Supporting Information

Ph_3As-catalyzed Wittig-Type Olefination of Aldehydes with Diazoacetate in the Presence of $Na_2S_2O_4$

Peng Cao[a], *Chuan-Ying Li*[a], *Yan-Biao Kang*[a], *Zuowei Xie*[b], *Xiu-Li Sun*[a], *Yong Tang*[a *],

[a] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

[b] Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

e-mail: tangy@mail.sioc.ac.cn

Contents

General Information All reactions were carried out under N_2 unless otherwise noted. All carbonyl compounds and solvents were purified according to standard methods unless otherwise noted.

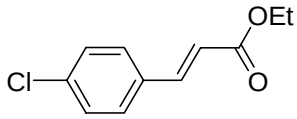
^{1}H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d. All signals are reported in ppm with the internal TMS signal at 0.0 ppm or chloroform signal at 7.26 ppm as a standard. The data are reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d. All signals are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

Fe(TCP)Cl was synthesized according to literature procedure.[1]

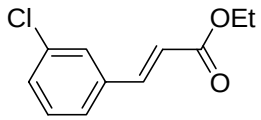
Part I Experimental Part

1. **General procedure for Iron(III) Porphyrin and Triphenylarsine-catalyzed Olefination Reaction.** Fe(TCP)Cl (2.5 mg, 0.003 mmol), Ph_3As (37 mg, 0.12 mmol) and $Na_2S_2O_4$ (210 mg, 1.2 mmol) were mixed in a Schlenk tube. The tube was evacuated and backfilled with nitrogen. Aldehyde (0.6 mmol) was added, followed by toluene (3.0 mL) and water (1.25 mL). The reaction mixture was heated to 80 ^oC and 2.0 equiv of EDA (126 uL, 1.2 mmol) was added within 8 h via a syringe pump or in portions. After the reaction was complete, the resulting mixture was cooled to room temperature, extracted with CH_2Cl_2, dried with Na_2SO_4 and concentrated. The residue was purified by flash chromatography (silica gel) to give the product.

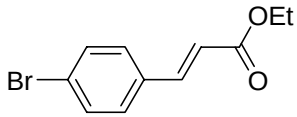
Characterization data of Compounds



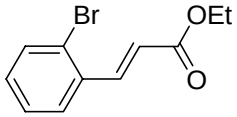
(E)-ethyl 3-(4-chlorophenyl)acrylate 3a[2] (Table 1, entry 1) was synthesized from 4-chlorobenzaldehyde **1a**. 97% yield. ^1H NMR (300 MHz,$CDCl_3$/TMS) δ 7.64 (d, *J* = 16.0 Hz, 1 H), 7.46 (d, *J* = 8.7 Hz, 2 H), 7.36 (d, *J* = 8.7 Hz, 2 H), 6.41 (d, *J* = 16.0 Hz, 1 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 1.34 (t, *J* = 7.2 Hz, 3 H).



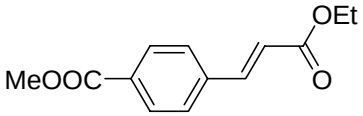
(E)-ethyl 3-(3-chlorophenyl)acrylate 3b[3] (Table 1, entry 2) was synthesized from 3-chlorobenzaldehyde **1b**. 95% yield. ^1H NMR (300 MHz, $CDCl_3$/TMS) δ 7.69 (d, *J* = 15.9 Hz, 1 H), 7.54-7.51 (m, 2 H), 7.39-7.37 (m, 2 H), 6.43 (d, *J* = 15.9 Hz, 1 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 1.34 (t, *J* = 7.2 Hz, 3 H).



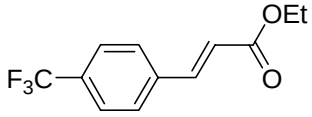
(E)-ethyl 3-(4-bromophenyl)acrylate 3c[4] (Table 1, entry 3) was synthesized from 4-bromobenzaldehyde **1c**. 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.62 (d, *J* = 16.2 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 6.43 (d, *J* = 16.2 Hz, 1 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 1.34 (t, *J* = 7.2 Hz, 3 H).



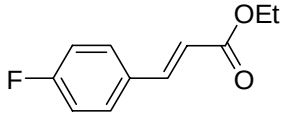
(E)-ethyl 3-(2-bromophenyl)acrylate 3d[5] (Table 1, entry 4) was synthesized from 2-bromobenzaldehyde **1d**. 91% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 8.05 (d, *J* = 16.2 Hz, 1 H), 7.61-7.59 (m, 2 H), 7.35-7.20 (m, 2 H), 7.26-7.19 (m, 1 H), 6.38 (d, *J* = 16.2 Hz, 1 H), 4.28 (q, *J* = 7.2 Hz, 2 H), 1.35 (t, *J* = 7.2 Hz, 3 H).



(E)-methyl 4-(3-ethoxy-3-oxoprop-1-enyl)benzoate 3e[6] (Table 1, entry 5) was synthesized from methyl 4-formylbenzoate **1e**. 99% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 8.05 (d, *J* = 8.7 Hz，2 H), 7.70 (d, *J* =15.9 Hz, 1 H), 7.59 (d, *J* = 8.7 Hz, 2 H), 6.52 (d, *J* = 15.9 Hz, 1 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 3.94 (s, 3 H), 1.35 (t, *J* = 7.2 Hz, 3 H).

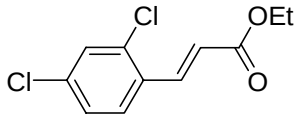


(E)-ethyl 3-(4-(trifluoromethyl)phenyl)acrylate 3f[7] (Table 1, entry 6) was synthesized from 4-(trifluoromethyl)benzaldehyde **1f**. 89% yield. ^{1}H NMR (300 MHz, $CDCl_3$/ TMS) δ 7.70 (d, *J* = 15.9 Hz, 1 H), 7.65 (s, 4 H), 6.53 (d, *J* = 15.9 Hz, 1 H), 4.30 (q, *J* = 7.2 Hz, 2 H), 1.37 (t, *J* = 7.2 Hz, 3 H).

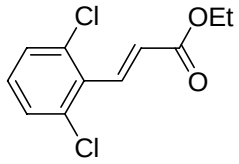


(E)-ethyl 3-(4-fluorophenyl)acrylate 3g[8] (Table 1, entry 7) was synthesized from 4-fluorobenzaldehyde **1g**. 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.65 (d，*J* =15.9 Hz，1 H)，7.54-7.49 (m，2 H)，7.11-7.05 (m，2 H)，

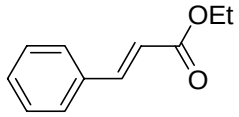
6.36 (d，*J* =15.9 Hz，1 H) ，4.27 (q, *J* = 7.2 Hz, 2 H), 1.34 (t, *J* = 7.2 Hz, 3 H).



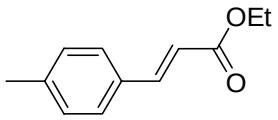
(E)-ethyl 3-(2,4-dichlorophenyl)acrylate 3h[9] (Table 1, entry 8) was synthesized from 2,4-dichlorobenzaldehyde **1h**. 96% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 8.01 (d, *J* = 15.9 Hz，1 H)，7.57-7.54 (m，1 H)，7.45-7.44 (m，1 H)，7.28-7.25(m，1 H)，6.42 (d, *J* = 15.9 HZ，1 H)，4.28 (q, *J* = 7.2 Hz, 2 H), 1.35 (t, *J* = 7.2 Hz, 3 H).



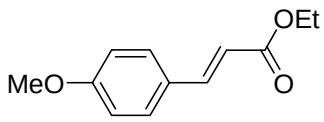
(E)-ethyl 3-(2,6-dichlorophenyl)acrylate 3i[10] (Table 1, entry 9) was synthesize from 2,6-dichlorobenzaldehyde **1i**. 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.78 (d, *J* = 15.9 Hz, 1 H), 7.39-7.34 (m, 2 H), 7.21-7.16 (m, 1 H), 6.59 (d, *J* = 15.9 Hz, 1 H), 4.28 (q, *J* = 7.2 Hz, 2 H), 1.35 (t, *J* = 7.2 Hz, 3 H).



ethyl cinnamate 3j[11] (Table 1, entry 10) was synthesized from benzaldehyde **1j**. 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.70 (d, *J* = 15.9 Hz, 1 H), 7.55-7.52 (m, 2 H), 7.40-7.38 (m, 3 H), 6.45 (d, *J* = 15.9 Hz, 1 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 1.35 (t, *J* = 7.2 Hz, 3 H).

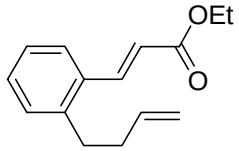


(E)-ethyl 3-p-tolylacrylate 3k[12] (Table 1, entry 11) was synthesized from 4-methylbenzaldehyde **1k**. 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.66 (d, *J* = 15.9 Hz, 1 H), 7.41 (d, *J* = 8.1 Hz, 2 H), 7.18 (d, *J* = 8.1 Hz, 2 H), 6.39 (d, *J* = 15.9 Hz, 1 H), 4.25 (q, *J* = 7.2 Hz, 2 H), 2.37 (s, 3 H), 1.33 (t, *J* = 7.2 Hz, 3 H).

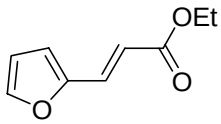


(E)-ethyl 3-(4-methoxyphenyl)acrylate 3l[13] (Table 1, entry 12) was synthesized from 4-methoxybenzaldehyde **1l**. 81% yield. ^{1}H NMR (300 MHz,$CDCl_3$/TMS) δ 7.64

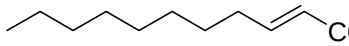
(d, J = 15.6 Hz, 1 H), 7.47 (d, J = 8.7 Hz, 2 H), 6.90 (d, J = 8.7 Hz, 2 H), 6.31 (d, J = 15.6 Hz, 1 H), 4.25 (q, J = 7.2 Hz, 2 H), 3.83 (s, 3 H), 1.33 (t, J = 7.2 Hz, 3 H).



