Dehydrogenative oxidation of Aryl Methanol using oxygen bridged [Cu-O-Se] bimetallic catalyst .

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1. Table of Content

2. Materials

Solvents such as Toluene (99.8%), 1,4-Dioxane (99.8%), Acetonitrile (99.8%), DMSO (99.9%), DMF (99.8%), THF (99.9%), t-BuOH (99.5%), DCM (99.8%) and Deuteriated NMR solvents $CDCl_3$ (99.8%), CD_3CN (99.8%) and $CuSeO_3$. $2H_2O$ (99%) is purchased from Sigma-Aldrich. All other solvents is purchased from Merck of high purity grade. Toluene and Acetonitrile was sparged with nitrogen (N_2) for 5 min at room temperature and stored under nitrogen atmosphere. KOH (99%), KO^tBu(99%) Cs_2CO_3 (*ReagentPlus®*, 99%) and K_2CO_3 (99%), KOAc (99%), NaOAc (99%), NaH (95%) was purchased from Sigma-Aldrich. All alcohols were purchased from Sigma, Merck, alfa-aesar, HImedia, SRI, Thomas baker, Spectrochem and TCI used directly as received. Some alcohols were synthesized by direct reduction of acetophenones by $NaBH_4$ in ethanol. Organic solutions were concentrated under reduced pressure on a Büchi or Aditya rotary evaporator using a water bath.

3. Instrumentation

NMR spectra were recorded on Bruker Avance III, 400 MHz (IISER Berhampur) spectrometers in appropriate solvents $CDCl_3$ (DMSO-d_6 when required) using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Deuterated solvents were purchased from Sigma-aldrich and used as received. All ^1H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvents. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets…etc, br = broad), coupling constant (Hz) and integration. All ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (77.0 ppm). 1,4-diiodobenzene was used as an internal standard for NMR yields from proton analysis. Elemental analysis is performed in 2400 Series II CHNS/O analyzer in CHNS mode. Flash column chromatography was performed by using a 70-100 times weight excess of flash silica gel 60-200 µm from Aldrich. Fractions were analyzed by TLC using TLC silica gel 60 F_{254} 250 µm precoated-plates from Merck and stains (permanganate, 2,4-dnp and CAM) was used for UV-inactive compounds. Melting point is determined in Digital melting point apparatus, Electronics India (EI)-2935 model; Visualized through LCD Screen and is uncorrected by ±5 ^oC. DFT study is performed using using *Gaussian16* using the M06L density functional and LANL2DZ basis set and effective core potential with the automatically generated density fitting functions. Single point calculations were performed using the M06-2X[5] functional and the 6-311+G(2d,p)[6,7] basis set on nonmetal atoms and SDD basis set. IR spectra is recorded on Bruker FT IR. Powdered XRD recorded on using thin film method. The powder XRD patterns at room temperature were recorded by using Rigaku model TTRX-III equipped with rotating anode-based Cu-Kα radiation (λ= 1.5418 A^o). X-ray diffractometer was operating at 100mA and 50kV. XRD machine was operated with the following conditions: (i) 2θ-θ scanning mode,, (ii) fixed monochromater (iii) continuous scanning, and (iv) measurement angle between 10- 80^o with 0.02^o step.

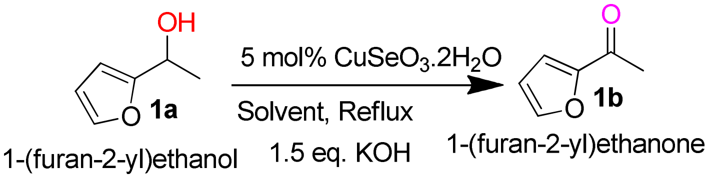
4. General Procedure Alcohol Oxidation

A oven dried 25 mL of two necked round bottom flask (one end with teflon cork and another end connected to reflux condensor) was charged with a stir bar. The flask was then charged with catalyst $CuSeO_3$. $2H_2O$ (5 mol%, 11 mg), toluene (2 ml), alcohols (1 mmol), KOH (84 mg, 1.5 eq.). The reaction mixture was then placed into an oil bath maintained at reflux temperature 80-100 °C.

The reaction is monitored after every 2 h to 30h with the help of TLC and 2,4-DNP stain. After the time specified in the reaction schemes, the reaction mixture was cooled, filtered. The organic layer was separated by with ethylacetate and concentrated in rotor. Then the solid crude was diretly subjected to culoumn for flash column chromatography using 100-200 Silica Gel ethylacetate and hexane as eluent. All yields are reported after column chromatography. The products were identified and cited with reported literature.

5. Standardization table of oxidation of 1-(furan-2-yl)ethanol with $CuSeO_3 . 2H_2O$

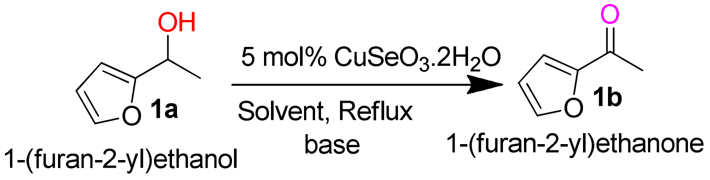
Table 1. Standardization of Solvent



Entry	Catalyst	Base	Solvent	Yield(%)[a] [b]
1	$CuSeO_3 . 2H_2O$	**KOH**	**Toluene**	**91/95***
2	$CuSeO_3 . 2H_2O$	**KOH**	**CH_3CN**	**80**
3	$CuSeO_3 . 2H_2O$	KOH	1,4-dioxane	60
4	$CuSeO_3 . 2H_2O$	KOH	DMF	55
5	$CuSeO_3 . 2H_2O$	KOH	*t*-BuOH	40
6	$CuSeO_3 . 2H_2O$	KOH	THF	0
7	$CuSeO_3 . 2H_2O$	KOH	DMSO	10
8	$CuSeO_3 . 2H_2O$	KOH	i-PrOH	0

[a] 1-(furan-2-yl)ethanol (1 mmol, 112 mg), $CuSeO_3 . 2H_2O$ (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml flask in 2 ml solvent for 28 h [b] Isolated yield

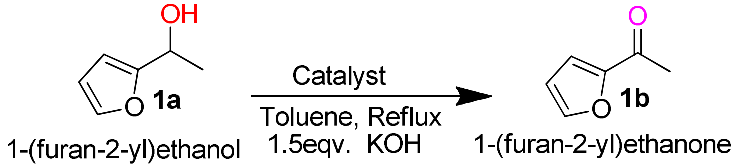
Table 2. Standardization of Base



Entry	Catalyst	Base	equivalent	Solvent	Yield (%)[a,b]
1	$CuSeO_3.2H_2O$	KOAc	1.5	Toluene	40
2	$CuSeO_3.2H_2O$	NaOAc	1.5	Toluene	5
3	$CuSeO_3.2H_2O$	NaH	1.5	Toluene	50
4	$CuSeO_3.2H_2O$	K-O^{t}Bu	1.5	Toluene	70
5	$CuSeO_3.2H_2O$	Cs_2CO_3	1.5	Toluene	30
6	$CuSeO_3.2H_2O$	K_2CO_3	1.5	Toluene	30
7	$CuSeO_3.2H_2O$	Na_2CO_3	1.5	Toluene	20
8	$CuSeO_3.2H_2O$	K_3PO_4	1.5	Toluene	0
9	$CuSeO_3.2H_2O$	Pyridine	1.5	Toluene	45
10	$CuSeO_3.2H_2O$	NEt_3	1.5	Toluene	10
11	$CuSeO_3.2H_2O$	KOH	1.5	Toluene	91
12	$CuSeO_3.2H_2O$	KOH	1	Toluene	80
13	$CuSeO_3.2H_2O$	KOH	0.75	Toluene	65
14	$CuSeO_3.2H_2O$	KOH	0.5	Toluene	45
15	$CuSeO_3.2H_2O$	KOH	0.25	Toluene	25
16	$CuSeO_3.2H_2O$	-	No base	Toluene	0
17	$CuSeO_3.2H_2O$	KOH	2	Toluene	91

[a] 1-(furan-2-yl)ethanol (1 mmol, 112 mg), $CuSeO_3.\ 2H_2O$ (5 mol%, 11 mg), base (0-2 equiv.,) were refluxed in a 25 ml flask in 2 ml solvent for 28 h [b] Isolated yield

Table 3. Standardization of Catalyst

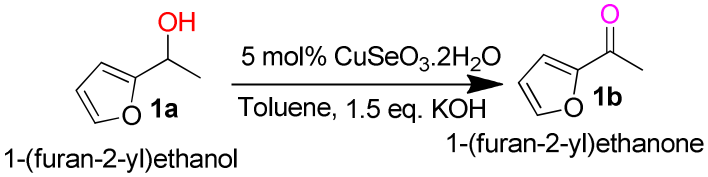


Entry	Catalyst	(mol%)	Base	Solvent	Yield (%)[a,b]
1	No catalyst	0	KOH	Toluene	10[c]
2	$CuSeO_3.2H_2O$	5	-	Toluene	0[d]
3	SeO_2	5	KOH	Toluene	0
4	CuO	5	KOH	Toluene	10
5	$CuCl_2\ 2H_2O$	5	KOH	Toluene	10

7	$CuSeO_3.2H_2O$	5	KOH	Toluene	91
8	$CuSeO_3.2H_2O$	2.5	KOH	Toluene	88
9	$CuSeO_3.2H_2O$	1.0	KOH	Toluene	80
10	$CuSeO_3.2H_2O$	0.5	KOH	Toluene	75
11	$CuSeO_3.2H_2O$	10	KOH	Toluene	91
12	$CuSeO_3.2H_2O$	20	KOH	Toluene	91

[a] 1-(furan-2-yl)ethanol (1 mmol, 112 mg), catalyst (0-20 mol%), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml flask in 2 ml solvent for 28 h [b] Isolated yield

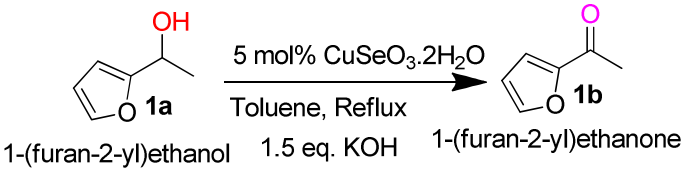
Table 4. Standardization of Temperature



Entry	Catalyst	Temperature (^{o}C)	Base	Solvent	Yield (%)^{a,b}
1	$CuSeO_3.2H_2O$	25	KOH	Toluene	5
2	$CuSeO_3.2H_2O$	33	KOH	Toluene	15
3	$CuSeO_3.2H_2O$	55	KOH	Toluene	45
4	$CuSeO_3.2H_2O$	65	KOH	Toluene	55
5	$CuSeO_3.2H_2O$	80	KOH	Toluene	78
6	$CuSeO_3.2H_2O$	90	KOH	Toluene	84
7	$CuSeO_3.2H_2O$	100	KOH	Toluene	88
8	$CuSeO_3.2H_2O$	Reflux	KOH	Toluene	91

[a] 1-(furan-2-yl) ethanol (1 mmol, 112 mg), $CuSeO_3.$ $2H_2O$ (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml flask in 2 ml solvent for 28 h from 25 ^{o}C to reflux temperature [b] Isolated yield

Table 5. Standardization of molecular oxygen and additives

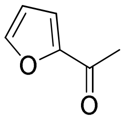


Entry	Gas bubbled	Gas ballon used	Additives (mol%)	Yield (%)[a,b]
1	O_2	O_2	-	91
2	O_2	No	-	91
3	No	O_2	-	91
4	N_2	N_2	-	50

6. Characterization of Products (alcohol 1b-33b) by NMR

1-(2-Acetylfuran) [1,4]

1-(furan-2-yl)ethanol 112 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

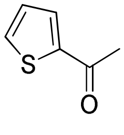


Colorless liquid, 91% yield; 100 mg

^{1}H $CDCl_3$(400 MHz): δ 2.44(s, 3H), 6.51-6.49 (m, 1H), 7.23(d, 1H, *J*= 4 Hz), 7.55(s, 1H), ; ^{13}C $CDCl_3$ (100 MHz): δ 25.9, 112.2, 117.2, 146.4, 152.8, 186.8.

2-Acetylthiofuran [2,4]

1-(thiofuran-2-yl)ethanol 128 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

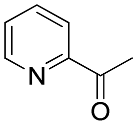


Orange Liquid, 85% yield; 107 mg

^{1}H $CDCl_3$ (400 MHz): δ 2.55(s, 3H); 7.63 (t, 1H, *J*= 4 Hz), 7.63 (d, 1H, *J*= 8 Hz), 7.69 (d, 1H, *J*= 8 Hz), ^{13}C $CDCl_3$ (100 MHz): δ 26.9, 128.1, 132.4, 133.7, 144.5, 190.7.

2-Acetyl pyridine [2,4]

1-(pyridin-2-yl)ethanol 123 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.



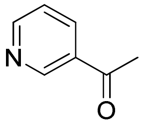
Liquid, 82% yield; 99 mg

^{1}H $CDCl_3$(400 MHz): δ 2.69 (s, 3H), 7.44 (s, 2H, *J*= 8 Hz), 7.80 (s, 1H, *J*= 8 Hz), 8.00 (s, 1H, *J*= 8 Hz), 8.66 (s, 1H, *J*= 8 Hz).

^{13}C $CDCl_3$ (100 MHz): δ 25.7, 121.6, 127.0, 136.8, 148.9, 153.5, 200.1.

3-Acetyl pyridine [3,4]

1-(pyridin-3-yl)ethanol 123 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

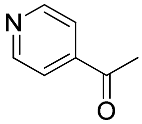


Orange Liquid, 77% yield; 93 mg

^{1}H $CDCl_3$(400 MHz): δ 2.60 (s, 3H), 7.40-7.37(m, 1H), 8.20 (d, 1H, *J*= 8 Hz), 8.74 (d, 1H, *J*= 8 Hz), 9.129(s, 1H); ^{13}C $CDCl_3$ (100 MHz): δ 26.6, 132.2, 135.3, 149.8, 153.4, 196.6.

4-Acetyl pyridine[4]

1-(pyridin-4-yl)ethanol 123 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

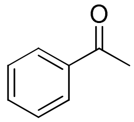


Liquid, 80% yield; 97 mg

^{1}H $CDCl_3$(400 MHz): δ 2.54 (s, 3H), 7.65 (d, 2H, *J*= 8 Hz), 8.72 (d, 2H, *J*= 8 Hz); ^{13}C $CDCl_3$ (100 MHz): δ 26.4, 121.1, 142.5, 150.7, 197.2.

Acetophenone: [3]

(Phenyl)-ethanol 120 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

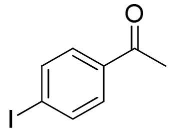


Colorless Liquid, 82% yield; 98 mg

^{1}H CDCl$_3$ (400 MHZ): δ 2.58 (s, 3H), 7.44(t, 2H, *J*= 8 Hz), 7.54(t, 2H, J= 8 Hz), 7.95-7.93 (m, 2H); ^{13}C CDCl$_3$ (100 MHz): δ 26.5, 128.2, 128.6, 133.0, 137.0, 198.1.

1-(4-Iodomophenyl)ethanone [4]

1-(4-iodophenyl)-ethanol 247 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

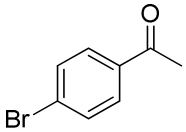


White solid Mp= 80 °C, 70% yield; 171 mg

^{1}H CDCl$_3$(400 MHz): δ 2.57 (s, 3H), 7.66 (d, 2H, *J*= 8 Hz), 7.83(d, 2H, *J*= 8 Hz); ^{13}C CDCl$_3$(100 MHz): δ 26.4, 101.1, 129.7, 136. 3, 137.9, 197.3.

1-(4-Bromophenyl)ethanone[1]

1-(4-bromophenyl)-ethanol 199 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

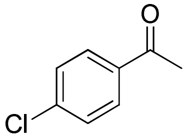


White solid Mp= 50 °C, 75% yield; 148 mg

^{1}H CDCl$_3$(400 MHz): δ 2.57 (s, 3H), 7.60 (d, 2H, *J*= 8 Hz), 7.81(d, 2H, *J*= 8 Hz); ^{13}C CDCl$_3$(100 MHz): δ 26.5, 128.3, 129.8, 131.9, 135.8, 196.9.

1-(4-Chlorophenyl)ethanone [1]

1-(4-chlorophenyl)-ethanol 156 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

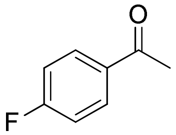


Liquid, 80% yield; 123 mg

^{1}H CDCl$_3$(400 MHz): δ 2.48 (s, 3H), 7.32(d, 2H, J= 8 Hz), 7.79 (d, 2H, J= 8 Hz); ^{13}C CDCl$_3$ (100 MHz): δ 26.2, 128.6, 129.5, 135.2, 139.2, 196.4.

1-(4-Fluorophenyl)ethanone [1]

1-(4-fluorophenyl)-ethanol 140 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

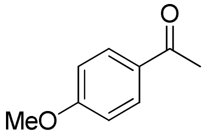


Colorless Liquid, 88% yield; 121 mg

^{1}H CDCl$_3$(400 MHz): δ 2.52 (s, 3H), 7.05(t, 2H, J= 8 Hz), 7.93-7.90 (m, 2H); ^{13}C CDCl$_3$(100 MHz): δ 26.5, 115.6, 115.8, 131.0, 131.1, 133.7, 133.7, 164.5, 167.1, 196.5.

1-(4-Methoxyphenyl)ethanone [1]

1-(4-methoxyphenyl)-ethanol 152 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

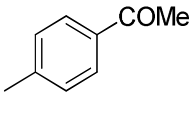


Colorless Liquid, 93% yield; 139 mg

^{1}H CDCl$_3$(400 MHz): δ 2.52 (s, 3H), 3.83 (s, 3H), 6.90 (d, 2H, J= 8 Hz), 7.91 (d, 2H, J= 8 Hz); ^{13}C CDCl$_3$(100 MHz): δ 26.2, 55.3, 113.5, 130.2, 130.5, 163.4, 196.7.

4-Methylacetophenone [1]

1-(4-methylphenyl)-ethanol 136 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

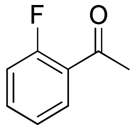


Colorless Liquid, 87% yield; 116 mg

^{1}H $CDCl_3$(400 MHz): δ 2.37(s, 3H), 2.53 (s, 3H), 7.23 (d, 2H, J= 8 Hz), 7.84 (d, 2H, J= 8 Hz); ^{13}C $CDCl_3$(100 MHz): δ 21.3, 26.2, 128.2, 129.0, 134.5, 143.6, 197.5.

2-Fluoro acetophenone[4]

1-(2-fluorophenyl)-ethanol 140 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

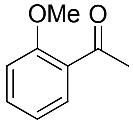


Liquid, 87% yield; 120 mg

^{1}H $CDCl_3$(400 MHz): δ 2.60 (s, 3H), 7.17 (dd, 2H, *J*= 4 Hz, 8 Hz), 7.17 (dt, 2H, *J*=4 Hz, 8 Hz), 7.50-7.44 (m, 1H), 7.83 (dt, 2H, *J*= 4 Hz, 8 Hz), ^{13}C $CDCl_3$ (100 MHz): δ 31.2, 31.3, 116.6, 124.2, 124.2, 125.5, 125.6, 130.4, 130.4, 134.5, 134.6, 160.8, 163.4, 163.4, 195. 7.

1-(2-methoxyphenyl)ethanone [4, 5]

1-(2-methoxyphenyl)-ethanol 152 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

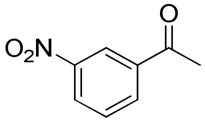


Liquid, 88% yield; 132 mg

^{1}H $CDCl_3$(400 MHz): δ 2.59 (s, 3H), 2.88 (s, 3H), 7.45 (d, 2H, *J*= 8 Hz), 7.71(d, 2H, *J*= 8 Hz); ^{13}C $CDCl_3$(100 MHz): δ 31.7, 55.3, 114.5, 120.4, 128.1, 130.2, 133.5, 158. 8, 199.7.

1-(3-Nitrophenyl)ethanone[4]

1-(3-nitrophenyl)-ethanol 167 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

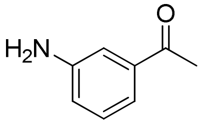


White solid Mp= 75 °C, 88% yield; 145 mg

^{1}H $CDCl_3$(100 MHz): δ 2.67 (s, 3H), 7.68(t, 1H, *J*= 8 Hz), 8.28(d, 1H, *J*= 8 Hz), 8.40(dd, 1H, *J*=5Hz, 8 Hz), 8.74(d 1H, *J*= 8 Hz); ^{13}C $CDCl_3$ (100 MHz): δ 26.6, 123.1, 127.3, 129.9, 133.7, 138.2, 148.4, 195.6.

3-Amino acetophenone[4]

1-(3-aminophenyl)-ethanol 137 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.



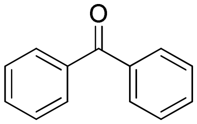
White solid Mp= 95 °C, 82% yield; 111 mg

^{1}H $CDCl_3$(400 MHz): δ 7.36 (d, 1H, J= 8 Hz), 7.29-7.28(m, 2H,), 6.98 (d, 1H, J= 8 Hz), 3.84 (s, 2H), 2.58(s, 3H).

^{13}C $CDCl_3$ (100 MHz): δ 198.4, 146.7, 138.2, 129.4, 119.6, 118.8, 113.9, 26.6

Benzophenone[3]

Benzyhydrol 184 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

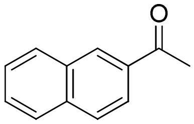


White solid Mp= 49 °C, 93% yield; 169 mg

^{1}H $CDCl_3$(400 MHZ): δ 7.82 (d 4H, *J*= 8 Hz), 7.59(dd, 2H, *J*=4Hz, 8 Hz), 7.49 (t, 4H, *J*= 8 Hz), ^{13}C $CDCl_3$ (100 MHZ): δ 196.7, 135.6, 132.4, 130.1, 128.2.

2-(Naphthalen-2-yl)ethanone [4]

1-(naphthalen-2-yl)ethanol 172 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

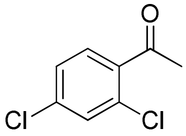


White solid Mp=56 °C, 91% yield; 154 mg

^{1}H $CDCl_3$ (400 MHZ): δ 2.75 (s, 3H), 7.62-7.54(m, 2H), 7.88(t, 2H, *J*= 8 Hz), 7.98(d, 1H, *J*= 8 Hz), 8.05(d, 1H, *J*= 8 Hz), 8.47 (s, 1H), ^{13}C $CDCl_3$ (100 MHZ): δ 25.8, 123.1, 125.9, 126.9, 127.51, 127.6, 128.6, 129.3, 131.6, 133.6, 134.7, 197.2.

1-(2,4-Dichlorophenyl)ethanone [1]

1-(2,4-dichlorophenyl)ethanol 189 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

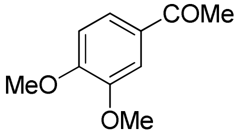


White solid Mp=33 °C, 86% yield; 160 mg

^{1}H $CDCl_3$(400 MHz): δ 2.66 (s, 3H), 7.32-7.29(m, 1H), 7.44(d, 1H, *J*= 8 Hz), 7.54(d, 1H, *J*= 8 Hz); ^{13}C $CDCl_3$ (100 MHz): δ 30.0, 127.3, 130.5, 130.7, 132.5, 137.2, 137.7, 198.9.

3,4-Dimethoxy acetophenone[1]

1-(3,4-dimethoxyphenyl)ethanol 183 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.

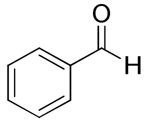


White solid Mp= 48 °C, 90% yield; 162 mg

^{1}H $CDCl_3$ (400 MHZ): δ 2.55 (s, 3H), 3.92 (s, 6H), 6.88(s, 1H), 7.51 (s, 1H), 7.57 (d, 2H, *J*= 8 Hz); ^{13}C $CDCl_3$ (100 MHZ): δ 26.1, 55.9, 109.8, 109.9, 123.2, 130.4, 148.9, 153.2, 196.7.

Benzaldehyde [3]

Benzyalcohol 108 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.



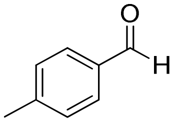
Colorless liquid, 85% yield; 90 mg

^{1}H $CDCl_3$(400 MHz): δ 7.49-7.45 (m, 2H), 7.59-7.56 (m, 1H), 7.84-7.82 (m, 2H), 9.97 (s, 1H).

^{13}C $CDCl_3$(100 MHz): δ 128.8, 129.5, 134.2, 136.2, 192. 7.

4-Methylbenzaldehyde[3]

4-methylbenzylalcohol 122 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.



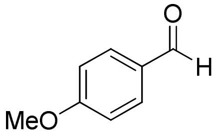
Colorless liquid, 91% yield; 109 mg

^{1}H $CDCl_3$(400 MHz): δ 2.39 (s, 3H), 7.30 (d, 2H, *J*=8 Hz), 7.75 (d, 2H, *J*= 8 Hz), 9.92 (s, 1H).

^{13}C $CDCl_3$(100 MHz): δ 21.7, 129.5, 129.7, 134.1, 145.4, 191.8.

4-Methoxybenzaldehyde [3]

4-methoxybenzylalcohol 138 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.



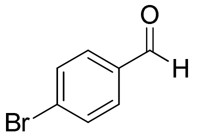
Colorless liquid, 93% yield; 126 mg

^{1}H $CDCl_3$(400 MHz): δ 3.84(s, 3H), 6.95 (d, 2H, *J*= 8 Hz), 7.81 (d, 2H, *J*= 8 Hz), 9.84(s, 1H).

^{13}C $CDCl_3$(100 MHz): δ 55.48, 114.22, 129.85, 131.88, 164.53, 190.74.

4-Bromobenzaldehyde[3]

4-bromobenzylalcohol 187 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.



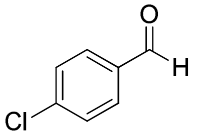
White solid Mp= 55 °C, 80% yield; 148 mg

^{1}H $CDCl_3$(400 MHz): δ 7.69-7.67(m, 1H), 7.75-7.73 (m, 2H), 9.97 (s, 1H).

^{13}C $CDCl_3$(100 MHz): δ 129.76, 130.94, 132.42, 135.06, 191.04.

4-Cholorobenzaldehyde[3]

4-chlorobenzylalcohol 142 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.



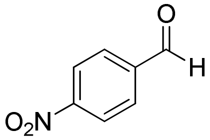
White solid Mp= 47 °C, 83% yield; 116 mg

^{1}H $CDCl_3$(400 MHz): δ 7.53 (d, 2H, J= 8 Hz), 7.84 (d, 2H, J= 8 Hz), 9.99 (s, 1H).

^{13}C $CDCl_3$(100 MHz): δ 128.93, 129.47, 130.92, 130.6,190.9,

4-Nitrobenzaldehyde [3]

4-nitrobenzylalcohol 153 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.



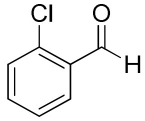
White solid Mp= 103 °C, 85 % yield; 128 mg

^{1}H $CDCl_3$(400 MHz): δ 8.08 (d, 2H, J= 8 Hz), 8.39(d, 2H, J= 8 Hz), 10.15 (s, 1H).

^{13}C $CDCl_3$(100 MHz): δ 124.2, 124.3, 124.3, 130.5, 140.0, 190.3.

2-chlorobenzaldehyde[1]

4-chlorobenzylalcohol 142 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.



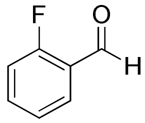
Liquid, 80% yield; 112 mg

^{1}H CDCl$_3$(400 MHz): δ 7.37(t, 1H, *J*= 8 Hz), 7.42(d, 1H, *J*= 8 Hz), 7.51 (t, 1H, *J*= 8 Hz), 7.91 (d, 1H, *J*= 8 Hz), 10.46 (s, 1H).

^{13}C CDCl$_3$(100 MHz): δ 127.3, 129.3, 130.5, 135.1, 189.1.

2-Fluorobenzaldehyde[1]

2-fluorobenzylalcohol 124 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.



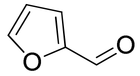
Liquid, 82% yield; 101 mg

^{1}H CDCl$_3$(400 MHz): δ 10.39 (s, 1H), 7.89 (t, 1H, *J*= 8 Hz), 7.62 (q, 1H, *J*= 8 Hz), 7.29 (t, 1H, *J*= 8 Hz), 7.19 (q, 1H, *J*= 8 Hz).

^{13}C CDCl$_3$(100 MHz): δ 187.2, 165.9, 163.4, 136.4, 136.3,132.7, 128.7, 124.6, 116.6, 116.4.

2-Furfuraldehyde [2]

Furan-2-ylmethanol 96 mg (1 mmol), catalyst (5 mol%, 11 mg), KOH(1.5 equiv., 84 mg) were refluxed in a 25 ml round bottom flask in 2 ml solvent as in general procedure.



Colorless liquid, 90% yield; 86 mg

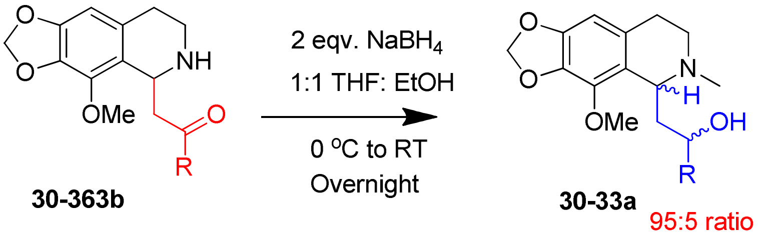
^{1}H CDCl$_3$(400 MHz): δ 6.58 (d, 1H, *J*= 8 Hz), 7.23(d, 1H, *J*= 8 Hz), 7.67(s, 1H), 9.63 (s, 1H).

^{13}C CDCl$_3$(100 MHz): δ 112.5, 120.9, 148.0, 152.9, 177.8.

7.General Procedure for Synthesis tetrahydroisoquinoline based ketone 30-33b

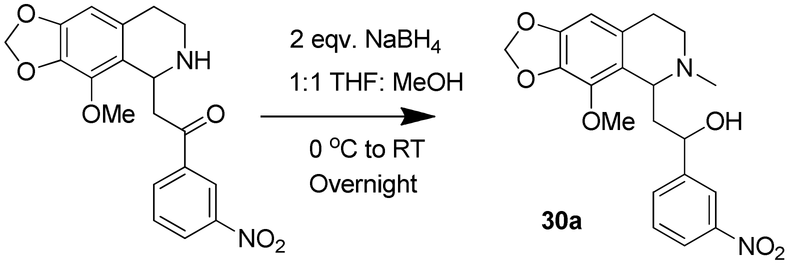
In 10 mL round bottom flask, 1 mmol of cotarnine was dissolved in 1 ml of methanol. The solution is stirred for 2 minute. To this solution, 1 mmol of acyl ketones (2-napthylacetone/ 2,4-dichlorophenylacetone /4-chlorophenyl acetone/3-aminophenyl acetone/ 3-nitrophenyl acetone) were added and stirred for 30-120 minutes (in most of the cases, the spontaneous precipitation of product during 10 minutes of stirring is formed). The product was collected by simple filtration with Whatman filter paper-40, washed with cold methanol (1 mL), and dried under vacuum. Sometime the liquid product was subjected to very short column purification to afford **30-33**. The compounds were synthesized according to the reported procedure by our group.[6]

8. General Procedure for Synthesis of tetrahydroisoquinoline based alcohol 30-33a by $NaBH_4$ Reduction



In 50 mL round bottom flask, 1 mmol of **30-33b** arylacetone was dissolved in 10 ml of tetrahydrofuran. To this 10 ml of ethanol was added followed by 2 equivalent of $NaBH_4$ slowly under ice cold condition. The solution is stirred for overnight. Progress of reaction is monitored by TLC. Finally, the reaction was quenched with 5 ml of methanol. Subsequently, 20 ml of aqueous NH_4Cl was added and organic layered was separated and concentrated. The crude product was purified in short silica column chromatography to afford reduced alcohol in 95:5 diastereomers **30-33a**.[6]

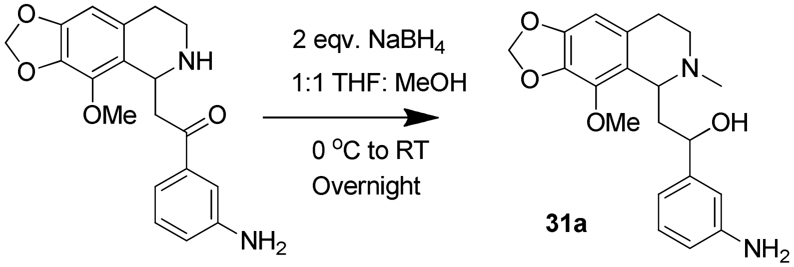
2-(4-methoxy-6-methyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-]isoquinolin-5-yl)-1-(3-nitrophenyl) ethanol 30a; (154 mg, 82%) yellow gummy liquid



^{1}**H NMR** (400 MHz, CDCl$_3$): *δ* 2.09–2.06(m, 1H), 2.32–2.28(m, 1H), 2.31 (s, 3H), 2.55–2.52 (m, 1H), 2.83- 2.72(m, 2H), 3.33–3.27 (m, 1H), 3.53 (dd, *J*=4.0 Hz, 8.0 Hz, 1H), 3.74(s, 3H), 4.01 (s, 1 OH), 4.98 (t, *J* = 4.0 Hz, 1H), 5.78(d, *J* = 4.0 Hz, 2H), 6.23 (s, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz,1H), 8.31(s, 1H).

^{13}**C NMR** (100 MHz, CDCl$_3$): *δ* 22.8, 37.8, 40.8, 44.6, 56.6, 58.7, 71.9, 100.3, 102.3, 119.7, 120.4, 121.3, 127.7, 128.6, 131.7, 133.8, 139.8, 147.7, 147.9, 148.1.

