Supporting Information

Highly Stereoselective Synthesis of (*Z,E*)-1-halo-1,3-dienol Esters via Rearrangement of Fischer Chromium Chloro-carbenes using Microwave Irradiation †‡

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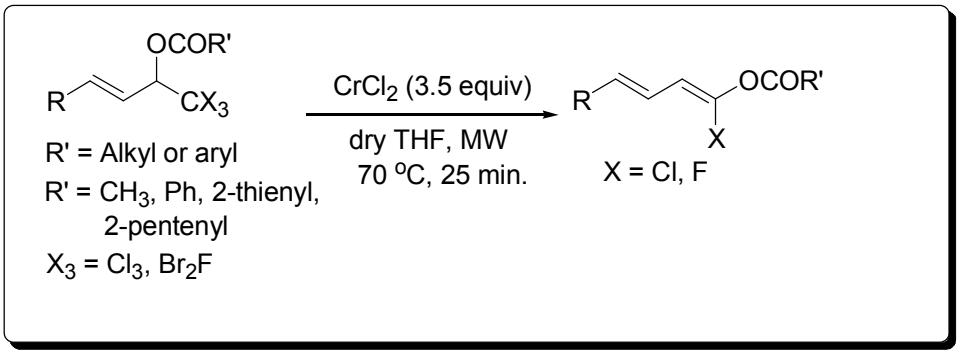
CONTENTS

1. General procedure for the preparation of 1-halo-1,3-dienol esters under microwave conditions

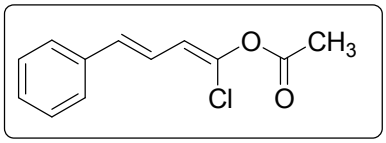
To a solution of allylic 1,1,1-trichloromethylcarbinol ester (1 equiv) in dry THF was added $CrCl_2$ (3.5 equiv) and the mixture was degassed with argon for 10 min and allowed to be irradiated under microwaves at 70 ^oC for 25 min. After completion of the reaction (TLC), the reaction mixture was cooled to RT, diluted with water and extracted with diethyl ether. The organic layers were washed with water, brine and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave the crude product which was purified by silica gel column chromatography. Elution of the column with diethyl ether/*n*-pentane gave the desired (*Z,E*)-1-halo-1,3-dienol esters.

CAUTION: 1-halo-1,3-dienol esters are highly reactive molecules that may be harmful (characteristic pungent smell) upon prolonged exposure during manipulations and purification steps. It is suggested to use proper precautions (well ventilated fume hood) while working with compounds.



(1Z,3E)-1-chloro-4-phenylbuta-1,3-dienyl acetate (2)

Colorless low melting solid



Yield: 84% (conventional heating)

92% (microwave conditions)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.24 (s, 3H), 6.20 (d, J = 10.3 Hz, 1H), 6.65 (d, J = 15.9 Hz, 1H), 6.88 (dd, J_1 = 10.2 Hz, J_2 = 5.2 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 7.37-7.35 (m, 2H), 7.44 (d, J = 7.1 Hz, 2H).

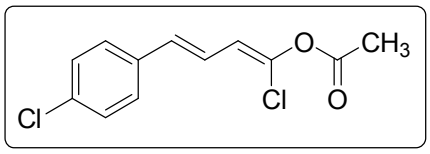
^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.96, 119.20, 122.36, 127.05, 128.62, 129.10, 135.53, 135.62, 137.09, 168.15.

FTIR (neat) ν_{max} 2923, 2853, 1783, 1638, 1368, 1176, 1079, 962, 747, 690 cm^{-1}

GCMS (EI): 222.1 (M^+).

(1Z,3E)-1-chloro-4-(4-chlorophenyl) buta-1,3-dienyl acetate (4)

White colored low melting solid



Yield: 24% (conventional heating)

74% (microwave conditions)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.23 (s, 3H), 6.17 (d, J = 10.2 Hz, 1H), 6.58 (d, J = 15.9 Hz, 1H), 6.83 (dd, J_1 = 10.6 Hz, J_2 = 5.2 Hz, 1H), 7.30 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H).

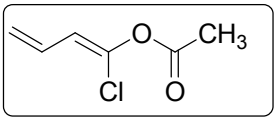
^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.96, 118.96, 122.95, 128.19, 129.29, 134.07, 134.21, 135.58, 136.09, 168.07.

FTIR (neat) ν_{max} 2922, 2852, 1783, 1638, 1490, 1369, 1175, 1077, 963, 805, 637, 630 cm^{-1}

GCMS (CI): 257.1 (M+1)

(Z)-1-chlorobuta-1,3-dienyl acetate (6)

Colorless liquid



Yield: (>90% conversion from crude ^{1}H-NMR spectrum)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.21 (s, 3H), 5.31 (ddd, J_1 = 18.0 Hz, J_2 = 10.9 Hz, J_3 = 3.2 Hz, 2H), 6.03 (d, J = 10.4, 1H), 6.47 (dt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, 1H).

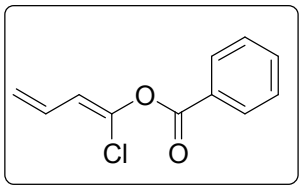
^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.64, 119.07, 120.65, 130.39, 135.73, 167.73.

FTIR (neat) ν_{max} 2924, 2853, 1787, 1732, 1217, 1185, 1101, 669 cm^{-1}

GCMS (CI): 147.0 (M+1)

(Z)-1-chlorobuta-1,3-dienyl benzoate (8)

Colorless liquid



Yield: 68%

^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.36 (ddd, J_1 = 16.8, J_2 = 10.2, J_3 = 8.1 Hz, 2H), 6.18 (d, J = 10.2, 1H), 6.56 (dt, J_1 = 17.1, J_2 = 10.5 Hz, 1H), 7.53-7.48 (m, 2H), 7.68-7.63 (m, 1H), 8.05 (d, J = 8.1 Hz, 2H).

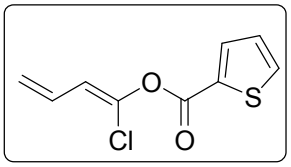
^{13}C-NMR (75 MHz, $CDCl_3$) δ 110.00, 119.62, 120.92, 128.53, 129.14, 130.77, 134.66, 136.33, 163.90.

FTIR (neat) ν_{max} 3062, 2926, 1753, 1695, 1451, 1259, 1091, 1037, 1012, 870, 735, 703, 649 cm^{-1}

GCMS (CI): 209.1 (M+1)

(Z)-1-chlorobuta-1,3-dienyl thiophene-2-carboxylate (10)

Colorless liquid



Yield: 81%

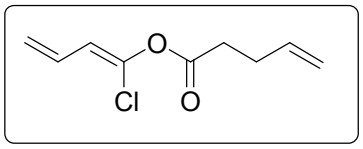
^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.31 (d, J = 10.2 Hz, 1H), 5.42-5.30 (m, 1H), 6.18 (d, J = 10.2 Hz, 1H), 6.53 (dt, J_1 = 17.1 Hz, J_2 = 10.5 Hz, 1H), 7.18 (td, J_1 = 4.2 Hz, J_2 = 0.1 Hz, 1H), 7.77 (t, J = 2.9 Hz, 1H), 7.95 (t, J = 2.6, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 119.58, 119.84, 120.87, 121.13, 128.63, 130.59, 131.50, 135.00, 135.18, 135.88, 136.00, 136.18, 159.22.

FTIR (neat) ν_{max} 2922, 2851, 1781, 1737, 1661, 1519, 1411, 1246, 1077, 1043, 997, 858, 720 cm^{-1}

GCMS (CI): 215.1 (M+1)

(Z)-1-chlorobuta-1,3-dienyl pent-4-enoate (12)



Colorless liquid, 85%

^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.55-2.41 (m, 2H), 2.58 (t, J_1 = 6.8 Hz, J_2 = 1.5 Hz, 2H), 5.15-5.05 (m, 2H), 5.80-5.78 (m, 2H), 5.85 (dddd, J_1 = 17.3 Hz, J_2 = 10.1 Hz, J_3 = 5.0 Hz, 1H), 6.02 (dd, J_1 = 10.6 Hz, J_2 = 2.4 Hz, 1H), 6.47 (dtd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, J_3 = 2.4 Hz, 1H).

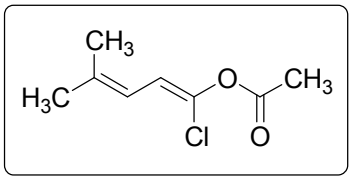
^{13}C-NMR (75 MHz, $CDCl_3$) 28.84, 33.49, 116.62, 119.21, 120.75, 130.61, 135.96, 136.10, 170.11.

FTIR (neat) ν_{max} 2924, 2853, 1777, 1645, 1417, 1256, 1080, 913, 681 cm^{-1}

GCMS (CI): 187.1 (M+1)

(Z)-1-chloro-4-methylpenta-1,3-dienyl acetate (14)

Colorless liquid



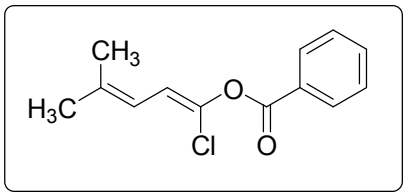
Yield: (>90% conversion from crude ^{1}H-NMR spectrum)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.74 (s, 3H), 1.85 (s, 3H), 2.21 (s, 3H), 5.2 (dt, J_1 = 10.9 Hz, J_2 = 2.1 Hz, 1H), 6.18 (d, J = 10.8 Hz, 1H).

FTIR (neat) ν_{max} 2979, 2931, 1697, 1655, 1416, 1286, 1132, 1081, 978, 669 cm^{-1}

GCMS (CI): 175.1 (M+1)

(Z)-1-chloro-4-methylpenta-1,3-dienyl benzoate (16)



Colorless liquid 77%

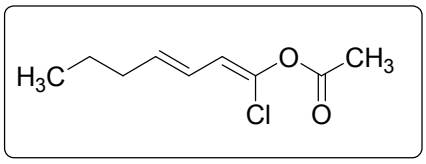
^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.76 (s, 3H), 1.88 (s, 3H), 6.01 (dt, J_1 = 11.0 Hz, J_2 = 2.1 Hz, 1H), 6.32 (d, J = 10.8 Hz, 1H), 7.45 (d, J_1 = 8.4 Hz, J_2 = 7.2 Hz, 2H), 7.75 (t, J = 7.2 Hz, 1H), 8.11 (d, J = 8.4 Hz, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.35, 26.72, 115.69, 118.62, 128.78, 129.06, 130.73, 133.77, 134.46, 140.19, 164.38.

FTIR (neat) ν_{max} 2981, 2933, 1789, 1756, 1697, 1287, 1242, 1082, 709 cm^{-1}

GCMS (CI): 237.1 (M+1)

(1Z,3E)-1-chlorohepta-1,3-dienyl acetate (18)



Colorless liquid

Yield: 90%

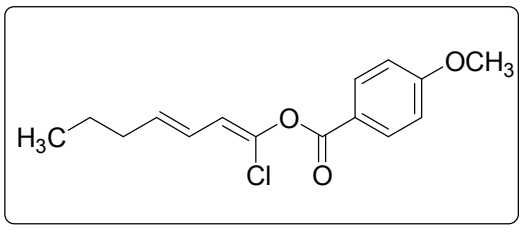
^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 7.1 Hz, 3H), 1.47-1.40 (quintet, 2H), 2.09 (q, J = 7.0 Hz, 2H), 2.19 (s, 3H), 5.82 (dt, J_1 = 13.8 Hz, J_2 = 6.9 Hz, 1H), 5.98 (d, J = 10.8 Hz, 1H), 6.18-6.13 (m, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.06, 20.87, 20.93, 22.58, 35.46, 118.92, 123.78, 133.31, 138.81, 168.29.

FTIR (neat) ν_{max} 2960, 2930, 2874, 1786, 1699, 1658, 1370, 1182, 1074, 968, 879, 668 cm^{-1}

GCMS (CI): 189.1 (M+1)

(1Z,3E)-1-chlorohepta-1,3-dienyl 4-methoxybenzoate (20)



Colorless liquid

Yield: 83%

^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz), 1.49-1.42 (m, 2H), 2.14 (q, J = 7.4 Hz), 3.8 (s, 3H), 5.85 (dq, J_1 = 14.9 Hz, J_2 = 6.6 Hz, 1H), 6.1 (d, J = 10.6 Hz, 1H), 6.27-6.13 (m, 1H), 6.95 (d, J = 9.0 Hz, 2H), 8.04 (d, J = 9.0 Hz, 2H)

^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.07, 22.64, 35.52, 55.93, 114.36, 119.09, 120.85, 124.00, 132.92, 133.83, 138.59, 163.88, 164.72.

