Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

(1a) Comparison of gas chromatograms (GC-MS) of the methylated culture extract of strain HxN1 with the synthetic standards (*S*)-**13e**, (*S*)-**9b**, **7e** and (3*R**,4*S*)-**11b** including co-injection experiments.

(1b) Comparison of mass spectra (extracted from the GC-MS data) of the metabolites with the synthetic standards (*S*)-**13e**, (*S*)-**9b**, **7e** and (3*R**,4*S*)-**11b**.

Pages S2 – S11

(2) Mass spectrum of synthetic standard (*S*)-**12b**.

Page S12

(3) ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of all synthetic compounds reported in this manuscript.

Pages S13 – S29

(4) Detailed data for Mosher ester analysis of compound (3*R*,4*S*)-**11b**, including ^{1}H and HSQC NMR data as well as the comparatively analysis of the ^{1}H NMR data of both diastereomeric MTPA esters.

Pages S30 – S32

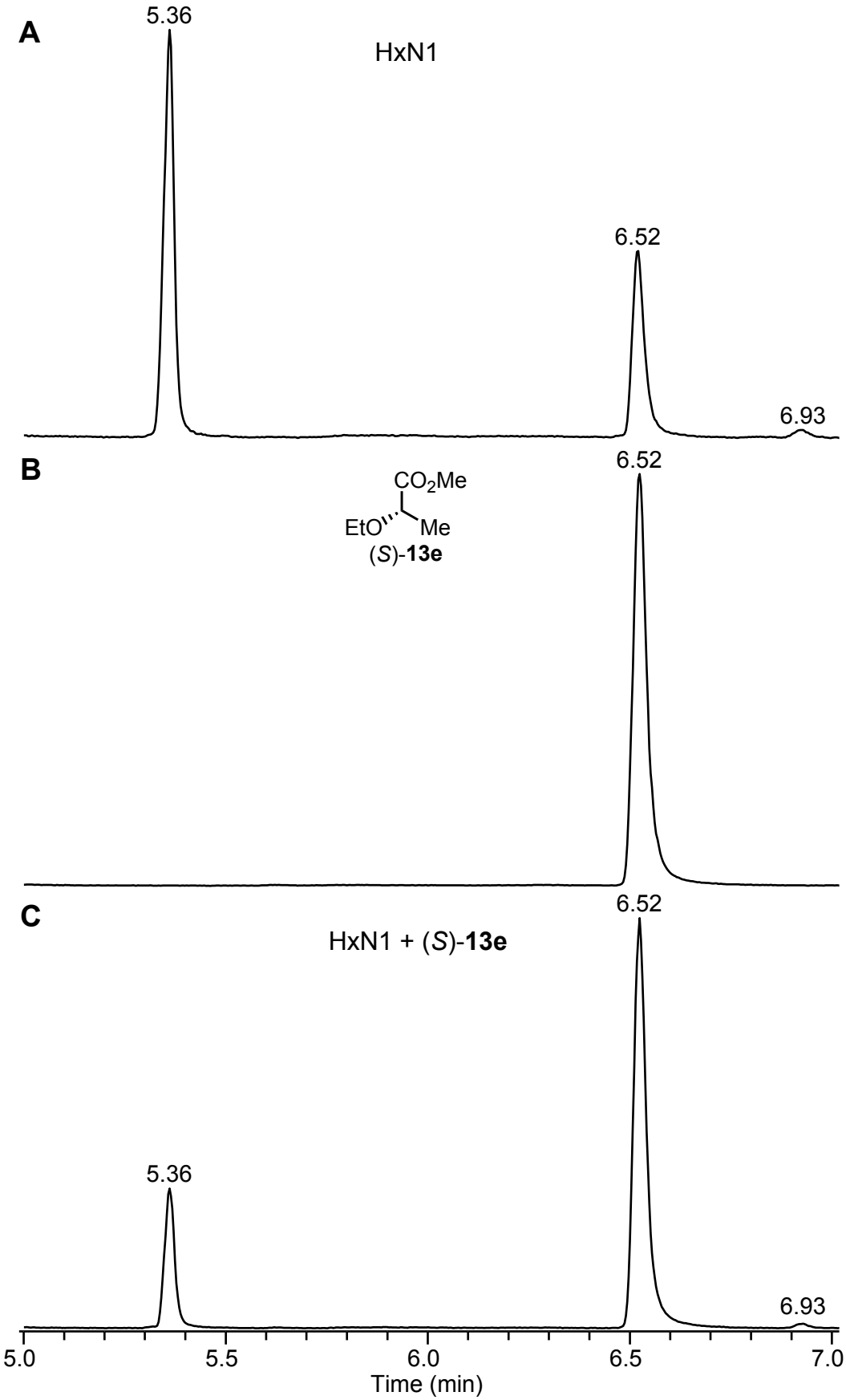


Figure S1. Gas chromatographic separation of (A) the methylated culture extract of strain HxN1, (B) the reference standard (*S*)-**13e** and (C) a co-injected mixture of the reference standard (*S*)-**13e** and the methylated culture extract of strain HxN1.

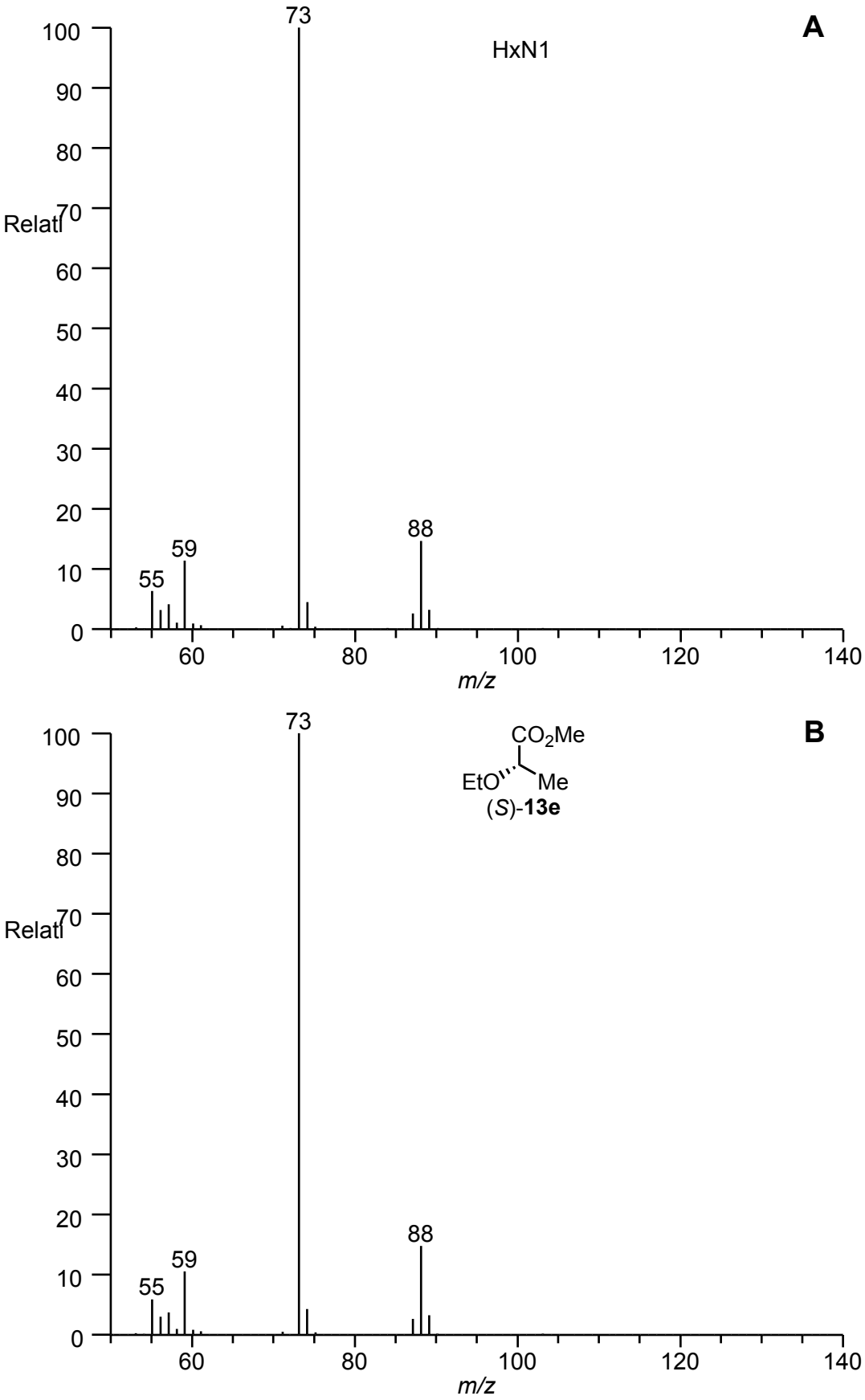


Figure S2. Mass spectra of (A) a metabolite specifically formed during anaerobic growth of strain HxN1 eluting at 6.52 min and (B) the reference standard (*S*)-**13e** eluting at 6.52 min.

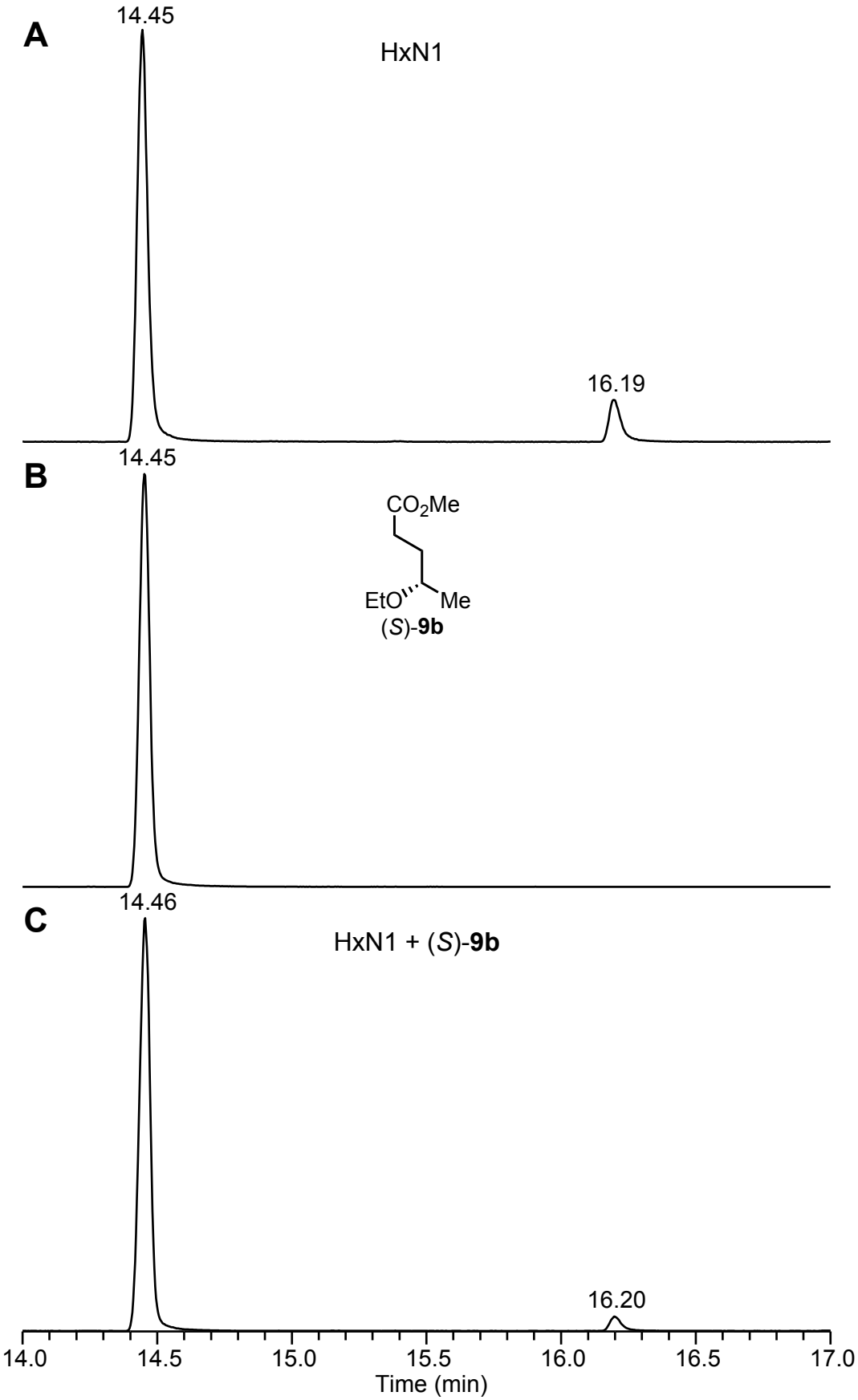


Figure S3. Gas chromatographic separation of (A) the methylated culture extract of strain HxN1, (B) the reference standard (*S*)-**9b** and (C) a co-injected mixture of the reference standard (*S*)-**9b** and the methylated culture extract of strain HxN1.

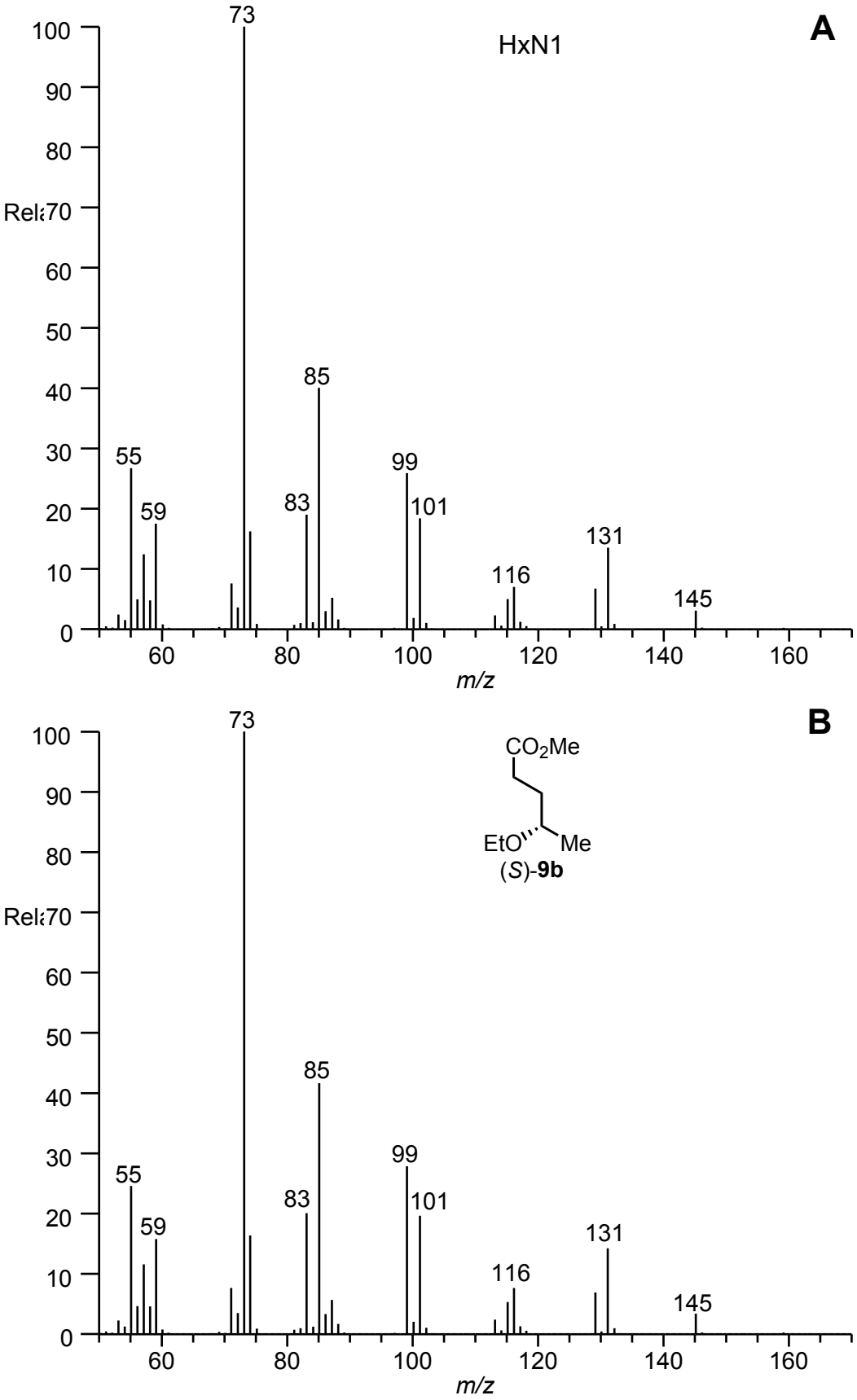


Figure S4. Mass spectra of (A) a metabolite specifically formed during anaerobic growth of strain HxN1 eluting at 14.45 min and (B) the reference standard (*S*)-**9b** eluting at 14.45 min.

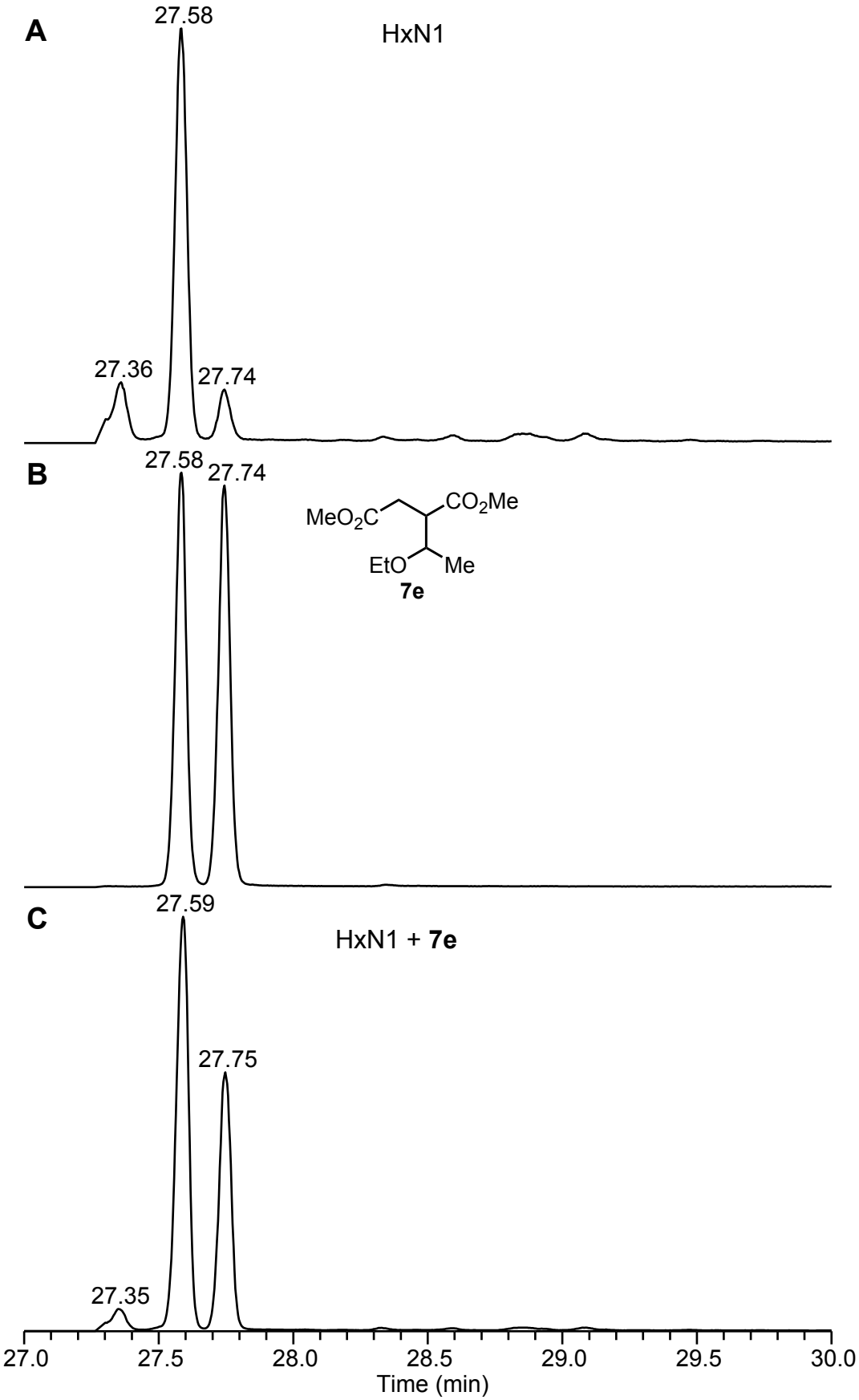


Figure S5. Gas chromatographic separation of (A) the methylated culture extract of strain HxN1, (B) the reference standard **7e** and (C) a co-injected mixture of the reference standard **7e** and the methylated culture extract of strain HxN1.

