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Solventless green synthesis of 4-O-aryloxy carbonates from aryl/alkyl-oxy propanediols and dimethyl carbonate over nano-crystalline alkali promoted alkaline earth metal oxide

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1. Reaction mechanism & Kinetics

1. Adsorption of 3-aryloxy-1,2-propanediol (A) on the vacant site S_1 is given by:

$$A + S_1 \overset{K_A}{\rightleftarrows} AS_1 \quad (1)$$

Similarly adsorption of dimethyl carbonate (B) on the vacant site $S_2$is presented by:

$$B + S_2 \overset{K_B}{\rightleftarrows} BS_2 \quad (2)$$

2. Surface reaction of AS with BS (dimethyl carbonate), in the vicinity of the site, leading to formation of 4-O-aryloxy-1,3-dioxolan-2-one (DS) and methanol (MS) on the site.

$$AS_1 + BS_2 \overset{K_2}{\rightleftarrows} DS_1 + MS_2 \quad (3)$$

Desorption of 4-O-aryloxy-1,3-dioxolan-2-one (DS_1) and methanol (MS_2)

$$DS_1 \overset{1/K_E}{\rightleftarrows} D + S_1 \quad (4)$$

$$DS_2 \overset{1/K_W}{\rightleftarrows} M + S_2 \quad (5)$$

The total concentration of the sites, $Ct = C_{t_1} + C_{t_2}$ expressed as,

$$C_{t_1} = C_{S_1} + C_{AS_1} + C_{DS_1} \quad (6)$$

$$C_{t_2} = C_{S_2} + C_{BS_2} + C_{MS_2} \quad (7)$$

By substituting for the concentrations of surface species, the following is obtained.

$$C_{S_1} = \frac{C_{t_1}}{1 + K_A C_A K_D C_D} \quad (8)$$

$$C_{S_2} = \frac{C_{t_2}}{1 + K_B C_B + K_M C_M} \quad (9)$$

If surface reaction controls the rate of reaction, then the rate of reaction of A is given by

$$-r_A = \frac{-dC_A}{dt} = k_2 C_{AS_1} C_{BS_2} - k_2^{'} C_{DS_1} C_{MS_2} \quad (10)$$

$$\frac{-dC_A}{dt} = \frac{k_2\{K_A K_B C_A C_B - (K_D K_M C_D C_M)/k_2\} C_{t_1} C_{t_2}}{(1+K_A C_A + K_D C_D)(1+K_B C_B + K_M C_M)} \quad (11)$$

When the reaction is far away from the equilibrium

$$\frac{-dC_A}{dt} = \frac{k_2\{K_A K_B C_A C_B\} C_{t_1} C_{t_2}}{(1+K_A C_A + K_D C_D)(1+K_B C_B + K_M C_M)} \quad (12)$$

$$\frac{-dC_A}{dt} = \frac{k_2 w K_A K_B C_A C_B}{(1+K_A C_A + K_D C_D)(1+K_B C_B + K_M C_M)} \quad (13)$$

Where, $k_{R2} w = k_2 C_{t_1} C_{t_2}$ (14)

When the reactants are strongly adsorbed, When

$K_A C_A \gg (1+K_D C_D)$ *and* $K_B C_B >> (1+K_M C_M)$

And *w* is catalyst loading, then the above equation reduces to

$$-\frac{dC_A}{dt} = k_{R2} w \quad (15)$$

Integration of the above equation leads to the following:

$$C_{A_0} - C_A = k_{R_2} wt \quad (16)$$

Which in terms of fractional conversion becomes:

