Supporting Information

Regioselective Palladium-Catalyzed Electrophilic Allylic Substitution in the Presence of Hexamethylditin

Olov A. Wallner and Kálmán J. Szabó*

Stockholm University, Arrhenius Laboratory, Department of Organic Chemistry

SE-106 91 Stockholm, Sweden. E-mail: kalman@organ.su.se. Fax: +46-8-15 49 08

The starting materials were purchased from Aldrich or Lancaster. Allyl acetate **3b** and allyl chlorides **4** and **5** were prepared using standard procedures reported in literature[1-4]. Allylic chloride **2** was prepared using the procedure reported below. The solvents were freshly distilled prior to use. All reactions were conducted under argon atmosphere by employing standard manifold techniques. The ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at room temperature by Varian 400 spectrometer. The chemical shifts (ppm) were obtained using $CDCl_3$ as an internal standard (7.26 ppm, ^{1}H; 77.36 ppm, ^{13}C). Mass spectra were recorded on a Finnigan Thermoquest 2000A spectrometer. Merck silica gel 60 (230-400 mesh) was used for the chromatography.

Ethyl-2-chloro-but-3-enoate (2). N-chlorosuccinimide (1.90 g, 14.2 mmol) was suspended in THF (25 ml) and this mixture was cooled to 0°C. Thereafter, triphenylphosphine (3.60 g, 13.8 mmol) in THF (13 ml) was added and the resulting mixture was stirred for 5 min. The temperature was then increased to 25°C and this mixture was stirred for an additional 30 min. Thereafter, ethyl-2-hydroxy-but-3-enoate[1] (1.23g, 9.50 mmol) was added and the reaction mixture was stirred for 23 h. After evaporation of the solvent the purification was done by silica gel chromatography using pentane-diethyl ether (20:1) as eluent providing ethyl-2-chloro-but-3-enoate (1.0 g, 67% yield). ^{1}H NMR: δ 6.05 (ddd, 17.0 Hz, 10.2 Hz, 8.2 Hz, 1H), 5.47 (d, 16.8 Hz, 0.8 Hz, 1H), 5.35 (dt, 8.0 Hz,0.8 Hz, 1H), 4.76 (dt, 8.0 Hz,1.0 Hz, 1H), 4.25 (q, 7.1 Hz, 2H), 1.31 (t, 7.1 Hz, 3H). ^{13}C NMR: δ 168.4, 132.8, 120.6, 62.7, 58.3, 14.3.

1-(4-Nitrophenyl)-2-phenyl-but-3-en-1-ol (10). The product was purified by silica gel chromatography using pentane-ethyl acetate (3:1) as eluent giving a mixture of diastereomers. NMR data given for the major diastereomer. ^{1}H NMR: δ 8.05 (m, 2H), 7.18-7.30 (m, 5H), 7.04 (m, 2H), 6.23 (ddd, 17.0 Hz, 10.1 Hz, 9.1 Hz, 1H), 5.32 (d, 10.1 Hz, 1H), 5.27 (d, 17.0 Hz, 1H), 4.93 (dd, 7.8 Hz, 2.2 Hz, 1H), 3.48 (t, 8.4 Hz, 1H), 2.48 (t, 2.5 Hz, 1H). ^{13}C NMR: δ 149.5, 139.8, 137.2, 129.1, 128.5, 127.8, 127.5, 123.4, 119.9, 76.7, 59.9.

N-(1,2-Diphenyl-but-3-enyl)-benzenesulfonamide (11). The product was purified by silica gel chromatography using pentane-diethyl ether (2:1) as eluent yielding a single diastereomer. ^{1}H NMR: δ 7.47-7.51 (m, 2H), 7.37-7.42 (m, 1H), 7.22-7.25 (m, 5H), 7.06-

7.13 (m, 3H), 6.95-6.99 (m, 2H), 6.88-6.92 (m, 2H), 5.79 (ddd, 17.0 Hz, 10.2 Hz, 8.3 Hz, 1H), 5.00 (d, 10.2 Hz, 1H), 4.98 (d, 7.4 Hz, 1H), 4.88 (dt, 17.0 Hz, 1.3 Hz, 1H), 4.59 (dd, 7.4 Hz, 6.7 Hz, 1H), 3.55 (t, 8.0 Hz, 1H). ^{13}C NMR: δ 140.4, 139.3, 138.5, 136.7, 132.4, 129.1, 128.9, 128.7, 128.2, 128.1, 127.7, 127.6, 127.3, 118.5, 62.0, 56.8.

