Zinc(II) Catalyzed Conversion of Alkynes to Vinyl Triflates in the Presence of Silyl Triflates

Mohammed H. Al-huniti and Salvatore D. Lepore*

Department of Chemistry, Florida Atlantic University, Boca Raton, FL 33431-0991.

Table of Contents

General Information. Reactions were carried out under an argon atmosphere (unless otherwise stated) in oven dried glassware with magnetic stirring. Purification of reaction products was carried out using flash silica gel 40-63μ. Analytical thin layer chromatography was performed on 0.25mm silica gel 60-F plates. Visualization was accomplished with UV light and aqueous potassium permanganate solution staining followed by air drying. ^{1}H NMR was recorded on a 400 MHz spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as: (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet; coupling constant(s) in Hz, integration). ^{13}C NMR were recorded on 100 MHz spectrometer. Chemical shifts are reported in ppm, with solvent resonance employed as the internal standard (CDCl3 at 77.16 ppm).

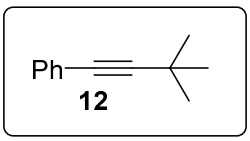
Materials: All reagents were purchased form commercially available sources and were used without further purification.

General procedure for the formation of vinyl triflate

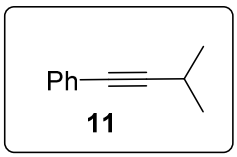
In an oven dried vial containing a teflon-clad magnetic stirrer was added alkyne (1mmol), zinc (II) triflate (0.1mmol) and $CDCl_3$ (3 mL).To that solution was added TMSOTf (1.5 mmol) in one portion and the reaction was allowed to stir at room temperature while monitoring by ^{1}H NMR. After completion, silica gel (200 mg) was added (to hydrolyze excess TMSOTf) and the mixture was filtered through cotton rinsing with dry chloroform. The resulting solution was evaporated under a stream of argon then under high vacuum (0.01 torr) for 1 h.

Spectral data:

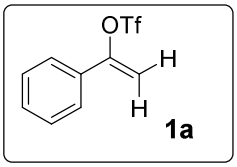
(3,3-dimethylbut-1-yn-1-yl)benzene[1]**:** ^{1}H-NMR (400MHz, $CDCl_3$): δ 1.32 (s, 9H), 7.25-7.27 (m, 3H), 7.27-7.39 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 28.1, 31.3, 79.2, 98.7, 124.3, 127.6, 128.3, 131.7.



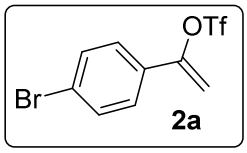
(3-methylbut-1-yn-1-yl)benzene[2]**:** ^{1}H-NMR (400MHz, $CDCl_3$): δ 1.39 (d, 9H), 2.8 (m, 1H), 7.26-7.29 (m, 3H), 7.40-7.42 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 21.4, 23.3, 80.0, 96.0, 124.3, 127.7, 128.4 131.8. HRMS calc. for $C_{11}H_{13}$ $[M+H]^+$: 145.1017 Found: 145.1020



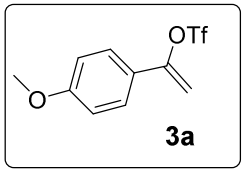
1-phenylvinyl trifluoromethanesulfonate[3]**:** ^{1}H-NMR (400MHz, C6D6): δ 4.85 (d, *J* = 4Hz, 1H), 4.89 (d, *J* = 4Hz, 1H), 7.41 (d, *J* = 8 Hz, 2H), 7.56 (d, *J = 8 Hz*, 2H);^{13}C-NMR (100 MHz, C_6D_6): δ 105.0, 118.6 (q, $J^1_{C\text{-}F}$ = 318 Hz), 125.5, 128.3, 128.9, 130.2, 153.7).



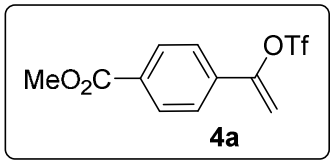
1-(4-bromophenyl)vinyl trifluoromethanesulfonate[4]**:** ^{1}H-NMR (400MHz, $CDCl_3$): δ 4.42 (d, *J* = 4Hz, 1H), 5.62 (d, *J* = 4 Hz, 1H), 7.41 (d, *J* = 8 Hz, 2H), 7.56 (d, *J* = 8Hz, 2H);^{13}C-NMR (100 MHz, $CDCl_3$): δ 105.0, 118.6 (q, $J^1_{C\text{-}F}$ = 318 Hz), 124.9, 126.9, 131.1, 132.3, 152.6.



1-(4-methoxyphenyl)vinyl trifluoromethanesulfonate: ^{1}H-NMR (400MHz, $CDCl_3$): δ 3.02 (s, 3H), 5.25 (d, *J* = 4 Hz, 1H), 5.46 (d, *J* = 4 Hz, 1H), 6.92 (d, *J* = 12 Hz, 2H), 7.48 (d, *J* = 12 Hz, 2H). This compound was hydrolyzed and 4'-methoxyacetopheneone was isolated; ^{1}H-NMR (400MHz, $CDCl_3$): δ 2.54 (s, 3H), 3.85 (s, 3H), 6.91 (d, *J* = 8 Hz, 2H), 7.93 (d, *J* = 8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 26.42, 55.5, 113.7, 127.9, 130.7, 163.5, 196.9.

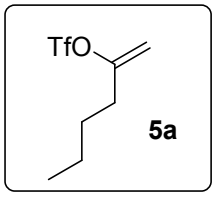


methyl 4-(1-(((trifluoromethyl)sulfonyl)oxy)vinyl)benzoate: ^{1}H-NMR (400MHz, $CDCl_3$): δ 1.04 (t, *J* = 7.2 Hz, 3H), 4.39 (t, *J* = 7.2 Hz, 2H), 5.49 (d, *J* = 8Hz, 1H), 7.16 (d, *J* = 8Hz, 1H), 7.61 (d, *J* = 8 Hz, 2H) 8.09 (d, *J* = 8 Hz, 2H);^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.8, 61.5, 106.4, 118.6(q, $J^1_{C\text{-}F}$ = 318 Hz),125.4, 130.2, 132.2, 136.0, 152.6, 165.8.



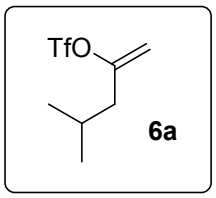
[1] Cahiez, G.; Gager, O. ; Buendia, J. *Angew. Chem. Int. Ed.* **2010**, 49, 1278-1281.
[2] Egi, M.; Kawai, T.; Umermura, M.; Akai, S. *J. Org. Chem.* **2012**, 77, 7092-7097
[3] Yang, Y.; Moscetta, E. G.; Rioux, R. M.; *Chem. Cat. Chem*. **2013**, 10, 3005-3013.
[4] Saulnier, M. G.; Kadow, J. F.; Tun, M. M.; Langley, D. R.; Vyas, D. M. *J Am. Chem Soc,* **1998**, 111, 8320.

hex-1-en-2-yl trifluoromethanesulfonate[7,6]**:** ^{1}H-NMR (400MHz, $CDCl_3$): δ 0.93 (t, *J* = 8 Hz, 3H), 1.39 (m, 2H), 1.51 (m, 2H), 2.34 (t, *J* = 8 Hz, 2H), 4.93 (d, *J* = 4Hz, 1H), 5.09 (d, *J* = 4Hz, 1H) ;^{13}C-NMR (100 MHz, $CDCl_3$): δ 13.8, 21.9, 28.2, 33.7, 104.1, 118.6 (q, $J^{1}_{C\text{-}F}$ = 318 Hz), 157.2.



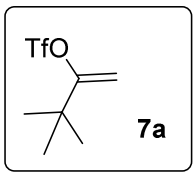
5a

4-methylpent-1-en-2-yl trifluoromethanesulfonate: ^{1}H-NMR (400MHz, $CDCl_3$): δ 0.96 (d, *J* = 6.8 Hz, 6H), 1.85-1.95 (m, 1H), 2.2 (d, *J* = 7.2 Hz, 2H), 4.92 (dd, *J* = 3.4, 0.4 Hz, 1H), 5.12 (d, *J* = 3.2 Hz, 1H) ;^{13}C-NMR (100 MHz, $CDCl_3$): δ 21.9, 25.6, 43.3, 105.3, 118.5 (q, $J^{1}_{C\text{-}F}$ = 315Hz), 156.2.



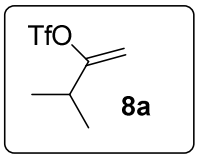
6a

3,3-dimethylbut-1-en-2-yl trifluoromethanesulfonate[7,6]**:** ^{1}H-NMR (400MHz, $CDCl_3$): δ 1.18 (s, 9H), 4.96 (d, *J* = 4 Hz, 1H), 5.06 (d, *J* = 4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 27.6, 36.6, 99.9, 118.5 (q, $J^{1}_{C\text{-}F}$ = 318 Hz),146.6.



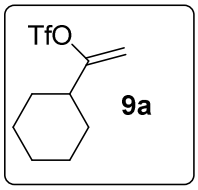
7a

3-methylbut-1-en-2-yl trifluoromethanesulfonate[5]**:** ^{1}H-NMR (400MHz, $CDCl_3$): δ 1.16 (d, *J* = 8 Hz, 1H), 2.56 (m, 1H), 4.93 (dd, *J* = 1.12, 3.6 Hz, 1H), 5.07 (d, J = 3.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.9, 33.1, 101.7, 118.6 (q, $J^{1}_{C\text{-}F}$ = 318 Hz), 162.3.



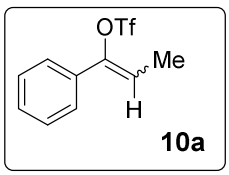
8a

1-cyclohexylvinyl trifluoromethanesulfonate : ^{1}H-NMR (400MHz, $CDCl_3$): δ 1.17-1.31 (m, 6H),1.17-1.18 (m, 4H), 2.15-2.29 (m, 1H), 4.88 (dd, J = 4, 2.8 Hz, 1H), 5.05 (d, J = 4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.7, 25.9, 30.4, 42.4, 101.9, 117.1, 161.6.[6]



9a

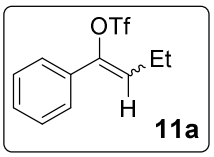
1-phenylprop-1-en-1-yl trifluoromethanesulfonate[7]**:** Two isomers were observed 68:32 *Z:E*, for Z isomer (major) ^{1}H-NMR (400MHz, $CDCl_3$): δ 1.85 (d, *J* = 8 Hz, 1H), 5.95 (q, J = 8 Hz, 1H), 7.37-7.46 (m, 5H). For E isomer (minor) ^{1}H-NMR (400MHz, $CDCl_3$): δ 1.95 (d, J = 8Hz, 1H), 5.94 (q, *J* = 8 Hz, 1H), 7.37-7.46 (m, 5H).