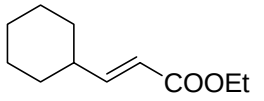
(E)-ethyl 3-(2-(but-3-enyl)phenyl)acrylate 3m (Table 1, entry 13) was synthesized from 2-(but-3-enyl)benzaldehyde **1m**. Fe(TCP)Cl was added in portions, 3.0 equivalent EDA was added to the system within 12h. 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 8.02 (d, J = 15.9 Hz, 1 H), 7.58 (d, J=8.1 Hz, 1 H), 7.35-7.21 (m, 3 H), 6.38 (d, J = 15.9 Hz, 1 H), 5.93-5.80 (m, 1 H), 5.10-5.00 (m, 2 H), 4.28 (q, J = 7.2 Hz, 2 H), 2.90-2.84 (m, 2 H), 2.37-2.30 (m, 2 H), 1.36 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 142.0, 141.3, 137.4, 132.9, 130.0, 129.9 126.5, 126.4, 119.5, 115.3, 60.4, 35.4, 32.7, 14.3; IR(KBr) ν/cm^{-1} 1716, 1634, 1313, 1177; MS (EI, m/z, rel. intensity) 230 (2.6), 157 (27), 117 (100), 115 (86), 91 (28); HRMS(EI) calcd for $C_{15}H_{18}O_2$: 230.1307; found: 230.1309.



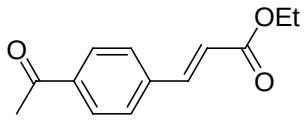
(E)-ethyl 3-(furan-2-yl)acrylate 3n[14] (Table 1, entry 14) was synthesized from furan-2-carbaldehyde **1n**. 87% yield. ^{1}H NMR (300 MHz,$CDCl_3$/TMS) δ 7.48 (s, 1 H), 7.43 (d, J = 15.9 Hz, 1 H), 6.60 (d, J = 2.1 Hz, 1 H), 6.48-6.46 (m, 1 H), 6.32 (d, J = 15.9 Hz, 1 H), 4.25 (q, J = 7.2 Hz, 2 H), 1.32 (t, J = 7.2 Hz, 3 H).



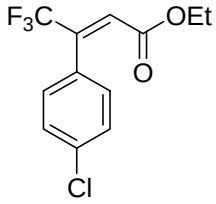
(E)-ethyl undec-2-enoate 3o[15] (Table 1, entry 15) was synthesized from nonanal **1o**. Fe(TCP)Cl was added in portions, 3.0 equivalent EDA was added to the system within 12 h. 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.96 (dt, J = 15.6, 6.9 Hz, 1 H), 5.81 (dt, J = 15.6, 1.5 Hz, 1 H), 4.18 (q, J = 7.2 Hz, 2 H), 2.22-2.15 (m, 2 H), 1.51-1.41 (m, 2 H), 1.32-1.22 (m, 13 H), 0.87 (t, J = 6.8 Hz, 3 H).



(E)-ethyl 3-cyclohexylacrylate 3p[16] (Table 1, entry 16) was synthesized from cyclohexanecarbaldehyde **1p**. 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.92 (dd, *J* = 6.6, 15.9 Hz, 1 H), 5.77 (dd, *J* = 15.9, 1.5 Hz, 1 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 2.15-2.12 (m, 1 H); 1.78-1.70 (m, 4 H), 1.36-1.12 (m, 9 H).



(E)-ethyl 3-(4-acetylphenyl)acrylate 3q[17] (Table 1, entry 17) was synthesized from 4-acetylbenzaldehyde **1q.** 93% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.98 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 16.2 Hz, 1 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 6.53 (d, *J* = 16.2 Hz, 1 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 2.63 (s, 3 H), 1.36 (t, *J* = 7.2 Hz, 3 H).



(E)-ethyl 3-(4-chlorophenyl)-4,4,4-trifluorobut-2-enoate 3r[18] (Table 1, entry 18) was synthesized from 1-(4-chlorophenyl)-2,2,2-trifluoroethanone **1r**. 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.38 (d, *J* = 8.4 Hz,2 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 6.62 (s,1 H), 4.07 (q, *J* = 7.2 Hz, 2 H), 1.12 (t, *J* = 7.2 Hz, 3 H).

References

1. Borovkov, V. V.; Lintuluoto, J. M.; Inove, Y. *Synlett.* **1999**, 61-62.

2.Reddy, M. P.; Rao, G. S. K. *Synthesis* **1980**, *10*, 815.

3.Christoforou, D.; Happer, D. A. R. *Aust. J. Chem.* **1982**, *35*, 729.

4.Costa,Ana.; Najera, C.; Sansano, J. M. *J. Org. Chem.* **2002**, *67*, 5216.

5.Costa,Ana.; Najera, C.; Sansano, J. M. *J. Org. Chem.* **2002**, *67*, 5216.

6. Chen, Y.; Huang, L. Y.; Ranade, M. A.; Zhang, X. P. *J. Org. Chem*. **2003**, *6*, 3714.

7. Murray, R. W.; Shiang, D. L. *J. Chem. Soc., Perkin Trans.2,* **1990**, 349.

8. Masllorens, J.; Moreno, M. M.; Roglans, A. *Org. Lett.* **2003**,*5*, 1559.

9. Kotti, S. R. S. S. ; Xu, X.; Wang, Y. N.; Headley, A. D.; Li, G. G. *Tetrahedron Lett.* **2004**, *45*,

7209

10. Blakemore, P. R.; Ho, D. K.; Nap, W. M. *Org, Biomol, Chem*. **2005**, *8*, 1365

11. Rozen, S.; Lerman, O.; Kol, M. *J. Chem. Soc., Chem. Commun.* **1981**, 443.

12. Kikukawa, K.; Nagira, K.; Wada, F.; Matsuda, T. *Tetrahedron* **1981,** *37*, 31.

13. Reddy, M. P.; Rao, G. S. K. *Synthesis* **1980**, *10*, 815-818.

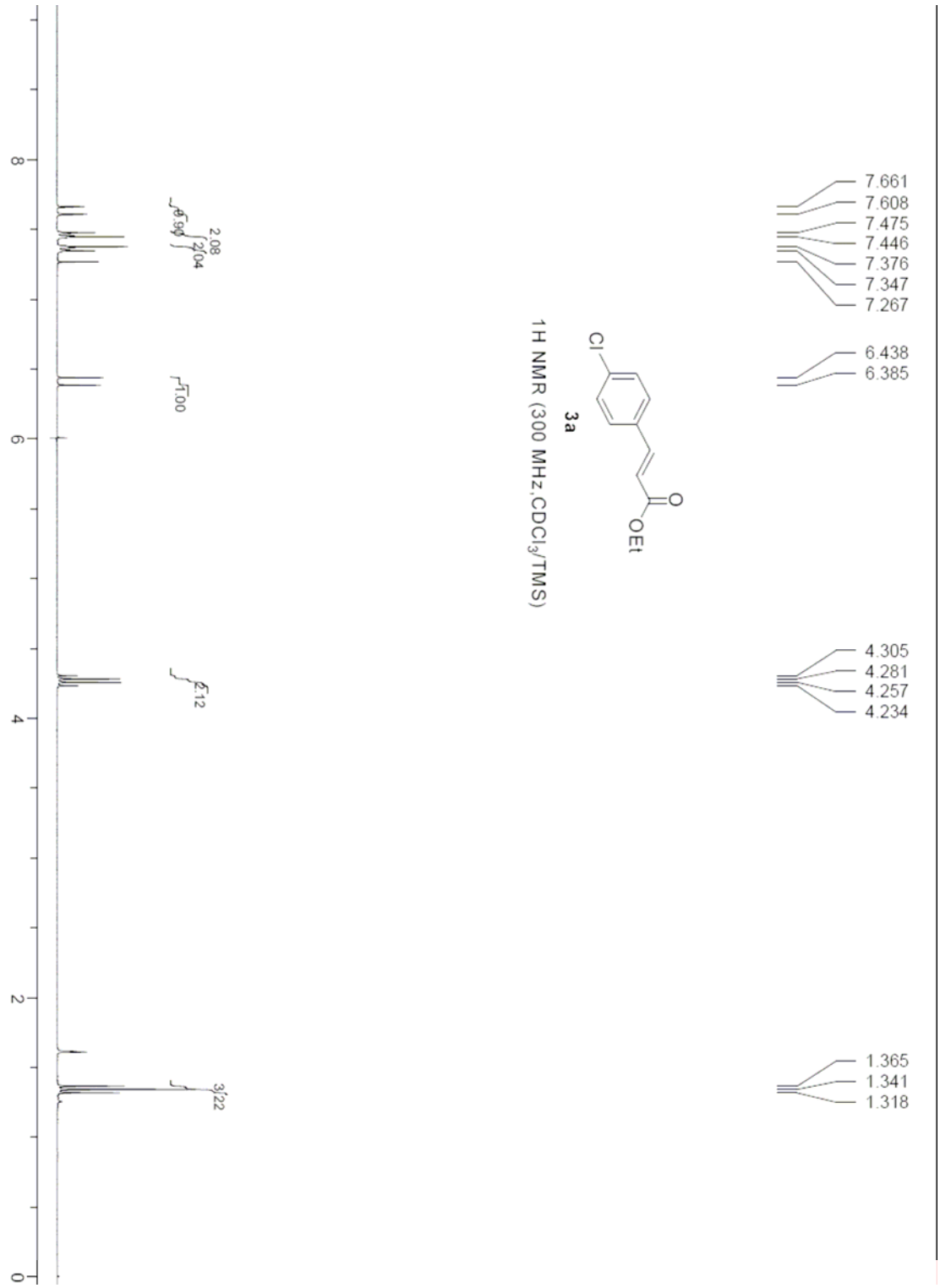
14. Augustinv,M.; Jahreis,G.; Rudorf, W.-D. *Synthesis* **1977**, 472.

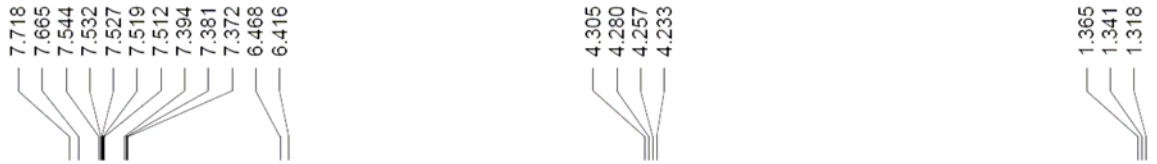
15.Stephan, V.; Andrea, V.; Paul, K.; *J. Org. Chem.61(21),* **1996**, 7473

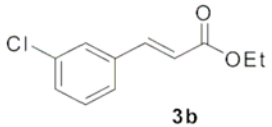
16. Hase, T. A.; Kukkola, P. *Synth. Commun.* **1980**, *10(*6), 451.