4,4-Dicyano-1,5,6-triphenyl-1,7-octadiene (12). The product was purified by silica gel chromatography using pentane-ethyl acetate (10:1) as eluent. Using this eluent system the two diastereomers of **12** could be completely separated. Diastereomer A: ^{1}H NMR: δ 6.97-7.44 (m, 15H), 6.44 (d, 15.7 Hz, 1H), 6.32 (dt, 17.0 Hz, 10.1 Hz, 1H), 6.18 (dt, 15.7 Hz, 7.4 Hz, 1H), 5.66 (d, 16.9 Hz, 1H), 5.36 (dd, 10.0 Hz, 1.3 Hz, 1H), 4.10 (t, 10.7 Hz, 1H), 3.48 (d, 11.2 Hz, 1H), 2.50 (ddd, 37.2 Hz, 14.1 Hz, 7.5 Hz, 2H). ^{13}C NMR: δ 141.2, 138.6, 138.0, 136.3, 135.9, 129.2, 129.0, 128.9, 128.8, 128.6, 127.9, 127.0, 127.0, 120.2, 119.6, 116.8, 115.1, 57.1, 56.2, 42.2, 41.2. Diastereomer B: ^{1}H NMR: δ 7.27-7.46 (m, 15H), 6.36 (dt, 15.7 Hz, 1.1 Hz, 1H), 6.08 (dt, 15.6 Hz, 7.4 Hz, 1H), 5.88 (ddd, 16.8 Hz, 10.2 Hz, 8.9 Hz, 1H), 5.01 (dt, 16.8 Hz, 1.2 Hz, 1H), 4.97 (m, 1H), 4.19 (t, 9.3 Hz, 1H), 3.38 (d, 9.4 Hz, 1H), 2.41 (dt, 7.4 Hz, 1.4 Hz, 2H). ^{13}C NMR: δ 140.8, 138.0, 137.8, 136.2, 135.8, 129.7, 129.5, 129.4, 129.2, 129.0, 128.9, 128.6, 128.4, 119.6, 118.4, 115.3, 114.8, 56.4, 54.1, 42.1, 41.9. MS (EI): *m/z* (rel intens) 388 (M^+, 10), 361 (4), 297 (8), 207 (9), 117 (100).

Ethyl-2-(hydroxy-(4-nitrophenyl)-methyl)-but-3-enoate (13). The product was purified by silica gel chromatography using pentane-ethyl acetate (4:1) as eluent giving a mixture of diastereomers. Diastereomer A: ^{1}H NMR: δ 8.14 (m, 2H), 7.46-7.52 (m, 2H), 5.87 (ddd, 17.4 Hz, 10.2 Hz, 9.0 Hz, 1H), 5.23 (dd, 10.2 Hz, 1.0 Hz, 1H), 5.16 (dd, 5.0 Hz, 2.5 Hz, 1H), 5.07 (dt, 17.4 Hz, 1.0 Hz, 1H), 4.11 (q, 7.1 Hz, 2H), 3.46 (d, 2.7 Hz, 1H), 3.28 (dd, 9.0 Hz, 5.0 Hz, 1H), 1.17 (t, 7.1 Hz, 3H). Diastereomer B: ^{1}H NMR: δ 8.14 (m, 2H), 7.46-7.52 (m, 2H), 5.70 (ddd, 17.2 Hz, 10.3 Hz, 8.9 Hz, 1H), 5.12 (d, 10.3 Hz, 1H), 4.99-5.05 (m, 2H), 4.15 (q, 7.1 Hz, 2H), 3.50 (d, 5.5 Hz, 1H), 3.36 (dd, 8.5 Hz, 8.5 Hz, 1H), 1.21 (t, 7.1 Hz, 3H). ^{13}C NMR for diastereomers A and B: δ 172.7, 148.8, 148.3, 147.8, 147.7, 131.7, 130.7, 127.8, 127.6, 123.7 (2 C), 121.7, 120.7, 74.5, 73.1, 61.7, 58.0, 57.8, 14.3, 14.3. MS (EI): *m/z* (rel intens) 265 (M^+, 2), 248 (6), 152 (18), 114 (46), 86 (100).

