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Palladium-Catalyzed Reaction of Allyl Halides with α-Diazocarbonyl Compounds

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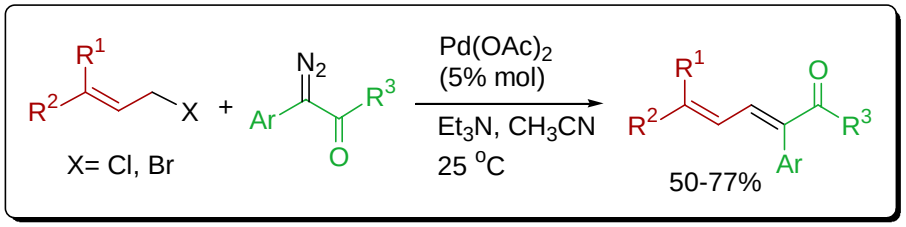
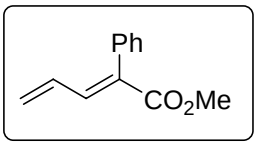


Contents

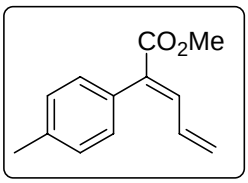
General All solvents were distilled prior to use. $PhCH_3$ and THF were distilled over sodium. CH_3CN was distilled over calcium hydride. All reactions were carried out under a nitrogen atmosphere and anhydrous conditions unless otherwise noted. Reagents purchased from commercial sources were used without further purification unless otherwise stated. Allylic bromide was distilled prior to use. The substituted allylic chlorides were prepared according to the literature methods.[1] For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 300 MHz (or 200 MHz) and 75 MHz (or 50 MHz) with Varian Mercury 300 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane (TMS) as internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer.

(*E*)-Methyl 2-phenylpenta-2,4-dienoate (2a)[2]



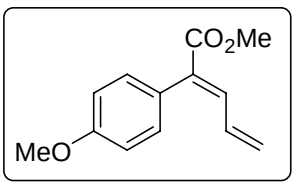
Yield 77%; ^1H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 3H), 5.42 (ddd, *J* = 0.6, 1.5, 10.8 Hz, 1H), 5.66 (ddd, *J* = 0.6, 1.5, 16.8 Hz, 1H), 6.39 (ddd, *J* = 10.2, 11.4, 16.8 Hz, 1H), 7.21~7.26 (m, 2H), 7.32~7.42 (m, 3H), 7.46 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 125.7, 127.7, 127.9, 128.2, 130.1, 133.1, 134.8, 140.7, 167.8.

(*E*)-Methyl 2-p-tolylpenta-2,4-dienoate (2b)



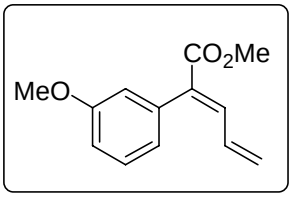
Yield 77%; IR (neat) 1718, 1514, 1435, 1245 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.76 (s, 3H), 5.40 (ddd, *J* = 0.6, 1.5, 9.9 Hz, 1H), 5.65 (ddd, *J* = 0.6, 1.5, 16.8 Hz, 1H), 6.41 (ddd, *J* = 10.2, 11.4, 16.8 Hz, 1H), 7.11~7.28 (M, 5H), 7.45 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 52.1, 125.4, 128.7, 130.0, 131.9, 133.2, 133.3, 137.5, 140.4, 168.0; EI-MS (*m/z*, relative intensity): 202 (M^+, 30), 143 (100). HRMS calcd for $C_{13}H_{14}O_2$: 202.0994. Found: 202.0992.

(*E*)-Methyl 2-(4-methoxyphenyl)penta-2,4-dienoate (2c)



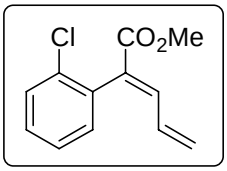
Yield 53%; IR (neat) 1736, 1613, 1513, 1247 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.84 (s, 3H), 5.41 (ddd, *J* = 0.6, 1.8, 10.2 Hz, 1H), 5.66 (ddd, *J* = 0.6, 1.8, 16.5 Hz, 1H), 6.43 (ddd, *J* = 10.2, 11.4, 16.5 Hz, 1H), 6.90~6.95 (m, 2H), 7.14~7.19 (m, 2H), 7.43 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 55.2, 113.4, 125.3, 127.0, 131.3, 132.7, 133.3, 140.3, 159.1, 168.1; EI-MS (*m/z*, relative intensity): 218 (M^+, 20), 159 (48), 121(100). HRMS calcd for $C_{13}H_{14}O_3$: 218.0943. Found: 218.0943.

(*E*)-Methyl 2-(3-methoxyphenyl)penta-2,4-dienoate (2d)



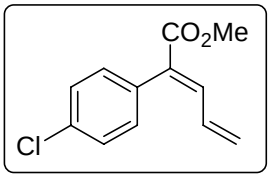
Yield 71%; IR (neat) 1713, 1601, 1585, 1246 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.82 (s, 3H), 5.42 (ddd, *J* = 1.2, 1.8, 10.2 Hz, 1H), 5.66 (ddd, *J* = 0.9, 1.8, 16.8 Hz, 1H), 6.40 (ddd, *J* = 10.2, 11.4, 16.8 Hz, 1H), 6.76~6.82 (m, 2H), 6.88~6.91 (m, 1H), 7.27~7.33 (m, 1H), 7.45 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 55.2, 113.2, 115.7, 122.5, 125.8, 129.0, 133.0, 133.1, 136.1, 140.8, 159.1, 167.7; EI-MS (*m/z*, relative intensity): 218 (M^+, 50), 159(100). HRMS calcd for $C_{13}H_{14}O_3$: 218.0943. Found: 218.0944.

(*E*)-Methyl 2-(2-chlorophenyl)penta-2,4-dienoate (2e)



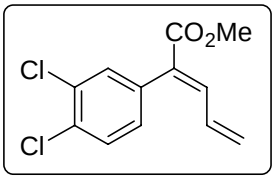
Yield 61%; IR (neat) 1715, 1629, 1434, 1242 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.76 (s, 3H), 4.46 (dd, *J* = 1.5, 9.9 Hz, 1H), 5.70 (dd, *J* = 1.5, 16.8 Hz, 1H), 6.17 (ddd, *J* = 10.2, 11.4, 17.1 Hz, 1H), 7.17~7.46 (m, 4H), 7.51 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.3, 126.5, 126.6, 129.3, 129.4, 131.0, 131.7, 132.5, 134.0, 134.1, 141.8, 167.0; EI-MS (*m/z*, relative intensity): 222 (M^+, 17), 187 (59), 128 (100). HRMS calcd for $C_{12}H_{11}O_2Cl$: 222.0448. Found: 222.0444.

(*E*)-Methyl 2-(4-chlorophenyl)penta-2,4-dienoate (2f)



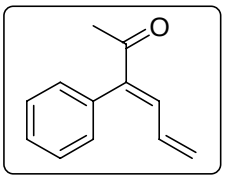
Yield 73%; IR (neat) 1713, 1624, 1493, 1420, 1242 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 5.46 (dd, *J* = 1.2, 10.2 Hz, 1H), 5.69 (dd, *J* = 0.9, 16.8 Hz, 1H), 6.36 (ddd, *J* = 10.2, 11.4, 16.8 Hz, 1H), 7.15~7.19 (m, 2H), 7.35~7.38 (m, 2H), 7.47 (d, *J* = 11.4 Hz, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.3, 126.4, 128.2, 131.5, 131.6, 131.9, 132.7, 133.1, 141.2, 167.4; EI-MS (*m*/z, relative intensity): 222 (M^+, 28), 128 (100). HRMS calcd for $C_{12}H_{11}O_2Cl$: 222.0448. Found: 222.0449.

(*E*)-Methyl 2-(3,4-dichlorophenyl)penta-2,4-dienoate (2g)



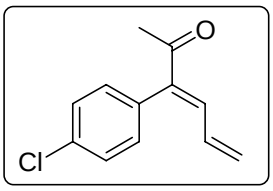
Yield 50 %; IR (neat) 1714, 1580, 1475, 1244 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H), 5.52 (d, *J* = 10.5 Hz, 1H), 5.73 (d, *J* = 16.8 Hz, 1H), 6.34 (ddd, *J* = 10.5, 11.4, 16.8 Hz, 1H), 7.07 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.27~7.34 (m, 1H), 7.45~7.51 (m, 2H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.4, 127.3, 128.0, 129.6, 130.0, 130.7, 132.0, 132.2, 132.4, 134.7, 141.8, 167.0; EI-MS (*m*/z, relative intensity): 256 (M^+, 23), 162 (100). HRMS calcd for $C_{12}H_{10}O_2Cl_2$: 256.0058. Found: 256.0065.

(*E*)-3-phenylhexa-3,5-dien-2-one (2h)



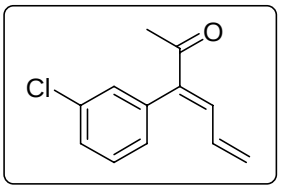
Yield 55%; IR (neat) 1665, 1615, 1249, 1226 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 5.45 (d, *J* = 9.9 Hz, 1H), 5.70 (d, *J* = 16.8 Hz, 1H), 6.34 (td, *J* = 10.5, 16.8 Hz, 1H), 7.14~7.43 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 126.1, 127.7, 128.2, 129.9, 133.5, 135.5, 139.4, 141.8, 198.8; EI-MS (*m/z*, relative intensity): 172 (M^+, 36), 129 (100). HRMS calcd for $C_{12}H_{12}O$: 172.0888. Found: 172.0884.

(*E*)-3-(4-chlorophenyl)hexa-3,5-dien-2-one (2i)



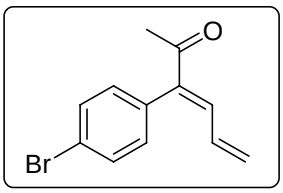
Yield 68%; IR (neat) 1668, 1619, 1491, 1250, 1090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 5.49 (d, *J* = 10.2 Hz, 1H), 5.73 (d, *J* = 16.8 Hz, 1H), 6.33 (td, *J* = 10.2, 16.8 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.26~7.29 (m, 1H), 7.38 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.2, 126.8, 128.4, 131.3, 133.2, 133.7, 133.8, 140.3, 140.7, 198.3; EI-MS (*m/z*, relative intensity): 206 (M^+, 45), 128 (75), 43 (100). HRMS calcd for $C_{12}H_{11}OCl$: 206.0498. Found: 206.0496.

(*E*)-3-(3-chlorophenyl)hexa-3,5-dien-2-one (2j)



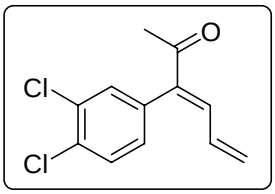
Yield 70%; IR (neat) 1668, 1621, 1423, 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 5.51 (d, *J* = 10.2 Hz, 1H), 5.74 (d, *J* = 16.8 Hz, 1H), 6.32 (td, *J* = 10.8, 16.8 Hz, 1H), 7.02~7.05 (m, 1H), 7.15 (s, 1H), 7.26~7.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.2, 127.0, 127.9, 128.2, 129.5, 129.9, 133.2, 134.1, 137.2, 140.4, 140.5, 198.1; EI-MS (*m/z*, relative intensity): 206 (M^+, 22), 128 (49), 43 (100). HRMS calcd for $C_{12}H_{11}OCl$: 206.0498. Found: 206.0494.

(*E*)-3-(4-bromophenyl)hexa-3,5-dien-2-one (2k)



Yield 63%; IR (neat) 1667, 1615, 1487, 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 5.49 (d, *J* = 9.9 Hz, 1H), 5.73 (d, *J* = 16.8 Hz, 1H), 6.33 (td, *J* = 10.8, 16.8 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 11.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.1, 122.0, 126.8, 131.3, 131.6, 133.2, 134.1, 140.3, 140.7, 198.2; EI-MS (*m/z*, relative intensity): 252 (M^+, 19), 128 (75), 43 (100). HRMS calcd for $C_{12}H_{11}OBr$: 249.9993. Found: 249.9981.

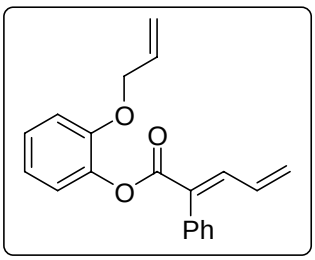
(*E*)-3-(3,4-dichlorophenyl)hexa-3,5-dien-2-one (2l)



Yield 60%; IR (neat) 1666, 1621, 1473, 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 5.54 (d, *J* = 10.2 Hz, 1H), 5.77 (d, *J* = 16.8 Hz, 1H), 6.33 (td, *J* = 10.8, 16.8 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 7.26~7.31

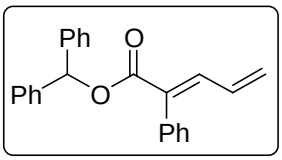
(m, 2H), 7.48 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.9, 127.5, 129.5, 130.2, 131.8, 132.1, 132.3, 132.9, 135.1, 139.5, 141.0, 197.8; EI-MS (*m/z*, relative intensity): 240 (M^+, 81), 162 (100). HRMS calcd for $C_{12}H_{10}OCl_2$: 240.0109. Found: 240.0099.

(*E*)-2-(Allyloxy)phenyl 2-phenylpenta-2,4-dienoate (2m)



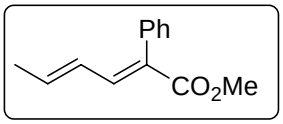
Yield 77%; IR (neat) 1730, 1604, 1498, 1183, 1157 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.55 (dt, J = 1.5, 5.1 Hz, 2H), 5.25 (dt, J = 1.5, 10.8 Hz, 1H), 5.40 (ddd, J = 1.8, 3.3, 17.4 Hz, 1H), 5.49 (d, J = 9.9 Hz, 1H), 5.73 (d, J = 16.8 Hz, 1H), 6.01 (m, 1H), 6.51 (m, 1H), 6.96 (d, J = 7.5 Hz, 2H), 7.05~7.19 (m, 2H), 7.30~7.38 (m, 5H), 7.67 (d, J = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 69.3, 113.8, 117.3, 121.0, 122.9, 126.4, 126.6, 127.8, 127.9, 130.3, 132.5, 132.9, 133.1, 134.6, 140.4, 141.9, 150.0, 165.5; EI-MS (*m/z*, relative intensity): 306 (M^+, 12), 157 (89), 129 (100). HRMS calcd for $C_{20}H_{18}O_3$: 306.1256. Found: 306.1265.

(*E*)-Benzhydryl 2-phenylpenta-2,4-dienoate (2n)



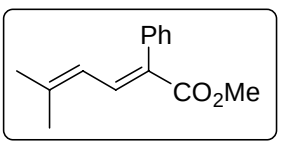
Yield 69%; IR (neat) 1711, 1495, 1232, 1175 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.41 (dd, J = 0.6, 10.5 Hz, 1H), 5.66 (d, J = 17.1 Hz, 1H), 6.41 (ddd, J = 10.2, 11.1, 17.1, Hz, 1H), 6.97 (s, 1H), 7.23~7.44 (m, 5H), 7.54 (d, J = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 77.3, 125.9, 126.9, 127.1, 127.4, 127.7, 127.9, 128.2, 128.4, 128.6, 129.3, 130.1, 133.1, 134.7, 140.3, 140.9, 166.1; EI-MS (*m/z*, relative intensity): 340 (M^+, 17), 167 (100). HRMS calcd for $C_{24}H_{20}O_2$: 340.1463. Found: 340.1464.

(*2E,4E*)-Methyl 2-phenylhexa-2,4-dienoate (4a)[3]



Yield 63%; IR (neat) 1710, 1637, 1434, 1233 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.78 (d, J = 6.6 Hz, 3H), 3.75 (s, 3H), 6.06~6.26 (m, 2H), 7.22~7.26 (m, 2H), 7.32~7.42 (m, 3H), 7.46 (d, J = 10.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.9, 52.1, 127.4, 127.9, 128.1, 130.1, 135.0, 135.2, 139.9, 141.1, 168.1; EI-MS (*m/z*, relative intensity): 202 (M^+, 23), 143 (100). HRMS calcd for $C_{13}H_{14}O_2$: 202.0994. Found: 202.0995.