17. Chen,Y.; Huang, L.; Ranade, M.; Zhang, X. P. *J. Org. Chem.* **2003**, *68(9)*, 3714.

18. Chen,Y.; Huang, L.; Zhang, X. P. *J. Org. Chem.* **2003**, *68(15)*, 5925.

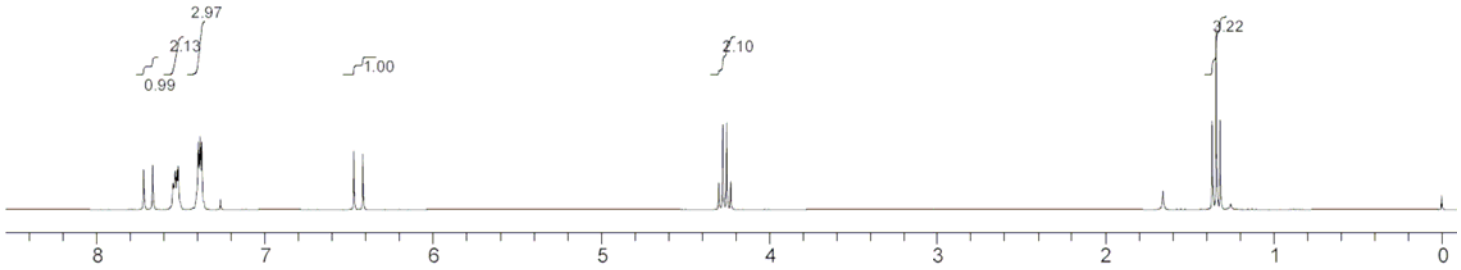

7.661
7.608
7.475
7.446
7.376
7.347
7.267
6.438
6.385
4.305
4.281
4.257
4.234
1.365
1.341
1.318
Cl
O
OEt
3a
1H NMR (300 MHz,CDCl3/TMS)
2.08
2.04
1.00
2.12
3.22
8
6
4
2
0

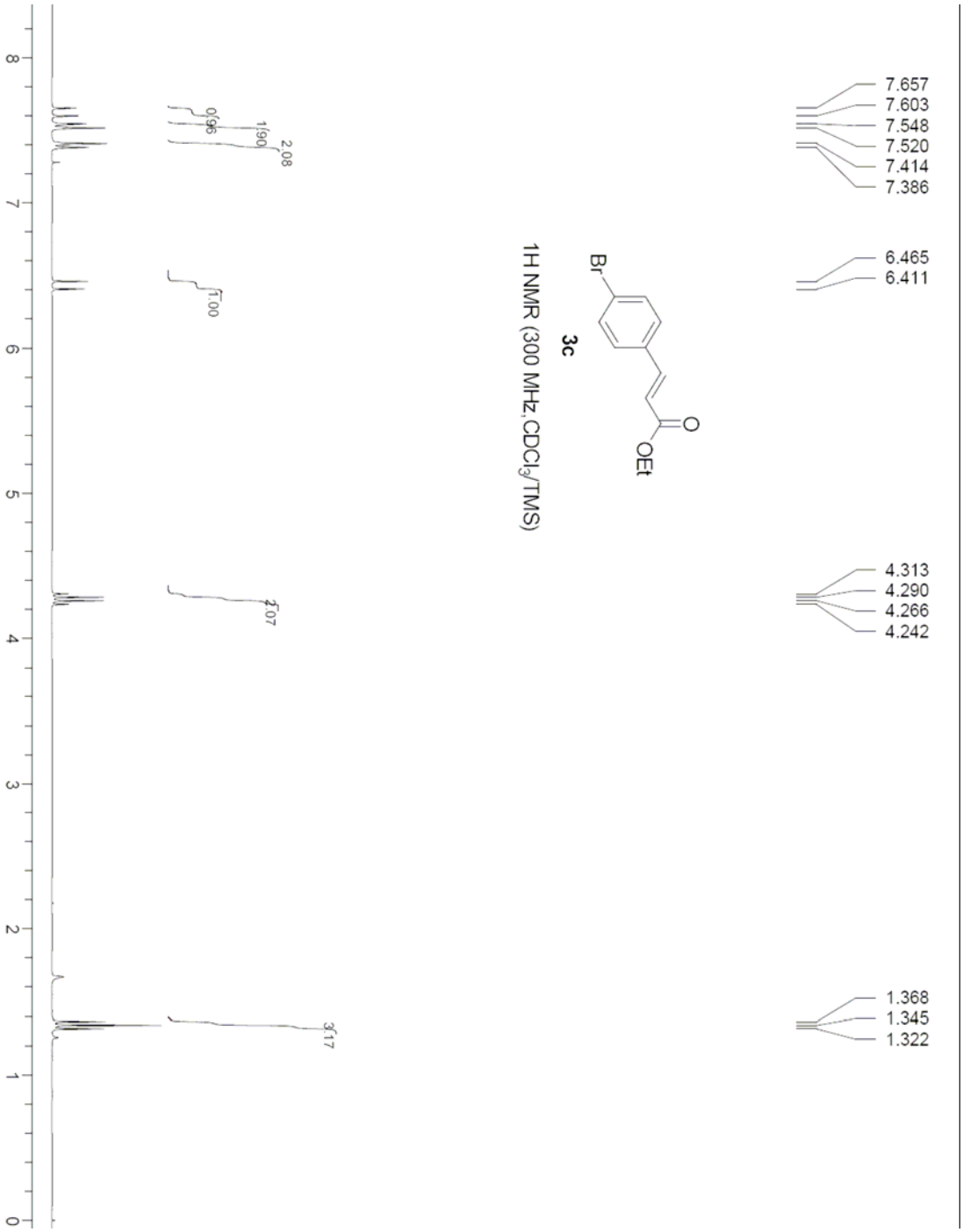


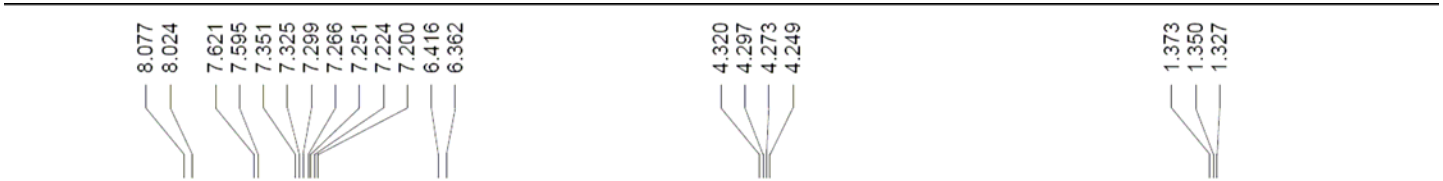


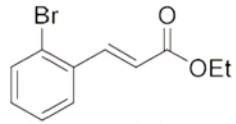
3b

^{1}H NMR (300 MHz, $CDCl_3$/TMS)



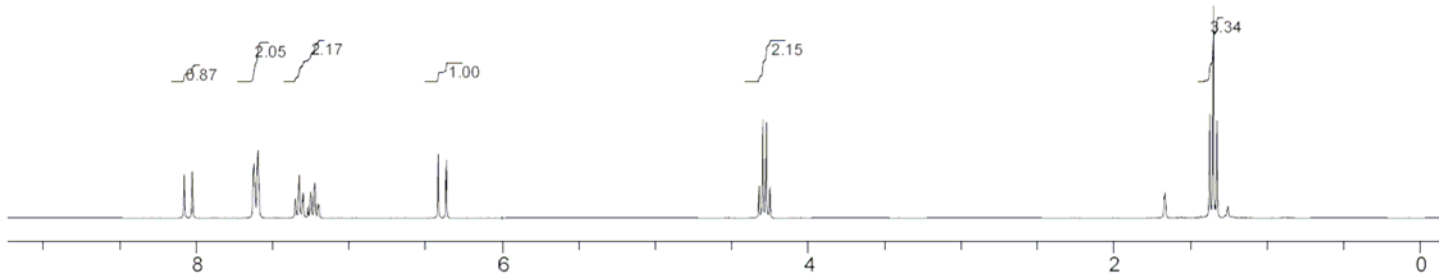

7.657
7.603
7.548
7.520
7.414
7.386
6.465
6.411
4.313
4.290
4.266
4.242
1.368
1.345
1.322
Br
O
OEt
3c
1H NMR (300 MHz,CDCl3/TMS)
2.08
1.90
0.96
1.00
2.07
3.17
8
7
6
5
4
3
2
1
0

