Supporting Information

DABCO-Catalyzed Regioselective Cyclization Reactions of β,γ-Unsaturated α-Ketophosphonates or β,γ-Unsaturated α-Ketoesters with Allenic Esters.

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CONTENTS

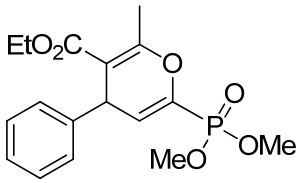
General Remarks: ^{1}H NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer for solution in CDCl3 with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. THF, toluene and Et_2O were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN, 1,2-dichloroethane and dichloromethane were distilled from CaH_2 under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All the β,γ-unsaturated α-ketophosphonates and β,γ-unsaturated α-ketoesters were prepared according to the literature.[1]

Reference:

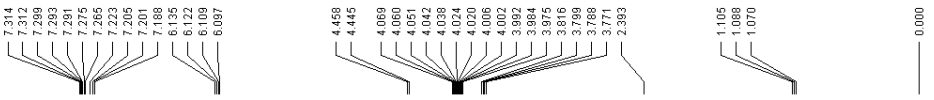
1. (a) D. A. Evans, J. S. Johnson and E. J. Olhava, *J. Am. Chem. Soc.,* 2000, **122**, 1635; (b) A. Kumar, S. Sharma, V. D. Tripathi, R. A. Maurya, S. P. Srivastava, G. Bhatia, A. K. Tamrakar and A. K. Srivastava, *Bioorg. Med. Chem*., 2010, **18**, 4138.

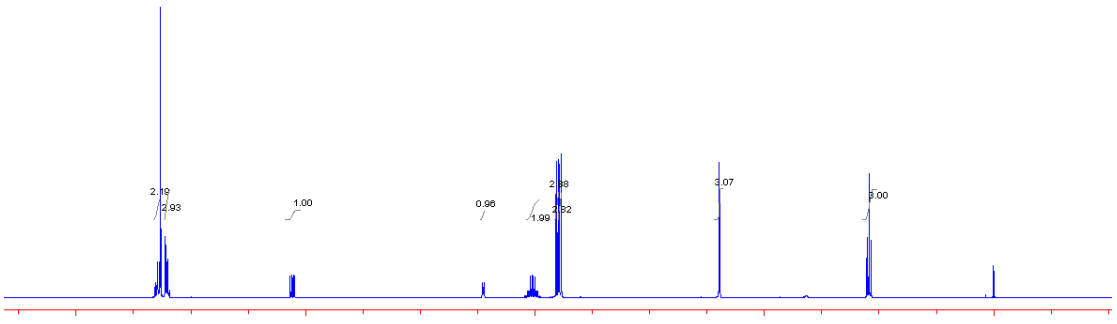
General Procedure for the Preparation of 3 from the Reaction of 1a with 2a Using 3a as an Example in the Presence of DABCO

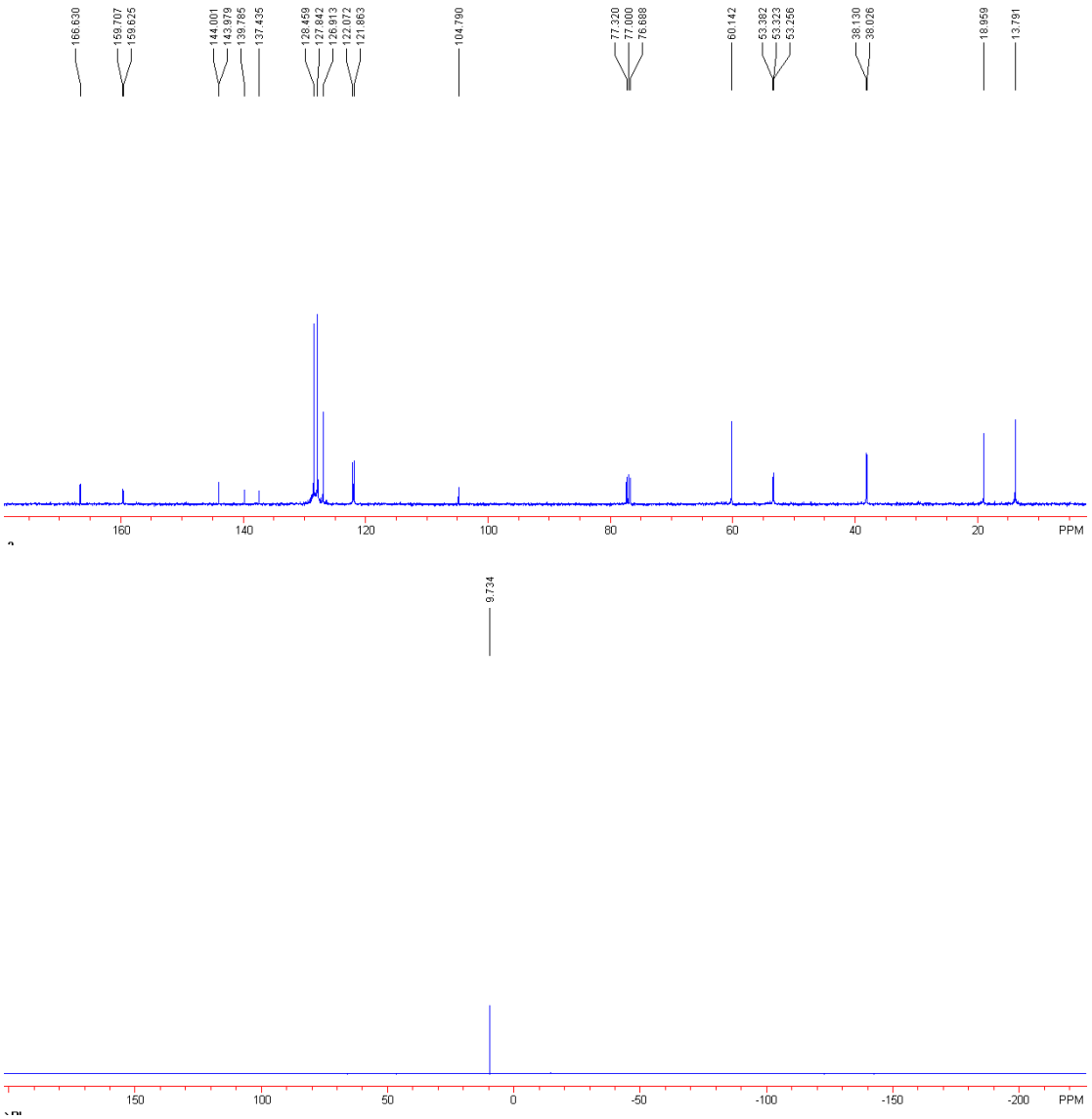
To a mixture of **1a** (0.10 mmol, 24.0 mg**)**, **2a** (0.12 mmol, 13.6 μL) and DABCO (2.2 mg, 0.02 mmol) was added 2.0 mL of dichloromethane at -40 ^{o}C. The reaction solution was monitored by TLC .After the reaction complete, the solution was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc/PE = 1/6) to give the target product **3aa** and **4aa.**

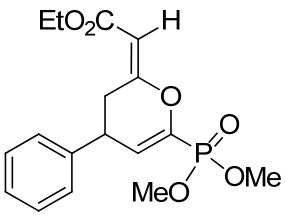


Ethyl 6-(dimethoxyphosphoryl)-2-methyl-4-phenyl-4H-pyran-3-carboxylate **3aa**: a colorless oil (16.7 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09 (t, *J* = 7.2 Hz, 3H), 2.39 (s, 3H), 3.78 (d, *J* = 11.2 Hz, 3H), 3.80 (d, *J* = 11.2 Hz, 3H), 3.96-4.07 (m, 2H), 4.45 (d, *J* = 5.2 Hz, 1H), 6.12 (dd, *J* = 10.0 Hz, 5.2 Hz, 1H), 7.19-7.22 (m, 3H), 7.29-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 19.0, 38.1 (d, *J* = 10.4 Hz), 53.3 (d, *J* = 6.7 Hz), 53.4 (d, *J* = 5.9 Hz), 60.1, 104.8, 122.0 (d, *J* = 20.9 Hz), 126.9, 127.8, 128.5, 137.4, 139.8, 144.0 (d, *J* = 2.2 Hz), 159.7 (d, *J* = 8.2 Hz), 166.6; ^{31}P NMR (161.93 MHz, $CDCl_3$, 85% H_3PO_4): δ 9.734;. IR (CH_2Cl_2) ν 2966, 2902, 1715, 1659, 1473, 1373, 1260, 1176, 1105, 1026, 947, 800, 741, 700 cm^{-1}; MS (ESI) *m/z* 353.0 (M+H^{+}). HRMS (ESI) Calcd. for $C_{17}H_{22}O_6P$ requires (M+H^{+}): 353.1149, Found: 353.1156.



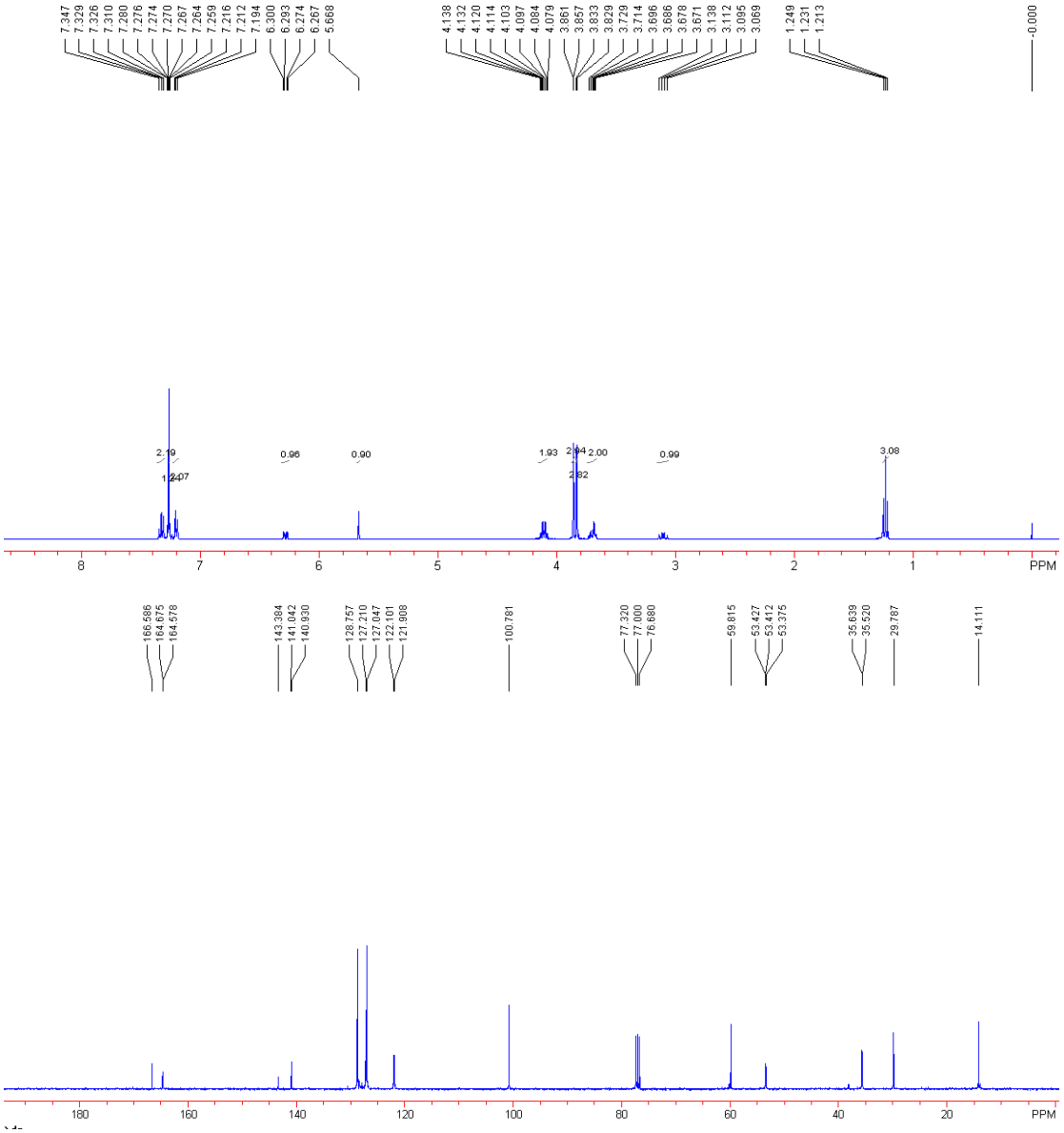


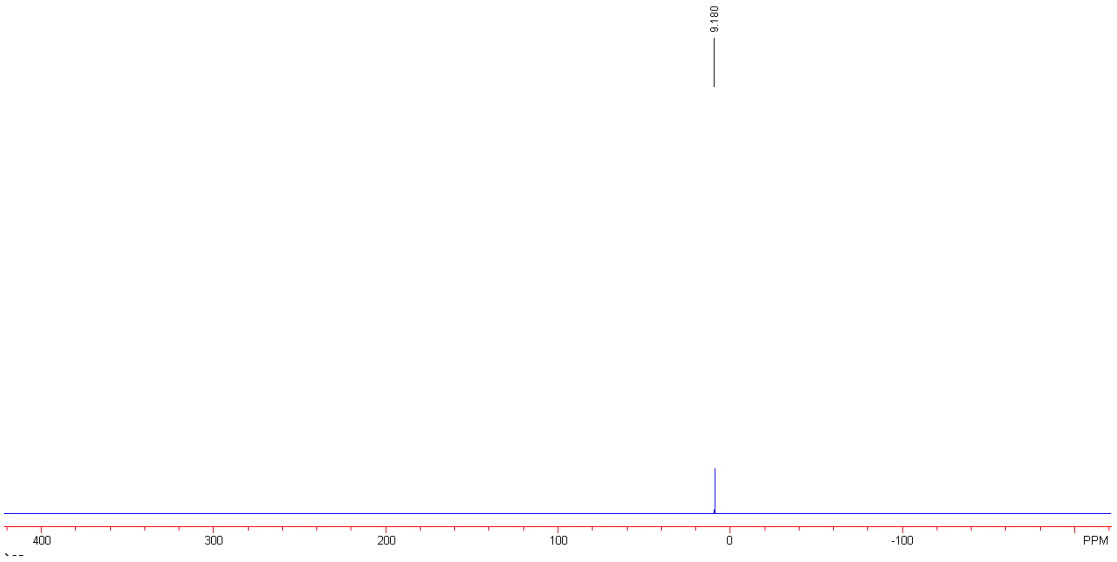


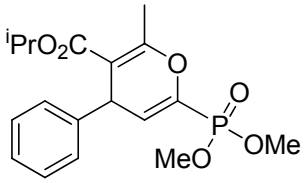


(*E*)-Ethyl 2-(6-(dimethoxyphosphoryl)-4-phenyl-3,4-dihydro-2H-pyran-2-ylidene)acetate **4aa**: a colorless oil (5.5 mg, 16%); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.23 (t, *J* = 7.2 Hz, 3H), 3.10 (dd, *J* = 10.4 Hz, 6.8 Hz, 1H), 3.67-3.73 (m, 2H), 3.84 (d, *J* = 11.2 Hz, 3H), 3.85 (d, *J* = 11.2 Hz, 3H), 4.08-4.14 (m, 2H), 5.67 (s, 1H), 6.28 (dd, *J* = 10.4 Hz, 2.8 Hz, 1H), 7.19-7.22 (m, 2H), 7.26-7.28 (m, 1H), 7.31-7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 29.8, 35.6 (d, *J* = 11.9 Hz), 53.39 (d, *J* = 3.7 Hz), 53.40 (d, *J* = 6.2 Hz), 59.8, 100.8, 122.0 (d, *J* =

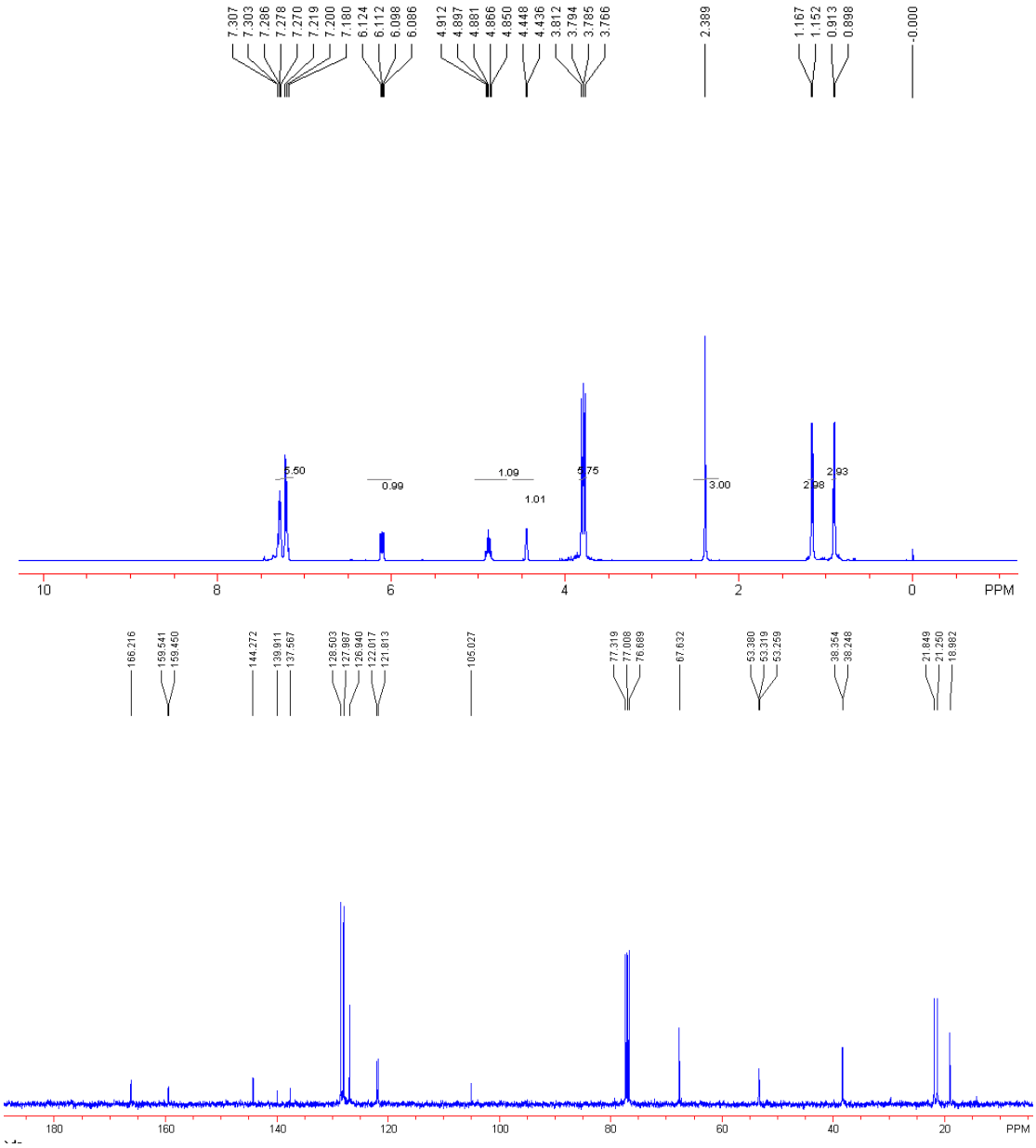
19.3 Hz), 127.0, 127.2, 128.8, 141.0 (d, J = 11.2 Hz), 143.4, 164.6 (d, J = 9.7 Hz), 166.6; ^{31}P NMR (161.93 MHz, $CDCl_3$, 85% H_3PO_4): δ 9.180; IR (neat) ν 2966, 2902, 1712, 1656, 1494, 1449, 1374, 1261, 1172, 1111, 1026, 824, 764, 700 cm^{-1}; MS (ESI) *m/z* 353.1 ($M+H^+$); HRMS (ESI) Calcd. for $C_{17}H_{22}O_6P$ requires ($M+H^+$): 353.1149, Found: 353.1159.

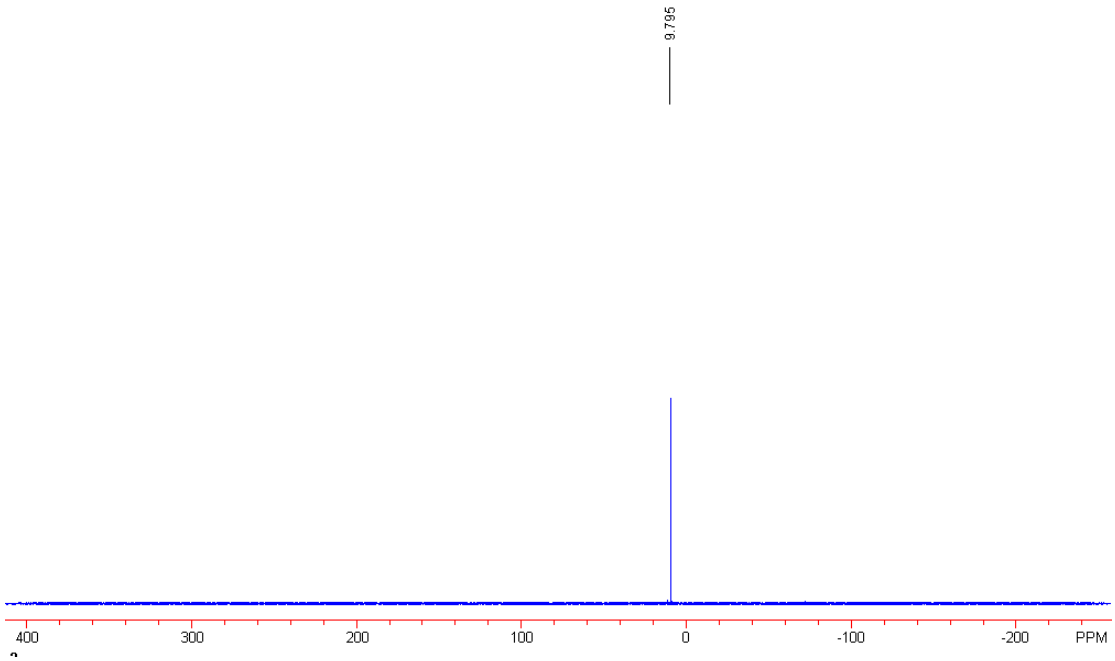


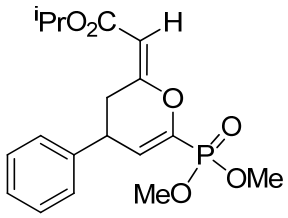




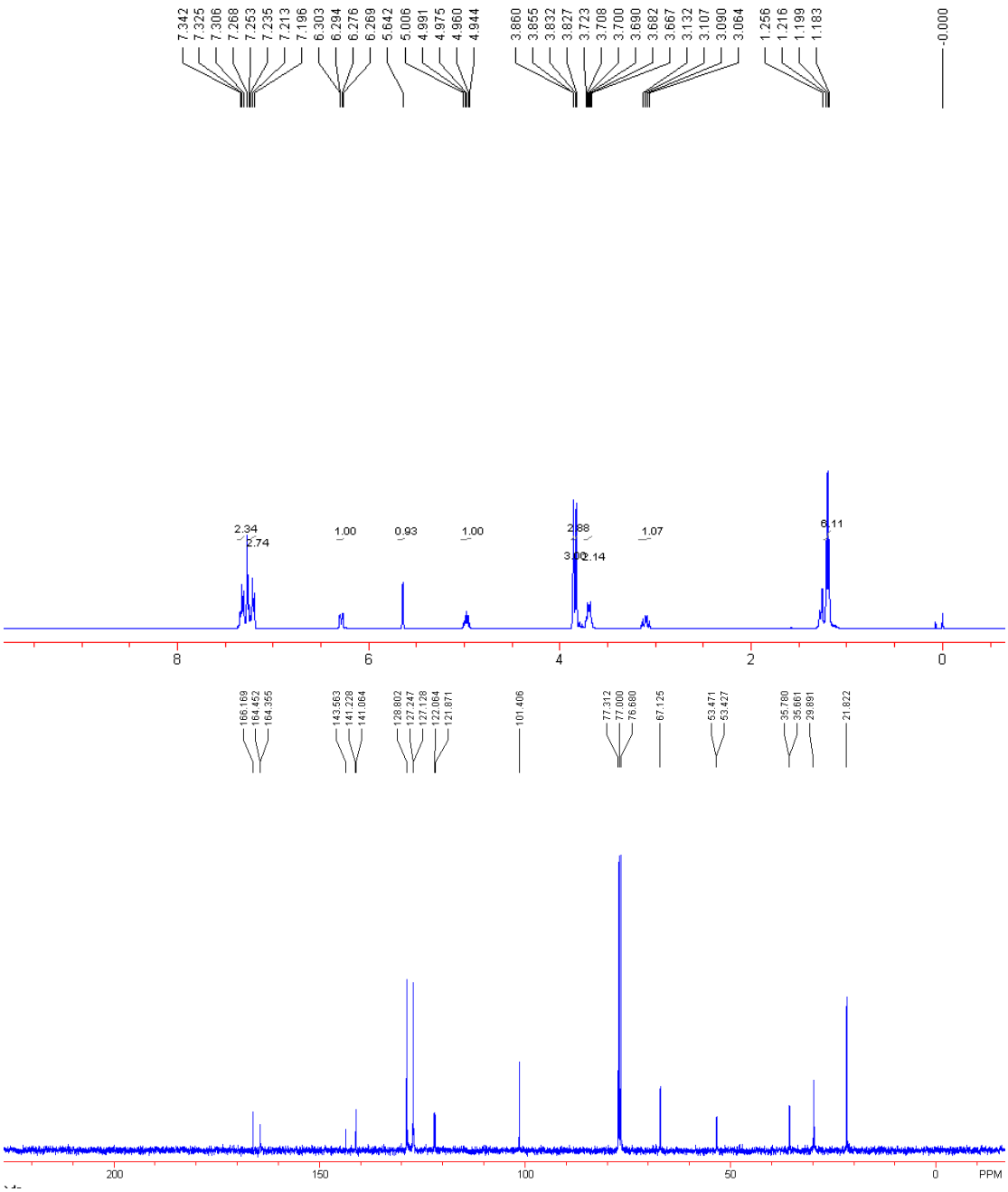
Isopropyl 6-(dimethoxyphosphoryl)-2-methyl-4-phenyl-4H-pyran-3-carboxylate **3ab**: a slight yellow liquid (22.0 mg, 60%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.91 (d, J = 6.0 Hz, 3H), 1.16 (d, J = 6.0 Hz, 3H), 2.39 (s, 3H), 3.78 (d, J = 11.2 Hz, 3H), 3.81 (d, J = 11.2 Hz, 3H), 4.44 (d, J = 4.8 Hz, 1H), 4.88 (sept, J = 6.0 Hz, 1H), 6.11 (dd, J = 10.4 Hz, 4.8 Hz, 1H), 7.18-7.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 21.3, 21.8, 38.3 (d, J = 10.6 Hz), 53.29 (d, J = 6.0 Hz), 53.35 (d, J = 6.0 Hz), 67.6, 105.0, 121.9 (d, J = 20.4 Hz), 126.9, 128.0, 128.5, 137.6, 139.9, 144.3, 159.5 (d, J = 9.1 Hz), 166.2; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 9.795; IR (CH_2Cl_2) ν 3061, 2980, 2902, 1713, 1659, 1628, 1374, 1262, 1177, 1104, 1047, 953, 803, 739, 701 cm^{-1}; MS (ESI) *m/z* 367.1 (M+H$^+$); HRMS (ESI) Calcd. for $C_{18}H_{23}O_6PNa$ requires (M+Na$^+$): 389.1125, Found: 389.1110.

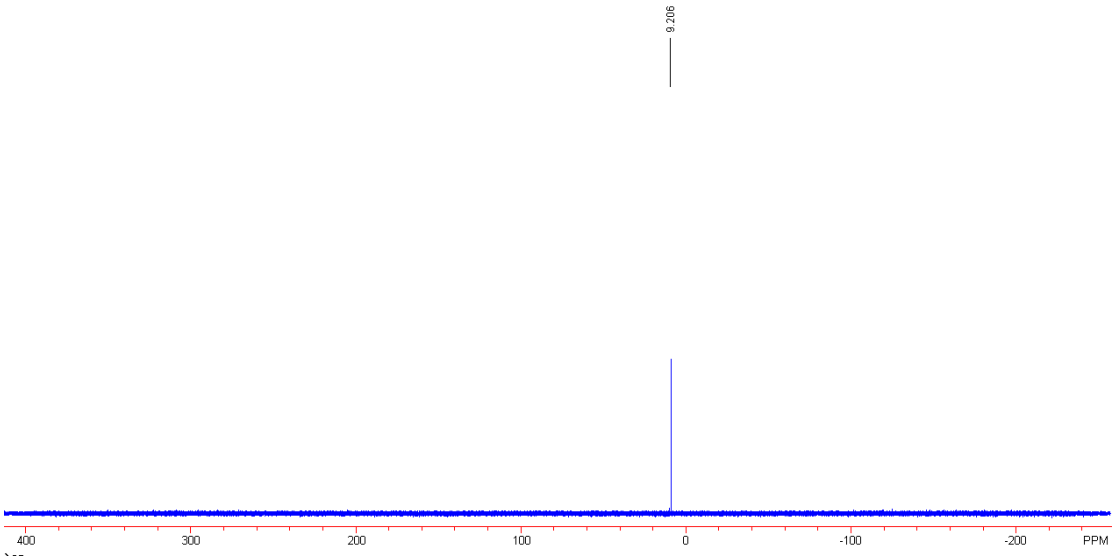


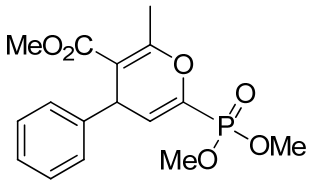




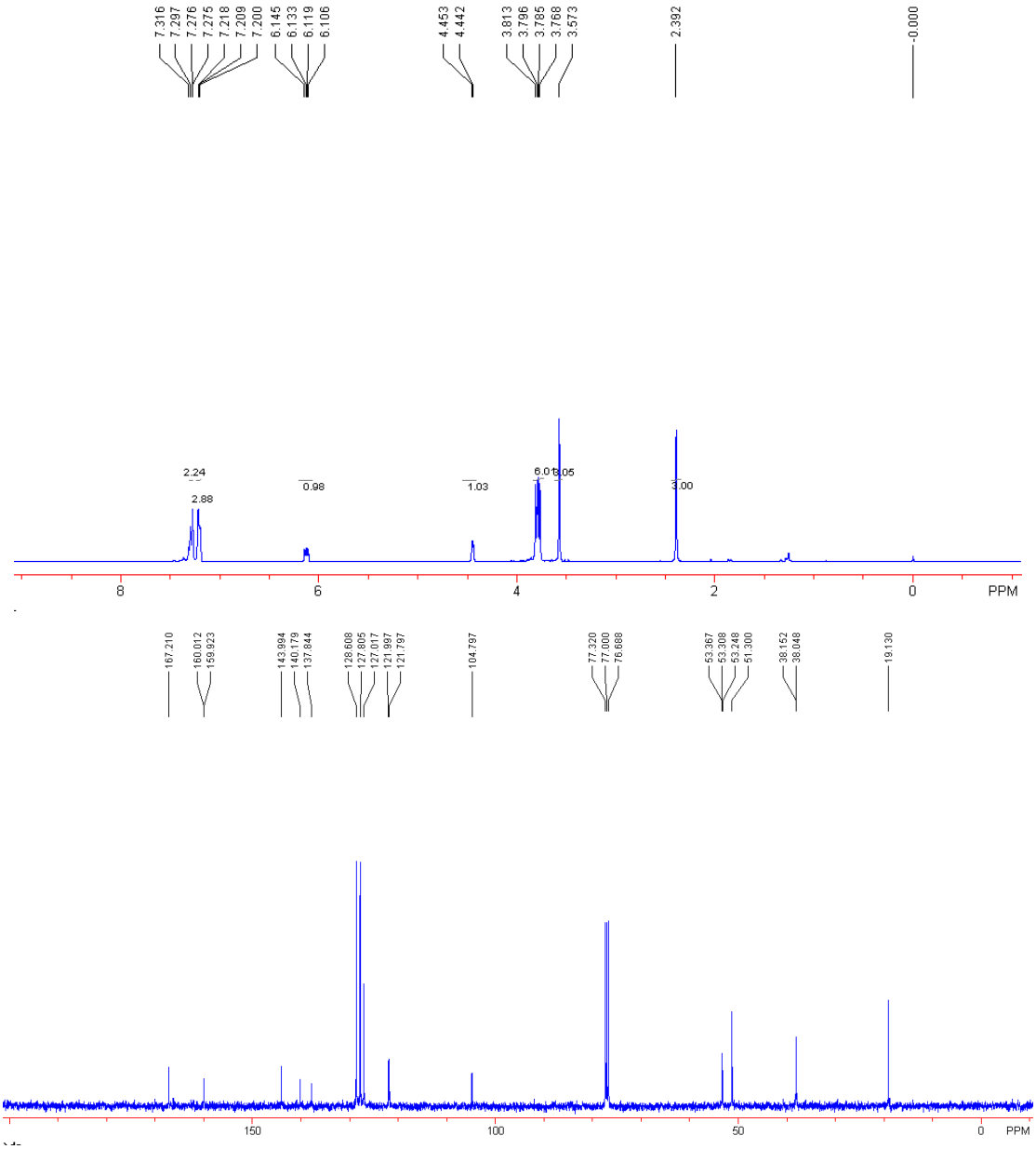
(*E*)-Isopropyl 2-(6-(dimethoxyphosphoryl)-4-phenyl-3,4-dihydro-2H-pyran-2-ylidene)acetate **4ab**: a slight yellow liquid (8.1 mg, 22%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.19 (d, *J* = 6.4 Hz, 3H), 1.22 (d, *J* = 6.4 Hz, 3H), 3.10 (dd, *J* = 17.2 Hz, 10.4 Hz, 1H), 3.68-3.72 (m, 2H), 3.84 (d, *J* = 11.2 Hz, 3H), 3.85 (d, *J* = 11.2 Hz, 3H), 4.98 (sept, *J* = 6.4 Hz, 1H), 5.64 (s, 1H), 6.29 (dd, *J* = 10.0 Hz, 2.8 Hz, 1H), 7.20-7.27 (m, 3H), 7.31-7.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 29.9, 35.7 (d, *J* = 11.9 Hz), 53.4 (d, *J* = 4.4 Hz), 67.1, 101.4, 121.5 (d, *J* = 19.3 Hz), 127.1, 127.2, 128.8, 141.1 (d, *J* = 16.4 Hz), 143.6, 164.4 (d, *J* = 9.7 Hz), 166.2; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 9.206; IR (CH_2Cl_2) ν 3062, 2979, 2905, 1706, 1655, 1452, 1374, 1260, 1170, 1100, 1023, 800, 761, 700 cm^{-1}; MS (ESI) *m/z* 367.2 ($M+H^+$); HRMS (ESI) Calcd. for $C_{18}H_{23}O_6PNa$ requires ($M+Na^+$): 389.1125, Found: 389.1112.







