Supporting Information

Ortho-Nitro Effect on the Diastereoselective Control in Sulfa-Staudinger and Staudinger Cycloadditions

Zhanhui Yang, Hassane Abdellaoui, Wei He, and Jiaxi Xu∗

State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, Faculty of Science, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

Email: jxxu@mail.buct.edu.cn

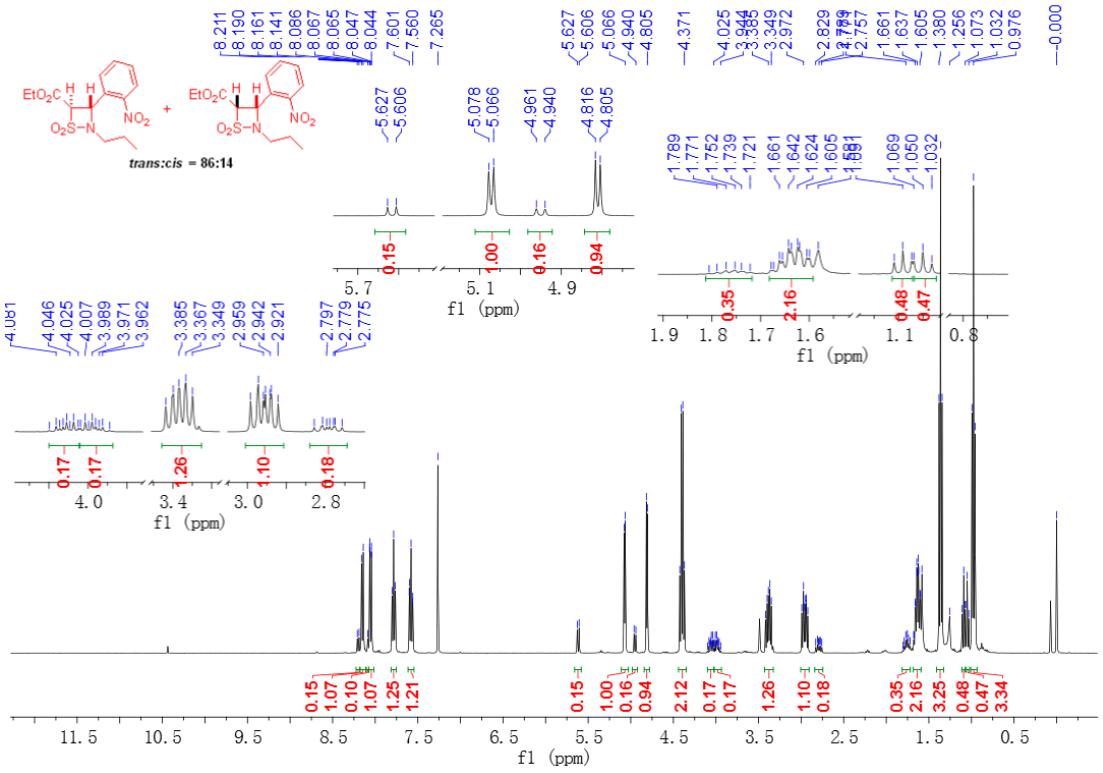
Contents

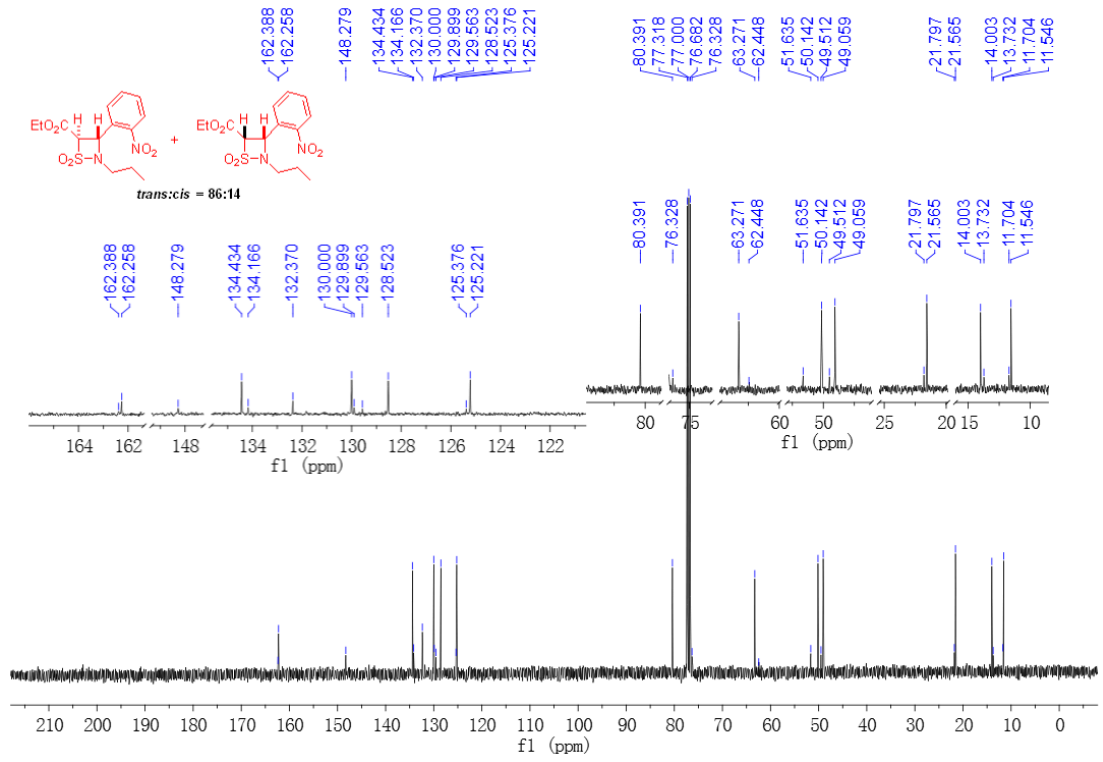
∗ Corresponding author. Tel.: +8610-6443-5565; fax: +8610-6443-5565; e-mail: jxxu@mail.buct.edu

1. Copies of ^{1}H and ^{13}C NMR spectra of unknown products

Ethyl trans-3-(2-nitrophenyl)-2-propyl-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(*trans*-3d)**

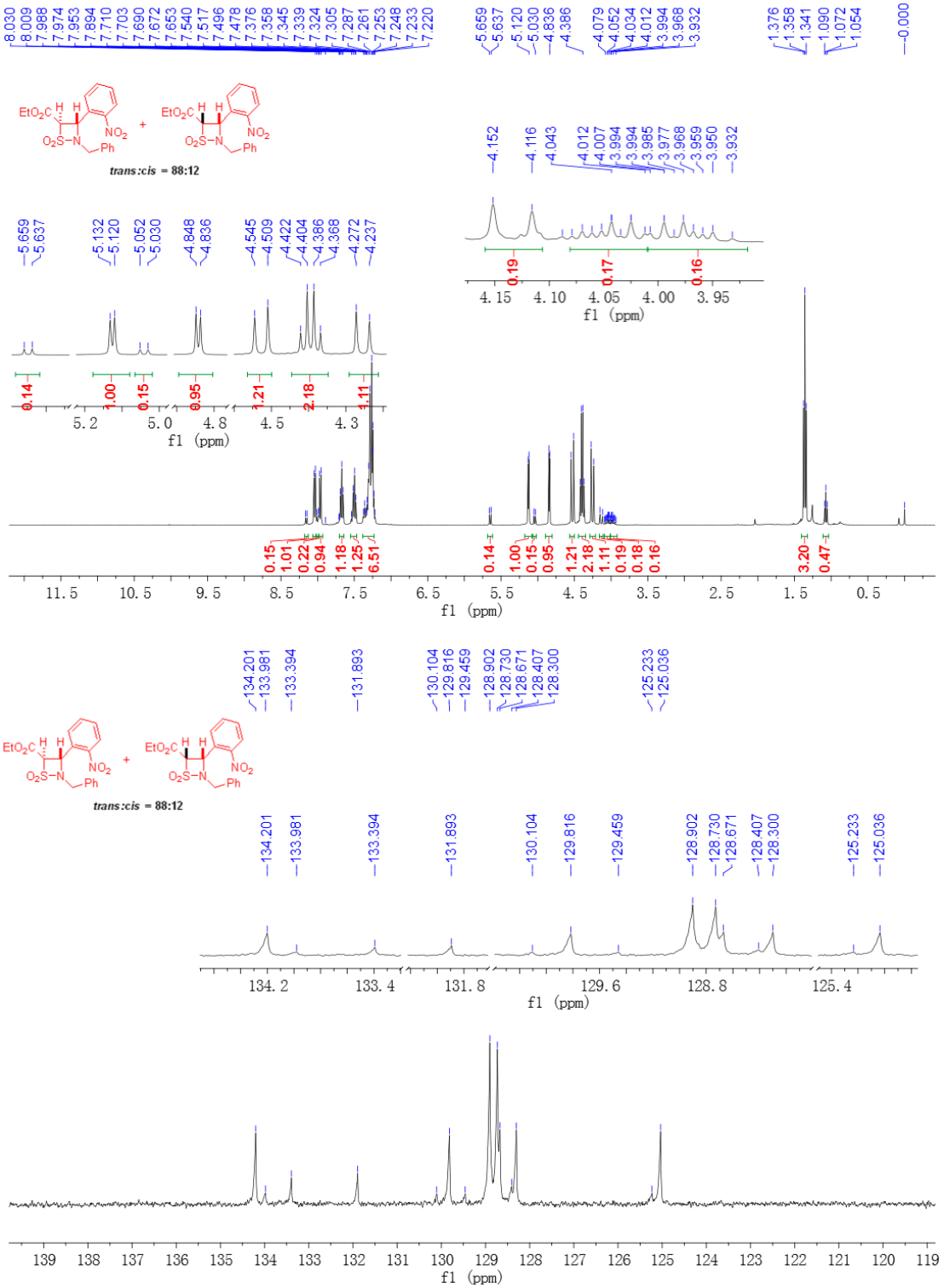
This product was isolated as a mixture of *cis*-**5d** (*trans/cis* = 86:14)





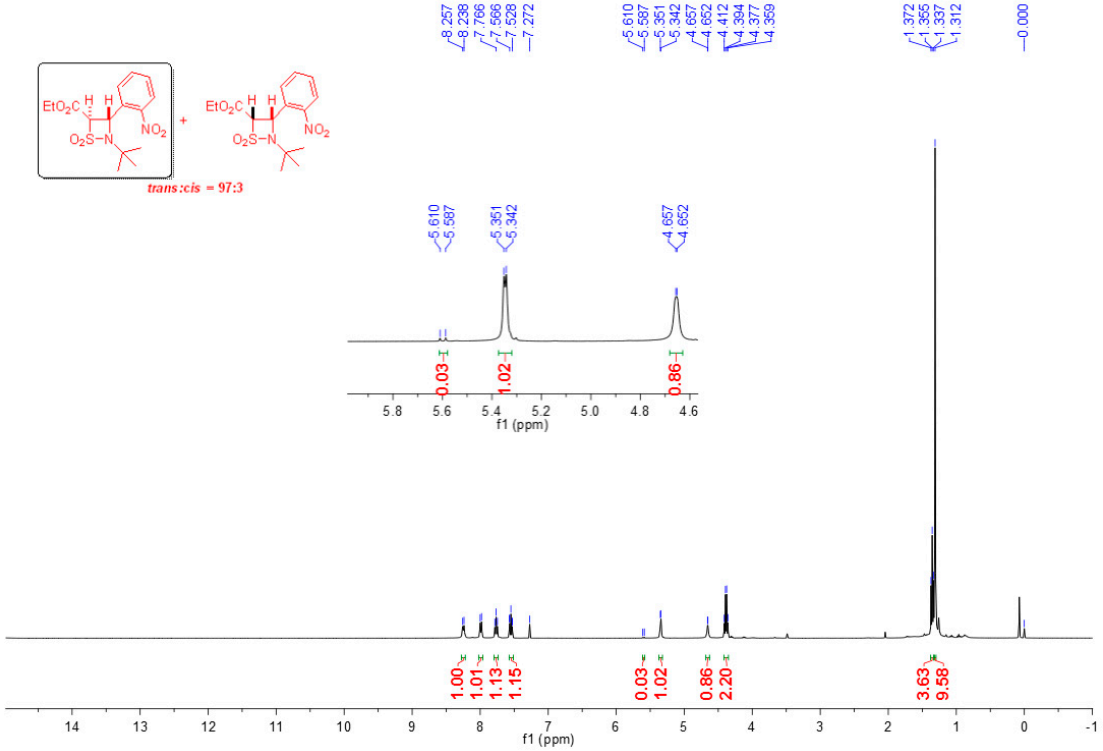
Ethyl trans-2-benzyl-3-(2-nitrophenyl)-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3e)**

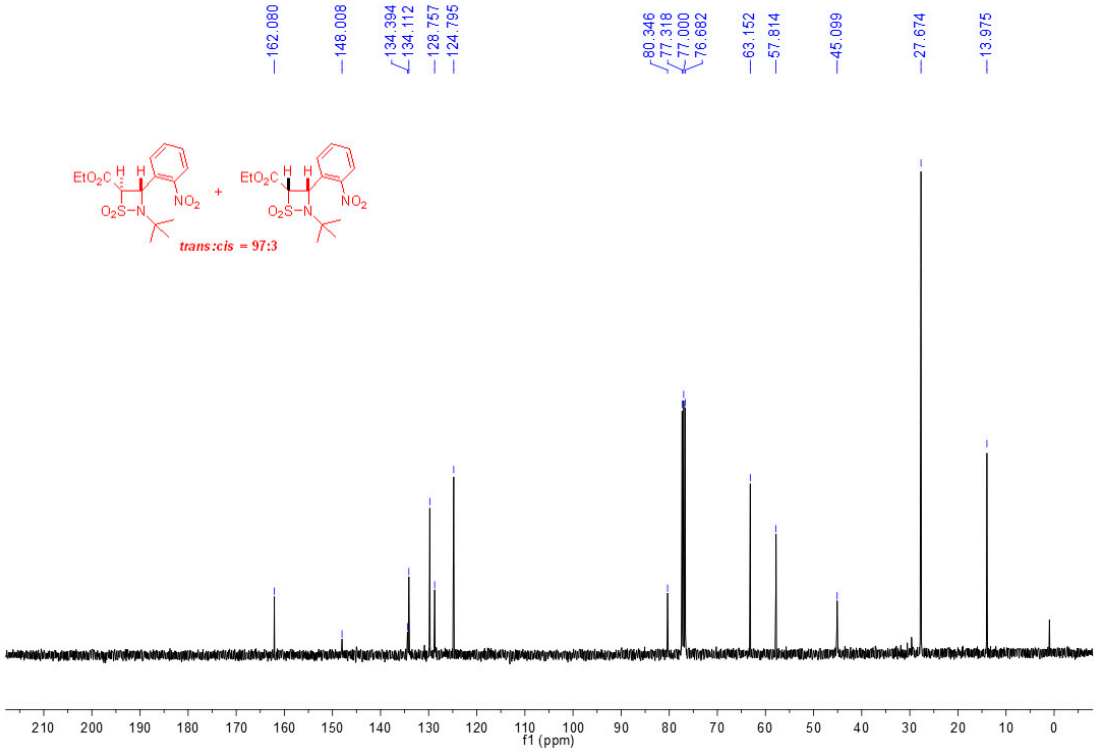
Compounds *trans*-**3e** and *cis*-**5e** were isolated as a mixture, with a *trans/cis* ratio of 88:12.



