Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Ozonation of Methylenecyclopropanes

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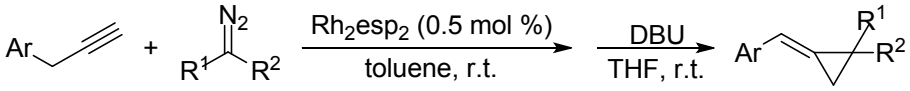
CONTENTS

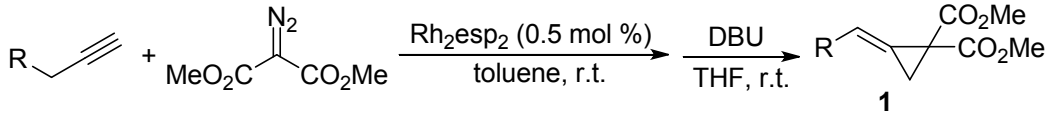
General remarks. ^{1}H and ^{13}C NMR spectra were recorded at 400 (or 300) MHz, respectively. HRMS spectra were recorded by EI or ESI method. The employed solvents were dry up by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

General Procedure for the Preparation of Substrates 1a-1k and 2a-2j.[1]

The preparation of MCPs 1a-1i, 1k and 2a-2i.



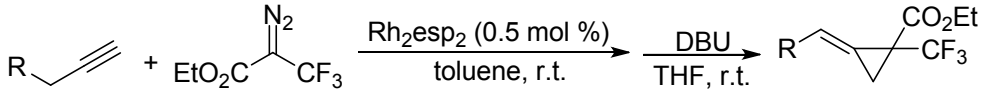
Under an argon atmosphere, to a solution of alkyne (2.0 mmol, 1.0 equiv) and catalyst $Rh_2(esp)_2$ (8 mg, 0.01 mmol, 0.005 equiv) in toluene (5.0 mL) was added dropwise a solution of diazo-compounds (6.0 mmol, 3.0 equiv) in toluene (10.0 mL) over 10 h at room temperature. After the resulting mixtures were stirred for 4 h, the solvent was removed under reduced pressure, then THF (2.0 mL) and DBU (0.6 mmol, 3.0 eq) was added at rt. After stirring for five hours, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products **1a-1i, 1k** and **2a-2i**.



1

entry[a]	R	**1**, yield/%[b]
1	Ph	**1a**, 89
2	4-BrC_6H_4	**1b**, 95
3	4-ClC_6H_4	**1c**, 92
4	4-MeC_6H_4	**1d**, 86
5	3-MeC_6H_4	**1e**, 90
6	2-MeC_6H_4	**1f**, 85
7	4-$MeOC_6H_4$	**1g**, 67
8	2-naphthyl	**1h**, 47
9	3,5-$Me_2C_6H_3$	**1i**, 96
10	3,5-$Br_2C_6H_3$	**1k**, 14

[a] Under an argon atmosphere, to a solution of alkyne (2.0 mmol, 1.0 equiv) and catalyst $Rh_2(esp)_2$ (8 mg, 0.01 mmol, 0.005 equiv) in toluene (5.0 mL) was added dropwise a solution of diazo-compounds (6.0 mmol, 3.0 equiv) in toluene (10.0 mL) over 10 h at room temperature. After the resulting mixtures were stirred for 4 h, the solvent was removed under reduced pressure, then THF (2.0 mL) and DBU (0.6 mmol, 3.0 eq) was added at rt. The resulting mixtures were stirred for 5 hours. [b] Isolated yields.

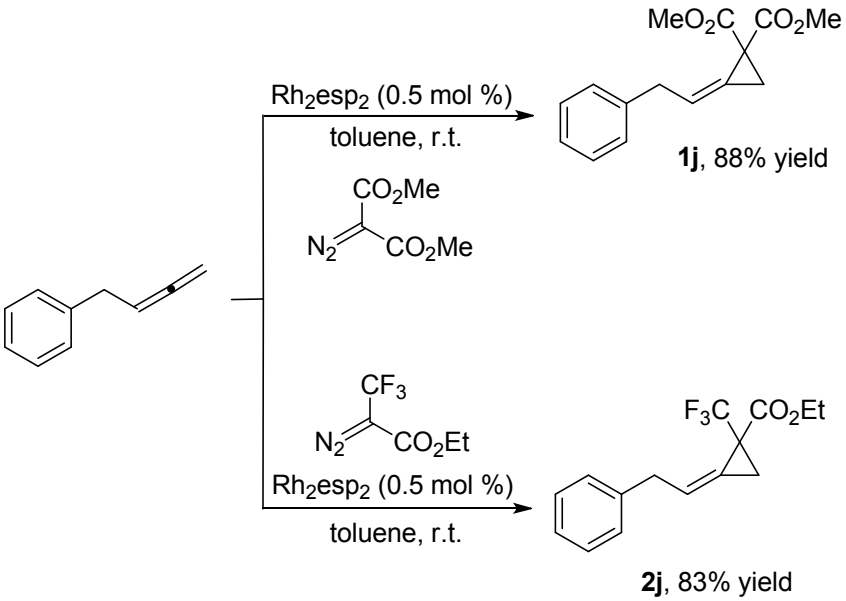


2

entry[a]	R	**2**, yield/%[b]
1	Ph	**2a**, 92
2	4-BrC_6H_4	**2b**, 90
3	4-ClC_6H_4	**2c**, 96
4	4-MeC_6H_4	**2d**, 89
5	3-MeC_6H_4	**2e**, 86
6	2-MeC_6H_4	**2f**, 91
7	4-MeOC_6H_4	**2g**, 89
8	2-naphthyl	**2h**, 89
9	3,5-$Me_2C_6H_3$	**2i**, 94

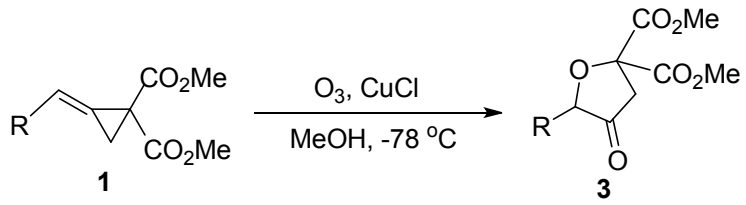
[a] Under an argon atmosphere, to a solution of alkyne (2.0 mmol, 1.0 equiv) and catalyst $Rh_2(esp)_2$ (8 mg, 0.01 mmol, 0.005 equiv) in toluene (5.0 mL) was added dropwise a solution of diazo-compounds (6.0 mmol, 3.0 equiv) in toluene (10.0 mL) over 10 h at room temperature. After the resulting mixtures were stirred for 4 h, the solvent was removed under reduced pressure, then THF (2.0 mL) and DBU (0.6 mmol, 3.0 eq) was added at rt. The resulting mixtures were stirred for 5 hours. [b] Isolated yields.

General Procedure for the Preparation of MCPs 1j and 2j.



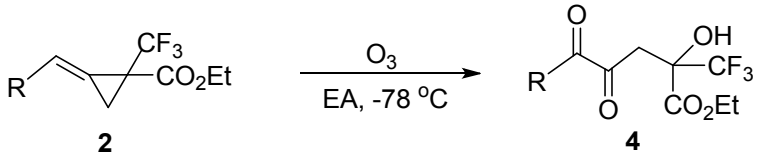
The two compounds were prepared according to the previous literature.[2]

General Procedure for the Ozonation of MCPs 1



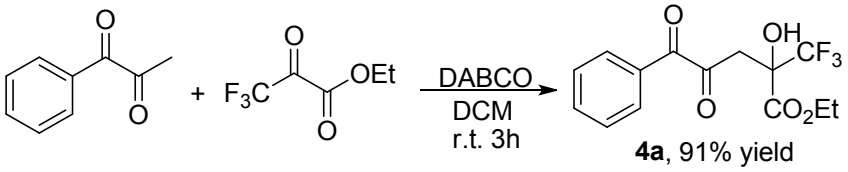
MCP **1** (0.5 mmol, 1 equiv) was dissolved in 5 mL MeOH at -78 °C, and then O_3 was slowly bubbled until the solvent became blue. CuCl (2 equiv) was added at -78 °C and the reaction mixture was naturally returned to room temperature with stirring and was further stirred for 5 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products **3a-3j**.

General procedure for the Ozonation of MCPs 2



MCP **2** (1.0 mmol, 1 equiv) was dissolved in 5 mL EA at -78 °C, and then O_3 was slowly bubbled until the solvent became blue. The reaction mixture was naturally returned to r.t. with stirring and was further stirred for 5 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products **4a-4j and 3j'**.

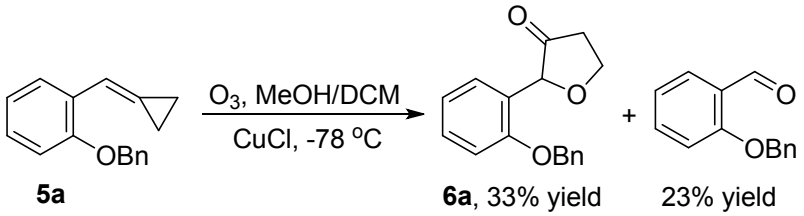
General Procedure for the Determination of the Structure of 4a.

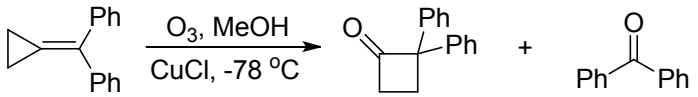


DABCO (3.0 mmol, 3.0 equiv) was dissolved in 10 mL DCM at 0 °C, and then ethyl 3,3,3-trifluoro-2-oxopropanoate (0.5 mmol, 1 equiv) and 1-phenylpropane-1,2-dione (3.0 mmol, 3.0

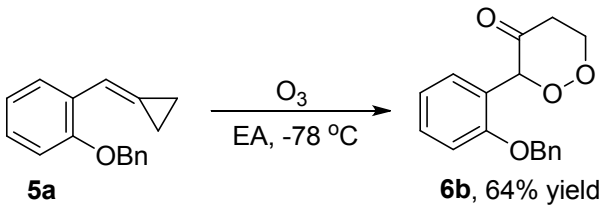
equiv) was added to the stirred reaction solution. The reaction mixture was naturally returned to r.t., and was further stirred for 3 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **4a**.

General Procedure for the Ozonation of MCPs 5a[3] and 5b[4]



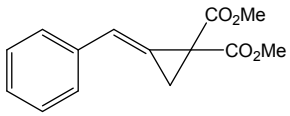


MCP **5** (1.0 mmol, 1.0 equiv) was dissolved in 5 mL MeOH at -78 °C, and then O_3 was slowly bubbled until the solvent became blue. CuCl (2.0 equiv) was added at -78 °C and the reaction mixture was naturally returned to room temperature with stirring and was further stirred for 5 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products **6a** and **6c**[5].



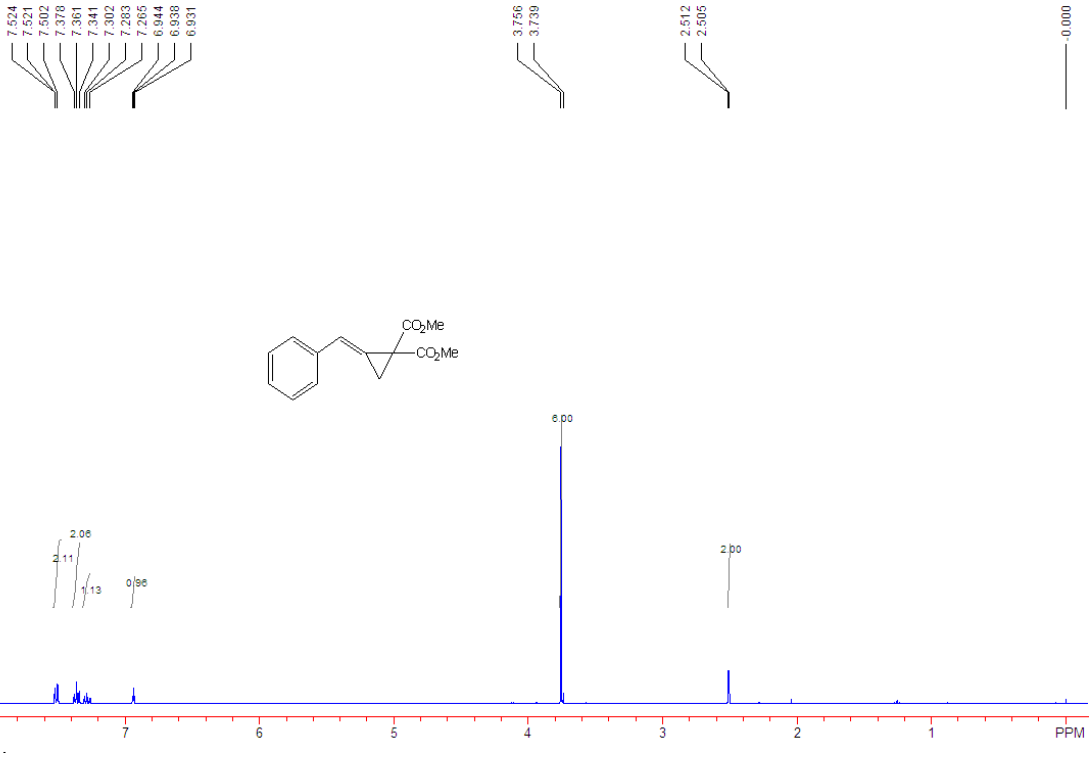
MCP **5a** (1.0 mmol, 1 equiv) was dissolved in 5 mL EA at -78 °C, and then O_3 was slowly bubbled until the solvent became blue. The reaction mixture was naturally returned to r.t. with stirring and was further stirred for 5 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **6b**.

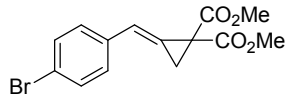
Spectroscopic Data and Charts of Compounds 1-9



Compound **1a** is a known compound and was synthesized according to the Previous literature procedure.[1]

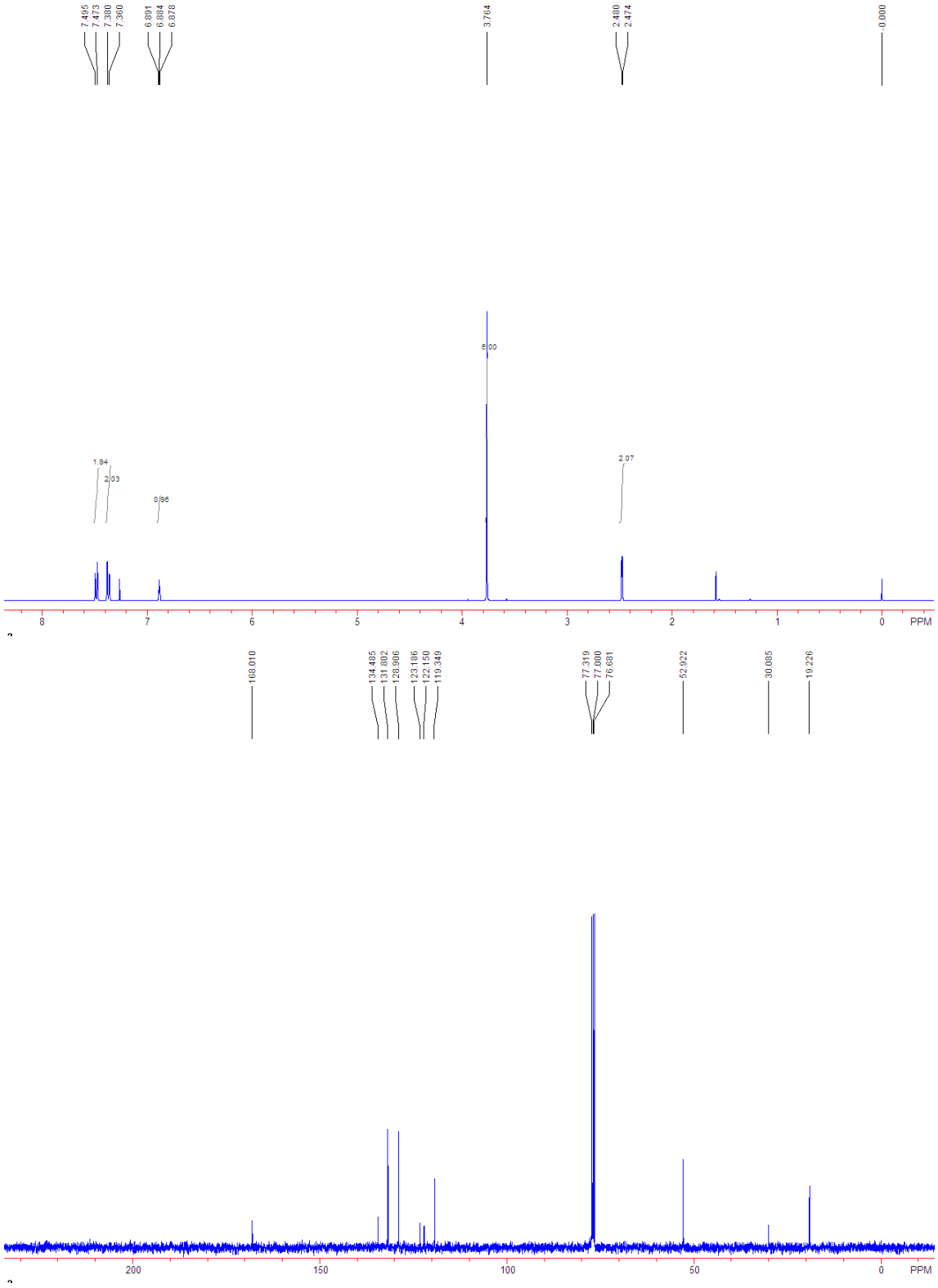
(E)-dimethyl 2-benzylidenecyclopropane-1,1-dicarboxylate **1a**: a light yellow oil. 44.1 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.51 (d, J = 3.2 Hz, 2H), 3.76 (s, 6H), 6.94 (t, J = 2.4 Hz, 1H), 7.27-7.30 (m, 1H), 7.34-7.38 (m, 2H), 7.50-7.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.31, 29.96, 52.79, 120.26, 122.37, 127.41, 128.16, 128.60, 135.47, 168.19. IR (ATR) ν 3062, 3026, 3007, 2956, 2846, 1731, 1436, 1264, 1104, 694 cm^{-1}. HRMS (ESI) calcd for [$C_{14}H_{14}O_4$+H] requires 247.0970, found 247.0973 [M^++H].

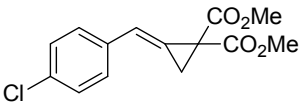




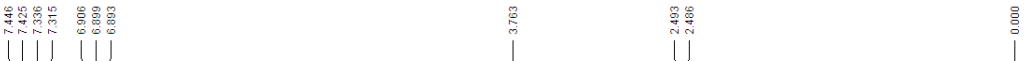
(E)-dimethyl 2-(4-bromobenzylidene)cyclopropane-1,1-dicarboxylate **1b**: a light yellow oil. 618.2 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.48 (d, J = 2.4 Hz, 2H), 3.76 (s,

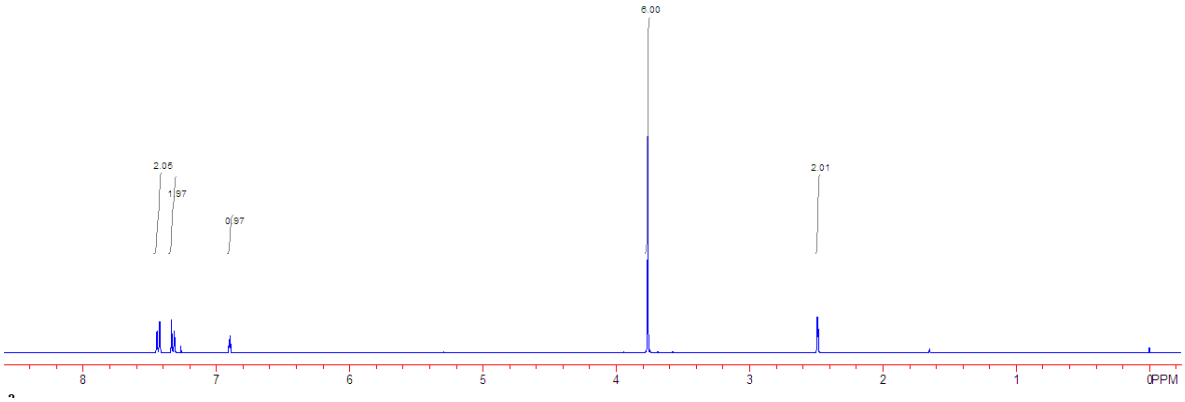
6H), 6.88 (t, J = 2.4 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.23, 30.09, 52.92, 119.35, 122.15, 123.19, 128.91, 131.80, 134.49, 168.01. IR (ATR) ν 2923, 1734, 1436, 1275, 1261, 1106, 764, 750 cm^{-1}. HRMS (ESI) calcd for [$C_{14}H_{13}BrO_4$+Na] requires 346.9889, found 346.9884 [M^++Na].

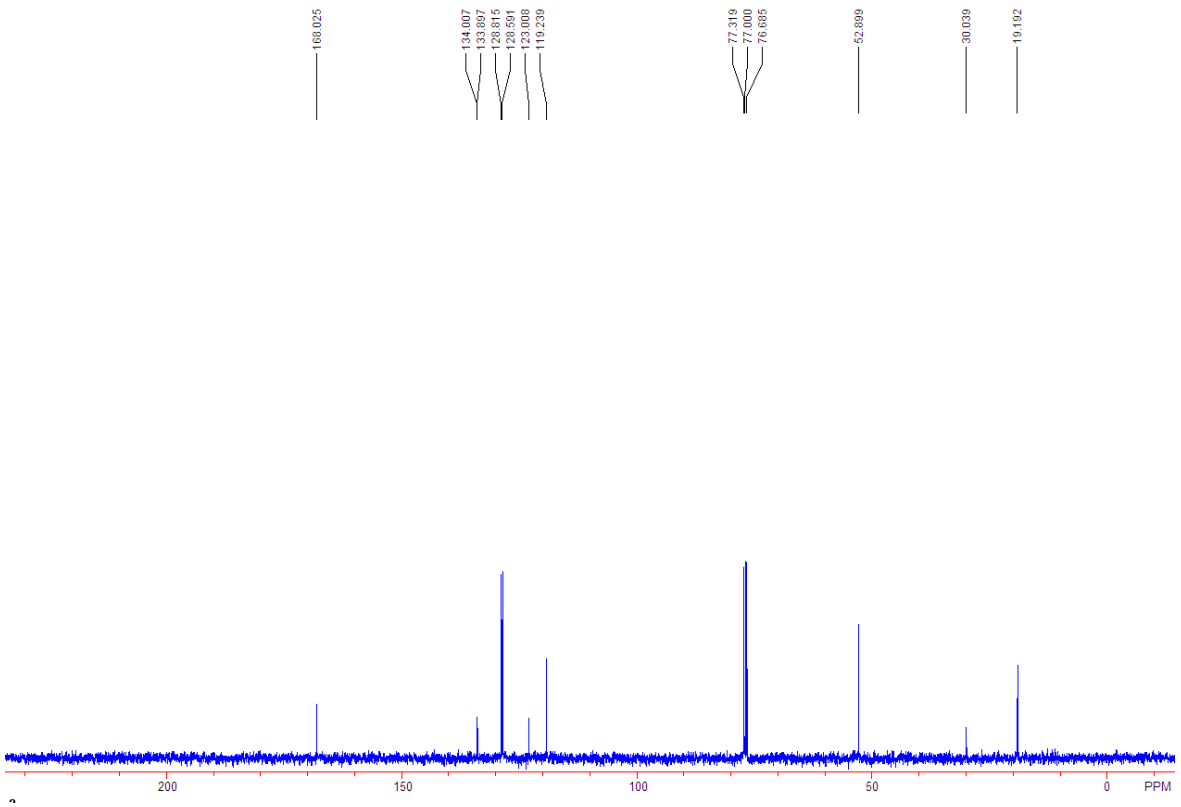


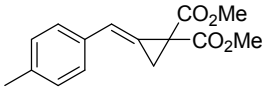


(E)-dimethyl 2-(4-chlorobenzylidene)cyclopropane-1,1-dicarboxylate **1c**: a light yellow oil. 589.7 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.49 (d, J = 2.8 Hz, 2H), 3.76 (s, 6H), 6.90 (t, J = 2.8 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.19, 30.04, 52.90, 119.24, 123.01, 128.59, 128.82, 133.90, 134.01, 168.03. IR (ATR) ν 2955. 2921, 1734, 1492, 1457, 1436, 1311, 1281, 1258, 1106, 1012, 820 cm^{-1}. HRMS (ESI) calcd for [$C_{14}H_{13}ClO_4$+Na] requires 303.0395, found 303.0392 [M^++Na].

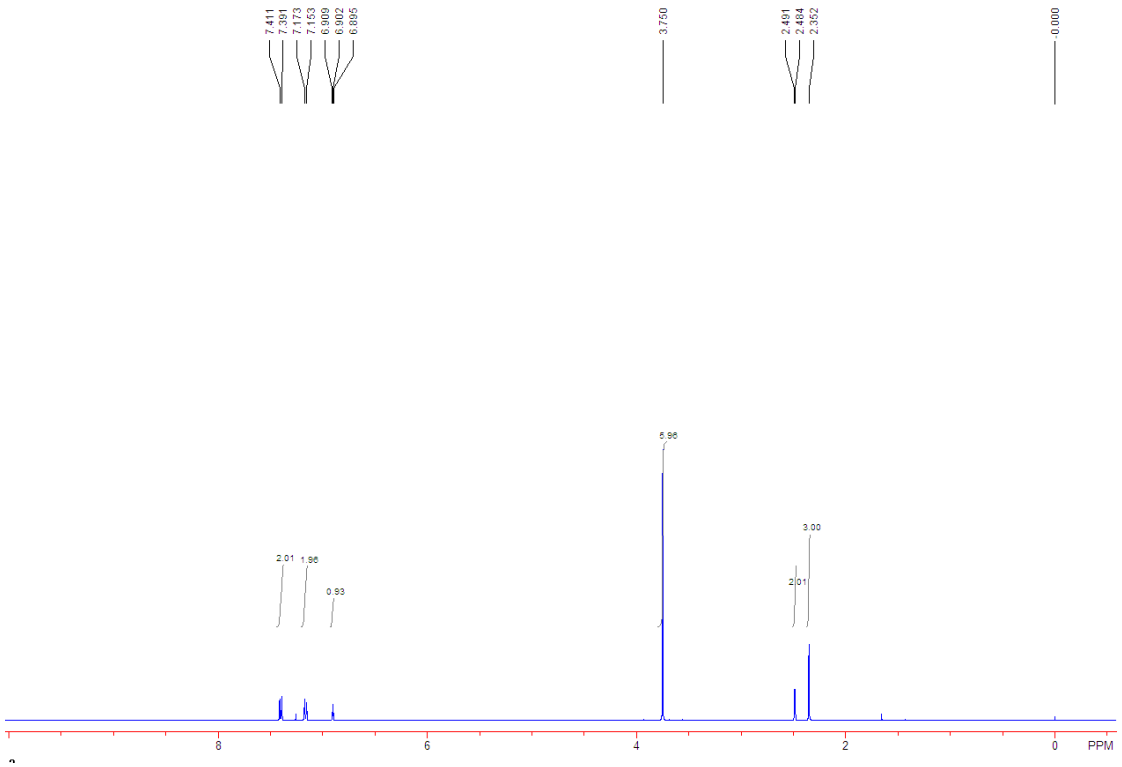


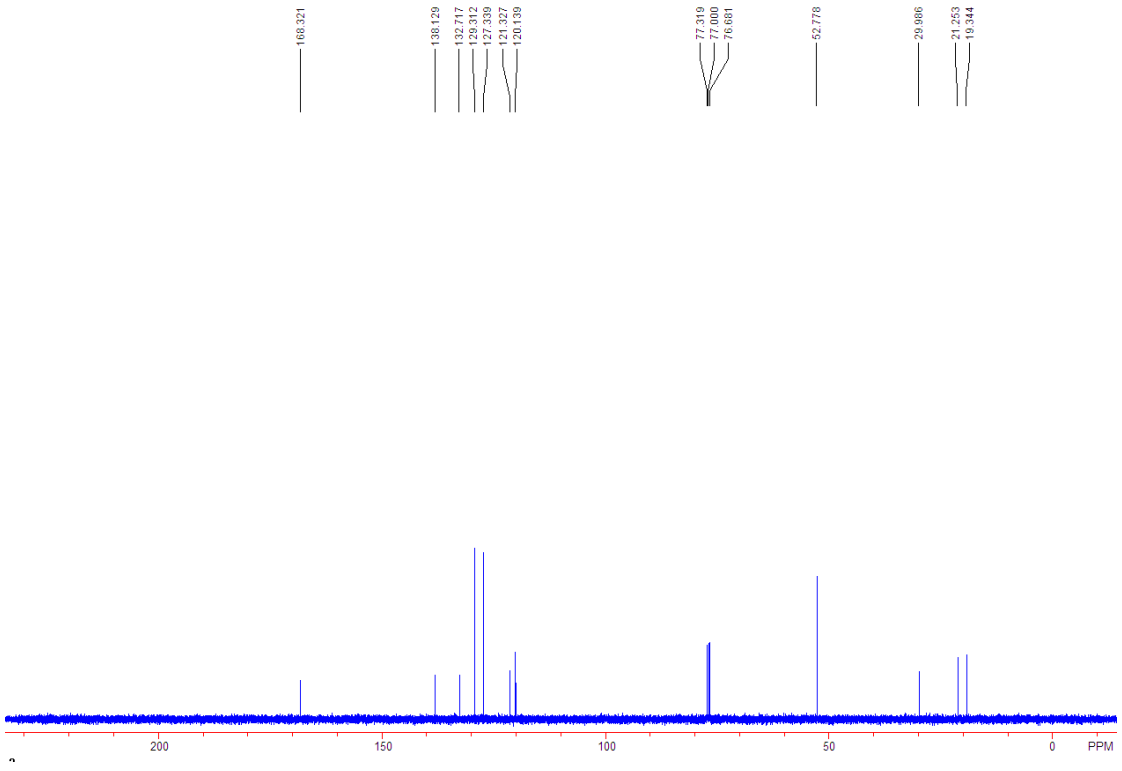


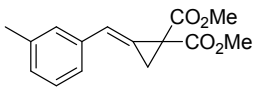




(E)-dimethyl 2-(4-methylbenzylidene)cyclopropane-1,1-dicarboxylate **1d**: a light yellow oil. 1.3475 g, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.35 (s, 3H), 2.49 (d, J = 3.2 Hz, 2H), 3.75 (s, 6H), 6.90 (t, J = 3.2 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.34, 21.25, 29.99, 52.78, 120.14, 121.33, 127.34, 129.34, 132.72, 138.13, 168.32. IR (ATR) ν 2955, 1735, 1507, 1437, 1275, 1261, 1107, 814, 764, 750 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{16}O_4$+H] requires 261.1121, found 261.1119 [M^++H].

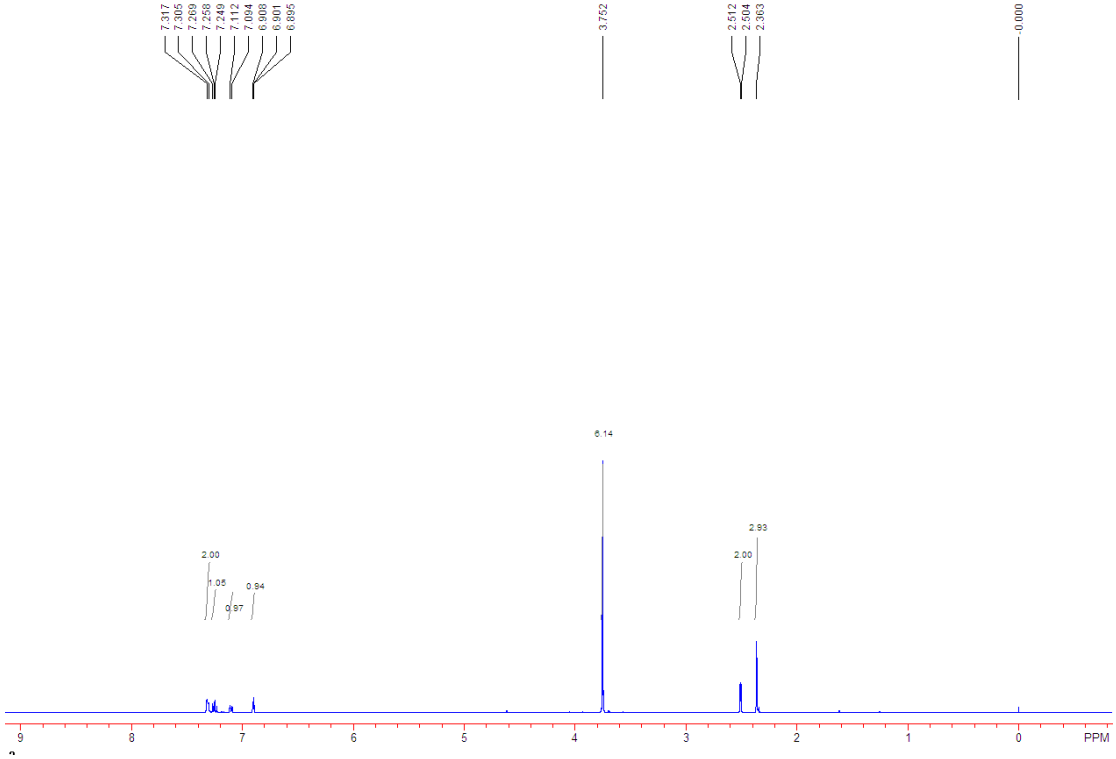


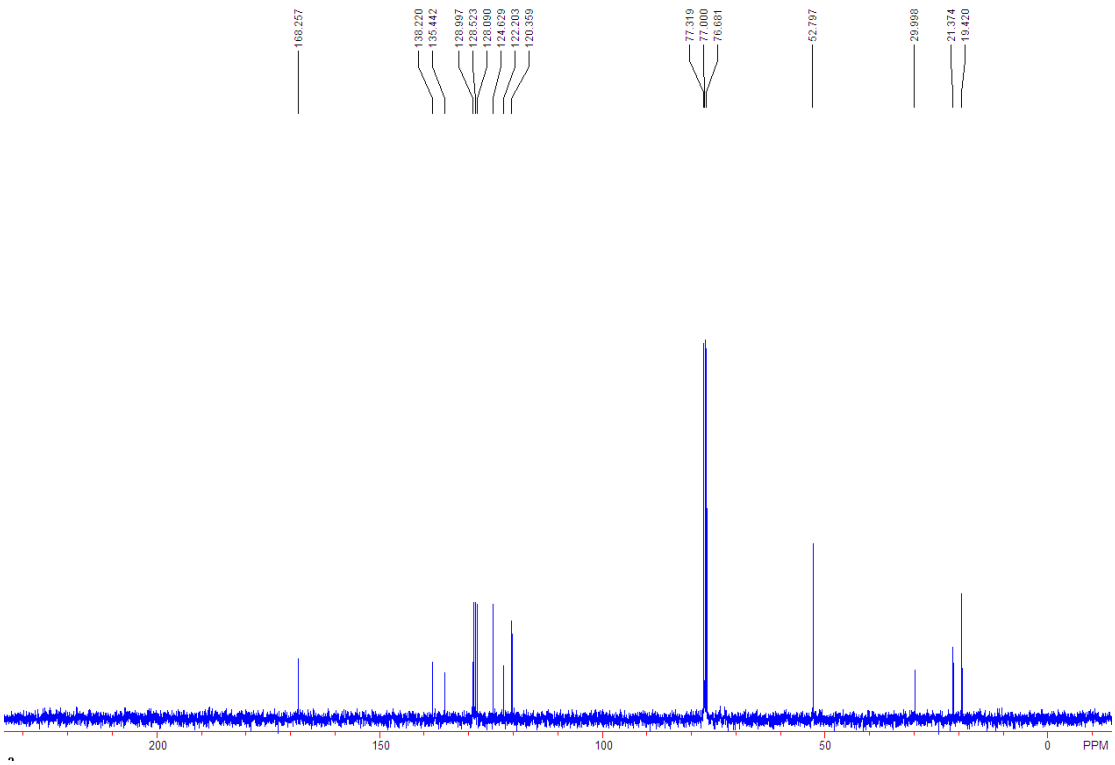


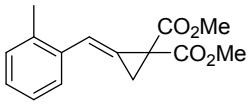


(E)-dimethyl 2-(3-methylbenzylidene)cyclopropane-1,1-dicarboxylate **1e**: a light yellow oil.

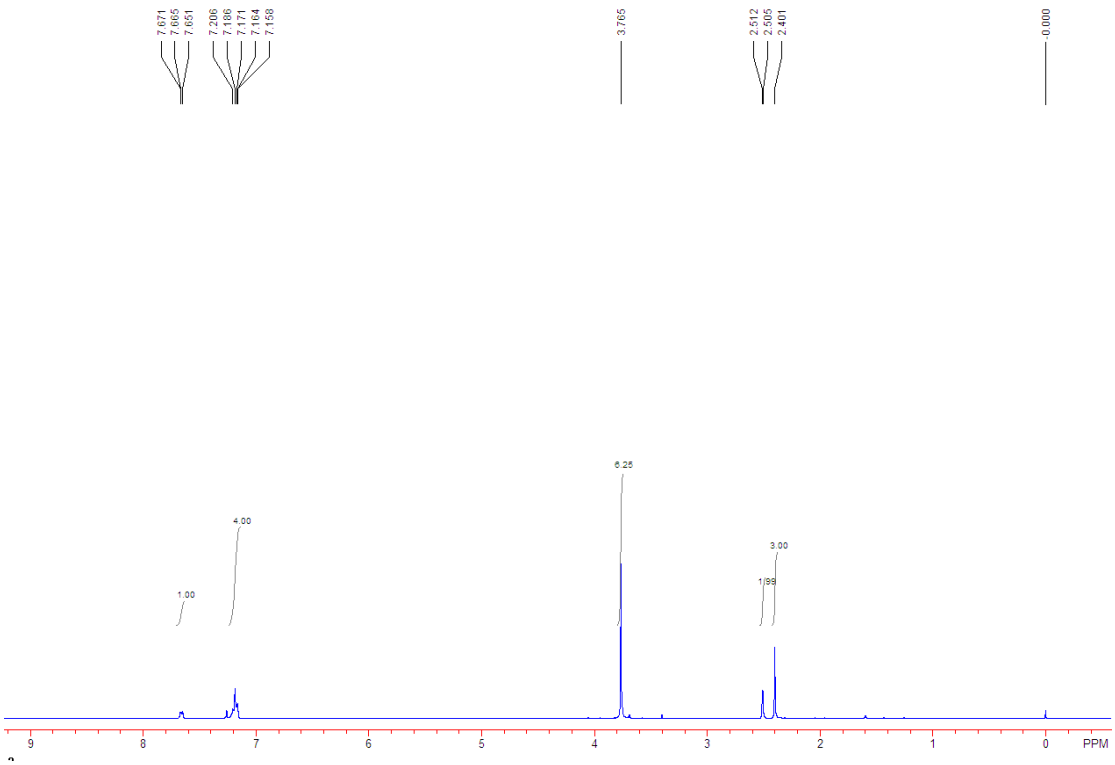
1.0538 g, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.36 (s, 3H), 2.51 (d, J = 2.4 Hz, 2H), 3.75 (s, 6H), 6.90 (t, d, J = 2.4 Hz, 1H), 7.09-7.11 (m, 1H), 7.25-7.27 (m, 1H), 7.31-7.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.42, 21.37, 30.00, 52.80, 120.36, 122.20, 124.63, 128.09, 128.52, 129.00, 135.44, 138.22, 168.26. IR (ATR) ν 3853, 3649, 2955, 1734, 1605, 1559, 1507, 1436, 1311, 1275, 1261, 1193, 1106, 764, 750, 693 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{16}O_4$+H] requires 261.1121, found 261.1119 [M^++H].

