J. Braz. Chem. Soc., Vol. 23, No. 5, S1-S39, 2012.
Printed in Brazil - ©2012 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Supplementary Information

Knoevenagel Condensation of Aromatic Aldehydes with Ethyl 4-Chloro-3-oxobutanoate in Ionic Liquids

Bruno R. S. de Paula,[a] Dávila S. Zampieri,[a] Julio Zukerman-Schpector,[b] Edward R. T. Tiekink,[c] José Augusto R. Rodrigues[a] and Paulo J. S. Moran*,[a]

[a]*Institute of Chemistry, University of Campinas, CP 6154, 13084-971 Campinas-SP, Brazil*

[b]*Department of Chemistry, Federal University of São Carlos, 13565-905 São Carlos-SP, Brazil*

[c]*Department of Chemistry, University of Malaya, 50603 Kuala Lampur, Malaysia*

Ethyl (*E*)-2-chloroacetyl-3-phenylpropenoate, (*E*)-**3a**

Following the general procedure, a mixture of (*E*/*Z*)-**3a** was obtained in 79% yield after column chromatography. The (*E*)-isomer was obtained as pale yellow oil; retention time on GC/MS: 11.903 min; EI-MS *m/z* 252/254 (25/8) [M$^+$], 207/209 (13/5), 203 (100), 175 (11), 135 (24), 131 (21), 107 (23), 103 (21), 102 (22), 91 (8), 77/79 (19/6); IR (film) ν/cm^{-1} 3060, 2983, 2936, 1723, 1699, 1621, 1258, 1199, 767, 692; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.34 (t, 3H, *J* 7.25 Hz), 4.29 (s, 2H), 4.32 (q, 2H, *J* 7.25 Hz), 7.37-7.43 (m, 5H), 7.85 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 49.2, 61.9, 129.1, 129.8, 130.5, 131.0, 132.4, 144.1, 163.8, 196.6; EI-HRMS (M$^+$) calcd.: 252.0553/254.0528. Found: 252.0511/254.0516.

Ethyl (*Z*)-2-chloroacetyl-3-phenylpropenoate, (*Z*)-**3a**

Following the general procedure, a mixture of (*E*/*Z*)-**3a** was obtained in 79% yield after column chromatography. The (*Z*)-isomer was obtained as pale yellow oil; retention time on GC/MS: 11.980 min; EI-MS *m/z* 252/254 (25/8) [M$^+$], 207/209 (17/5), 203 (100), 175 (11), 135 (23), 131 (21), 107 (23), 103 (21), 102 (23), 91 (8), 77/79 (19/6); IR (film) ν/cm^{-1} 3056, 2983, 2938, 1728, 1687, 1621, 1598, 1227, 1179, 755, 693; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.25 (t, 3H, *J* 7.25 Hz), 4.32 (q, 2H, *J* 7.25 Hz), 4.48 (s, 2H), 7.39-7.47 (m, 5H), 7.79 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 13.7, 46.0, 62.0, 128.8, 129.9, 130.9, 131.1, 132.8, 144.4, 167.0, 188.3; EI-HRMS (M$^+$) calcd.: 252.0553/254.0528. Found: 252.0523/254.0511.

*e-mail: moran@iqm.unicamp.br

Ethyl (*E*)-2-chloroacetyl-3-(4'-chlorophenyl)propenoate, (*E*)-**3b**

Following the general procedure, a mixture of (*E*/*Z*)-**3b** was obtained in 57% yield after column chromatography. The (*E*)-isomer was obtained as pale yellow oil; retention time on GC/MS: 12.767 min; EI-MS *m/z* 286/288/290 (9/6/1) [M$^+$], 241/243/245 (11/6/1), 237/239 (100/35), 209/211 (12/4), 169/171 (18/6), 165/167 (20/6), 141/143 (20/7), 115 (7), 101 (17), 77/79 (9/3); IR (film) ν/cm^{-1} 2983, 2936, 1724, 1703, 1622, 1591, 1492, 1256, 1197, 1092, 828; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.34 (t, 3H, *J* 7.25 Hz), 4.30 (s, 2H), 4.32 (q, 2H, *J* 7.25 Hz), 7.30-7.39 (m, 4H), 7.79 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 14.1, 49.0, 62.0, 129.4, 130.8, 131.0, 137.3, 142.8, 163.6, 196.5; EI-HRMS (M$^+$) calcd.: 286.0164/288.0136. Found: 286.0153/288.0125.

Ethyl (*Z*)-2-chloroacetyl-3-(4'-chlorophenyl)propenoate, (*Z*)-**3b**

Following the general procedure, a mixture of (*E*/*Z*)-**3b** was obtained in 57% yield after column chromatography. The (*Z*)-isomer was obtained as white solid; mp 72.5-74.6 °C; retention time on GC/MS: 12.822 min; EI-MS *m/z* 286/288/290 (10/6/1) [M$^+$], 241/243/245 (12/8/1), 237/239 (100/33), 209/211 (11/4), 169/171 (19/6), 165/167 (22/6), 141/143 (20/7), 115 (7), 101 (17), 77/79 (9/3); IR (KBr) ν/cm^{-1} 3058, 2988, 2936, 1702, 1590, 1562, 1492, 1377, 1236, 1092, 1030, 833, 765; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.27 (t, 3H, *J* 7.25 Hz), 4.46 (s, 2H), 4.32 (q, 2H, *J* 7.25 Hz), 7.30-7.39 (m, 4H), 7.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 13.8, 46.2, 62.1, 129.1, 131.1, 131.2, 131.2, 137.3, 143.1, 166.7, 188.2; EI-HRMS (M$^+$) calcd.: 286.0164/288.0136. Found: 286.0169/288.0142.

Ethyl (*E*)-2-chloroacetyl-3-(4'-methoxyphenyl)propenoate, (*E*)-**3c**

Following the general procedure, a mixture of (*E*/*Z*)-**3c** was obtained in 67% yield after column chromatography. The (*E*)-isomer was obtained as pale yellow solid; mp 43-44 °C; retention time on GC/MS:13.524 min; EI-MS *m/z* 282/284 (15/5) [M^+], 237/239 (10/4), 233 (100), 205 (12), 189 (6), 161 (12), 145 (16), 137 (14), 133 (7), 117 (16), 89 (19), 77/79 (9/2); IR (KBr) ν/cm^{-1} 2988, 2944, 2846, 1716, 1618, 1602, 1568, 1513, 1259, 1205, 1181, 831, 758; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.33 (t, 3H, *J* 7.25 Hz), 3.84 (s, 3H), 4.32 (q, 2H, *J* 7.25 Hz), 4.34 (s, 2H), 6.75 (d, 2H, *J* 8.75 Hz), 7.34 (d, 2H, *J* 8.75 Hz), 7.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 14.2, 49.3, 55.4, 61.7, 114.6, 124.9, 127.6, 132.0, 144.0, 162.0, 164.2, 197.0; EI-HRMS (M^+) calcd.: 282.0659/284.0634. Found: 282.0650/284.0633.

Ethyl (*Z*)-2-chloroacetyl-3-(4'-methoxyphenyl)propenoate, (*Z*)-**3c**

Following the general procedure, a mixture of (*E*/*Z*)-**3c** was obtained in 67% yield after column chromatography. The (*Z*)-isomer was obtained as pale yellow solid; mp 42-43 °C; retention time on GC/MS: 13.679 min; EI-MS *m/z* 282/284 (16/6) [M^+], 237/239 (11/4), 233 (100), 205 (13), 189 (7), 161 (14), 145 (6), 137 (15), 133 (8), 117 (10), 89 (12), 77/79 (12/3); IR (film) 2981, 2939, 2842, 1725, 1681, 1599, 1569, 1513, 1324, 1309, 1265, 1223, 1176, 1131, 1111, 1027, 830, 776; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.31 (t, 3H, *J* 7.25 Hz), 3.86 (s, 3H), 4.36 (q, 2H, *J* 7.25 Hz), 4.46 (s, 2H), 6.91 (d, 2H, *J* 8.75 Hz), 7.45 (d, 2H, *J* 8.75 Hz), 7.71 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 13.9, 46.2, 55.4, 61.9, 114.4, 125.1, 128.3, 132.4, 144.2, 162.3, 167.5, 188.3; EI-HRMS (M^+) calcd.: 282.0659/284.0634. Found: 282.0657/284.0648.

Ethyl (*E*)-2-chloroacetyl-3-(3',4'-methylenedioxyphenyl) propenoate, (*E*)-**3d**

Following the general procedure, a mixture of (*E*/*Z*)-**3d** was obtained in 82% yield after column chromatography. The (*E*)-isomer was obtained as white solid; mp 94.1-94.4 °C; retention time on GC/MS: 13.926 min; EI-MS *m/z* 296/298 (29/10) [M^+], 251/253 (9/3), 247 (100), 219 (9), 203 (6), 189 (11), 179 (15), 173 (15), 151 (11), 145 (21), 117 (8), 89 (14), 77/79 (7/2); IR (KBr) ν/cm^{-1} 2990, 2929, 1729, 1686, 1619, 1597, 1504, 1452, 1386, 1290, 1265, 1253, 1035, 925, 811, 776; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.33 (t, 3H, *J* 7.25 Hz), 4.30 (q, 2H, *J* 7.25 Hz), 4.33 (s, 2H), 6.02 (s, 3H), 6.81-6.96 (m, 3H), 7.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 14.2, 49.2, 61.8, 101.9, 108.9, 126.5, 128.4, 144.0, 148.5, 150.3, 164.0, 196.9; EI-HRMS (M^+) calcd.: 296.0452/298.0428. Found: 296.0320/298.0342.

Ethyl (*Z*)-2-chloroacetyl-3-(3',4'-methylenedioxyphenyl) propenoate, (*Z*)-**3d**

Following the general procedure, a mixture of (*E*/*Z*)-**3d** was obtained in 82% yield after column chromatography. The (*Z*)-isomer was obtained as yellow oil; retention time on GC/MS: 14.058 min; EI-MS *m/z* 296/298 (32/11) [M^+], 251/253 (12/4), 247 (100), 219 (9), 203 (6), 189 (11), 179 (14), 173 (16), 151 (10), 145 (21), 117 (8), 89 (15), 77/79 (8/2); IR (film) 2984, 2940, 2906, 1724, 1684, 1619, 1596, 1505, 1491, 1451, 1266, 1235, 1179, 1105, 1039, 928, 811, 787; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.33 (t, 3H, *J* 7.25 Hz), 4.36 (q, 2H, *J* 7.25 Hz), 4.44 (s, 2H), 6.03 (s, 3H), 6.82-7.03 (m, 3H), 7.65 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.9, 46.2, 62.0, 101.9, 108.7, 108.8, 126.7, 127.4, 128.7, 144.0, 148.3, 150.6, 167.3, 188.2; EI-HRMS (M^+) calcd.: 296.0452/298.0428. Found: 296.0308/298.0331.

Ethyl (*E*)-2-chloroacetyl-3-(2'-furanyl)propenoate, (*E*)-**3e**

Following the general procedure, a mixture of (*E*/*Z*)-**3e** was obtained in 84% yield after column chromatography. The (*E*)-isomer was obtained as yellow oil; retention time on GC/MS: 11.315 min; EI-MS *m/z* 242/244 (17/6) [M^+], 197/199 (11/4), 193 (100), 165 (21), 149 (8), 121 (25), 97 (9), 77/79 (10/2); IR (film) ν/cm^{-1} 3135, 2984, 2946, 1718, 1698, 1626, 1471, 1392, 1370, 1260, 1247, 1211, 1022, 759; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.33 (t, 3H, *J* 7.50 Hz), 4.29 (q, 2H, *J* 7.50 Hz), 4.48 (s, 2H), 6.52 (dd, 1H, *J* 2.00, 3.50 Hz), 6.84 (d, 1H, *J* 3.50 Hz), 7.52 (s, 1H), 7.55 (d, 1H, *J* 2.00 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 49.1, 61.7, 112.9, 119.0, 125.8, 128.8, 146.8, 148.8, 163.9, 195.3; EI-HRMS (M^+) calcd.: 242.0346/244.0320. Found: 242.0320/244.0329.

Ethyl (*Z*)-2-chloroacetyl-3-(2'-furanyl)propenoate, (*Z*)-**3e**

Following the general procedure, a mixture of (*E*/*Z*)-**3e** was obtained in 84% yield after column chromatography. The (*Z*)-isomer was obtained as light tan solid; mp 65.5-66.3 °C; retention time on GC/MS: 11.517 min; EI-MS *m/z* 242/244 (16/5) [M^+], 197/199 (13/4), 193 (100), 165 (20), 149 (8), 121 (27), 97 (9), 77/79 (12/3); IR (KBr) 3149, 3131, 2994, 2981, 2942, 1725, 1678, 1621, 1471, 1378, 1281, 1240, 1211, 1185, 1171, 1019, 774, 590; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.39 (t, 3H, *J* 7.50 Hz), 4.42 (q, 2H, *J* 7.50 Hz), 4.44 (s, 2H), 6.56 (dd,

1H, *J* 2.00, 3.50 Hz), 6.99 (d, 1H, *J* 3.50 Hz), 7.52 (s, 1H), 7.59 (d, 1H, *J* 2.00 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 14.1, 46.3, 61.9, 113.3, 120.7, 125.9, 129.2, 147.1, 149.0, 166.6, 187.8; EI-HRMS (M^+) calcd.: 242.0346/244.0320. Found: 242.0320/244.0329.

Ethyl (*E*)-2-chloroacetyl-3-(2'-thiofuranyl)propenoate, (*E*)-**3f**

Following the general procedure, a mixture of (*E*/*Z*)-**3f** was obtained in 44% yield after column chromatography. The (*E*)-isomer was obtained as yellow oil; retention time on GC/MS: 12.270 min; EI-MS *m/z* 258/260 (14/5) [M^+], 213/215 (10/4), 209 (100), 181 (18), 165 (9), 141 (12), 137 (18), 121 (5), 113 (13), 109 (16), 97 (4), 82 (3), 77/79 (6/2); IR (film) ν/cm^{-1} 3106, 2981, 2930, 2852, 1698, 1607, 1417, 1395, 1368, 1270, 1249, 1204, 1029, 720; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.36 (t, 3H, *J* 7.00 Hz), 4.33 (q, 2H, *J* 7.00 Hz), 4.51 (s, 2H), 7.13 (dd, 1H, *J* 4.00, 5.00 Hz), 7.43 (d, 1H, *J* 4.00 Hz), 7.60 (d, 1H, *J* 5.00 Hz), 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.2, 49.1, 61.8, 125.2, 128.1, 133.6, 135.8, 136.7, 138.4, 164.5, 195.4; EI-HRMS (M^+) calcd.: 258.0117/260.0090. Found: 258.0172/260.0238.

Ethyl (*Z*) -2-chloroacetyl-3-(2'-thiofuranyl)propenoate, (*Z*)-**3f**

Following the general procedure, a mixture of (*E*/*Z*)-**3f** was obtained in 44% yield after column chromatography. The (*Z*)-isomer was obtained as pale yellow oil; retention time on GC/MS: 12.478 min; EI-MS *m/z* 258/260 (13/5) [M^+], 213/215 (11/4), 209 (100), 181 (17), 165 (10), 141 (12), 137 (19), 121 (5), 113 (13), 109 (16), 97 (5), 82 (4), 77/79 (7/2); IR (film) ν/cm^{-1} 3106, 2983, 2938, 1722, 1683, 1605, 1578, 1418, 1266, 1206, 1171, 1126, 1022, 860, 720; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.41 (t, 3H, *J* 7.50 Hz), 4.44 (q, 2H, *J* 7.50 Hz), 4.48 (s, 2H), 7.14 (dd, 1H, *J* 4.00, 5.00 Hz), 7.54 (d, 1H, *J* 4.00 Hz), 7.67 (d, 1H, *J* 5.00 Hz), 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0, 47.0, 62.0, 125.3, 127.8, 134.6, 136.1, 138.3, 138.6, 166.1, 189.2; EI-HRMS (M^+) calcd.: 258.0117/260.0090. Found: 258.0083/260.0353.

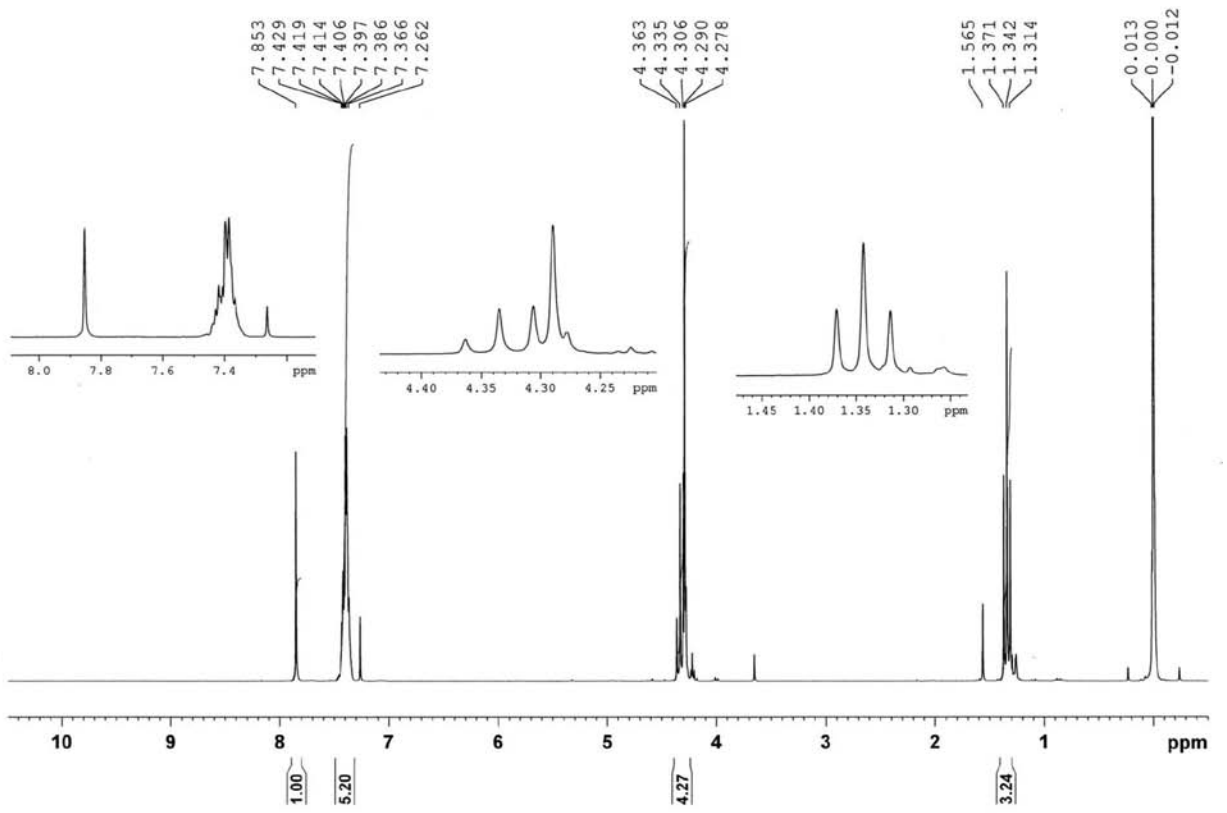


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of ethyl (*E*)-2-chloroacetyl-3-phenylpropenoate (*E*-**3a**).

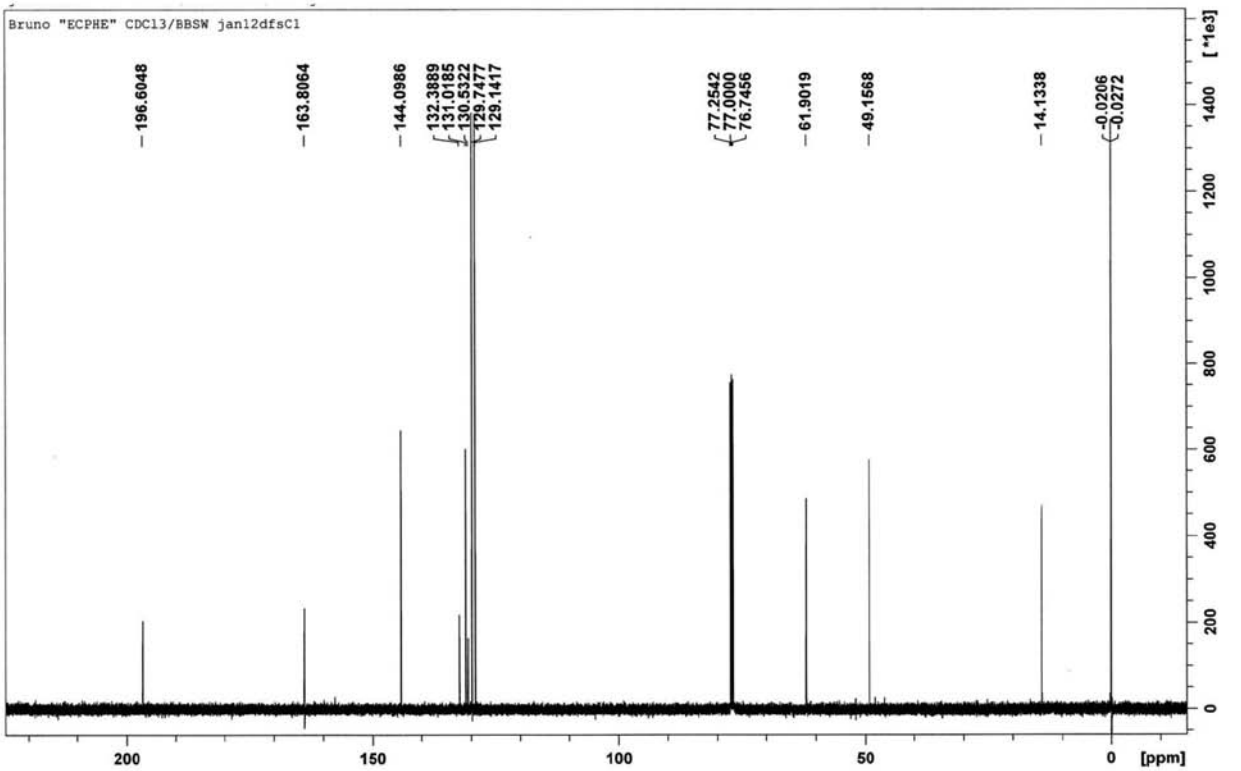


Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of ethyl (*E*)-2-chloroacetyl-3-phenylpropenoate (*E*-**3a**).

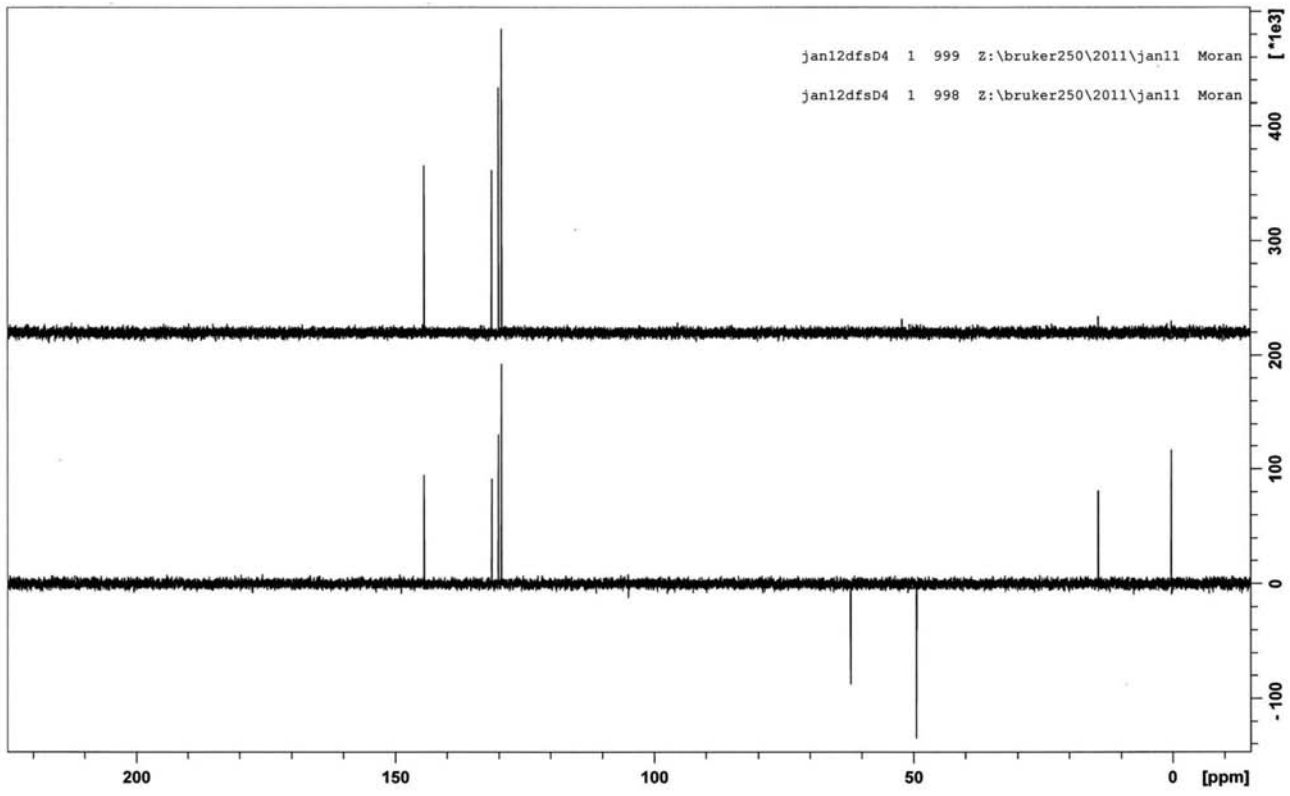


Figure S3. DEPT-90 and DEPT-135 spectra ($CDCl_3$, 125 MHz) of ethyl (*E*)-2-chloroacetyl-3-phenylpropenoate (*E*-**3a**).

