

# Silver-Catalysed Protodecarboxylation of Carboxylic Acids

Lukas J. Goßen, Christophe Linder, Nuria Rodríguez, Paul P. Lange and Andreas Fromm

*FB Chemie – Organische Chemie, TU Kaiserslautern,*

*Erwin-Schrödinger-Strasse, Geb. 54, 67663 Kaiserslautern, Germany*

## Supporting Information

General Procedures	S2-S5
Spectroscopic data	S6-S18
Absolute energies of the calculated structures	S19
Optimized geometries of the calculated structures	S22-S29
References	S34

## Experimental procedures and data

**General Methods.** Reactions were performed in oven-dried glassware under a nitrogen atmosphere containing a Teflon-coated stirrer bar and dry septum. For the exclusion of atmospheric oxygen from the reaction media, three freeze-pump thaw cycles were performed before the reagents were mixed. Solvents were purified by standard procedures prior to use. All reactions were monitored by GC using *n*-tetradecane as an internal standard. Response factors of the products with regard to *n*-tetradecane were obtained experimentally by analyzing known quantities of the substances. GC analyses were carried out using an HP-5 capillary column (Phenyl Methyl Siloxane 30 m x 320 x 0.25, 100/2.3-30-300/3) and a time program beginning with 2 min at 60 °C followed by 30 °C/min ramp to 300 °C, then 3 min at this temp. NMR spectra were obtained on Bruker AMX 400 or on Bruker Avance 600 systems using CDCl<sub>3</sub>, as solvent, with proton and carbon resonances at 400/600 MHz and 101/151 MHz, respectively. Mass spectral data were acquired on a GC-MS Saturn 2100 T (Varian).

1-Methyl-2-pyrrolidone (NMP) was dried by removing water as a toluene azeotrope. All inorganic bases were dried for 2 h *in vacuo* at room temperature prior to use. All other compounds are commercially available and were used without further purification.

**General procedure for the decarboxylation study (Table 3).** An oven-dried vessel was charged with the carboxylic acid (**1a-t**) (2.00 mmol), AgOAc (33.7 mg, 0.20 mmol) and K<sub>2</sub>CO<sub>3</sub> (41.5 mg, 0.30 mmol). After flushing the vessel with alternating vacuum and nitrogen purge cycles, degassed NMP (4 mL) was added *via* syringe and the resulting mixture was stirred at 120 °C for 16 h. Then, it was allowed to cool to room temperature, diluted with diethyl ether (2 mL), poured into aqueous HCl (1N, 2 mL) and extracted repeatedly with diethyl ether (2 mL portions). The combined organic layers were washed with aqueous solution of NaHCO<sub>3</sub> (4 mL) and brine (4 mL), dried over MgSO<sub>4</sub> and filtered. The corresponding arene (**2a-j, l, m, o, p**) was obtained in pure form after removal of the solvent by distillation over a Vigreux column.

**Synthesis of anisole (2a).** Compound **2a** was prepared from 2-methoxybenzoic acid (**1a**) (304 mg, 2.00 mmol) yielding **2a** as a colorless liquid (178 mg, 83 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for anisole [100-66-3]. Compound **2a** was also prepared from 3-methoxybenzoic acid (**1w**) (152 mg, 1.00 mmol) and 4-methoxybenzoic acid (**1x**) (152 mg, 1.00 mmol), performing the reaction at 160 °C and using *n*-tetradecane (50 µL) as an internal gas chromatographic standard. The yield of compound **2a** was determined by quantitative GC to be 38 % and 14 % respectively, based on a response factor obtained using commercial anisole [100-66-3].

**Synthesis of nitrobenzene (2b).** Compound **2b** was prepared from 2-nitrobenzoic acid (**1b**) (334 mg, 2.00 mmol) yielding **2b** as a yellow liquid (225 mg, 92 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for nitrobenzene [98-95-3].

**Synthesis of 4-nitroanisole (2c).** Compound **2c** was prepared from 5-methoxy-2-nitrobenzoic acid (**1c**) (394 mg, 2.00 mmol) yielding **2c** as a yellow solid (m.p. 51-53 °C, 270 mg, 88 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for 4-nitroanisole [100-17-4].

**Synthesis of 1,2,4-trimethoxybenzene (2d).** Compound **2d** was prepared from 2,4,5-trimethoxybenzoic acid (**1d**) (424 mg, 2.00 mmol) yielding **2d** as a colorless liquid (145 mg, 43 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for 1,2,4-trimethoxybenzene [135-77-3].

**Synthesis of 1,3-dimethoxybenzene (2e).** Compound **2e** was prepared from 2,4-dimethoxybenzoic acid (**1e**) (364 mg, 2.00 mmol) yielding **2e** as a colorless liquid (246 mg, 89 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for 1,3-dimethoxybenzene [151-10-0]. Compound **2e** was also prepared from 2,6-dimethoxybenzoic acid (**1f**) (364 mg, 2.00 mmol) to give compound **2e** in 87 % yield (239 mg).

**Synthesis of bromobenzene (2f).** Compound **2f** was prepared from 2-bromobenzoic acid (**1g**) (402 mg, 2.00 mmol) yielding **2f** as a colorless liquid (237 mg, 76 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for bromobenzene [108-86-1].

**Synthesis of 4-bromoveratrole (2g).** Compound **2g** was prepared from 2-bromo-4,5-dimethoxybenzoic acid (**1h**) (522 mg, 2.00 mmol) yielding **2g** as a colorless liquid (412 mg, 95 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for 4-bromoveratrole [2859-78-1].

**Synthesis of 1,3-dichlorobenzene (2h).** Compound **2h** was prepared from 2,6-dichlorobenzoic acid (**1i**) (382 mg, 2.00 mmol) yielding **2h** as a colorless liquid (223 mg, 76 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for 1,3-dichlorobenzene [541-73-1]. Compound **2h** was also prepared from 2,4-dichlorobenzoic acid (**1j**) (328 mg, 2.00 mmol) to give compound **2h** in 74 % yield (218 mg).

**Synthesis of 1-chloro-4-nitrobenzene (2i).** Compound **2i** was prepared from 2-chloro-5-nitrobenzoic acid (**1k**) (403 mg, 2.00 mmol) yielding **2i** as a colorless liquid (268 mg, 85 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for 1-chloro-4-nitrobenzene [100-00-5].

**Synthesis of methyl phenyl sulfone (2j).** Compound **2j** was prepared from 2-(methylsulfonyl)benzoic acid (**1l**) (400 mg, 2.00 mmol) yielding **2j** as a white solid (m.p. 87-88 °C, 280 mg, 90 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for methyl phenyl sulfone [3112-85-4].

**Synthesis of trifluoromethylbenzene (2k).** Compound **2k** was prepared from 2-(trifluoromethyl)benzoic acid (**1m**) (190 mg, 1.00 mmol) and using *n*-tetradecane (50 µL) as an internal gas chromatographic standard. The yield of compound **2k** was determined by quantitative GC to be 91 %, based on a response factor obtained using commercial trifluoromethylbenzene [98-08-8].

**Synthesis of isopropyl benzoate (2l).** Compound **2l** was prepared from 2-(isopropoxyloxycarbonyl)benzoic acid (**1n**) (416 mg, 2.00 mmol) yielding **2l** as a yellow liquid (234 mg, 71 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for isopropyl benzoate [939-48-0].

**Synthesis of acetophenone (2m).** Compound **2m** was prepared from 2-acetylbenzoic acid (**1o**) (328 mg, 2.00 mmol) yielding **2m** as a yellow liquid (139 mg, 58 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for acetophenone [98-86-2].

**Synthesis of benzonitrile (2n).** Compound **2n** was prepared from 2-cyanobenzoic acid (**1p**) (147 mg, 1.00 mmol) and using *n*-tetradecane (50  $\mu$ L) as an internal gas chromatographic standard. The yield of compound **2n** was determined by quantitative GC to be 11 %, based on a response factor obtained using commercial benzonitrile [100-47-0].

**Synthesis of phenol (2o).** Compound **2o** was prepared from 4-hydroxybenzoic acid (**1q**) (276 mg, 2.00 mmol) yielding **2o** as a yellow liquid (32 mg, 17 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for phenol [108-95-2].

**Synthesis of naphthalene (2p).** Compound **2p** was prepared from 1-naphthoic acid (**1r**) (344 mg, 2.00 mmol) yielding **2p** as a white solid (m.p. 78-80 °C, 115 mg, 45 %). The spectroscopic data (NMR, GC-MS) matched those reported in the literature for naphthalene [91-20-3].

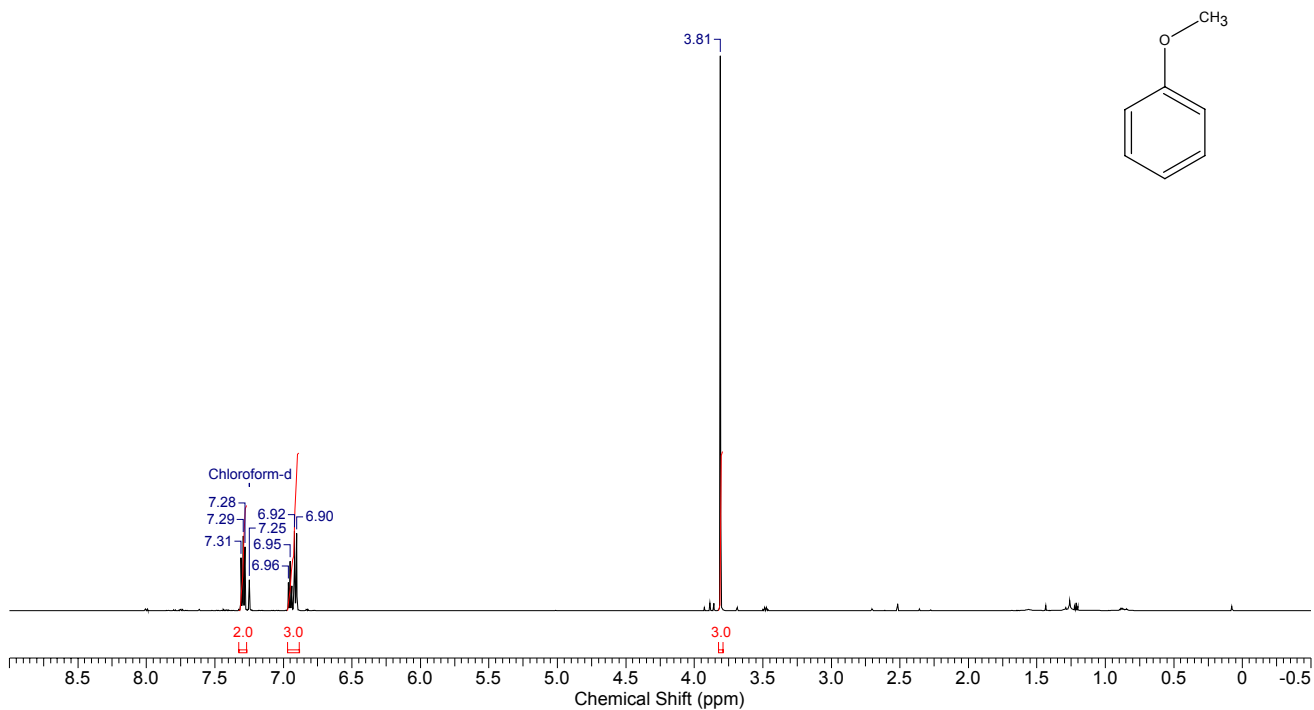
**Synthesis of thiophene (2q).** Compound **2q** was prepared from thiophene-2-carboxylic acid (**1s**) (128 mg, 1.00 mmol) and using *n*-tetradecane (50  $\mu$ L) as an internal gas chromatographic standard. The yield of compound **2q** was determined by quantitative GC to be 80 %, based on a response factor obtained using commercial thiophene [110-02-1]. Compound **2q** was also prepared from thiophene-3-carboxylic acid (**1t**) (128 mg, 1.00 mmol) to give compound **2q** in 36 %.

**Synthesis of styrene (2r).** Compound **2r** was prepared from cinnamic acid (**1u**) (148 mg, 1.00 mmol) in DMAC (4 mL) at 140 °C, and using *n*-tetradecane (50  $\mu$ L) as an internal gas chromatographic standard. The yield of compound **2r** was determined by quantitative GC to be 76 %, based on a response factor obtained using commercial styrene [100-42-5].