$$X_A = \frac{k_{R_2} wt}{C_{A_0}} = k_1 t \quad (17)$$

Where,

$$k_1 = \frac{k_{R_2} w}{C_{A_0}}$$

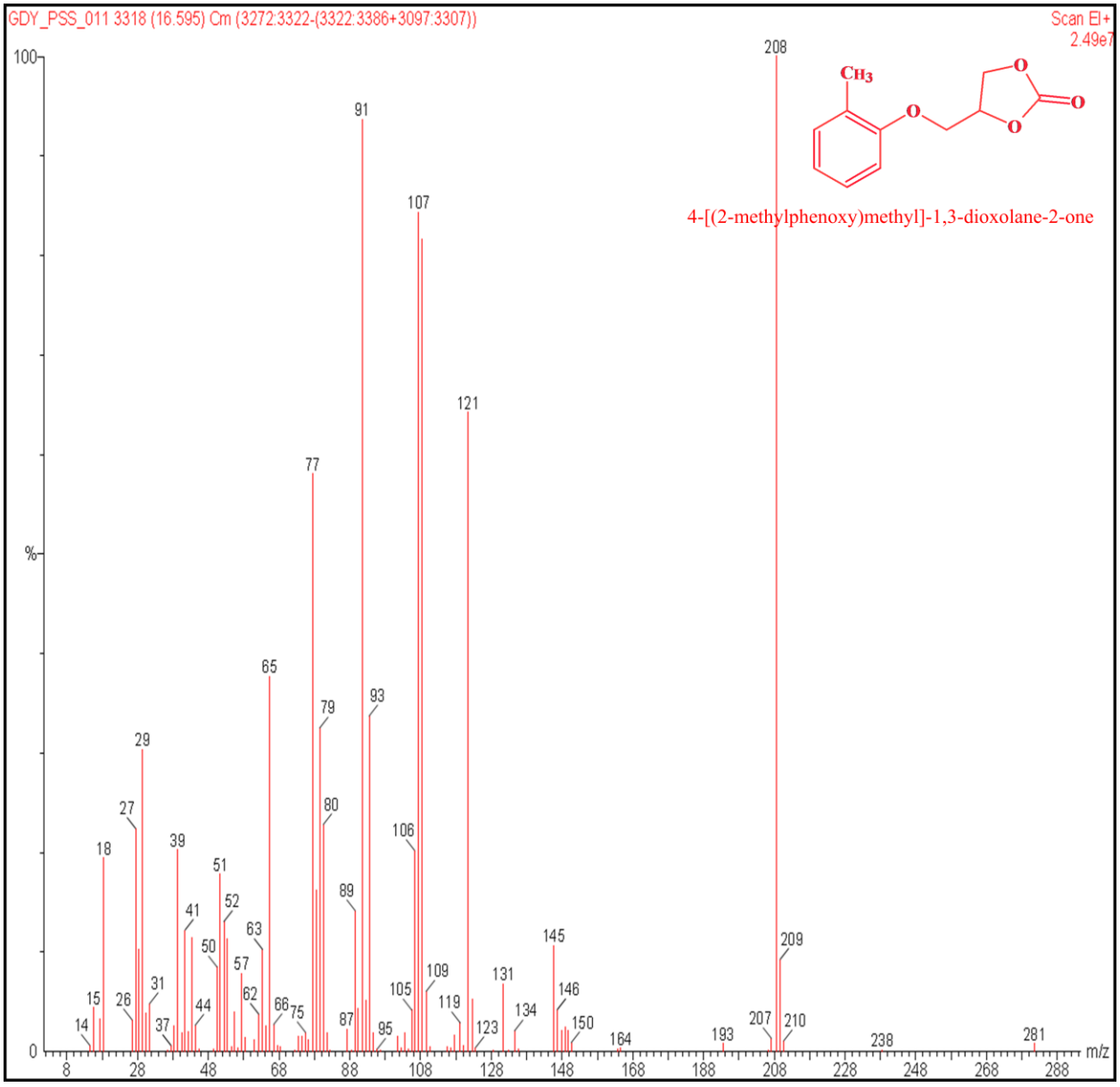
2. Green chemistry aspects

Considering 90% recovery of the excess reactant, calculated E-factor is 0.3 which is much less, which is the proof of less waste product formation. Also methanol is recycled and thus there is no waste and hence for practical purposes the E factor is zero. Table shown below shows different green chemistry factors, which proves greenness of the reaction. It was found that 0.1% lithium ion promoted MgO is highly active, cleaner and green catalyst. Considering corrosive nature, toxicity and handling problems of reagent reported in prior art such as phosgene, triphosgene, isocynate as carboxylting agent and high temperature and pressure conditions required, dimethyl carbonate offers cleaner, greener method of carboxylation in the synthesis of 4-O-aryl/alkyl-oxy-1,3-dioxolan-2-one.

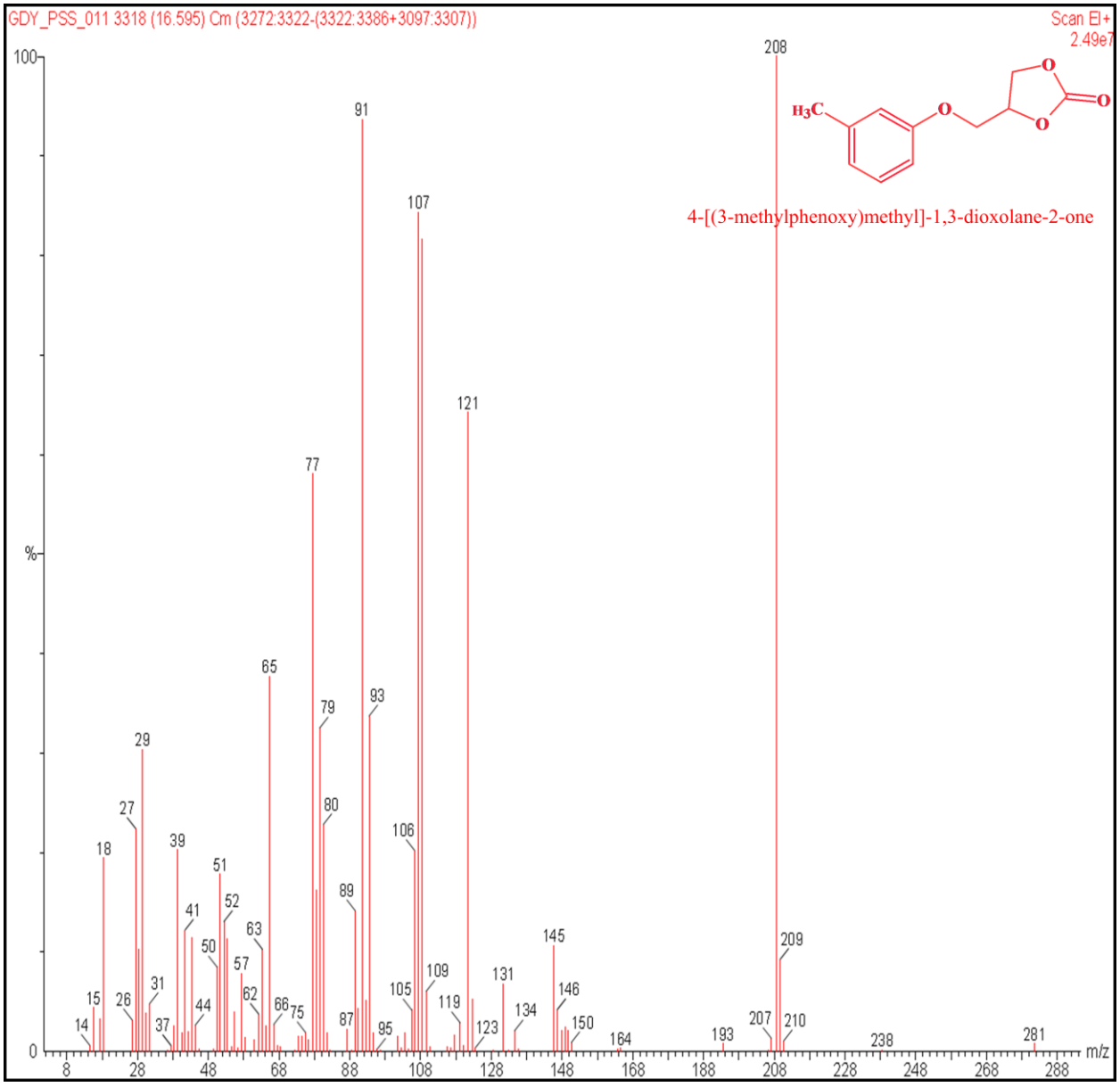
Carboxylating agent	E-Factor	Mass intensity	Atom economy	Yield
Phosgene	7.1	18.04	74.04	60
Dialkyl carbonate [a]	0.3	7.52	86.66	98.52

[a] Methanol as co-product recycled on plant scale. Hence, there is no waste and E can be viewed as zero.

