Supporting Information

Two Novel 1,2,4,5-Tetrazines that Participate in Inverse Electron Demand Diels–Alder Reactions with an Unexpected Regioselectivity

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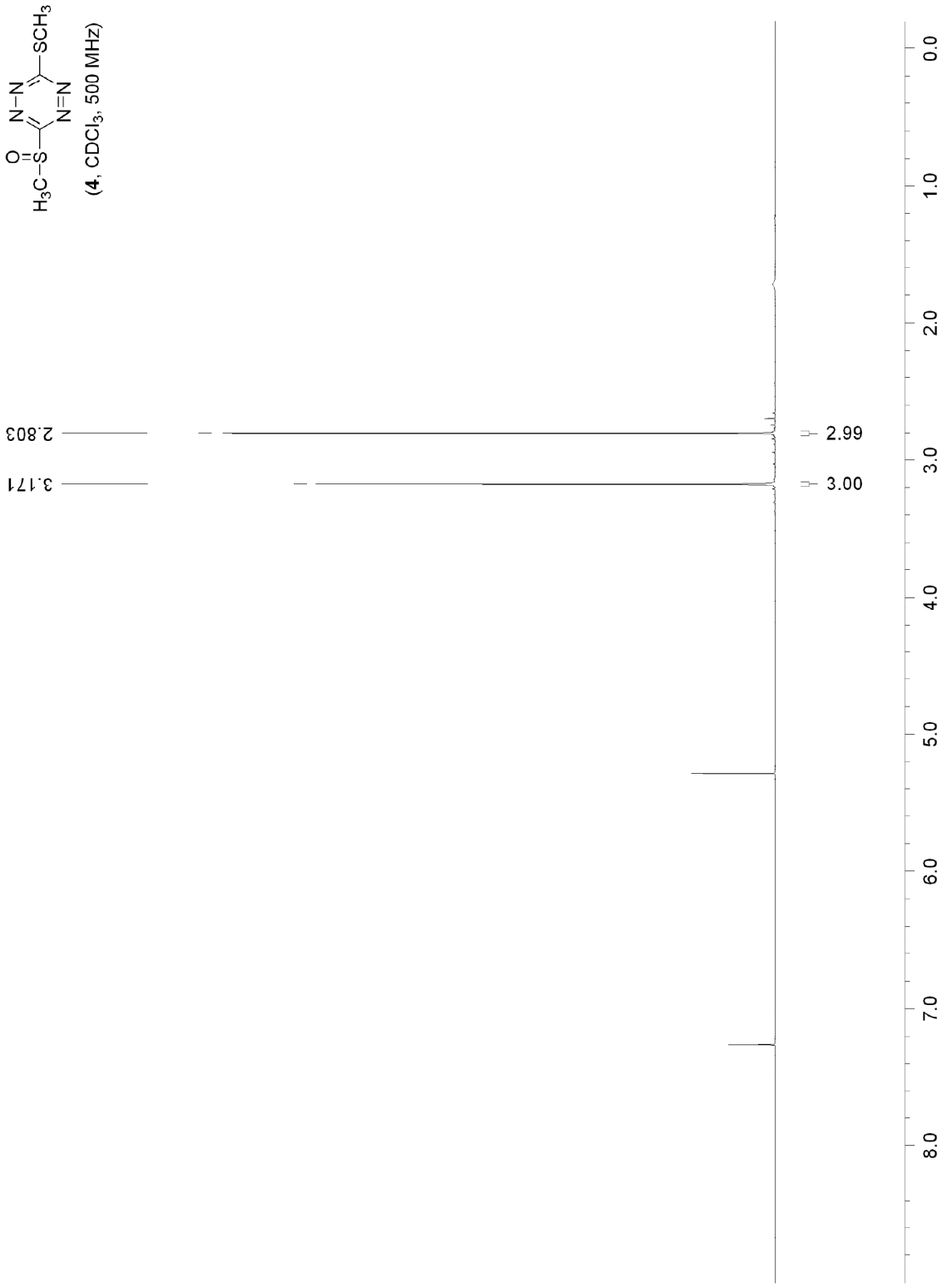
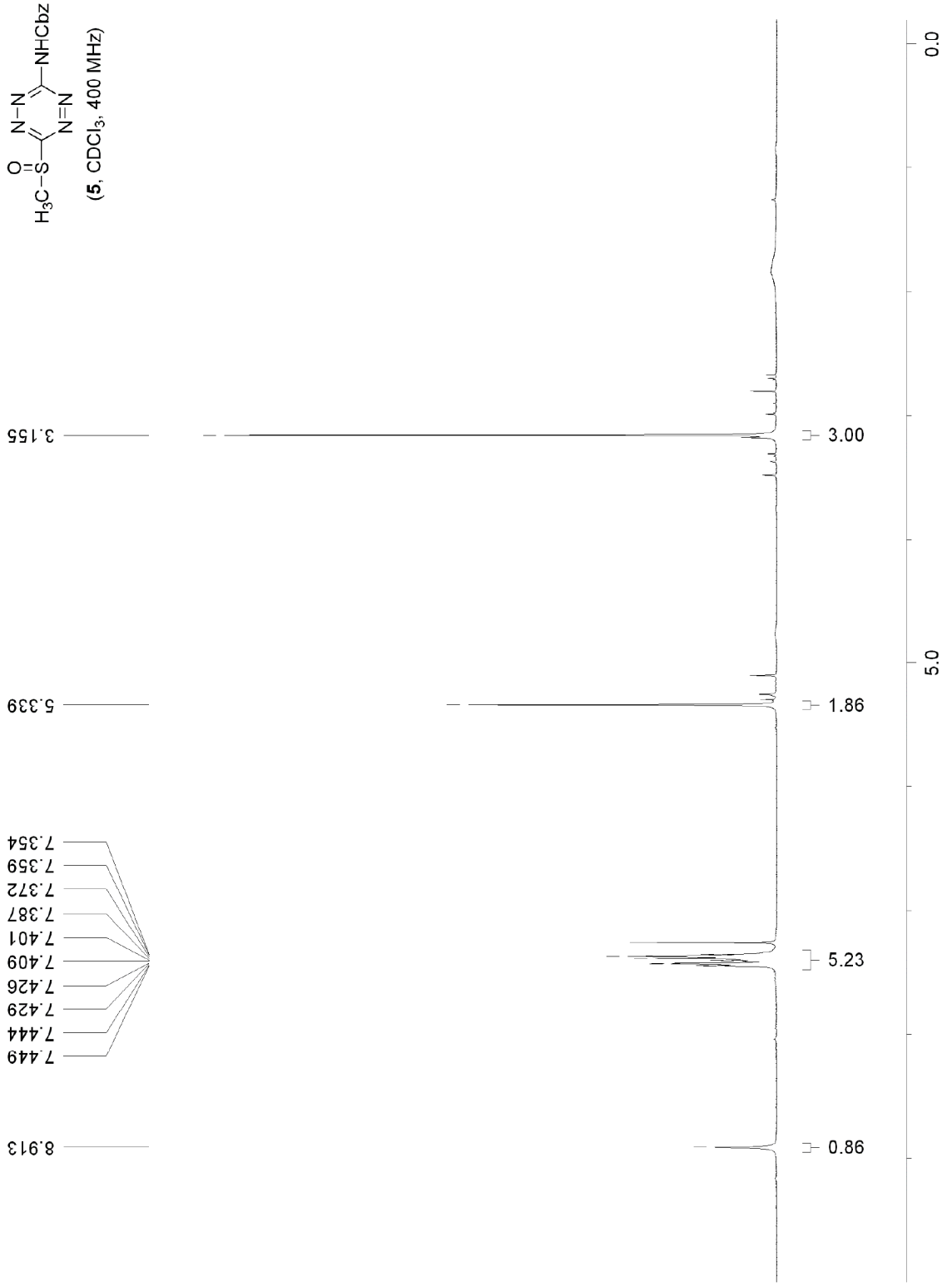
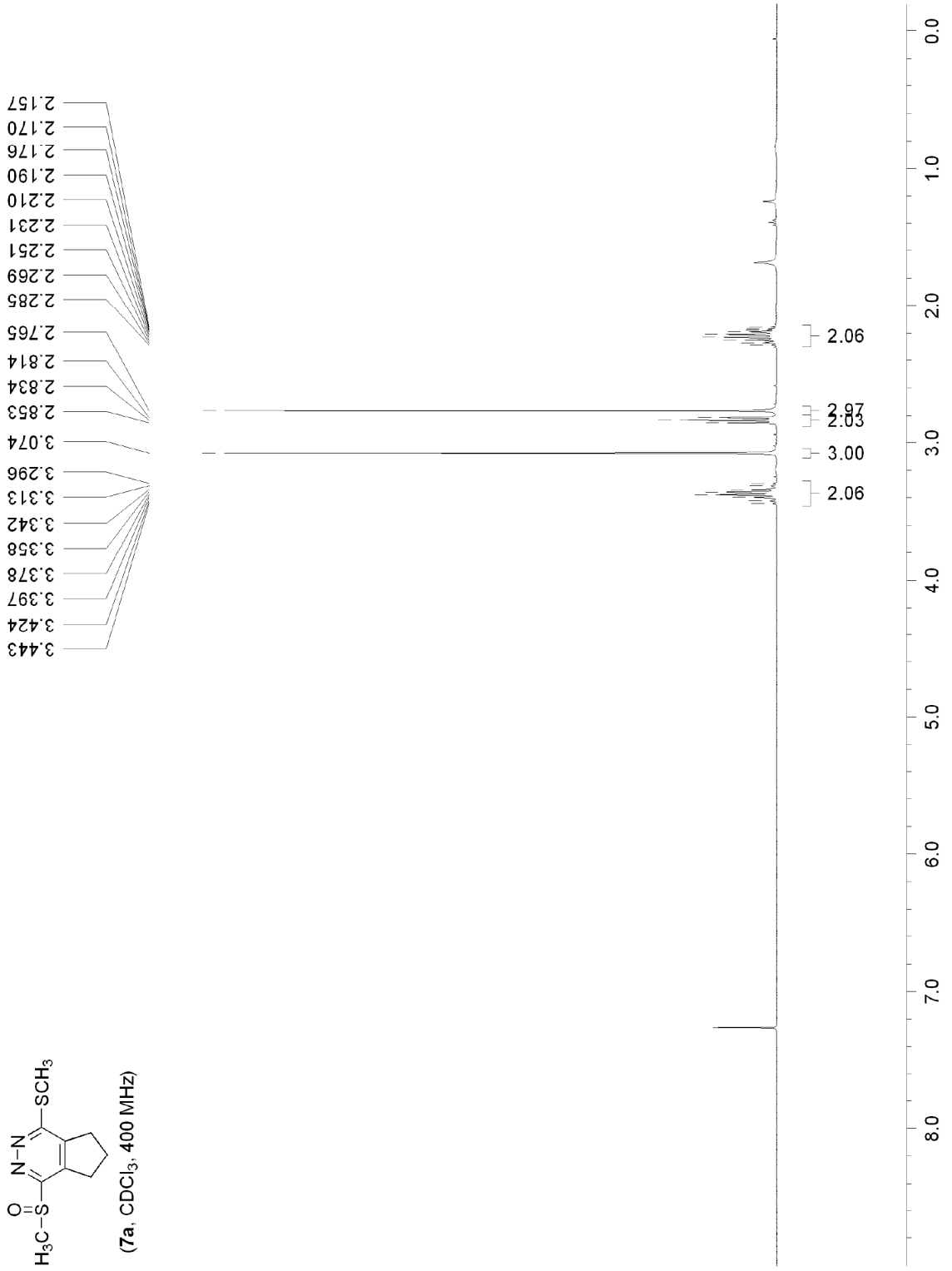
^{1}H NMR of **4**	S3
^{1}H NMR of **5**	S4
^{1}H NMR of **7a**	S4
^{1}H NMR of **7b**	S6
^{1}H NMR of **7c**	S7
^{1}H NMR of **7d**	S8
^{1}H NMR of **7e**	S9
^{1}H NMR of **7f**	S10
^{1}H NMR of **7g**	S11
^{1}H NMR of **7h**	S12
^{1}H NMR of **7i**	S13
^{1}H NMR of **7j**	S14
^{1}H NMR of **7k**	S15
^{1}H NMR of **7l**	S16
^{1}H NMR of **9a**	S17
^{1}H NMR of **9b**	S18
^{1}H NMR of **9c**	S19
^{1}H NMR of **9d**	S20
^{1}H NMR of **9e**	S21
^{1}H NMR of **9f**	S22