10a

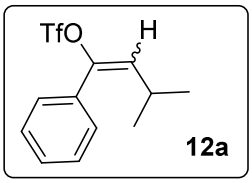
[5] Summerville, R. H.; Senkler, C. A.; Schleyer, P. V.; Dueber ,T. E.; Stang, P. J. *J. Am. Chem. Soc*. **1974**, 96, 1100.
[6] Matsubara, S.; Hibino, J.-I.; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Organomet. Chem.* **1985**, *285*, 163.
[7] Luan, L.; Song, J-S. ; Bullock, M. *J. Org. Chem*. **1995**, 60, 7170.

1-phenylbut-1-en-1-yl trifluoromethanesulfonate: two isomers were observed 75:25 *Z:E*, for Z isomer (major), 1H-NMR (400MHz, $CDCl_3$): δ 1.09 (t, *J* = 8 Hz, 3H), 2.23 (p, *J* = 8 Hz, 2H) 5.85 (t, *J* = 8 Hz, 1H), 7.37-7.46 (m, 5H);^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.1, 21.1, 118.6 (q, J^1_{C-F} = 318 Hz), 125.9, 128.6, 128.7, 130.0, 131.8, 146.7. For *E* isomer (minor), ^{1}H-NMR (400MHz, $CDCl_3$): 1.14 (t, J = 8 Hz, 3H), 2.39 (p, *J* = 8 Hz, 2H), 5.83 (t, *J* = 8 Hz, 2H), 7.37-7.46 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 13.4, 20.4, 118.6 (q, J^1_{C-F} = 318 Hz), 125.8, 128.7, 128.8, 129.5, 131.7, 146.7. Hydrolysis of compoud **11a** gives Butyrophenone[8] :^{1}H-NMR (400MHz, $CDCl_3$): δ 1.00 (t, *J* = 7.4 Hz, 3H), 1.77 (m, 2H) 2.94 (t, *J* = 7.4 Hz, 2H), 7.43-7.53 (m, 2H) 7.53-7.56 (m, 1H), 7.95-7.97 (m, 2H);^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.0, 17.8, 40.5, 128.1, 128.6, 132.9, 137.1, 200.5.



11a

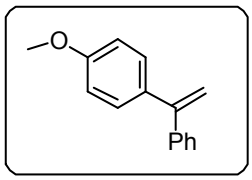
3-methyl-1-phenylbut-1-en-1-yl trifluoromethanesulfonate^{1}H-NMR (400MHz, $CDCl_3$): δ 1.09 (d, *J* = 4Hz, 6H), 2.54 (m, 1H), 5.67 (d, 1H), 7.36-7.44 (m, 5H);^{13}C-NMR (100 MHz, $CDCl_3$): δ 23.0, 27.5, 118.6 (q, J^1_{C-F} = 318 Hz), 126.0, 128.7, 128.9, 130.0, 131.2, 145.6.



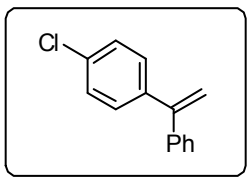
12a

Spectral data for Suzuki coupling products:

1-methoxy-4-(1-phenylvinyl)benzene[9]: (74% two step yield); 1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.29 (m, 5H), 7.26 (d, J = 8.8 Hz, 2H), 6.84 (d, *J* = 8 Hz, 2H), 5.38 (d, *J* = 1.2 Hz, 1H), 5.34 (d, I = 1.2 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl3): δ 55.36, 113.0, 113.6, 127.8, 128.2, 128.4, 129.5, 134.0, 141.9, 149.6, 159.4; HRMS calc. for $C_{15}H_{15}O$ $[M+H]^+$: 211.1117. Found: 211.1118

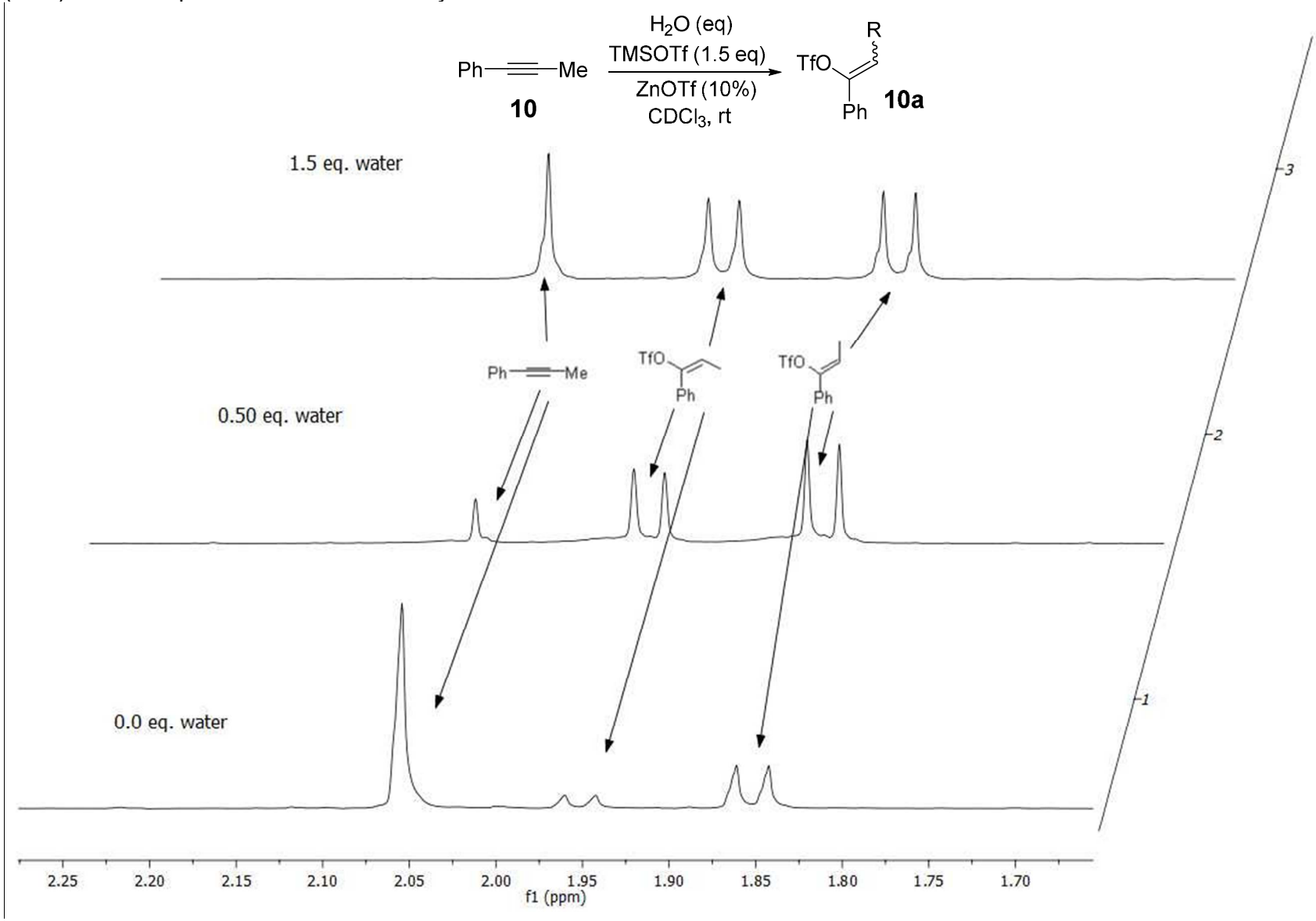


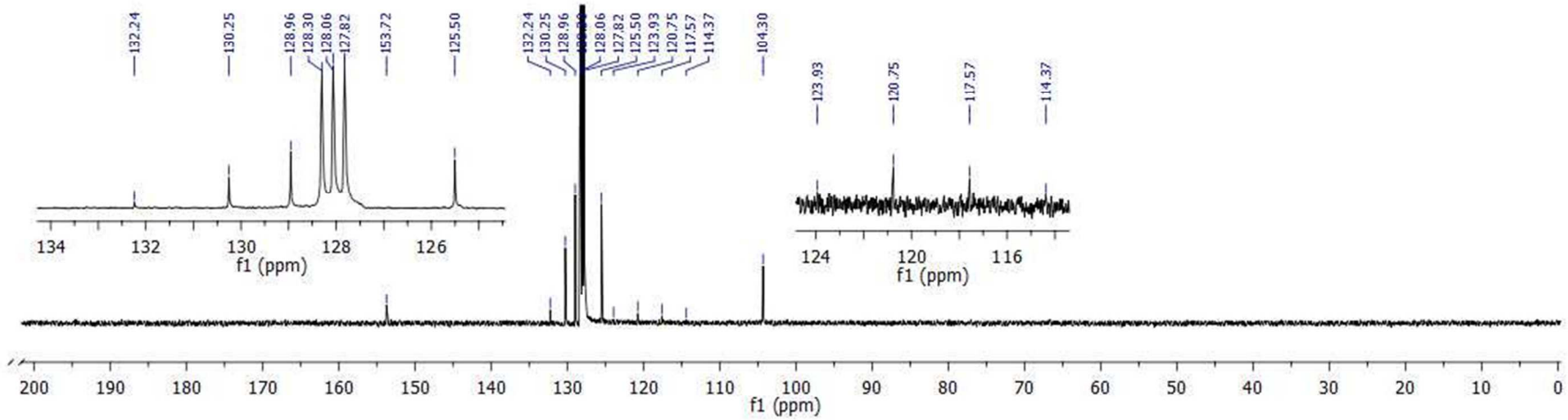
1-chloro-4-(1-phenylvinyl)benzene[10]: (71% two-step yield); ^{1}H-NMR (400MHz, $CDCl_3$): δ 5.47 (s, 1H), 5.49 (s, 1H), 7.28-7.35 (m, 8H);^{13}C-NMR (100 MHz, $CDCl_3$): δ 114.8, 128.0, 128.3, 128.4, 128.5, 129.7, 133.7, 140.1, 141.1, 149.1.