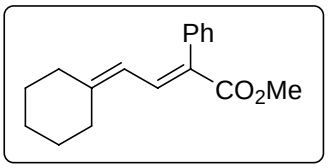
(*E*)-Methyl 5-methyl-2-phenylhexa-2,4-dienoate (4b)[4]



Yield 72%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.79 (s, 3H), 1.95 (s, 3H), 3.76 (s, 3H), 5.87 (d, J = 12.0 Hz, 1H), 7.20~7.23 (m, 2H), 7.29~7.42 (m, 3H),

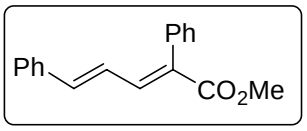
7.77 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1, 26.9, 52.0, 121.9, 127.3, 127.9, 129.4, 130.2, 135.5, 136.9, 146.8, 168.5.

(*E*)-Methyl 4-cyclohexylidene-2-phenylbut-2-enoate (4c)



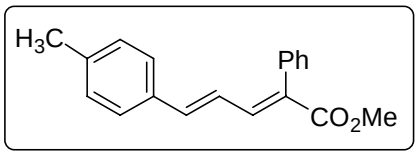
Yield 71 %; IR (neat) 2931, 1710, 1627, 1434, 1242 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59~1.60 (br, m, 6H), 2.11~2.13 (br, m, 2H), 2.45~2.47 (br, m, 2H), 3.75 (s, 3H), 5.83 (d, *J* = 12.0 Hz, 1H), 7.21~7.27 (m, 2H), 7.33~7.40 (m, 3H), 7.84 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 27.9, 28.5, 29.9, 38.0, 52.0, 118.7, 127.3, 127.9, 129.6, 130.3, 135.5, 136.1, 154.9, 168.5; EI-MS (*m/z*, relative intensity): 256 (M^+, 100), 197 (98). HRMS calcd for $C_{17}H_{20}O_2$: 256.1463. Found: 256.1459.

(*2E,4E*)-Methyl 2,5-diphenylpenta-2,4-dienoate (4d)



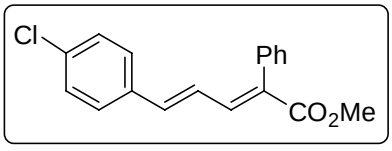
Yield 66%; IR (neat) 1707, 1616, 1434, 1232 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.81 (dd, *J* = 11.4, 15.6 Hz, 1H), 7.48 (d, *J* = 15.6 Hz, 1H), 7.25~7.44 (m, 10H), 7.66 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 124.7, 127.2, 127.7, 128.0, 128.7, 128.9, 130.3, 132.2, 135.1, 136.2, 140.6, 140.7, 167.9; EI-MS (*m/z*, relative intensity): 264 (M^+, 57), 205 (100). HRMS calcd for $C_{18}H_{16}O_2$: 264.1150. Found: 264.1142.

(*2E,4E*)-Methyl 2-phenyl-5-p-tolylpenta-2,4-dienoate (4e)



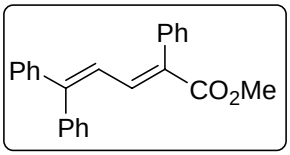
Yield 57%; IR (neat) 1708, 1603, 1434, 1233 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.79 (s, 3H), 6.76 (dd, *J* = 11.4, 15.6 Hz, 1H), 6.95 (d, *J* = 15.6 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.23~7.31 (m, 4H), 7.36~7.45 (m, 3H), 7.65 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 52.1, 123.8, 127.2, 127.7, 128.0, 129.4, 130.4, 131.7, 133.5, 135.2, 139.1, 140.7, 141.0, 168.0. EI-MS (*m/z*, relative intensity): 278 (M^+, 60), 219 (100). HRMS calcd for $C_{19}H_{18}O_2$: 278.1307. Found: 278.1305.

(*2E,4E*)-Methyl 5-(4-chlorophenyl)-2-phenylpenta-2,4-dienoate (4f)



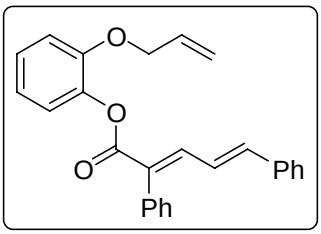
Yield 65%; IR (neat) 1708, 1616, 1490, 1232 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.76 (dd, *J* = 11.1, 15.6 Hz, 1H), 6.91 (d, *J* = 15.6 Hz, 1H), 7.26~7.30 (m, 6H), 7.39~7.47 (m, 3H), 7.63 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 125.2, 127.8, 128.1, 128.3, 128.9, 130.3, 132.8, 134.5, 134.7, 135.0, 139.0, 140.3, 167.8; EI-MS (*m/z*, relative intensity): 298 (M^+, 64), 204 (100). HRMS calcd for $C_{18}H_{15}O_2Cl$: 298.0761. Found: 298.0760.

(*E*)-Methyl 2,5,5-triphenylpenta-2,4-dienoate (4g)



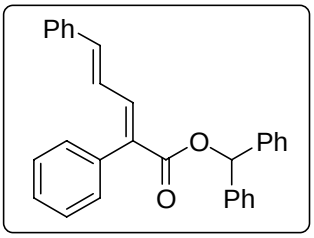
Yield 65%; IR (neat) 1707, 1604, 1434, 1262, 1234 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.69 (s, 3H), 6.70 (d, *J* = 11.7 Hz, 1H), 7.17~7.43 (m, 15H), 7.57 (d, *J* = 11.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.1, 123.7, 127.7, 128.0, 128.2, 128.3, 128.4, 130.3, 130.5, 133.1, 135.2, 138.1, 138.8, 141.6, 150.8, 168.0; EI-MS (*m/z*, relative intensity): 340 (M^+, 93), 281 (100). HRMS calcd for $C_{24}H_{20}O_2$: 340.1463. Found: 340.1469.

(2*E*,4*E*)-2-(allyloxy)phenyl 2,5-diphenylpenta-2,4-dienoate (4h)



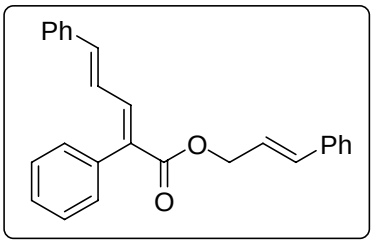
Yield 70%; IR (neat) 1724, 1614, 1497, 1183 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.56 (d, *J* = 4.8 Hz, 2H), 5.26 (dd, *J* = 1.2, 10.5 Hz, 1H), 5.41 (dd, *J* = 1.5, 17.4 Hz, 1H), 6.02 (ddd, *J* = 5.4, 10.5, 12.0 Hz, 1H), 6.88~7.45 (m, 16H), 7.86 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 69.3, 113.8, 117.2, 121.0, 123.0, 124.7, 126.5, 127.3, 127.8, 128.0, 128.7, 129.0, 130.5, 131.5, 132.9, 134.9, 136.2, 140.6, 141.3, 142.0, 150.1, 165.6; EI-MS (*m/z*, relative intensity): 382 (M^+, 6), 233 (100). HRMS calcd for $C_{26}H_{22}O_3$: 382.1569. Found: 382.1558.

(2*E*,4*E*)-benzhydryl 2,5-diphenylpenta-2,4-dienoate (4i)



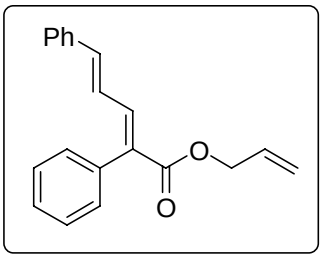
Yield 60%; IR (neat) 1706, 1223 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.84 (dd, *J* = 11.4, 15.6 Hz, 1H), 6.97~7.02 (m, 2H), 7.24~7.44 (m, 20H), 7.73 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 77.3, 124.7, 126.9, 127.2, 127.7, 128.0, 128.4, 128.7, 128.9, 130.4, 132.4, 135.0, 136.2, 140.4, 140.8, 140.9, 166.2; EI-MS (*m/z*, relative intensity): 416 (M^+, 3), 167 (100). HRMS calcd for $C_{30}H_{24}O_2$: 416.1776. Found: 416.1762.

(2*E*,4*E*)-cinnamyl 2,5-diphenylpenta-2,4-dienoate (4j)



Yield 58%; IR (neat) 1703, 1223 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.87 (d, *J* = 6.0 Hz, 2H), 6.34 (td, *J* = 6.0, 15.9 Hz, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.83 (dd, *J* = 11.4, 15.6 Hz, 1H), 6.99 (d, *J* = 15.6 Hz, 1H), 7.26~7.47 (m, 15H), 7.69 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.5, 123.3, 124.7, 126.6, 127.2, 127.8, 128.0, 128.1, 128.6, 128.7, 128.9, 130.4, 132.3, 133.8, 135.0, 136.2, 140.7, 140.8, 167.1; EI-MS (*m/z*, relative intensity): 366 (M^+, 3), 117 (100). HRMS calcd for $C_{26}H_{22}O_2$: 366.1620. Found: 366.1628.

(2*E*,4*E*)-allyl 2,5-diphenylpenta-2,4-dienoate (4k)



Yield 51%; IR (neat) 1707, 1224 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.71 (d, *J* = 5.4 Hz, 2H), 5.23 (dd, *J* = 0.9, 10.5 Hz, 1H), 5.30 (dd, *J* = 1.2, 17.1 Hz, 1H), 5.97 (ddd, *J* = 5.4, 10.8, 15.9 Hz, 1H), 6.83 (dd, *J* = 11.4, 15.6 Hz, 1H), 6.99 (d, *J* = 15.6 Hz, 1H), 7.26~7.46 (m, 10H), 7.68 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.5, 117.9, 124.7, 127.2, 127.7, 128.0, 128.7, 128.9, 130.4, 132.2, 135.0, 136.2, 140.7, 140.8, 167.0; EI-MS (*m/z*, relative intensity): 290 (M^+, 55), 205 (100). HRMS calcd for $C_{20}H_{18}O_2$: 290.1307. Found: 290.1318.

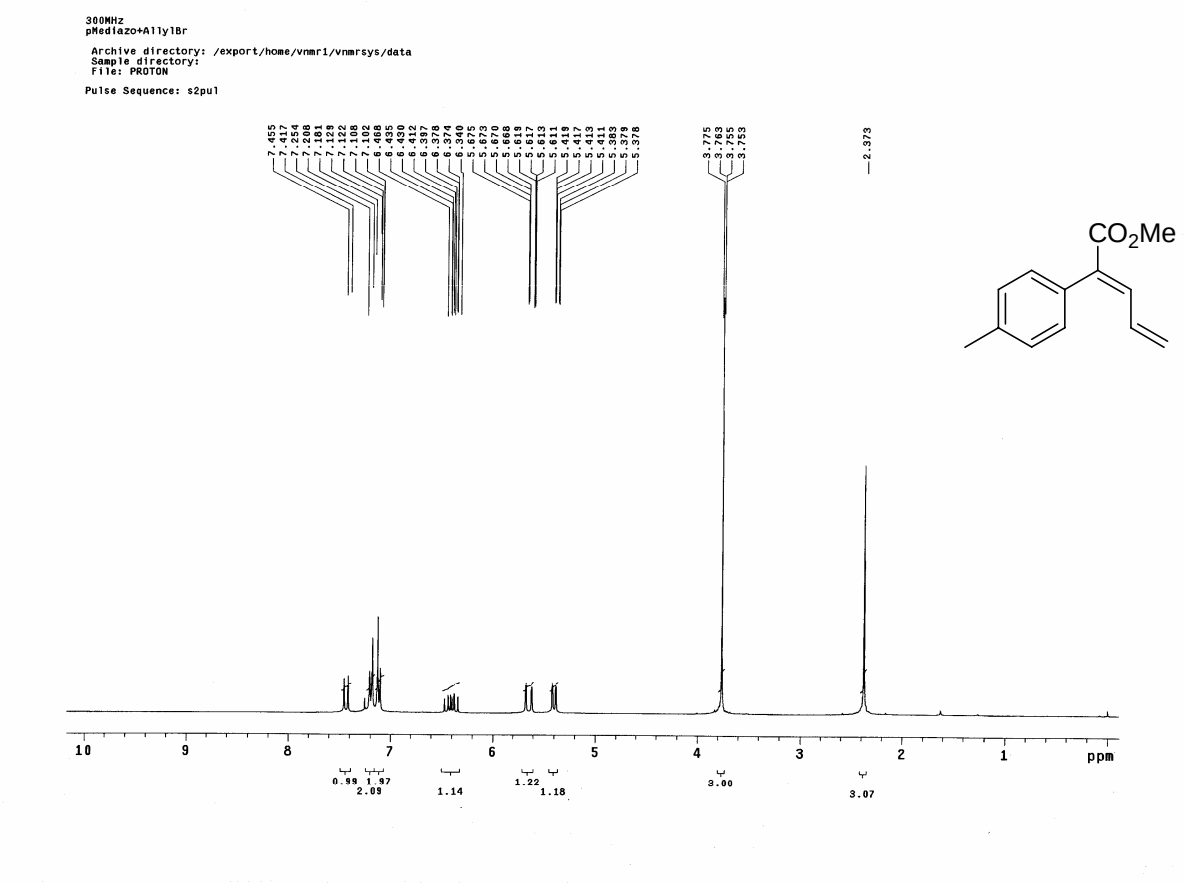
References

1 (a) T. Fekner, H. Muller-Bunz, P. J. Guiry, *Org. Lett*. 2006, **8**, 5109-5112. (b) V. K. Yadav, K. G. Babu, *Tetrahedron*. 2003, **59**, 9111-9116.