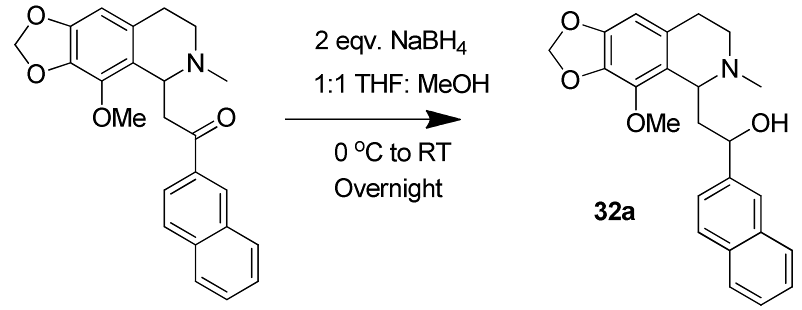
1-(3-aminophenyl)-2-(4-methoxy-6-methyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]isoquinolin-5-yl) ethanol 31a; (142 mg, 80%) Gummy liquid



31a

^{1}H NMR (300 MHz, CDCl$_3$): *δ* 2.11–2.06(m, 1H), 2.31–2.25(m, 1H), 2.39 (s, 3H), 2.60–2.56 (m, 1H), 2.78- 2.74(m, 2H), 3.38–3.30 (m, 1H), 3.80 (dd, *J*=4.0 Hz, 8.0 Hz, 1H), 3.80(s, 3H), 4.03 (s, 1H), 4.88 (t, *J* = 4.0 Hz, 1H), 5.85(d, *J* = 4.0 Hz, 2H), 6. 30 (s, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.85-6.80 (m, 2H), 7.16 (t , *J* = 8.0 Hz, 1H),
^{13}C NMR (100 MHz, CDCl$_3$): *δ* 38.4, 40.9, 44.8, 56.4, 58.8, 72.9, 100.4, 102.4, 120.7, 123.9, 124.4, 125.2, 125.7, 127.2, 127.5, 127.9, 132.4, 133.4, 140.1, 143.1, 147. 7.

2-(4-methoxy-6-methyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-]isoquinolin-5-yl)-1-(naphthalen-2-yl)ethanol; 32a: (162 mg, 83%) . Colorless gummy liquid.

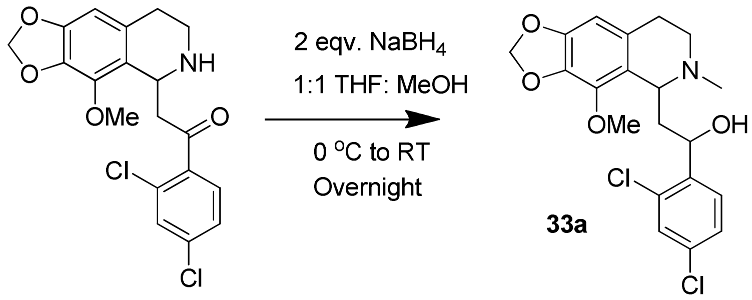


32a

^{1}H NMR (400 MHz, CDCl$_3$): δ 2.25-2.19 (m, 1H), 2.36 (s, 3H), 2.42-2.38 (m, 1H), 2.59–2.56 (m, 1H), 2.80-2.75 (m, 2H), 3.40-3.37 (m, 1H), 3.65-3.62 (dd, J = 4 Hz, 8 Hz, 1H), 3.69 (s, 3H), 3.75(t, J = 8.0 Hz, 1H), 4.05 (s, 1 OH), 5.14 (t, J = 4.0 Hz, 1H), 5.29(s, 3H), 5.83 (d, J = 4 Hz, 2H), 6.28 (s, 1H), 7.52-7.45(m, 3H), 7.87 (d, J =8 Hz, 2H), 7.90 (d, J =8 Hz, 1H), 8.02(s, 1H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 23.1, 38.2, 40.9, 44.8, 56.4, 58.7, 72.9, 100.4, 102.4, 120.7, 123.9, 124.4, 125.2, 125.7, 127.2, 127.5, 127. 9, 132.4, 133.4, 140.1, 143.1, 147.7.

1-(2,4-dichlorophenyl)-2-(4-methoxy-6-methyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-]isoquinolin-5-yl)ethanol; 33a: (174 mg, 85%). Colorless gummy liquid.



33a

^{1}H NMR(400 MHz, CDCl$_3$): δ 2.07-2.02 (m, 1H), 2.22-2.15(m, 1H), 2.33 (s, 3H), 2.50-2.46 (m, 1H), 2.70-2.67 (m, 1H), 2.82-2.78 (m, 1H), 3.30-3.23 (m, 1H), 3.53 (dd, J=4.0 Hz, 8.0 Hz, 1H), 3.69 (s, 3H), 3.95 (s, 1OH), 5.07 (t, J=4.0 Hz, 1H), 5.74 (s, 2H), 6.19 (s, 1H), 7.28-7.24(m, 2H), 7.62 (d, J=8.0 Hz, 2H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 23.1, 35.6, 39.7, 40.9 42.7, 56.8, 58.7, 59.8, 59.7, 70.4, 71.9, 100.5, 102.1, 119.8, 126.7, 127.1, 127.8, 128.1, 128.6, 128.7, 128.7, 131.8, 132.5, 133.7, 139.9, 141.3, 147.8.

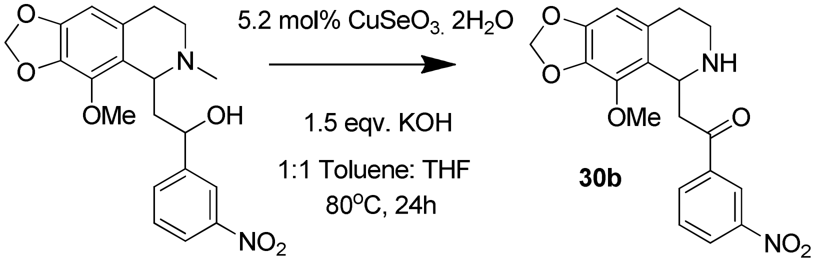
9. General Procedure for oxidation of tetrahydroisoquinoline based alcohol 45-49a

The tetrahydroisoquinoline based alcohol **30-33a** has been subjected to oxidation as same procedure adapted for alcohol oxidation. A oven dried 25 mL of two necked round bottom flask (one end with teflon cork and another end connected to reflux condensor) was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with KOH (84 mg, 1.5 eq.), alcohols (0.25 mmol), 5.2 mol% $CuSeO_3.2H_2O$ (3 mg) in 2 ml of 1:1 THF: toluene. The reaction mixture was then placed into an oil bath maintained at reflux temperature 60-80°C.

The reaction is monitored after every 2 h to 48h with the help of TLC and 2,4-dnp stain. After the time specified in the reaction schemes, the reaction mixture was cooled, filtered and concentrated in rotor. Then the solid crude was diretly subjected to culoumn for flash column chromatography using with 230-400 Silica Gel using ethylacetate and hexane as eluent to afford corresponding product. All yields are reported after column chromatography. The products were identified and cited with reorted literature

2-(4-Methoxy-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-]-isoquinolin-5-yl)-1-(3-nitrophenyl) ethan-1-one (30b):[5]

Alcohol **30a** 96 mg (0.25 mmol), catalyst (5.2 mol%, 2 mg), KOH(1.5 equiv., 21 mg) were refluxed in a 25 ml round bottom flask flask in 2 ml of 1:1 mixture of toluene: THF solvent as in general procedure.

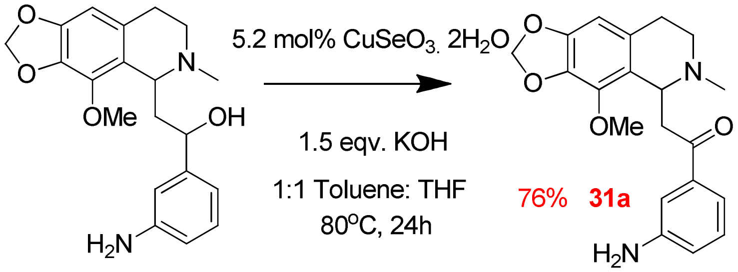


White powder ; Mp: 113 °C; (72 mg, 75%).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 2.44–2.37 (m, 1 H), 2.92–2.74 (m, 2 H), 3.24–3.13 (m, 2 H), 3.38–3.32 (m, 1 H), 4.05 (s, 3 H), 4.38 (dd, J = 6 Hz, 12 Hz, 1 H), 5.87 (s, 2 H), 6.31 (s, 1 H), 7.67 (t, J = 9 Hz, 1 H), 8.35 (d, J = 9 Hz, 1 H), 8.40 (d, J = 9 Hz, 1 H), 8.86 (t, J = 0.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.9, 40.8, 43.1, 54.5, 58.3, 99.5, 101.6, 120. 1, 122.2, 125.9, 126.9, 128.7, 132.7, 132.9, 137.4, 139.1, 146.9, 147.2, 195.9.

1-(3-aminophenyl)-2-(4-methoxy-6-methyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]isoquinolin-5-yl)ethanol (31b):[6] Alcohol **31a** 89 mg (0.25 mmol), catalyst (5.2 mol%, 3 mg), KOH(1.5 equiv., 21 mg) were refluxed in a 25 ml flask in 2 ml of 1:1 mixture of toluene: THF solvent as in general procedure.



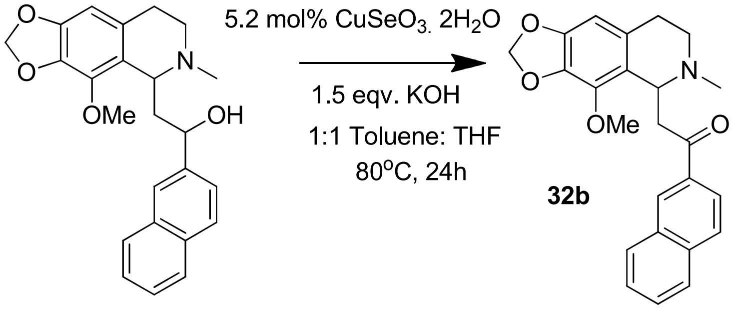
White powder ; Mp: 158 °C, (71 mg, 76%) was obtained as

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 2.51-2.45(m, 1H), 2.73-2.93(m, 2H), 3.12-3.23 (m, 3H), 3.77(s, 2 NH), 3.93(s, 3H), 4.46(m, 1H), 5,85 (s, 2H), 6.30 (s, 1H), 6.86 (s, 1H), 7.22-7.37 (m, 3H),

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.8, 41.9, 43.5, 44.4, 54.9, 59.1, 100.4, 102.5, 114.2, 118.6, 119.2, 122.4, 127.9, 129.2, 133.8, 138.3, 140.1, 146.5, 147.7, 198.9

2-(4-methoxy-6-methyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]isoquinolin-5-yl)-1-(naphthalen-1-yl)ethanol (32b):[5]

Alcohol **32a** 98 mg (0.25 mmol), catalyst (5.2 mol%, 3 mg), KOH(1.5 equiv., 21 mg) were refluxed in a 25 ml round bottom flask in 2 ml of 1:1 mixture of toluene: THF solvent as in general procedure.

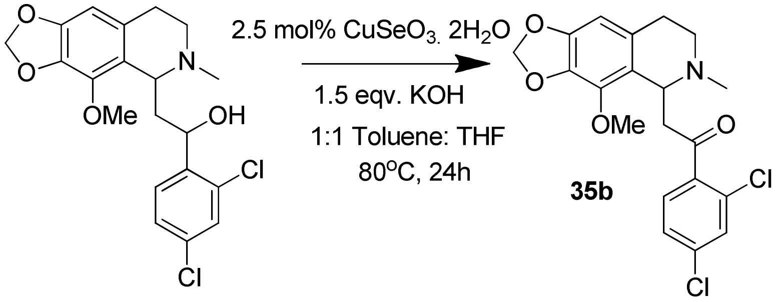


Off-white solid; Mp: 132 °C; (71 mg, 73%)

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 2.48–2.42 (m, 1H), 2.95–2.74 (m, 2H), 3.25–3.15 (m, 1H), 3.36 (d, J = 6.3 Hz, 2H), 3.48(s, 1H), 3.98 (s, 3H), 4.53 (t, J = 6.0 Hz, 1H), 5.86 (d, J = 5.7 Hz, 2H), 6.33 (s, 1H), 7.61–7.51 (m, 2H), 7.95– 7.86 (m, 3H), 8.12 (dd, J = 3 Hz, 9 Hz, 1H), 8.52 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 22.5, 40.8, 42.6, 43.3, 54.2, 58.1, 99.3, 1010.5, 121.1, 123.2, 125.5, 126.6, 126.9, 127.1, 128.4, 128.6, 131.4, 132.7, 133.5, 134.3, 139.1, 146. 7, 197.7.

1-(2,4-dichlorophenyl)-2-(4-methoxy-6-methyl-5,6,7,8-tetrahydro- [1,3]dioxolo[4,5-g]isoquinolin-5-yl)ethan-1-one (33b):[6] Alcohol **33a** 102 mg (0.25 mmol), catalyst (2.5 mol%, 6 mg), KOH(1.5 equiv., 21 mg) were refluxed in a 25 ml flask in 2 ml of 1:1 mixture of toluene: THF solvent as in general procedure.



White crystalline solid. Mp: 96 °C; (76 mg, 75%)

^{1}H NMR(300 MHz, $CDCl_3$): δ 2.25 (s, 3H), 2.38–2.31 (m, 1H), 2.89–2.68(m, 2H), 3.13– 3.05 (m, 2H), 3.38–3.31 (m, 1H), 3.99 (s, 3H), 4.17–4.13 (m, 1H), 5.85 (s, 2H), 6.28(s, 1H), 7.31–7.26 (m, 1H), 7.48–7.42 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9, 40.5, 42.9, 46.5, 58.1, 54.1, 99.4, 101.5, 120.1, 125.9, 128.9, 126.9, 129.5, 130.7, 132.7, 135.4, 136.9, 139.1, 146.8, 200.2.

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C. Florent, L. Johannes, G. Phaomei; E. Bertounesque *Eur J. Org. Chem*, **2017**, *35*, 5275; d) S. K. Sahu, P. K. Behera, S. Panda, P. Choudhury, L. Rout, *Tetrahedron*, **2020**, *76*, 131663

10. Mechanism and DFT Study:

1-phenyl ethanol has been take as standard for optimization of DFT for mechanism study. All compound structures is optimized using *Gaussian16*[1] using the M06L[2] density functional and LANL2DZ[3,4] basis set and effective core potential with the automatically generated density fitting functions. Transition state and minima were confirmed by calculations of vibrational frequency. Single point calculations were performed using the M06-2X[5] functional and the 6-311+G(2d,p)[6,7] basis set on nonmetal atoms and SDD basis set and effective core potential[8,9] for copper and selenium. The SMD implicit solvent model[10] with toluene was used in these single point calculations to account for solvent effect. The thermodynamic correction from the optimization calculations were used with the energies from the single point calculations for calculations of relative Gibbs energies. To calculate the relative Gibbs energies, the thermodynamic correction from the optimization calculations were used with the energies from the single point calculations. Cartesian coordinates for all structures and gas phase Gibbs energy and Gibbs energy including solvation correction are listed below. [To obtain the Gibbs free energy with relevant standard state reference, $G^o(298K, 1M) = G^{o*}(298K, 1atm) + RT \ln(0.08206T)$, where R is the gas constant and T is the temperature. $\Delta G0(298K, 1M) = \Delta G0^*(298K, 1atm)$ when there is no mole change from the reactant to the product.

1. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

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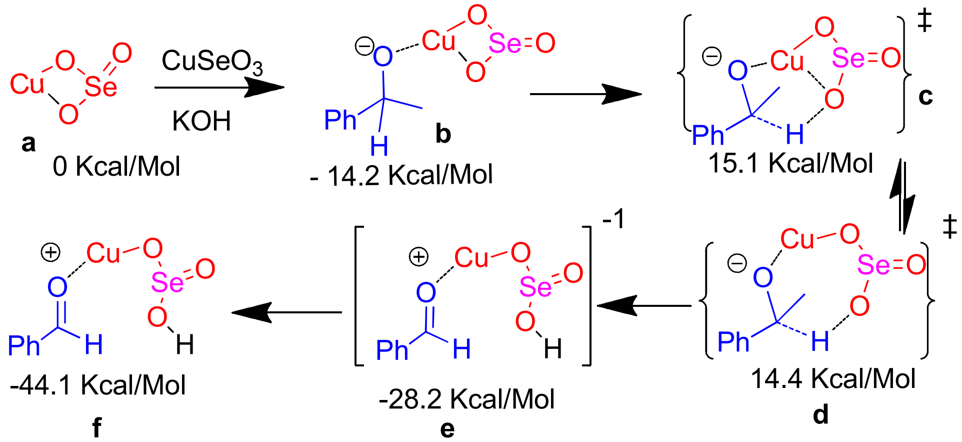
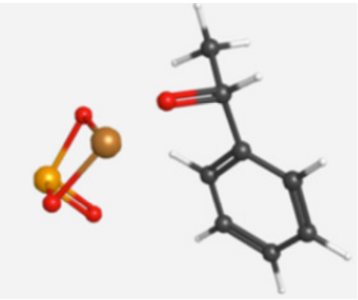
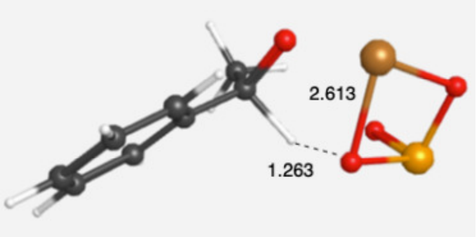
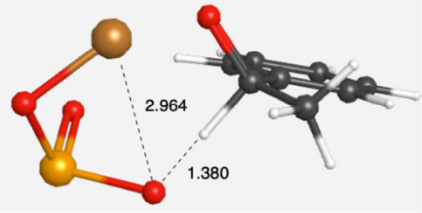
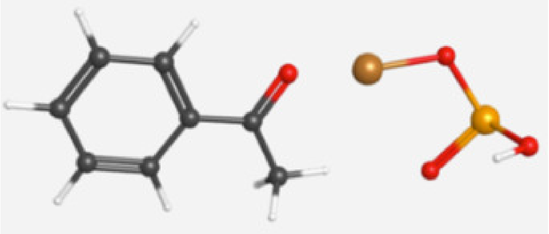
Mechanism:

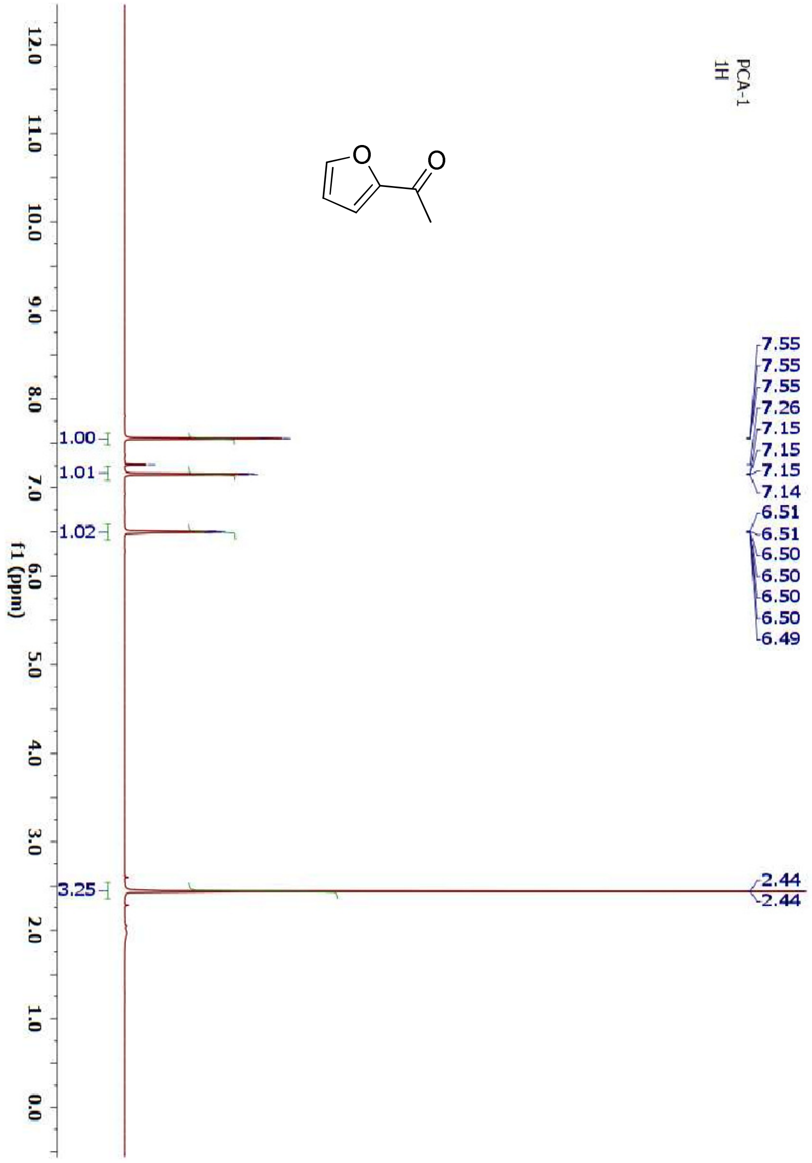
$CuSeO_3$ with 1-phenylethanol shown in the figure below. There is simultaneous hydrogen transfer and Cu-O bond breaking and the transition state has a barrier height of 29.3 kcal/mol. Interestingly, we also found another transition state **[d]** where the Cu-O bond has already been broken. Unfortunately, we have not been able to find the preceding intermediate. It has a slightly lower energy than the other intermediate **[c]**.

Mechanism and DFT study:



Rel. G (kcal/mol) using M06L/6-31G(d)/auto geometry optimizations followed by M06-2x/6-311+G(2d,p)/SDD single point incuding SMD/toluene. Orange =Se, Orange Yellow=Cu, Red= O, Black =C and White =H.

