Supporting Information

Mild-Condition Synthesis of Allenes from Alkynes and Aldehydes Mediated by Tetrahydroisoquinoline (THIQ)

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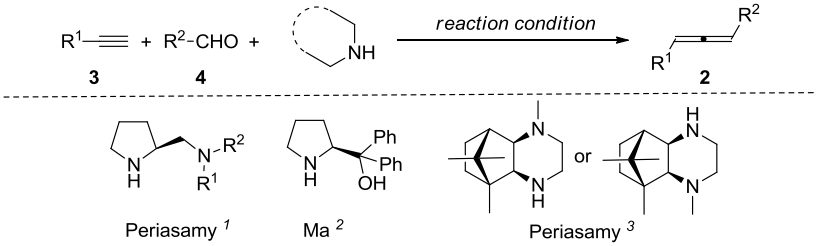
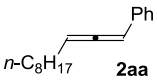
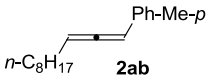
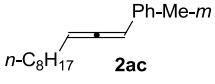
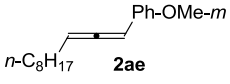
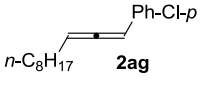
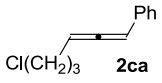
Contents

1. Comparison of the Allene Syntheses

Table S1. Comparison of the Allene Synthesis Using Three Different Protocols



entry	R^1/R^2	2	yield (%)[a] Ma	Periasamy	present method
1	R^1 = *n*-C_8H_{17} R^2 = Ph	 **2aa**	55 [2]	72 [1]	63
2	R^1 = *n*-C_8H_{17} R^2 = *p*-Me-Ph	 **2ab**	40 [2]	63 [3]	73
3	R^1 = *n*-C_8H_{17} R^2 = *m*-Me-Ph	 **2ac**	48 [2]	67 [3]	77
4	R^1 = *n*-C_8H_{17} R^2 = *m*-MeO-Ph	 **2ae**	47 [2]	65 [3]	60
5	R^1 = *n*-C_8H_{17} R^2 = *p*-Cl-Ph	 **2ag**	47 [2]	71 [3]	67
6	R^1 = $Cl(CH_2)_3$ R^2 = Ph	 **2ca**	43 [2]	68 [3]	63

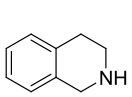
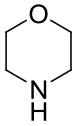
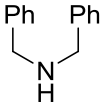
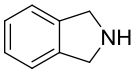
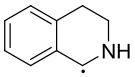
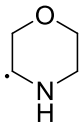
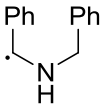
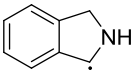
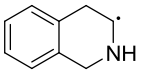
[a] Isolated yield.

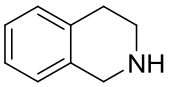
2. Calculations of C-H Bond Dissociation Energies and Computed Structures

All DFT calculations were carried out with the Gaussian 03 program package.[4] The geometry optimization of all the minima and transition states were performed at (U)B3LYP[5] level of theory with the 6-31G(d)[6] basis set. The vibrational frequencies were computed at the same level of theory to check whether every optimized structure is an energy minimum and to evaluate its zero-point vibration energy (ZPE). The bond dissociation energies were computed based on the following scheme.

$$\text{A-B(g)} \longrightarrow \text{A•(g)} + \text{B•(g)}$$

$$\text{BDE} = \Delta H_{gas} = H_{gas}(\text{A•}) + H_{gas}(\text{B•}) - H_{gas}(\text{A-B})$$

Structure							
H_{gas} (Hartree)	-404.137553	-287.650543	-212.445565	-213.638068	-596.998066	-364.847459	-0.497912
Structure							
H_{gas} (Hartree)	-403.520991	-286.994358	-211.806955	-212.997872	-596.377142	-364.228446	-403.483586



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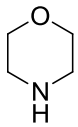
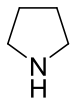
C	-2.56180900	-0.69227800	0.02428000
C	-1.35038100	-1.37937800	0.04298500
C	-0.12889000	-0.69439400	0.01685700
C	-0.12606300	0.71009300	-0.02582400
C	-1.35038300	1.39238200	-0.04247900
C	1.18362000	-1.46830700	0.07169800
N	2.37843000	-0.71158300	-0.30497200
C	2.38348300	0.60839000	0.33131100
C	1.18383200	1.47836200	-0.07704600
H	-3.49932200	1.25302400	-0.03052200
H	-3.50025500	-1.24051300	0.03967700
H	-1.34726000	-2.46776300	0.07651400
H	-1.34798500	2.48047300	-0.07335900
H	1.12293100	-2.35839400	-0.56618400
H	1.33624700	-1.84079200	1.09640000
H	2.38321700	-0.58519300	-1.31733700
H	3.32476400	1.11558400	0.08995900
H	2.37679900	0.44704100	1.41769500
H	1.34609300	1.85166300	-1.10047400
H	1.12243700	2.37090900	0.56045000



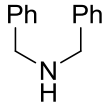
C	-1.17799000	-0.75005400	0.19942800
C	-1.20711700	0.72292800	-0.21963300
N	0.00002900	1.45473200	0.18723000
C	1.20714900	0.72288100	-0.21962700
C	1.17796000	-0.75010300	0.19942200
O	-0.00003200	-1.39359400	-0.27510700
H	-2.02213900	-1.30708000	-0.22152700
H	-1.22977400	-0.82643300	1.30145700
H	-1.27994000	0.78019900	-1.31367100
H	-2.08796800	1.22573100	0.19803400
H	0.00003000	1.54714700	1.20413100
H	2.08801400	1.22564900	0.19805100
H	1.27998200	0.78015900	-1.31366300
H	1.22975400	-0.82650000	1.30144900
H	2.02208200	-1.30715800	-0.22154900



C	-0.77707400	1.03057200	-0.05638300
C	-1.16223600	-0.44662300	0.17193400
N	-0.00167100	-1.17004900	-0.35653800
C	1.16059600	-0.45012600	0.17286900
C	0.78048300	1.02786100	-0.05761200
H	-1.19624600	1.67923500	0.71903300
H	-1.15961600	1.38063900	-1.01981000
H	-2.07595600	-0.73966900	-0.35686600
H	-1.32631200	-0.62640900	1.25188200
H	-0.00329100	-2.14856300	-0.07521700
H	2.07407400	-0.74671900	-0.35437000
H	1.32254800	-0.62930500	1.25326100
H	1.20332300	1.67680600	0.71557100
H	1.16256000	1.37422000	-1.02257000

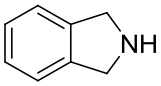
C	-2.46216600	-0.37092500	-0.03308800
C	-1.22233200	0.51873800	0.02239000

N	-0.00000500	-0.27642200	-0.07185000
C	1.22233500	0.51878900	0.02196900
C	2.46214100	-0.37094700	-0.03289600
H	-3.37728100	0.23060100	-0.00027100
H	-2.46658500	-0.96670000	-0.95161700
H	-2.49023200	-1.06308600	0.81848600
H	-1.25447500	1.14636500	0.93582900
H	-1.23132700	1.21565800	-0.82670600
H	0.00017100	-0.96467000	0.68188700
H	1.23143000	1.21519500	-0.82755300
H	1.25443600	1.14694900	0.93504400
H	3.37727600	0.23056900	-0.00050400
H	2.49020200	-1.06253500	0.81914200
H	2.46655000	-0.96732200	-0.95104100

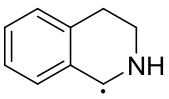


C	-2.46831800	-0.42768000	0.21821800
C	-1.22046200	-1.18665200	0.62317200
N	-0.00004600	-0.46548300	0.26324500
C	1.22047900	-1.18660700	0.62281400
C	2.46828600	-0.42750100	0.21791100
C	3.55004300	-1.09467200	-0.36774600
C	4.71409700	-0.40519300	-0.71378400
C	4.80666500	0.96783300	-0.48447300
C	3.72927000	1.64467800	0.09286800
C	2.57020900	0.95260300	0.44240700
C	-3.54930300	-1.09457100	-0.36915600
C	-4.71333200	-0.40512700	-0.71538700
C	-4.80662900	0.96757900	-0.48451400
C	-3.72999600	1.64416500	0.09457400
C	-2.57097200	0.95212700	0.44426700
H	-1.26027100	-2.20684500	0.19532800
H	-1.20459400	-1.31979100	1.71554600
H	-0.00020500	-0.28306500	-0.73981600
H	1.26030900	-2.20671000	0.19474600
H	1.20478500	-1.32002600	1.71516200
H	3.48027500	-2.16415700	-0.55562900
H	5.54398600	-0.94020500	-1.16839400
H	5.70965700	1.50812800	-0.75652800
H	3.79287000	2.71510300	0.27195000
H	1.72697300	1.47611800	0.88304300

H	-3.47896100	-2.16380800	-0.55822000
H	-5.54262600	-0.93991900	-1.17134100
H	-5.70960100	1.50784800	-0.75668800
H	-3.79418400	2.71434600	0.27489200
H	-1.72831600	1.47547400	0.88622000

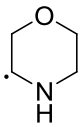


C	2.24363700	0.69921600	-0.02206100
C	2.24363700	-0.69921700	-0.02206200
C	1.03911200	-1.40917700	0.00192100
C	-0.15822700	-0.69878400	0.02456500
C	-0.15822700	0.69878400	0.02456400
C	1.03911300	1.40917700	0.00192100
C	-1.58149700	-1.20092000	0.07630700
N	-2.36133400	0.00000000	-0.27506000
C	-1.58149800	1.20092000	0.07630700
H	3.18705400	1.23835400	-0.04590700
H	3.18705500	-1.23835200	-0.04590800
H	1.04293700	-2.49669000	-0.00195200
H	1.04293700	2.49669000	-0.00195100
H	-1.77556500	-2.01181900	-0.63876500
H	-1.80925300	-1.59946200	1.08388500
H	-3.27730900	0.00000000	0.16213100
H	-1.77556400	2.01182000	-0.63876600
H	-1.80925200	1.59946200	1.08388500

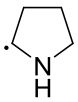


C	2.52962300	-0.71393700	0.07401200
C	2.53859900	0.68961600	0.08027300
C	1.35140200	1.40025900	0.01438400
C	0.10040500	0.72647200	-0.06205900
C	0.10226800	-0.70557300	-0.09207900
C	1.30684800	-1.39271400	-0.01325500
C	-1.12360600	1.42671000	-0.10781600
N	-2.33865600	0.76157400	-0.12176500
C	-2.36253500	-0.60863400	0.39058300
C	-1.22750100	-1.40768100	-0.26145900
H	3.46056000	-1.27024500	0.13400100
H	3.48294600	1.22504100	0.14193100

H	1.36294800	2.48806900	0.02877500
H	1.29580100	-2.48143500	-0.02855200
H	-1.16069400	2.50834800	-0.17483700
H	-3.13718300	1.32655000	0.13912700
H	-3.33547000	-1.05135300	0.15364300
H	-2.23901600	-0.62460700	1.48671100
H	-1.45748200	-1.52217000	-1.33129000
H	-1.19483100	-2.41633100	0.16733800



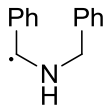
C	1.41073400	-0.24611500	0.20970300
C	0.46283300	-1.31656800	-0.22471800
N	-0.87716200	-1.15901600	0.23519500
C	-1.39115200	0.15447500	-0.22951500
C	-0.42252400	1.27907200	0.17304300
O	0.90219500	1.02379800	-0.27336600
H	2.40953100	-0.34754700	-0.22220300
H	1.49921700	-0.20311700	1.30942900
H	0.54748400	-1.68911100	-1.24574300
H	-0.87112400	-1.13317400	1.25806500
H	-2.39022400	0.32649000	0.19033900
H	-1.48061900	0.11362600	-1.32089800
H	-0.43681300	1.39360200	1.27307900
H	-0.71422400	2.23677500	-0.27257900



C	1.25341400	0.27913100	0.14620900
C	0.13894400	1.25173200	-0.10869400
N	-1.08623700	0.56575000	-0.17625700
C	-0.88731700	-0.84363200	0.18053600
C	0.58659200	-1.07505600	-0.19298100
H	1.58649100	0.28590400	1.20099900
H	2.14918200	0.46450100	-0.46078200
H	0.14641900	2.30268700	0.15650600
H	-1.90041500	1.02020000	0.22287400
H	-1.57778700	-1.49376500	-0.36873500
H	-1.04095200	-1.01949000	1.25906000

H	1.02498700	-1.92291700	0.34156000
H	0.66592900	-1.27042400	-1.26809900

C	2.42652800	-0.36858100	0.11137900
C	1.21532500	0.52321800	-0.15091700
N	-0.03153600	-0.21435800	0.02775500
C	-1.23906500	0.49214800	0.00098600
C	-2.50973000	-0.29553900	0.01304700
H	3.35645900	0.19866700	-0.00427600
H	2.39270100	-0.78235700	1.12452500
H	2.46203400	-1.20723000	-0.59595000
H	1.28733700	0.97426800	-1.15613800
H	1.20527000	1.35606800	0.56343600
H	-0.05795000	-1.06186800	-0.53470000
H	-1.20630100	1.44193400	0.53278900
H	-3.37238400	0.36437400	-0.12818400
H	-2.53257400	-1.03944400	-0.79775100
H	-2.67218700	-0.85138300	0.95499200



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N	-0.02992800	-0.43748500	0.08283700
C	1.21117800	-0.99109200	0.32891000
C	2.44810900	-0.33633200	0.12545600
C	3.66177700	-1.01917700	0.43381700
C	4.89563800	-0.42488400	0.23029000
C	4.98746400	0.87713900	-0.28621800
C	3.80966800	1.57148700	-0.58806600
C	2.56535000	0.98883700	-0.38843800
C	-3.48909000	-0.73205500	-0.97000200
C	-4.69172900	-0.02353300	-0.92269100
C	-4.90424100	0.92461700	0.07814000
C	-3.90935500	1.15891900	1.03102700
C	-2.71169200	0.44651400	0.98483400
H	-1.16183300	-1.90114700	-0.98041800
H	-1.16856900	-2.01501200	0.77891300

H	-0.03915300	0.35424800	-0.55065200
H	1.19354200	-1.98036400	0.77558400
H	3.60585600	-2.03012100	0.83206400
H	5.80088100	-0.97577600	0.47435200
H	5.95675600	1.34067000	-0.44459400
H	3.86499800	2.58454600	-0.97983300
H	1.67399900	1.56939800	-0.61420200
H	-3.32454100	-1.46519900	-1.75678400
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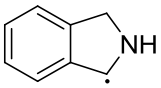

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C	0.18314800	0.74438800	0.01485300
C	0.20635900	-0.68264700	0.00660500
C	-0.96408700	-1.41754000	-0.00956600
C	1.51490900	1.20436900	0.01139700
N	2.39105900	0.12710300	-0.12191700
C	1.64884200	-1.13770300	0.03336100
H	-3.12424200	-1.30406100	-0.02212300
H	-3.18979800	1.17289300	0.00080700
H	-1.10091100	2.50309600	0.01414100
H	-0.94018100	-2.50534300	-0.01934400
H	1.88835700	2.21924900	-0.00728700
H	3.30138700	0.18996600	0.31699100
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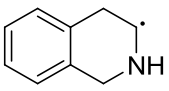

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C	-0.06410300	-0.68698700	0.04107000
C	-0.09130500	0.71918000	-0.01078300

C	-1.32695700	1.37708500	-0.04781200
C	1.26407000	-1.43784100	0.09341700
N	2.40744300	-0.61580900	-0.35932500
C	2.37075000	0.63697300	0.30931000
C	1.21513600	1.52870600	-0.03398000
H	-3.47288000	1.19354000	-0.05891700
H	-3.42439700	-1.29849500	0.02730800
H	-1.24898100	-2.48295300	0.08931700
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H	1.21715800	-2.34687100	-0.51916900
H	1.47406300	-1.76293100	1.12169400
H	2.28641400	-0.45627800	-1.36116200
H	2.73602900	0.61201400	1.33553500
H	1.34021500	1.96443700	-1.04049500
H	1.14380700	2.37747700	0.65713700

3. References

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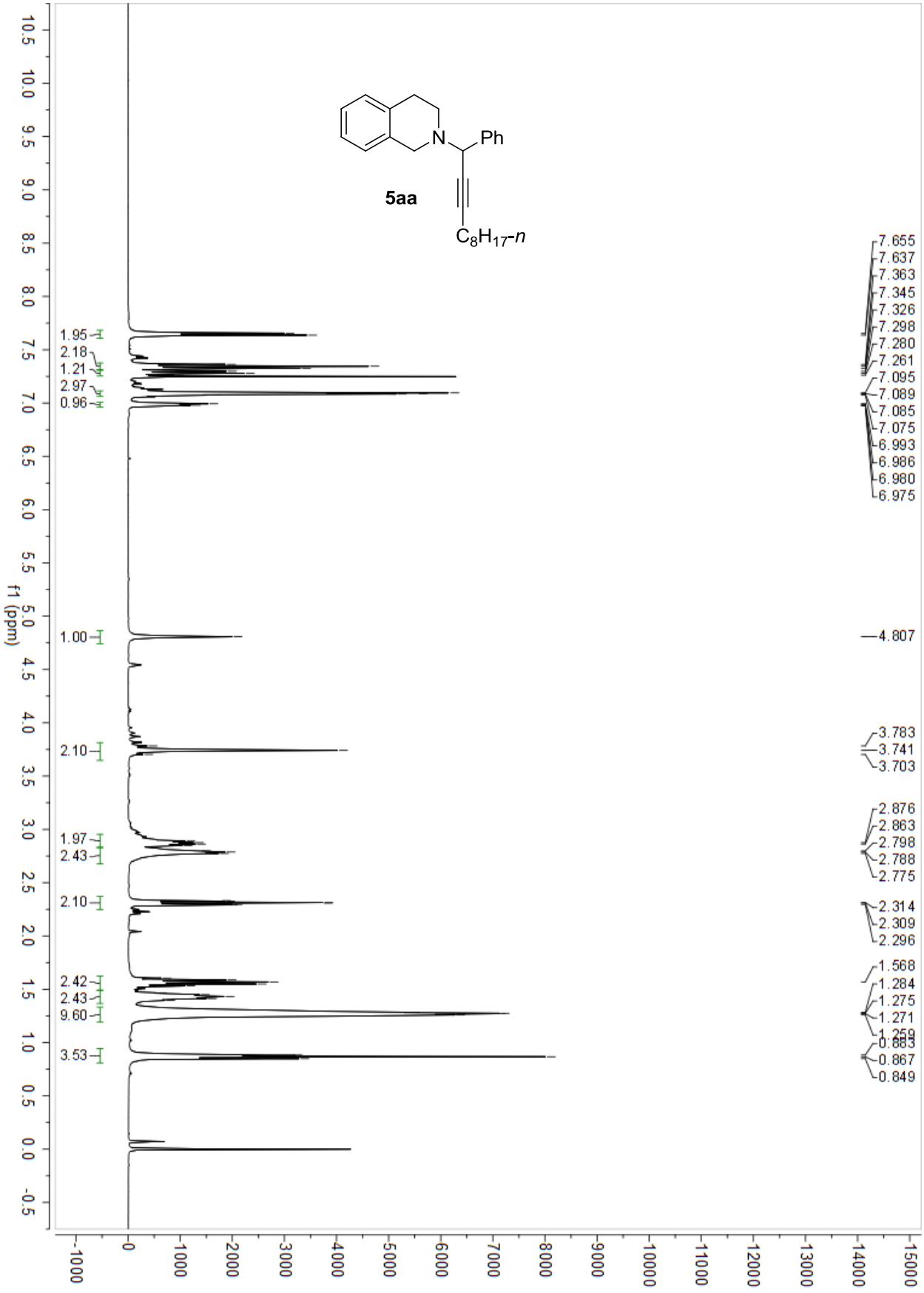
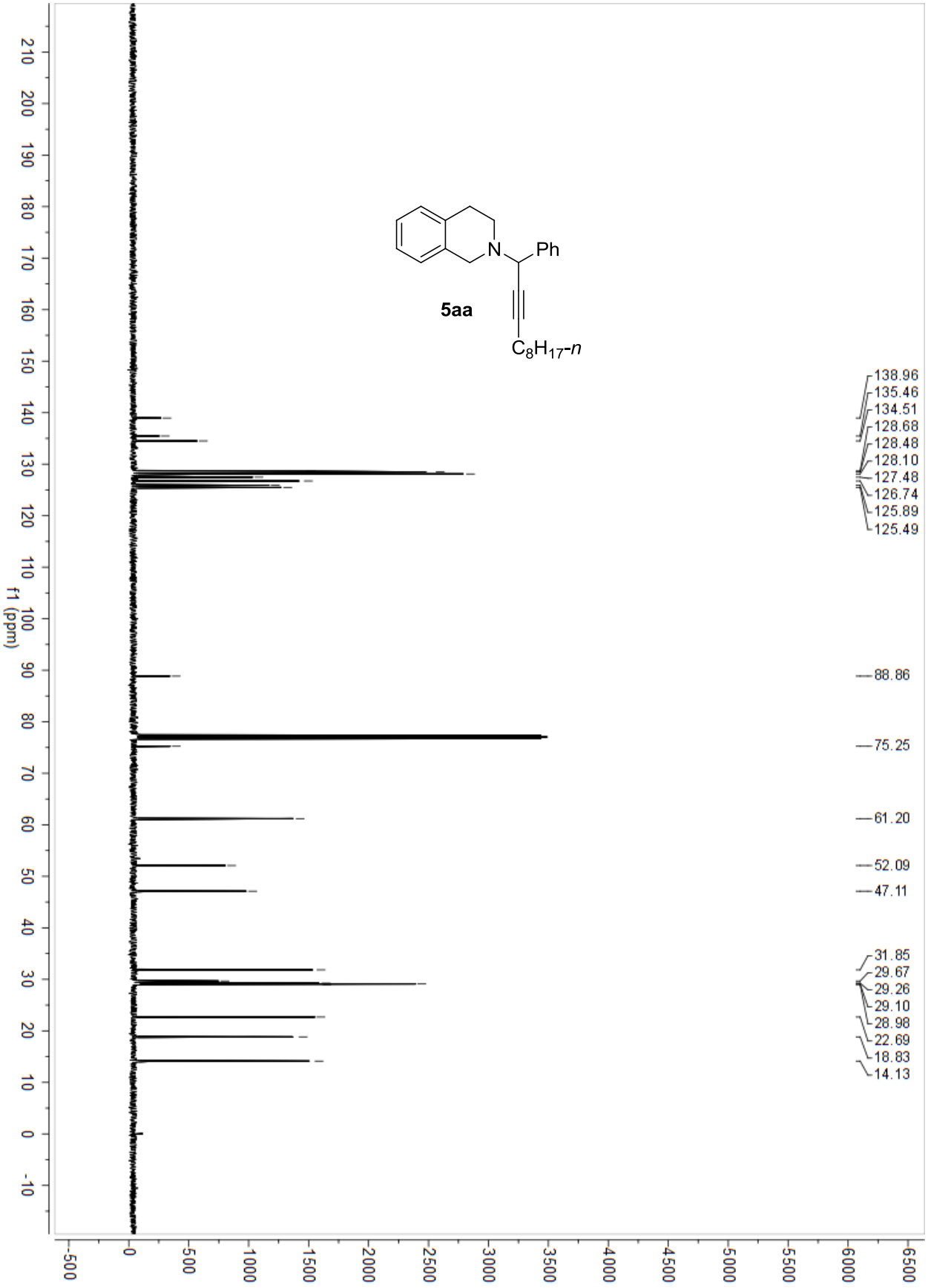
4. ^{1}H and ^{13}C-NMR Spectra for New and Reported Compounds