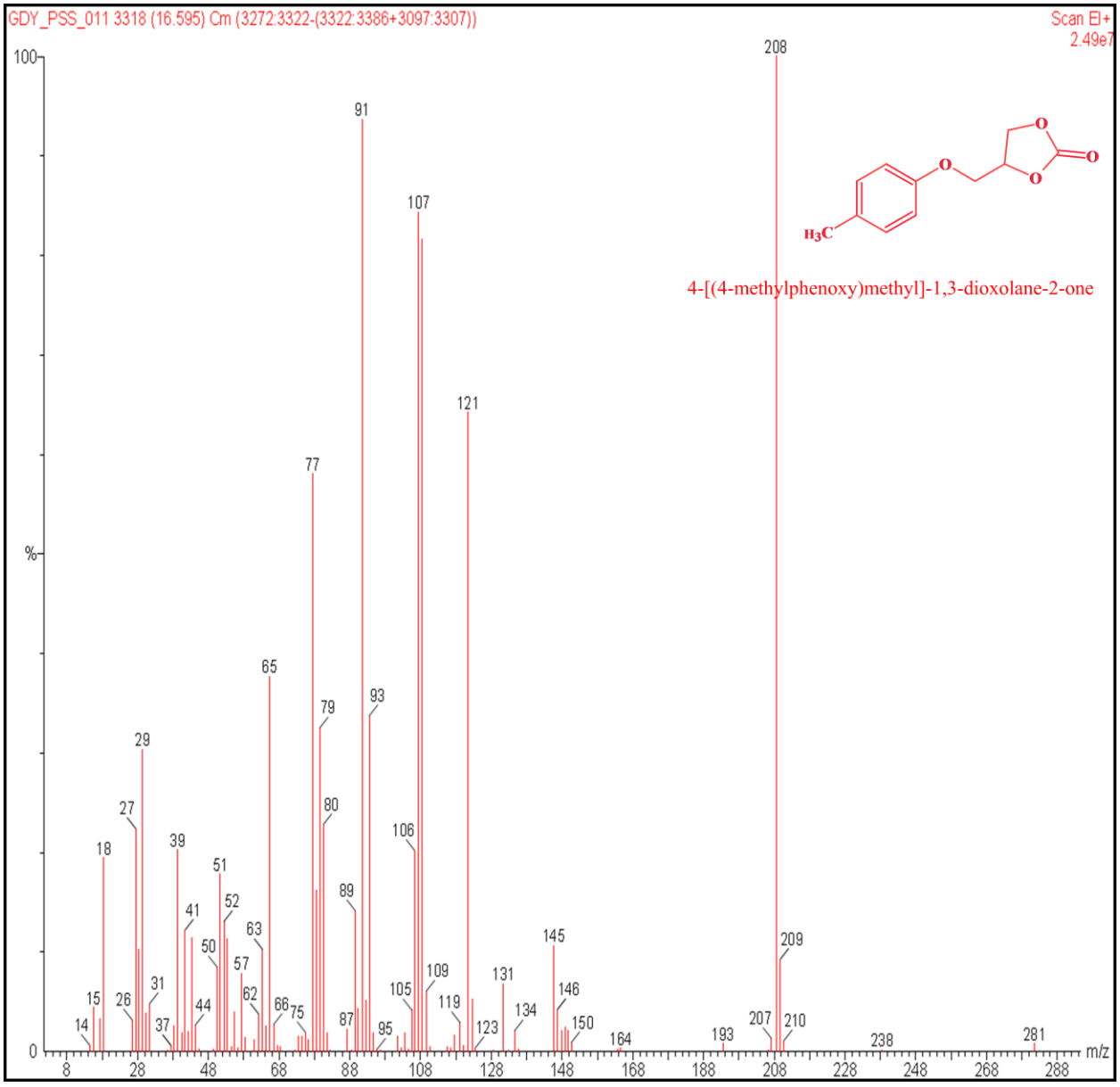
3. GC-MS of 4-[(2-methylphenoxy)methyl]-1,3-dioxolane-2-one



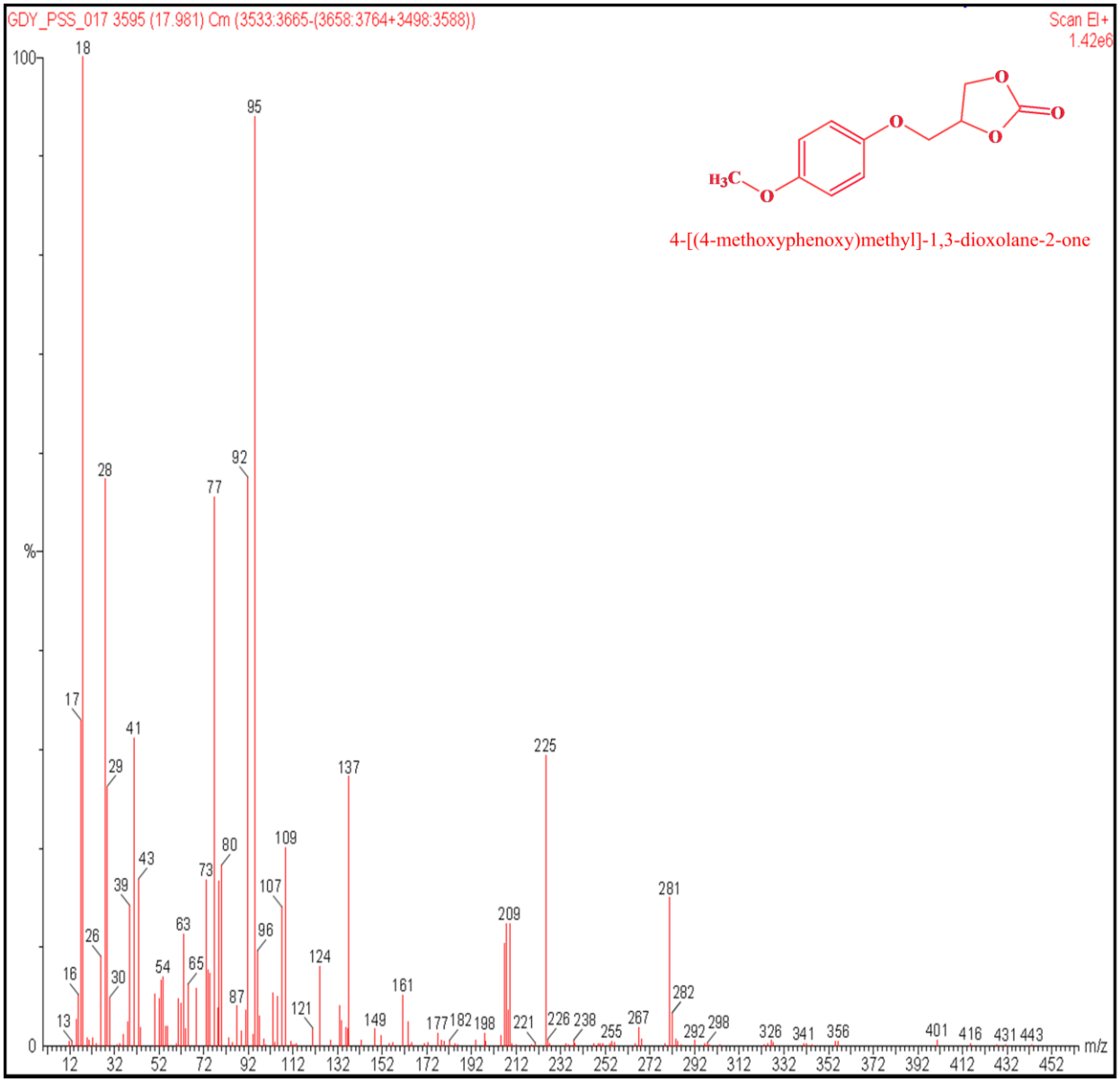
4. GC-MS of 4-[(3-methylphenoxy)methyl]-1,3-dioxolane-2-one