 CuSeO$_3$ coordinated to Oxygen	 TS state for 1-phenyl ethanol with Cu-O bond breaking and H-transfer	
 TS of 1-Phenyl ethanol with Cu-O bond broken	 CuSeO$_2$(OH) coordinated toketone	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6.50
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6.49
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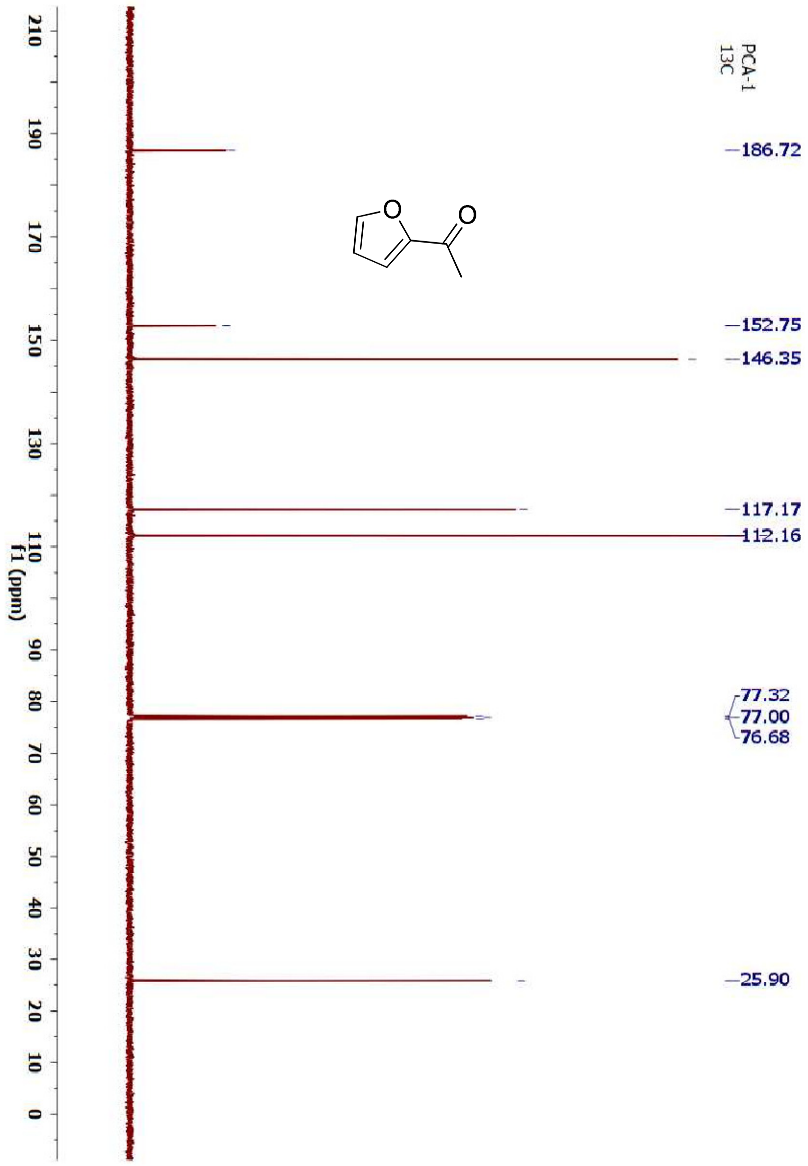
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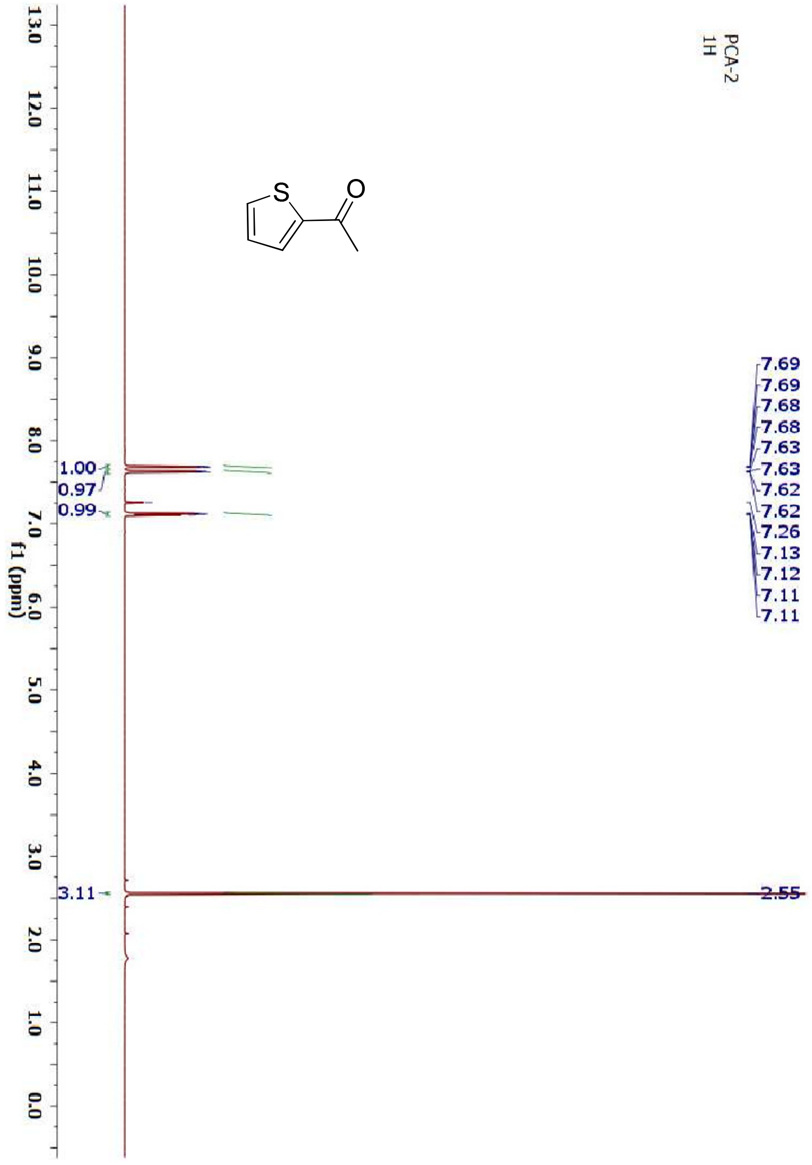
f1 (ppm)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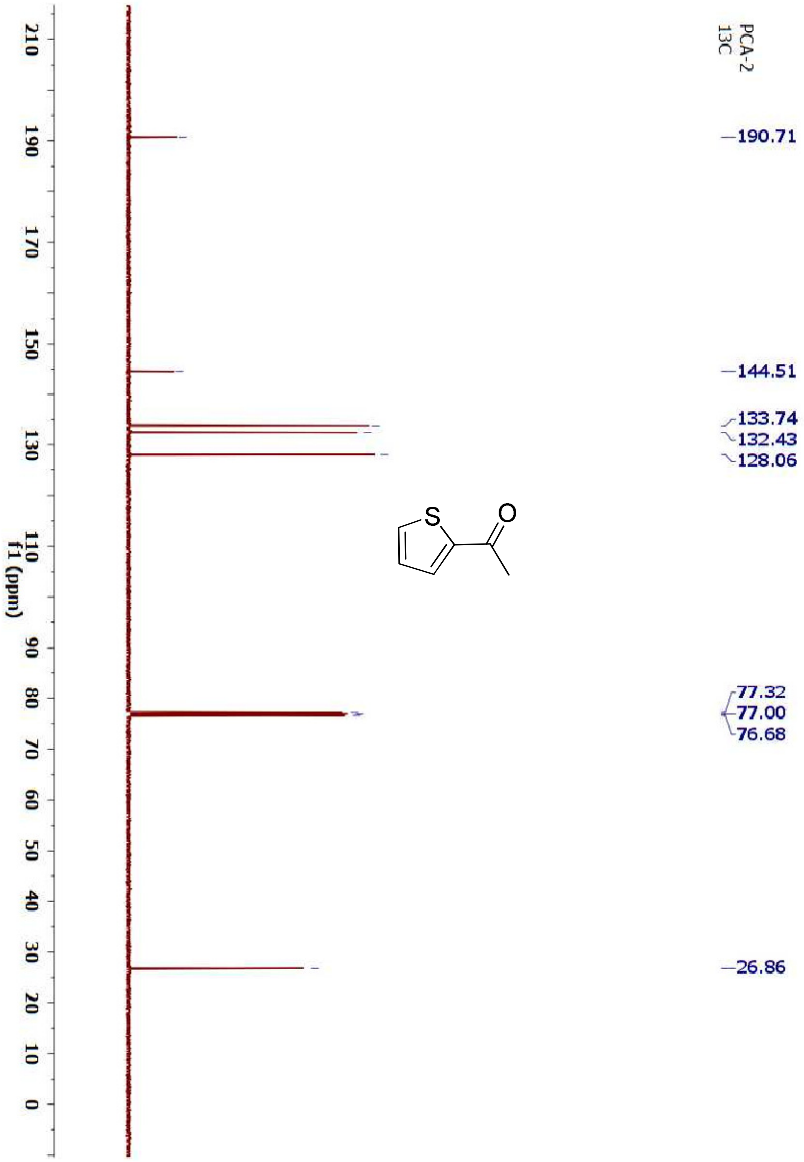
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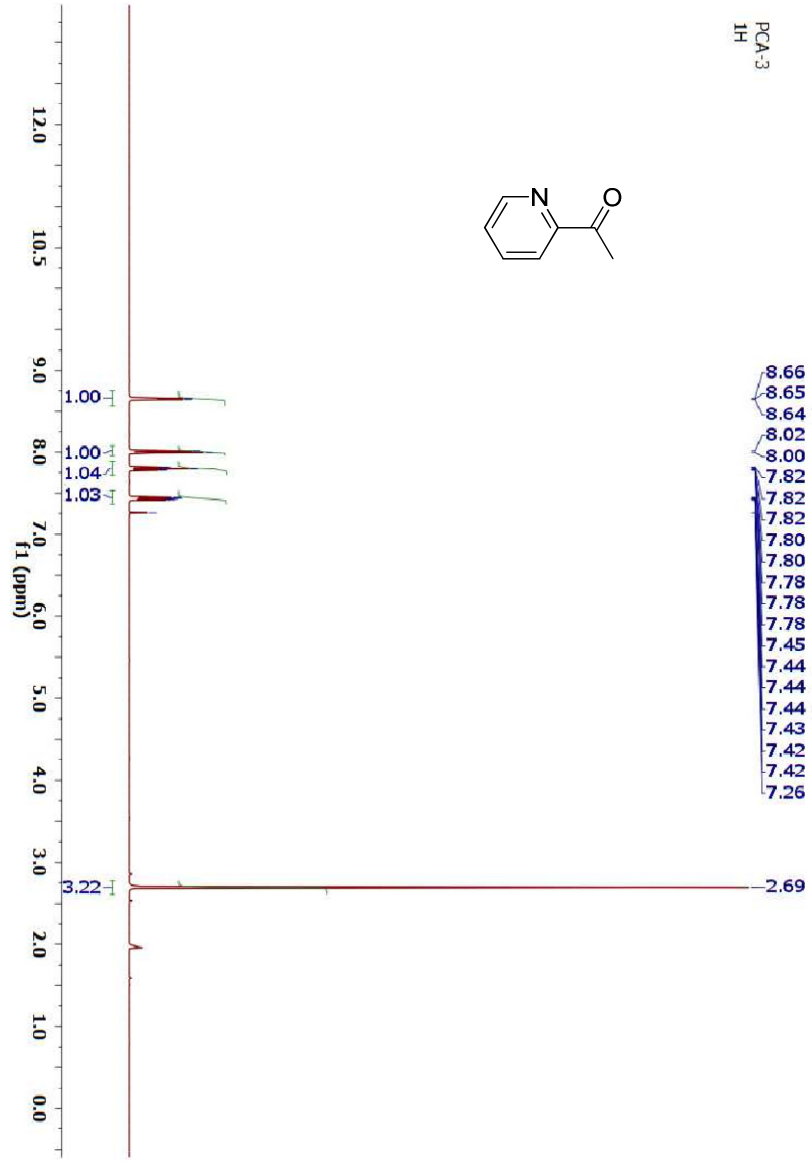
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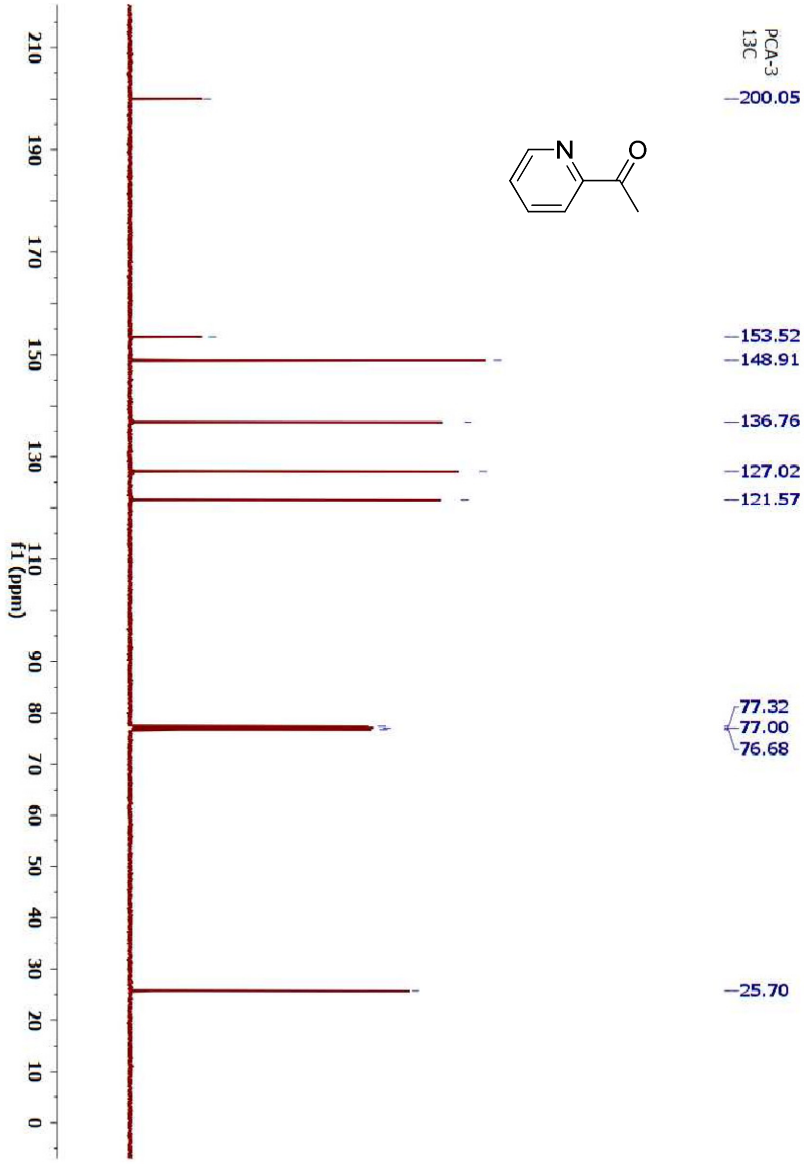
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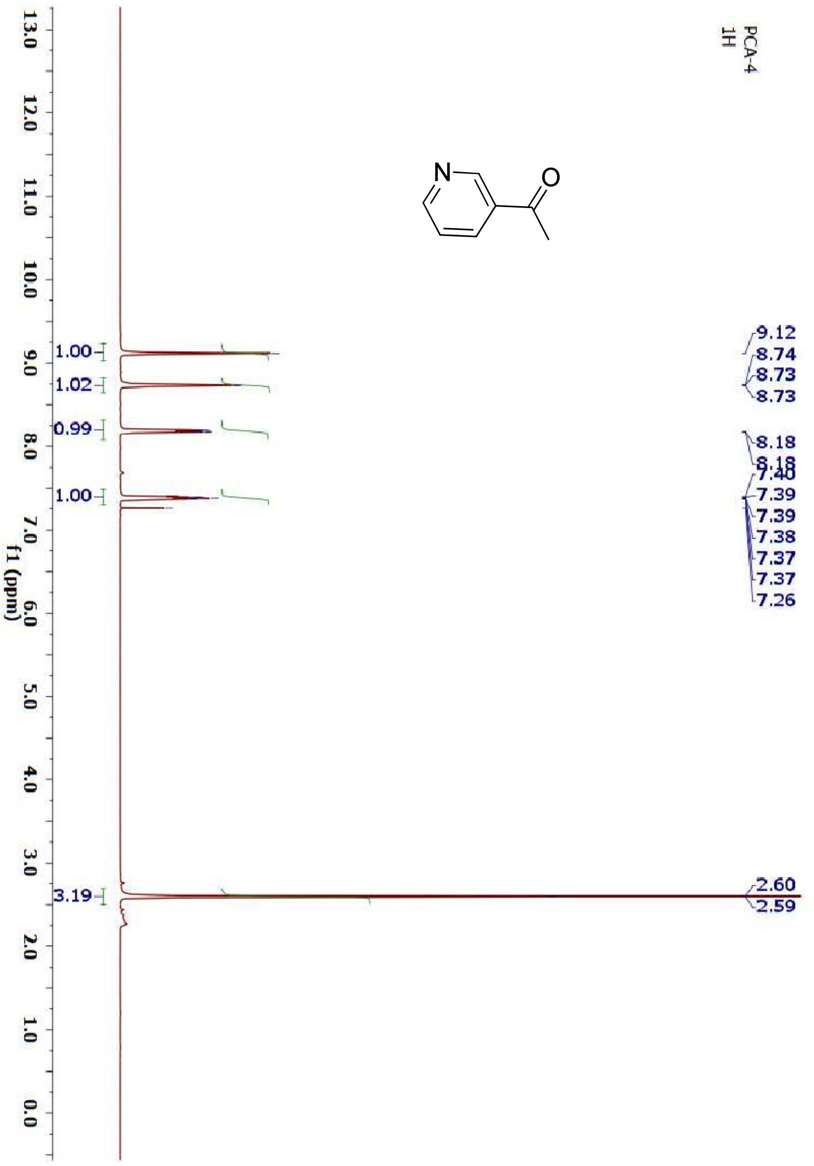
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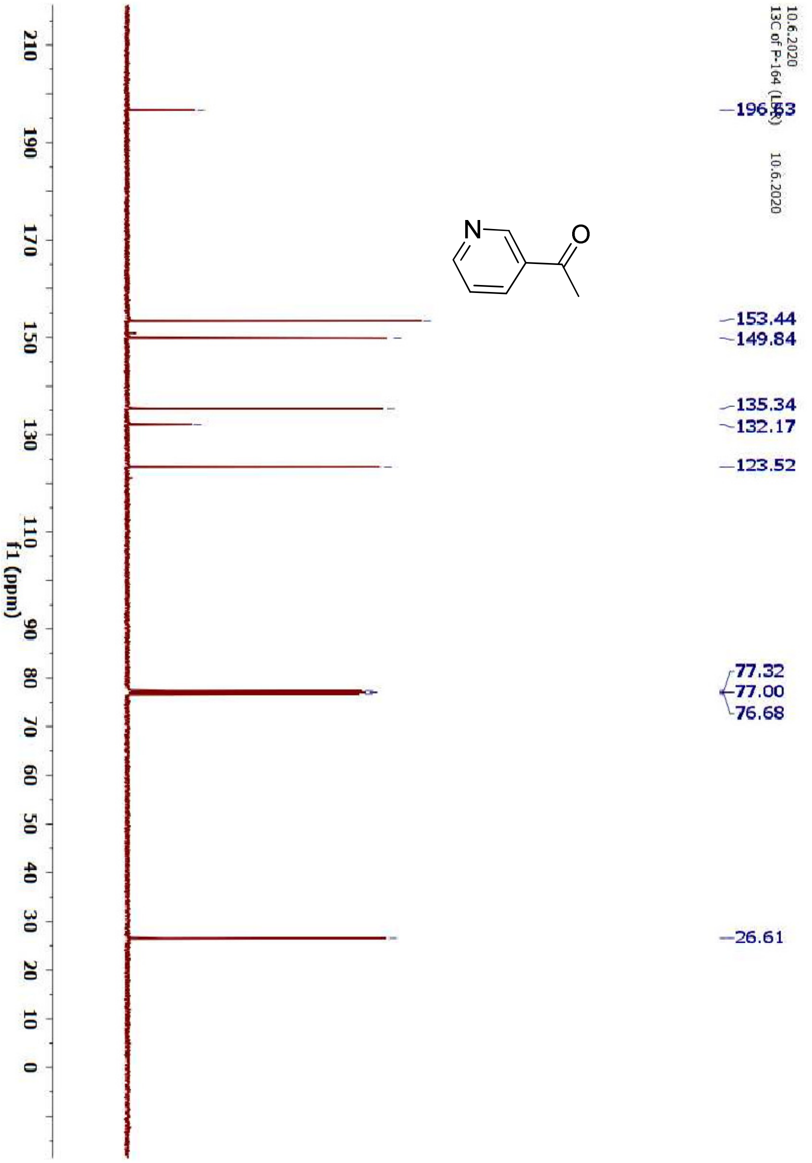
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10.6.2020
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130
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f1 (ppm)
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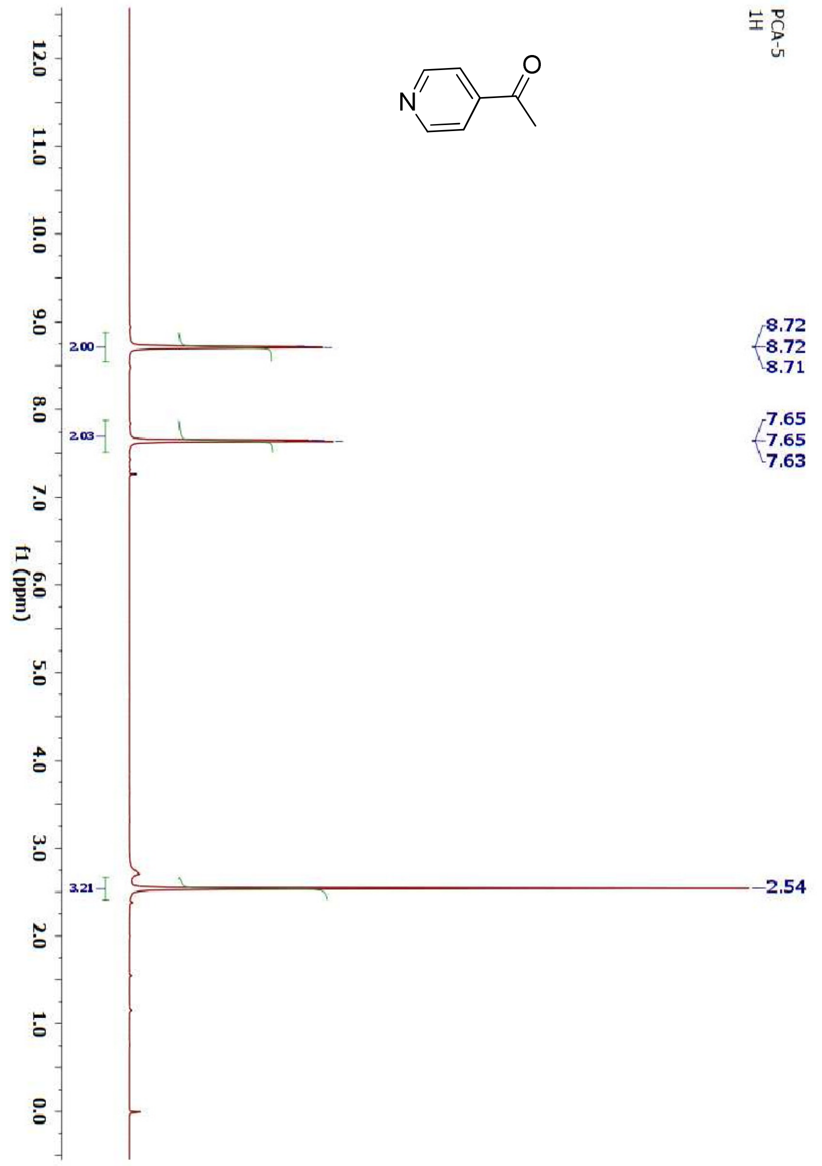
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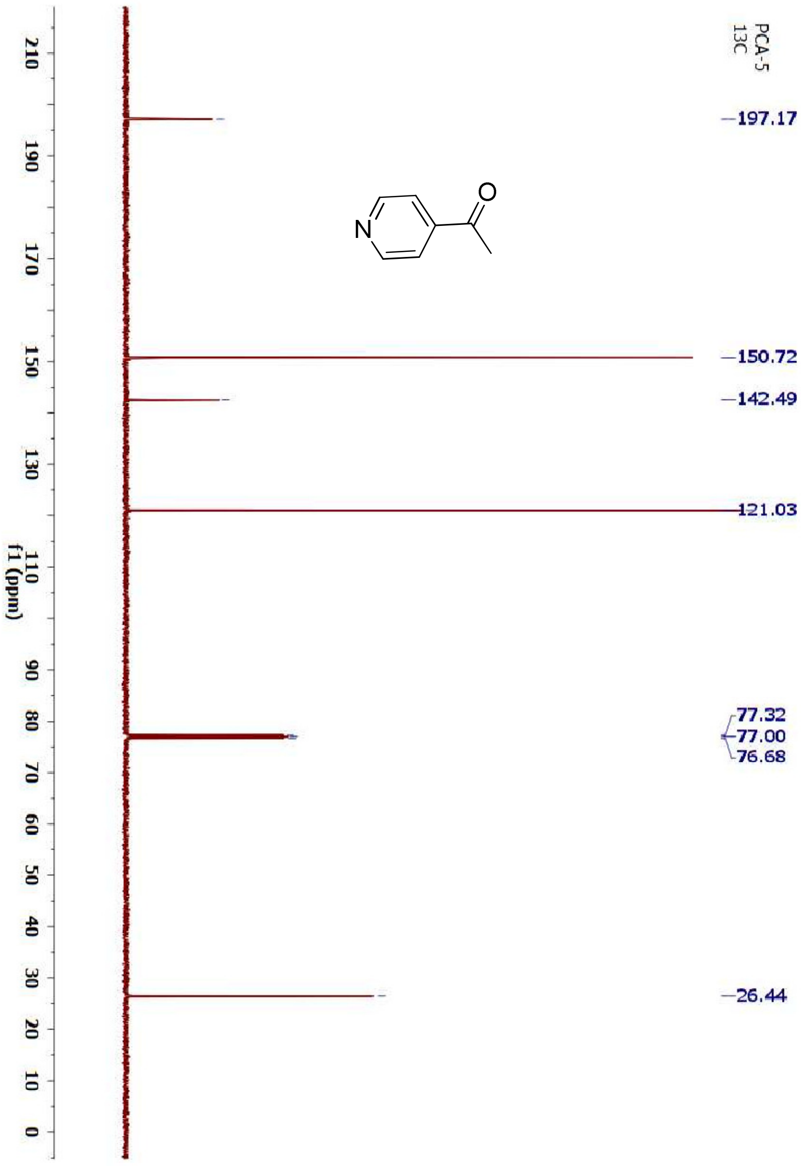
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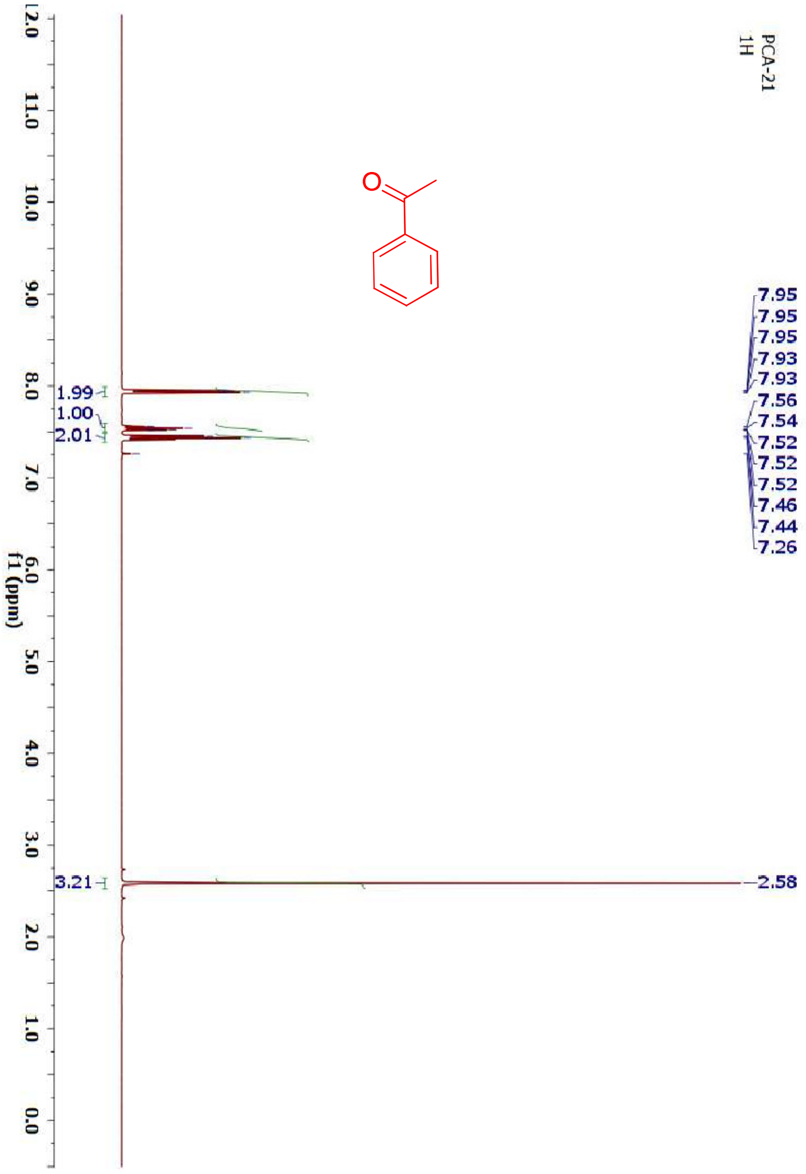
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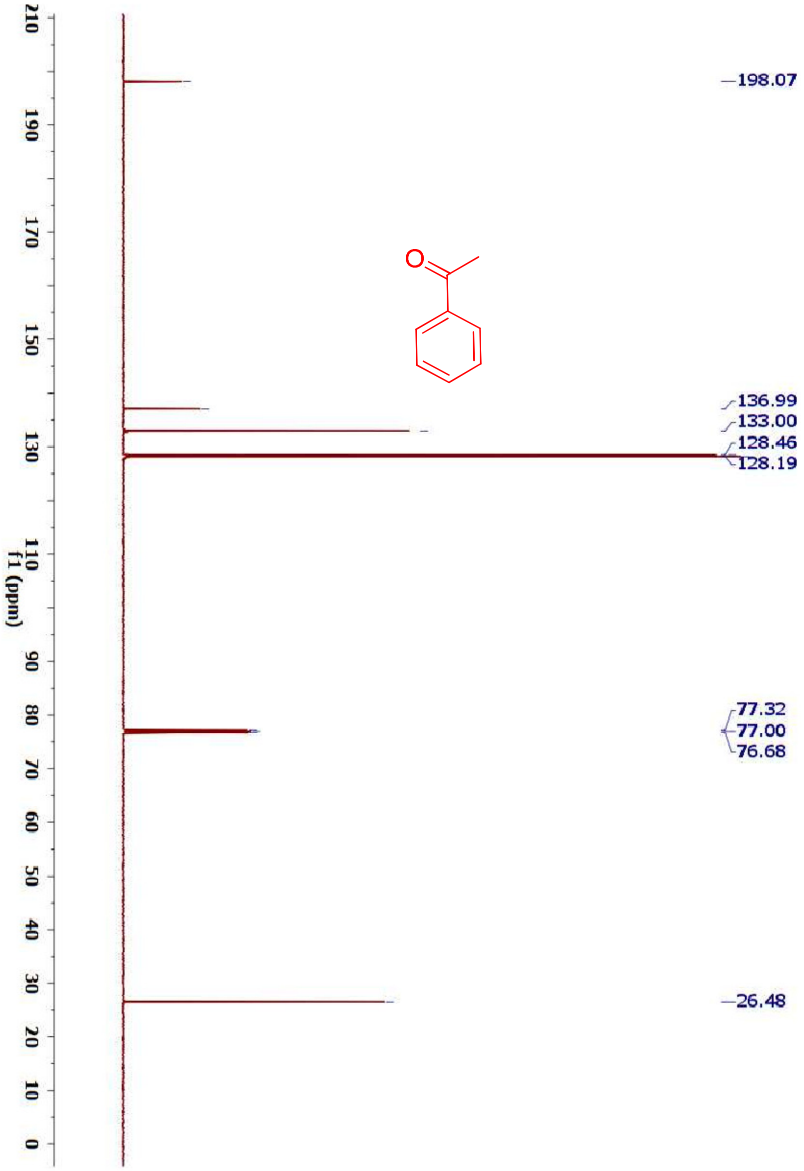
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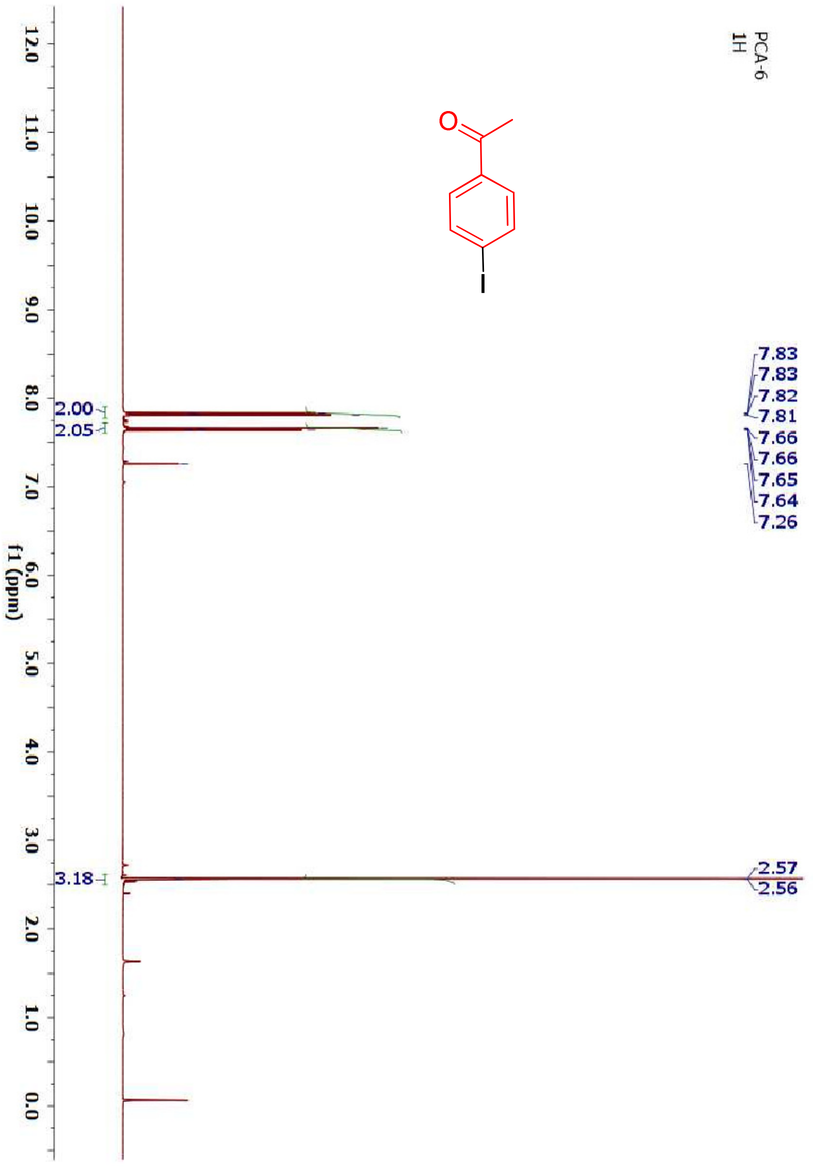
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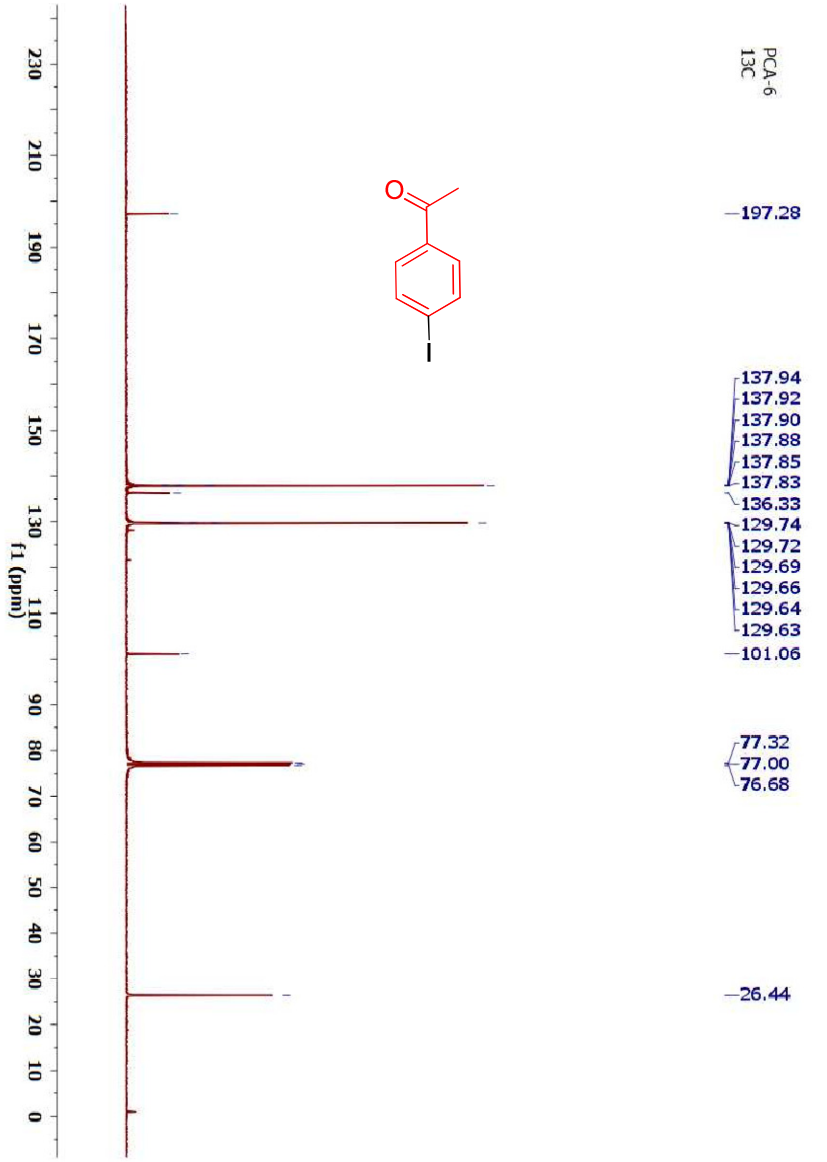
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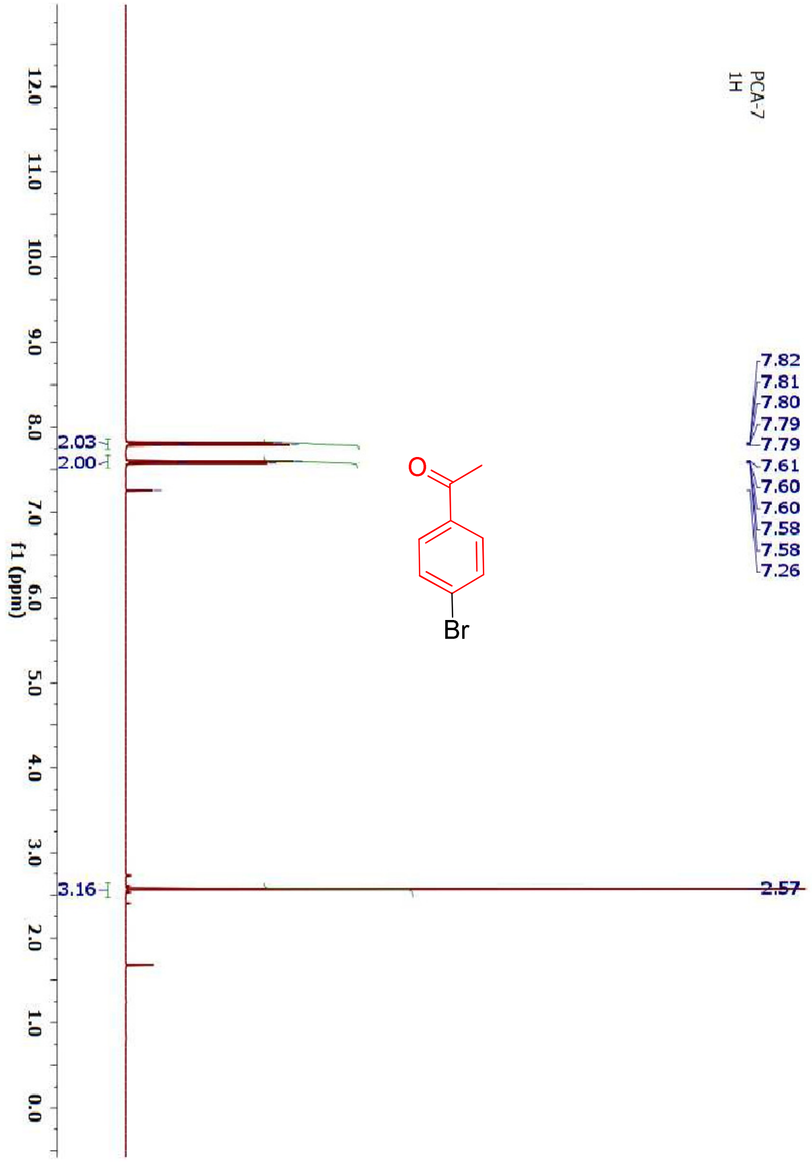
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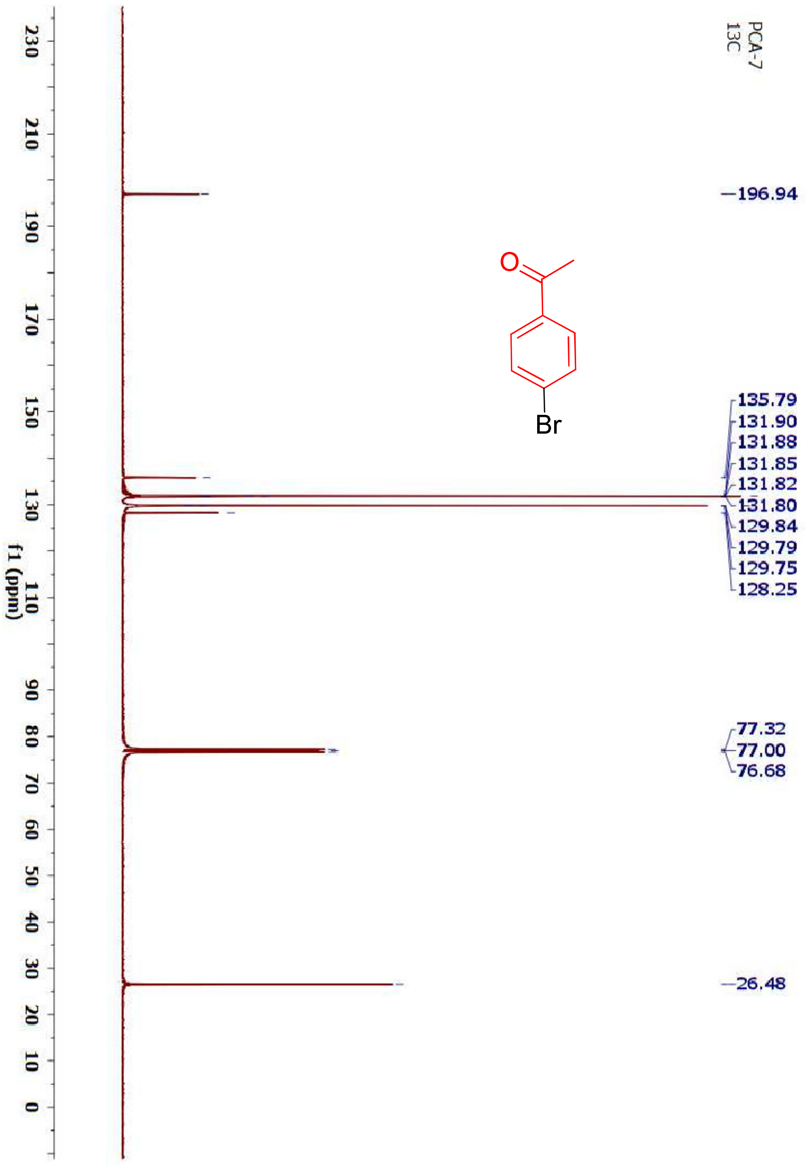
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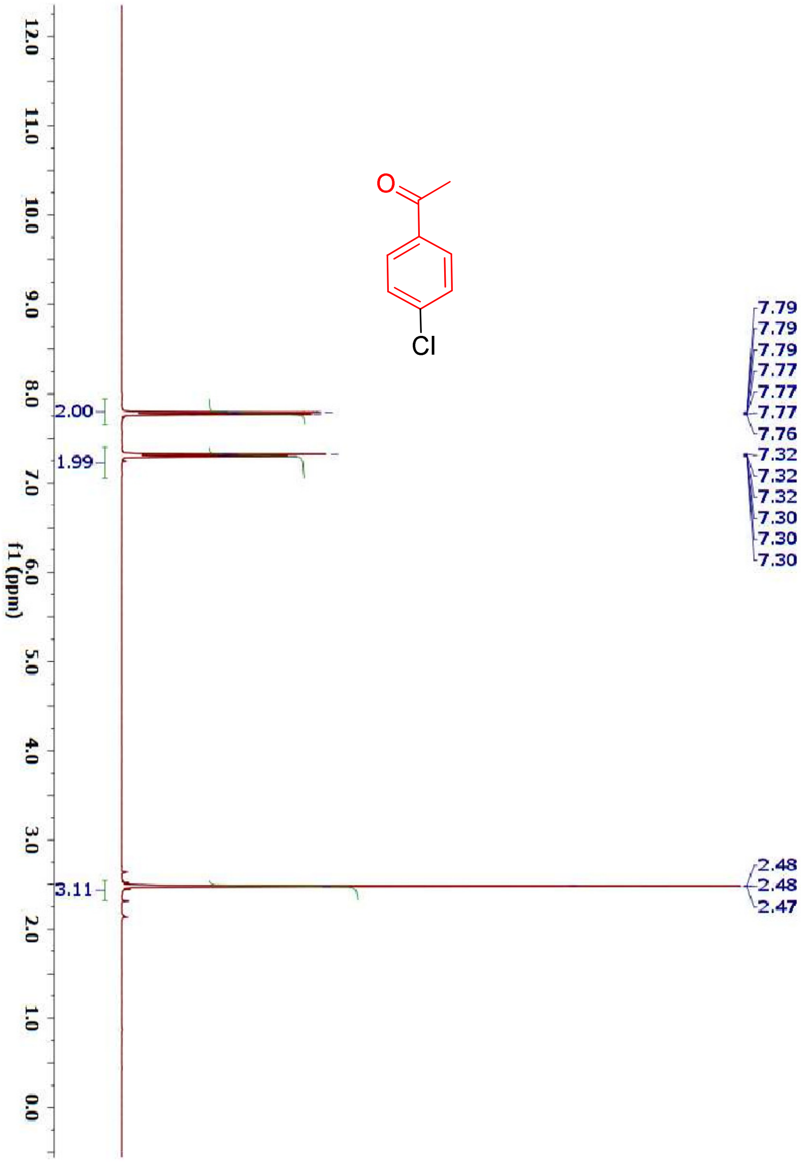
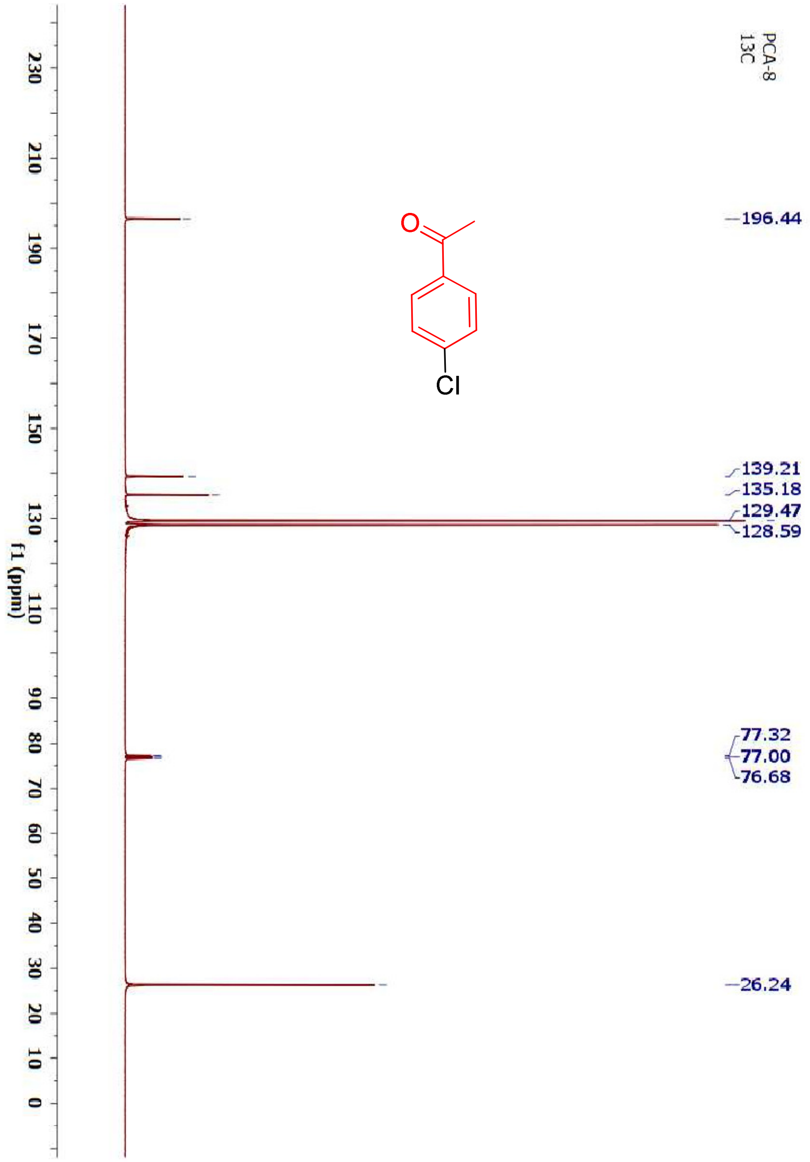
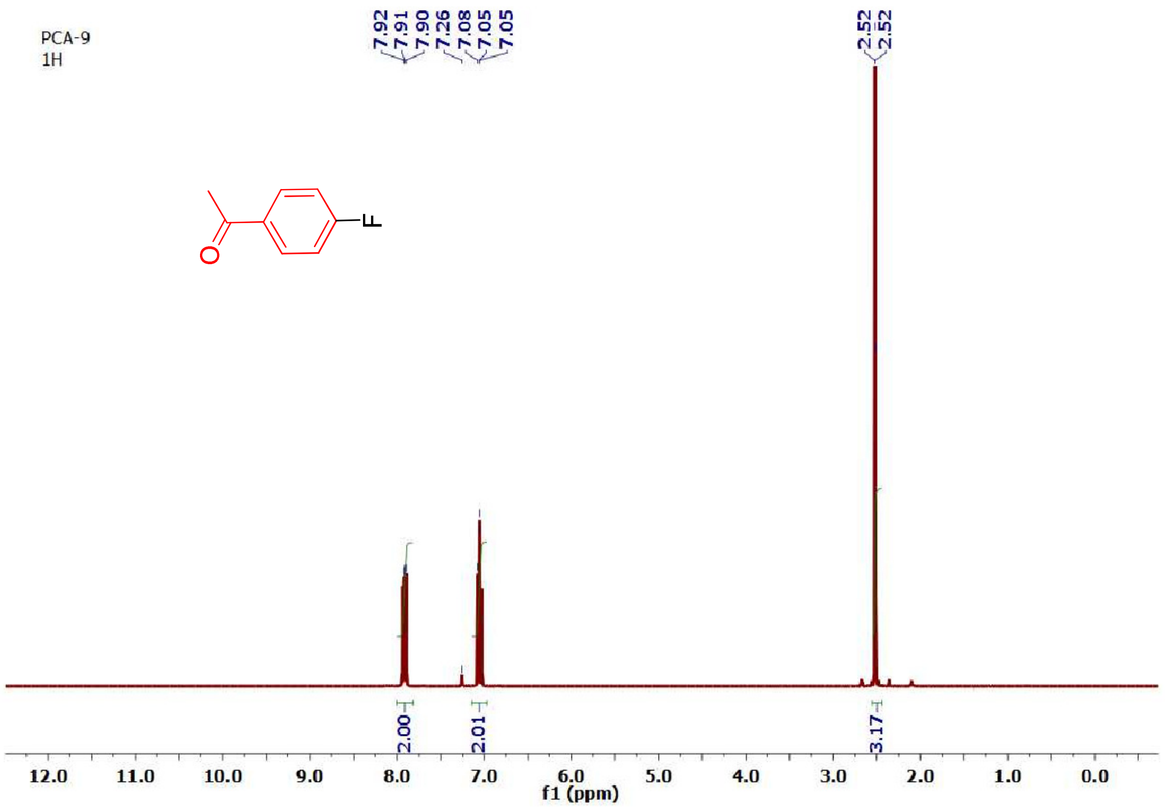
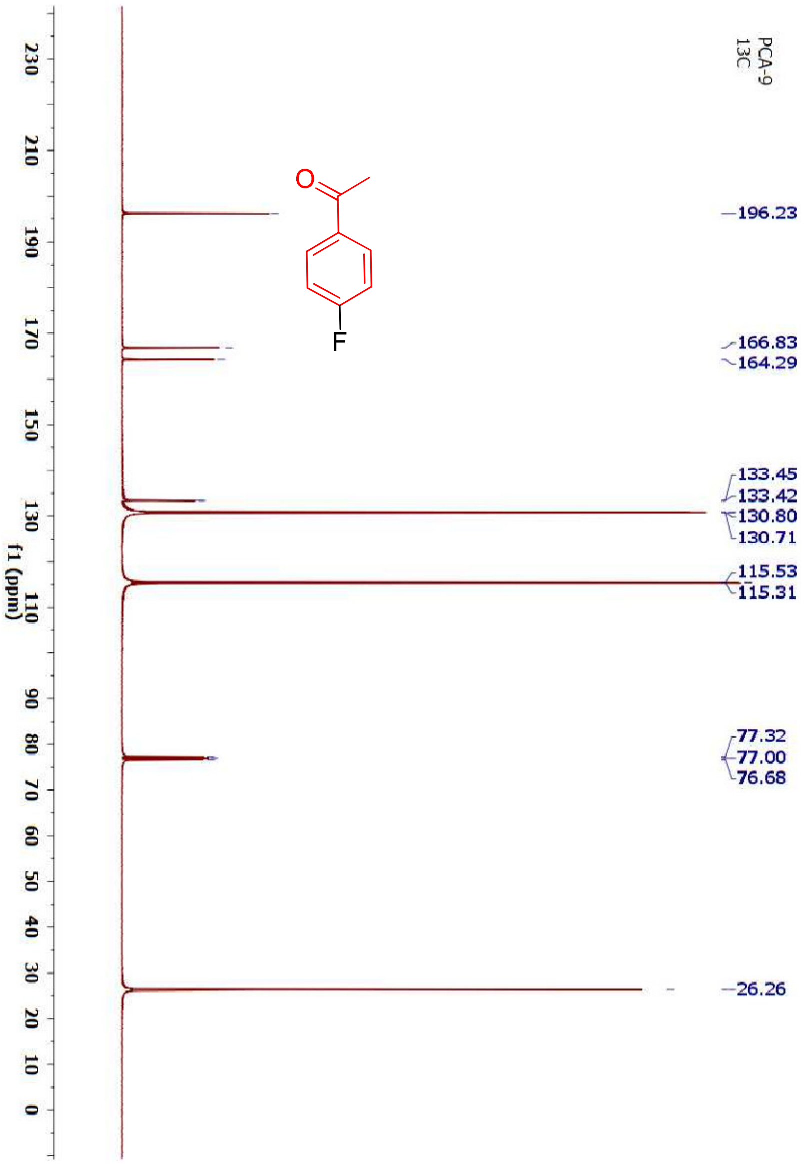
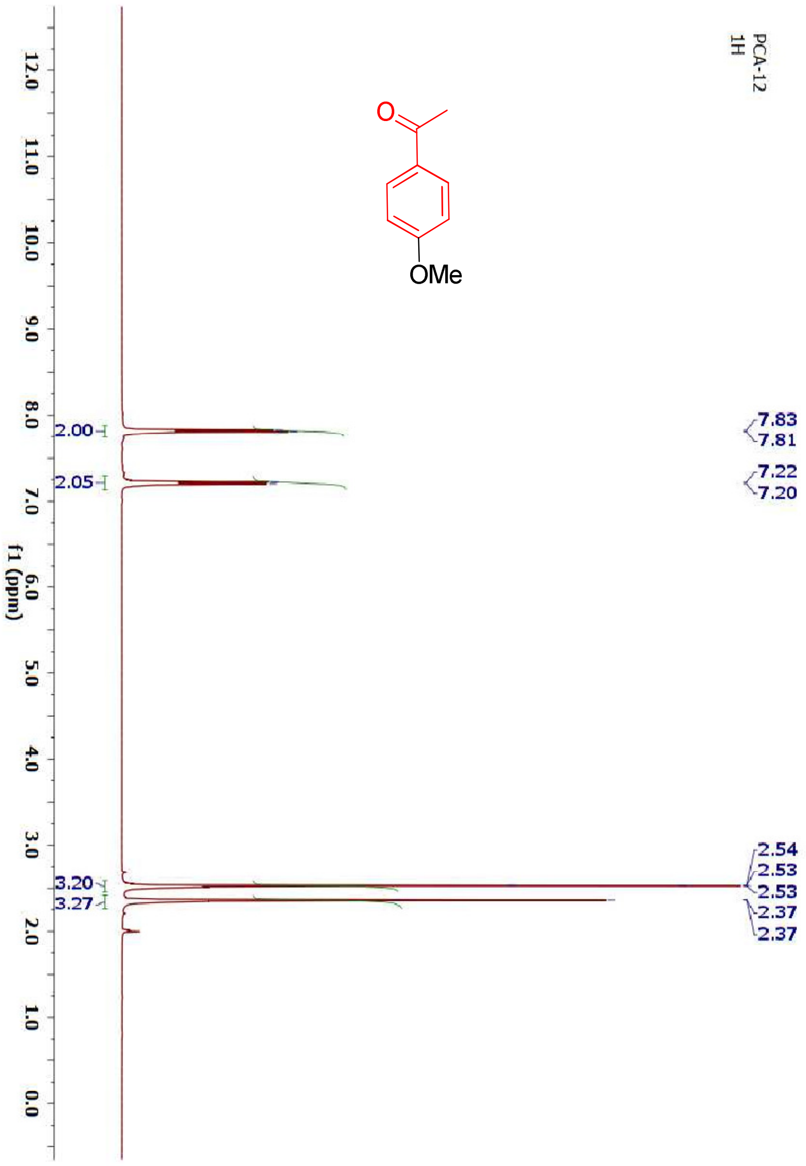
0
f1 (ppm)