Methyl 6-(dimethoxyphosphoryl)-2-methyl-4-phenyl-4H-pyran-3-carboxylate **3ac**: a slight yellow liquid (21.6 mg, 64%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.39 (s, 3H), 3.57 (s, 3H), 3.78 (d, *J* = 11.2 Hz, 3H), 3.80 (d, *J* = 11.2 Hz, 3H), 4.45 (d, *J* = 4.8 Hz, 1H), 6.13 (dd, *J* = 10.4 Hz, 4.8 Hz, 1H), 7.20-7.22 (m, 3H), 7.28-7.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 38.1 (d, *J* = 10.4 Hz), 51.3, 53.27 (d, *J* = 6.0 Hz), 53.34 (d, *J* = 5.9 Hz), 104.8, 121.9 (d, *J* = 20.0 Hz), 127.0, 127.8, 128.6, 137.8, 140.2, 144.0, 160.0 (d, *J* = 8.9 Hz), 167.2; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 9.654. IR (CH_2Cl_2) ν 3062, 2963, 2904, 1717, 1660, 1627, 1437, 1375, 1262, 1174, 1037, 840, 803, 702 cm^{-1}; MS (ESI) *m/z* 339.1 ($M+H^+$); HRMS (ESI) Calcd. for $C_{16}H_{19}O_6PNa$ requires ($M+Na^+$): 361.0812, Found: 361.0801.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3.813
3.796
3.785
3.768
3.573
2.392
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2.24
2.88
0.98
1.03
6.01
6.05
3.00
8
6
4
2
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PPM
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160.012
158.923
143.984
140.179
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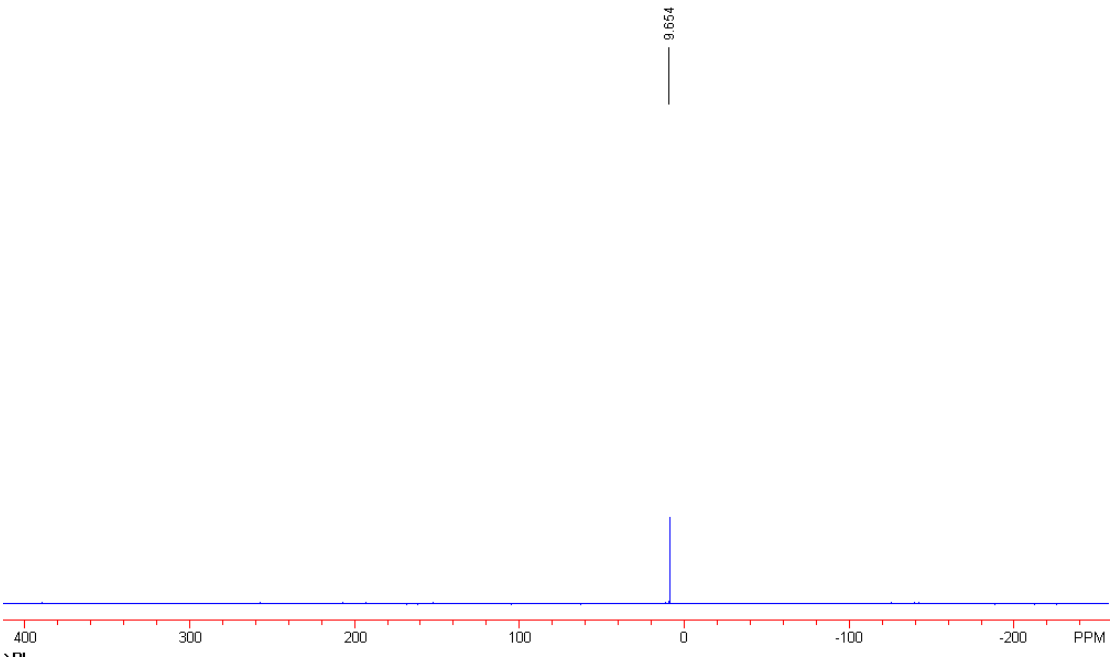
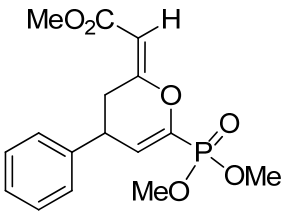
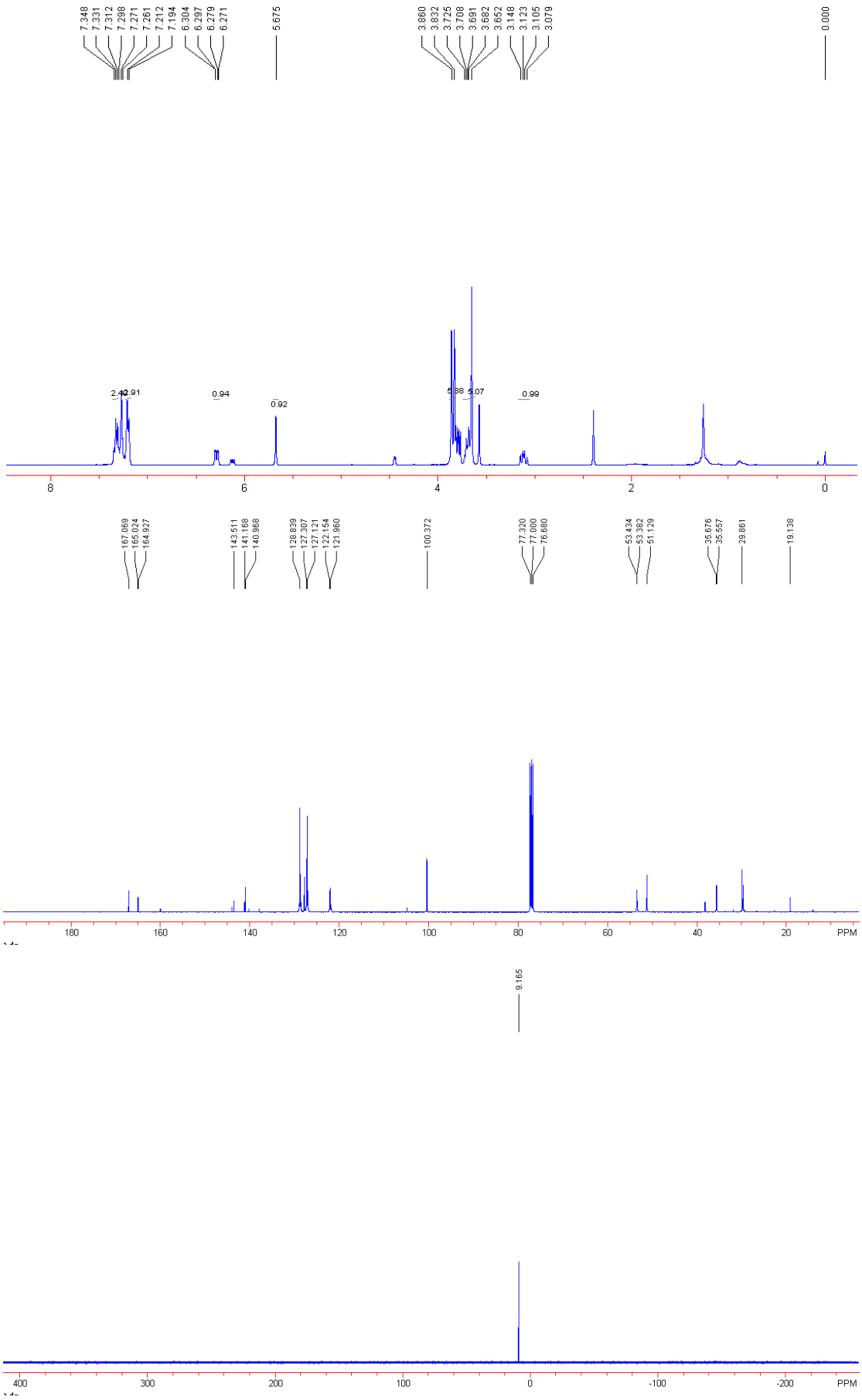
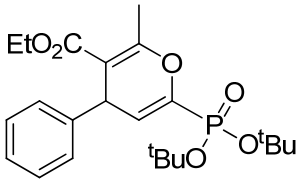
PPM



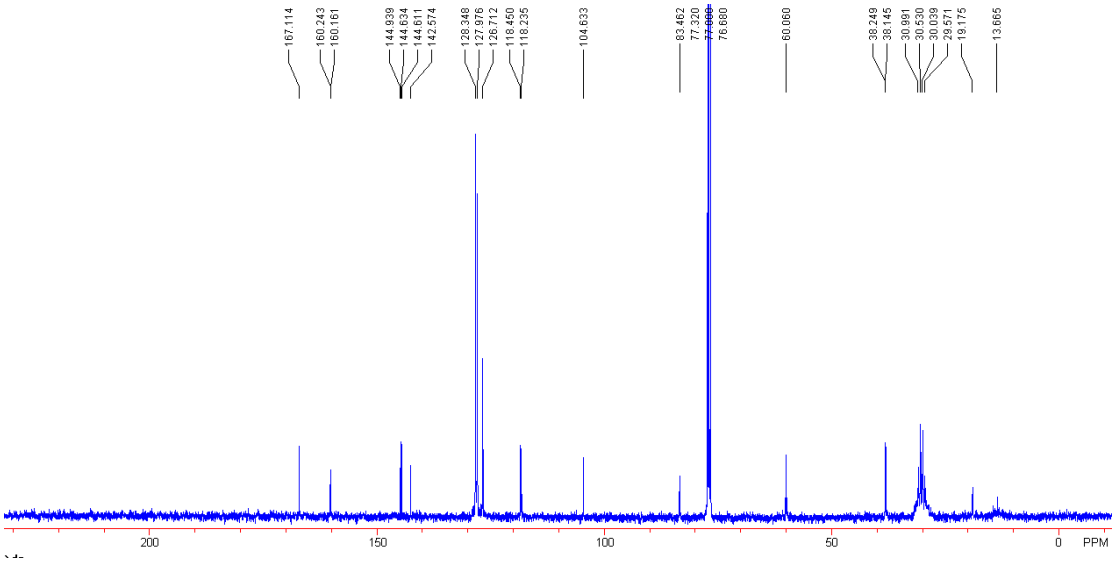


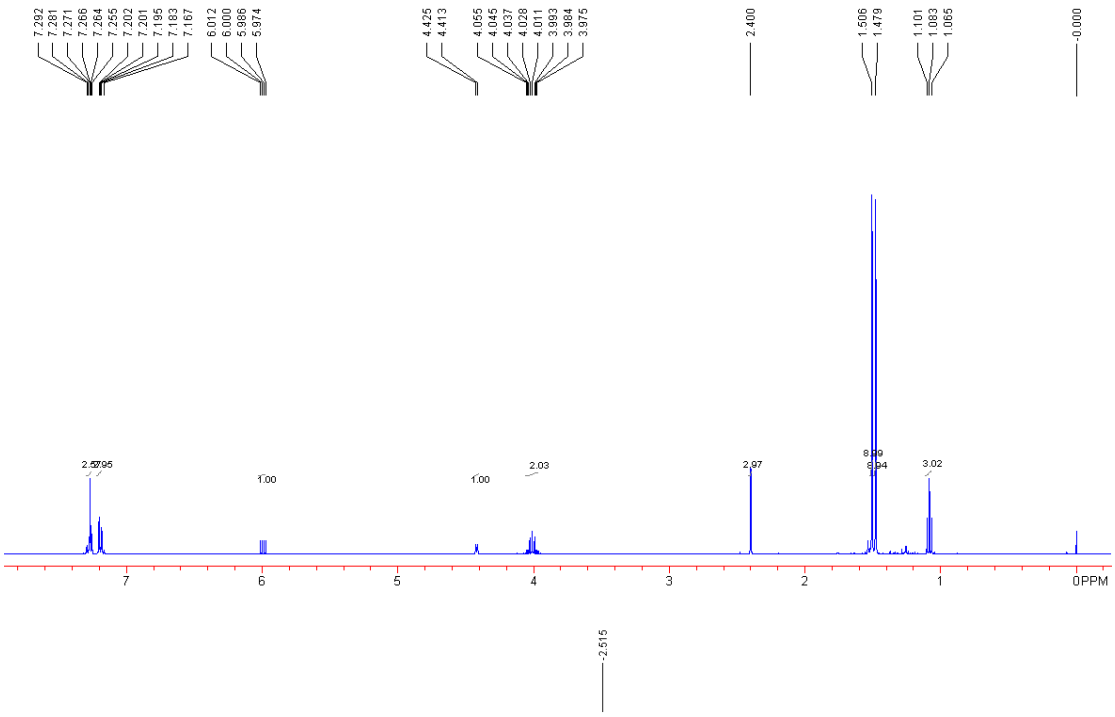
(*E*)-Methyl 2-(6-(dimethoxyphosphoryl)-4-phenyl-3,4-dihydro-2H-pyran-2-ylidene)acetate **4ac** (8.8 mg, 26%): a slight yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.11 (dd, *J* = 17.6 Hz, 10.4 Hz, 1H), 3.65 (s, 3H), 3.68-3.73 (m, 2H), 3.85 (d, *J* = 11.2 Hz, 6H), 5.68 (s, 1H), 6.29 (dd, *J* = 10.4 Hz, 3.2 Hz, 1H), 7.19-7.27 (m, 3H), 7.33-7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 29.9, 35.6 (d, *J* = 11.9 Hz), 51.1, 53.4 (d, *J* = 5.2 Hz), 100.4, 122.1 (d, *J* = 19.4 Hz), 127.1, 127.3, 128.8, 141.1 (d, *J* = 20.0 Hz), 143.5, 164.5 (d, *J* = 9.7 Hz), 167.1; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 9.165; IR (CH_2Cl_2) ν 3061, 2963, 2904, 1714, 1655, 1372, 1262, 1168, 1114, 1028, 803, 764, 701, 651 cm^{-1}; MS (ESI) *m/z* 339.2 ($M+H^+$); HRMS (ESI) Calcd. for $C_{16}H_{20}O_6P$ requires ($M+H^+$): 339.1001, Found: 339.0992.

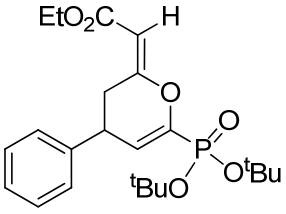




Ethyl 6-(di-tert-butoxyphosphoryl)-2-methyl-4-phenyl-4H-pyran-3-carboxylate **3ba**: a slight yellow liquid (27.5 mg, 63%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.08 (t, J = 7.2 Hz, 3H), 1.46 (s, 9H), 1.51 (s, 9H), 2.40 (s, 3H), 3.96-4.06 (m, 2H), 4.42 (d, J = 4.8 Hz, 1H), 5.99 (dd, J = 10.4 Hz, 4.8 Hz, 1H), 7.17-7.20 (m, 3H), 7.26-7.29 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.7, 19.2, 29.6-31.0 (m, 6C), 38.2 (d, J = 10.4 Hz), 60.1, 83.5, 104.6, 118.3 (d, J = 21.5 Hz), 126.7, 128.0, 128.3, 142.6, 144.6, 144.9, 160.2 (d, J = 8.2 Hz), 167.1; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ -2.515; IR (CH_2Cl_2) ν 2980, 2902, 2884, 1714, 1659, 1626, 1476, 1372, 1262, 1171, 1108, 1041, 992, 804, 700 cm^{-1}; MS (ESI) *m/z* 459.3 (M+Na^{+}); HRMS (ESI) Calcd. for $C_{23}H_{33}O_6PNa$ requires (M+Na^{+}): 459.1907, Found: 459.1919.

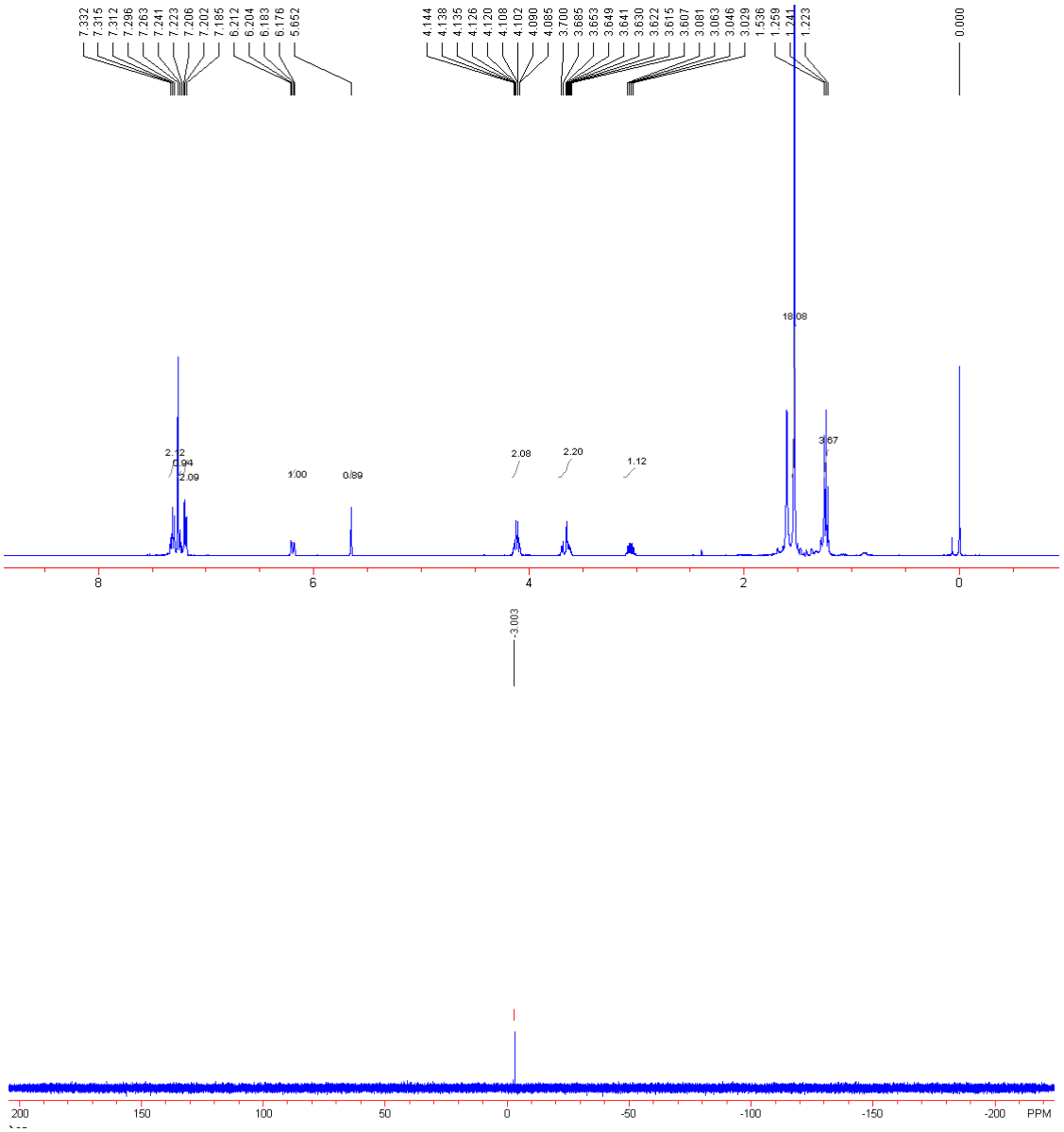


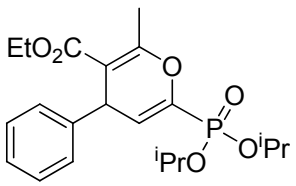




(*E*)-ethyl 2-(6-(di-tert-butoxyphosphoryl)-4-phenyl-3,4-dihydro-2H-pyran-2-ylidene)acetate **4ba**: a slight yellow liquid (3.1 mg, 7%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, J = 7.2 Hz, 3H), 1.54 (s, 18H), 3.05 (dd, J = 13.6 Hz, 6.8 Hz, 1H), 3.61-3.70 (m, 2H), 4.09-4.14 (m, 2H), 5.65 (s, 1H), 6.19 (dd, J = 11.2 Hz, 2.8 Hz, 1H), 7.19-7.21 (m, 2H), 7.22-7.26 (m, 1H), 7.30-7.33 (m, 2H); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ -3.003; IR (CH_2Cl_2) ν 2977, 2903, 1713, 1655, 1373, 1261, 1170, 1114, 1042, 1014, 801, 739, 700 cm^{-1}; MS (ESI) *m/z*

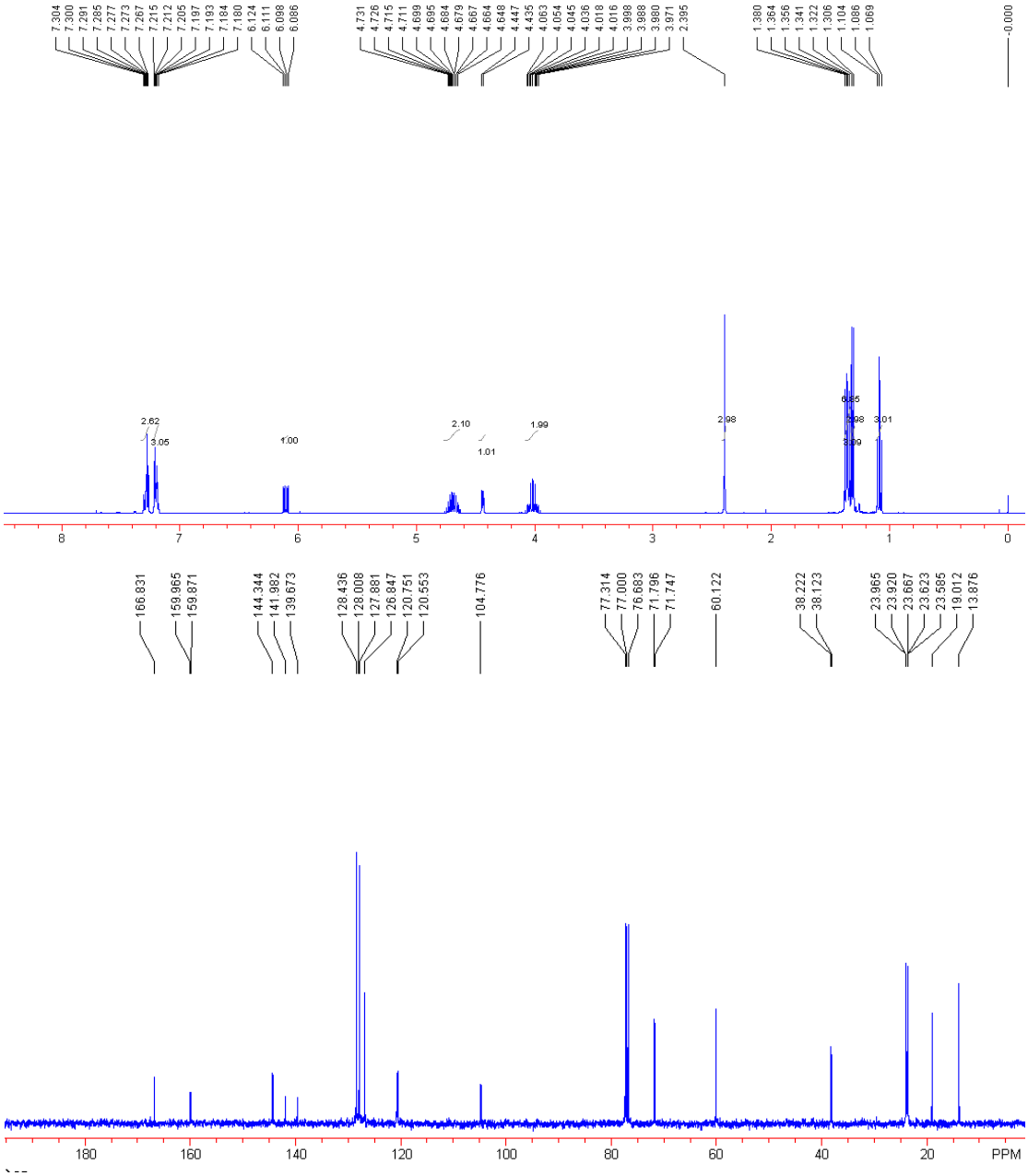
459.2 (M+Na$^+$); HRMS (ESI) Calcd. for $C_{23}H_{33}O_6PNa$ requires (M+Na$^+$): 459.1907, Found: 459.1915.

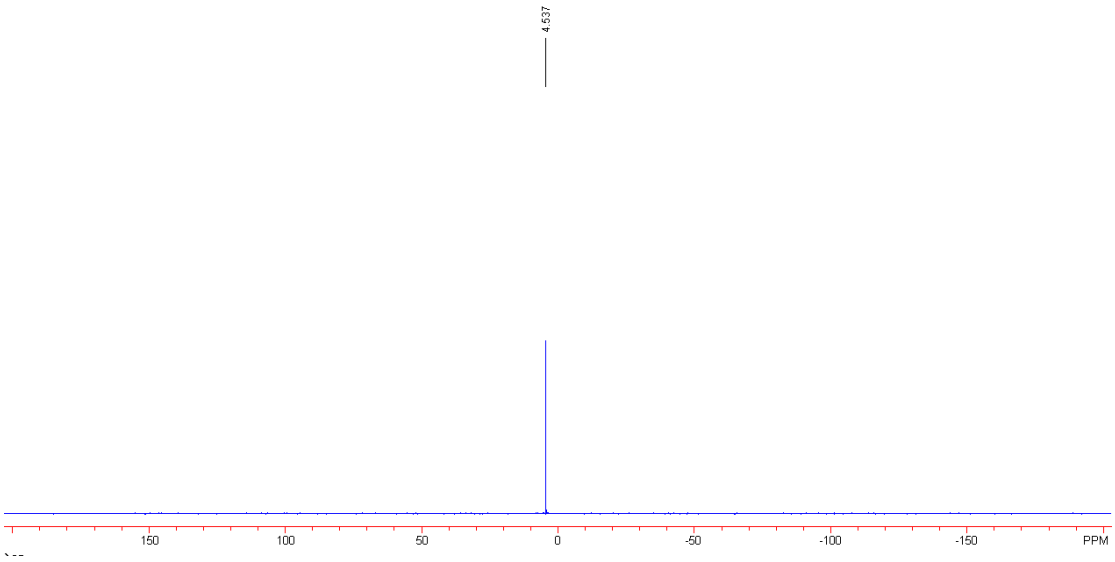


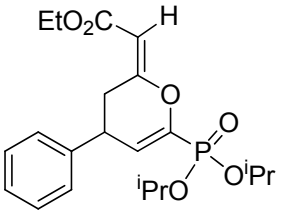


Ethyl 6-(diisopropoxyphosphoryl)-2-methyl-4-phenyl-4H-pyran-3-carboxylate **3ca**: a slight yellow liquid (31.4 mg, 77%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (t, J = 6.8 Hz, 3H), 1.31 (d, J = 6.4 Hz, 6H), 1.35 (d, J = 6.4 Hz, 3H), 1.37 (d, J = 6.4 Hz, 3H), 2.40 (s, 3H), 3.97-4.06 (m, 2H), 4.44 (d, J = 4.8 Hz, 1H), 4.65-4.73 (m, 2H), 6.10 (dd, J = 10.4 Hz, 4.8 Hz,

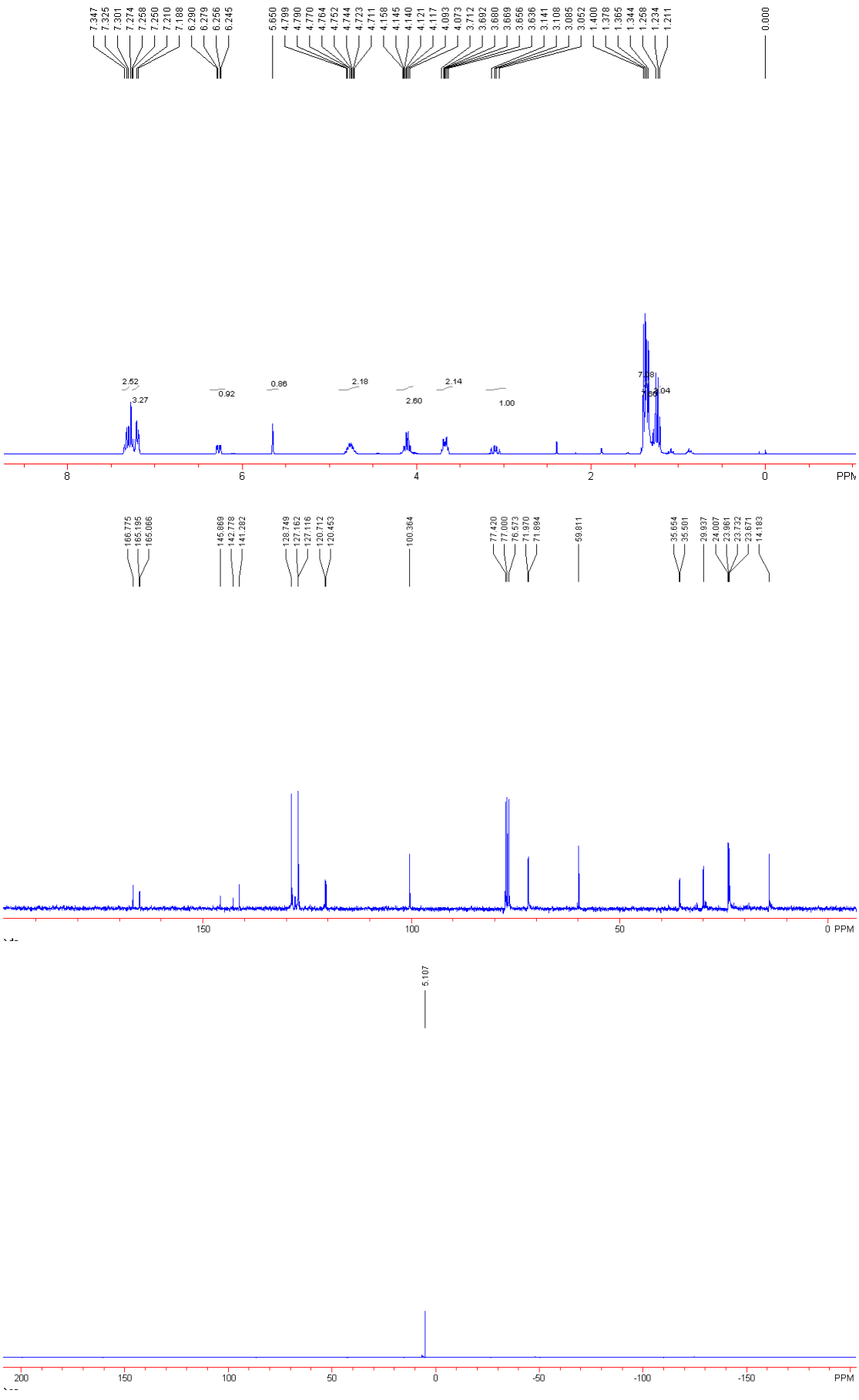
1H), 7.18-7.22 (m, 3H), 7.28-7.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 19.0, 23.60 (d, *J* = 3.8 Hz), 23.65 (d, *J* = 4.4 Hz), 23.9 (d, *J* = 4.5 Hz), 38.2 (d, *J* = 9.9 Hz), 60.1, 71.8 (d, *J* = 4.9 Hz), 104.8, 120.7 (d, *J* = 19.8 Hz), 126.8, 127.9, 128.0, 128.4, 139.7, 142.0, 144.3, 159.9 (d, *J* = 9.4 Hz), 166.8; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.537; IR (CH_2Cl_2) ν 2982, 2905, 2876, 1769, 1720, 1658, 1376, 1261, 1098, 1009, 800, 701 cm^{-1}; MS (ESI) *m/z* 409.2 ($M+H^+$); HRMS (ESI) Calcd. for $C_{21}H_{29}O_6PNa$ requires ($M+Na^+$): 431.1594, Found: 431.1595.







(*E*)-Ethyl 2-(6-(diisopropoxyphosphoryl)-4-phenyl-3,4-dihydro-2H-pyran-2-ylidene)acetate **4ca**: a slight yellow liquid (3.2 mg, 8%); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.23 (t, *J* = 7.2 Hz, 3H), 1.35 (d, *J* = 6.3 Hz, 6H), 1.39 (d, *J* = 6.3 Hz, 6H), 3.10 (dd, *J* = 16.8 Hz, 9.9 Hz, 1H), 3.64-3.71 (m, 2H), 4.07-4.16 (m, 2H), 4.71-4.80 (m, 2H), 5.65 (s, 1H), 6.27 (dd, *J* = 10.2 Hz, 6.9 Hz, 1H), 7.19-7.26 (m, 3H), 7.30-7.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.2, 23.7 (d, *J* = 4.6 Hz), 24.0 (d, *J* = 3.5 Hz), 29.9, 35.6 (d, *J* = 11.4 Hz), 59.8, 71.9 (d, *J* = 5.7 Hz), 100.4, 120.6 (d, *J* = 19.4 Hz), 127.1, 127.2, 128.7, 141.3, 142.8, 145.9, 165.1 (d, *J* = 9.7 Hz), 166.8; ^{31}P NMR ($CDCl_3$, 121.453 MHz, 85% H_3PO_4) δ 5.107; IR (CH_2Cl_2) ν 3063, 2980, 2937, 2902, 1711, 1654, 1352, 1259, 1170, 1110, 1044, 985, 886, 762, 700 cm^{-1}; MS (ESI) *m/z* 409.2 ($M+H^+$); HRMS (ESI) Calcd. for $C_{21}H_{29}O_6PNa$ requires ($M+Na^+$): 431.1594, Found: 431.1579.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1.365
1.344
1.258
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3.27
0.92
0.86
2.18
2.60
2.14
1.00
7.08
7.04
8
6
4
2
0
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165.195
165.066
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141.282
128.749
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127.116
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77.420
77.000
76.573
71.970
71.894
59.811
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35.501
29.937
24.007
23.961
23.732
23.671
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100
50
0 PPM
5.107
200
150
100
50
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-100
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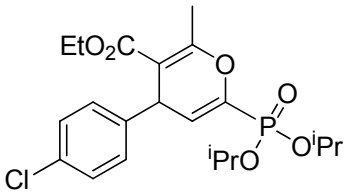
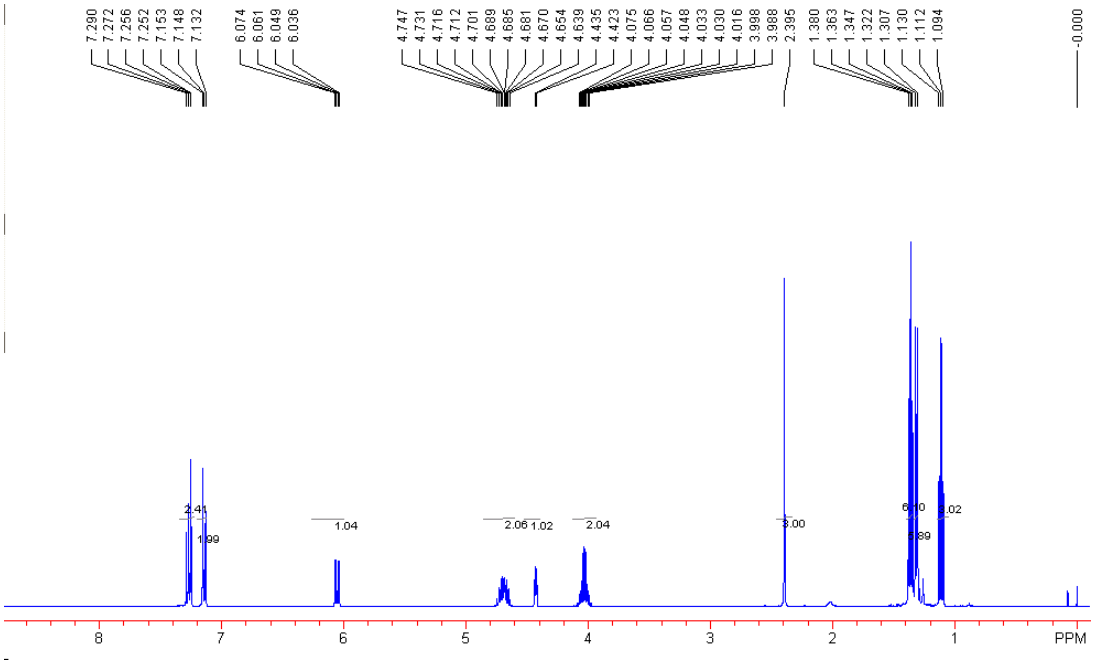
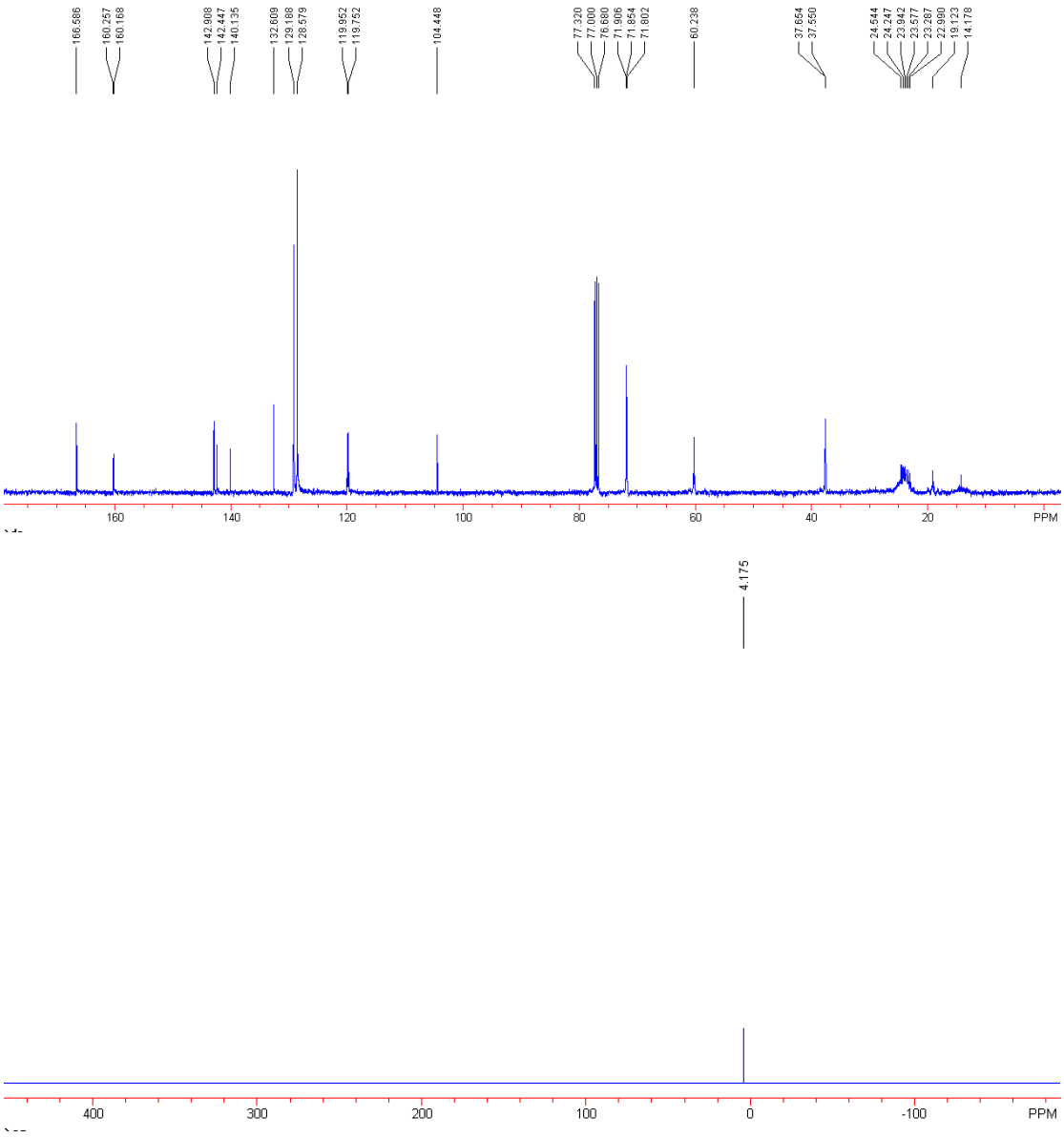
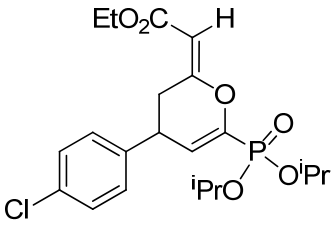
PPM



Ethyl 4-(4-chlorophenyl)-6-(diisopropoxyphosphoryl)-2-methyl-4H-pyran-3-carboxylate **3da**: a slight yellow liquid (34.9 mg, 79%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, *J* = 7.2 Hz, 3H), 1.31 (d, *J* = 6.0 Hz, 6H), 1.36 (d, *J* = 6.0 Hz, 3H), 1.37 (d, *J* = 6.0 Hz, 3H), 2.40 (s, 3H), 4.00-4.08 (m, 2H), 4.43 (d, *J* = 4.8 Hz, 1H), 4.64-4.75 (m, 2H), 6.06 (dd, *J* = 10.0 Hz, 4.8 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.2, 19.1, 23.0-24.5 (m, 4C), 37.6 (d, *J* = 10.4 Hz), 60.2, 71.8 (d, *J* = 5.2 Hz), 71.9 (d, *J* = 5.2 Hz), 104.4, 119.9 (d, *J* = 20.0 Hz), 128.6, 129.2, 132.6, 140.1, 142.4, 142.9, 160.2 (d, *J* = 8.9 Hz), 166.6; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.175; IR (CH_2Cl_2) ν 2980, 2942, 2904, 1714, 1663, 1625, 1488, 1376, 1259, 1176, 1104, 986, 946, 804, 685 cm^{-1}; MS (ESI) *m/z* 443.3 ($M+H^+$); HRMS (ESI) Calcd. for $C_{21}H_{28}O_6PNa$ requires ($M+Na^+$): 465.1204, Found: 465.1193.