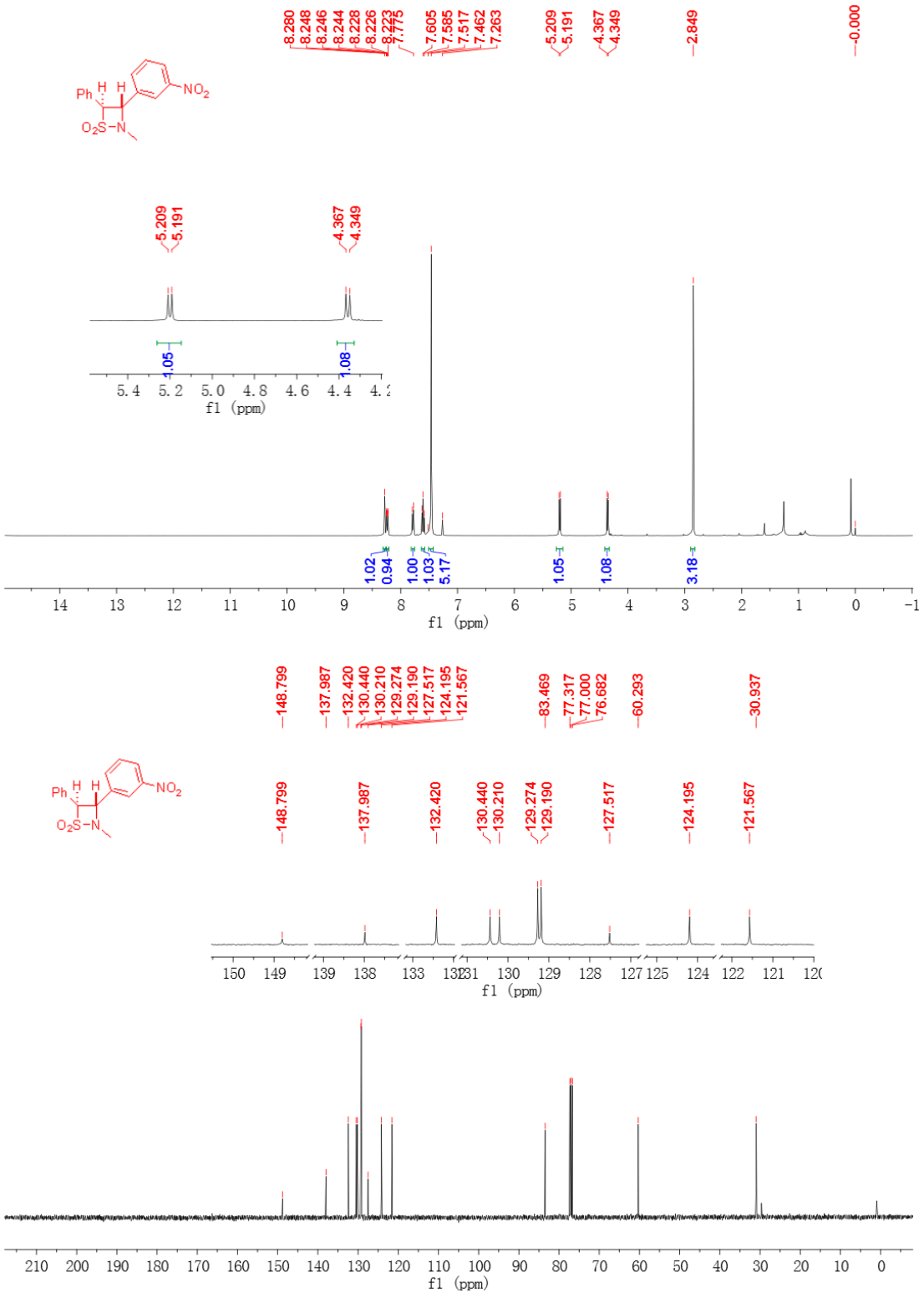
Ethyl trans-2-(tert-butyl)-3-(2-nitrophenyl)-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3f)**

Compounds *trans*-**3f** and *cis*-**5f** were isolated as a mixture, with a *trans/cis* ratio of 97:3.

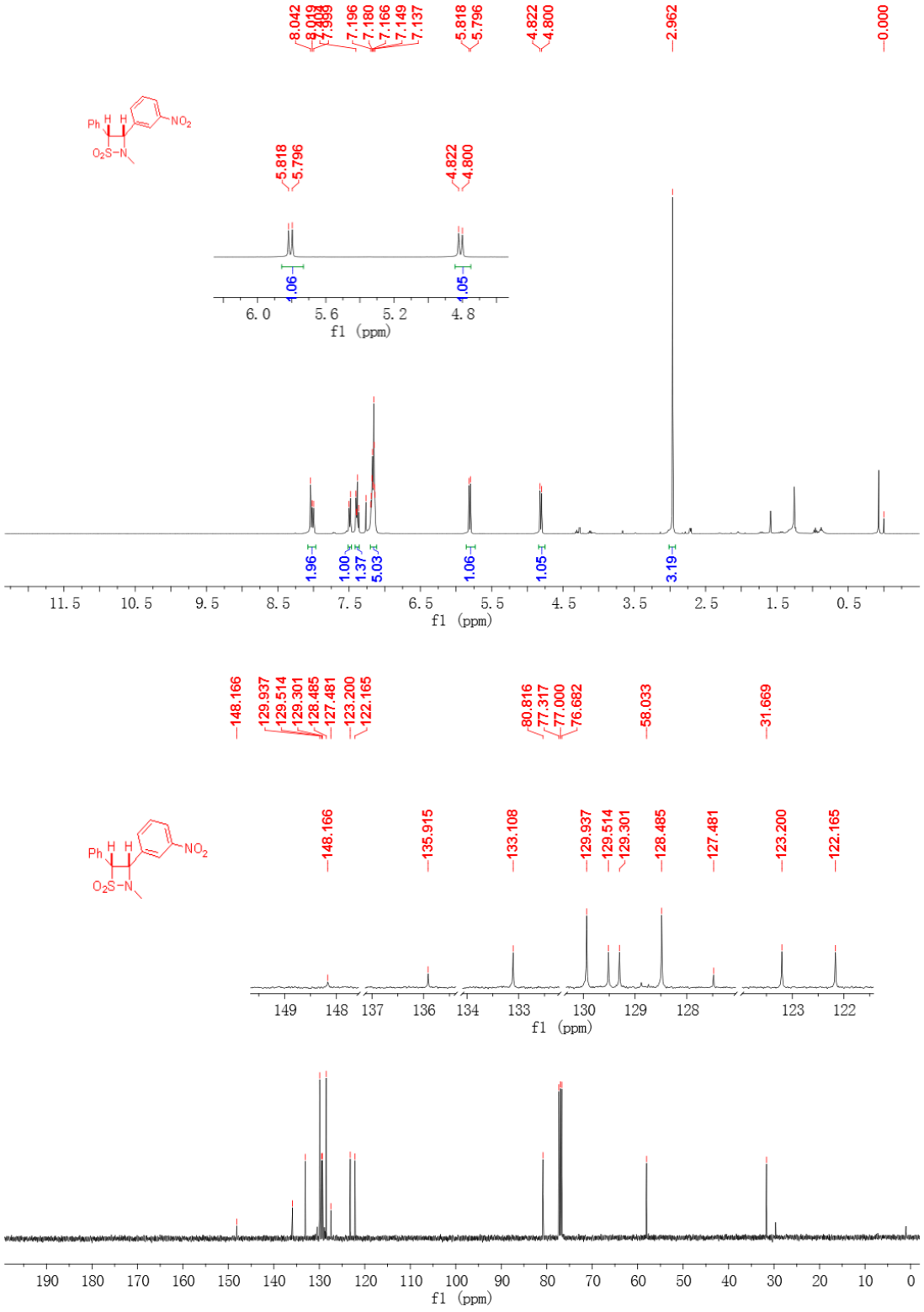




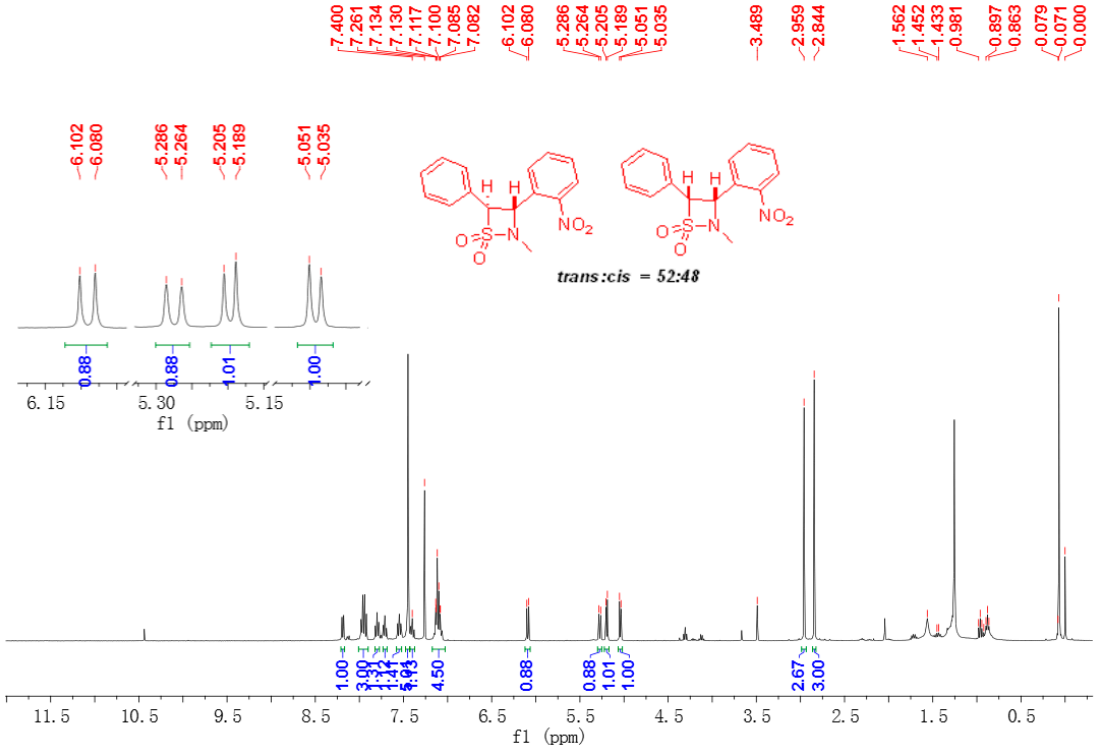
trans-2-Methyl-3-(3-nitrophenyl)-4-phenyl-1,2-thiazetidine 1,1-dioxide **(3bc)**

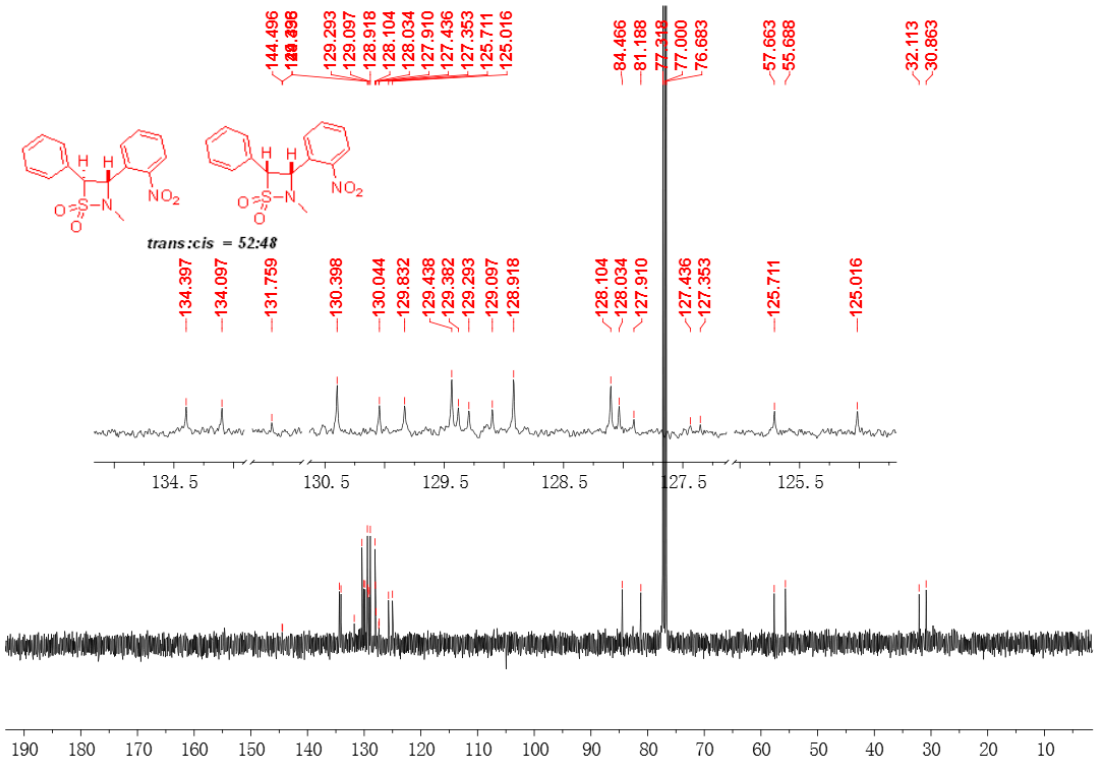


Cis-2-methyl-3-(3-nitrophenyl)-4-phenyl-1,2-thiazetidine 1,1-dioxide (*cis*-**5bc)**



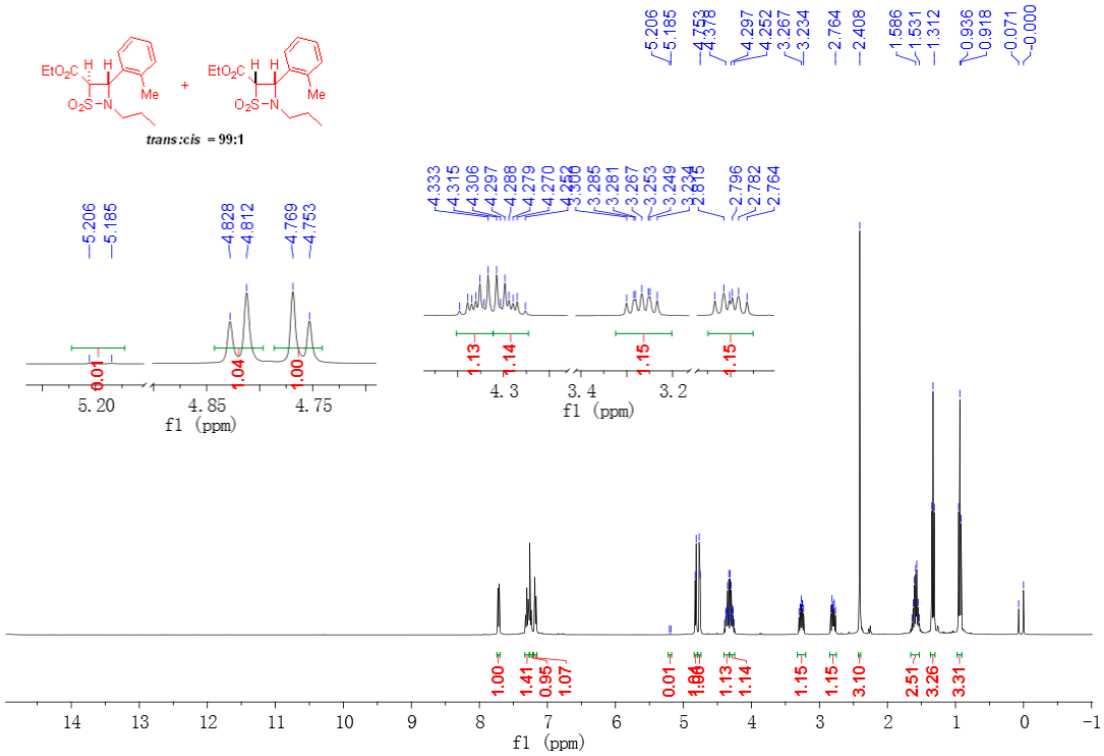
trans and cis-2-Methyl-3-(2-nitrophenyl)-4-phenyl-1,2-thiazetidine 1,1-dioxides **(3ac** and **5ac)**
Isolated as a mixture, trans/cis = 52:48.

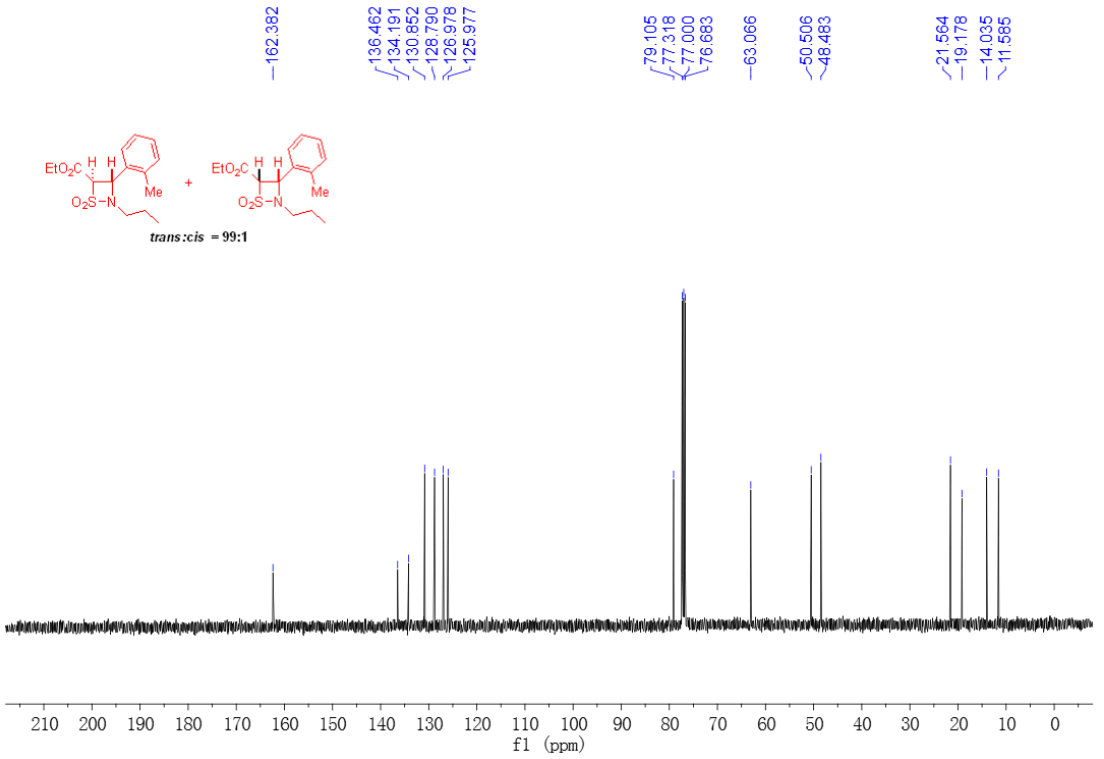




Ethyl trans-2-propyl-3-(o-tolyl)-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3g)**