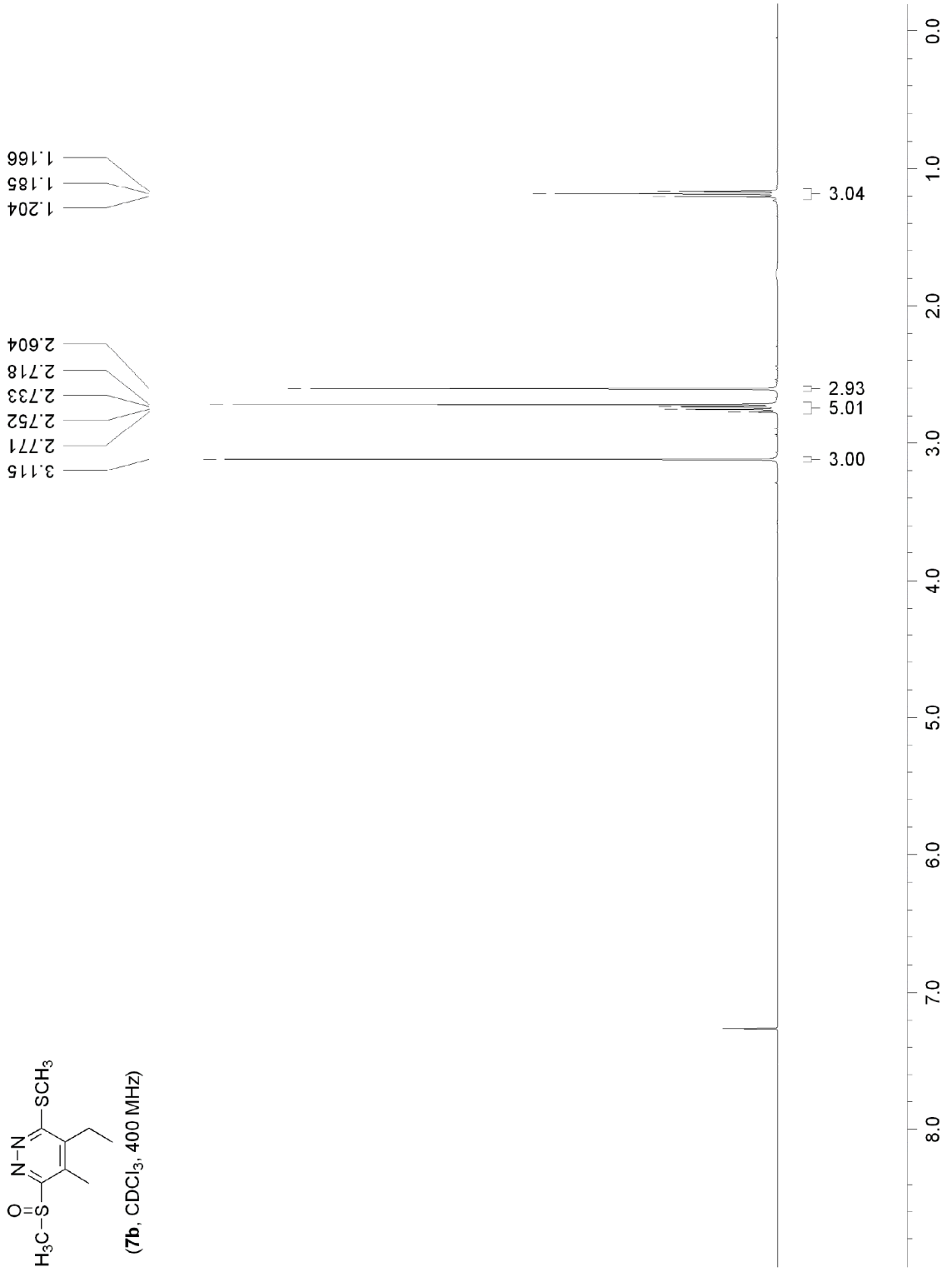
^{1}H NMR of **9g** S23
^{1}H NMR of **9h** S24
^{1}H NMR of **9i** S25
^{1}H NMR of **9j** S26
^{1}H NMR of **10a** S27
^{1}H NMR of **10b** S28
^{1}H NMR of **10c** S29
^{1}H NMR of **10d** S30


(4, CDCl3, 500 MHz)
2.803
3.171
2.99
3.00
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0


(5, CDCl3, 400 MHz)
3.155
5.339
7.354
7.359
7.372
7.387
7.401
7.409
7.426
7.429
7.444
7.449
8.913
3.00
1.86
5.23
0.86
0.0
5.0

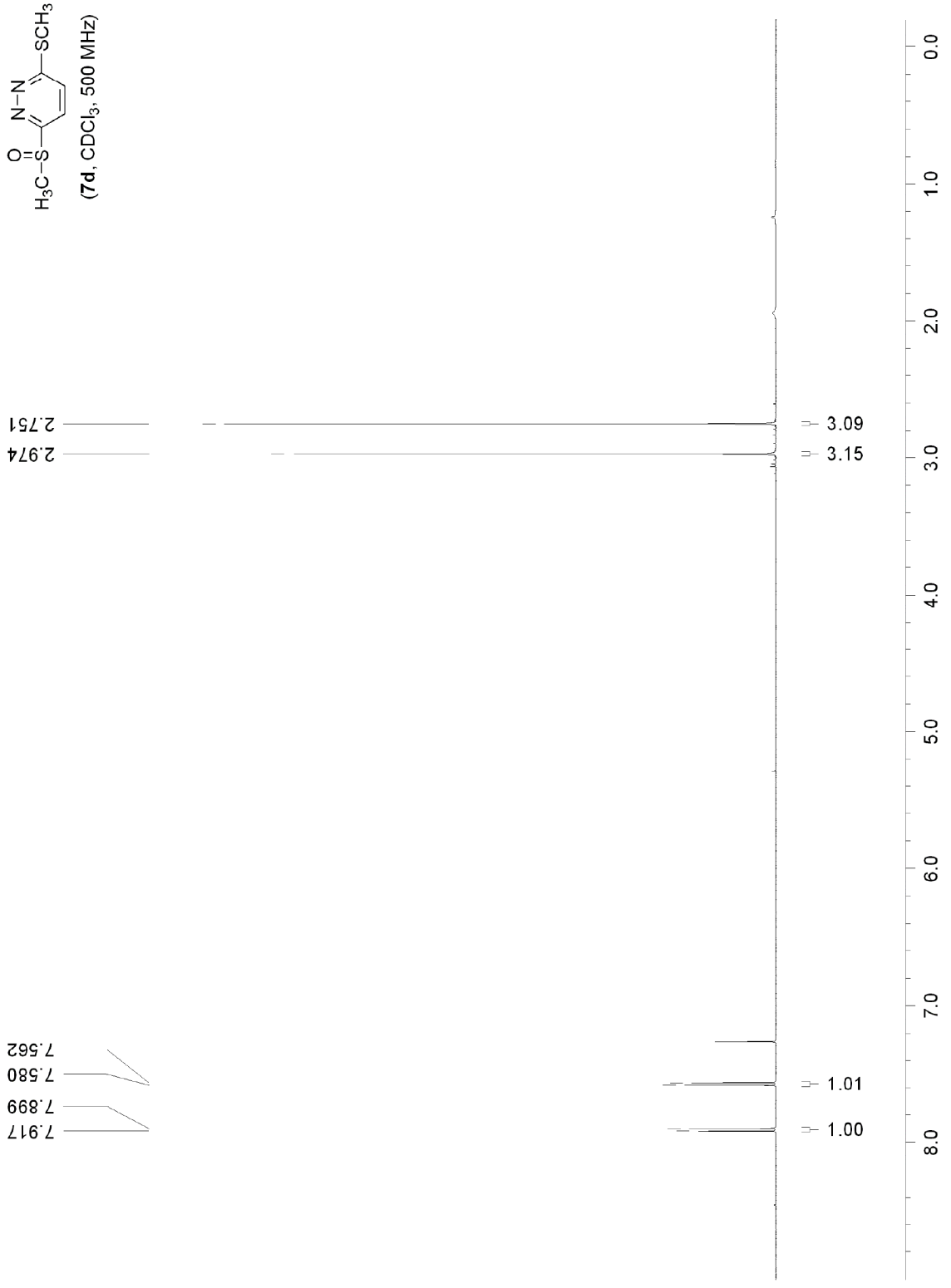


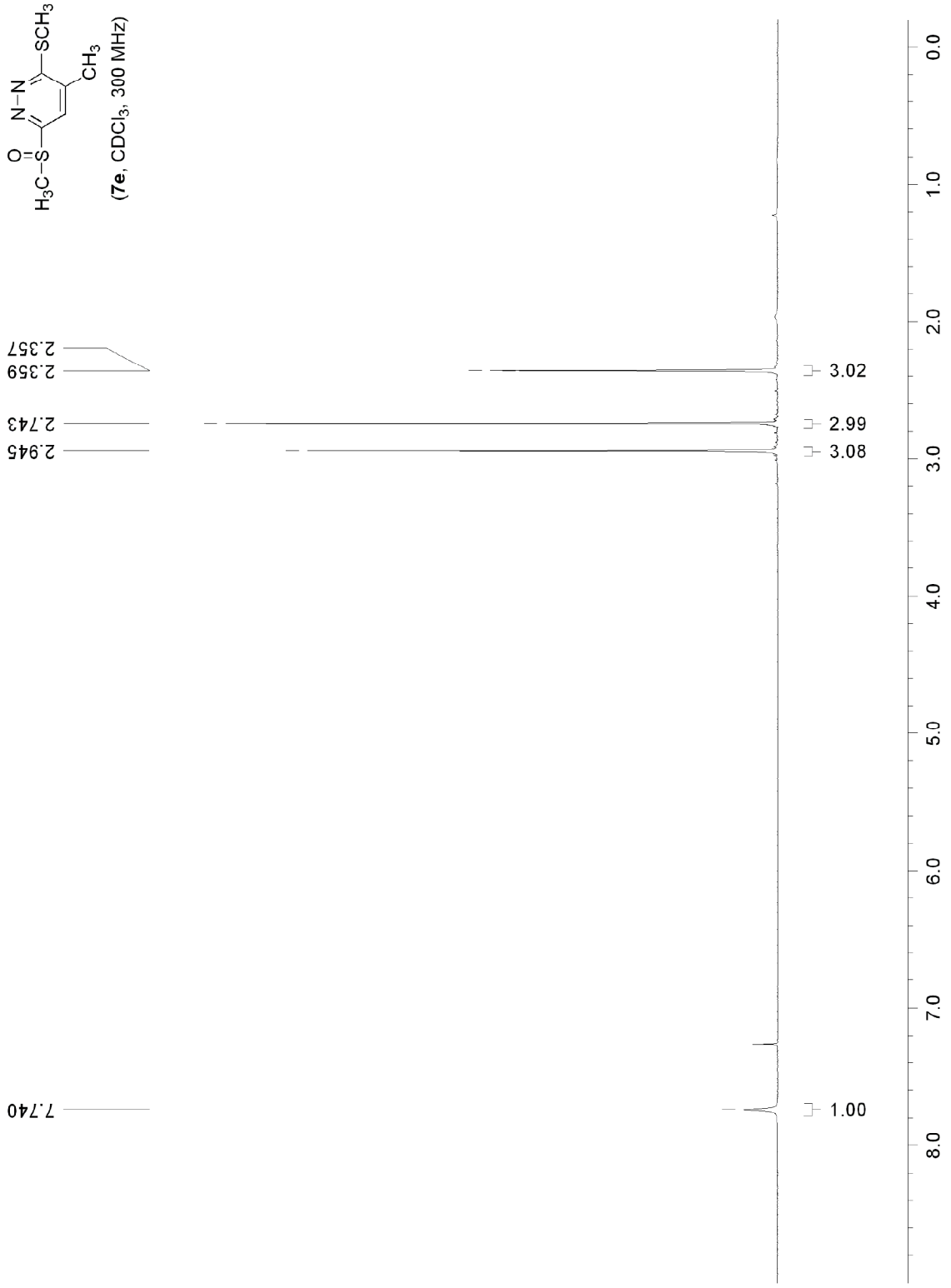
(**7a**, $CDCl_3$, 400 MHz)

