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Supporting Information

Efficient Palladium-catalyzed Asymmetric Allylic Alkylation of Ketones and Aldehydes

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Contents

1. General Methods.

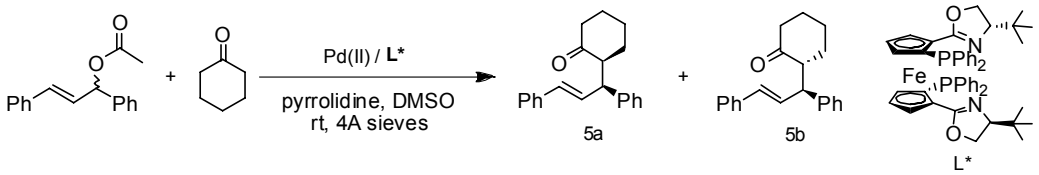
All reactions were performed under a nitrogen atmosphere, and the workup was carried out in air. The reaction solvents were distilled prior to use (Tetrahydrofuran was distilled from sodium-benzophenone ketyl. Dichloromethane, *N*,*N*-dimethylformamide and toluene were distilled from CaH_2). The commercially available reagents were used without further purification. The substrate of asymmetric allylic alkylation was prepared according to literature procedure.[1] TLC was run on 2 cm × 5 cm silica plate. Column chromatography was run on silica gel (100-200 mesh). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian MERCURY plus-400 spectrometer. The ee values were determined by HPLC using Daicel Chiralcel AD-H, OD-H, OJ-H column.

2. Synthesis and Characterization Data.

General procedure for palladium-catalyzed asymmetric allylic alkylation.

A mixture of ligand (for **1** and **2** 7.5 μmol; for **3** and **4** 15 μmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.3 mg, 6.3 μmol) in dry DMSO (1 mL) was stirred at room temperature under N_2 atmosphere for 1 h and 1,3-diphenyl-2-propenyl acetate (126 mg, 0.500 mmol) was added for another 10 min followed by the addition of pyrrolidine (0.50 mmol) and ketone or aldehyde (1.50 mmol). The reaction was monitored by TLC for the disappearance of 1,3-diphenyl-2-propenyl acetate. The reaction mixture was quenched by iced saturated NH_4Cl solution (10 mL) for 2 h and the aqueous layer was extracted with ethyl ether (5 mL×3). The combined organic extracts were washed with water, brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The ratio of *anti* and *syn*-configuration was determined by ^{1}H NMR of the mixture and the residue was purified on silica gel column chromatography with petrol ether-ethyl acetate (10:1) to afford pure product of *anti*-configuration and *syn*-configuration, respectively. For the determination of ee value by HPLC, a mixture of the products of *anti* and *syn*-configuration was used.

Table 1. Allylic Alkylation of 1,3-Diphenyl-2-Propenyl Acetate of Cyclohexane[a]



Entry	Time / h	Yield / %[b]	Anti / Syn[c,d]	Ee / %[e]
1	16	95	63 / 37	98 / 97

[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/pyrrolidine/ketone =5.0/6.0/200/200/600; Reactions were conducted under nitrogen; The catalysts were prepared by treating $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with ligands in a suitable solvent at 20 °C for 1 h before use. [b] Isolated yield. [c] Determined by ^{1}H NMR. [d] The absolute configuration of *syn* / *anti*-products was determined according to ref. 2. [e] Determined by the HPLC using chiral AD-H column.

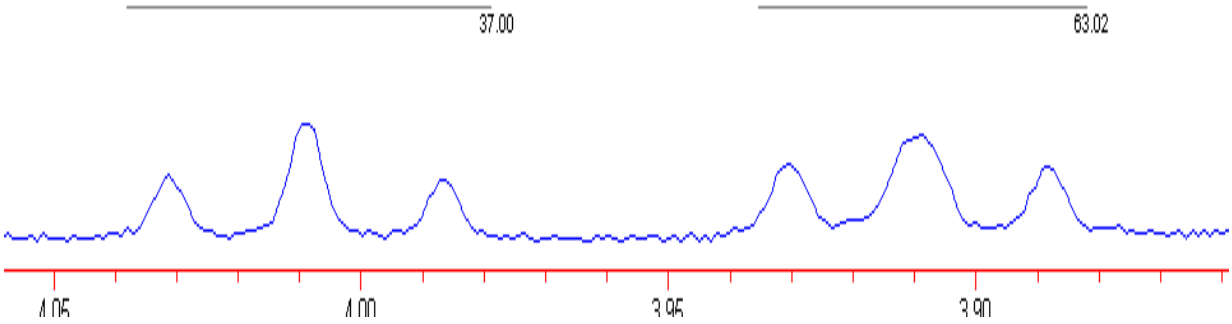
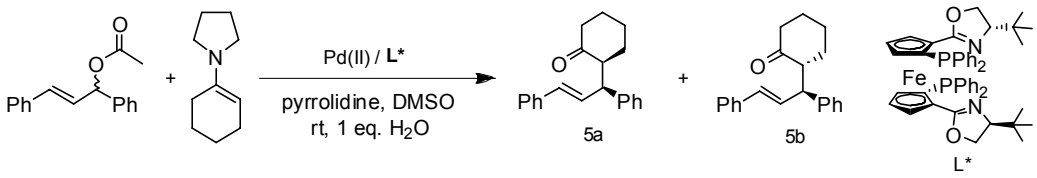


Table 2. Allylic Alkylation of 1,3-Diphenyl-2-Propenyl Acetate of Enamine[a]



Entry	Time / h	Yield / %[b]	Anti / Syn[c,d]	Ee / %[e]
1	12	80	75 / 25	98 / 97

[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/enamine=2.5/6.0/ 200/600; Reactions were conducted under nitrogen; The catalysts were prepared by treating $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with ligands in a suitable solvent at 20 °C for 1 h before use. [b] Isolated yield. [c] Determined by ^1H NMR. [d] The absolute configuration of *syn* / *anti*-products was determined according to ref. 2. [e] Determined by the HPLC using chiral AD-H column.

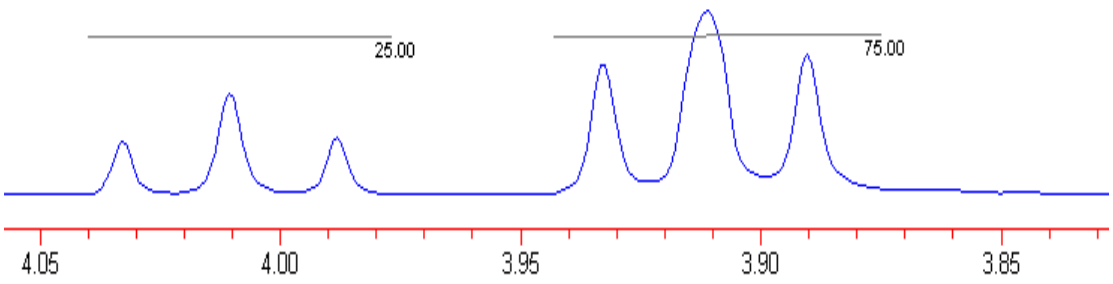
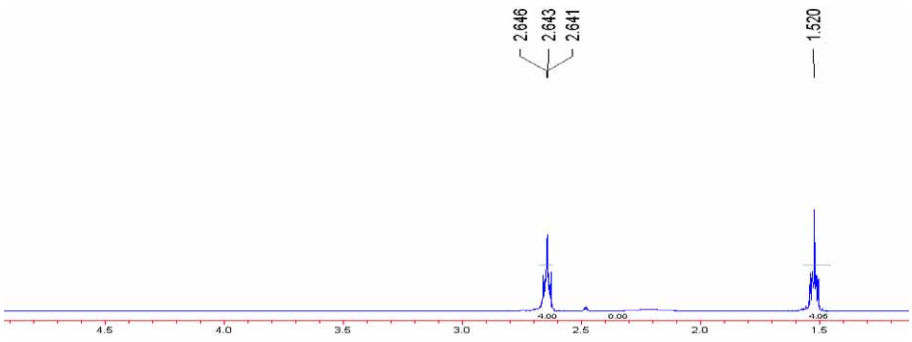
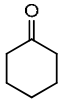
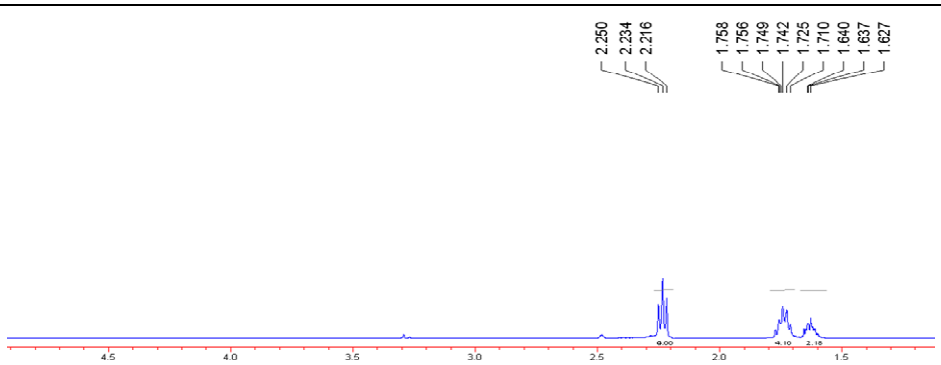
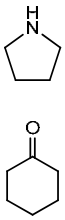
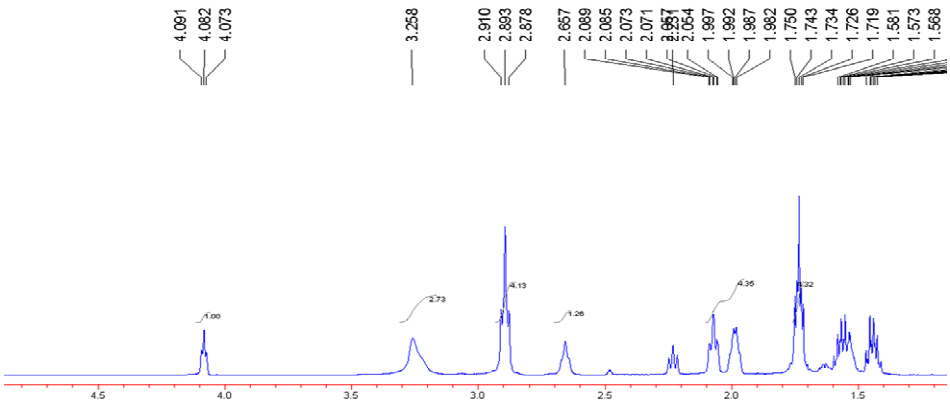
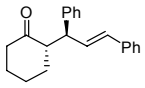


Table 3 ^{1}H NMR Spectra of Pyrrolidine, Cyclohexanone and Enamine Generated in situ in d_6-DMSO

	^{1}H NMR spectra
d_6-DMSO 	
d_6-DMSO 	
d_6-DMSO  (in situ)[a]	

[a] Pyrrolidine (0.020 ml, 1 equiv.) and cyclohexanone (0.026 ml, 1equiv.) were added to NMR tube in d^6-DMSO, a set of new peaks appeared after 10 minutes, which attributed to the formation of enamine. ^{1}H NMR (d^6-DMSO, 400 Hz): δ 1.70-1.78 (m, 4H), 1.94-2.11 (m, 4H), 2.61-2.69 (m, 1H), 2.84-2.95 (m, 4H), 3.17-3.35 (m, 3H), 4.05-4.11 (m, 1H).

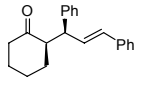
(*S*)-2-((*S,E*)-1,3-diphenylallyl)cyclohexanone (**5a**)



5a

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 1.33-1.41 (m, 1H), 1.56-1.63 (m, 1H), 1.70-1.81 (m, 3H), 1.90-1.95 (m, 1H), 2.31-2.46 (m, 2H), 2.83-2.89 (m, 1H), 3.87 (t, *J*=8.4 Hz, 1H), 6.32 (d, *J*=16 Hz, 1H), 6.44 (dd, *J*=8.0, 16 Hz, 1H), 7.12-7.32 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 24.2, 28.8, 32.4, 42.5, 48.6, 56.1, 126.5, 126.8, 127.4, 128.6, 128.7, 128.9, 130.7, 132.2, 137.6, 140.1, 212.7.

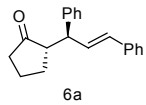
(*R*)-2-((*S,E*)-1,3-diphenylallyl)cyclohexanone (**5b**)



5b

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 1.57-1.77 (m, 3H), 1.86-2.10 (m, 2H), 2.15-2.37 (m, 3H), 2.85-2.91 (m, 1H), 3.97 (t, *J*=8.4 Hz, 1H), 6.25 (dd, *J*=9.6, 15.6 Hz, 1H), 6.45 (d, *J*=15.6 Hz, 1H), 7.14-7.33 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 24.8, 28.6, 32.1, 42.6, 48.7, 55.9, 126.5, 126.6, 127.5, 128.1, 128.7, 128.8, 131.3, 131.6, 137.5, 143.5, 211.8.

