:

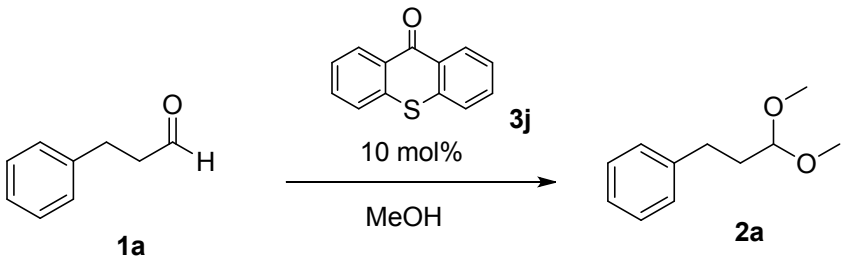
$$\text{Mol } Fe^{2+} = \frac{V \times \Delta A}{l \times \varepsilon} = \frac{0.00235\ \text{L} \times 0.382}{1.0\ \text{cm} \times 11.100\ \text{L mol}^{-1}\ \text{cm}^{-1}} = 8.09 \times 10^{-8}\ \text{mol}$$

In this equation, V is the total volume of the solution after addition of the phenanthroline (0.00235 L), ΔA is the difference in the absorbance at 510 nm between the irradiated and the non-irradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11.100 L mol^{-1} cm^{-1}). The photon flux then calculated:

$$\text{Flux} = \frac{\text{Mol } Fe^{2+}}{\Phi \times t \times f} = \frac{8.09 \times 10^{-8}\ \text{mol}}{1.35 \times 90\ \text{sec} \times 0.9999} = 6.66 \times 10^{-10}\ \text{einsteins}^{-1}$$

In this equation, Φ is the quantum yield of the ferrioxalate actinometer,[22] t is the time of the irradiation (90 seconds), and f is the fraction of the light absorbed at the lamps (that is calculated above). Thus, the photon flux of the spectrophotometer was calculated to be 6.66×10^{-10} einstein s^{-1}.

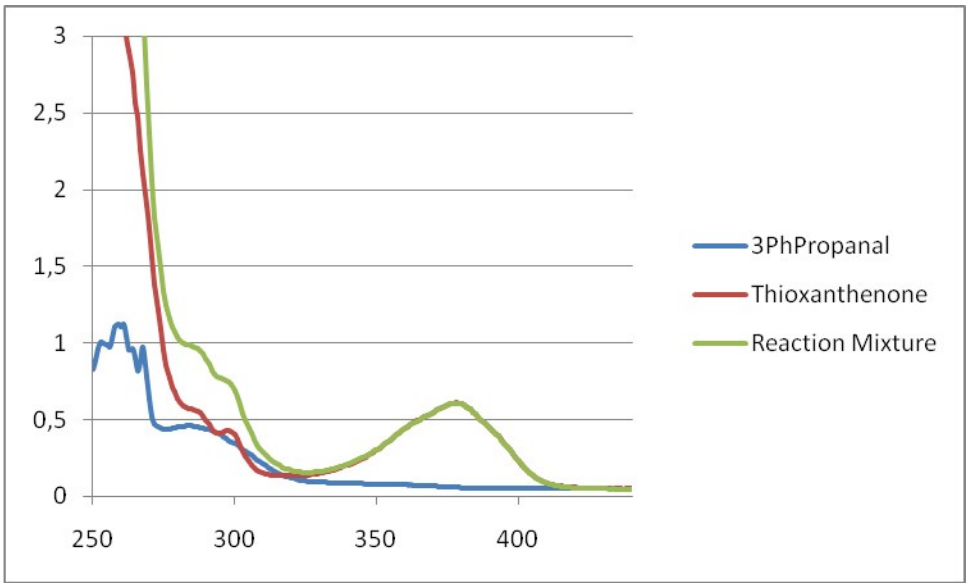
Determination of the quantum yield



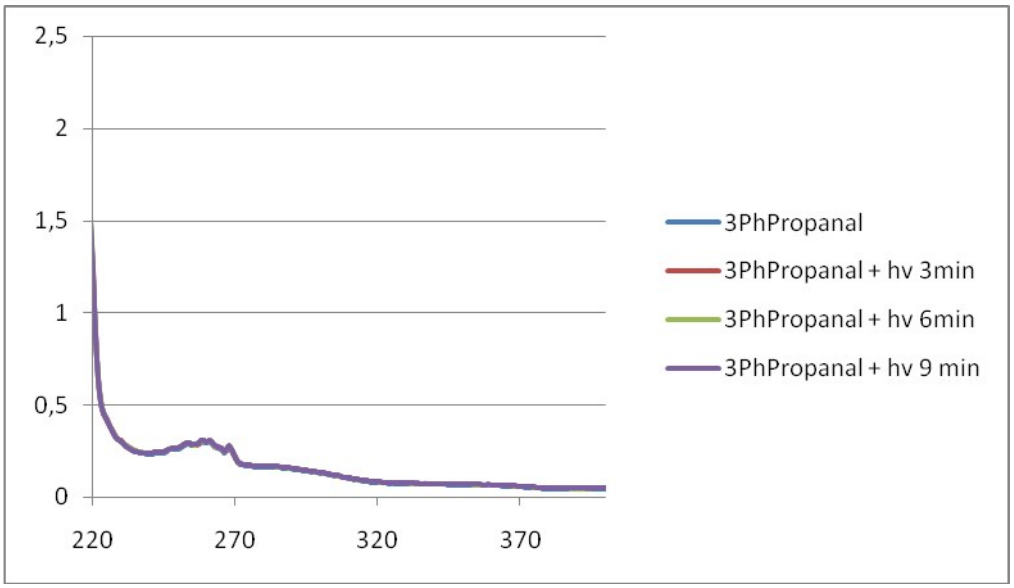
A cuvette was charged with 3-phenylpropionaldehyde (16.7 mg, 0.12 mmol), thioxanthene-9-one (2 mg, 0.01 mmol) in methanol (0.5 mL). The sample was stirred and then irradiated under CFL irradiation for 1800 s (0.5 h). After irradiation, the solvent was removed and the yield of the product was determined by ^{1}H NMR (92%). The quantum yield was determined with the following equation:

$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f} = \frac{0.115 \times 10^{-3}\ \text{mol}}{6.66 \times 10^{-10}\ \text{einstein}\ s^{-1} \times 1800\ s \times 0.9999} = 96$$

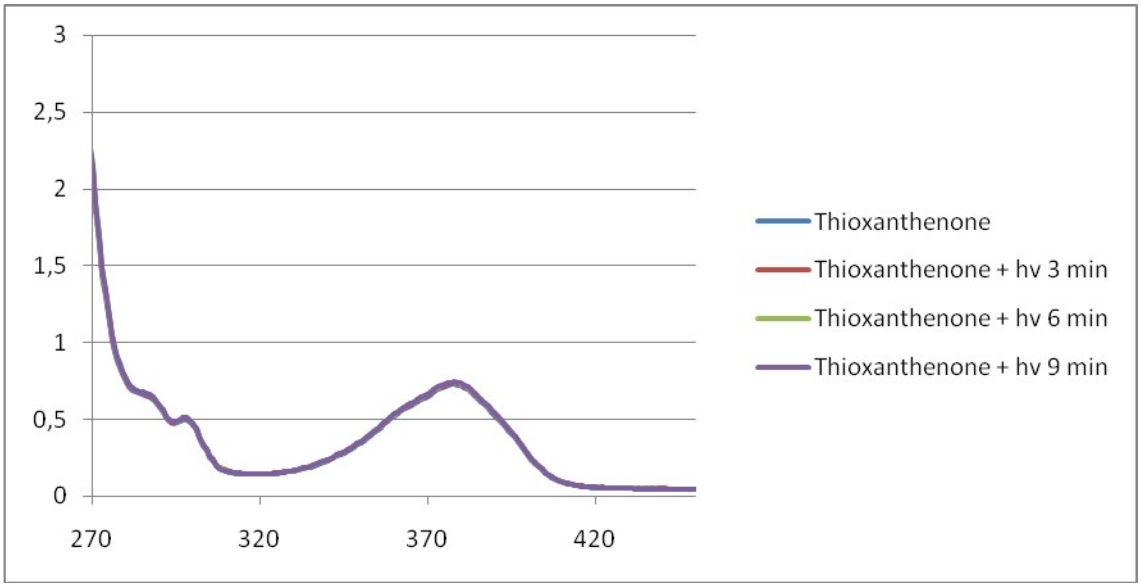
Mechanistic Investigations with UV-Vis Absorption Spectra



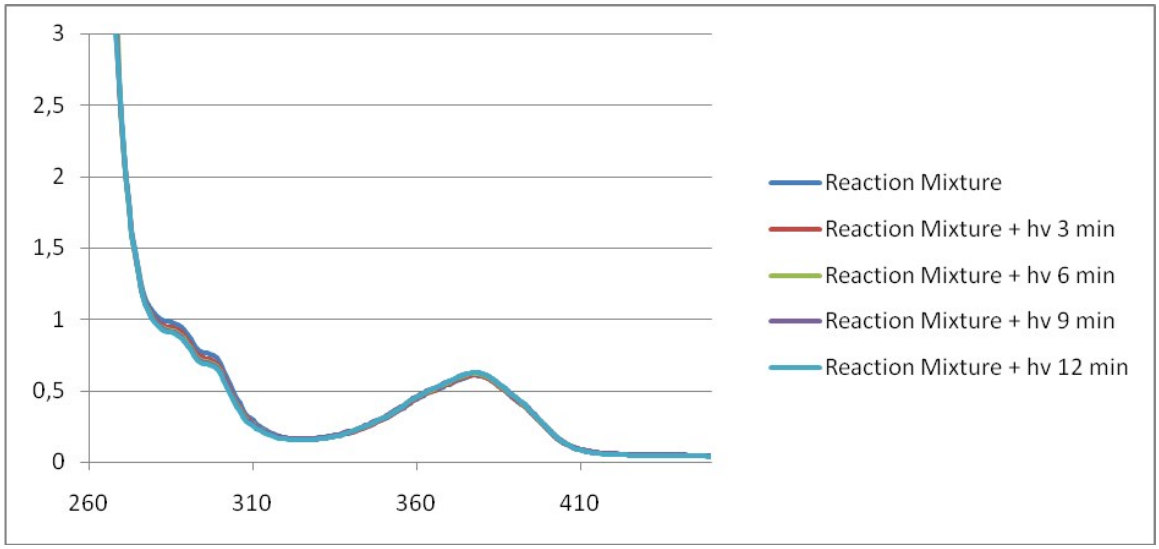
Mixtures of 3-phenylpropanal (3 x 10^{-4} M) in MeOH, thioxanthen-9-one (2 x 10^{-5} M) in MeOH and the reaction mixture



3-Phenylpropanal (3 x 10^{-4} M) in MeOH after consecutive irradiation



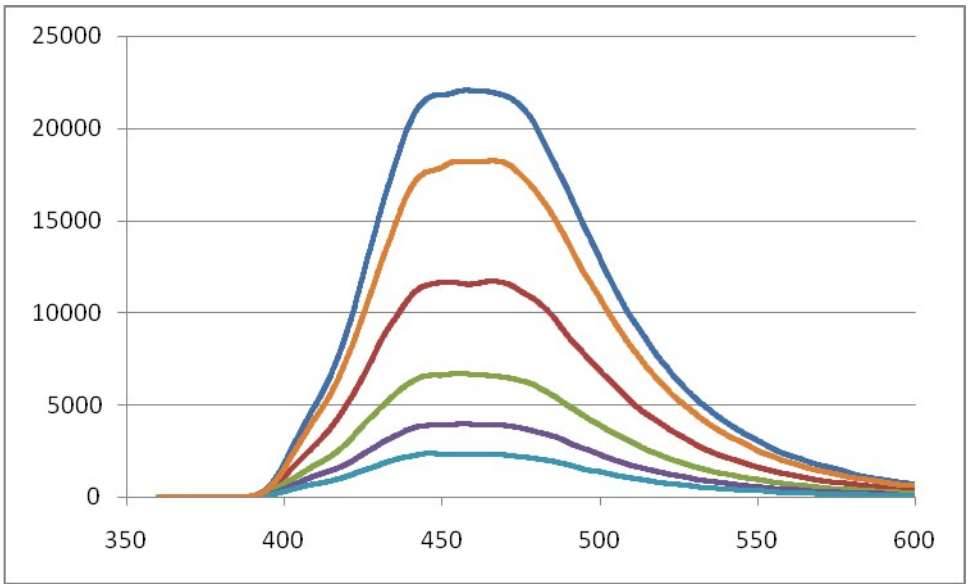
Thioxanthen-9-one (2 x 10^{-5} M) in MeOH after consecutive irradiation

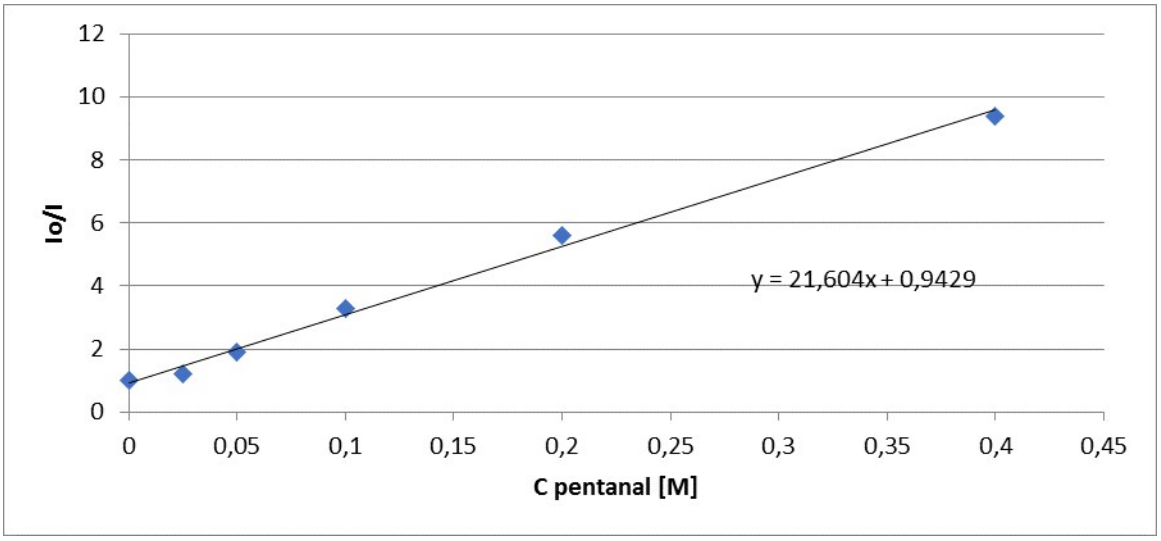


3-Phenylpropanal (3 x 10^{-4} M) and thioxanethen-9-one (2 x 10^{-5} M) in MeOH after consecutive irradiation

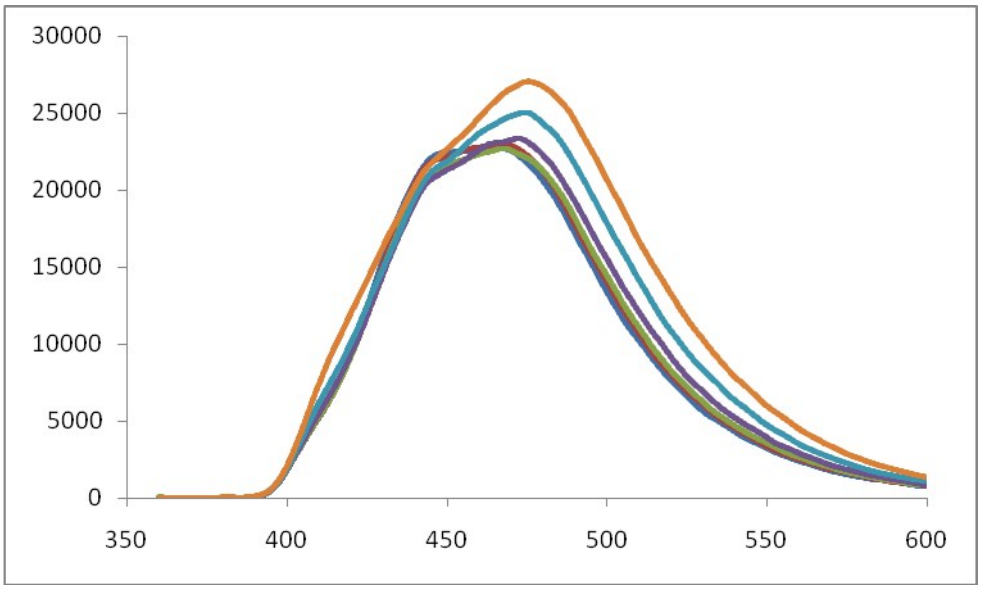
Fluorescence Quenching Studies

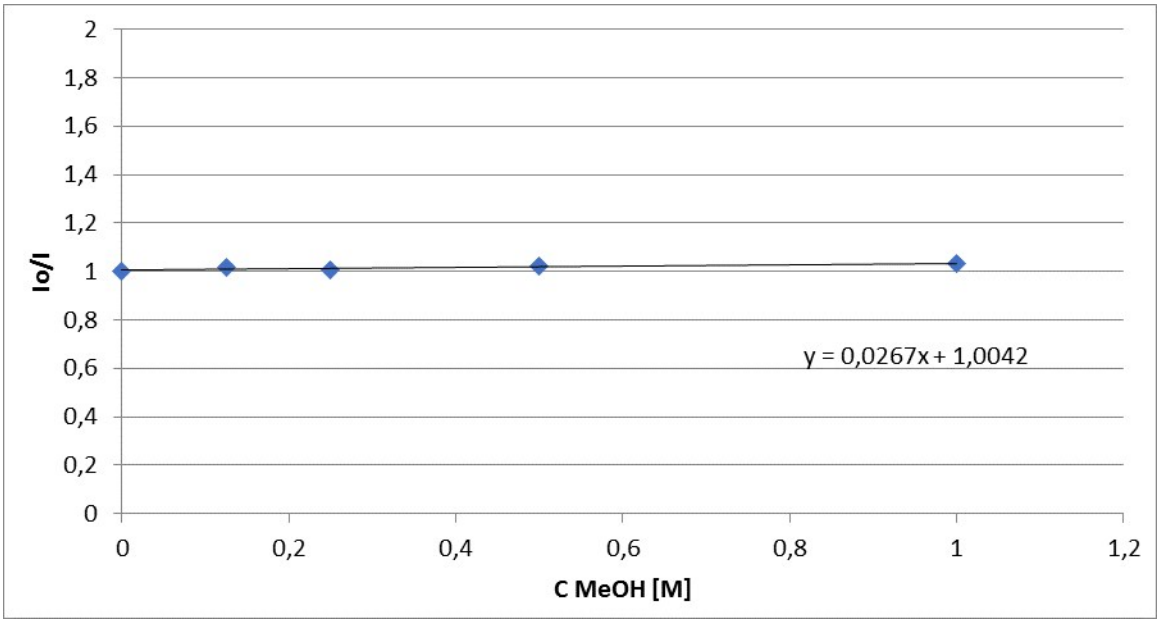
After irradiation of thioxanthen-9-one (10^{-3}M in MeCN) at 312 nm, its fluorescence was measured at 450 nm. Increasing the amount of the added pentanal, a constant decrease in the fluoroscence was observed.



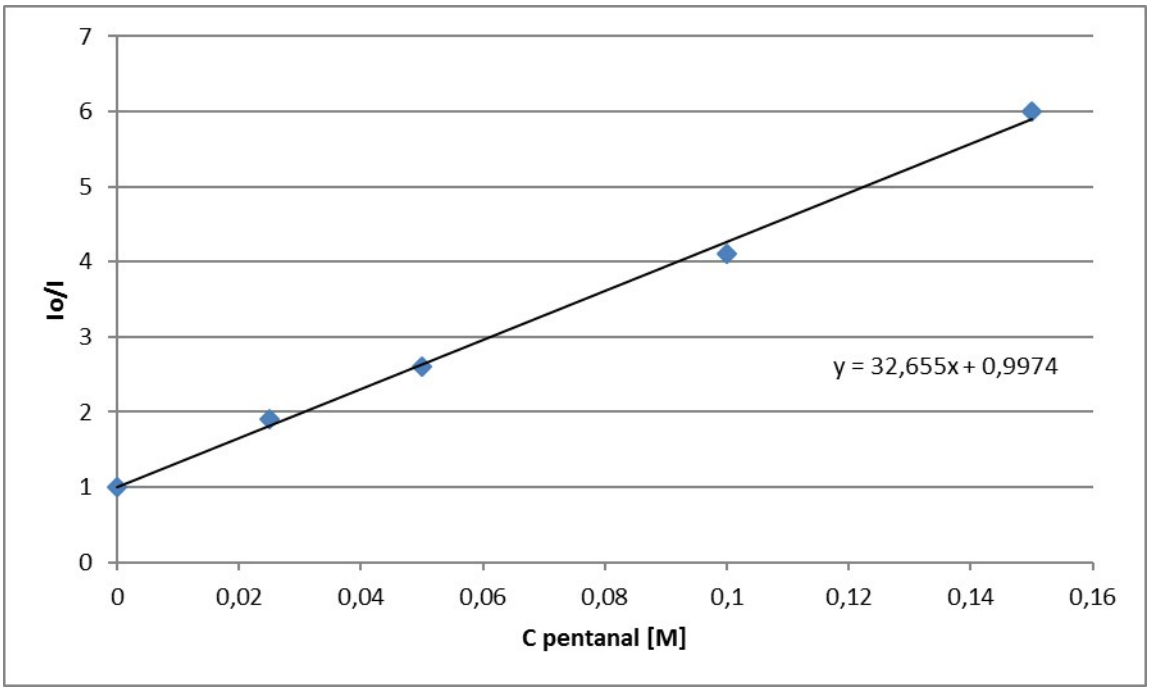


After irradiation of thioxanthen-9-one (10^{-3}M in MeCN) at 312 nm, its fluorescence was measured at 450 nm. Increasing the amount of the added methanol, no changes in the fluoroscence were observed.

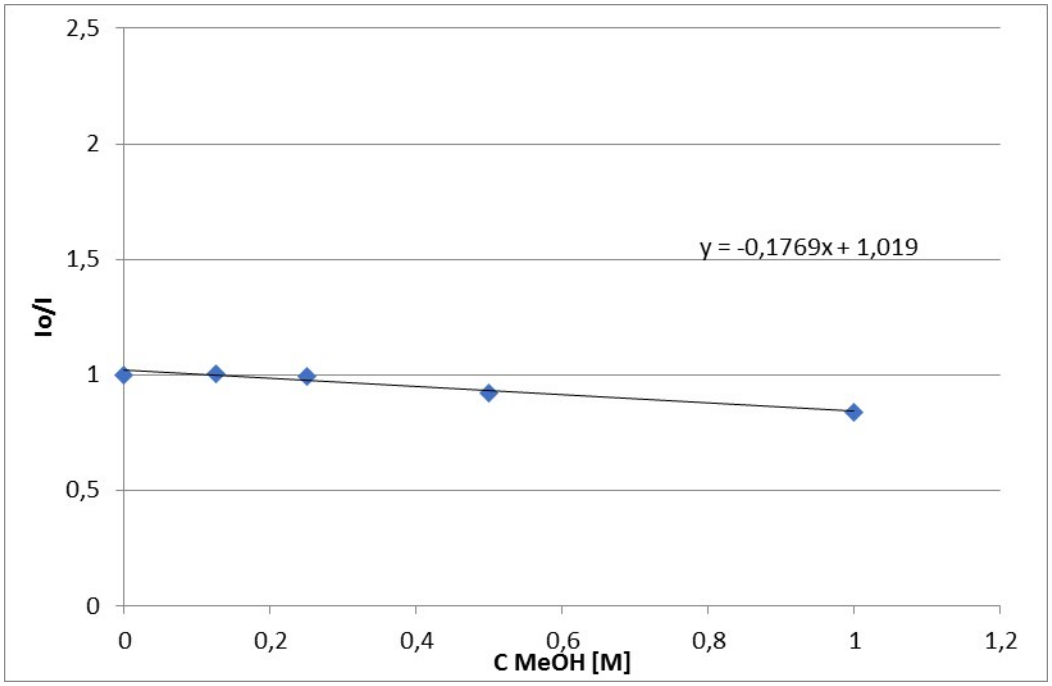




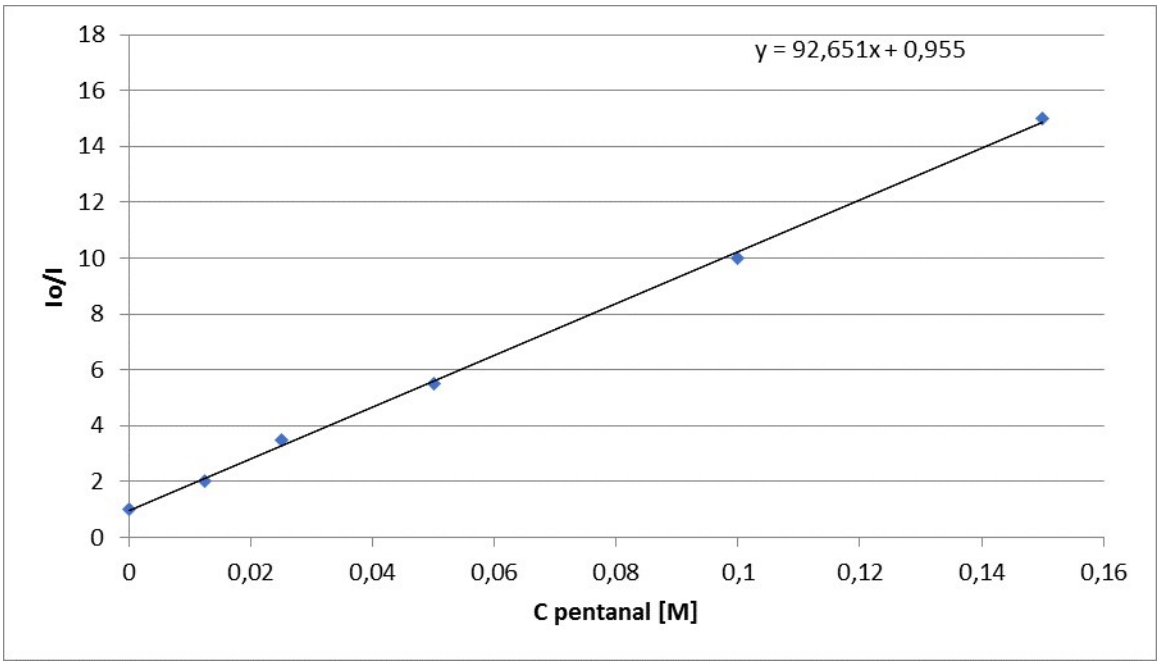
Similar fluorescence quenching experiments took place in a variety of solvents, in order to determine the dependence of the quenching of the photocatalyst by pentanal and methanol.