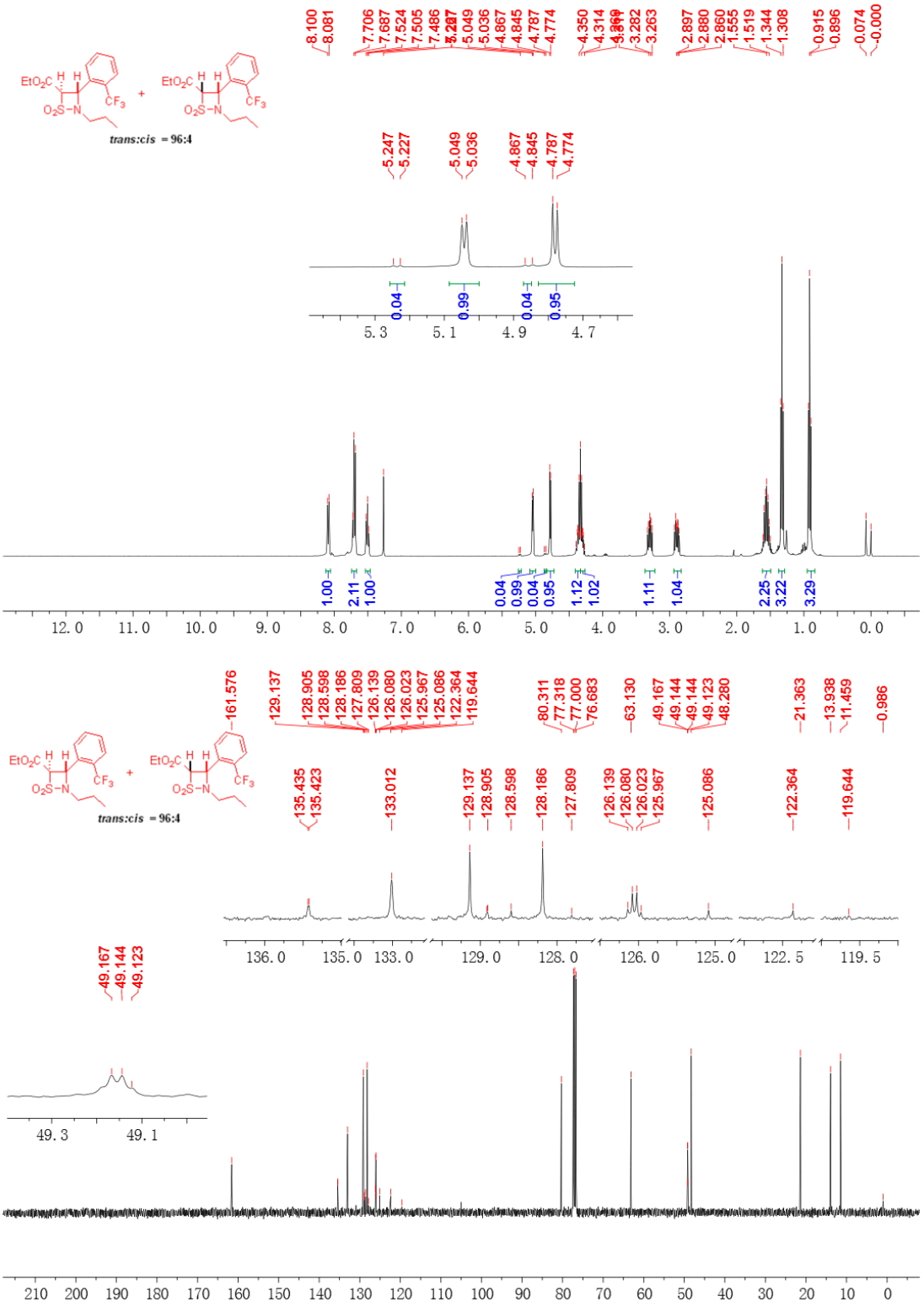
Compounds *trans*-**3g** and *cis*-**5g** were isolated as a mixture, with a *trans/cis* ratio of 99:1.





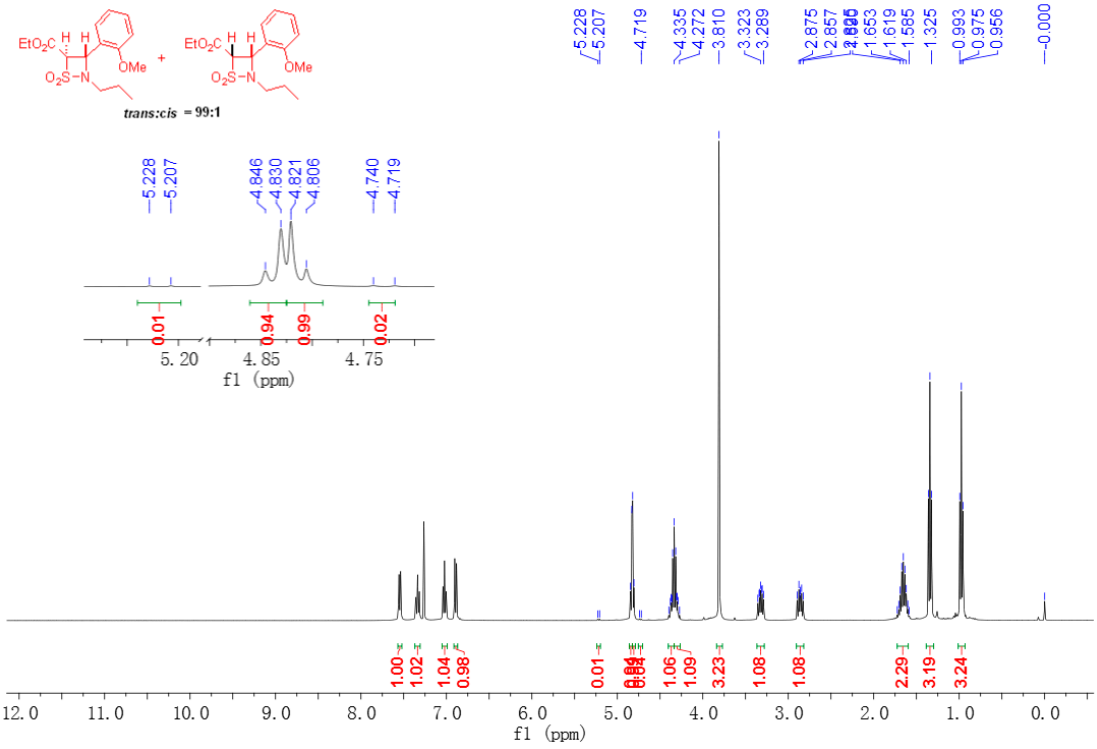
Ethyl trans-2-propyl-3-(2-(trifluoromethyl)phenyl)-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3h)**

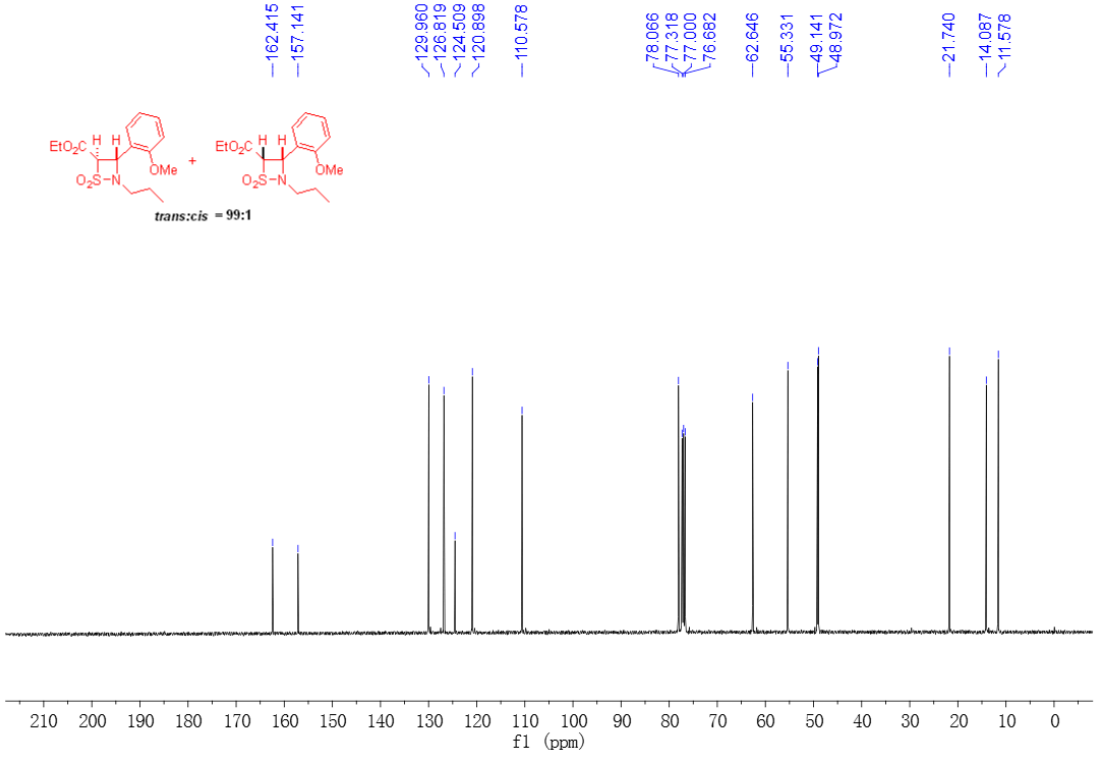
Compounds *trans*-**3h** and *cis*-**5h** were isolated as a mixture, with a *trans/cis* ratio of 97:3.



Ethyl trans-3-(2-methoxyphenyl)-2-propyl-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3i)**

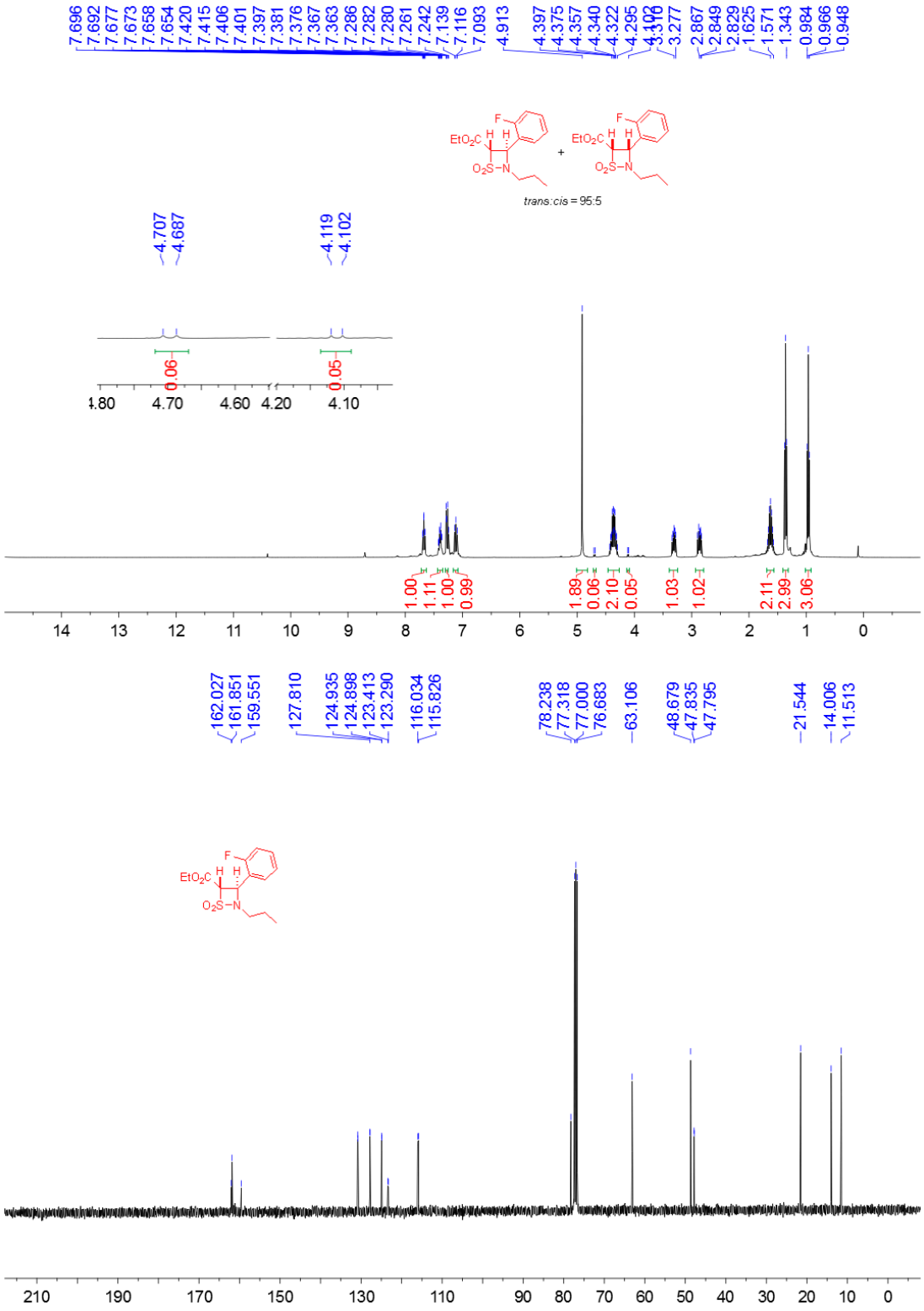
Compounds *trans*-**3i** and *cis*-**5i** were isolated as a mixture, with a *trans/cis* ratio of 99:1.





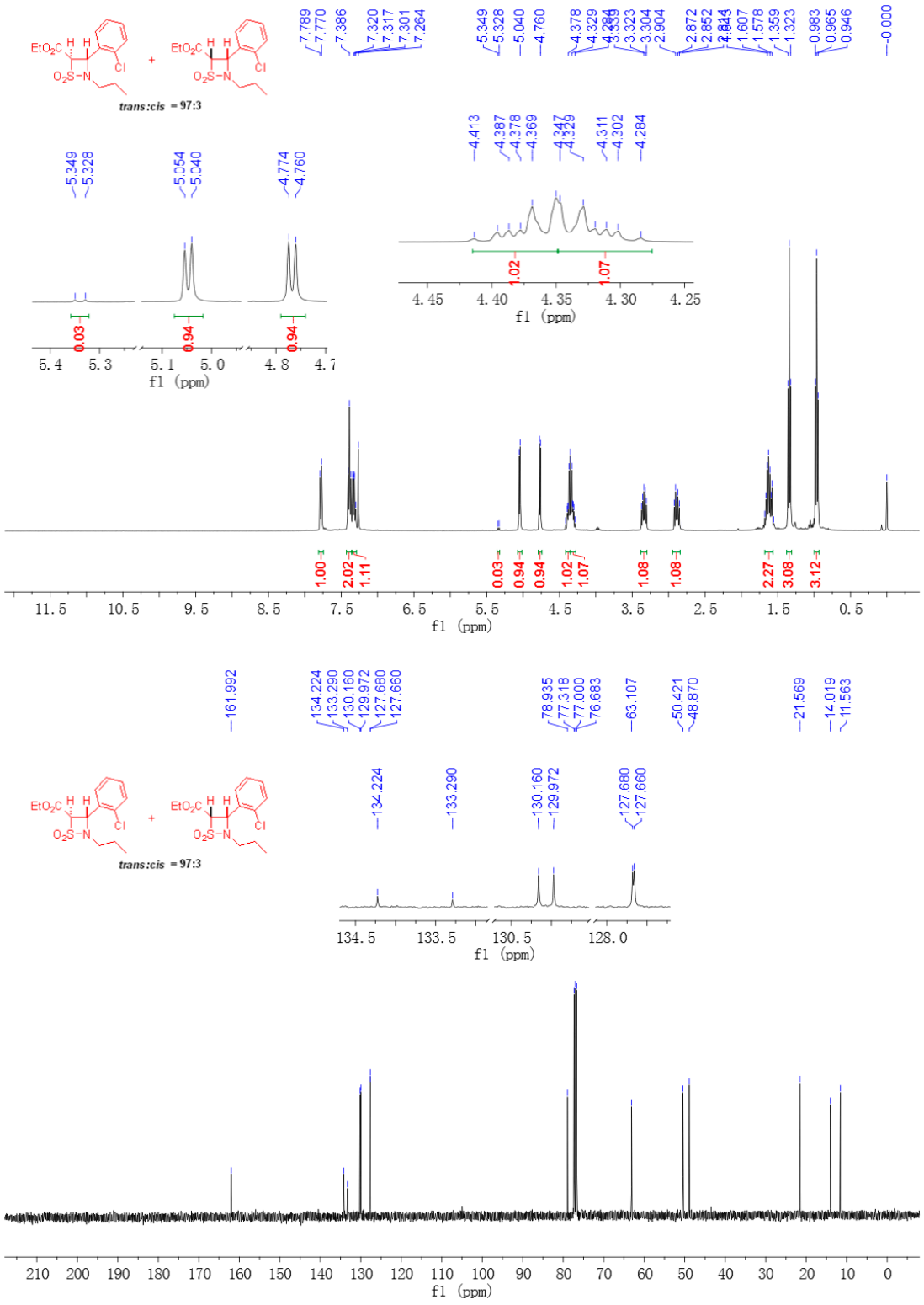
Ethyl trans-3-(2-fluorophenyl)-2-propyl-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3j)**

Compounds *trans*-**3j** and *cis*-**5j** were isolated as a mixture, with a *trans/cis* ratio of 97:3.