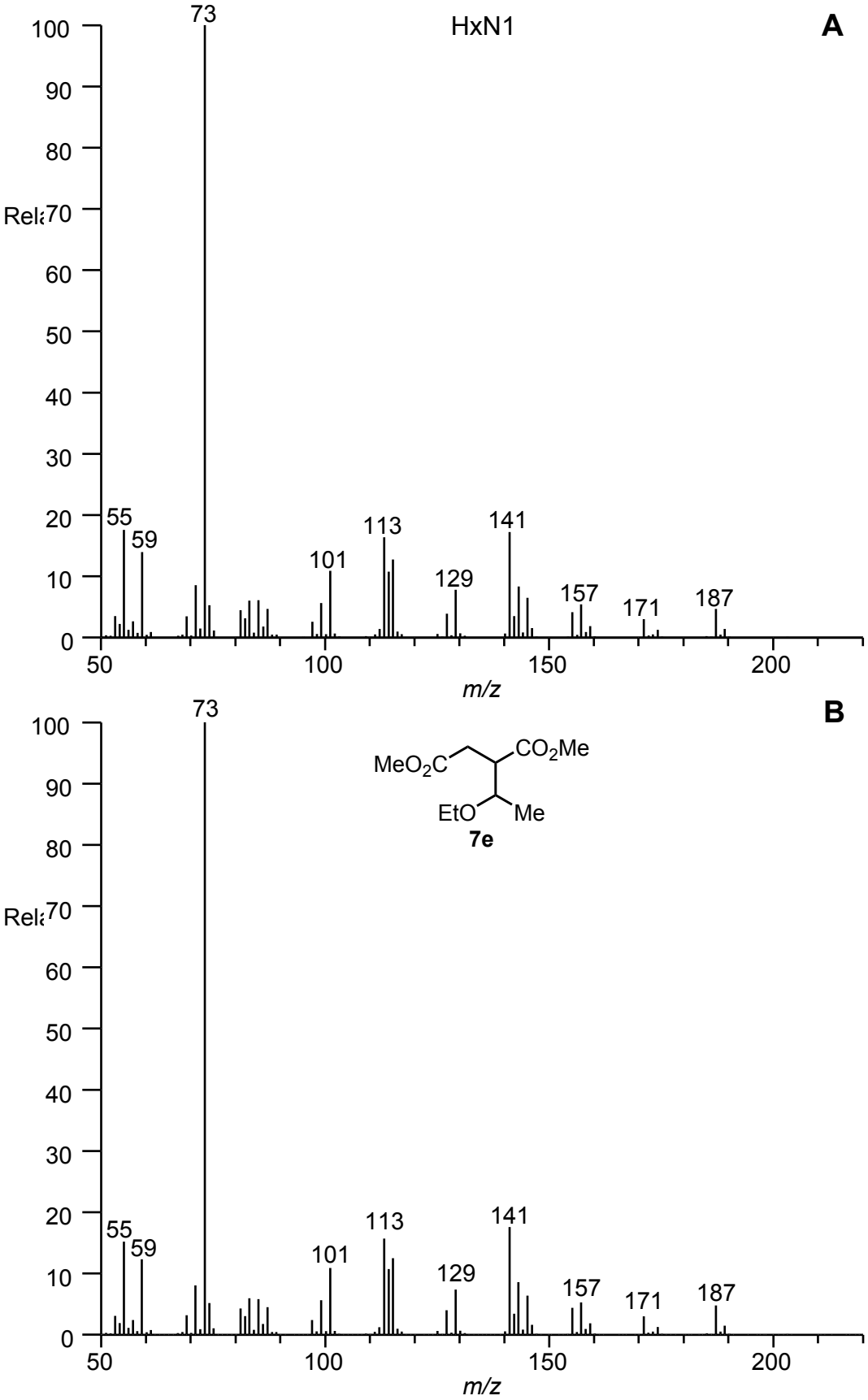


Figure S6. Mass spectra of (A) a metabolite specifically formed during anaerobic growth of strain eluting at 27.58 min and (B) the first diastereoisomer of the reference standard **7e** eluting at 27.58 min.

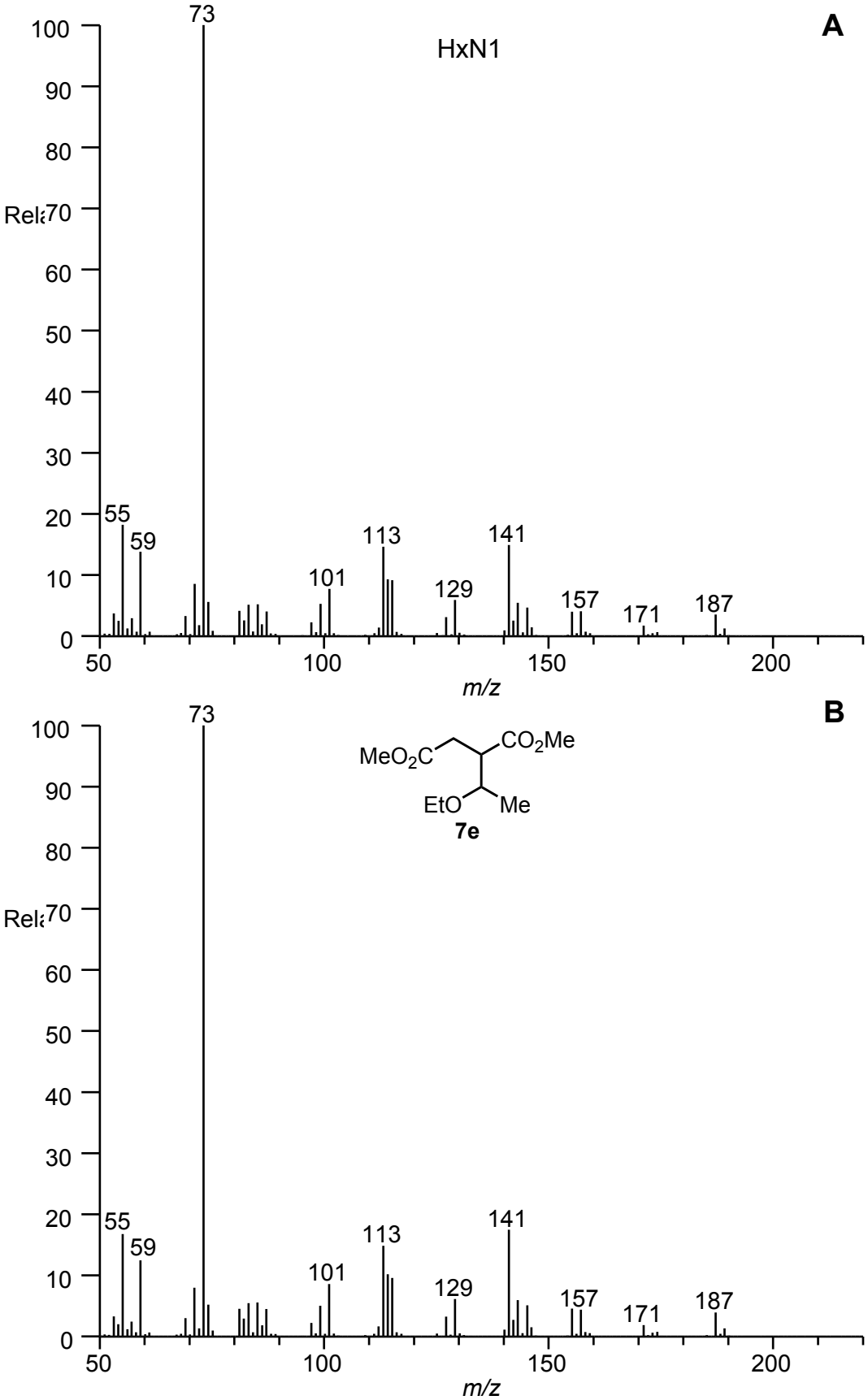


Figure S7. Mass spectra of (A) a metabolite specifically formed during anaerobic growth of strain HxN1 eluting at 27.74 min and (B) the second diastereoisomer of the reference standard **7e** eluting at 27.74 min.

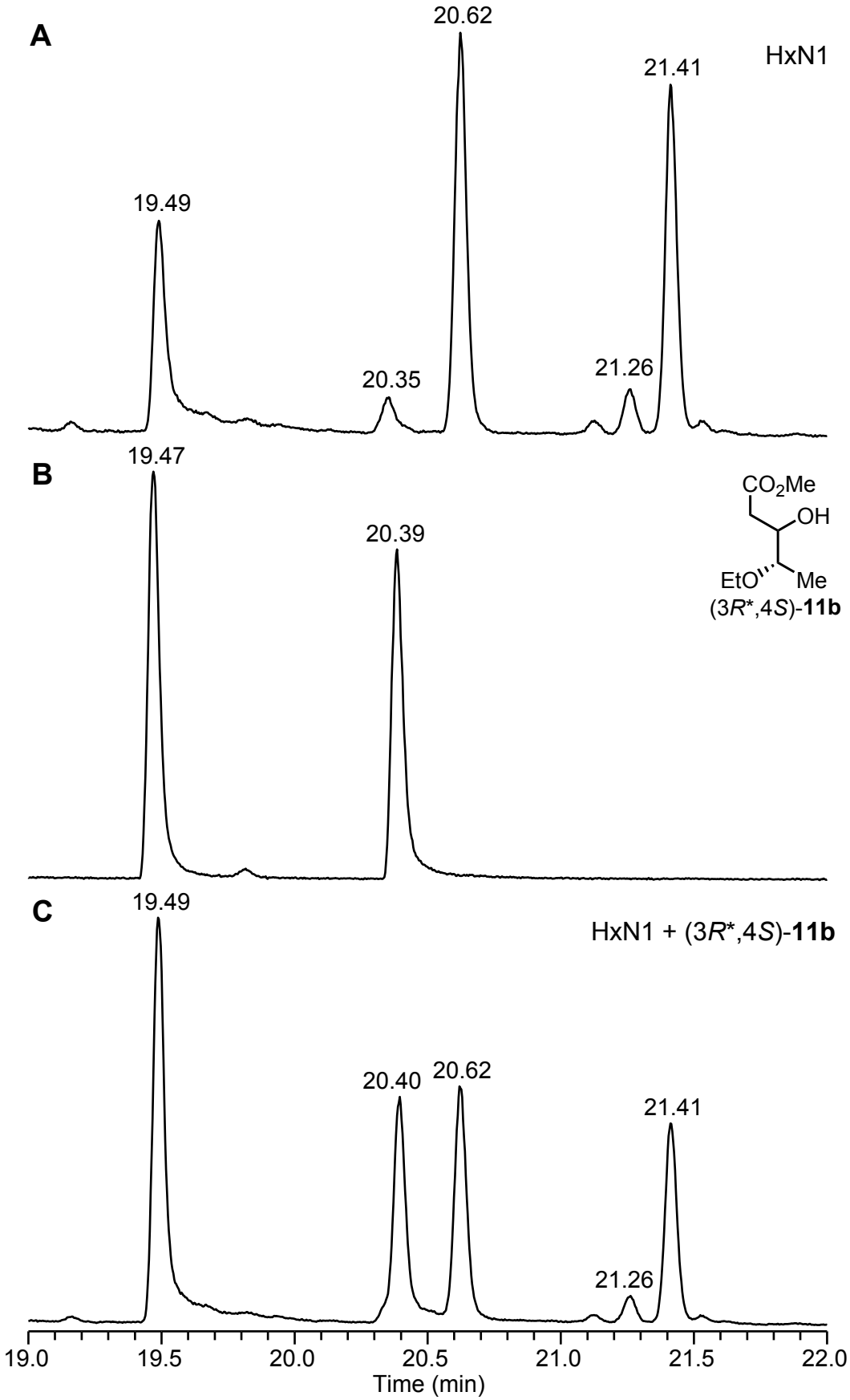


Figure S8. Gas chromatographic separation of (A) the methylated culture extract of strain HxN1, (B) both diastereoisomers of the reference standard (3*R**,4*S*)-**11b** and (C) a co-injected mixture of the reference standard (3*R**,4*S*)-**11b** and the methylated culture extract of strain HxN1. According to its mass spectral fragmentation pattern, the compound eluting at 20.35 min from the extract is not compound (3*R**,4*S*)-**11b**.

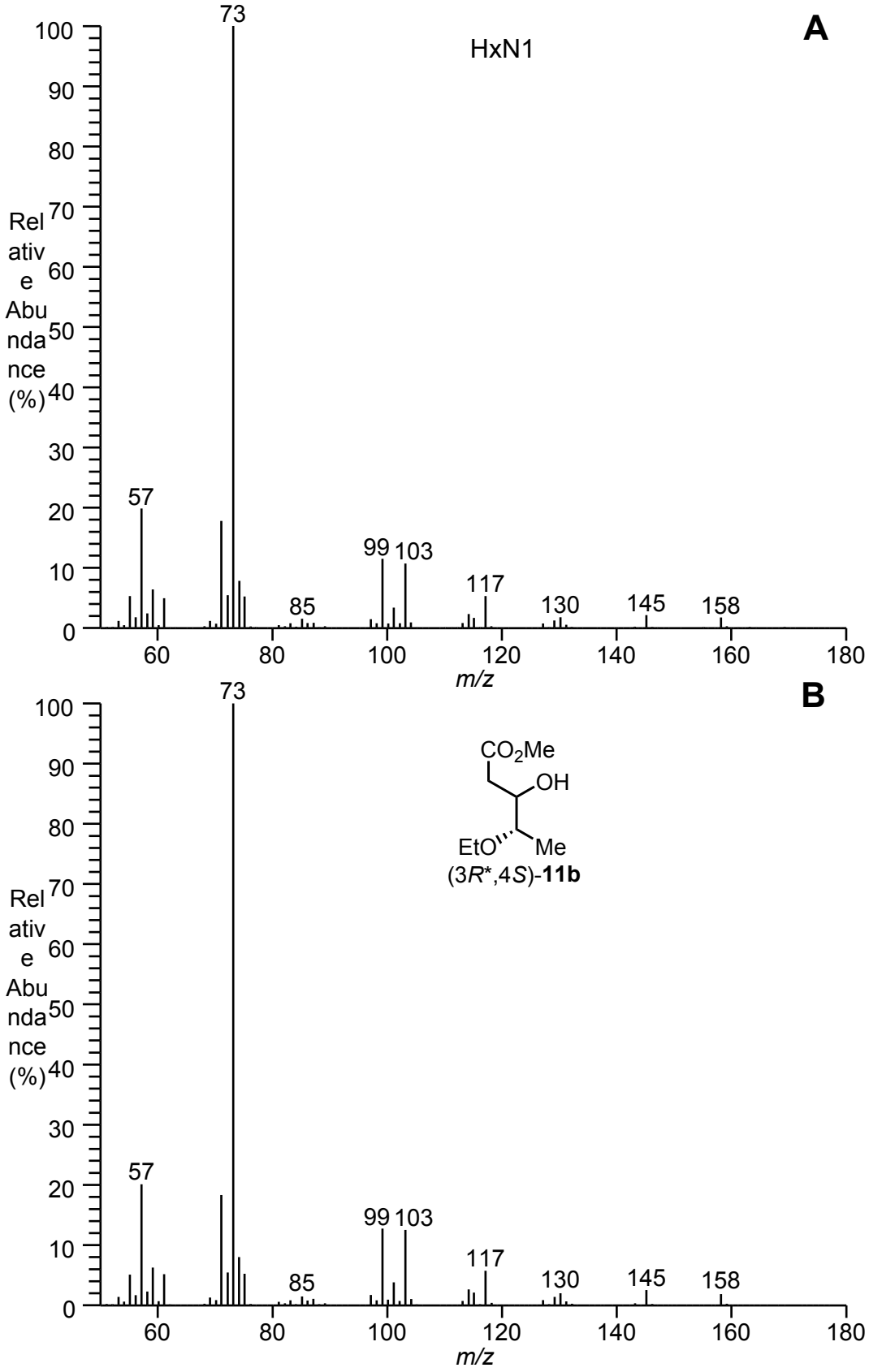


Figure S9. Mass spectra of (A) a metabolite specifically formed during anaerobic growth of strain HxN1 eluting at 19.49 min and (B) one diastereoisomer of the reference standard (3*R**,4*S*)-**11b** eluting at 19.47 min. The second diastereoisomers was not detected in the extracts

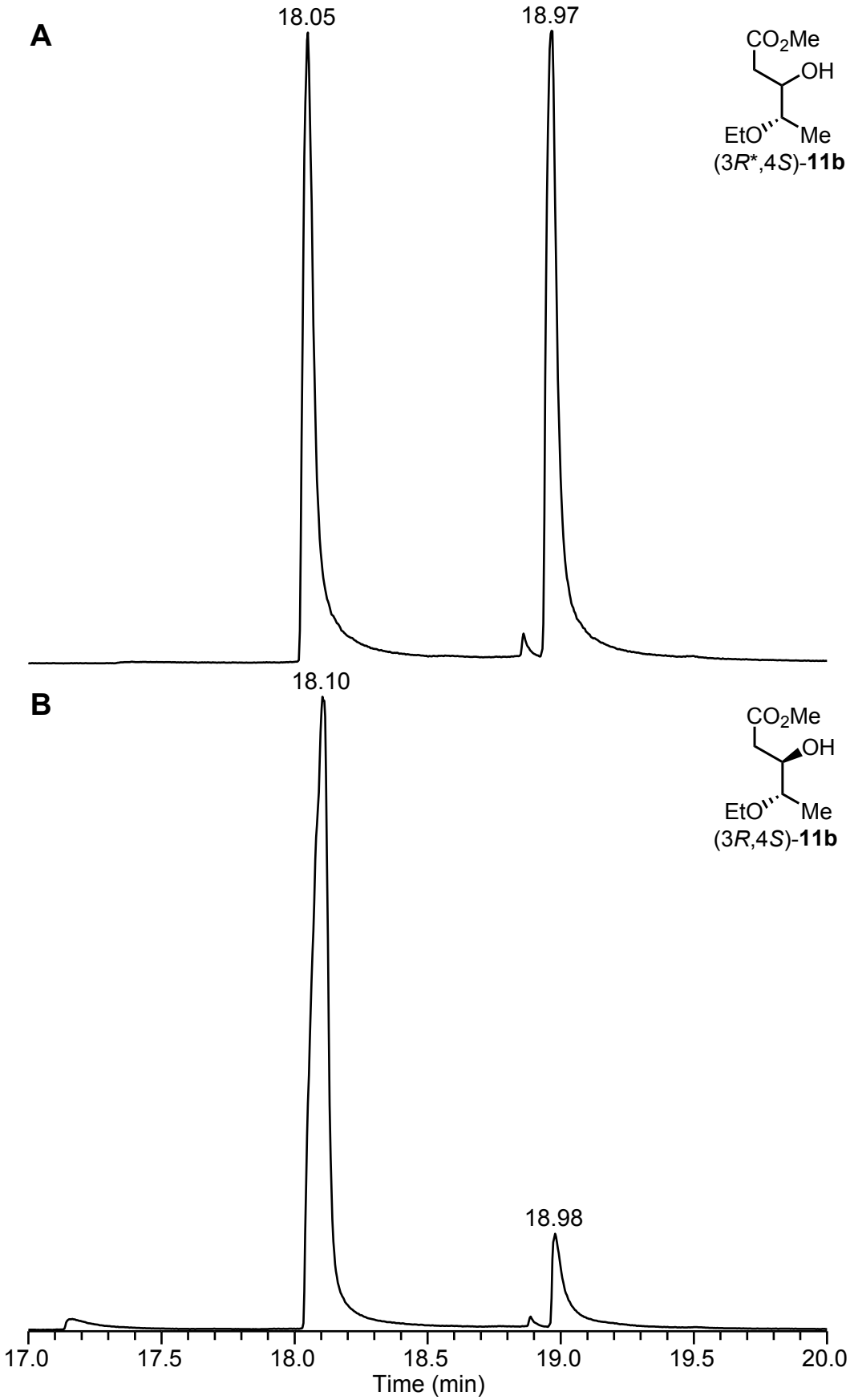


Figure S10. Gas chromatographic separation of (A) the reference standard (3*R**,4*S*)-**11b** and (B) the reference standard (3*R*,4*S*)-**11b**. The retention times do not match with those of Figure S10 because the column was shortened.

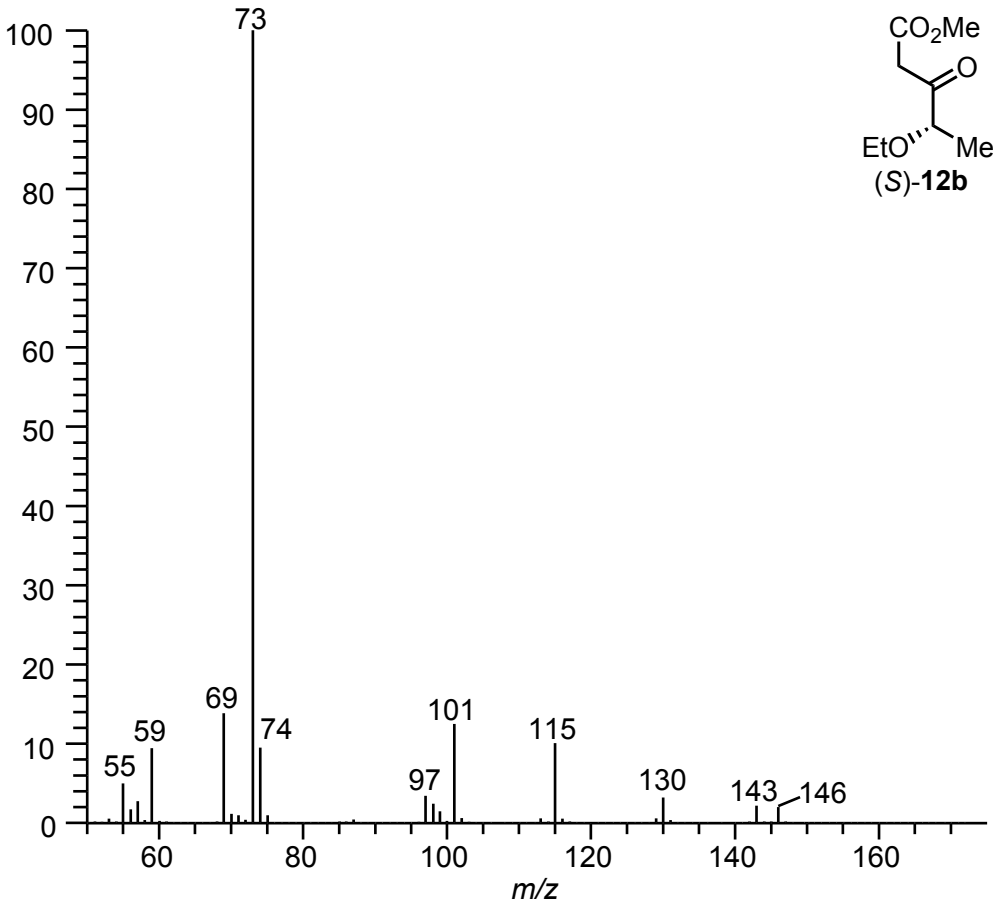
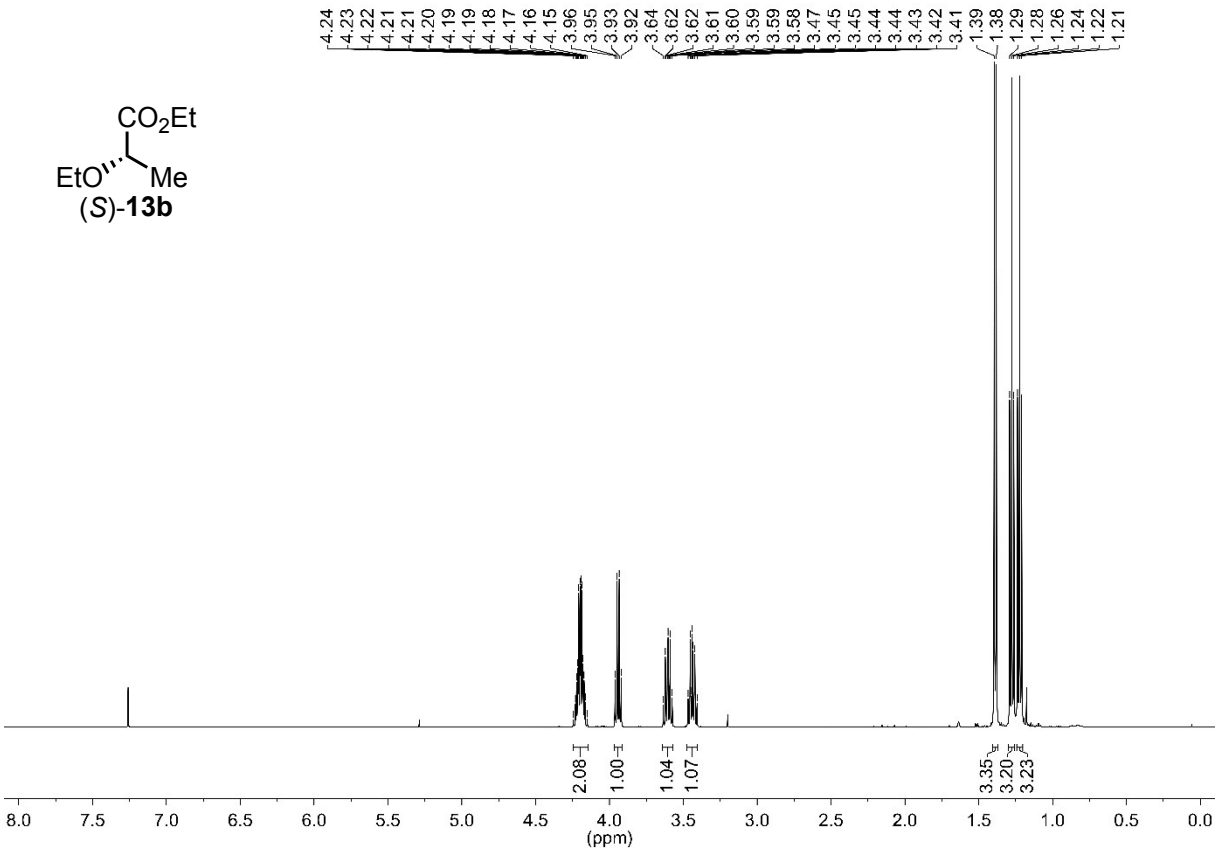