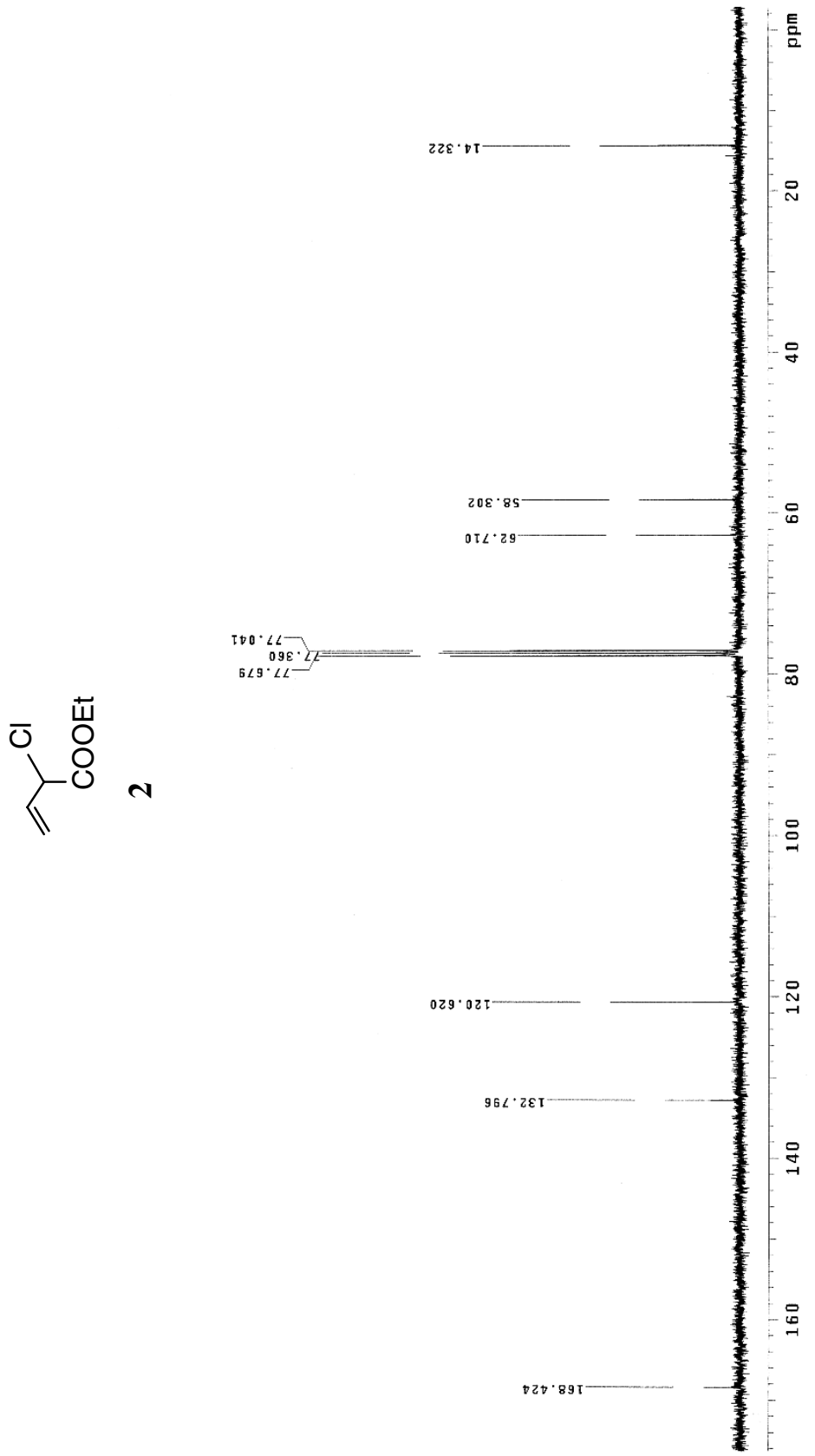
Ethyl-2-(phenyl-(phenysulfonyl)-amino)-methyl)-but-3-enoate (14). The product was purified by silica gel chromatography using pentane-ethyl acetate (4:1) as eluent providing a single diastereomer. ^{1}H NMR: δ 7.61-7.65 (m, 2H), 7.36-7.40 (m, 1H), 7.23-7.29 (m, 2H), 7.09-7.13 (m, 3H), 7.00-7.04 (m, 2H), 6.24 (d, 9.4 Hz, 1H), 5.73 (ddd, 17.5 Hz, 10.0 Hz, 8.5 Hz, 1H), 5.10 (m, 2H), 4.77 (dd, 9.4 Hz, 6.5 Hz, 1H), 4.06 (q, 7.1 Hz, 2H), 3.41 (dd, 8.4 Hz, 6.4 Hz, 1H), 1.15 (t, 7.1 Hz, 3H). ^{13}C NMR: δ 172.0, 141.0, 138.2, 132.4, 132.2, 128.8, 128.6, 127.9, 127.2, 127.0, 120.4, 61.5, 59.6, 56.6, 14.3. MS (EI): *m/z* (rel intens) 359 (M^+, 4), 246 (100), 141 (43), 77 (45).