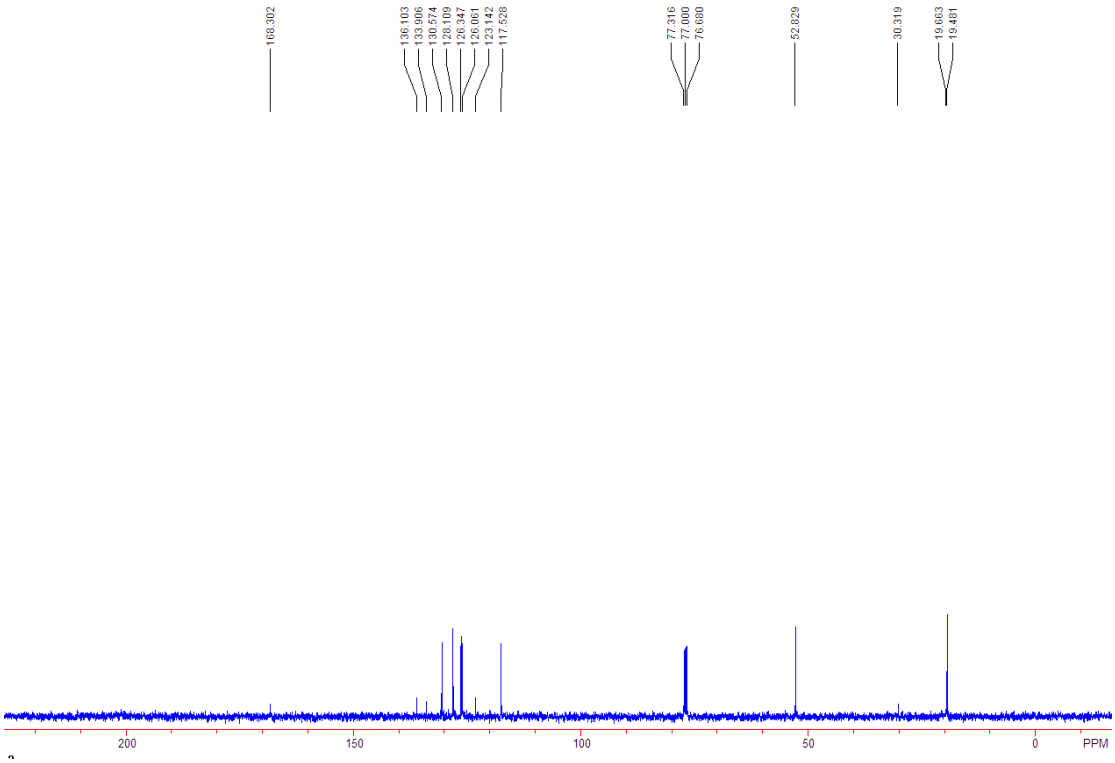


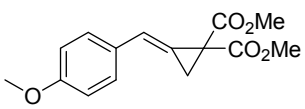




(E)-dimethyl 2-(2-methylbenzylidene)cyclopropane-1,1-dicarboxylate **1f**: a light yellow oil. 442.5 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.40 (s, 3H), 2.51 (d, J = 2.8 Hz, 2H), 3.77 (s, 6H), 7.16-7.21 (m, 4H), 7.65-7.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.48, 19.66, 30.32, 52.83, 117.53, 123.14, 126.06, 126.35, 128.11, 130.57, 133.91, 136.10, 168.30. IR (ATR) ν 2954, 2921, 1732, 1559, 1507, 1436, 1310, 1275, 1261, 1192, 1147, 1106, 888, 764, 750 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{16}O_4$+Na] requires 283.0941, found 283.0944 [M^++Na].

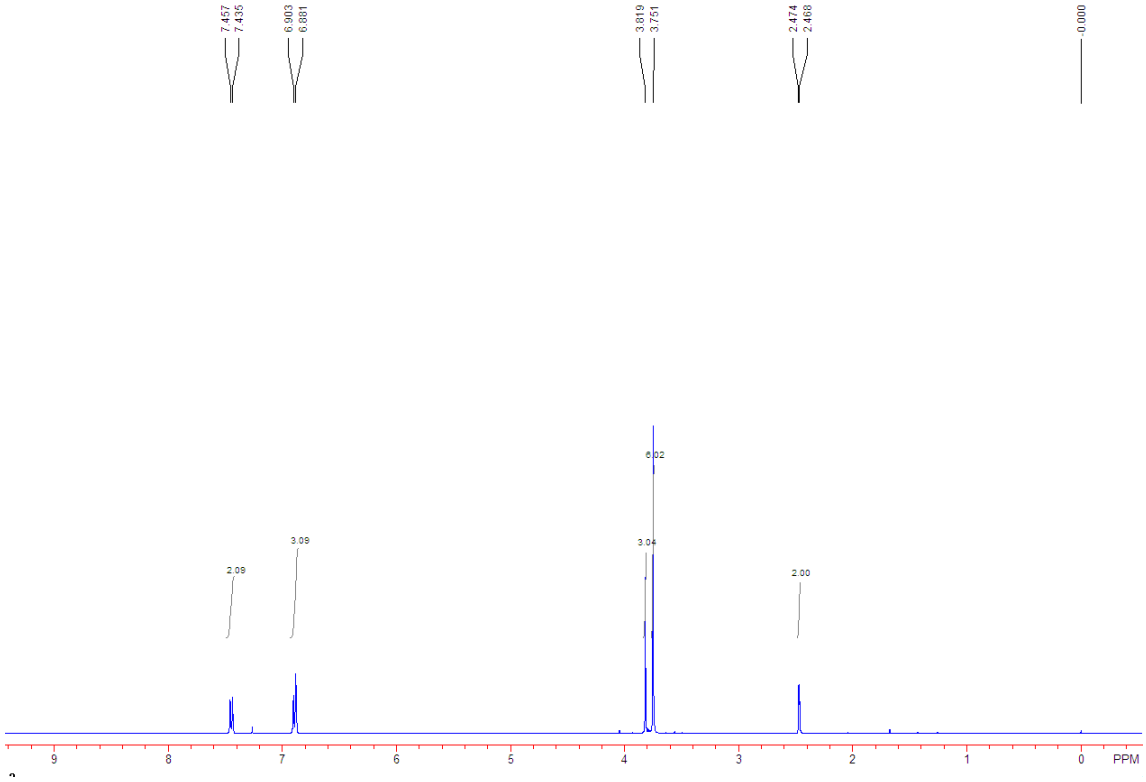


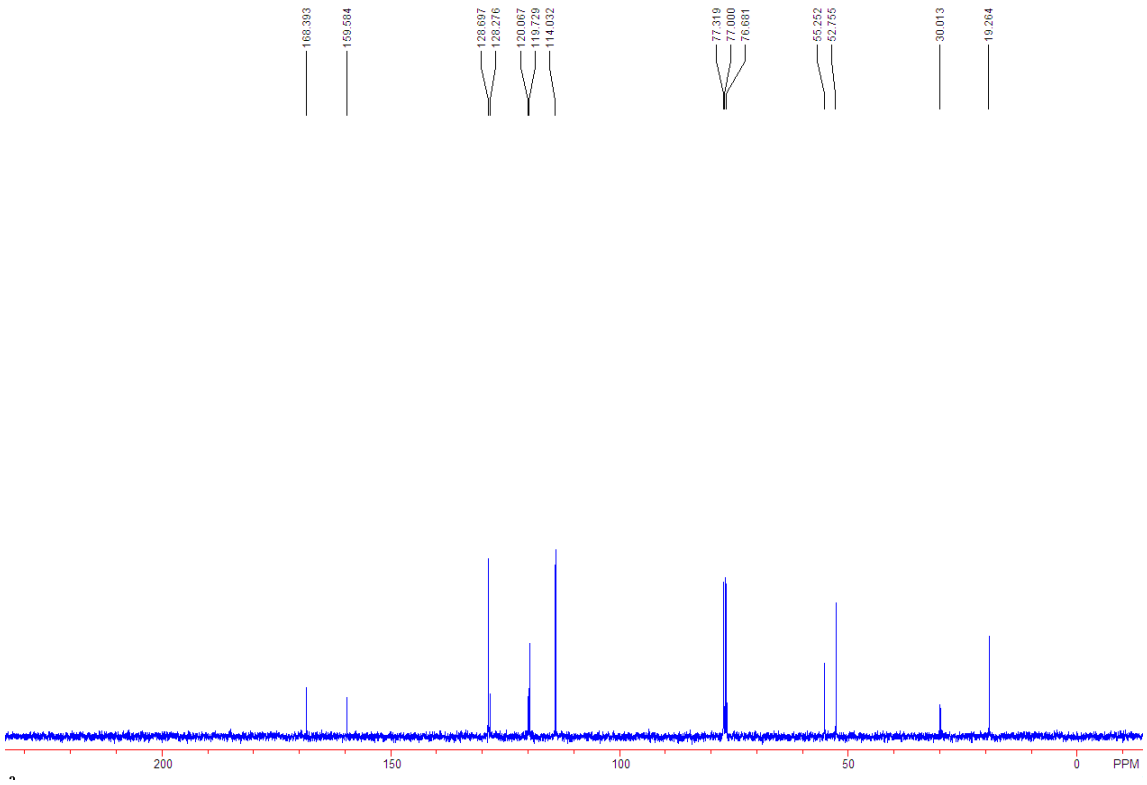


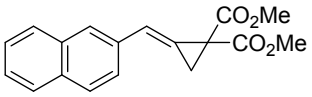


(E)-dimethyl 2-(4-methoxybenzylidene)cyclopropane-1,1-dicarboxylate **1g**: a white solid. 417.1 mg, 67% yield. m.p. 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.47 (d, J = 2.4 Hz,

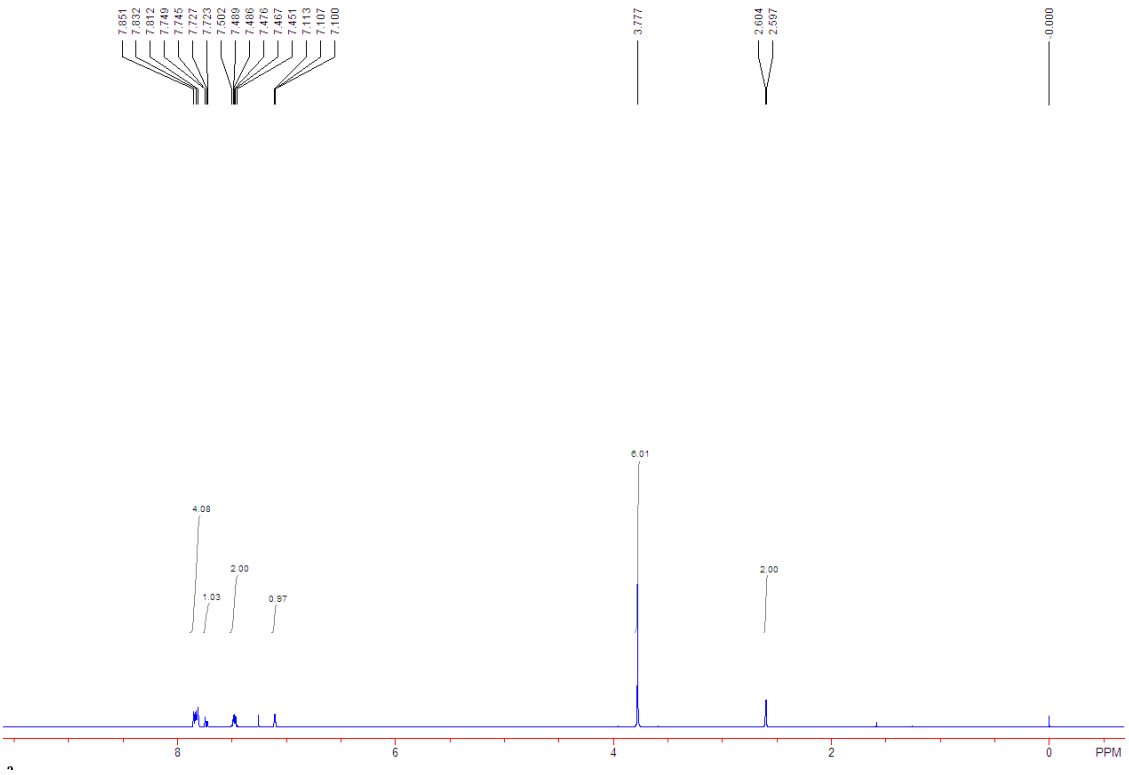
2H), 3.75 (s, 6H), 3.82 (s, 3H), 6.88 (s, 1H), 6.89 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.26, 30.01, 52.76, 55.25, 114.03, 119.73, 120.07, 128.28, 128.70, 159.58, 168.39. IR (ATR) ν 2954, 2839, 1726, 1605, 1577, 1512, 1435, 1361, 1298, 1247, 1173, 1143, 1101, 1030, 972, 889, 827, 764, 750 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{16}O_5$+H] requires 277.1071, found 277.1062 [M^++H].

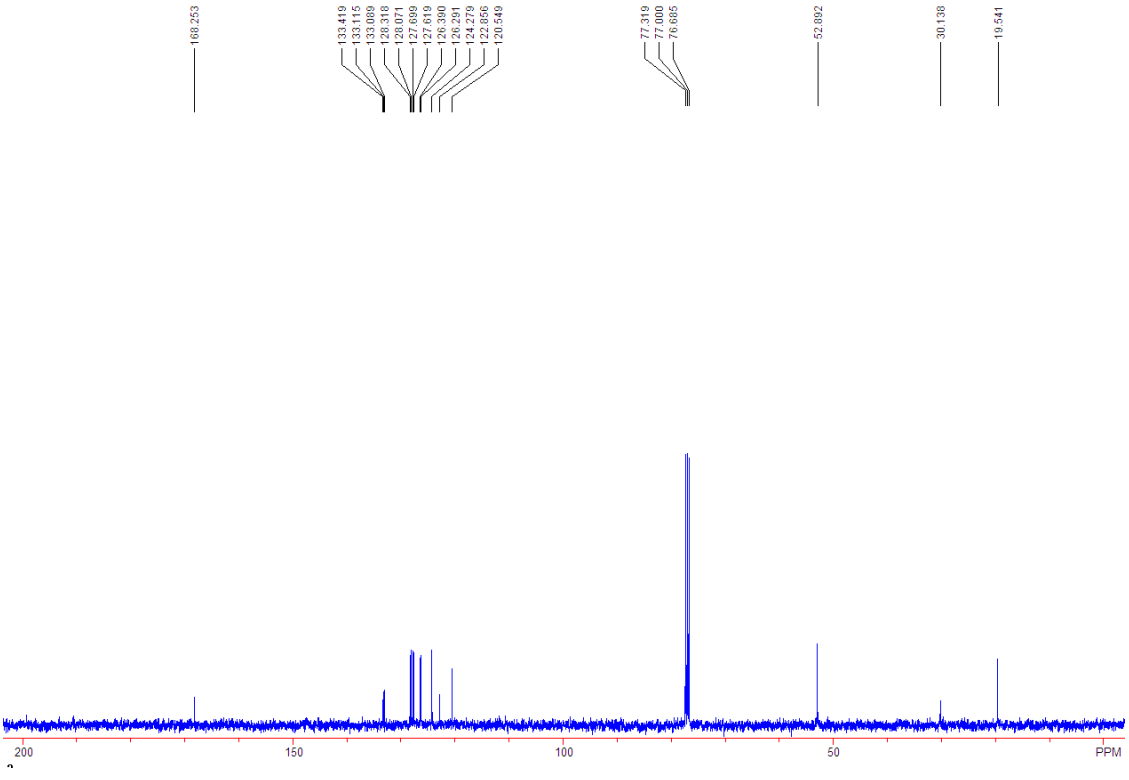


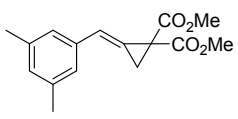




(E)-dimethyl 2-(naphthalen-2-ylmethylene)cyclopropane-1,1-dicarboxylate **1h**: a white solid. 140.0 mg, 47% yield. m.p. 107 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.60 (d, J = 2.4 Hz, 2H), 3.78 (s, 6H), 7.11 (t, J = 2.4 Hz, 1H), 7.45-7.50 (m, 2H), 7.72-7.75 (m, 1H), 7.81-7.85 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.54, 30.14, 52.89, 120.55, 122.86, 124.28, 126.29, 126.39, 127.62, 127.70, 128.07, 128.32, 133.09, 133.12, 133.42, 168.25. IR (ATR) ν 2954, 2922, 1732, 1508, 1435, 1310, 1275, 1261, 1193, 1145, 1105, 966, 901, 817, 764, 750 cm^{-1}. HRMS (ESI) calcd for [$C_{18}H_{16}O_4$+Na] requires 319.0941, found 319.0939 [M^++Na].

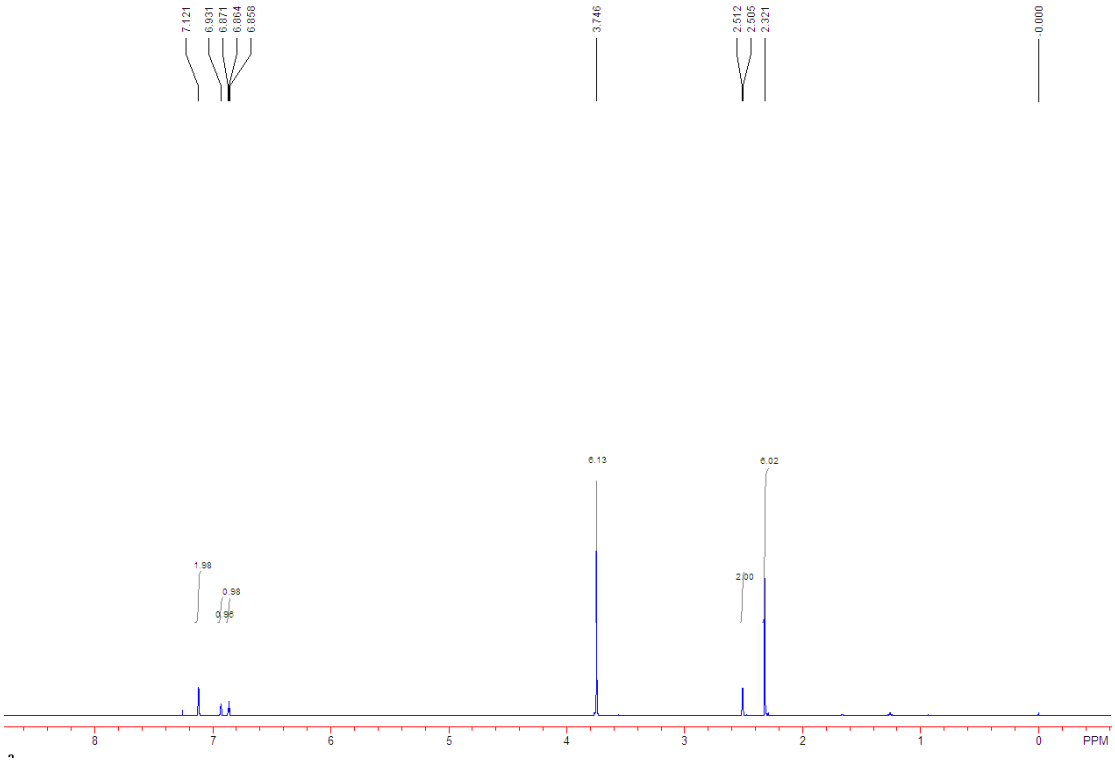


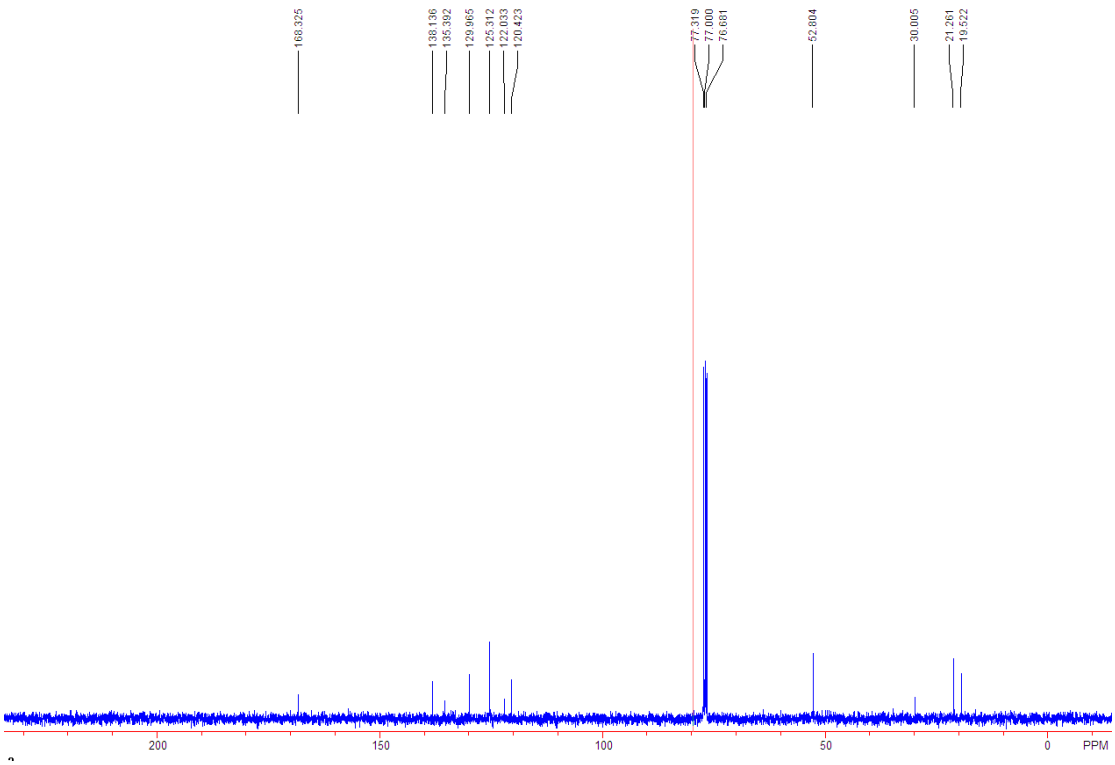


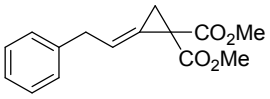


(E)-dimethyl 2-(3,5-dimethylbenzylidene)cyclopropane-1,1-dicarboxylate **1i**: a white solid. 1.0524 g, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.32 (s, 6H), 2.51 (d, J = 2.8 Hz,

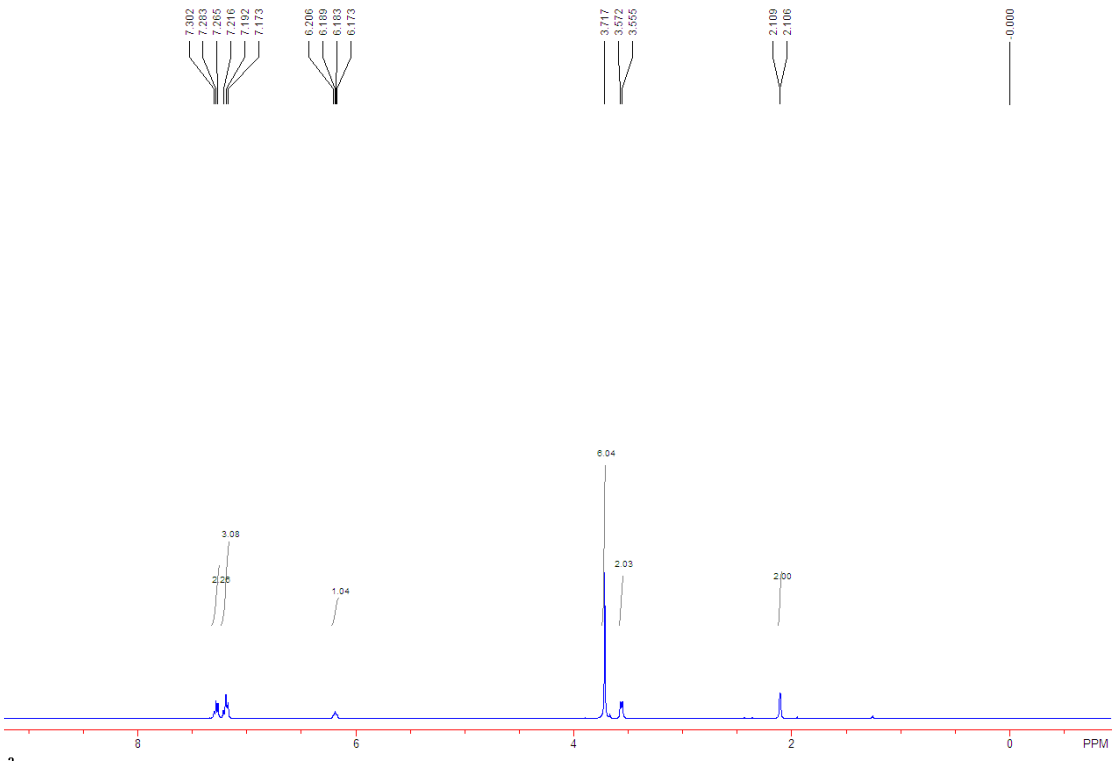
2H), 3.75 (s, 6H), 6.86 (t, J = 2.8 Hz, 1H), 6.93 (s, 1H), 7.12 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.52, 21.26, 30.00, 52.80, 120.42, 122.03, 125.31, 129.97, 135.39, 138.14, 168.33. IR (ATR) ν 2954, 1733, 1602, 1559, 1507, 1436, 1353, 1310, 1275, 1262, 1193, 1142, 1106, 982, 888, 842, 764, 750, 691 cm^{-1}. HRMS (ESI) calcd for [$C_{16}H_{18}O_4$+Na] requires 297.1097, found 297.1099 [M^++Na].

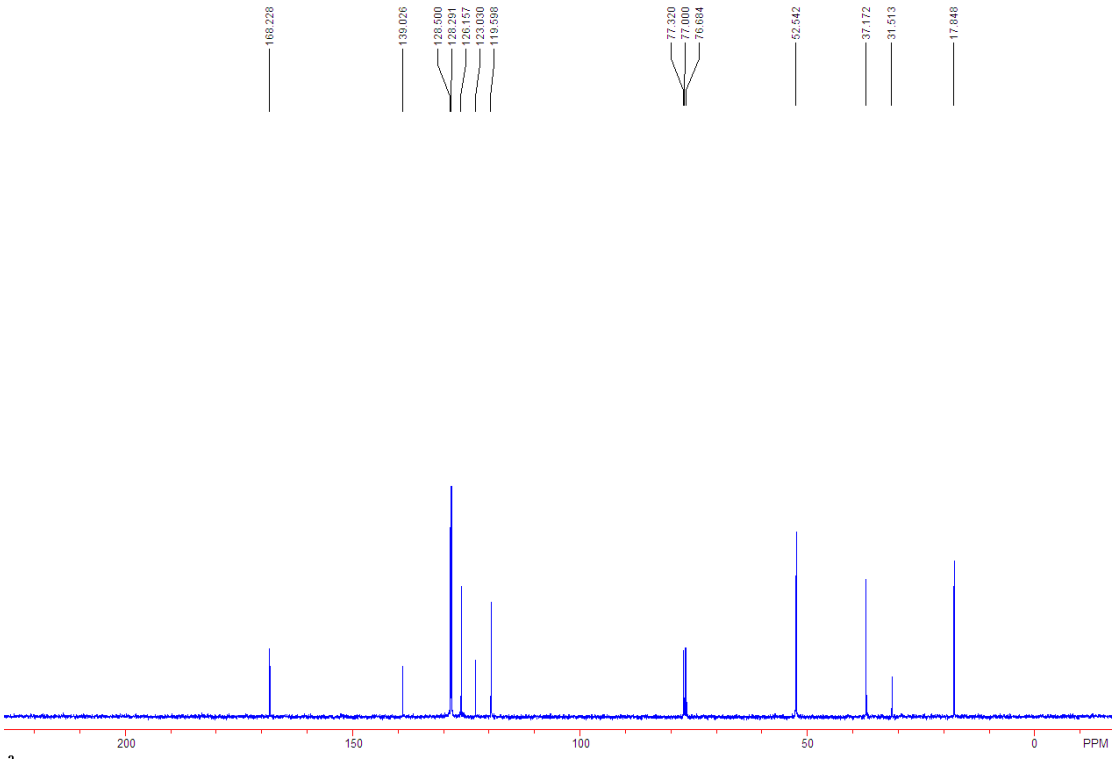


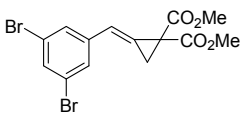




(E)-dimethyl 2-(2-phenylethylidene)cyclopropane-1,1-dicarboxylate **1j**: a light yellow oil. 912.1 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.11 (d, J = 1.2 Hz, 2H), 3.56 (d, J = 6.8 Hz, 2H), 3.72 (s, 6H), 6.17-6.21 (m, 1H), 7.17-7.22 (m, 3H), 7.27-7.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.85, 31.51, 37.17, 52.54, 119.60, 123.03, 126.16, 128.29, 128.50, 139.03, 168.23. IR (ATR) ν 2953, 1728, 1603, 1496, 1453, 1435, 1311, 1258, 1192, 1150, 1103, 1030, 980, 885, 829, 749, 698 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{16}O_4$+H] requires 261.1121, found 261.1115 [M^++H].

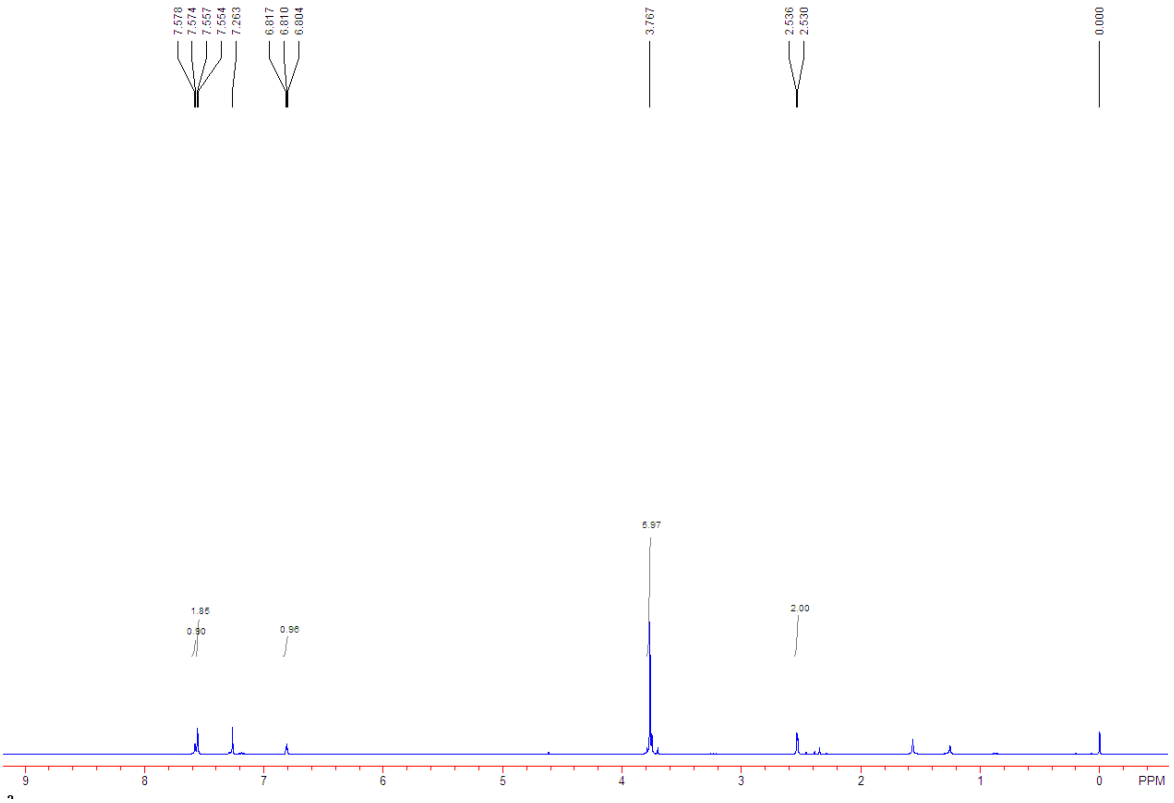


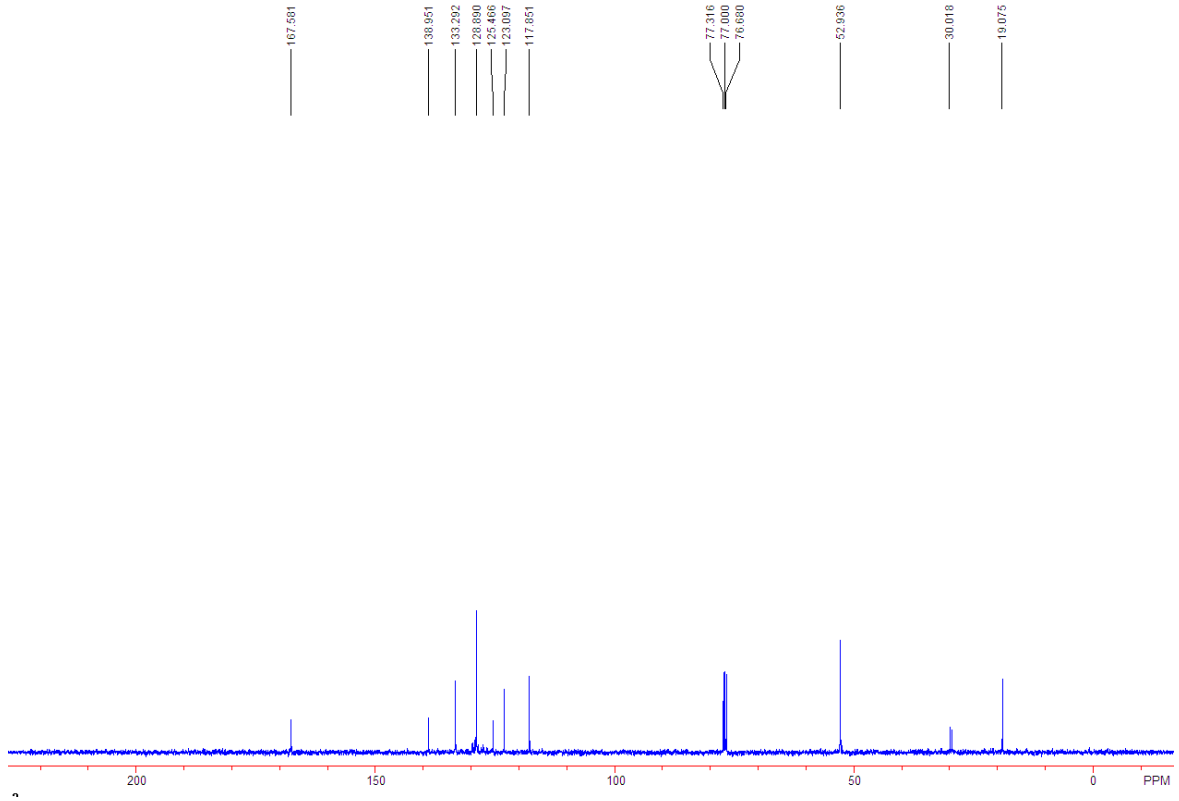


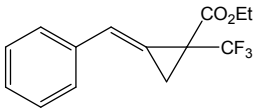


(E)-dimethyl 2-(3,5-dibromobenzylidene)cyclopropane-1,1-dicarboxylate **1k**: a white solid. 165.2 mg, 14% yield. m.p. 128 ^{o}C ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.53 (d, J = 2.4 Hz,

2H), 3.77 (s, 6H), 6.81 (t, J = 2.4 Hz, 1H), 7.55-7.56 (m, 2H), 7.57-7.58 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.08, 30.02, 52.94, 117.85, 123.10, 125.47, 128.89, 133.29, 138.95, 167.58. IR (ATR) ν 2952, 2850, 1731, 1580, 1548, 1434, 1338, 1307, 1259, 1191, 1147, 1104, 968, 892, 841, 748, 734, 670 cm^{-1}. MS (EI) m/z 402. HRMS (EI) calcd for [$C_{14}H_{12}Br_2O_4$] requires 401.9102, found 401.9098.