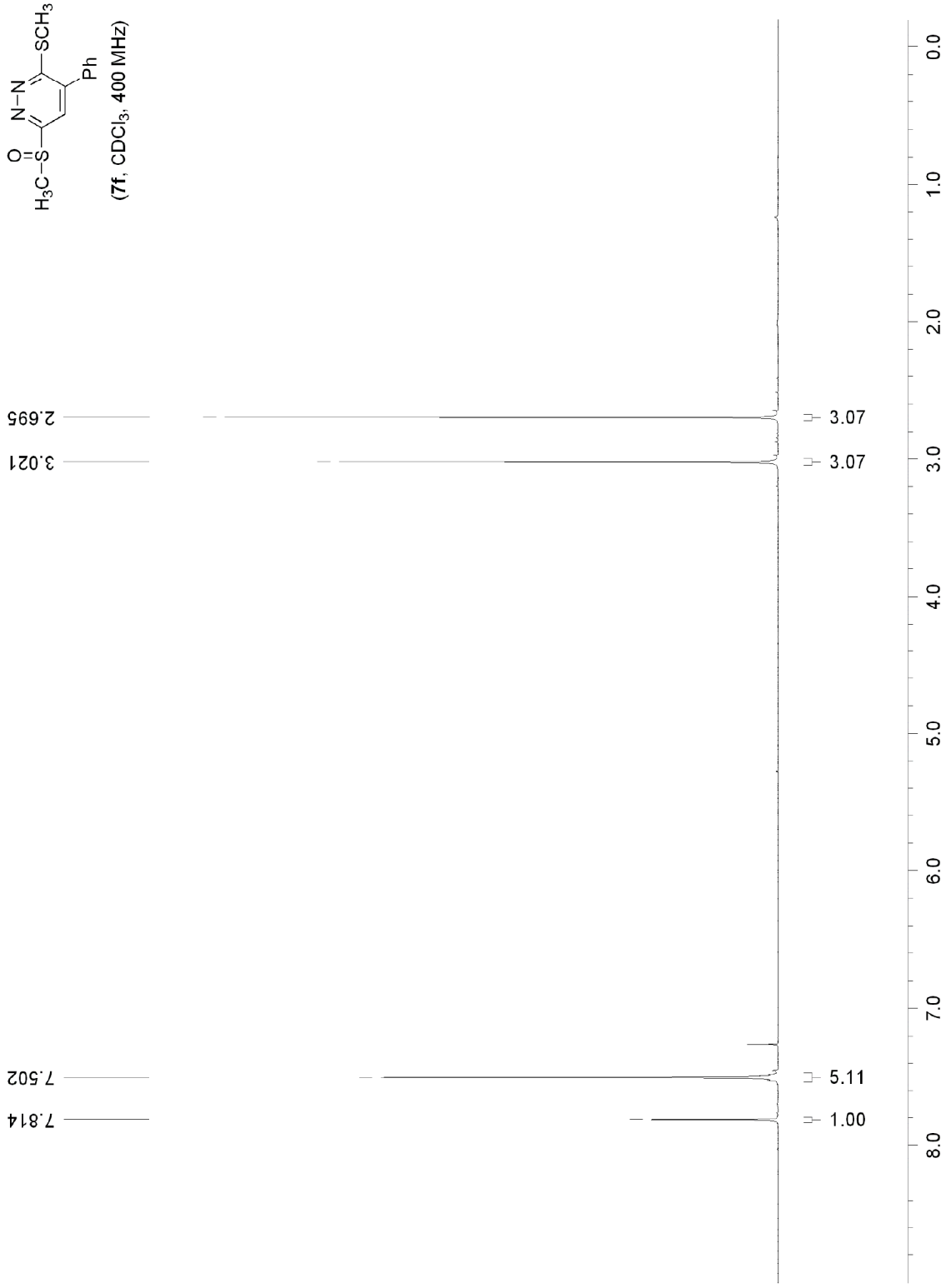


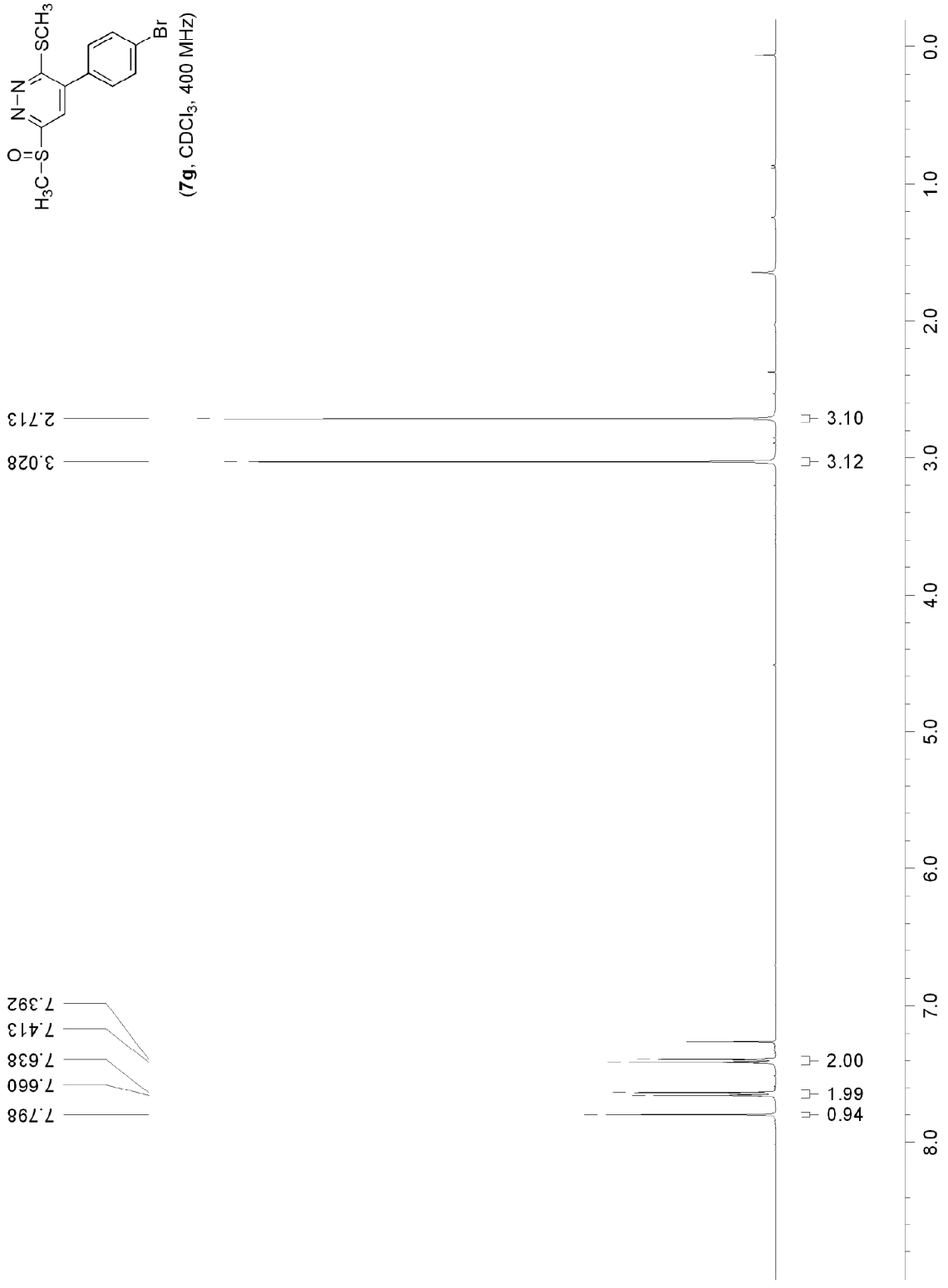
(**7b**, $CDCl_3$, 400 MHz)

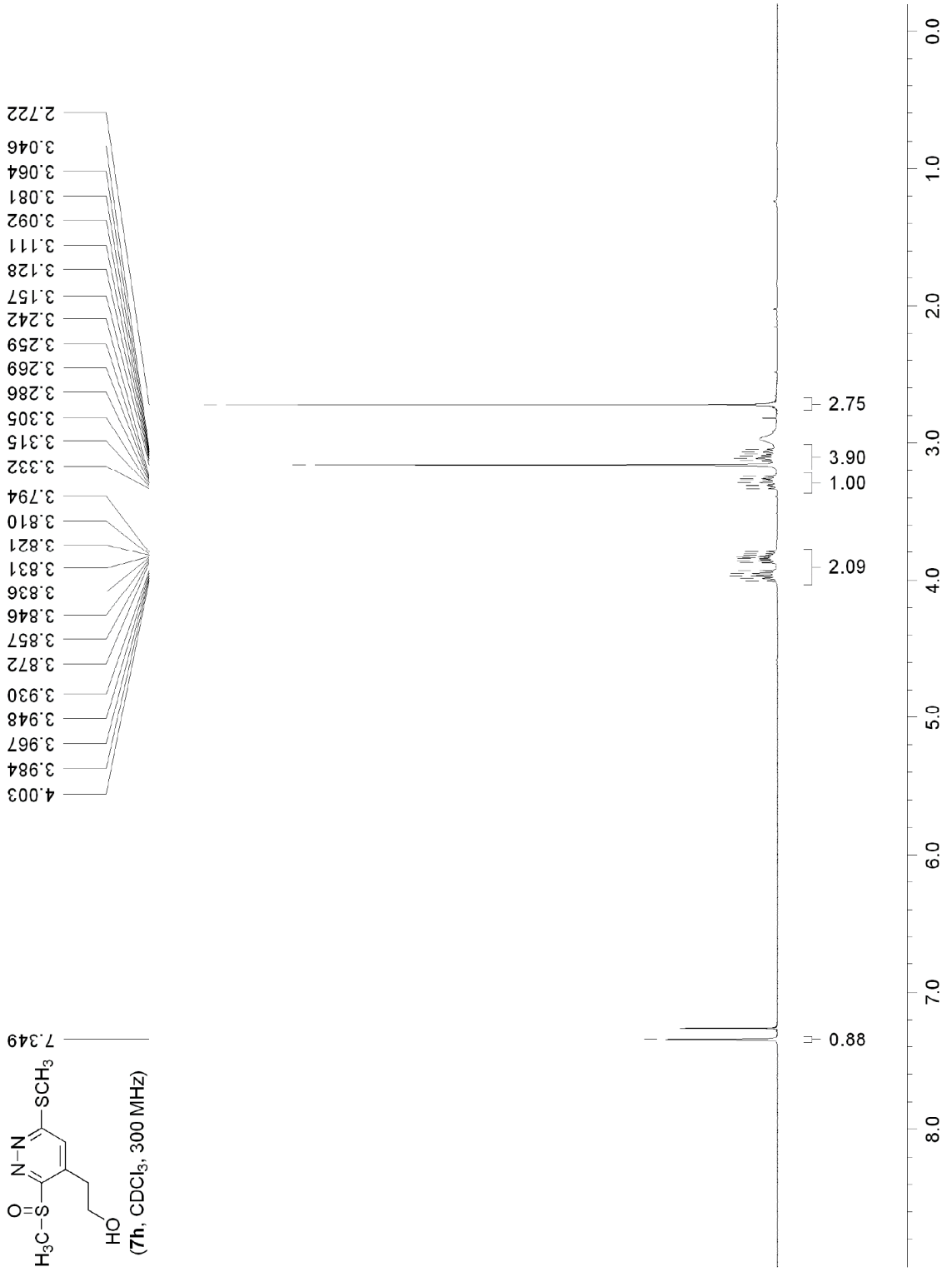
(**7c**, $CDCl_3$, 400 MHz)

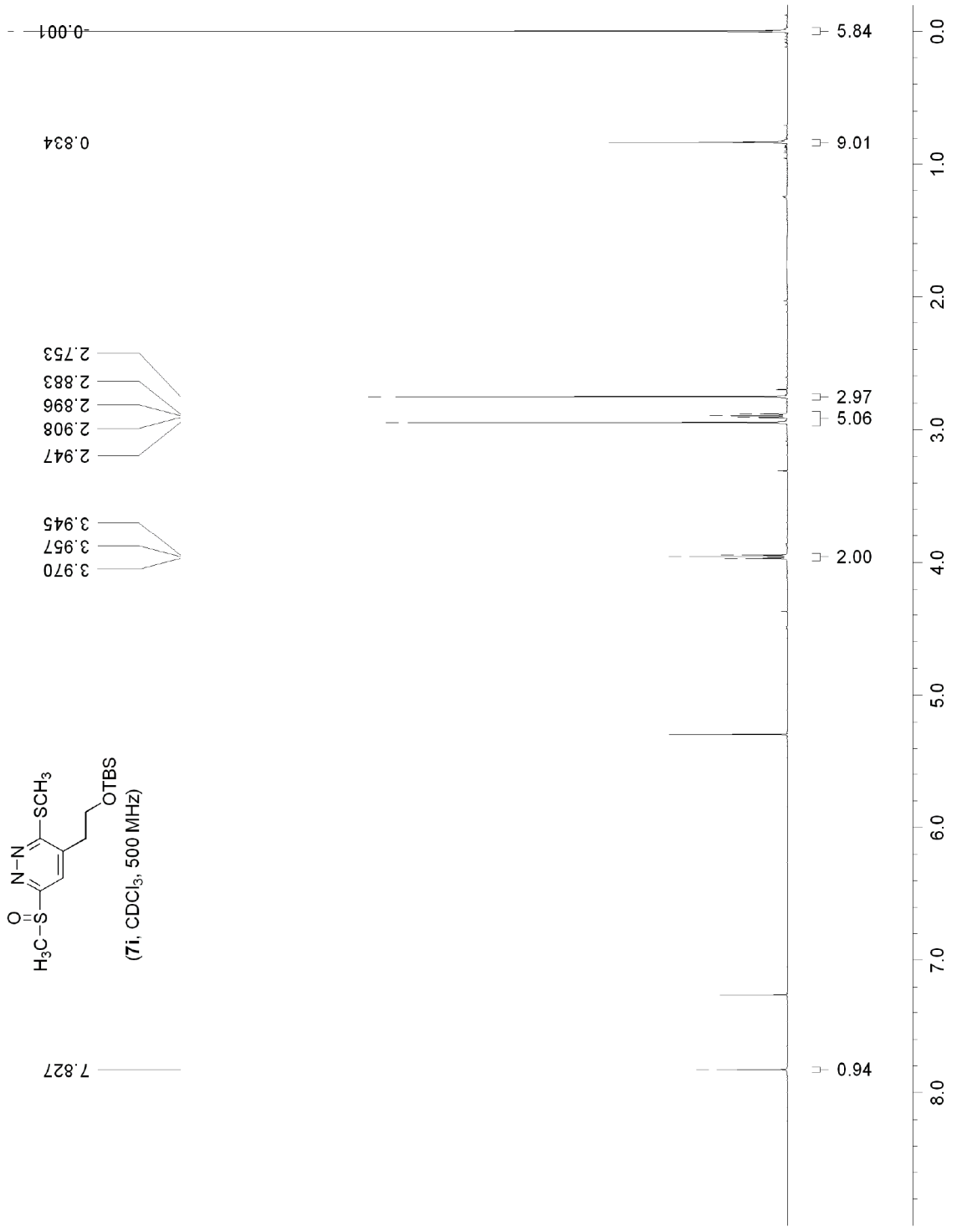

(7d, CDCl3, 500 MHz)
2.751
2.974
7.562
7.580
7.899
7.917
3.09
3.15
1.01
1.00
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0


(7e, CDCl3, 300 MHz)
2.357
2.359
2.743
2.945
7.740
3.02
2.99
3.08
1.00
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

