Hydrosilane and Bismuth-accelerated Palladium Catalyzed Aerobic Oxidative Esterification of Benzylic Alcohols with Air

Xing-Feng Bai[a], Fei Ye[a], Long-Sheng Zheng[a], Guo-Qiao Lai[a], Chun-Gu Xia[b], and Li-Wen Xu*[a,b]

[a] *Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education Hangzhou Normal University, Hangzhou 310012, China*
[b] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P. R. China*
Fax: (+86)-571-28865135
E-mail: licpxulw@yahoo.com and liwenxu@hznu.edu.cn

Supporting Information

Table of Contents

1. General information

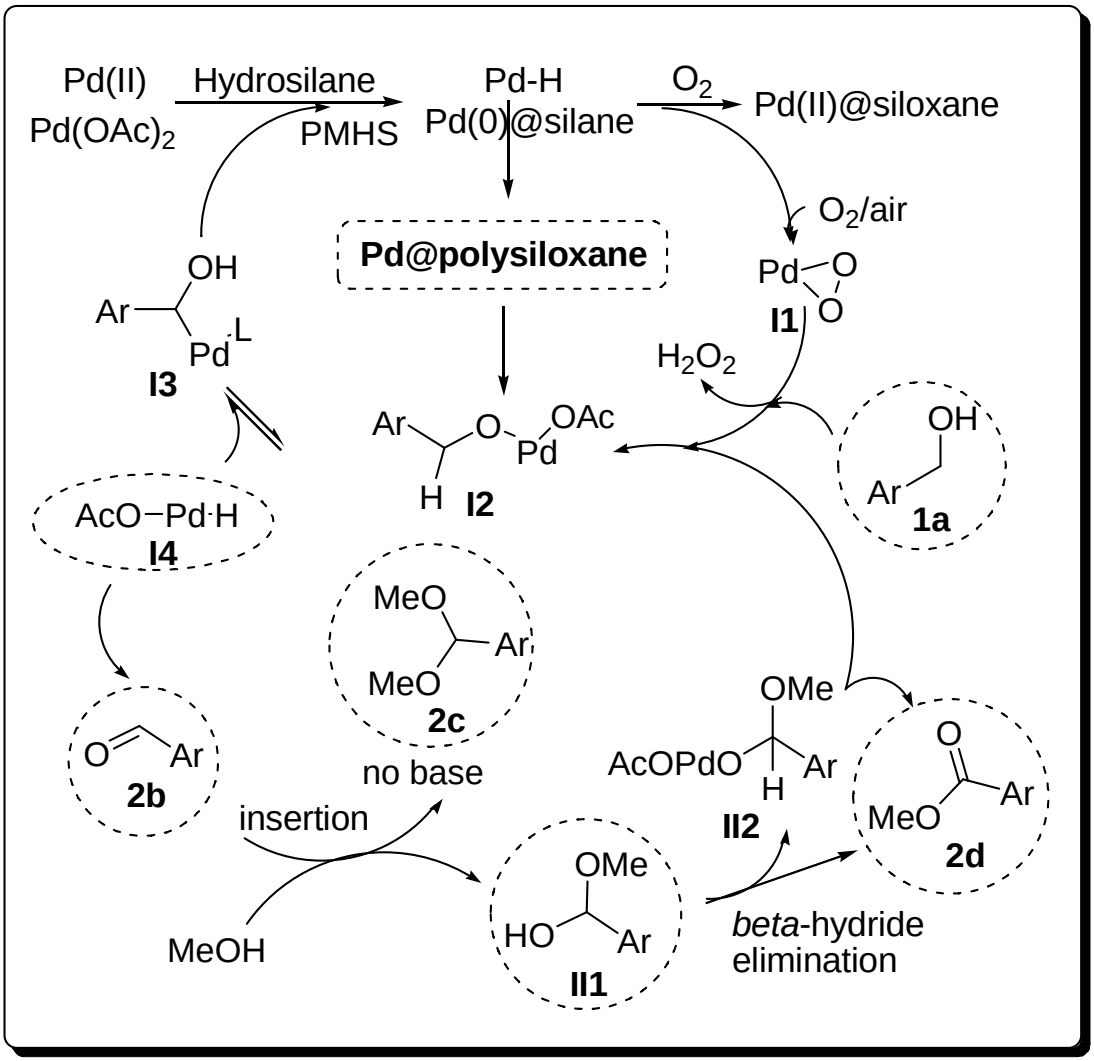
Solvents used in the reactions were distilled from CaH_2. The polymethylhydrosiloxane (PMHS) (Mw ≈ 2500, Viscosity(25°C), mm2/MS:10 - 50; Hydroxyl content: 1.55 - 1.60 w/w%; density (25°C), g/cm^3: 0.995 - 1.015) was purchasing from Chengxing County Chemical Co., Ltd., located in Kaihua, Zhejiang province, China. Other reagents are commercially available and used directly without further purification. Flash column chromatography was performed over silica (200-300 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 and 100 MHz, respectively on Advance (Brucker) 400 MHz Nuclear Magnetic Resonance Spectrometry, and were referenced to the internal solvent signals. Thin layer chromatography was performed using silica gel; GF_{254} TLC plates and visualized with ultraviolet light. The products of the oxidation reaction was known and confirmed by GC-Mass, and usual spectral methods (^{1}H-NMR).

2. A typical procedure for the oxidation of benzylic alcohol to methyl benzoate.

Under air atmosphere, benzylic alcohol (0.5 mmol) was added to a dry tube containing $Pd(OAc)_2$ (0.025mmol), $BiCl_3$ (0.05 mmol), K_2CO_3 (1 mmol), PMHS (0.1mmol, calculated on the Si-H hydrogen content) and methanol (2 mL). And the mixture was stirring at room temperature for 2 hour. After the reaction was completed, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were subsequently concentrated and the crude product was purified by flash chromatography. The products of oxidative esterification are known compounds and confirmed by NMR and GC-MS.

It should be noted that no ester was detected with only bismuth catalyst in the absence of palladium catalyst.

Scheme S1. Proposed mechanism of palladium-catalyzed transformation of benzyl alcohol to various products (Table 1) in the presence of hydrosilane or PMHS

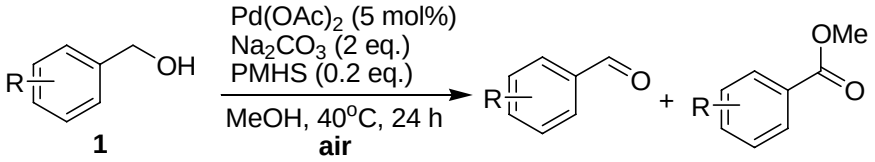


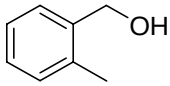
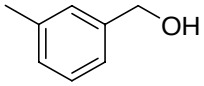
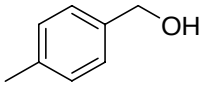
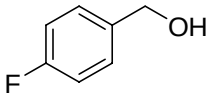
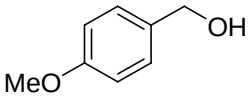
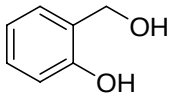
Note:

For the product **2b** (benzaldehyde): The palladium(II) was activated by hydrosilane to form activated Pd(0) catalyst, and then the oxidative addition of oxygen to Pd(0) generated the intermediate (**I1**). The following alcoholysis step selectively occurred with alcohol to generate the alkoxy palladium intermediate **I2** with the aid of a base. In the last step, direct β-hydride elimination to afford the aldehyde and the palladium hydride intermediate **I4** which undergoes reductive elimination to regenerate Pd(0) species.

For the product **2c** (1-(dimethoxymethyl)benzene): In the absence of base, the acetal **2c** was formed from the reaction of benzaldehyde and methanol directly.

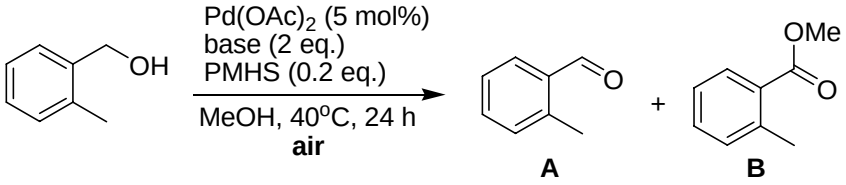
Table S1. Palladium-catalyzed oxidation in the presence of PMHS



Entry	Substrate	Conversion %	Yield %[a]	
			Aldehyde	Ester
1		47	43	<5
2		40	15	25
3		>99	69	31
4		23	0	23
5		51	50	<5
6		>99	95	<5

[a] Reaction conditions: alcohol (0.5 mmol), 5 mol% of $Pd(OAc)_2$, 20 mol% of PMHS, and 2 eq. Na_2CO_3, 3 mL of MeOH, 40°C, for 12 hrs. The yield was determined by GC.

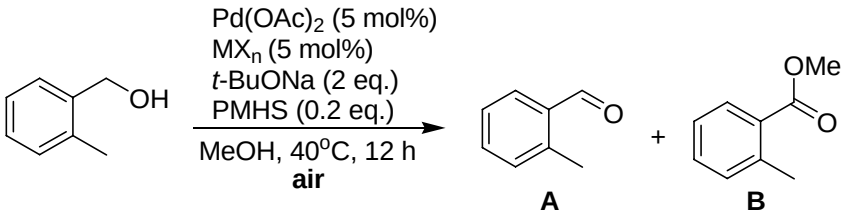
Table S2. The effects of bases on palladium-catalyzed oxidation



Entry	Base	Temperature/°C	Conversion %	Yield%/A	Yield/B
1	Na_2CO_3	40	47	43	<5
2	K_2CO_3	40	76	65	11
3	Cs_2CO_3	40	59	53	6
4	*t*-BuONa	40	92	76	16
5	*t*-BuOK	40	81	70	11
6	NEt_3	40	21	19	<5
7	Pyridine	40	Trace	-	-
8	*t*-BuONa	60	94	70	24

[a] Reaction conditions: alcohol (0.5 mmol), 5 mol% of $Pd(OAc)_2$, 20 mol% of PMHS, and 2 eq. base, 3 mL of MeOH, 40°C, for 24 hrs. The yield was determined by GC.

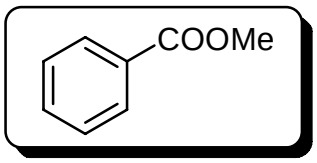
Table S3. The effects of metal salts on the palladium-catalyzed oxidative esterification



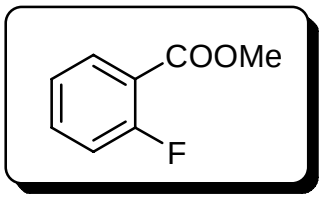
Entry	Base	MX_n	Conversion %	Yield %[a]		
				Aldehyde/A	Ester/B	Other side-products[b]
1	-	$NaBF_4$	Trace	-	-	-
2	-	KPF_6	Trace	-	-	-
3	-	$Na_2SiO_3{\cdot}9H_2O$	44	44	0	-
4	*t*-BuONa	CuCl	17	8	0	9
5	*t*-BuONa	CuI	4	<5	0	-
6	*t*-BuONa	Cu_2O	35	35	0	-
7	*t*-BuONa	AgF	98	52	31	15
8	*t*-BuONa	AgOAc	>99	13	78	9
9	*t*-BuONa	$AgNO_3$	91	41	48	<5
10[c]	K_2CO_3	$BiCl_3$	>99	<1	>99	-
11[c]	K_2CO_3	$BiBr_3$	>99	<1	>99	-
12[c]	K_2CO_3	BiI_3	trace	-	-	-
13[c]	K_2CO_3	$Bi(OTf)_3$	>99	<1	>99	-
14[d]	K_2CO_3	$BiCl_3$	>99	<1	>99	-

[a] Reaction conditions: alcohol (0.5 mmol), 5 mol% of $Pd(OAc)_2$, 5 mol% of metal salt additive, 20 mol% of PMHS, and 2 eq. base, 3 mL of MeOH, 40°C, for 12 hrs. The yield was determined by GC. [b] The side products included decarbonyl product and acid. [c] The reaction was carried out for 8 hrs. [d] The reaction was carried out at room temperature for 2 hours in the presence of 10 mol% of $BiCl_3$.