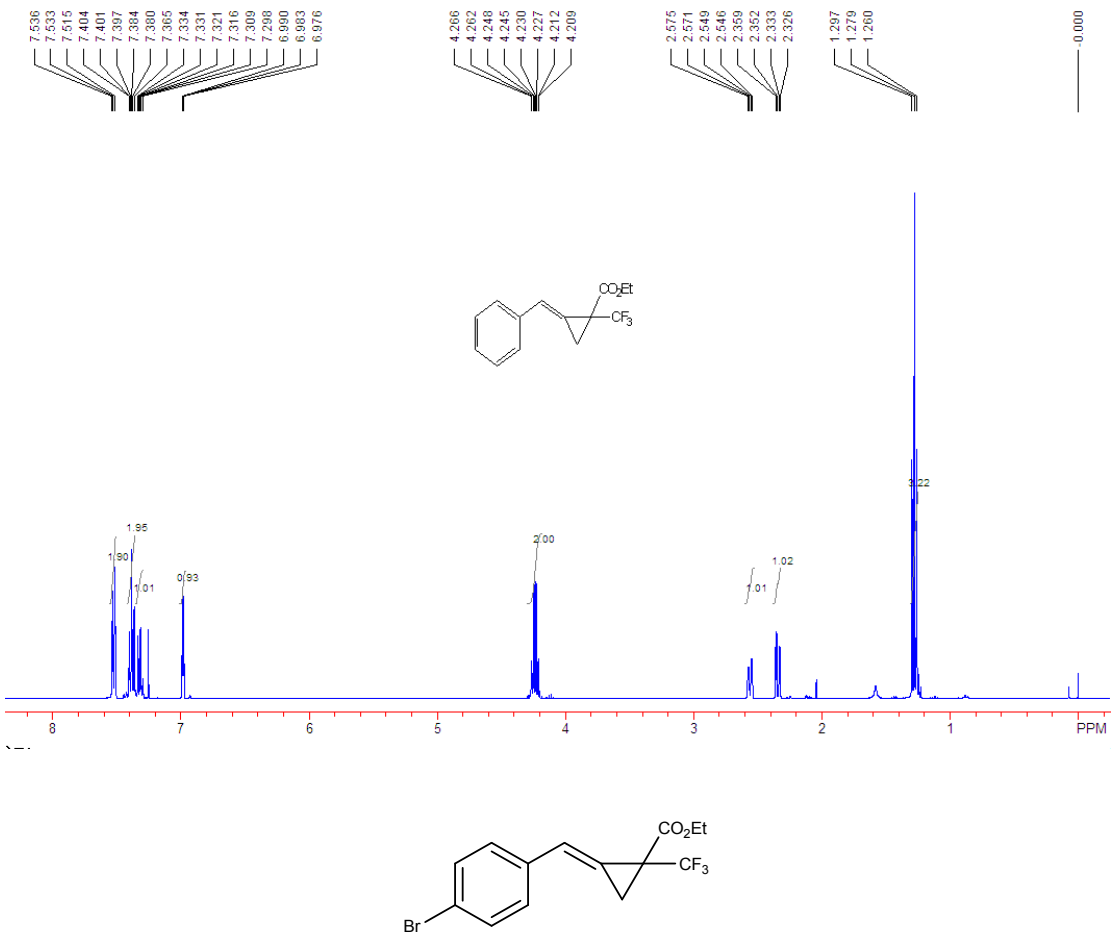






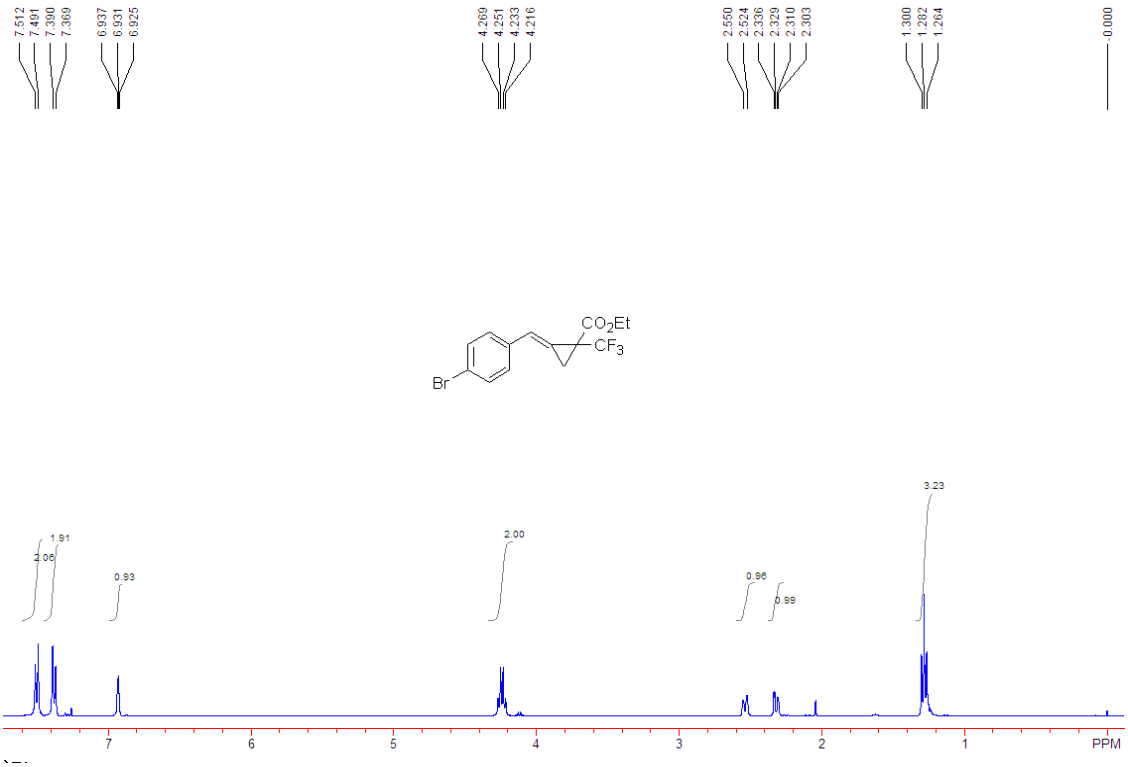
Compound **2a** is a known compound and was synthesized according to the literature procedure.[1]

(E)-ethyl 2-benzylidene-1-(trifluoromethyl)cyclopropanecarboxylate **2a**: a light yellow oil. 49.7 mg. 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.28 (t, J = 7.2 Hz, 3H), 2.34 (dd, J = 10.4 Hz, 2.8 Hz, 1H), 2.56 (dd, J = 10.4 Hz, 1.6 Hz, 1H), 4.24 (qd, J = 7.2 Hz, 1.2 Hz, 2H), 6.98 (t, J = 2.8 Hz, 1H), 7.30-7.33 (m, 1H), 7.37-7.40 (m, 2H), 7.52-7.54 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -66.73. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.98, 16.50 (q, J = 2.3 Hz), 27.98 (q, J = 34.7 Hz), 62.01, 119.18, 121.62, 124.58 (q, J = 272.9 Hz), 127.58, 128.56, 128.72, 135.11, 166.44. IR (ATR) ν 3062, 2985, 2963, 2926, 1734, 1454, 1370, 1339, 1293, 1275, 1154, 1124, 1069, 1016, 800, 751, 690 cm^{-1}. HRMS (ESI) calcd for [$C_{14}H_{13}F_3O_2$+NH_4] requires 288.1211, found 288.1213 [M^++NH_4].



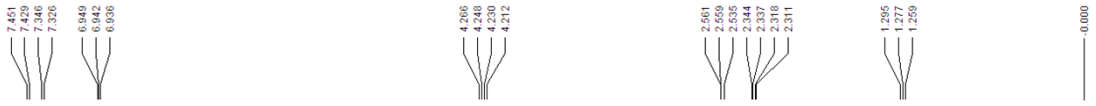
Compound **2b** is a known compound and was synthesized according to the literature procedure.[1]

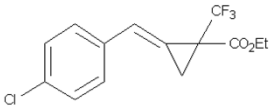
ethyl 2-(4-bromobenzyl)-1-(trifluoromethyl)cycloprop-2-enecarboxylate **2b**: a light yellow oil. 70.1 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.28 (t, *J* = 7.2 Hz, 3H), 2.32 (dd, *J* = 10.4 Hz, 2.8 Hz, 1H), 2.53 (d, *J* = 10.4 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 6.93 (t, *J* = 2.8 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -66.67. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.95, 16.41 (q, *J* = 2.3 Hz), 28.04 (q, *J* = 34.9 Hz), 62.12, 119.95, 120.61, 122.55, 123.34 (q, *J* = 273.3 Hz), 128.99, 131.87, 133.99, 166.17. IR (ATR) *ν* 2985, 2926, 2854, 1734, 1489, 1370, 1337, 1302, 1282, 1267, 1155, 1126, 1069, 1009, 877, 822 cm^{-1}. HRMS (ESI) calcd for [$C_{14}H_{12}BrF_3O_2$+NH_4] requires 366.0311, found 366.0322 [M^++NH_4].

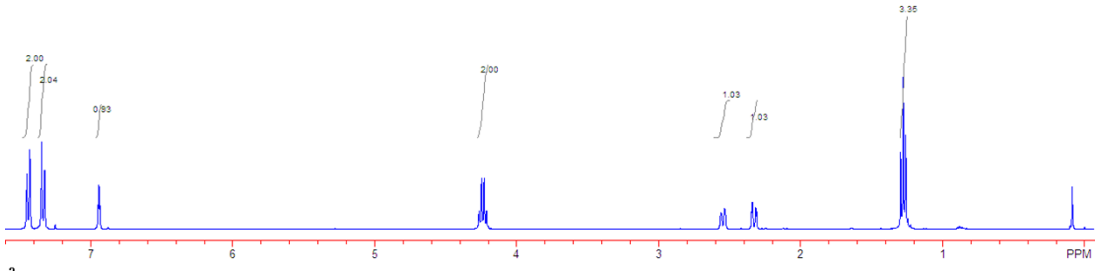


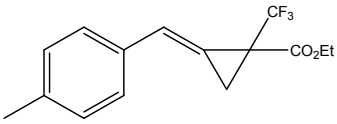
Compound **2c** is a known compound and was synthesized according to the literature procedure.[1]

(E)-ethyl 2-(4-chlorobenzylidene)-1-(trifluoromethyl)cyclopropanecarboxylate **2c**: a light yellow oil. 58.2 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.28 (t, J = 7.2 Hz, 3H), 2.33 (dd, J = 10.4 Hz, J = 2.8 Hz, 1H), 2.55 (dd, J = 10.4 Hz, J = 2.8 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 6.94 (t, J = 2.8 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -66.75. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.92, 16.35 (q, J = 2.3 Hz), 28.03 (q, J = 34.9 Hz), 62.08, 119.82, 120.52, 123.39 (q, J = 273.3 Hz), 128.71, 128.90, 133.57, 134.32, 166.18. IR (ATR) ν 2981, 2879, 2363, 1735, 1494, 1371, 1339, 1303, 1282, 1268, 1161, 1129, 1091, 1073, 1014, 764, 750 cm^{-1}. MS (ESI) *m/z* 304.0478. HRMS (ESI) calcd for [$C_{14}H_{12}ClF_3O_2$+NH_4] requires 322.0816, found 322.0826 [M^++NH_4].



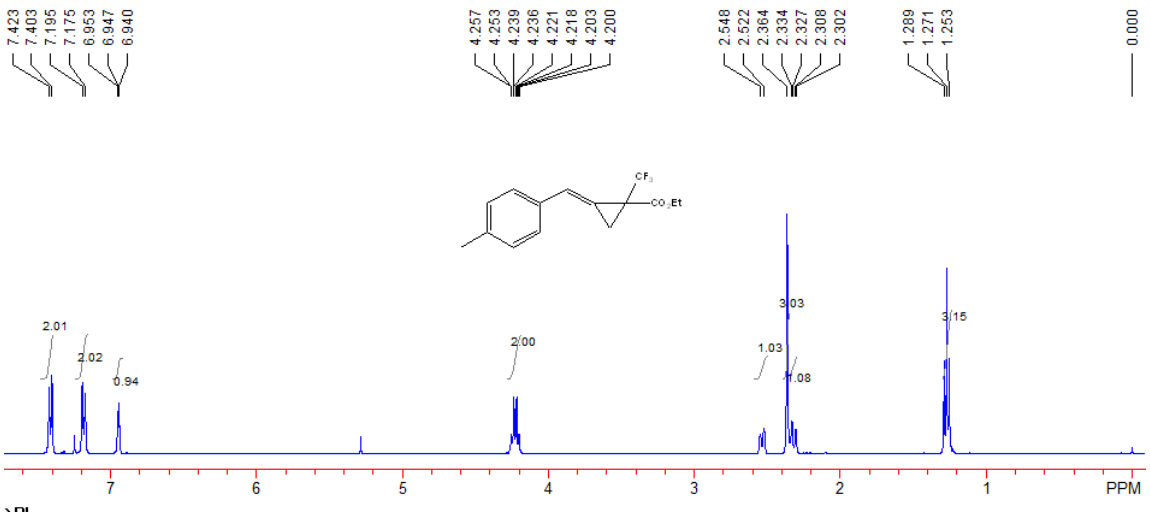


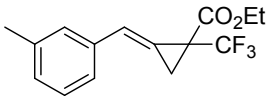




Compound **2d** is a known compound and was synthesized according to the literature procedure.[1]

(E)-ethyl 2-(4-methylbenzylidene)-1-(trifluoromethyl)cyclopropanecarboxylate **2d**: a light yellow oil. 50.3 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.27 (t, *J* = 7.2 Hz, 3H), 2.32 (dd, *J* = 10.4 Hz, 2.4 Hz, 1H), 2.36 (s, 3H), 2.54 (d, *J* = 10.4 Hz, 1H), 4.23 (qd, *J* = 7.2 Hz, 1.2 Hz, 2H), 6.95 (t, *J* = 2.8 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -66.75. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.97, 16.47, 21.29, 27.80 (q, *J* = 34.6 Hz), 61.94, 118.10, 121.47, 123.56 (q, *J* = 272.6 Hz), 127.49, 129.41, 132.36, 138.59, 166.55. IR (ATR) *ν* 2959, 2924, 2846, 2358, 1733, 1457, 1314, 1300, 1270, 1147, 1073, 1042, 800, 721 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{15}F_3O_2$+NH_4] requires 302.1362, found 302.1367 [M^++NH_4].





(E)-ethyl 2-(3-methylbenzylidene)-1-(trifluoromethyl)cyclopropanecarboxylate **2e**: a light yellow oil. 734.8 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (t, *J* = 7.2 Hz, 3H), 2.34 (dd, *J* = 10.8 Hz, 2.4 Hz, 1H), 2.36 (s, 3H), 2.56 (dd, *J* = 10.8 Hz, 1.2 Hz, 1H), 4.22 (qd, *J* = 7.2 Hz, 1.6 Hz, 2H), 6.94 (t, *J* = 3.2 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.315-7.322 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -66.70. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.90, 16.49 (q, *J* = 2.6 Hz), 21.29, 27.91 (q, *J* = 35.0 Hz), 61.91, 118.90 (q, *J* = 1.5 Hz), 121.65, 123.52 (q, *J* = 273.2 Hz), 124.73, 128.18, 128.58, 129.32, 135.00, 138.31, 166.42. IR (ATR) *ν* 2987, 1735, 1607, 1465, 1370, 1338, 1275, 1260, 1201, 1157, 1125, 1071, 1019, 923, 884, 764, 750, 689 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{15}F_3O_2$+NH_4] requires 302.1362, found 302.1365 [M^++NH_4].


7.322
7.312
7.279
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7.240
7.130
7.112
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6.943
6.936
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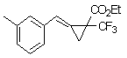
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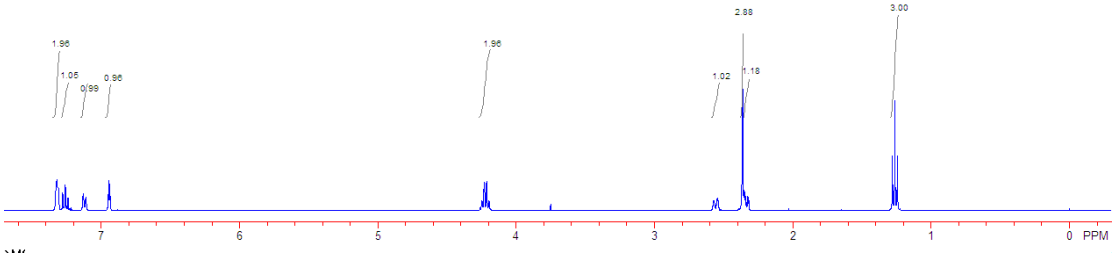
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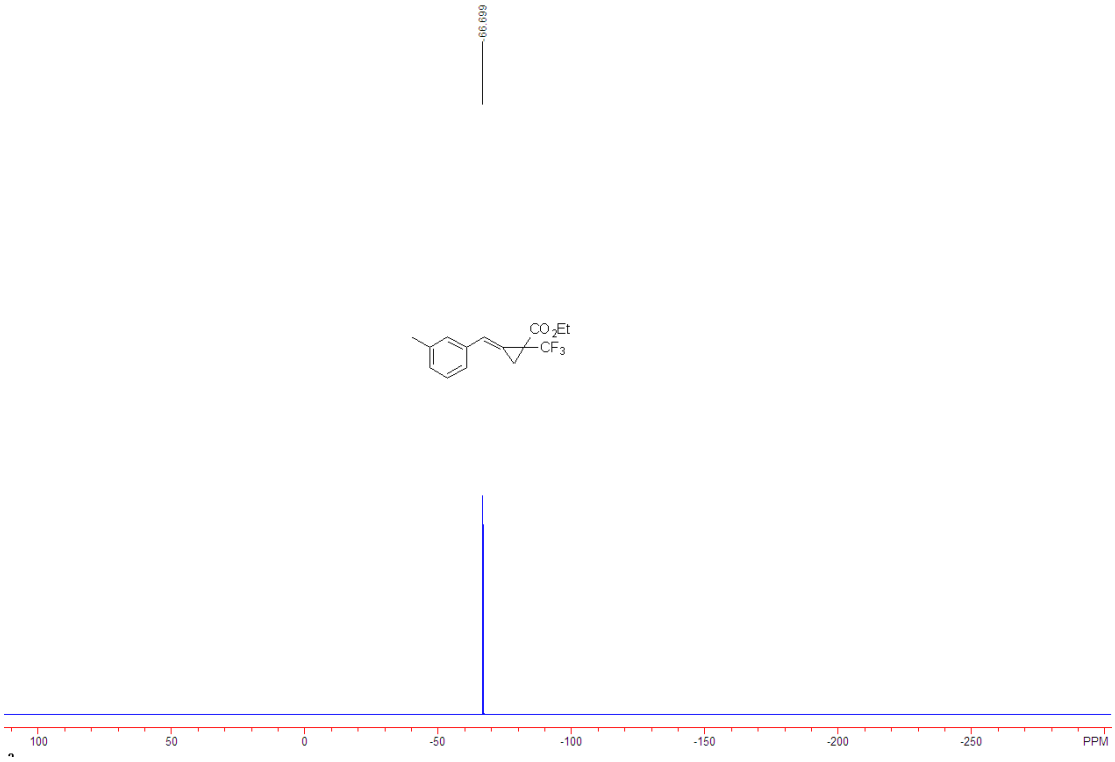
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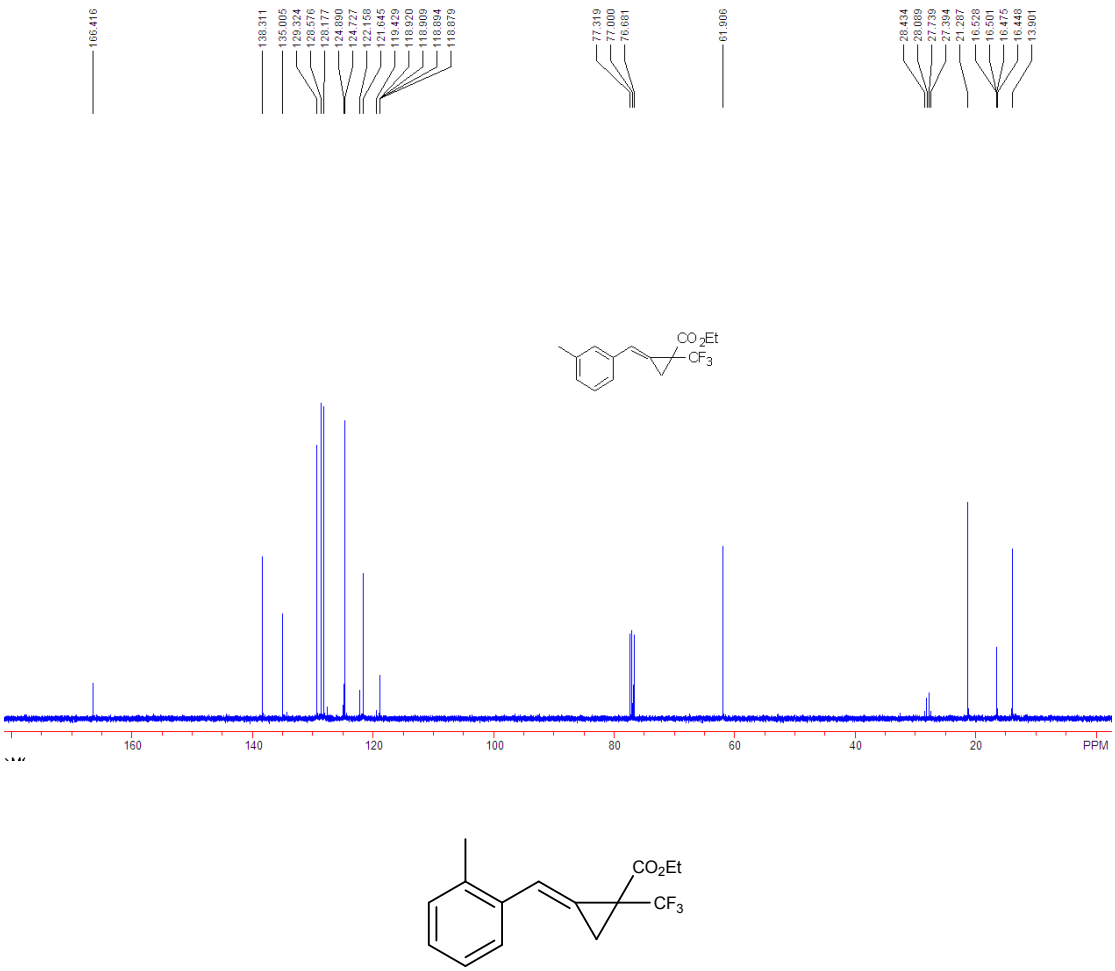
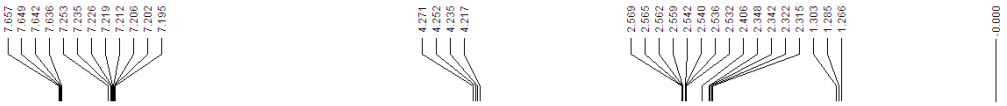


(E)-ethyl 2-(2-methylbenzylidene)-1-(trifluoromethyl)cyclopropanecarboxylate **2f**: a light yellow oil. 767.1 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.29 (t, J = 7.2 Hz, 3H), 2.33 (dd, J = 10.4 Hz, 2.4 Hz, 1H), 2.41 (s, 3H), 2.55 (ddd, J = 10.8 Hz, 3.2 Hz, 1.6 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 7.20-7.25 (m, 4H), 7.64-7.66 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -66.74. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.99, 16.58 (q, J = 2.7 Hz), 19.63, 28.30 (q, J = 34.9 Hz), 61.97, 118.97, 119.99, 123.55 (q, J = 273.3 Hz), 126.13, 126.51, 128.46, 130.64, 133.62, 136.29, 166.52. IR (ATR) ν 2988, 1735, 1559, 1457, 1370, 1339, 1275, 1261, 1157, 1131, 1102, 1072, 764, 750 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{15}F_3O_2$+NH_4] requires 302.1362, found 302.1366 [M^++NH_4].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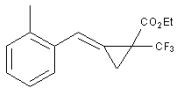
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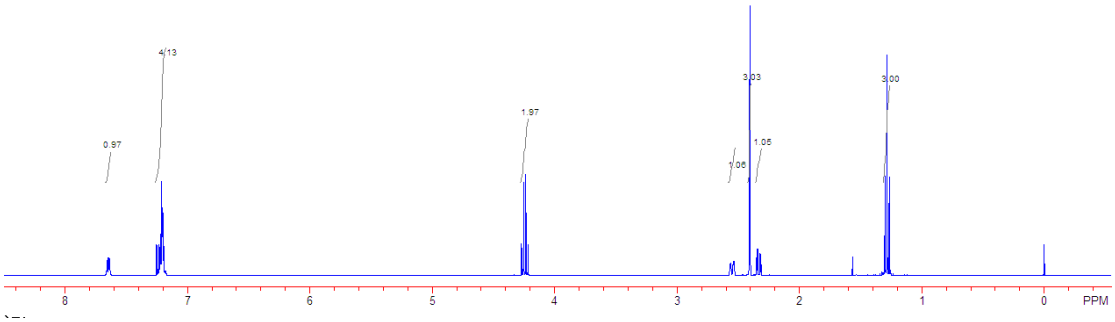
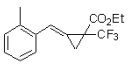
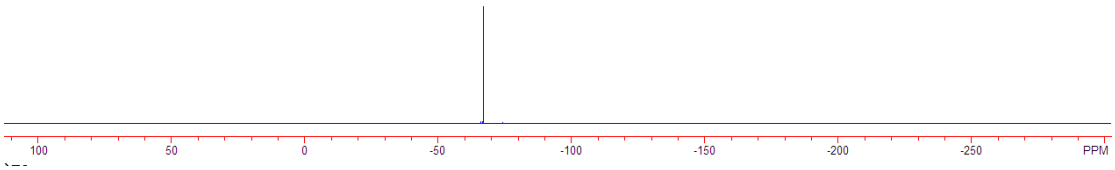

0.97
4.13
1.97
1.06
3.03
1.05
3.00
8
7
6
5
4
3
2
1
0
PPM

-66.742


CO2Et
CF3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-150
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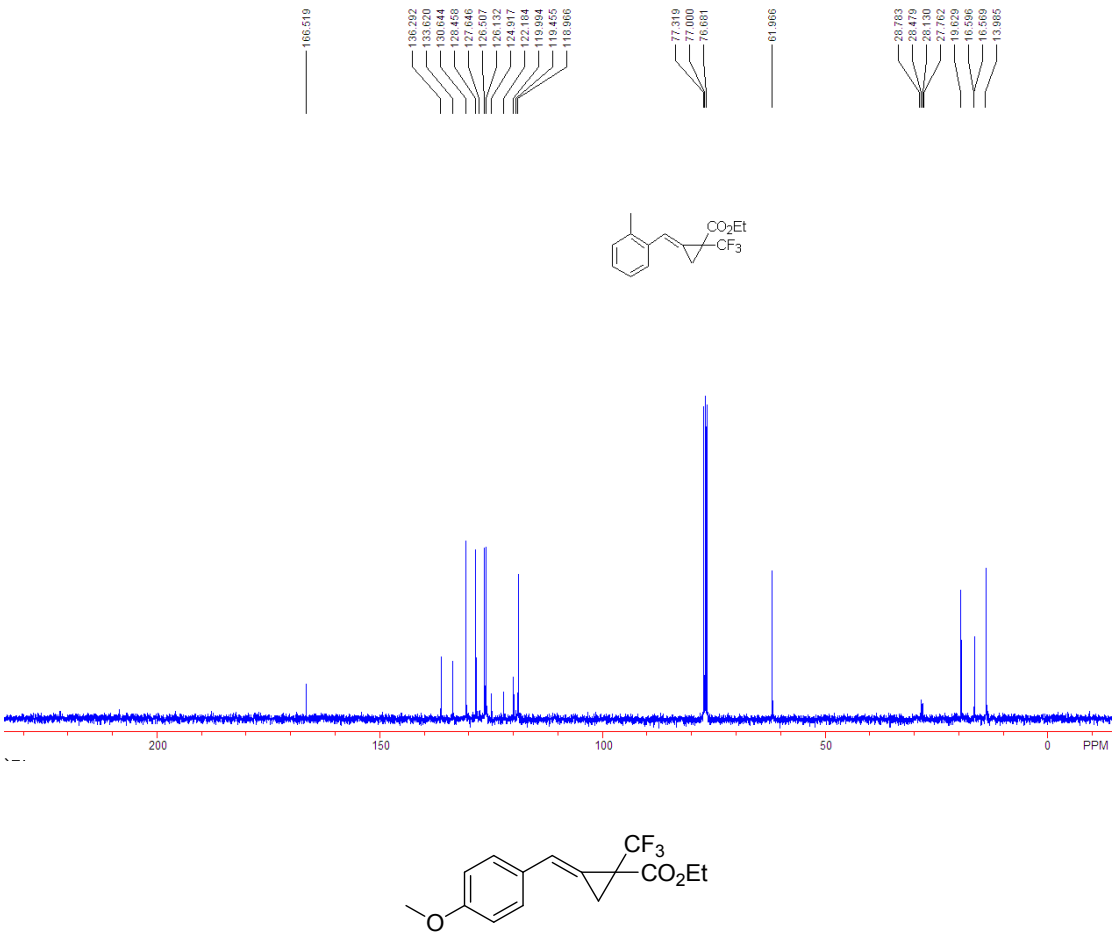
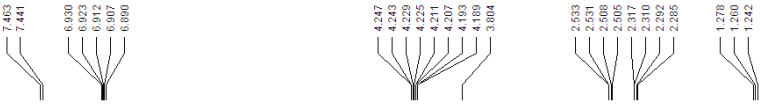
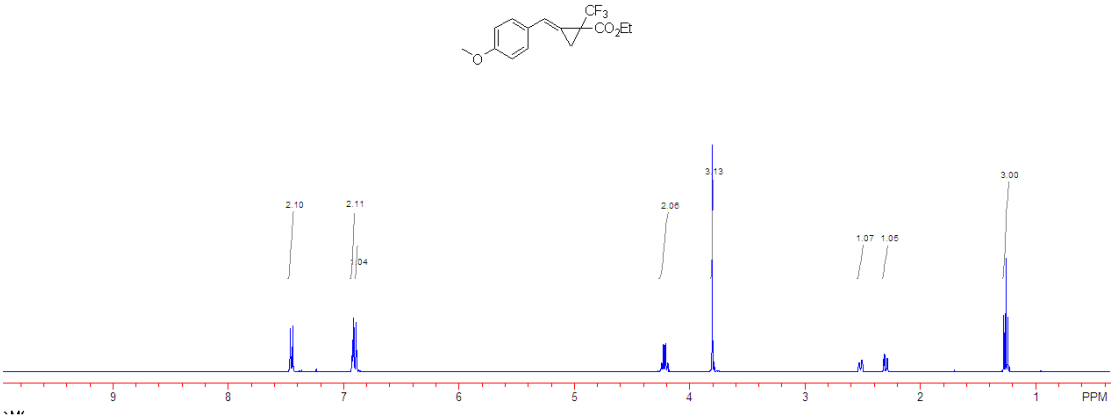
PPM

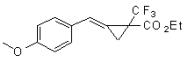


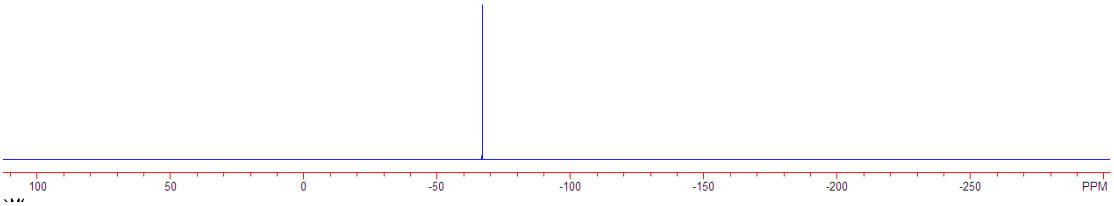
(E)-ethyl 2-(4-methoxybenzylidene)-1-(trifluoromethyl)cyclopropanecarboxylate **2g**: a white solid. 798.8 mg, 89% yield. m.p. 83 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (t, J = 7.2 Hz, 3H), 2.30 (dd, J = 10.0 Hz, 2.8 Hz, 1H), 2.52 (dd, J = 10.0 Hz, 0.8 Hz, 1H), 3.80 (s, 3H), 4.22 (qd, J = 7.2 Hz, 1.6 Hz, 2H), 6.89 (s, 1H), 6.91-6.93 (m, 2H), 7.44-7.46 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -66.73. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.88, 16.33 (q, J = 2.3 Hz), 27.94 (q, J = 34.6 Hz), 55.18, 61.85, 114.09, 116.75, 121.01, 123.59 (q, J = 272.9 Hz), 127.83, 128.83, 159.87, 166.56. IR (ATR) ν 2988, 1735, 1608, 1514, 1465, 1371, 1339, 1300, 1276, 1260, 1156, 1125, 1072, 1033, 764, 750 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{15}F_3O_3$+H] requires 301.1046, found 301.1036 [M^++H].

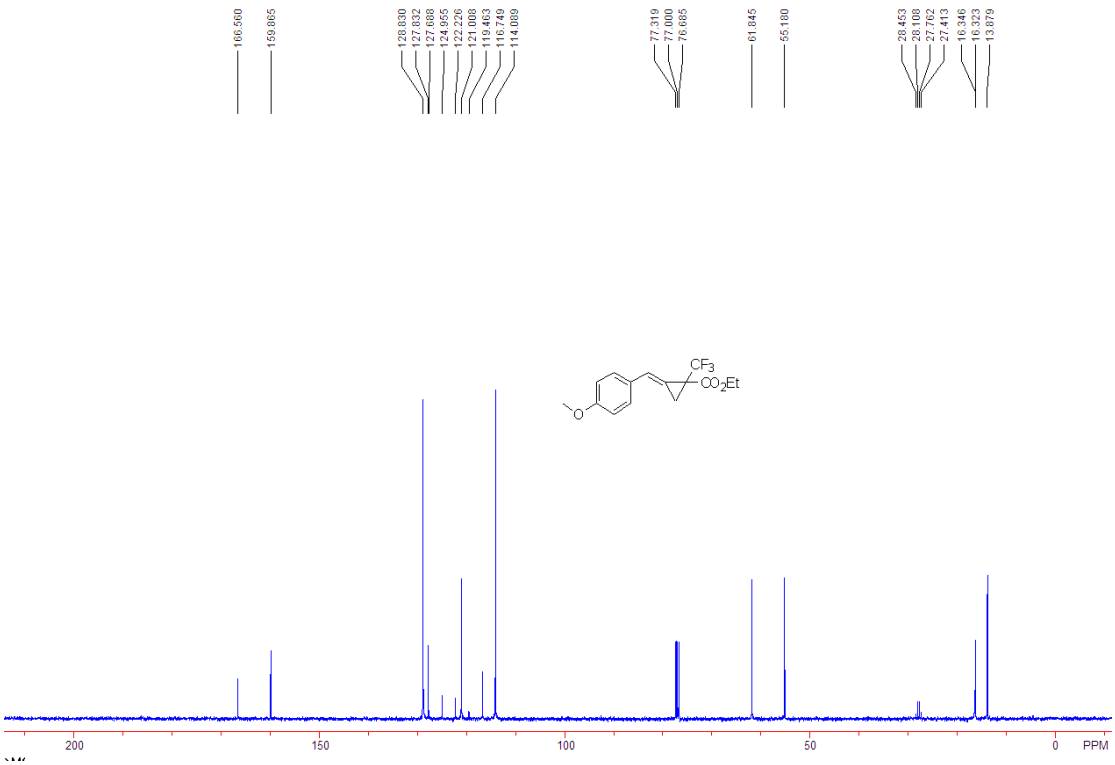

7.463
7.441
6.930
6.923
6.912
6.907
6.890
4.247
4.243
4.229
4.225
4.211
4.207
4.193
4.189
3.804
2.533
2.531
2.508
2.505
2.317
2.310
2.292
2.285
1.278
1.260
1.242

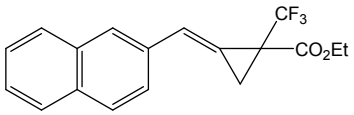

CF3
CO2Et
O
2.10
2.11
1.04
2.06
3.13
1.07
1.05
3.00
9
8
7
6
5
4
3
2
1
PPM

-66.733


CF3
CO2Et
O

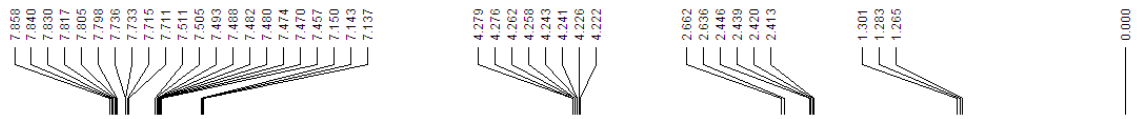

100
50
0
-50
-100
-150
-200
-250
PPM

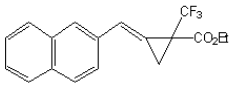


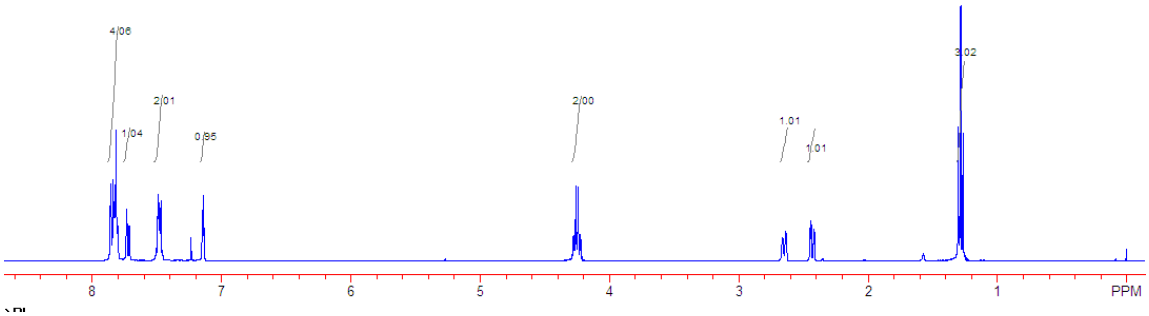


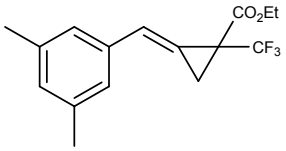
Compound **2h** is a known compound and was synthesized according to the literature procedure.[1]

(E)-ethyl 2-(naphthalen-2-ylmethylene)-1-(trifluoromethyl)cyclopropanecarboxylate **2h**: a white solid. 57.1 mg, 89% yield. m.p. 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.28 (t, J = 7.2 Hz, 3H), 2.43 (dd, J = 10.4 Hz, 2.8 Hz, 1H), 2.65 (d, J = 10.4 Hz, 1H), 4.25 (qd, J = 7.2 Hz, 1.6 Hz, 2H), 7.14 (t, J = 2.8 Hz, 1H), 7.46-7.51 (m, 2H), 7.72 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.80-7.86 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -66.62. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.98, 16.67 (q, J = 2.2 Hz), 28.09 (q, J = 34.6 Hz), 62.04, 119.56, 121.84, 123.54 (q, J = 273.3 Hz), 124.19, 126.50, 127.71, 127.90, 128.12, 128.41, 132.63, 133.25, 133.37, 166.44. IR (ATR) ν 3322, 2934, 2831, 1734, 1330, 1267, 1157, 1077, 1023, 734, 704 cm^{-1}. HRMS (ESI) calcd for [$C_{18}H_{15}F_3O_2$+NH_4] requires 338.1362, found 338.1366 [M^++NH_4].