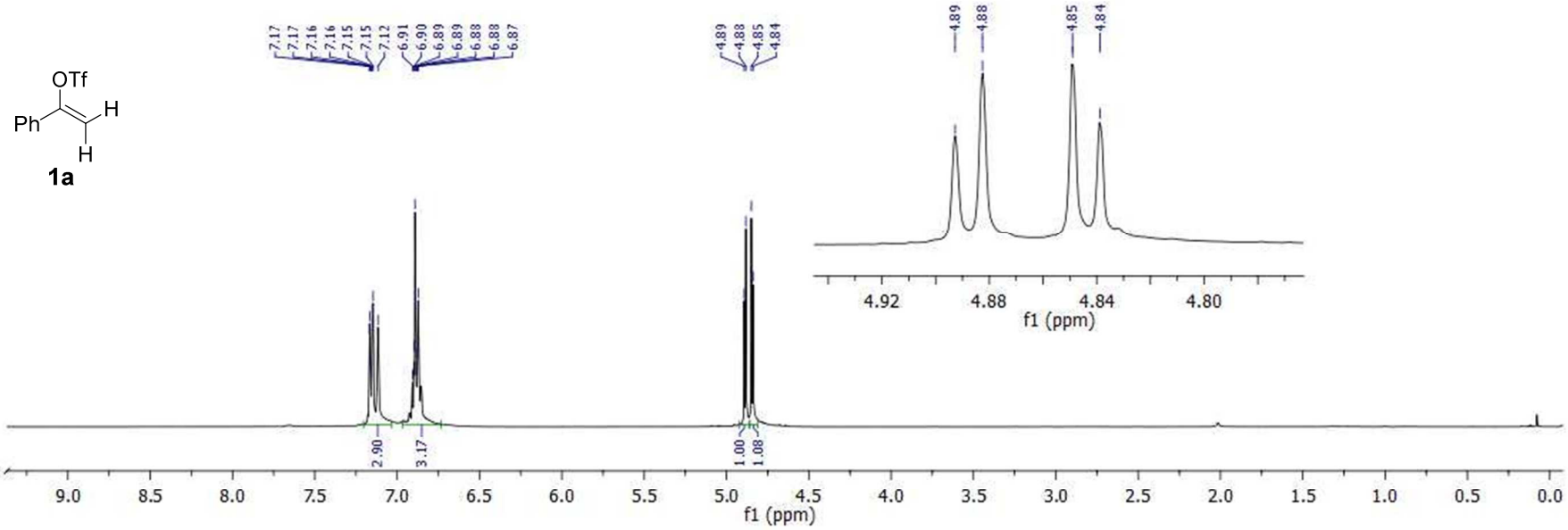


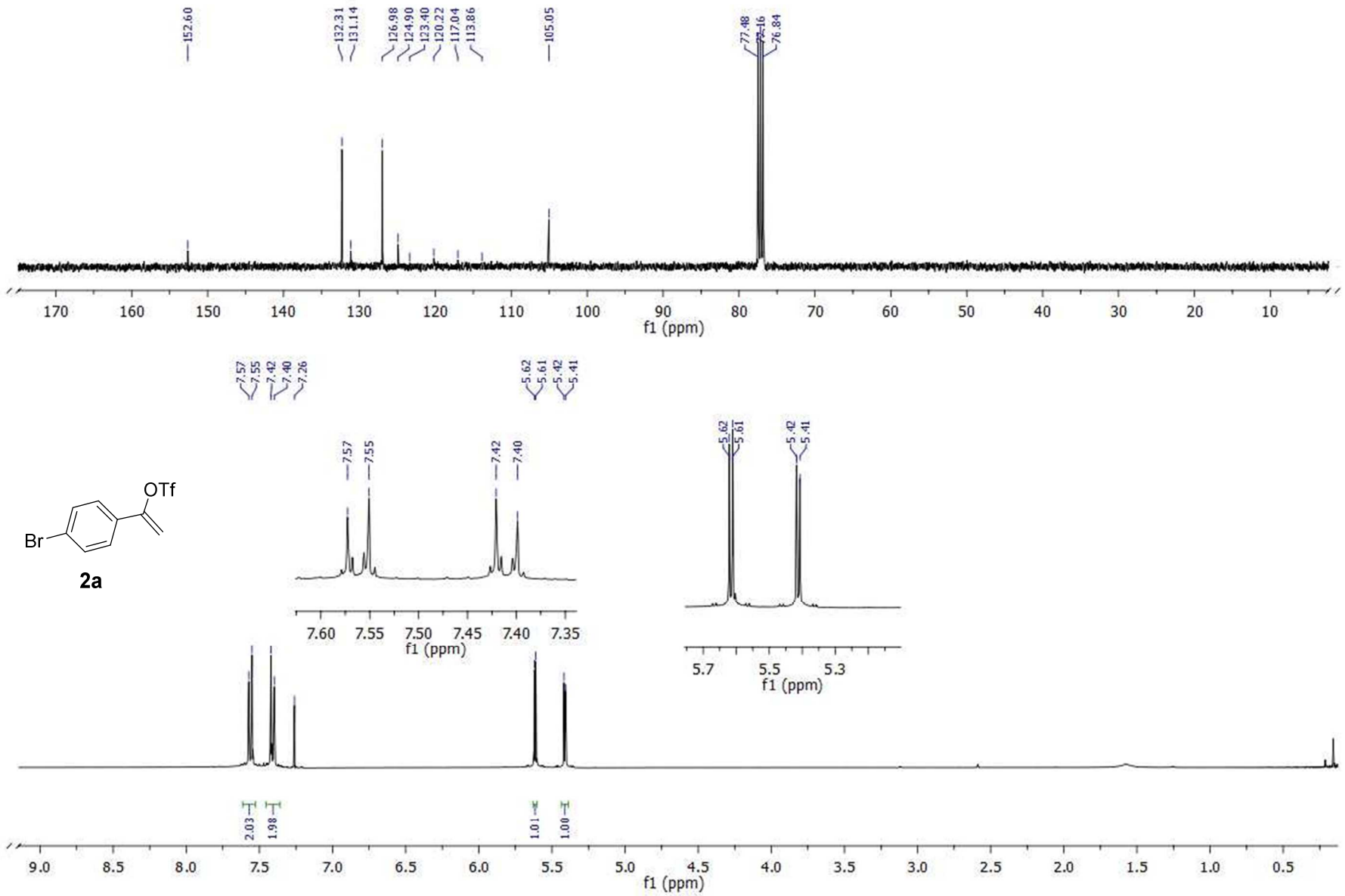
[8] Meng, L.; Su, J.; Zha, Z.; Zhang, L.; Zhang, Z.; Wang, Z. *Chem. Eur. J.* **2013**, 19, 5542-5545
[9] Alacid, E.; Najera, C. *J. Org. Chem*. **2008**, 73, 2315
[10] Zou, Y.; Qin, L.; Ren, X.; Lu, Y.; Li, Y. Zhou, J. *Chem Eur. J.* **2013**, 3504-3511.

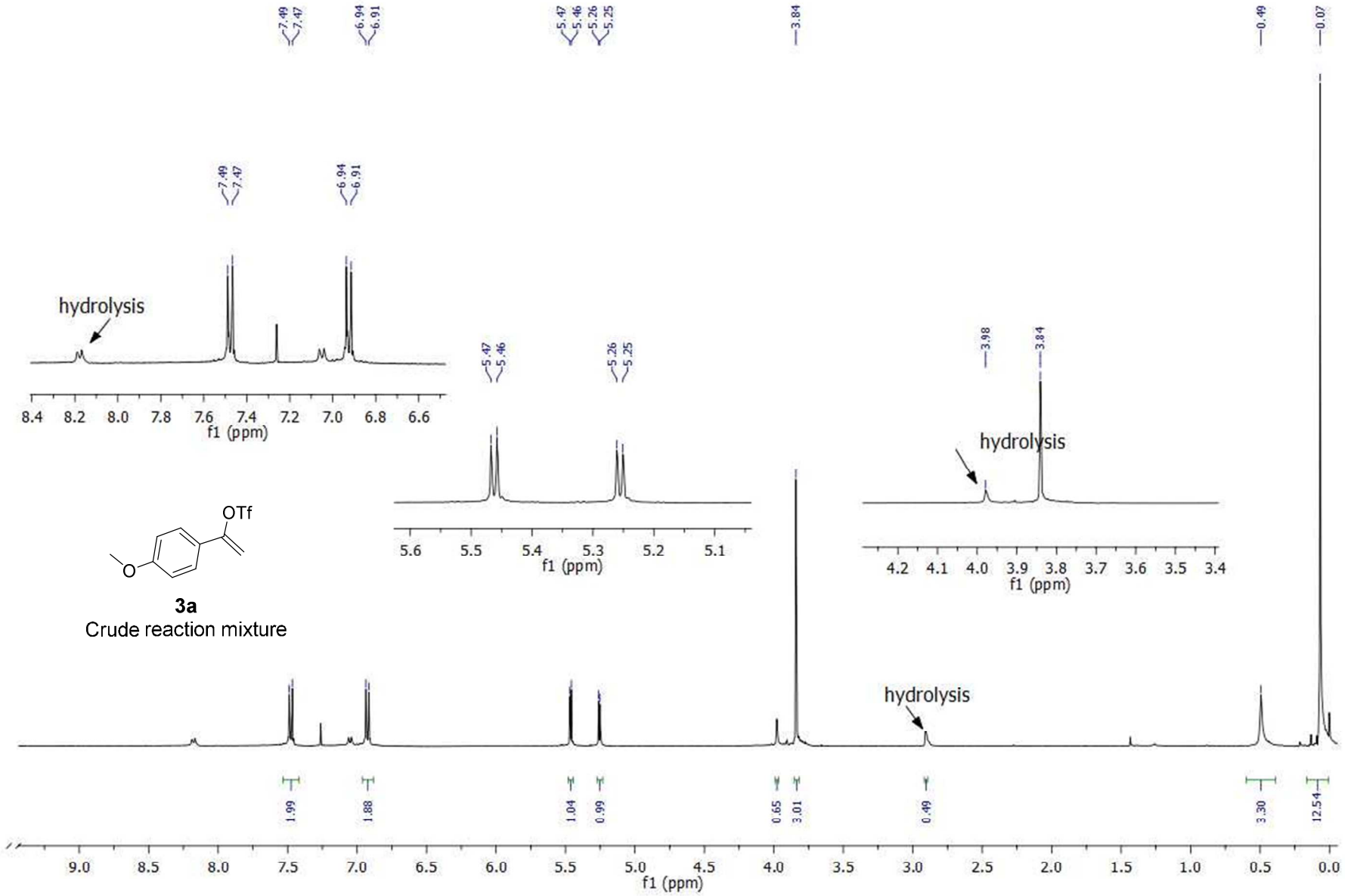
The spectra show the formation of vinyl triflate **10a** in reactions containing varying amounts of water after 3 h (Table 4). With high vacuum dried $Zn(OTf)_2$ and no added water, the reaction gives low conversion to product though in a 3:1 *Z:E* ratio. With 0.50 eq of water, 90% conversion is achieved but the *Z:E* ratio is reduced to 1.2:1. Larger amounts of water (1.5 eq) actually led to reduced conversion (70%) and a complete loss of *Z:E* selectivity.