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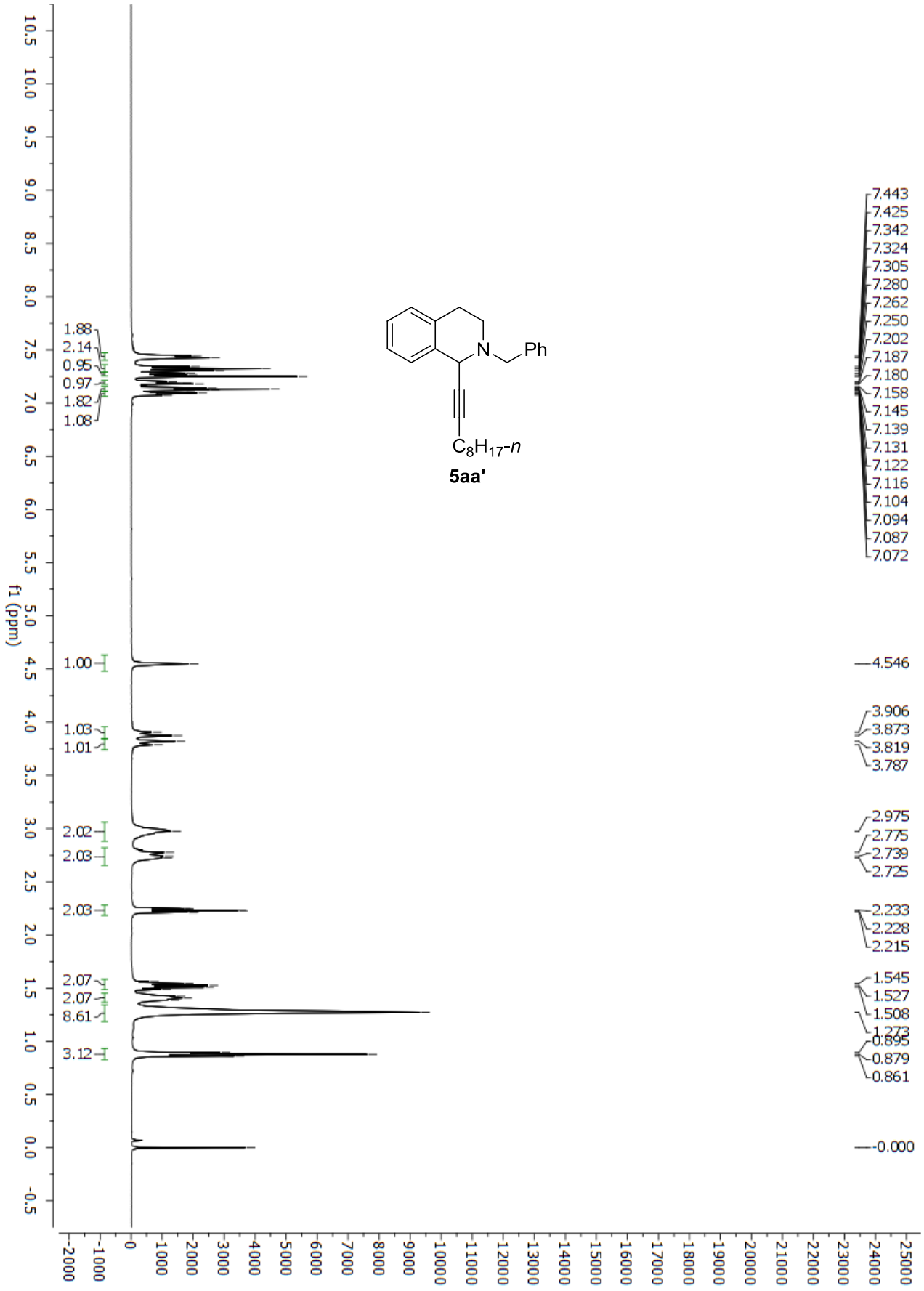
128.48
128.10
127.48
126.74
125.89
125.49
88.86
75.25
61.20
52.09
47.11
31.85
29.67
29.26
29.10
28.98
22.69
18.83
14.13
f1 (ppm)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7.250
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7.180
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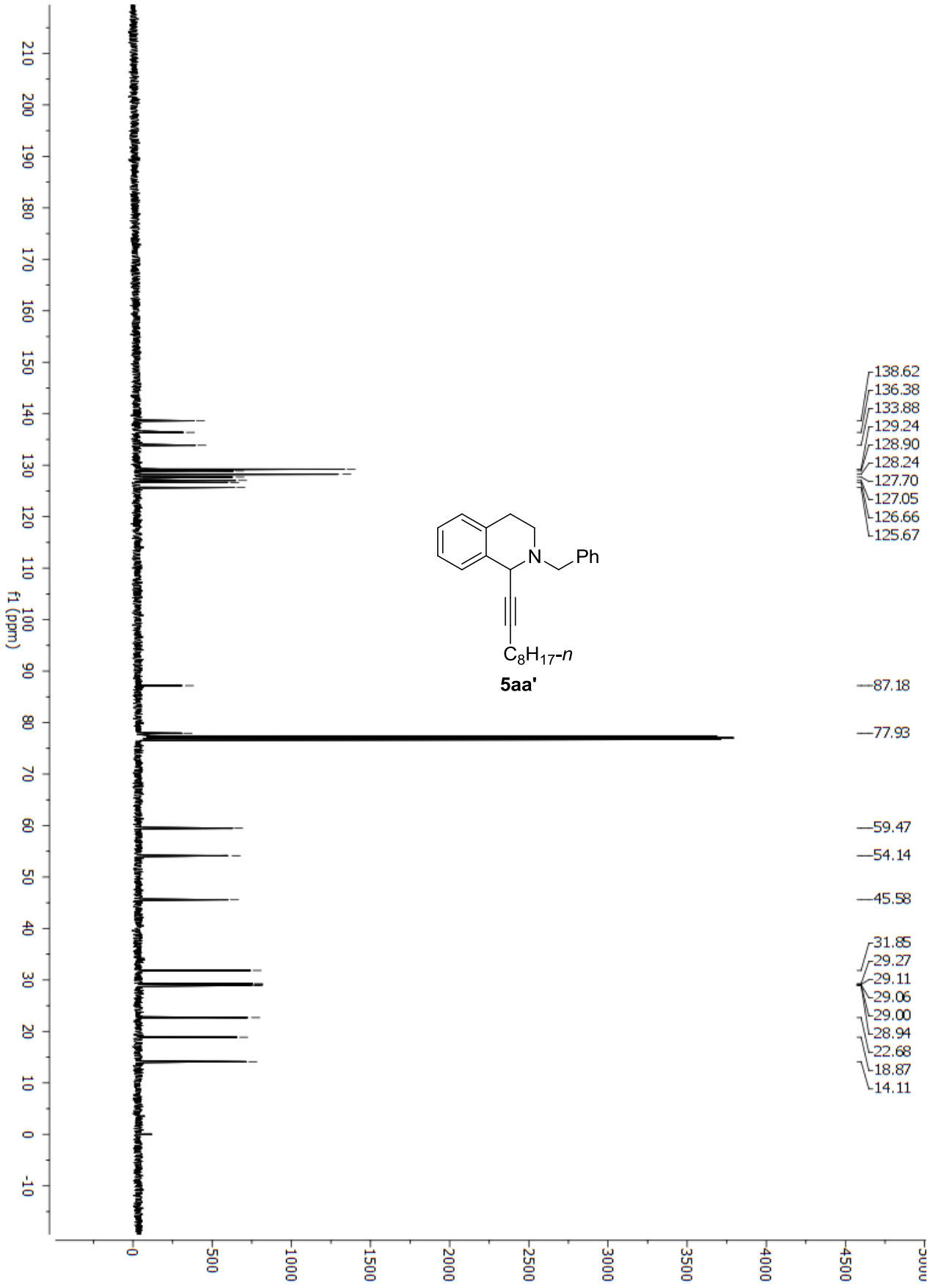
7.145
7.139
7.131
7.122
7.116
7.104
7.094
7.087
7.072
4.546
3.906
3.873
3.819
3.787
2.975
2.775
2.739
2.725
2.233
2.228
2.215
1.545
1.527
1.508
1.273
0.895
0.879
0.861
-0.000
1.88
2.14
0.95
0.97
1.82
1.08
1.00
1.03
1.01
2.02
2.03
2.03
2.07
2.07
8.61
3.12
N
Ph
C8H17-n
5aa'
f1 (ppm)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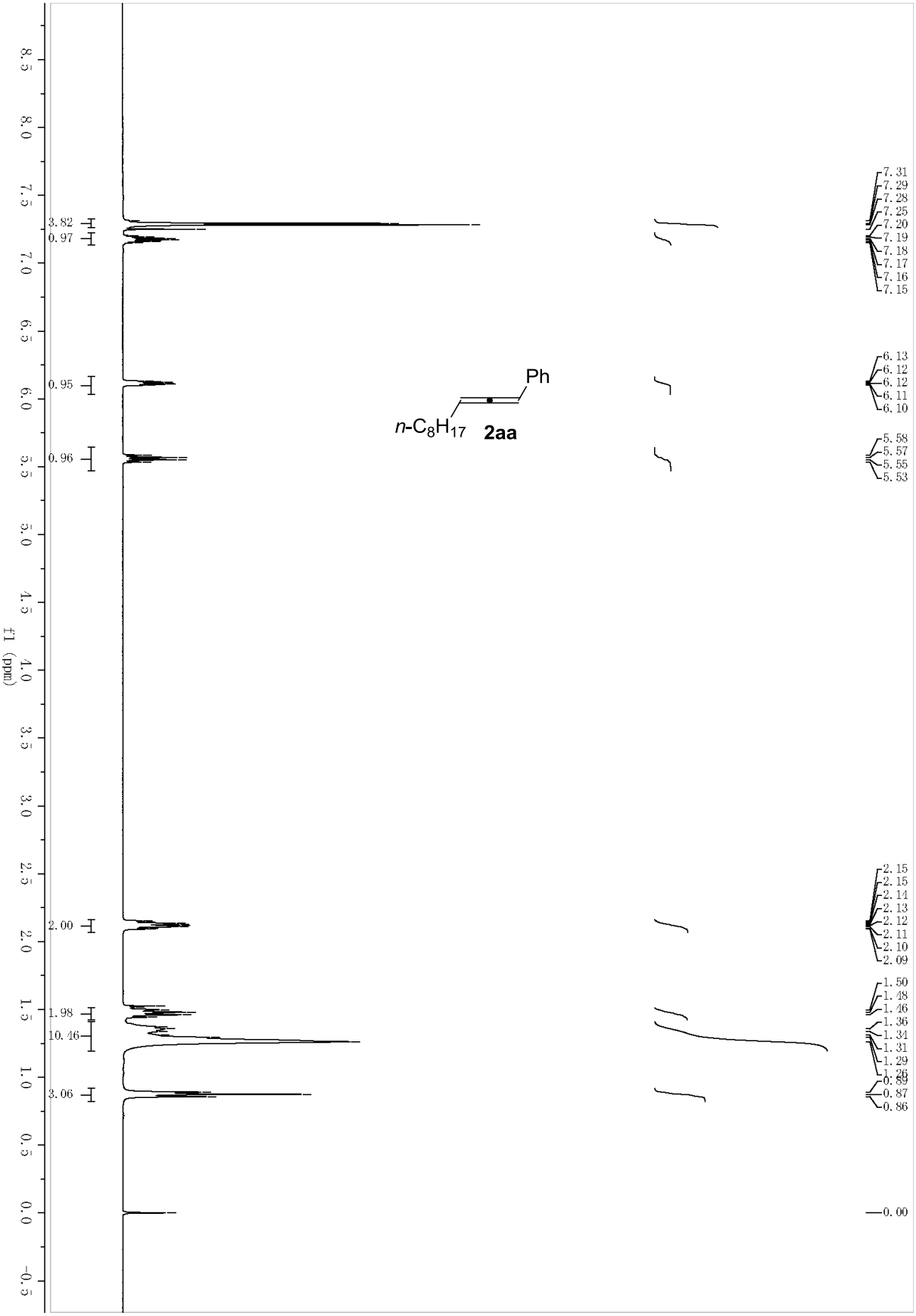
128.24
127.70
127.05
126.66
125.67
87.18
77.93
59.47
54.14
45.58
31.85
29.27
29.11
29.06
29.00
28.94
22.68
18.87
14.11
N
Ph
C8H17-n
5aa'
f1 (ppm)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0.96
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1.98
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3.06
7.31
7.29
7.28
7.25
7.20
7.19
7.18
7.17
7.16
7.15
6.13
6.12
6.12
6.11
6.10
5.58
5.57
5.55
5.53
2.15
2.15
2.14
2.13
2.12
2.11
2.10
2.09
1.50
1.48
1.46
1.36
1.34
1.31
1.29
1.26
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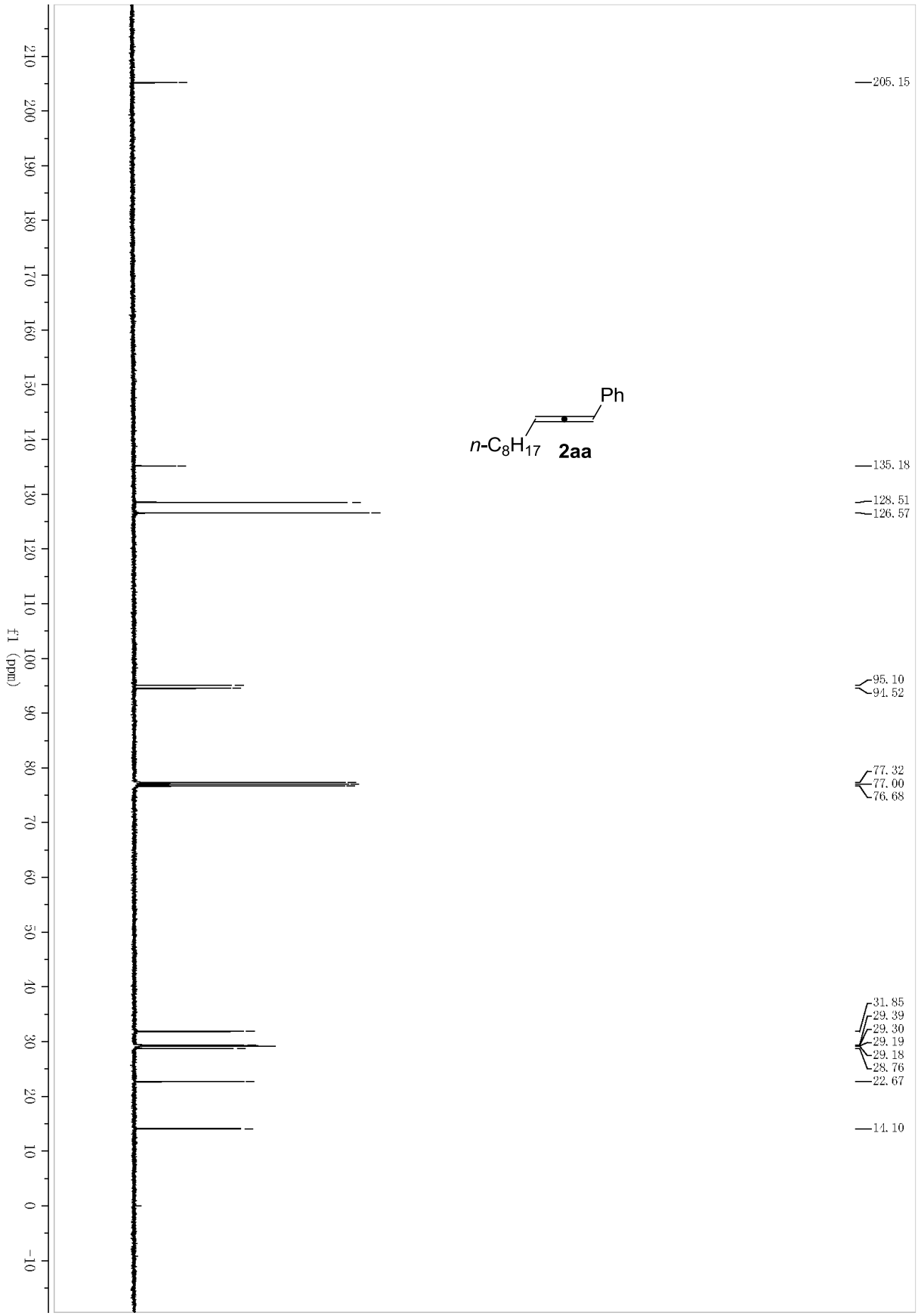
0.86
0.00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2aa
205.15
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95.10
94.52
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29.18
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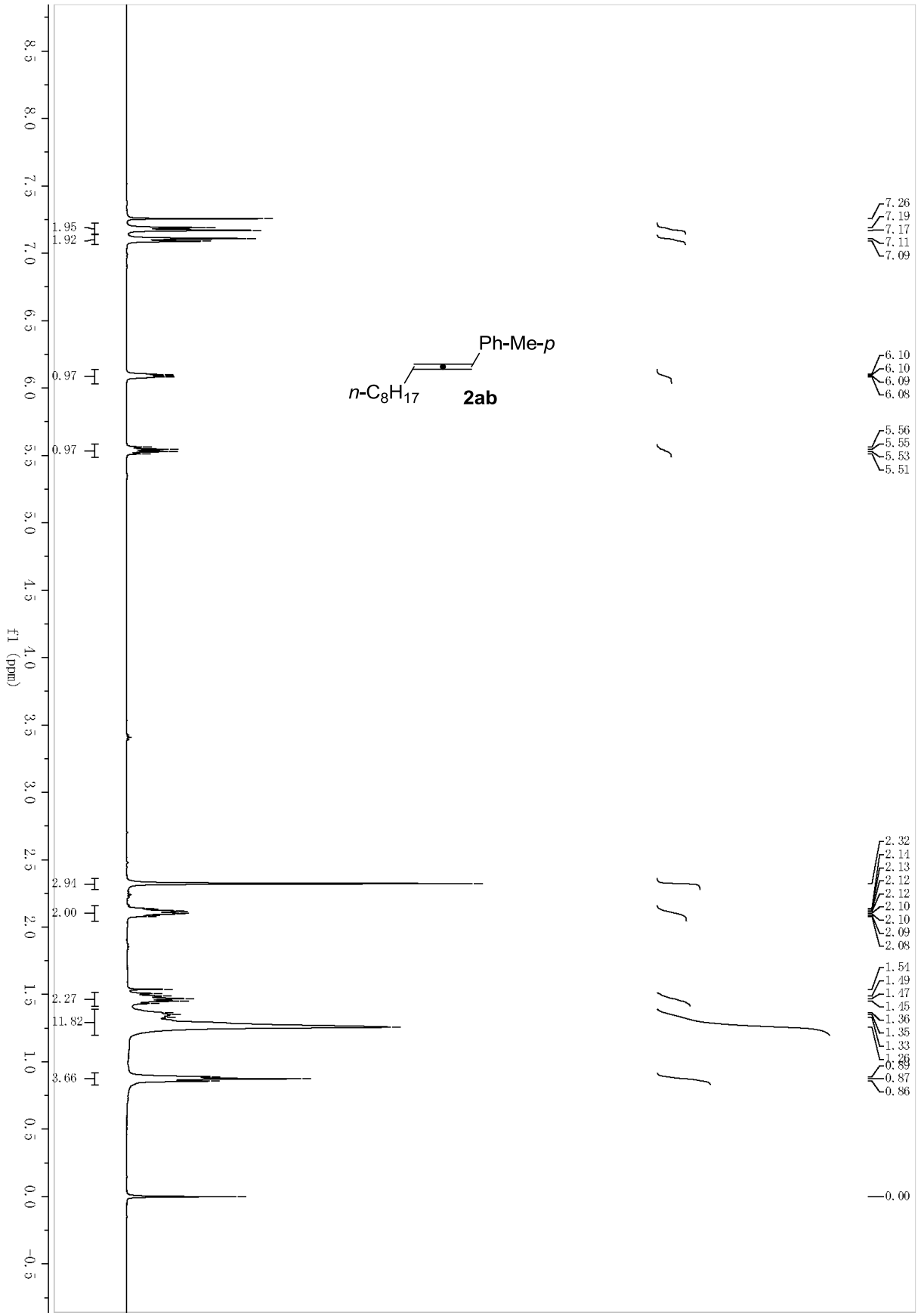
22.67
14.10
f1 (ppm)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3.66
7.26
7.19
7.17
7.11
7.09
6.10
6.10
6.09
6.08
5.56
5.55
5.53
5.51
2.32
2.14
2.13
2.12
2.12
2.10
2.10
2.09
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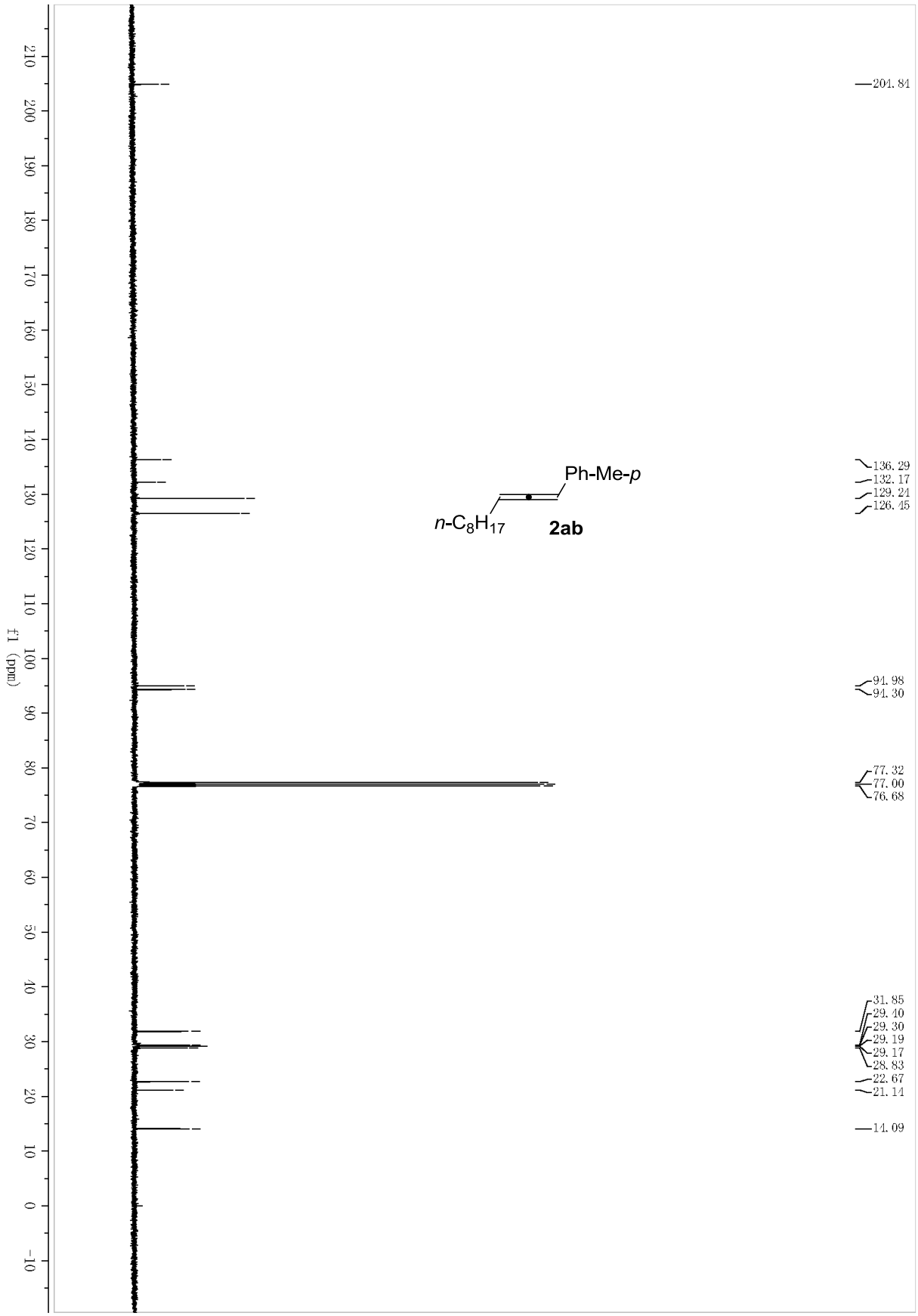
1.49
1.47
1.45
1.36
1.35
1.33
0.89
0.87
0.86
0.00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76.68
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29.40
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29.19
29.17
28.83
22.67
21.14
14.09
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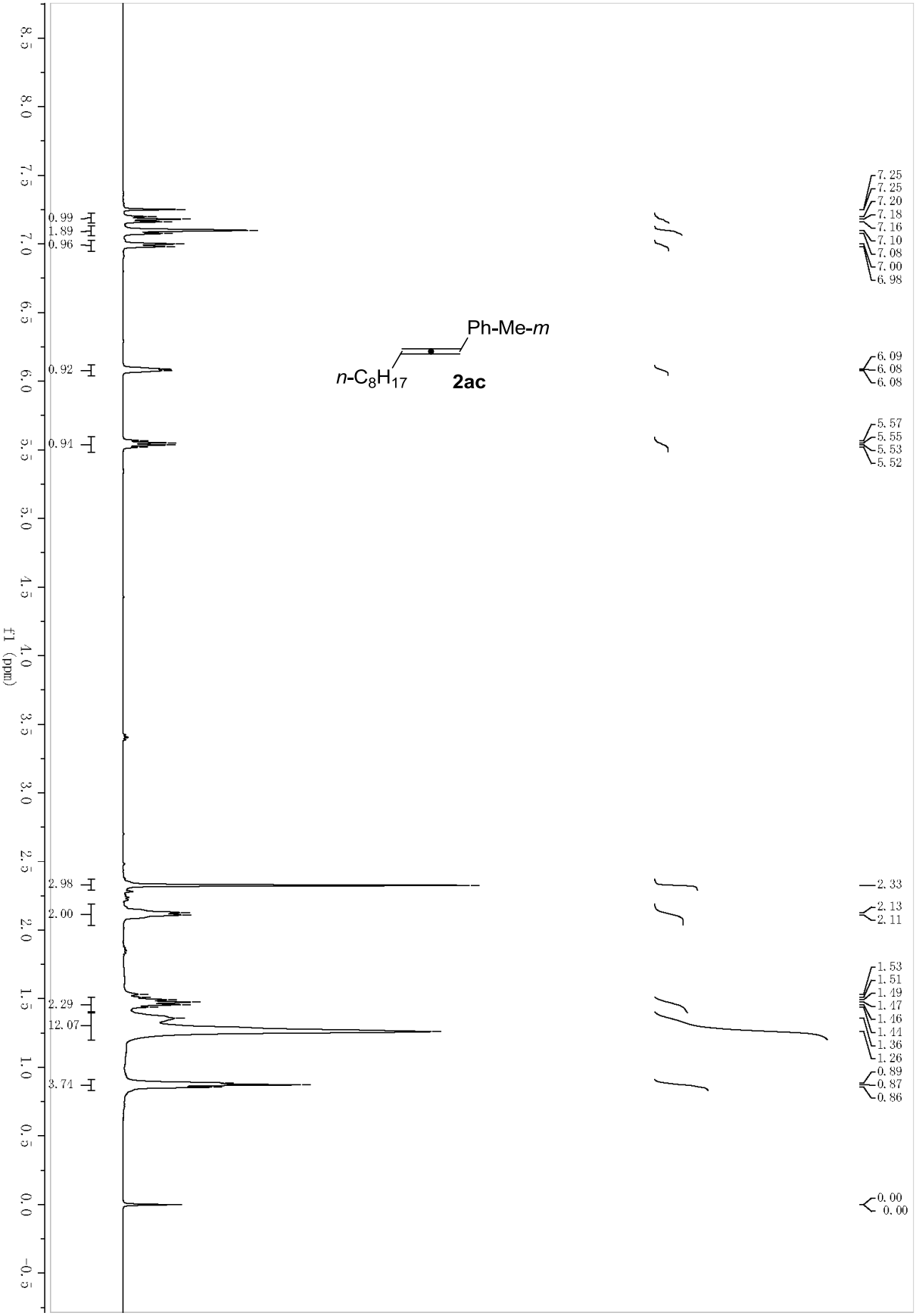
n-C8H17
2ab
