Supporting Information

Selective Synthesis of Oxygen-containing Heterocycles *via* Tandem Reactions of 1,2-Allenic Ketones with Ethyl 4-Chloroacetoacetate

Qiang Wang,[a, b] Zhouqing Xu[b] and Xuesen Fan[a]*

[a] *School of Chemistry and Chemical Engineering, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Key Laboratory for Environmental Pollution Control, Henan Normal University, Xinxiang, Henan 453007, P. R. China.*
[b] *School of Physics-Chemistry, Henan Polytechnic University, Jiaozuo, Henan, 454003, P. R. China.*
E-mail: xuesen.fan@htu.cn; xuesen.fan@yahoo.com

Table of Contents

I. General Experimental Information

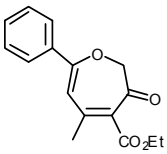
The ^{1}H, ^{13}C NMR spectra were recorded at 400 MHz or 100 MHz, respectively. Chemical shifts were reported in ppm from $CDCl_3$ as standard. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets); td (triplet of doublets); qd (quartet of doublets); br s (broad singlet), etc. and coupling constants were given in Hz. The conversion of starting materials were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm) and components were visualized by observation under UV light (254 and 365 nm). Mass spectra were obtained using a Waters Acquity SQ HPLC-mass spectrometer. High resolution mass spectra (HRMS) were performed on a time-of-flight (microTOF) mass spectrometer.

II. Experimental Procedures and Spectroscopic Data

1-Aryl substituted allenic ketones were prepared through oxidation of the corresponding homopropargyl alcohols,[1] which were prepared through zinc promoted propargylation of aldehydes.[2] 1,4-Disubsituted allenic ketones were prepared from 1-(triphenylphosphoranylidene)-2-propanone or 2-(triphenyl phosphoranylidene)acetophenone with phenylacetyl chloride based on a literature procedure.[3]

1. Typical procedure for the preparation of ethyl 5-methyl-3-oxo-7-phenyl-2,3-dihydrooxepine-4-carboxylate (3a)

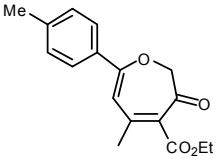
To a flask containing 1-phenylbuta-2,3-dien-1-one (**1a**, 1 mmol) and ethyl 4-chloroacetoacetate (**2**, 1.2 mmol) in CH_3CN (5 mL) were added anhydrous K_2CO_3 (1.0 mmol). The solution was stirred at room temperature for 1 h. The reaction then was quenched with aqueous NH_4Cl and extracted with ethyl acetate (5 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography over silica gel using ethyl acetate/hexane (v/v = 1:10) as eluent to give **3a** (68%). **3b**-**3s** were obtained in a similar manner.



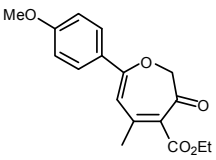
Ethyl 5-methyl-3-oxo-7-phenyl-2,3-dihydrooxepine-4-carboxylate (3a)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, J = 8.0 Hz, 2H), 7.40-7.46 (m, 3H), 6.02 (s, 1H), 4.69 (s, 2H), 4.34 (q, J = 7.6 Hz, 2H), 2.21 (s, 3H), 1.35 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.2, 167.7, 165.1, 149.4, 134.3, 133.4, 131.2, 128.7, 127.1, 106.9, 77.5, 61.5, 24.8, 14.2. MS(ESI): m/z 295.4 $[M+Na]^+$. HRMS (ESI) Calcd for $C_{16}H_{17}O_4$: $[M+H]^+$ 273.1127, found: 273.1137.

Ethyl 5-methyl-3-oxo-7-*p*-tolyl-2,3-dihydrooxepine-4-carboxylate (3b)



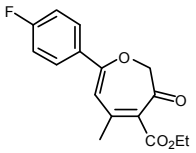
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 5.98 (s, 1H), 4.66 (s, 2H), 4.33 (q, J = 7.2 Hz, 2H), 2.38 (s, 3H), 2.19 (s, 3H), 1.34 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.2, 167.8, 165.4, 149.7, 141.9, 133.9, 130.6, 129.5, 127.2, 106.2, 77.5, 61.4, 24.8, 21.4, 14.1. HRMS (ESI) Calcd for $C_{17}H_{19}O_4$: $[M+H]^+$ 287.1283, found: 287.1288.



Ethyl 7-(4-methoxyphenyl)-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3c)

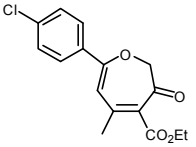
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.91 (s, 1H), 4.63 (s, 2H), 4.31 (q, *J* = 6.8 Hz, 2H), 3.82 (s, 3H), 2.18 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.9, 167.9, 165.3, 162.2, 150.2, 133.4, 129.0, 125.7, 114.1, 105.3, 77.4, 61.3, 55.4, 24.9, 14.1. HRMS (ESI) Calcd for $C_{17}H_{19}O_5$: $[M+H]^+$ 303.1232, found: 303.1240.

Ethyl 7-(4-fluorophenyl)-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3d)



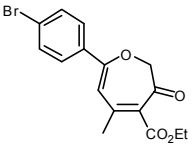
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67-7.70 (m, 2H), 7.06-7.10 (m, 2H), 5.94 (s, 1H), 4.66 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.19 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.0, 167.6, 163.9, 163.3, 149.3, 134.3, 129.7, 129.6, 129.4, 129.3, 115.9, 115.7, 106.6, 77.5, 61.5, 24.8, 14.1. HRMS (ESI) Calcd for $C_{16}H_{16}FO_4$: $[M+H]^+$ 291.1033, found: 291.1039.

Ethyl 7-(4-chlorophenyl)-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3e)



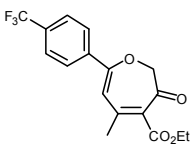
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 5.98 (s, 1H), 4.65 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.19 (s, 3H), 1.33 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.1, 167.5, 163.6, 148.9, 137.3, 134.6, 131.9, 128.9, 128.3, 107.1, 77.4, 61.5, 24.8, 14.1. MS(ESI): m/z 329.2, 329.5 $[M+Na]^+$.HRMS (ESI) Calcd for $C_{16}H_{16}ClO_4$: $[M+H]^+$ 307.0737, found: 307.0743.

Ethyl 7-(4-bromophenyl)-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3f)



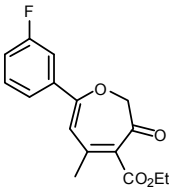
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51-7.56 (m, 4H), 5.99 (s, 1H), 4.66 (s, 2H), , 4.32 (q, *J* = 6.8 Hz, 2H), 2.19 (s, 3H), 1.33 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.1, 167.5, 163.7, 149.0, 134.6, 132.3, 131.9, 128.5, 125.8, 107.1, 77.4, 61.5, 24.8, 14.2. MS(ESI): m/z 373.3, 375.4 $[M+Na]^+$. HRMS (ESI) Calcd for $C_{16}H_{16}BrO_4$: $[M+H]^+$ 351.0232, found: 351.0239.

Ethyl 5-methyl-3-oxo-7-(4-(trifluoromethyl)phenyl)-2,3-dihydrooxepine-4-carboxylate (3g)



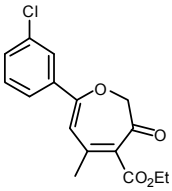
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 6.07

(s, 1H), 4.68 (s, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.21 (s, 3H), 1.34 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.2, 167.3, 162.8, 148.4, 136.9, 135.3, 132.2, 127.1, 125.65, 125.61, 125.58, 108.5, 77.5, 24.7, 14.1. HRMS (ESI) Calcd for $C_{17}H_{16}F_3O_4$: $[M+H]^+$ 341.1001, found: 341.1011.



Ethyl 7-(3-fluorophenyl)-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3h)

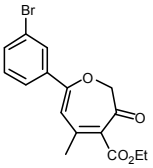
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 8.0 Hz, 1H), 7.34-7.39 (m, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.00 (s, 1H), 4.65 (s, 2H), 4.32 (q, *J* = 7.6 Hz, 2H), 2.18 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.2, 167.4, 164.0, 163.2, 161.6, 148.7, 135.74, 135.66, 134.89, 130.33, 130.26, 122.57, 122.54, 117.98, 117.78, 113.9, 113.7, 107.7, 77.4, 61.5, 14.1. HRMS (ESI) Calcd for $C_{16}H_{16}FO_4$: $[M+H]^+$ 291.1033, found: 291.1037.



Ethyl 7-(3-chlorophenyl)-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3i)

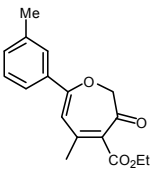
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 1H) 7.40 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 4.66 (s, 2H), 5.99 (s, 1H), 4.33 (q, *J* = 7.6 Hz, 2H), 2.19 (s, 3H), 1.34 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.2, 167.4, 163.01, 148.7, 135.3, 134.9, 134.8, 130.9, 129.9, 126.9, 125.0, 107.7, 77.5, 61.5, 24.7, 14.1. HRMS (ESI) Calcd for $C_{16}H_{16}ClO_4$: $[M+H]^+$ 307.0737, found: 307.0741.

Ethyl 7-(3-bromophenyl)-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3j)



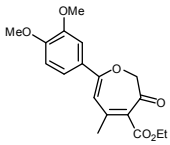
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 5.98 (s, 1H), 4.66 (s, 2H), 4.33 (q, *J* = 6.8 Hz, 2H), 2.19 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.2, 162.9, 148.6, 148.6, 135.5, 134.9, 133.8, 130.2, 129.9, 125.5, 122.9, 107.7, 77.5, 61.5, 24.7, 14.1. HRMS (ESI) Calcd for $C_{16}H_{16}BrO_4$: $[M+H]^+$ 351.0232, found: 351.0238.

Ethyl 5-methyl-3-oxo-7-m-tolyl-2, 3-dihydrooxepine-4-carboxylate (3k)



^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48-7.50 (m, 2H), 7.24-7.31 (m, 2H), 5.99 (s, 1H), 4.65 (s, 2H), 4.33 (q, *J* = 6.8 Hz, 2H), 2.38 (s, 3H), 2.19 (s, 3H), 1.34 (t, *J* = 6.8 Hz, 3H). ^{13}C

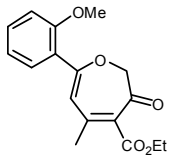
NMR (100 MHz, $CDCl_3$) δ: 187.2, 167.7, 165.3, 149.5, 138.4, 134.2, 133.4, 132.0, 128.6, 127.7, 124.3, 106.9, 77.5, 61.4, 24.8, 21.4, 14.1. HRMS (ESI) Calcd for $C_{17}H_{19}O_4$: $[M+H]^+$ 287.1283, found: 287.1289.



Ethyl 7-(3,4-dimethoxyphenyl)-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3l)

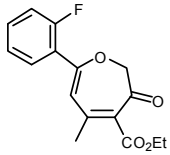
^1H NMR (400 MHz, $CDCl_3$) δ: 7.33 (dd, J_1 = 2.0 Hz, J_2 = 10.4 Hz, 1H), 7.16 (d, J = 1.6 Hz, 1H), 6. 88 (d, J = 8.8 Hz, 1H), 5.92 (s, 1H), 4.67 (s, 2H), 4.33 (q, J = 7.2 Hz, 2H), 3.92 (s, 6H), 2.20 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.9, 167.8, 165.3, 151.9, 149.9, 148.9, 133.5, 125.9, 121.1, 110.9, 109.8, 105.5, 77.5, 65.9, 61.4, 24.9, 14.1. HRMS (ESI) Calcd for $C_{18}H_{21}O_6$: $[M+H]^+$ 333.1338, found: 333.1343.

Ethyl 7-(2-methoxyphenyl)-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3m)



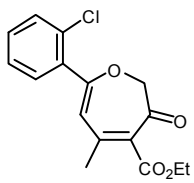
^1H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.52 (m, 1H), 7.36-7.40 (m, 1H), 6.93-6.99 (m, 2H), 6.13 (s, 1H), 4.64 (s, 2H), 4.33 (q, J = 6.8 Hz, 2H), 3.87 (s, 3H), 2.16 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.5, 167.8, 163.1, 158.0, 149.4, 134.2, 132.0, 130.3, 123.4, 120.6, 112.3, 111.5, 77.5, 61.3, 55.8, 24.7, 14.1. HRMS (ESI) Calcd for $C_{17}H_{19}O_5$: $[M+H]^+$ 303.1232, found: 303.1242.

Ethyl 7-(2-fluorophenyl)-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3n)



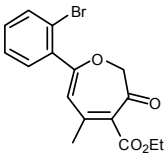
^1H NMR (400 MHz, $CDCl_3$) δ: 7.58-7.62 (m, 1H), 7.36-7.39 (m, 1H), 7.15-7.19 (m, 1H), 7.07-7.12 (m, 1H), 6.08 (s, 1H), 4.65 (s, 2H), 4.32 (q, J = 6.8 Hz, 2H), 2.16 (s, 3H), 1.33 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.9, 167.5, 161.7, 159.8, 159.8, 159.2, 148.7, 134.9, 132.4, 132.3, 130.1, 124.4, 124.3, 122.2, 122.0, 116.6, 116.4, 112.4, 112.3, 77.5, 61.4, 24.7, 14.1. MS(ESI): m/z 313.6 $[M+Na]^+$. HRMS (ESI) Calcd for $C_{16}H_{16}FO_4$: $[M+H]^+$ 291.1033, found: 291.1043.

Ethyl 7-(2-chlorophenyl)-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3o)



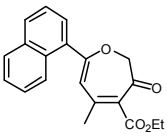
^1H NMR (400 MHz, $CDCl_3$) δ: 7.39-7.41 (m, 2H), 7.32-7.36 (m, 1H), 7.25-7.29 (m, 1H), 5.68 (s, 1H), 4.69 (s, 2H), 4.32 (q, J = 6.8 Hz, 2H), 2.14 (s, 3H), 1.33 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.5, 167.4, 148.3, 134.9, 134.1, 133.9, 131.6, 131.4, 130.4,

126.8, 112.0, 77.4, 61.5, 24.5, 14.1. HRMS (ESI) Calcd for $C_{16}H_{16}ClO_4$: $[M+H]^+$ 307.0737, found: 307.0744.



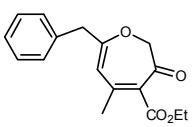
Ethyl 7-(2-bromophenyl)-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3p)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, J = 7.6 Hz, 1H), 7.37 (dd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.24 (dt, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1H), 5.61 (s, 1H), 4.69 (s, 2H), 4.29 (q, J = 7.2 Hz, 2H), 2.12 (s, 3H), 1.31 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.3, 167.4, 164.9, 148.3, 136.1, 134.9, 133.5, 131.7, 127.4, 123.1, 111.6, 77.6, 61.4, 30.8, 24.5, 14.1. HRMS (ESI) Calcd for $C_{16}H_{16}BrO_4$: $[M+H]^+$ 351.0232, found: 351.0243.



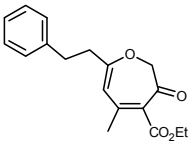
Ethyl 5-methyl-7-(naphthalen-1-yl)-3-oxo-2,3-dihydrooxepine-4-carboxylate (3q)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (d, J = 8.4 Hz, 1H), 7.86-7.92 (m, 2H), 7.44-7.60 (m, 4H), 5.81 (s, 1H), 4.82 (s, 2H), 4.38 (q, J = 6.8 Hz, 2H), 2.21 (s, 3H), 1.38 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.7, 167.7, 166.5, 149.2, 134.4, 133.7, 132.7, 131.3, 131.1, 128.7, 128.6, 127.2, 126.3, 124.9, 124.9, 111.8, 77.5, 61.5, 24.8, 14.2. HRMS (ESI) Calcd for $C_{20}H_{19}O_4$: $[M+H]^+$ 323.1283, found: 323.1291.



Ethyl 7-benzyl-5-methyl-3-oxo-2,3-dihydrooxepine-4-carboxylate (3r)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30-7.34 (m, 2H), 7.21-7.28 (m, 3H), 5.29 (s, 1H), 4.42 (s, 2H), 4.29 (q, J = 7.2 Hz, 2H), 3.56 (s, 2H), 2.03 (s, 3H), 1.31 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.0, 168.9, 167.6, 148.9, 136.2, 133.9, 128.9, 128.7, 127.1, 108.9, 77.1, 61.3, 42.1, 24.5, 14.1. HRMS (ESI) Calcd for $C_{17}H_{19}O_4$: $[M+H]^+$ 287.1283, found: 287.1289.

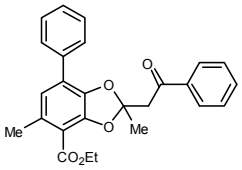


Ethyl 5-methyl-3-oxo-7-phenethyl-2,3-dihydrooxepine-4-carboxylate (3s)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25-7.29 (m, 2H), 7.13-7.20 (m, 3H), 5.19 (s, 1H), 4.41 (s, 2H), 4.28 (q, J = 7.2 Hz, 2H), 2.85 (t, J = 8.0 Hz, 2H), 2.57 (t, J = 7.6 Hz, 2H), 1.98 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.9, 169.5, 167.6, 149.2, 140.2, 133.6, 128.5, 128.3, 126.3, 108.6, 76.8, 61.3, 37.6, 33.4, 24.4, 14.1. HRMS (ESI) Calcd for $C_{18}H_{21}O_4$: $[M+H]^+$ 301.1440, found: 301.1449.

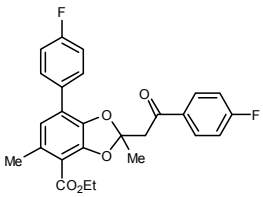
2. Typical procedure for the preparation of ethyl 2,5-dimethyl-2-(2-oxo-2-phenylethyl)-7-phenyl benzo[d][1,3]dioxole-4-carboxylate (4a)

To a flask containing 1-phenylbuta-2,3-dien-1-one (**1a**, 2.0 mmol) and ethyl 4-chloroacetoacetate (**2**, 1.0 mmol) in toluene (5 mL) were added anhydrous K_2CO_3 (2.5 mmol) and tetrabutyl ammonium bromide (0.05 mmol). The solution was stirred at room temperature for 1 h. The reaction then was quenched with aqueous NH_4Cl and extracted with ethyl acetate (5 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (v/v: 1/10) to give **4a** (62%). **4b-4n** were obtained in a similar manner.



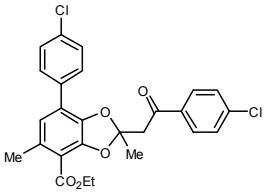
Ethyl 2,5-dimethyl-2-(2-oxo-2-phenylethyl)-7-phenylbenzo[*d*][1,3]dioxole-4-carboxylate (4a)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.34-7.41 (m, 4H), 6.89 (s, 1H), 4.25-4.33 (m, 2H), 3.64 (d, *J* = 14.8 Hz, 1H), 3.63 (d, *J* = 14.8 Hz, 1H), 2.49 (s, 3H), 1.93 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.1, 165.4, 147.9, 142.8, 137.2, 135.1, 133.2, 131.6, 128.6, 128.5, 128.5, 127.9, 127.8, 124.4, 122.8, 117.8, 112.9, 60.7, 46.9, 24.8, 20.8,14.2. HRMS (ESI) Calcd for $C_{26}H_{25}O_5$: $[M+H]^+$ 417.1702, found: 417.1711.



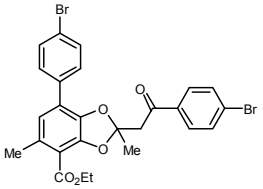
Ethyl 7-(4-fluorophenyl)-2-(2-(4-fluorophenyl)-2-oxoethyl)-2,5-dimethyl benzo[*d*][1,3]dioxole-4-carboxylate (4b)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88-7.92 (m, 2H), 7.56-7.59 (m, 2H), 6.98-7.07 (m, 4H), 6.81 (s, 1H), 4.30 (qd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 2H), 3.62 (d, *J* = 14.4 Hz, 1H), 3.55 (d, *J* = 14.4 Hz, 1H), 2.45 (s, 3H), 1.91 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.5, 167.1, 165.2, 164.6, 163.7, 161.2, 147.8, 142.5, 133.63, 133.60, 131.8, 131.4, 131.3, 131.04, 131.01, 129.7, 129.6, 123.4, 122.5, 117.7, 115.6, 115.55, 115.38, 115.33, 112.9, 60.8, 47.0, 24.8, 20.8, 14.1. HRMS (ESI) Calcd for $C_{26}H_{23}F_2O_5$: $[M+H]^+$ 453.1514, found: 453.1525.



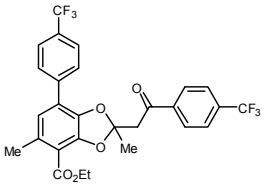
Ethyl 7-(4-chlorophenyl)-2-(2-(4-chlorophenyl)-2-oxoethyl)-2,5-dimethyl benzo[*d*][1,3]dioxole-4-carboxylate (4c)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78-7.80 (m, 2H), 7.51-7.54 (m, 2H), 7.28-7.34 (m, 4H), 6.82 (s, 1H), 4.30 (q, *J* = 7.6 Hz, 2H), 3.61 (d, *J* = 14.8 Hz, 1H), 3.54 (d, *J* = 14.0 Hz, 1H), 2.45 (s, 3H), 1.91 (s, 3H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.9, 165.12 147.8, 142.6, 139.8, 135.4, 133.9, 133.4, 131.9, 130.0, 129.1, 128.7, 123.1, 122.4, 117.7, 113.3, 60.8, 47.0, 24.9, 20.8, 14.2. HRMS (ESI) Calcd for $C_{26}H_{23}Cl_2O_5$: $[M+H]^+$ 485.0923, found: 485.0932.



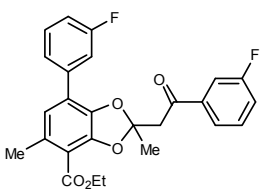
Ethyl 7-(4-bromophenyl)-2-(2-(4-bromophenyl)-2-oxoethyl)-2,5-dimethyl benzo[*d*][1,3]dioxole-4-carboxylate (4d)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 8.0 Hz, 2H), 7.42-7.48 (m, 6H), 6.80 (s, 1H), 4.28 (q, *J* = 6.8 Hz, 2H), 3.58 (d, *J* = 14.4 Hz, 1H), 3.51 (d, *J* = 14.4 Hz, 1H), 2.43 (s, 3H), 1.89 (s, 3H), 1.28 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 194.1, 165.1, 147.8, 142.6, 135.8, 133.8, 131.9, 131.7, 131.7, 130.1, 129.4, 128.5, 123.1, 122.3, 122.2, 117.7, 113.3, 60.8, 47.0, 24.8, 20.8, 14.2. HRMS (ESI) Calcd for $C_{26}H_{23}Br_2O_5$: $[M+H]^+$ 572.9912, found: 572.9921.



Ethyl 2,5-dimethyl-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-7-(4-(tri fluoromethyl)phenyl)benzo[*d*][1,3]dioxole-4-carboxylate (4e)

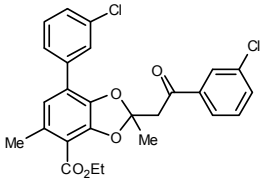
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.8 Hz, 4H), 6.85 (s, 1H), 4.29 (q, *J* = 6.8 Hz, 2H), 3.68 (d, *J* = 14.4 Hz, 1H), 3.60 (d, *J* = 14.4 Hz, 1H), 2.44 (s, 3H), 1.92 (s, 3H), 1.28 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.1, 165.0, 147.8, 142.9, 139.6, 138.5, 132.0, 128.9, 128.1, 125.5, 125.44, 125.41, 125.37, 125.3, 122.7, 122.67, 122.6, 117.8, 113.9, 60.9, 47.3, 24.9, 20.7, 14.4. HRMS (ESI) Calcd for $C_{28}H_{23}F_6O_5$: $[M+H]^+$ 553.1450, found: 553.1456.



Ethyl 7-(3-fluorophenyl)-2-(2-(3-fluorophenyl)-2-oxoethyl)-2,5-dimethyl benzo[*d*][1,3] dioxole-4-carboxylate (4f)

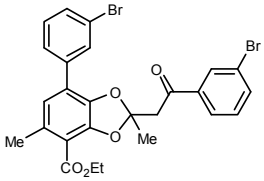
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.30 (t, *J* = 7.6 Hz, 3H), 1.92 (s, 3H), 2.45 (s, 3H), 3.57 (d, *J* = 14.4 Hz, 1H), 3.63 (d, *J* = 14.4 Hz, 1H), 4.30 (qd, J_1 = 1.6 Hz, J_2 = 6.8 Hz, 2H), 6.85

(s, 1H), 6.97-7.01 (m, 1H), 7.16-7.21 (m, 1H), 7.29-7.35 (m, 3H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.56-7.59 (m, 1H), 7.65 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.8, 165.2, 164.0, 163.9, 161.6, 161.5, 147.9, 142.8, 139.2, 139.1, 137.1, 137.05, 131.9, 130.2, 130.1, 130.01, 129.9, 124.4, 124.39,123.48, 123.45, 123.0, 120.4, 120.2, 117.8, 115.3, 115.0, 114.88, 114.86, 114.7, 113.4, 60.8, 47.1, 24.9, 20.8, 14.1. HRMS (ESI) Calcd for $C_{26}H_{23}F_2O_5$: $[M+H]^+$ 453.1514, found: 453.1520.



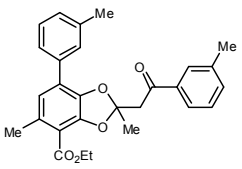
Ethyl 7-(3-chlorophenyl)-2-(2-(3-chlorophenyl)-2-oxoethyl)-2,5-dimethyl benzo[*d*][1,3]dioxole-4-carboxylate (4g)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82-7.83 (m, 1H), 7.70-7.73 (m, 1H), 7.56-7.57 (m, 1H), 7.42-7.49 (m, 2H), 7.24-7.30 (m, 3H), 6.83 (s, 1H), 4.27-4.34 (m, 2H), 3.64 (d, *J* = 14.4 Hz, 1H), 3.57 (d, *J* = 14.4 Hz, 1H), 2.45 (s, 3H), 1.92 (s, 3H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.8, 165.1, 147.9, 142.7, 138.6, 136.7, 134.9, 134.4, 133.1, 131.9, 129.8, 129.7, 128,5, 127.9, 127.8, 126.7, 126.1, 122.8, 122.5, 117.8, 113.4, 60.8, 47.0, 24.9, 20.8,14.2. HRMS (ESI) Calcd for $C_{26}H_{23}Cl_2O_5$: $[M+H]^+$ 485.0923, found: 485.0929.



Ethyl 7-(3-bromophenyl)-2-(2-(3-bromophenyl)-2-oxoethyl)-2,5-dimethyl benzo[*d*][1,3]dioxole-4-carboxylate (4h)

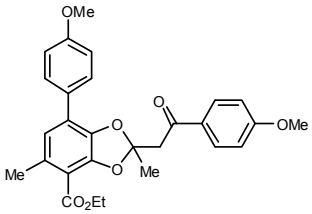
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (t, *J* = 2.0 Hz, 1H), 7.76-7.78 (m, 1H), 7.72 (t, *J* = 1.6 Hz, 1H), 7.59-7.62 (m, 1H), 7.51-7.54 (m, 1H), 7.42-7.45 (m, 1H), 7.22 (q, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 0.8 Hz, 1H), 4.28-4.34 (m, 2H), 3.62 (d, *J* = 14.4 Hz, 1H), 3.55 (d, *J* = 14.4 Hz, 1H), 2.46 (s, 3H), 1.92 (s, 3H), 1.30 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.8, 165.1, 147.9, 142.7, 138.8, 137.0, 136.1, 131.8, 131.4, 130.9, 130.6, 130.0, 127.1, 126.6, 122.9, 122.8, 122.7, 122.5, 117.8, 113.5, 60.9, 47.0, 24.9, 20.8, 14.2. HRMS (ESI) Calcd for $C_{26}H_{23}Br_2O_5$: $[M+H]^+$ 572.9912, found: 572.9919.



Ethyl 2,5-dimethyl-2-(2-oxo-2-m-tolylethyl)-7-m-tolylbenzo[*d*][1,3]dioxole-4-carboxylate (4i)

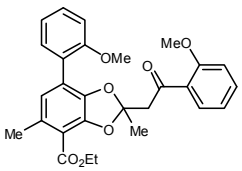
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 6.8 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 4.8 Hz, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 0.4 Hz, 1H),

4.27-4.35 (m, 2H), 3.67 (d, *J* = 14.4 Hz, 1H), 3.61 (d, *J* = 14.4 Hz, 1H), 2.50 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H), 1.95 (s, 3H), 1.30 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.4, 165.5, 148.0, 142.8, 138.3, 138.1, 137.3, 135.0, 134.0, 131.6, 129.1, 128.7, 128.5, 128.4, 125.9, 125.1, 124.6, 122.8, 117.8, 112.8, 60.7, 46.9, 24.8, 21.5, 21.2, 20.9, 14.2. HRMS (ESI) Calcd for $C_{28}H_{29}O_5$: $[M+H]^+$ 445.2015, found: 445.2020.



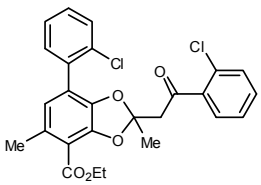
Ethyl 7-(4-methoxyphenyl)-2-(2-(4-methoxyphenyl)-2-oxoethyl)-2,5-dimethylbenzo[*d*][1,3]dioxole-4-carboxylate (4j)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85-7.89 (m, 2H), 7.55-7.59 (m, 2H), 6.87-6.91(m, 2H), 6.85 (s, 1H), 6.78-6.82 (m, 2H), 4.26-4.32 (m, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.59 (d, *J* = 14.4 Hz, 1H), 3.52 (d, *J* = 14.4 Hz, 1H), 2.47 (s, 3H), 1.91 (s, 3H), 1.28 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.7, 165.5, 163.7, 159.4, 148.0, 142.4, 131.6, 131.1, 130.4, 129.1, 127.5, 124.2, 122.2, 117.7, 113.9, 113.6, 112.3, 60.7, 55.4, 55.2, 46.8, 24.7, 20.9, 14.1. HRMS (ESI) Calcd for $C_{28}H_{29}O_7$: $[M+H]^+$ 477.1913, found: 477.1921.



Ethyl 7-(2-methoxyphenyl)-2-(2-(2-methoxyphenyl)-2-oxoethyl)-2,5-dimethyl benzo[*d*][1,3]dioxole-4-carboxylate (4k)

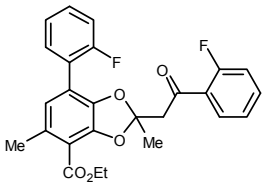
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58-7.60 (m, 1H), 7.38-7.42 (m, 1H), 7.30-7.35 (m, 1H), 7.25-7.27 (m, 1H), 6.90-7.00 (m, 3H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.72 (s, 1H), 4.24-4.32 (m, 2H), 3.80 (d, *J* = 15.2 Hz, 1H), 3.64 (d, *J* = 15.2 Hz, 1H), 3.77 (s, 3H) 3.74 (s, 3H), 2.42 (s, 3H), 1.87 (s, 3H), 1.29 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.2, 165.7, 158.4, 156.7, 147.7, 143.6, 133.6, 130.8, 130.3, 129.4, 128.6, 124.7, 124.7, 121.9, 120.5, 120.5, 117.8, 112.4, 111.4, 111.2, 60.5, 55.5, 55.3, 51.6, 25.0, 20.7, 14.2. HRMS (ESI) Calcd for $C_{28}H_{29}O_7$: $[M+H]^+$ 477.1913, found: 477.1920.



Ethyl 7-(2-chlorophenyl)-2-(2-(2-chlorophenyl)-2-oxoethyl)-2,5-dimethyl benzo[*d*][1,3]dioxole-4-carboxylate (4l)

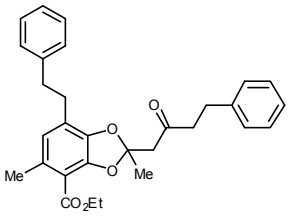
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42-7.45 (m, 1H), 7.25-7.35 (m, 6H), 7.16-7.20 (m, 1H), 6.64 (s, 1H), 4.34 (q, *J* = 6.8 Hz, 2H), 3.68 (d, *J* = 15.2 Hz, 1H), 3.61 (d, *J* = 15.2 Hz, 1H), 2.43 (s, 3H), 1.89 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.9, 165.4, 147.3,

143.2, 139.3, 134. 5, 133.1, 131.7, 131.3, 130.9, 130.8, 130.3, 129.8, 129.3, 129.2, 126.7, 126.7, 124.7, 122.6, 117.8, 113.5, 60.8, 50.9, 25.1, 20.6, 14.2. HRMS (ESI) Calcd for $C_{26}H_{23}Cl_2O_5$: $[M+H]^+$ 485.0923, found: 485.0931.



Ethyl 7-(2-fluorophenyl)-2-(2-(2-fluorophenyl)-2-oxoethyl)-2,5-dimethyl benzo[*d*][1,3]dioxole-4-carboxylate (4m)

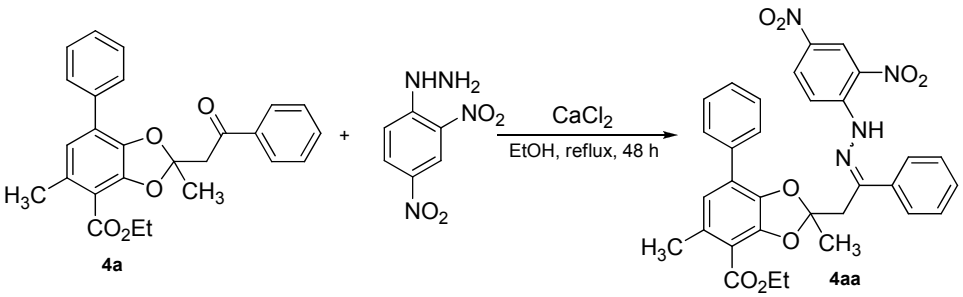
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69-7.74 (m, 1H), 7.38-7.47 (m, 2H), 7.29-7.34 (m, 1H), 7.09-7.17 (m, 3H), 6.99-7.04 (m, 1H), 6.76 (s, 1H), 4.27-4.35 (m, 2H), 3.69 (d, *J* = 15.6 Hz, 1H), 3.66 (d, *J* = 15.6 Hz, 1H), 2.44 (s, 3H), 1.89 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.38, 193.35, 165.4, 162.9, 160.9, 160.3, 158.4, 147.7, 143.4, 131.03, 131.0, 130.54, 130.51, 129.7, 129.65, 126.3, 126.2, 124.42, 124.38, 124.30, 124.27, 124.05, 124.02, 123.2, 123.1, 119.1, 117.7, 116.6, 116.4, 116.1, 115.9, 113.2, 60.7, 51.3, 51.2, 25.1, 20.7, 14.2. HRMS (ESI) Calcd for $C_{26}H_{22}F_2NaO_5$: $[M+Na]^+$ 475.1333, found: 475.1330.



Ethyl 2,5-dimethyl-2-(2-oxo-4-phenylbutyl)-7-phenethylbenzo[*d*][1,3] dioxole-4-carboxylate (4n)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25-7.31 (m, 4H), 7.17-7.22 (m, 6H), 6.53 (s, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.01 (d, *J* = 13.6 Hz, 1H), 2.95 (d, *J* = 13.6 Hz, 1H), 2.83-2.94 (m, 8H), 2.45 (s, 3H), 1.75 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.9, 165.6, 146.9, 143.7, 141.2, 140.8, 131.4, 128.5, 128.5, 128.3, 128.3, 126.1, 126.0, 125.5, 124.4, 116.8, 112.1, 60.7, 51.3, 45.7, 35.6, 31.4, 29.4, 24.5, 20.8, 14.3. HRMS (ESI) Calcd for $C_{30}H_{33}O_5$: $[M+H]^+$ 473.2328, found: 473.2331.

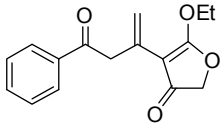
3. Procedure for the synthesis of (*Z/E*)-ethyl 2-(2-(2-(2,4-dinitrophenyl)hydrazono)-2-phenylethyl) -2,5-dimethyl-7-phenylbenzo[*d*][1,3]dioxole-4-carboxylate (4aa)



To a flask containing ethyl 2,5-dimethyl-2-(2-oxo-2-phenylethyl)-7-phenylbenzo[*d*][1,3]dioxole-4-carboxylate (**4a**, 1.0 mmol) and (2,4-dinitrophenyl)hydrazine (1.0 mmol) in ethanol (5 mL) were added anhydrous $CaCl_2$ (2.0 mmol). The solution was stirred at reflux for 48 h, and then concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (1:5) to give **4aa** as a mixture of *E*/*Z* isomers with a total yield of 52% (E:Z = 10:3). Single crystal of (*E*)-**4aa** was obtained by slow evaporation of its chloroform/petroleum ether solution at room temperature.

4. Typical procedure for the preparation of 5-ethoxy-4-(3-methyl-4-oxo-4-phenylbut-1-en-2-yl) furan-3(2H)-one (5b)

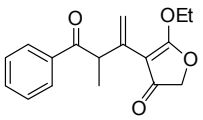
To a flask containing 2-methyl-1-phenylbuta-2,3-dien-1-one (1 mmol) and ethyl 4-chloro acetoacetate (**2**, 1.2 mmol) in CH_3CN (5 mL) were added anhydrous K_2CO_3 (1.0 mmol). The solution was stirred at room temperature for 1 h. The reaction then was quenched with aqueous NH_4Cl and extracted with ethyl acetate (5 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography over silica gel using ethyl acetate/hexane (v/v = 1/10) as eluent to give **5b** (52%). **5a**, **5c** and **5d** were obtained in a similar manner.



5-Ethoxy-4-(4-oxo-4-phenylbut-1-en-2-yl)furan-3(2H)-one (5a)

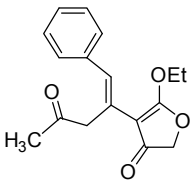
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.93-7.90 (m, 2H), 7.47-7.44 (m, 1H), 7.38-7.34 (m, 2H), 5.87 (s, 1H), 4.89 (s, 1H), 4.41 (s, 2H), 4.28-4.23 (m, 2H), 3.97 (s, 2H),

1.09-1.05 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ:197.5, 194.0, 180.1, 136.9, 132.8, 130.1, 128.4, 128.0, 114.8, 93.8, 74.3, 66.6, 45.1, 14.3. HRMS(ESI): calcd for $C_{16}H_{17}O_4$: $[M+H]^+$ 273.1127, found 273.1124.