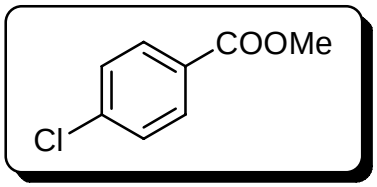
3.The analytical and spectral characterization data of the methyl benzoates.



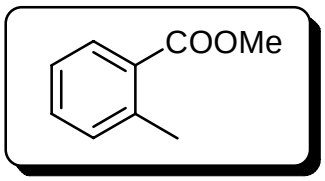
Methyl benzoate (2d) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, J = 8.0 Hz, 2 H), 7.57 (t, J = 7.2 Hz, 1 H), 7.45 (t, J = 8.0 Hz, 2 H), 3.93 (s, 3 H).



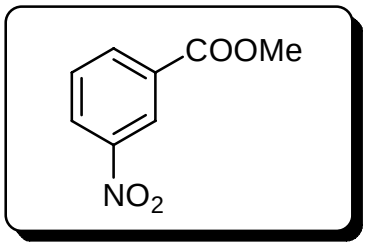
Methyl 2-fluorobenzoate (3a) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (dt, J = 7.6, 1.6 Hz, 1 H), 7.55 – 7.50 (m, 1 H), 7.21 (dt, J = 8.0, 1.2 Hz, 1 H), 7.17 – 7.12 (m, 1 H), 3.94 (s, 1 H).



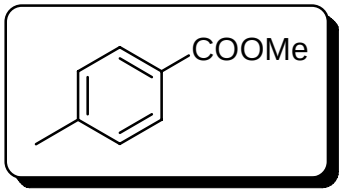
Methyl 4-chlorobenzoate (3b) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, J = 8.4 Hz, 2 H), 7.43 (d, J = 8.4 Hz, 2 H), 3.93 (s, 3 H).



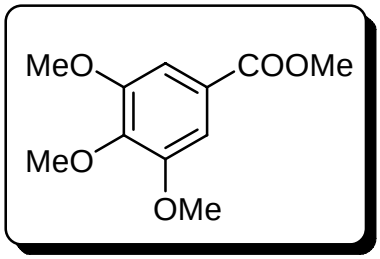
Methyl 2-methylbenzoate (3c) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, J = 7.6 Hz, 1 H), 7.41 (t, J = 7.6 Hz, 1 H), 7.25 (t, J = 6.8 Hz, 2 H), 3.91 (s, 3 H), 2.61 (s, 3 H).



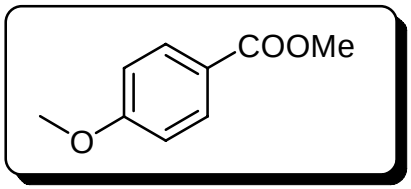
Methyl 3-nitrobenzoate (3d) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.89 (t, J = 2.0 Hz, 1 H), 8.45 - 8.42 (m, 1 H), 8.40 - 8.37 (m, 1 H), 7.67 (t, J = 8.0 Hz, 1 H), 4.00 (s, 3 H).



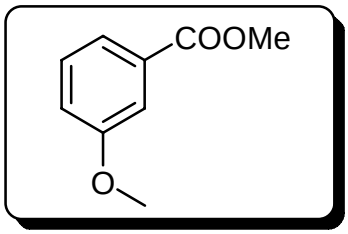
Methyl 4-methylbenzoate (3e) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, J = 8.0 Hz, 2 H), 7.25 (d, J = 8.0 Hz, 2 H), 3.92 (s, 3 H), 2.42 (s, 3 H).



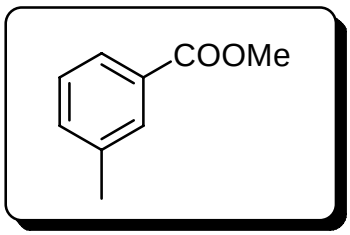
Methyl 3,4,5-trimethoxybenzoate (3f) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 (s, 2 H), 3.92 (s, 12 H).



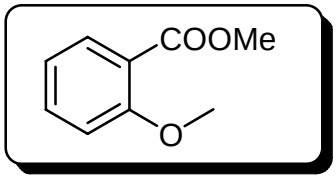
Methyl 4-methoxybenzoate (3g) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (d, J = 8.8 Hz, 2 H), 6.93 (d, J = 8.8 Hz, 2 H), 3.90 (s, 3 H), 3.87 (s, 3 H).



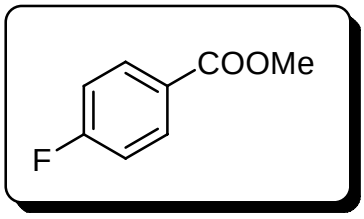
Methyl 3-methoxybenzoate (3h) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, J = 8.0 Hz, 1 H), 7.57 (d, J = 4.0 Hz, 1 H), 7.35 (t, J = 8.0 Hz, 1 H), 7.11 (dd, J = 8.0, 2.0 Hz, 1 H), 3.93 (s, 3 H), 3.87 (s, 3 H).



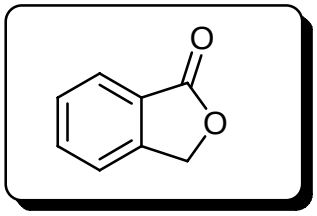
Methyl 3-methylbenzoate (3i) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (s, 1 H), 7.85 (d, J = 8.4 Hz, 1 H), 7.38 – 7.31 (m, 2 H), 3.91 (s, 3 H), 2.41 (s, 3 H).



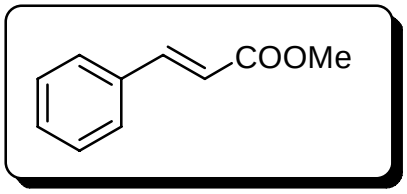
Methyl 2-methoxybenzoate (3j) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (dd, J = 8.0, 2.0 Hz, 1 H), 7.47 (dt, J = 8.0, 1.6 Hz, 1 H), 6.96 – 7.00 (m, 2 H), 3.91 (s, 3 H), 3.90 (s, 3 H).



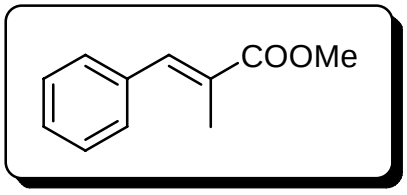
Methyl 4-fluorobenzoate (3k) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (t, J = 6.8 Hz, 2 H), 7.12 (t, J = 8.4 Hz, 2 H), 3.93 (s, 3 H).



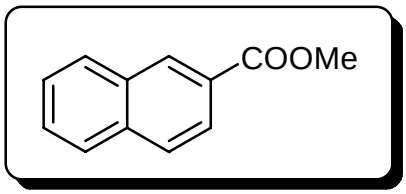
Isobenzofuran-1(3H)-one (3l) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, J = 8.0 Hz, 1 H), 7.70 (t, J = 7.6 Hz, 1 H), 7.55 (t, J = 7.6 Hz, 1 H), 7.51 (d, J = 7.6 Hz, 1 H), 6.34 (s, 2 H).



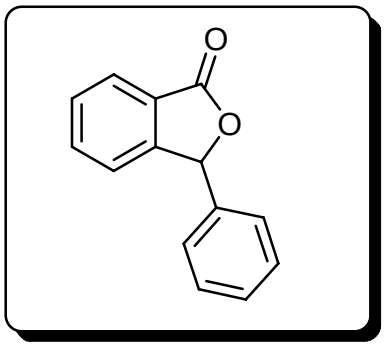
Methyl cinnamate (3m) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, J = 16.0 Hz, 1 H), 7.54 (q, J = 3.2 Hz, 2 H), 7.40 (t, J = 3.2 Hz, 3 H), 6.46 (d, J = 16.0 Hz, 1 H), 3.83 (s, 3 H).



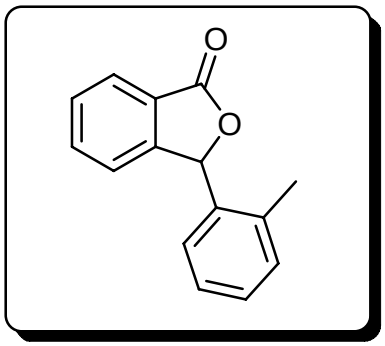
(E)-methyl 2-methyl-3-phenylacrylate (3n) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (s, 1 H), 7.41 (d, J = 4.0 Hz, 4 H), 7.37 – 7.31 (m, 1 H), 3.84 (s, 3 H), 2.14 (s, 3 H).



Methyl 2-naphthoate (3o) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.63 (s, 1 H), 8.08 (dd, J = 8.4, 1.6 Hz, 1 H), 7.97 (d, J = 8.0 Hz, 1 H), 7.90 (d, J = 8.4 Hz, 2 H), 7.63 – 7.54 (m, 2 H), 4.00 (s, 3 H).

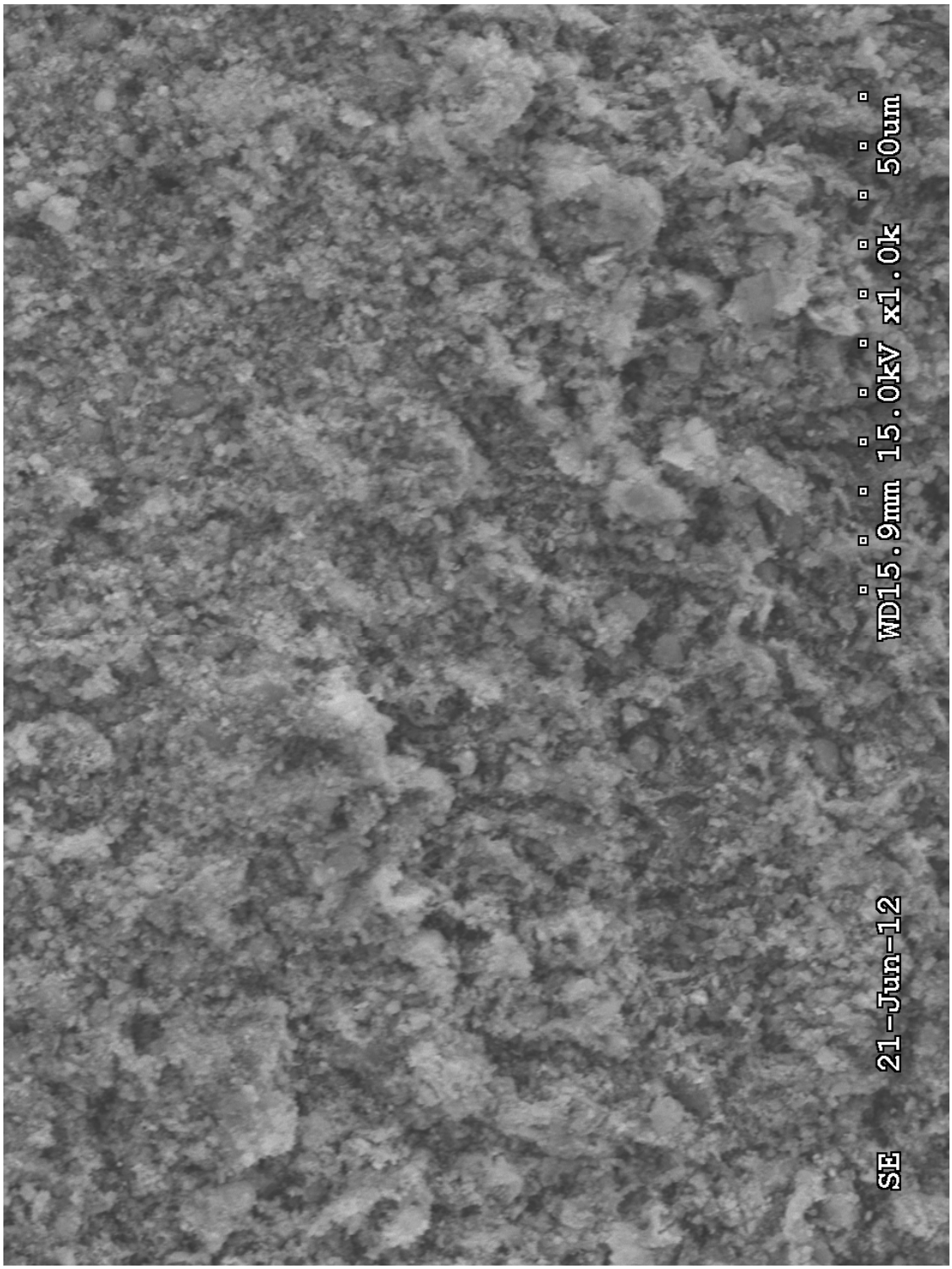


3-phenylisobenzofuran-1(3H)-one(5a) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (d, J = 7.6 Hz, 1 H), 7.66 (dt, J = 7.6, 1.2 Hz, 1 H), 7.57 (t, J = 7.6 Hz, 1 H), 7.41 - 7.39 (m, 3 H), 7.35 (d, J = 7.6 Hz, 1 H), 7.31 - 7.28 (m, 2 H), 6.42 (s, 1 H).