f1 (ppm)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2.29
12.07
3.74
7.25
7.25
7.20
7.18
7.16
7.10
7.08
7.00
6.98
6.09
6.08
6.08
5.57
5.55
5.53
5.52
2.33
2.13
2.11
1.53
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1.46
1.44
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1.26
0.89
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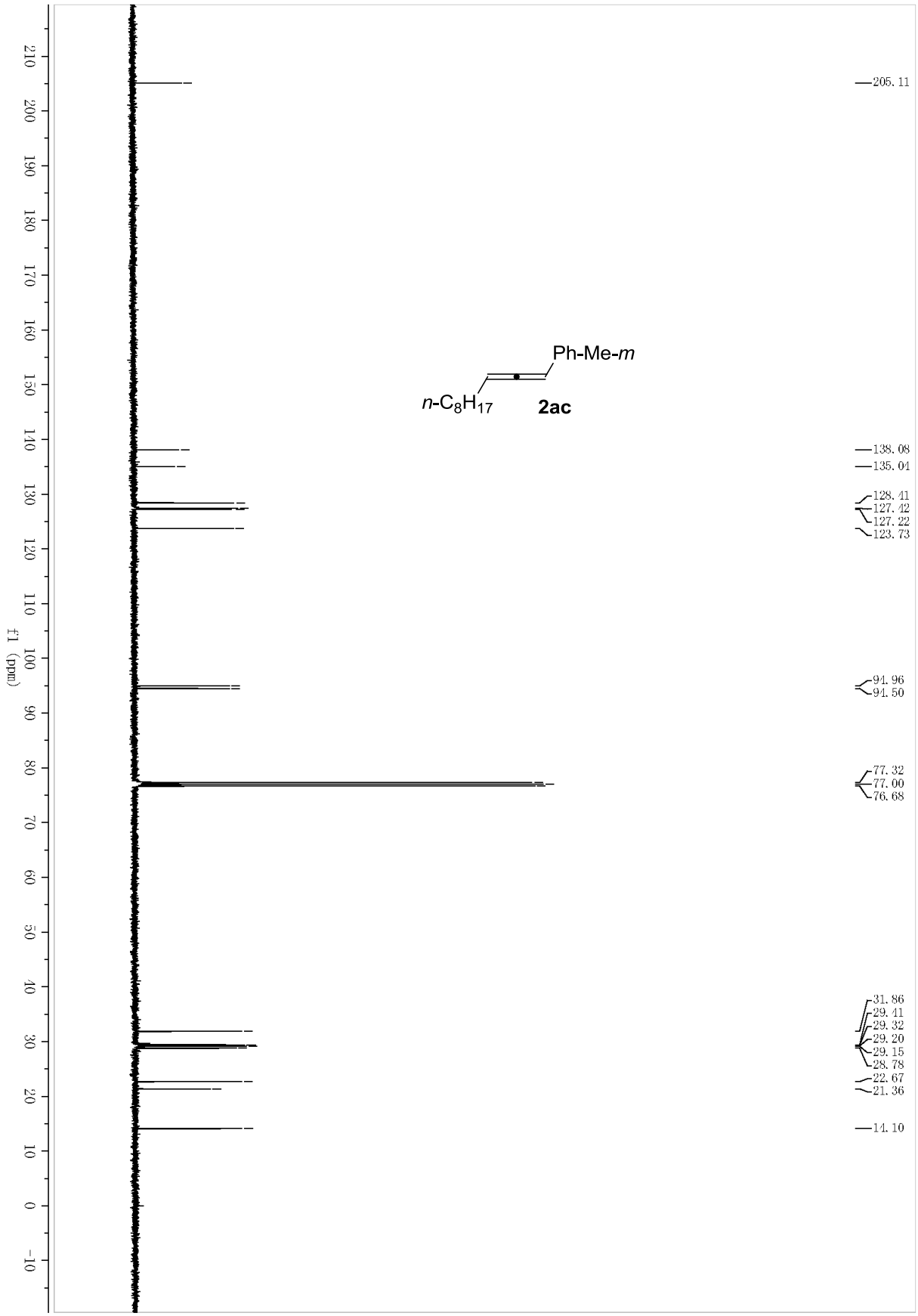
0.00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77.00
76.68
31.86
29.41
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21.36
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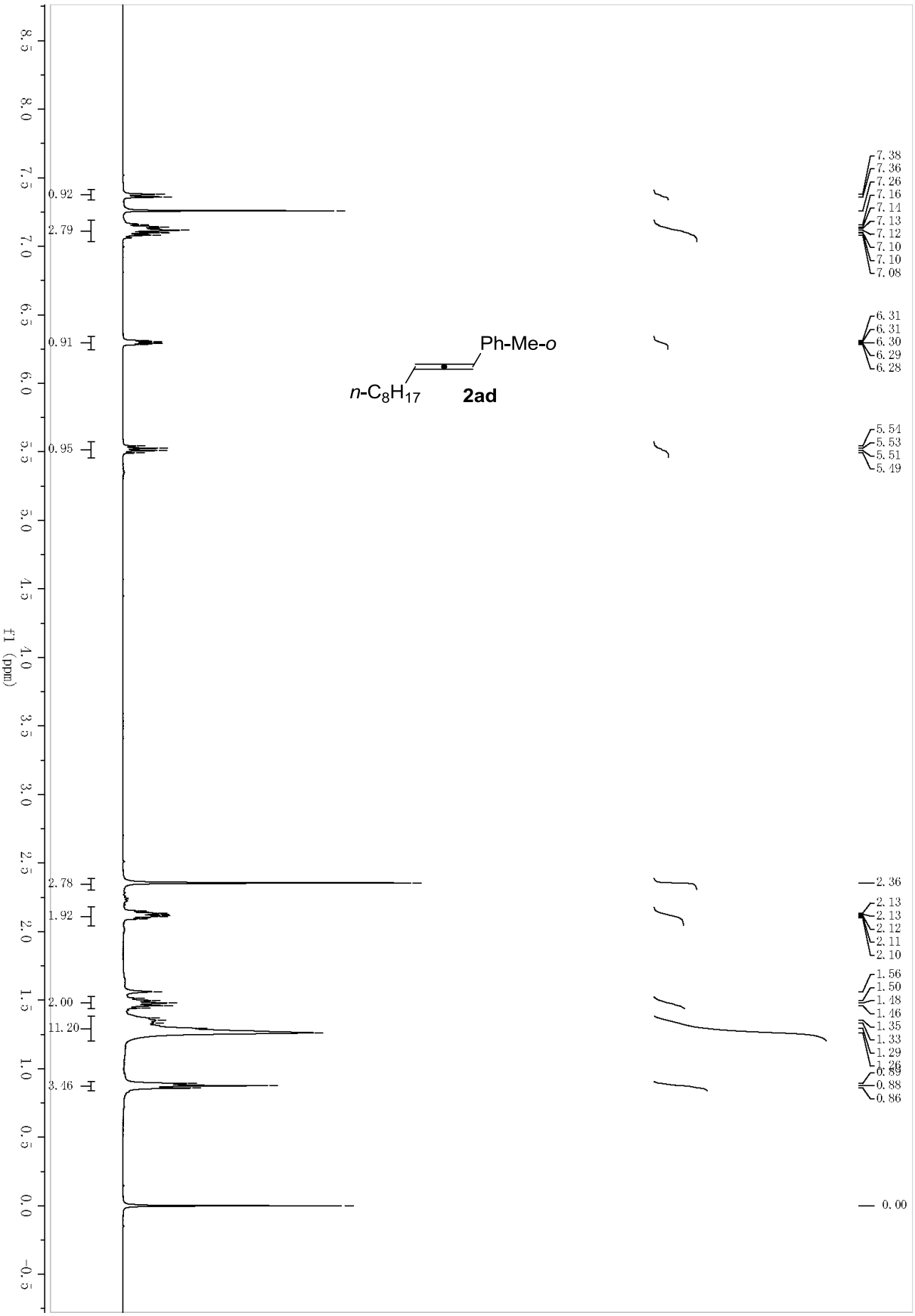
2ac
f1 (ppm)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3.46
7.38
7.36
7.26
7.16
7.14
7.13
7.12
7.10
7.10
7.08
6.31
6.31
6.30
6.29
6.28
5.54
5.53
5.51
5.49
2.36
2.13
2.13
2.12
2.11
2.10
1.56
1.50
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1.33
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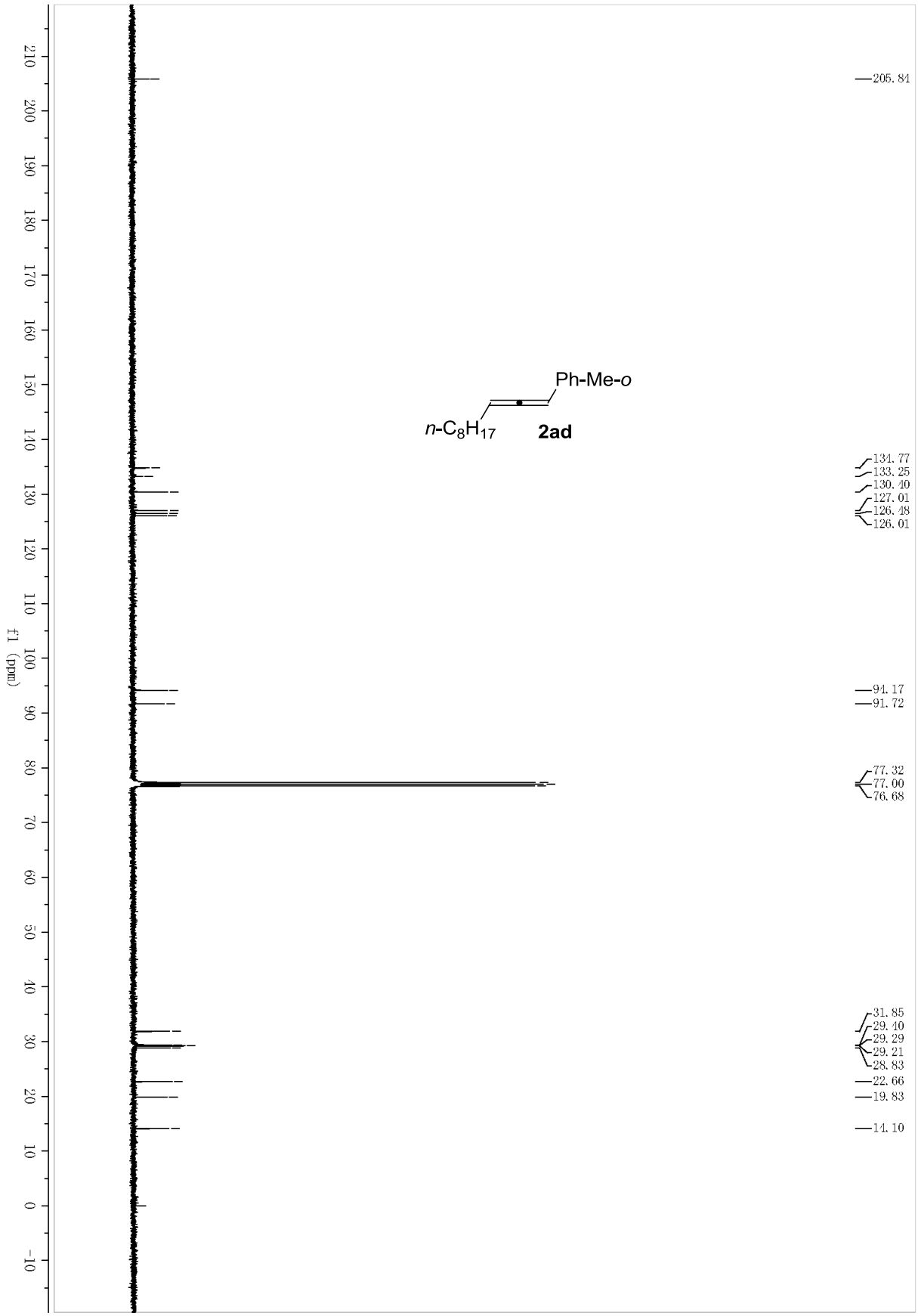
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31.85
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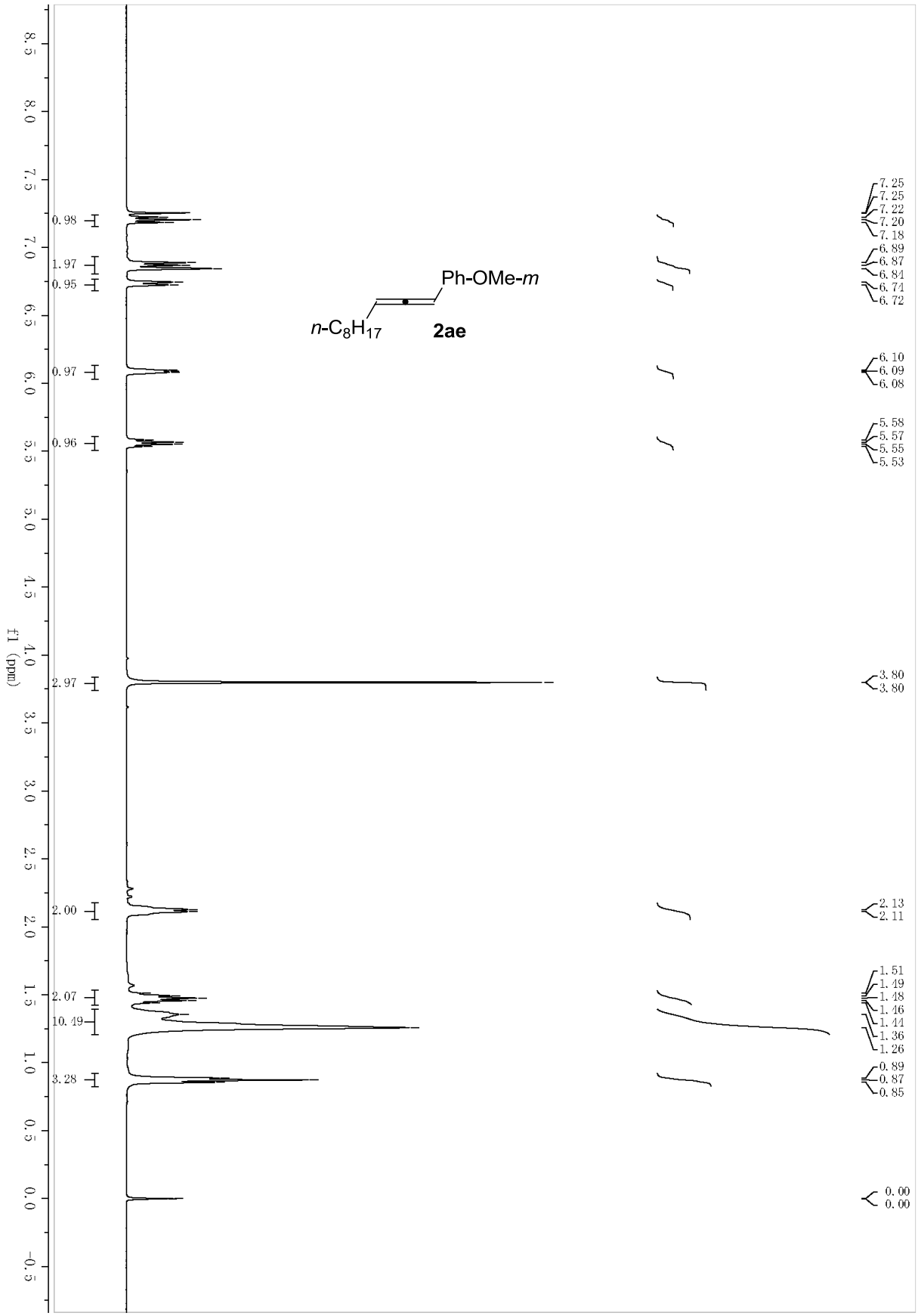
Ph-Me-o
n-C8H17
2ad
f1 (ppm)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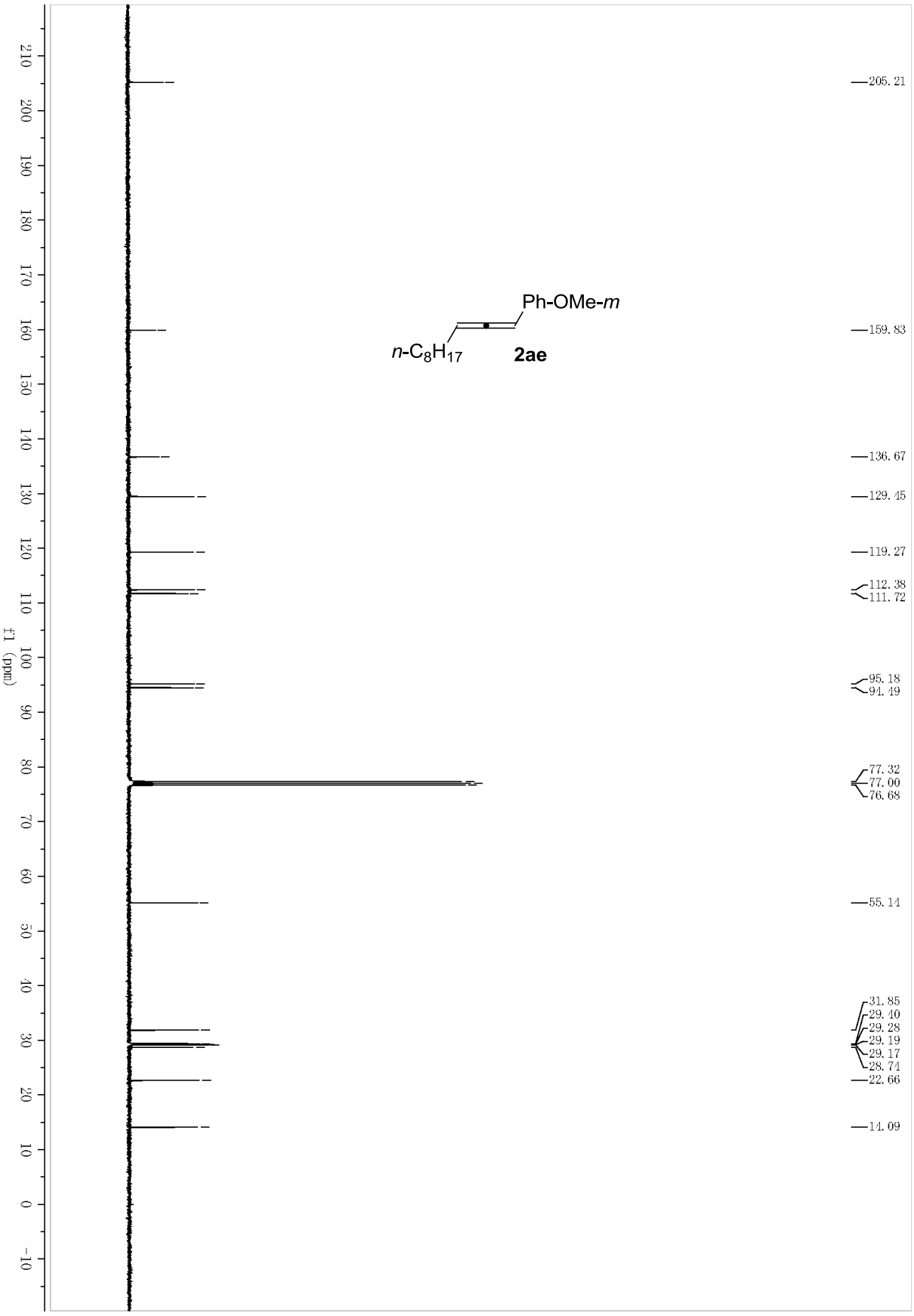
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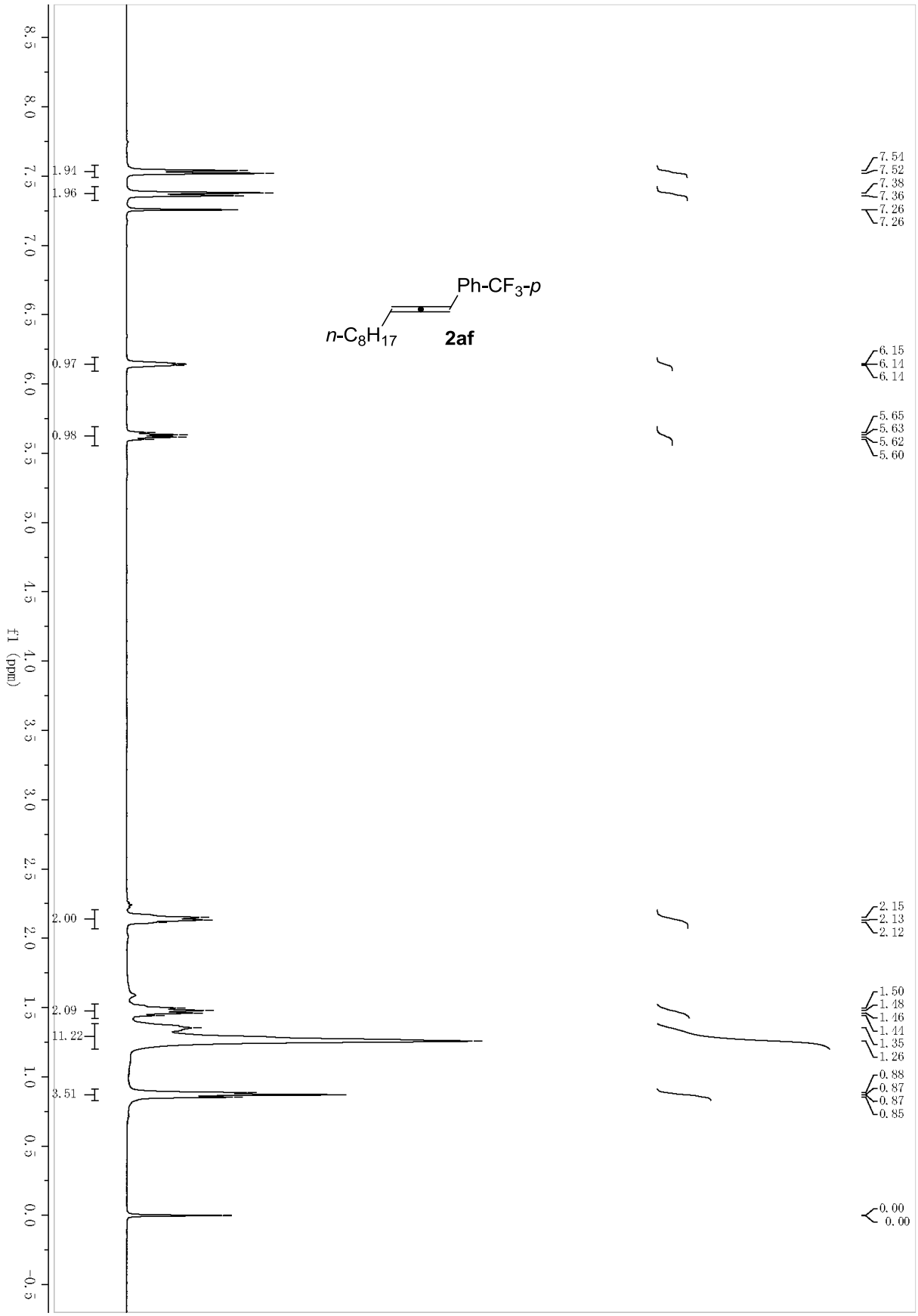
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3.51
7.54
7.52
7.38
7.36
7.26
7.26
6.15
6.14
6.14
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5.63
5.62
5.60
2.15
2.13
2.12
1.50
1.48
1.46
1.44
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1.26
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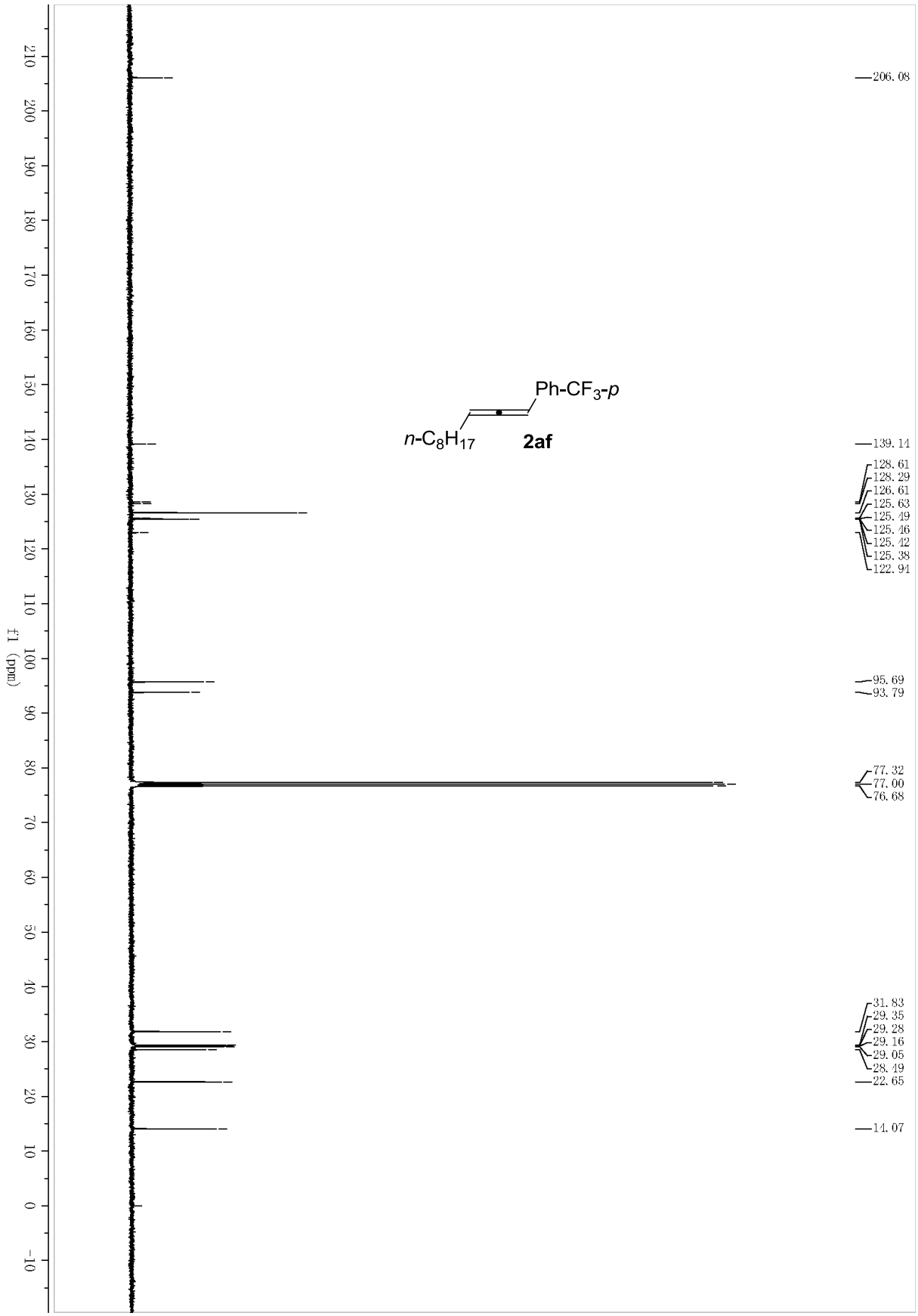
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125.42
125.38
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93.79
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77.00
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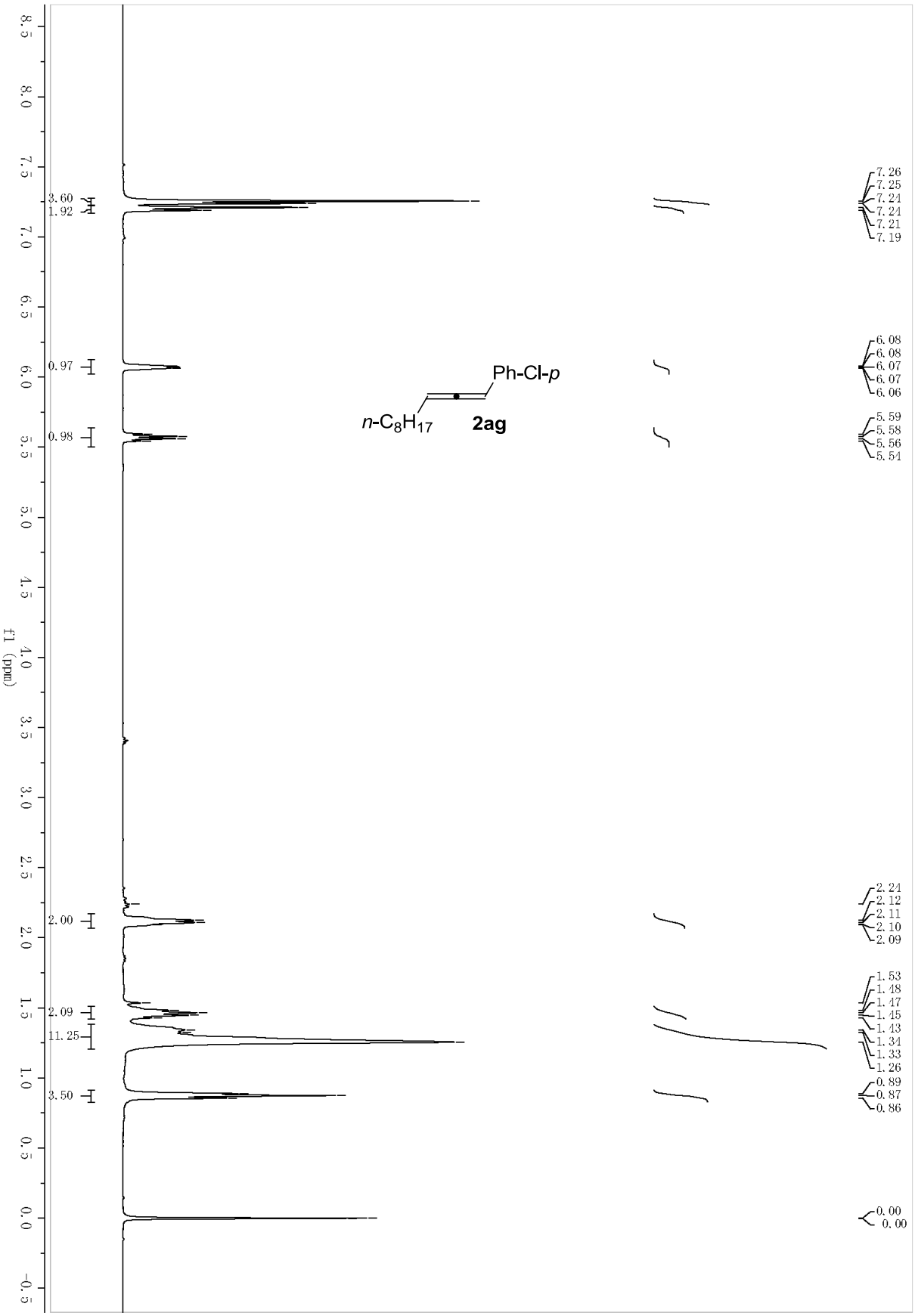
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6.08
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1.26
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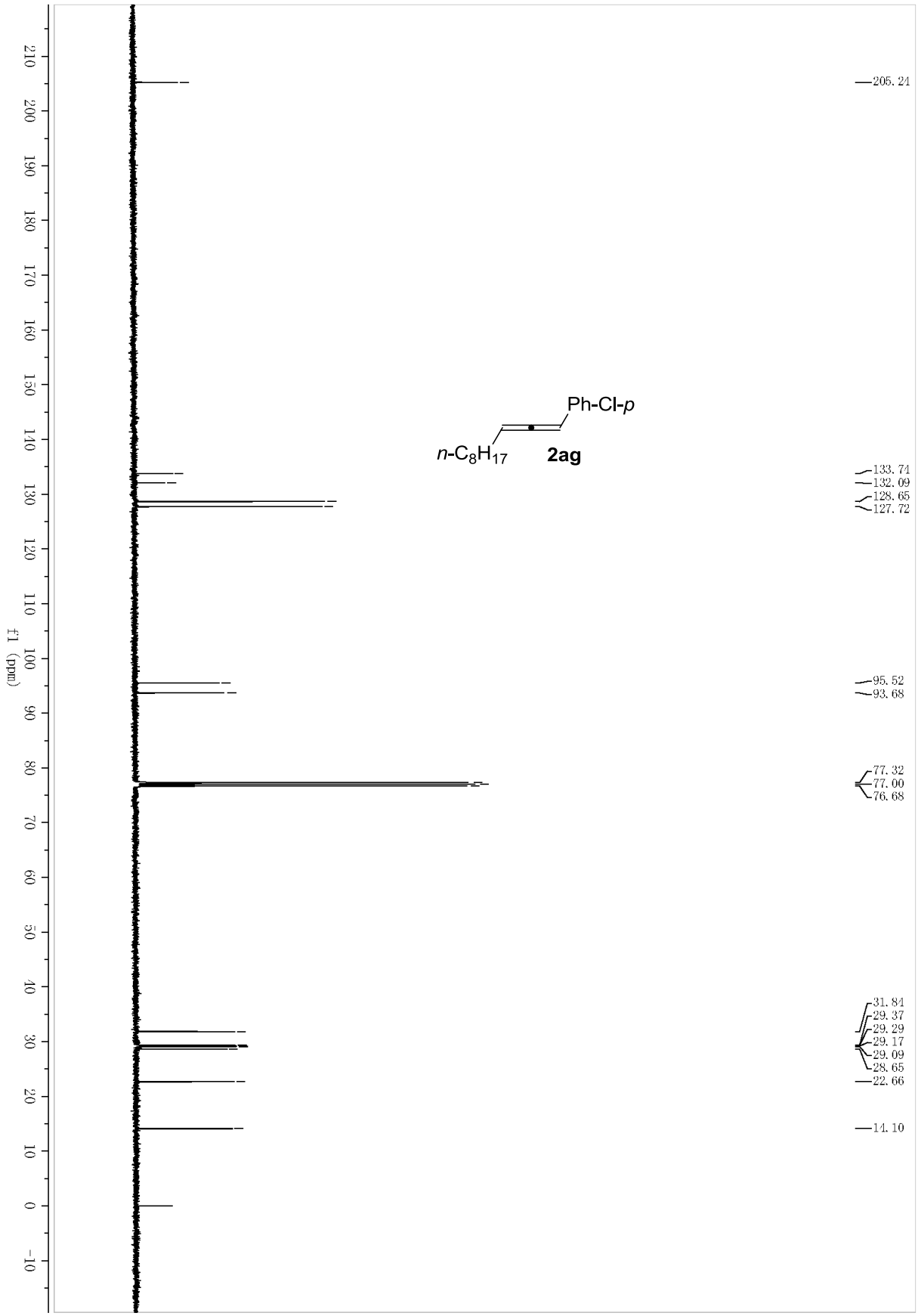
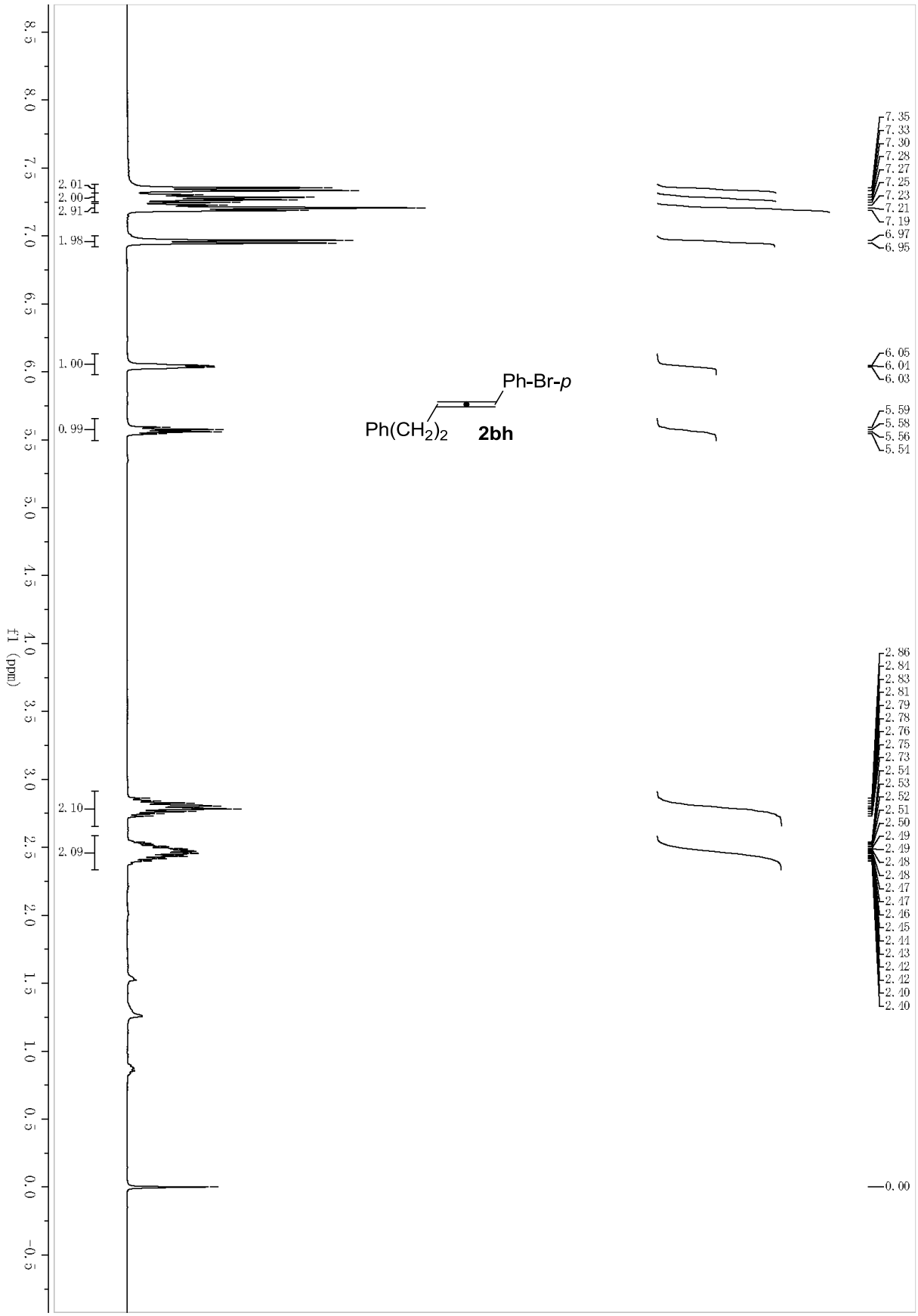
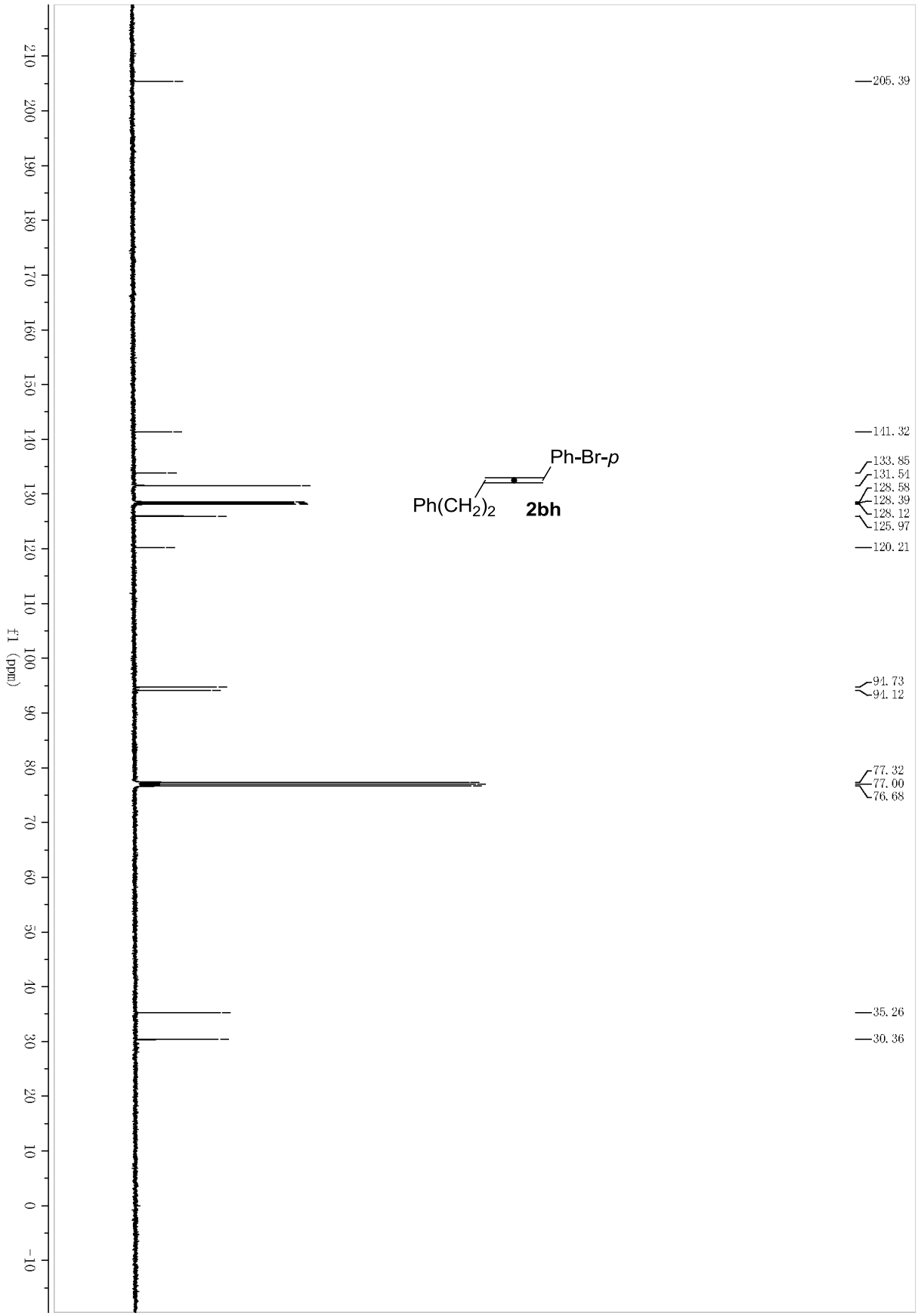
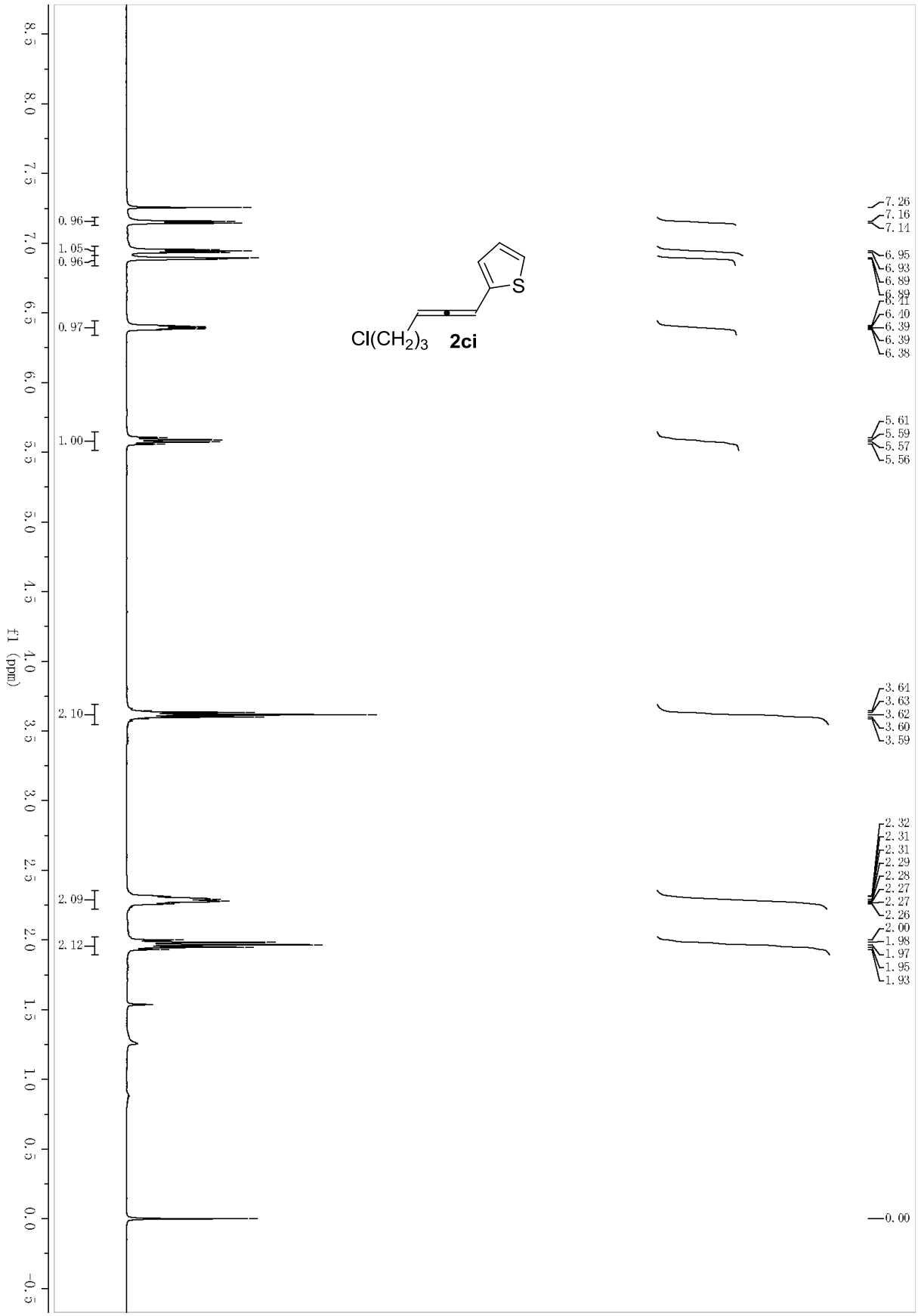
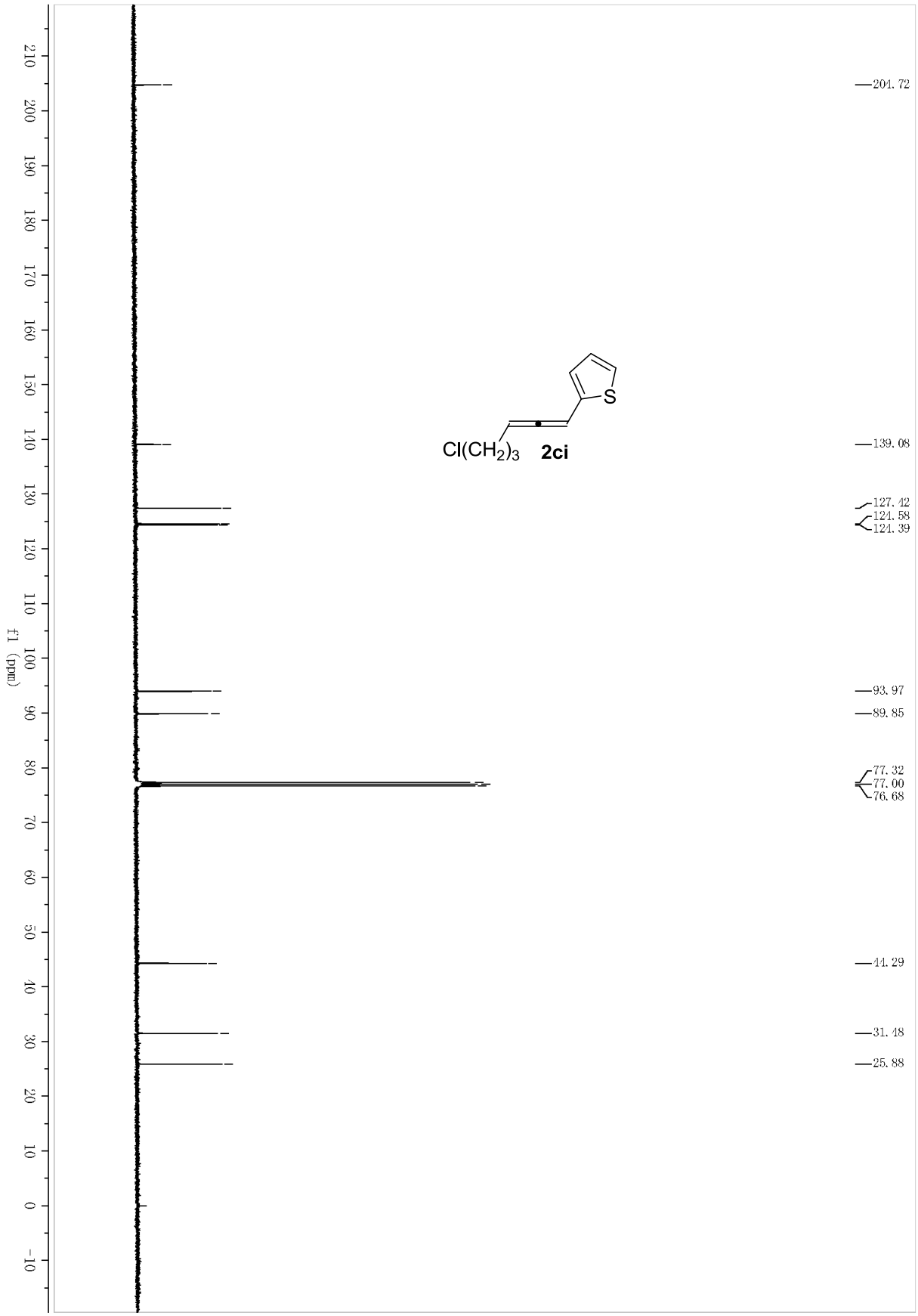
0.00
0.00