2 N. S. Mani, C. M. Mapes, J. Wu, X. Deng, T. K. Jones, *J. Org. Chem.* 2006, **71**, 5039-5042.

3 A. Llebaria, F. Camps, J. M. Moretó, *Tetrahedron*. 1993, **49**, 1283-1296.

4 F. G. Stakem, R. F. Heck, *J. Org. Chem.* 1980, **45**, 3584-3593.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Sample directory:
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7.254
7.208
7.181
7.128
7.122
7.106
7.102
6.468
6.435
6.430
6.412
6.397
6.378
6.374
6.340
5.675
5.673
5.670
5.668
5.619
5.617
5.613
5.411
5.408
5.417
5.413
5.411
5.383
5.379
5.378
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3.763
3.755
3.753
2.373
CO2Me
10
9
8
7
6
5
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3
2
1
ppm
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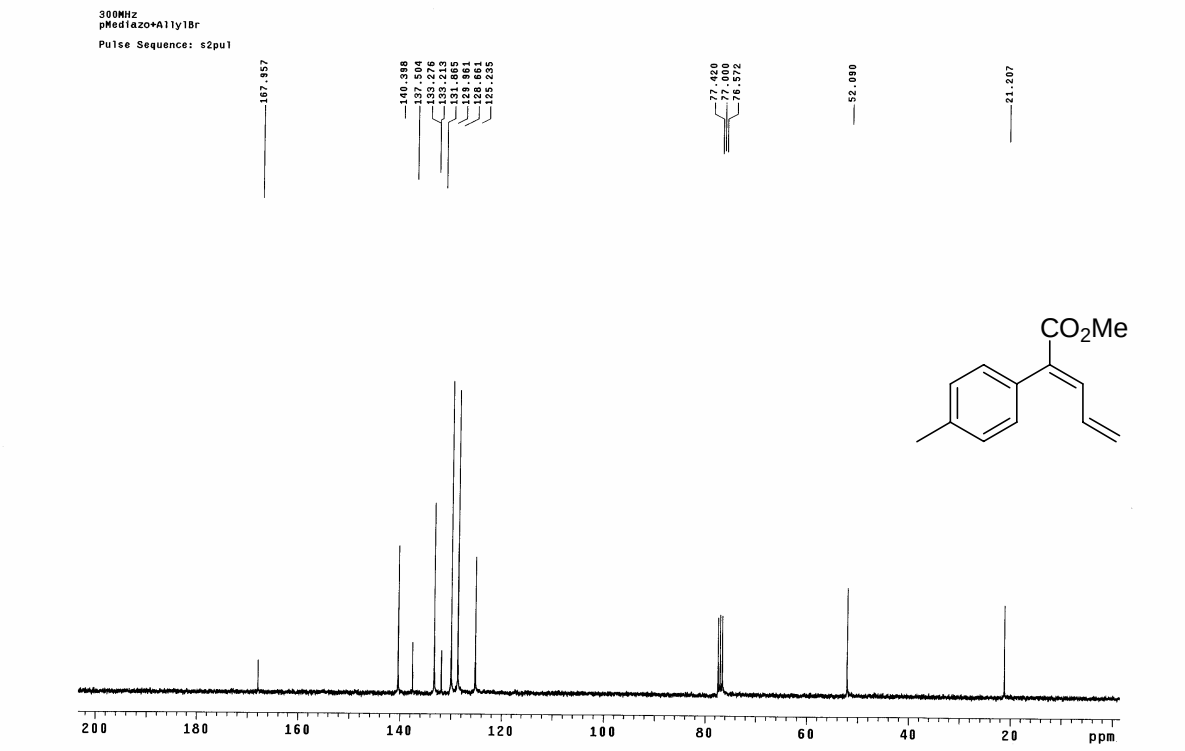
2.09
1.14
1.22
1.18
3.00
3.07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52.090
21.207
CO2Me
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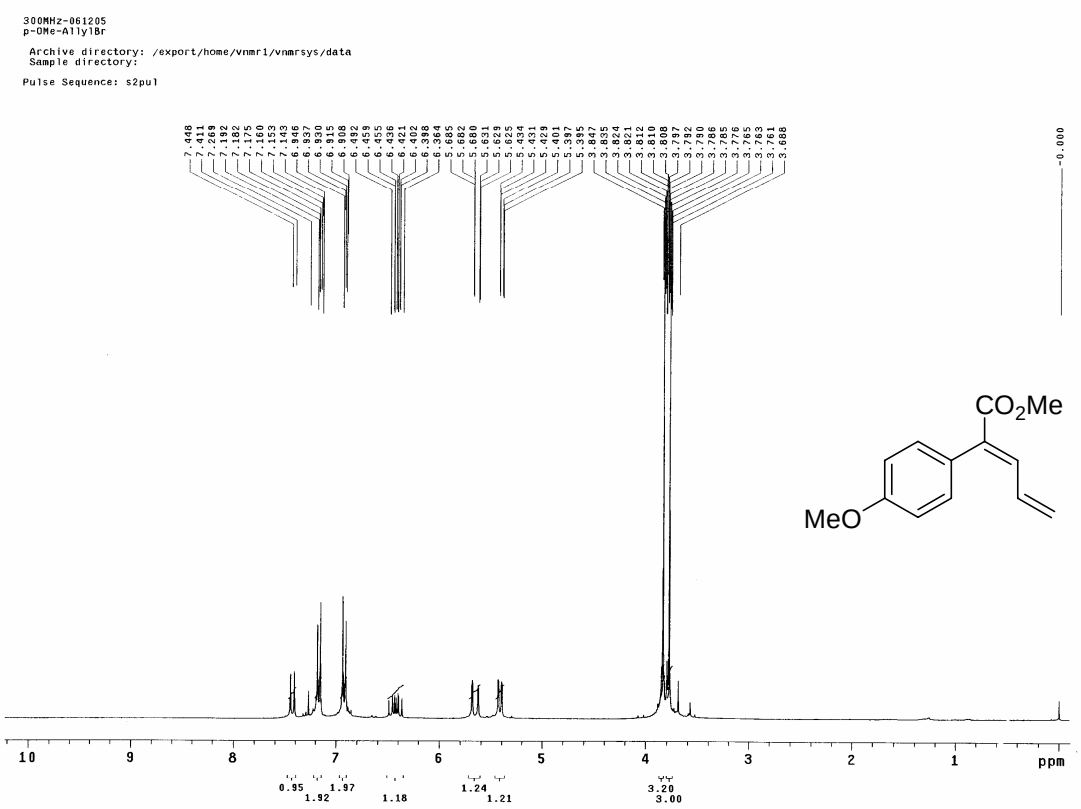
140
120
100
80
60
40
20
ppm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Sample directory:
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7.160
7.153
7.143
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6.908
6.492
6.459
6.455
6.436
6.421
6.402
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5.685
5.682
5.680
5.651
5.629
5.625
5.434
5.431
5.429
5.401
5.397
5.395
3.847
3.835
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3.808
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3.765
3.763
3.761
3.688
0.000
CO2Me
MeO
10
9
8
7
6
5
4
3
2
1
ppm
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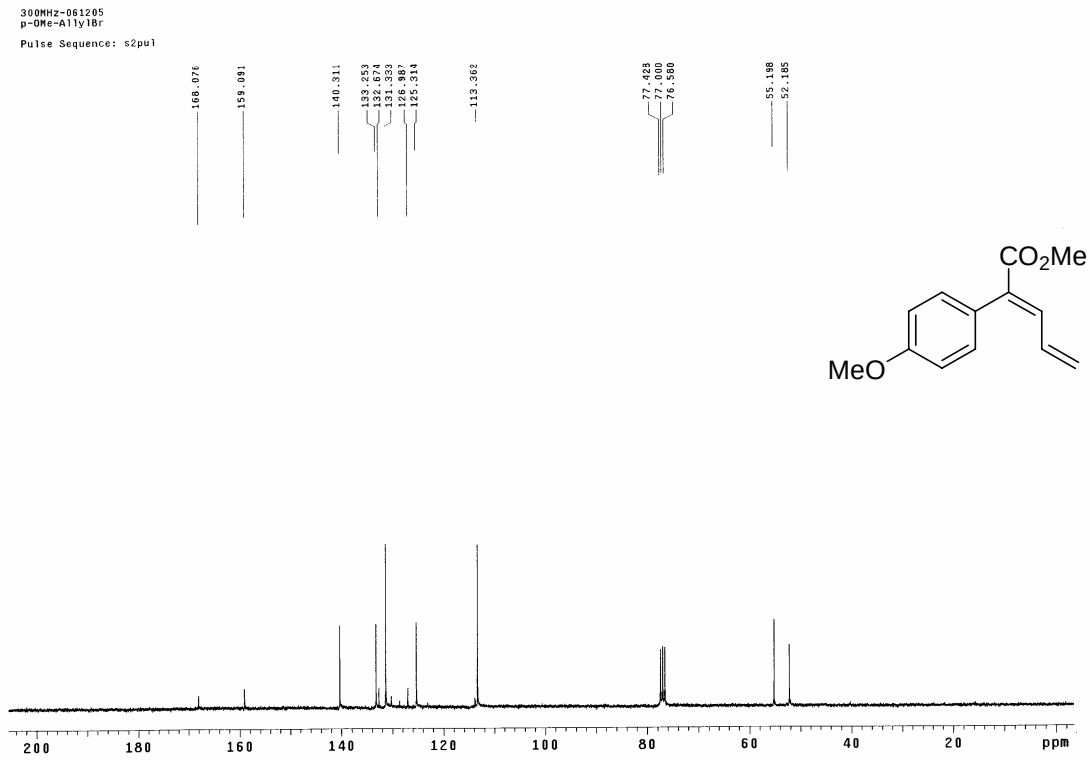
1.92
1.18
1.24
1.21
3.20
3.00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52.185
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MeO
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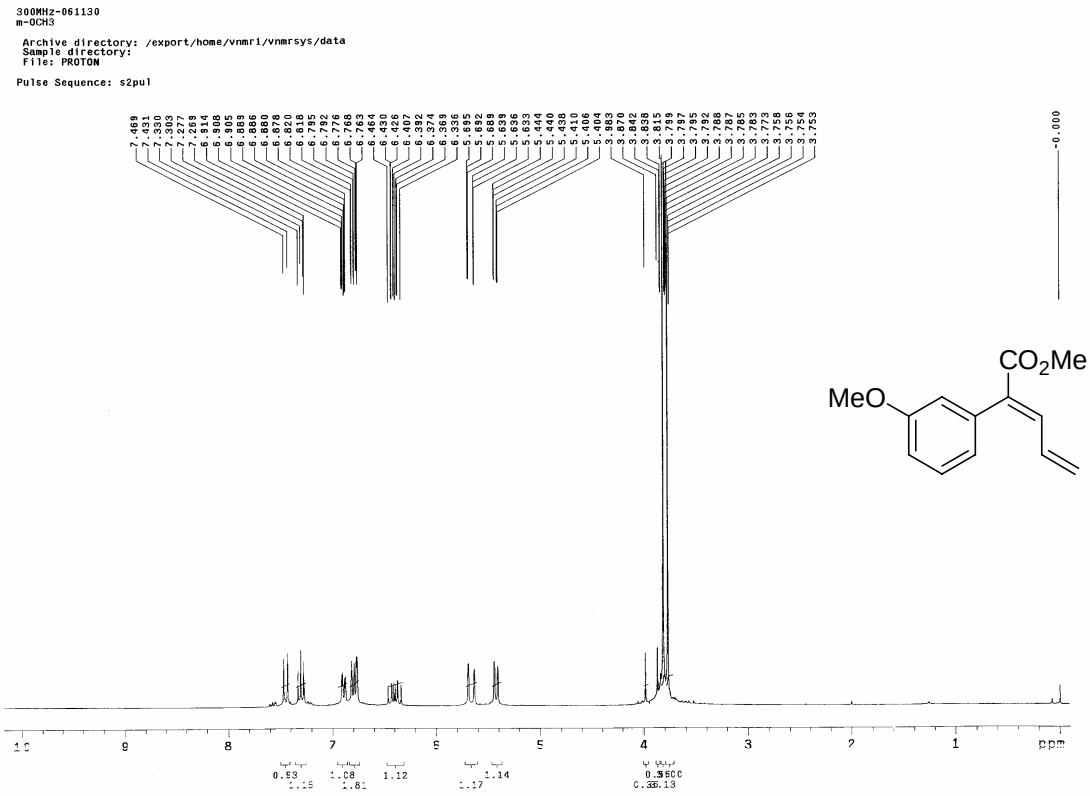
40
20
ppm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Sample directory:
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7.277
7.268
6.914
6.908
6.905
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6.818
6.795
6.792
6.776
6.768
6.765
6.464
6.430
6.426
6.407
6.392
6.374
6.364
6.336
5.695
5.692
5.689
5.638
5.636
5.633
5.444
5.440
5.438
5.410
5.406
5.404
3.983
3.870
3.842
3.838
3.815
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3.797
3.795
3.792
3.788
3.787
3.785
3.773
3.773
3.758
3.756
3.754
3.753
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MeO
ppm
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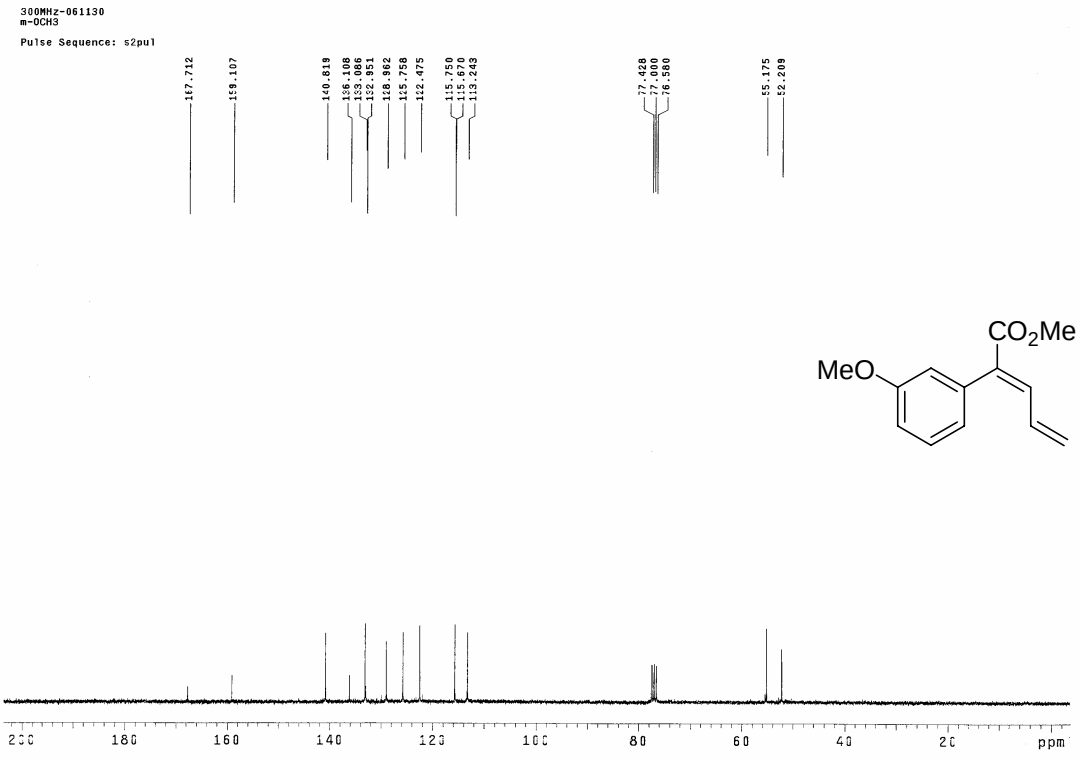
1.08
1.81
1.12
1.17
1.14
3.13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55.175
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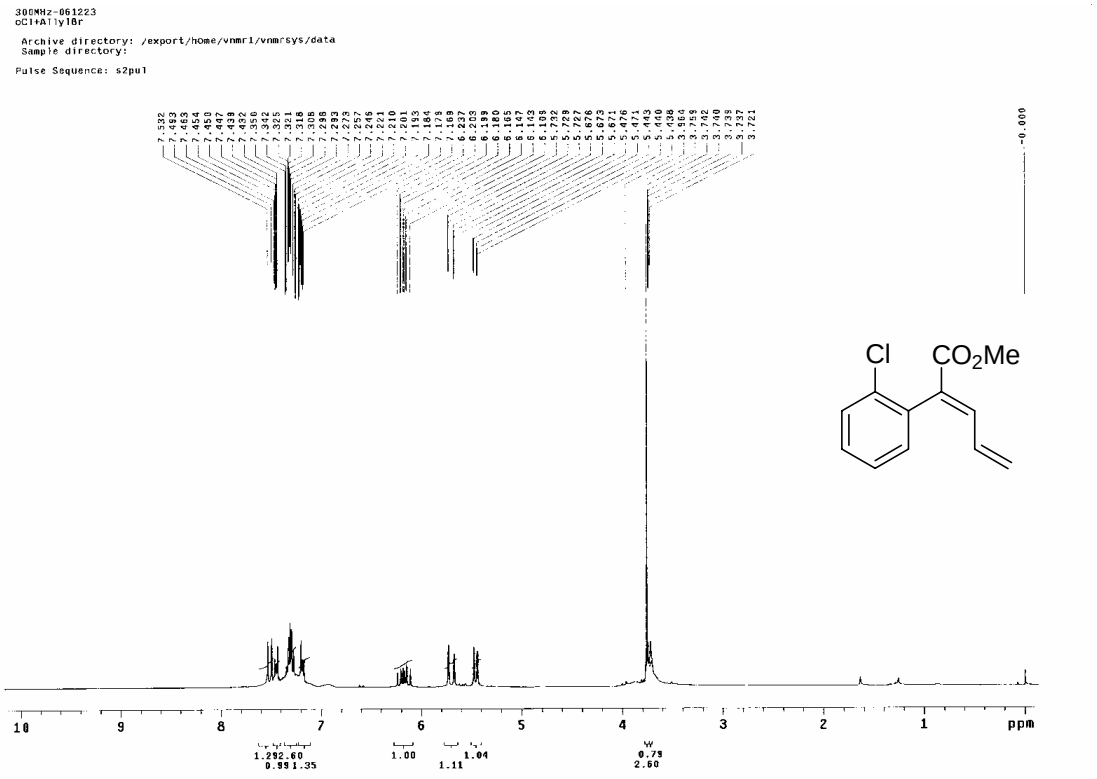
CO2Me
MeO