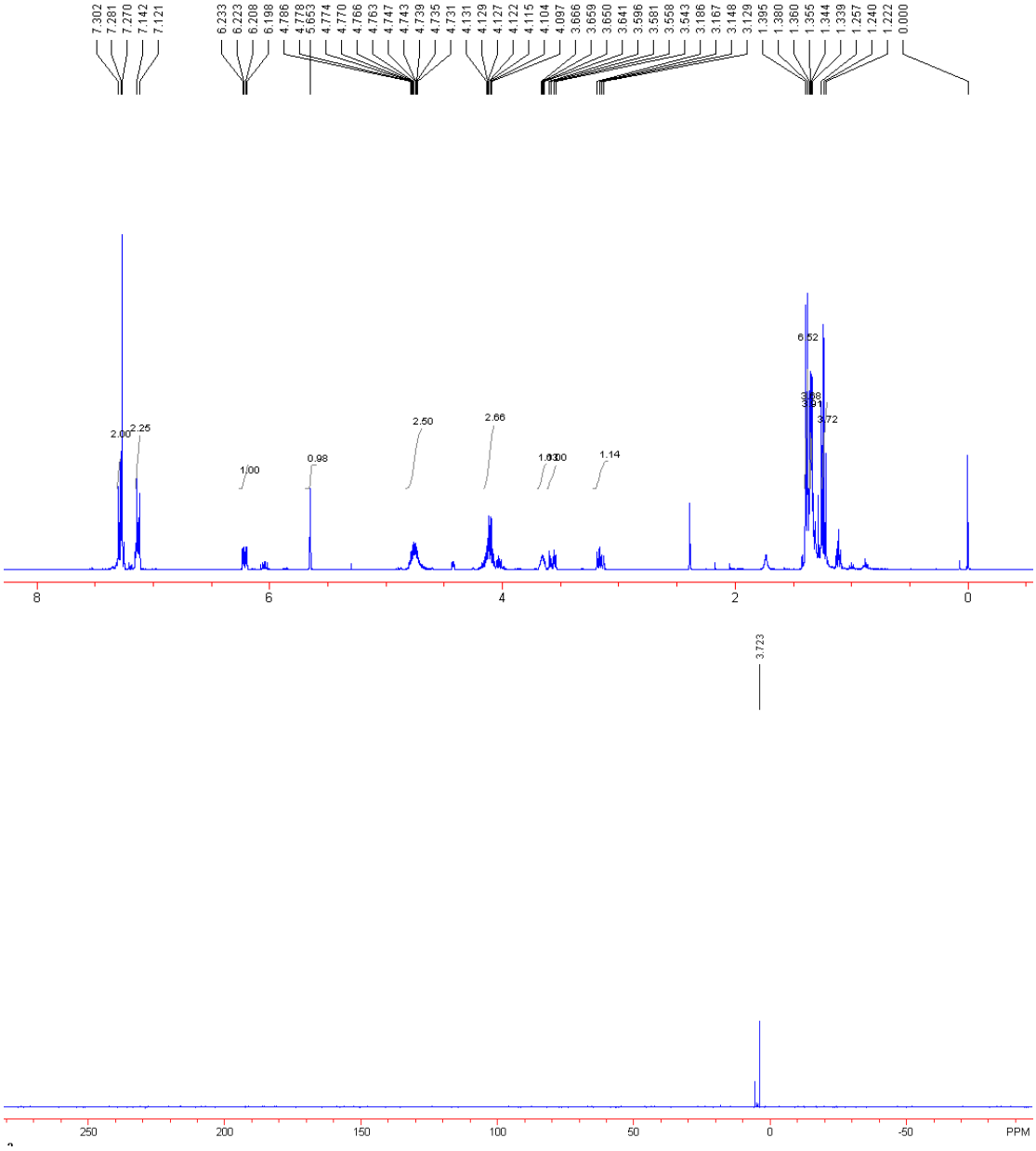


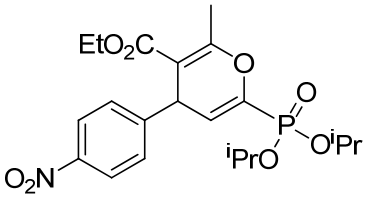
(*E*)-Ethyl

2-(4-(4-chlorophenyl)-6-(diisopropoxyphosphoryl)-3,4-dihydro-2H-pyran-2-ylidene)acetate

4da: a slight yellow liquid (3.5 mg, 8%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, J = 7.2 Hz, 3H), 1.34 (d, J = 6.4 Hz, 3H), 1.35 (d, J = 6.4 Hz, 3H), 1.39 (d, J = 6.0 Hz, 6H); 3.16 (dd, J = 15.2 Hz, 7.6 Hz, 1H), 3.55 (dd, J = 15.2 Hz, 6.0 Hz, 1H); 3.64-3.67 (m, 1H), 4.09-4.13 (m, 2H), 4.73-4.79 (m, 2H), 5.65 (s, 1H), 6.22 (dd, J = 10.0 Hz, 4.0 Hz, 1H), 7.13 (d, J = 8.4 Hz,

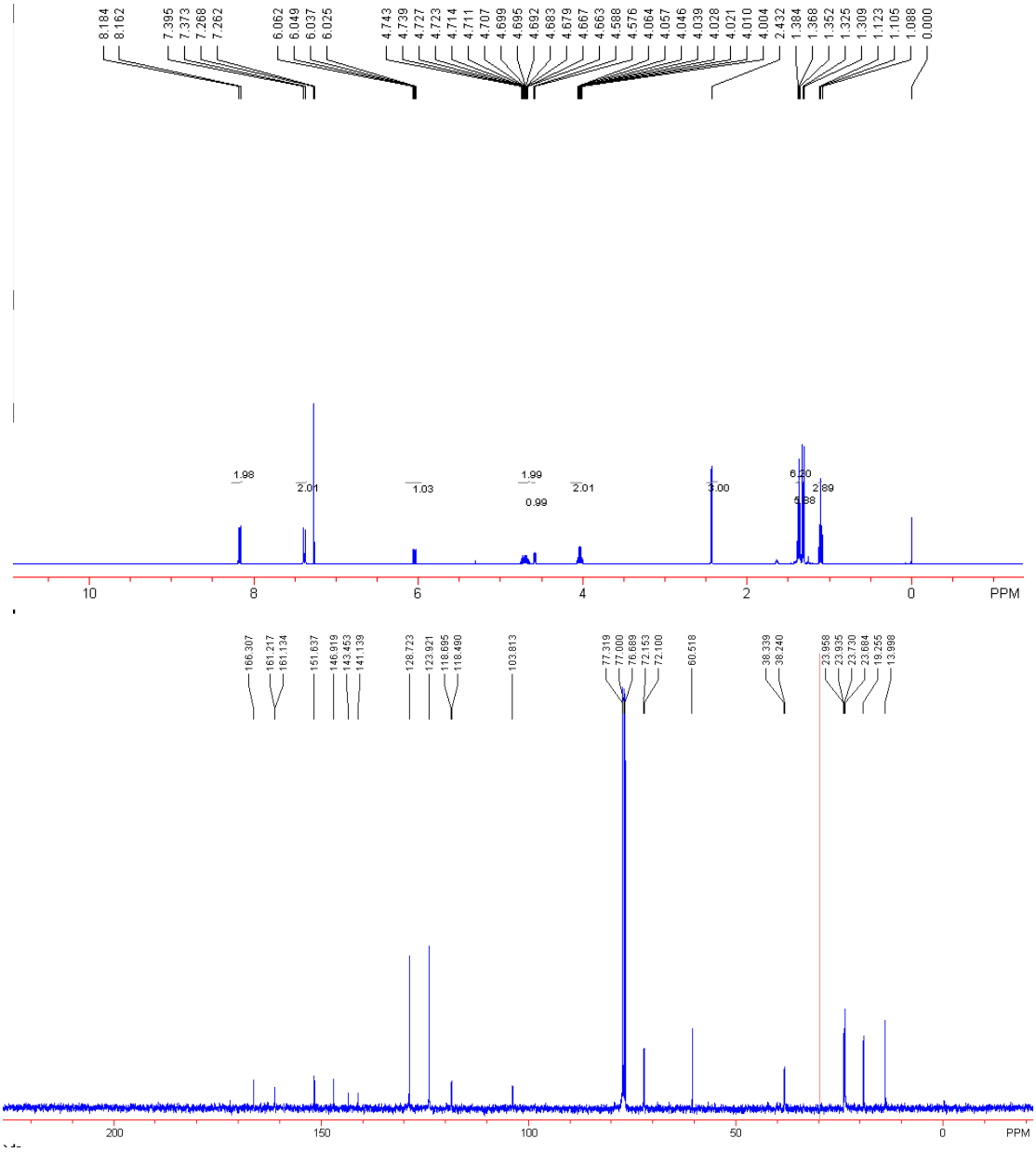
2H), 7.29 (d, J = 8.4 Hz, 2H); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 3.723; IR (CH_2Cl_2) ν 2980, 2942, 2902, 1713, 1657, 1492, 1375, 1261, 1172, 1116, 1045, 994, 820, 739, 703 cm^{-1}; MS (ESI) *m/z* 443.2 ($M+H^+$); HRMS (ESI) Calcd. for $C_{21}H_{28}O_6PNa$ requires ($M+Na^+$): 465.1204, Found: 465.1213.

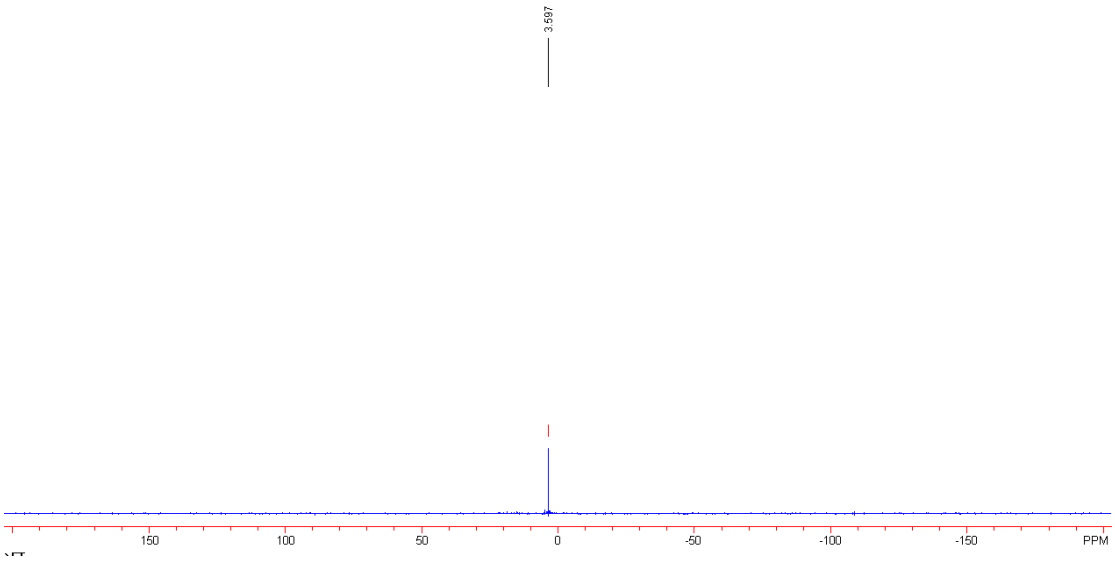


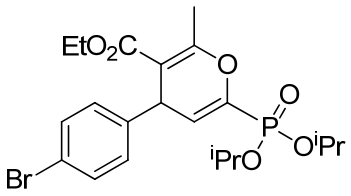


Ethyl 6-(diisopropoxyphosphoryl)-2-methyl-4-(4-nitrophenyl)-4H-pyran-3-carboxylate **3da**: a slight yellow liquid (36.2 mg, 80%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, J = 7.2 Hz,

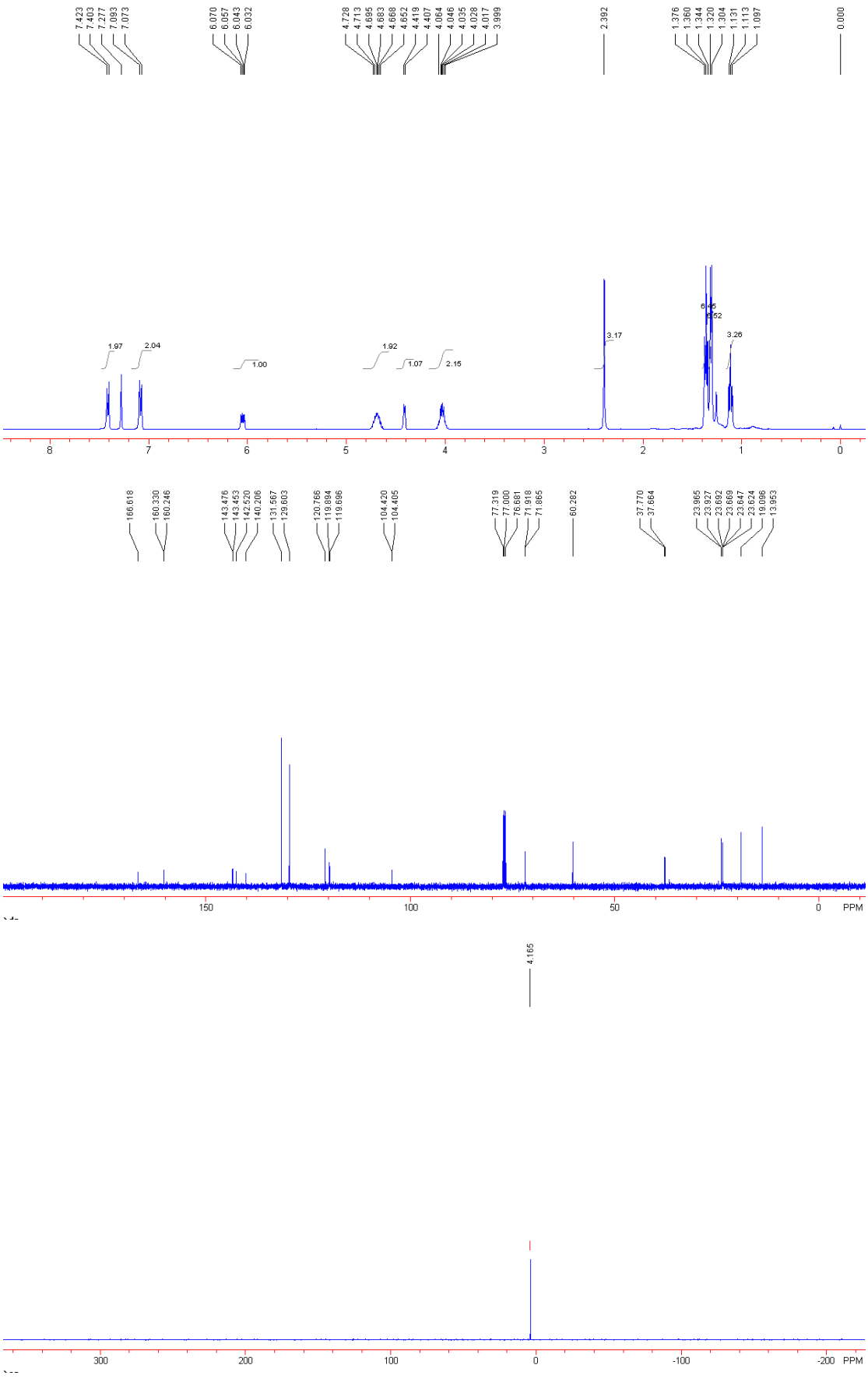
3H), 1.32 (d, J = 6.4 Hz, 6H), 1.36 (d, J = 6.4 Hz, 3H), 1.38 (d, J = 6.4 Hz, 3H), 2.43 (s, 3H), 4.00-4.06 (m, 2H), 4.58 (d, J = 4.8 Hz, 1H), 4.67-4.74 (m, 2H), 6.04 (dd, J = 10.0 Hz, 4.8 Hz, 1H), 7.38 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 19.3, 23.7 (d, J = 4.6 Hz), 23.9 (d, J = 2.3 Hz), 38.3 (d, J = 9.9 Hz), 60.5, 72.1 (d, J = 5.3 Hz), 103.8, 118.6 (d, J = 19.5 Hz), 123.9, 128.7 141.1, 143.5, 146.9, 151.6, 161.2 (d, J = 8.3 Hz), 166.3; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 3.597; IR (CH_2Cl_2) ν 3074, 2981, 2906, 2874, 1715, 1662, 1626, 1521, 1375, 1347, 1176, 1105, 988, 854, 806, 700 cm^{-1}; MS (ESI) *m/z* 454.2 (M+H$^+$); HRMS (ESI) Calcd. for $C_{21}H_{28}NO_8PNa$ requires (M+Na$^+$): 476.1445, Found: 476.1461.







Ethyl 4-(4-bromophenyl)-6-(diisopropoxyphosphoryl)-2-methyl-4H-pyran-3-carboxylate **3fa**: a slight yellow liquid (38.3 mg, 79%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, *J* = 6.8 Hz, 3H), 1.31 (d, *J* = 6.4 Hz, 6H), 1.35 (d, *J* = 6.4 Hz, 3H), 1.37 (d, *J* = 6.4 Hz, 3H), 2.39 (s, 3H), 4.00-4.06 (m, 2H), 4.41 (d, *J* = 4.8 Hz, 1H), 4.65-4.73 (m, 2H), 6.05 (dd, *J* = 10.4 Hz, 4.8 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 19.1, 23.64 (d, *J* = 2.3 Hz), 23.68 (d, *J* = 2.3 Hz), 23.9 (d, *J* = 3.8 Hz), 37.7 (d, *J* = 10.6 Hz), 60.3, 71.9 (d, *J* = 5.3 Hz), 104.4 (d, *J* = 1.5 Hz), 119.8 (d, *J* = 19.8 Hz), 120.8, 129.6, 131.6, 140.2, 142.5, 143.5 (d, *J* = 2.3 Hz), 160.2 (d, *J* = 8.4 Hz), 166.6; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.165; IR (CH_2Cl_2) ν 2979, 2934, 2906, 1713, 1657, 1488, 1448, 1261, 1170, 1111, 1010, 802, 740, 702, 668 cm^{-1}; MS (ESI) *m/z* 487.3 ($M+H^+$); HRMS (ESI) Calcd. for $C_{21}H_{28}O_6PBrNa$ requires ($M+Na^+$): 509.0699, Found: 509.0705.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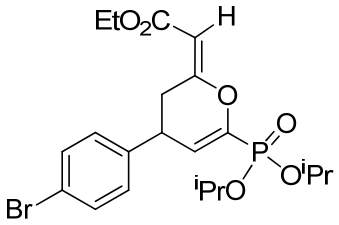
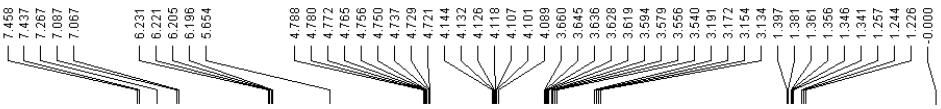
PPM

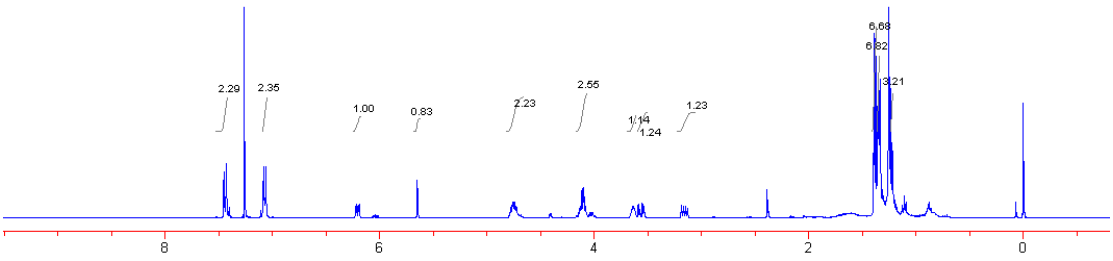


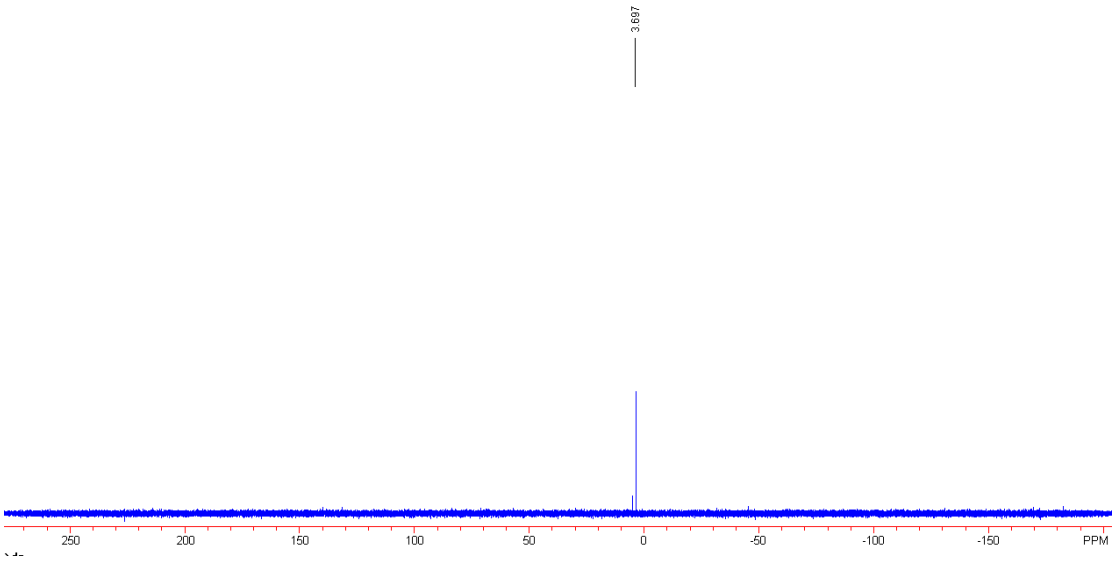
(*E*)-Ethyl

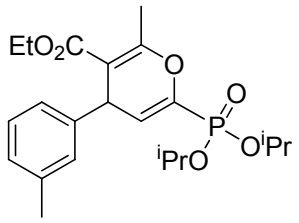
2-(4-(4-bromophenyl)-6-(diisopropoxyphosphoryl)-3,4-dihydro-2H-pyran-2-ylidene)acetate

4fa: a slight yellow liquid (3.1 mg, 6%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.35 (d, *J* = 6.4 Hz, 3H), 1.36 (d, *J* = 6.4 Hz, 3H), 1.39 (d, *J* = 6.4 Hz, 6H); 3.16 (dd, *J* = 15.2 Hz, 7.6 Hz, 1H), 3.57 (dd, *J* = 15.2 Hz, 6.4 Hz, 1H), 3.62-3.66 (m, 1H), 4.09-4.14 (m, 2H), 4.72-4.79 (m, 2H), 5.65 (s, 1H), 6.21 (dd, *J* = 10.0 Hz, 4.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 3.697; IR (CH_2Cl_2) ν 2980, 2939, 2902, 1714, 1661, 1626, 1485, 1376, 1260, 1176, 1106, 992, 805, 740, 664 cm^{-1}; MS (ESI) *m/z* 487.3 ($M+H^+$); HRMS (ESI) Calcd. for $C_{21}H_{28}O_6PBrNa$ requires ($M+Na^+$): 509.0699, Found: 509.0708.

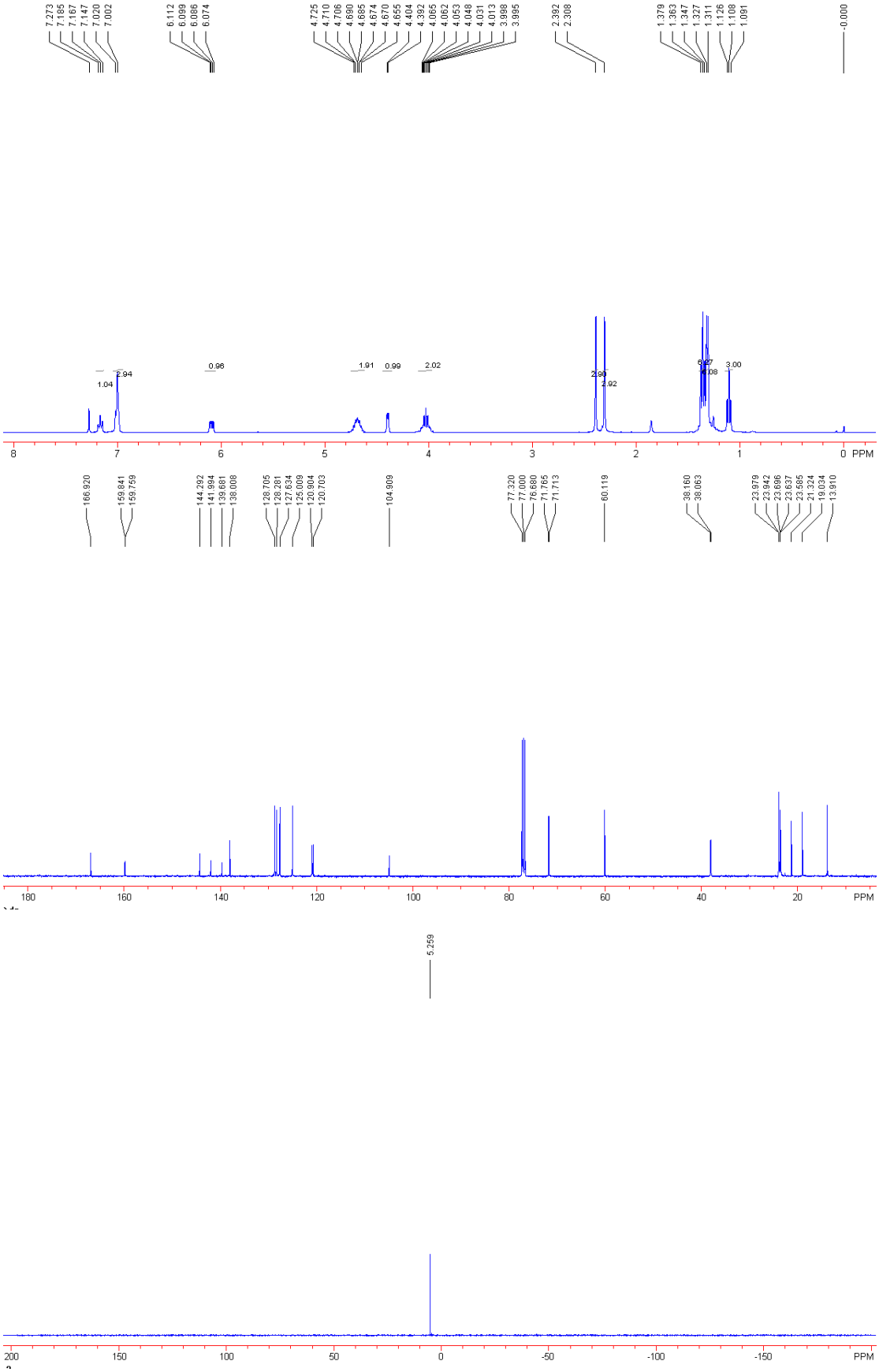


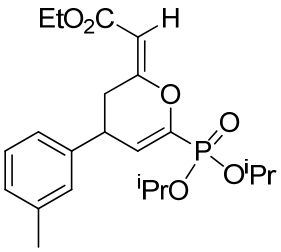




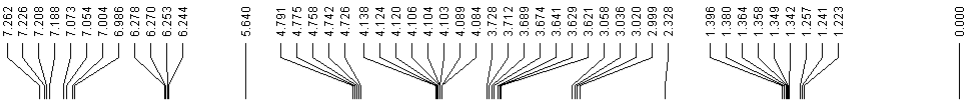


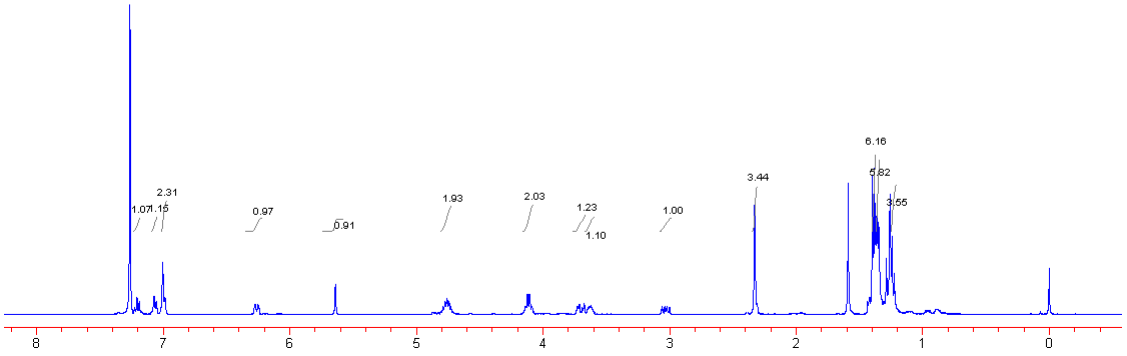
Ethyl 6-(diisopropoxyphosphoryl)-2-methyl-4-m-tolyl-4H-pyran-3-carboxylate **3ga**: a slight yellow liquid (32.6 mg, 77%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, J = 7.2 Hz, 3H), 1.32 (d, J = 6.4 Hz, 6H), 1.35 (d, J = 6.4 Hz, 3H), 1.37 (d, J = 6.4 Hz, 3H), 2.31 (s, 3H), 2.39 (s, 3H), 4.00-4.07 (m, 2H), 4.40 (d, J = 4.8 Hz, 1H), 4.66-4.73 (m, 2H), 6.09 (dd, J = 10.0 Hz, 4.8 Hz, 1H), 7.00-7.02 (m, 3H), 7.17 (t, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 19.0, 21.3, 23.6 (d, J = 5.2 Hz), 23.7 (d, J = 5.9 Hz), 24.0 (d, J = 3.7 Hz), 38.1 (d, J = 9.7 Hz), 60.1, 71.7 (d, J = 5.2 Hz), 104.9, 120.8 (d, J = 20.1 Hz), 125.0, 127.6, 128.3, 128.7, 138.0, 139.7, 142.0, 144.3, 159.8 (d, J = 8.2 Hz), 166.9; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 5.259; IR (CH_2Cl_2) ν 2979, 2901, 2884, 1715, 1660, 1626, 1475, 1376, 1261, 1171, 1107, 1011, 801, 739, 703 cm^{-1}; MS (ESI) *m/z* 423.3 ($M+H^+$); HRMS (ESI) Calcd. for $C_{22}H_{31}O_6PNa$ requires ($M+Na^+$): 445.1751, Found: 445.1743.

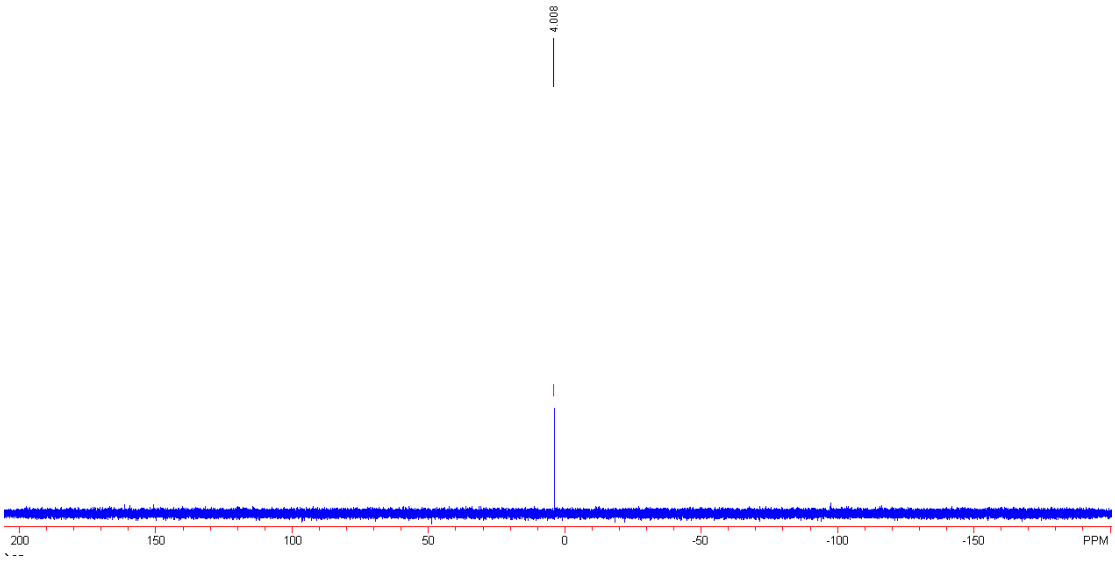


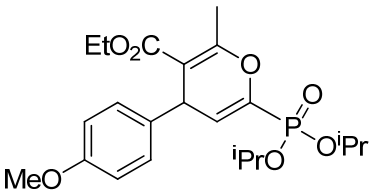


(*E*)-Ethyl 2-(6-(diisopropoxyphosphoryl)-4-m-tolyl-3,4-dihydro-2H-pyran-2-ylidene)acetate **4ga**: a slight yellow liquid (3.3 mg, 8%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.35 (d, *J* = 6.4 Hz, 3H), 1.36 (d, *J* = 6.4 Hz, 3H), 1.39 (d, *J* = 6.4 Hz, 6H), 2.33 (s, 3H), 3.03 (dd, *J* = 15.2 Hz, 8.4 Hz, 1H), 3.62-3.64 (m, 1H), 3.70 (dd, *J* = 15.2 Hz, 6.0 Hz, 1H), 4.08-4.14 (m, 2H), 4.73-4.79 (m, 2H), 5.64 (s, 1H), 6.26 (dd, *J* = 10.4 Hz, 3.6 Hz, 1H), 6.99-7.00 (m, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.008; IR (CH_2Cl_2) ν 2979, 2903, 1713, 1656, 1375, 1260, 1175, 1112, 1044, 1013, 800, 739, 703 cm^{-1}; MS (ESI) *m/z* 423.3 ($M+H^+$); HRMS (ESI) Calcd. for $C_{22}H_{31}O_6PNa$ requires ($M+Na^+$): 445.1751, Found: 445.1744.

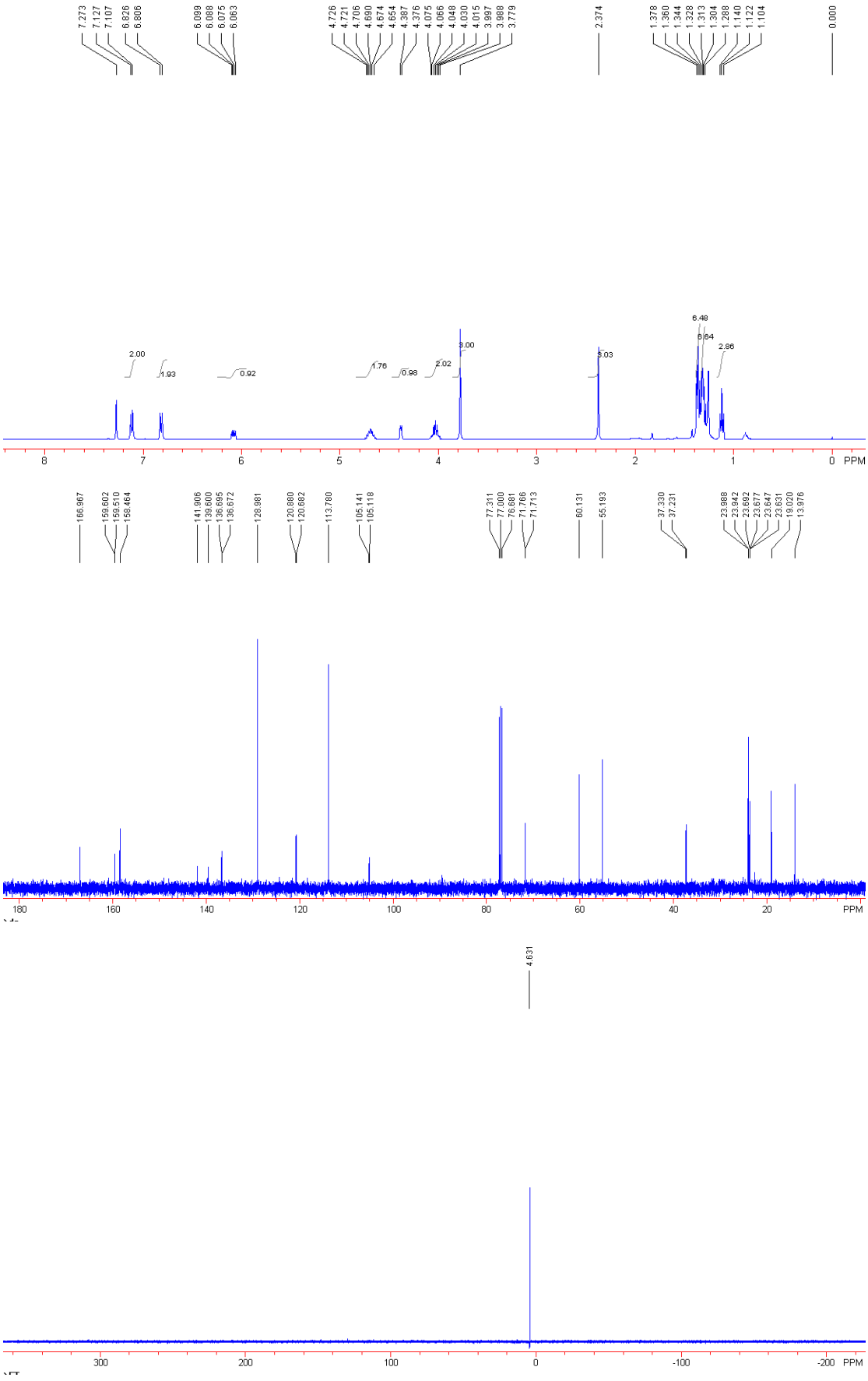








Ethyl 6-(diisopropoxyphosphoryl)-4-(4-methoxyphenyl)-2-methyl-4H-pyran-3-carboxylate **3ha**: a slight yellow liquid (29.2 mg, 67%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (t, *J* = 7.2 Hz, 3H), 1.30 (d, *J* = 6.4 Hz, 3H), 1.32 (d, *J* = 6.4 Hz, 3H), 1.35 (d, *J* = 6.4 Hz, 3H), 1.37 (d, *J* = 6.4 Hz, 3H), 2.37 (s, 3H), 3.78 (s, 3H), 4.00-4.08 (m, 2H), 4.38 (d, *J* = 4.8 Hz, 1H), 4.65-4.73 (m, 2H), 6.08 (dd, *J* = 10.0 Hz, 4.8 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 19.0, 23.6 (d, *J* = 1.4 Hz), 23.7 (d, *J* = 1.4 Hz), 24.0 (d, *J* = 4.6 Hz), 37.3 (d, *J* = 9.9 Hz), 55.2, 60.1, 71.7 (d, *J* = 5.3 Hz), 105.1 (d, *J* = 2.3 Hz), 113.8, 120.8 (d, *J* = 19.8 Hz), 129.0, 136.7 (d, *J* = 2.3 Hz), 139.6, 141.9, 158.5, 159.6 (d, *J* = 9.2 Hz), 167.0; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.631; IR (CH_2Cl_2) ν 2980, 2937, 2906, 1714, 1626, 1510, 1376, 1259, 1176, 1106, 1070, 991, 946, 805, 745 cm^{-1}; MS (ESI) *m/z* 439.3 ($M+H^+$); HRMS (ESI) Calcd. for $C_{22}H_{31}O_7PNa$ requires ($M+Na^+$): 461.1700, Found: 461.1699.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4.674
4.654
4.387
4.376
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4.066
4.048
4.030
4.015
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1.360
1.344
1.328
1.313
1.304
1.288
1.140
1.122
1.104
0.000
2.00
1.93
0.92
1.76
0.98
2.02
3.00
3.03
6.48
6.64
2.86
8
7
6
5
4
3
2
1
0 PPM
166.967
159.602
159.510
158.464
141.906
139.600
136.695
136.672
128.981
120.880
120.682
113.780
105.141
105.118
77.311
77.000
76.681
71.766
71.713
60.131
55.193
37.330
37.231
23.988
23.942
23.692
23.677
23.647
23.631
19.020
13.976
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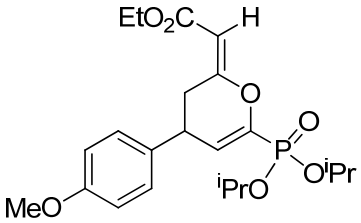
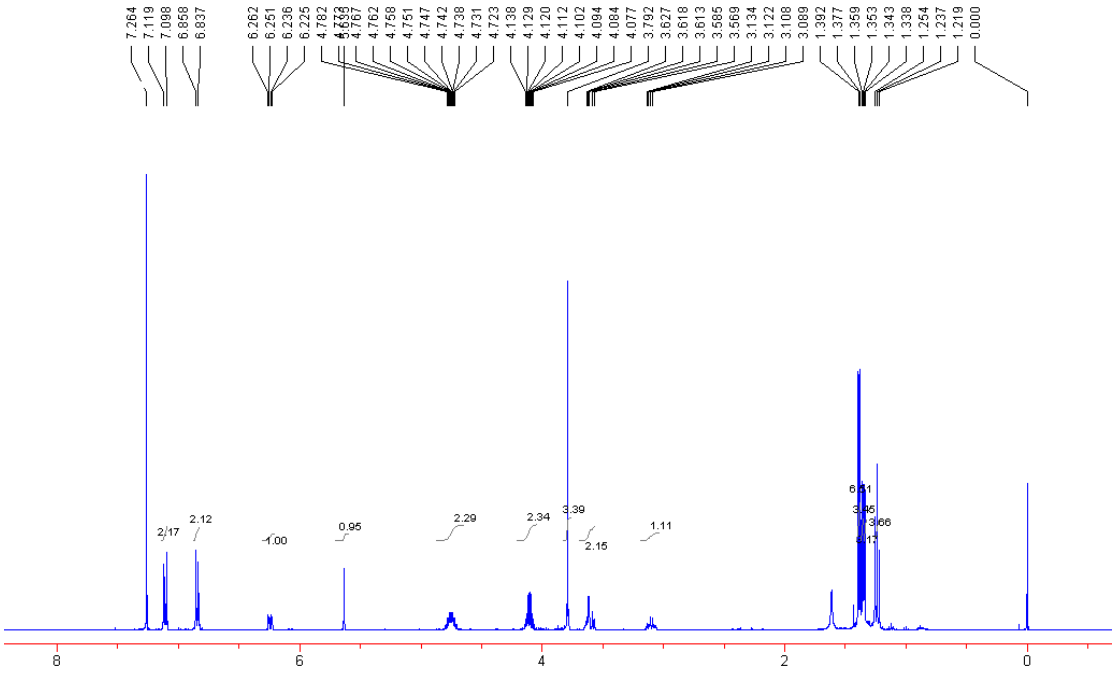
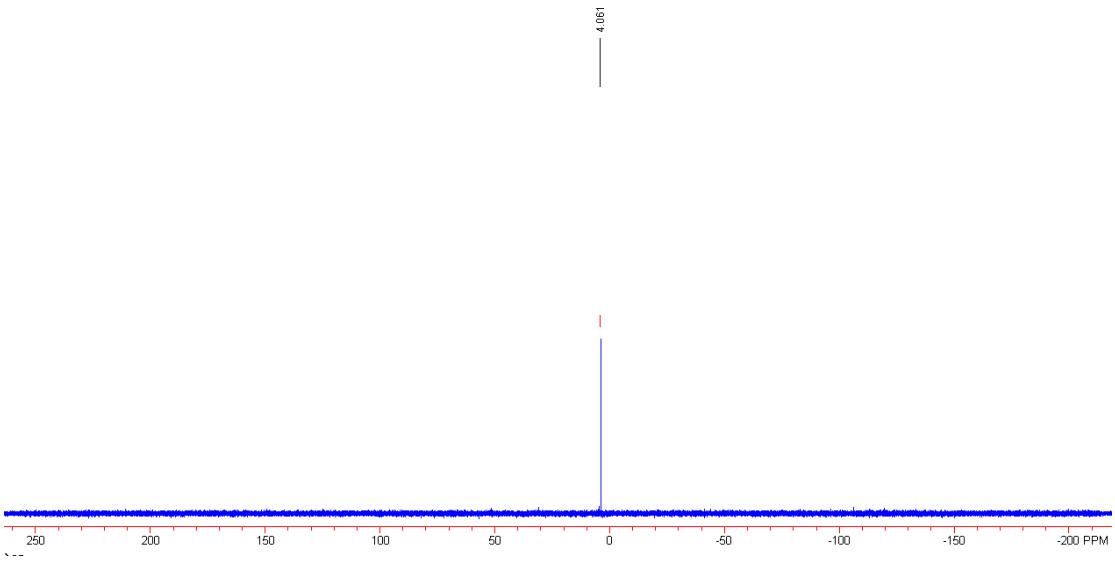
160
140
120
100
80
60
40
20
PPM
4.631
300
200
100
0
-100
-200
PPM