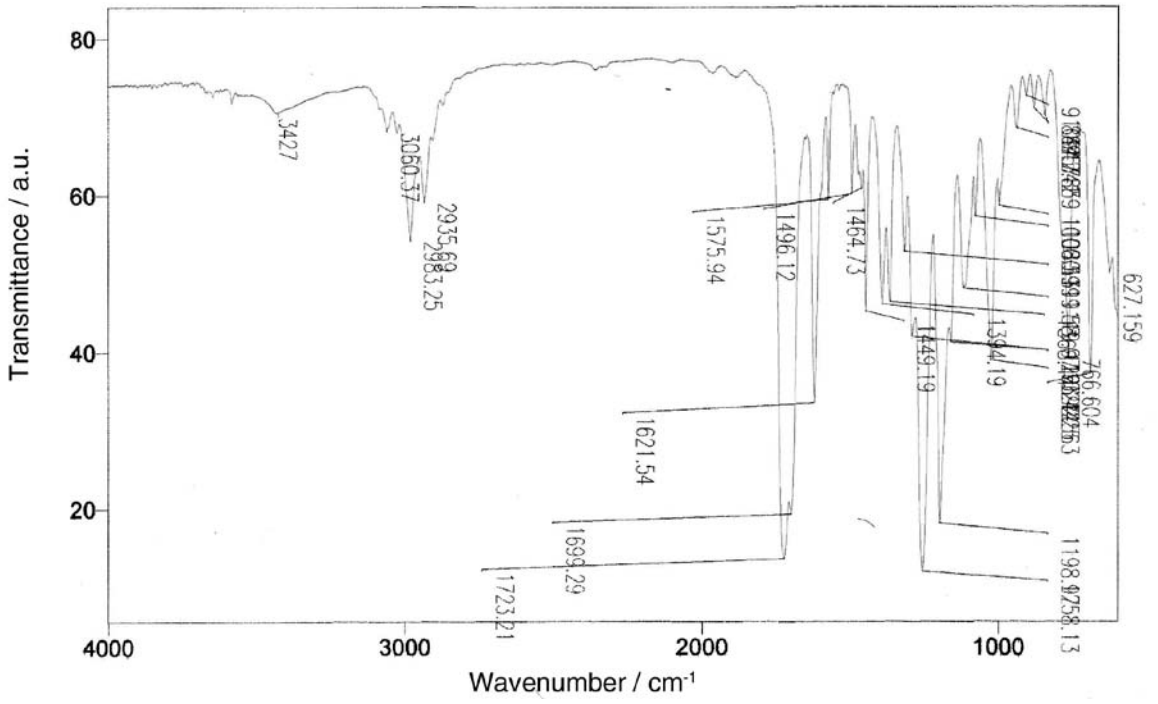


Figure S4. IR spectrum (film) of ethyl (*E*)-2-chloroacetyl-3-phenylpropenoate (*E*-**3a**).

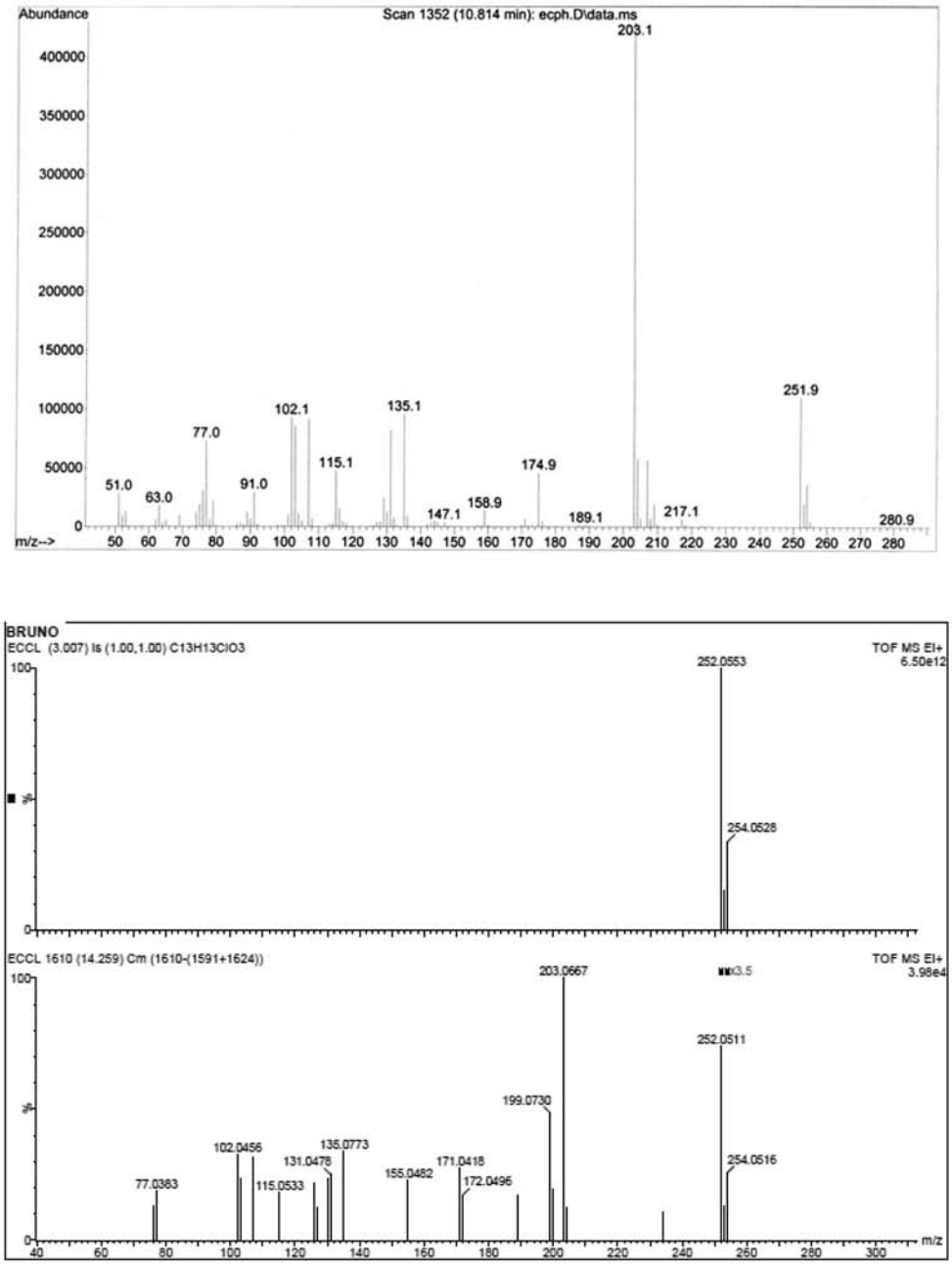


Figure S5. MS and HRMS (EI) spectra of ethyl (*E*)-2-chloroacetyl-3-phenylpropenoate (*E*-**3a**).

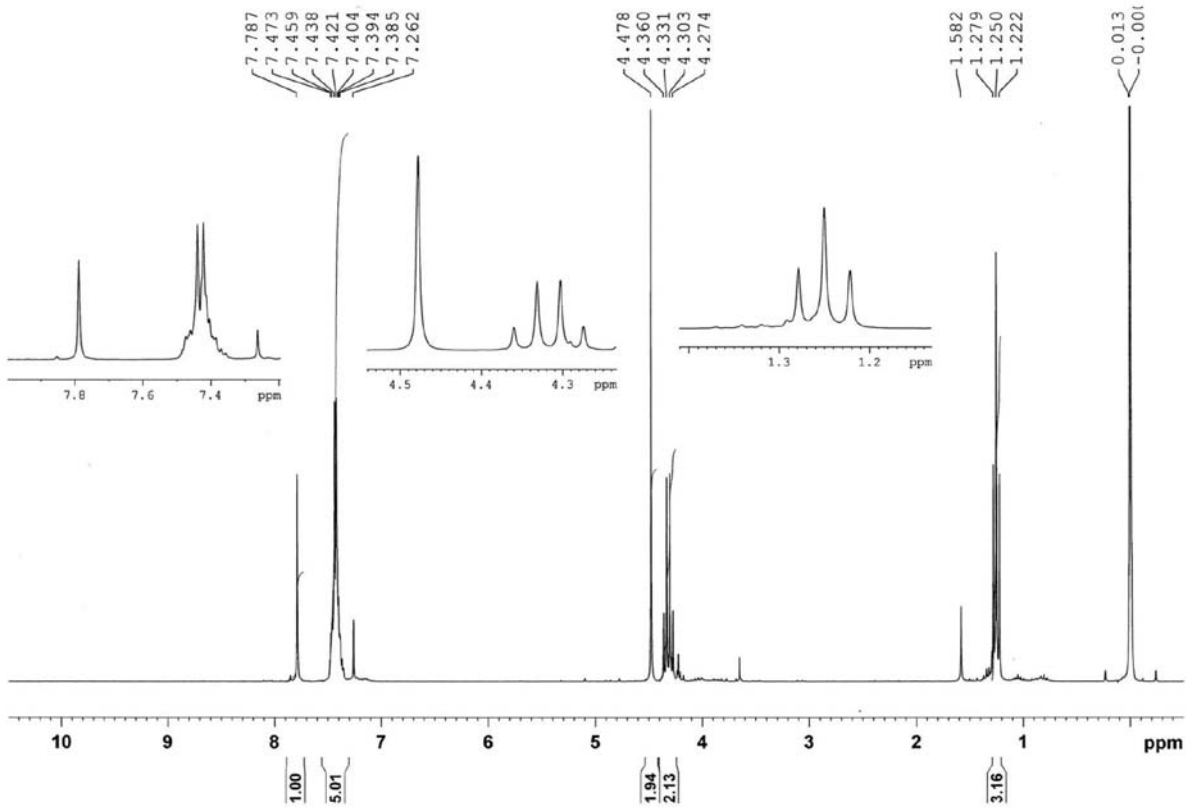


Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of ethyl (*Z*)-2-chloroacetyl-3-phenylpropenoate (*Z*-**3a**).

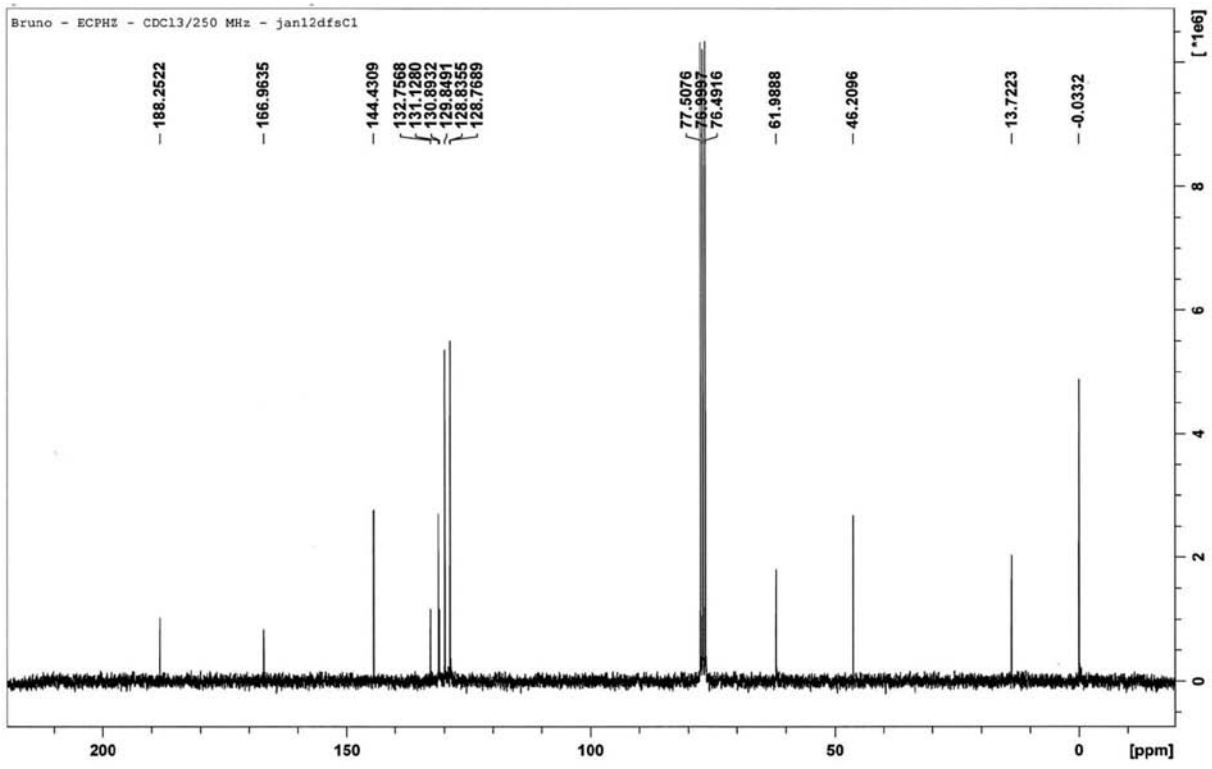


Figure S7. ^{13}C NMR spectrum ($CDCl_3$, 62.5 MHz) of ethyl (*Z*)-2-chloroacetyl-3-phenylpropenoate (*Z*-**3a**).

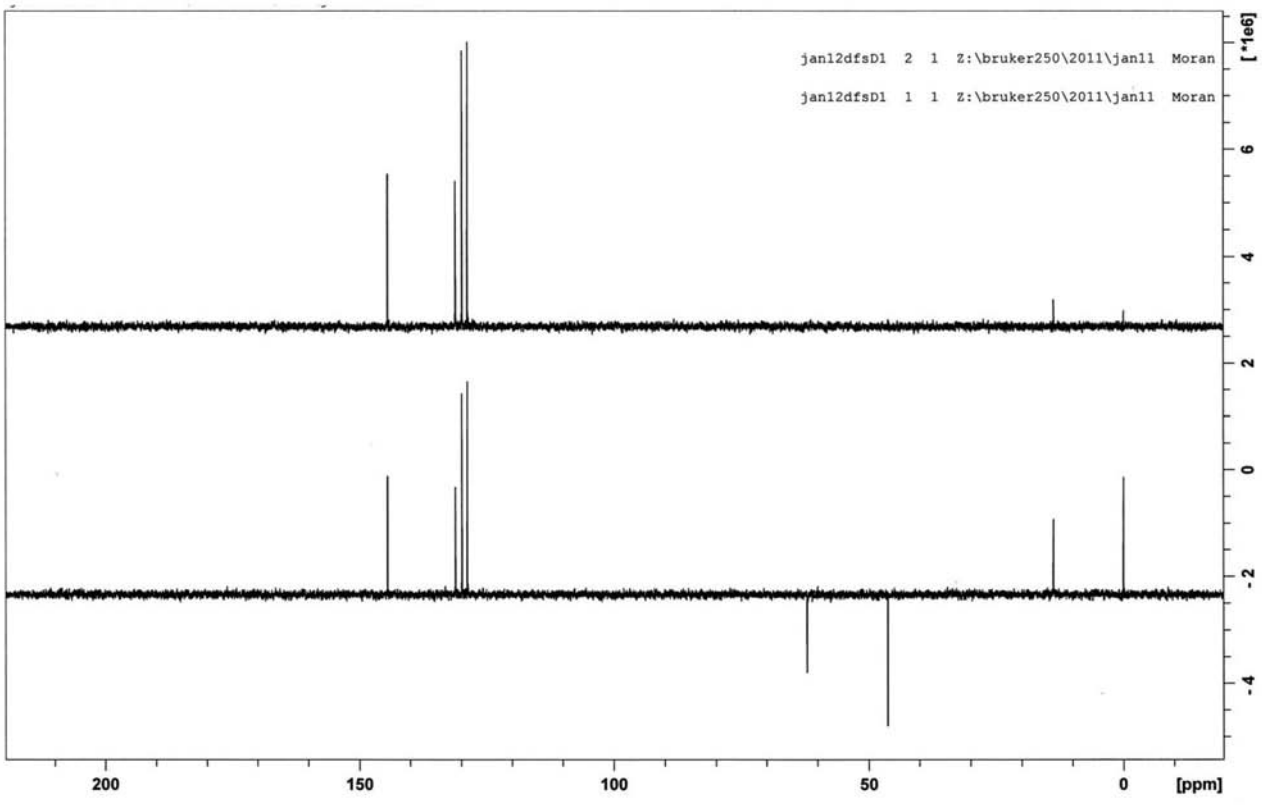


Figure S8. DEPT-90 and DEPT-135 spectra ($CDCl_3$, 62.5 MHz) of ethyl (*Z*)-2-chloroacetyl-3-phenylpropenoate (*Z*-**3a**).

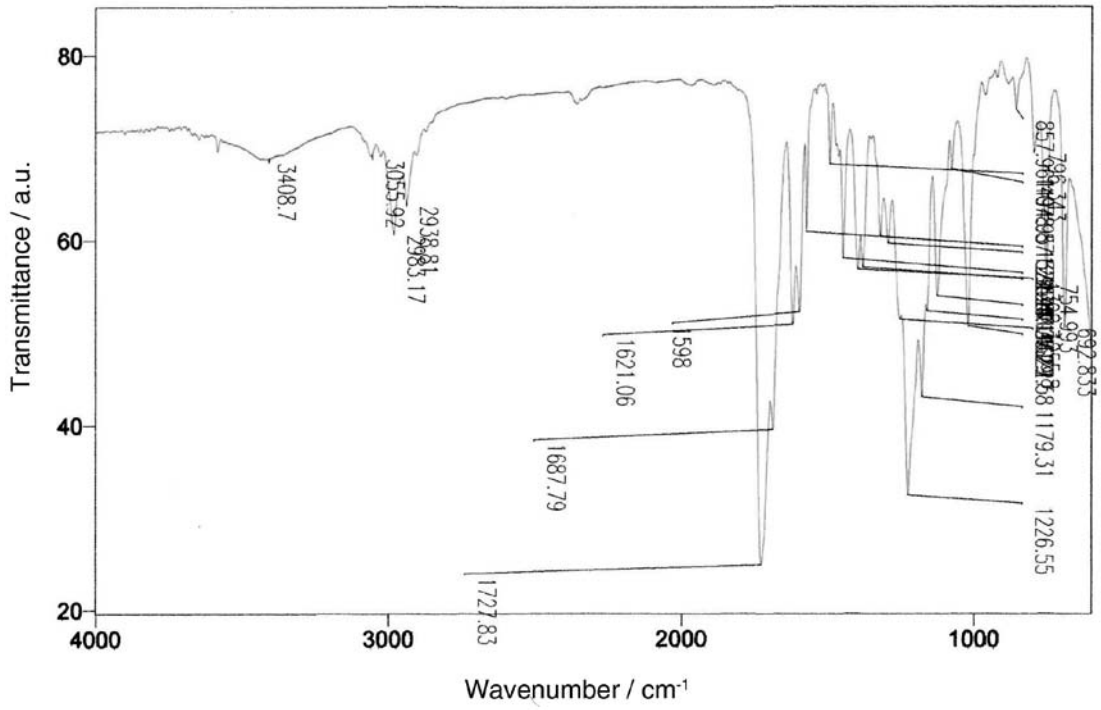
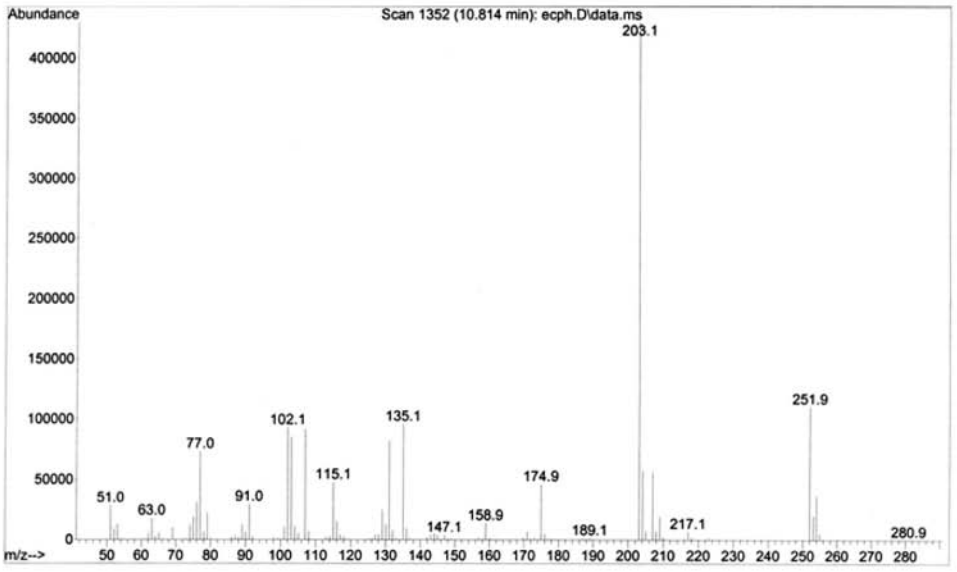


Figure S9. IR spectrum (film) of ethyl (*Z*)-2-chloroacetyl-3-phenylpropenoate (*Z*-**3a**).



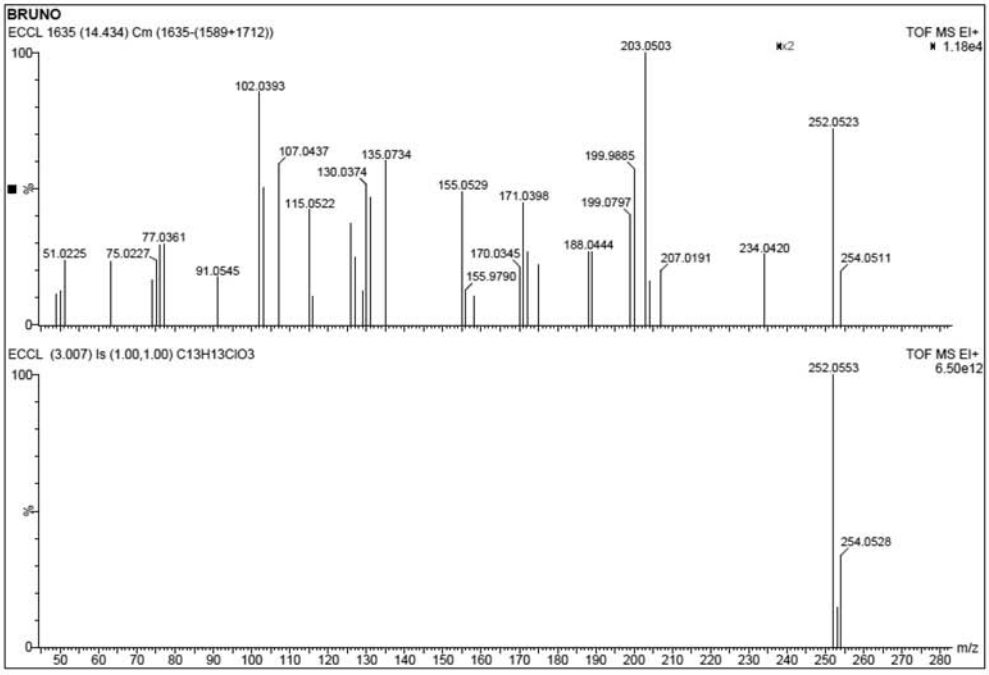


Figure S10. MS and HRMS (EI) spectra of ethyl (*Z*)-2-chloroacetyl-3-phenylpropenoate (*Z*-**3a**).

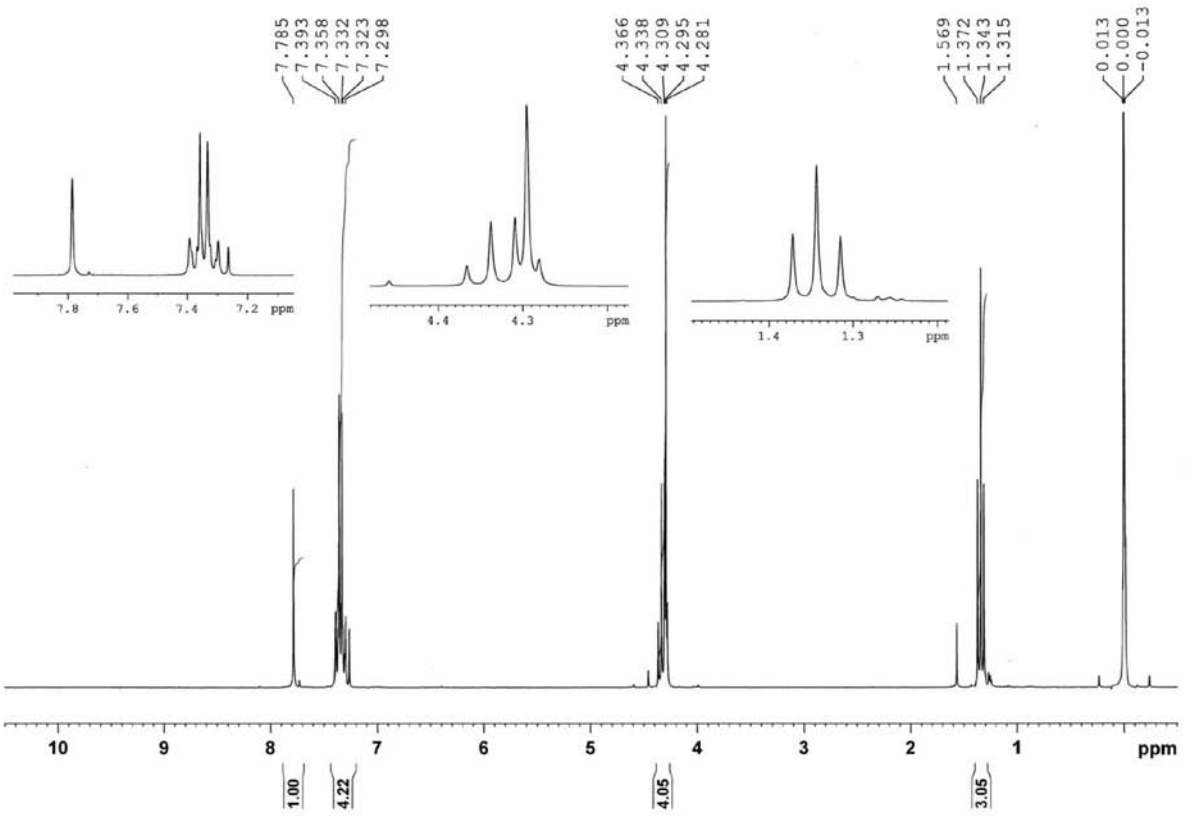


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of ethyl (*E*)-2-chloroacetyl-3-(4'-chlorophenyl)propenoate (*E*-**3b**).