ppm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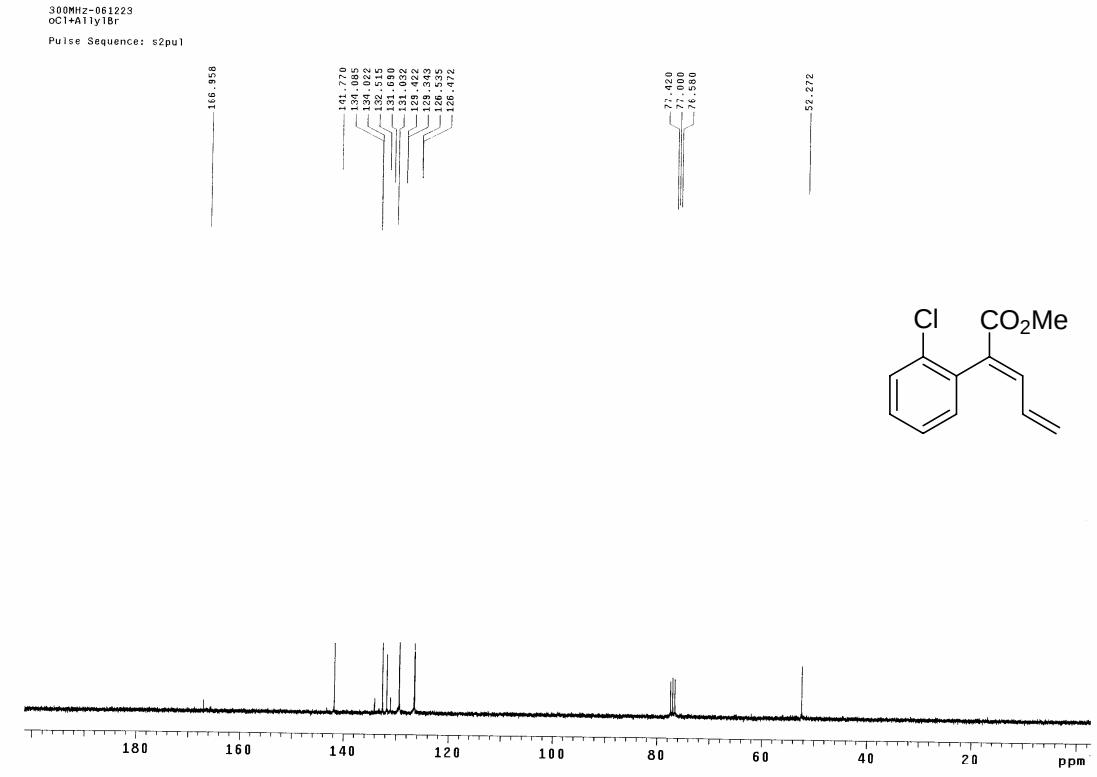
9
8
7
6
5
4
3
2
1
ppm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CO2Me
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160
140
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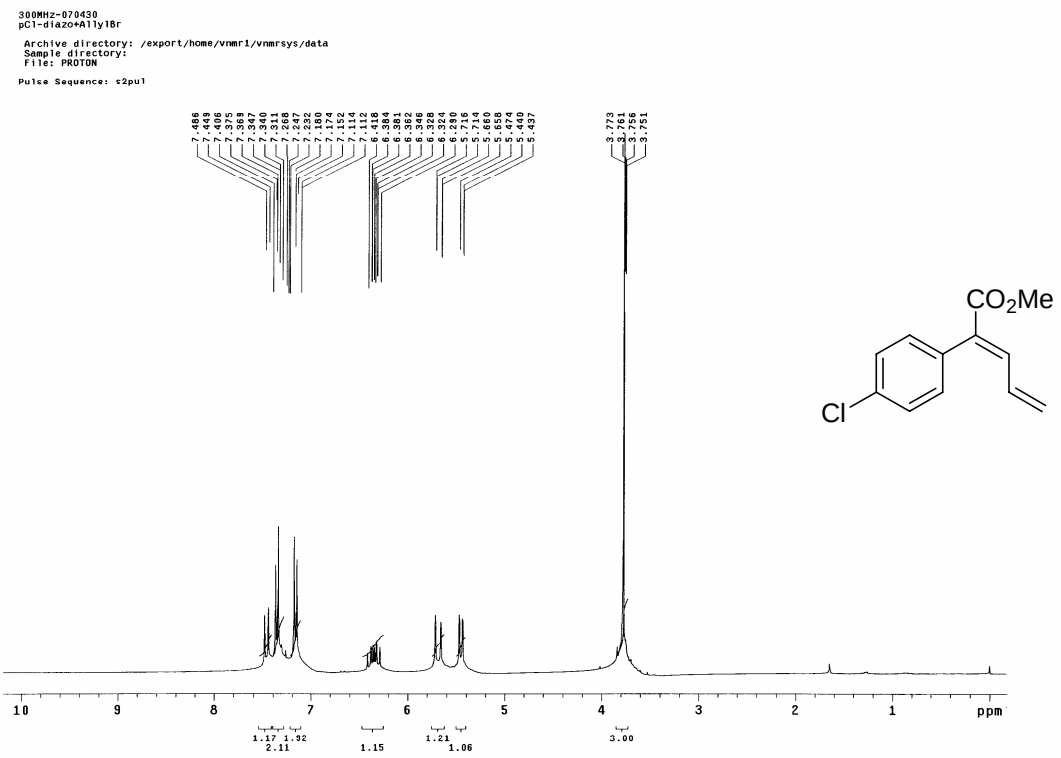
80
60
40
20
ppm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6.362
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5.474
5.460
5.437
3.773
3.761
3.756
3.751
CO2Me
Cl
10
9
8
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2
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2.11
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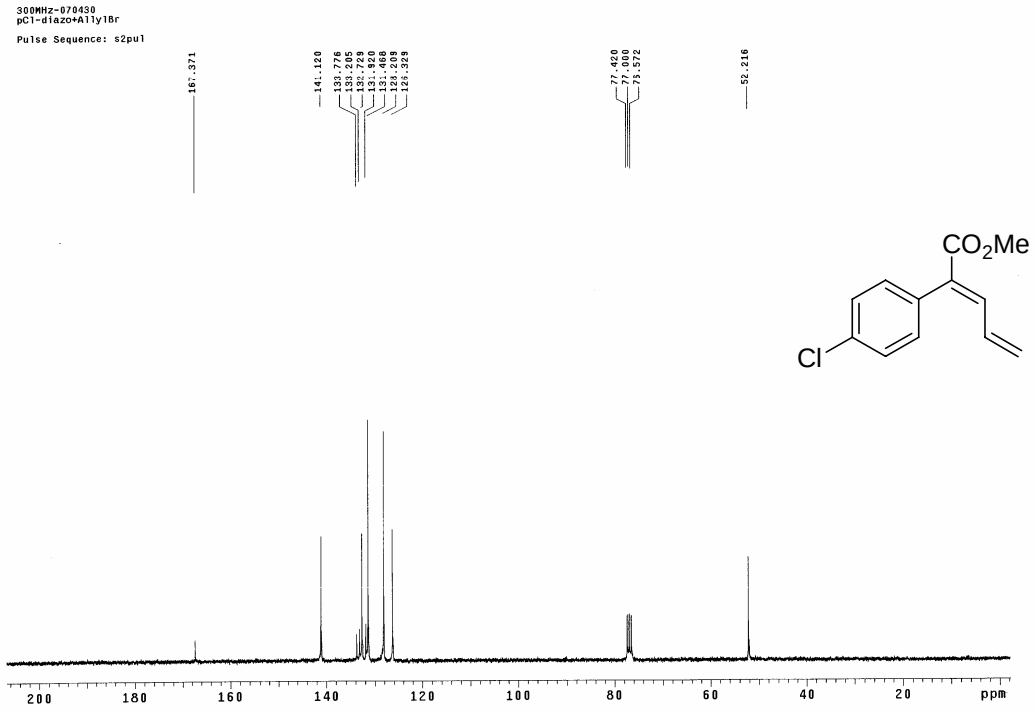
1.21
1.06
3.00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Pulse Sequence: s2pul
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131.208
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52.216
CO2Me
Cl
200
180
160
140
120
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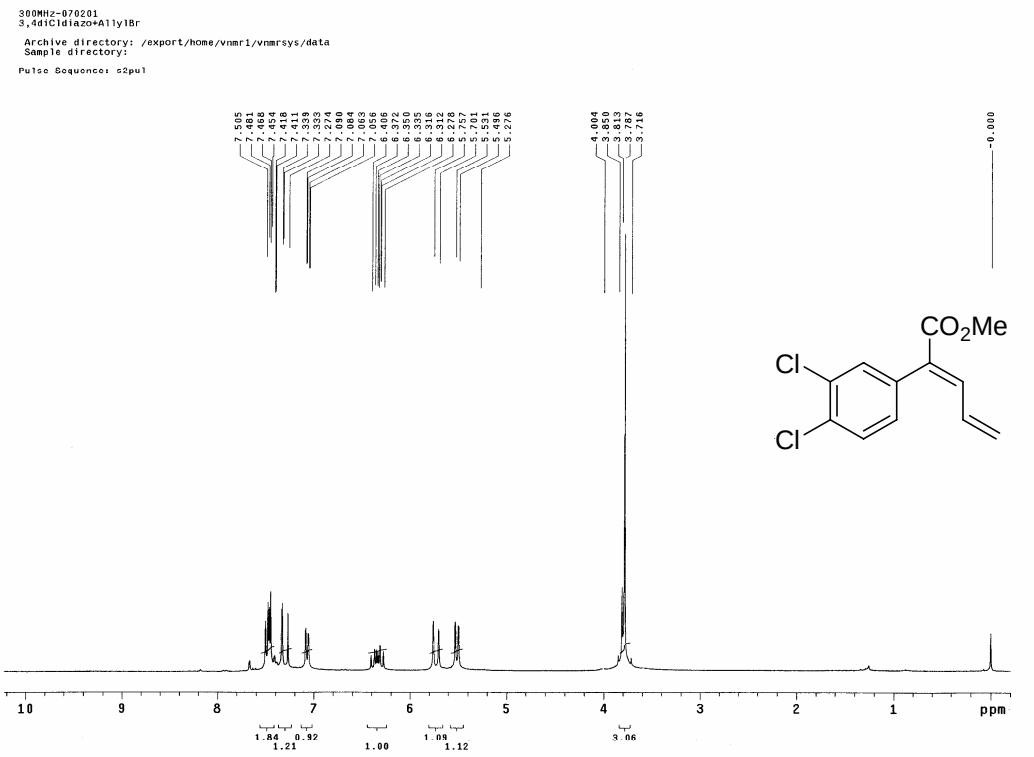
80
60
40
20
ppm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7.411
7.339
7.333
7.224
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7.084
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6.272
6.278
5.757
5.701
5.531
5.496
5.276
4.004
3.850
3.813
3.787
3.716
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CO2Me
Cl
Cl
10
9
8
7
6
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4
3
2
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ppm
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1.21
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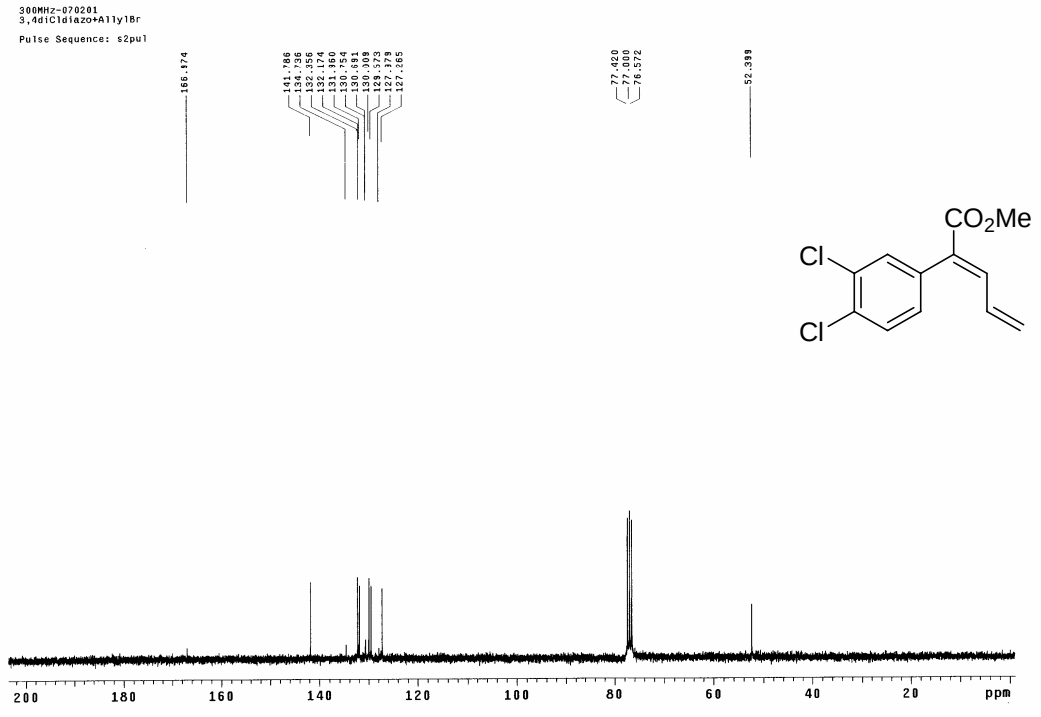
1.08
1.12
3.06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130.309
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77.420
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CO2Me
Cl
Cl
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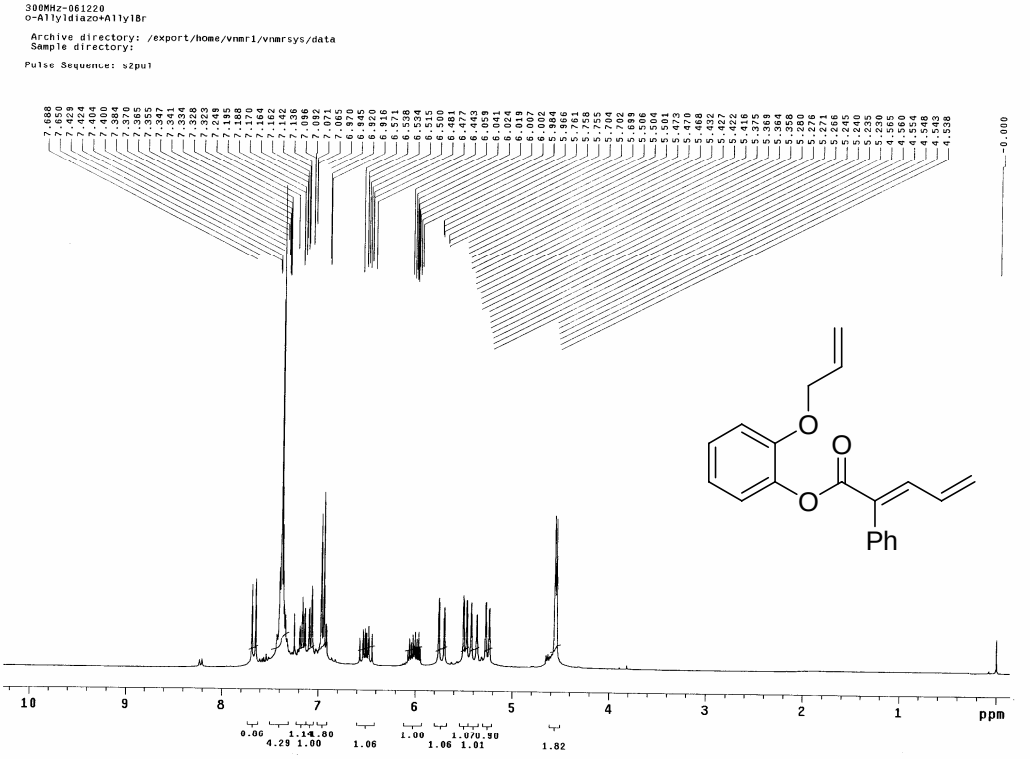
160
140
120
100
80
60
40
20
ppm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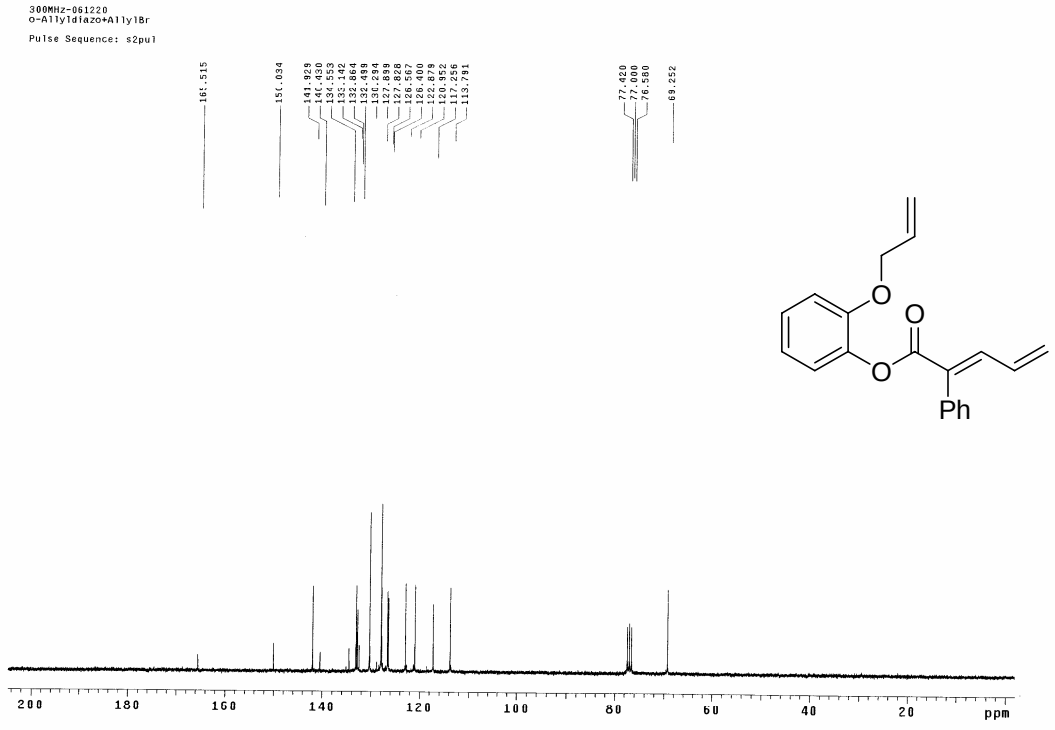
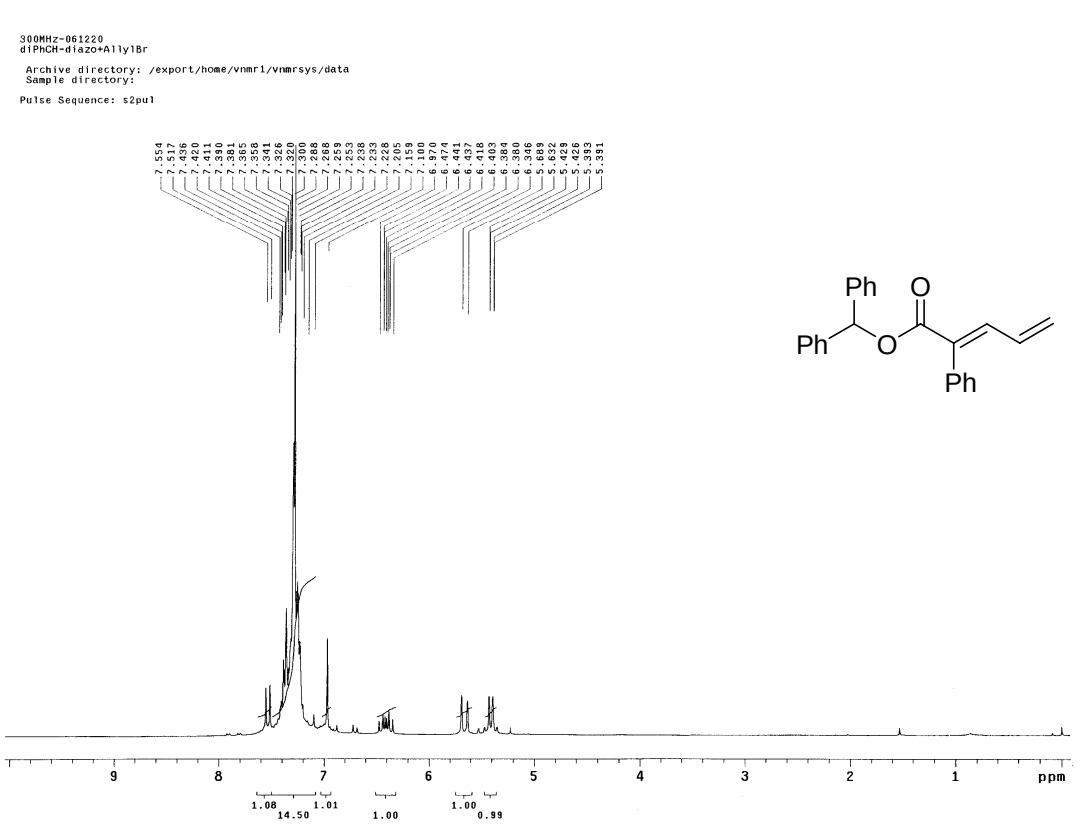
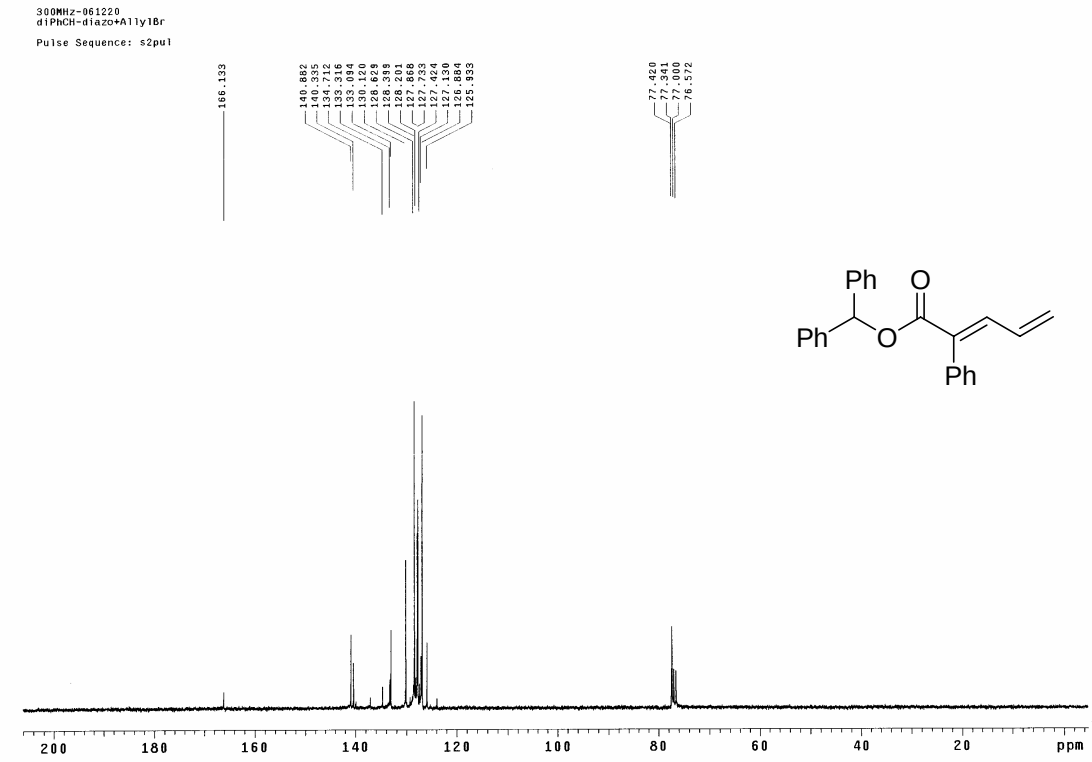
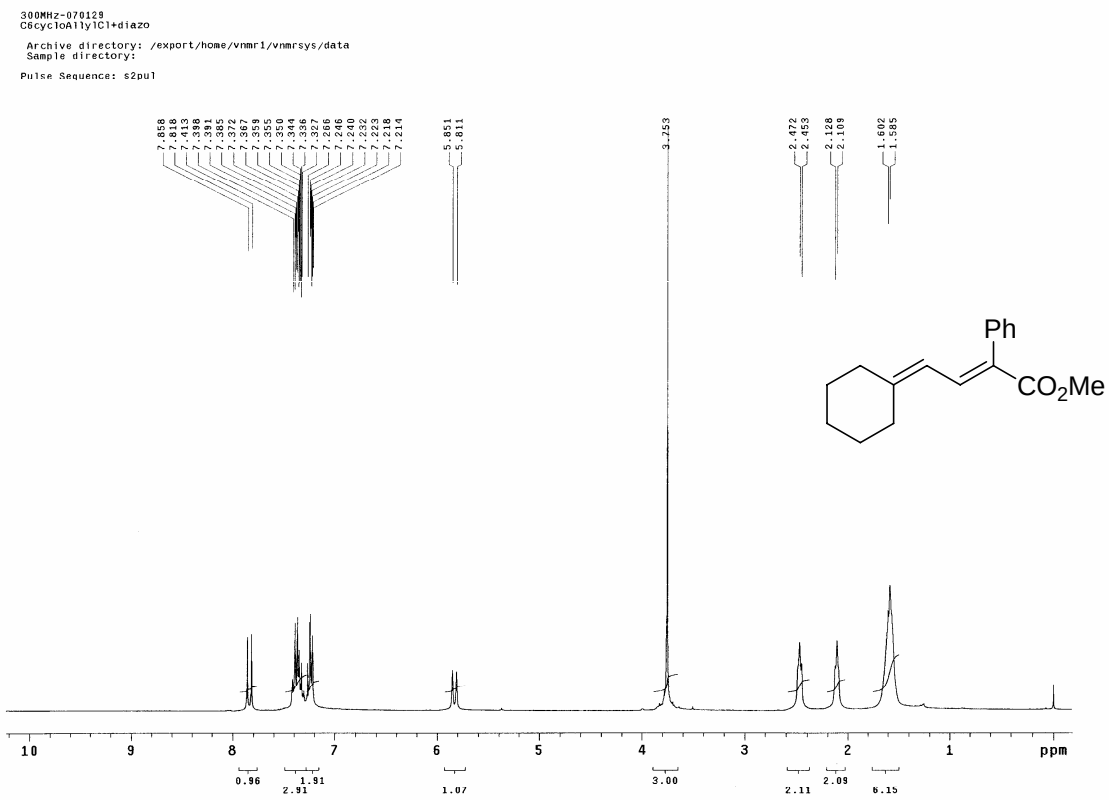
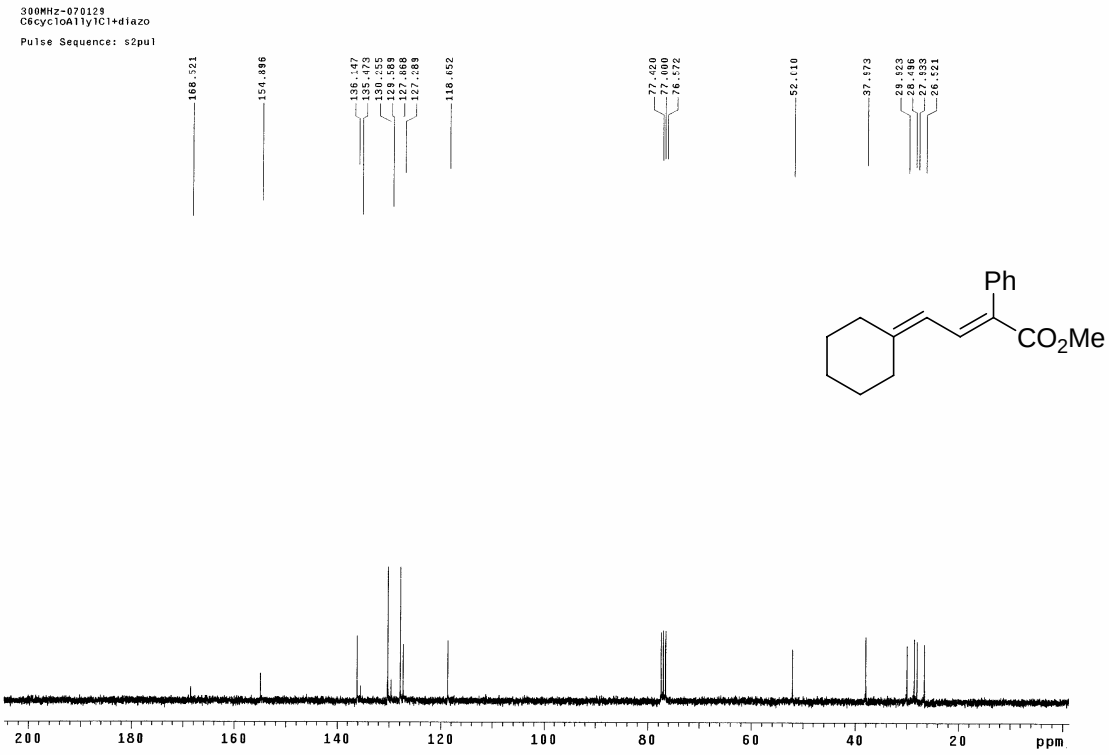
7.429
7.414
7.404
7.400
7.384
7.370
7.355
7.347
7.341
7.334
7.328
7.323
7.249
7.195
7.188
7.170
7.164
7.162
7.142
7.138
7.096
7.092
7.071
7.065
6.970
6.965
6.920
6.916
6.571
6.538
6.534
6.515
6.500
6.481
6.477
6.449
6.445
6.058
6.041
6.024
6.019
6.007
6.002
5.984
5.966
5.761
5.758
5.755
5.704
5.702
5.699
5.506
5.504
5.501
5.473
5.470
5.468
5.467
5.427
5.422
5.416
5.375
5.369
5.364
5.358
5.280
5.276
5.271
5.268
5.245
5.240
5.235
5.230
4.565
4.560
4.554
4.548
4.543
4.538
0.000
O
O
O
Ph
10
9
8
7
6
5
4
3
2
1
ppm
0.06
1.14
4.80
4.29
1.00
1.06
1.00
1.06
1.07
0.90
1.01
1.82