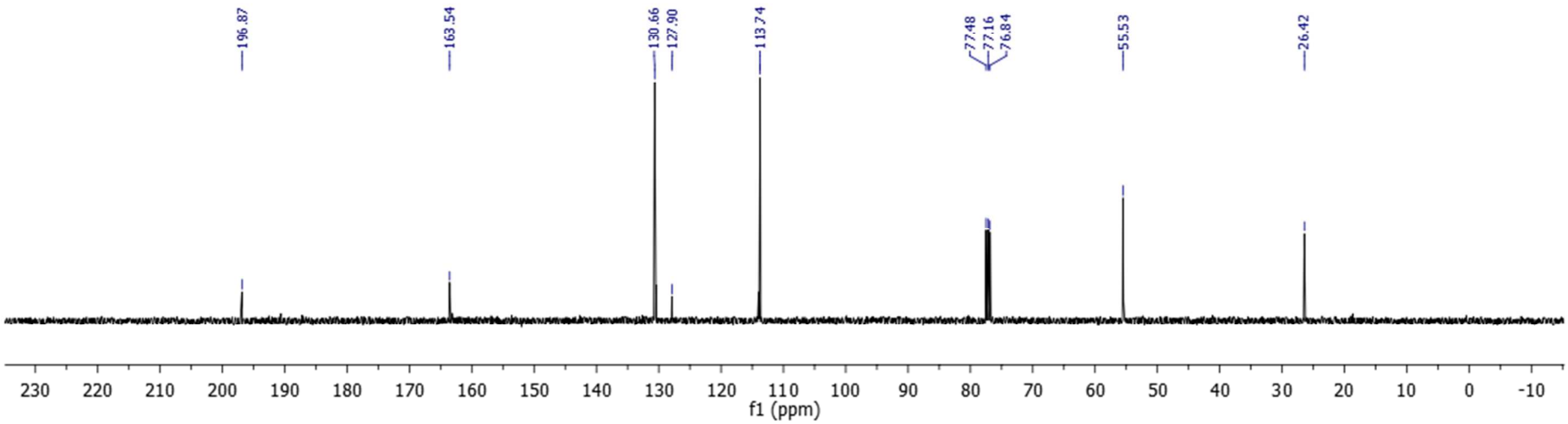


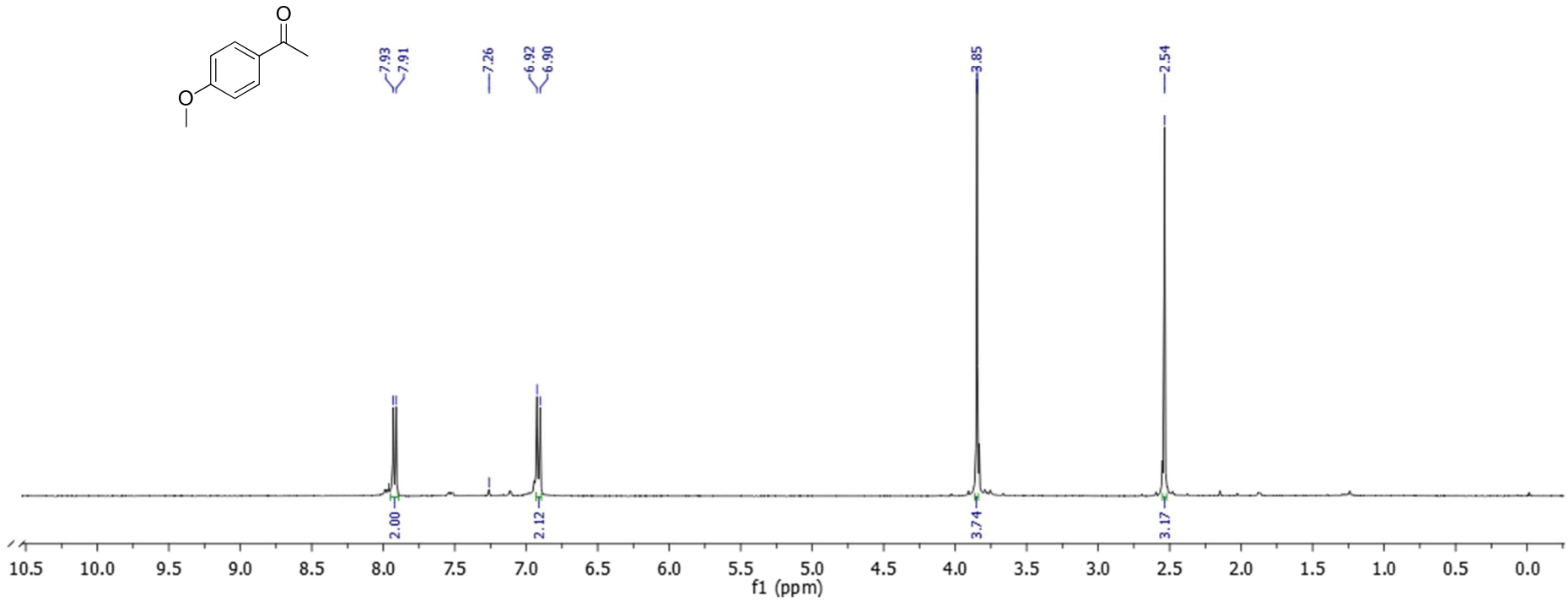

132.24
130.25
128.96
128.30
128.06
127.82
153.72
125.50
104.30
123.93
120.75
117.57
114.37
f1 (ppm)
f1 (ppm)
f1 (ppm)

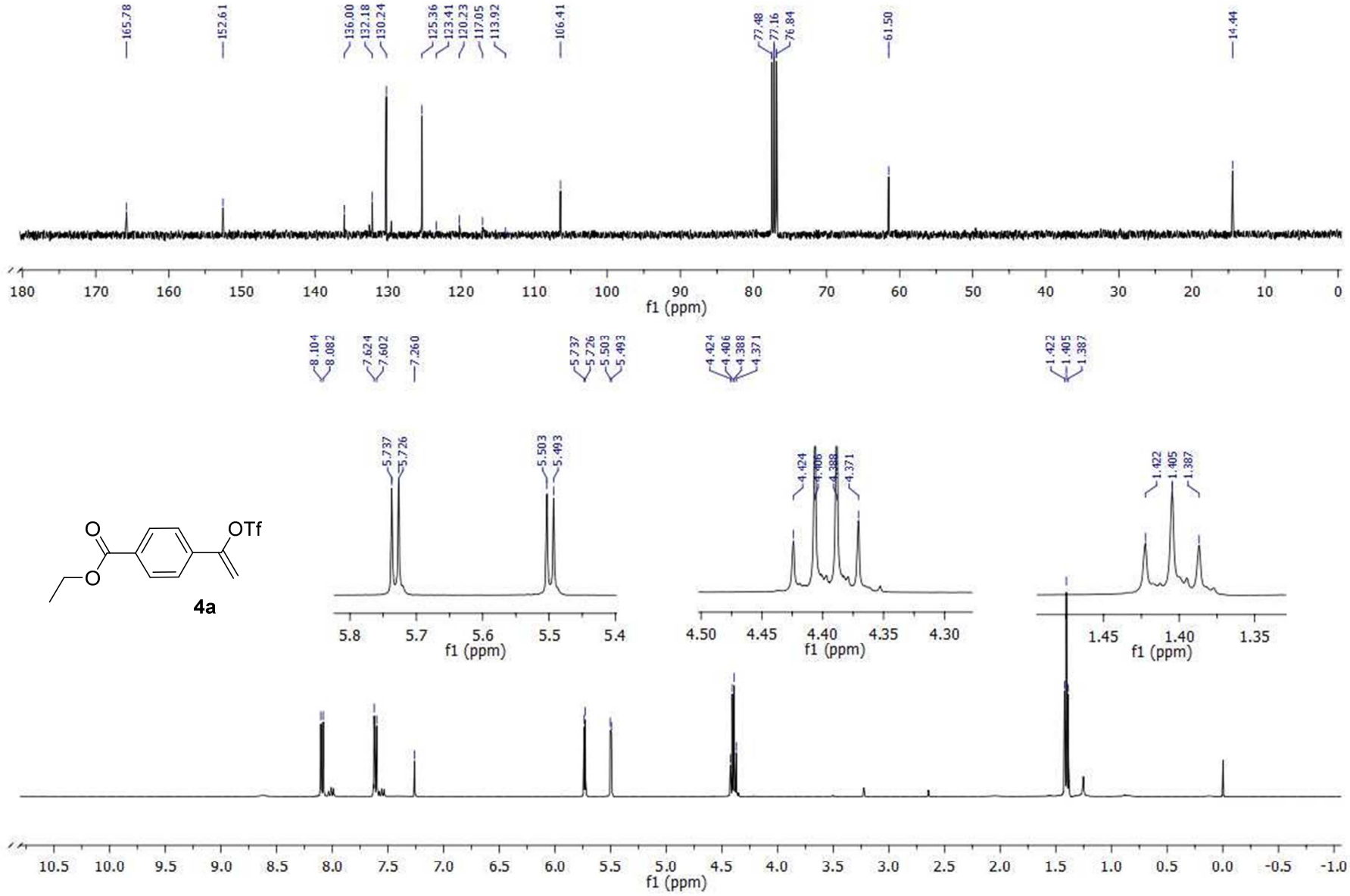

OTf
Ph
H
H
1a
7.17
7.16
7.15
7.12
6.91
6.90
6.89
6.88
6.87
4.89
4.88
4.85
4.84
2.90
3.17
1.00
1.08
f1 (ppm)
f1 (ppm)

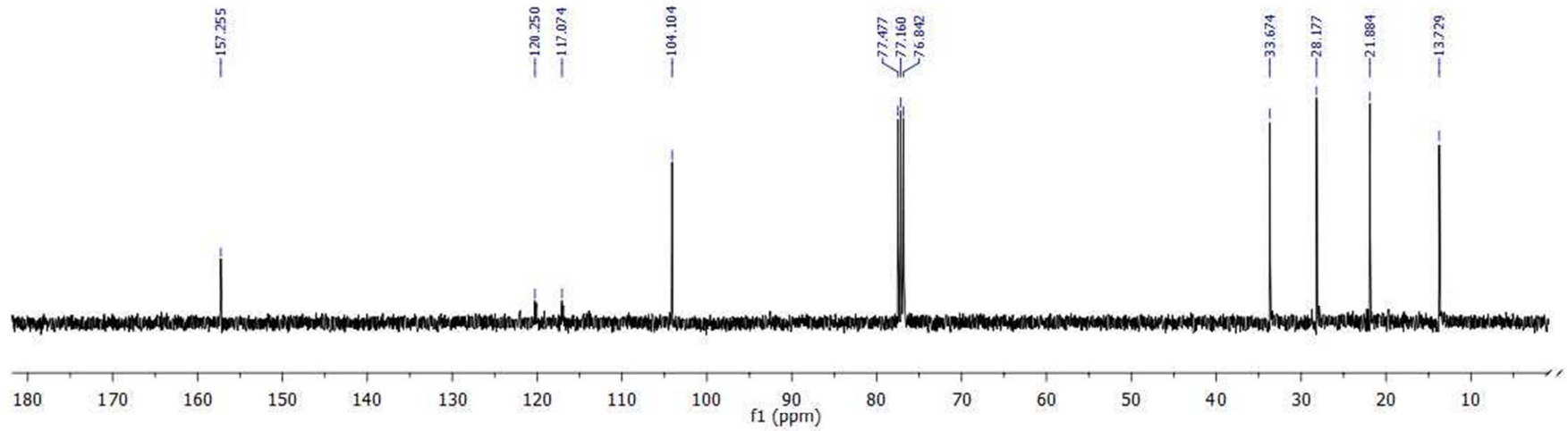

152.60
132.31
131.14
126.98
124.90
123.40
120.22
117.04
113.86
105.05
77.48
77.16
76.84
f1 (ppm)
7.57
7.55
7.42
7.40
7.26
5.62
5.61
5.42
5.41
OTf
Br
2a
2.03
1.98
1.01
1.00
f1 (ppm)