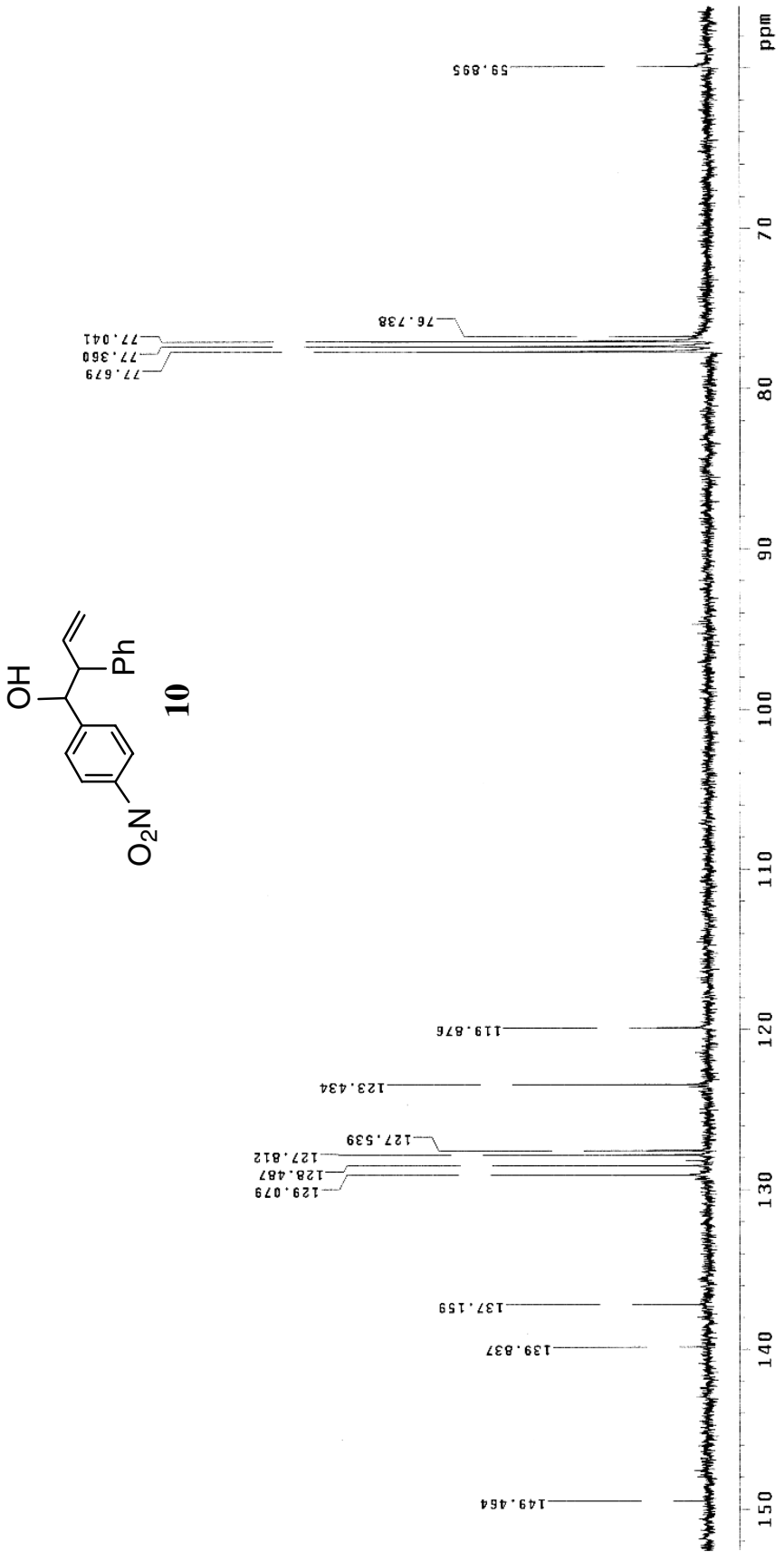
Diethyl-5,5-dicyano-6-phenyl-7-vinyloct-2-enedioate (15). The product was purified by silica gel chromatography using pentane-ethyl acetate (7:1) as eluent giving a mixture of diastereomers. Diastereomer A: ^{1}H NMR: δ 7.30-7.41 (m, 5H), 6.86 (dt, 15.1 Hz, 7.8 Hz, 1H), 5.95 (dt, 15.5 Hz, 1.4 Hz, 1H), 5.57 (dt, 17.0 Hz, 9.7 Hz, 1H), 5.22 (d, 17.0 Hz, 1H), 5.11 (dd, 10.0 Hz, 0.9 Hz, 1H), 4.16-4.24 (m, 4H), 3.79-3.96 (m, 1H), 3.69 (d, 9.2 Hz, 1H), 2.55 (m, 2H), 1.24-1.31 (m, 6H). Diastereomer B: ^{1}H NMR: δ 7.30-7.41 (m, 5H), 6.82 (dt, 15.5 Hz, 7.4 Hz, 1H), 6.06 (dt, 16.9 Hz, 10.0 Hz, 1H), 5.89 (dt, 15.3 Hz, 1.3 Hz, 1H), 5.74 (d, 16.6 Hz, 1H), 5.51 (dd, 9.9 Hz, 1.0 Hz, 1H), 4.16-4.24 (m, 4H), 3.79-3.96 (m, 1H), 3.59 (d, 11.4 Hz, 1H), 2.43 (m, 2H), 1.24-1.31 (m, 6H). ^{13}C NMR for diastereomers A and B: δ 171.7, 170.5, 165.1, 136.9, 136.9, 134.5, 133.3, 132.7, 132.6, 130.2, 129.8, 129.7, 129.5, 129.1, 128.9, 124.2, 121.3, 115.4, 114.4, 114.1, 114.0, 62.3, 61.5, 61.2, 61.2, 57.3, 53.3, 52.3, 52.1, 41.1, 40.5, 40.1, 39.4, 14.5, 14.2, 14.0. MS (EI): *m/z* (rel intens) 381 (M^++1, 6), 307 (30), 261 (36), 157 (43), 129 (100).