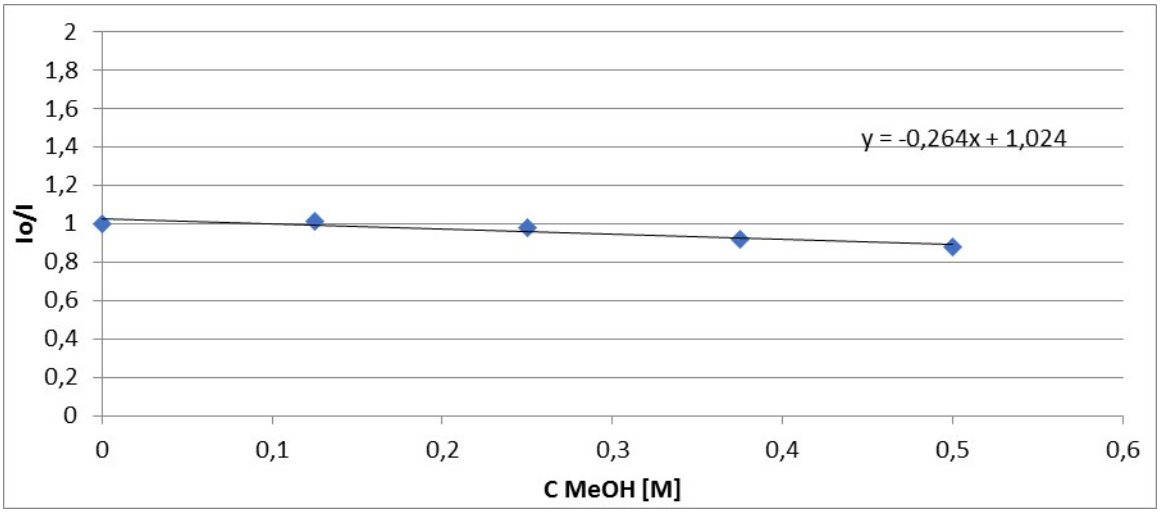
in AcOEt



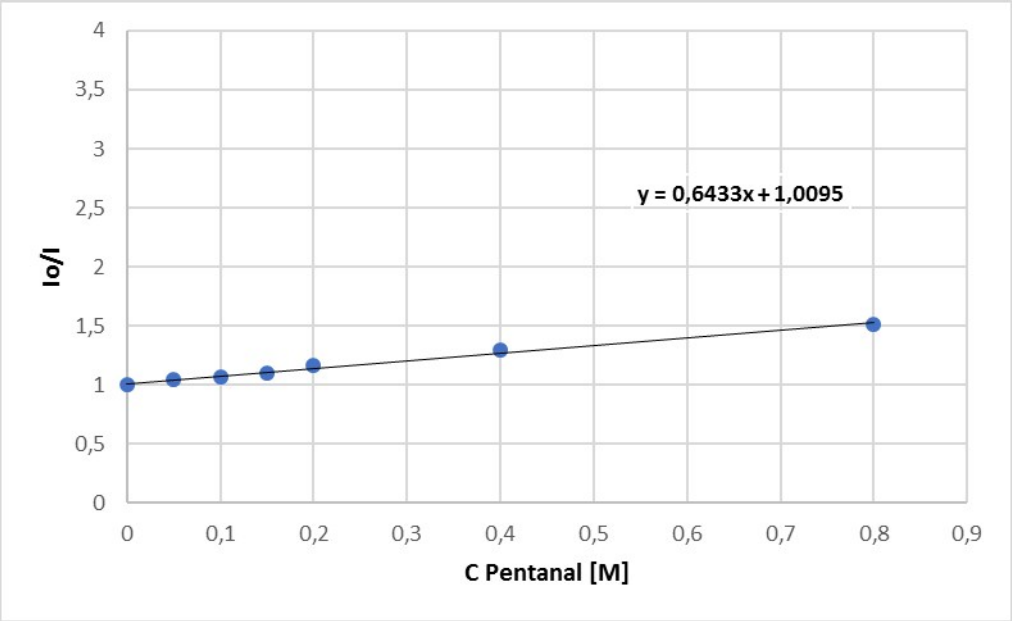
In AcOEt



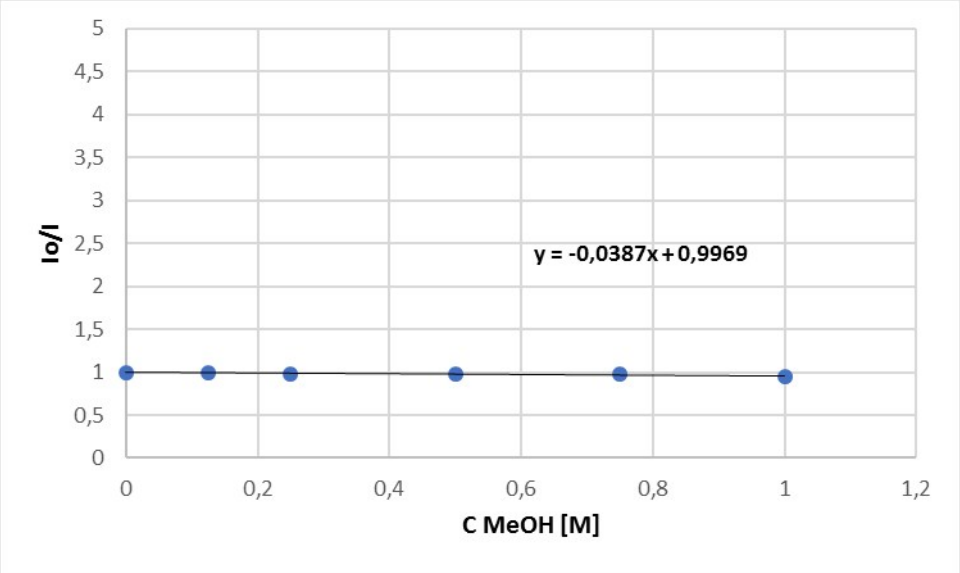
In CH_2Cl_2



In CH_2Cl_2


y = 0,6433x + 1,0095
Io/I
C Pentanal [M]
0
0,5
1
1,5
2
2,5
3
3,5
4
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9

In H_2O

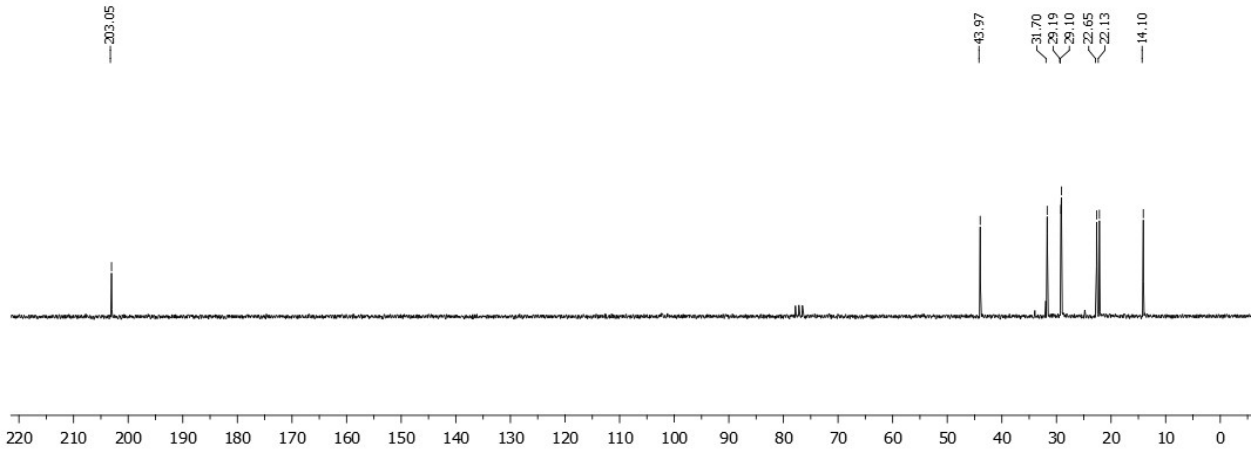

y = -0,0387x + 0,9969
Io/I
C MeOH [M]
0
0,5
1
1,5
2
2,5
3
3,5
4
4,5
5
0,2
0,4
0,6
0,8
1
1,2

In H_2O

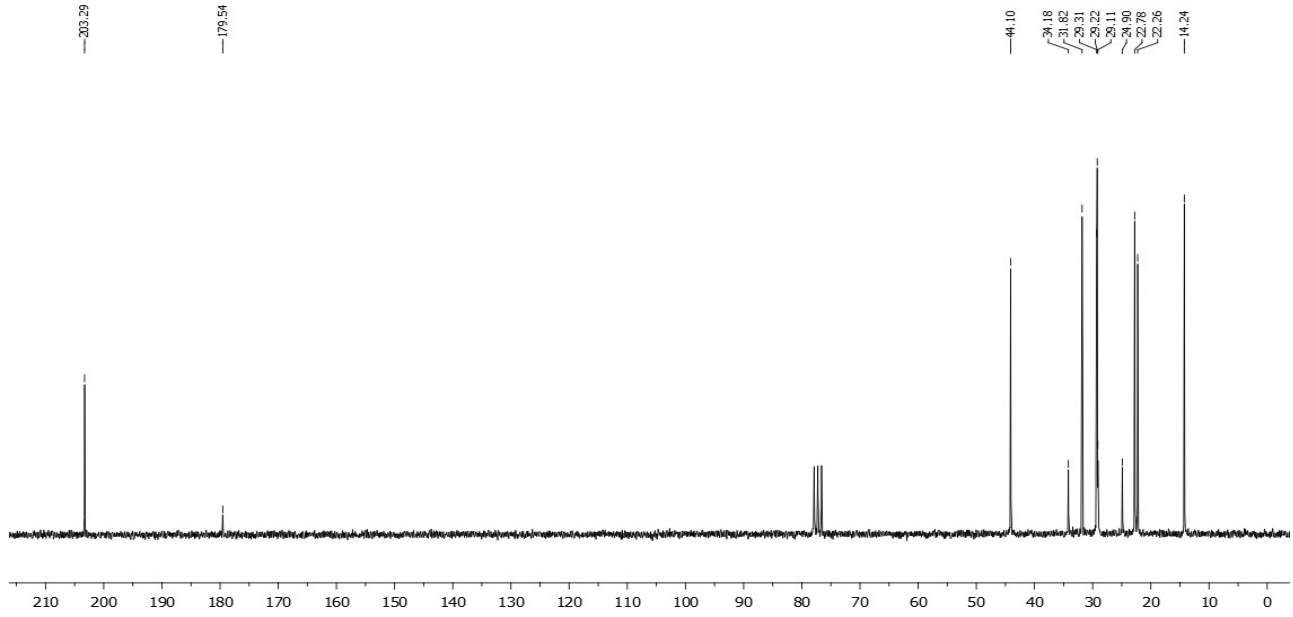
Taking into consideration, the similarity in fluorescence quenching, shown in the Stern-Volmer plots in solvents with different polarity, we can assume an energy transfer mechanism is in place.[23]

^{13}C-NMR Mechanistic Experiments

The ^{13}C-NMR spectra of octanal in $CDCl_3$ were recorded before and after irradiation for 30 min (in MeOH, then evaporation). After irradiation, the corresponding carboxylic acid was also observed.

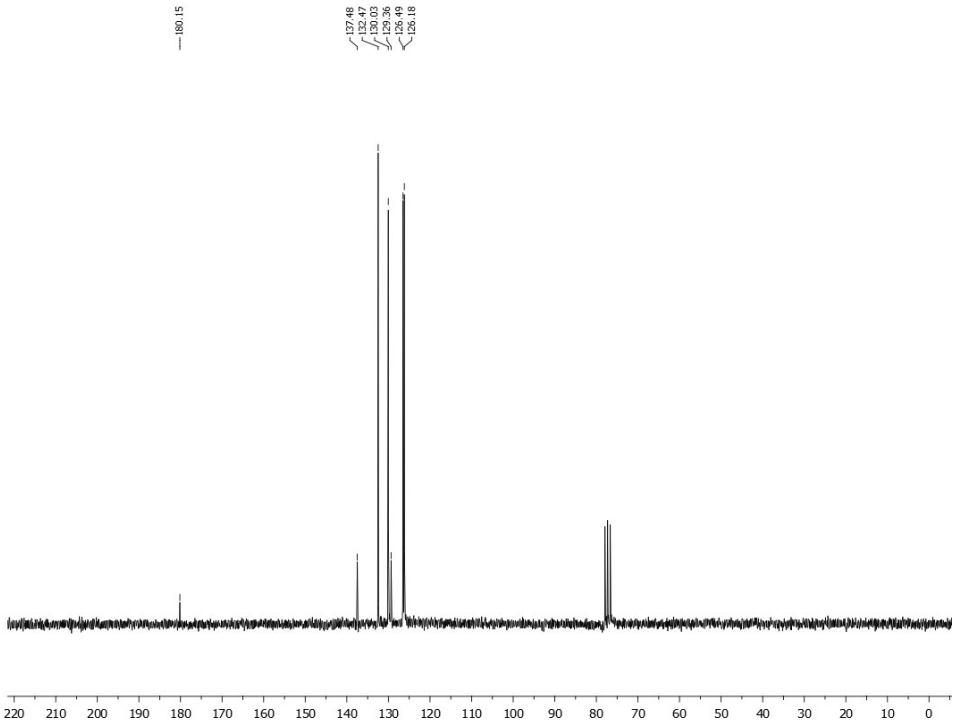


^{13}C-NMR spectrum of octanal in $CDCl_3$

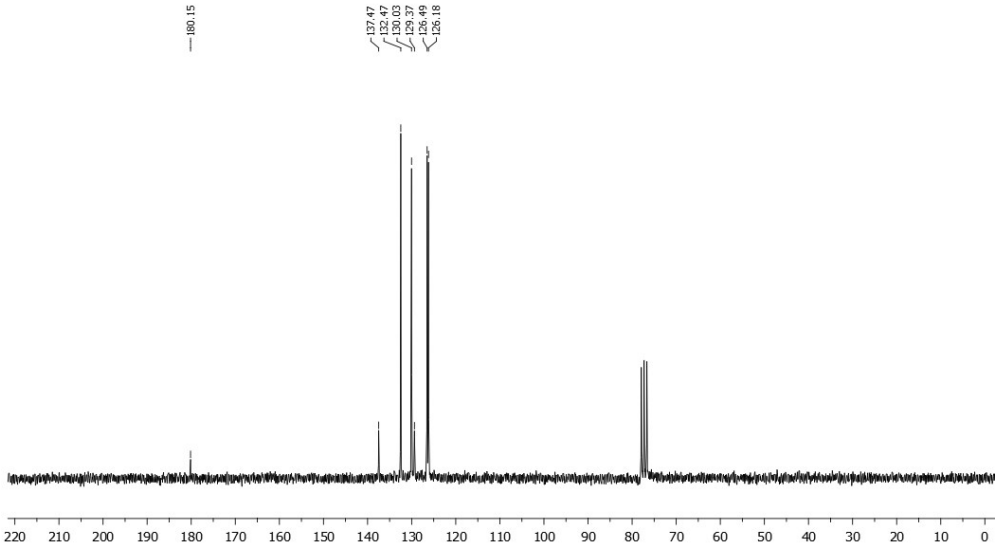


^{13}C-NMR spectrum of octanal in $CDCl_3$ after irradiation for 30 min (in MeOH)

^{13}C-NMR spectra (in $CDCl_3$) of thioxanthen-9-one, before and after irradiation for 30 min (in MeOH) were recorded. After irradiation, not significant change occurred, in order to assume a plausible degradation mechanism.

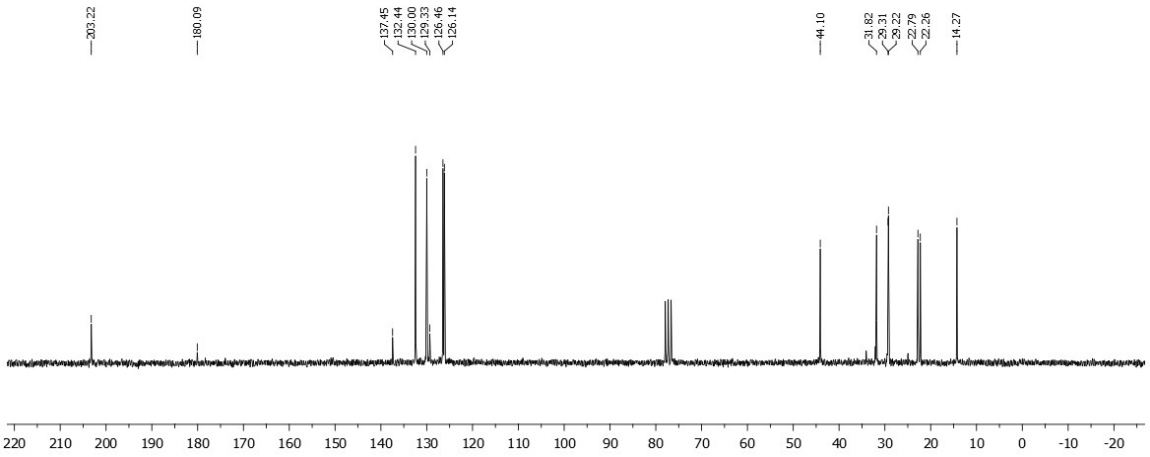


^{13}C-NMR spectrum of thioxanthen-9-one in $CDCl_3$

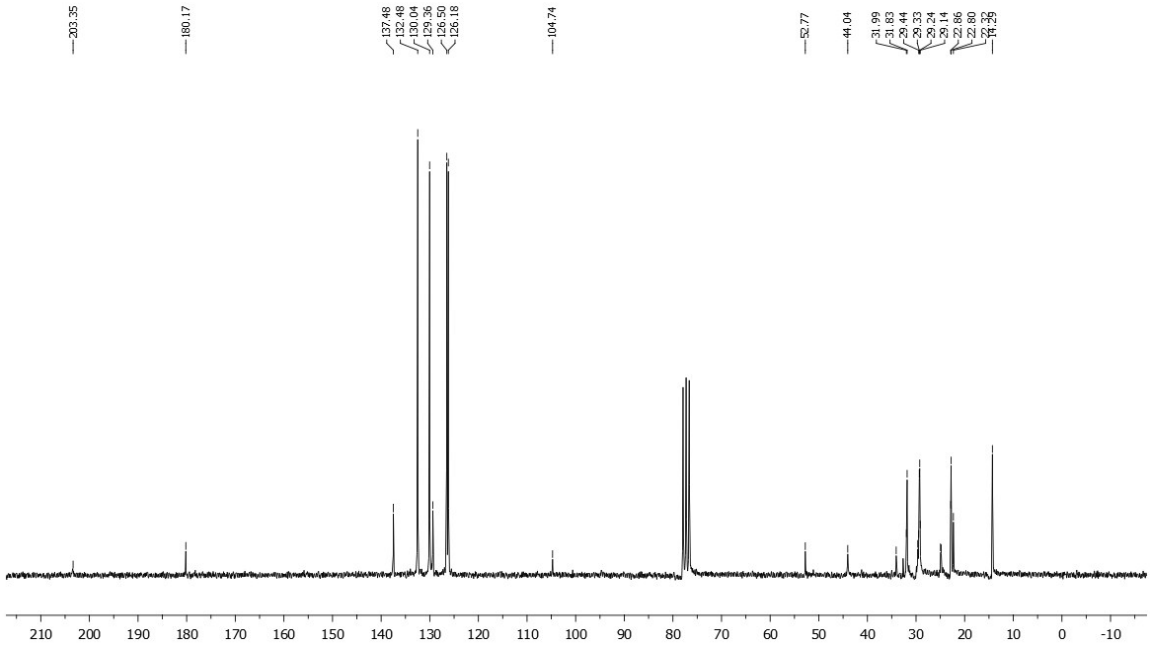


^{13}C-NMR spectrum of thioxanthen-9-one in $CDCl_3$ after irradiation for 30 min (in MeOH)

Finally, the reaction mixture (octanal and thioxanthen-9-one) (in $CDCl_3$) presented all expected signals. As it was expected after 30 min of irradiation of the reaction, no decomposition to the carboxylic acid was observed and the product has also started being formed.



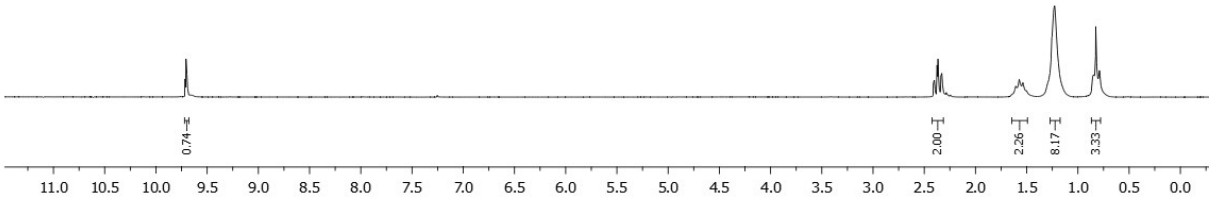
^{13}C NMR spectrum of the reaction mixture in $CDCl_3$



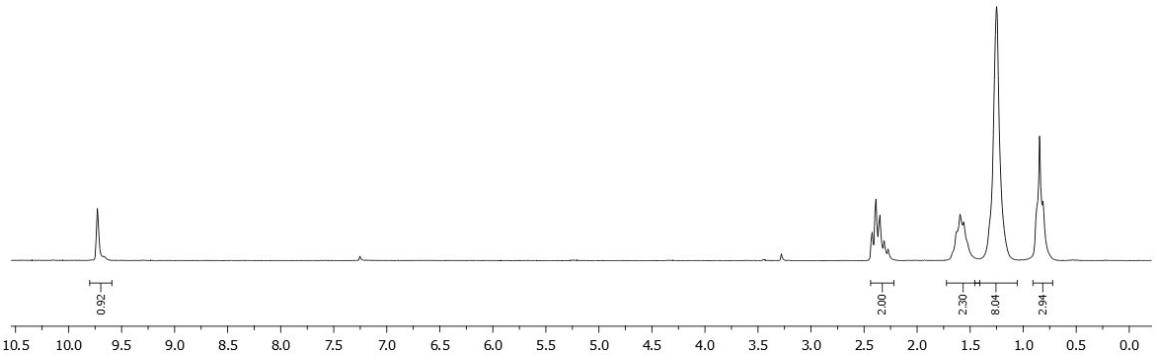
^{13}C NMR spectrum of the reaction mixture in $CDCl_3$ after irradiation for 30 min (in MeOH)

^{1}H-NMR Mechanistic Experiments

The ^{1}H-NMR spectra of octanal in $CDCl_3$ were recorded before and after irradiation for 30 min (in MeOH, then evaporation). After irradiation, the corresponding carboxylic acid was also observed.

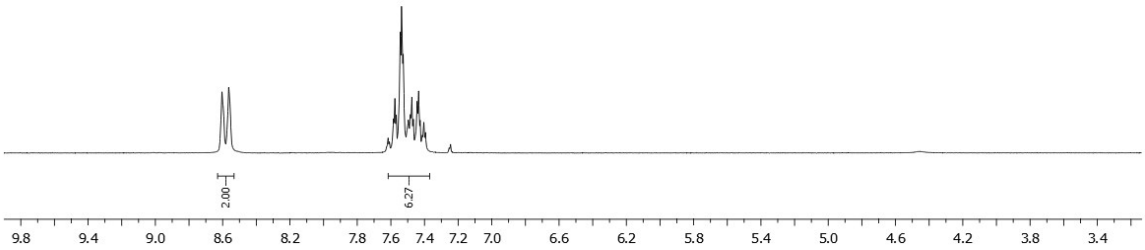


^{1}H NMR spectrum of octanal in $CDCl_3$

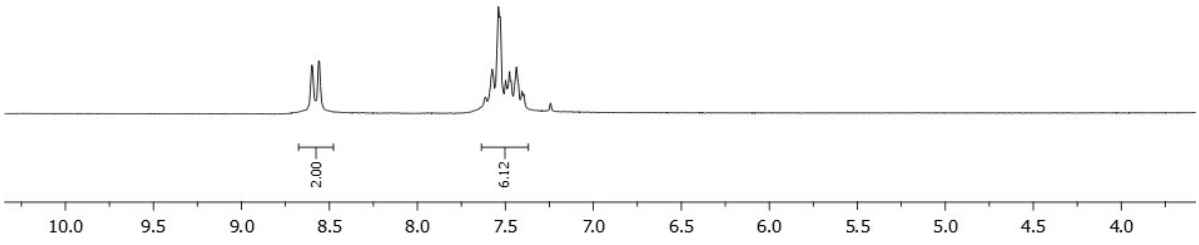


^{1}H NMR spectrum of octanal in $CDCl_3$ after irradiation for 30 min (in MeOH)

^{1}H-NMR spectra (in $CDCl_3$) of thioxanthen-9-one, before and after irradiation for 30 min (in MeOH) were recorded. After irradiation, not significant change occurred, in order to assume a plausible degradation mechanism.

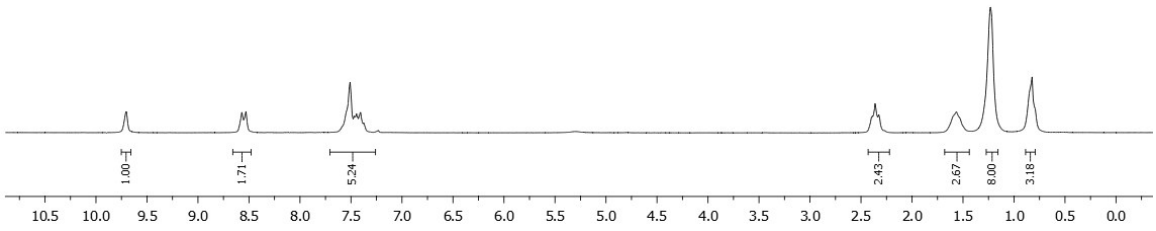


^{1}H NMR spectrum of thioxanthen-9-one in $CDCl_3$

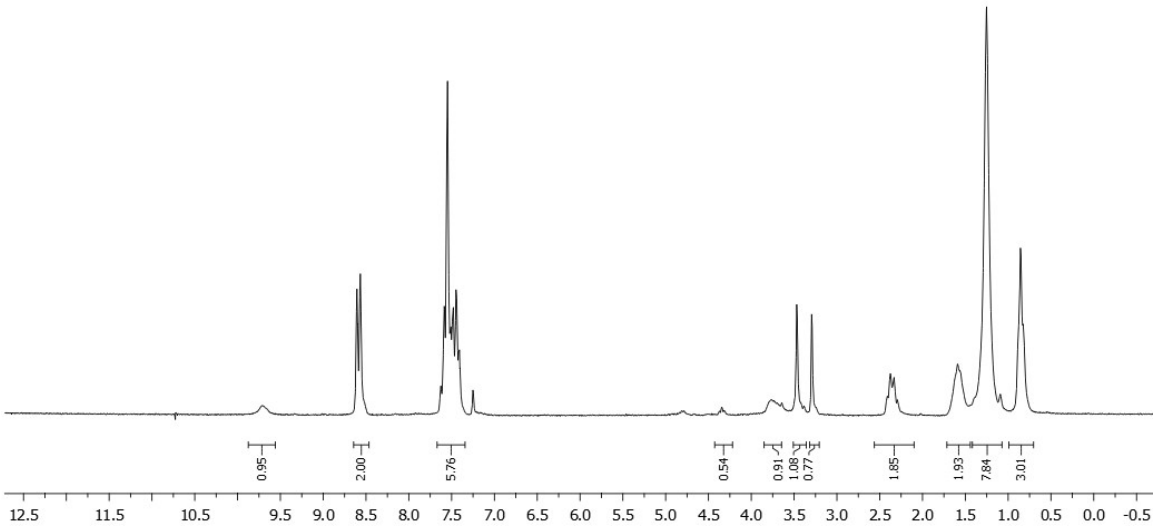


^{1}H NMR spectrum of thioxanthen-9-one in $CDCl_3$ after irradiation for 30 min (in MeOH)

Finally, the reaction mixture (octanal and thioxanthen-9-one) (in $CDCl_3$) presented all expected signals. As it was expected after 30 min of irradiation of the reaction, no decomposition to the carboxylic acid was observed and the product has also started being formed.