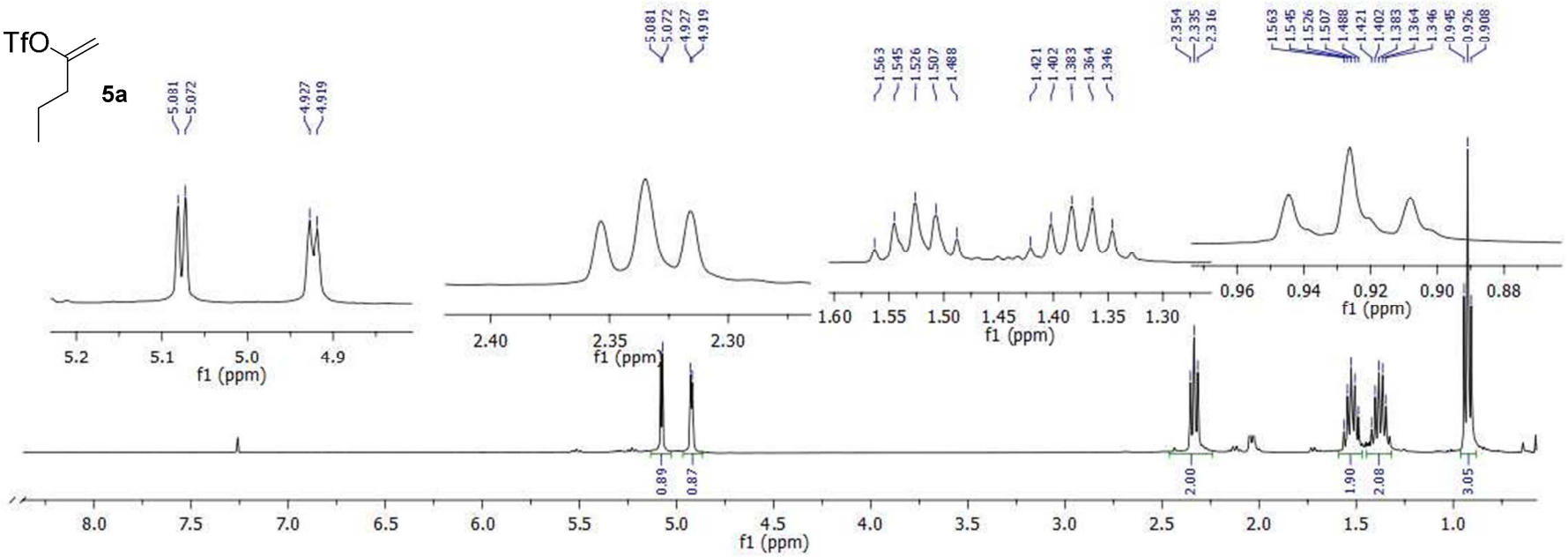

7.49
7.47
6.94
6.91
5.47
5.46
5.26
5.25
3.84
0.49
0.07
hydrolysis
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
f1 (ppm)
5.6 5.5 5.4 5.3 5.2 5.1
f1 (ppm)
3.98
3.84
hydrolysis
4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4
f1 (ppm)
OTf
O
3a
Crude reaction mixture
hydrolysis
1.99
1.88
1.04
0.99
0.65
3.01
0.49
3.30
12.54
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

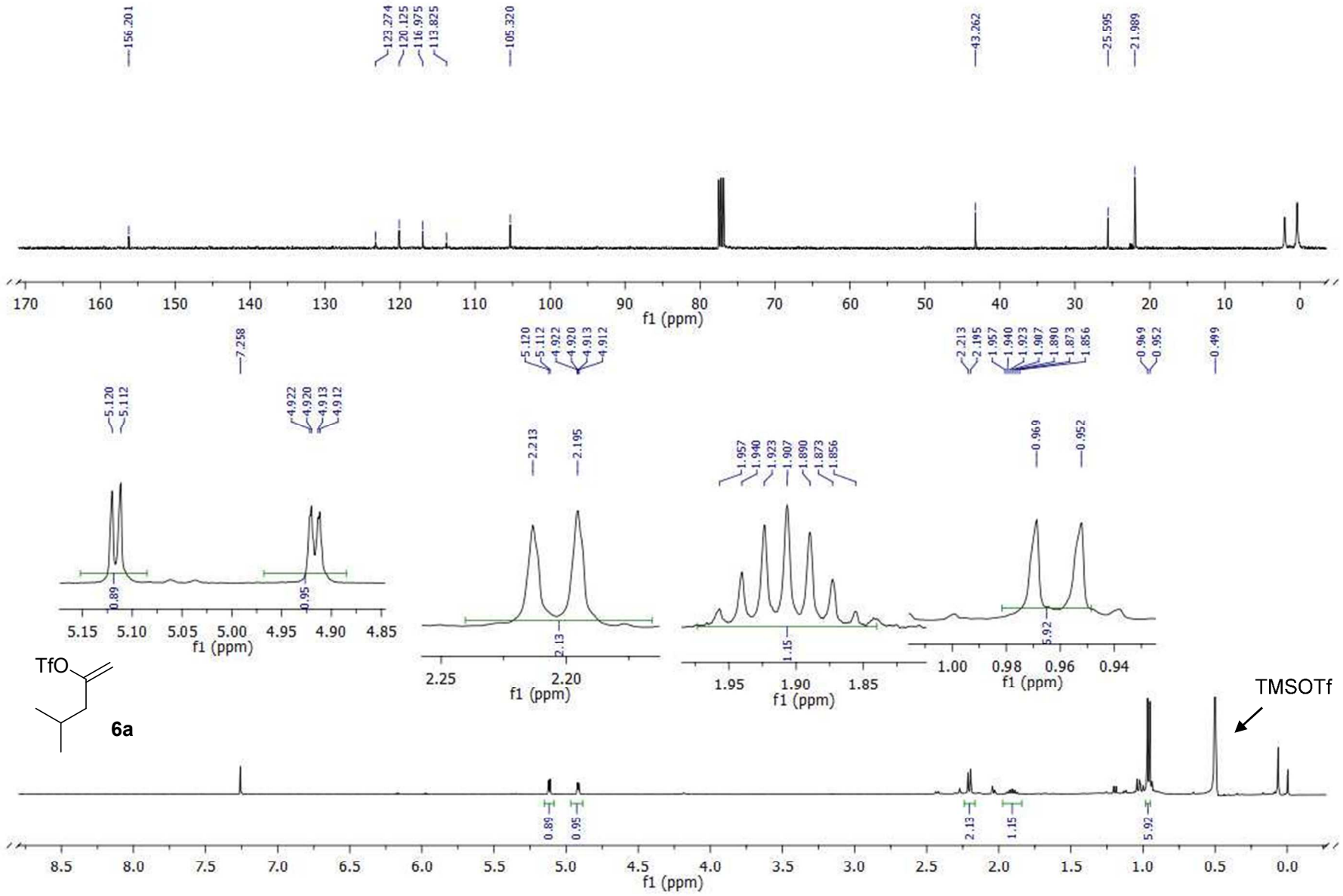

196.87
163.54
130.66
127.90
113.74
77.48
77.16
76.84
55.53
26.42
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

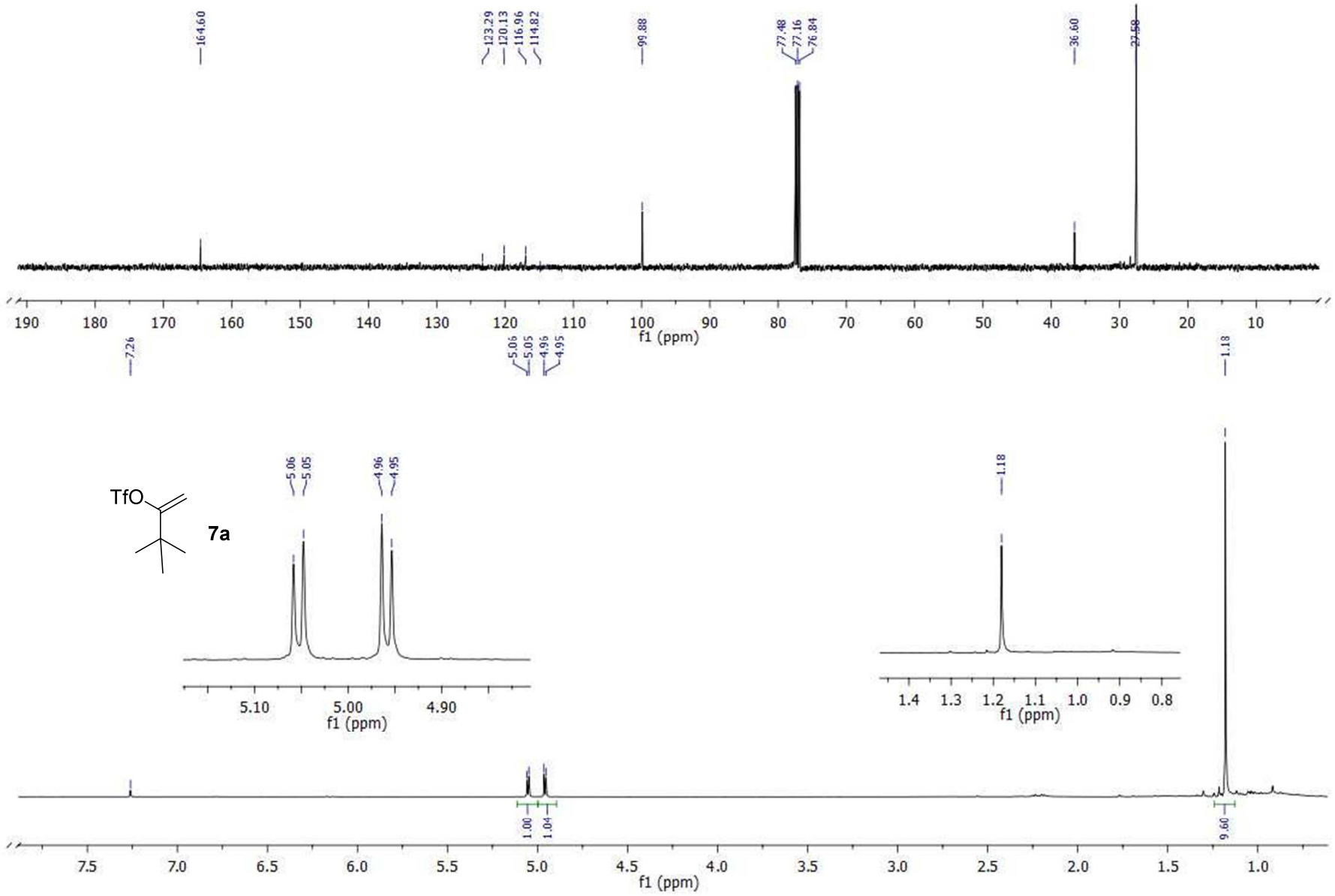

O
O
7.93
7.91
7.26
6.92
6.90
3.85
2.54
2.00
2.12
3.74
3.17
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