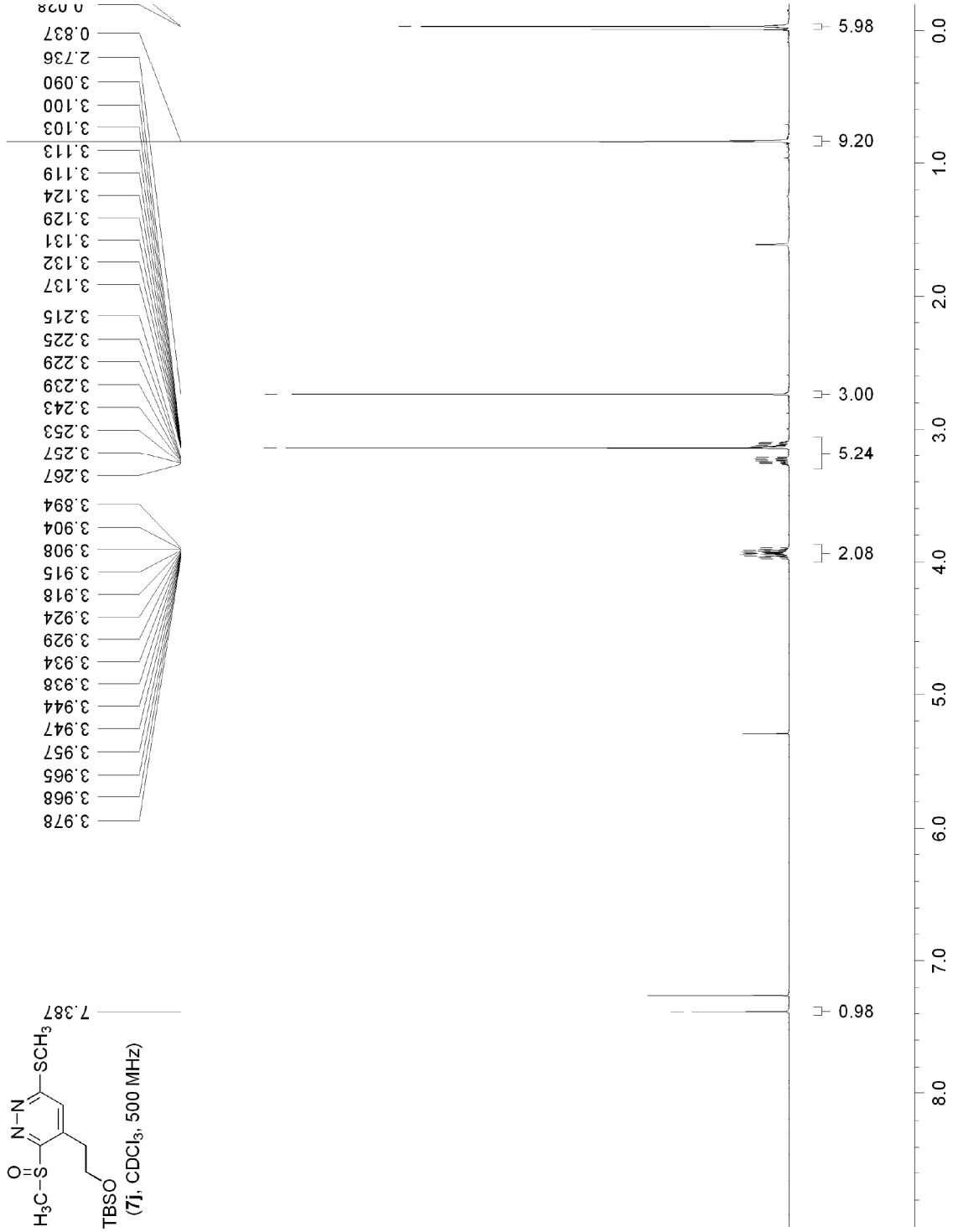

(7f, CDCl3, 400 MHz)
2.695
3.021
7.502
7.814
3.07
3.07
5.11
1.00
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

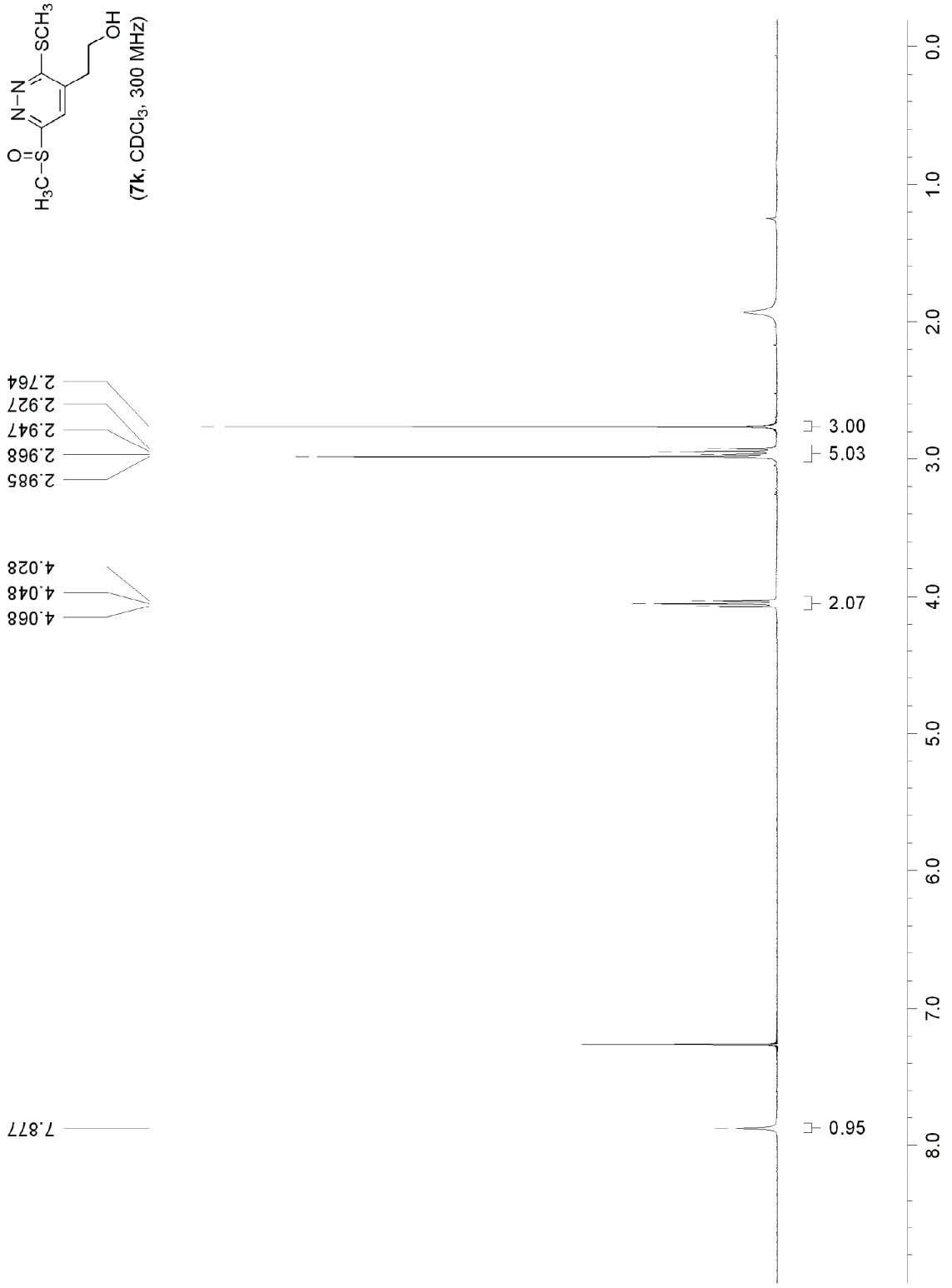

(7g, CDCl3, 400 MHz)
2.713
3.028
7.392
7.413
7.638
7.660
7.798
3.10
3.12
2.00
1.99
0.94
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

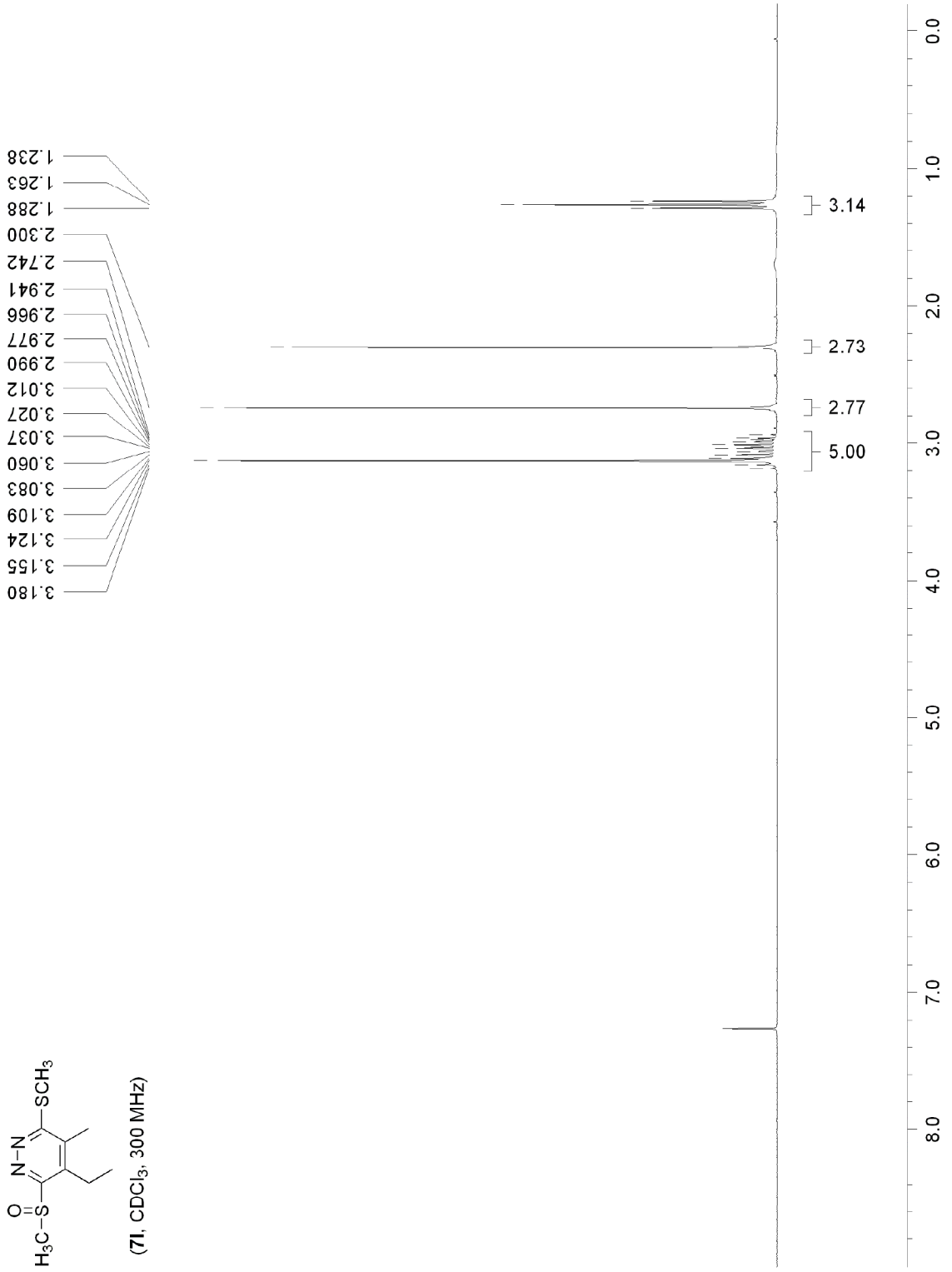

7.349
4.003
3.984
3.967
3.948
3.930
3.872
3.857
3.846
3.836
3.831
3.821
3.810
3.794
3.332
3.315
3.305
3.286
3.269
3.259
3.242
3.157
3.128
3.111
3.092
3.081
3.064
3.046
2.722
0.88
2.09
1.00
3.90
2.75
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
(7h, CDCl3, 300 MHz)



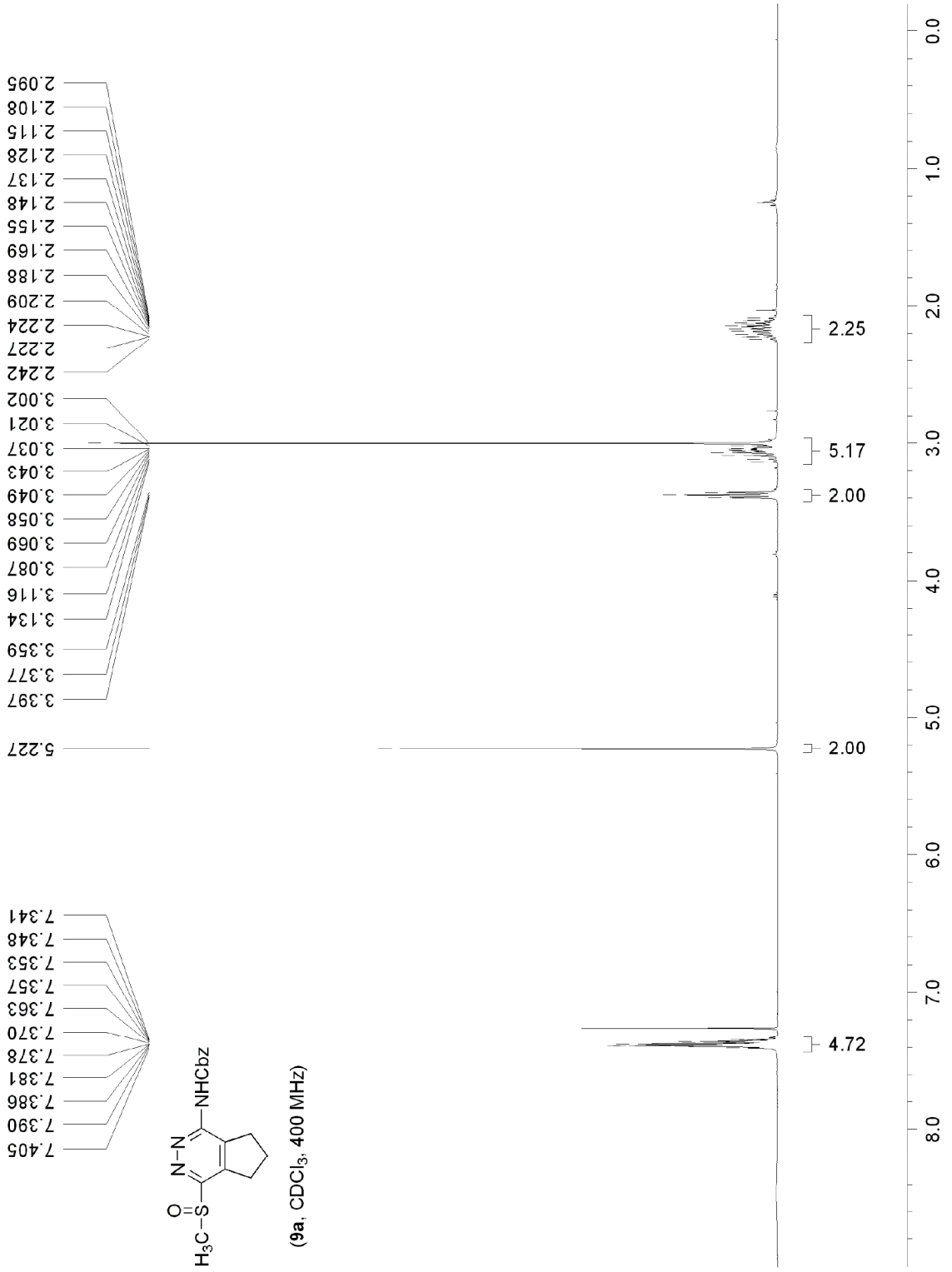
(**7i**, $CDCl_3$, 500 MHz)