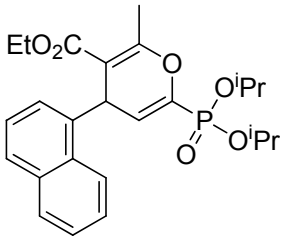


(*E*)-ethyl

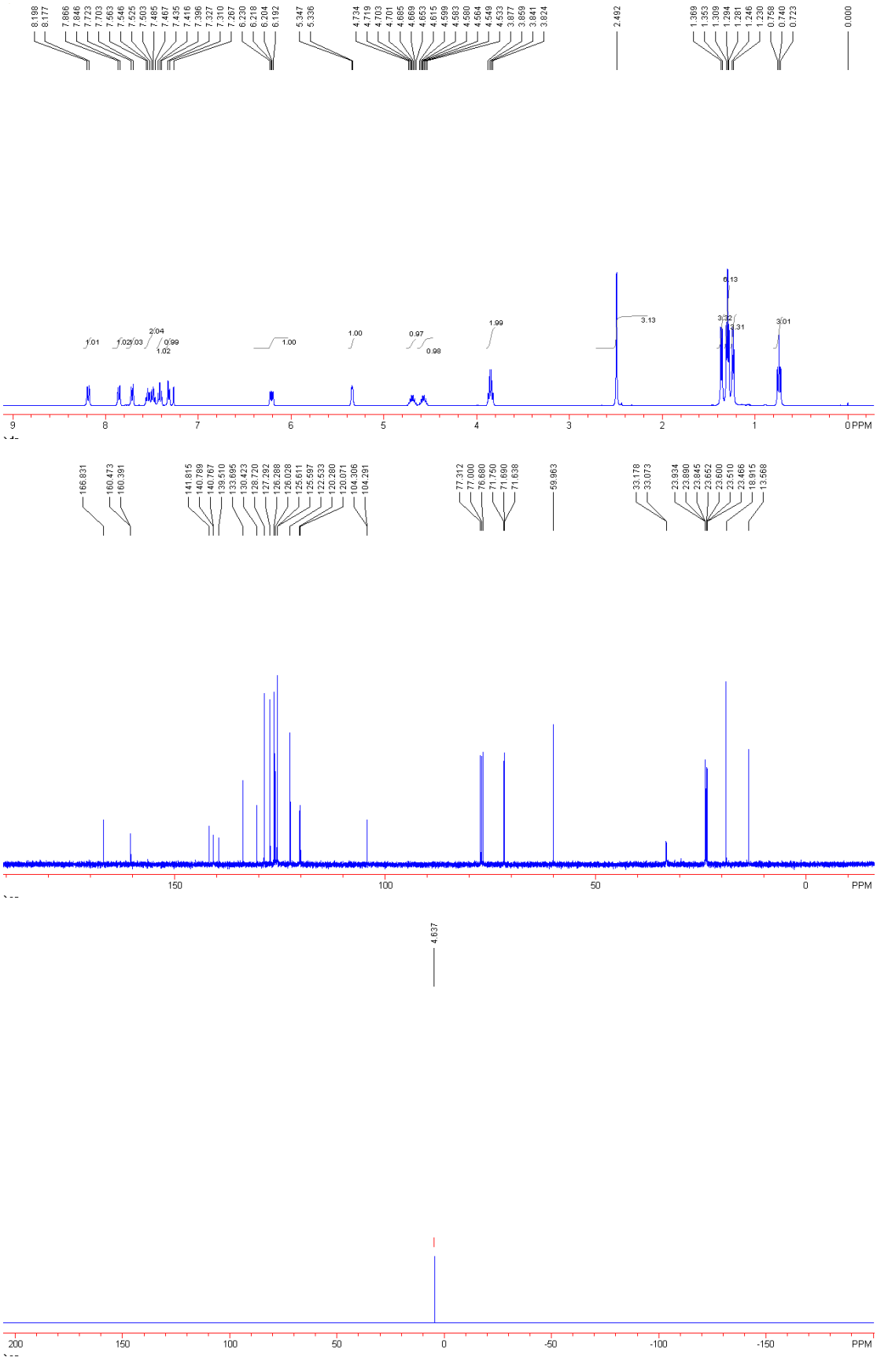
2-(6-(diisopropoxyphosphoryl)-4-(4-methoxyphenyl)-3,4-dihydro-2H-pyran-2-ylidene)acetate **4ha**: a slight yellow liquid (3.7 mg, 8%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.35 (d, *J* = 6.4 Hz, 3H), 1.36 (d, *J* = 6.4 Hz, 3H), 1.38 (d, *J* = 6.0 Hz, 6H), 3.11 (dd, *J* = 10.4 Hz, 4.8 Hz, 1H), 3.57-3.63 (m, 2H), 3.79 (s, 3H), 4.08-4.14 (m, 2H), 4.72-4.78 (m, 2H), 5.64 (s, 1H), 6.24 (dd, *J* = 10.4 Hz, 4.4 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.061; IR (CH_2Cl_2) ν 2968, 2902, 2839, 1713, 1657, 1513, 1474, 1447, 1375, 1172, 1109, 1046, 1016, 803, 738, 702 cm^{-1}; MS (ESI) *m/z* 439.3 ($M+H^+$); HRMS (ESI) Calcd. for $C_{22}H_{31}O_7PNa$ requires ($M+Na^+$): 461.1700, Found: 461.1694.







Ethyl 6-(diisopropoxyphosphoryl)-2-methyl-4-(naphthalen-1-yl)-4H-pyran-3-carboxylate **3ia**: a slight yellow liquid (36.2 mg, 79%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.74 (t, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 6.4 Hz, 3H), 1.29 (d, *J* = 5.2 Hz, 3H), 1.30 (d, *J* = 6.0 Hz, 3H), 1.36 (d, *J* = 6.4 Hz, 3H), 2.49 (s, 3H), 3.85 (q, *J* = 7.2 Hz, 2H), 4.53-4.62 (m, 1H), 4.65-4.73 (m, 1H), 5.34 (d, *J* = 4.8 Hz, 1H), 6.21 (dd, *J* = 10.4 Hz, 4.8 Hz, 1H), 7.32 (d, *J* = 6.8 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.47-7.56 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.6, 18.9, 23.5 (d, *J* = 4.4 Hz), 23.6 (d, *J* = 5.2 Hz), 23.87 (d, *J* = 4.4 Hz), 23.91 (d, *J* = 4.4 Hz), 33.1 (d, *J* = 10.5 Hz), 60.0, 71.66 (d, *J* = 5.2 Hz), 71.72 (d, *J* = 6.0 Hz), 104.3 (d, *J* = 1.5 Hz), 120.2 (d, *J* = 21.1 Hz), 122.5, 125.60, 125.61, 126.3, 127.3, 128.7, 130.4, 133.7, 139.5, 140.8 (d, *J* = 2.2 Hz), 141.8, 160.4 (d, *J* = 8.2 Hz), 166.8; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.637; IR (CH_2Cl_2) ν 3059, 2980, 2939, 1713, 1665, 1627, 1375, 1327, 1258, 1106, 984, 798, 776, 740, 702 cm^{-1}; MS (ESI) *m/z* 459.3 ($M+H^+$); HRMS (ESI) Calcd. for $C_{25}H_{31}O_6PNa$ requires ($M+Na^+$): 481.1751, Found: 481.1760.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4.719
4.703
4.701
4.685
4.669
4.653
4.615
4.599
4.583
4.580
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4.549
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3.877
3.859
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3.824
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1.353
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1.294
1.281
1.246
1.230
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0.723
0.000
1.01
1.02
1.03
2.04
0.99
1.02
1.00
1.00
0.97
0.98
1.99
3.13
6.13
3.32
3.31
3.01
9
8
7
6
5
4
3
2
1
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23.600
23.510
23.466
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PPM
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100
50
0
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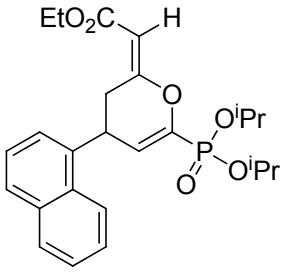
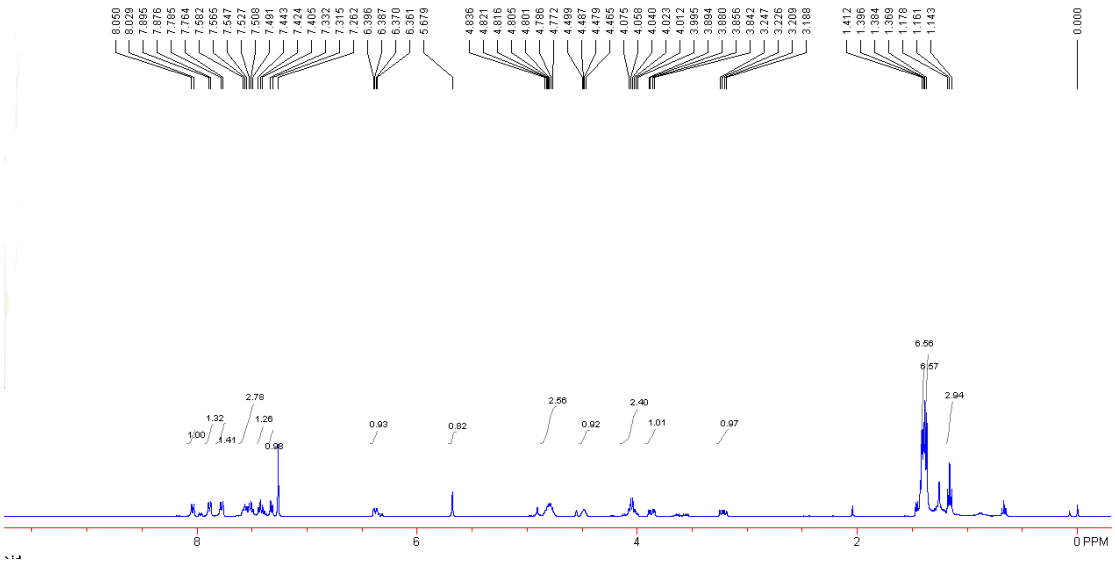
-100
-150
PPM

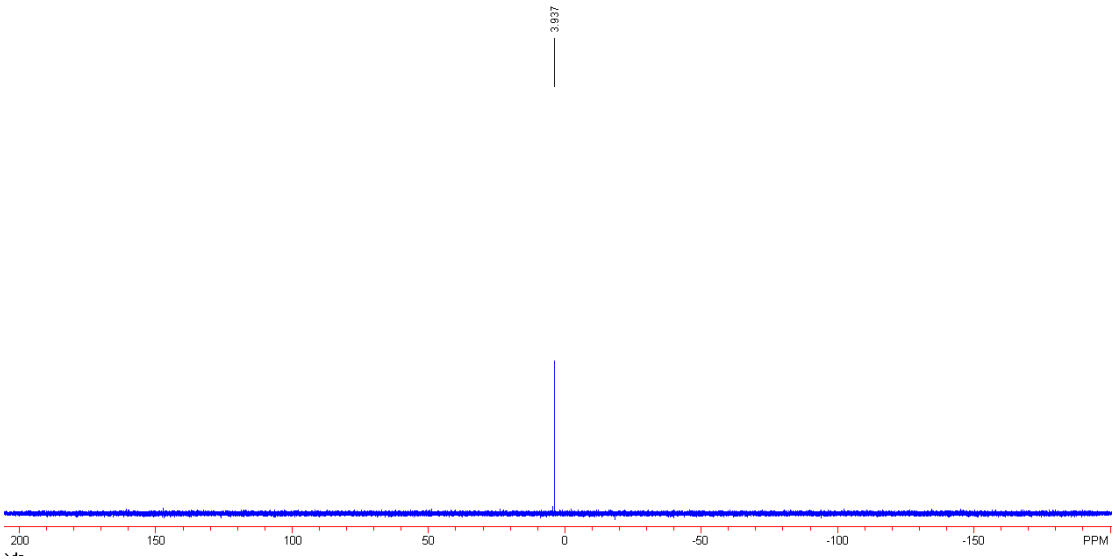


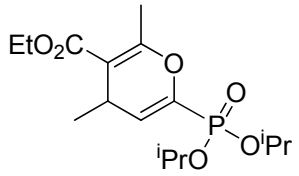
(*E*)-Ethyl

2-(6-(diisopropoxyphosphoryl)-4-(naphthalen-1-yl)-3,4-dihydro-2H-pyran-2-ylidene)acetate

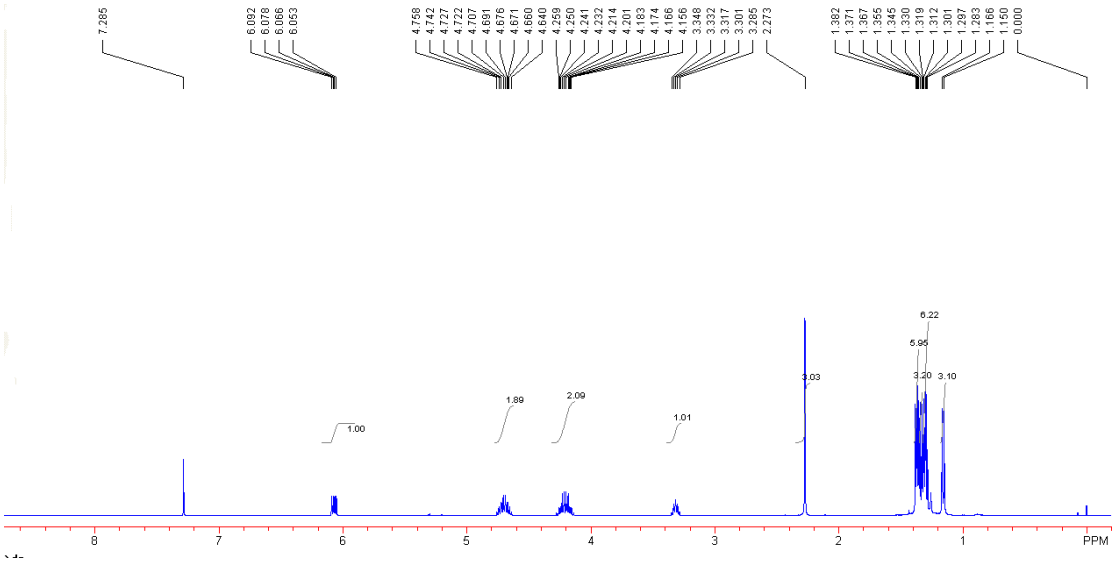
4ia: a slight yellow liquid (2.6 mg, 6%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.16 (t, *J* = 7.2 Hz, 3H), 1.38 (d, *J* = 6.0 Hz, 6H), 1.40 (d, *J* = 6.0 Hz, 6H), 3.22 (dd, *J* = 15.2 Hz, 8.4 Hz, 1H), 3.87 (dd, *J* = 15.2 Hz, 5.6 Hz, 1H), 4.00-4.08 (m, 2H), 4.47-4.50 (m, 1H), 4.77-4.84 (m, 2H), 5.68 (s, 1H), 6.38 (dd, *J* = 10.4 Hz, 3.6 Hz, 1H), 7.32 (d, *J* = 6.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.49-7.58 (m, 2H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 3.937; IR (CH_2Cl_2) ν 2981, 2901, 1712, 1657, 1474, 1374, 1261, 1175, 1116, 1046, 1013, 88, 801, 739 cm^{-1}; MS (ESI) *m/z* 459.3 ($M+H^+$); HRMS (ESI) Calcd. for $C_{25}H_{31}O_6PNa$ requires ($M+Na^+$): 481.1751, Found: 481.1743.







Ethyl 6-(diisopropoxyphosphoryl)-2,4-dimethyl-4H-pyran-3-carboxylate **3ja**: a slight yellow liquid (20.8 mg, 60%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.16 (d, J = 6.4 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.30 (d, J = 6.0 Hz, 3H), 1.34 (d, J = 6.0 Hz, 3H), 1.36 (d, J = 6.0 Hz, 3H), 1.38 (d, J = 6.0 Hz, 3H), 2.27 (s, 3H), 3.29-3.35 (m, 1H), 4.16-4.26 (m, 2H), 4.64-4.76 (m, 2H), 6.07 (dd, J = 10.0 Hz, 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.2, 19.1, 23.4 (d, J = 2.7 Hz), 23.6 (d, J = 4.5 Hz), 24.0 (d, J = 3.8 Hz), 26.7 (d, J = 10.2 Hz), 60.1, 71.6 (d, J = 5.3 Hz), 71.7 (d, J = 5.3 Hz), 106.4, 122.6 (d, J = 20.1 Hz), 140.5, 142.8, 160.0 (d, J = 8.4 Hz), 167.3; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.672; IR (CH_2Cl_2) ν 2980, 2937, 2905, 2874, 1713, 1665, 1625, 1375, 1259, 1163, 1056, 989, 945, 801, 662, 611 cm^{-1}; MS (ESI) *m/z* 347.2 ($M+H^+$); HRMS (ESI) Calcd. for $C_{16}H_{27}O_6PNa$ requires ($M+Na^+$): 369.1438, Found: 369.1439.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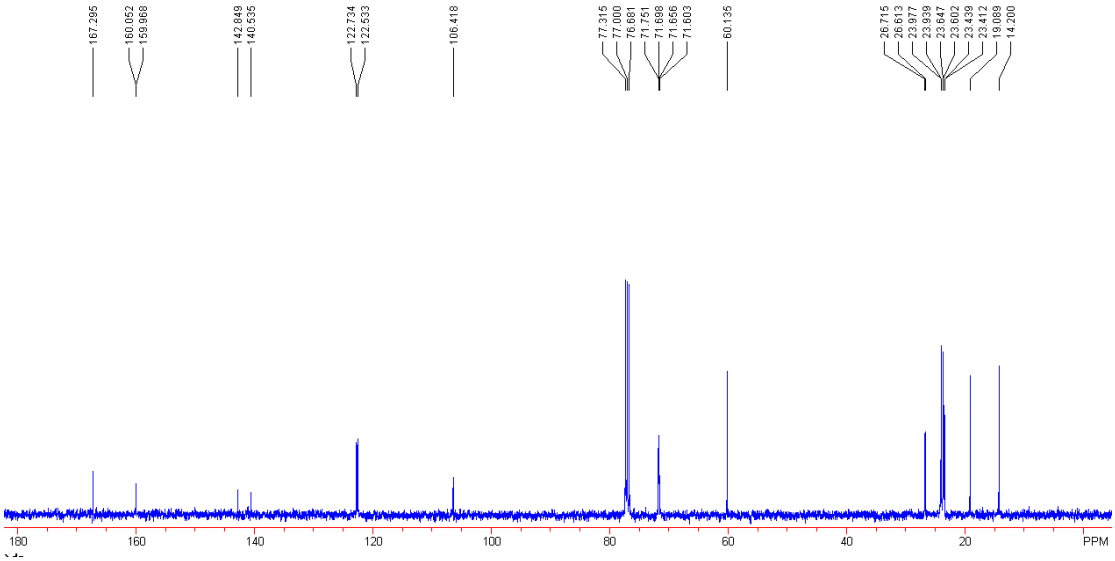
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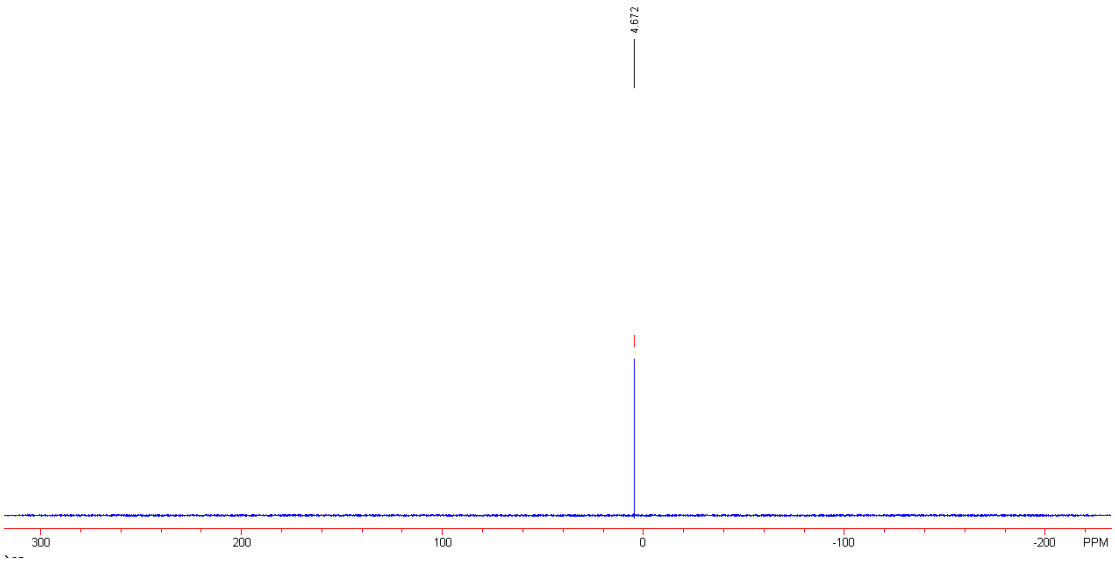
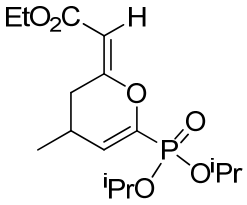
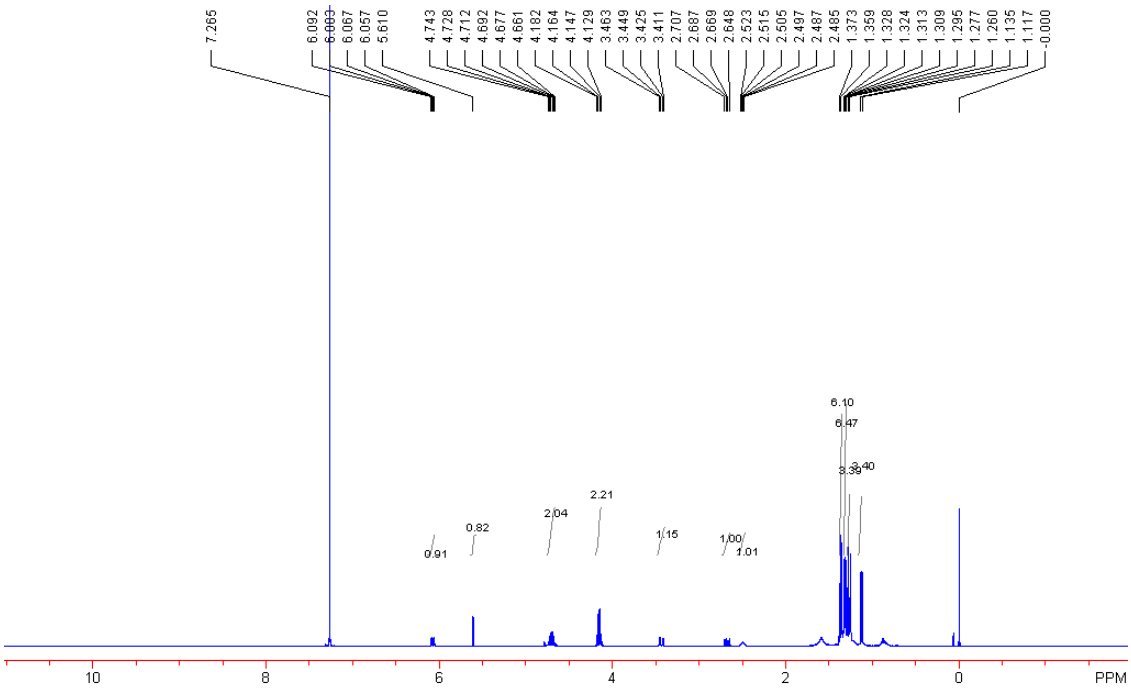
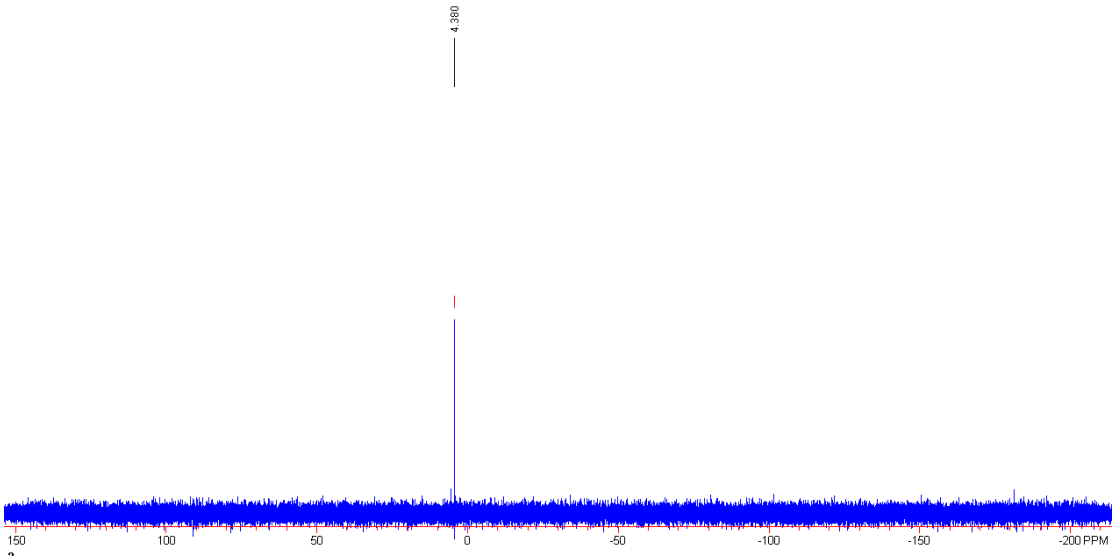
PPM


4.672
PPM



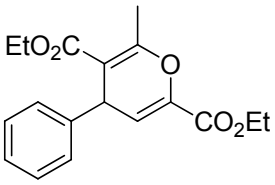
(*E*)-Ethyl 2-(6-(diisopropoxyphosphoryl)-4-methyl-3,4-dihydro-2H-pyran-2-ylidene)acetate **4ja**: a slight yellow liquid (5.2 mg, 15%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.13 (d, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.32 (d, *J* = 6.4 Hz, 3H), 1.33 (d, *J* = 6.4 Hz, 3H), 1.37 (d, *J* = 5.6 Hz, 6H), 2.45-2.92 (m, 1H), 2.68 (dd, *J* = 14.8 Hz, 8.4 Hz, 1H), 3.44 (dd, *J* = 14.8 Hz, 5.6 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.66-4.74 (m, 2H), 5.61 (s, 1H), 6.08 (dd, *J* = 10.4 Hz, 4.0 Hz, 1H); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.380; IR (CH_2Cl_2) ν 2978, 2906, 1713, 1657, 1375, 1351, 1261, 1114, 1048, 1014, 803, 739, 703 cm^{-1}; MS (ESI) *m/z* 347.2 ($M+H^+$); HRMS (ESI) Calcd. for $C_{16}H_{27}O_6PNa$ requires ($M+Na^+$): 369.1438, Found: 369.1421.



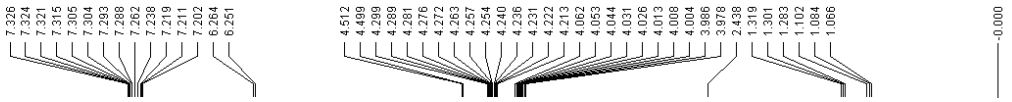


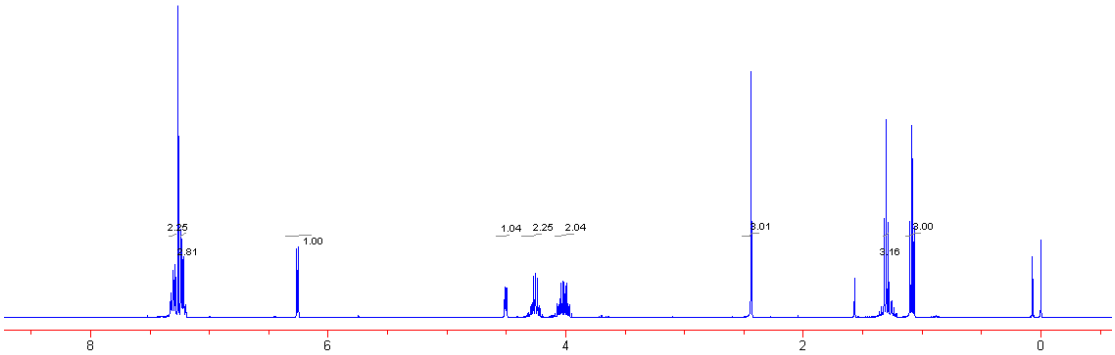
General Procedure for the Preparation of 6 and 7 from the Reaction of 5a with 2a Using 6aa and 7aa as an Example in the Presence of DABCO

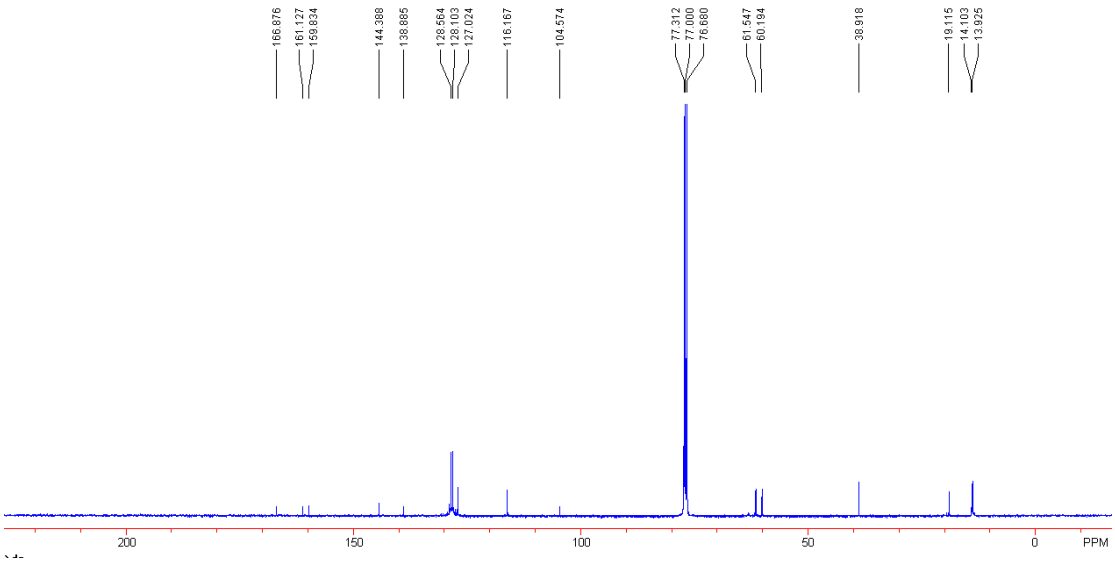
To a mixture of **1a** (0.10 mmol, 20.4 mg**)**, **2a** (0.12 mmol, 13.6 μL) and DABCO (2.2 mg, 0.02 mmol) was added 3.0 mL of THF at -10 ^{o}C. The reaction solution was monitored by TLC .After the reaction complete, the solution was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc/PE = 1/6) to give the target product **6aa** and **7aa.**

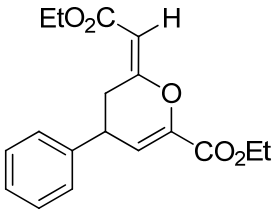


Diethyl 6-methyl-4-phenyl-4H-pyran-2,5-dicarboxylate **6aa**: a slight yellow liquid (2.7 mg, 7%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.08 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 2.44 (s, 3H), 3.99-4.06 (m, 2H), 4.21-4.30 (m, 2H), 4.51 (d, *J* = 5.2 Hz, 1H), 6.26 (d, *J* = 5.2 Hz, 1H), 7.20-7.24 (m, 3H), 7.29-7.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 14.1, 19.1, 38.9, 60.2, 61.5, 104.6, 116.2, 127.0, 128.1, 128.6, 138.9, 144.4, 159.8, 161.1, 166.9; IR (CH_2Cl_2) ν 2980, 2903, 1736, 1714, 1658, 1448, 1374, 1260, 1118, 1018, 860, 802, 761, 739, 700 cm^{-1}; MS (ESI) *m/z* 317.2 (M+H^{+}); HRMS (ESI) Calcd. for $C_{18}H_{20}O_5Na$ requires (M+Na^{+}): 339.1203, Found: 339.1206.

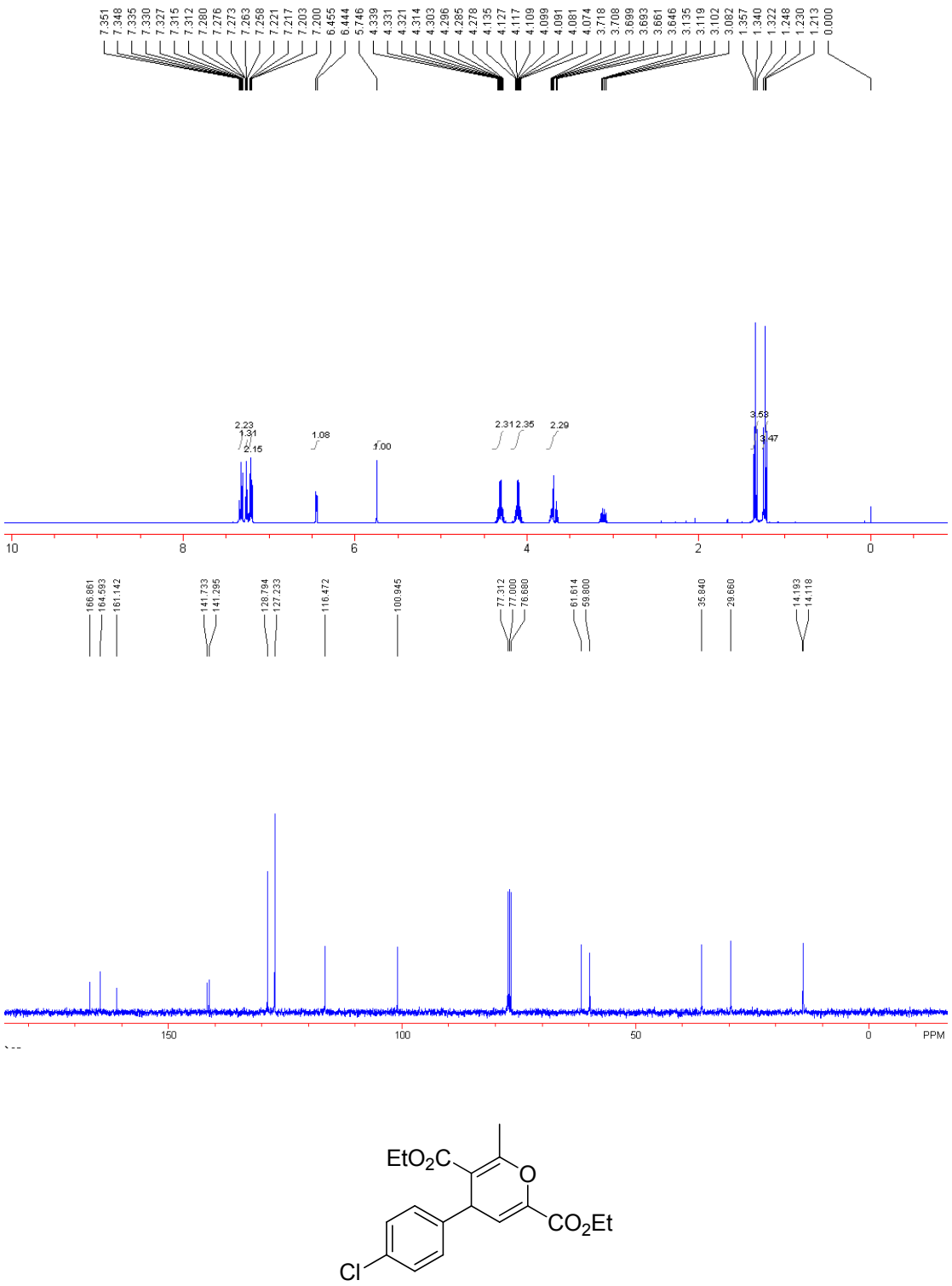






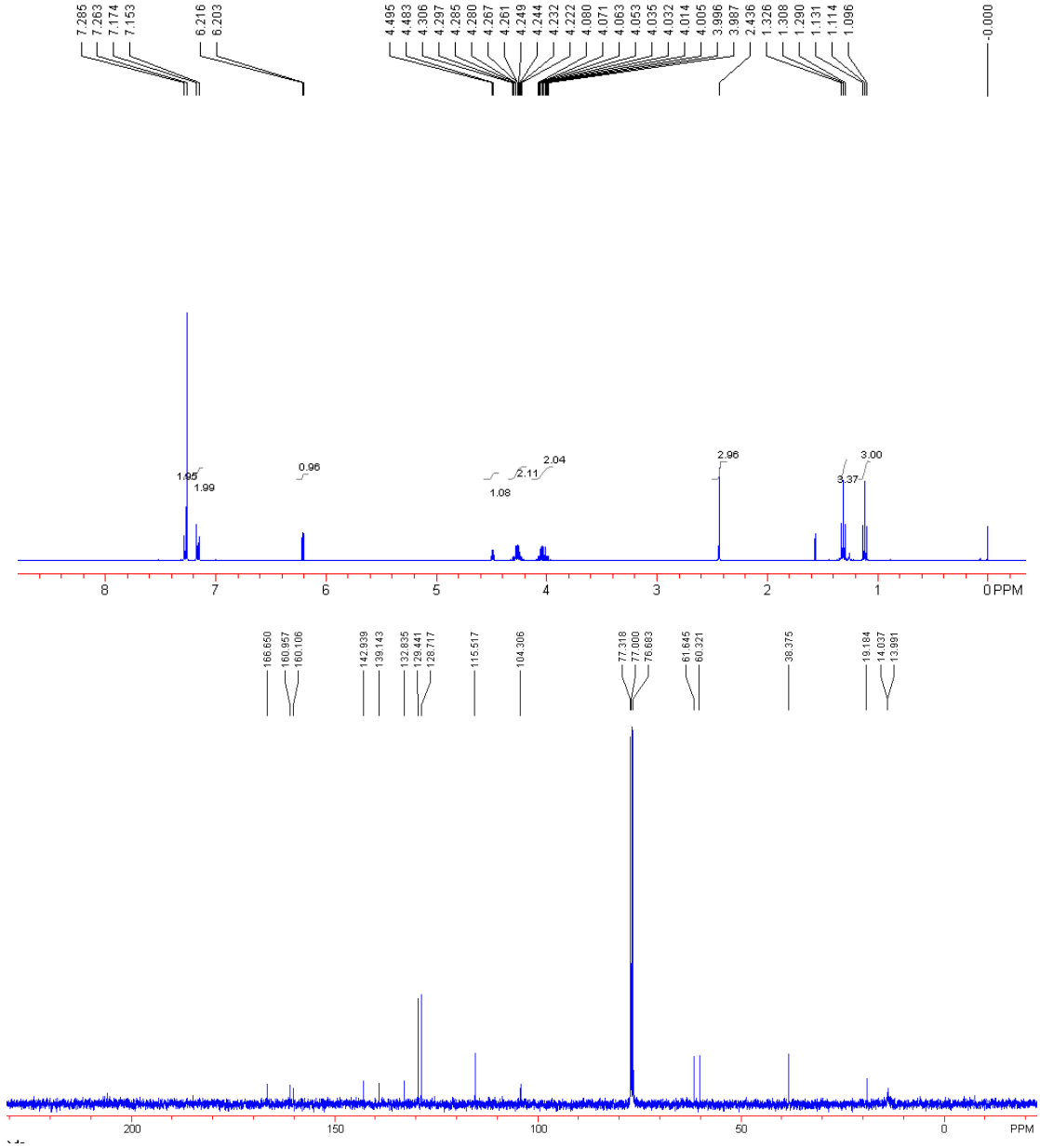


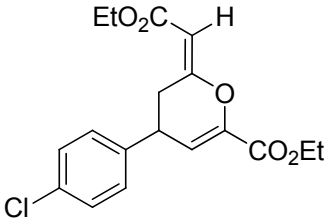
(*E*)-Ethyl 2-(2-ethoxy-2-oxoethylidene)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate **7aa**: a slight yellow liquid (30.0 mg, 95%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (t, *J* = 7.2 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 3.11 (dd, *J* = 8.0 Hz, 4.8 Hz, 1H), 3.68-3.72 (m, 2H), 4.07-4.14 (m, 2H), 4.28-4.34 (m, 2H), 5.75 (s, 1H), 6.45 (d, *J* = 4.8 Hz, 1H), 7.20-7.22 (m, 2H), 7.26-7.28 (m, 1H), 7.31-7.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 14.2, 29.7, 35.8, 59.8, 61.6, 101.0, 116.5, 127.2, 128.8, 141.3, 141.7, 161.1, 164.6, 166.9; IR (CH_2Cl_2) ν 2981, 2903, 2875, 1736, 1711, 1660, 1493, 1373, 1258, 1170, 1118, 1046, 1015, 821, 760 cm^{-1}; MS (ESI) *m/z* 317.2 ($M+H^+$). HRMS (ESI) Calcd. for $C_{18}H_{20}O_5$ requires ($M+Na^+$): 339.1203, Found: 339.1206.