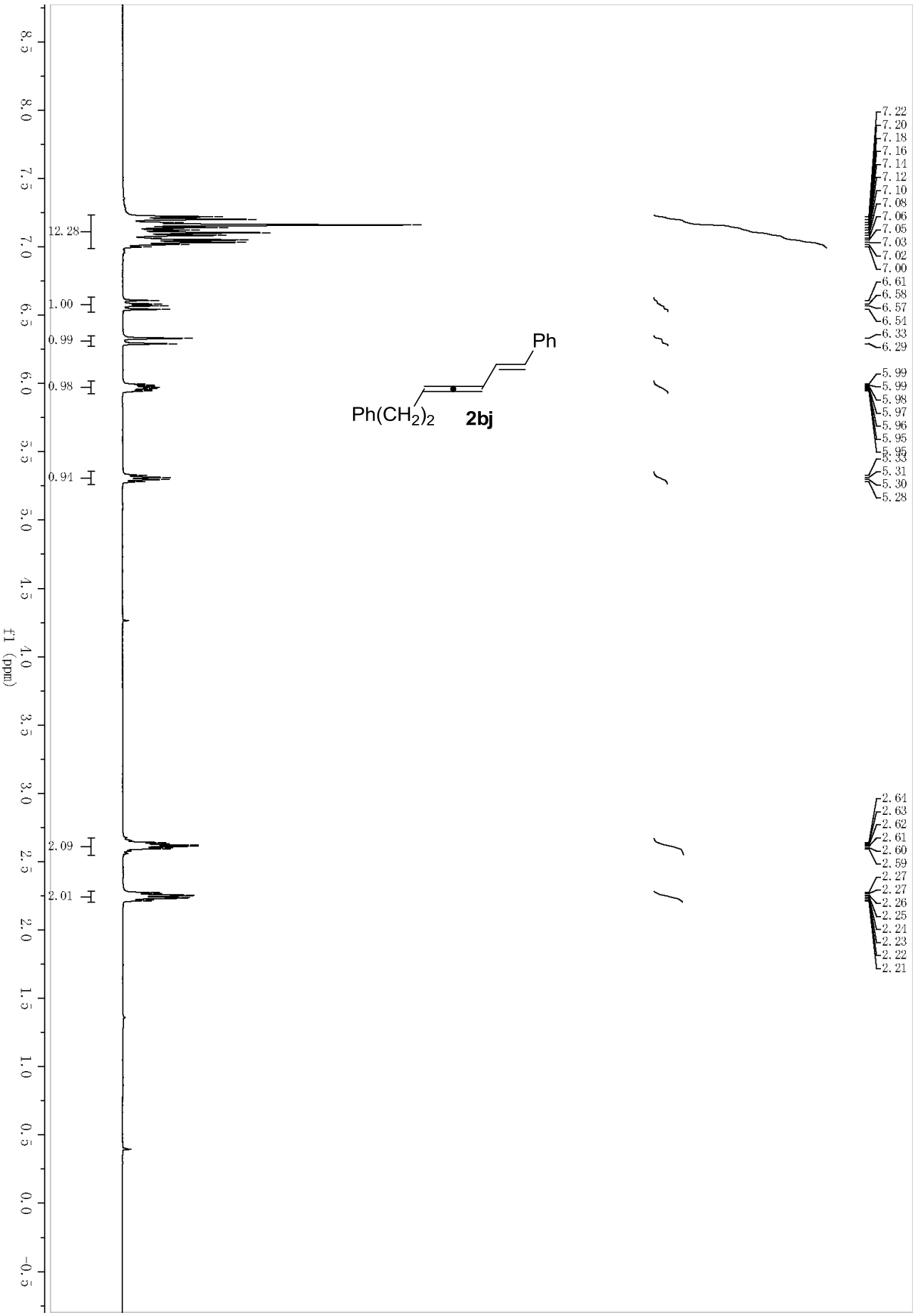

205.24
133.74
132.09
128.65
127.72
95.52
93.68
77.32
77.00
76.68
31.84
29.37
29.29
29.17
29.09
28.65
22.66
14.10
Ph-Cl-p
n-C8H17
2ag
f1 (ppm)

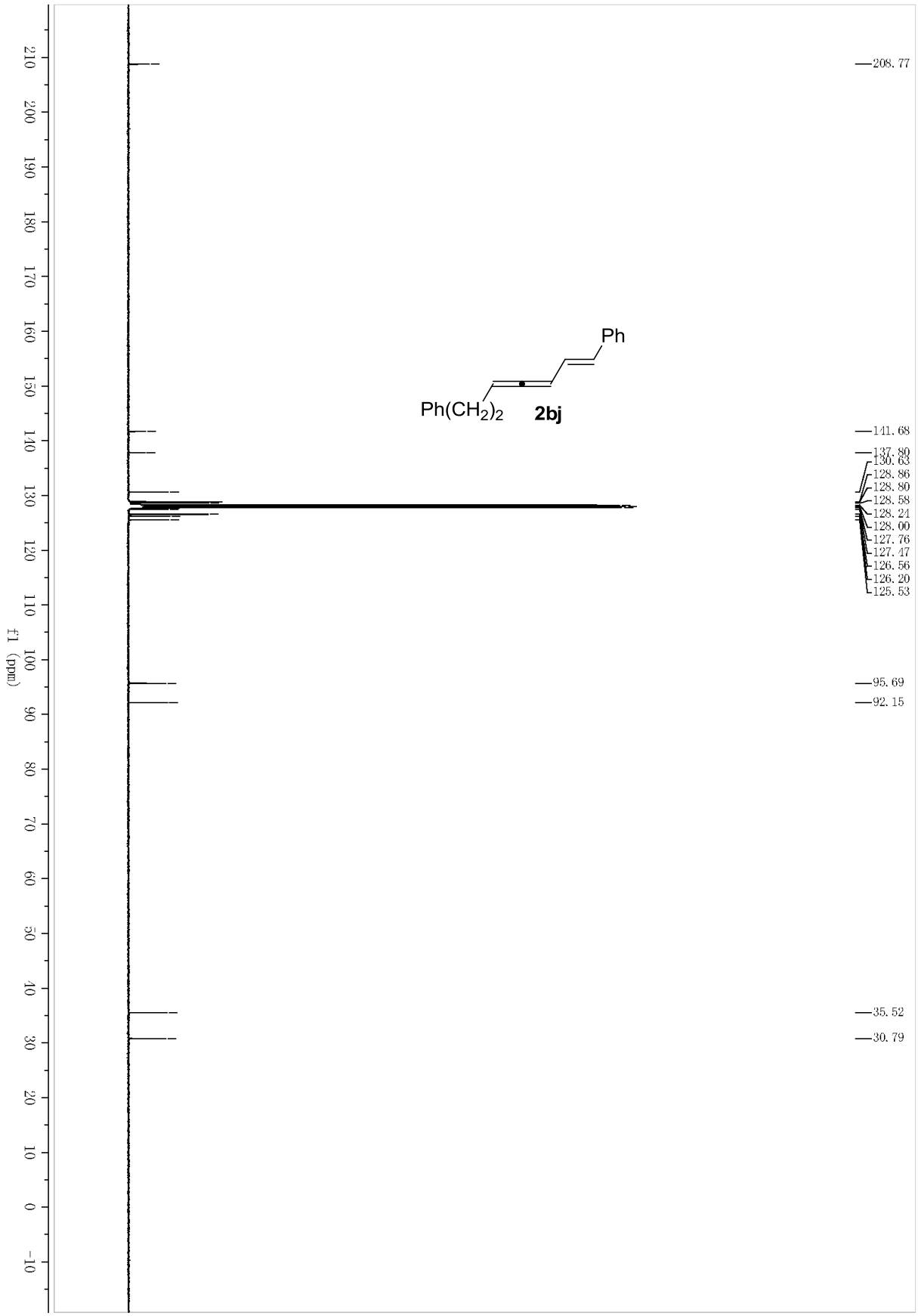

Ph-Br-p
Ph(CH2)2
2bh
f1 (ppm)
2.01
2.00
2.91
1.98
1.00
0.99
2.10
2.09
7.35
7.33
7.30
7.28
7.27
7.25
7.23
7.21
7.19
6.97
6.95
6.05
6.04
6.03
5.59
5.58
5.56
5.54
2.86
2.84
2.83
2.81
2.79
2.78
2.76
2.75
2.73
2.54
2.53
2.52
2.51
2.50
2.49
2.49
2.48
2.48
2.47
2.47
2.46
2.45
2.44
2.43
2.42
2.42
2.40
2.40
0.00

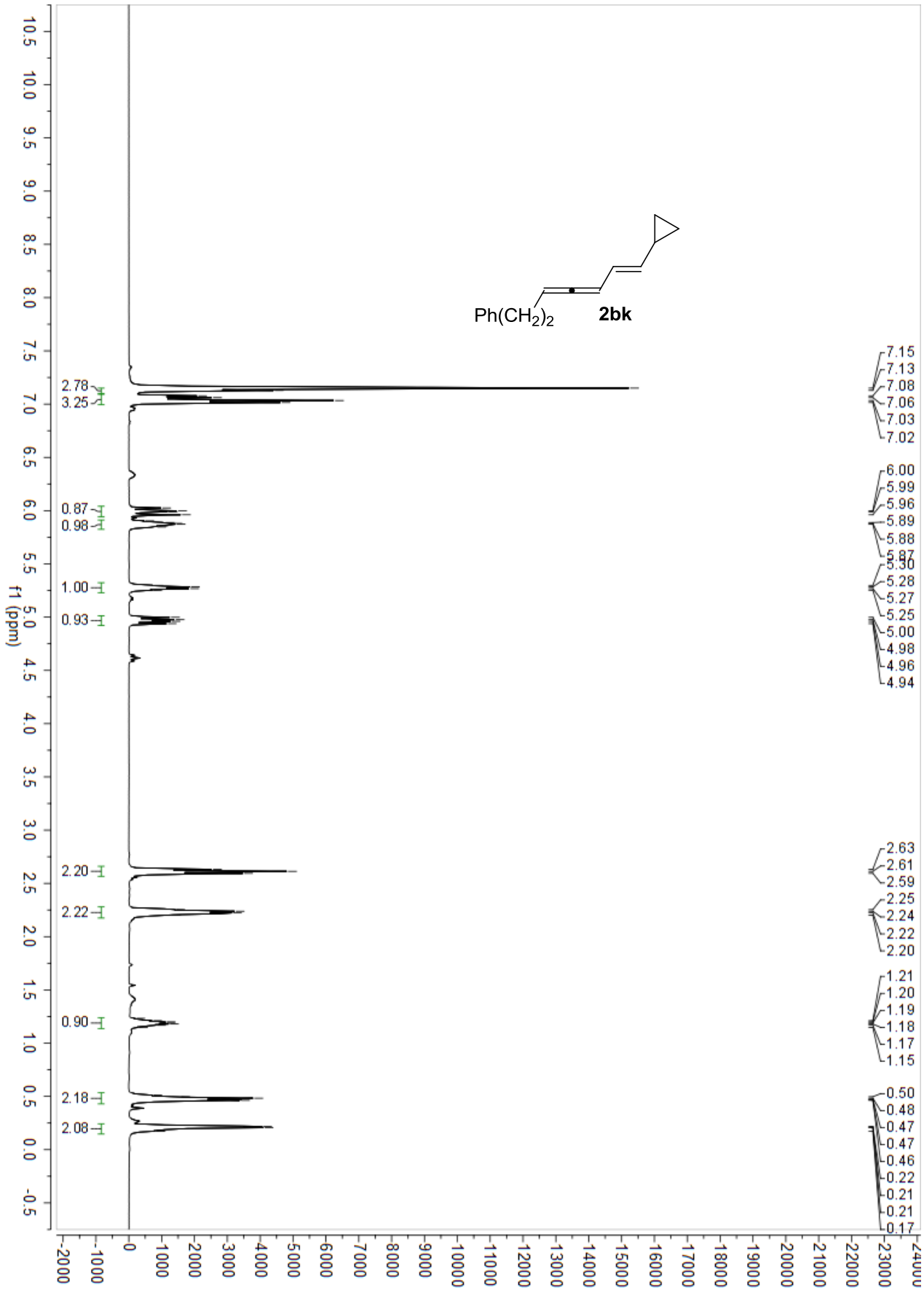

205.39
141.32
133.85
131.54
128.58
128.39
128.12
125.97
120.21
94.73
94.12
77.32
77.00
76.68
35.26
30.36
Ph-Br-p
Ph(CH2)2
2bh
f1 (ppm)

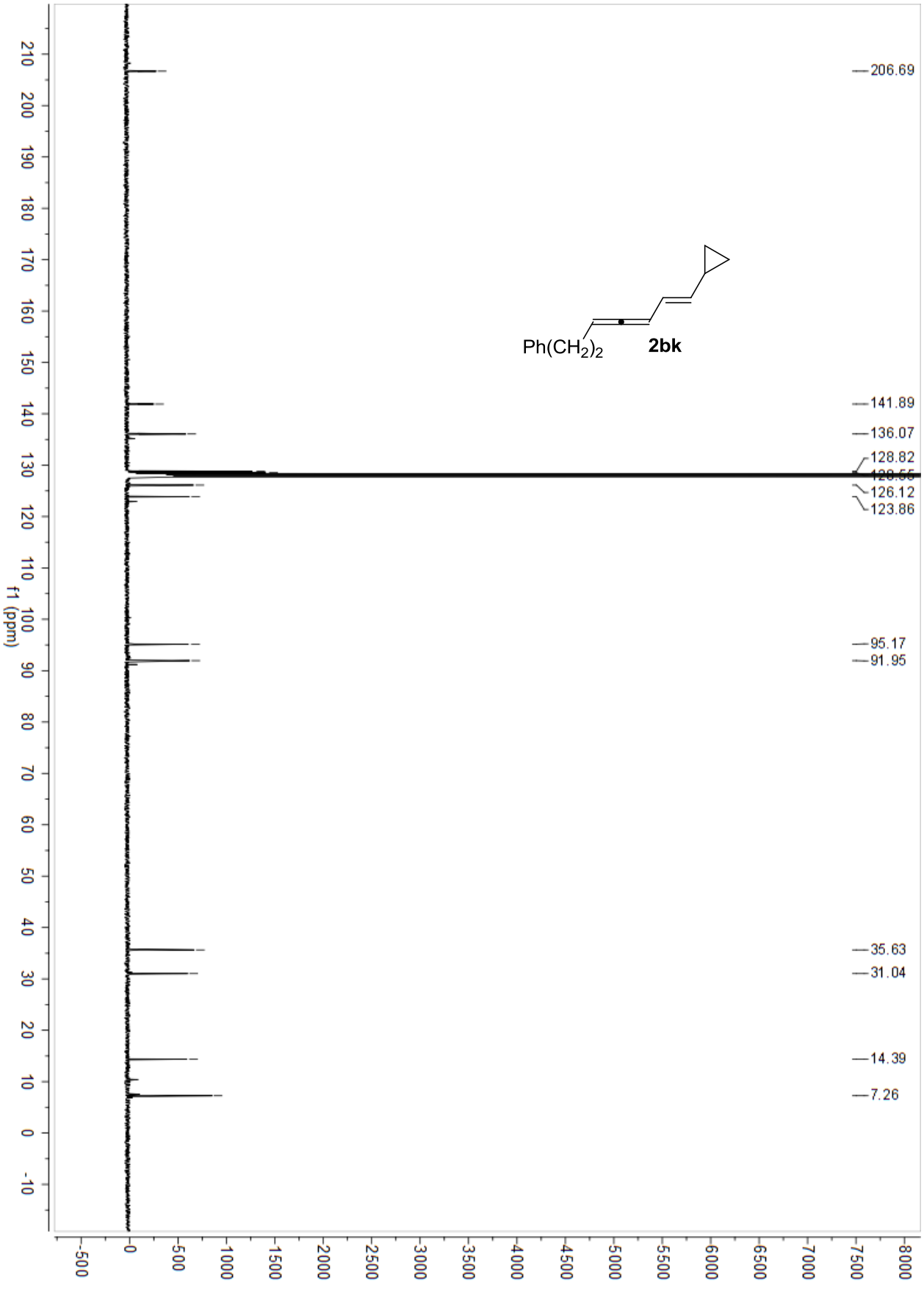

f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0.96
1.05
0.96
0.97
1.00
2.10
2.09
2.12
S
Cl(CH2)3
2ci
7.26
7.16
7.14
6.95
6.93
6.89
6.89
6.41
6.40
6.39
6.39
6.38
5.61
5.59
5.57
5.56
3.64
3.63
3.62
3.60
3.59
2.32
2.31
2.31
2.29
2.28
2.27
2.27
2.26
2.00
1.98
1.97
1.95
1.93
0.00

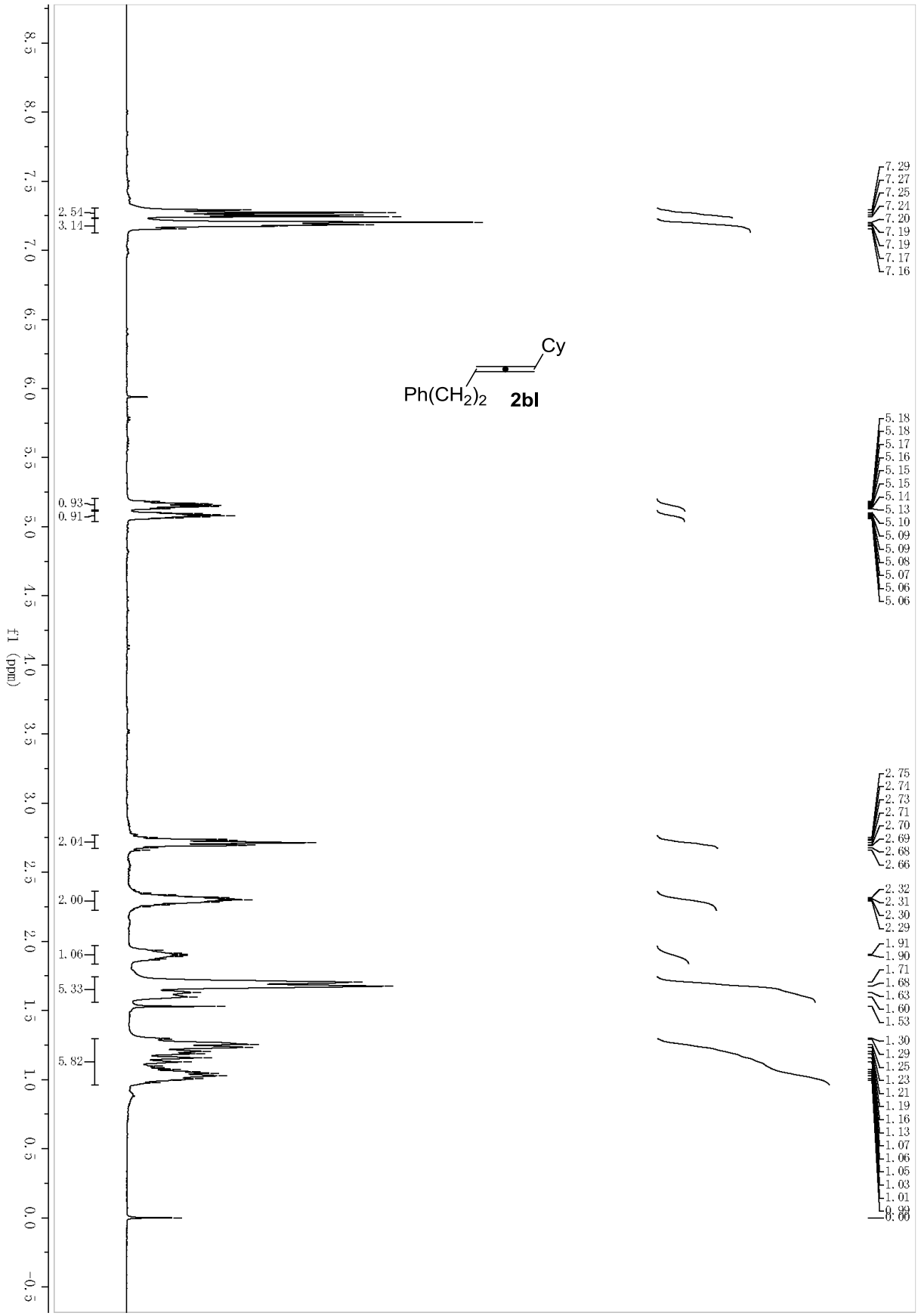

204.72
139.08
127.42
124.58
124.39
93.97
89.85
77.32
77.00
76.68
44.29
31.48
25.88
f1 (ppm)
Cl(CH2)3
2ci
S

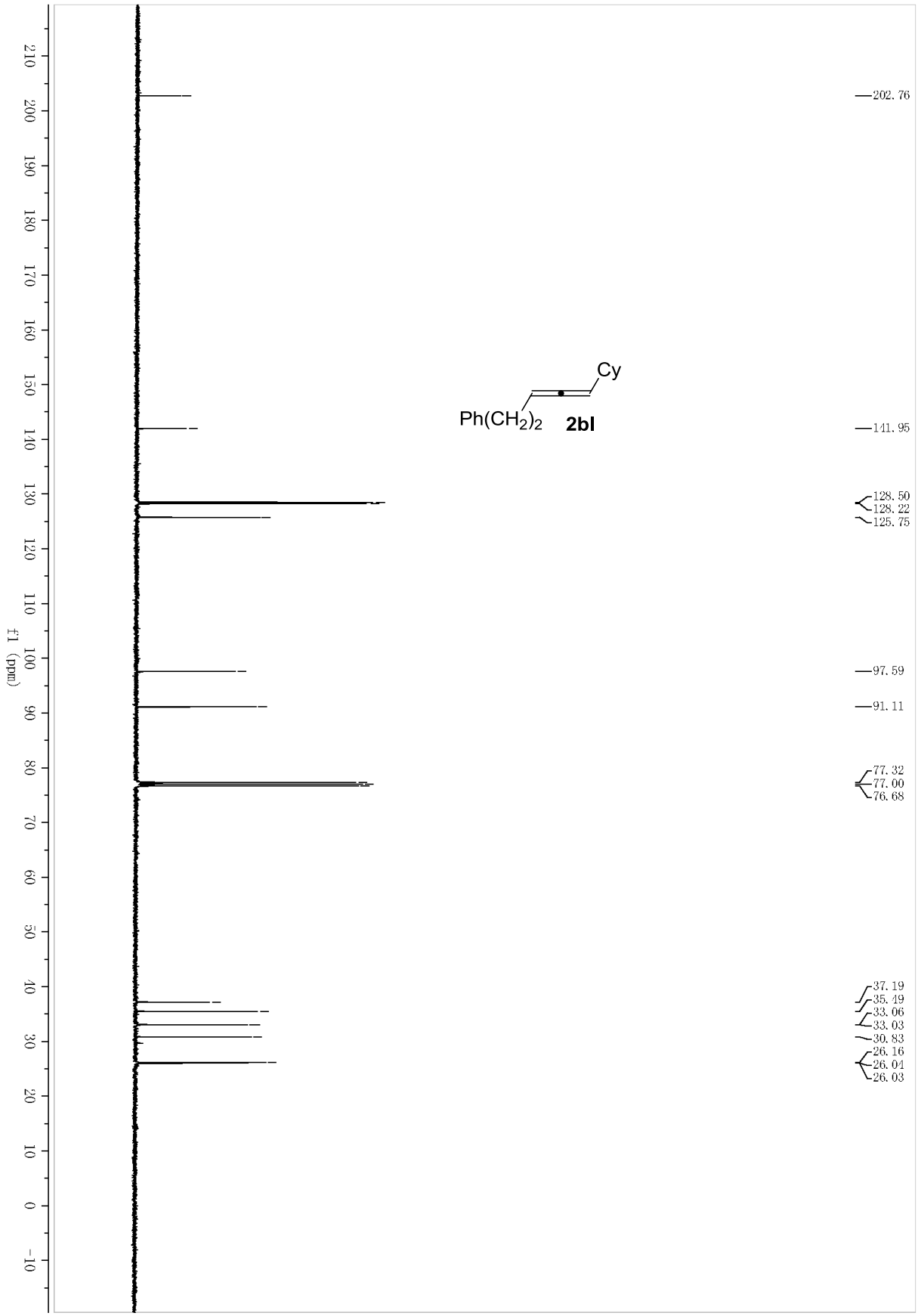

Ph
Ph(CH2)2
2bj
f1 (ppm)
12.28
1.00
0.99
0.98
0.94
2.09
2.01
7.22
7.20
7.18
7.16
7.14
7.12
7.10
7.08
7.06
7.05
7.03
7.02
7.00
6.61
6.58
6.57
6.54
6.33
6.29
5.99
5.99
5.98
5.97
5.96
5.95
5.95
5.33
5.31
5.30
5.28
2.64
2.63
2.62
2.61
2.60
2.59
2.27
2.27
2.26
2.25
2.24
2.23
2.22
2.21

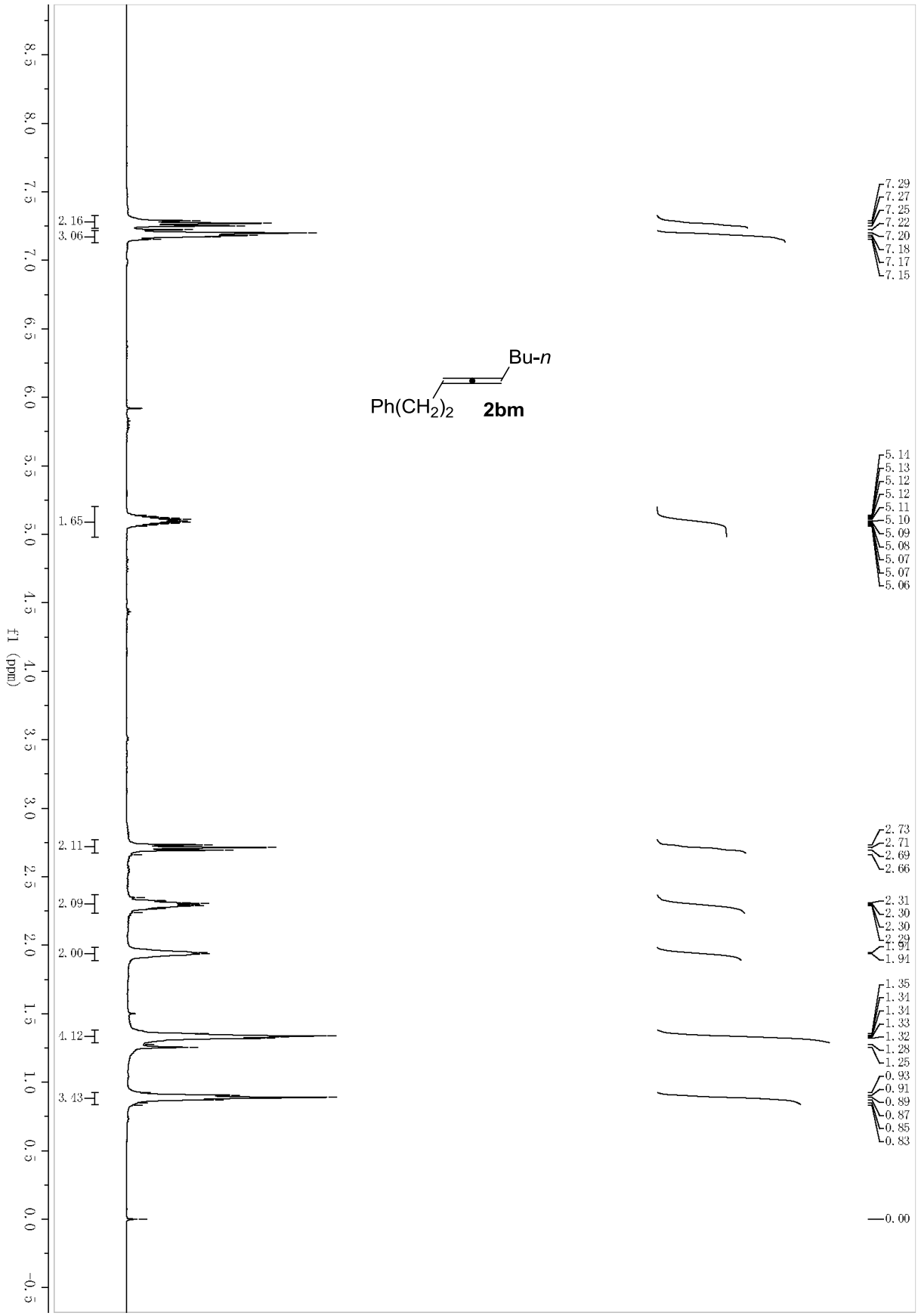

208.77
141.68
137.80
130.63
128.86
128.80
128.58
128.24
128.00
127.76
127.47
126.56
126.20
125.53
95.69
92.15
35.52
30.79
f1 (ppm)
Ph
Ph(CH2)2
2bj

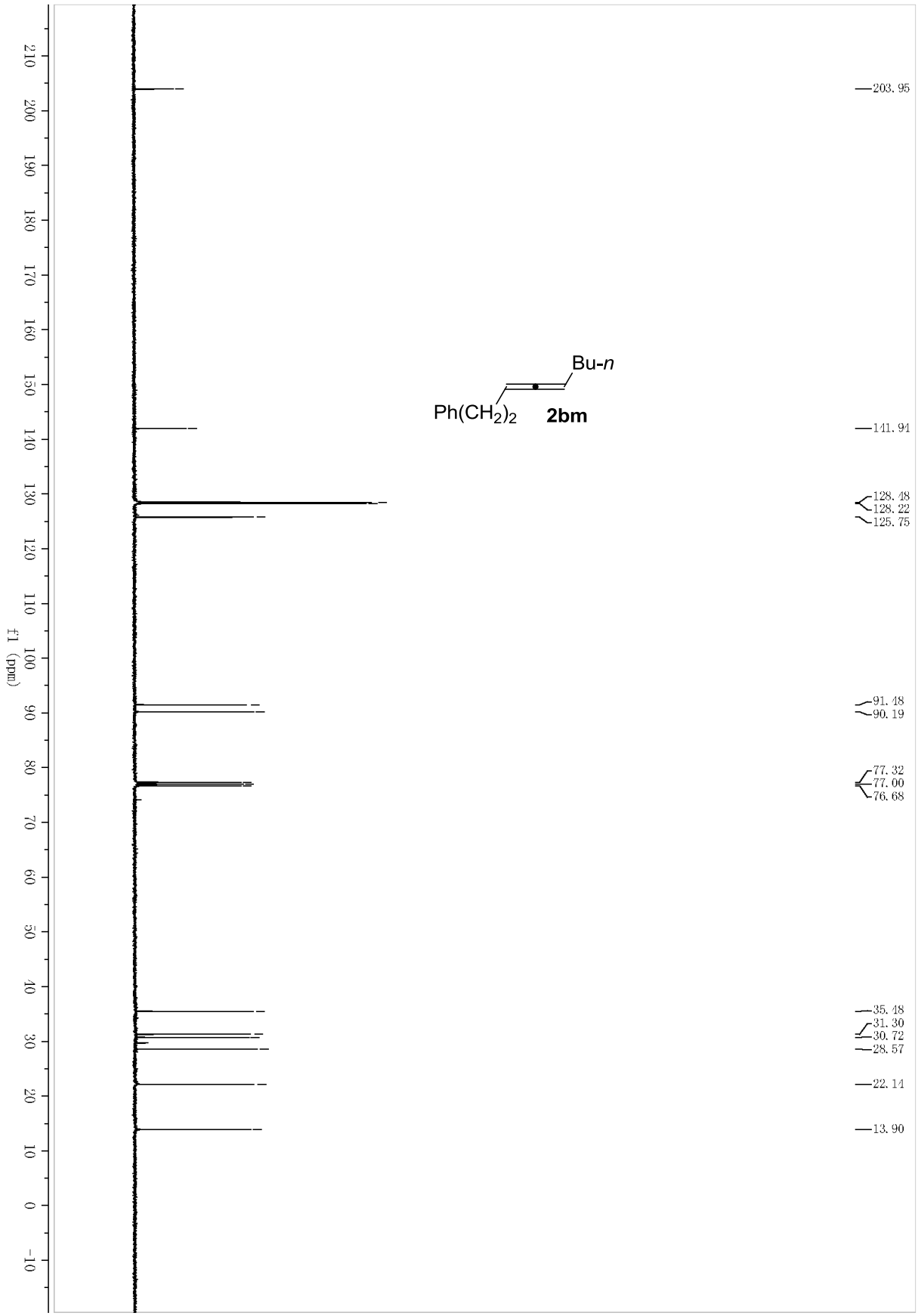

Ph(CH2)2
2bk
f1 (ppm)
2.78
3.25
0.87
0.98
1.00
0.93
2.20
2.22
0.90
2.18
2.08
7.15
7.13
7.08
7.06
7.03
7.02
6.00
5.99
5.96
5.89
5.88
5.87
5.30
5.28
5.27
5.25
5.00
4.98
4.96
4.94
2.63
2.61
2.59
2.25
2.24
2.22
2.20
1.21
1.20
1.19
1.18
1.17
1.15
0.50
0.48
0.47
0.47
0.46
0.22
0.21
0.21
0.17