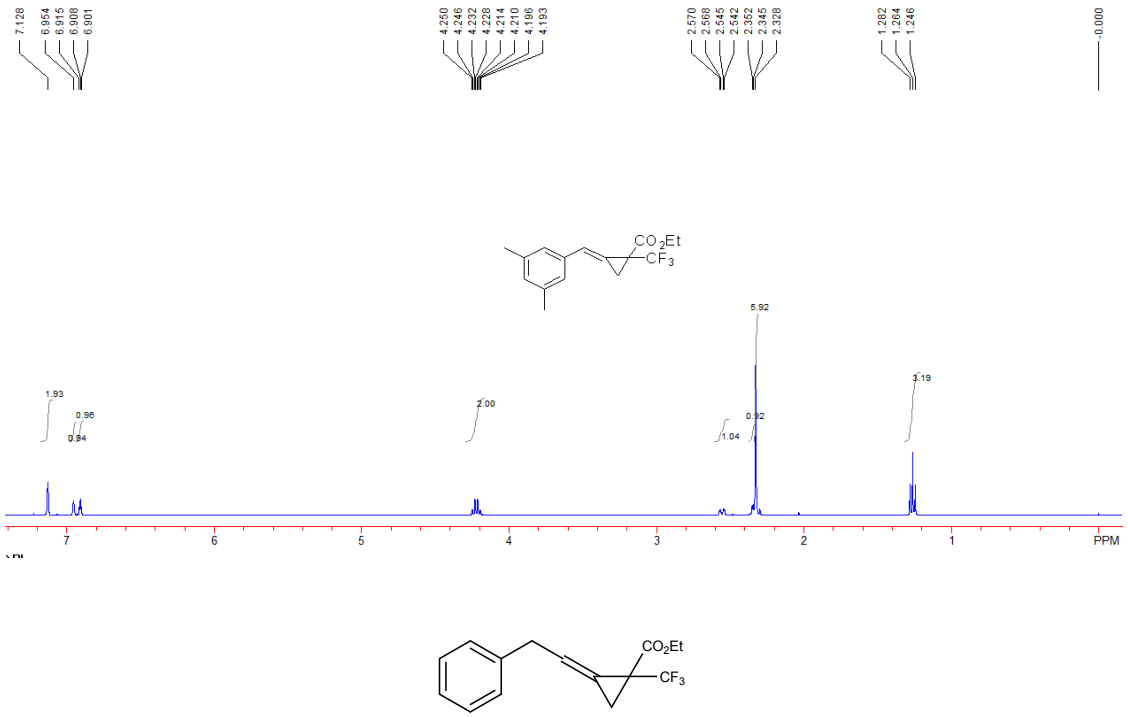




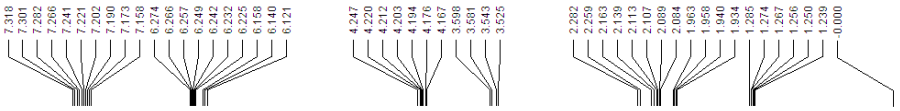


Compound **2i** is a known compound and was synthesized according to the literature procedure.[1]

ethyl 2-(3,5-dimethylbenzyl)-1-(trifluoromethyl)cycloprop-2-enecarboxylate **2i**: a light yellow oil. 56.1 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (t, J = 7.2 Hz, 3H), 2.34 (d, J = 10.0 Hz, 1H), 2.35 (s, 6H), 2.56 (d, J = 10.0 Hz, 0.8 Hz, 1H), 4.12 (qd, J = 7.2 Hz, 1.6 Hz, 2H), 6.91 (t, J = 0.8 Hz, 1H), 6.95 (s, 1H), 7.13 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -66.75. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.93, 16.55 (q, J = 2.2 Hz), 21.18, 27.92 (q, J = 34.6 Hz), 61.88, 118.70, 121.72, 123.54 (q, J = 272.9 Hz), 125.40, 130.27, 134.97, 138.21, 166.48. IR (ATR) ν 2985, 2924, 1736, 1603, 1465, 1370, 1358, 1389, 1282, 1160, 1127, 1073, 904, 872, 738, 689 cm^{-1}. HRMS (ESI) calcd for [$C_{16}H_{17}F_3O_2$+NH_4] requires 316.1519, found 316.1522 [M^++NH_4].



ethyl 2-(2-phenylethylidene)-1-(trifluoromethyl)cyclopropanecarboxylate **2j** (E:Z=4:1): a light yellow oil. 942 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.24-1.29 (m, 3.75H), 1.95 (dd, *J* = 9.6 Hz, 2.4 Hz, 1H), 2.10 (dd, *J* = 9.2 Hz, 2.0 Hz, 0.25H), 2.15 (d, *J* = 9.6 Hz, 1H), 2.27 (d, *J* = 9.2 Hz, 0.25H), 3.53 (d, *J* = 7.2 Hz, 0.5H), 3.59 (d, *J* = 6.8 Hz, 2H), 4.17-4.25 (m, 2.5H), 6.14 (t, *J* = 7.2 Hz, 0.25H), 6.23-6.27 (m, 1H), 7.16-7.24 (m, 3.75H), 7.27-7.32 (m, 2.5H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -66.96, -65.91. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.92, 13.95, 15.11 (q, *J* = 2.3 Hz), 15.58 (q, *J* = 2.2 Hz), 29.45 (q, *J* = 34.0 Hz), 37.32, 37.83, 61.78, 61.83, 120.24, 121.27, 121.47, 123.48 (q, *J* = 272.5 Hz), 126.42, 128.36, 128.47, 128.54, 128.60, 138.81, 166.58. IR (ATR) *ν* 3005, 2988, 1735, 1496, 1454, 1370, 1339, 1275, 1260, 1153, 1128, 1070, 1018, 858, 803, 749, 697 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{15}F_3O_2$+NH_4] requires 302.1362, found 302.1366 [M^++NH_4].


7.318
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7.282
7.266
7.241
7.221
7.202
7.190
7.173
7.158
6.274
6.266
6.257
6.249
6.242
6.232
6.225
6.158
6.140
6.121
4.247
4.220
4.212
4.203
4.194
4.176
4.167
3.598
3.581
3.543
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2.282
2.259
2.163
2.139
2.113
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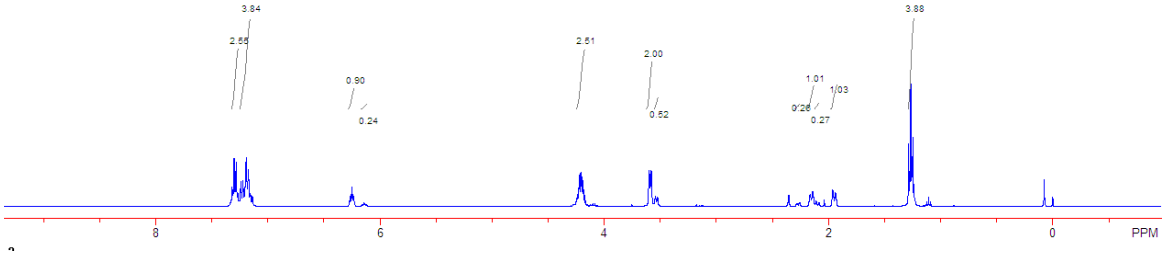
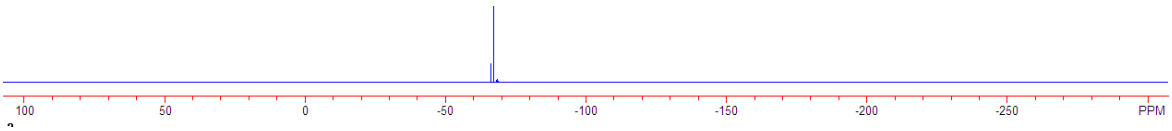
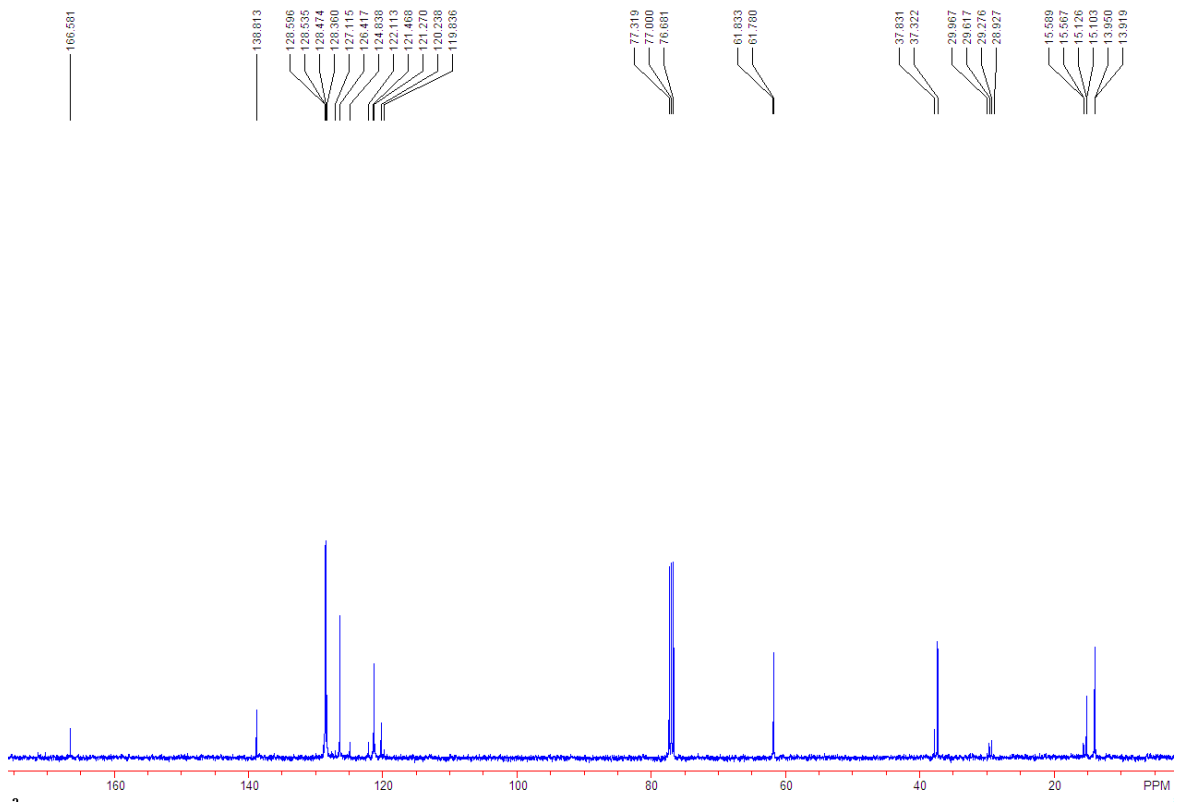
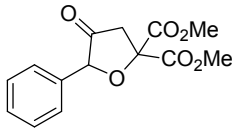
1.267
1.256
1.250
1.239
-0.000


3.84
2.55
0.90
0.24
2.51
2.00
0.52
1.01
0.26
1.03
0.27
3.88
8
6
4
2
0
PPM

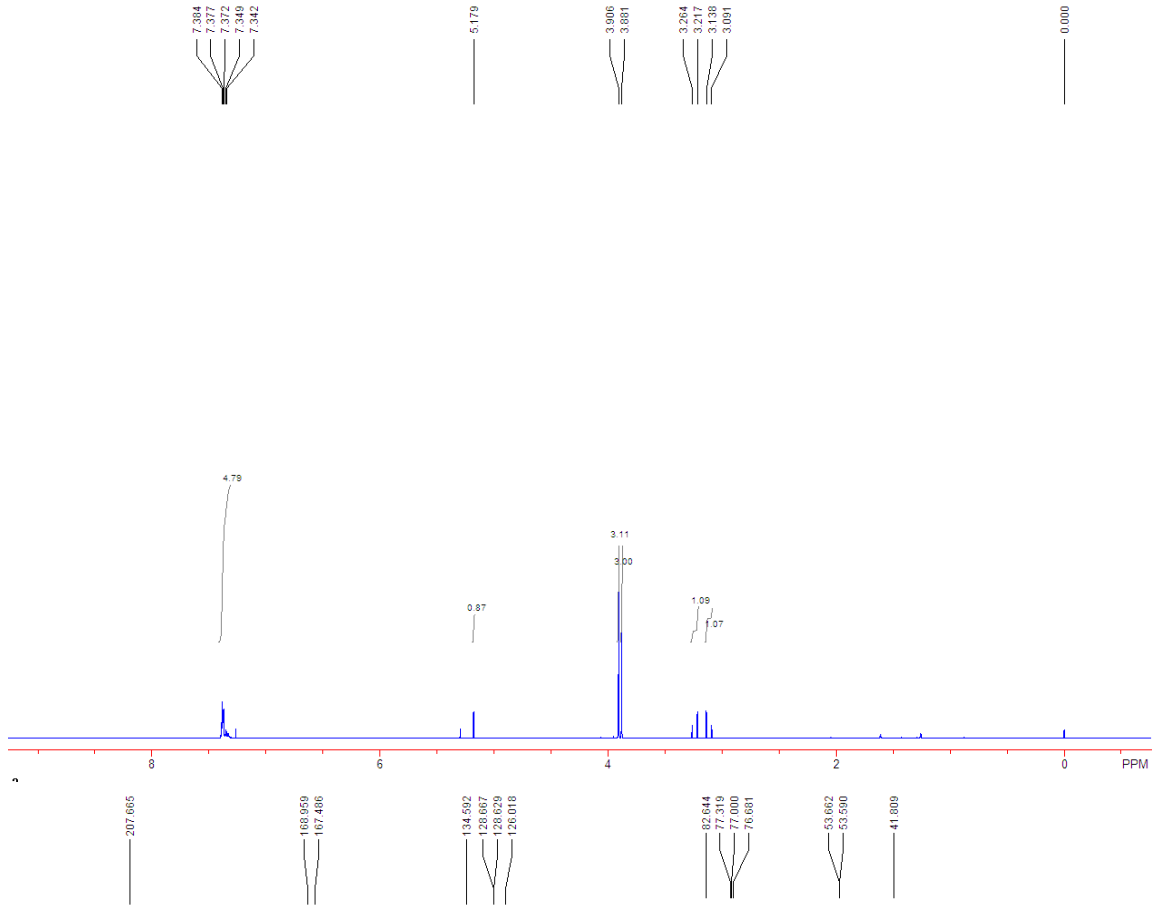

65.907
66.963


100
50
0
-50
-100
-150
-200
-250
PPM





dimethyl 4-oxo-5-phenyldihydrofuran-2,2(3H)-dicarboxylate **3a**: a light yellow oil. 123.6 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.11 (d, J = 18.8 Hz, 1H), 3.24 (d, J = 18.8 Hz, 1H), 3.88 (s, 3H), 3.91 (s, 3H), 5.18 (s, 1H), 7.34-7.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.81, 53.59, 53.66, 82.64 (2C), 126.02, 128.63, 128.67, 134.59, 167.49, 168.96, 207.67. ^{13}C NMR (100 MHz, $CD_3C(O)CD_3$) δ 42.26, 53.67 (2C), 83.26, 83.51, 127.32, 129.26, 129.28, 136.67, 168.43, 169.80, 208.63. IR (ATR) ν 2956. 2923, 1737, 1498, 1455, 1434, 1318, 1288, 1254, 1107, 1001, 821 cm^{-1}. HRMS (ESI) calcd for [$C_{14}H_{14}O_6$+NH_4] requires 296.1129, found 296.1122 [M^++NH_4].


7.384
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7.372
7.349
7.342
5.179
3.906
3.881
3.264
3.217
3.138
3.091
0.000
4.79
0.87
3.11
3.00
1.09
1.07
8
6
4
2
0
PPM
207.665
168.959
167.486
134.592
128.667
128.629
126.018
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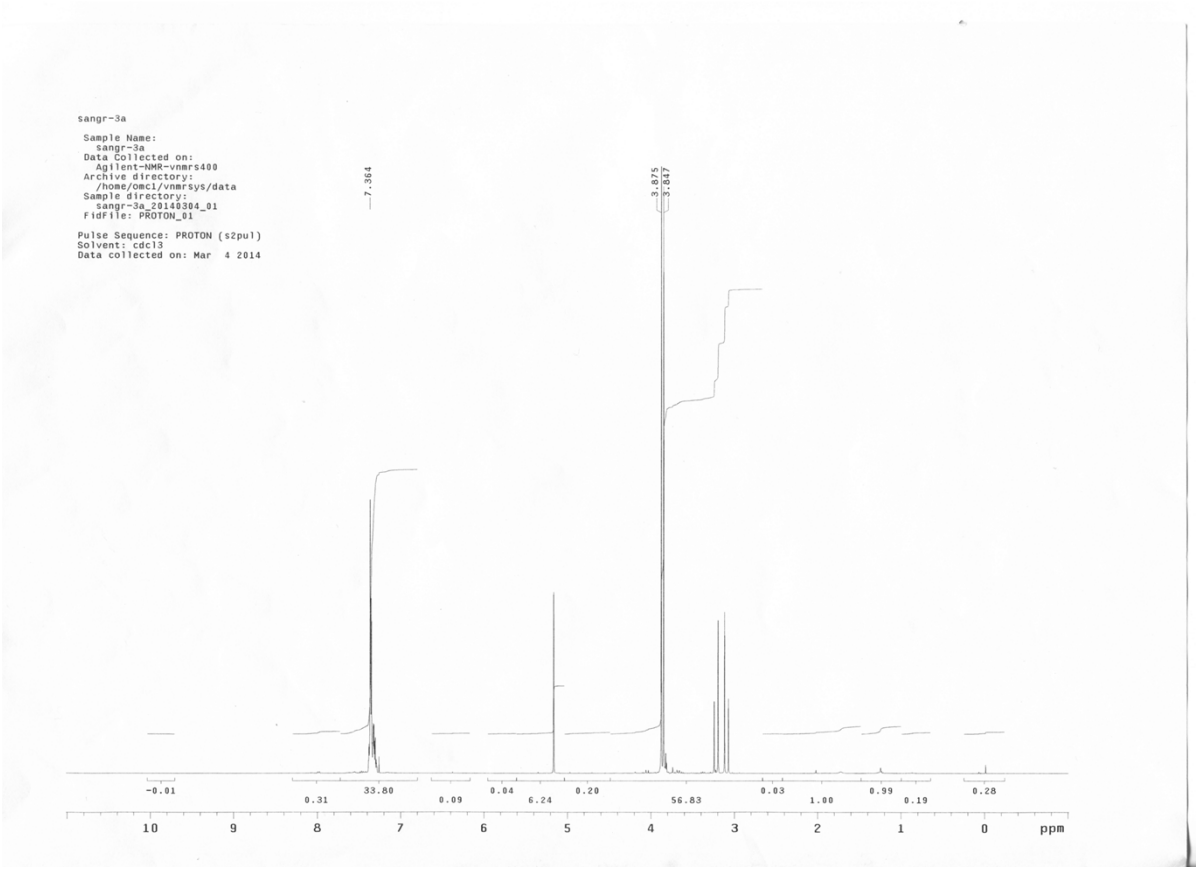
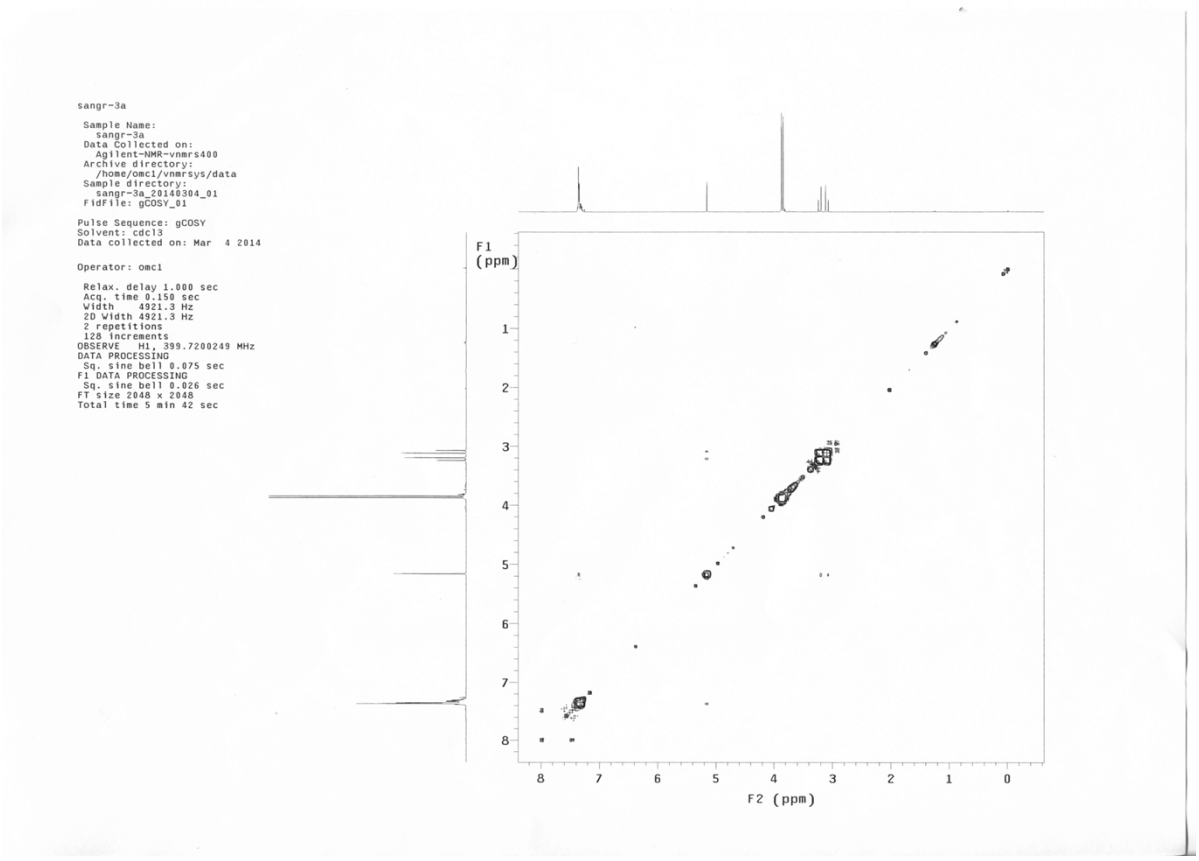
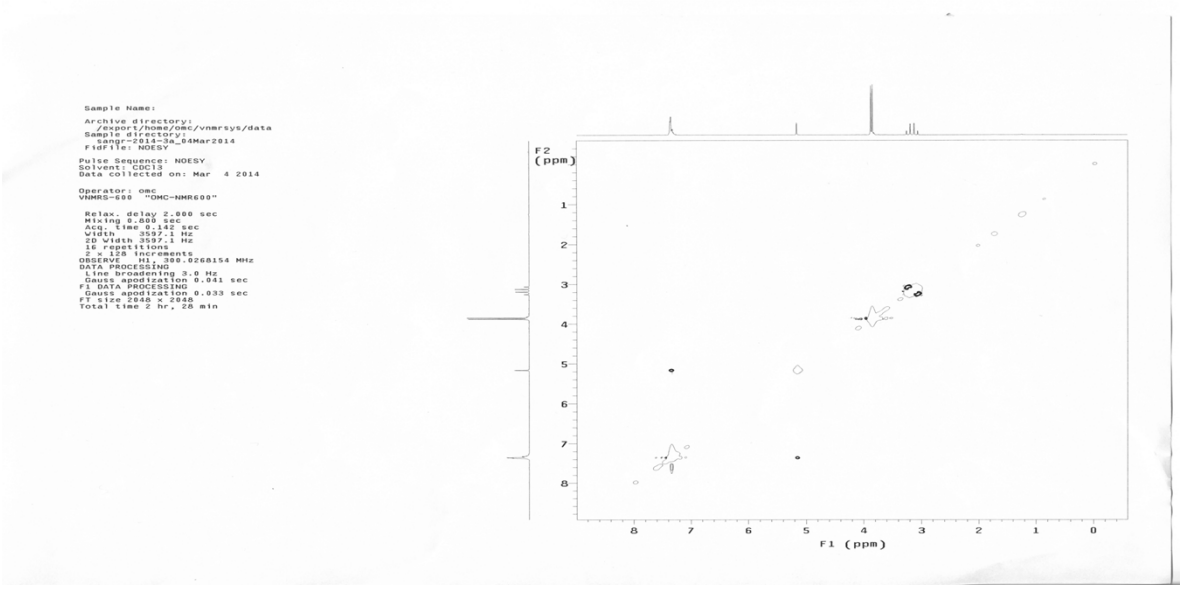
77.319
77.000
76.681
53.662
53.590
41.809
200
150
100
50
0
PPM



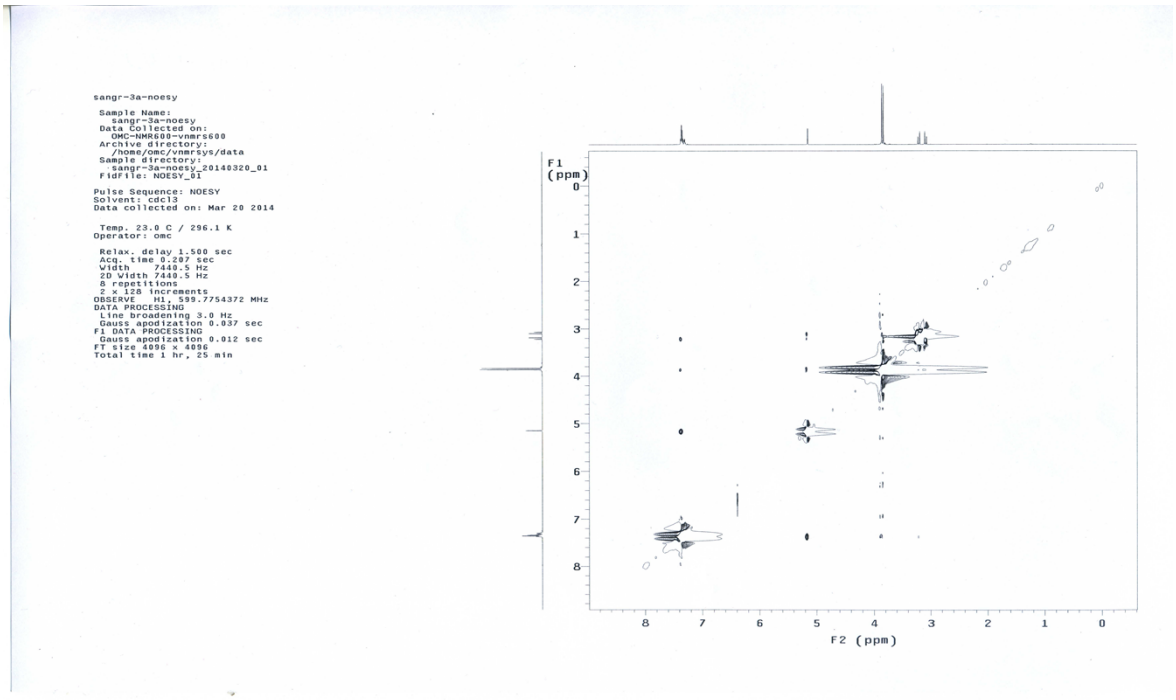
^{1}H-NMR



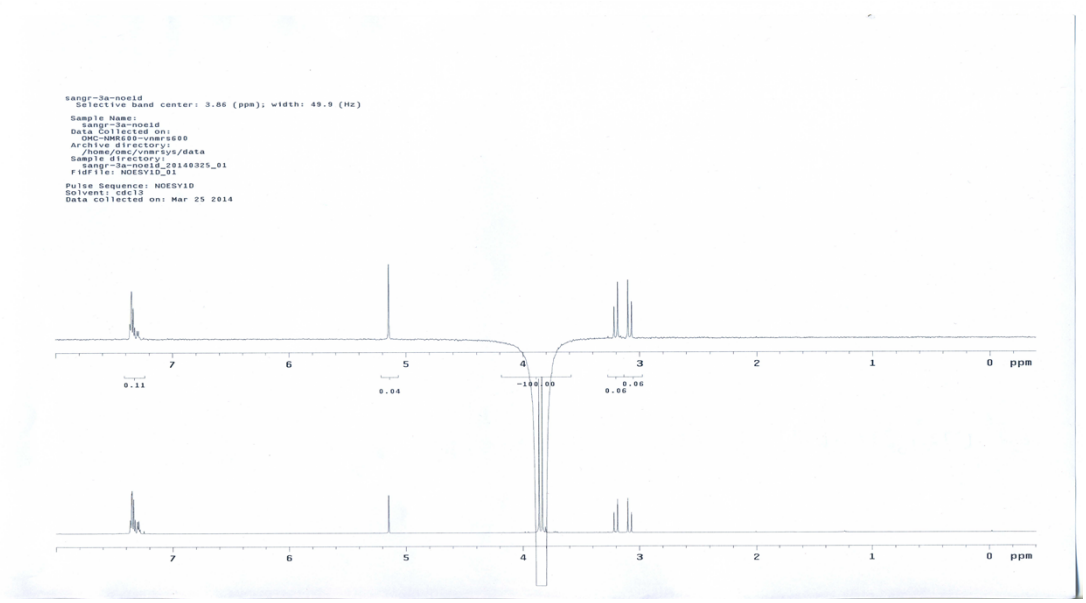
3a-gCOSY



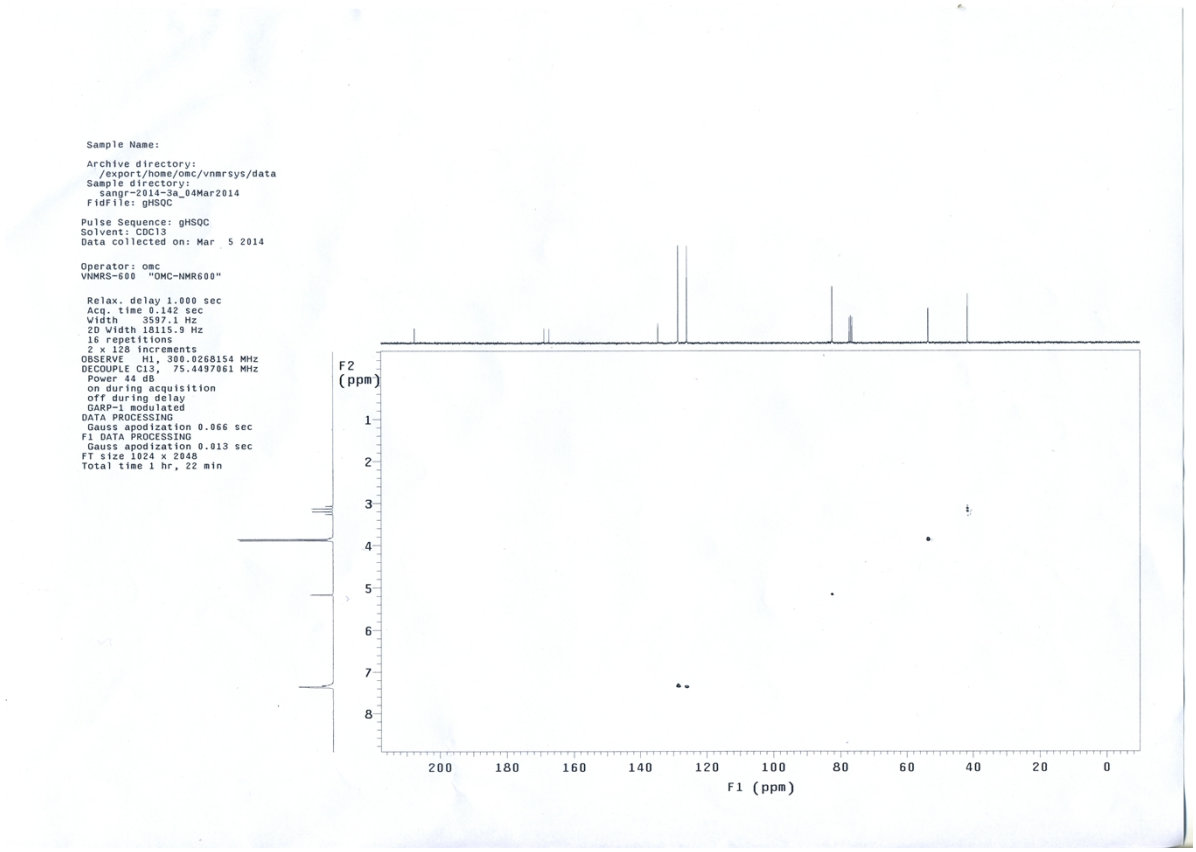
3a-NOESY (300 MHz)



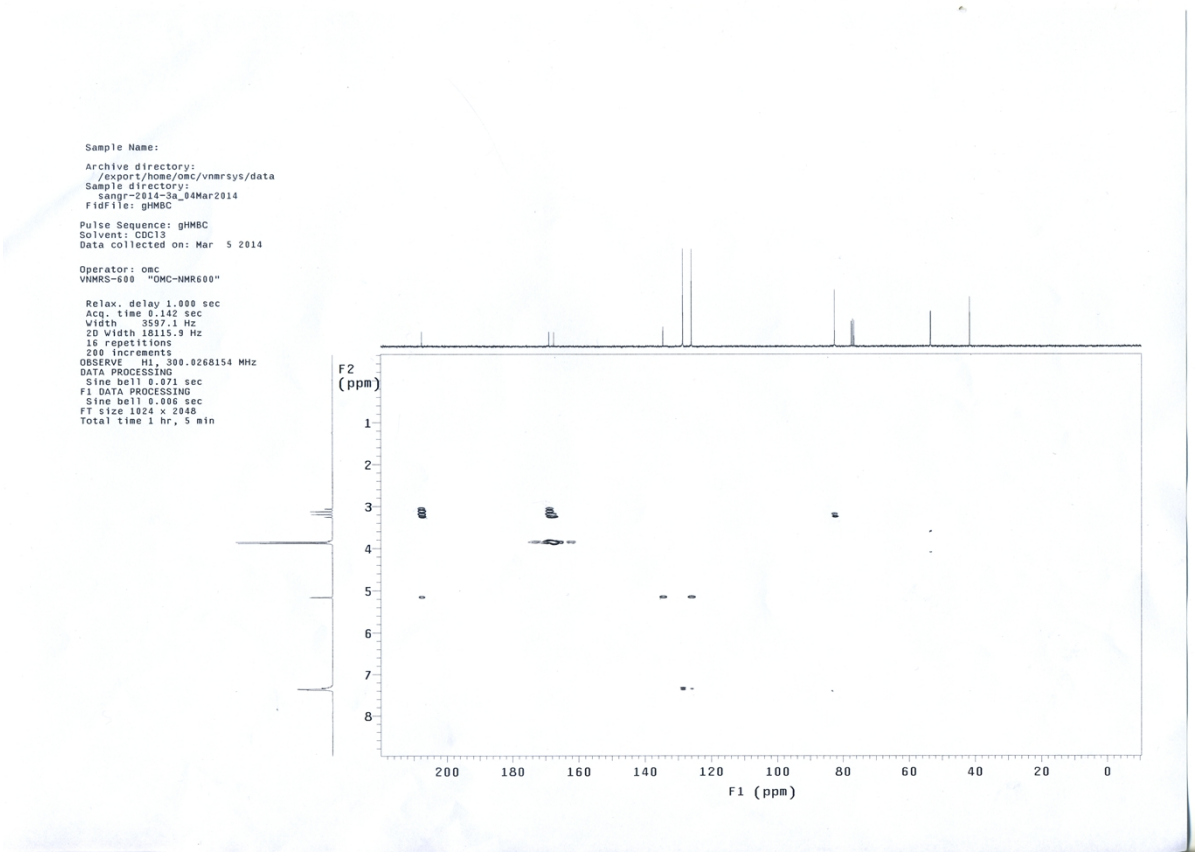
3a-NOESY (6000 MHz)



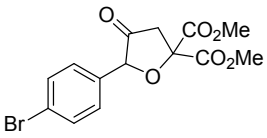
3a-NOE1D



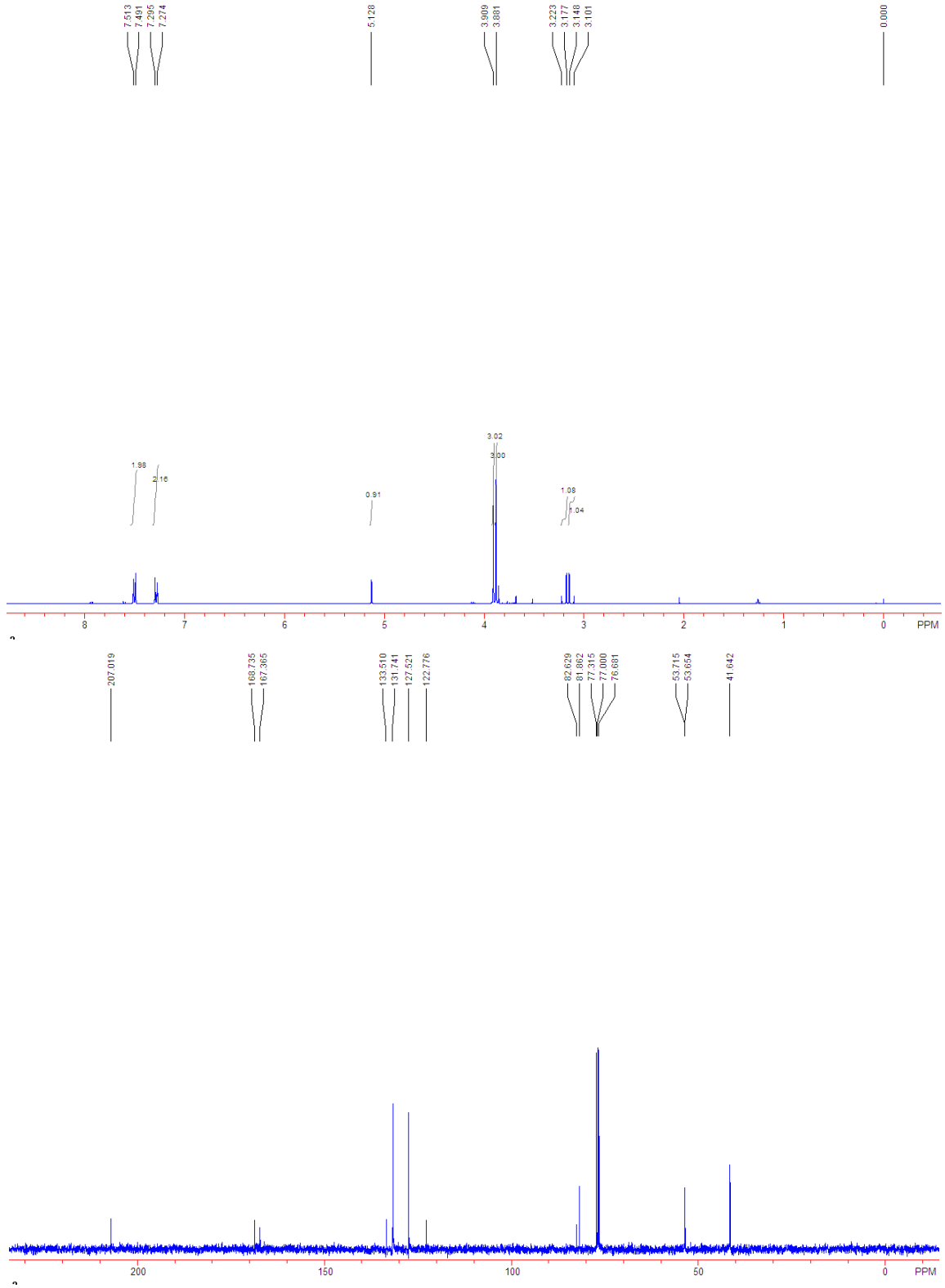
3a-gHSQC

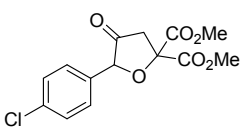


3a-gHMBC



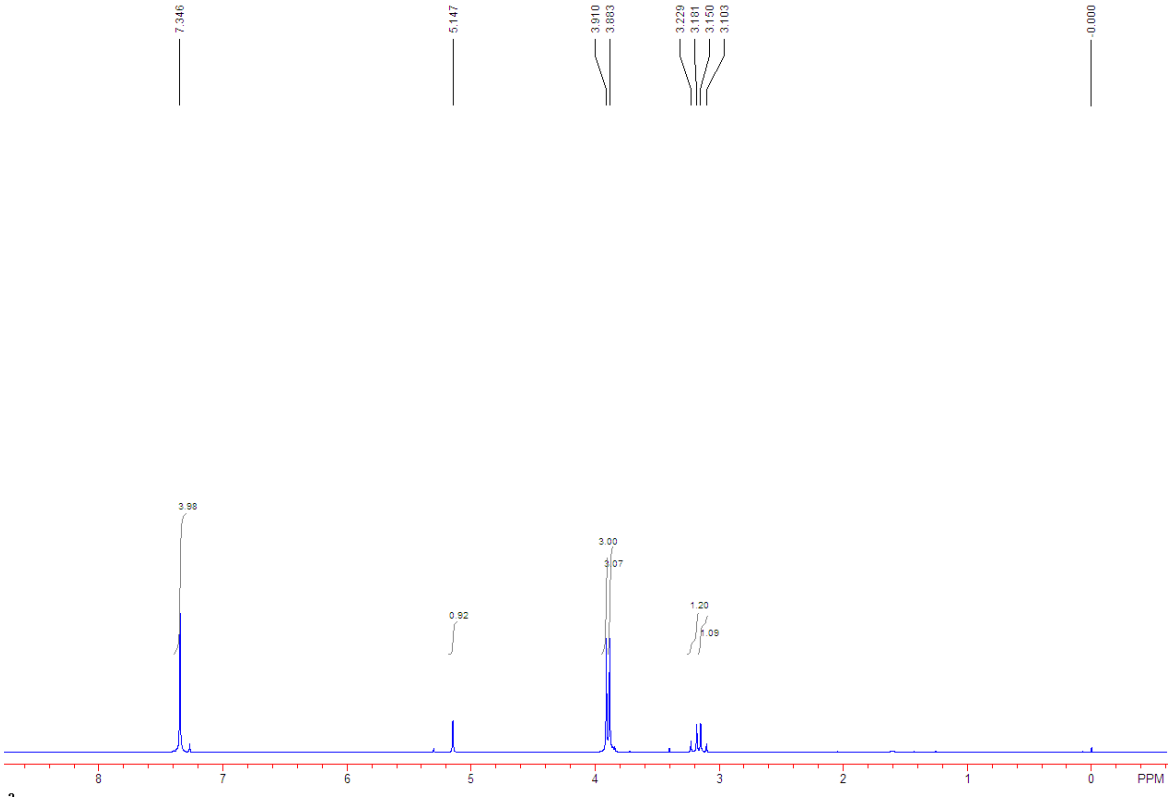
dimethyl 5-(4-bromophenyl)-4-oxodihydrofuran-2,2(3H)-dicarboxylate **3b**: a light yellow oil. 121.5 mg, 57% yield.^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.12 (d, J = 18.8 Hz, 1H), 3.20 (d, J = 18.8 Hz, 1H), 3.88 (s, 3H), 3.91 (s, 3H), 5.13 (s, 1H), 7.28 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.64, 53.65, 53.72, 81.86, 82.63, 122.78, 127.52, 131.74, 133.51, 167.37, 168.74, 207.02. IR (ATR) ν 3005, 2989, 2318, 1738, 1589, 1487, 1435, 1399, 1275, 1260, 1154, 1120, 1100, 1068, 1010, 959, 896, 821, 746 cm^{-1}. MS (EI) *m/z* 356. HRMS (EI) calcd for [$C_{14}H_{13}BrO_6$] requires 355.9895, found 355.9901.