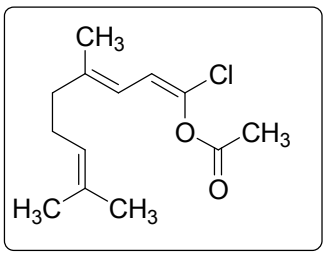
FTIR (neat) ν_{max} 2960, 2931, 2873, 1786, 1699, 1658, 1370, 1183, 1074, 968, 880 cm^{-1}

GCMS (CI): 281.2 (M+1)

(1E,3E)-1-chloro-4,8-dimethylnona-1,3,7-trienyl acetate (22a)

Colorless liquid

Yield: 12%



^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.56 (s, 3H), 1.62 (s, 3H), 1.70 (s, 3H), 1.85 (s, 3H), 2.12 (s, 3H), 2.24 (s, 3H), 5.08 (m, 1H), 5.62 (s, 1H), 7.30 (s, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.09, 18.57, 20.99, 26.07, 26.75, 40.33, 116.69, 119.33, 123.26, 132.62, 133.26, 144.06, 167.77.

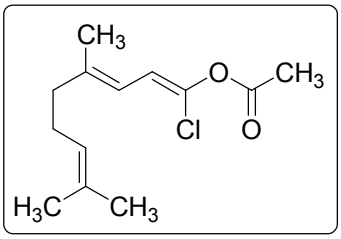
FTIR (neat) ν_{max} 2964, 2925, 2854, 1764, 1706, 1619, 1435, 1371, 1207, 1046 cm^{-1}

GCMS (CI): 243.2 (M+1)

(1Z,3E)-1-chloro-4,8-dimethylnona-1,3,7-trienyl acetate(22b)

Colorless liquid

Yield: 64%



^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.62 (s, 3H), 1.69 (s, 3H), 1.74 (d, J = 1.3 Hz, 3H), 2.13 (t, J = 2.7 Hz, 4H), 2.21 (s, 3H), 5.10 (bs, 1H), 5.93 (d, J = 10.9 Hz, 1H), 6.19 (d, J = 10.9 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.77, 18.14, 20.99, 26.10, 26.86, 40.52, 115.41, 118.15, 124.06, 132.44, 133.69, 143.79, 168.58.

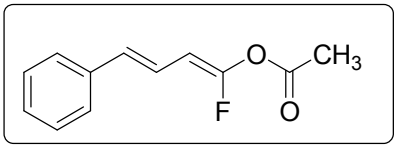
FTIR (neat) ν_{max} 2971, 2922, 2854, 1785, 1613, 1441, 1369, 1178, 1076, 881, 720, 669 cm^{-1}

GCMS (CI): 243.2 (M+1)

(1Z,3E)-1-fluoro-4-phenylbuta-1,3-dienyl acetate (24)

White low melting solid

Yield: 74%



^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.27 (s, 3H), 5.4 (dd, J_1 = 25.8 Hz, J_2 = 10.8 Hz, 1H), 6.55 (d, J = 15.8 Hz, 1H), 6.88 (dd, J_1 = 15.9 Hz, J_2 = 10.8 Hz, 1H), 7.47-7.29 (m, 5H)

^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.72 (d, J = 21.9 Hz, CH_3-F coupling), 96.32 (d, J = 74.93 Hz, C-F coupling), 119.39, 126.73, 128.10, 129.074, 132.27, 137.38, 149.17, 153.00, 167.44

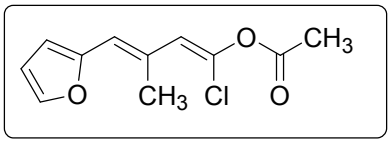
^{19}F-NMR (75 MHz, $CDCl_3$) δ -84.25 (d, 25.9 Hz).

FTIR (neat) ν_{max} 3060, 3027, 2925, 1791, 1690, 1369, 1188, 1150, 1131, 1010, 985, 964, 928, 867, 747, 691 cm^{-1}

GCMS (CI): 207.1 (M+1)

(1Z,3E)-1-chloro-4-(furan-2-yl)-3-methylbuta-1,3-dienyl acetate (26)

White colored low melting solid



Yield: 68%

^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.22 (d, *J* = 9.6, 3H), 2.28 (s, 3H), 6.05 (s, 1H), 6.38 (d, *J* = 3.2 Hz, 1H), 3.43 (bs, 1H), 7.42 (bs, 1H).

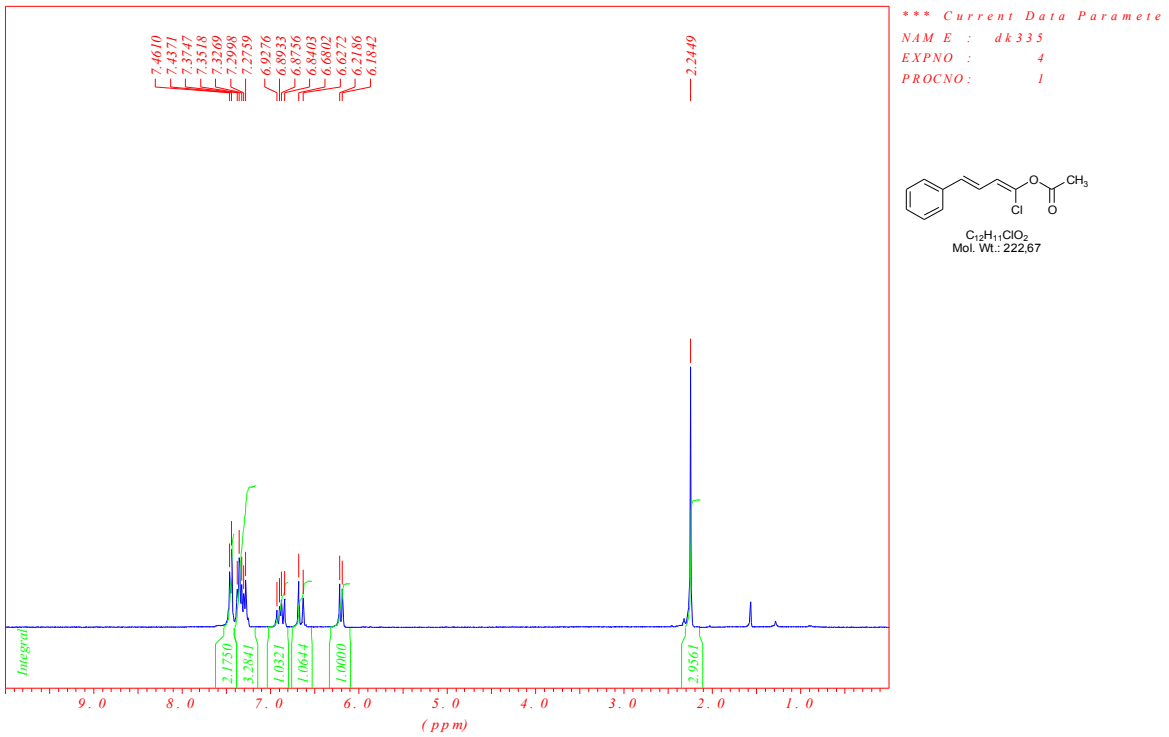
^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.82, 20.96, 111.23, 111.96, 121.75, 123.12, 128.65, 133.07, 142.52, 153.16, 168.31.

FTIR (neat) ν_{max} 2922, 1777, 1629, 1368, 1180, 1068, 1027, 884, 734, 668, 608 cm^{-1}

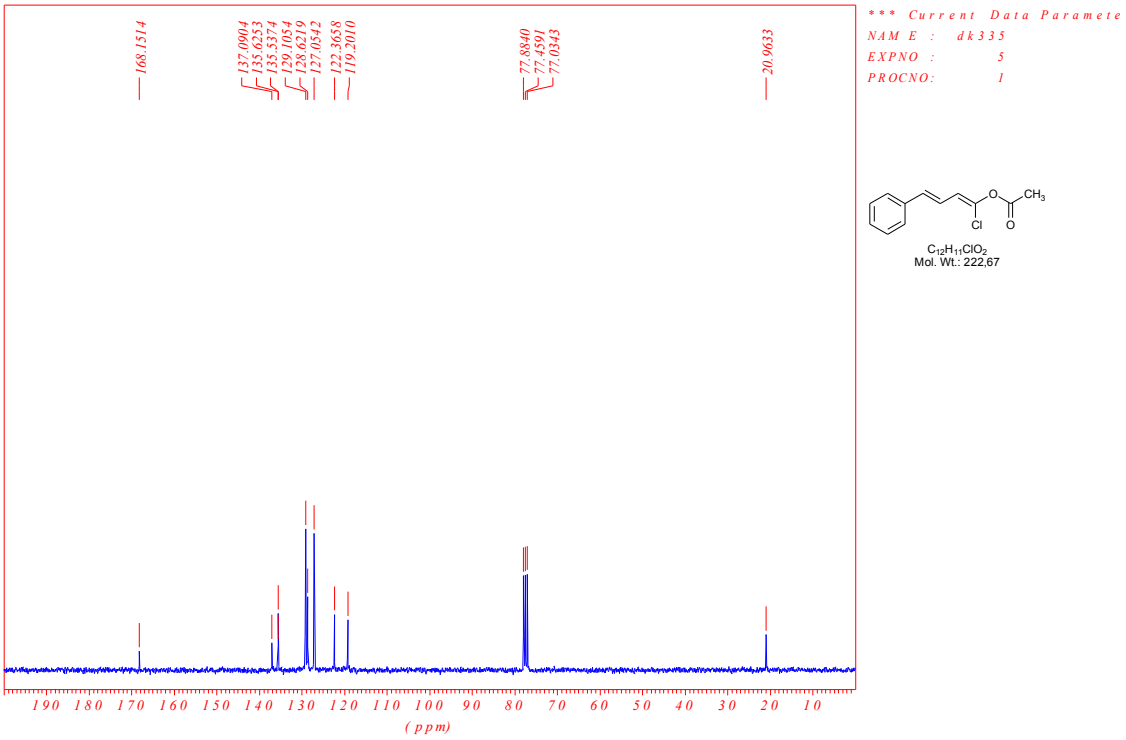
GCMS (EI): 226.1 (M^+)

2. Data of original compounds

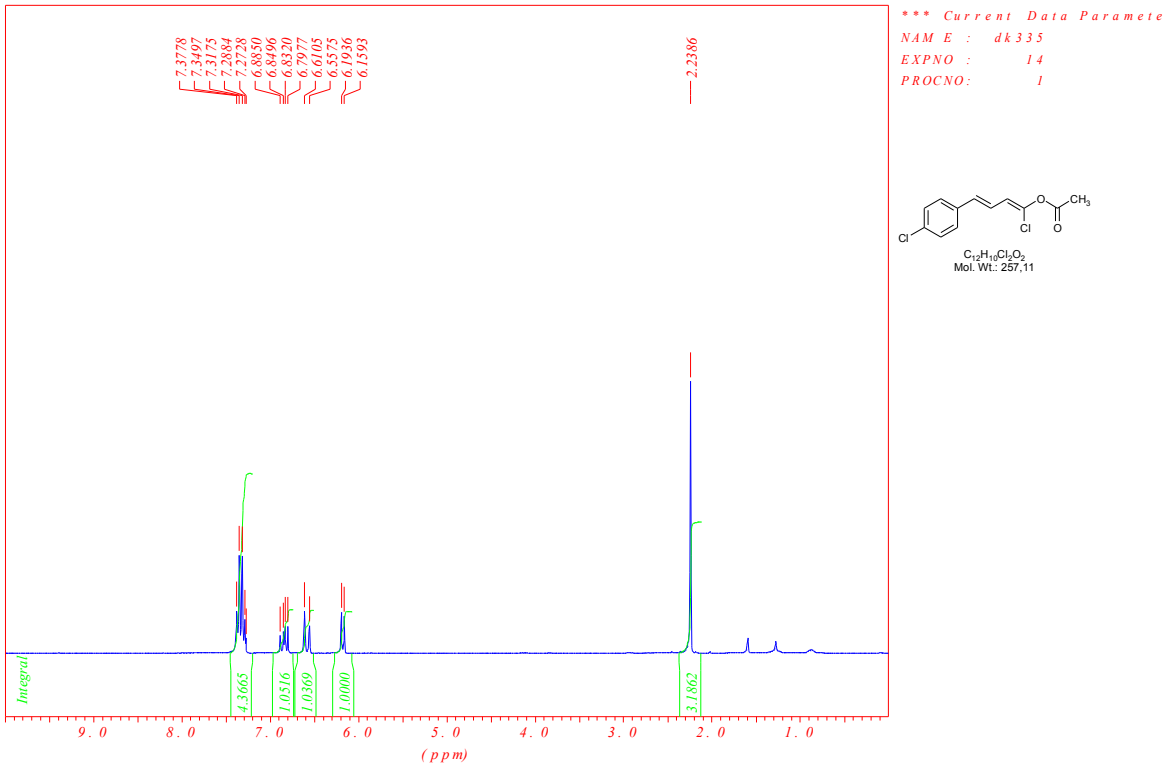
^{1}H-NMR spectrum of dienol ester (2)