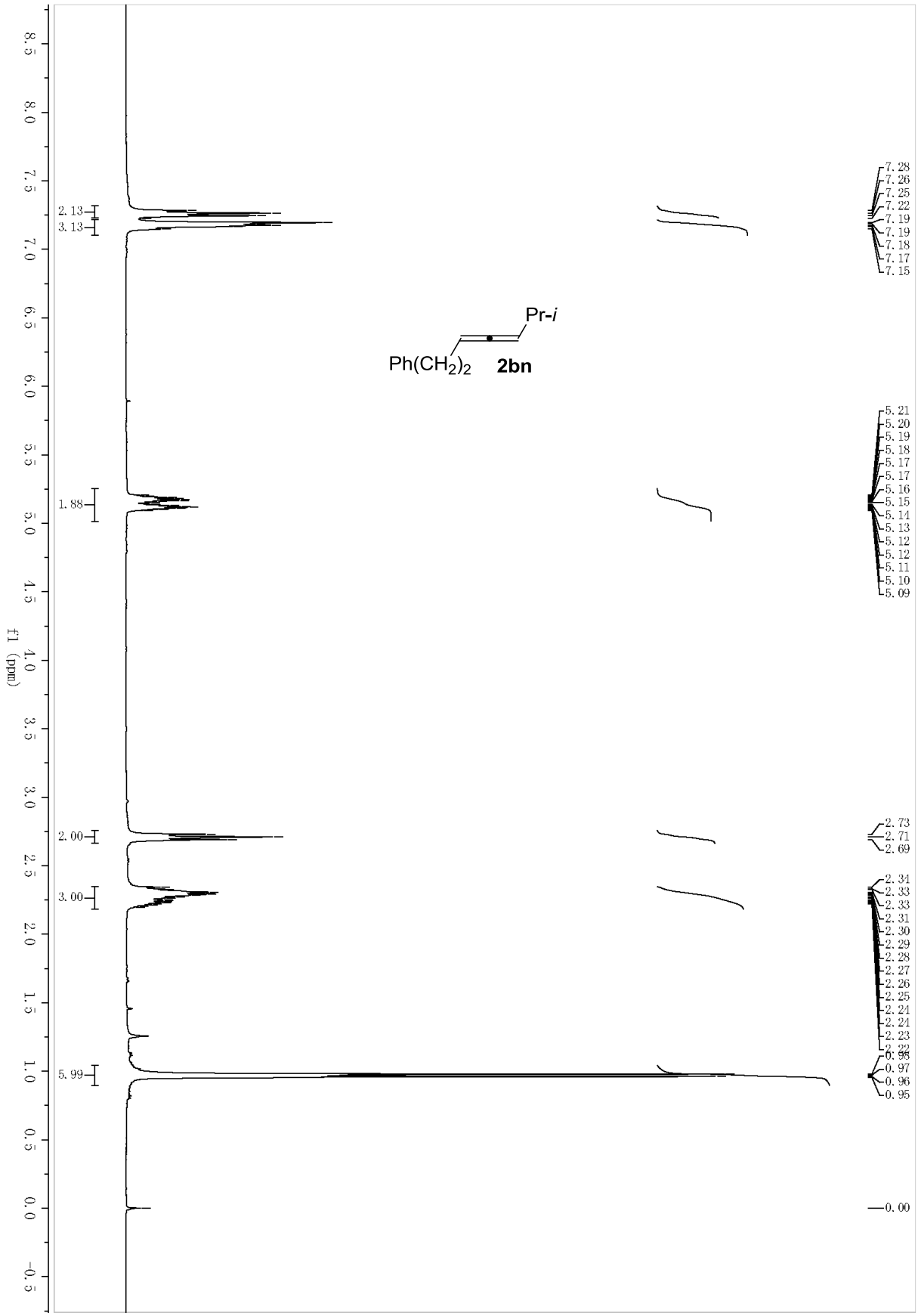

206.69
141.89
136.07
128.82
126.12
123.86
95.17
91.95
35.63
31.04
14.39
7.26
Ph(CH2)2
2bk
f1 (ppm)

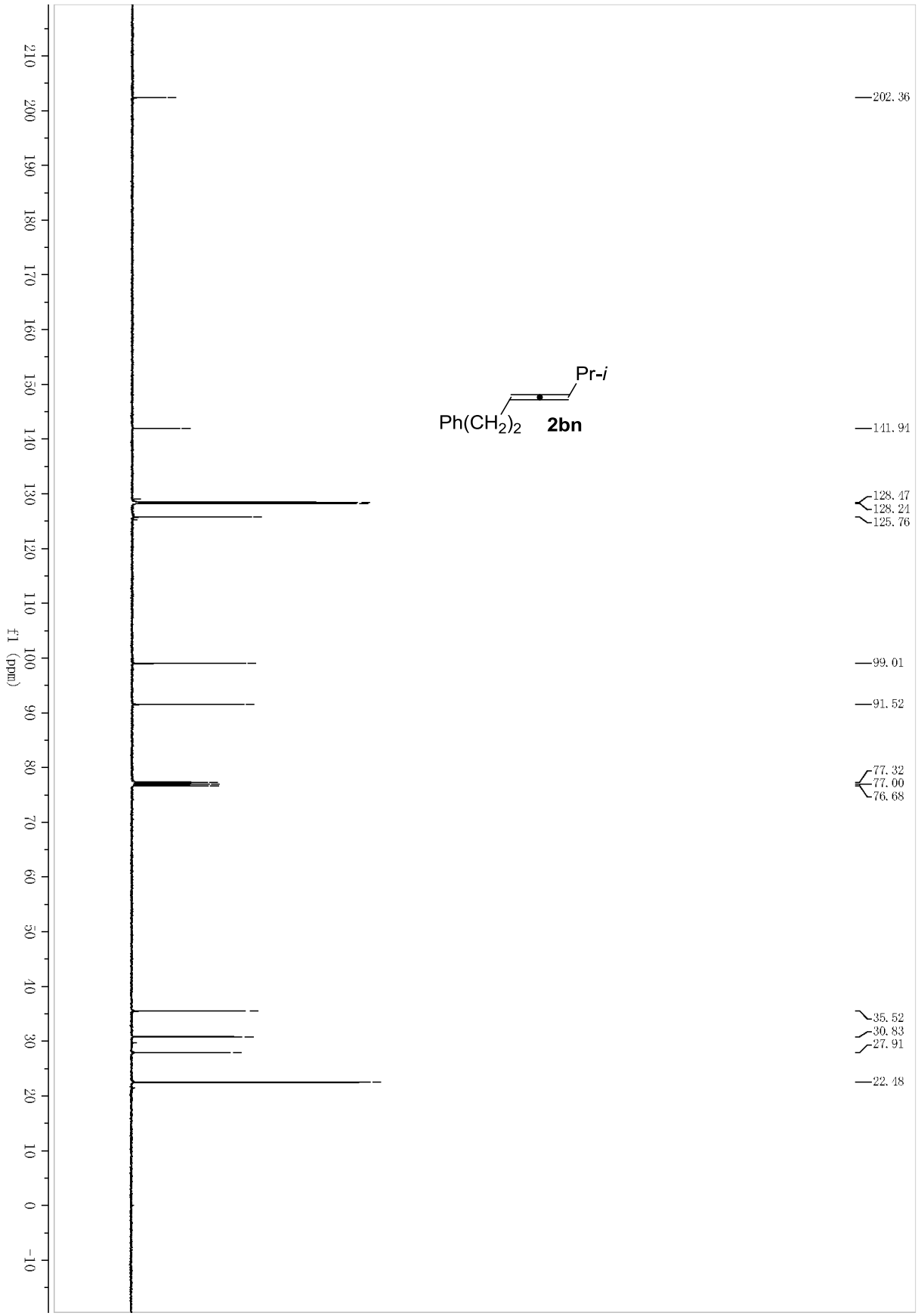

Cy
Ph(CH2)2
2bl
f1 (ppm)
2.54
3.14
0.93
0.91
2.04
2.00
1.06
5.33
5.82
7.29
7.27
7.25
7.24
7.20
7.19
7.19
7.17
7.16
5.18
5.18
5.17
5.16
5.15
5.15
5.14
5.13
5.10
5.09
5.09
5.08
5.07
5.06
5.06
2.75
2.74
2.73
2.71
2.70
2.69
2.68
2.66
2.32
2.31
2.30
2.29
1.91
1.90
1.71
1.68
1.63
1.60
1.53
1.30
1.29
1.25
1.23
1.21
1.19
1.16
1.13
1.07
1.06
1.05
1.03
1.01
0.99
0.00

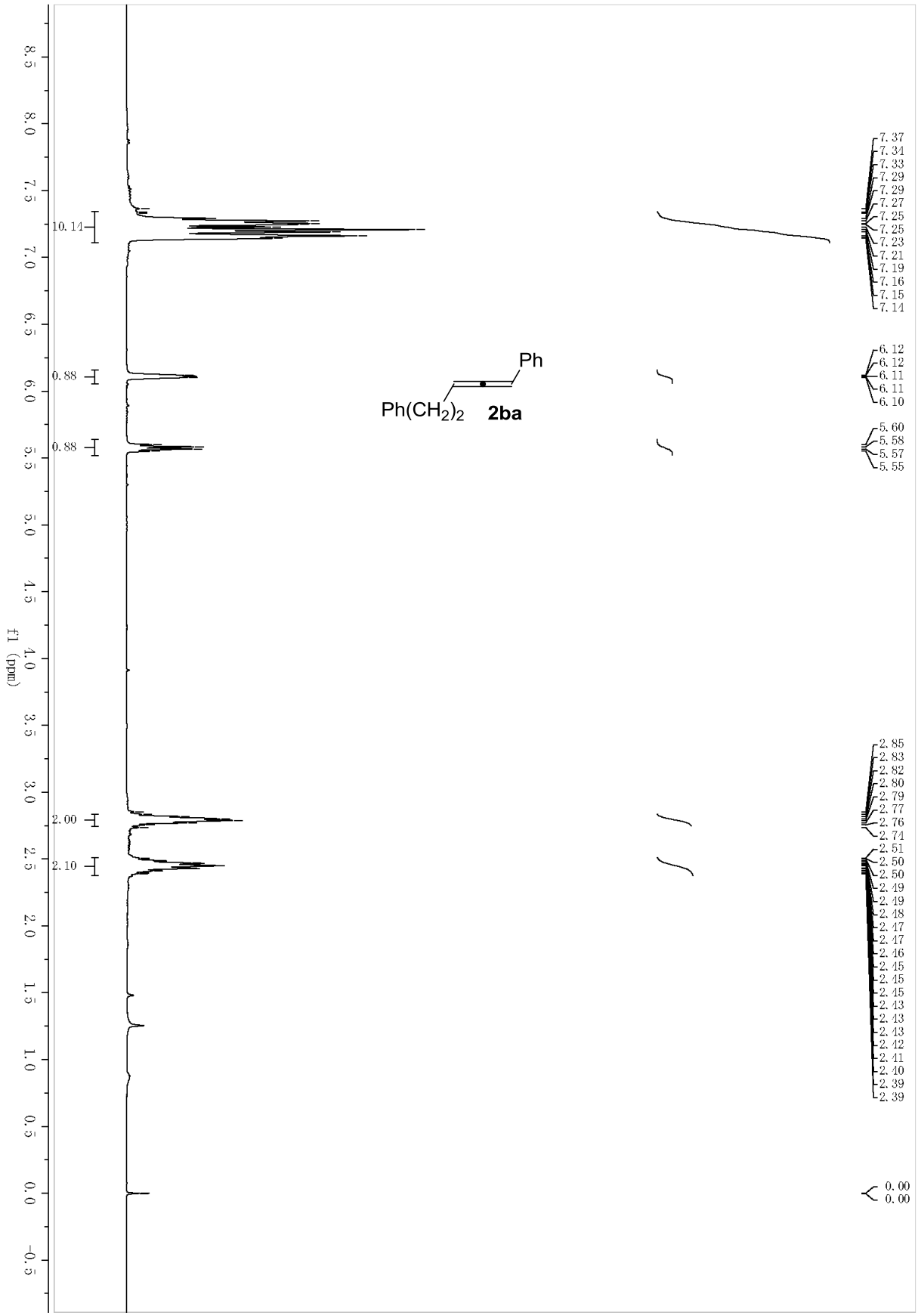

Cy
Ph(CH2)2
2bl
202.76
141.95
128.50
128.22
125.75
97.59
91.11
77.32
77.00
76.68
37.19
35.49
33.06
33.03
30.83
26.16
26.04
26.03
f1 (ppm)

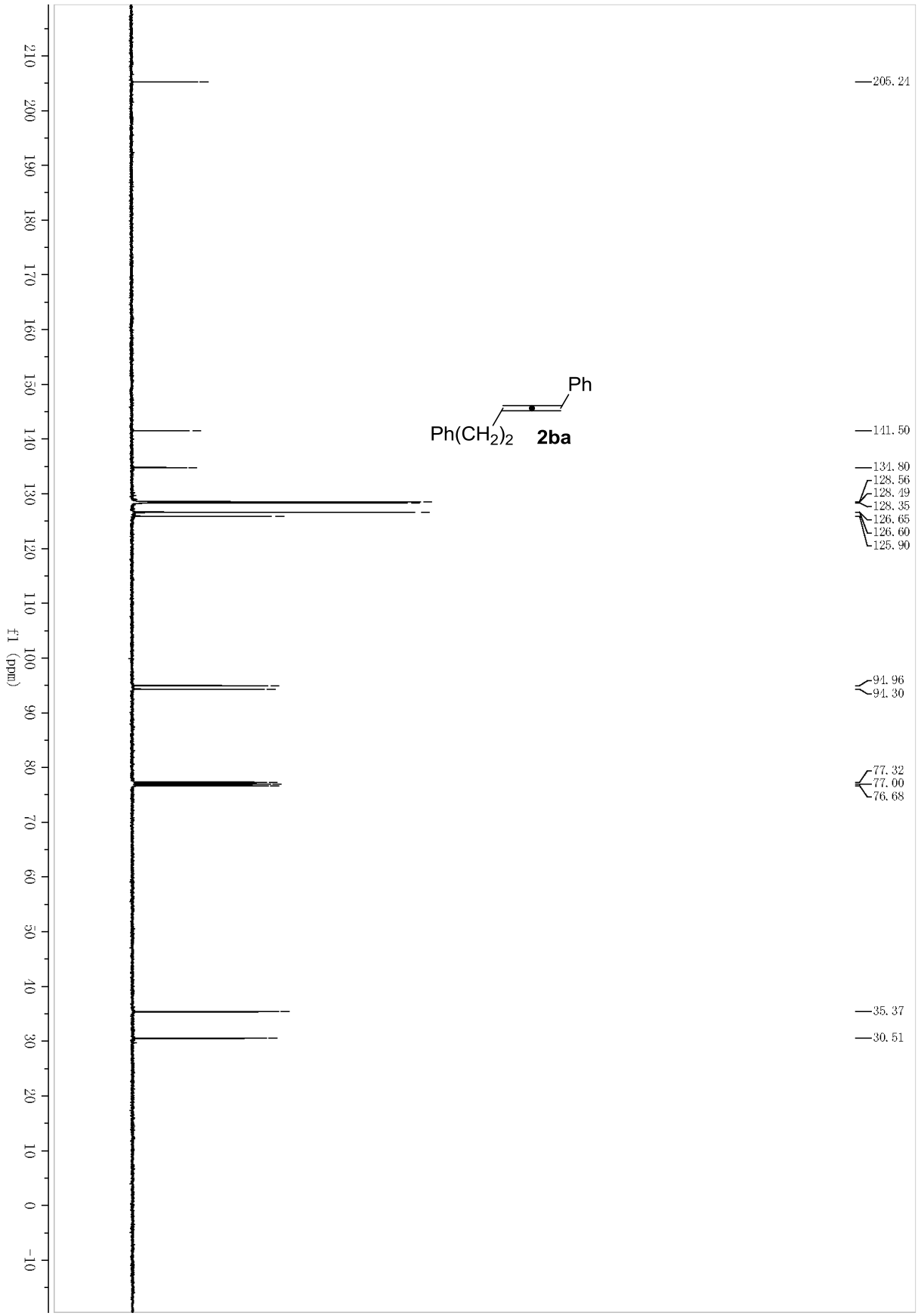

Bu-n
Ph(CH2)2
2bm
f1 (ppm)
2.16
3.06
1.65
2.11
2.09
2.00
4.12
3.43
7.29
7.27
7.25
7.22
7.20
7.18
7.17
7.15
5.14
5.13
5.12
5.12
5.11
5.10
5.09
5.08
5.07
5.07
5.06
2.73
2.71
2.69
2.66
2.31
2.30
2.30
2.29
1.94
1.94
1.35
1.34
1.34
1.33
1.32
1.28
1.25
0.93
0.91
0.89
0.87
0.85
0.83
0.00

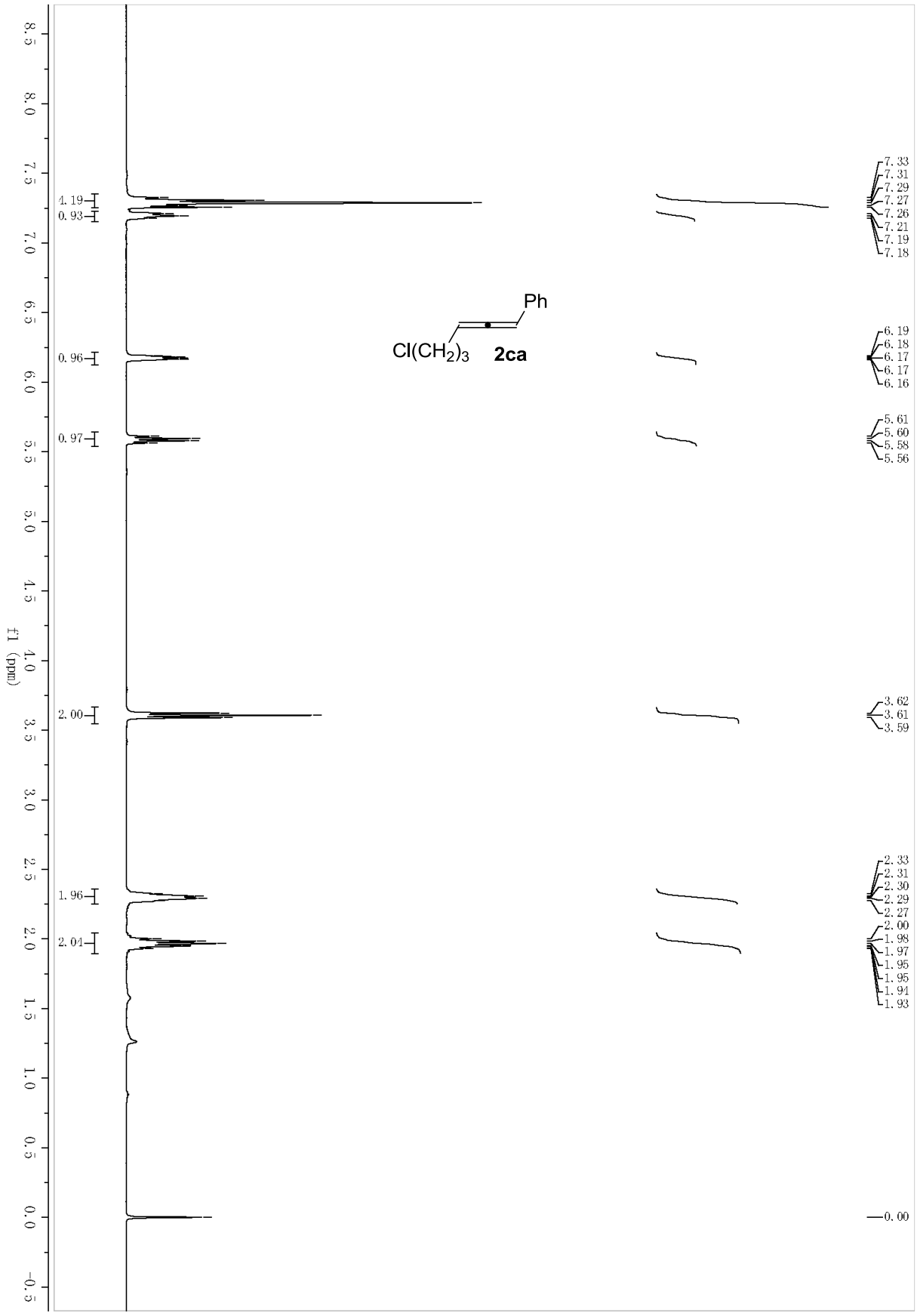

Bu-n
Ph(CH2)2
2bm
203.95
141.94
128.48
128.22
125.75
91.48
90.19
77.32
77.00
76.68
35.48
31.30
30.72
28.57
22.14
13.90
f1 (ppm)

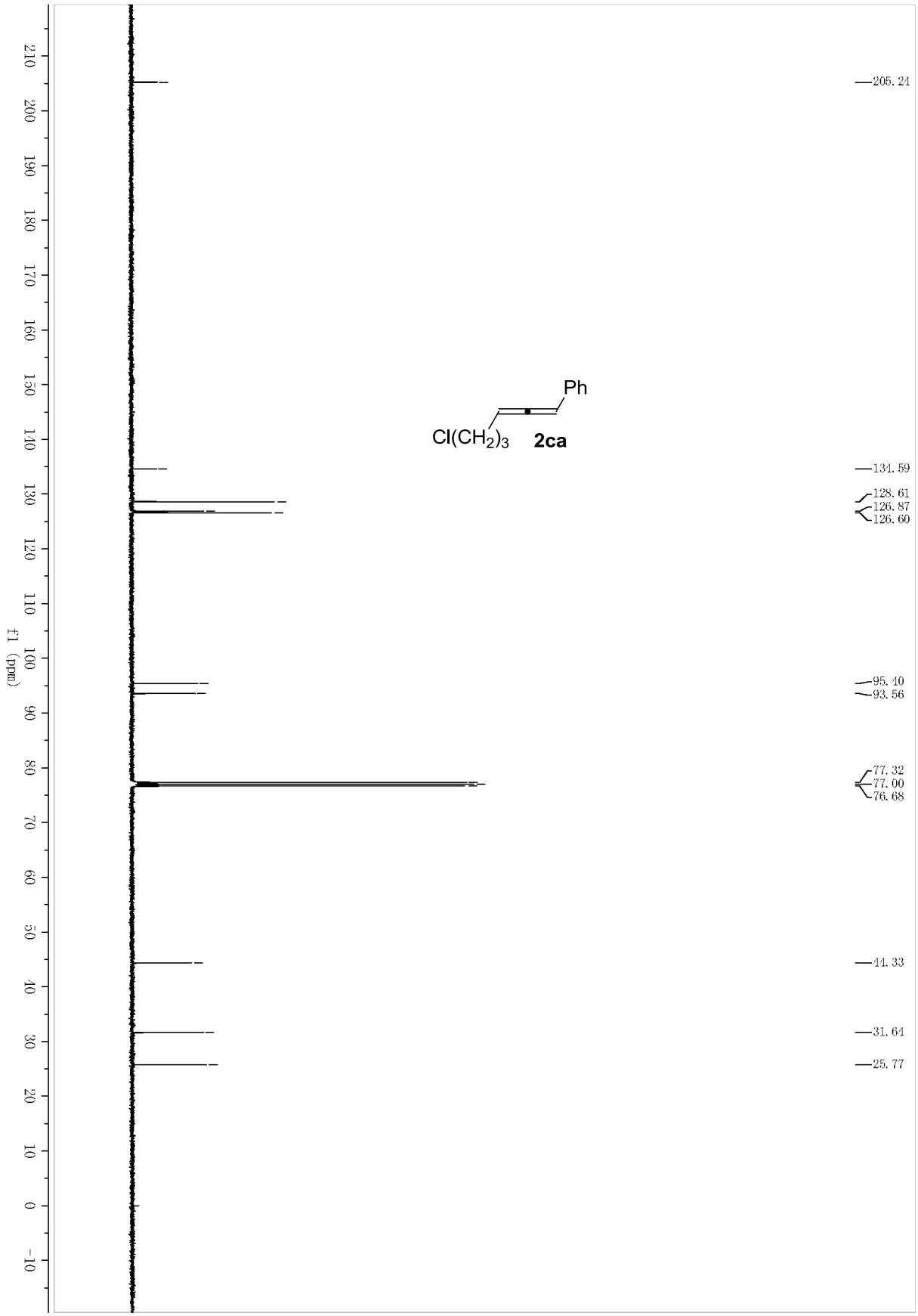

Pr-i
Ph(CH2)2
2bn
f1 (ppm)
2.13
3.13
1.88
2.00
3.00
5.99
7.28
7.26
7.25
7.22
7.19
7.19
7.18
7.17
7.15
5.21
5.20
5.19
5.18
5.17
5.17
5.16
5.15
5.14
5.13
5.12
5.12
5.11
5.10
5.09
2.73
2.71
2.69
2.34
2.33
2.33
2.31
2.30
2.29
2.28
2.27
2.26
2.25
2.24
2.24
2.23
0.98
0.97
0.96
0.95
0.00

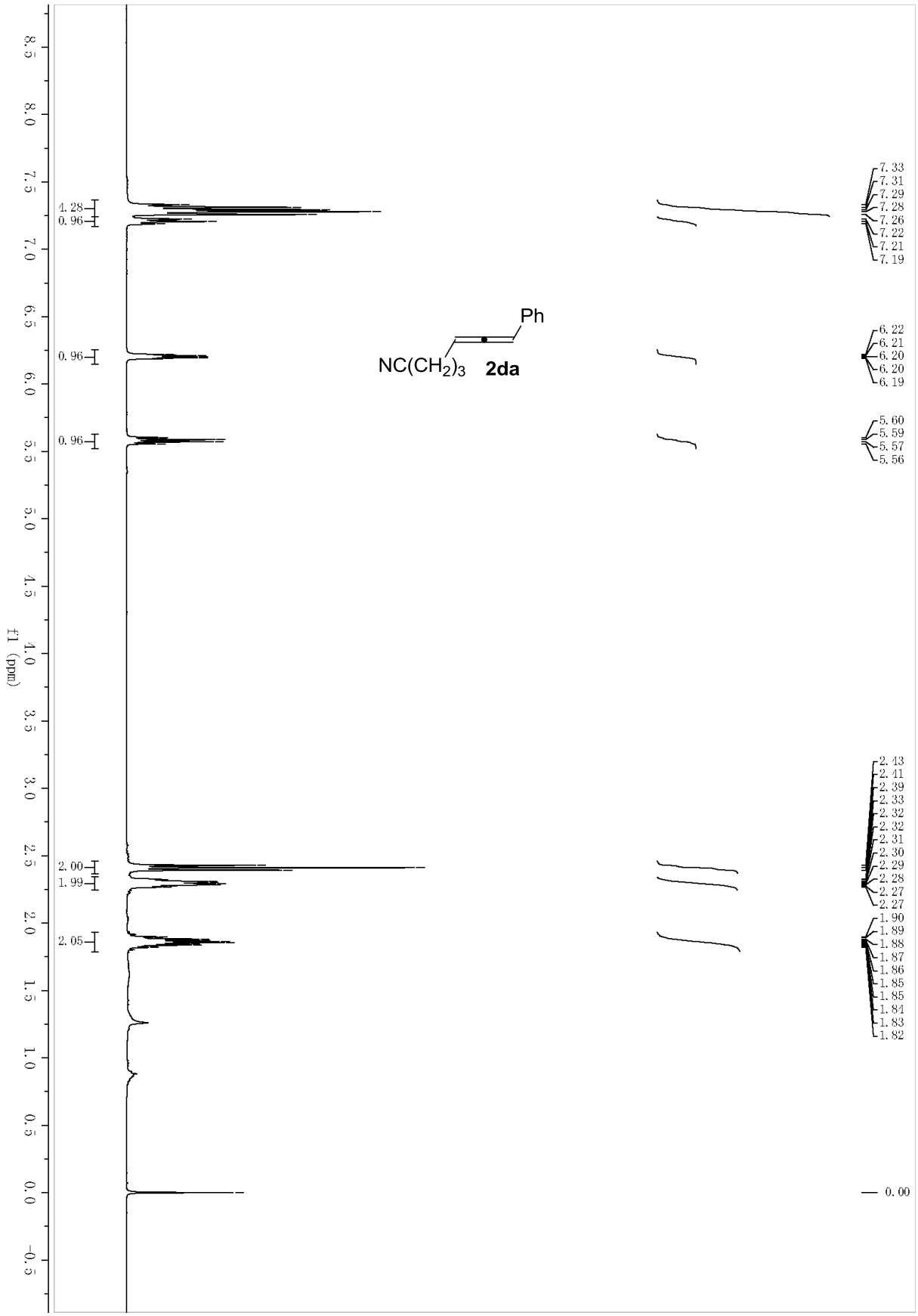

Pr-i
Ph(CH2)2
2bn
202.36
141.94
128.47
128.24
125.76
99.01
91.52
77.32
77.00
76.68
35.52
30.83
27.91
22.48
f1 (ppm)

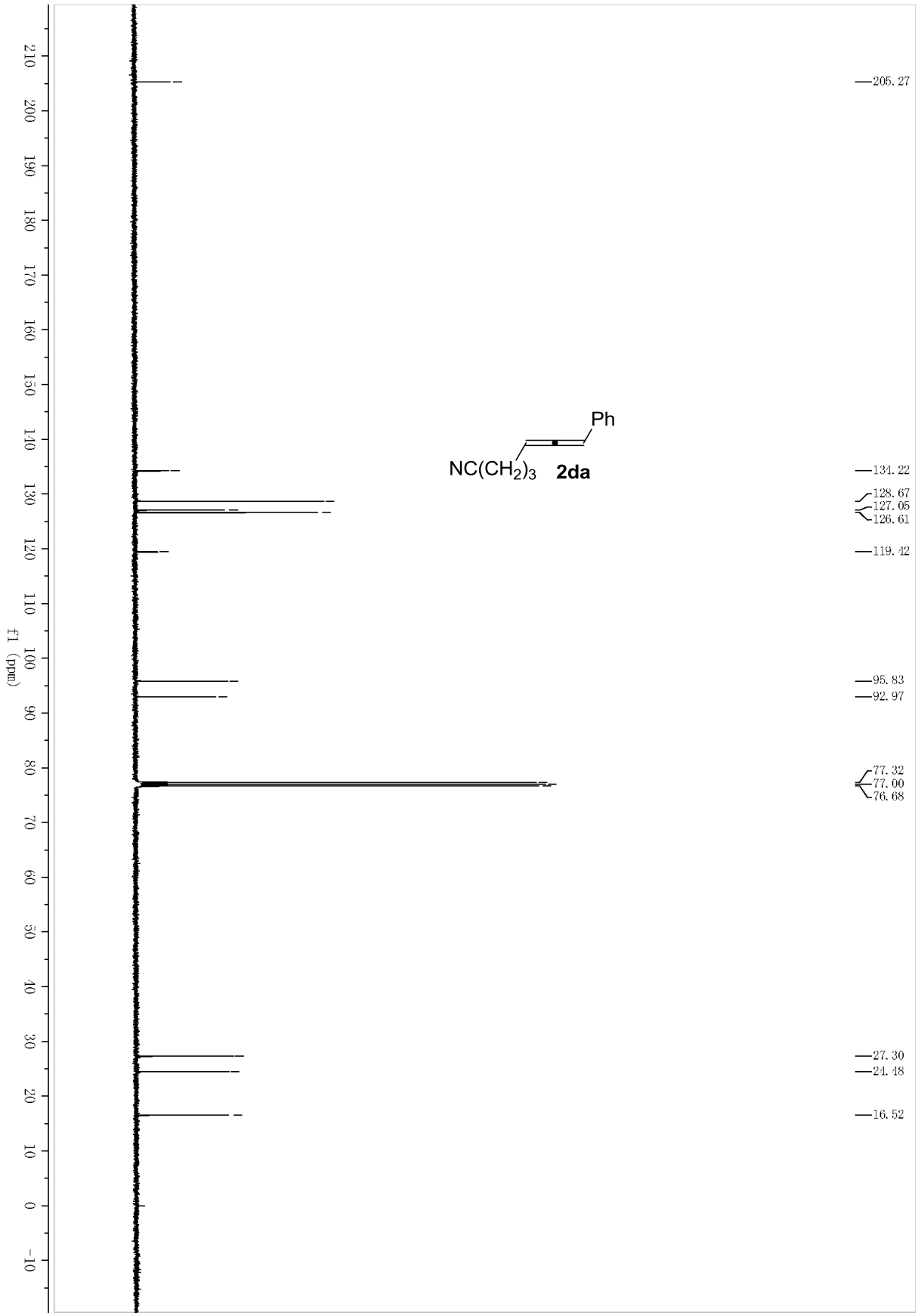

Ph
Ph(CH2)2
2ba
f1 (ppm)
10.14
0.88
0.88
2.00
2.10
7.37
7.34
7.33
7.29
7.29
7.27
7.25
7.25
7.23
7.21
7.19
7.16
7.15
7.14
6.12
6.12
6.11
6.11
6.10
5.60
5.58
5.57
5.55
2.85
2.83
2.82
2.80
2.79
2.77
2.76
2.74
2.51
2.50
2.50
2.49
2.49
2.48
2.47
2.47
2.46
2.45
2.45
2.45
2.43
2.43
2.43
2.42
2.41
2.40
2.39
2.39
0.00
0.00