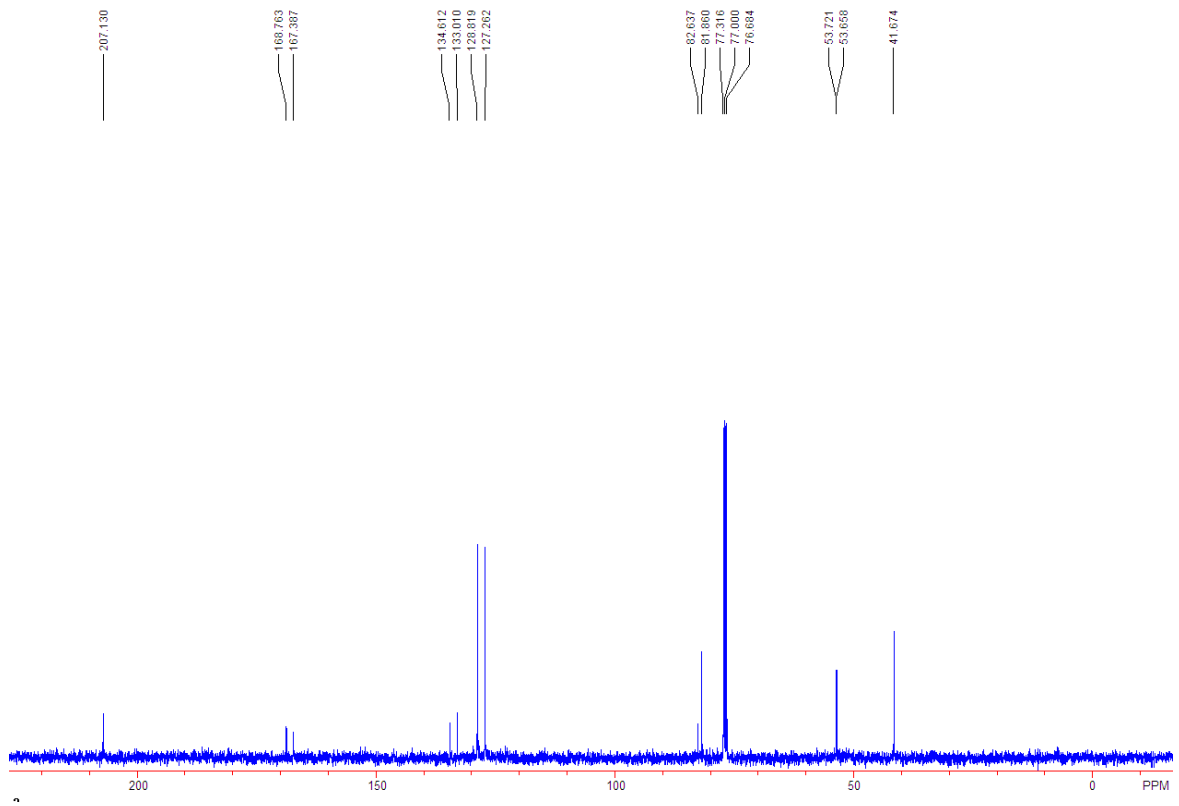


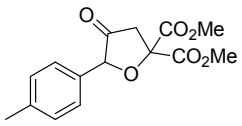


dimethyl 5-(4-chlorophenyl)-4-oxodihydrofuran-2,2(3H)-dicarboxylate **3c**: a light yellow oil.

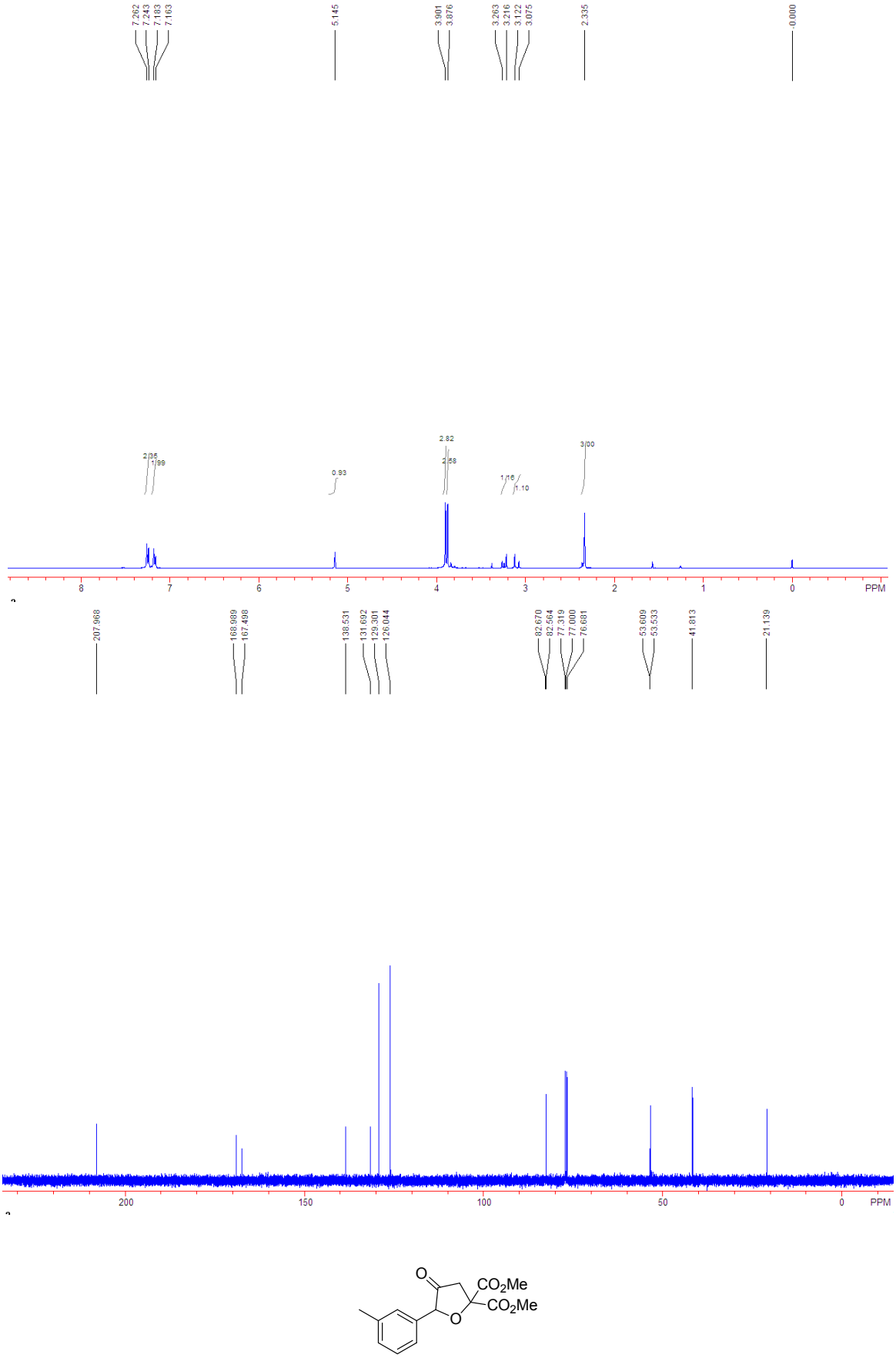
193.4 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.13 (d, J = 18.8 Hz, 1H), 3.21 (d, J = 18.8 Hz, 1H), 3.88 (s, 3H), 3.91 (s, 3H), 5.14 (s, 1H), 7.35 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.67, 53.66, 53.72, 81.86, 82.64, 127.26, 128.82, 133.01, 134.61, 167.39, 168.76, 207.13. IR (ATR) ν 2924, 1740, 1595, 1437, 1403, 1276, 1261, 1093, 1015, 764, 750 cm^{-1}. HRMS (ESI) calcd for [$C_{14}H_{13}ClO_6$+NH_4] requires 330.0739, found 330.0747 [M^++NH_4].





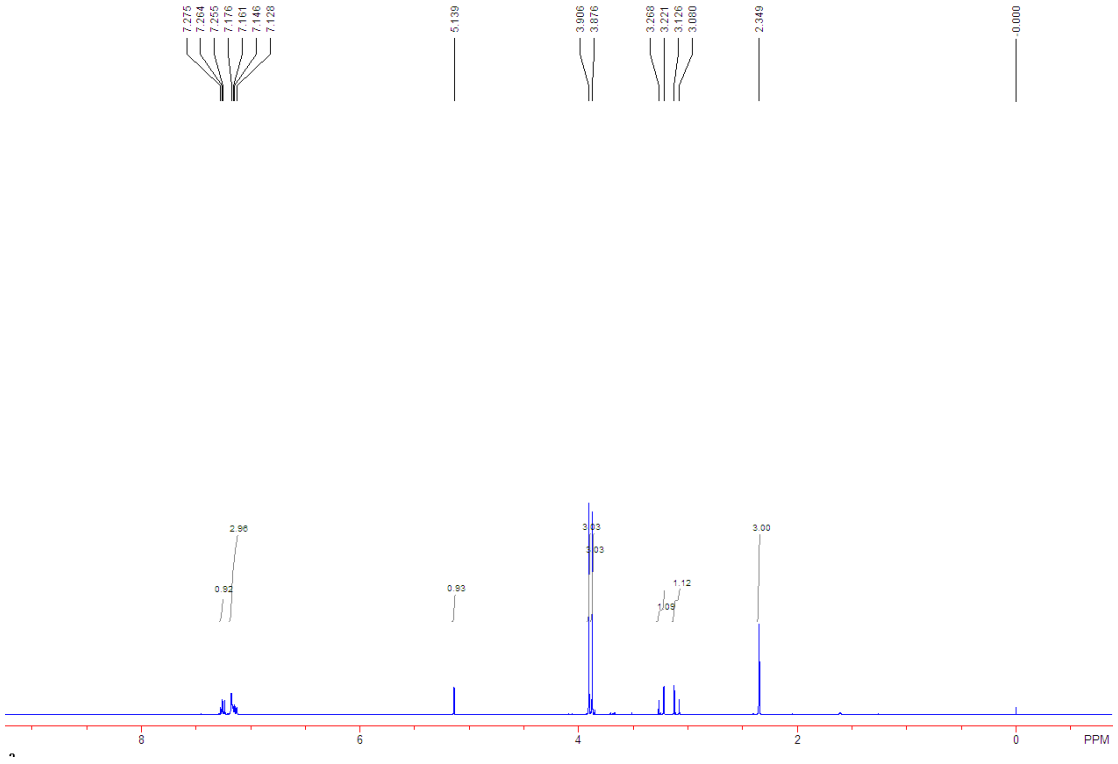


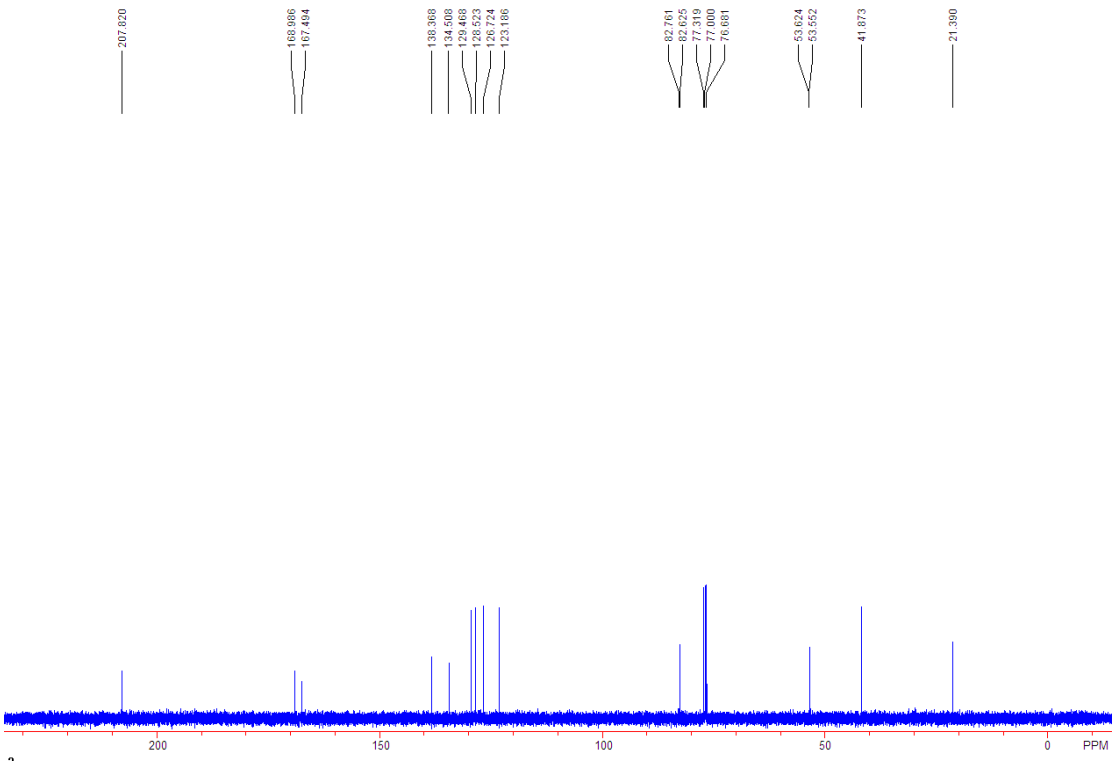
dimethyl 4-oxo-5-(p-tolyl)dihydrofuran-2,2(3H)-dicarboxylate **3d**: a light yellow oil. 181.2 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.33 (s, 3H), 3.10 (d, J = 18.8 Hz, 1H), 3.24 (d, J = 18.8 Hz, 1H), 3.88 (s, 3H), 3.90 (s, 3H), 5.14 (s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.14, 41.81, 53.53, 53.61, 82.56, 82.67, 126.04, 129.30, 131.69, 138.53, 167.50, 168.99, 207.97. IR (ATR) ν 2956, 1740, 1611, 1512, 1436, 1283, 1244, 1178, 1100, 1020, 962, 818, 752, 691 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{16}O_6$+NH_4] requires 310.1285, found 310.1284 [M^++NH_4].

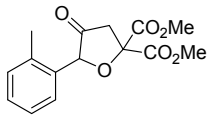


dimethyl 4-oxo-5-(m-tolyl)dihydrofuran-2,2(3H)-dicarboxylate **3e**: a light yellow oil. 215.6

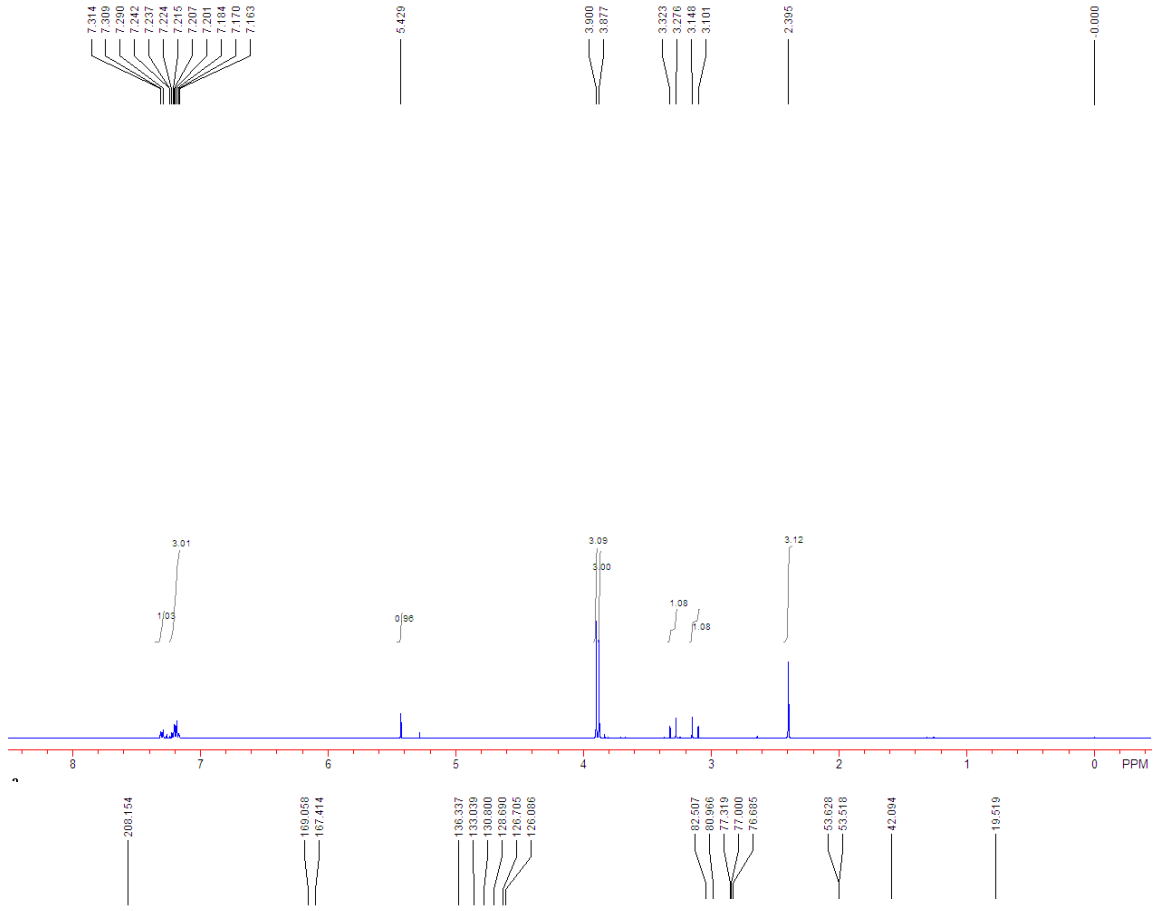
mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.35 (s, 3H), 3.10 (d, J = 18.4 Hz, 1H), 3.24 (d, J = 18.4 Hz, 1H), 3.88 (s, 3H), 3.91 (s, 3H), 5.14 (s, 1H), 7.13-7.18 (m, 3H), 7.26-7.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.39, 41.87, 53.55, 53.62, 82.63, 82.76, 123.19, 126.72, 128.52, 129.47, 134.51, 138.37, 167.49, 168.99, 207.82. IR (ATR) ν 2957, 1739, 1608, 1590, 1436, 1276, 1260, 1196, 1104, 1081, 954, 793, 764, 749, 703, 682 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{16}O_6$+NH_4] requires 310.1285, found 310.1273 [M^++NH_4].

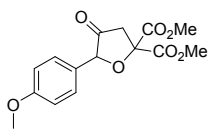






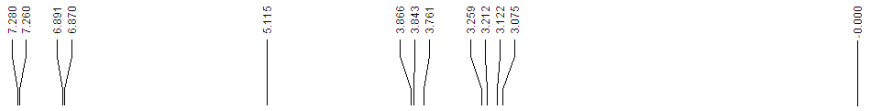
dimethyl 4-oxo-5-(o-tolyl)dihydrofuran-2,2(3H)-dicarboxylate **3f**: a light yellow oil. 195.8 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.40 (s, 3H), 3.12 (d, J = 18.8 Hz, 1H), 3.30 (d, J = 18.8 Hz, 1H), 3.88 (s, 3H), 3.90 (s, 3H), 5.43 (s, 1H), 7.16-7.24 (m, 3H), 7.29-7.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.52, 42.09, 53.52, 53.63, 80.97, 82.51, 126.09, 126.71, 128.69, 130.80, 133.04, 136.34, 167.41, 169.06, 208.15. IR (ATR) ν 2958, 2924, 1745, 1260, 1019, 799 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{16}O_6$+NH_4] requires 310.1285, found 310.1285 [M^++NH_4].

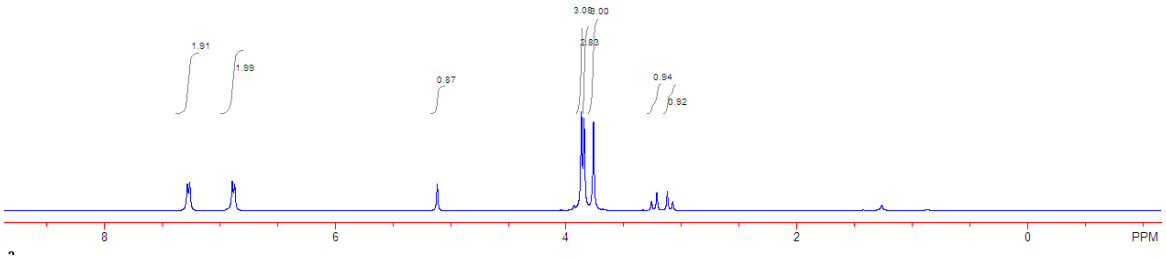


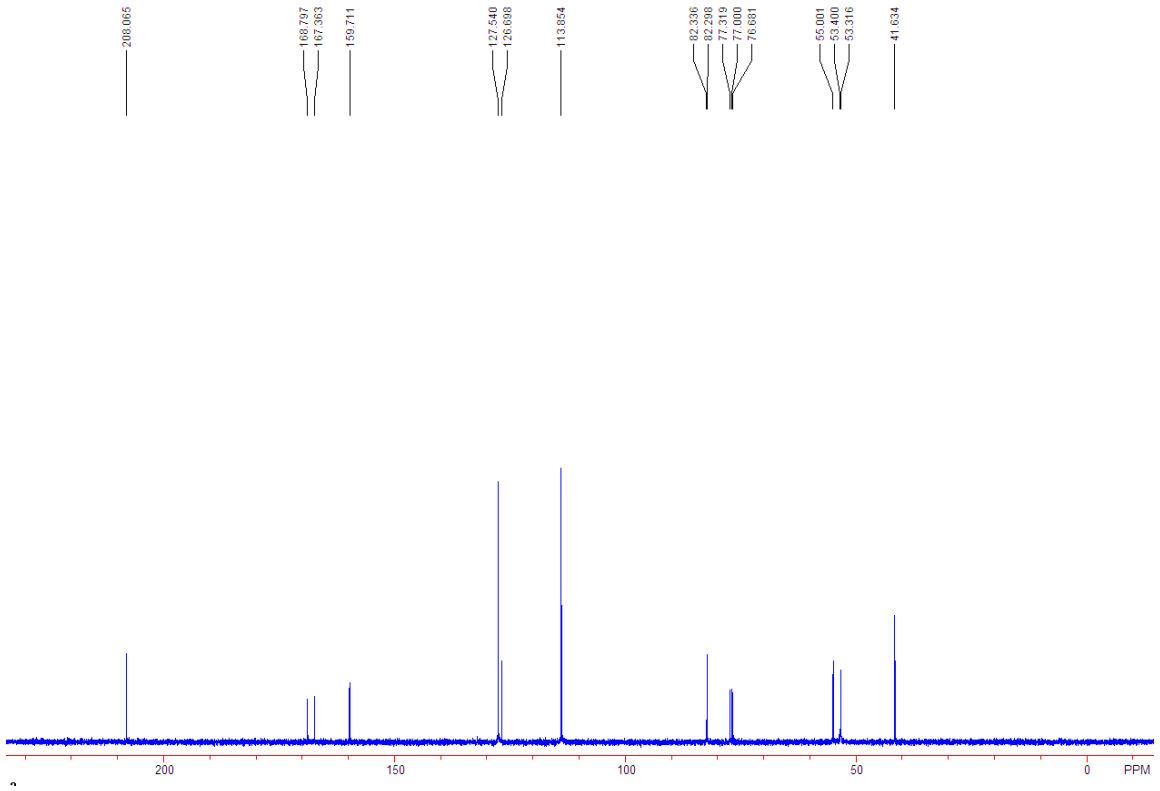


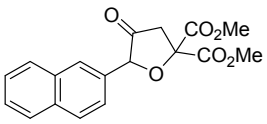
dimethyl 5-(4-methoxyphenyl)-4-oxodihydrofuran-2,2(3H)-dicarboxylate **3g**: a light yellow

oil. 417.1 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.10 (d, J = 18.8 Hz, 1H), 3.24 (d, J = 18.8 Hz, 1H), 3.76 (s, 3H), 3.84 (s, 3H), 3.87 (s, 3H), 5.12 (s, 1H), 6.88 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.63, 53.32, 53.40, 55.00, 82.30, 82.34, 113.85, 126.70, 127.54, 159.71, 167.36, 168.80, 208.07. IR (ATR) ν 2958, 2842, 1857, 1741, 1605, 1512, 1436, 1283, 1247, 1161, 1121, 1060, 1027, 959, 889, 828, 797, 769, 735, 697. HRMS (ESI) calcd for [$C_{15}H_{16}O_7$+H] requires 309.0969, found 309.0975 [M^++H].

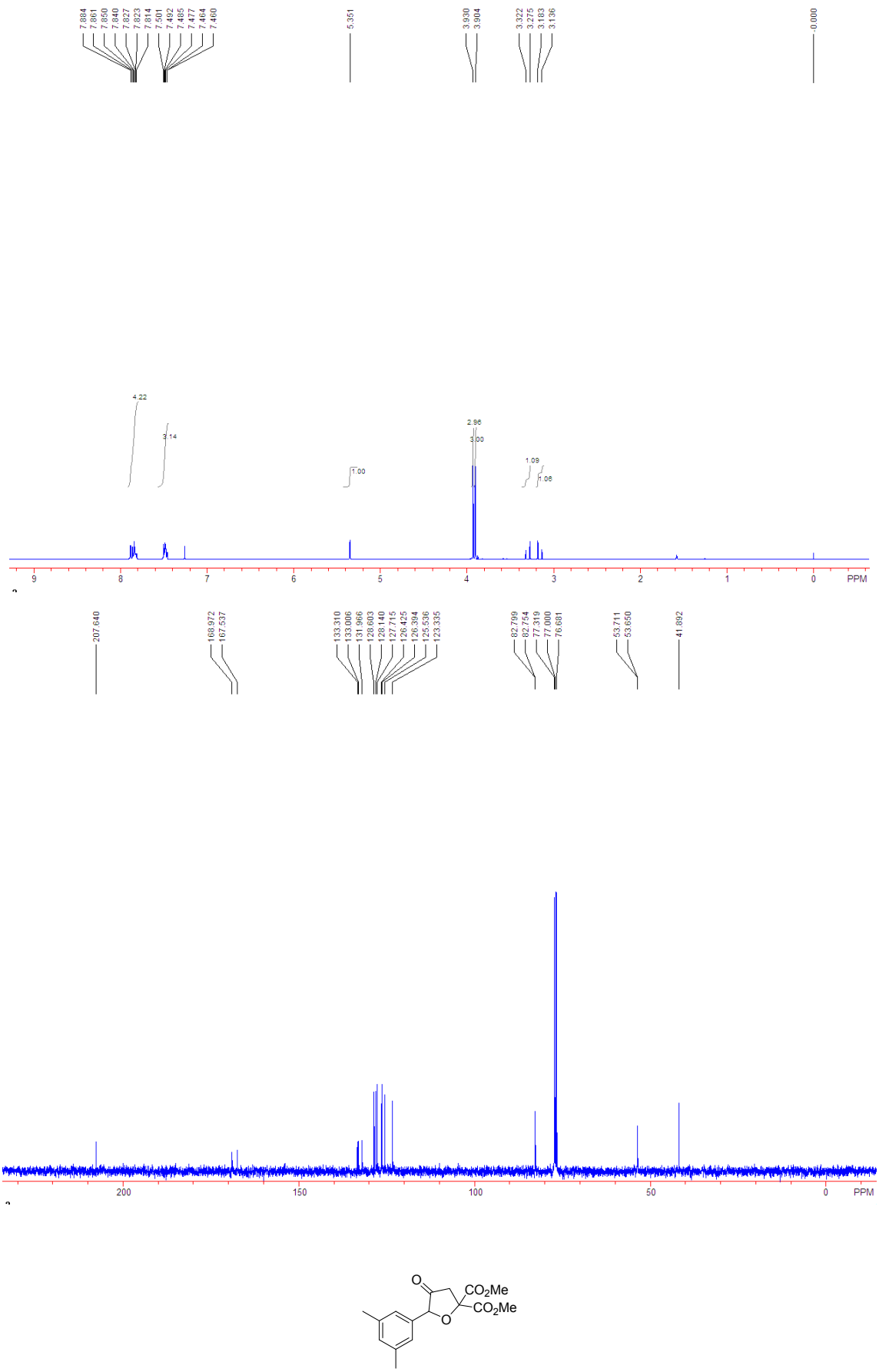






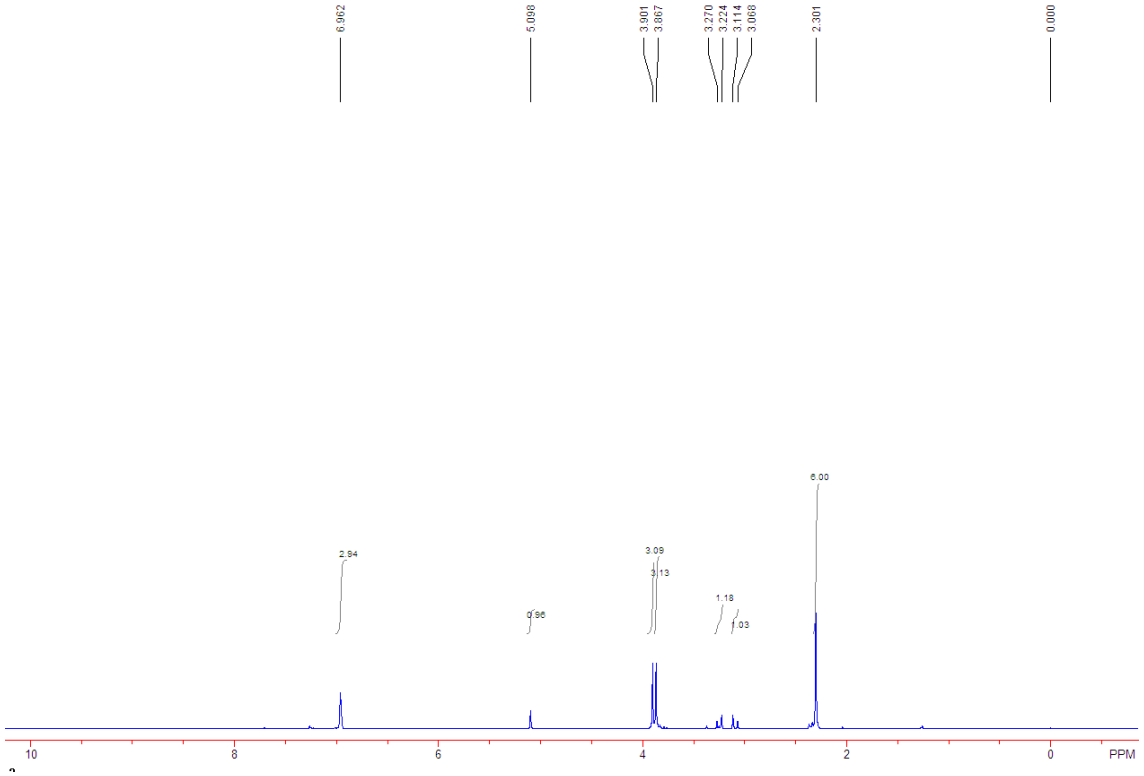


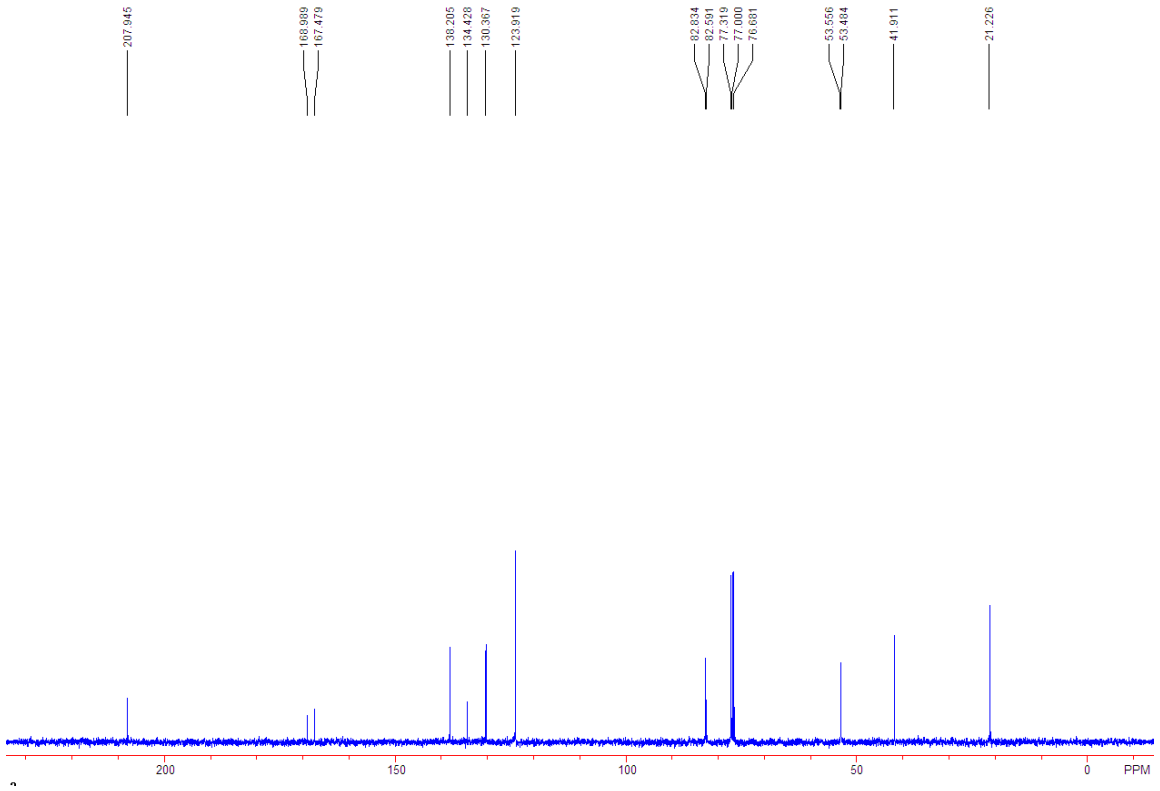
dimethyl 5-(naphthalen-2-yl)-4-oxodihydrofuran-2,2(3H)-dicarboxylate **3h**: a white solid. 141.1 mg, 43% yield. m.p. 89 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.16 (d, J = 18.8 Hz, 1H), 3.30 (d, J = 18.8 Hz, 1H), 3.90 (s, 3H), 3.93 (s, 3H), 5.35 (s, 1H), 7.46-7.50 (m, 3H), 7.81-7.88 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.89, 53.65, 53.71, 82.75, 82.80, 123.34, 125.54, 126.39, 126.43, 127.72, 128.14, 128.60, 131.97, 133.01, 133.31, 167.54, 168.97, 207.64. IR (ATR) ν 3005, 2989, 2318, 1740, 1462, 1275, 1260, 895, 749 cm^{-1}. MS (EI) *m/z* 328. HRMS (EI) calcd for [$C_{18}H_{16}O_6$] requires 328.0947, found 328.0946.

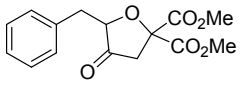


dimethyl 5-(3,5-dimethylphenyl)-4-oxodihydrofuran-2,2(3H)-dicarboxylate **3i**: a light yellow

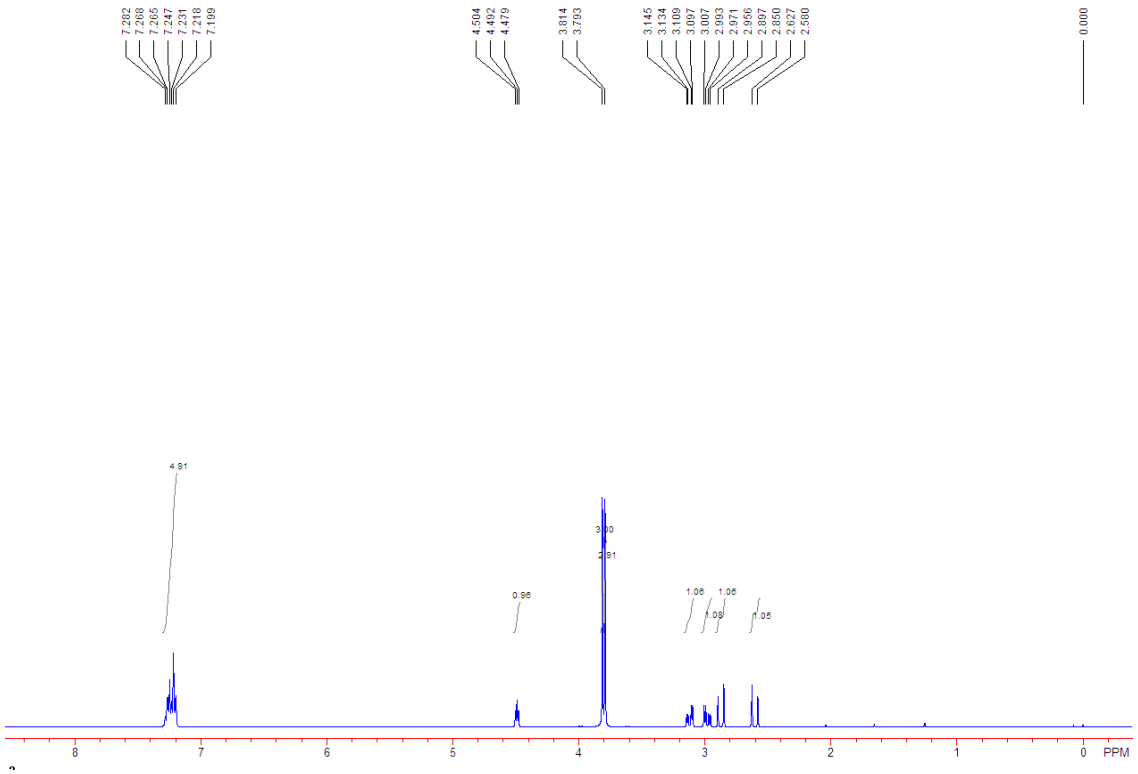
oil. 282.6 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.30 (s, 6H), 3.09 (d, J = 18.4 Hz, 1H), 3.25 (d, J = 18.4 Hz, 1H), 3.87 (s, 3H), 3.90 (s, 3H), 5.10 (s, 1H), 6.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.23, 41.91, 53.48, 53.56, 82.59, 82.83, 123.92, 130.37, 134.43, 138.21, 167.48, 168.99, 207.95. IR (ATR) ν 2956, 1744, 1608, 1507, 1436, 1314, 1275, 1260, 1206, 1075, 949, 871, 764, 750, 678 cm^{-1}. HRMS (ESI) calcd for [$C_{16}H_{18}O_6$+NH_4] requires 324.1442, found 324.1443 [M^++NH_4].