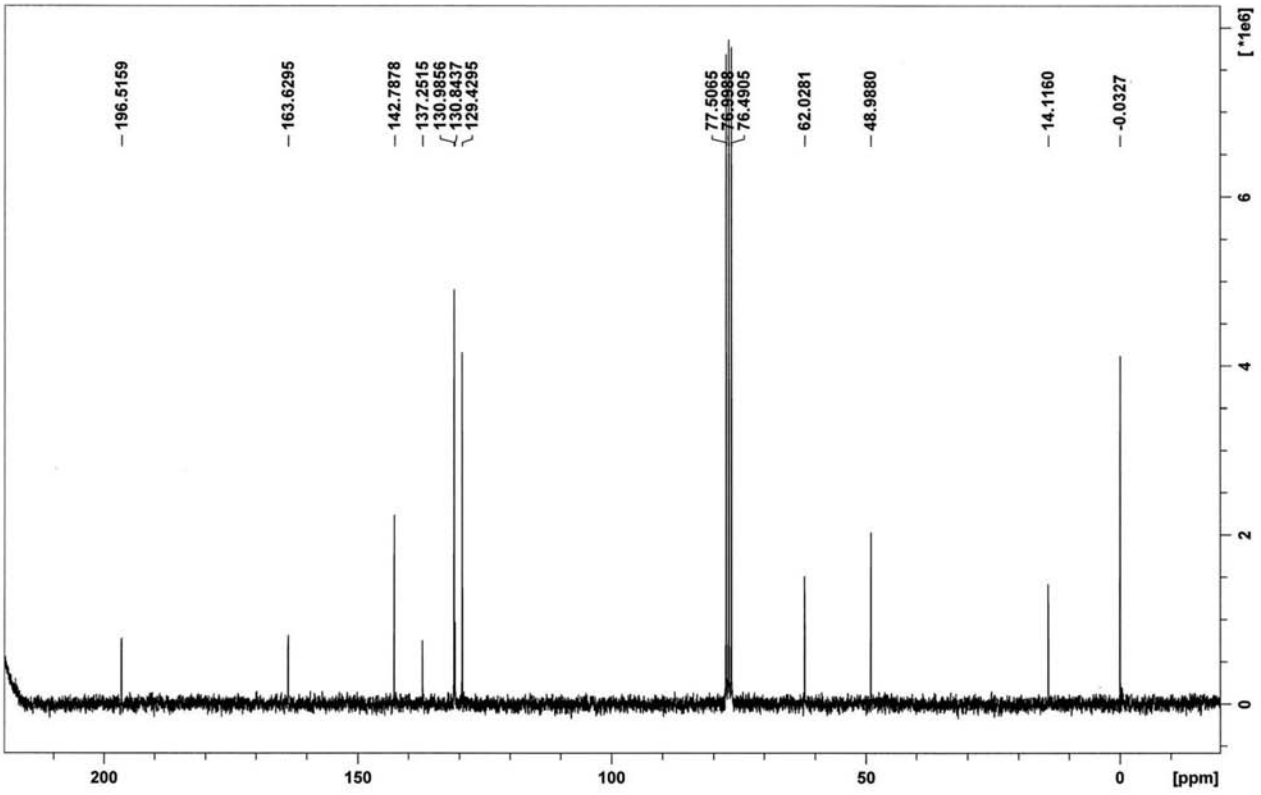


Figure S12. ^{13}C NMR spectrum ($CDCl_3$, 62.5 MHz) of ethyl (*E*)-2-chloroacetyl-3-(4'-chlorophenyl)propenoate (*E*-**3b**).

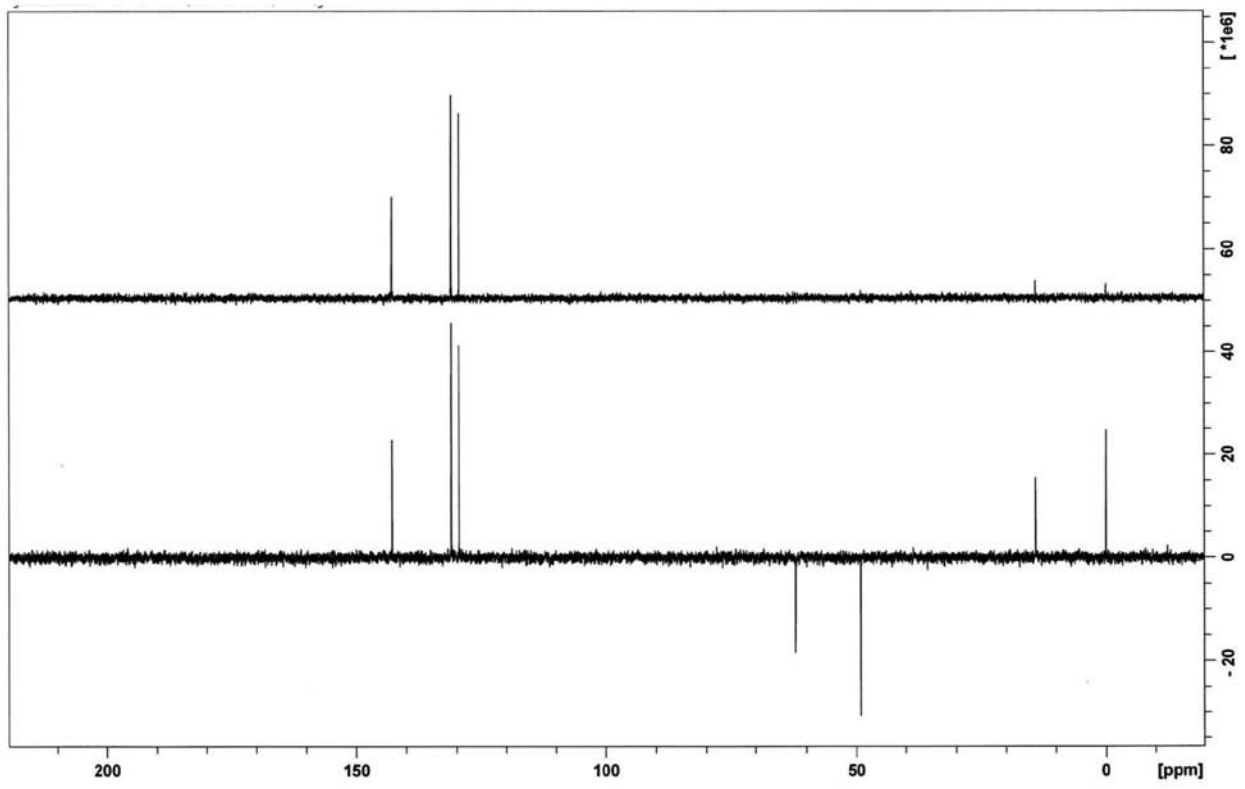


Figure S13. DEPT-90 and DEPT-135 spectra ($CDCl_3$, 62.5 MHz) of ethyl (*E*)-2-chloroacetyl-3-(4'-chlorophenyl)propenoate (*E*-**3b**).

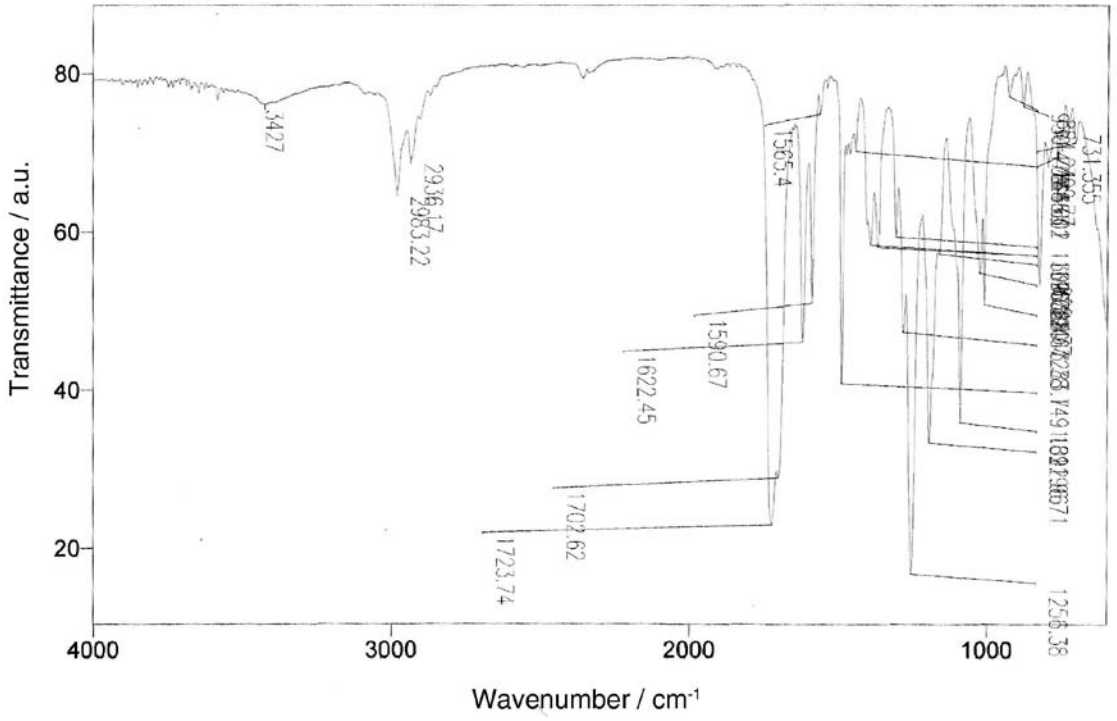


Figure S14. IR spectrum (film) of ethyl (*E*)-2-chloroacetyl-3-(4' chlorophenyl)propenoate (*E*-**3b**).

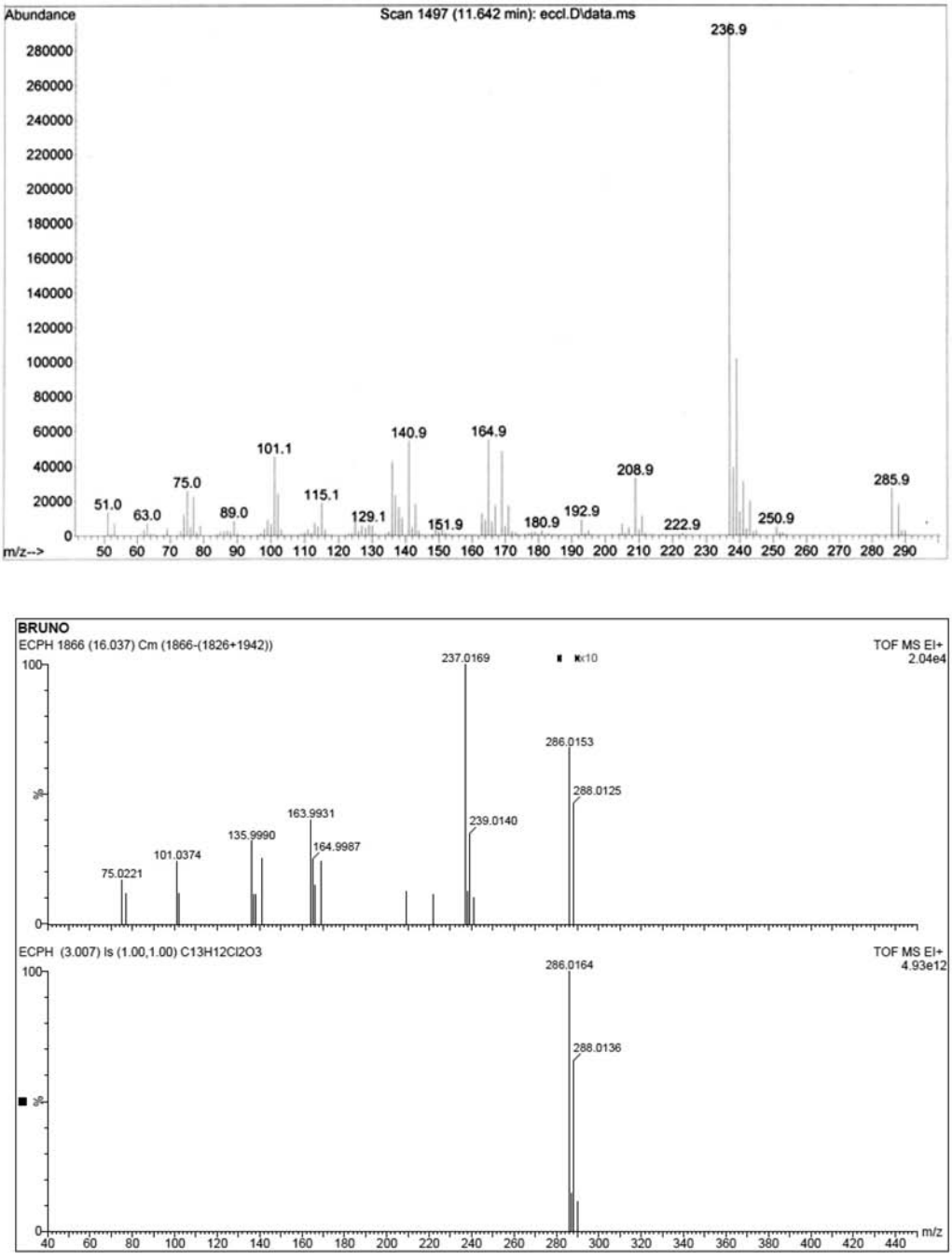


Figure S15. MS and HRMS (EI) spectra of ethyl (*E*)-2-chloroacetyl-3-(4'-chlorophenyl)propenoate (*E*-**3b**).

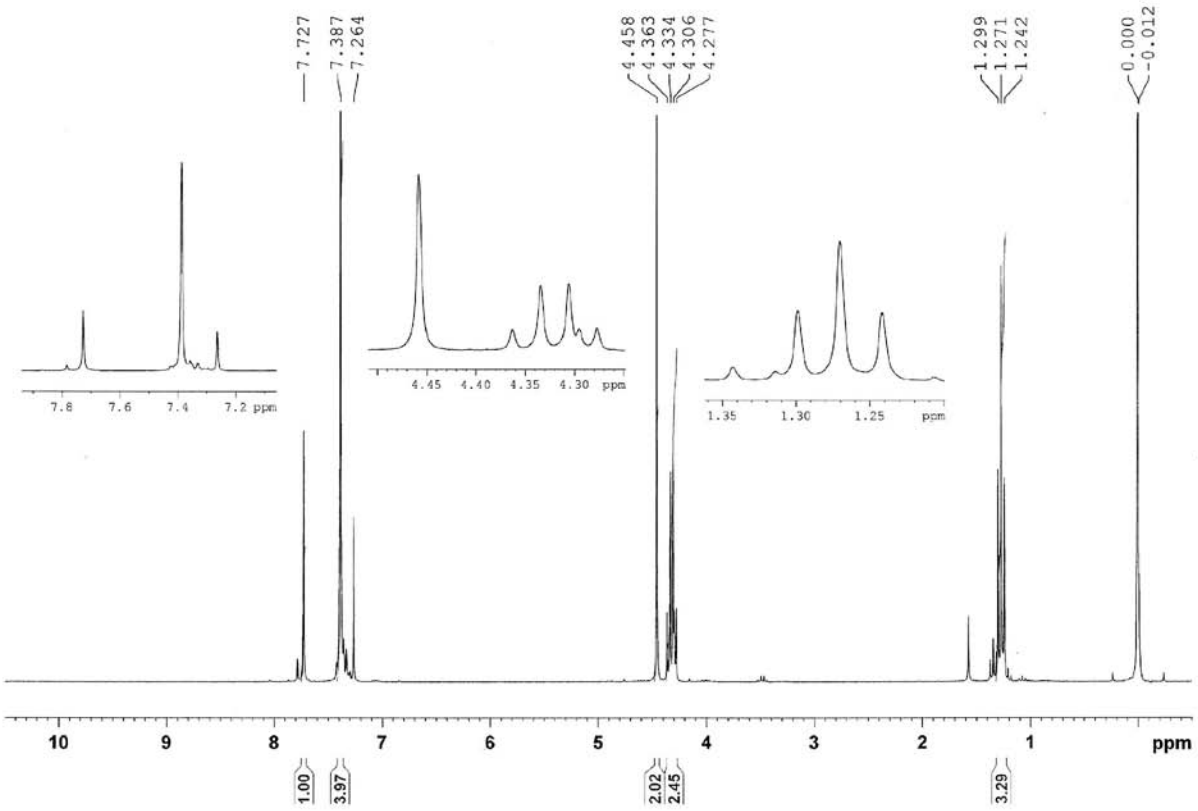


Figure S16. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(4'-chlorophenyl)propenoate (*Z*-**3b**).

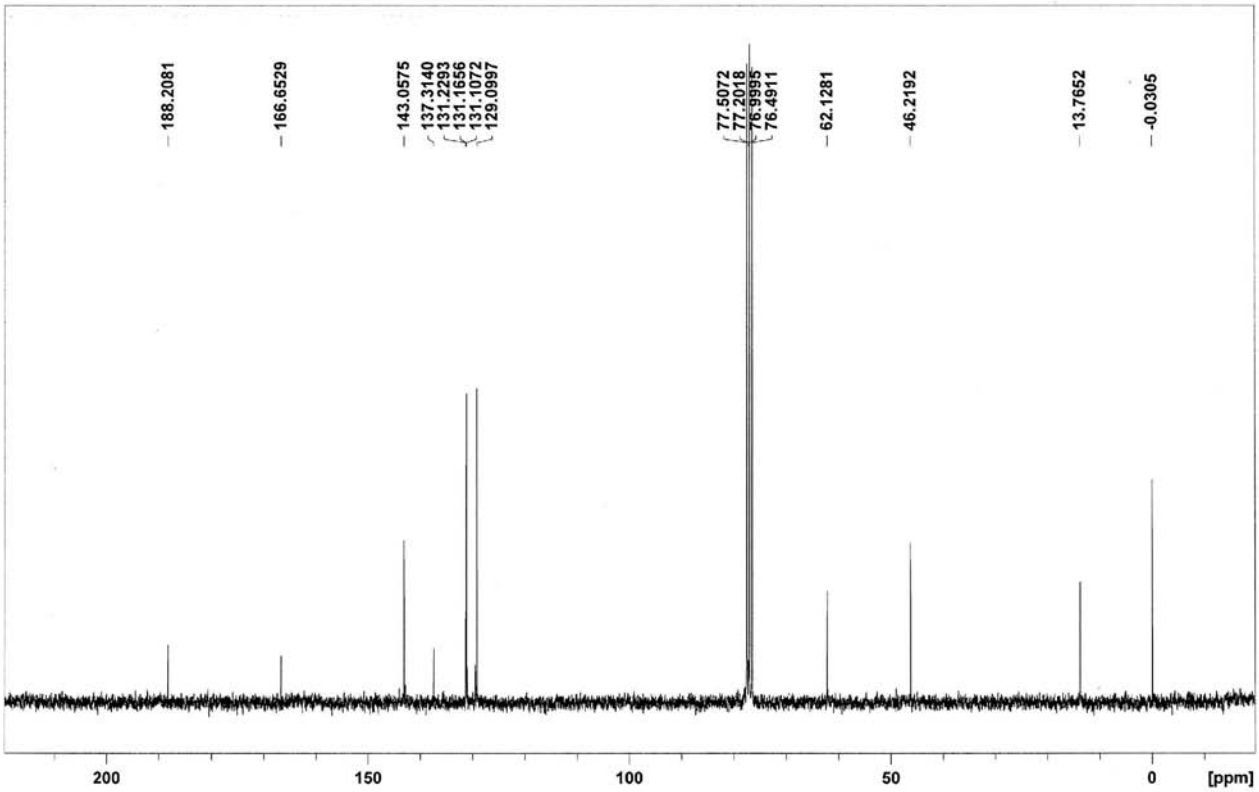


Figure S17. ^{13}C NMR spectrum ($CDCl_3$, 62.5 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(4'-chlorophenyl)propenoate (*Z*-**3b**).

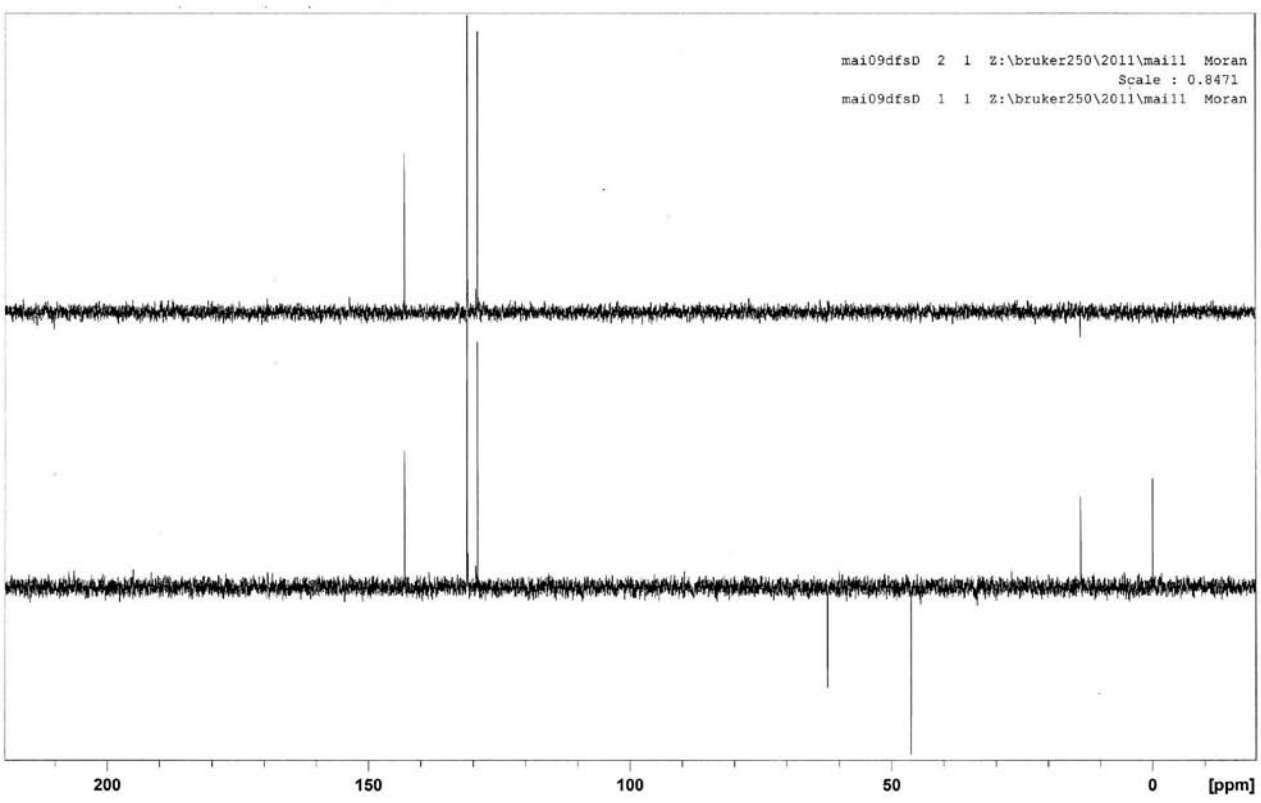


Figure S18. DEPT-90 and DEPT-135 spectra ($CDCl_3$, 62.5 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(4'-chlorophenyl)propenoate (*Z*-**3b**).

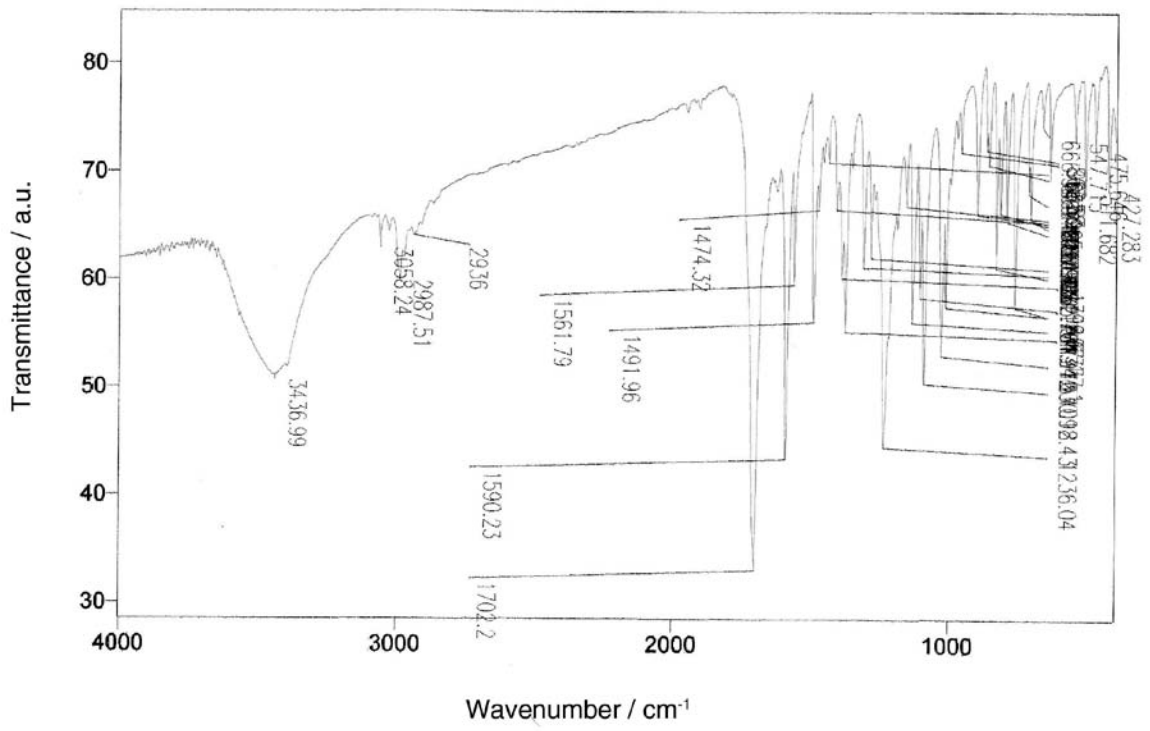


Figure S19. IR spectrum (KBr) of ethyl (*Z*)-2-chloroacetyl-3-(4'-chlorophenyl)propenoate (*Z*-**3b**).

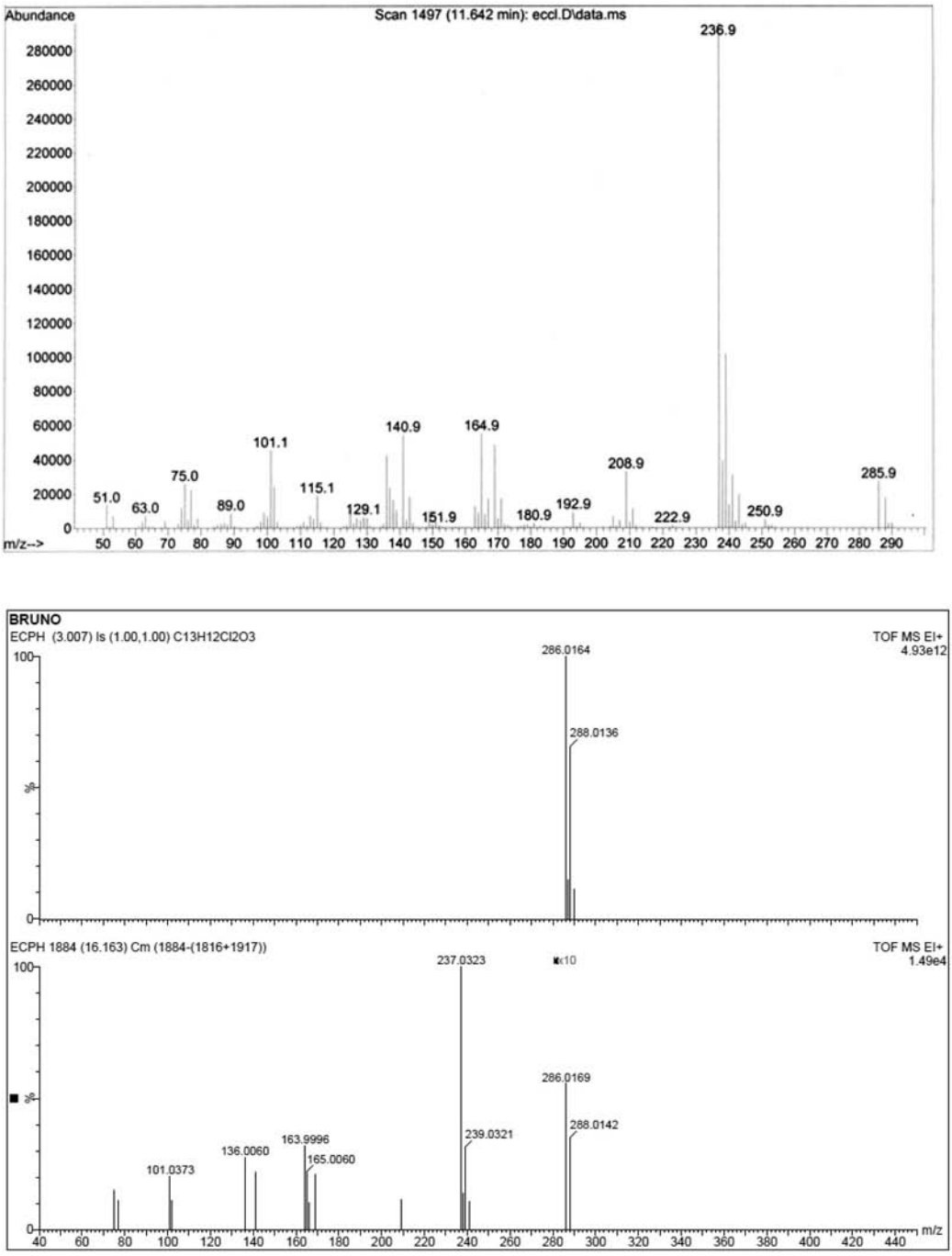


Figure S20. MS and HRMS (EI) spectra of ethyl (*Z*)-2-chloroacetyl-3-(4'-chlorophenyl)propenoate (*Z*-**3b**).