0.028
0.837
2.736
3.090
3.100
3.103
3.113
3.119
3.124
3.129
3.131
3.132
3.137
3.215
3.225
3.229
3.239
3.243
3.253
3.257
3.267
3.894
3.904
3.908
3.915
3.918
3.924
3.929
3.934
3.938
3.944
3.947
3.957
3.965
3.968
3.978
7.387
5.98
9.20
3.00
5.24
2.08
0.98
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
SCH3
N–N
O=S
H3C–S
TBSO
(7j, CDCl3, 500 MHz)

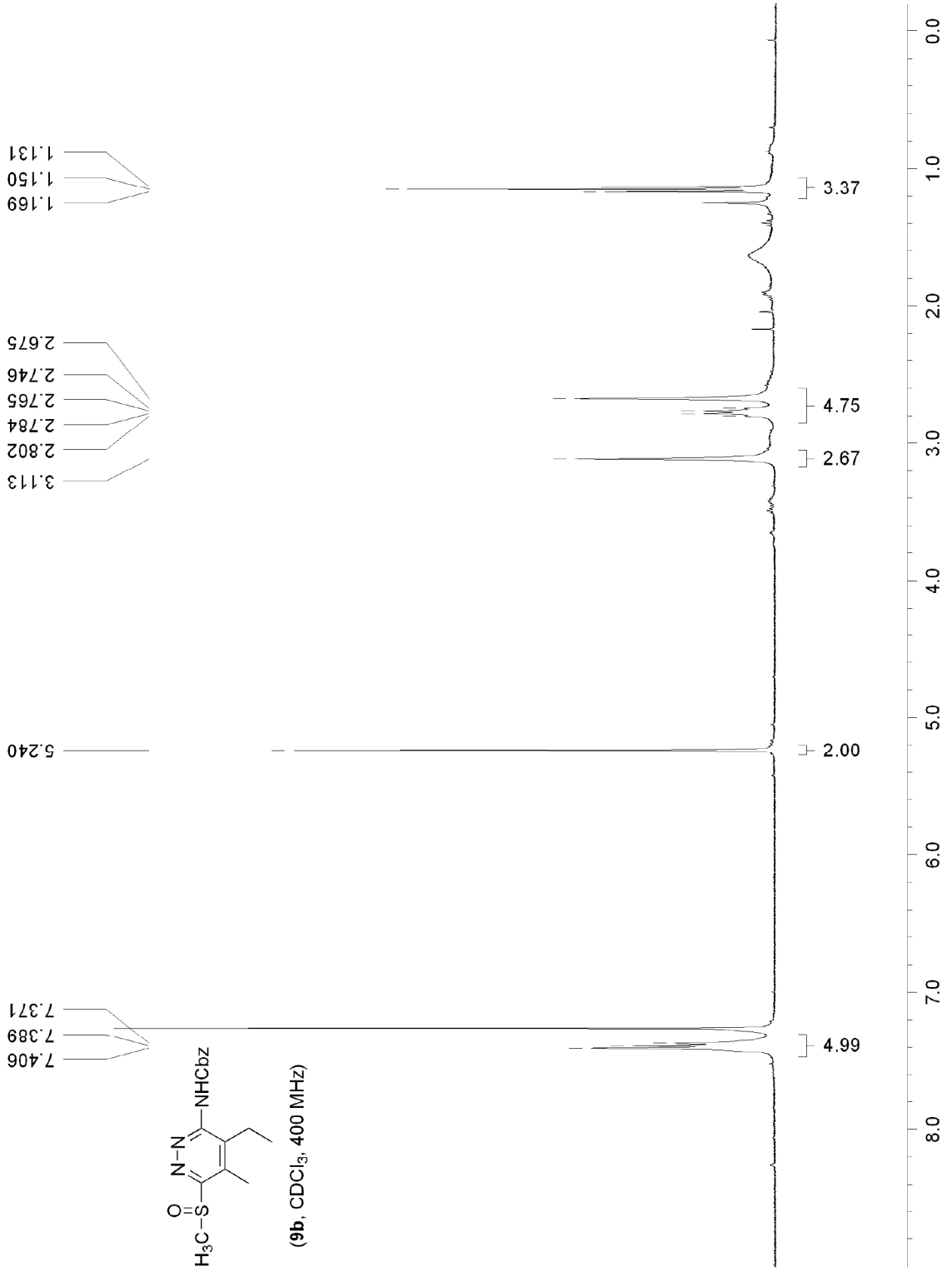

(7k, CDCl3, 300 MHz)
7.877
4.068
4.048
4.028
2.985
2.968
2.947
2.927
2.764
0.95
2.07
5.03
3.00
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

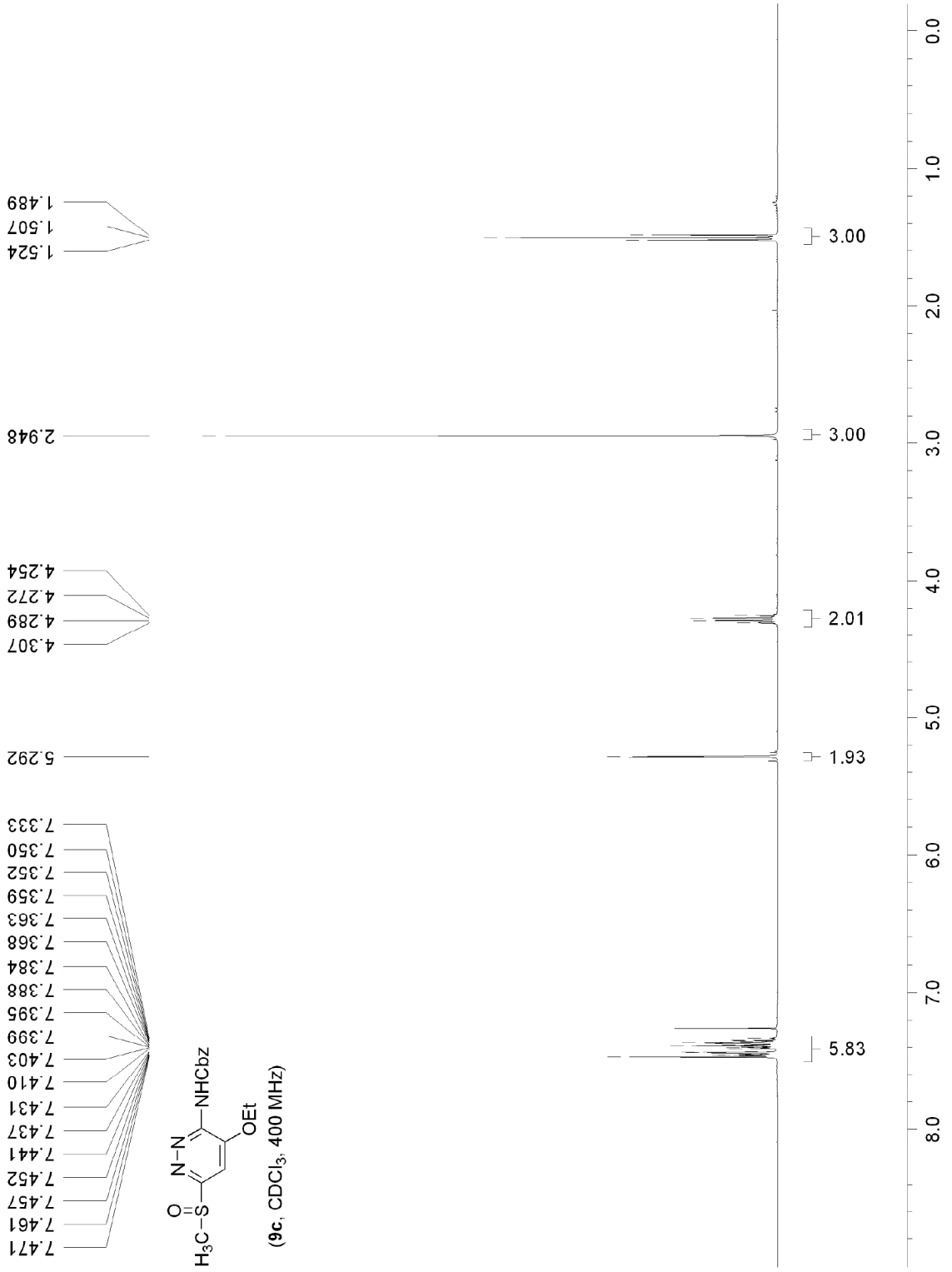


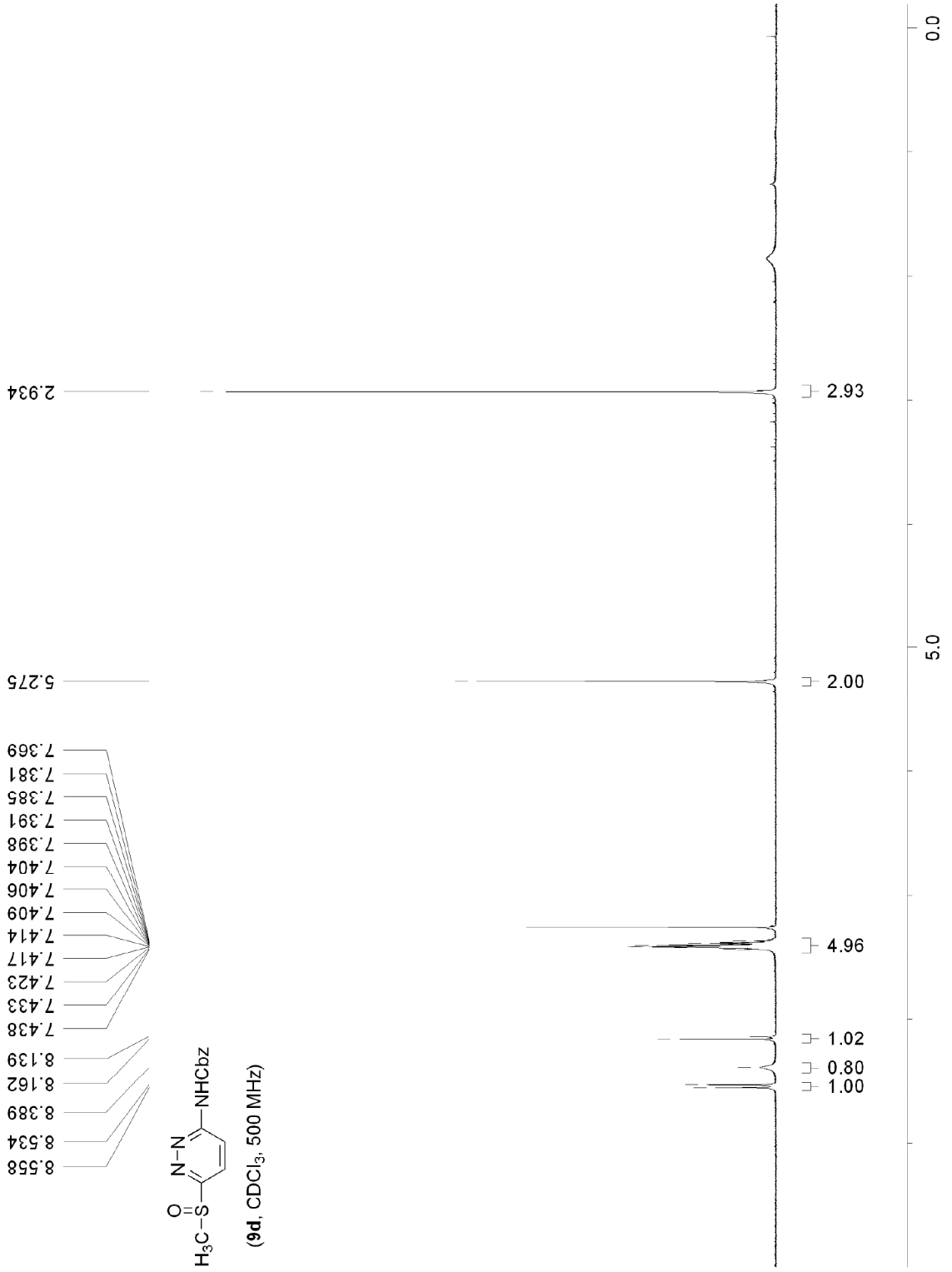
(**7l**, $CDCl_3$, 300 MHz)