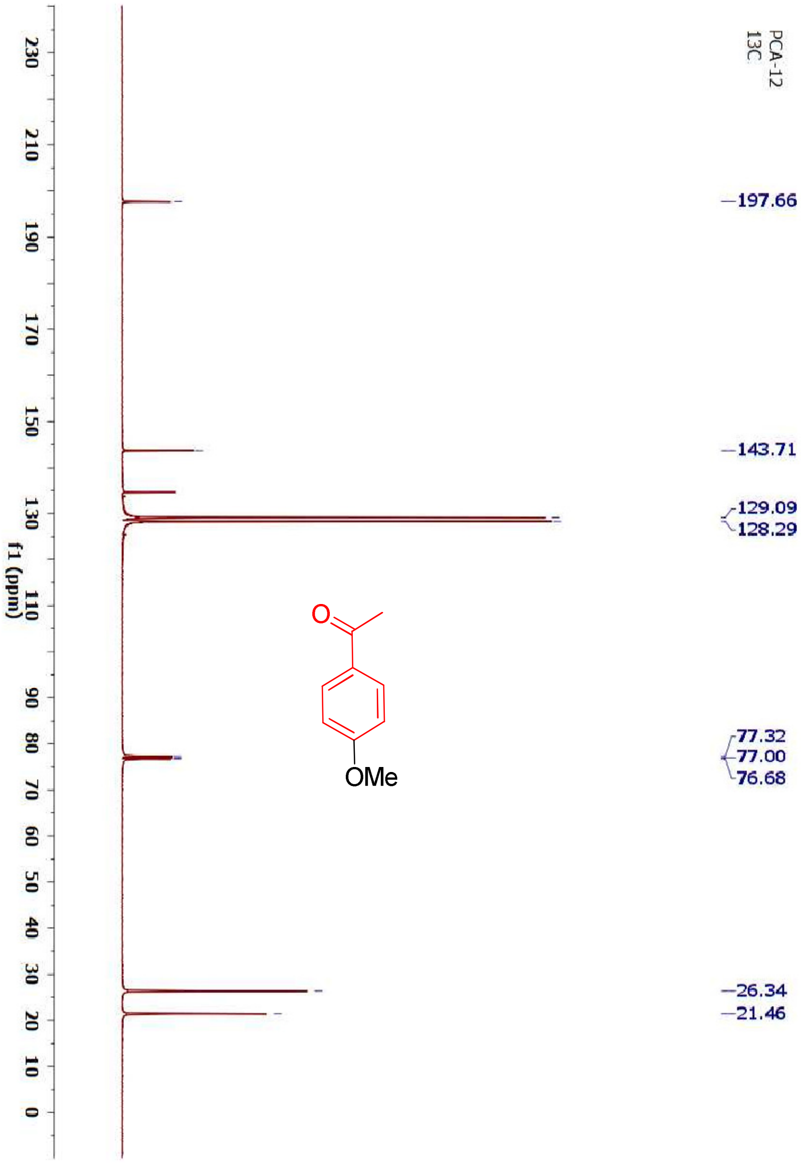

O
Cl
7.79
7.79
7.79
7.77
7.77
7.77
7.76
7.32
7.32
7.32
7.30
7.30
7.30
2.48
2.48
2.47
2.00
1.99
3.11
12.0
11.0
10.0
9.0
8.0
7.0
6.0
f1 (ppm)
5.0
4.0
3.0
2.0
1.0
0.0

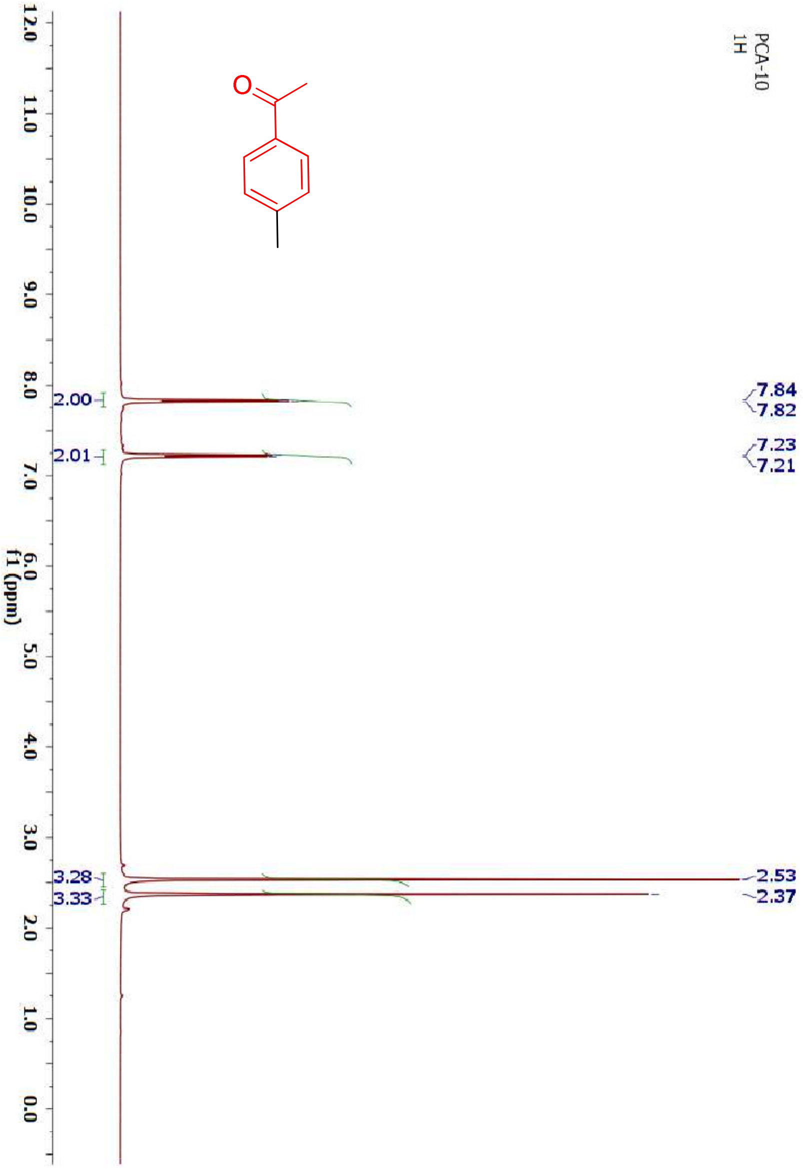

PCA-8
13C
O
Cl
196.44
139.21
135.18
129.47
128.59
77.32
77.00
76.68
26.24
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

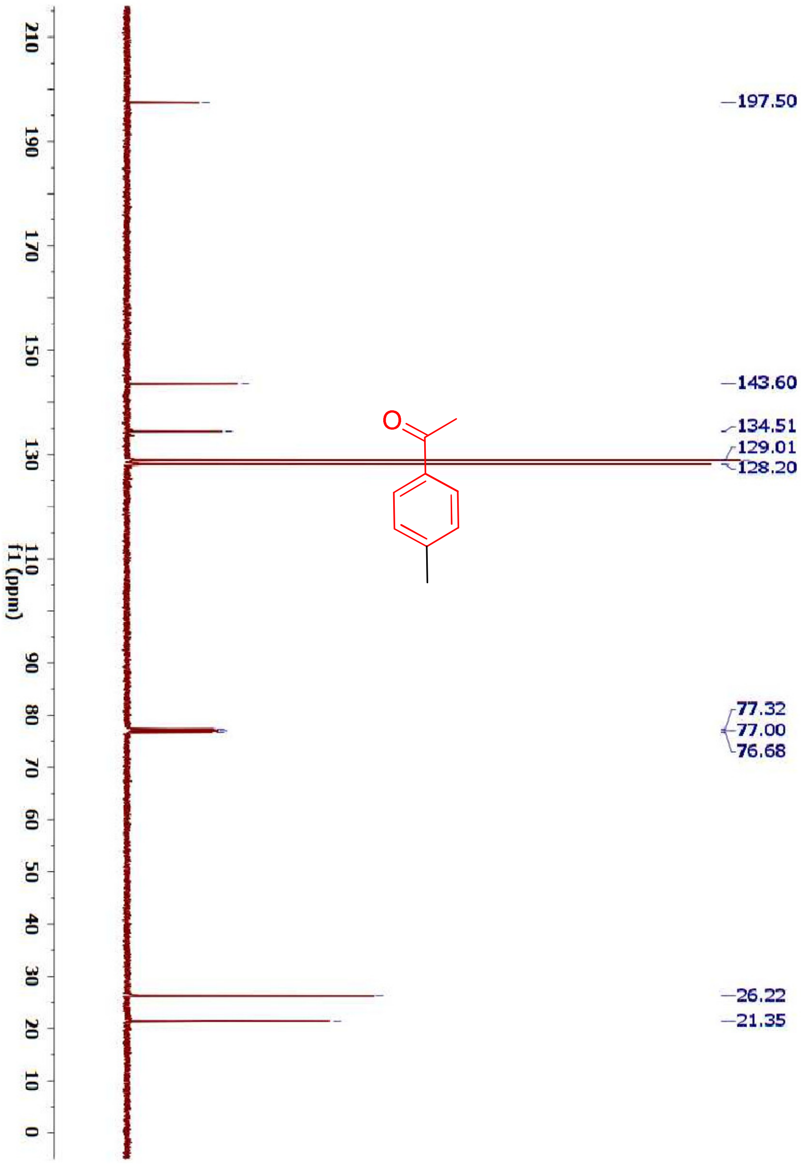

PCA-9
1H
O
F
7.92
7.91
7.90
7.26
7.08
7.05
7.05
2.52
2.52
2.00
2.01
3.17
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


PCA-9
13C
O
F
196.23
166.83
164.29
133.45
133.42
130.80
130.71
115.53
115.31
77.32
77.00
76.68
26.26
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

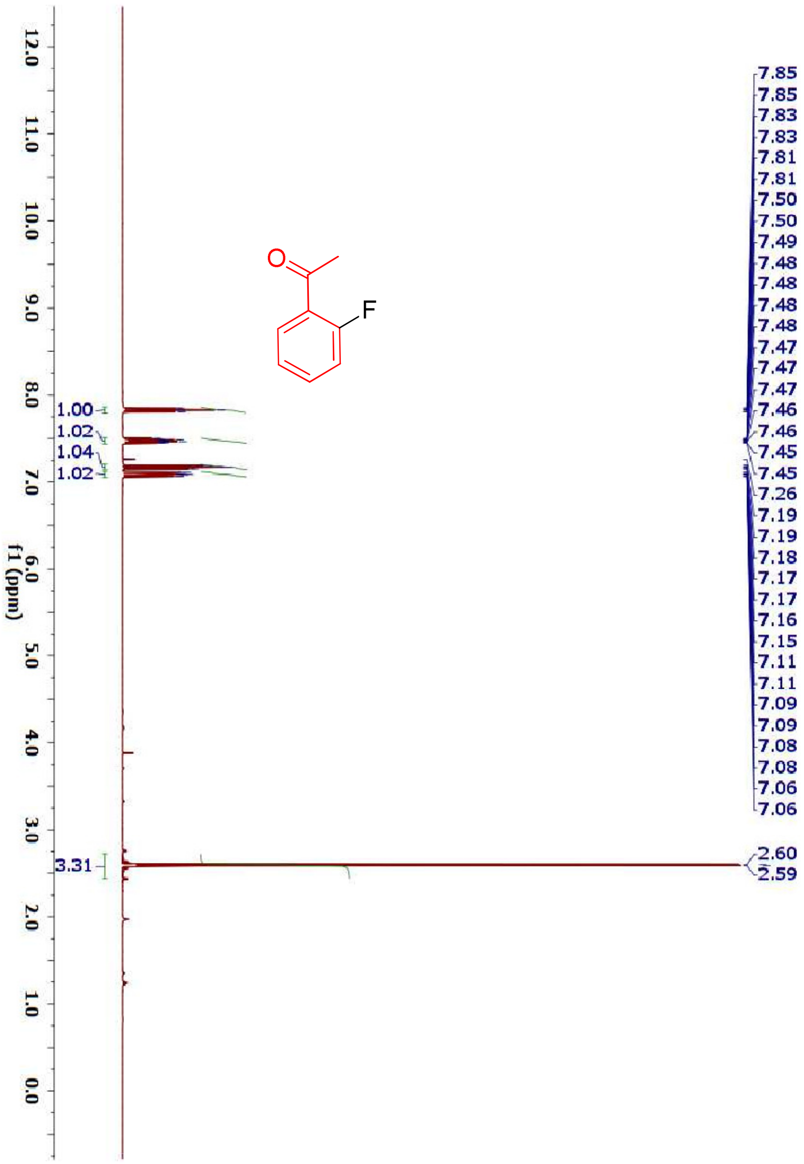

PCA-12
1H
O
OMe
7.83
7.81
7.22
7.20
2.54
2.53
2.53
2.37
2.37
2.00
2.05
3.20
3.27
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

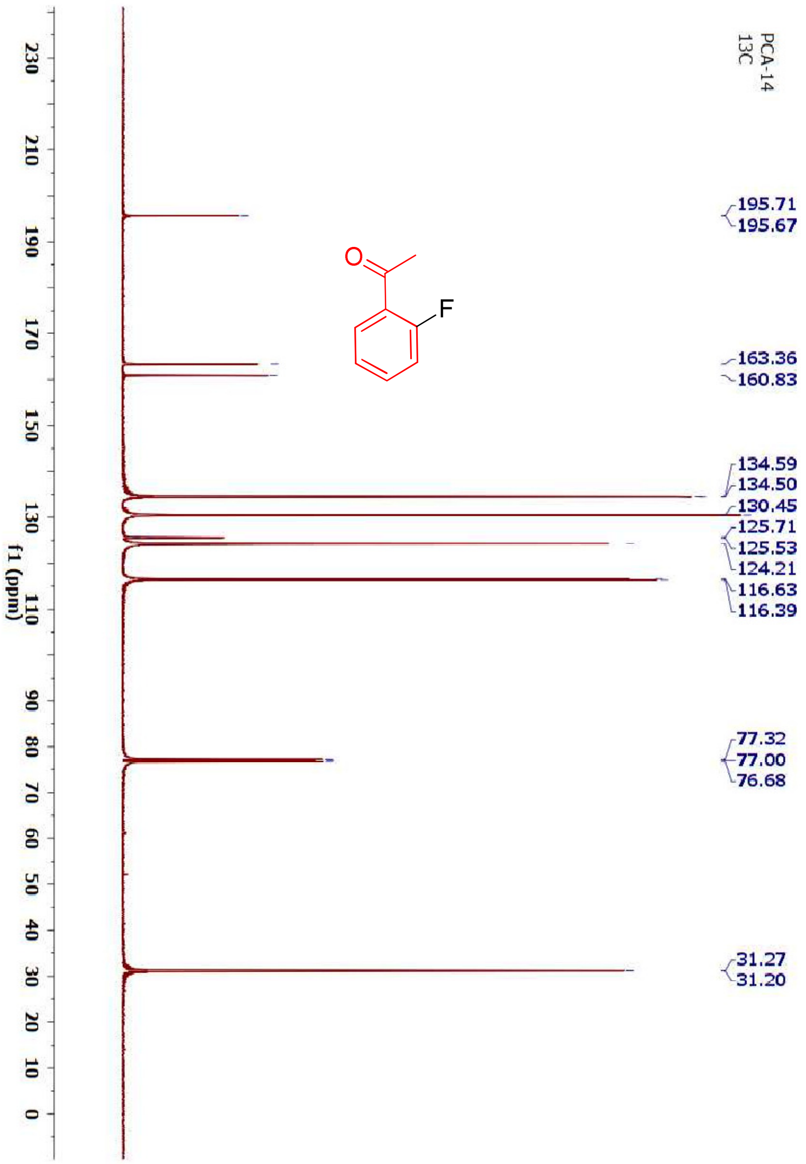

PCA-12
13C
197.66
143.71
129.09
128.29
77.32
77.00
76.68
26.34
21.46
O
OMe
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

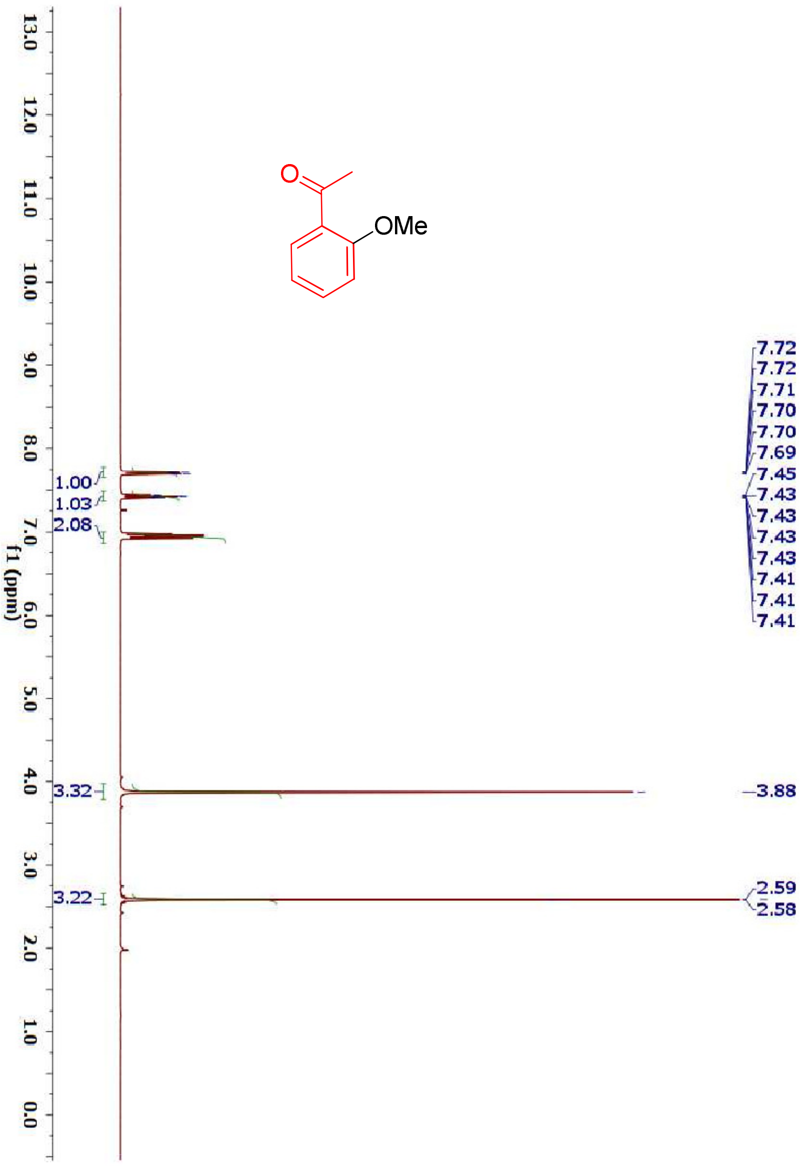

PCA-10
1H
O
7.84
7.82
7.23
7.21
2.53
2.37
2.00
2.01
3.28
3.33
12.0
11.0
10.0
9.0
8.0
7.0
6.0
f1 (ppm)
5.0
4.0
3.0
2.0
1.0
0.0