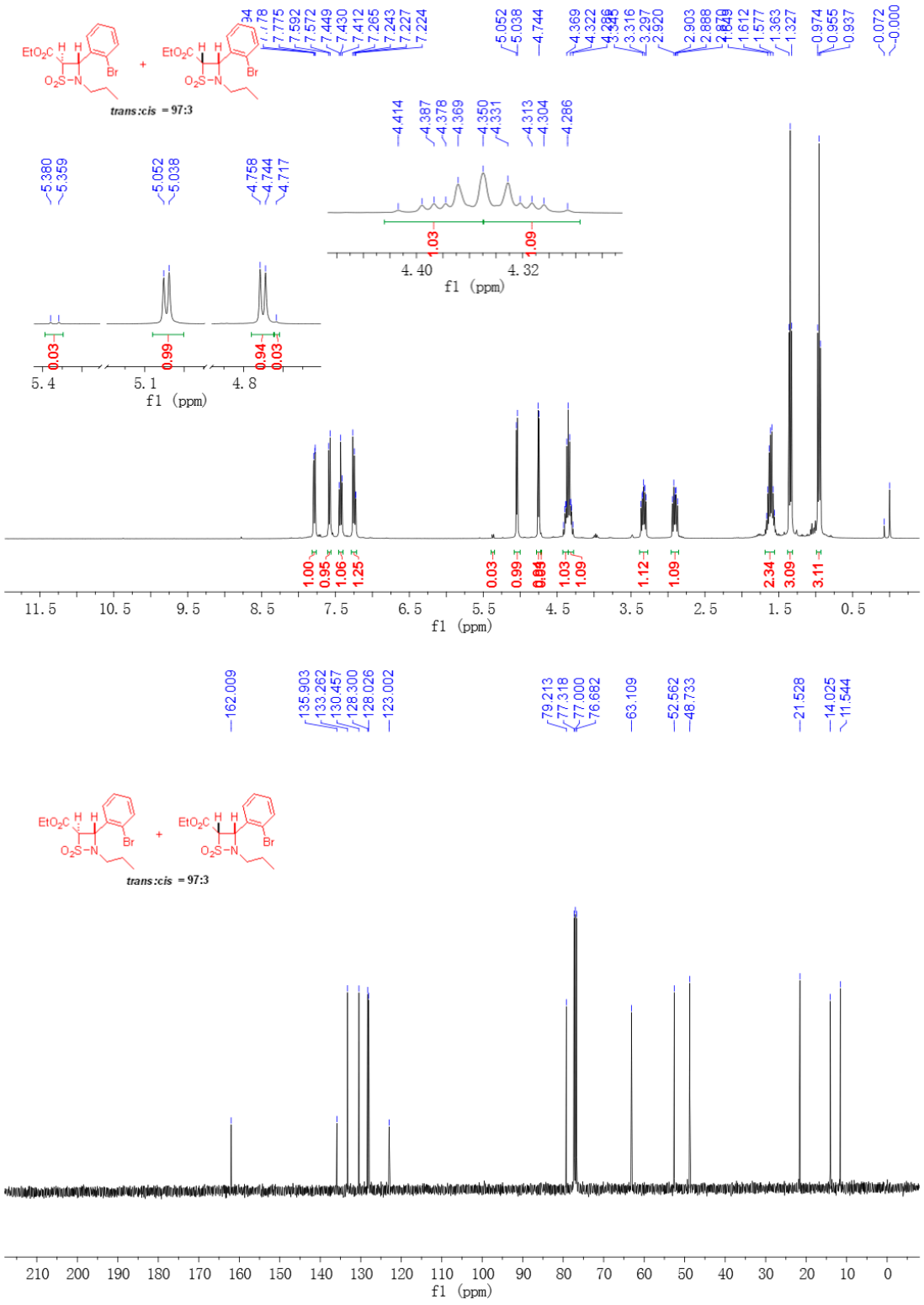
Ethyl trans-3-(2-chlorophenyl)-2-propyl-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3k)**

Compounds *trans*-**3j** and *cis*-**5j** were isolated as a mixture, with a *trans/cis* ratio of 97:3.



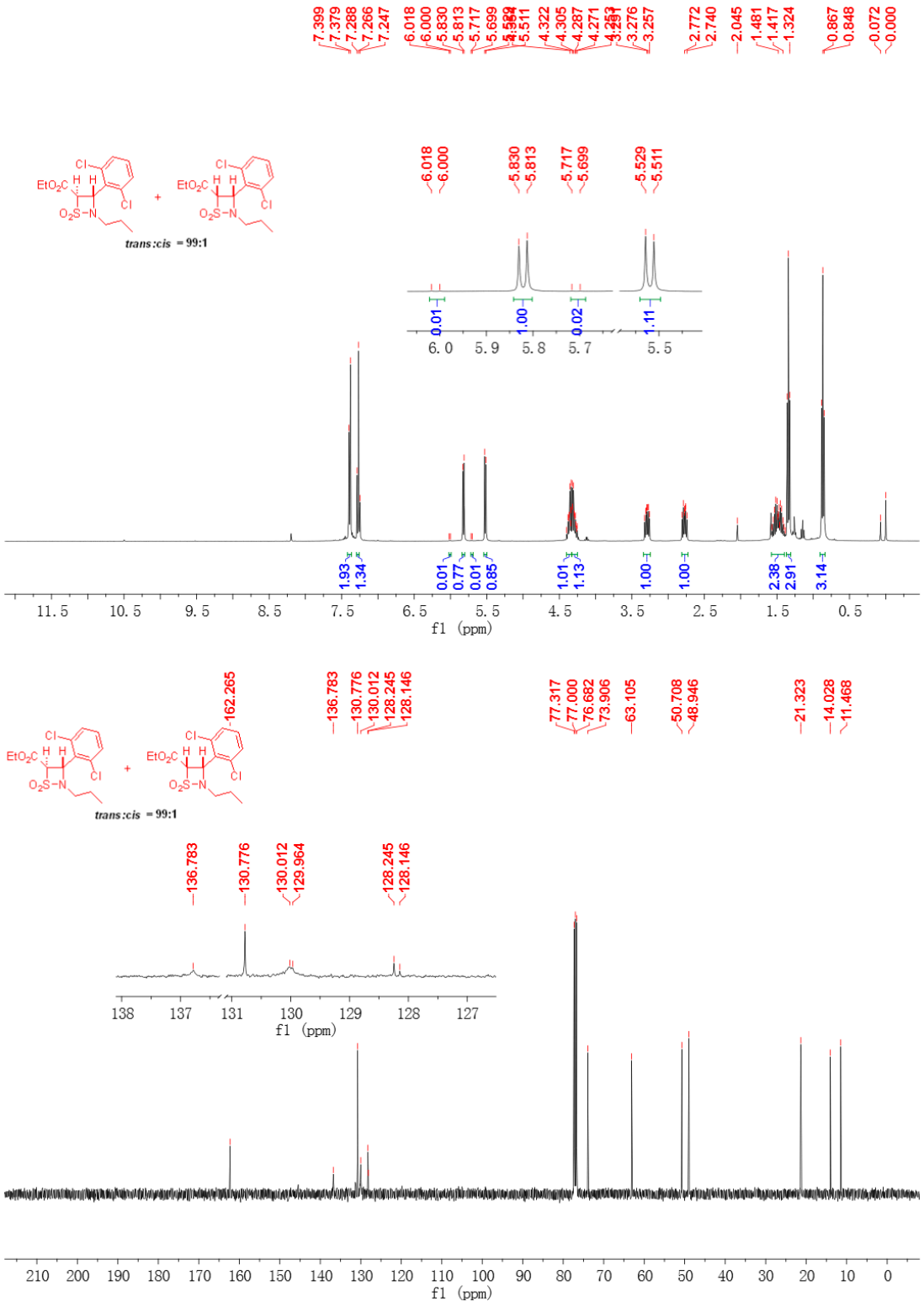
Ethyl trans-3-(2-bromophenyl)-2-propyl-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3l)**

Compounds *trans*-**3k** and *cis*-**5k** were isolated as a mixture, with a *trans/cis* ratio as 97:3.

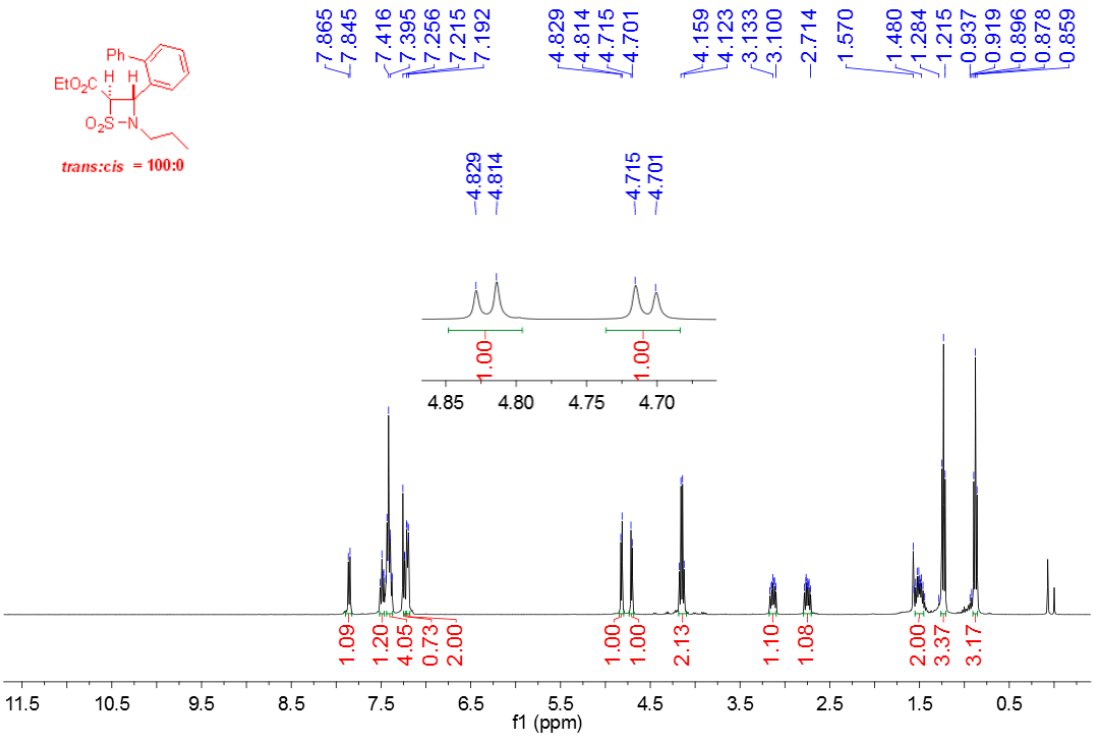


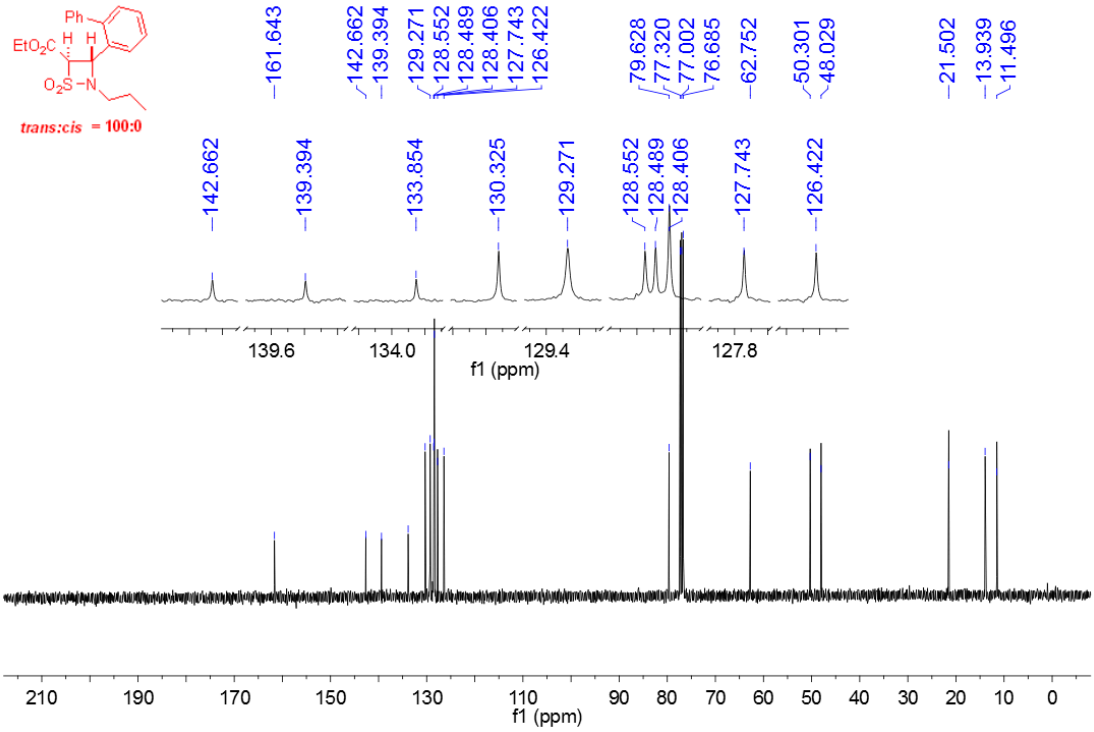
Ethyl trans-3-(2,6-dichlorophenyl)-2-propyl-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3m)**

Compounds *trans*-**3l** and *cis*-**5l** were isolated as a mixture, with a *trans/cis* ratio of 99:1.

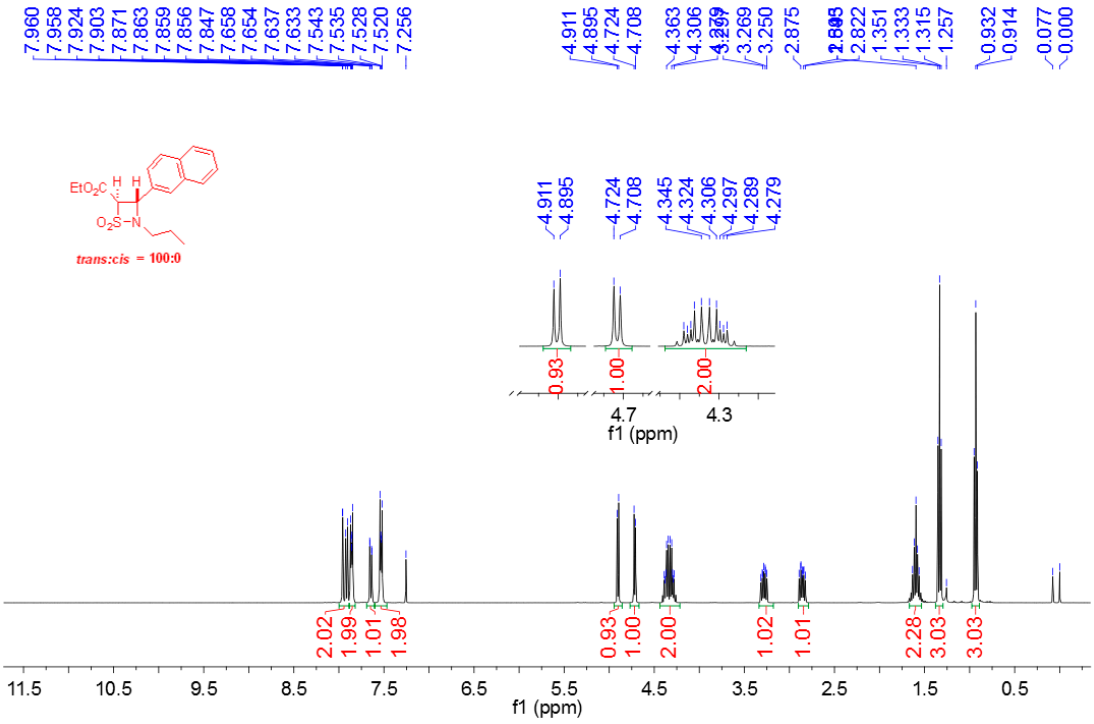


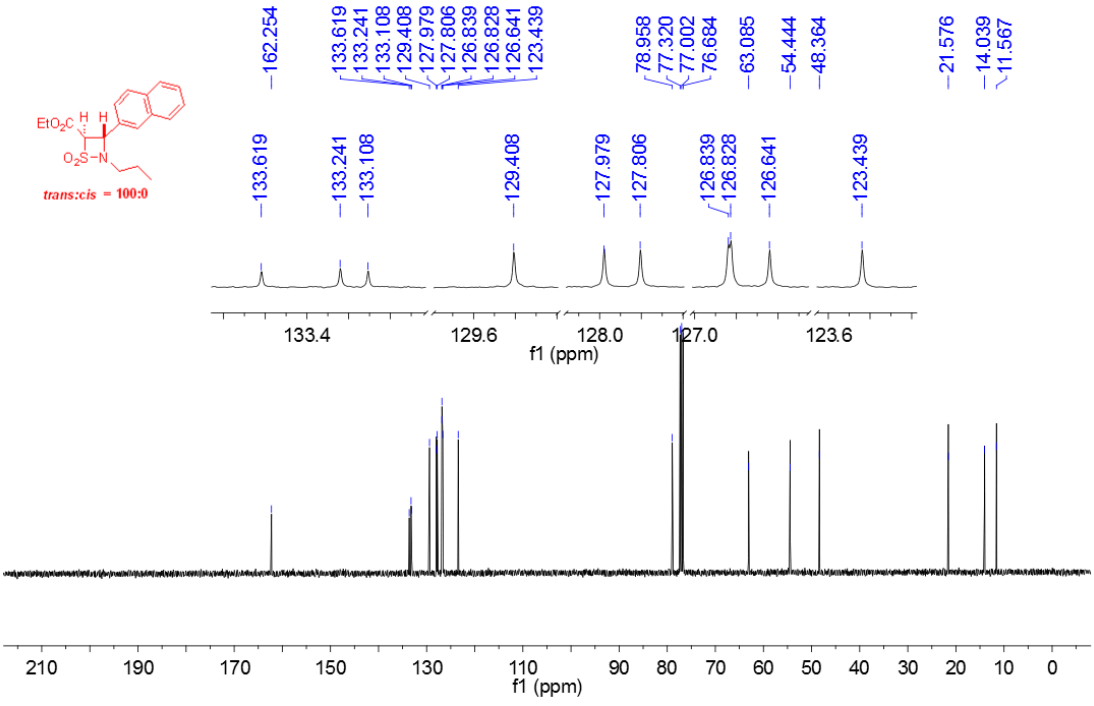
Ethyl trans-3-([1,1'-biphenyl]-2-yl)-2-propyl-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3n)**