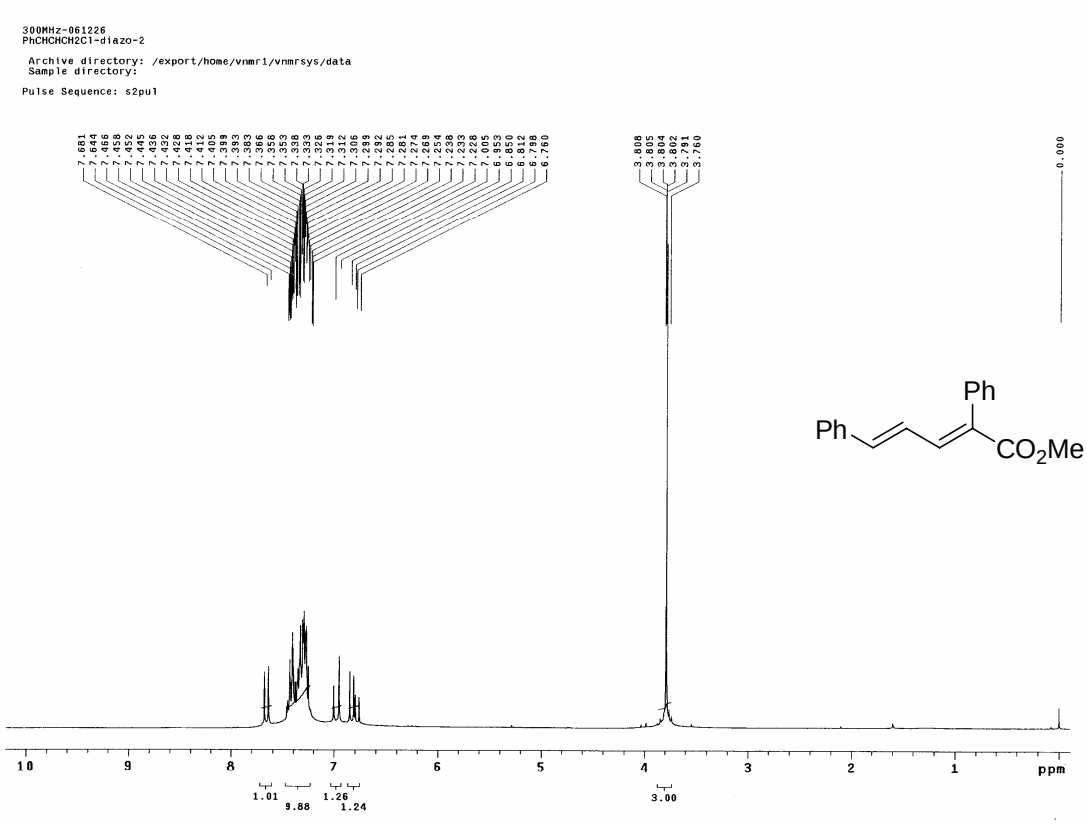

300MHz-061220
o-Allyldiazo+AllylBr
Pulse Sequence: s2pul
167.515
150.034
141.929
140.430
138.455
135.142
132.864
132.499
130.294
128.888
127.828
126.567
126.400
122.879
120.552
117.256
113.781
77.420
77.000
76.580
69.252
O
O
O
Ph
200
180
160
140
120
100
80
60
40
20
ppm