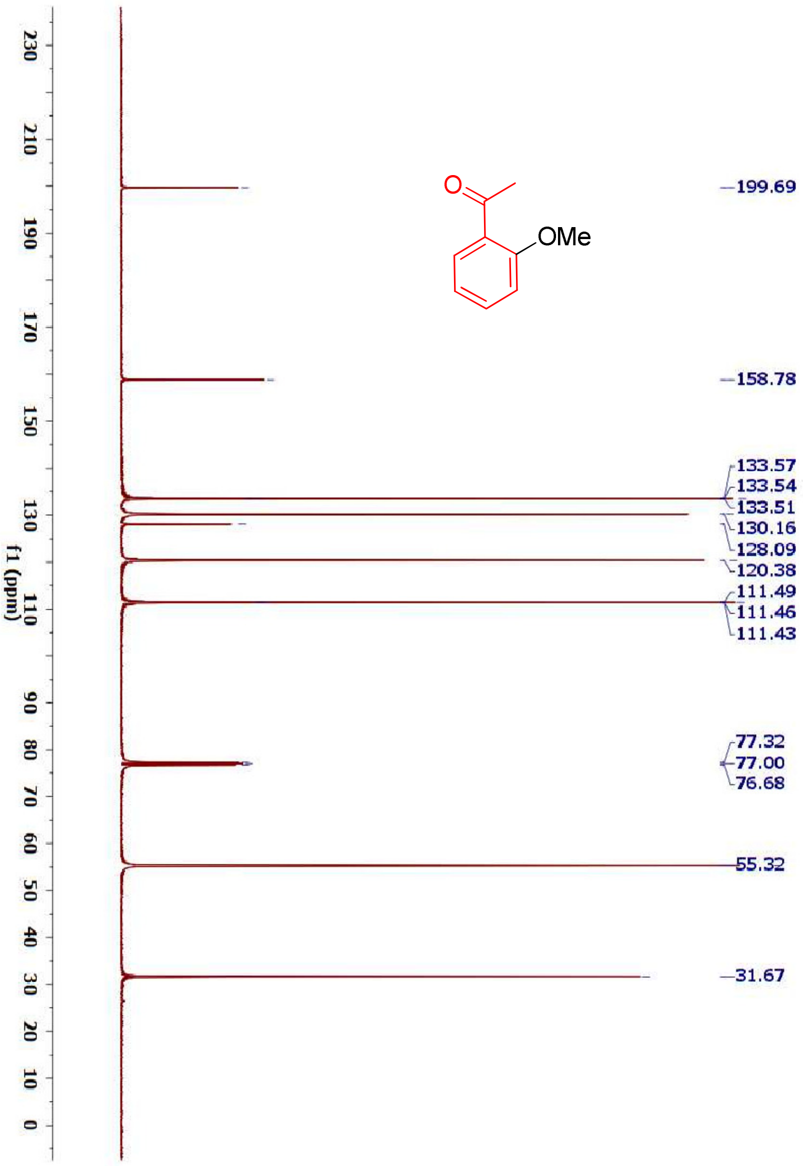
197.50
143.60
134.51
129.01
128.20
77.32
77.00
76.68
26.22
21.35
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
F
12.0
11.0
10.0
9.0
8.0
7.0
6.0
f1 (ppm)
5.0
4.0
3.0
2.0
1.0
0.0
1.00
1.02
1.04
1.02
3.31
7.85
7.85
7.83
7.83
7.81
7.81
7.50
7.50
7.49
7.48
7.48
7.48
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.26
7.19
7.19
7.18
7.17
7.17
7.16
7.15
7.11
7.11
7.09
7.09
7.08
7.08
7.06
7.06
2.60
2.59

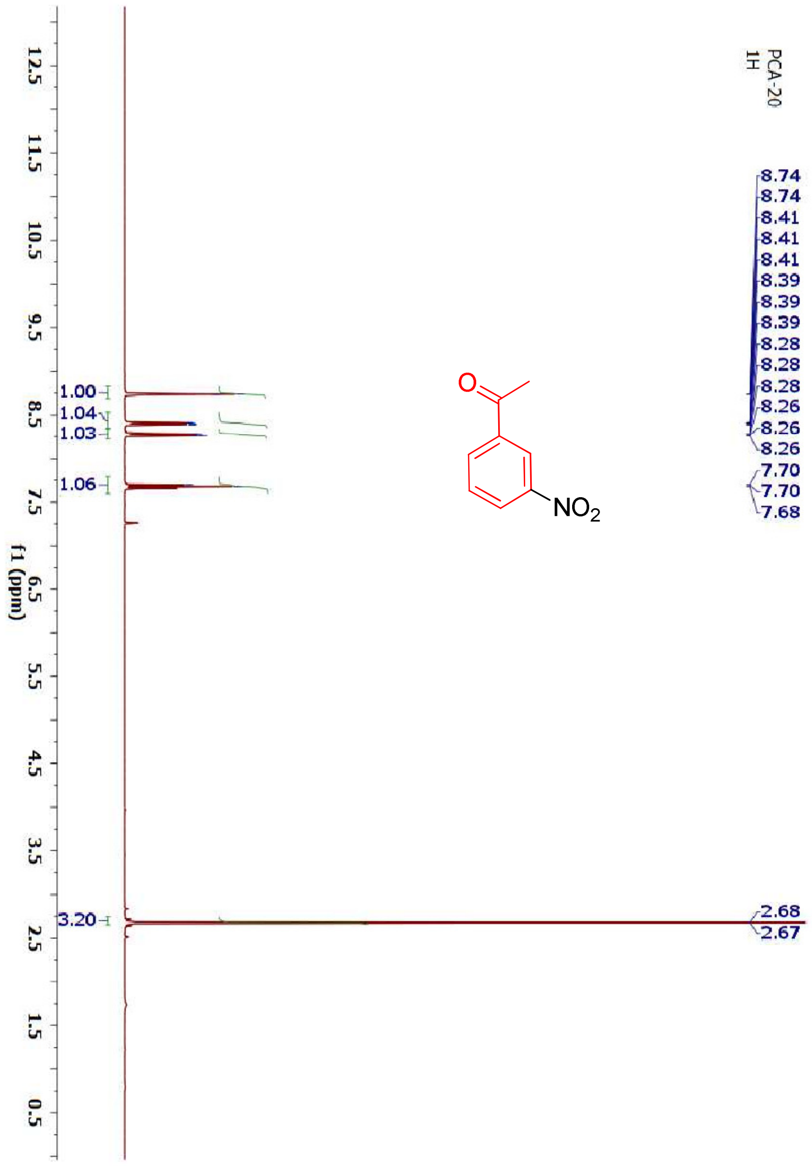

PCA-14
13C
195.71
195.67
163.36
160.83
134.59
134.50
130.45
125.71
125.53
124.21
116.63
116.39
77.32
77.00
76.68
31.27
31.20
O
F
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

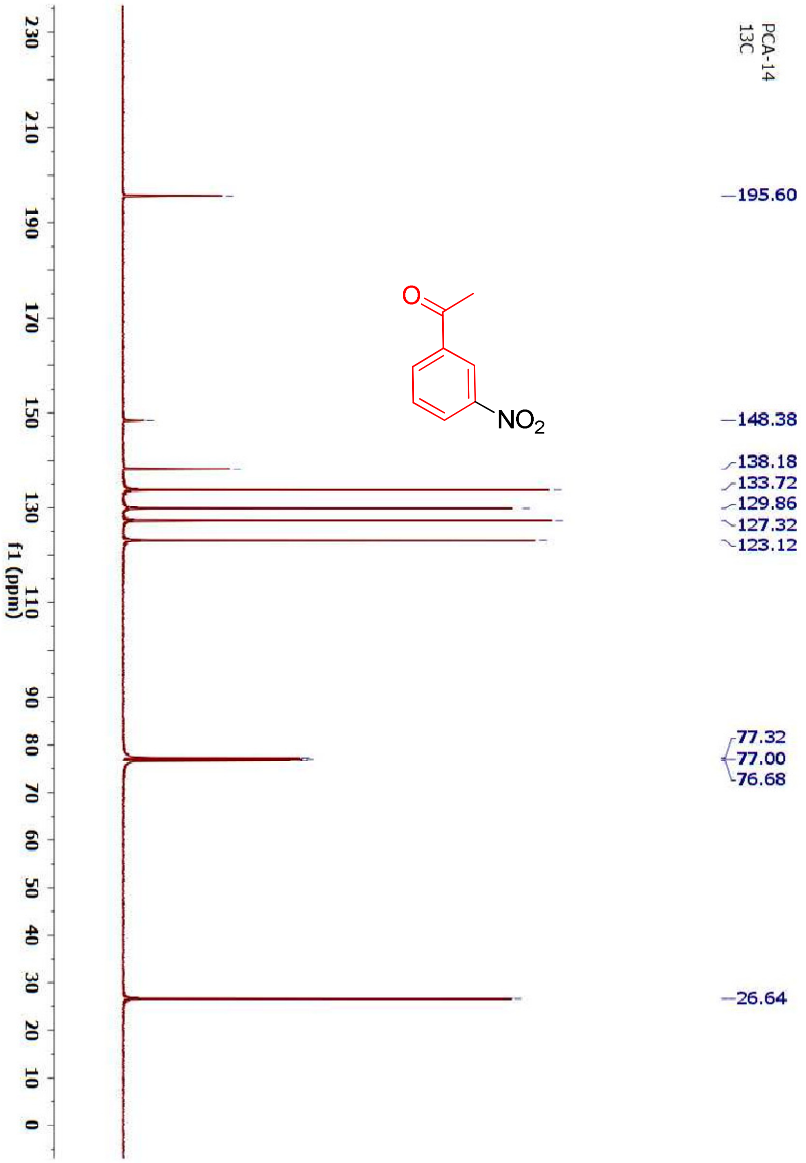


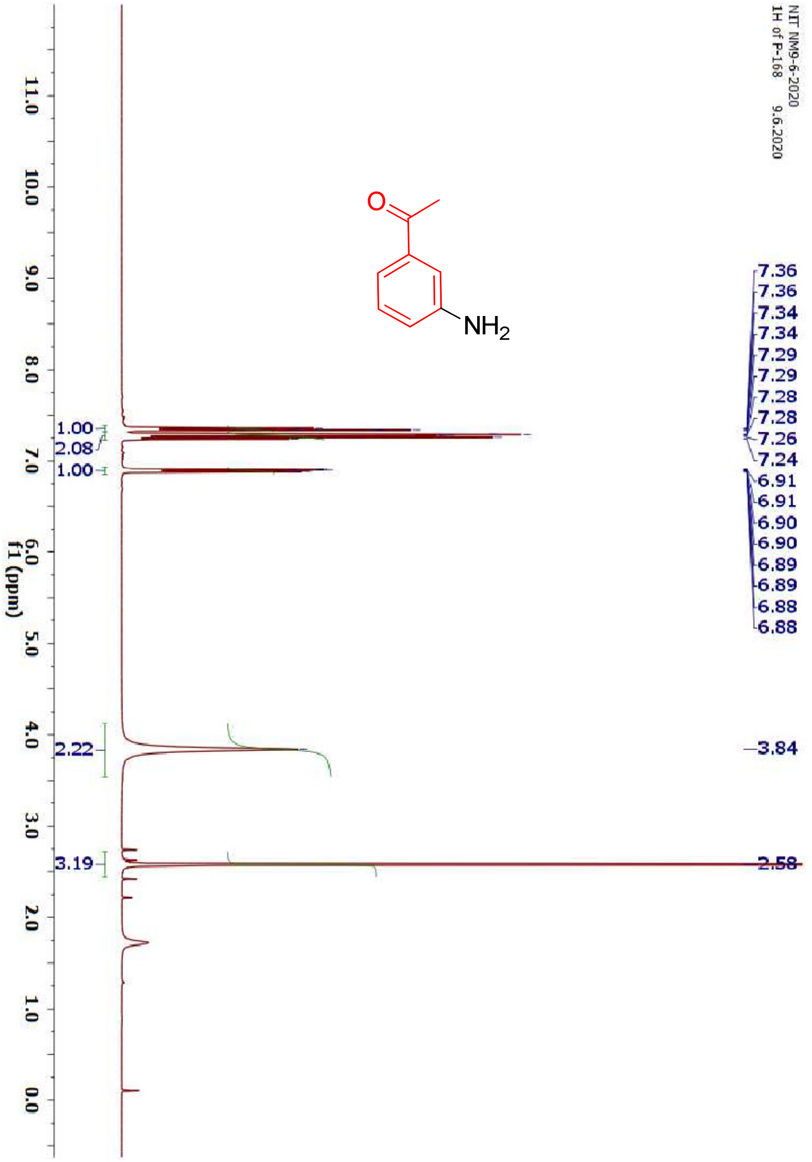
OMe
O
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
1.00
1.03
2.08
3.32
3.22
7.72
7.72
7.71
7.70
7.70
7.69
7.45
7.43
7.43
7.43
7.43
7.41
7.41
7.41
3.88
2.59
2.58

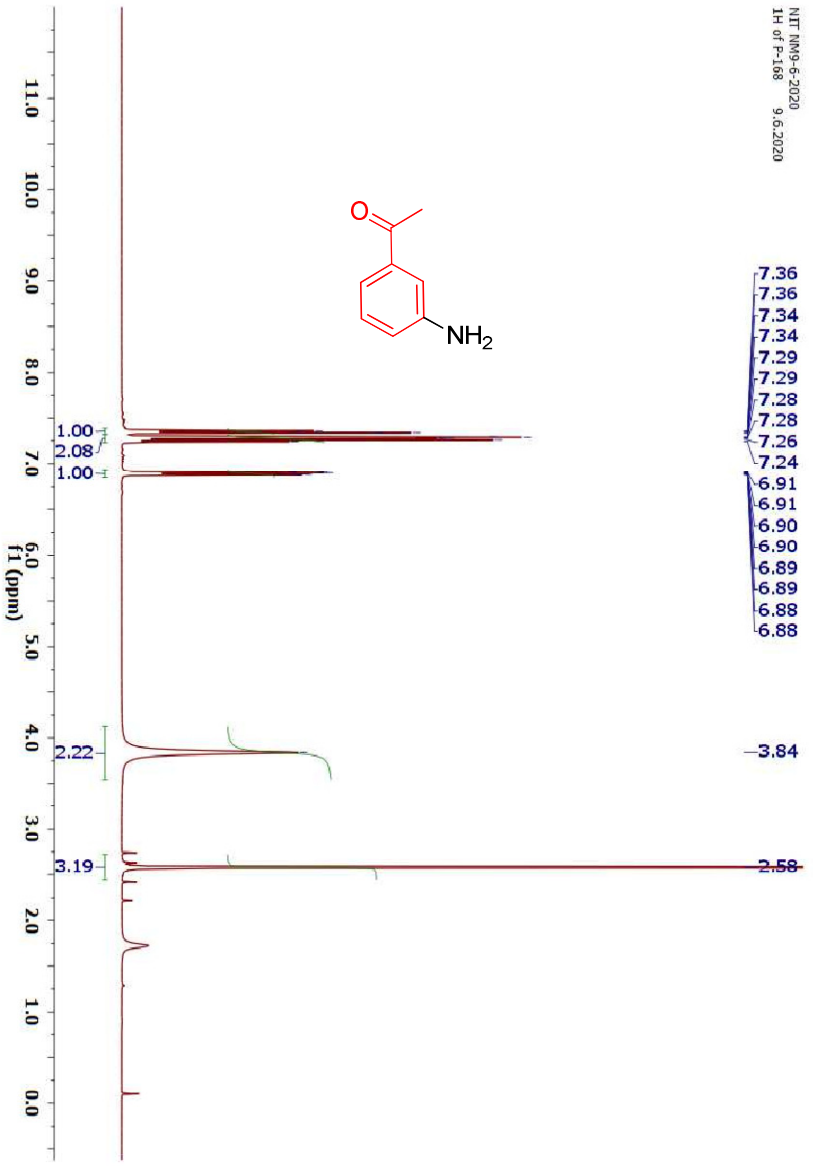


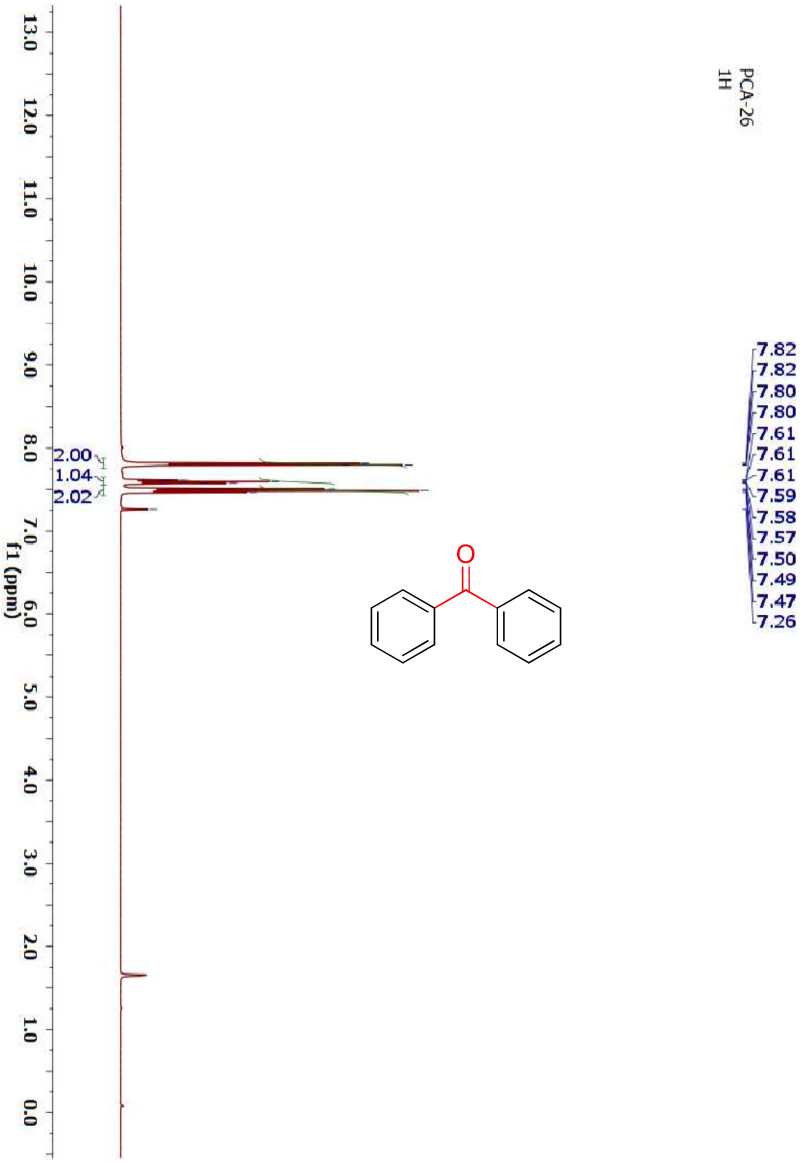
O
OMe
199.69
158.78
133.57
133.54
133.51
130.16
128.09
120.38
111.49
111.46
111.43
77.32
77.00
76.68
55.32
31.67
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

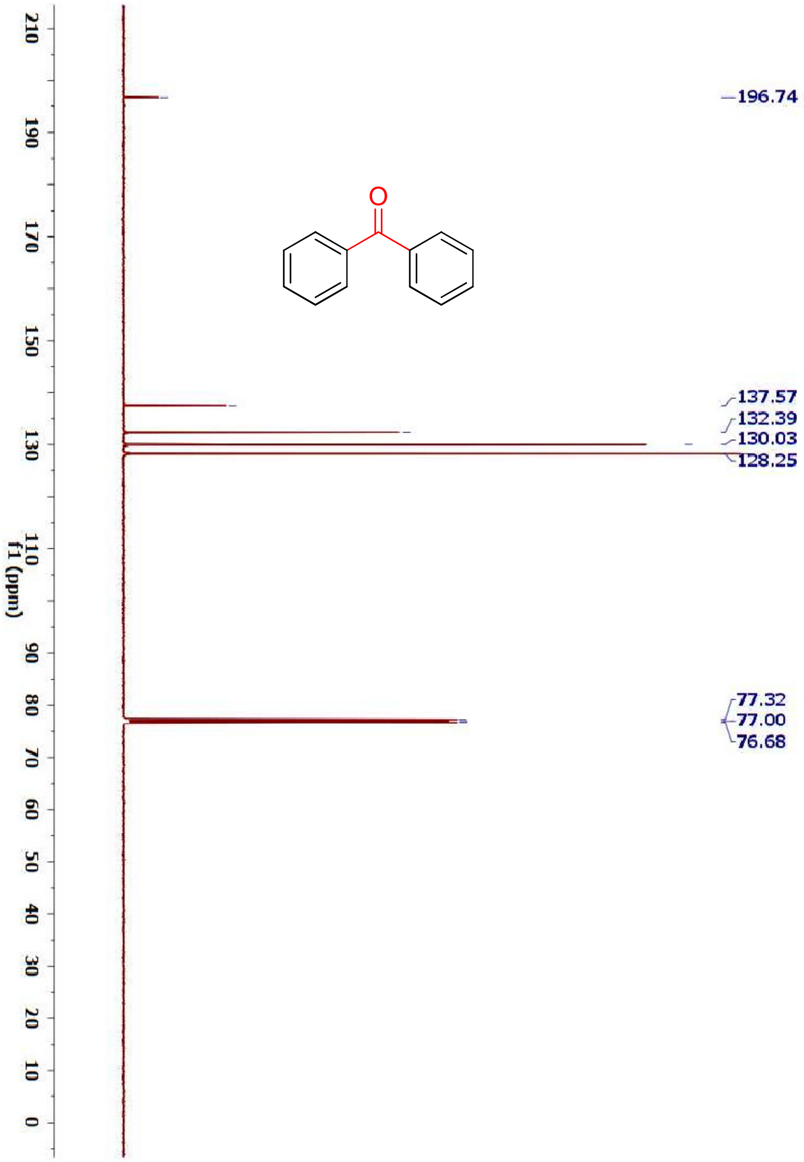

PCA-20
1H
8.74
8.74
8.41
8.41
8.41
8.39
8.39
8.39
8.28
8.28
8.28
8.26
8.26
8.26
7.70
7.70
7.68
2.68
2.67
O
NO2
1.00
1.04
1.03
1.06
3.20
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

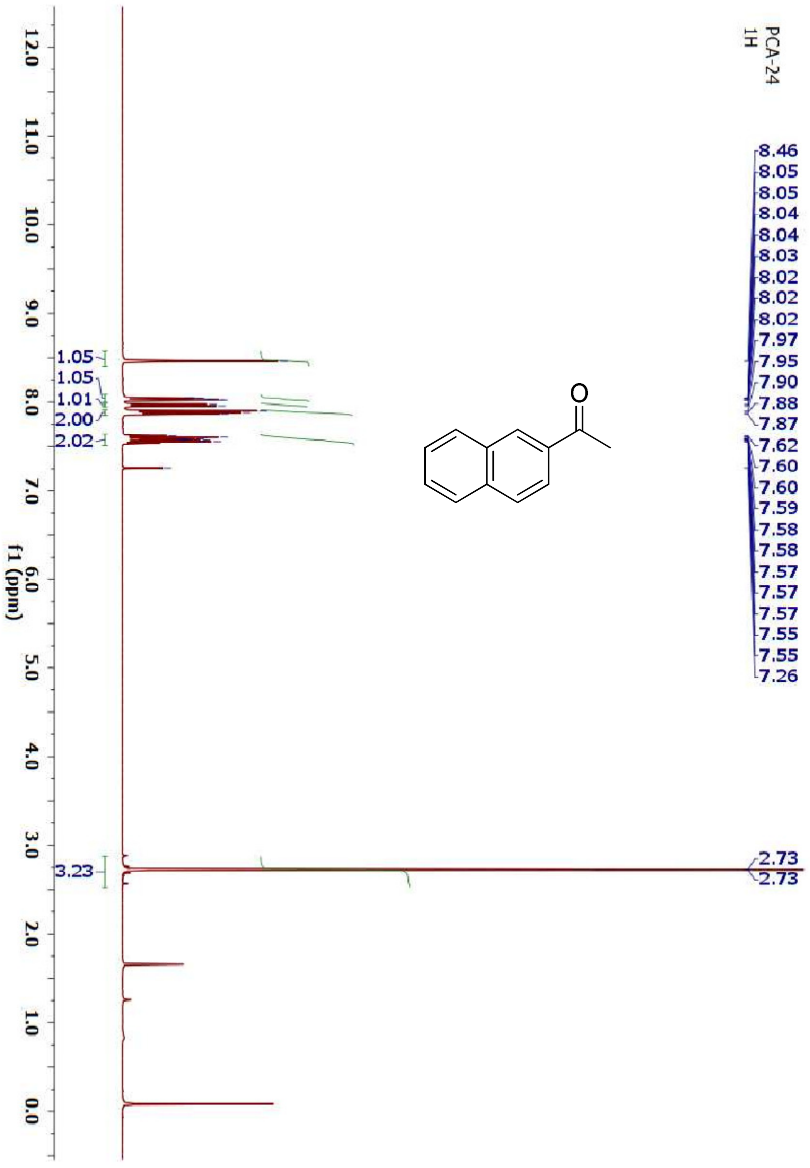

PCA-14
13C
195.60
148.38
138.18
133.72
129.86
127.32
123.12
77.32
77.00
76.68
26.64
O
NO2
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

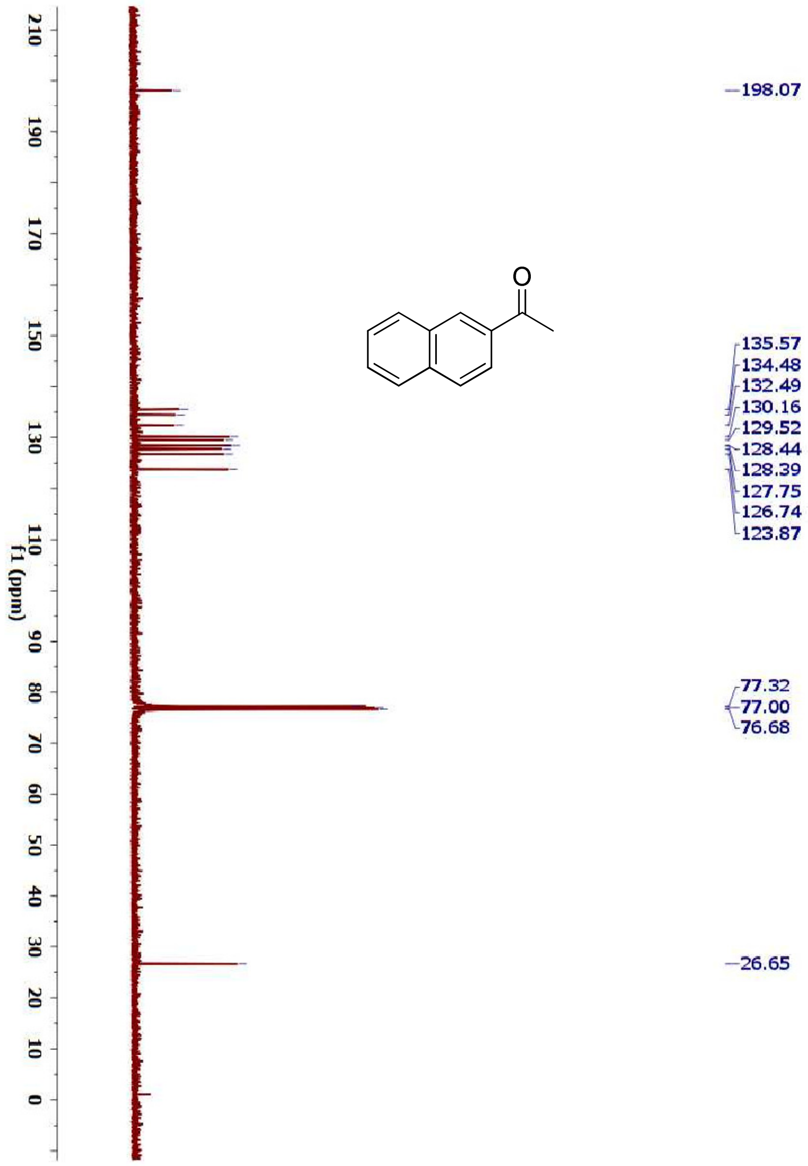

NIT NM9-6-2020
1H of P-168 9.6.2020
O
NH2
7.36
7.36
7.34
7.34
7.29
7.29
7.28
7.28
7.26
7.24
6.91
6.91
6.90
6.90
6.89
6.89
6.88
6.88
3.84
2.58
1.00
2.08
1.00
2.22
3.19
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

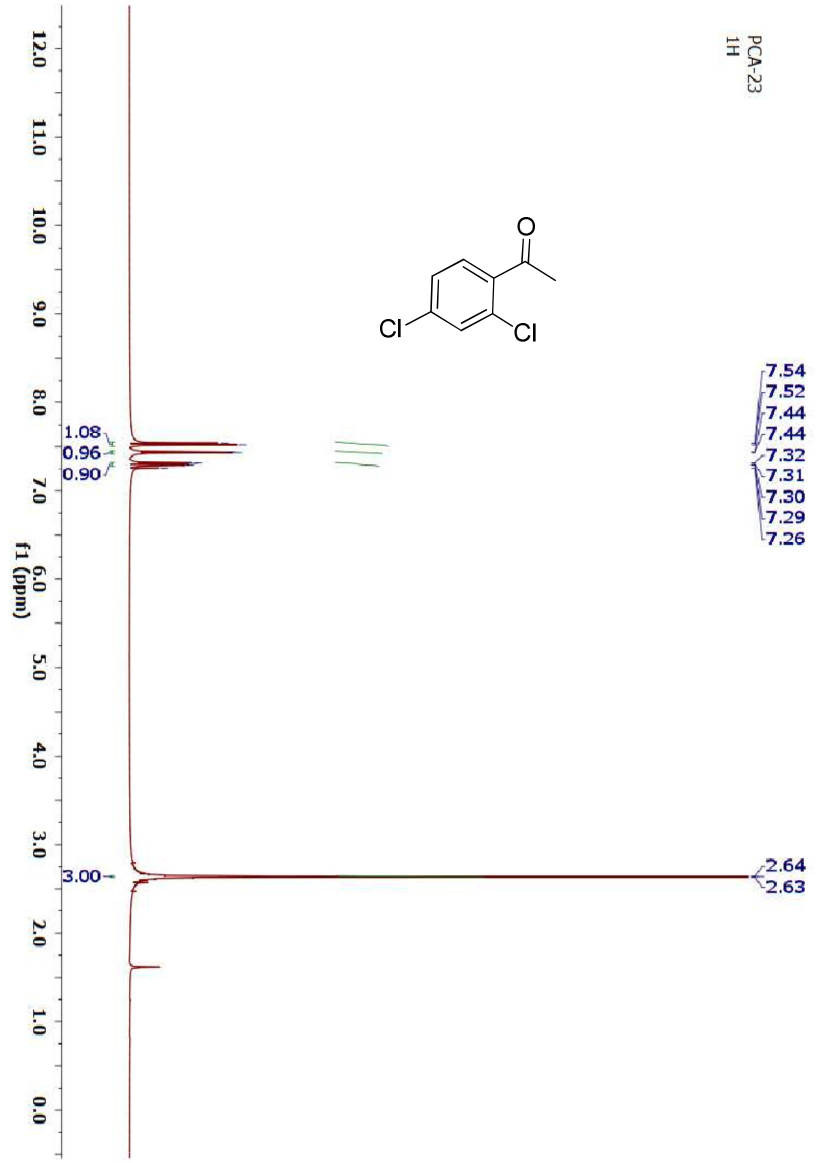

NIT NM9-6-2020
1H of P-168 9.6.2020
O
NH2
7.36
7.36
7.34
7.34
7.29
7.29
7.28
7.28
7.26
7.24
6.91
6.91
6.90
6.90
6.89
6.89
6.88
6.88
3.84
2.58
1.00
2.08
1.00
2.22
3.19
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

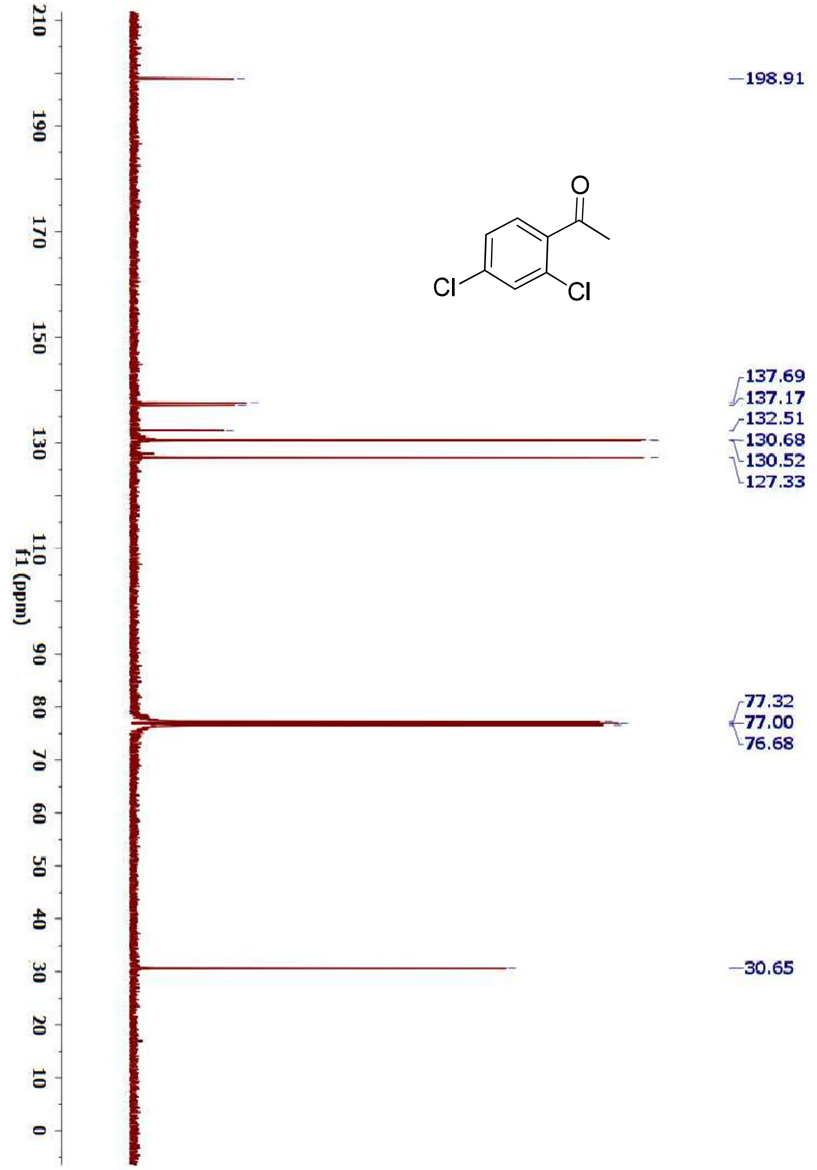

PCA-26
1H
7.82
7.82
7.80
7.80
7.61
7.61
7.61
7.59
7.58
7.57
7.50
7.49
7.47
7.26
2.00
1.04
2.02
O
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