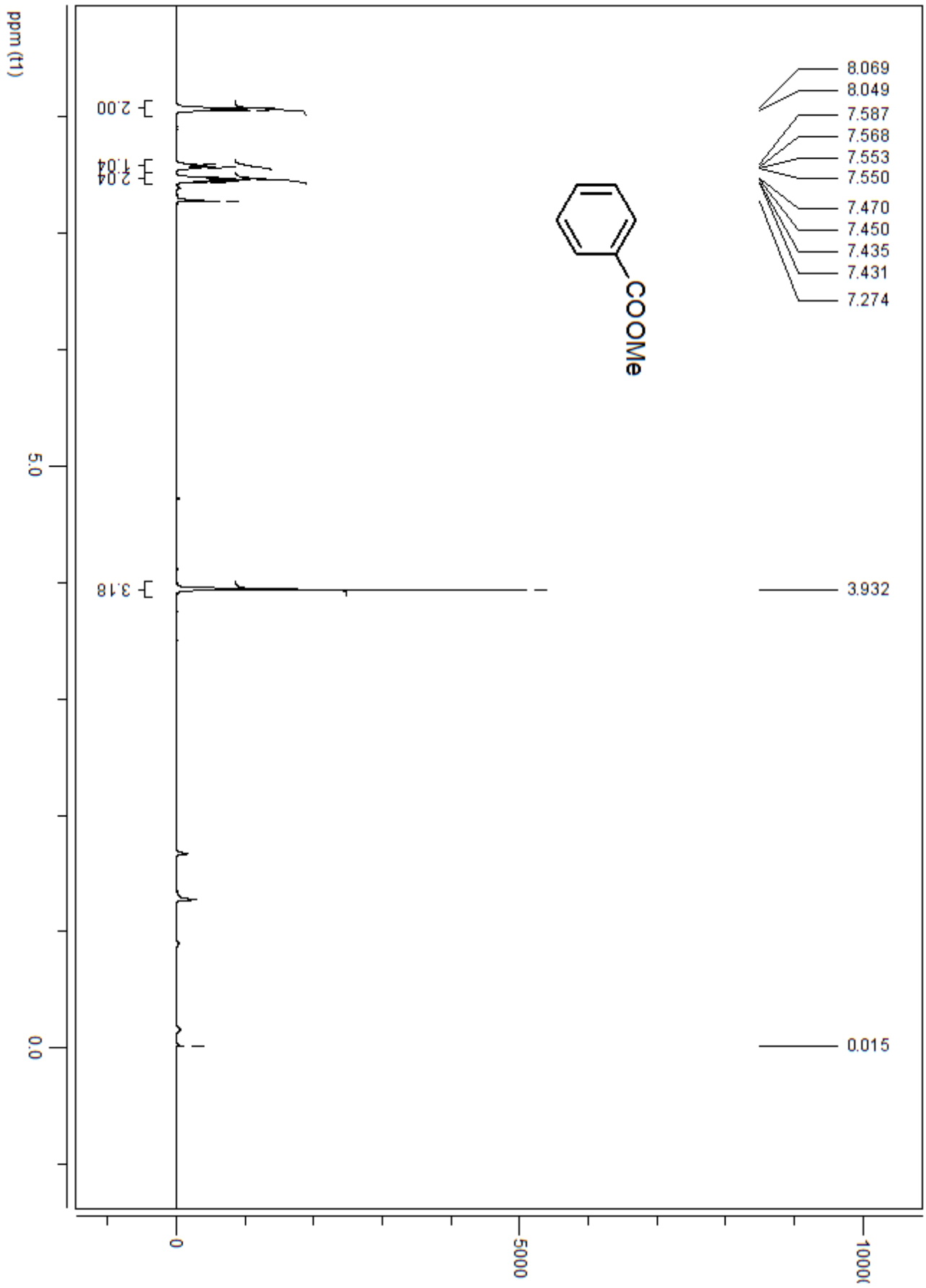


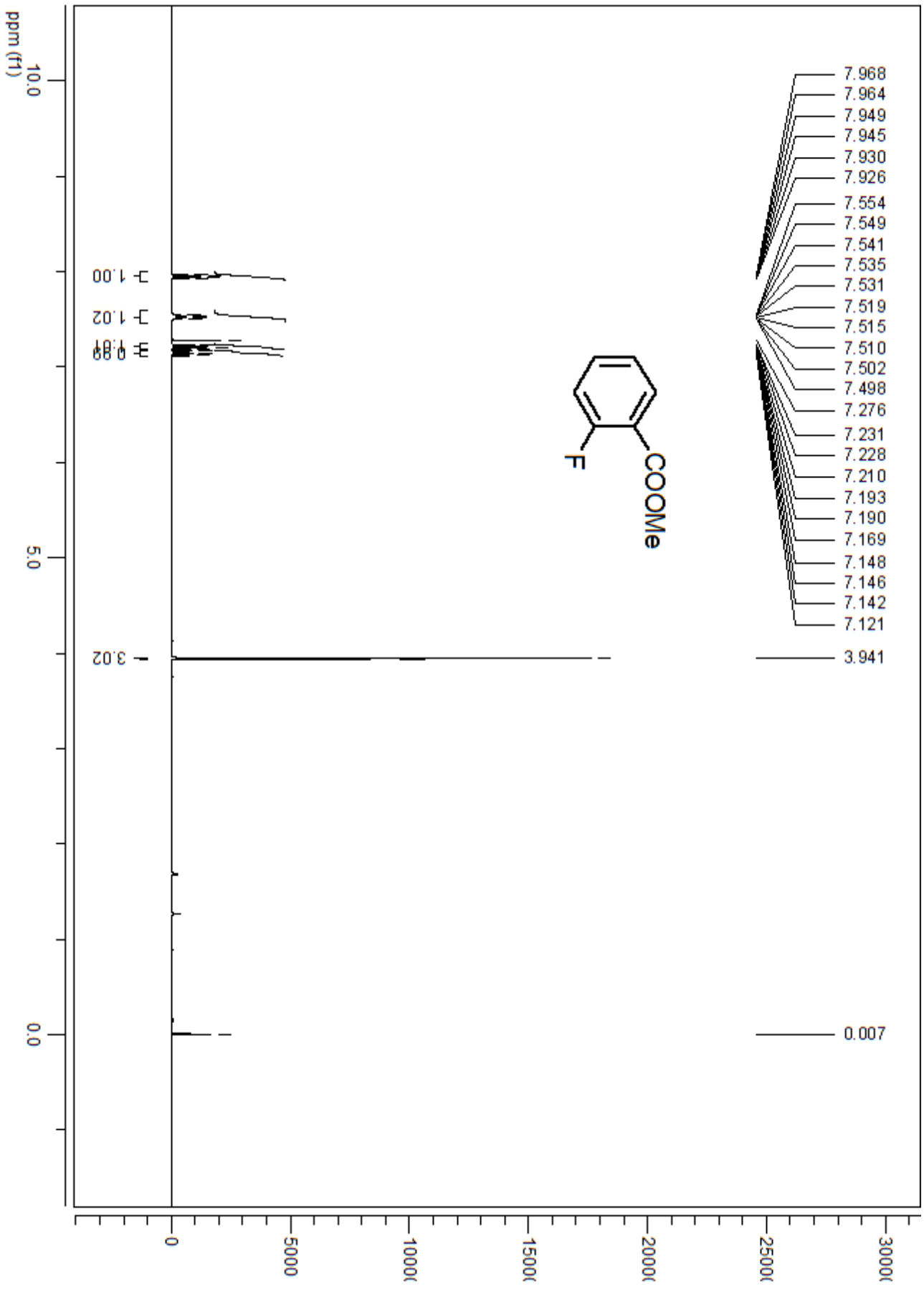
3-o-tolylisobenzofuran-1(3H)-one(5b) : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, J = 7.6 Hz, 1 H), 7.69 (t, J = 3.6 Hz, 1 H), 7.59 (t, J = 3.6 Hz, 1 H), 7.36 (d, J = 7.6 Hz, 1 H), 7.31 - 7.26 (m, 2 H), 7.14 (dt, J = 8.0, 2.8 Hz, 1 H), 6.94 (d, J = 8.0 Hz, 1 H), 6.70 (s, 1 H), 2.51 (s, 3 H).

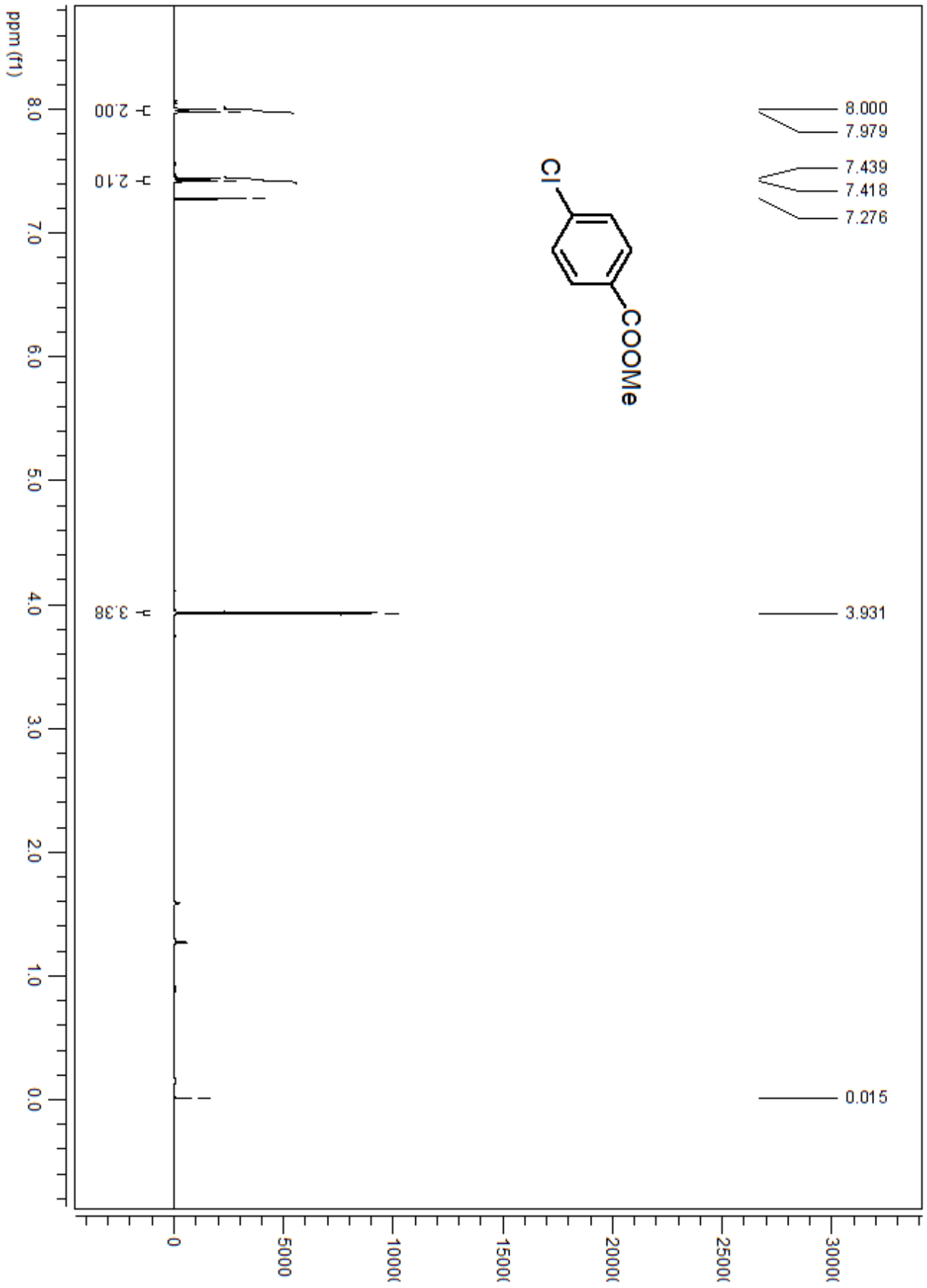
Figure S1. SEM image of the polysiloxnae(PMHS)-stabilized Pd@PMS after reaction

