Electronic Supplementary Material (ESI) for Green Chemistry.

PhotoOrganocatalytic Synthesis of Lactones via a Selective C-H Activation-alkylation of Alcohols

Nikolaos Kaplaneris, Aikaterini Bisticha, Giorgos N. Papadopoulos,
Dimitris Limnios and Christoforos G. Kokotos*

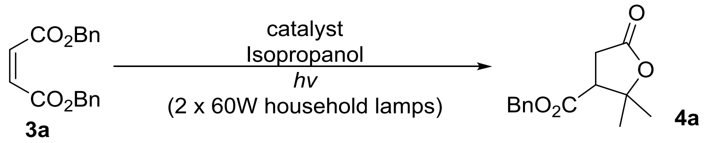
Laboratory of Organic Chemistry, Department of Chemistry, National and Kapodistrian
University of Athens,
Panepistimiopolis, Athens 15771, Greece

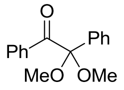
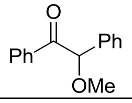
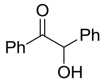
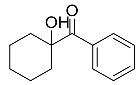
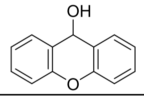
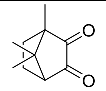
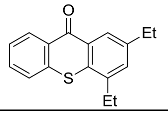
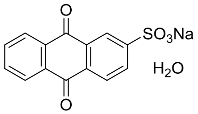
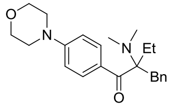
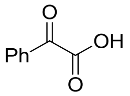
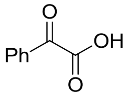
SUPPORTING INFORMATION

General Remarks

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

Catalyst Optimization for the PhotoOrganocatalytic Reaction Between Dibenzyl Maleate and Isopropanol



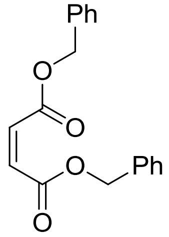
Entry	Catalyst[a]	Catalyst Loading (mol%)	Reaction Time (days)	Yield (%)[b]
1		30	3	60
2		30	3	75
3		30	3	83
4		30	3	87
5		30	3	20
6		30	3	83
7		30	3	40
8		30	3	78
9		30	3	33
10		30	3	98
11		20	3	90
12		10	3	58
13	-	-	3	0
14[c]		30	3	traces
15[d]		30	-	97

[a] Reaction conditions: **3a** (0.5 mmol), catalyst (0.15 mmol) and isopropanol (2 mL). [b] Isolated yield. [c] Reaction was kept in the dark. [d] Reaction was carried out utilizing sunlight (from 09:00 until 17:00, 27 July 2016, Athens, Greece, 37.97° N, 23.72° E).

General Procedure for the Synthesis of Dibenzyl Maleates

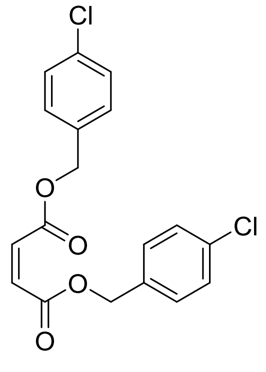
In a round bottom flask maleic acid (1 equiv.) and K_2CO_3 (1.1 equiv.) were dissolved in DMF (0.5 M). The reaction mixture was stirred at 0 °C for 30 min. Benzyl bromide or chloride (2 equiv.) was added dropwise. After 24-48 h, the reaction mixture was concentrated under reduced pressure and the crude product was purified by silica gel chromatography (pet. ether/EtOAc) to provide the desired dibenzyl maleate.

Dibenzyl maleate (3a)[1]



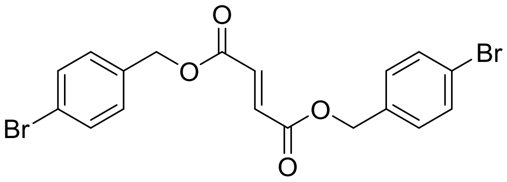
Colorless oil (85%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.37 (10H, s, ArH), 6.28 (2H, s, 2 x HC=C), 5.17 (4H, s, 2 x CH_2Ph); **^{13}C NMR** (50 MHz, $CDCl_3$) δ 163.4, 136.1, 132.4, 128.9, 127.6, 65.9; **MS (ESI) m/z(%)** 297 [M+1, 100%].

Bis(4-chlorobenzyl) maleate (3b)



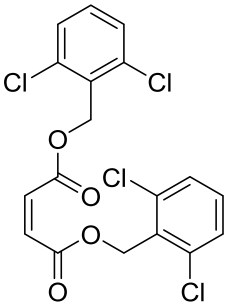
White solid (73%), m.p. 66-68 °C; **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.30 (4H, d, J = 8.8 Hz, ArH), 7.23 (4H, d, J = 8.8 Hz, ArH), 6.28 (2H, s, 2 x HC=C), 5.09 (4H, s, 2 x CH_2Ar); **^{13}C NMR** (50 MHz, $CDCl_3$) δ 164.6, 134.2, 133.5, 129.6, 128.6, 128.5, 66.0; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{18}H_{15}Cl_2O_4^+$) requires *m/z* 365.0342, found *m/z* 365.0349.

Bis(4-bromobenzyl) fumarate (3c)



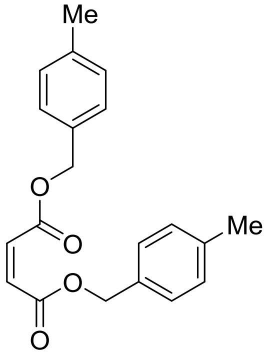
White solid (78%), m.p. 58-60 °C; **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.48 (4H, d, J = 8.3 Hz, ArH), 7.23 (4H, d, J = 8.3 Hz, ArH), 6.90 (2H, s, 2 x HC=C), 5.16 (4H, s, 2 x CH_2Ar); **^{13}C NMR** (50 MHz, $CDCl_3$) δ 164.4, 134.6, 133.6, 131.7, 130.0, 122.6, 66.3; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{18}H_{15}Br_2O_4^+$) requires *m/z* 452.9332, found *m/z* 452.9336.

Bis(2,6-dichlorobenzyl) maleate (3d)



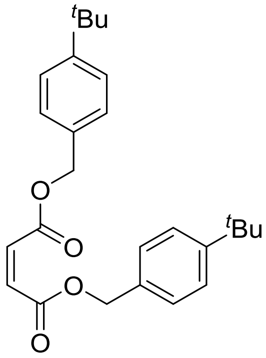
White solid (45%), m.p. 36-38 °C; **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.35-7.10 (6H, m, 6 x ArH), 6.25 (2H, s, 2 x HC=C), 5.45 (4H, s, 2 x CH_2Ar); **^{13}C NMR** (50 MHz, $CDCl_3$) δ 164.4, 137.0, 130.6, 130.5, 129.6, 128.3, 61.7; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{18}H_{13}Cl_4O_4^+$) requires *m/z* 432.9562, found *m/z* 432.9562.

Bis(4-methylbenzyl) maleate (3e)



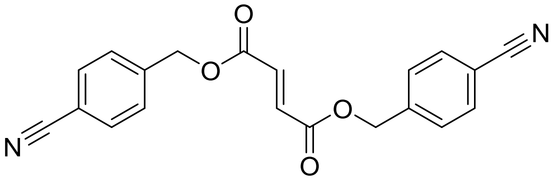
White solid (81%), m.p. 41-43 °C; **^{1}H NMR** (200 MHz, CDCl$_3$) δ 7.26 (4H, d, J = 7.9 Hz, ArH), 7.18 (4H, d, J = 7.9 Hz, ArH), 6.27 (2H, s, 2 x HC=C), 5.13 (4H, s, 2 x CH$_2$Ar), 2.37 (6H, s, 2 x CH$_3$); **^{13}C NMR** (50 MHz, CDCl$_3$) δ 164.8, 138.1, 132.0, 129.7, 129.1, 128.5, 66.9, 21.1; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{20}H_{21}O_4^+$) requires *m/z* 325.1434, found *m/z* 325.1437.

Bis(4-(tert-butyl)benzyl) maleate (3f)



White solid (45%), m.p. 60-64 °C; **^{1}H NMR** (200 MHz, CDCl$_3$) δ 7.38 (4H, d, J = 8.5 Hz, ArH), 7.27 (4H, d, J = 8.5 Hz, ArH). 6.26 (2H, s, 2 x HC=C), 5.10 (4H, s, 2 x CH$_2$Ar), 1.30 (18H, s, 6 x CH$_3$); **^{13}C NMR** (50 MHz, CDCl$_3$) δ 164.6, 151.1, 131.8, 129.4, 128.2, 125.1, 66.5, 34.2, 31.0; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{26}H_{33}O_4^+$) requires *m/z* 409.2373, found *m/z* 409.2374.

Bis(4-cyanobenzyl) fumarate (3g)

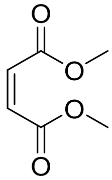


Colorless oil (49%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.66 (4H, d, J = 8.2 Hz, ArH), 7.46 (4H, d, J = 8.2 Hz, ArH). 6.96 (2H, s, 2 x HC=C), 5.28 (4H, s, 2 x CH_2Ar); **^{13}C NMR** (50 MHz, $CDCl_3$) δ 164.1, 140.2, 133.5, 132.4, 118.3, 112.3, 65.7; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{20}H_{15}N_2O_4^+$) requires *m/z* 347.1026, found *m/z* 347.1026.

General Procedure for the Synthesis of Dialkyl Maleates

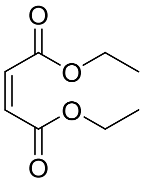
In a round bottom flask maleic acid (5.00 mmol, 0.58 g, 1 equiv.), alcohol (10 mL) and conc. H_2SO_4 (0.2 mL) were added. The reaction mixture was stirred at 80 ^oC for 16 h. After 16 h, the reaction mixture was cooled, concentrated under reduced pressure and the crude product was purified by silica gel chromatography (pet. ether/EtOAc) to provide the desired dialkyl maleate.

Dimethyl maleate (3h)[2]



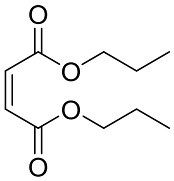
Colorless oil (40%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 6.09 (2H, s, 2 x HC=C), 3.57 (6H, s, 2 x OCH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) δ 167.6, 129.6, 52.5; **MS (ESI) m/z(%)** 144 [M+1, 100%].

Diethyl maleate (3i)[3]



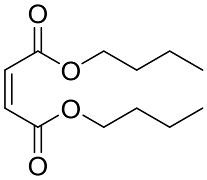
Colorless oil (36%); ^{1}**H NMR** (200 MHz, $CDCl_3$) *δ* 6.06 (2H, s, 2 x HC=C), 4.05 (4H, q, *J* = 7.1 Hz, OCH_2), 1.06 (6H, t, *J* = 7.1 Hz, 2 x CH_3); ^{13}**C NMR** (50 MHz, $CDCl_3$) *δ* 167.6, 129.6, 61.5, 13.6; **MS (ESI) m/z(%)** 172 [M+1, 100%].

Dipropyl maleate (3j)[4]



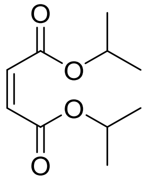
Colorless oil (58%); ^{1}**H NMR** (200 MHz, $CDCl_3$) *δ* 6.06 (2H, s, 2 x HC=C), 3.94 (4H, t, *J* = 6.7 Hz, 2 x OCH_2), 1.52-1.48 (4H, m, 2 x CH_2CH_3), 0.78 (6H, t, *J* = 7.4 Hz, 2 x CH_3); ^{13}**C NMR** (50 MHz, $CDCl_3$) *δ* 165.3, 129.8, 66.7, 21.8, 10.3; **MS (ESI) m/z(%)** 200 [M+1, 100%].

Dibutyl maleate (3k)[5]



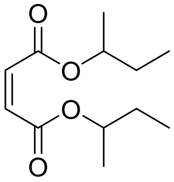
Colorless oil (60%); ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 6.06 (2H, s, 2 x HC=C), 3.94 (4H, t, *J* = 6.6 Hz, 2 x OCH_2), 1.44-1.37 (4H, m, 2 x CH_2), 1.21-1.10 (4H, m, 2 x CH_2), 0.70 (6H, t, *J* = 7.2 Hz, 2 x CH_3); ^{13}**C NMR** (50 MHz, $CDCl_3$) *δ* 165.2, 129.8, 64.9, 30.5, 19.1, 13.6; **MS (ESI) m/z(%)** 228 [M+1, 100%].

Diisopropyl maleate (3l)



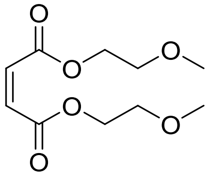
Colorless oil (20%); **^{1}H NMR** (200 MHz, $CDCl_3$) *δ* 6.15 (2H, s, 2 x HC=C), 5.00 (2H, hept, *J* = 6.3 Hz, 2 x OCH), 1.18 (12H, d, *J* = 6.3 Hz, 4 x CH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) *δ* 164.9, 130.1, 69.1, 21.8; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{10}H_{17}O_4^+$) requires *m/z* 201.1121, found *m/z* 201.1129.

Di-*sec*-butyl maleate (3m)



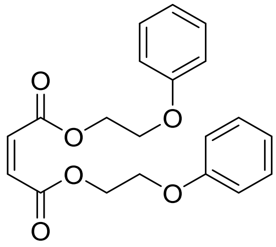
Colorless oil (24%); **^{1}H NMR** (200 MHz, $CDCl_3$) *δ* 6.11 (2H, s, 2 x HC=C), 4.87-4.80 (2H, m, 2 x OCH), 1.58-1.43 (4H, m, 2 x CH_2), 1.17 (6H, d, *J* = 6.3 Hz, 2 x CH_3CH), 0.82 (6H, t, *J* = 7.4 Hz, 2 x C$H_3$$CH_2$); **^{13}C NMR** (50 MHz, $CDCl_3$) *δ* 165.1, 130.0, 73.5, 28.8, 19.3, 9.7; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{12}H_{21}O_4^+$) requires *m/z* 229.1434, found *m/z* 229.1438.

Bis(2-methoxyethyl) maleate (3n)



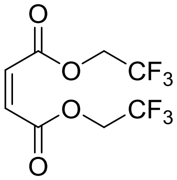
Colorless oil (41%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 6.21 (2H, s, 2 x HC=C), 4.30-4.13 (4H, m, 2 x CH_2OCO), 3.56-3.45 (4H, m, 2 x CH_2OCH_3), 3.28 (6H, s, 2 x OCH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) *δ* 164.9, 129.6, 69.8, 63.9, 58.6; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{10}H_{17}O_6^+$) requires *m/z* 233.1020, found *m/z* 233.1021.

Bis(2-phenoxyethyl) maleate (3o)



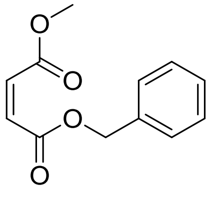
Colorless oil (25%); **^{1}H NMR** (200 MHz, $CDCl_3$) *δ* 7.41-7.25 (4H, m, 4 x ArH), 7.08-6.82 (6H, m, 6 x ArH), 6.31 (2H, s, 2 x HC=C), 4.61-4.45 (4H, m, 2 x CH_2O), 4.25-4.09 (4H, m, 2 x CH_2O); **^{13}C NMR** (50 MHz, $CDCl_3$) *δ* 164.9, 158.2, 129.7, 129.4, 121.0, 114.4, 65.2, 63.4; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{20}H_{21}O_6^+$) requires *m/z* 357.1333, found *m/z* 357.1339.

Bis(2,2,2-trifluoroethyl) maleate (3p)



Pale yellow oil (85%); **^{1}H NMR** (200 MHz, $CDCl_3$) *δ* 6.35 (2H, s, 2 x HC=C), 4.50 (4H, q, *J* = 8.4 Hz, 2 x CH_2CF_3); **^{13}C NMR** (50 MHz, $CDCl_3$) *δ* 163.0, 129.6, 122.6 (q, *J* = 276.9 Hz), 60.9 (q, *J* = 37.2 Hz); **^{19}F NMR** (188 MHz, $CDCl_3$) *δ* 5.05 (t, *J* = 8.3 Hz); **HRMS** exact mass calculated for $[M+H]^+$ ($C_8H_7F_6O_4^+$) requires *m/z* 281.0243, found *m/z* 281.0248.

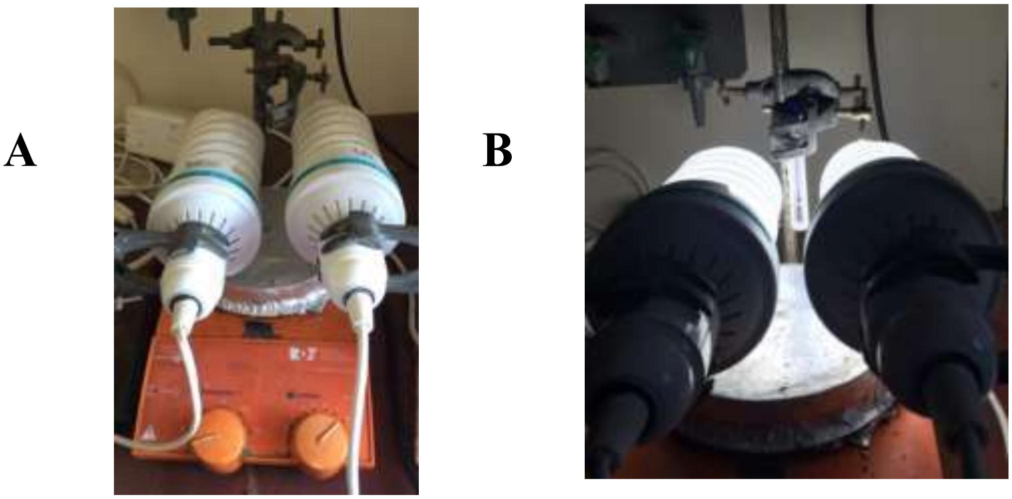
Benzyl methyl maleate (3q)



Low melting point solid; **^{1}H NMR** (200 MHz, $CDCl_3$) *δ* 7.36-7.32 (5H, m, 5 x ArH), 6.89 (2H, s, 2 x HC=C), 5.22 (2H, s, CH_2Ph), 3.78 (3H, s, OCH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) *δ* 165.2, 164.6, 135.1, 133.5, 133.4, 128.5, 128.4, 128.2, 67.0, 52.2; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{12}H_{13}O_4^+$) requires *m/z* 221.0808, found *m/z* 221.0814.

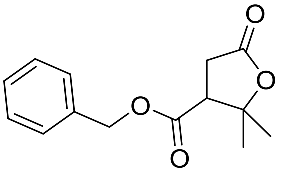
General Procedure for the Photocatalytic Synthesis of γ-Lactones

In a glass vial with a screw cap containing phenylglyoxilic acid (23 mg, 0.15 mmol, 0.3 equiv.) in the corresponding alcohol (2 mL), diester of maleic acid (0.50 mmol, 1 equiv.) was added. The vial was sealed with a screw cap and left stirring under household bulb irradiation (2 x 85W household lamps, see photos below) for 3 days. The reaction progress can be monitored by GC-MS. After completion of the reaction, the product was isolated by flash silica chromatography of the crude mixture.



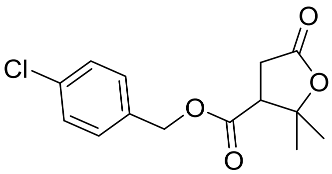
Scheme. A: 2 x 85W fluorescent household lamps utilized for the photocatalytic reaction. Bulbs are placed symmetrically 3 cm away from the reaction tube. **B**: Beginning of the reaction.

Benzyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4a)



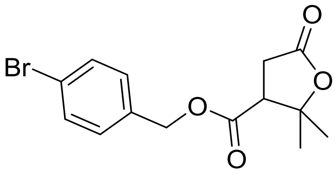
White solid (98%), m.p. 92-94 °C; **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.41-7.25 (5H, m, ArH), 5.20 (1H, d, *J* = 12.1 Hz, OC*H*HAr), 5.11 (1H, d, *J* = 12.1 Hz, OC*H*HAr), 3.27-2.93 (2H, m, CH and C*H*H), 2.67 (1H, dd, *J* = 17.3 and 8.2 Hz, C*H*H), 1.54 (3H, s, CH_3), 1.18 (3H, s, CH$_3$); ^{13}**C NMR** (50 MHz, CDCl$_3$) δ 173.8, 169.5, 134.8, 128.6, 128.5, 84.2, 67.2, 50.2, 31.6, 28.3, 23.0; **HRMS** exact mass calculated for [M+Na]$^+$ (C$_{14}$H$_{16}$NaO$_4^+$) requires *m/z* 271.0941, found *m/z* 271.0941.

4-Chlorobenzyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4b)



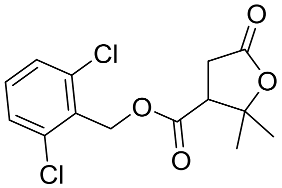
White solid (95%), m.p. 91-93 °C; ^{1}**H NMR** (200 MHz, CDCl$_3$) δ 7.34 (2H, d, *J* = 8.6 Hz, ArH), 7.28 (2H, d, *J* = 8.6 Hz, ArH), 5.17 (1H, d, *J* = 12.1 Hz, OC*H*HAr), 5.09 (1H, d, *J* = 12.1 Hz, OC*H*HAr), 3.25-2.97 (2H, m, CH and C*H*H), 2.69 (1H, dd, *J* = 17.2 and 8.2 Hz, C*H*H), 1.55 (3H, s, CH$_3$), 1.20 (3H, s, CH$_3$); ^{13}**C NMR** (50 MHz, CDCl$_3$) δ 173.8, 169.5, 134.6, 133.3, 130.0, 128.9, 84.3, 66.4, 50.3, 31.7, 28.4, 23.2; **HRMS** exact mass calculated for [M+Na]$^+$ (C$_{14}$H$_{15}$ClNaO$_4^+$) requires *m/z* 305.0551, found *m/z* 305.0553.

4-Bromobenzyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4c)



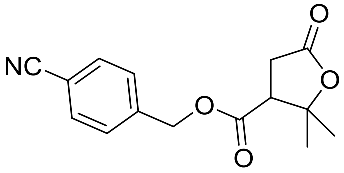
Colorless oil (93%); ^{1}**H NMR** (200 MHz, CDCl$_3$) δ 7.49 (2H, d, *J* = 8.4 Hz, ArH), 7.22 (2H, d, *J* = 8.4 Hz, ArH), 5.15 (1H, d, *J* = 12.2 Hz, OC*H*HAr), 5.07 (1H, d, *J* = 12.2 Hz, OC*H*HAr), 3.27-2.97 (2H, m, CH and C*H*H), 2.68 (1H, dd, *J* = 17.2 and 8.2 Hz, C*H*H), 1.54 (3H, s, CH$_3$), 1.20 (3H, s, CH$_3$); ^{13}**C NMR** (50 MHz, CDCl$_3$) δ 173.8, 169.5, 133.8, 131.8, 130.3, 122.8, 84.3, 66.4, 50.2, 31.6, 28.4, 23.2; **HRMS** exact mass calculated for [M+Na]$^+$ (C$_{14}$H$_{15}$BrNaO$_4^+$) requires *m/z* 349.0046, found *m/z* 349.0056.

2,6-Dichlorobenzyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4d)



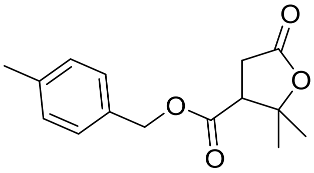
Colorless oil (92%); ^{1}**H NMR** (200 MHz, CDCl$_3$) *δ* 7.41-7.25 (3H, m, ArH), 5.47 (1H, d, *J* = 11.6 Hz, OC*H*HAr), 5.40 (1H, d, *J* = 11.6 Hz, OC*H*HAr) 3.31-3.04 (2H, m, CH and C*H*H), 2.71 (1H, dd, *J* = 15.7 and 7.2 Hz, C*H*H), 1.56 (3H, s, CH$_3$), 1.33 (3H, s, CH$_3$); ^{13}**C NMR** (50 MHz, CDCl$_3$) δ 173.9, 169.5, 136.9, 131.0, 130.4, 128.6, 84.4, 62.3, 50.3, 31.7, 28.4, 23.3; **HRMS** exact mass calculated for [M+Na]$^+$ ($C_{14}H_{14}Cl_2NaO_4^+$) requires *m/z* 339.0161, found *m/z* 339.0166.

4-Cyanobenzyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4e)



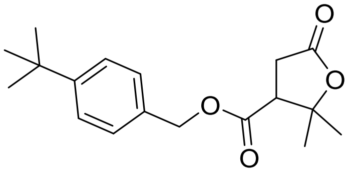
Colorless oil (92%); ^{1}**H NMR** (200 MHz, CDCl$_3$) *δ* 7.67 (2H, d, *J* = 7.5 Hz, ArH), 7.57 (2H, d, *J* = 7.5 Hz, ArH), 5.21 (2H, s, OCH$_2$Ar), 3.32-2.97 (2H, m, CH and C*H*H), 2.69 (1H, dd, *J* = 17.6 and 8.6 Hz, C*H*H), 1.57 (3H, s, CH$_3$), 1.22 (3H, s, CH$_3$); ^{13}**C NMR** (50 MHz, CDCl$_3$) *δ* 173.6, 169.4, 139.9, 132.3, 128.8, 118.3, 112.5, 84.2, 66.1, 50.3, 31.7, 28.4, 23.3; **HRMS** exact mass calculated for [M+Na]$^+$ ($C_{15}H_{15}NNaO_4^+$) requires *m/z* 296.0896, found *m/z* 296.0906.

4-Methylbenzyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4f)



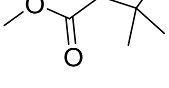
White solid (95%), m.p. 85-87 °C; **^{1}H NMR** (200 MHz, CDCl$_3$) δ 7.25 (2H, d, J = 8.0 Hz, ArH), 7.17 (2H, d, J = 8.0 Hz, ArH), 5.18 (1H, d, J = 11.8 Hz, OC*H*HAr), 5.09 (1H, d, J = 11.8 Hz, OC*H*HAr), 3.26-3.02 (2H, m, CH and C*H*H), 2.68 (1H, dd, J = 16.5 and 7.5 Hz, C*H*HCO), 2.35 (3H, s, CH$_3$), 1.56 (3H, s, CH$_3$), 1.20 (3H, s, CH$_3$); **^{13}C NMR** (50 MHz, CDCl$_3$) δ 173.9, 169.6, 138.5, 131.9, 129.3, 128.7, 84.3, 67.2, 50.3, 31.6, 28.4, 23.1, 21.1; **HRMS** exact mass calculated for [M+Na]$^+$ ($C_{15}H_{18}NaO_4^+$) requires *m/z* 285.1097, found *m/z* 285.1102.