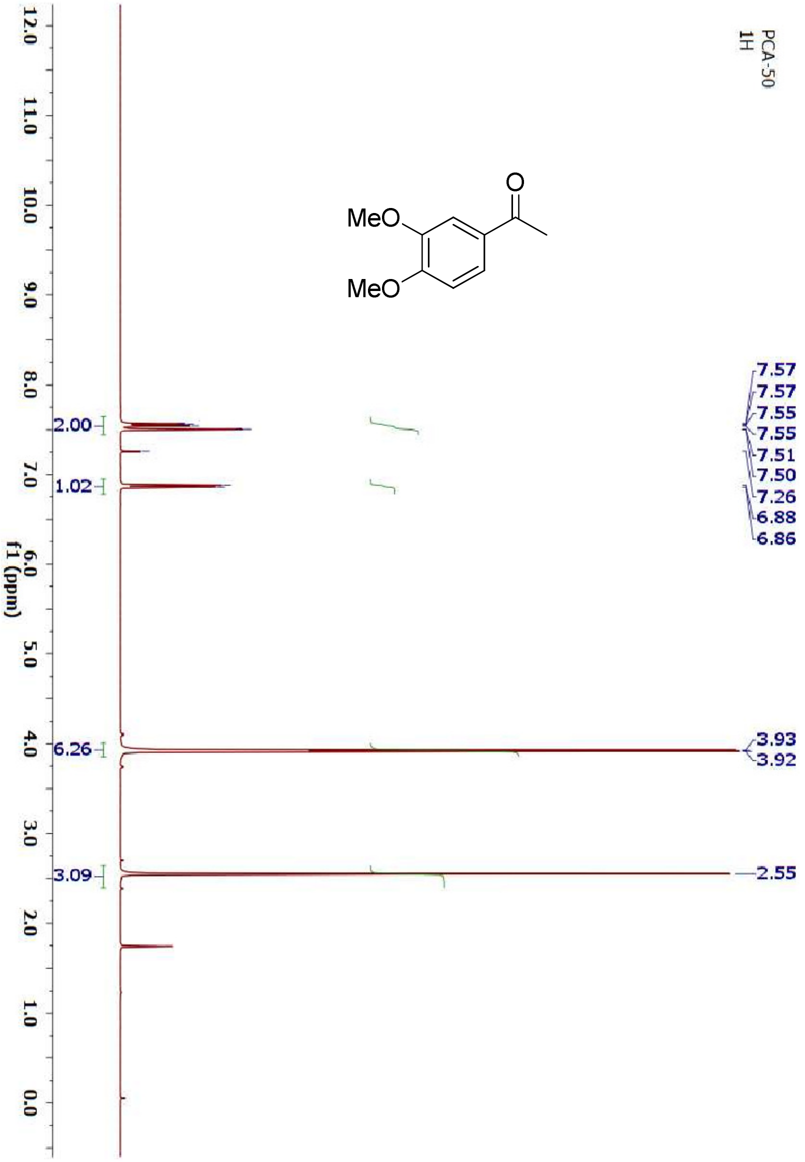

210
190
170
150
130
110
f1 (ppm)
90
80
70
60
50
40
30
20
10
0
196.74
137.57
132.39
130.03
128.25
77.32
77.00
76.68
O

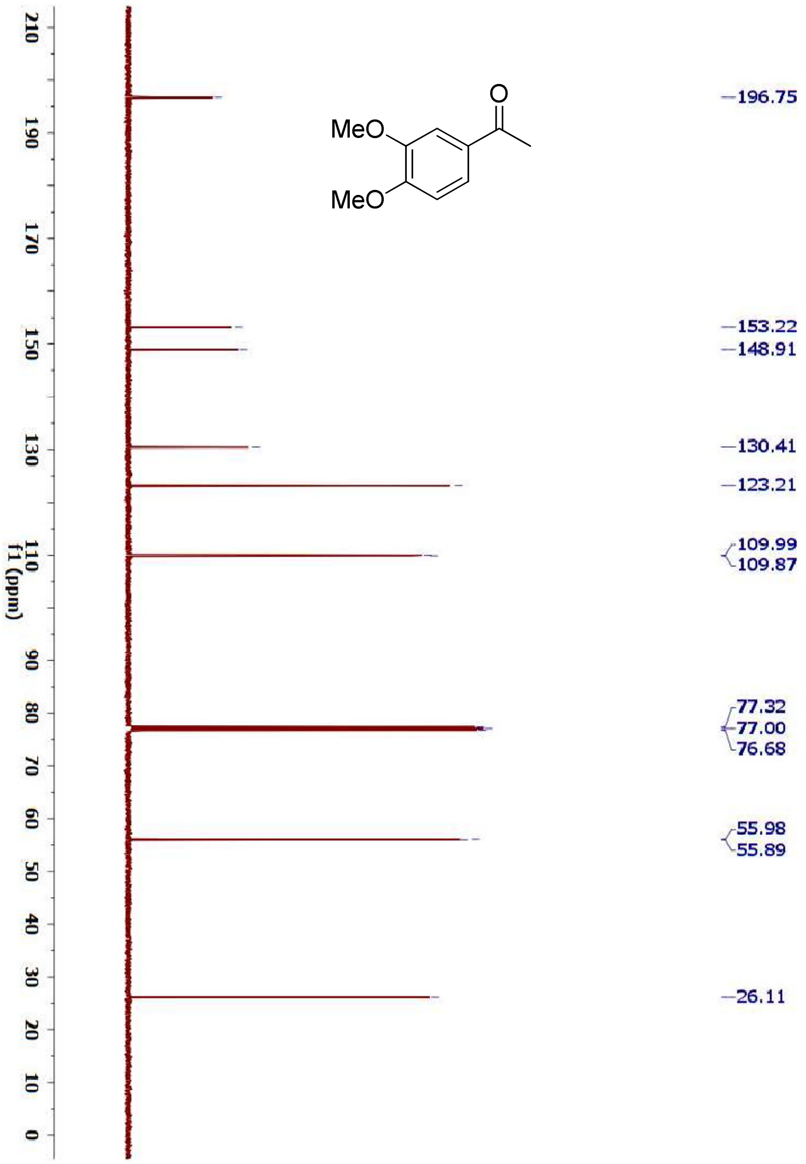

PCA-24
1H
8.46
8.05
8.05
8.04
8.04
8.03
8.02
8.02
8.02
7.97
7.95
7.90
7.88
7.87
7.62
7.60
7.60
7.59
7.58
7.58
7.57
7.57
7.57
7.55
7.55
7.26
2.73
2.73
1.05
1.05
1.01
2.00
2.02
3.23
12.0
11.0
10.0
9.0
8.0
7.0
6.0
f1 (ppm)
5.0
4.0
3.0
2.0
1.0
0.0
O


210
190
170
150
130
110
f1 (ppm)
90
80
70
60
50
40
30
20
10
0
O
198.07
135.57
134.48
132.49
130.16
129.52
128.44
128.39
127.75
126.74
123.87
77.32
77.00
76.68
26.65

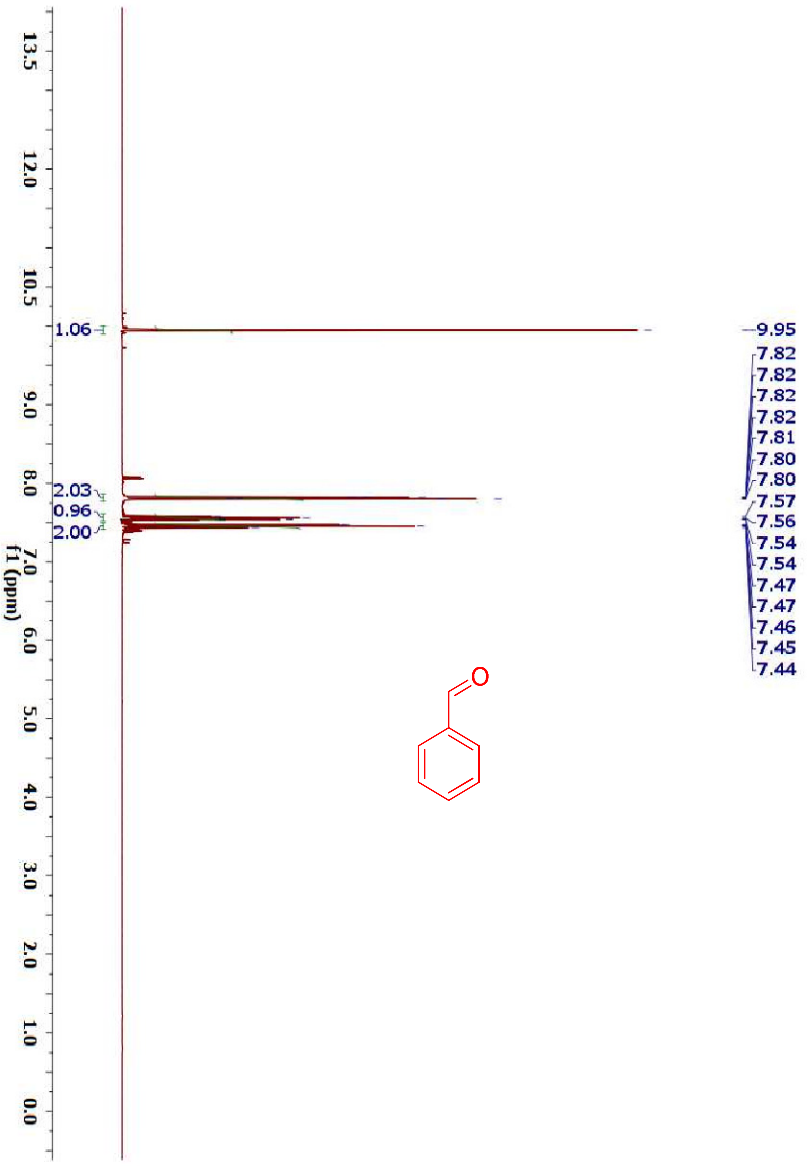

PCA-23
1H
O
Cl
Cl
7.54
7.52
7.44
7.44
7.32
7.31
7.30
7.29
7.26
2.64
2.63
1.08
0.96
0.90
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
f1 (ppm)
5.0
4.0
3.0
2.0
1.0
0.0


Cl
Cl
O
198.91
137.69
137.17
132.51
130.68
130.52
127.33
77.32
77.00
76.68
30.65
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

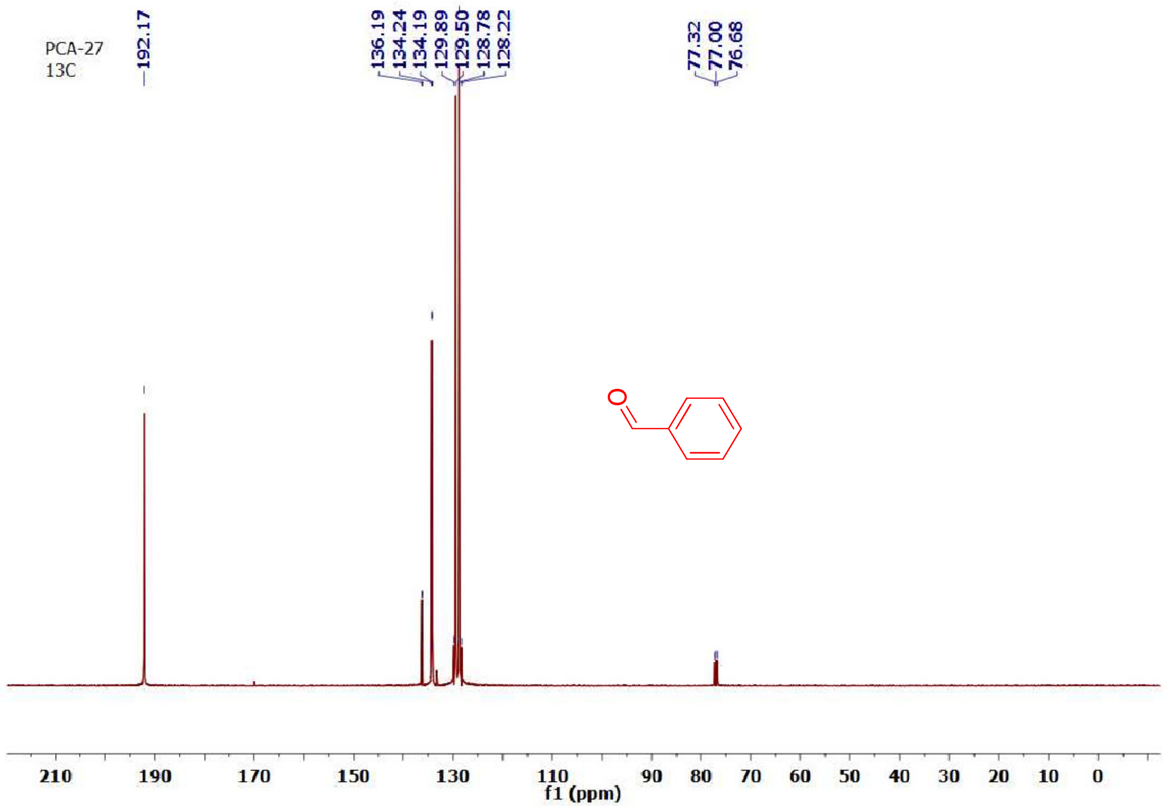

PCA-50
1H
MeO
MeO
O
7.57
7.57
7.55
7.55
7.51
7.50
7.26
6.88
6.86
3.93
3.92
2.55
2.00
1.02
6.26
3.09
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

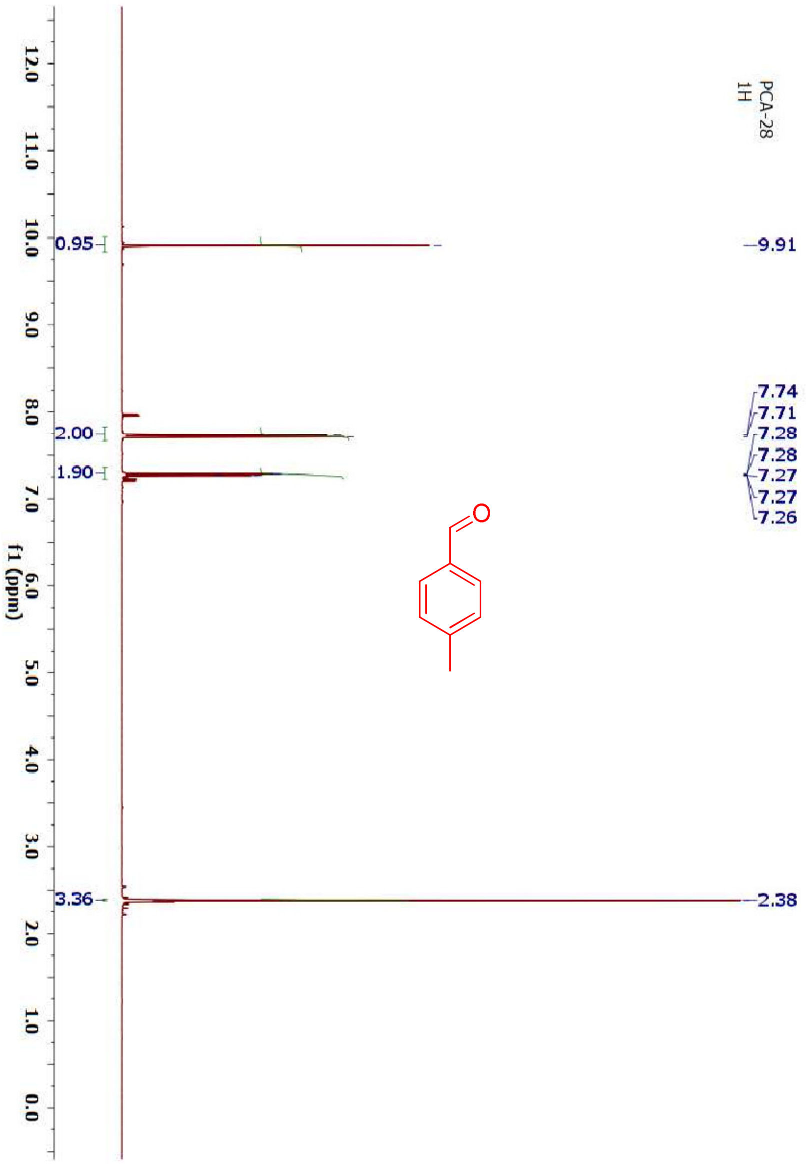


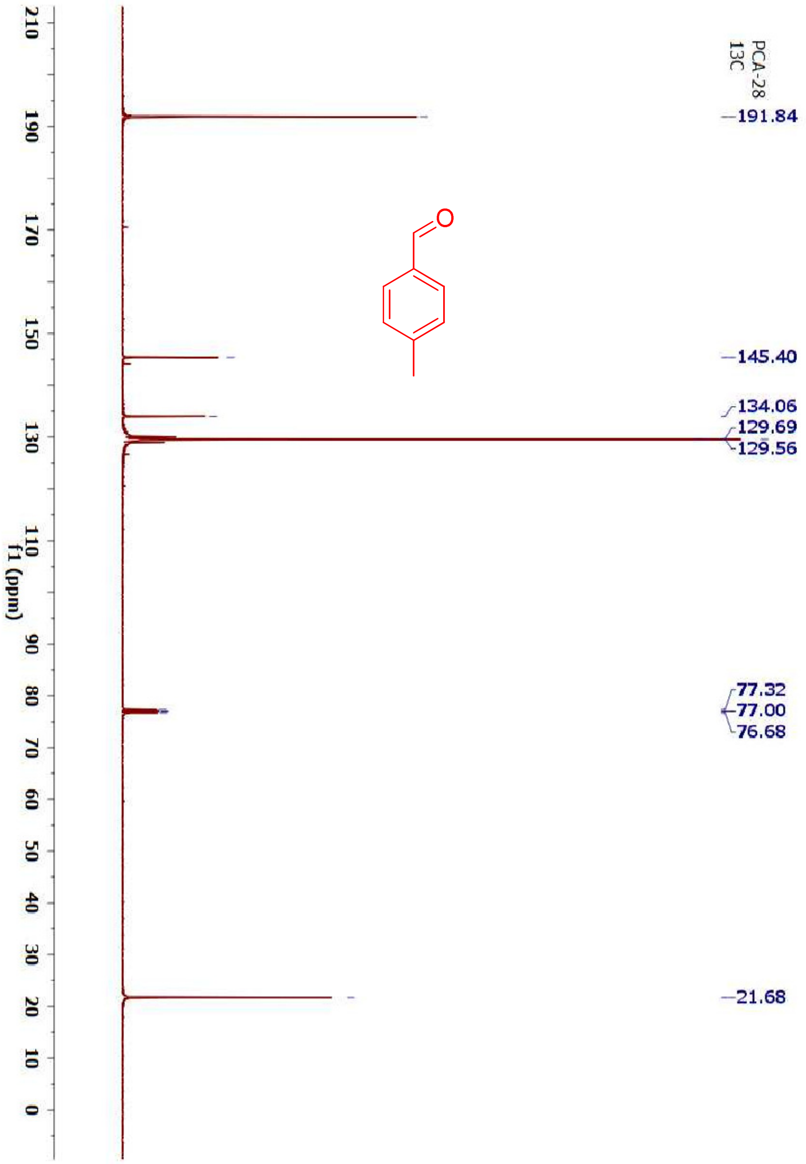
MeO
MeO
O
196.75
153.22
148.91
130.41
123.21
109.99
109.87
77.32
77.00
76.68
55.98
55.89
26.11
210
190
170
150
130
110
f1 (ppm)
90
80
70
60
50
40
30
20
10
0

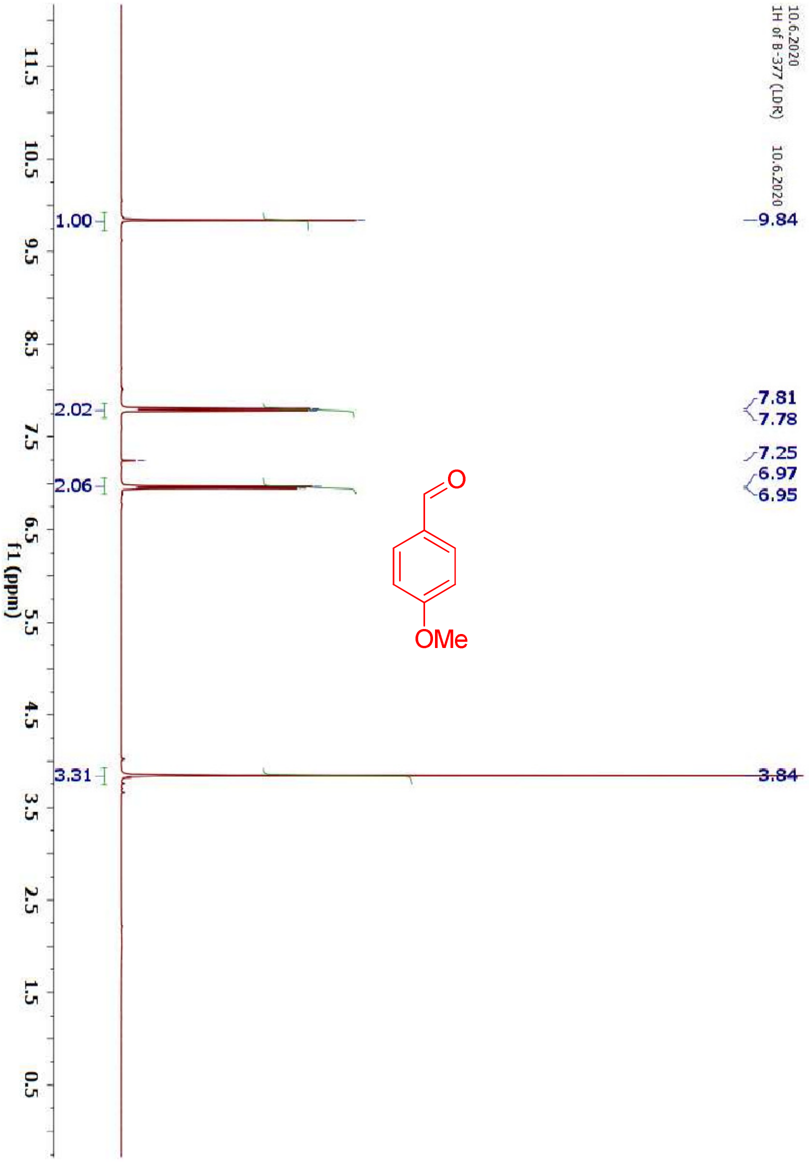


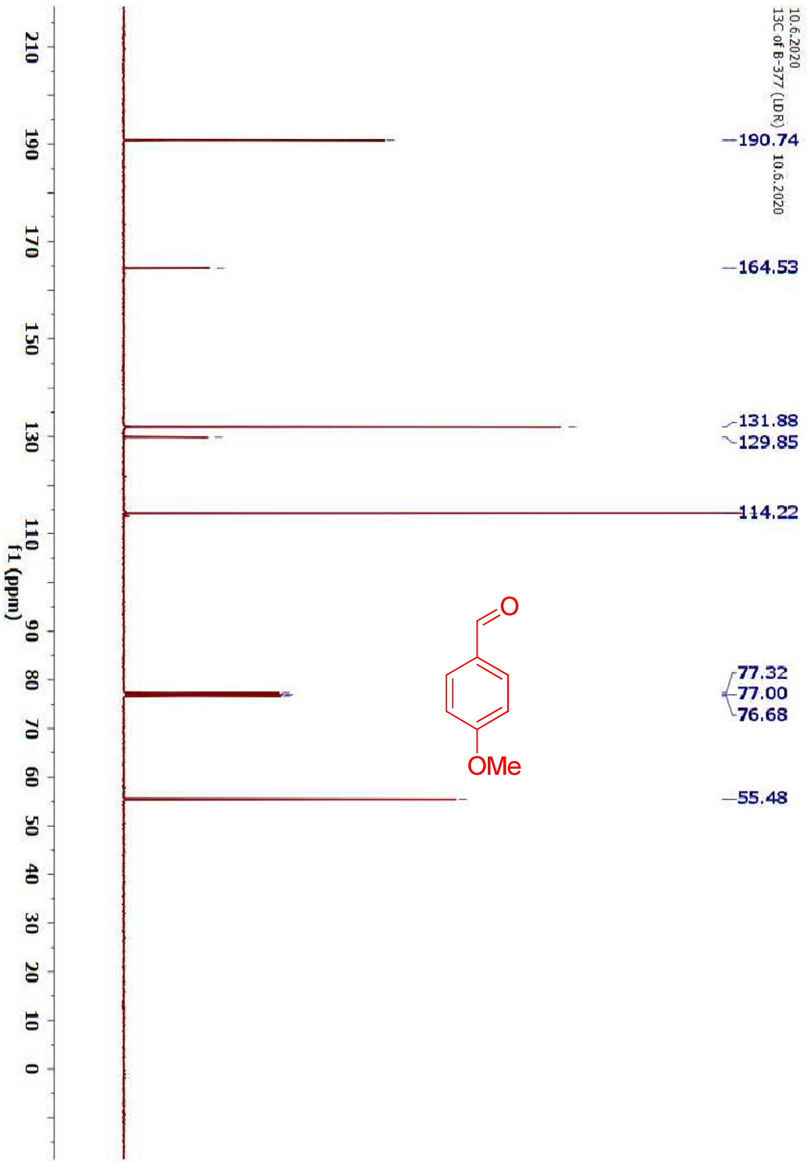
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
1.06
2.03
0.96
2.00
9.95
7.82
7.82
7.82
7.82
7.81
7.80
7.80
7.57
7.56
7.54
7.54
7.47
7.47
7.46
7.45
7.44
O

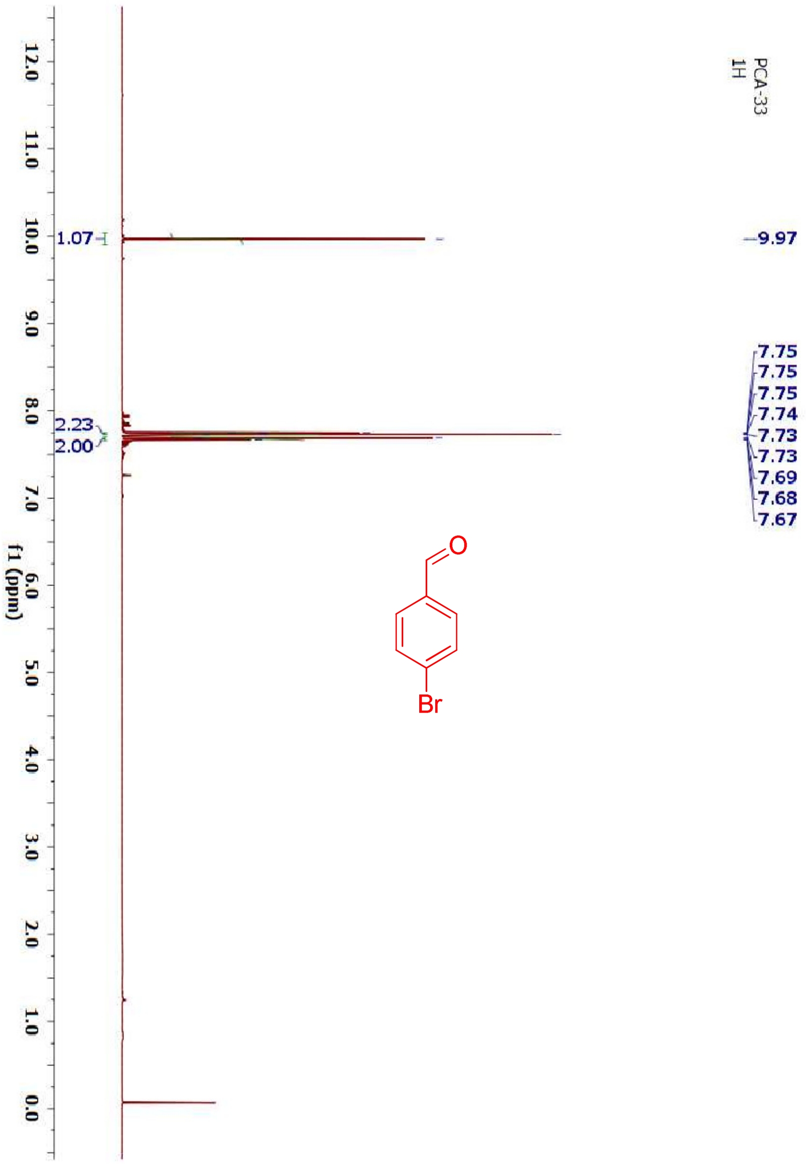

PCA-27
13C
192.17
136.19
134.24
134.19
129.89
129.50
128.78
128.22
77.32
77.00
76.68
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

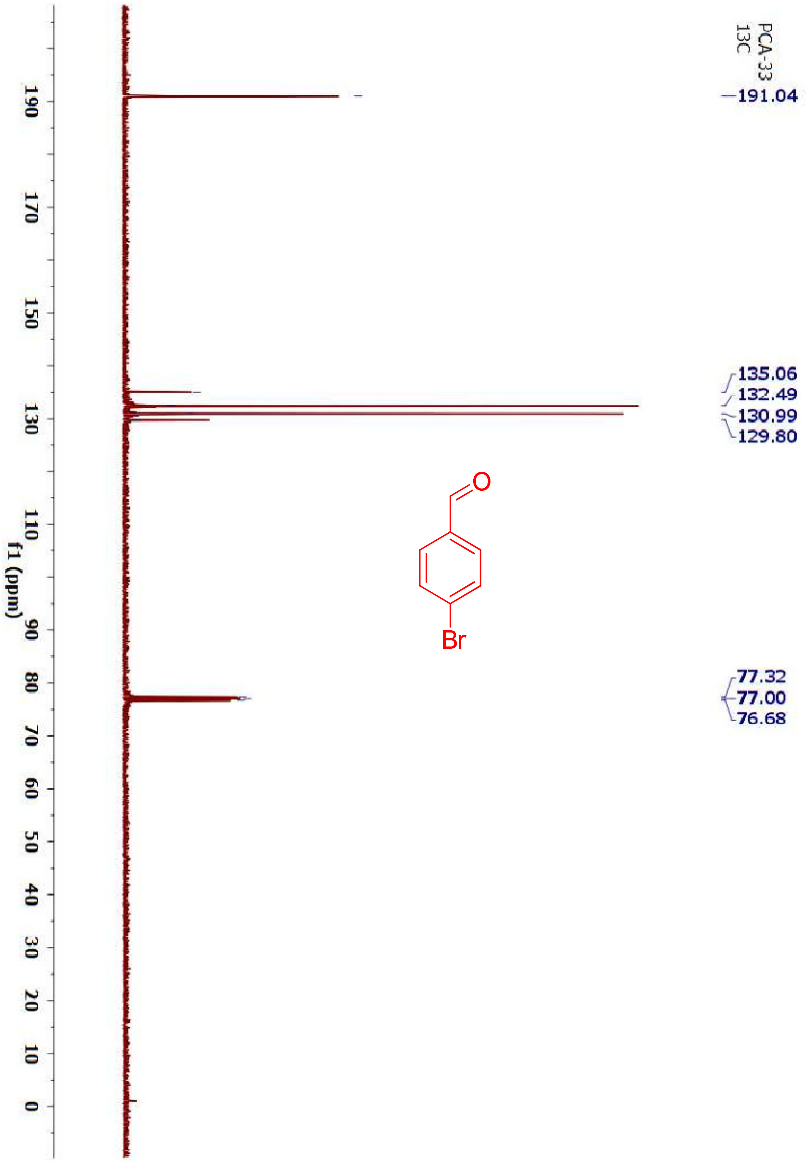

PCA-28
1H
9.91
7.74
7.71
7.28
7.28
7.27
7.27
7.26
2.38
0.95
2.00
1.90
3.36
O
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