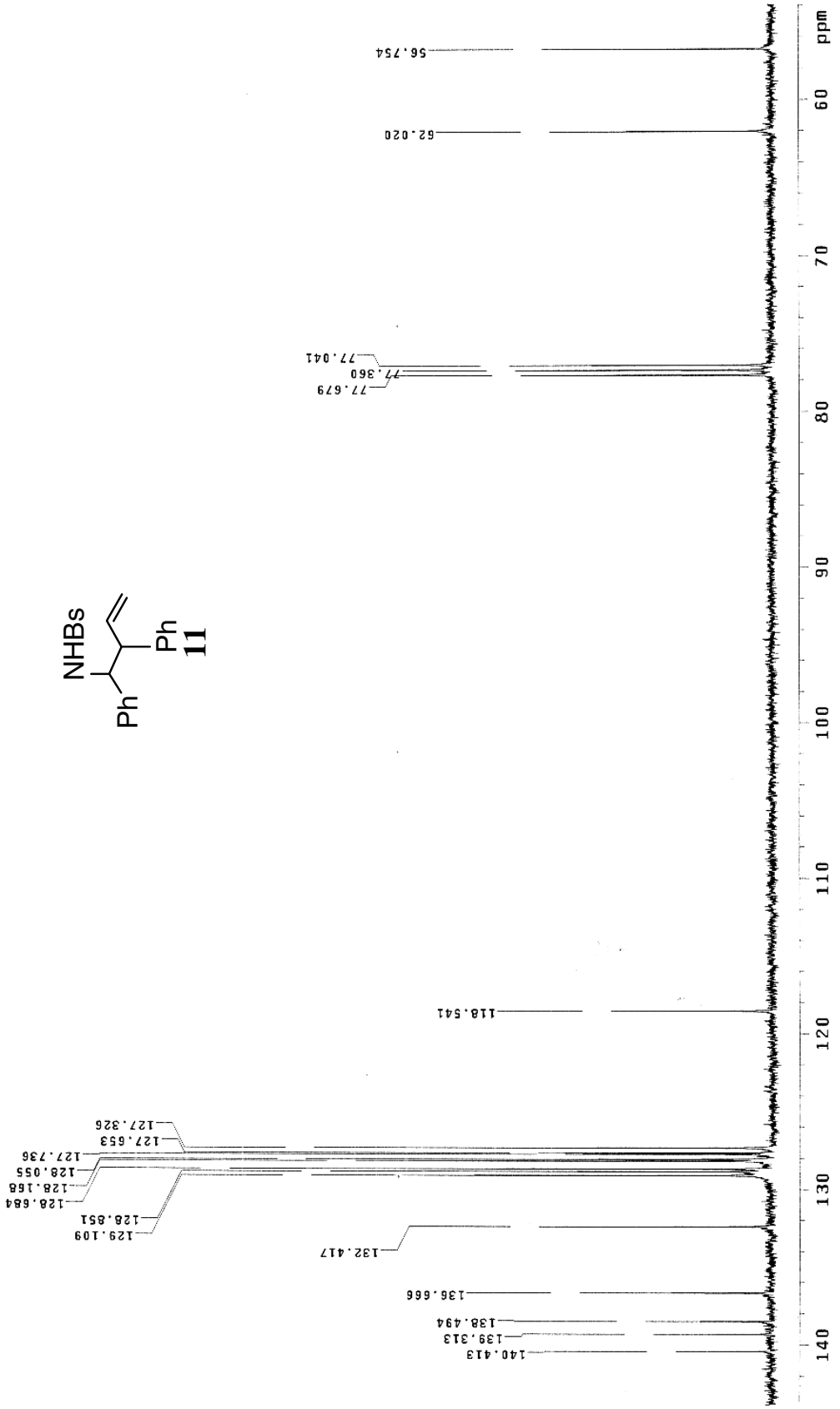
1-(Hydroxy-(4-nitrophenyl)-methyl-allylcyanide (16). The product was purified by silica gel chromatography using pentane-ethyl acetate (7:1) as eluent giving a mixture of diastereomers. ^{1}H NMR: δ 8.25 (m, 2H), 7.61 (m, 2H), 5.68-5.78 (m, 1H), 5.42-5.59 (m, 2H), 5.03 (dd, 14.1 Hz, 6.1 Hz, 1H), 3.64-3.69 (m, 1H), 2.47-2.74 (bs, 1H). ^{13}C NMR: δ 148.3, 146.7, 146.5, 128.2, 127.9, 127.7, 127.6, 124.1, 124.0, 122.4, 122.2, 117.6, 117.3, 73.4, 73.3, 44.9, 44.4. MS (EI): *m/z* (rel intens) 218 (M^+, 3), 201 (51), 152 (100), 122 (20), 77 (41).

