Electronic Supplementary Material (ESI) for Green Chemistry.

Photochemical Synthesis of Acetals utilizing Schreiner's Thiourea as the Catalyst

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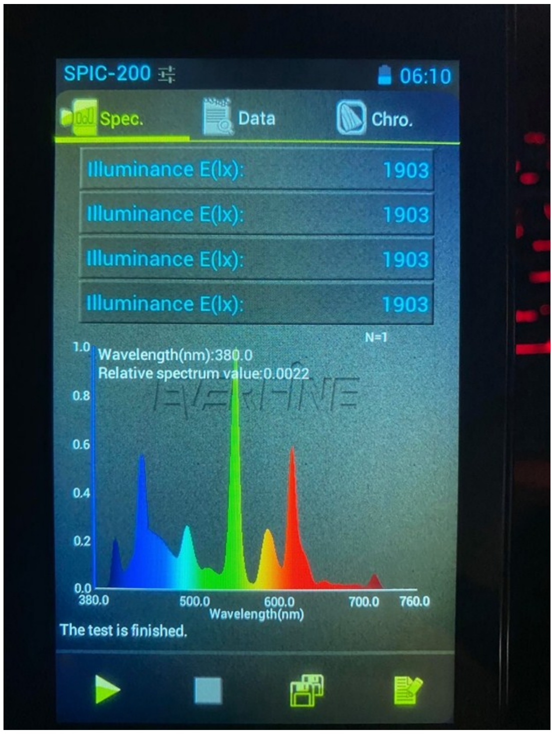
General Remarks

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), or a Bruker 400 MHz, 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 signal), 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-NMR 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 °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.

Emission Spectrum of the Light Source

The emission spectrum of the lamps was measured with a SPIC-200 spectral irradiance colorimeter. The lamp was placed in a dark room in a 30 cm distance from the lamp.



Illuminance E(lx): 1903

Illuminance E(lx): 1903

Illuminance E(lx): 1903

Illuminance E(lx): 1903

Wavelength(nm):380.0

Relative spectrum value:0.0022

The test is finished.

CCT(K) 6201

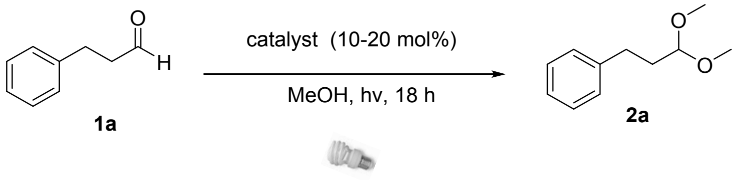
TLCI-2012: 59

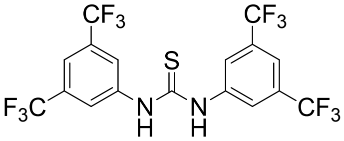
Duv 0.00143

u ' 0.2009

v ' 0.4702

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

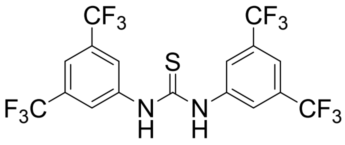




3a

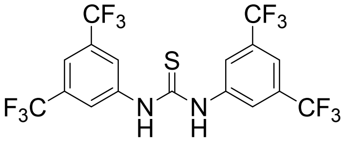
20 mol%, 81%[a]

10 mol%, 59%[a]



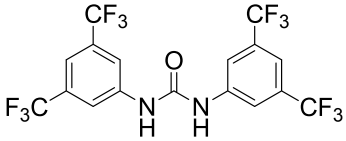
3a

20 mol%, 0%[b]



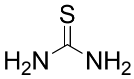
3a

20 mol%, 13%[c]



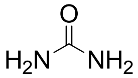
3b

20 mol%, 12%



3c

20 mol%, 20%

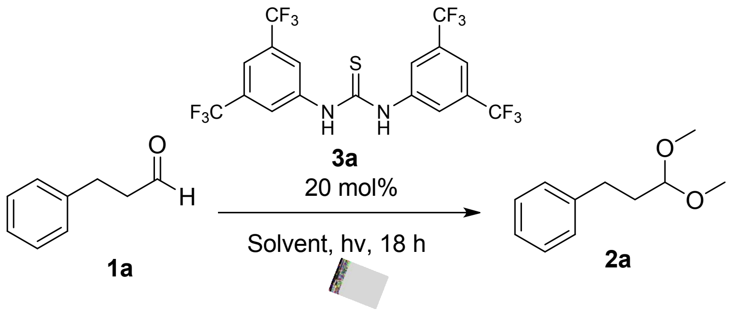


3d

20 mol%, 10%

no catalyst, 9%

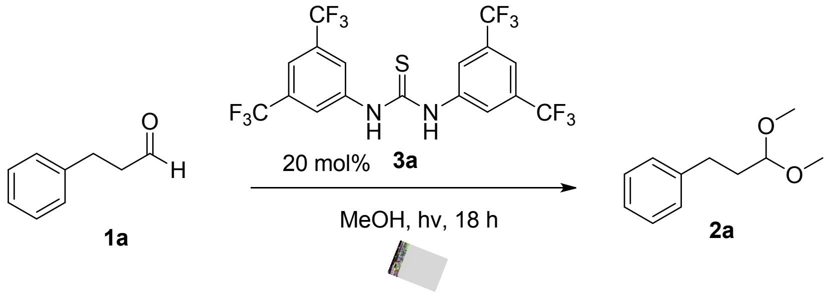
[a] Yield of isolated product
[b] Reaction was kept in the dark
[c] Reaction took place at 50 ºC



Entry	**Solvent**	**Yield (%)[a]**
1[b]	MeOH	81
2	MeOH/MeCN (1:1)	24
3	MeOH/$CHCl_3$ (1:1)	67
4	MeOH/EtOAc (1:1)	traces
5	MeOH/Pet.Ether (1:1)	61
6	MeOH/CH_2Cl_2 (1:1)	63
7	MeOH/toluene (1:1)	50
8	MeOH/Et_2O (1:1)	50
9[c]	MeOH	72
10[d]	MeOH	50

[a] Yield of isolated product
[b] Reaction time: 3 h
[c] Blue LED instead of CFL lamps
[d] Green LED instead of CFL lamps

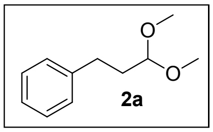
Mechanistic Investigations with Scavengers for the Photocatalytic Reaction of 3-Phenyl-propanal with Methanol



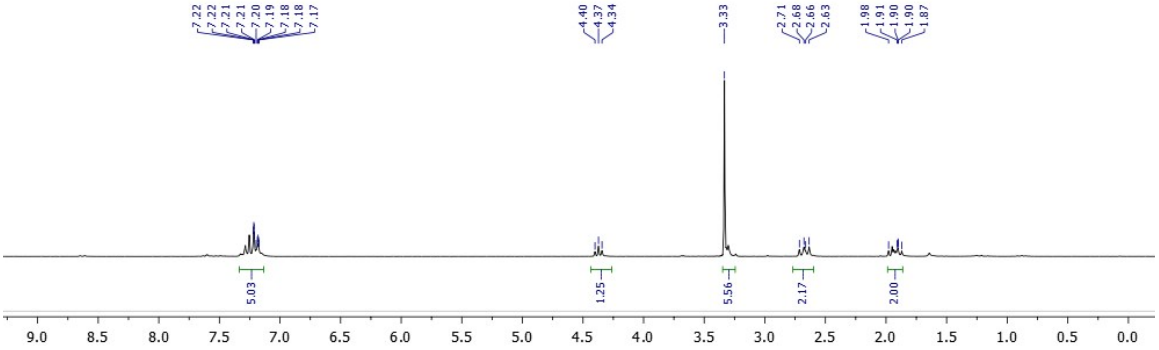
Entry	Quencher (equiv.)	Notes	Yield (%)[a]
1	Ar atmosphere	-	79
2	Open air	-	100 (81)

[a] Yield determined by ^{1}H-NMR, isolated yield in parentheses

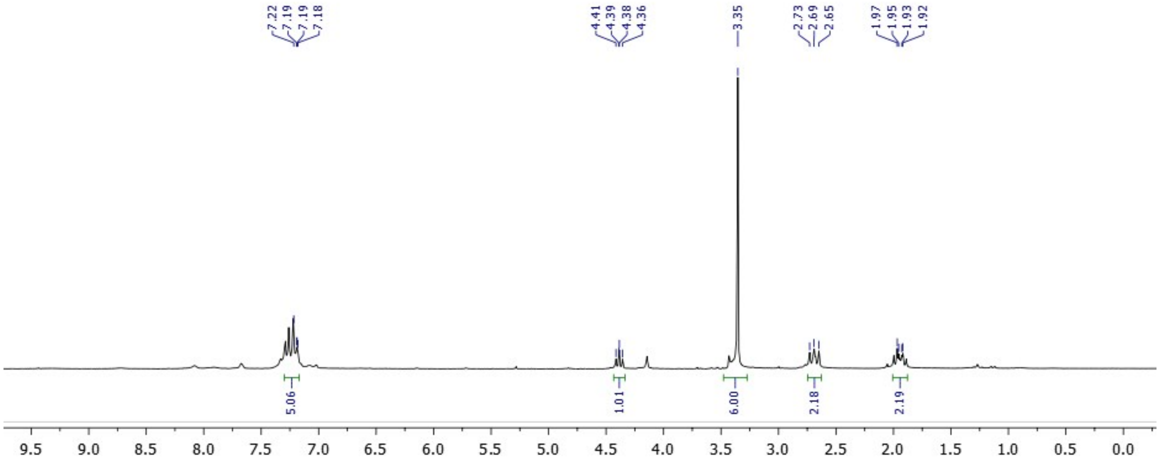
Purification of the Product utilizing Extractions



2a



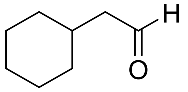
^{1}H-NMR (in $CDCl_3$) of 2a, after purification by column chromatography



^{1}H-NMR in ($CDCl_3$) of the reaction mixture for 2a, after $NaHCO_3$ (aqueous, 10%) wash (without column chromatography)

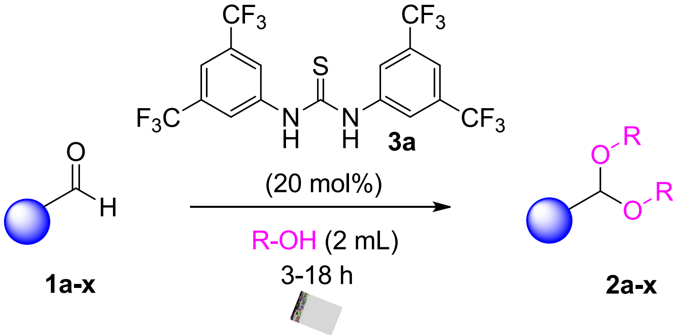
Synthesis of Starting Materials

2-Cyclohexyl acetaldehyde (1o) [1]



A flame dry round-bottom flask was charged with a solution of oxalyl chloride (2M) (0.60 mL, 1.20 mmol, 1.2 equiv.) in dry CH_2Cl_2 (1.5 mL) under argon atmosphere at -78 ^oC. Dimethylsulfoxide (0.08 mL, 1.10 mmol, 1.1 equiv.) in dry CH_2Cl_2 (1.5 mL) was added dropwise and the reaction mixture was left stirring for 30 min. 2-Cyclohexyl ethanol (128 mg, 1.00 mmol, 1.0 equiv.) was dissolved in dry CH_2Cl_2 (1.5 mL) and was added in the reaction mixture. After 30 min, triethylamine (0.45 mL, 5.00 mmol, 5.0 equiv.) was added and the reaction mixture was stirred at -78 ^oC for 15 min. The reaction mixture was extracted with CH_2Cl_2 (3 x 5 mL) and ice-water (10 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 reaction mixture was purified by column chromatography eluting with petroleum ether:ethyl acetate (9:1- 8:2). Colorless Oil; 62% yield; ^1H NMR (200 MHz, $CDCl_3$) δ: 9.68 (1H, t, *J*= 2.3 Hz, CHO), 2.22 (2H, dd, *J* = 6.8 and 2.3 Hz, $COCH_2$), 1.87-1.74 (1H, m, CH), 1.72-1.55 (5H, m, 5 x C*H*H), 1.34-1.15 (2H, m, 2 x C*H*H), 1.06-0.98 (1H, m, C*H*H), 0.97-0.87 (2H, m, 2 x C*H*H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 202.8, 51.4, 33.2, 32.7, 26.1, 26.1; MS 127 $[M+H]^+$.

General Procedure for the Photochemical Synthesis of Acetals

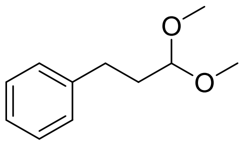


In a glass vial with a screw cap containing *N*,*N*′-bis[3,5-bis(trifluoromethyl) phenyl]-thiourea (**3a**) (Schreiner′s thiourea) (50 mg, 0.10 mmol) in alcohol (2 mL), aldehyde (0.50 mmol) was added. The vial was sealed with a screw cap and left stirring under household bulb irradiation (2 x 80W household lamps, see photos below) for 3-18 h. The desired product was isolated after purification by column chromatography or base aqueous wash (when full consumption of aldehyde took place).

A **B**

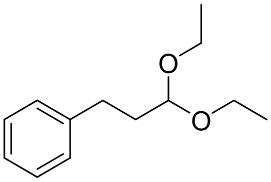
Scheme. **A**: 2 x 80W fluorescent household lamps utilized for the photocatalytic reaction. Bulbs are placed symmetrically 3 cm away from the reaction tube. **B**: Beginning of the reaction.

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



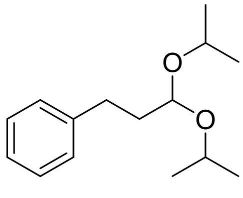
Reaction time: 3 h; colorless oil; 81% yield; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 7.38-7.08 (5H, m, ArH), 4.37 (1H, t, J = 5.8 Hz, OCH), 3.33 (6H, s, 2 x OCH$_3$), 2.68 (2H, t, J = 7.5 Hz, PhCH$_2$), 2.00-1.86 (2H, m, CH$_2$); ^{13}C NMR (50 MHZ, CDCl$_3$) δ: 141.6, 128.4, 125.9, 103.7, 52.7, 34.0, 30.8; MS (ESI) m/z 181 [M+H]$^+$.