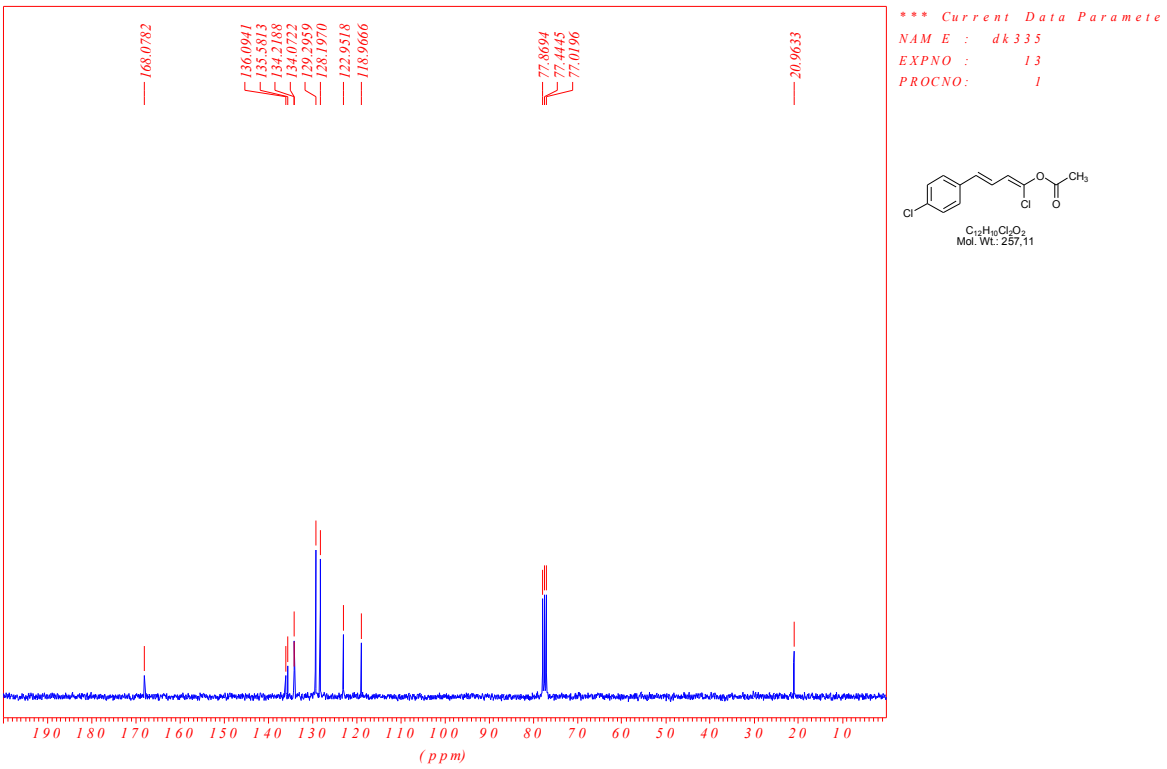
^{13}C-NMR spectrum of dienol ester (2)



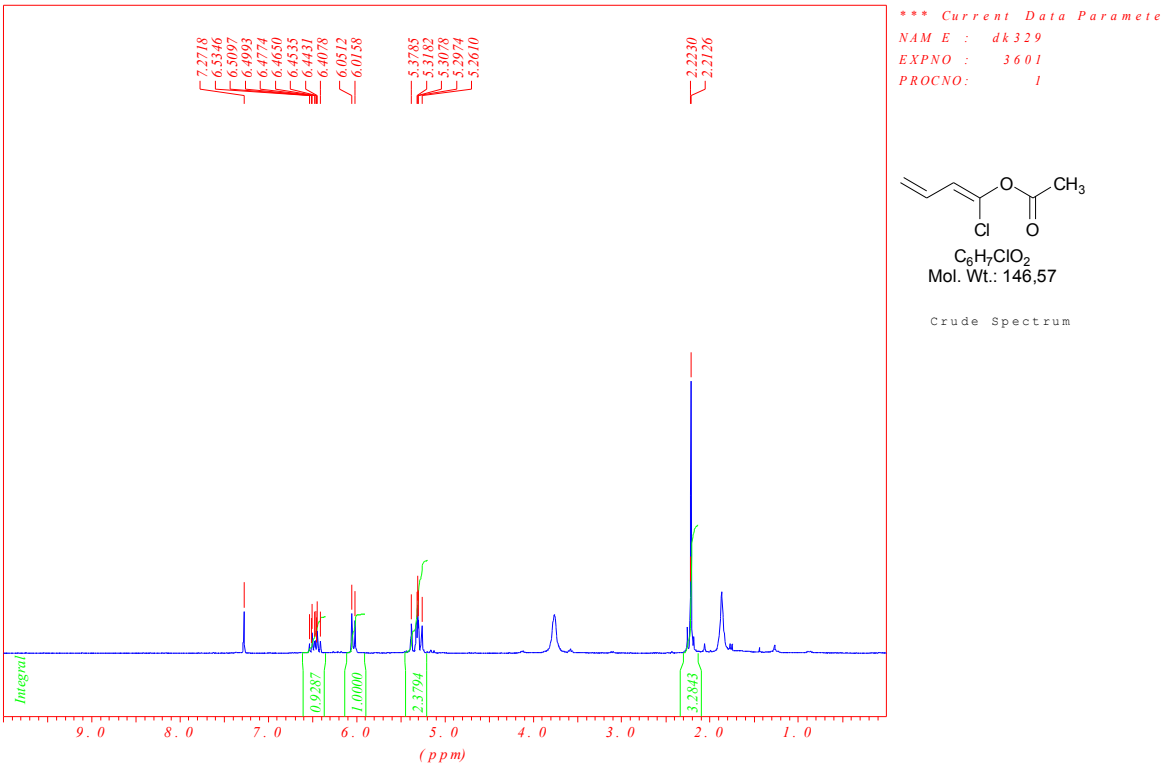
[1]H-NMR spectrum of dienol ester (4)



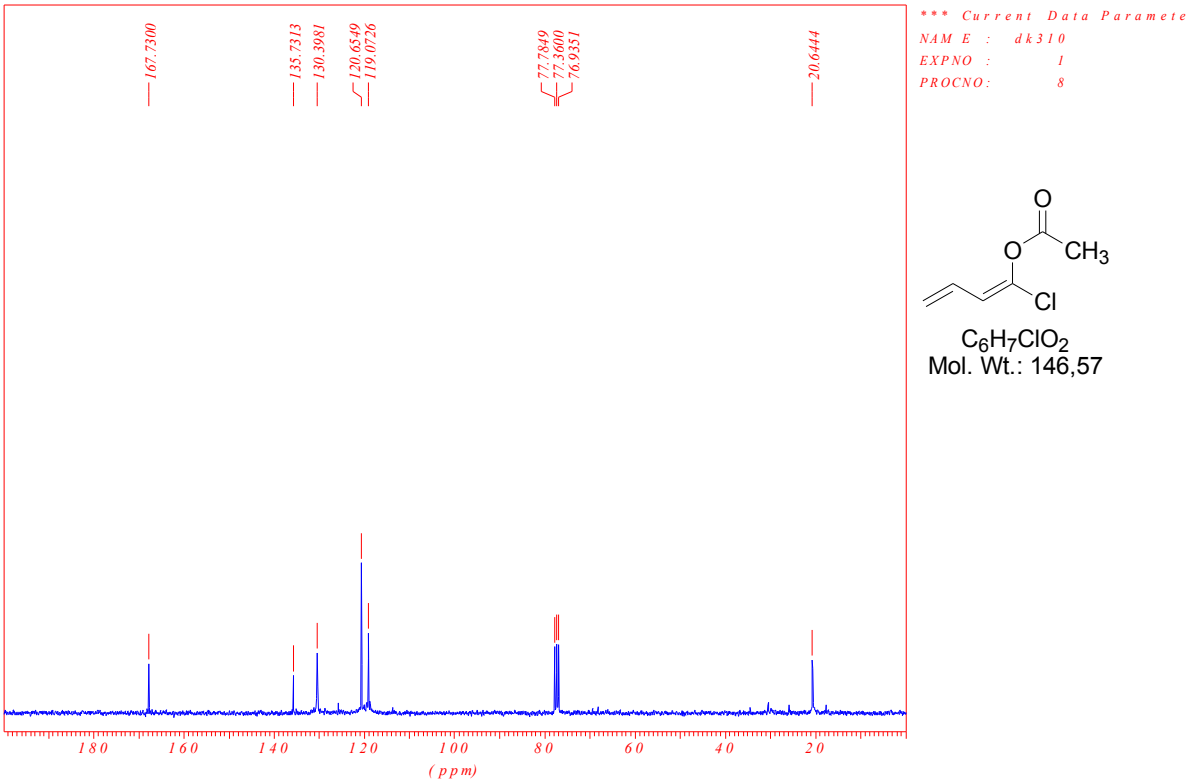
[13]C-NMR spectrum of dienol ester (4)



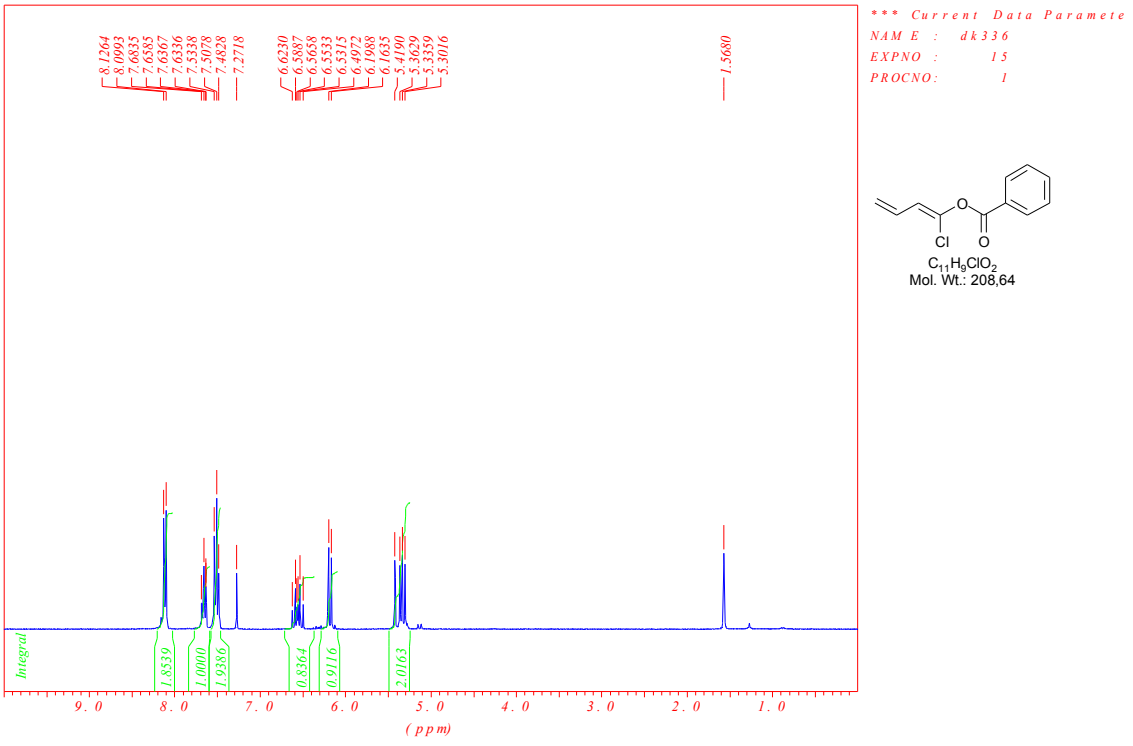
^{1}H-NMR spectrum of crude reaction mixture of dienol ester (6)