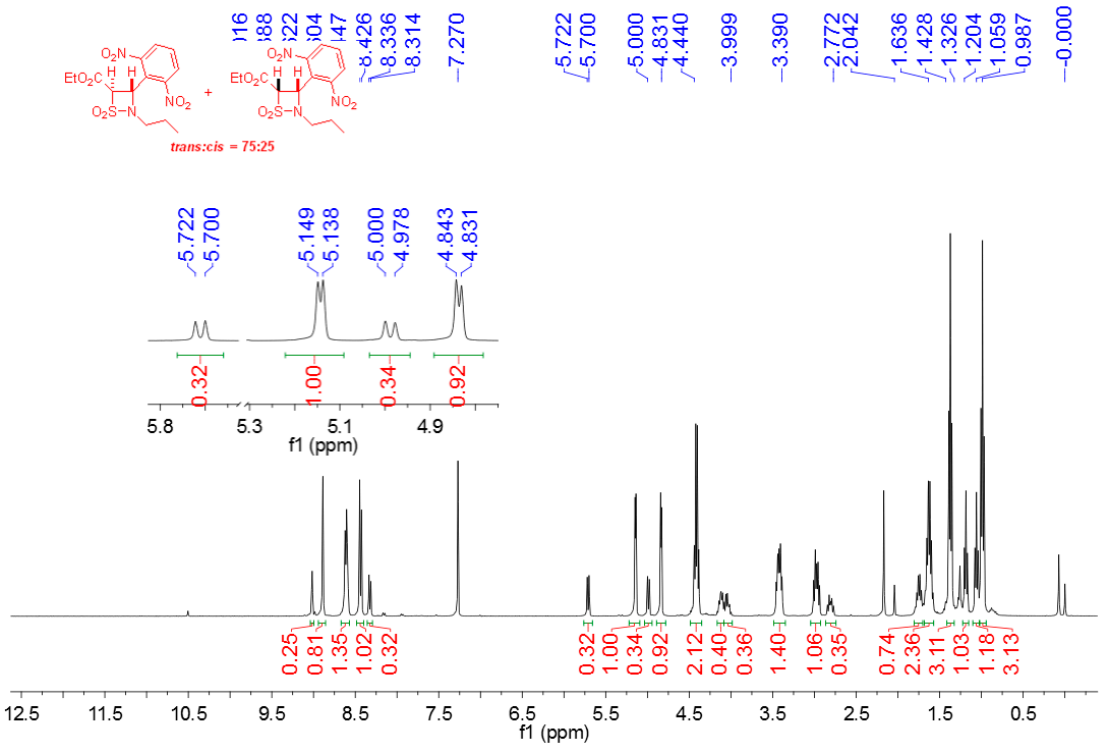
Ethyl trans-3-(naphthalen-2-yl)-2-propyl-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3o)**

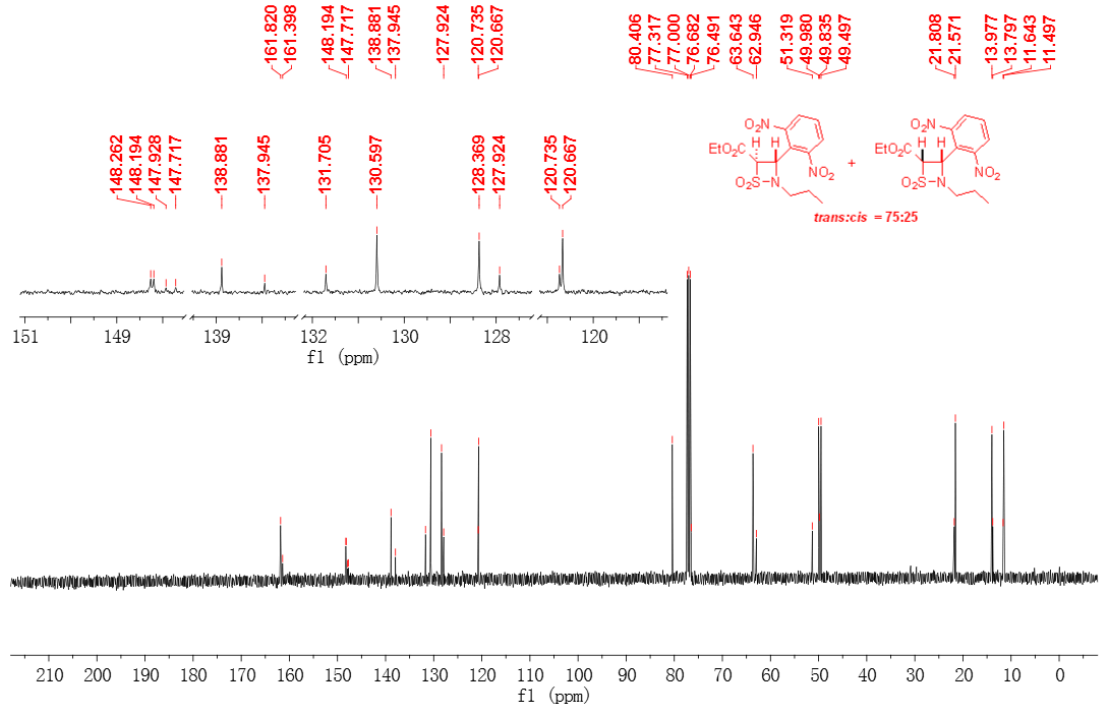




Ethyl trans-3-(2,4-dinitrophenyl)-2-propyl-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3p)**

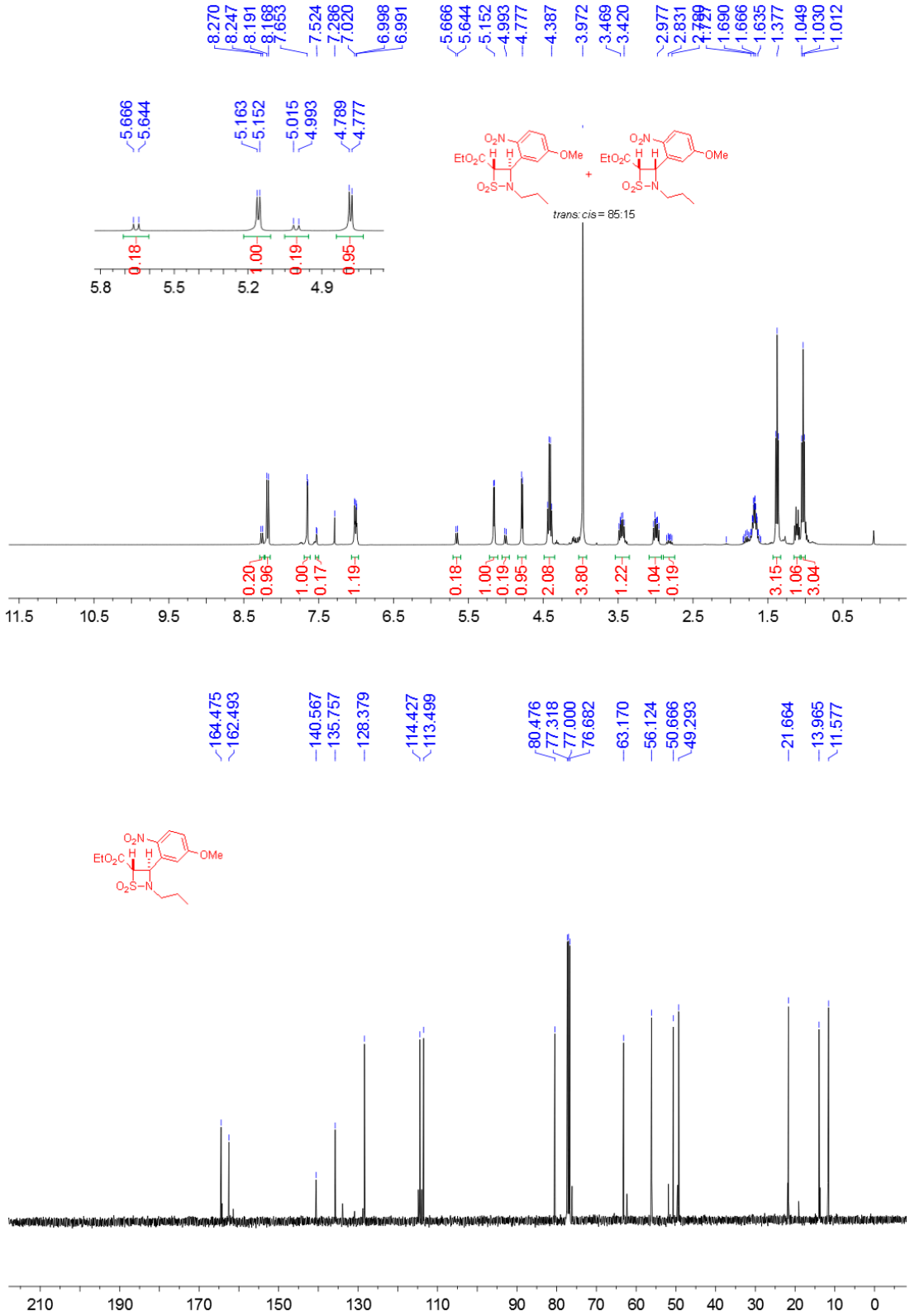
Compounds *trans*-**3o** and *cis*-**5o** were isolated as a mixture, with a *trans/cis* ratio of 75:25.

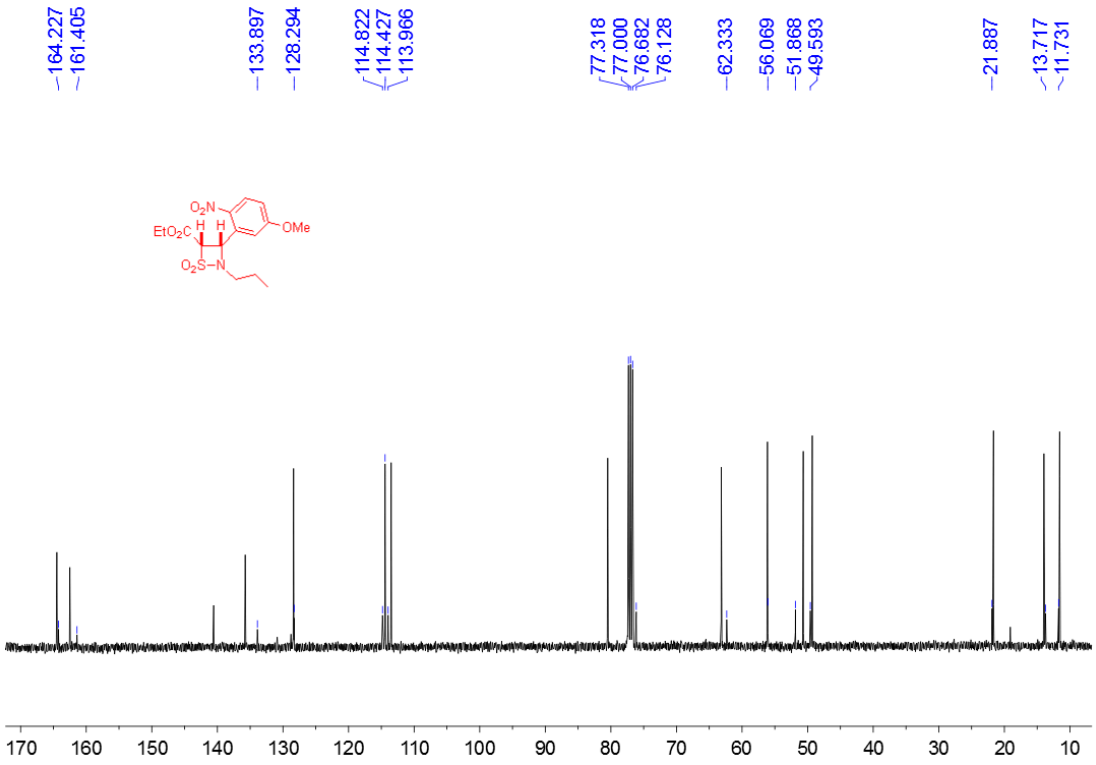




Ethyl trans- and cis-3-(5-methoxy-2-nitrophenyl)-2-propyl-1,2-thiazetidine-4-carboxylate 1,1-dioxide **(3q)**

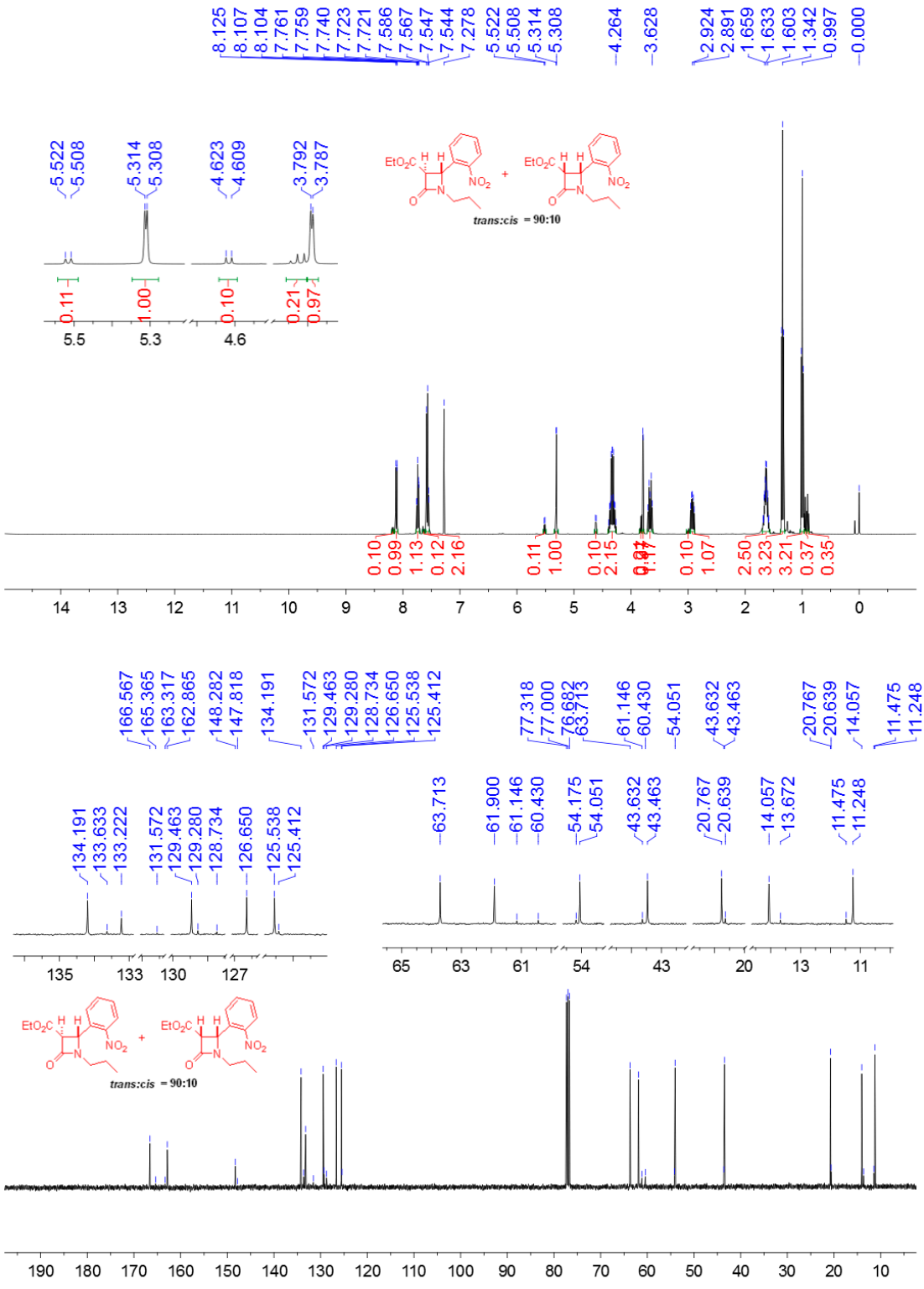
Compounds *trans*-**3q** and *cis*-**5q** were isolated as a mixture, with a *trans/cis* ratio of 75:25.