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



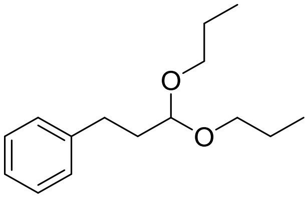
Reaction time: 3 h; Colorless oil; 83% yield; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 7.34- 7.15 (5H, m, ArH), 4.48 (1H, t, J = 5.7 Hz, OCH), 3.81-3.35 (4H, m, 2 x OCH$_2$), 2.69 (2H, t, J = 7.5 Hz, PhCH$_2$), 2.06-1.84 (2H, m, CH$_2$), 1.21 (6H, t, J = 7.1 Hz, 2 x CH$_3$); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 141.7, 128.4, 128.3, 125.8, 102.1, 61.0, 35.0, 31.0, 15.4; MS (ESI) m/z 209 [M+H]$^+$.

(3,3-Diisopropoxypropyl)benzene (2c)[4]



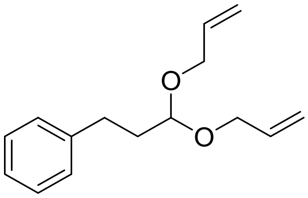
Reaction time: 3 h; Colorless oil; 64% yield; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 7.34-7.10 (5H, m, ArH), 4.56 (1H, t, J = 5.5 Hz, OCH), 3.86 (2H, hept, J = 6.1 Hz, 2 x OCH), 2.70 (2H, t, J = 7.6 Hz, PhCH$_2$), 1.97-1.87 (2H, m, CH$_2$), 1.21 (6H, d, J = 6.1 Hz, 2 x CH$_3$), 1.14 (2H, d, *J* = 6.1 Hz, 2 x CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) *δ*: 141.9, 128.3, 128.2, 125.7, 99.6, 67.7, 36.9, 31.0, 23.4, 22.6; MS (ESI) m/z 237 $[M+H]^+$.

(3,3-Dipropoxypropyl)benzene (2d)[5]



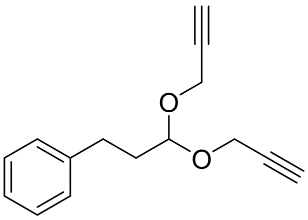
Reaction time: 3 h; Colorless oil; 77% yield; ^1H NMR (200 MHz, $CDCl_3$) *δ*: 7.33-7.08 (5H, m, ArH), 4.49 (1H, t, *J* = 5.8 Hz, OCH), 3.62-3.51 (2H, m, OCH_2), 3.45- 3.32 (2H, m, OCH_2), 2.70 (2H, t, *J* = 7.6 Hz, $PhCH_2$), 2.06-1.89 (2H, m, CH_2), 1.71-1.50 (4H, m, 2 x CH_2), 0.95 (6H, t, *J* = 7.4 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; MS (ESI) m/z 237 $[M+H]^+$.

(3,3-Bis(allyloxy)propyl)benzene (2e)[5]



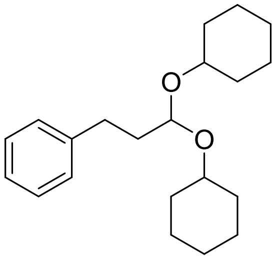
Reaction time: 3 h; Colorless oil; 96% yield; ^1H NMR (200 MHz, $CDCl_3$) *δ*: 7.34-7.13 (5H, m, ArH), 6.10-5.82 (2H m, 2 x =CH), 5.44-5.11 (4H, m, 2 x =CH_2), 4.63 (1H, t, *J* = 6.1 Hz, OCH), 4.17-3.96 (4H, m, 2 x OCH_2), 2.73 (2H, t, *J* = 7.6 Hz, $PhCH_2$), 2.11-1.93 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) *δ*: 141.5, 134.6, 128.3, 125.8, 116.7, 101.5, 66.3, 34.9, 30.9; MS (ESI) m/z 233 $[M+H]^+$.

(3,3-Bis(prop-2-yn-1-yloxy)propyl)benzene (2f)[5]



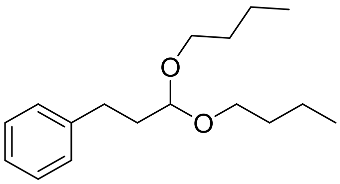
Reaction time: 3 h; Colorless oil; 74% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.30-7.19 (5H, m, ArH), 4.83 (1H, t, J = 5.7 Hz, OCH), 4.25 (4H, d, J = 2.4 Hz, 2 x OCH_2), 2.73 (2H, t, J = 7.3 Hz, $PhCH_2$), 2.44 (2H, t, J = 2.4 Hz, ≡CH), 2.06-1.91 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 141.2, 128.4, 128.3, 125.9, 100.9, 79.6, 74.3, 53.1, 34.7, 30.6; MS (ESI) m/z 229 $[M+H]^+$.

((3-Phenylpropane-1,1-diyl)bis(oxy))dicyclohexane (2g)[5]



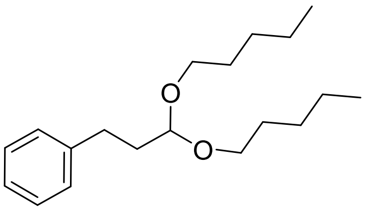
Reaction time: 3 h; Colorless oil; 61% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.31-7.12 (5H, m, ArH), 4.66 (1H, t, J = 5.5 Hz, OCH), 3.56-3.45 (2H, m, 2 x OCH), 2.69 (2H, t, J = 7.8 Hz, $PhCH_2$), 1.99-1.61 (10H, m, 5 x CH_2), 1.58-1.15 (12H, m, 6 x CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 142.0, 128.3, 128.2, 125.7, 99.2, 73.6, 37.1, 33.6, 32.8, 31.2, 25.7, 24.4, 24.2; MS (ESI) m/z 317 $[M+H]^+$.

(3,3-Dibutoxypropyl)benzene (2h)[6]



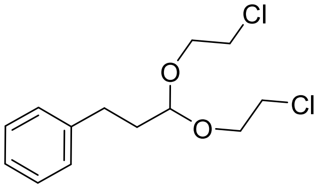
Reaction time: 3 h; Colorless oil; 87% yield; ^{1}H NMR (200 MHz, $CDCl_3$) *δ*: 7.36-6.98 (5H, m, ArH), 4.49 (1H, t, *J* = 5.8 Hz, OCH), 3.67-3.50 (2H, m, OCH_2), 3.48-3.37 (2H, m, OCH_2), 2.70 (2H, t, *J* = 7.7 Hz, $PhCH_2$), 2.06-1.86 (2H, m, CH_2), 1.65-1.23 (8H, m, 4 x CH_2), 0.94 (6H, t, *J* = 7.2 Hz, 2 x CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) *δ*: 141.7, 128.3, 128.2, 125.7, 102.2, 65.2, 34.9, 31.9, 31.0, 19.4, 13.9; MS (ESI) m/z 265 $[M+H]^+$.

(3,3-Bis(pentyloxy)propyl)benzene (2i)[5]



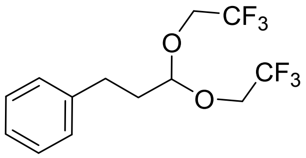
Reaction time: 3 h; Colorless oil; 83% yield; ^{1}H NMR (200 MHz, $CDCl_3$) *δ*: 7.43-7.03 (5H, m, ArH), 4.48(1H, t, *J* = 5.8 Hz, OCH), 3.70-3.53 (2H, m, OCH_2), 3.49-3.32 (2H, m, OCH_2), 2.69 (2H, t, *J* = 7.9 Hz, $PhCH_2$), 2.04-1.89 (2H, m, CH_2), 1.69-1.49 (4H, m, 2 x CH_2), 1.40-1.29 (8H, m, 4 x CH_2), 0.91 (6H, t, *J* = 6.9 Hz, 2 x CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) *δ*: 141.8, 128.4, 128.3, 125.7, 102.2, 65.5, 34.9, 31.0, 29.6, 28.4, 22.3, 14.1; MS (ESI) m/z 293 $[M+H]^+$.

(3,3-Bis(2-chloroethoxy)propyl)benzene (2j)[5]



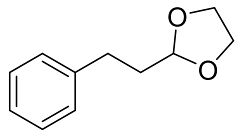
Reaction time: 3 h; Yellow oil; 94% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.34-7.08 (5H, m, ArH), 4.64 (1H, t, J = 5.9 Hz, OCH), 3.95-3.72 (4H, m, 2 x OCH_2), 3.65 (4H, t, J = 6.0 Hz, 2 x CH_2Cl), 2.73 (2H, t, J = 6.7 Hz, $PhCH_2$), 2.12-1.84 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 141.1, 128.4, 128.3, 126.0, 102.3, 65.3, 43.3, 34.4, 30.8; MS (ESI) m/z 277 $[M+H]^+$.

(3,3-Bis(2,2,2-trifluoroethoxy)propyl)benzene (2k)[5]



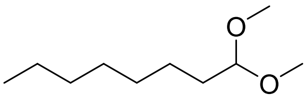
Reaction time: 18 h; Colorless oil; 45% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.33-7.11 (5H, m, ArH), 4.75 (1H, t, J = 5.9 Hz, OCH), 3.90 (4H, q, J = 8.6 Hz, 2 x CH_2CF_3), 2.71 (2H, t, J = 6.5 Hz, $PhCH_2$), 1.99 (2H, td, J = 6.5 and 5.9 Hz, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 140.2, 128.6, 128.3, 126.3, 123.5 (q, J = 275 Hz), 102.3, 62.1 (q, J = 34 Hz), 33.9, 30.5; ^{19}F (188 MHz, $CDCl_3$) δ: -32.3 (t, J = 8.5 Hz); MS (ESI) m/z 317 $[M+H]^+$.

2-Phenethyl-1,3-dioxolane (2l)[3]



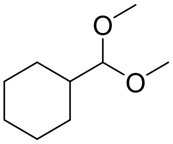
Reaction time: 3 h; Colorless oil; 85% yield; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 7.36-7.05 (5H, m, ArH), 4.89 (1H, t, J = 4.8 Hz, OCH), 4.06-3.81 (4H, m, 2 x OCH$_2$), 2.75 (2H, t, J = 7.6 Hz, PhCH$_2$), 2.05-1.91 (2H, m, CH$_2$); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 141.5, 128.5, 128.4, 125.8, 103.8, 64.9, 35.5, 30.1; MS (ESI) m/z 179 [M+H]$^+$.

1,1-Dimethoxyoctane (2m)[2]



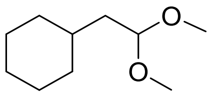
Reaction time: 18 h; Colorless oil; 81% yield; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 4.34 (1H, t, J = 5.7 Hz, OCH), 3.29 (6H, s, 2 x OCH$_3$), 1.63-1.51 (2H, m, CH$_2$), 1.29-1.25 (10H, m, 5 x CH$_2$), 0.84 (3H, t, J = 6.4 Hz, CH$_3$); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 104.5, 52.5, 32.4, 31.8, 29.4, 29.2, 24.6, 22.6, 14.1; MS (ESI) m/z 175 [M+H]$^+$.

Dimethoxymethyl)cyclohexane (2n)[7]



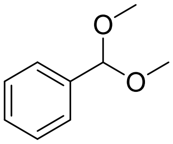
Reaction time: 18 h; Colorless oil; 74% yield; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 3.99 (1H, d, J = 7.1 Hz, OCH), 3.33 (6H, s, 2 x OCH$_3$), 1.77-1.59 (6H, m, 5 x C*H*H and CH), 1.26-0.95 (5H, m, 5 x CH*H*); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 108.5, 53.5, 40.0, 28.0, 26.3, 25.7; MS (ESI) m/z 84 [M+H]$^+$.

(2,2-Dimethoxyethyl)cyclohexane (2o)[8]



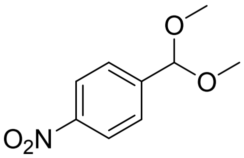
Reaction time: 18 h; Colorless oil; 63% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.46 (1H, t, J = 5.7 Hz, OCH), 3.29 (6H, s, 2 x OCH_3), 1.79-1.59 (5H, m, 2 x CH_2 and CH), 1.48-1.32 (2H, m, CH_2), 1.25-1.04 (4H, m, 2 x CH_2), 0.99-0.83 (2H, m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 102.7, 52.3, 39.9, 33.7, 33.5, 26.5, 26.2; MS (ESI) m/z 173 [M+H]$^+$.

(Dimethoxymethyl)benzene (2p)[2]



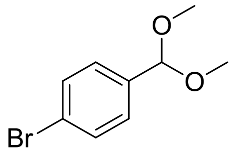
Reaction time: 18 h; Colorless oil, 80% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.54-7.20 (5H, m, ArH), 5.40 (1H, s, OCH), 3.33 (6H, s, 2 x OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.0, 128.4, 128.2, 126.6, 103.1, 52.7; MS (ESI) m/z 153 [M+H]$^+$.

1-(Dimethoxymethyl)-4-nitrobenzene (2q)[2]



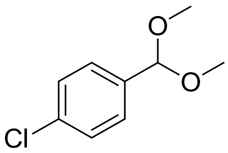
Reaction time: 18 h; Colorless oil, 94% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.22 (2H, d, J = 7.7 Hz, ArH), 7.63 (2H, d, J = 7.7 Hz, ArH), 5.47 (1H, s, OCH), 3.32 (6H, s, 2 x OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 145.0, 127.8, 123.4, 120.6, 101.5, 52.7; MS (ESI) m/z 198 [M+H]$^+$.

1-Bromo-4-(dimethoxymethyl)benzene (2r)[2]



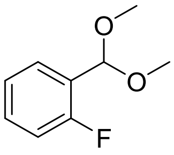
Reaction time: 18 h; Colorless oil, 46% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.48 (2H, d, J = 8.5 Hz, ArH), 7.31 (2H, d, J = 8.5 Hz, ArH), 5.34 (1H, s, OCH), 3.29 (6H, s, 2 x OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 137.0, 131.3, 128.4, 122.4, 102.2, 52.5; MS (ESI) m/z 231 $[M+H]^+$.

1-Chloro-4-(dimethoxymethyl)benzene (2s)[2]



Reaction time: 18 h; Colorless oil, 36% 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: 136.6, 134.2, 128.3, 128.1, 102.2, 52.5; MS (ESI) m/z 187 $[M+H]^+$.

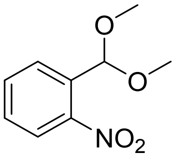
1-(Dimethoxymethyl)-2-fluorobenzene (2t)[9]



Reaction time: 18 h; Colorless oil, 87% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.60-7.52 (1H, m, ArH), 7.37-7.27 (1H, m, ArH), 7.19-6.99 (2H, 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 = 248.0 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 =

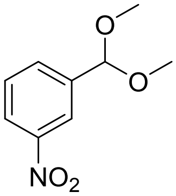
21.2 Hz), 98.5 (d, *J* = 3.6 Hz), 53.5; ^{19}F (188 MHz, CDCl$_3$) *δ*: -77.6 (m); MS (ESI) m/z 171 [M+H]$^+$.