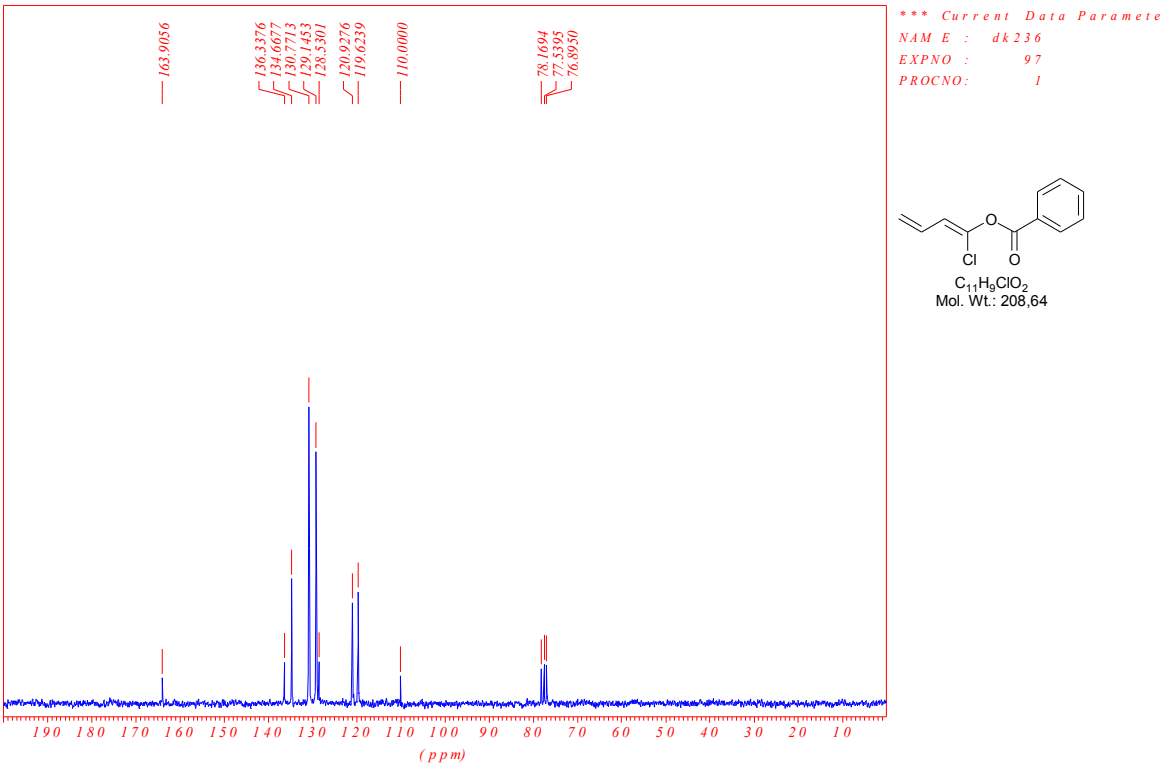
^{13}C-NMR spectrum of crude reaction mixture of dienol ester (6)



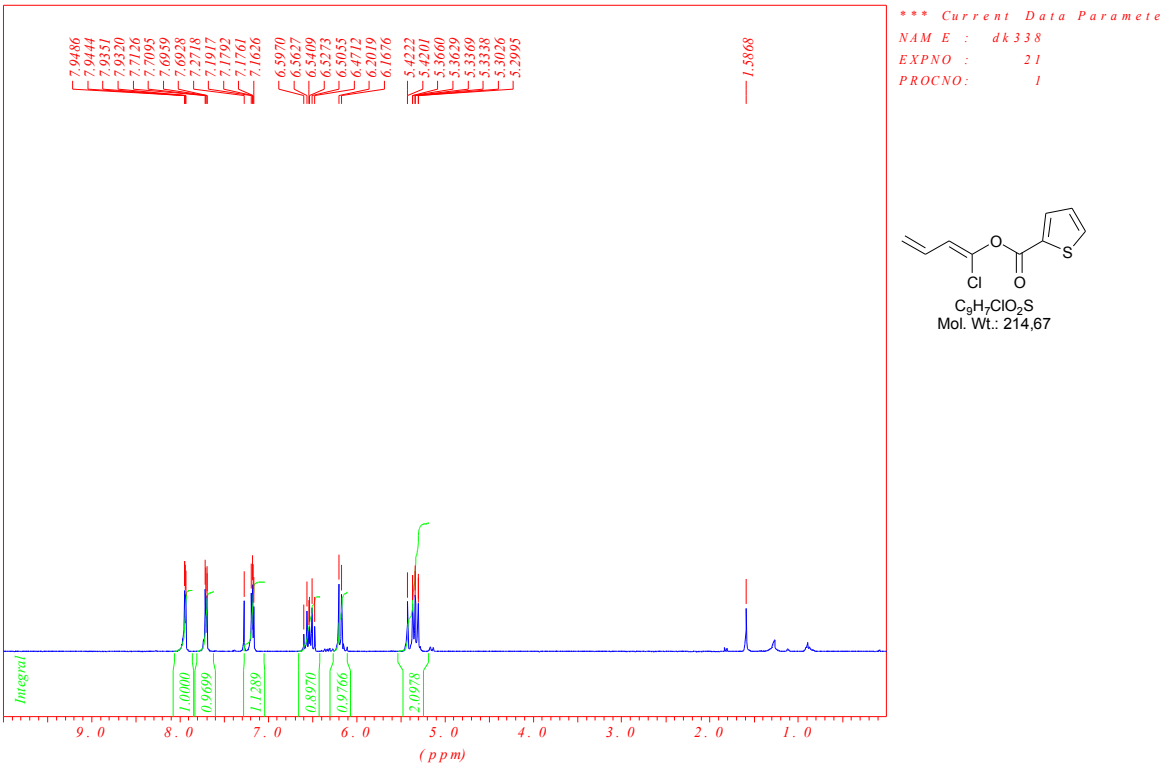
^{1}H-NMR spectrum of dienol ester (8)



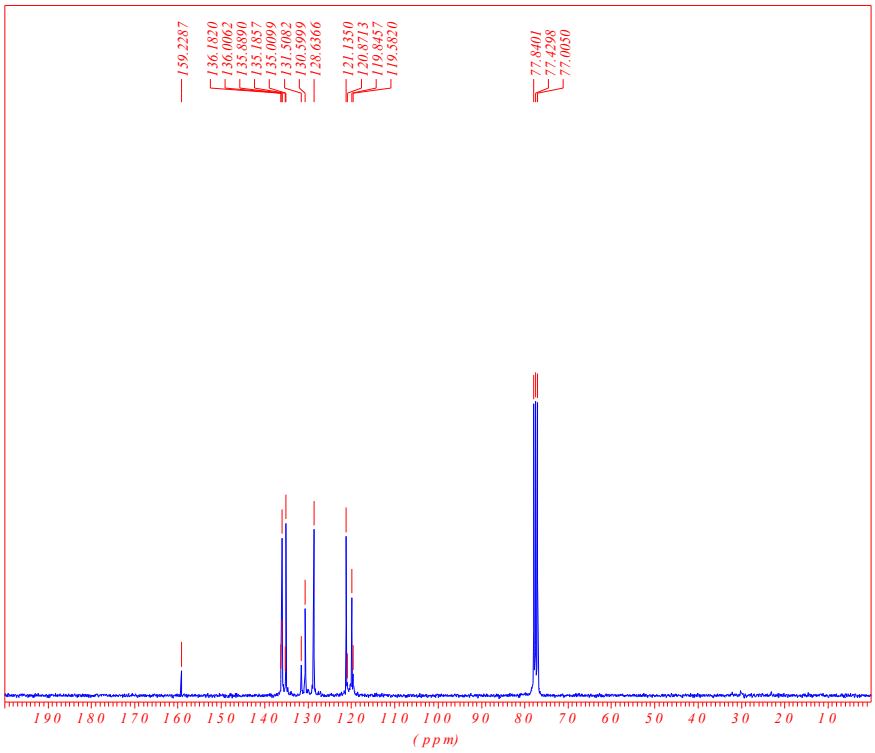
^{13}C-NMR spectrum of dienol ester (8)



^{1}H-NMR spectrum of dienol ester (10)



^{13}C-NMR spectrum of dienol ester (10)



*** Current Data Paramete
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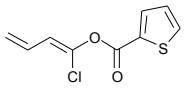
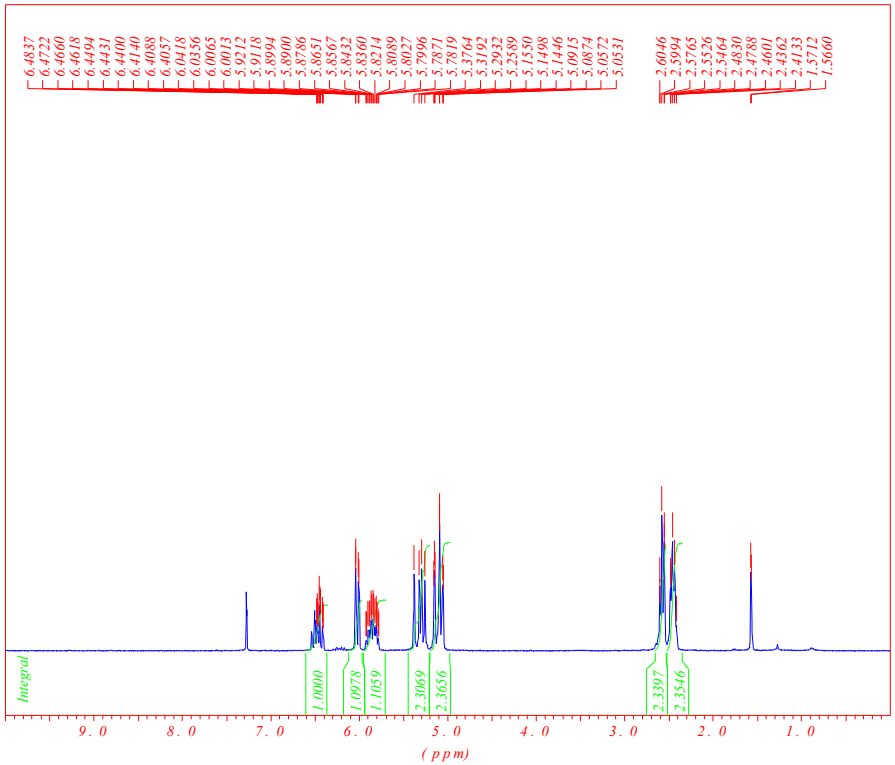
EXPNO : 22
PROCNO: 1



$C_9H_7ClO_2S$
Mol. Wt.: 214,67

^{1}H-NMR spectrum of dienol ester (12)