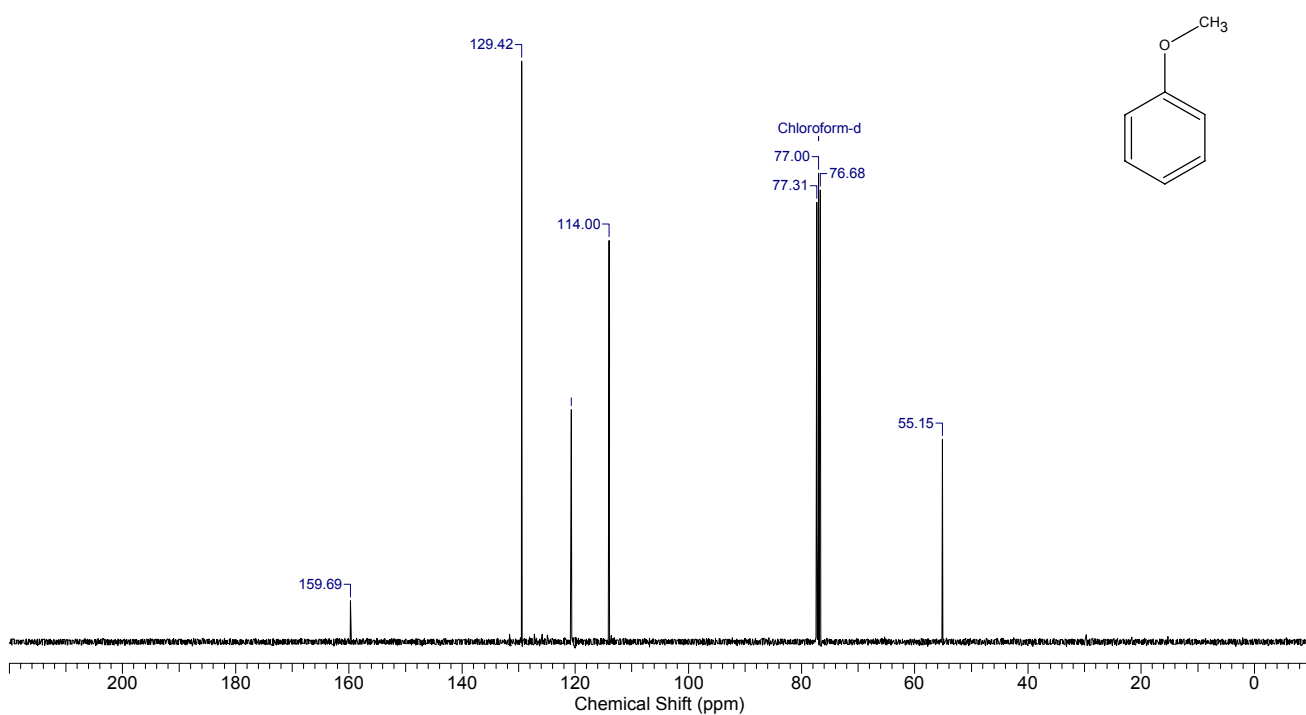
**Synthesis of 2-thiophenecarboxaldehyde (2s).** Compound **2s** was prepared from 2-thiopheneglyoxylic acid (**1v**) (156 mg, 1.00 mmol) and using *n*-tetradecane (50  $\mu$ L) as an internal gas chromatographic standard. The yield of compound **2s** was determined by quantitative GC to be 41 %, based on a response factor obtained using commercial 2-thiophenecarboxaldehyde [98-03-3].

## Anisole (2a)

<sup>1</sup>H NMR (Chloroform-d, 600 MHz)

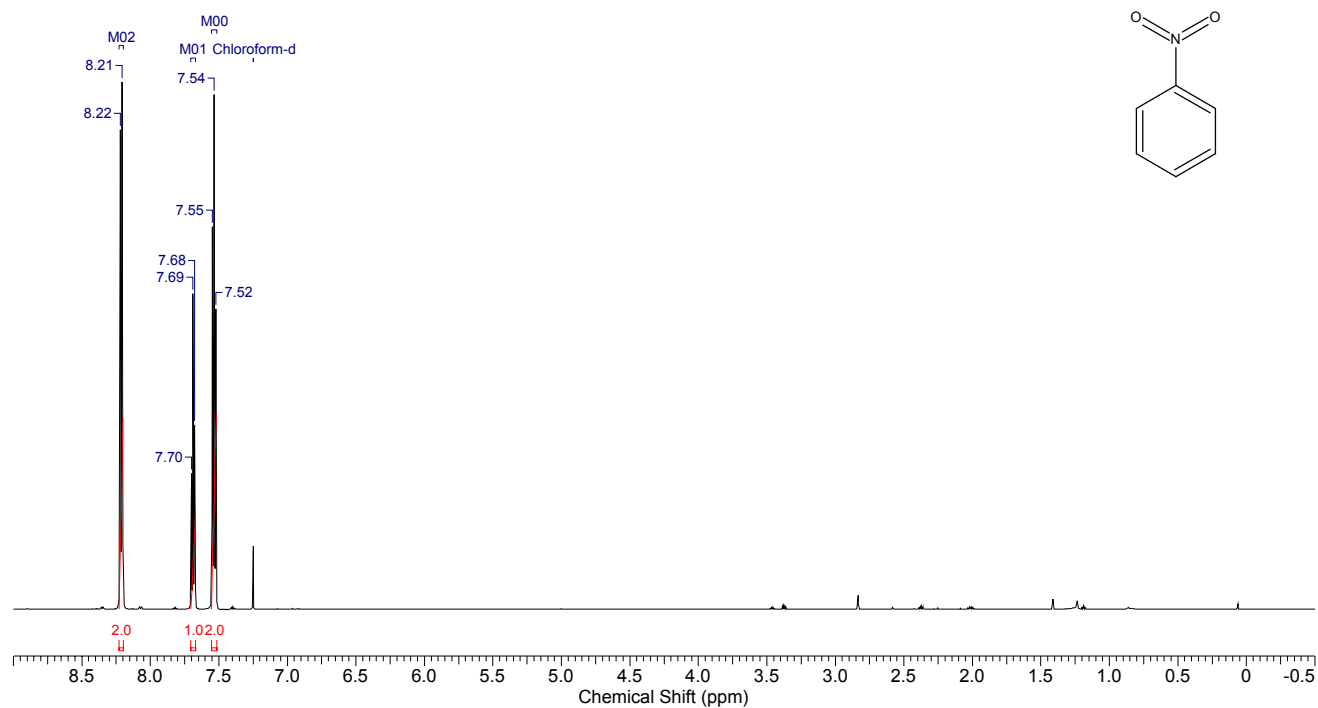


<sup>13</sup>C NMR (Chloroform-d, 101 MHz)

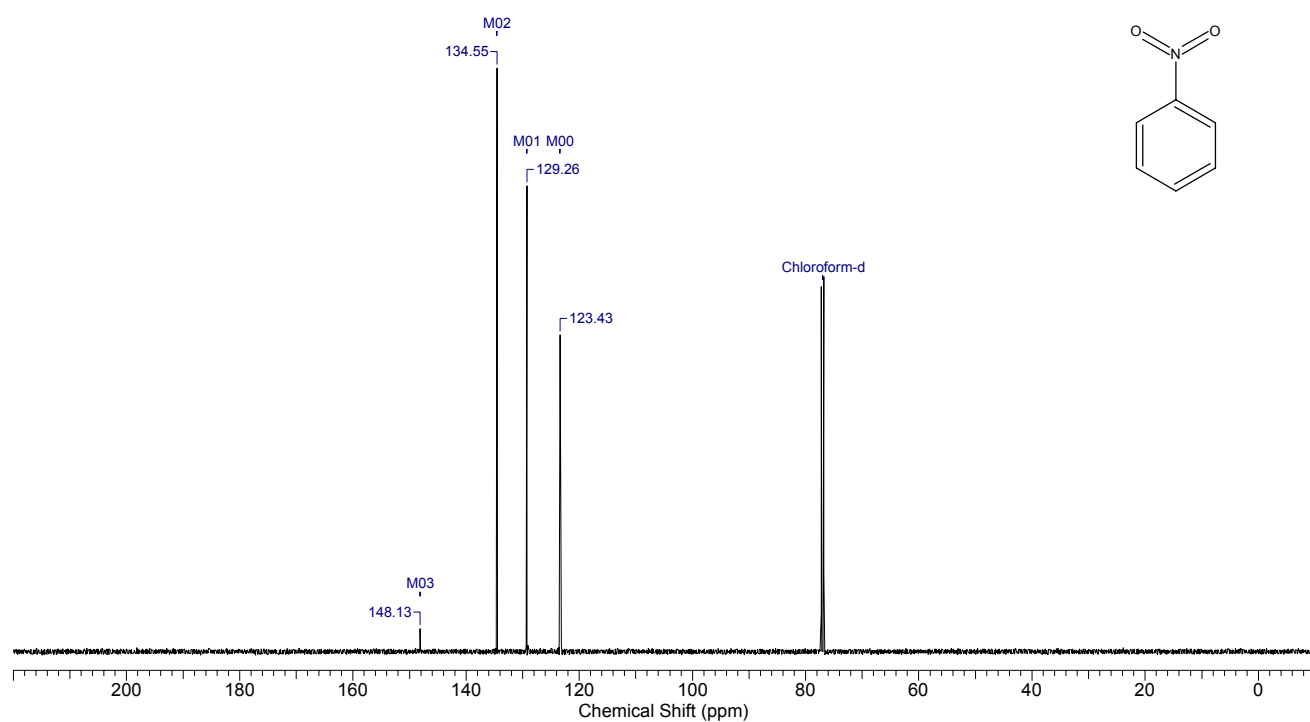


## Nitrobenzene (2b)

<sup>1</sup>H NMR (Chloroform-d, 600 MHz)

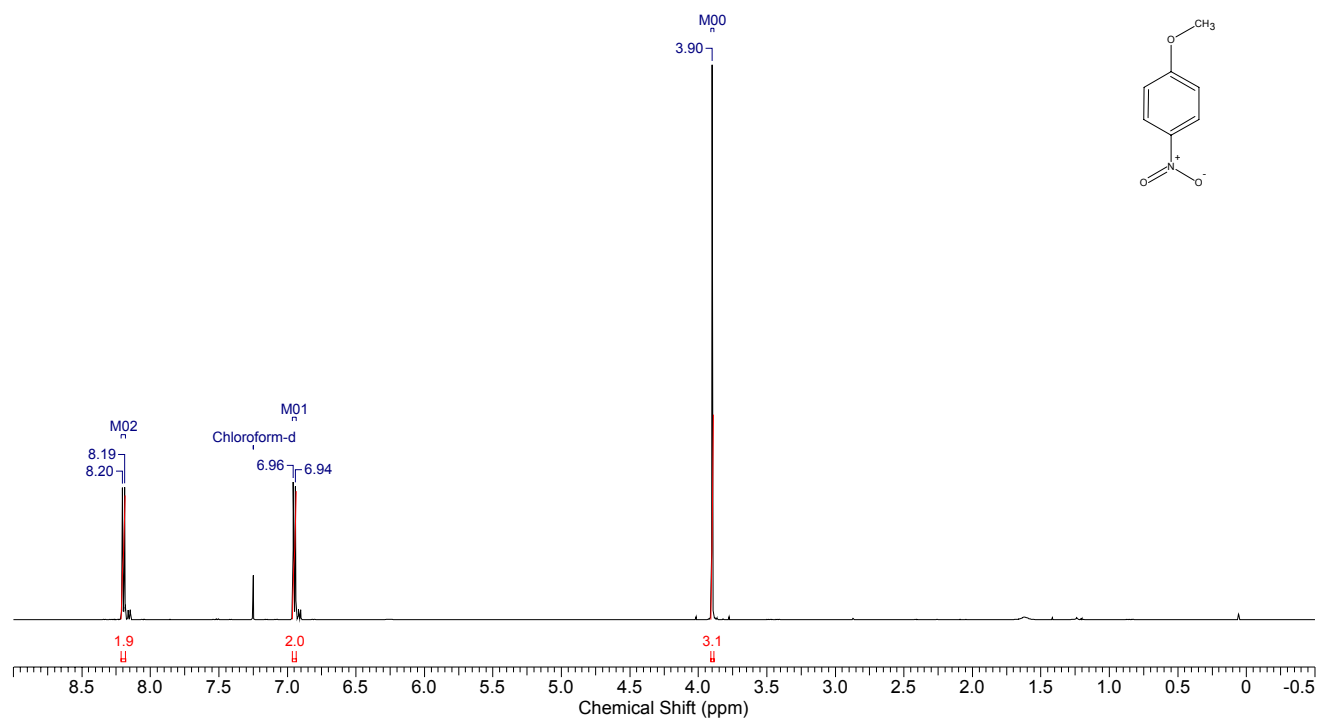


<sup>13</sup>C NMR (Chloroform-d, 151 MHz)

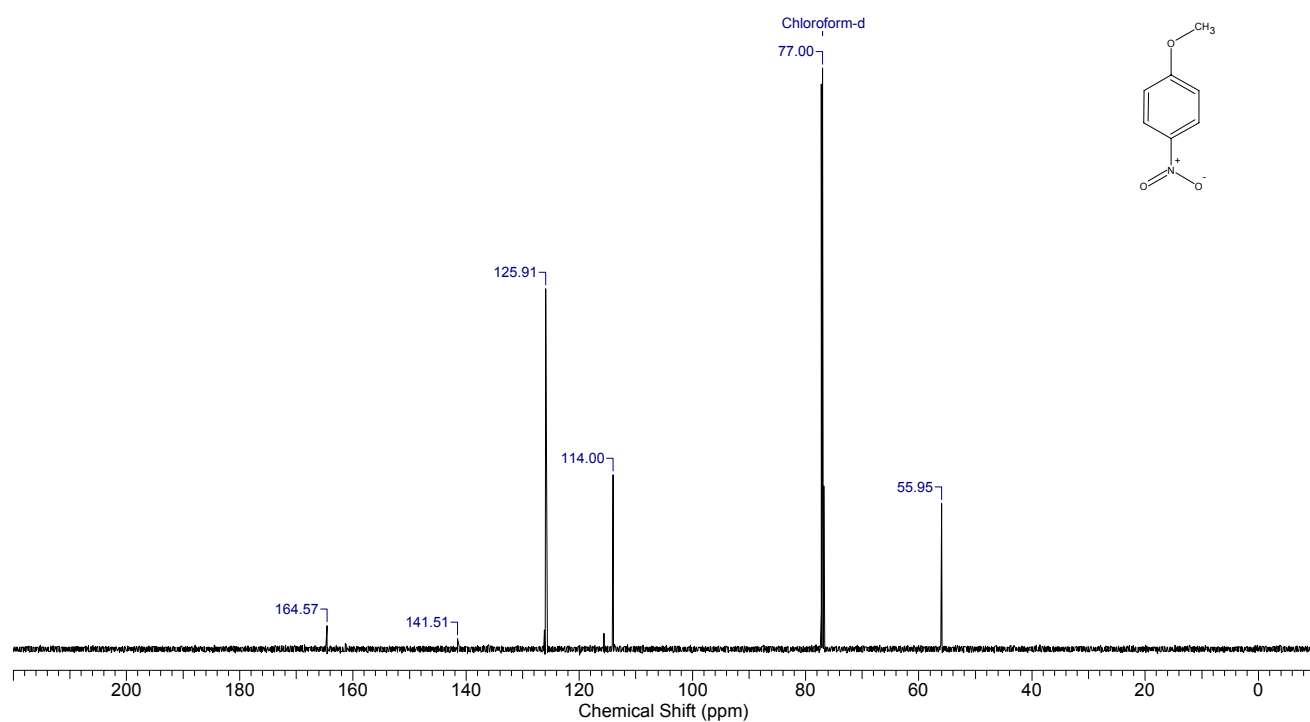


## 4-Nitroanisole (2c)

<sup>1</sup>H NMR (Chloroform-d, 600 MHz)