1-(*o*-Nitrophenyl)-1,1-dimethoxymethane (2u)[10]



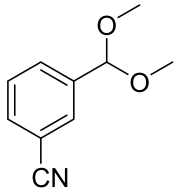
Reaction time: 18 h; Colorless oil, 88% yield; ^{1}H NMR (200 MHz, CDCl$_3$) *δ*: 7.85-7.72 (2H, m, ArH), 7.63-7.55 (1H, m, ArH), 7.52-7.38 (1H, m, ArH) 5.91 (1H, s, OCH), 3.99 (6H, s, 2 x OCH$_3$); ^{13}C NMR (50 MHz, CDCl$_3$) *δ*: 149.0, 132.7, 132.5, 129.4, 128.1, 124.2, 99.9, 54.6; MS (ESI) m/z 198 [M+H]$^+$.

1-(Dimethoxymethyl)-3-nitrobenzene (2v)[10]



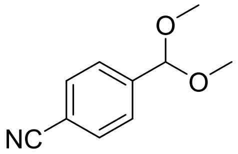
Reaction time: 18 h; Colorless oil, 44% yield; ^{1}H NMR (200 MHz, CDCl$_3$) *δ*: 8.29 (1H, s, ArH), 8.14 (1H, d, *J* = 7.7 Hz, ArH), 7.75 (1H, d, *J* = 7.7 Hz, ArH), 7.51 (1H, t, *J* = 7.7 Hz, ArH), 5.44 (1H, s, OCH), 3.31 (6H, s, 2 x OCH$_3$); ^{13}C NMR (50 MHz, CDCl$_3$) *δ*: 148.2, 140.3, 132.8, 129.1, 123.3, 121.9, 101.4, 52.6; MS (ESI) m/z 198 [M+H]$^+$.

3-(Dimethoxymethyl)benzonitrile (2w)[11]



Reaction time: 18 h; Colorless oil, 80% yield; ^{1}H NMR (200 MHz, CDCl$_3$) *δ*: 7.75-7.73 (1H, m, ArH), 7.69-7.55 (2H, m, ArH), 7.45-7.41 (1H, m, ArH), 5.39 (1H, s, OCH), 3.29 (6H, s, 2 x CH$_3$); ^{13}C NMR (50 MHz, CDCl$_3$) *δ*: 139.6, 132.0, 131.1, 130.5, 129.0, 118.6, 112.4, 101.4, 52.6; MS (ESI) m/z 178 [M+H]$^+$.

4-(Dimethoxymethyl)benzonitrile (2x)[10]



Reaction time: 18 h; Colorless oil, 78% yield; ^{1}H NMR (200 MHz, CDCl$_3$) *δ*: 7.66-7.52 (4H, m, ArH), 5.40 (1H, s, OCH), 3.29 (6H, s, 2 x OCH$_3$); ^{13}C NMR (50 MHz, CDCl$_3$) *δ*: 143.1, 132.0, 127.5, 118.6, 112.2, 101.6, 52.6; MS (ESI) m/z 178 [M+H]$^+$.

Determination of the Quantum Yield

Determination of the photon flux of the lamps

The photon flux of the spectrophotometer was determined following the procedure described in *Green Chem.,* **2019**, *21*, 669-674. 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 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:

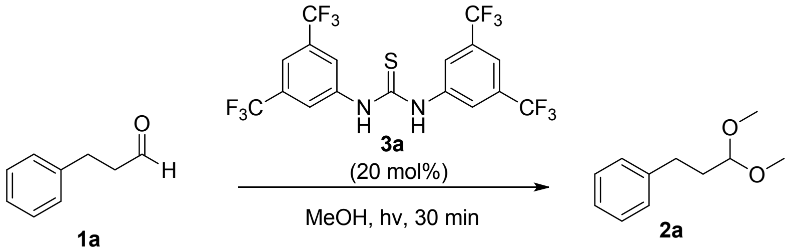
$$\text{Mol Fe}^{2+} = \frac{V \times \Delta A}{l \times \varepsilon} = \frac{0.00235\ \text{L} \times 0.382}{1.0\ \text{cm} \times 11.100\ \text{L mol}^{-1}\ \text{cm}^{-1}} = 8.09 \times 10^{-8}\ \text{mol}$$

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 is then calculated:

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

In this equation, Φ is the quantum yield of the ferrioxalate actinometer,[12] t is the time of the irradiation (90 seconds), and f is the fraction of the light absorbed at lamps (that is calculated above). Thus, the photon flux of the spectrophotometer was calculated to be 6.66×10^{-10} einstein s^{-1}.

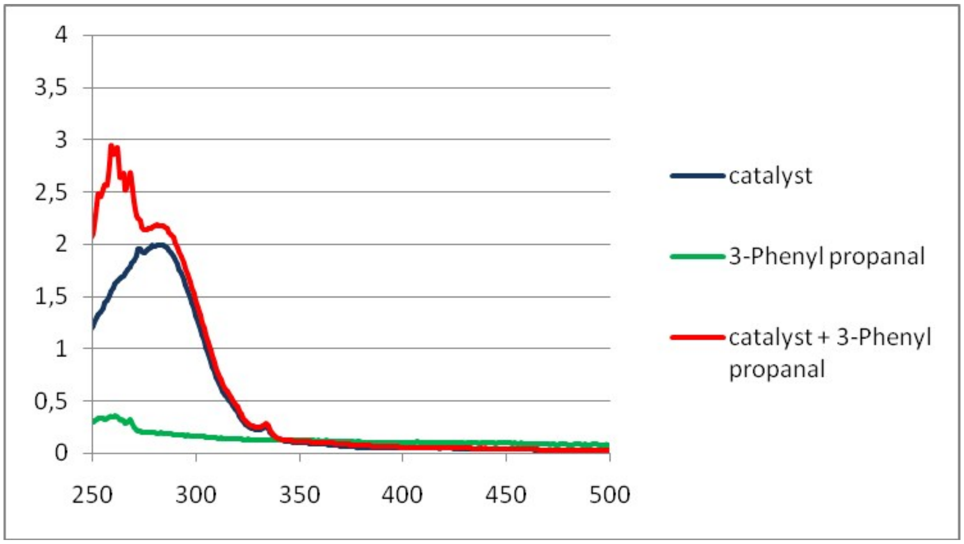
Determination of the quantum yield



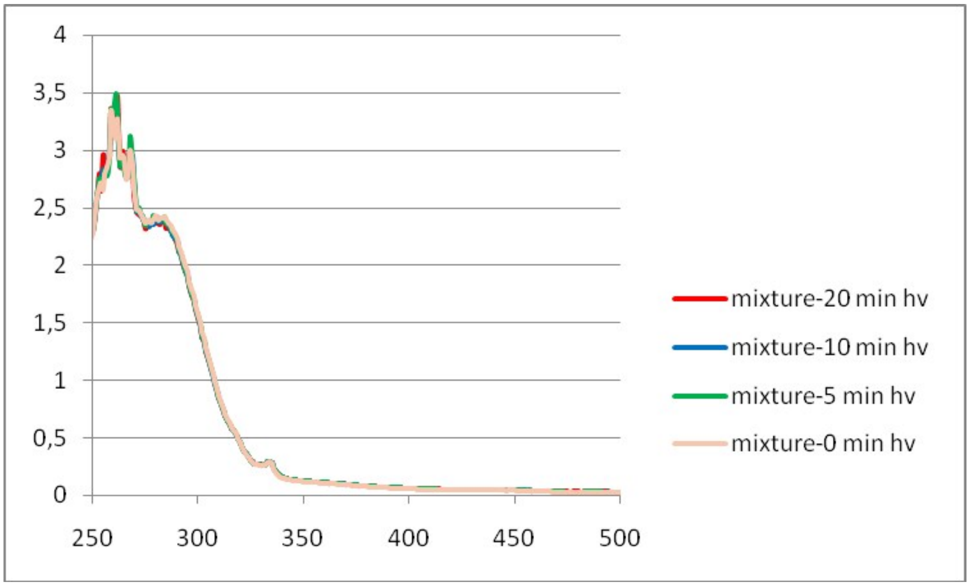
A cuvette was charged with 3-phenyl-propanal (**1a**) (13.5 mg, 0.10 mmol), Schreiner's thiourea (**3a**) (10 mg, 0.02 mmol) in methanol (0.5 mL). The reaction mixture was stirred and irradiated under CFL irradiation for 1800 s (0.5 h). After irradiation, the solvent was removed and the yield of the product was determined by ^{1}H-NMR (55%). The quantum yield was determined with the following equation:

$$\Phi = \frac{\text{mol product}}{\text{flux} \times \text{t} \times \text{f}} = \frac{55 \times 10^{-6}\ \text{mol}}{6.66 \times 10^{-10}\ \text{einstein s}^{-1} \times 1800\ \text{s} \times 0.9999} = 46$$

Mechanistic Investigations with UV-Vis Absorption Spectra

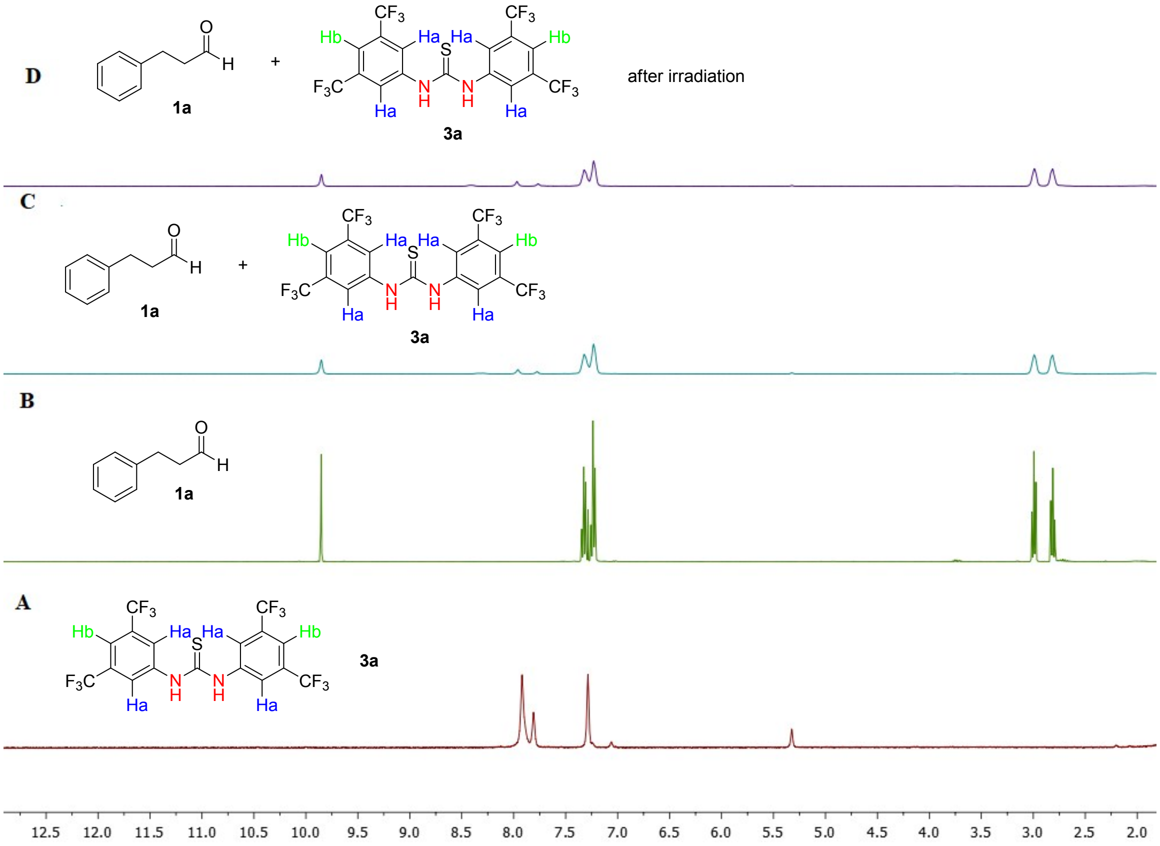


UV absorbance of 3-phenyl-propanal (**1a**) (1 x 10^{-3} M) in MeOH, Schreiner's thiourea **3a** (6 x 10^{-5} M) in MeOH and the reaction mixture (3-phenyl-propanal 1 x 10^{-3} M and Schreiner's thiourea 6 x 10^{-5} M) in MeOH

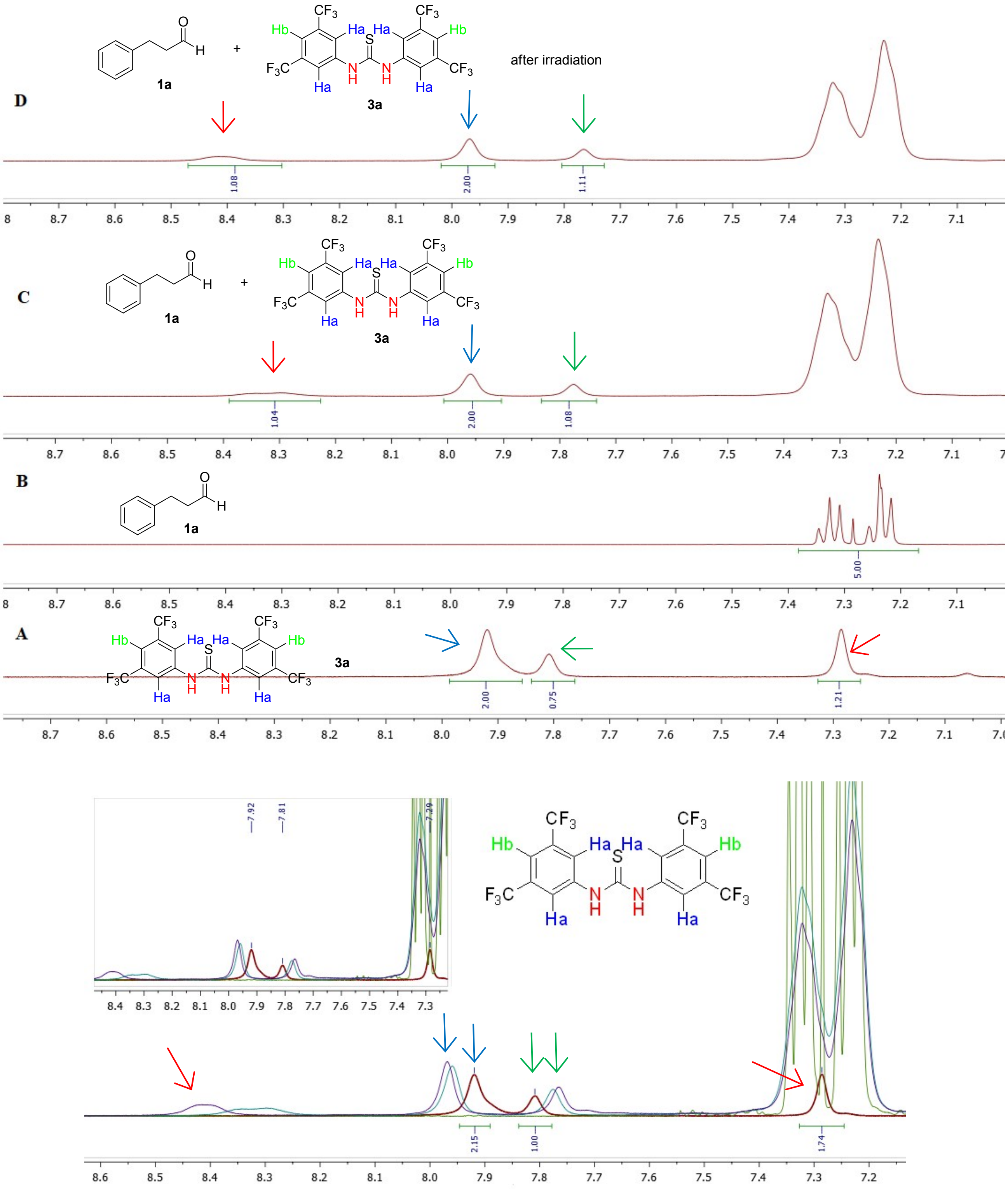


UV absorbance of the reaction mixture [3-phenyl-propanal (4 x 10^{-3} M) and Schreiner's thiourea catalyst (6 x 10^{-5} M)] in MeOH, after consecutive irradiation