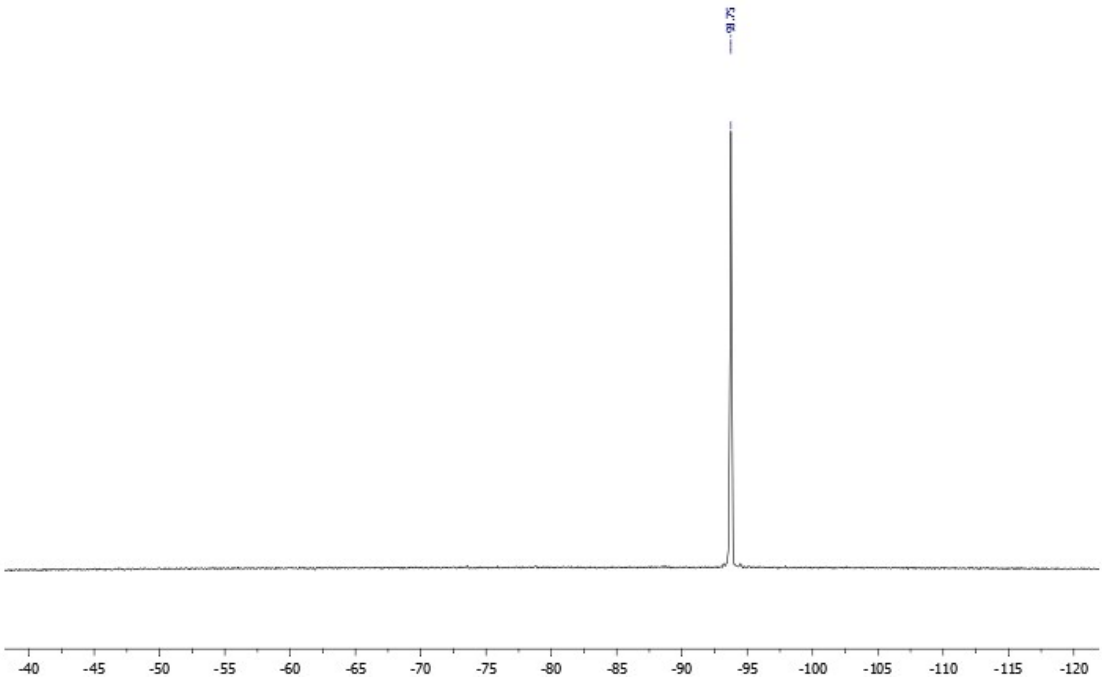
^{1}H NMR spectrum of the reaction mixture in $CDCl_3$ (in MeOH)



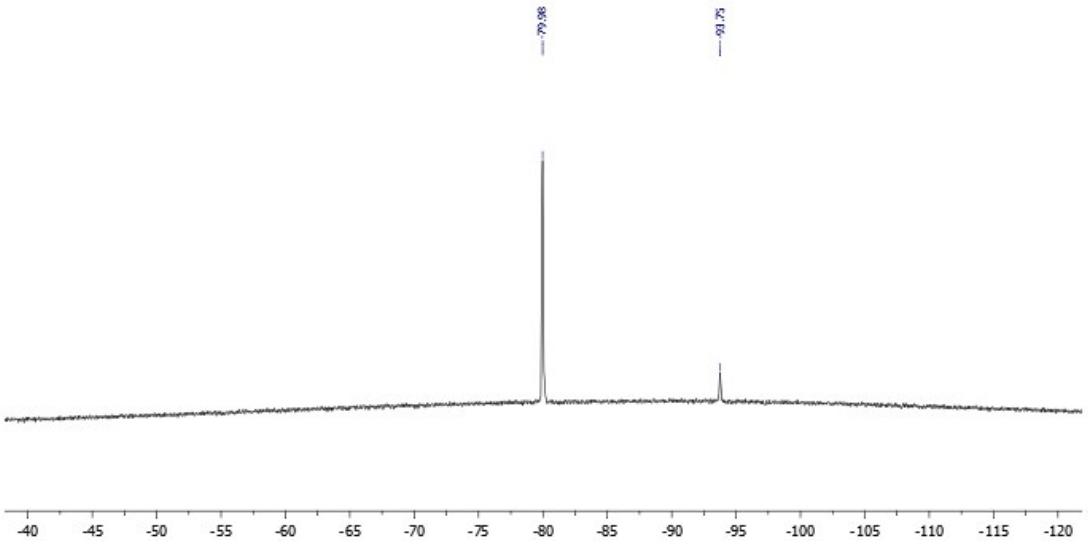
^{1}H NMR spectrum of the reaction mixture in $CDCl_3$ after irradiation for 30 min (in MeOH)

^{19}F-NMR Mechanistic Experiments

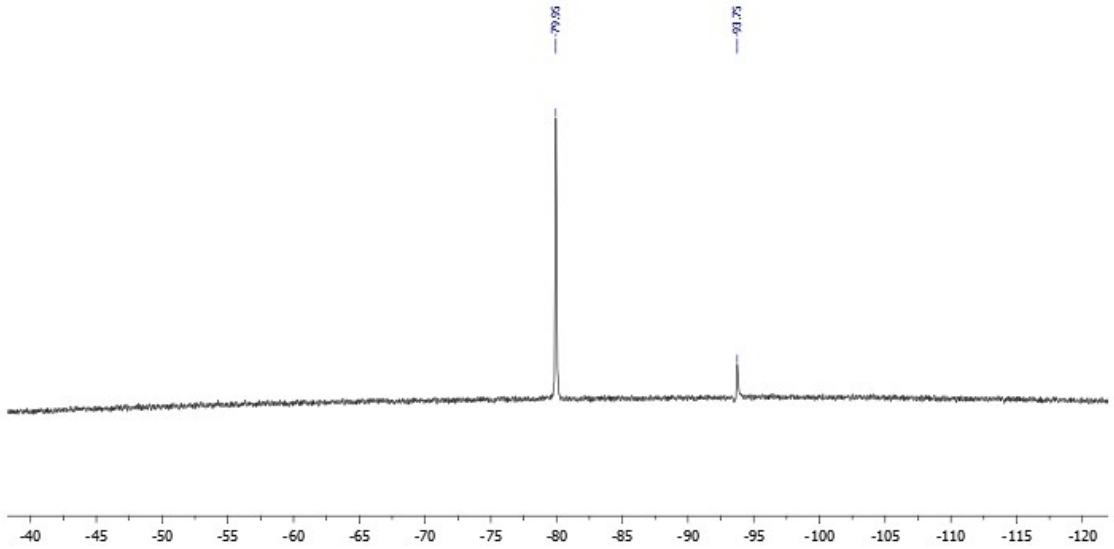
The ^{19}F-NMR spectra of 2-fluorobenzaldehyde in $CDCl_3$ were recorded before and after addition of thioxanthenone, utilizing 4-fluoroanisol (-93.75 ppm) as the internal standard. In the following spectra is obvious that upon the addition of thioxanthenone in a solution of 2-fluorobenzaldehyde, a slight difference in the chemical shift of the aldehyde is occurred, which can be attributed to the formation of an EDA complex between an aldehyde and thioxanthenone.



^{19}F NMR spectrum of the 4-fluoroanisol in $CDCl_3$ as internal standard



^{19}F NMR spectrum of the 2-fluorobenzaldehyde in $CDCl_3$ before addition of thioxanthone (-79.98 ppm) (4-fluoroanisol as internal standard)

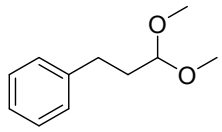


^{19}F NMR spectrum of the 2-fluorobenzaldehyde in $CDCl_3$ after addition of thioxanthone (-79.95 ppm) (4-fluoroanisol as internal standard)

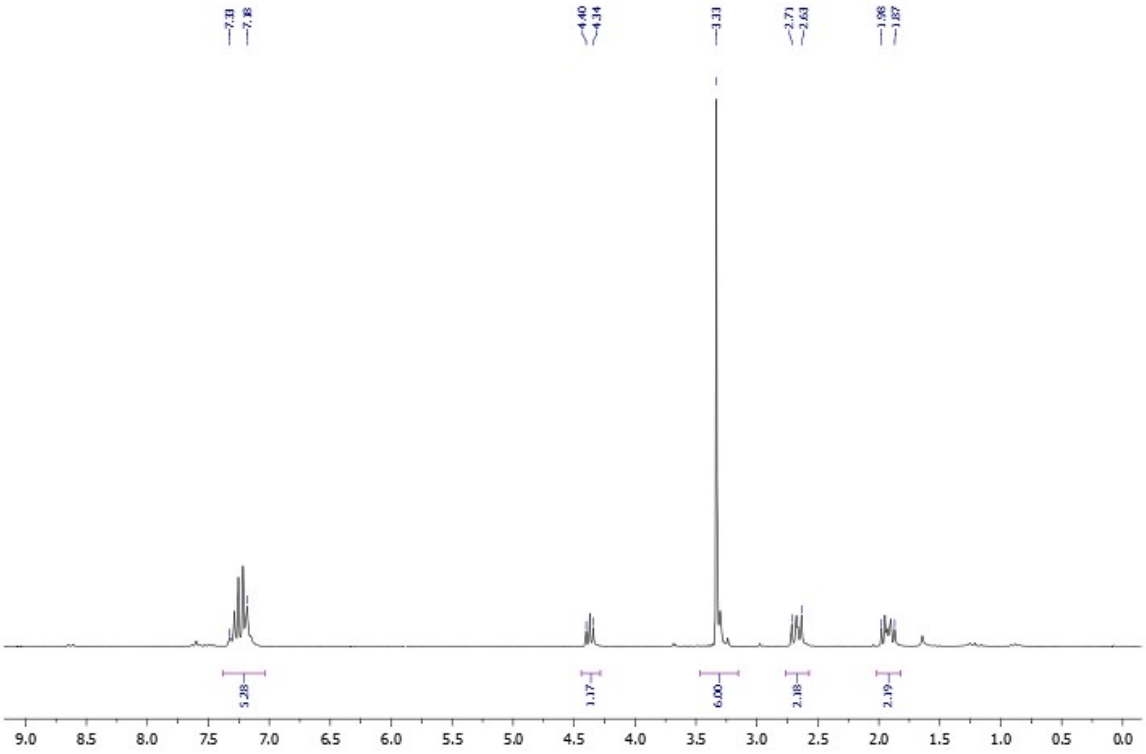
References

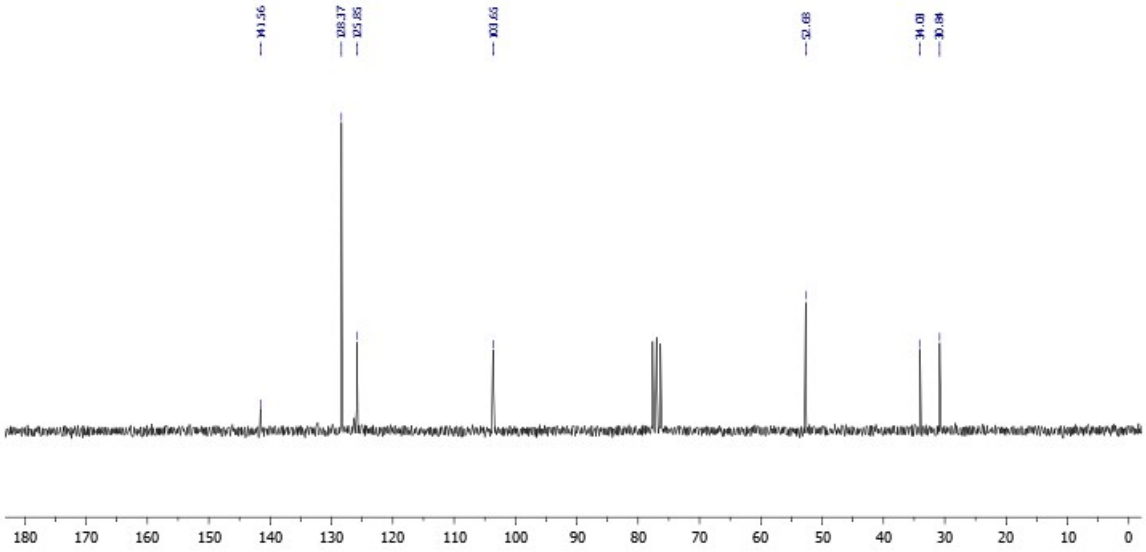
1. C.-M. Wang, D. Song, P.-J. Xia, J. Wang, H.-Y. Xiang, H. Yang, *Chem. Asian J.*, **2018**, *13*, 271.
2. M. L. Buck, D. M. Evans, V. A. Evans, D. Herkt, H. Sharp, J. Hollinshead, F. Mitschang, P. J. Murphy, R. J. Nash, J. Wenbourne, *Tetrahedron*, **2017**, 73, 4545.
3. D. Bezier, S. Park, M. Brookhart, *Org. Lett.*, **2013**, *15*, 496.
4. K. Heckenbichler, A. Schweiger, L. A. Brandner, A. Binter, M. Toplak, P. Macheroux, K. Gruber, R. Breinbauer, *Angew. Chem., Int. Ed*., **2018**, *57*, 7240.
5. V. Chudasama, A. R. Akhbar, K. A. Bahou, R. J. Fitzmaurice, S. Caddick, *Org. Biomol. Chem.*, **2013**, *11*, 7301.
6. Q. Zhou, T. Jia. X.-X. Li, L. Zhou, C.-J. Li, Y. S. Feng, *Synth. Commun.*, **2018**, *48*, 1068.
7. R. A. Ugarte, T. W. Hudnail, *Green Chem.*, **2017**, *19*, 1990.
8. A. Bauer, N. Maulide, *Org. Lett.*, **2018**, *20*, 1461.
9. M. Kunishima, D. Nakata, T. Sakuma, K. Kono, S. Sato, S. Tani, *Chem. Pharm. Bull.*, **2001**, *49*, 1.
10. H. M. Liu, C. Y. Chang, Y. C. Lai, M. D. Yang, C. Y. Chang, *Tetrahedron: Asymmetry*, **2014**, *25*, 187.
11. H. Yi, L. Niu, S. Wang, T. Liu, A. K. Singh, A. Lei, *Org. Lett.*, **2017**, *19*, 122.
12. F. J. Fananás, M. Álvarez-Pérez, F. Rodríquez, *Chem. Eur. J.* , **2005**, *11*, 5938.
13. R. Guryn, M. Staszewski, P. Kopczacki, K. Walczyski, *Med. Chem*., **2016**, *13*, 65.
14. Y. Yu, L. S. Liebeskind, *J. Org. Chem*., **2004**, *69*, 3554.
15. T. Schlager, D. Schepmann, B. Wunsch, *Synthesis*, **2011**, *24*, 3965.
16. S. Nonaka, K. Sugimoto, H. Ueda, H. Tokuyama, *Adv. Synth. Catal*., **2016**, *358*, 380.
17. K. Christiansen, V. Mahadevan, C. V. Viswanathan, R. T. Holman, *Lipids*, **1969**, *4,* 421.
18. M. Maryska, L. Fojtikova, R. Jurok, B. Holubova, O. Lapcik, M. Kuchar, *RSC Adv*., **2018**, *8*, 16243.

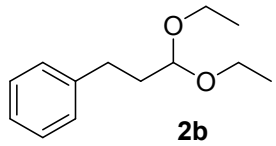
19. (a) Y. Masaki, T. Miura, M. Ochiai, *Bull. Chem. Soc. Jpn*., **1996**, *69*, 195. (b) W. Kuhnz, H. Rembold, *Org. Magn. Reson*., **1981**, *16*, 138. (c) T. Akihisa, K. Watanabe, R. Yoneima, T. Suzuki, Y. Kimura, *J. Nat. Prod*., **2006**, *69*, 604.
20. L. Qin, P. Wang, Y. Zhang, Z. Ren, X. Zhang, C. S. Da, *Synlett.*, **2016**, *27*, 571.
21. H. Li, Y.-F. Han, Y.-Ji. Lin, Z.-W. Guo, G.-X. Jin, *J. Am. Chem. Soc*., **2014**, *136*, 2982.
22. (a) J. Lee, H. H. Seliger, *J. Chem. Phys.*, **1964**, *40*, 519. (b) J. N. Demas, W. D. Bowman, E. F. Zalewskl, R. A. Velapoldl, *J. Phys. Chem*. **1981**, *85*, 2766. (c) J. R. Bolton, M. I. Stefan, P.-S. Shaw, K. R. Lykke, *J. Photochem. Photobiol. A: Chemistry*, **2011**, *222*, 166.
23. (a) F. Strieth-Kalthoff, M. J. James, M. Teders, L. Pitzer, F. Glorius, *Chem. Soc. Rev.*, **2018**, *47*, 7190. (b) N. J. Turro, *Modern Molecular Photochemistry*, University Science Books, Sausalito, **1991**. (c) V. Balzani, P. Ceroni, A. Juris, *Photochemistry and Photophysics: Concepts, Research, Applications*, Wiley-VCH, Weinheim, **2014**.



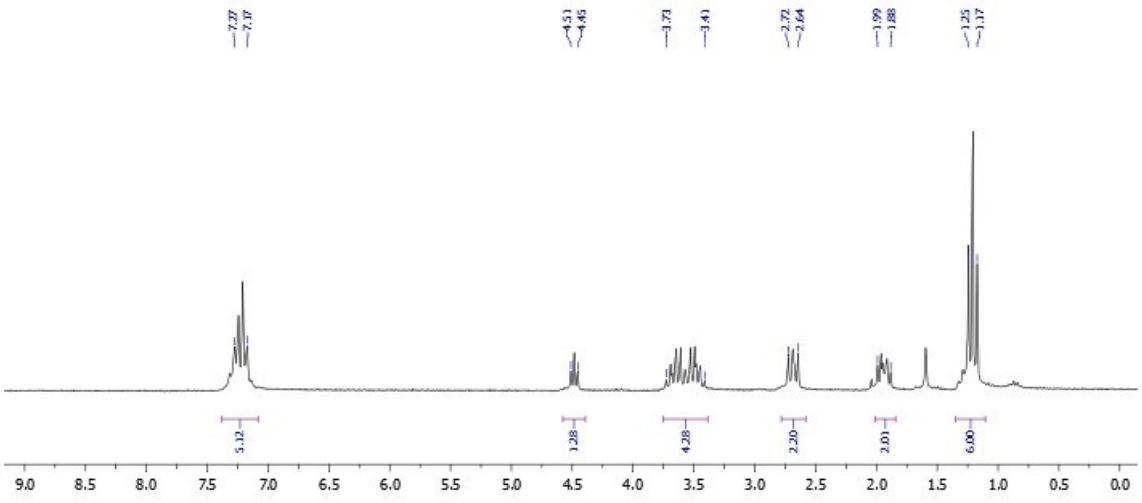
2a

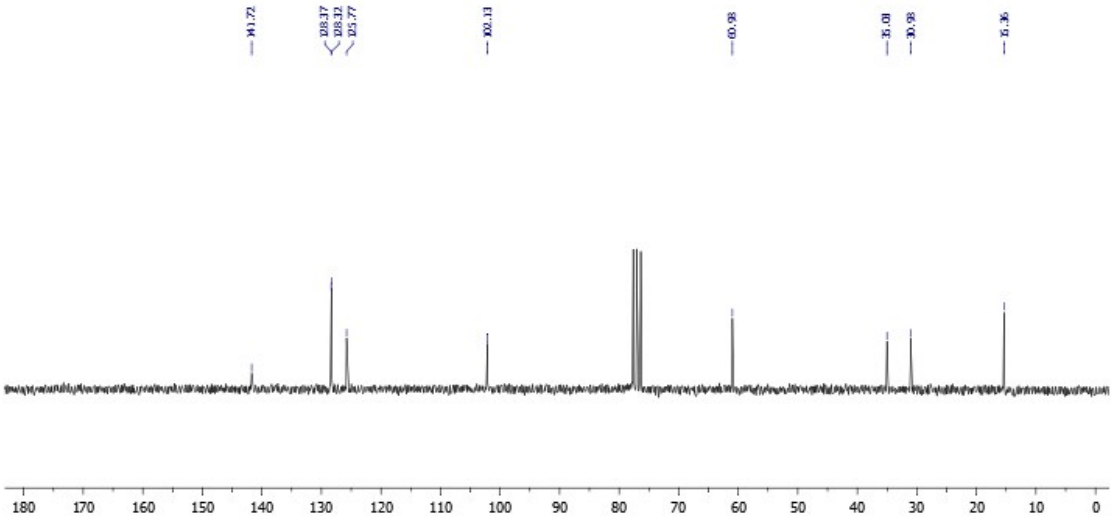

7.33
7.28
4.40
4.34
3.33
2.71
2.63
1.98
1.87
5.28
1.17
6.00
2.18
2.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

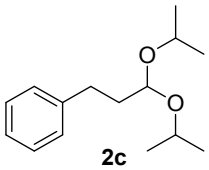

141.56
128.37
125.85
103.65
52.68
34.01
30.84
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



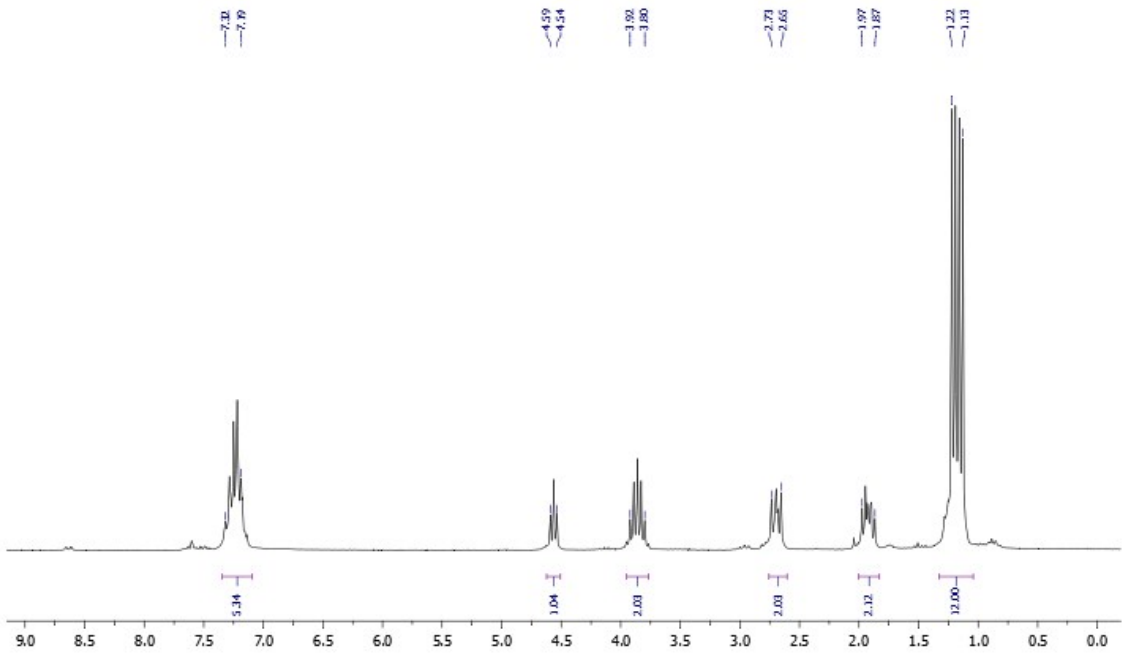
2b

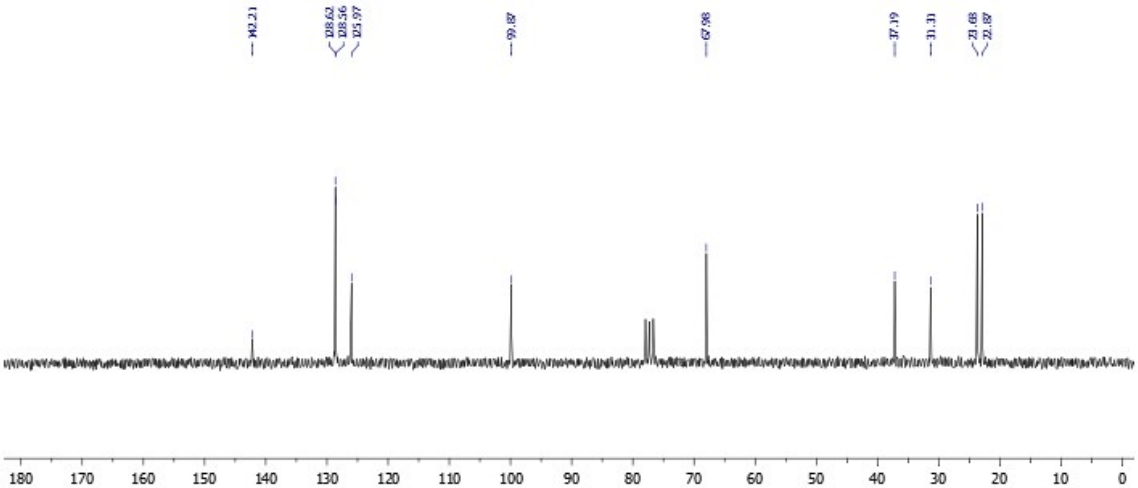

7.27
7.19
4.51
4.45
3.73
3.41
2.72
2.64
1.99
1.88
1.25
1.17
5.12
1.28
4.28
2.20
2.01
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

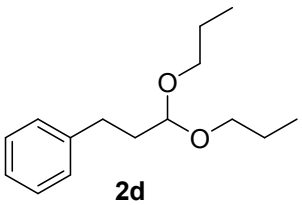

141.72
128.37
128.32
125.77
102.13
60.98
35.01
30.98
15.36
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
O

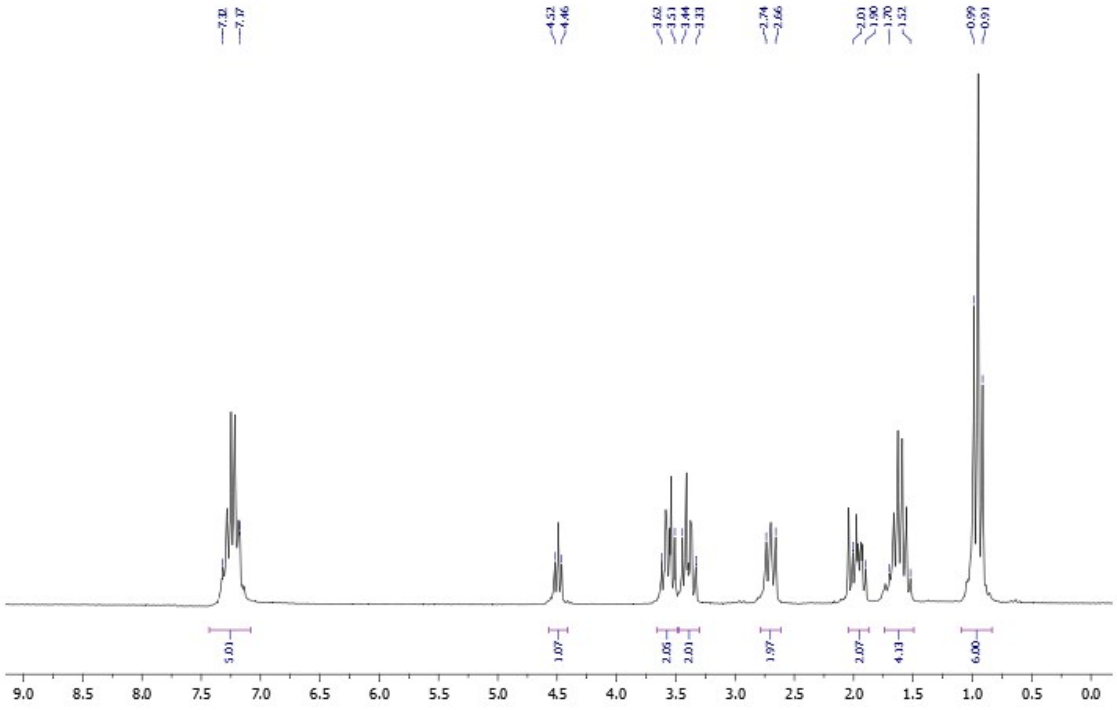
2c

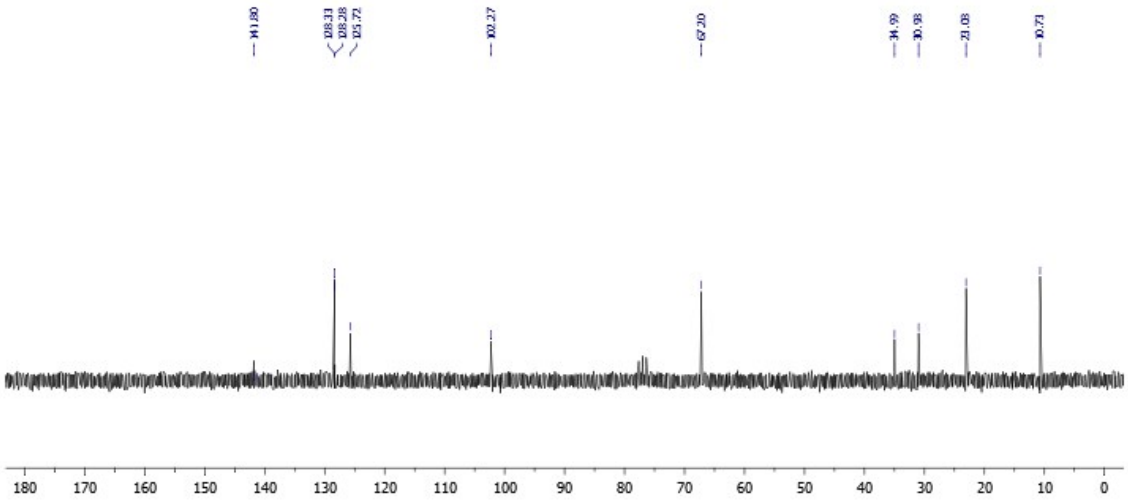

7.32
7.29
4.59
4.54
3.92
3.80
2.73
2.65
1.97
1.87
1.22
1.13
5.34
1.04
2.03
2.03
2.12
12.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