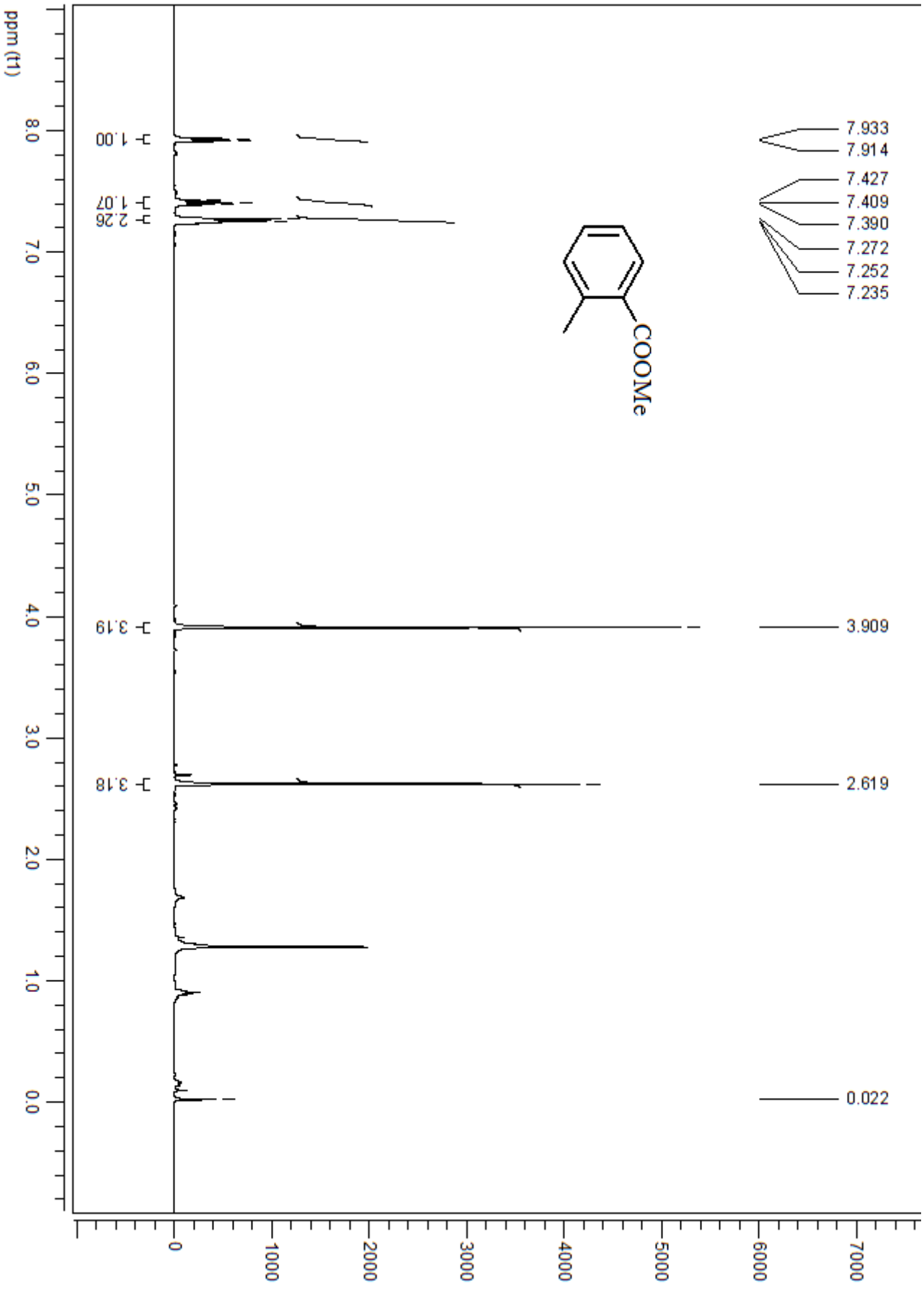


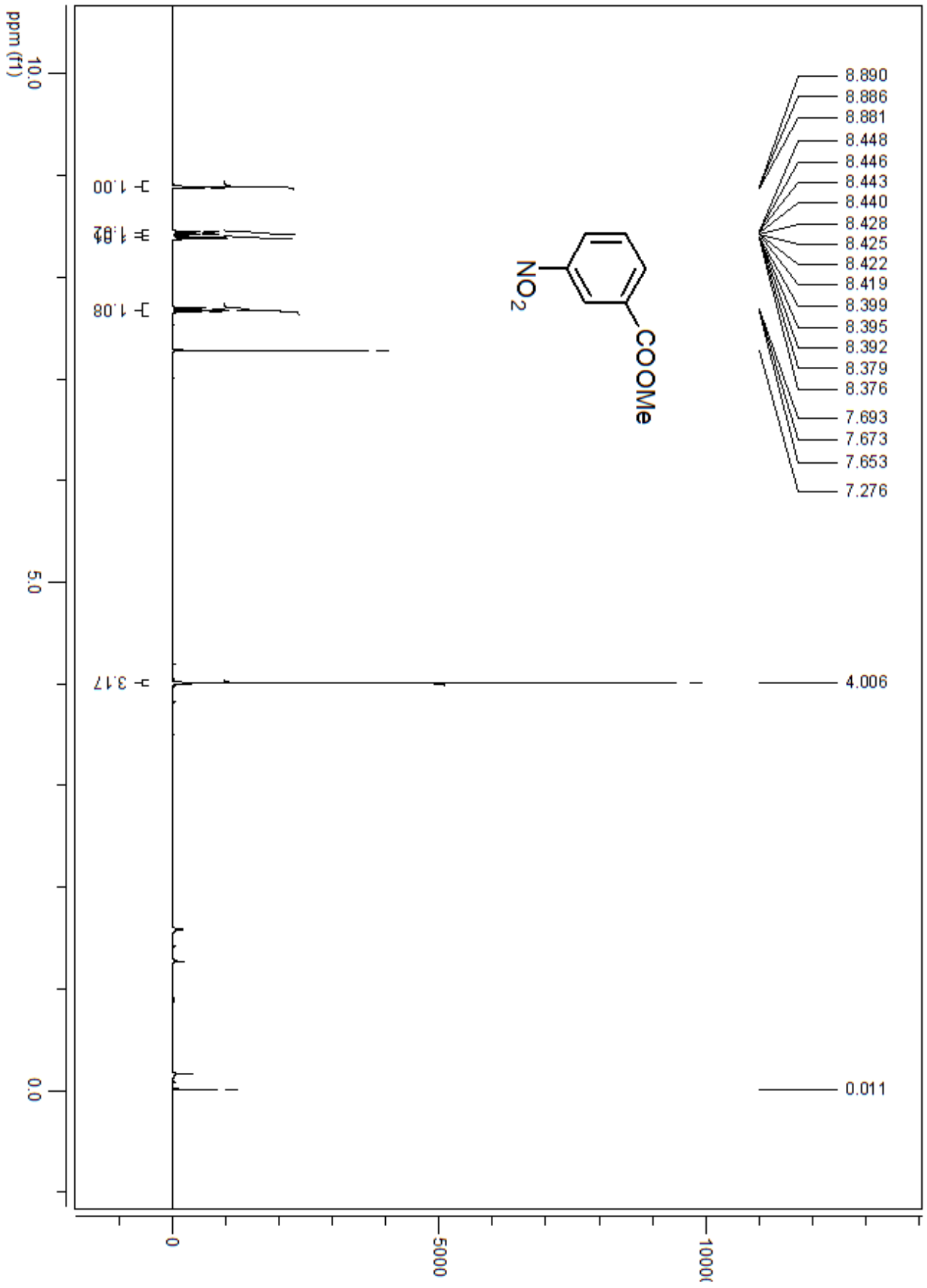
4. ^{1}*H-NMR of* methyl benzoates.