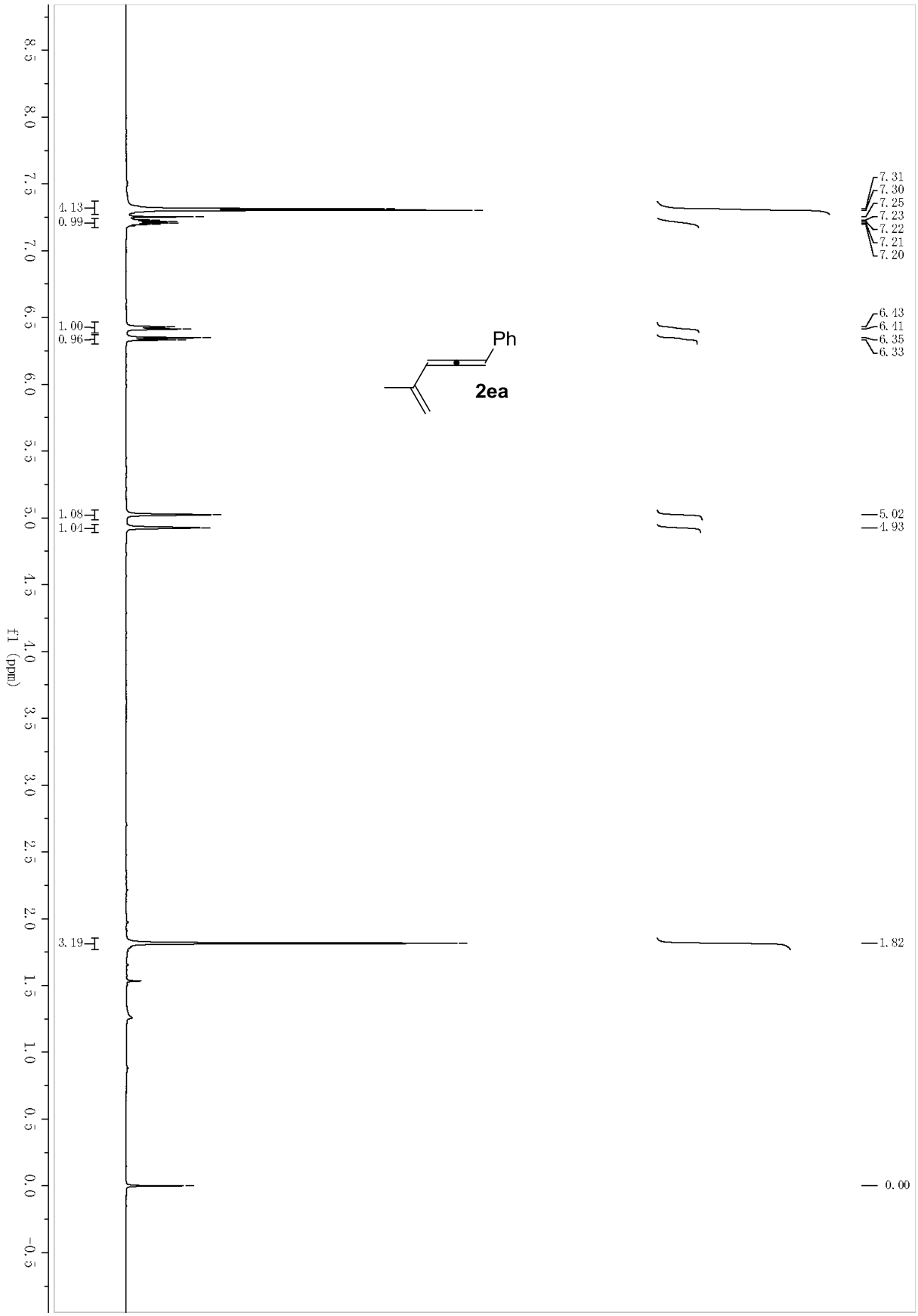

205.24
141.50
134.80
128.56
128.49
128.35
126.65
126.60
125.90
94.96
94.30
77.32
77.00
76.68
35.37
30.51
f1 (ppm)
Ph
Ph(CH2)2
2ba

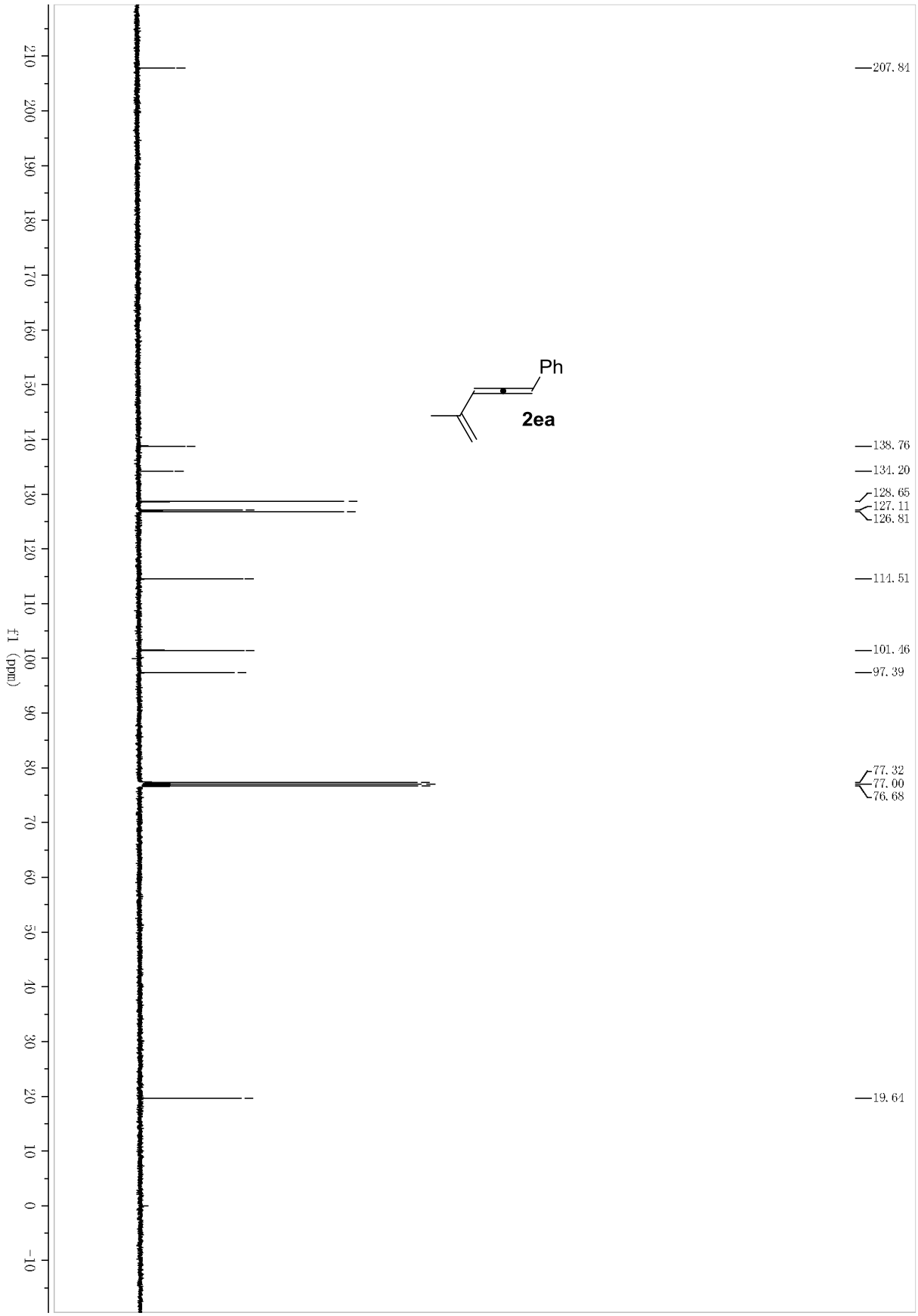

Ph
Cl(CH2)3
2ca
f1 (ppm)
4.19
0.93
0.96
0.97
2.00
1.96
2.04
7.33
7.31
7.29
7.27
7.26
7.21
7.19
7.18
6.19
6.18
6.17
6.17
6.16
5.61
5.60
5.58
5.56
3.62
3.61
3.59
2.33
2.31
2.30
2.29
2.27
2.00
1.98
1.97
1.95
1.95
1.94
1.93
0.00

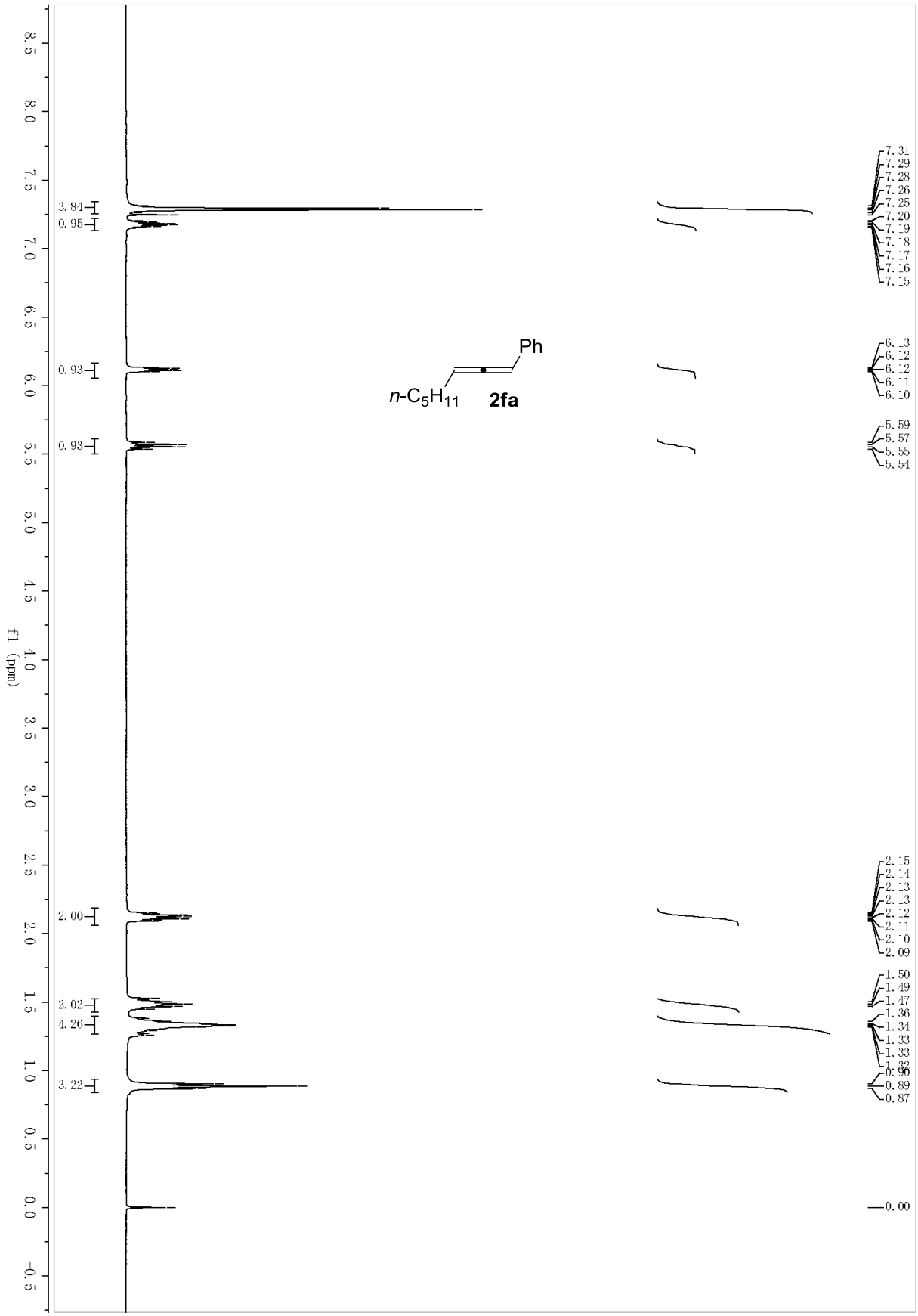

205.24
134.59
128.61
126.87
126.60
95.40
93.56
77.32
77.00
76.68
44.33
31.64
25.77
f1 (ppm)
Ph
Cl(CH2)3
2ca

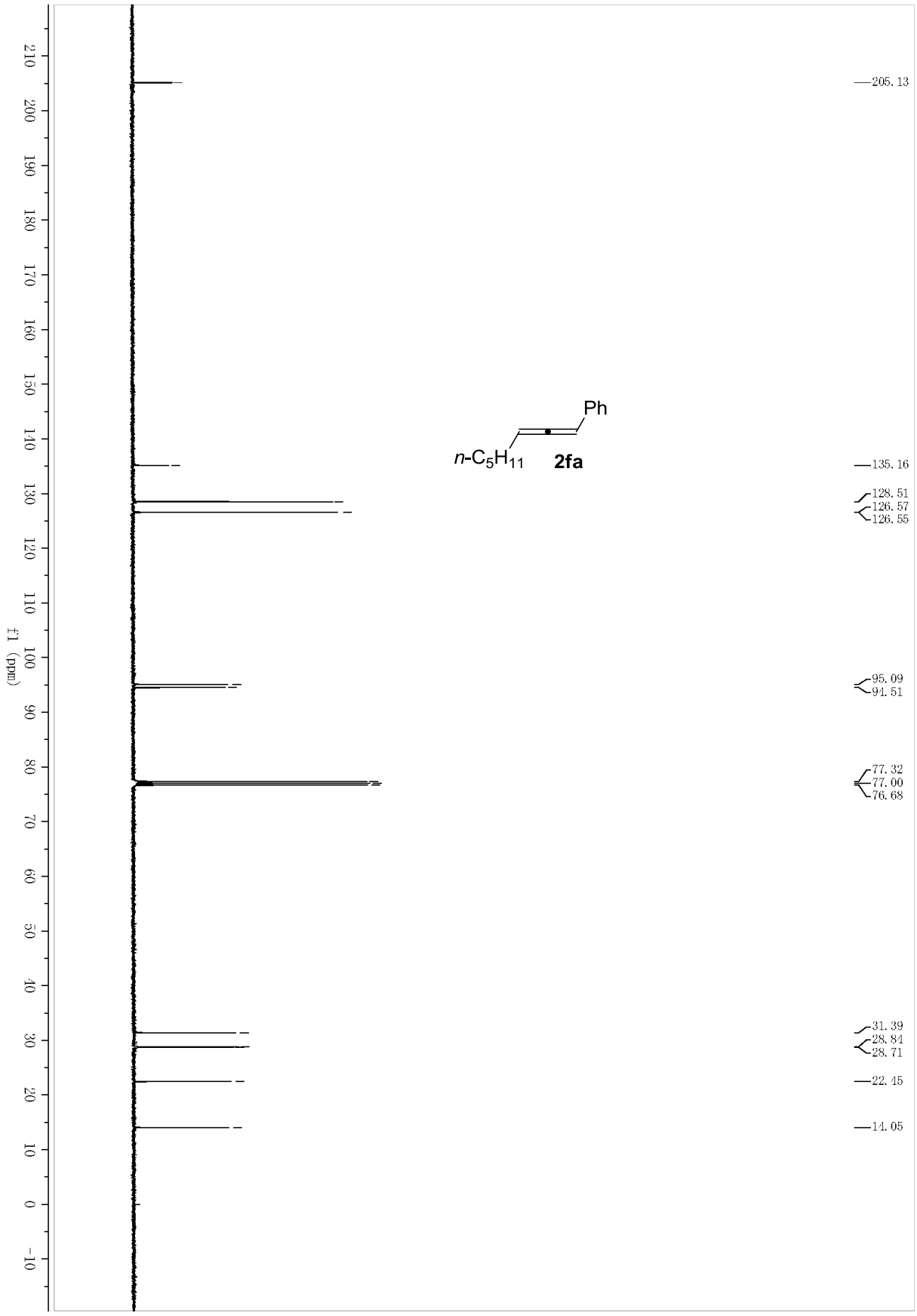

Ph
NC(CH2)3
2da
f1 (ppm)
4.28
0.96
0.96
0.96
2.00
1.99
2.05
7.33
7.31
7.29
7.28
7.26
7.22
7.21
7.19
6.22
6.21
6.20
6.20
6.19
5.60
5.59
5.57
5.56
2.43
2.41
2.39
2.33
2.32
2.32
2.31
2.30
2.29
2.28
2.27
2.27
1.90
1.89
1.88
1.87
1.86
1.85
1.85
1.84
1.83
1.82
0.00

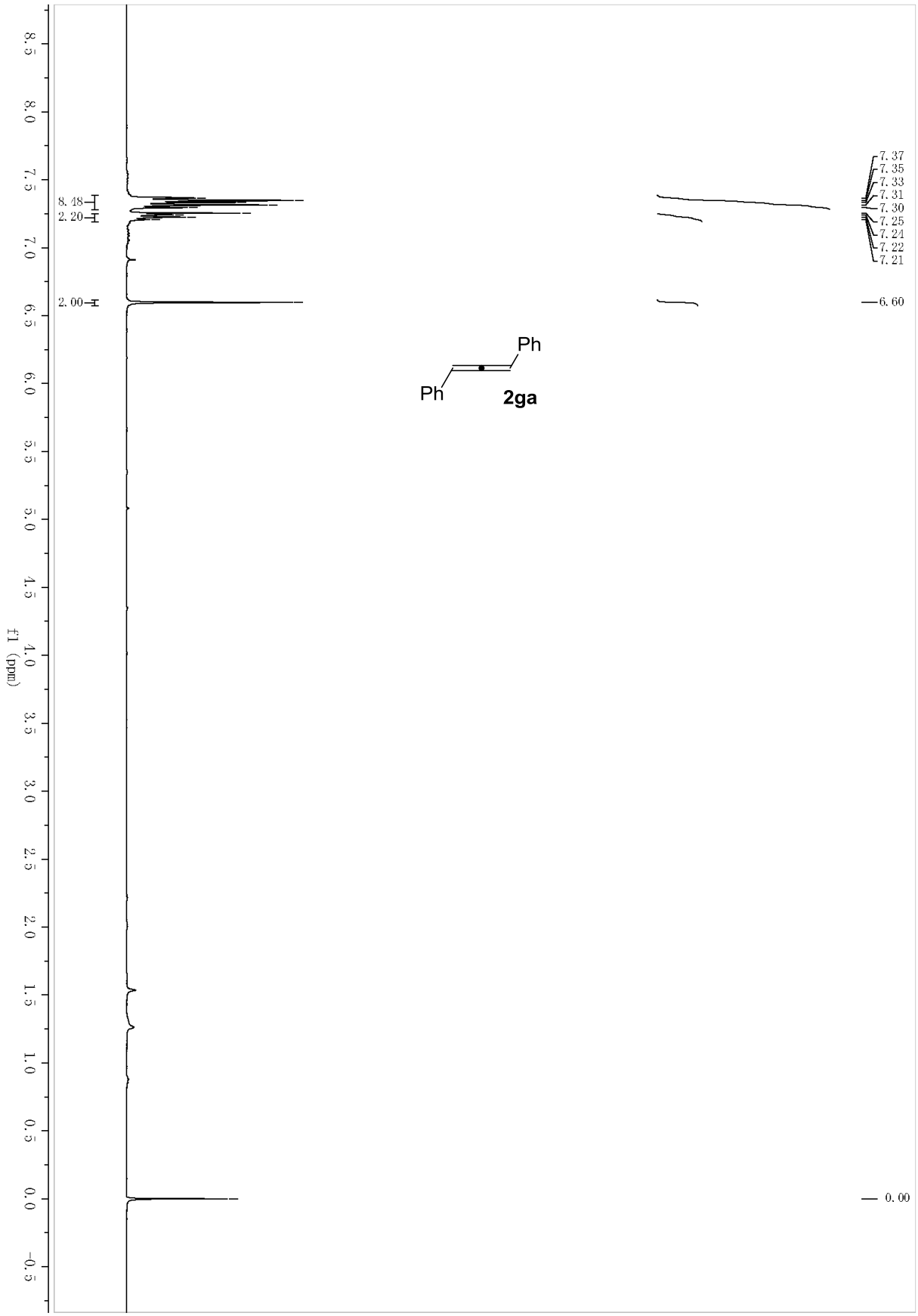

Ph
NC(CH2)3
2da
205.27
134.22
128.67
127.05
126.61
119.42
95.83
92.97
77.32
77.00
76.68
27.30
24.48
16.52
f1 (ppm)

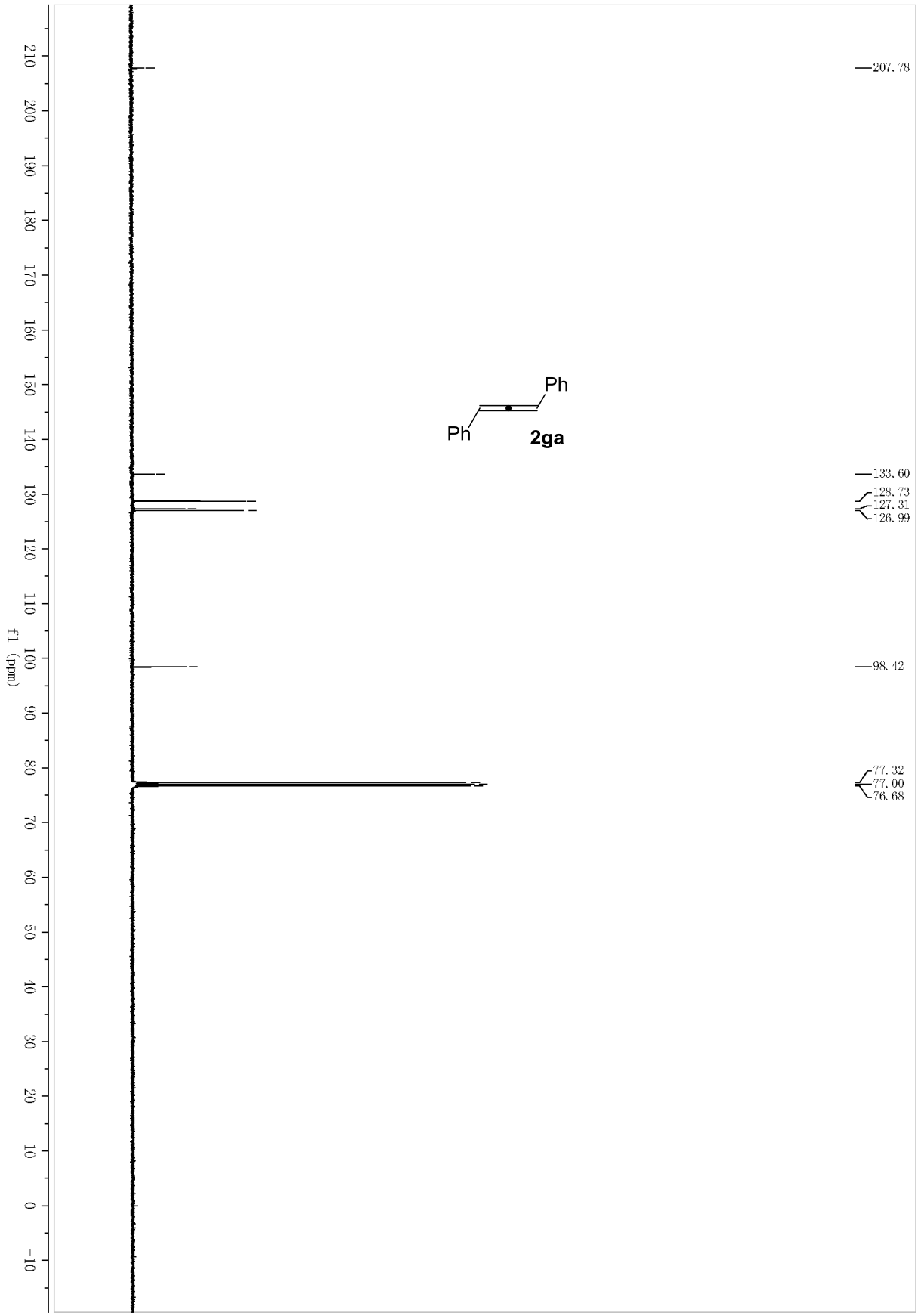

Ph
2ea
f1 (ppm)
4.13
0.99
1.00
0.96
1.08
1.04
3.19
7.31
7.30
7.25
7.23
7.22
7.21
7.20
6.43
6.41
6.35
6.33
5.02
4.93
1.82
0.00

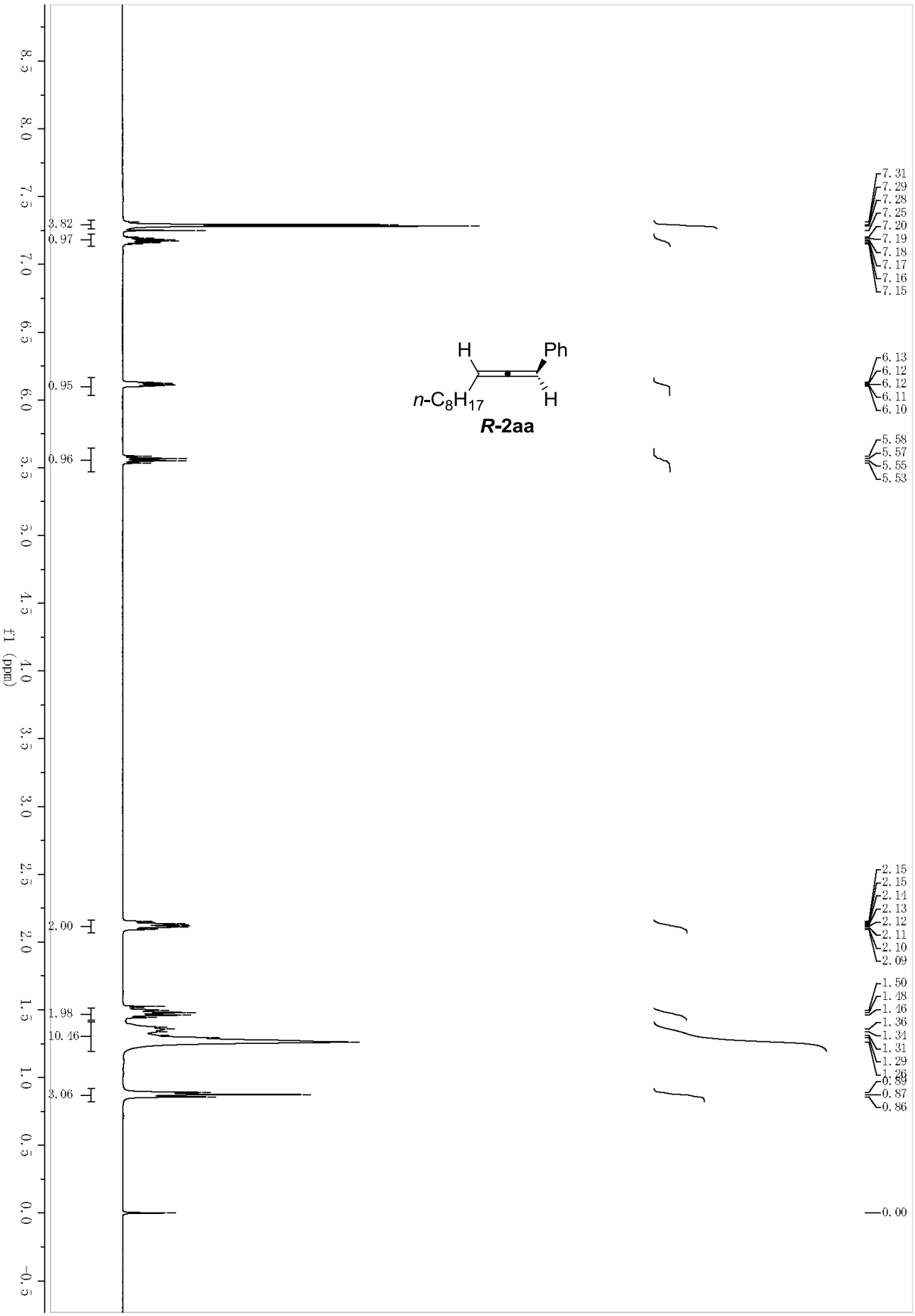

Ph
2ea
207.84
138.76
134.20
128.65
127.11
126.81
114.51
101.46
97.39
77.32
77.00
76.68
19.64
f1 (ppm)

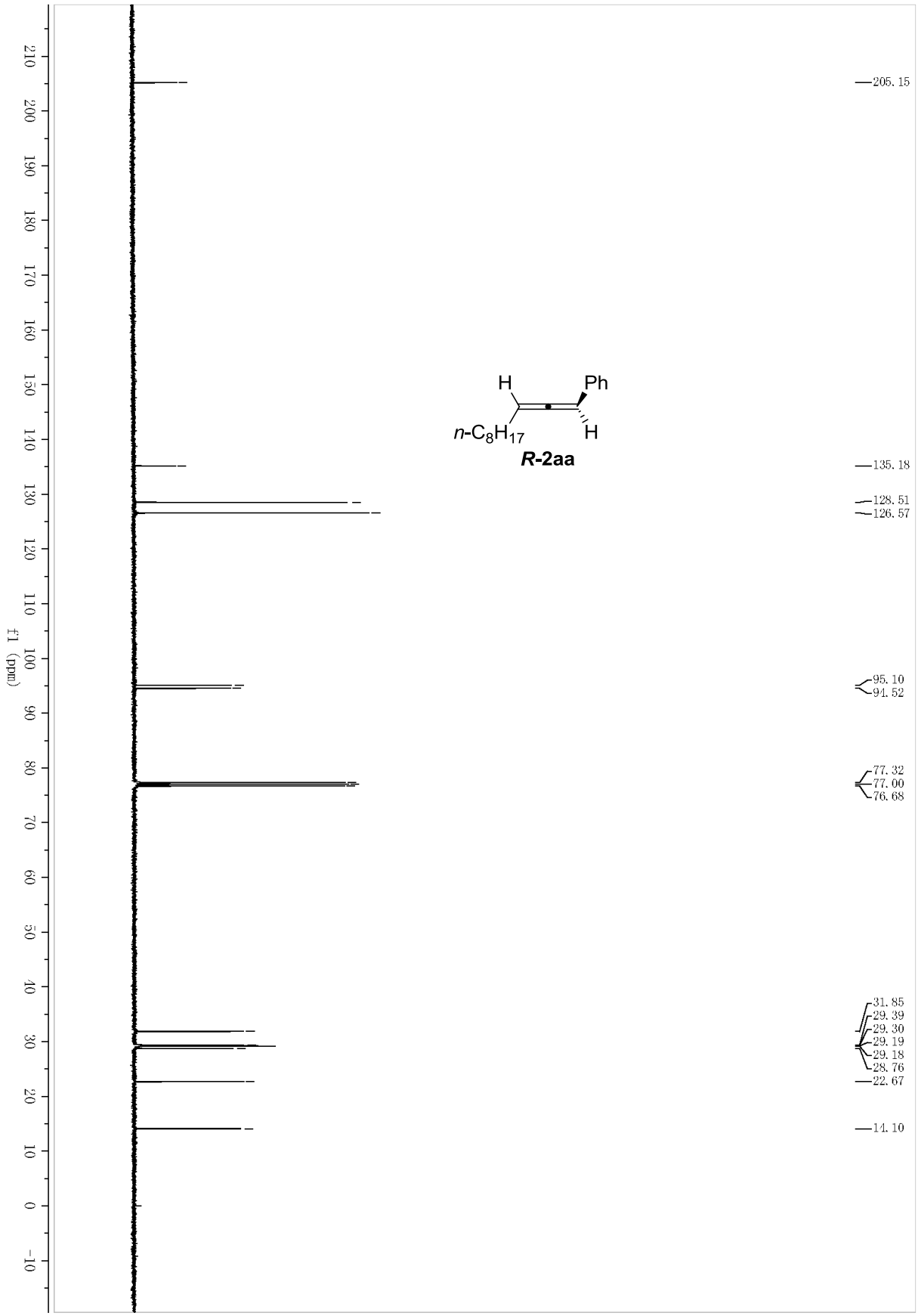

Ph
n-C5H11
2fa
f1 (ppm)
3.84
0.95
0.93
0.93
2.00
2.02
4.26
3.22
7.31
7.29
7.28
7.26
7.25
7.20
7.19
7.18
7.17
7.16
7.15
6.13
6.12
6.12
6.11
6.10
5.59
5.57
5.55
5.54
2.15
2.14
2.13
2.13
2.12
2.11
2.10
2.09
1.50
1.49
1.47
1.36
1.34
1.33
1.33
0.90
0.89
0.87
0.00