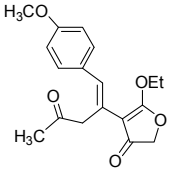
5-Ethoxy-4-(3-methyl-4-oxo-4-phenylbut-1-en-2-yl)furan-3(2H)-one (5b)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.03-8.01 (m, 2H), 7.51-7.49 (m, 1H), 7.43-7.39 (m, 2H), 5.55 (s, 1H), 4.97 (q, *J* = 7.2 Hz, 1H), 4.95 (s, 1H), 4.57 (s, 2H), 4.45 (q, *J* = 7.2 Hz, 2H), 1.38-1.33 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 201.1, 194.0, 180.7, 136.8, 136.6, 132.4, 128.7, 128.3, 113.1, 94.0, 74.3, 66.7, 43.9, 16.8, 14.6. HRMS(ESI): calcd for $C_{17}H_{19}O_4$: $[M+H]^+$ 287.1283, found 287.1279.



5-Ethoxy-4-(4-oxo-1-phenylpent-1-en-2-yl)furan-3(2H)-one (5c)

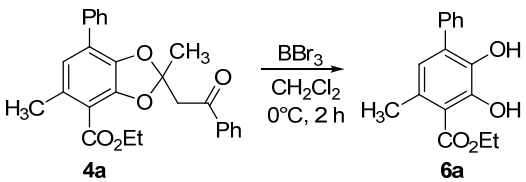
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.25-7.21 (m, 2H), 7.42 (m, 1H), 7.16-7.11 (m, 2H), 4.48 (s, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 3.63 (s, 2H), 2.14 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 206.8, 194.1, 180.2, 137.6, 128.5, 128.1, 126.5, 123.7, 94.6, 74.1, 66.9, 44.5, 29.4, 14.7. HRMS(ESI): calcd for $C_{17}H_{19}O_4$: $[M+H]^+$ 287.1283, found 287.1278.



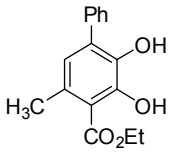
5-Ethoxy-4-(1-(4-methoxyphenyl)-4-oxopent-1-en-2-yl)furan-3(2H)-one (5d)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.37 (s, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.54 (s, 2H), 4.50 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 3.68 (s, 2H), 2.19 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 207.1, 180.2, 158.4, 130.1, 129.7, 128.6, 122.5, 113.6, 95.0, 74.1, 66.8, 55.2, 44.6, 29.5, 14.7. HRMS(ESI): calcd for $C_{18}H_{21}O_5$: $[M + H]^+$ 317.1389, found 317.1386.

5. Procedure for the synthesis of ethyl 2,3-dihydroxy-5-methylbiphenyl-4-carboxylate (6a) from 4a

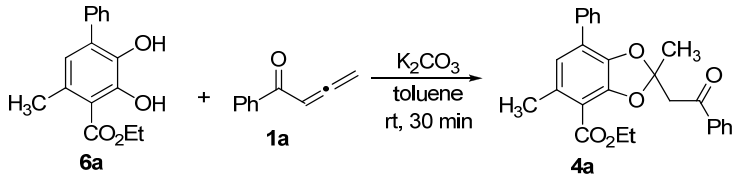


To a flask containing ethyl 2,5-dimethyl-2-(2-oxo-2-phenylethyl)-7-phenylbenzo[d][1,3]dioxole-4-carboxylate (**4a**, 1.0 mmol) in CH_2Cl_2 (5 mL) was added BBr_3 (5.0 mmol, 1M solution in methylene chloride) at 0 °C. The mixture was stirred at 0 °C for 2 h. Upon completion, the mixture was quenched with water and extracted with CH_2Cl_2 (5 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (v/v = 1/25) to give **6a** (80%).



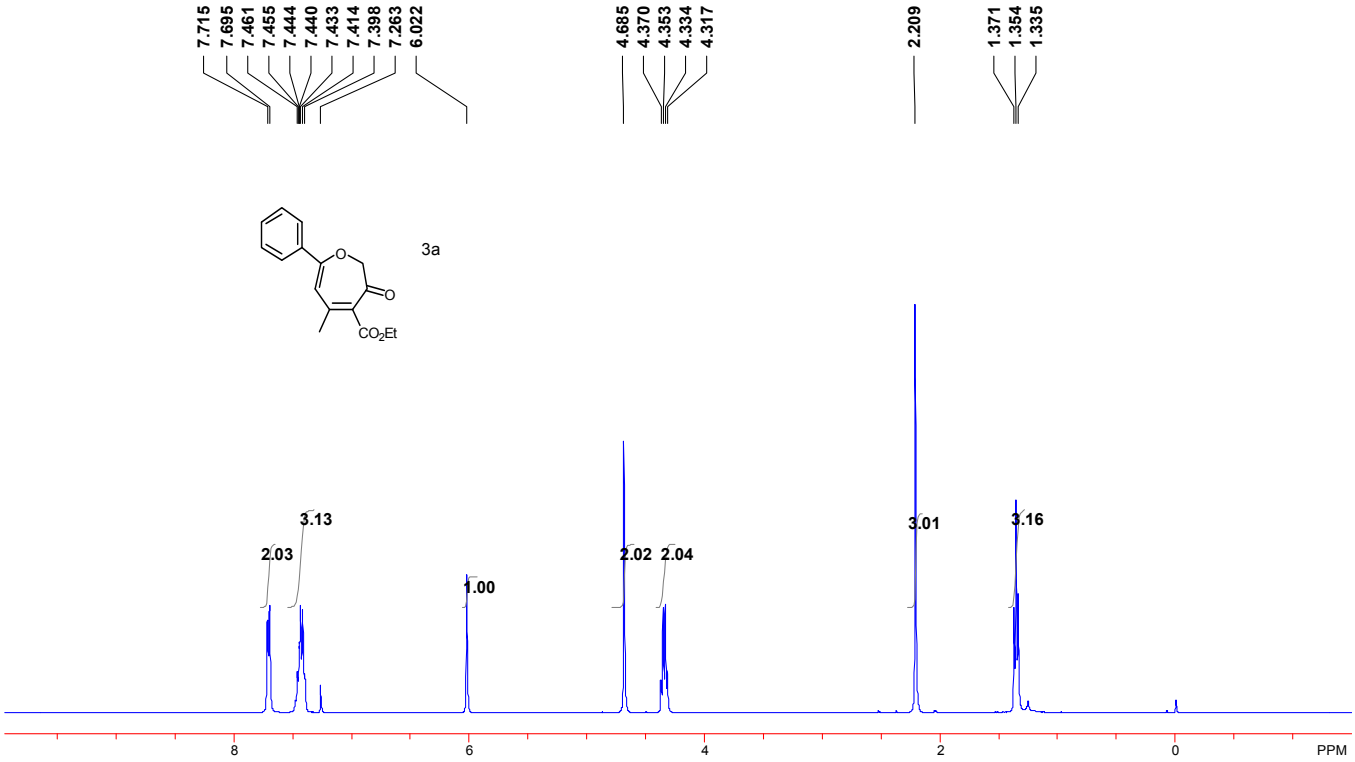
^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.93 (s, 1H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 5.92 (s, 1H), 6.76 (s, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 2.54 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 150.4, 140.3, 136.9, 130.9, 130.93, 129.0, 128.6, 128.2, 127.8, 126.9, 123.4, 110.6, 61.8, 23.4, 14.2. HRMS (ESI) Calcd for $C_{16}H_{16}NaO_4$: $[M+Na]^+$ 295.0946, found: 295.0951.

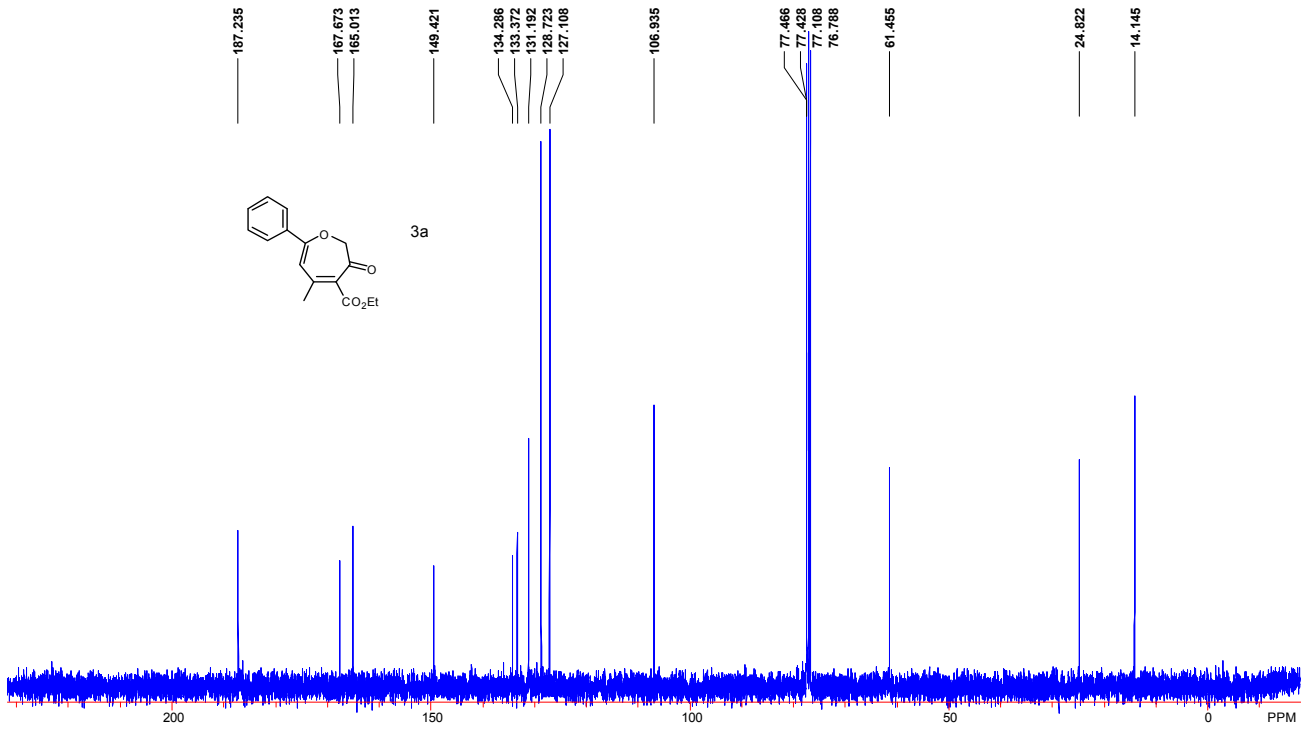
6. Procedure for the preparation of 4a through the reacion of 1a with 6a

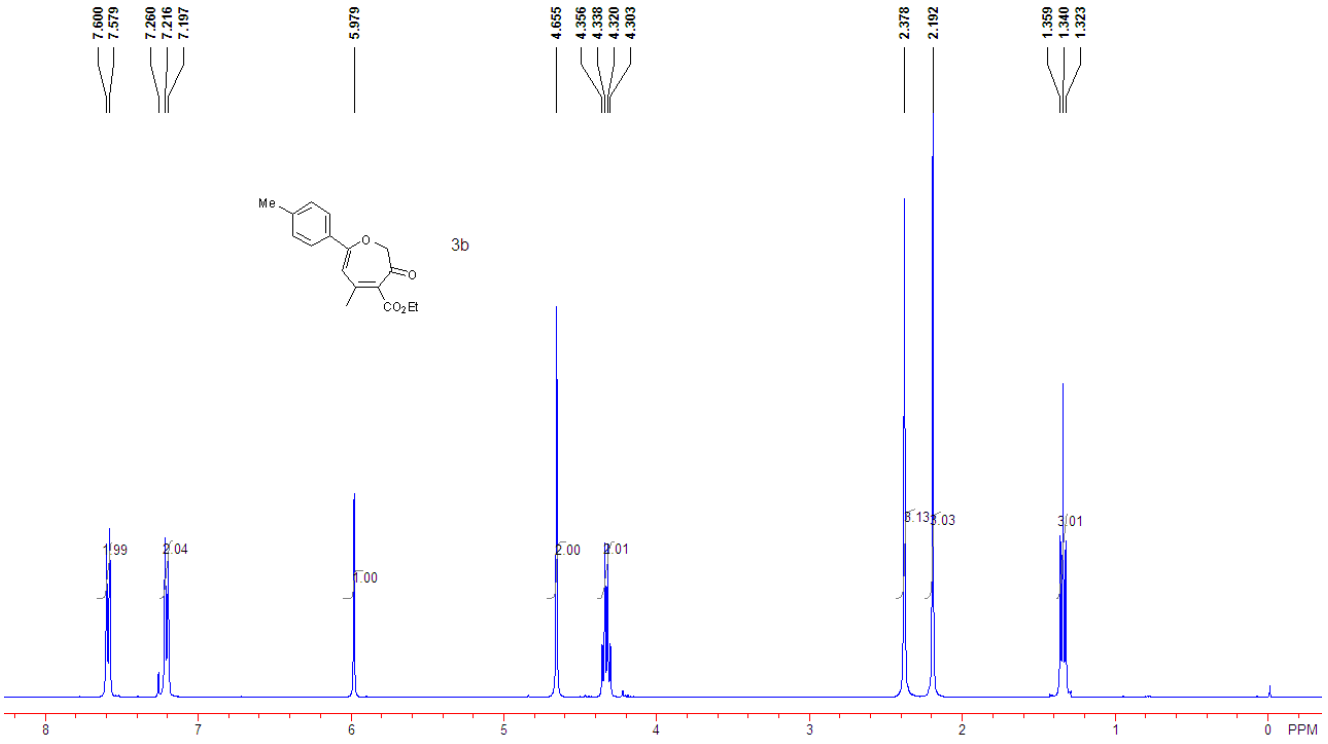


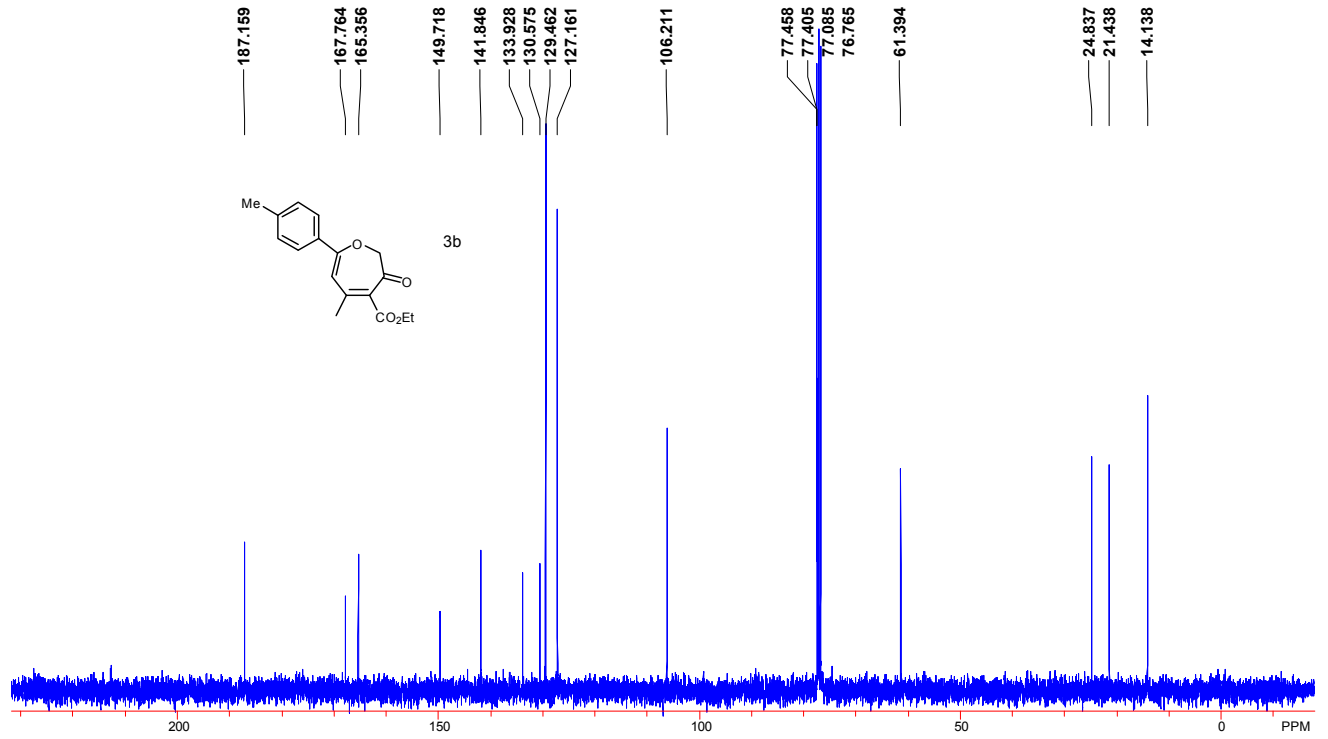
To a flask containing 1-phenylbuta-2,3-dien-1-one (**1a**, 0.5 mmol) and ethyl 2,3-dihydroxy-5-methyl biphenyl-4-carboxylate (**6a**, 0.5 mmol) in toluene (5 mL) were added anhydrous K_2CO_3 (0.75 mmol) and tetrabutyl ammonium bromide (TBAB) (0.03 mmol). The solution was stirred at room temperature for 30 min. The reaction then was quenched with aqueous NH_4Cl and extracted with ethyl acetate (5 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (v/v = 1/10) to give ethyl 2,5-dimethyl-2-(2-oxo-2-phenylethyl)-7-phenylbenzo[d][1,3]dioxole-4-carboxylate (**4a,** 86%).

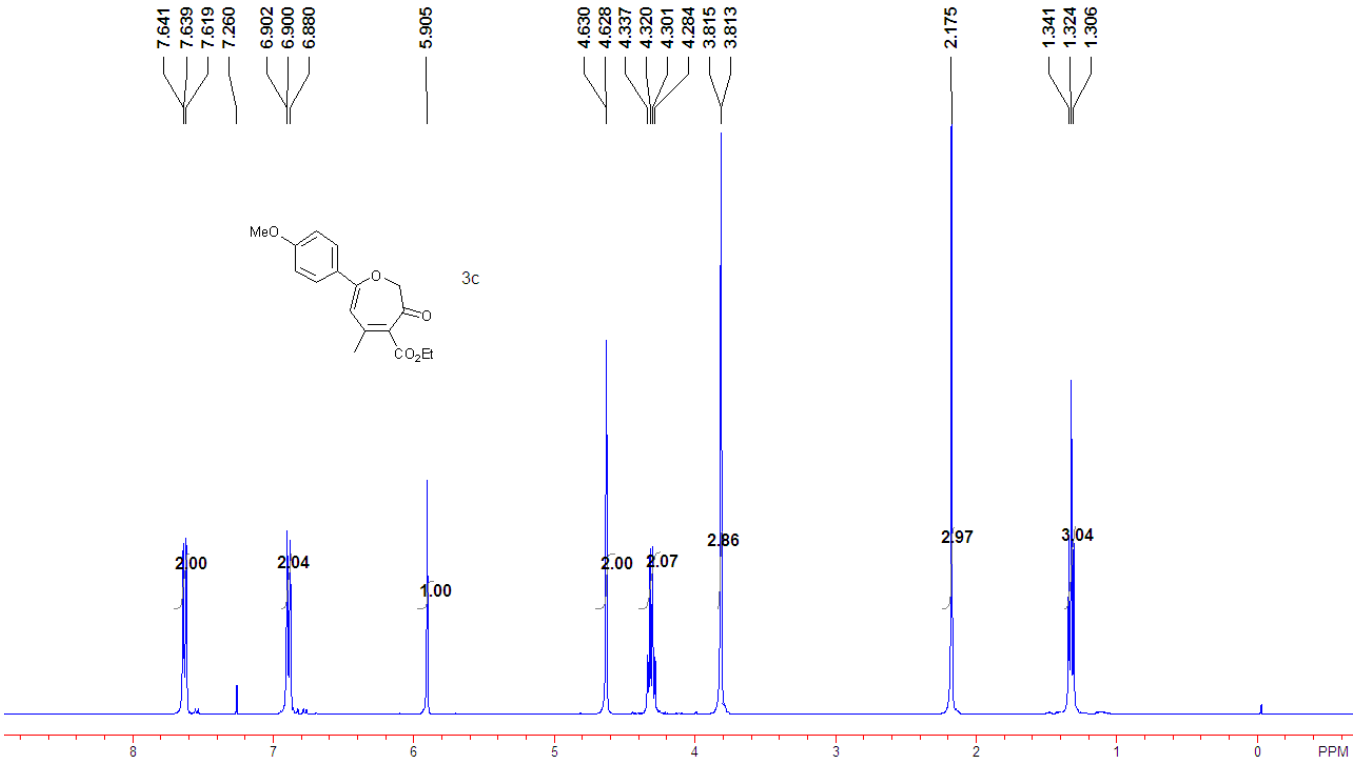
III. Copies of ^{1}H and ^{13}C NMR spectra of 3a-3s, 4a-4n, 5a-5d and 6a

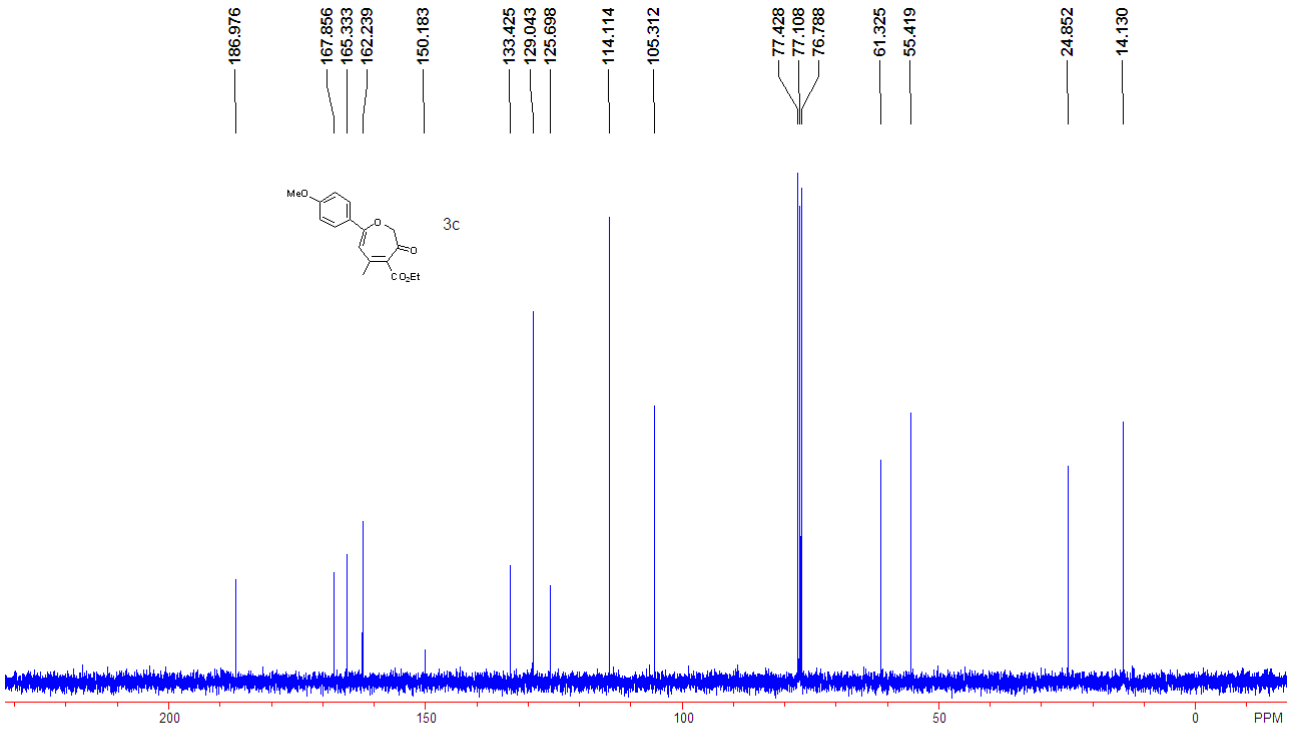


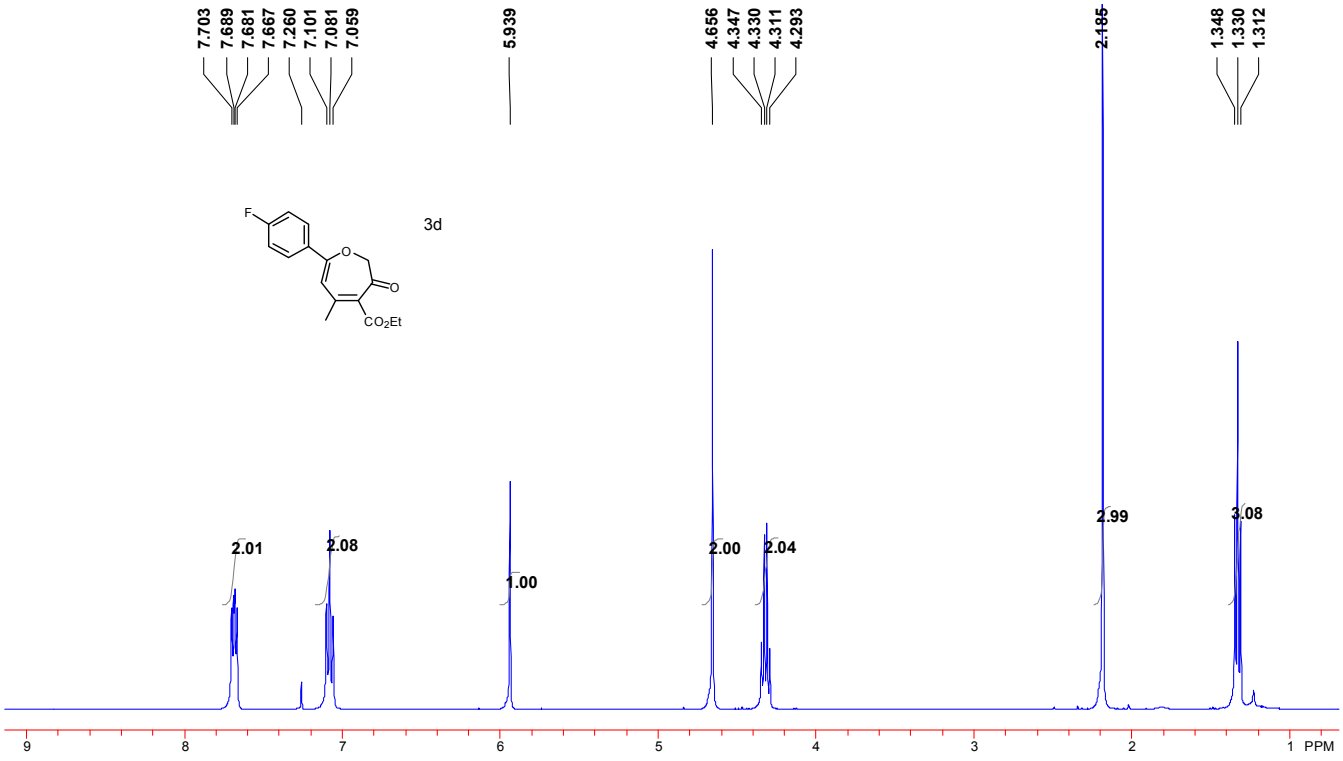


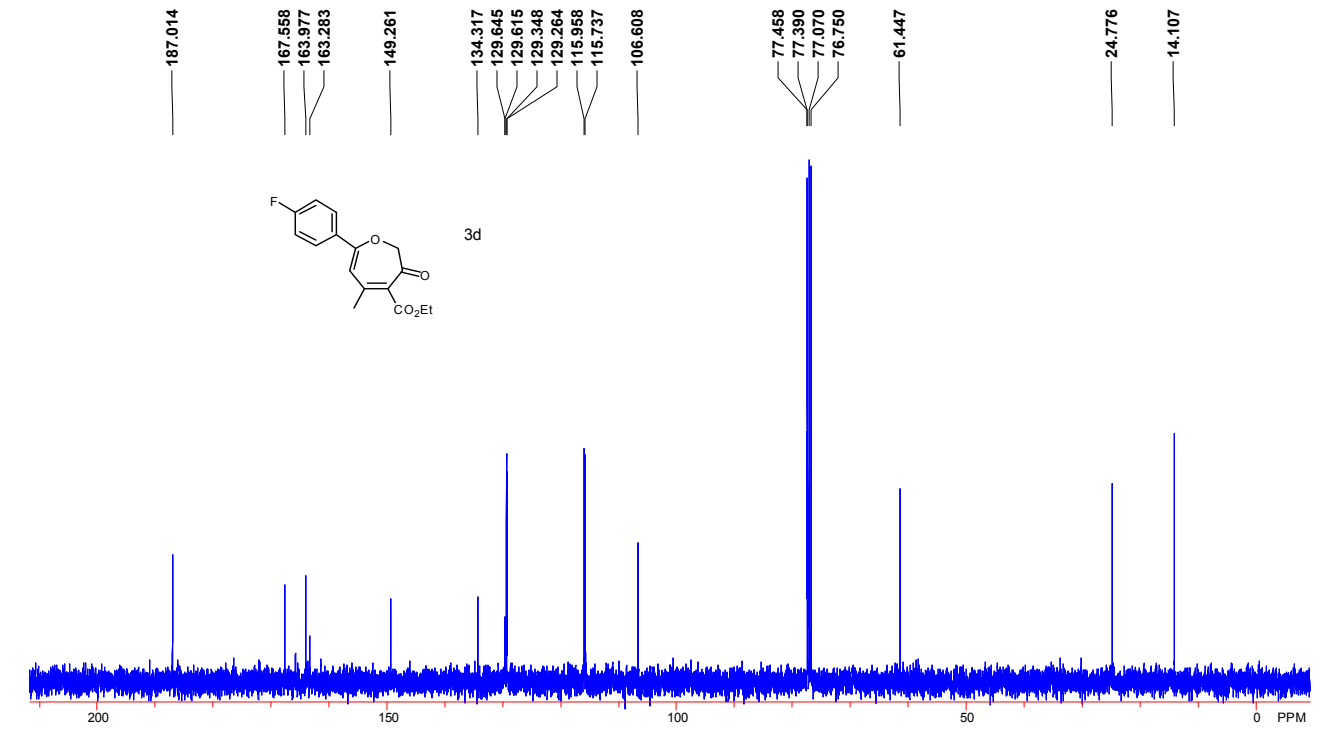

7.600
7.579
7.260
7.216
7.197
5.979
4.655
4.356
4.338
4.320
4.303
2.378
2.192
1.359
1.340
1.323
Me
O
O
CO2Et
3b
1.99
2.04
1.00
2.00
2.01
6.13
6.03
3.01
8
7
6
5
4
3
2
1
0
PPM

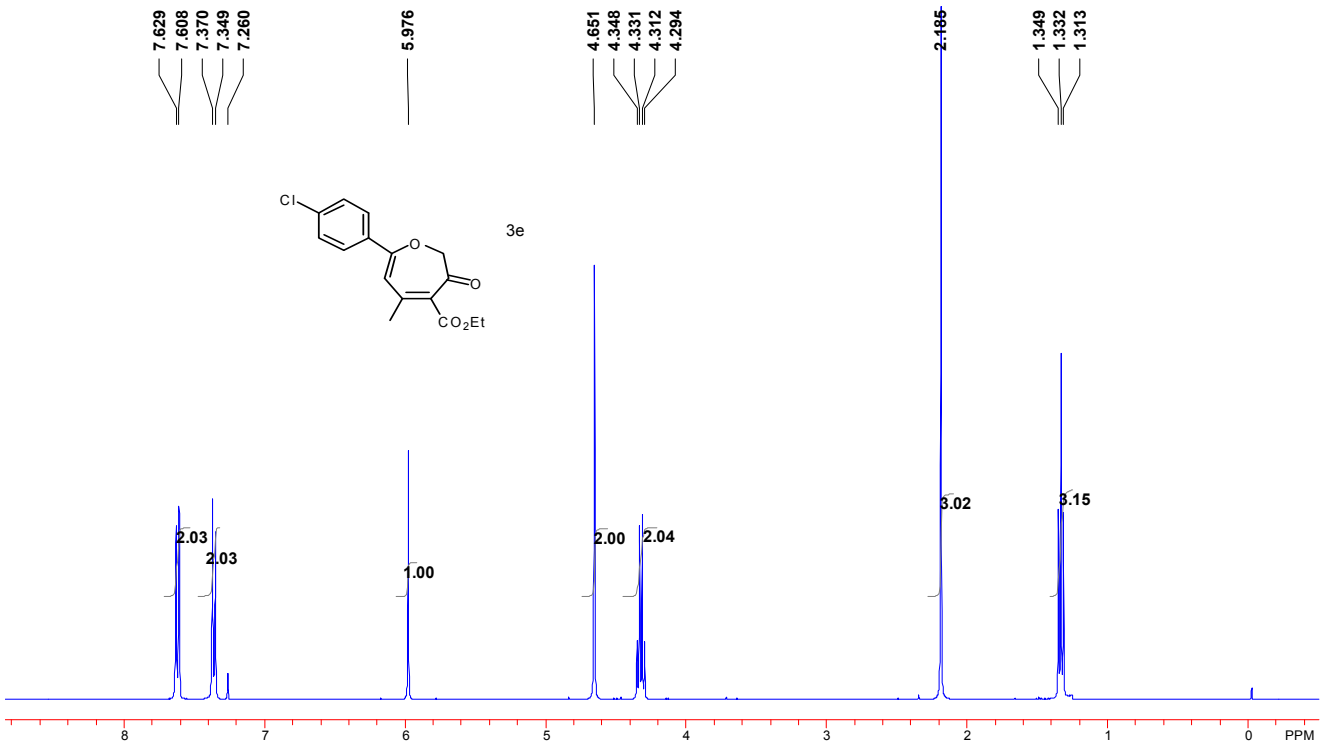

187.159
167.764
165.356
149.718
141.846
133.928
130.575
129.462
127.161
106.211
77.458
77.405
77.085
76.765
61.394
24.837
21.438
14.138
Me
O
O
CO2Et
3b
200
150
100
50
0
PPM

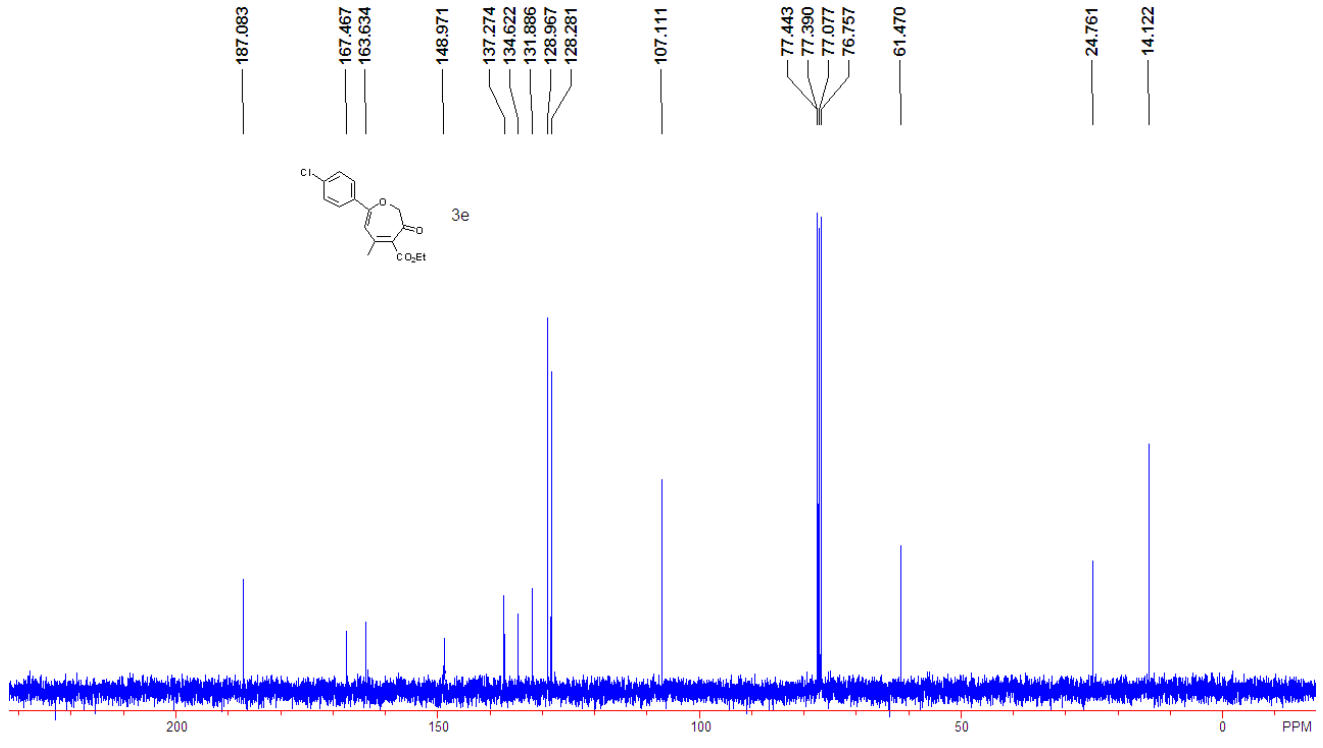

7.641
7.639
7.619
7.260
6.902
6.900
6.880
5.905
4.630
4.628
4.337
4.320
4.301
4.284
3.815
3.813
2.175
1.341
1.324
1.306
MeO
O
O
CO2Et
3c
2.00
2.04
1.00
2.00
2.07
2.86
2.97
3.04
8
7
6
5
4
3
2
1
0
PPM