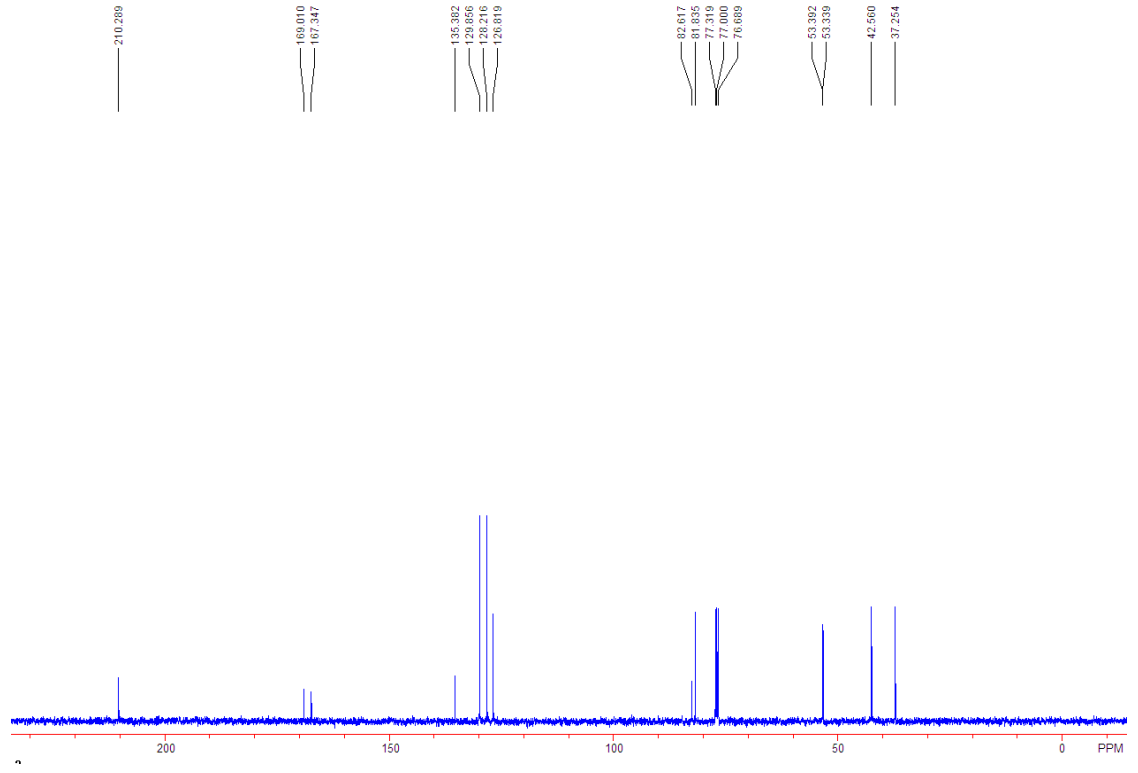


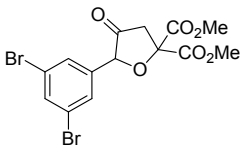




dimethyl 5-benzyl-4-oxodihydrofuran-2,2(3H)-dicarboxylate **3j**: a light yellow oil. 233.0 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.60 (d, J = 18.8 Hz, 1H), 2.87 (d, J = 18.8 Hz, 1H), 2.99 (dd, J = 14.4 Hz, 5.6 Hz, 1H), 3.12 (dd, J = 14.4 Hz, 4.8 Hz, 1H), 3.79 (s, 3H), 3.81 (s, 3H), 4.49 (t, J = 5.2 Hz , 1H), 7.20-7.28 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.25, 42.56, 53.34, 53.39, 81.84, 82.62, 126.82, 128.22, 129.86, 135.38, 167.34, 169.01, 210.23. IR (ATR) ν 32996, 1745, 1496, 1455, 1436, 1301, 1275, 1261, 1197, 1157, 1121, 1075, 956, 764, 750, 702 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{16}O_6$+H] requires 293.1020, found 293.1026 [M^++H].

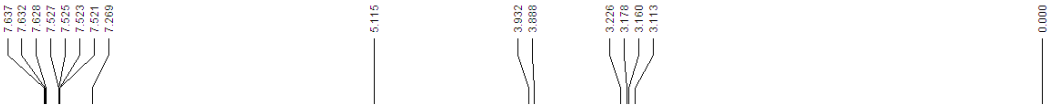


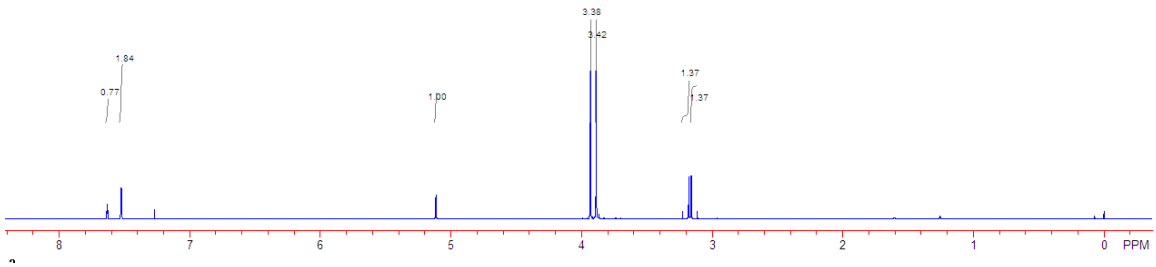


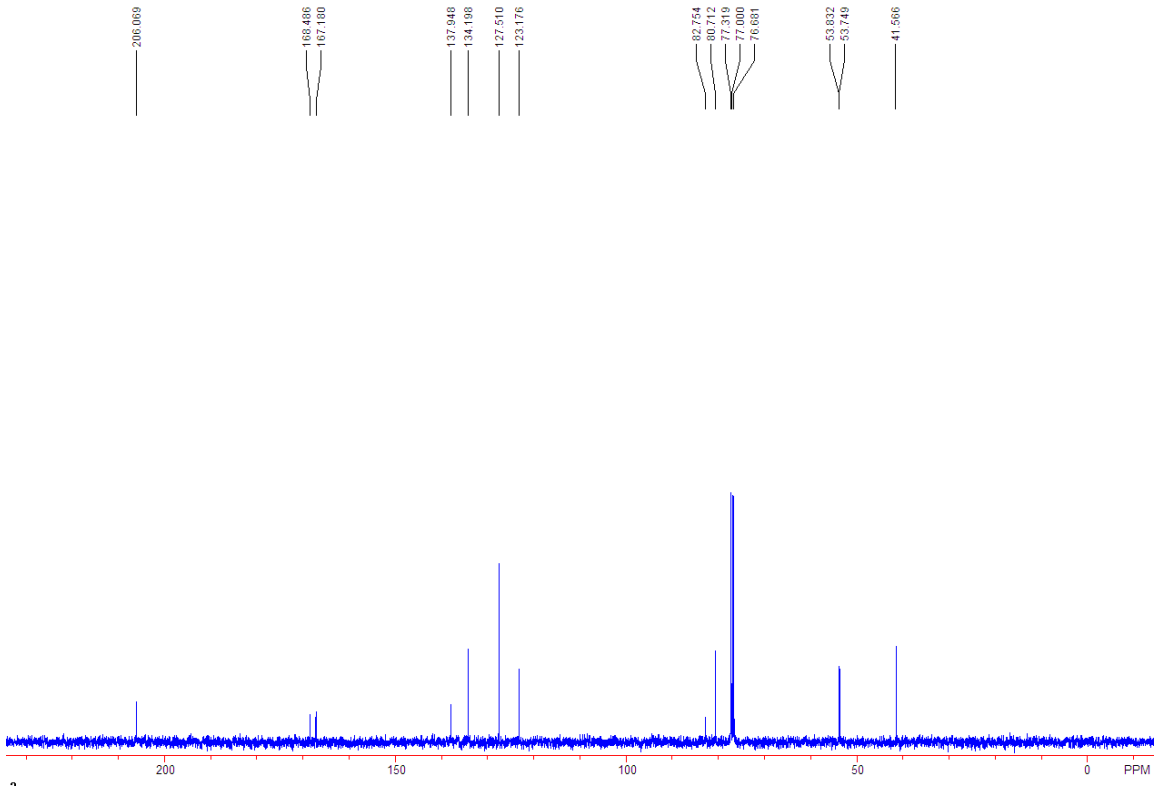


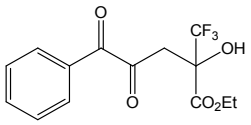
dimethyl 5-(3,5-dibromophenyl)-4-oxodihydrofuran-2,2(3H)-dicarboxylate **3k**: a white solid.

66.4 mg, 38% yield. m.p. 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.14 (d, *J* = 18.8 Hz, 1H), 3.20 (d, *J* = 18.8 Hz, 1H), 3.89 (s, 3H), 3.92 (s, 3H), 5.12 (s, 1H), 7.52 (dd, *J* = 1.6 Hz, 0.8 Hz, 2H), 7.63 (t, *J* = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.57, 53.75, 53.84, 80.71, 82.75, 123.18, 127.51, 134.20, 137.95, 167.18, 168.49, 206.07. IR (ATR) ν 3068, 2955, 1742, 1585, 1558, 1434, 1270, 1242, 1153, 1121, 1067, 1046, 958, 857, 830, 736, 699, 659 cm^{-1}. MS (EI) *m/z* 434. HRMS (EI) calcd for [$C_{14}H_{12}Br_2O_6$-OCH_3] requires 402.8817, found 402.8815[M^+-OCH_3].

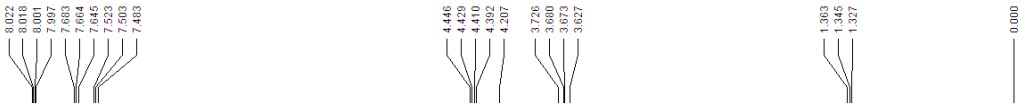








ethyl 2-hydroxy-4,5-dioxo-5-phenyl-2-(trifluoromethyl)pentanoate **4a**: a light yellow oil. 121.4 mg. 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.35 (t, J = 7.2 Hz, 3H), 3.67 (d, J = 18.4 Hz, 1H), 3.68 (d, J = 18.4 Hz, 1H), 4.21 (s, 1H), 4.42 (q, J = 7.2 Hz, 2H), 7.50 (t, J = 8.0 Hz, 2H), 7.66 (t, J = 8.0 Hz, 1H), 8.01 (dd, J = 8.4 Hz, 1.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -79.27. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.80, 40.47, 64.18, 74.72 (q, J = 30.0 Hz), 122.91 (q, J = 285.1 Hz), 128.90, 130.48, 131.24, 135.01, 168.53, 189.42, 196.53. IR (ATR) ν 3476, 2956, 1746, 1599, 1448, 1407, 1367, 1308, 1222, 1189, 1136, 1096, 1011, 858, 800, 707 cm^{-1}. HRMS (ESI) calcd for [$C_{14}H_{13}F_3O_5$] requires 318.0715, found 318.0711 [M].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7.645
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4.392
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3.726
3.680
3.673
3.627
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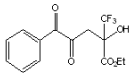
1.327
0.000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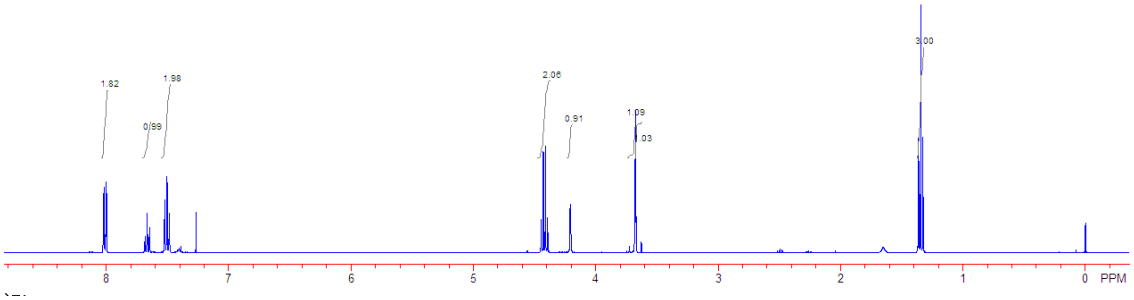
CF3
OH
O
CO2Et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0.91
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1.03
3.00
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7
6
5
4
3
2
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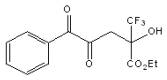
0
PPM

79.273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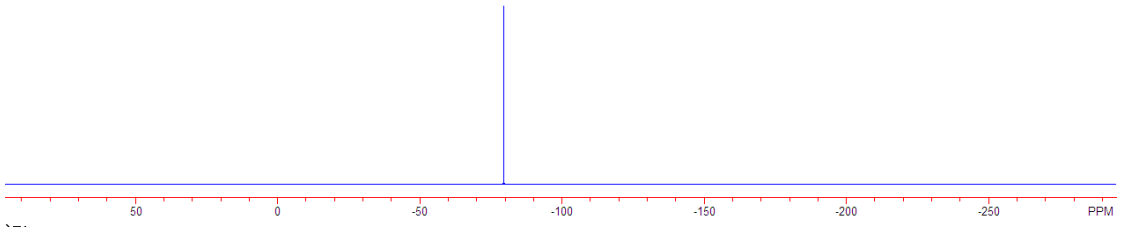
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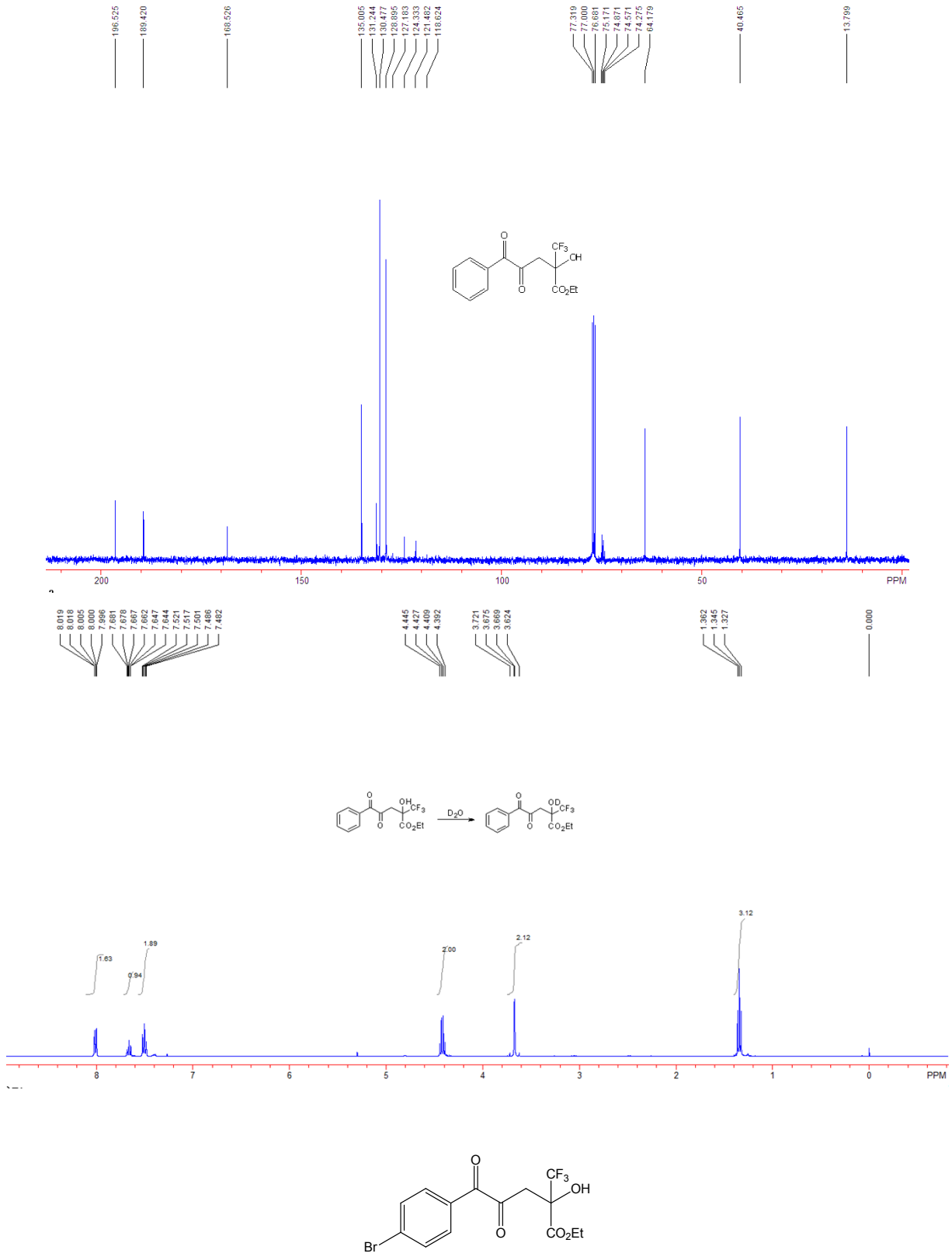
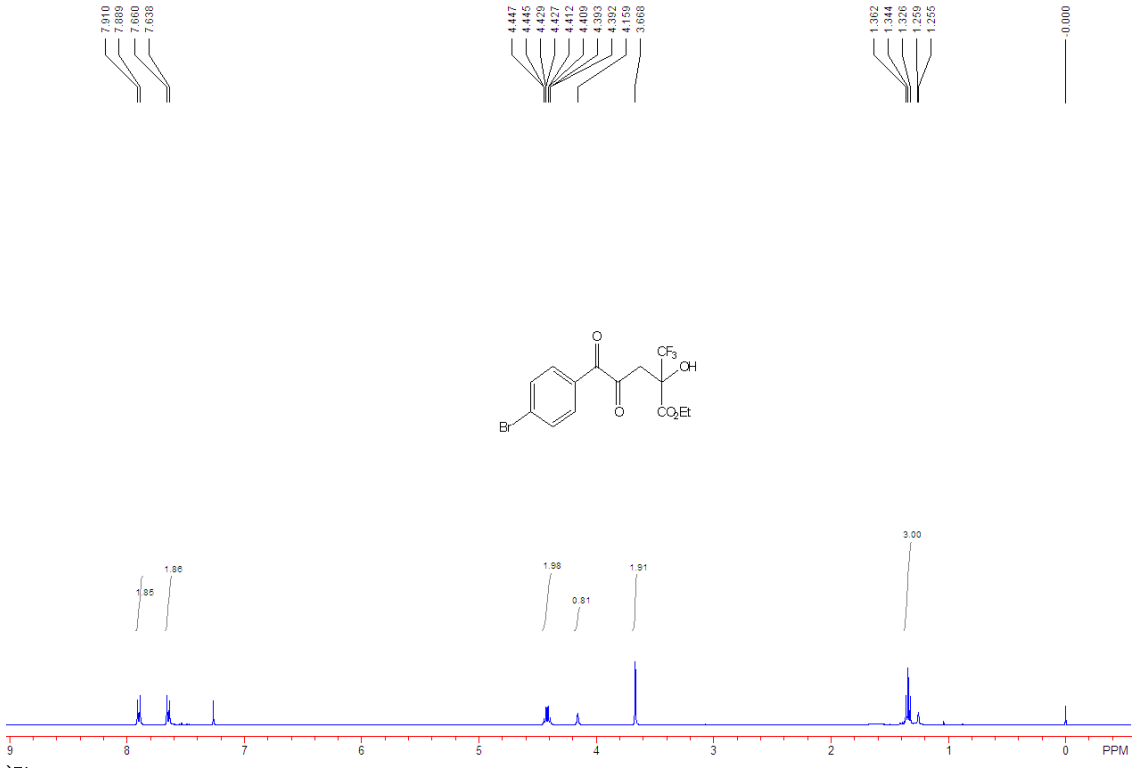
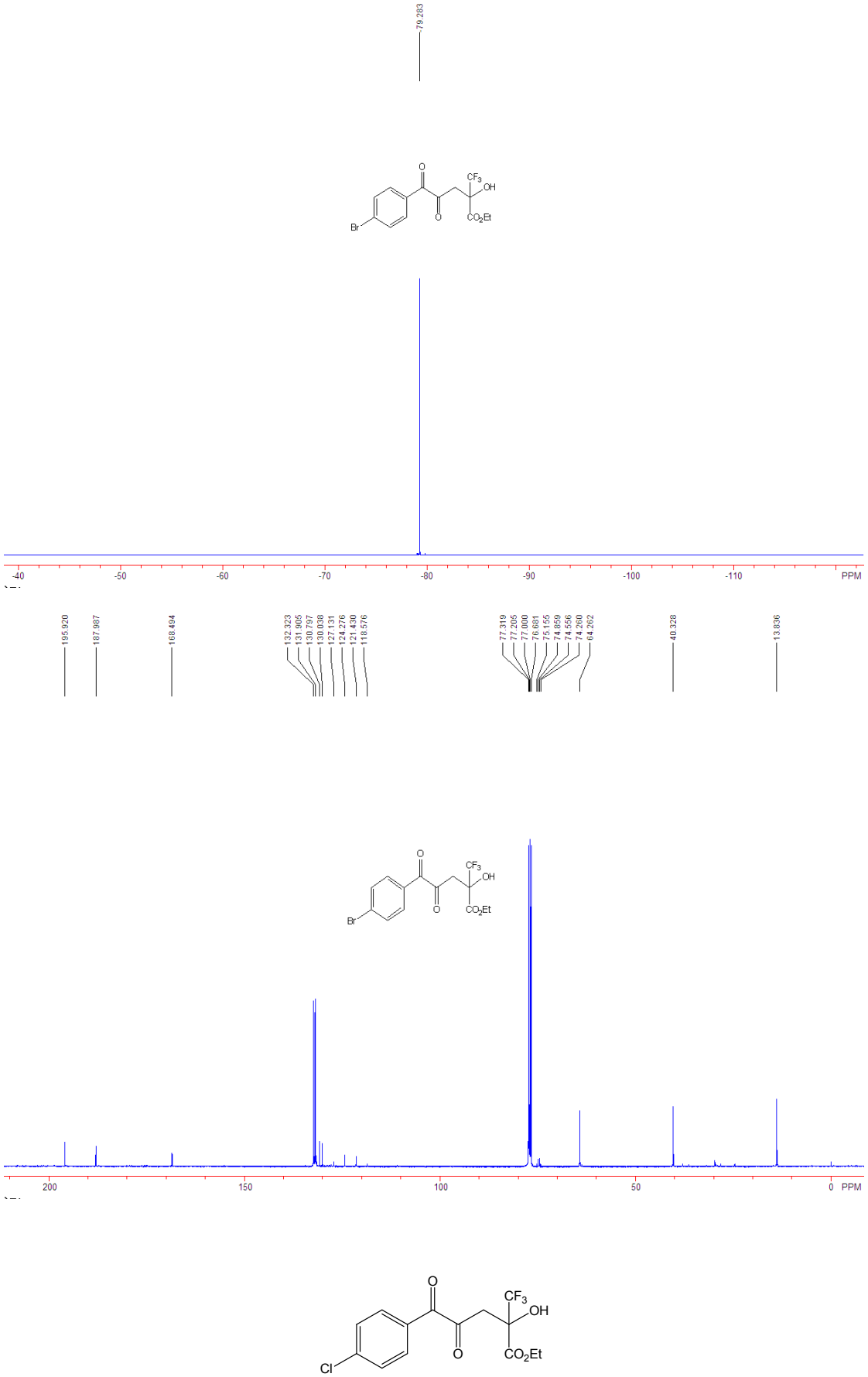
PPM



ethyl 5-(4-bromophenyl)-2-hydroxy-4,5-dioxo-2-(trifluoromethyl)pentanoate **4b**: a light yellow oil. 68.0 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.34 (t, J = 7.2 Hz, 3H), 3.67 (s, 2H), 4.16 (s, 1H), 4.42 (qd, J = 7.2 Hz, 1.2 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.90 (d,

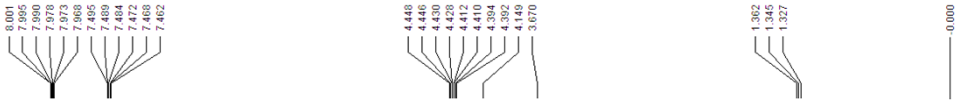
J = 8.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -79.28. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.84, 40.33, 64.26, 74.71 (q, J = 30.3 Hz), 122.85 (q, J = 284.6 Hz), 130.04, 130.80, 131.91, 132.32, 168.49, 187.99, 195.92. IR (ATR) ν 3005, 2988, 1736, 1677, 1584, 1438, 1399, 1275, 1260, 1190, 1135, 1105, 1070, 1010, 895, 816, 749, 703 cm^{-1}. HRMS (EI) calcd for [$C_{14}H_{12}BrF_3O_5$] requires 395.9820, found 395.9817.

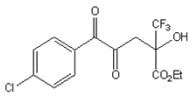


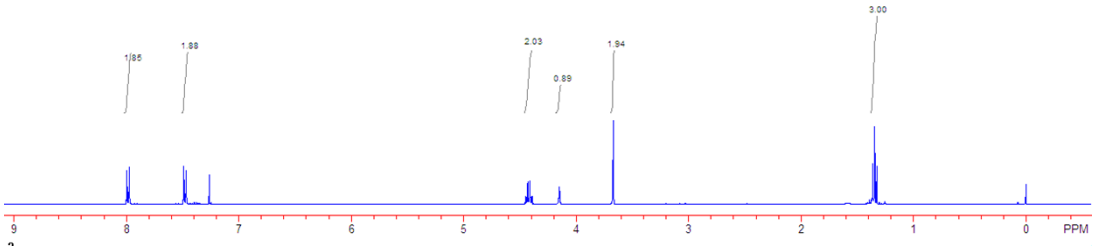


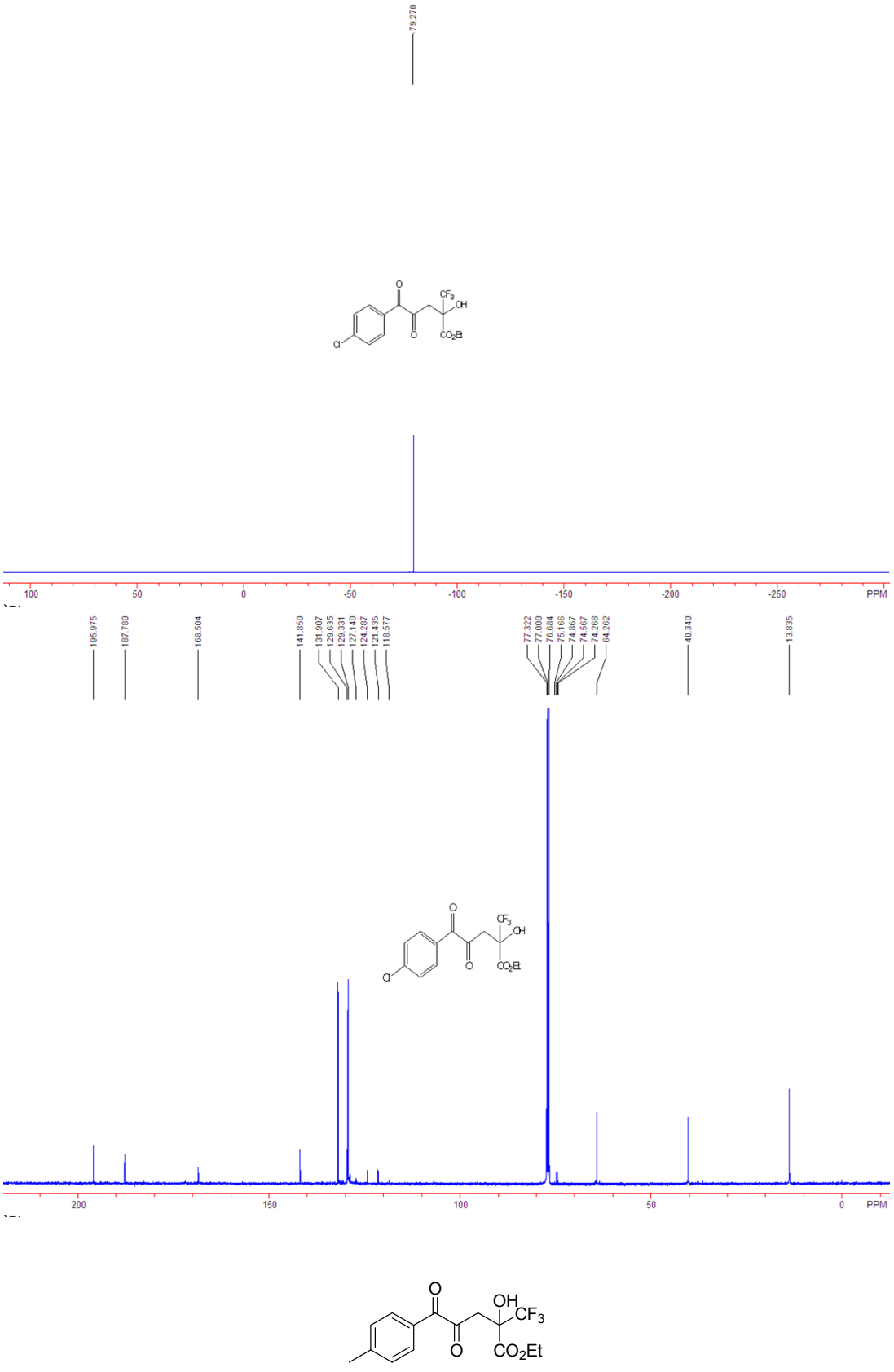
ethyl 5-(4-chlorophenyl)-2-hydroxy-4,5-dioxo-2-(trifluoromethyl)pentanoate **4c**: a light

yellow oil. 108.1 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.35 (t, J = 7.2 Hz, 3H), 3.67 (s, 2H), 4.15 (s, 1H), 4.42 (qd, J = 7.2 Hz, 0.8 Hz, 2H), 7.48 (dt, J = 8.4 Hz, 2.4 Hz, 2H), 7.98 (dt, J = 8.4 Hz, 2.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -79.27. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.84, 40.34, 64.26, 74.72 (q, J = 30.0 Hz), 122.86 (q, J = 285.2 Hz), 129.33, 129.64, 131.91, 141.85, 168.50, 187.78, 195.98. IR (ATR) ν 3005, 2989, 1740, 1587, 1462, 1275. 1260, 1193, 1092, 1014, 897, 749 cm^{-1}. MS (EI) *m/z* 352. HRMS (EI) calcd for [$C_{14}H_{12}ClF_3O_5$-CO_2Et] requires 279.0036, found 279.0034 [M-CO_2Et].



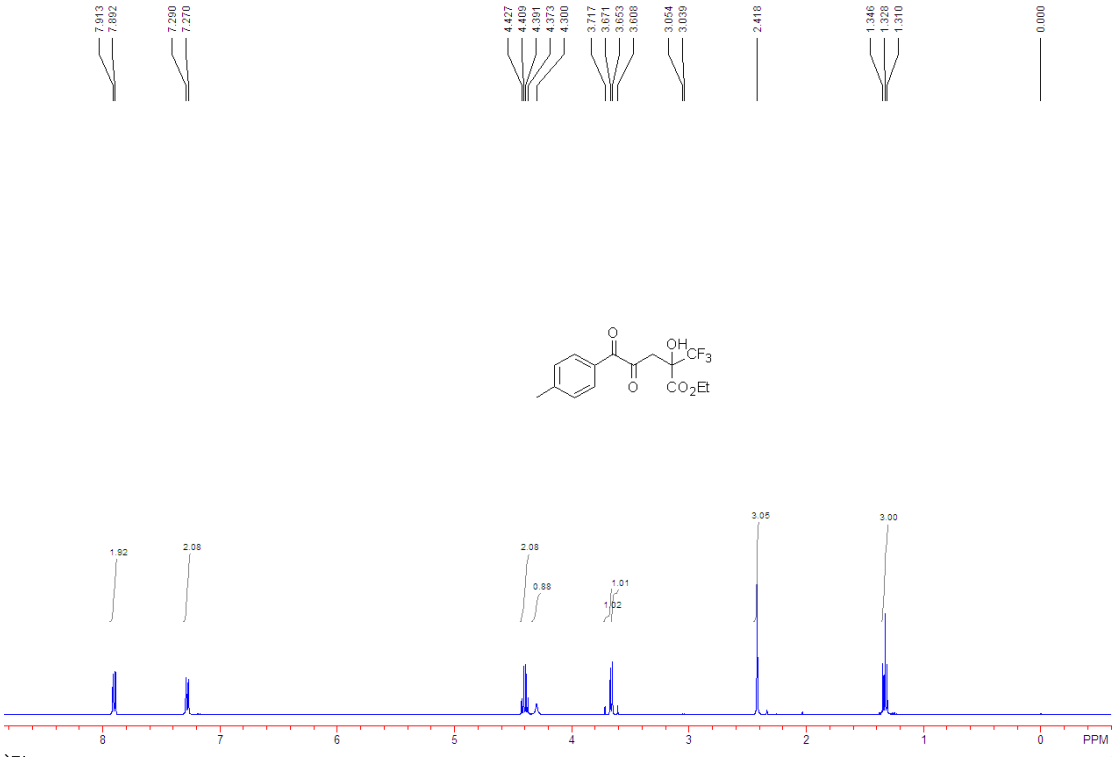


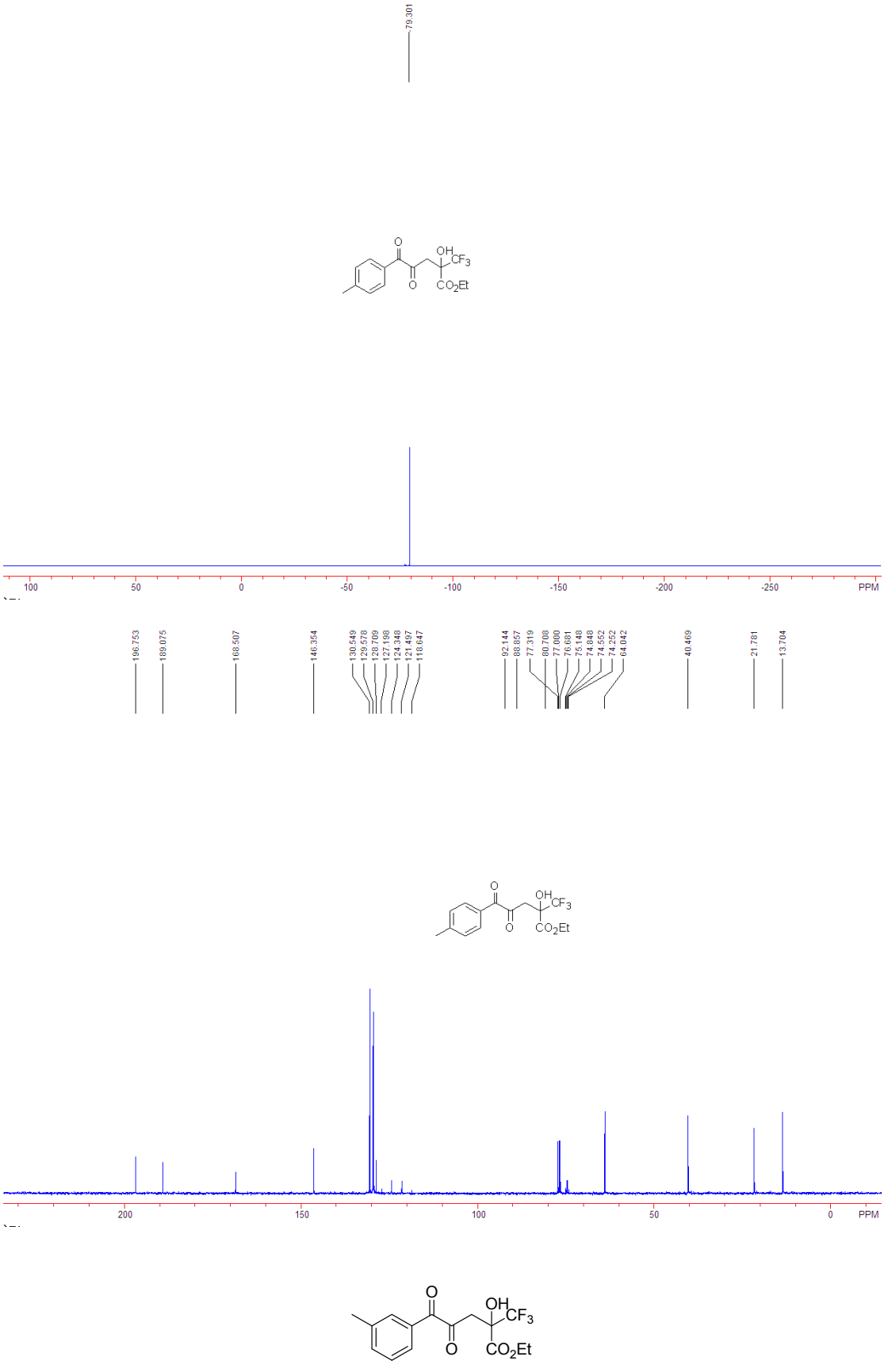




ethyl 2-hydroxy-4,5-dioxo-5-(p-tolyl)-2-(trifluoromethyl)pentanoate **4d**: a light yellow oil. 418.1 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.33 (t, *J* = 7.2 Hz, 3H), 2.42 (s, 3H), 3.63 (d, *J* = 18.0 Hz, 1H), 3.69 (d, *J* = 18.0 Hz, 1H), 4.30 (s, 1H), 4.40 (q, *J* = 7.2 Hz,

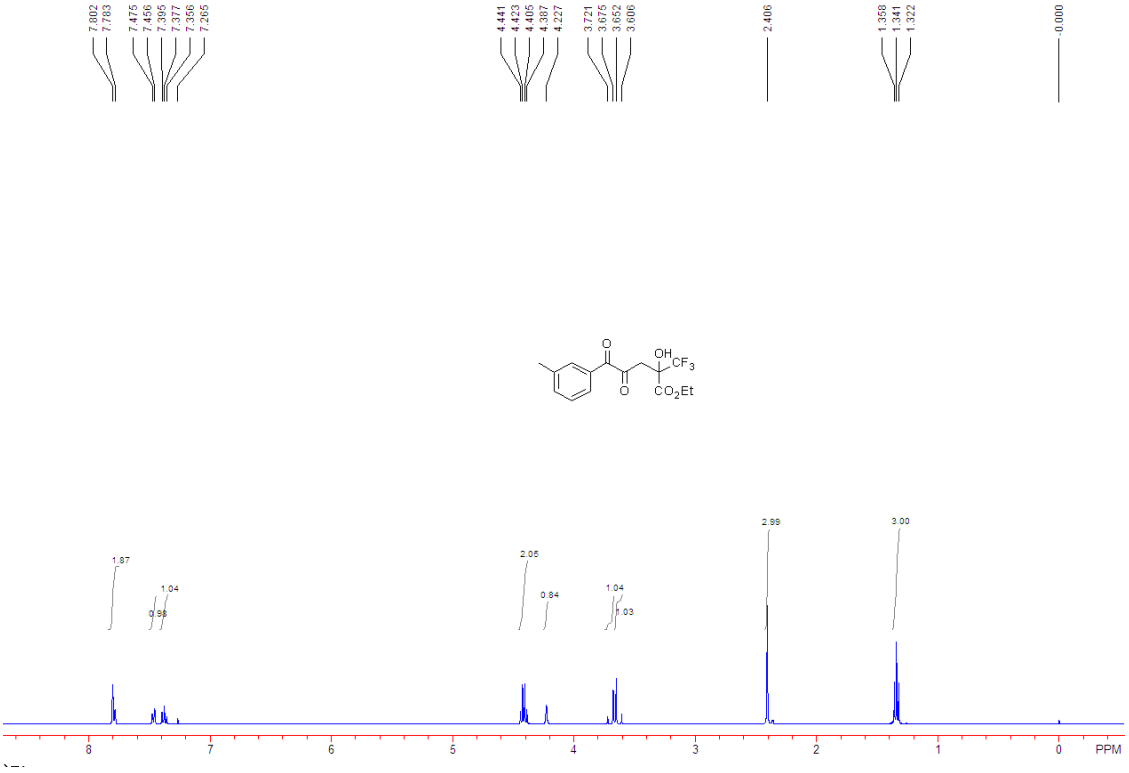
2H), 7.28 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -79.30. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.70, 21.78, 40.47, 64.04, 74.70 (q, J = 29.6 Hz), 122.92 (q, J = 285.1 Hz), 128.71, 129.58, 130.55, 146.35, 168.51, 189.08, 196.75. IR (ATR) ν 3463, 2988, 1747, 1724, 1668, 1605, 1573, 1447, 1409, 1370, 1277, 1243, 1219, 1184, 1132, 1067, 1010, 988, 921, 894, 856, 826, 765, 750, 703, 682 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{15}F_3O_5$+NH_4] requires 350.1210, found 350.1202 [M^++NH_4].