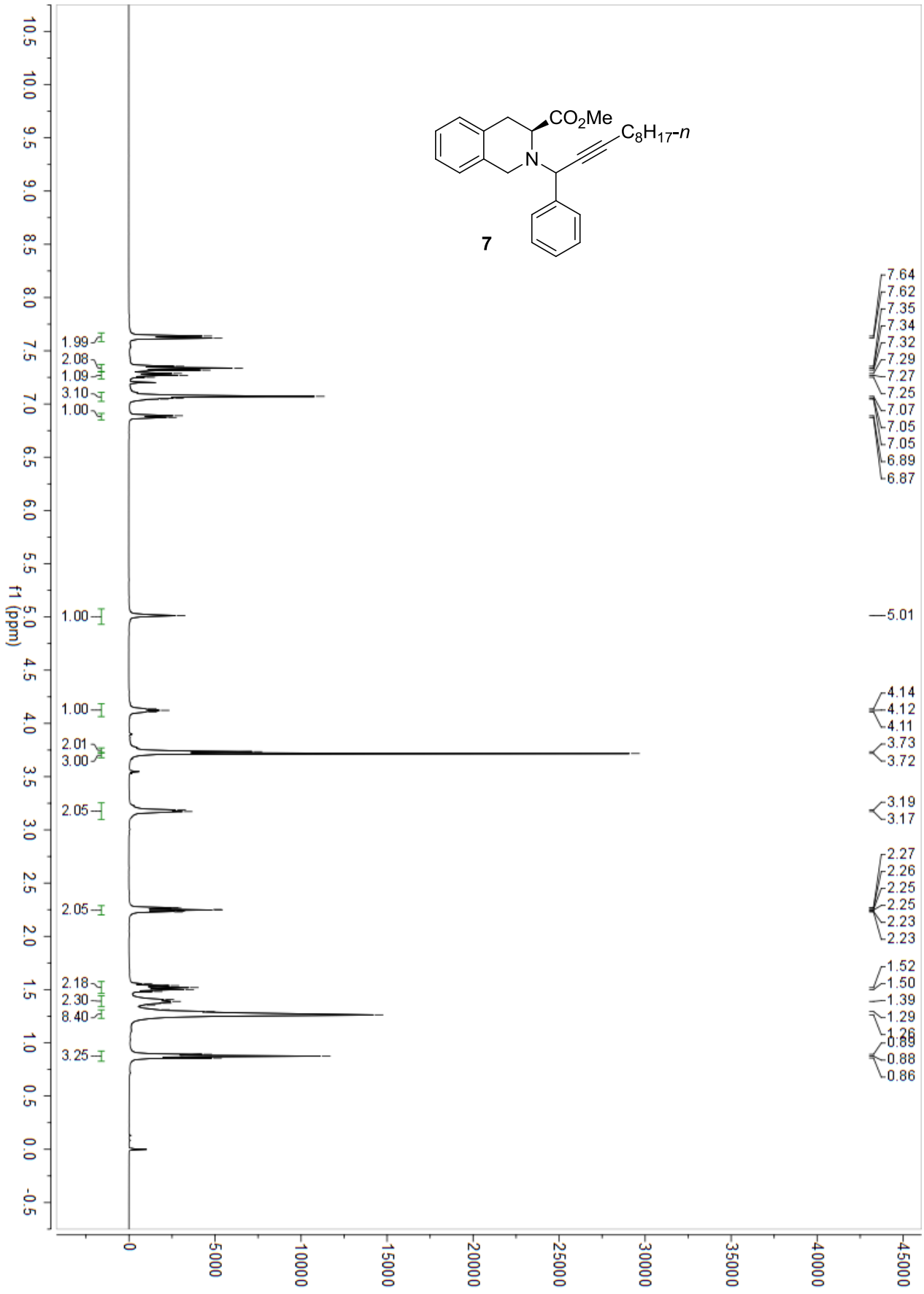

205.13
135.16
128.51
126.57
126.55
95.09
94.51
77.32
77.00
76.68
31.39
28.84
28.71
22.45
14.05
f1 (ppm)
Ph
n-C5H11
2fa

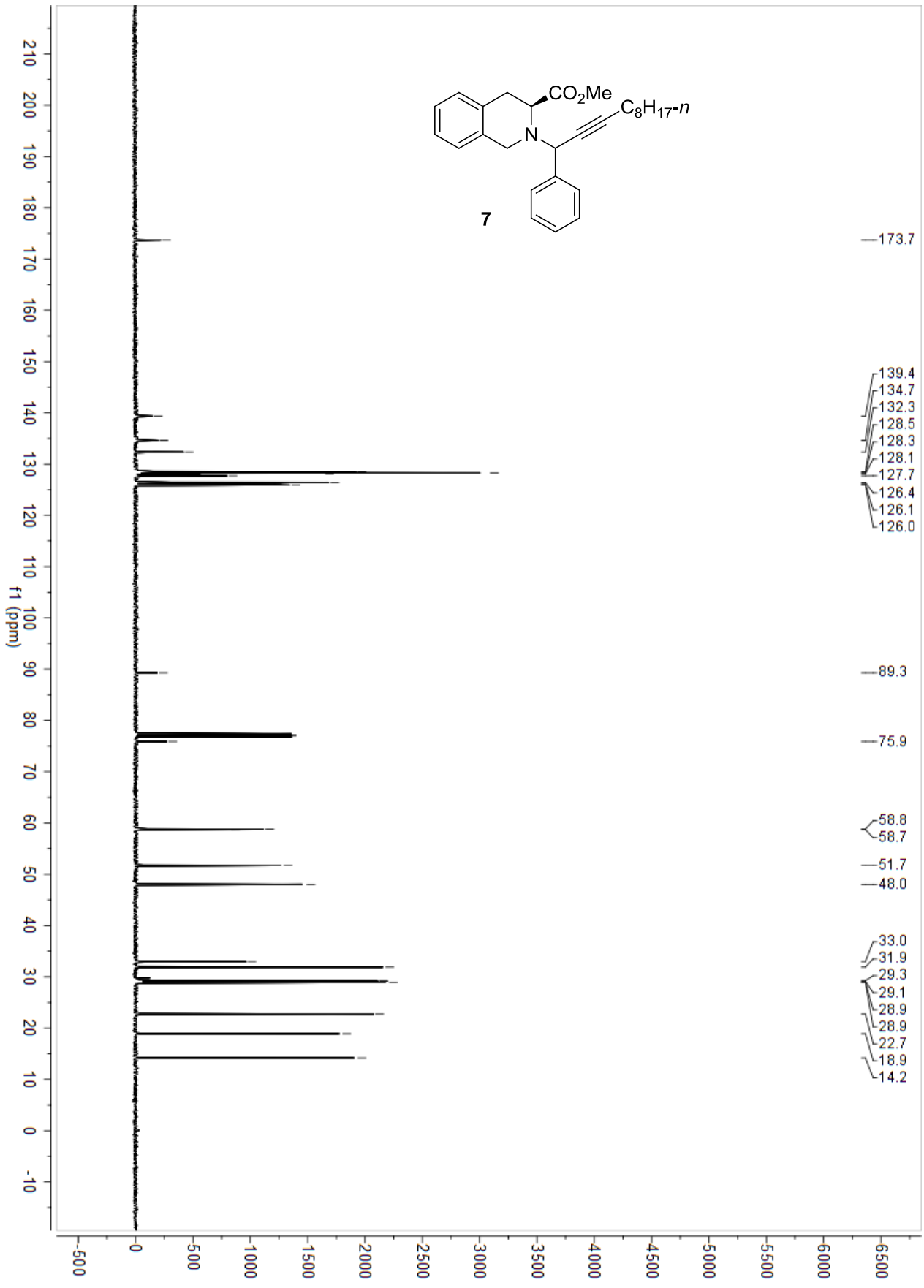

8.48
2.20
2.00
7.37
7.35
7.33
7.31
7.30
7.25
7.24
7.22
7.21
6.60
0.00
Ph
Ph
2ga
f1 (ppm)

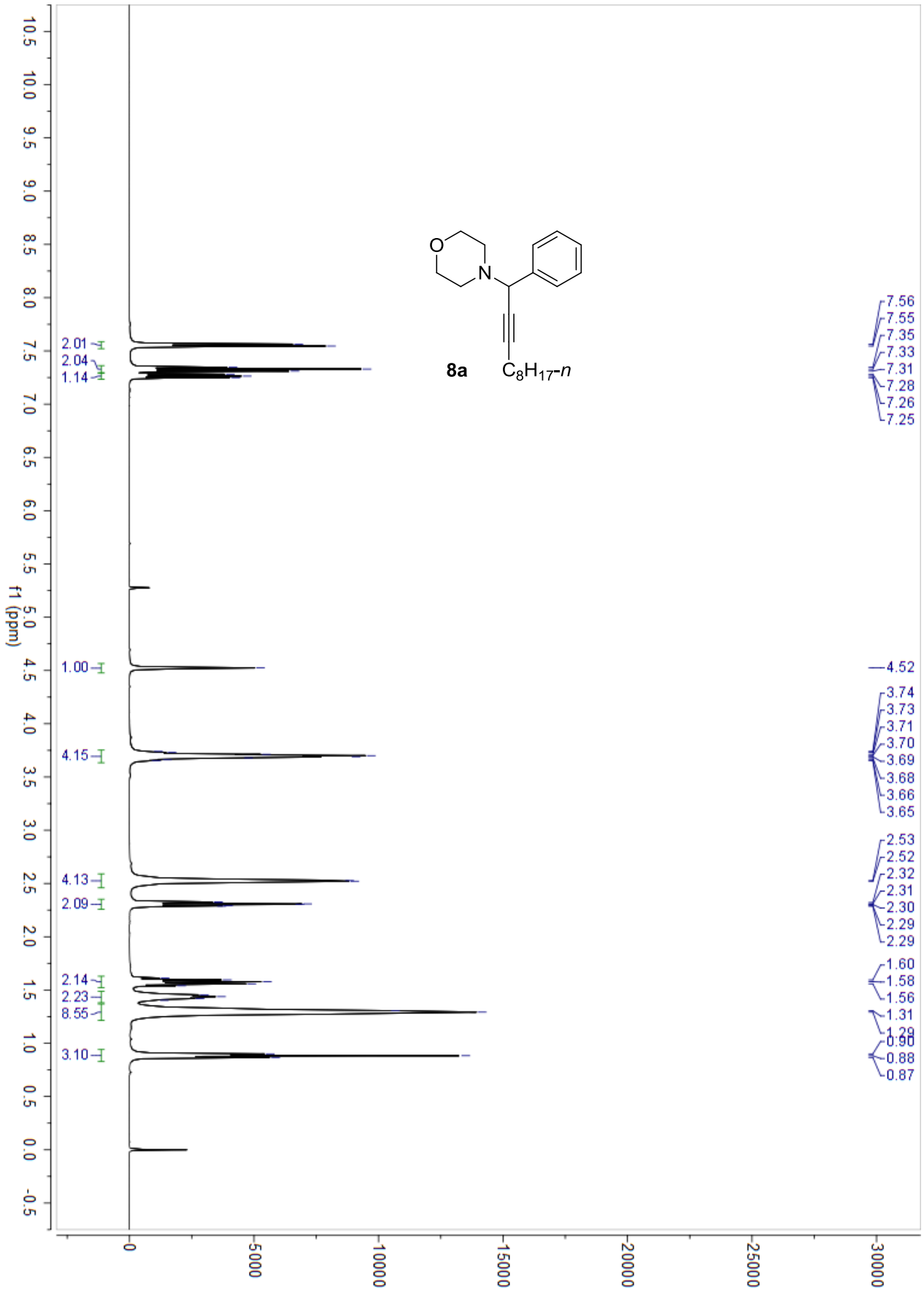

207.78
133.60
128.73
127.31
126.99
98.42
77.32
77.00
76.68
Ph
Ph
2ga
f1 (ppm)

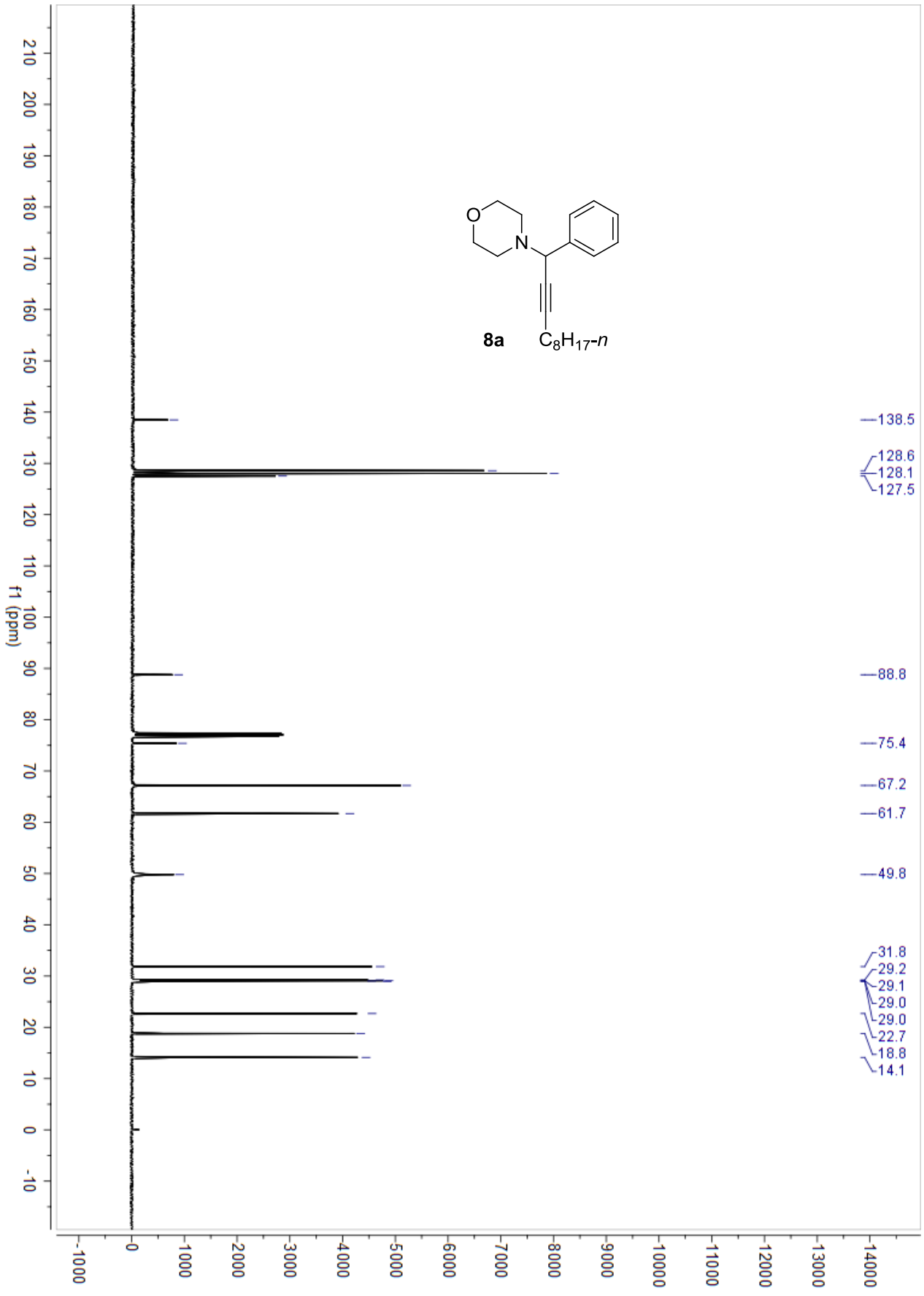

H
Ph
n-C8H17
H
R-2aa
f1 (ppm)
3.82
0.97
0.95
0.96
2.00
1.98
10.46
3.06
7.31
7.29
7.28
7.25
7.20
7.19
7.18
7.17
7.16
7.15
6.13
6.12
6.12
6.11
6.10
5.58
5.57
5.55
5.53
2.15
2.15
2.14
2.13
2.12
2.11
2.10
2.09
1.50
1.48
1.46
1.36
1.34
1.31
1.29
1.26
0.89
0.87
0.86
0.00

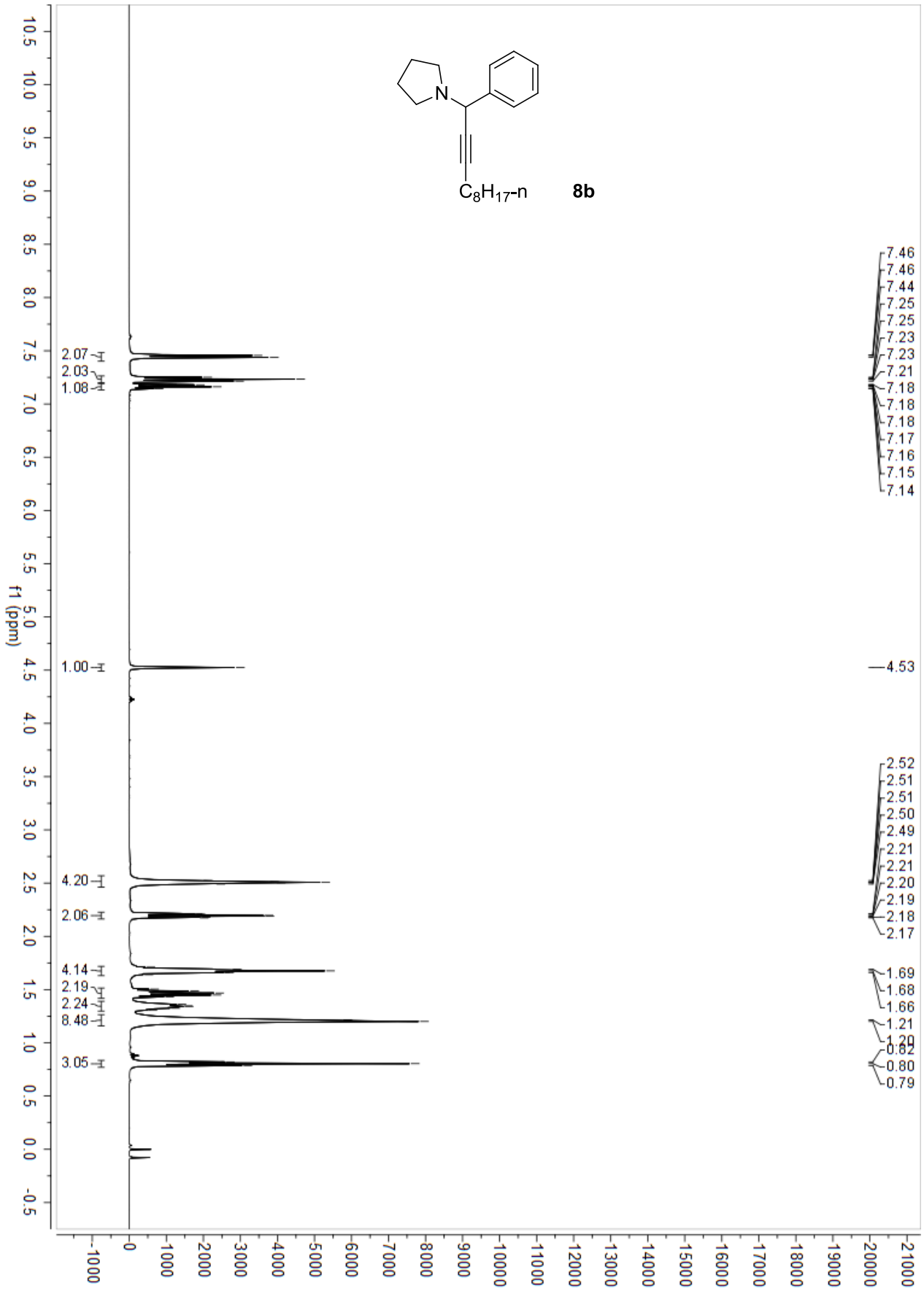

H
Ph
n-C8H17
H
R-2aa
205.15
135.18
128.51
126.57
95.10
94.52
77.32
77.00
76.68
31.85
29.39
29.30
29.19
29.18
28.76
22.67
14.10
f1 (ppm)

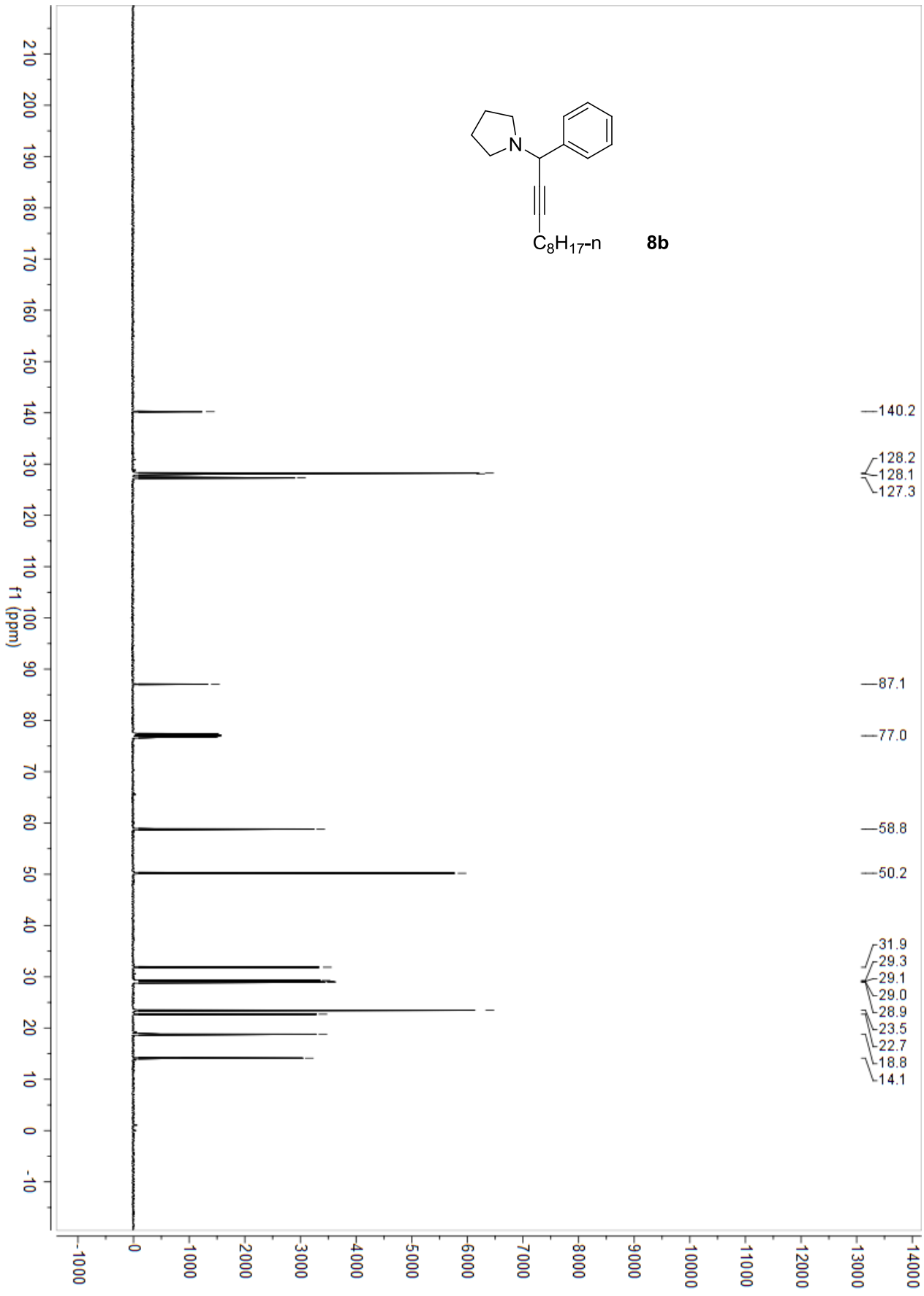

CO2Me
C8H17-n
N
7
f1 (ppm)
1.99
2.08
1.09
3.10
1.00
1.00
1.00
2.01
3.00
2.05
2.05
2.18
2.30
8.40
3.25
7.64
7.62
7.35
7.34
7.32
7.29
7.27
7.25
7.07
7.05
7.05
6.89
6.87
5.01
4.14
4.12
4.11
3.73
3.72
3.19
3.17
2.27
2.26
2.25
2.25
2.23
2.23
1.52
1.50
1.39
1.29
0.89
0.88
0.86

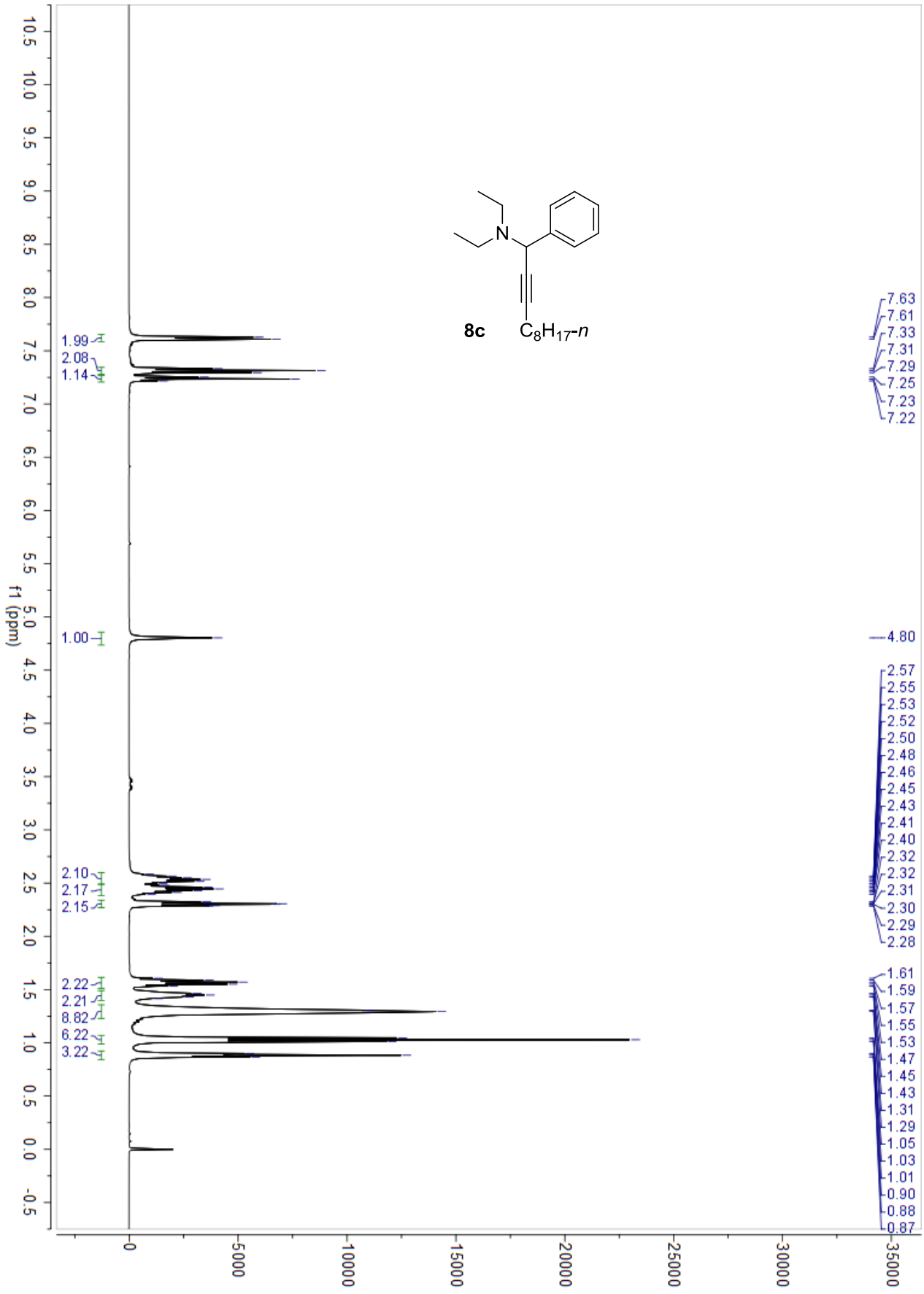

CO2Me
C8H17-n
N
7
173.7
139.4
134.7
132.3
128.5
128.3
128.1
127.7
126.4
126.1
126.0
89.3
75.9
58.8
58.7
51.7
48.0
33.0
31.9
29.3
29.1
28.9
28.9
22.7
18.9
14.2
f1 (ppm)

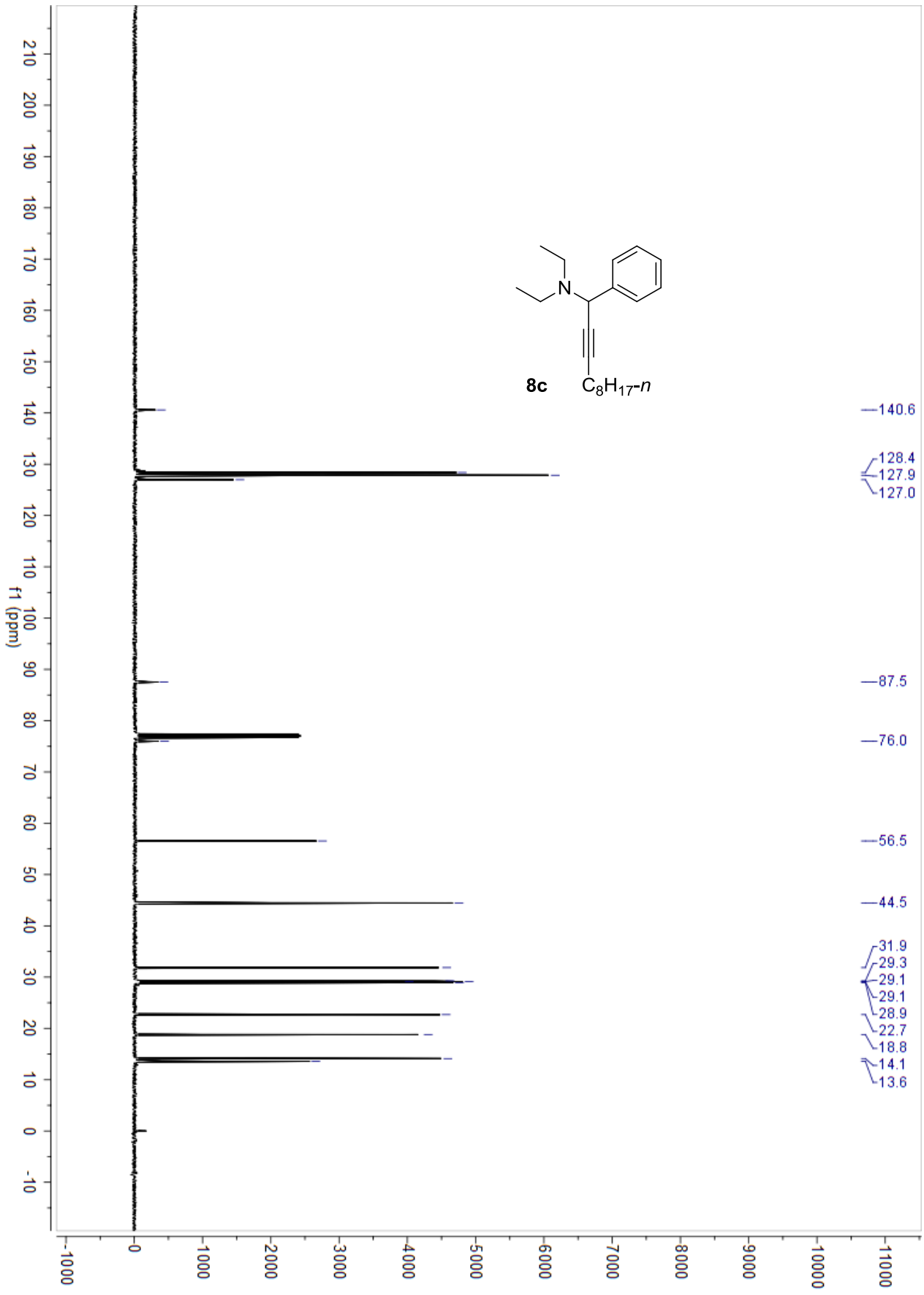

O
N
8a
C_8H_{17}-*n*
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
2.01
2.04
1.14
1.00
4.15
4.13
2.09
2.14
2.23
8.55
3.10
7.56
7.55
7.35
7.33
7.31
7.28
7.26
7.25
4.52
3.74
3.73
3.71
3.70
3.69
3.68
3.66
3.65
2.53
2.52
2.32
2.31
2.30
2.29
2.29
1.60
1.58
1.56
1.31
0.90
0.88
0.87
0
5000
10000
15000
20000
25000
30000