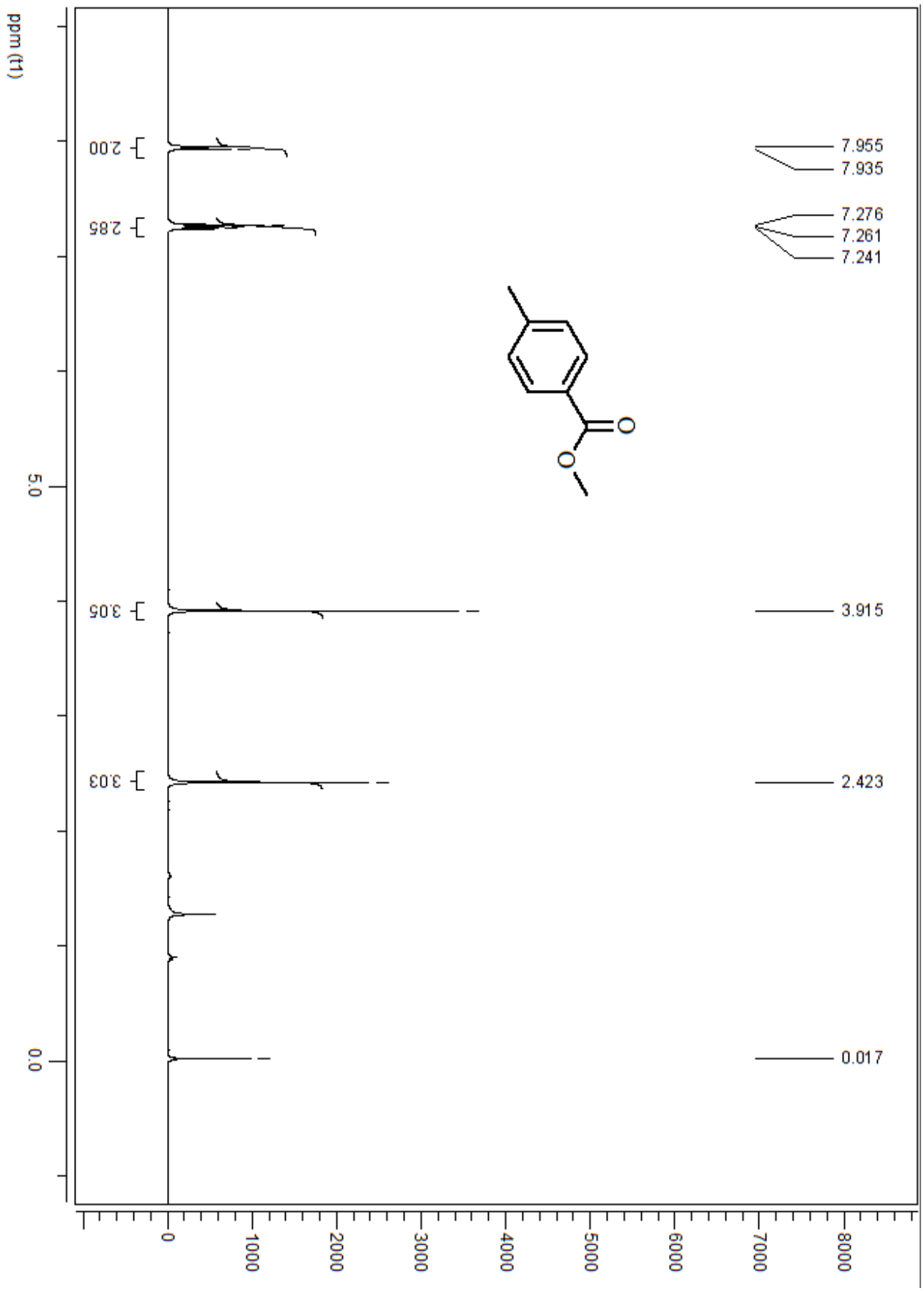


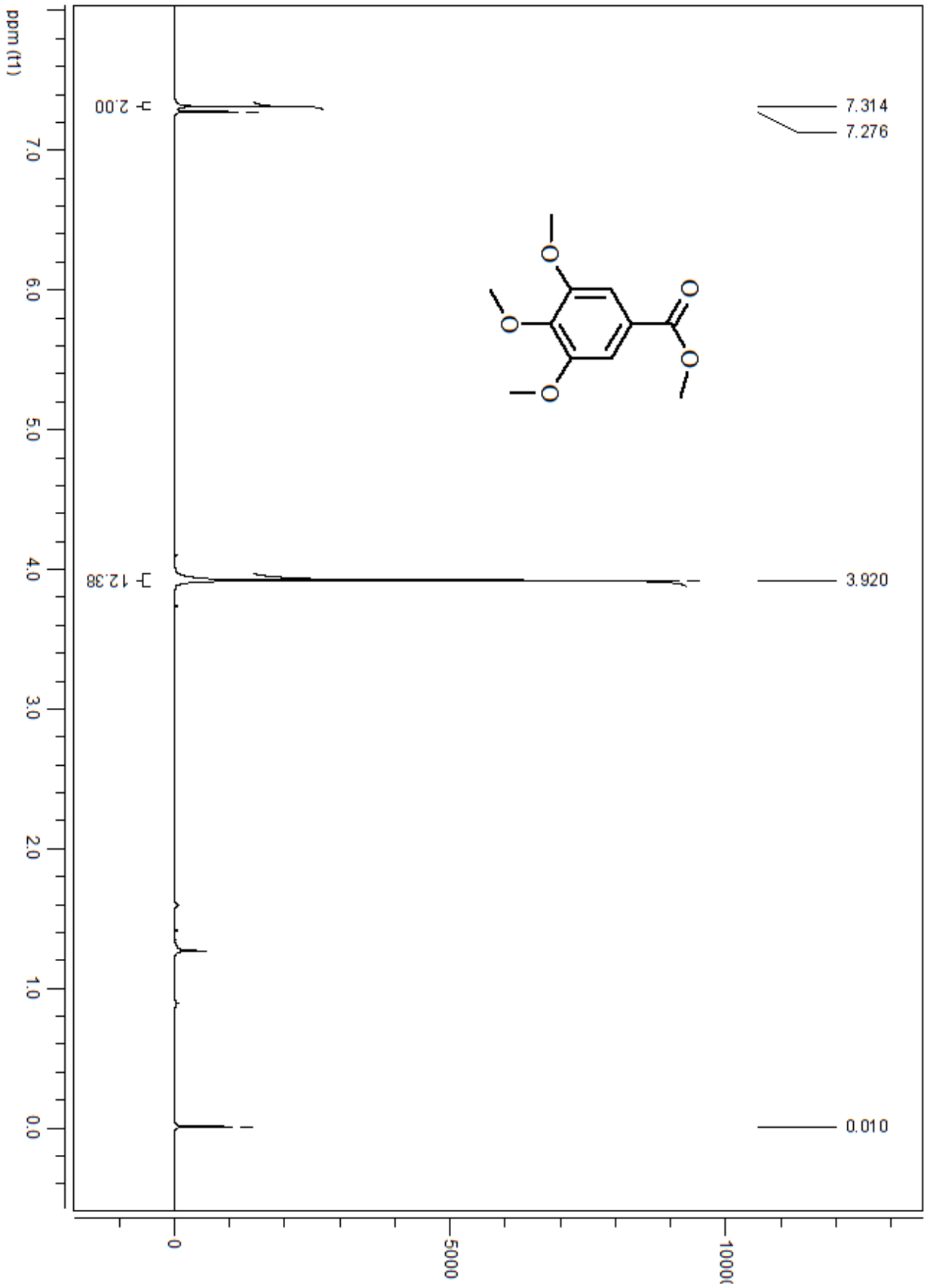


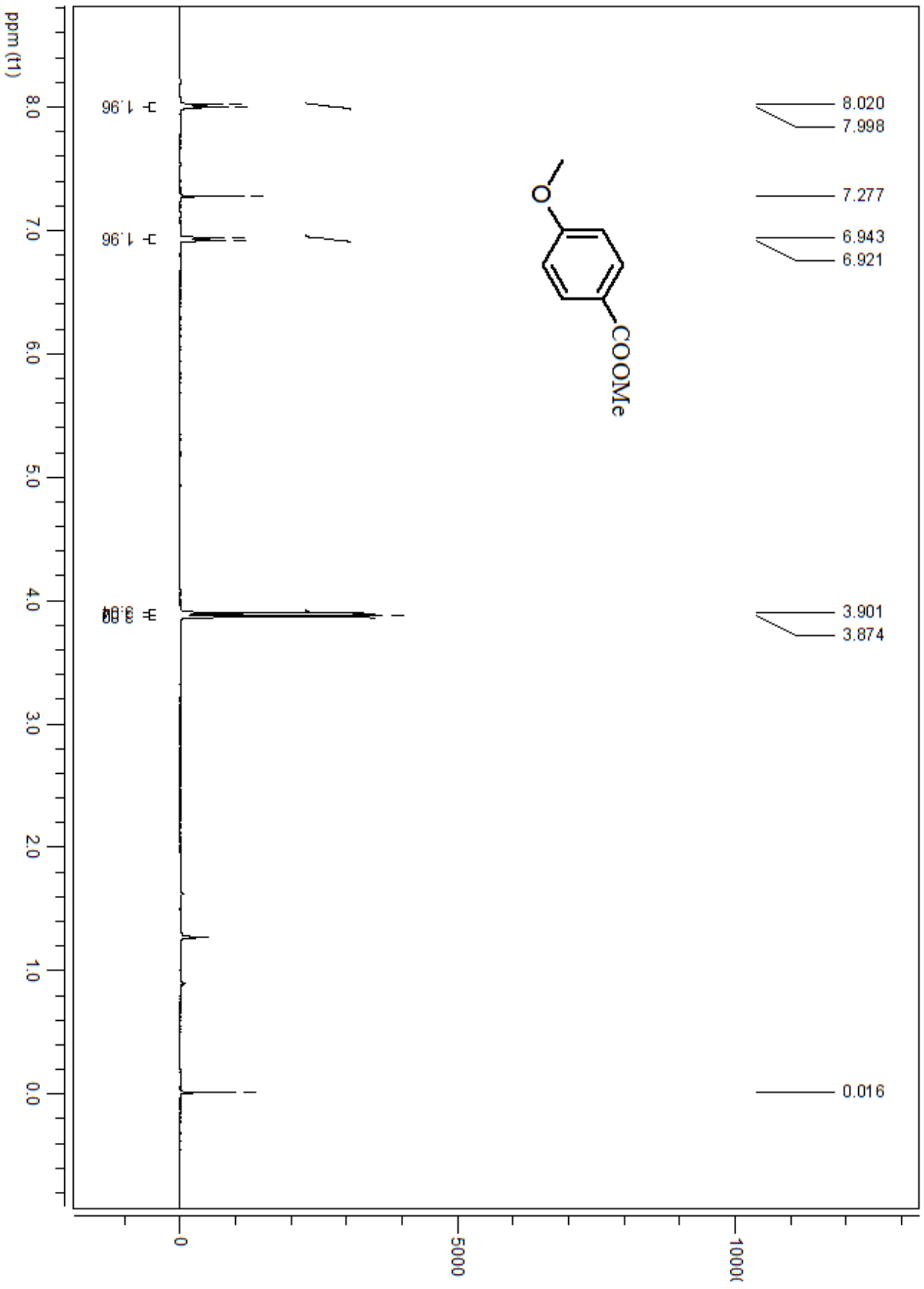


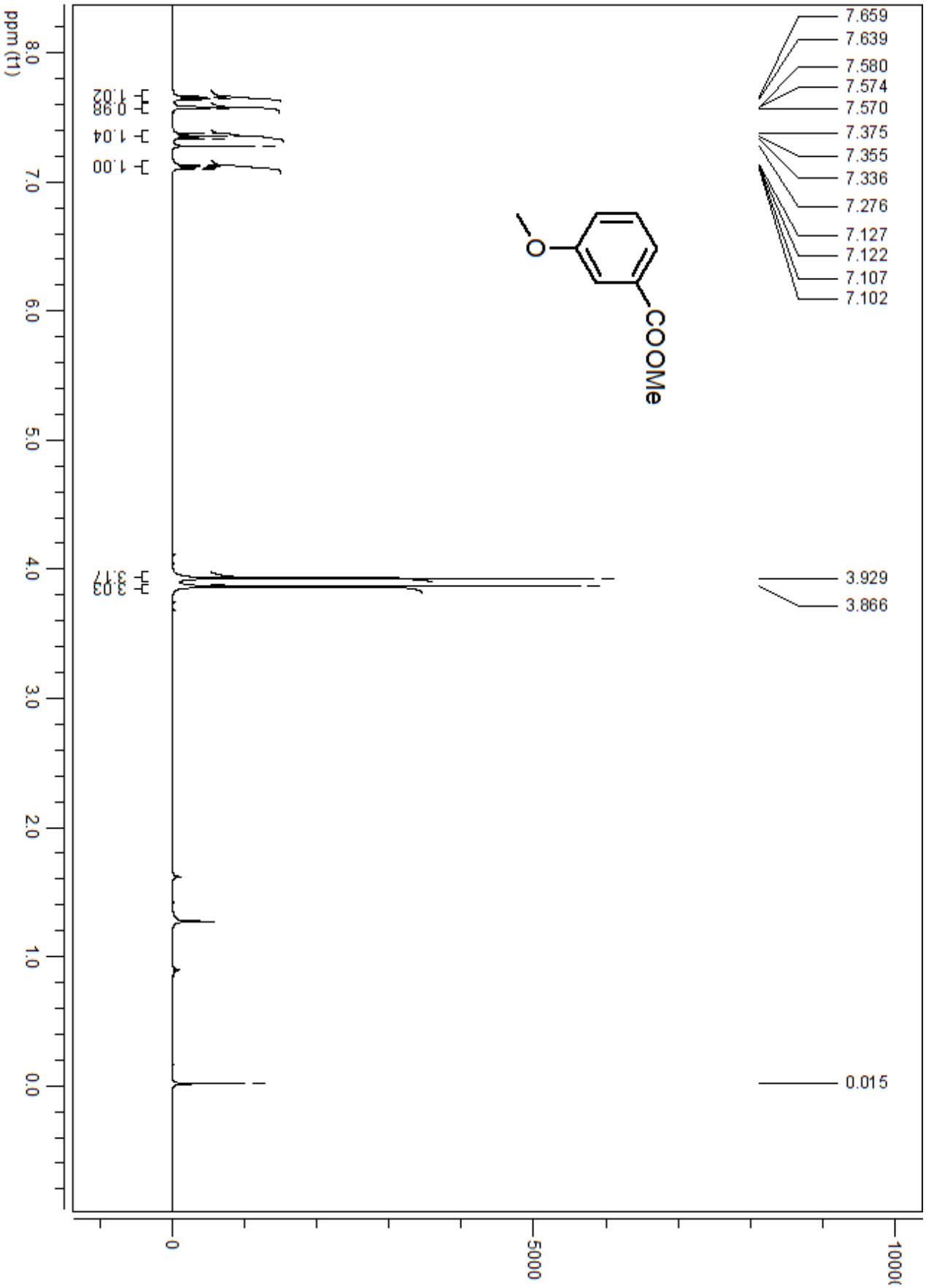

ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.00
1.07
2.26
3.19
3.18
7.933
7.914
7.427
7.409
7.390
7.272
7.252
7.235
3.909
2.619
0.022
COOMe
0
1000
2000
3000
4000
5000
6000
7000