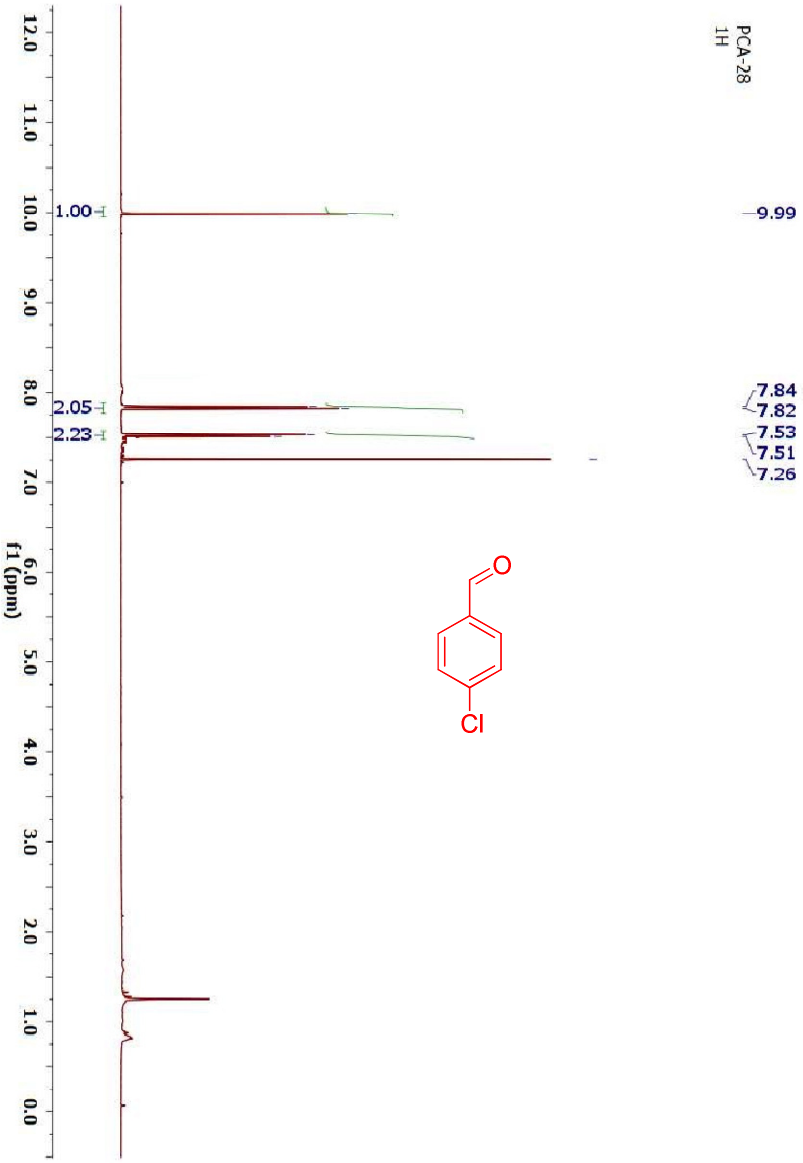

PCA-28
13C
191.84
145.40
134.06
129.69
129.56
77.32
77.00
76.68
21.68
210
190
170
150
130
110
f1 (ppm)
90
80
70
60
50
40
30
20
10
0
O

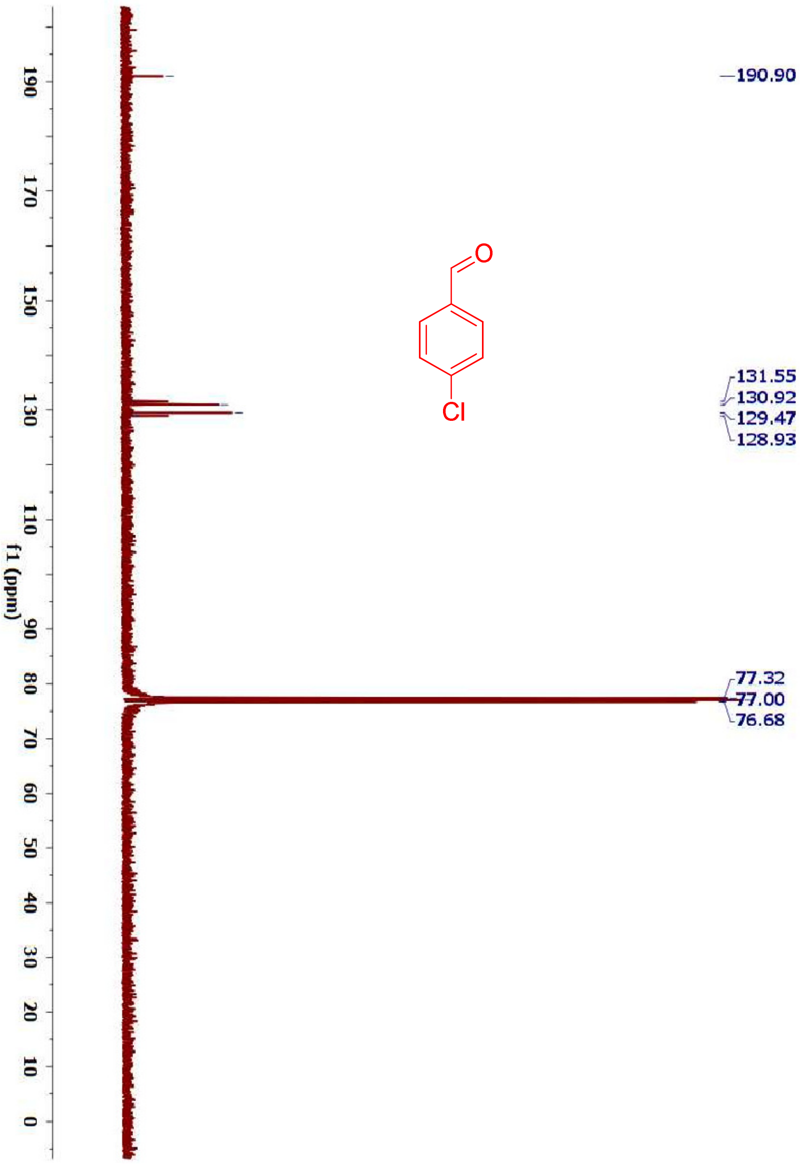

10.6.2020
1H of B-377 (LDR)
10.6.2020
9.84
7.81
7.78
7.25
6.97
6.95
3.84
1.00
2.02
2.06
3.31
O
OMe
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


10.6.2020
13C of B-377 (LDR) 10.6.2020
190.74
164.53
131.88
129.85
114.22
77.32
77.00
76.68
55.48
O
OMe
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


PCA-33
1H
9.97
7.75
7.75
7.75
7.74
7.73
7.73
7.69
7.68
7.67
1.07
2.23
2.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
O
Br


PCA-33
13C
191.04
135.06
132.49
130.99
129.80
77.32
77.00
76.68
O
Br
190
170
150
130
110
f1 (ppm)
90
80
70
60
50
40
30
20
10
0


PCA-28
1H
9.99
7.84
7.82
7.53
7.51
7.26
1.00
2.05
2.23
12.0
11.0
10.0
9.0
8.0
7.0
6.0
f1 (ppm)
5.0
4.0
3.0
2.0
1.0
0.0
O
Cl


190.90
131.55
130.92
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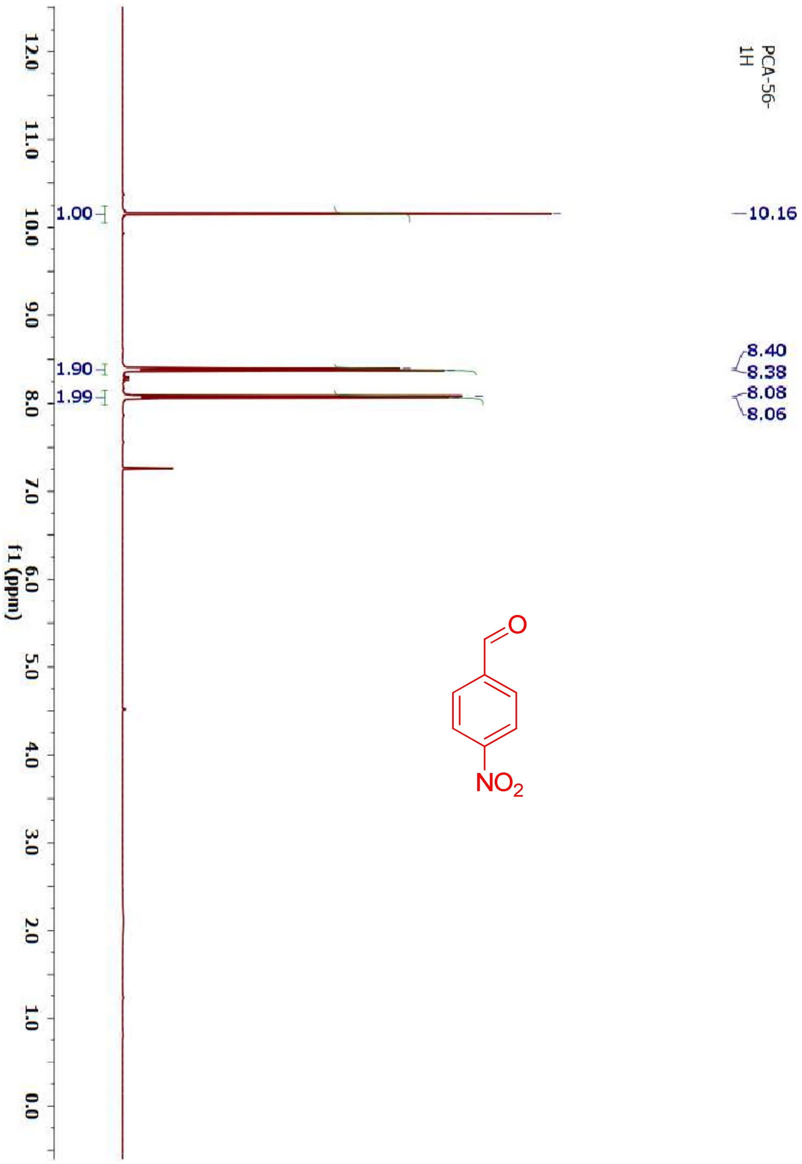
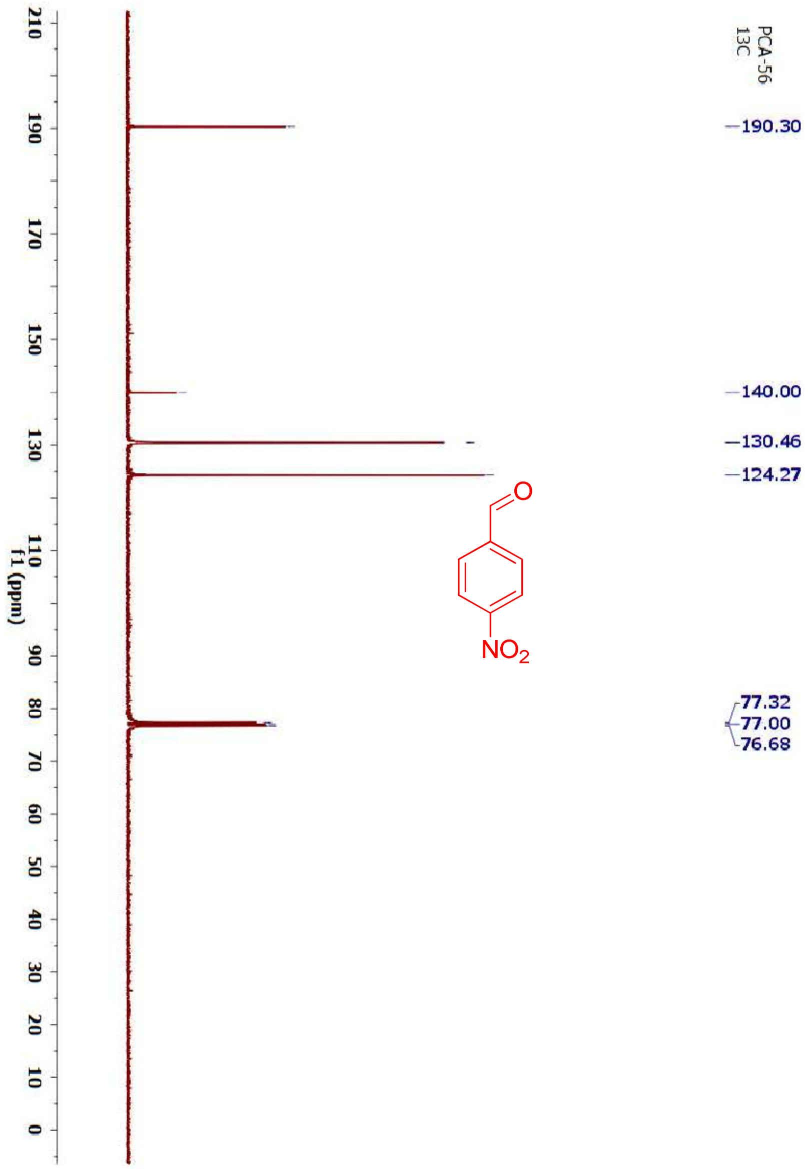
77.32
77.00
76.68
O
Cl
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


PCA-56-
1H
10.16
8.40
8.38
8.08
8.06
1.00
1.90
1.99
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
O
NO2


PCA-56
13C
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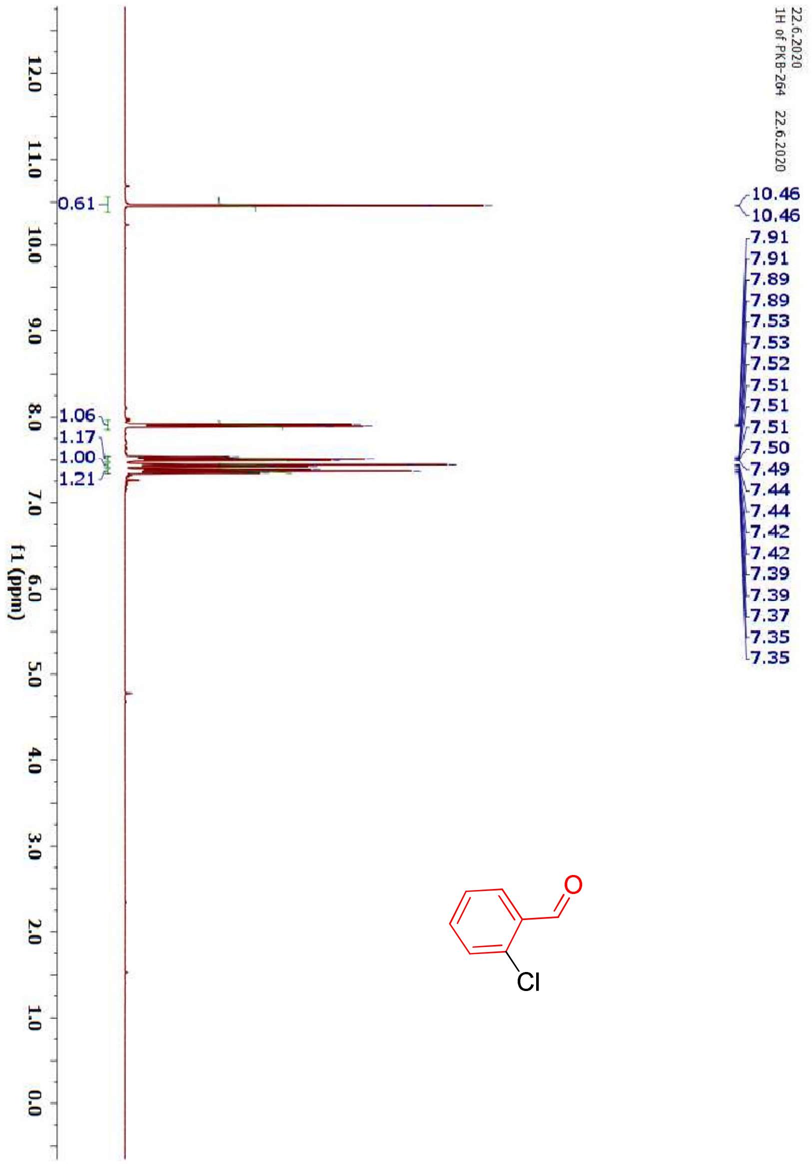
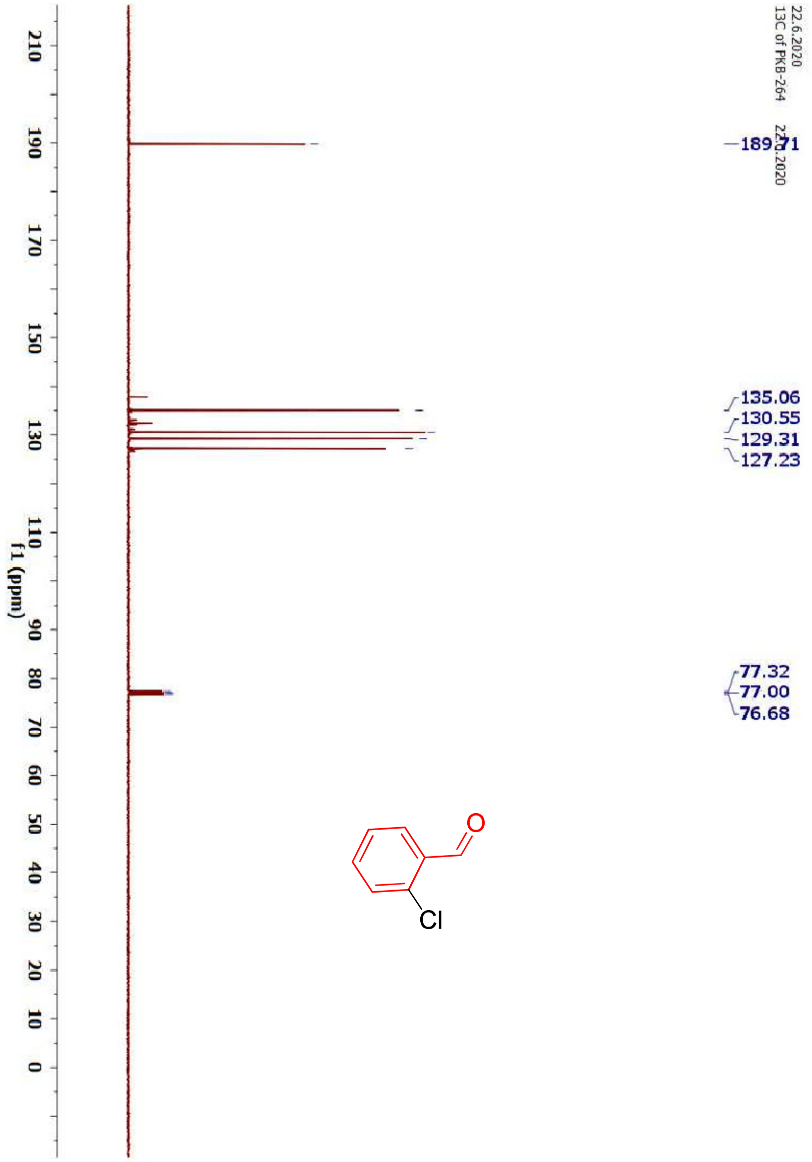
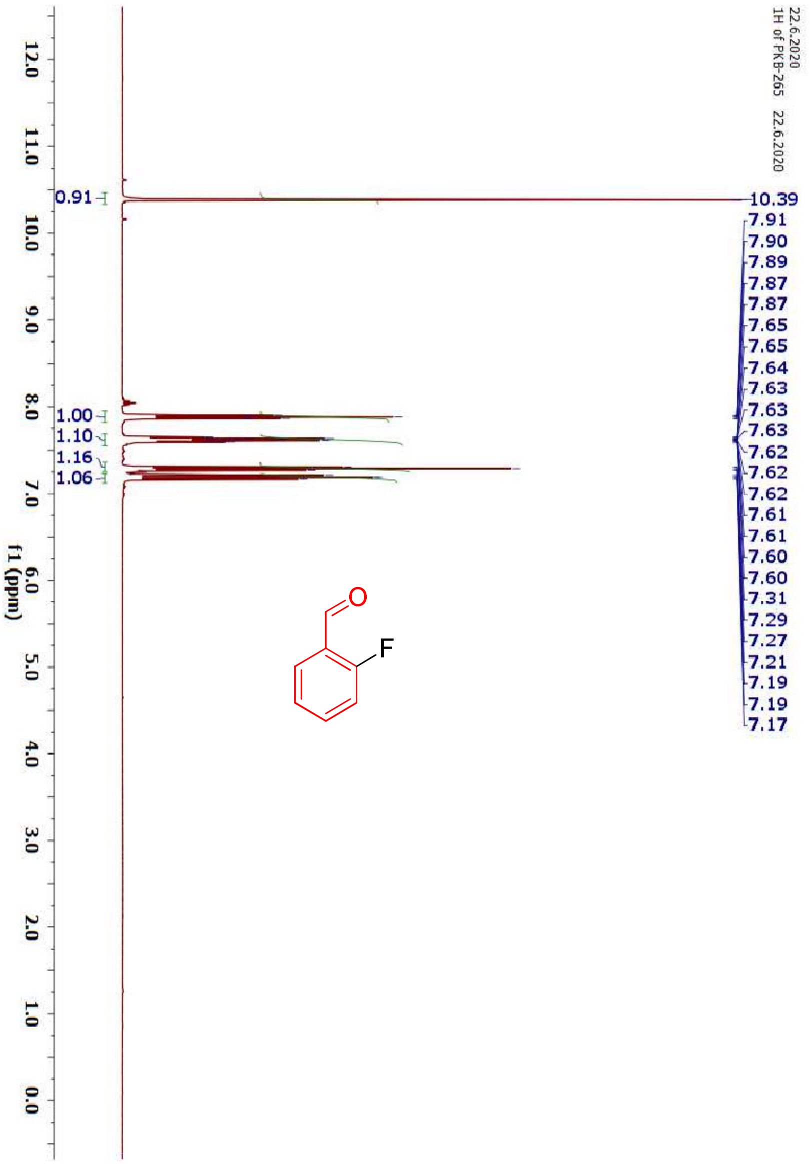
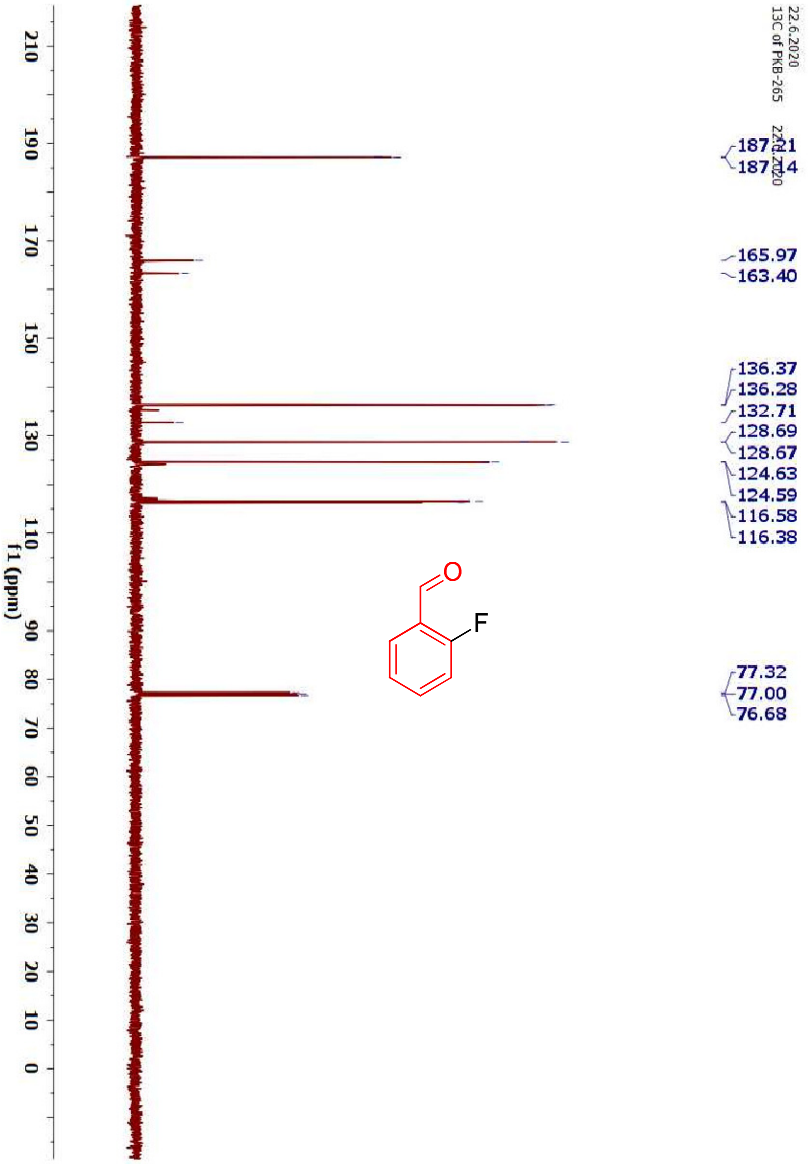
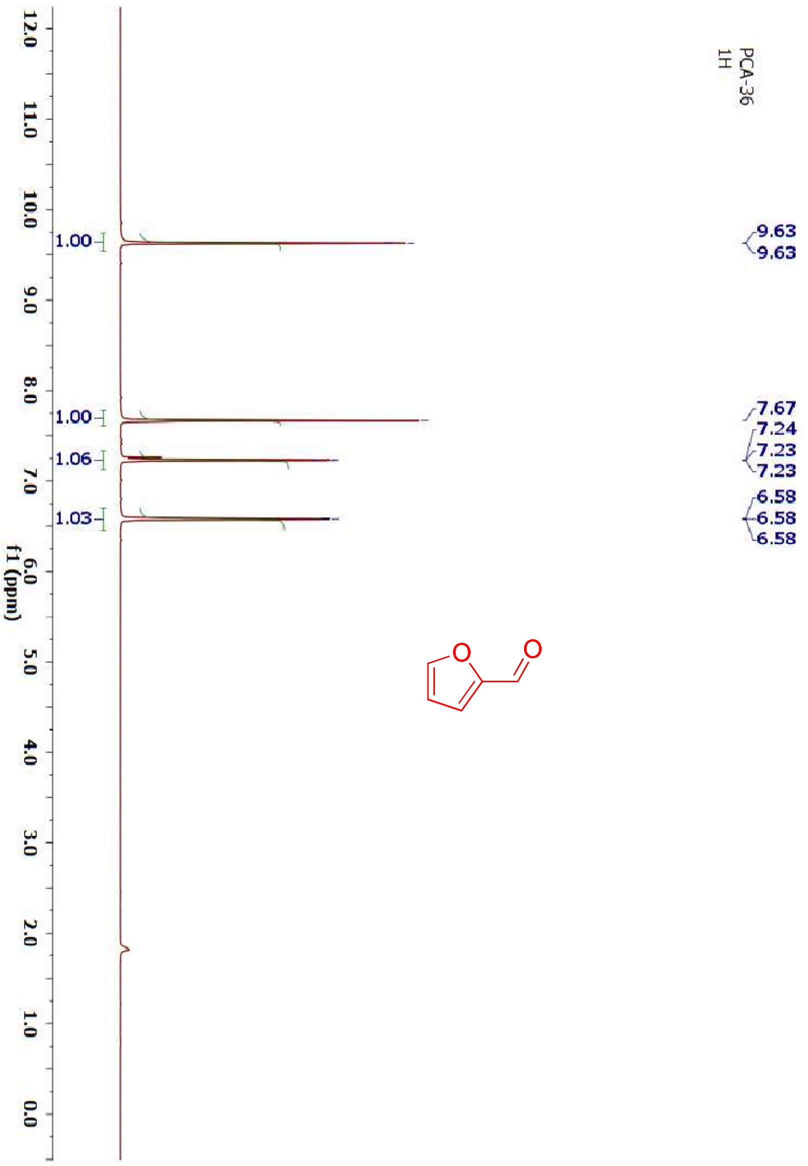
140.00
130.46
124.27
77.32
77.00
76.68
O
NO2
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

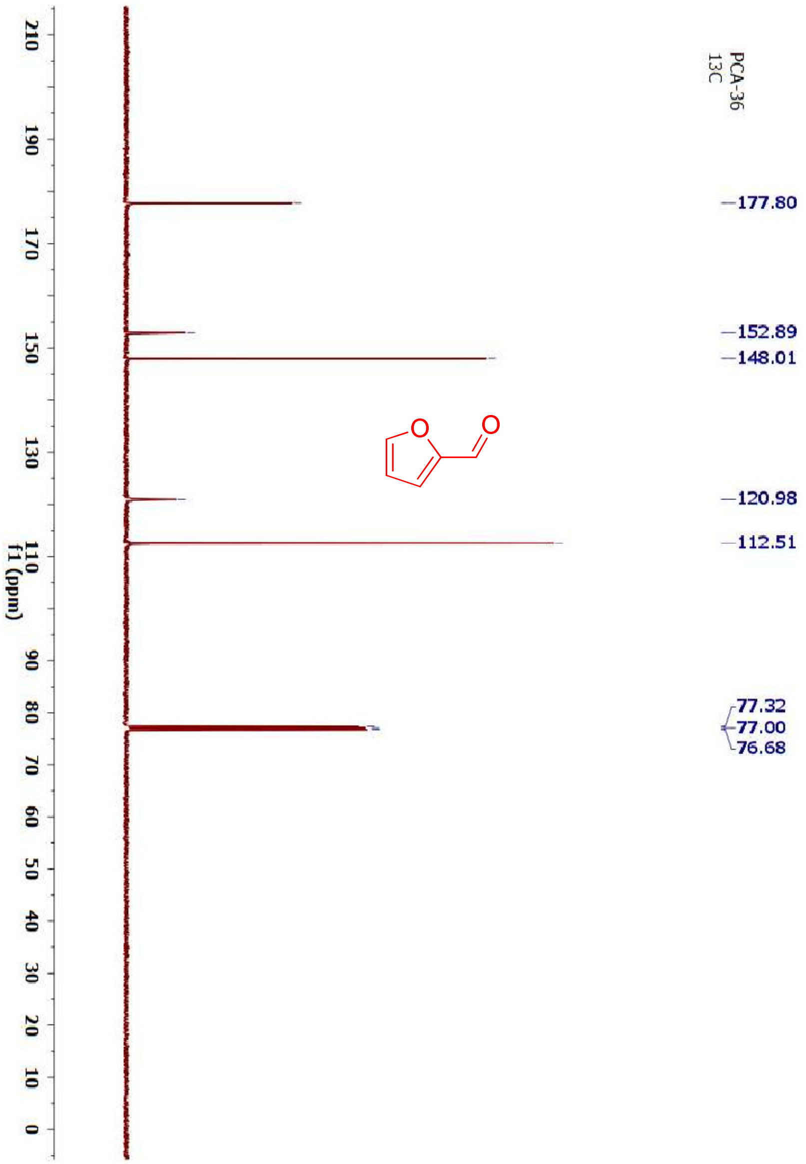

22.6.2020
1H of PKB-264 22.6.2020
10.46
10.46
7.91
7.91
7.89
7.89
7.53
7.53
7.52
7.51
7.51
7.51
7.50
7.49
7.44
7.44
7.42
7.42
7.39
7.39
7.37
7.35
7.35
0.61
1.06
1.17
1.00
1.21
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
O
Cl

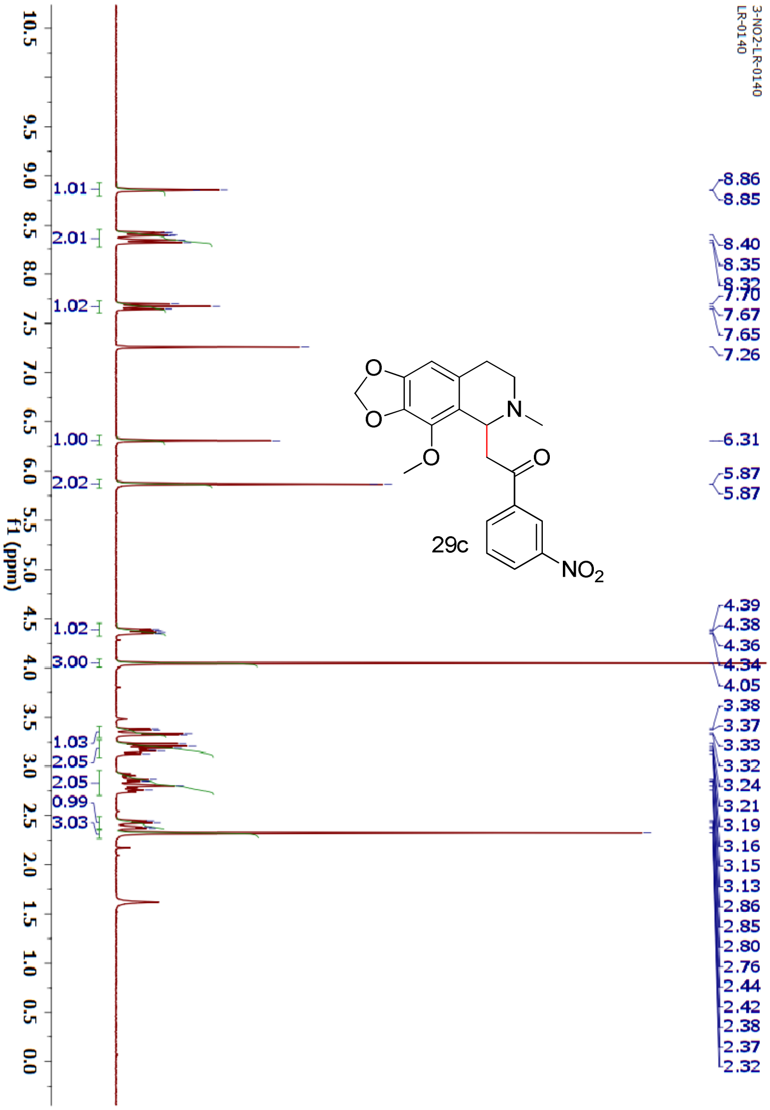

22.6.2020
13C of PKB-264
22.6.2020
189.71
135.06
130.55
129.31
127.23
77.32
77.00
76.68
O
Cl
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