Figure S11. Mass spectrum of the reference standard (*S*)-**12b** eluting at 18.65 min.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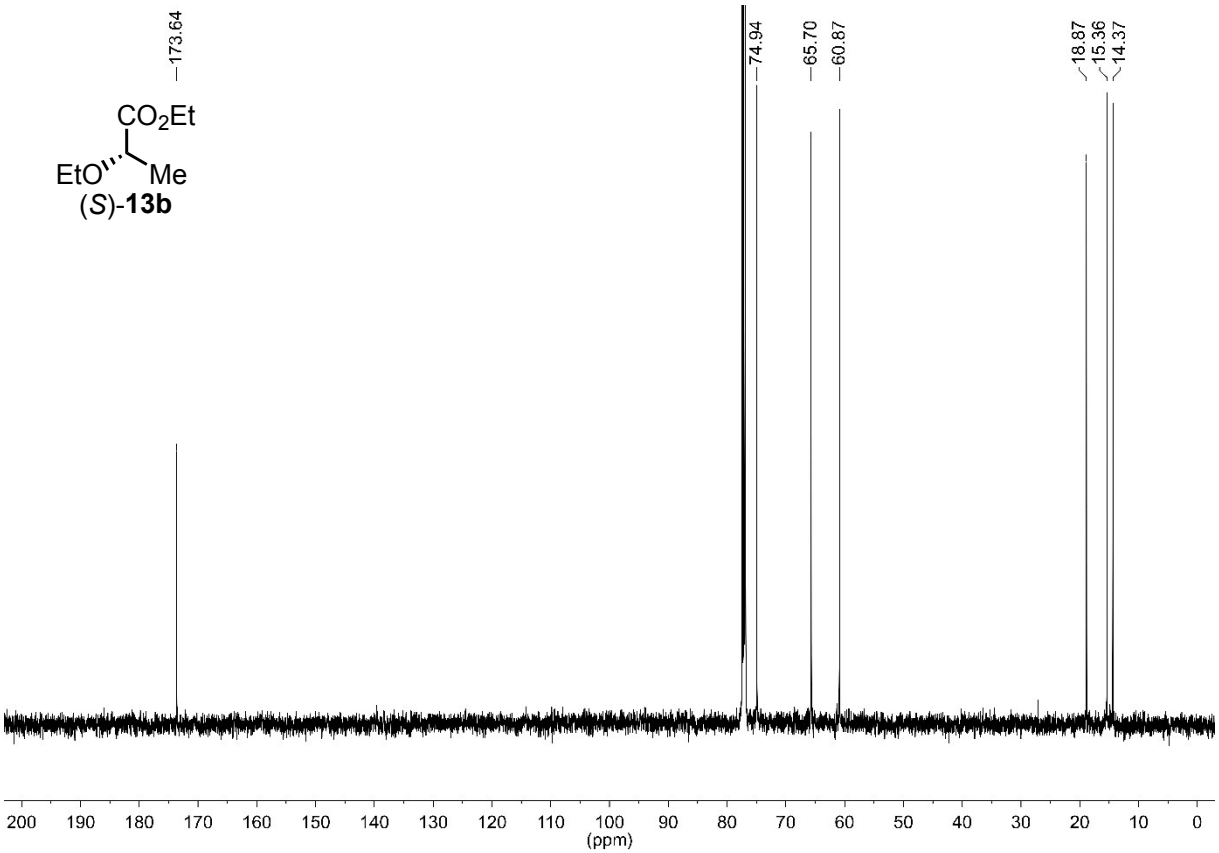
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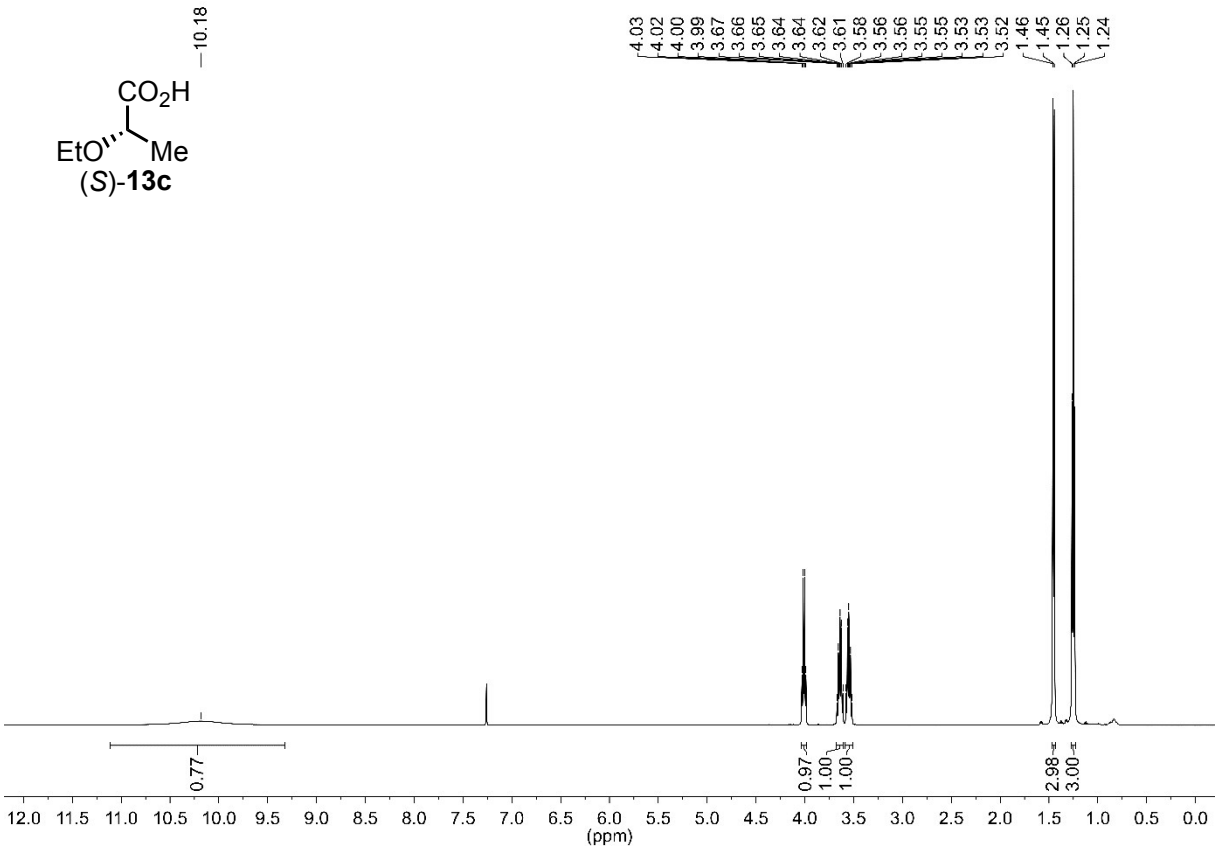
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1.25
1.24
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1.00
2.98
3.00
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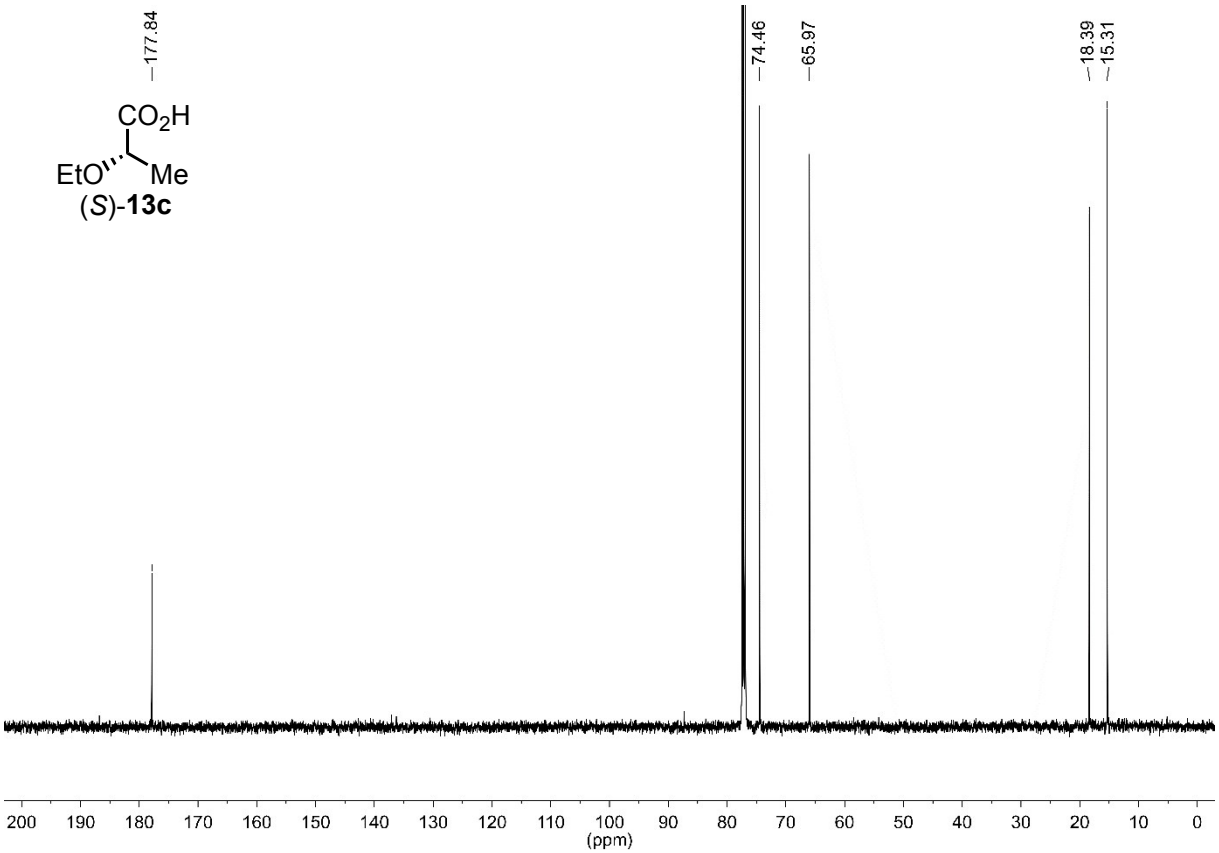
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Me
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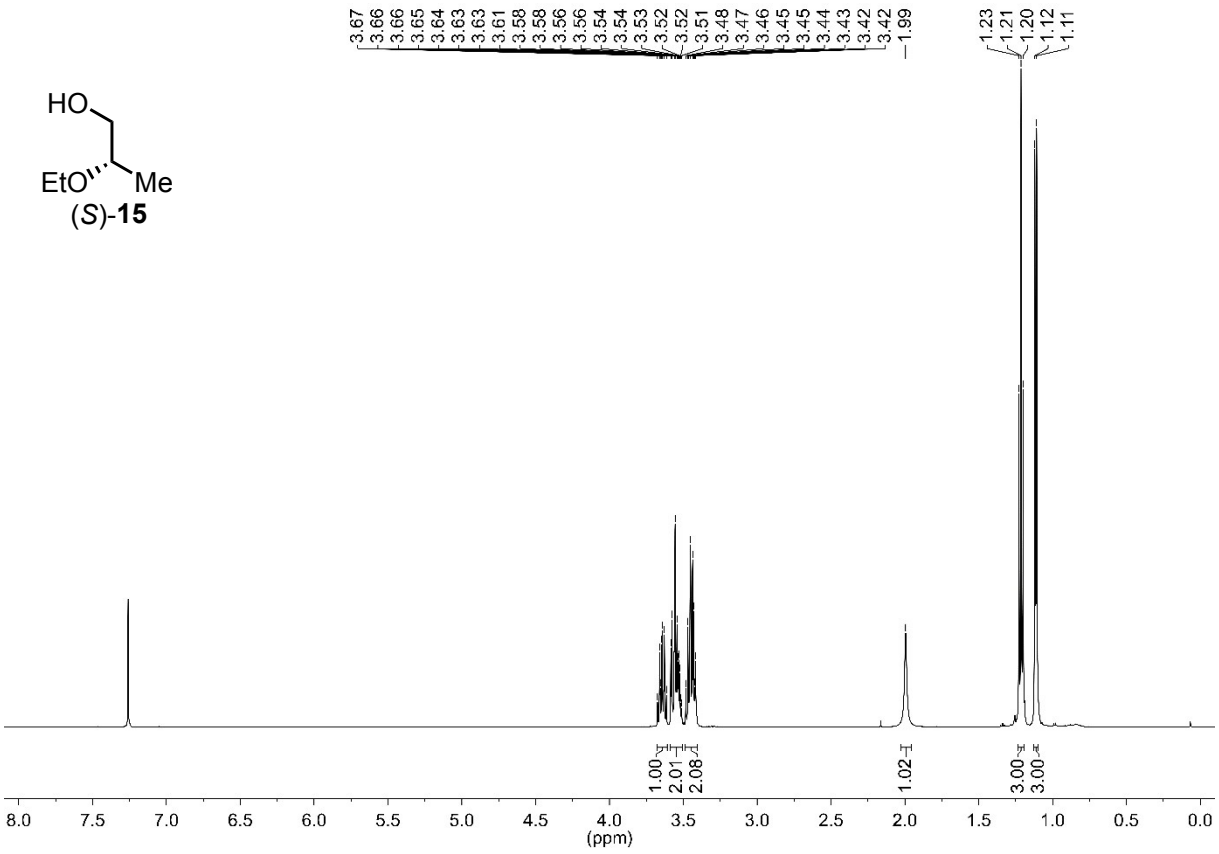
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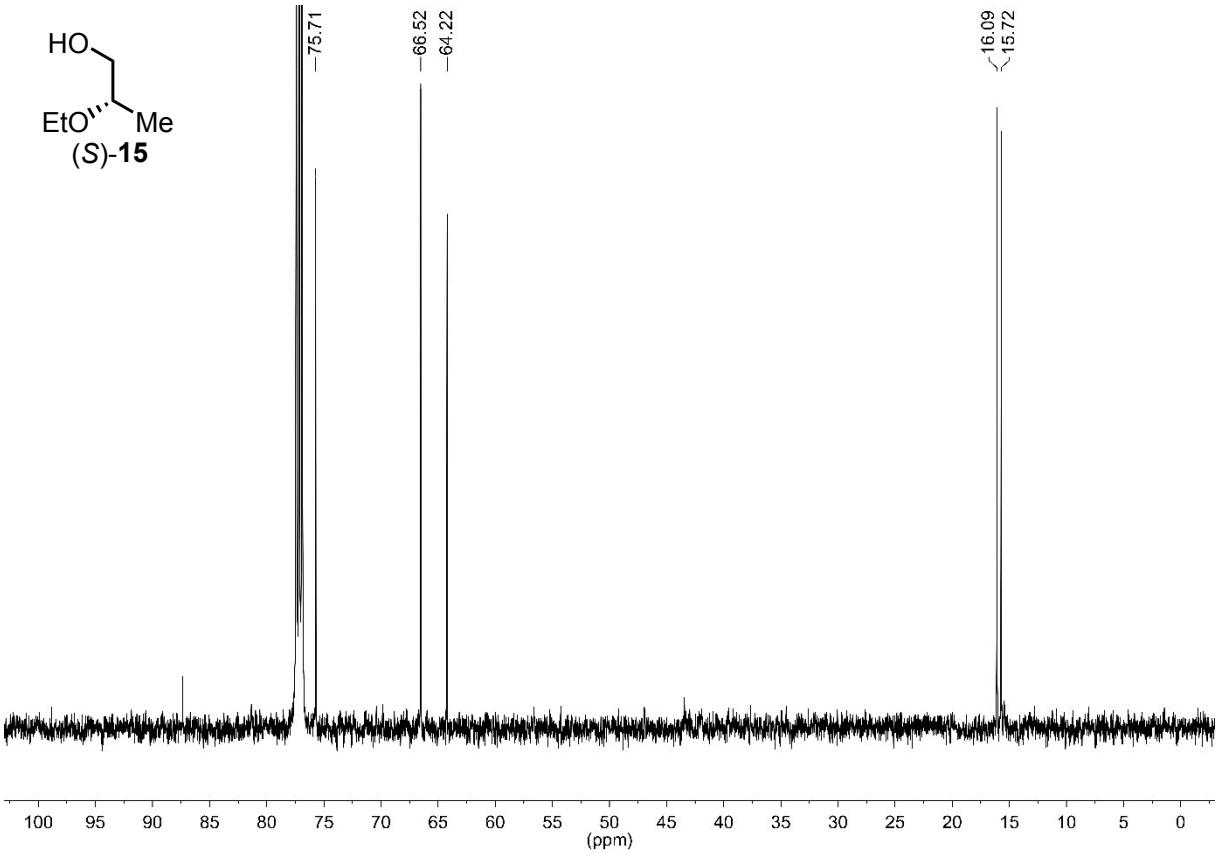
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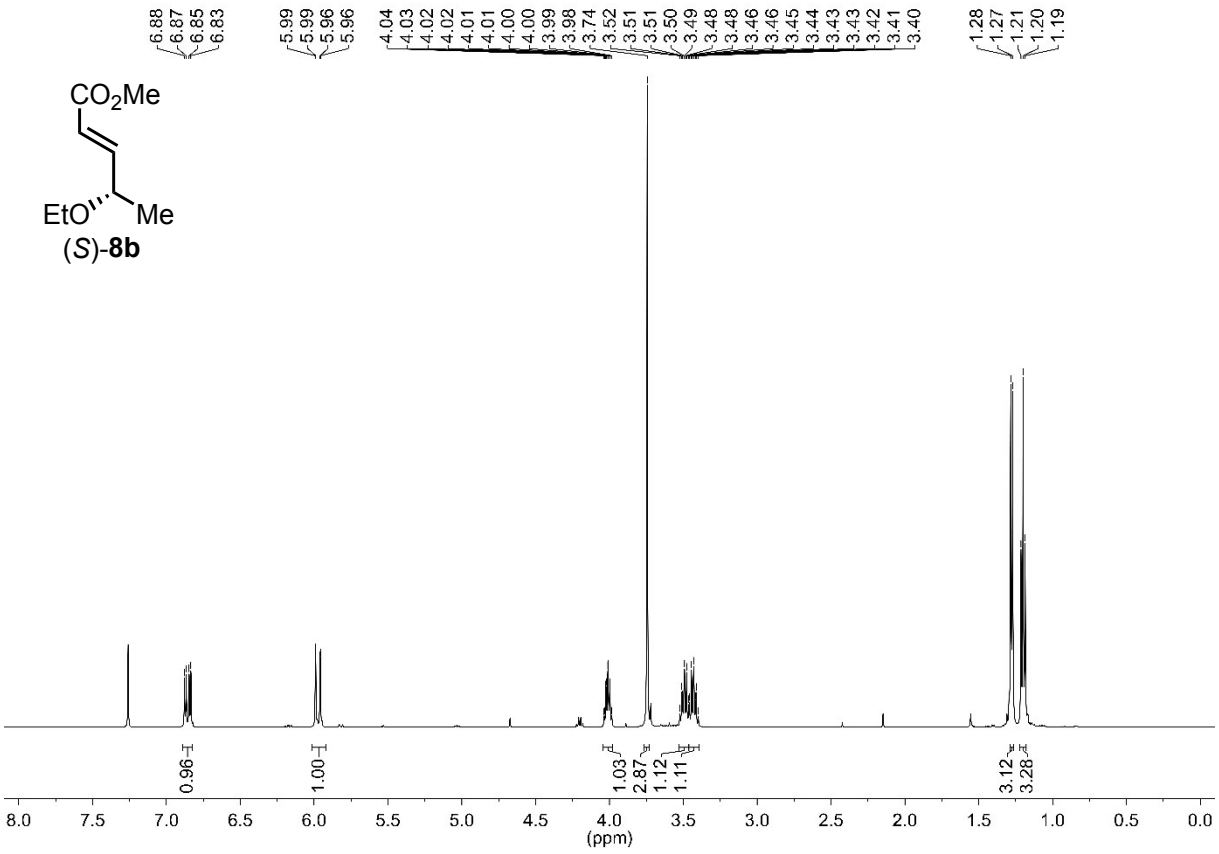