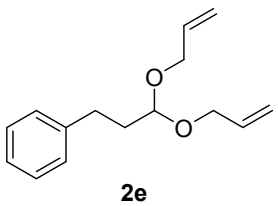

142.21
128.62
128.56
125.97
99.87
67.98
37.19
31.31
21.68
21.87
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



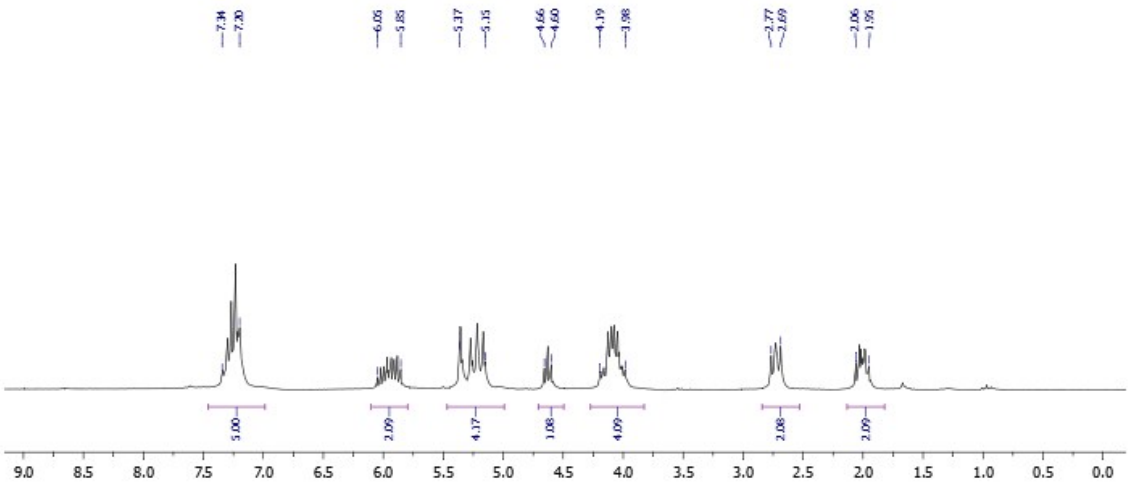
2d

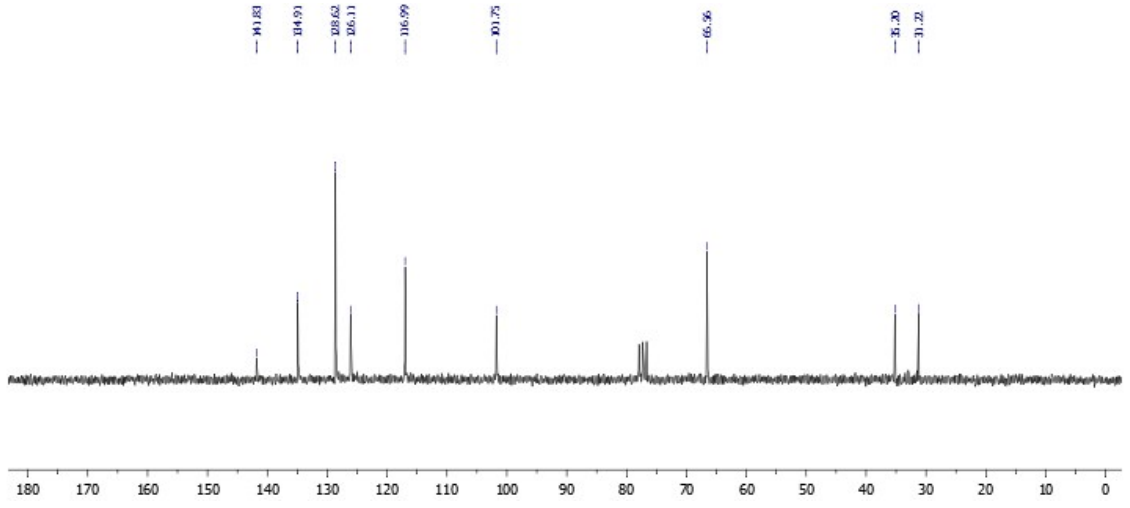


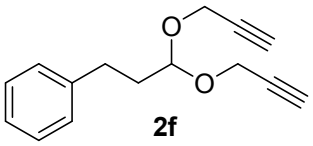




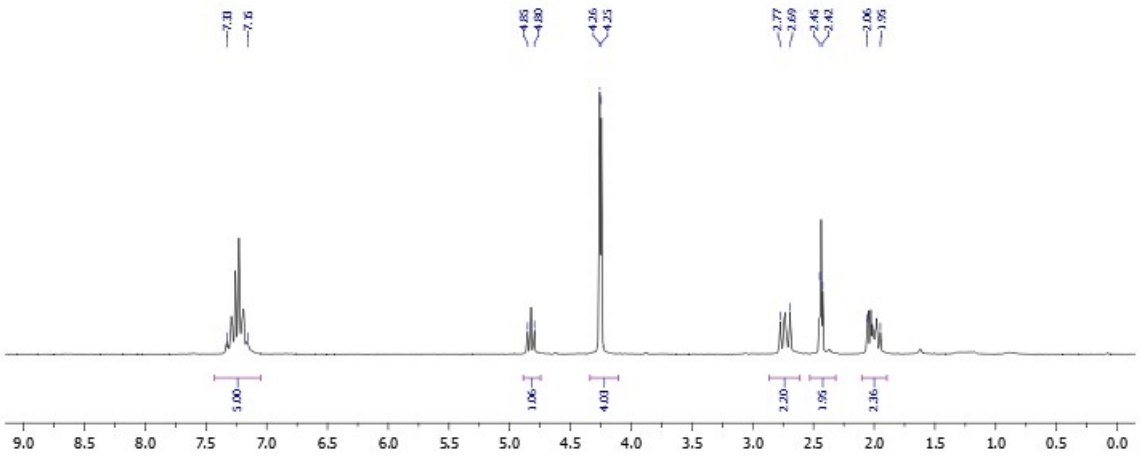
2e

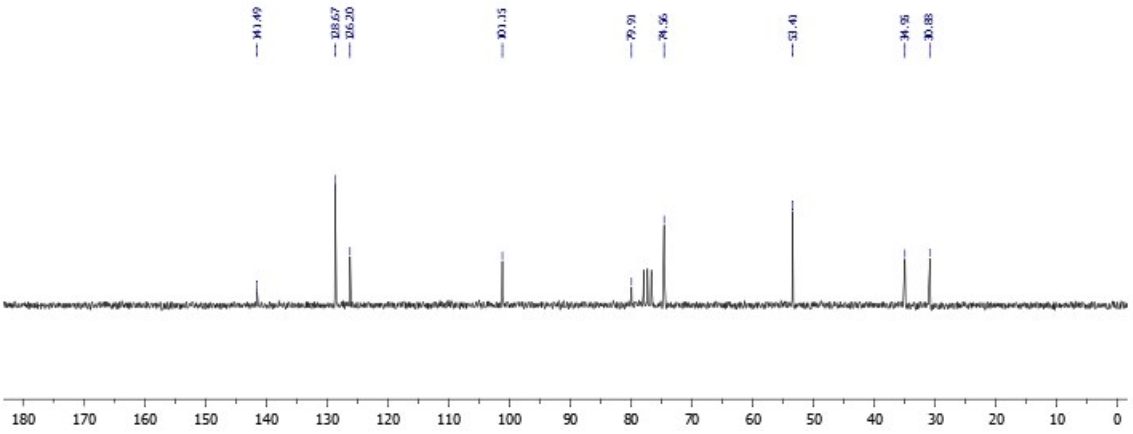

7.34
7.30
6.05
5.85
5.17
5.15
4.66
4.60
4.19
3.98
2.77
2.69
2.06
1.95
5.00
2.09
4.17
1.08
4.09
2.08
2.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

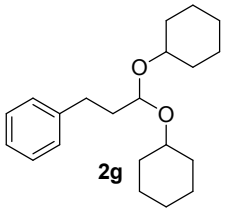

141.83
134.91
128.62
126.11
116.99
101.75
65.36
35.20
31.22
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



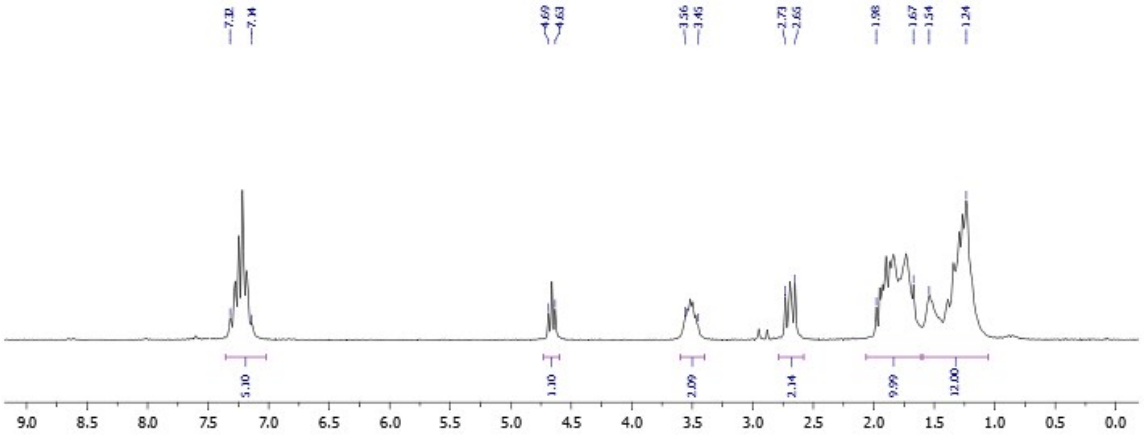
2f

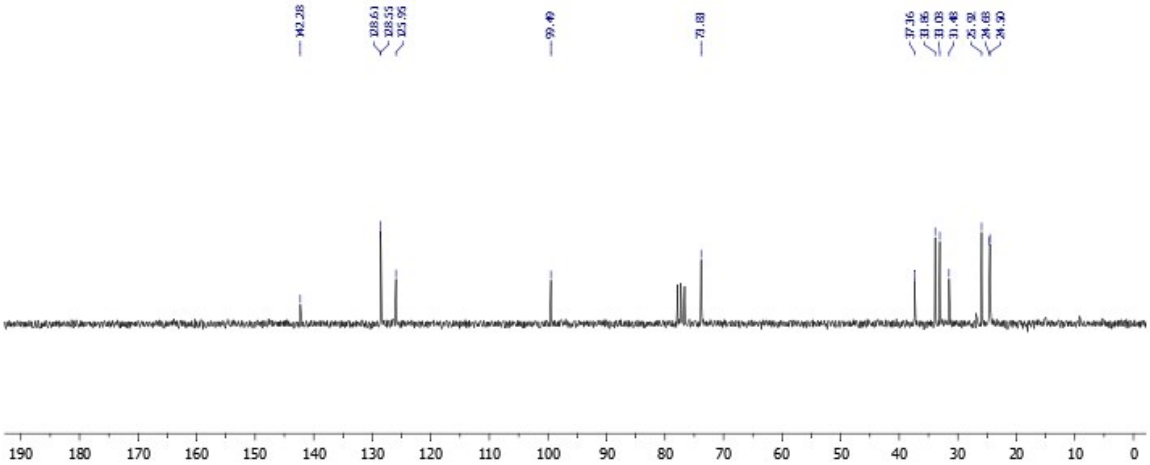

7.33
7.16
4.85
4.80
4.26
4.25
2.77
2.69
2.45
2.42
2.06
1.95
5.00
1.06
4.03
2.20
1.99
2.36
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

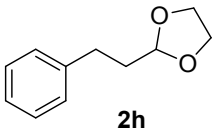

141.49
128.67
126.20
101.15
79.91
74.56
53.41
34.05
30.88
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
O

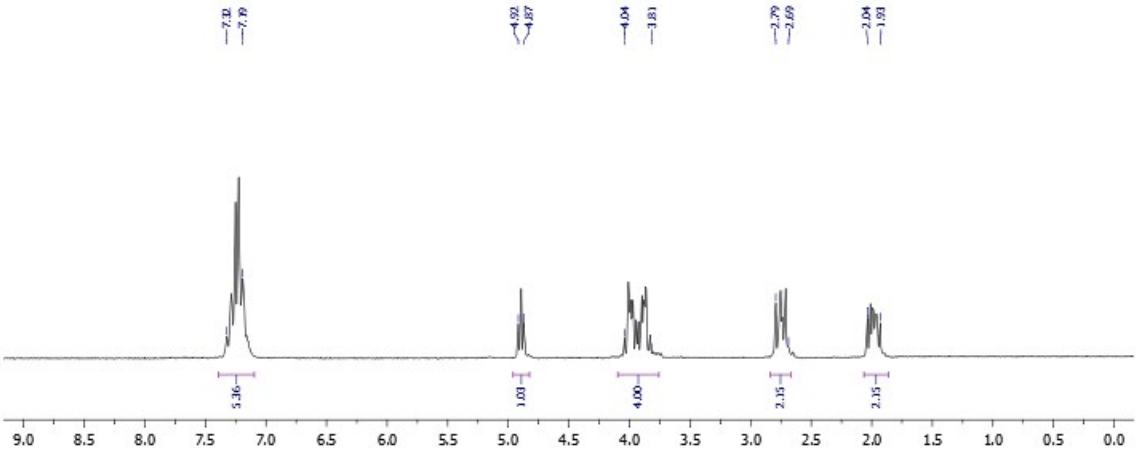
2g

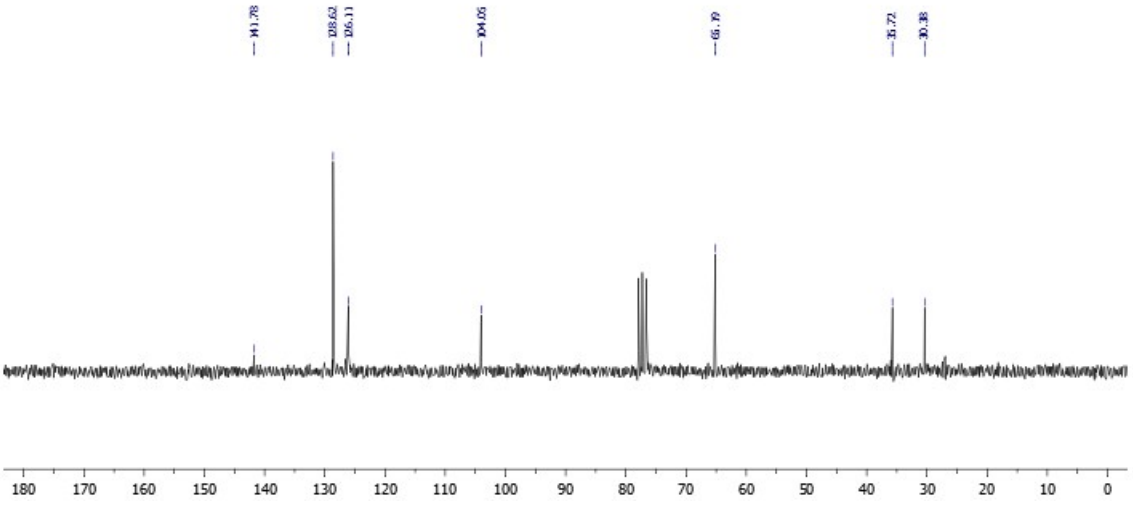

7.32
7.14
4.69
4.63
3.56
3.45
2.73
2.65
1.98
1.67
1.54
1.24
5.10
1.10
2.09
2.14
9.99
12.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

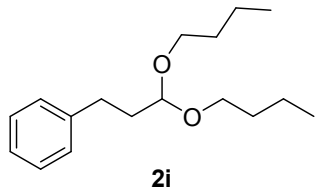

142.28
128.61
128.55
125.99
99.49
71.88
37.36
31.86
31.08
31.48
25.92
24.68
24.30
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



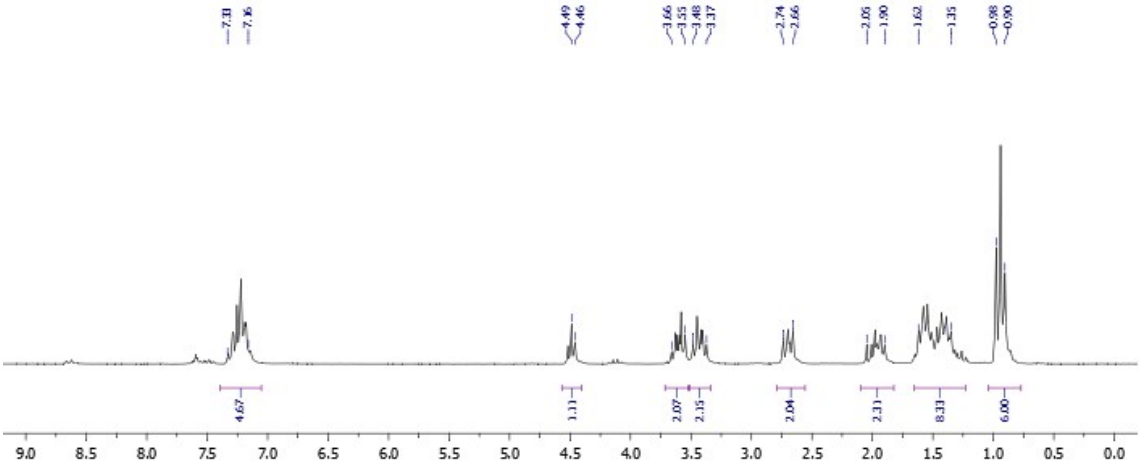
2h

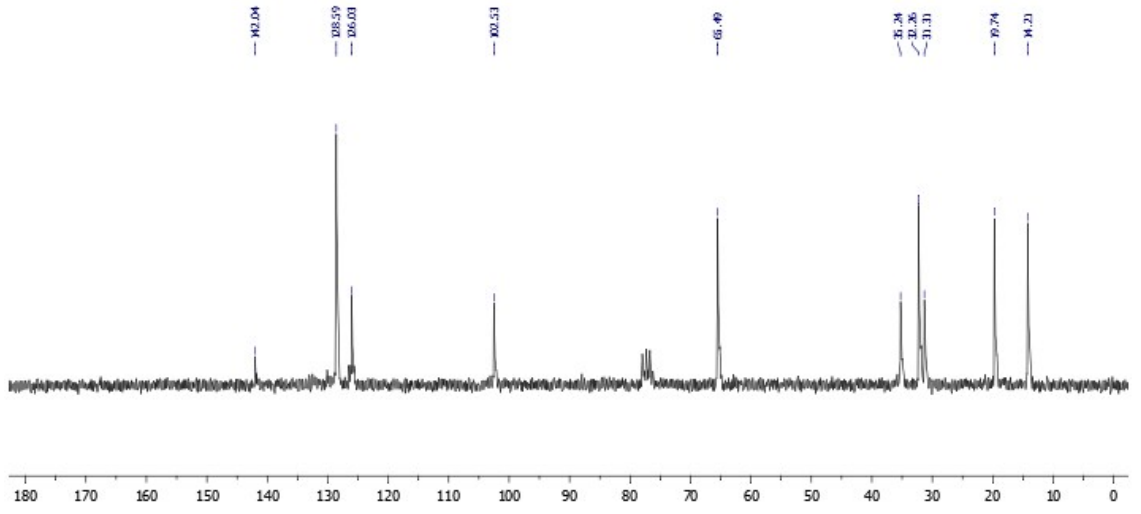

7.32
7.19
4.92
4.87
4.04
3.81
2.79
2.69
2.04
1.93
5.36
1.03
4.00
2.15
2.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

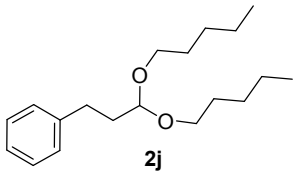

141.78
128.62
126.11
104.05
65.19
35.72
30.38
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



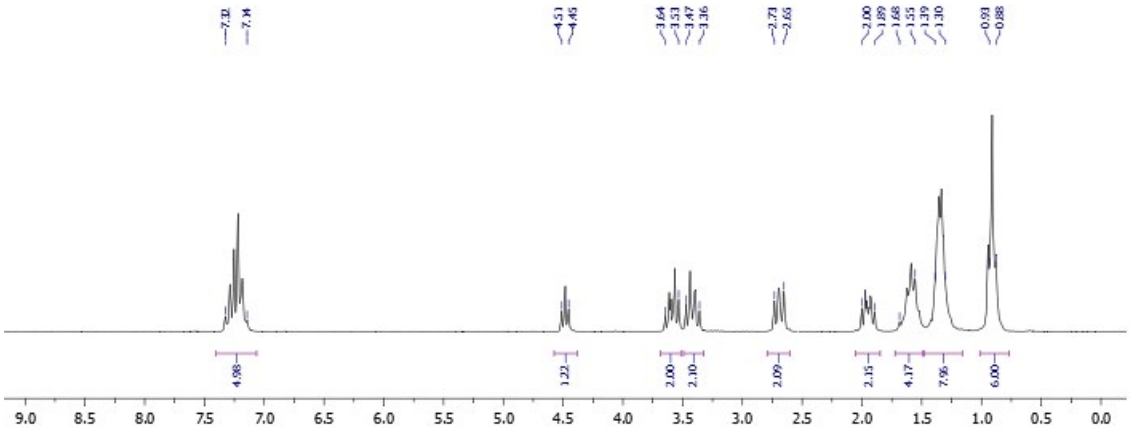
2i

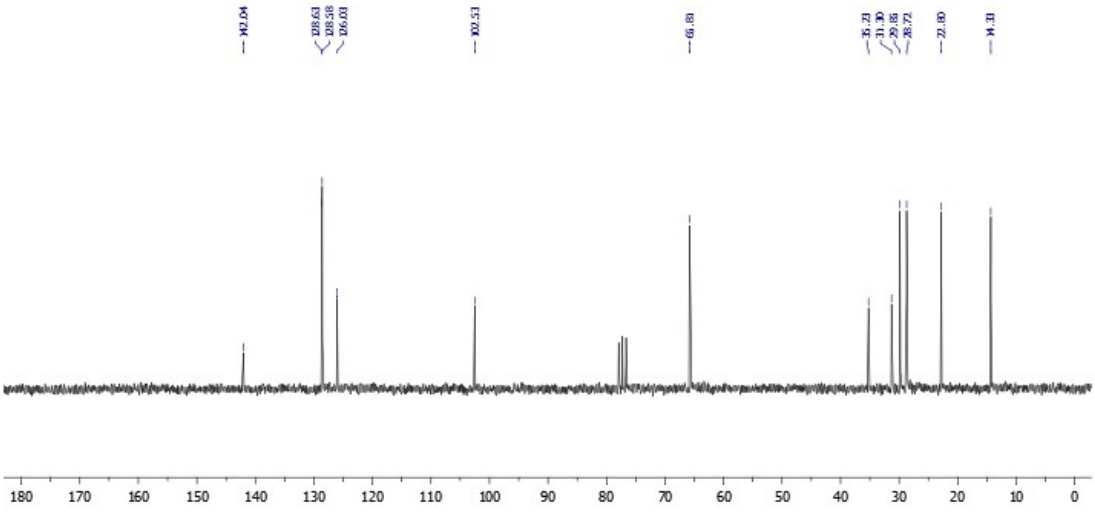

7.31
7.16
4.49
4.46
3.66
3.55
3.48
3.37
2.74
2.66
2.05
1.90
1.62
1.35
0.98
0.90
4.67
1.11
2.07
2.15
2.04
2.31
8.33
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

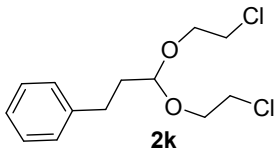

142.04
128.59
126.03
102.53
65.49
36.24
32.26
31.31
19.74
14.21
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