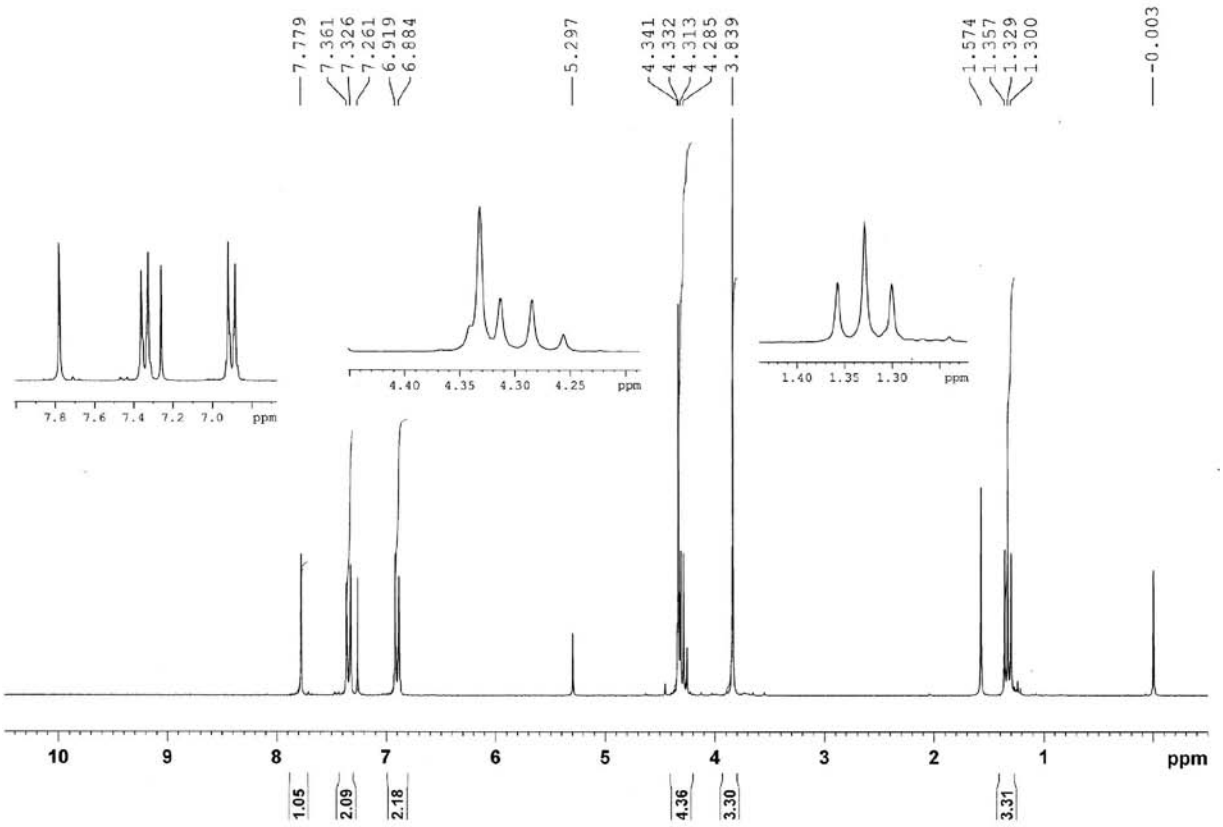


Figure S21. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of ethyl (*E*)-2-chloroacetyl-3-(4'-methoxyphenyl)propenoate (*E*-**3c**).

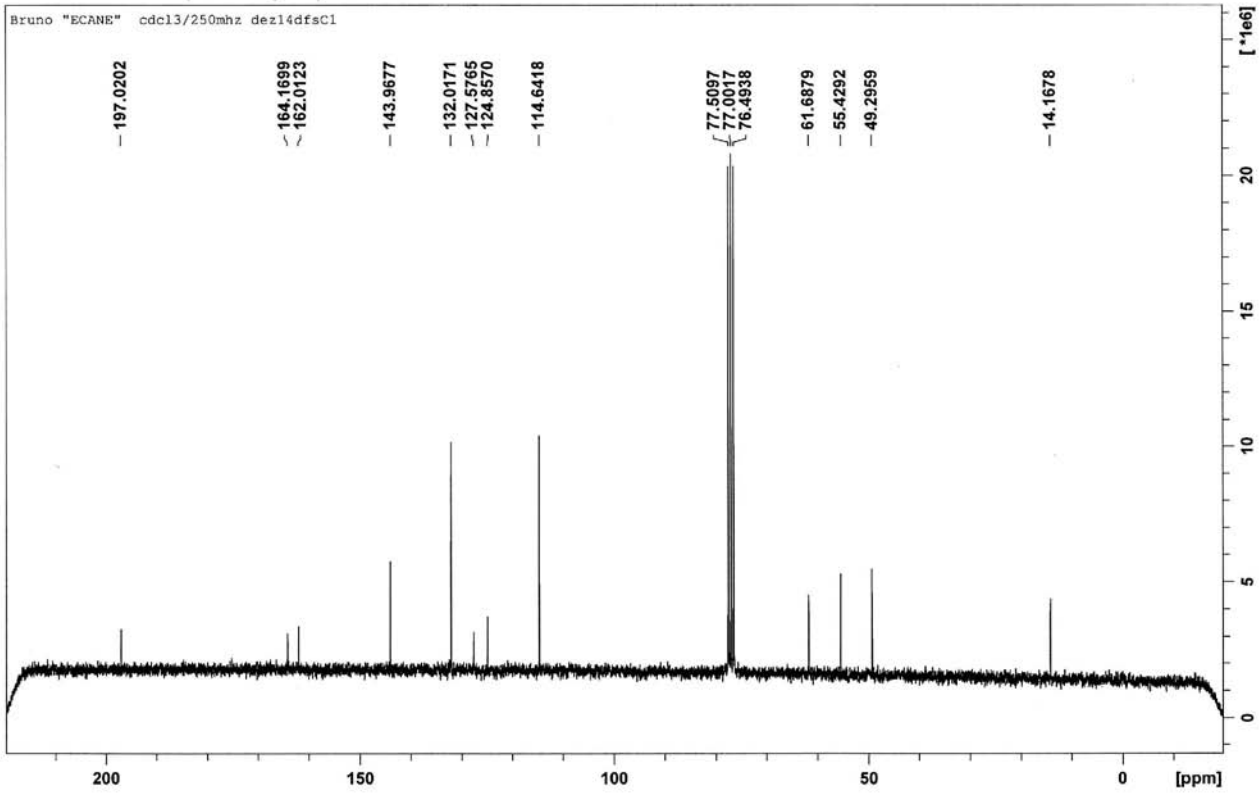


Figure S22. ^{13}C NMR spectrum ($CDCl_3$, 62.5 MHz) of ethyl (*E*)-2-chloroacetyl-3-(4'-methoxyphenyl)propenoate (*E*-**3c**).

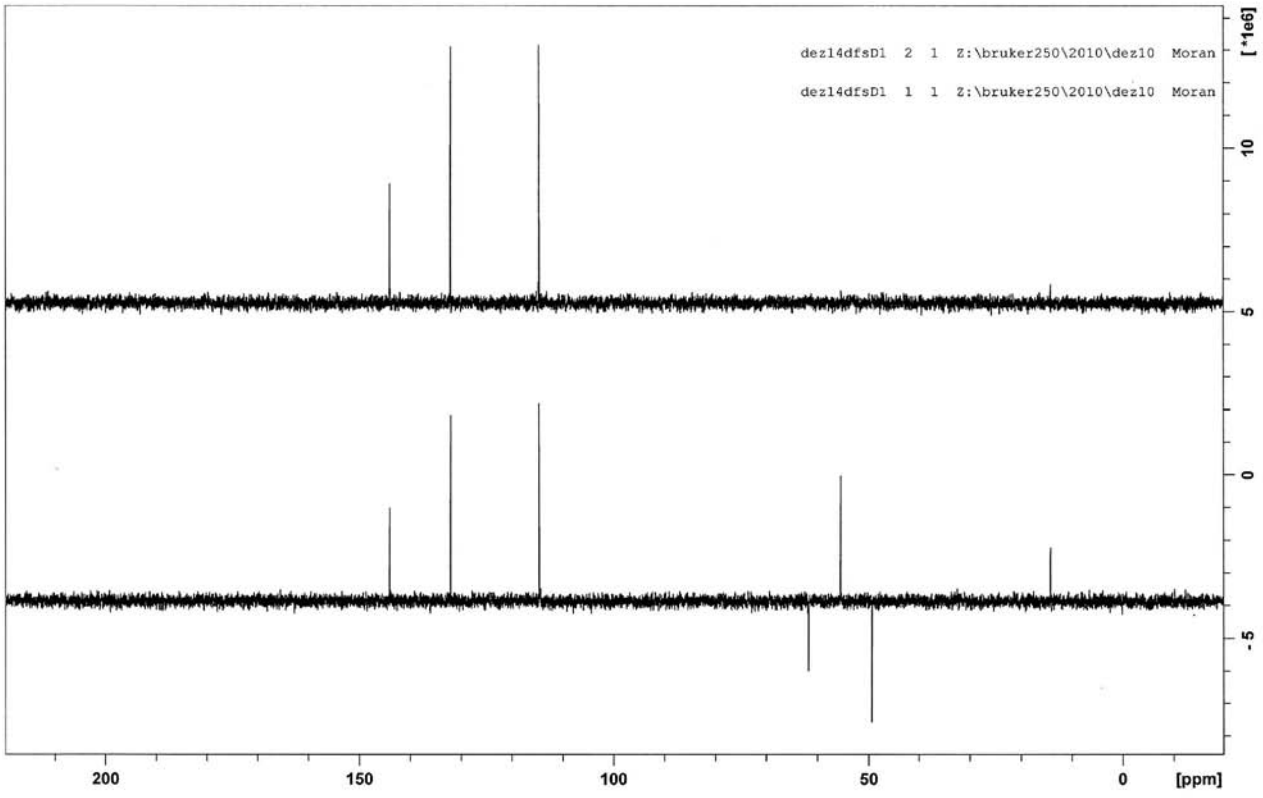


Figure S23. DEPT-90 and DEPT-135 spectra ($CDCl_3$, 62.5 MHz) of ethyl (*E*)-2-chloroacetyl-3-(4'-methoxyphenyl)propenoate (*E*-**3c**).

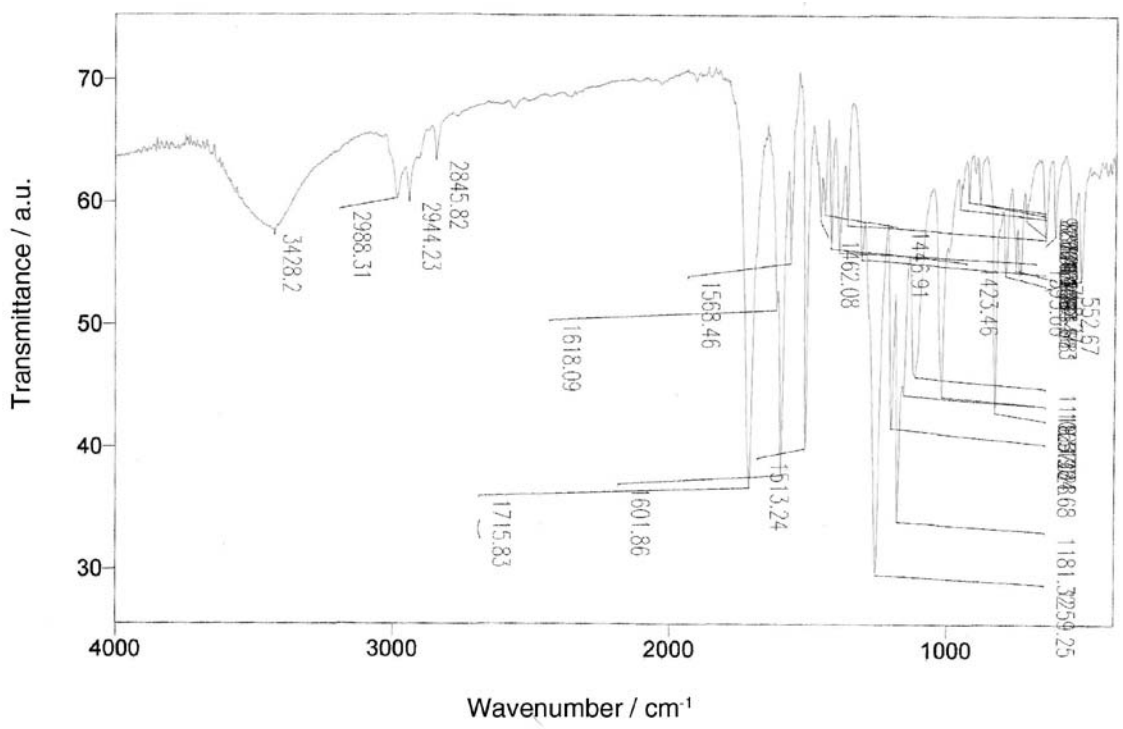


Figure S24. IR spectrum (KBr) of ethyl (*E*)-2-chloroacetyl-3-(4'-methoxyphenyl)propenoate (*E*-**3c**).

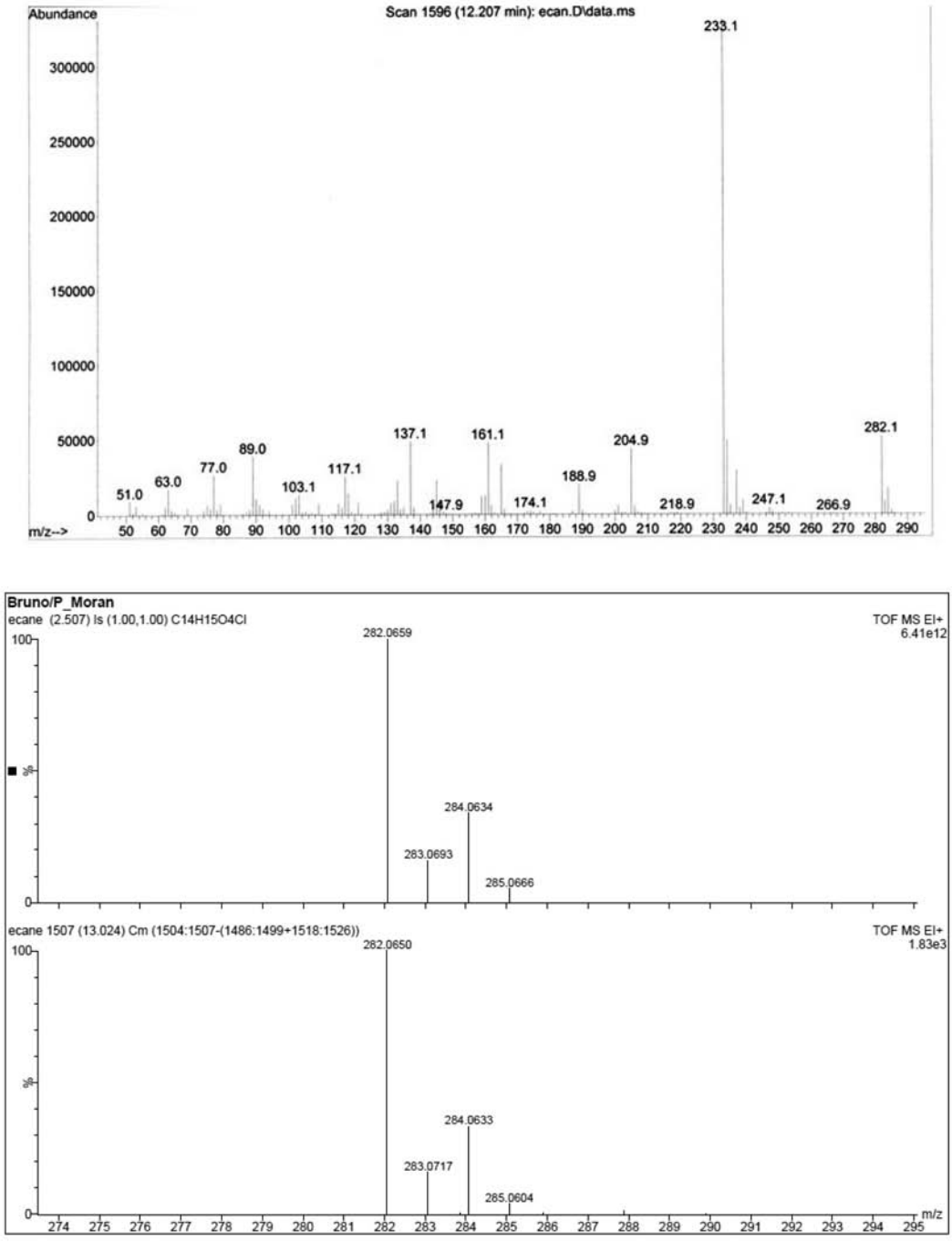


Figure S25. MS and HRMS (EI) spectra of ethyl (*E*)-2-chloroacetyl-3-(4'-methoxyphenyl)propenoate (*E*-**3c**).

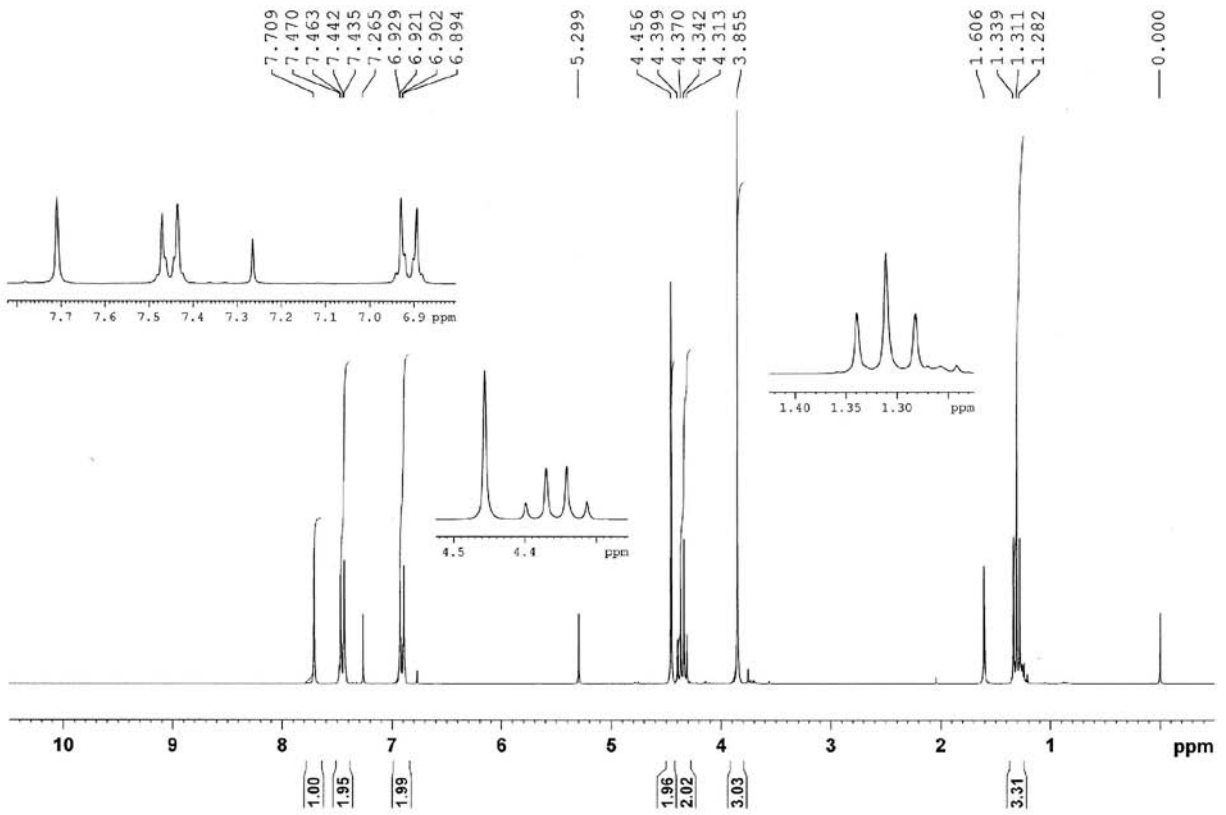


Figure S26. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(4'-methoxyphenyl)propenoate (*Z*-**3c**).

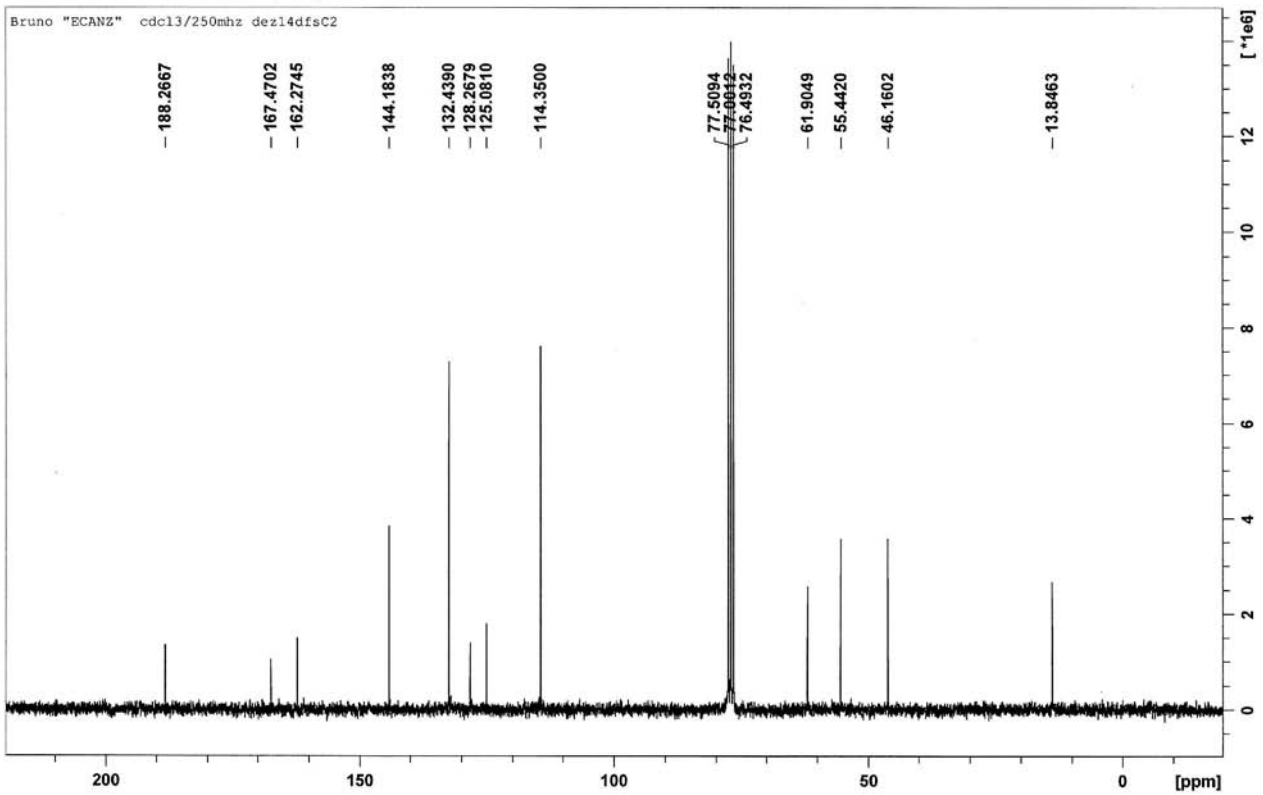


Figure S27. ^{13}C NMR spectrum ($CDCl_3$, 62.5 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(4'-methoxyphenyl)propenoate (*Z*-**3c**).