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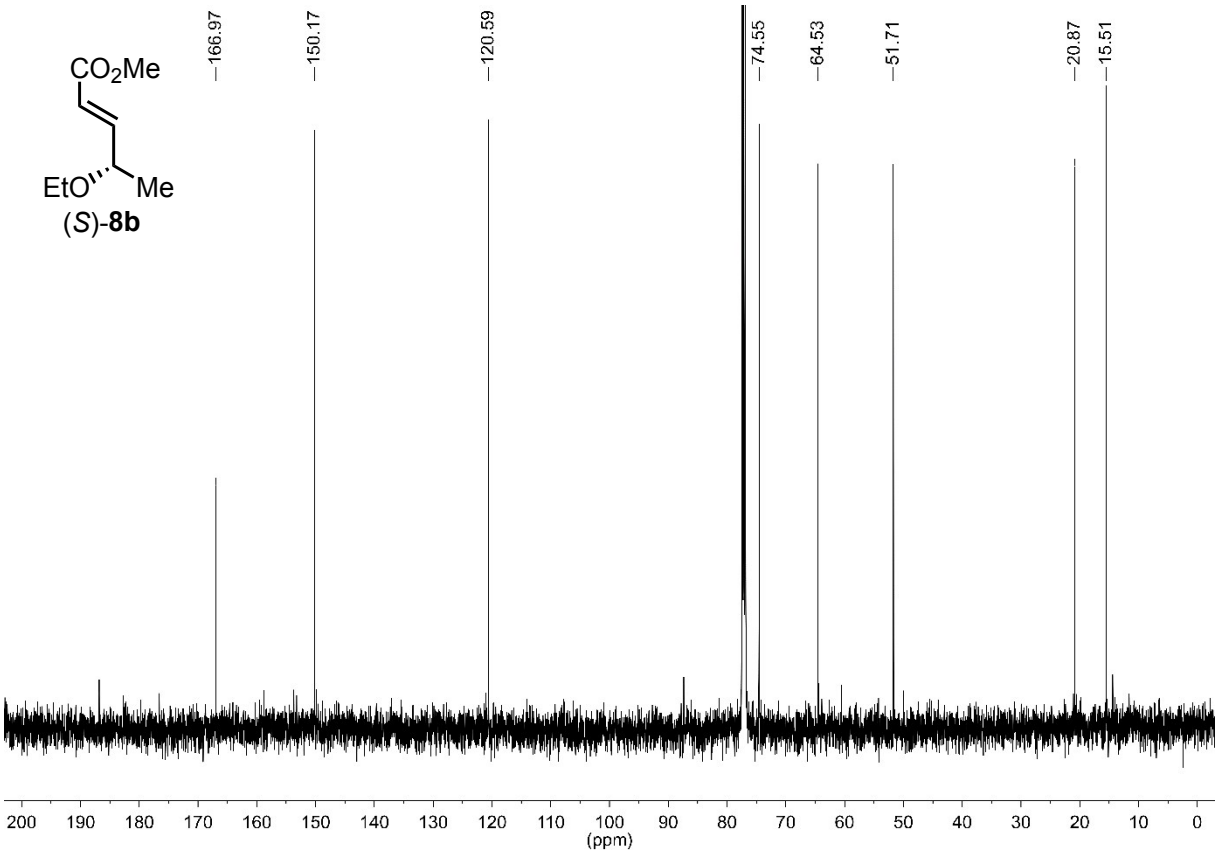
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Me
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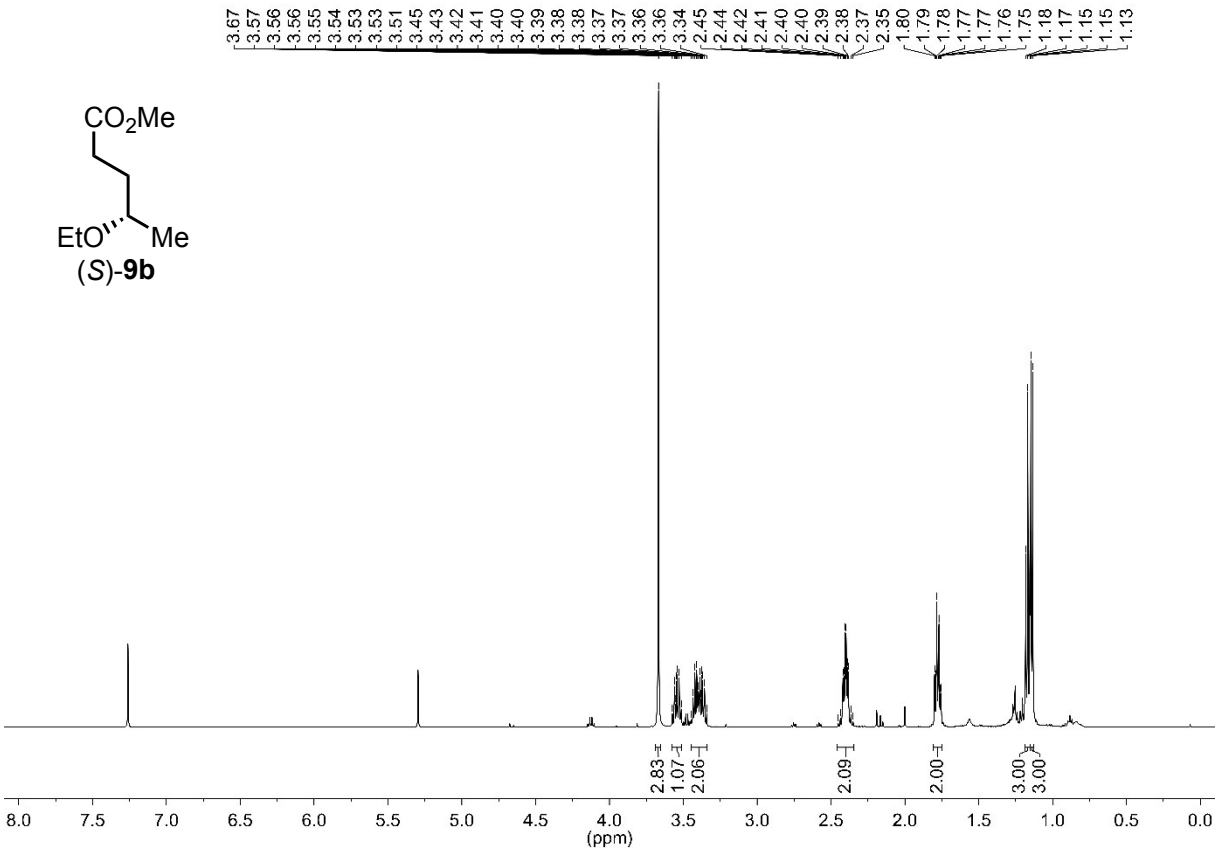
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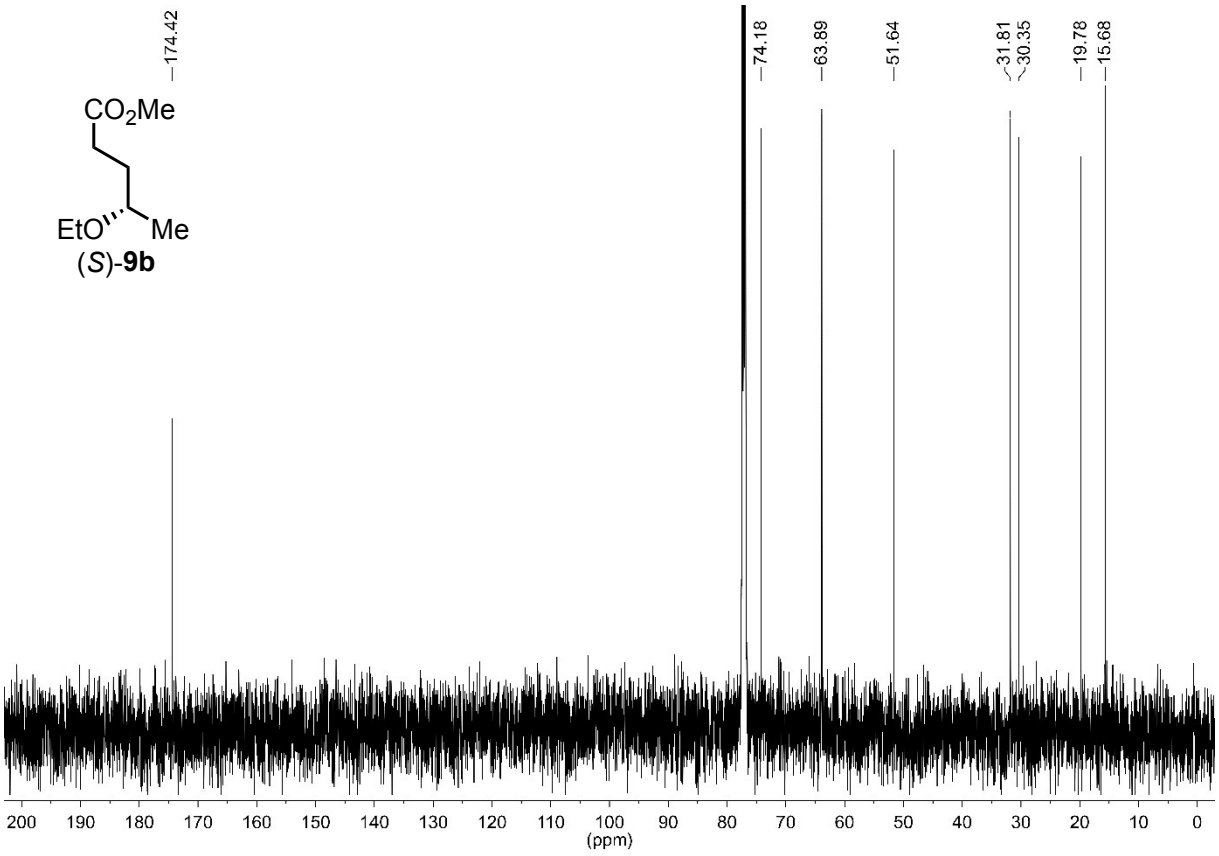
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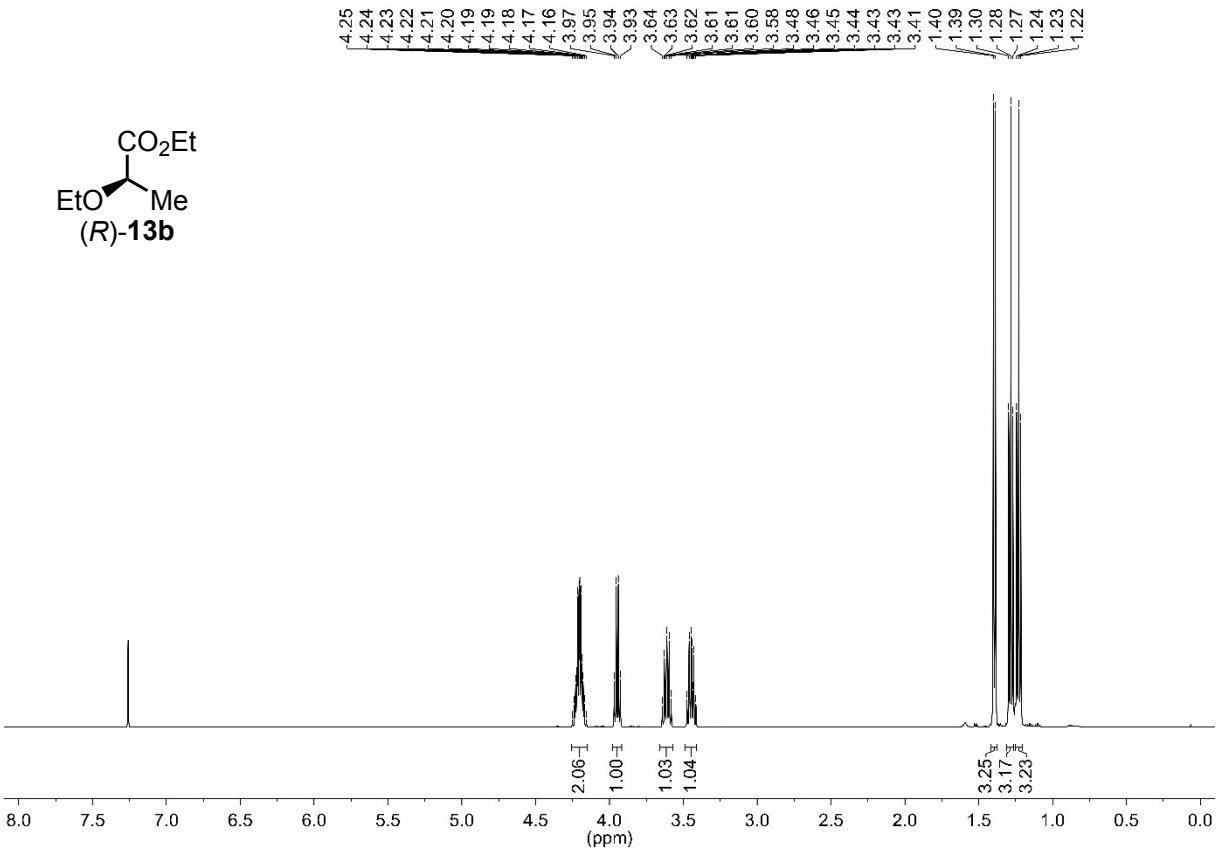
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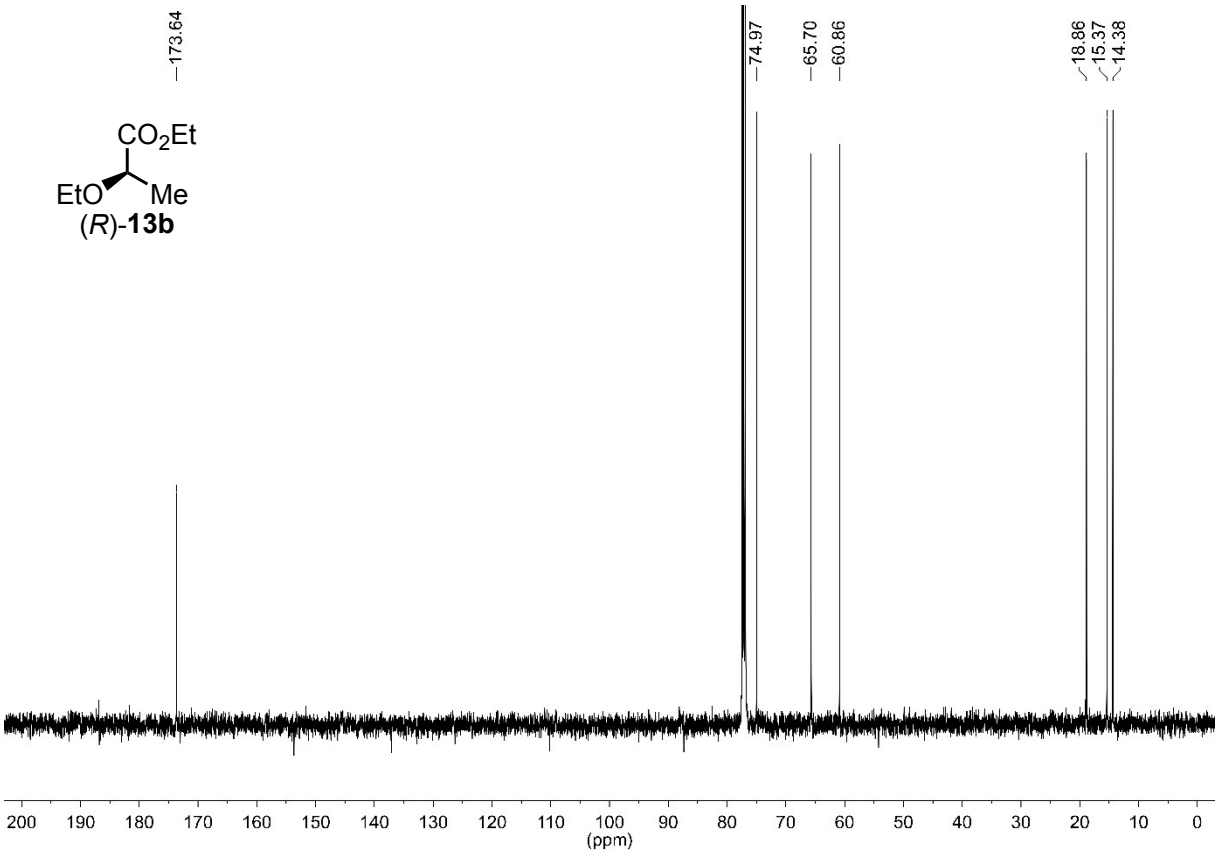
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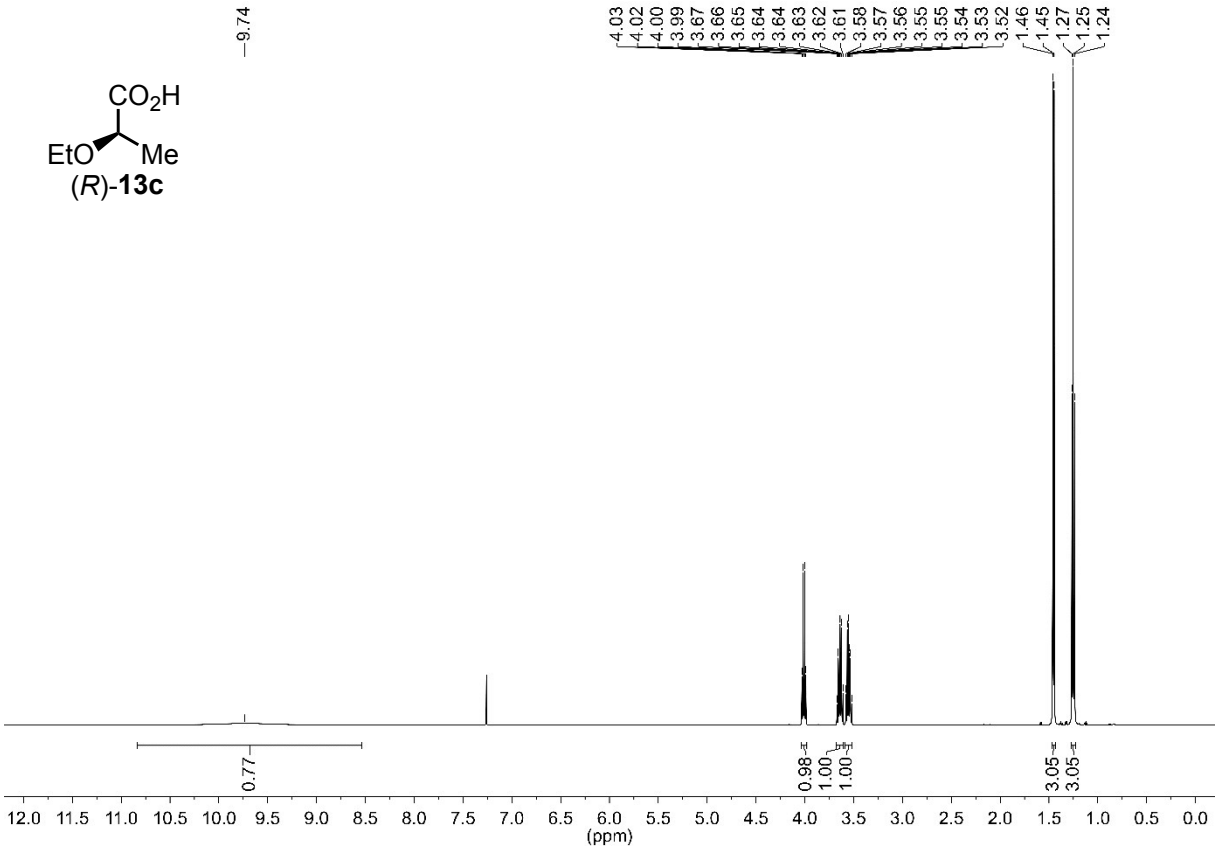
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1.25
1.24
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3.05
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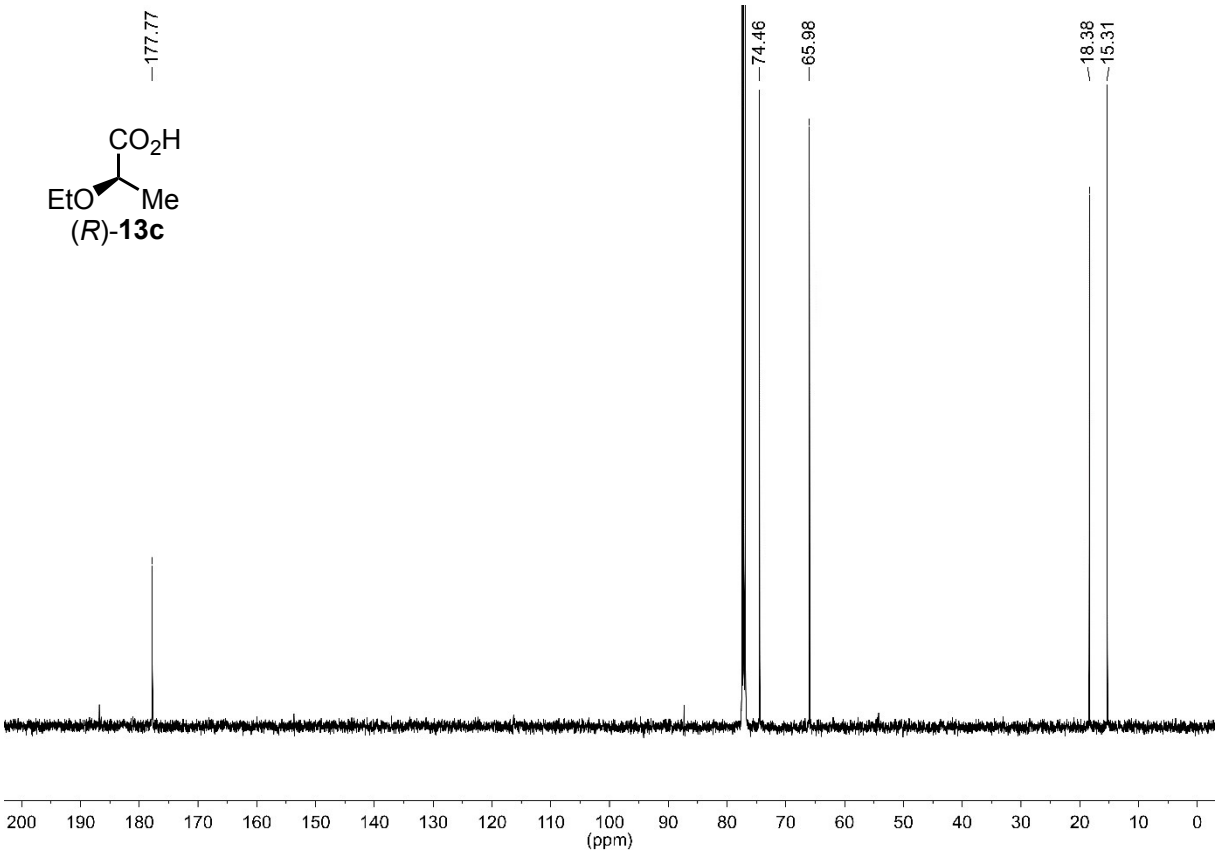