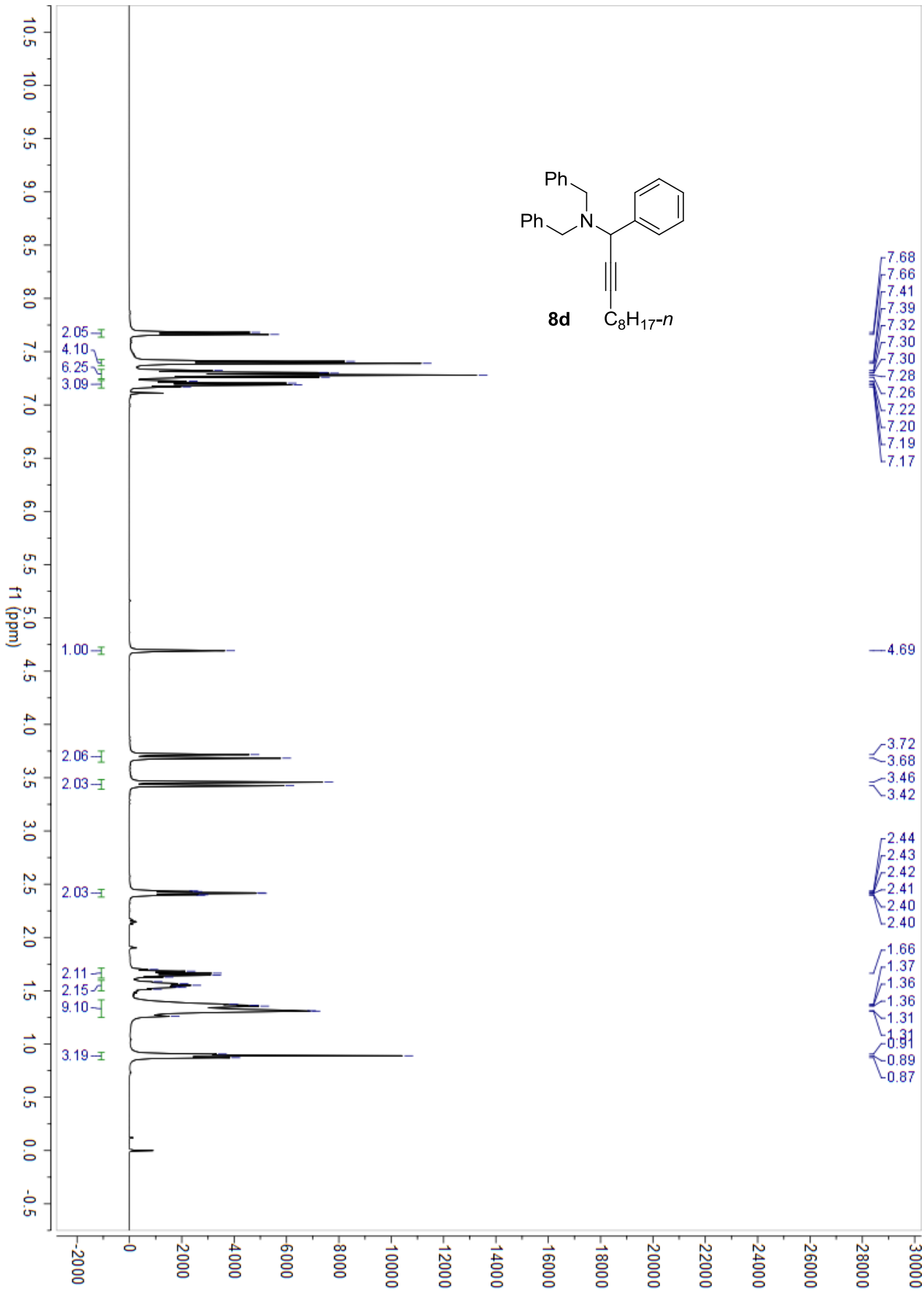

O
N
8a
C_8H_{17}-*n*
138.5
128.6
128.1
127.5
88.8
75.4
67.2
61.7
49.8
31.8
29.2
29.1
29.0
29.0
22.7
18.8
14.1
f1 (ppm)

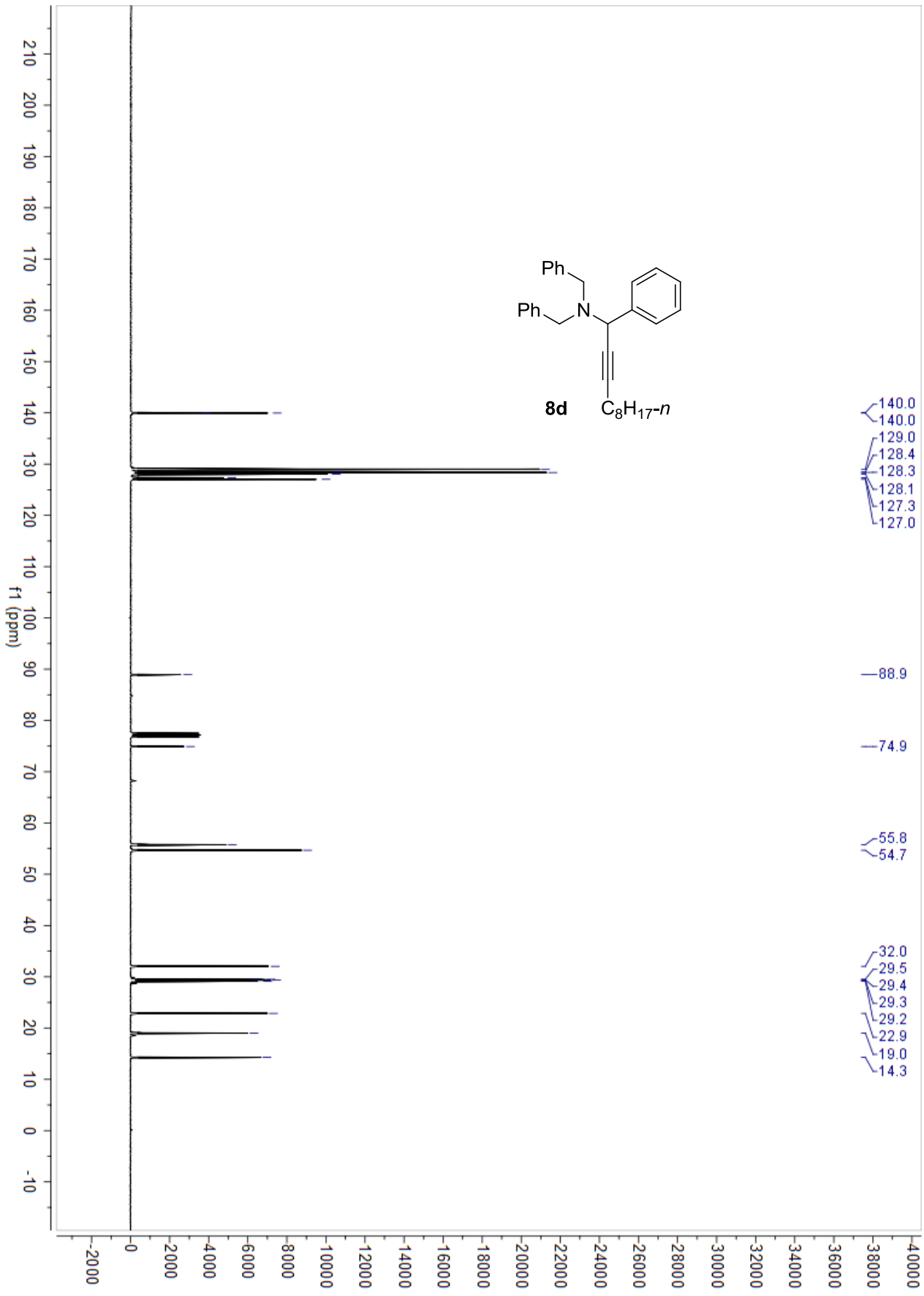

N
C8H17-n
8b
f1 (ppm)
7.46
7.46
7.44
7.25
7.25
7.23
7.23
7.21
7.18
7.18
7.18
7.17
7.16
7.15
7.14
2.07
2.03
1.08
1.00
4.53
2.52
2.51
2.51
2.50
2.49
2.21
2.21
2.20
2.19
2.18
2.17
4.20
2.06
4.14
2.19
2.24
8.48
3.05
1.69
1.68
1.66
1.21
1.20
0.82
0.80
0.79

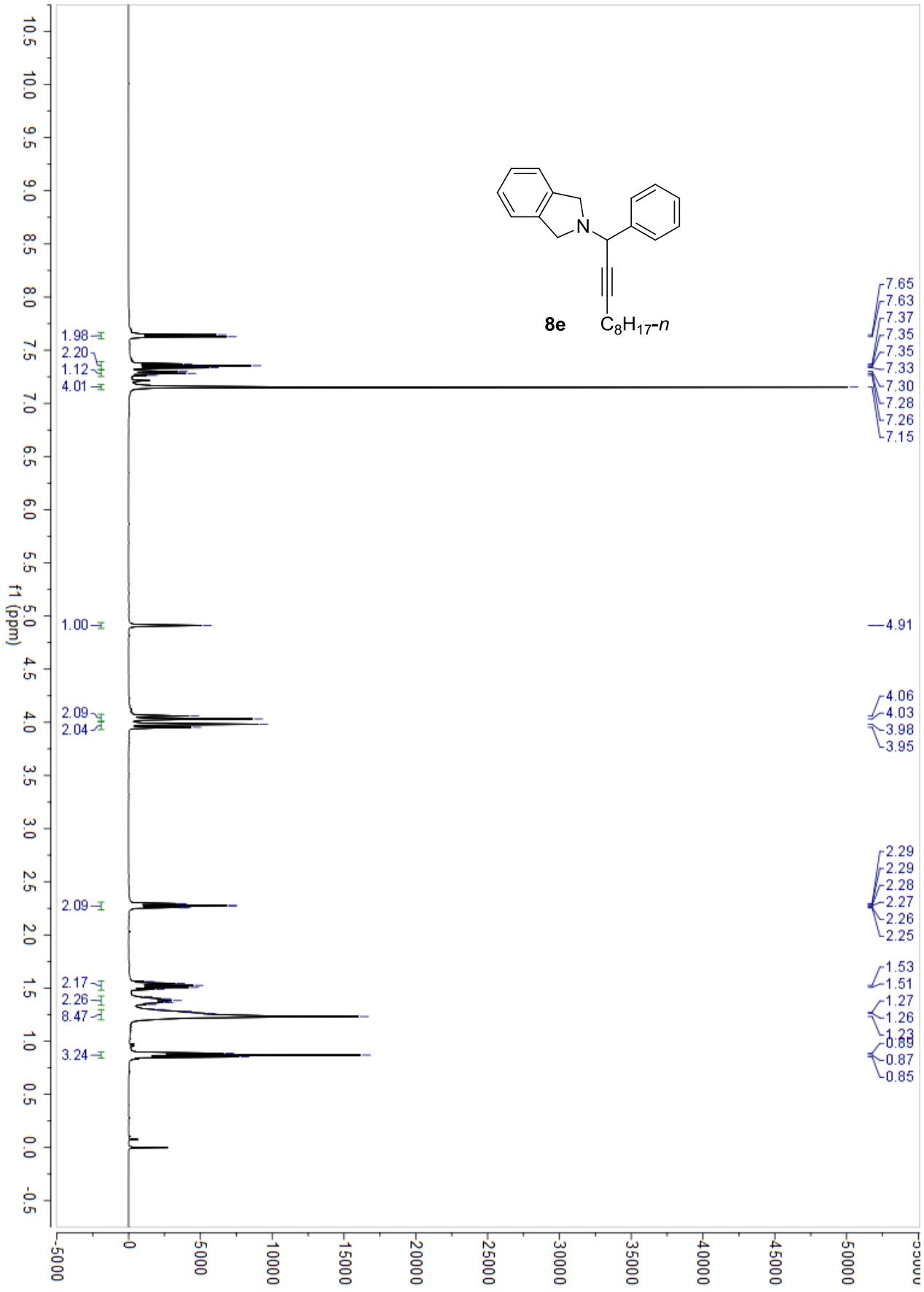

N
C8H17-n
8b
140.2
128.2
128.1
127.3
87.1
77.0
58.8
50.2
31.9
29.3
29.1
29.0
28.9
23.5
22.7
18.8
14.1
f1 (ppm)

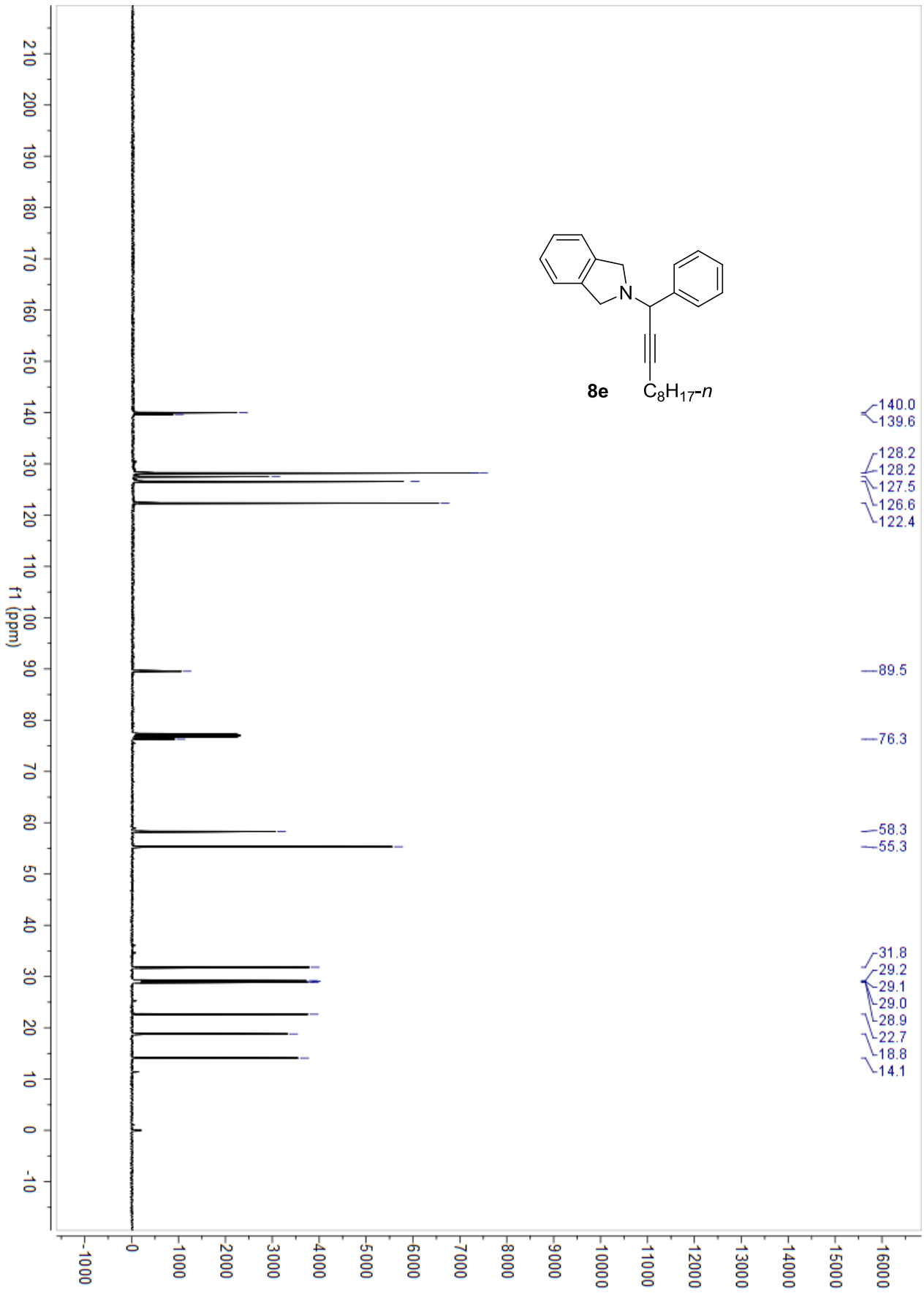

N
8c
C_8H_{17}-*n*
f1 (ppm)
1.99
2.08
1.14
1.00
2.10
2.17
2.15
2.22
2.21
8.82
6.22
3.22
7.63
7.61
7.33
7.31
7.29
7.25
7.23
7.22
4.80
2.57
2.55
2.53
2.52
2.50
2.48
2.46
2.45
2.43
2.41
2.40
2.32
2.32
2.31
2.30
2.29
2.28
1.61
1.59
1.57
1.55
1.53
1.47
1.45
1.43
1.31
1.29
1.05
1.03
1.01
0.90
0.88
0.87


8c
C_8H_{17}-*n*
140.6
128.4
127.9
127.0
87.5
76.0
56.5
44.5
31.9
29.3
29.1
29.1
28.9
22.7
18.8
14.1
13.6
f1 (ppm)


Ph
Ph
N
8d
C_8H_{17}-*n*
f1 (ppm)
2.05
4.10
6.25
3.09
1.00
2.06
2.03
2.03
2.11
2.15
9.10
3.19
7.68
7.66
7.41
7.39
7.32
7.30
7.30
7.28
7.26
7.22
7.20
7.19
7.17
4.69
3.72
3.68
3.46
3.42
2.44
2.43
2.42
2.41
2.40
2.40
1.66
1.37
1.36
1.36
1.31
1.31
0.91
0.89
0.87


Ph
Ph
N
8d
C_8H_{17}-*n*
140.0
140.0
129.0
128.4
128.3
128.1
127.3
127.0
88.9
74.9
55.8
54.7
32.0
29.5
29.4
29.3
29.2
22.9
19.0
14.3
f1 (ppm)

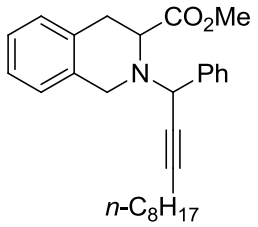

8e
C_8H_{17}-*n*
f1 (ppm)
1.98
2.20
1.12
4.01
1.00
2.09
2.04
2.09
2.17
2.26
8.47
3.24
7.65
7.63
7.37
7.35
7.35
7.33
7.30
7.28
7.26
7.15
4.91
4.06
4.03
3.98
3.95
2.29
2.29
2.28
2.27
2.26
2.25
1.53
1.51
1.27
1.26
1.23
0.89
0.87
0.85

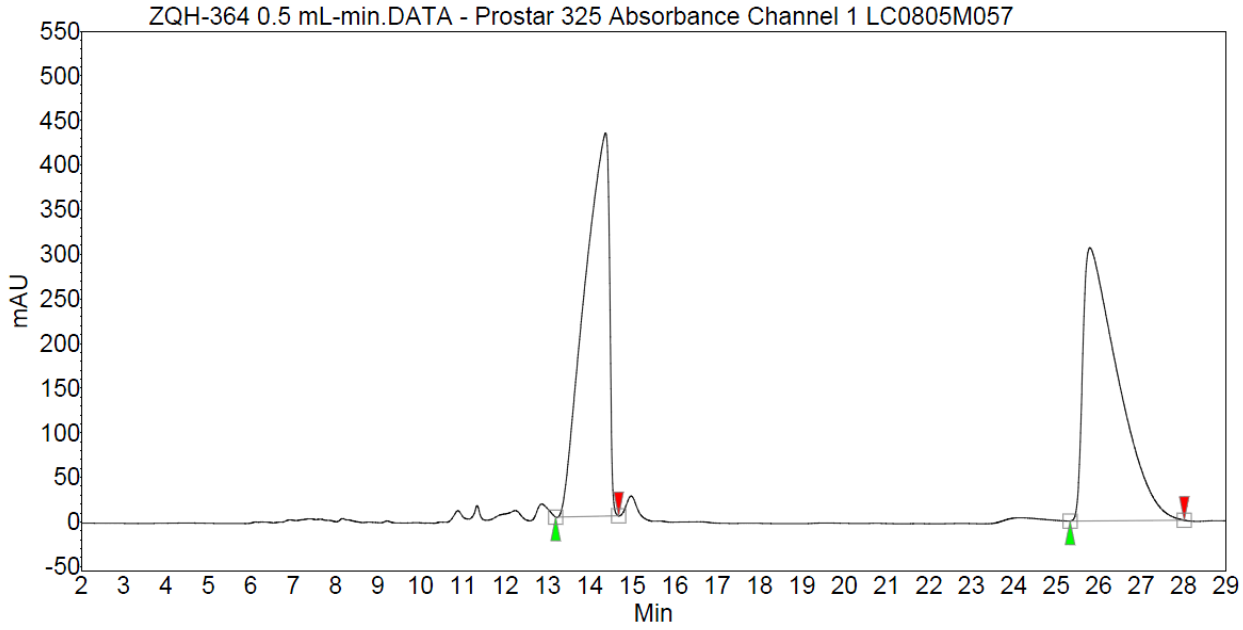

8e
C8H17-n
140.0
139.6
128.2
128.2
127.5
126.6
122.4
89.5
76.3
58.3
55.3
31.8
29.2
29.1
29.0
28.9
22.7
18.8
14.1
f1 (ppm)

5. Copies of HPLC Profiles

HPLC Conditions of rac-7 and 7: chiralcel AD-H column, hexanes/*i*-PrOH = 99/1, flow rate 0.5 mL/min, 254 nm, retention time 14.0 min and 25.1 min (**rac-7** was prepared by the similar way of the synthesis of 7 except that racemic **6b** was used)

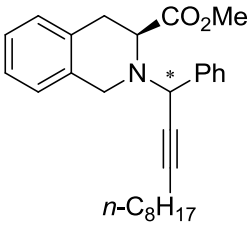
HPLC Profile of rac-7

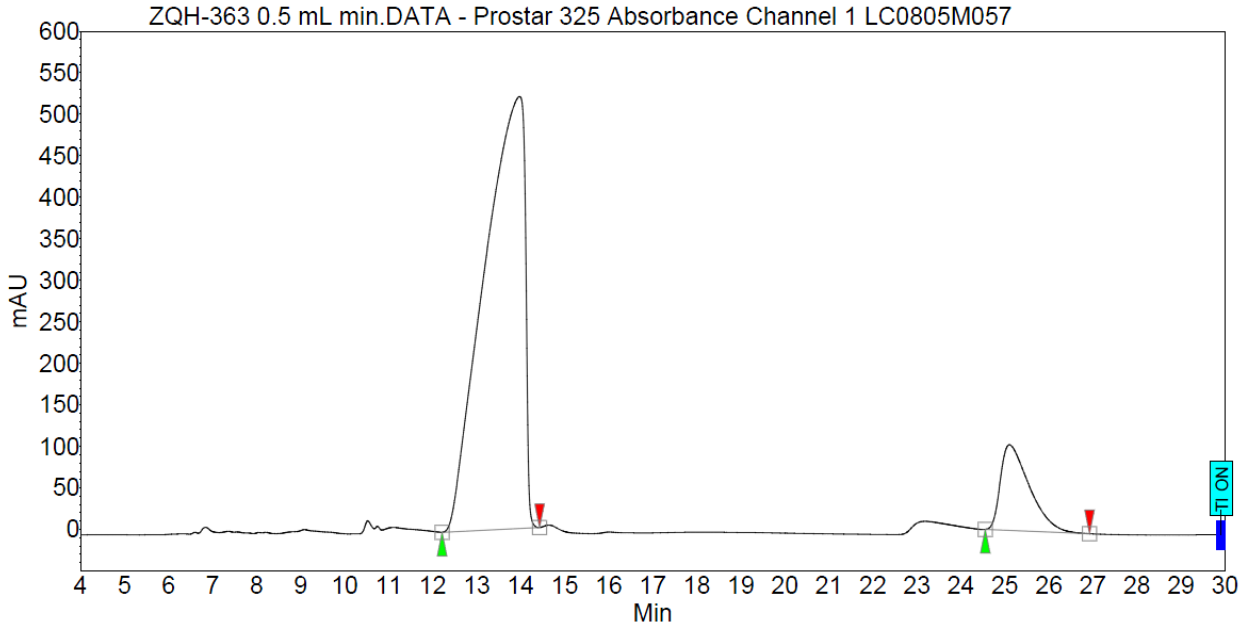




No.	Ret.Time (min)	Height (mAU)	Rel.Area (%)
1	14.37	429.4	49.77
2	25.79	306.1	50.23

HPLC Profile of 7

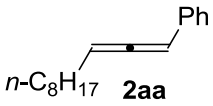


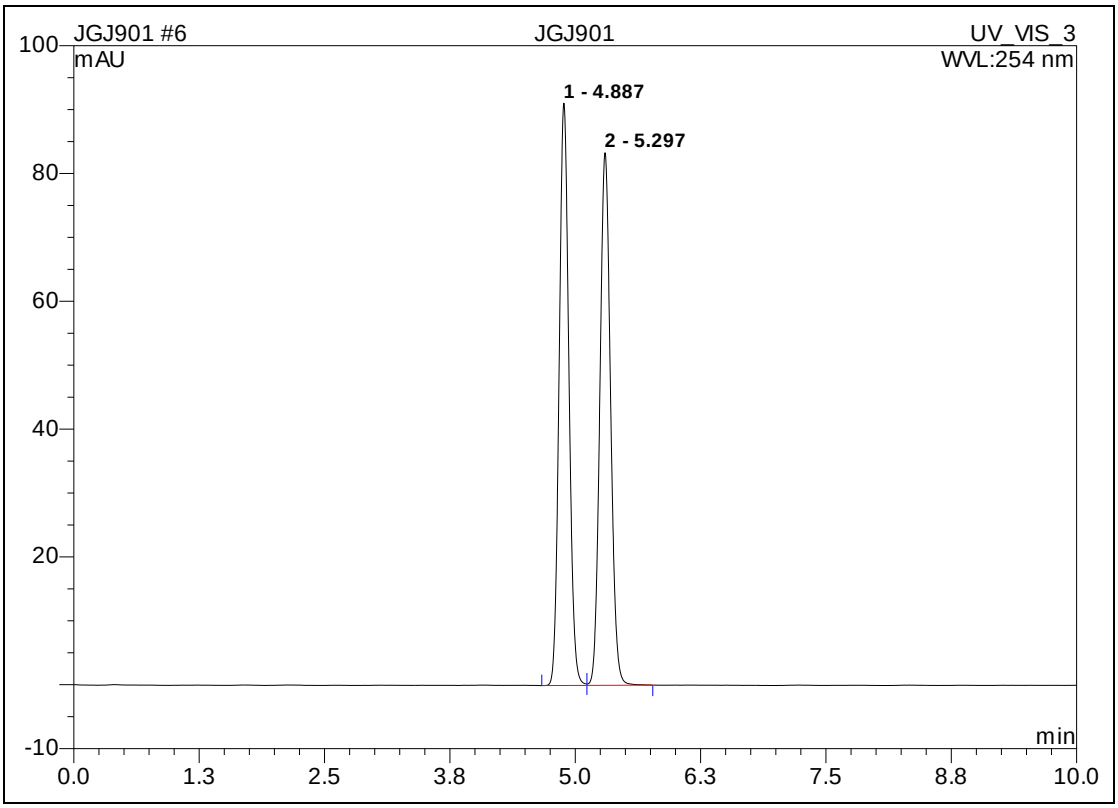


No.	Ret.Time (min)	Height (mAU)	Rel.Area (%)
1	13.97	520.2	87.62
2	25.11	103.2	12.38

HPLC Conditions of 2aa and *R*-2aa: chiralcel OD-H column, hexanes/*i*-PrOH = 100/0, flow rate 1.5 mL/min, 254 nm, retention time 4.9 min (*R*) and 5.2 min (*S*).

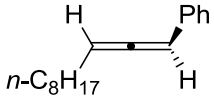
HPLC Profile of 2aa



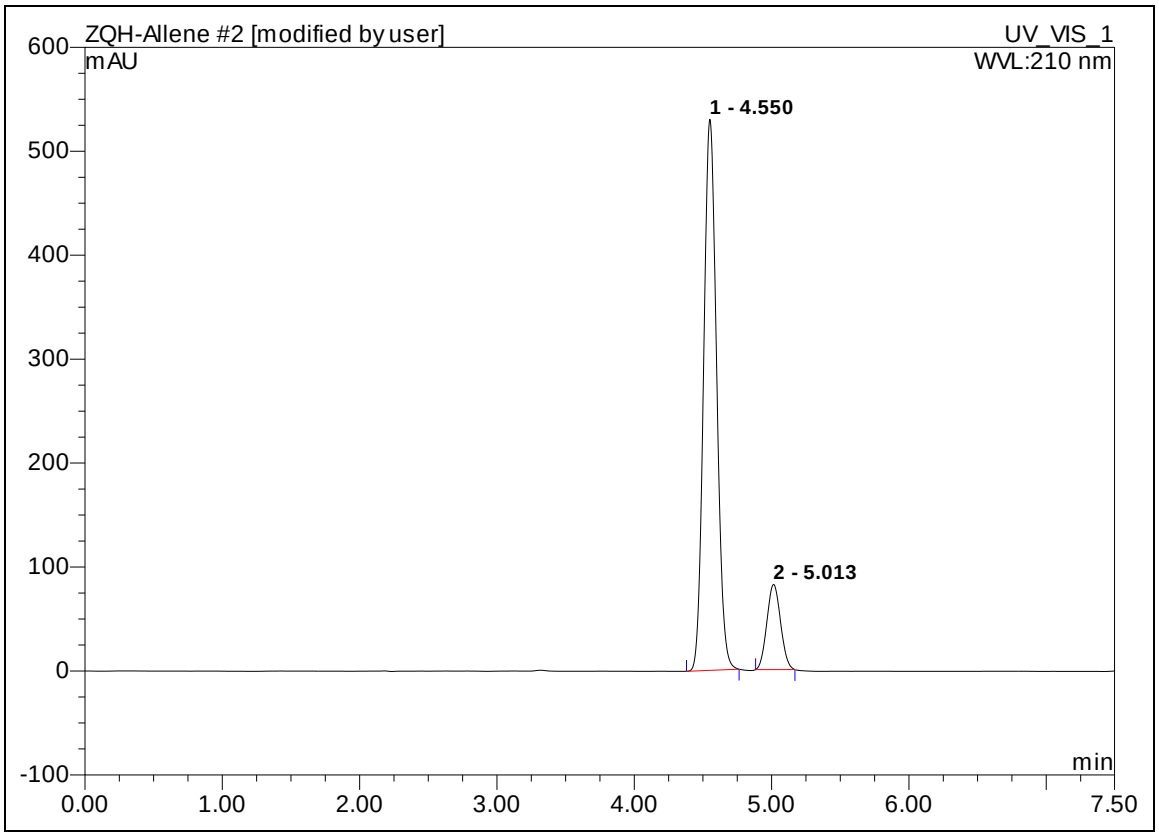


No.	Ret.Time (min)	Height (mAU)	Area (mAU*min)	Rel.Area (%)
1	4.887	91.123	10.295	49.95
2	5.297	83.341	10.317	50.05

HPLC Profile of *R*-2aa (synthesized by using purified propargyl amine intermediate 7)

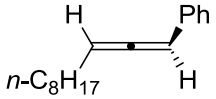


***R*-2aa**

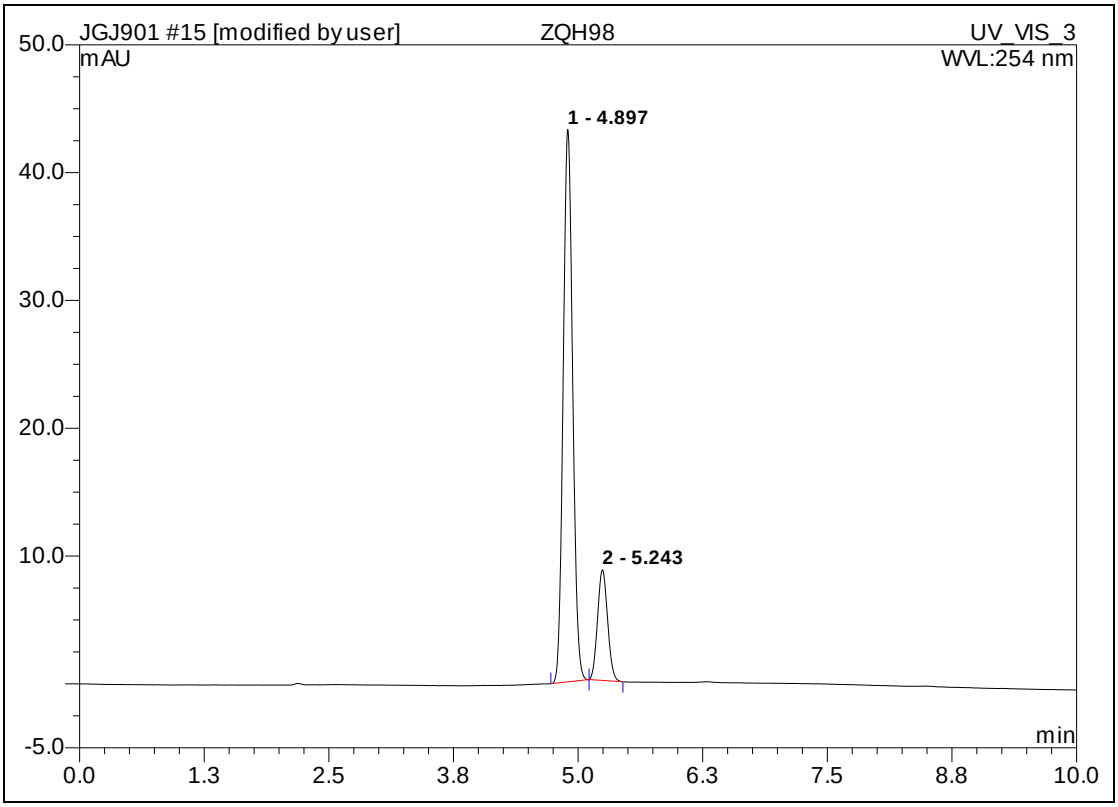


No.	Ret.Time (min)	Height (mAU)	Area (mAU*min)	Rel.Area (%)
1	4.55	530.121	57.889	85.95
2	5.01	81.874	9.465	14.05

HPLC Profile of *R*-2aa (using unpurified propargyl amine intermediate)



***R*-2aa**



No.	Ret.Time (min)	Height (mAU)	Area (mAU*min)	Rel.Area (%)
1	4.897	43.212	4.756	82.48
2	5.243	8.647	1.010	17.52