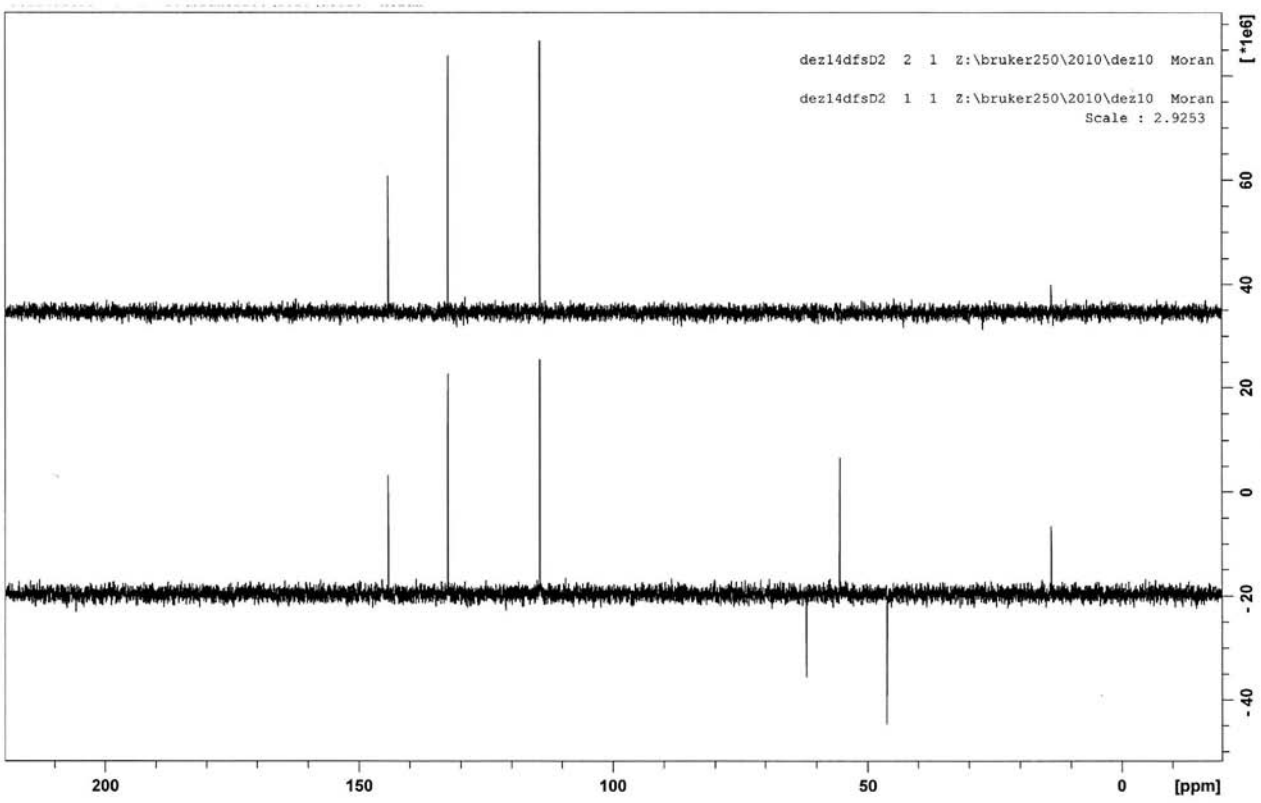


Figure S28. DEPT-90 and DEPT-135 spectra ($CDCl_3$, 62.5 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(4'-methoxyphenyl)propenoate (*Z*-**3c**).

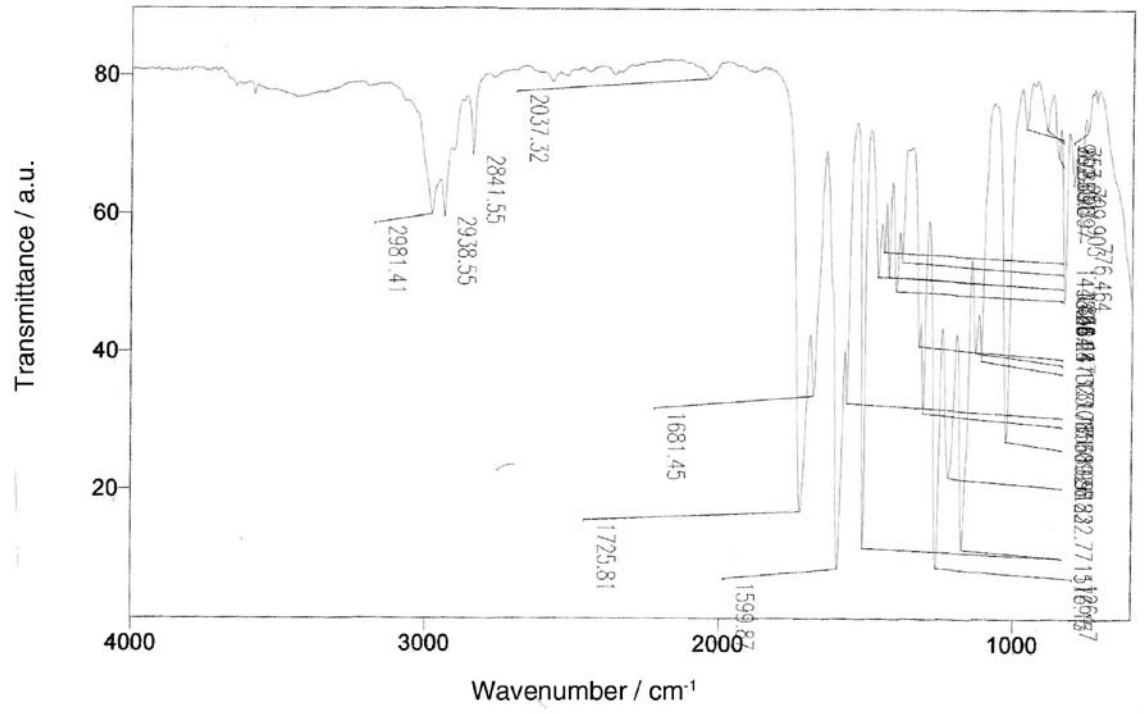


Figure S29. IR spectrum (film) of ethyl (*Z*)-2-chloroacetyl-3-(4'-methoxyphenyl)propenoate (*Z*-**3c**).

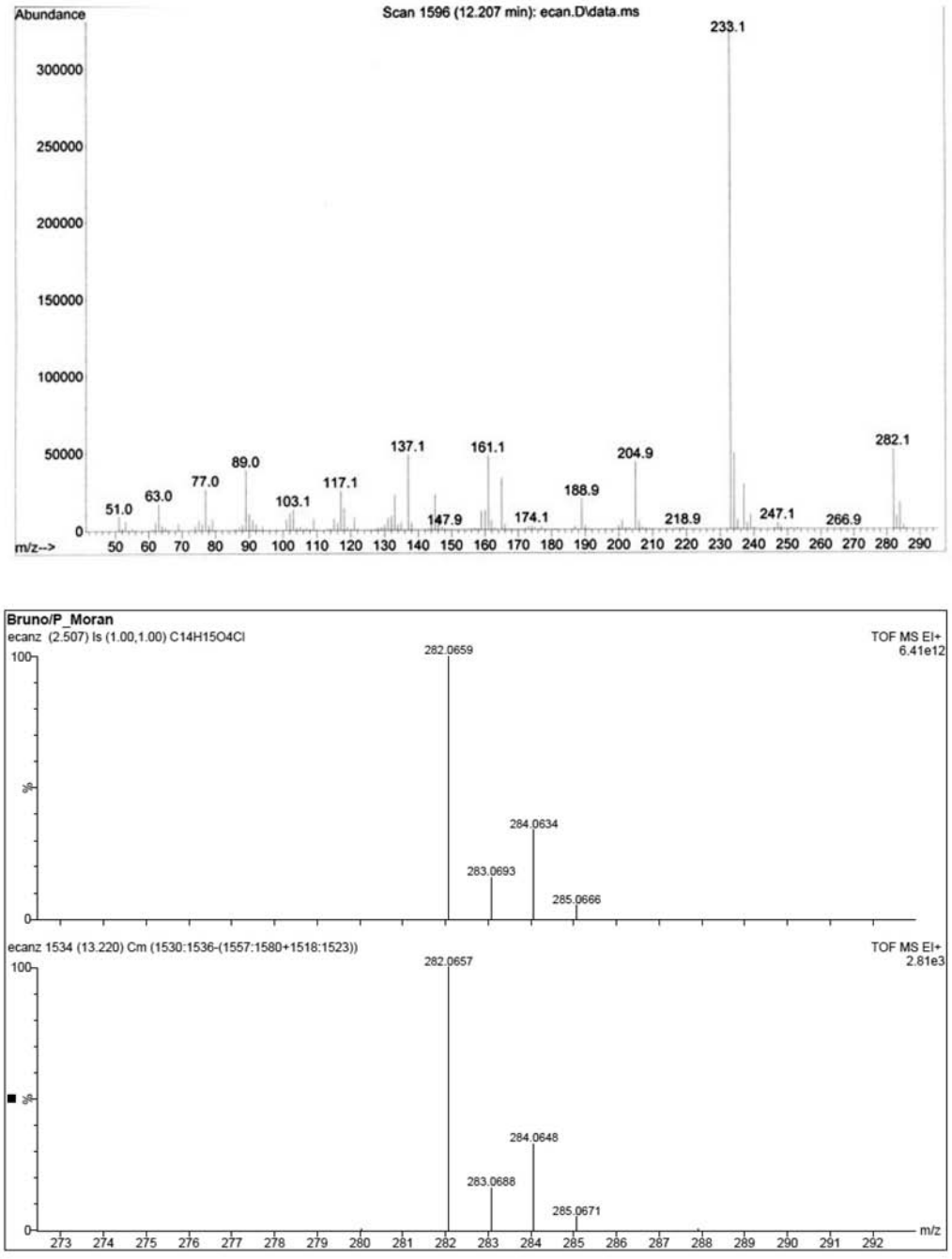


Figure S30. MS and HRMS (EI) spectra of ethyl (*Z*)-2-chloroacetyl-3-(4'-methoxyphenyl)propenoate (*Z*-**3c**).

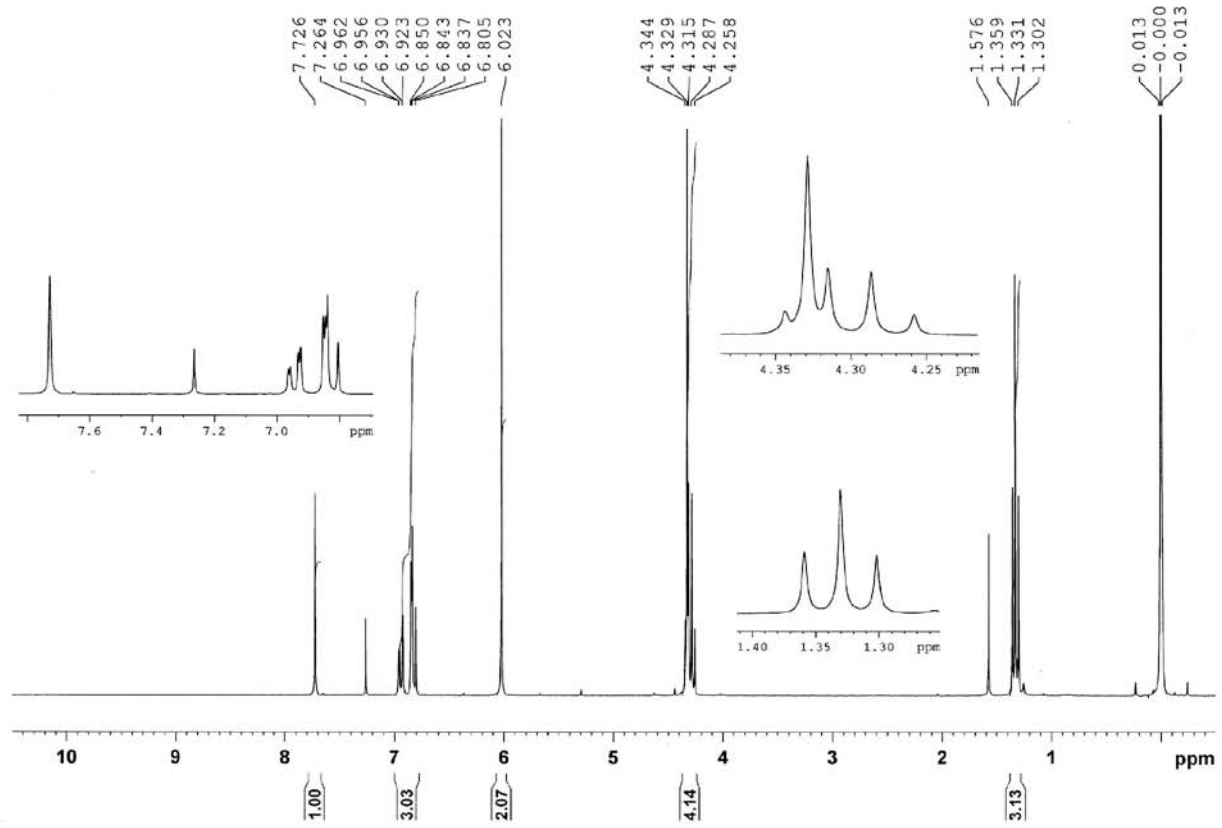


Figure S31. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of ethyl (*E*)-2-chloroacetyl-3-(3',4'-methylenedioxyphenyl)propenoate (*E*-**3d**).

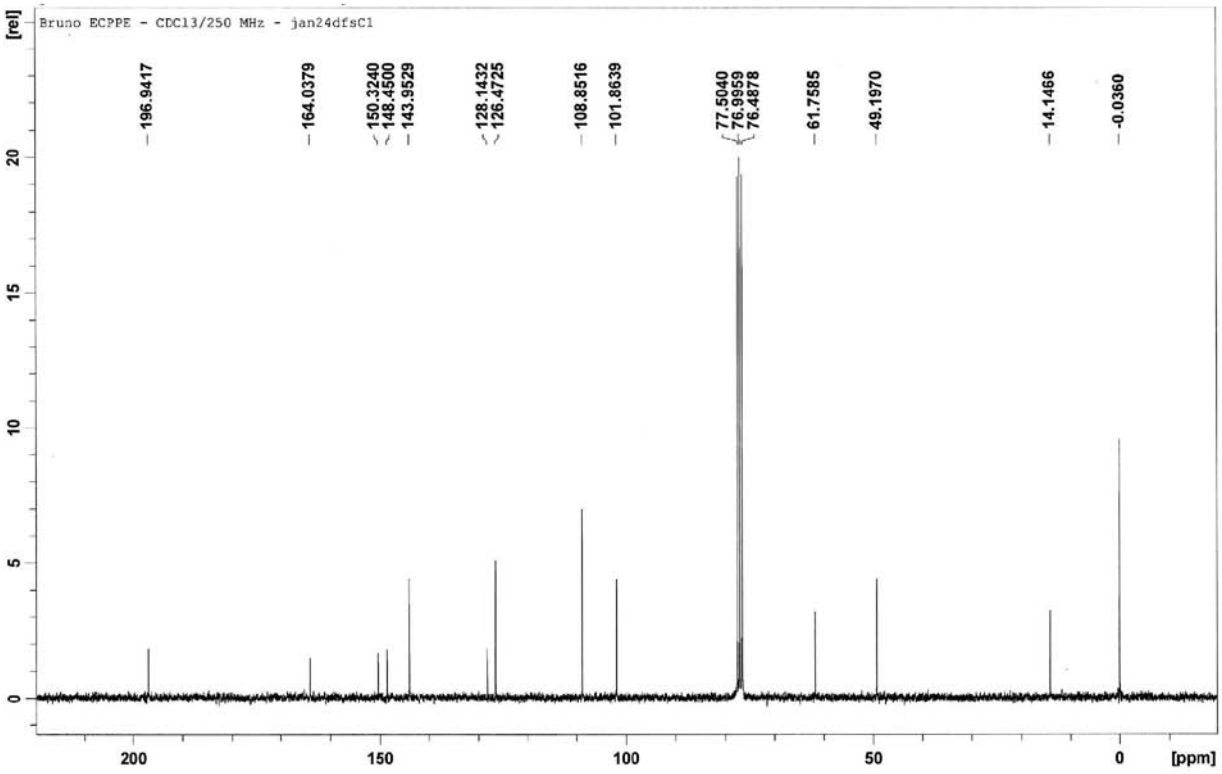


Figure S32. ^{13}C NMR spectrum ($CDCl_3$, 62.5 MHz) of ethyl (*E*)-2-chloroacetyl-3-(3',4'-methylenedioxyphenyl)propenoate (*E*-**3d**).

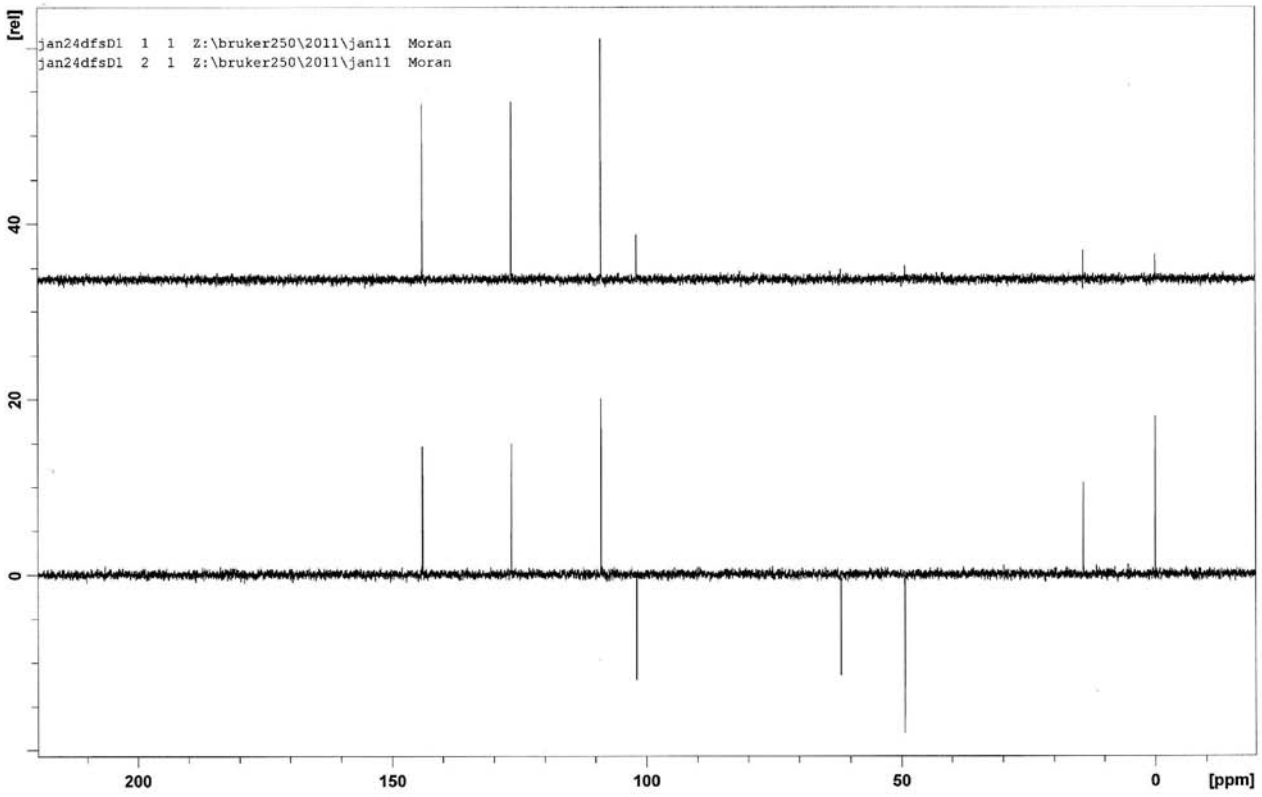


Figure S33. DEPT-90 and DEPT-135 spectra ($CDCl_3$, 62.5 MHz) of ethyl (*E*)-2-chloroacetyl-3-(3',4'-methylenedioxyphenyl)propenoate (*E*-**3d**).

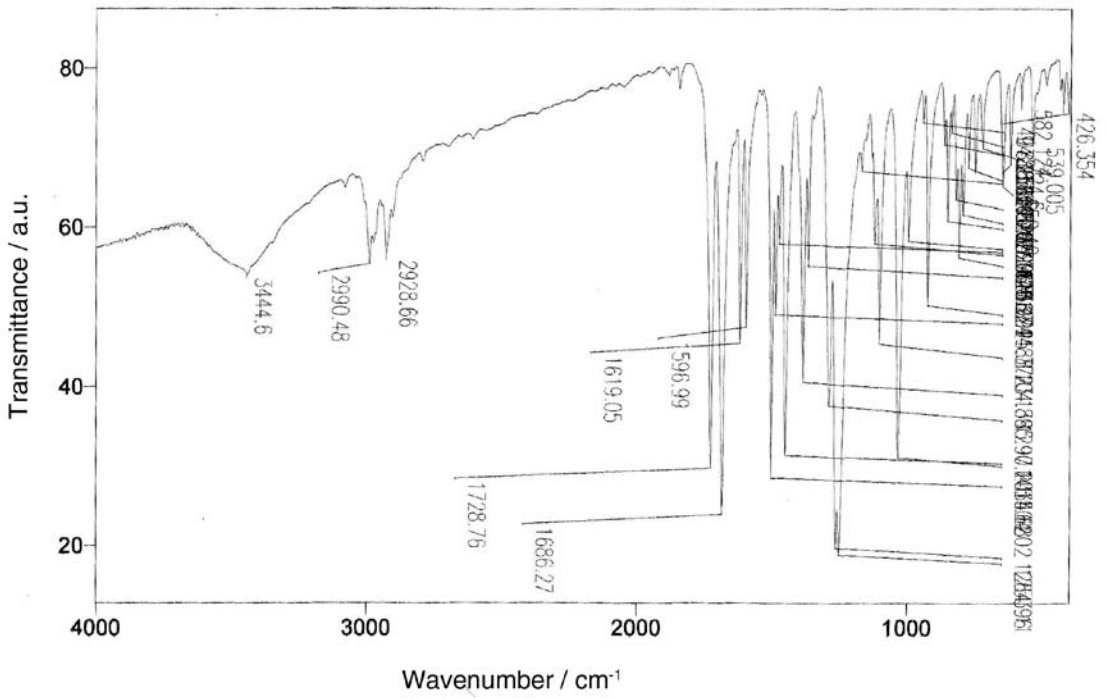


Figure S34. IR (KBr) spectrum of ethyl (*E*)-2-chloroacetyl-3-(3', 4'-methylenedioxyphenyl)propenoate (*E*-**3d**).

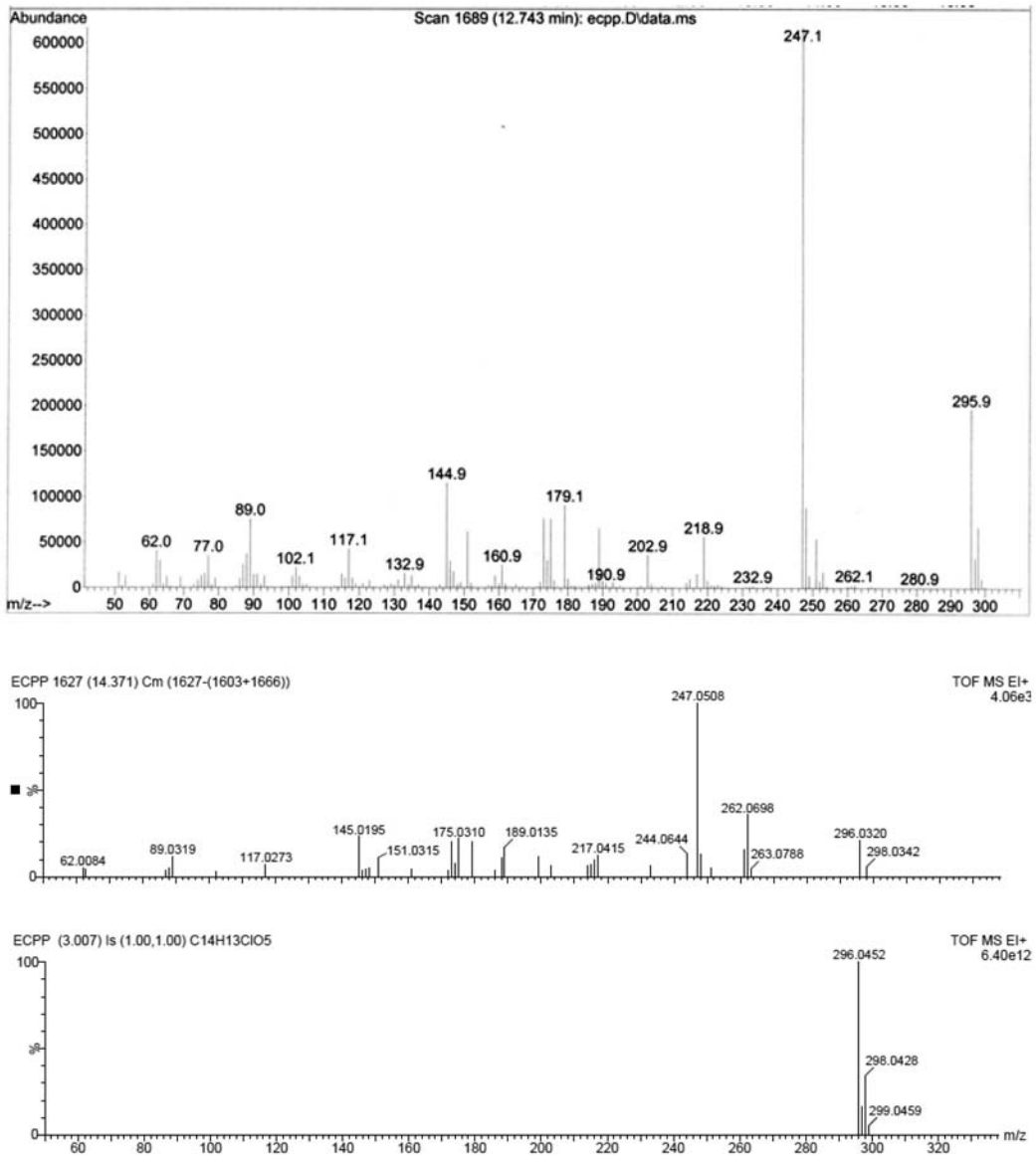


Figure S35. MS and HRMS (EI) spectra of ethyl (*E*)-2-chloroacetyl-3-(3',4'-methylenedioxyphenyl)propenoate (*E*-**3d**).

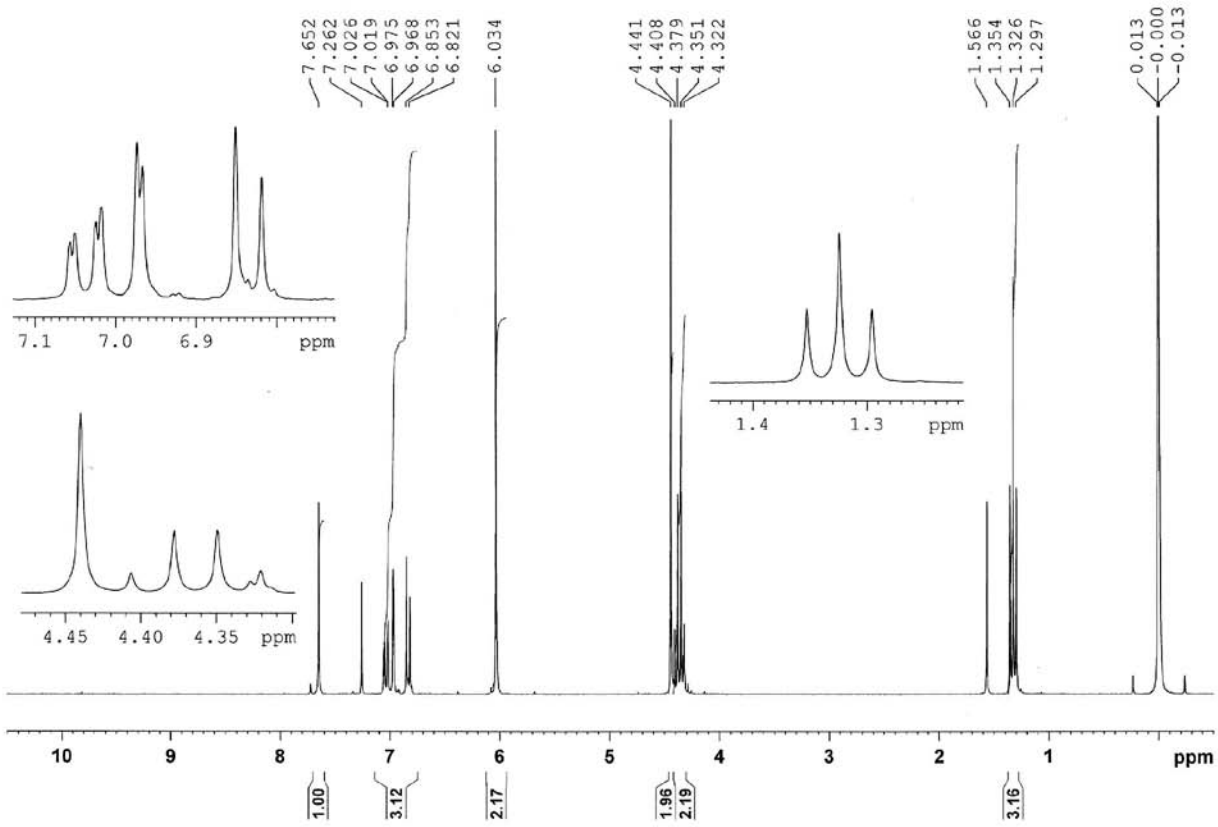


Figure S36. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(3',4'-methylenedioxyphenyl)propenoate (*Z*-**3d**).