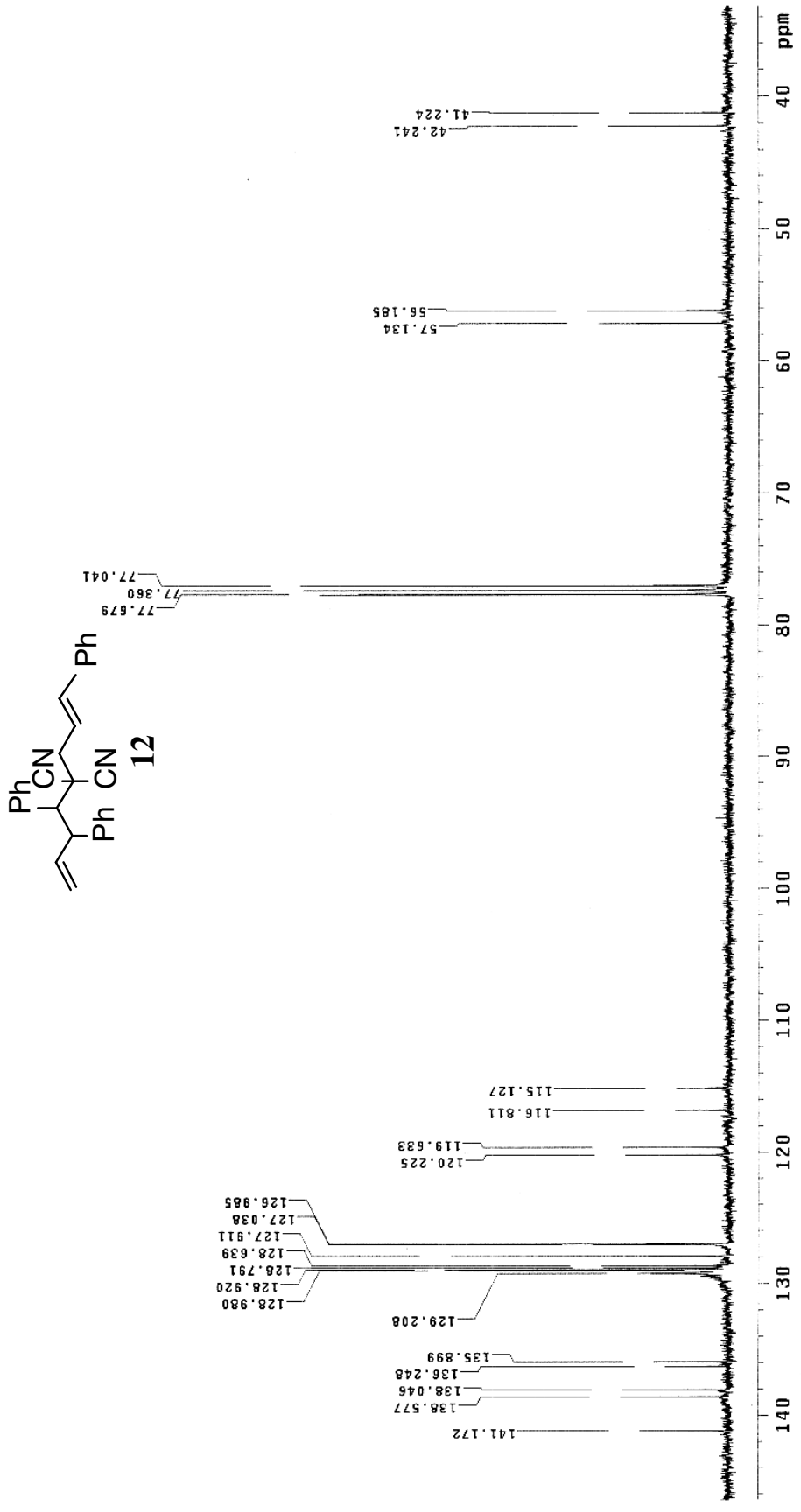
3-(Hydroxy-(2-nitrophenyl)-methyl)-pent-4-en-2-one (17). The product was purified by silica gel chromatography using pentane-ethyl acetate (4:1) as eluent. Using this eluent system the two diastereomers of **17** could be completely separated. Diastereomer A: ^{1}H NMR: δ 7.97-8.00 (m, 1H), 7.74-7.78 (m, 1H), 7.59-7.64 (m, 1H), 7.39-7.44 (m, 1H), 5.89 (ddd, 17.2 Hz, 10.1 Hz, 9.6 Hz, 1H), 5.78 (d, 1.9 Hz, 1H), 5.25 (dd, 10.2 Hz, 1.3 Hz, 1H), 4.97 (d, 17.2 Hz, 1H), 3.81 (bs, 1H), 3.66 (dd, 9.6 Hz, 2.0 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR: δ 211.2, 147.3, 136.9, 133.5, 130.3, 130.2, 128.5, 124.8, 122.9, 68.6, 62.2, 29.6. Diastereomer B: ^{1}H NMR: 7.87-7.90 (m, 1H), 7.68-7.72 (m, 1H), 7.60-7.65 (m, 1H), 7.40-7.45 (m, 1H), 5.72 (ddd, 17.1 Hz, 10.0 Hz, 9.7 Hz, 1H), 5.66 (dd, 7.1 Hz, 5.20 Hz), 5.15 (dd, 10.2 Hz, 1.2 Hz, 1H), 5.09 (d, 17.0 Hz, 1H), 3.75 (bd, 5.6 Hz, 1H), 3.64 (dd, 9.3 Hz, 7.4 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR: δ 210.1, 137.1, 133.6, 132.1, 129.4, 128.9, 124.7, 121.6, 70.6, 64.3, 30.7.