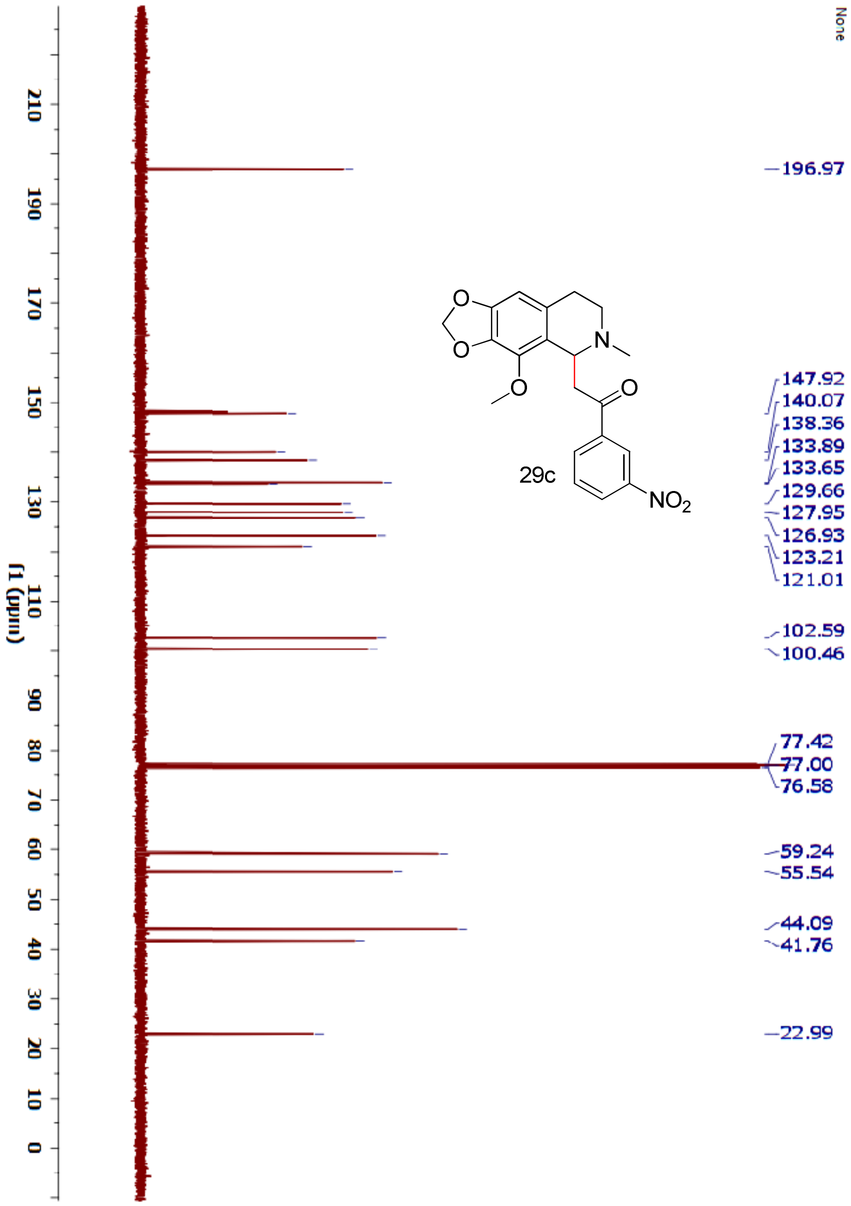

22.6.2020
1H of PKB-265 22.6.2020
10.39
7.91
7.90
7.89
7.87
7.87
7.65
7.65
7.64
7.63
7.63
7.63
7.62
7.62
7.62
7.61
7.61
7.60
7.60
7.31
7.29
7.27
7.21
7.19
7.19
7.17
0.91
1.00
1.10
1.16
1.06
O
F
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


22.6.2020
13C of PKB-265
187.21
187.14
165.97
163.40
136.37
136.28
132.71
128.69
128.67
124.63
124.59
116.58
116.38
77.32
77.00
76.68
O
F
210
190
170
150
130
110
f1 (ppm)
90
80
70
60
50
40
30
20
10
0

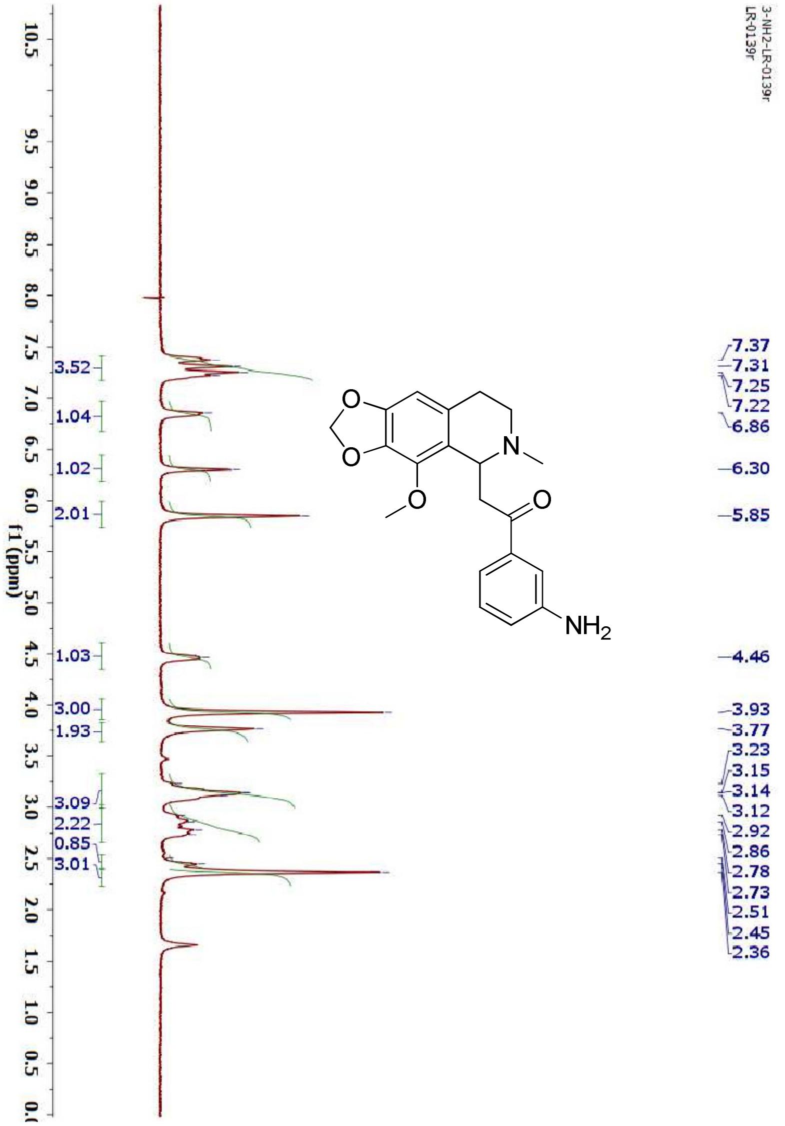

PCA-36
1H
9.63
9.63
7.67
7.24
7.23
7.23
6.58
6.58
6.58
1.00
1.00
1.06
1.03
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
O
O

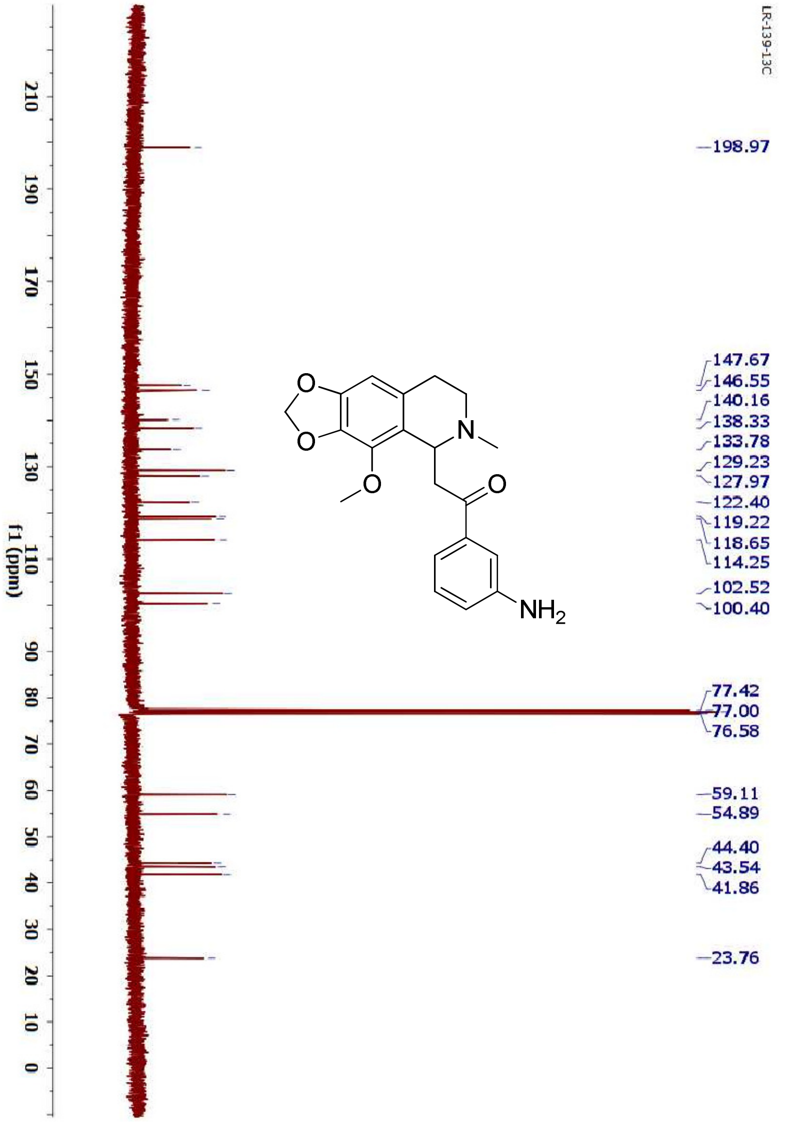

PCA-36
13C
177.80
152.89
148.01
120.98
112.51
77.32
77.00
76.68
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

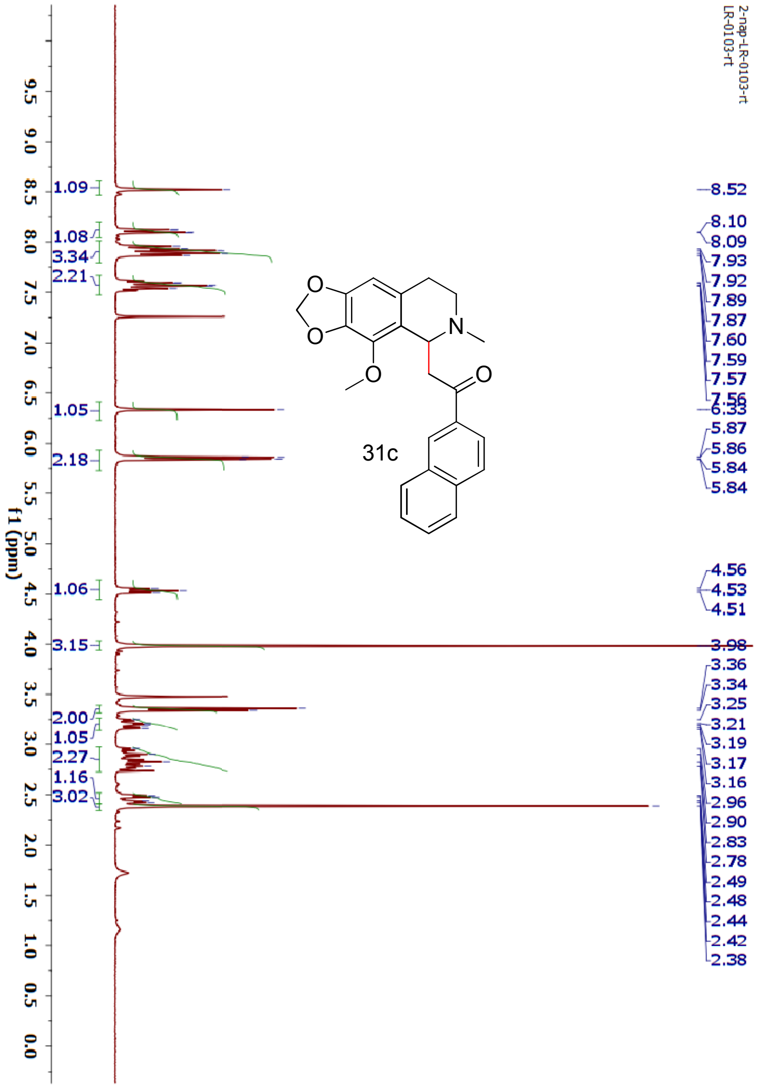

3-NO2-LR-0140
LR-0140
29c
NO2
N
O
O
O
O
8.86
8.85
8.40
8.35
8.32
7.70
7.67
7.65
7.26
6.31
5.87
5.87
4.39
4.38
4.36
4.34
4.05
3.38
3.37
3.33
3.32
3.24
3.21
3.19
3.16
3.15
3.13
2.86
2.85
2.80
2.76
2.44
2.42
2.38
2.37
2.32
1.01
2.01
1.02
1.00
2.02
1.02
3.00
1.03
2.05
2.05
0.99
3.03
10.5
9.5
9.0
8.5
8.0
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
f1 (ppm)

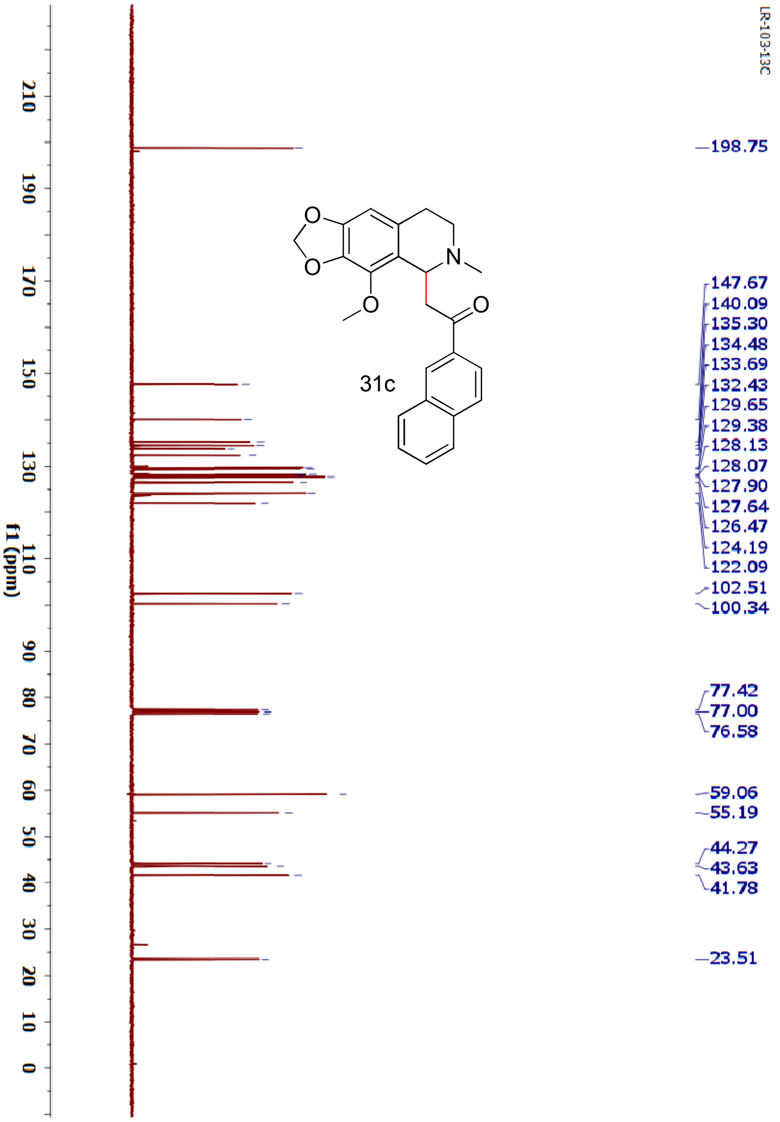

None
196.97
147.92
140.07
138.36
133.89
133.65
129.66
127.95
126.93
123.21
121.01
102.59
100.46
77.42
77.00
76.58
59.24
55.54
44.09
41.76
22.99
210
190
170
150
130
110
f1 (ppm)
90
80
70
60
50
40
30
20
10
0
O
O
N
O
O
NO_2

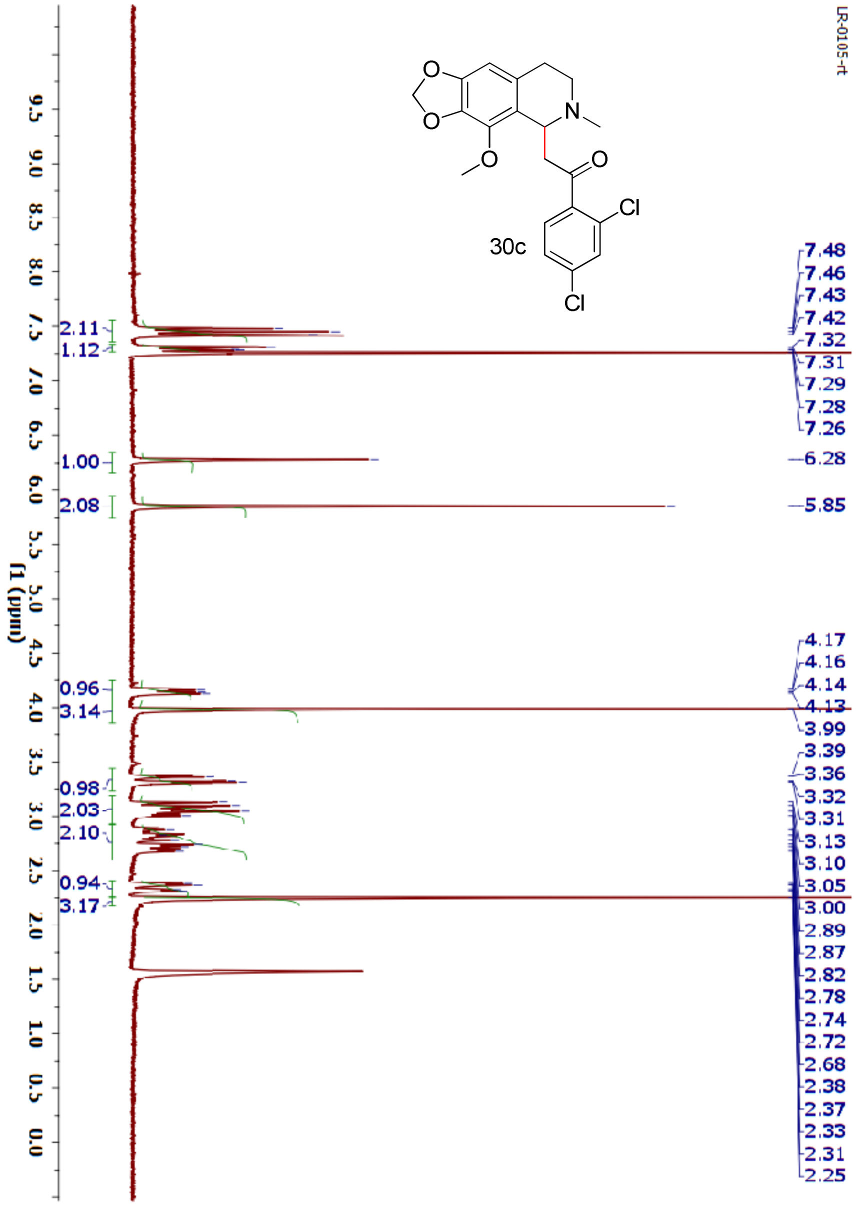
29c

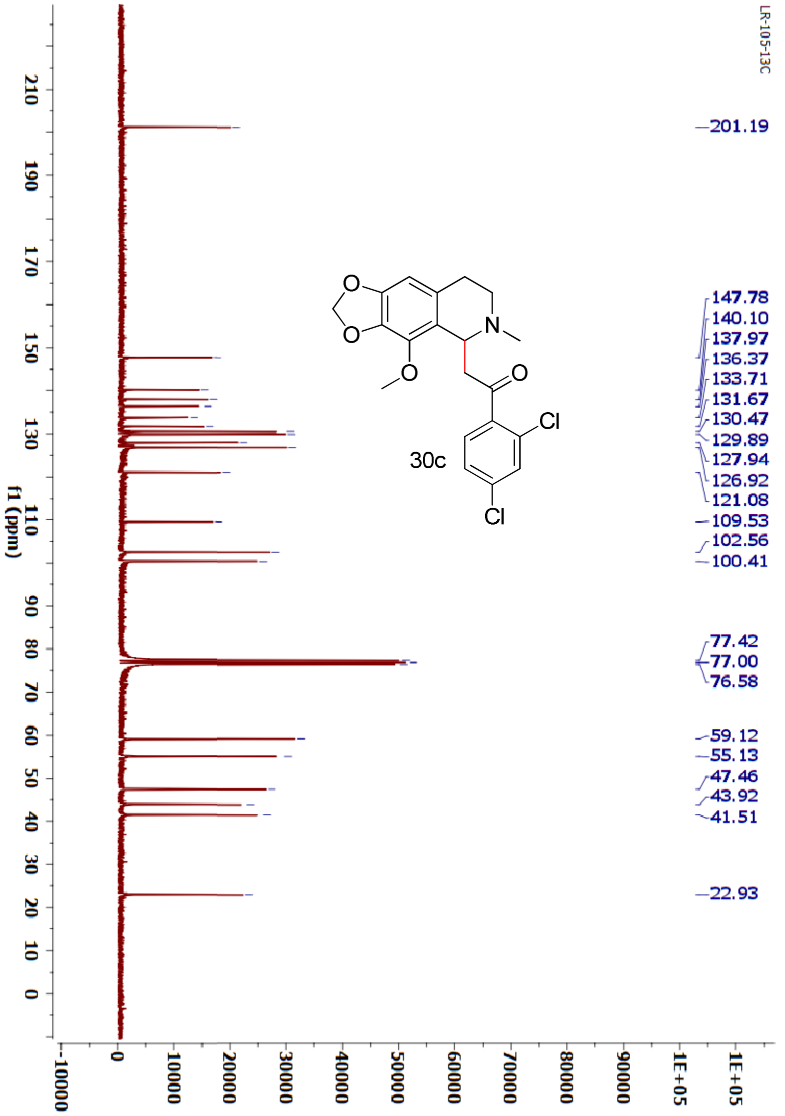

3-NH2-LR-0139r
LR-0139r
7.37
7.31
7.25
7.22
6.86
6.30
5.85
4.46
3.93
3.77
3.23
3.15
3.14
3.12
2.92
2.86
2.78
2.73
2.51
2.45
2.36
3.52
1.04
1.02
2.01
1.03
3.00
1.93
3.09
2.22
0.85
3.01
f1 (ppm)
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
O
O
N
O
O
NH2

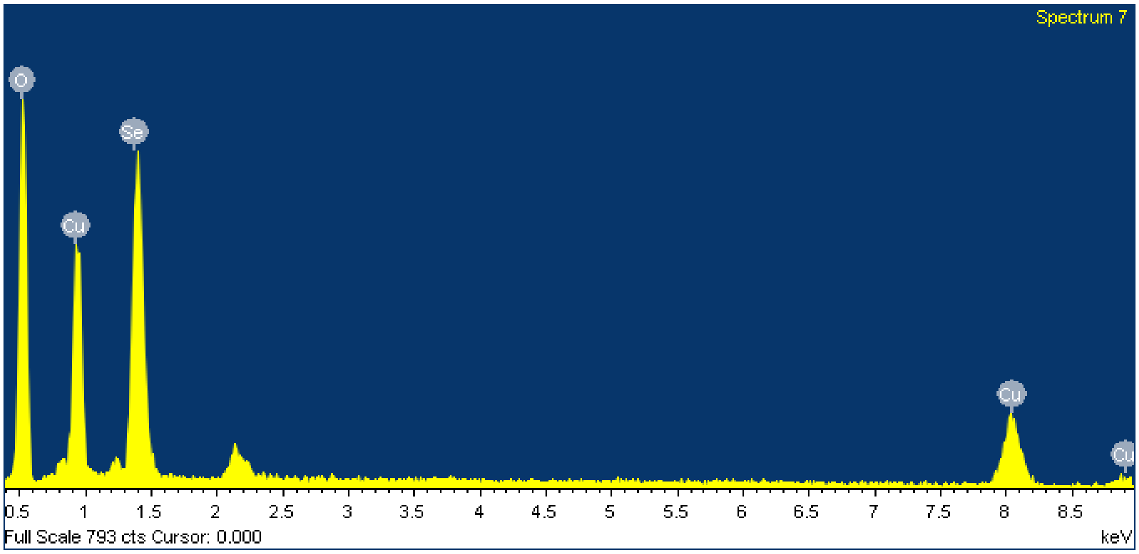

LR-139-13C
198.97
147.67
146.55
140.16
138.33
133.78
129.23
127.97
122.40
119.22
118.65
114.25
102.52
100.40
77.42
77.00
76.58
59.11
54.89
44.40
43.54
41.86
23.76
210
190
170
150
130
110
f1 (ppm)
90
80
70
60
50
40
30
20
10
0
O
O
N
O
O
NH2

2-nap-LR-0103-rt
LR-0103-rt
31c
8.52
8.10
8.09
7.93
7.92
7.89
7.87
7.60
7.59
7.57
7.56
6.33
5.87
5.86
5.84
5.84
4.56
4.53
4.51
3.98
3.36
3.34
3.25
3.21
3.19
3.17
3.16
2.96
2.90
2.83
2.78
2.49
2.48
2.44
2.42
2.38
1.09
1.08
3.34
2.21
1.05
2.18
1.06
3.15
2.00
1.05
2.27
1.16
3.02
9.5
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
f1 (ppm)
O
O
O
N
O


LR-103-13C
210
190
170
150
130
110
f1 (ppm)
90
80
70
60
50
40
30
20
10
0
198.75
147.67
140.09
135.30
134.48
133.69
132.43
129.65
129.38
128.13
128.07
127.90
127.64
126.47
124.19
122.09
102.51
100.34
77.42
77.00
76.58
59.06
55.19
44.27
43.63
41.78
23.51
O
O
O
N
O
31c

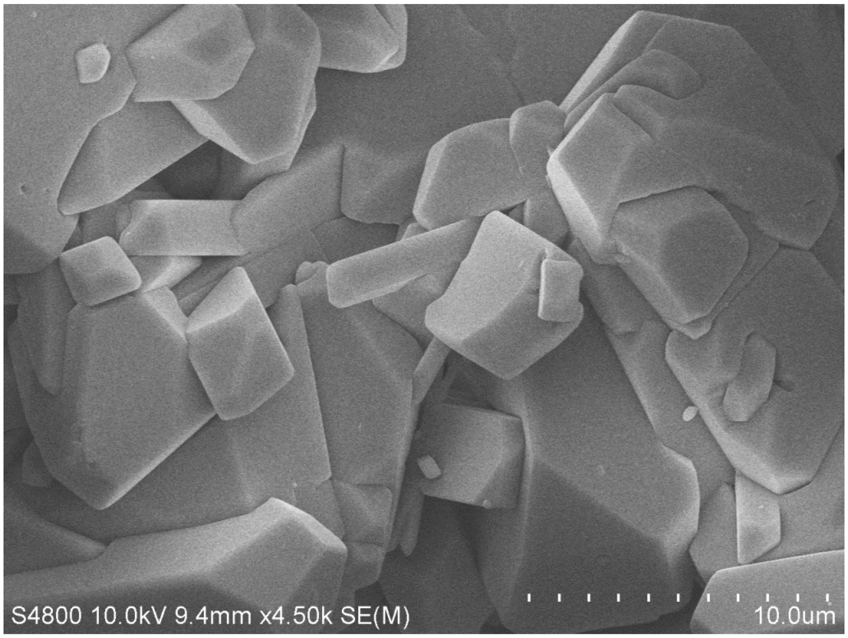

LR-0105-rt
30c
O
O
O
N
O
Cl
Cl
7.48
7.46
7.43
7.42
7.32
7.31
7.29
7.28
7.26
6.28
5.85
4.17
4.16
4.14
4.13
3.99
3.39
3.36
3.32
3.31
3.13
3.10
3.05
3.00
2.89
2.87
2.82
2.78
2.74
2.72
2.68
2.38
2.37
2.33
2.31
2.25
2.11
1.12
1.00
2.08
0.96
3.14
0.98
2.03
2.10
0.94
3.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


LR-105-13C
30c
O
O
N
O
O
Cl
Cl
201.19
147.78
140.10
137.97
136.37
133.71
131.67
130.47
129.89
127.94
126.92
121.08
109.53
102.56
100.41
77.42
77.00
76.58
59.12
55.13
47.46
43.92
41.51
22.93
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
-10000
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
1E+05
1E+05

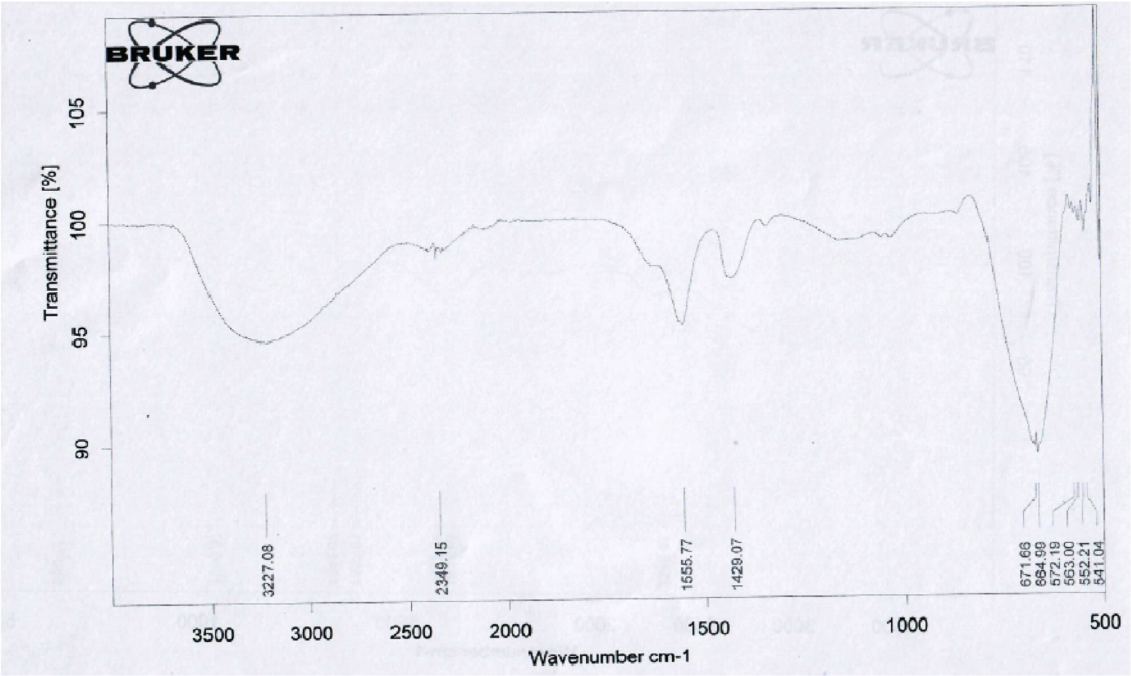


Fugure 1: EDXRF spectra of $CuSeO_3$. $2H_2O$

Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
O K	34.83	1.2604	37.44	0.60	72.66
Cu L	12.66	0.5983	28.68	0.59	14.02
Se L	13.69	0.5471	33.88	0.58	13.32
Totals			100.00		

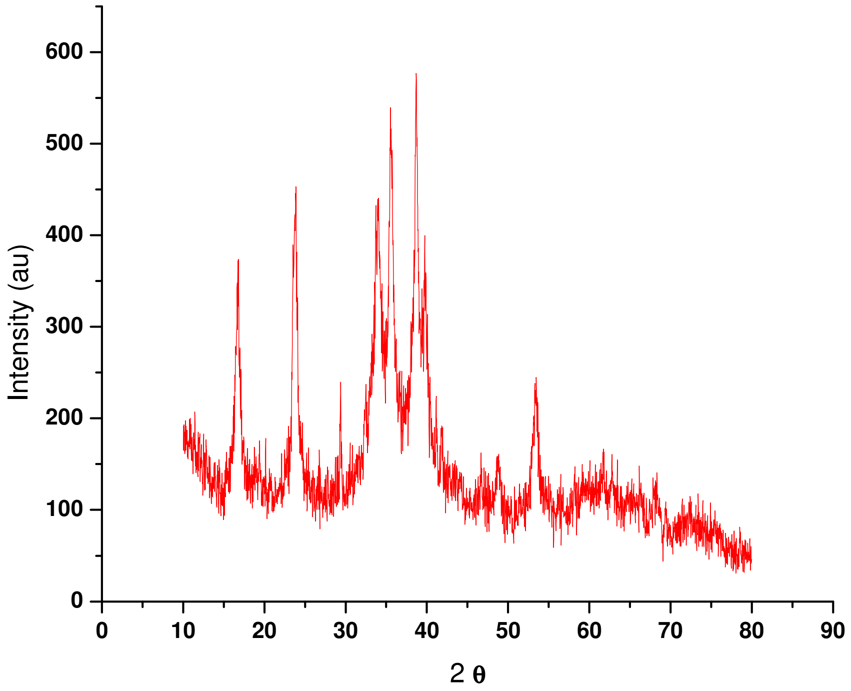


Fugure 2: Catalytic Surface of CuSeO$_3$. 2H$_2$O in FE-SEM



IR characterisation: 3327 cm^{-1} (O-H vibration), 1555 cm^{-1} (Se-O streching), 1429 cm^{-1} (Se=O streching), 671 cm^{-1} (Cu-O streching), 584 cm^{-1} (Cu-O-Se streching frequency).

Reference: a) R.J.M. Konings, A.S. Booij , A. Kovacs, Chemical Physics Letters **1998**, 292, 447–45; b) N. Dukstiene, L. Tatariskinaite, M. Andrulevicius, Materials Science-Poland, **2010**, 28, 93-103.



The X-ray diffraction analysis has been used to study the crystal structure of materilas. The powder XRD patterns at room temperature were recorded by using Rigaku model TTRX-III equipped with rotating anode-based Cu-Kα radiation (λ= 1.5418 A^o). X-ray diffractometer was operating at 100mA and 50kV. XRD machine was operated with the following conditions: (i) 2θ-θ scanning mode, (ii) fixed monochromater (iii) continuous scanning, and (iv) measurement angle between 10-80^o with 0.02^o step.