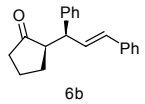
(*S*)-2-((*R,E*)-1,3-diphenylallyl)cyclopentanone (**6a**)



6a

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 1.70-1.78 (m, 1H), 1.93-2.03 (m, 3H), 2.16-2.23 (m, 1H), 2.27-2.34 (m, 1H), 2.55-2.61 (m, 1H), 4.09-4.12 (m, 1H), 6.40 (d, *J*=4.4 Hz, 1H), 6.41 (s, 1H), 7.17-7.35 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 20.9, 26.1, 39.1, 48.0, 55.1, 126.5, 126.7, 127.6, 128.1, 128.7, 128.8, 129.3, 132.6, 137.4, 143.0, 219.3.

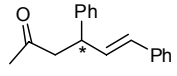
(*R*)-2-((*R,E*)-1,3-diphenylallyl)cyclopentanone (**6b**)



6b

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 1.70-1.86 (m, 1H), 1.94-2.11 (m, 3H), 2.18-2.28 (m, 1H), 2.29-2.38 (m, 1H), 2.58-2.64 (m, 1H), 4.05-4.10 (m, 1H), 6.44 (d, *J*=3.2 Hz, 1H), 6.45 (s, 1H), 7.20-7.41 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 21.0, 26.1, 39.1, 48.0, 55.1, 126.4, 126.6, 128.7, 129.2, 129.3, 132.5, 132.6, 132.7, 137.4, 143.1, 219.3.

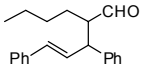
(*E*)-4,6-diphenylhex-5-en-2-one (**7**)



7

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 2.11 (s, 3H), 2.93-2.97 (m, 2H),4.05-4.12 (dd, *J*=6.8, 7.2 Hz, 1H), 6.28-6.41 (m, 2H), 7.17-7.36 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 21.0, 26.1, 39.1, 48.0, 55.1, 126.4, 126.6, 128.7, 129.2, 129.3, 132.5, 132.6, 132.7, 137.4, 143.1, 219.3.

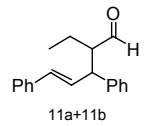
(*E*)-2-(1,3-diphenylallyl)hexanal (**10a** and **10b**)



10a+10b

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 0.77-0.81 (t, *J*=9.6 Hz, 3H), 0.83-0.88 (t, *J*=9.6 Hz, 3H), 1.11-1.38 (m, 8H), 1.47-1.72 (m, 4H), 2.72-2.82 (m, 2H), 3.67-3.77 (m, 2H), 6.25-6.52 (m, 4H), 7.16-7.38 (m, 20H), 9.47-9.50 (d, *J*=4.0 Hz, 1H), 9.62-9.66 (d, *J*=4.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 14.0, 14.1, 22.8, 22.9, 27.6, 27.7, 29.3, 29.5, 50.2, 50.4, 56.6, 56.8, 126.5, 126.6, 127.1, 127.2, 127.7, 128.1, 128.2, 128.7, 128.8, 129.0, 129.1, 130.4, 130.8, 131.6, 131.9, 137.0, 137.1, 141.5, 141.6, 204.6, 204.9. HRMS (EI^+) *m/z* calculated for $C_{21}H_{24}O$ $[M+1]^+$: 293.1905; found 293.1911. IR(v/cm^{-1}): 3086, 3063, 3030, 2957, 2929, 2871, 2860, 1724, 1693, 1638, 1603, 1566, 1493, 1455, 1416, 1379, 966, 749, 699.

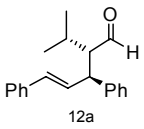
(*E*)-2-ethyl-3,5-diphenylpent-4-enal (**11a** and **11b**)



11a+11b

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 0.82-0.87 (t, *J*=7.2 Hz, 3H), 0.91-0.96 (t, *J*=7.2 Hz, 3H), 1.39-1.79 (m, 4H), 2.69-2.77 (m, 2H), 3.71-3.77 (m, 2H), 6.27-6.51 (m, 2H), 7.18-7.40 (m, 20H), 9.49-9.51 (d, *J*=4.4 Hz, 1H), 9.65-9.68 (d, *J*=4.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 11.7, 11.7, 21.1, 21.2, 49.9, 50.2, 126.5, 126.6, 127.1, 127.2, 127.7, 128.1, 128.3, 128.6, 128.7, 128.8, 129.0, 129.1, 129.2, 130.5, 130.8, 131.6, 131.9.

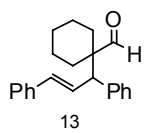
(*S*)-2-((*S,E*)-1,3-diphenylallyl)cyclohexanone (**12a**)



12a

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 0.96-1.02 (t, *J*=7.2 Hz, 6H), 1.75-1.79 (m, 1H), 2.67-2.73 (m, 1H), 3.96-4.01 (t, *J*=7.2 Hz, 1H), 2.31-2.46 (m, 2H), 2.83-2.89 (m, 1H), 3.87 (t, *J*=9.6 Hz, 1H), 6.25-6.31 (dd, *J*=8.4, 8.8 Hz, 1H), 6.42-6.47 (d, *J*=16.0 Hz, 1H), 7.19-7.37 (m, 10H), 9.79-9.81 (d, *J*=5.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 17.6, 21.8, 28.2, 48.0, 61.7, 126.5, 127.1, 127.7, 128.1, 128.7, 129.1, 131.0, 131.6, 137.0, 141.7, 205.9. HRMS (EI^+) *m/z* calculated for $C_{20}H_{22}O$ $[M+1]^+$: 278.1671; found 278.1668. IR(v/cm^{-1}): 3088, 3060, 3027, 2960, 2926, 2871, 2855, 1721, 1659, 1599, 1578, 1494, 1464, 1452, 1389, 1371, 965, 799, 745, 697.

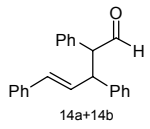
(*E*)-1-(1,3-diphenylallyl)cyclohexanecarbaldehyde (**13**)



13

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 0.09-1.58 (m, 8H), 1.99-2.03 (d, *J*=12.4 Hz, 1H), 2.16-2.19 (d, *J*=12.4 Hz, 1H), 3.46-3.48 (d, *J*=9.6 Hz, 1H), 6.44-6.68 (d, *J*=15.6 Hz, 1H), 6.56-6.62 (dd, *J*=9.6, 15.6 Hz, 1H), 7.19-7.40 (m, 10H), 9.61(s, 1H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 23.1, 23.2, 25.7, 30.5, 30.6, 53.2, 57.9, 126.6, 127.1, 127.7, 128.1, 128.6, 128.8, 129.3, 133.1, 137.3, 139.9, 208.5. HRMS (EI^+) *m/z* calculated for $C_{22}H_{24}O$ $[M+1]^+$: 304.1827; found 304.1833. IR (v/cm^{-1}): 3086, 3060, 3028, 2931, 2855, 1703, 1600, 1582, 1495, 1451, 1415, 965, 770, 745, 701.

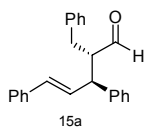
(*E*)-2,3,5-triphenylpent-4-enal (**14a** and **14b**)



14a+14b

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 4.09-4.13 (m, 2H), 4.31-4.37 (m, 2H), 6.12-6.24 (m, 2H), 6.43-6.57 (m, 2H), 7.08-7.45 (m, 30H), 9.66-9.68 (d, *J*=2.8 Hz, 1H), 9.83-9.85 (d, *J*=3.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 49.8, 50.2, 64.1, 64.5, 126.4, 126.6, 126.8, 127.3, 127.5, 127.7, 127.8, 128.1, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 129.0, 129.1, 129.2, 129.3, 129.7, 130.0, 130.3, 130.9, 131.9, 132.1, 134.4, 134.5, 137.1, 137.3, 140.7, 141.6, 199.4, 199.8. HRMS (EI^+) *m/z* calculated for $C_{23}H_{20}O$ $[M+1]^+$: 312.1514; found 312.1512. IR(v/cm^{-1}): 3082, 3060, 3027, 2924, 2852, 2818, 2716, 1723, 1683, 1664, 1599, 1577, 1493, 1452, 1387, 965, 745, 697.

(*2S,3R,E*)-2-benzyl-3,5-diphenylpent-4-enal (**15a**)



15a

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 2.68-2.96 (m, 2H), 3.20-3.28 (m, 1H), 3.76-3.83 (t, *J*=8.0 Hz, 1H), 6.34-6.49 (m, 2H), 7.05-7.43 (m, 15H), 9.73-9.75 (d, *J*=2.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 34.3, 50.0, 58.3, 126.6, 126.7, 127.3, 127.9, 128.3, 128.7, 128.8, 129.1, 129.2, 129.8, 132.4, 136.9, 138.8, 141.4,

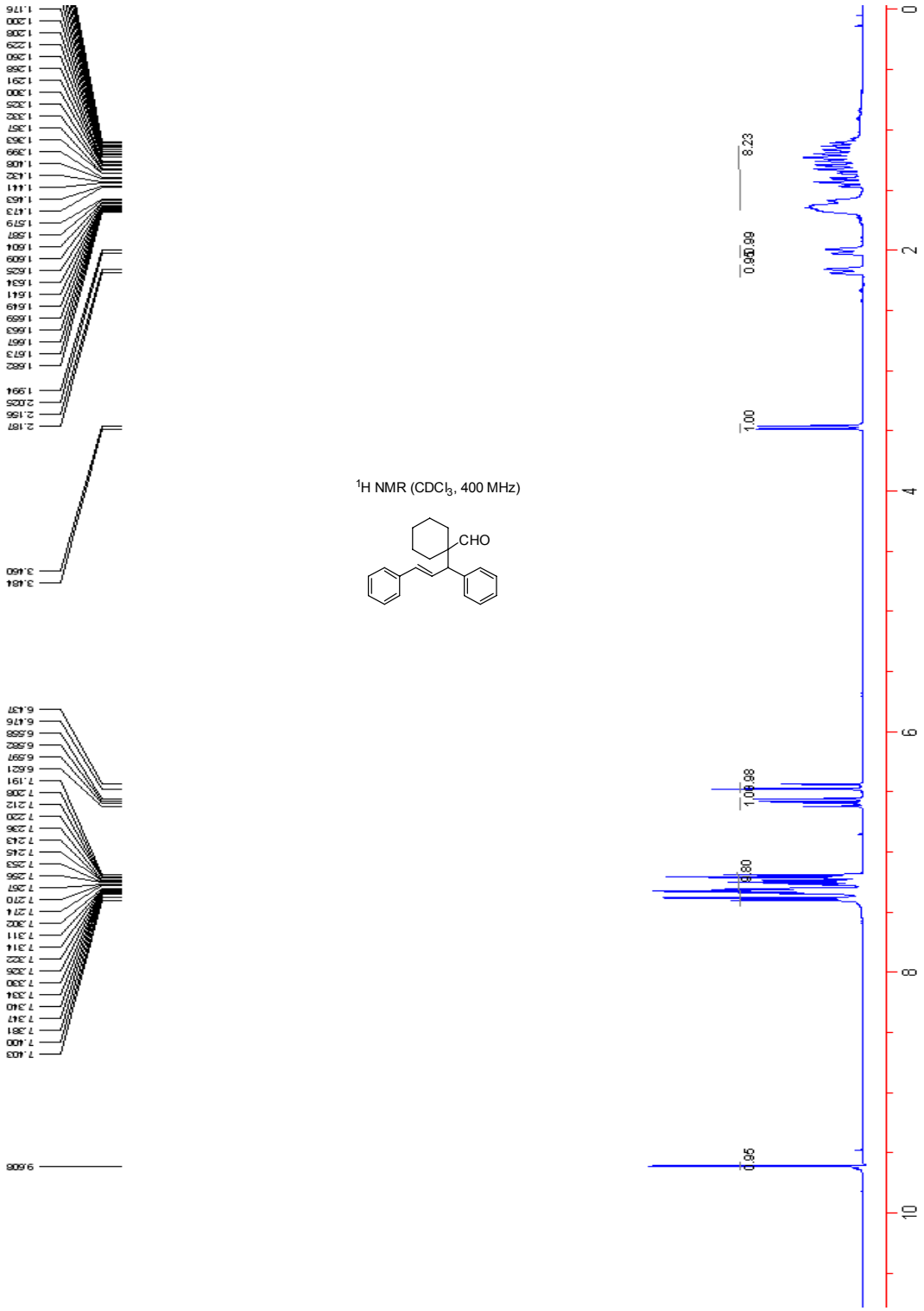
204.4. HRMS (EI^+) *m/z* calculated for $C_{24}H_{22}O$ $[M+1]^+$: 326.1701; found 326.1671. IR(v/cm^{-1}): 3083, 3060, 3027, 2924, 2851, 2724, 1724, 1681, 1600, 1583, 1494, 1453, 1393, 966, 745, 698.