4-(*tert*-Butyl)benzyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4g)



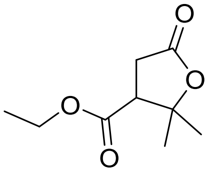
Colorless oil (84%); **^{1}H NMR** (200 MHz, CDCl$_3$) δ 7.45-7.21 (4H, m, ArH), 5.16 (2H, s, OCH$_2$Ar), 3.27-2.99 (2H, m, CH and C*H*H), 2.67 (1H, dd, J = 17.1 and 8.0 Hz, C*H*H), 1.57 (3H, s, CH$_3$), 1.34 (9H, s, 3 x CH$_3$), 1.23 (3H, s, CH$_3$); **^{13}C NMR** (50 MHz, CDCl$_3$) δ 173.9, 169.6, 151.8, 131.8, 128.4, 125.6, 84.4, 67.2, 50.3, 34.0, 31.7, 31.2, 28.4, 23.1; **HRMS** exact mass calculated for [M+Na]$^+$ ($C_{18}H_{24}NaO_4^+$) requires *m/z* 327.1567, found *m/z* 327.1579.

Methyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4h)[6]



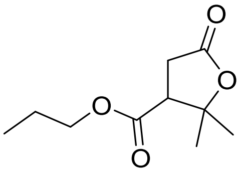
Colorless oil (92%); ^{1}**H NMR** (200 MHz, CDCl$_3$) δ 3.72 (3H, s, OCH$_3$), 3.21-3.09 (2H, m, CH and C*H*H), 2.66 (1H, dd, J = 17.1 and 8.2 Hz, C*H*H), 1.55 (3H, s, CH$_3$), 1.26 (3H, s, CH$_3$); ^{13}**C NMR** (50 MHz, CDCl$_3$) δ 173.9, 170.2, 84.3, 52.4, 50.2, 31.7, 28.3, 23.2; **HRMS** exact mass calculated for [M+Na]$^+$ ($C_8H_{12}NaO_4^+$) requires *m/z* 195.0628, found *m/z* 195.0626.

Ethyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4i)[6]



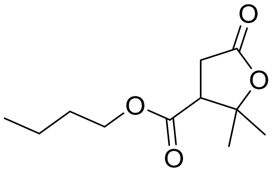
Colorless oil (96%); ^{1}**H NMR** (200 MHz, CDCl$_3$) δ 4.21 (2H, q, *J* = 4.2 Hz, OCH$_2$), 3.14-2.92 (2H, m, CH and C*H*H), 2.66 (1H, dd, *J* = 16.4 and 7.4 Hz C*H*H), 1.57 (3H, s, CH$_3$), 1.32-1.29 (6H, m, 2 x CH$_3$); ^{13}**C NMR** (50 MHz, CDCl$_3$) δ 174.0, 169.7, 84.3, 61.4, 50.3, 31.6, 28.4, 23.2, 14.1; **HRMS** exact mass calculated for [M+Na]$^+$ ($C_9H_{14}NaO_4^+$) requires *m/z* 209.0784, found *m/z* 209.0782.

Propyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4j)



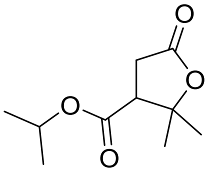
Colorless oil (70%); ^{1}**H NMR** (200 MHz, CDCl$_3$) δ 4.10 (2H, t, *J* = 6.5 Hz, OCH$_2$), 3.16-2.99 (2H, m, CH and C*H*H), 2.65 (1H, dd, *J* = 17.1 and 8.1 Hz, C*H*H), 1.65-1.52 (5H, m, CH$_2$ and CH$_3$), 1.56 (3H, s, CH$_3$), 0.92 (3H, t, *J* = 7.4 Hz, CH$_3$); ^{13}**C NMR** (50 MHz, CDCl$_3$) δ 176.1, 173.3, 80.9, 66.5, 50.6, 33.7, 24.2, 24.9, 22.2, 10.3; **HRMS** exact mass calculated for [M+Na]$^+$ ($C_{10}H_{16}NaO_4^+$) requires *m/z* 223.0941, found *m/z* 223.0941.

Butyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4k)



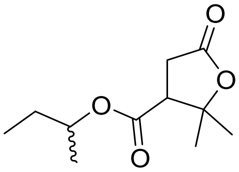
Colorless oil (96%); **^{1}H NMR** (200 MHz, $CDCl_3$) *δ* 4.10 (2H, t, *J* = 6.6 Hz, OCH_2), 3.19-2.95 (2H, m, CH and C*H*H), 2.64 (1H, dd, *J* = 17.1 and 8.1 Hz, C*H*H), 1.54-1.52 (5H, m, CH_2 and CH_3), 1.31-1.25 (5H, m, CH_2 and CH_3), 0.84 (3H, t, *J* = 7.3 Hz, CH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) *δ* 173.9, 169.8, 84.3, 65.3, 50.3, 31.6, 30.3, 28.3, 23.1, 19.0, 13.5; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{11}H_{18}NaO_4^+$) requires *m/z* 237.1097, found *m/z* 237.1099.

Isopropyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4l)[7]



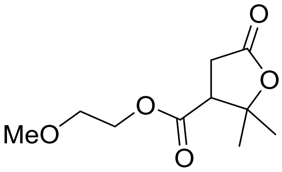
After 72 h, AcOH (2 equiv.) were added and stirred for additional 24 h. Colorless oil (81%); **^{1}H NMR** (200 MHz, $CDCl_3$) *δ* 5.14-4.96 (1H, m, OCH), 3.28-2.95 (2H, m, CH and C*H*H), 2.71 (1H, dd, *J* = 13.7 and 9.0 Hz, C*H*H), 1.59 (3H, s, CH_3) 1.31-1.22 (9H, m, 3 x CH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) *δ* 174.2, 169.2, 84.4, 69.3, 50.6, 31.6, 28.2, 23.2, 21.8, 21.7; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{10}H_{16}NaO_4^+$) requires *m/z* 223.0941, found *m/z* 223.0943.

sec-Butyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4m)



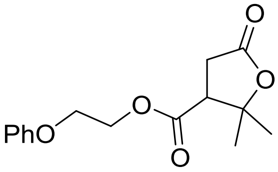
Colorless oil (85%, mixture of diastereomers); **^{1}H NMR** (200 MHz, $CDCl_3$) *δ* 4.89-4.80 (1H, m, OCH), 3.12-2.99 (2H, m, CH and C*H*H), 2.63 (1H, dd, *J* = 16.5 and 7.5 Hz, C*H*H) 1.67-1.42 (5H, m, CH_2 and CH_3), 1.27-1.17 (6H, m, 2 x CH_3), 0.87 (3H, t, *J* = 7.4 Hz, CH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) δ 174.2, 169.3, 169.2, 84.3, 73.9, 73.7, 50.6, 50.4, 31.7, 31.6, 28.5, 28.3, 23.1, 23.0, 19.1, 9.6, 9.5; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{11}H_{18}NaO_4^+$) requires *m/z* 237.1097, found *m/z* 237.1101.

2-Methoxyethyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4n)



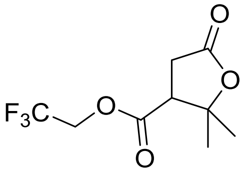
Colorless oil (83%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 4.34 (1H, dt, *J* = 12.0 and 4.6 Hz, C*H*HO), 4.22 (1H, dt, *J* = 12.0 and 4.6 Hz, C*H*HO), 3.58 (2H, t, *J* = 4.6 Hz, OC*H$_2$*), 3.34 (3H, s, OCH_3), 3.18-2.98 (2H, m, CH and C*H*H), 2.67 (1H, dd, *J* = 17.4 and 8.3 Hz, C*H*H), 1.58 (3H, s, CH_3), 1.30 (3H, s, CH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) δ 174.0, 169.8, 84.4, 70.0, 64.1, 58.7, 50.2, 31.6, 28.3, 23.1; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{10}H_{16}F_2NaO_5^+$) requires *m/z* 239.0890, found *m/z* 239.0899.

2-Phenoxyethyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4o)



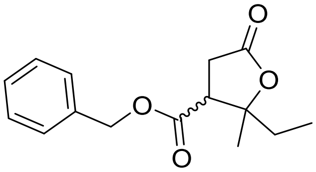
Colorless oil (92%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.38-7.23 (2H, m, ArH), 7.04-6.82 (3H, m, ArH), 4.59 (1H, dt, *J* = 14.9 and 5.1 Hz, C*H*HOCO), 4.41 (1H, dt, *J* = 14.9 and 5.1 Hz, C*H*HOCO), 4.22-4.14 (2H, m, C*H$_2$*O), 3.29-3.01 (2H, m, CH and C*H*H), 2.70 (1H, dd, *J* = 17.1 and 8.1 Hz, C*H*H), 1.59 (3H, s, CH_3), 1.32 (3H, s, CH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) δ 173.9, 169.7, 158.0, 129.5, 121.3, 114.3, 84.4, 65.2, 63.6, 50.2, 31.5, 28.3, 23.1; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}O_5^+$) requires *m/z* 279.1227, found *m/z* 279.1227.

2,2,2-Trifluoroethyl 2,2-dimethyl-5-oxotetrahydrofuran-3-carboxylate (4p)



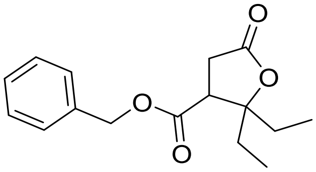
Colorless oil (87%); ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 4.66 (1H, dq, *J* = 12.7 and 8.3 Hz, C*H*HCF$_3$), 4.42 (1H, dq, *J* = 12.7 and 8.3, C*H*HCF$_3$), 3.30 (1H, dd, *J* = 9.7 and 8.8 Hz, CH), 3.07 (1H, dd, *J* = 17.8 and 9.7 Hz, C*H*H), 2.73 (1H, dd, *J* = 17.8 and 8.8 Hz, C*H*H), 1.60 (3H, s, CH_3), 1.30 (3H, s, CH_3); ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 173.2, 168.4, 122.4 (q, *J* = 277.3 Hz), 84.0, 60.7 (q, *J* = 36.9 Hz), 50.0, 31.5, 28.2, 23.1; ^{19}**F NMR** (188 MHz, $CDCl_3$) δ 5.66 (t, *J* = 8.3 Hz); **HRMS** exact mass calculated for $[M+Na]^+$ ($C_9H_{11}F_3NaO_4^+$) requires *m/z* 263.0502, found *m/z* 263.0506.

Benzyl 2-ethyl-2-methyl-5-oxotetrahydrofuran-3-carboxylate (6b)



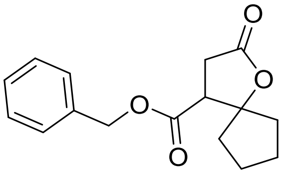
Colorless oil (82%, 53:47 mixture of diasteromers); ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 7.41-7.31 (5H, m, ArH), 5.20 (1H, d, *J* = 12.6 Hz, OC*H*HPh), 5.13 (1H, d, *J* = 12.6 Hz, OC*H*HPh), 3.34-2.96 (2H, m, CHCO and C*H*HCO), 2.68 (1H, dd, *J* =17.6 and 8.7 Hz, C*H*HCO), 1.90-1.09 (5H, m, CCH_3 and C*H*$_2$CH$_3$), 1.03-0.85 (3H, m, C*H*$_3$CH$_2$); ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 174.1, 169.8, 169.6, 134.9, 134.8, 128.6, 128.6, 128.5, 86.8, 86.7, 67.3, 50.7, 47.8, 33.6, 31.8, 31.6, 29.0, 25.1, 21.0, 7.8, 7.7; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{15}H_{18}NaO_4^+$) requires *m/z* 285.1097, found *m/z* 287.1087.

Benzyl 2,2-diethyl-5-oxotetrahydrofuran-3-carboxylate (6c)



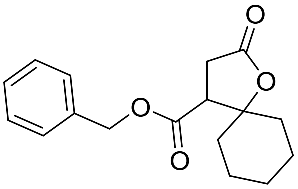
Colorless oil (85%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.41-7.32 (5H, m, ArH), 5.19 (1H, d, J = 12.3 Hz, OC*H*HPh), 5.13 (1H, d, J = 12.3 Hz, OC*H*HPh), 3.34 (1H, t, J = 9.1 Hz, CHCO), 3.09 (1H, dd, J = 18.0 and 9.1 Hz, C*H*HCO), 2.69 (1H, dd, J = 18.0 and 9.1 Hz, C*H*HCO), 1.93-1.42 (4H, m, 4 x C*H*H), 0.95 (3H, t, J = 7.4 Hz, CH_3), 0.86 (3H, t, J = 7.4 Hz, CH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) δ 174.4, 170.1, 134.8, 128.6, 128.6, 89.2, 67.3, 46.6, 32.1, 29.6, 27.6, 7.5; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{16}H_{20}NaO_4^+$) requires *m/z* 299.1254, found *m/z* 299.1269.

Benzyl 2-oxo-1-oxaspiro[4.4]nonane-4-carboxylate (6d)



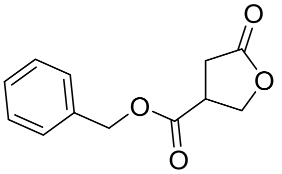
Colorless oil (93%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.43-7.25 (5H, m, ArH), 5.21 (1H, d, J = 12.1 Hz, OC*H*HPh), 5.13 (1H, d, J = 12.1 Hz, OC*H*HPh), 3.38 (1H, t, J = 8.4 Hz, CHCO), 3.01 (1H, dd, J = 17.6 and 8.4 Hz, C*H*HCO), 2.70 (1H, dd, J = 17.6 and 8.4 Hz, C*H*HCO), 2.11-1.91 (2H, m, 2 x C*H*H), 1.89-1.44 (6H, m, 6 x C*H*H); **^{13}C NMR** (50 MHz, $CDCl_3$) δ 174.2, 170.0, 134.9, 128.7, 128.6, 94.8, 67.2, 47.9, 38.7, 34.4, 32.6, 23.7, 23.2; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{16}H_{18}NaO_4^+$) requires *m/z* 297.1097, found *m/z* 297.1103.

Benzyl 2-oxo-1-oxaspiro[4.5]decane-4-carboxylate (6e)



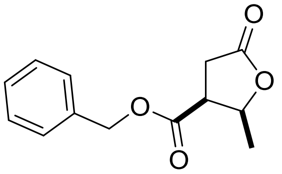
Colorless oil (82%); ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 7.41-7.34 (5H, m, ArH), 5.23 (1H, d, *J* = 12.1 Hz, OC*H*HPh), 5.13 (1H, d, *J* = 12.1 Hz, OC*H*HPh), 3.16-2.97 (2H, m, CH and C*H*H), 2.69 (1H, dd, J = 17.1 and 8.1 Hz, C*H*H), 1.96-1.39 (6H, m, 6 x C*H*H), 1.37-0.85 (4H, m, 4 x C*H*H); ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 174.7, 170.1, 135.2, 129.0 128.9, 86.3, 67.5, 50.7, 37.5, 32.5, 31.8, 25.0, 22.6, 21.8; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{17}H_{20}NaO_4^+$) requires *m/z* 311.1254, found *m/z* 311.1259.

Benzyl 5-oxotetrahydrofuran-3-carboxylate (6f)[8]



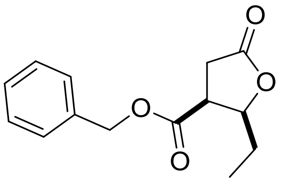
Colorless oil (42%); ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 7.45-7.28 (5H, m, 5 x ArH), 5.18 (2H, s, OCH_2Ph), 4.58-4.36 (2H, m, OCH_2), 3.58-3.35 (1H, m, CHCO), 2.93-2.62 (2H, m, 2 x C*H*HCO); ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 175.0, 170.9, 134.9, 128.7, 128.4, 68.9, 67.5, 39.9, 30.8; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{12}H_{12}NaO_4^+$) requires *m/z* 243.0628, found *m/z* 243.0636.

Benzyl 2-methyl-5-oxotetrahydrofuran-3-carboxylate (6g)



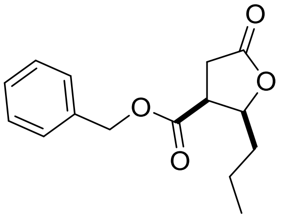
Colorless oil (48%, *cis* diastereomer); ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 7.45-7.28 (5H, m, 5 x ArH), 5.21-5.15 (2H, m, OCH_2Ph), 4.73-4.55 (1H, m, OCH), 3.12-2.68 (3H, m, CHCO and 2 x C*H*HCO), 1.49 (3H, d, *J* = 6.3 Hz, CH_3); ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 174.2, 170.5, 134.9, 128.7, 128.6, 128.5, 128.3, 127.6, 126.9, 78.1, 67.4, 47.5, 32.2, 20.7; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{13}H_{14}NaO_4^+$) requires *m/z* 257.0784, found *m/z* 257.0791.

Benzyl 2-ethyl-5-oxotetrahydrofuran-3-carboxylate (6h)



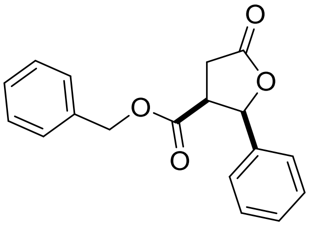
Colorless oil (75%, *cis* diastereomer); **^{1}H NMR** (200 MHz, CDCl$_3$) δ 7.45-7.28 (5H, m, 5 x ArH), 5.17 (2H, s, OCH$_2$Ph), 4.52 (1H, td, *J* = 7.0 and 5.4 Hz, OCH), 3.07 (1H, m, ddd, *J* = 11.6, 9.4 and 5.4 Hz, CHCO), 2.93-2.67 (2H, m, 2 x C*H*HCO), 1.88-1.58 (2H, m, 2 x C*H*H), 1.00 (3H, t, *J* = 7.4 Hz, CH$_3$); **^{13}C NMR** (50 MHz, CDCl$_3$) δ 174.4, 170.9, 134.9, 128.7, 128.6, 128.3, 82.9, 67.4, 45.2, 32.2, 28.2, 9.4; **HRMS** exact mass calculated for [M+Na]$^+$ (C$_{14}$H$_{16}$NaO$_4$$^+$) requires *m/z* 271.0941, found *m/z* 271.0946.

Benzyl 5-oxo-2-propyltetrahydrofuran-3-carboxylate (6i)



Colorless oil (89%, *cis* diastereomer); **^{1}H NMR** (200 MHz, CDCl$_3$) δ 7.39-7.28 (5H, m, ArH), 5.22 (1H, d, *J* = 12.0 Hz, OC*H*HPh), 5.13 (1H, d, *J* = 12.0 Hz, OC*H*HPh), 4.65-4.54 (1H, m, OCH), 3.53-3.37 (1H, m, CHCO), 2.90 (1H, dd, *J* = 17.6 and 5.7 Hz, C*H*HCO), 2.65 (1H, dd, *J* = 17.6 and 8.6 Hz, C*H*HCO), 1.62-1.31 (4H, m, 4 x C*H*H), 0.82 (3H, t, *J* = 7.1 Hz, CH$_3$); **^{13}C NMR** (50 MHz, CDCl$_3$) δ 174.9, 170.2, 134.9, 128.8, 128.7, 128.6, 80.2, 67.2, 44.2, 33.3, 31.7, 19.0, 13.6; **HRMS** exact mass calculated for [M+Na]$^+$ (C$_{15}$H$_{18}$NaO$_4$$^+$) requires *m/z* 285.1097, found *m/z* 287.1089.

Benzyl 5-oxo-2-phenyltetrahydrofuran-3-carboxylate (6j)



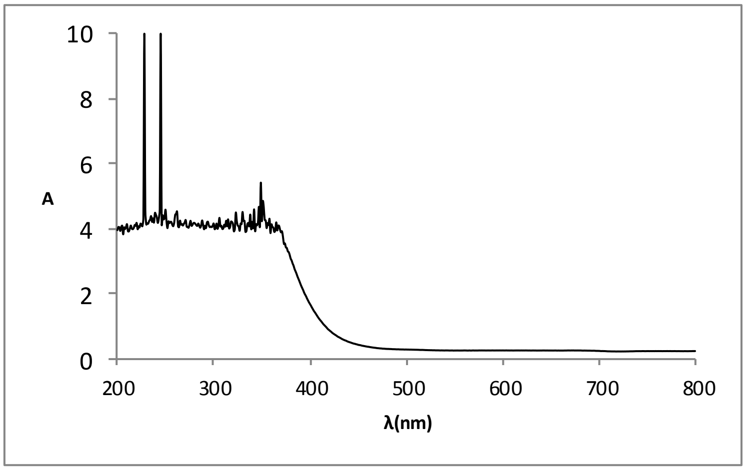
Colorless oil (55%, *cis* diastereomer); ^{1}**H NMR** (200 MHz, CDCl$_3$) δ 7.40-7.24 (10H, m, ArH), 5.62 (1H, d, *J* = 7.3 Hz, OCHPh), 5.24 (1H, d, *J* = 12.2 Hz, OC*H*HPh), 5.15 (1H, d, *J* = 12.2 Hz, OC*H*HPh), 3.37 (1H, ddd, *J* = 12.2, 9.7 and 8.8 Hz, CHCO), 3.02 (1H, dd, *J* = 17.9 and 8.8 Hz, C*H*HCO), 2.89 (1H, dd, *J* = 17.9 and 9.7 Hz, C*H*HCO); ^{13}**C NMR** (50 MHz, CDCl$_3$) δ 174.0, 170.5, 137.8, 134.8, 128.8, 128.7, 128.6, 128.5, 128.3, 125.4, 82.1, 67.5, 48.7, 32.2; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{18}H_{16}NaO_4^+$) requires *m/z* 319.0941, found *m/z* 319.0936.

Determination of Quantum Yields

Determination of the photon flux at 248 nm

The photon flux of the spectrophotometer was determined following the work of Yoon and coworkers,[8] utilizing standard ferrioxalate actinometry.[9,10] A 0.006M solution of potassium ferrioxalate was prepared by dissolving 120 mg of potassium ferrioxalate hydrate in 40 mL of 0.05M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 10 mg of phenanthroline and 2.25 g of sodium acetate in 250 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the photometer, 2.0 mL of the solution of potassium ferrioxalate was placed in a cuvette, UV-Vis absorbance recorded (absorbance of interest at 510 nm) and shown below, and irradiated for 90 seconds at 248 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was allowed to rest for 1 h (complete coordination of ferrous ions to phenanthroline). The absorbance of the solution was then measured at 510 nm.

Absorbance of the ferrioxalate actinometer solution



The absorbance of the above ferrioxalate solution at 248 nm was measured to be 4.9987. The fraction of light absorbed (f) by this solution was calculated, using this absorbance (A):

$$f = 1 - 10^{-A} = 1 - 10^{-4.9987} = 0.999947$$

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

$$\text{Mol Fe}^{2+} = \frac{V \times \Delta A}{l \times \varepsilon} = \frac{0.00235 \text{ L} \times 0.246}{1.0 \text{ cm} \times 11.100 \text{ L mol}^{-1} \text{ cm}^{-1}} = 5.21 \times 10^{-8} \text{ mol}$$

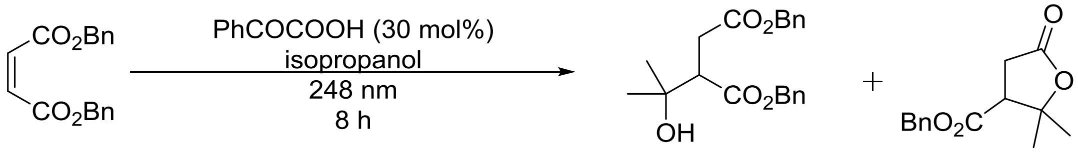
In this equation, V is the total volume of the solution after addition of the phenanthroline (0.00235 L), ΔA is the difference in the absorbance at 510 nm between the irradiated and the non-irradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11.100 L mol^{-1}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

The photon flux is then calculated:

$$\text{photon flux} = \frac{\text{Mol Fe}^{2+}}{\Phi \times t \times f} = \frac{5.21 \times 10^{-8} \text{ mol}}{1.35 \times 90 \text{ sec} \times 0.999947} = 4.29 \times 10^{-10} \text{ einstein s}^{-1}$$

In this equation, Φ is the quantum yield of the ferrioxalate actinometer (1.35 for a 0.006M solution at 248 nm),[9] t is the time of the irradiation (90 seconds), and f is the fraction of the light absorbed at 248 nm (that is calculated above). Thus, the photon flux of the spectrophotometer was calculated to be 4.29 × 10^{-10} einstein s^{-1}.

Determination of the quantum yield



A cuvette was charged with phenylglyoxylic acid (22.5 mg, 0.15 mmol) in isopropanol (2 mL) and dibenzyl maleate (148 mg, 0.50 mmol) is added. The sample was stirred and then irradiated at 248 nm for 28800 s (8 h). After irradiation, the solvent was removed and the yield of the product was determined by ^{1}H NMR utilizing anisole as internal standard (0.65% yield, 0.00325 mmol of the product). The quantum yield was determined with the following equation:

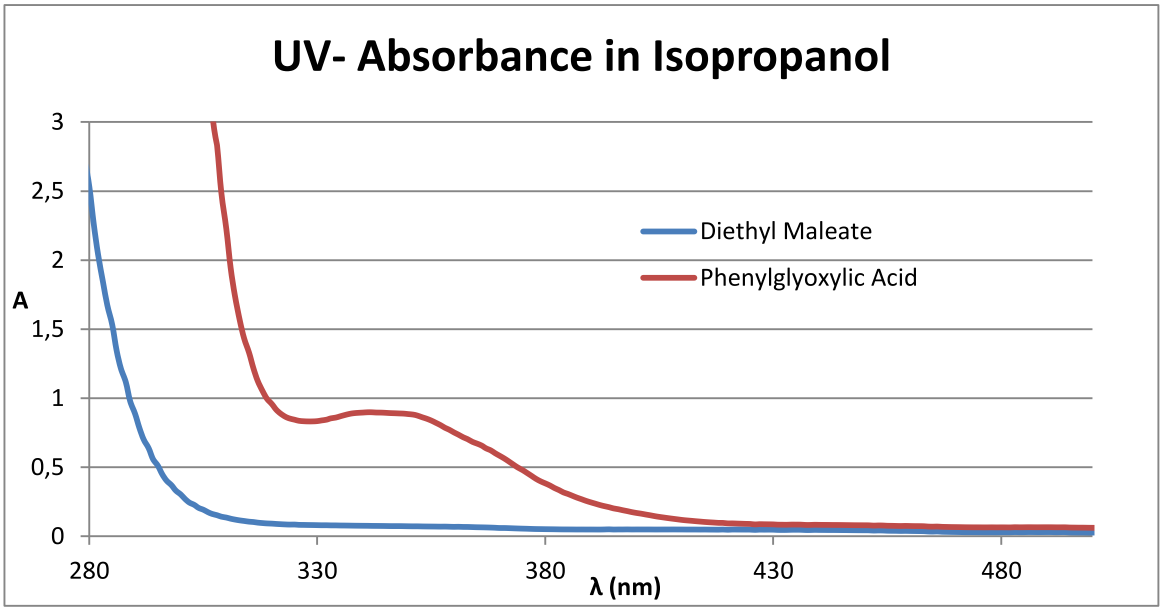
$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f} = \frac{0.00325 \times 10^{-3} \text{ mol}}{4.29 \times 10^{-10} \text{ einstein s}^{-1} \text{ } 28800 \text{ s} \times 0.999947} = 0.26$$

The same experimental procedure was carried out for various wavelength values and the photon flux and quantum yields were determined.