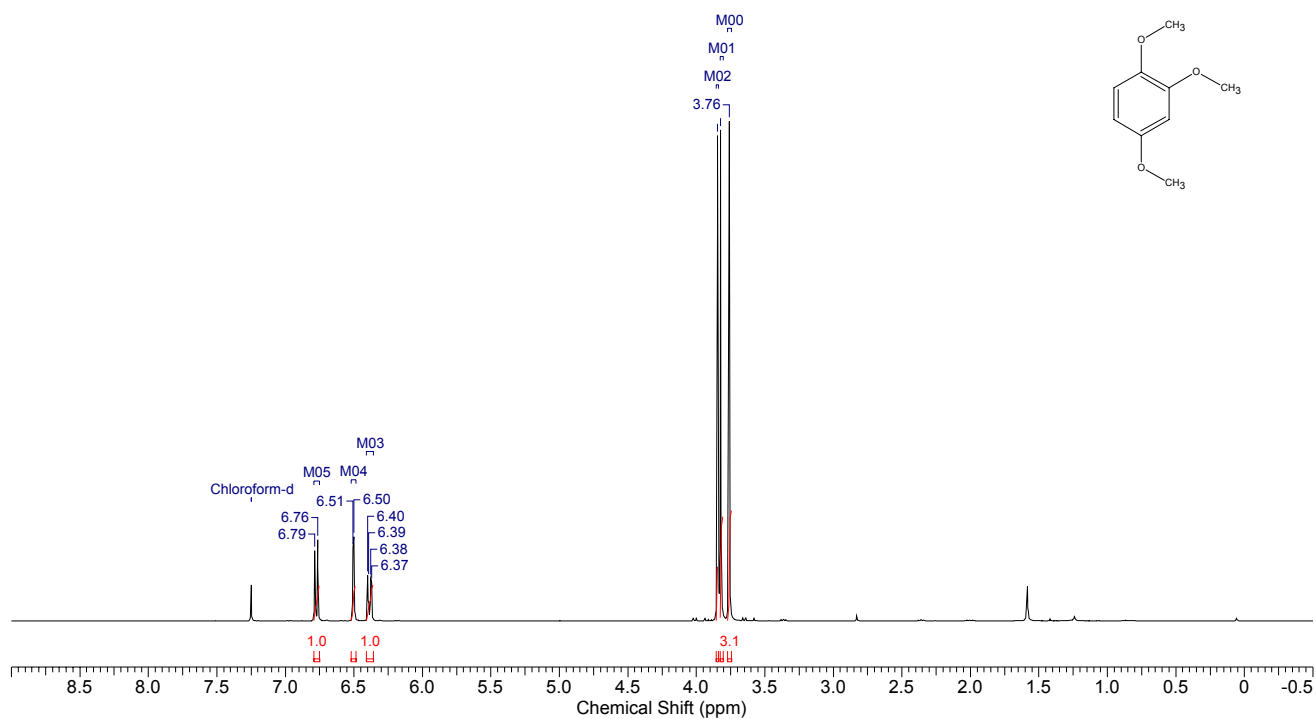


<sup>13</sup>C NMR (Chloroform-d, 151 MHz)

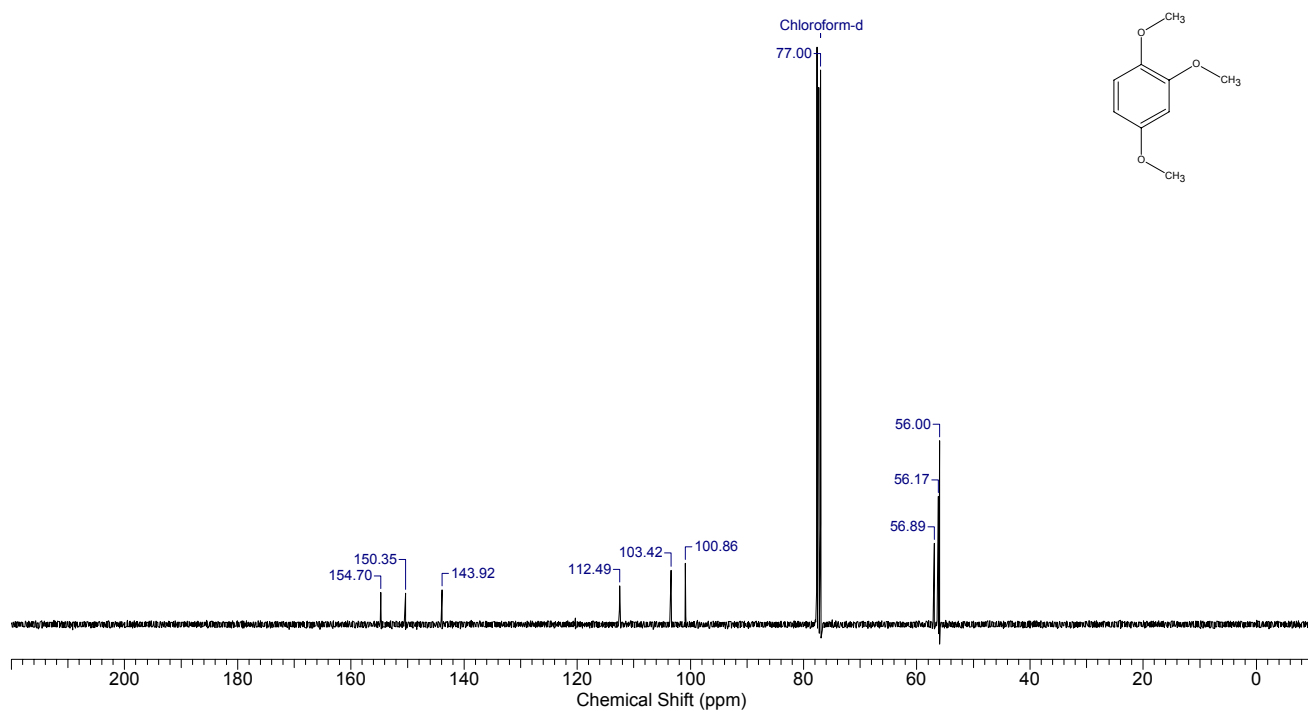


## 1,2,4-Trimethoxybenzene (2d)

<sup>1</sup>H NMR (Chloroform-d, 400 MHz)

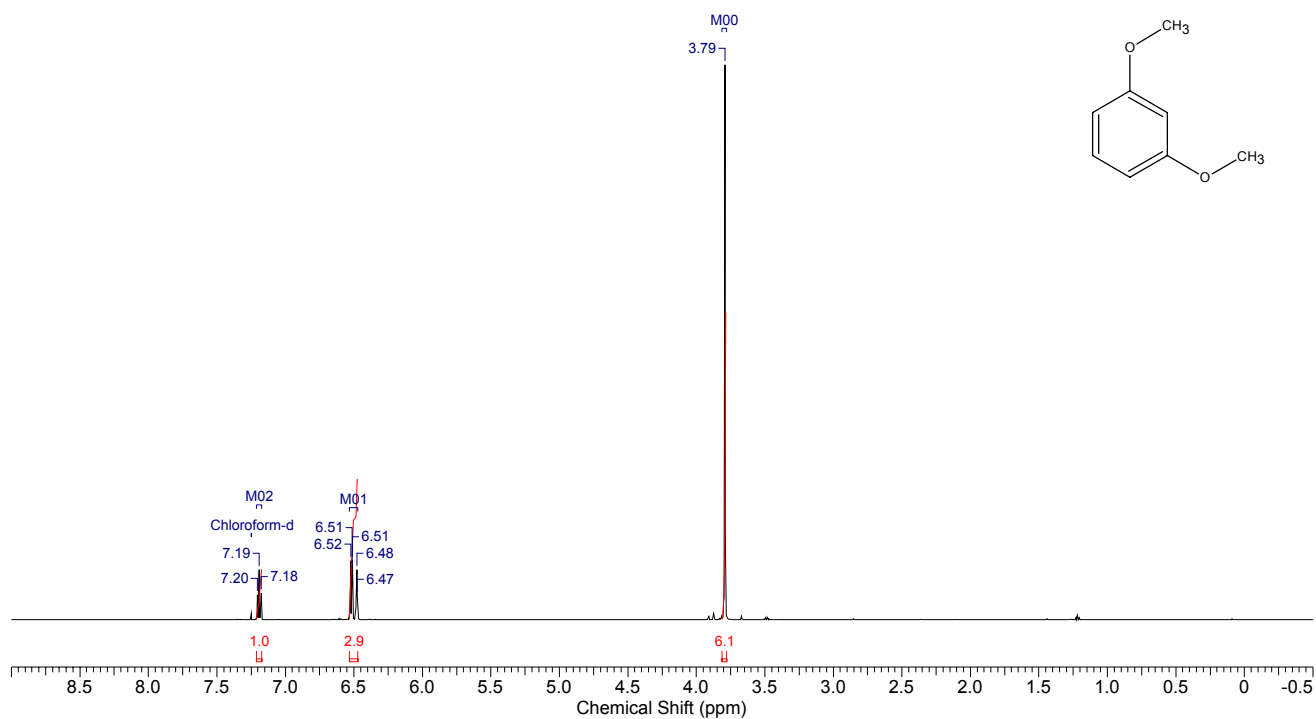


<sup>13</sup>C NMR (Chloroform-d, 101 MHz)

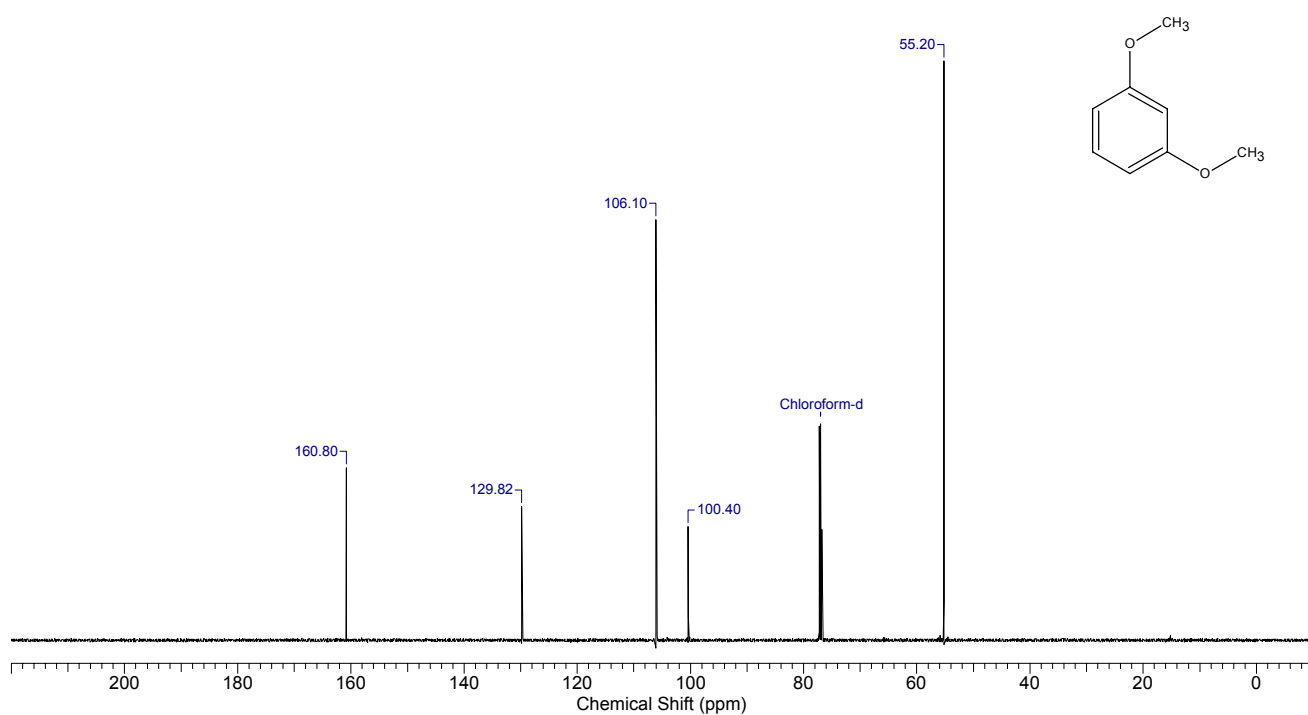


### 1,3-Dimethoxybenzene (2e)

<sup>1</sup>H NMR (Chloroform-d, 600 MHz)