^{1}H-NMR Mechanistic Experiments



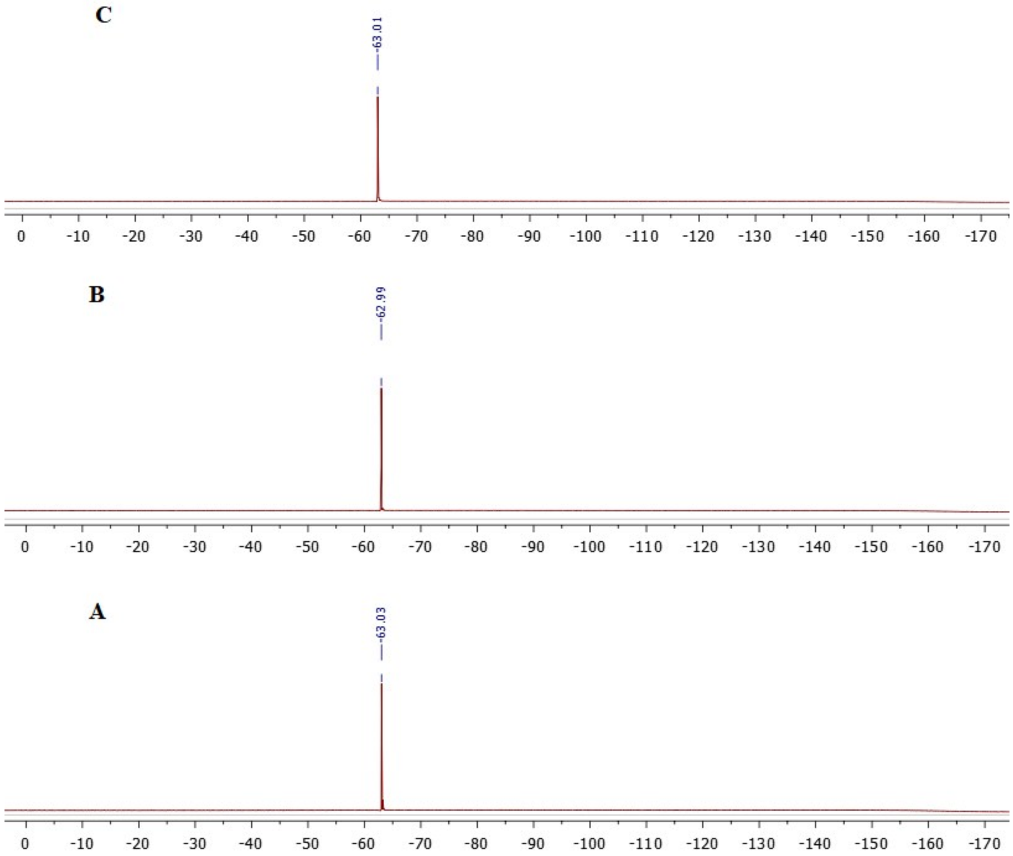
^{1}H-NMR (in $CDCl_3$) of **A**) Schreiner's thiourea **3a**, **B**) 3-phenyl-propanal (**1a**), **C**) reaction mixture before irradiation and **D**) reaction mixture after irradiation.



Zoom in (8.70-7.00 ppm) of ^{1}H –NMR (in $CDCl_3$) of **A**) Schreiner's thiourea **3a**, **B**) 3-phenyl-propanal (**1a**), **C**) reaction mixture before irradiation and **D**) reaction mixture after irradiation.

For better understanding of the hydrogen bond effect, several mechanistic experiments were performed. Initially, the ^{1}H-NMR (in $CDCl_3$) of Schreiner's thiourea **3a** was recorded (**A**). Two sets of aromatic signals were recorded at 7.92 ppm and 7.81 ppm, while the *NH* appeared at 7.29 ppm. The addition of 3-phenyl-propanal (**1a**) (**B**) to a solution of thiourea in $CDCl_3$, led to remarkable changes in ^{1}H-NMR chemical shifts of the catalyst, as it is presented above (**C**). The peak at 7.92 ppm shifted downfield to 7.96 ppm, the peak at 7.81 ppm shifted upfield to 7.78 ppm, while the *NH* protons shifted downfield from 7.29 ppm to 8.31 ppm. These results confirm the presence of hydrogen bonds among the substrate and the thiourea, supporting the formation of an aldehyde-catalyst complex. After irradiation, similar observations can be drawn in (**D**).

^{19}F-NMR Mechanistic Experiments



^{19}F-NMR (in $CDCl_3$) of **A**) Schreiner's thiourea **3a**, **B**) reaction mixture before irradiation and **C**) reaction mixture after irradiation.

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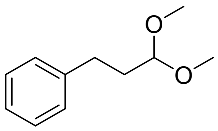
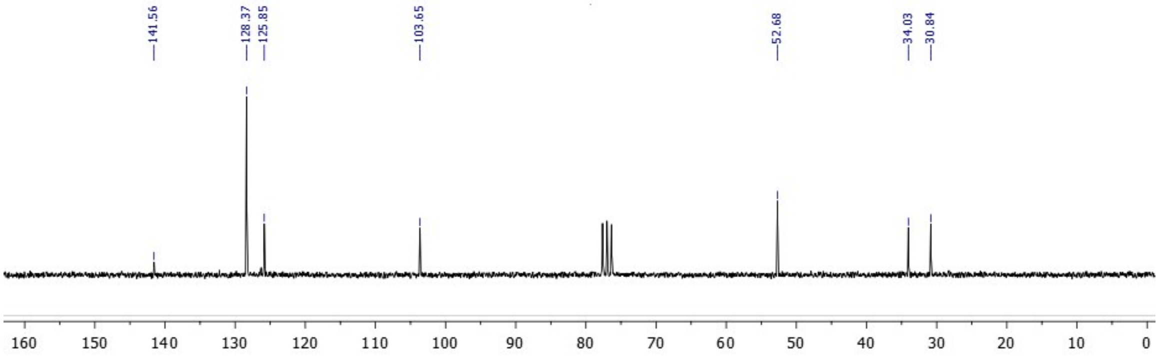

O
O

2a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103.65
52.68
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30.84
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130
120
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100
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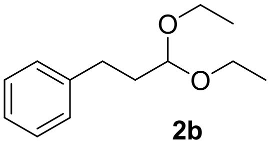
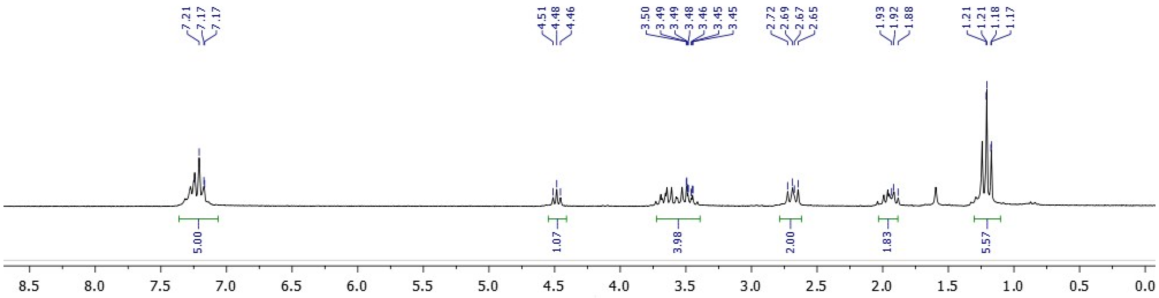
40
30
20
10
0



2b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3.50
3.49
3.49
3.48
3.46
3.45
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2.72
2.69
2.67
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1.88
1.21
1.21
1.18
1.17
5.00
1.07
3.98
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5.57
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8.0
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7.0
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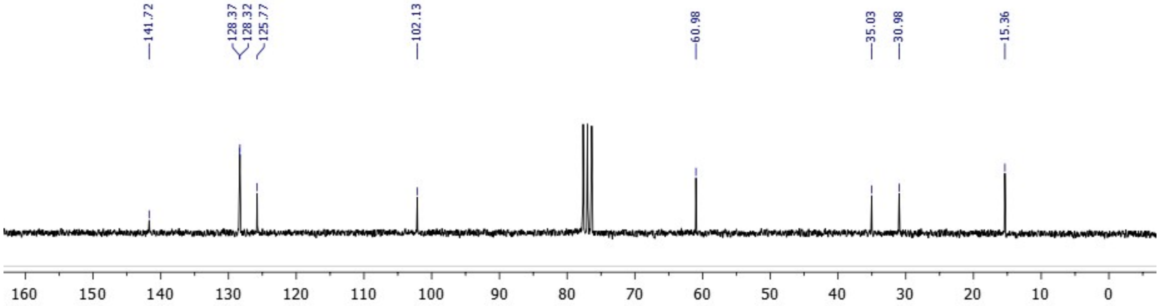
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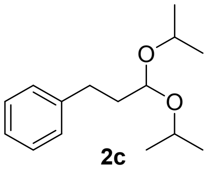
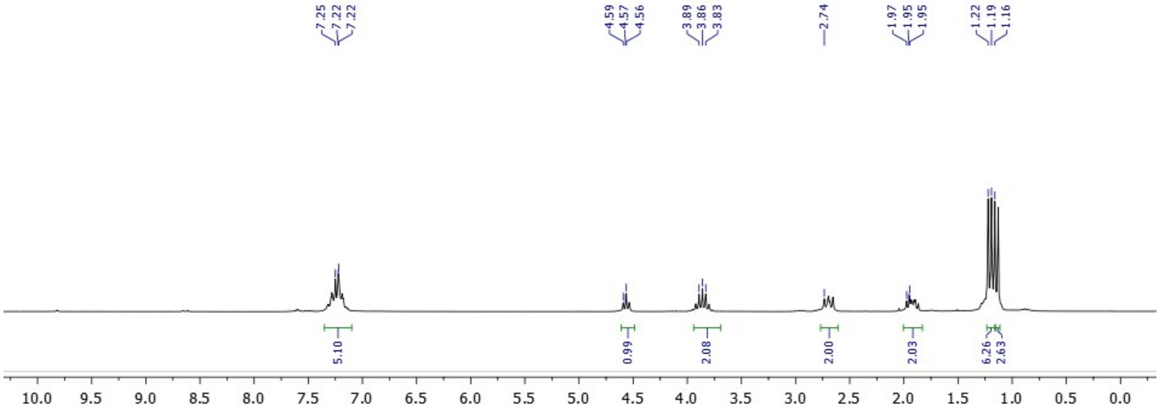


2c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1.95
1.22
1.19
1.16
5.10
0.99
2.08
2.00
2.03
6.26
2.63
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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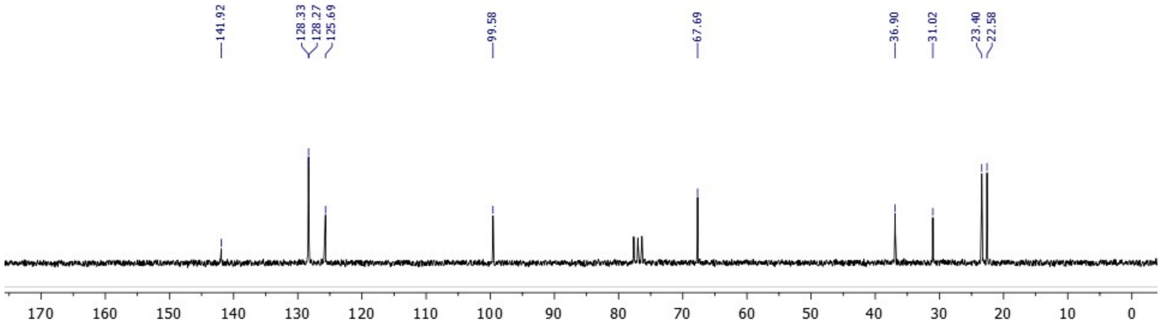
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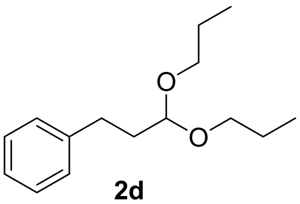