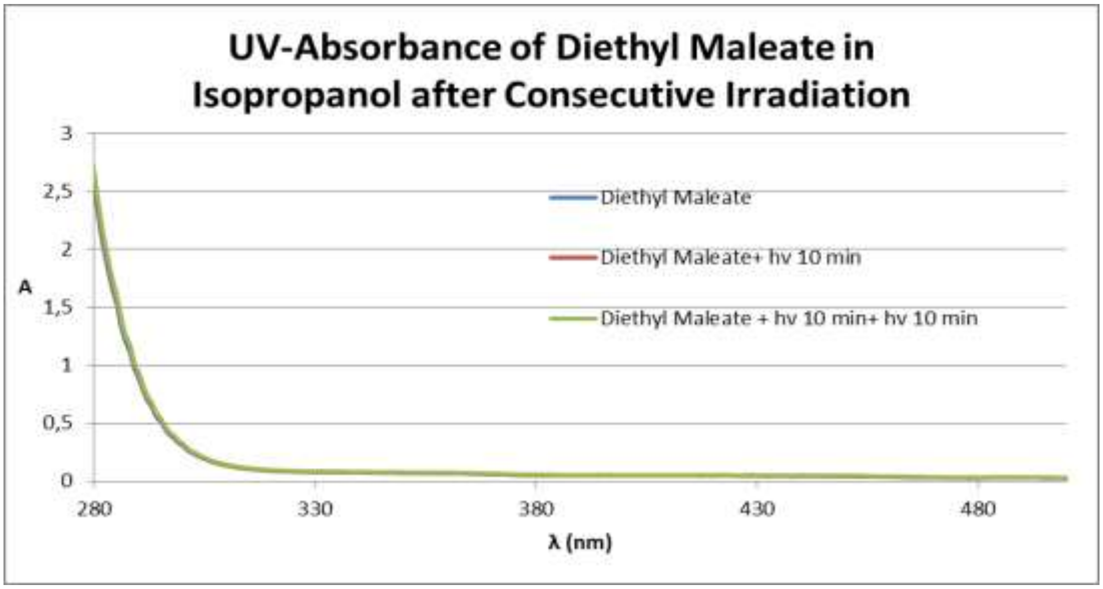
Wavelength (nm)	**Photon Flux (einstein s^{-1})**	**Yield (%)**	**Quantum Yield**
248	4.29×10^{-10}	0.65	0.26
334	5.00×10^{-10}	0.90	0.30
365	4.28×10^{-10}	0.54	0.22
405	4.65×10^{-10}	0.49	0.19

The same experimental procedure was carried out utilizing the exact light source and setup (20 h of irradiation, 75% yield) and the photon flux and quantum yields were determined. The quantum yield was measured to be 88, verifying literature precedent that an open chain radical propagation is in place.

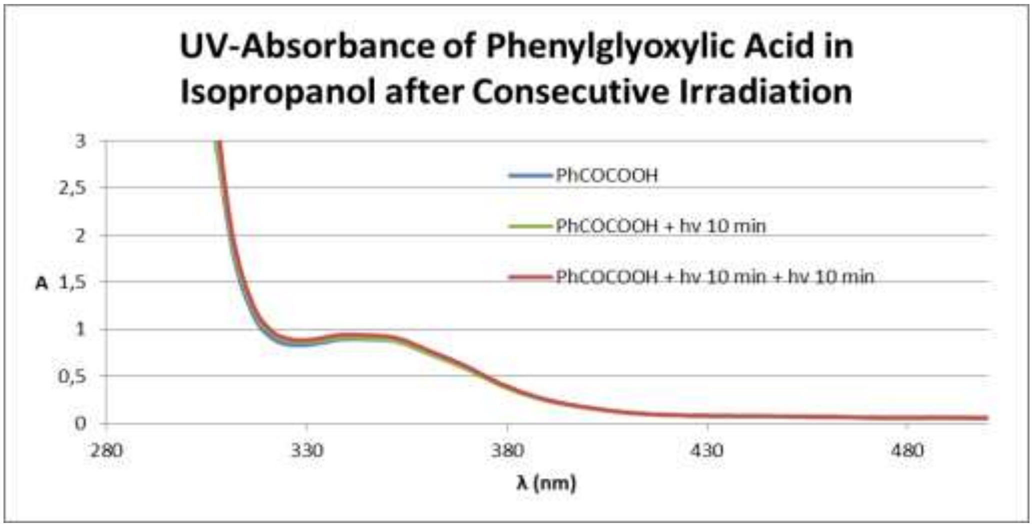
Mechanistic Investigations with UV-Vis Absorption Spectra



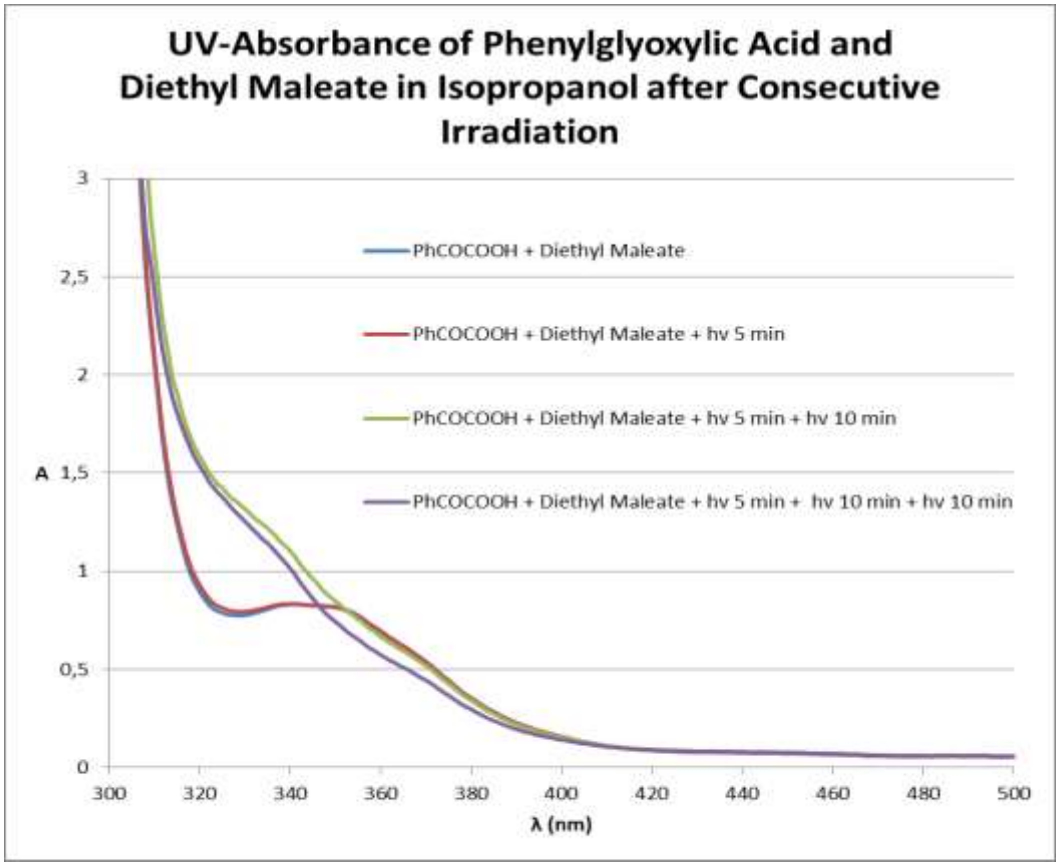
Phenylglyoxylic Acid (10^{-2} M), Diethyl Maleate (0.25 M)



Diethyl Maleate (0.25 M)



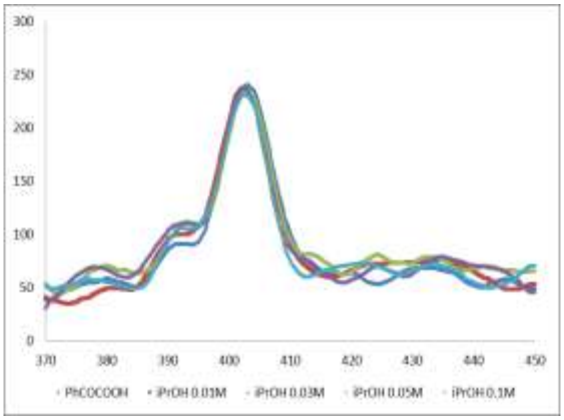
Phenylglyoxylic Acid (10^{-2} M)

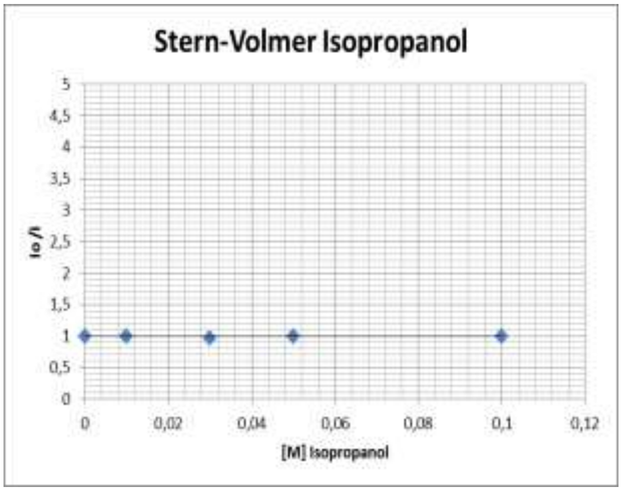


Phenylglyoxylic Acid (10^{-2} M), Diethyl Maleate (0.25 M)

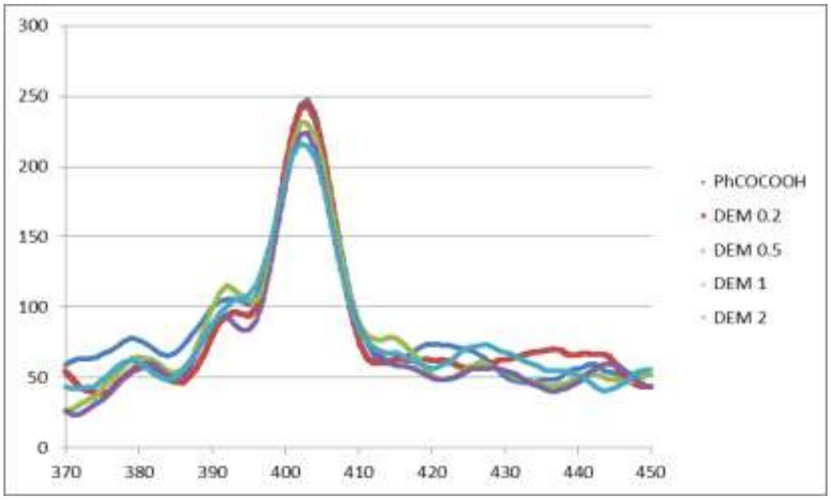
Fluorescence Studies

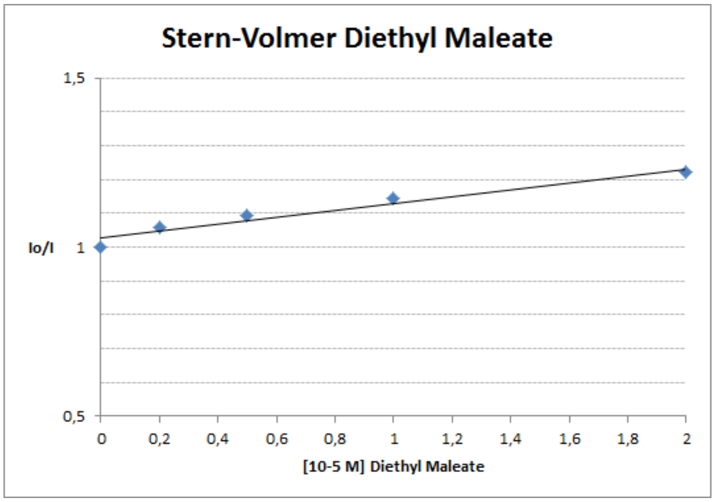
After irradiation of phenylglyoxylic acid (1mM in MeCN) at 360 nm, its fluorescence is measured at 402 nm. Increasing the added amount of isopropanol, no changes in the fluoroscence were observed.



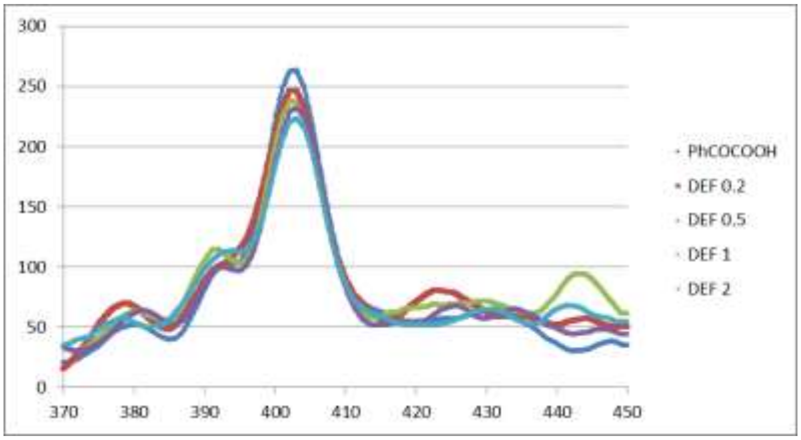


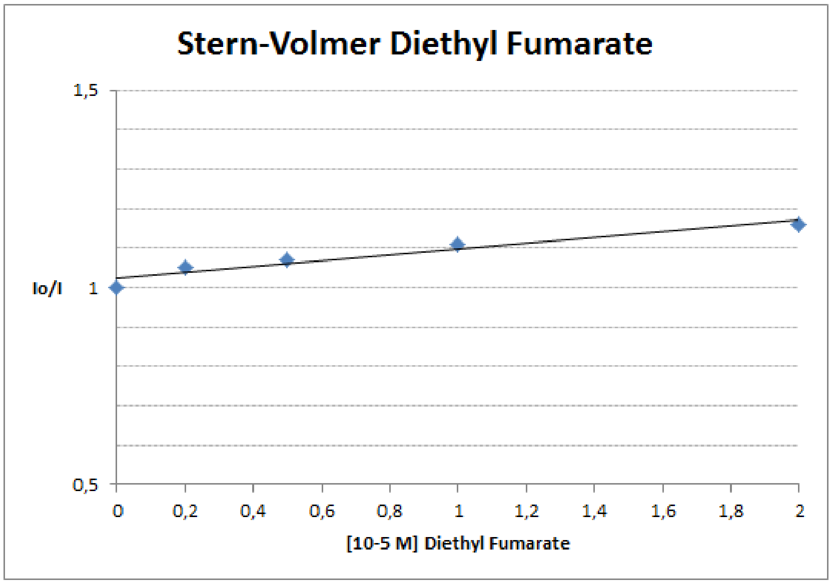
Increasing the added amount of diethyl maleate (10^{-5}M), a constant decrease in the fluoroscence was observed. This constitutes a proof for the interaction between the excited phenylglyoxylic acid and diethyl maleate.





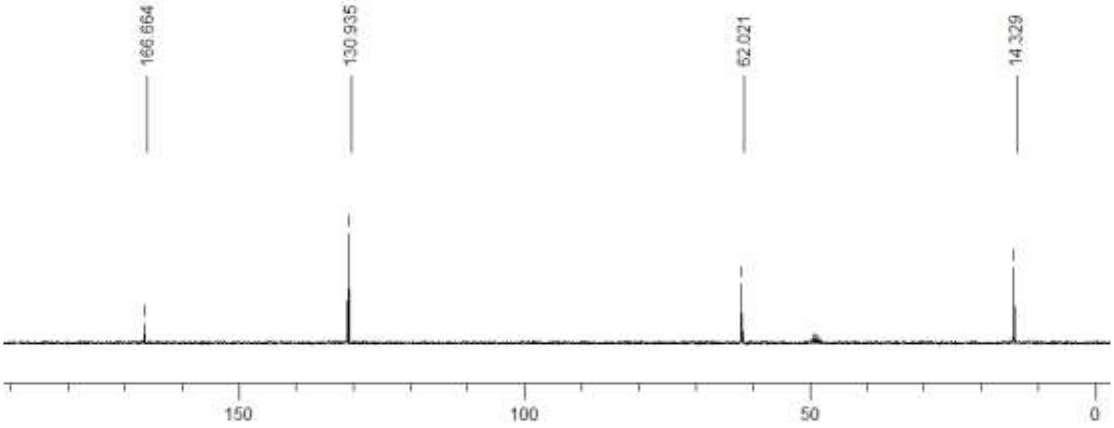
Similar trend is also observed in the case of diethyl fumarate. Increasing the added amount of diethyl fumarate (10^{-5}M), a constant decrease in the fluoroscence was observed. In this case, the decrease is more obvious and this can be attributed also to *cis-trans* isomerization.



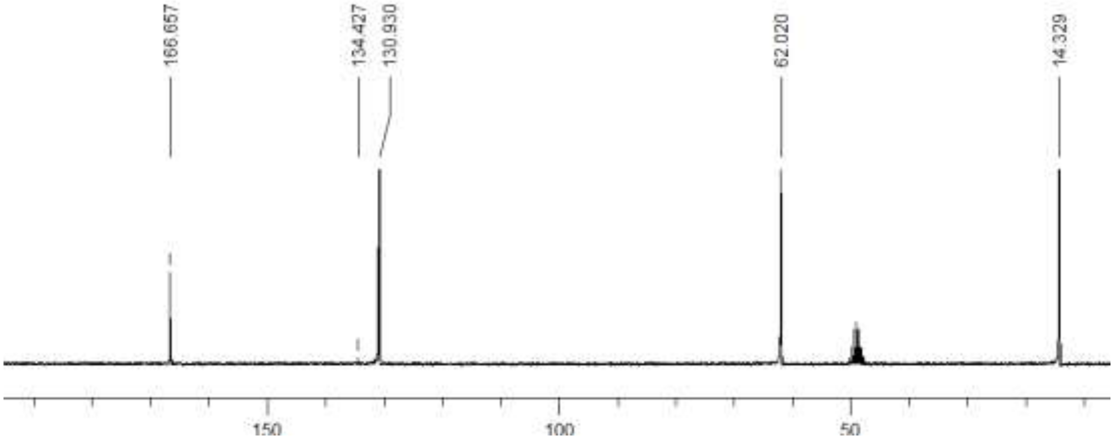


^{13}C-NMR Experiments for the Reaction Mechanism

Initially, the ^{13}C-NMR spectra of diethyl maleate in CD_3OD were recorded before and after irradiation for 30 min.

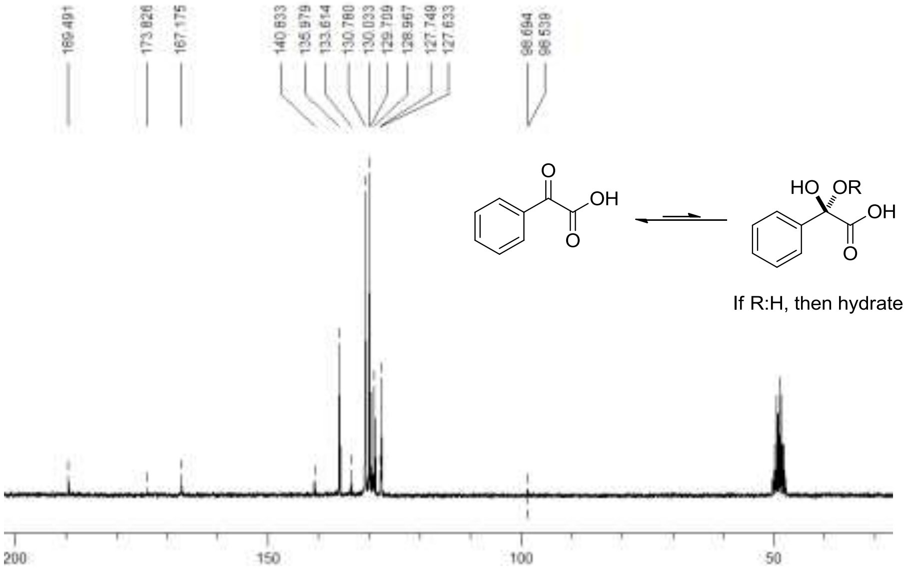


^{13}C NMR spectrum of diethyl maleate in CD_3OD

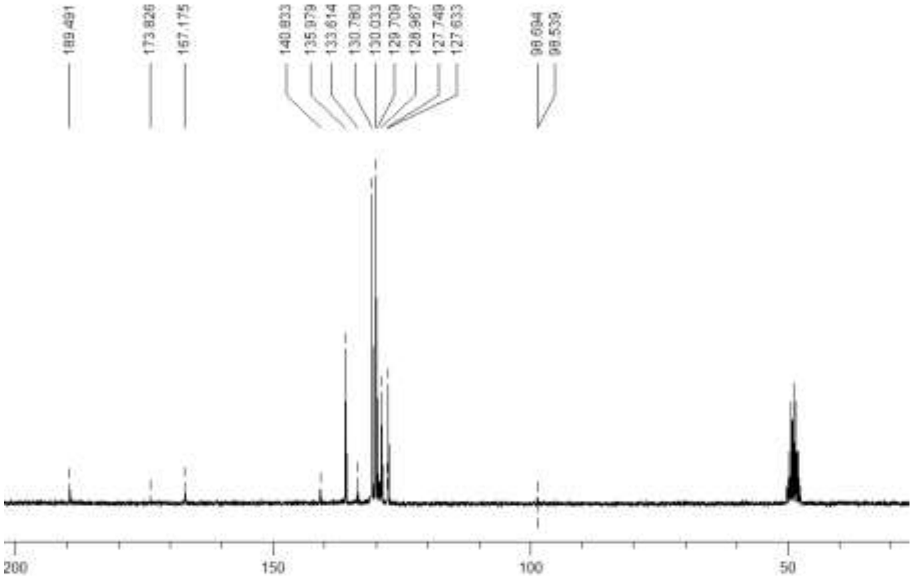


^{13}C NMR spectrum of diethyl maleate in CD_3OD after irradiation for 20 min

Then, the ^{13}C-NMR spectra of phenylglyoxylic acid in CD_3OD were recorded before and after irradiation for 30 min. There is an equilibrium between the keto form (189.5 and 167.2 ppm) and the acetal (probably the gem diol hydrate form) (173.8 and 98.5 ppm). No differences were observed after irradiation.