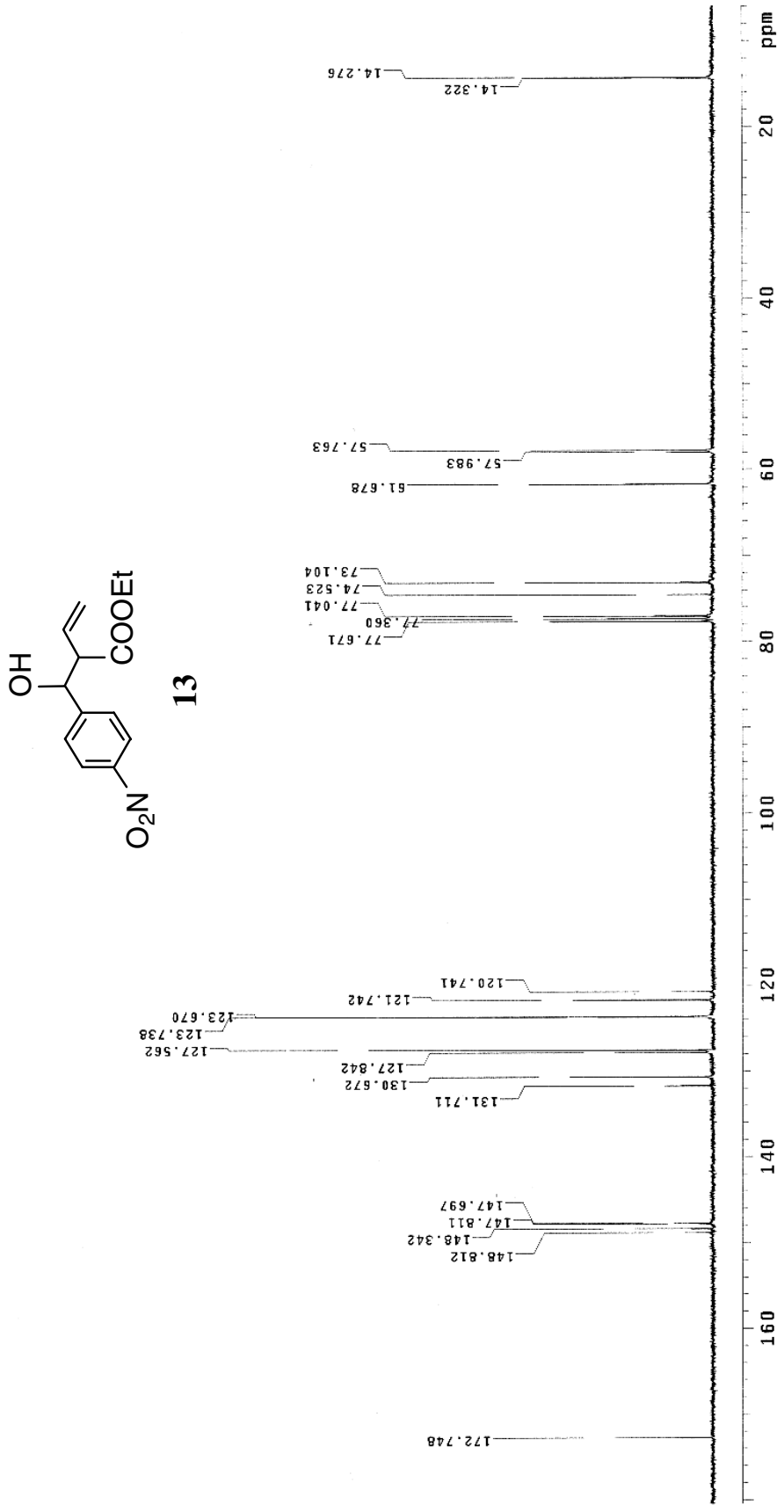
N-(2-acetyl-1-phenyl-but-3-enyl)-benzenesulfonamide (18). The typical procedure given in the communication was followed except that an additional portion of hexamethylditin (0.03 g, 0.1 mmol) was added to the reaction mixture after 24 h. The product was purified by silica gel chromatography using pentane-ethyl acetate (7:1) as eluent giving a mixture of diastereomers. Diastereomer A: ^{1}H NMR: δ 7.58-7.64 (m, 2H), 7.35-7.44 (m, 1H), 7.22-7.32 (m, 2H), 6.98-7.13 (m, 5H), 6.35 (d, 9.3 Hz, 1H), 5.59-5.71 (m, 1H), 5.16 (d, 5.3 Hz, 1H), 5.12 (s, 1H), 4.73 (dd, 9.2 Hz, 6.4 Hz, 1H), 3.56 (dd, 8.9 Hz, 6.5 Hz, 1H), 2.03 (s, 3H). Diastereomer B: ^{1}H NMR: δ 7.58-7.64 (m, 2H), 7.35-7.44 (m,1H), 7.22-7.32 (m, 2H), 6.98-7.13 (m, 5H), 5.59-5.71 (m, 2H), 5.30 (s, 1H), 5.26 (d, 7.4 Hz, 1H), 4.64 (dd, 9.3 Hz, 7.1 Hz, 1H), 3.51 (t, 9.4 Hz, 1H), 1.83 (s, 3H). ^{13}C NMR for diastereomers A and B: δ 208.8, 206.6, 140.9, 140.5, 138.6, 138.4, 133.2, 132.6, 132.4 (2 C), 128.9 (2 C), 128.6, 128.0, 127.8, 127.4, 127.2, (2 C), 122.2, 121.2, 64.5, 63.3, 59.6, 58.8, 30.5, 30.3.