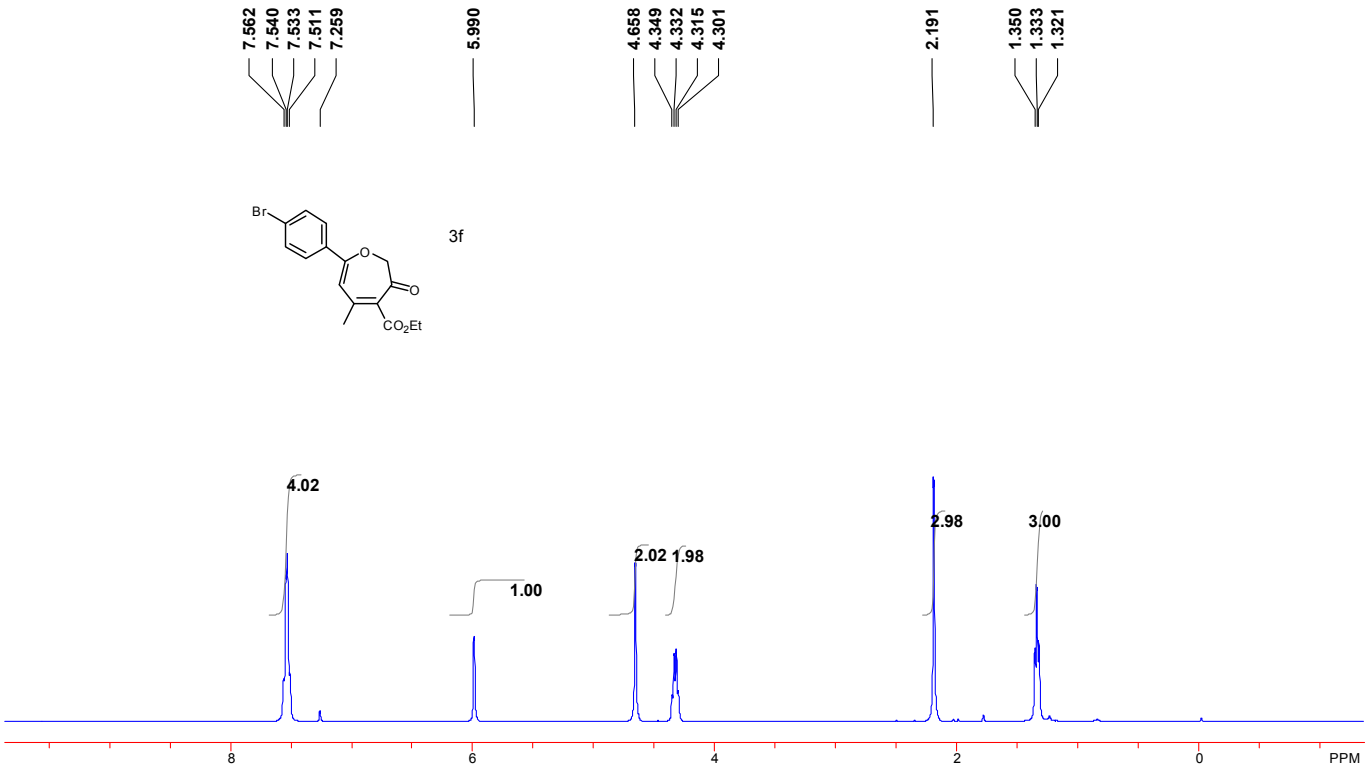

186.976
167.856
165.333
162.239
150.183
133.425
129.043
125.698
114.114
105.312
77.428
77.108
76.788
61.325
55.419
24.852
14.130
MeO
O
O
CO2Et
3c
200
150
100
50
0
PPM

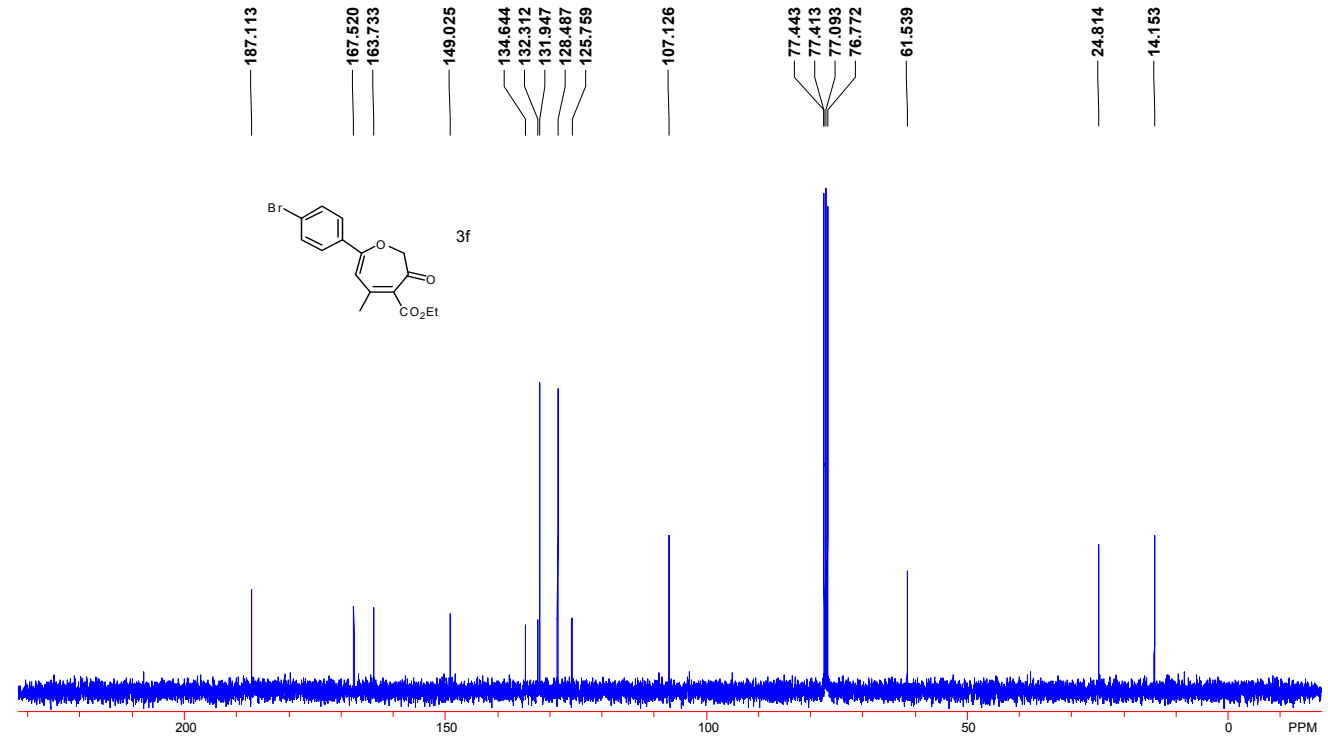


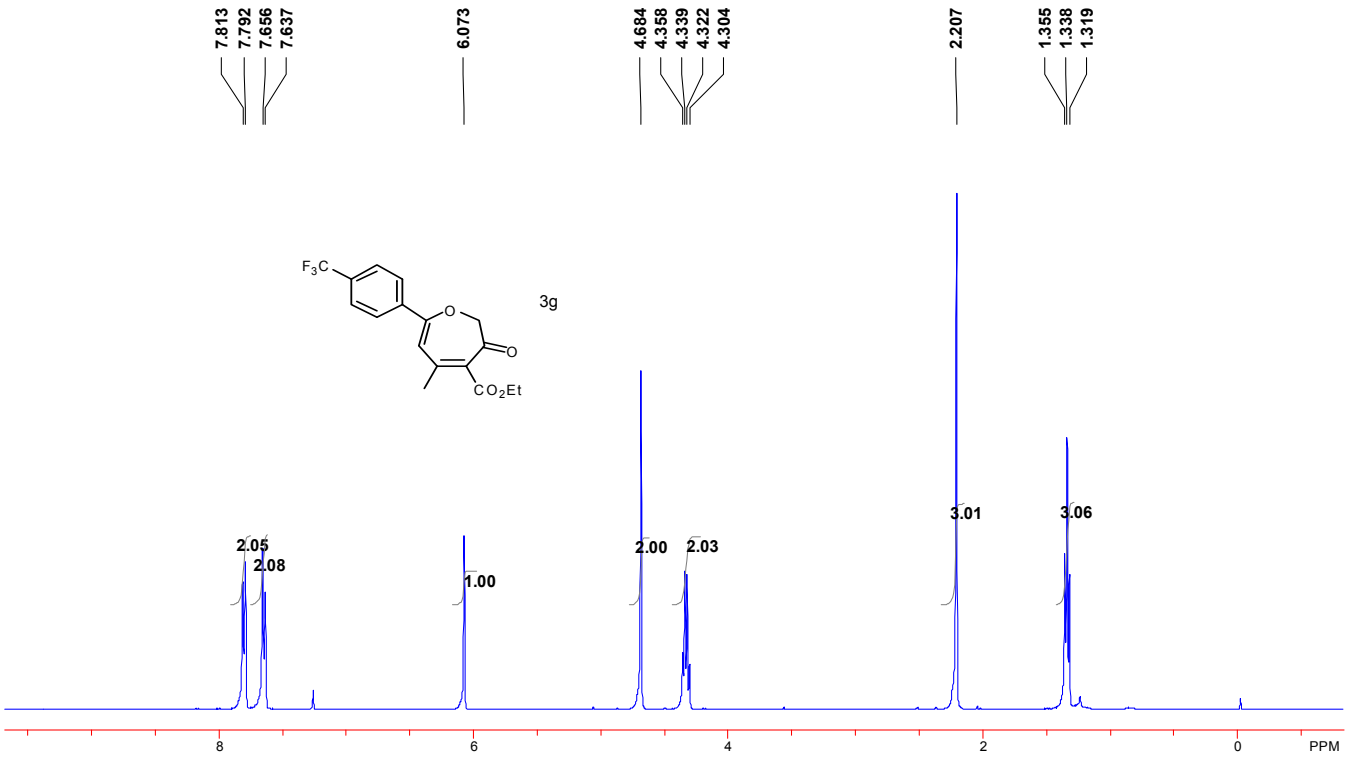


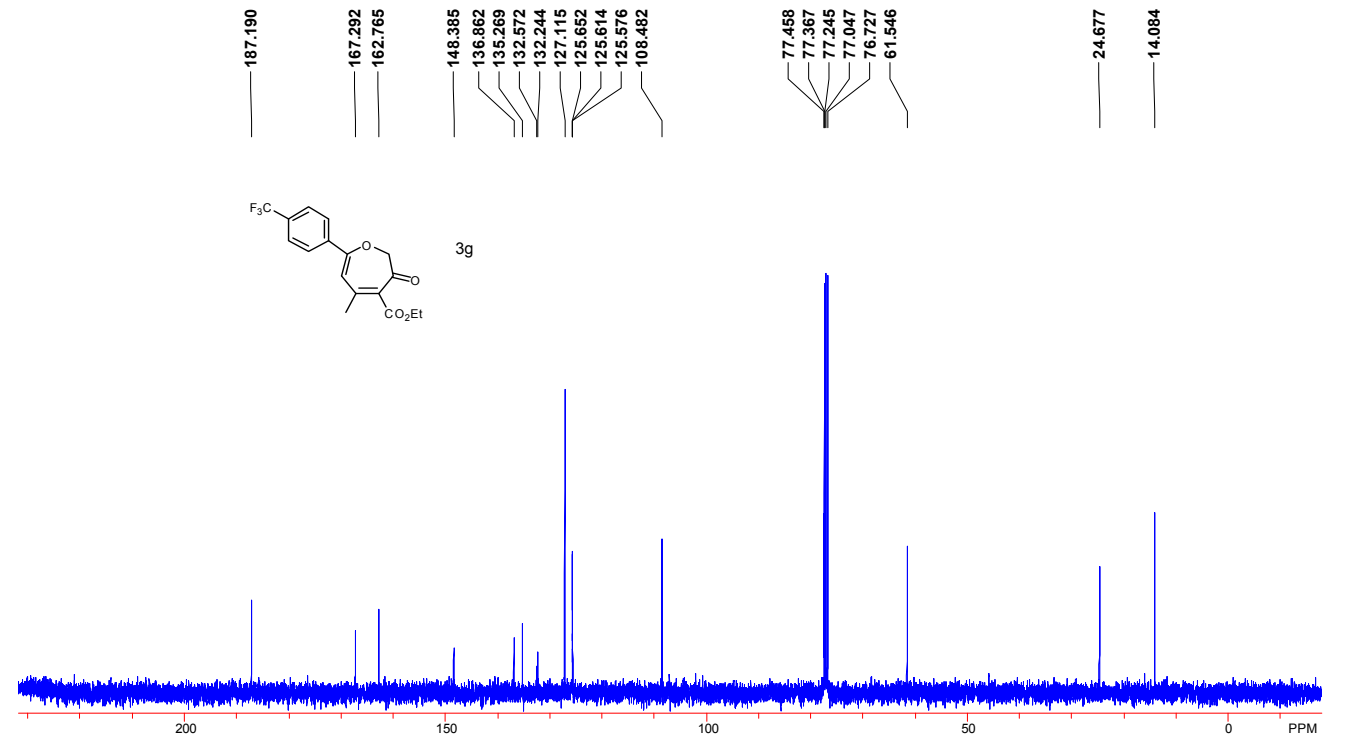

7.629
7.608
7.370
7.349
7.260
5.976
4.651
4.348
4.331
4.312
4.294
2.185
1.349
1.332
1.313
Cl
O
O
CO2Et
3e
2.03
2.03
1.00
2.00
2.04
3.02
3.15
8
7
6
5
4
3
2
1
0
PPM

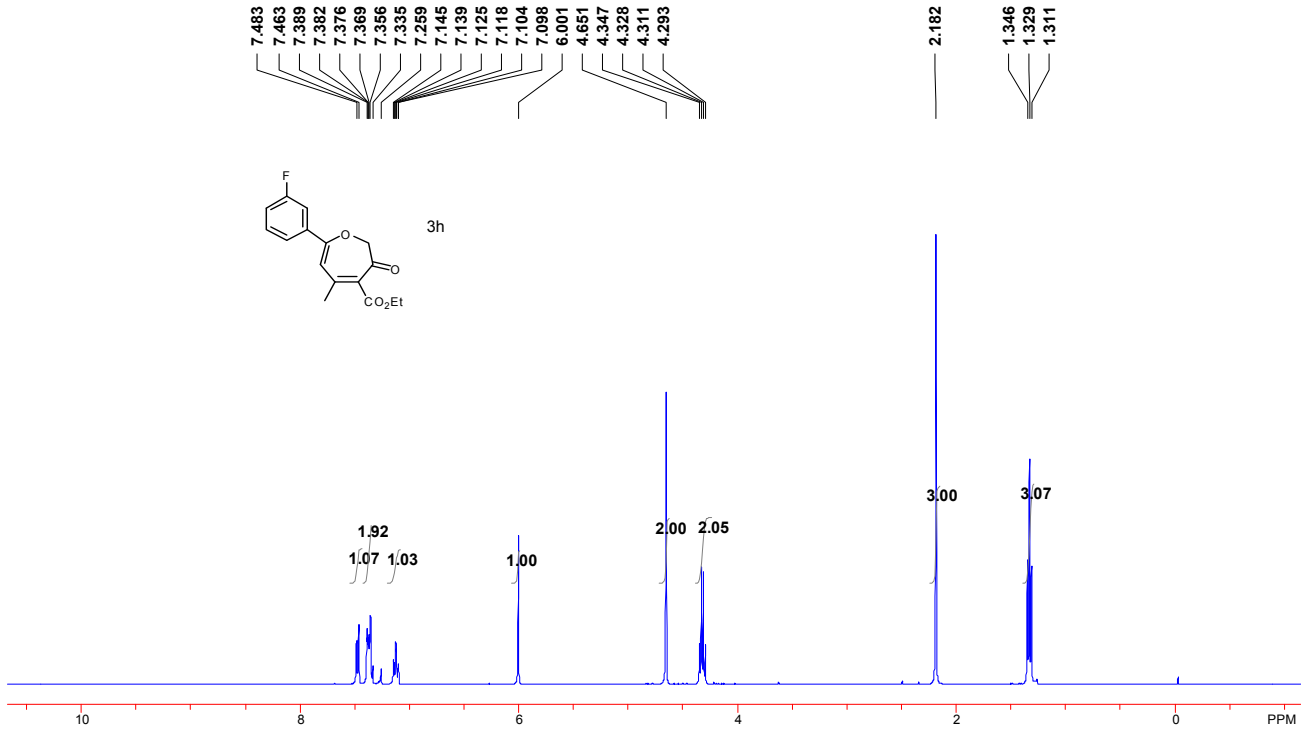

187.083
167.467
163.634
148.971
137.274
134.622
131.886
128.967
128.281
107.111
77.443
77.390
77.077
76.757
61.470
24.761
14.122
Cl
O
O
CO2Et
3e
200
150
100
50
0
PPM

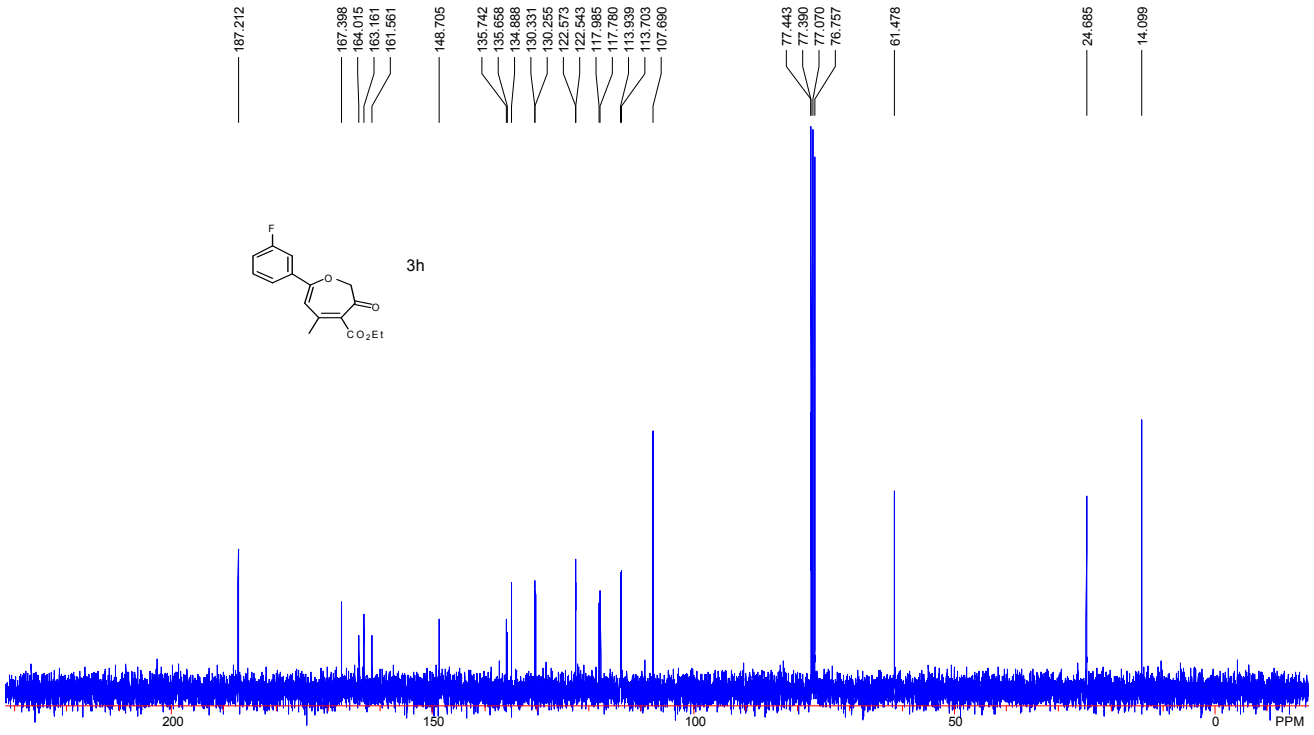


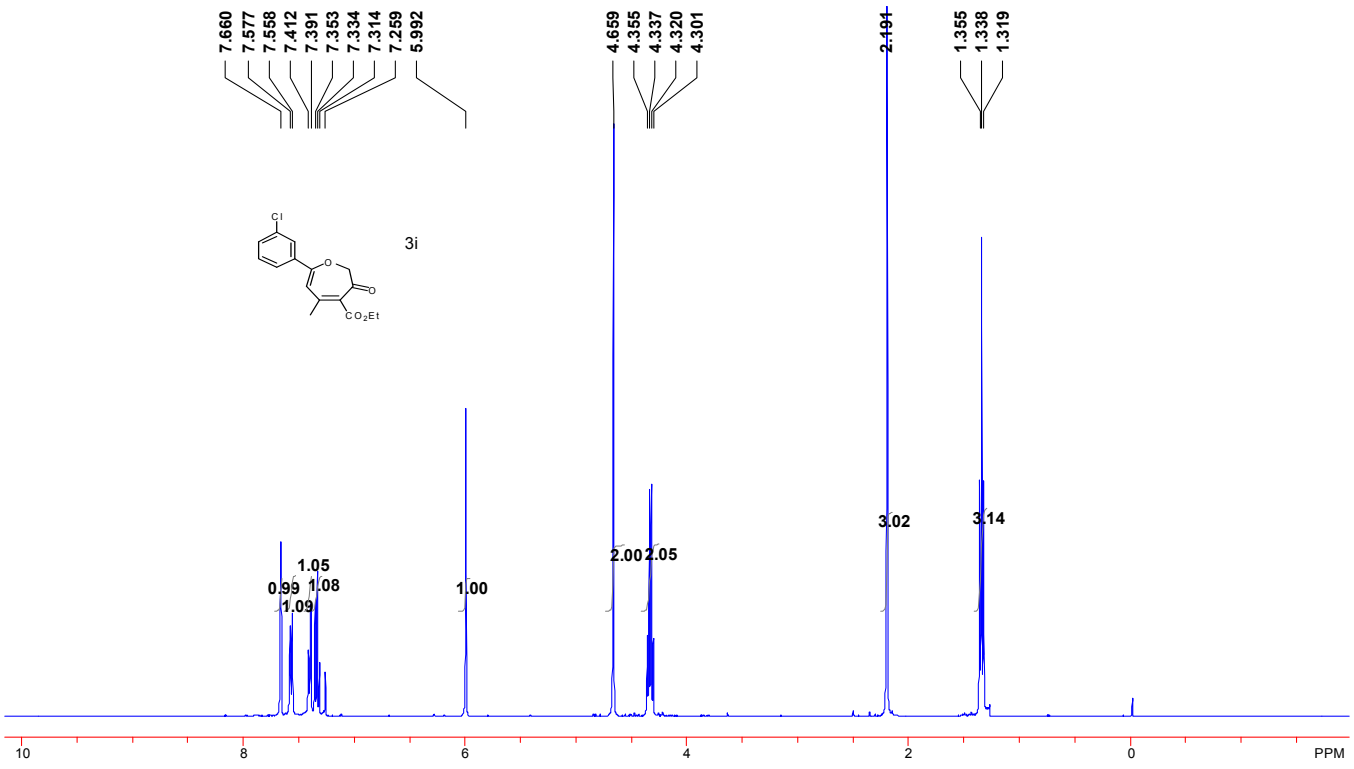


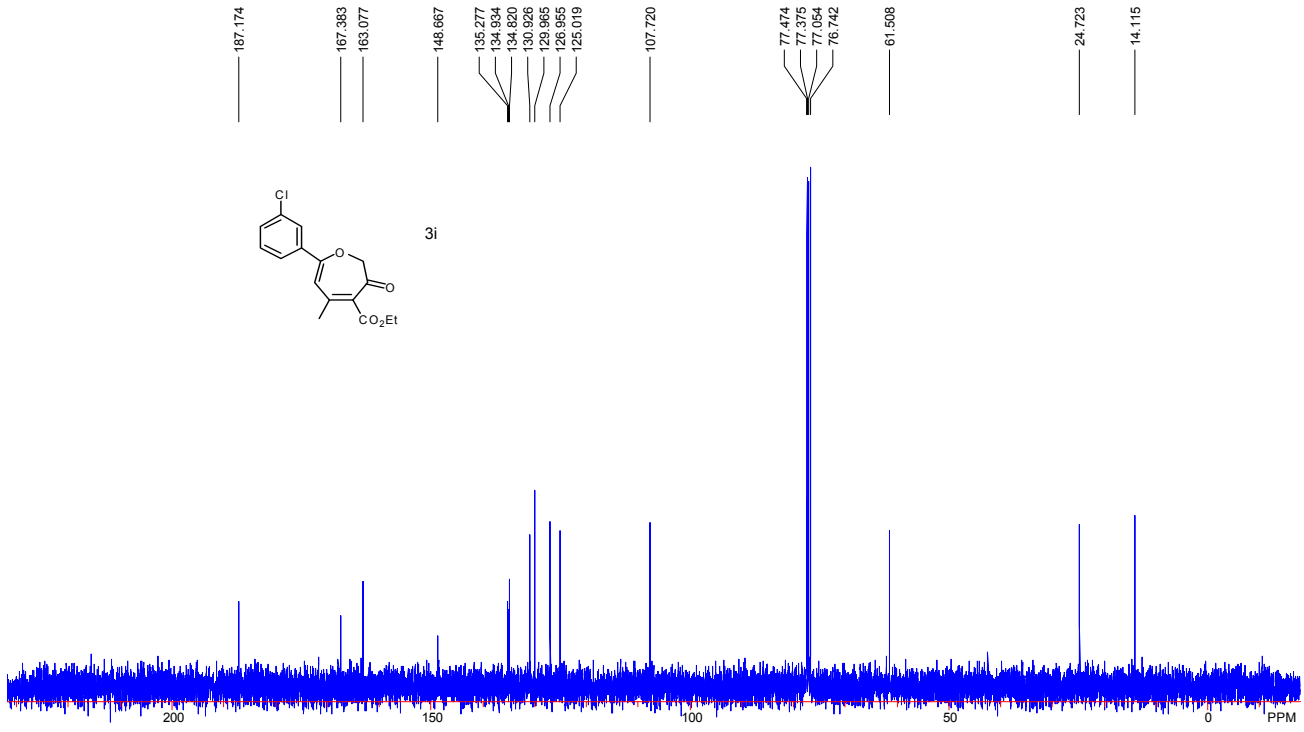

7.813
7.792
7.656
7.637
6.073
4.684
4.358
4.339
4.322
4.304
2.207
1.355
1.338
1.319
F3C
O
O
CO2Et
3g
2.05
2.08
1.00
2.00
2.03
3.01
3.06
8
6
4
2
0
PPM

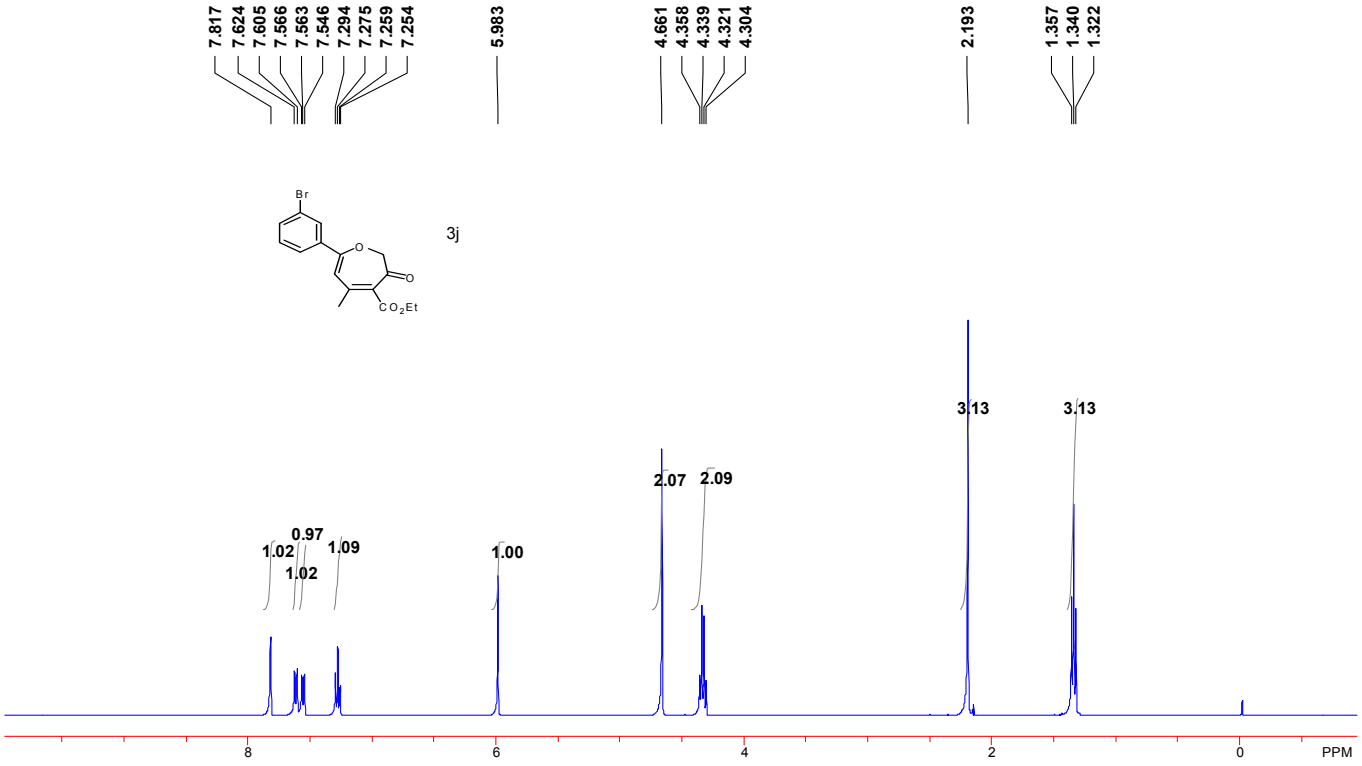

187.190
167.292
162.765
148.385
136.862
135.269
132.572
132.244
127.115
125.652
125.614
125.576
108.482
77.458
77.367
77.245
77.047
76.727
61.546
24.677
14.084
F3C
O
O
CO2Et
3g
200
150
100
50
0
PPM

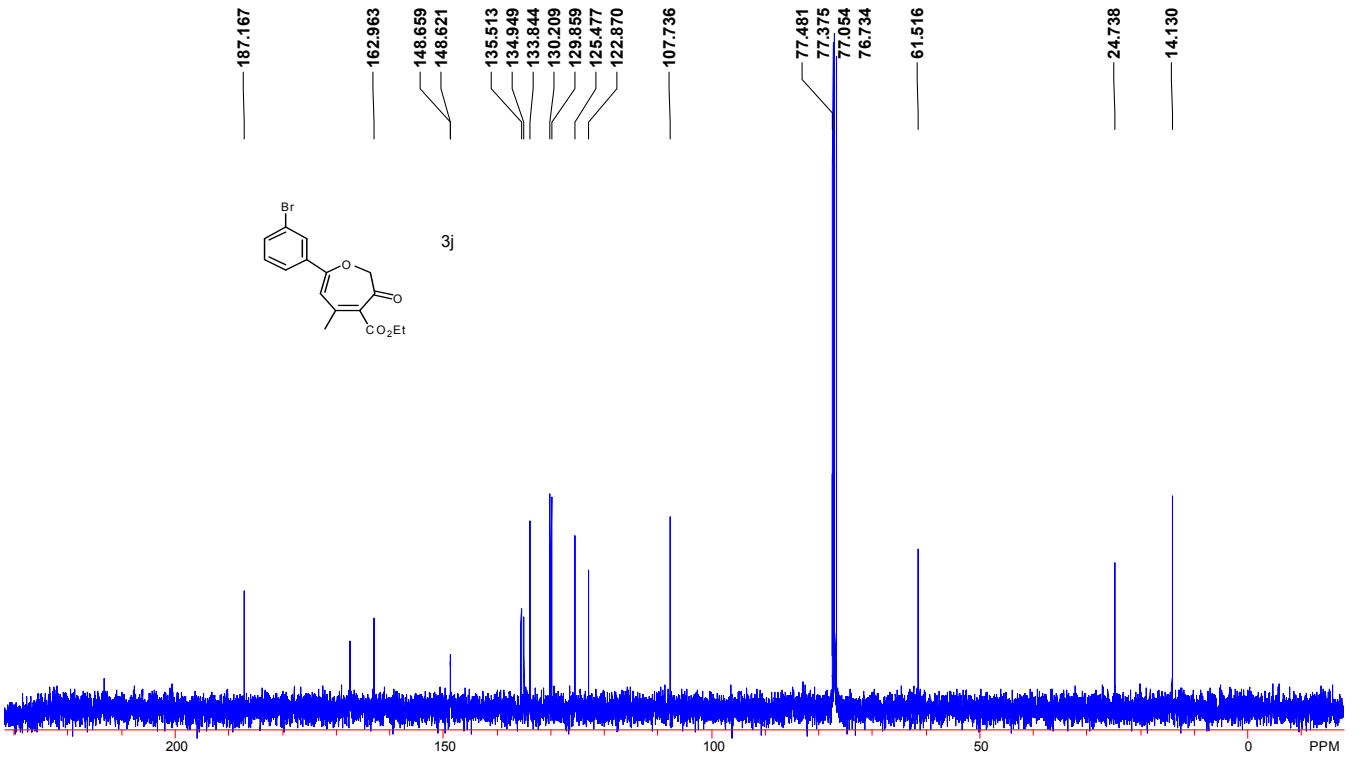


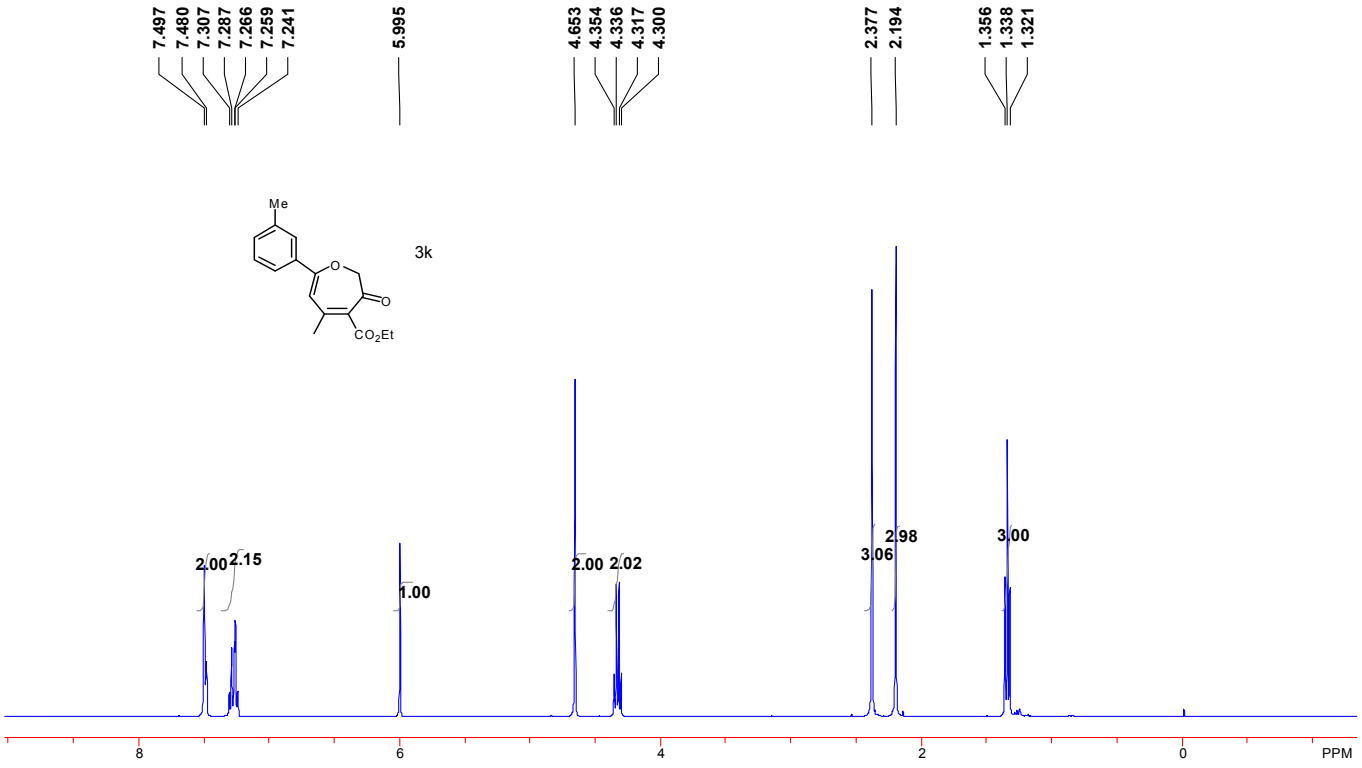


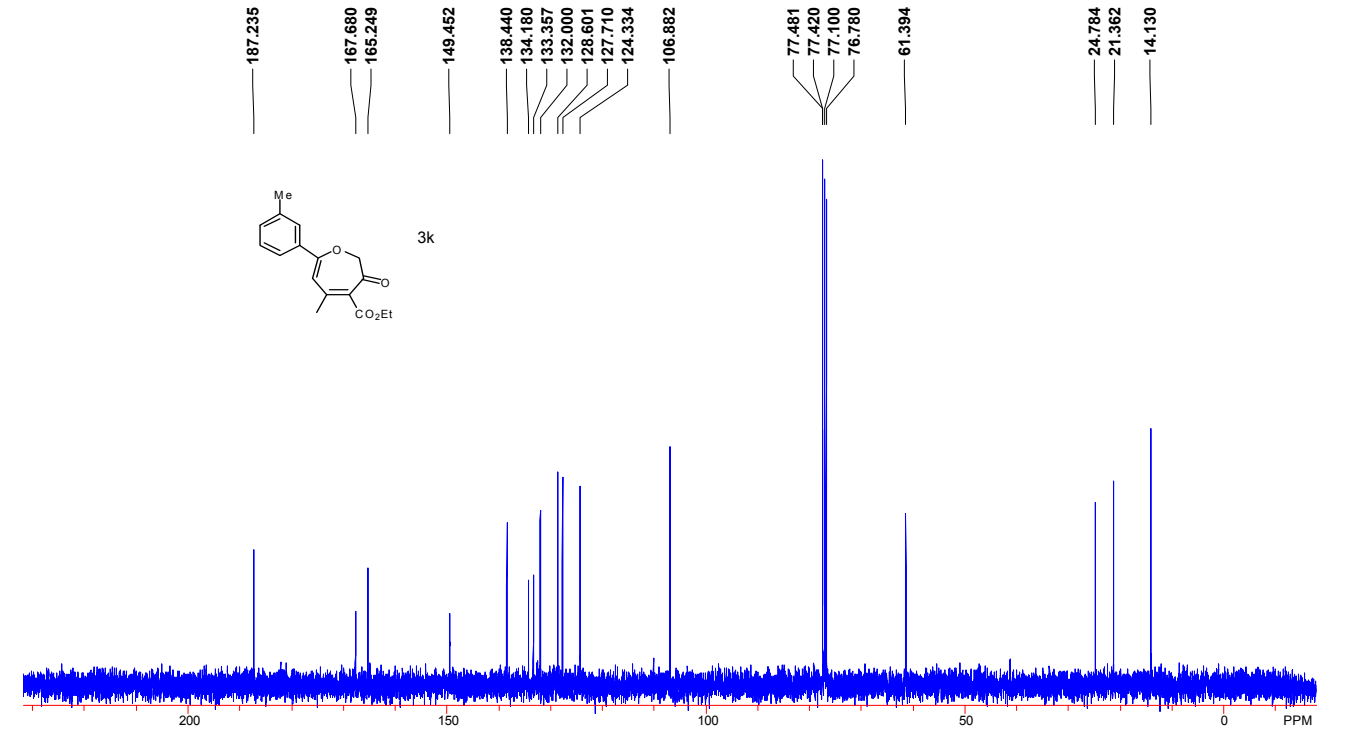

7.660
7.577
7.558
7.412
7.391
7.353
7.334
7.314
7.259
5.992
4.659
4.355
4.337
4.320
4.301
2.491
1.355
1.338
1.319
Cl
O
O
CO2Et
3i
0.99
1.05
1.09
1.08
1.00
2.00
2.05
3.02
3.14
10
8
6
4
2
0
PPM