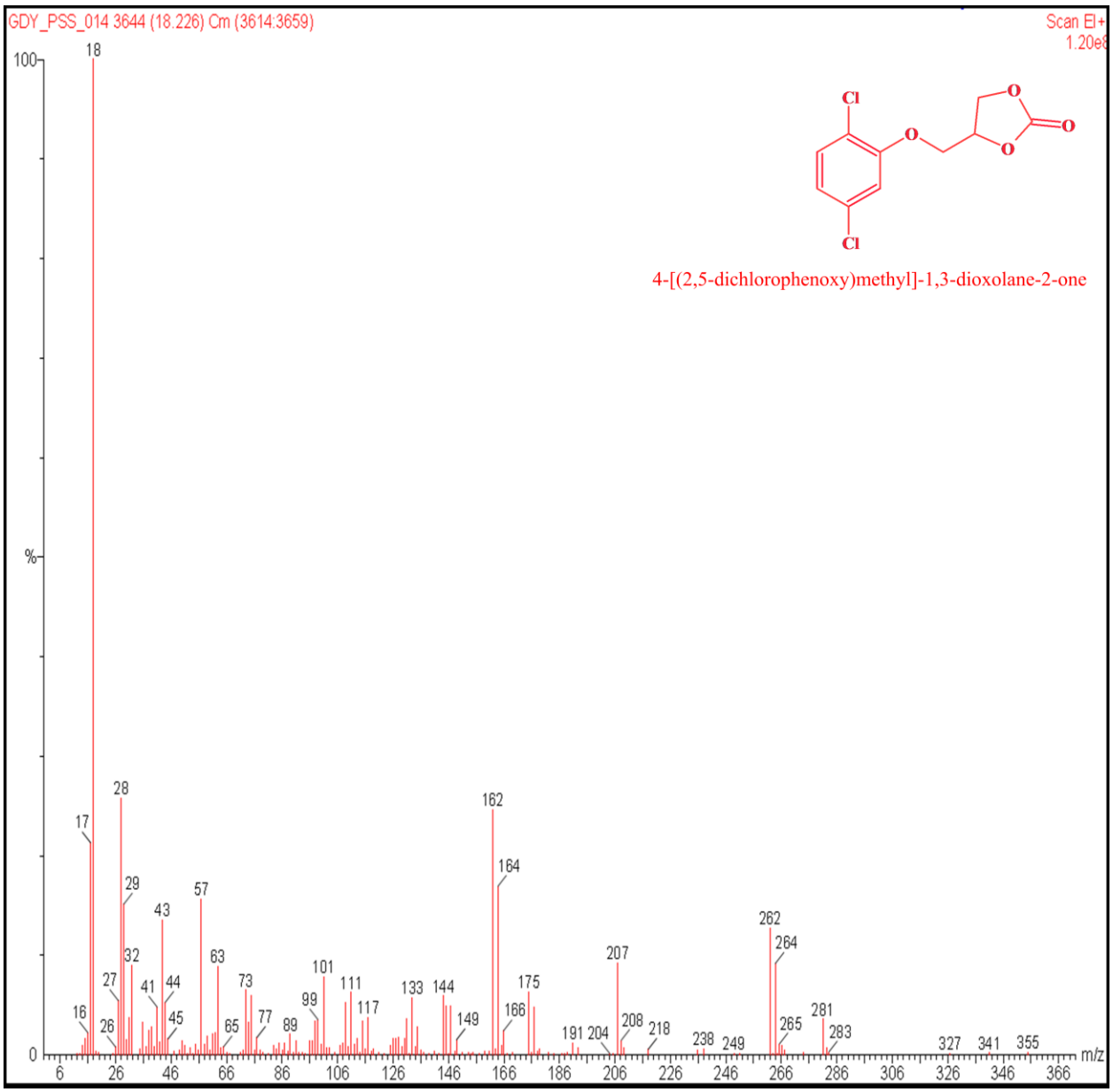
5. GC-MS of 4-[(4-methylphenoxy)methyl]-1,3-dioxolane-2-one



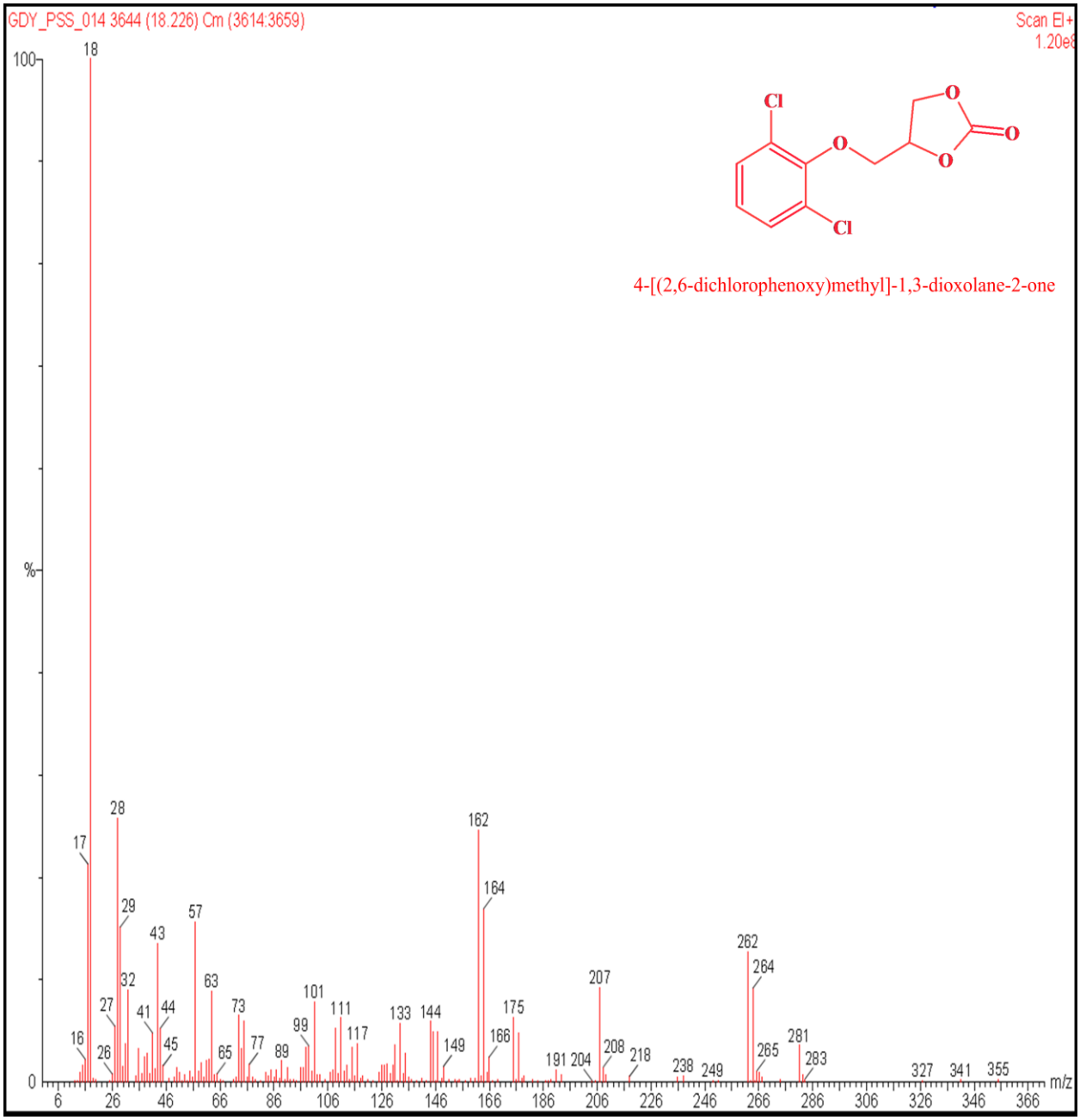
6. GC-MS of 4-[(4-methoxyphenoxy)methyl]-1,3-dioxolane-2-one