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EXPNO : 9
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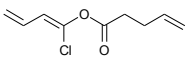
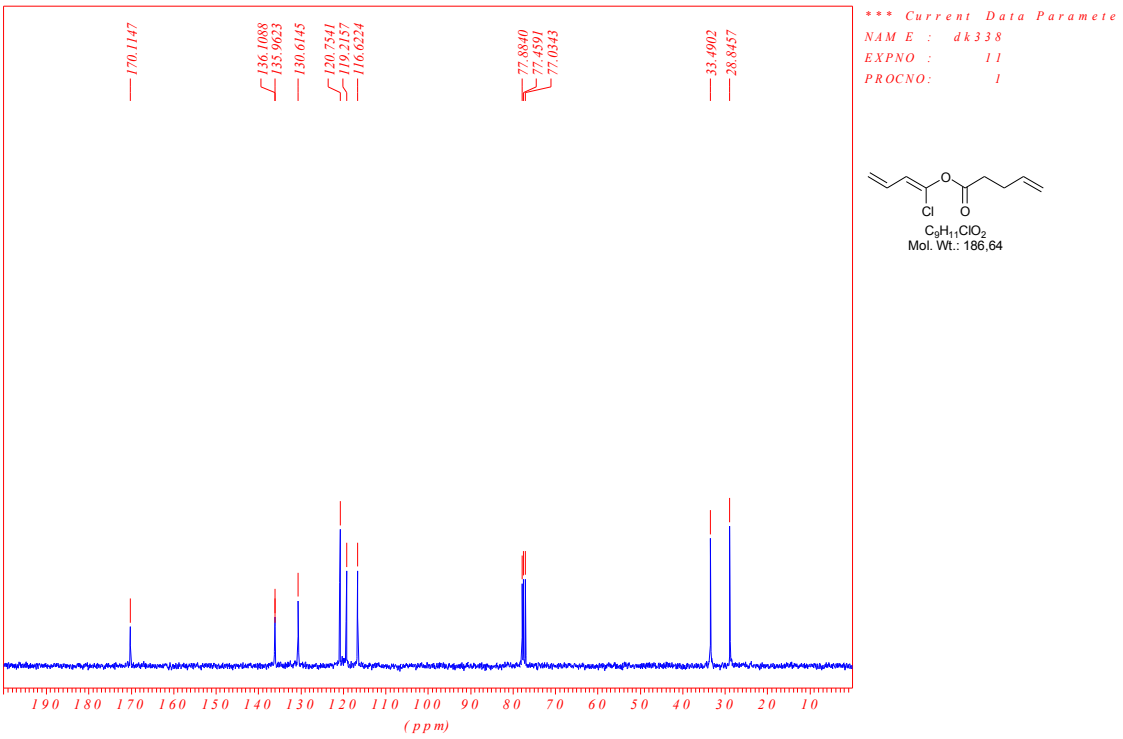
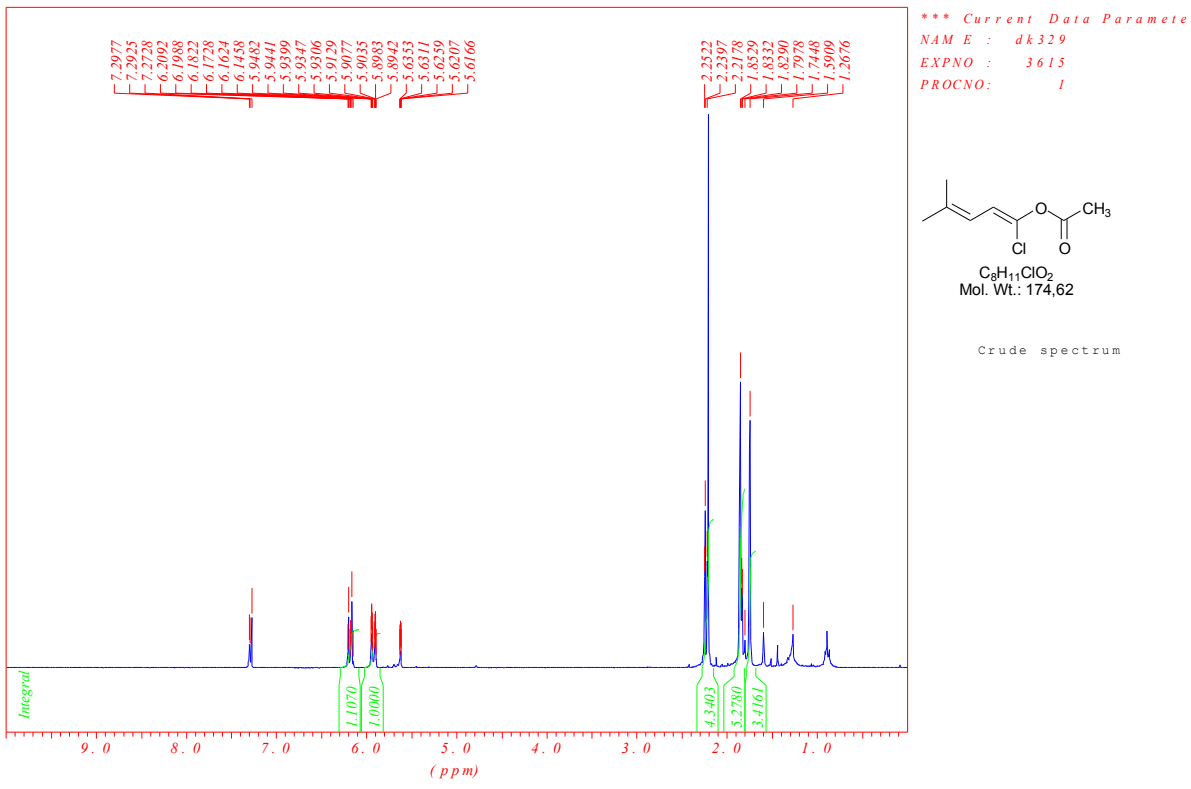


$C_9H_{11}ClO_2$
Mol. Wt.: 186,64

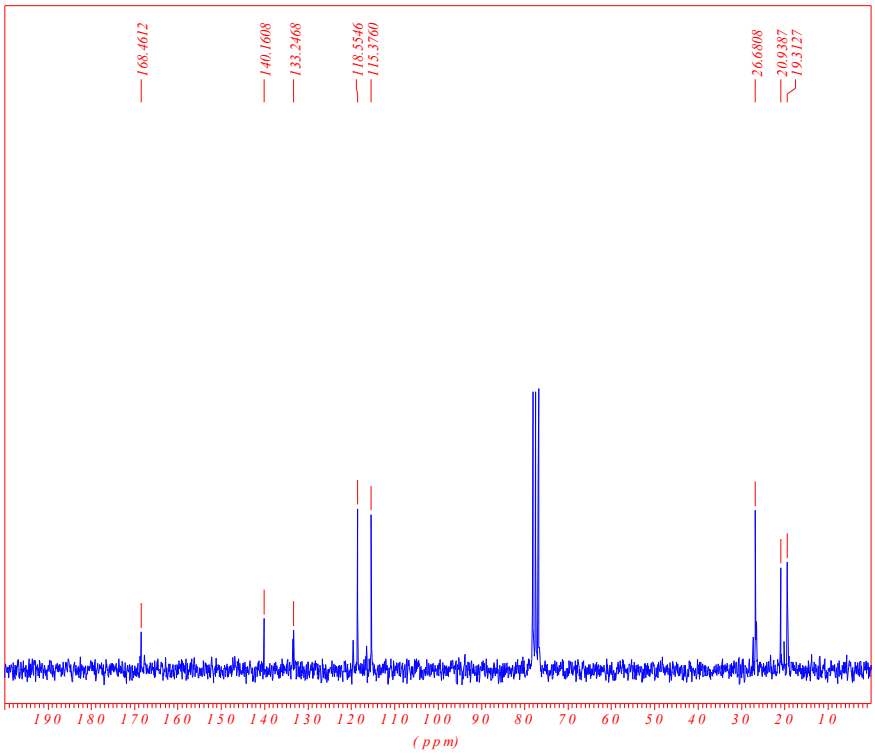
^{13}C-NMR spectrum of dienol ester (12)



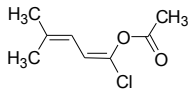
^{1}H-NMR spectrum of crude reaction mixture of dienol ester (14)



^{13}C-NMR spectrum of crude reaction mixture of dienol ester (14)

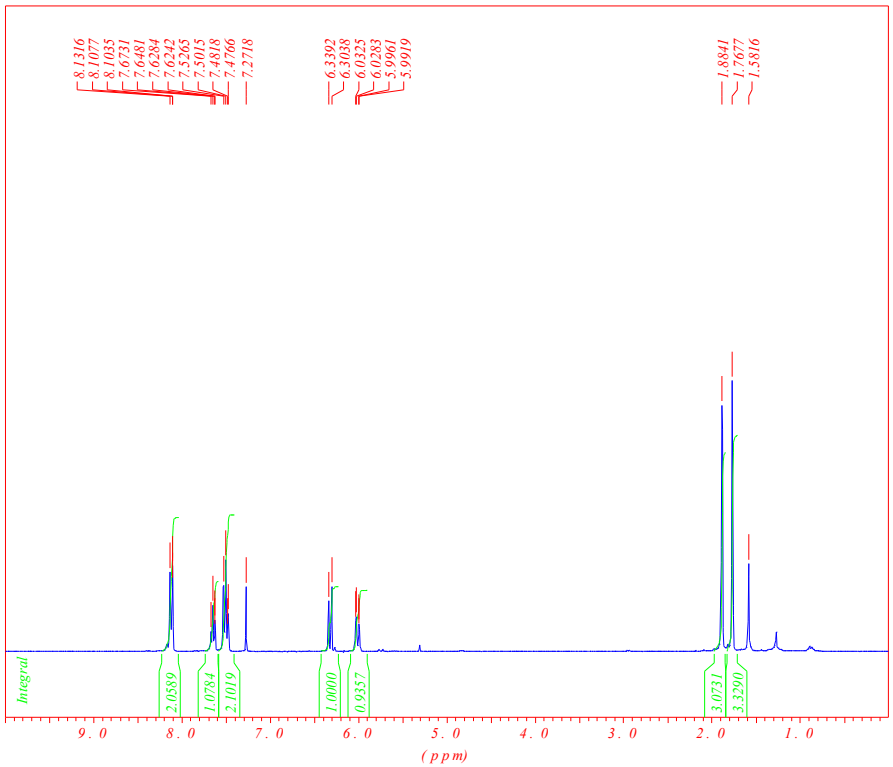


*** Current Data Paramete
NAME : dk225
EXPNO : 14
PROCNO: 1



$C_8H_{11}ClO_2$
Mol. Wt.: 174,62
Crude Spectrum

^{1}H-NMR spectrum of dienol ester (16)



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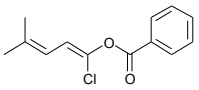
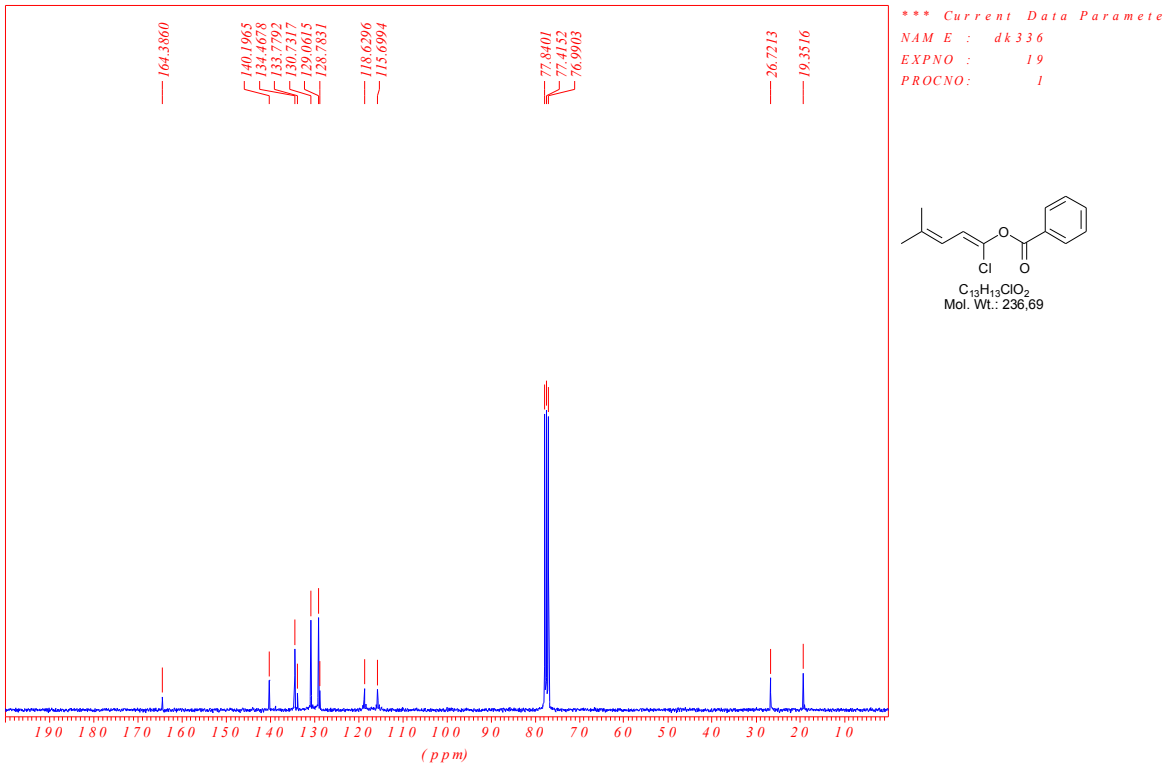
EXPNO : 16
PROCNO: 1