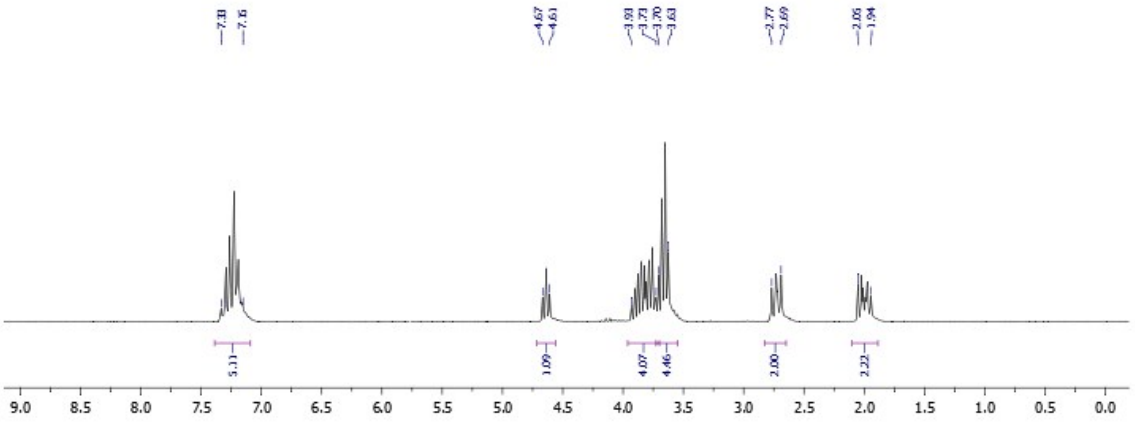
2j

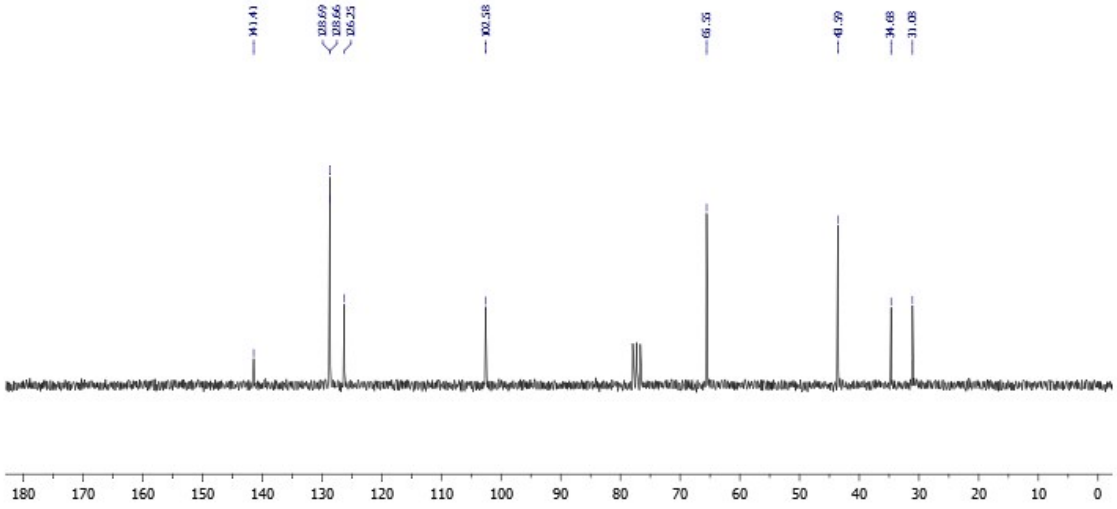


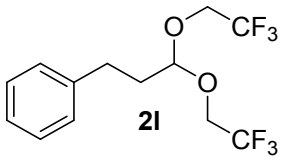



Cl
O
O
Cl

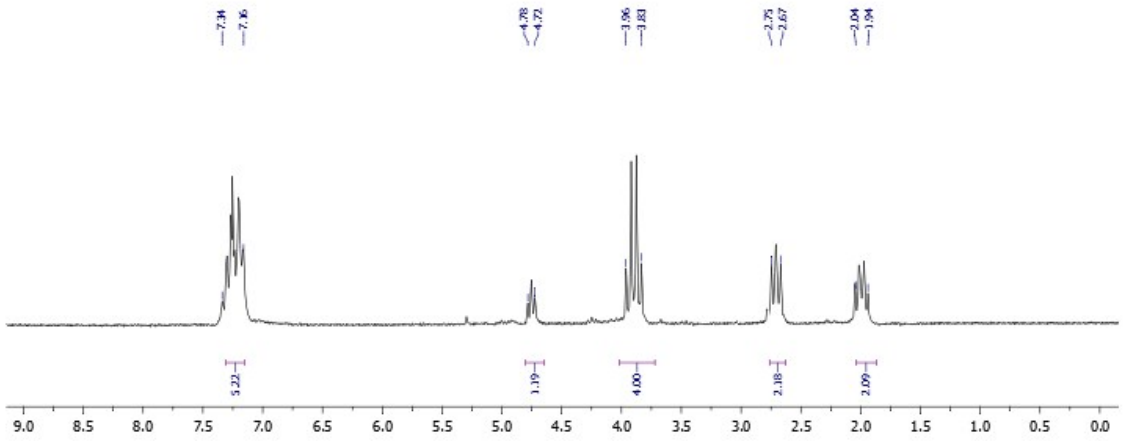
2k

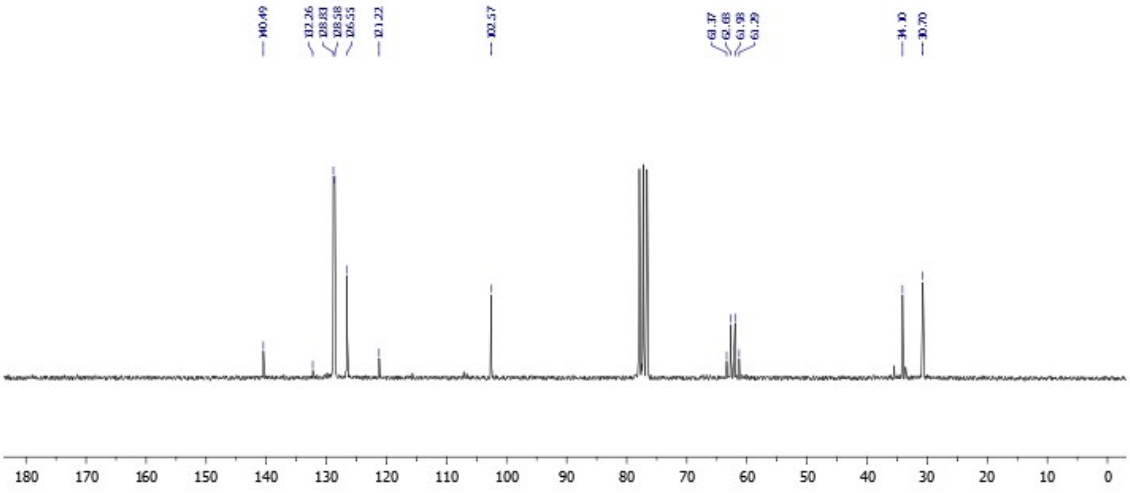

7.33
7.16
4.67
4.61
3.93
3.73
3.70
3.63
2.77
2.69
2.05
1.94
5.11
1.09
4.07
4.46
2.00
2.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

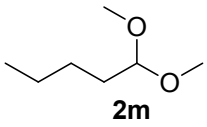

141.41
128.69
128.66
126.25
102.58
65.55
41.99
34.68
31.08
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
CF3
O
CF3

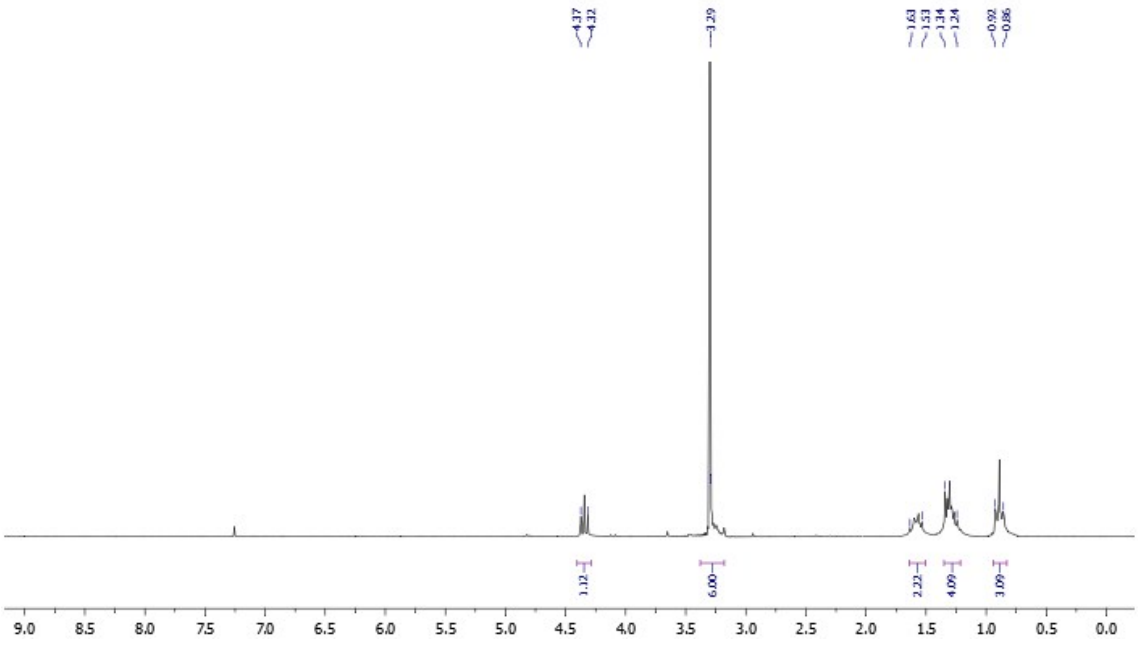
2l

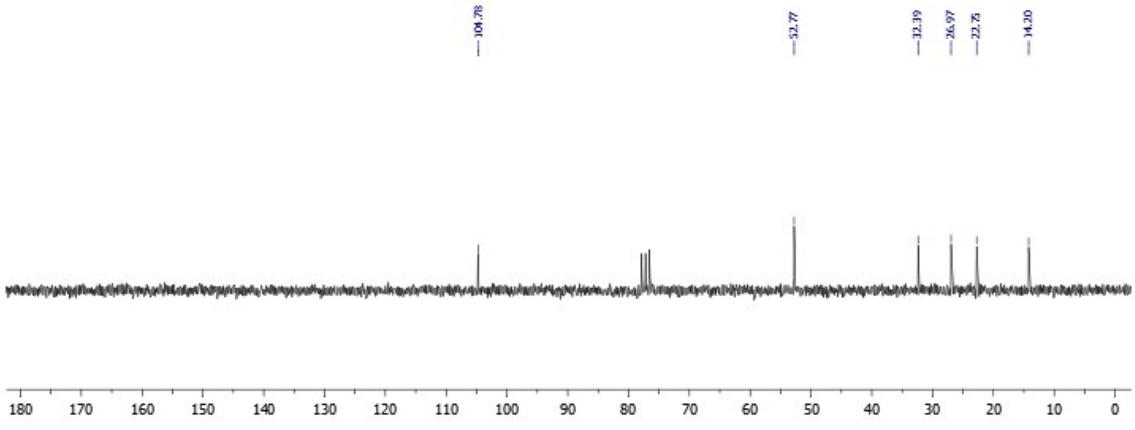

7.34
7.16
4.78
4.72
3.96
3.83
2.75
2.67
2.04
1.94
5.22
1.19
4.00
2.18
2.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

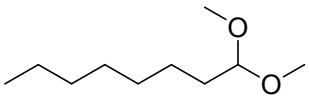

140.49
132.26
128.83
128.58
126.55
121.22
102.57
61.37
62.68
61.98
61.29
34.10
30.70
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



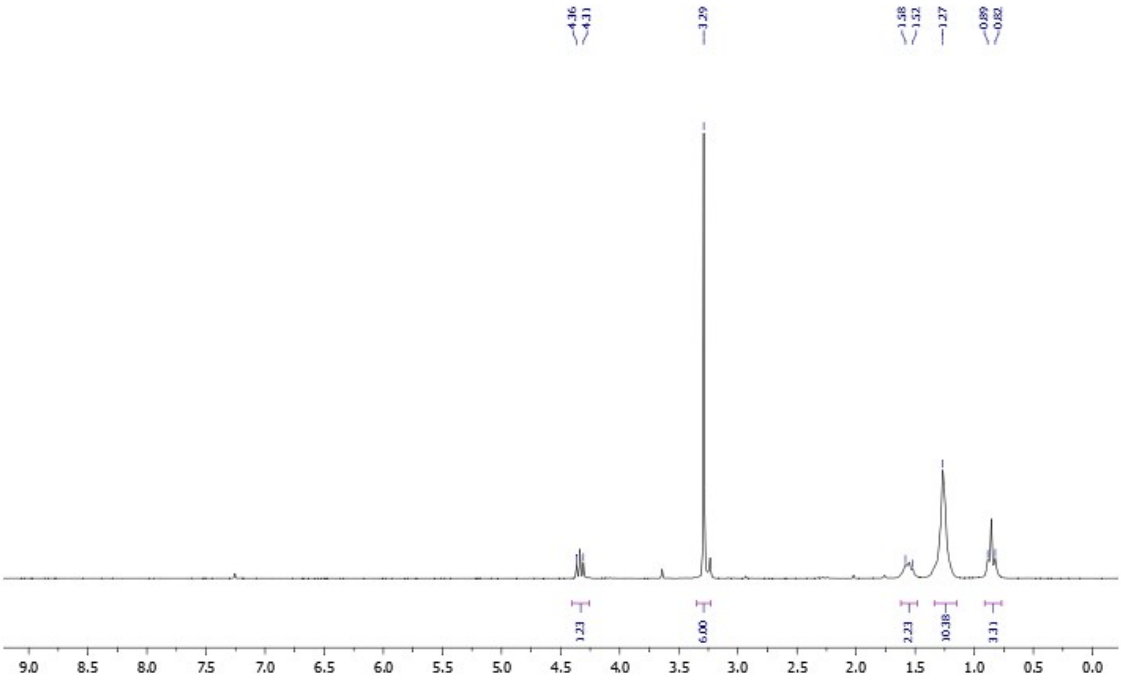
2m

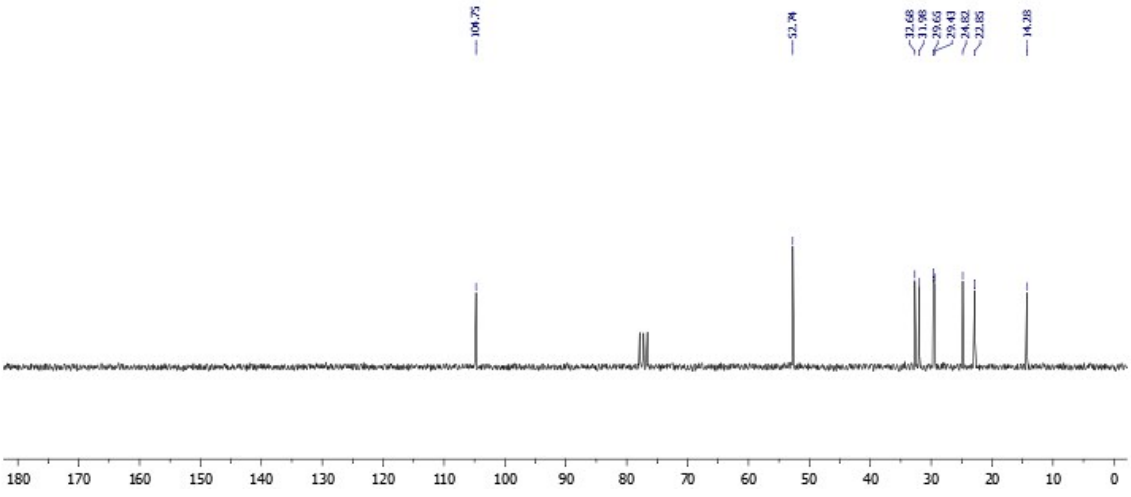

4.37
4.32
3.29
1.63
1.53
1.34
1.24
0.92
0.86
1.12
6.00
2.22
4.09
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

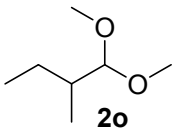

104.78
52.77
32.39
26.97
22.75
14.20
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



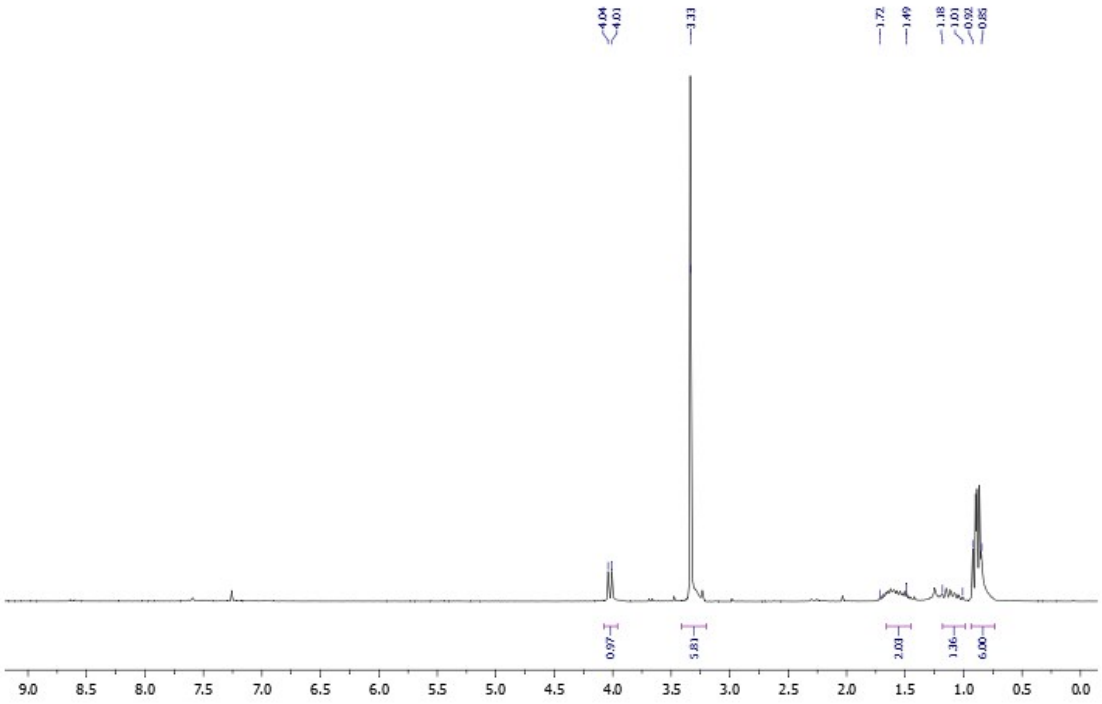
2n

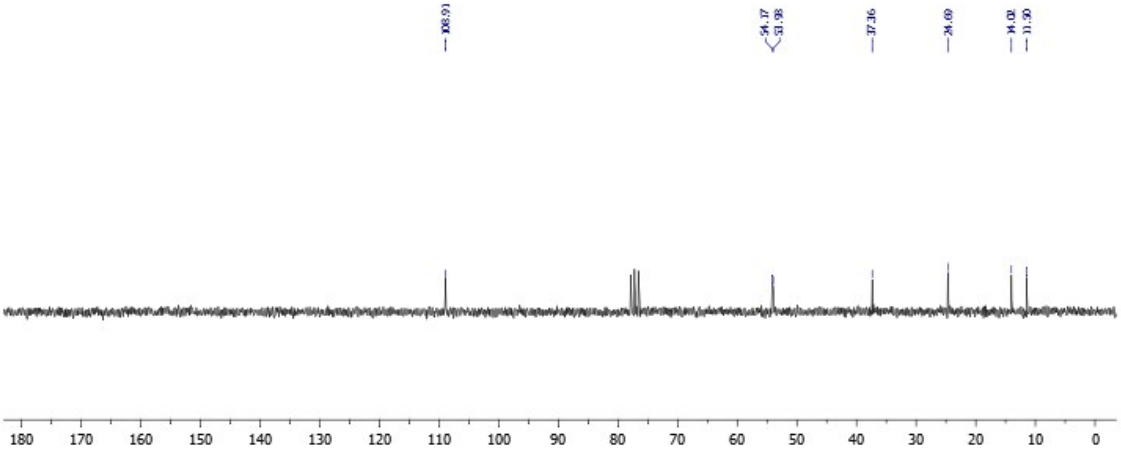

4.36
4.31
3.29
1.58
1.52
1.27
0.89
0.82
1.23
6.00
2.23
10.38
3.31
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

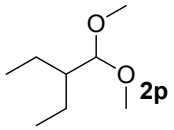

104.75
52.74
32.68
31.98
29.65
29.43
24.82
22.85
14.28
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

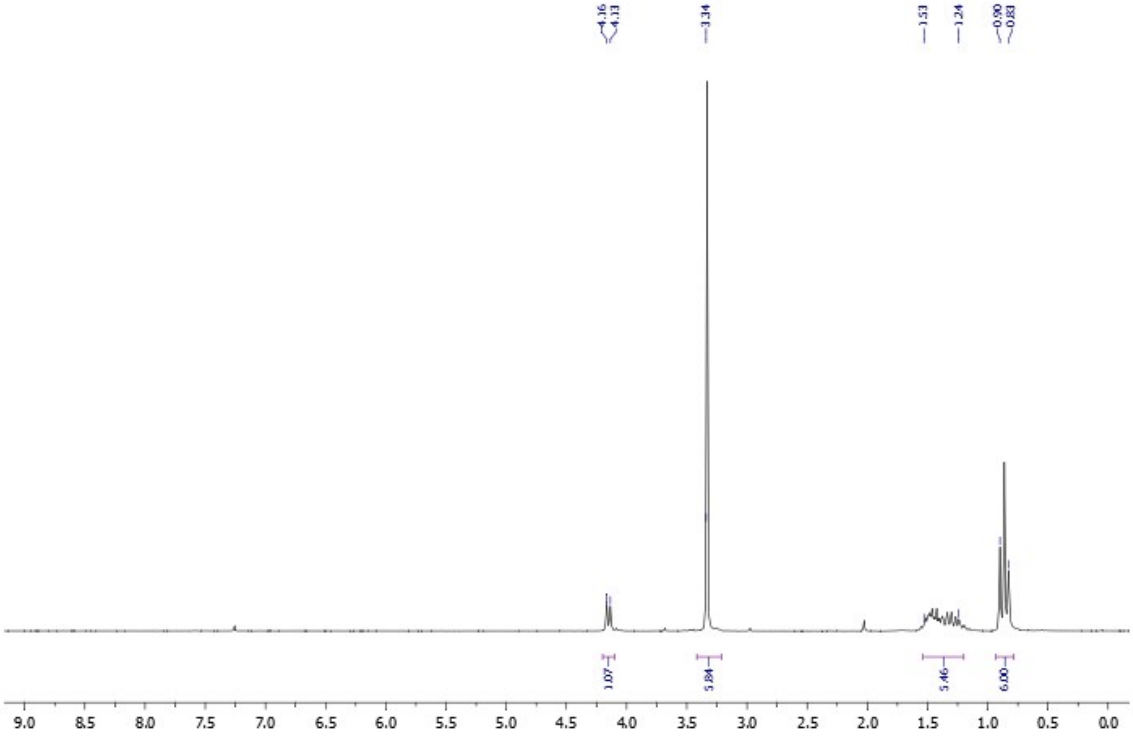

O
O

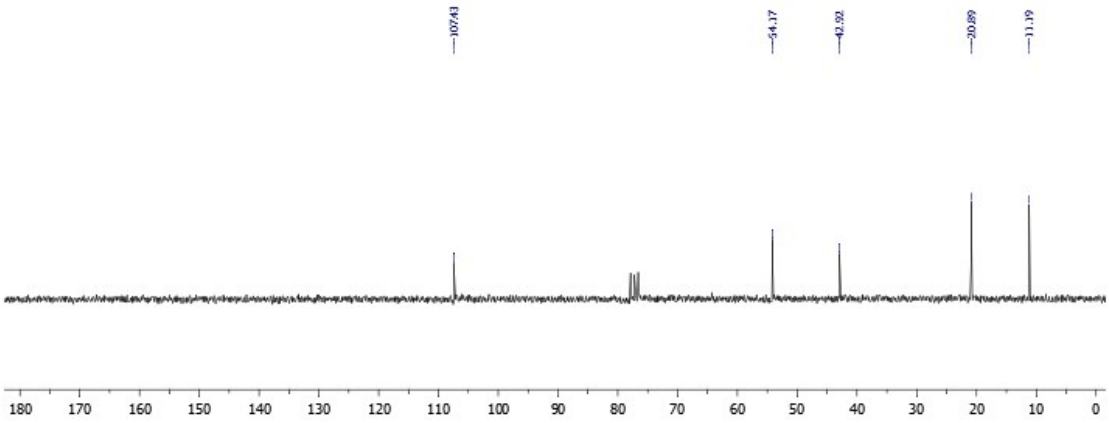
2o

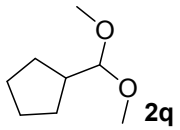

4.04
4.01
3.33
1.72
1.49
1.18
1.01
0.92
0.85
0.97
5.81
2.03
1.36
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

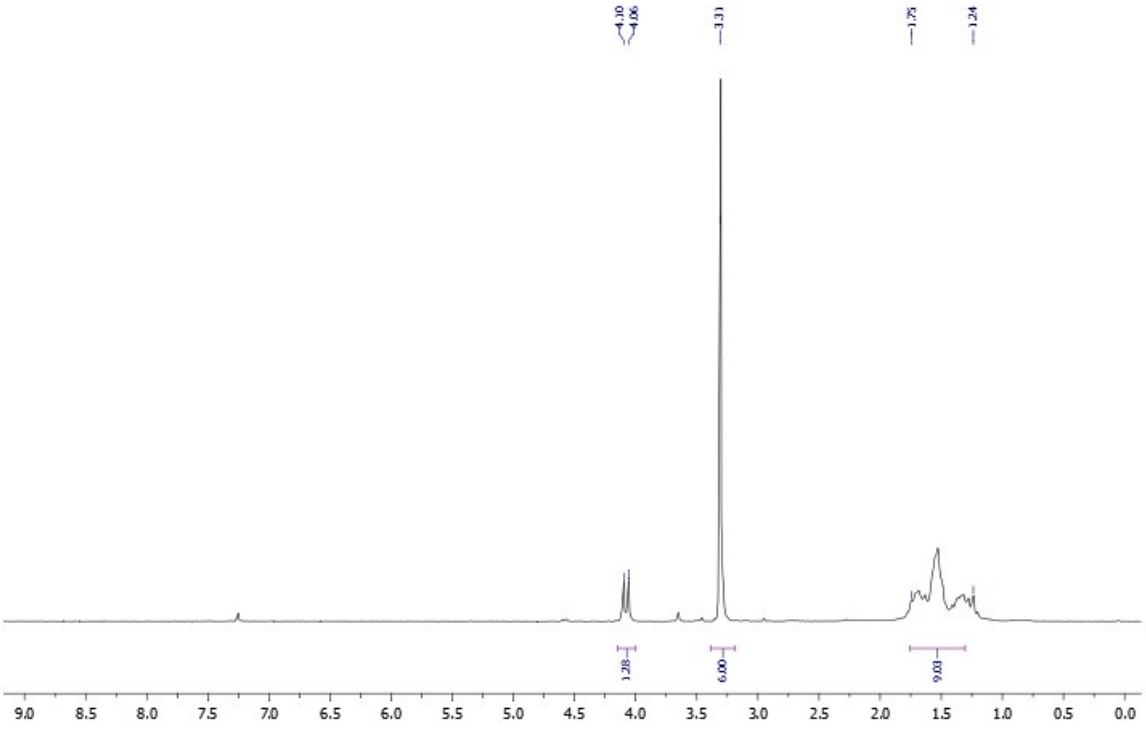

108.91
54.17
53.38
37.46
24.69
14.02
11.30
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

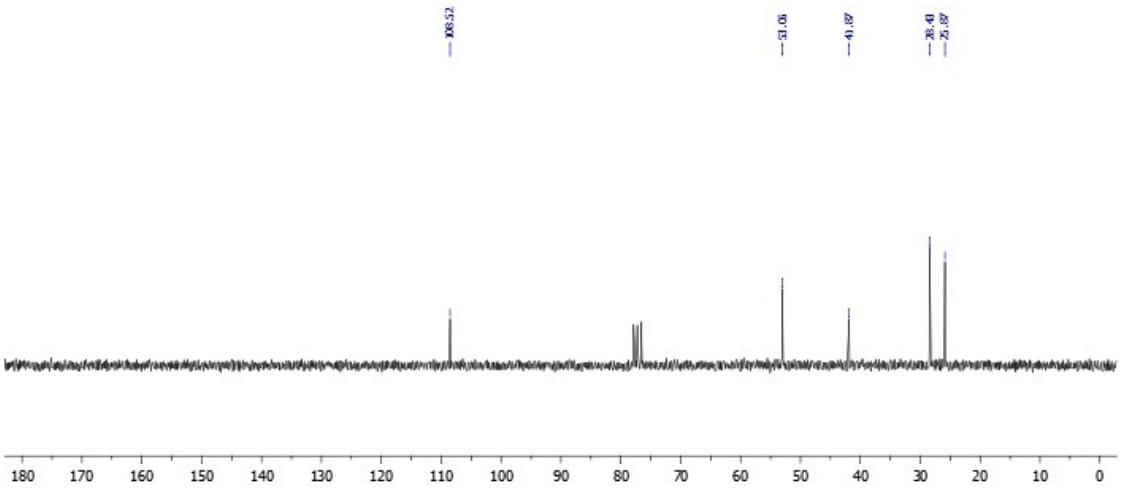

O
O
2p

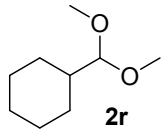

4.16
4.13
3.34
1.53
1.24
0.90
0.83
1.07
5.84
5.46
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


107.43
54.17
42.92
20.89
11.19
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