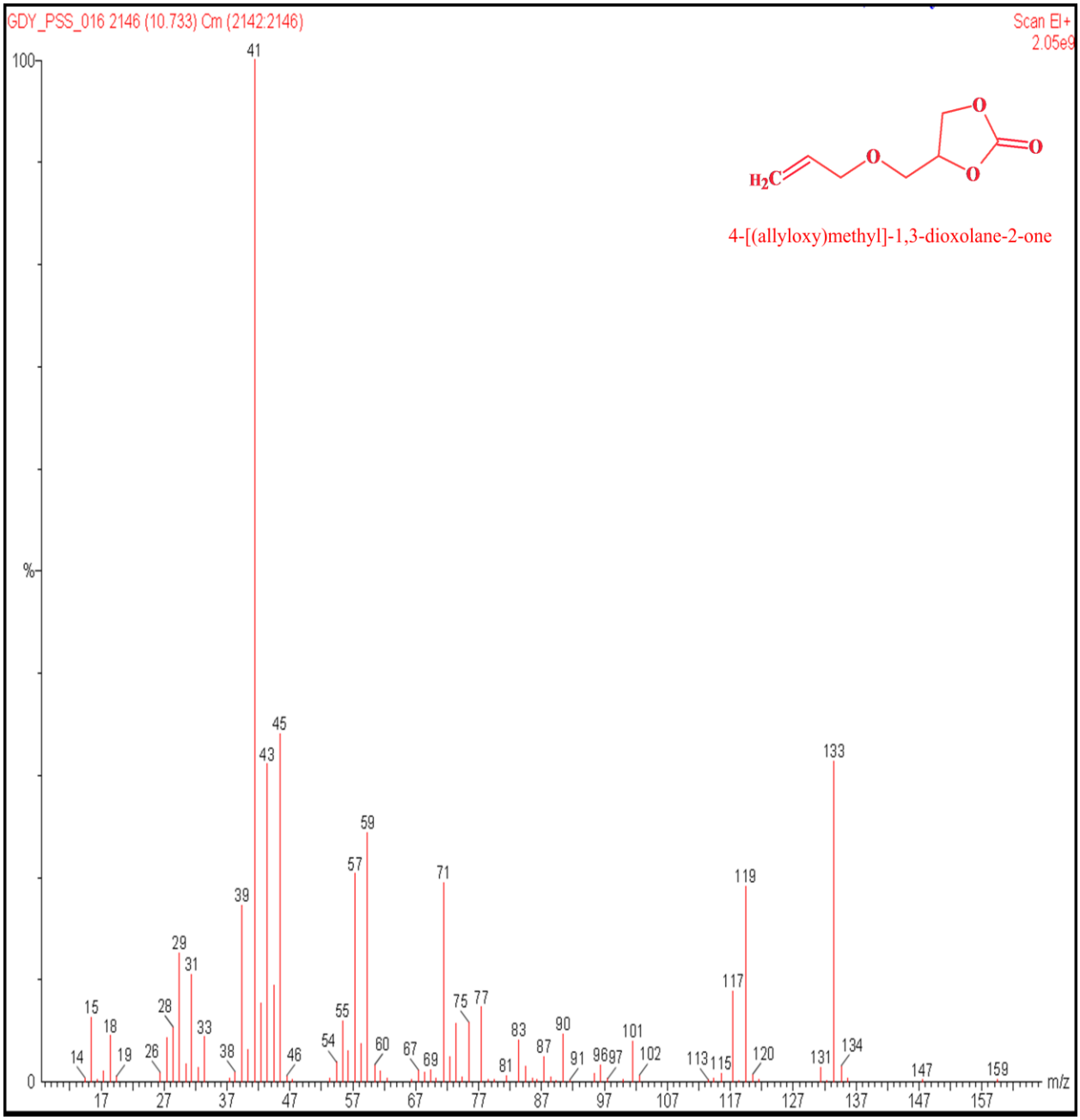
7. GC-MS of 4-[(2,5-dichlorophenoxy)methyl]-1,3-dioxolane-2-one



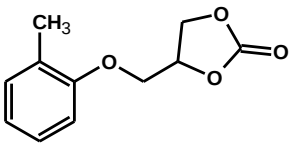
8. GC-MS of 4-[(2,6-dichlorophenoxy)methyl]-1,3-dioxolane-2-one



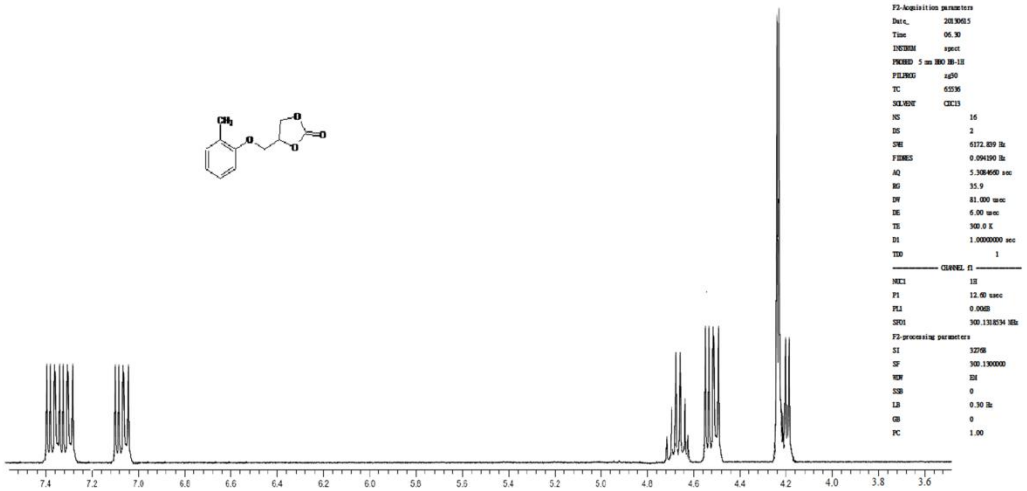
9. GC-MS of 4-[(allyloxy)methyl]-1,3-dioxolane-2-one



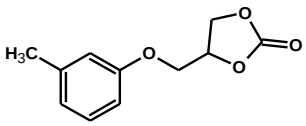
10. H^1 NMR of 4-[(2-methylphenoxy)methyl]-1,3-dioxolane-2-one