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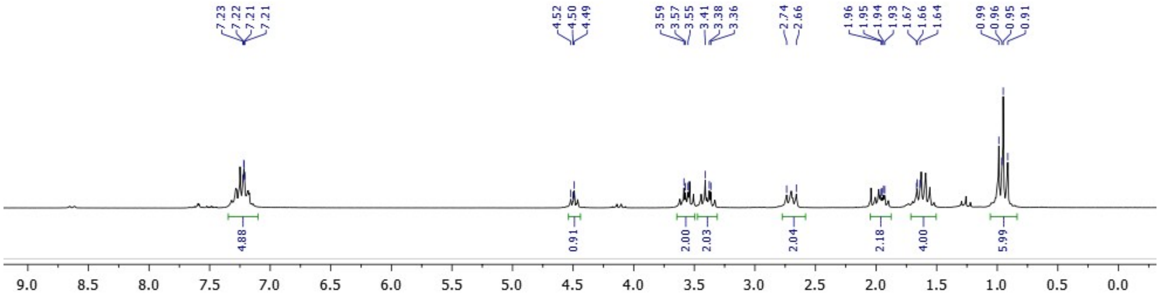
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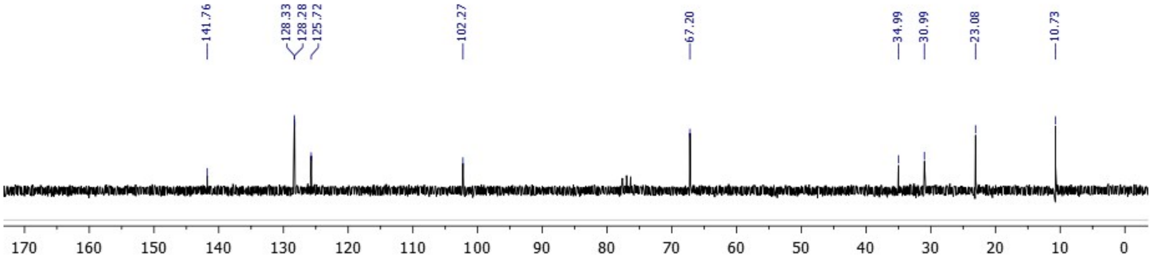
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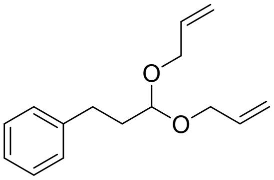

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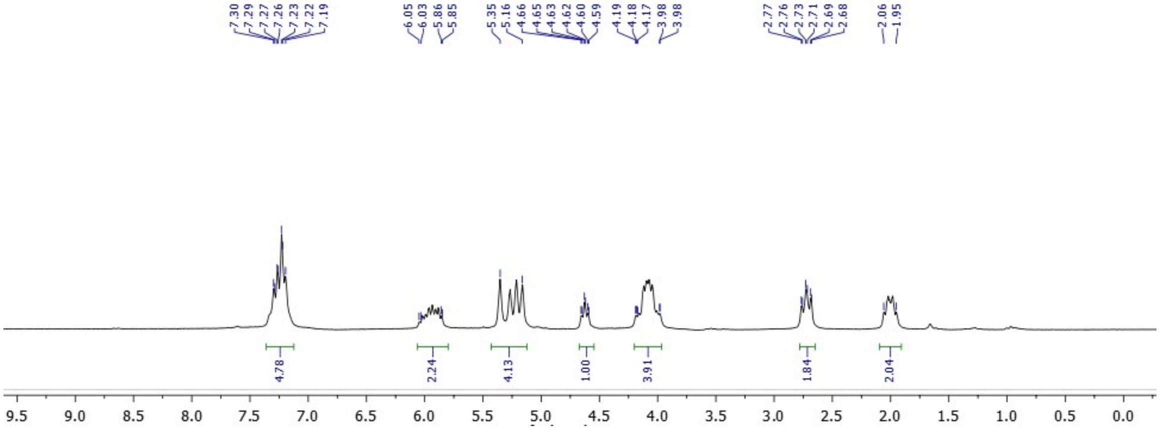
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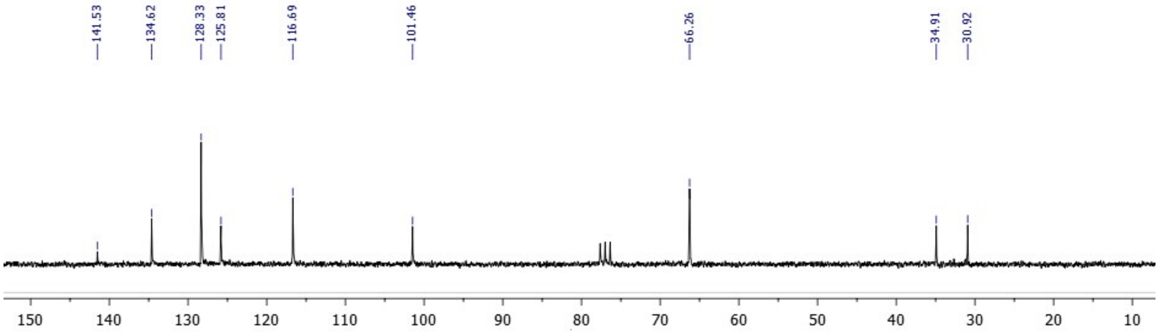
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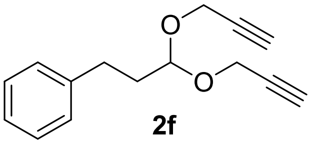

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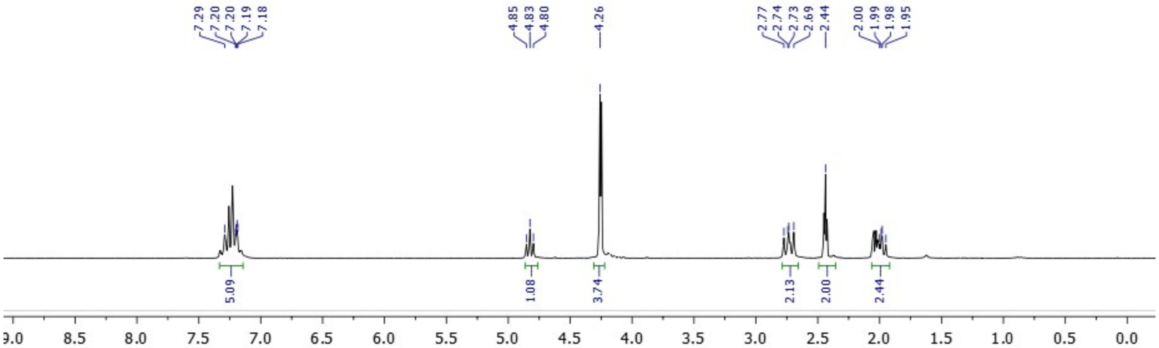
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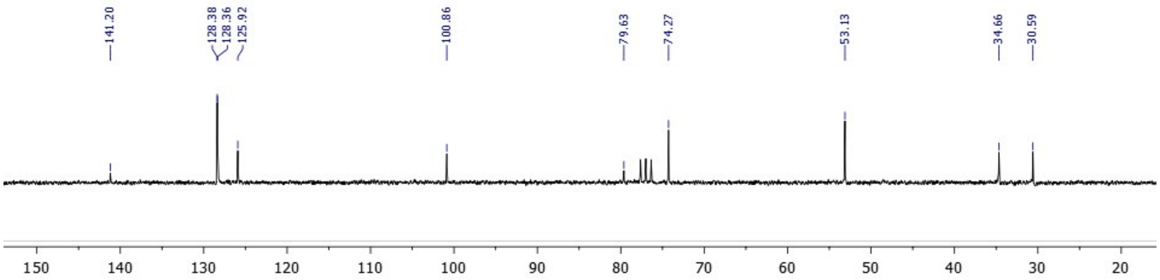
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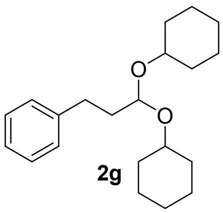

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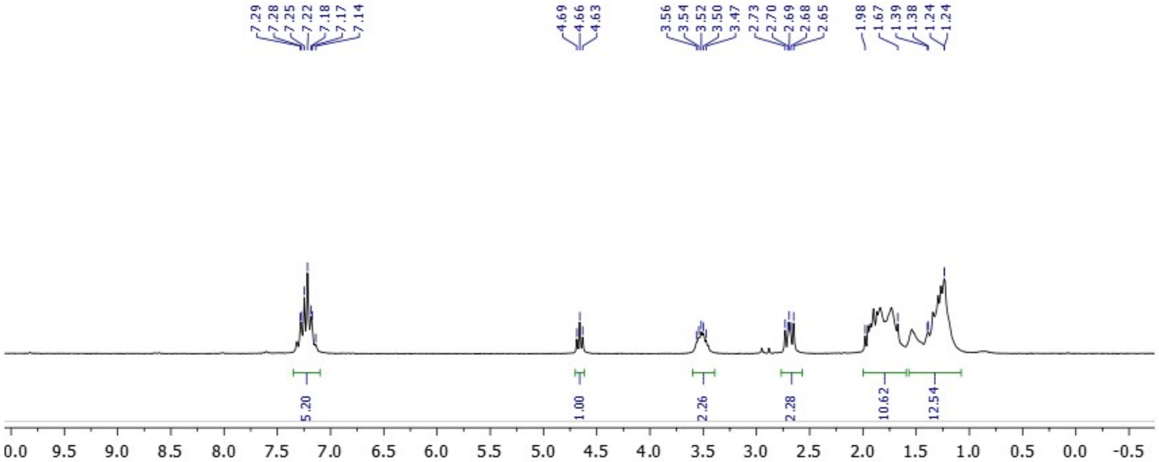
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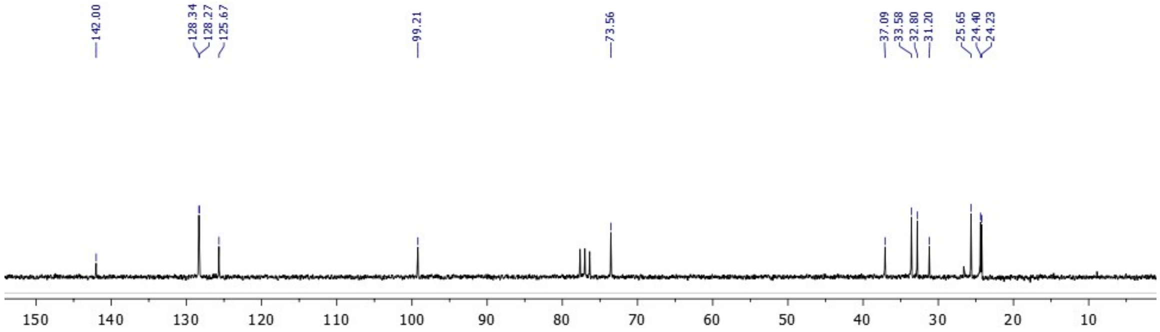
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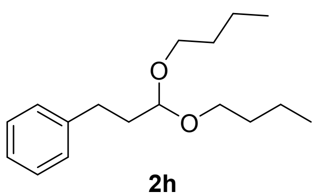
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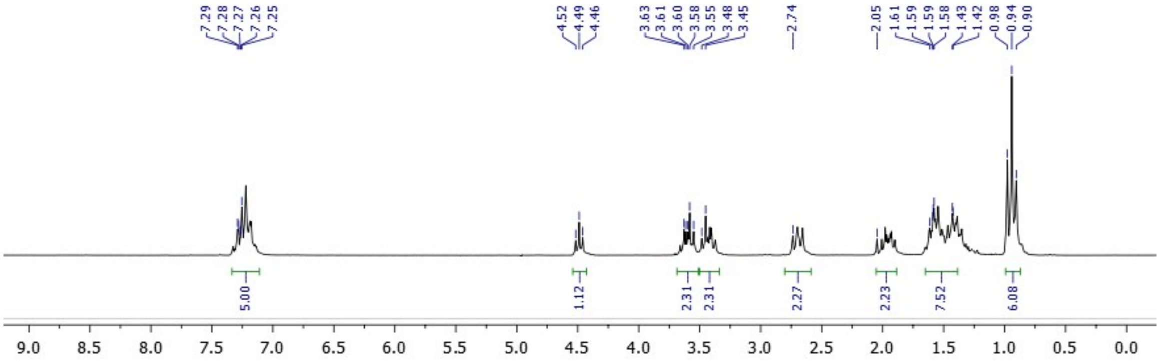
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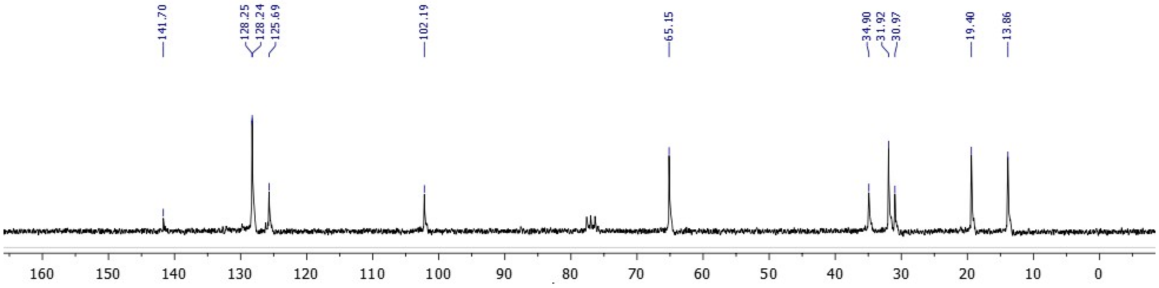
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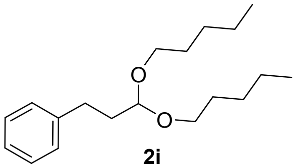