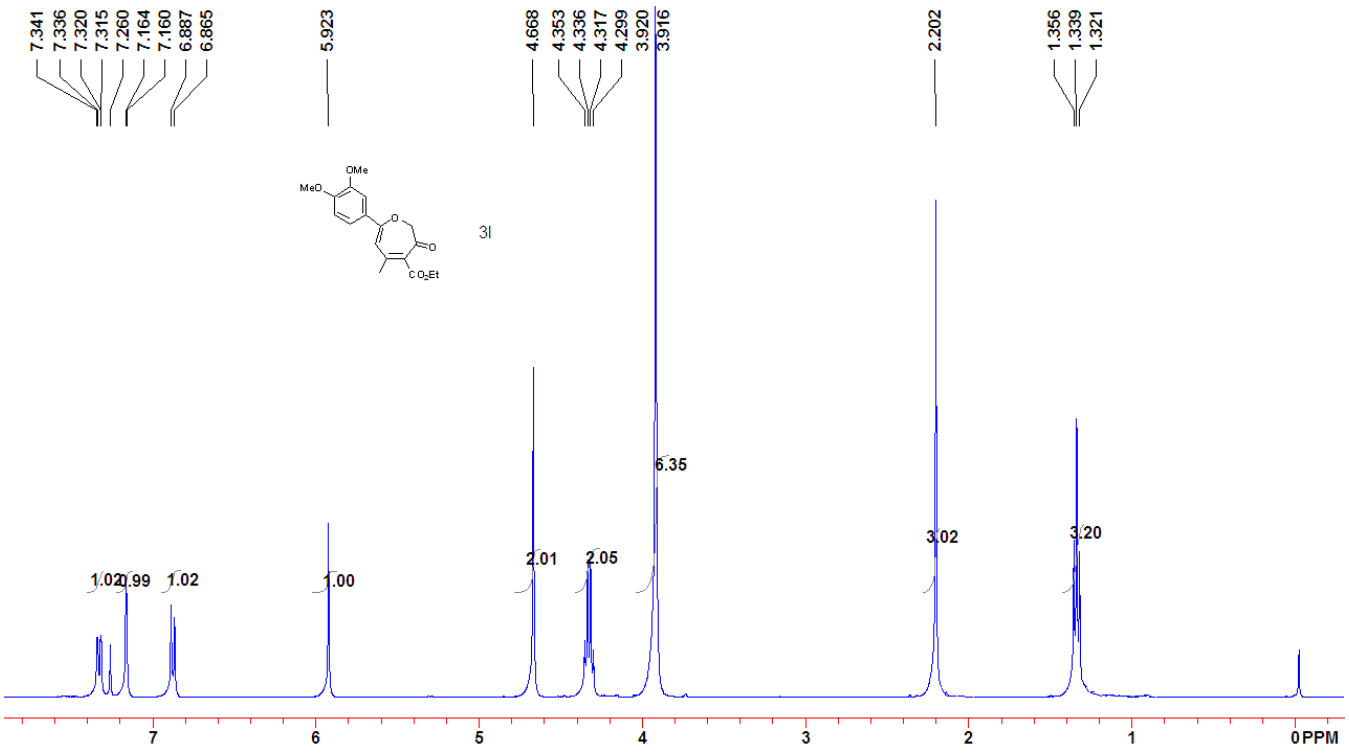

187.174
167.383
163.077
148.667
135.277
134.934
134.820
130.926
129.965
126.955
125.019
107.720
77.474
77.375
77.054
76.742
61.508
24.723
14.115
Cl
O
O
CO2Et
3i
200
150
100
50
0
PPM

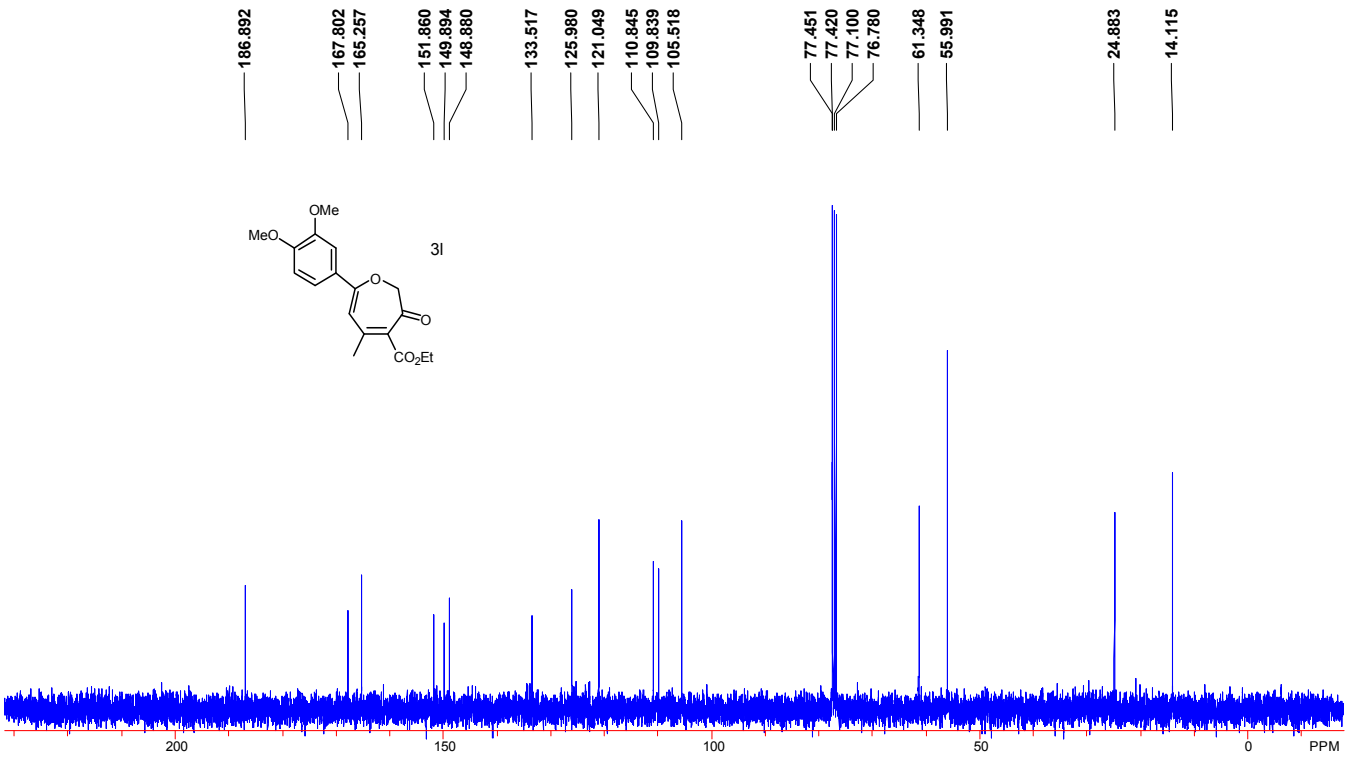

7.817
7.624
7.605
7.566
7.563
7.546
7.294
7.275
7.259
7.254
5.983
4.661
4.358
4.339
4.321
4.304
2.193
1.357
1.340
1.322
Br
O
O
CO2Et
3j
3.13
3.13
2.07
2.09
0.97
1.02
1.09
1.00
1.02
8
6
4
2
0
PPM

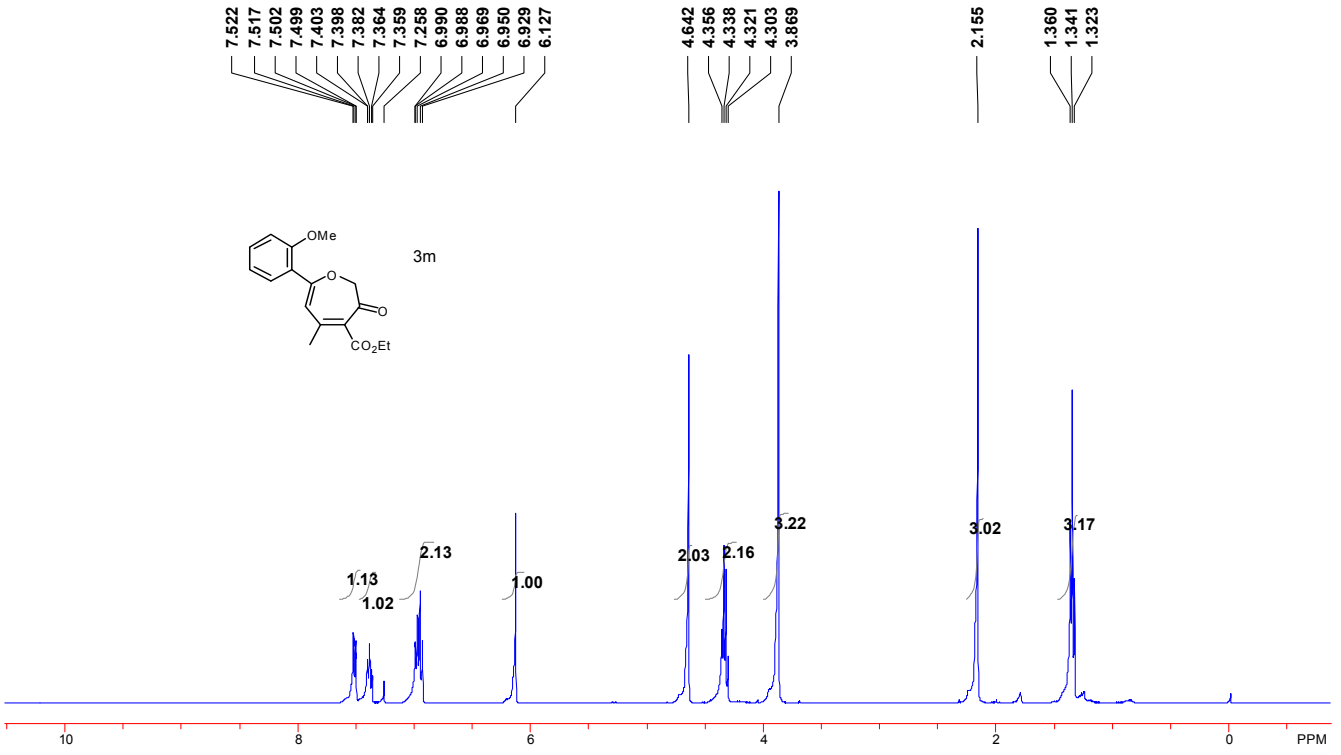

187.167
162.963
148.659
148.621
135.513
134.949
133.844
130.209
129.859
125.477
122.870
107.736
77.481
77.375
77.054
76.734
61.516
24.738
14.130
Br
O
O
CO2Et
3j
200
150
100
50
0
PPM

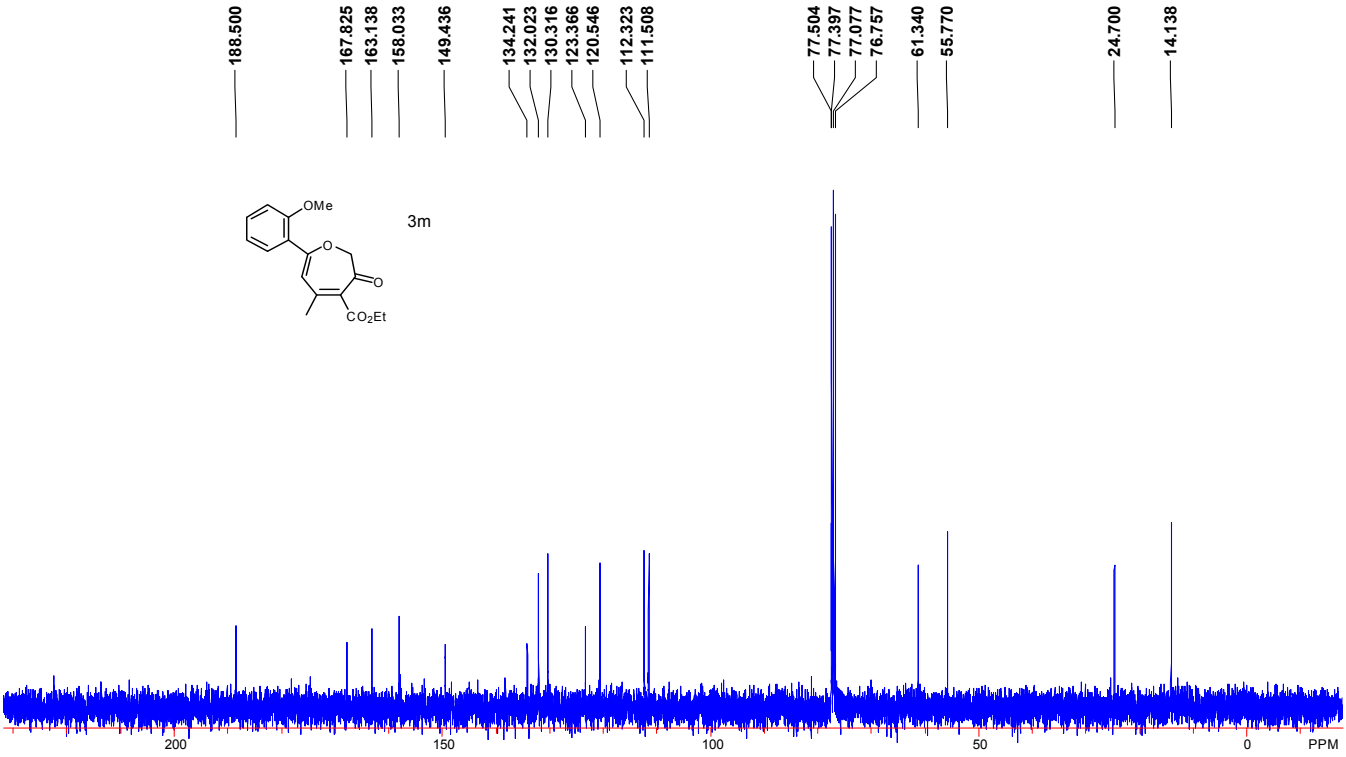


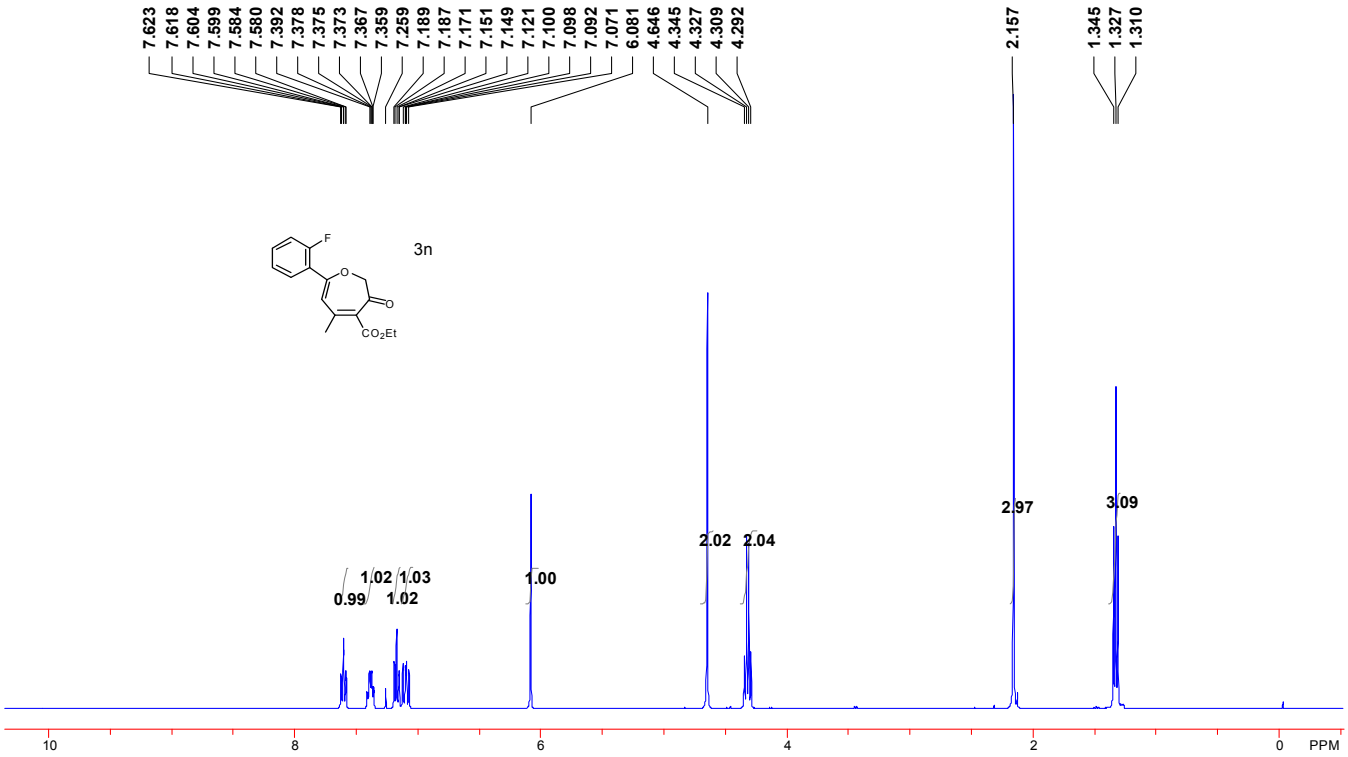


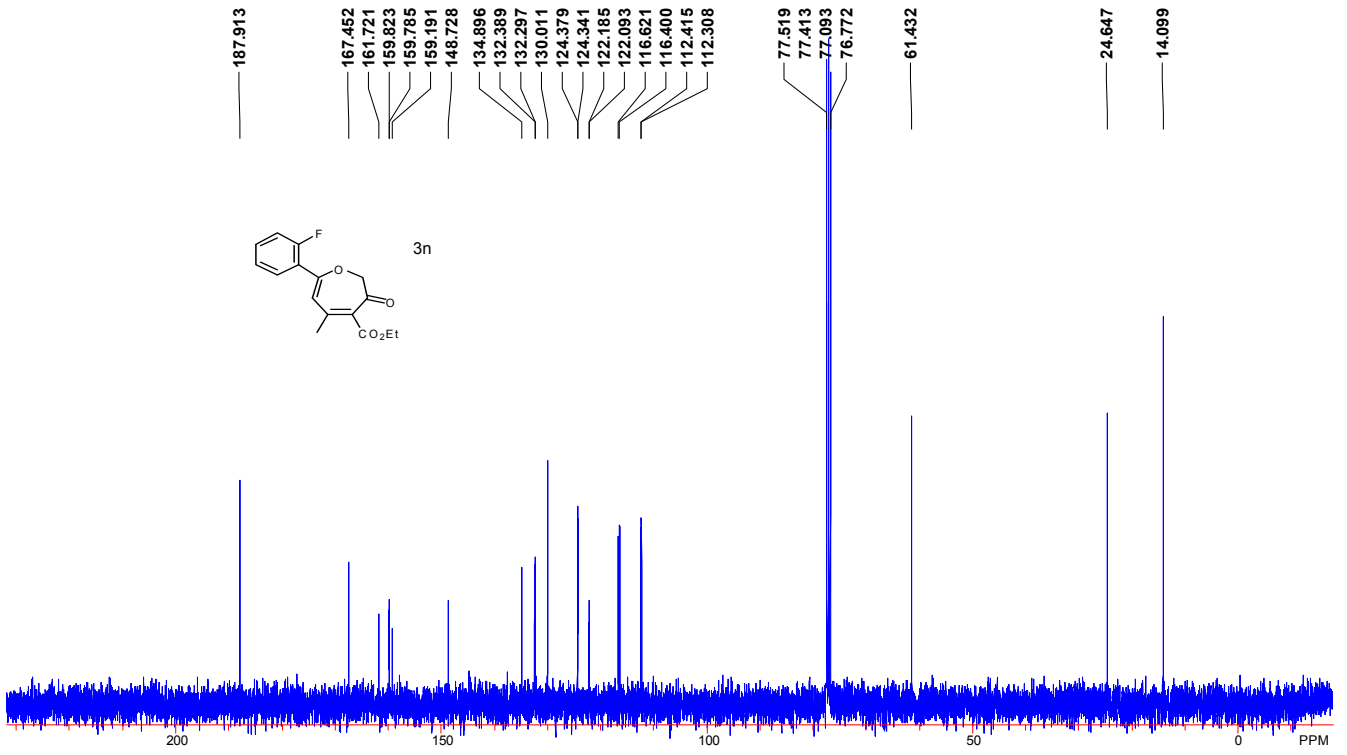

7.341
7.336
7.320
7.315
7.260
7.164
7.160
6.887
6.865
5.923
4.668
4.353
4.336
4.317
4.299
3.920
3.916
2.202
1.356
1.339
1.321
OMe
MeO
O
O
CO2Et
3l
6.35
3.02
3.20
2.01
2.05
1.02
0.99
1.02
1.00
7
6
5
4
3
2
1
0 PPM

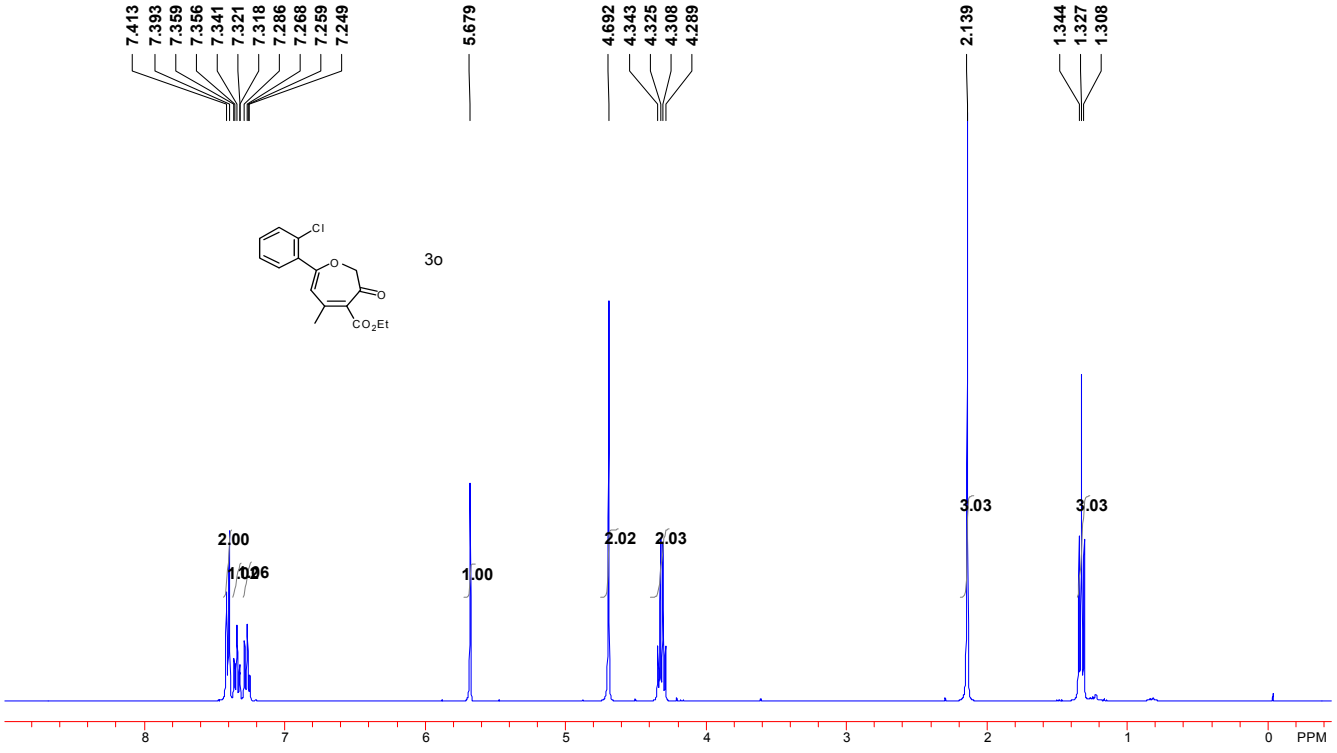

186.892
167.802
165.257
151.860
149.894
148.880
133.517
125.980
121.049
110.845
109.839
105.518
77.451
77.420
77.100
76.780
61.348
55.991
24.883
14.115
OMe
MeO
O
O
CO2Et
3l
200
150
100
50
0
PPM