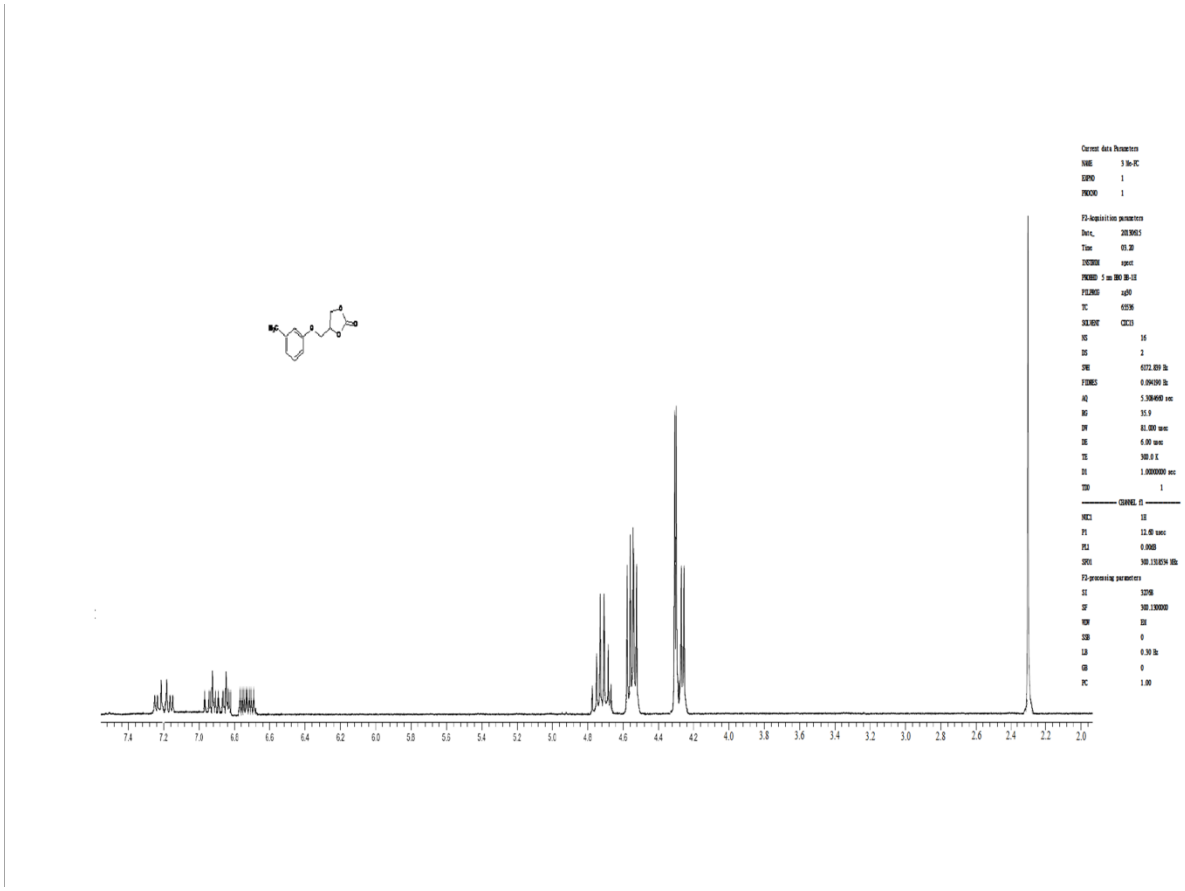
2.140 (1, 3H), 6.833 (3, 1H, ddd, J=8.018, J=7.467, J=1.319), 7.235 (4, 1H, ddd, J=8.289, J=7.467, J=1.248), 7.082 (5, 1H, ddd, J=8.018, J=4.727, J=1.248), 6.854 (6, 1H, ddd, J=8.289, J=4.727, J=1.319), 4.505 (7, 1H, dd, J=15.297, J=8.060), 4.504 (7, 1H, dd, J=15.297, J=4.250), 4.243 (8, 2H, d, J=3.943), 4.679 (15, 1H, ddt, J=8.060, J=4.250, J=3.943)



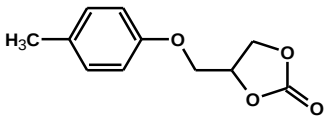
11. H^1 NMR of 4-[(3-methylphenoxy)methyl]-1,3-dioxolane-2-one



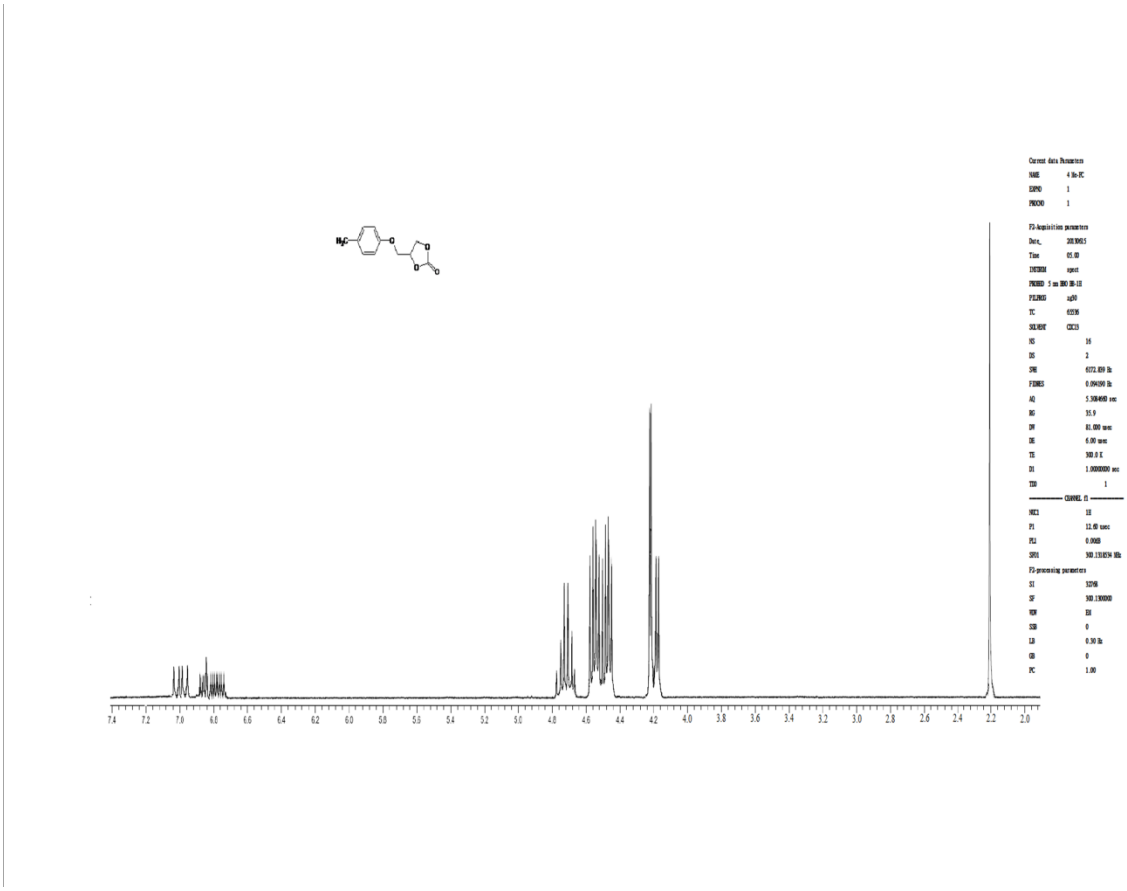
2.314 (1, 3H), 7.201 (3, 1H, ddd, J=8.240, J=8.046, J=4.434), 6.903 (4, 1H, ddd, J=8.046, J=2.803, J=2.007), 6.899 (5, 1H, ddd, J=8.240, J=2.803, J=2.801), 6.747 (6, 1H, ddd, J=4.434, J=2.801, J=2.007), 4.504 (7, 1H, dd, J=8.060, J=0.000), 4.504 (7, 1H, dd, J=4.250, J=0.000), 4.247 (8, 2H, d, J=3.938), 4.677 (15, 1H, ddt, J=8.060, J=4.250, J=3.938)