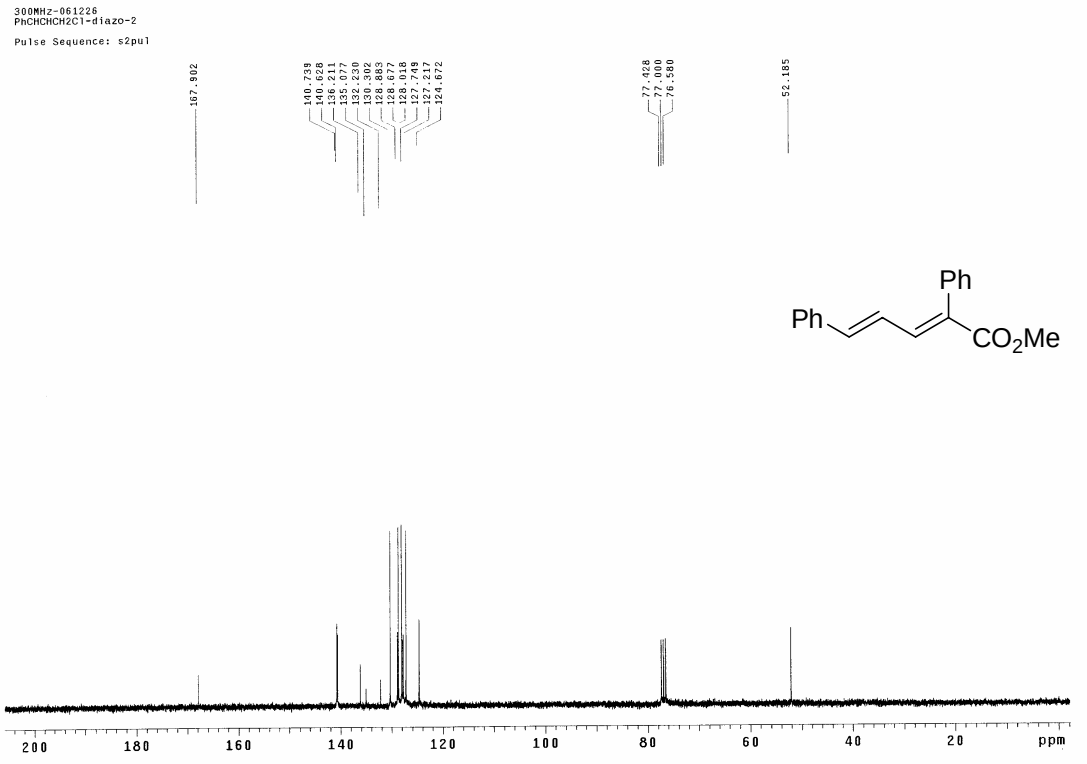

300MHz-061220
diPhCH-diazo+AllylBr
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
7.554
7.517
7.436
7.420
7.411
7.390
7.381
7.365
7.358
7.341
7.326
7.320
7.300
7.288
7.268
7.259
7.253
7.238
7.233
7.228
7.205
7.159
7.100
6.470
6.441
6.437
6.418
6.403
6.384
6.360
6.346
5.689
5.632
5.429
5.426
5.383
5.381
Ph
O
Ph
O
Ph
9
8
7
6
5
4
3
2
1
ppm
1.08
1.01
14.50
1.00
1.00
0.99

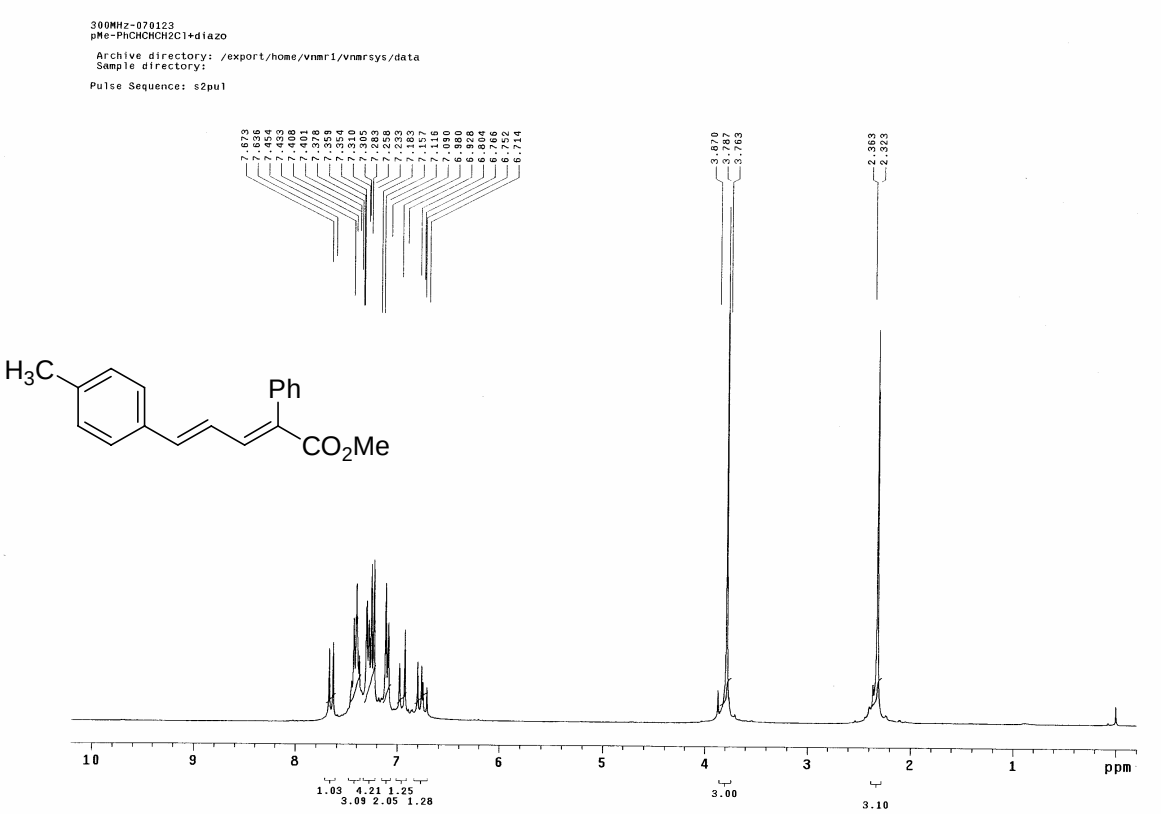

300MHz-061220
diPhCH-diazo+AllylBr
Pulse Sequence: s2pul
166.133
140.882
140.335
134.712
133.316
133.094
130.120
128.629
128.398
128.201
127.868
127.733
127.454
127.130
126.884
125.933
77.420
77.341
77.000
76.572
Ph
O
Ph
O
Ph
200
180
160
140
120
100
80
60
40
20
ppm


300MHz-070129
C6cycloAllylCl+diazo
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
7.858
7.818
7.413
7.398
7.391
7.385
7.372
7.367
7.359
7.355
7.350
7.344
7.336
7.327
7.266
7.246
7.240
7.232
7.223
7.218
7.214
5.851
5.811
3.753
2.472
2.453
2.128
2.109
1.602
1.585
Ph
CO2Me
10
9
8
7
6
5
4
3
2
1
ppm
0.96
1.91
2.91
1.07
3.00
2.11
2.09
6.15


300MHz-070129
C6cycloAllylCl+diazo
Pulse Sequence: s2pul
168.521
154.896
136.147
135.473
130.255
129.589
127.868
127.289
118.652
77.420
77.000
76.572
52.610
37.573
29.523
28.496
27.533
26.521
Ph
CO2Me
200
180
160
140
120
100
80
60
40
20
ppm


300MHz-061226
PhCHCHCH2Cl-diazo-2
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
7.681
7.644
7.466
7.458
7.452
7.445
7.436
7.432
7.418
7.416
7.412
7.405
7.399
7.393
7.383
7.366
7.358
7.353
7.338
7.333
7.326
7.319
7.312
7.306
7.299
7.292
7.285
7.281
7.274
7.268
7.254
7.238
7.233
7.228
7.005
6.853
6.850
6.812
6.798
6.760
3.808
3.805
3.804
3.802
3.791
3.760
0.000
Ph
Ph
CO2Me
10
9
8
7
6
5
4
3
2
1
ppm
1.01
9.88
1.26
1.24
3.00


300MHz-061226
PhCHCHCH2Cl-diazo-2
Pulse Sequence: s2pul
167.902
140.739
140.628
136.211
135.077
132.230
130.302
128.883
128.677
128.018
127.748
127.217
124.672
77.428
77.000
76.580
52.185
Ph
Ph
CO2Me
200
180
160
140
120
100
80
60
40
20
ppm


300MHz-070123
pMe-PhCHCHCH2Cl+diazo
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
7.673
7.636
7.454
7.433
7.408
7.401
7.378
7.354
7.310
7.305
7.283
7.258
7.233
7.183
7.157
7.116
7.090
6.980
6.928
6.876
6.824
6.766
6.752
6.714
3.870
3.787
3.763
2.363
2.323
H3C
Ph
CO2Me
10
9
8
7
6
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ppm
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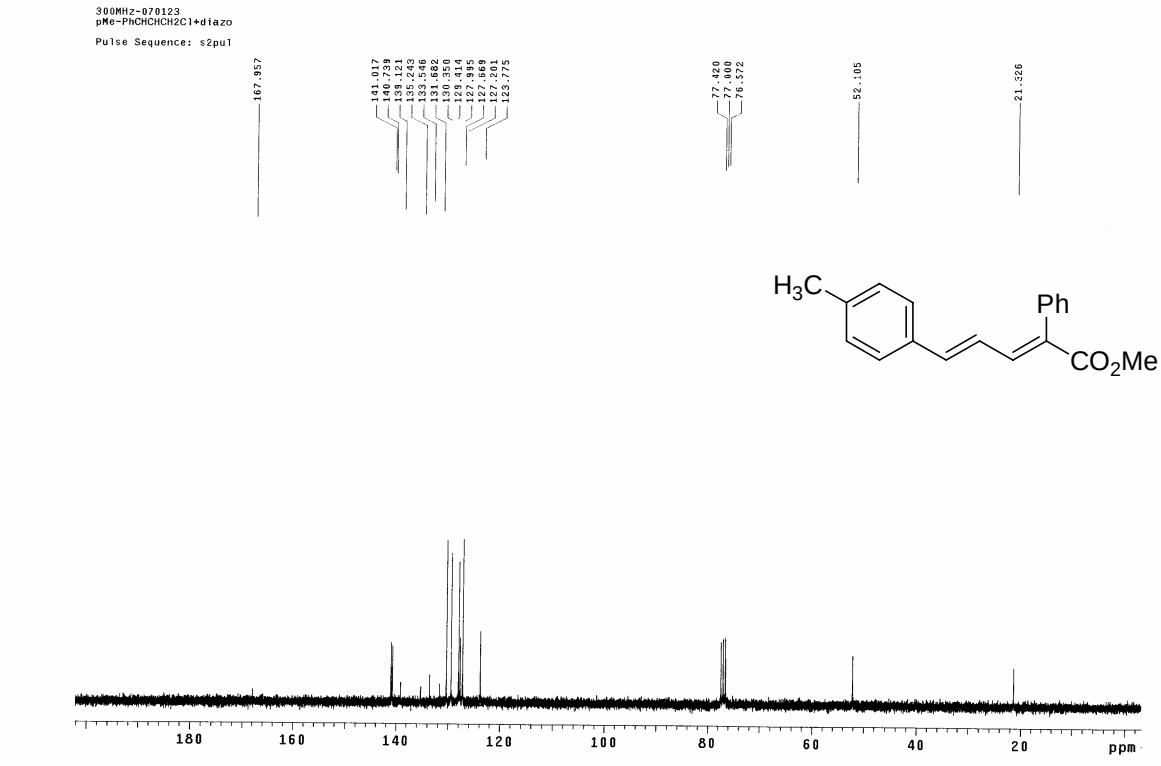
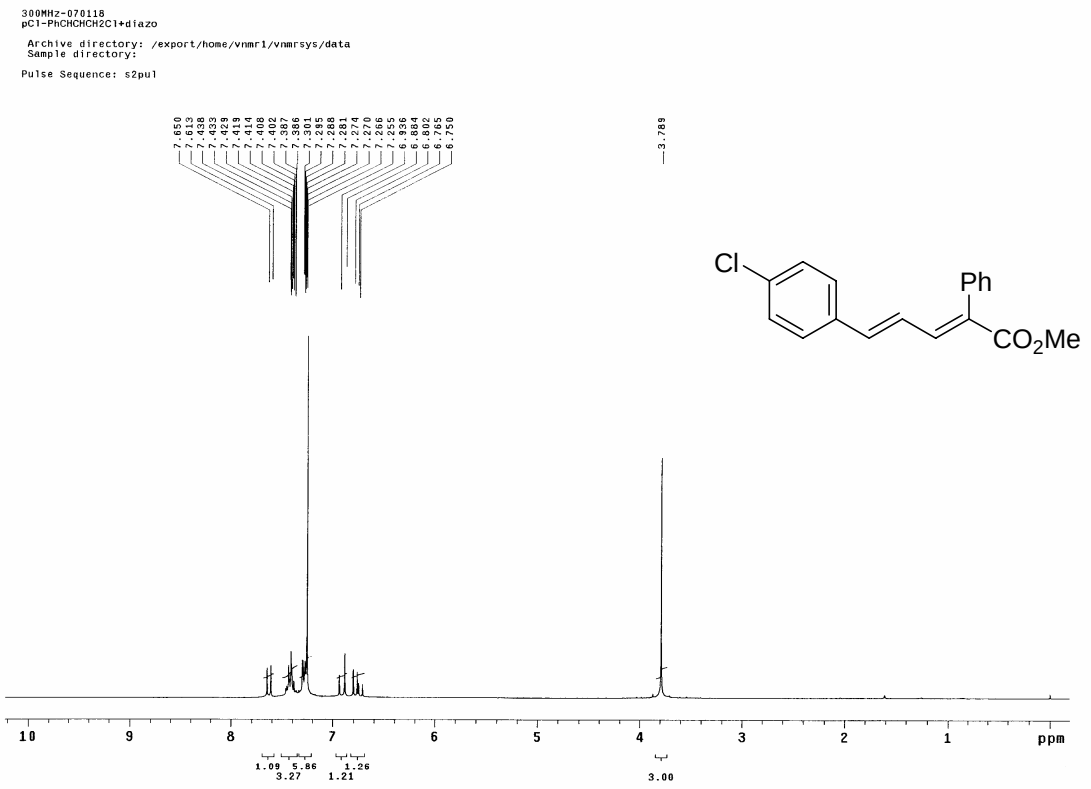
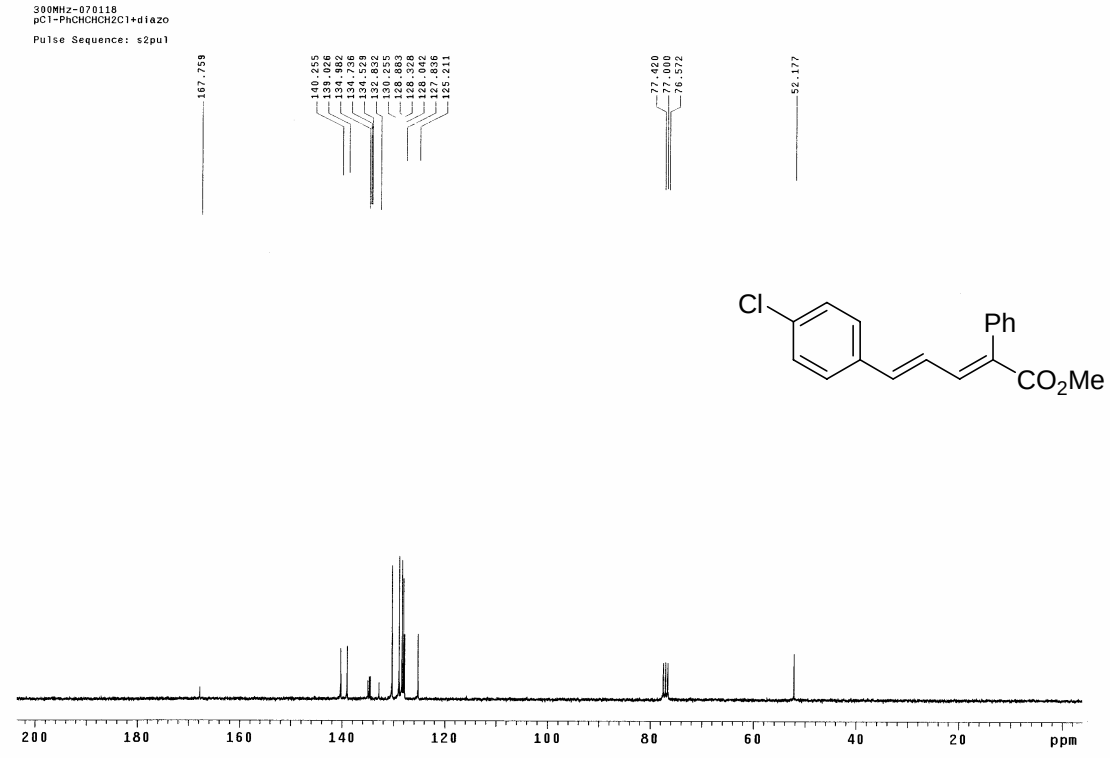
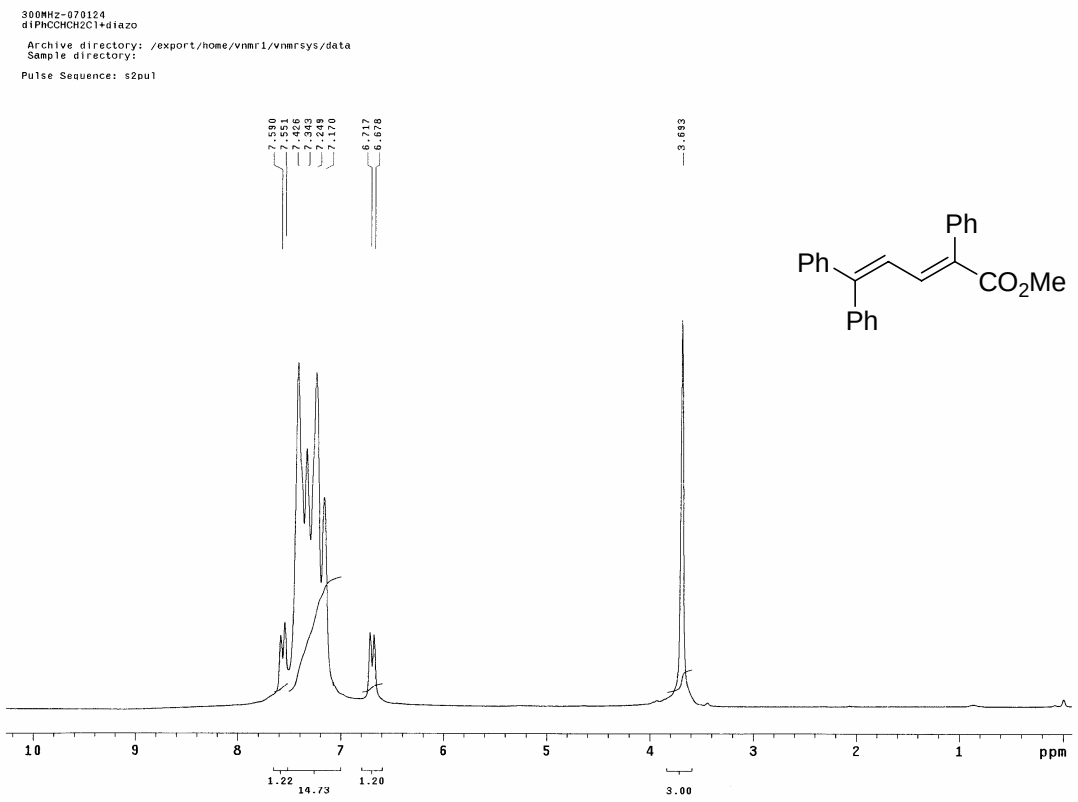
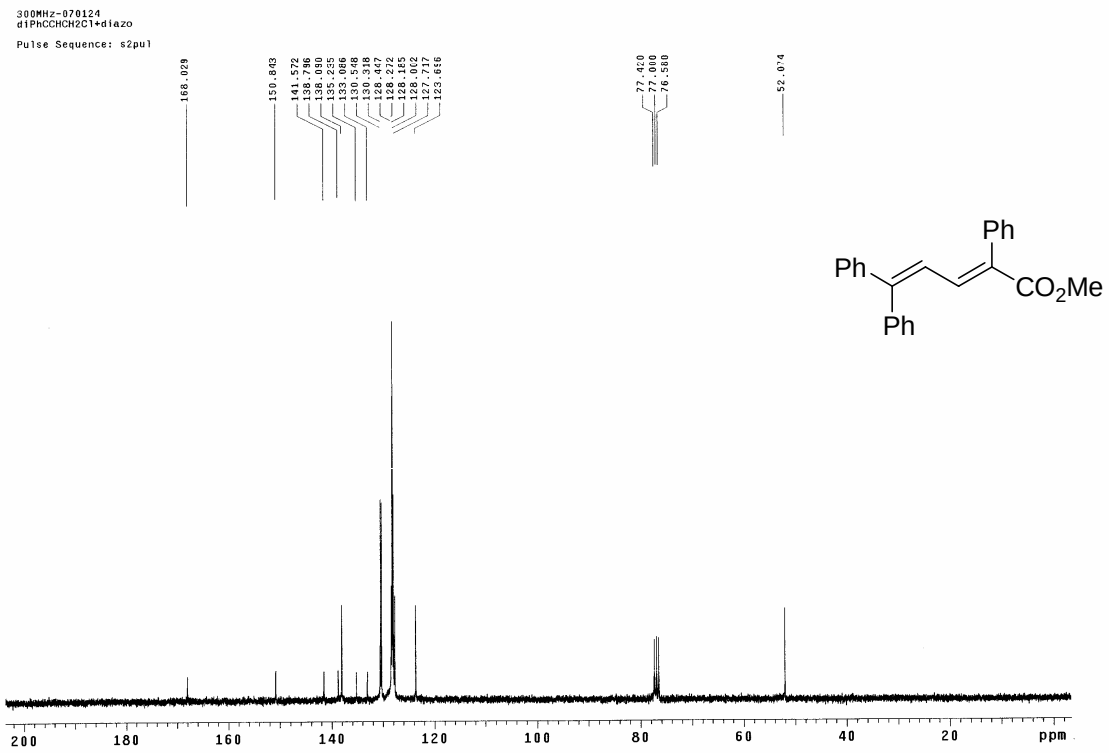
4.21
1.25
3.09
2.05
1.28
3.00
3.10