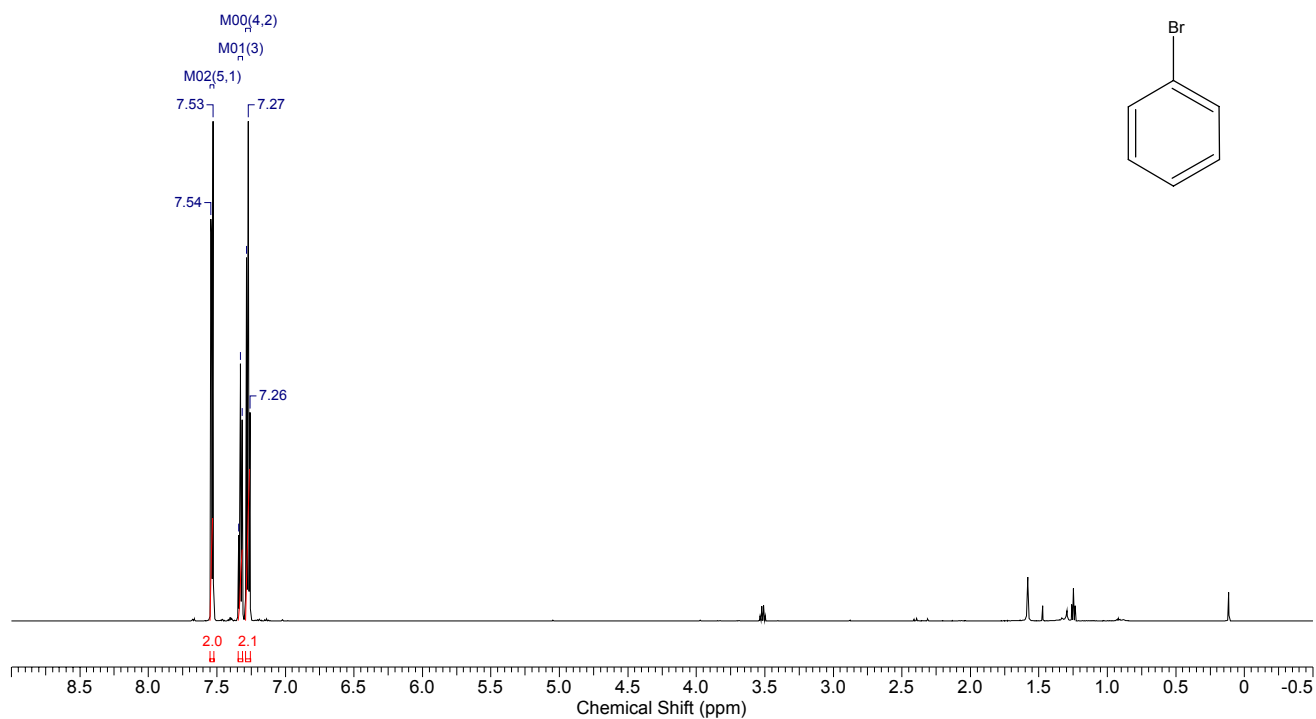


<sup>13</sup>C NMR (Chloroform-d, 151 MHz)

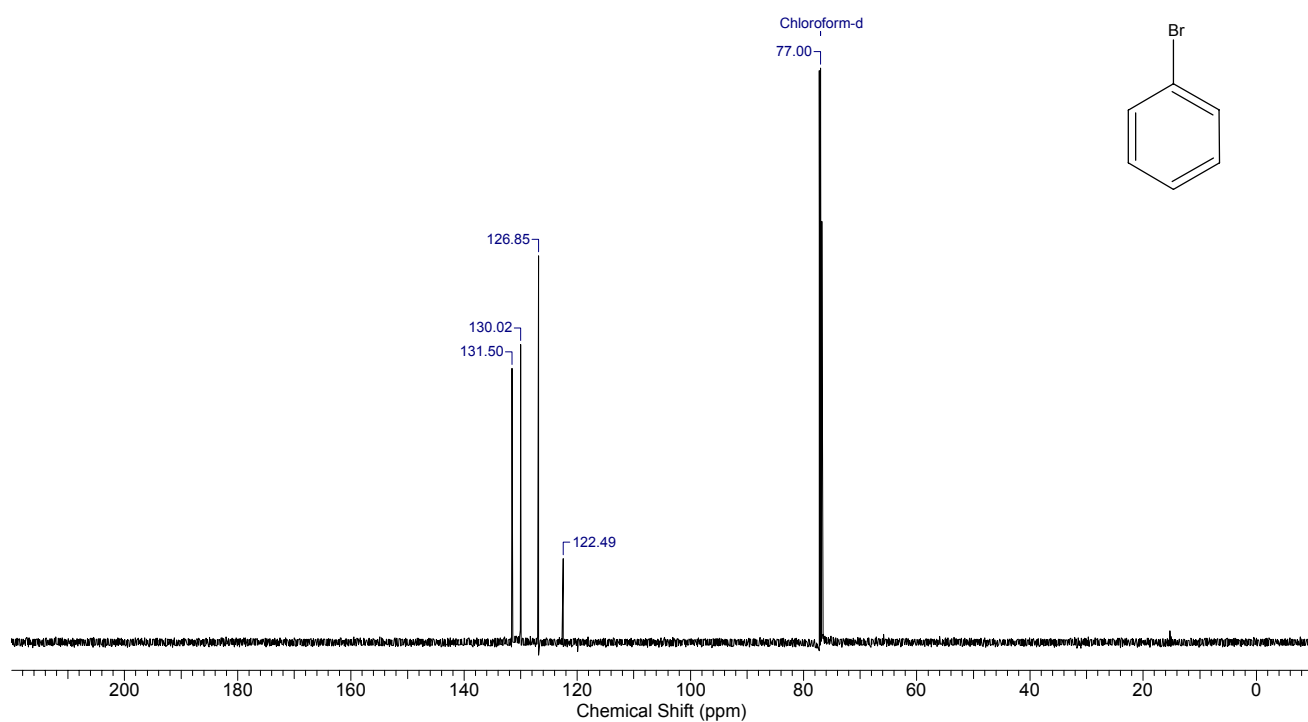


## Bromobenzene (2f)

<sup>1</sup>H NMR (Chloroform-d, 600 MHz)

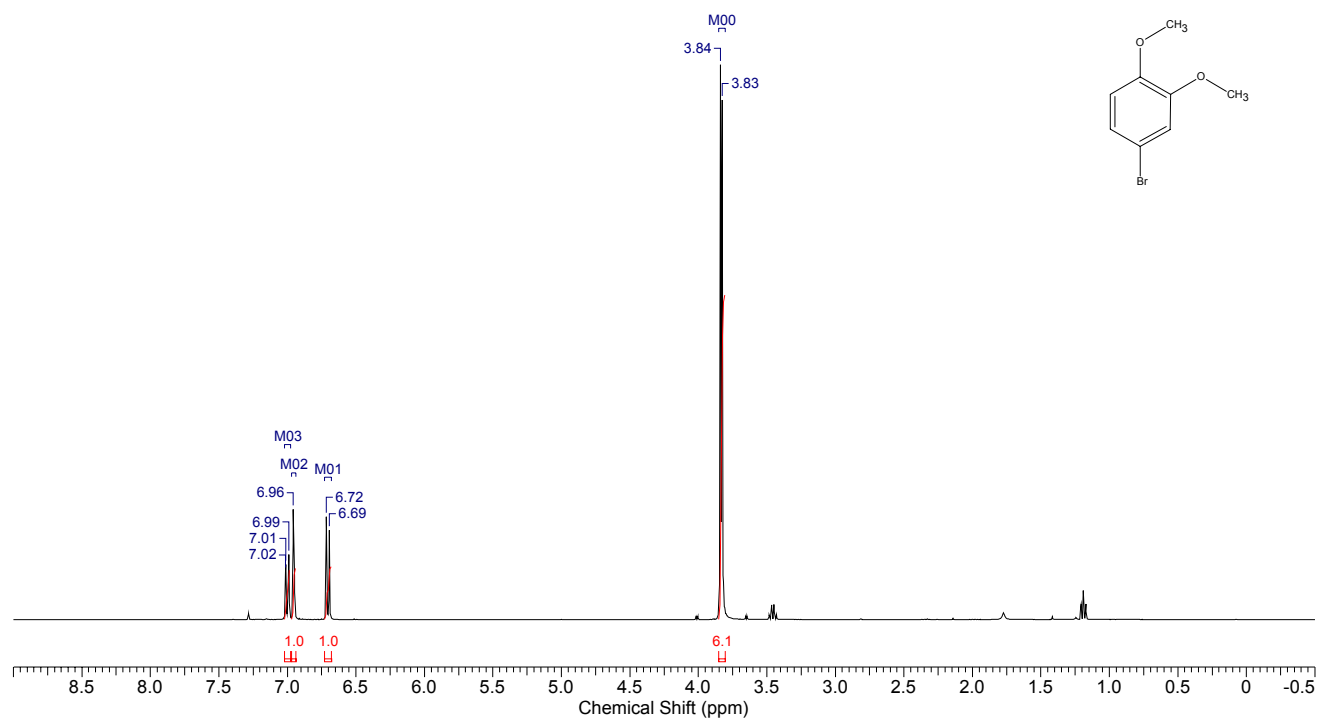


<sup>13</sup>C NMR (Chloroform-d, 151 MHz)

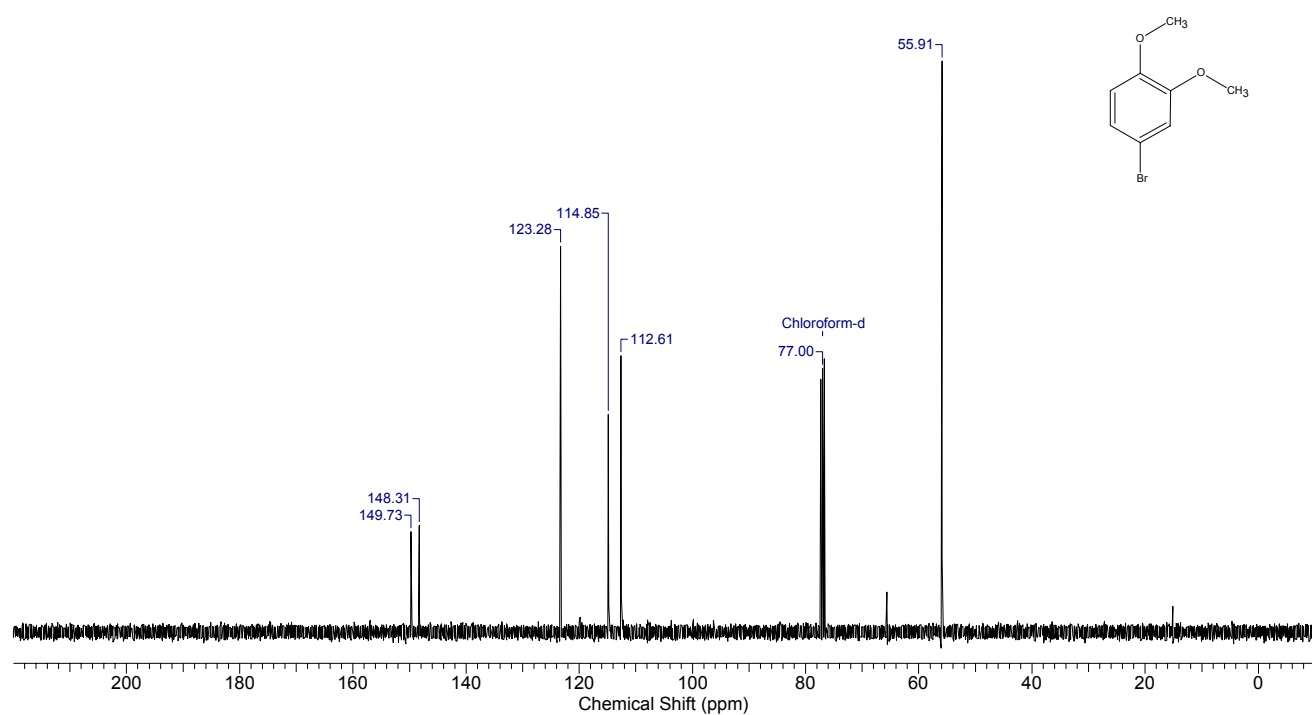


## 4-Bromoveratrole (2g)

<sup>1</sup>H NMR (Chloroform-d, 400 MHz)

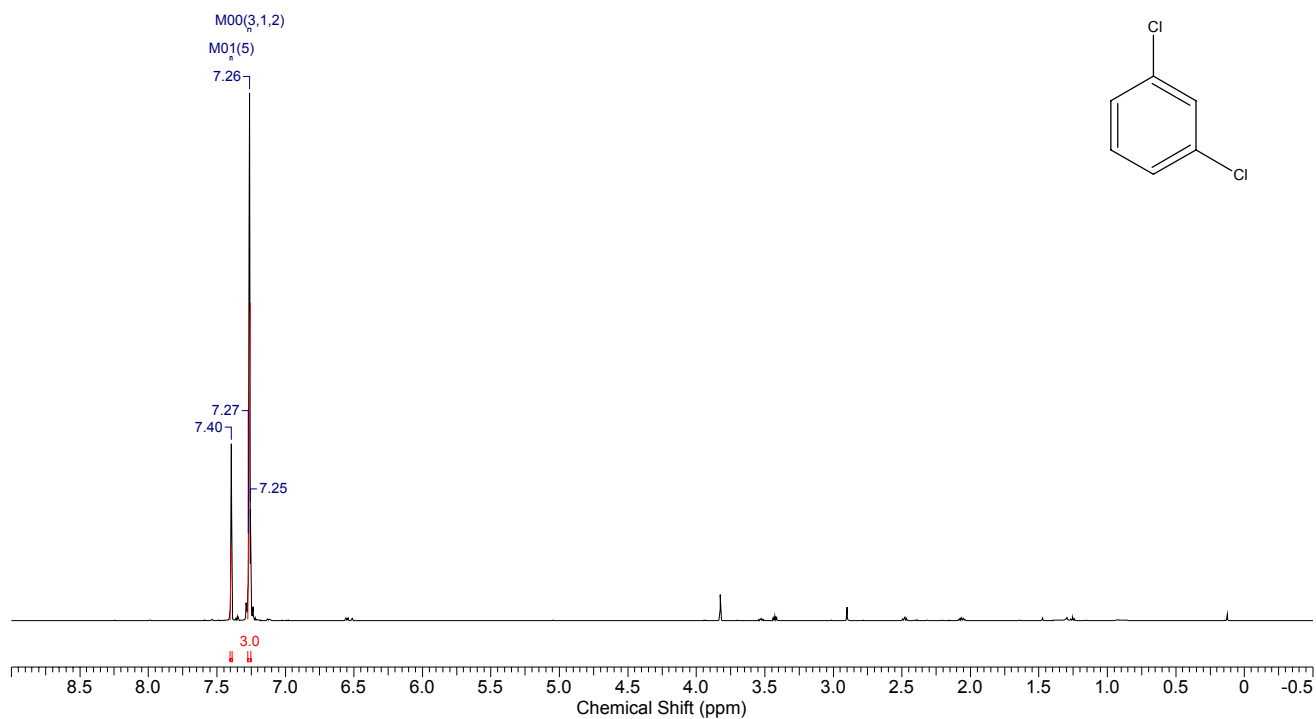


<sup>13</sup>C NMR (Chloroform-d, 101 MHz)