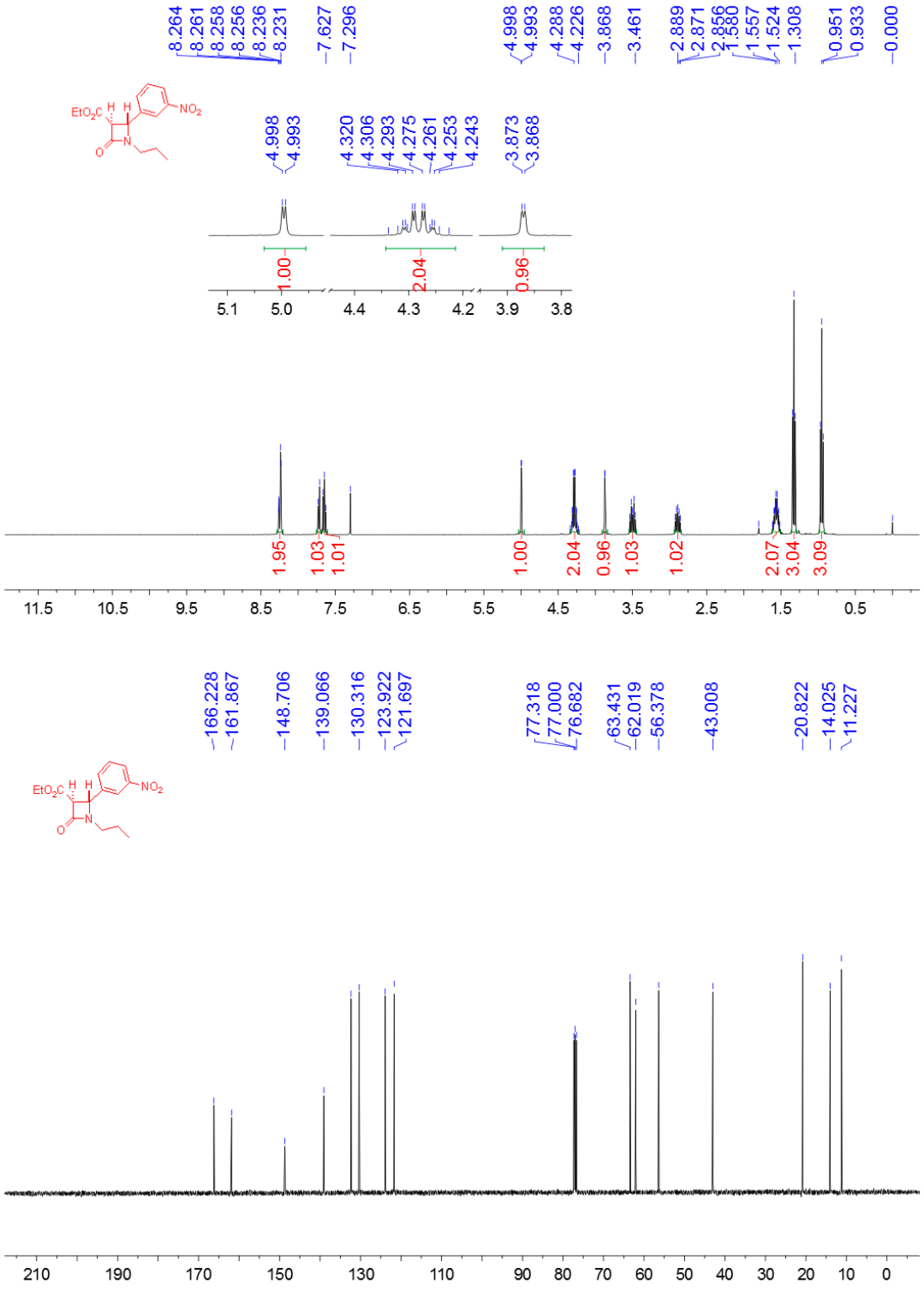

164.227
161.405
133.897
128.294
114.822
114.427
113.966
77.318
77.000
76.682
76.128
62.333
56.069
51.868
49.593
21.887
13.717
11.731
O2N
EtO2C
H
H
OMe
O2S–N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

Ethyl trans-4-(2-nitrophenyl)-1-propylazetidin-2-one-3-carboxylate **(4d)**

Compounds *trans*-**4d** and *cis*-**6d** were isolated as a mixture, with a *trans/cis* ratio of 90:10.

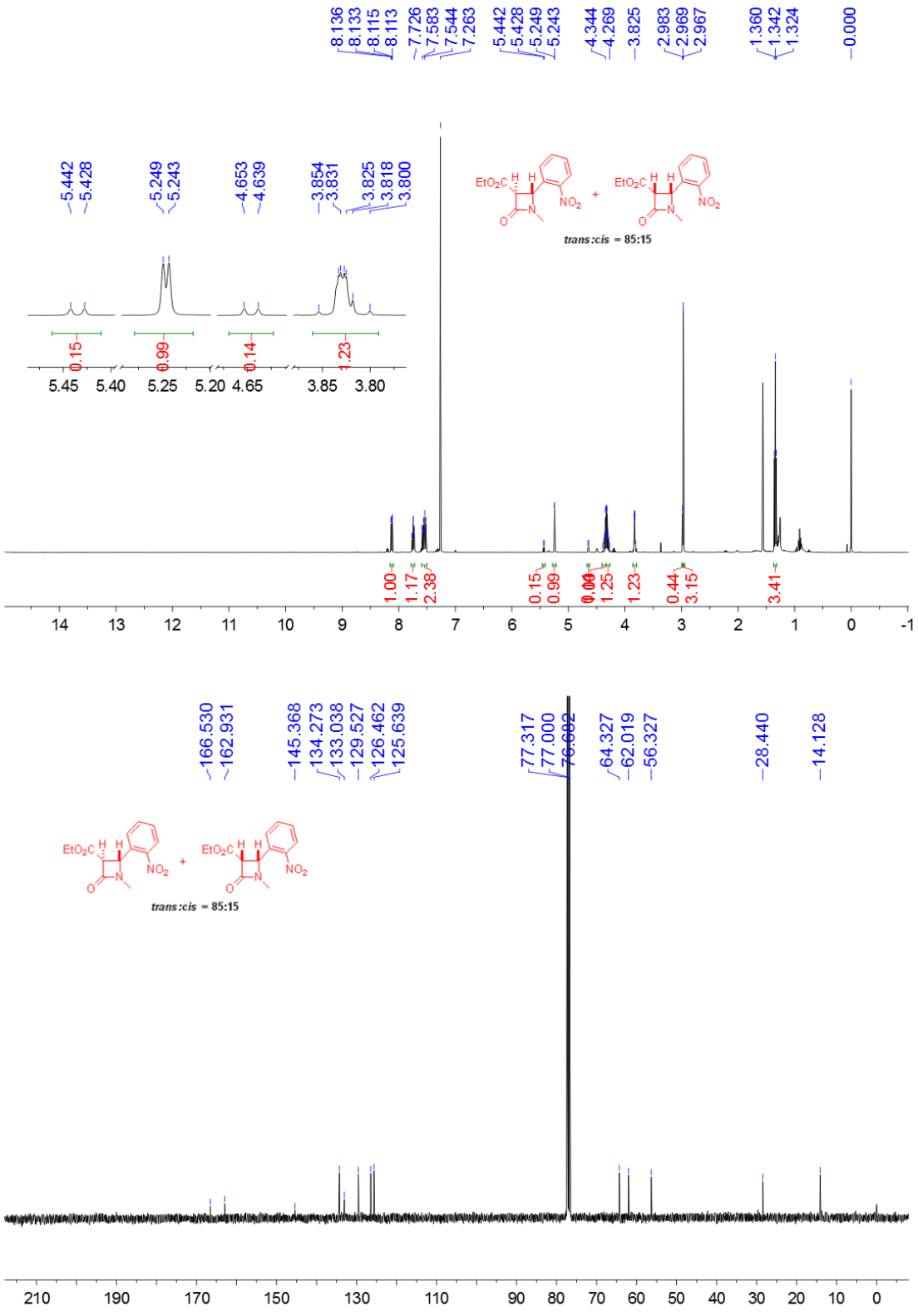


Ethyl trans-4-(3-nitrophenyl)-1-propylazetidin-2-one-3-carboxylate **(4r)**



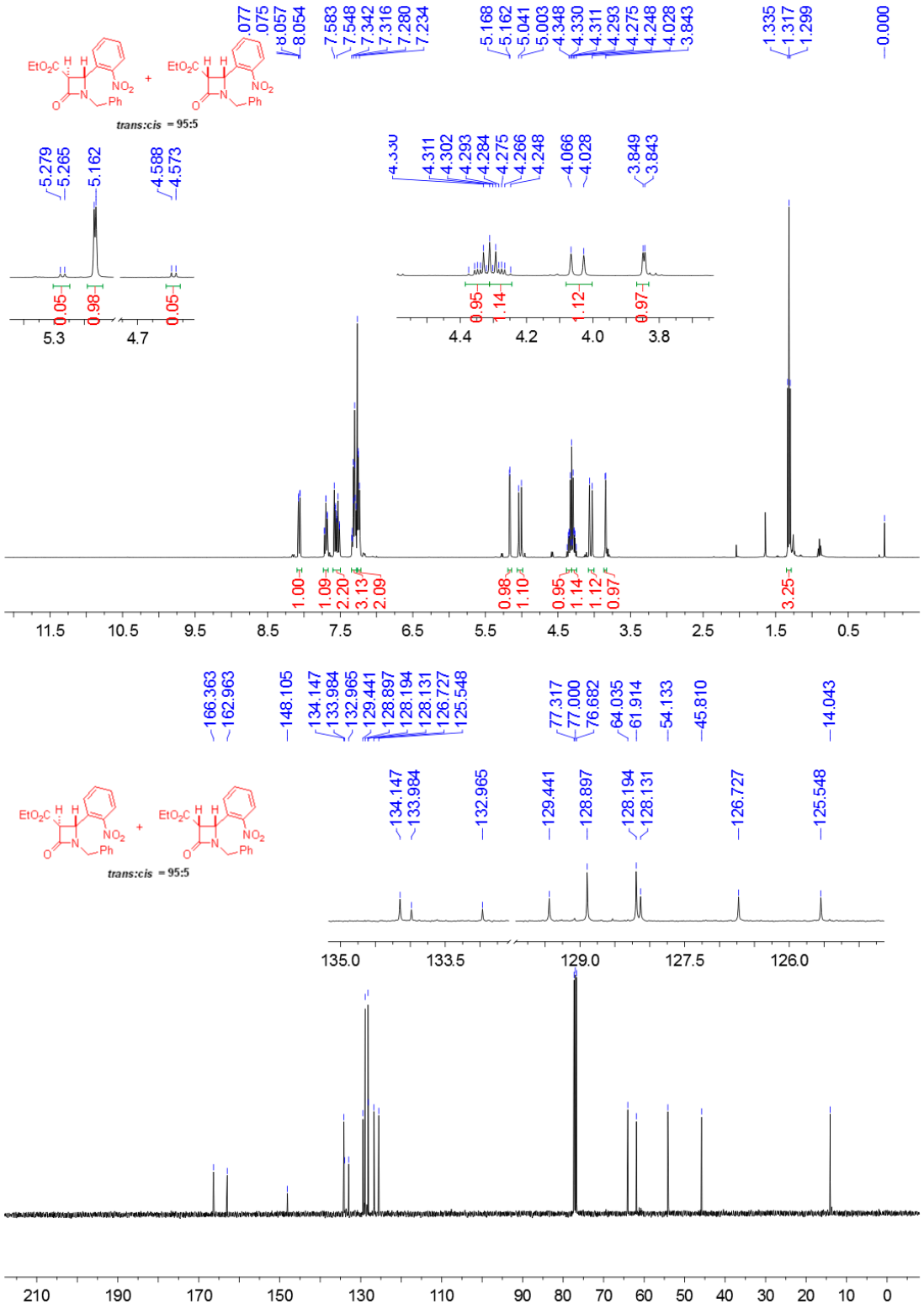
Ethyl trans-1-methyl-2-(2-nitrophenyl)-4-oxoazetidine-3-carboxylate **(4a)**

Compounds *trans*-**4a** and *cis*-**6a** were isolated as a mixture, with a *trans/cis* ratio of 85:15.

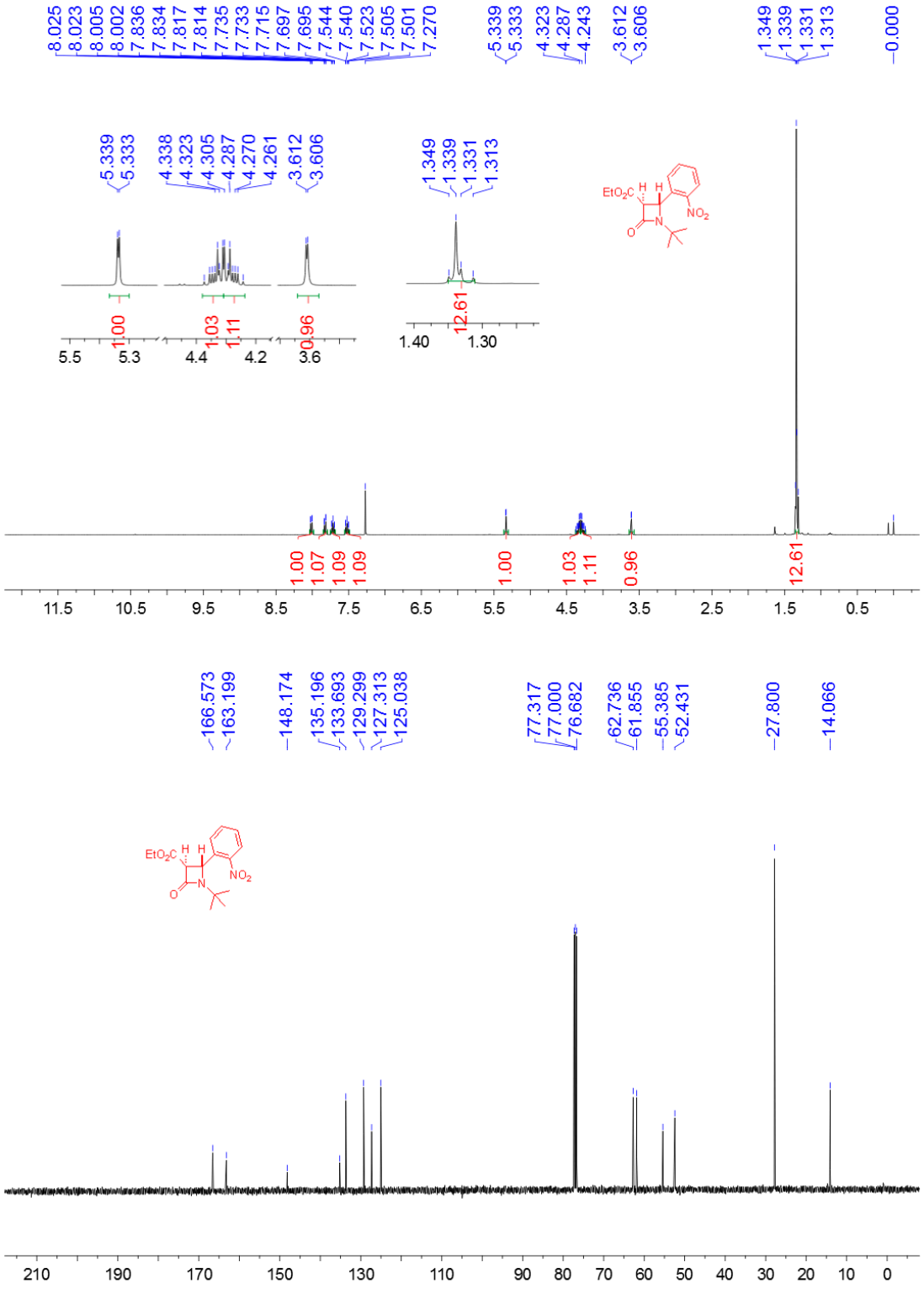


Ethyl trans-1-benzyl-2-(2-nitrophenyl)-4-oxoazetidine-3-carboxylate (**4e**)

Compounds *trans*-**4e** and *cis*-**6e** were isolated as a mixture, with a *trans/cis* ratio of 95:5.