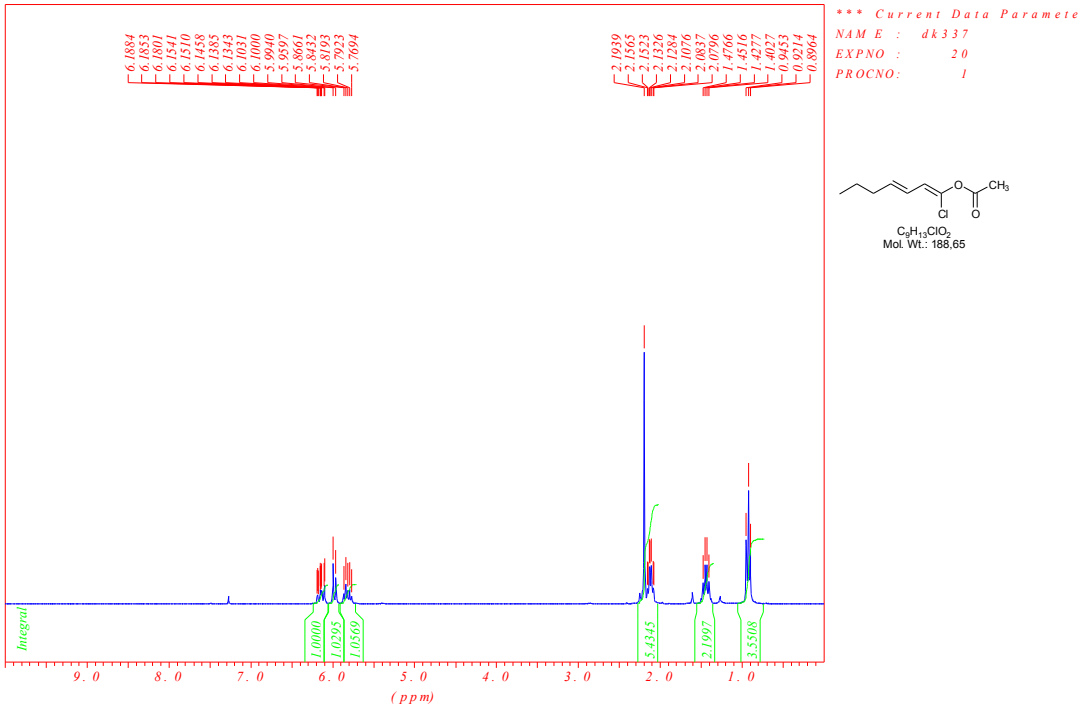


$C_{13}H_{13}ClO_2$
Mol. Wt.: 236,69

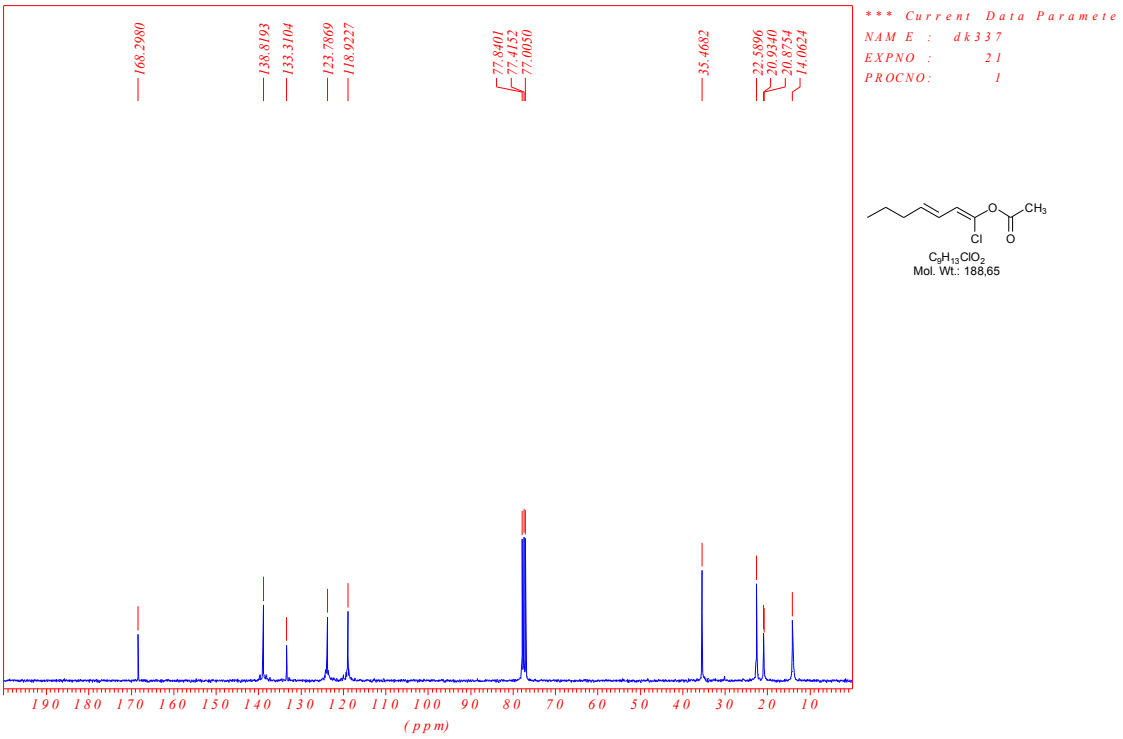
^{13}C-NMR spectrum of dienol ester (16)



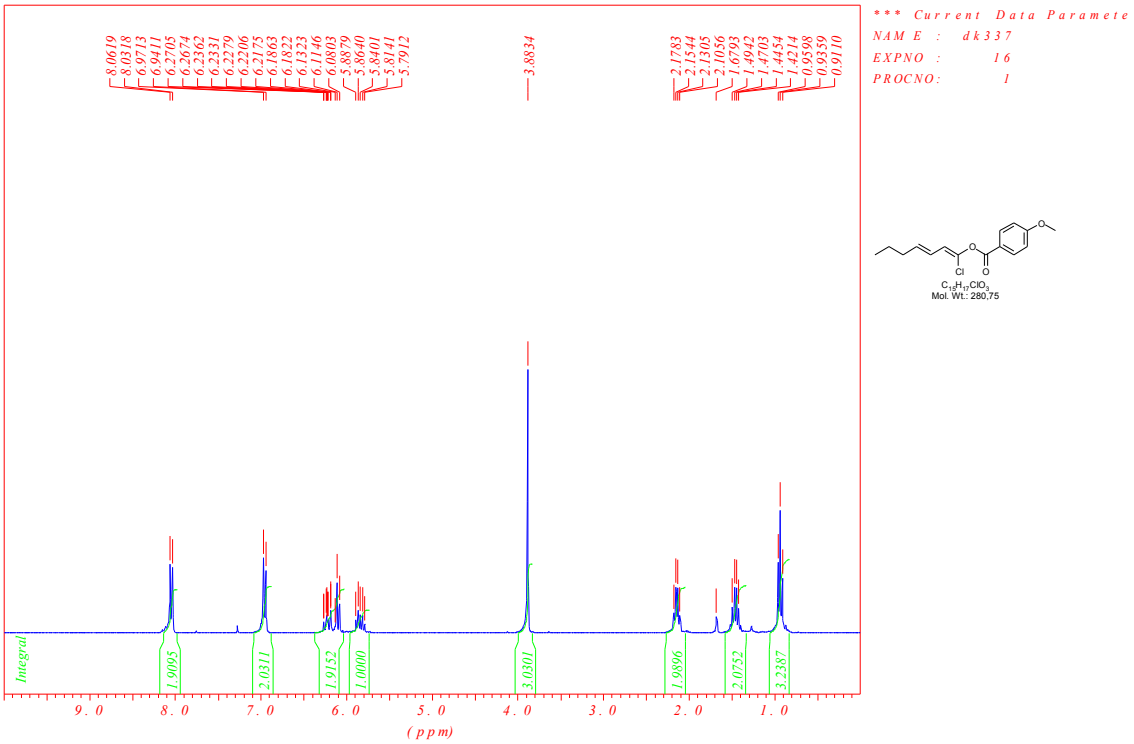
^{1}H-NMR spectrum of dienol ester (18)



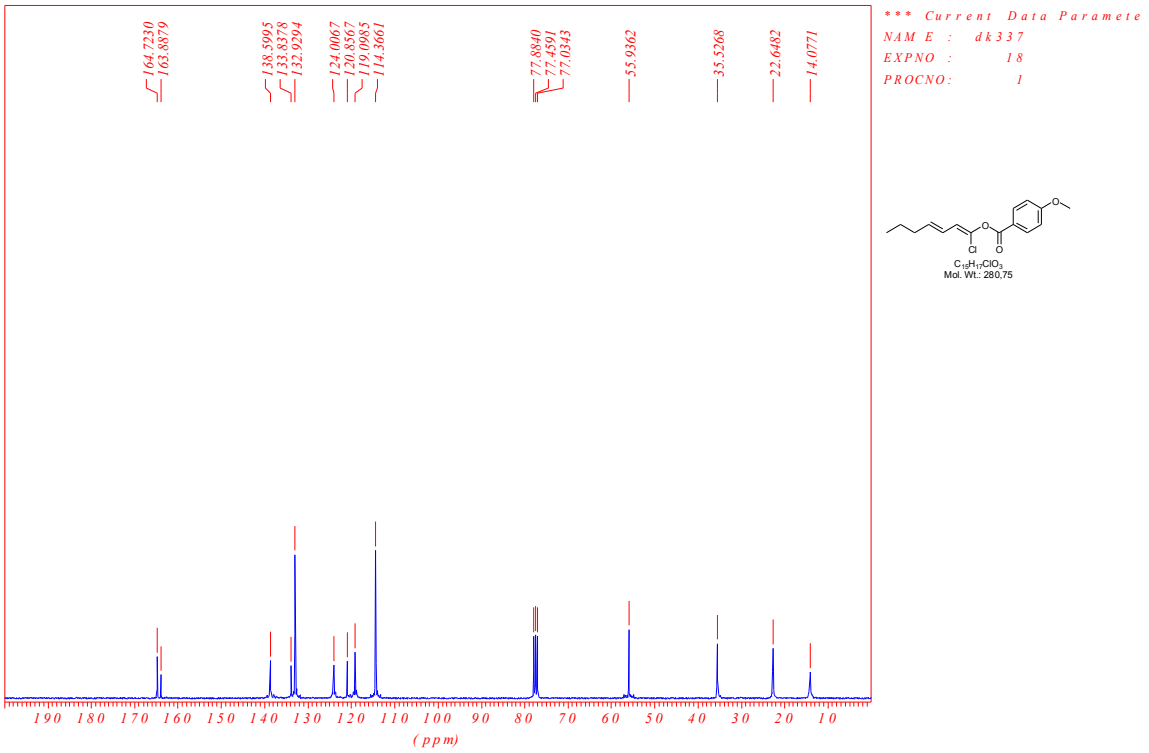
^{13}C-NMR spectrum of dienol ester (18)