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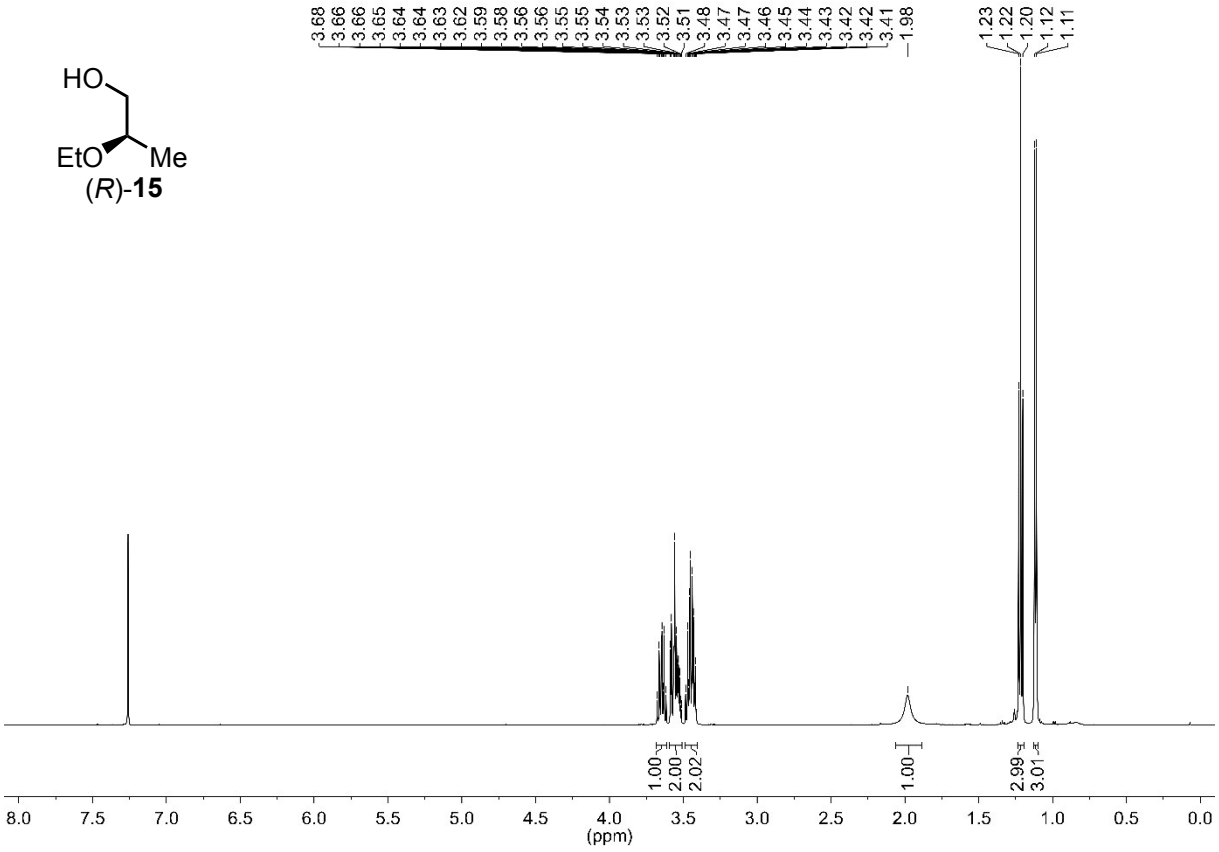
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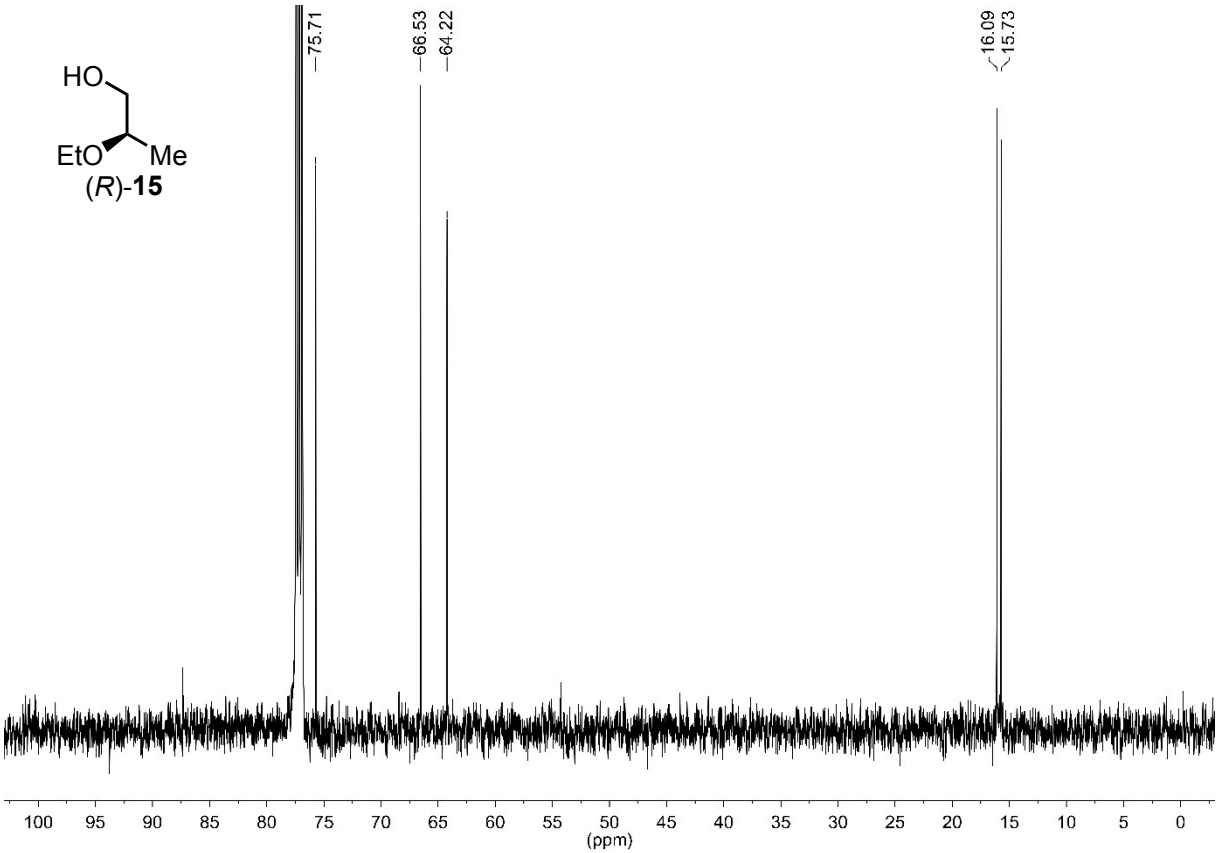
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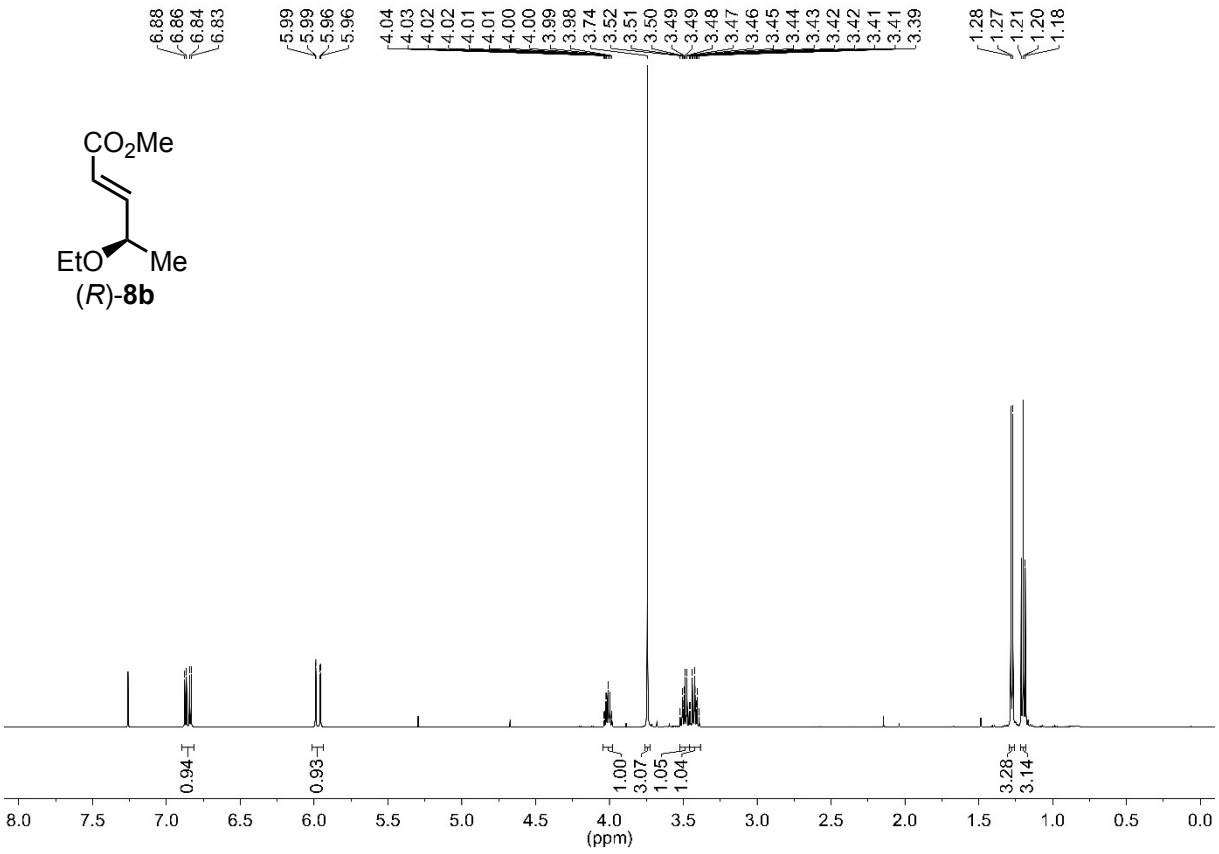
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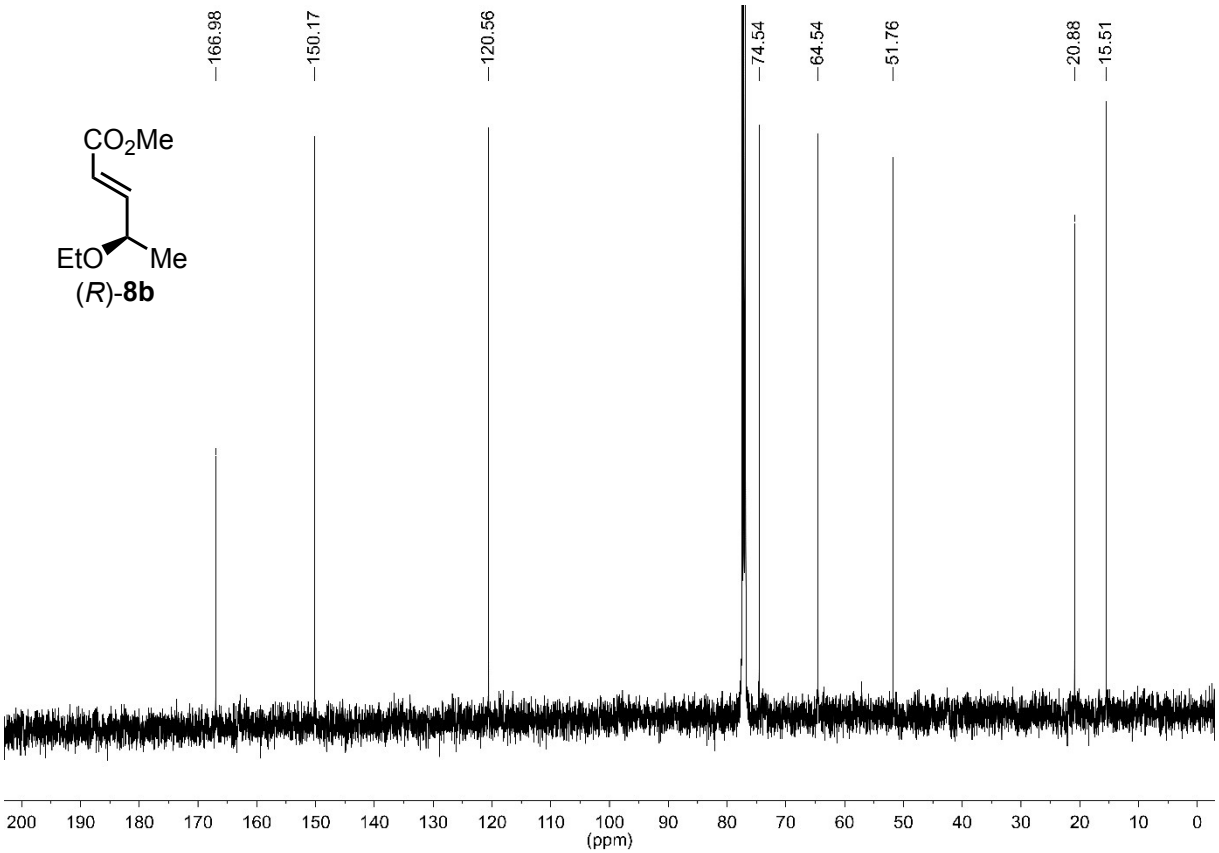
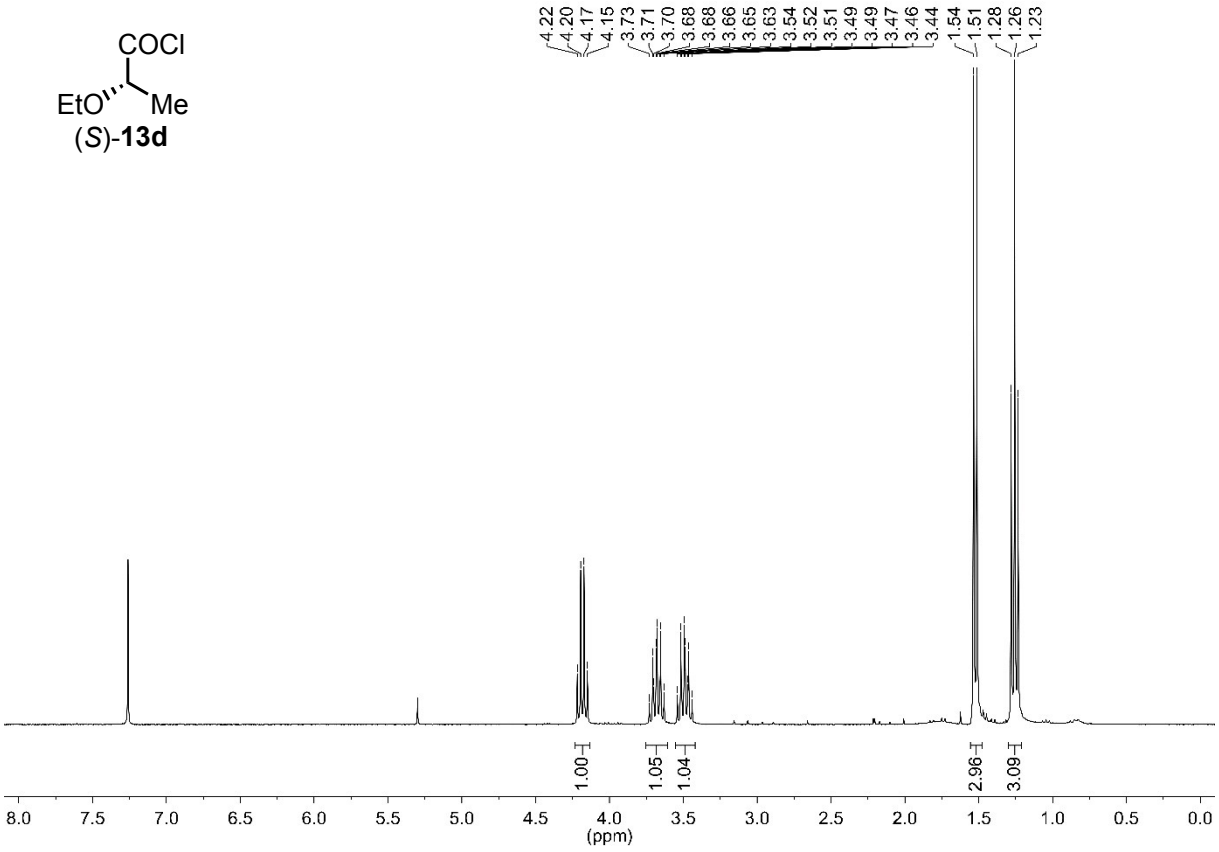
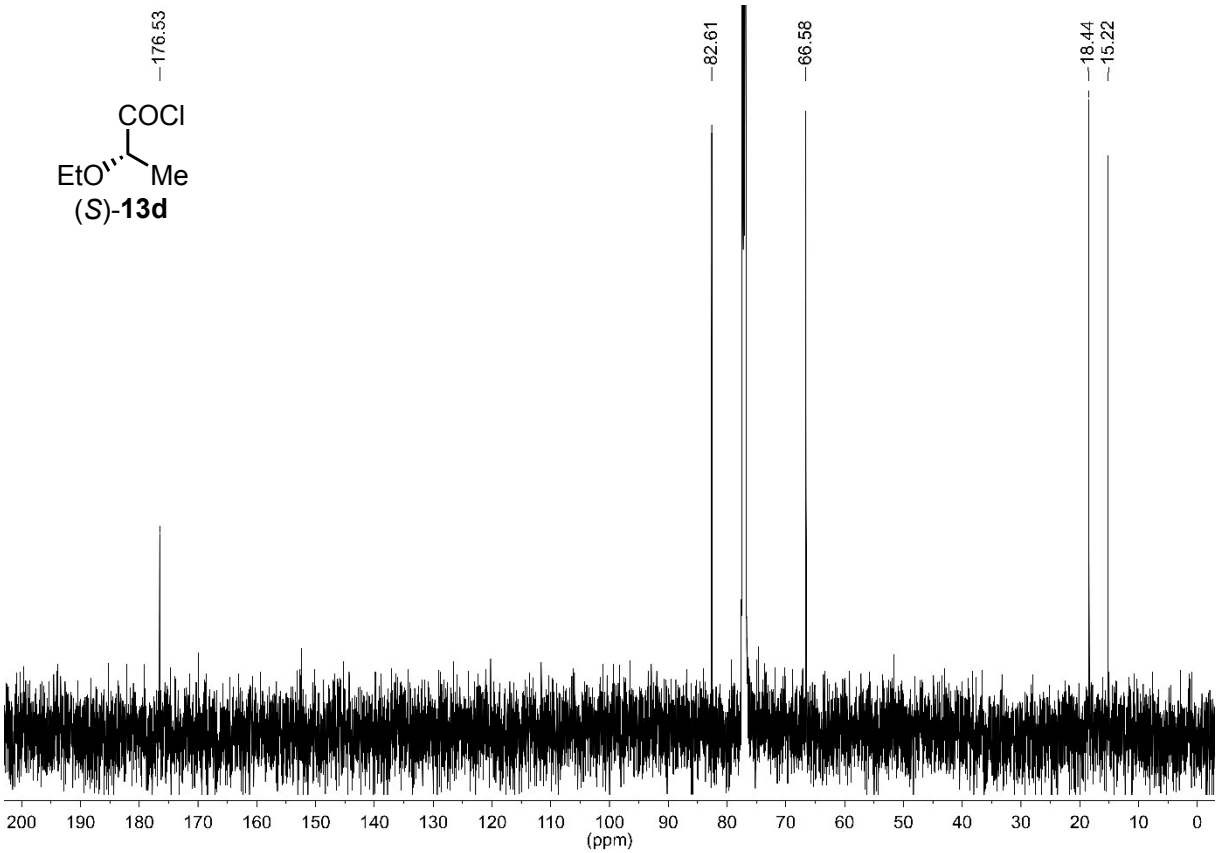
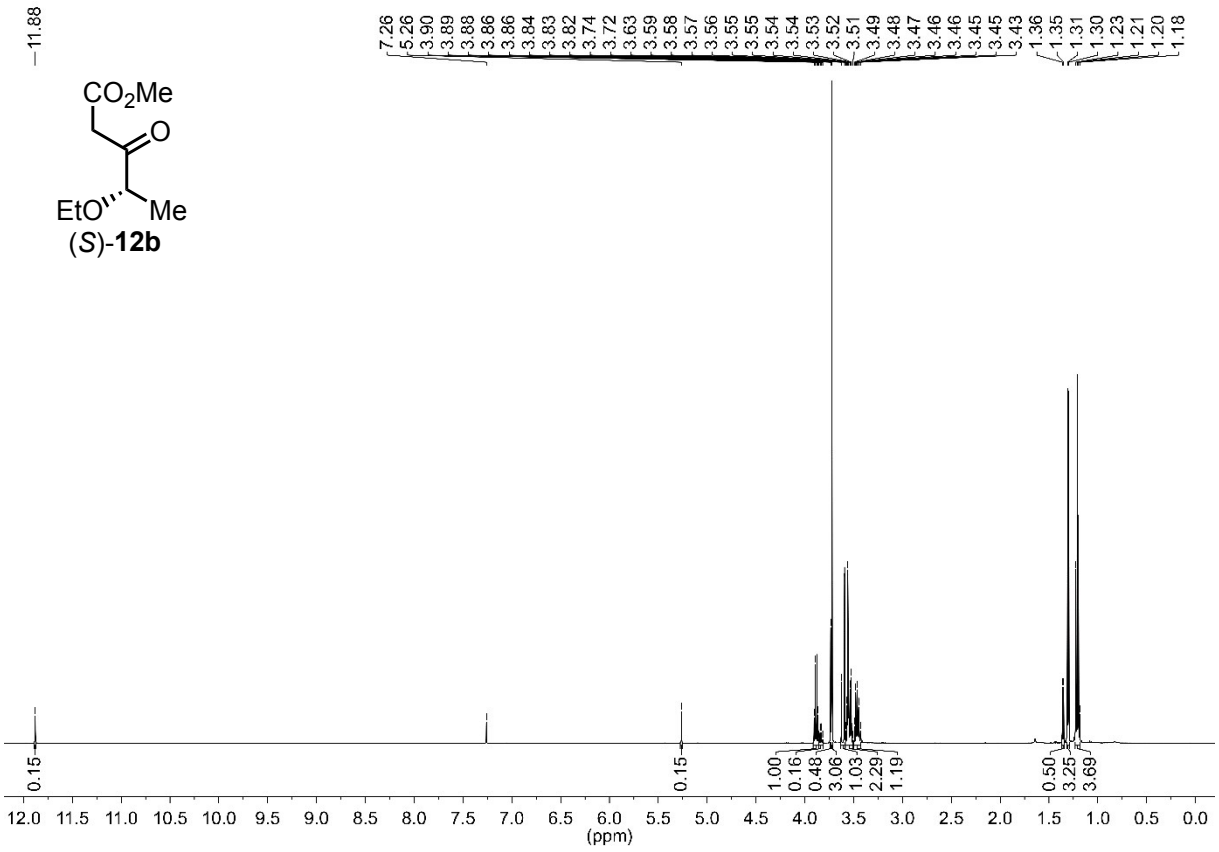
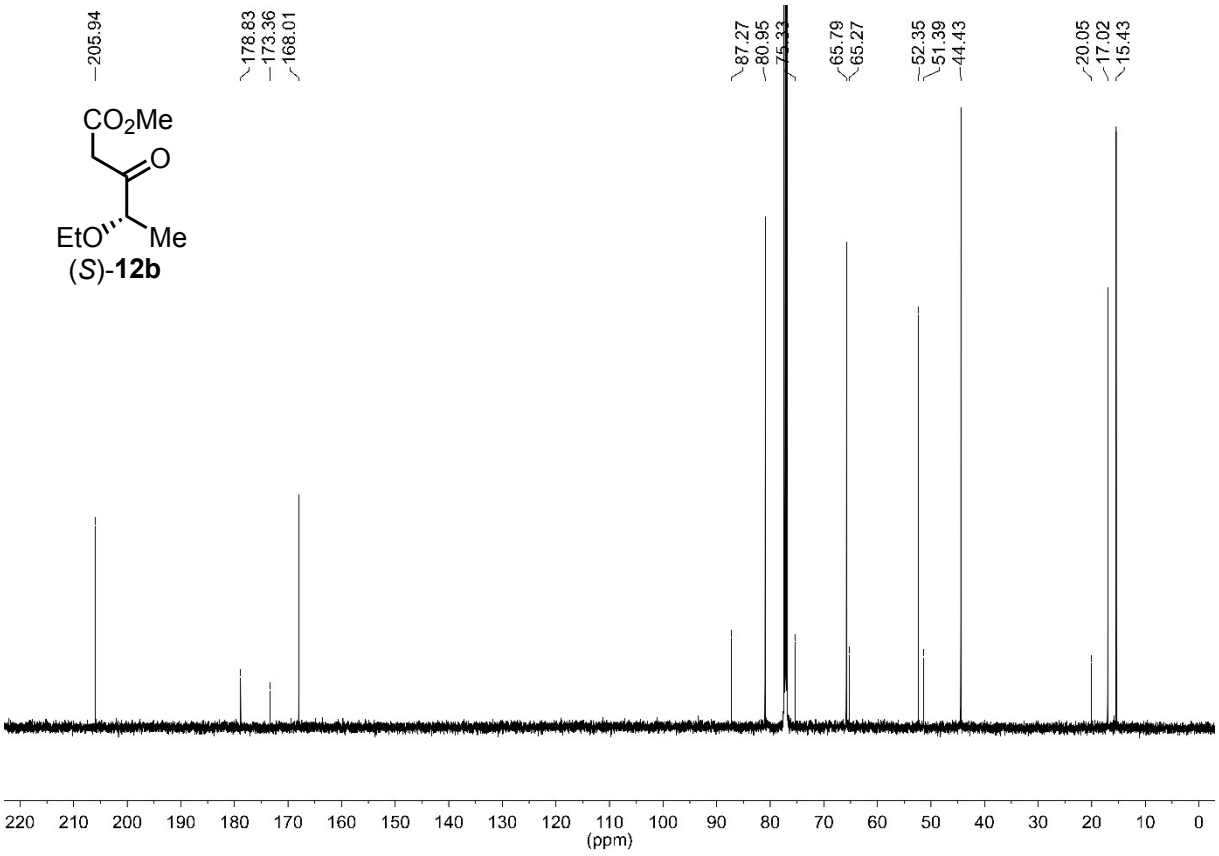
4.00
3.99
3.98
3.74
3.52
3.51
3.50
3.49
3.49
3.48
3.47
3.46
3.45
3.44
3.43
3.42
3.42
3.41
3.41
3.39
1.28
1.27
1.21
1.20
1.18
CO2Me
EtO
Me
(R)-8b
0.94
0.93
1.00
3.07
1.05
1.04
3.28
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