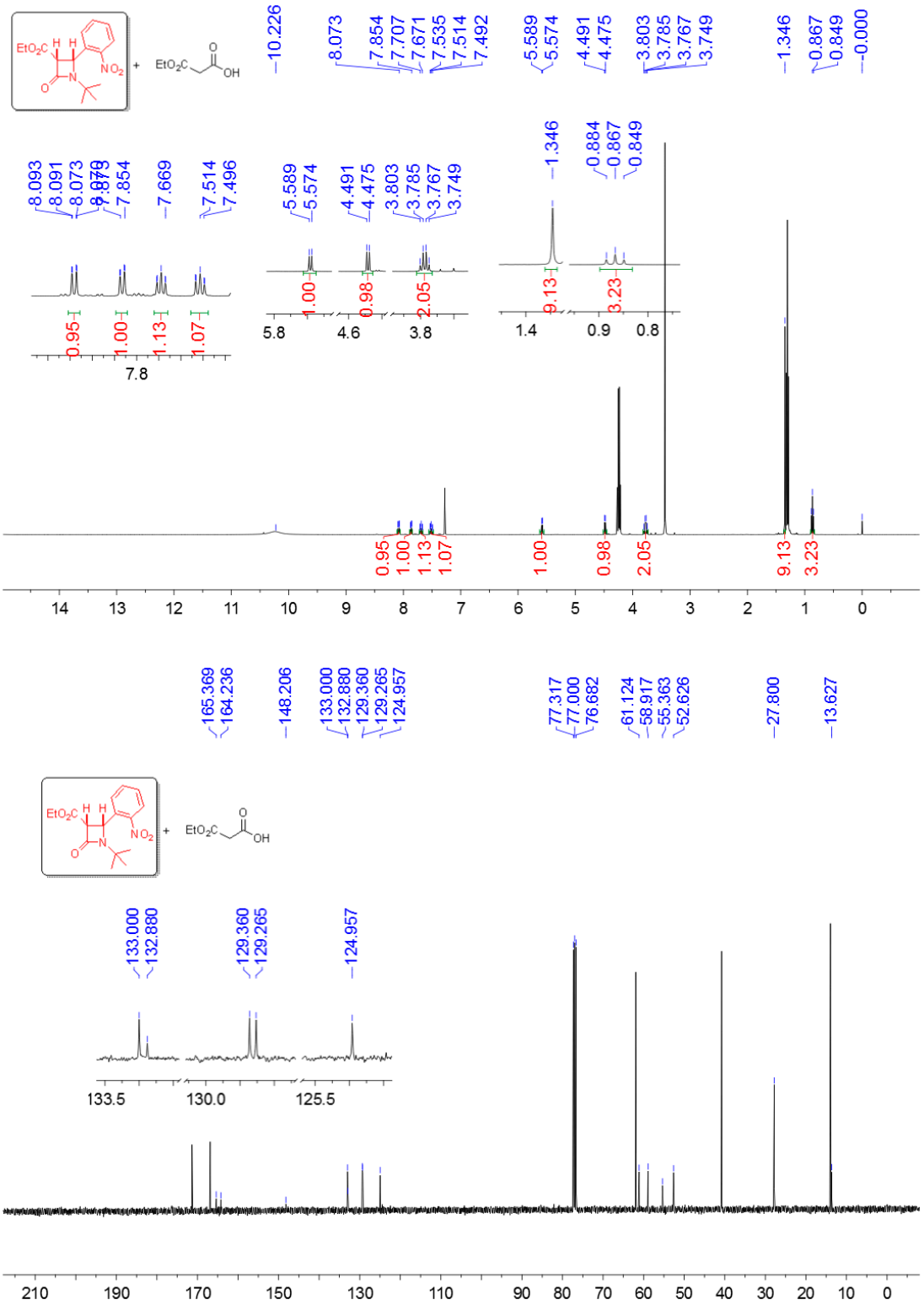


Ethyl trans-1-(tert-butyl)-2-(2-nitrophenyl)-4-oxoazetidine-3-carboxylate **(4f)**



Ethyl cis-1-(tert-butyl)-2-(2-nitrophenyl)-4-oxoazetidine-3-carboxylate **(6f)**

This compound was isolated as a mixture with EtO_2CCH_2COOH; however, further purification of the mixture by treating the column chromatography with Et_3N led to isomerization of *cis*-**6f** into *trans*-**4f**. Thus, herein we present ^{1}H and ^{13}C NMR spectra of the mixture.



2. Copies of representative ^{1}H spectra of reaction mixtures.

Note: Most of *cis*- and *trans*-products involving the *ortho*-nitro effect were inseparable, as indicated in the experimental section. For sulfa-Staudinger reactions, determining the *trans/cis* ratios by the isolated mixtures or crude reaction mixtures gave the same results. For Staudinger reactions, the ratios were determined by their ^{1}H NMR spectra of the crude reaction mixtures, because Et_3N added in the purification step by column chromatography led to the isomerization of *cis*-products into *trans*-products. Herein, only some of spectra of crude reaction mixtures are given.

Table 1, entry 10.

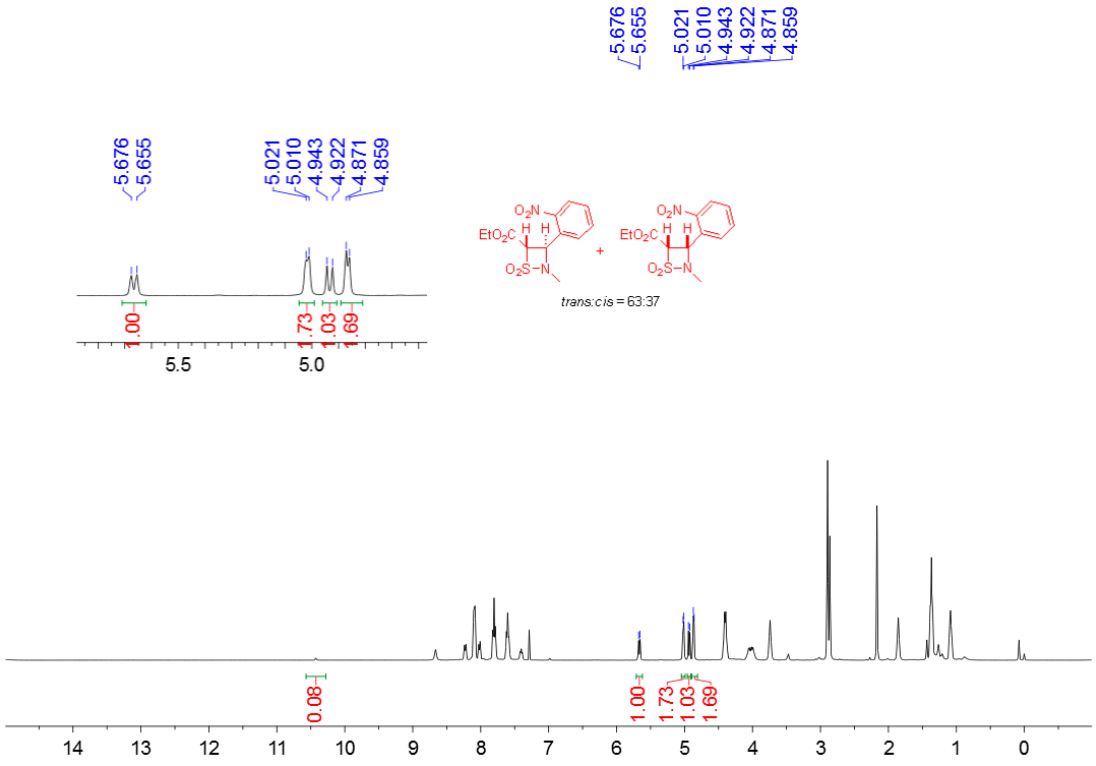


Table 1, entry 11

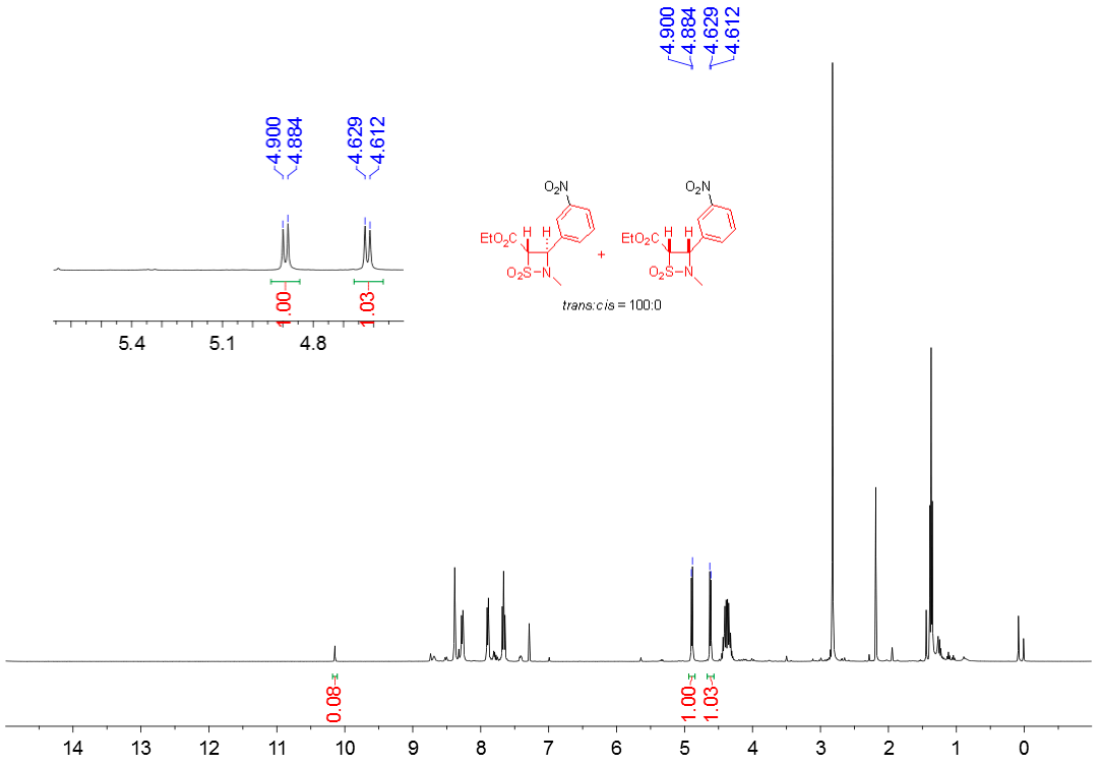
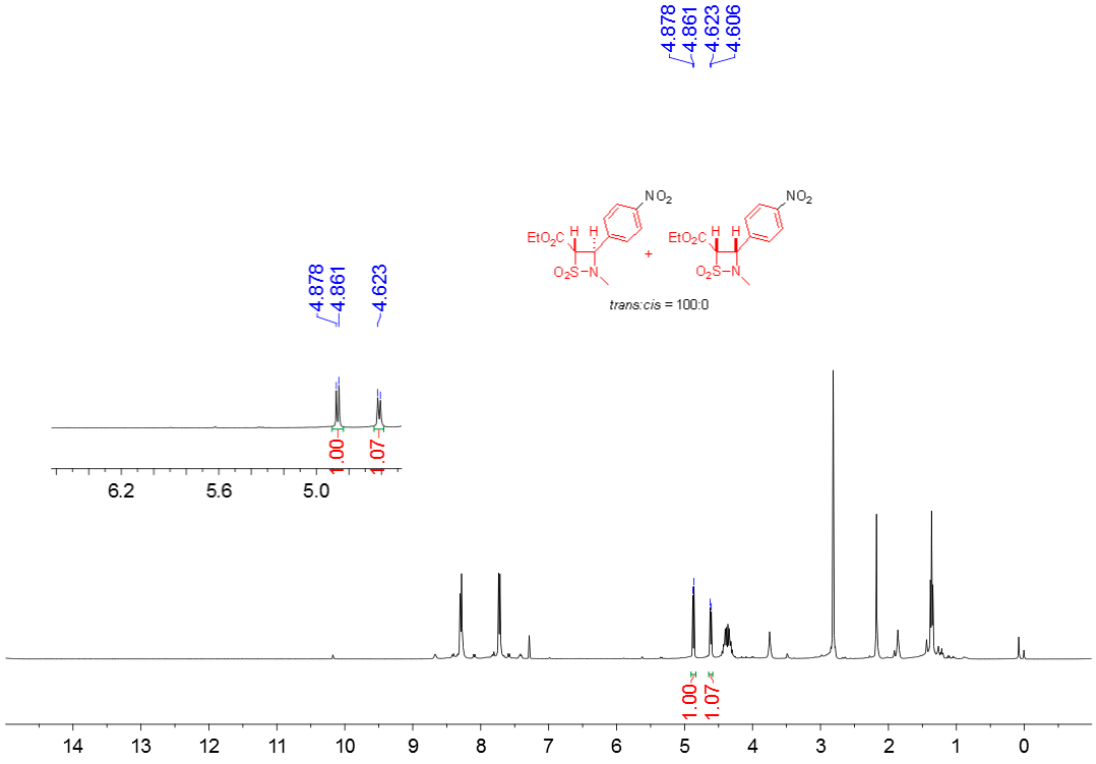
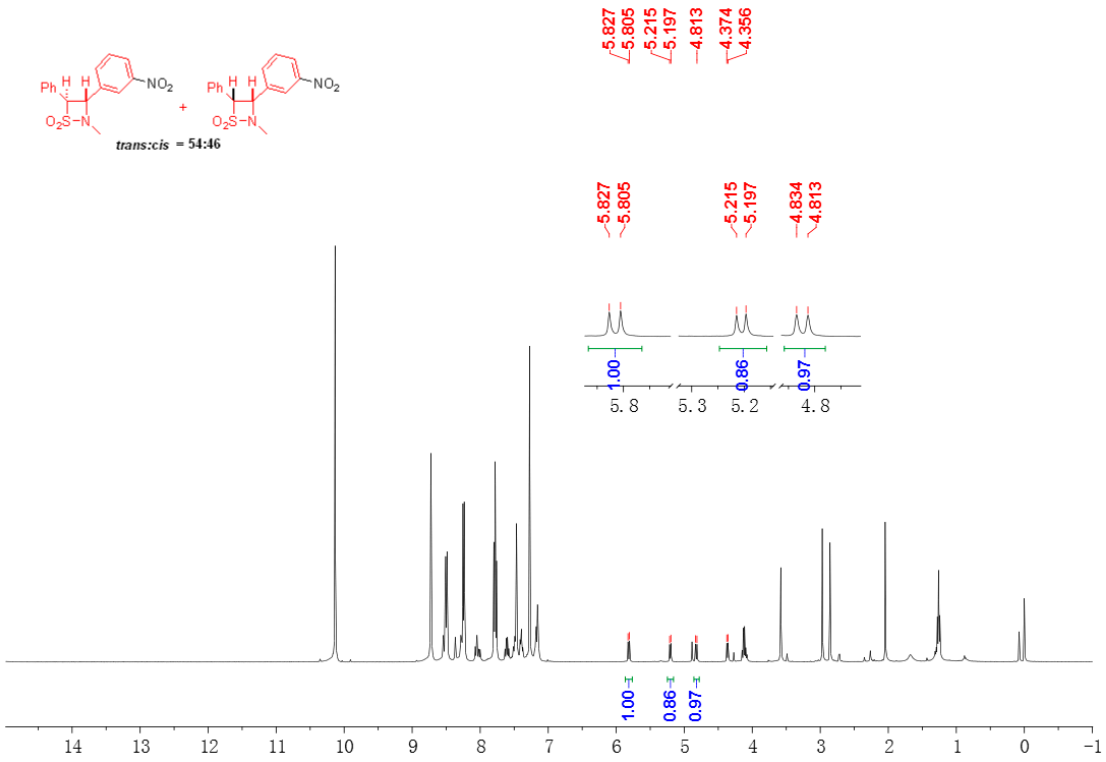
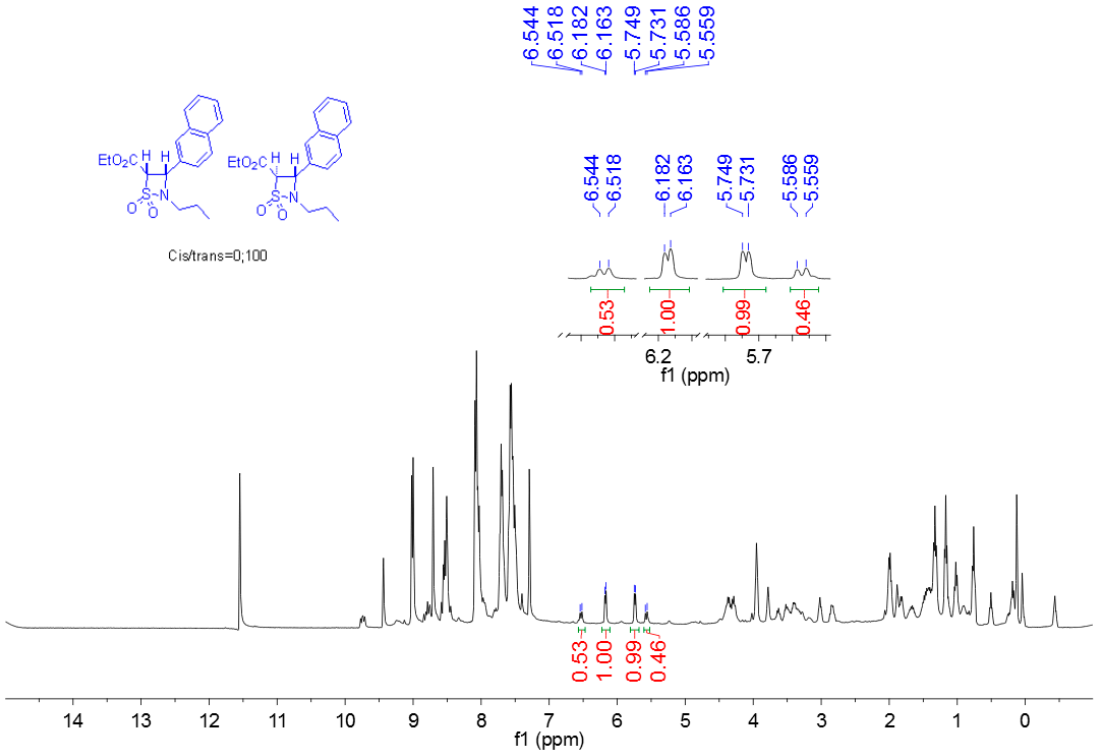