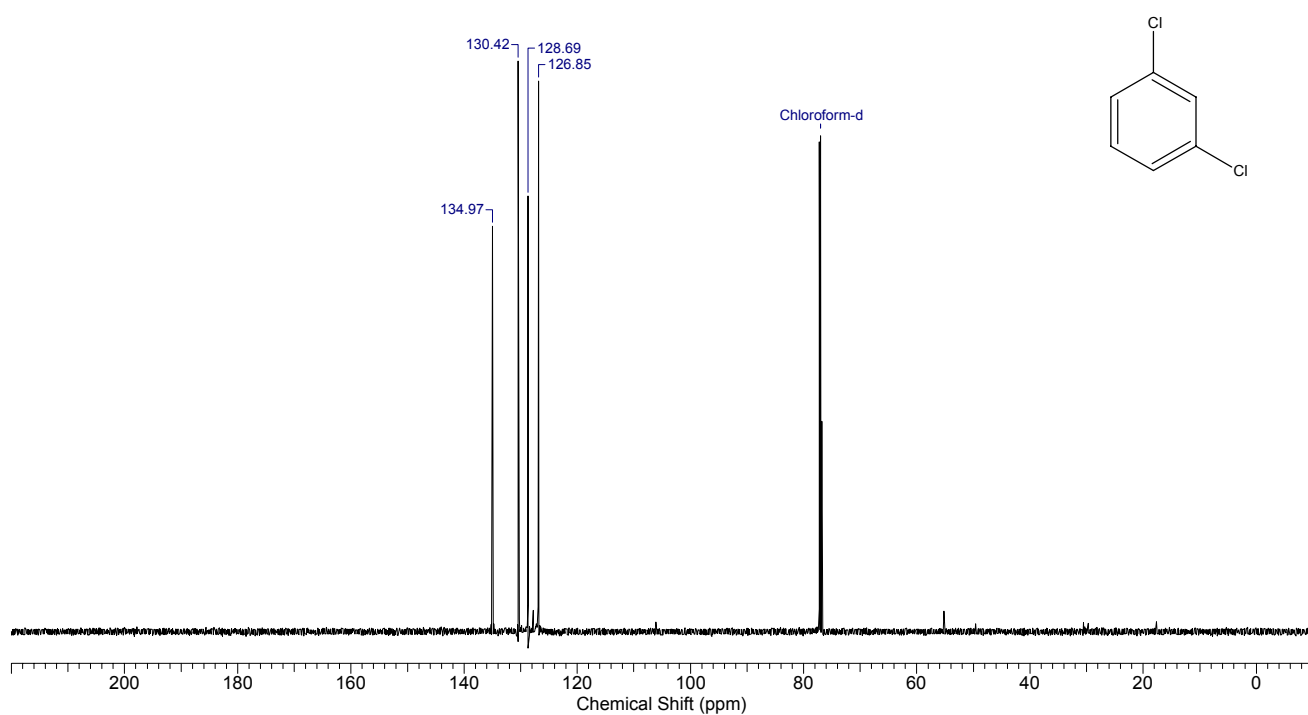


## 1,3-Dichlorobenzene (2h)

<sup>1</sup>H NMR (Chloroform-d, 600 MHz)

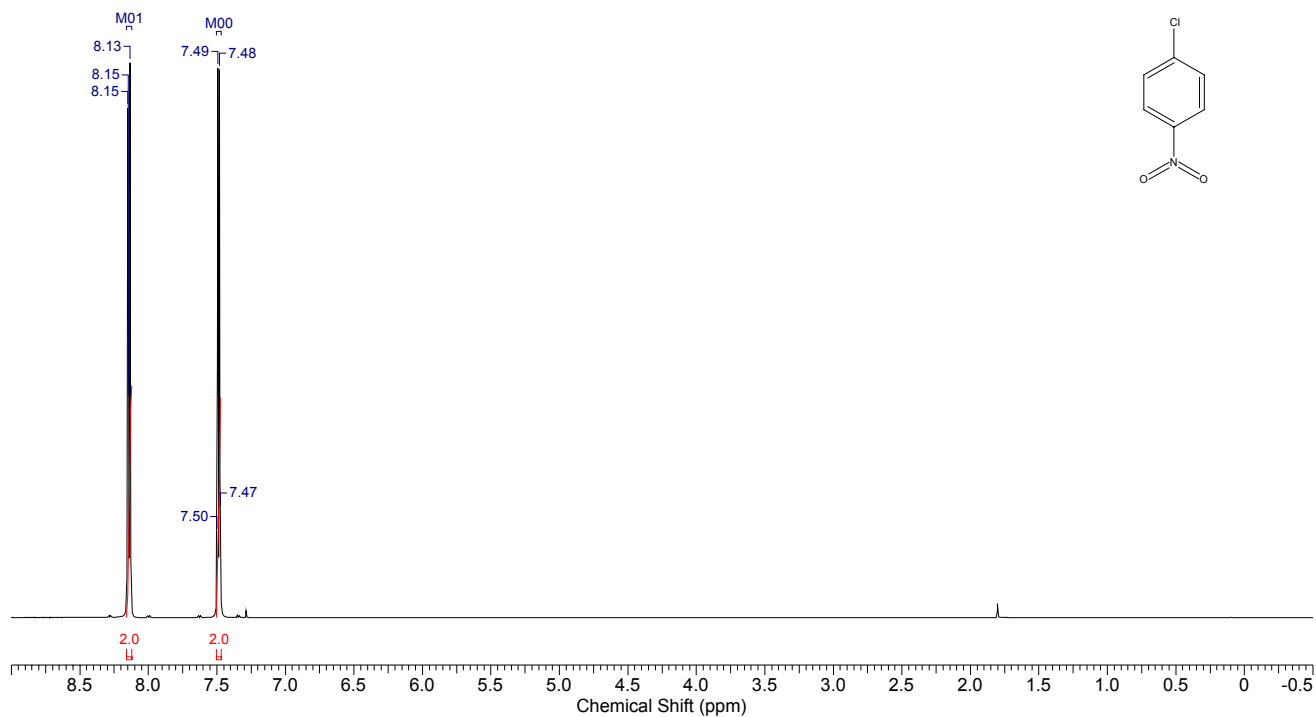


<sup>13</sup>C NMR (Chloroform-d, 151 MHz)

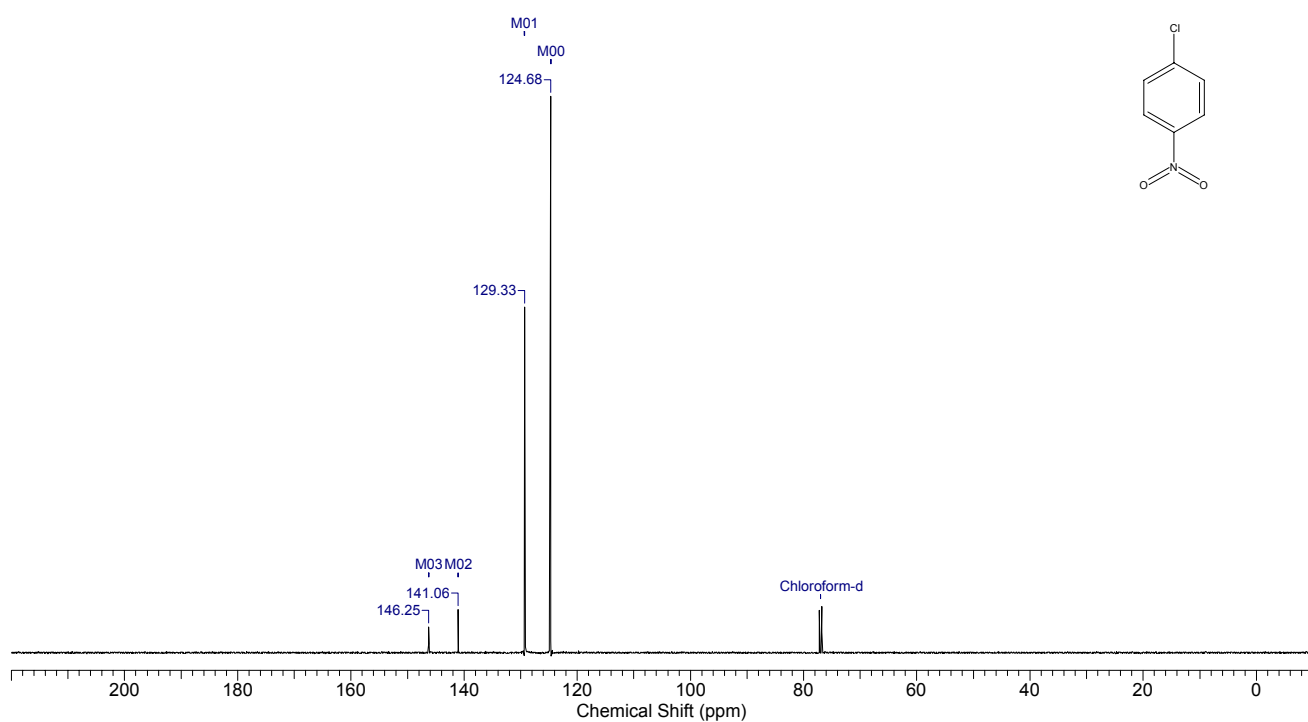


## 1-Chloro-4-nitrobenzene (2i)

<sup>1</sup>H NMR (Chloroform-d, 600 MHz)

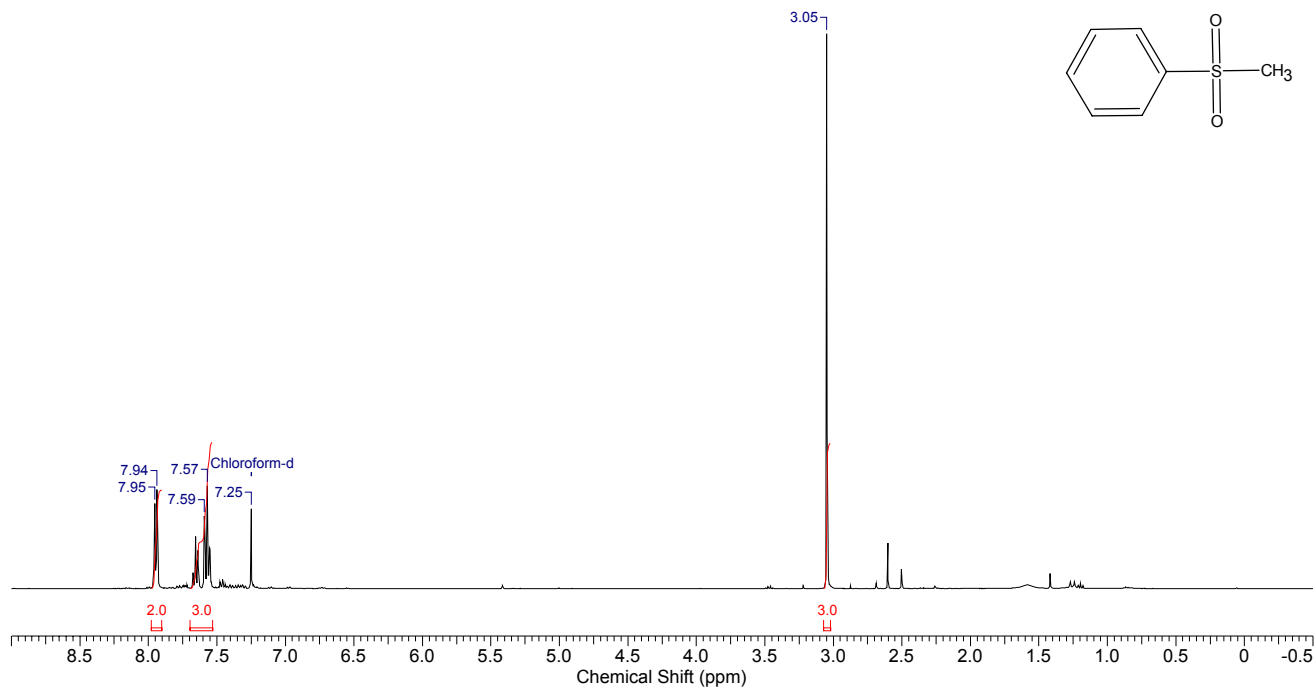


<sup>13</sup>C NMR (Chloroform-d, 151 MHz)