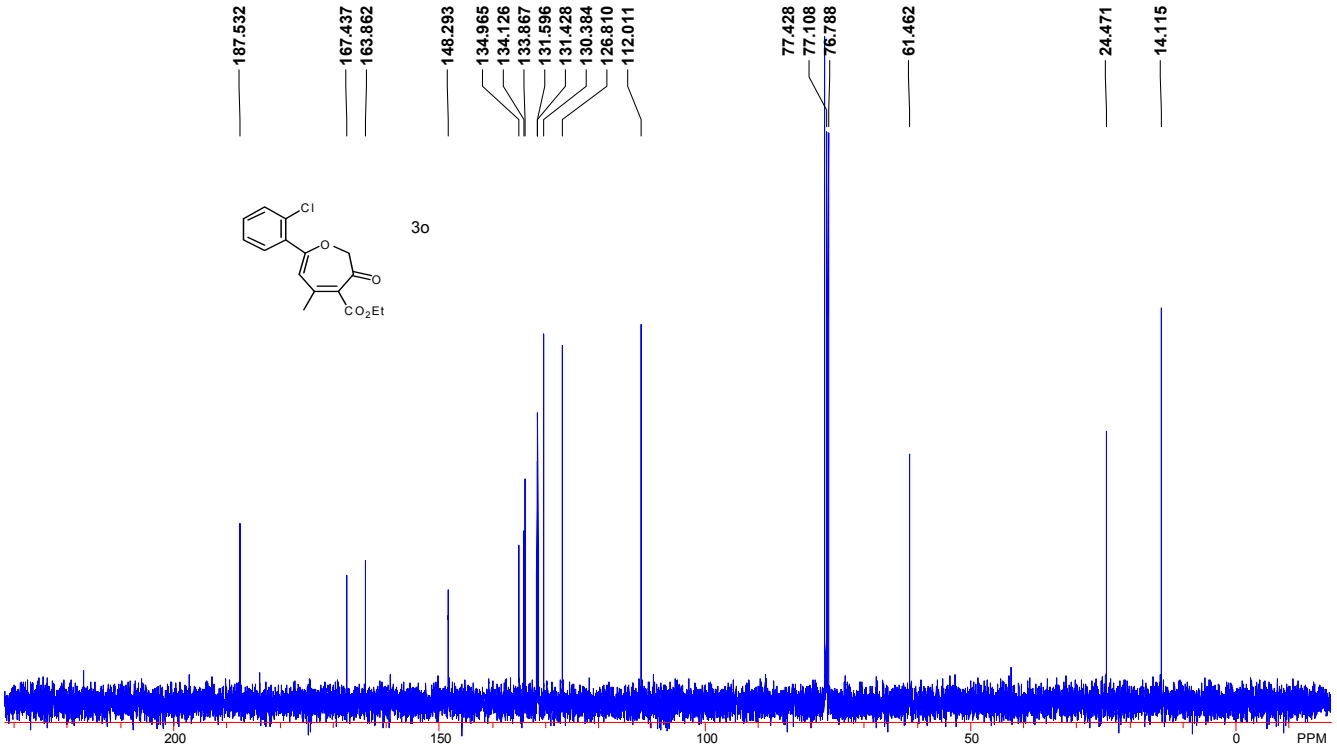


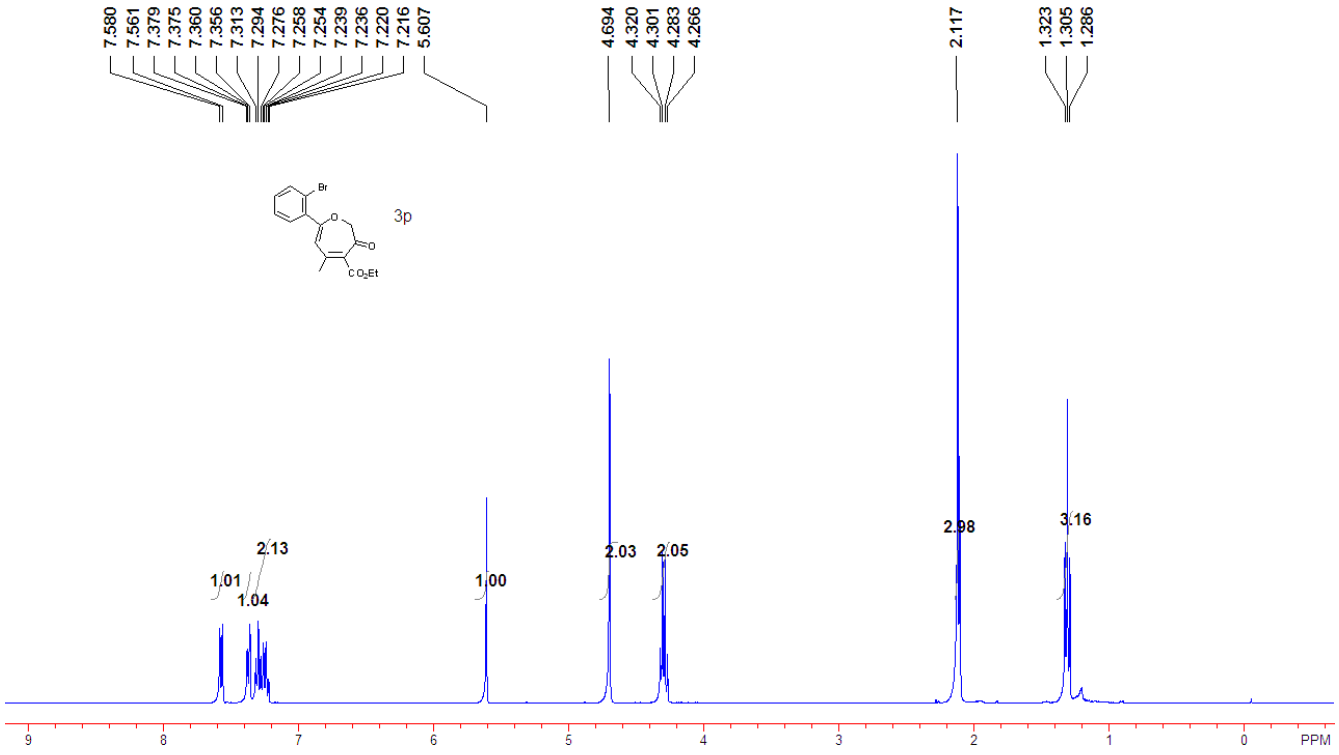


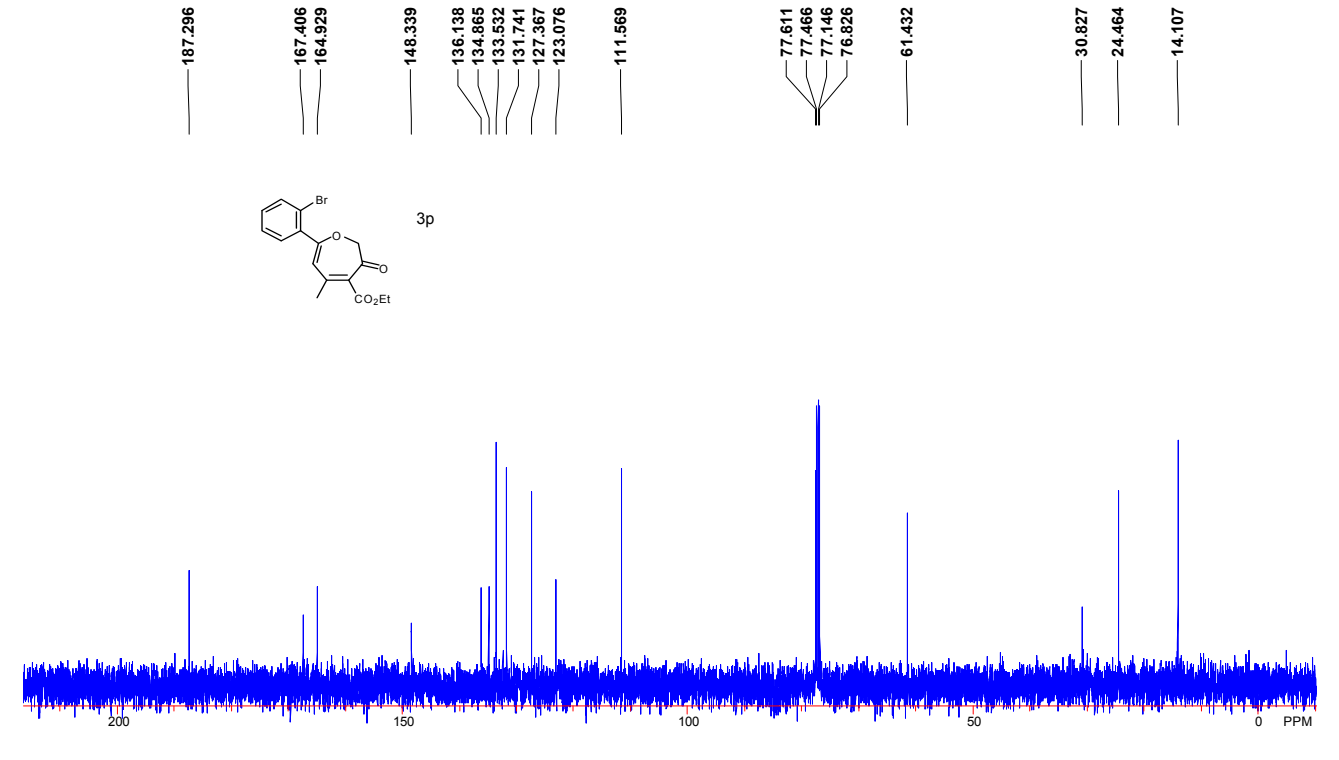


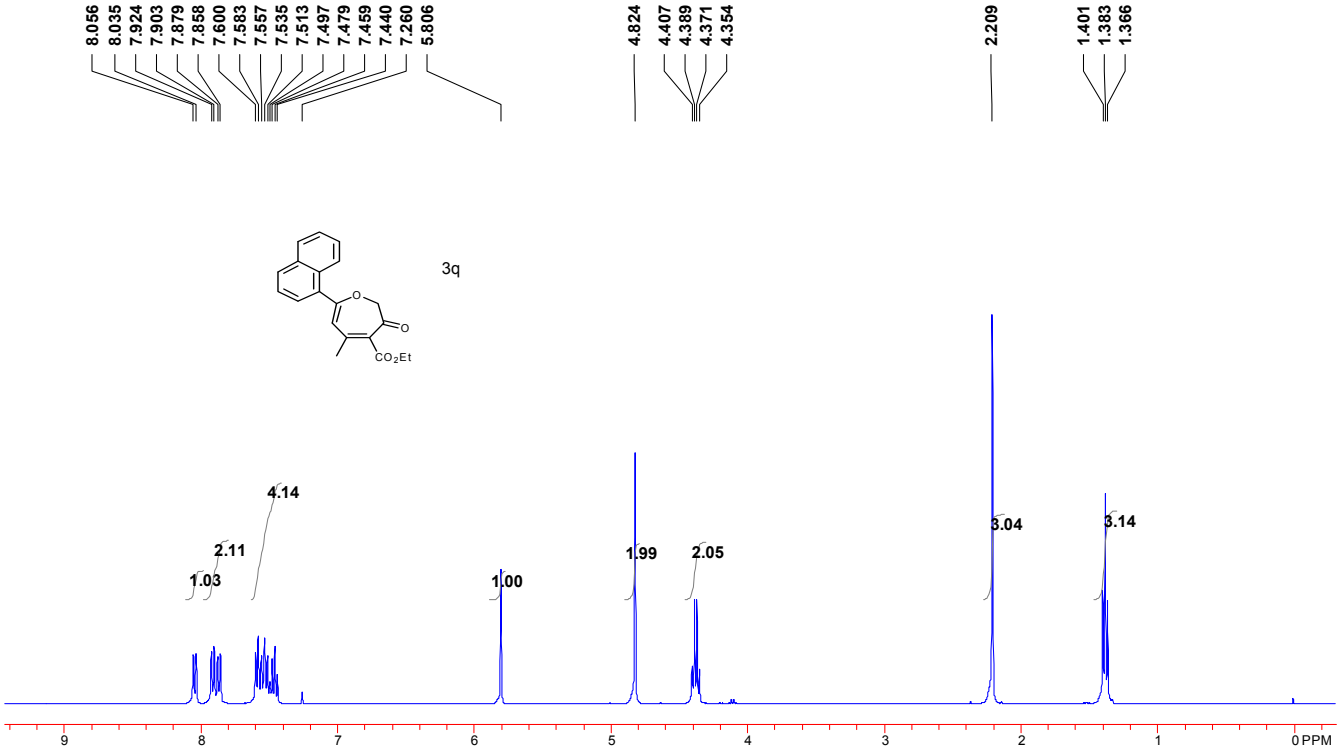


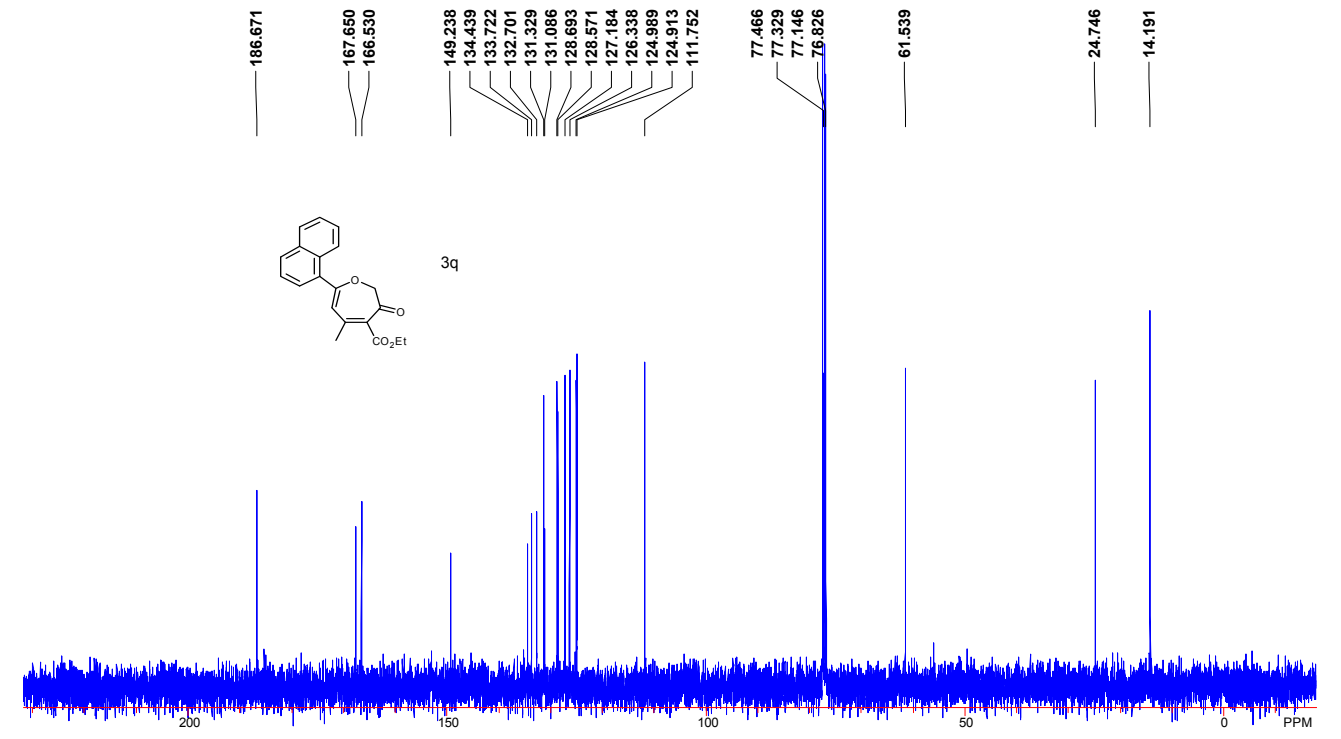


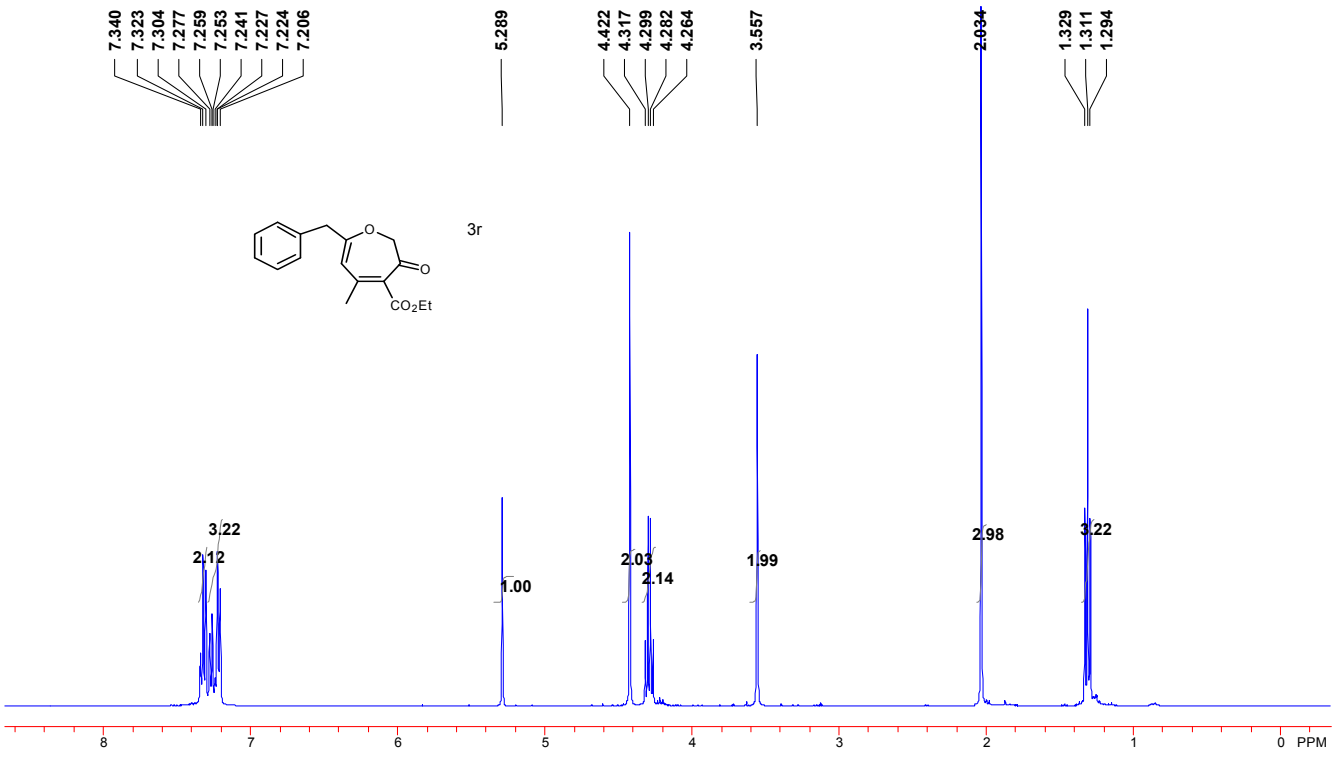


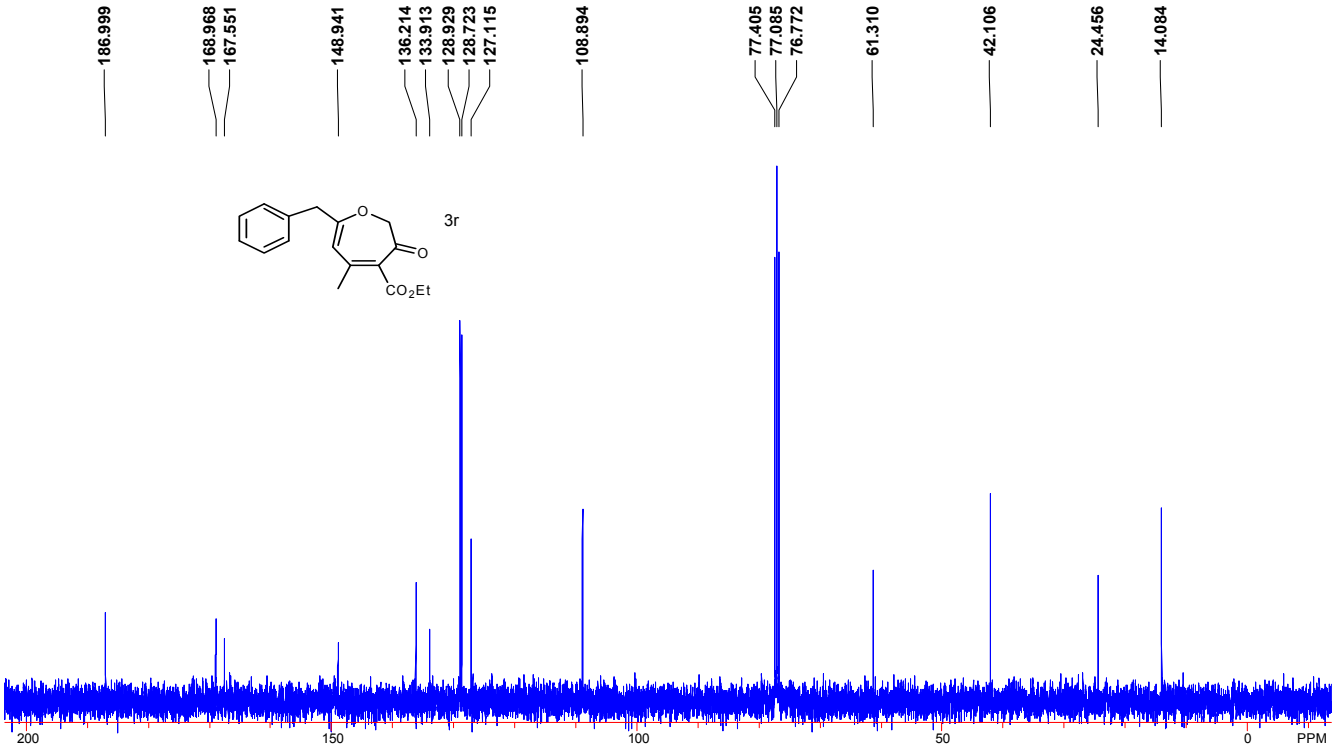


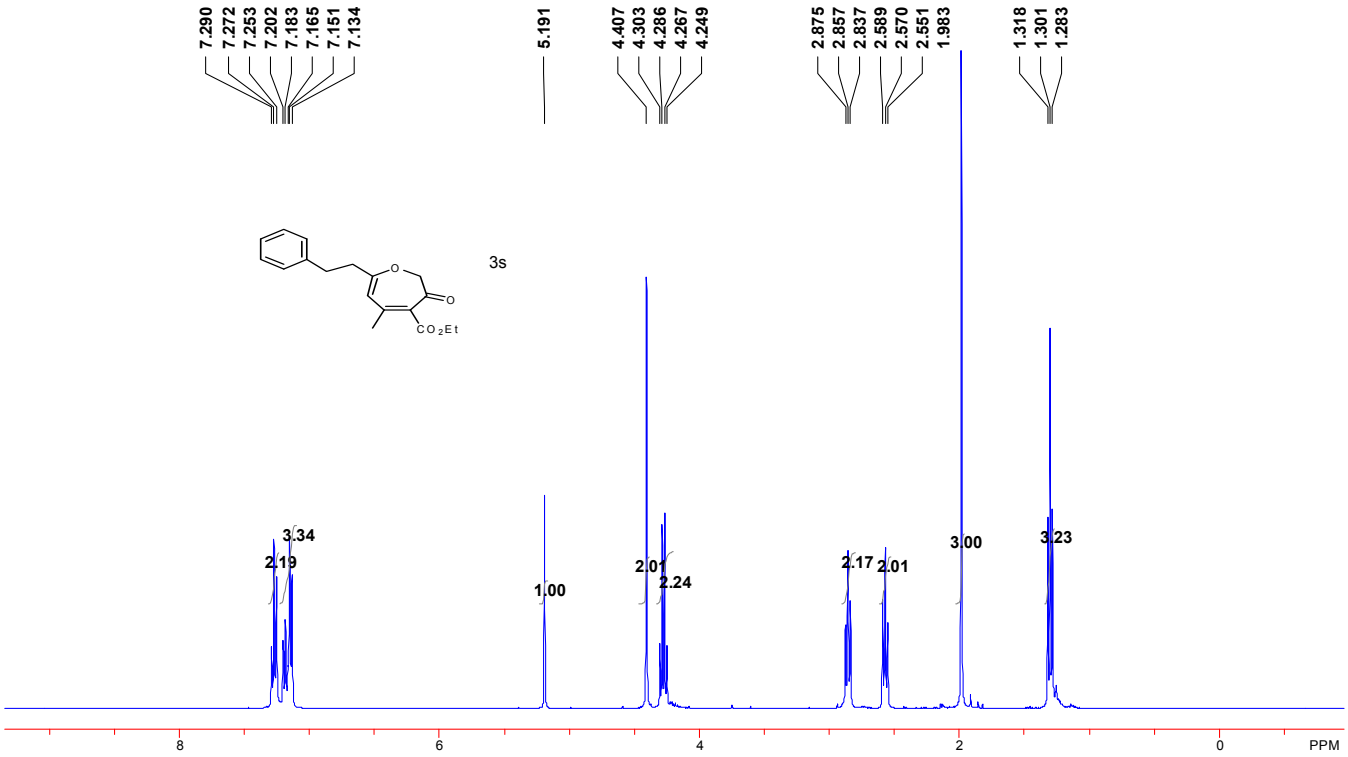


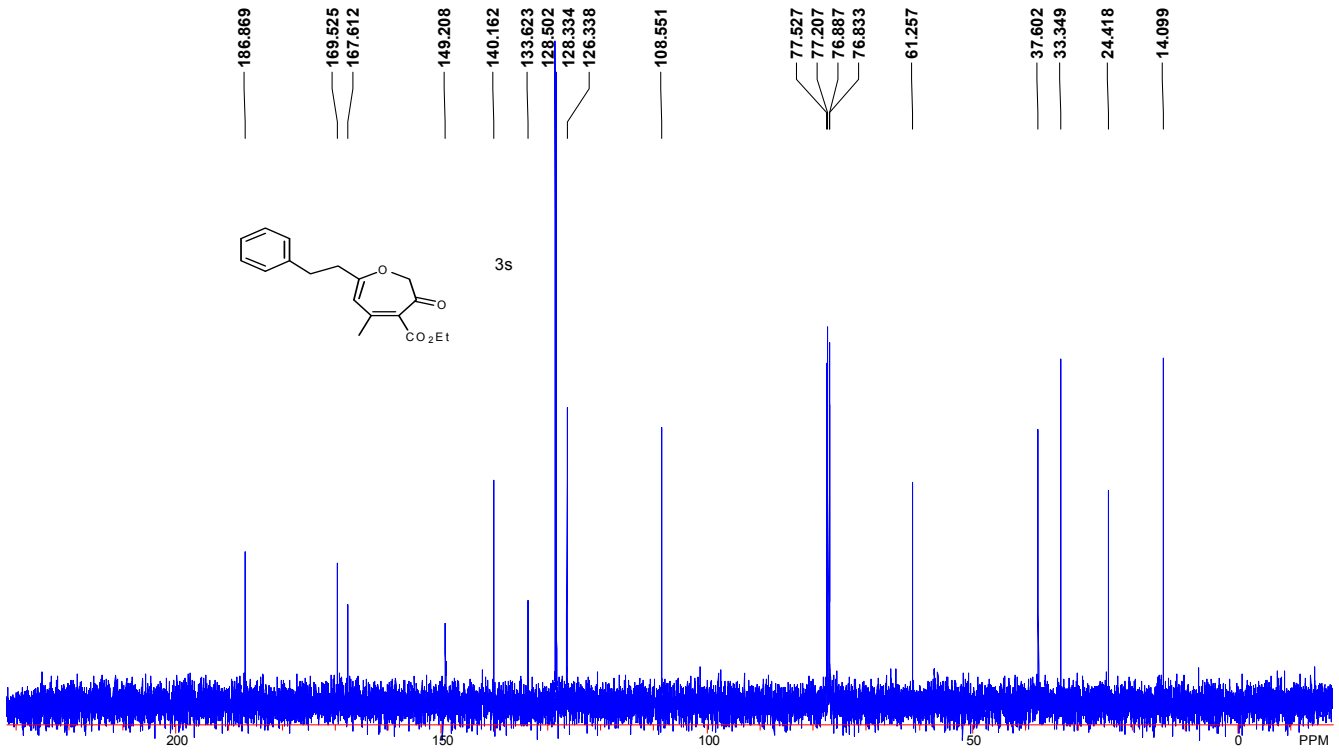


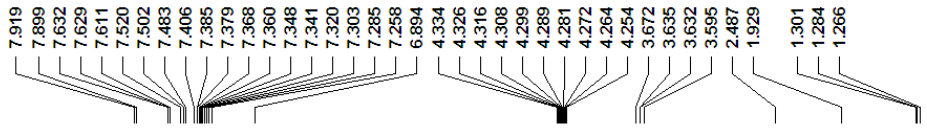


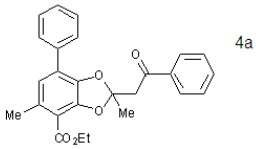

7.340
7.323
7.304
7.277
7.259
7.253
7.241
7.227
7.224
7.206
5.289
4.422
4.317
4.299
4.282
4.264
3.557
2.034
1.329
1.311
1.294
3r
O
O
CO2Et
3.22
2.12
1.00
2.03
2.14
1.99
2.98
3.22
8
7
6
5
4
3
2
1
0
PPM

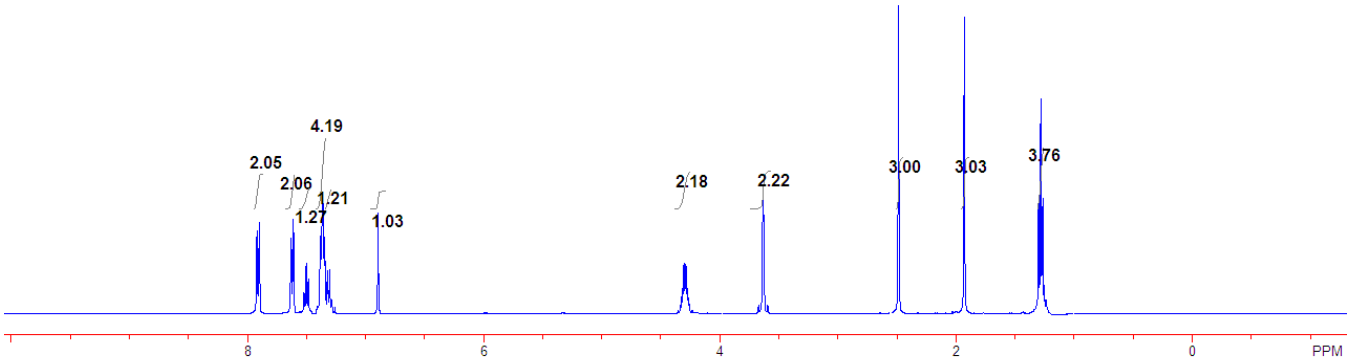

186.999
168.968
167.551
148.941
136.214
133.913
128.929
128.723
127.115
108.894
77.405
77.085
76.772
61.310
42.106
24.456
14.084
3r
O
O
CO2Et
200
150
100
50
0
PPM

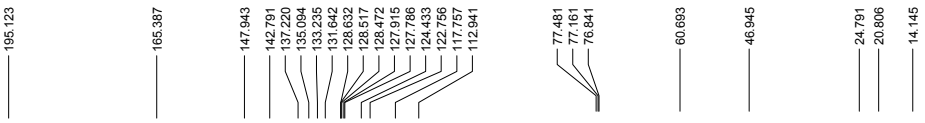


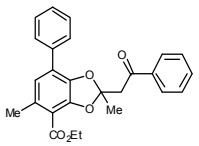


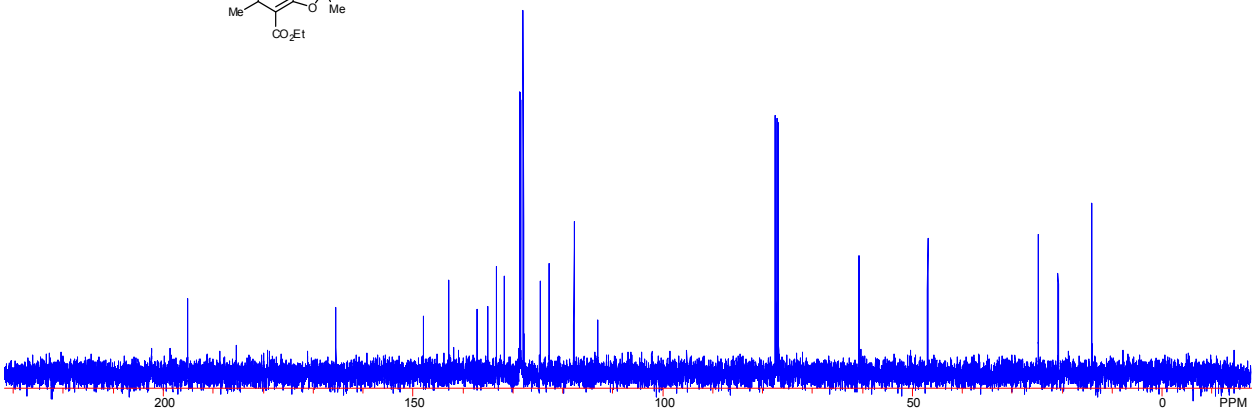

7.919
7.899
7.632
7.629
7.611
7.520
7.502
7.483
7.406
7.385
7.379
7.368
7.360
7.348
7.341
7.320
7.303
7.285
7.258
6.894
4.334
4.326
4.316
4.308
4.299
4.289
4.281
4.272
4.264
4.254
3.672
3.635
3.632
3.595
2.487
1.929
1.301
1.284
1.266

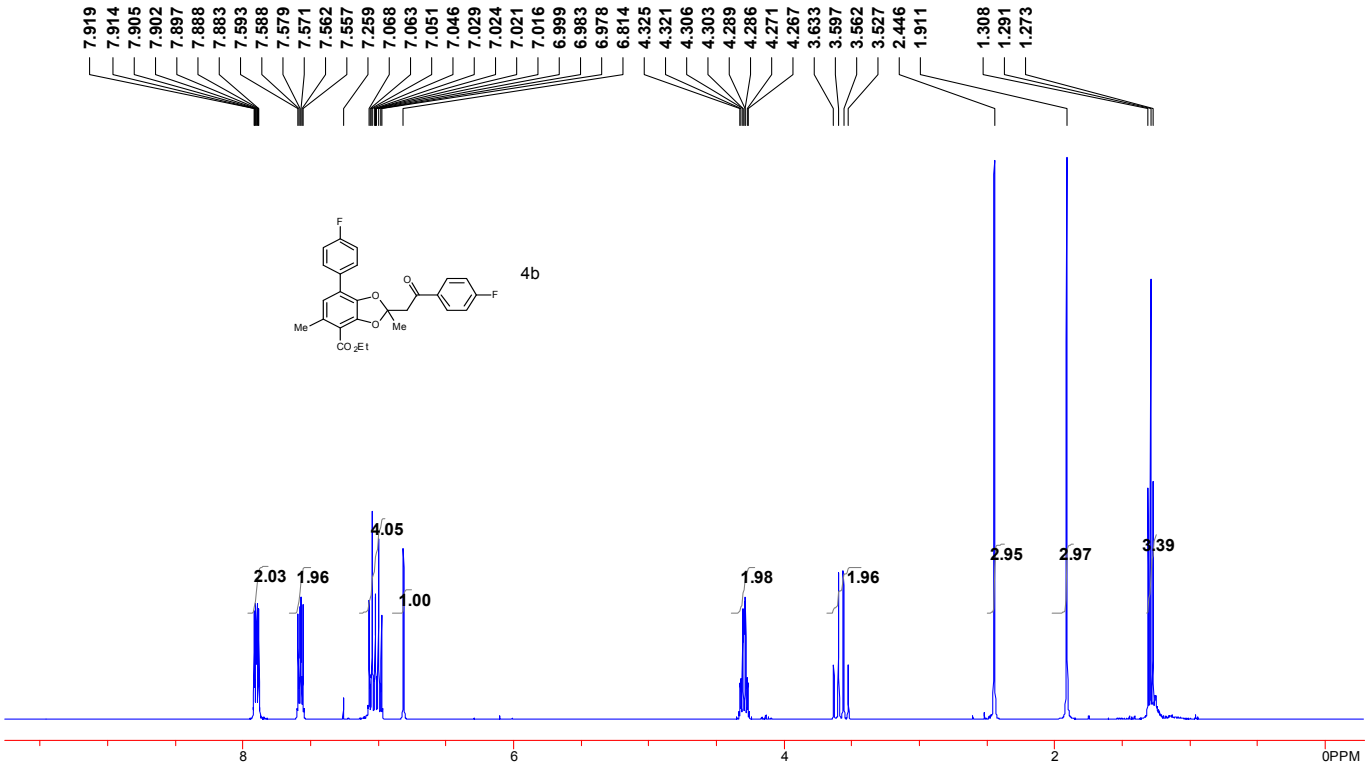

4a
Me
Me
CO2Et

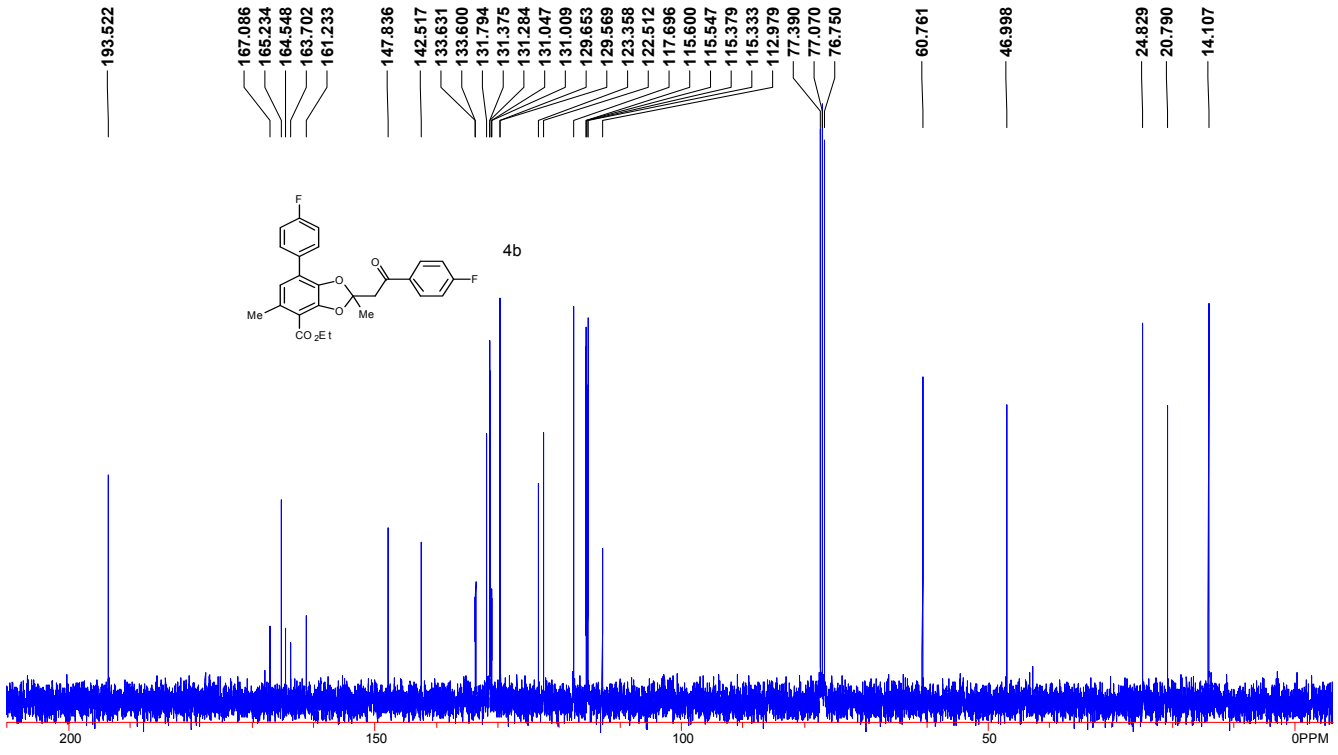

4.19
2.05
2.06
1.21
1.27
1.03
2.18
2.22
3.00
3.03
3.76
8
6
4
2
0
PPM

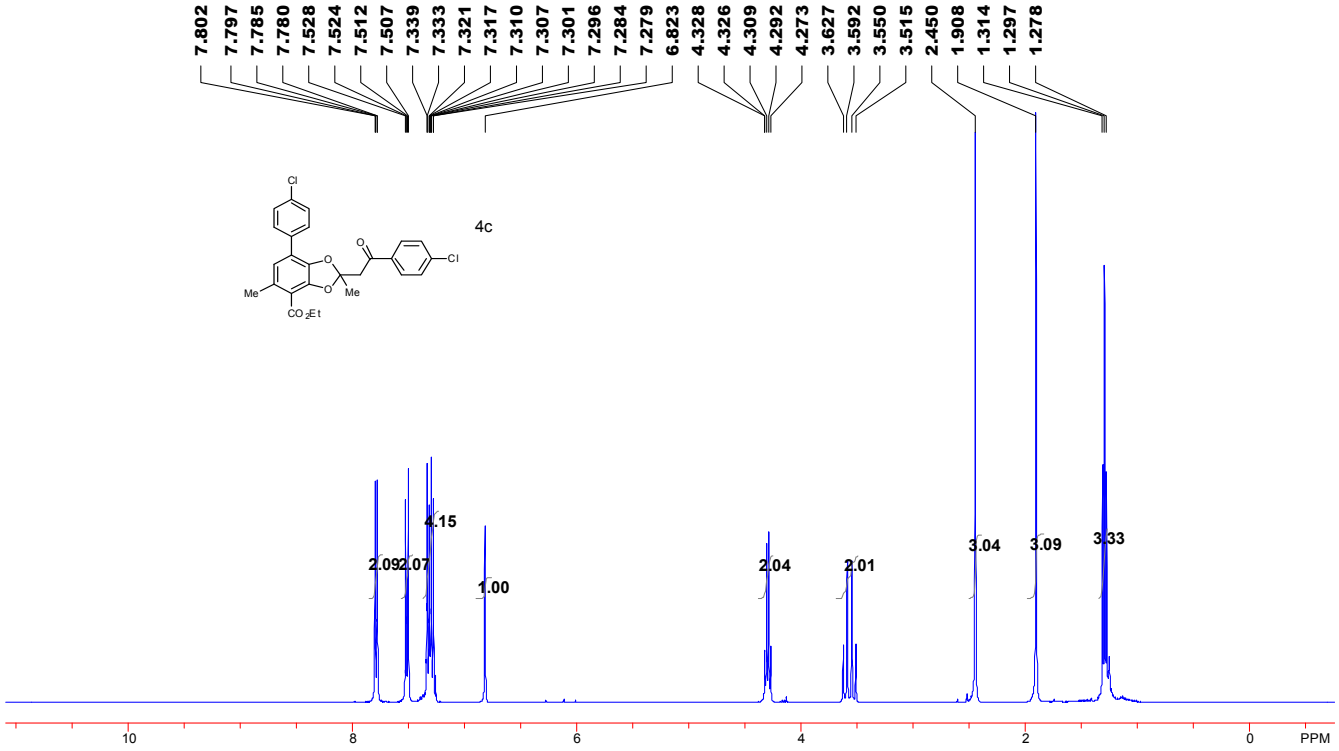

195.123
165.387
147.943
142.791
137.220
135.094
133.235
131.642
128.632
128.517
128.472
127.915
127.786
124.433
122.756
117.757
112.941
77.481
77.161
76.841
60.693
46.945
24.791
20.806
14.145

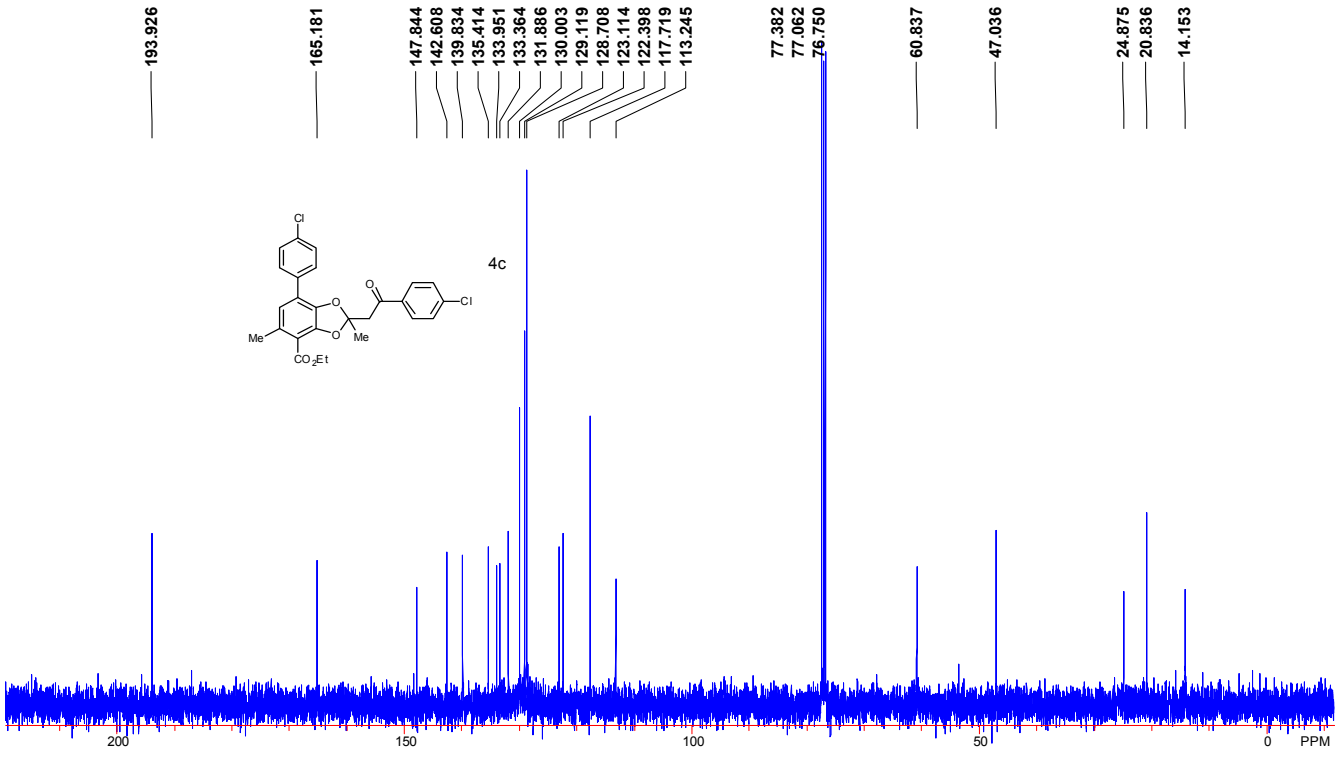

4a
Me
Me
CO2Et

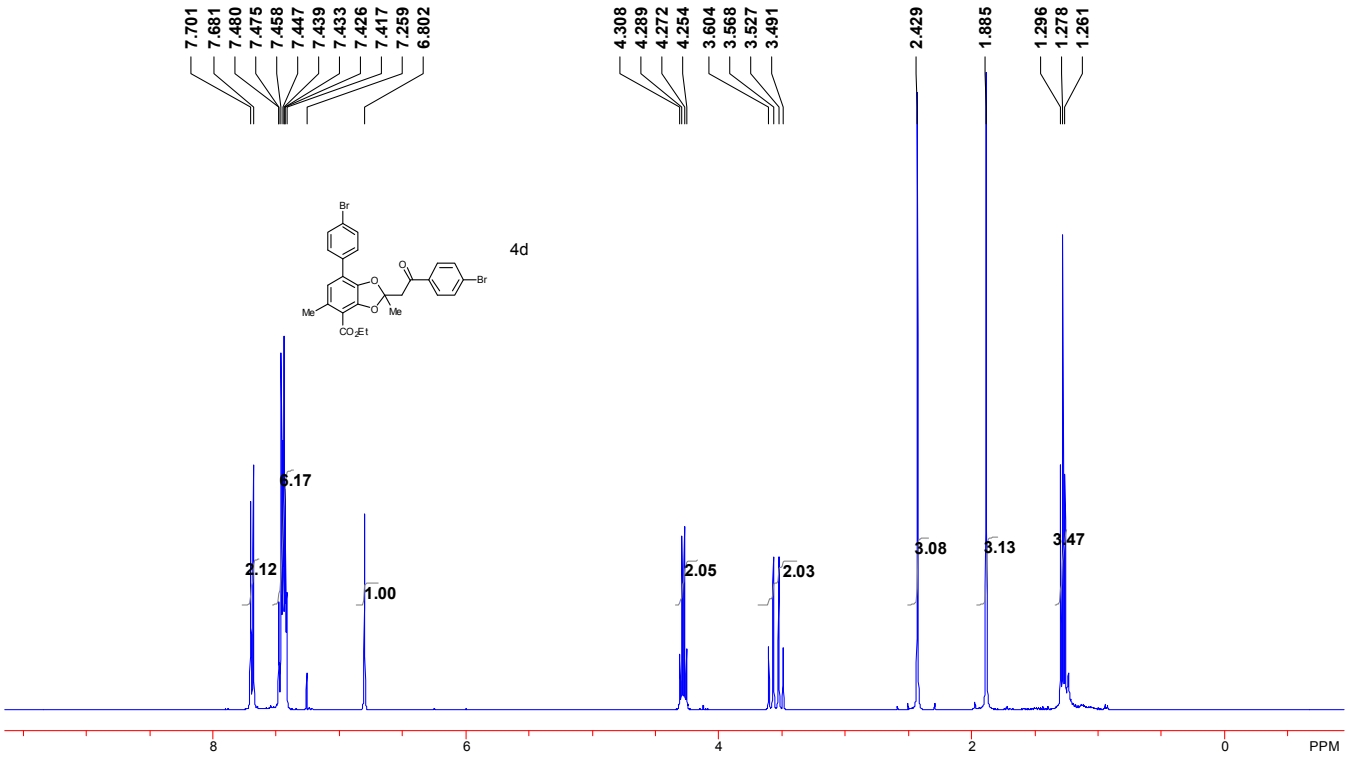

200
150
100
50
0
PPM

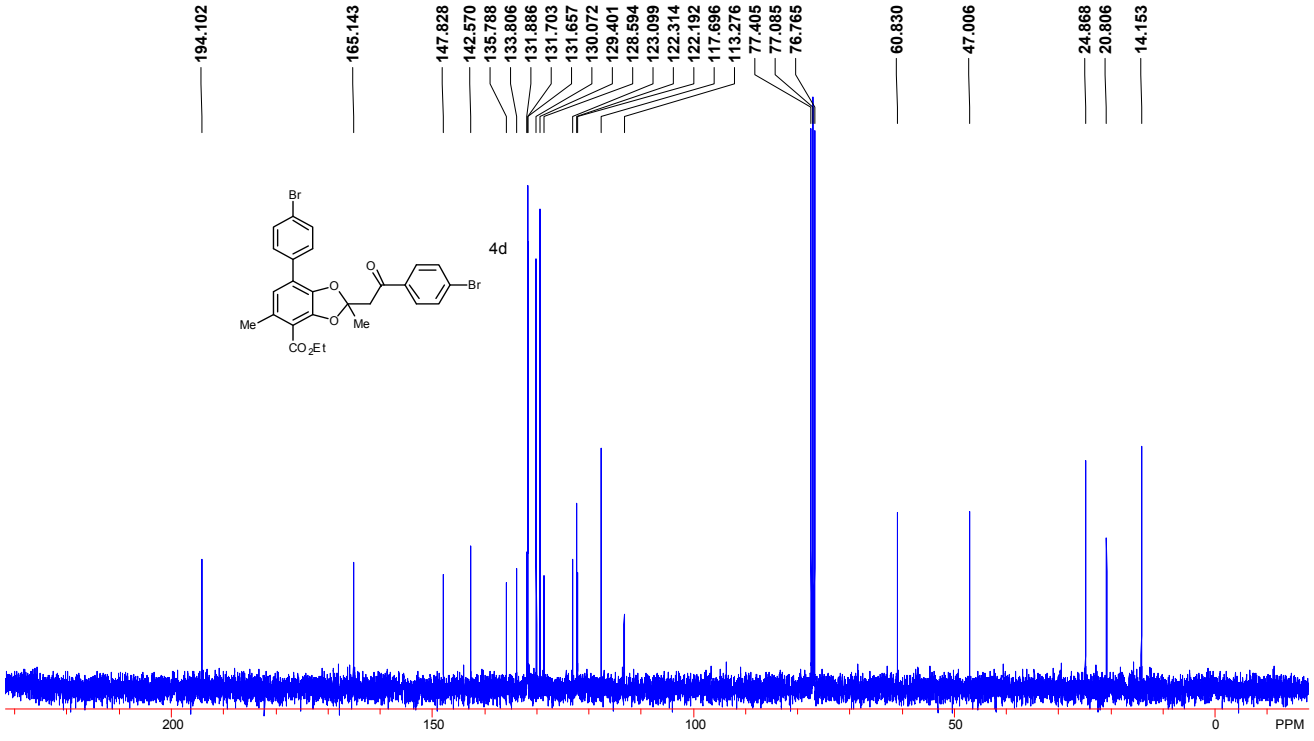

7.919
7.914
7.905
7.902
7.897
7.888
7.883
7.593
7.588
7.579
7.571
7.562
7.557
7.259
7.068
7.063
7.051
7.046
7.029
7.024
7.021
7.016
6.999
6.983
6.978
6.814
4.325
4.321
4.306
4.303
4.289
4.286
4.271
4.267
3.633
3.597
3.562
3.527
2.446
1.911
1.308
1.291
1.273
4b
2.03
1.96
4.05
1.00
1.98
1.96
2.95
2.97
3.39
8
6
4
2
0PPM