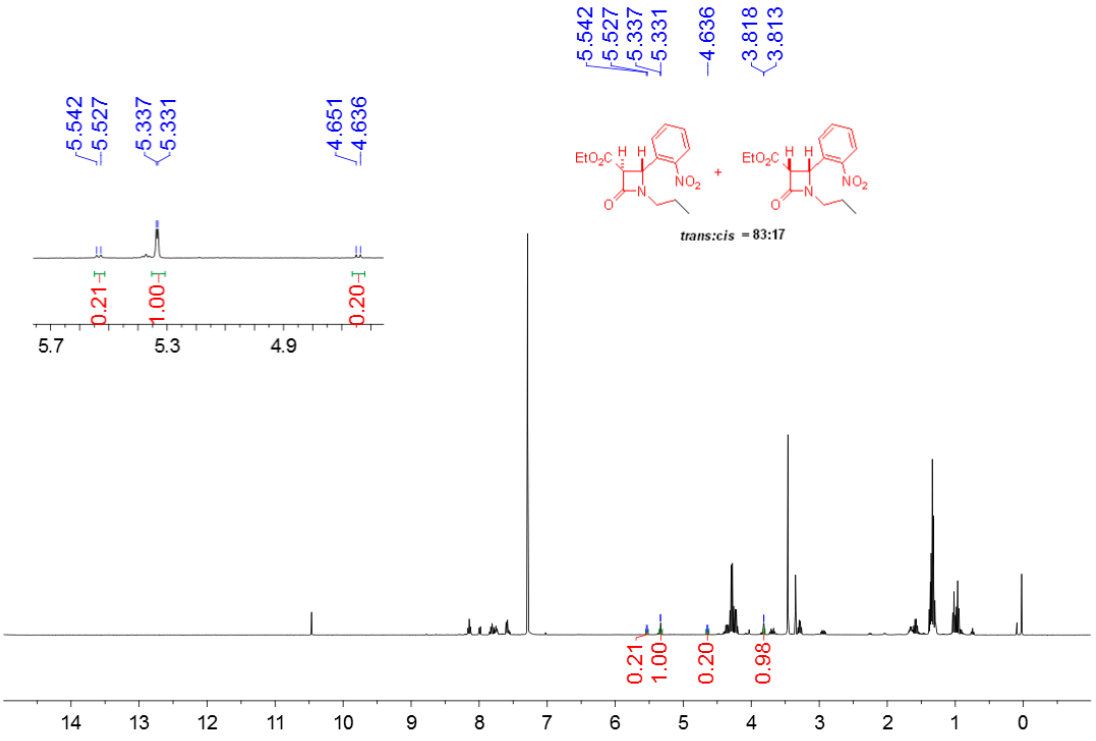
Table 1, entry 12

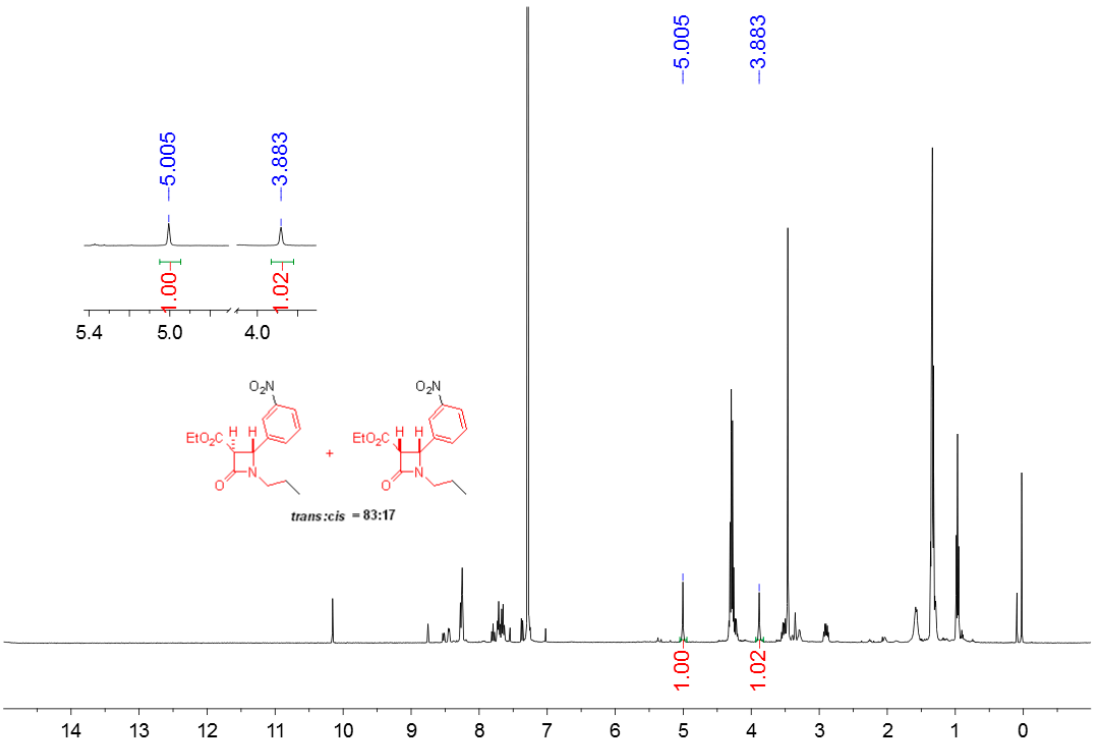




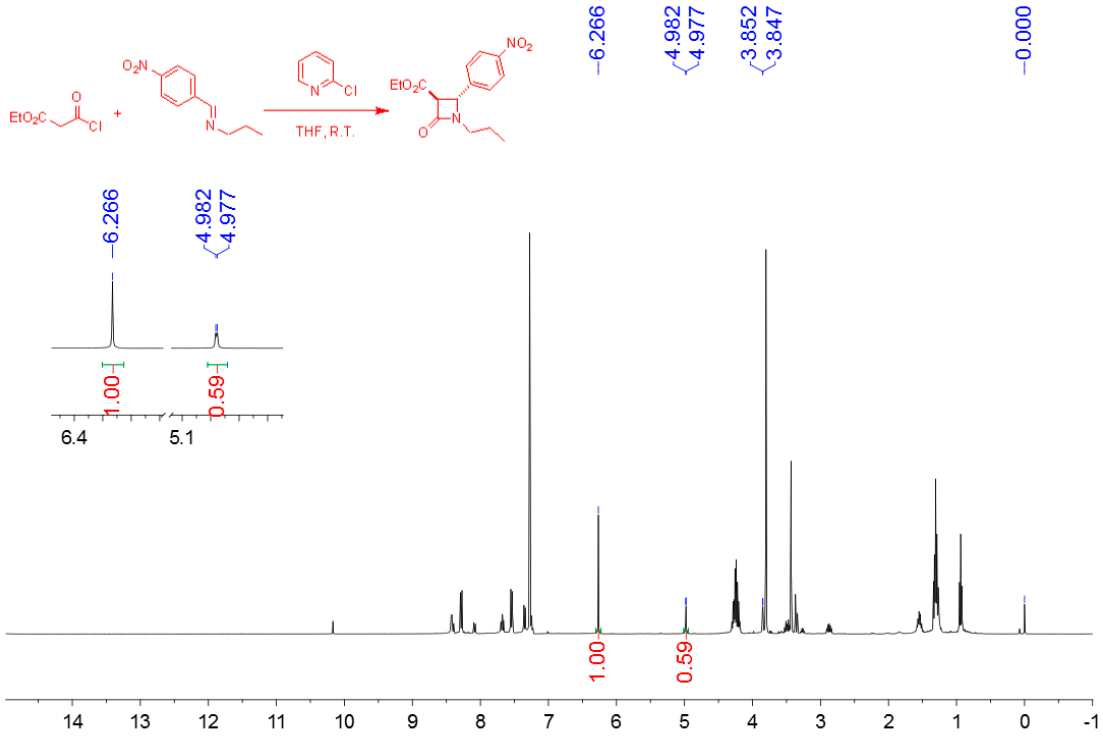
Chemical shifts 6.53 and 5.87 ppm were not the characteristic peaks of *cis*-products, based on the following facts: (a) the coupling constant of 10.4 Hz is too great; (b) *cis*-product was not isolated.

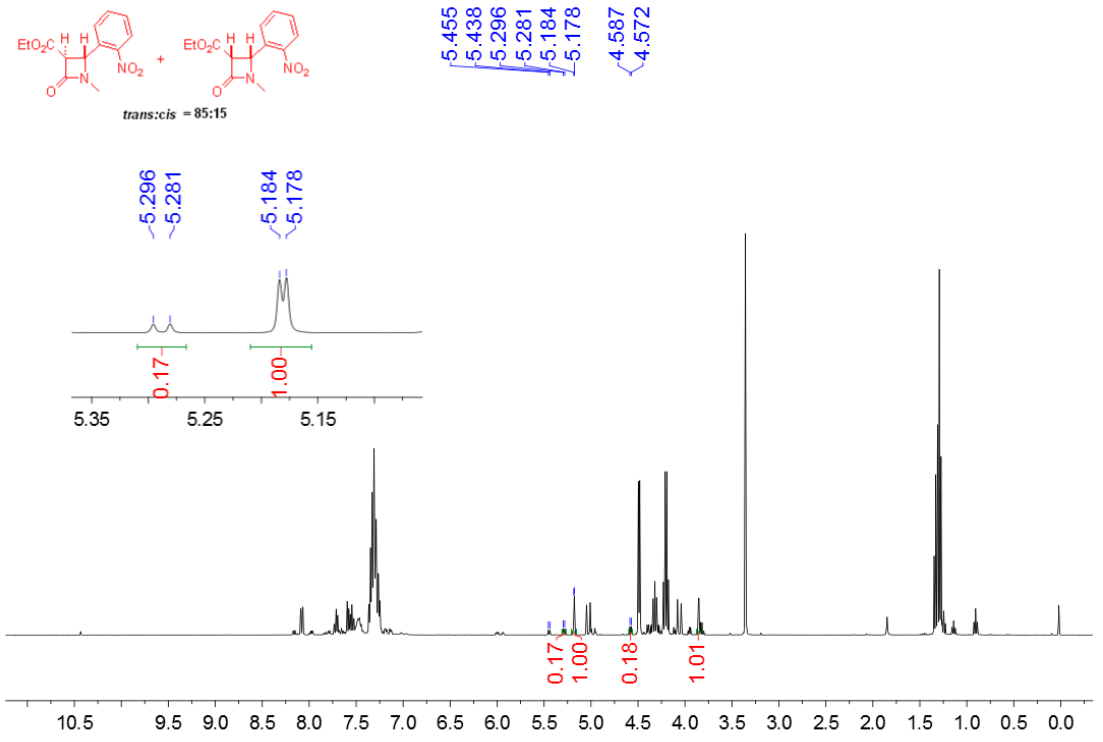


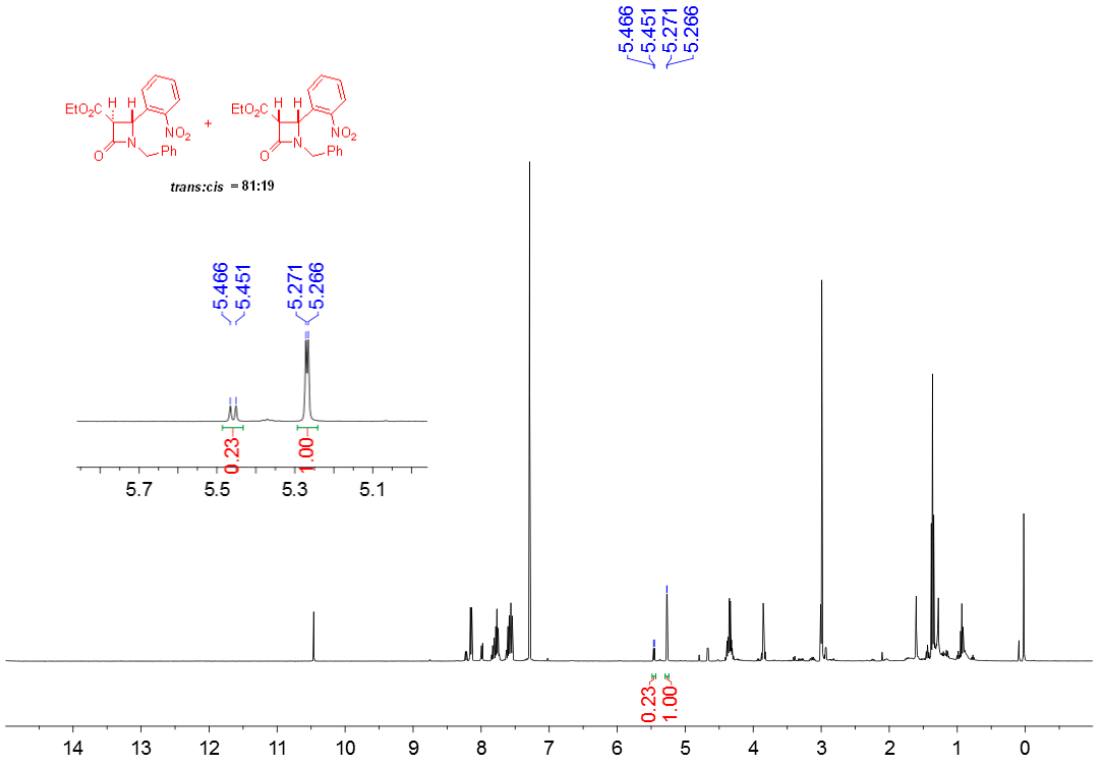

5.542
5.527
5.337
5.331
4.636
3.818
3.813
5.542
5.527
5.337
5.331
4.651
4.636
0.21
1.00
0.20
5.7
5.3
4.9
trans:cis = 83:17
0.21
1.00
0.20
0.98
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0

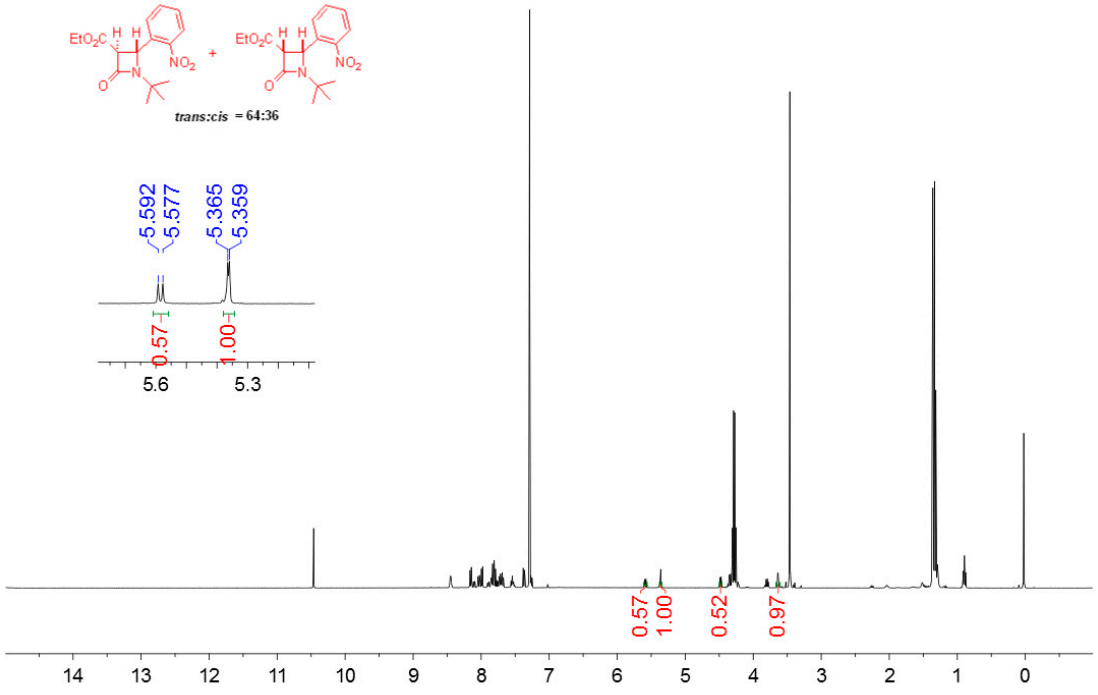

5.005
3.883
5.005
3.883
1.00
1.02
5.4
5.0
4.0
trans:cis = 83:17
1.00
1.02
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0

Trans/cis = 100:0. Dimethyl malonate (6.27 and 3.85 ppm) was added as an internal standard to determine the yield (59%).






5.466
5.451
5.271
5.266
trans:cis = 81:19
0.23
1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0


5.592
5.577
5.365
5.359
trans:cis = 64:36
0.57
1.00
0.52
0.97
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0