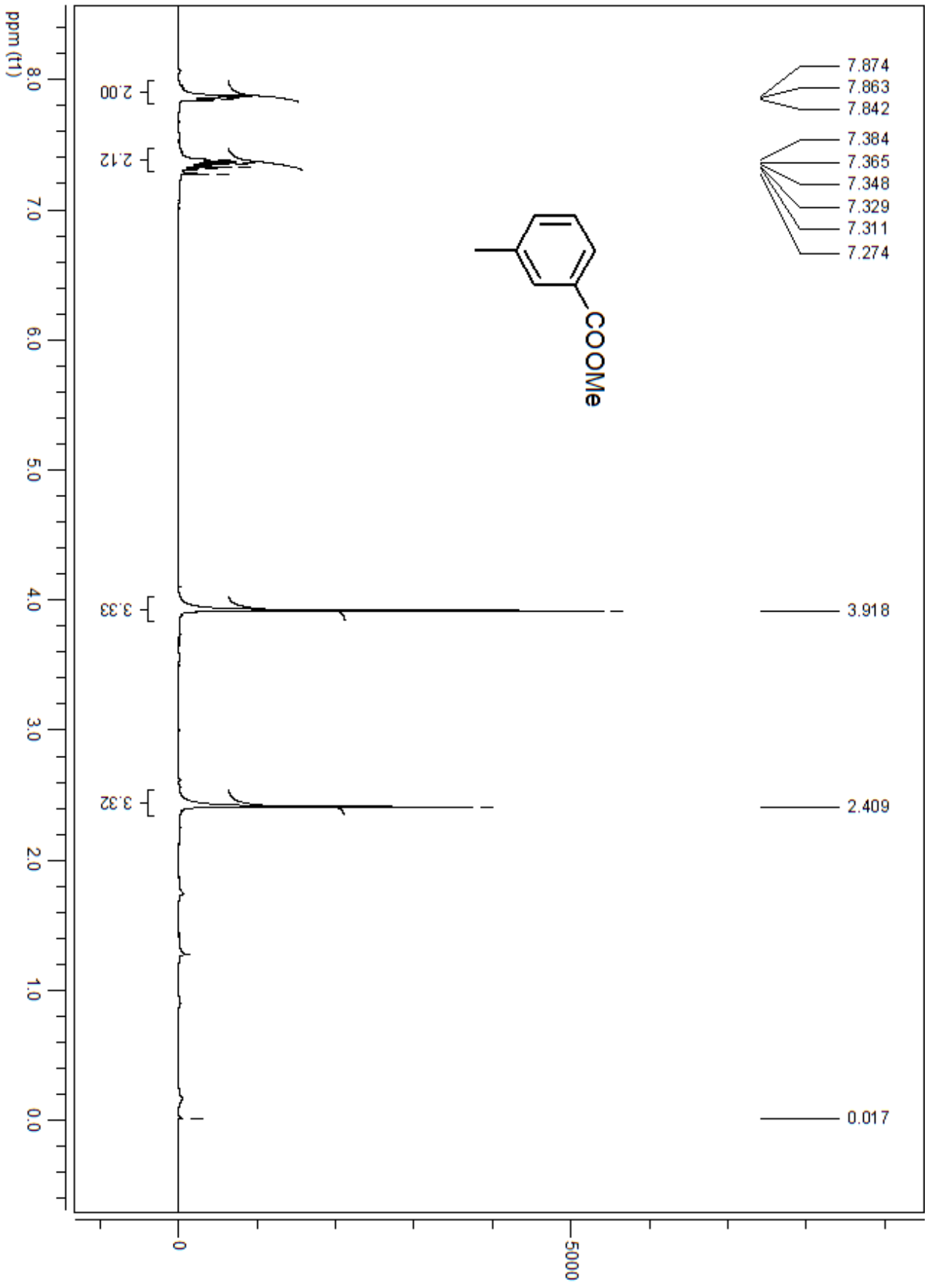

ppm (f1)
10.0
5.0
0.0
1.00
1.02
1.08
3.17
4.006
0.011
8.890
8.886
8.881
8.448
8.446
8.443
8.440
8.428
8.425
8.422
8.419
8.399
8.395
8.392
8.379
8.376
7.693
7.673
7.653
7.276
NO2
COOMe
0
5000
10000

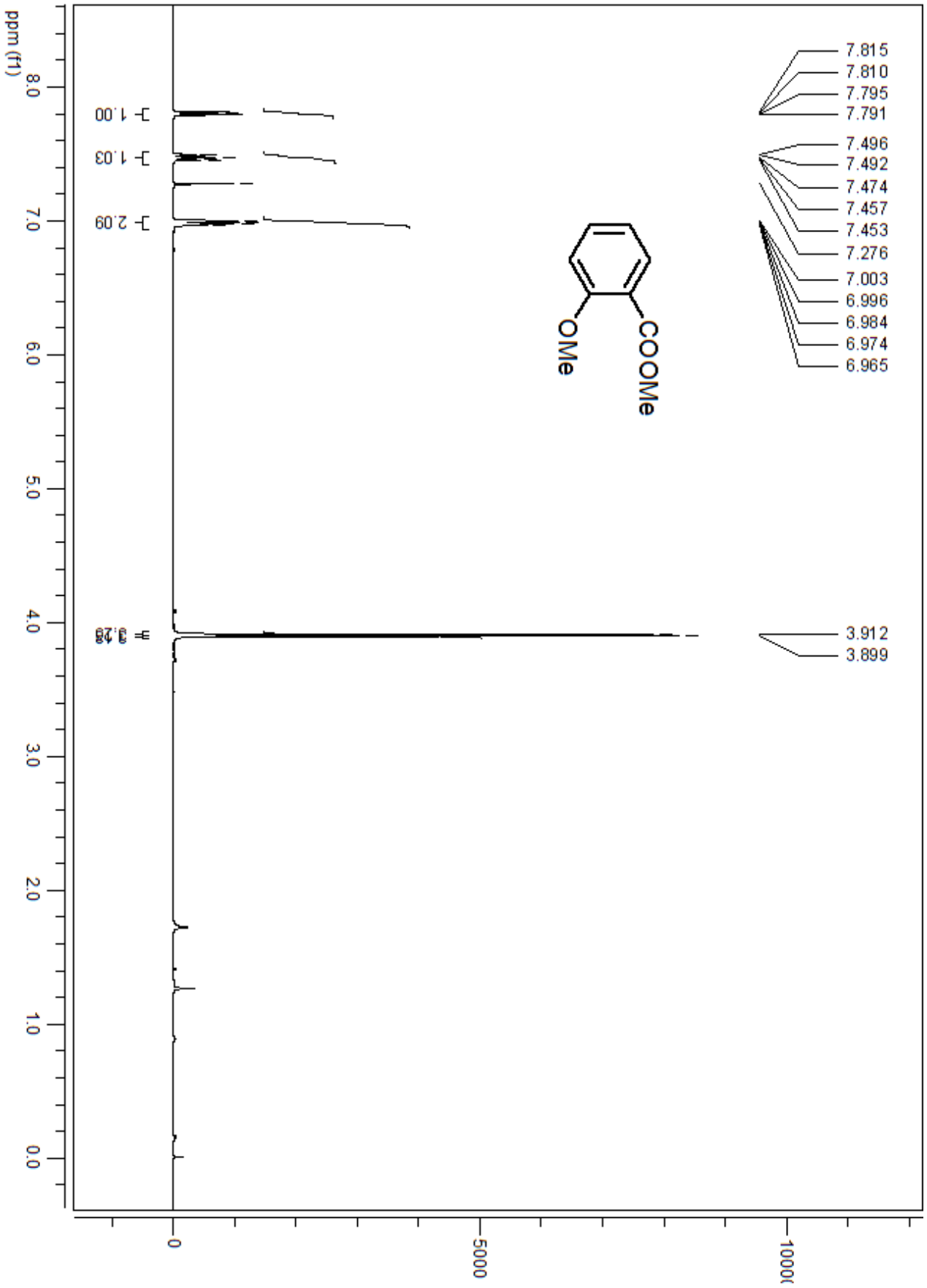

ppm (t1)
5.0
0.0
2.00
2.85
3.05
3.03
7.955
7.935
7.276
7.261
7.241
3.915
2.423
0.017
O
O
0
1000
2000
3000
4000
5000
6000
7000
8000

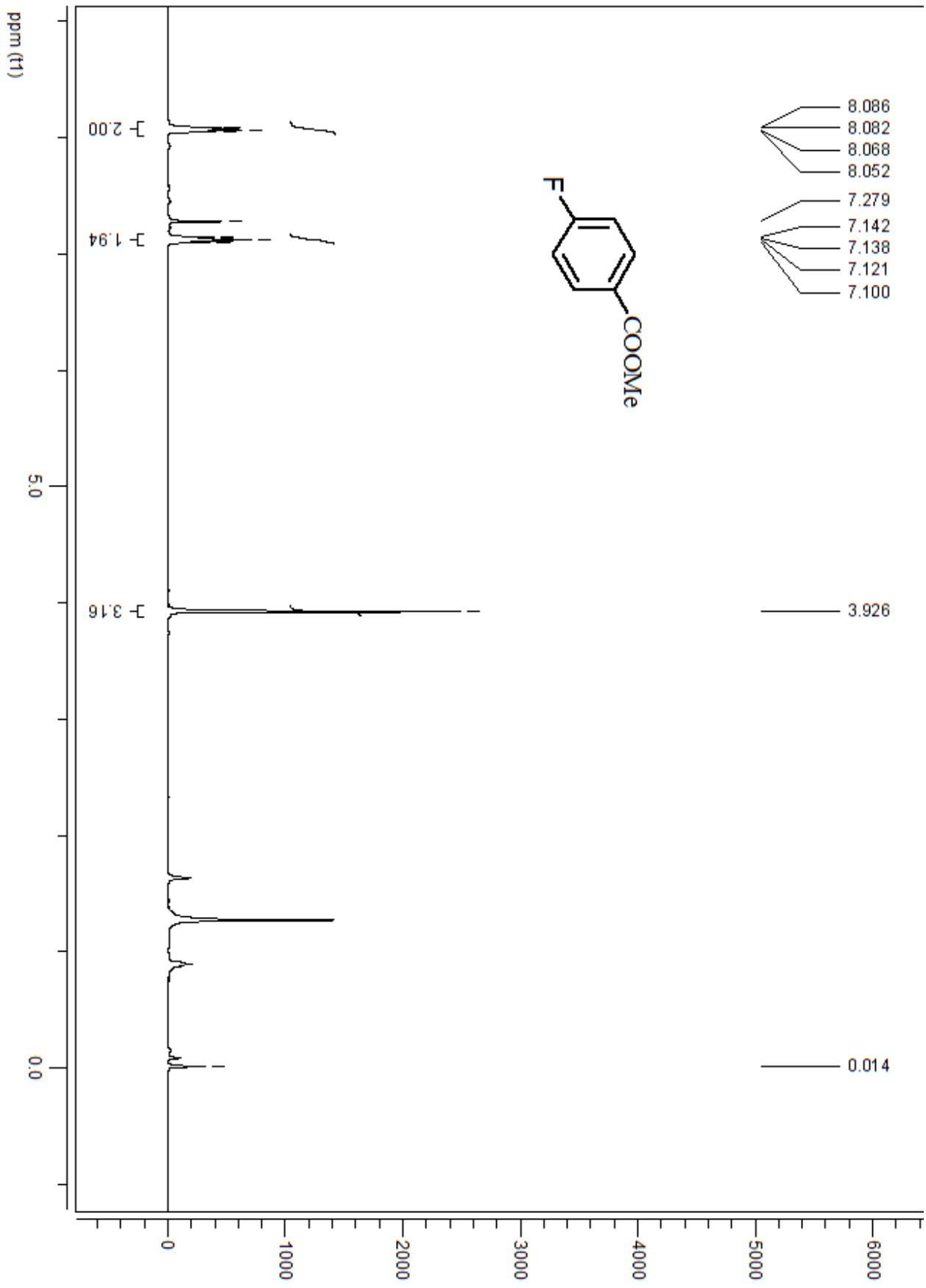

ppm (t1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.00
12.38
7.314
7.276
3.920
0.010
O
O
O
O
O
O
0
5000
10000