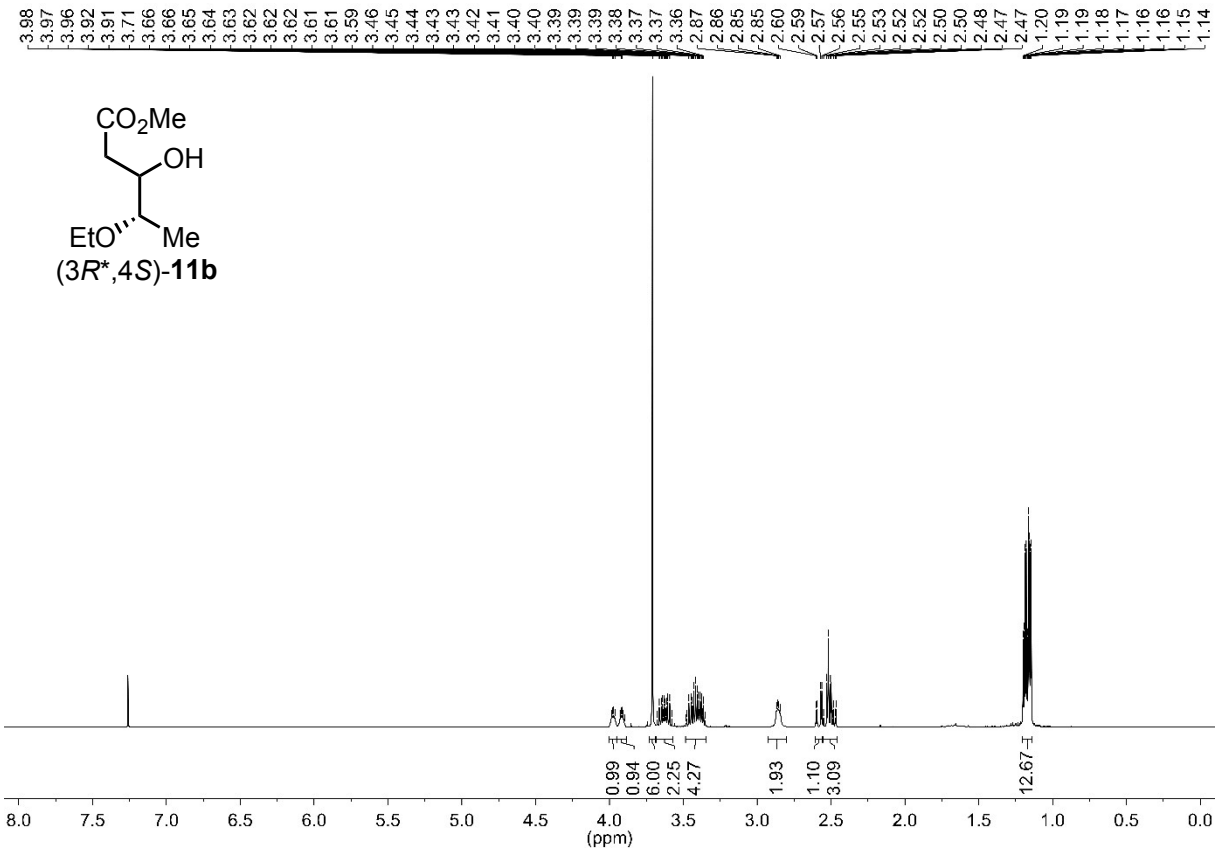

166.98
150.17
120.56
74.54
64.54
51.76
20.88
15.51
CO2Me
EtO
Me
(R)-8b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

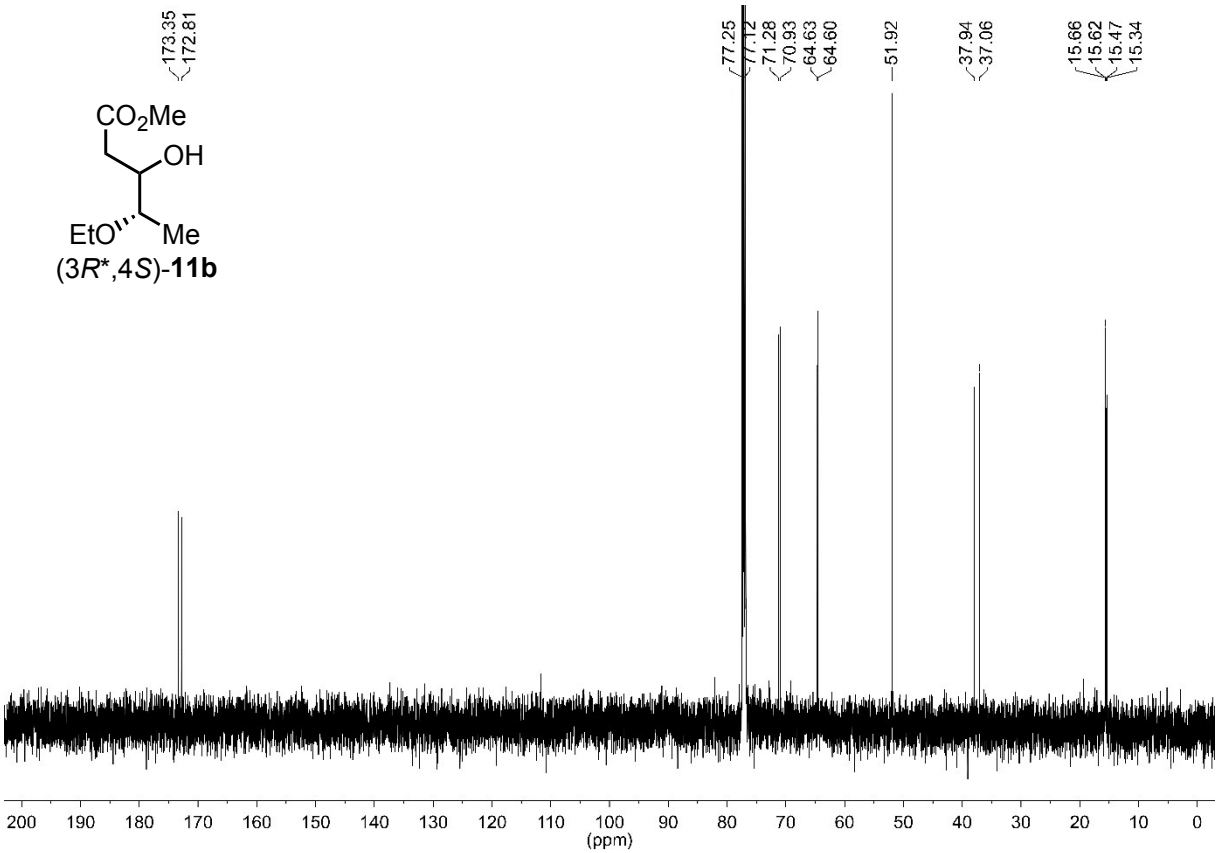

COCl
EtO
Me
(S)-13d
4.22
4.20
4.17
4.15
3.73
3.71
3.70
3.68
3.68
3.66
3.65
3.63
3.54
3.52
3.51
3.49
3.49
3.47
3.46
3.44
1.54
1.51
1.28
1.26
1.23
1.00
1.05
1.04
2.96
3.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

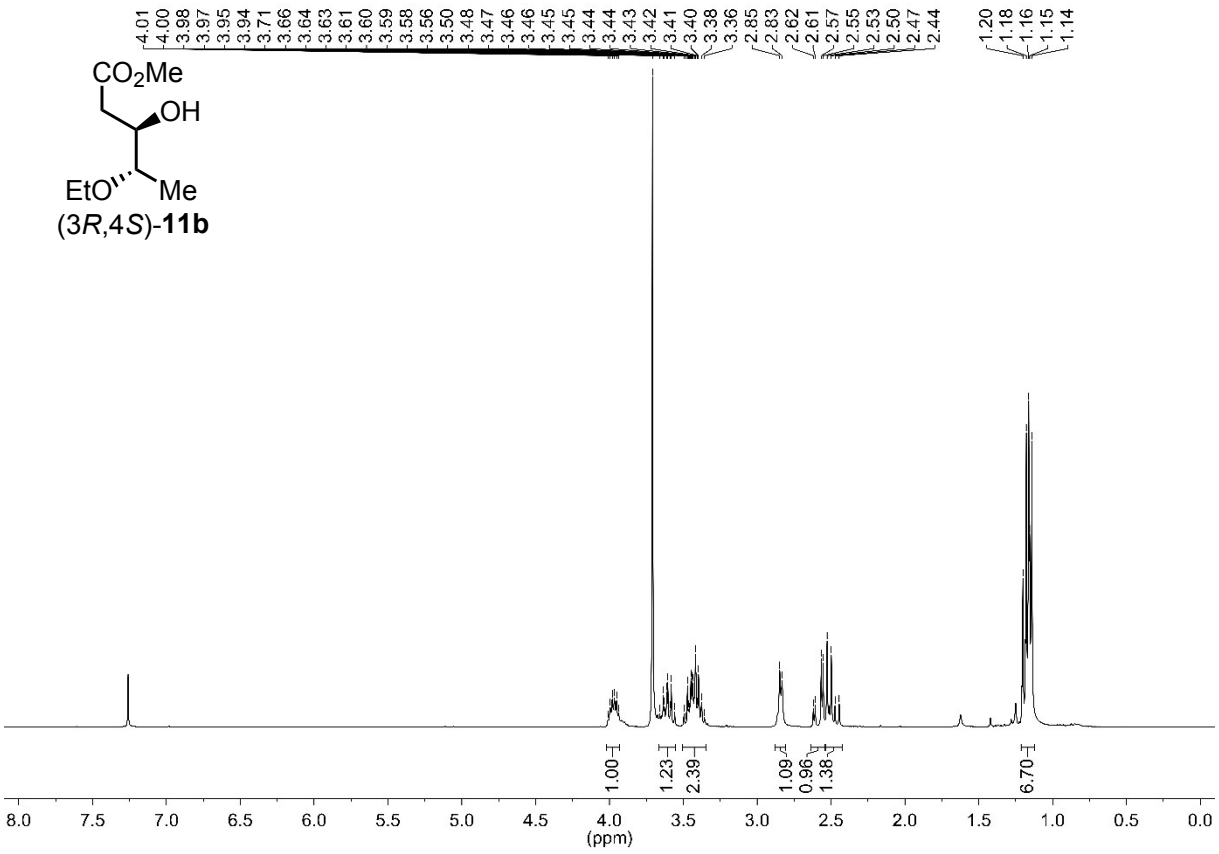

COCl
EtO
Me
(S)-13d
176.53
82.61
66.58
18.44
15.22
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

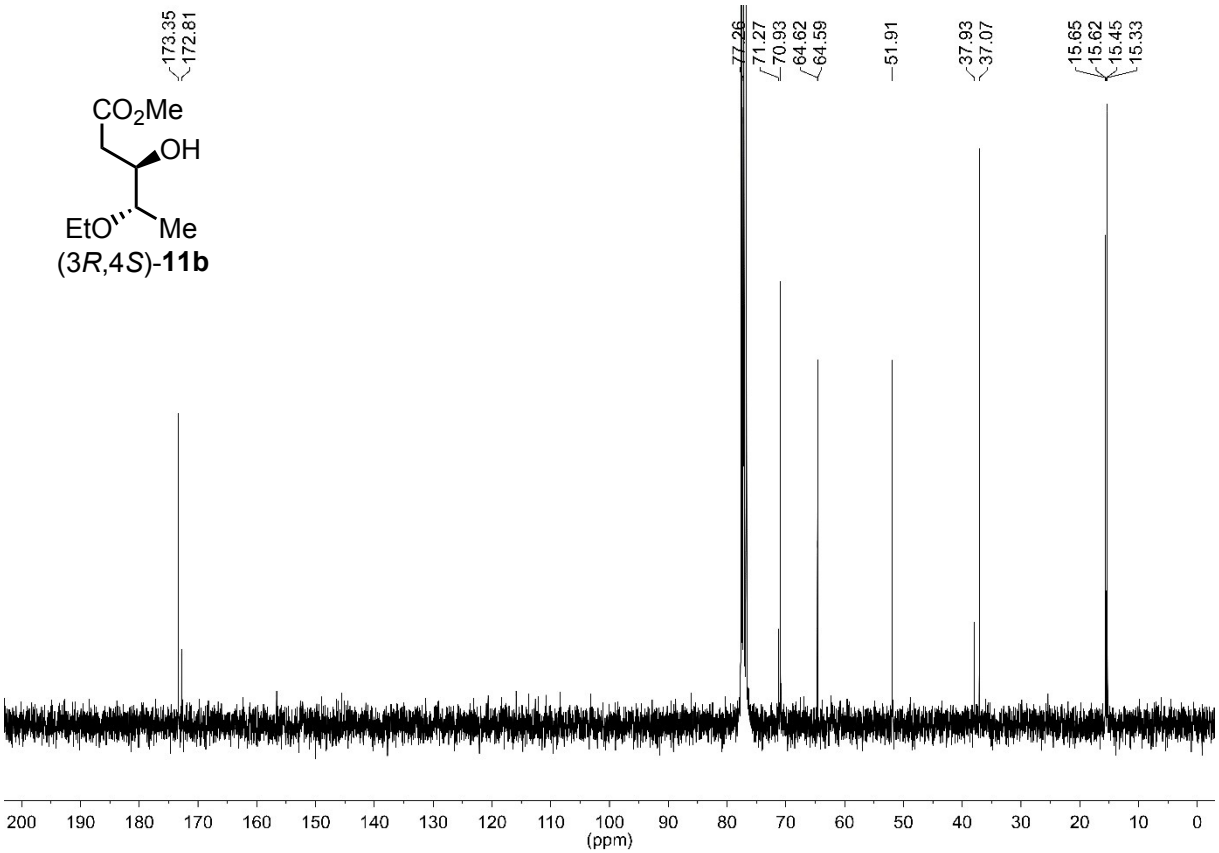

11.88
7.26
5.26
3.90
3.89
3.88
3.86
3.86
3.84
3.83
3.82
3.74
3.72
3.63
3.59
3.58
3.57
3.56
3.55
3.55
3.54
3.54
3.53
3.52
3.51
3.49
3.48
3.47
3.46
3.46
3.45
3.45
3.43
1.36
1.35
1.31
1.30
1.23
1.21
1.20
1.18
CO2Me
O
EtO
Me
(S)-12b
0.15
0.15
1.00
0.16
0.48
3.06
1.03
2.29
1.19
0.50
3.25
3.69
12.0 11.5 11.0 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
(ppm)

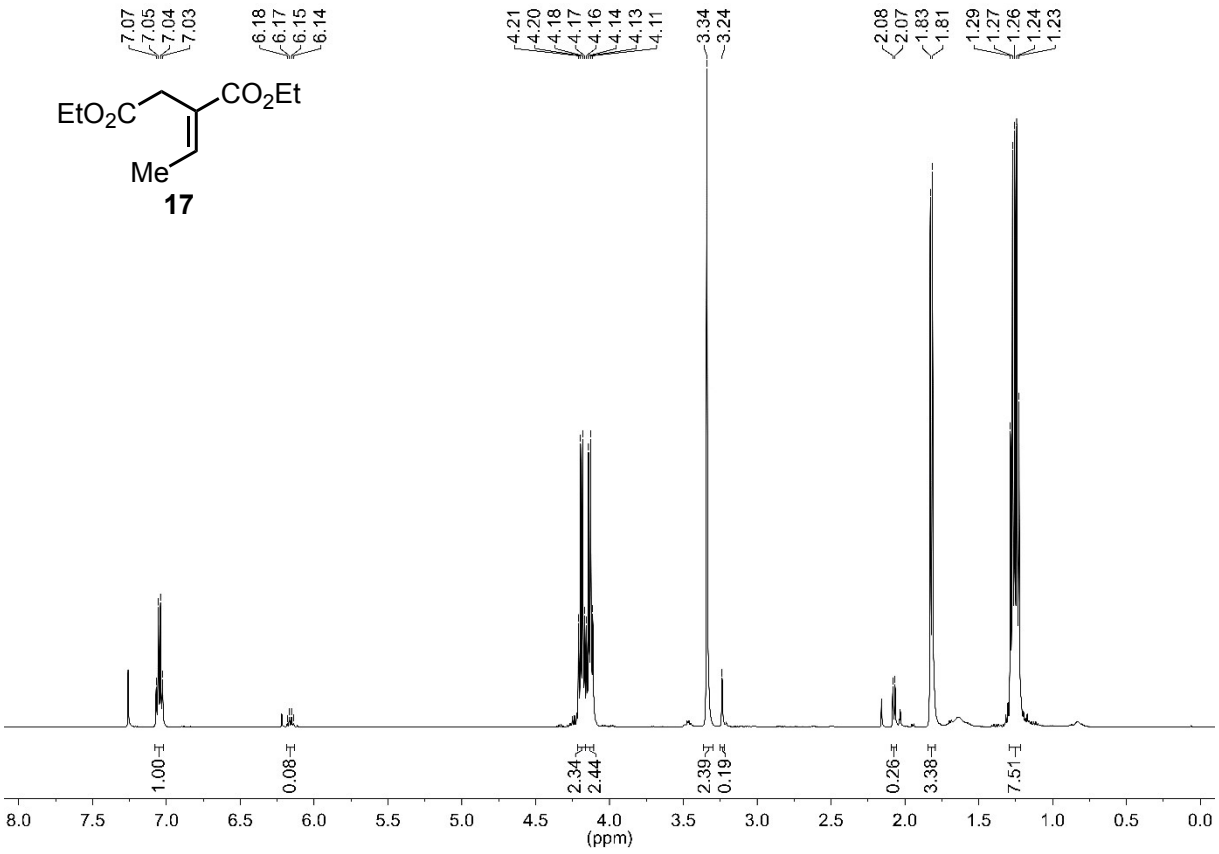

205.94
178.83
173.36
168.01
87.27
80.95
75.33
65.79
65.27
52.35
51.39
44.43
20.05
17.02
15.43
CO2Me
O
EtO
Me
(S)-12b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