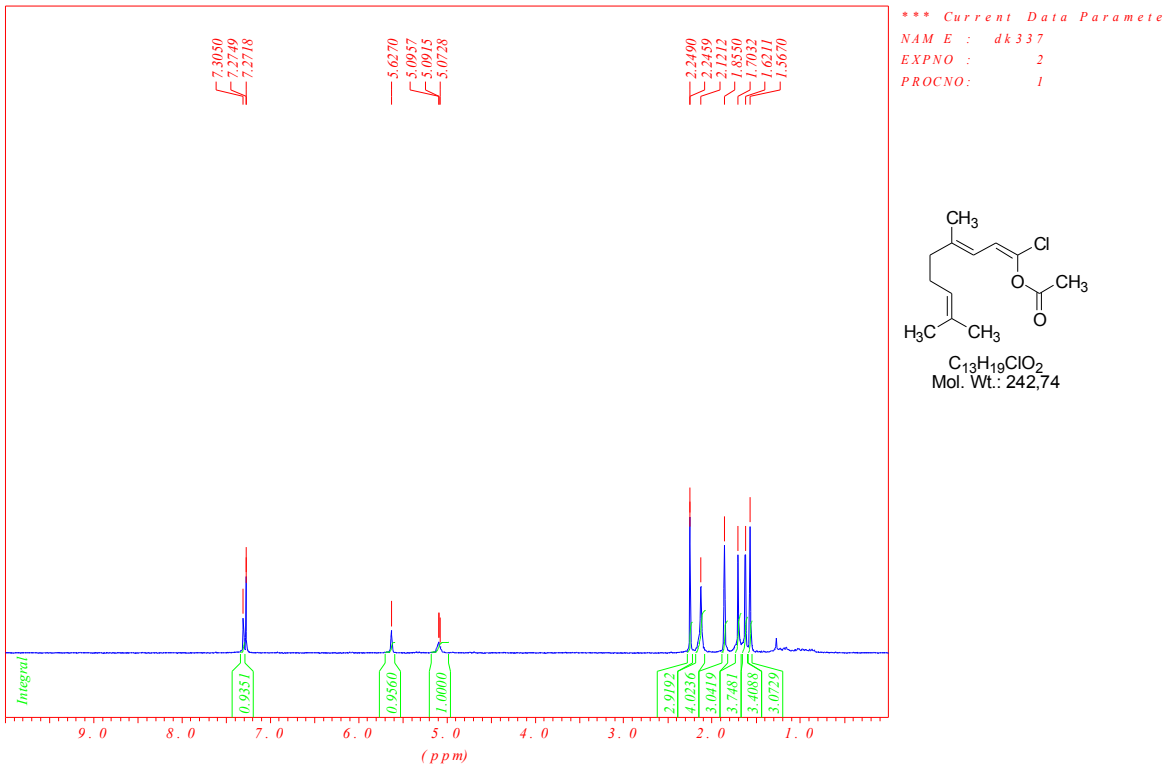
^{1}H-NMR spectrum of dienol ester (20)



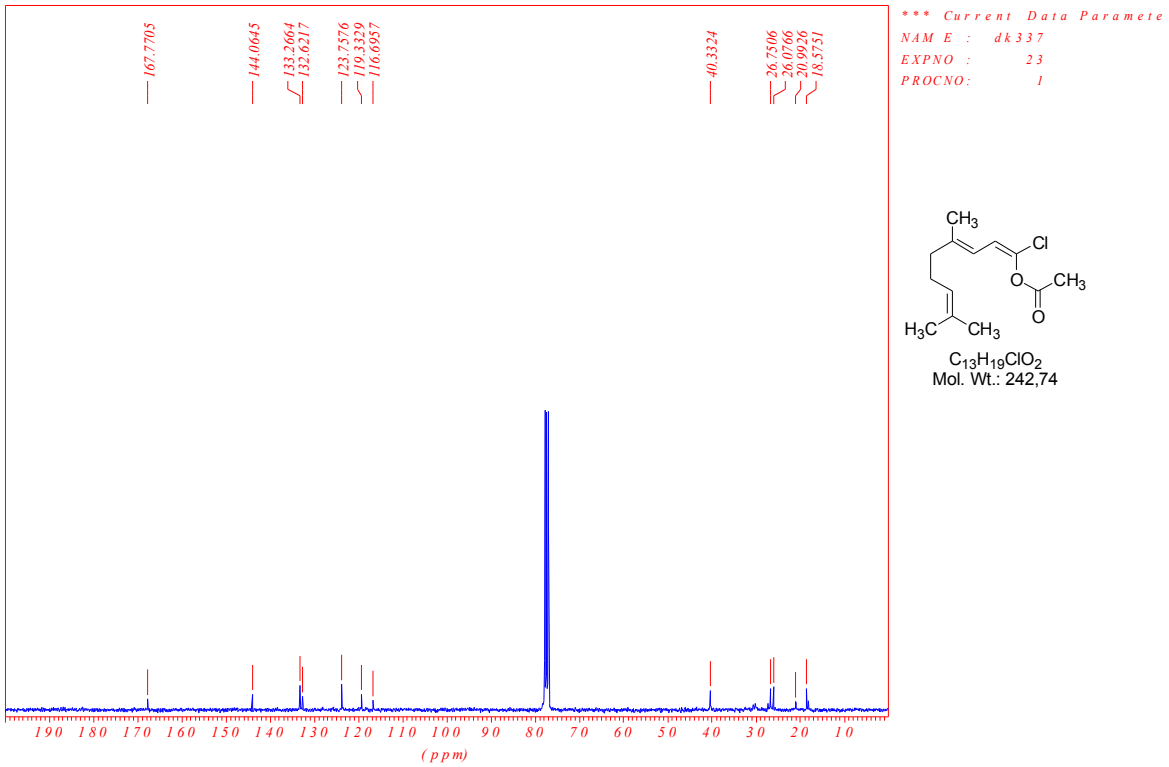
^{13}C-NMR spectrum of dienol ester (20)



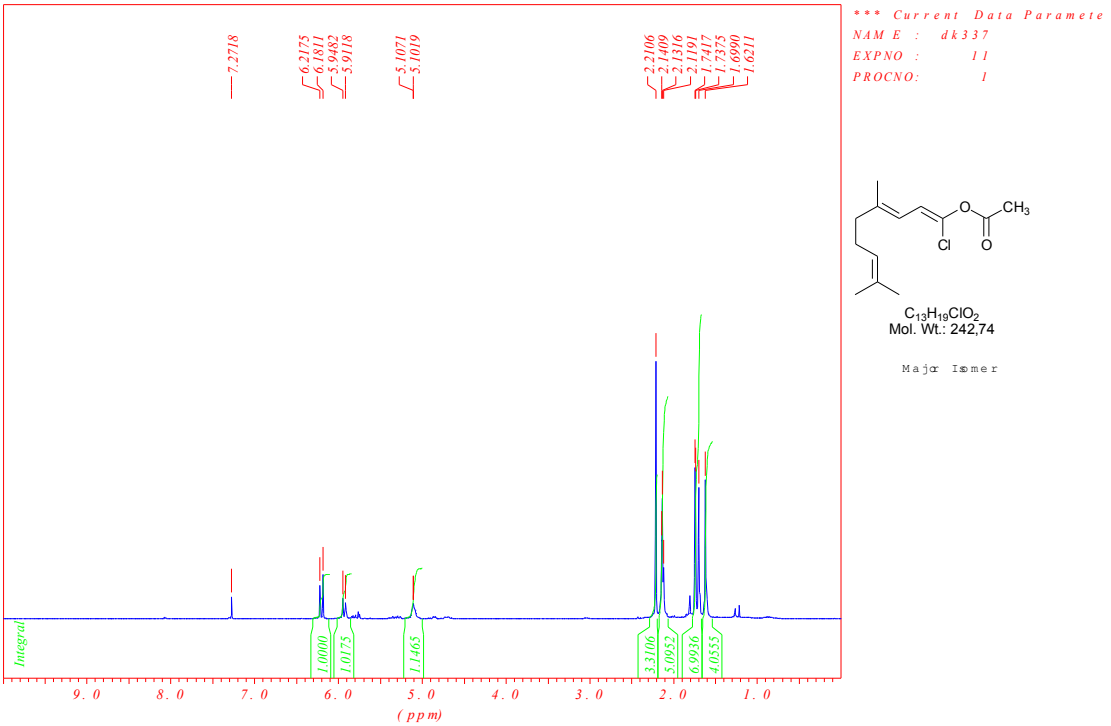
^{1}H-NMR spectrum of (*E,E*)-1-chloro-1,3-dienol ester (22a, MINOR ISOMER)



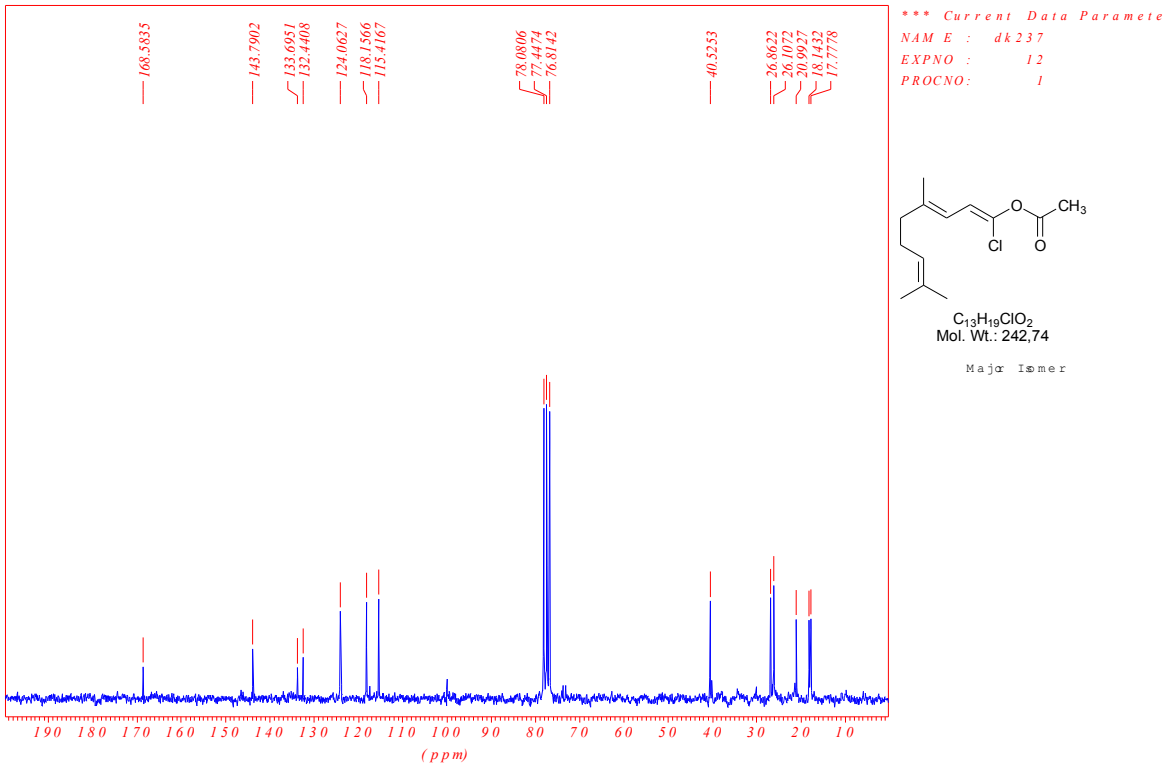
^{13}C-NMR spectrum of (*E*,*E*)-1-chloro-1,3-dienol ester (22a, MINOR ISOMER)