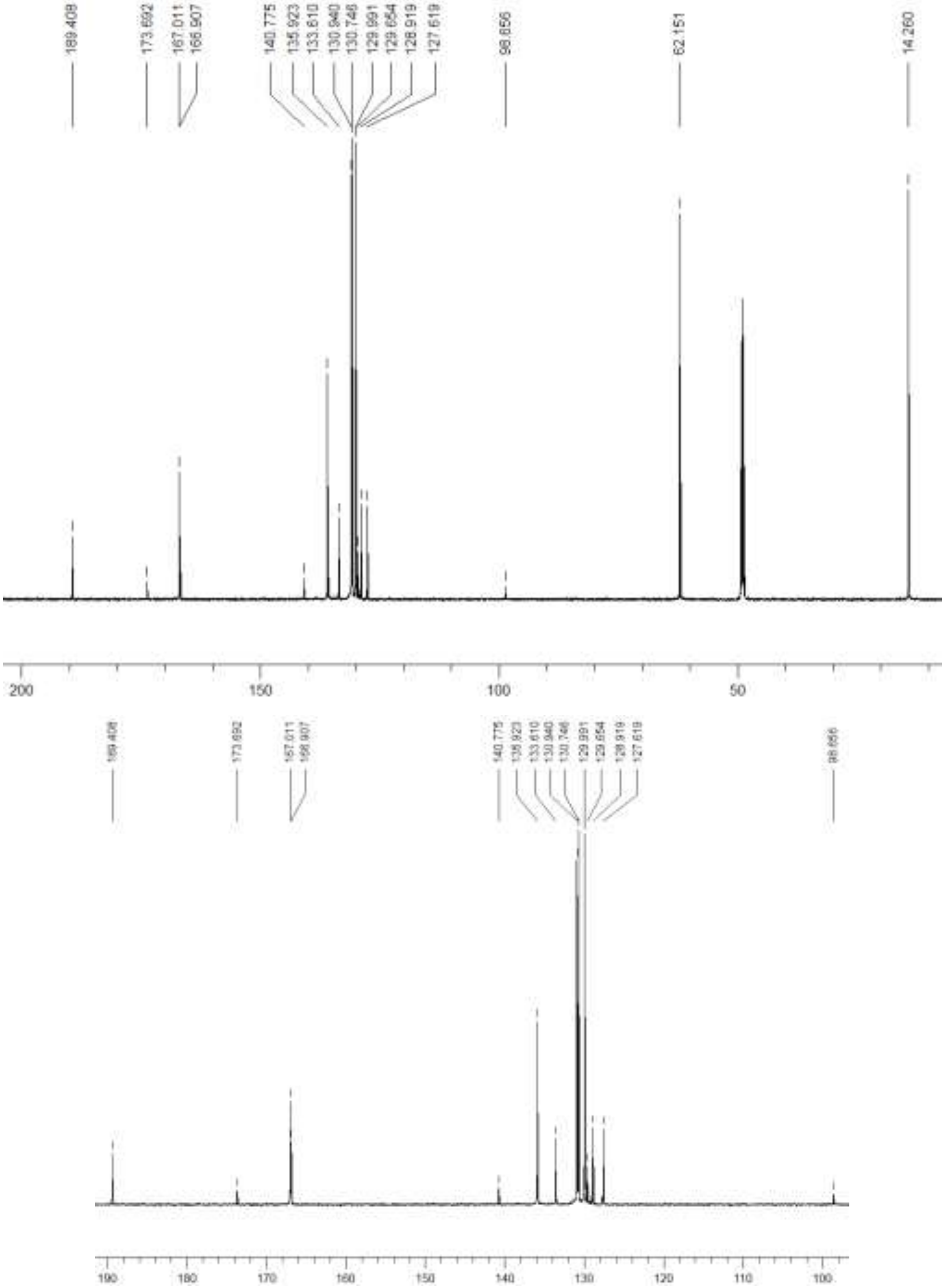


^{13}C NMR spectrum of phenylglyoxylic acid in CD_3OD

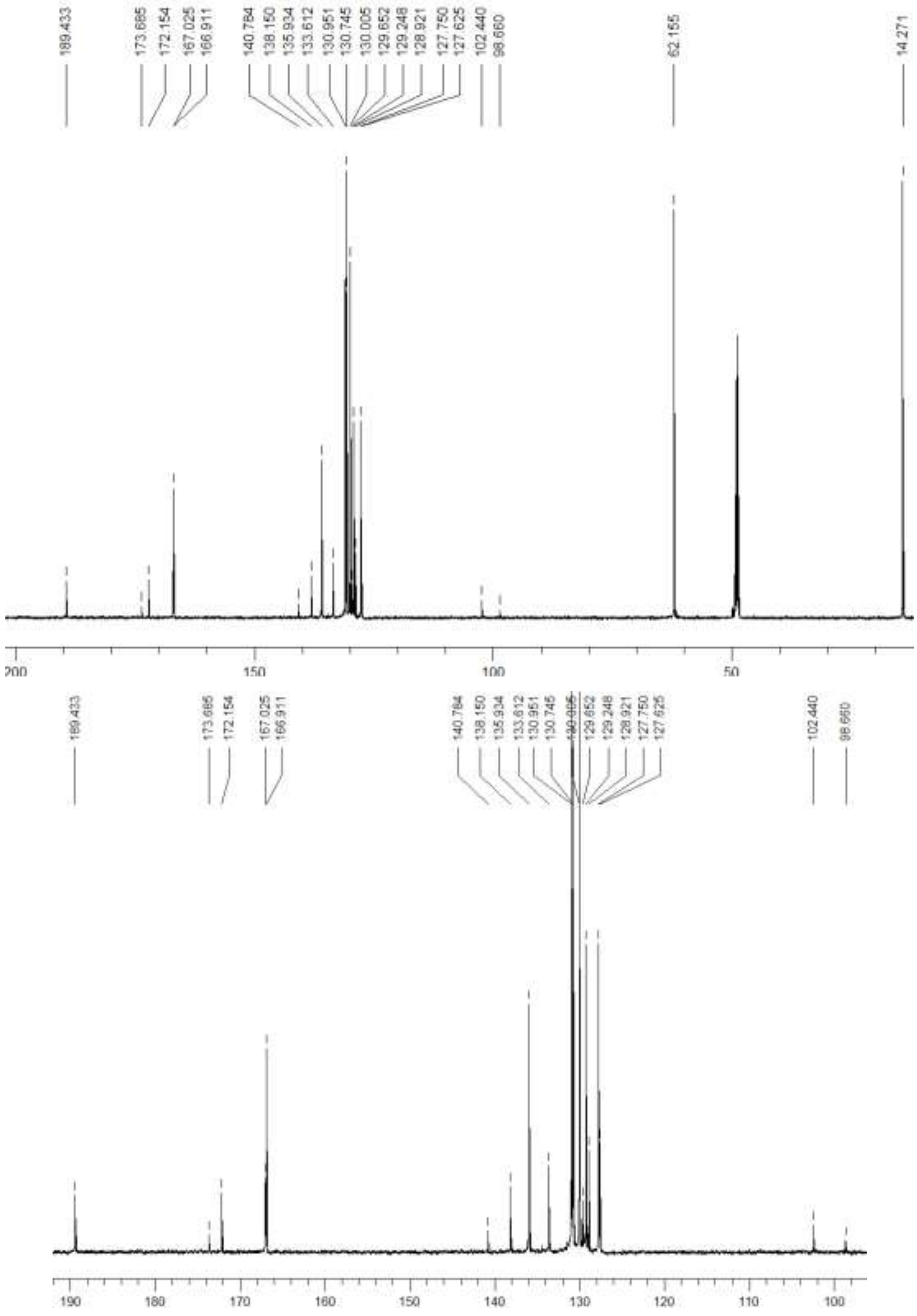


^{13}C NMR spectrum of phenylglyoxylic acid in CD_3OD after irradiation for 20 min

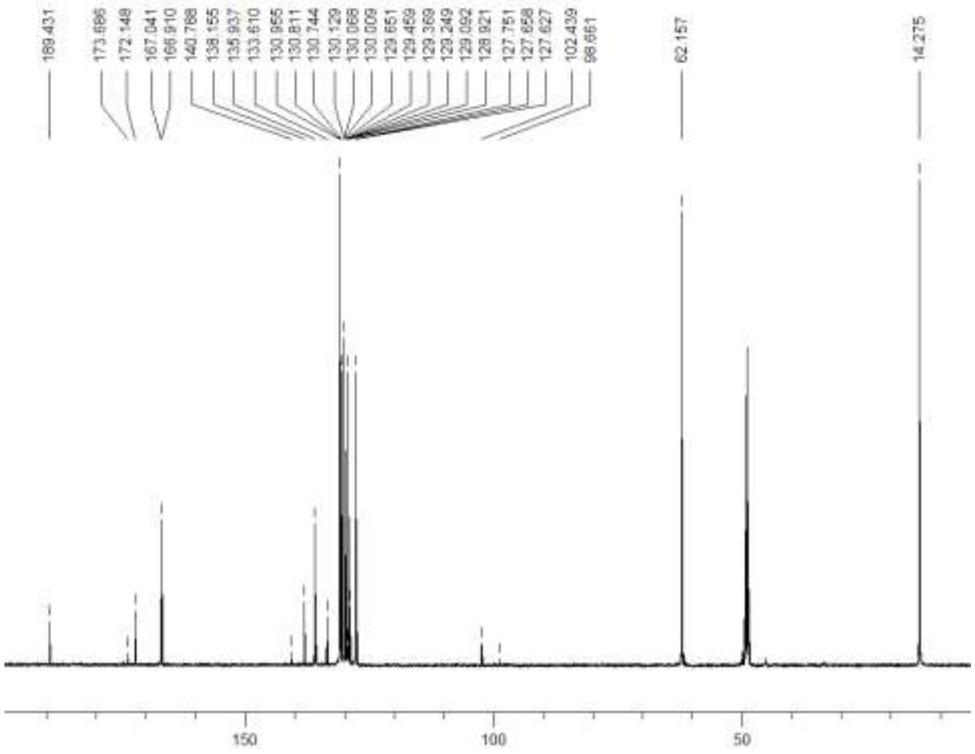
The mixture of phenylglyoxylic acid and diethyl maleate (in CD_3OD) presented all expected signals. After irradiation of the reaction mixture (in CD_3OD) for 20 min, new signals appear and more specifically additional carbonyl peaks and the aromatic carbons appear. The new peak for the quaternary carbon atom appears at 102 ppm for diphenyl tartaric acid.

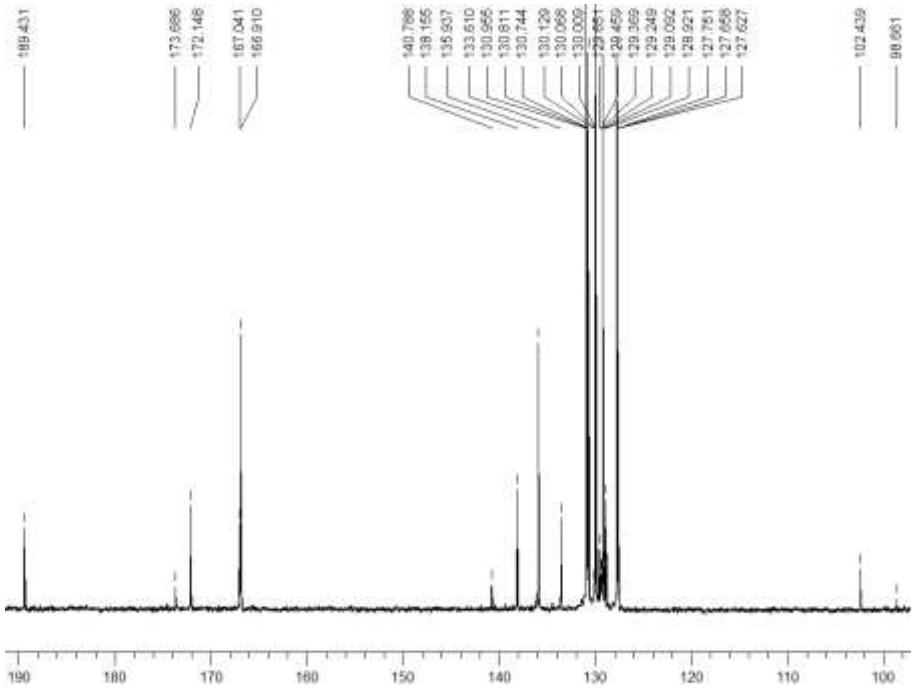


^{13}C NMR spectrum of phenylglyoxylic acid with diethyl maleate in CD_3OD

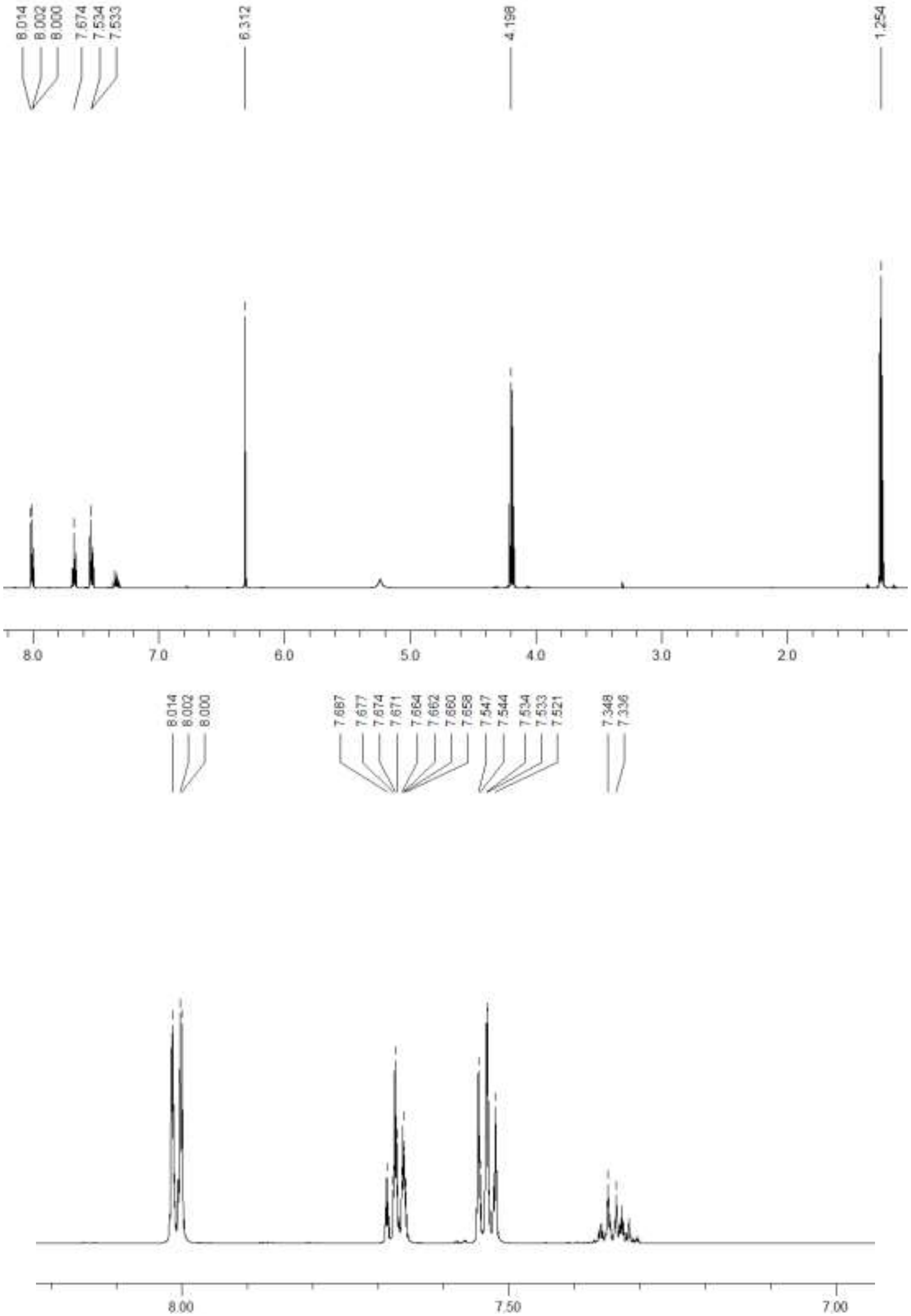


^{13}C NMR spectrum of phenylglyoxylic acid with diethyl maleate in CD$_3$OD after irradiation for 20 min

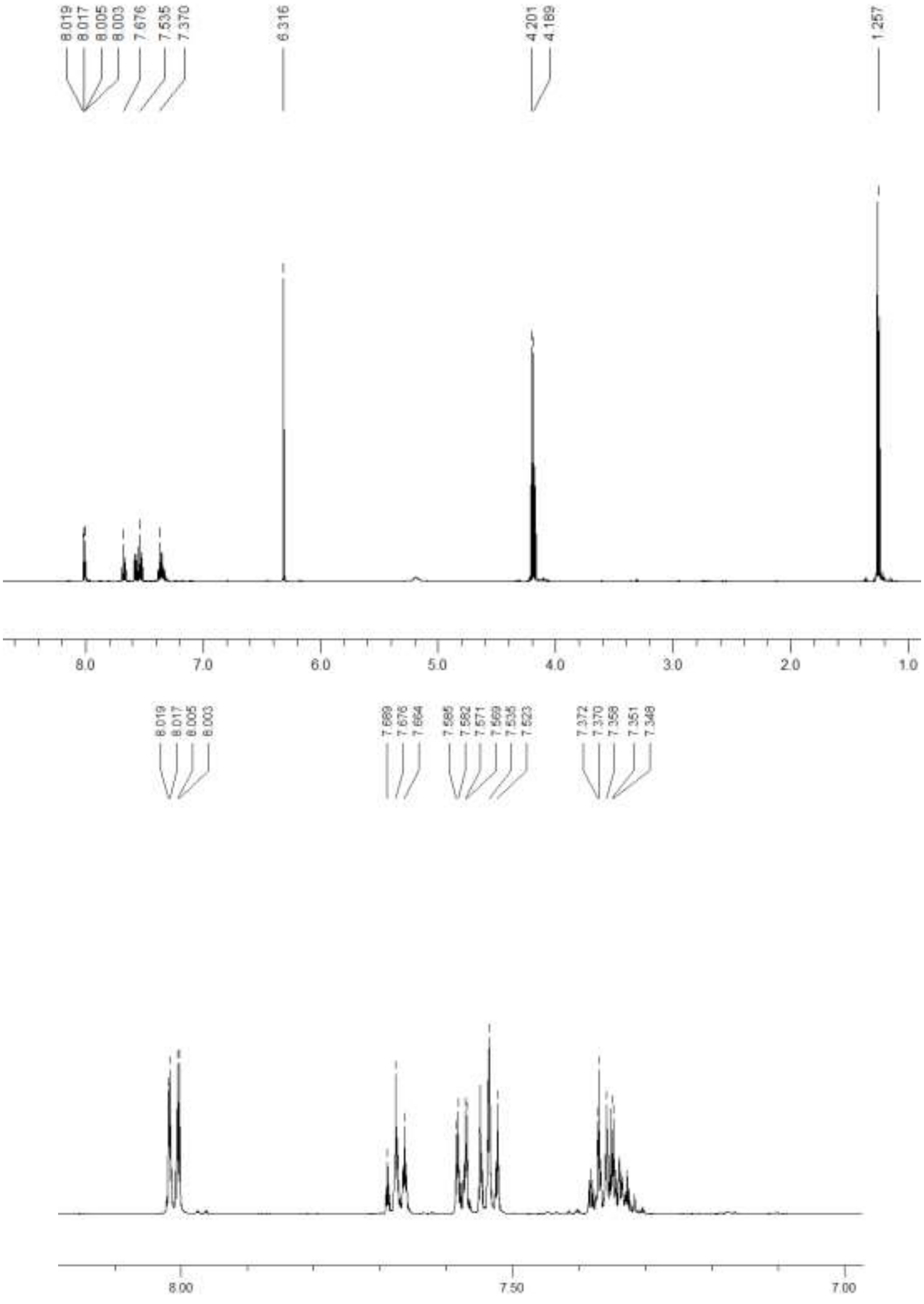




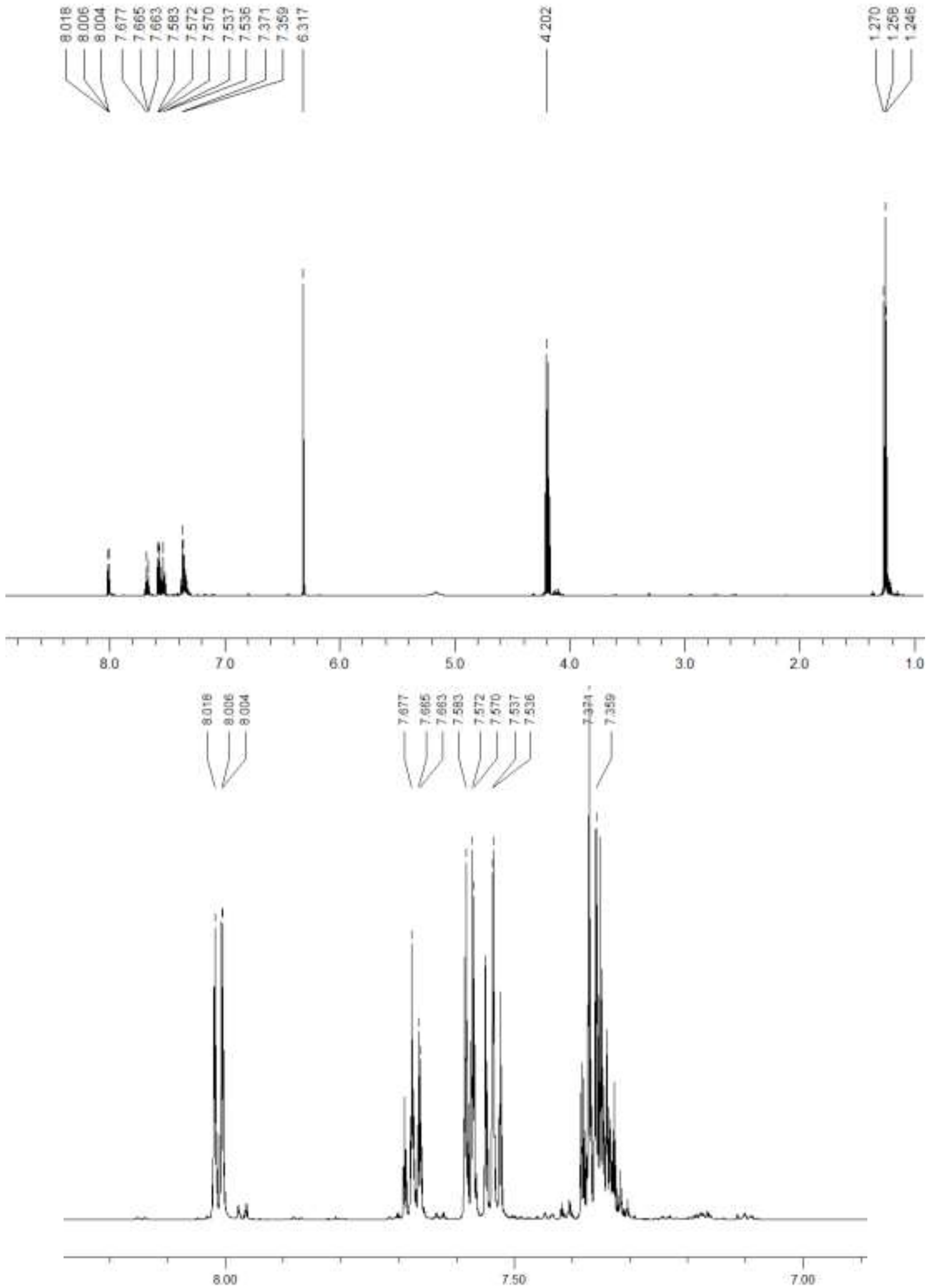
^{13}C NMR spectrum of phenylglyoxylic acid with diethyl maleate in CD_3OD after irradiation for 40 min



^{1}H NMR spectrum of phenylglyoxylic acid with diethyl maleate in CD_3OD



^{1}H NMR spectrum of phenylglyoxylic acid with diethyl maleate in CD_3OD after irradiation for 20 min

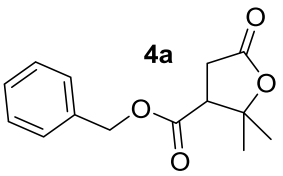


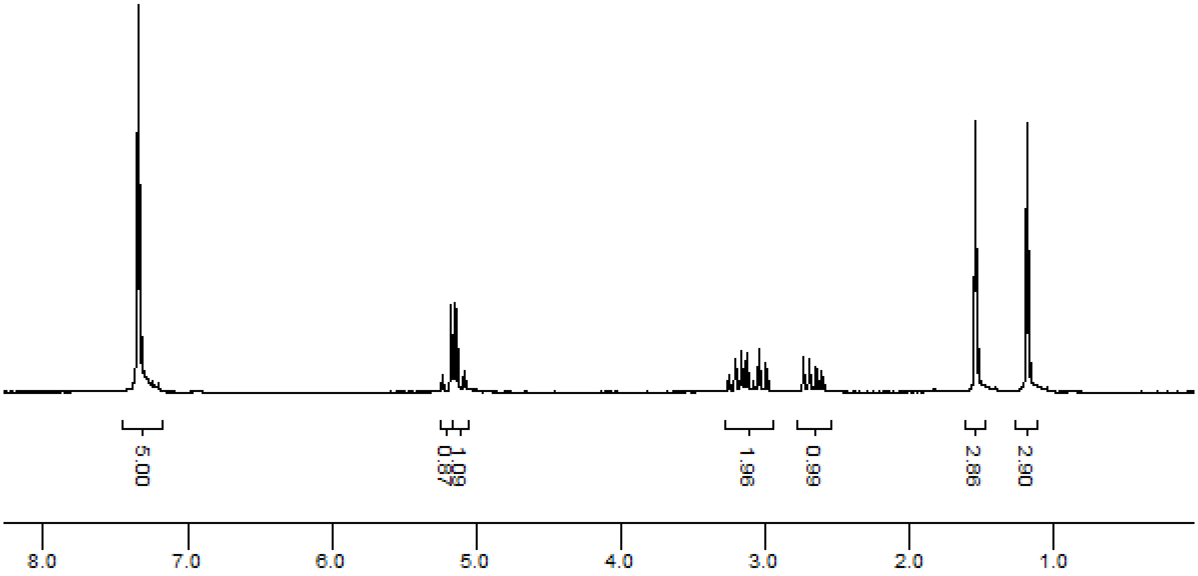
^{1}H NMR spectrum of phenylglyoxylic acid with diethyl maleate in CD_3OD after irradiation for 40 min

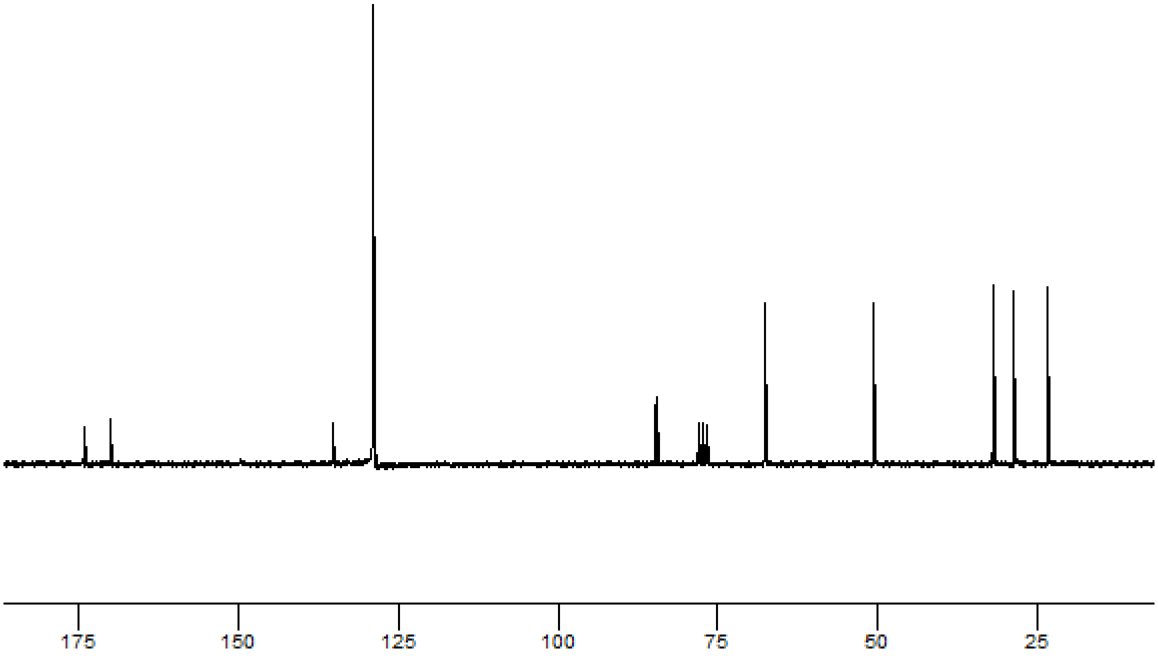
References

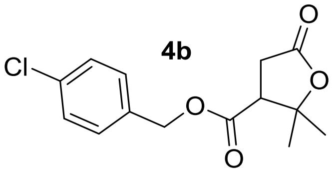
1. A. Thaqi, A. McClusky, J. L. Scott, *Tetrahedron Lett.* **2008**, 48, 6962-6964.
2. B. Font, J. F. Trant, A. D. Wong, E. R. Gillies, *J. Am. Chem. Soc*. **2014**, 136,10116-10123.
3. X. Xu, C. Li, Z. Tao, Y. Pan, *Adv. Synth. Catal.* **2015**, 357, 3341-3345.
4. D. M. Hodgson, D. Angrish, *Chem. Eur. J.* **2007**, 13, 3470-3479.
5. M Ramalingam, S. Manickam, K. R. Srinivasalu, M. B. Ismail, E. Deivanayagam, *Eur. J. Inorg. Chem.* **20016**, 1697-1705.
6. A. Comini, C. Forzato, P. Nitti, G. Pitacco. E. Valentin, *Tetrahedron: Asymmetry* **2004**, 15, 617-625.
7. J. Kucera, J. Moravec, *Collect. Czech. Chem. Commun.* **1980**, 45, 3564-3570.
8. M. A. Cismesia, T. P. Yoon, *Chem. Sci.*, **2015**, *6*, 5426-5434.
9. E. Fernandez, J. M. Figuera, A. Tobar, *J. Photochem.*, **1979**, *11*, 69-71.
10. W. D. Bowman, J. N. Demas, *J. Phys. Chem.*, **1976**, *20*, 2434-2435.