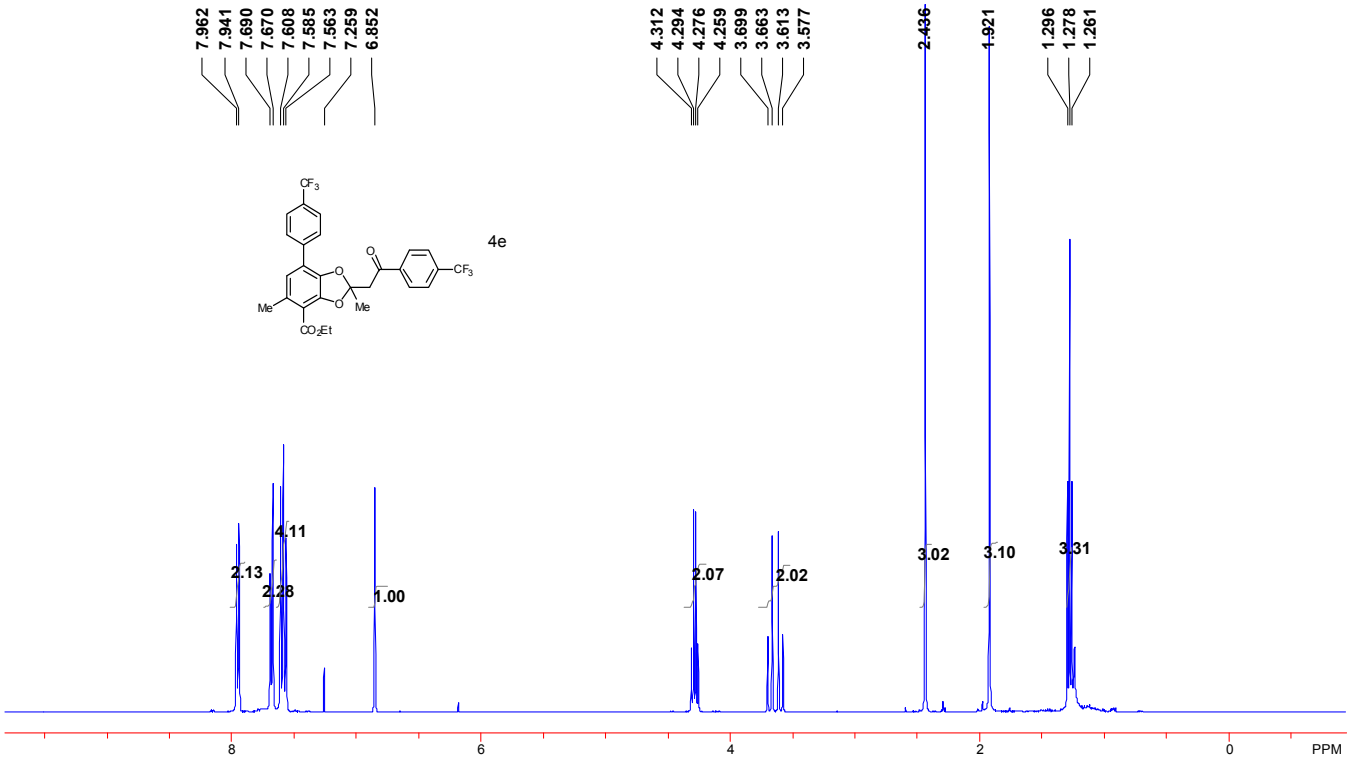

193.522
167.086
165.234
164.548
163.702
161.233
147.836
142.517
133.631
133.600
131.794
131.375
131.284
131.047
131.009
129.653
129.569
123.358
122.512
117.696
115.600
115.547
115.379
115.333
112.979
77.390
77.070
76.750
60.761
46.998
24.829
20.790
14.107
4b
200
150
100
50
0PPM

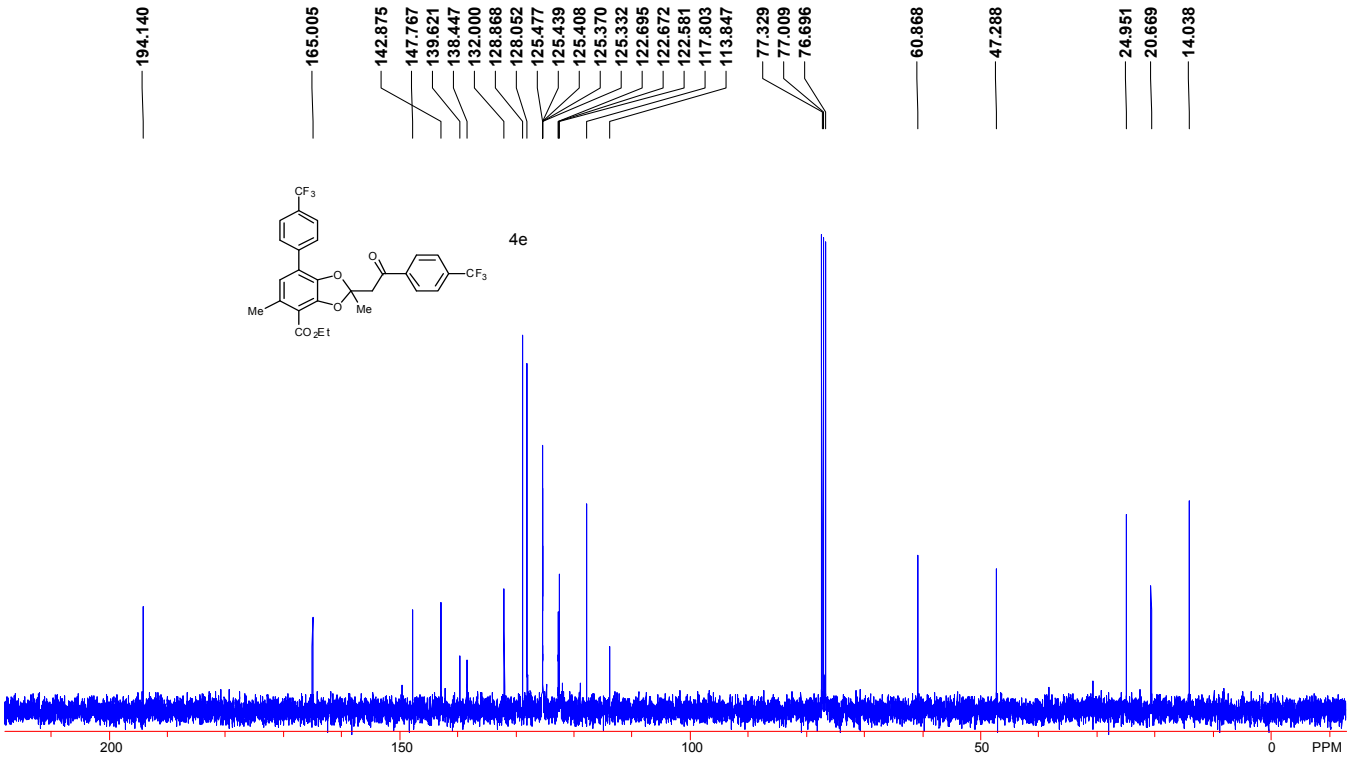

7.802
7.797
7.785
7.780
7.528
7.524
7.512
7.507
7.339
7.333
7.321
7.317
7.310
7.307
7.301
7.296
7.284
7.279
6.823
4.328
4.326
4.309
4.292
4.273
3.627
3.592
3.550
3.515
2.450
1.908
1.314
1.297
1.278
4c
4.15
2.09
2.07
1.00
2.04
2.01
3.04
3.09
3.33
10
8
6
4
2
0
PPM

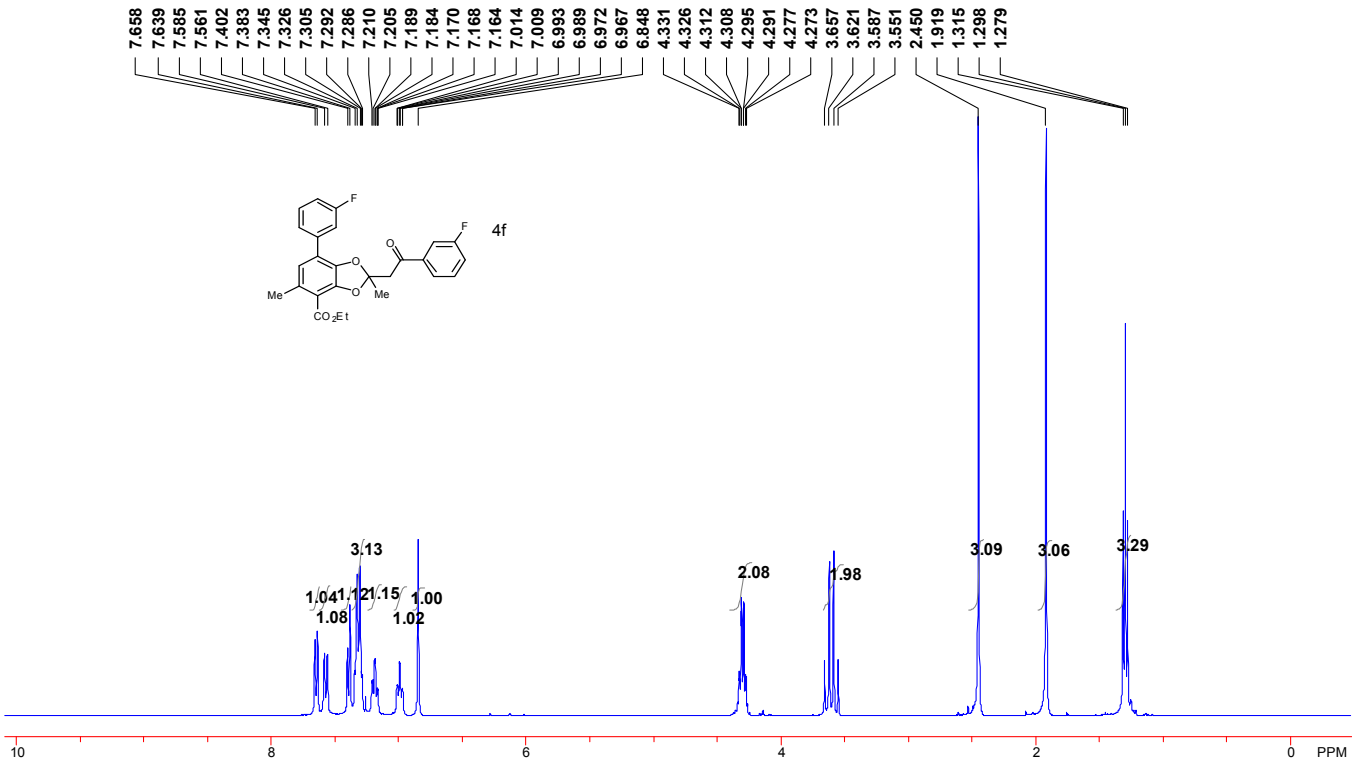

193.926
165.181
147.844
142.608
139.834
135.414
133.951
133.364
131.886
130.003
129.119
128.708
123.114
122.398
117.719
113.245
77.382
77.062
76.750
60.837
47.036
24.875
20.836
14.153
4c
200
150
100
50
0
PPM

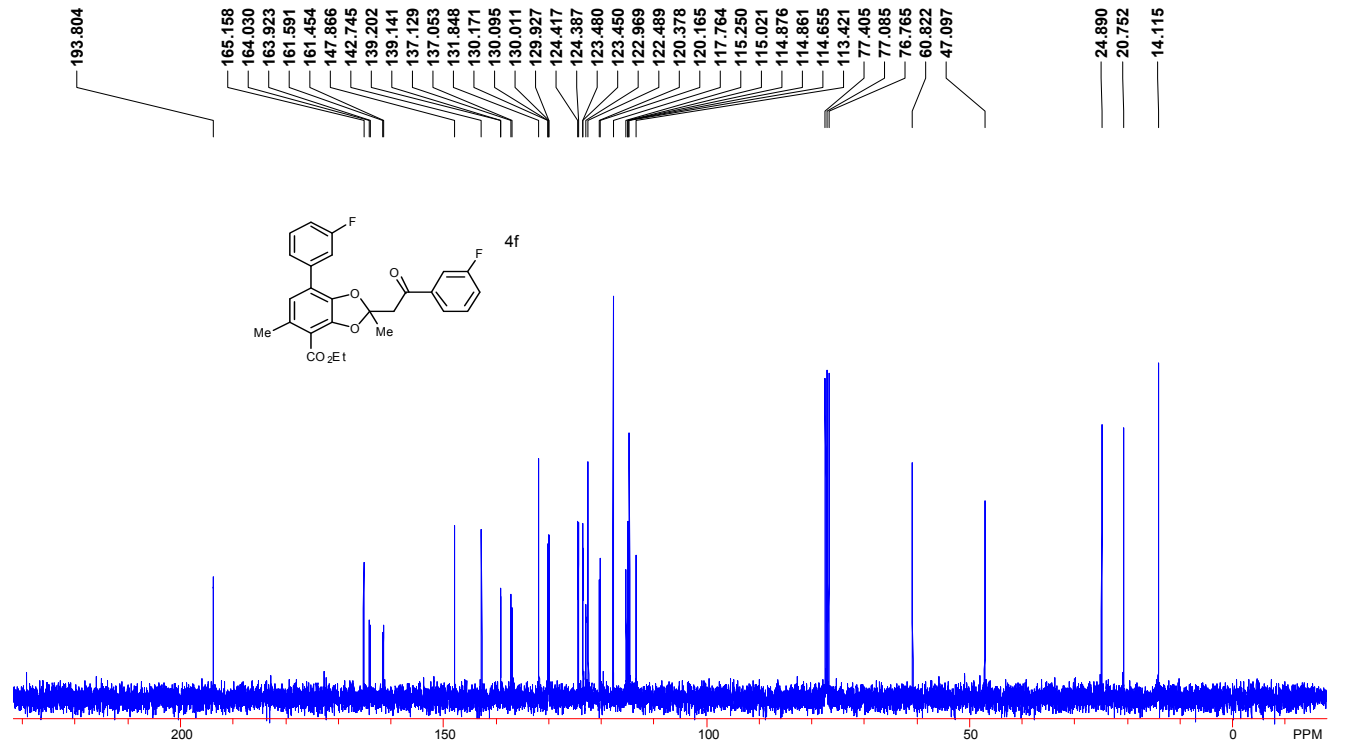


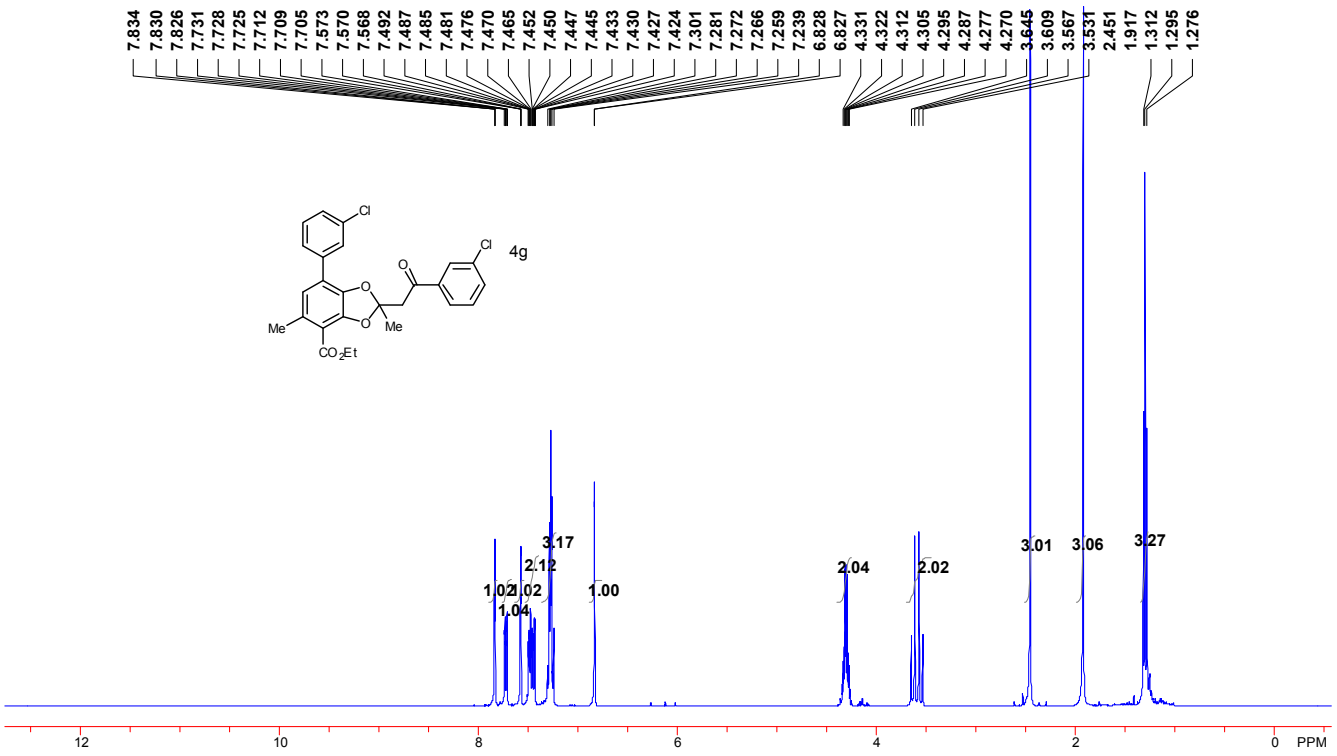


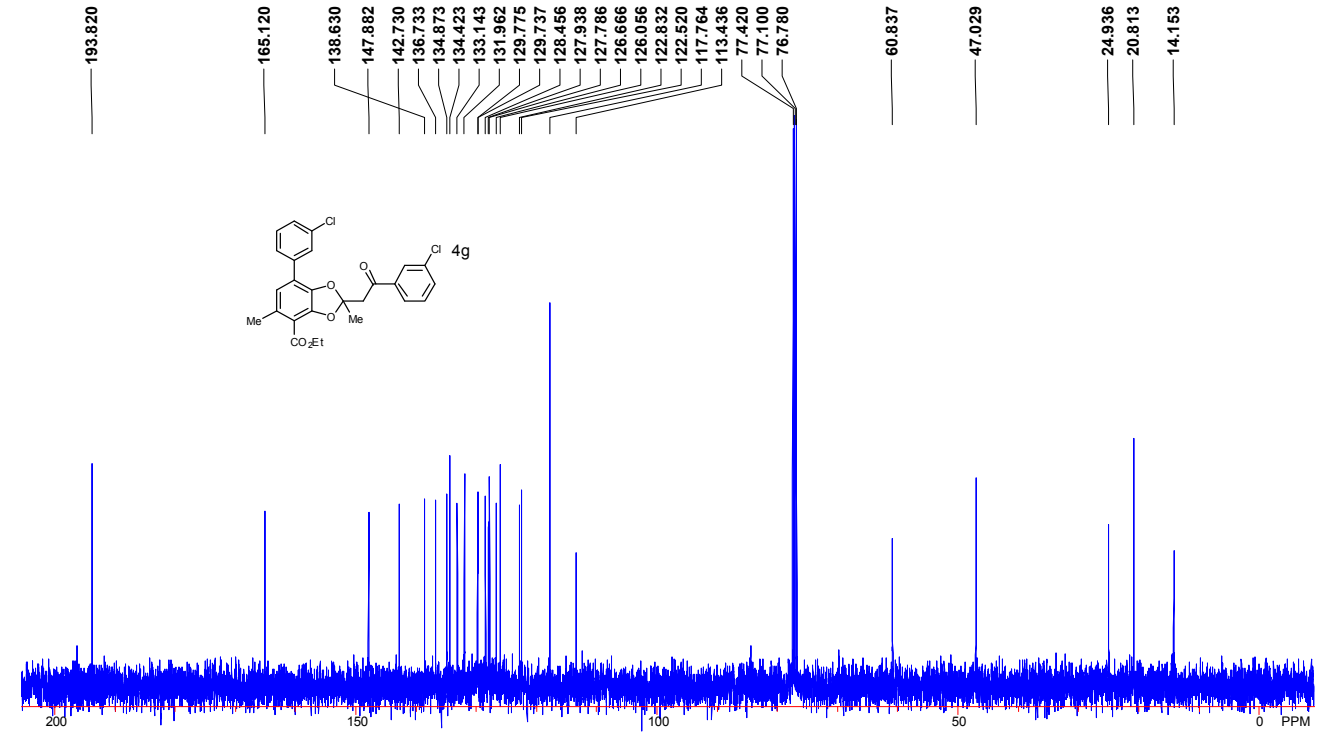


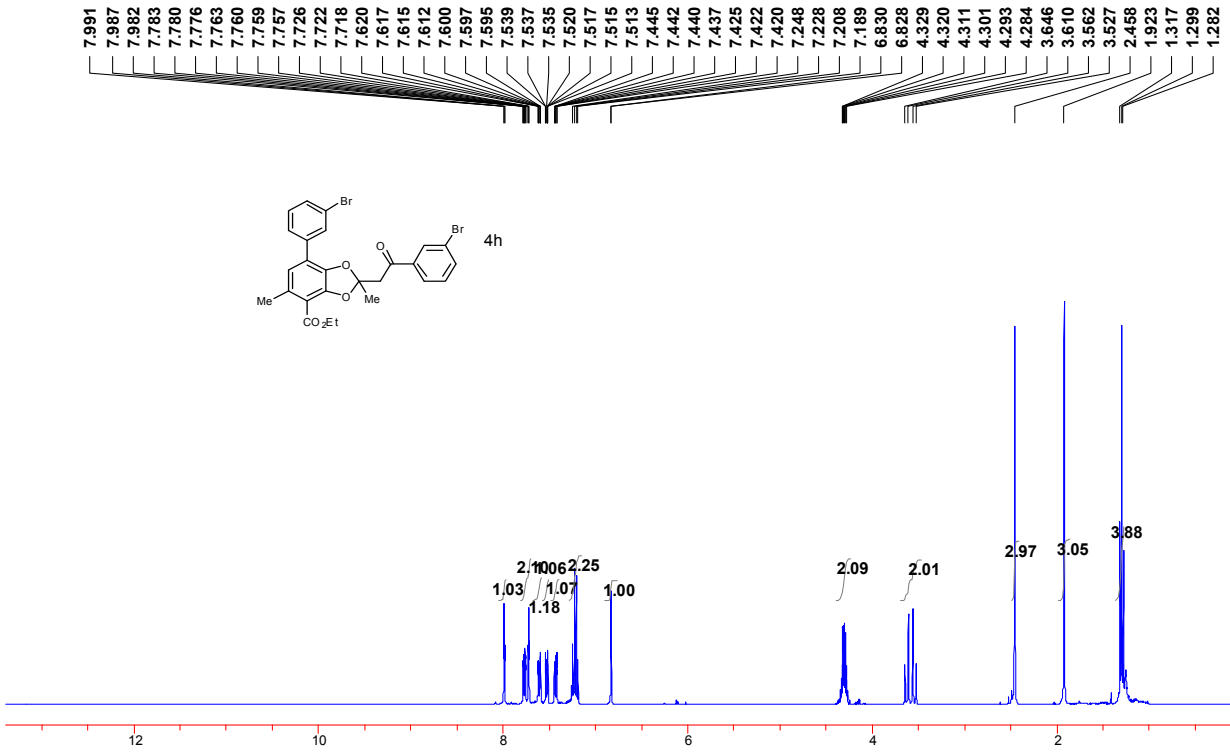


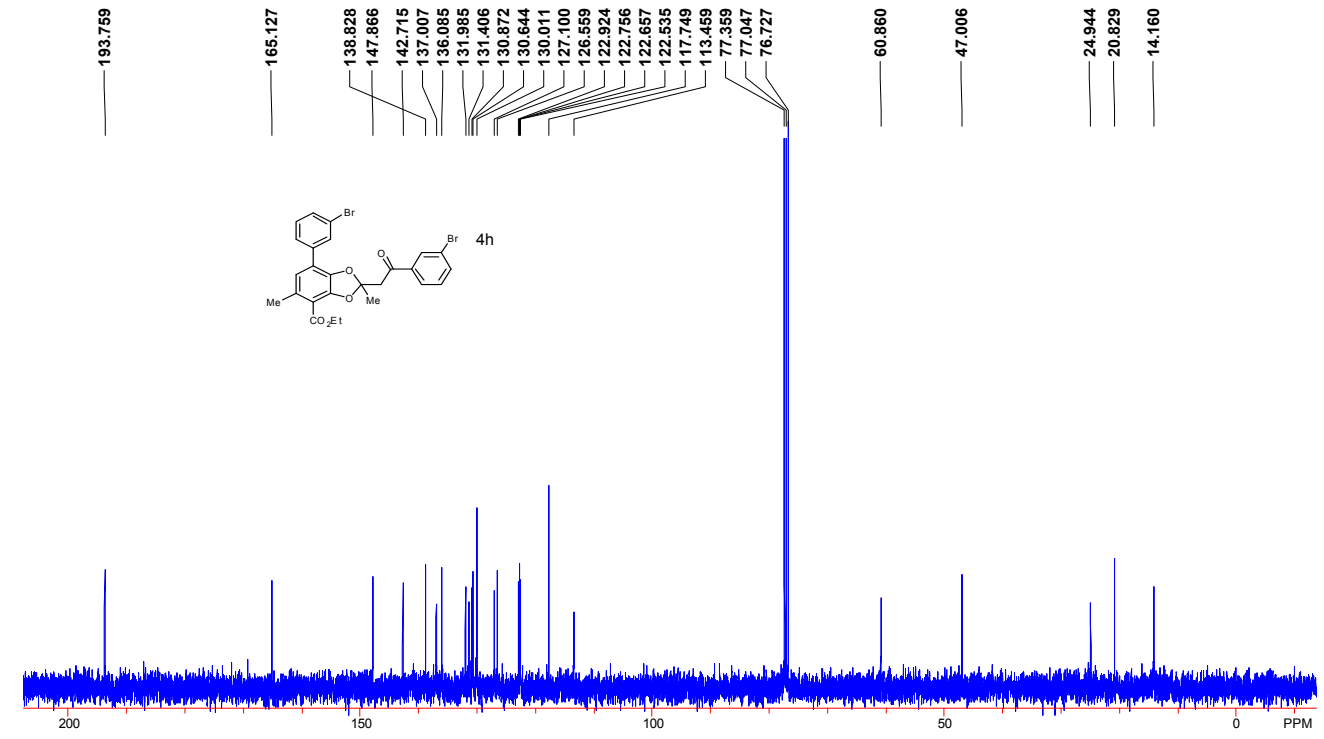


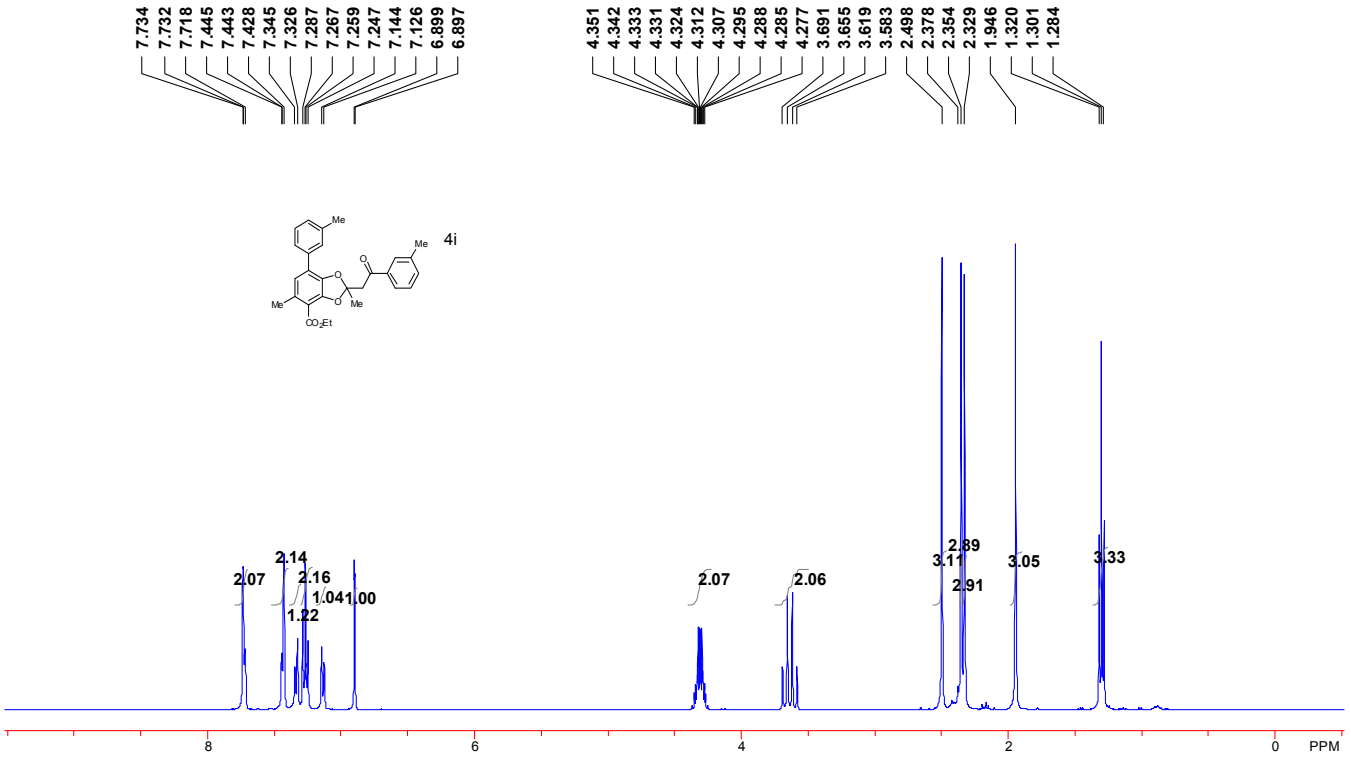


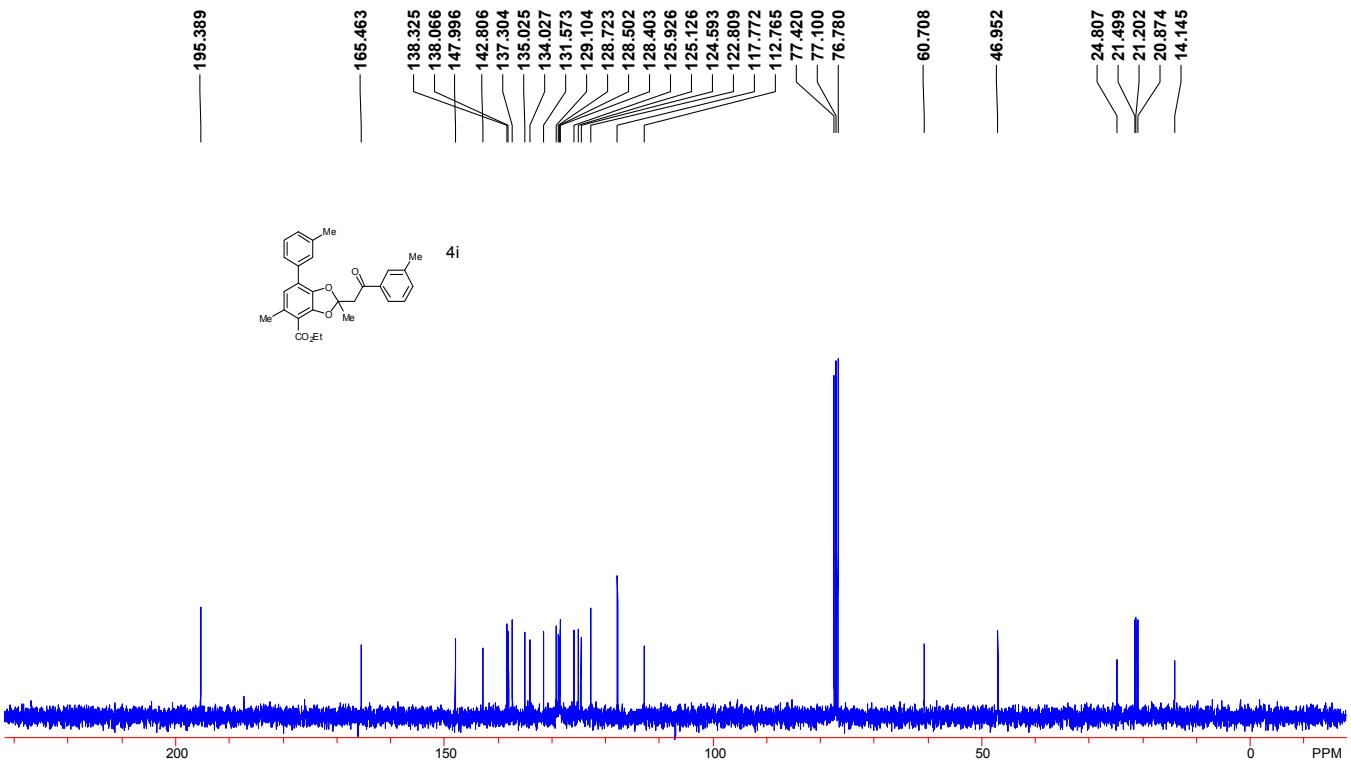

7.834
7.830
7.826
7.731
7.728
7.725
7.712
7.709
7.705
7.573
7.570
7.568
7.492
7.487
7.485
7.481
7.476
7.470
7.465
7.452
7.450
7.447
7.445
7.433
7.430
7.427
7.424
7.301
7.281
7.272
7.266
7.259
7.239
6.828
6.827
4.331
4.322
4.312
4.305
4.295
4.287
4.277
4.270
3.645
3.609
3.567
3.531
2.451
1.917
1.312
1.295
1.276
Cl
Cl
O
O
O
Me
Me
CO2Et
4g
3.17
2.12
1.02
1.02
1.04
1.00
2.04
2.02
3.01
3.06
3.27
12
10
8
6
4
2
0
PPM