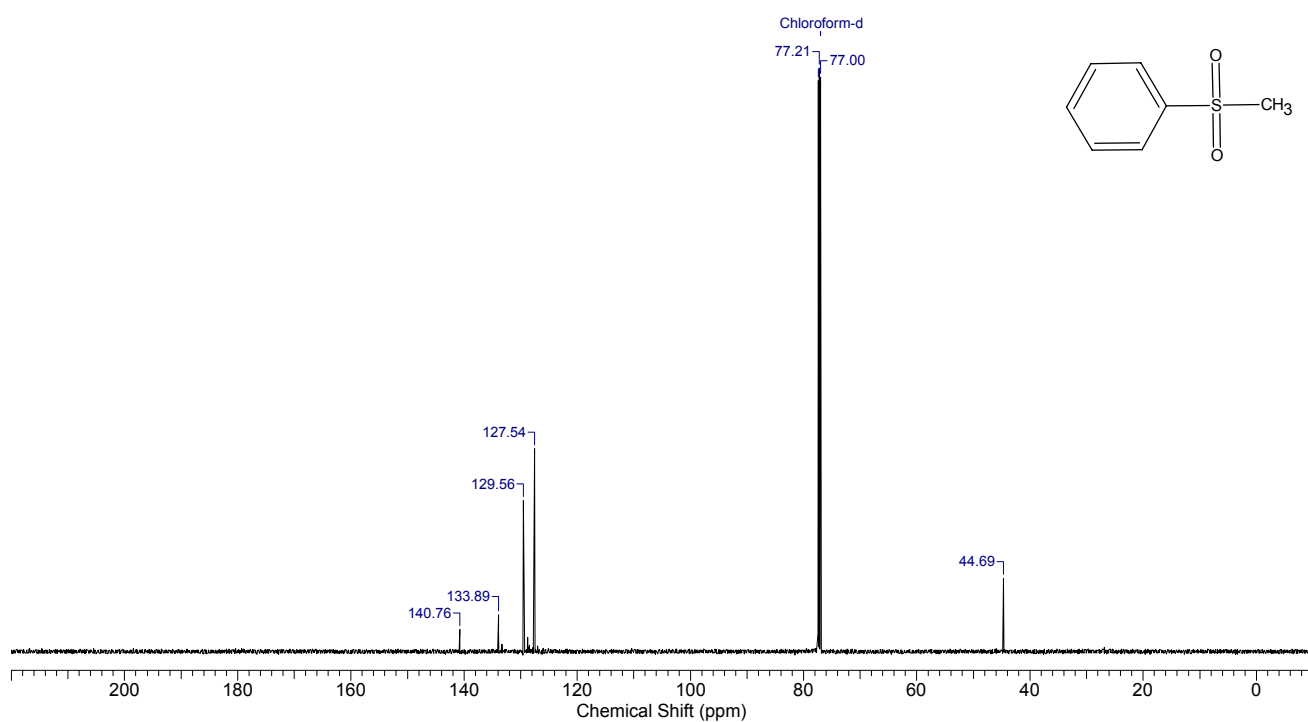


## Methyl phenyl sulfone (2j)

<sup>1</sup>H NMR (Chloroform-d, 600 MHz)

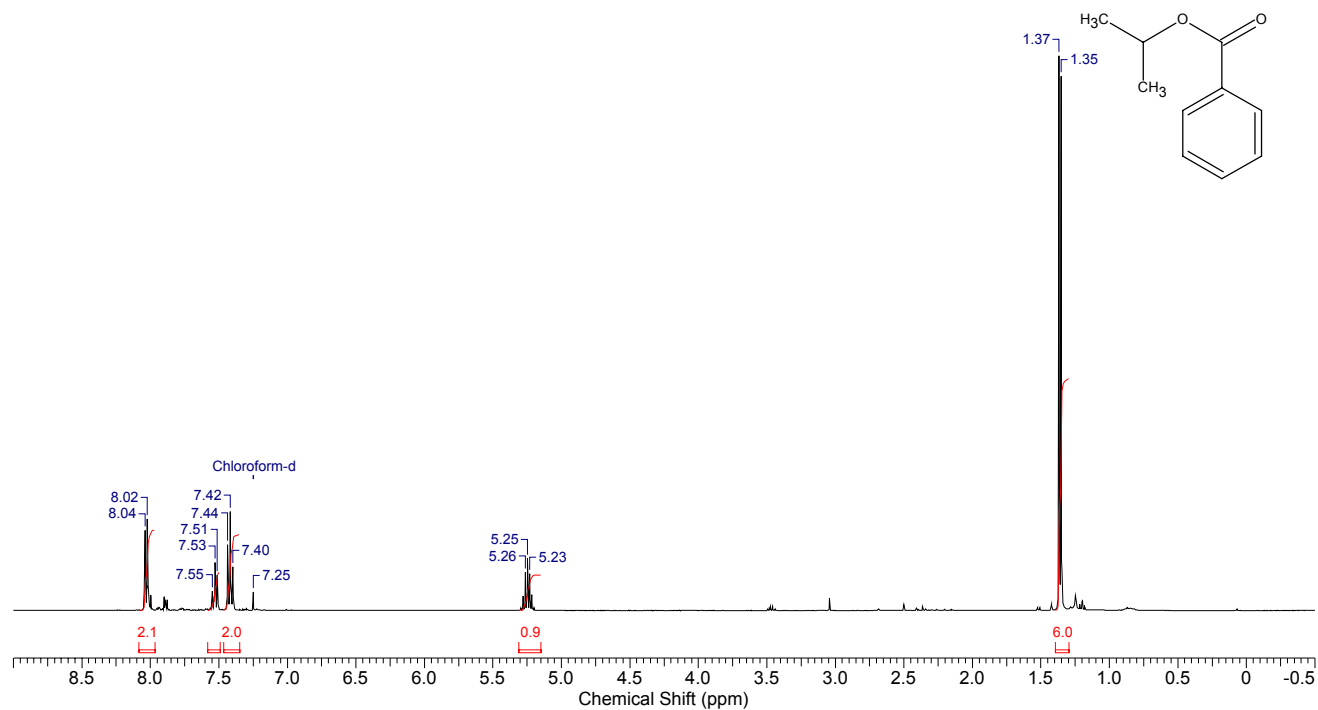


<sup>13</sup>C NMR (Chloroform-d, 151 MHz)

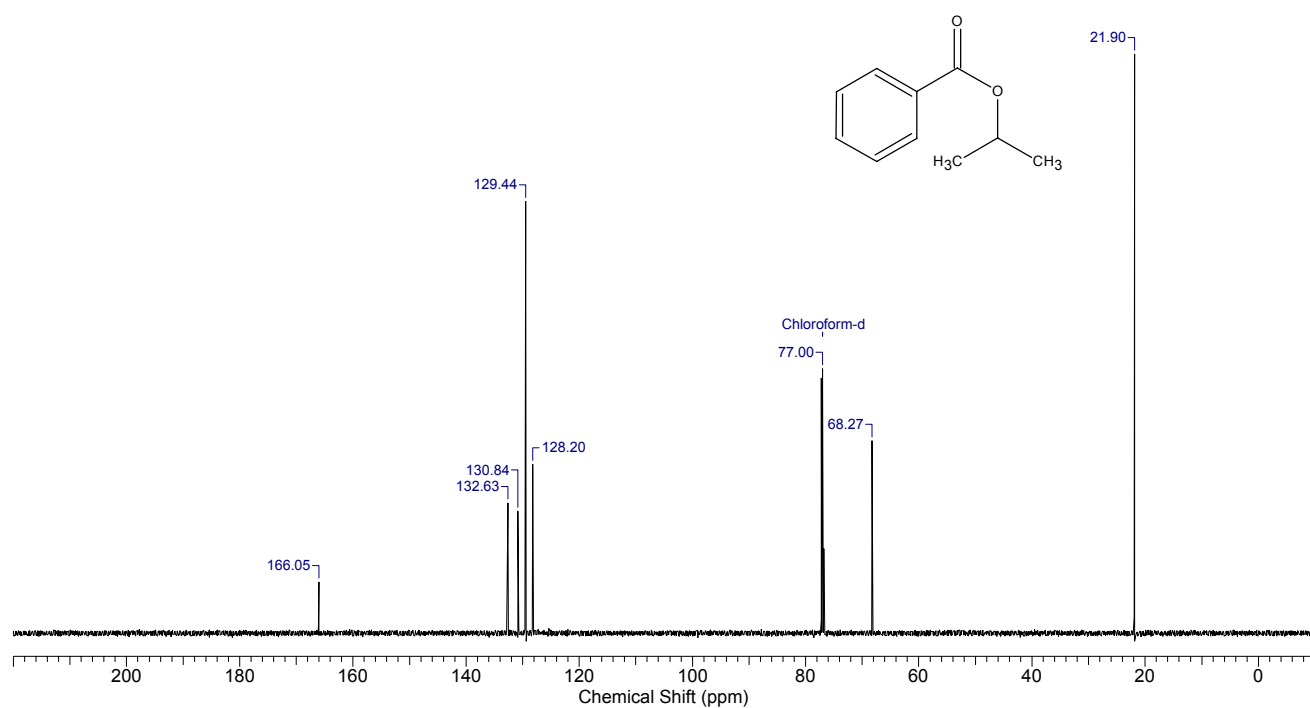


## Isopropyl benzoate (2l)

<sup>1</sup>H NMR (Chloroform-d, 600 MHz)

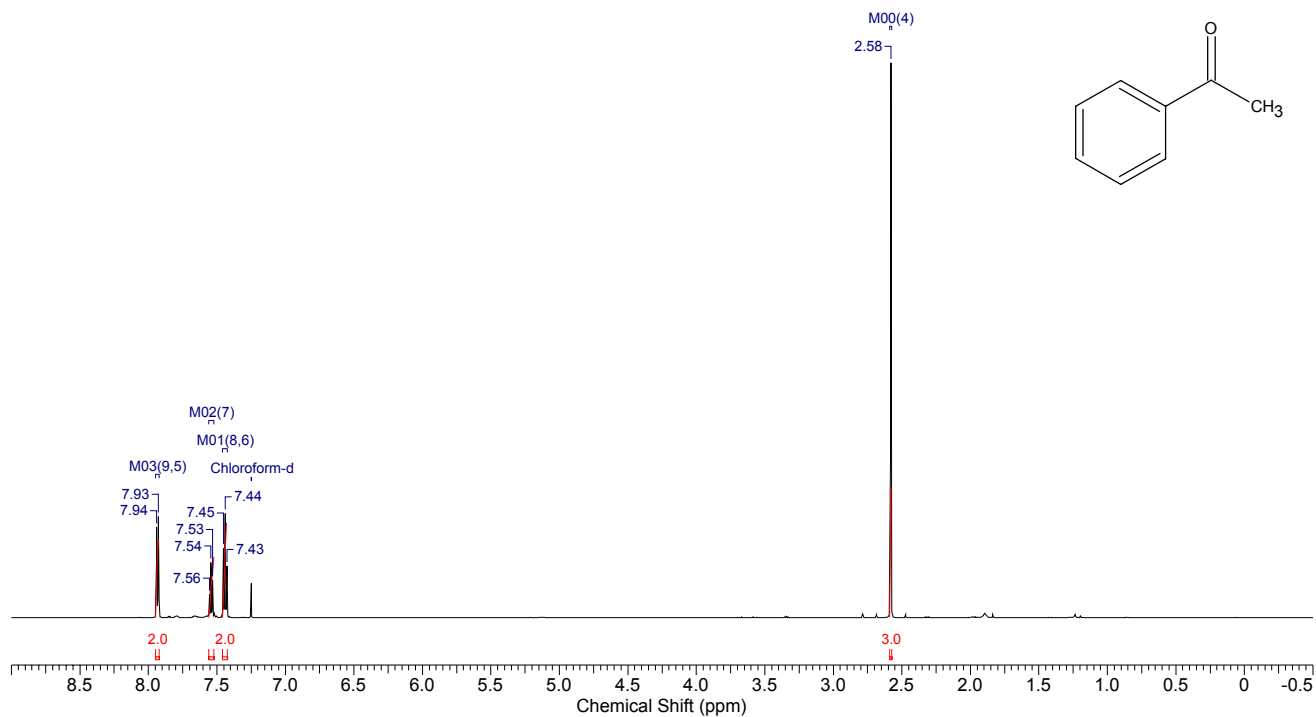


<sup>13</sup>C NMR (Chloroform-d, 151 MHz)