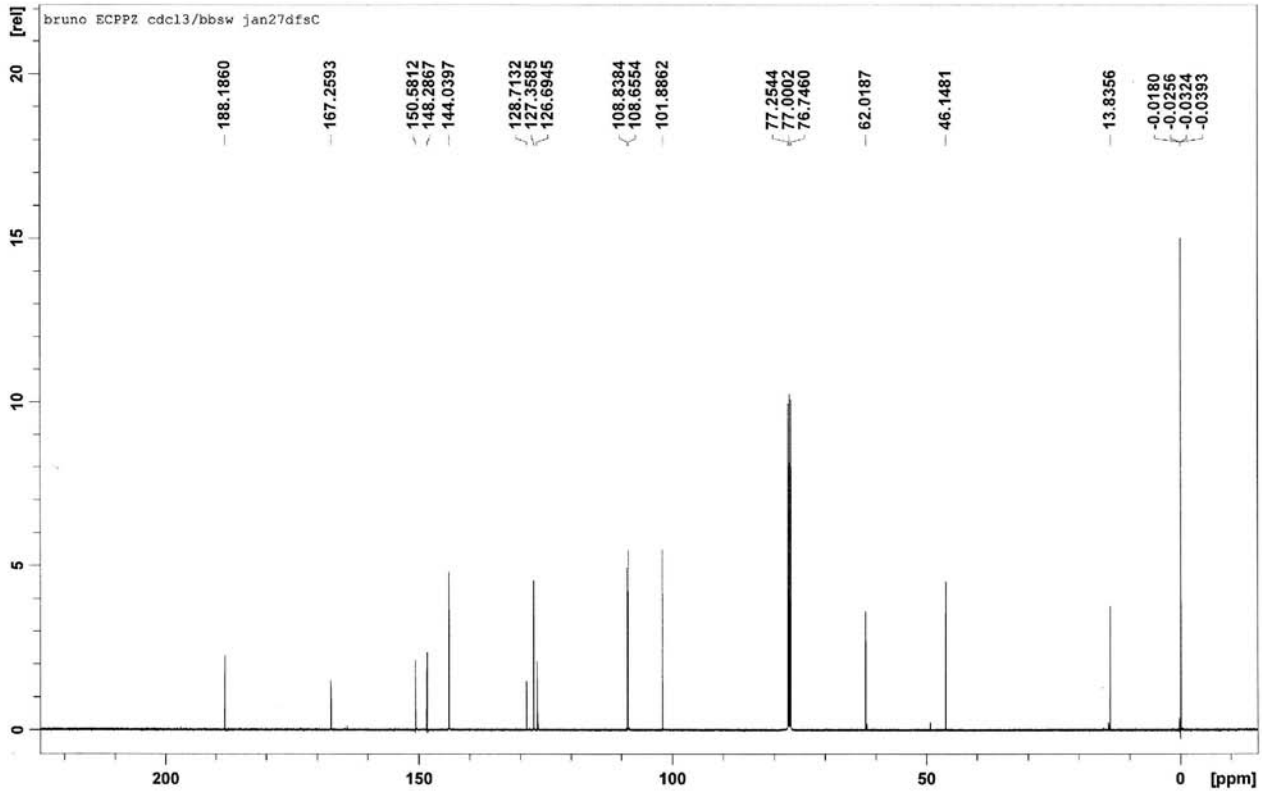


Figure S37. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(3',4'-methylenedioxyphenyl)propenoate (*Z*-**3d**).

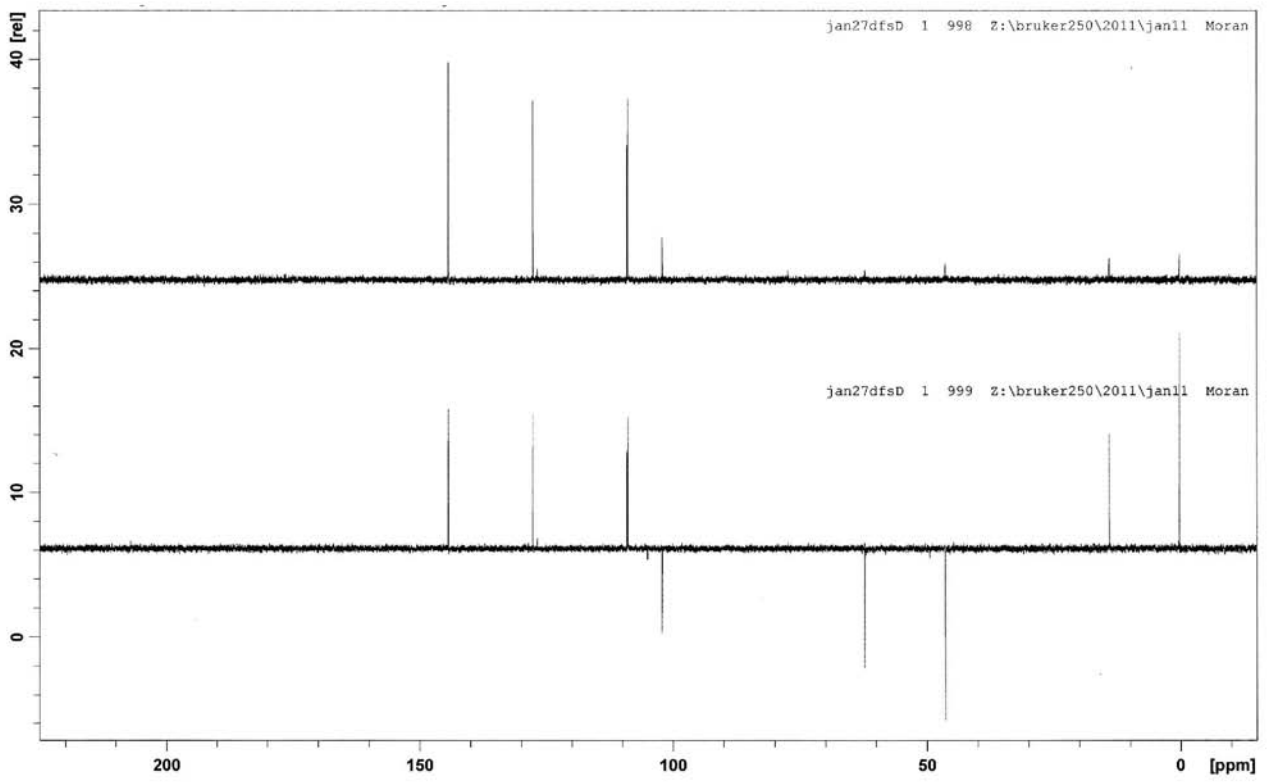


Figure S38. DEPT-90 and DEPT-135 spectra ($CDCl_3$, 125 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(3',4'-methylenedioxyphenyl)propenoate (*Z*-**3d**).

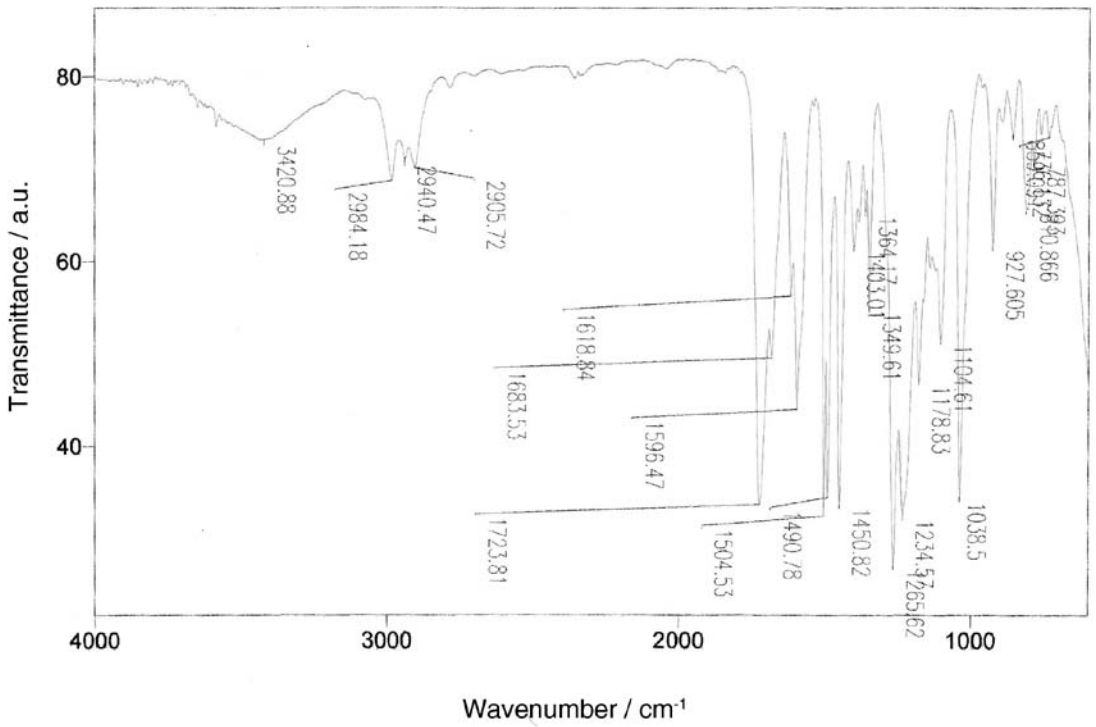


Figure S39. IR spectrum (film) of ethyl (*Z*)-2-chloroacetyl-3-(3',4'-methylenedioxyphenyl)propenoate (*Z*-**3d**).

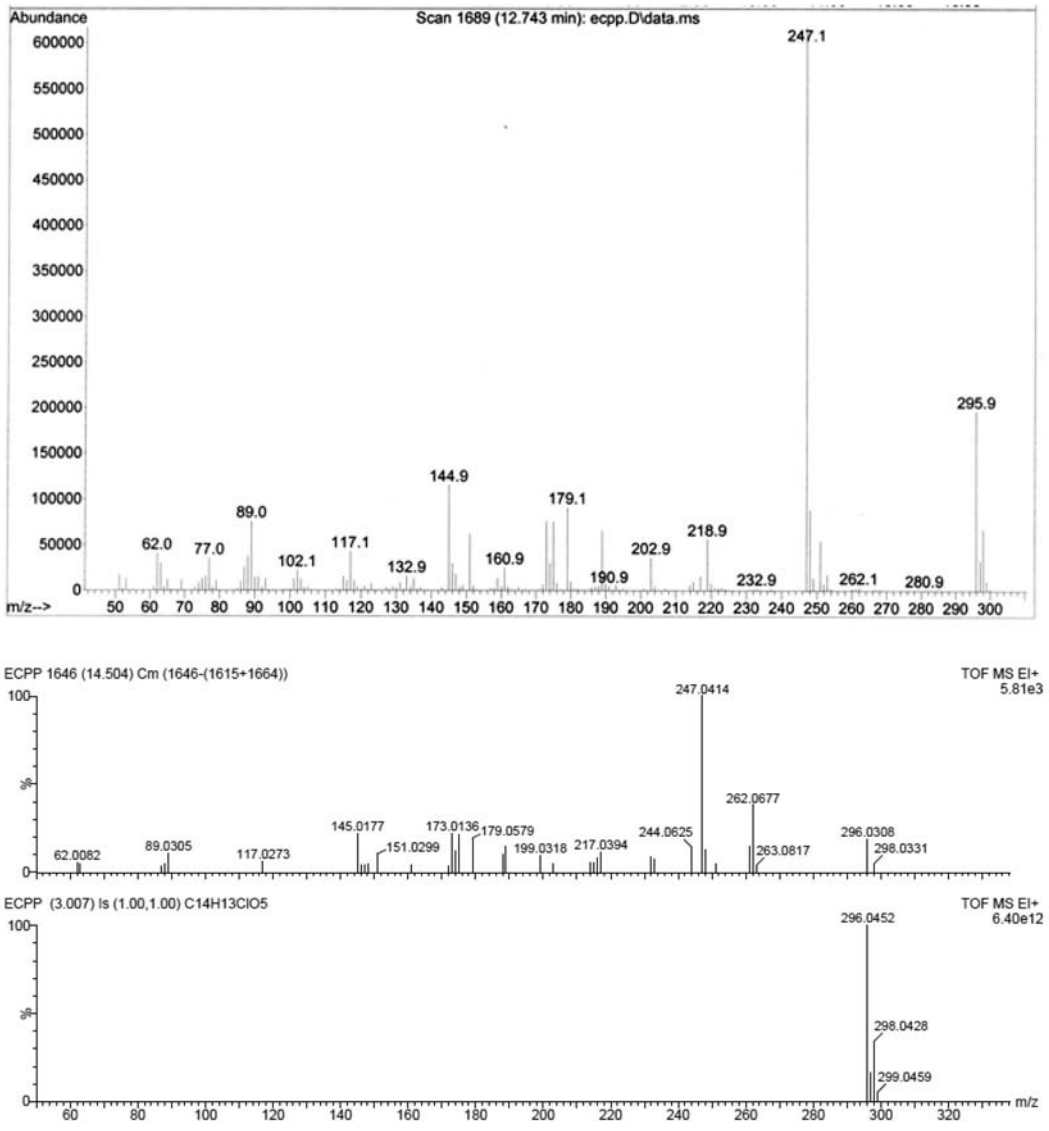


Figure S40. MS and HRMS (EI) spectra of ethyl (*Z*)-2-chloroacetyl-3-(3',4'-methylenedioxyphenyl)propenoate (*Z*-**3d**).

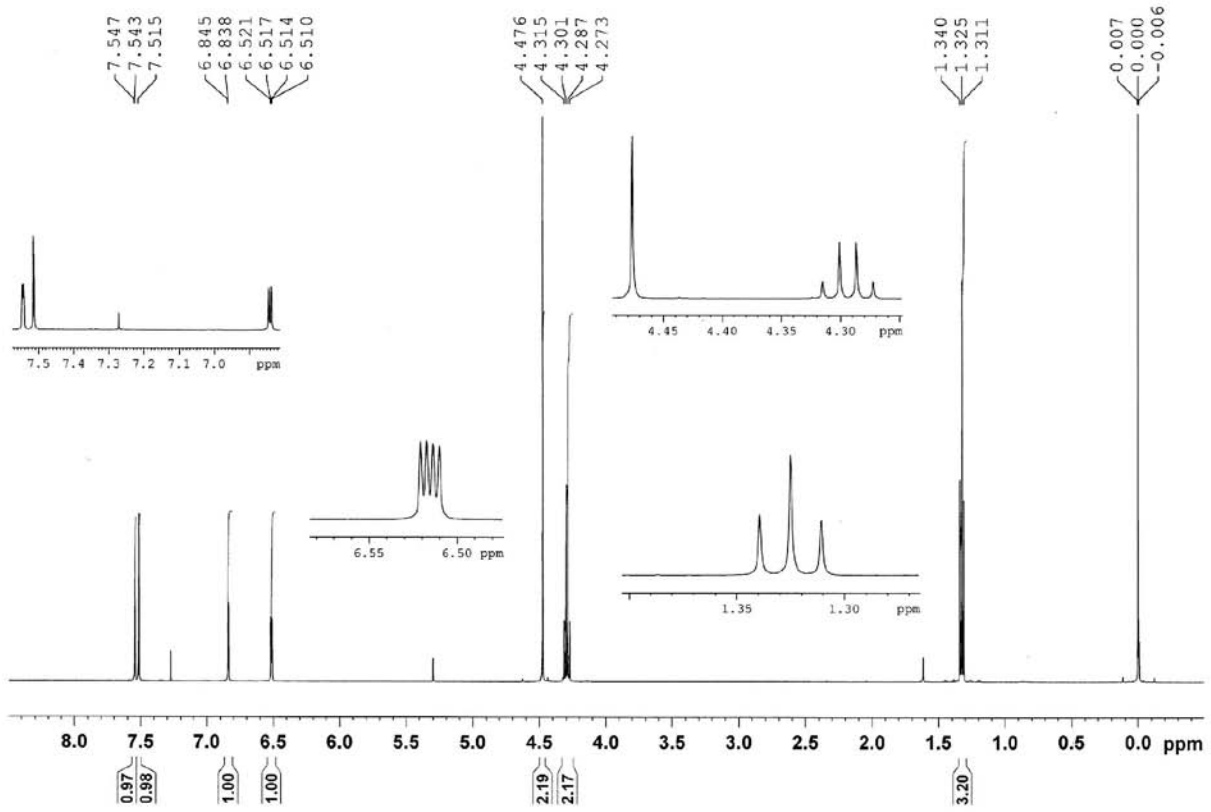


Figure S41. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of ethyl (*E*)-2-chloroacetyl-3-(2'-furanyl)propenoate (*E*-**3e**).

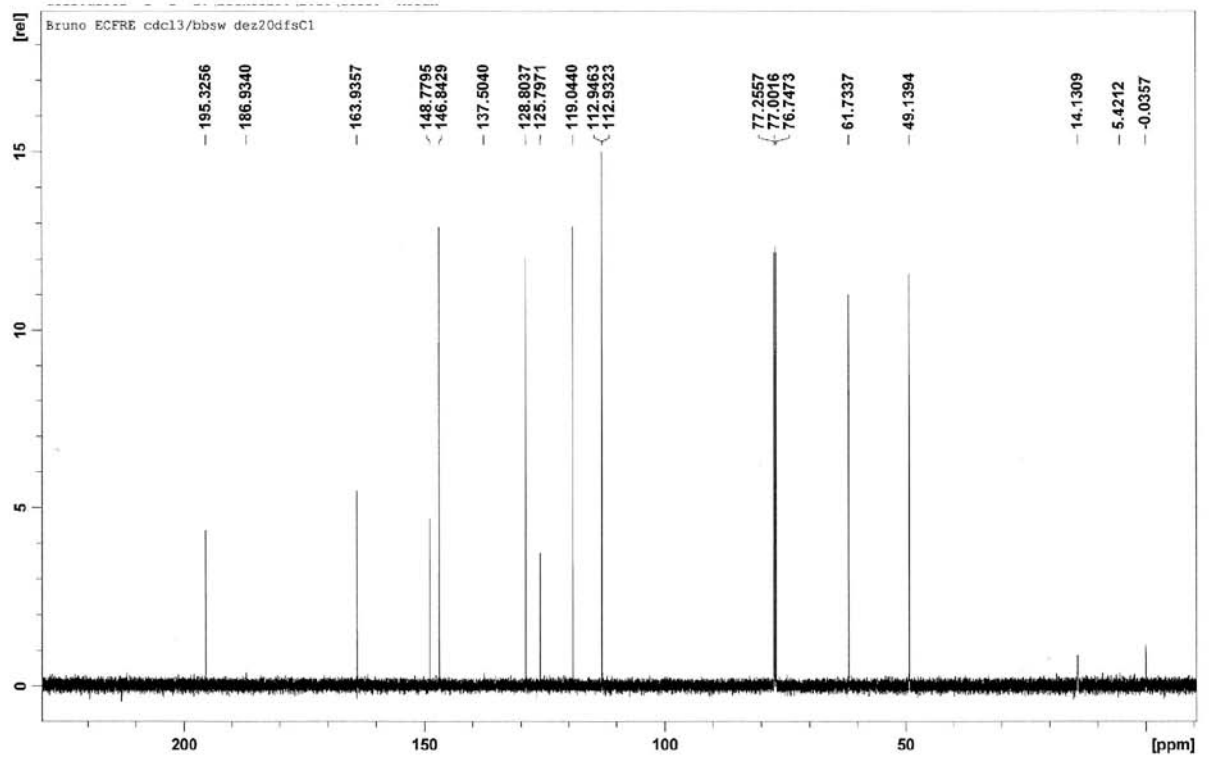


Figure S42. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of ethyl (*E*)-2-chloroacetyl-3-(2'-furanyl)propenoate (*E*-**3e**).

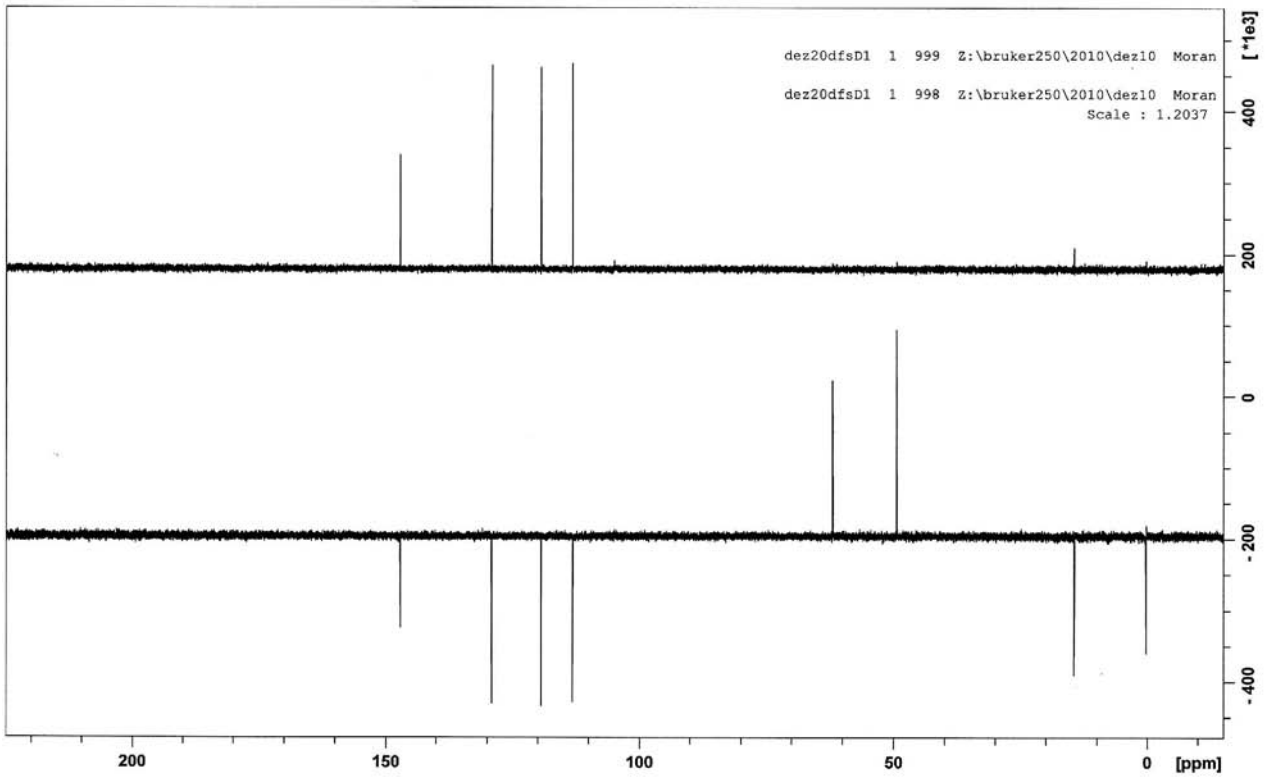


Figure S43. DEPT-90 and DEPT-135 spectra ($CDCl_3$, 125 MHz) of ethyl (*E*)-2-chloroacetyl-3-(2'-furanyl)propenoate (*E*-**3e**).

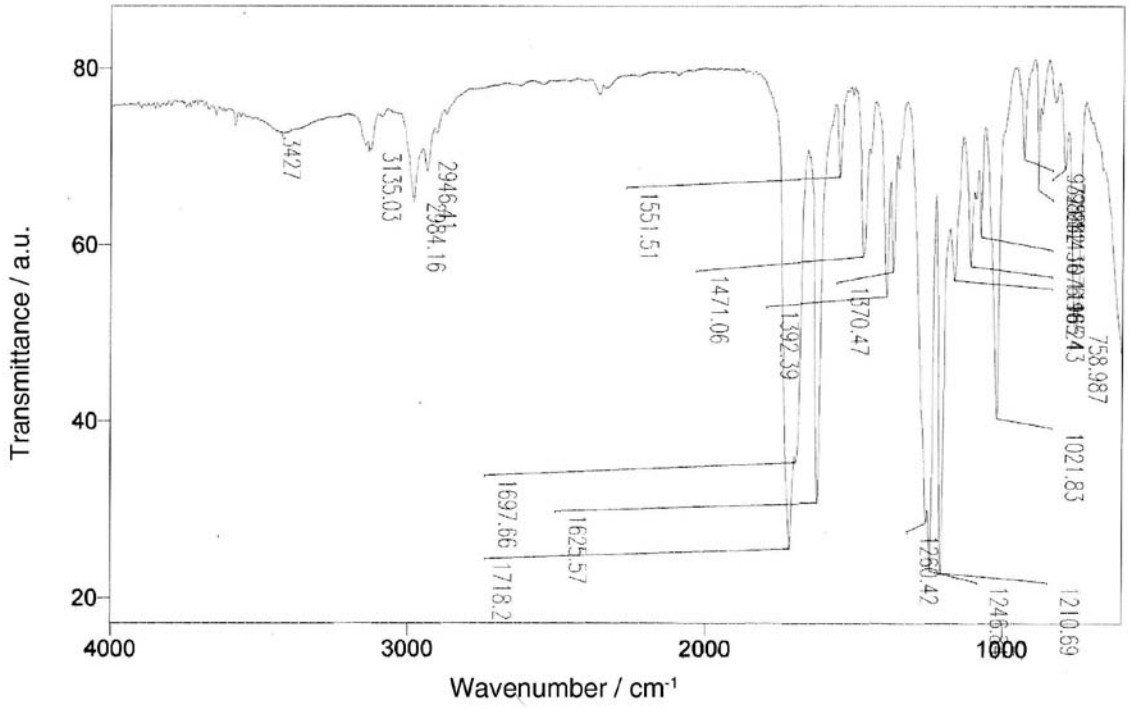


Figure S44. IR spectrum (film) of ethyl (*E*)-2-chloroacetyl-3-(2'-furanyl)propenoate (*E*-**3e**).