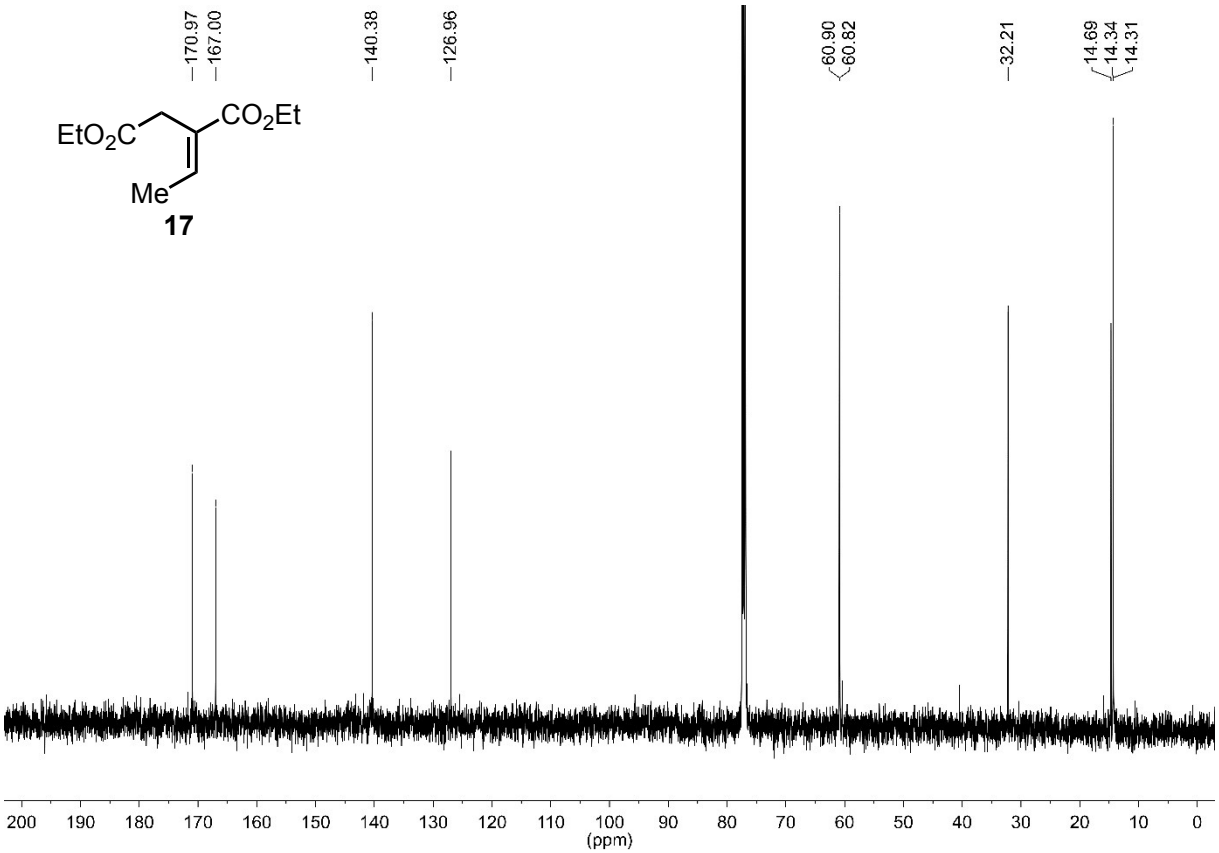

3.98 3.97 3.96 3.92 3.91 3.71 3.66 3.66 3.65 3.64 3.63 3.62 3.62 3.62 3.61 3.61 3.59 3.46 3.45 3.44 3.43 3.43 3.42 3.41 3.40 3.40 3.39 3.39 3.39 3.38 3.37 3.37 3.36 2.87 2.86 2.85 2.85 2.60 2.59 2.57 2.56 2.55 2.53 2.52 2.52 2.50 2.50 2.48 2.47 2.47 1.20 1.19 1.19 1.18 1.17 1.16 1.16 1.15 1.14
CO2Me
OH
EtO
Me
(3R*,4S)-11b
0.99 0.94 6.00 2.25 4.27 1.93 1.10 3.09 12.67
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
(ppm)

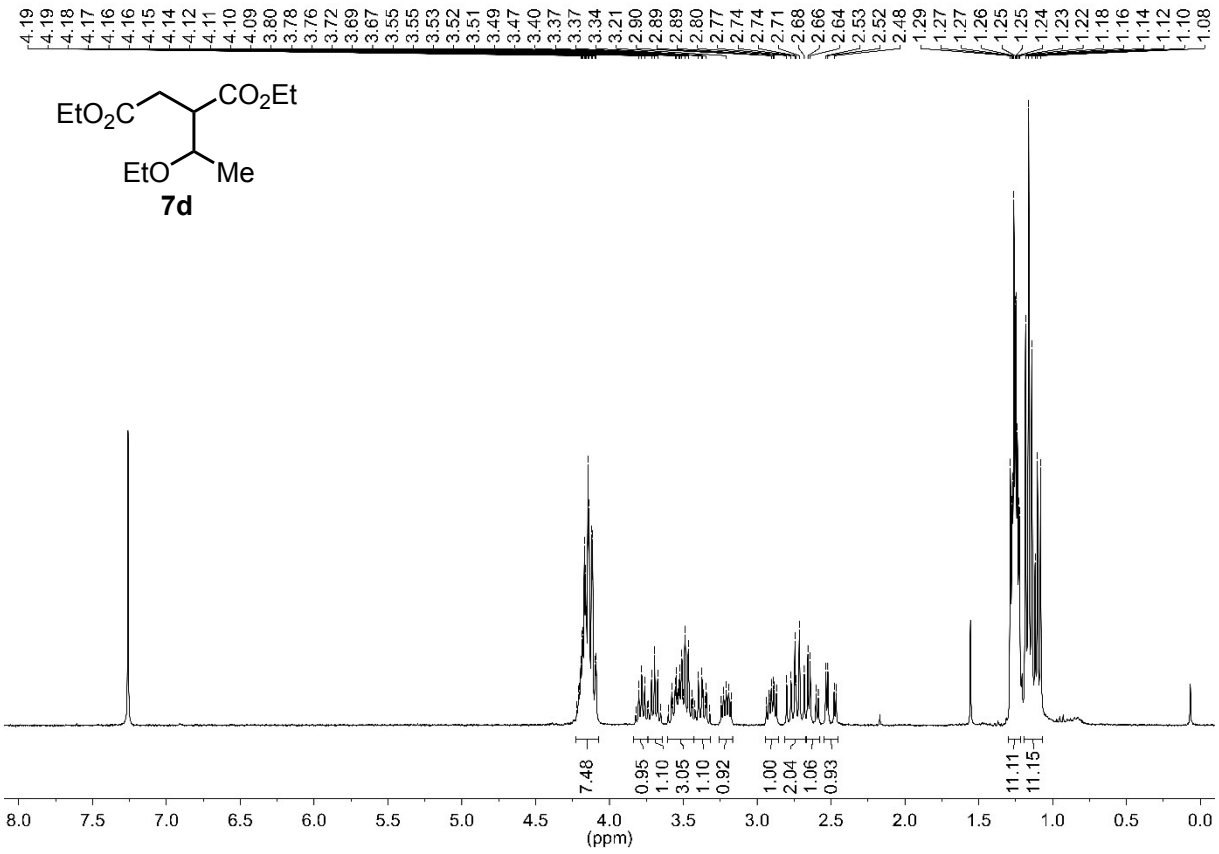

173.35 172.81
77.25 77.12 71.28 70.93 64.63 64.60 51.92 37.94 37.06 15.66 15.62 15.47 15.34
CO2Me
OH
EtO
Me
(3R*,4S)-11b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

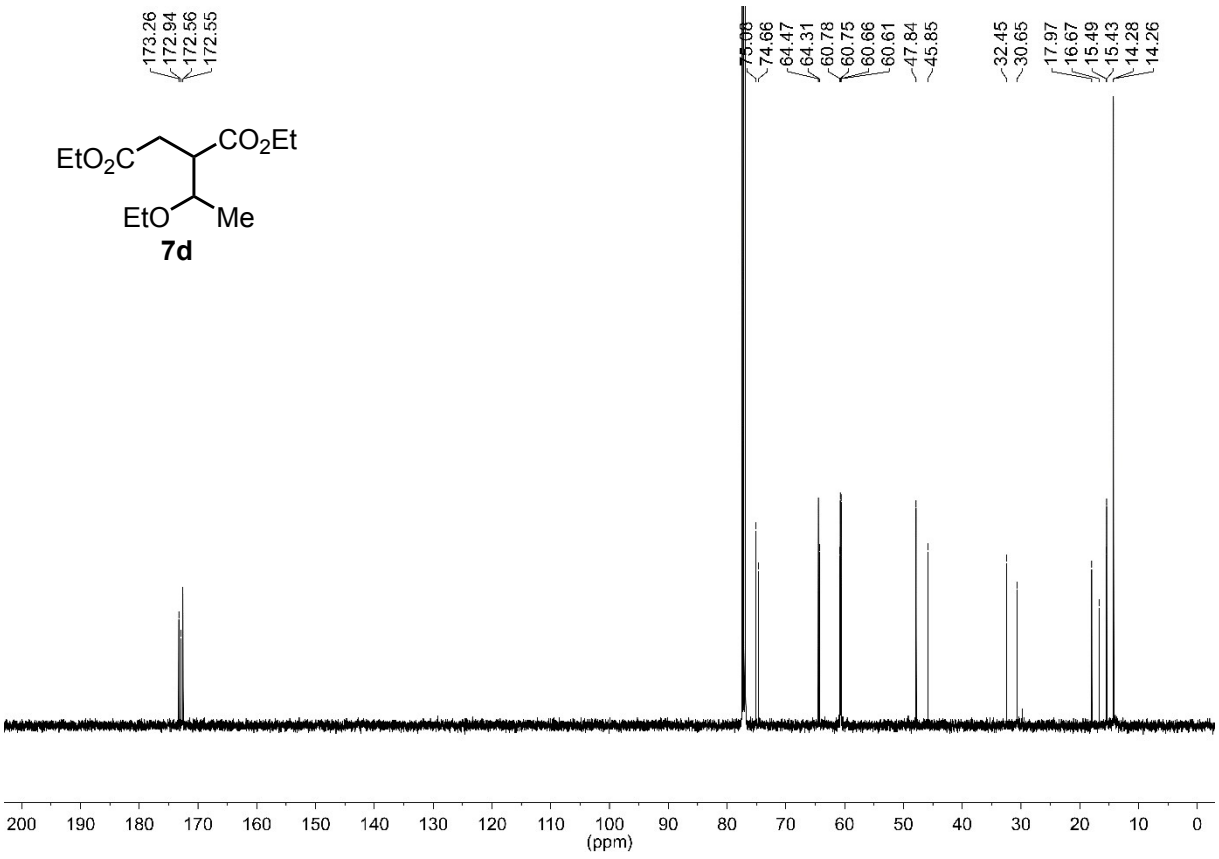

4.01
4.00
3.98
3.97
3.95
3.94
3.71
3.66
3.64
3.63
3.61
3.60
3.59
3.58
3.56
3.50
3.48
3.47
3.46
3.46
3.45
3.45
3.44
3.44
3.43
3.42
3.41
3.40
3.38
3.36
2.85
2.83
2.62
2.61
2.57
2.55
2.53
2.50
2.47
2.44
1.20
1.18
1.16
1.15
1.14
CO2Me
OH
EtO
Me
(3R,4S)-11b
1.00
1.23
2.39
1.09
0.96
1.38
6.70
8.0
7.5
7.0
6.5
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
(ppm)

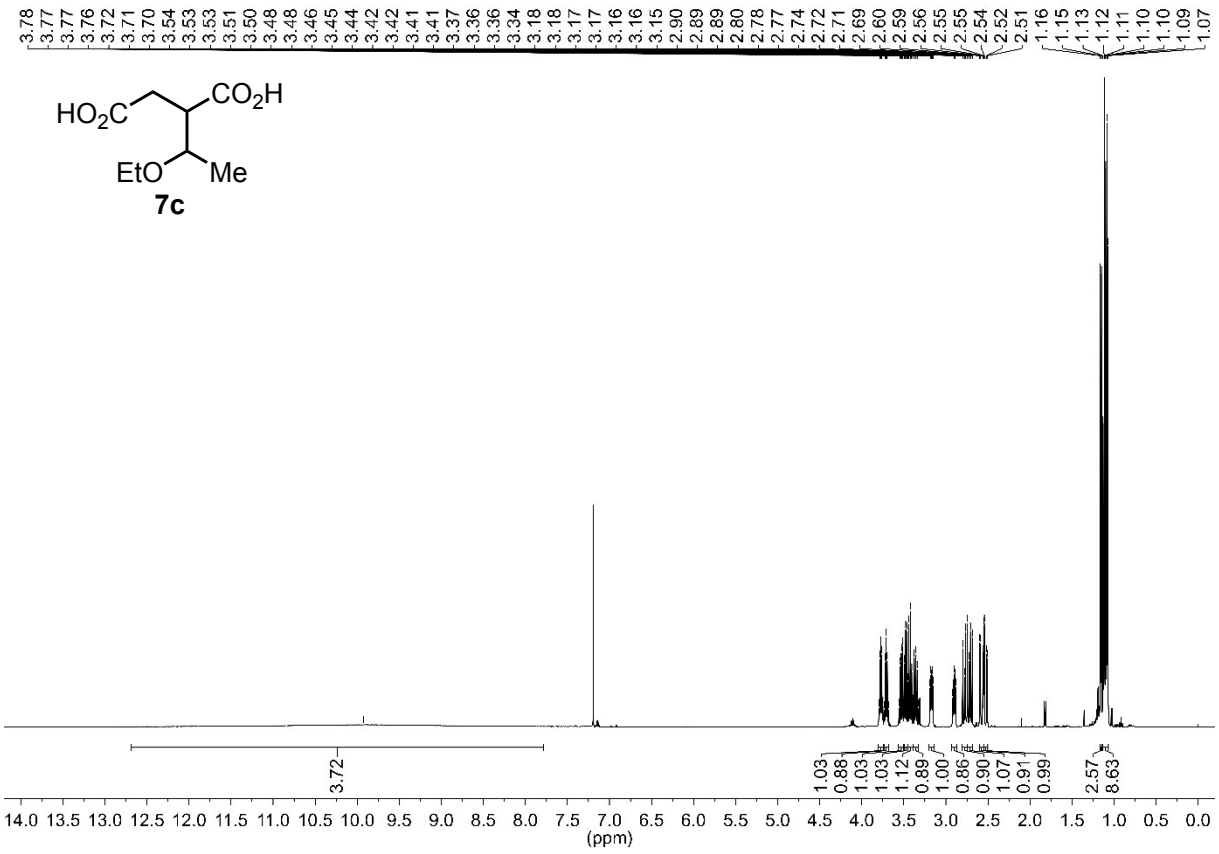

173.35
172.81
77.26
71.27
70.93
64.62
64.59
51.91
37.93
37.07
15.65
15.62
15.45
15.33
CO2Me
OH
EtO
Me
(3R,4S)-11b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

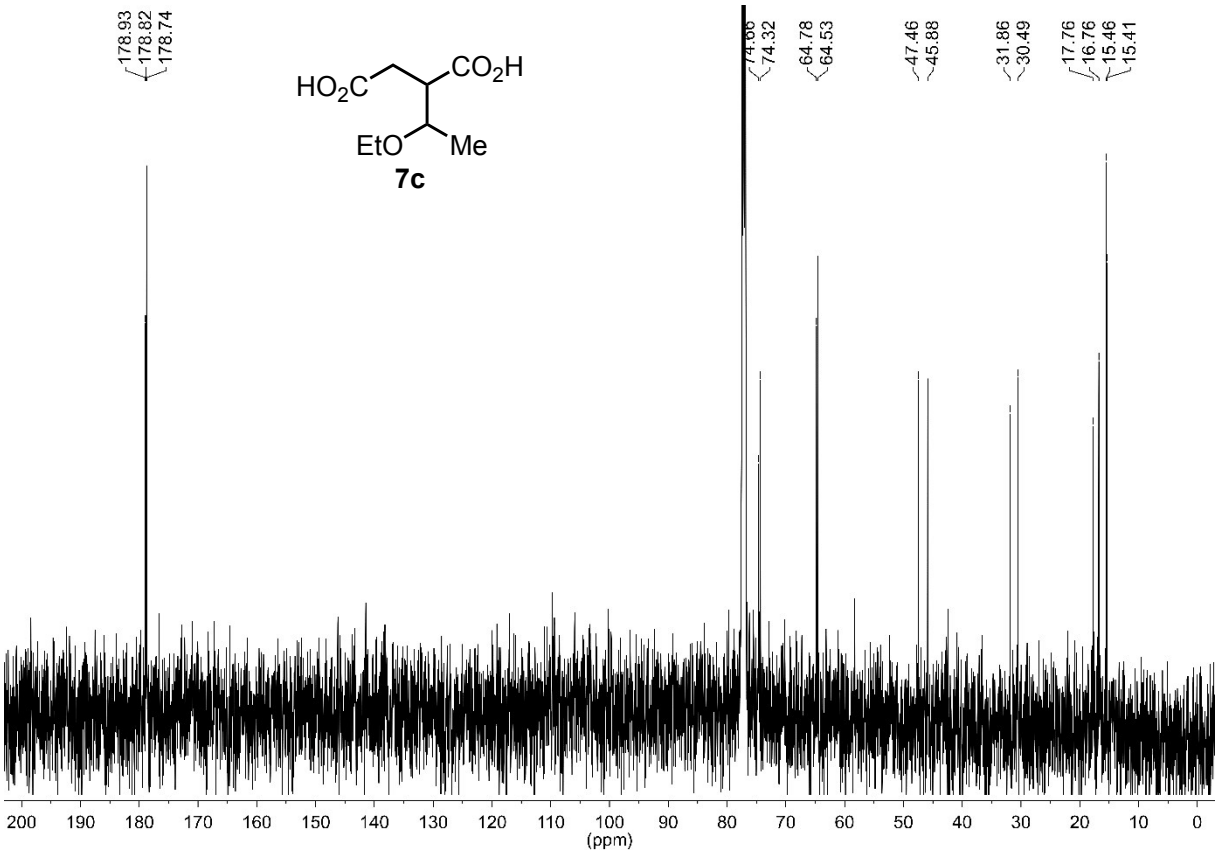

7.07
7.05
7.04
7.03
6.18
6.17
6.15
6.14
4.21
4.20
4.18
4.17
4.16
4.14
4.13
4.11
3.34
3.24
2.08
2.07
1.83
1.81
1.29
1.27
1.26
1.24
1.23
EtO2C
CO2Et
Me
17
1.00
0.08
2.34
2.44
2.39
0.19
0.26
3.38
7.51
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

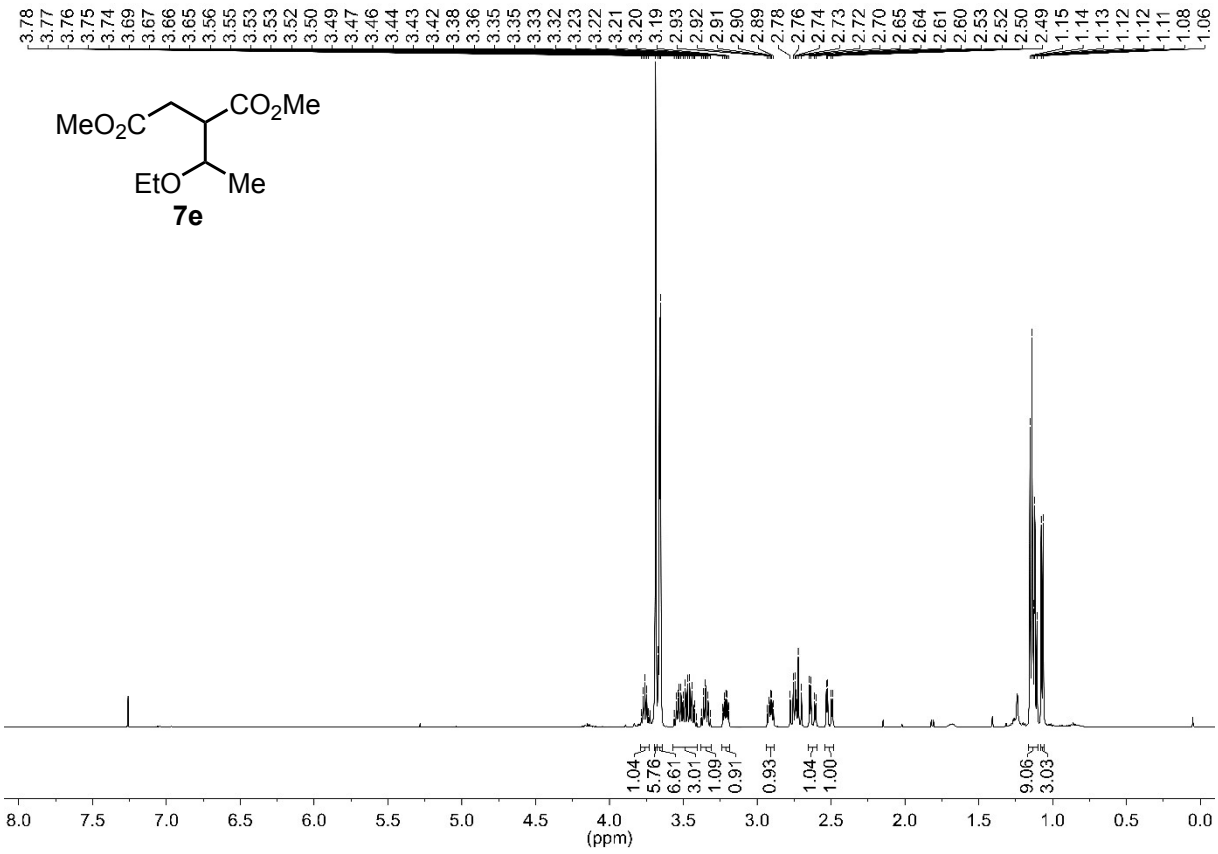

170.97
167.00
140.38
126.96
60.90
60.82
32.21
14.69
14.34
14.31
EtO2C
CO2Et
Me
17
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