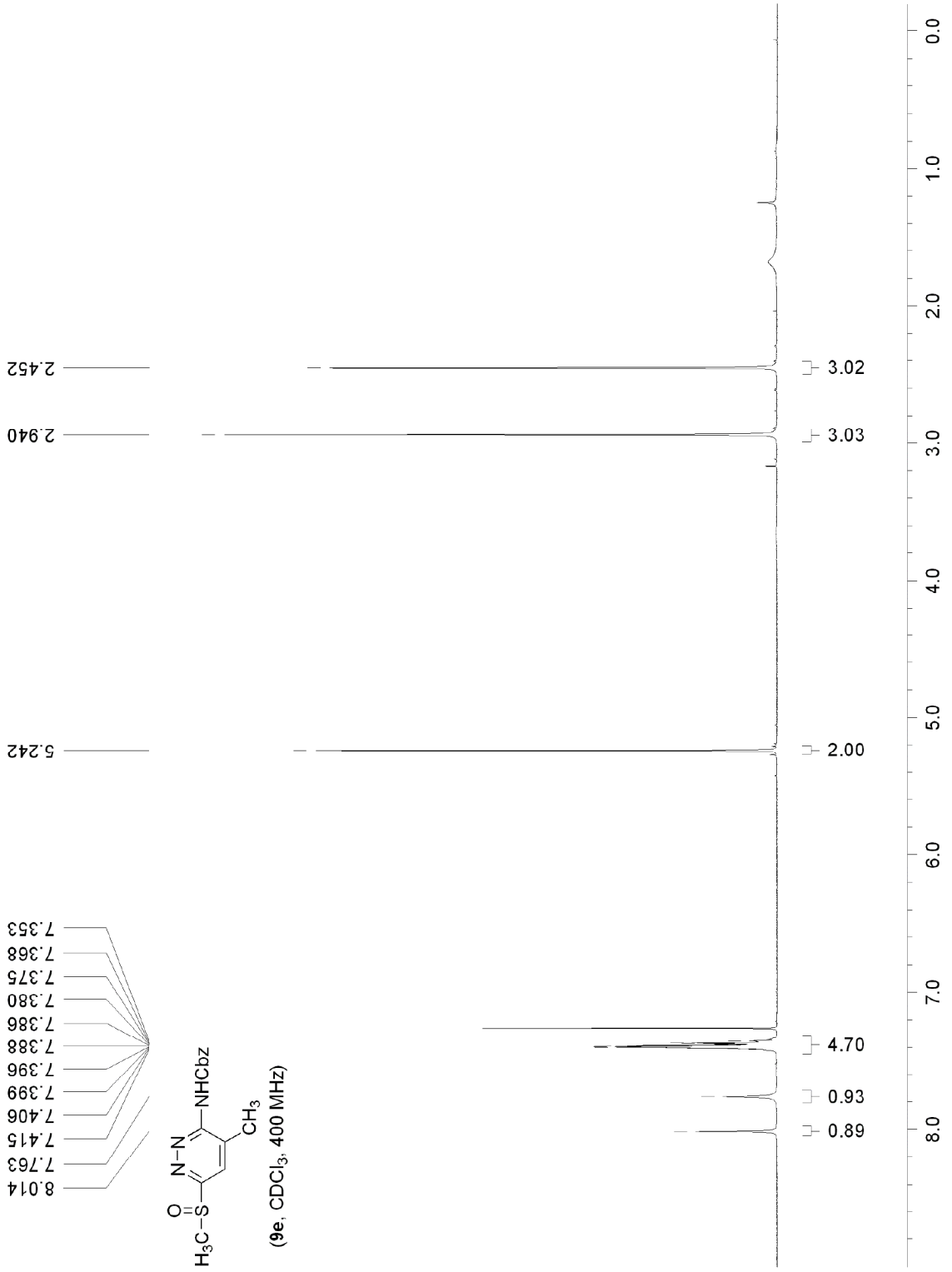


(**9a**, $CDCl_3$, 400 MHz)

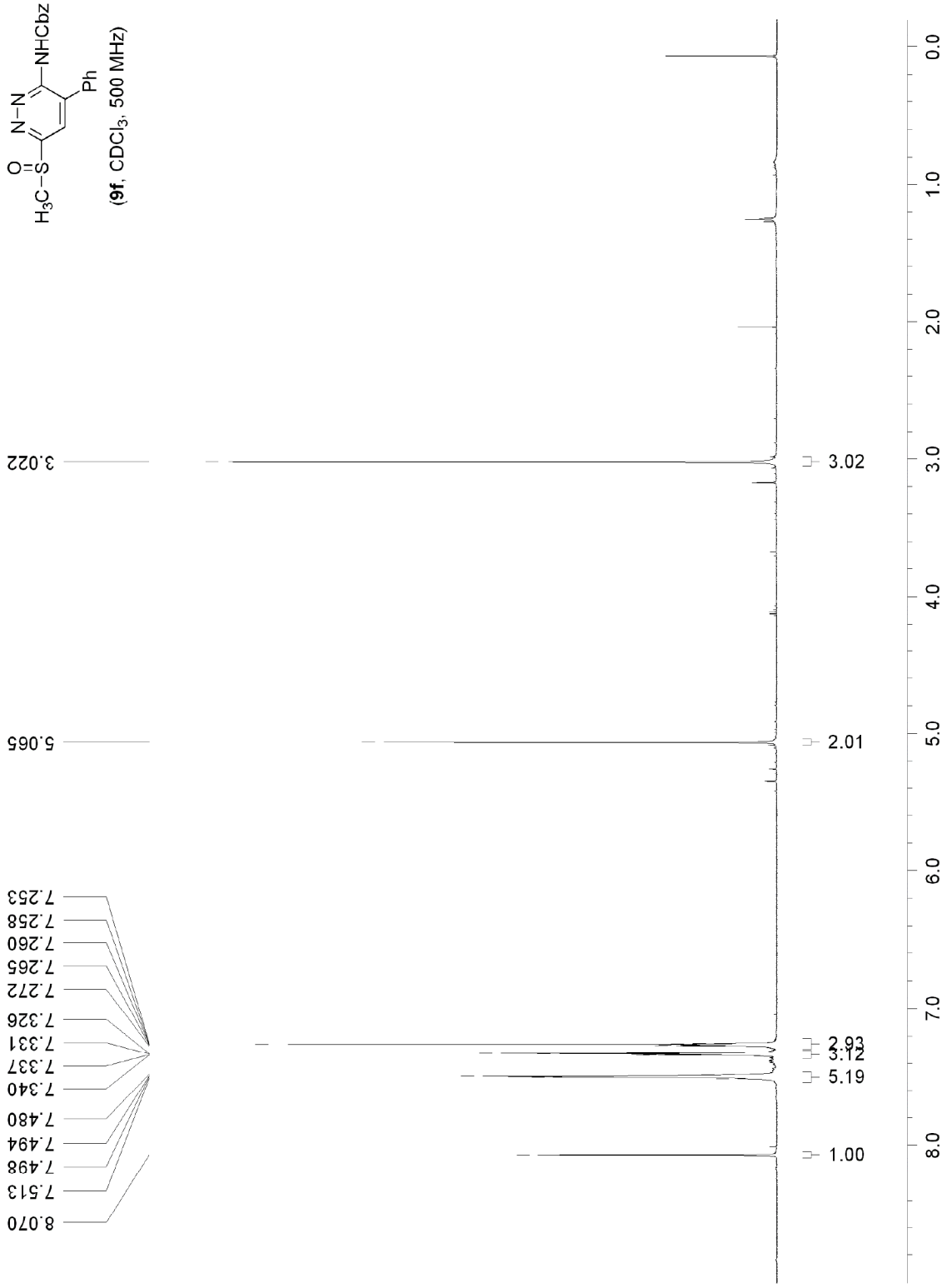

1.131
1.150
1.169
2.675
2.746
2.765
2.784
2.802
3.113
5.240
7.371
7.389
7.406
3.37
4.75
2.67
2.00
4.99
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
NHCbz
N–N
O=S
H3C
(9b, CDCl3, 400 MHz)

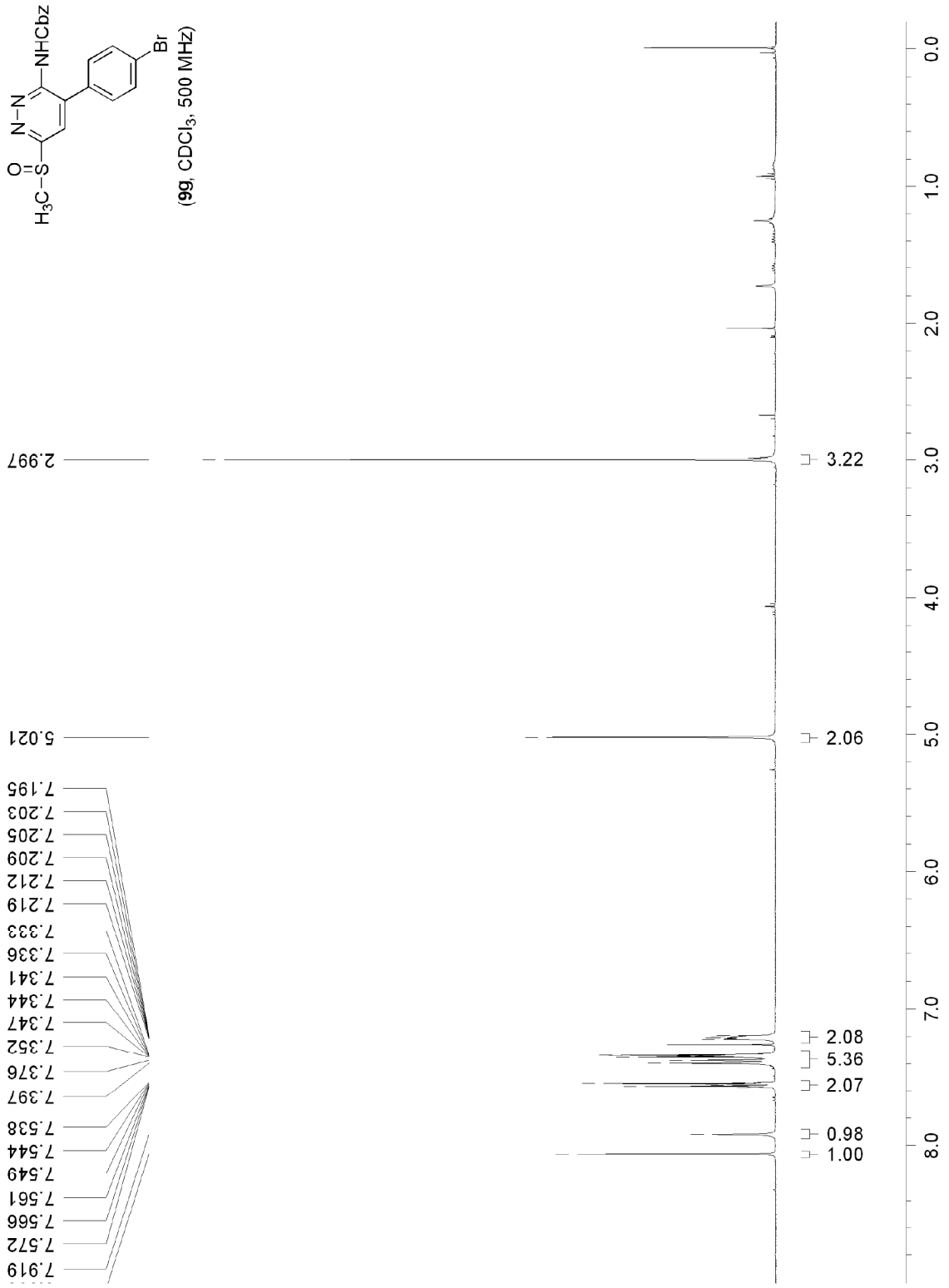

1.489
1.507
1.524
2.948
4.254
4.272
4.289
4.307
5.292
7.333
7.350
7.352
7.359
7.363
7.368
7.384
7.388
7.395
7.399
7.403
7.410
7.431
7.437
7.441
7.452
7.457
7.461
7.471
3.00
3.00
2.01
1.93
5.83
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
NHCbz
OEt
N–N
O=S
H3C
(9c, CDCl3, 400 MHz)

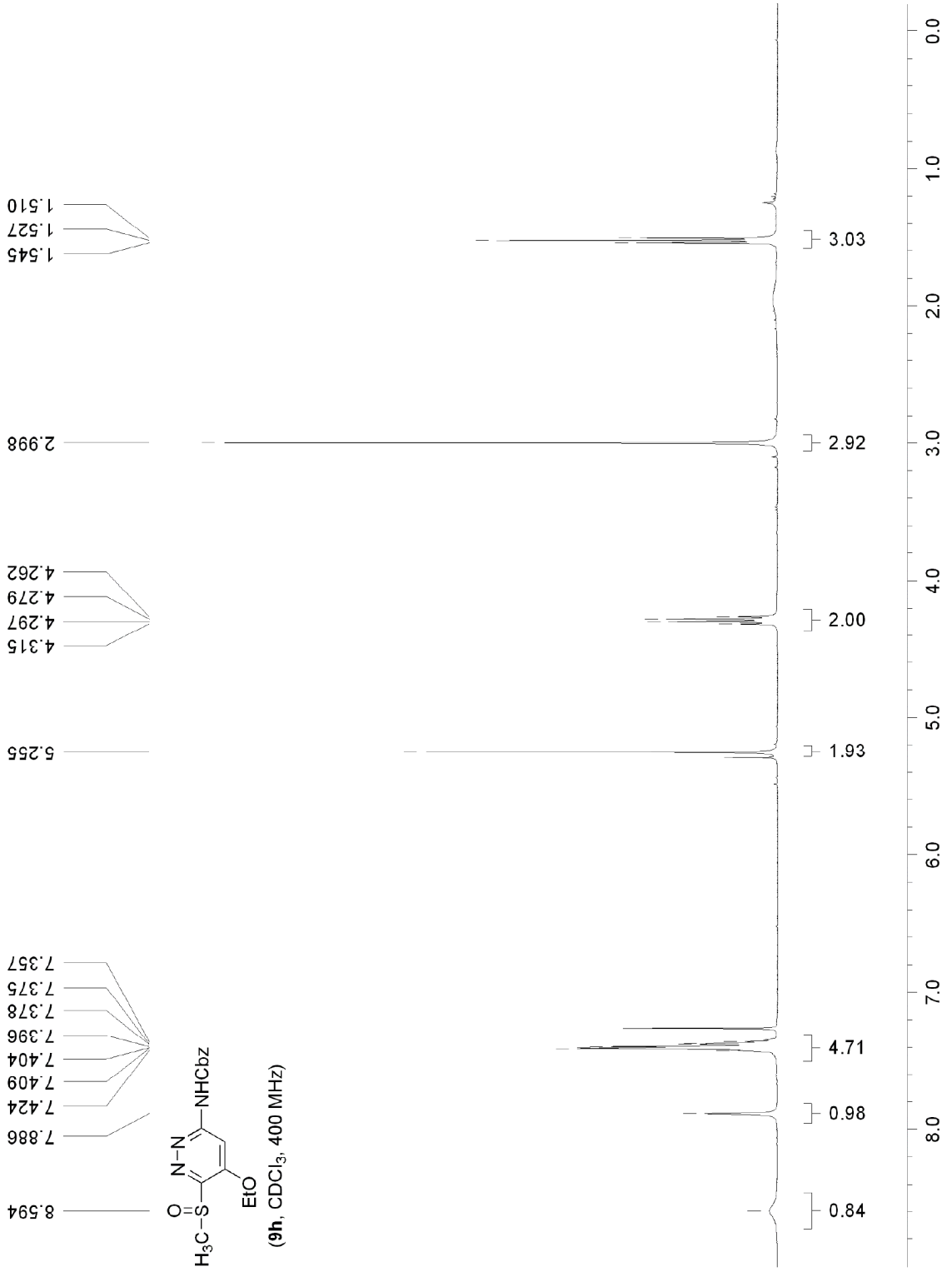

2.934
5.275
7.369
7.381
7.385
7.391
7.398
7.404
7.406
7.409
7.414
7.417
7.423
7.433
7.438
8.139
8.162
8.389
8.534
8.558
NHCbz
N–N
O=S
H3C
(9d, CDCl3, 500 MHz)
2.93
2.00
4.96
1.02
0.80
1.00
0.0
5.0