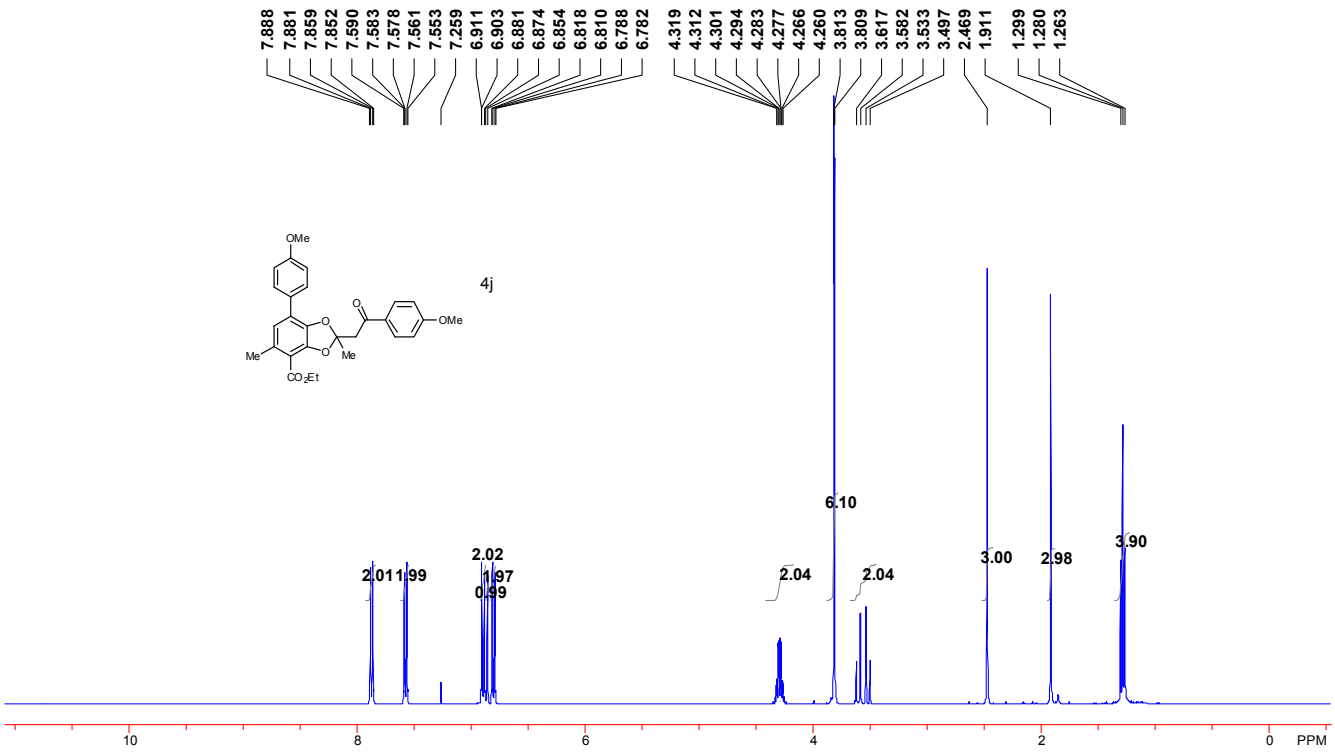

193.820
165.120
138.630
147.882
142.730
136.733
134.873
134.423
133.143
131.962
129.775
129.737
128.456
127.938
127.786
126.666
126.056
122.832
122.520
117.764
113.436
77.420
77.100
76.780
60.837
47.029
24.936
20.813
14.153
Cl
Cl
O
O
O
Me
Me
CO2Et
4g
200
150
100
50
0
PPM

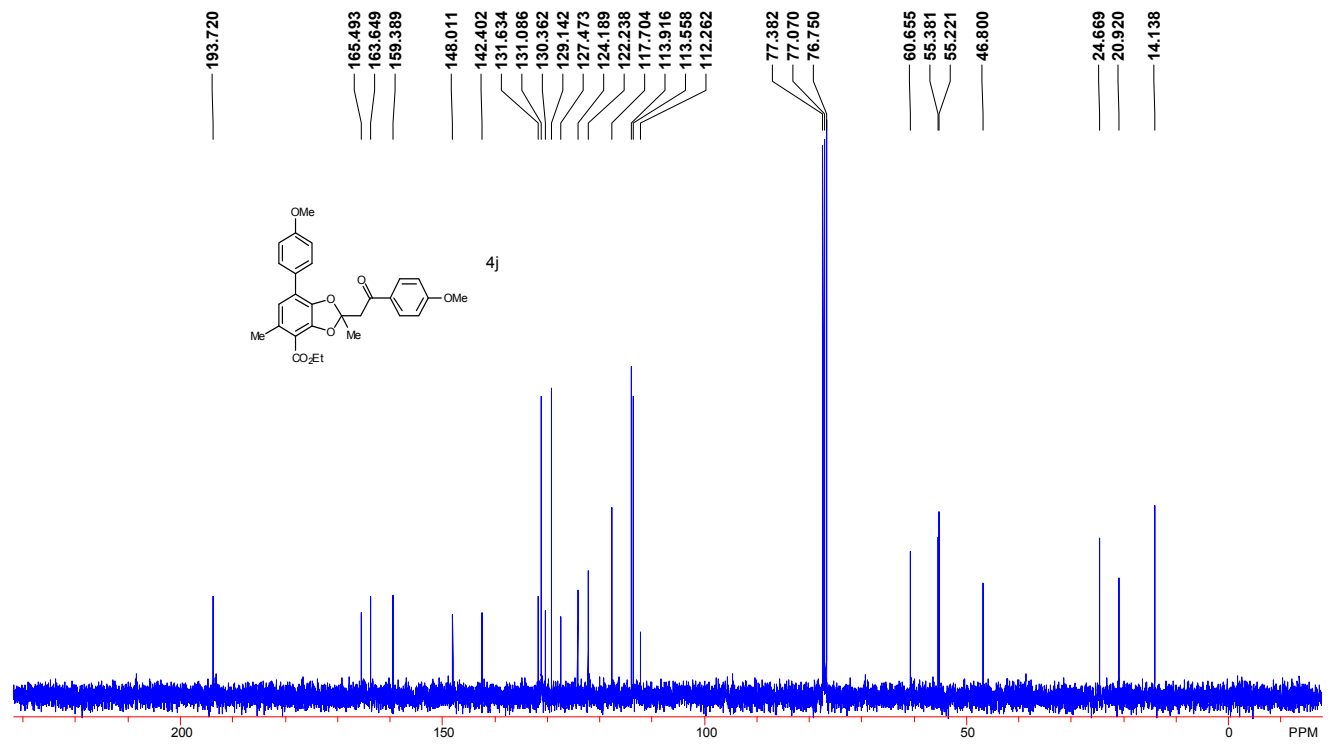


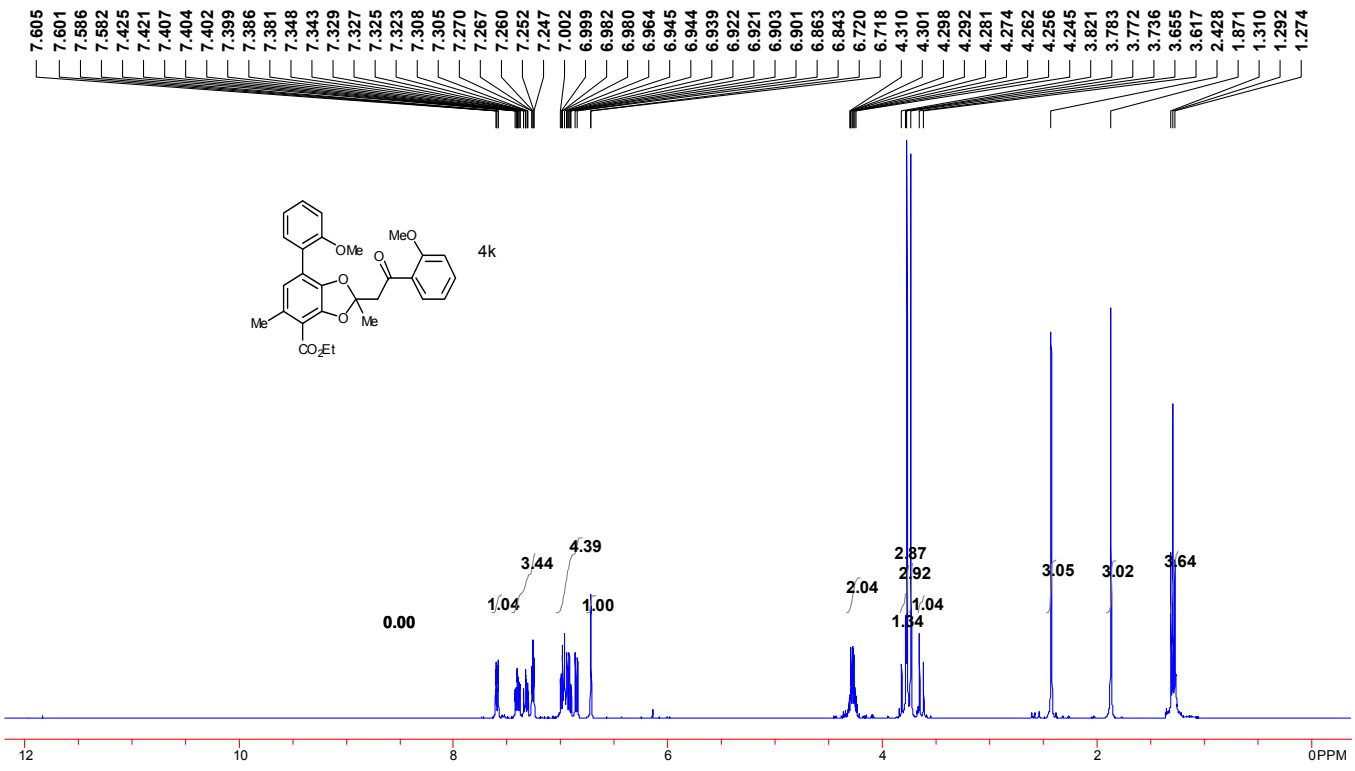


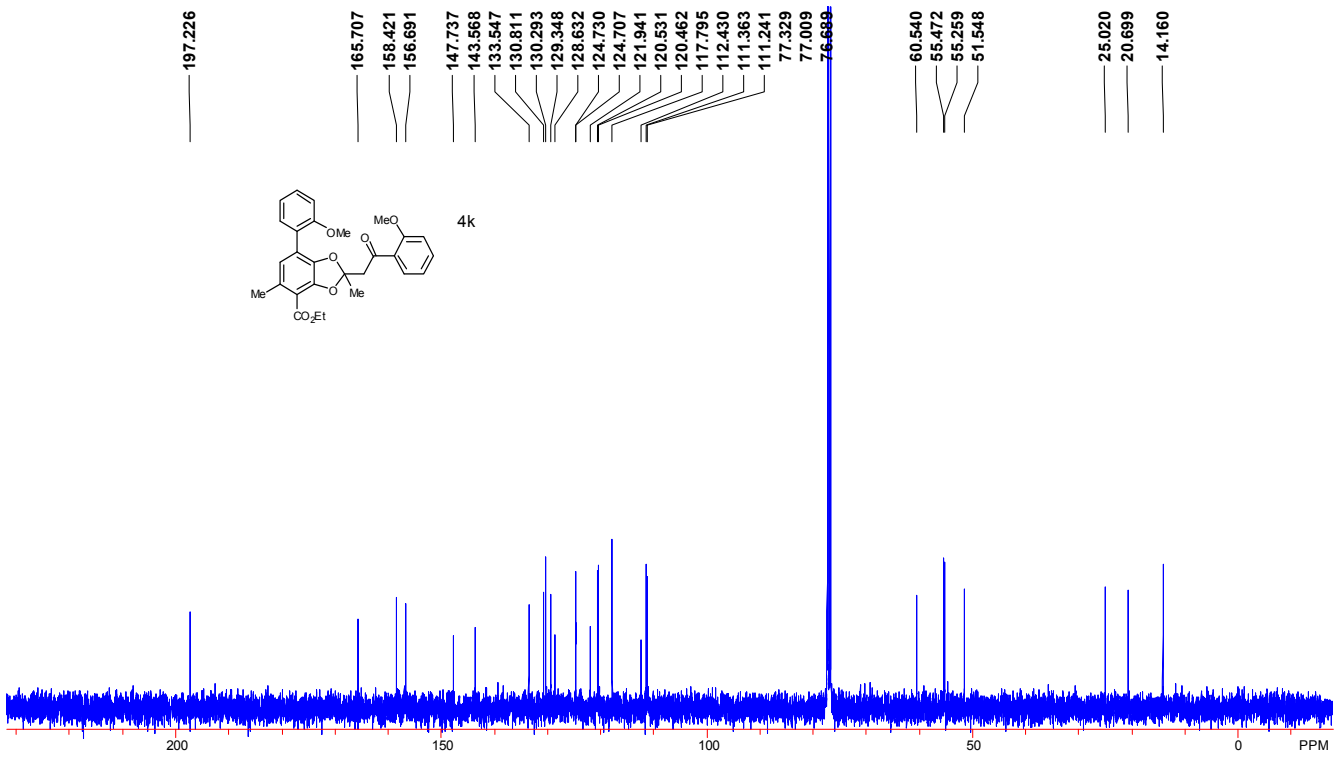

7.734
7.732
7.718
7.445
7.443
7.428
7.345
7.326
7.287
7.267
7.259
7.247
7.144
7.126
6.899
6.897
4.351
4.342
4.333
4.331
4.324
4.312
4.307
4.295
4.288
4.285
4.277
3.691
3.655
3.619
3.583
2.498
2.378
2.354
2.329
1.946
1.320
1.301
1.284
4i
2.07
2.14
2.16
1.04
1.00
1.22
2.07
2.06
3.11
2.89
2.91
3.05
3.33
8
6
4
2
0
PPM

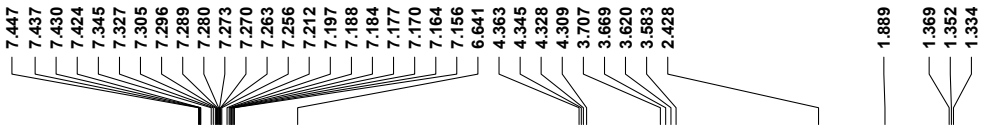

195.389
165.463
138.325
138.066
147.996
142.806
137.304
135.025
134.027
131.573
129.104
128.723
128.502
128.403
125.926
125.126
124.593
122.809
117.772
112.765
77.420
77.100
76.780
60.708
46.952
24.807
21.499
21.202
20.874
14.145
4i
200
150
100
50
0
PPM

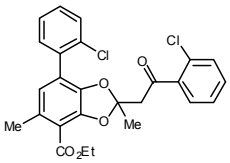




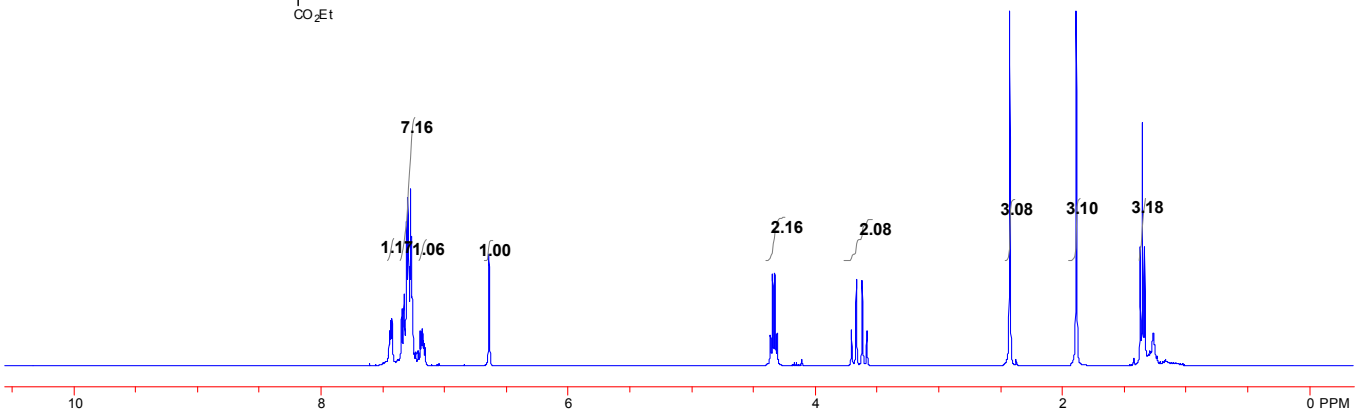


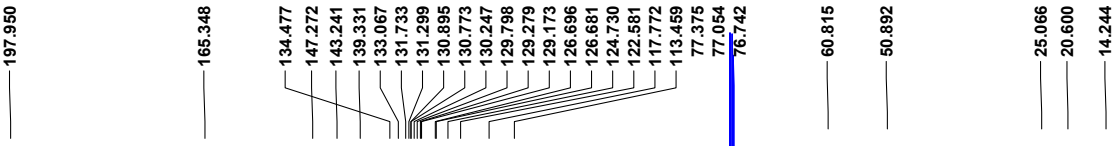


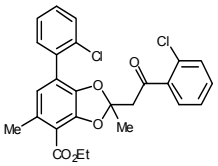

7.447
7.437
7.430
7.424
7.345
7.327
7.305
7.296
7.289
7.280
7.273
7.270
7.263
7.256
7.212
7.197
7.188
7.184
7.177
7.170
7.164
7.156
6.641
4.363
4.345
4.328
4.309
3.707
3.669
3.620
3.583
2.428
1.889
1.369
1.352
1.334


Cl
Cl
O
O
O
Me
Me
CO2Et

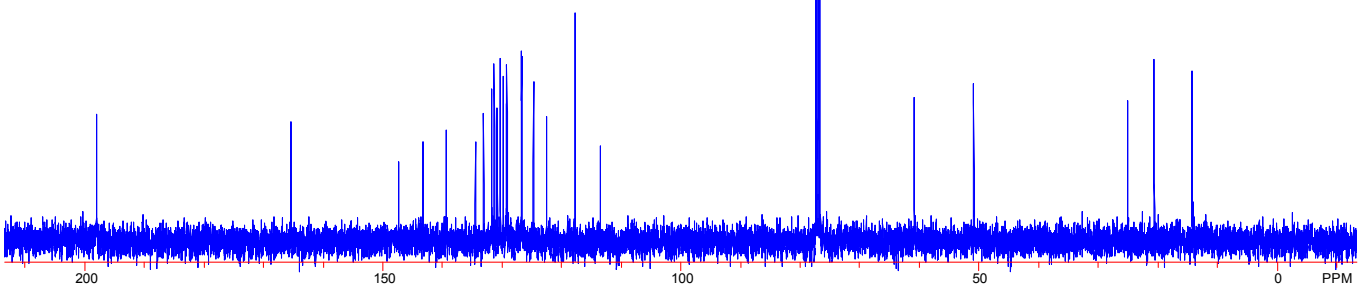
4l

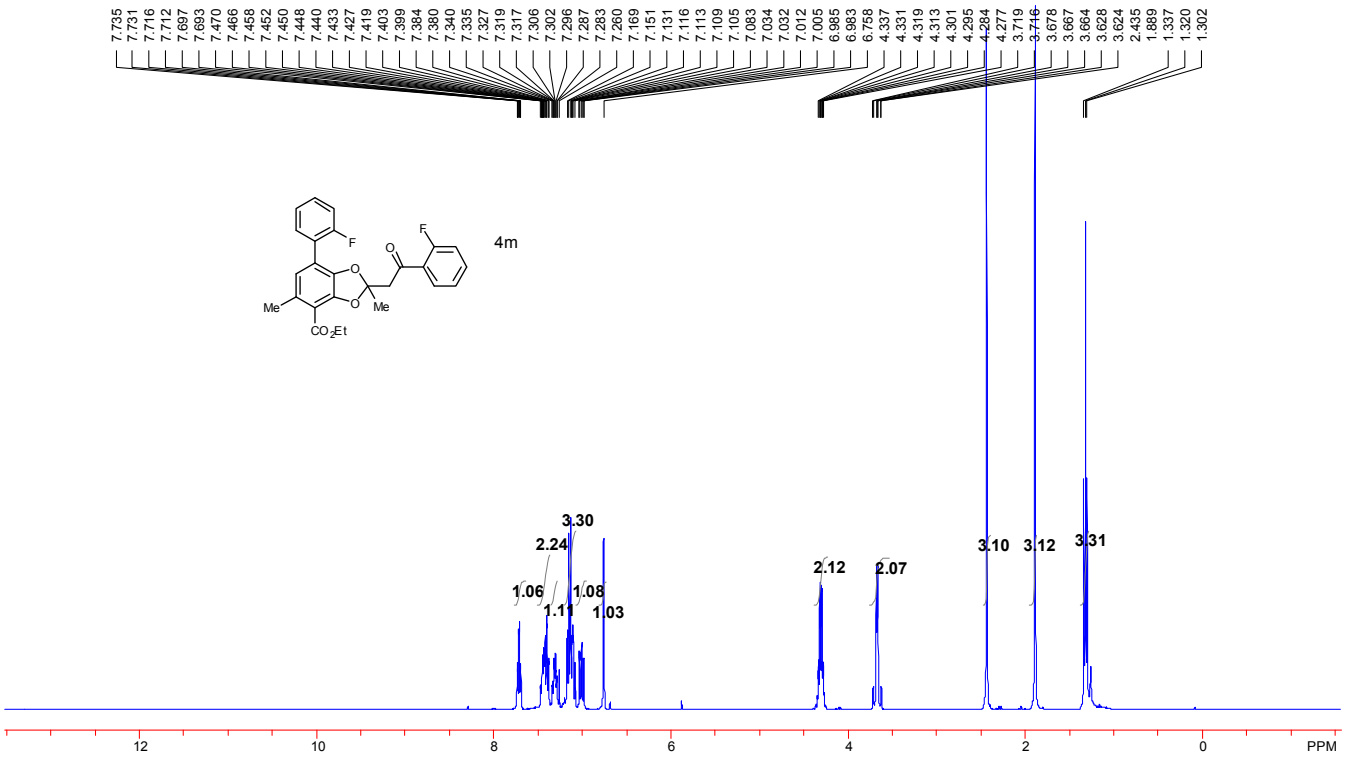

7.16
1.17
1.06
1.00
2.16
2.08
3.08
3.10
3.18
10
8
6
4
2
0 PPM

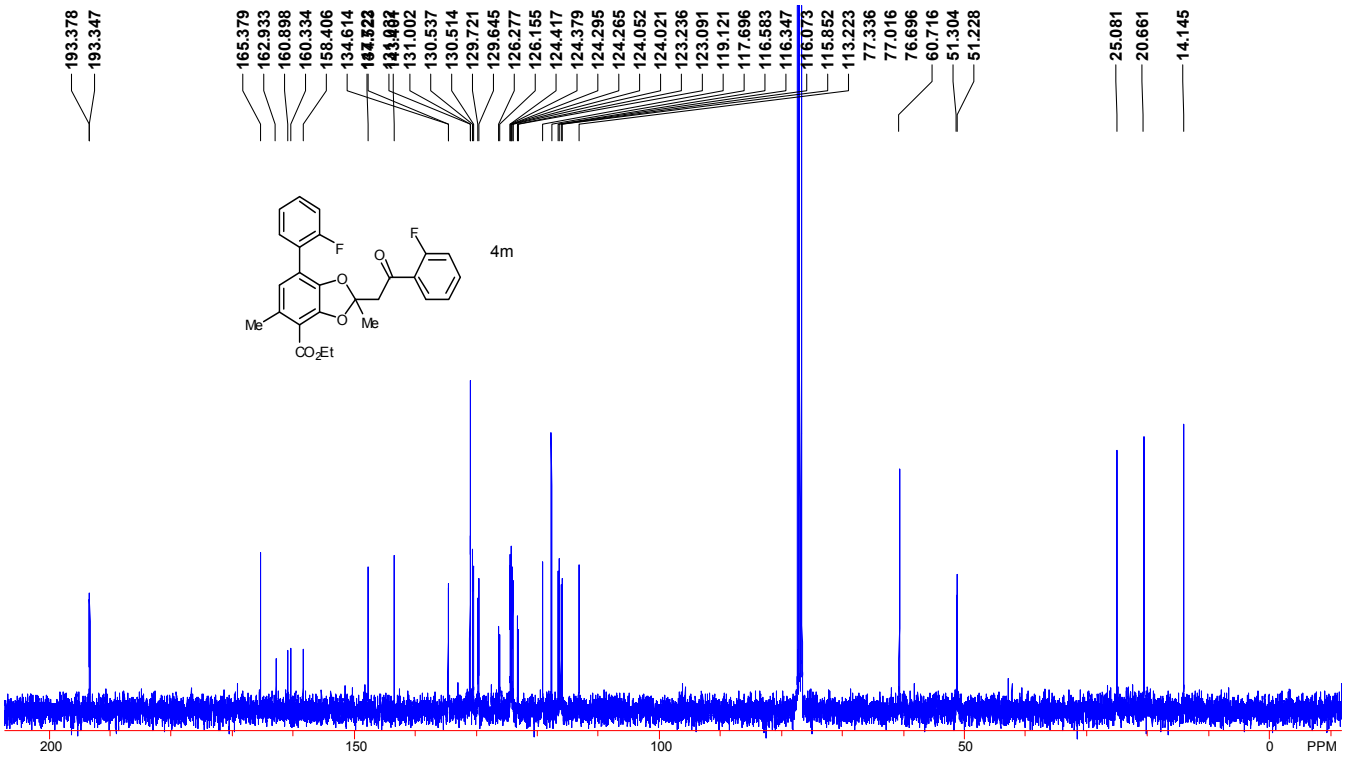

197.950
165.348
134.477
147.272
143.241
139.331
133.067
131.733
131.299
130.895
130.773
130.247
129.798
129.279
129.173
126.696
126.681
124.730
122.581
117.772
113.459
77.375
77.054
76.742
60.815
50.892
25.066
20.600
14.244

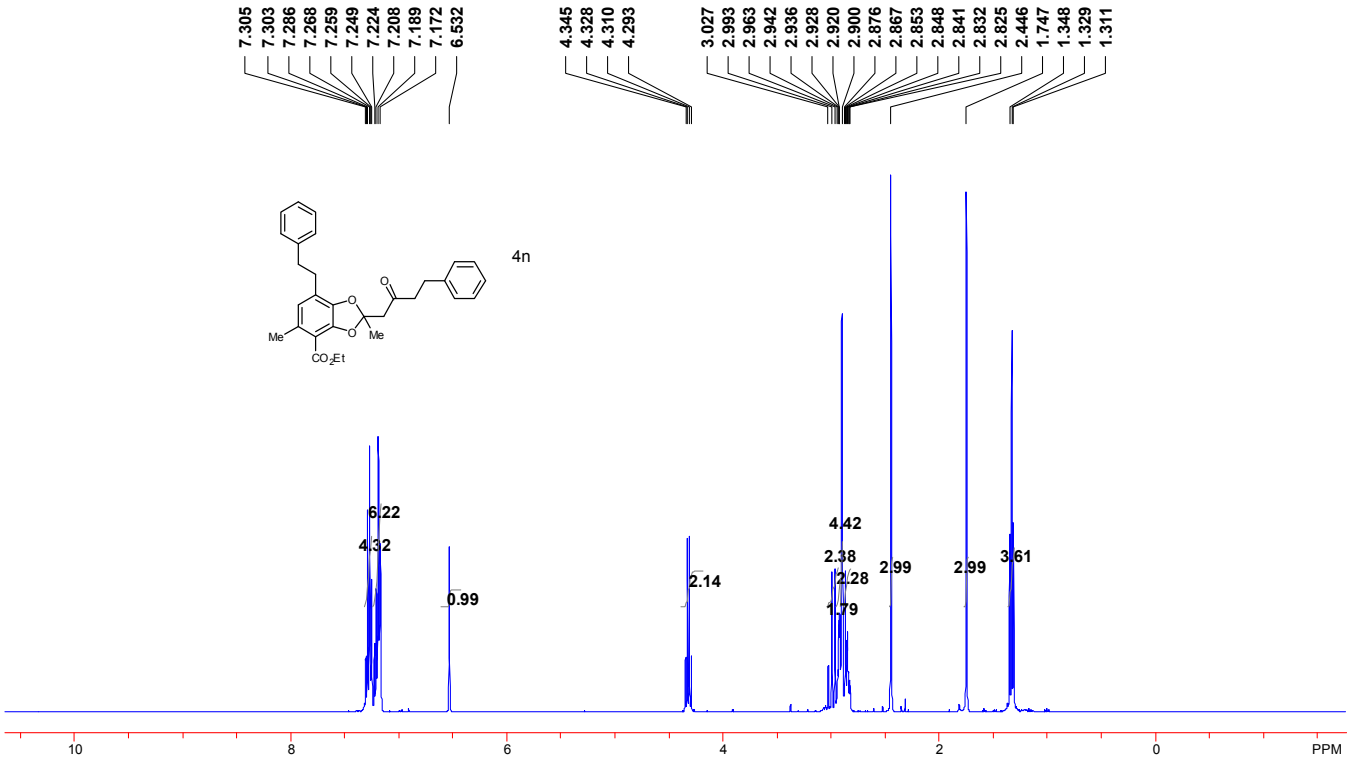

Cl
Cl
O
O
O
Me
Me
CO2Et

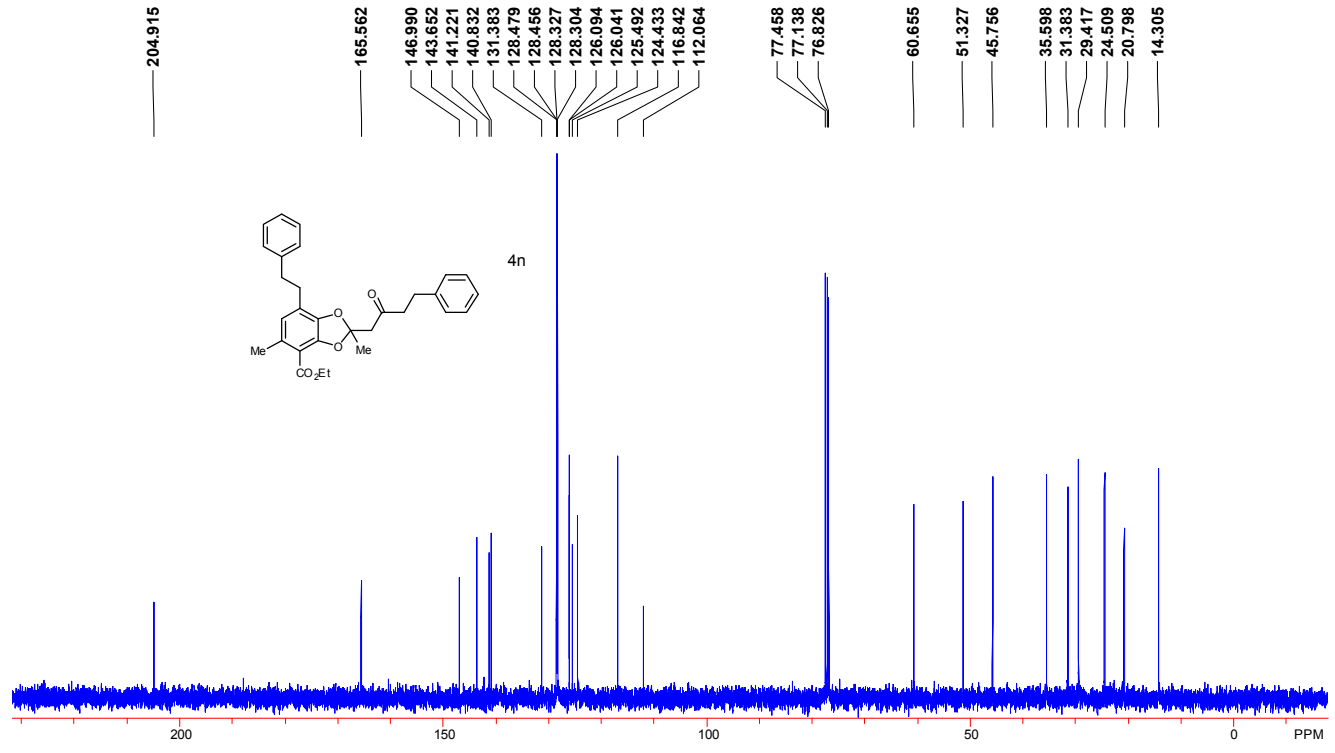
4l

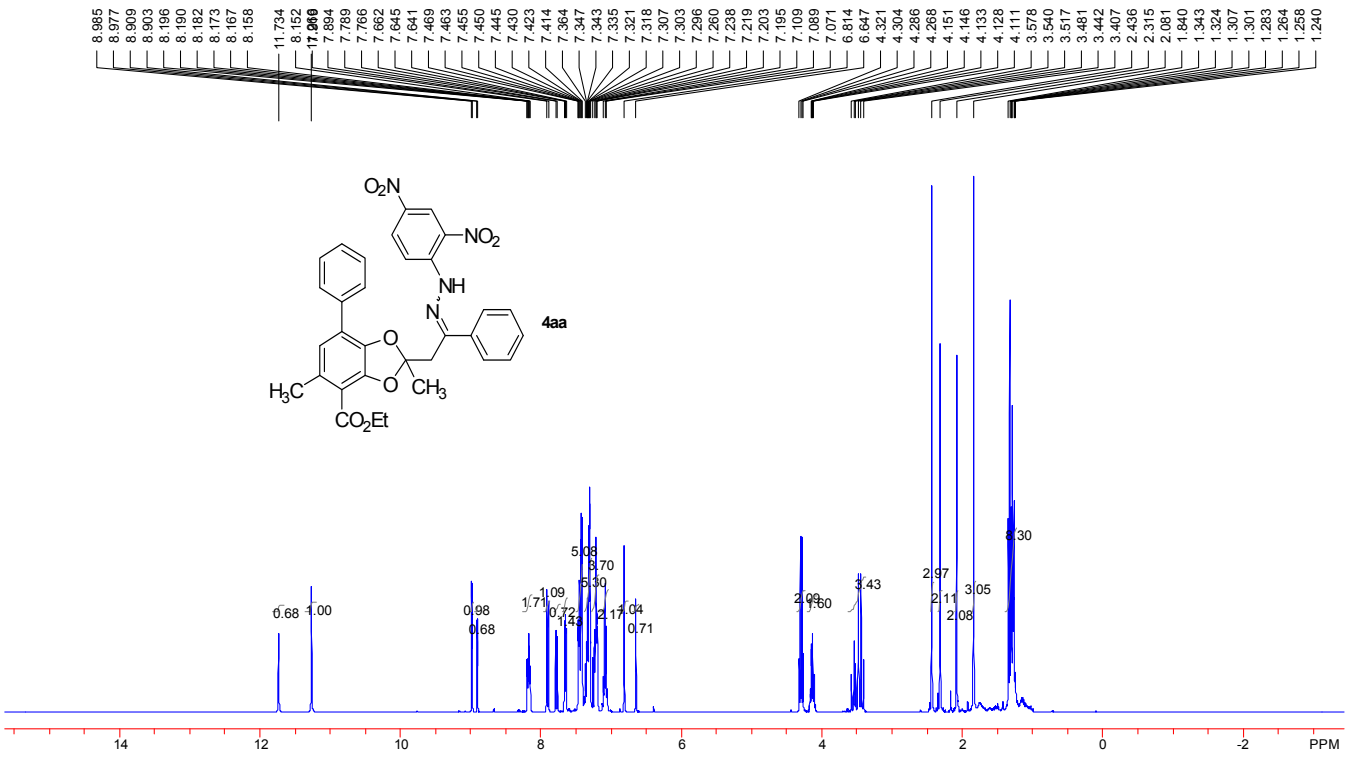

200
150
100
50
0
PPM


7.735 7.731 7.716 7.712 7.697 7.693 7.470 7.466 7.458 7.452 7.450 7.448 7.440 7.433 7.427 7.419 7.403 7.399 7.384 7.380 7.340 7.335 7.327 7.319 7.317 7.306 7.302 7.296 7.287 7.283 7.260 7.169 7.151 7.131 7.116 7.113 7.109 7.105 7.083 7.034 7.032 7.012 7.005 6.985 6.983 6.758 4.337 4.331 4.319 4.313 4.301 4.295 4.284 4.277 3.719 3.716 3.678 3.667 3.664 3.628 3.624 2.435 1.889 1.337 1.320 1.302
4m
3.30
2.24
1.06
1.11
1.08
1.03
2.12
2.07
3.10
3.12
3.31
12
10
8
6
4
2
0
PPM

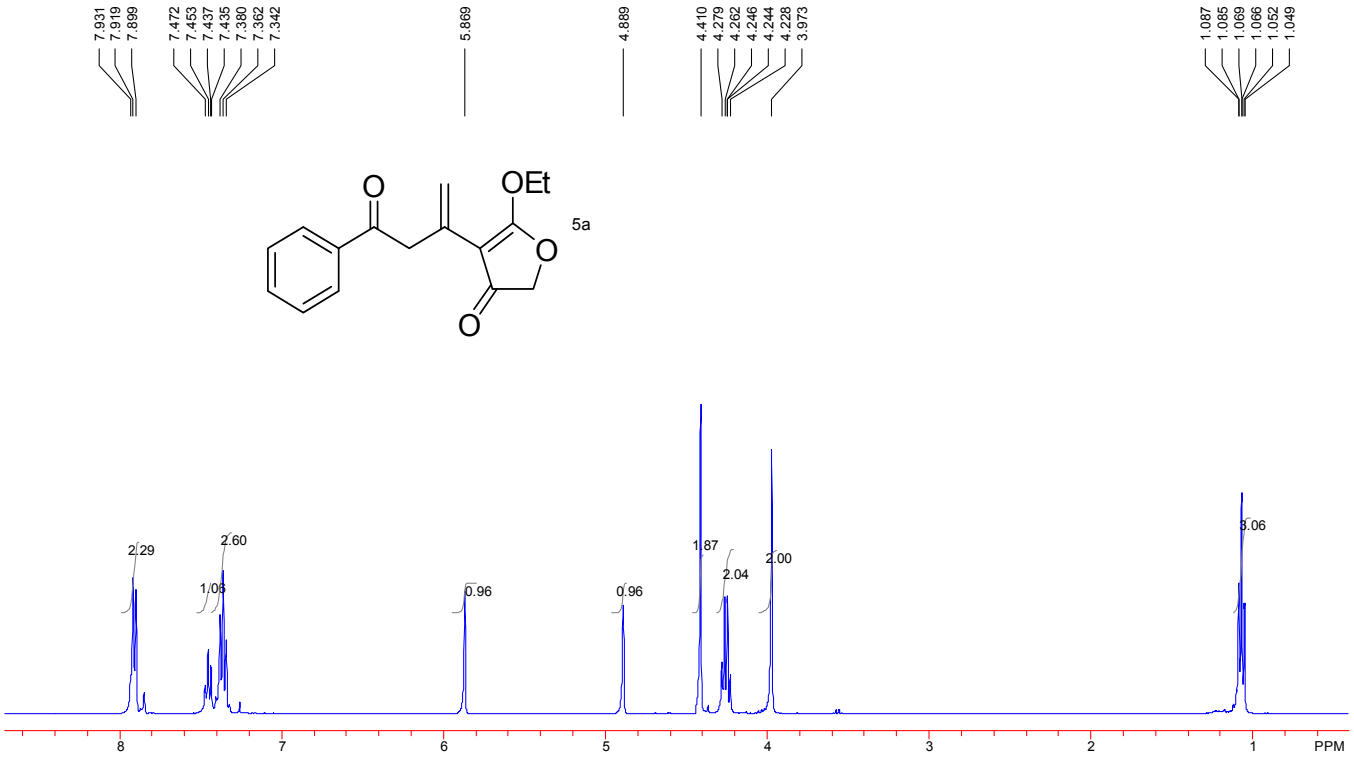

193.378 193.347 165.379 162.933 160.898 160.334 158.406 134.614 131.002 130.537 130.514 129.721 129.645 126.277 126.155 124.417 124.379 124.295 124.265 124.052 124.021 123.236 123.091 119.121 117.696 116.583 116.347 116.073 115.852 113.223 77.336 77.016 76.696 60.716 51.304 51.228 25.081 20.661 14.145
4m
200
150
100
50
0
PPM