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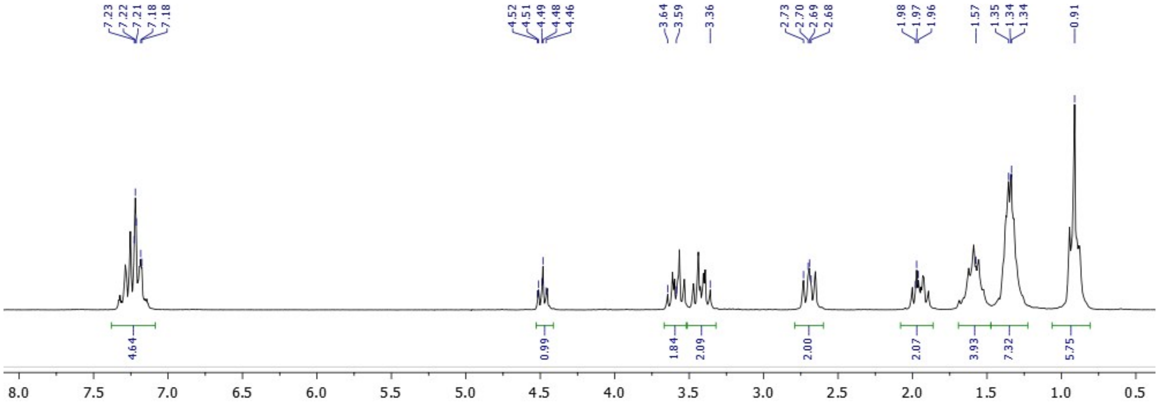
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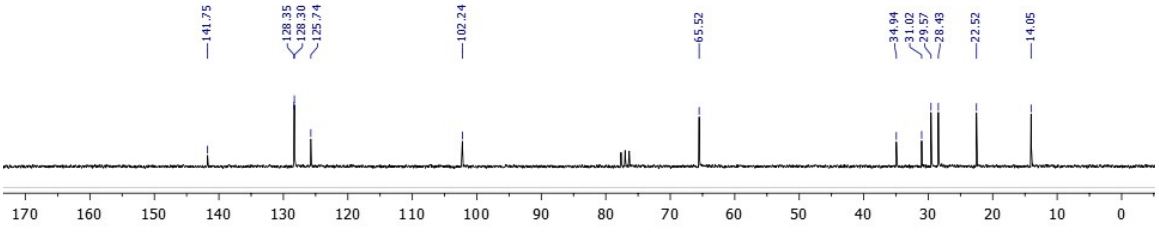
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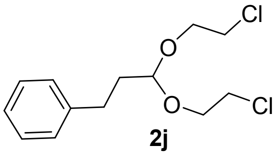
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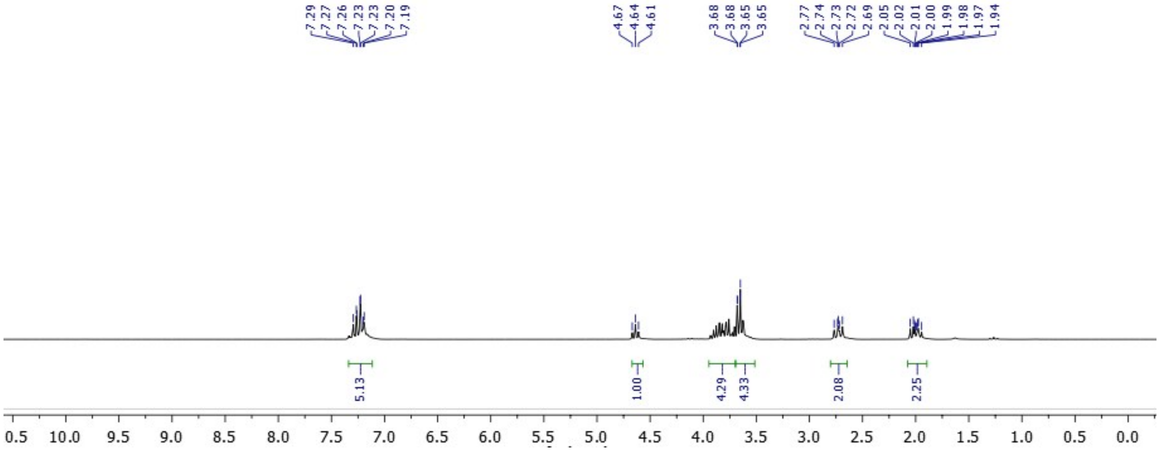
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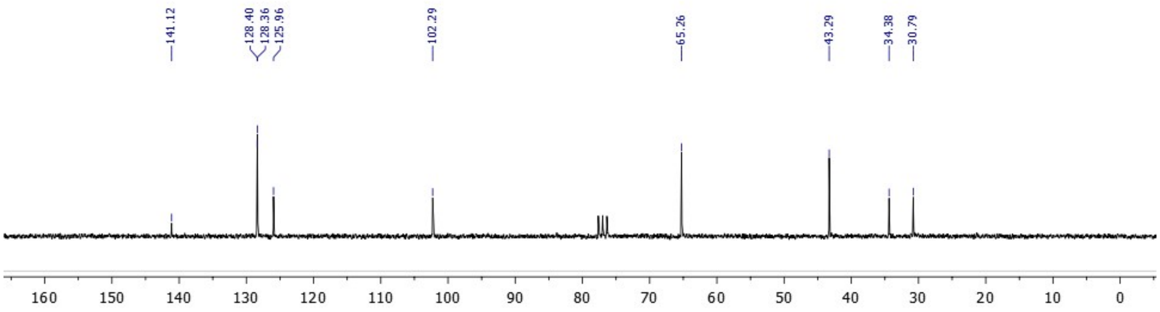
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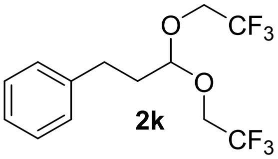
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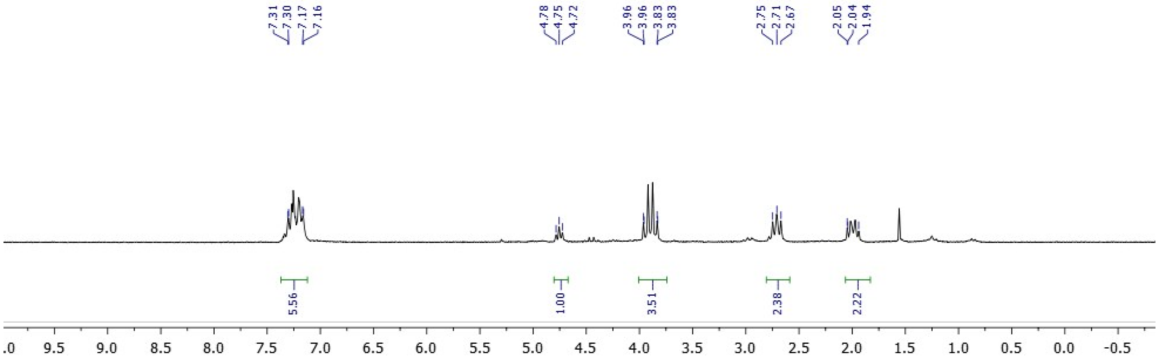
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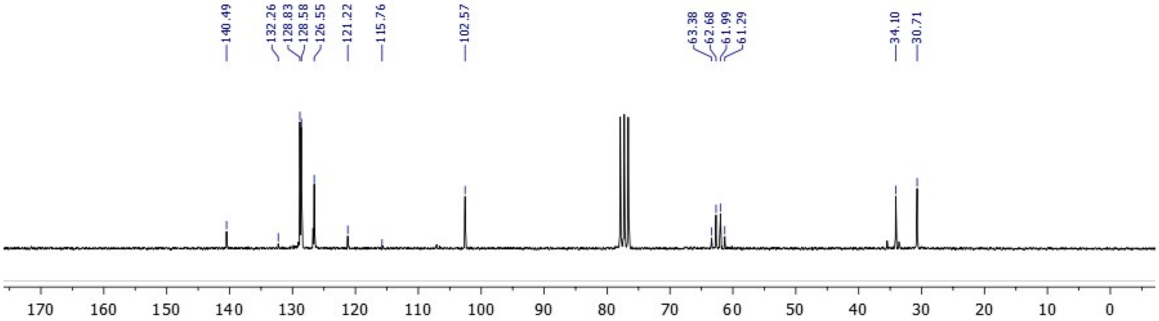
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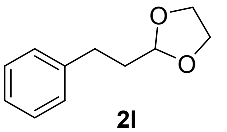

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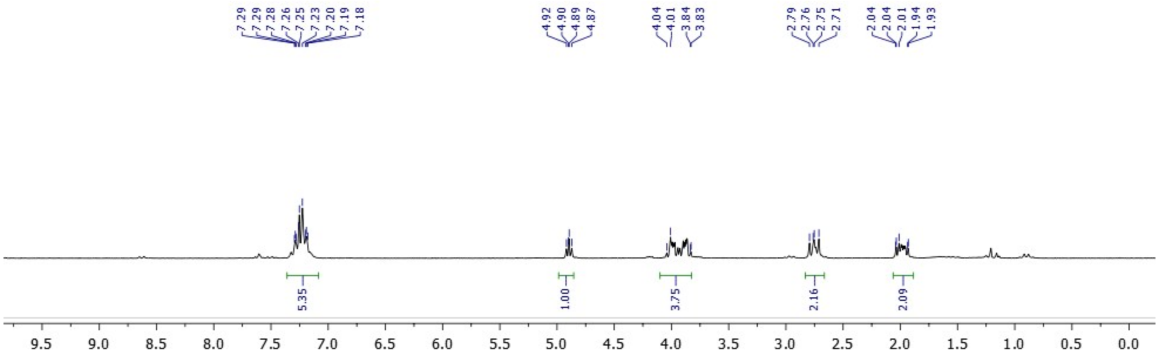
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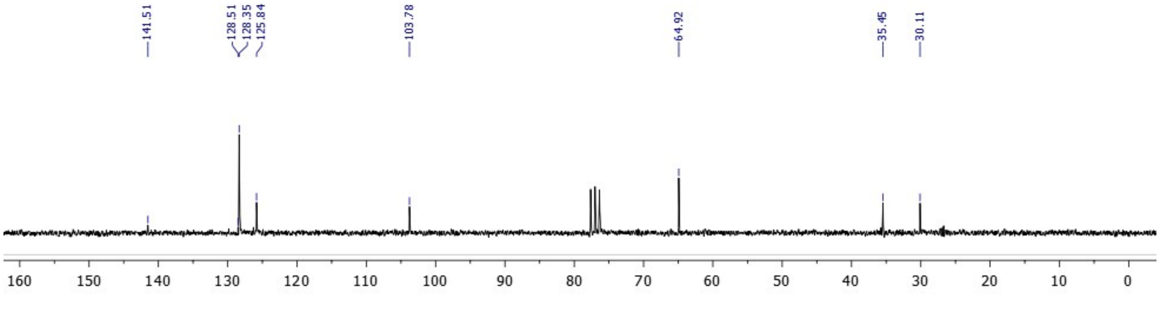
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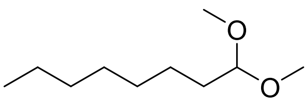
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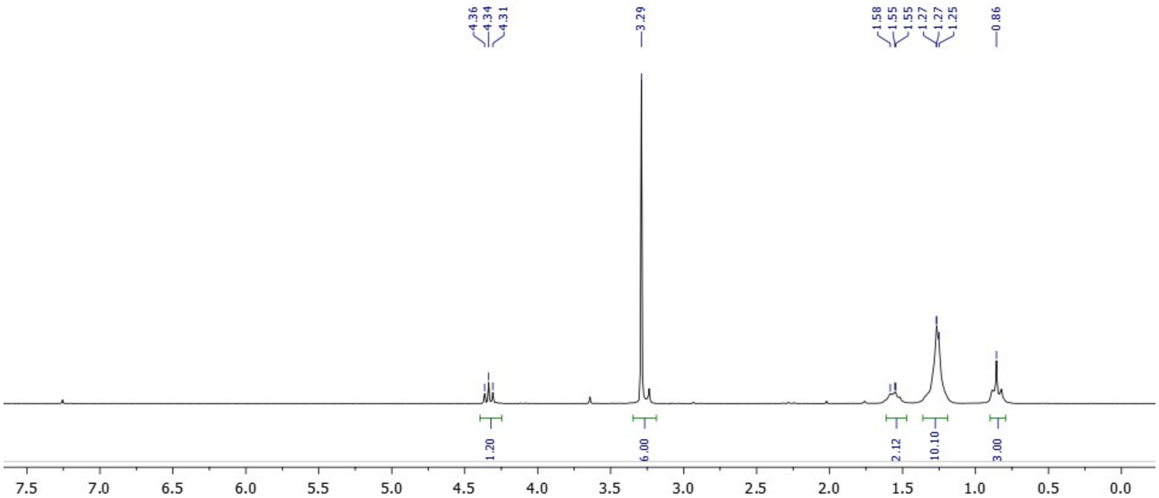
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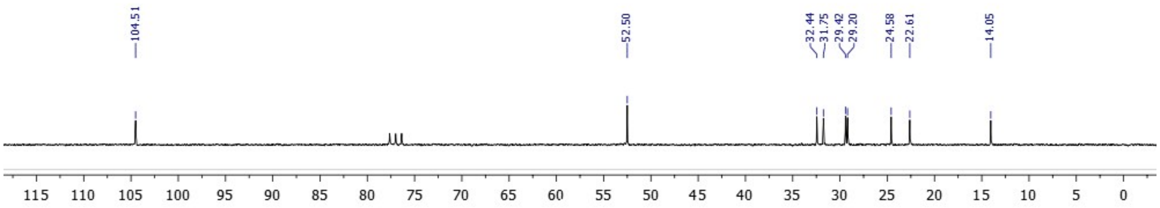
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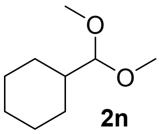

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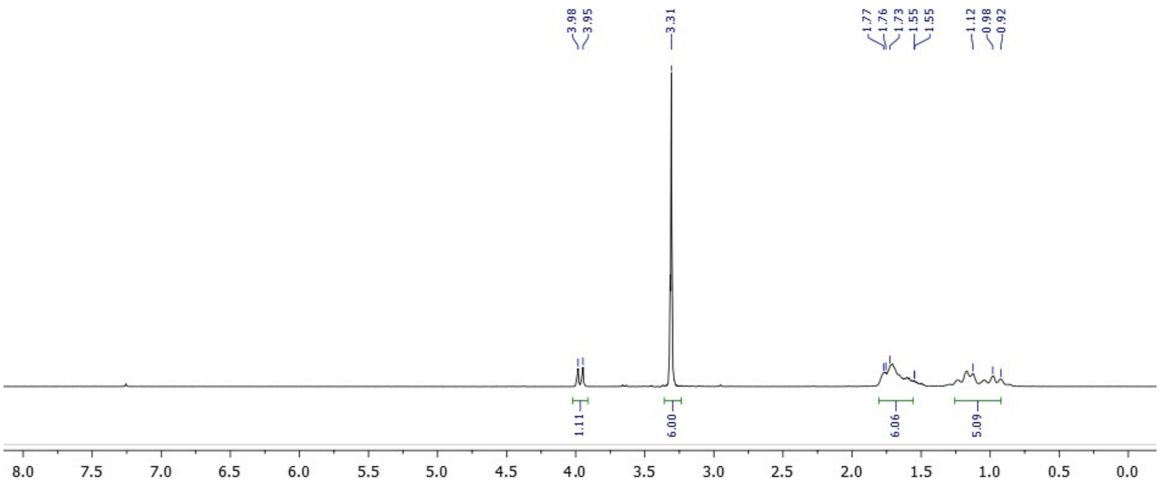
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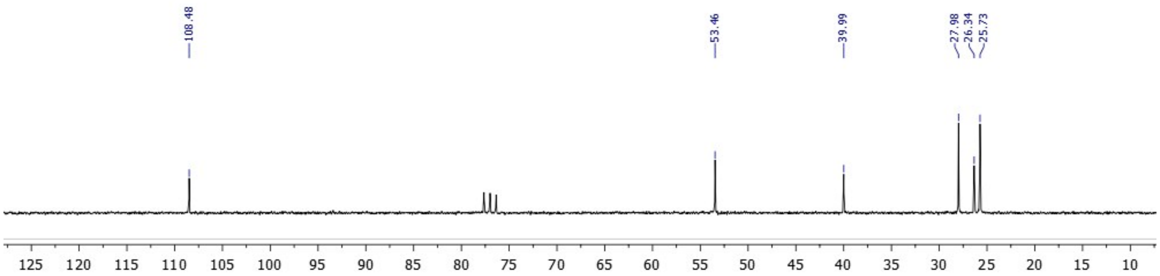
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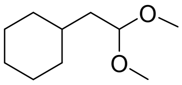