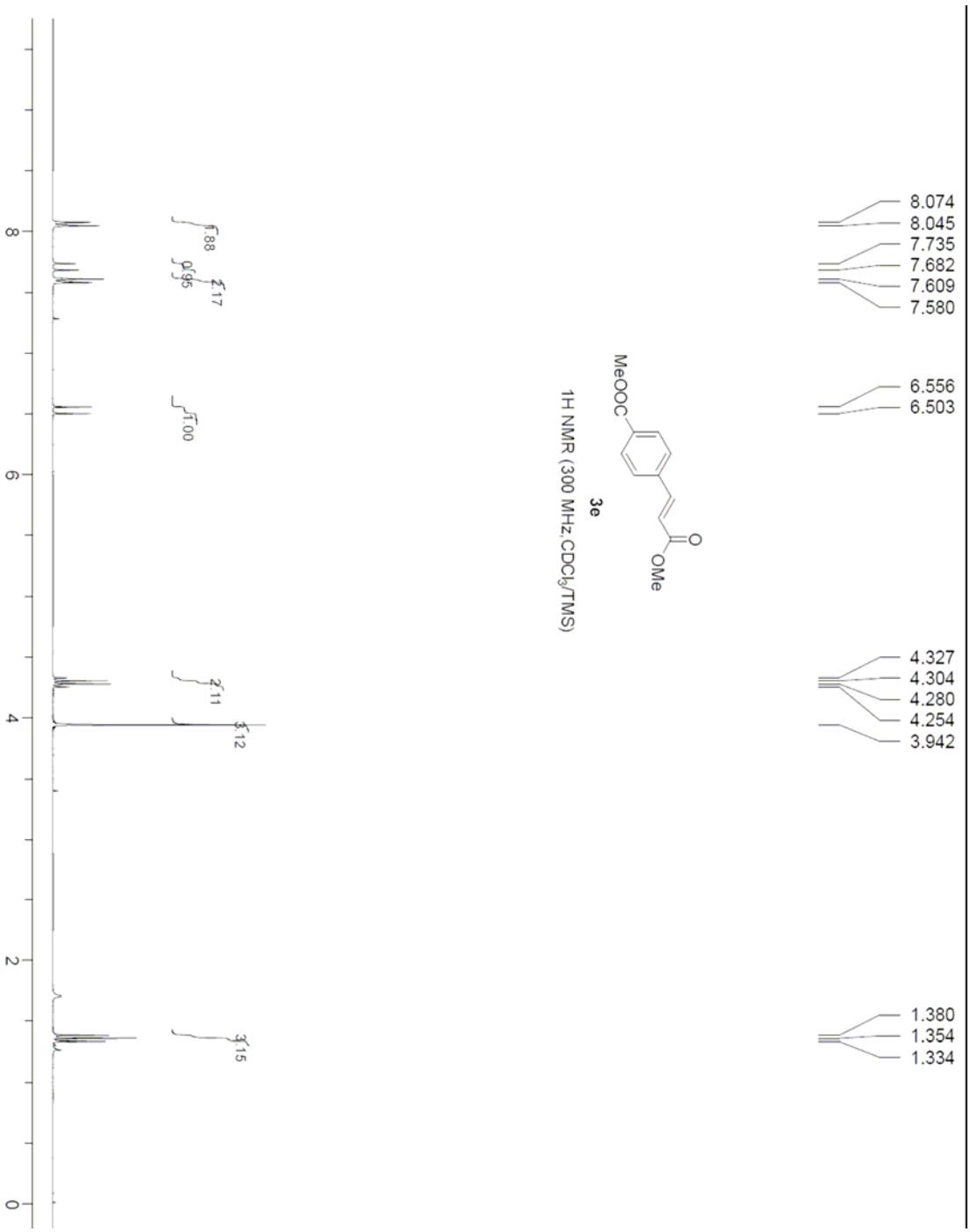


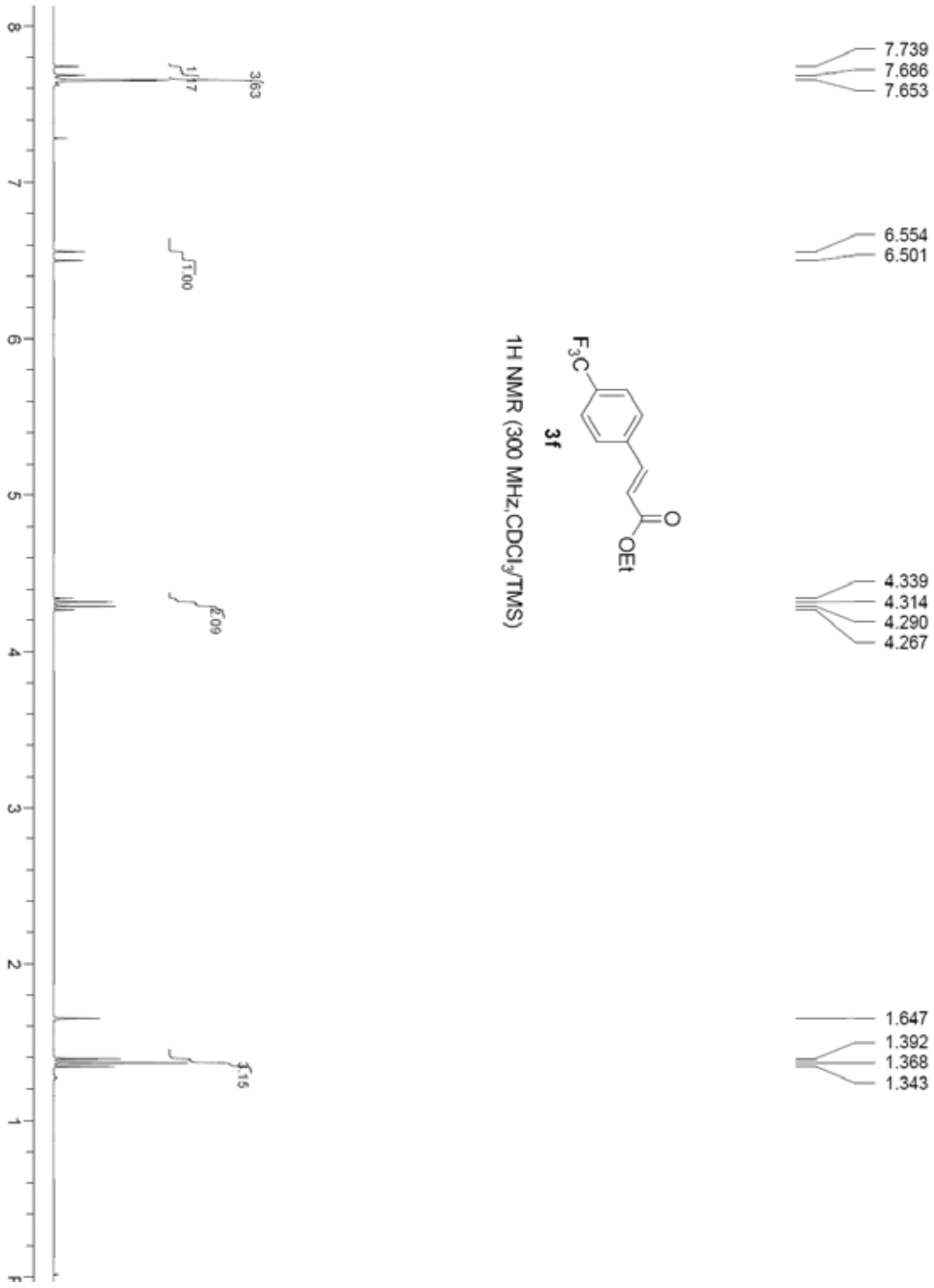


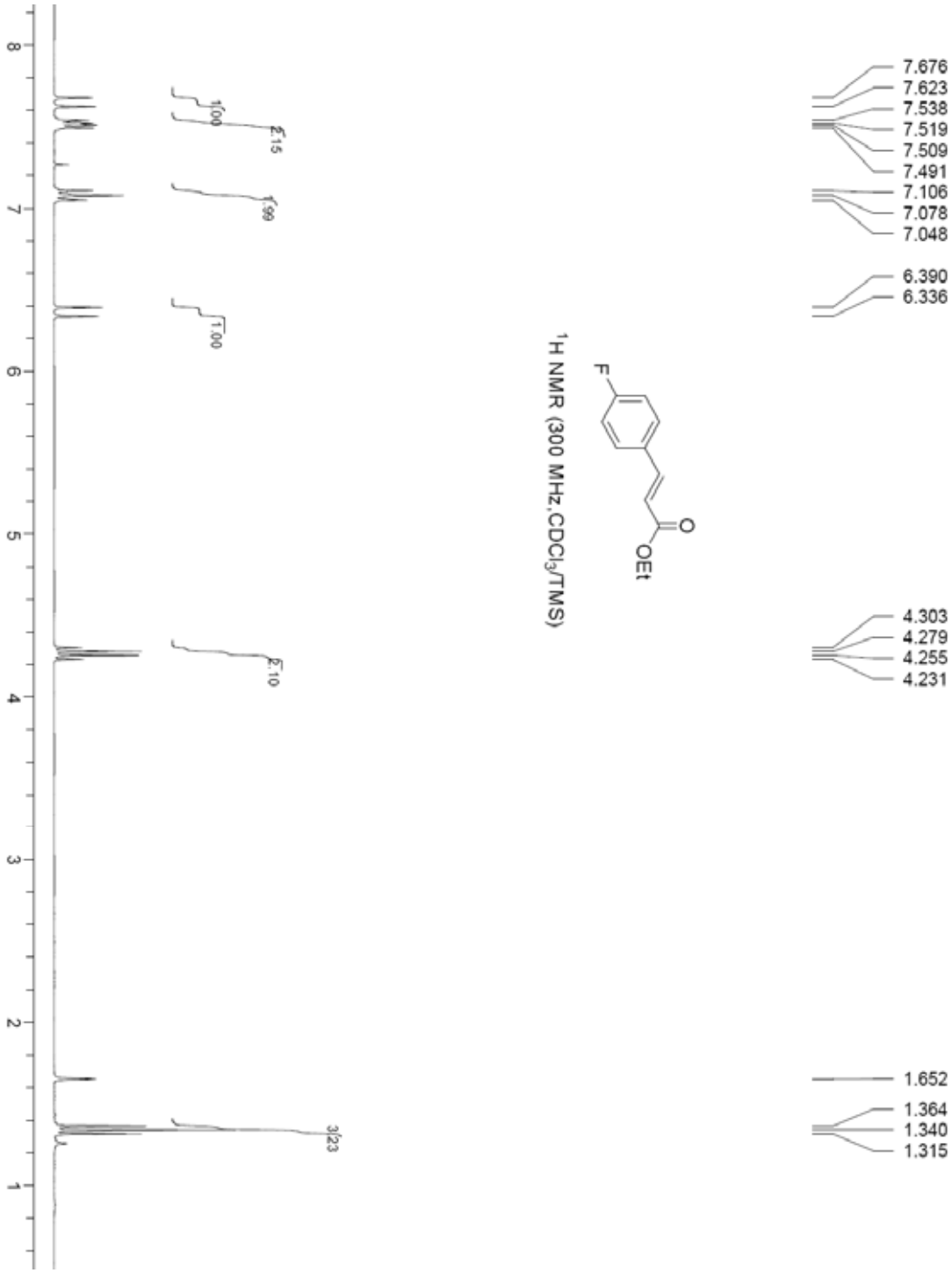
3d

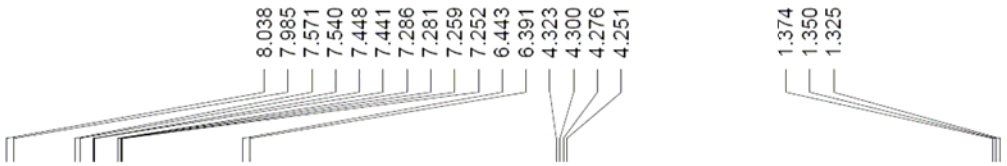
^{1}H NMR (300 MHz, $CDCl_3$/TMS)

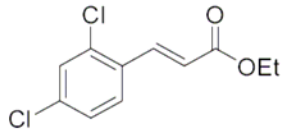



8.074
8.045
7.735
7.682
7.609
7.580
6.556
6.503
4.327
4.304
4.280
4.254
3.942
1.380
1.354
1.334
MeOOC
OMe
3e
1H NMR (300 MHz,CDCl3/TMS)
1.88
2.95
2.17
1.00
2.11
3.12
3.15
0
2
4
6
8