References

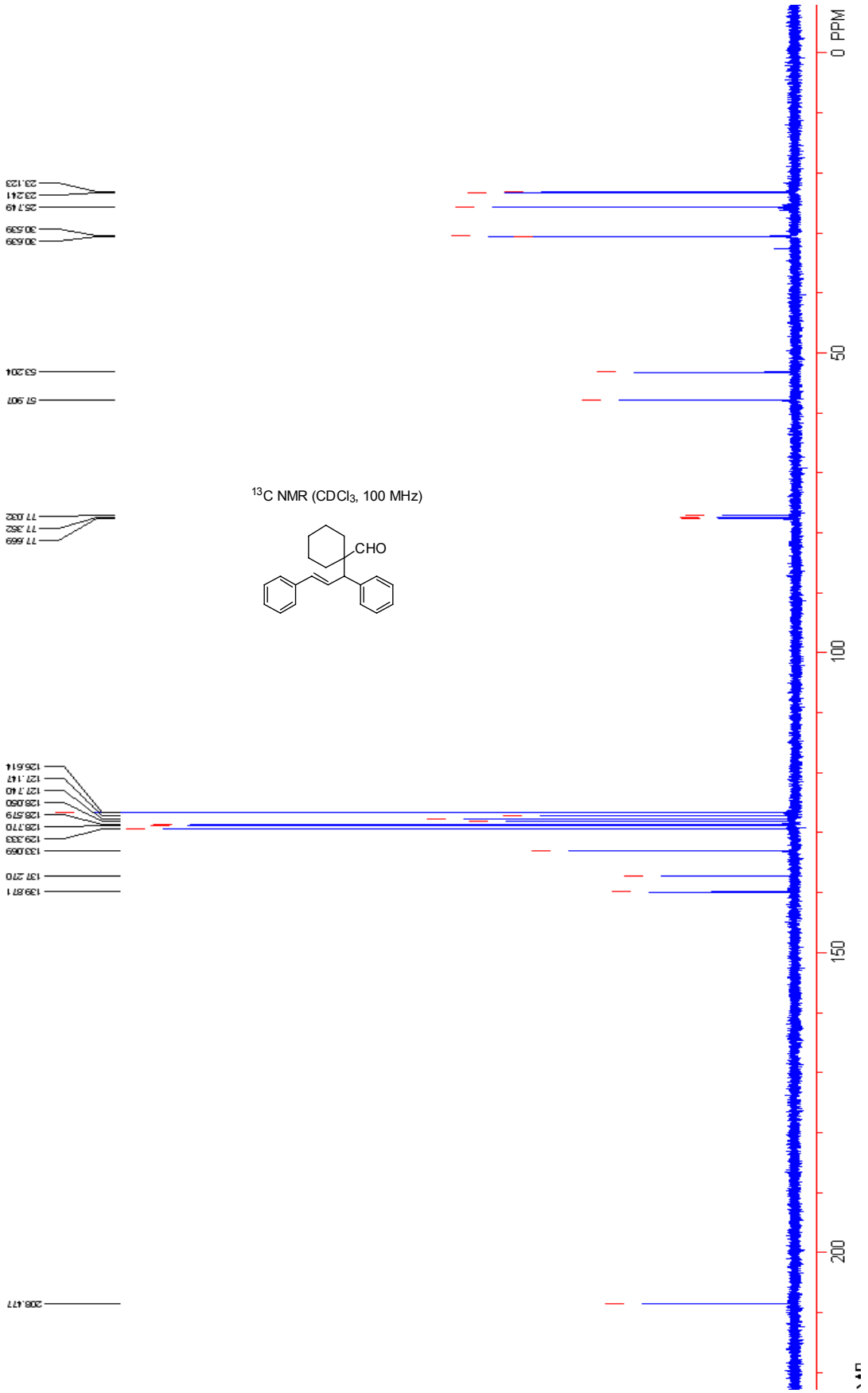
1 Watson, L. D. G.; Styler, S. A.; Yudin, A. K. *J. Am. Chem. Soc*. **2004**, *126*, 5086-5087.

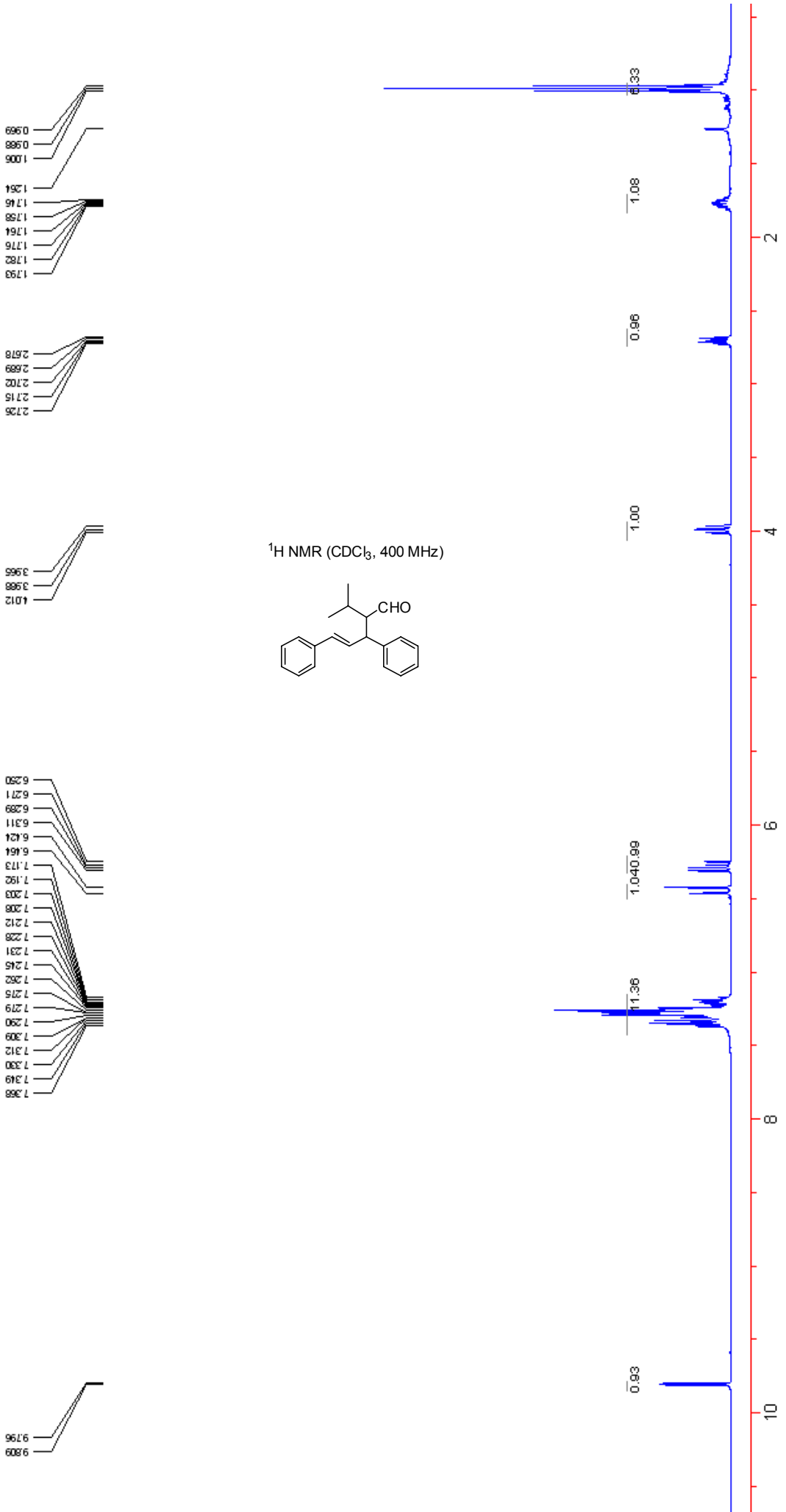
2 Braun, M.; Laicher, F.; Meier, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 3494-3497.

3. Copies of NMR Spectra

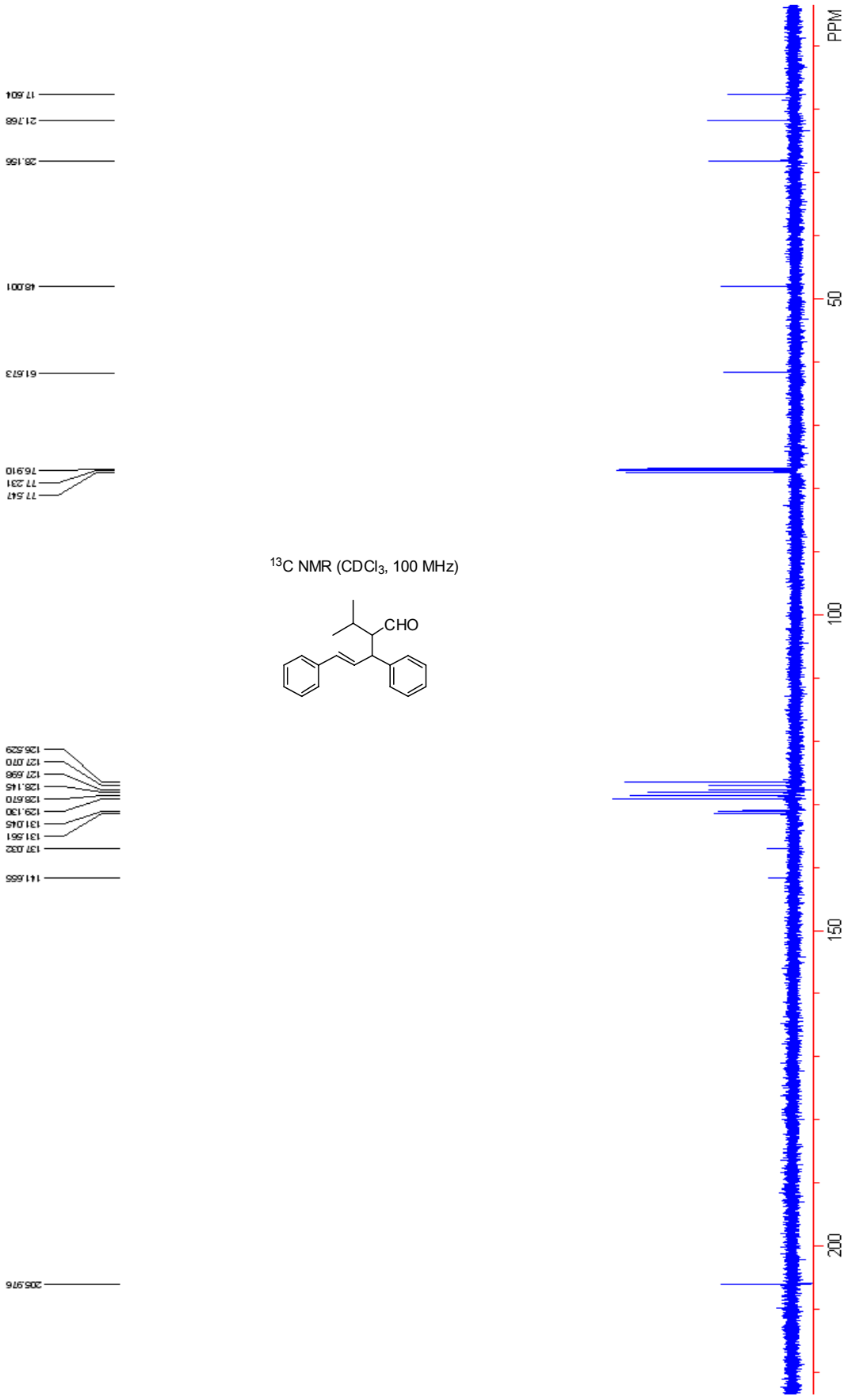


^{1}H NMR ($CDCl_3$, 400 MHz)