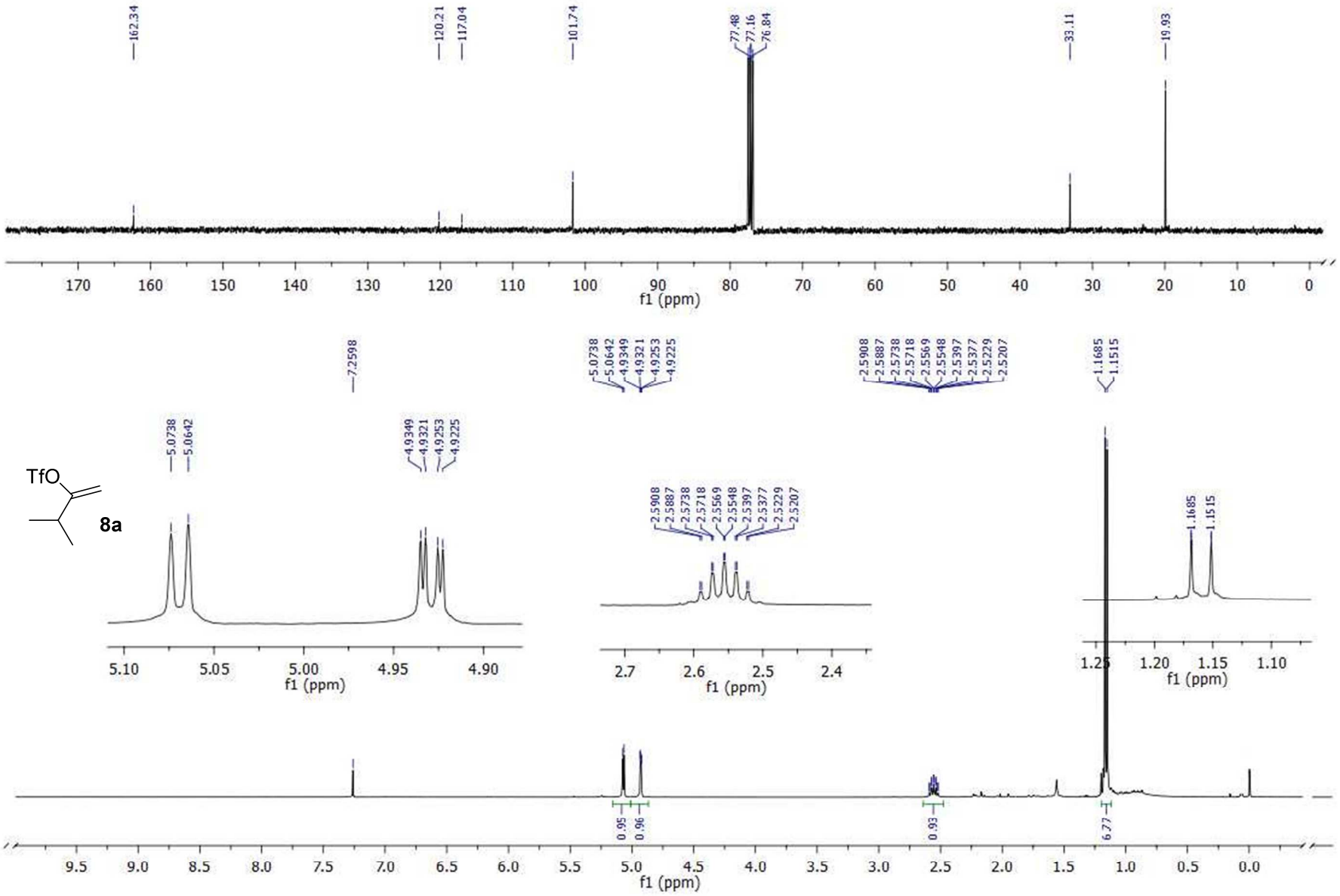

165.78
152.61
136.00
132.18
130.24
125.36
123.41
120.23
117.05
113.92
106.41
77.48
77.16
76.84
61.50
14.44
f1 (ppm)
8.104
8.082
7.624
7.602
7.260
5.737
5.726
5.503
5.493
4.424
4.406
4.388
4.371
1.422
1.405
1.387
O
OTf
O
4a
f1 (ppm)

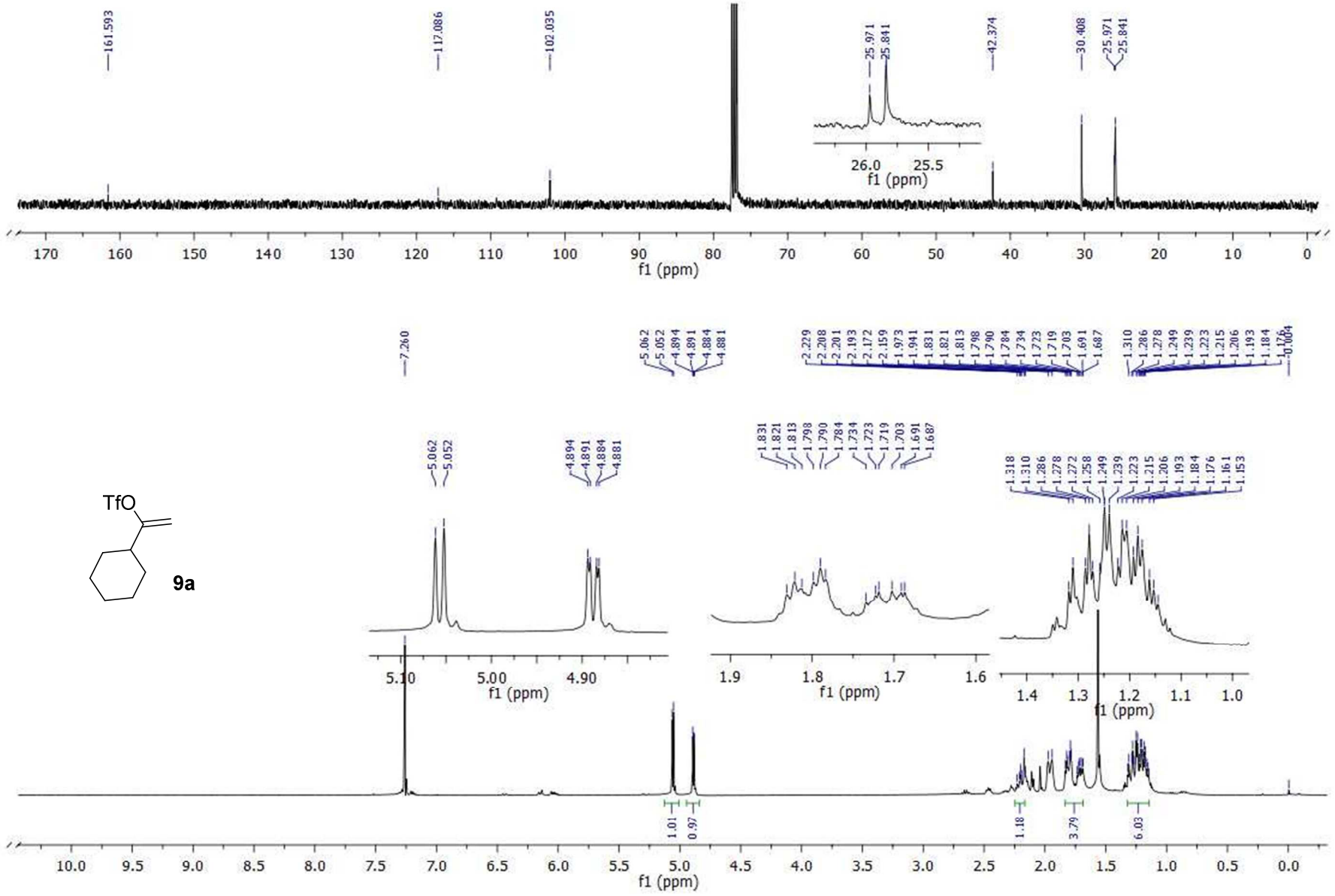

157.255
120.250
117.074
104.104
77.477
77.160
76.842
33.674
28.177
21.884
13.729
f1 (ppm)

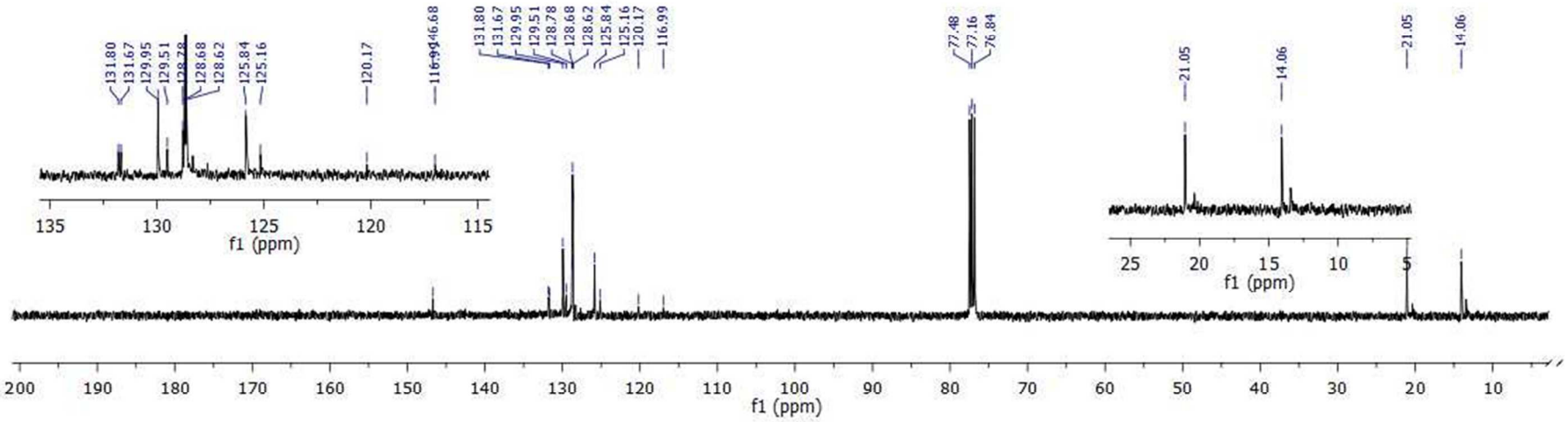

TfO
5a
5.081
5.072
4.927
4.919
1.563
1.545
1.526
1.507
1.488
1.421
1.402
1.383
1.364
1.346
2.354
2.335
2.316
0.945
0.926
0.908
f1 (ppm)
0.89
0.87
2.00
1.90
2.08
3.05