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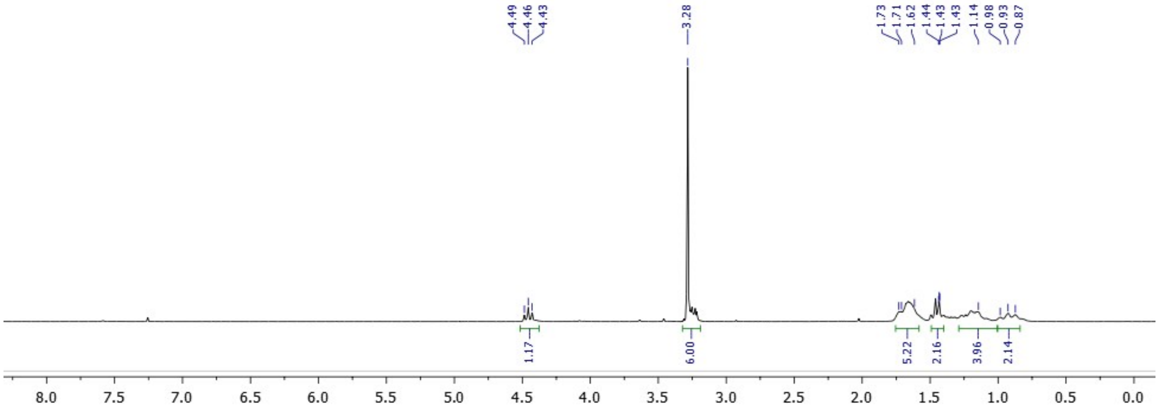
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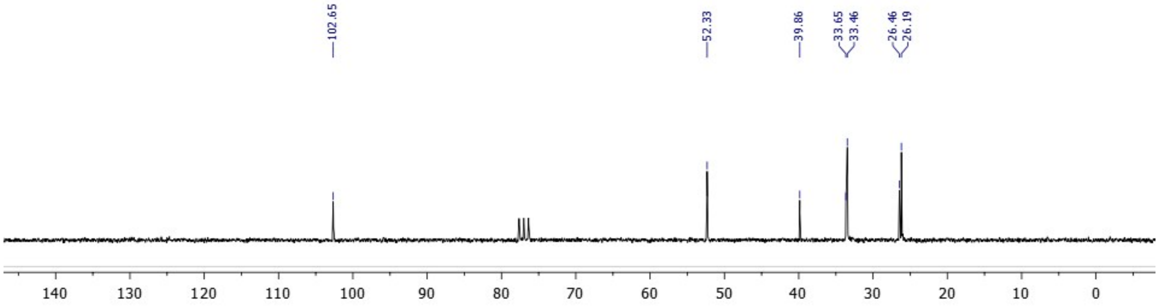
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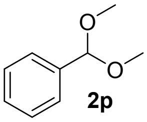
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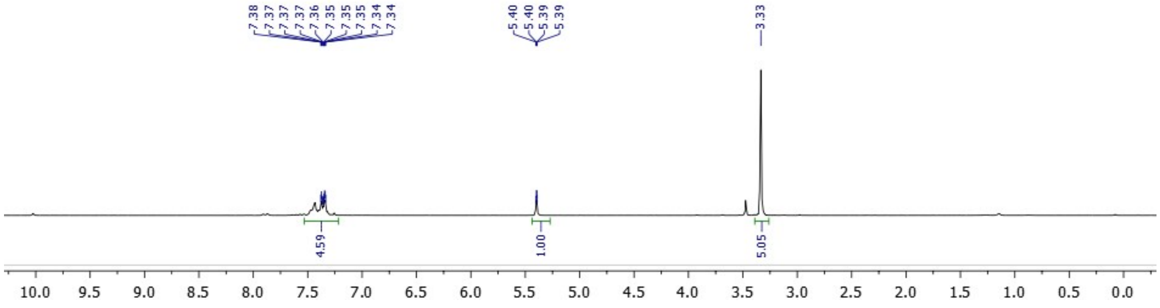
2p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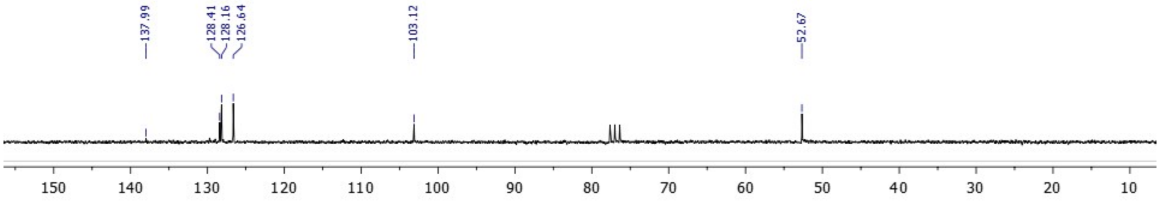
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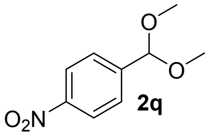
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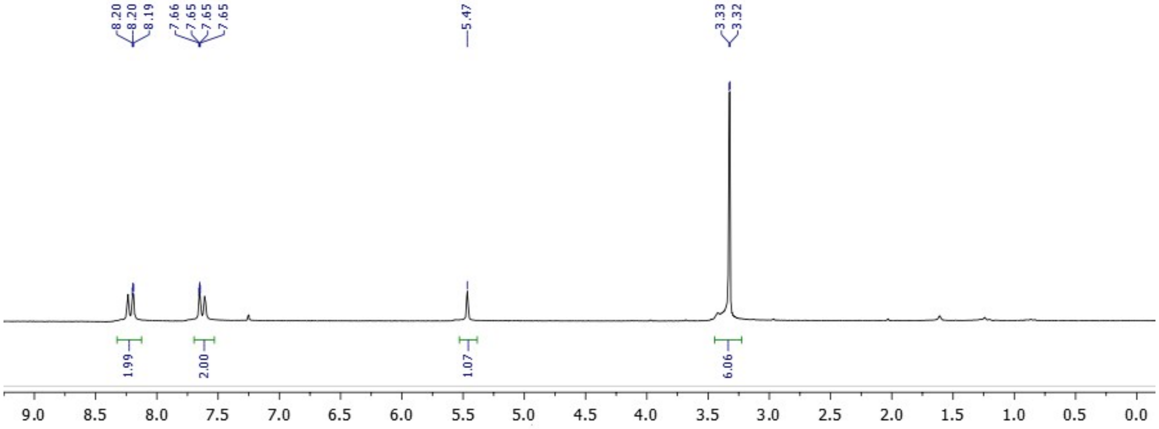
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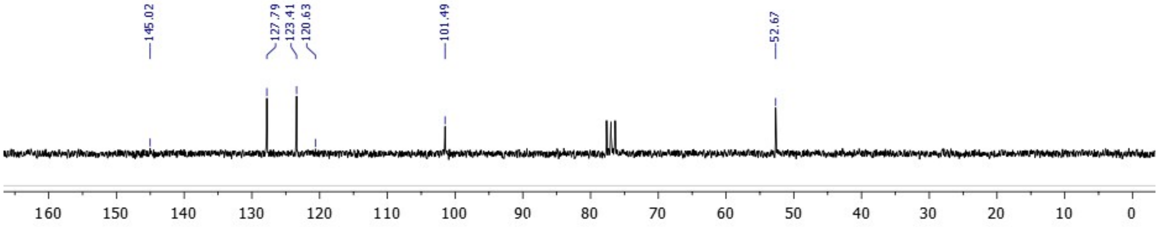
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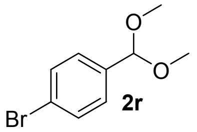
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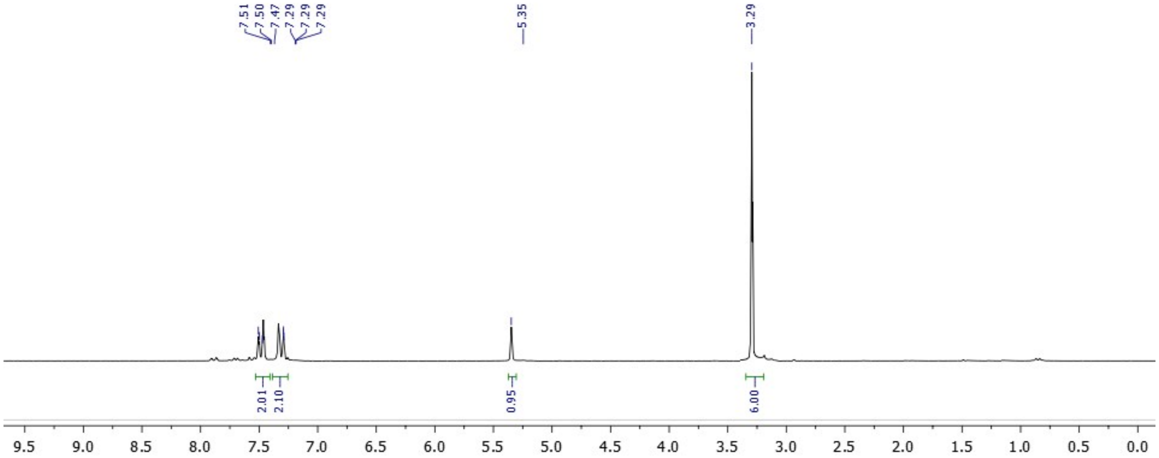
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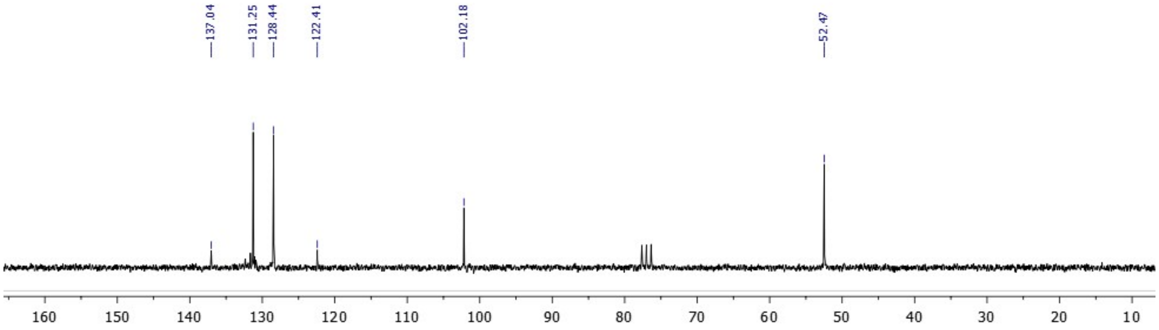
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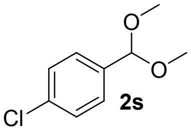
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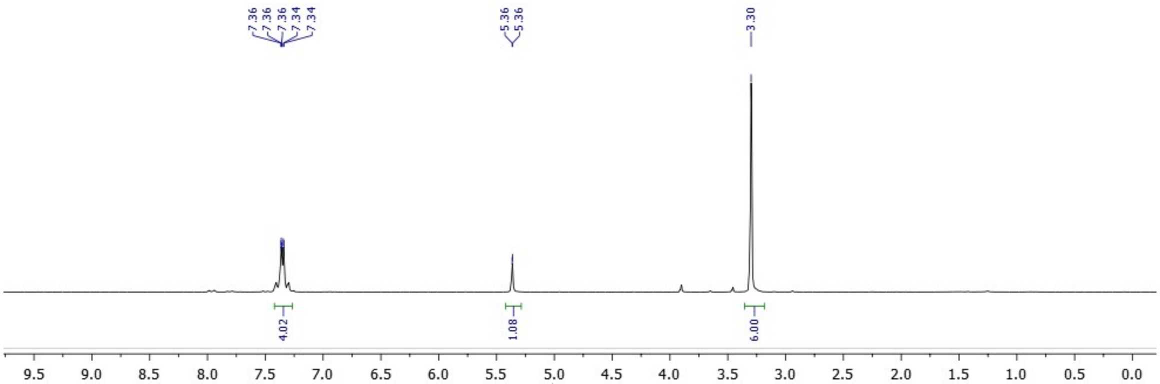
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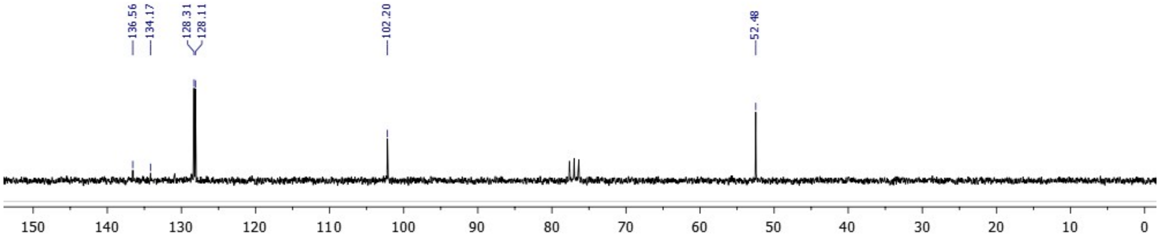
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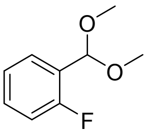