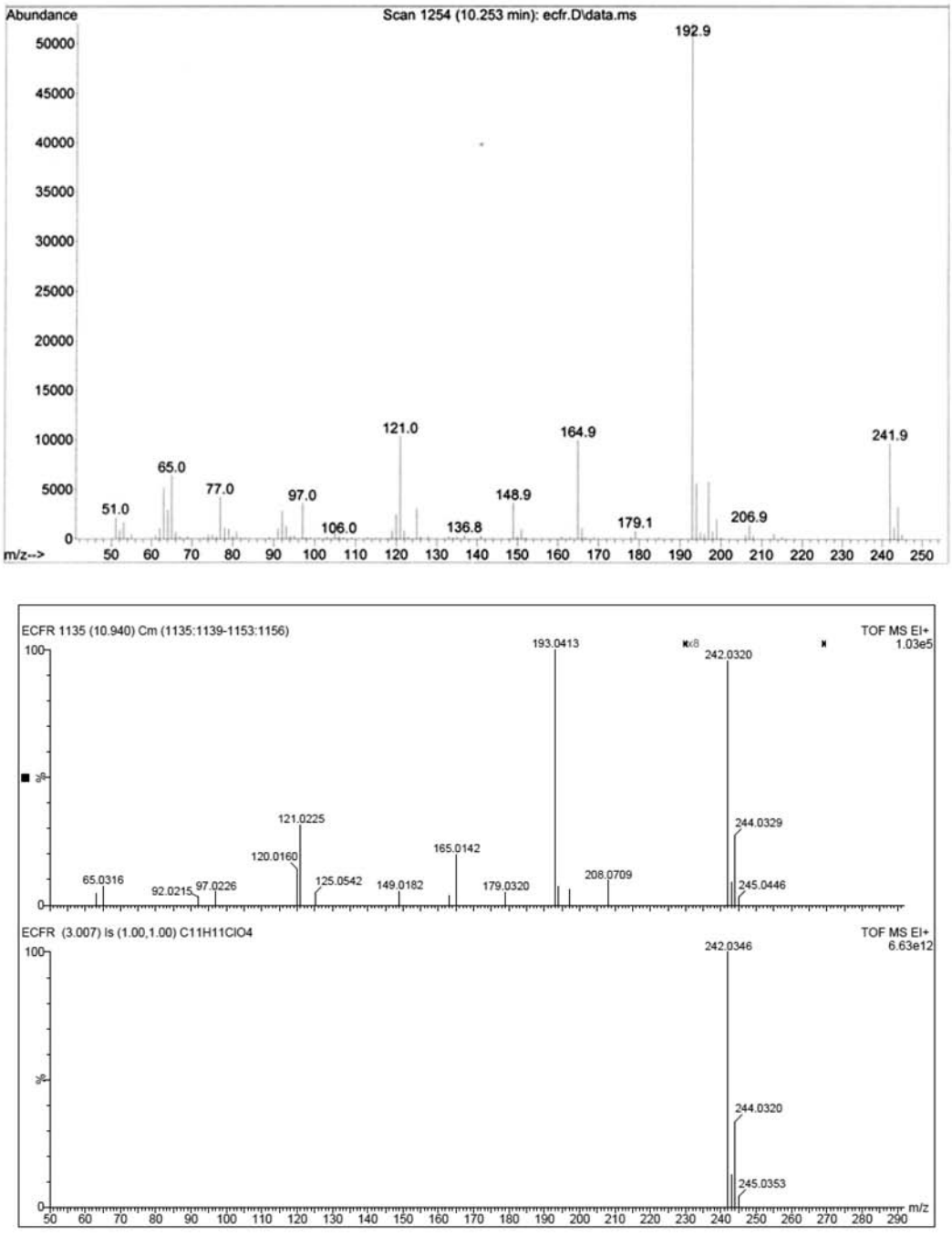


Figure S45. MS and HRMS (EI) spectra of ethyl (*E*)-2-chloroacetyl-3-(2'-furanyl)propenoate (*E*-**3e**).

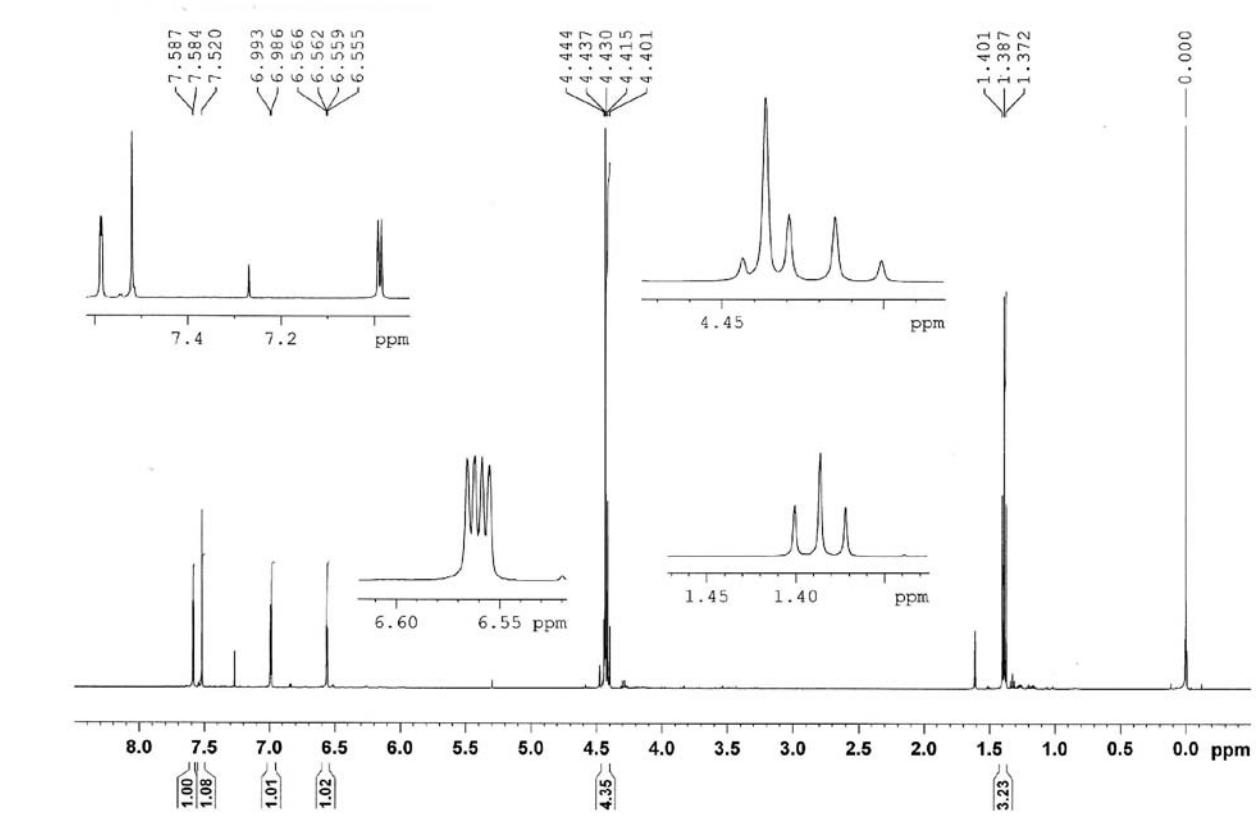


Figure S46. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(2'-furanyl)propenoate (*Z*-**3e**).

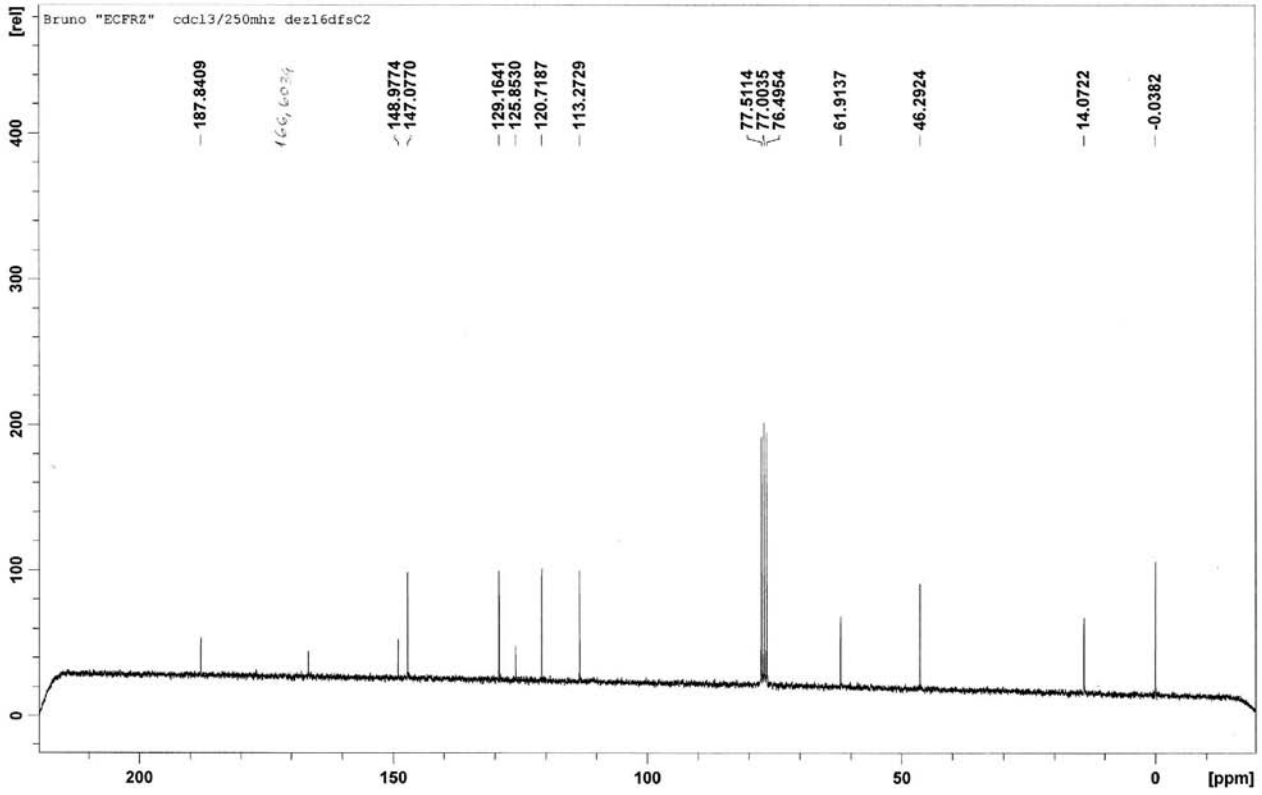


Figure S47. ^{13}C NMR spectrum ($CDCl_3$, 62.5 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(2'-furanyl)propenoate (*Z*-**3e**).

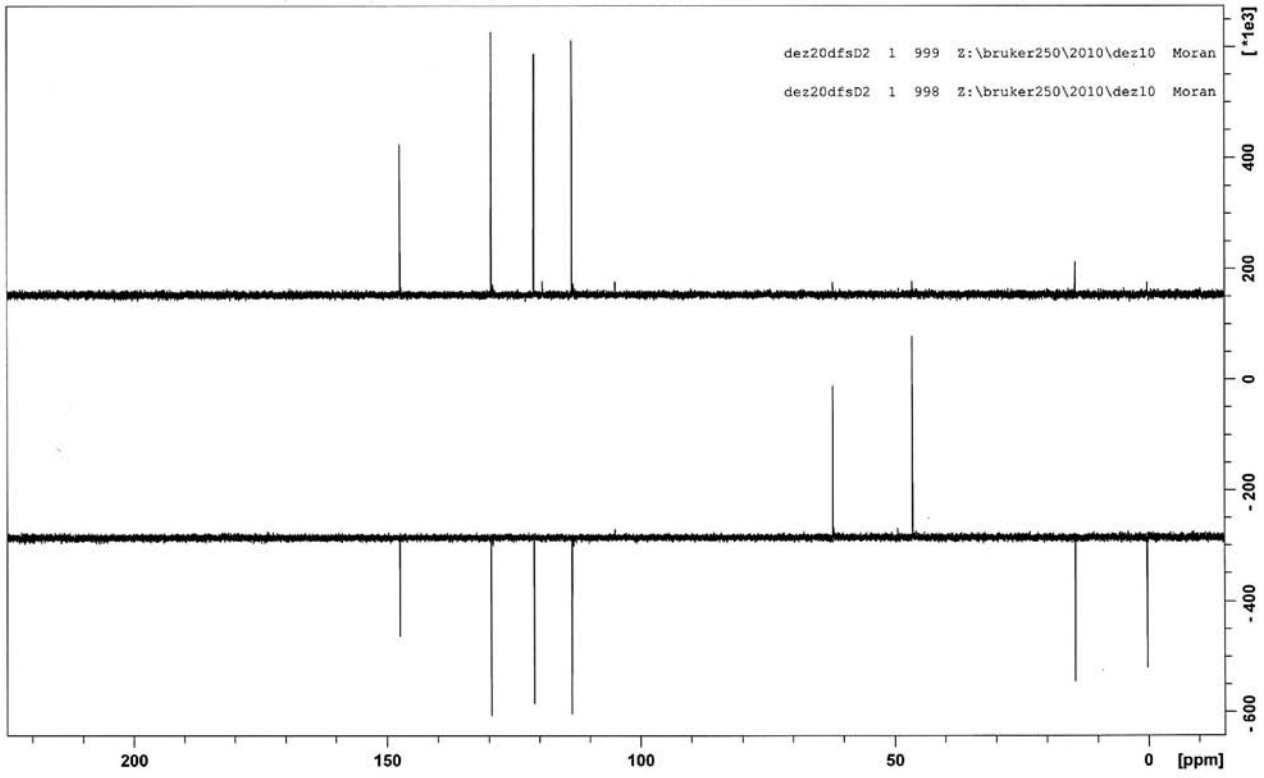


Figure S48. DEPT-90 and DEPT-135 spectra ($CDCl_3$, 62.5 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(2'-furanyl)propenoate (*Z*-**3e**).

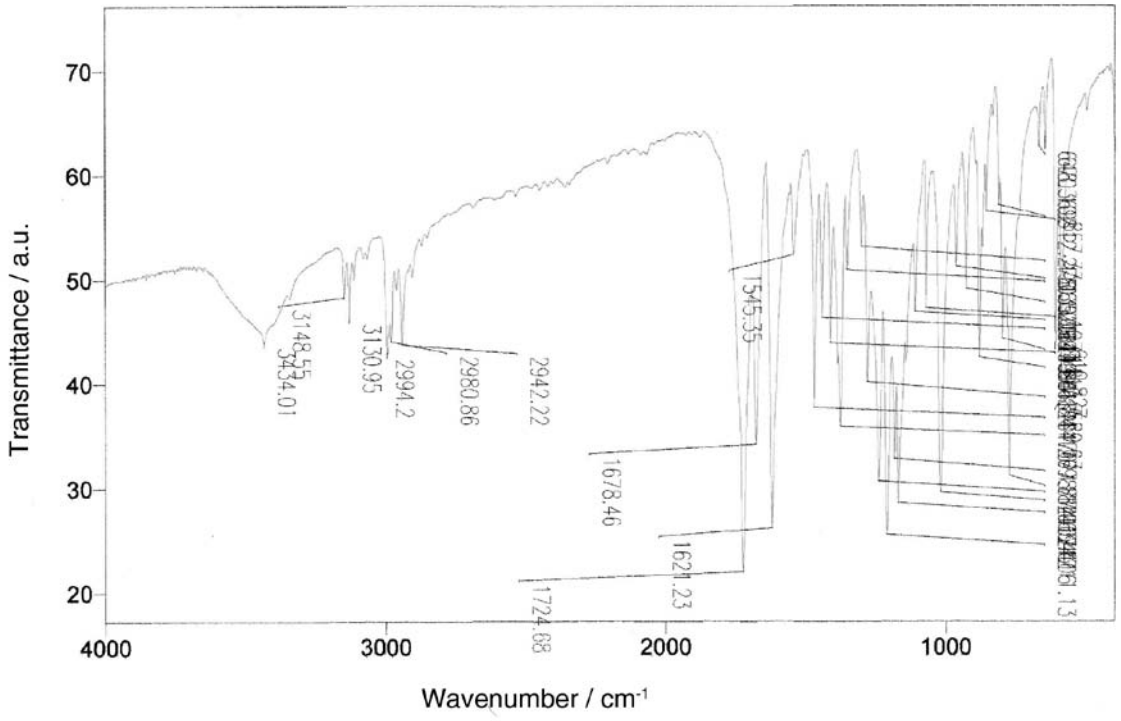


Figure S49. IR spectrum (film) of ethyl (*Z*)-2-chloroacetyl-3-(2'-furanyl)propenoate (*Z*-**3e**).

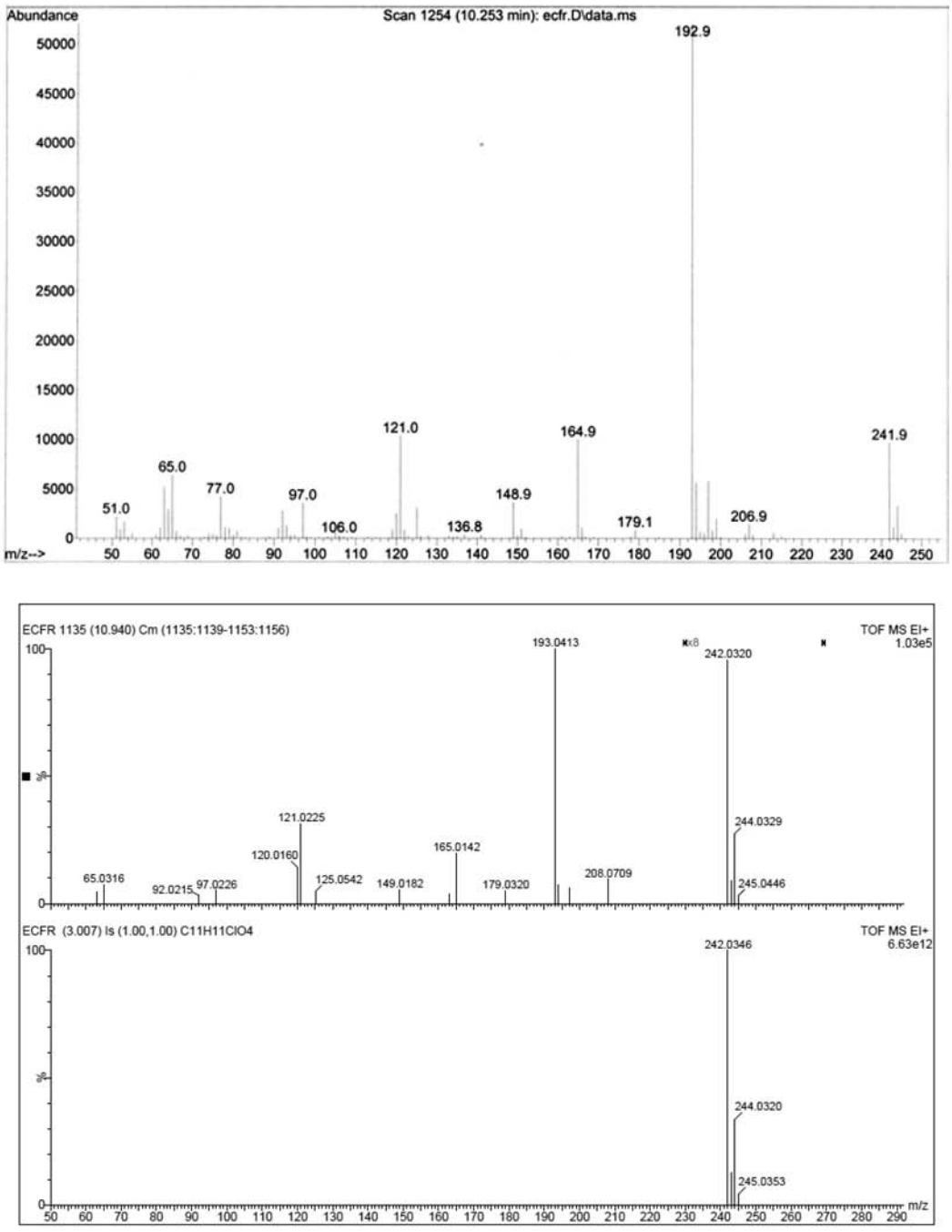


Figure S50. MS and HRMS (EI) spectra of ethyl (*Z*)-2-chloroacetyl-3-(2'-furanyl)propenoate (*Z*-**3e**).

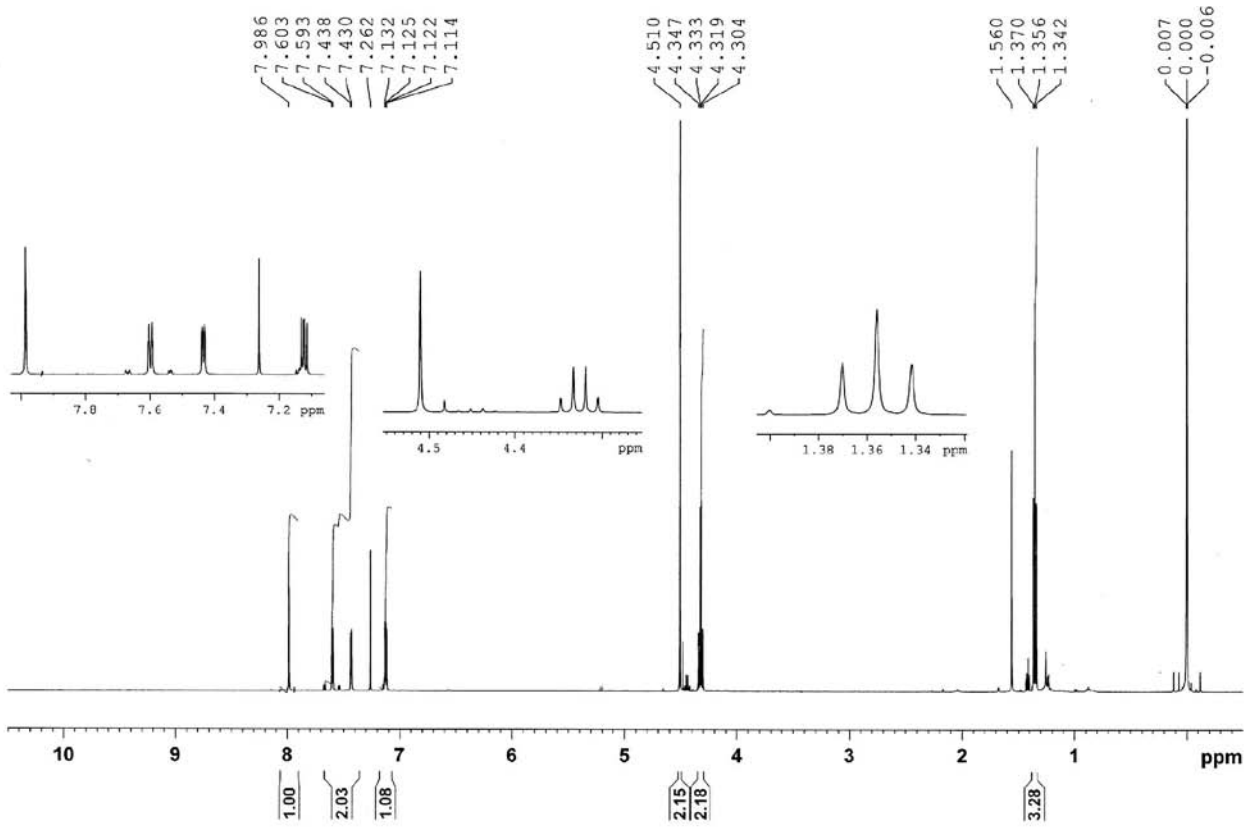


Figure S51. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of ethyl (*E*)-2-chloroacetyl-3-(2'-thiofuranyl)propenoate (*E*-**3f**).

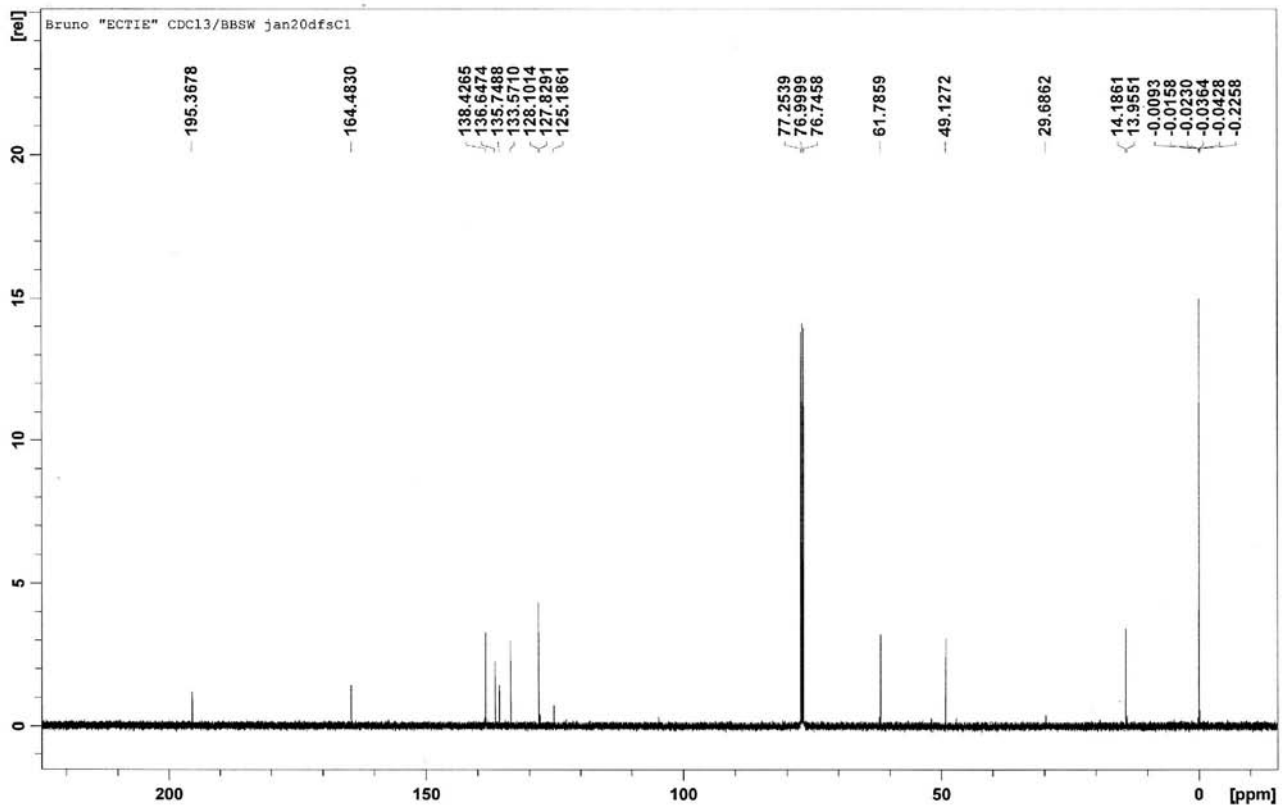


Figure S52. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of ethyl (*E*)-2-chloroacetyl-3-(2'-thiofuranyl)propenoate (*E*-**3f**).