156.201
123.274
120.125
116.975
113.825
105.320
43.262
25.595
21.989
f1 (ppm)
7.258
5.120
5.112
4.922
4.920
4.913
4.912
2.213
2.195
1.957
1.940
1.923
1.907
1.890
1.873
1.856
0.969
0.952
0.499
0.89
0.95
2.13
1.15
5.92
TfO
6a
TMSOTf


164.60
123.29
120.13
116.96
114.82
99.88
77.48
77.16
76.84
36.60
27.58
f1 (ppm)
7.26
5.06
5.05
4.96
4.95
1.18
TfO
7a
1.00
1.04
9.60


162.34
120.21
117.04
101.74
77.48
77.16
76.84
33.11
19.93
f1 (ppm)
7.2598
5.0738
5.0642
4.9349
4.9321
4.9253
4.9225
2.5908
2.5887
2.5738
2.5718
2.5569
2.5548
2.5397
2.5377
2.5229
2.5207
1.1685
1.1515
TfO
8a
0.95
0.96
0.93
6.77


161.593
117.086
102.035
25.971
25.841
42.374
30.408
25.971
25.841
f1 (ppm)
7.260
5.062
5.052
4.894
4.891
4.884
4.881
2.229
2.208
2.201
2.193
2.172
2.159
1.973
1.941
1.831
1.821
1.813
1.798
1.790
1.784
1.734
1.723
1.719
1.703
1.691
1.687
1.310
1.286
1.278
1.249
1.239
1.223
1.215
1.206
1.193
1.184
1.176
0.004
TfO
9a
1.01
0.97
1.18
3.79
6.03
f1 (ppm)

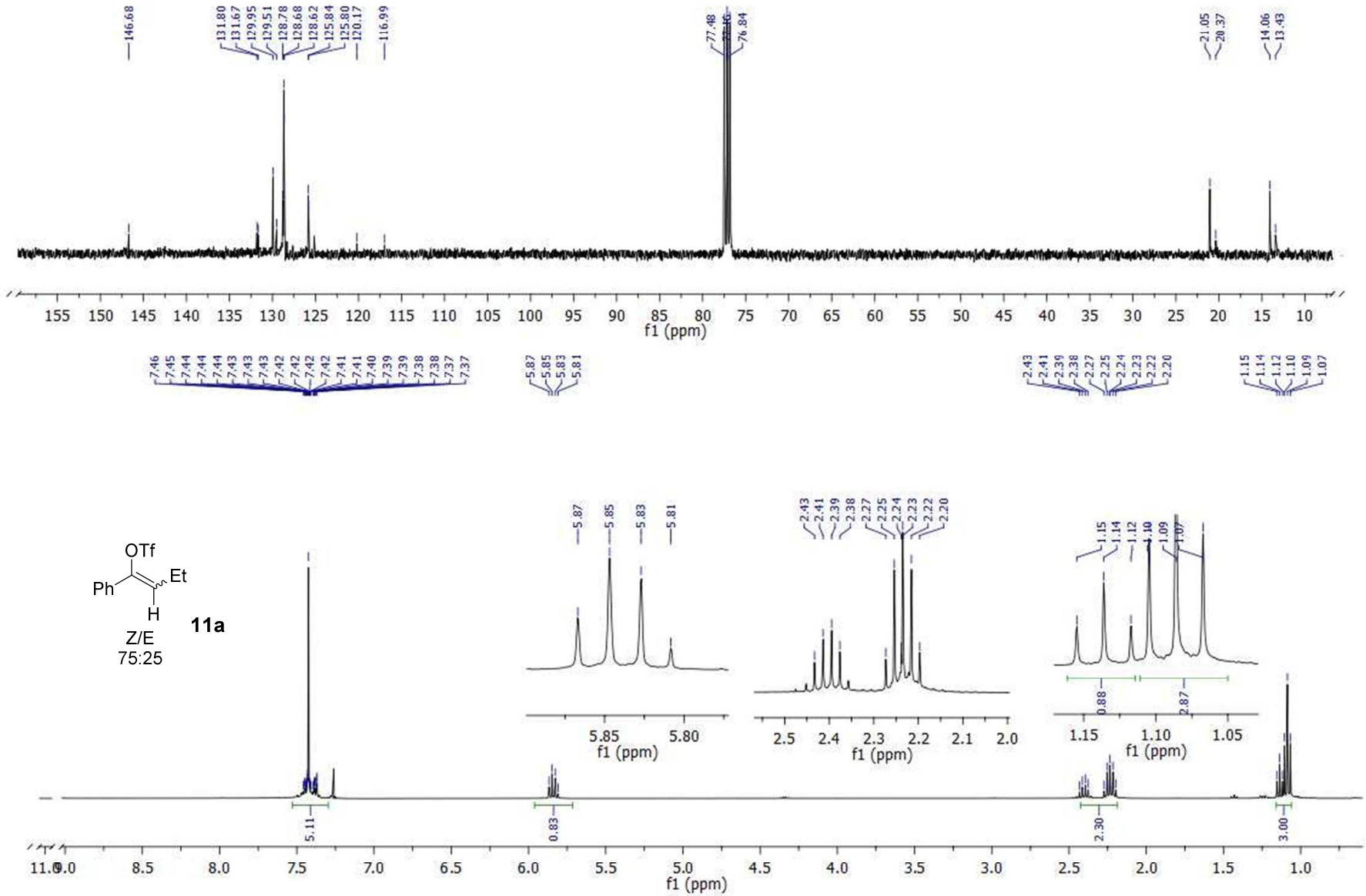

131.80
131.67
129.95
129.51
128.78
128.68
128.62
125.84
125.16
120.17
116.99
77.48
77.16
76.84
21.05
14.06
f1 (ppm)