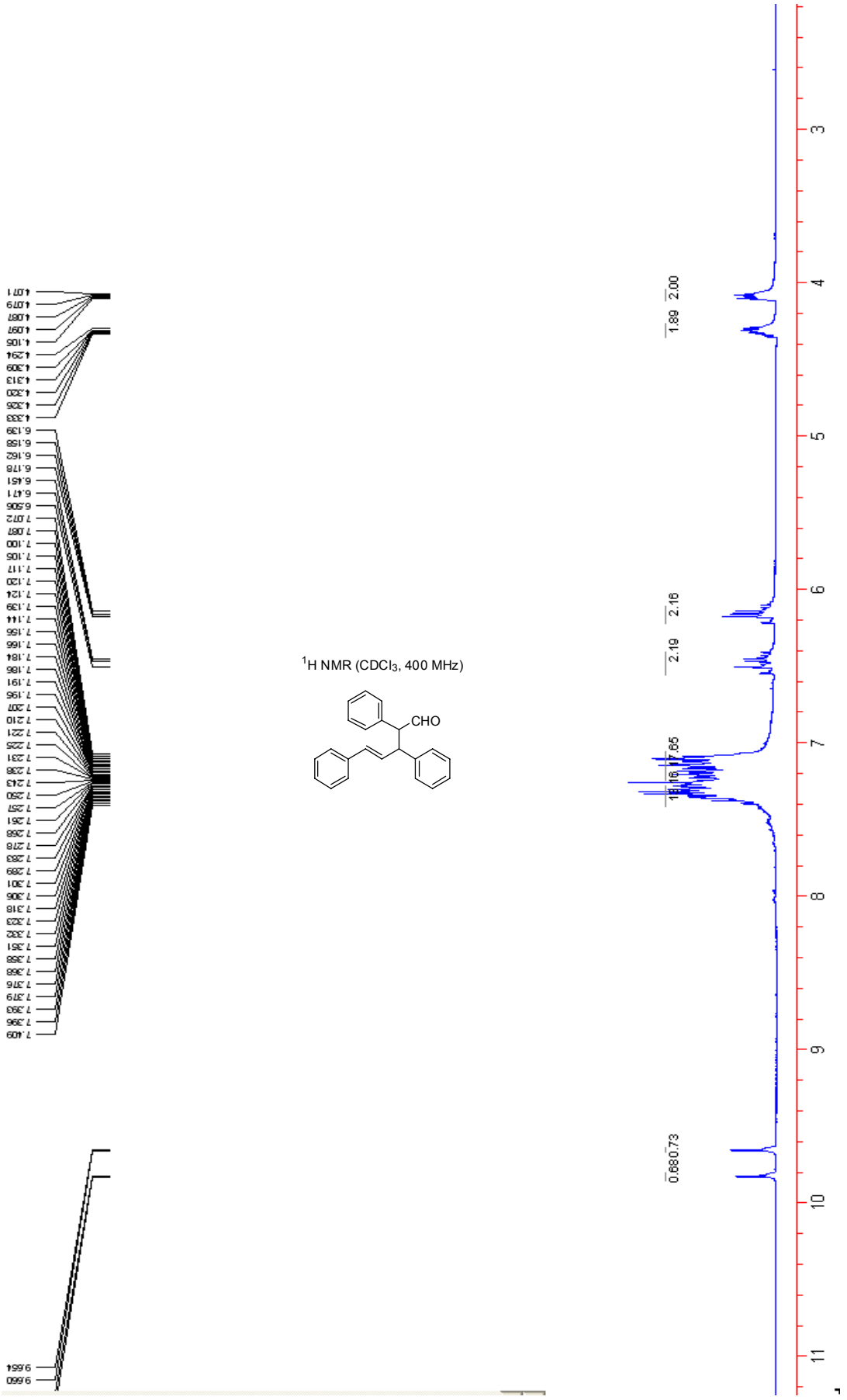

^{13}C NMR ($CDCl_3$, 100 MHz)
CHO
0 PPM
50
100
150
200

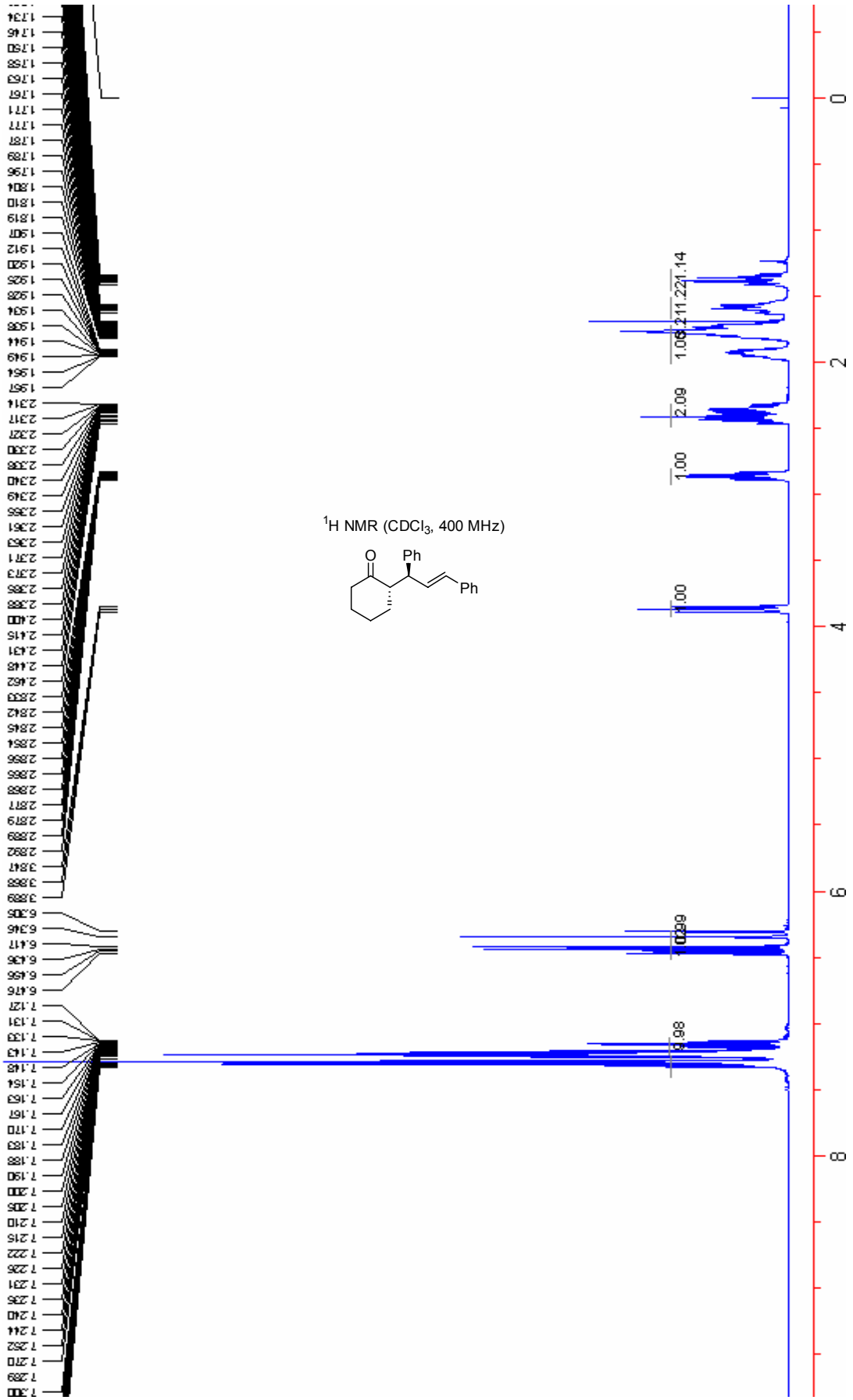


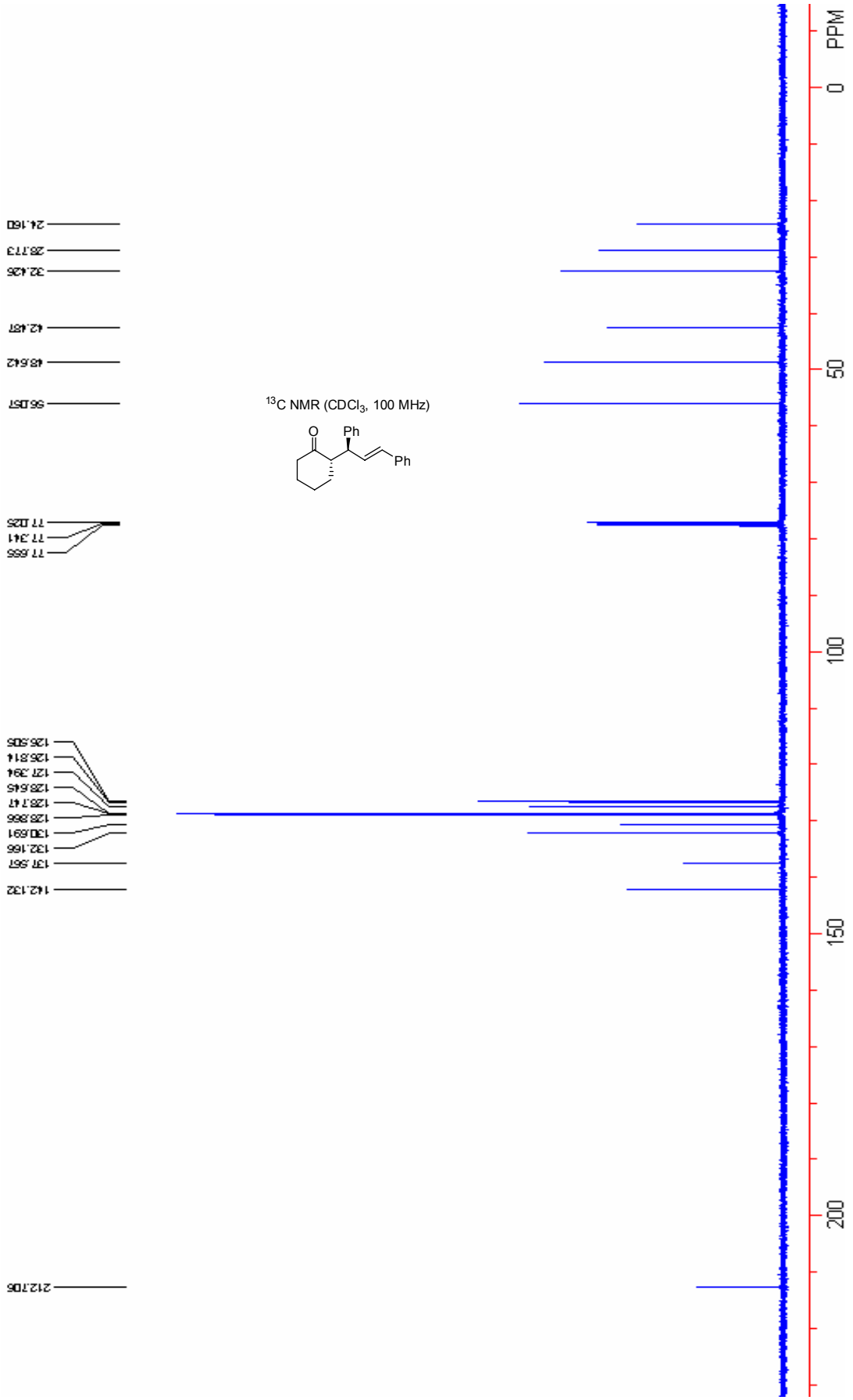
^{1}H NMR ($CDCl_3$, 400 MHz)