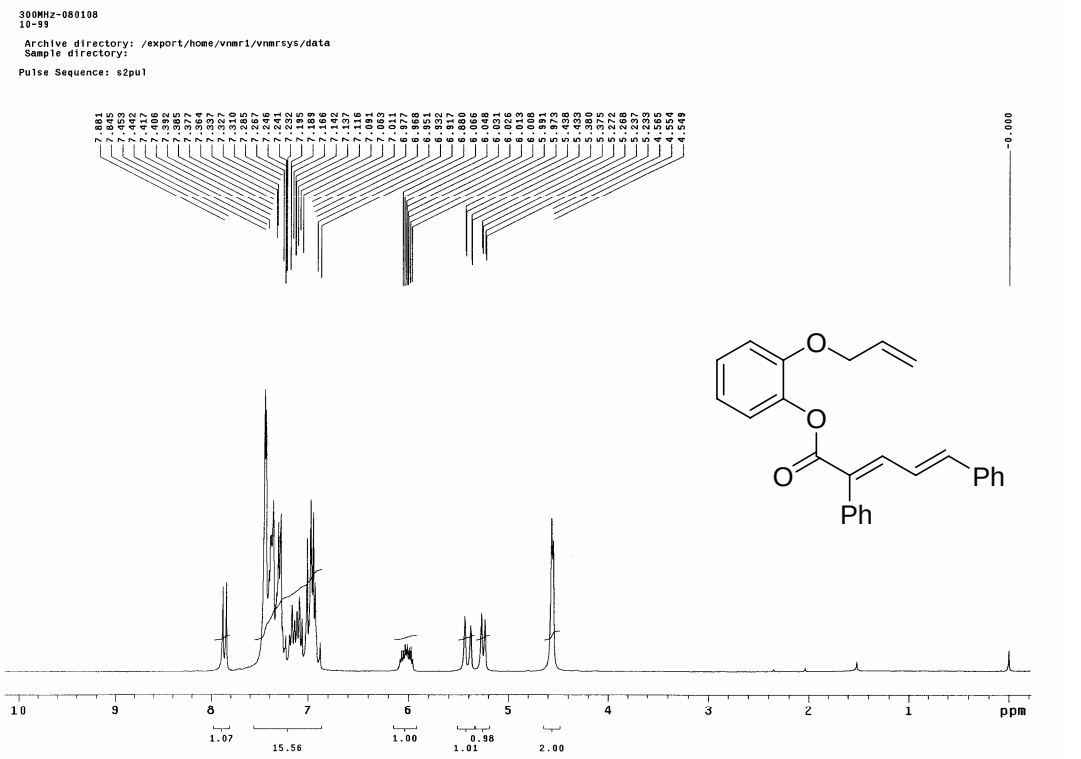

300MHz-070123
pMe-PhCHCHCH2Cl+diazo
Pulse Sequence: s2pul
167.957
141.017
140.739
139.171
135.243
133.546
131.682
130.350
129.414
127.995
127.598
127.201
123.775
77.420
77.000
76.572
52.105
21.326
H3C
Ph
CO2Me
180
160
140
120
100
80
60
40
20
ppm

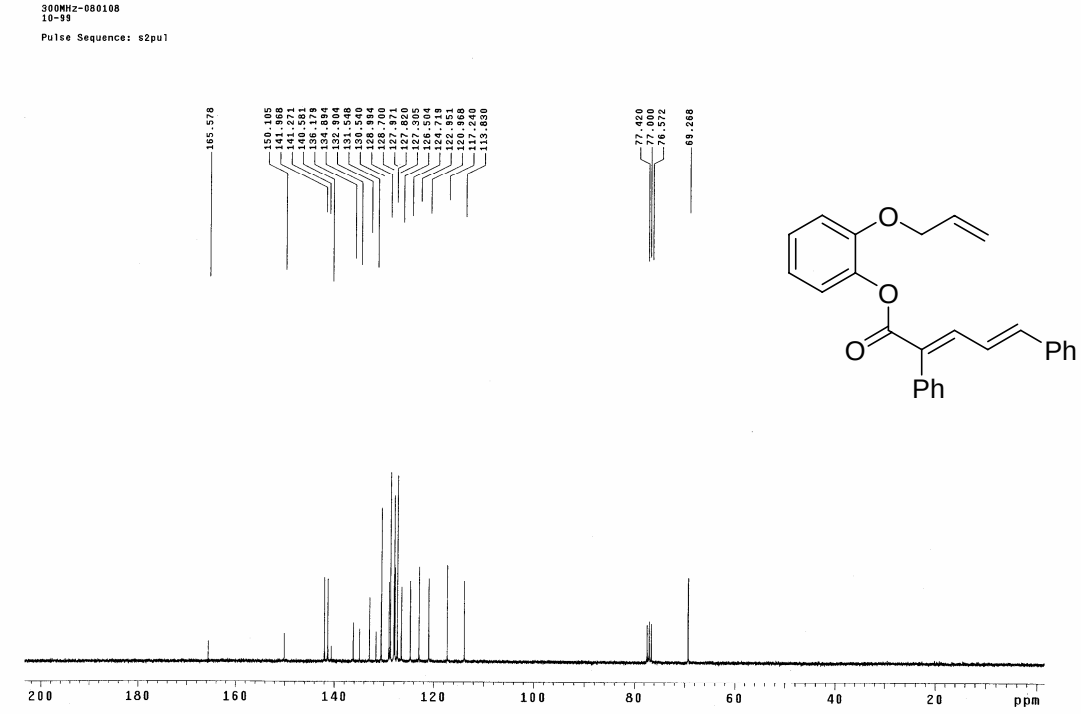

300MHz-070118
pC1-PhCHCHCH2C1+diazo
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
7.650
7.613
7.438
7.433
7.429
7.419
7.414
7.408
7.402
7.397
7.306
7.301
7.295
7.288
7.281
7.274
7.270
7.266
7.255
6.936
6.884
6.802
6.765
6.750
3.789
Cl
Ph
CO2Me
10
9
8
7
6
5
4
3
2
1
ppm
1.09
5.86
3.27
1.21
1.26
3.00

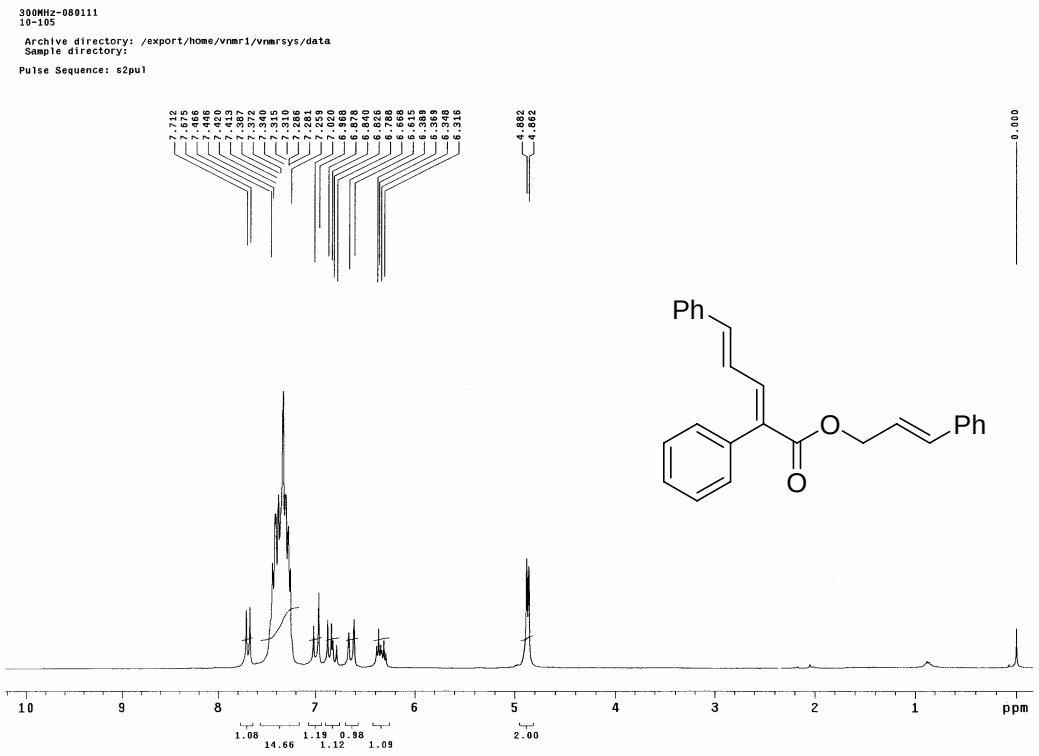

300MHz-070118
pC1-PhCHCHCH2C1+diazo
Pulse Sequence: s2pul
167.759
140.255
139.026
138.882
134.796
134.529
132.832
130.255
128.883
128.328
128.040
127.836
125.211
77.420
77.000
76.572
52.177
Cl
Ph
CO2Me
200
180
160
140
120
100
80
60
40
20
ppm


300MHz-070124
diPhCCHCH2Cl+diazo
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
7.590
7.571
7.426
7.343
7.249
7.170
6.717
6.678
3.693
Ph
Ph
Ph
CO2Me
10
9
8
7
6
5
4
3
2
1
ppm
1.22
14.73
1.20
3.00


300MHz-070124
diPhCCHCH2Cl+diazo
Pulse Sequence: s2pul
168.029
150.843
141.572
138.796
138.090
135.255
133.066
130.548
130.338
128.447
128.272
128.165
128.062
127.717
123.656
77.420
77.000
76.580
52.074
Ph
Ph
Ph
CO2Me
200
180
160
140
120
100
80
60
40
20
ppm