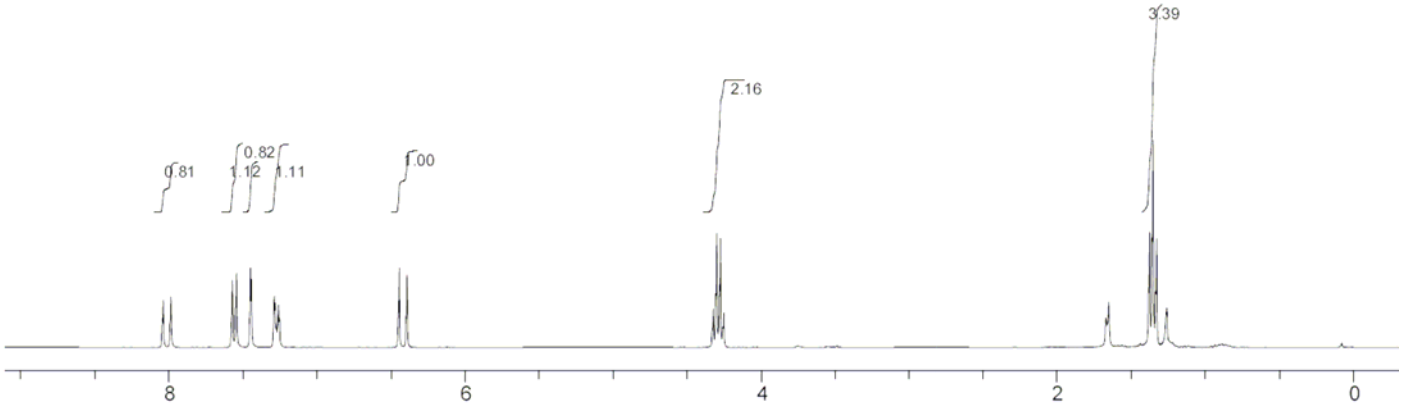

7.739
7.686
7.653
6.554
6.501
4.339
4.314
4.290
4.267
1.647
1.392
1.368
1.343
3.63
1.17
1.00
2.09
3.15
F3C
O
OEt
3f
1H NMR (300 MHz, CDCl3/TMS)

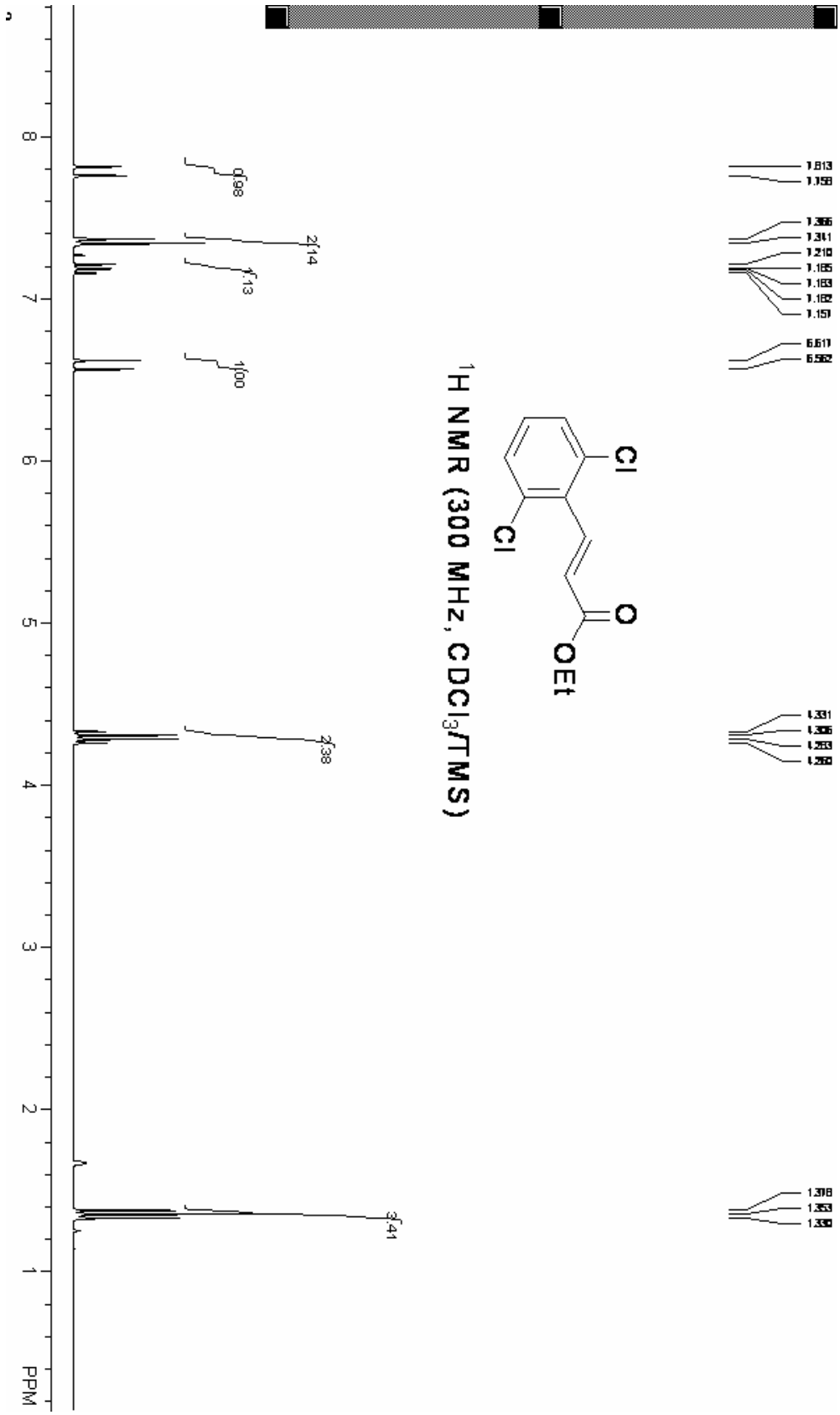

7.676
7.623
7.538
7.519
7.509
7.491
7.106
7.078
7.048
6.390
6.336
4.303
4.279
4.255
4.231
1.652
1.364
1.340
1.315
^{1}H NMR (300 MHz,CDCl$_3$/TMS)
F
O
OEt
1.00
2.15
1.99
1.00
2.10
3.23