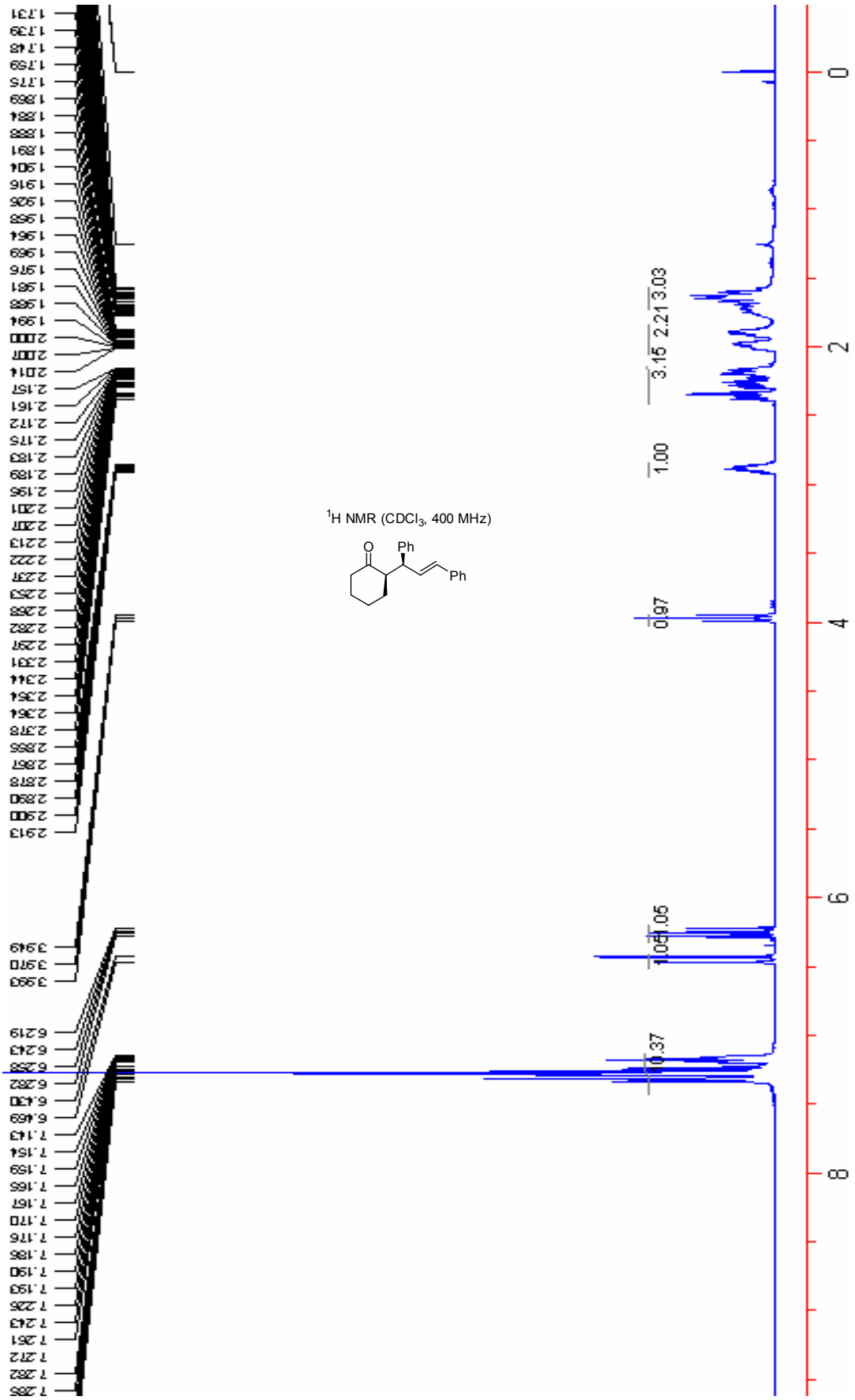


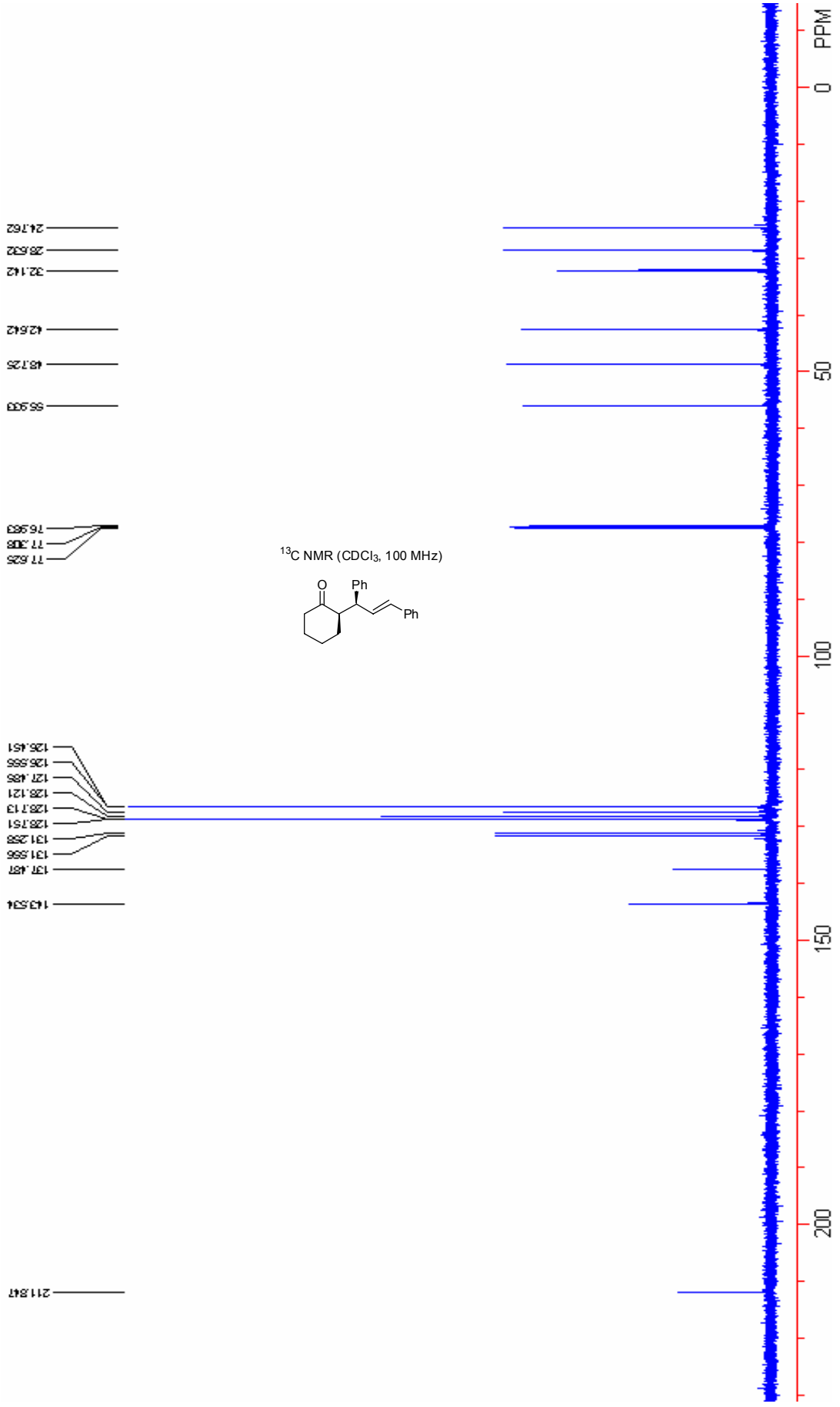
^{13}C NMR ($CDCl_3$, 100 MHz)

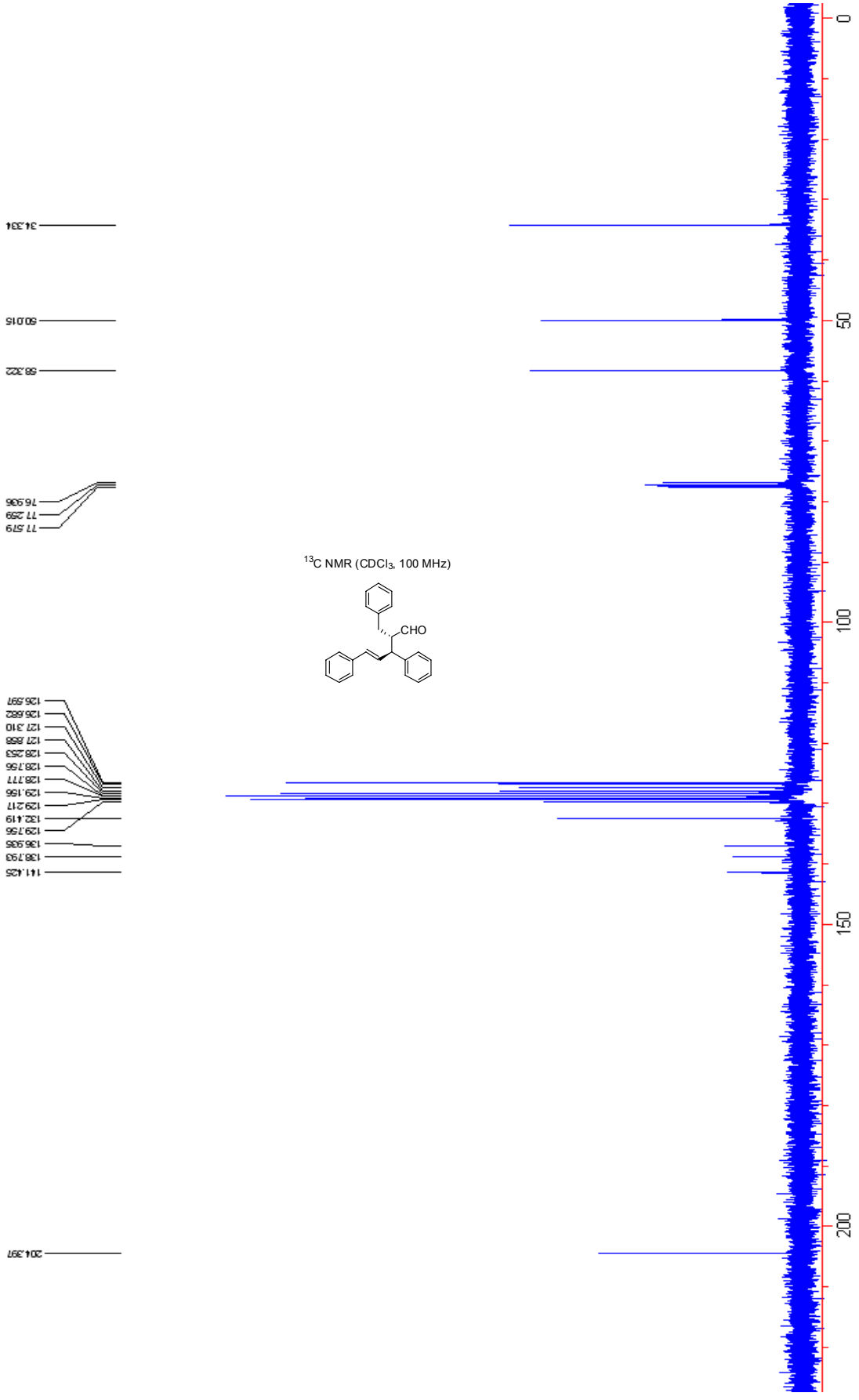

1H NMR (CDCl3, 400 MHz)
CHO
2.00
1.89
2.16
2.19
7.65
0.68
0.73
3
4
5
6
7
8
9
10
11

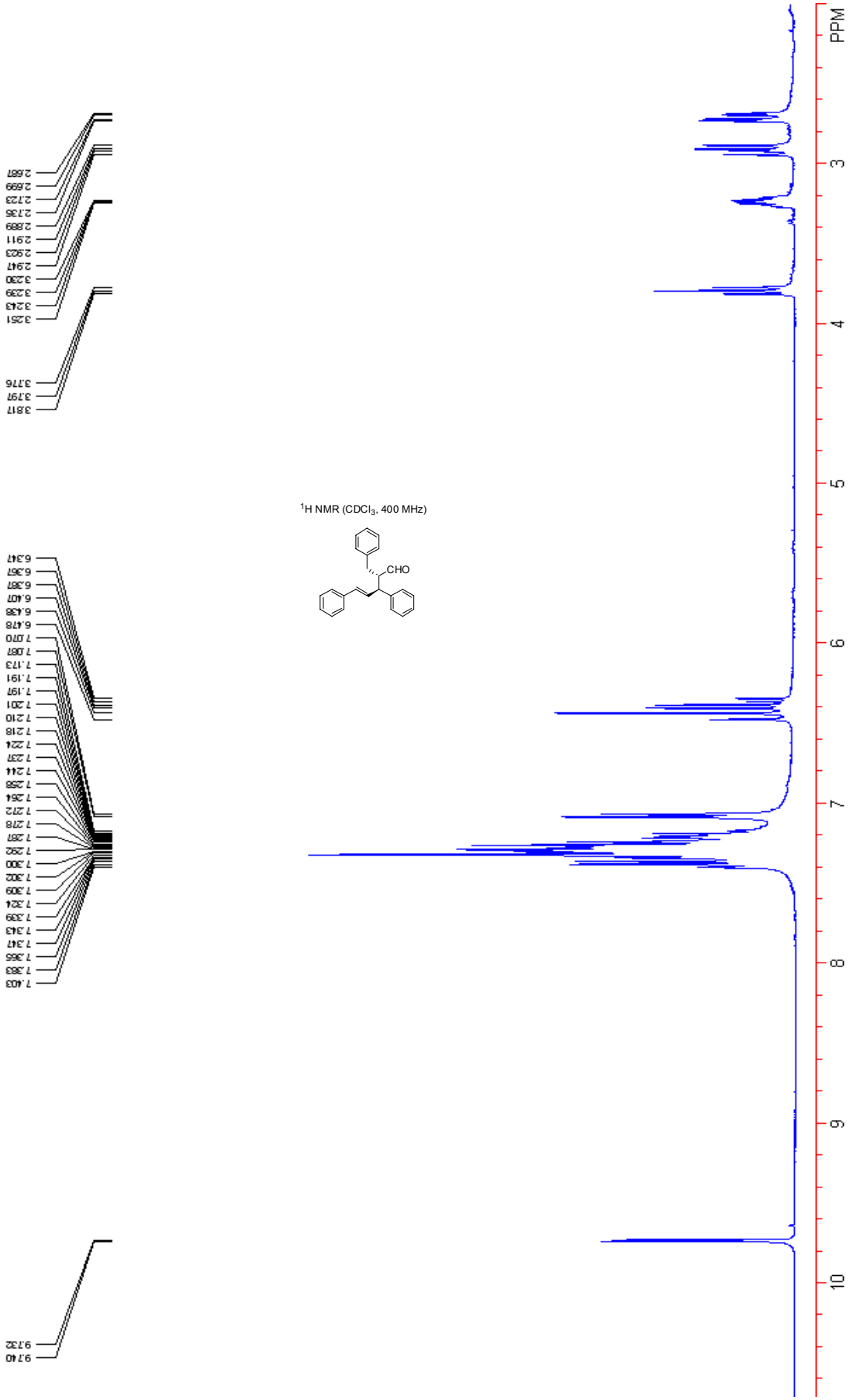

^{1}H NMR ($CDCl_3$, 400 MHz)
O
Ph
Ph
1.14
1.22
1.06
2.09
1.00
1.00
1.00
1.98
0
2
4
6
8


^{13}C NMR ($CDCl_3$, 100 MHz)
O
Ph
Ph
PPM
0
50
100
150
200
24.160
28.173
32.436
42.487
48.642
56.057
77.025
77.341
77.655
126.505
126.814
127.394
128.645
128.747
128.866
130.691
132.166
137.567
142.132
212.705