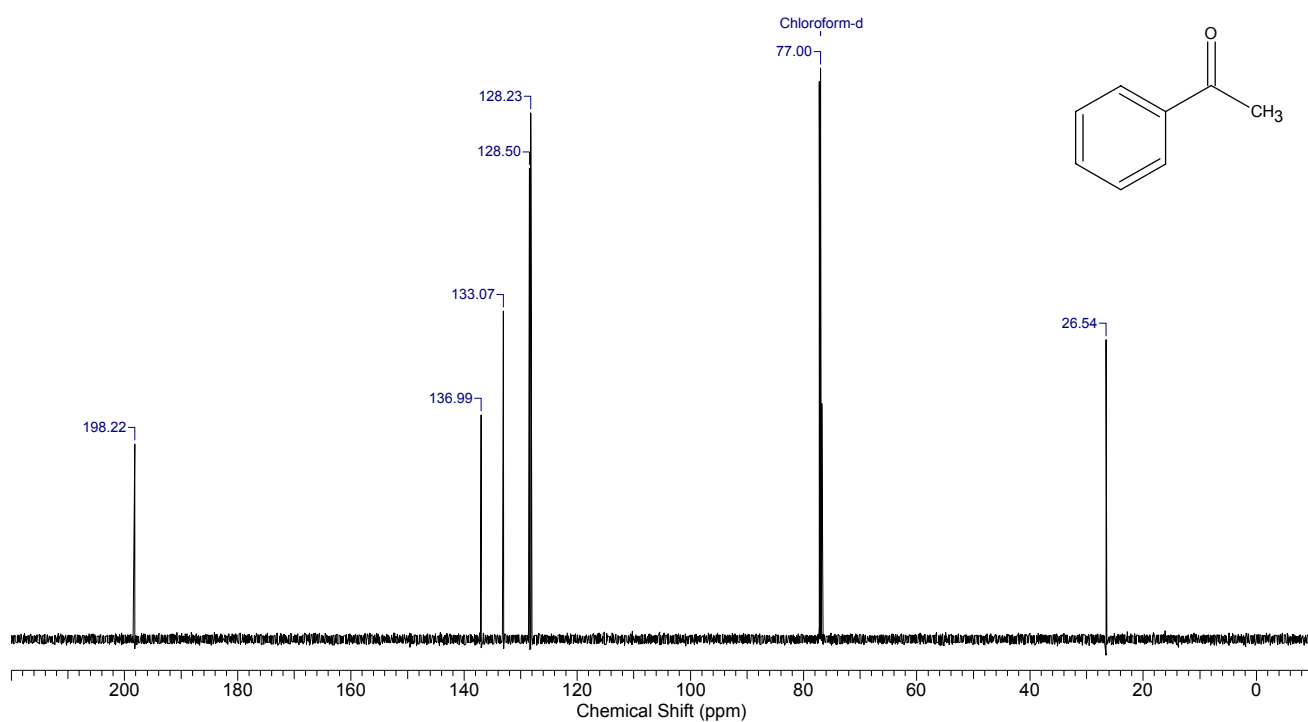


## Acetophenone (2m)

<sup>1</sup>H NMR (Chloroform-d, 600 MHz)

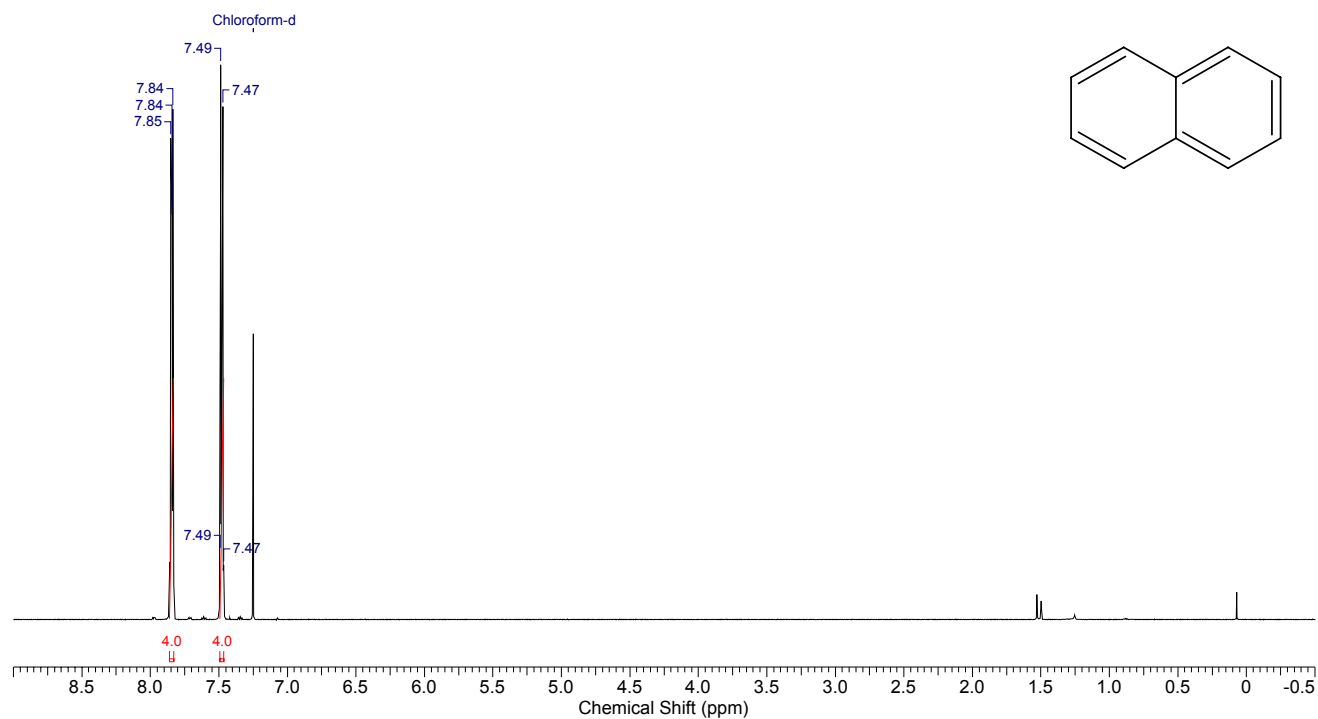


<sup>13</sup>C NMR (Chloroform-d, 151 MHz)

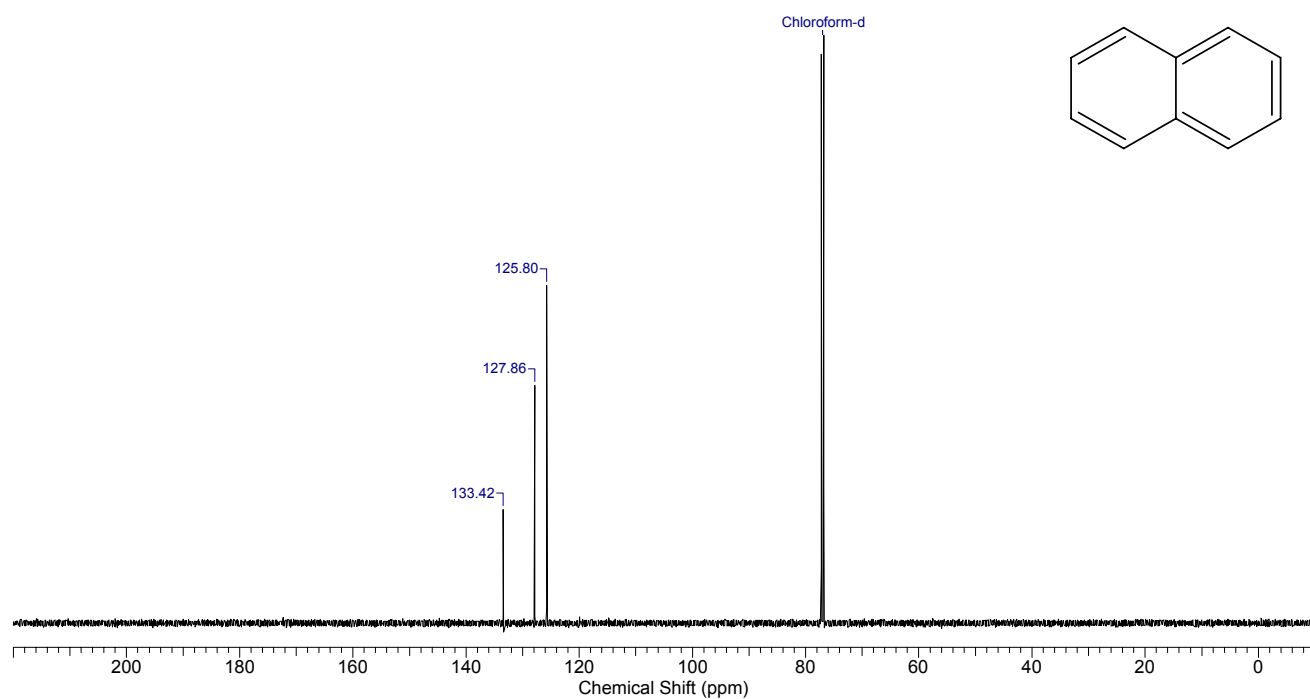


## Naphthalene (2p)

$^1\text{H}$  NMR (Chloroform-d, 600 MHz)



$^{13}\text{C}$  NMR (Chloroform-d, 151 MHz)



**Quantum Chemical Calculations.** All calculations were performed with the Gaussian03 program package<sup>[1]</sup> and the B3LYP density functional.<sup>[2]</sup> The atoms H, C, F, N and O were described by the 6-31G(d) basis,<sup>[3]</sup> while the Stuttgart RSC 1997 ECP pseudopotential was used to represent Ag and Cu.<sup>[4]</sup> All geometries of minima and transition states were fully optimized. Harmonic force constants were calculated for the optimized geometries to characterize the stationary points either as minima or transition states. Thermal Corrections from the frequency calculations were scaled with Wong's scaling factor ( $f = 0.9804$ ) for B3LYP/6-31G(d).<sup>[5]</sup> Transition states were located using the STQN (synchronous transit-guided quasi-Newton) method. The nature of the transition states **[3a-4a]**<sup>‡</sup> and **[5-6]**<sup>‡</sup> were verified by following the intrinsic reaction coordinates. Additional single point energy calculation were performed on all structures employing the 6-311+G(2d,p) basis<sup>[6]</sup> for the atoms H, C, F, N and O. All ball and stick models were rendered with GaussView.<sup>[7]</sup>

**Table 1:** Total energies (hartree) from B3LYP/6-311+G(2d,p) single point energy calculations.

	Total energy
7 (CO <sub>2</sub> )	-188.65030454
8 (NMP)	-326.04653810
3a	-1288.81257755
[3a-4a] <sup>‡</sup>	-1288.76101330
4a	-1100.14010662
3'a	-1238.44597020
[3'a-4'a] <sup>‡</sup>	-1238.39599074
4'a	-1049.77807905
5	-1318.76961038
[5-6] <sup>‡</sup>	-1318.72312897
6	-804.05146302

**Table 2:** Unscaled thermal corrections (hartree) from B3LYP/6-31G(d) frequency calculations at 298.15 K.

	$E_{298}$	$U_{298}$	$H_{298}$	$G_{298}$
7	0.011619	0.014260	0.015204	-0.009098
8	0.139765	0.146682	0.147626	0.108891
3a	0.269548	0.289937	0.290881	0.216656
[3a-4a] <sup>‡</sup>	0.266505	0.287055	0.287999	0.214631
4a	0.254429	0.272023	0.272967	0.206562
3'a	0.268822	0.289623	0.290567	0.213962
[3'a-4'a] <sup>‡</sup>	0.265893	0.286941	0.287886	0.211030
4'a	0.253866	0.271815	0.272759	0.204396
5	0.377889	0.405515	0.406460	0.310761
[5-6] <sup>‡</sup>	0.375036	0.402800	0.403744	0.310105
6	0.222509	0.238202	0.239146	0.174202

$E_{298}$  unscaled zero-point vibrational energy correction at 298.15 K

$U_{298}$  unscaled thermal correction to energy at 298.15 K

$H_{298}$             unscaled thermal correction to enthalpy at 298.15 K  
 $G_{298}$             unscaled thermal correction to Gibbs free enthalpy at 298.15 K

Optimized Cartesian coordinates (Å) from B3LYP/6-31G(d) calculations.

**Structure 7**

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.169590
O	0.000000	0.000000	-1.169590

**Structure 8**

C	-0.225431	-0.445327	-0.020858
C	0.099610	0.587543	1.061643
N	1.439274	0.470513	1.348260
C	2.106046	-0.606423	0.632578
C	1.147266	-0.899521	-0.543254
H	3.102019	-0.292248	0.296653
H	2.240654	-1.486088	1.283200
H	1.437225	-0.296077	-1.410011
H	1.176060	-1.950224	-0.844235
H	-0.780814	-1.265289	0.452897
H	-0.877140	-0.009620	-0.782338
C	2.064106	1.183290	2.439315
H	2.351868	0.500515	3.251560
H	2.962996	1.712078	2.097752
H	1.339068	1.905800	2.819795
O	-0.677765	1.361892	1.597922

**Structure 3a**

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.404256
C	1.251341	0.000000	2.036957
C	2.444933	0.000062	1.316425
C	2.409609	0.000126	-0.076226
C	1.179316	0.000086	-0.739418
C	-1.342199	-0.000022	2.112037
O	-2.370494	-0.001240	1.418756
F	1.362678	-0.000120	3.377996

O	-1.286982	0.001387	3.404676
Cu	-2.879546	0.001043	4.400440
N	-4.009208	0.001179	6.053858
C	-5.359842	0.000623	5.869061
C	-6.278326	0.000854	6.948353
C	-5.745899	0.001631	8.256549
C	-4.375751	0.002150	8.432506
C	-3.540024	0.001912	7.301848
C	-7.688041	0.000340	6.670679
C	-8.155102	-0.000344	5.389251
C	-7.252464	-0.000616	4.273152
C	-5.856664	-0.000188	4.512116
C	-7.667743	-0.001296	2.920830
C	-6.718966	-0.001550	1.916790
C	-5.348680	-0.001168	2.258568
N	-4.940842	-0.000511	3.520428
H	3.381377	0.000042	1.865481
H	3.340002	0.000191	-0.638206
H	-7.010347	-0.002053	0.871212
H	-4.549050	-0.001415	1.521181
H	-8.729472	-0.001612	2.686617
H	-9.224317	-0.000694	5.193862
H	-2.460066	0.002335	7.407457
H	-3.933261	0.002756	9.423048
H	-6.418505	0.001814	9.110390
H	-8.378817	0.000525	7.509522
H	1.141833	0.000119	-1.825284
H	-0.970408	-0.000083	-0.484716

Structure [3a-4a]<sup>‡</sup>

C	-0.186565	-0.566685	0.044231
C	-0.223135	-0.300632	1.381665
C	0.976842	0.001345	2.111599
C	2.213270	0.039308	1.422314
C	2.249974	-0.239523	0.004528