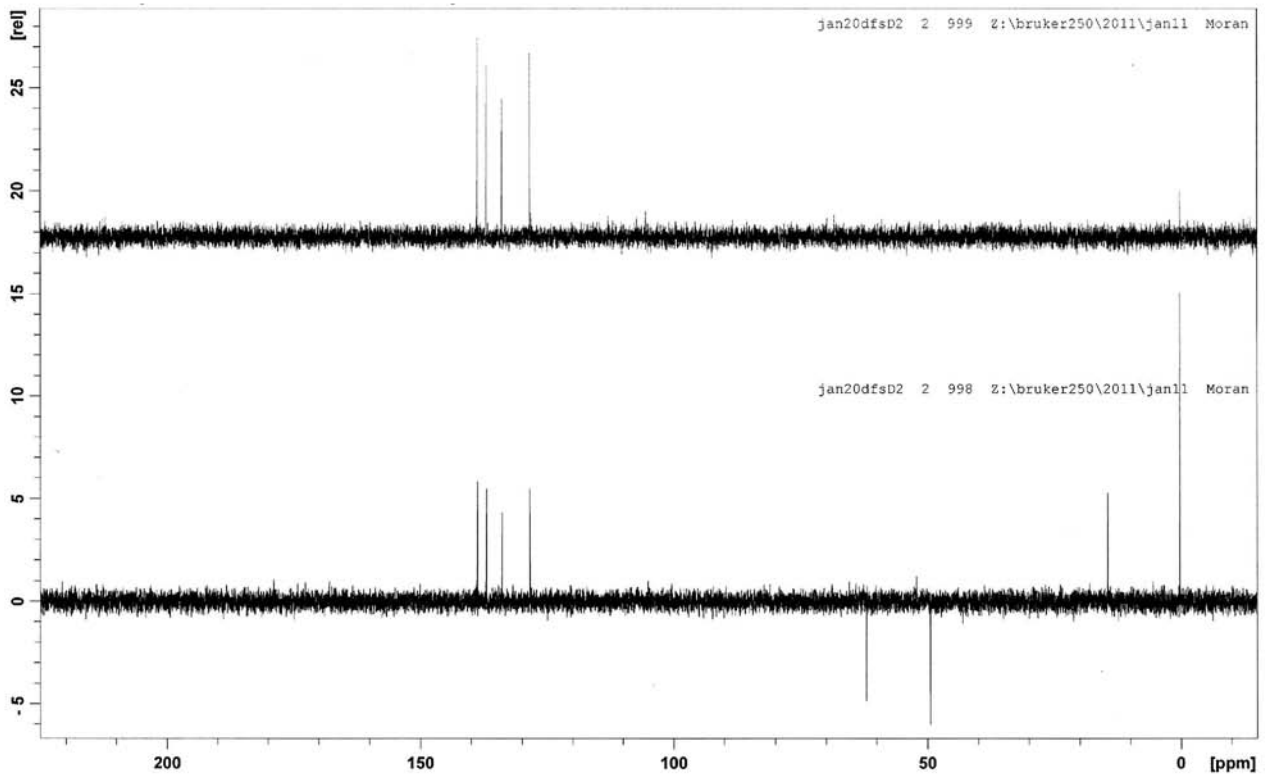


Figure S53. DEPT-90 and DEPT-135 spectra ($CDCl_3$, 125 MHz) of ethyl (*E*)-2-chloroacetyl-3-(2'-thiofuranyl)propenoate (*E*-**3f**).

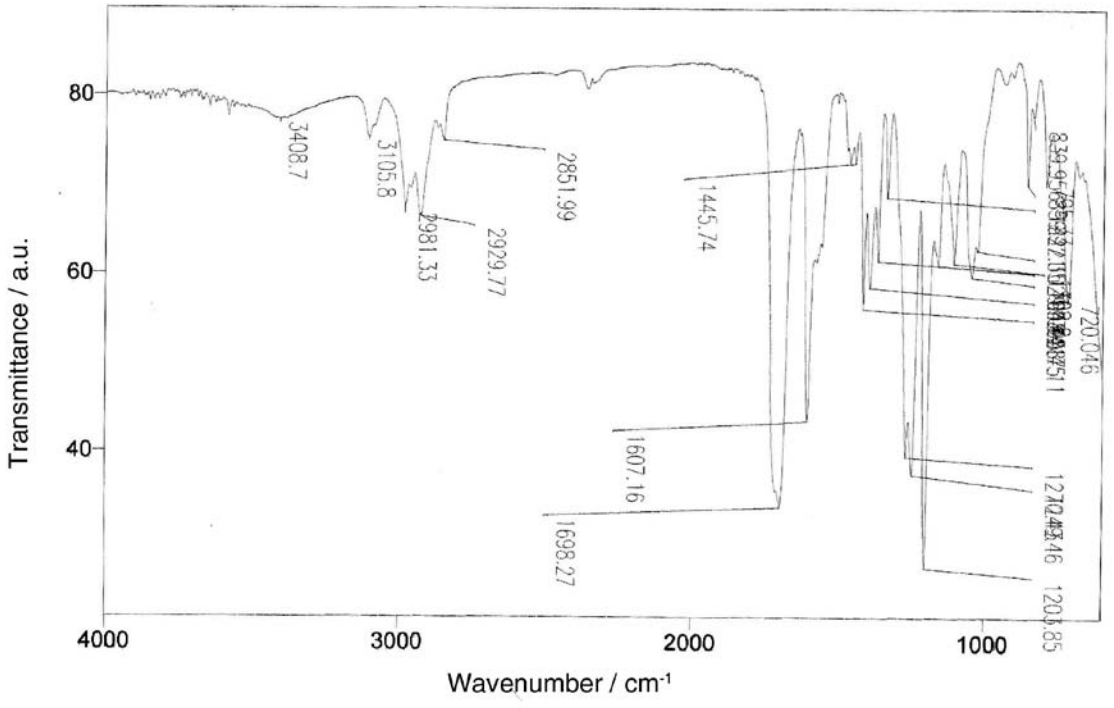


Figure S54. IR spectrum (film) of ethyl (*E*)-2-chloroacetyl-3-(2'-thiofuranyl)propenoate (*E*-**3f**).

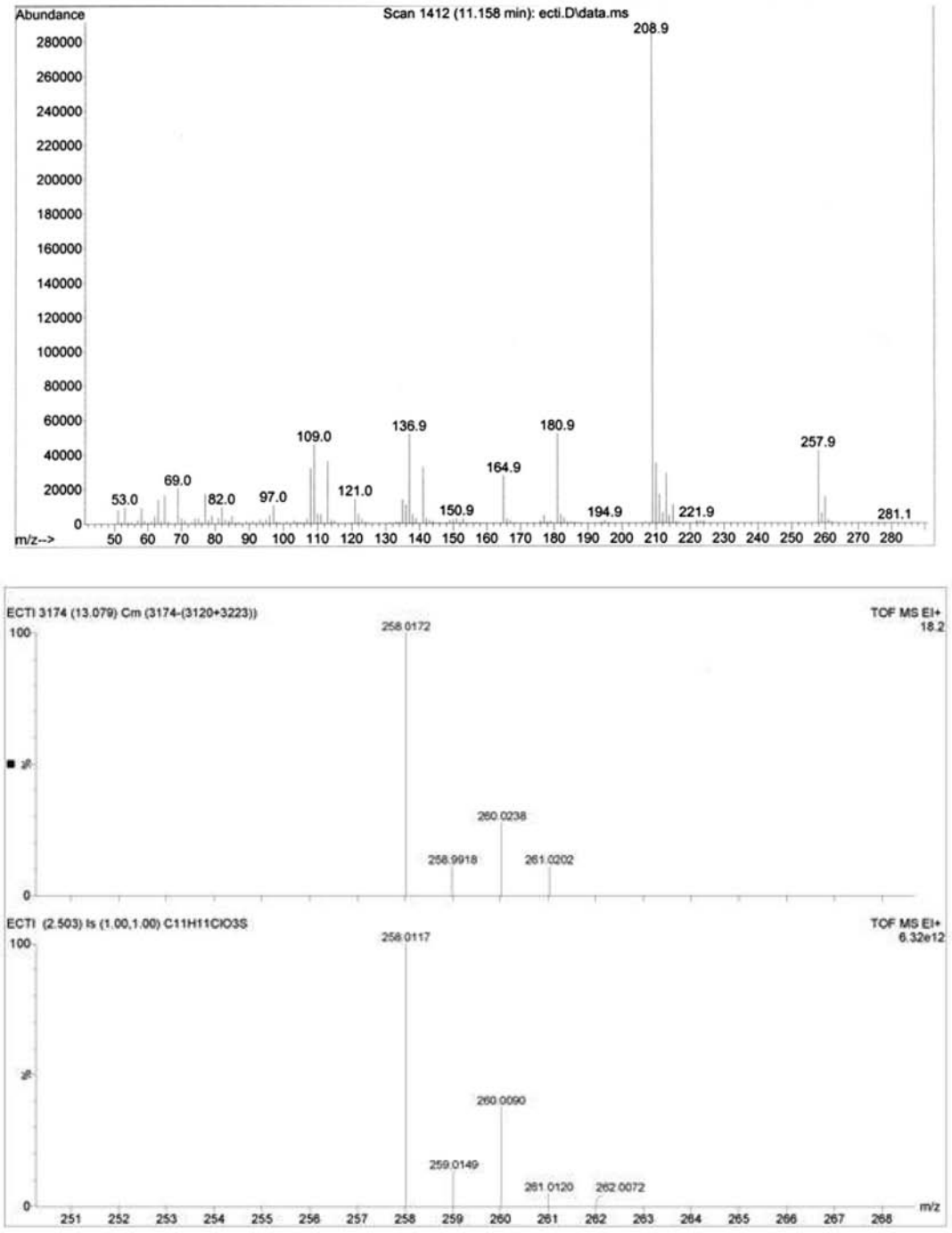


Figure S55. MS and HRMS (EI) spectra of ethyl (*E*)-2-chloroacetyl-3-(2'-thiofuranyl)propenoate (*E*-**3f**).

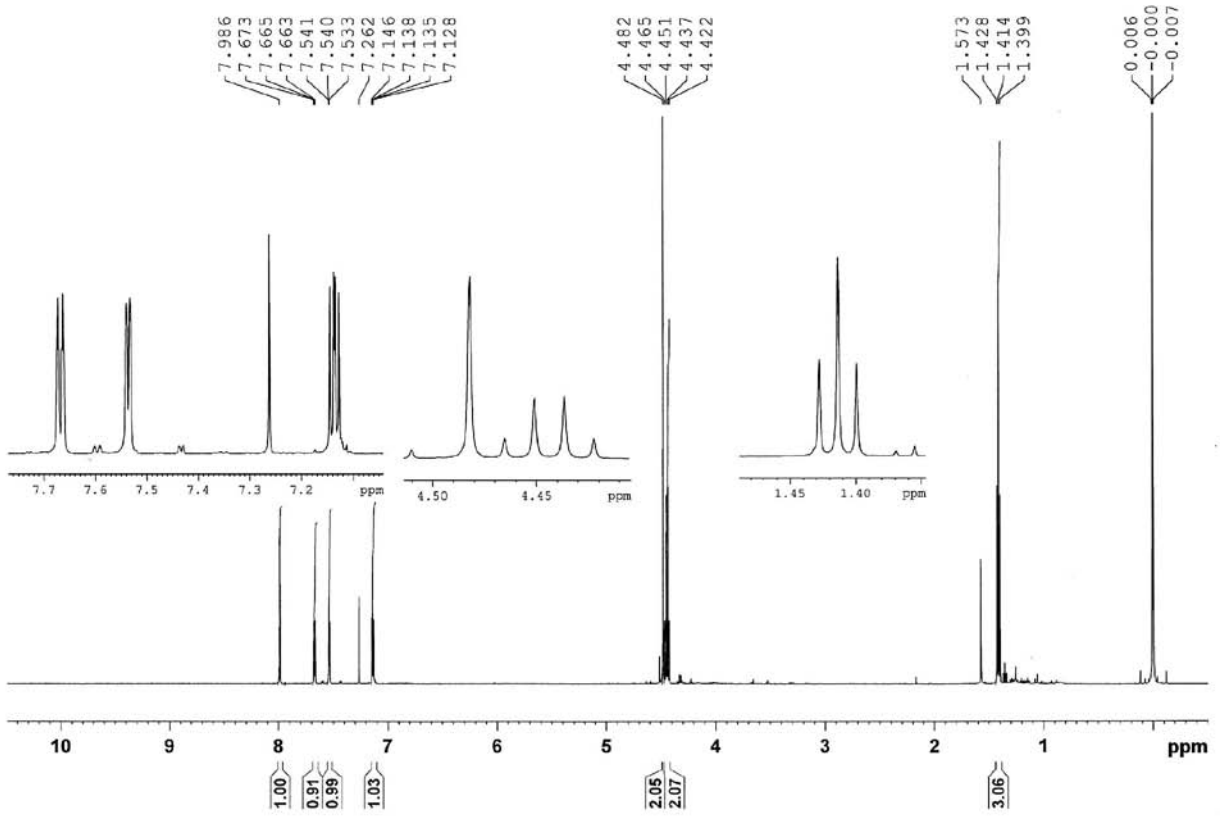


Figure S56. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(2'-thiofuranyl)propenoate (*Z*-**3f**).

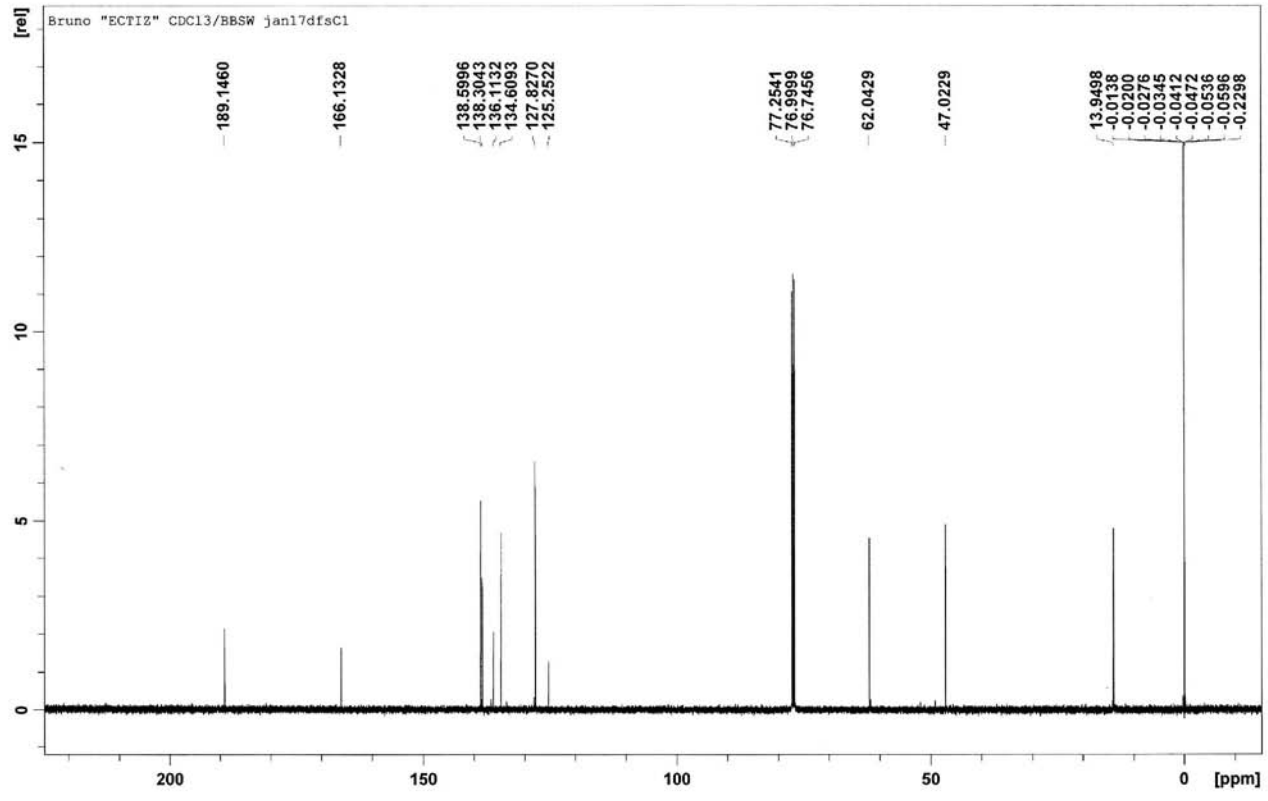


Figure S57. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(2'-thiofuranyl)propenoate (*Z*-**3f**).

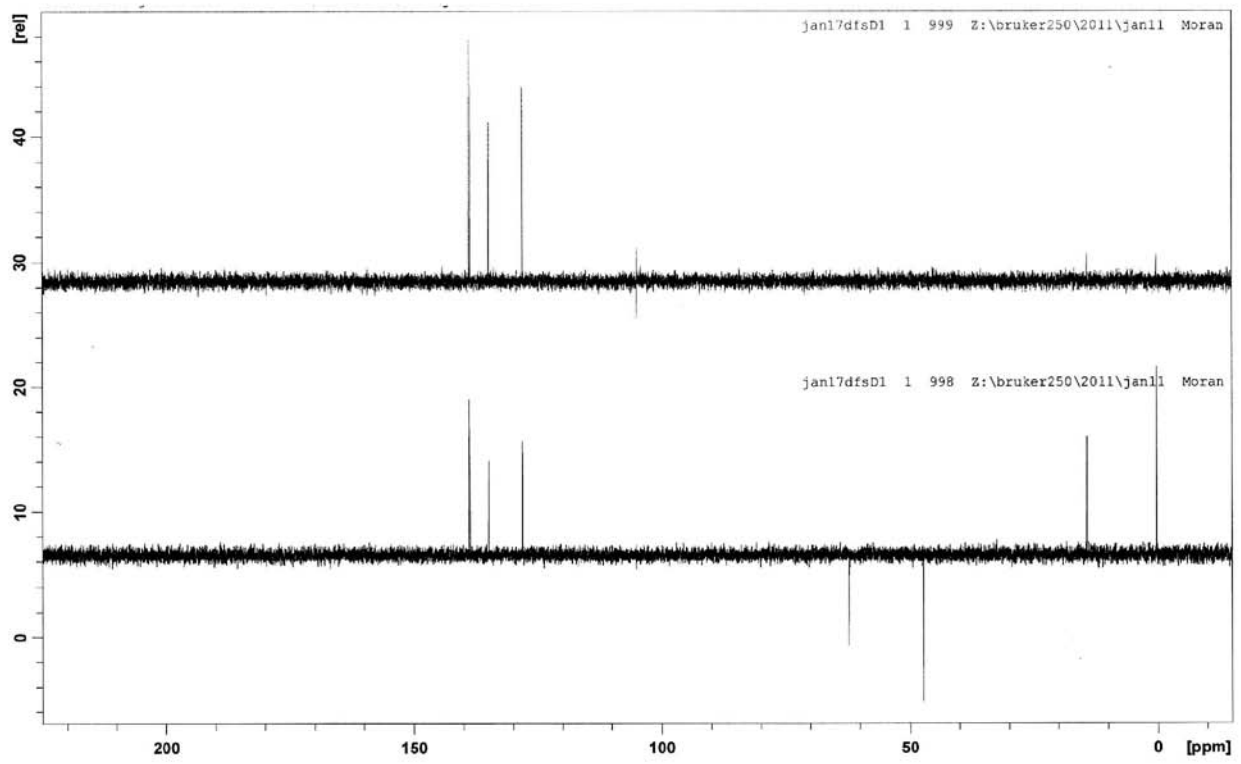


Figure S58. DEPT-90 and DEPT-135 spectra ($CDCl_3$, 125 MHz) of ethyl (*Z*)-2-chloroacetyl-3-(2'-thiofuranyl)propenoate (*Z*-**3f**).

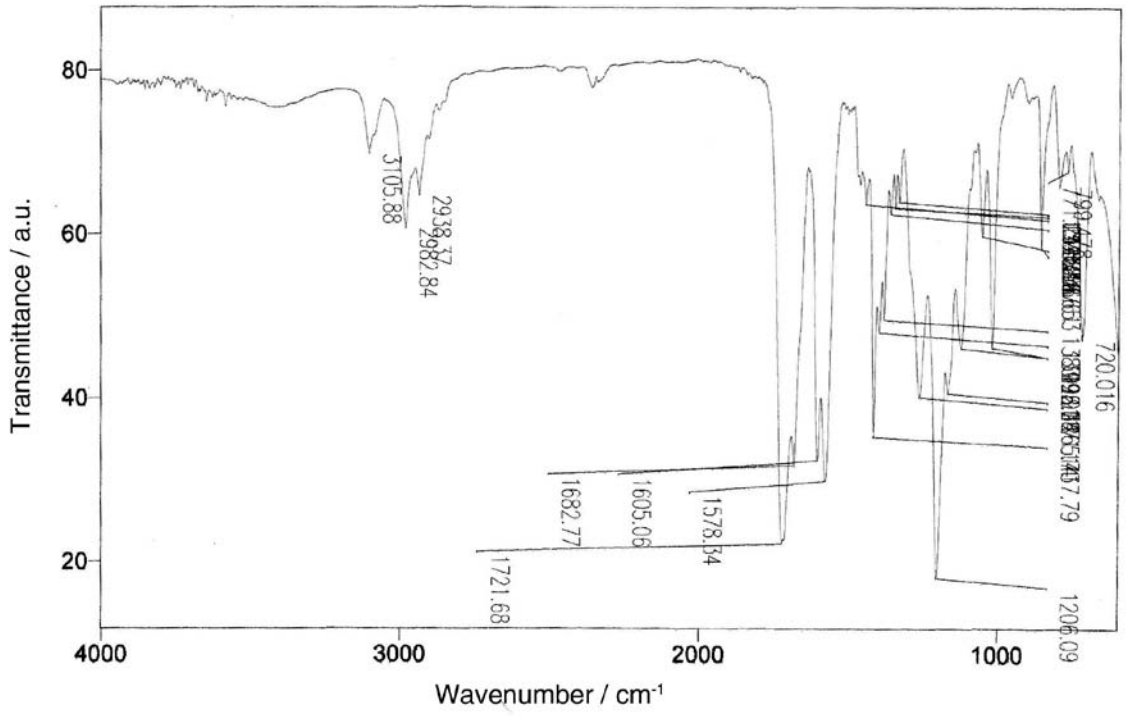


Figure S59. IR spectrum (film) of ethyl (*Z*)-2-chloroacetyl-3-(2'-thiofuranyl)propenoate (*Z*-**3f**).

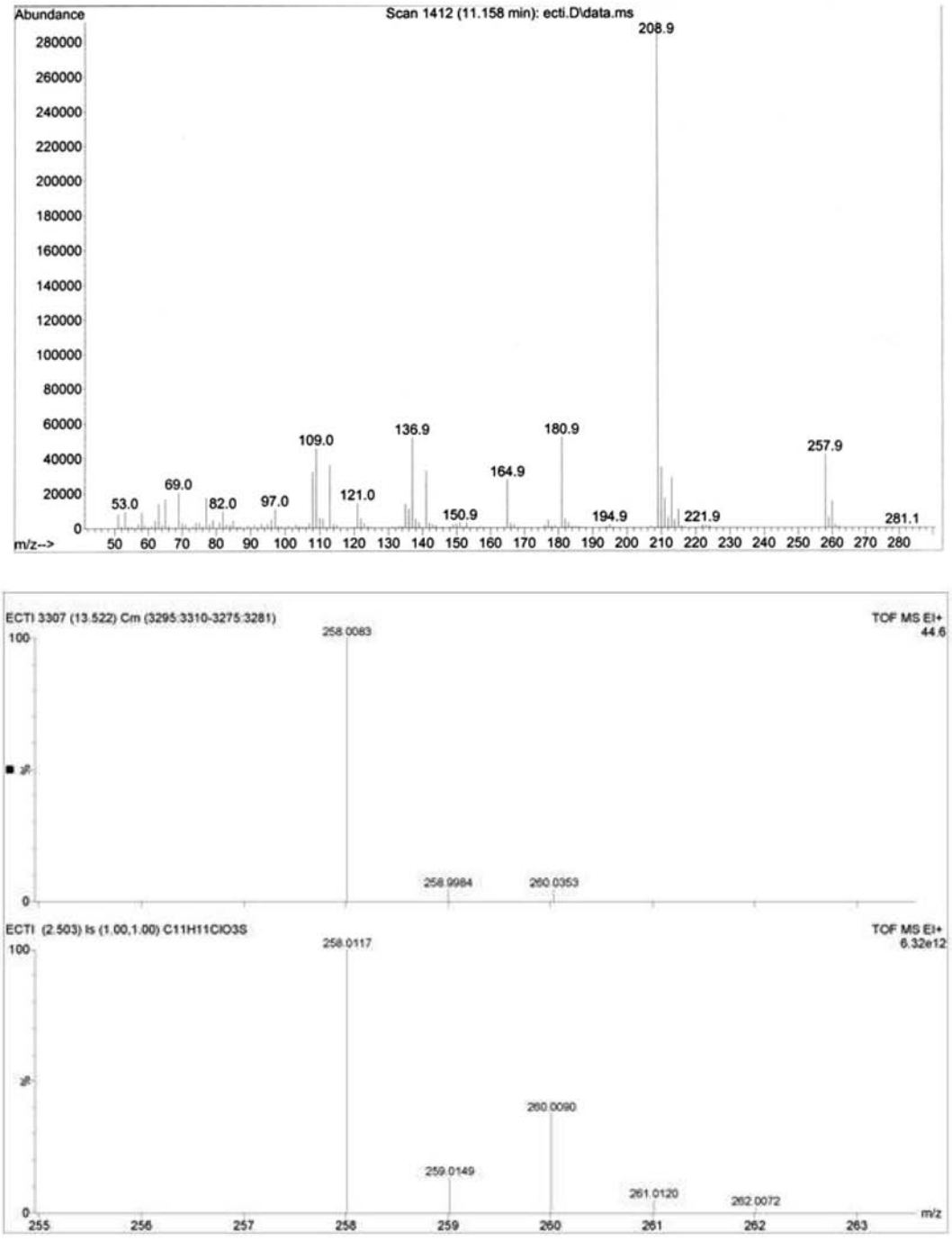


Figure S60. MS and HRMS (EI) spectra of ethyl (*Z*)-2-chloroacetyl-3-(2'-thiofuranyl)propenoate (*Z*-**3f**).