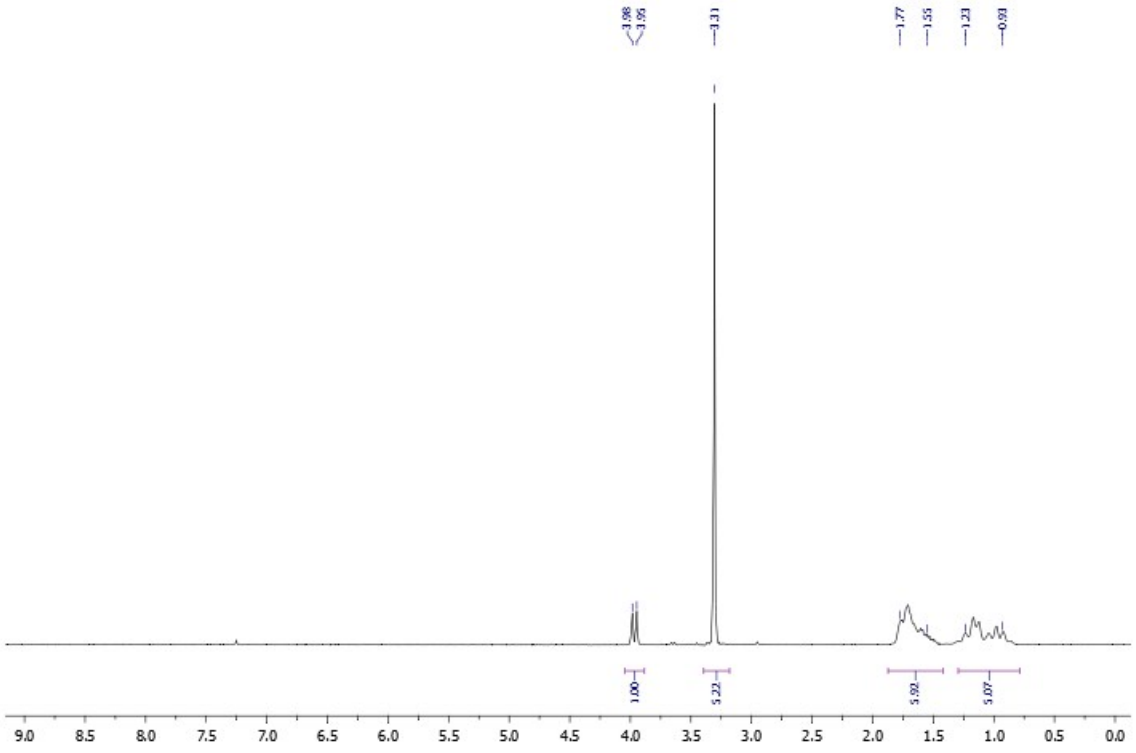

O
O
2q

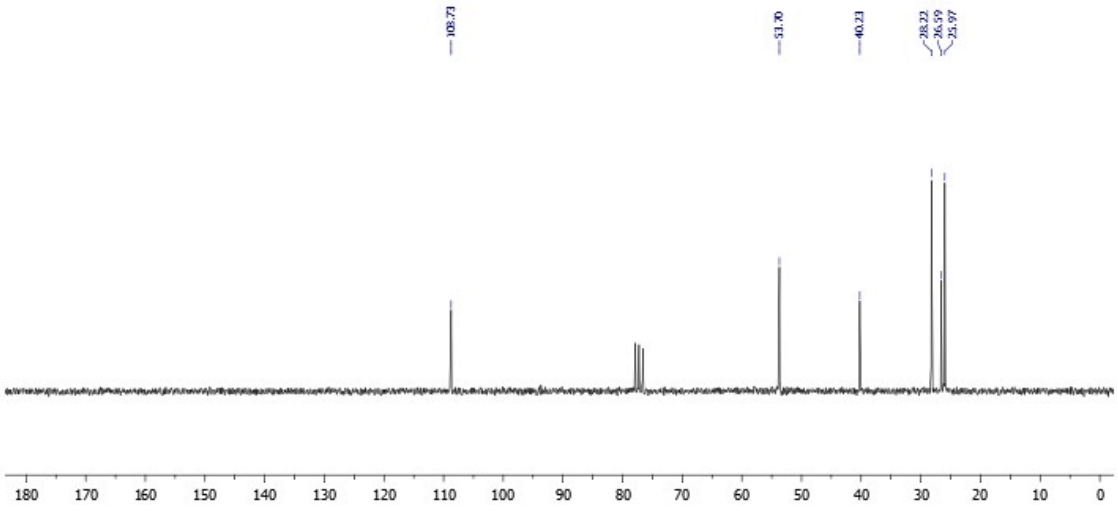

4.10
4.06
3.31
1.75
1.24
1.28
6.00
9.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

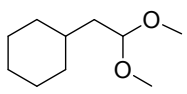

108.52
51.06
41.87
28.41
25.87
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
O

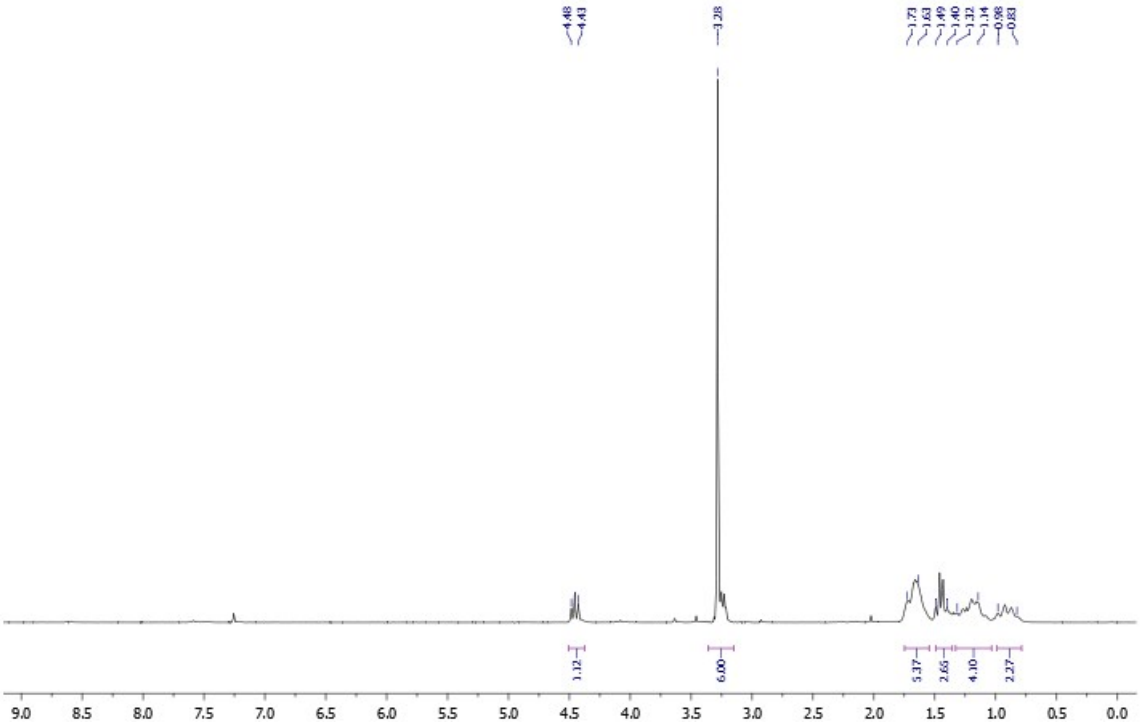
2r

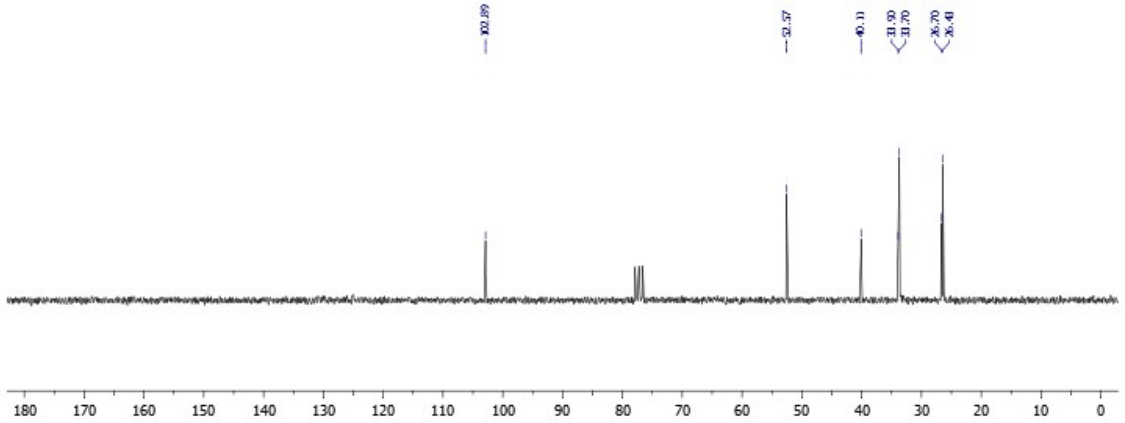

3.98
3.95
3.31
1.77
1.55
1.23
0.93
1.00
5.22
5.92
5.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

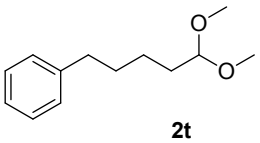

108.73
53.70
40.23
28.22
26.59
25.97
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
O

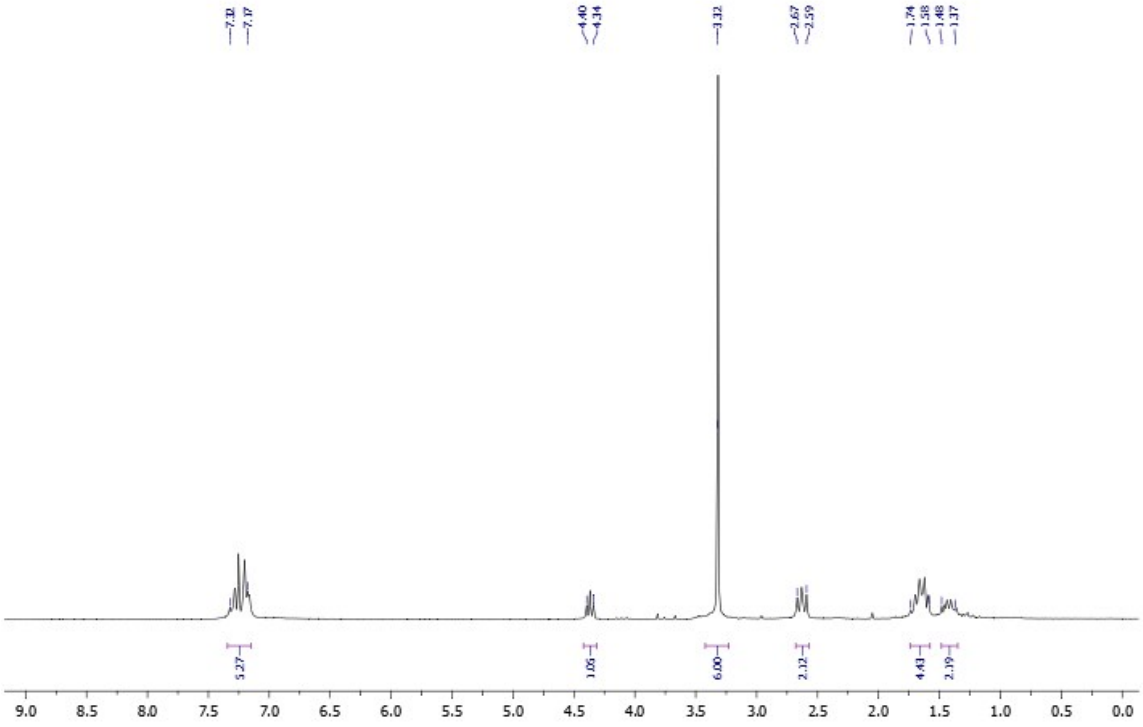
2s

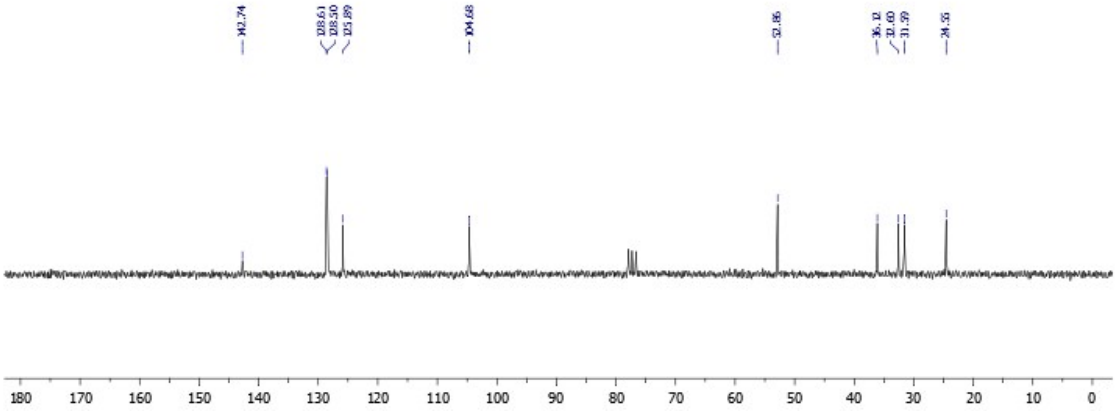

4.48
4.41
3.28
1.73
1.63
1.49
1.40
1.32
1.14
0.98
0.83
1.12
6.00
5.37
2.65
4.10
2.27
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

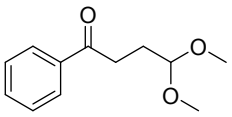

102.89
52.57
40.11
31.90
31.70
26.70
26.41
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



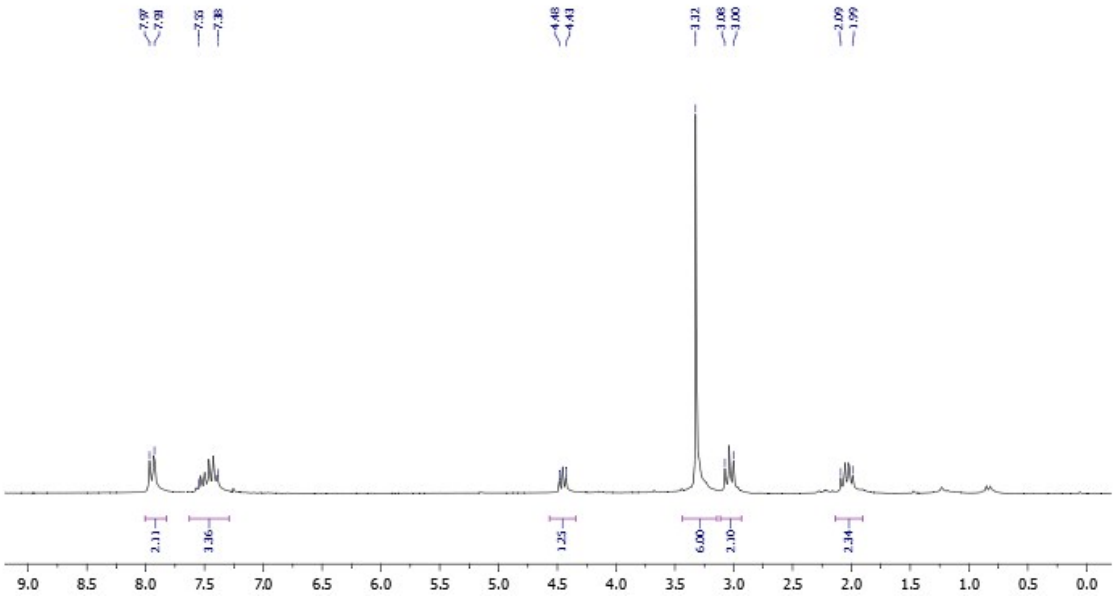
2t

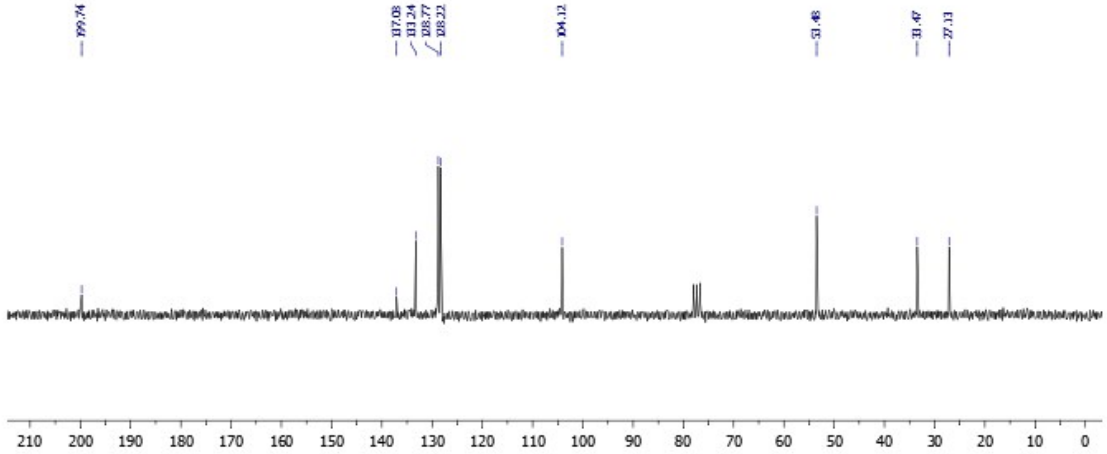

7.22
7.17
4.40
4.34
3.32
2.67
2.59
1.74
1.58
1.48
1.37
5.27
1.05
6.00
2.12
4.43
2.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

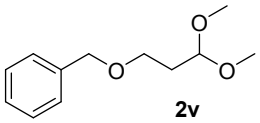

142.74
128.61
128.50
125.89
104.68
52.86
36.12
32.60
31.59
24.55
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



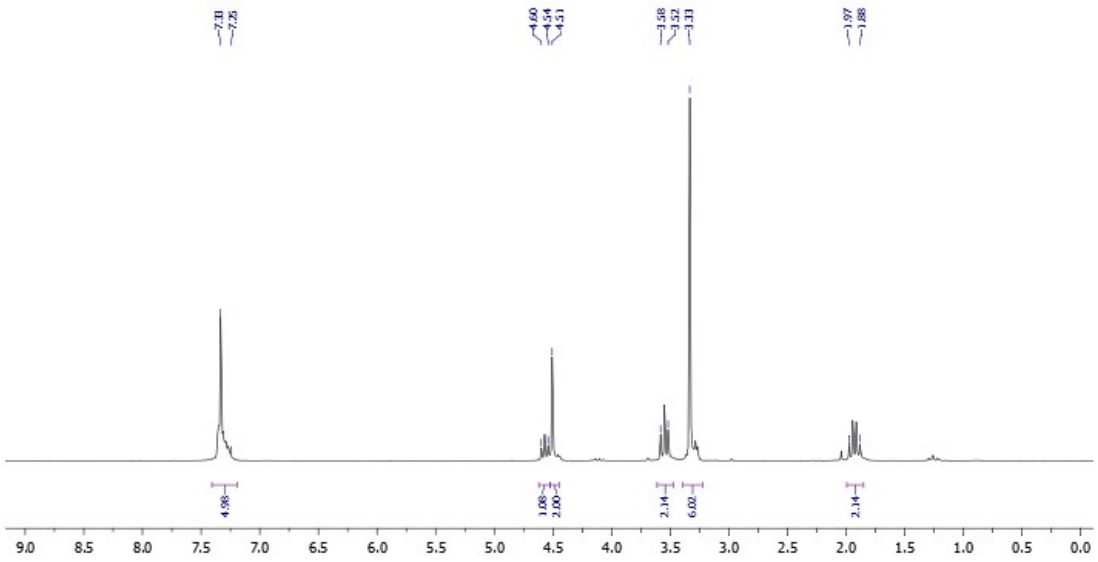
2u

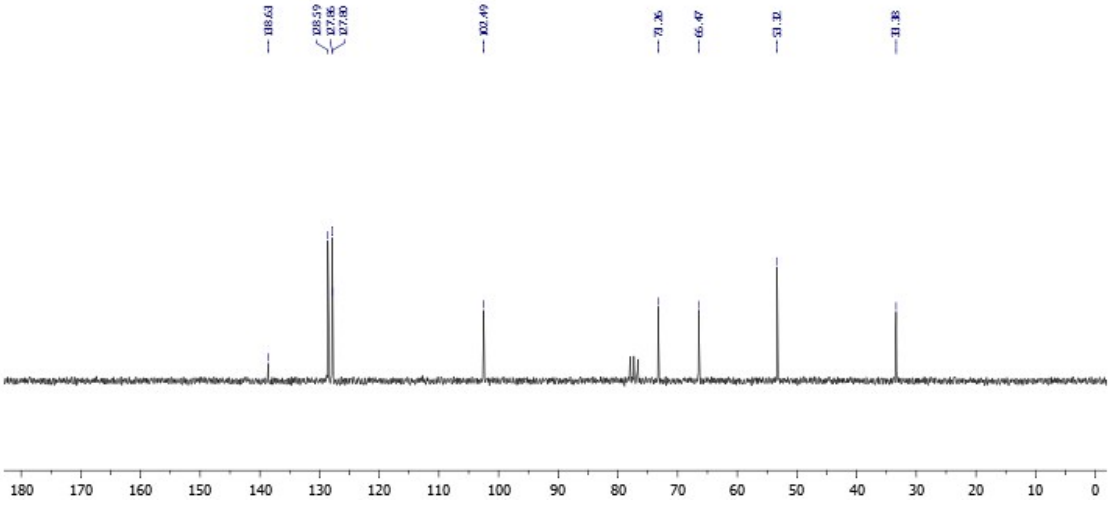

7.97
7.93
7.55
7.38
4.48
4.43
3.32
3.08
3.00
2.09
1.99
2.11
3.36
1.25
6.00
2.10
2.34
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

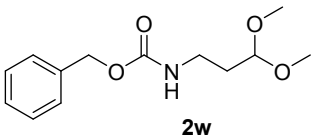

199.74
137.08
133.24
128.77
128.22
104.12
53.48
31.47
27.13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



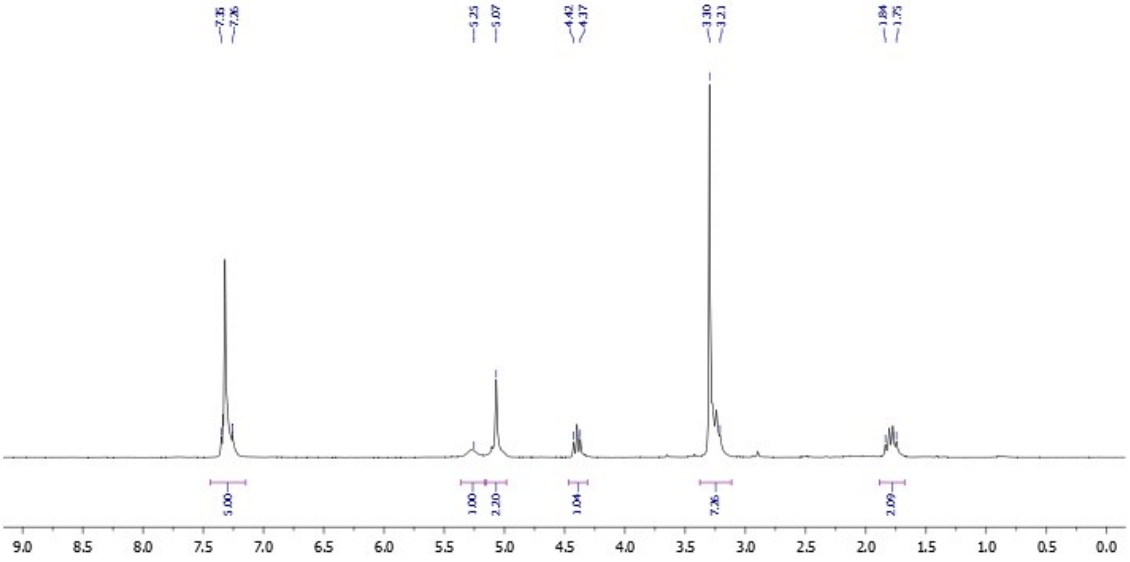
2v

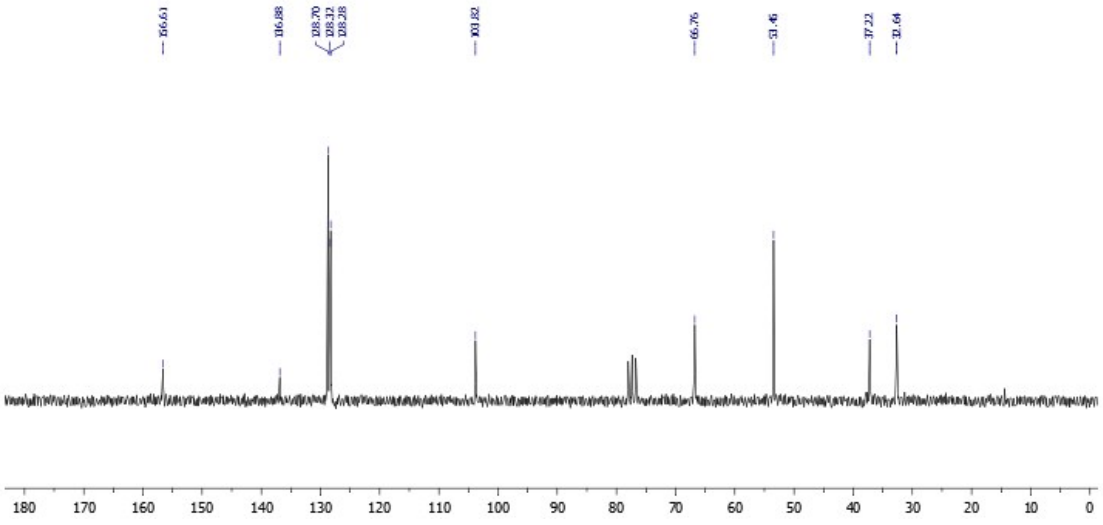


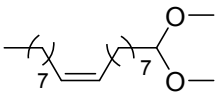




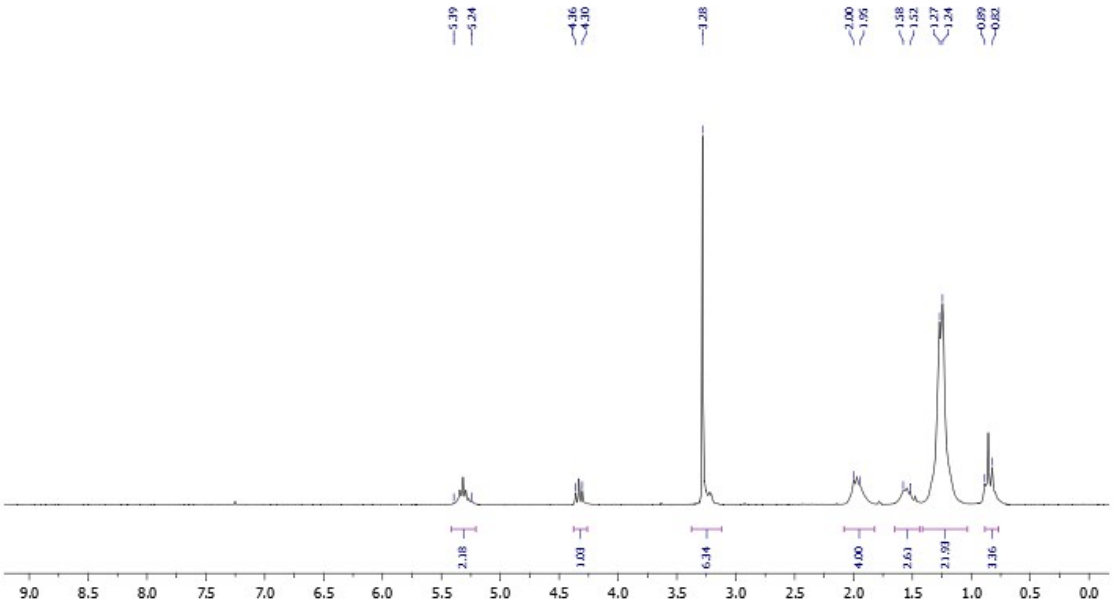
2w

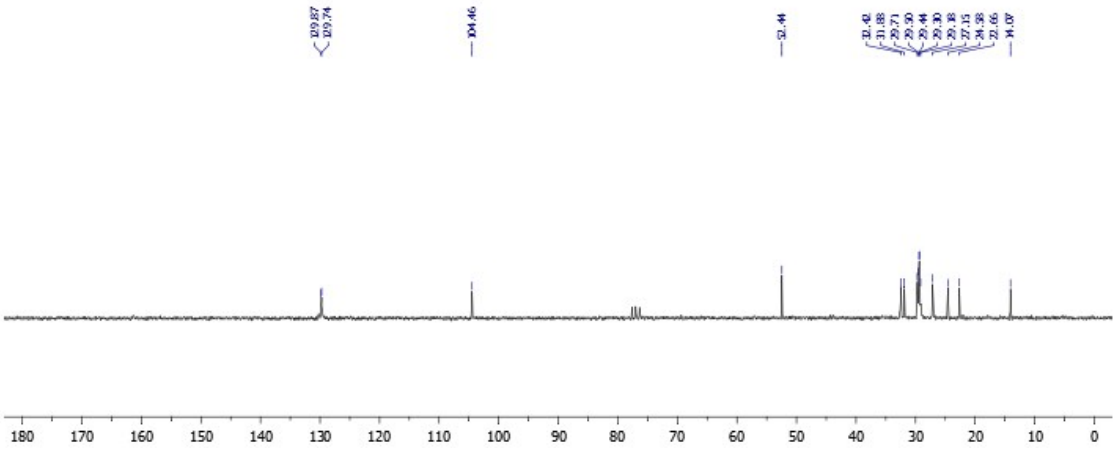

7.35
7.26
5.25
5.07
4.42
4.37
3.30
3.21
1.84
1.75
5.00
1.00
2.20
1.04
7.26
2.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