Diethyl 4-(4-chlorophenyl)-6-methyl-4H-pyran-2,5-dicarboxylate **6ba**: a slight yellow liquid (2.0 mg, 6%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, J = 7.2 Hz, 3H), 1.31 (t, J = 7.2 Hz, 3H), 2.44 (s, 3H), 4.00-4.08 (m, 2H), 4.22-4.31 (m, 2H), 4.49 (d, J = 4.8 Hz, 1H), 6.21 (d, J = 4.8 Hz, 1H), 7.16 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.00, 14.04, 19.2, 38.4, 60.3, 61.6, 104.3, 115.5, 128.7, 129.4, 132.8, 139.1, 142.9,

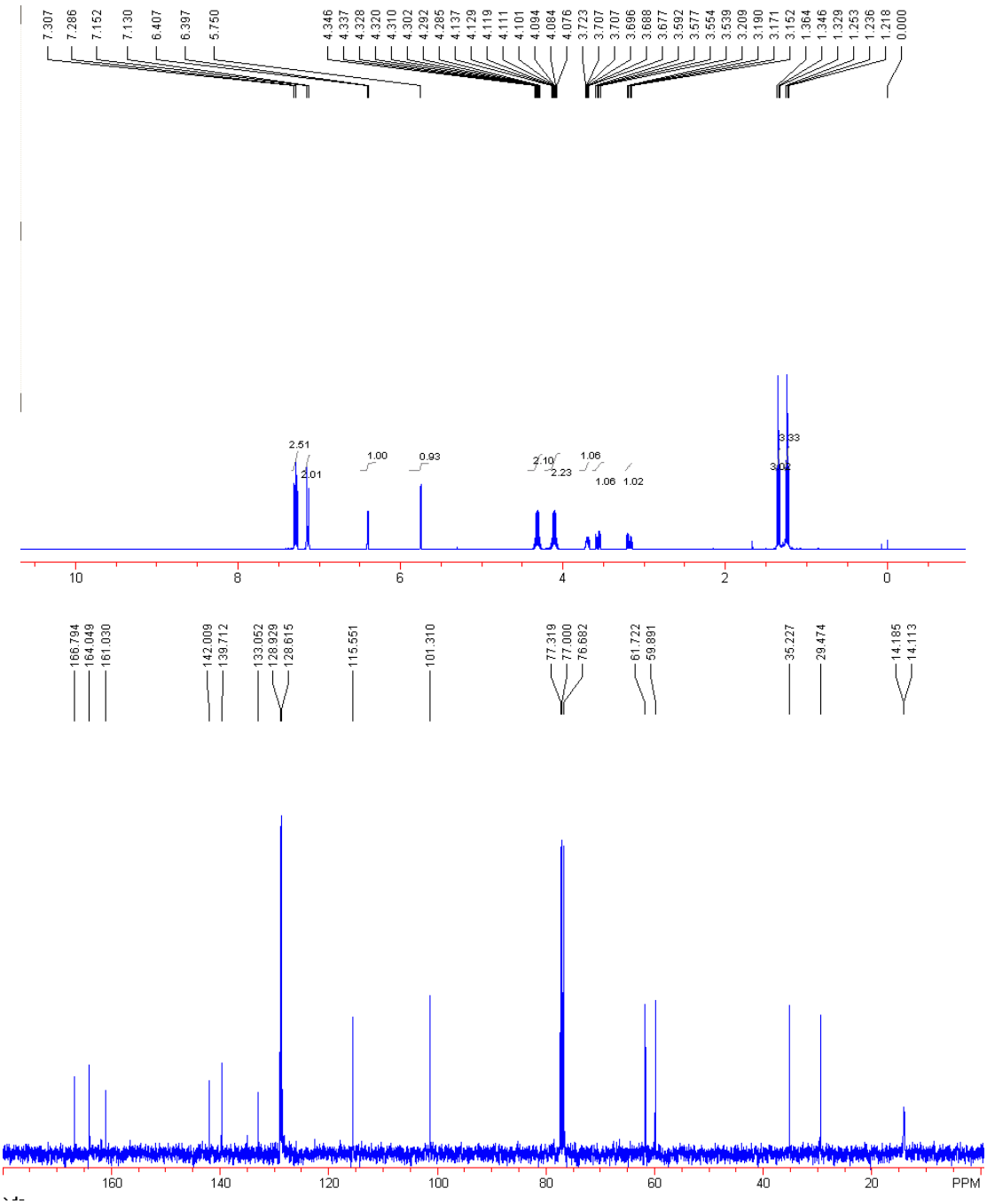
160.1, 161.0, 166.7; IR (CH_2Cl_2) ν 2981, 2904, 1739, 1715, 1629, 1488, 1372, 1327, 1268, 1106, 1049, 1015, 946, 805, 739 cm^{-1}; MS (ESI) *m/z* 373.2 ($M+Na^+$); HRMS (ESI) Calcd. for $C_{18}H_{19}ClNaO_5$ requires ($M+Na^+$): 373.0816, Found: 373.0813.

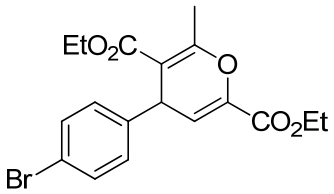




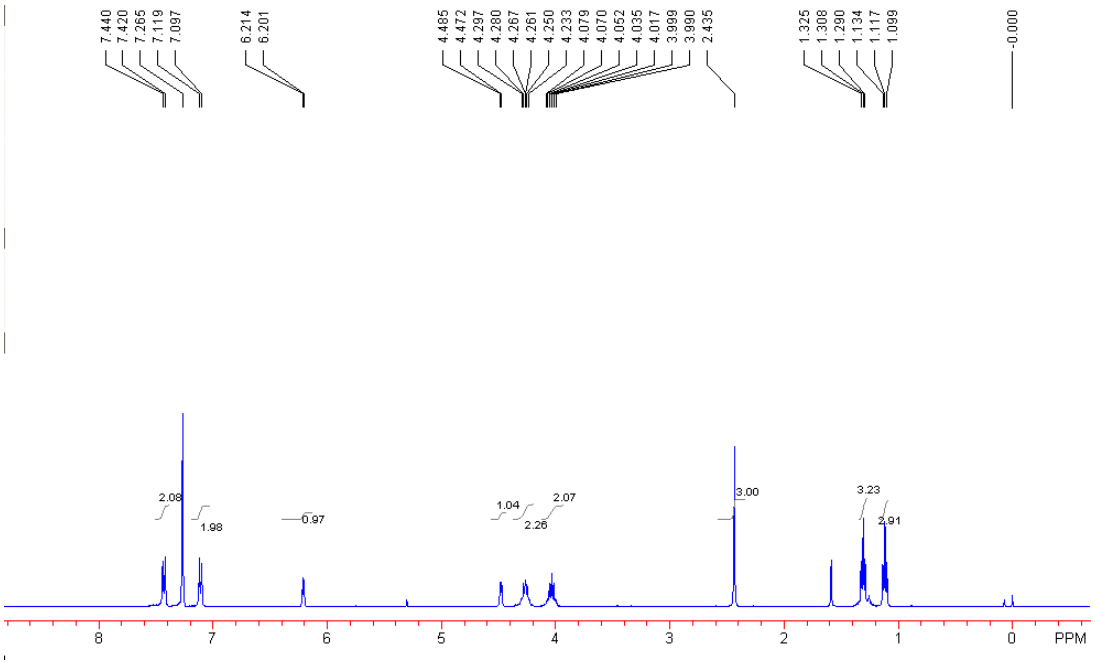
(*E*)-Ethyl 4-(4-chlorophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-carboxylate **7ba**: a

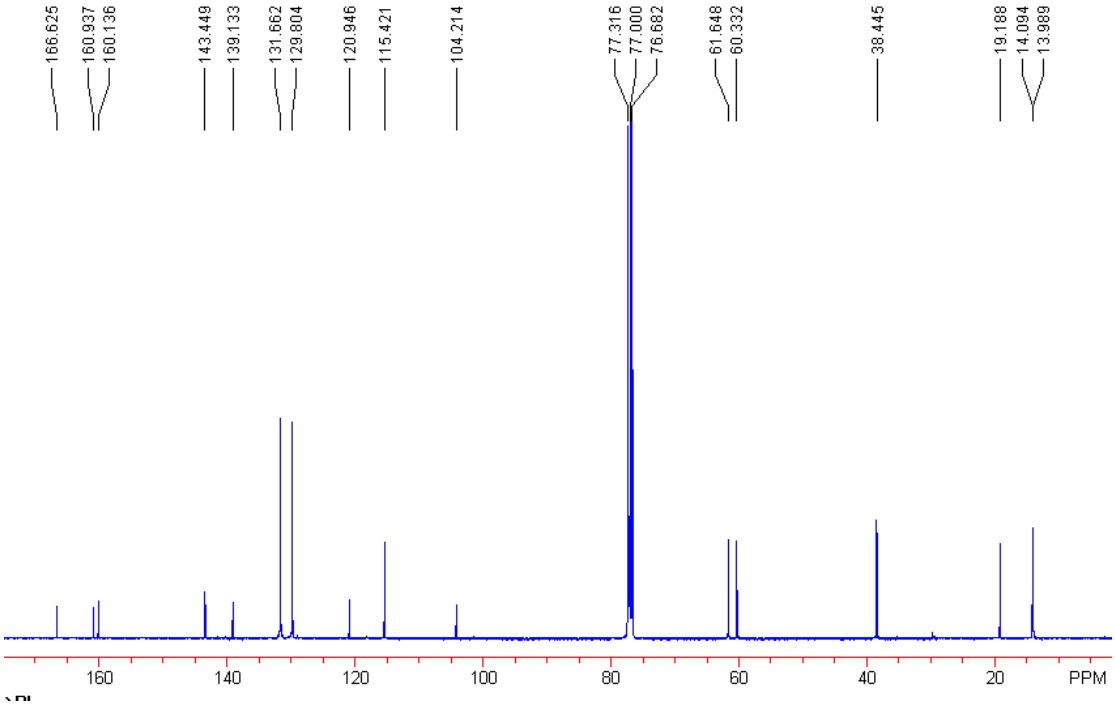
slight yellow liquid (28.1 mg, 80%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 3.18 (dd, *J* = 15.2 Hz, 7.6 Hz, 1H), 3.57 (dd, *J* = 15.2 Hz, 6.0 Hz, 1H), 3.68-3.72 (m, 1H), 4.08-4.14 (m, 2H), 4.29-4.35 (m, 2H), 5.75 (s, 1H), 6.40 (d, *J* = 4.0 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 14.2, 29.5, 35.2, 59.9, 61.7, 101.3, 115.6, 128.6, 128.9, 133.1, 139.7, 142.0, 161.0, 164.0, 166.8; IR (CH_2Cl_2) ν 2981, 2903, 2875, 1736, 1711, 1660, 1493, 1373, 1258, 1170, 1118, 1046, 1015, 821, 760 cm^{-1}; MS (ESI) *m/z* 373.2 ($M+Na^+$); HRMS (ESI) Calcd. for $C_{18}H_{19}ClO_5$ requires ($M+Na^+$): 373.0813, Found: 373.0821.

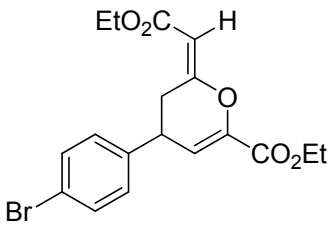




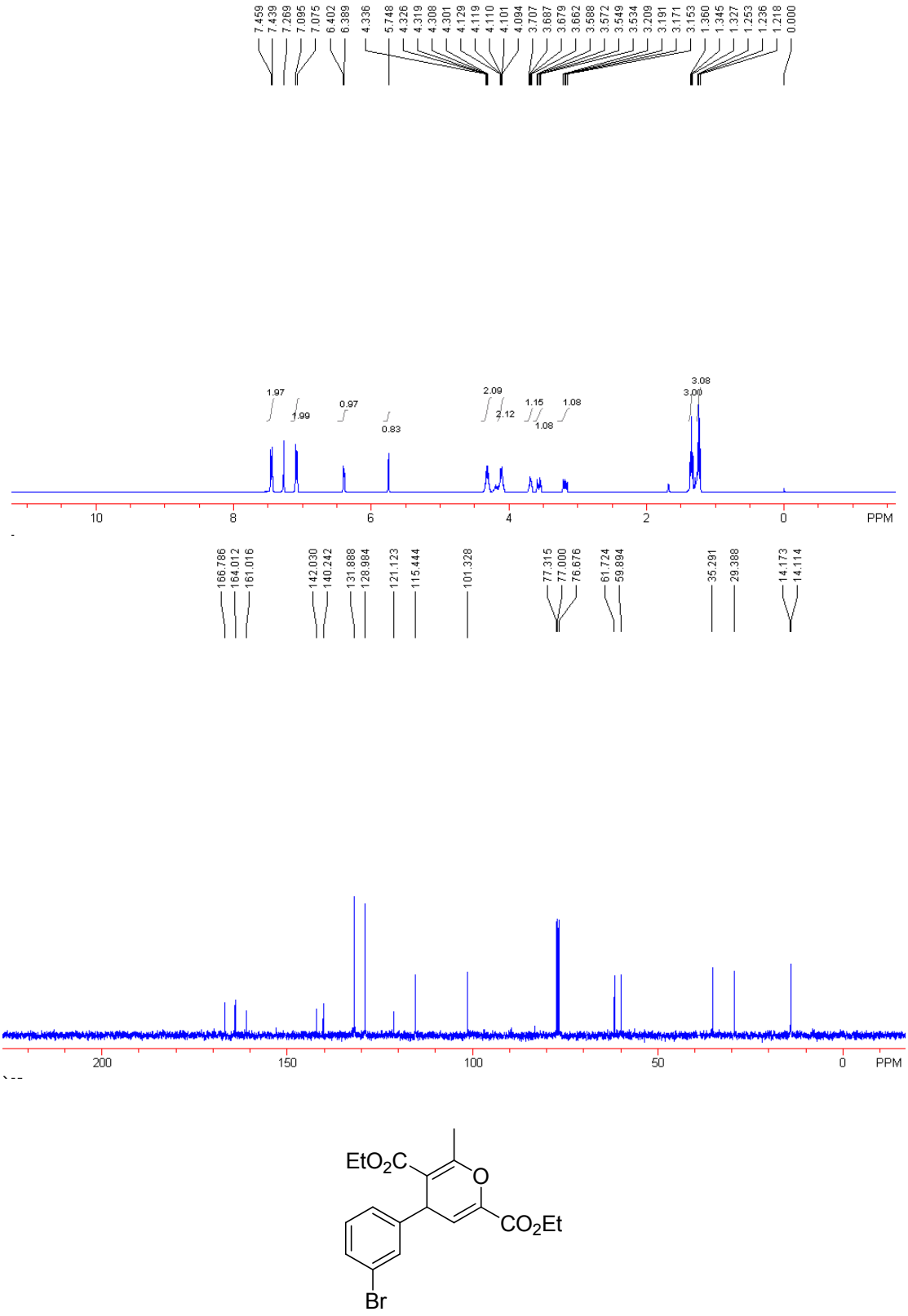
Diethyl 4-(4-bromophenyl)-6-methyl-4H-pyran-2,5-dicarboxylate **6ca**: a slight yellow liquid (3.1 mg, 8%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (t, J = 7.2 Hz, 3H), 1.31 (t, J = 7.2 Hz, 3H), 2.44 (s, 3H), 3.99-4.08 (m, 2H), 4.23-4.30 (m, 2H), 4.48 (d, J = 5.2 Hz, 1H), 6.21 (d, J = 5.2 Hz, 1H), 7.11 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 14.1, 19.2, 38.4, 60.3, 61.6, 104.2, 115.4, 120.9, 129.8, 131.7, 139.1, 143.4, 160.1, 160.9, 166.6; IR (CH_2Cl_2) ν 2979, 2902, 1716, 1660, 1373, 1263, 1173, 1107, 1048, 1013, 803, 762, 738, 703 cm^{-1}; MS (ESI) *m/z* 395.2 (M+H$^+$); HRMS (ESI) Calcd. for $C_{18}H_{19}BrO_5Na$ requires (M+Na$^+$): 417.0308, Found: 417.0320.





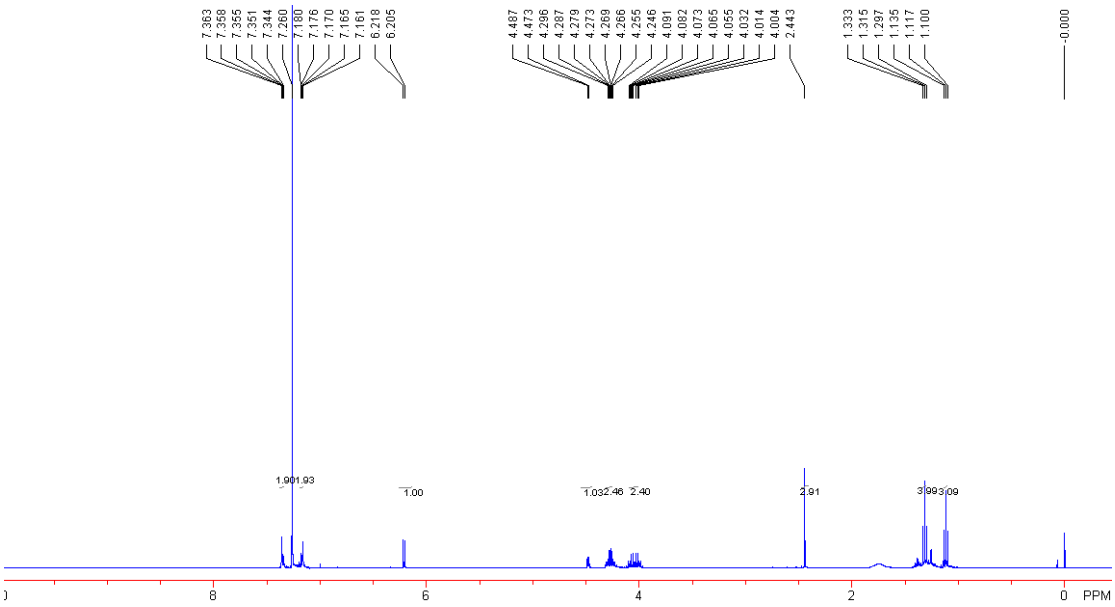


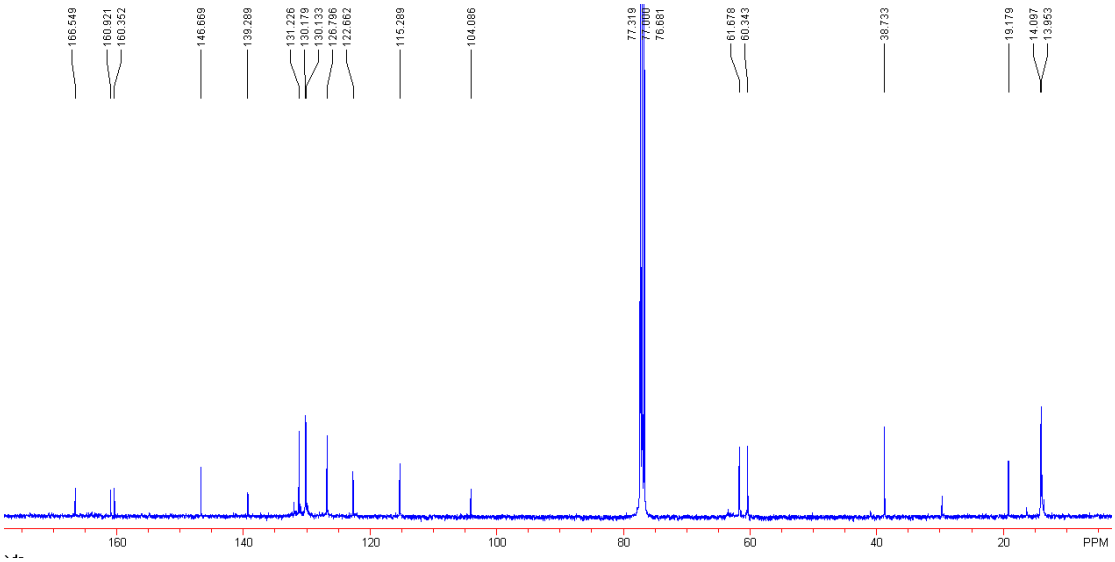
(*E*)-Ethyl 4-(4-bromophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-carboxylate **7ca**: a slight yellow liquid (31.2 mg, 80%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 3.18 (dd, *J* = 15.2 Hz, 7.2 Hz, 1H), 3.56 (dd, *J* = 15.2 Hz, 6.4 Hz, 1H), 3.66-3.71 (m, 1H), 4.09-4.13 (m, 2H), 4.30-4.34 (m, 2H), 5.75 (s, 1H), 6.40 (d, *J* = 5.2 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 14.2, 29.4, 35.3, 59.9, 61.7, 101.3, 115.4, 121.1, 129.0, 131.9, 140.2, 142.0, 161.0, 164.0, 166.8; IR (CH_2Cl_2) ν 3084, 2982, 2904, 1736, 1711, 1659, 1489, 1394, 1300, 1167, 1117, 1011, 859, 818, 760 cm^{-1}; MS (ESI) *m/z* 417.2 ($M+Na^+$); HRMS (ESI) Calcd. for $C_{18}H_{19}BrO_5Na$ requires ($M+Na^+$): 417.0308, Found: 417.0315.

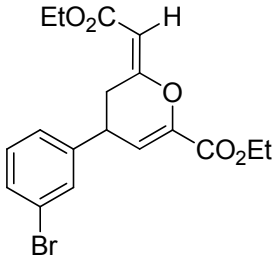


Diethyl 4-(3-bromophenyl)-6-methyl-4H-pyran-2,5-dicarboxylate **6da**: a slight yellow liquid (3.6 mg, 9%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H), 2.44 (s, 3H), 4.00-4.09 (m, 2H), 4.25-4.30 (m, 2H), 4.48 (d, J = 5.2 Hz, 1H), 6.21 (d, J = 5.2 Hz, 1H), 7.16-7.18 (m, 2H), 7.34-7.26 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0,

14.1, 19.2, 38.7, 60.3, 61.7, 104.1, 115.3, 122.7, 126.8, 130.1, 130.2, 131.2, 139.3, 146.7, 160.4, 160.9, 166.5; IR (CH_2Cl_2) ν 3058, 2980, 2873, 1714, 1627, 1590, 1472, 1328, 1267, 1096, 964, 839, 764, 739, 696 cm^{-1}; MS (ESI) *m/z* 395.2 ($M+H^+$); HRMS (ESI) Calcd. for $C_{18}H_{19}BrO_5Na$ requires ($M+Na^+$): 417.0308, Found: 417.0315.

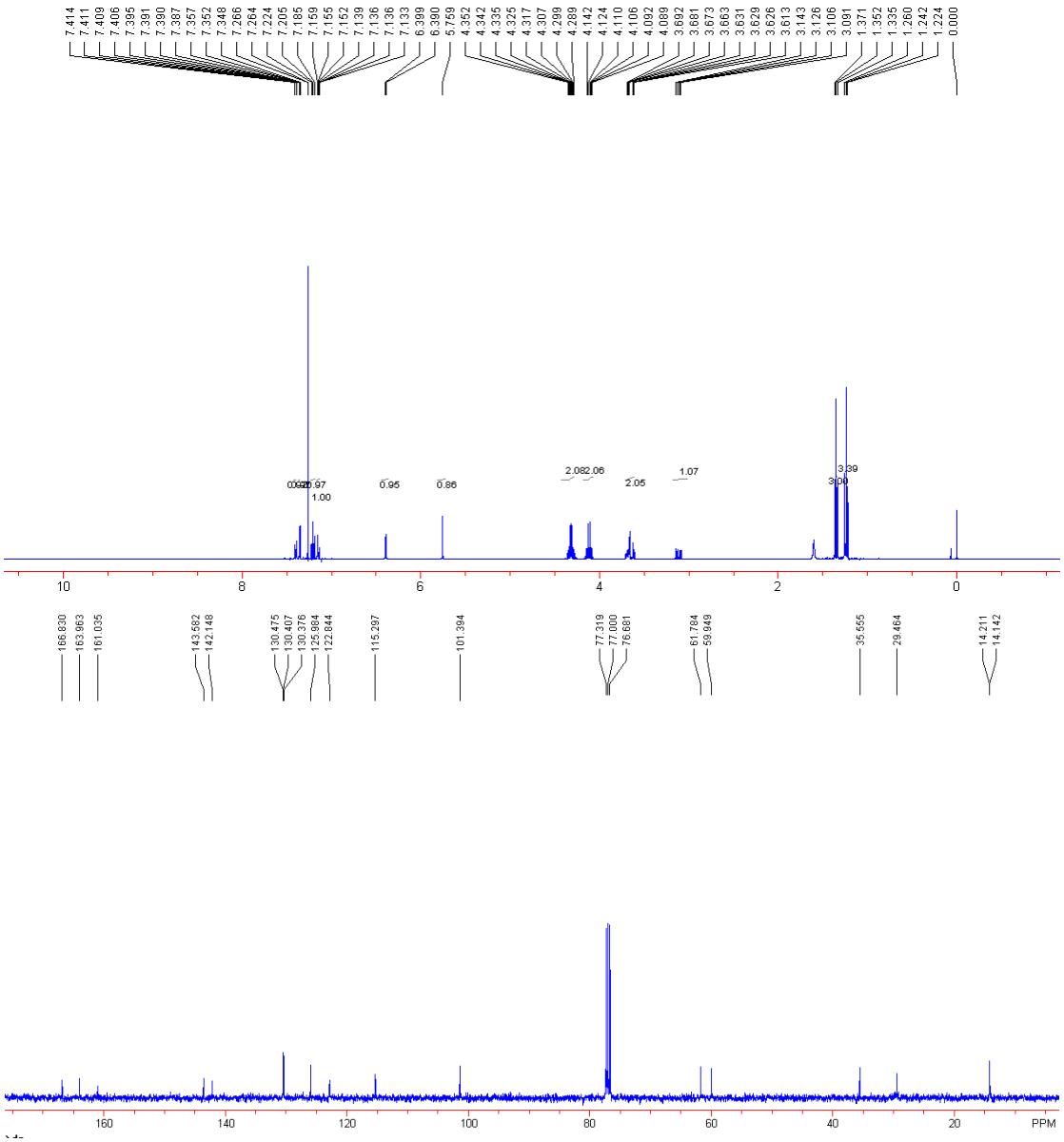


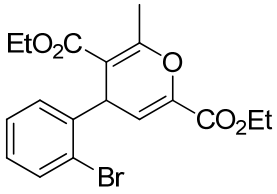




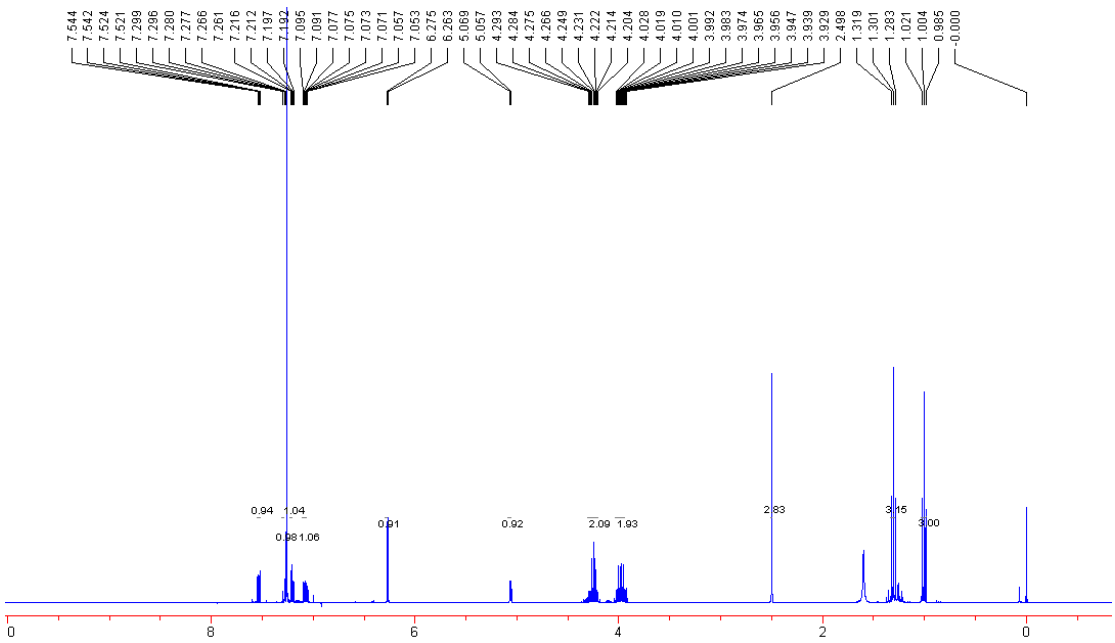
(*E*)-Ethyl

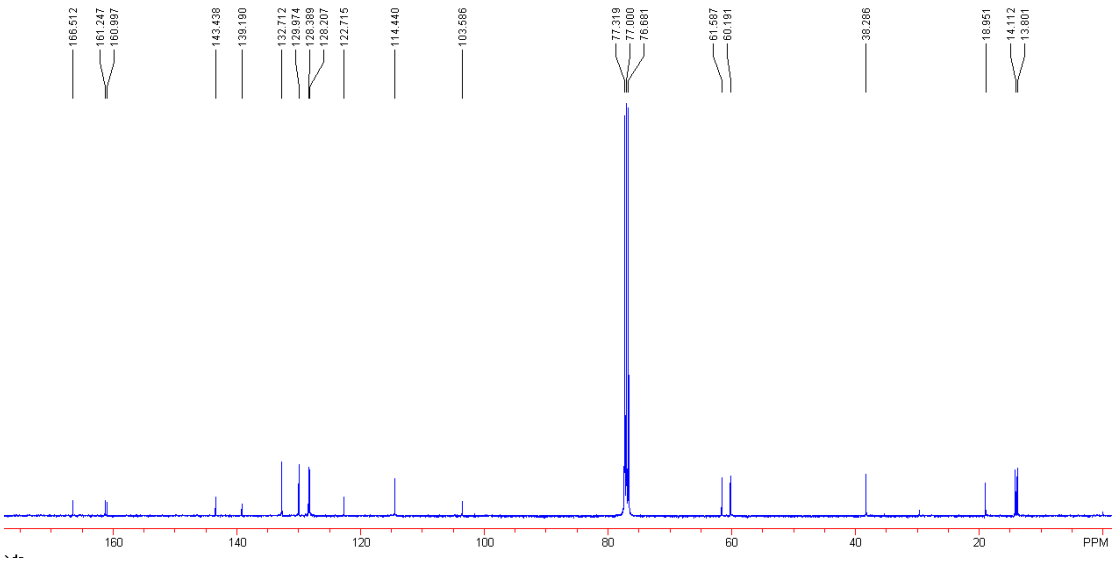
4-(3-bromophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-carboxylate **7da**: a slight yellow liquid (29.2 mg, 74%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 3.12 (dd, *J* = 14.8 Hz, 6.8 Hz, 1H), 3.61-3.69 (m, 2H), 4.09-4.14 (m, 2H), 4.29-4.35 (m, 2H), 5.76 (s, 1H), 6.39 (d, *J* = 3.6 Hz, 1H), 7.13-7.16 (m, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.35 (s, 1H), 7.39-7.41 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 14.2, 29.5, 35.6, 59.9, 61.8, 101.4, 115.3, 122.8, 126.0, 130.38, 130.41, 130.5, 142.1, 143.6, 161.0, 164.0, 166.8; IR (CH_2Cl_2) ν 3082, 2981, 2903, 2873, 1710, 1658, 1593, 1475, 1393, 1349, 1256, 1111, 1045, 1021, 855, 790, 676 cm^{-1}; MS (ESI) *m/z* 419.1 (M+Na^{+}); HRMS (ESI) Calcd. for $C_{18}H_{19}BrO_5Na$ requires (M+Na^{+}): 417.0308, Found: 417.0307.

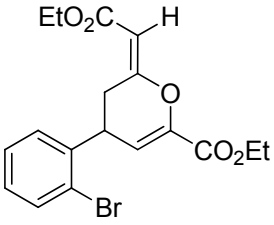




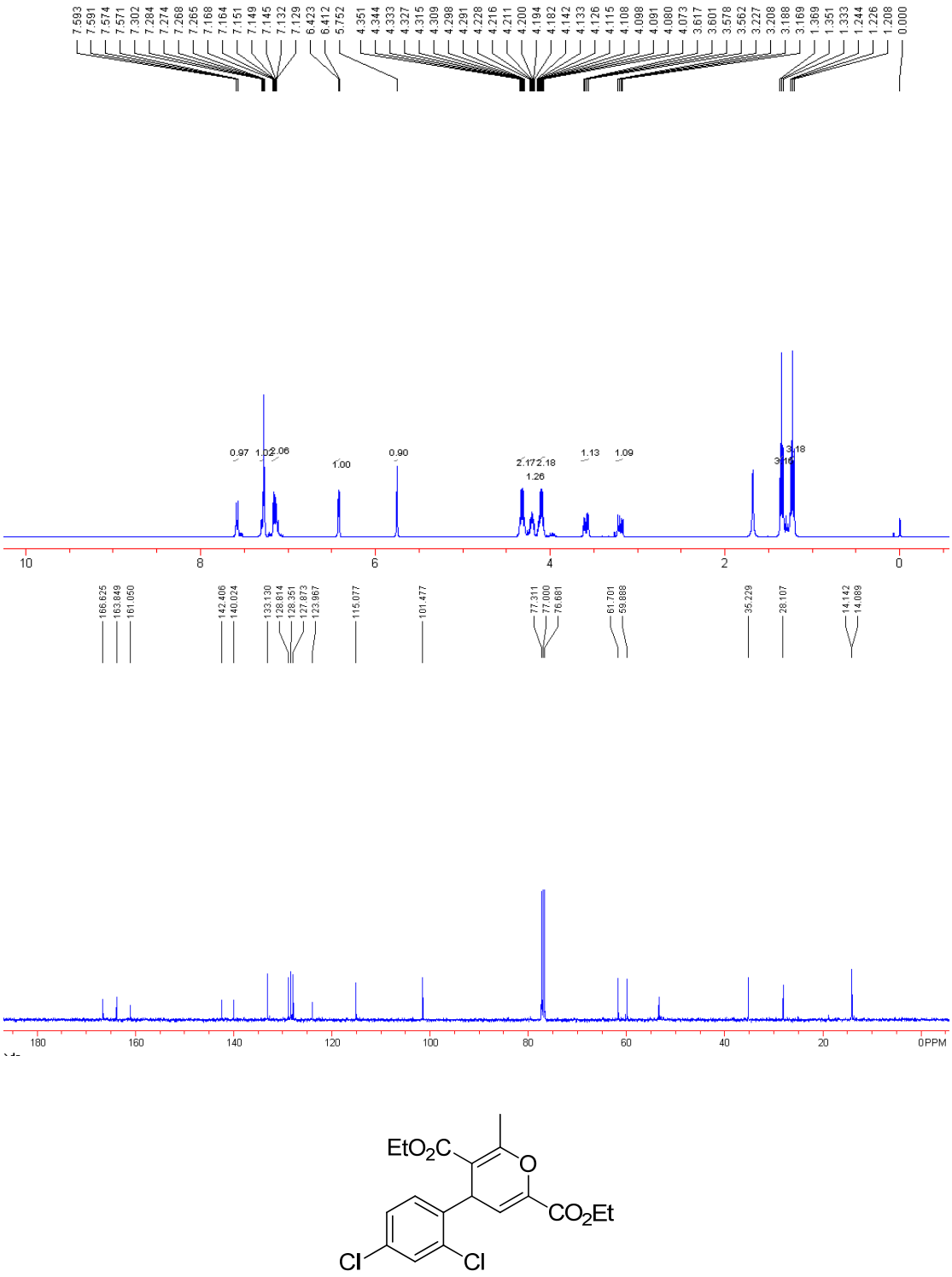
Diethyl 4-(2-bromophenyl)-6-methyl-4H-pyran-2,5-dicarboxylate **6ea**: a white solid (3.7 mg, 9%); m.p. 122-124 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.00 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 2.50 (s, 3H), 3.93-4.03 (m, 2H), 4.20-4.29 (m, 2H), 5.06 (d, *J* = 4.8 Hz, 1H), 6.27 (d, *J* = 4.8 Hz, 1H), 7.05-7.10 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.27-7.30 (m, 1H), 7.53 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 14.1, 19.0, 38.3, 60.2, 61.6, 103.6, 114.4, 122.7, 128.2, 128.4, 130.0, 132.7, 139.2, 143.4, 161.0, 161.2, 166.5; IR (CH_2Cl_2) ν 3058, 2980, 2873, 1714, 1627, 1590, 1472, 1328, 1267, 1096, 964, 839, 764, 739, 696 cm^{-1}; MS (ESI) *m/z* 395.2 (M+H$^+$); HRMS (ESI) Calcd. for $C_{18}H_{19}BrO_5Na$ requires (M+Na$^+$): 417.0308, Found: 417.0315.