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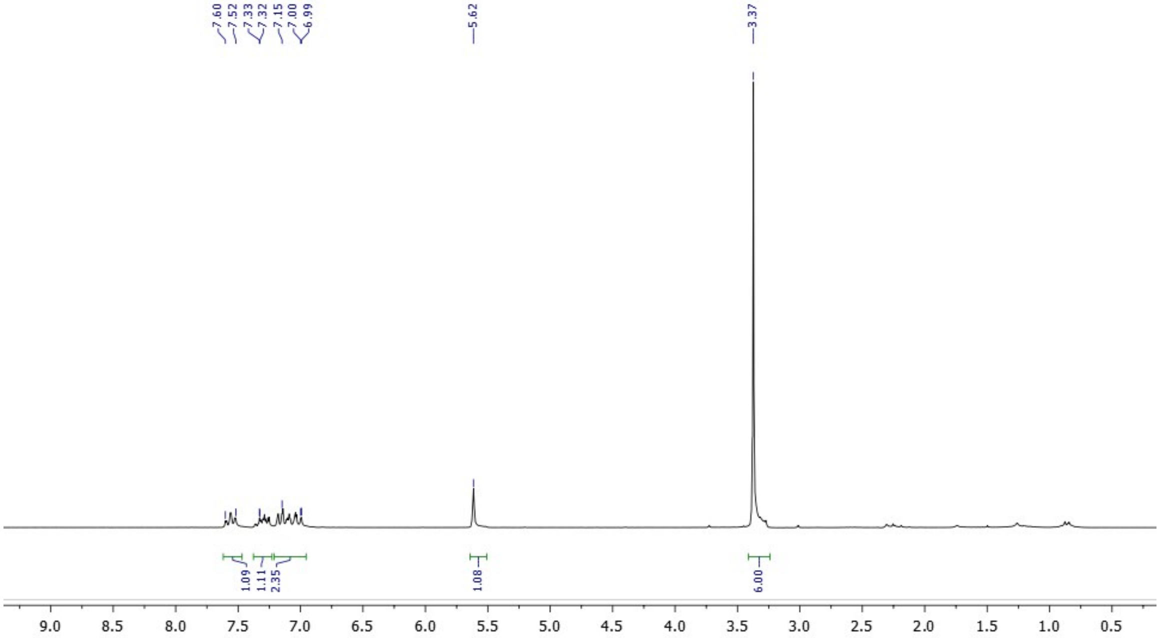
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8.0
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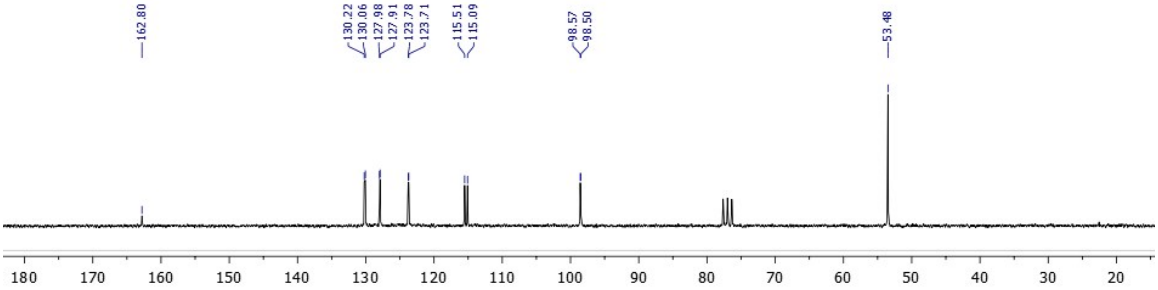
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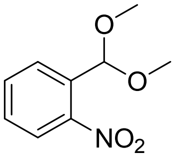
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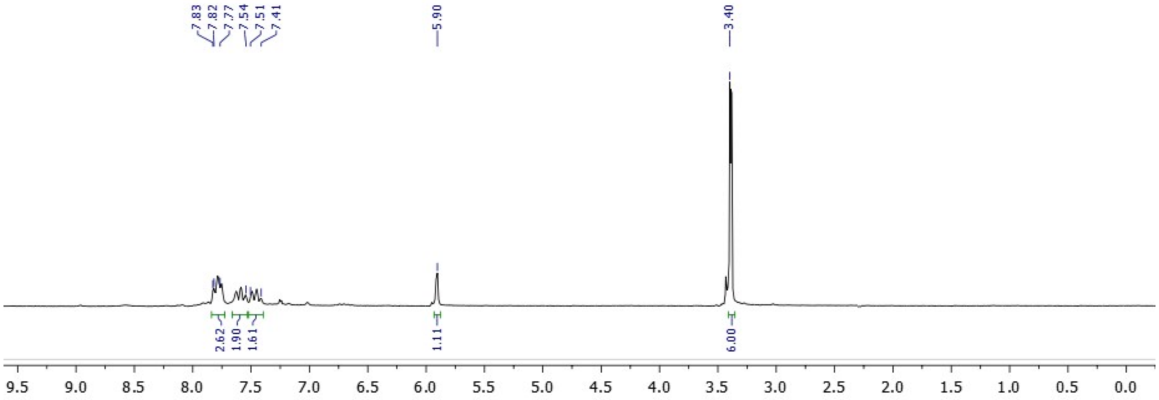
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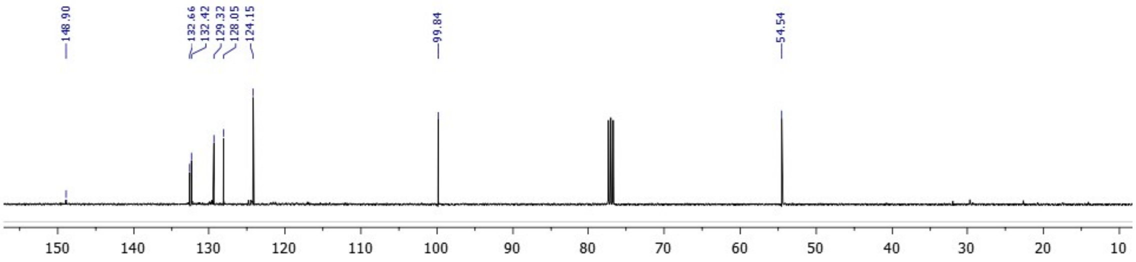
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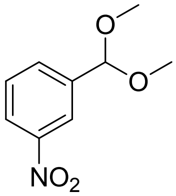
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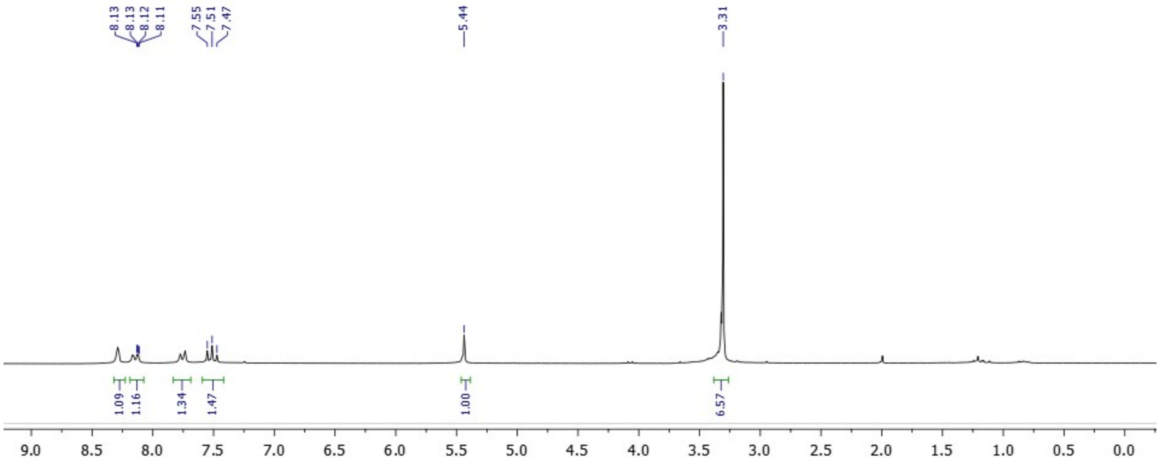
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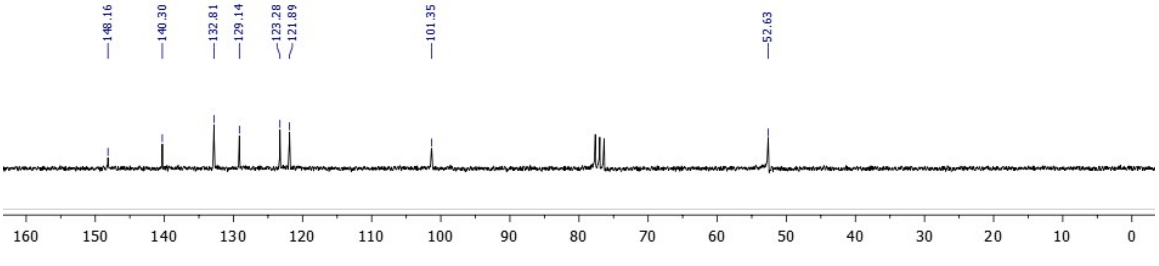
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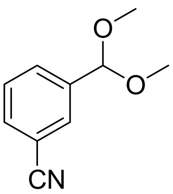
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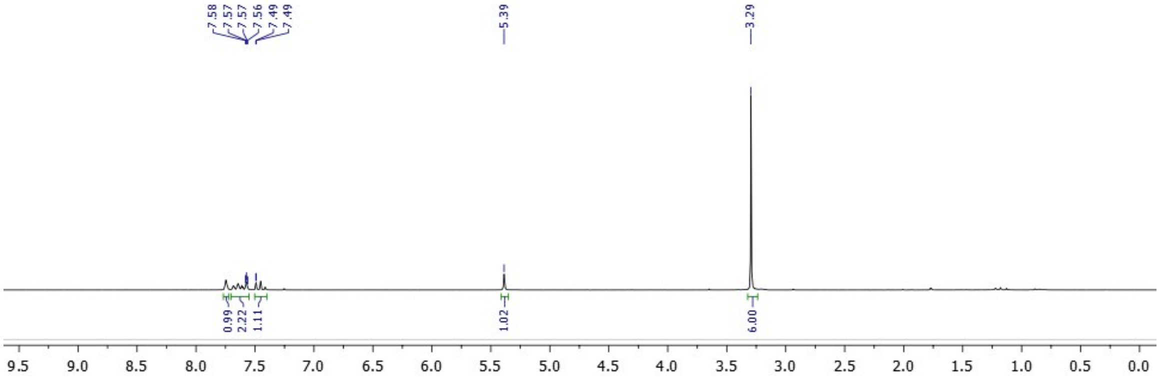
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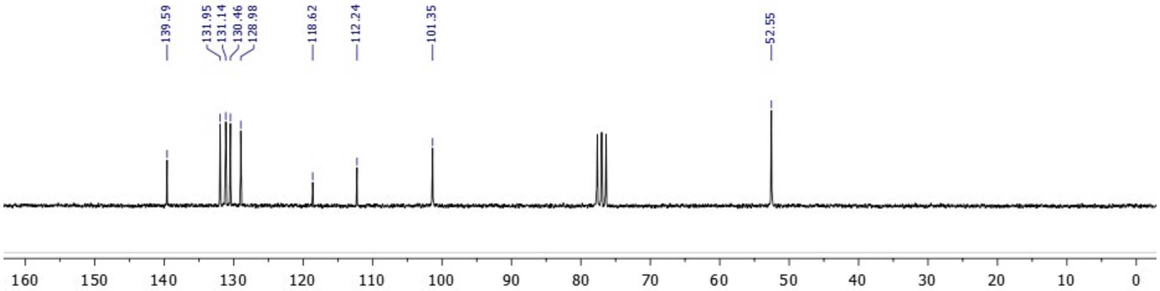
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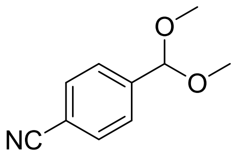
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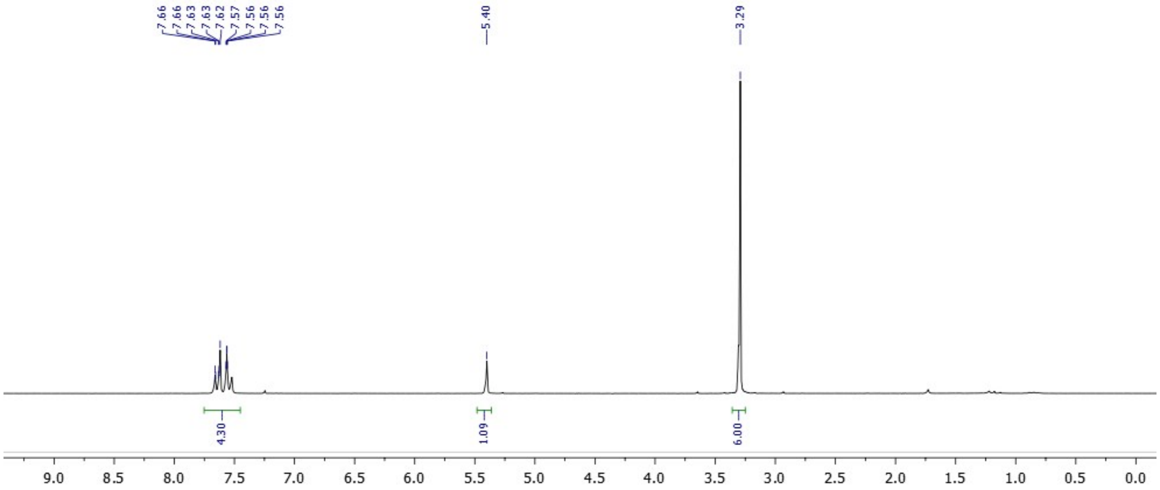
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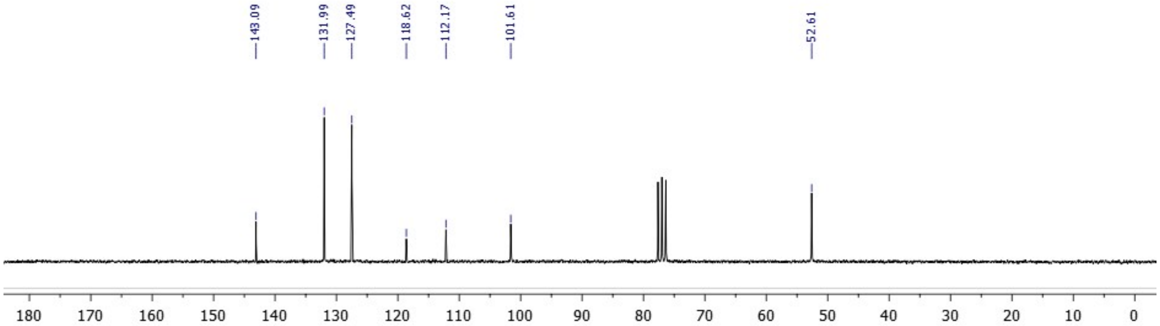
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