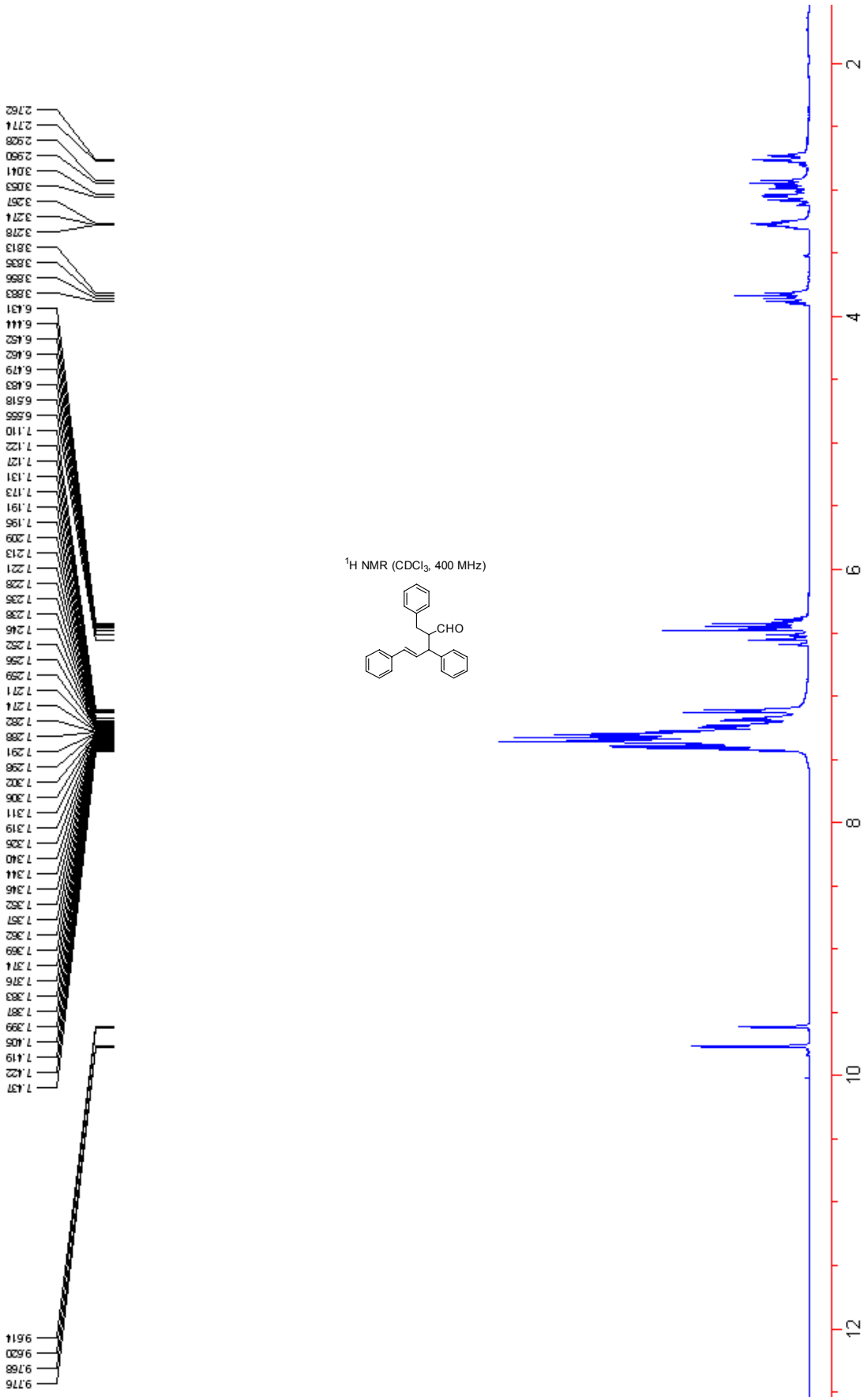

^{1}H NMR ($CDCl_3$, 400 MHz)
O
Ph
Ph
3.03
2.21
3.15
1.00
0.97
1.05
1.05
0.37
0
2
4
6
8

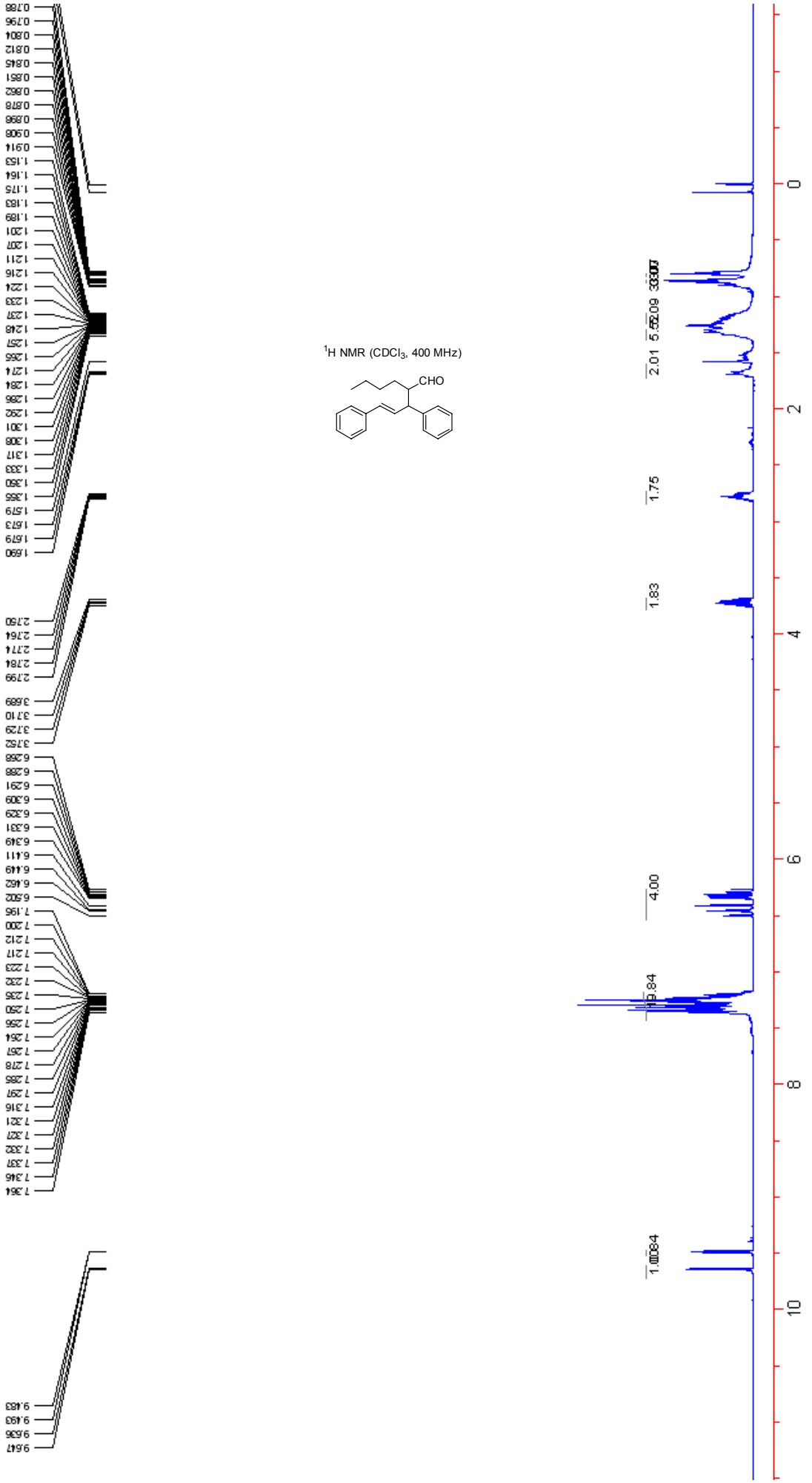

24.762
28.532
32.142
42.642
48.125
55.939
76.963
77.308
77.625
126.451
126.556
127.485
128.121
128.213
128.751
131.258
131.556
137.487
143.534
211.847
PPM
0
50
100
150
200
^{13}C NMR ($CDCl_3$, 100 MHz)
O
Ph
Ph

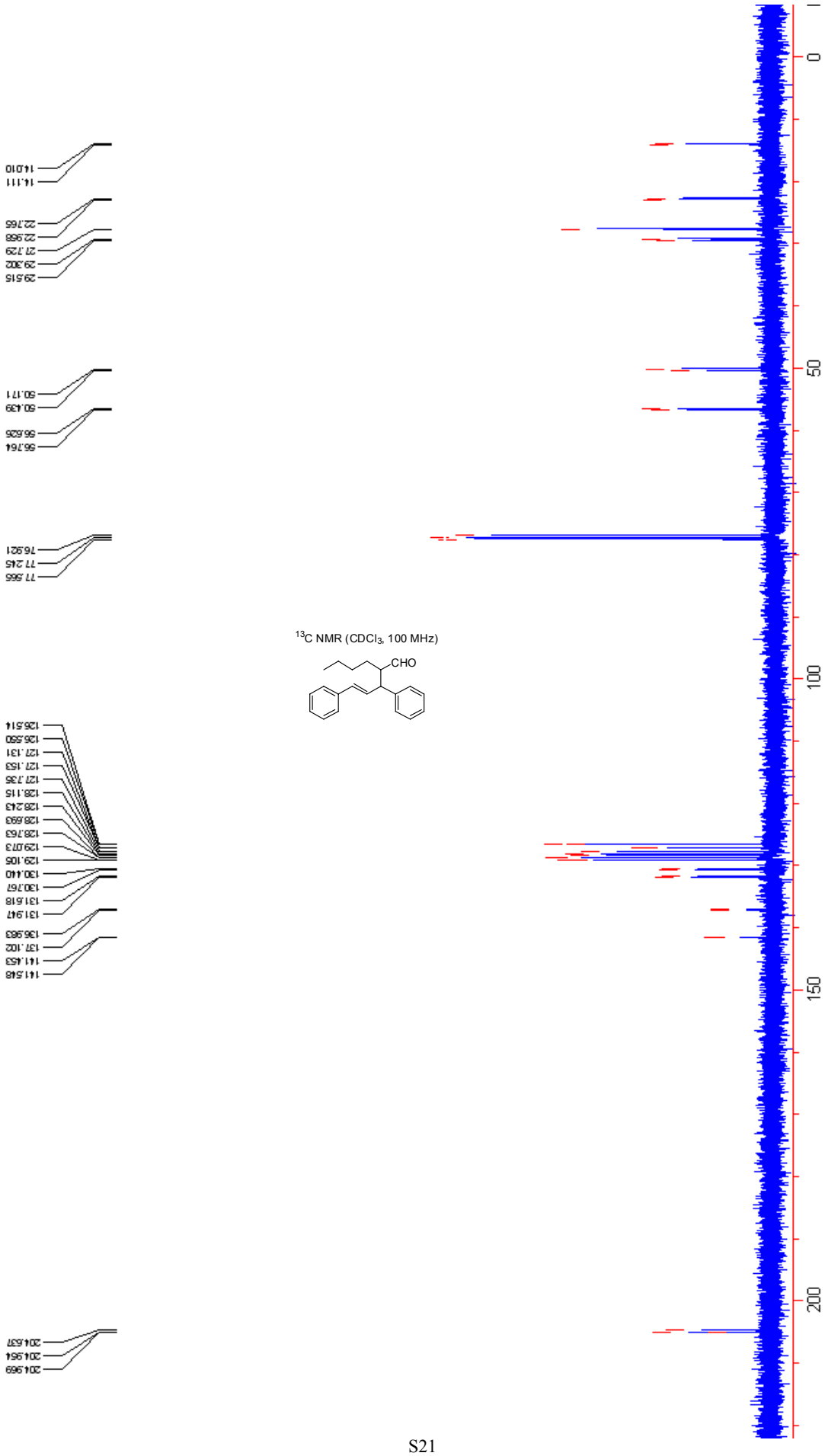

^{13}C NMR ($CDCl_3$, 100 MHz)
CHO
31.331
60.015
68.322
76.926
77.259
77.579
126.597
126.682
127.310
127.868
128.253
128.756
128.777
129.156
129.217
132.419
129.756
136.935
138.793
141.425
201.397
0
50
100
150
200



^{1}H NMR ($CDCl_3$, 400 MHz)


^{1}H NMR ($CDCl_3$, 400 MHz)
CHO
2.762
2.774
2.928
2.960
3.041
3.053
3.267
3.274
3.278
3.813
3.835
3.856
3.863
6.431
6.444
6.452
6.462
6.479
6.483
6.518
6.556
7.110
7.122
7.127
7.131
7.173
7.191
7.196
7.209
7.213
7.221
7.228
7.235
7.238
7.246
7.252
7.256
7.259
7.271
7.274
7.282
7.288
7.291
7.298
7.302
7.306
7.311
7.319
7.326
7.340
7.344
7.346
7.352
7.357
7.362
7.369
7.374
7.376
7.383
7.387
7.399
7.405
7.419
7.422
7.437
9.611
9.620
9.768
9.776
2
4
6
8
10
12


^{1}H NMR ($CDCl_3$, 400 MHz)
CHO
2.01
1.75
1.83
4.00
9.84
1.0084
0
2
4
6
8
10


14.010
14.111
22.766
22.968
27.729
29.302
29.515
50.171
50.439
56.626
56.764
76.921
77.245
77.566
125.514
125.560
127.131
127.153
127.736
128.115
128.243
128.693
128.763
129.073
129.105
130.440
130.767
131.518
131.947
136.963
137.102
141.453
141.518
201.537
201.964
201.969
^{13}C NMR ($CDCl_3$, 100 MHz)
CHO
0
50
100
150
200

4. Copies of HPLC Spectra

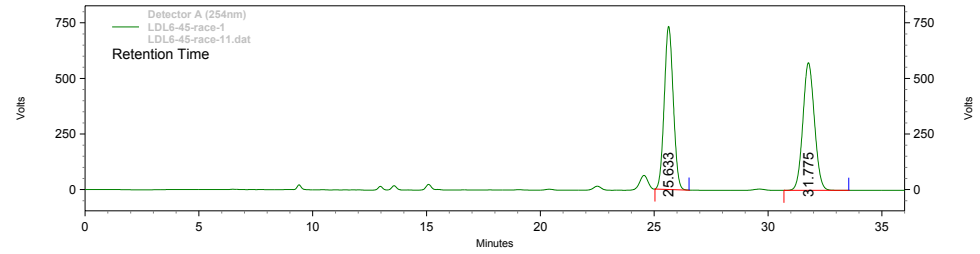


Figure 1. HPLC chromatogram showing the separation product using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min). *Anti*-product (**5a**) from asymmetric allylic alkylation using PPh_3 in DMSO at room temperature, racemic isomers.