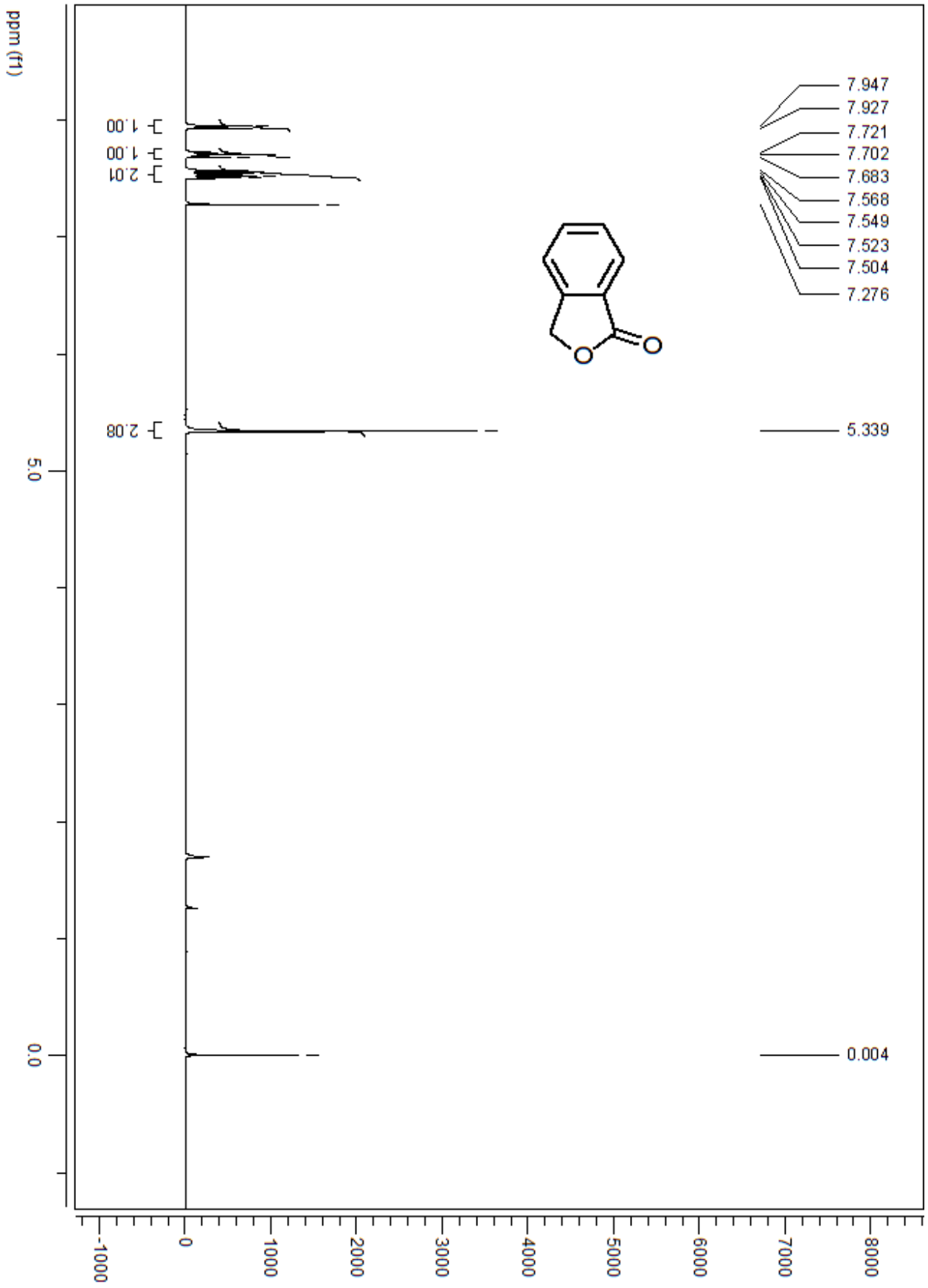


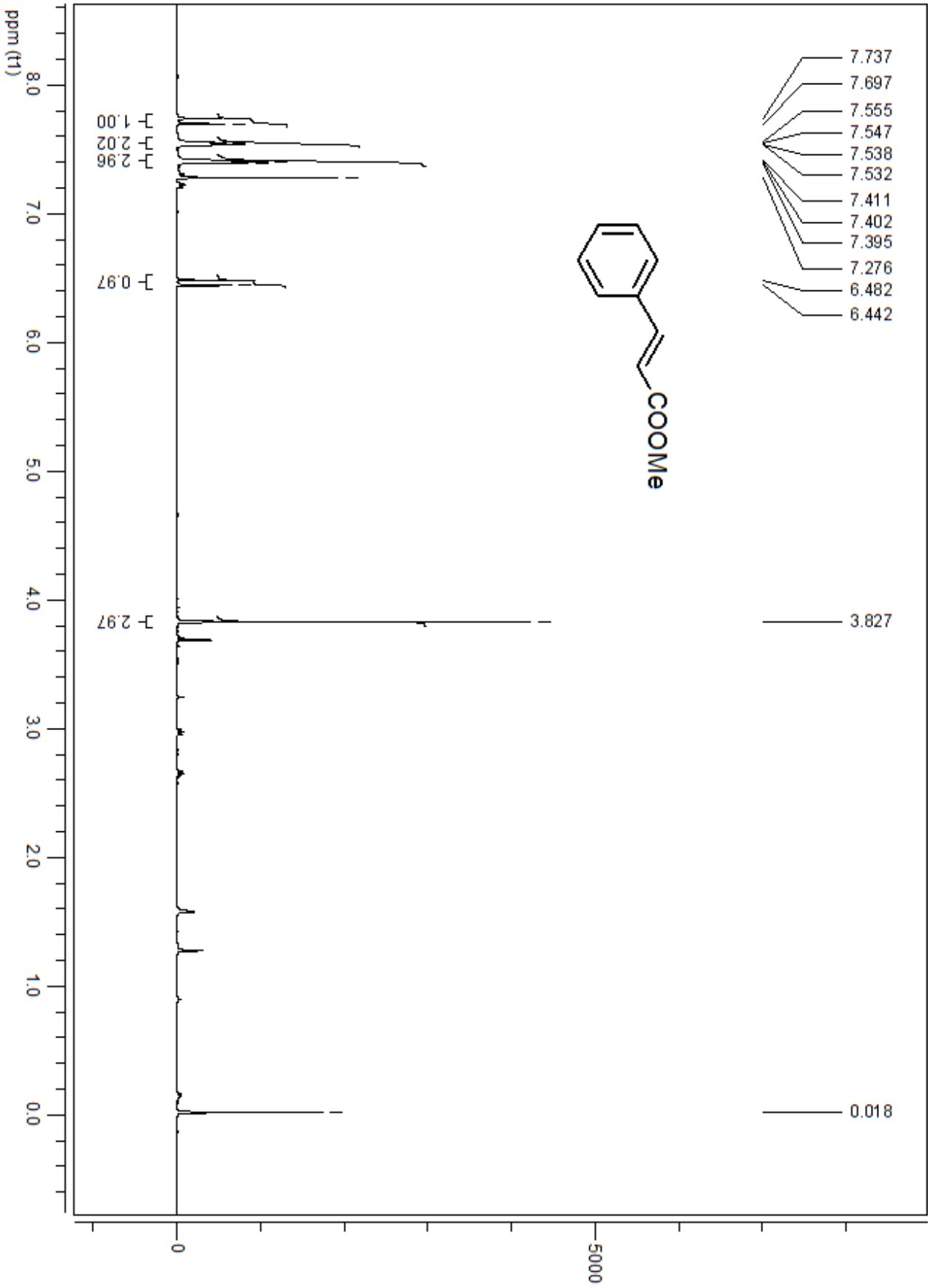

ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.02
0.98
1.04
1.00
3.03
3.17
7.659
7.639
7.580
7.574
7.570
7.375
7.355
7.336
7.276
7.127
7.122
7.107
7.102
3.929
3.866
0.015
O
COOMe
0
5000
10000

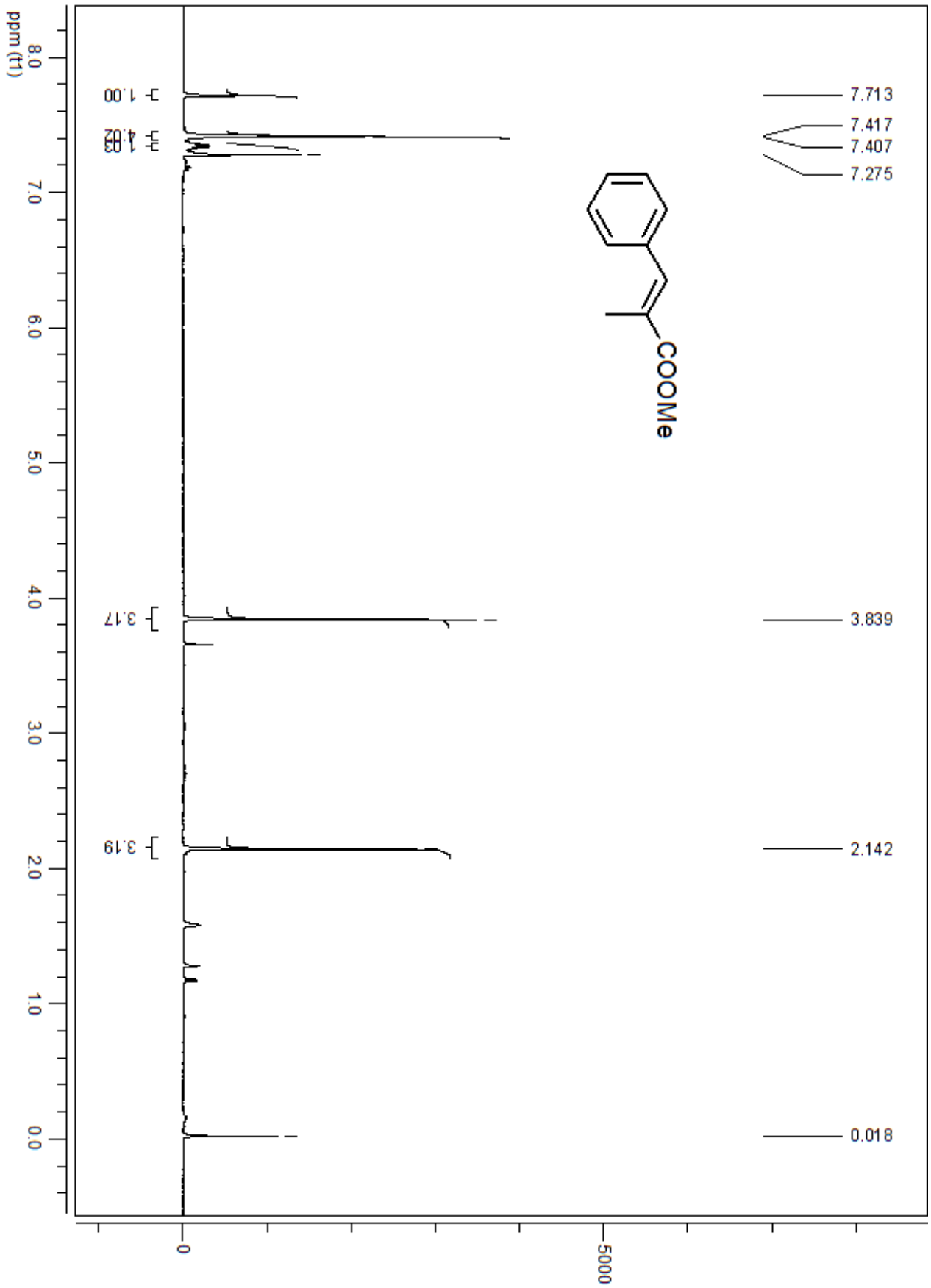

ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.00
2.12
3.33
3.32
7.874
7.863
7.842
7.384
7.365
7.348
7.329
7.311
7.274
3.918
2.409
0.017
COOMe
0
5000