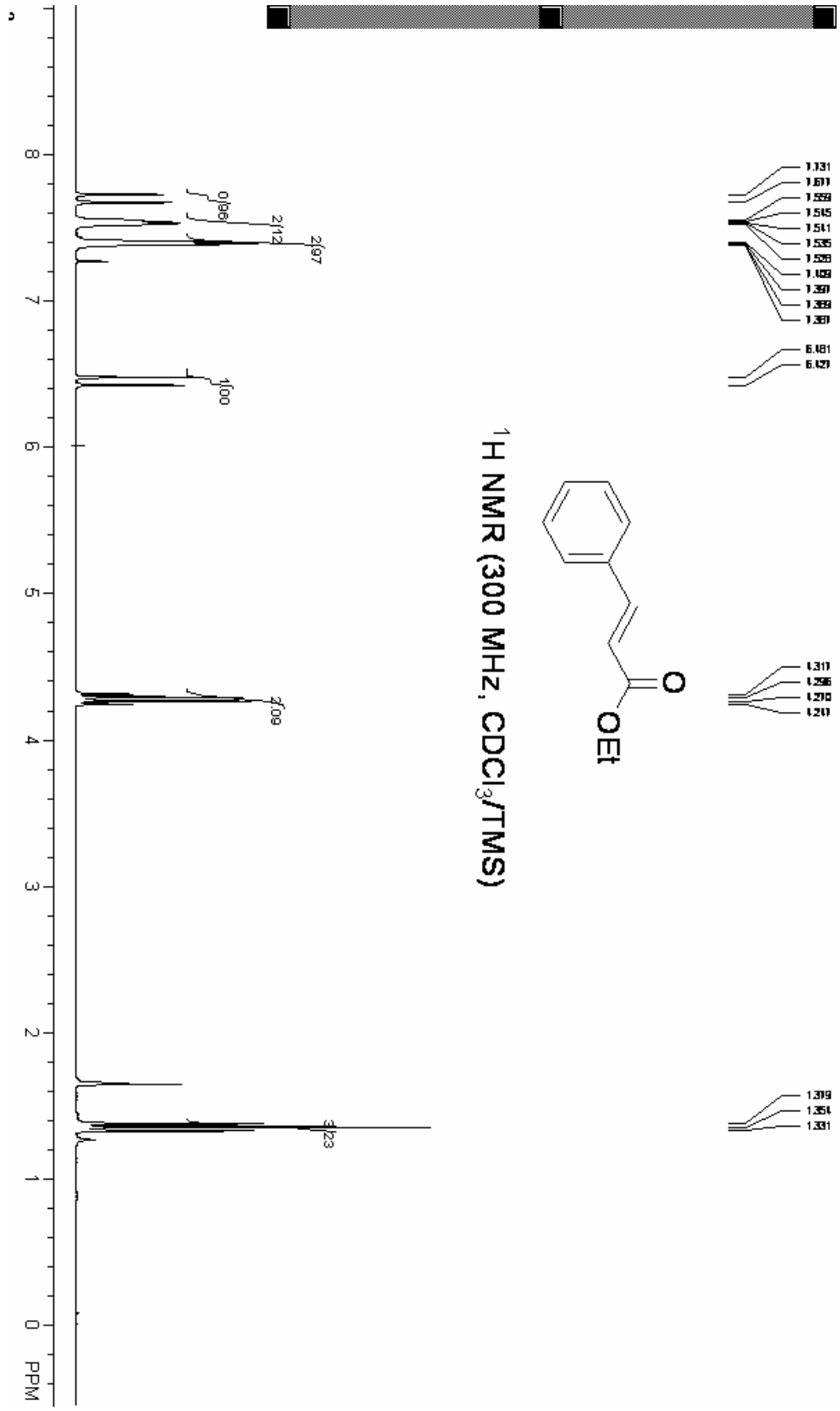


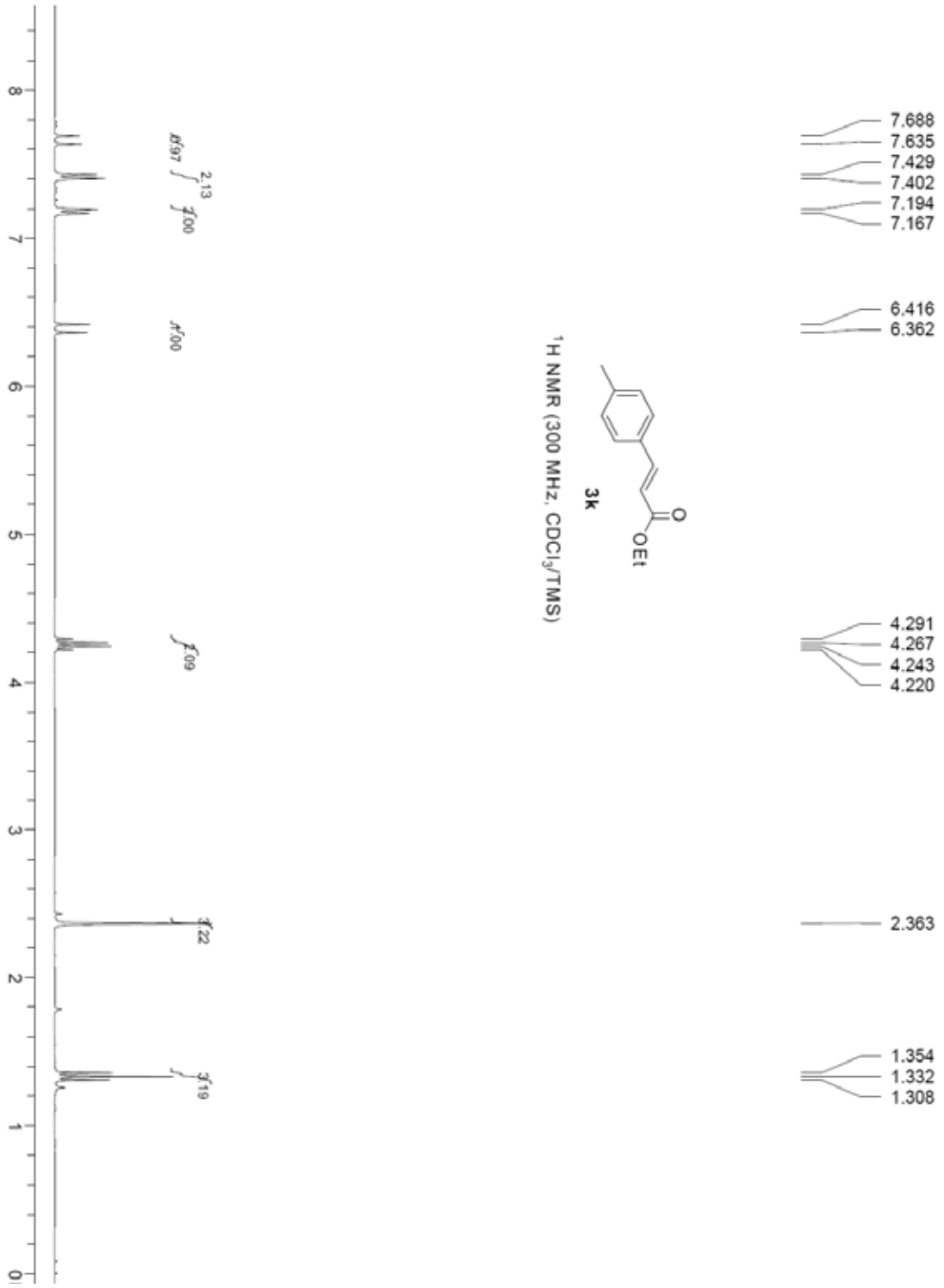


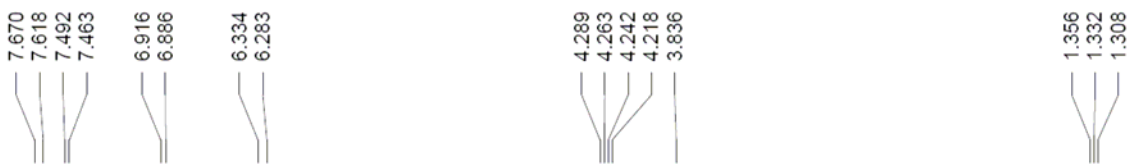
^{1}H NMR (300 MHz,$CDCl_3$/TMS)

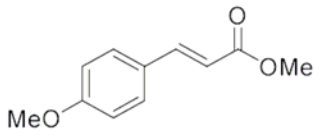



^{1}H NMR (300 MHz, CDCl$_3$/TMS)
Cl
Cl
O
OEt
PPM


^{1}H NMR (300 MHz, CDCl$_3$/TMS)
O
OEt
PPM

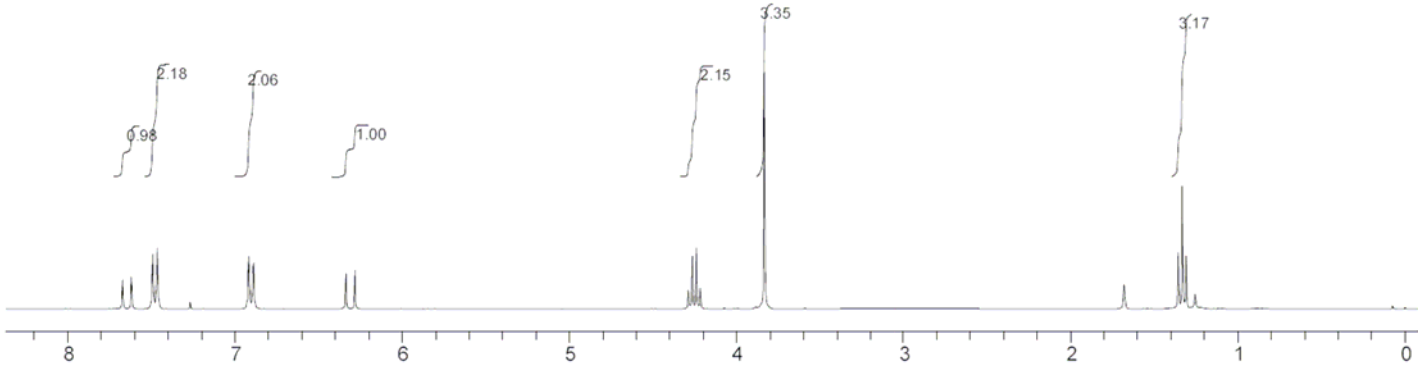

7.688
7.635
7.429
7.402
7.194
7.167
6.416
6.362
4.291
4.267
4.243
4.220
2.363
1.354
1.332
1.308
OEt
O
3k
^{1}H NMR (300 MHz, CDCl$_3$/TMS)