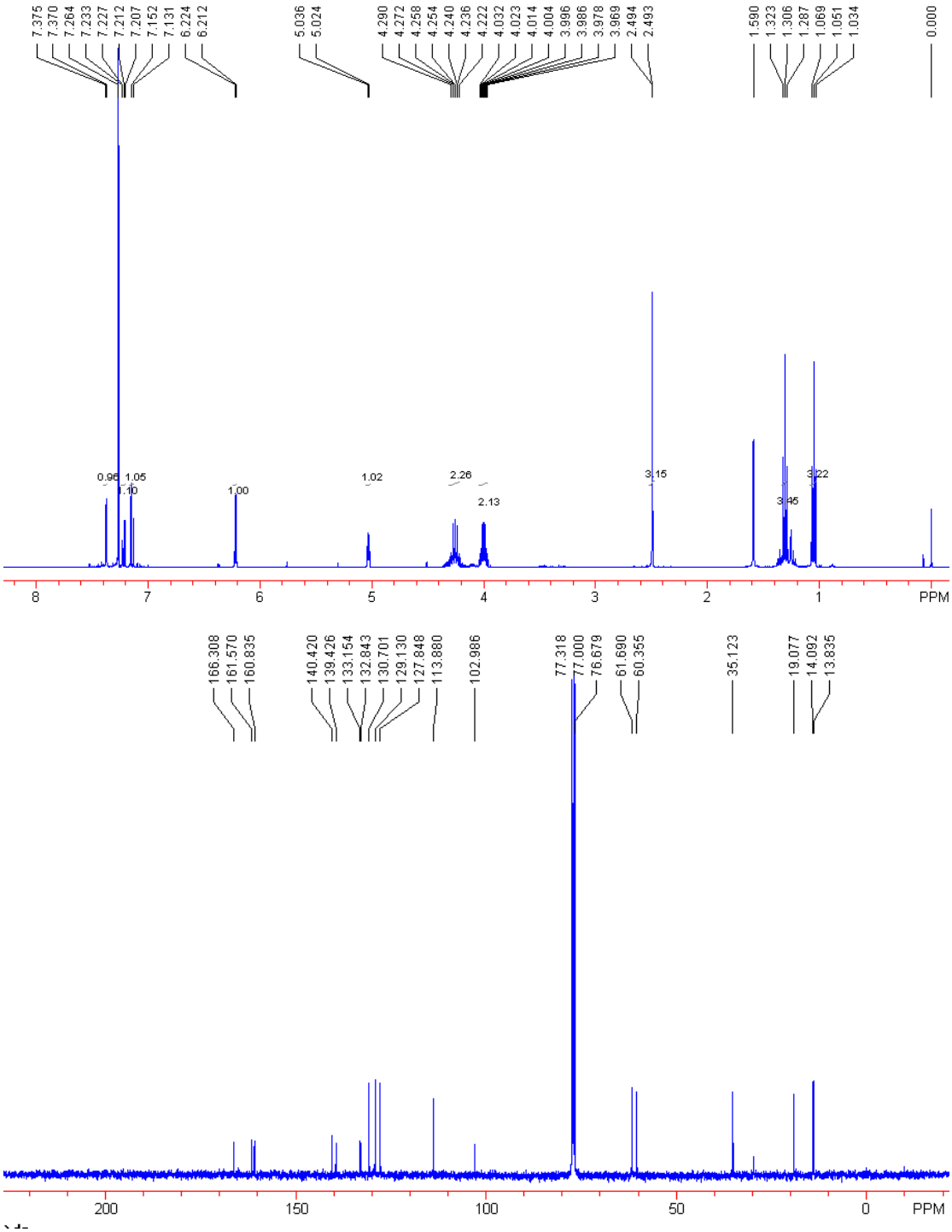


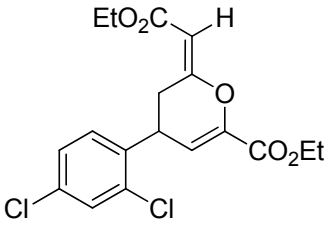
(*E*)-Ethyl 4-(2-bromophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-carboxylate **7ea**: a slight yellow liquid (29.8 mg, 76%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 3.20 (dd, *J* = 15.6 Hz, 7.6 Hz, 1H), 3.59 (dd, *J* = 15.6 Hz, 6.4 Hz, 1H), 4.07-4.14 (m, 2H), 4.18-4.23 (m, 1H), 4.29-4.35 (m, 2H), 5.75 (s, 1H), 6.42 (d, *J* = 4.4 Hz, 1H), 7.13-7.17 (m, 2H), 7.27-7.30 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.09, 14.14, 28.1, 35.2, 59.9, 61.7, 101.5, 115.1, 124.0, 127.9, 128.4, 128.8, 133.1, 140.0, 142.4, 161.1, 163.8, 166.6; IR (CH_2Cl_2) ν 3060, 2980, 2902, 1711, 1659, 1470, 1372, 1298, 1258, 1197, 1108, 1022, 856, 803, 754, 670 cm^{-1}; MS (ESI) *m/z* 395.0 ($M+H^+$); HRMS (ESI) Calcd. for $C_{18}H_{19}BrO_5Na$ requires ($M+Na^+$): 417.0308, Found: 417.0312.



Diethyl 4-(2,4-dichlorophenyl)-6-methyl-4H-pyran-2,5-dicarboxylate **6fa**: a slight yellow liquid (4.2 mg, 11%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.05 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 2.49 (s, 3H), 3.97-4.03 (m, 2H), 4.22-4.29 (m, 2H), 5.03 (d, *J* = 4.8 Hz, 1H), 6.22 (d, *J* = 4.8 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.37 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 14.1, 19.1, 35.1, 60.4, 61.7, 103.0, 113.9, 127.8, 129.1, 130.7, 132.8, 133.2, 139.4, 140.4, 160.8, 161.6, 166.3; IR (CH_2Cl_2) ν 3086, 2982, 2906, 1716,

1630, 1586, 1561, 1372, 1270, 1189, 1172, 1097, 1074, 964, 918, 767 cm^{-1}; MS (ESI) *m/z* 385.3. ($M+H^+$); HRMS (ESI) Calcd. for $C_{18}H_{18}Cl_2NaO_5$ requires ($M+Na^+$): 407.0424, Found: 407.0435.

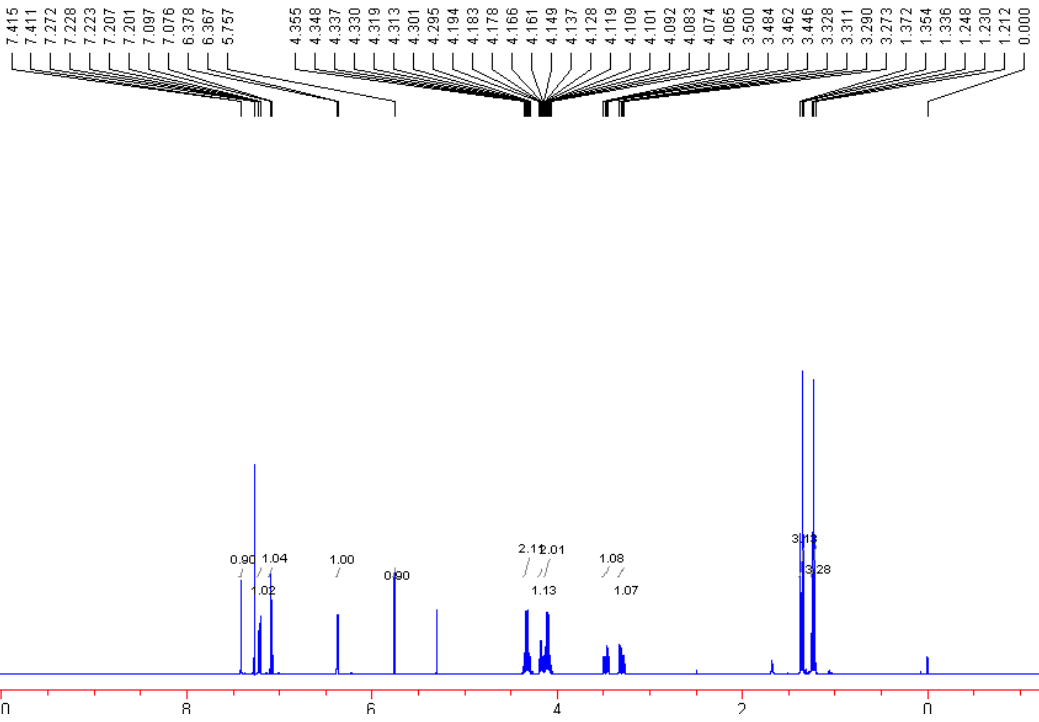


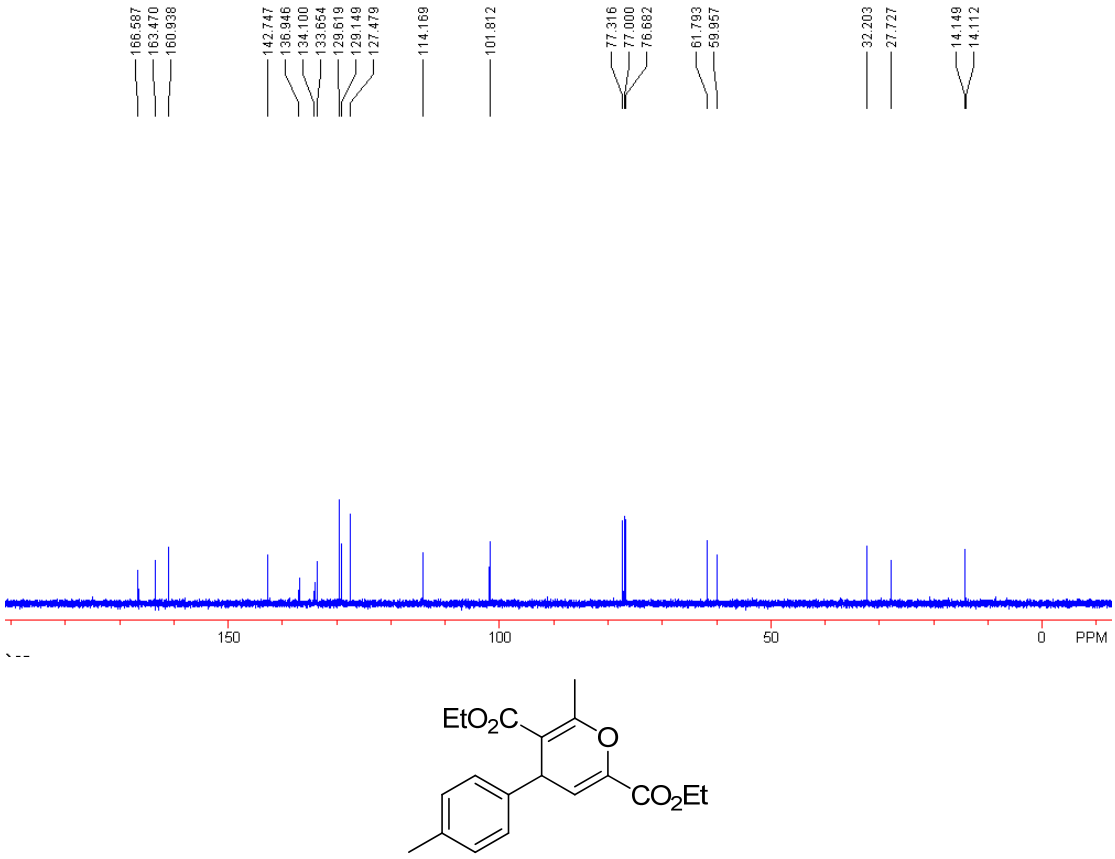


(*E*)-Ethyl

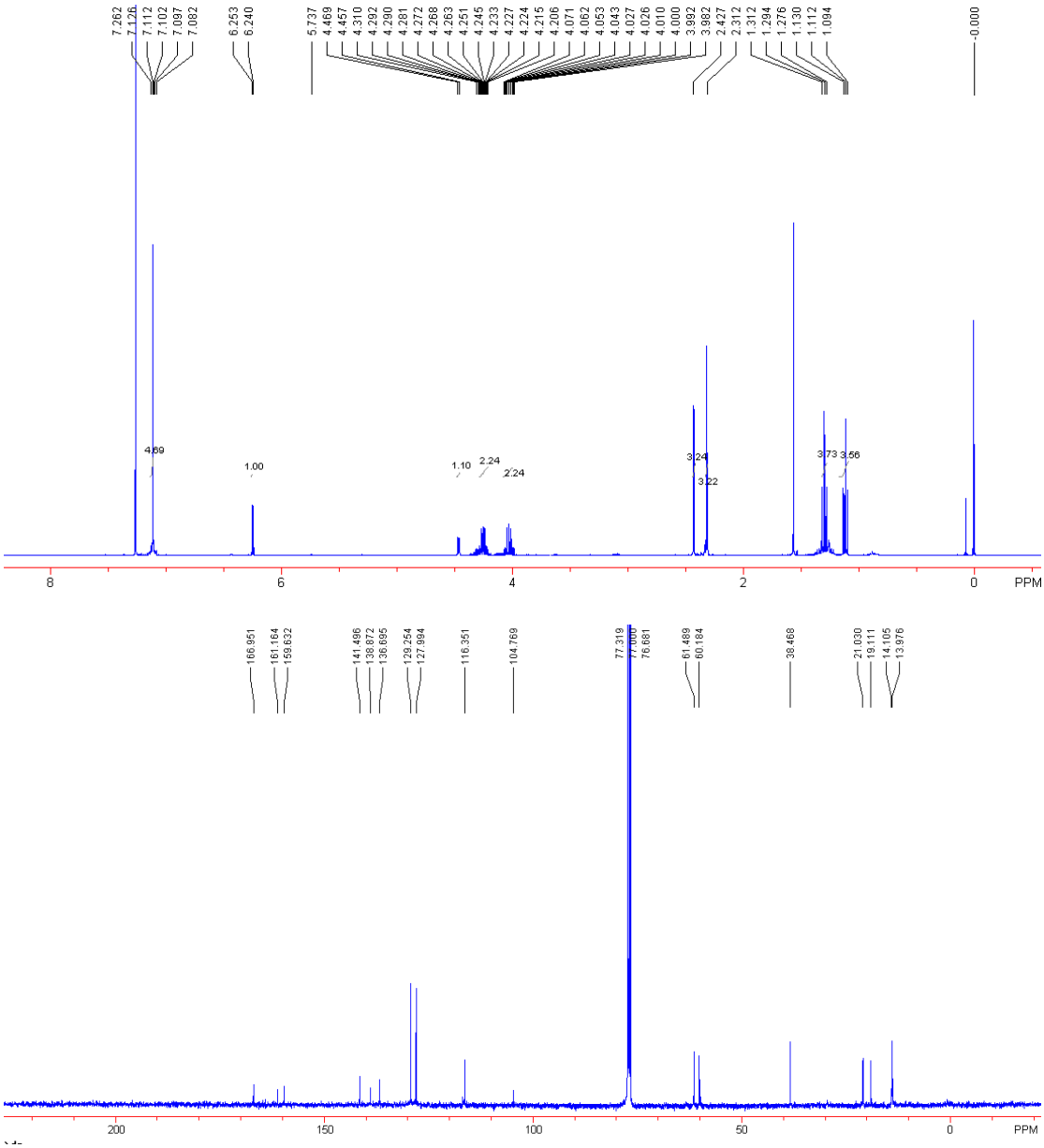
4-(2,4-dichlorophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-carboxylate

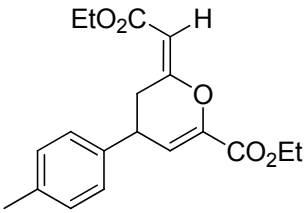
7fa: a slight yellow liquid (29.2 mg, 76%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 3.30 (dd, *J* = 15.2 Hz, 6.8 Hz, 1H), 3.47 (dd, *J* = 15.2 Hz, 6.4 Hz, 1H), 4.07-4.19 (m, 3H), 4.30-4.36 (m, 2H), 5.76 (s, 1H), 6.37 (d, *J* = 4.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.41 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.11, 14.15, 27.7, 32.2, 60.0, 61.8, 101.8, 114.2, 127.5, 129.1, 129.6, 133.7, 134.1, 136.9, 142.7, 160.9, 163.5, 166.6; IR (CH_2Cl_2) ν 3086, 2982, 2905, 1660, 1587, 1561, 1474, 1372, 1299, 1256, 1170, 1104, 1020, 861, 818, 760 cm^{-1}; MS (ESI) *m/z* 385.3. (M+H$^+$); HRMS (ESI) Calcd. for $C_{18}H_{18}Cl_2NaO_5$ requires (M+Na$^+$): 407.0424, Found: 407.0435.





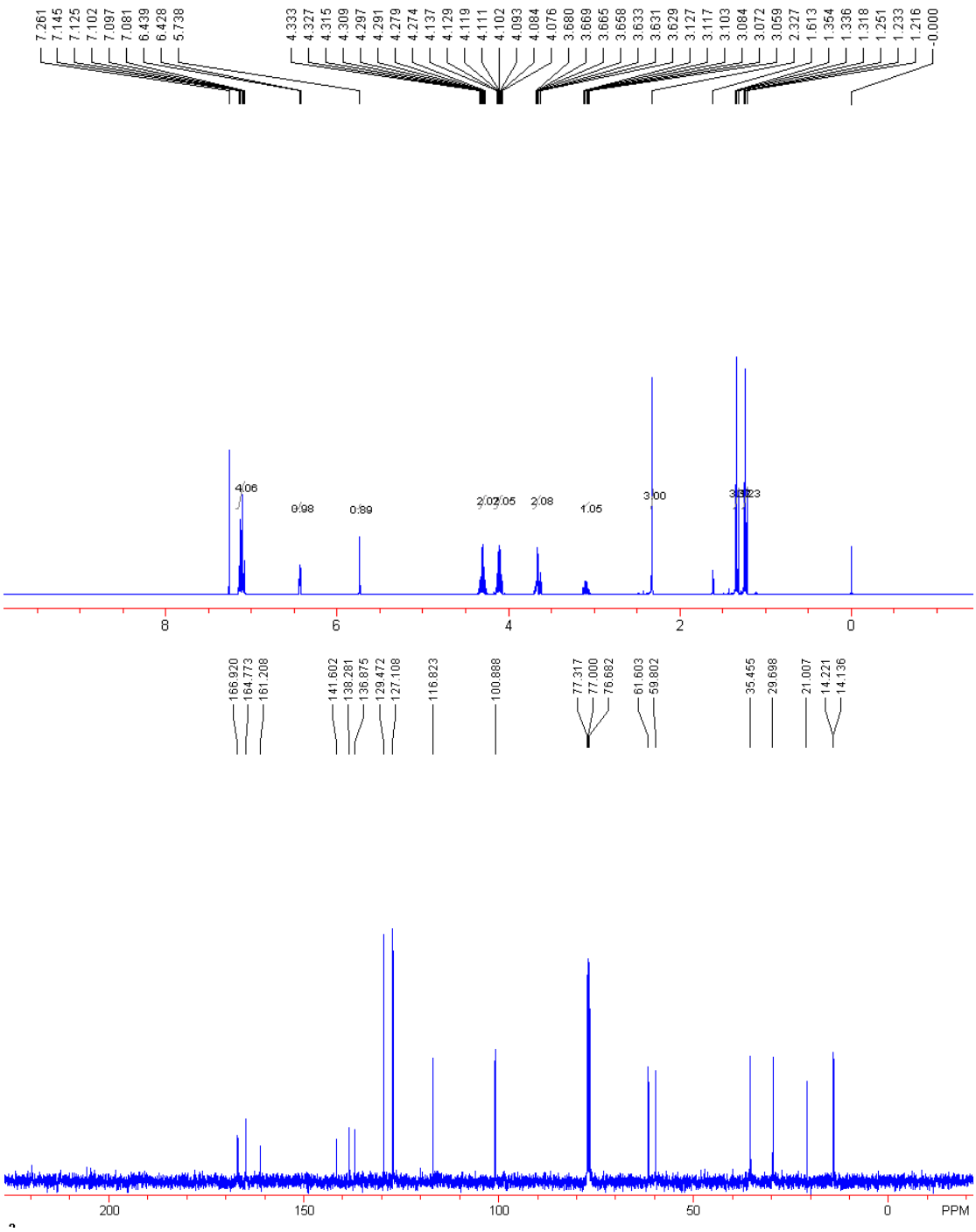
Diethyl 6-methyl-4-p-tolyl-4H-pyran-2,5-dicarboxylate **6ga**: a slight yellow liquid (2.2 mg, 7%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H), 2.31 (s, 3H), 2.43 (s, 3H), 3.98-4.07 (m, 2H), 4.21-3.31 (m, 2H), 4.46 (d, J = 4.8 Hz, 1H), 5.74 (s, 1H), 6.25 (d, J = 4.8 Hz, 1H), 7.08-7.13 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 14.1, 19.1, 21.0, 38.5, 60.2, 61.5, 104.8, 116.4, 128.0, 129.3, 136.7, 138.9, 141.5, 159.6, 161.2, 167.0; IR (CH_2Cl_2) ν 2979, 2902, 1715, 1659, 1629, 1511, 1446, 1373, 1324, 1263, 1172, 1106, 1021, 865, 803, 739 cm^{-1}; MS (ESI) *m/z* 353.1 (M+Na^{+}); HRMS (ESI) Calcd. for $C_{19}H_{22}O_5Na$ requires (M+Na^{+}): 353.1359, Found: 353.1371.

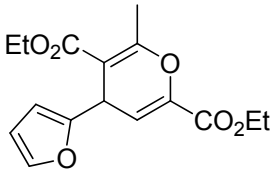




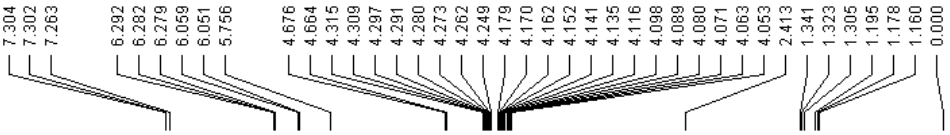
(*E*)-Ethyl 2-(2-ethoxy-2-oxoethylidene)-4-p-tolyl-3,4-dihydro-2H-pyran-6-carboxylate **7ga**: a slight yellow liquid (25.9 mg, 78%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (t, *J* = 7.2 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 2.33 (s, 3H), 3.06-3.13 (m, 1H), 3.62-3.69 (m, 2H), 4.08-4.14 (m, 2H), 4.27-4.33 (m, 2H), 5.74 (s, 1H), 6.43 (d, *J* = 4.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 14.2, 21.0, 29.7, 35.5, 59.8,

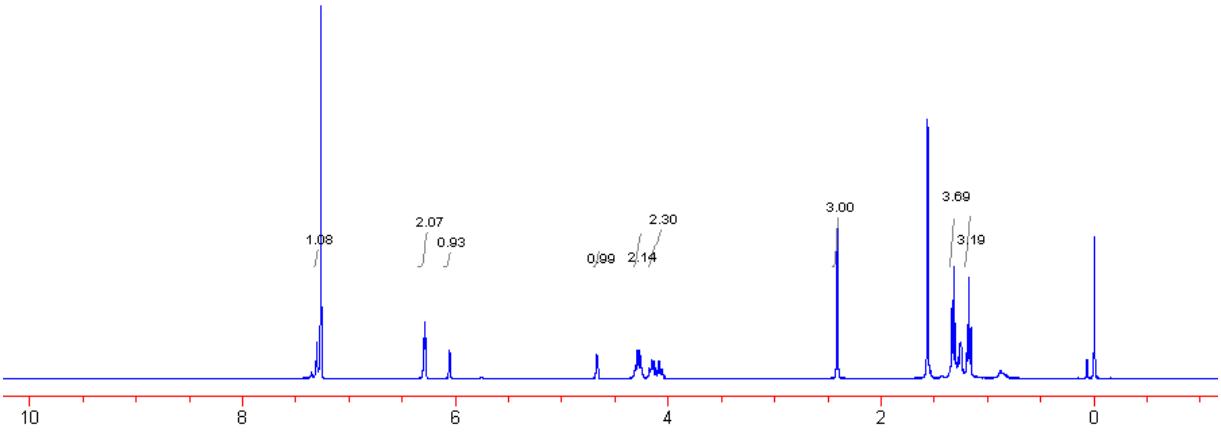
61.6, 100.9, 116.8, 127.1, 129.5, 136.9, 138.3, 141.6, 161.2, 164.8, 166.9; IR (CH_2Cl_2) ν 2980, 2902, 1736, 1712, 1658, 1514, 1373, 1297, 1167, 1113, 1045, 1020, 847, 808, 762 cm^{-1}; MS (ESI) *m/z* 353.1 ($M+Na^+$); HRMS (ESI) Calcd. for $C_{19}H_{22}O_5Na$ requires ($M+Na^+$): 353.1359, Found: 353.1371.

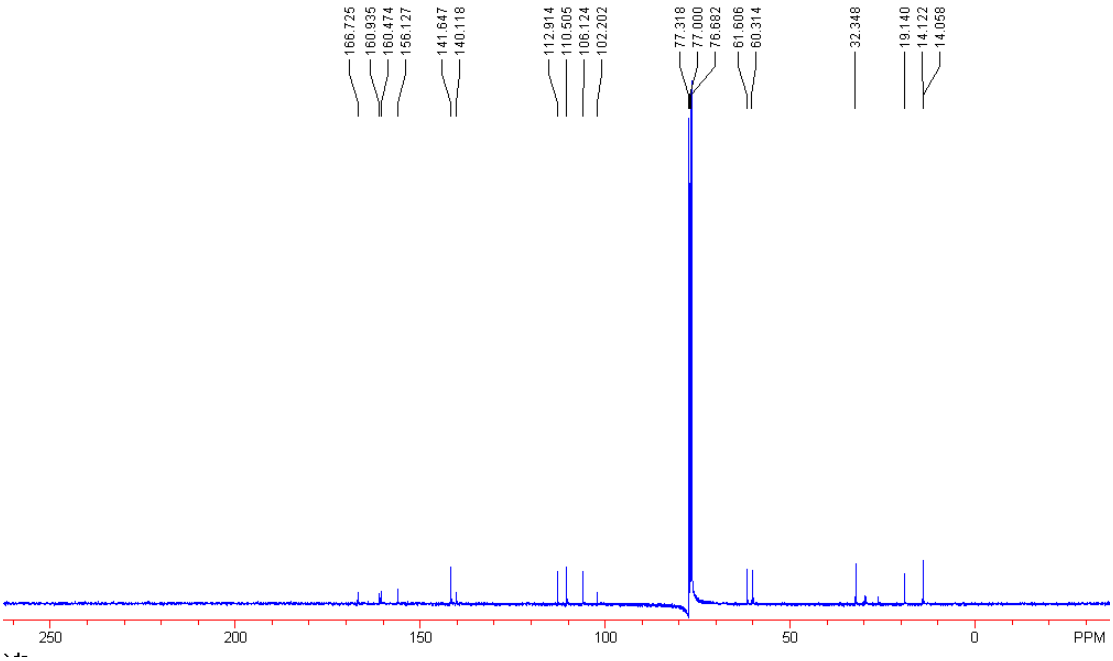


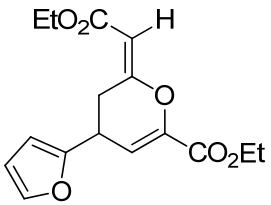


Diethyl 4-(furan-2-yl)-6-methyl-4H-pyran-2,5-dicarboxylate **6ha**: a slight yellow liquid (4.6 mg, 15%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.18 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 2.41 (s, 3H), 4.06-4.18 (m, 2H), 4.25-4.31 (m, 2H), 4.67 (d, *J* = 5.2 Hz, 1H), 6.05 (d, *J* = 5.2 Hz, 1H), 6.28-6.29 (m, 2H), 7.27-7.29 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.06, 14.12, 19.1, 32.3, 60.3, 61.6, 102.2, 106.1, 110.5, 112.9, 140.1, 141.6, 156.1, 160.5, 160.9, 166.7; IR (CH_2Cl_2) ν 2980, 2903, 2857, 1738, 1716, 1660, 1475, 1372, 1266, 1173, 1107, 1048, 1020, 798, 763, 739 cm^{-1}; MS (ESI) *m/z* 329.1 (M+Na^{+}); HRMS (ESI) Calcd. for $C_{16}H_{18}O_6Na$ requires (M+Na^{+}): 329.0996, Found: 329.1000.

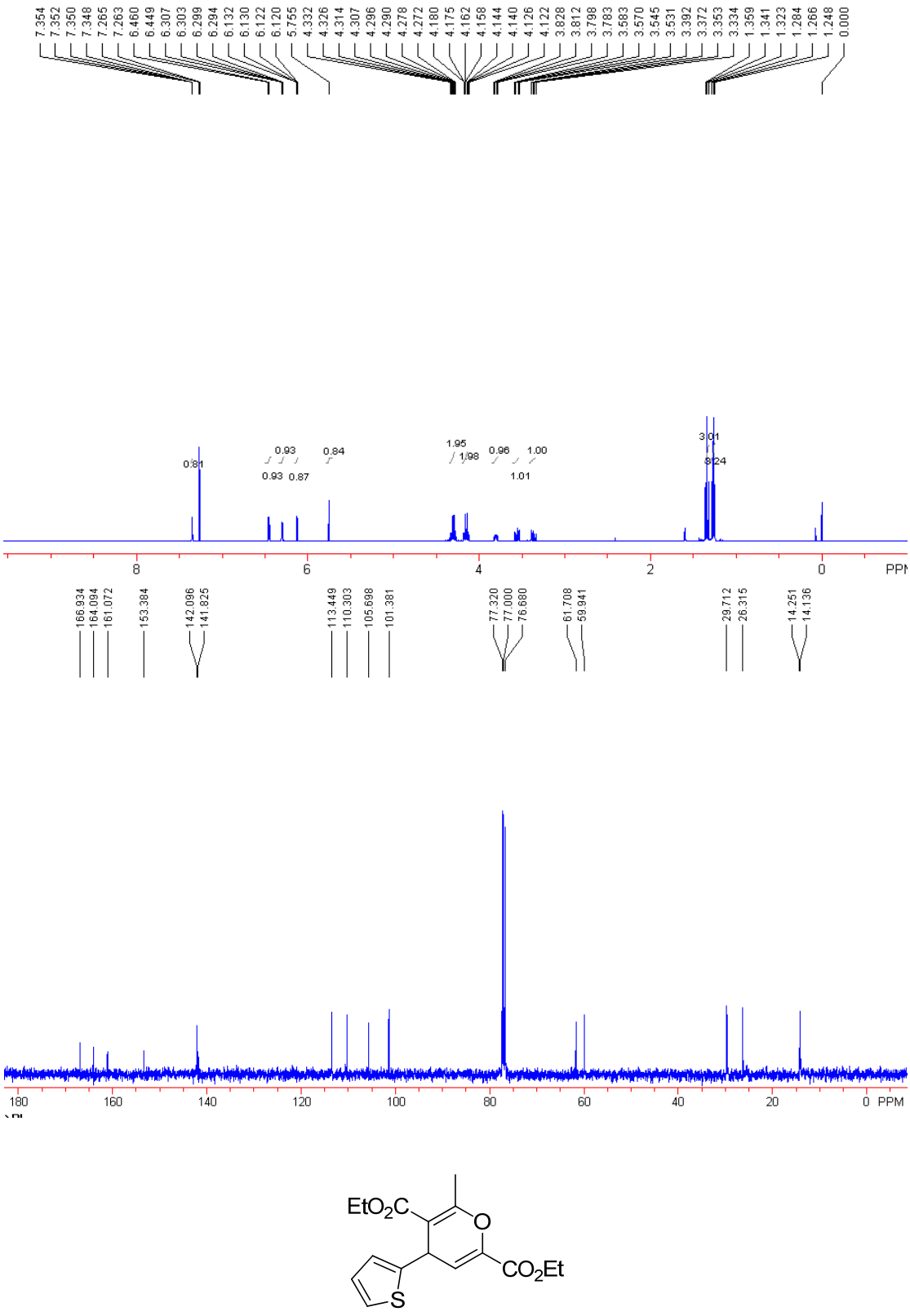






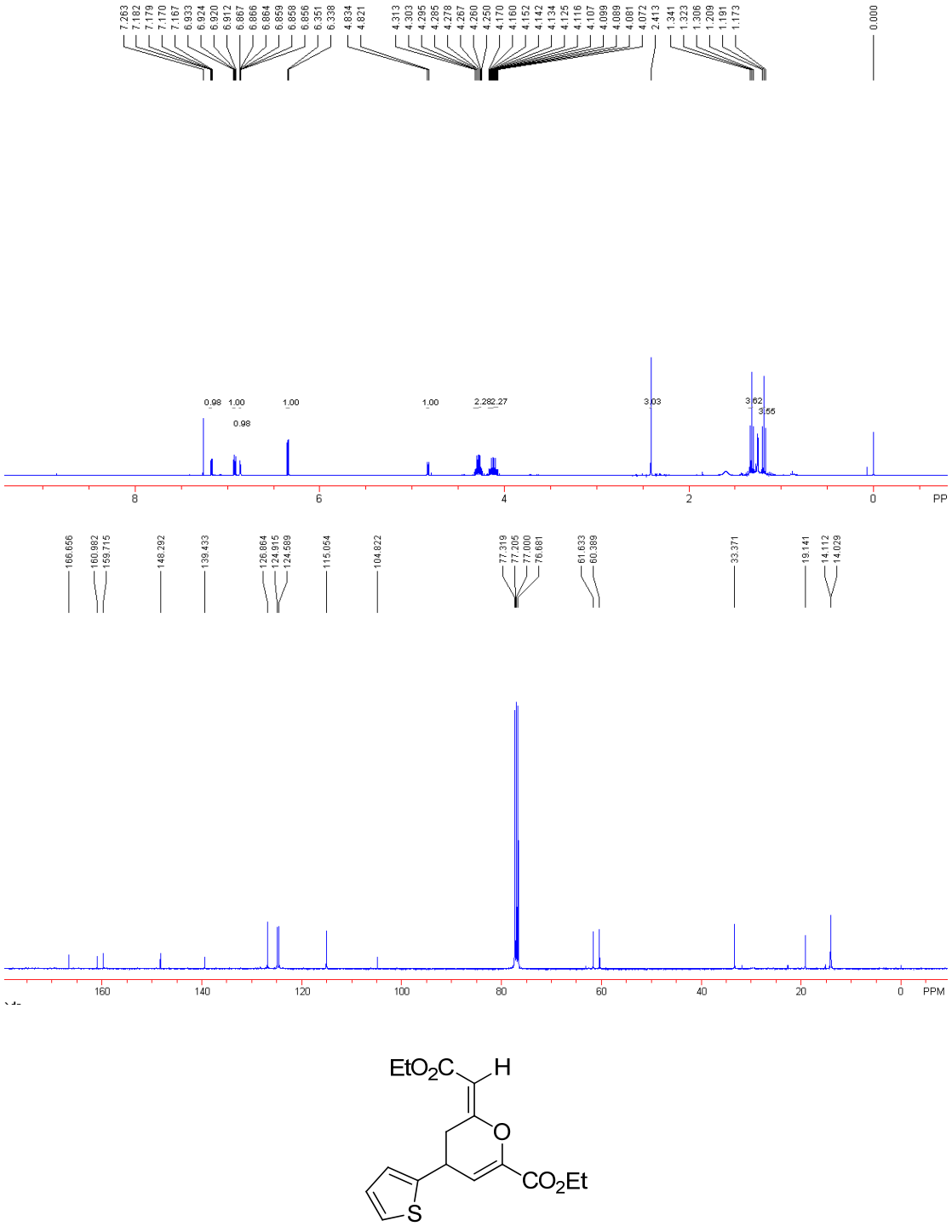


(*E*)-Ethyl 2-(2-ethoxy-2-oxoethylidene)-4-(furan-2-yl)-3,4-dihydro-2H-pyran-6-carboxylate **7ha**: a slight yellow liquid (13.8 mg, 45%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.27 (t, *J* = 7.2 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 3.36 (dd, *J* = 15.2 Hz, 8.0 Hz, 1H), 3.56 (dd, *J* = 15.2 Hz, 5.2 Hz, 1H), 3.78-3.83 (m, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 5.76 (s, 1H), 6.13-6.14 (m, 1H), 6.30-6.31 (m, 1H), 6.45 (d, *J* = 4.0 Hz, 1H), 7.35-7.36 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 14.3, 26.3, 29.7, 59.9, 61.7, 101.4, 105.7, 110.3, 113.4, 141.8, 142.1, 153.4, 161.1, 164.1, 166.9; IR (CH_2Cl_2) ν 2980, 2906, 2874, 1737, 1712, 1660, 1446, 1373, 1298, 1174, 1120, 1046, 1017, 801, 761, 739 cm^{-1}; MS (ESI) *m/z* 329.1 ($M+Na^+$); HRMS (ESI) Calcd. for $C_{16}H_{18}O_6Na$ requires ($M+Na^+$): 329.0996, Found: 329.1007.



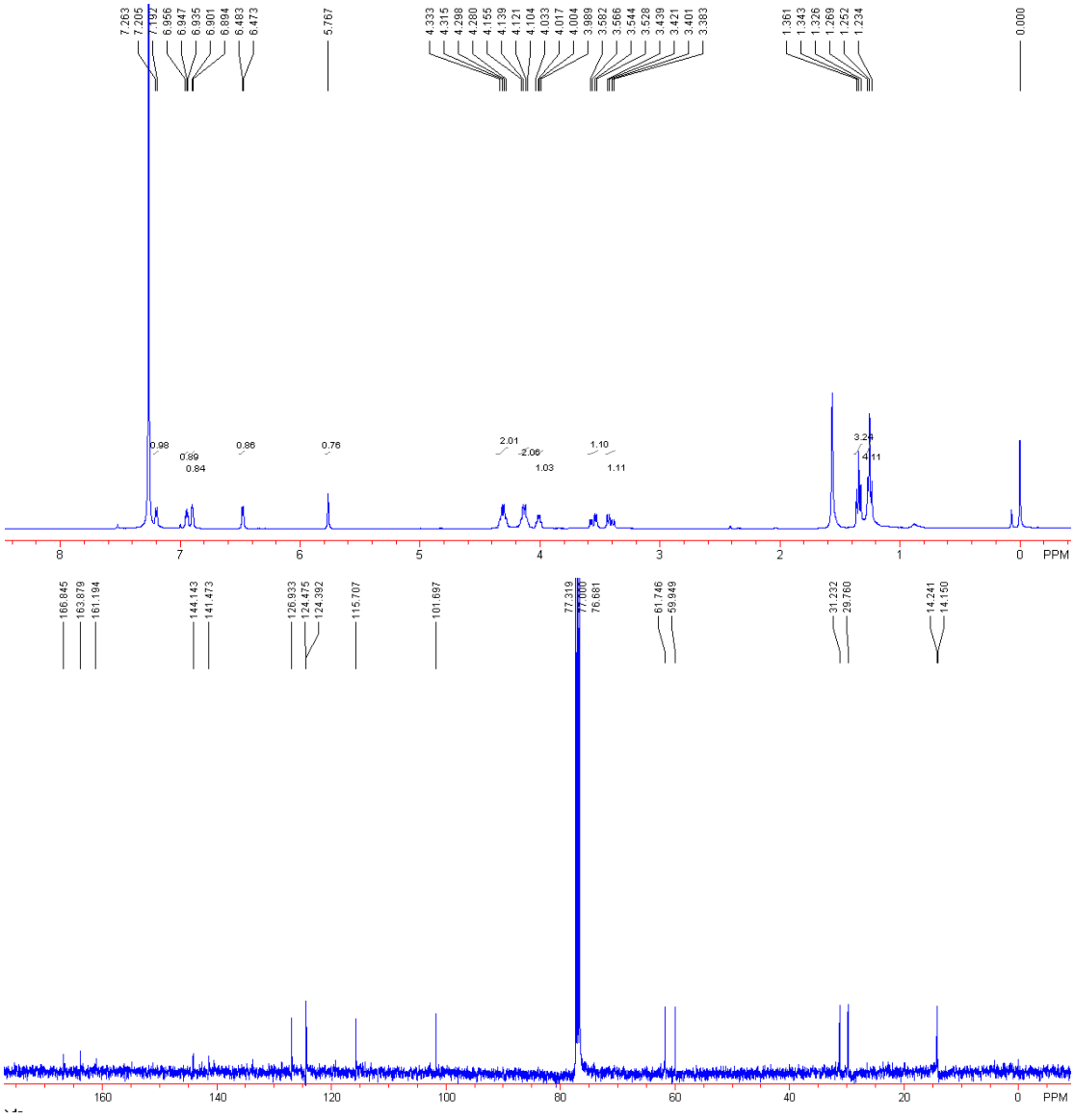
Diethyl 6-methyl-4-(thiophen-2-yl)-4H-pyran-2,5-dicarboxylate **6ia**: a slight yellow liquid (2.6 mg, 8%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.19 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H), 2.41 (s, 3H), 4.07-4.17 (m, 2H), 4.25-4.31 (m, 2H), 4.83 (d, J = 5.2 Hz, 1H), 6.34 (d, J = 5.2 Hz, 1H), 6.86-6.87 (m, 1H), 6.91 (dd, J = 4.8 Hz, 3.2 Hz, 1H), 7.17 (dd, J = 4.8 Hz, 1.2 Hz,

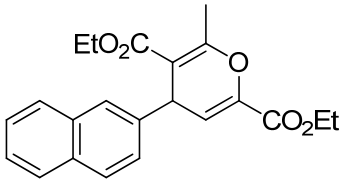
1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.03, 14.1, 19.1, 33.4, 60.4, 61.6, 104.8, 115.1, 124.6, 124.9, 126.9, 139.4, 148.3, 159.7, 161.0, 166.7; IR (CH_2Cl_2) ν 2980, 2903, 2857, 1738, 1716, 1660, 1475, 1372, 1266, 1173, 1107, 1048, 1020, 798, 763, 739 cm^{-1}; MS (ESI) *m/z* 345.1 ($M+Na^+$); HRMS (ESI) Calcd. for $C_{16}H_{18}O_5SNa$ requires ($M+Na^+$): 345.0767, Found: 345.0775.