300MHz-080108
10-99
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
7.881
7.845
7.453
7.442
7.417
7.406
7.392
7.385
7.377
7.364
7.357
7.327
7.310
7.285
7.267
7.246
7.241
7.232
7.195
7.188
7.156
7.142
7.137
7.116
7.091
7.063
7.011
6.977
6.968
6.951
6.932
6.917
6.880
6.066
6.048
6.031
6.026
6.013
6.008
5.991
5.973
5.438
5.433
5.380
5.375
5.272
5.268
5.237
5.233
4.555
4.554
4.549
-0.000
O
O
O
Ph
Ph
10
9
8
7
6
5
4
3
2
1
ppm
1.07
15.56
1.00
1.01
0.98
2.00


300MHz-080108
10-99
Pulse Sequence: s2pul
165.578
150.105
141.968
141.271
140.581
136.179
134.084
132.804
131.548
130.540
128.984
128.700
128.371
127.820
127.305
126.504
124.719
122.551
122.361
117.240
113.830
77.420
77.000
76.572
69.268
O
O
O
Ph
Ph
200
180
160
140
120
100
80
60
40
20
ppm


300MHz-080111
10-105
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
7.712
7.675
7.466
7.446
7.420
7.413
7.387
7.372
7.340
7.315
7.310
7.286
7.281
7.254
7.020
6.868
6.840
6.825
6.788
6.668
6.615
6.389
6.368
6.348
6.316
4.882
4.862
0.000
Ph
O
O
Ph
10
9
8
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6
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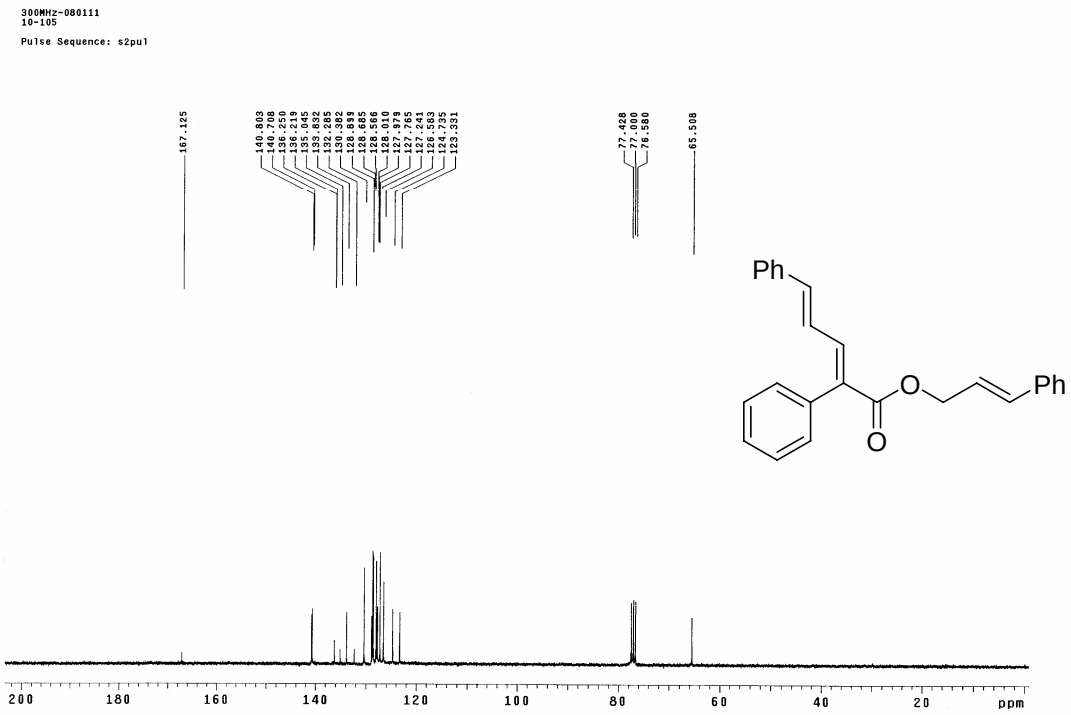
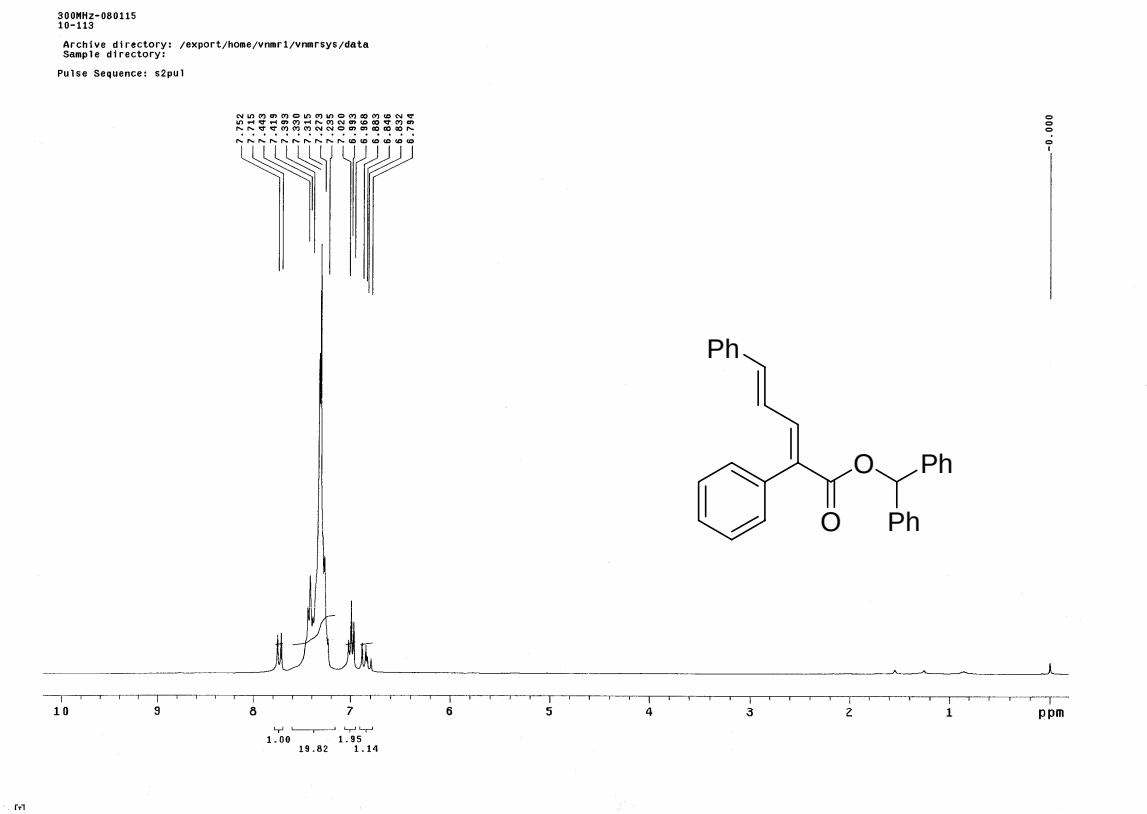
1.08
14.66
1.19
1.12
0.98
1.09
2.00


300MHz-080111
10-105
Pulse Sequence: s2pul
167.125
140.803
140.708
136.250
136.219
135.045
133.802
132.285
130.382
128.899
128.685
128.566
128.010
127.979
127.765
127.241
126.583
124.735
123.331
77.428
77.000
76.580
65.508
Ph
O
O
Ph
200
180
160
140
120
100
80
60
40
20
ppm


300MHz-080115
10-113
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
7.752
7.715
7.443
7.419
7.393
7.330
7.315
7.273
7.235
7.020
6.983
6.968
6.883
6.846
6.832
6.794
-0.000
Ph
O
Ph
O
Ph
10
9
8
7
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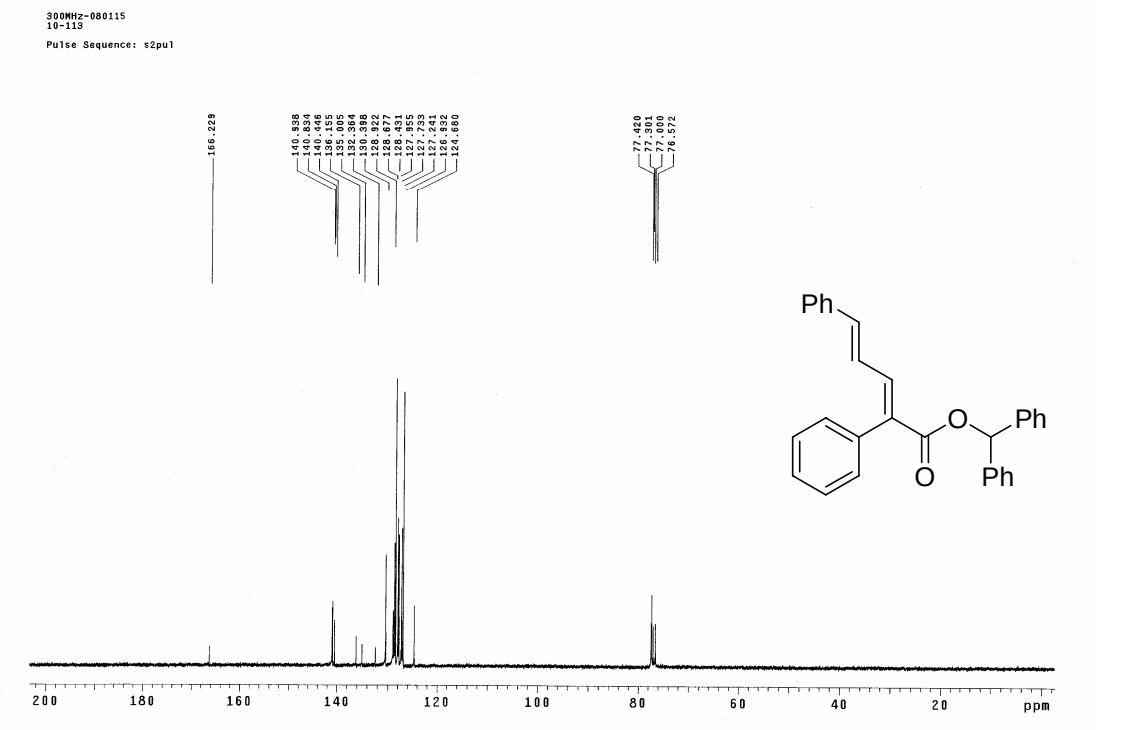
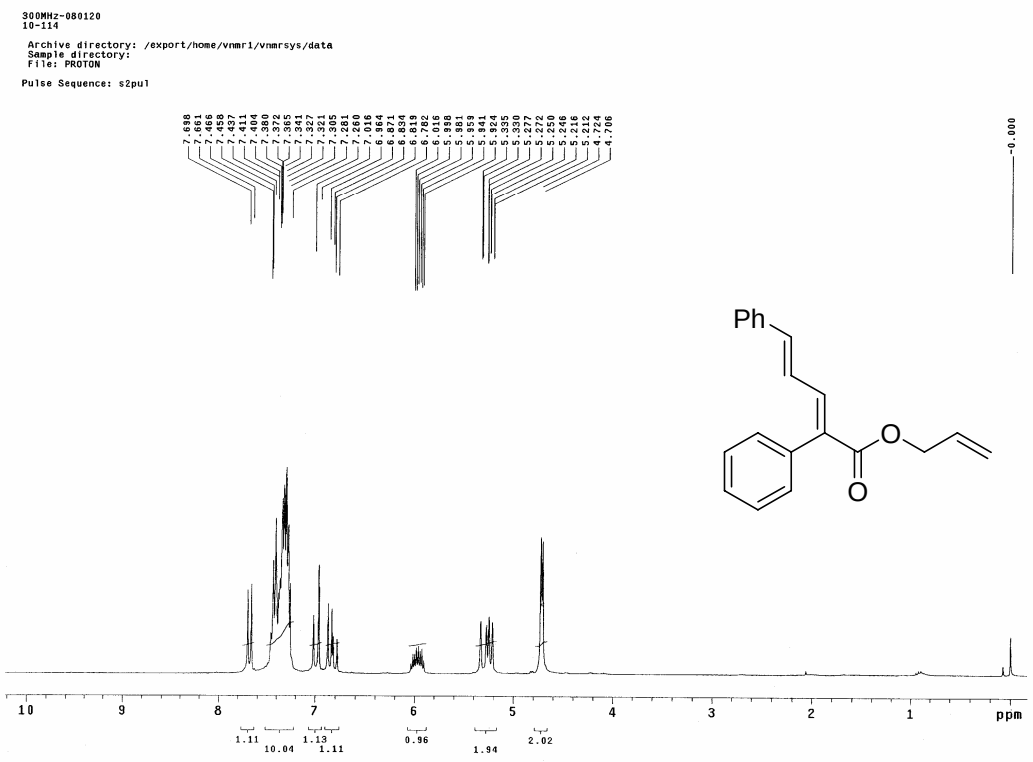
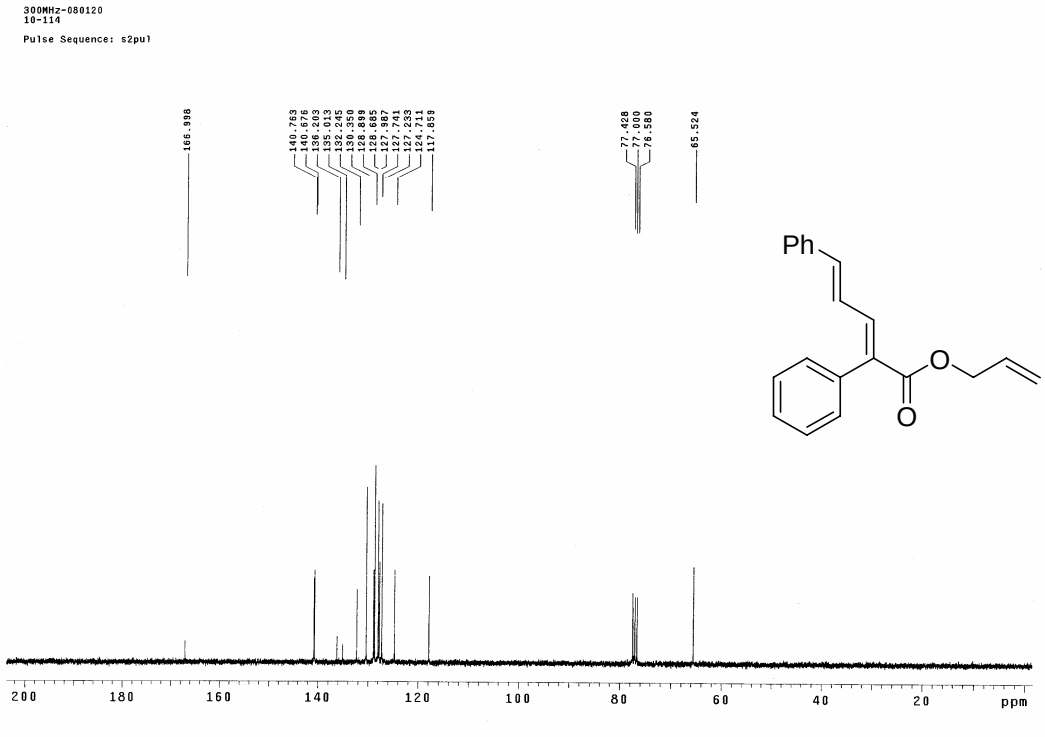
2
1
ppm
1.00
19.82
1.95
1.14


300MHz-080115
10-113
Pulse Sequence: s2pul
166.229
140.838
140.830
140.446
136.155
135.005
132.864
130.386
128.922
128.677
128.431
127.955
127.793
127.241
126.832
124.680
77.420
77.301
77.000
76.572
Ph
O
Ph
O
Ph
200
180
160
140
120
100
80
60
40
20
ppm


300MHz-080120
10-114
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
7.698
7.681
7.466
7.458
7.437
7.411
7.404
7.380
7.372
7.365
7.341
7.327
7.321
7.305
7.281
7.260
7.016
6.804
6.791
6.834
6.819
6.782
6.016
5.988
5.981
5.959
5.941
5.924
5.335
5.330
5.277
5.272
5.250
5.246
5.216
5.212
4.724
4.706
-0.000
Ph
O
O
10
9
8
7
6
5
4
3
2
1
ppm
1.11
10.04
1.13
1.11
0.96
1.94
2.02


300MHz-080120
10-114
Pulse Sequence: s2pul
166.998
140.763
140.576
136.205
135.013
132.245
130.350
128.689
128.465
127.987
127.741
127.233
124.711
117.859
77.428
77.000
76.580
65.524
Ph
O
O
200
180
160
140
120
100
80
60
40
20
ppm