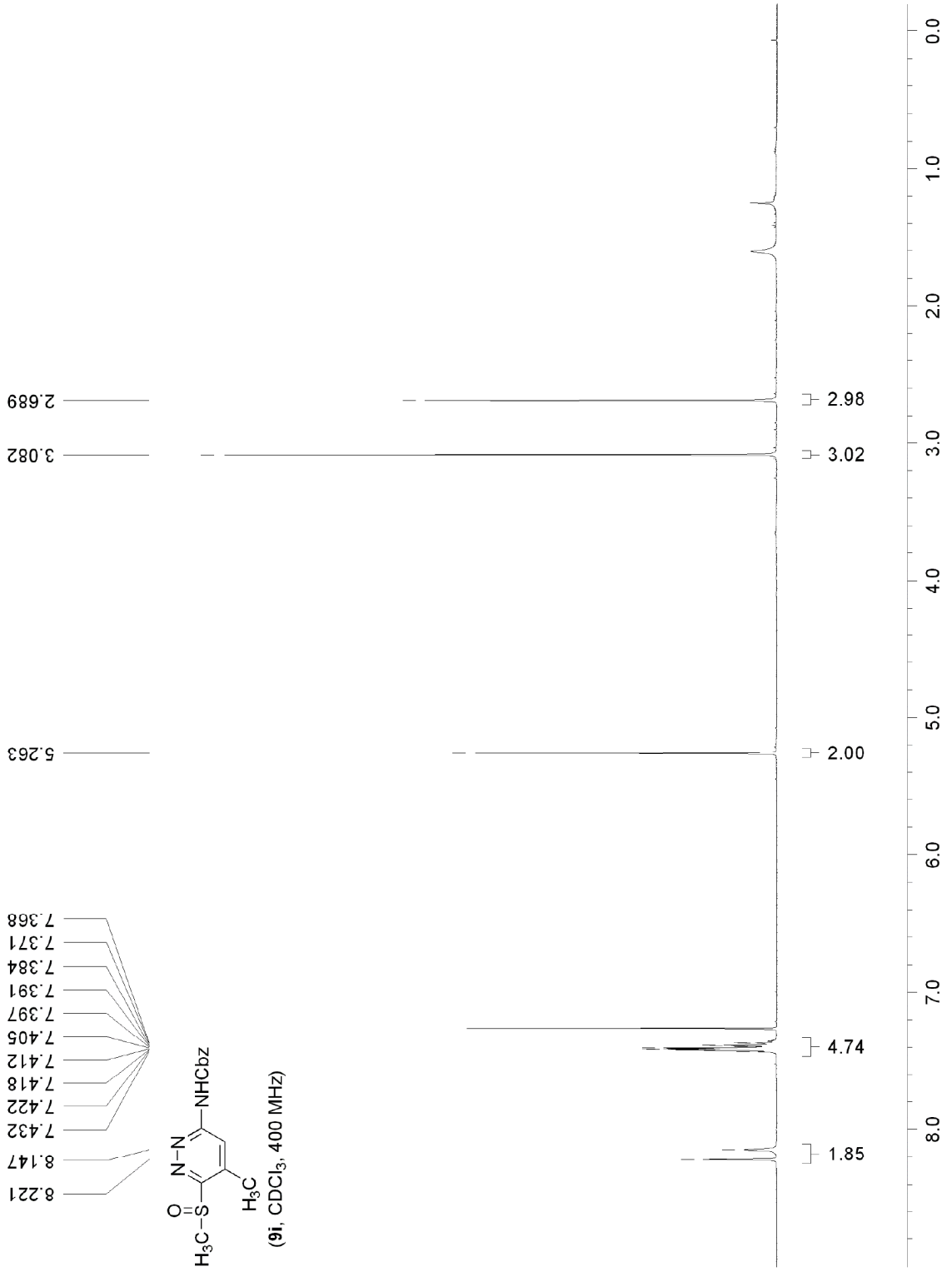


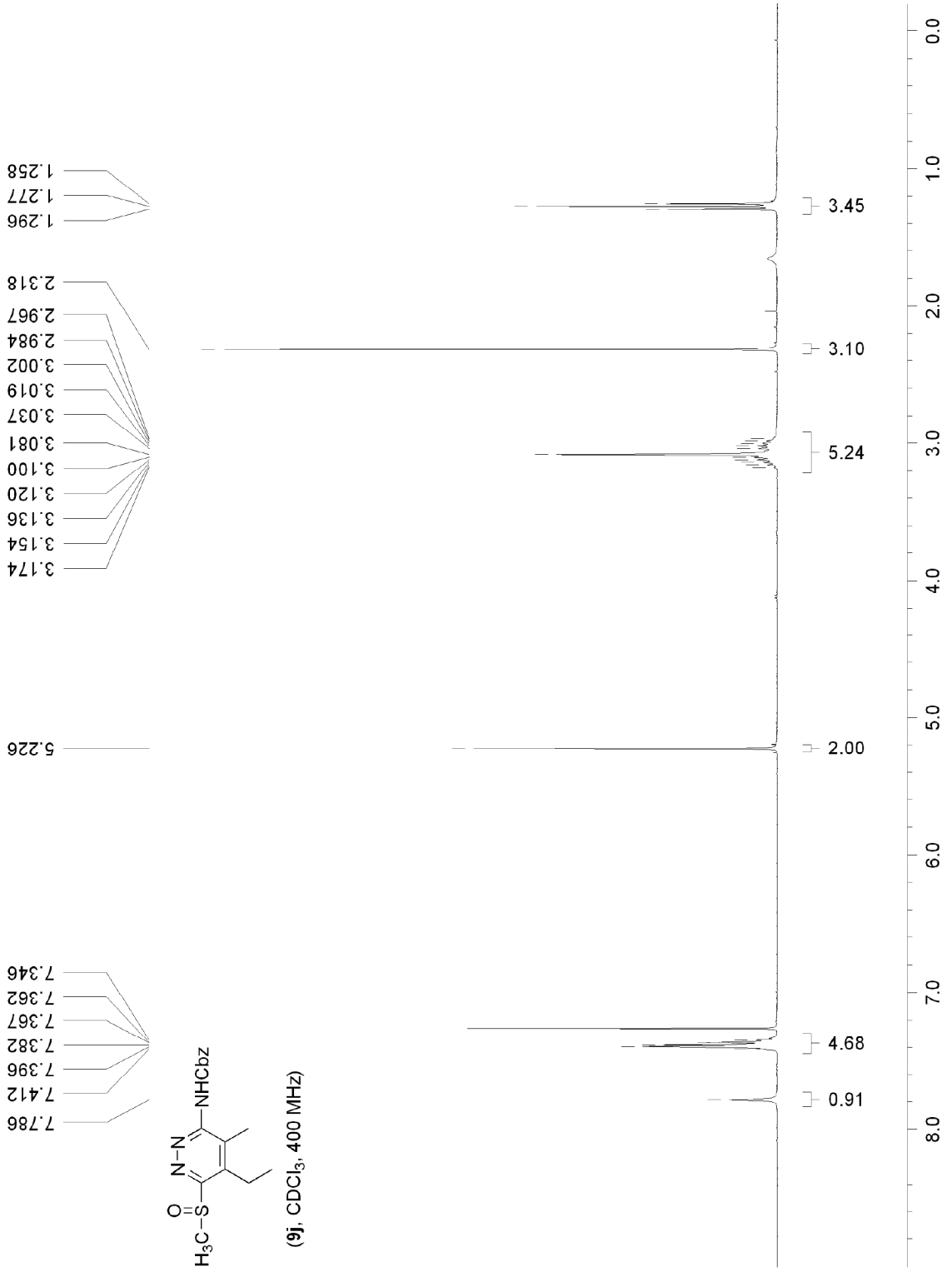
(**9e**, $CDCl_3$, 400 MHz)

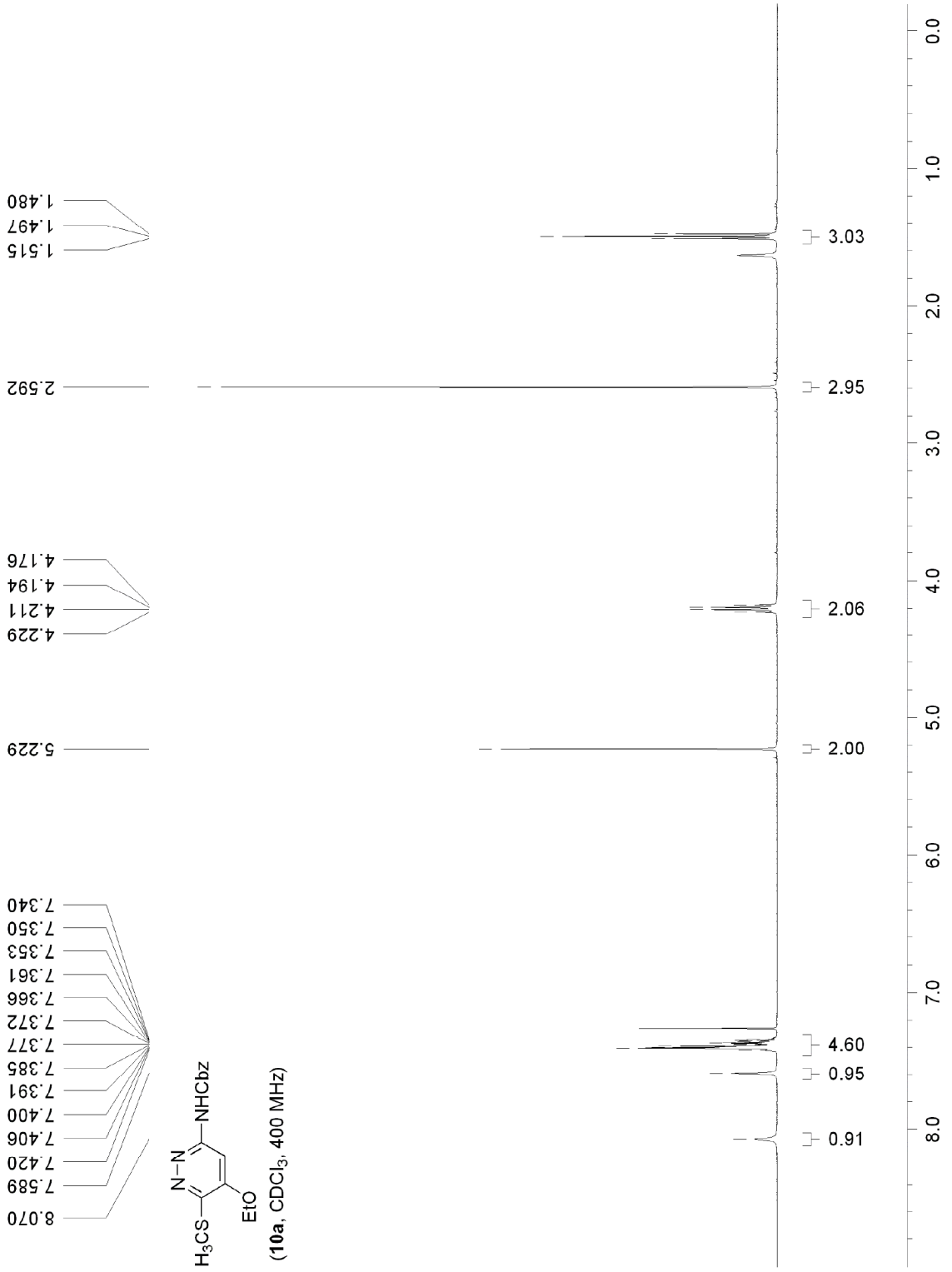

NHCbz
Ph
N–N
O
S
H3C–S
(9f, CDCl3, 500 MHz)
3.022
5.065
7.253
7.258
7.260
7.265
7.272
7.326
7.331
7.337
7.340
7.480
7.494
7.498
7.513
8.070
3.02
2.01
2.93
3.12
5.19
1.00
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