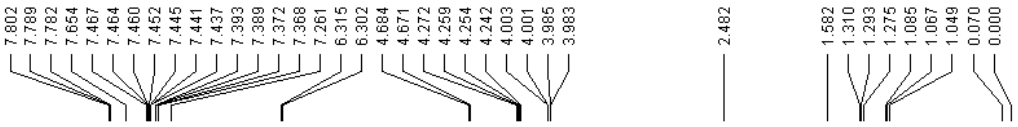
(*E*)-Ethyl

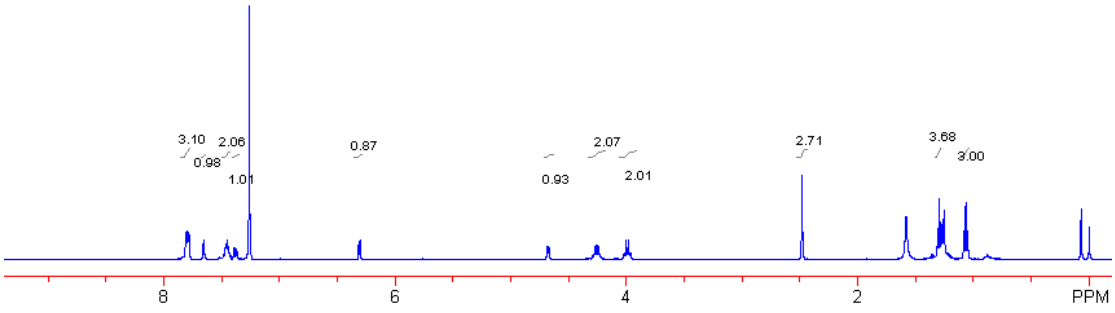
2-(2-ethoxy-2-oxoethylidene)-4-(thiophen-2-yl)-3,4-dihydro-2H-pyran-6-carboxylate **7ia**: a slight yellow liquid (15.7 mg, 49%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (t, *J* = 7.2 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 3.41 (dd, *J* = 15.2 Hz, 8.0 Hz, 1H), 3.56 (dd, *J* = 15.2 Hz, 5.2 Hz, 1H), 3.99-4.03 (m, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 5.77 (s, 1H), 6.48 (d, *J* = 4.0 Hz, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 6.95 (dd, *J* = 4.8 Hz, 3.6 Hz, 1H), 7.20 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.15, 14.24, 29.8, 31.2, 59.9, 61.7, 101.7, 115.7, 124.4, 124.5, 126.9, 141.5, 144.1, 161.2, 163.9, 166.8; IR (CH_2Cl_2) ν 3075, 2966, 2934, 1736, 1713, 1660, 1373, 1259, 1173, 1259, 1119, 1046, 1020, 802, 762, 738, 701 cm^{-1}; MS (ESI) *m/z* 345.2 ($M+Na^+$); HRMS (ESI) Calcd. for $C_{16}H_{18}O_5SNa$ requires ($M+Na^+$): 345.0767, Found: 345.0777.

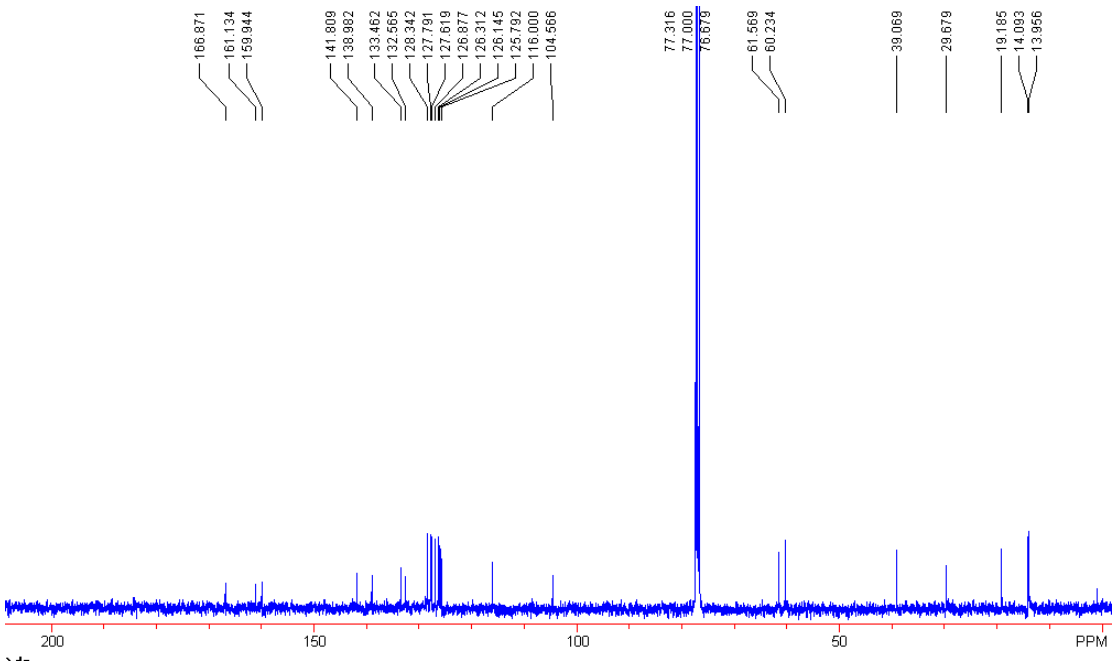


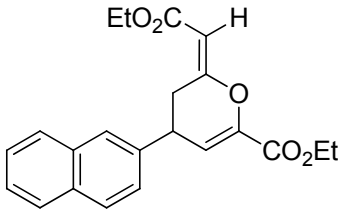


Diethyl 6-methyl-4-(naphthalen-2-yl)-4H-pyran-2,5-dicarboxylate **6ja**: a slight yellow liquid (3.3 mg, 9%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.07 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 2.48 (s, 3H), 3.98-4.00 (m, 2H), 4.24-4.27 (m, 2H), 4.68 (d, *J* = 5.2 Hz, 1H), 6.31 (d, *J* = 5.2 Hz, 1H), 7.38 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.44-7.47 (m, 2H), 7.65 (s, 1H), 7.78-7.80 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 14.1, 19.2, 39.1, 60.2, 61.6, 104.6, 116.0, 125.8, 126.1, 126.3, 126.9, 127.6, 127.8, 128.3, 132.6, 133.5, 139.0, 141.8, 159.9, 161.1, 166.9; IR (CH_2Cl_2) ν 3057, 2980, 2902, 1715, 1474, 1373, 1262, 1106, 1048, 1021, 956, 859, 801, 746, 702, 667 cm^{-1}; MS (ESI) *m/z* 389.2 (M+Na^{+}); HRMS (ESI) Calcd. for $C_{22}H_{22}O_5Na$ requires (M+Na^{+}): 389.1359, Found: 389.1374.



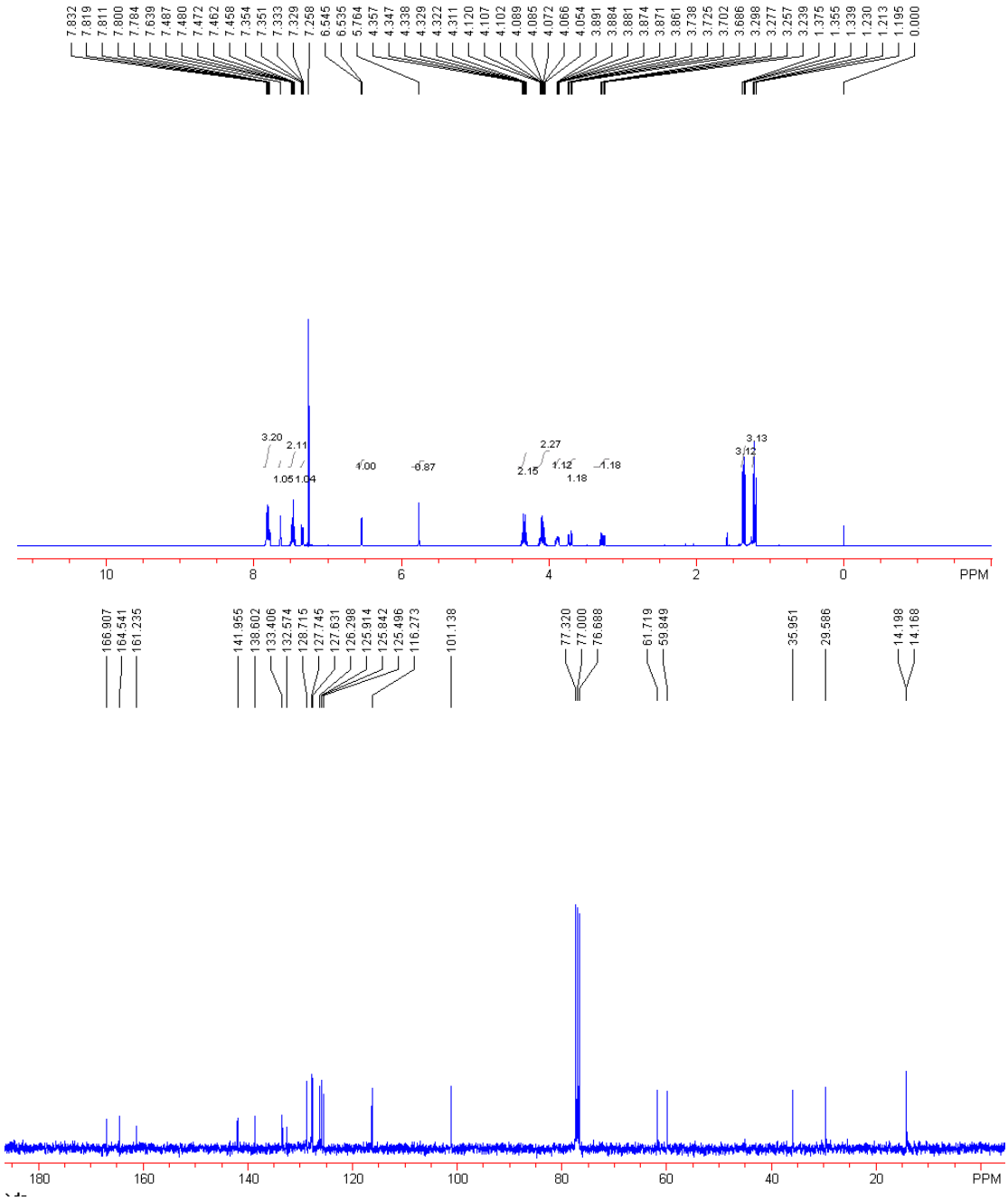


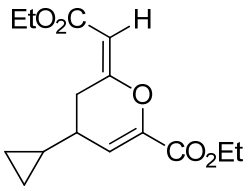




(*E*)-ethyl

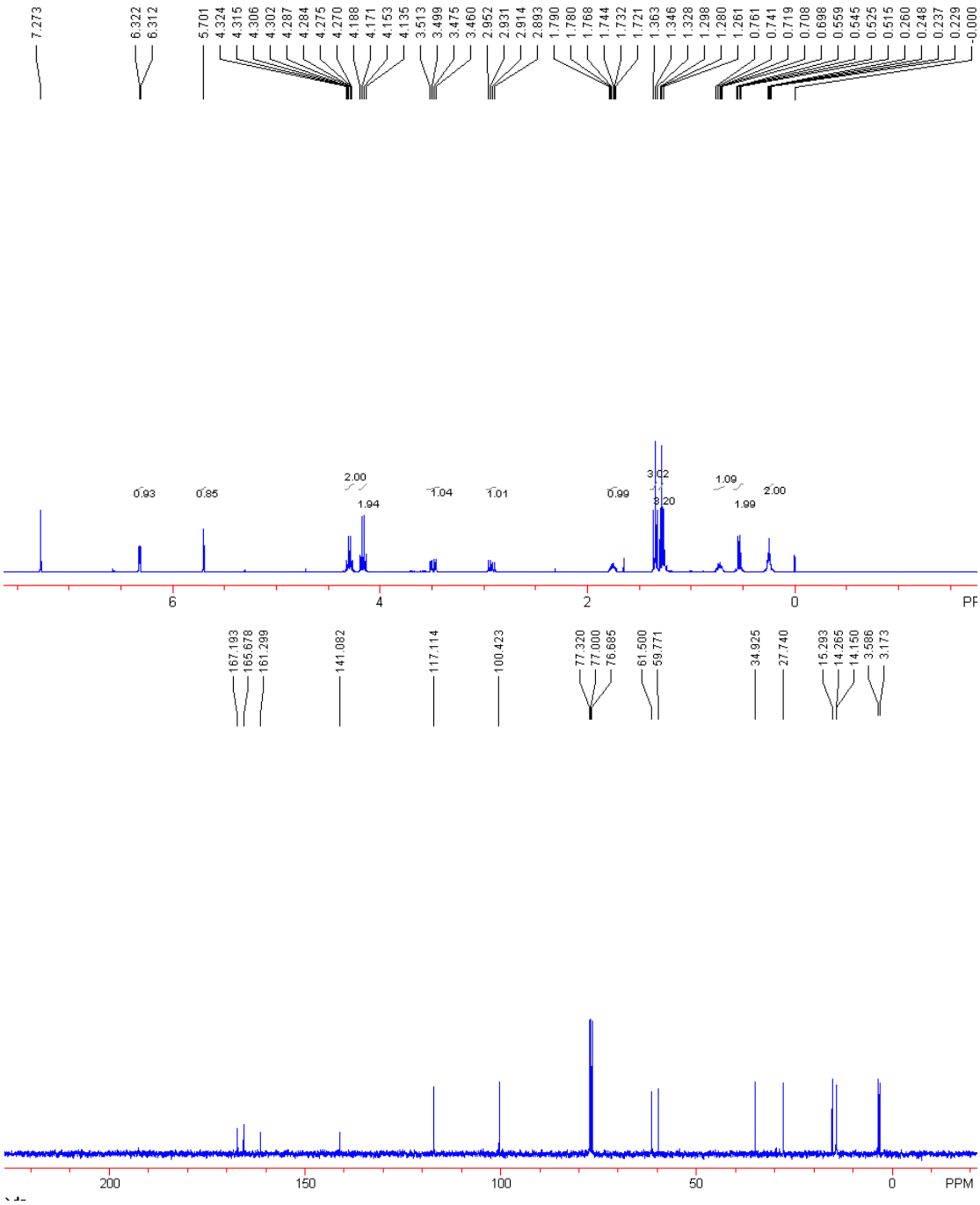
2-(2-ethoxy-2-oxoethylidene)-4-(naphthalen-2-yl)-3,4-dihydro-2H-pyran-6-carboxylate **7ja**: a slight yellow liquid (26.7 mg, 73%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.21 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 3.27 (dd, *J* = 14.8 Hz, 8.4 Hz, 1H), 3.71 (dd, *J* = 14.8 Hz, 5.2 Hz, 1H), 3.86-3.89 (m, 1H), 4.05-4.12 (m, 2H), 4.31-4.36 (m, 2H), 5.76 (s, 1H), 6.54 (d, *J* = 4.0 Hz, 1H), 7.34 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.46-7.49 (m, 2H), 7.64 (s, 1H), 7.78-7.83 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.17, 14.20, 29.6, 36.0, 59.8, 61.7, 101.3, 116.3, 125.5, 125.8, 125.9, 126.3, 127.6, 127.7, 128.7, 132.6, 133.4, 138.6, 142.0, 161.2, 164.5, 166.9; IR (CH_2Cl_2) ν 3056, 2982, 2904, 1734, 1709, 1659, 1508, 1474, 1445, 1372, 1298, 1254, 1172, 1115, 854, 817, 760 cm^{-1}; MS (ESI) *m/z* 389.2 (M+Na^{+}); HRMS (ESI) Calcd. for $C_{22}H_{22}O_5Na$ requires (M+Na^{+}): 389.1359, Found: 389.1364.





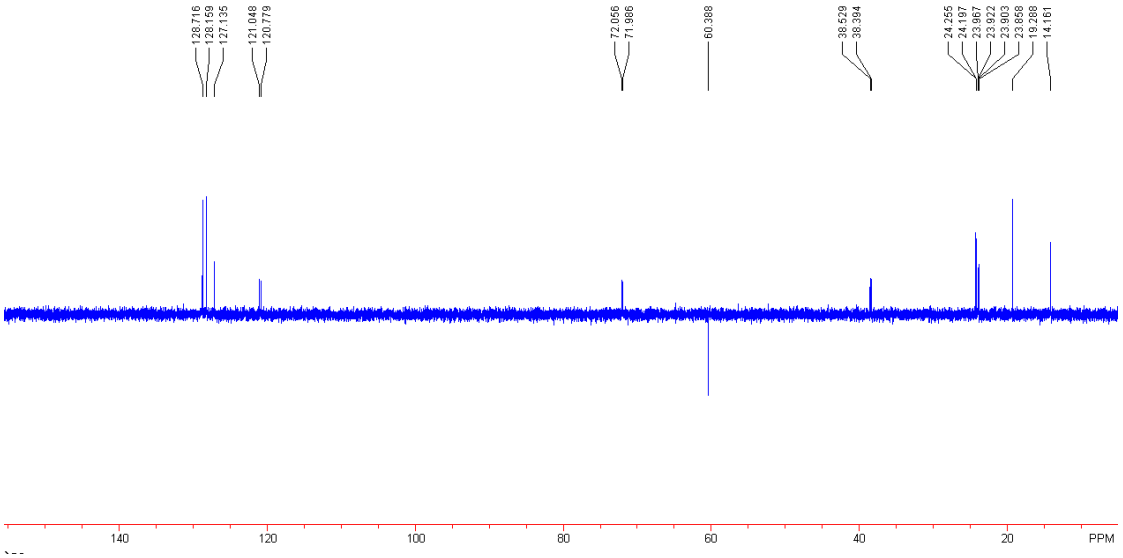
(*E*)-ethyl 4-cyclopropyl-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-carboxylate **7ka**: a slight yellow liquid (27.3 mg, 90%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.23-0.26 (m, 2H), 0.52-0.56 (m, 2H), 0.70-0.76 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.72-1.79 (m, 1H), 2.92 (dd, *J* = 15.2 Hz, 8.4 Hz, 1H), 3.48 (dd, *J* = 15.2 Hz, 5.6 Hz, 1H),

4.16 (q, J = 7.2 Hz, 2H), 4.27-4.32 (m, 2H), 5.70 (s, 1H), 6.32 (d, J = 4.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.2, 3.6, 14.1, 14.3, 15.3, 27.7, 34.9, 59.8, 61.5, 100.4, 117.1, 141.1, 161.3, 165.7, 167.2. IR (CH_2Cl_2) ν 3081, 2982, 2903, 1737, 1713, 1659, 1372, 1335, 1298, 1256, 1120, 1048, 1021, 854, 761, 740 cm^{-1}. MS (ESI) *m/z* 281.1 (M+H$^+$). HRMS (ESI) Calcd. for $C_{15}H_{20}O_5Na$ requires (M+Na$^+$): 303.1203, Found: 303.1209.

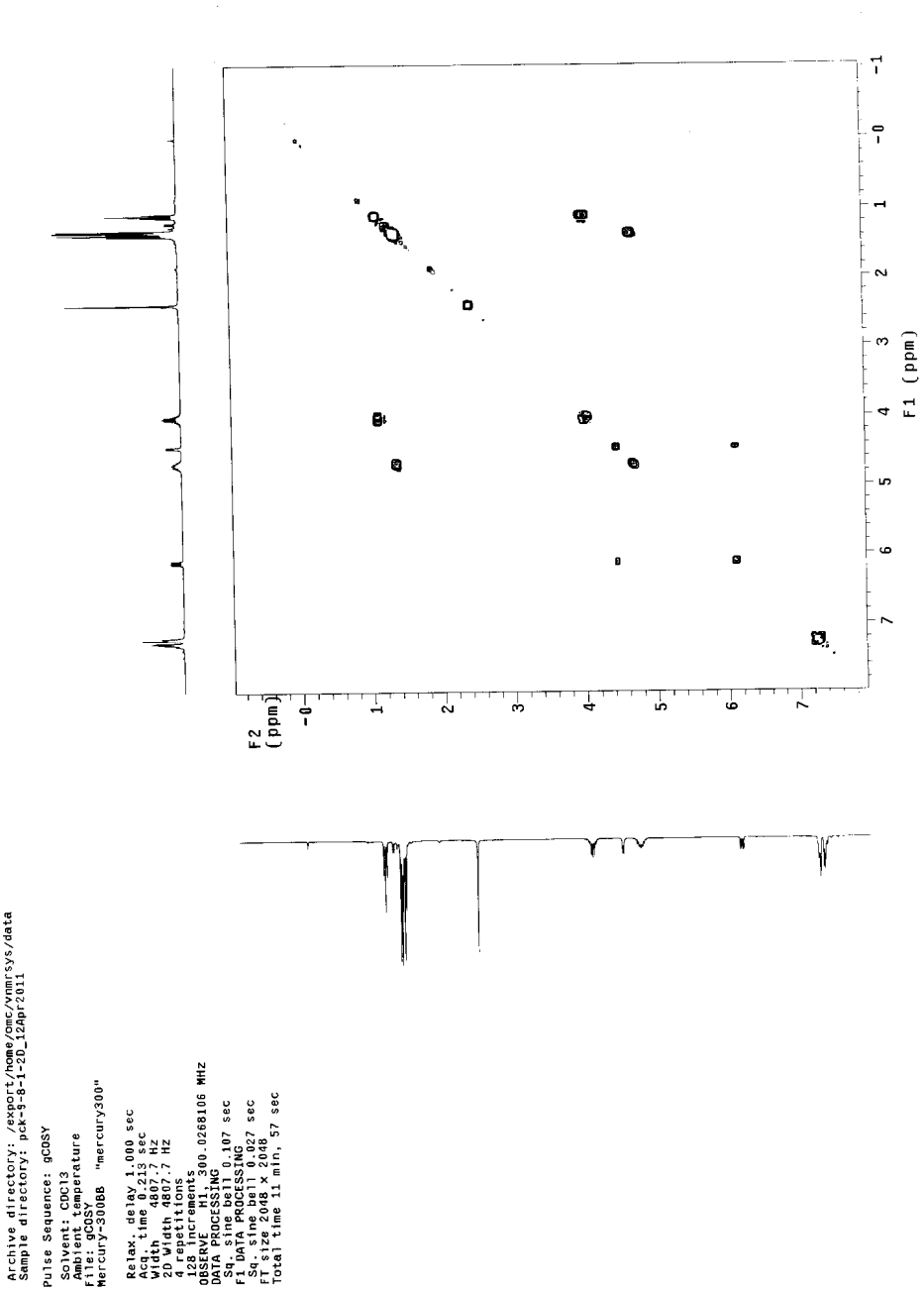


The 2-D NMR Spectroscopic Data of **3ca**, **4ca** and **7aa**

DEPT of **3ca**



gCOSY of **3ca**


F2 (ppm)
F1 (ppm)
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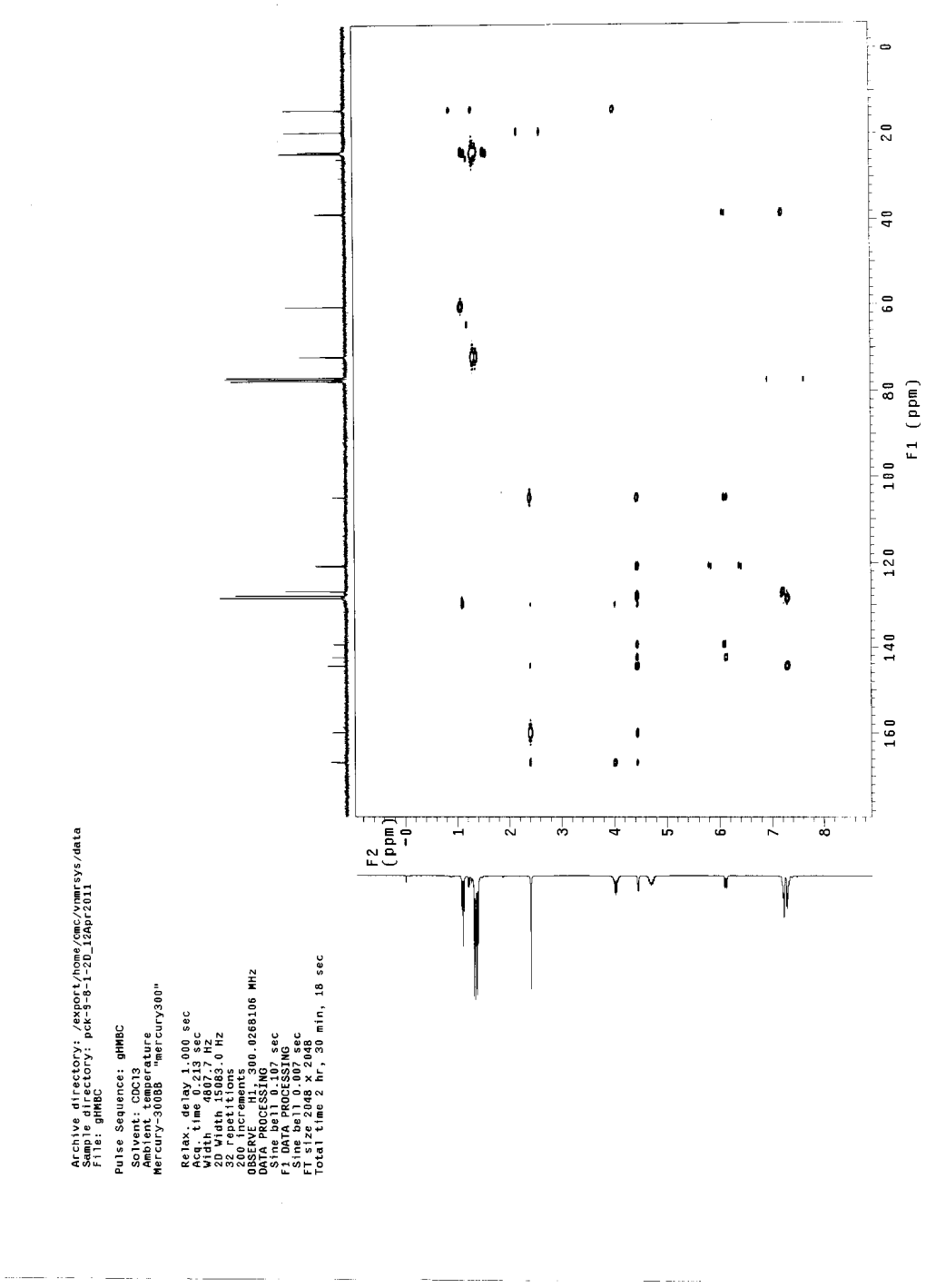
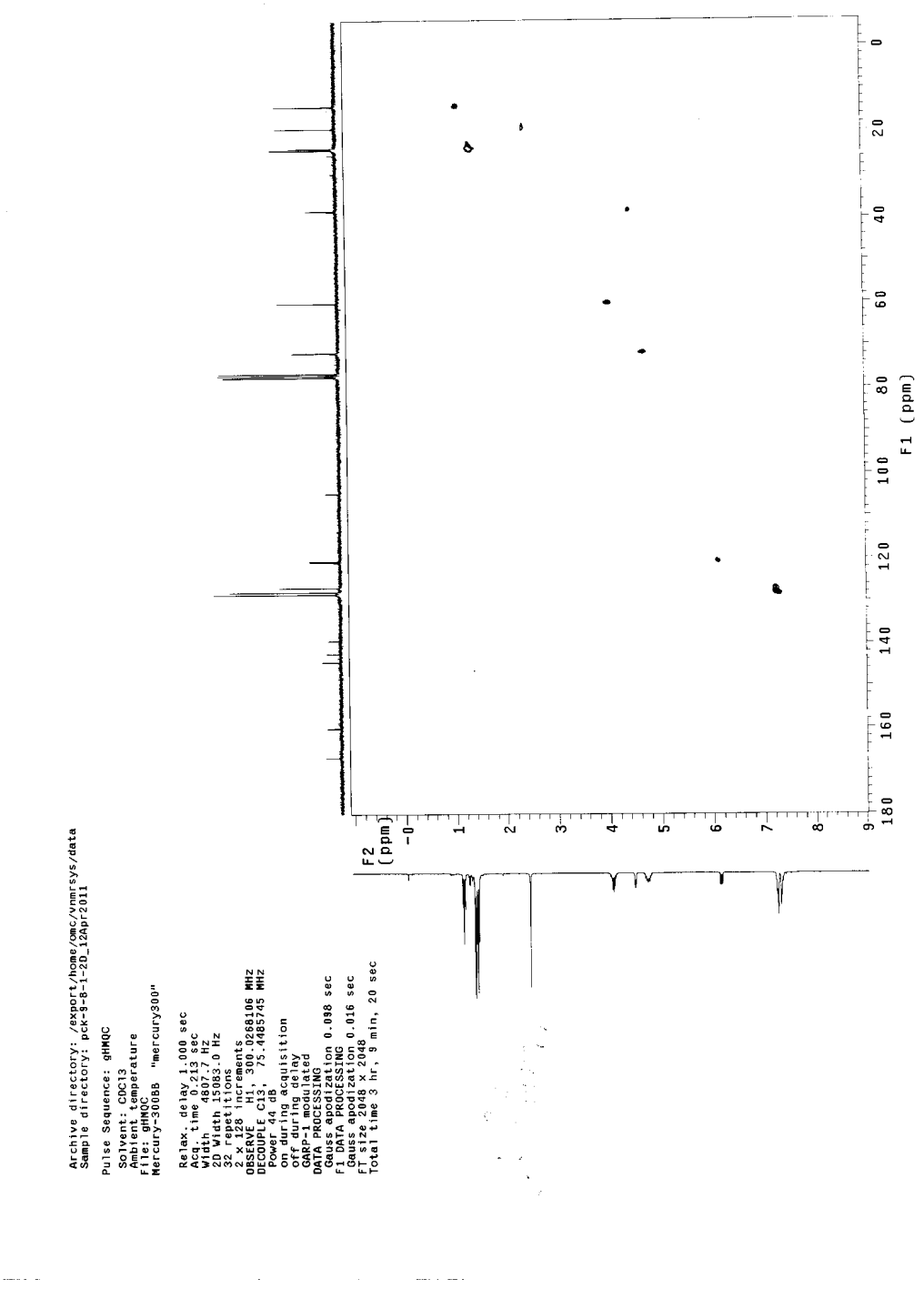
Sample directory: pck-9-8-1-2D_12Apr2011
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
File: gCOSY
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 4807.7 Hz
4 repetitions
128 increments
OBSERVE H1, 300.0268106 MHz
DATA PROCESSING
Sq. sine bell 0.107 sec
F1 DATA PROCESSING
Sq. sine bell 0.027 sec
FT size 2048 x 2048
Total time 11 min, 57 sec

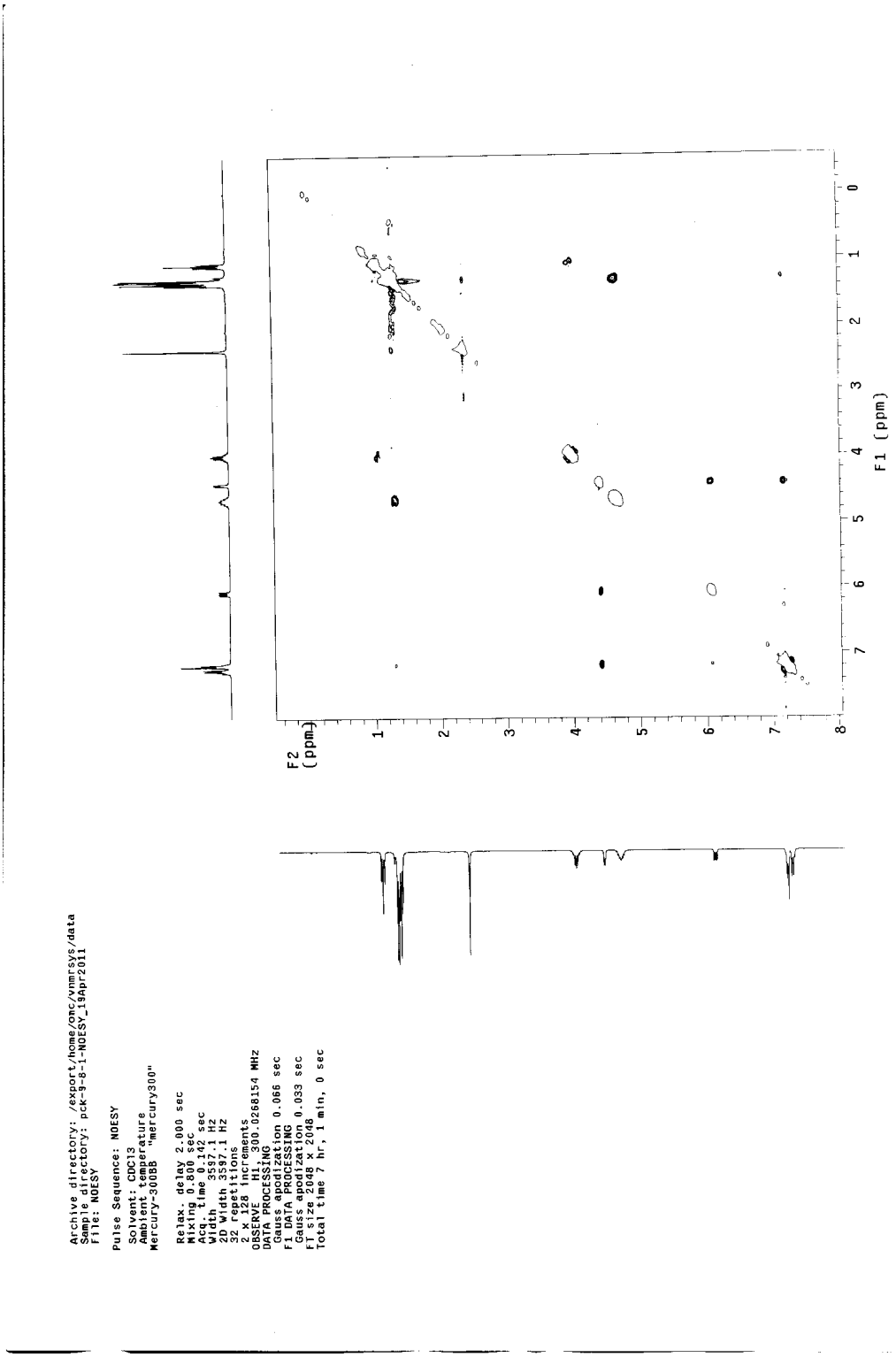
gHMBC of **3ca**


Archive directory: /export/home/cmc/vnmrsys/data
Sample directory: pck-3-8-1-2D_12Apr2011
File: gHMBC
Pulse Sequence: gHMBC
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 15083.0 Hz
32 repetitions
220 increments
OBSERVE H1, 300.0268106 MHz
DATA PROCESSING
Sine bell 0.107 sec
F1 DATA PROCESSING
Sine bell 0.007 sec
FT size 2048 x 2048
Total time 2 hr, 30 min, 18 sec
F2 (ppm)
F1 (ppm)

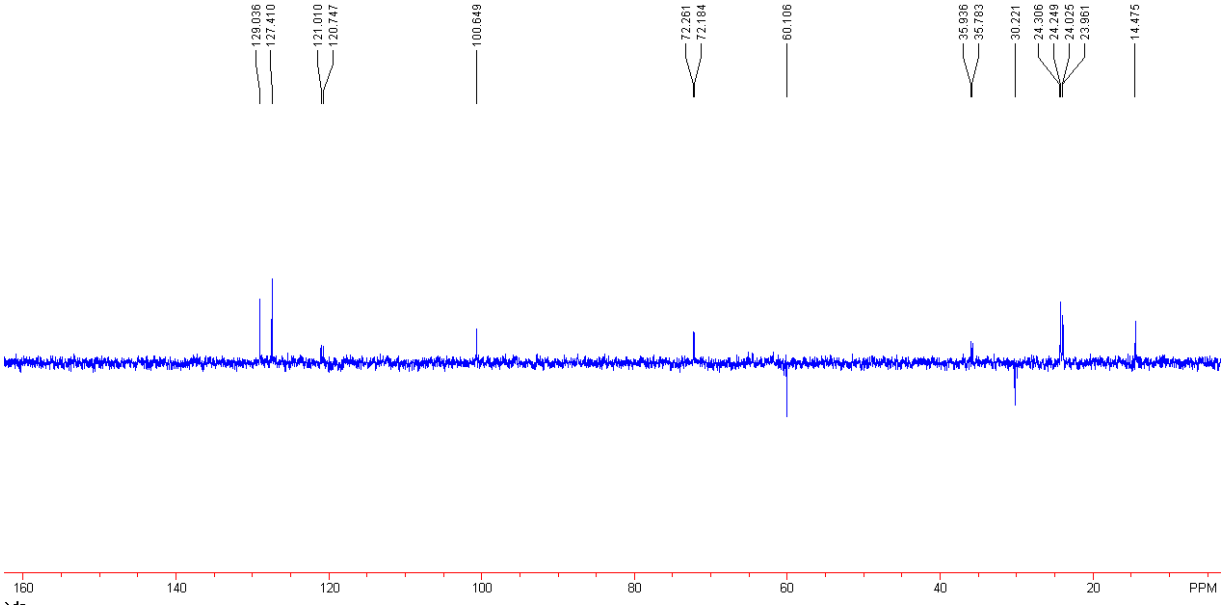
gHMQC of **3ca**


Archive directory: /export/home/omc/vnmrsys/data
Sample directory: pck-8-1-2D_12Apr2011
Pulse Sequence: gHMQC
Solvent: CDCl3
Ambient temperature
File: gHMQC
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 15083.0 Hz
32 repetitions
256 x 128 increments
OBSERVE H1, 300.0268106 MHz
DECOUPLE C13, 75.4485745 MHz
Power 44 dB
on during acquisition
off during delay
GARP-1 modulated
DATA PROCESSING
Gauss apodization 0.038 sec
FT DATA PROCESSING
Gauss apodization 0.016 sec
FT size 2048 x 2048
Total time 3 hr, 9 min, 20 sec
F2 (ppm)
F1 (ppm)