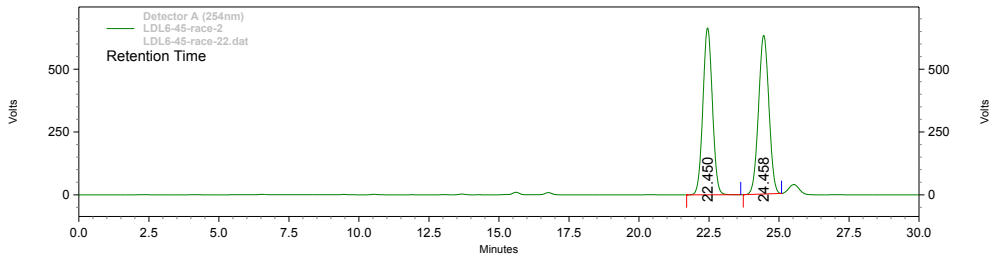


Figure 2. HPLC chromatogram showing the separation product using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min). *Syn*-product (**5b**) from asymmetric allylic alkylation using PPh_3 in DMSO at room temperature, racemic isomers.

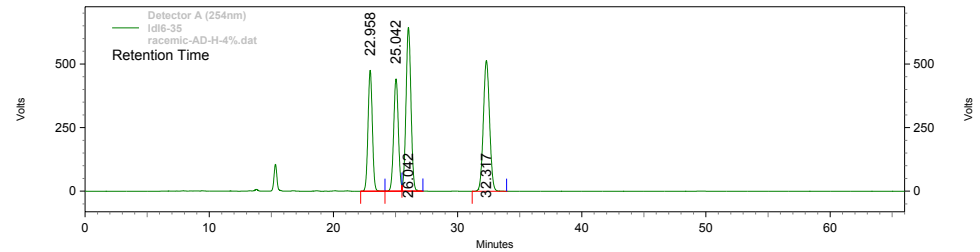


Figure 3. HPLC chromatogram showing the separation racemic mixture of *anti*- and *syn*-product (**5a and 5b**) using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min).

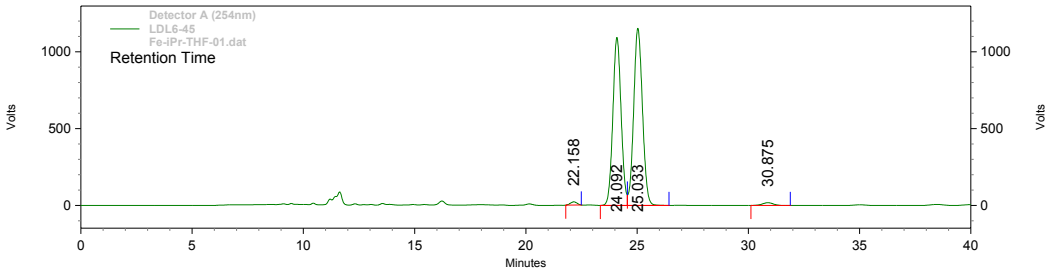


Figure 4. HPLC chromatogram using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**5a and 5b**) from asymmetric allylic alkylation using **1a** as a ligand in DMSO at room temperature (Table 1, entry 7), 94% *ee* (*anti*-) and 94% *ee* (*syn*-).

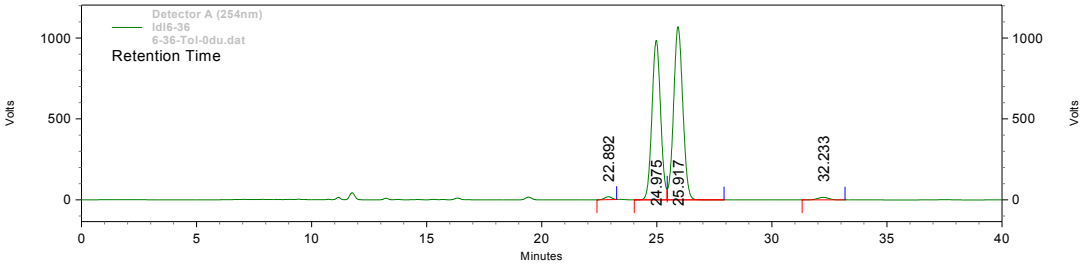


Figure 5. HPLC chromatogram using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**5a and 5b**) from asymmetric allylic alkylation using **1b** as aligand at room temperature in DMSO (Table 1, entry 15), 98% *ee* (*anti*-) and 97% *ee* (*syn*-).

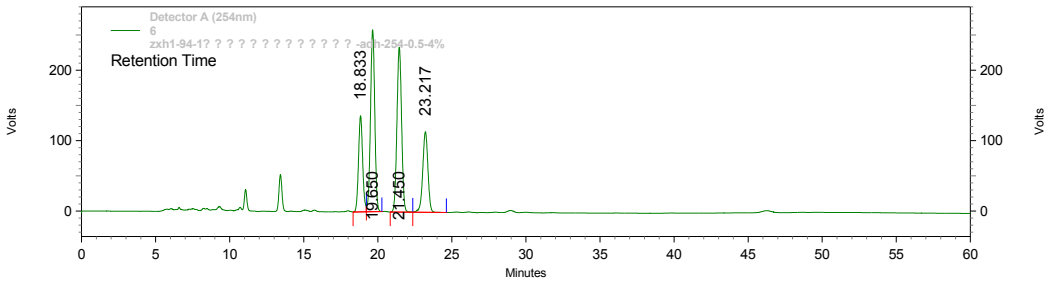


Figure 6. HPLC chromatogram showing the racemic mixture of *anti*- and *syn*-product (**6a** and **6b**) using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min).

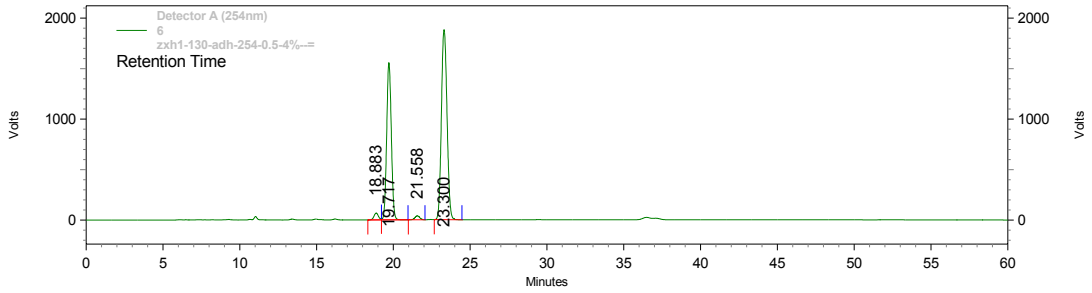


Figure 7. HPLC chromatogram using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**6a** and **6b**) from asymmetric allylic alkylation using **1b** as a ligand at room in DMSO temperature (Scheme 1), 97% *ee* (*anti*-) and 96 % *ee* (*syn*-).

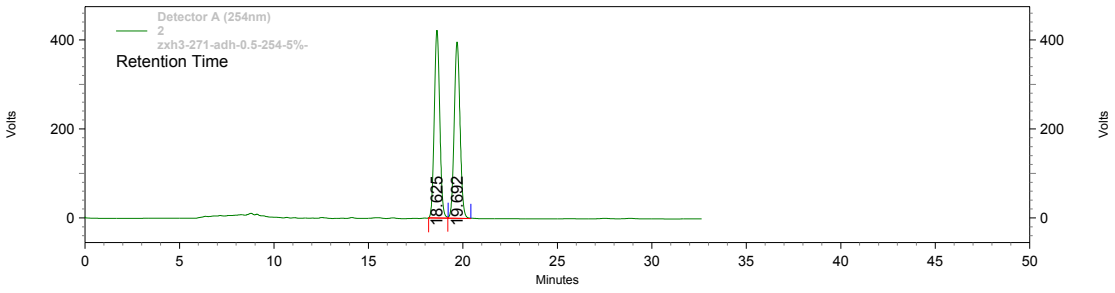


Figure 8. HPLC chromatogram showing the racemic product (**7**) using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 95: 5, flow=0.5mL/min).

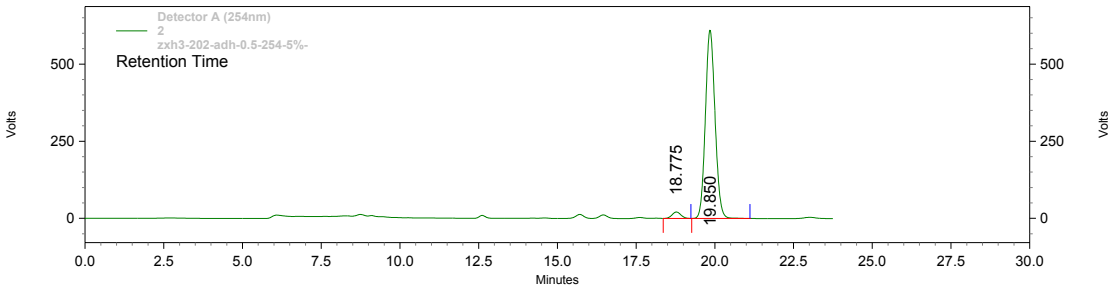


Figure 9. HPLC chromatogram using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 95: 5, flow = 0.5 mL/min). Enantioselective product (**7**) from asymmetric allylic alkylation using **1b** as a ligand in DMSO at room temperature (Scheme 2), 90% *ee* .

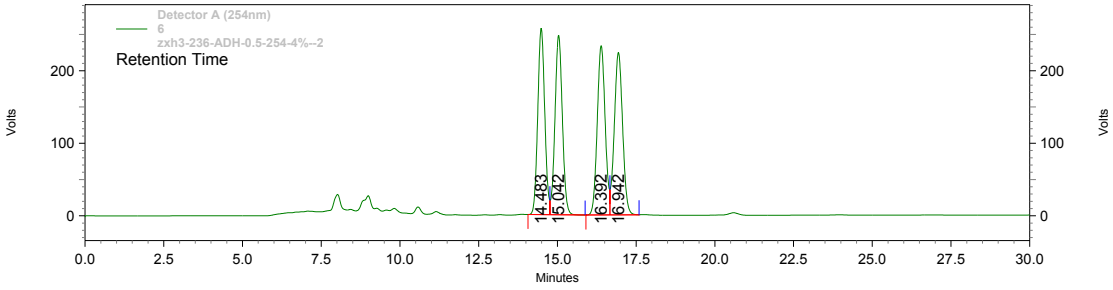


Figure 10. HPLC chromatogram showing the racemic mixture of *anti*- and *syn*-product (**10a** and **10b**) using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min).

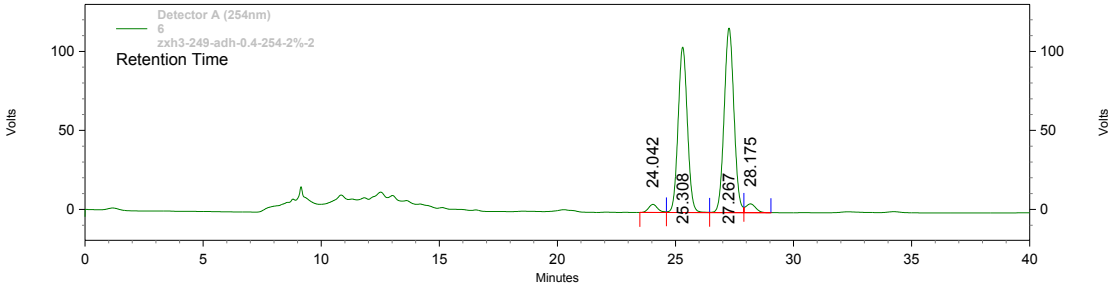


Figure 11. HPLC chromatogram using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 98: 2, flow = 0.4 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**10a** and **10b**) from asymmetric allylic alkylation using **4b** as a ligand in DMSO at room temperature (Table 2, entry 8), 91% *ee* (*anti*-) and 91% *ee* (*syn*-).