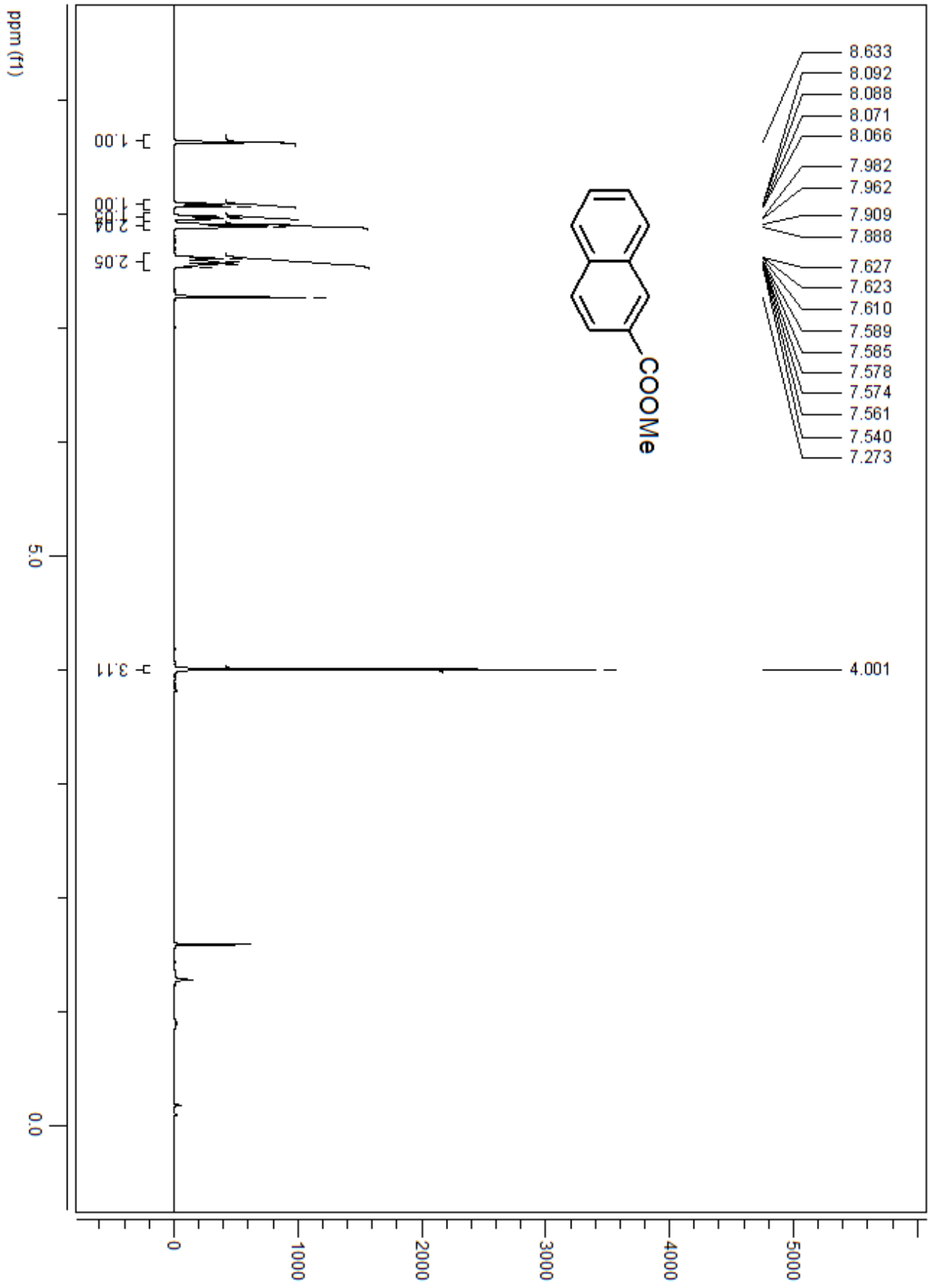

ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.00
1.03
2.09
3.29
7.815
7.810
7.795
7.791
7.496
7.492
7.474
7.457
7.453
7.276
7.003
6.996
6.984
6.974
6.965
3.912
3.899
OMe
COOMe
0
5000
1000

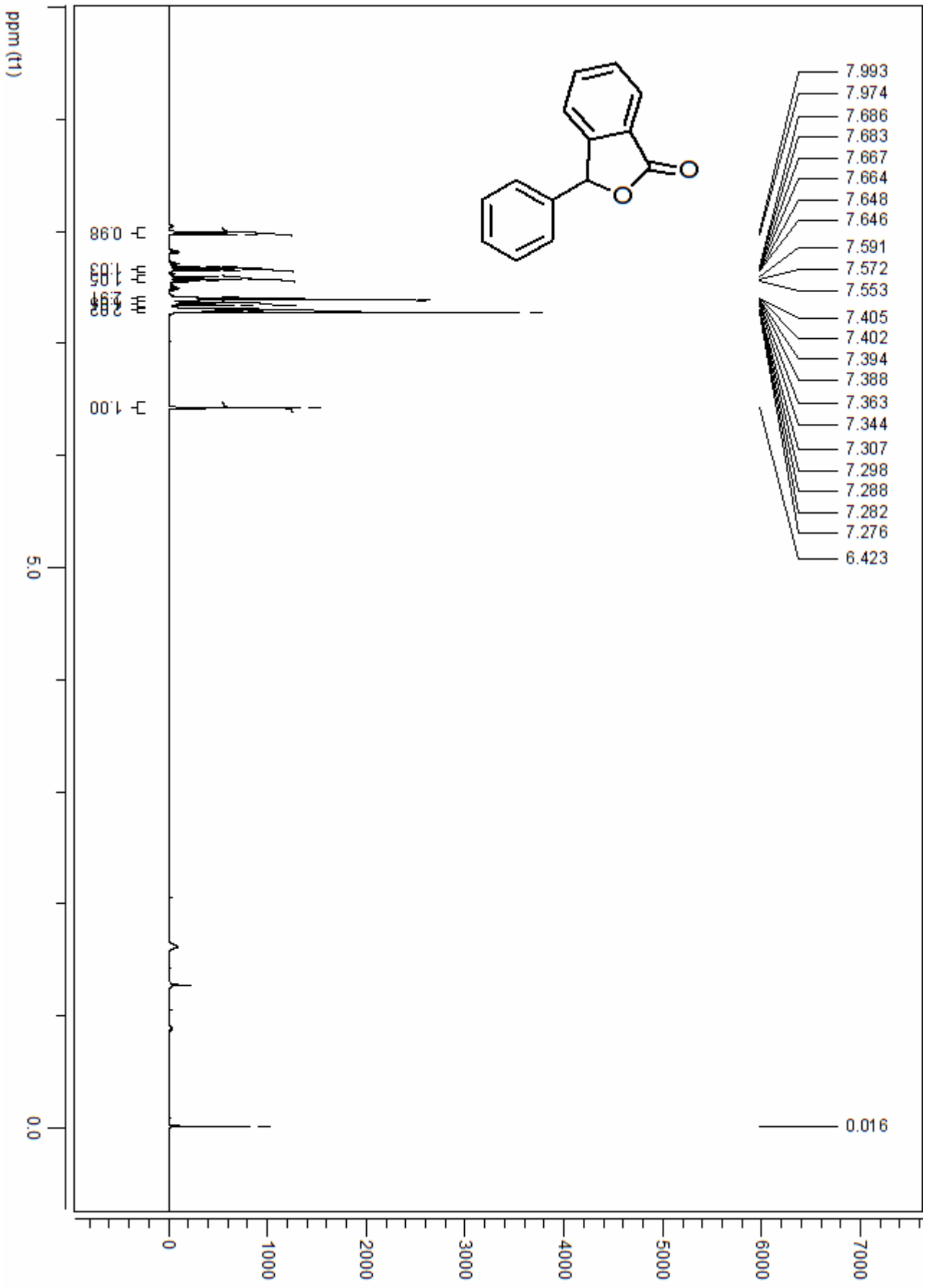

ppm (t1)
5.0
0.0
2.00
1.94
3.16
8.086
8.082
8.068
8.052
7.279
7.142
7.138
7.121
7.100
3.926
0.014
F
COOMe
0
1000
2000
3000
4000
5000
6000

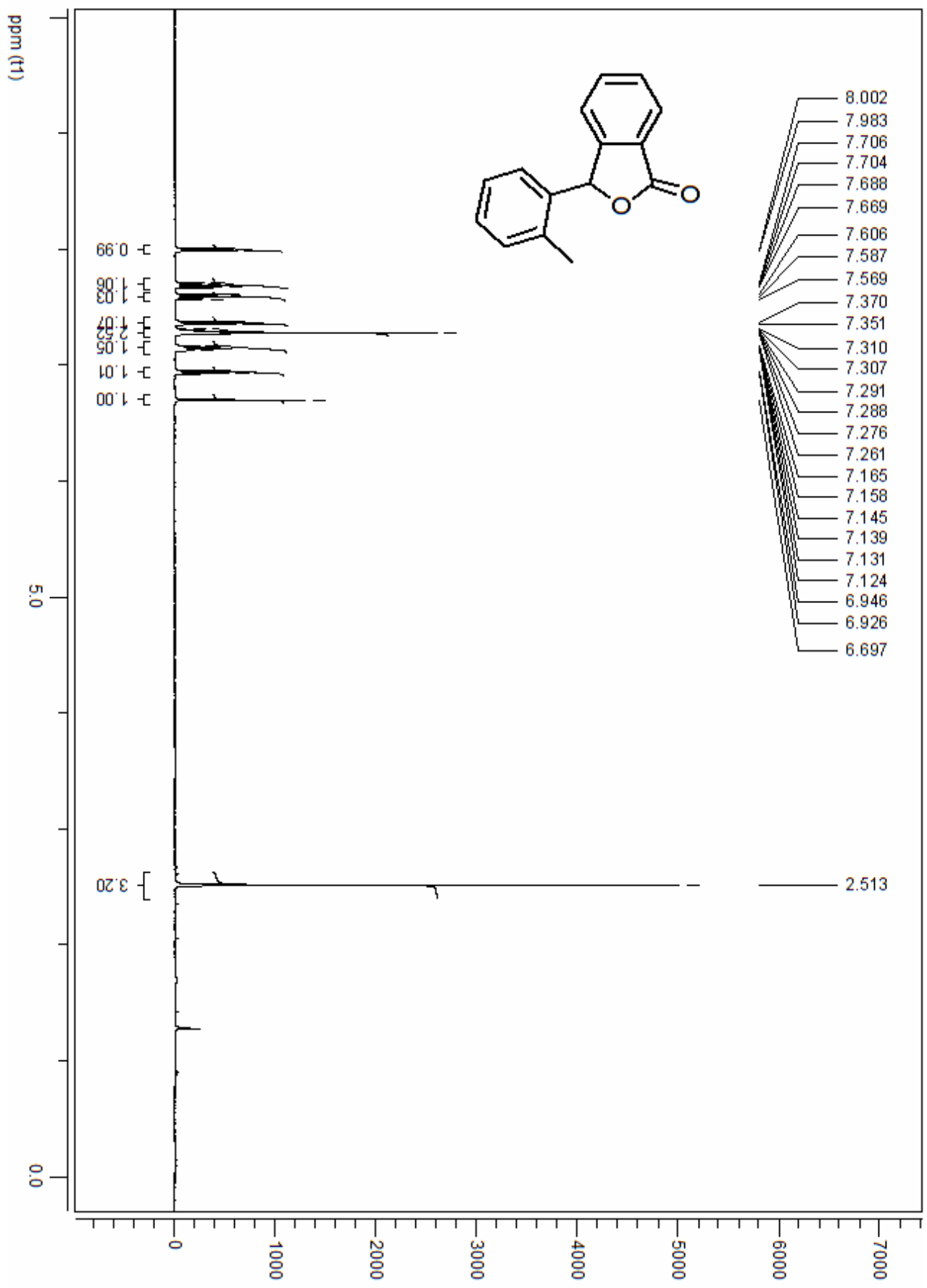

ppm (f1)
5.0
0.0
1.00
1.00
2.01
2.08
7.947
7.927
7.721
7.702
7.683
7.568
7.549
7.523
7.504
7.276
5.339
0.004
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000


ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.00
2.02
2.96
0.97
2.97
7.737
7.697
7.555
7.547
7.538
7.532
7.411
7.402
7.395
7.276
6.482
6.442
3.827
0.018
COOMe
0
5000




ppm (f1)
5.0
0.0
1.00
1.00
2.04
2.05
3.11
COOMe
8.633
8.092
8.088
8.071
8.066
7.982
7.962
7.909
7.888
7.627
7.623
7.610
7.589
7.585
7.578
7.574
7.561
7.540
7.273
4.001
0
1000
2000
3000
4000
5000


ppm (t1)
5.0
0.0
0.98
1.03
1.05
1.00
7.993
7.974
7.686
7.683
7.667
7.664
7.648
7.646
7.591
7.572
7.553
7.405
7.402
7.394
7.388
7.363
7.344
7.307
7.298
7.288
7.282
7.276
6.423
0.016
0
1000
2000
3000
4000
5000
6000
7000


ppm (t1)
8.002
7.983
7.706
7.704
7.688
7.669
7.606
7.587
7.569
7.370
7.351
7.310
7.307
7.291
7.288
7.276
7.261
7.165
7.158
7.145
7.139
7.131
7.124
6.946
6.926
6.697
2.513
0.99
1.06
1.03
1.07
2.52
1.05
1.01
1.00
3.20
5.0
0.0
0
1000
2000
3000
4000
5000
6000
7000