C	1.052733	-0.552417	-0.681920
C	1.006756	0.256588	3.501635
C	2.213846	0.515224	4.122456
C	3.392407	0.529307	3.351548
N	3.390908	0.308424	2.041766
C	1.161874	-0.844481	-2.061449
C	2.403038	-0.823256	-2.668219
C	3.540440	-0.496949	-1.902045
N	3.458102	-0.205969	-0.608465
Cu	4.995783	0.350288	0.686520
C	7.272831	2.219615	-0.022163
C	6.872342	1.123004	0.767834
C	7.228686	1.191668	2.121506
C	7.929932	2.249457	2.688627
C	8.300903	3.317027	1.867966
C	7.964631	3.307402	0.510882
F	6.830209	0.197537	2.964255
C	6.836265	-0.483889	-0.238838
O	6.832996	-0.214059	-1.434054
O	6.906076	-1.459194	0.496591
H	8.169439	2.230979	3.747734
H	8.855342	4.150991	2.290737
H	8.261444	4.134121	-0.129146
H	7.067394	2.164294	-1.087394
H	2.269112	0.703883	5.189496
H	4.363891	0.712922	3.801010
H	0.080540	0.239018	4.070272
H	-1.166252	-0.320476	1.921100
H	4.542189	-0.474688	-2.324944
H	2.517138	-1.053655	-3.722323
H	0.268128	-1.090221	-2.629353
H	-1.100572	-0.801283	-0.494779

**Structure 4a**

C	0.000061	-0.001087	-0.000179
---	----------	-----------	-----------

C	0.000291	0.000615	1.412911
C	1.277659	0.001226	1.972821
C	2.474931	-0.001581	1.266047
C	2.417605	-0.002447	-0.129497
C	1.173876	-0.002257	-0.763313
Cu	-1.548553	0.047139	2.533266
N	-1.450605	0.901488	4.755677
C	-2.699904	0.931984	5.265519
C	-2.994299	1.441353	6.556326
C	-1.907984	1.938649	7.312342
C	-0.634987	1.904189	6.778007
C	-0.449135	1.368731	5.485690
C	-4.349366	1.426686	7.029098
C	-5.355776	0.928433	6.256626
C	-5.095843	0.406757	4.943728
C	-3.769049	0.411288	4.441603
C	-6.108927	-0.117898	4.111672
C	-5.778006	-0.598952	2.860201
C	-4.436585	-0.548658	2.443295
N	-3.455755	-0.059153	3.202074
F	1.396050	-0.005340	3.348997
H	3.420861	-0.004395	1.800590
H	3.336961	-0.004799	-0.710023
H	-6.529982	-1.010131	2.194938
H	-4.143831	-0.914121	1.464395
H	-7.136658	-0.137476	4.465008
H	-6.379200	0.918159	6.622039
H	0.533958	1.307562	5.028047
H	0.218799	2.276311	7.335477
H	-2.086668	2.340585	8.306625
H	-4.558952	1.820162	8.020431
H	1.117188	-0.003087	-1.849819
H	-0.952117	-0.000454	-0.527931

Structure **3'a**

C	0.043561	0.000643	-0.047994
C	0.229618	0.000511	1.343901
C	1.553284	-0.000228	1.806305
C	2.641452	-0.000786	0.934786
C	2.422406	-0.000599	-0.441018
C	1.115456	0.000117	-0.936253
C	-1.001627	0.001171	2.228488
O	-2.120667	0.001069	1.680077
F	1.837992	-0.000478	3.120454
O	-0.788189	0.001854	3.499084
Ag	-2.658913	0.002393	4.523056
N	-4.160753	0.001911	6.308143
C	-5.486305	0.000788	6.008439
C	-6.486799	0.000344	7.017476
C	-6.059333	0.001122	8.363571
C	-4.709516	0.002274	8.651069
C	-3.791331	0.002633	7.585174
C	-7.873938	-0.000850	6.646532
C	-8.251978	-0.001573	5.337568
C	-7.273789	-0.001155	4.287843
C	-5.892831	0.000031	4.614177
C	-7.610698	-0.001864	2.914068
C	-6.609670	-0.001408	1.963089
C	-5.263374	-0.000210	2.386360
N	-4.930548	0.000491	3.669378
H	3.642126	-0.001361	1.355451
H	3.270436	-0.001023	-1.120955
H	-6.841482	-0.001959	0.902807
H	-4.426115	0.000165	1.691342
H	-8.658144	-0.002775	2.622523
H	-9.304816	-0.002475	5.067554
H	-2.722275	0.003521	7.776406
H	-4.347338	0.002895	9.673836
H	-6.799915	0.000810	9.159332
H	-8.619231	-0.001165	7.437395

H	0.935229	0.000260	-2.007726
H	-0.981911	0.001166	-0.401285

Structure [3'a-4'a]<sup>‡</sup>

C	-0.387474	-0.591208	0.048087
C	-0.366836	-0.474196	1.404851
C	0.855686	-0.195173	2.102380
C	2.062748	-0.029406	1.373118
C	2.041321	-0.152545	-0.074532
C	0.811819	-0.438765	-0.725768
C	0.926451	-0.078479	3.509554
C	2.139157	0.183347	4.114250
C	3.283026	0.331715	3.304378
N	3.240969	0.231041	1.982908
C	0.830358	-0.567737	-2.132603
C	2.019373	-0.419655	-2.816999
C	3.188323	-0.134854	-2.087381
N	3.199722	-0.000524	-0.765397
Ag	5.126022	0.459086	0.445166
C	7.840707	1.881301	-0.054268
C	7.218669	1.049766	0.902024
C	7.259424	1.518677	2.222935
C	7.862763	2.708408	2.610370
C	8.462463	3.500062	1.626429
C	8.447571	3.091194	0.290455
F	6.654905	0.787193	3.201591
C	7.420028	-0.810994	0.468274
O	7.451258	-0.920262	-0.747327
O	7.520090	-1.449699	1.492388
H	7.858154	3.002211	3.655867
H	8.944494	4.432159	1.910066
H	8.924902	3.702324	-0.471158
H	7.879985	1.518301	-1.078133
H	2.225507	0.273543	5.192147
H	4.260198	0.534493	3.734209

H	0.022346	-0.200281	4.100731
H	-1.278665	-0.594678	1.983700
H	4.143888	-0.017565	-2.590090
H	2.069184	-0.519350	-3.896153
H	-0.094162	-0.787413	-2.660369
H	-1.315436	-0.807017	-0.474523

**Structure 4'a**

C	0.261325	-0.189946	-0.227740
C	0.206385	-0.007796	1.168823
C	1.448544	0.149714	1.778315
C	2.674153	0.137463	1.121350
C	2.678678	-0.045831	-0.263252
C	1.468143	-0.209928	-0.938461
Ag	-1.508364	0.077527	2.362818
N	-1.566123	0.943010	4.805137
C	-2.806597	0.939714	5.334366
C	-3.072665	1.397262	6.652807
C	-1.973585	1.868599	7.407187
C	-0.710919	1.864938	6.849555
C	-0.552318	1.386662	5.531848
C	-4.413348	1.364890	7.162307
C	-5.440018	0.898511	6.398524
C	-5.213965	0.427134	5.061321
C	-3.900897	0.444924	4.517088
C	-6.257669	-0.062723	4.245967
C	-5.975649	-0.501302	2.968518
C	-4.645993	-0.444186	2.513797
N	-3.640023	0.011717	3.255197
F	1.499087	0.328947	3.145650
H	3.593969	0.267098	1.684900
H	3.621657	-0.060272	-0.804203
H	-6.752360	-0.884375	2.314924
H	-4.388357	-0.779647	1.513776
H	-7.272279	-0.088483	4.635335

H	-6.453975	0.874718	6.788924
H	0.421545	1.357956	5.049691
H	0.151771	2.219325	7.404826
H	-2.136717	2.227984	8.420280
H	-4.594270	1.719940	8.173593
H	1.461790	-0.353568	-2.016823
H	-0.664898	-0.320493	-0.783655

### Structure 5

C	1.509827	1.154326	1.049594
C	0.943732	0.791133	2.268795
C	1.727730	0.494041	3.394942
C	3.116821	0.593083	3.239673
C	3.706521	0.959881	2.032126
C	2.899582	1.238464	0.930563
C	1.021426	0.097064	4.678672
O	1.766225	-0.354822	5.621029
Ag	0.525293	-0.731073	7.395561
O	-1.511919	-1.150035	8.275102
F	3.960501	0.347695	4.266861
O	-0.218058	0.229922	4.730208
O	2.297904	-0.265121	9.024371
H	4.789001	1.020914	1.978710
H	3.356978	1.522558	-0.013498
H	0.872851	1.373330	0.197094
H	-0.131757	0.727982	2.394917
C	-2.486541	-1.286206	7.510202
N	-3.758596	-0.982213	7.854747
C	-4.708511	-1.117719	6.750927
C	-3.947006	-1.981466	5.720278
C	-2.462053	-1.779441	6.078055
H	-5.635220	-1.586348	7.101724
H	-4.964833	-0.124274	6.354733
H	-4.229070	-3.032382	5.841140
H	-4.182040	-1.688474	4.694440

H	-1.950136	-1.021354	5.469069
H	-1.863023	-2.692630	6.006723
C	-4.119484	-0.350525	9.108145
H	-4.457181	0.680640	8.940989
H	-4.926145	-0.908082	9.598144
H	-3.238984	-0.340825	9.752144
C	3.451107	0.001913	8.657296
N	4.220652	0.978386	9.209033
C	5.572898	1.042152	8.662144
C	5.468554	0.230428	7.352453
C	4.258285	-0.694296	7.572397
H	5.867826	2.085076	8.495790
H	6.291745	0.603506	9.371817
H	5.263049	0.898073	6.510566
H	6.393184	-0.309899	7.133441
H	4.547160	-1.683732	7.952549
H	3.649076	-0.829900	6.676410
C	3.806834	1.771567	10.346097
H	4.422605	1.546312	11.227543
H	3.896405	2.841758	10.123627
H	2.765041	1.530734	10.564300

Structure [5-6]<sup>‡</sup>

Ag	-0.203961	0.059502	-1.186127
C	-0.431187	-0.098967	1.006807
C	1.524881	0.472431	0.860413
O	2.205510	-0.517650	0.968648
O	1.535370	1.679138	0.766461
C	-0.741824	-1.398509	1.424320
C	-1.715051	-1.709798	2.366177
C	-2.444317	-0.663229	2.936682
C	-2.183856	0.657501	2.562048
C	-1.185853	0.923926	1.621780
F	-0.068415	-2.448730	0.871243
H	-1.892043	-2.745544	2.640756

H	-3.207992	-0.883914	3.678138
H	-2.742007	1.472616	3.015463
H	-0.935487	1.953187	1.376691
O	0.319806	-1.864328	-2.563761
O	-0.136657	1.478230	-2.989298
C	0.831357	-2.902908	-2.117019
N	0.334036	-4.149499	-2.321770
C	1.159559	-5.211798	-1.752899
C	2.073080	-4.458427	-0.762442
C	2.113919	-3.021413	-1.309750
H	0.528704	-5.964140	-1.265229
H	1.728693	-5.718771	-2.547656
H	1.613791	-4.451572	0.230284
H	3.059241	-4.921986	-0.678802
H	2.956567	-2.862229	-1.997131
H	2.161299	-2.254499	-0.533738
C	-0.826649	-4.422995	-3.141464
H	-0.548678	-4.998395	-4.034786
H	-1.571968	-4.995642	-2.576424
H	-1.257131	-3.468252	-3.448034
C	0.849105	2.190838	-3.244371
N	0.823413	3.236704	-4.104066
C	2.078357	3.985381	-4.149979
C	3.101623	3.012552	-3.523579
C	2.244201	2.071943	-2.656259
H	2.322673	4.256341	-5.183494
H	1.981977	4.917604	-3.573923
H	3.602780	2.445983	-4.315028
H	3.869061	3.540089	-2.952558
H	2.200931	2.374658	-1.602102
H	2.574759	1.029538	-2.672266
C	-0.385208	3.717113	-4.743342
H	-0.675757	4.696850	-4.341987
H	-0.232566	3.813032	-5.824584
H	-1.183037	2.998648	-4.549882

Structure 6

C	0.137543	-0.251531	0.143157
C	-0.033045	-0.280857	1.533031
C	1.019150	0.008718	2.421630
C	2.234773	0.324215	1.820231
C	2.451833	0.365984	0.447249
C	1.381478	0.072251	-0.400804
Ag	0.917376	0.001216	4.486343
O	0.917933	0.014101	6.683027
F	3.309174	0.618024	2.622399
H	3.434527	0.622446	0.061793
H	1.523773	0.097647	-1.478252
H	-0.700006	-0.481305	-0.511470
H	-1.013045	-0.536921	1.929610
C	1.926796	0.112383	7.407473
N	1.879723	0.157473	8.754856
C	3.201057	0.185385	9.384234
C	4.140679	0.591113	8.227840
C	3.376510	0.166989	6.960110
H	3.210410	0.900367	10.214127
H	3.443108	-0.806279	9.793233
H	4.284791	1.676112	8.232846
H	5.123706	0.122994	8.314893
H	3.659550	-0.834974	6.611664
H	3.495683	0.844207	6.110317
C	0.658375	0.010489	9.524417
H	0.667597	-0.931047	10.087724
H	0.553096	0.841781	10.230398
H	-0.185447	0.009054	8.833374

- 
- <sup>1</sup> Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- <sup>2</sup> C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; P. J. Stephens, J. F. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
- <sup>3</sup> P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
- <sup>4</sup> M. Dolg, U. Wedig, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1987, **86**, 866; D. Andrae, U. Hübnermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123.
- <sup>5</sup> M. W. Wong, *Chem. Phys. Lett.*, 1996, **256**, 391.
- <sup>6</sup> R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.
- <sup>7</sup> GaussView 4.1.2, Gaussian, Inc., Wallingford CT, 2006.