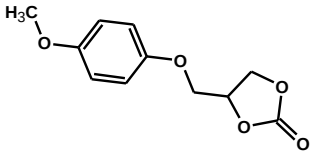
12. H^1 NMR of 4-[(4-methylphenoxy)methyl]-1,3-dioxolane-2-one



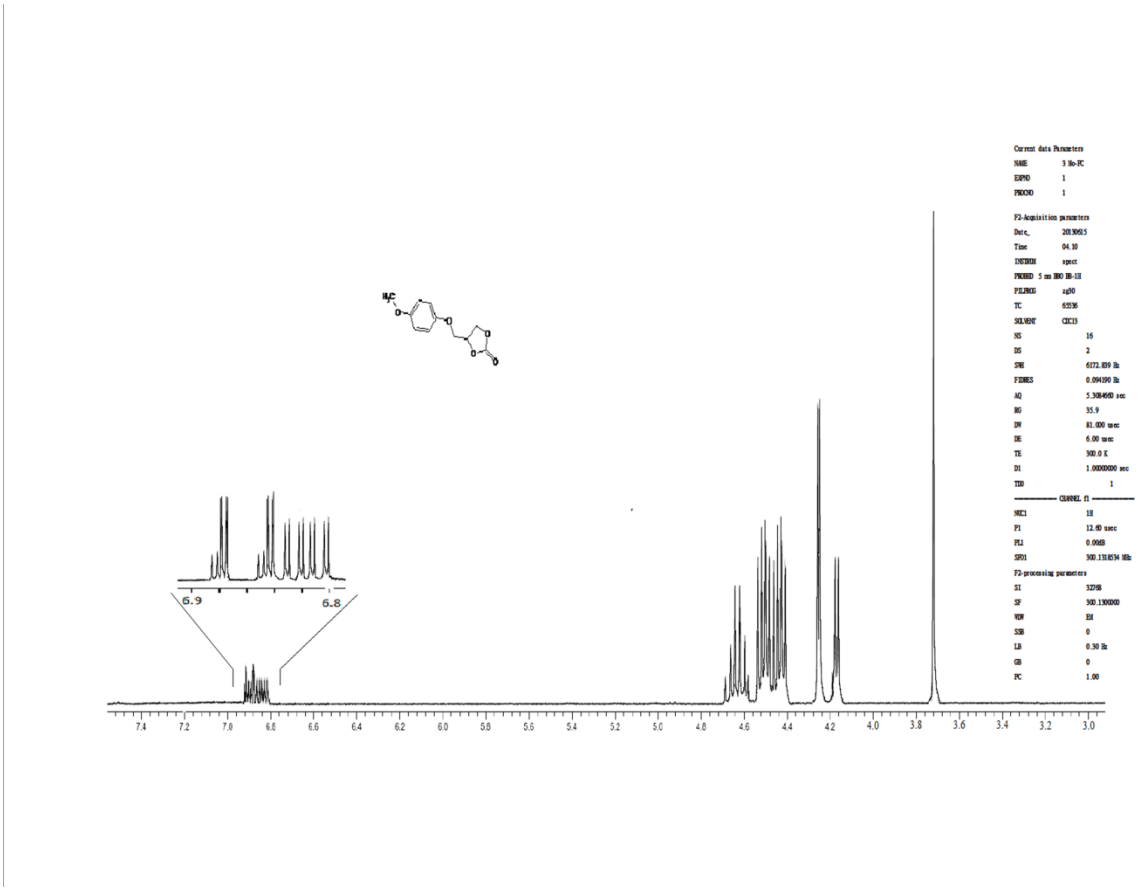
2.203 (1, 3H), 6.994 (3, 1H, ddd, J=8.800, J=4.899, J=0.000), 6.994 (4, 1H, ddd, J=8.800, J=5.398, J=0.000), 6.793 (5, 1H, ddd, J=8.800, J=5.398, J=2.242), 6.821 (6, 1H, ddd, J=8.800, J=4.899, J=2.242), 4.504 (7, 1H, dd, J=15.296, J=8.060), 4.503 (7, 1H, dd, J=15.296, J=4.250), 4.244 (8, 2H, d, J=3.946), 4.677 (15, 1H, ddt, J=8.060, J=4.250, J=3.946)



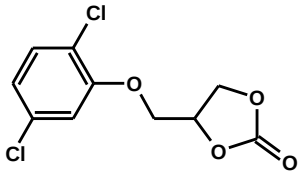
13. H^1 NMR of 4-[(4-methoxyphenoxy)methyl]-1,3-dioxolane-2-one



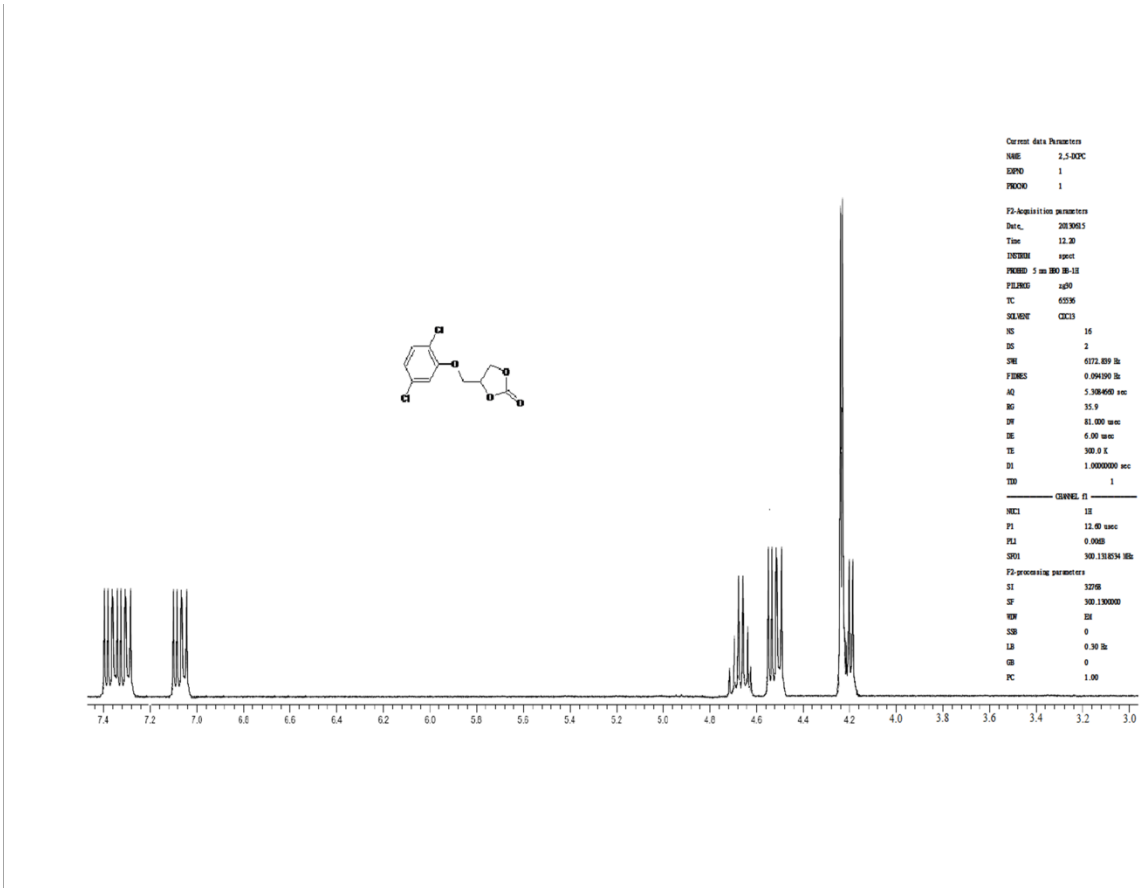
3.751 (1, 3H), 6.853 (3, 1H, ddd, J=8.731, J=1.050, J=0.000), 6.853 (4, 1H, ddd, J=8.714, J=1.844, J=0.000), 6.856 (5, 1H, ddd, J=8.731, J=2.714, J=1.844), 6.816 (6, 1H, ddd, J=8.714, J=2.714, J=1.050), 4.505 (7, 1H, dd, J=15.303, J=8.060), 4.504 (7, 1H, dd, J=15.303, J=4.250), 4.246 (8, 2H, d, J=3.941), 4.678 (16, 1H, ddt, J=8.060, J=4.250, J=3.941)