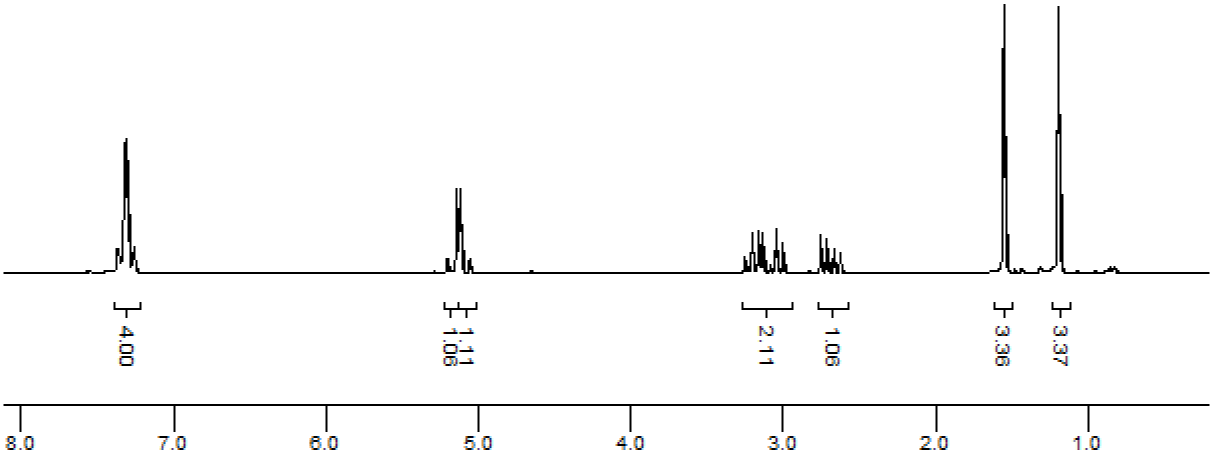
4a



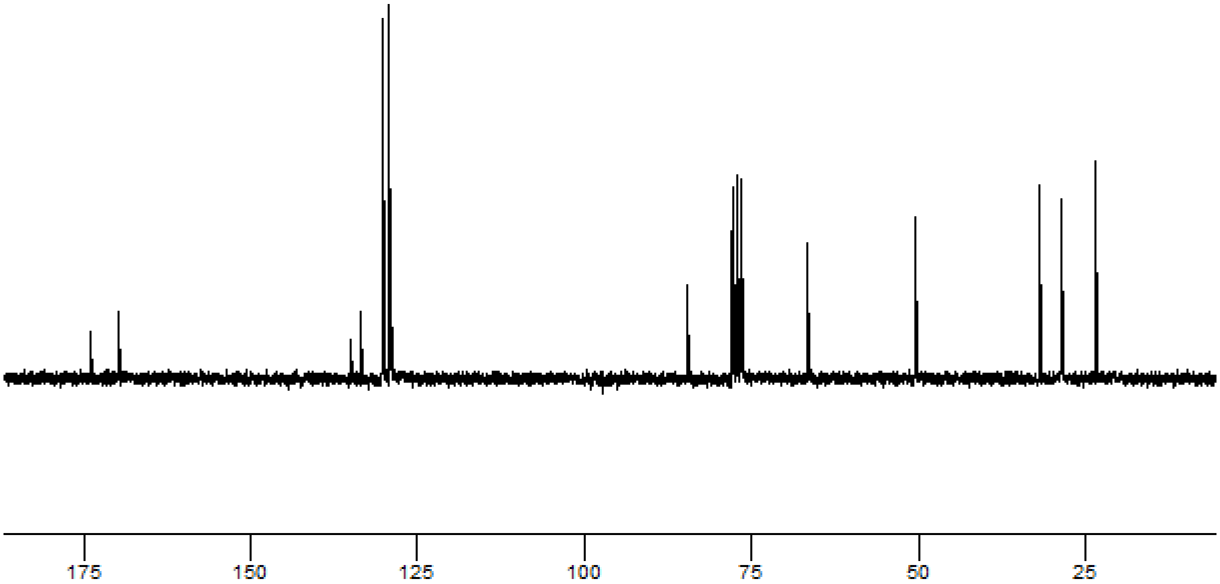

5.00
0.87
1.09
1.96
0.99
2.86
2.90
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25


4b

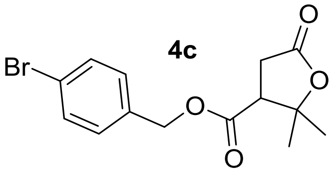


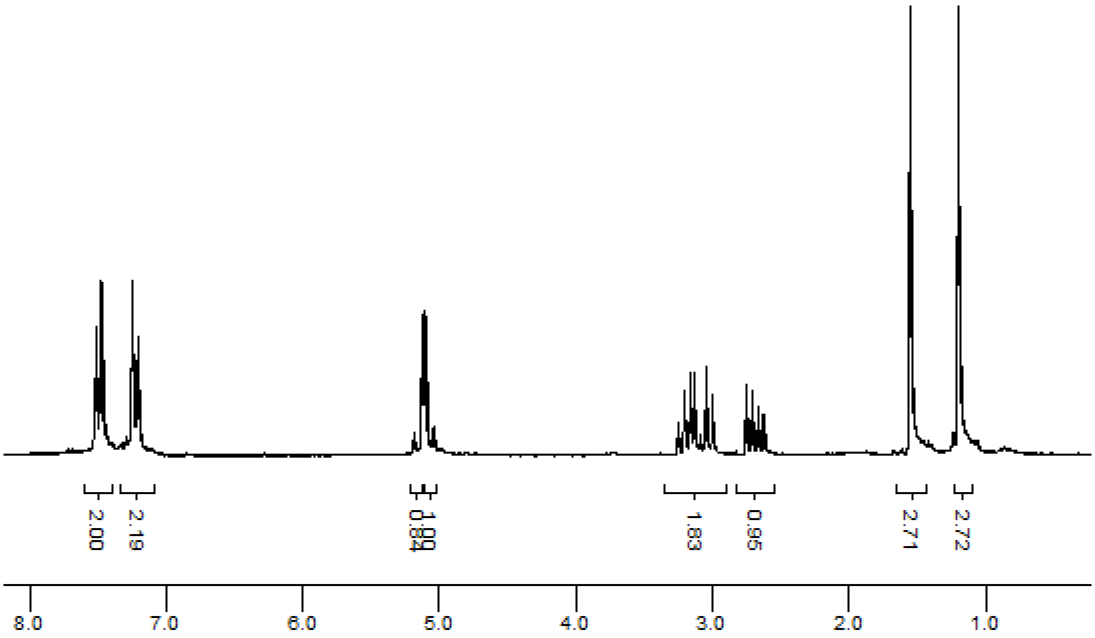
4.00
1.06
1.11
2.11
1.06
3.36
3.37
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

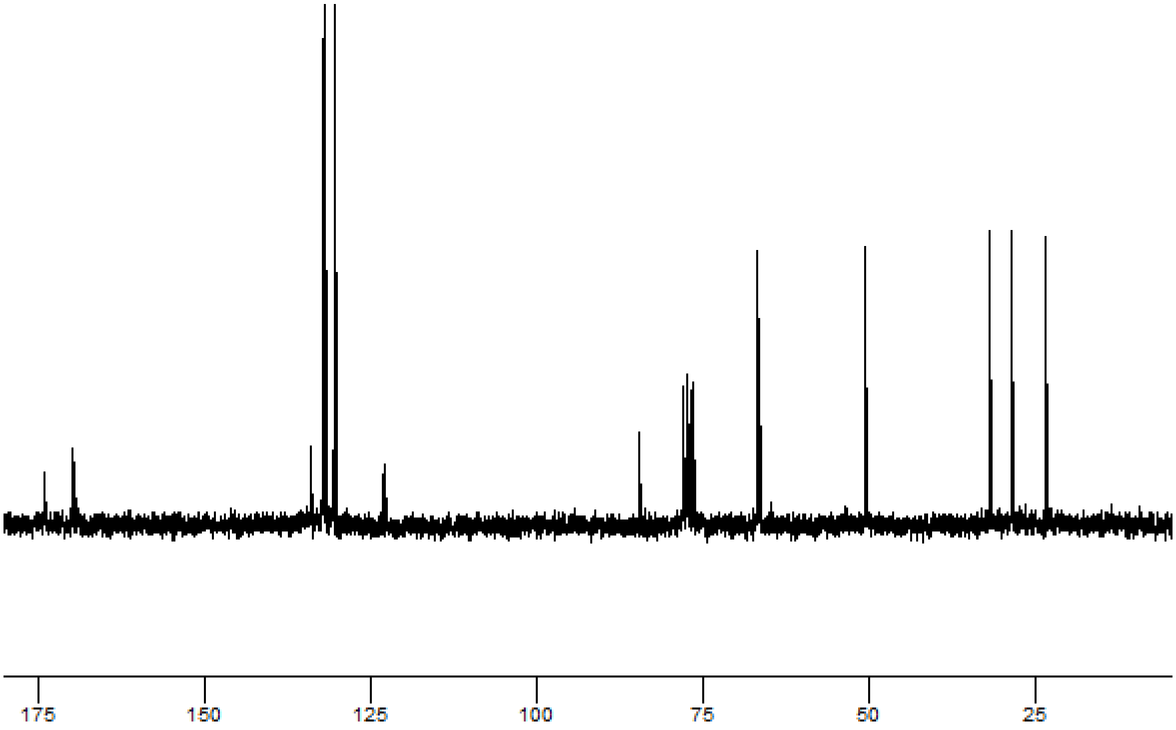


175
150
125
100
75
50
25

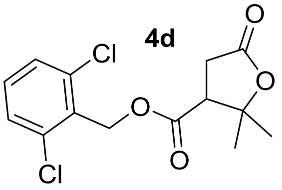
4c

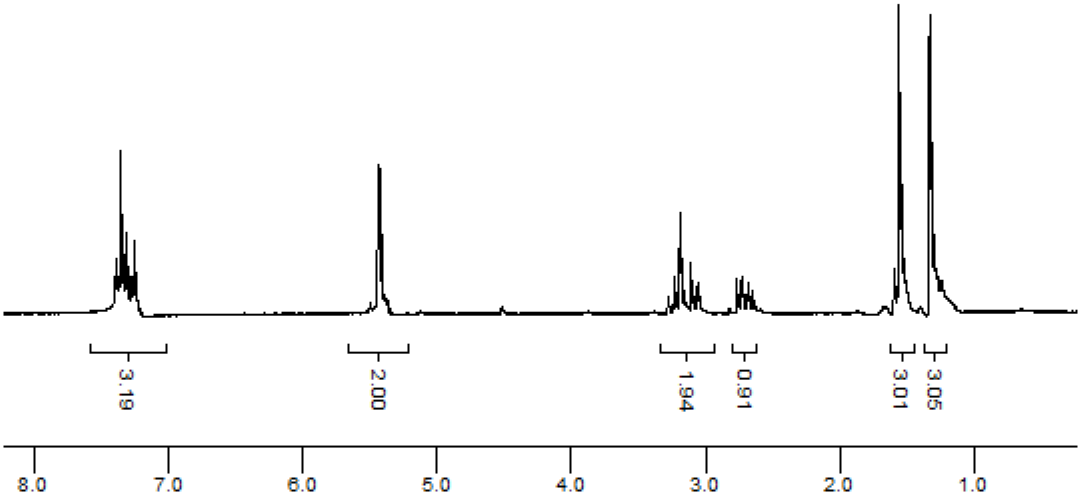

Br
O
O
O
O

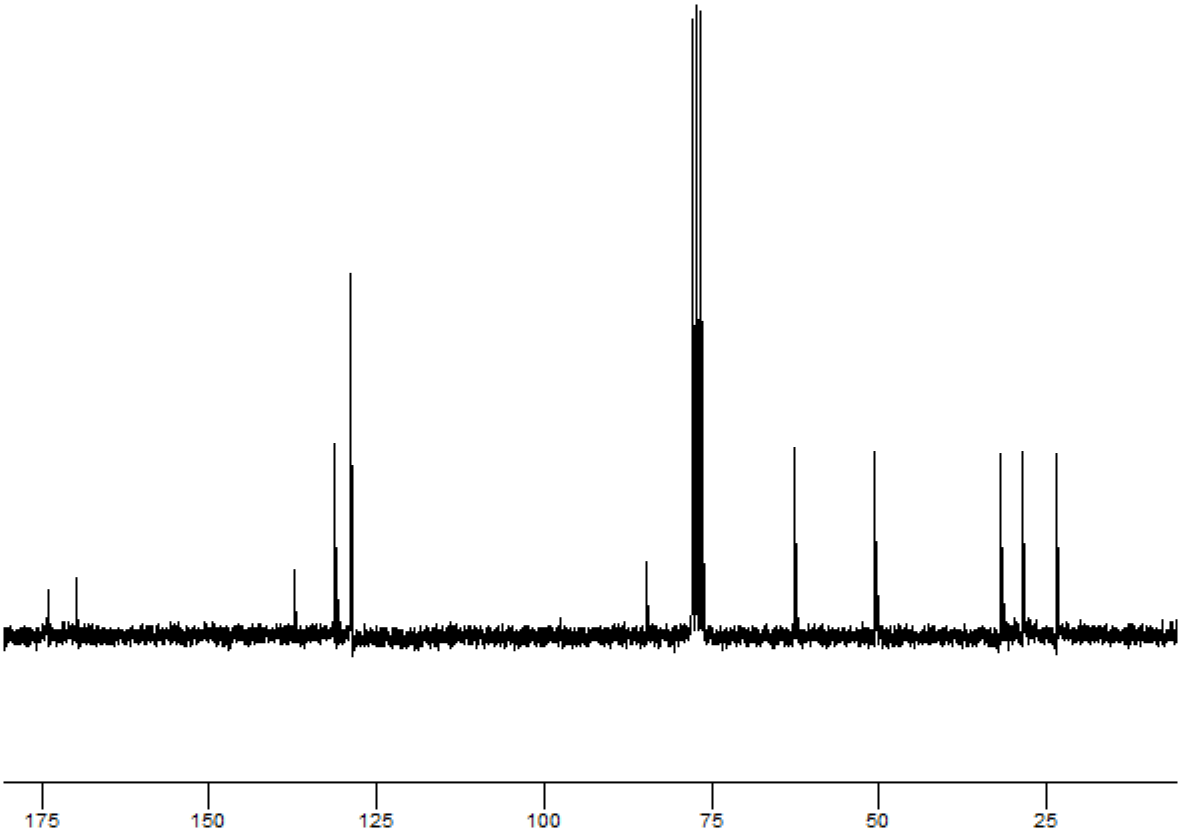

2.00
2.19
0.84
1.00
1.83
0.95
2.71
2.72
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

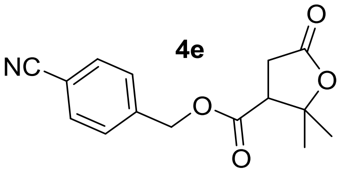

175
150
125
100
75
50
25

4d

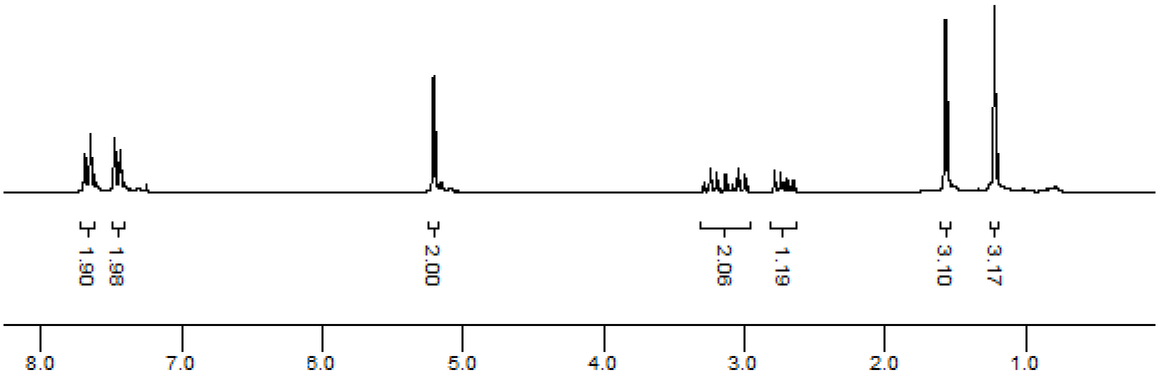

Cl
Cl
O
O
O
O

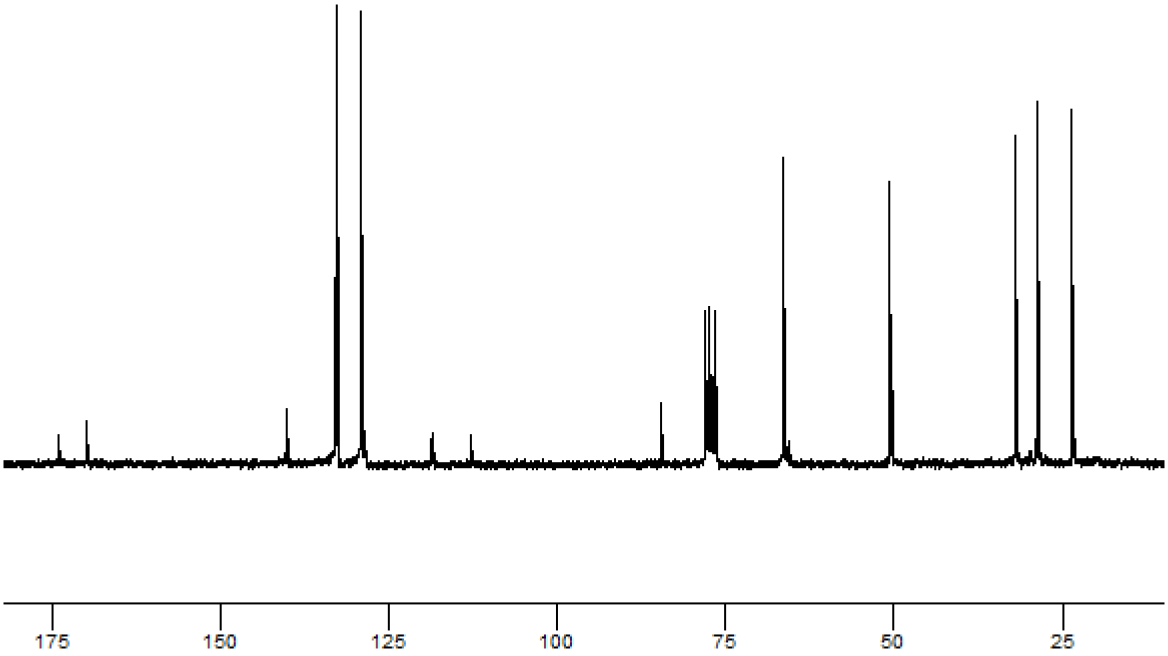

3.19
2.00
1.94
0.91
3.01
3.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

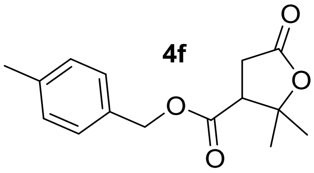

175
150
125
100
75
50
25


NC
O
O
O
O

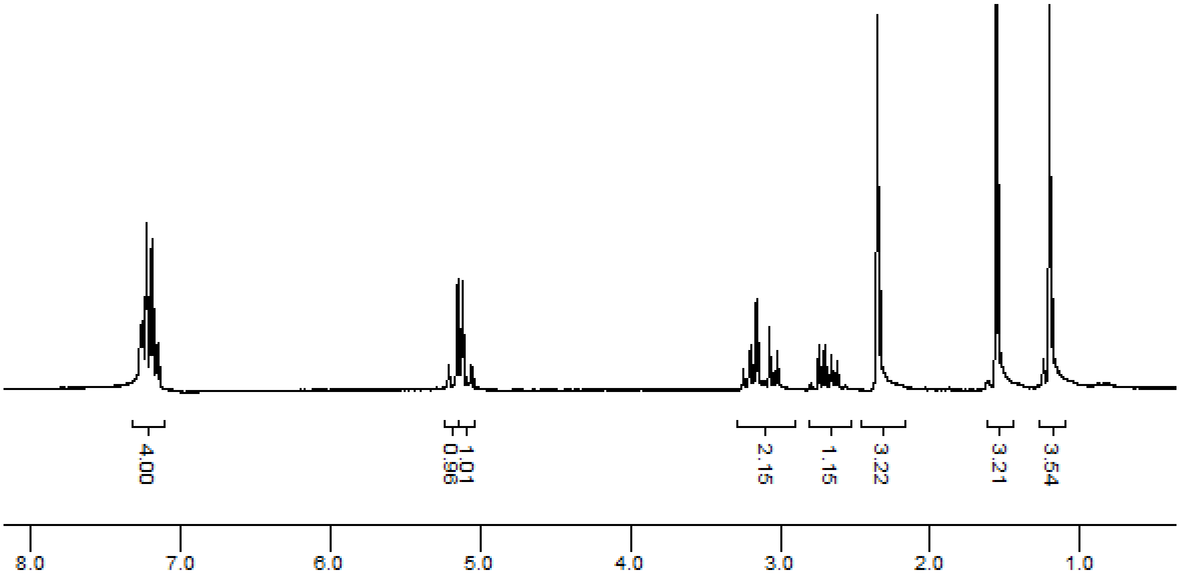
4e


1.90
1.98
2.00
2.06
1.19
3.10
3.17
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

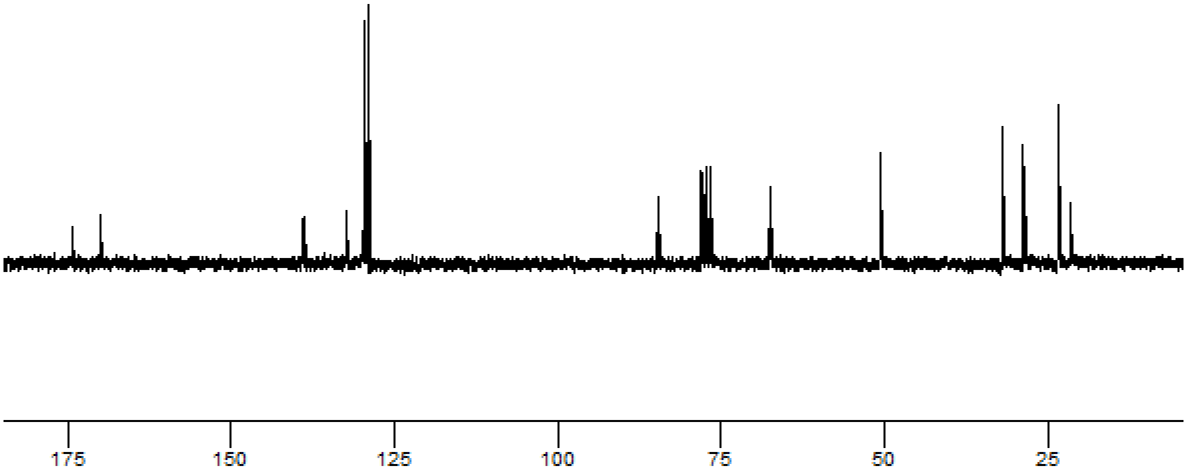

175
150
125
100
75
50
25



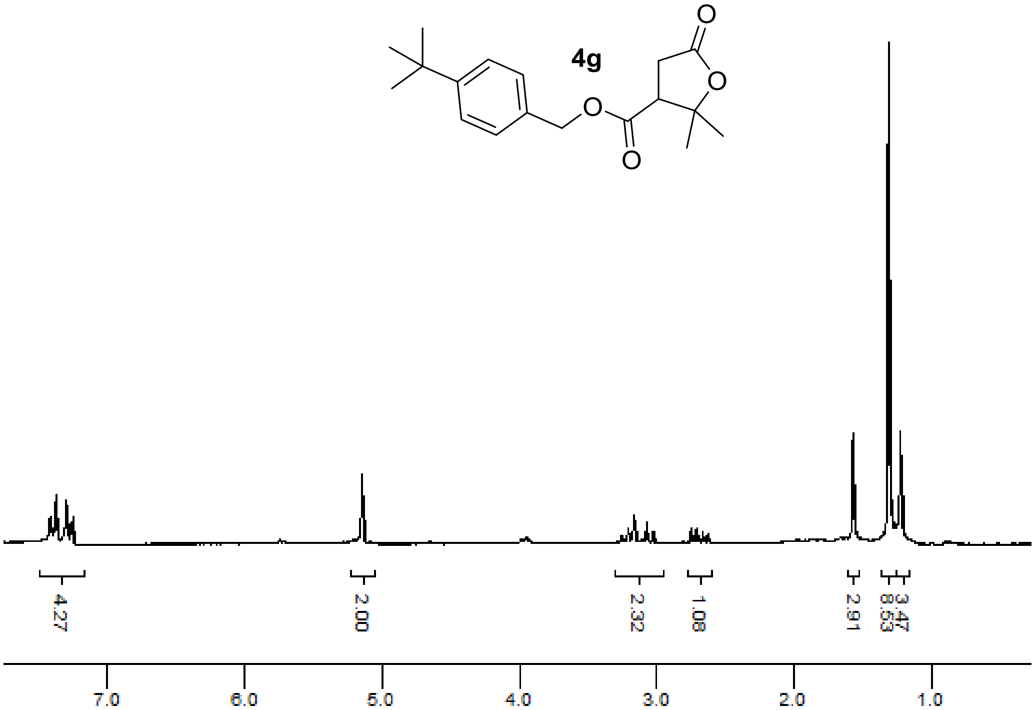
4f

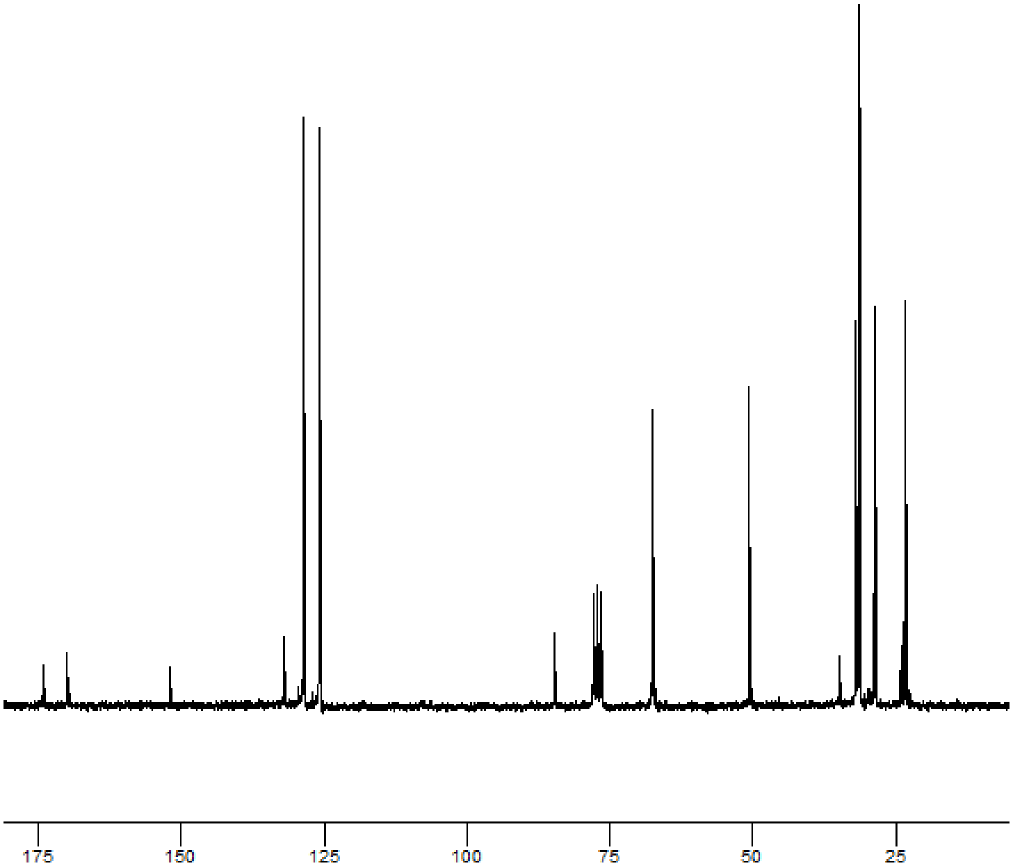


4.00
0.96
1.01
2.15
1.15
3.22
3.21
3.54
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