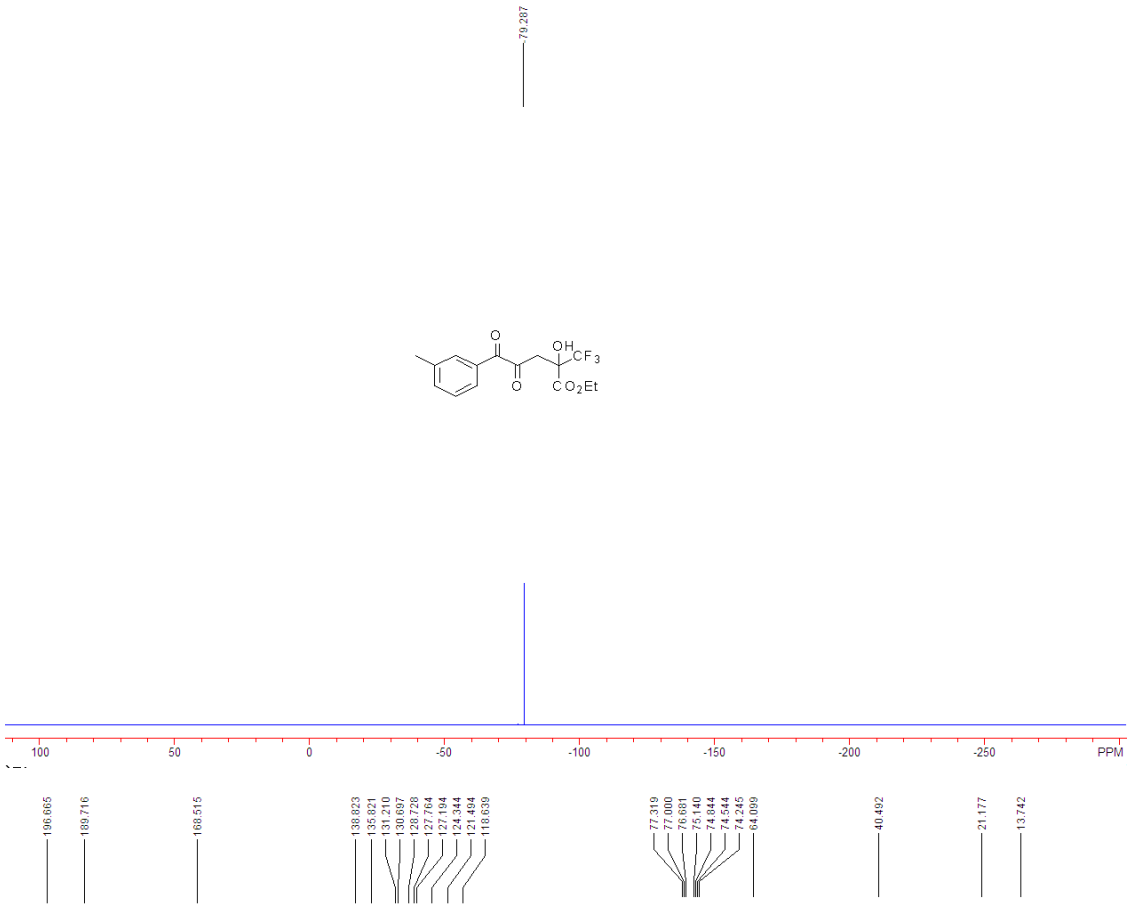


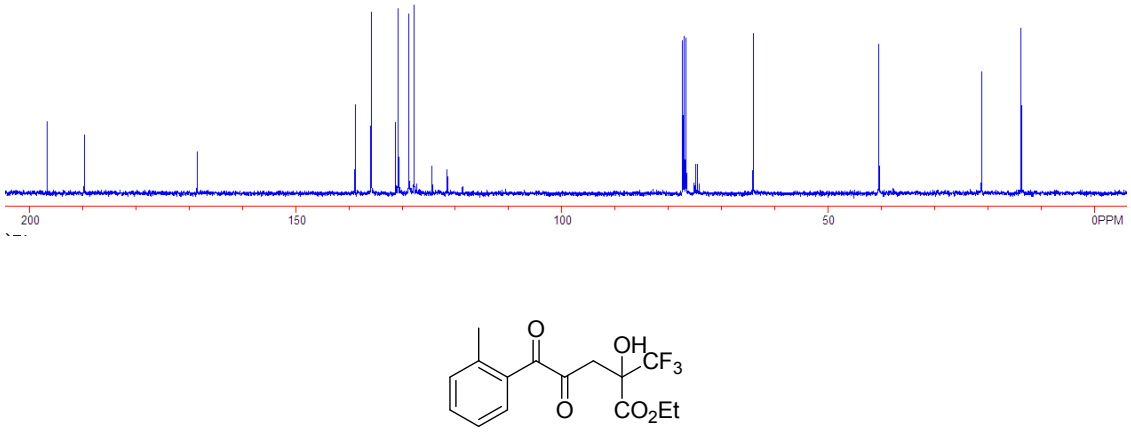


ethyl 2-hydroxy-4,5-dioxo-5-(m-tolyl)-2-(trifluoromethyl)pentanoate **4e**: a light yellow oil. 216.7 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.34 (t, J = 7.2 Hz, 3H), 2.41 (s,

3H), 3.63 (d, J = 18.4 Hz, 1H), 3.70 (d, J = 18.4 Hz, 1H), 4.23 (s, 1H), 4.41 (q, J = 7.2 Hz, 2H), 7.38 (t, J = 8.4 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -79.29. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.74, 21.18, 40.49, 64.10, 74.69 (q, J = 30.0 Hz), 122.92 (q, J = 285.0 Hz), 127.76, 128.73, 130.70, 131.21, 135.82, 138.82, 168.52, 189.72, 196.67. IR (ATR) ν 3470, 2986, 1749, 1672, 1603, 1585, 1371, 1282, 1246, 1223, 1191, 1133, 1104, 1068, 1012, 948, 857, 796, 766, 748, 700, 680 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{15}F_3O_5$+NH_4] requires 350.1210, found 350.1205 [M^++NH_4].

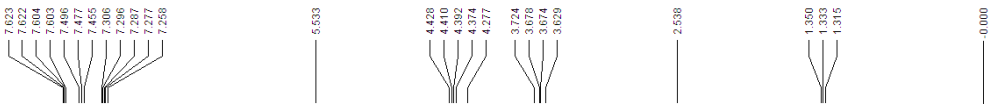


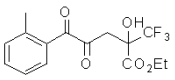


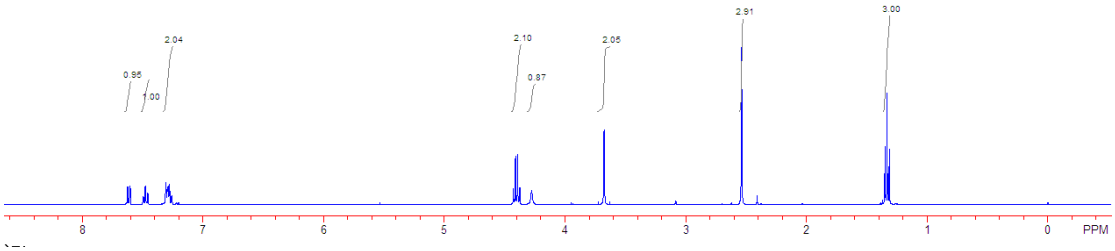


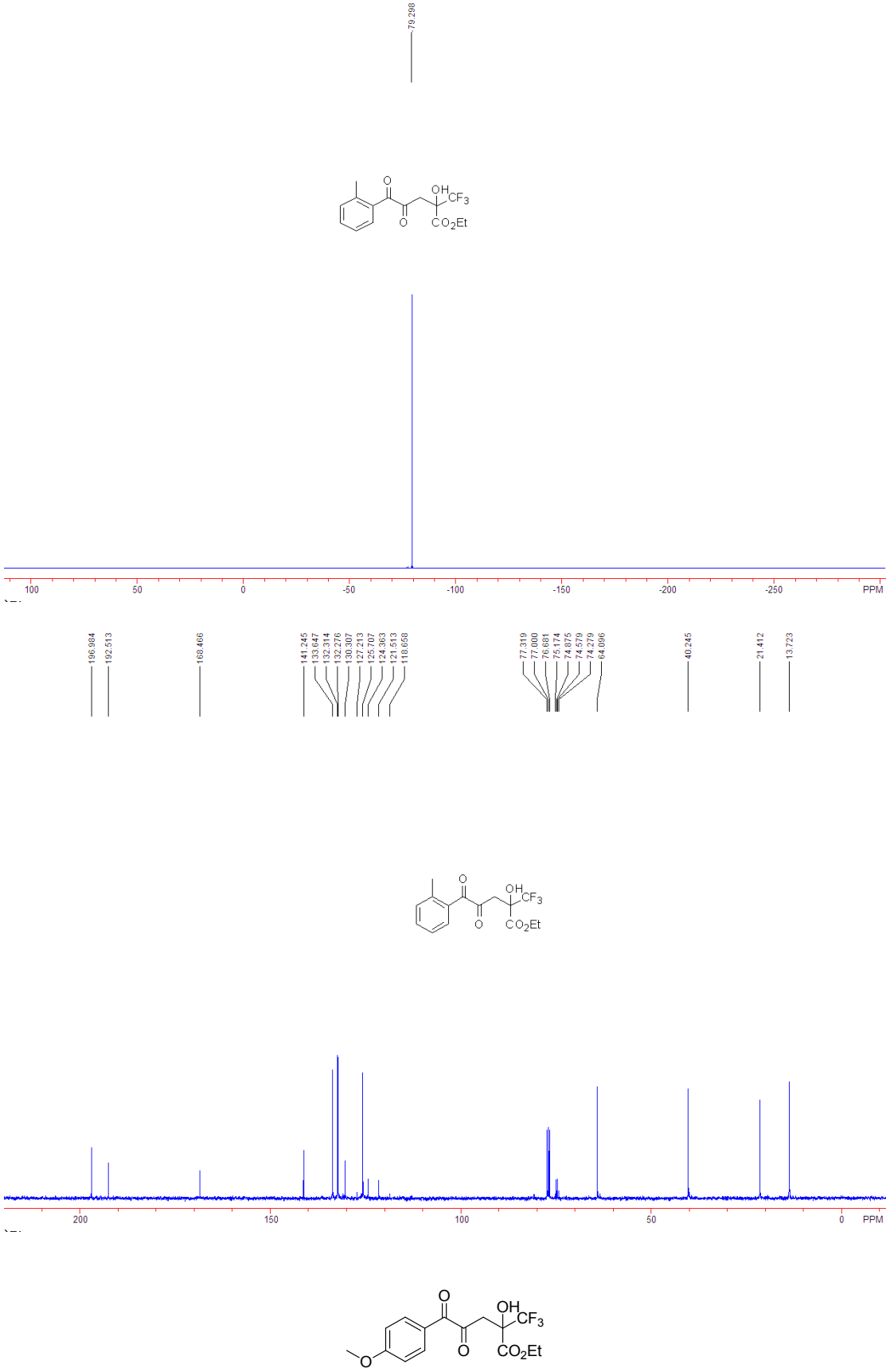
ethyl 2-hydroxy-4,5-dioxo-5-(o-tolyl)-2-(trifluoromethyl)pentanoate **4f**: a yellow oil. 405.1

mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.33 (t, J = 7.2 Hz, 3H), 2.54 (s, 3H), 3.67 (d, J = 18.0 Hz, 1H), 3.68 (d, J = 18.0 Hz, 1H), 4.28 (s, 1H), 4.40 (q, J = 7.2 Hz, 2H), 7.26-7.31 (m, 2H), 7.48 (t, J = 8.8 Hz, 1H), 7.61 (dd, J = 7.6 Hz, 0.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -79.30. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.72, 21.41, 40.25, 64.10, 74.73 (q, J = 29.6 Hz), 122.94 (q, J = 285.0 Hz), 125.71, 130.31, 132.28, 132.32, 133.65, 141.25, 168.47, 192.51, 196.98. IR (ATR) ν 3853, 3735, 3649, 2989, 1800, 1734, 1608, 1559, 1540, 1507, 1457, 1275, 1261, 1185, 764, 750 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{15}F_3O_5$+NH_4] requires 350.1210, found 350.1214 [M^++NH_4].



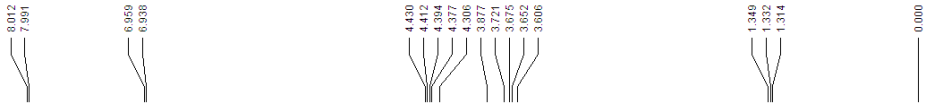


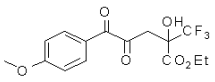


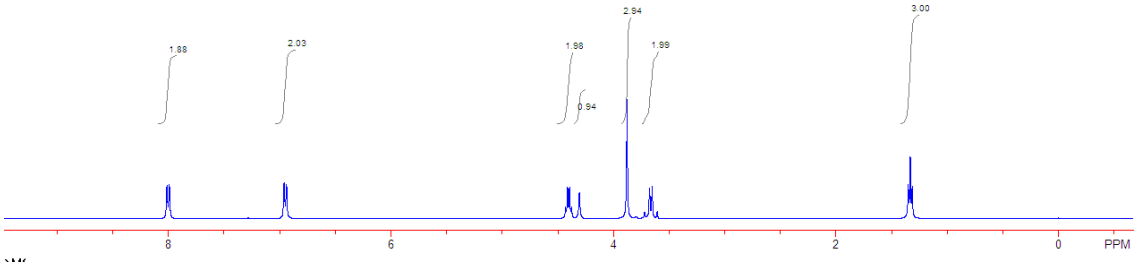


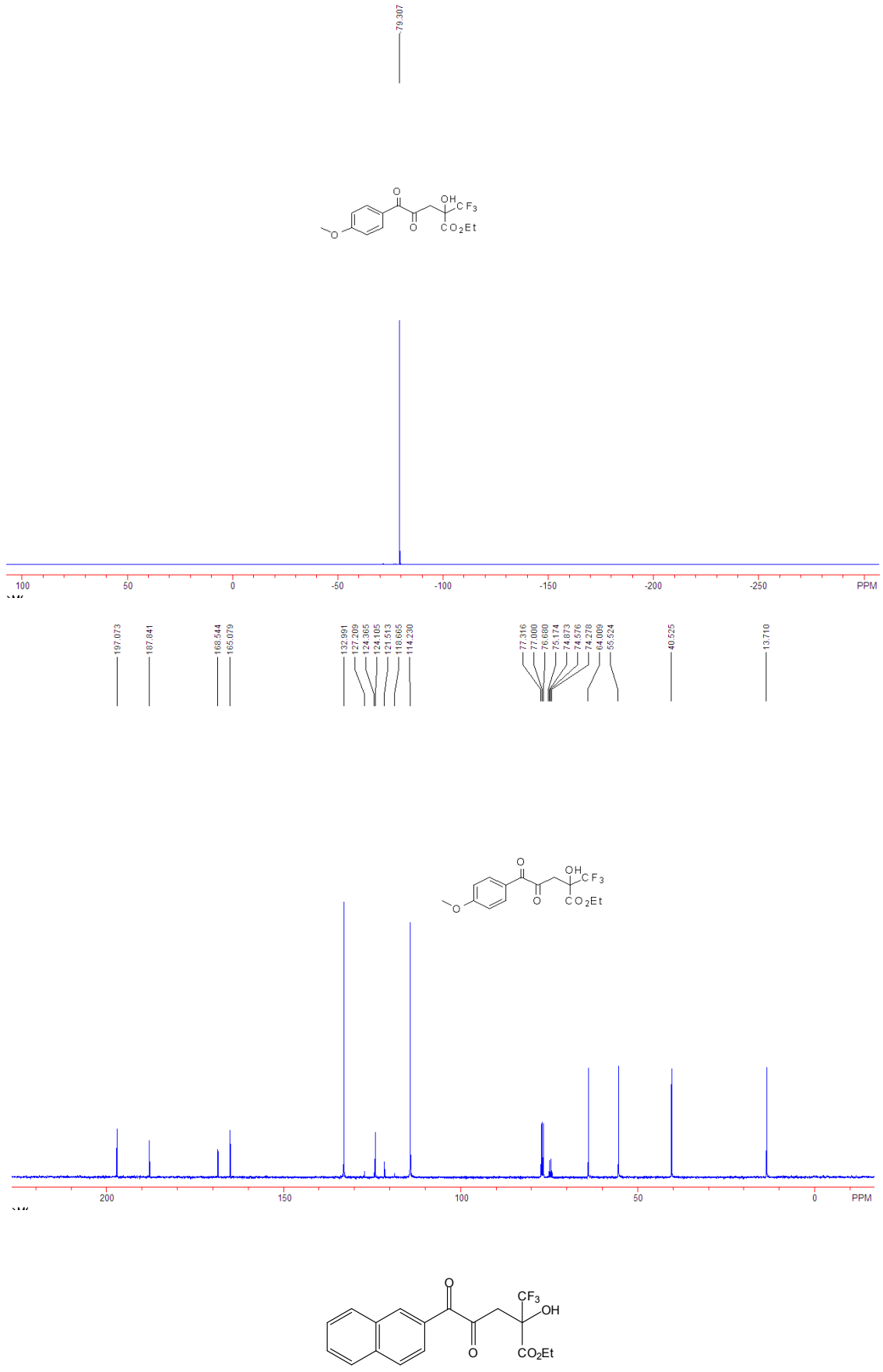
ethyl 2-hydroxy-5-(4-methoxyphenyl)-4,5-dioxo-2-(trifluoromethyl)pentanoate **4g**: a light yellow oil. 626.4 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.33 (t, J = 7.2 Hz, 3H),

3.63 (d, J = 18.4 Hz, 1H), 3.70 (d, J = 18.4 Hz, 1H), 3.88 (s, 3H), 4.31 (s, 1H), 4.40 (q, J = 7.2 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -79.31. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.71, 40.53, 55.52, 64.01, 74.72 (q, J = 29.7 Hz), 114.23, 122.94 (q, J = 285.2 Hz), 124.11, 132.99, 165.08, 168.54, 187.84, 197.07. IR (ATR) ν 3463, 2986, 1748, 1722, 1596, 1573, 1512, 1465, 1425, 1392, 1370, 1307, 1261, 1219, 1176, 1132, 1104, 1067, 1021, 988, 920, 894, 840, 805, 765, 750, 707 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{15}F_3O_6$+H] requires 349.0893, found 349.0883 [M^++H].



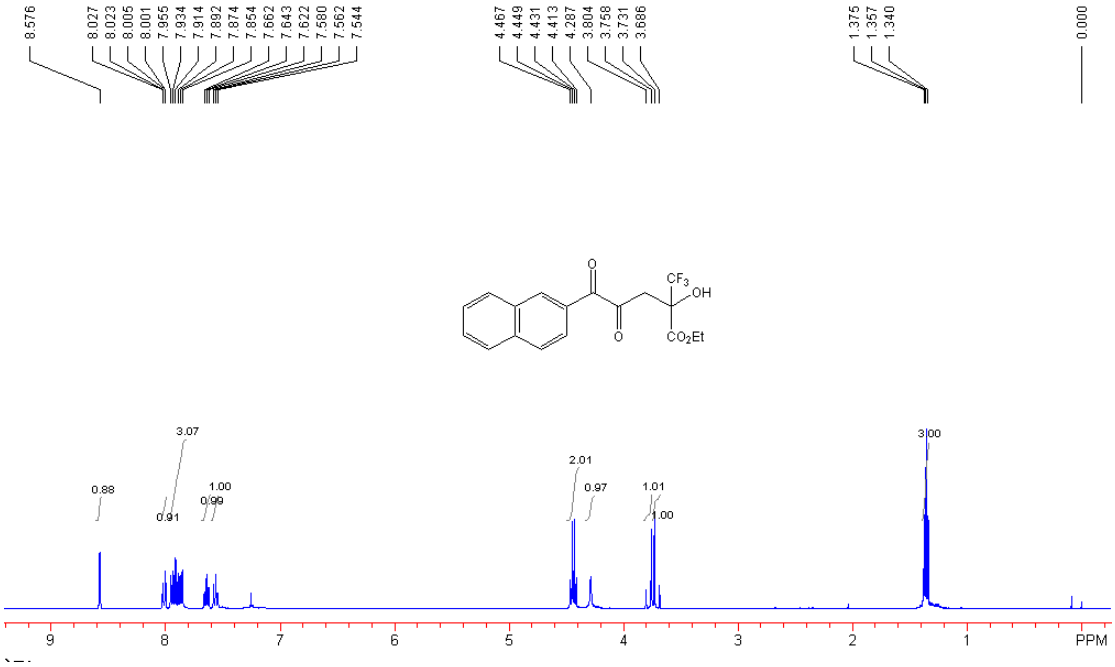


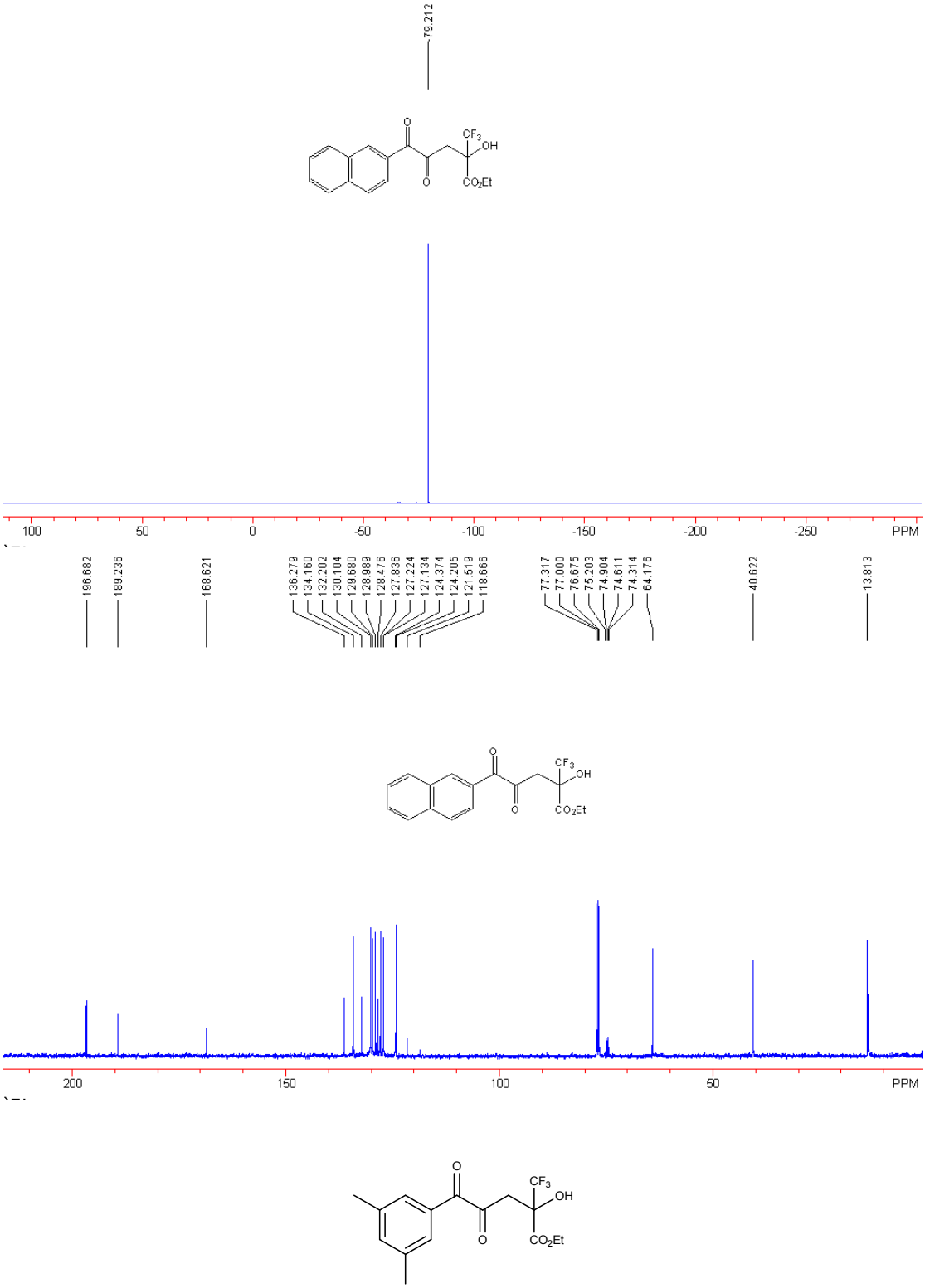




ethyl 2-hydroxy-5-(naphthalen-2-yl)-4,5-dioxo-2-(trifluoromethyl)pentanoate **4h**: a white

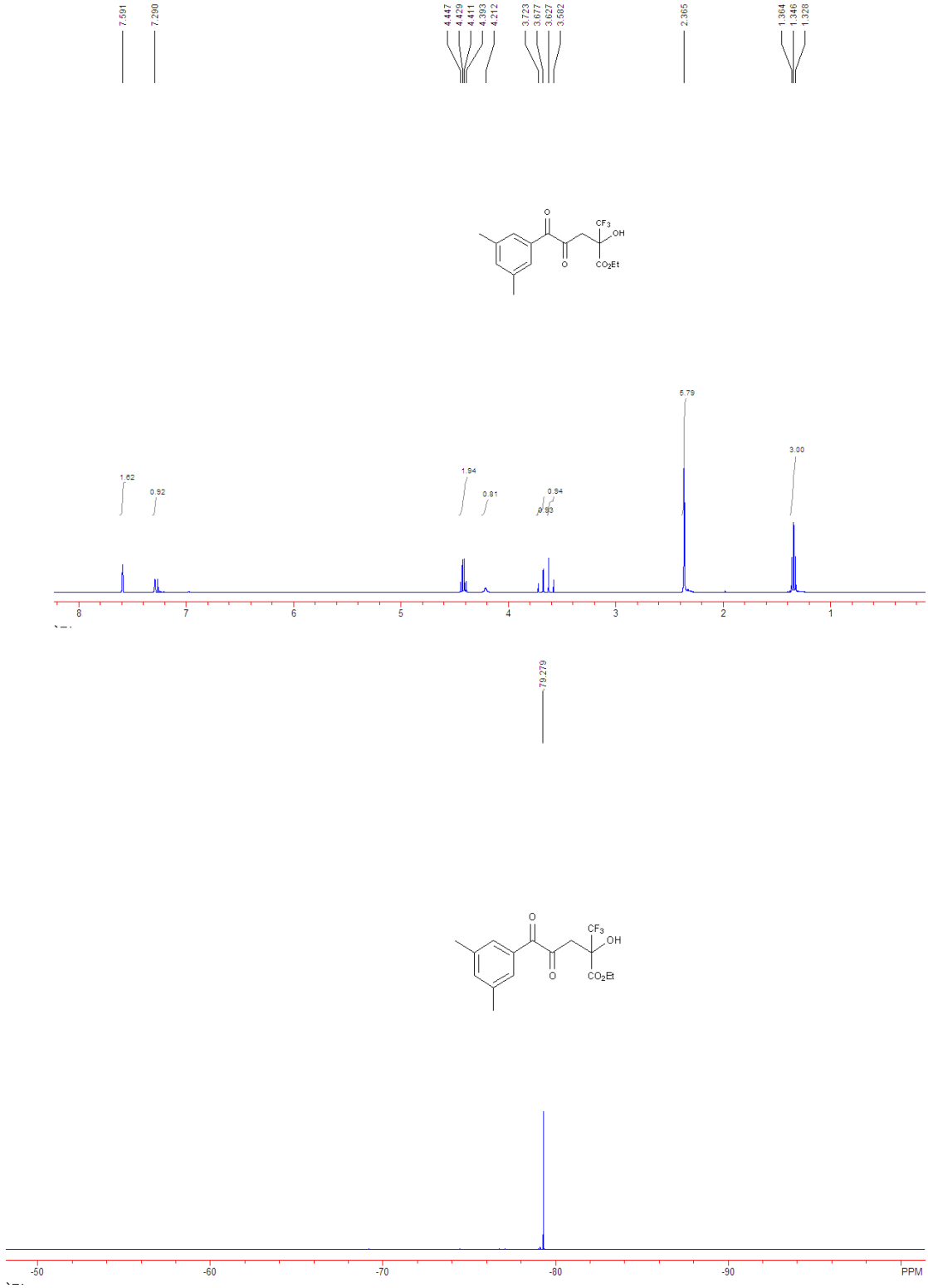
solid. 268.6 mg, 73% yield. m.p. 86 ^{o}C^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.36 (t, *J* = 7.2 Hz, 3H), 3.71 (d, *J* = 18.0 Hz, 1H), 3.78 (d, *J* = 18.0 Hz, 1H), 4.29 (s, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.85-7.96 (m, 3H), 8.01 (dd, *J* = 8.8 Hz, 1.6 Hz, 1H), 8.58 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -79.21. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.81, 40.62, 64.18, 74.76 (q, *J* = 29.3 Hz), 122.95 (q, *J* = 285.5 Hz), 124.21, 127.13, 127.84, 128.48, 129.00, 129.68, 130.10, 132.20, 134.16, 136.28, 168.62, 189.24, 196.68. IR (ATR) *ν* 3470, 2956, 1749, 1668, 1597, 1507, 1465, 1389, 1371. 1275, 1257, 1220, 1194, 1134, 1092, 1013, 927, 864, 822, 764, 751, 698 cm^{-1}. HRMS (ESI) calcd for [$C_{18}H_{15}F_3O_5$+NH_4] requires 386.1210, found 386.1196 [M^++NH_4].

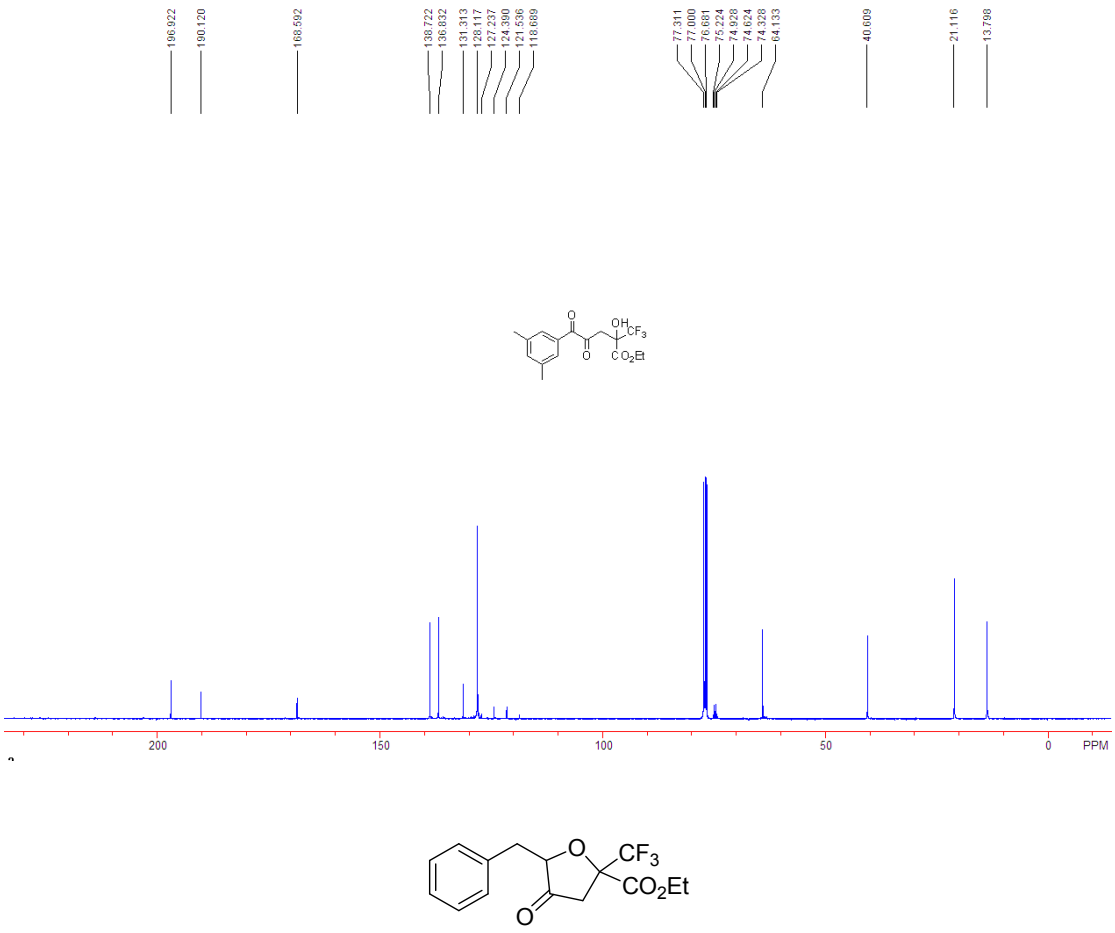




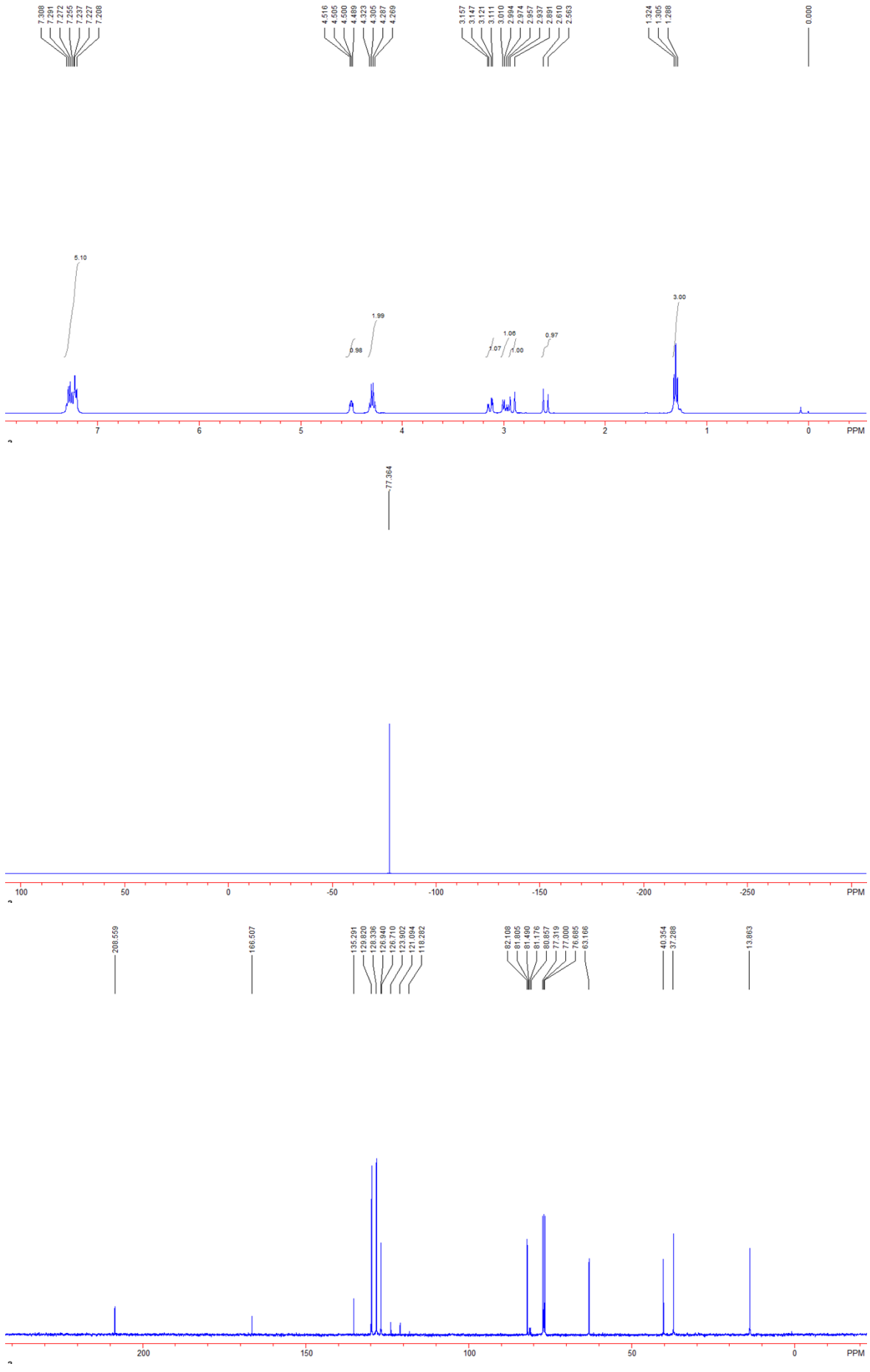
ethyl 5-(3,5-dimethylphenyl)-2-hydroxy-4,5-dioxo-2-(trifluoromethyl)pentanoate **4i**: a light yellow oil. 160.7 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.35 (t, J = 7.2 Hz, 3H), 2.37 (s, 6H), 3.60 (d, J = 18.0 Hz, 1H), 3.70 (d, J = 18.0 Hz, 1H), 4.21 (s, 1H), 4.42 (q, J = 7.2 Hz, 2H), 7.29 (s, 1H), 7.59 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -79.28. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.80, 21.12, 40.61, 64.13, 74.78 (q, J = 30.4 Hz), 122.96 (q, J = 285.4

Hz), 128.12, 131.31, 136.83, 138.72, 168.59, 190.12, 196.92. IR (ATR) ν 2990, 1749, 1600, 1507, 1457, 1308, 1275, 1260, 1194, 1137, 764, 750 cm^{-1}. HRMS (ESI) calcd for $[C_{16}H_{17}F_3O_5+NH_4]$ requires 364.1366, found 364.1374 $[M^+ + NH_4]$.





ethyl 5-benzyl-4-oxo-2-(trifluoromethyl)tetrahydrofuran-2-carboxylate **3j'**: a light yellow oil. 99.5 mg, 21% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.31 (t, J = 7.2 Hz, 3H), 2.59 (d, J = 18.8 Hz, 1H), 2.91 (d, J = 18.8 Hz, 1H), 2.98 (dd, J = 14.4 Hz, 6.4 Hz, 1H), 3.13 (dd, J = 14.4 Hz, 4.0 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 4.49-4.52 (m, 1H), 7.21-7.31 (m, 5H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -77.36. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.86, 37.28, 40.36, 63.17, 81.33 (q, J = 31.4 Hz), 82.11, 122.50 (q, J = 280.8 Hz), 126.94, 128.34, 129.82, 135.29, 166.51, 208.56. IR (ATR) ν 2988, 1765, 1275, 1260, 1160 1084 cm^{-1}. HRMS (ESI) calcd for [$C_{15}H_{15}F_3O_4$+NH_4] requires 334.1261, found 334.1255 [M^++NH_4].