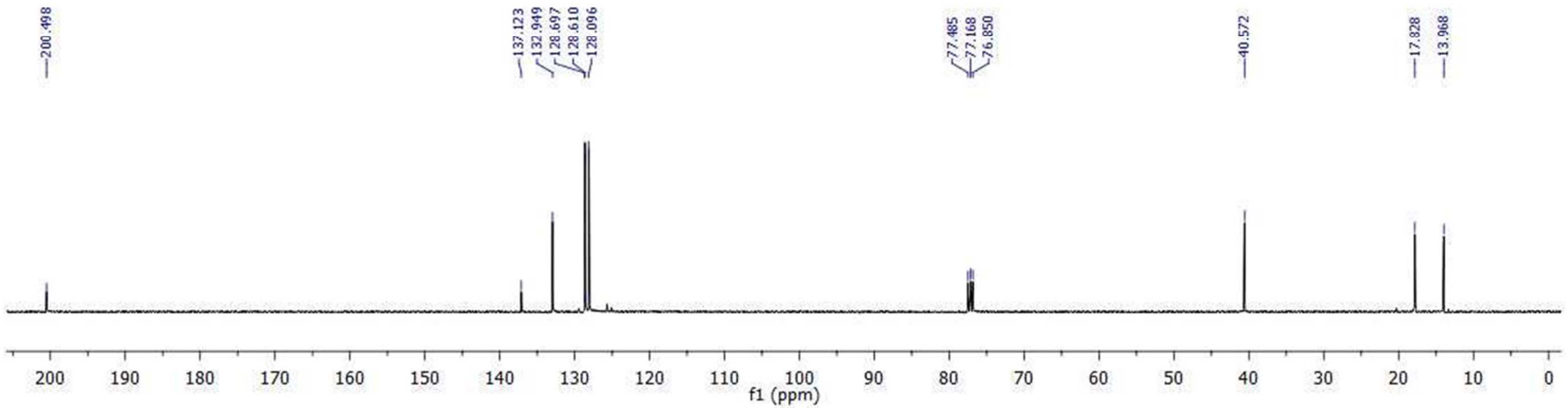

OTf
Ph
Me
H

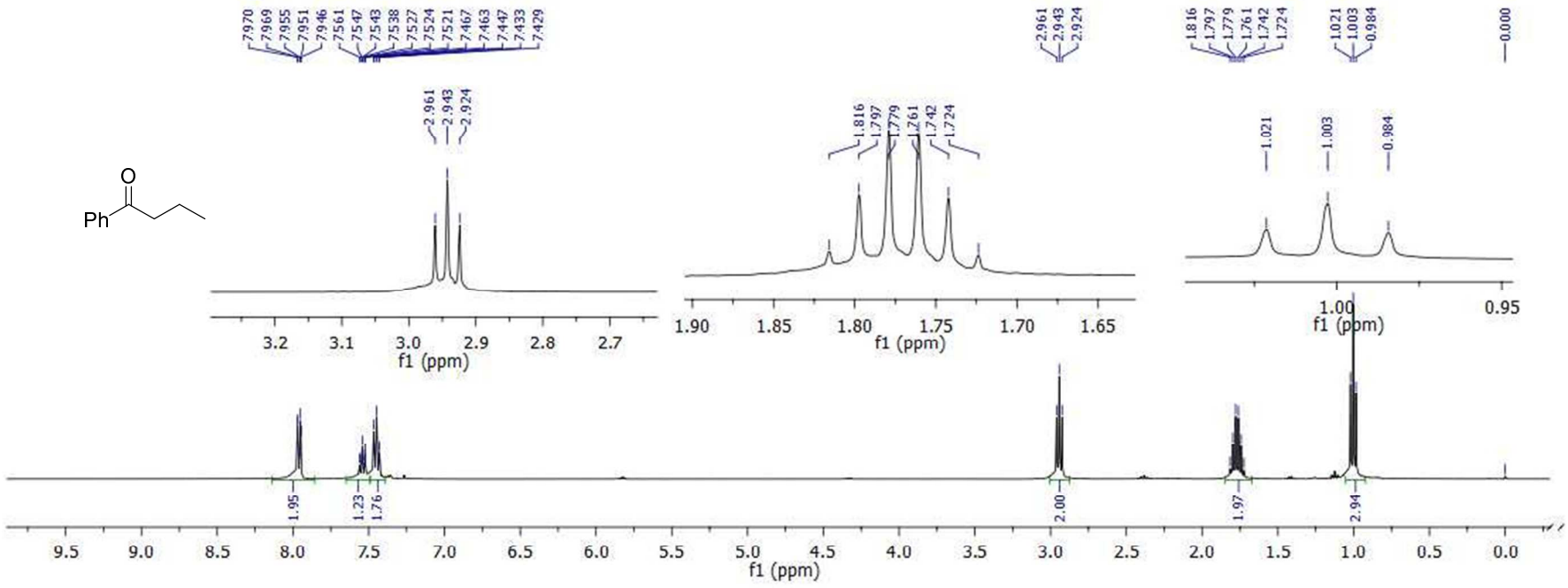
10a

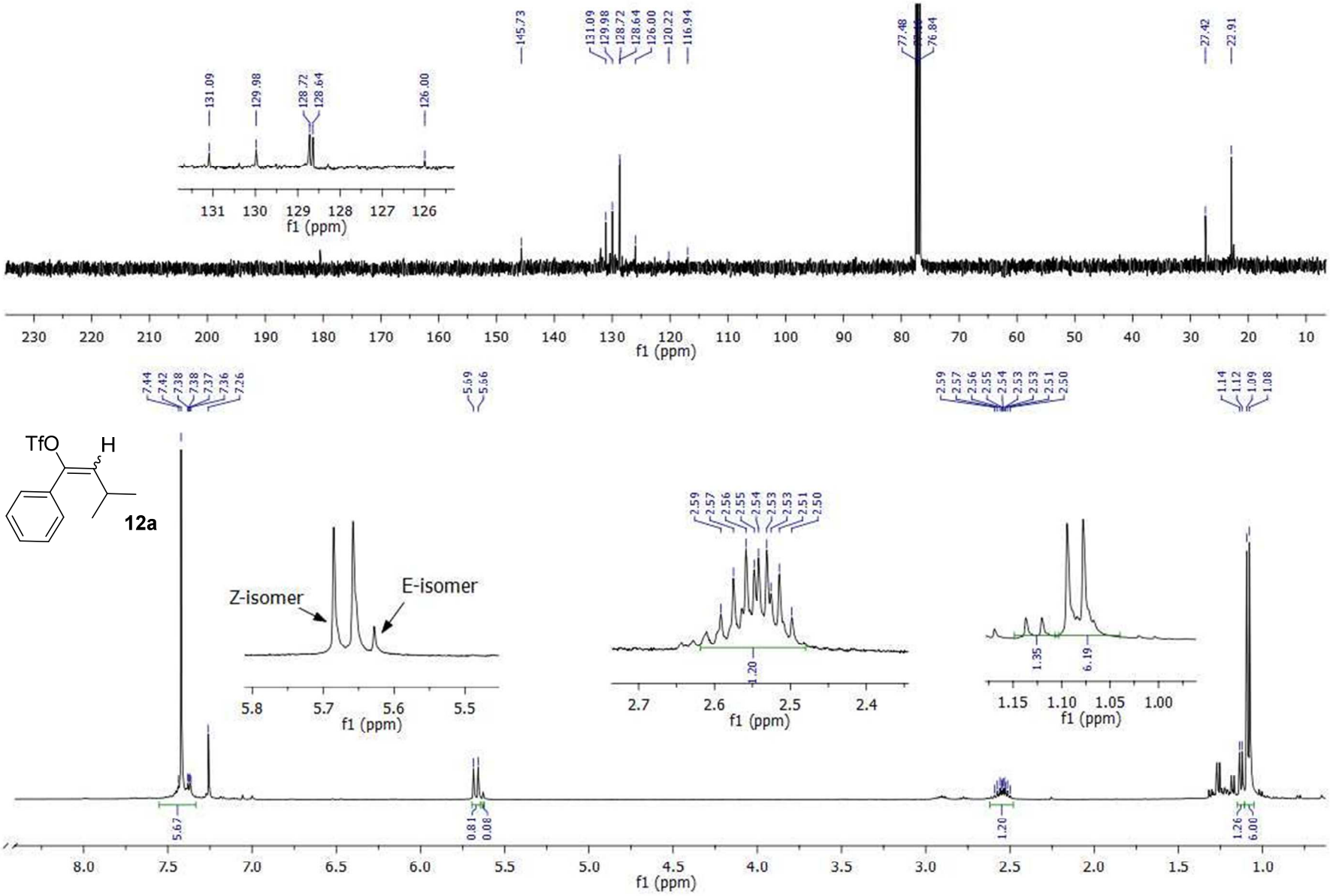
Z/E
68:32

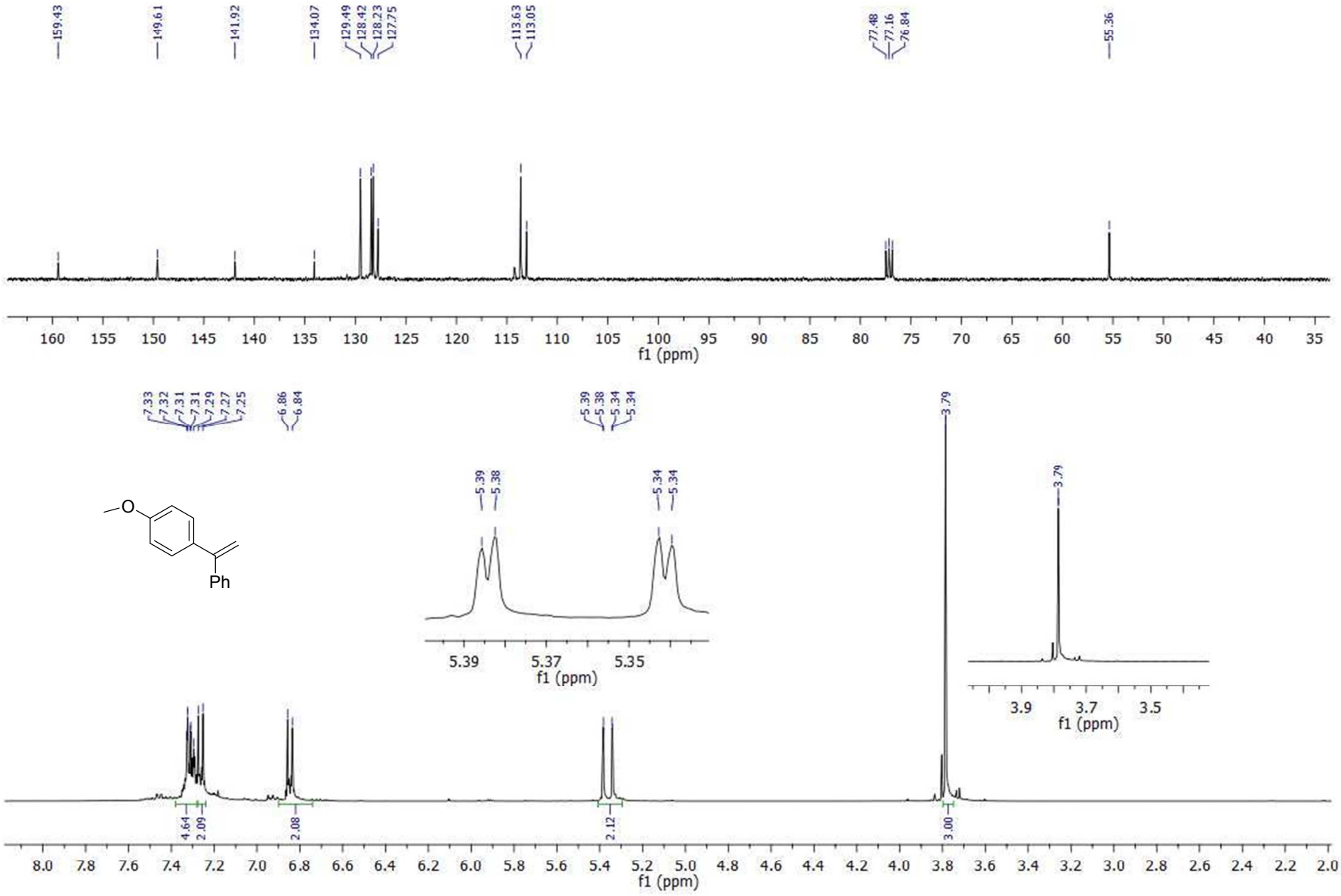
7.46
7.45
7.44
7.43
7.42
7.39
7.38
7.37
7.26
5.98
5.96
5.94
5.93
5.92
1.96
1.94
1.86
1.84
8.01
1.15
1.40
3.00
f1 (ppm)


146.68
131.80
131.67
129.95
129.51
128.78
128.68
128.62
125.84
125.80
120.17
116.99
77.48
77.16
76.84
21.05
20.37
14.06
13.43
f1 (ppm)
OTf
Et
Ph
H
Z/E
75:25
11a
5.11
0.83
2.30
3.00
0.88
2.87


200.498
137.123
132.949
128.697
128.610
128.096
77.485
77.168
76.850
40.572
17.828
13.968
f1 (ppm)


7.970
7.969
7.955
7.951
7.946
7.561
7.547
7.543
7.538
7.527
7.524
7.521
7.467
7.463
7.447
7.433
7.429
2.961
2.943
2.924
1.816
1.797
1.779
1.761
1.742
1.724
1.021
1.003
0.984
0.000
O
Ph
f1 (ppm)
1.95
1.23
1.76
2.00
1.97
2.94


145.73
131.09
129.98
128.72
128.64
126.00
120.22
116.94
77.48
76.84
27.42
22.91
f1 (ppm)
7.44
7.42
7.38
7.38
7.37
7.36
7.26
5.69
5.66
2.59
2.57
2.56
2.55
2.54
2.53
2.53
2.51
2.50
1.14
1.12
1.09
1.08
TfO
H
12a
Z-isomer
E-isomer
5.67
0.81
0.08
1.20
1.26
6.00
1.35
6.19


159.43
149.61
141.92
134.07
129.49
128.42
128.23
127.75
113.63
113.05
77.48
77.16
76.84
55.36
f1 (ppm)
7.33
7.32
7.31
7.31
7.29
7.27
7.25
6.86
6.84
5.39
5.38
5.34
5.34
3.79
O
Ph
5.39
5.38
5.34
5.34
5.39
5.37
5.35
f1 (ppm)
3.79
3.9
3.7
3.5
f1 (ppm)
4.64
2.09
2.08
2.12
3.00
f1 (ppm)