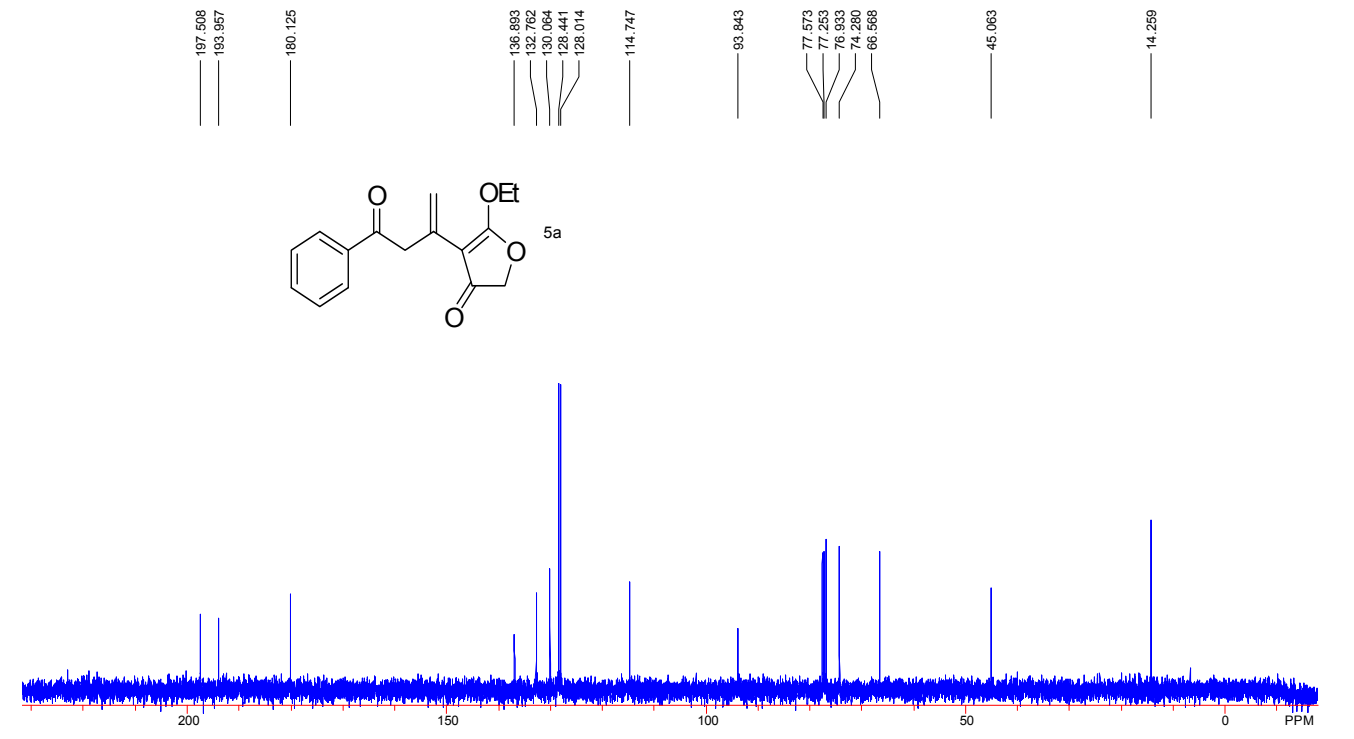


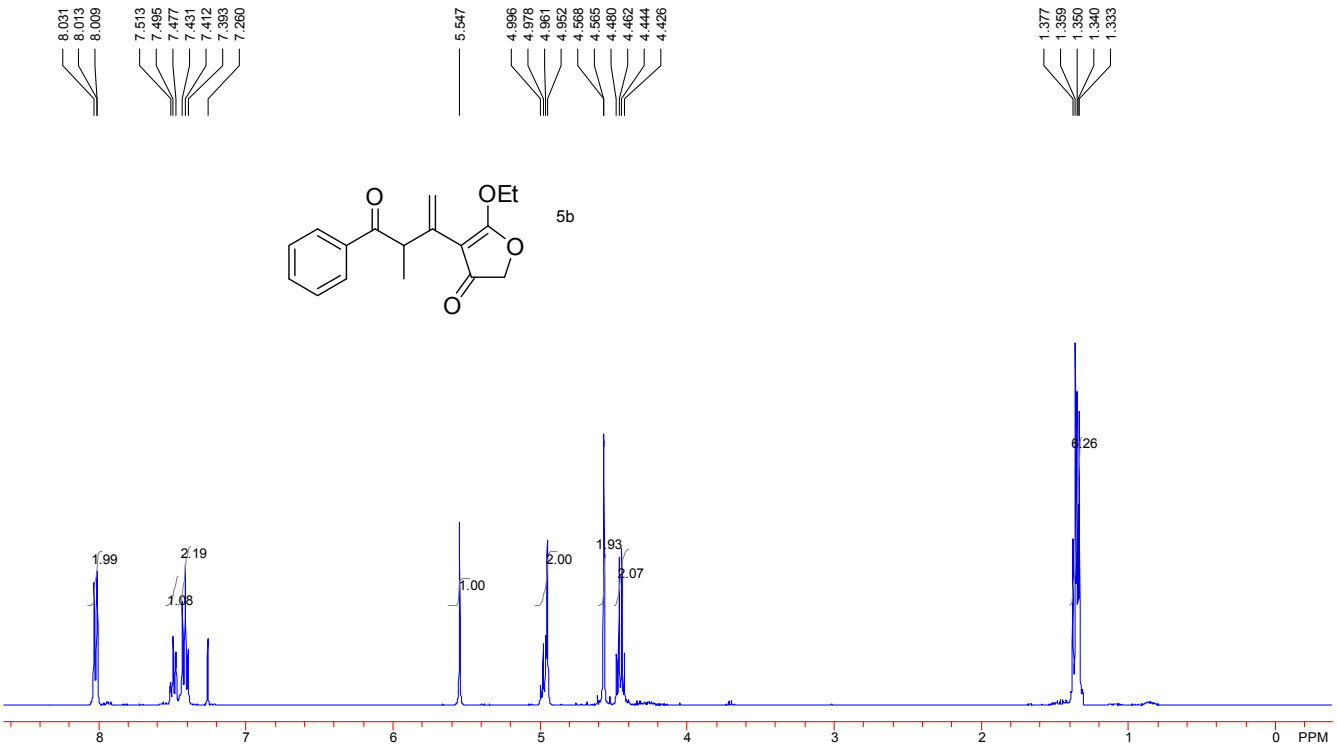


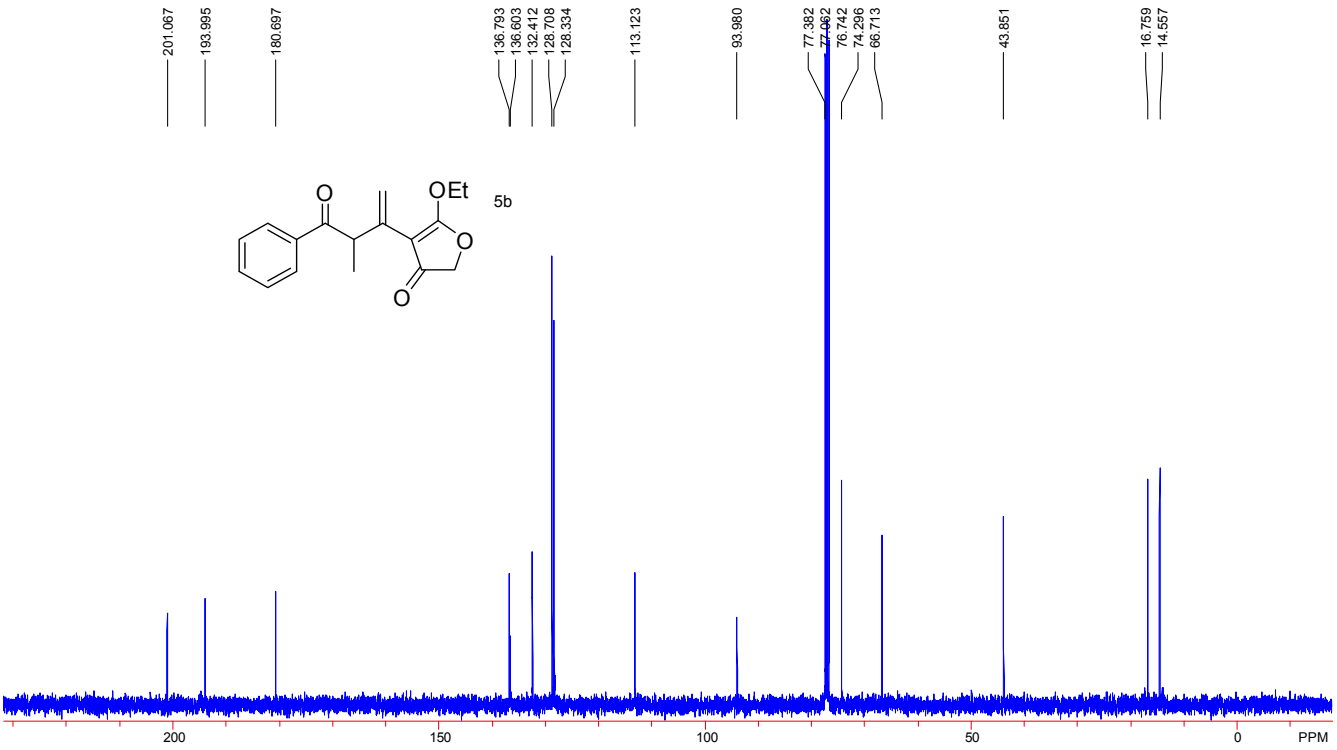


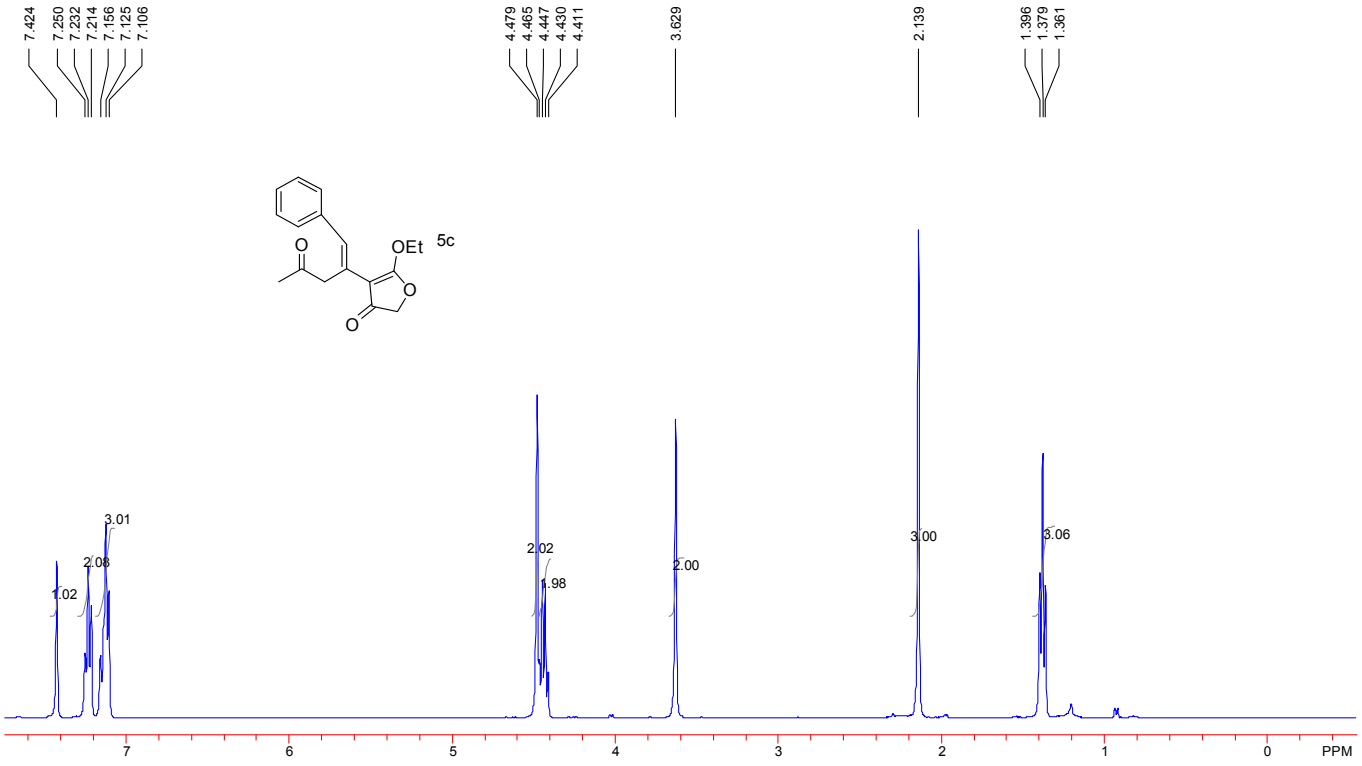
As a mixture a E/Z isomers (E/Z = 10/7)

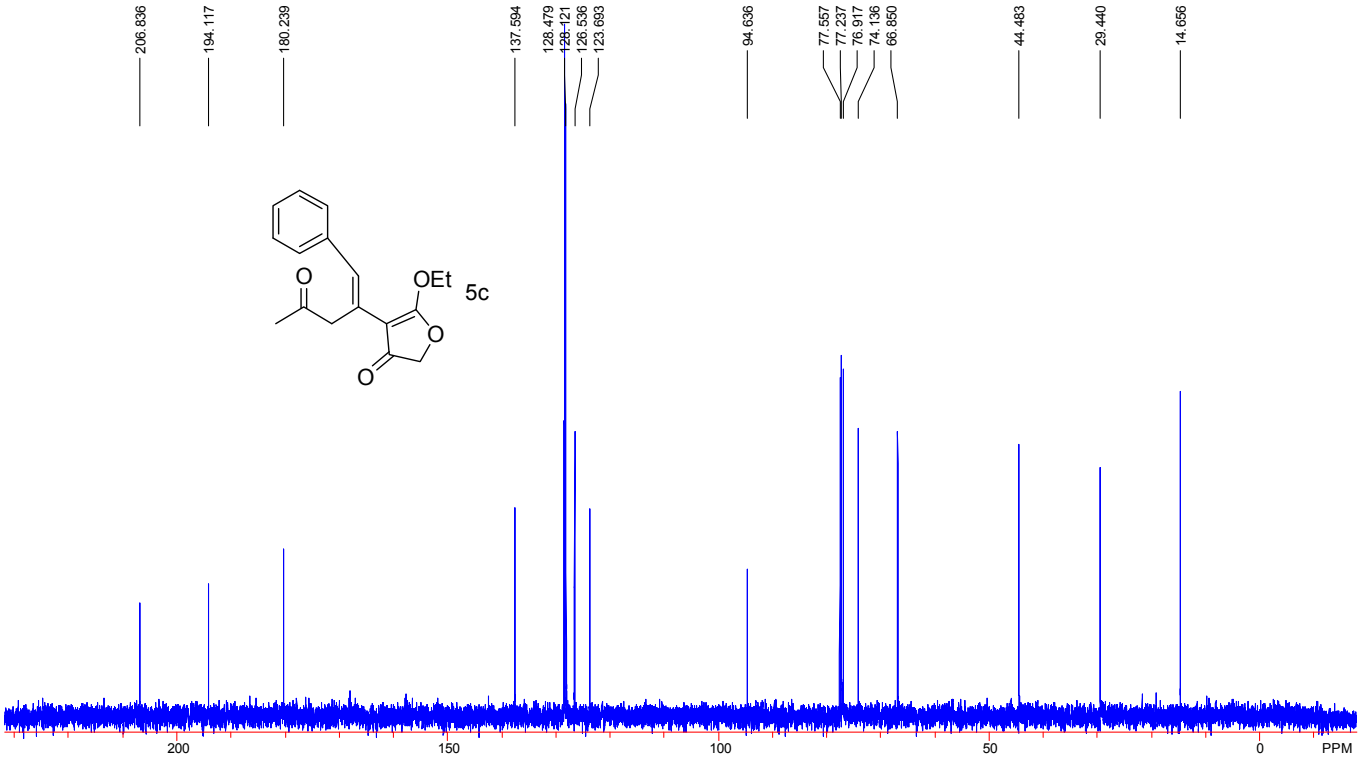


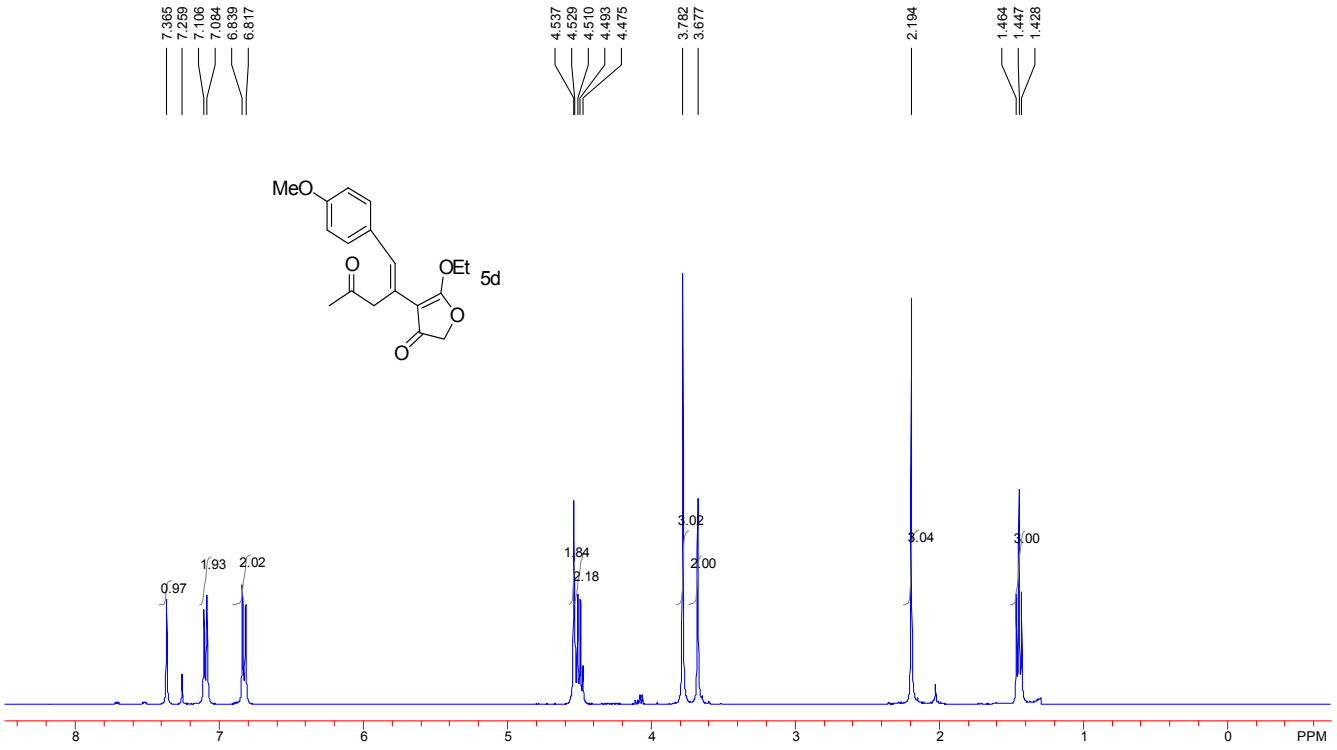


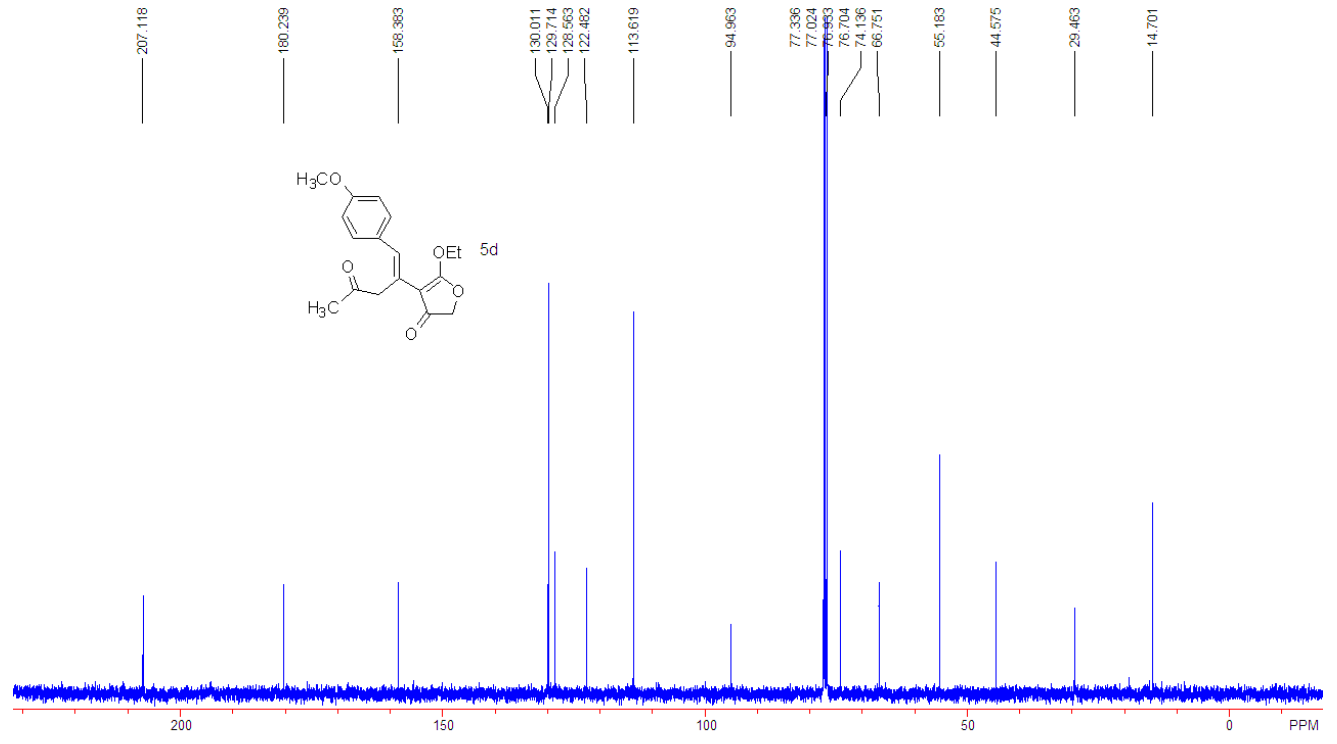


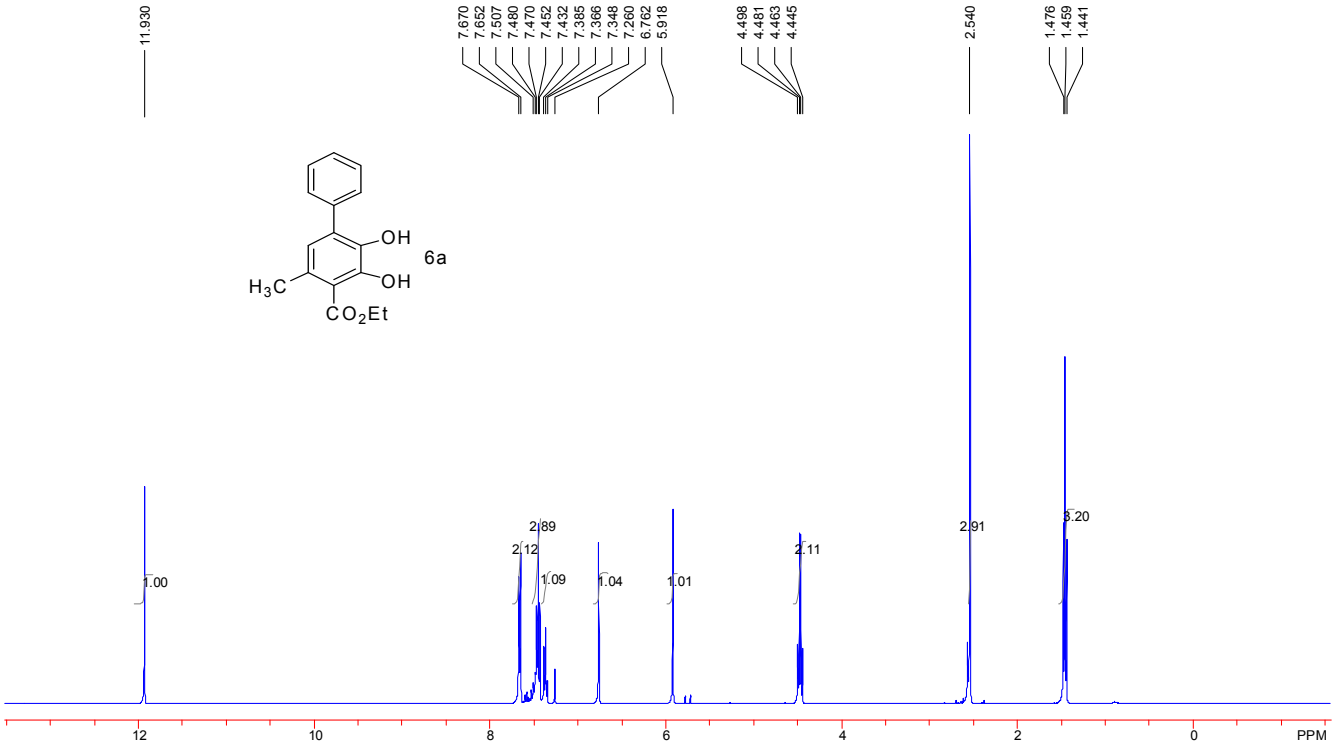


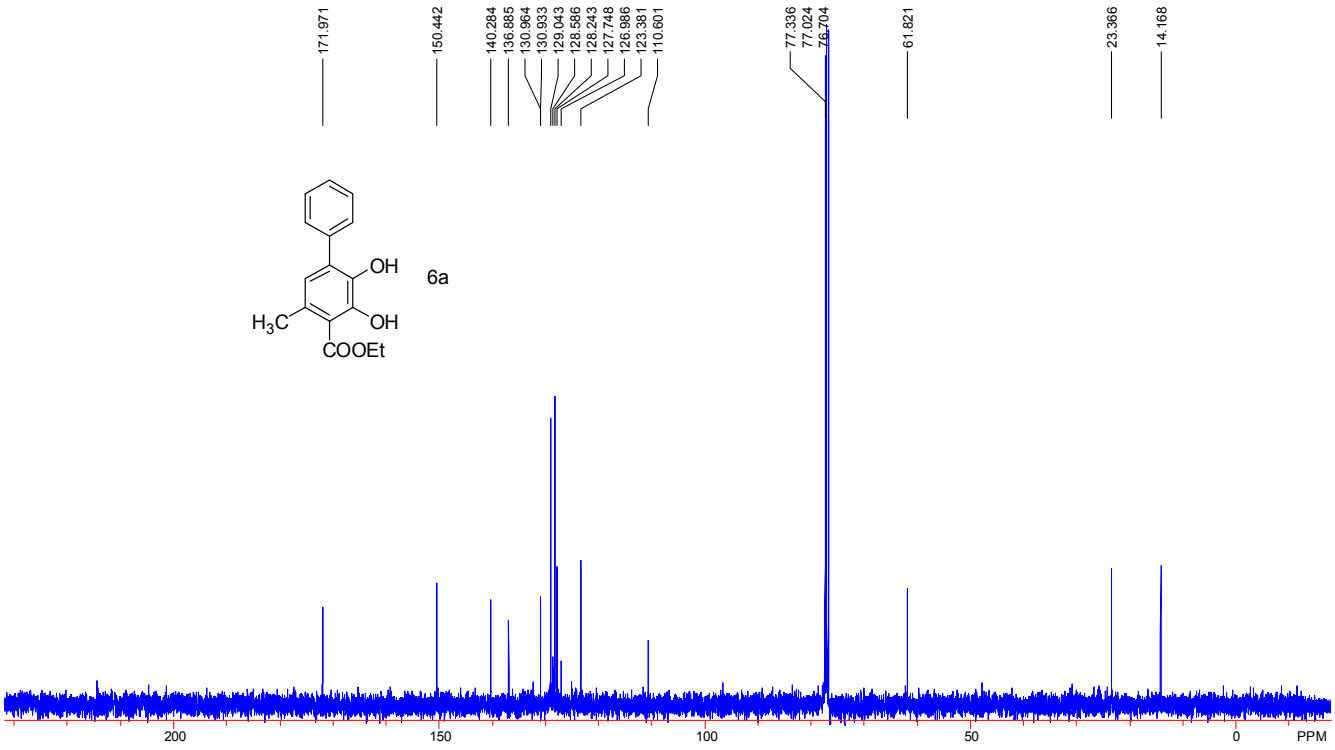








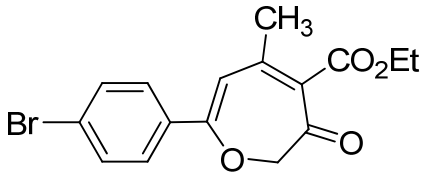

11.930
7.670
7.652
7.507
7.480
7.470
7.452
7.432
7.385
7.366
7.348
7.260
6.762
5.918
4.498
4.481
4.463
4.445
2.540
1.476
1.459
1.441
OH
OH
H3C
CO2Et
6a
1.00
2.12
2.89
1.09
1.04
1.01
2.11
2.91
3.20
12
10
8
6
4
2
0
PPM


171.971
150.442
140.284
136.885
130.964
130.933
129.043
128.586
128.243
127.748
126.986
123.381
110.601
77.336
77.024
76.704
61.821
23.366
14.168
OH
OH
H3C
COOEt
6a
200
150
100
50
0
PPM

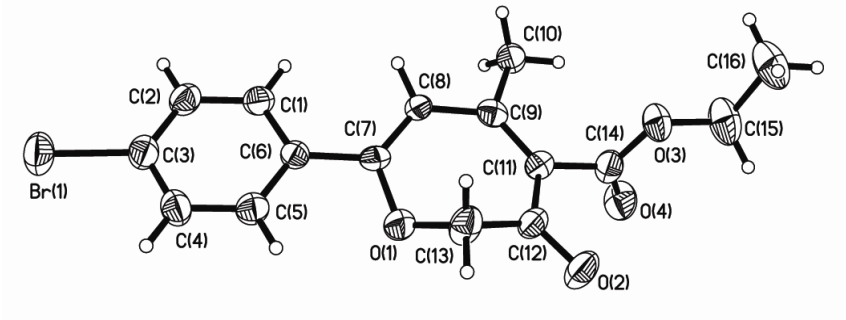
IV. X-ray crystallography

The crystallographic data (excluding structure factors) for **3f**, (*E*)-**4aa** (hydrazone of **4a)** and **5c** have been deposited at the Cambridge Crystallographic Data Centre. CCDC 892529, 913070 and 909448 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1. X-ray crystal structure of ethyl 7-(4-bromophenyl)-5-methyl-3-oxo-2,3-dihydrooxepine- 4-carboxylate (3f)

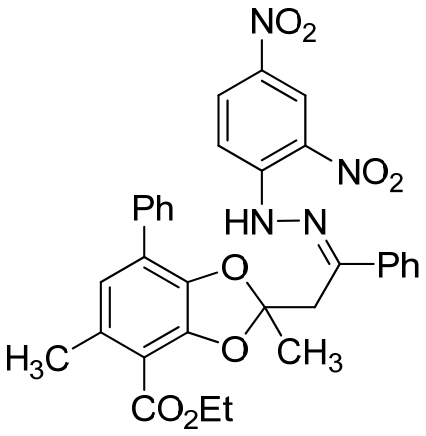


3f

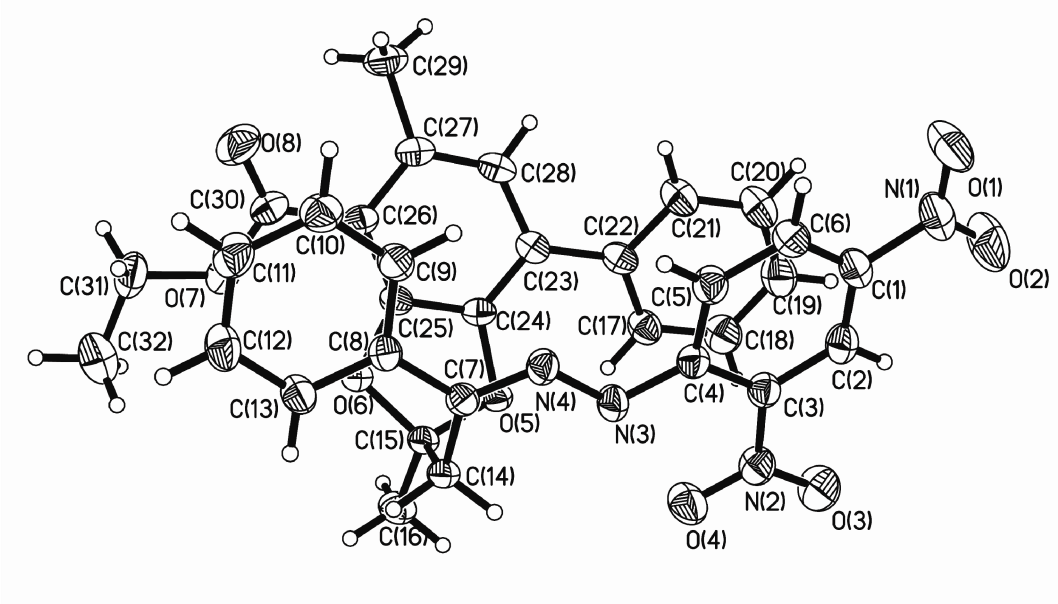


Fiure 1 The ORTEP drawing of 3f

2. X-ray crystal structure of (E)-ethyl 2-(2-(2-(2,4-dinitrophenyl)hydrazono)-2-phenylethyl)-2,5-dimethyl-7-phenylbenzo[d][1,3]dioxole-4-carboxylate (E-4aa)

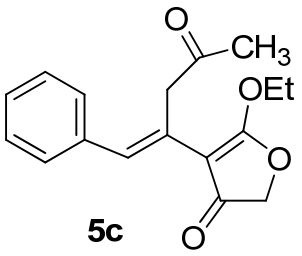


***(E)*-4aa**

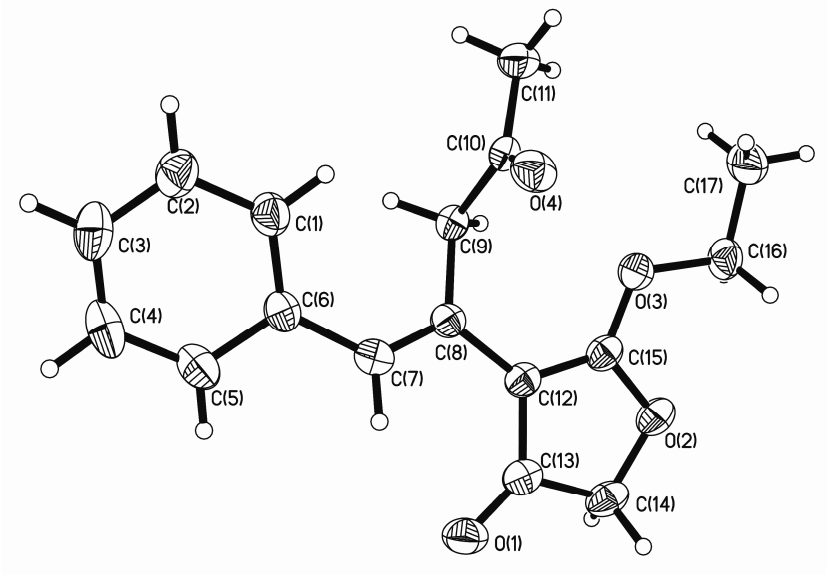


Fiure 2 The ORTEP drawing of (E)-4aa

3. X-ray crystal structure of 5-Ethoxy-4-(4-oxo-1-phenylpent-1-en-2-yl)furan-3(2H)-one (5c)



5c



Fiure 3 The ORTEP drawing of 5c

V. References

(1) A. Sniady, M. S. Morreale, R. Dembinski, *Org. Synth.,* **2007**, *84*, 199-208.

(2) W. Wu, Z. Yao, Y. Li, J. Li, Y. Xia, Y. Wu, *J. Org. Chem.*, **1995**, *60*, 3257-3259.

(3) N. A. Petasis, K. A. Teets, *J. Am. Chem. Soc.,* **1992**, *114,* 10328-10334.