7.308
7.291
7.272
7.255
7.237
7.227
7.208
4.516
4.505
4.500
4.489
4.323
4.305
4.287
4.269
3.157
3.147
3.121
3.111
3.010
2.994
2.974
2.957
2.937
2.891
2.610
2.563
1.324
1.305
1.288
0.000
5.10
1.99
0.98
1.06
1.07
1.00
0.97
3.00
PPM
77.364
PPM
208.559
166.507
135.291
129.820
128.336
126.940
126.710
123.902
121.094
118.282
82.108
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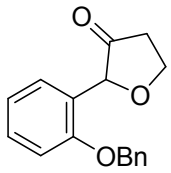
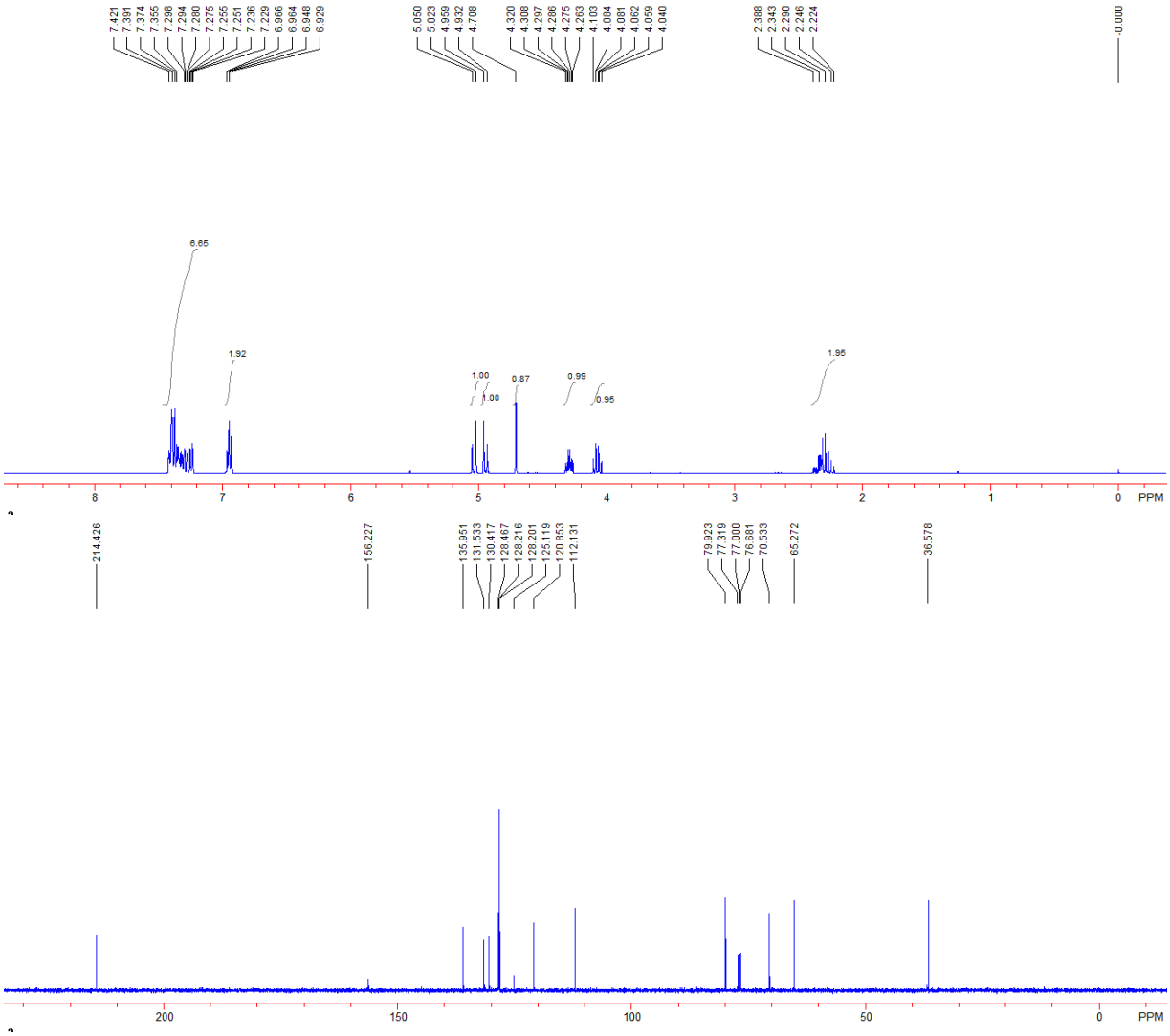
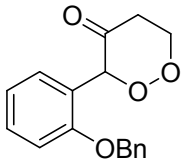
63.166
40.354
37.288
13.863
PPM

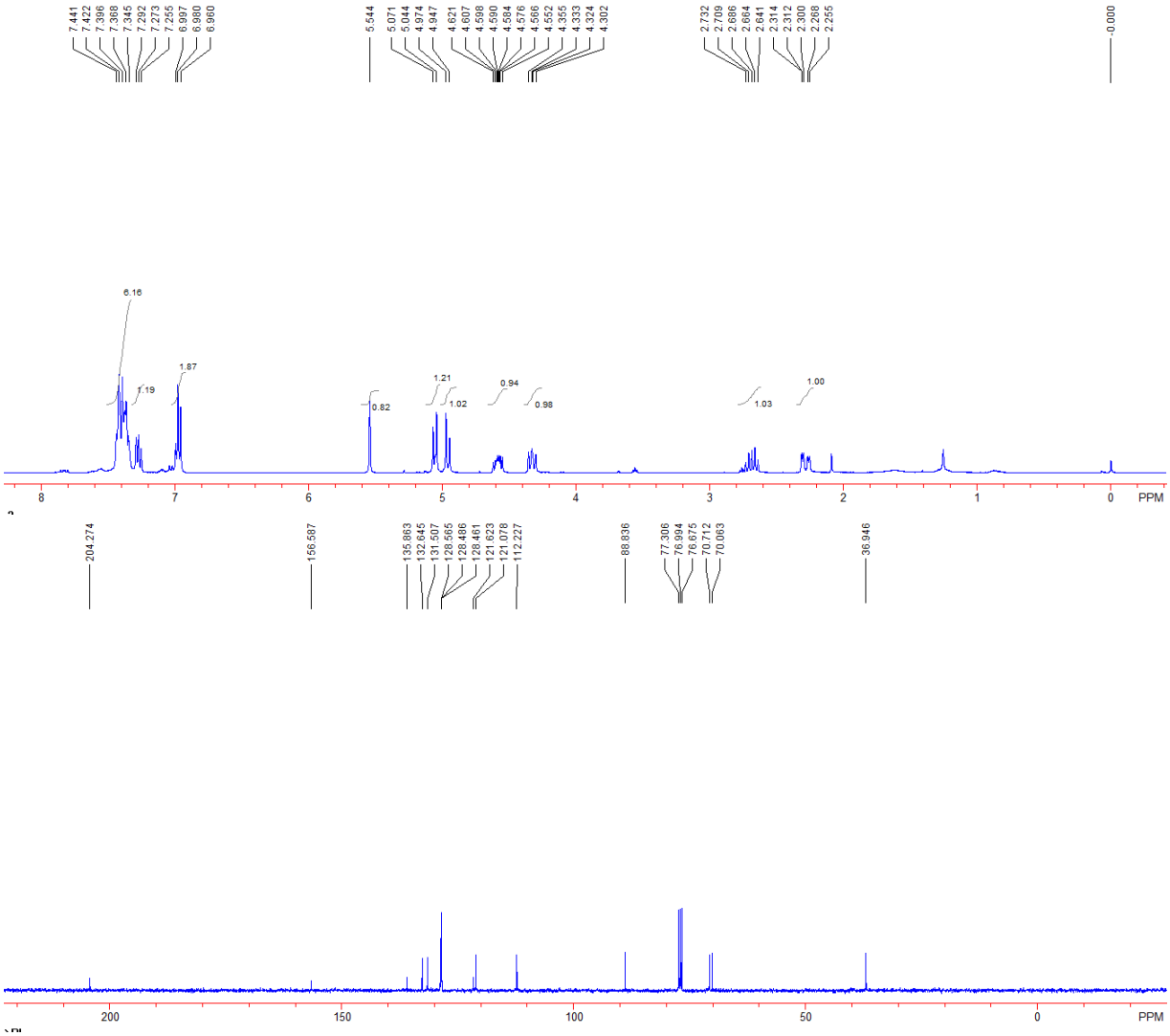


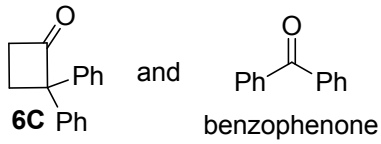
2-(2-(benzyloxy)phenyl)dihydrofuran-3(2H)-one **6a**: a white solid. 89.1 mg, 33% yield. m.p. 86 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.22-2.39 (m, 2H), 4.04-4.10 (m, 1H), 4.26-4.32 (m, 1H), 4.71 (s, 1H), 4.95 (d, J = 10.8 Hz, 1H), 5.04 (d, J = 10.8 Hz, 1H), 6.93-6.97 (m, 2H), 7.23-7.42 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.58, 65.27, 70.53, 79.92, 112.13, 120.85, 125.12, 128.20, 128.22, 128.47, 130.42, 131.53, 135.95, 156.23, 214.43. IR (ATR) ν 3855, 2924, 2854, 1754, 1601, 1589, 1492, 1453, 1401, 1378, 1239, 1194, 1145, 1118, 1039, 1020, 929, 857, 751, 697, 669 cm^{-1}. HRMS (ESI) calcd for [$C_{17}H_{16}O_3$+NH_4] requires 286.1438, found 286.1438 [M^++NH_4].





3-(2-(benzyloxy)phenyl)-1,2-dioxan-4-one **6b**: a white solid. 180.8 mg, 64% yield. m.p. 116 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.28 (dd, *J* = 18.4 Hz, 5.6 Hz, 1H), 2.64-2.78 (m, 1H), 4.33 (dd, *J* = 12.4 Hz, 8.8 Hz, 1H), 4.55-4.62 (m, 1H), 4.96 (d, *J* = 10.8 Hz, 1H), 5.06 (d, *J* = 10.8 Hz, 1H), 5.54 (s, 1H), 6.96-7.00 (m, 2H), 7.26-7.29 (m, 1H), 7.35-7.44 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.95, 70.06, 70.71, 88.84, 112.23, 121.08, 121.62, 128.46, 128.49, 128.57, 131.51, 132.65, 135.86, 156.59, 204.27. IR (ATR) *ν* 3855, 2925, 2853, 1719, 1598, 1491, 1454, 1378, 1267, 1238, 1158, 1116, 1024, 1000, 855, 763, 698 cm^{-1}. HRMS (ESI) calcd for [$C_{17}H_{16}O_4$+NH_4] requires 302.1387, found 302.1388 [M^++NH_4].

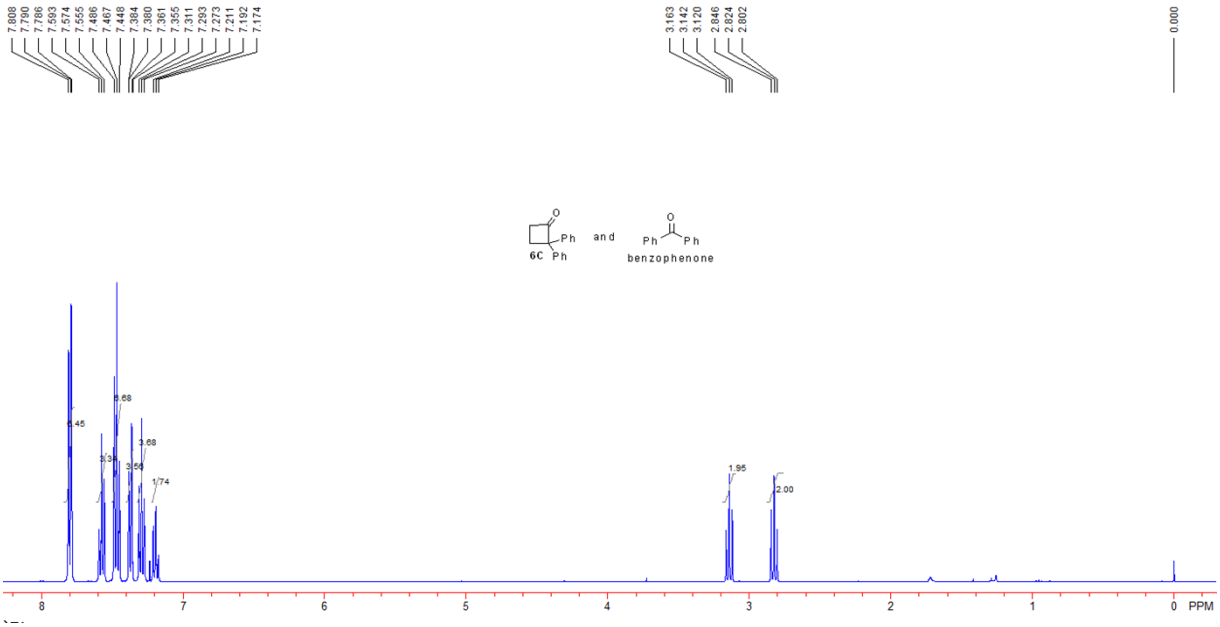


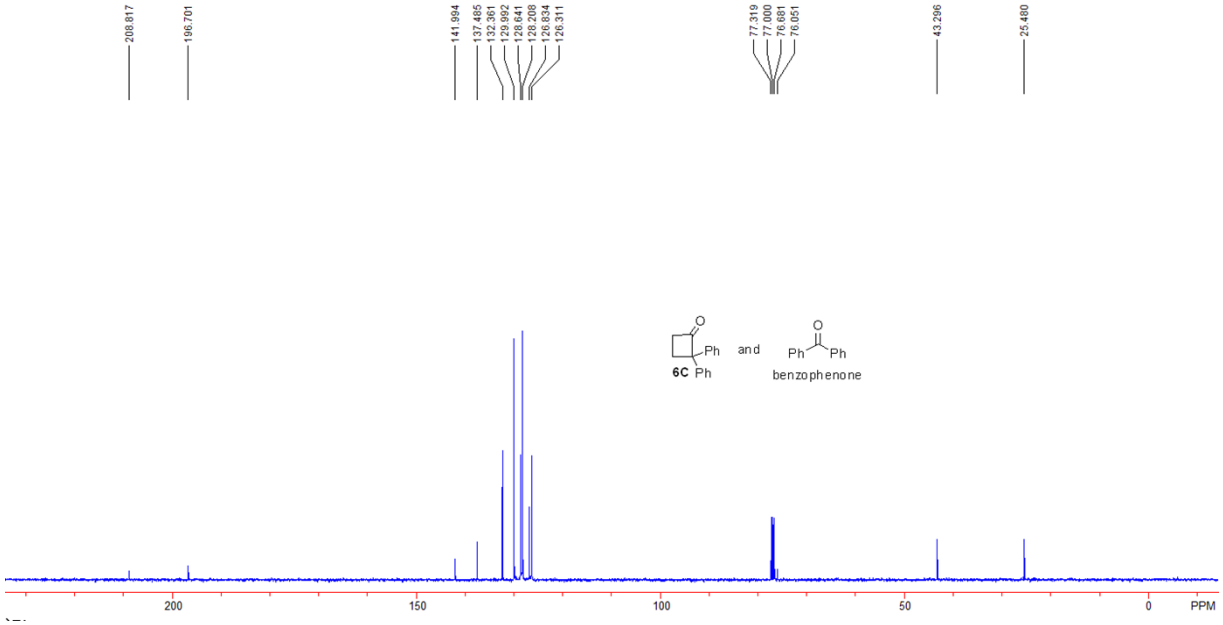


Compound **6c** is a known compound,[5] which can not be separated from benzophenone by column chromatography in this reaction. The yield was calculated by integration.

2,2-diphenylcyclobutanone **6c**: a light yellow oil. 61.8 mg, 28% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.82 (t, *J* = 8.8 Hz, 2H), 3.14 (t, *J* = 8.8 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 4H), 7.36-7.38 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$ TMS): δ 25.48, 43.30, 76.05, 126.31, 126.83, 128.64, 141.99, 208.82. MS (%): m/z = 222 [M] (1.68), 180 (100).

Benzophenone: 89.3 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 (t, *J* = 7.6 Hz, 4H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.79-7.81 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$ TMS): δ 128.22, 130.00, 132.37, 137.51, 196.71.

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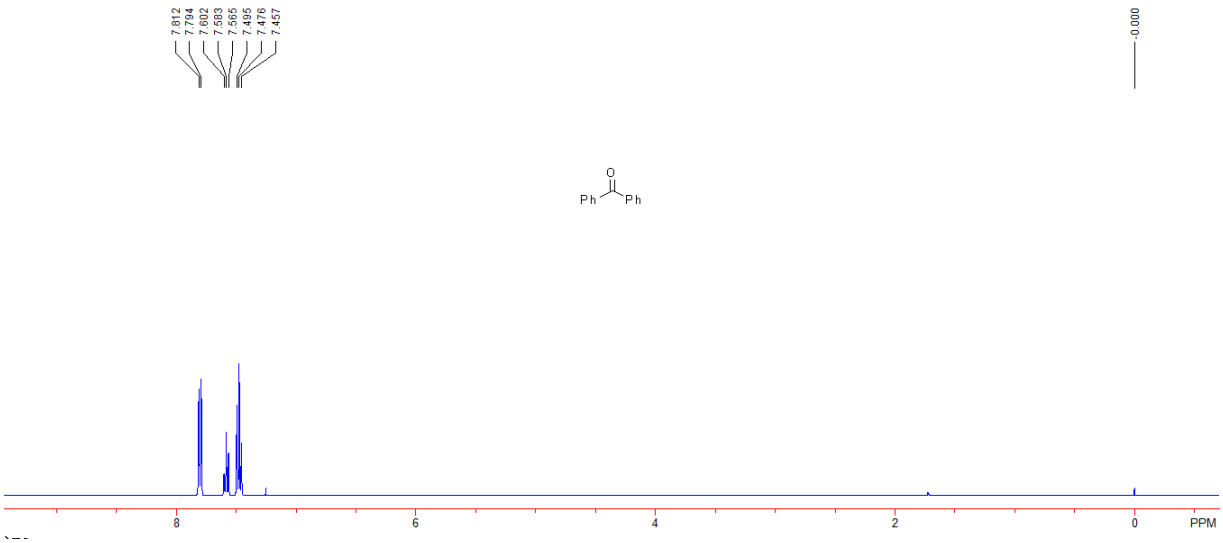
196.701
141.994
137.485
132.361
129.992
128.641
128.208
126.834
126.311
77.319
77.000
76.681
76.051
43.296
25.480
6C
Ph
Ph
and
Ph
Ph
benzophenone
200
150
100
50
0
PPM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7.794
7.602
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7.565
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7.457
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Ph
Ph
8
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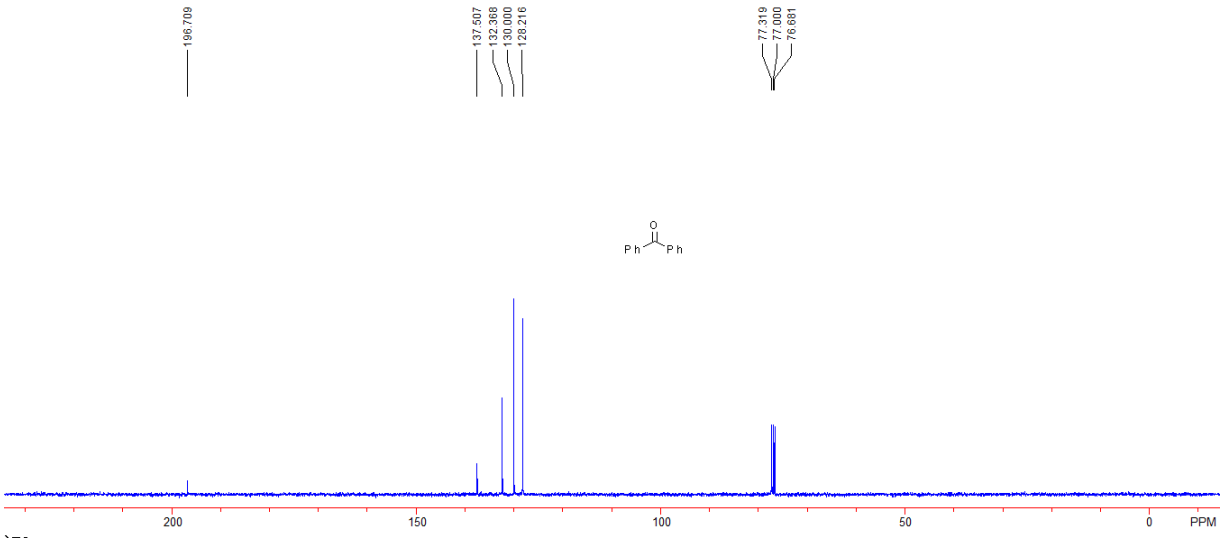
4
2
0
PPM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Ph
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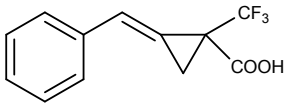
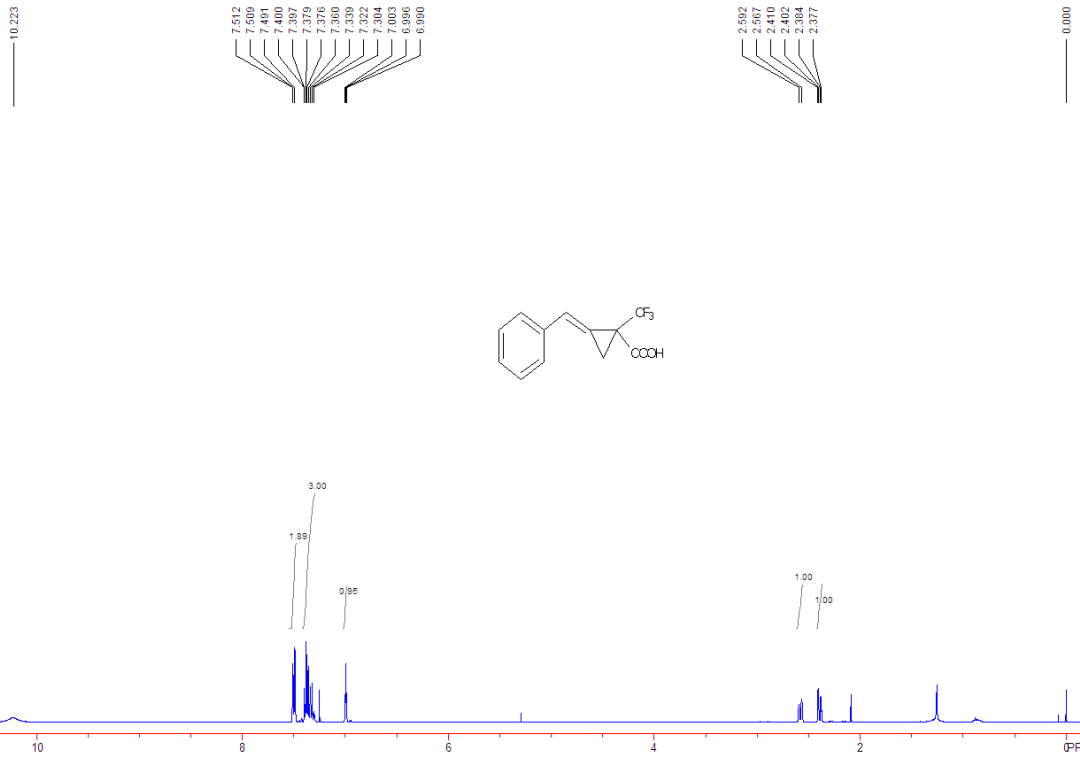
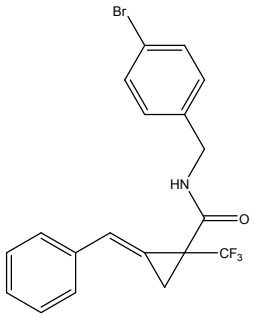
50
0
PPM



Compound **7a** is a known compound and was synthesized according to the literature procedure.[1]

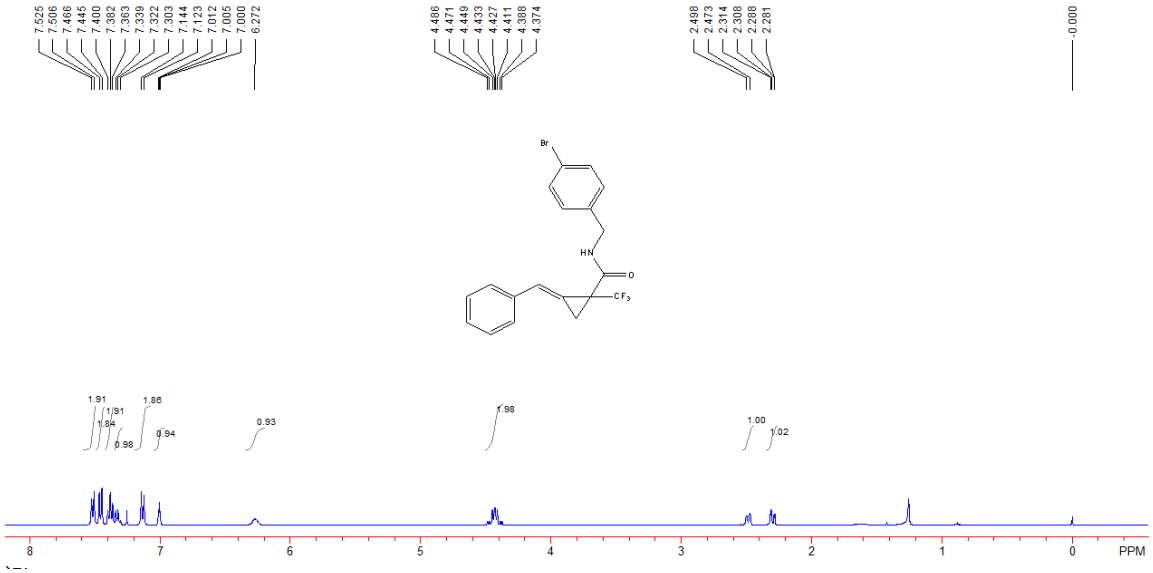
(E)-2-benzylidene-1-(trifluoromethyl)cyclopropanecarboxylic acid **7a**: a colorless solid. 221.1 mg, 91% yield. m.p. 167 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.39 (dd, *J* = 10.0 Hz, 2.8 Hz, 1H), 2.58 (d, *J* = 10.0 Hz, 1H), 7.00 (t, *J* = 2.8 Hz, 1H), 7.30-7.40 (m, 3H), 7.49-7.51 (m, 2H), 10.22 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -66.92. ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.25 (q, *J* = 1.9 Hz), 27.71 (q, *J* = 34.5 Hz), 118.80, 122.19, 123.22 (q, *J* = 273.3 Hz), 127.64, 128.77, 134.77, 172.84. IR (ATR) *ν* 3066, 2927, 2663, 1709, 1429, 1363, 1294, 1217, 1195, 1160, 1073, 920, 752, 688 cm^{-1}. HRMS (ESI) calcd for [$C_{12}H_9F_3O_2$+NH_4] requires 260.0893, found 260.0896 [M^++NH_4].

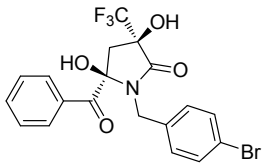




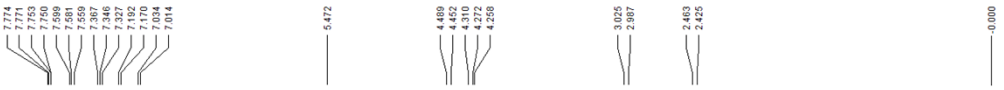
Compound **8a** is a known compound and was synthesized according to the literature procedure.[1]

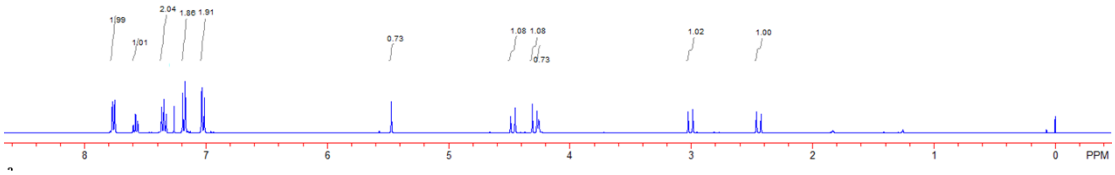
(E)-2-benzylidene-N-(4-bromobenzyl)-1-(trifluoromethyl)cyclopropanecarboxamide **8a**: a white solid. 742.8 mg, 87% yield. m.p. 126 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.30 (dd, *J* = 10.4 Hz, 2.4Hz, 1H), 2.49 (d, *J* = 10.4 Hz, 1H), 4.37-4.49 (m, 2H), 6.27 (s, 1H), 7.01 (t, *J* = 2.4 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.30-7.34 (m, 1H), 7.36-7.40 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -65.22. ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.48, 29.09 (q, *J* = 33.8 Hz), 43.35, 118.52, 121.59, 122.20, 124.19 (q, *J* = 273.2 Hz), 127.56, 128.73, 128.77, 129.25, 131.89, 134.93, 136.59, 164.37. IR (ATR) *ν* 3331, 3029, 2923, 2842, 1659, 1525, 1488, 1314, 1190, 1140, 1091, 1072, 1011, 755, 690 cm^{-1}. HRMS (ESI) calcd for [$C_{19}H_{15}BrF_3NO$+H] requires 410.0362, found 410.0361 [M^++H].

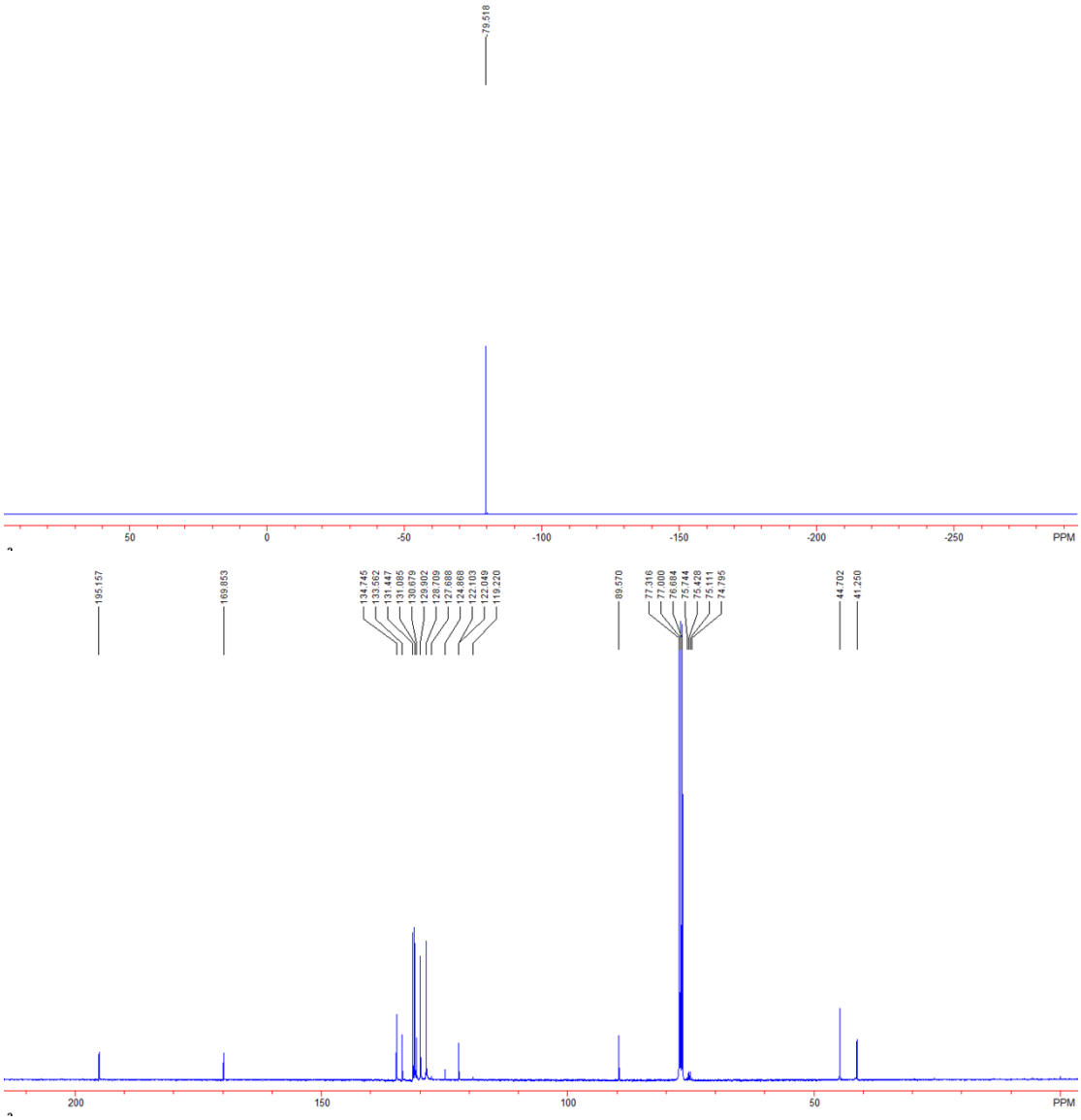




(3R,5R)-5-benzoyl-1-(4-bromobenzyl)-3,5-dihydroxy-3-(trifluoromethyl)pyrrolidin-2-one **9a**: a white solid. 73.3 mg, 32% yield. m.p. 137 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.44 (d, *J* = 15.2Hz, 1H), 3.01 (d, *J* = 15.2 Hz, 1H), 4.26 (s, 1H), 4.29 (d, *J* = 15.2 Hz, 1H), 4.47 (d, *J* = 15.2 Hz, 1H), 5.47 (s, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.76 (dd, *J* = 8.4 Hz, 1.2Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -79.51. ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.25, 44.70, 75.27 (q, *J* = 31.7 Hz), 89.57, 122.10, 123.46 (q, *J* = 273.2 Hz), 127.69, 128.71, 129.90, 130.68, 131.09, 131.45, 133.56, 134.75, 169.85, 195.16. IR (ATR) ν 3005, 2989, 2846, 2695, 2311, 1736, 1462, 1275, 1260, 749 cm^{-1}. HRMS (ESI) calcd for [$C_{19}H_{15}BrF_3NO_4$+H] requires 458.0209, found 458.0196 [M^++H].



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50
0
-50
-100
-150
-200
-250
PPM
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134.745
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131.447
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130.679
129.902
129.709
127.688
124.868
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122.049
119.220
89.570
77.316
77.000
76.684
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75.428
75.111
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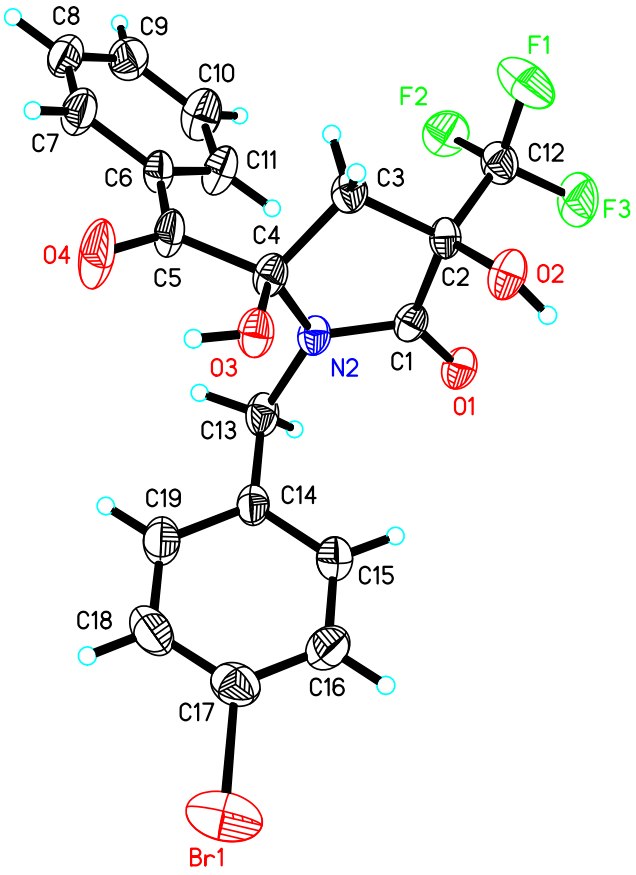
44.702
41.250
200
150
100
50
PPM

X-ray Crystal Data of Product 9a



The crystal data of **9a** have been deposited in CCDC with number 947607. Empirical Formula: $C_{19}H_{15}BrF_3NO_4$; Formula Weight: 458.23; Crystal Color, Habit: colorless; Crystal System: Monoclinic; Crystal size: 0.231 x 0.176 x 0.121; Lattice Parameters: a = 24.855(6)Å, b = 9.629(2)Å, c = 15.692(4)Å, α = 90°, β = 96.850(5)°, γ = 90°, V = 3728.7(15)Å^3; Space group: P2(1)/c; Z = 8; D_{calc} = 1.633 g/cm^3; F_{000} = 1840; Final R indices [I>2sigma(I)]: R1 = 0.0674; wR2 = 0.1646.

References

1. Sang, R.; Yang, H. B.; Shi, M. *Tetrahedron Lett.* **2013**, *54*, 3591.

2. Ma, S. M.; Lu, L. H. *J. Org. Chem.* **2005**, *70*, 7629-7633.

3. Shi, M.; Liu, L. P.; Tang, J. *J. Am. Chen. Soc.* **2006**, *128*, 7430-7431.

4. a) Shao, L. X.; Shi, M. *Eur. J. Org. Chem.* **2004**, 426-430; b) Hoppe, D. *Angew. Chem.* **1974**, *86*, 878-893; c) Chen, W. L.; Huang, X.; Zhou, H. W.; Huang, X. *Synlett* **2003**, 2080-2082.

5. Langler, R. F.; Raheja, R. K.; Schank, K.; Beck, H. *Helv. Chim. Acta.* **2001**, *84*, 1943-1951.