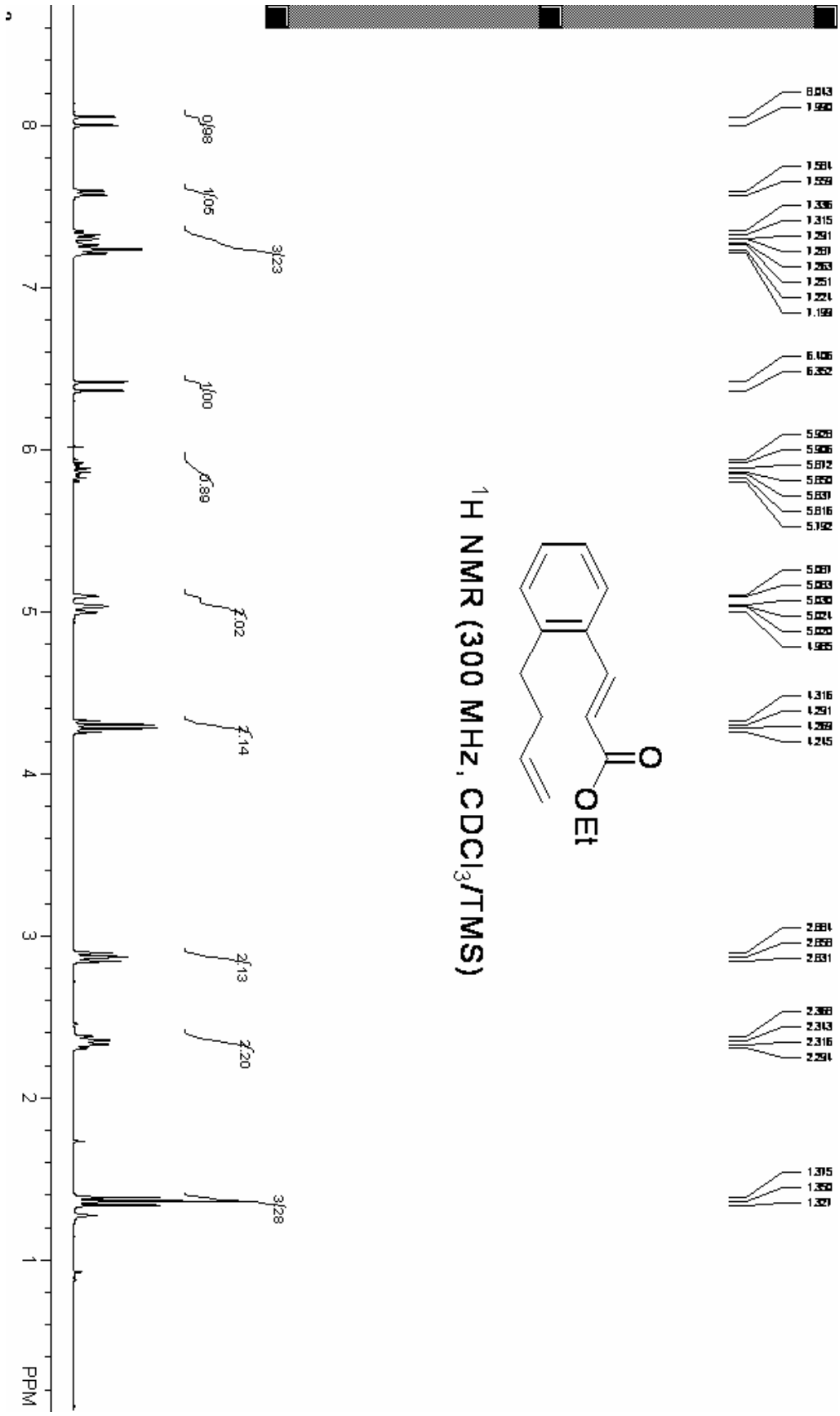


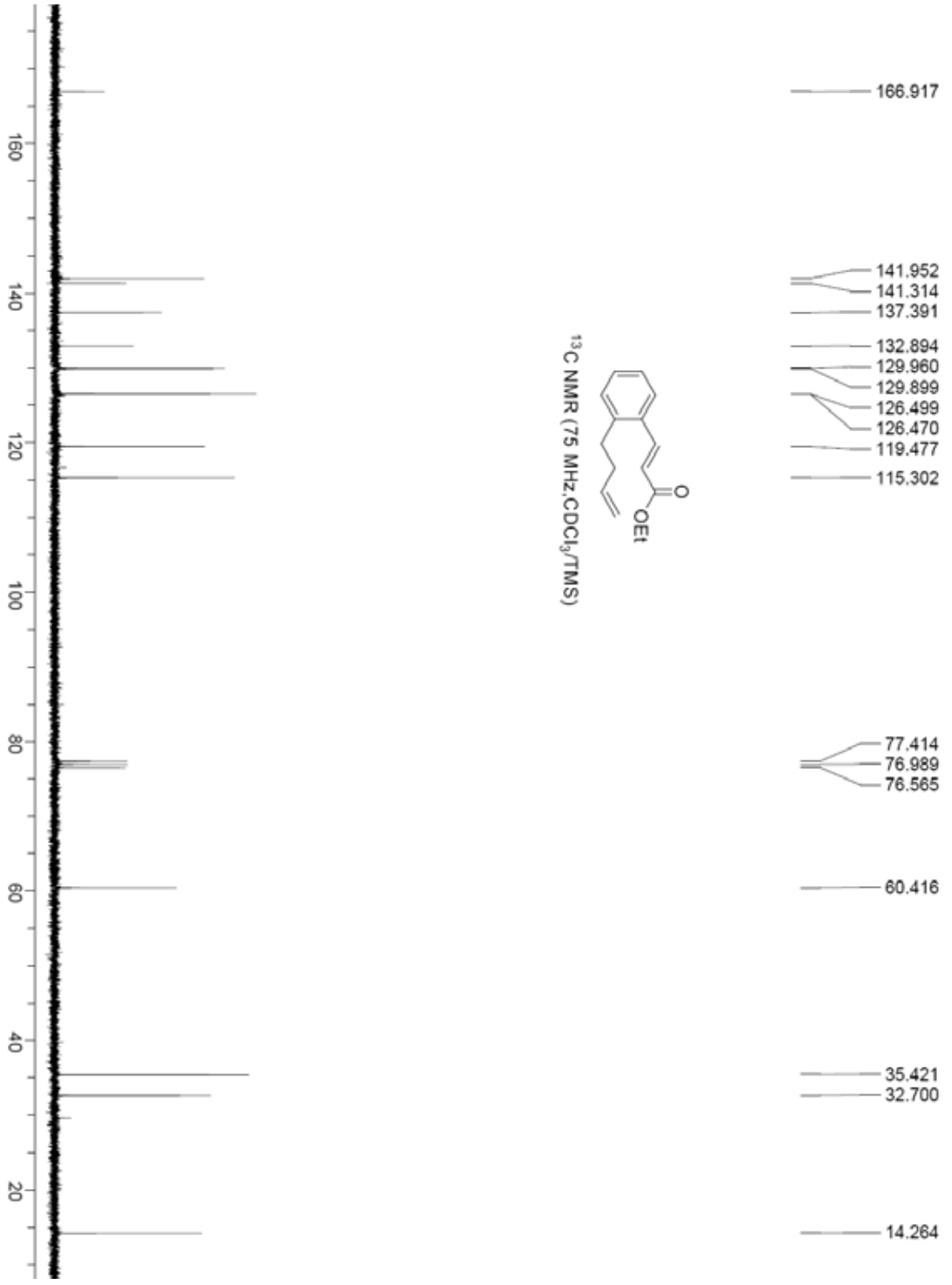


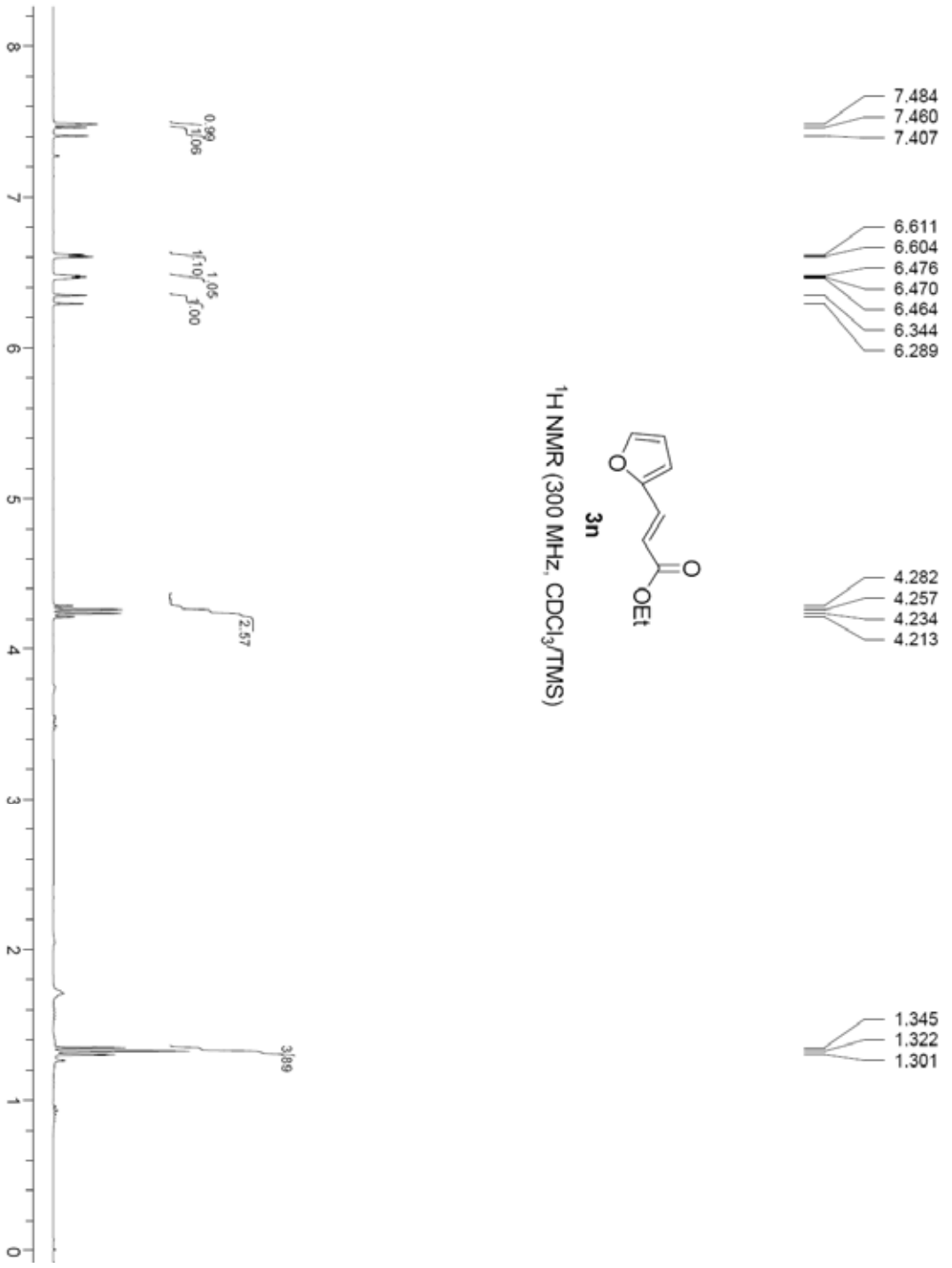
3l

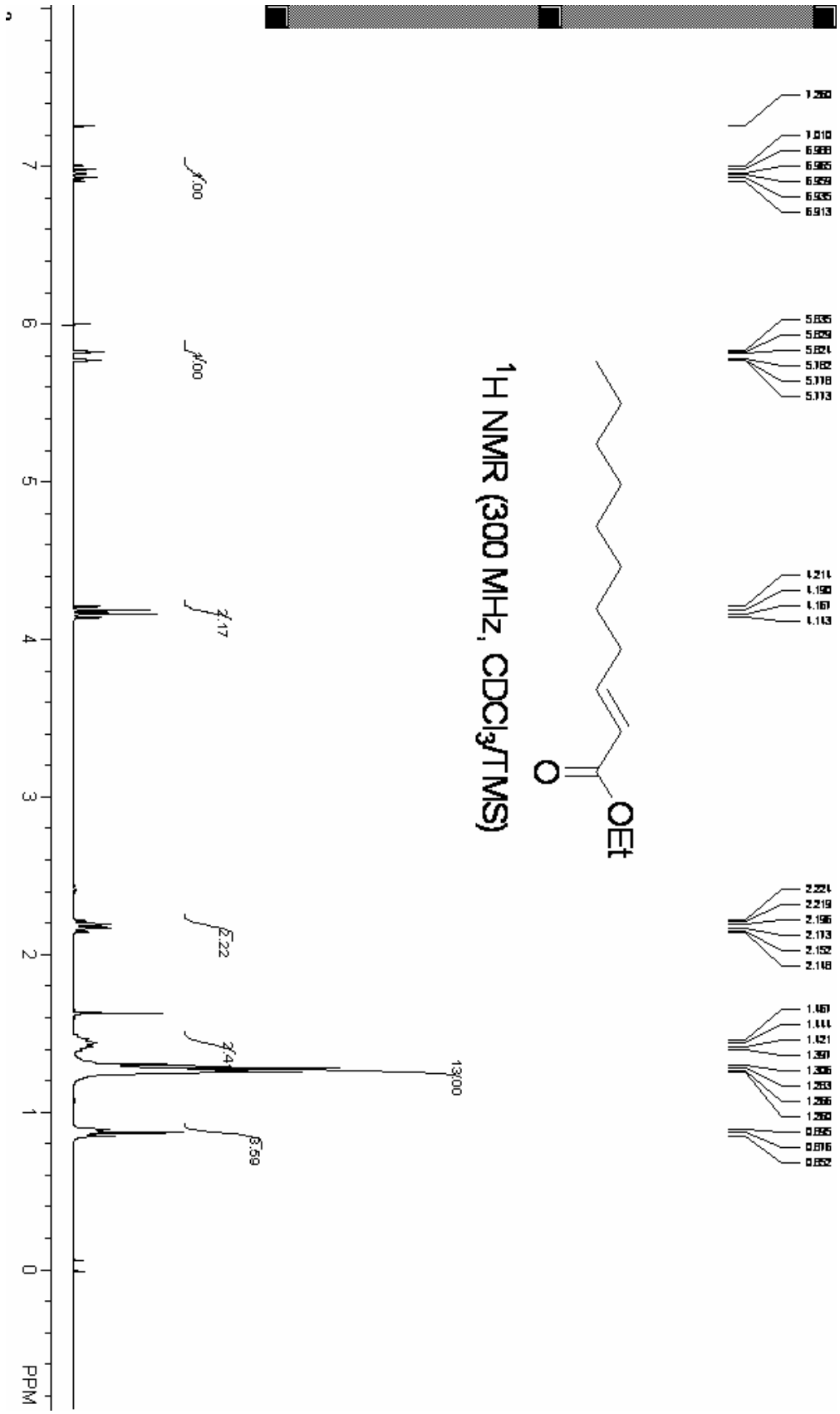
1H NMR (300 MHz,$CDCl_3$/TMS)