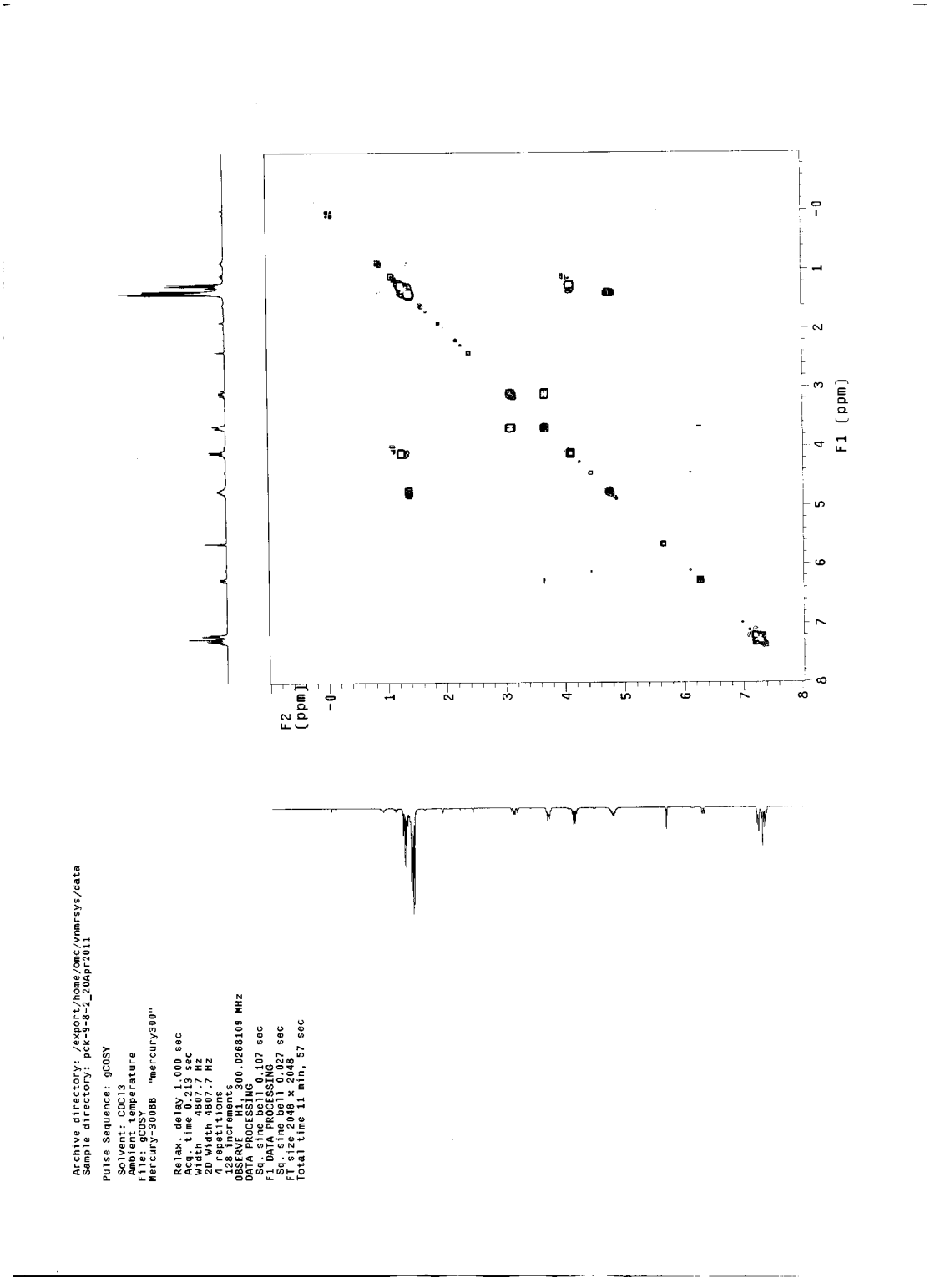
NOESY of **3ca**


F2 (ppm)
F1 (ppm)
Archive directory: /export/home/onc/vnmrsys/data
Sample_directory: pck-9-8-1-NOESY_19Apr2011
File: NOESY
Pulse Sequence: NOESY
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 2.000 sec
Mixing 0.800 sec
Acq. time 0.142 sec
Width 3597.1 Hz
2D Width 3597.1 Hz
32 repetitions
2 x 128 increments
OBSERVE H1, 300.0268154 MHz
DATA PROCESSING
Gauss apodization 0.066 sec
F1 DATA PROCESSING
Gauss apodization 0.033 sec
FT size 2048 x 2048
Total time 7 hr, 1 min, 0 sec

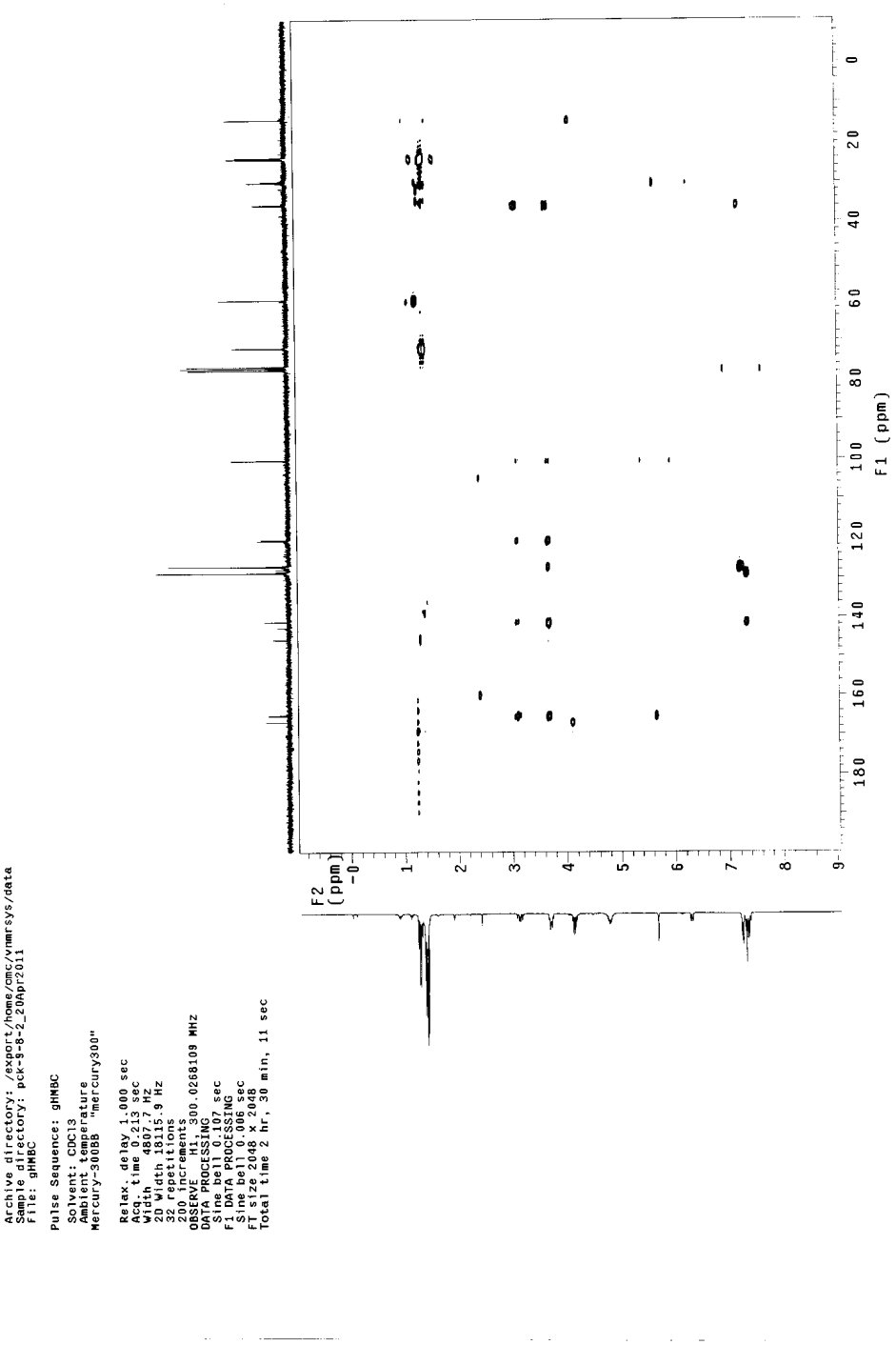
DEPT of **4ca**



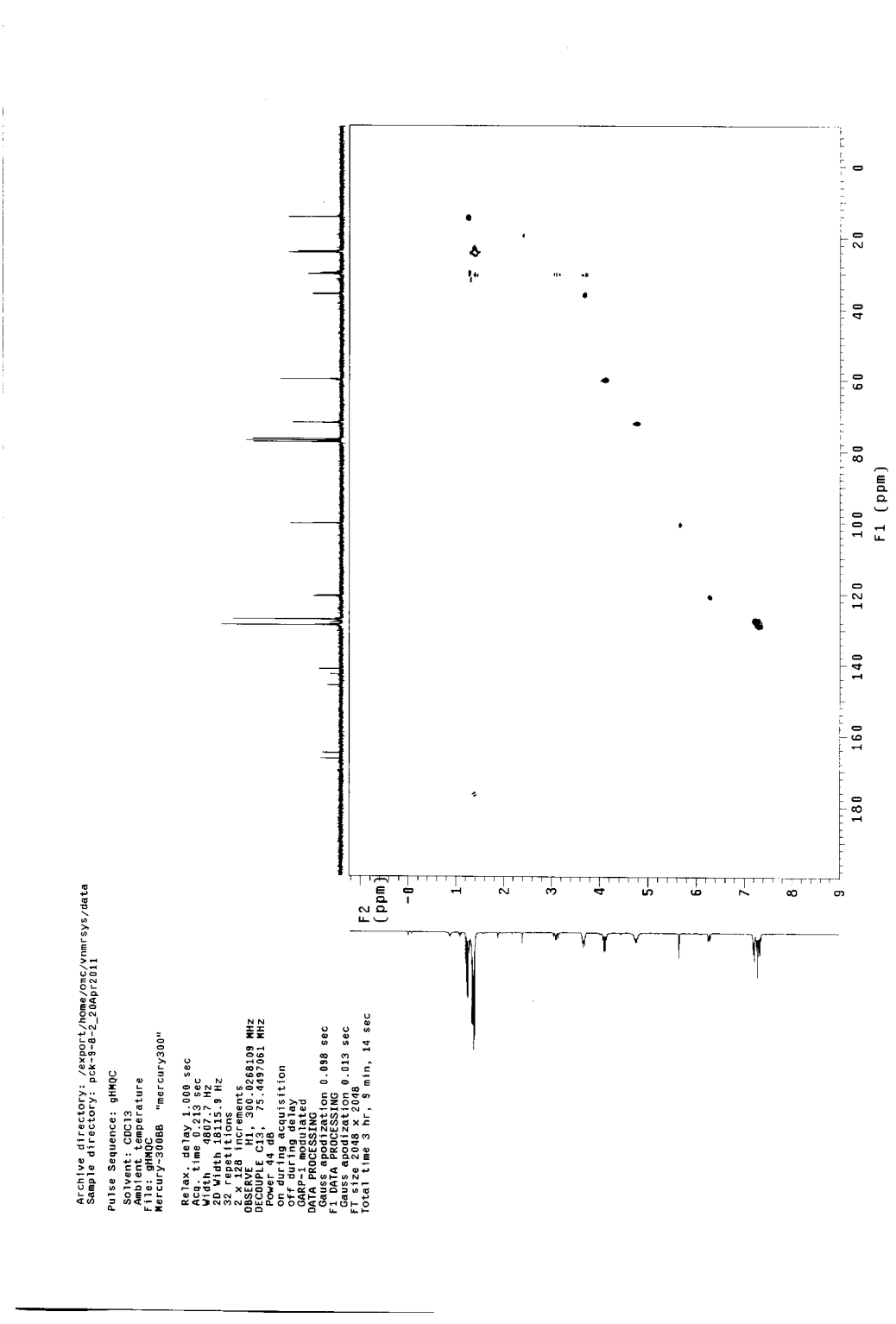
gCOSY of **4ca**


F2 (ppm)
F1 (ppm)
Archive directory: /export/home/omc/vnmrsys/data
Sample directory: pck-9-8-2_20Apr2011
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
File: gCOSY
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4807.7 HZ
2D Width 4807.7 HZ
4 repetitions
128 increments
OBSERVE H1, 300.0268109 MHz
DATA PROCESSING
Sq. sine bell 0.107 sec
FT DATA PROCESSING
Sq. sine bell 0.027 sec
FT size 2048 x 2048
Total time 11 min, 57 sec

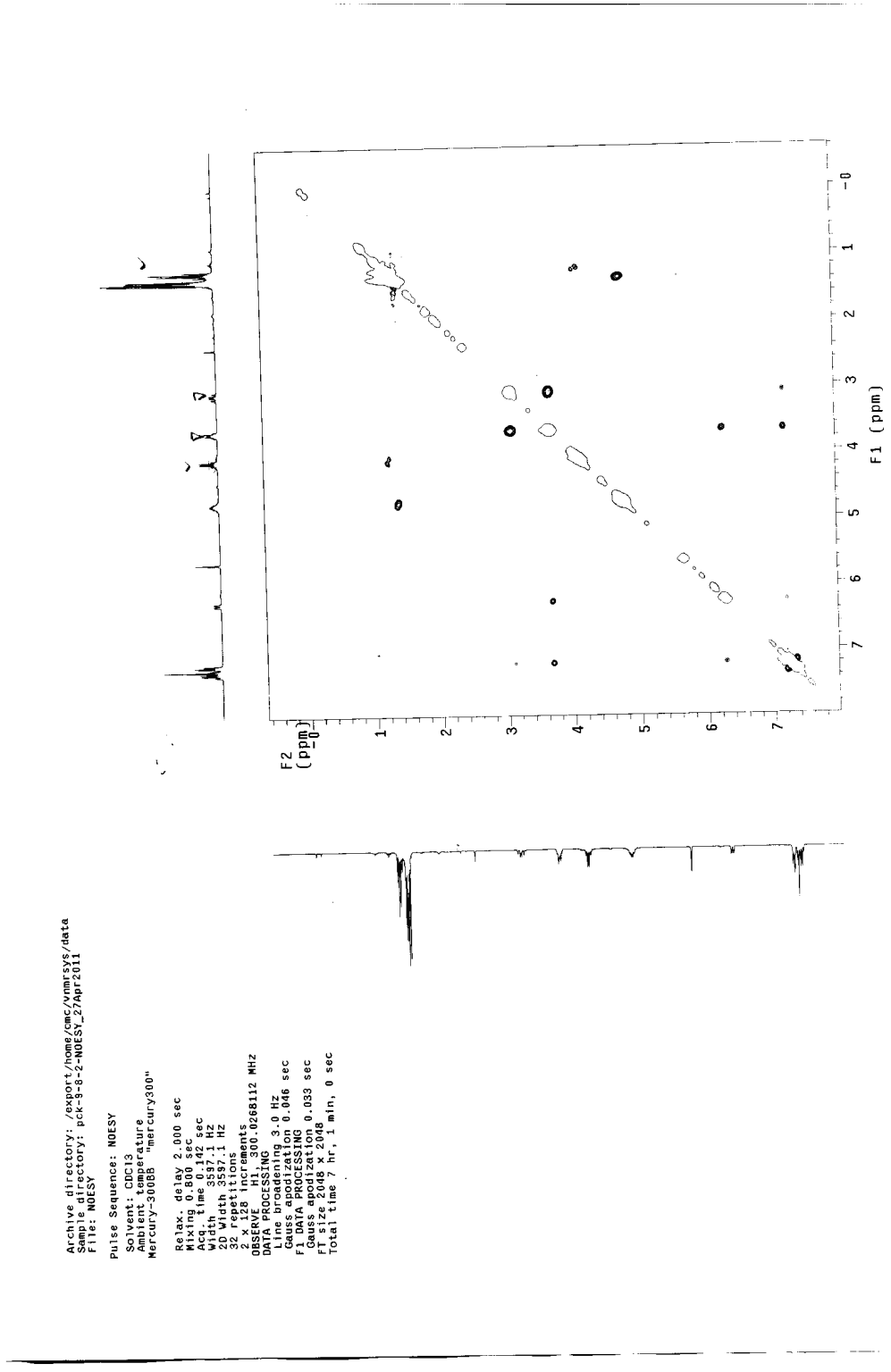
gHMBC Of **4ca**


Archive directory: /export/home/cmc/vnmrsys/data
Sample directory: pck-9-8-2_20Apr2011
File: gHMBC
Pulse Sequence: gHMBC
Solvent: CDCl3
Ambient temperature
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4801.7 Hz
2D width 19515.9 Hz
32 repetitions
200 increments
OBSERVE H1, 300.0268109 MHz
DATA PROCESSING
Sine bell 0.107 sec
F1 DATA PROCESSING
Sine bell 0.006 sec
FT size 2048 x 2048
Total time 2 hr, 30 min, 11 sec
F2 (ppm)
F1 (ppm)

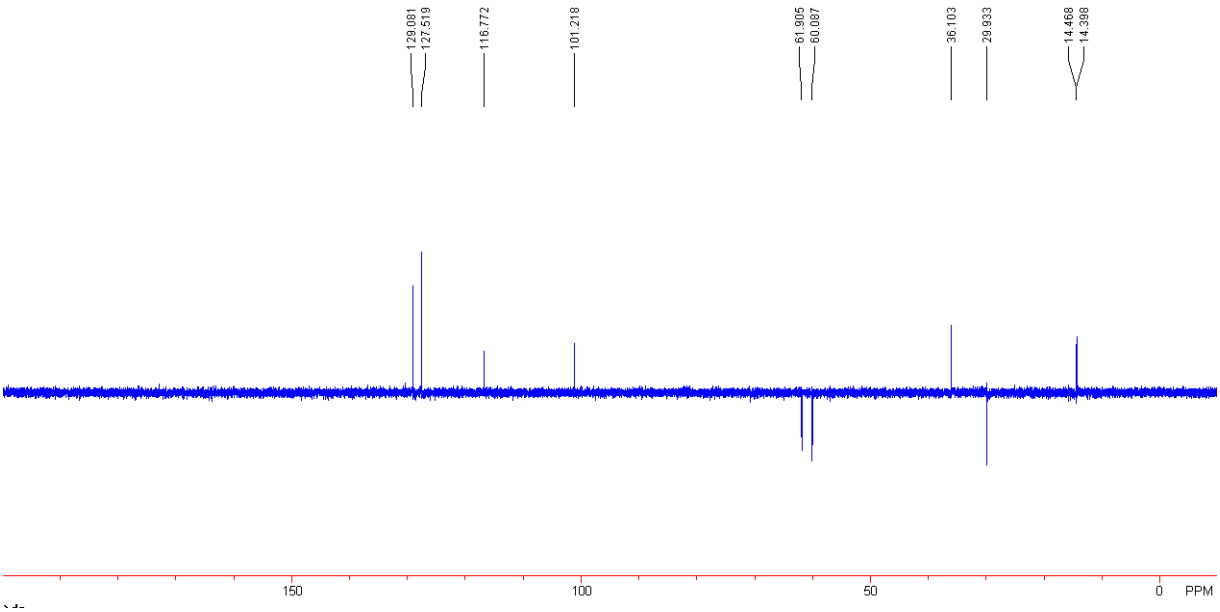
gHMQC of **4ca**


Archive directory: /export/home/onc/vnmrsys/data
Sample directory: pck-9-8-2_20Apr2011
Pulse Sequence: gHMQC
Solvent: CDCl3
Ambient temperature
File: gHMQC
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4811.7 Hz
2D Width 18115.9 Hz
32 repetitions
2 x 128 increments
OBSERVE H1, 300.0268109 MHz
DECOUPLE C13, 75.4497061 MHz
Power 44 dB
on during acquisition
off during delay
GARP-modulated
DATA PROCESSING
Gauss apodization 0.098 sec
F1 DATA PROCESSING
Gauss apodization 0.013 sec
FT size 2048 x 2048
Total time 3 hr, 9 min, 14 sec
F2 (ppm)
F1 (ppm)

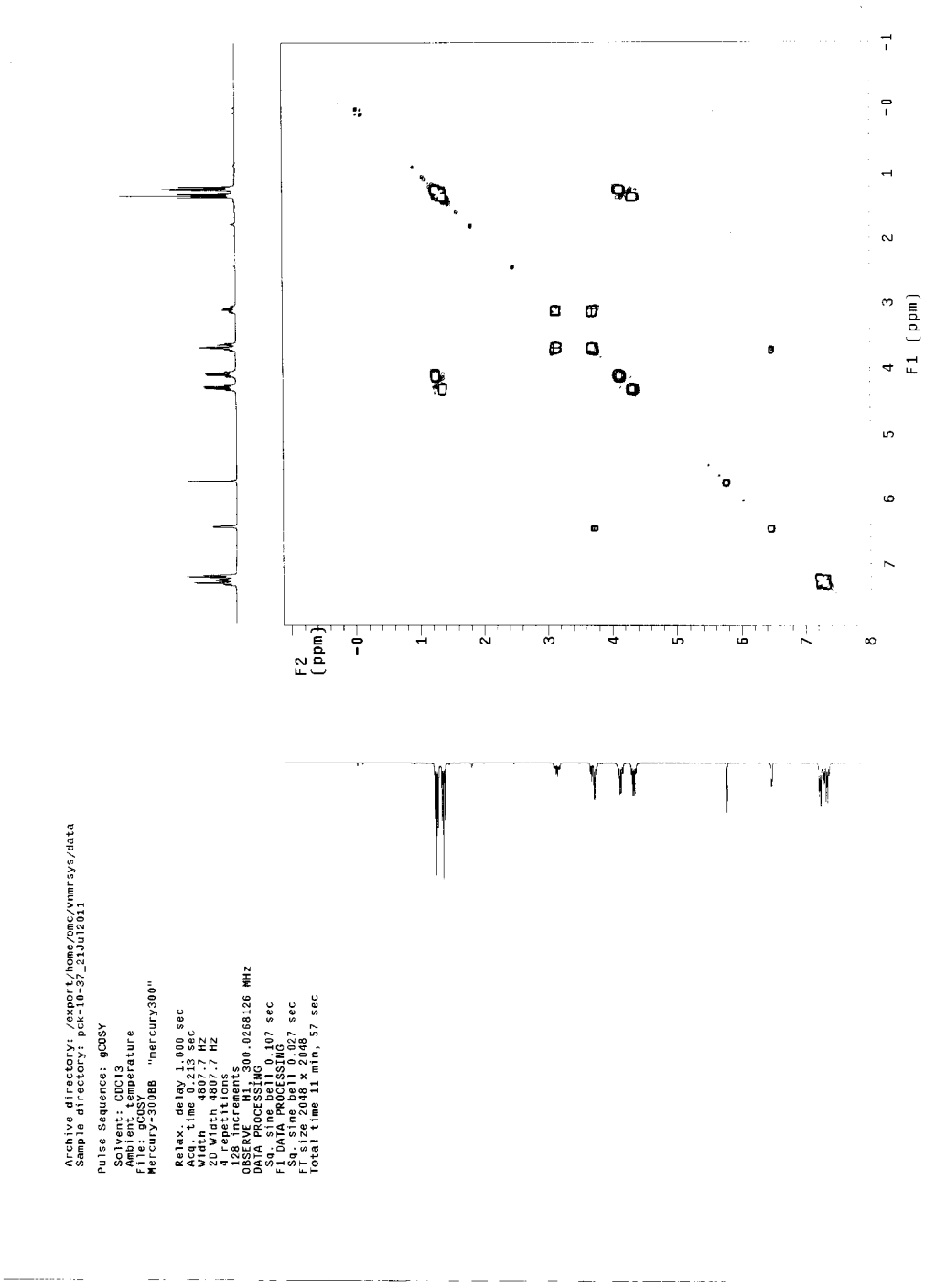
NOESY of **4ca**


F2 (ppm)
F1 (ppm)
Archive directory: /export/home/cmc/vnmrsys/data
Sample directory: pck-9-8-2-NOESY_27Apr2011
File: NOESY
Pulse Sequence: NOESY
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 2.000 sec
Mixing 0.800 sec
Acq. time 0.142 sec
Width 3597.1 Hz
2D Width 3597.1 Hz
32 repetitions
2 x 128 increments
OBSERVE H1, 300.0268112 MHz
DATA PROCESSING
Line broadening 3.0 Hz
Gauss apodization 0.046 sec
F1 DATA PROCESSING
Gauss apodization 0.033 sec
FT size 2048 x 2048
Total time 7 hr, 1 min, 0 sec

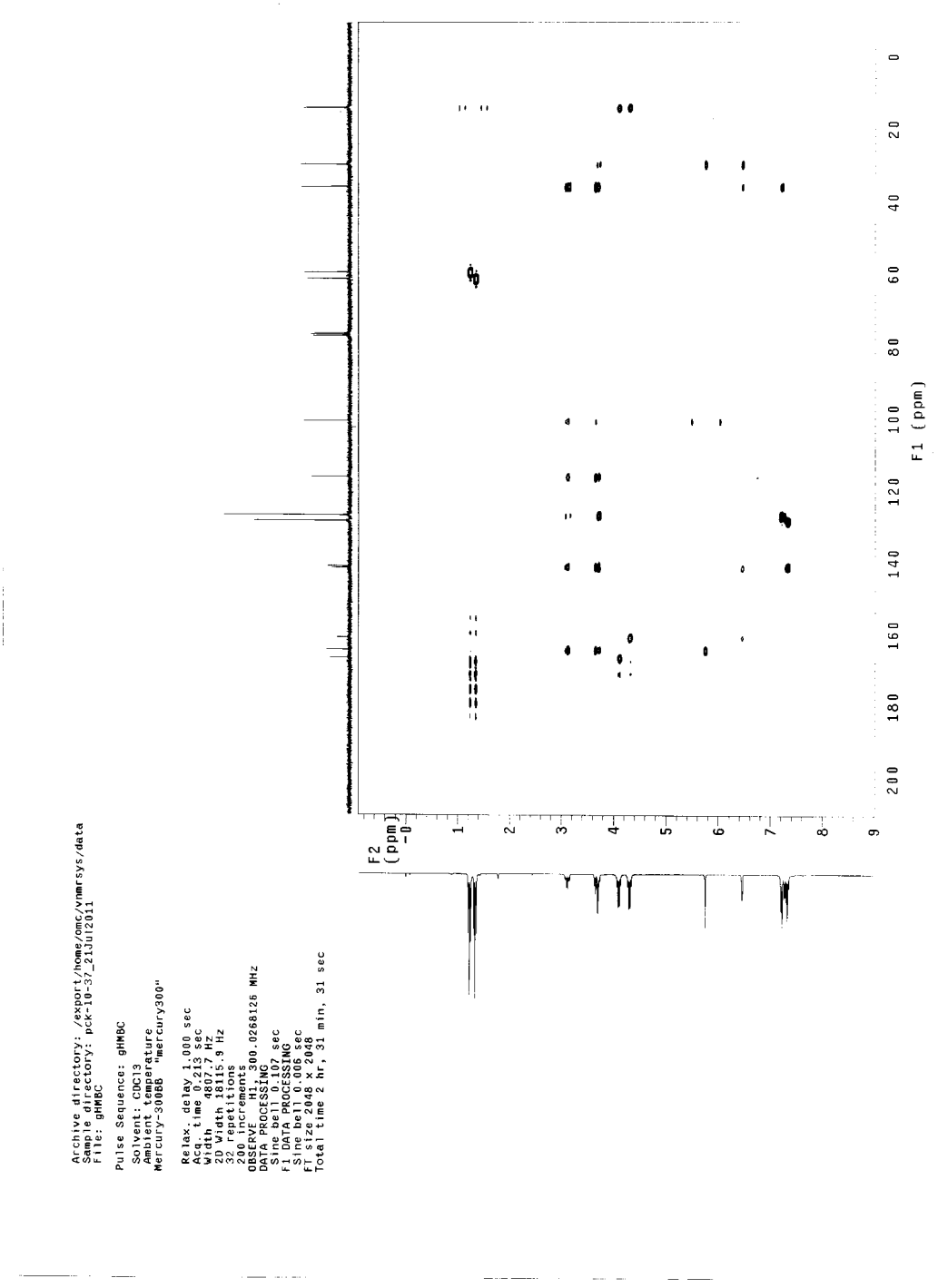
DEPT of **7aa**



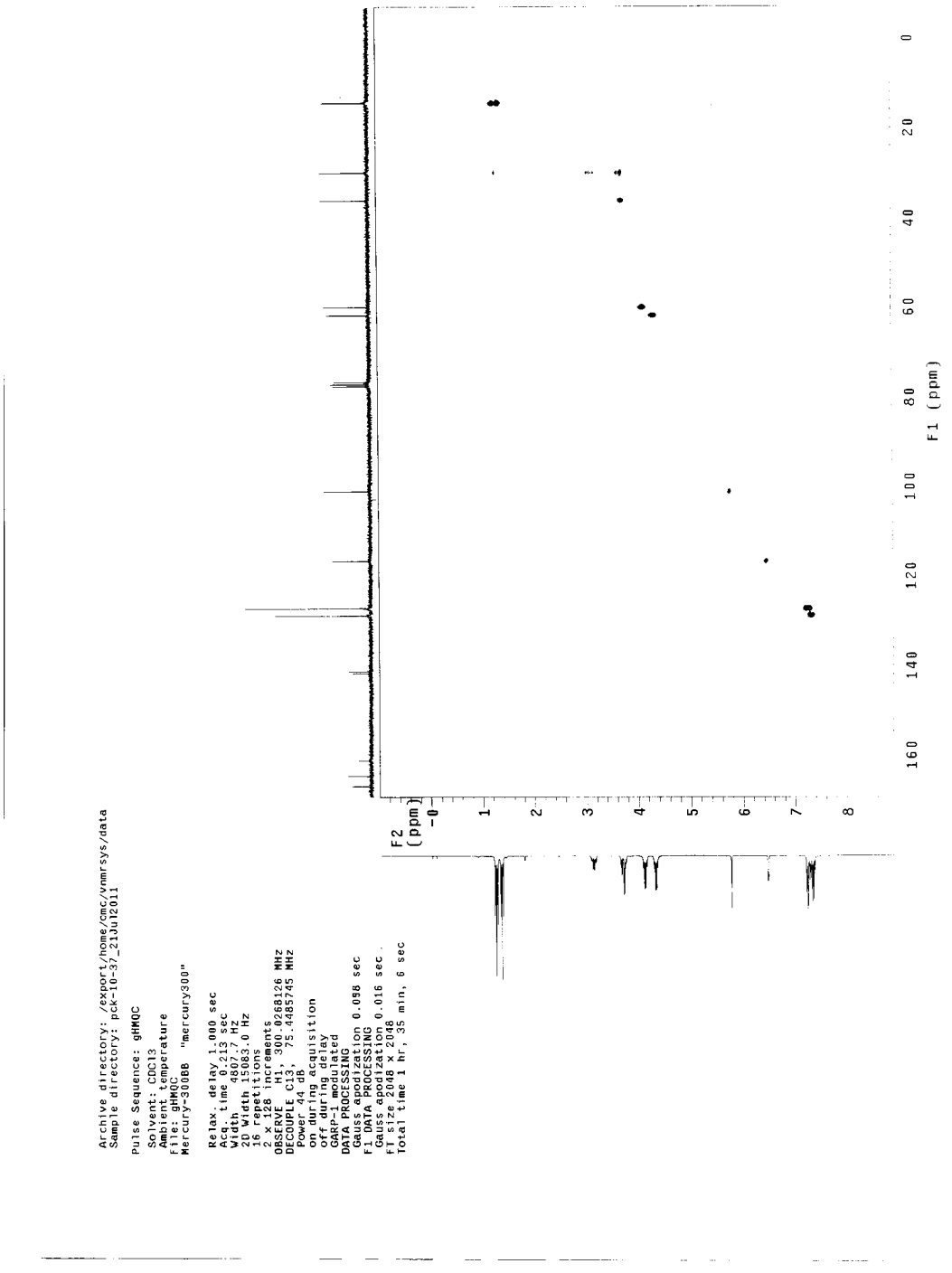
gCOSY of **7aa**


F2 (ppm)
F1 (ppm)
Archive directory: /export/home/cmc/vnmrsys/data
Sample directory: pck-10-37_21Jul2011
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
File: gCOSY
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 4807.7 Hz
4 repetitions
128 increments
OBSERVE H1, 300.0268126 MHz
DATA PROCESSING
Sq. sine bell 0.107 sec
F1 DATA PROCESSING
Sq. sine bell 0.027 sec
FT size 2048 x 2048
Total time 11 min, 57 sec

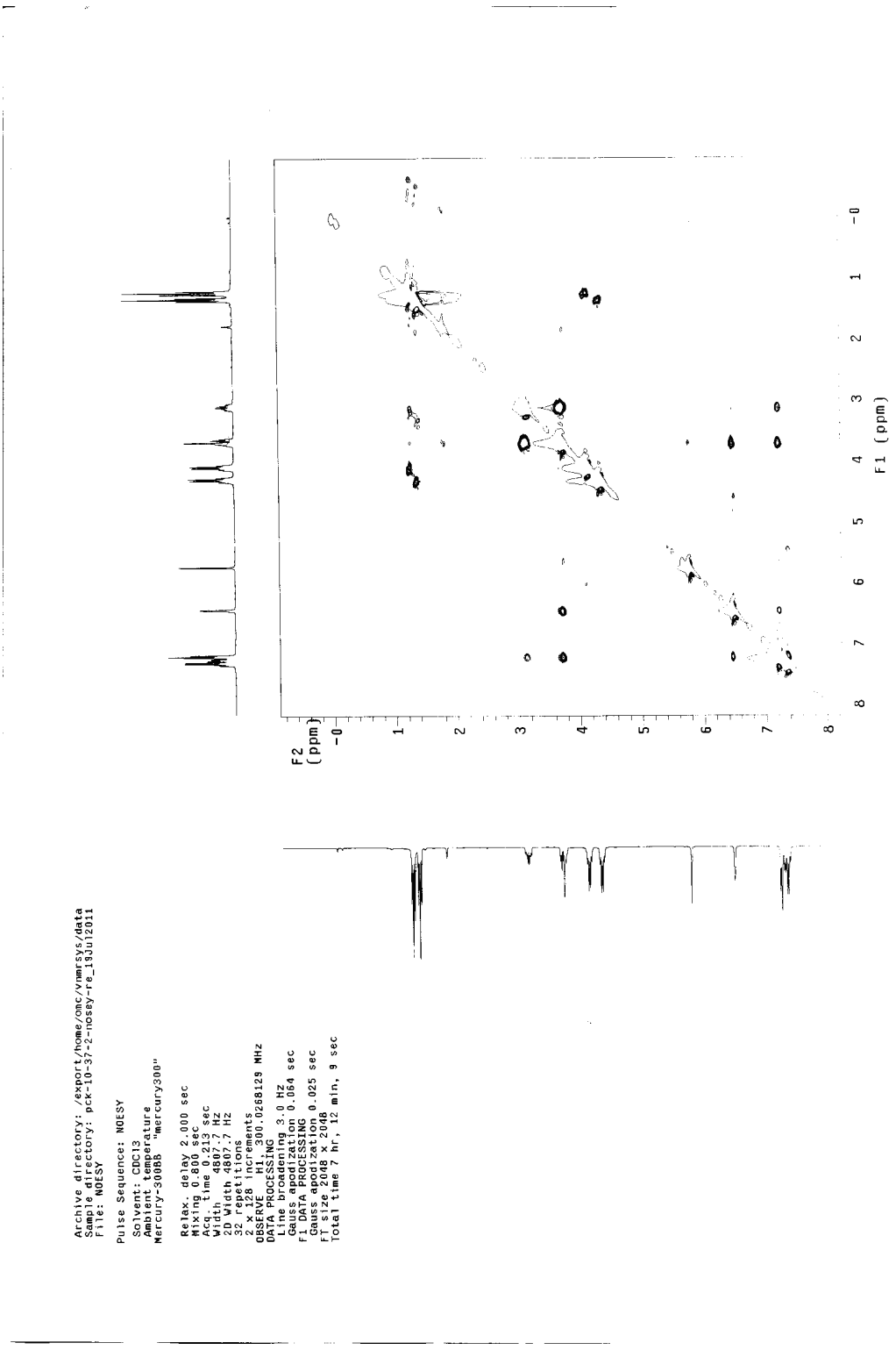
gHMBC of **7aa**


Archive directory: /export/home/omc/vnmrsys/data
Sample directory: pck-10-37_213ul2011
File: gHMBC
Pulse Sequence: gHMBC
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4807.7 HZ
2D Width 18115.9 Hz
32 repetitions
200 increments
OBSERVE H1, 300.0268126 MHz
DATA PROCESSING
Sine bell 0.107 sec
F1 DATA PROCESSING
Sine bell 0.006 sec
FT size 2048 x 2048
Total time 2 hr, 31 min, 31 sec
F2 (ppm)
F1 (ppm)

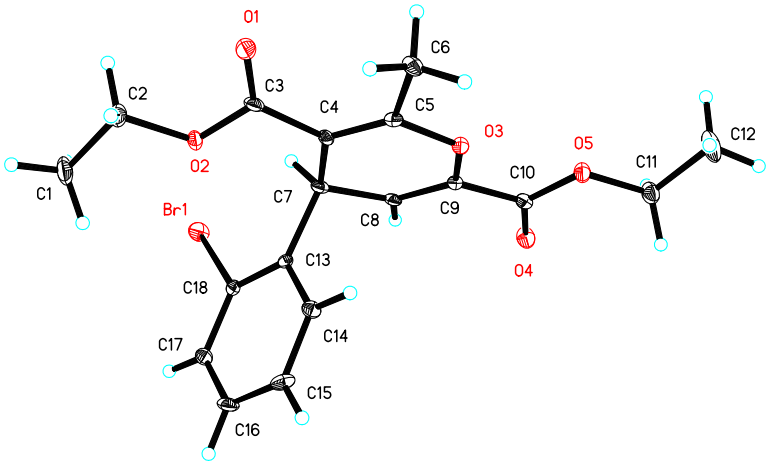
gHMQC of **7aa**


Archive directory: /export/home/cmc/vnmrsys/data
Sample directory: pck-10-37_21Jul2011
Pulse Sequence: gHMQC
Solvent: CDCl3
Ambient temperature
File: gHMQC
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 15083.0 Hz
16 repetitions
256 x 128 increments
OBSERVE H1, 300.0268126 MHz
DECOUPLE C13, 75.4485745 MHz
Power 44 dB
on during acquisition
off during delay
GARP-1 modulated
DATA PROCESSING
Gauss apodization 0.058 sec
FT of PROCESSING
Gauss apodization 0.016 sec.
FT size 2048 x 2048
Total time 1 hr, 35 min, 6 sec
F2 (ppm)
F1 (ppm)

NOSEY of **7aa**


F2 (ppm)
F1 (ppm)
Archive directory: /export/home/omc/vnmrsys/data
Sample directory: pck-10-37-2-nosey-re_19Jul2011
File: NOESY
Pulse Sequence: NOESY
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 2.000 sec
Mixing 0.800 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 4807.7 Hz
32 repetitions
2 x 128 increments
OBSERVE H1, 300.0268128 MHz
DATA PROCESSING
Line broadening 3.0 Hz
Gauss apodization 0.064 sec
F1 DATA PROCESSING
Gauss apodization 0.025 sec
FT size 2048 x 2048
Total time 7 hr, 12 min, 9 sec

The X-ray Crystal Data of 6ea



The crystal data of compound **6ea** have been deposited in CCDC with number 833190. Empirical Formula: $C_{18}H_{19}BrO_5$; Formula Weight: 395.24; Crystal Color, Habit: colorless; Crystal Dimensions: 0.28 x 0.15 x 0.10 mm; Crystal System: Triclinic; Lattice Type: Primitive; Lattice Parameters: a = 8.5579(17)Å, b = 9.7108(19)Å, c = 11.568(3)Å, α = 73.985(4)^o, β = 68.692(3)^o, γ = 73.448(3)^o, V = 842.4(3)Å^3; Space group: P-1; Z = 2; D_{calc}= 1.558 g/cm^3; F_{000} = 404; Final R indices [I>2sigma(I)]: R1 = 0.0438; wR2 = 0.1321.