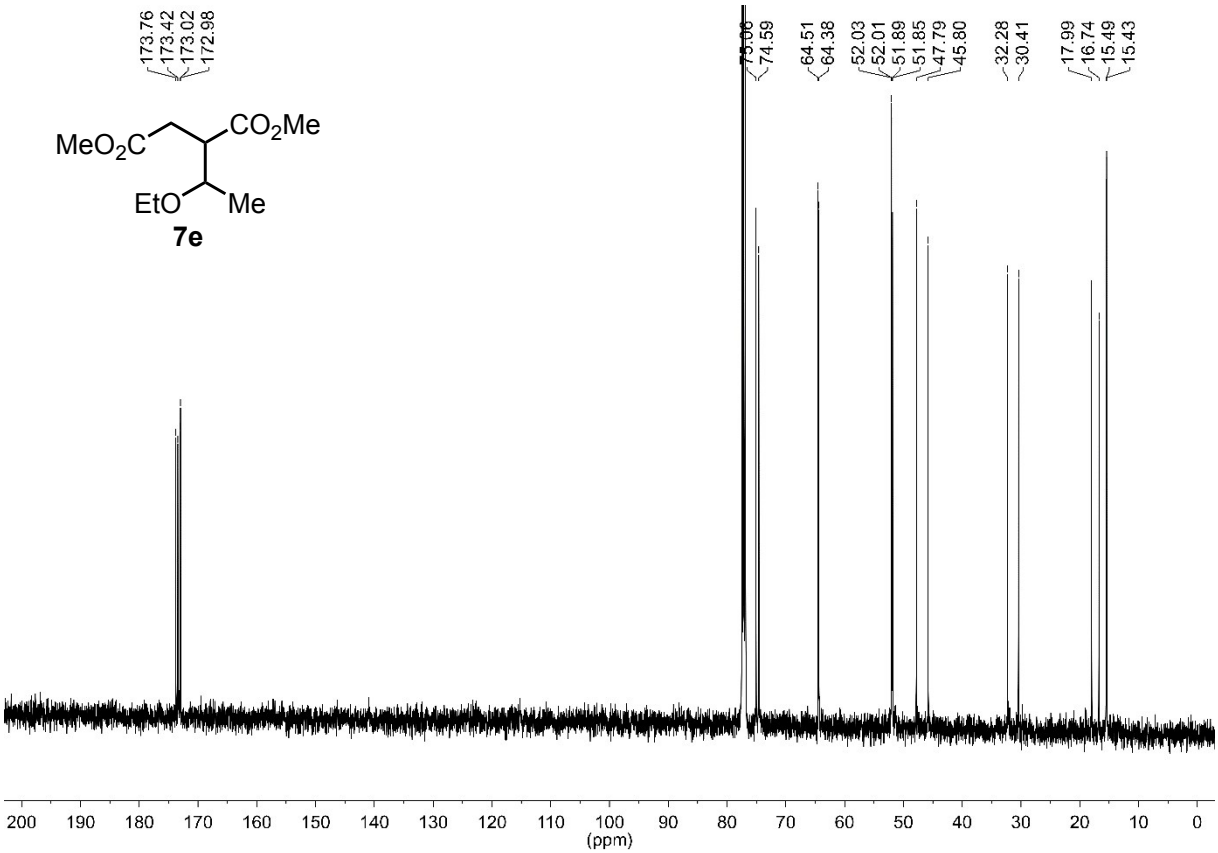

4.19 4.19 4.18 4.17 4.16 4.16 4.15 4.14 4.12 4.11 4.10 4.09 3.80 3.78 3.76 3.72 3.69 3.67 3.55 3.55 3.53 3.52 3.51 3.49 3.47 3.40 3.37 3.37 3.34 3.21 2.90 2.89 2.89 2.80 2.77 2.74 2.74 2.71 2.68 2.66 2.64 2.53 2.52 2.48 1.29 1.27 1.27 1.26 1.25 1.25 1.24 1.23 1.22 1.18 1.16 1.14 1.12 1.10 1.08
EtO2C
CO2Et
EtO
Me
7d
7.48
0.95
1.10
3.05
1.10
0.92
1.00
2.04
1.06
0.93
11.11
11.15
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
(ppm)

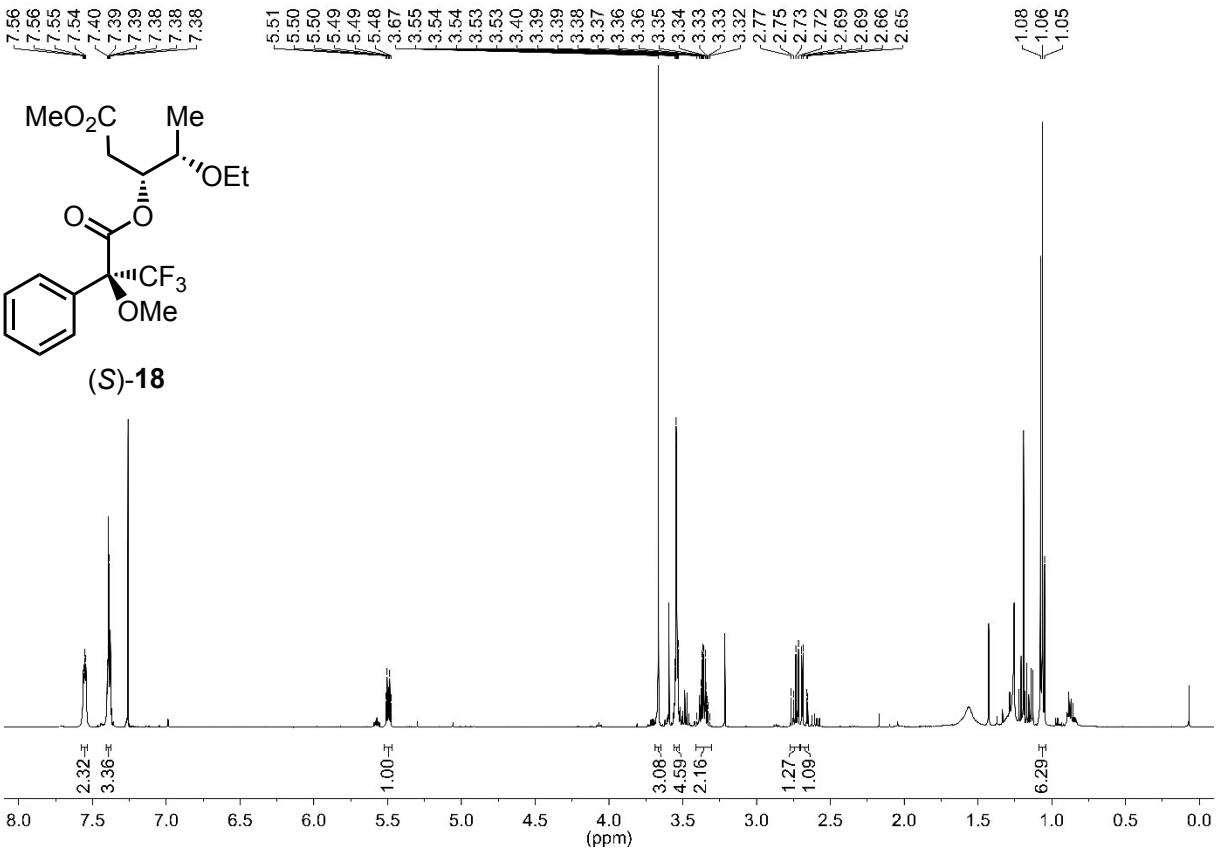

173.26 172.94 172.56 172.55
79.06 74.66 64.47 64.31 60.78 60.75 60.66 60.61 47.84 45.85 32.45 30.65 17.97 16.67 15.49 15.43 14.28 14.26
EtO2C
CO2Et
EtO
Me
7d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

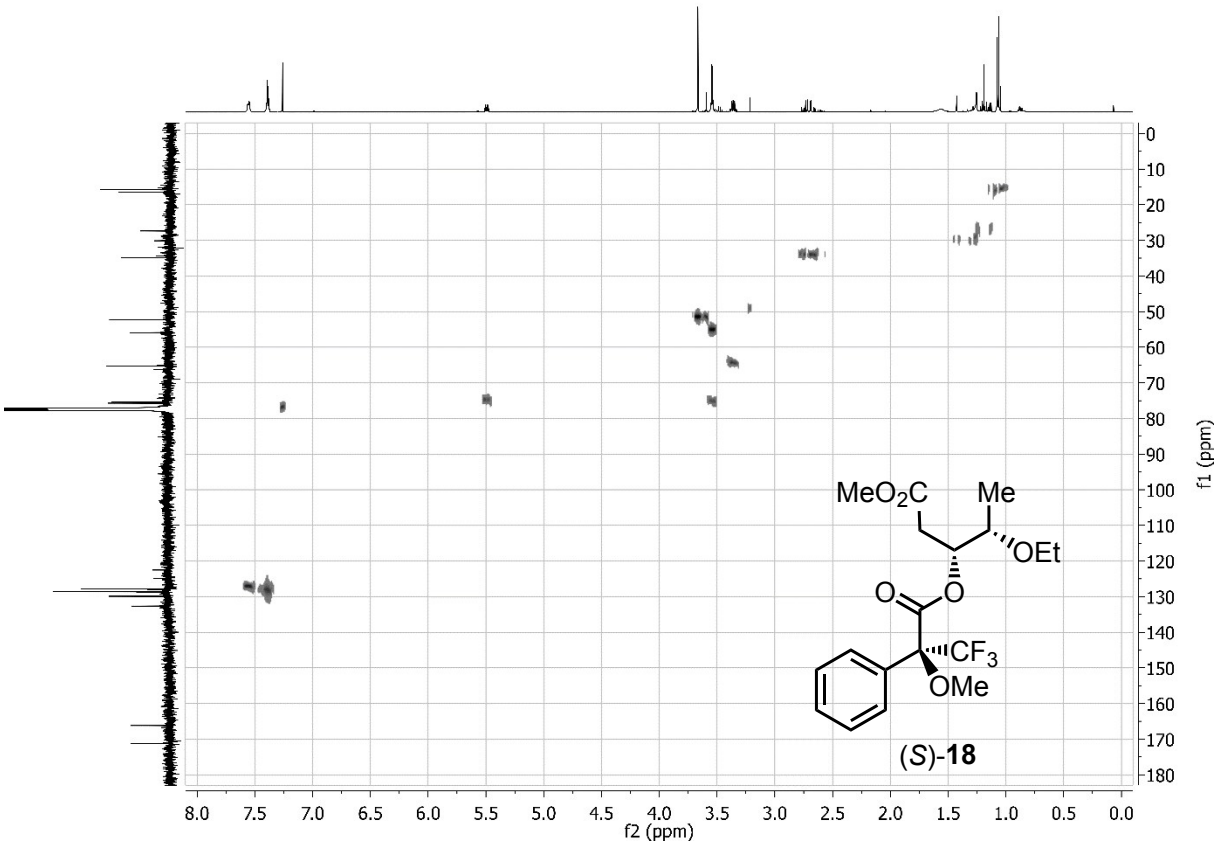

HO2C
CO2H
EtO
Me
7c
(ppm)

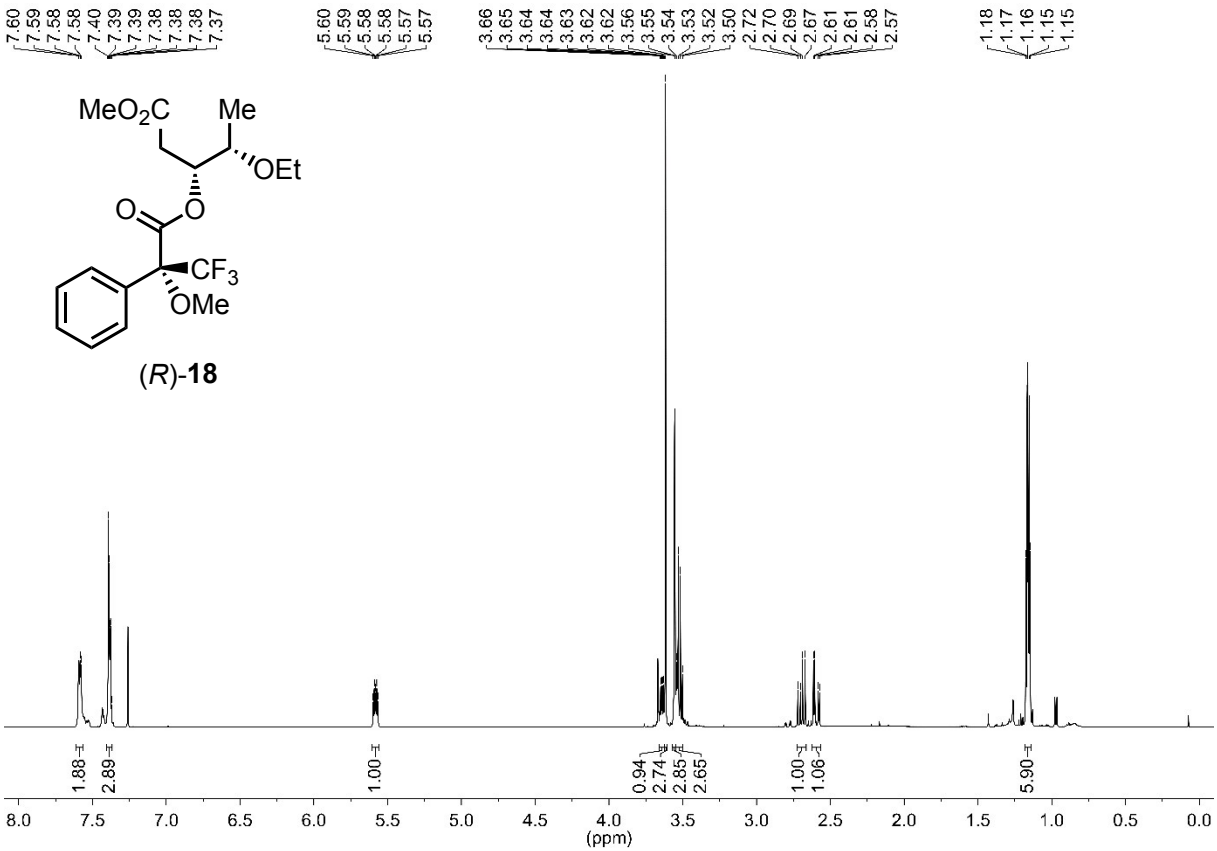

HO2C
CO2H
EtO
Me
7c
(ppm)


MeO2C
CO2Me
EtO
Me
7e
(ppm)


MeO2C
CO2Me
EtO
Me
7e
(ppm)


MeO2C
Me
OEt
O
O
CF3
OMe
(S)-18
(ppm)


MeO2C
Me
OEt
O
O
CF3
OMe
(S)-18
f2 (ppm)
f1 (ppm)


7.60 7.59 7.58 7.58 7.40 7.39 7.39 7.38 7.38 7.38 7.37
5.60 5.59 5.58 5.58 5.57 5.57
3.66 3.65 3.64 3.64 3.63 3.62 3.62 3.56 3.55 3.54 3.53 3.52 3.50
2.72 2.70 2.69 2.67 2.61 2.61 2.58 2.57
1.18 1.17 1.16 1.15 1.15
MeO2C
Me
OEt
O
O
CF3
OMe
(R)-18
1.88 2.89 1.00 0.94 2.74 2.85 2.65 1.00 1.06 5.90
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
(ppm)

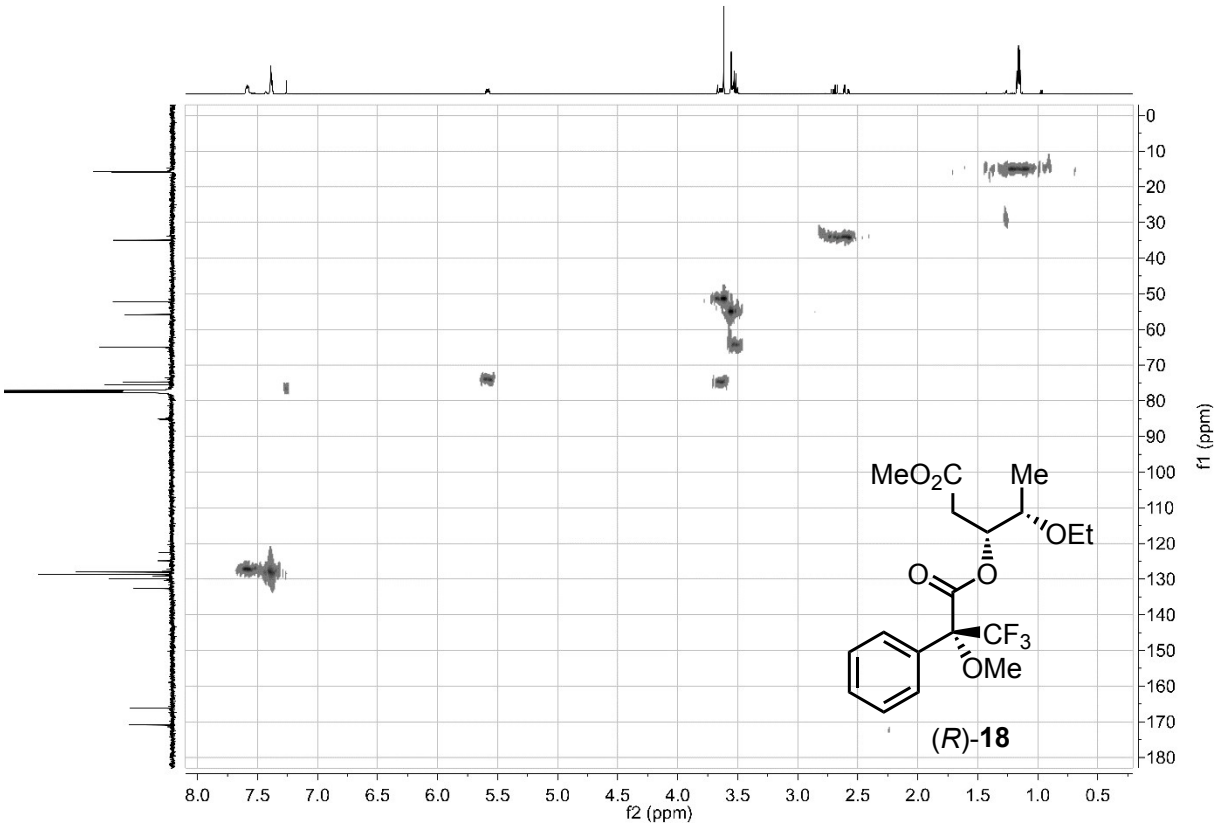
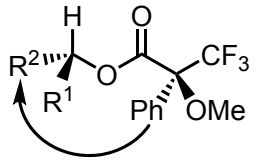

MeO2C
Me
OEt
O
O
CF3
OMe
(R)-18
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
f1 (ppm)

Table S1. $\Delta\delta_{SR}$ (= $\delta_S - \delta_R$) data for the (*S*)- and (*R*)-MTPA Mosher esters (*S*)-**18** and (*R*)-**18**

	δ_S ((*S*)-**18**) (ppm)	δ_R ((*R*)-**18**) (ppm)	$\Delta\delta_{SR}$ (= $\delta_S - \delta_R$)	
			ppm	Hz (500 MHz)
$CH_2CO_2\mathbf{CH_3}$	3.67	3.62	+0.05	+25
$\mathbf{CH_2}CO_2CH_3$	2.67	2.59	+0.08	+40
$\mathbf{CH_2}CO_2CH_3$	2.74	2.70	+0.04	+20
4-H	3.54	3.64	–0.10	–50
C-5 (CH_3)	1.07	1.16	–0.09	–45
$O\mathbf{CH_2}CH_3$	3.36	3.52	–0.16	–80
$OCH_2\mathbf{CH_3}$	1.06	1.16	–0.10	–50

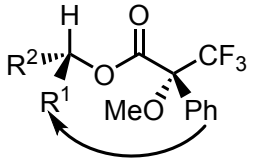


shielding

(*S*)-**18**

$R^1 = CH_2CO_2Me$

$R^2 = CH(CH_3)OCH_2CH_3$



shielding

(*R*)-**18**

$R^1 = CH_2CO_2Me$

$R^2 = CH(CH_3)OCH_2CH_3$

Figure S12. Mosher esters analysis of diastereomeric enriched (3*R*,4*S*)-**11b** by enantioselective reduction with baker's yeast. In case of mosher ester (*S*)-**18**, protons of the substructure of R^2 are relatively more shielded by the phenyl-group and therefore shifted upfield (towards lower ppm values) in the NMR spectrum. Reversely, in case of mosher ester (*R*)-**18**, the protons of the substructure of R^1 are relatively more shielded by the phenyl-group and therefore shifted upfield in the NMR spectrum.