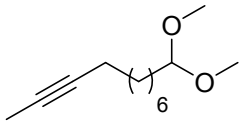

166.61
136.88
128.70
128.32
128.28
103.82
66.76
53.46
37.22
32.64
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



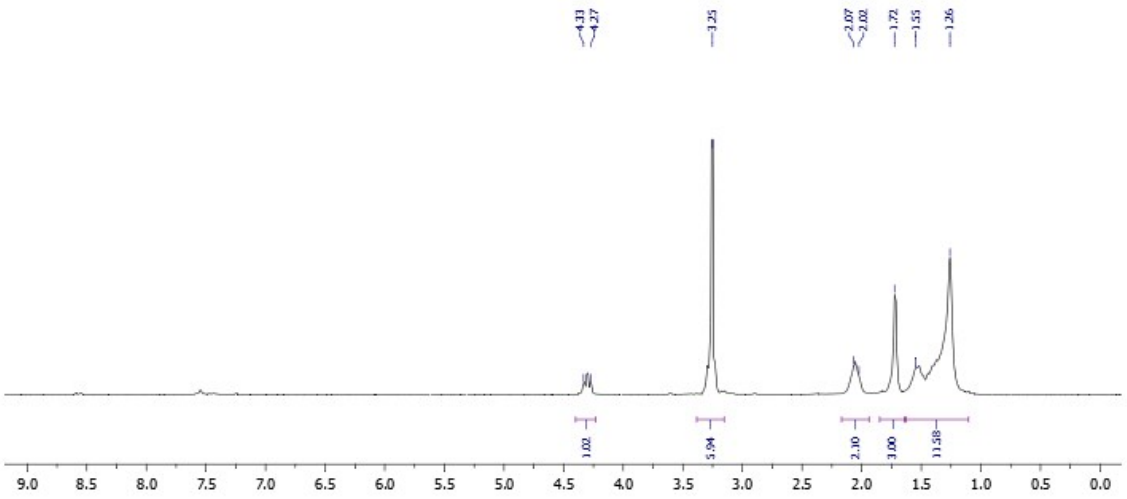
2x

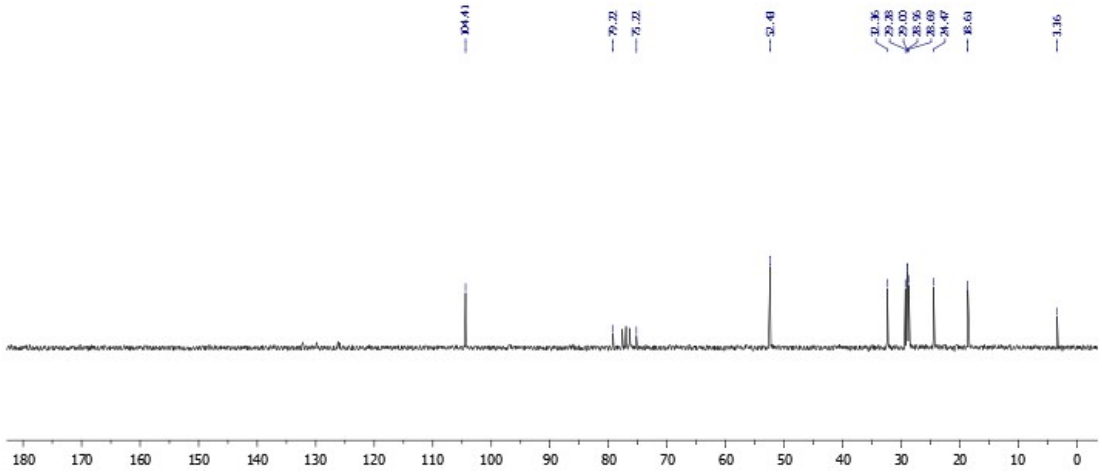


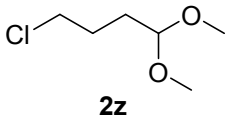



O
O
6

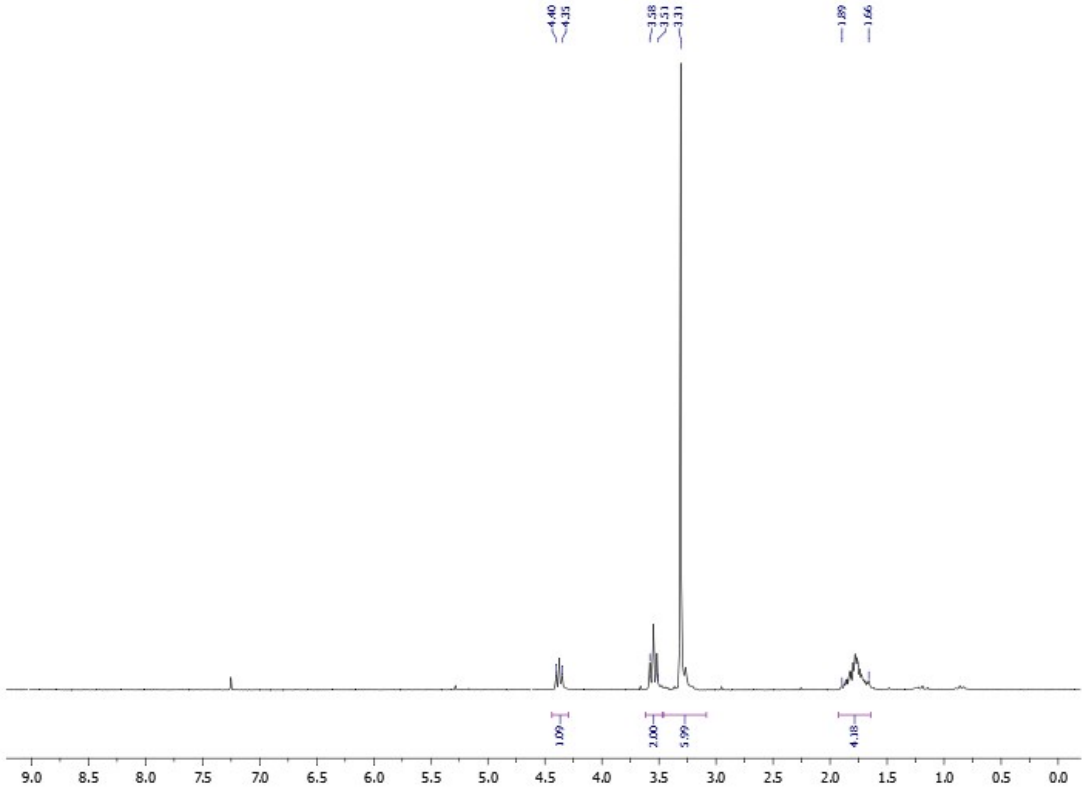
2y

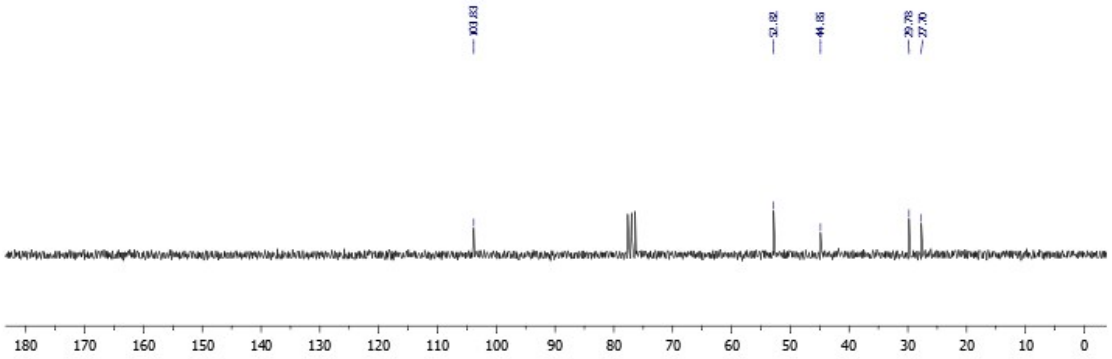

4.33
4.27
3.25
2.07
2.02
1.72
1.55
1.26
1.02
5.94
2.10
3.00
11.58
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

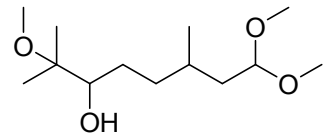

104.41
79.22
75.22
52.41
32.36
29.28
29.03
28.96
28.69
24.47
18.61
3.36
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Cl
O
O

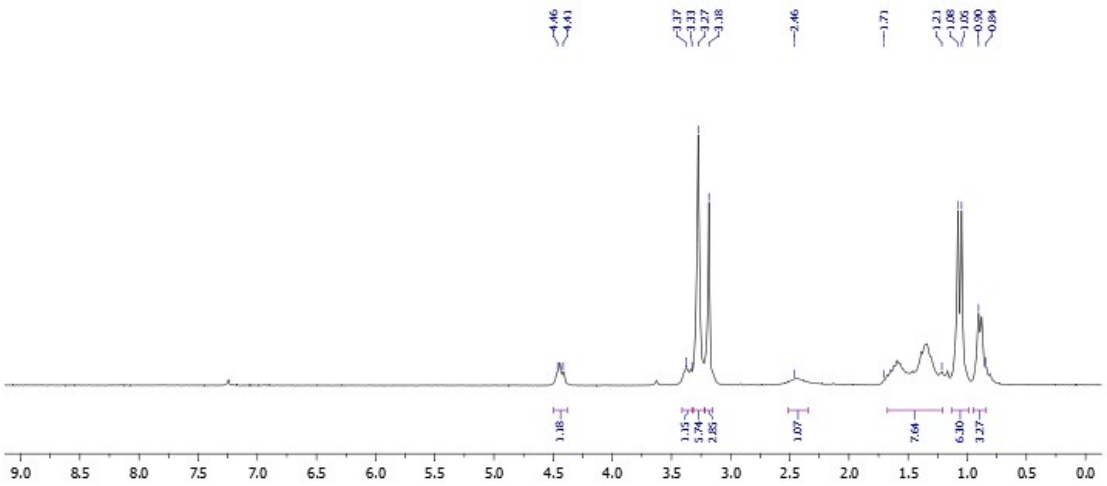
2z

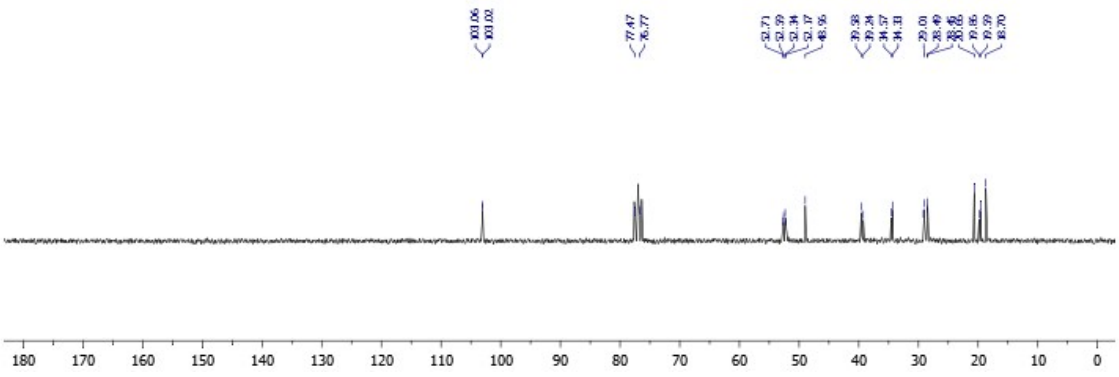

4.40
4.35
3.58
3.51
3.31
1.89
1.66
1.09
2.00
5.99
4.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


103.83
32.82
44.86
29.78
27.30
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

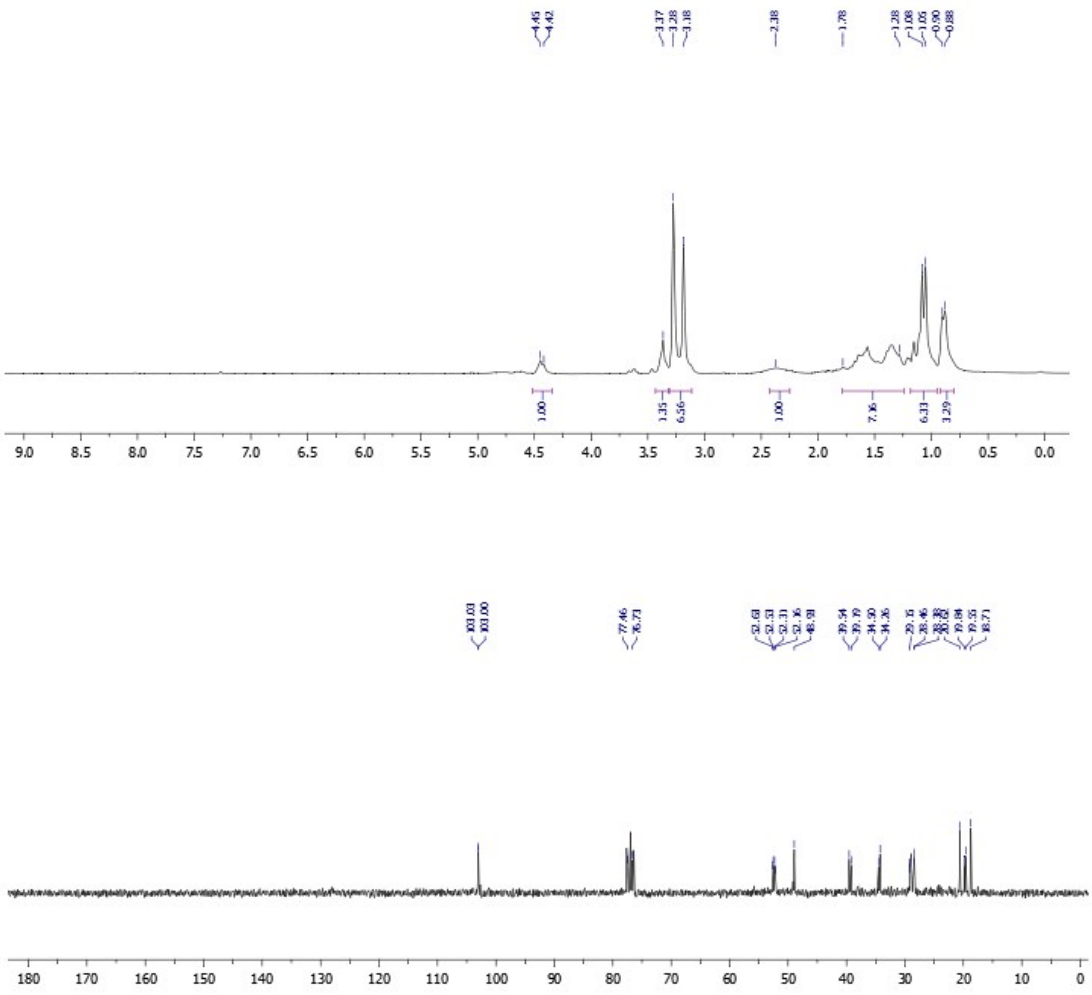


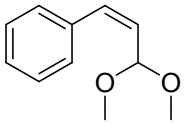
2aa



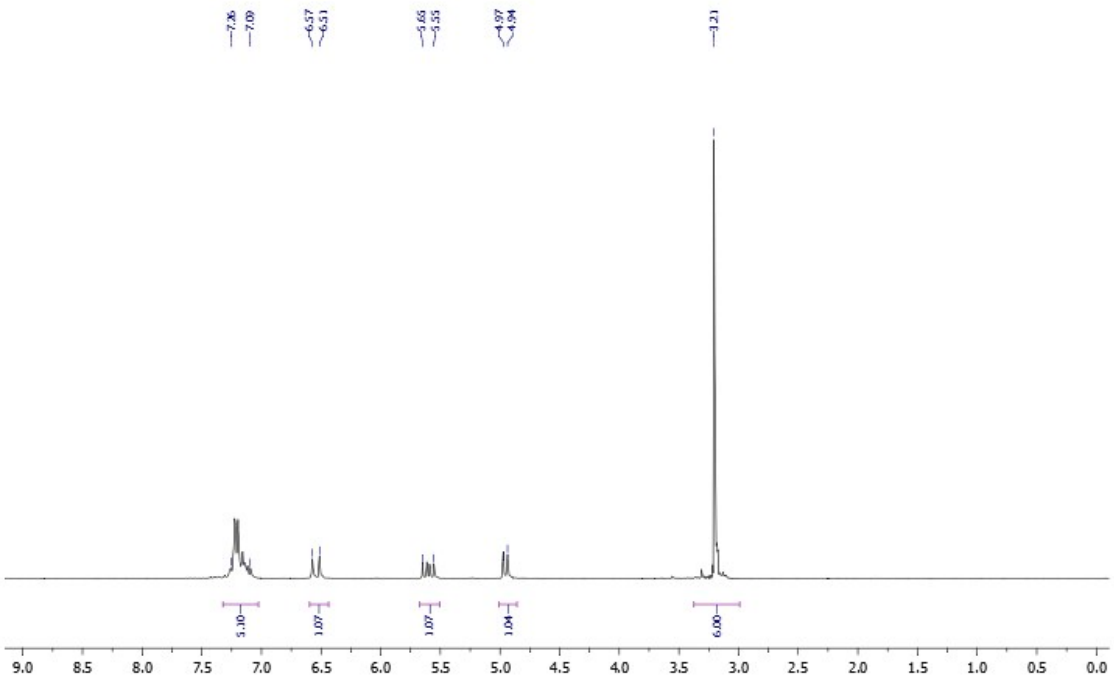


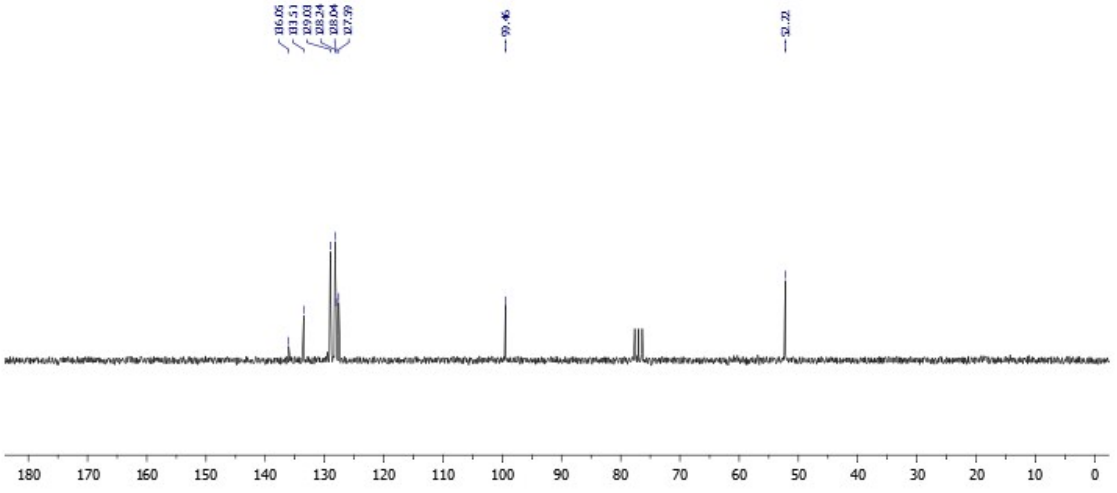
Spectra for **2aa**, obtained with the acidic formation of acetal from **1aa**

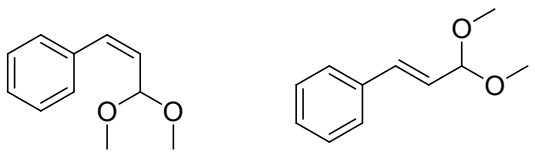




2ab

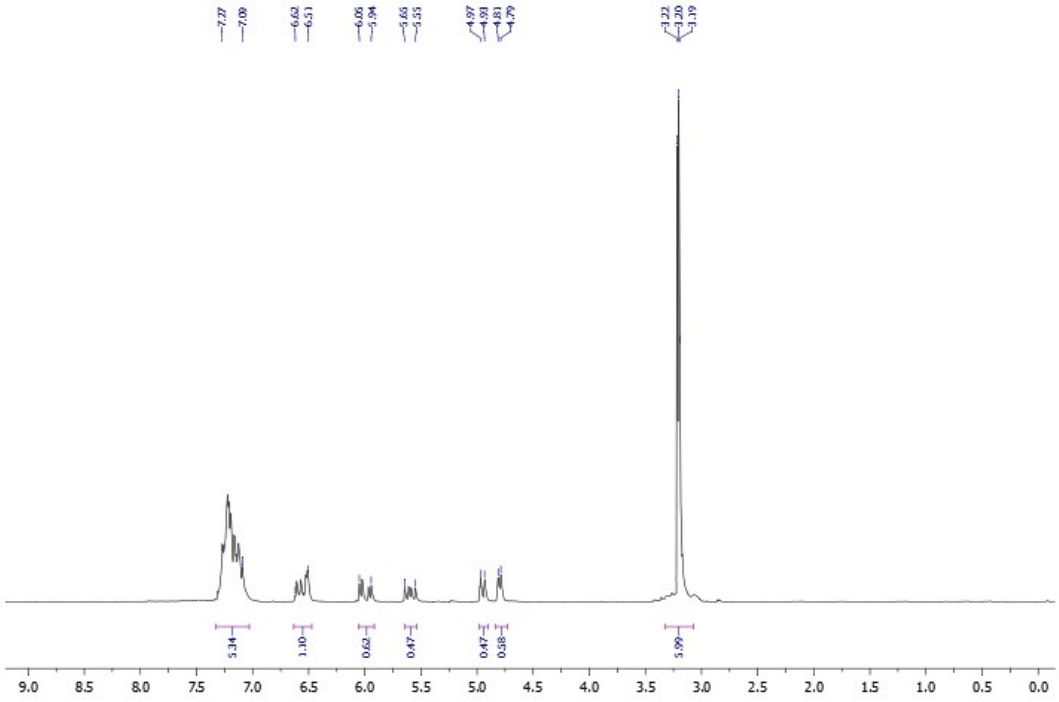

7.36
7.09
6.57
6.51
5.65
5.55
4.97
4.94
3.21
5.10
1.07
1.07
1.04
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

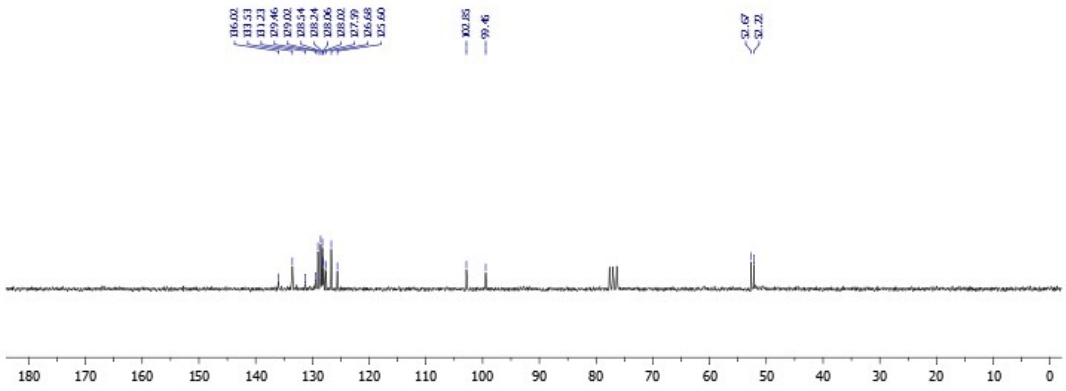

136.05
133.51
129.01
128.24
128.04
127.59
99.46
52.22
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