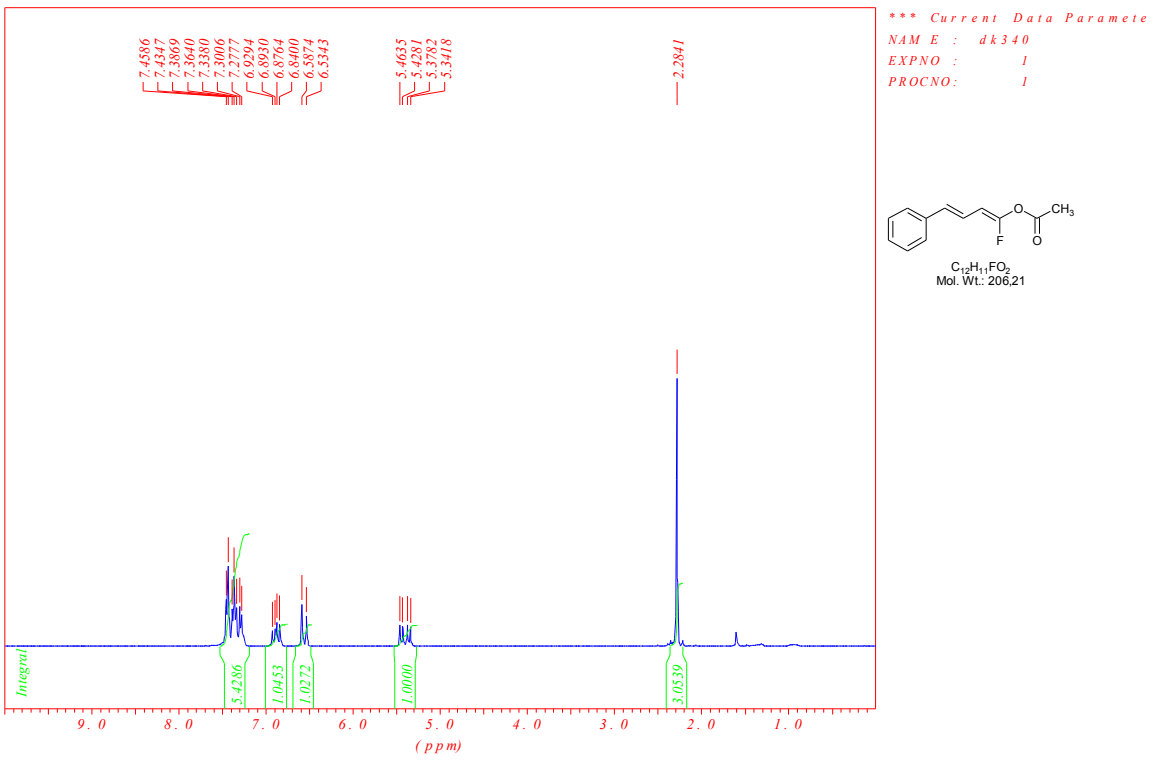
^{1}H-NMR spectrum of dienol ester (22b, MAJOR ISOMER)



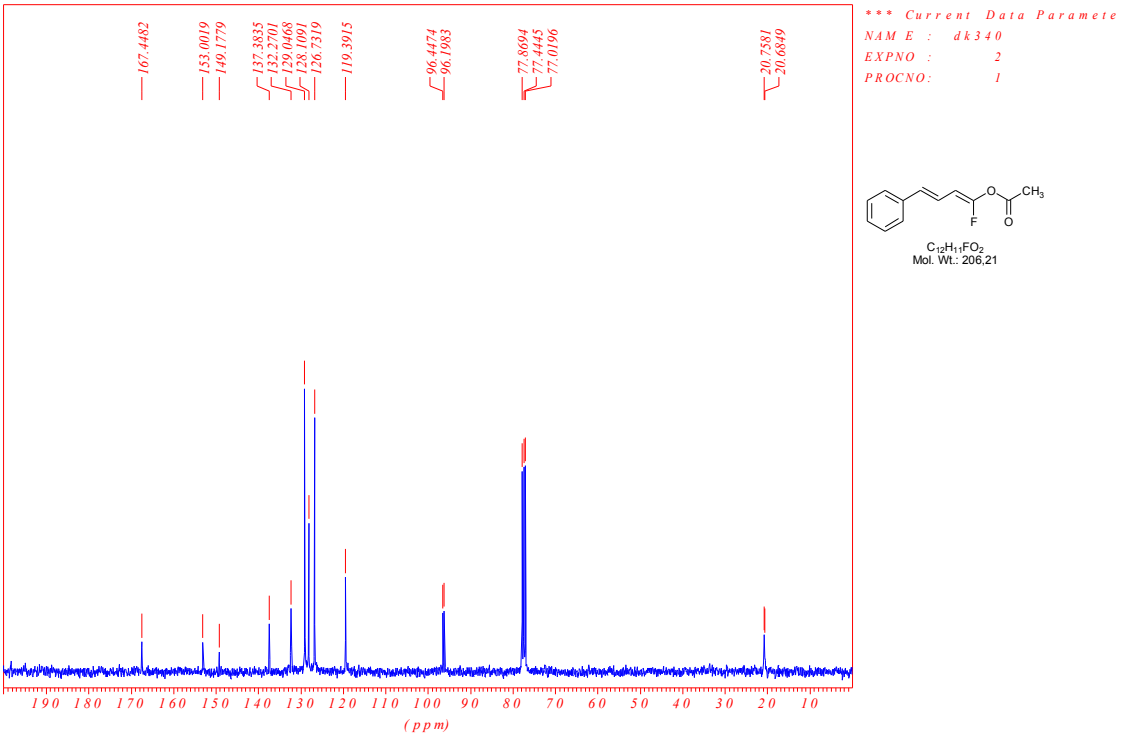
^{13}C-NMR spectrum of dienol ester (22b, MAJOR ISOMER)



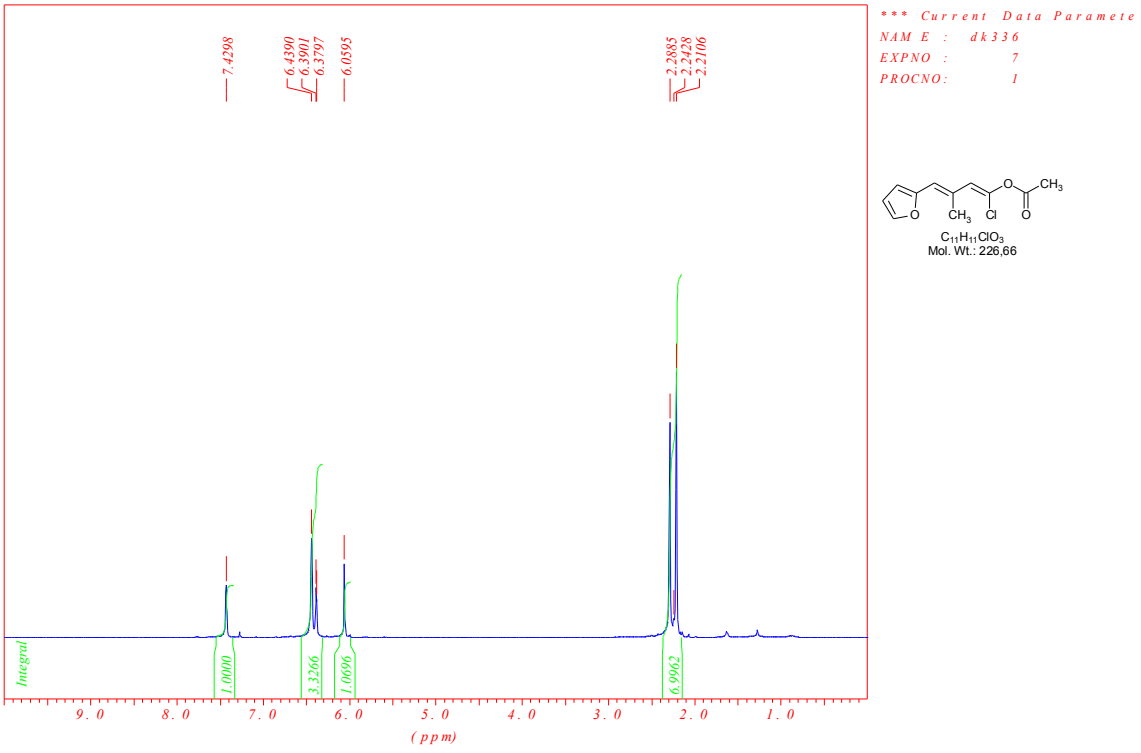
^{1}H-NMR spectrum of dienol ester (24)



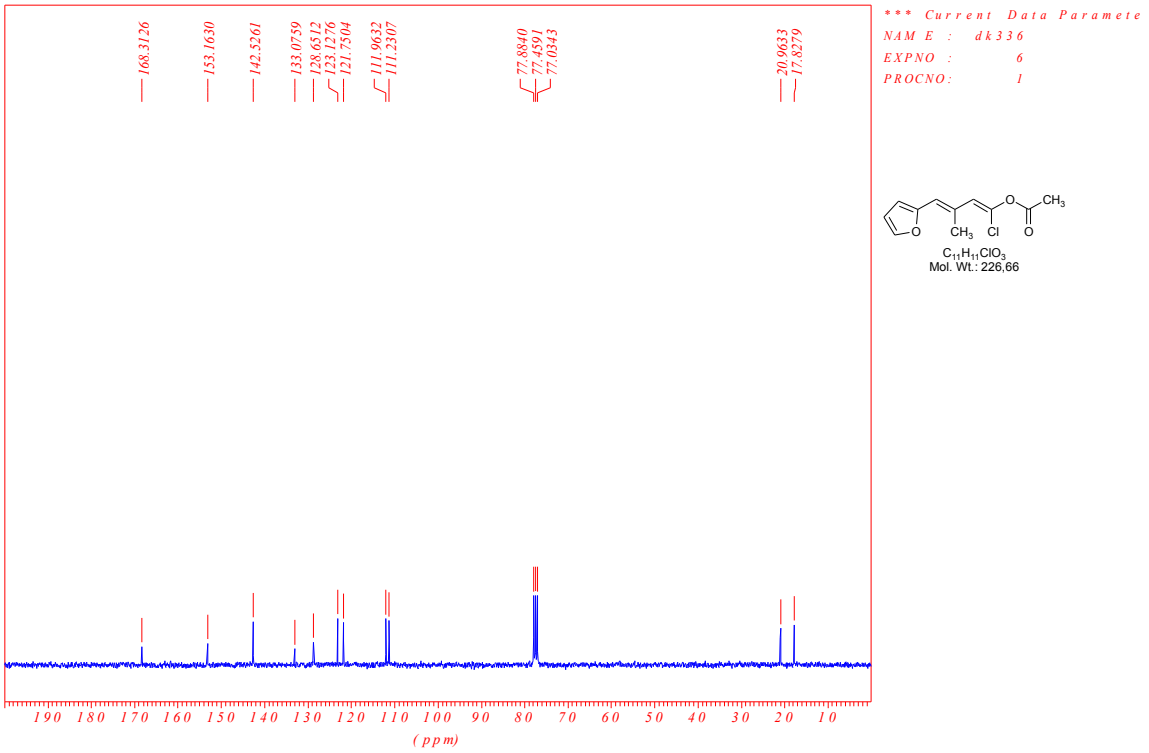
^{13}C-NMR spectrum of dienol ester (24)



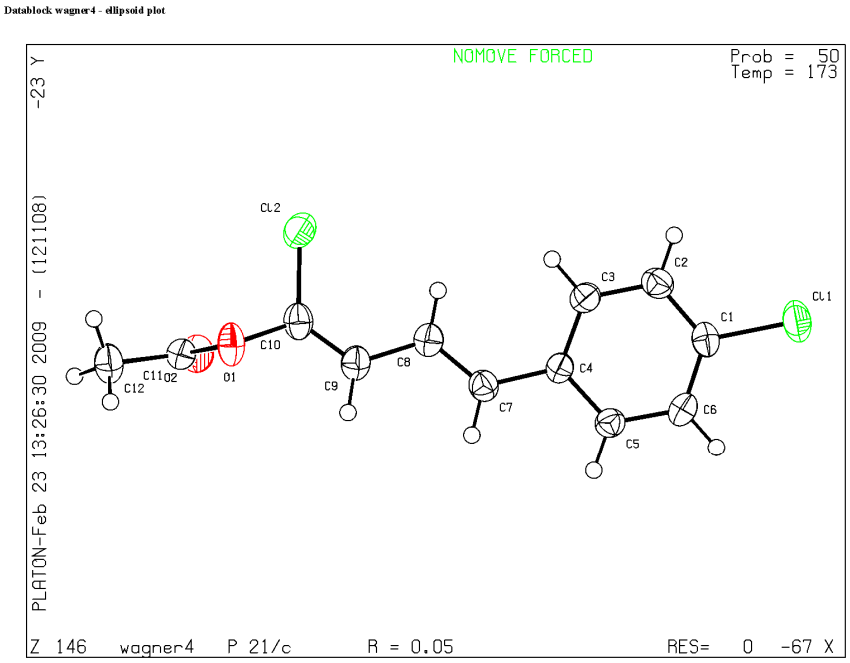
^{1}H-NMR spectrum of dienol ester (26)



^{13}C-NMR spectrum of dienol ester (26)



3. X-ray structure plot of **4** generated by Ortep-32 software



X-ray structure plot of **26** generated by Ortep-32 software