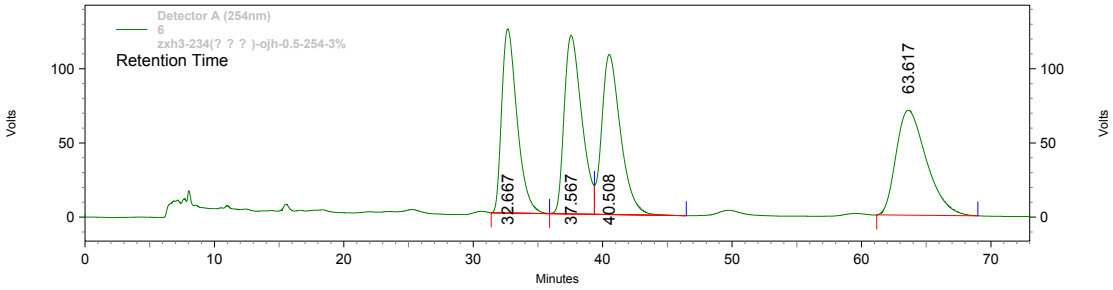


Figure 12. HPLC chromatogram showing the racemic mixture of *anti*-product and *syn*-product (**11a** and **11b**) using a Daicel Chiralcel OJ-H column (hexane: 2-propanol = 97: 3, flow = 0.5 mL/min).

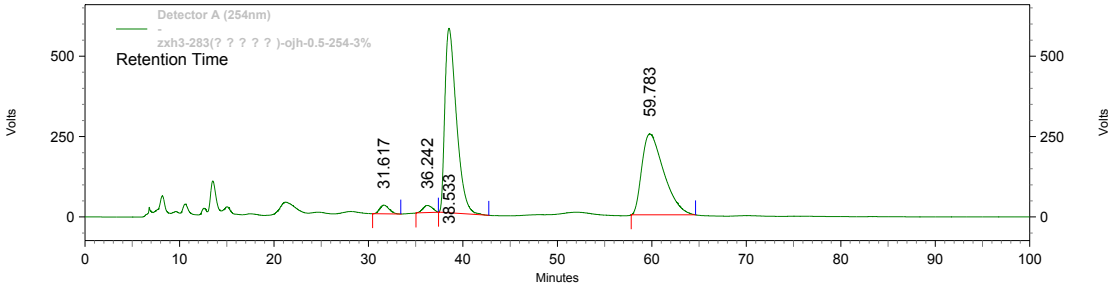


Figure 13. HPLC chromatogram using a Daicel Chiralcel OJ-H column (hexane: 2-propanol = 97: 3, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**11a** and **11b**) from asymmetric allylic alkylation using **4b** as a ligand in DMSO at room temperature (Table 3, entry 1), 92% *ee* (*anti*-) and 93 % *ee* (*syn*-).

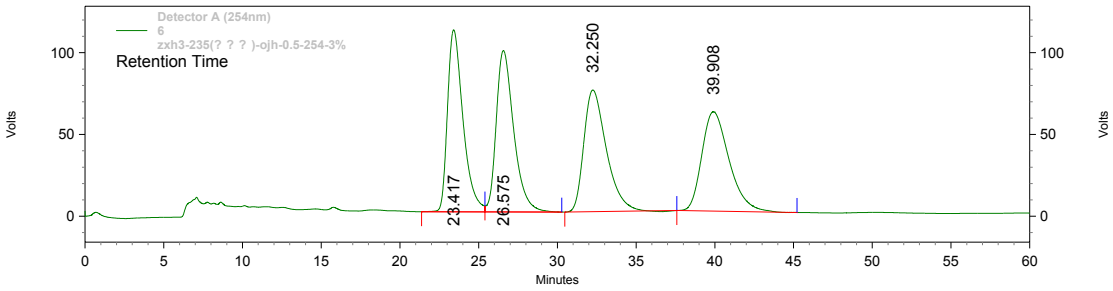


Figure 14. HPLC chromatogram showing the racemic mixture of *anti*- and *syn*-product (**12a** and **12b**) using a Daicel Chiralcel OJ-H column (hexane: 2-propanol = 97: 3, flow=0.5mL/min).

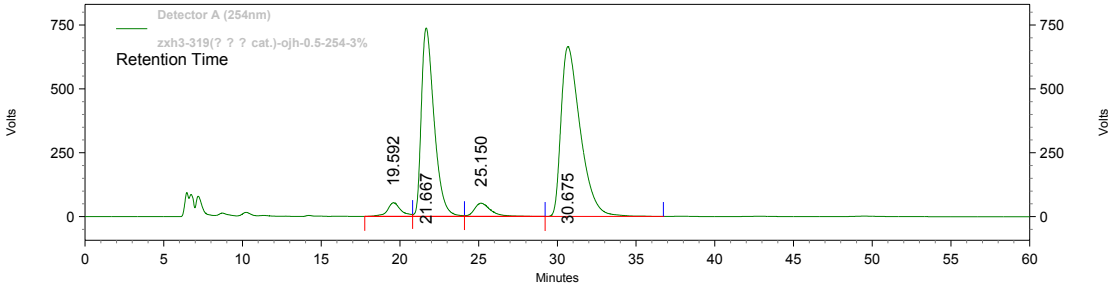


Figure 15. HPLC chromatogram using a Daicel Chiralcel OJ-H column (hexane: 2-propanol = 97: 3, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**12a** and **12b**) from asymmetric allylic alkylation using **4b** as a ligand in DMSO at room temperature (Table 3, entry 2), 89% *ee* (*anti*-) and 89 % *ee* (*syn*-)

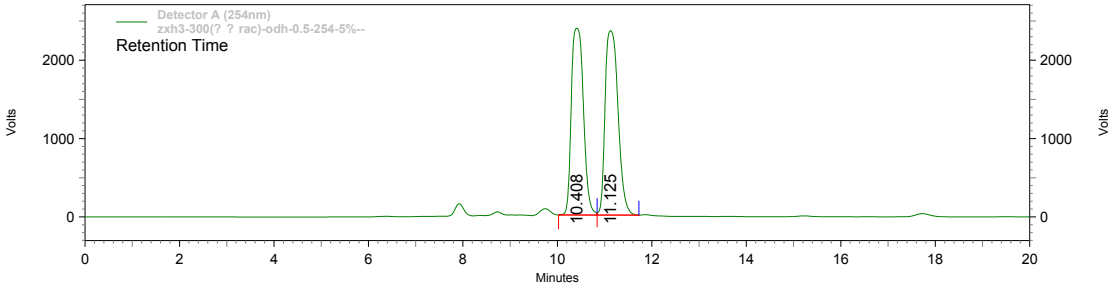


Figure 16. HPLC chromatogram showing the racemic product (**13**) using a Daicel Chiralcel OD-H column (hexane: 2-propanol = 95: 5, flow=0.5mL/min).

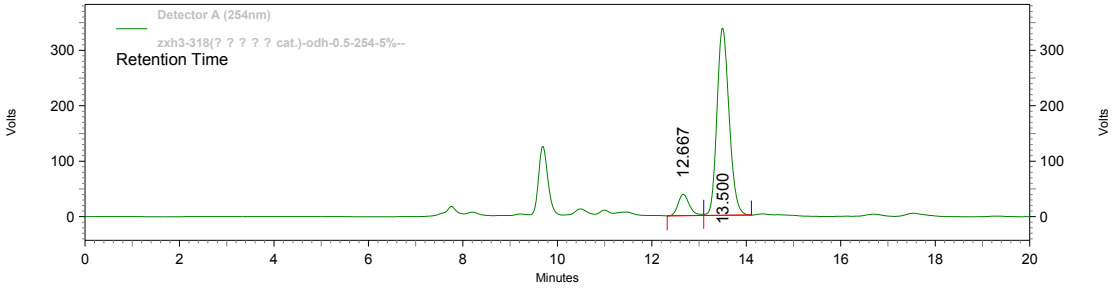


Figure 17. HPLC chromatogram using a Daicel Chiralcel OD-H column (hexane: 2-propanol = 95: 5, flow = 0.5 mL/min). Enantioselective product (**13**) from asymmetric allylic alkylation using **4b** as a ligand in DMSO at room temperature (Table 3, entry 3), 79 % *ee* .

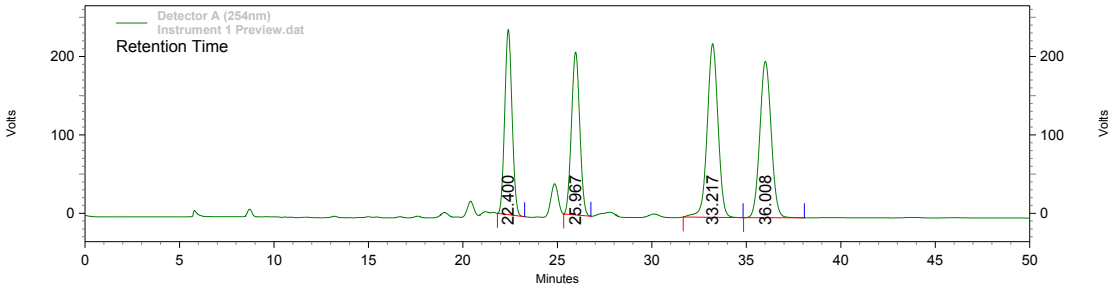


Figure 18. HPLC chromatogram showing the racemic mixture of *anti*- and *syn*-product (**14a** and **14b**) using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 95: 5, flow = 0.5 mL/min).

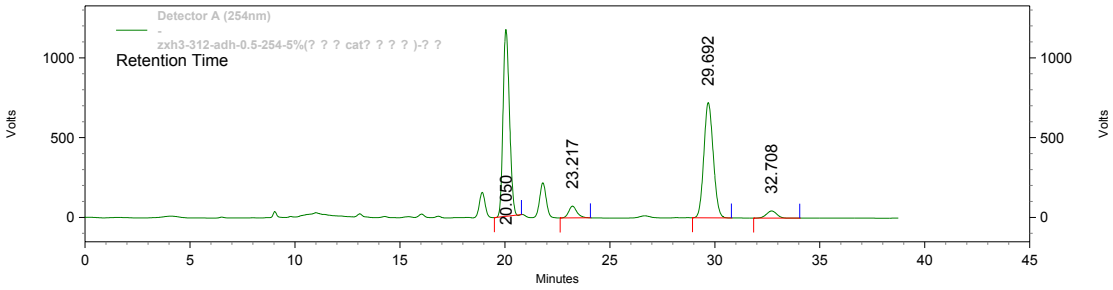


Figure 19. HPLC chromatogram using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 95: 5, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**14a** and **14b**) from asymmetric allylic alkylation using **4b** in DMSO at room temperature (Table 3, entry 4), 87% *ee*

(*anti*-) and 87 % *ee* (*syn*-).

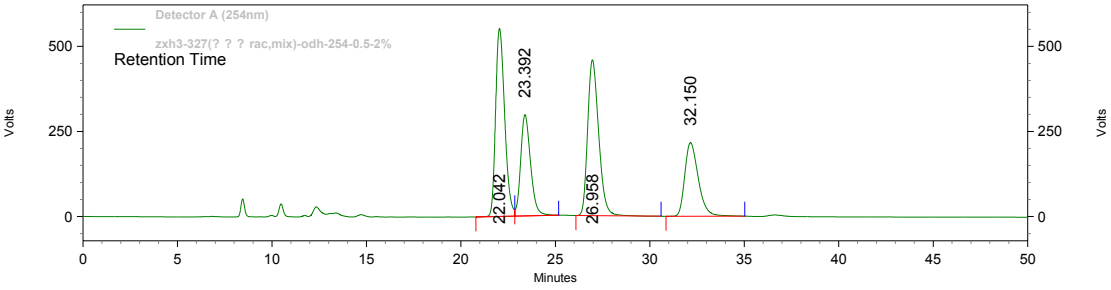


Figure 20. HPLC chromatogram showing the racemic mixture of *anti*- and *syn*-product (**15a** and **15b**) using a Daicel Chiralcel OD-H column (hexane: 2-propanol = 98: 2, flow = 0.5 mL/min).

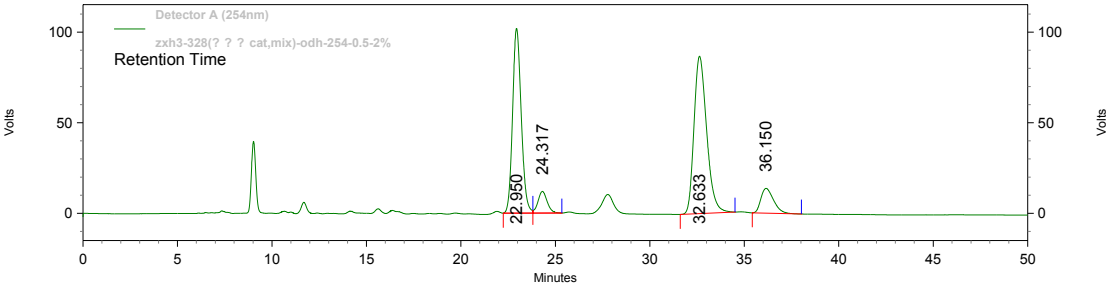


Figure 21. HPLC chromatogram using a Daicel Chiralcel OD-H column (hexane: 2-propanol = 98: 2 flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**15a** and **15b**) from asymmetric allylic alkylation using **4b** as a ligand in DMSO at room temperature (Table 3, entry 5), 90% *ee* (*anti*-) and 90 % *ee* (*syn*-).