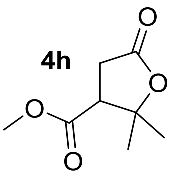


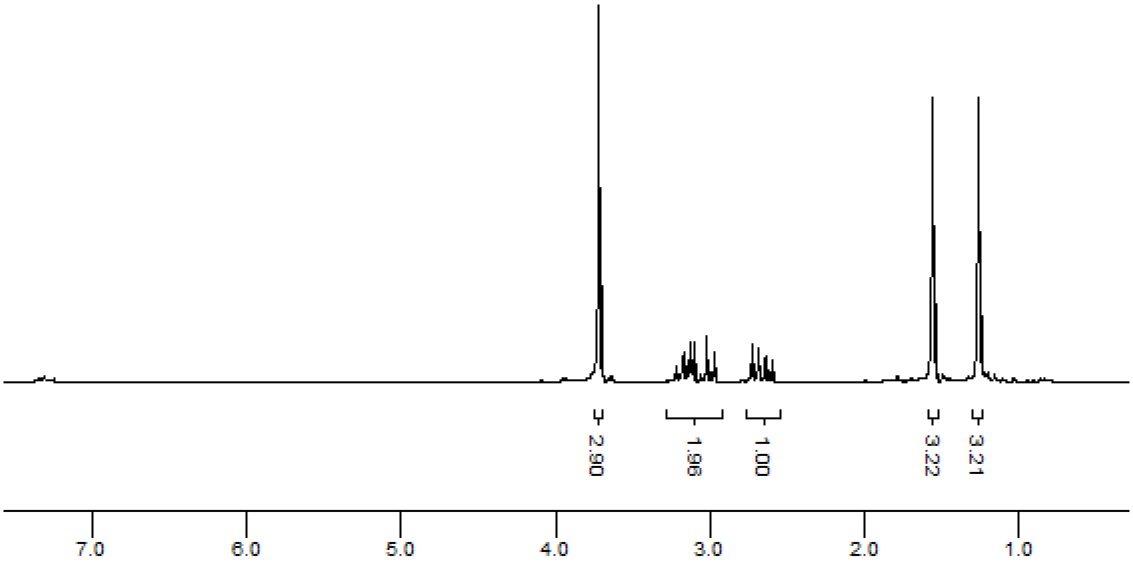
175
150
125
100
75
50
25

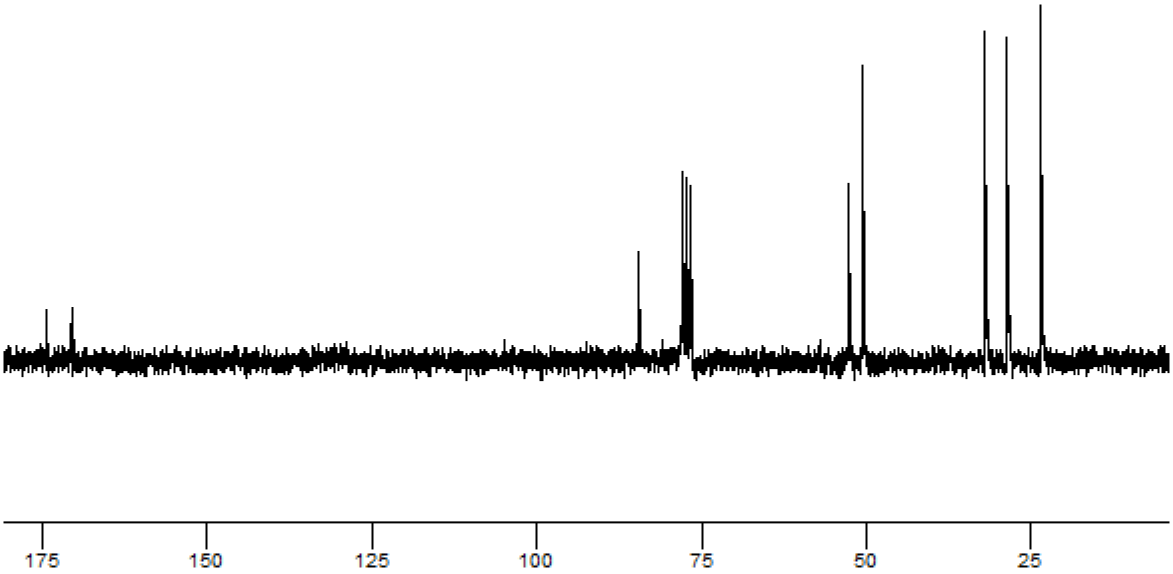

4g
O
O
O
O
4.27
2.00
2.32
1.08
2.91
8.53
3.47
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25

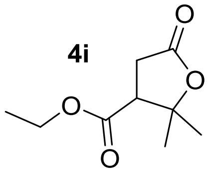
4h

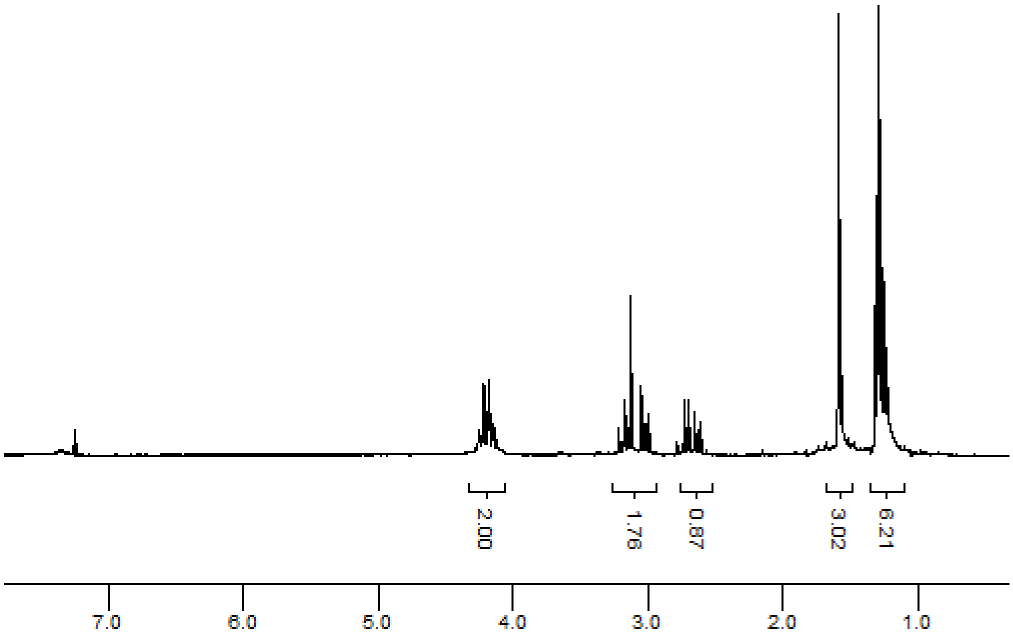

O
O
O
O

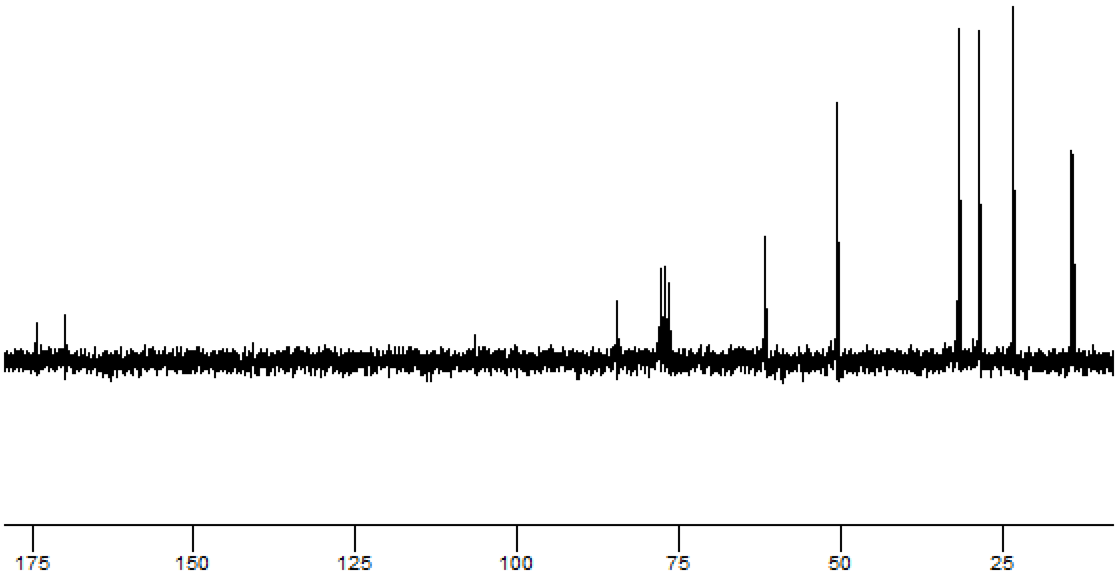

2.90
1.96
1.00
3.22
3.21
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25

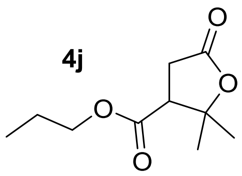
4i

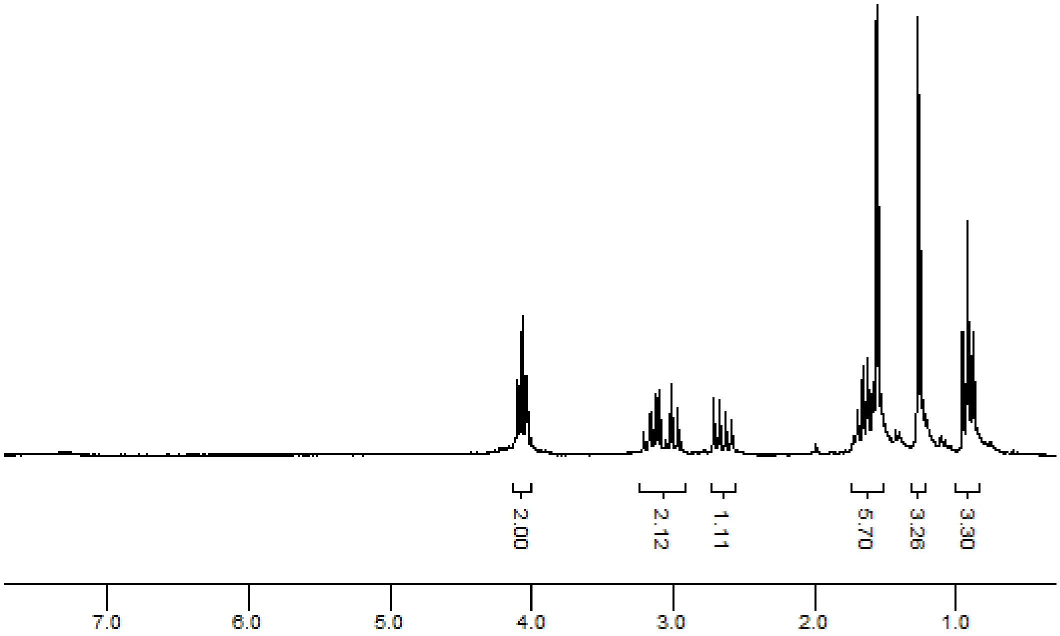

O
O
O
O

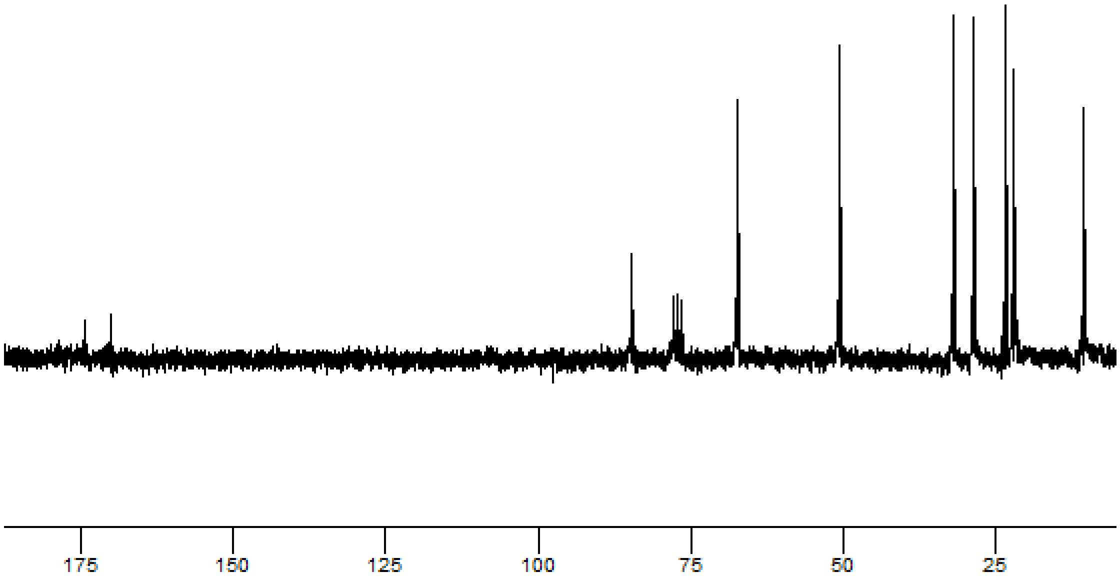

2.00
1.76
0.87
3.02
6.21
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25

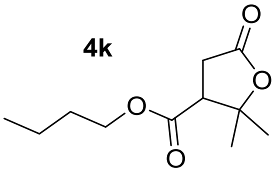
4j

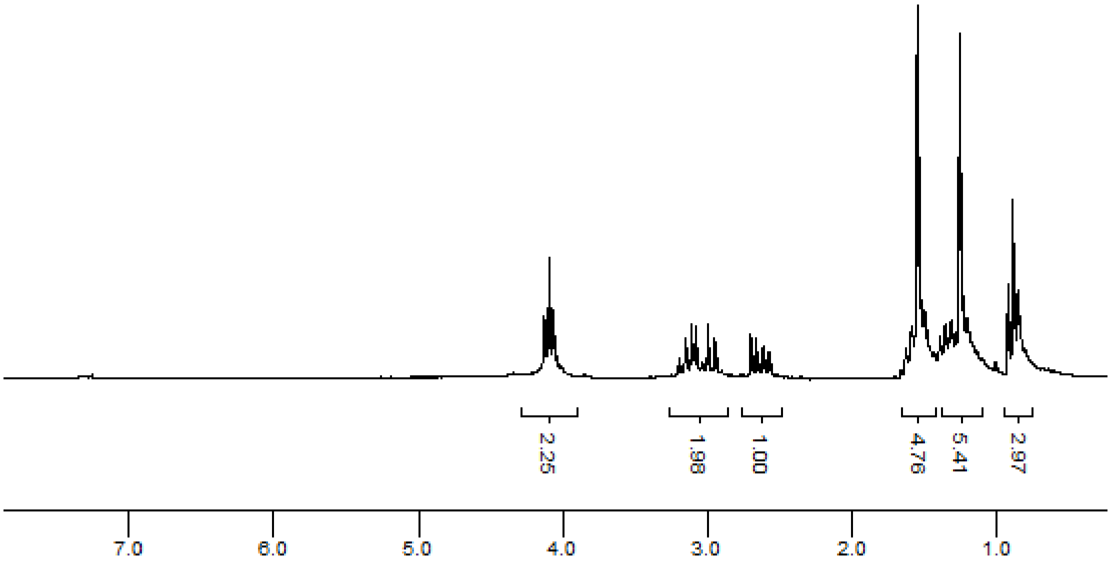

O
O
O
O

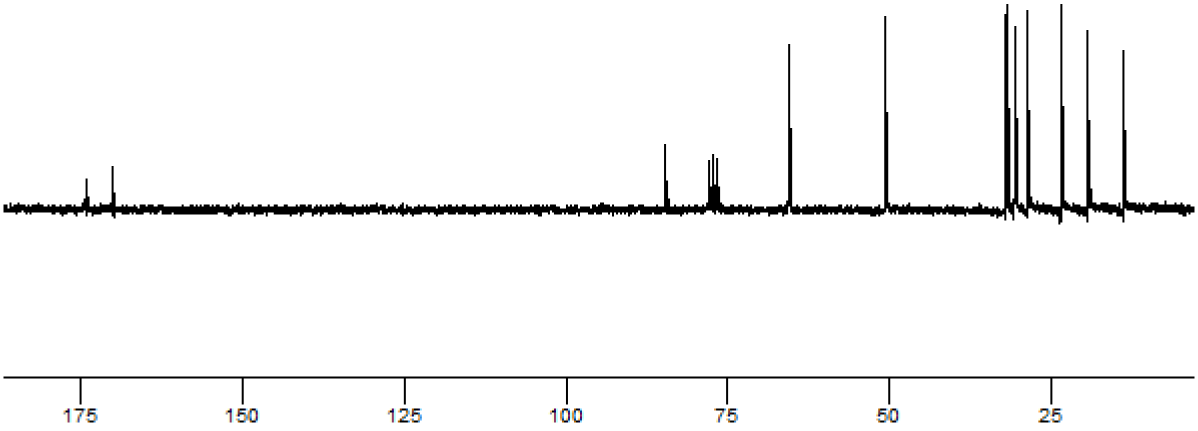

2.00
2.12
1.11
5.70
3.26
3.30
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25

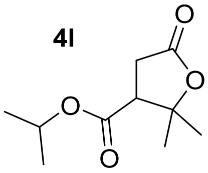
4k

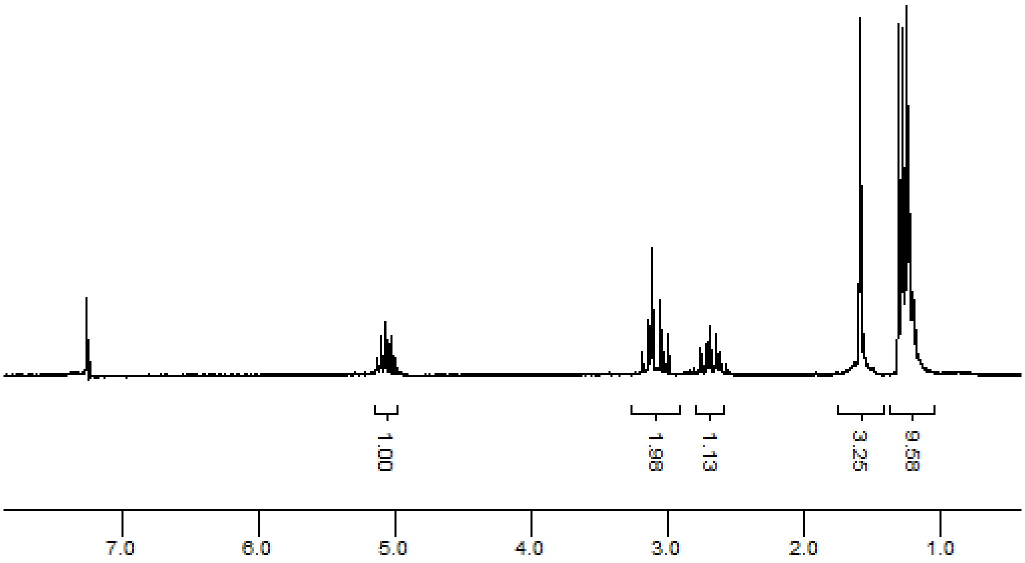

O
O
O
O

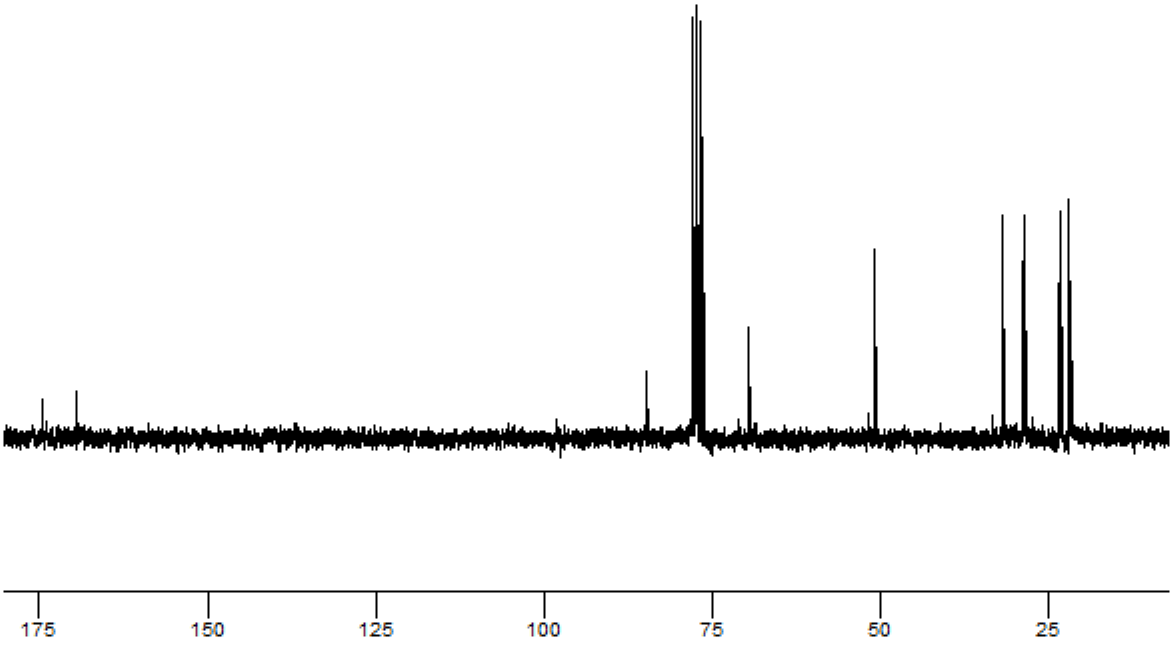

2.25
1.98
1.00
4.76
5.41
2.97
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25