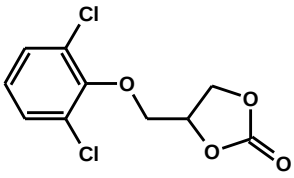
14. H^1 NMR of 4-[(2,5-dichlorophenoxy)methyl]-1,3-dioxolane-2-one



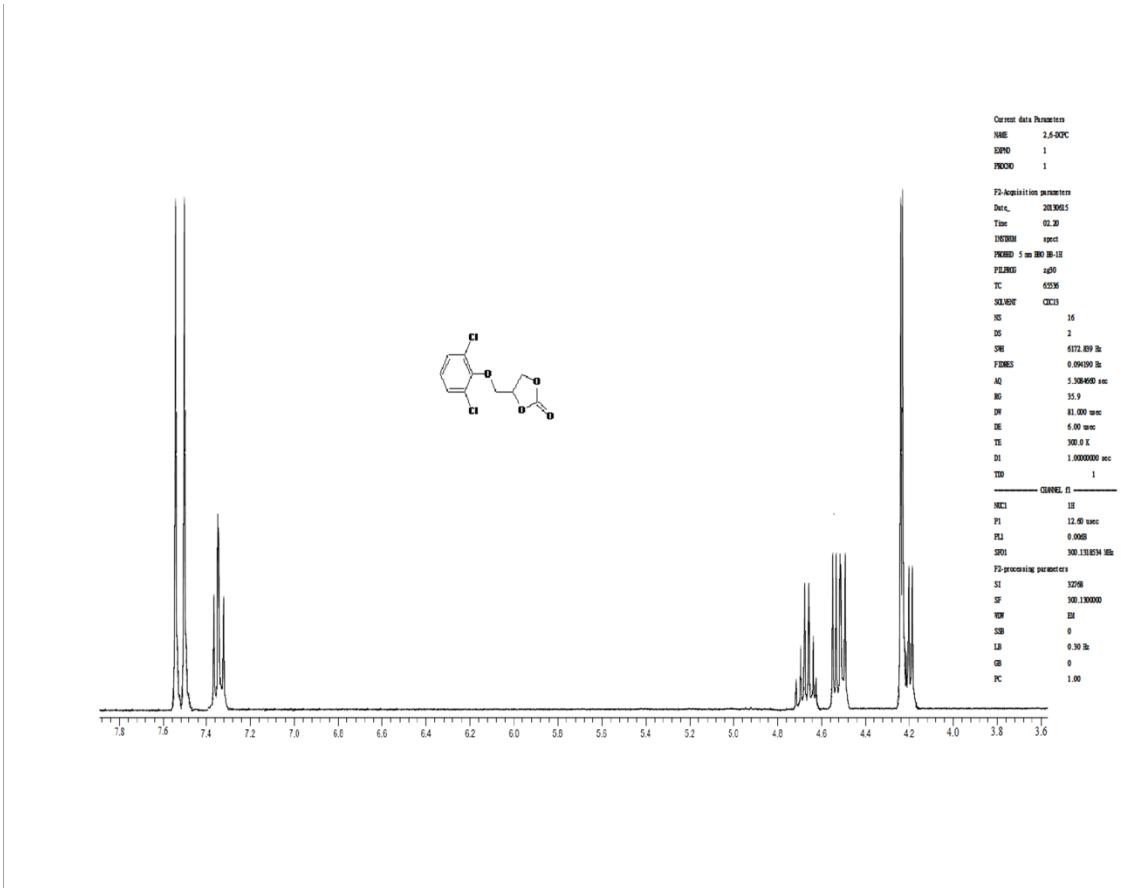
7.400 (4, 1H, dd, J=7.904, J=1.780), 7.375 (5, 1H, dd, J=7.904, J=5.416), 7.128 (6, 1H, dd, J=5.416, J=1.780), 4.509 (7, 1H, dd, J=8.060, J=0.000), 4.510 (7, 1H, dd, J=4.250, J=0.000), 4.236 (8, 2H, d, J=3.920), 4.648 (16, 1H, ddt, J=8.060, J=4.250, J=3.920)



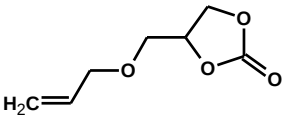
15. H^1 NMR of 4-[(2,6-dichlorophenoxy)methyl]-1,3-dioxolane-2-one



7.366 (4, 1H, t, J=7.649), 7.561 (5, 1H, dd, J=7.649, J=0.000), 7.561 (6, 1H, dd, J=7.649, J=0.000), 4.511 (7, 1H, dd, J=8.060, J=0.000), 4.511 (7, 1H, dd, J=4.250, J=0.000), 4.209 (8, 2H, d, J=3.928), 4.652 (16, 1H, ddt, J=8.060, J=4.250, J=3.928)



16.H^1 NMR of 4-[(allyloxy)methyl]-1,3-dioxolane-2-one



5.039 (1, 1H, dd, J=10.658, J=1.322), 4.980 (1, 1H, dd, J=17.231, J=1.322), 5.777 (3, 1H, ddt, J=17.231, J=10.658, J=6.044), 3.896 (4, 2H, d, J=6.044), 3.743 (5, 2H, d, J=4.018), 4.451 (6, 1H, dd, J=15.295, J=4.250), 4.468 (6, 1H, dd, J=15.295, J=8.060), 4.608 (11, 1H, ddt, J=8.060, J=4.250, J=4.018)