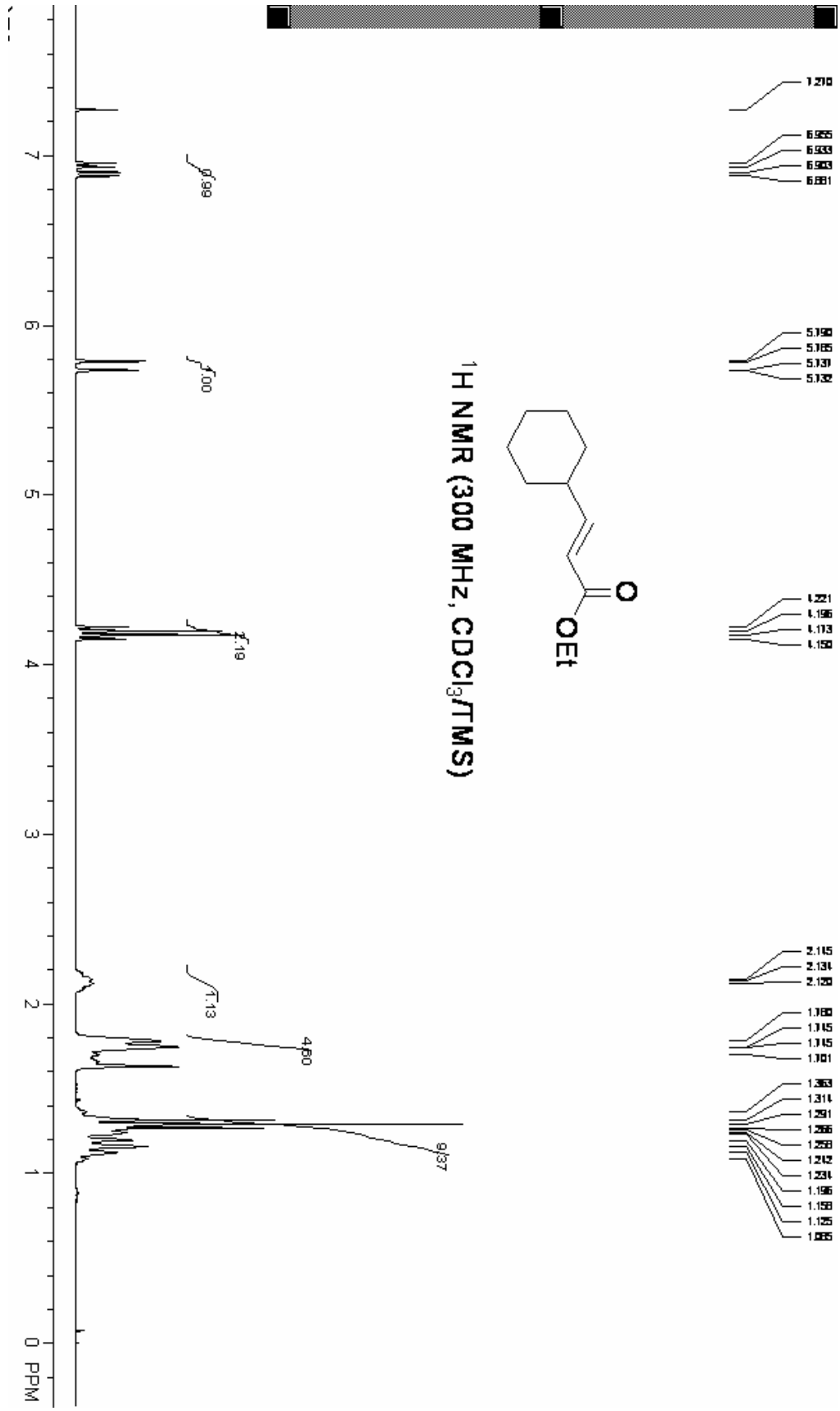


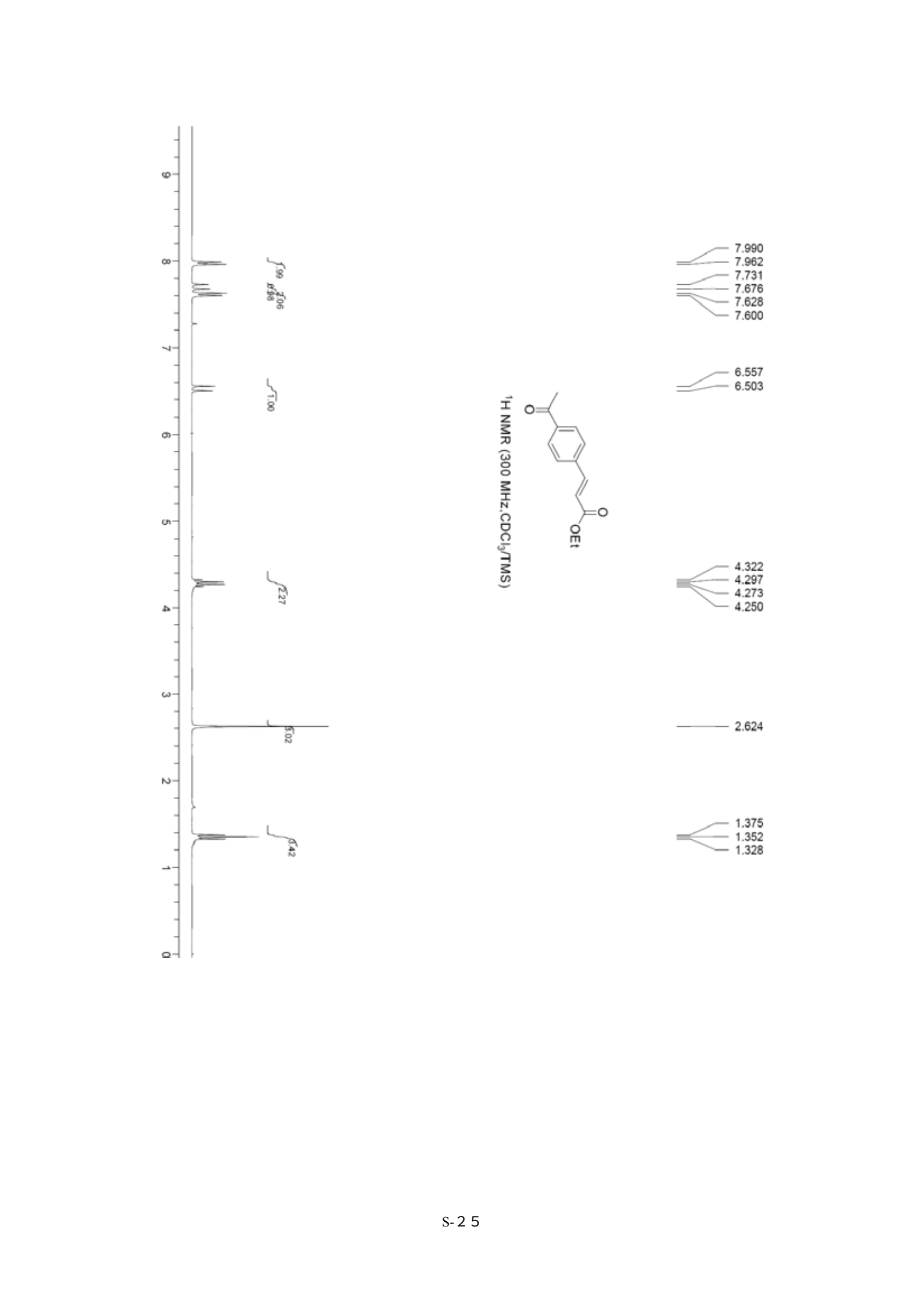

^{1}H NMR (300 MHz, CDCl$_3$/TMS)
OEt
O
8.043
7.994
7.559
7.529
7.336
7.315
7.291
7.269
7.263
7.251
7.224
7.199
6.406
6.352
5.926
5.906
5.872
5.850
5.831
5.816
5.192
5.069
5.063
5.030
5.024
5.020
4.995
4.316
4.291
4.269
4.215
2.884
2.858
2.831
2.368
2.343
2.316
2.294
1.315
1.350
1.329
0.98
1.05
3.23
1.00
0.89
2.02
2.14
2.13
2.20
3.28
8
7
6
5
4
3
2
1
PPM

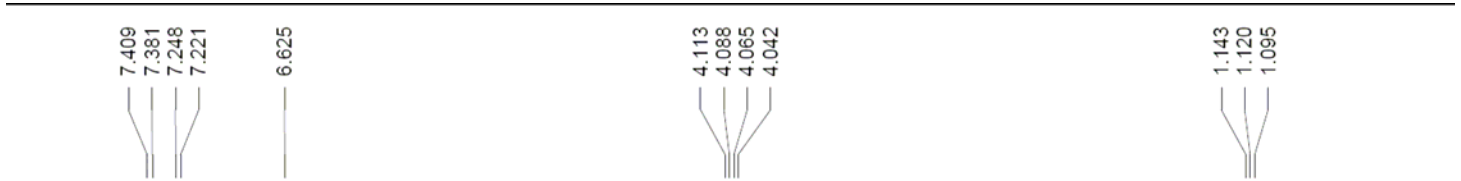

166.917
141.952
141.314
137.391
132.894
129.960
129.899
126.499
126.470
119.477
115.302
77.414
76.989
76.565
60.416
35.421
32.700
14.264
160
140
120
100
80
60
40
20
^{13}C NMR (75 MHz,CDCl$_3$/TMS)
O
OEt

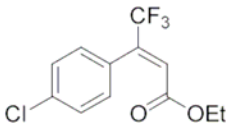

7.484
7.460
7.407
6.611
6.604
6.476
6.470
6.464
6.344
6.289
4.282
4.257
4.234
4.213
1.345
1.322
1.301
3n
OEt
O
O
^{1}H NMR (300 MHz, CDCl$_3$/TMS)
0.99
1.06
1.10
1.05
1.00
2.57
3.89
8
7
6
5
4
3
2
1
0


^{1}H NMR (300 MHz, CDCl$_3$/TMS)
OEt
O
PPM
1.00
1.00
2.17
2.22
2.14
13.00
3.59


^{1}H NMR (300 MHz, CDCl$_3$/TMS)
O
OEt
7.210
6.955
6.933
6.903
6.881
5.190
5.185
5.131
5.132
4.221
4.196
4.173
4.150
2.115
2.134
2.129
1.380
1.315
1.315
1.301
1.363
1.314
1.291
1.266
1.258
1.242
1.234
1.196
1.158
1.125
1.095
9.99
4.00
2.19
1.13
4.60
9.37
0 PPM


7.990
7.962
7.731
7.676
7.628
7.600
6.557
6.503
4.322
4.297
4.273
4.250
2.624
1.375
1.352
1.328
O
O
OEt
^{1}H NMR (300 MHz,CDCl$_3$/TMS)
1.99
2.06
1.98
1.00
2.27
5.02
3.42





3r

^{1}H NMR (300MHz,$CDCl_3$/TMS)