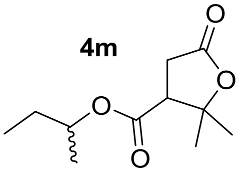
4l

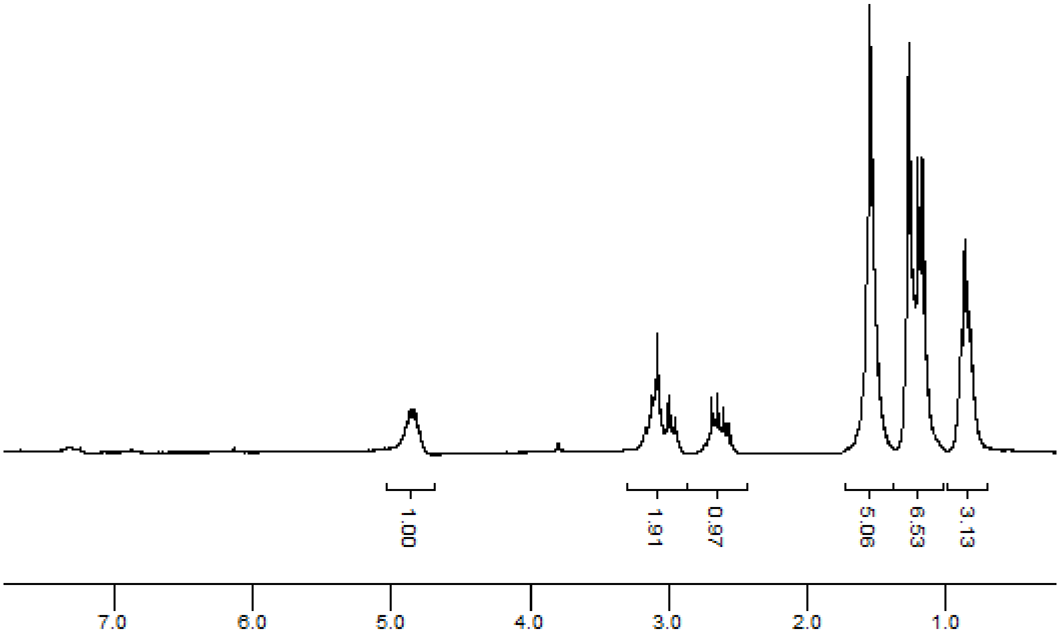


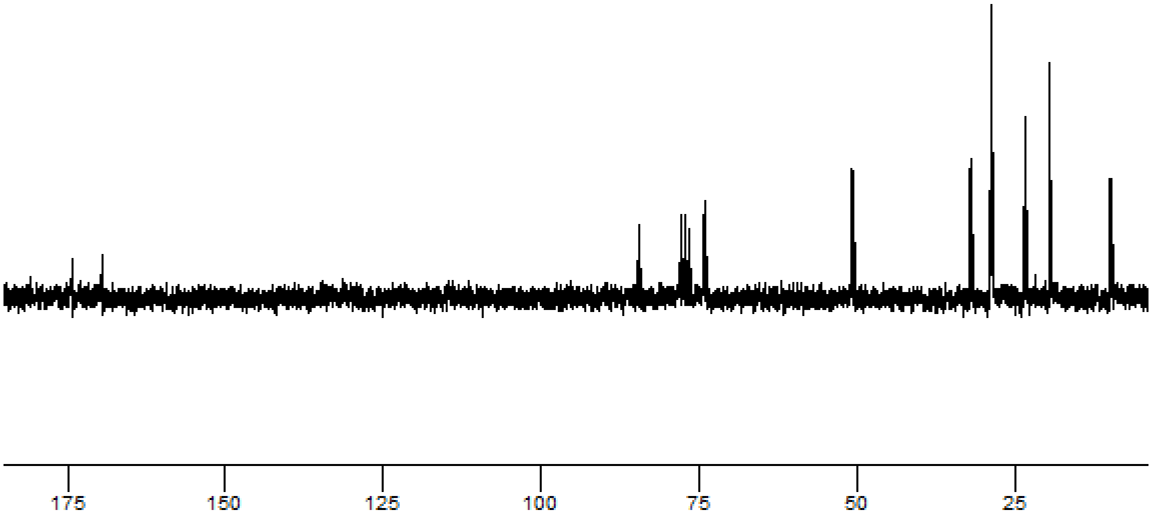




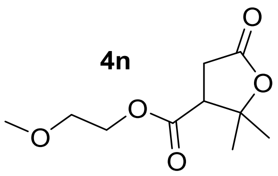
4m

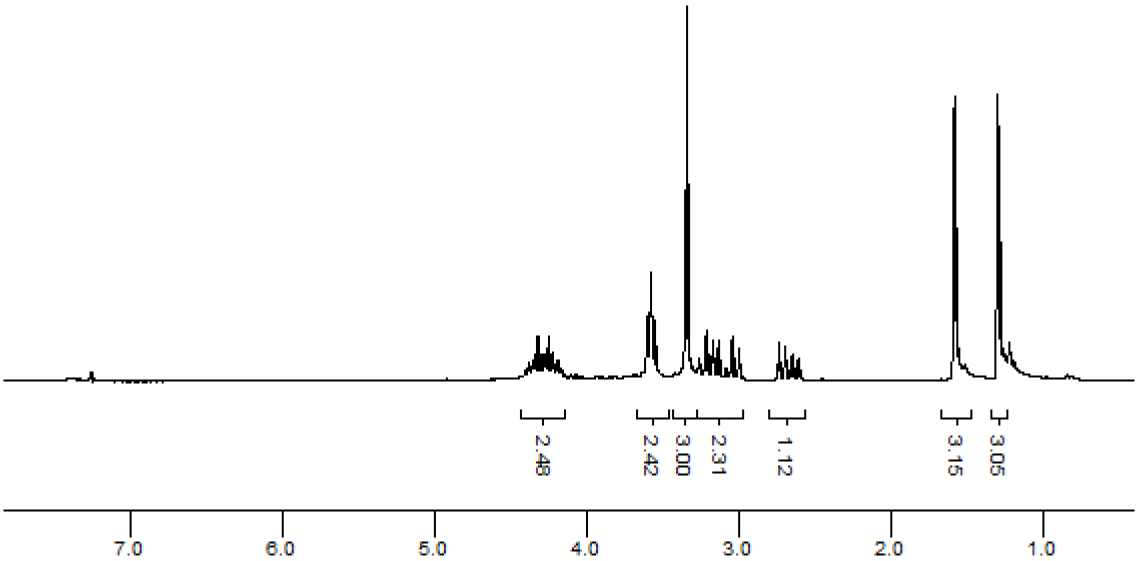


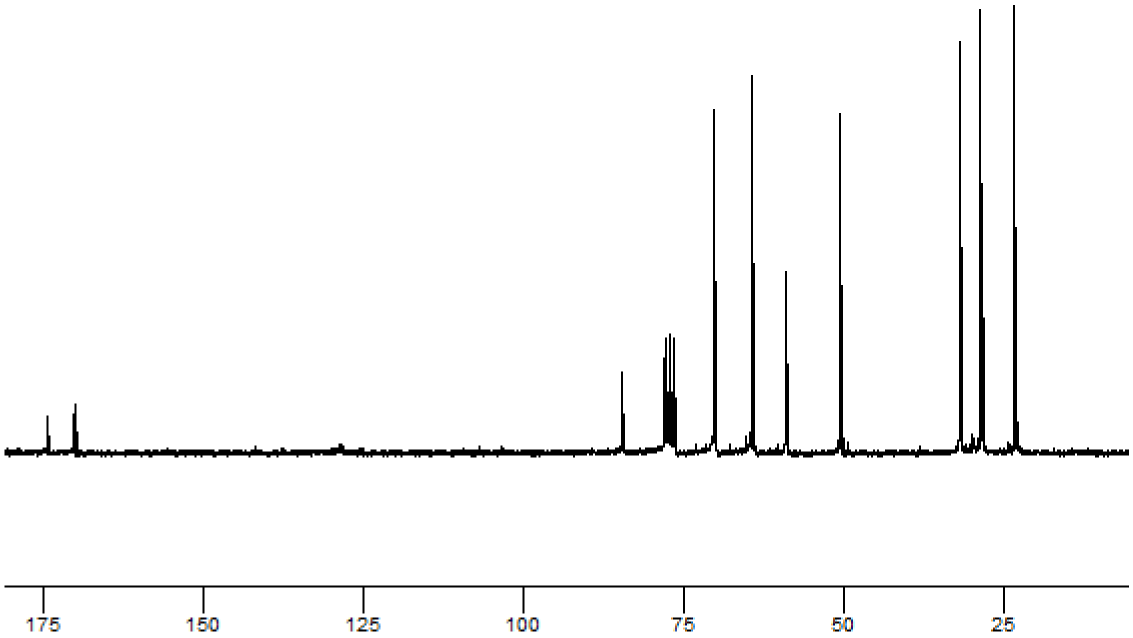

1.00
1.91
0.97
5.06
6.53
3.13
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25

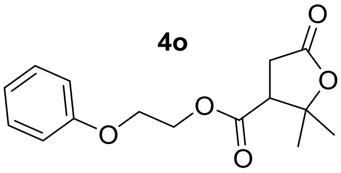
4n

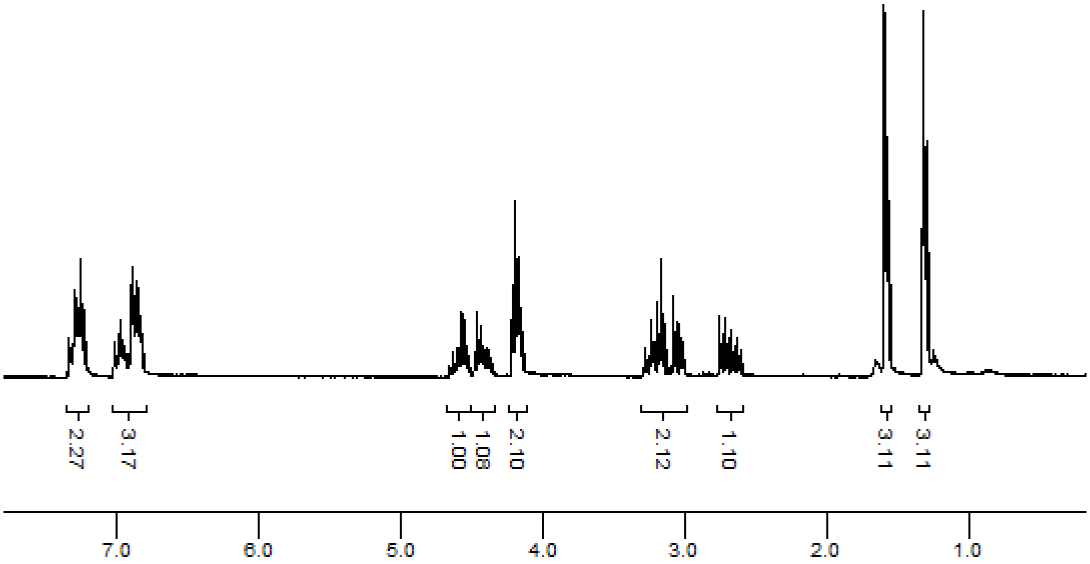


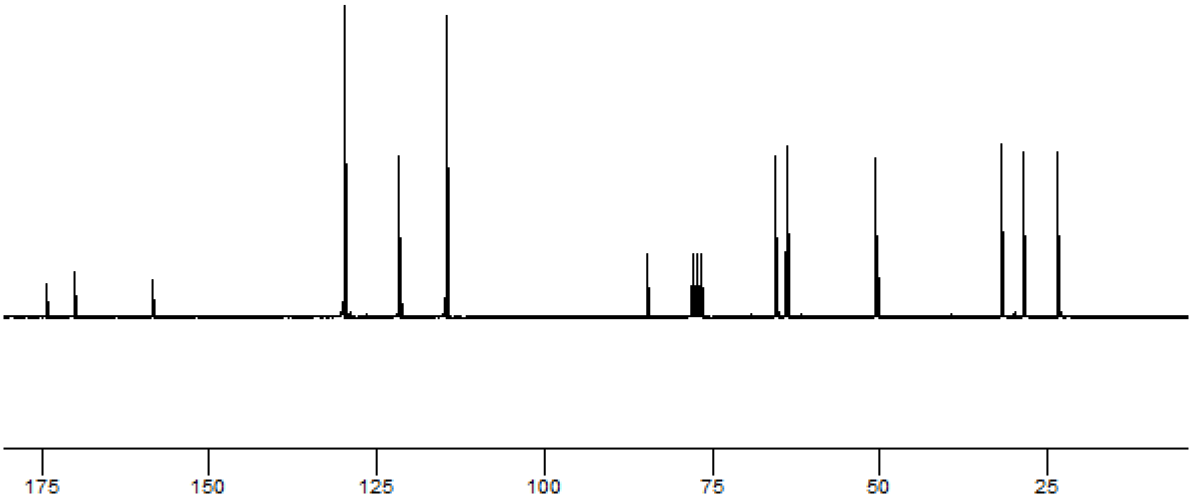

2.48
2.42
3.00
2.31
1.12
3.15
3.05
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25

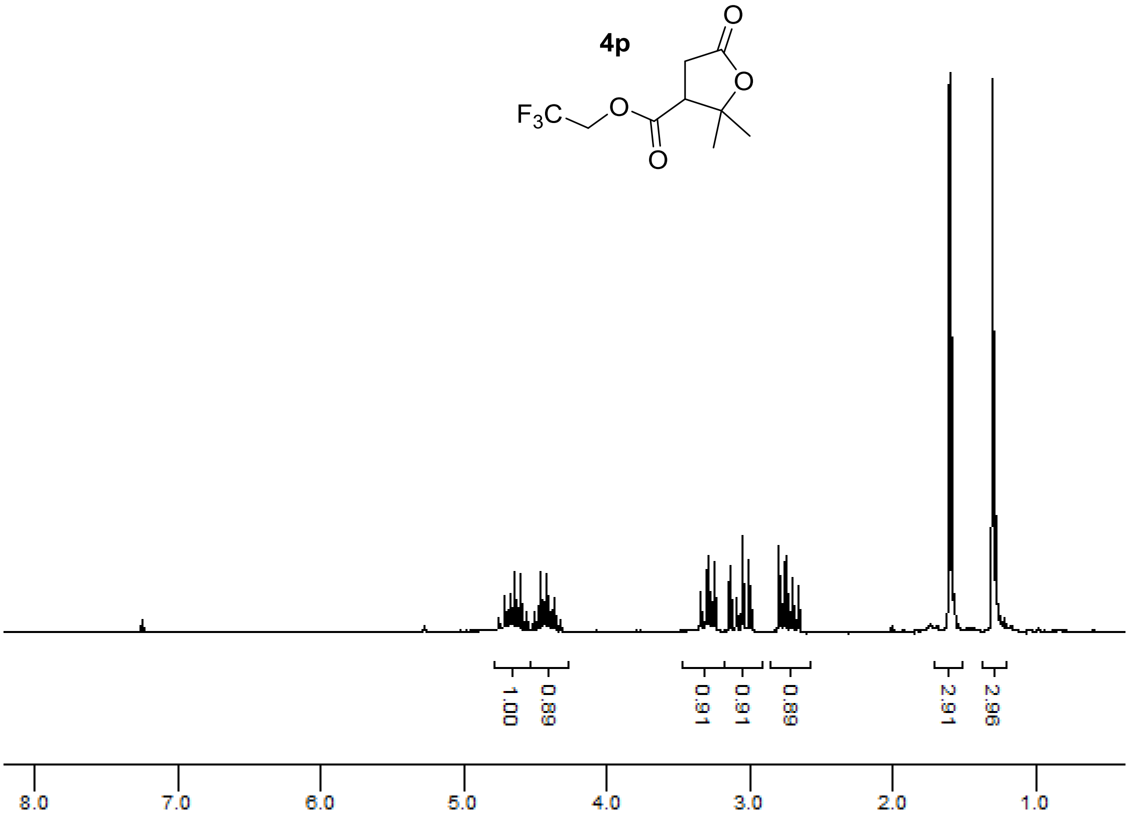
4o

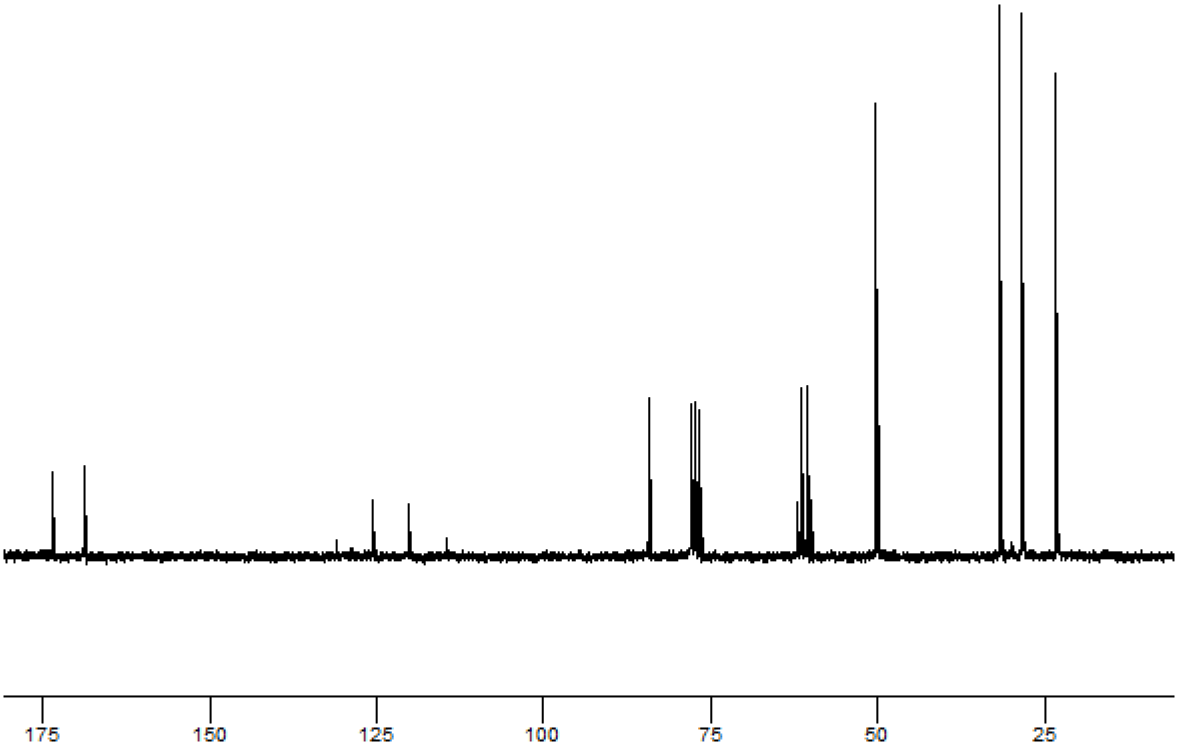



2.27
3.17
1.00
1.08
2.10
2.12
1.10
3.11
3.11
7.0
6.0
5.0
4.0
3.0
2.0
1.0

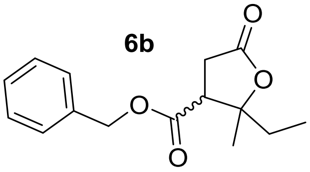

175
150
125
100
75
50
25

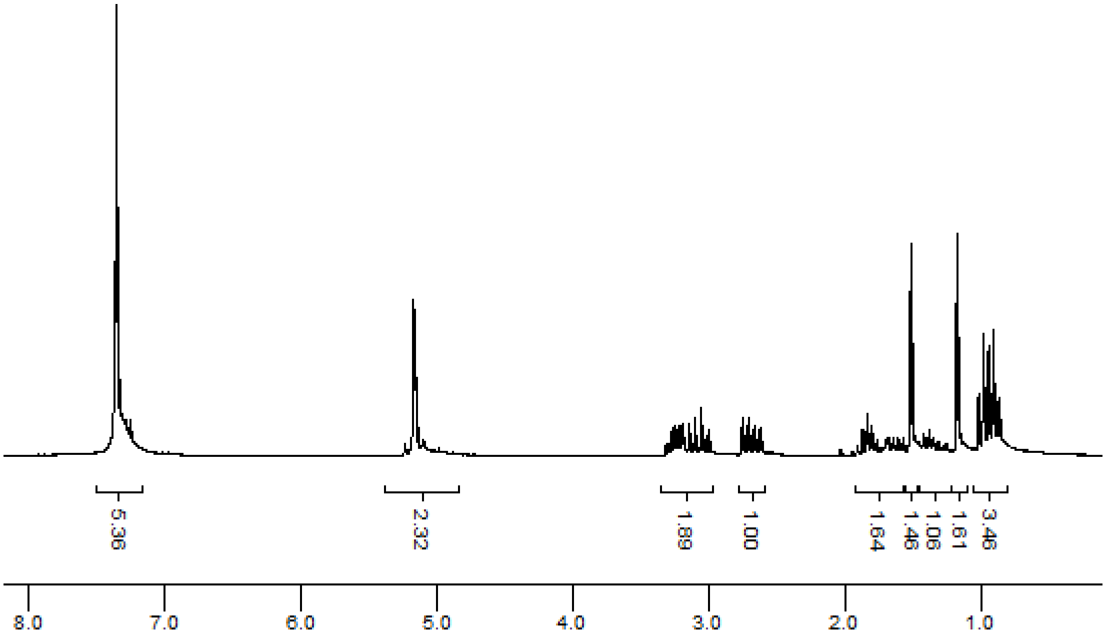
4p

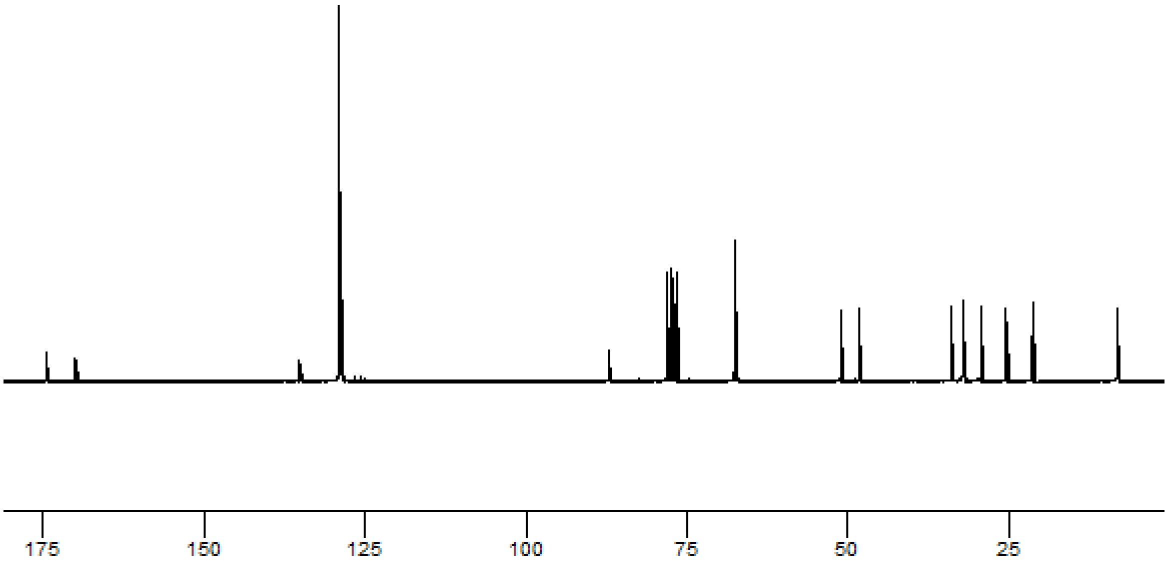

O
O
F$_3$C
O
O
1.00
0.89
0.91
0.91
0.89
2.91
2.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25

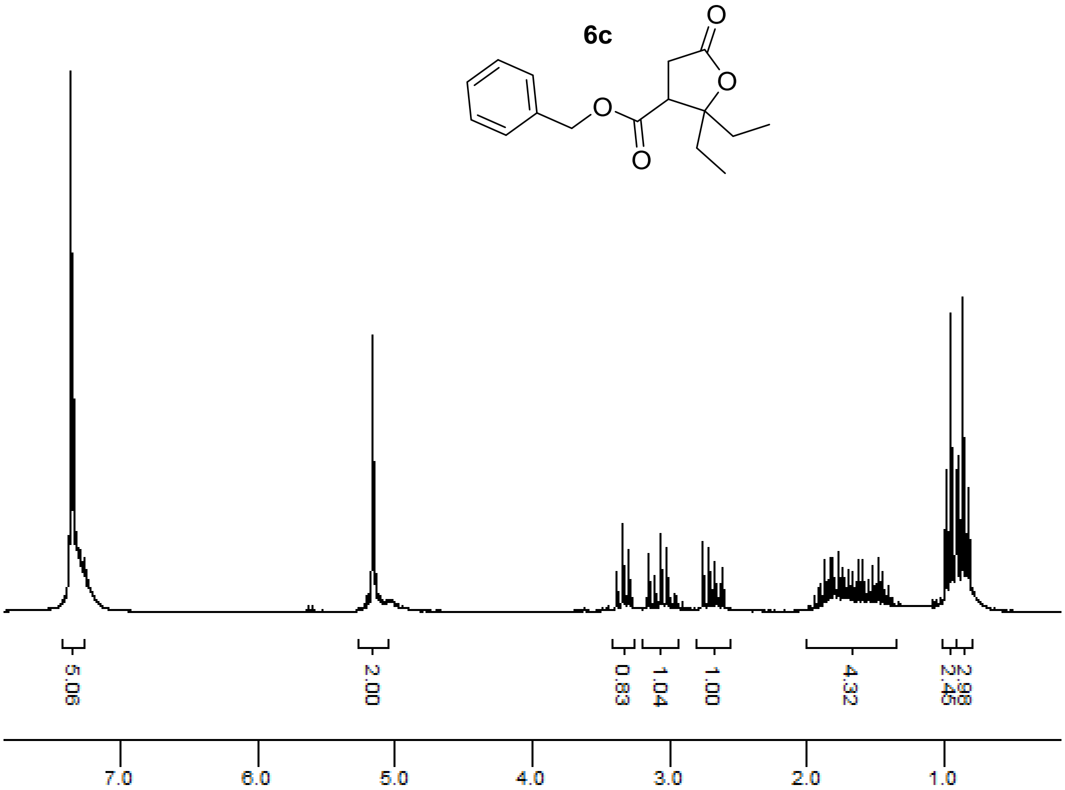
6b

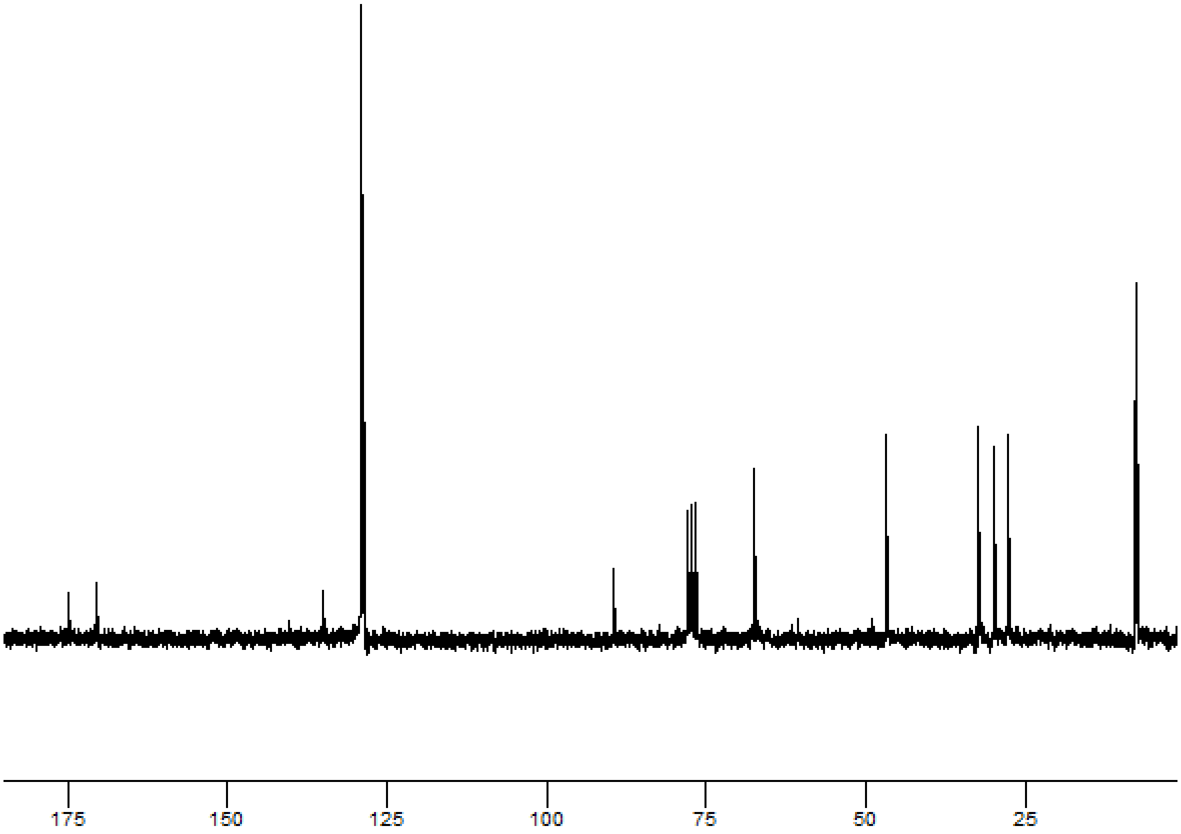



5.36
2.32
1.89
1.00
1.64
1.46
1.06
1.61
3.46
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