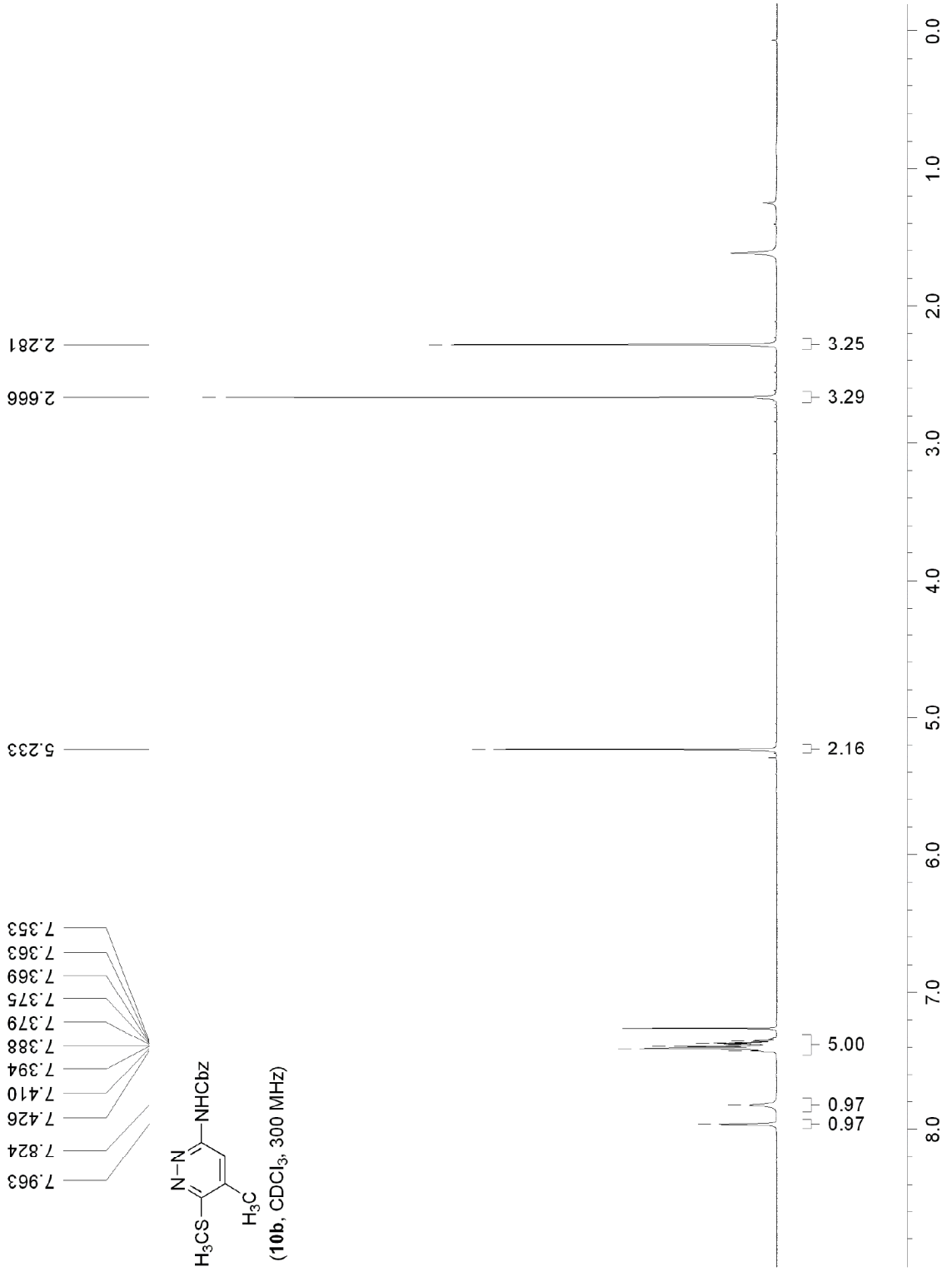

NHCbz
Br
N–N
O
H3C–S
(99, CDCl3, 500 MHz)
2.997
5.021
7.195
7.203
7.205
7.209
7.212
7.219
7.333
7.336
7.341
7.344
7.347
7.352
7.376
7.397
7.538
7.544
7.549
7.561
7.566
7.572
7.919
3.22
2.06
2.08
5.36
2.07
0.98
1.00
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

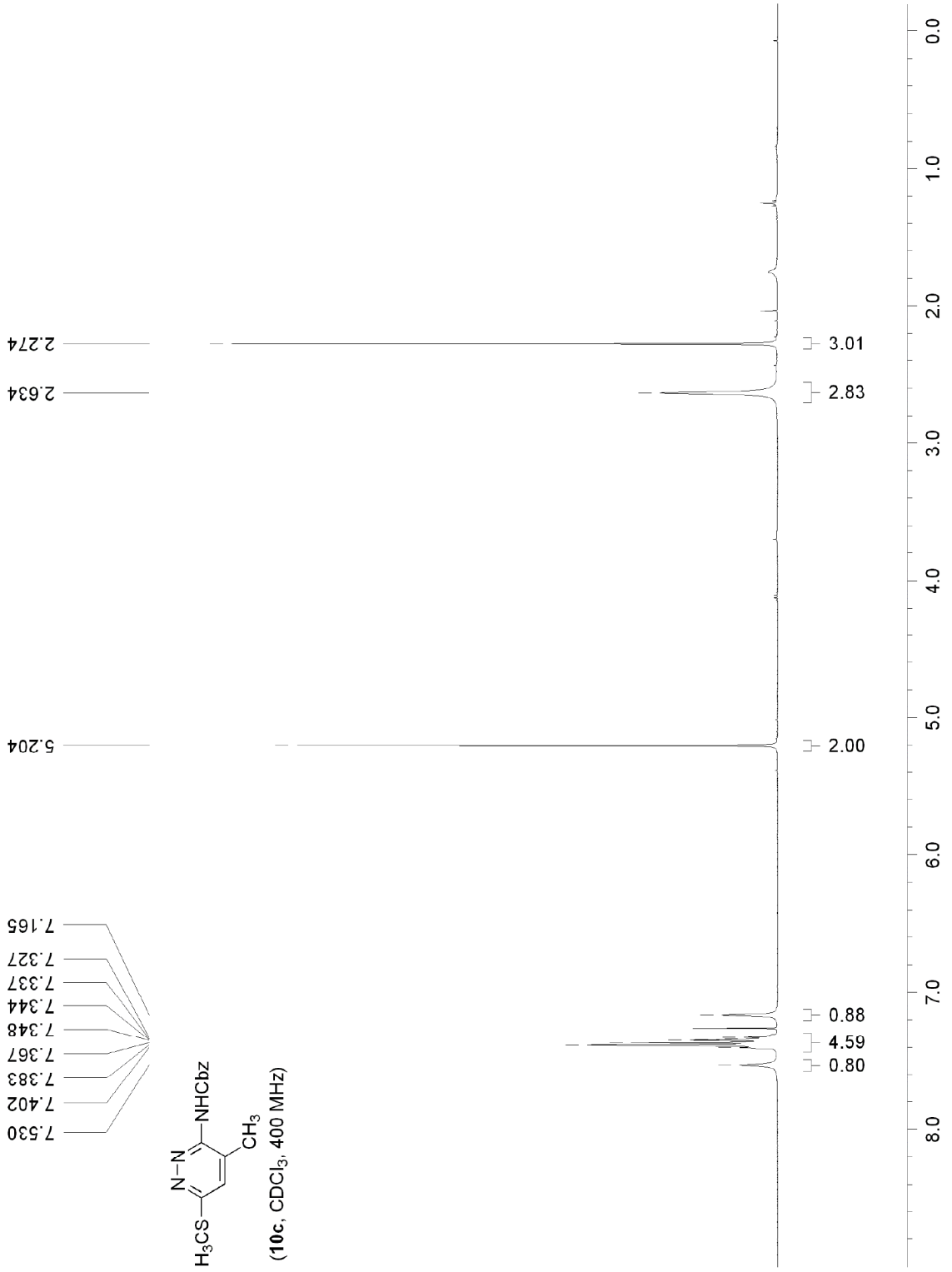

1.510
1.527
1.545
2.998
4.262
4.279
4.297
4.315
5.255
7.357
7.375
7.378
7.396
7.404
7.409
7.424
7.886
8.594
3.03
2.92
2.00
1.93
4.71
0.98
0.84
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
NHCbz
EtO
(9h, CDCl3, 400 MHz)

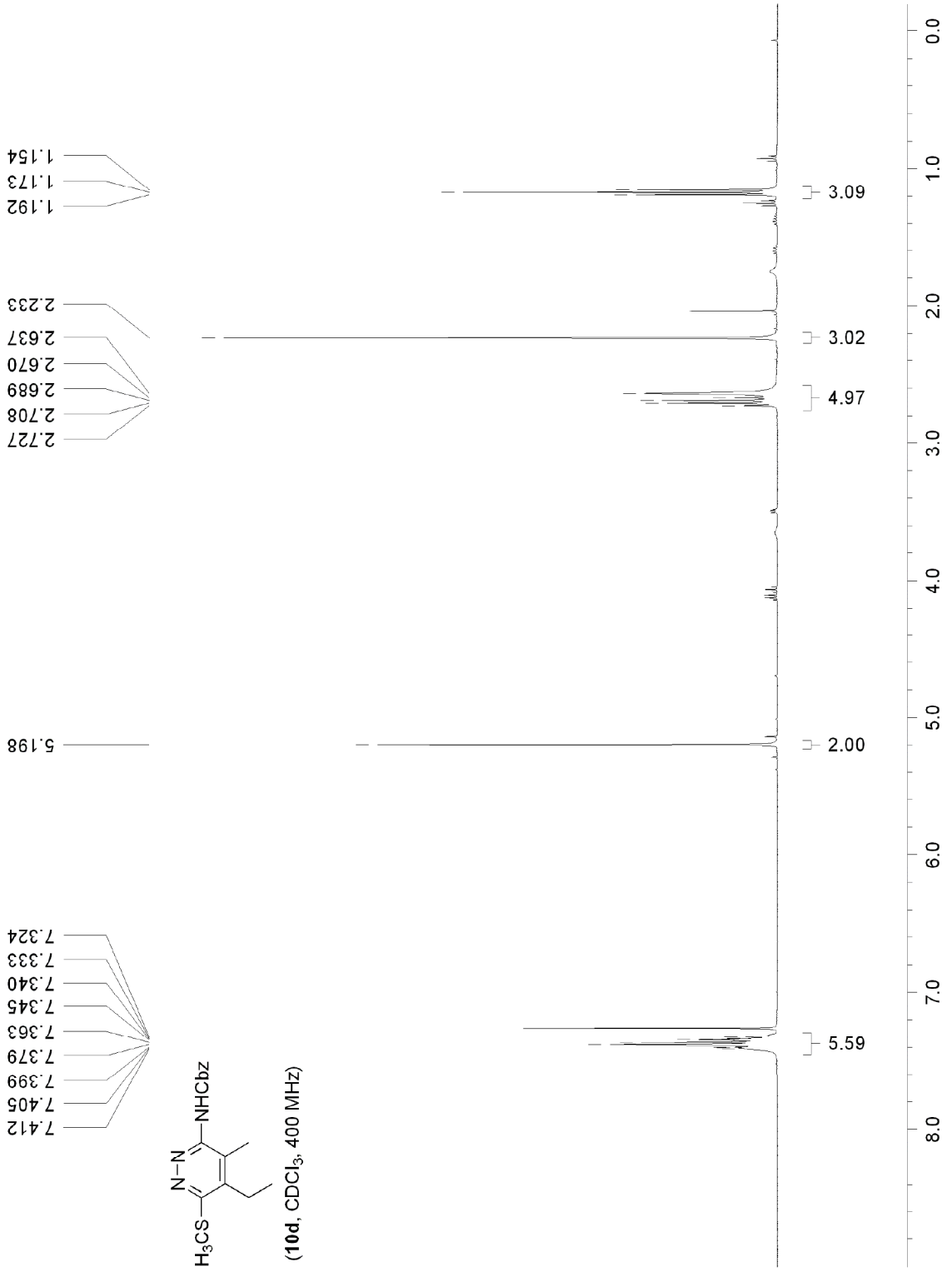

2.689
3.082
5.263
7.368
7.371
7.384
7.391
7.397
7.405
7.412
7.418
7.422
7.432
8.147
8.221
2.98
3.02
2.00
4.74
1.85
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
NHCbz
N–N
O=S
H3C
H3C
(9i, CDCl3, 400 MHz)


1.258
1.277
1.296
2.318
2.967
2.984
3.002
3.019
3.037
3.081
3.100
3.120
3.136
3.154
3.174
5.226
7.346
7.362
7.367
7.382
7.396
7.412
7.786
3.45
3.10
5.24
2.00
4.68
0.91
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
NHCbz
N–N
O=S
H3C
(9j, CDCl3, 400 MHz)


1.480
1.497
1.515
2.592
4.176
4.194
4.211
4.229
5.229
7.340
7.350
7.353
7.361
7.366
7.372
7.377
7.385
7.391
7.400
7.406
7.420
7.589
8.070
3.03
2.95
2.06
2.00
4.60
0.95
0.91
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
NHCbz
N–N
H3CS
EtO
(10a, CDCl3, 400 MHz)


7.963
7.824
7.426
7.410
7.394
7.388
7.379
7.375
7.369
7.363
7.353
5.233
2.666
2.281
3.25
3.29
2.16
5.00
0.97
0.97
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
NHCbz
N–N
H3CS
H3C
(10b, CDCl3, 300 MHz)


2.274
2.634
5.204
7.165
7.327
7.337
7.344
7.348
7.367
7.383
7.402
7.530
3.01
2.83
2.00
0.88
4.59
0.80
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
NHCbz
CH3
N–N
H3CS
(10c, CDCl3, 400 MHz)


1.154
1.173
1.192
2.233
2.637
2.670
2.689
2.708
2.727
5.198
7.324
7.333
7.340
7.345
7.363
7.379
7.399
7.405
7.412
3.09
3.02
4.97
2.00
5.59
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
NHCbz
N–N
H3CS
(10d, CDCl3, 400 MHz)