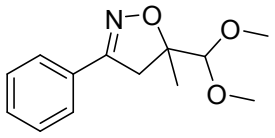


40 : 60

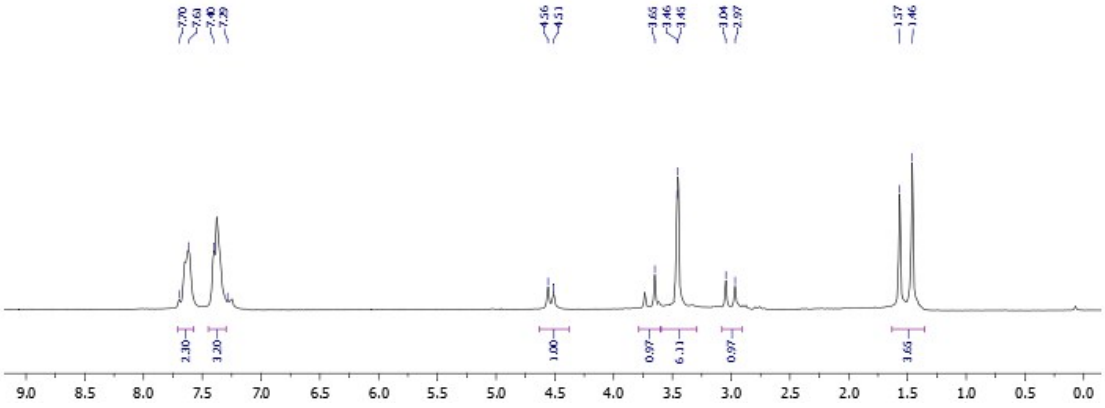
2ab

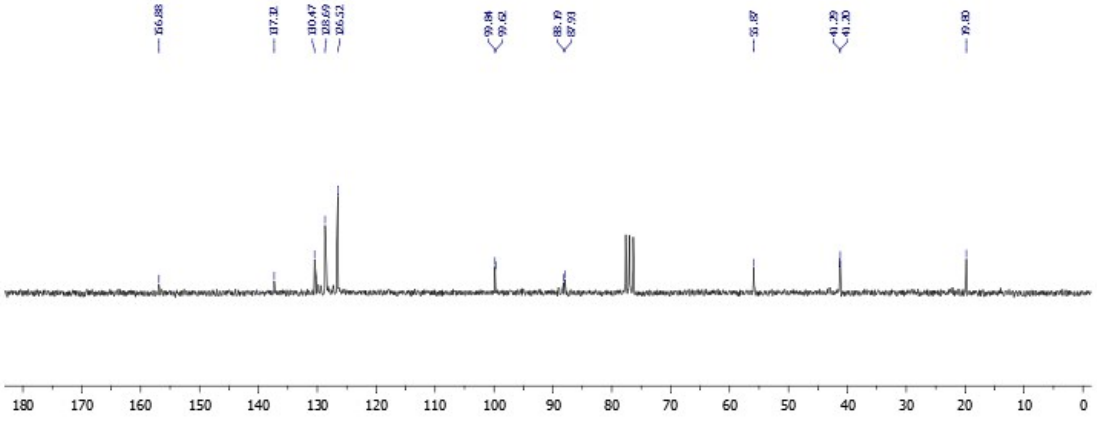


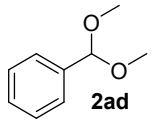




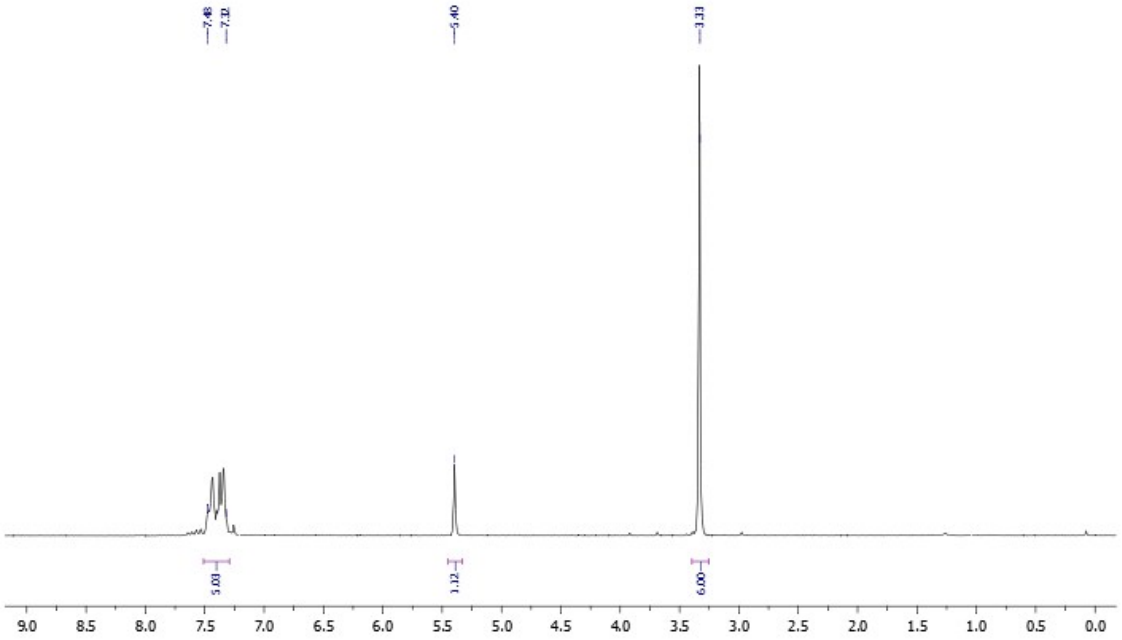
2ac

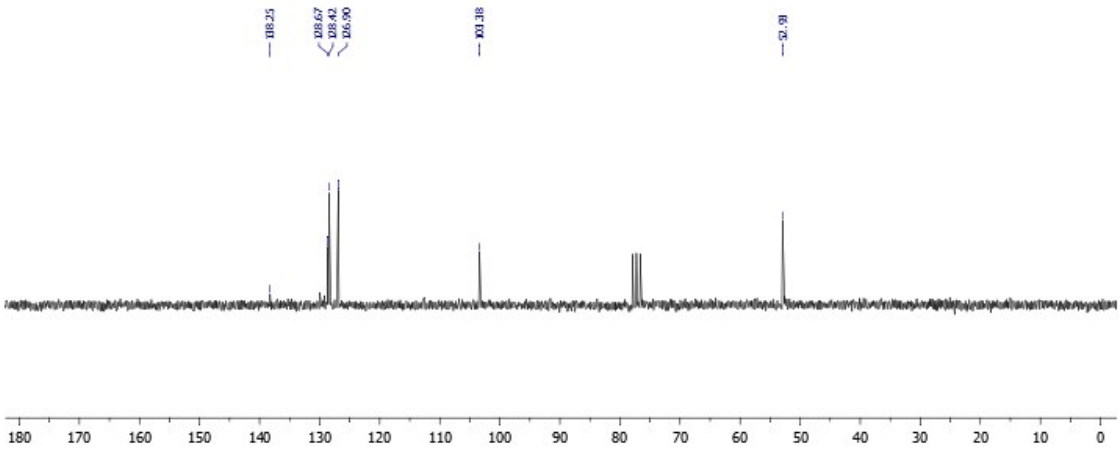

7.70
7.61
7.40
7.29
4.56
4.51
3.65
3.46
3.45
3.04
2.97
1.57
1.46
2.30
3.20
1.00
0.97
6.11
0.97
3.65
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

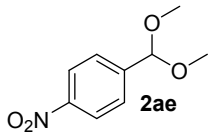

166.88
137.32
130.47
128.69
126.52
99.84
99.62
88.39
87.93
55.87
41.29
41.20
19.80
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
O

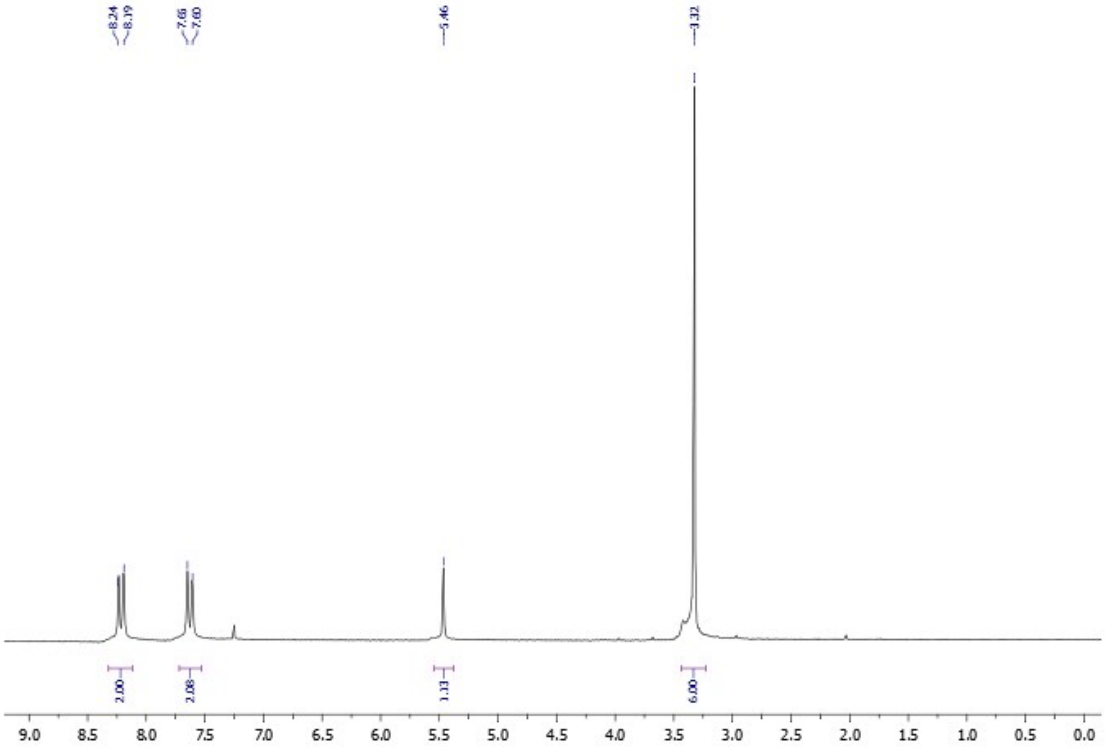
2ad

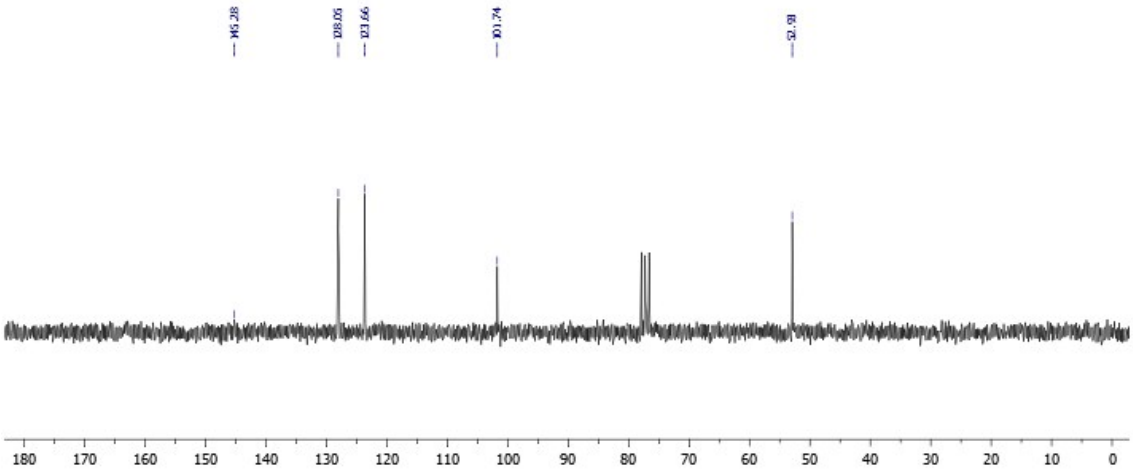

7.48
7.32
5.40
3.33
5.03
1.12
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

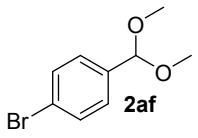

138.25
128.67
128.42
126.90
103.38
52.91
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
O
O2N

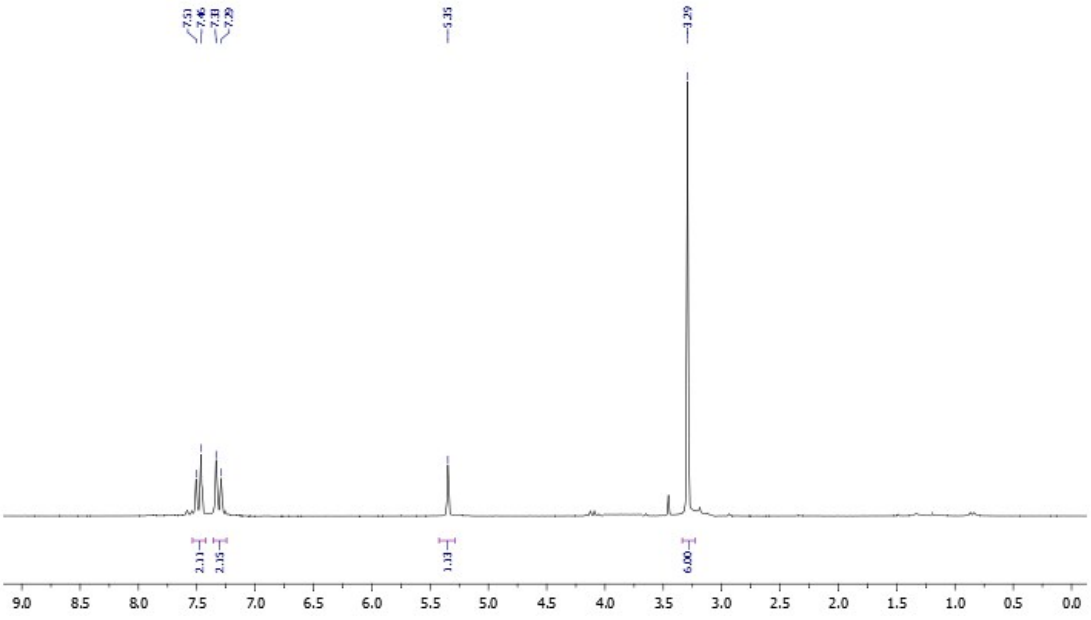
2ae

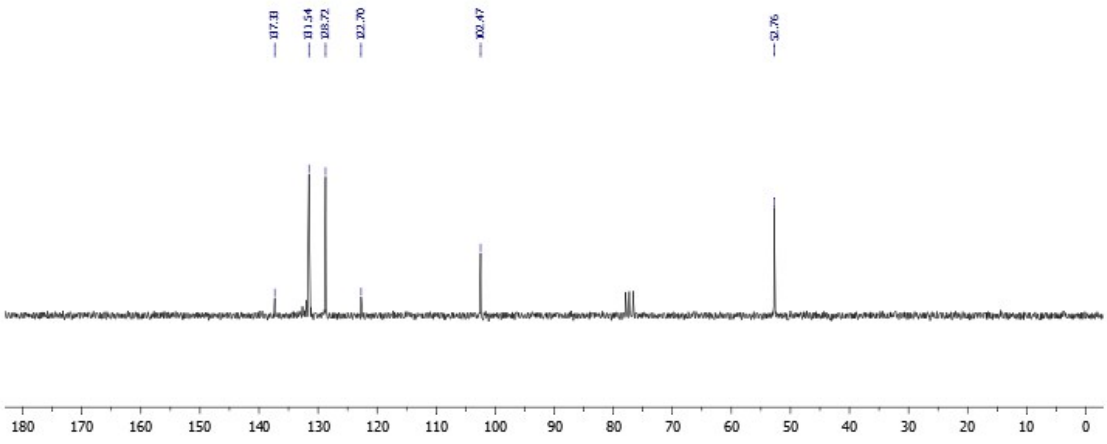

8.24
8.19
7.66
7.60
5.46
3.32
2.00
2.08
1.33
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

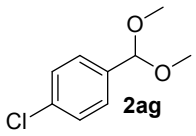

145.28
128.05
123.66
101.74
52.91
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
O
Br

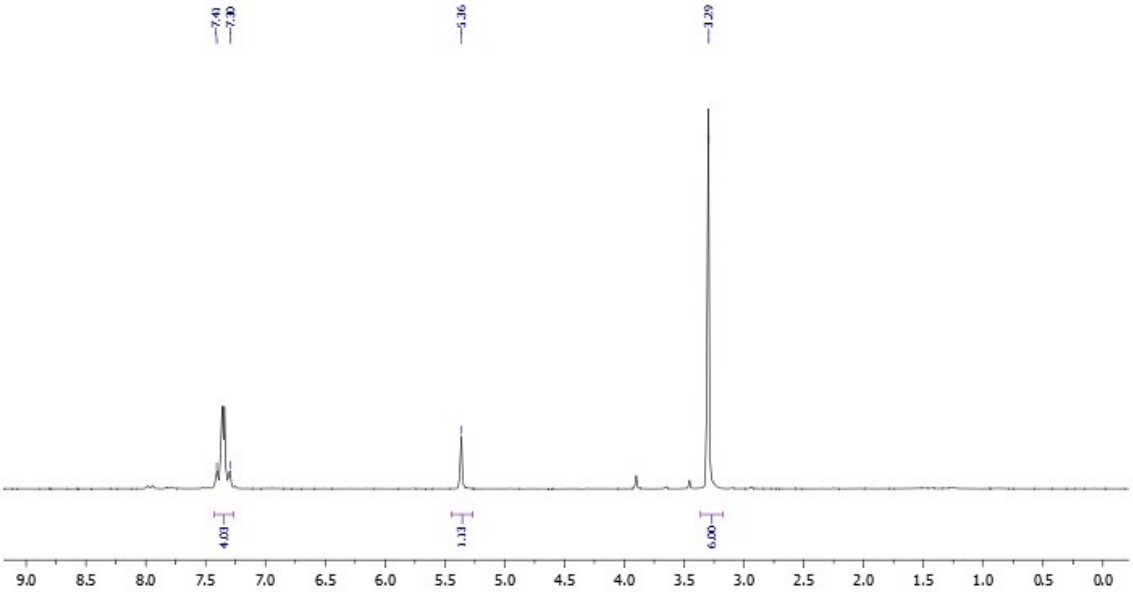
2af

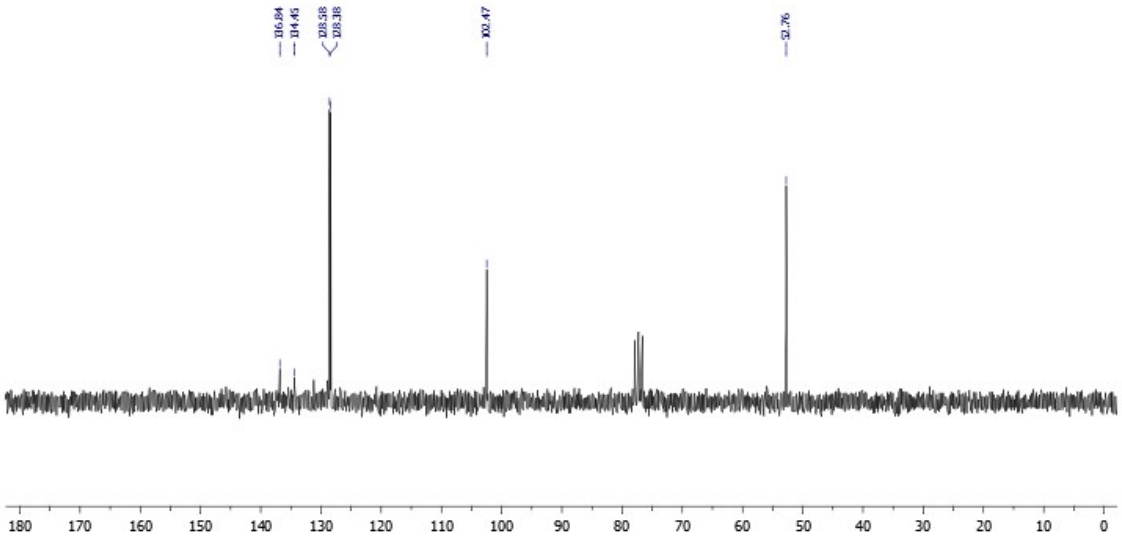

7.51
7.46
7.33
7.29
5.35
3.29
2.13
2.35
1.13
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

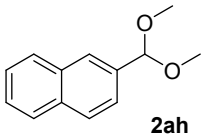

137.33
131.54
128.72
122.70
102.47
52.76
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
O
Cl

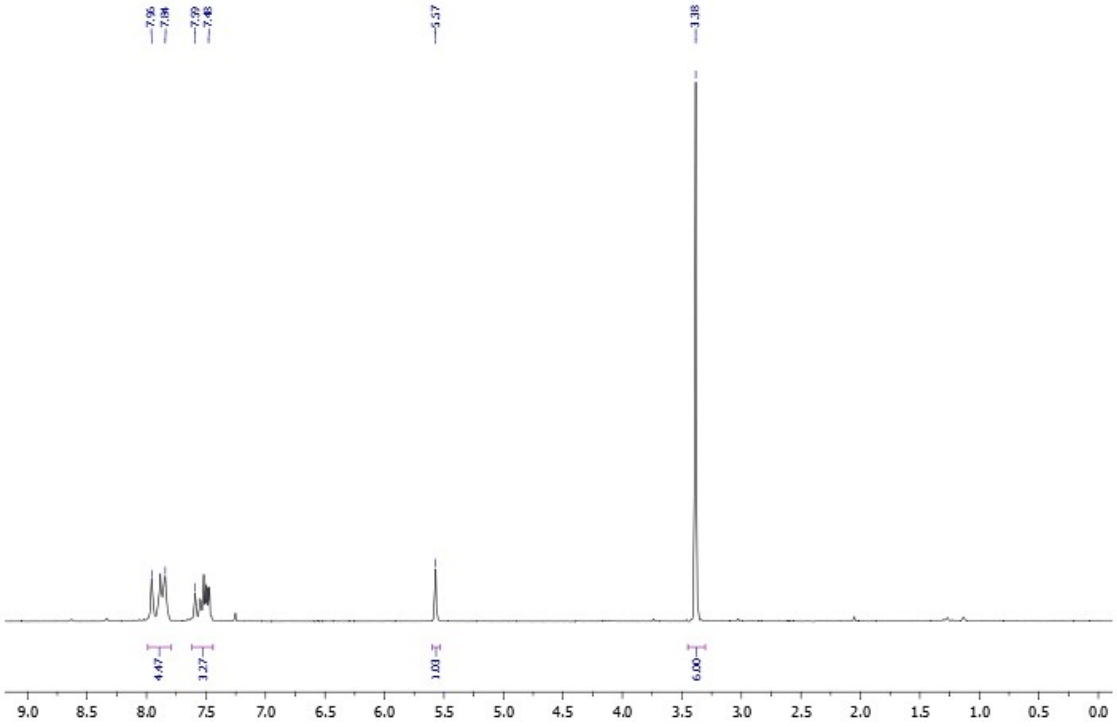
2ag

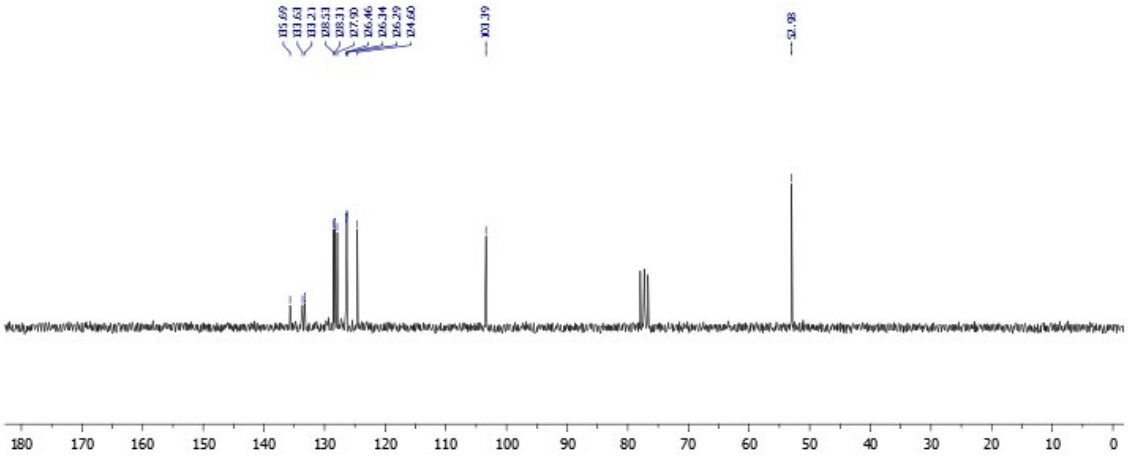

7.41
7.30
5.36
3.29
4.03
1.13
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

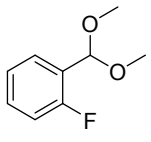

116.84
114.46
128.58
128.38
100.47
52.76
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



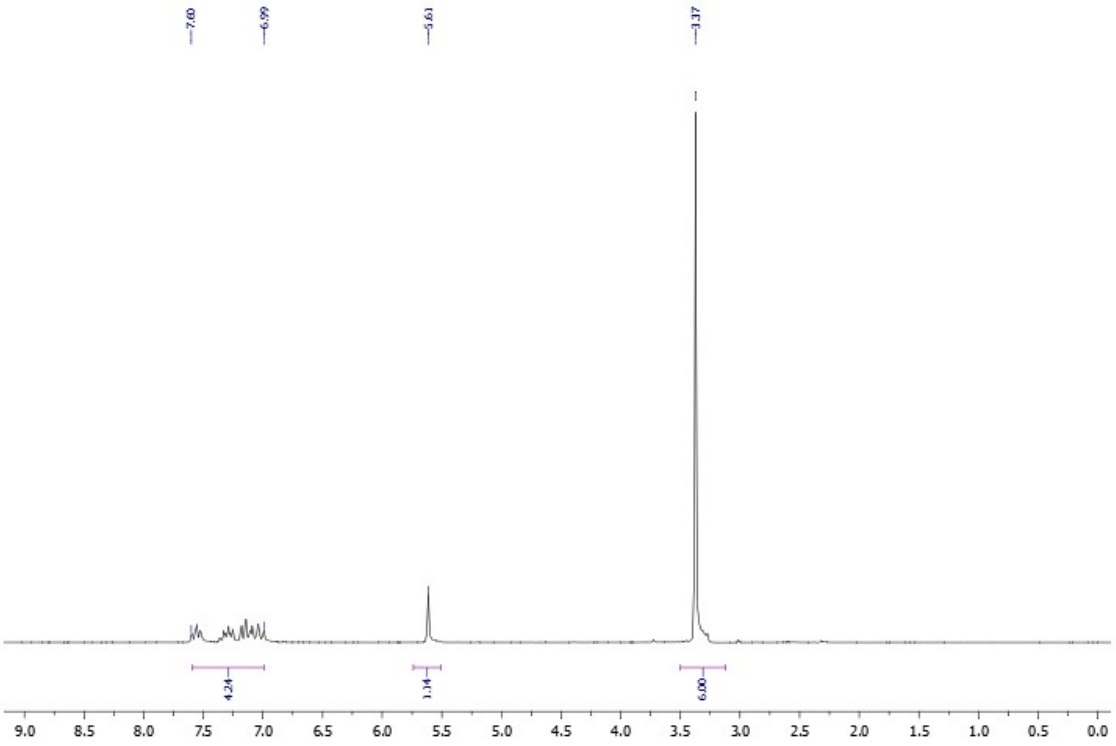
2ah

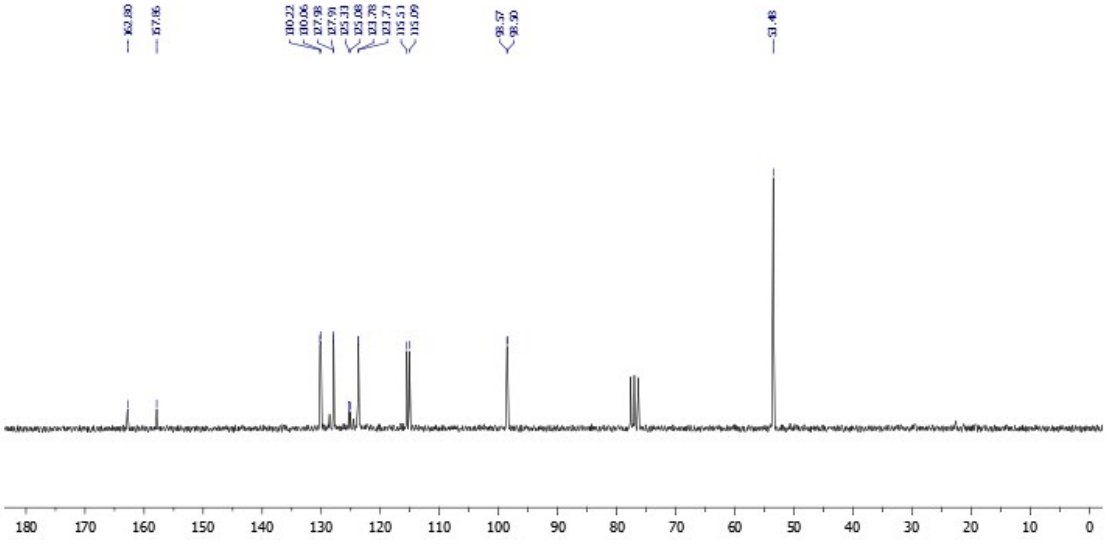

7.96
7.94
7.89
7.85
5.57
3.38
4.47
3.27
1.03
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


135.69
133.63
133.23
128.53
128.31
127.90
126.46
126.34
126.29
124.60
103.39
52.98
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
O
F

2ai


7.60
6.99
5.61
3.37
4.24
1.14
6.00
9.0
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
0.5
0.0


162.80
157.86
130.22
130.06
127.78
127.70
125.31
125.08
123.78
123.71
115.51
115.09
98.57
98.30
51.48
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0