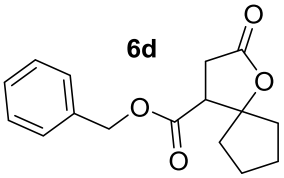

175
150
125
100
75
50
25

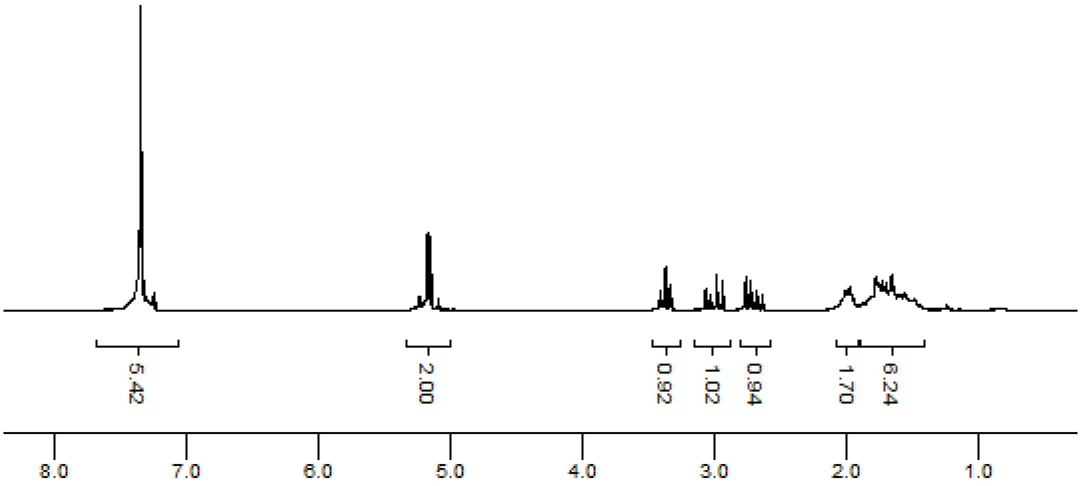
6c

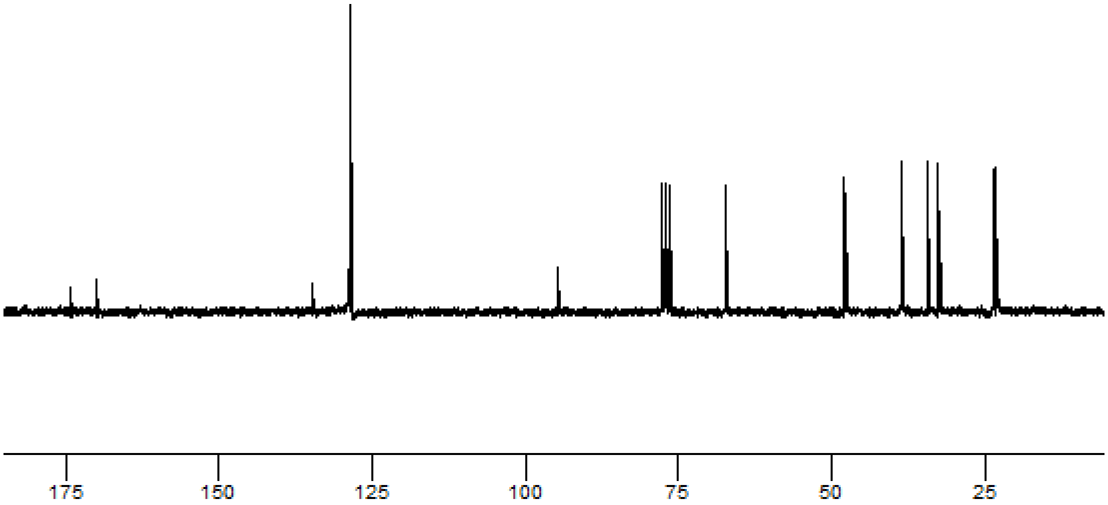

O
O
O
O
5.06
2.00
0.83
1.04
1.00
4.32
2.45
2.98
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25

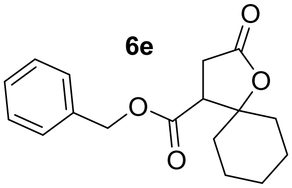
6d

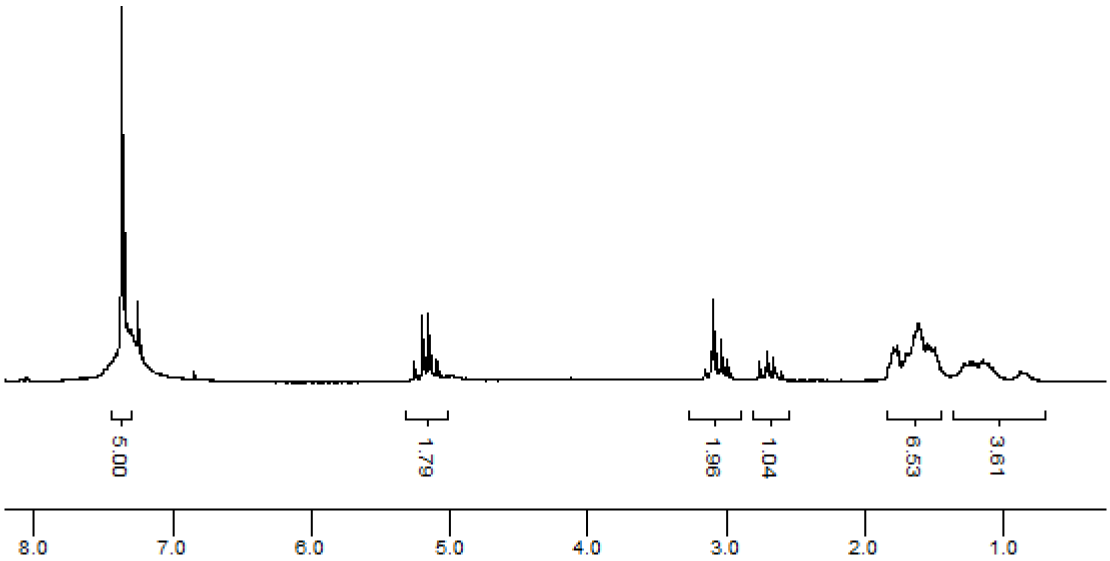


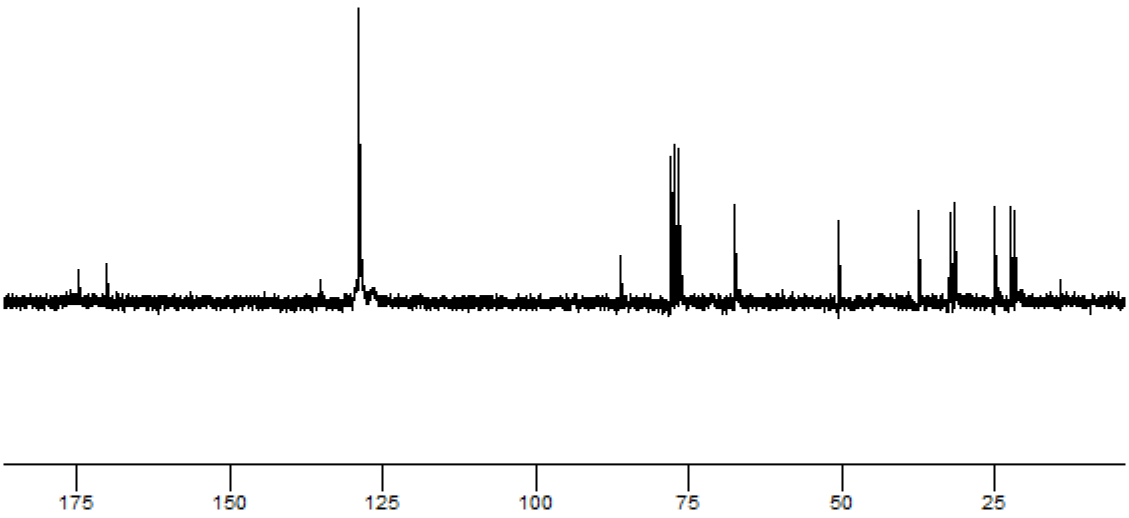

5.42
2.00
0.92
1.02
0.94
1.70
6.24
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25

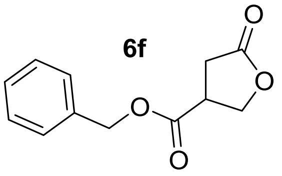
6e

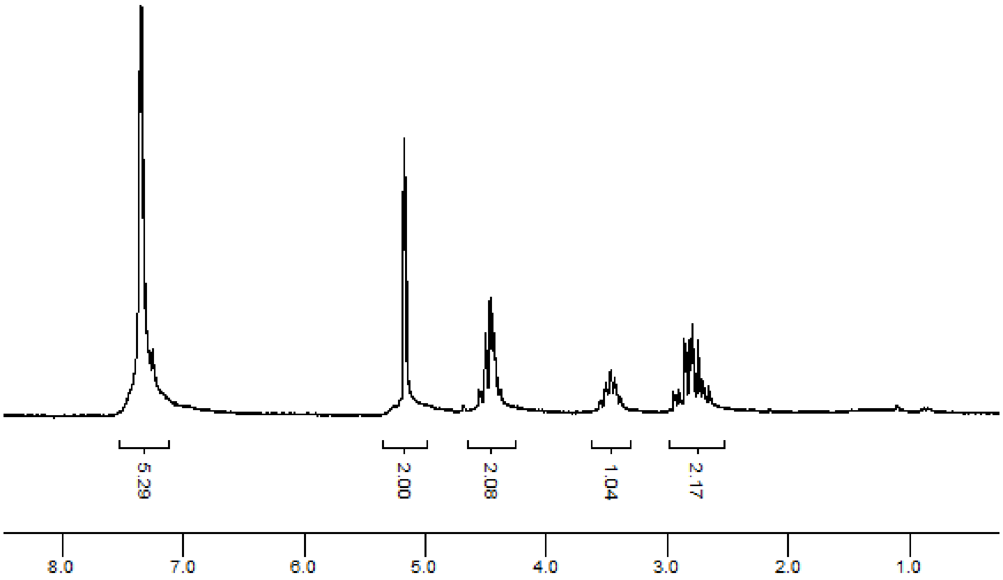


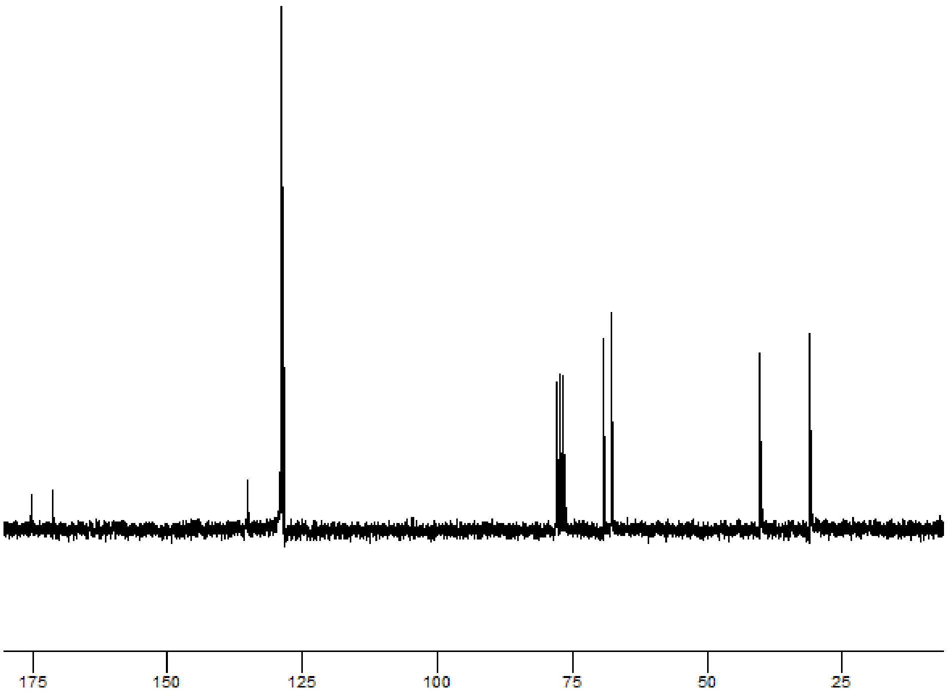

5.00
1.79
1.96
1.04
6.53
3.61
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

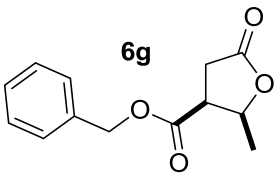

175
150
125
100
75
50
25

6f

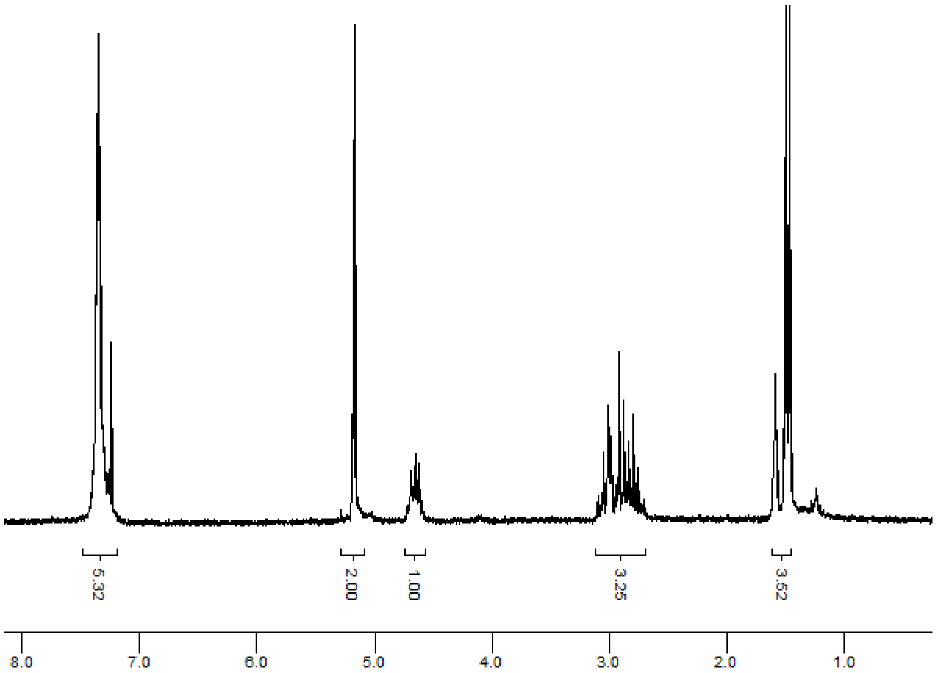

O
O
O
O

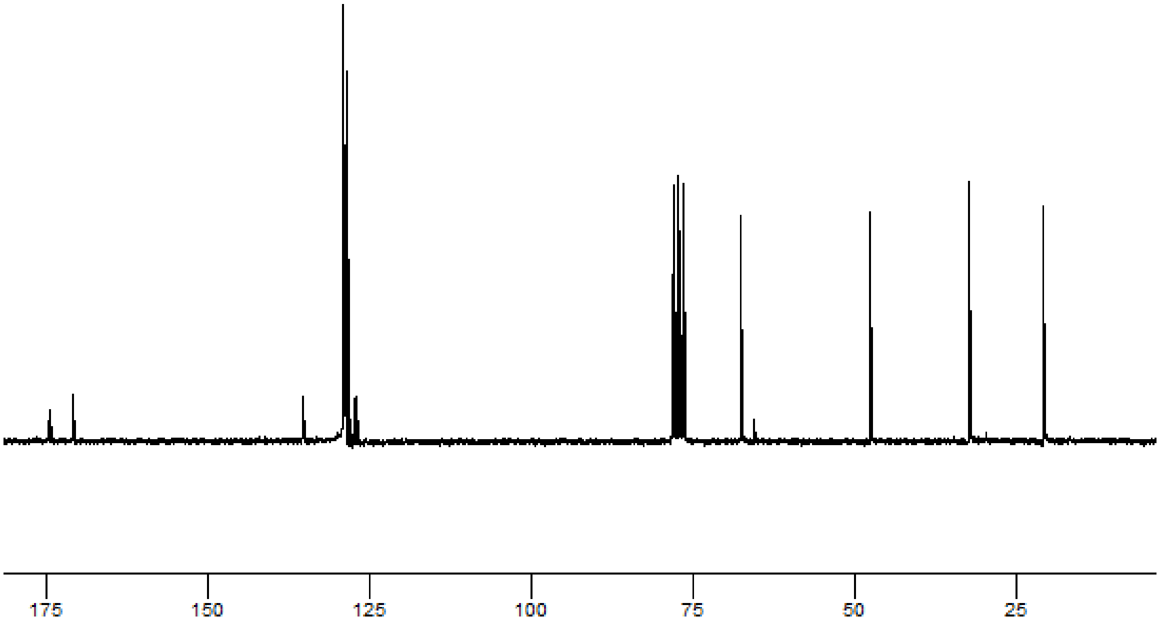

5.29
2.00
2.08
1.04
2.17
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25

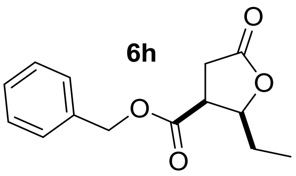


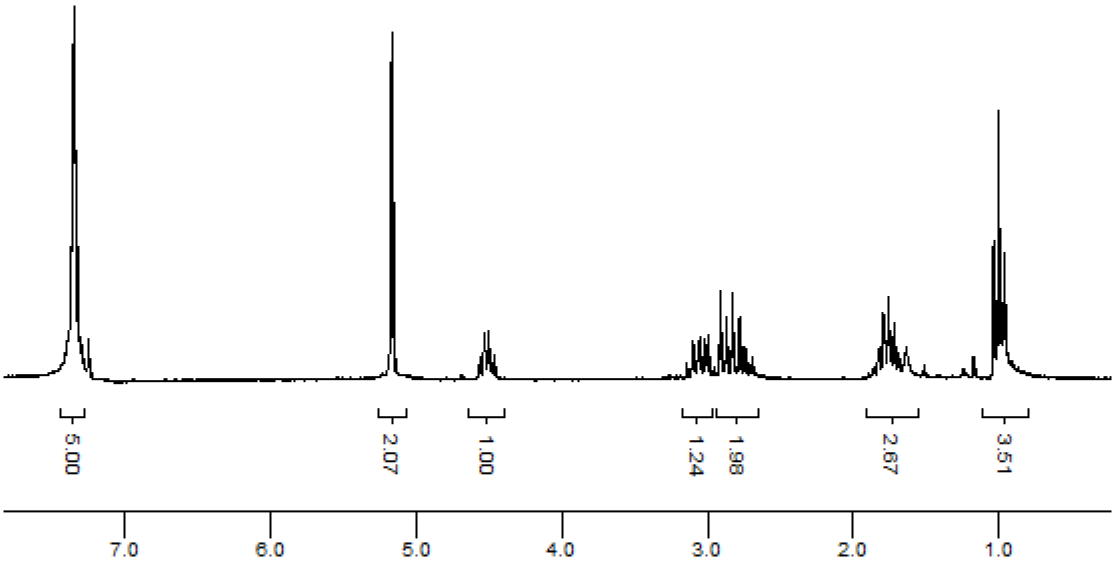
6g

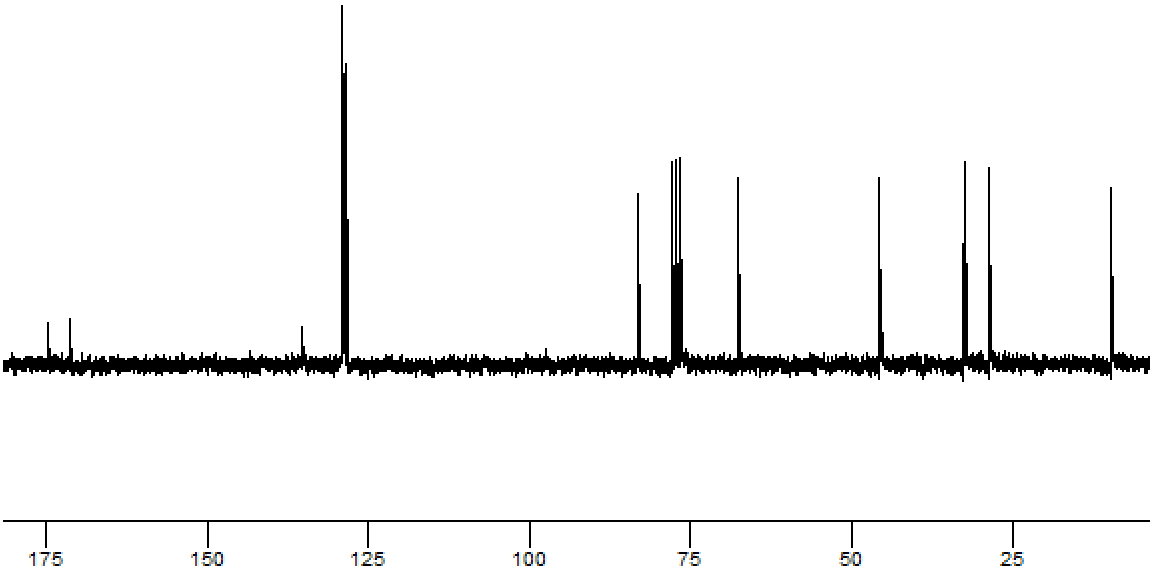




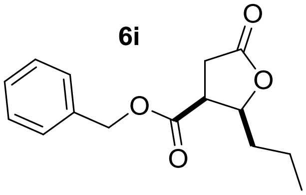
6h

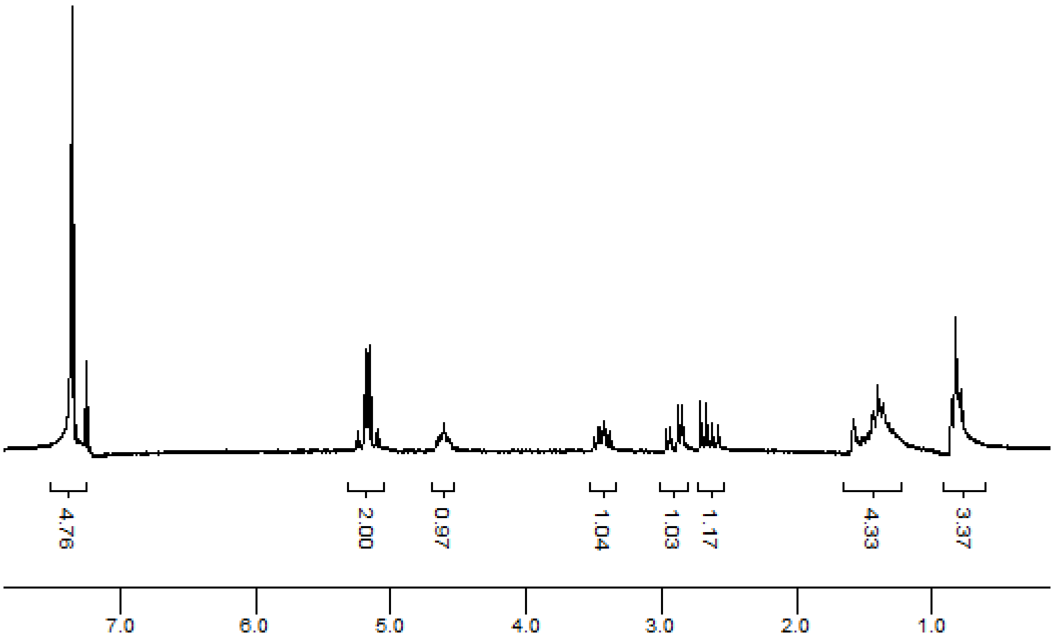

O
O
O
O

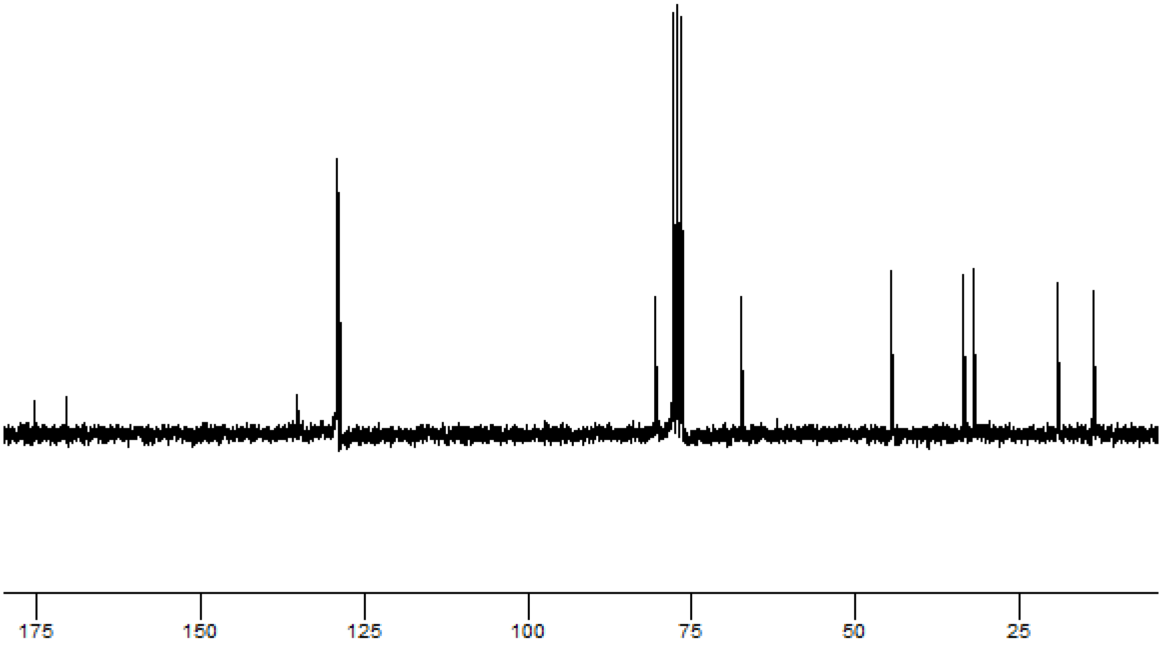

5.00
2.07
1.00
1.24
1.98
2.67
3.51
7.0
6.0
5.0
4.0
3.0
2.0
1.0

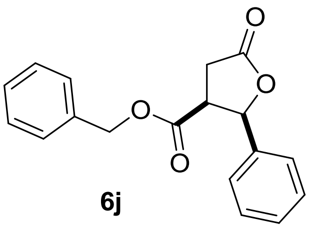

175
150
125
100
75
50
25

6i




4.76
2.00
0.97
1.04
1.03
1.17
4.33
3.37
7.0
6.0
5.0
4.0
3.0
2.0
1.0


175
150
125
100
75
50
25



6j