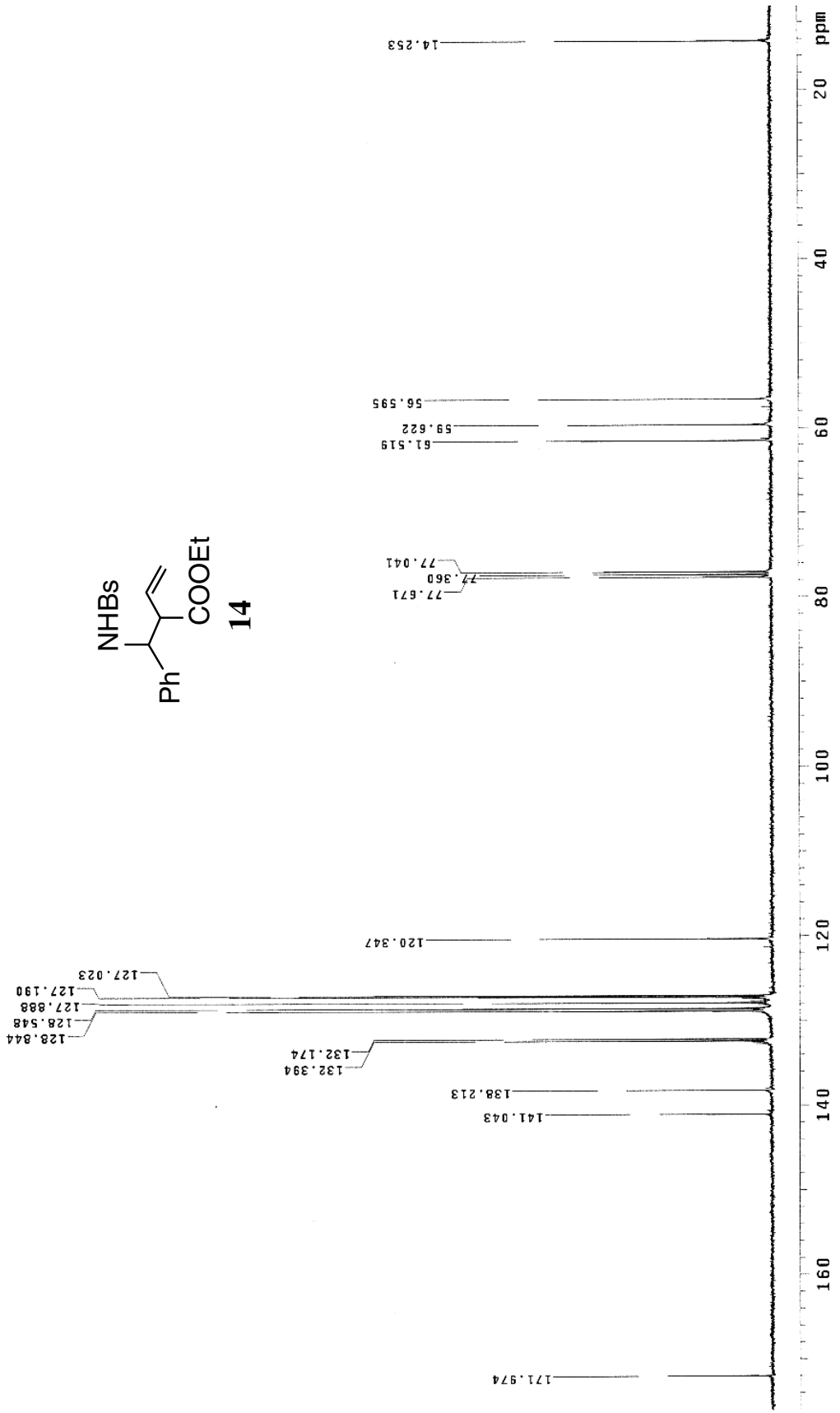

Cl
COOEt
2
168.424
132.796
120.620
77.679
77.360
77.041
62.710
58.302
14.322
ppm
160
140
120
100
80
60
40
20

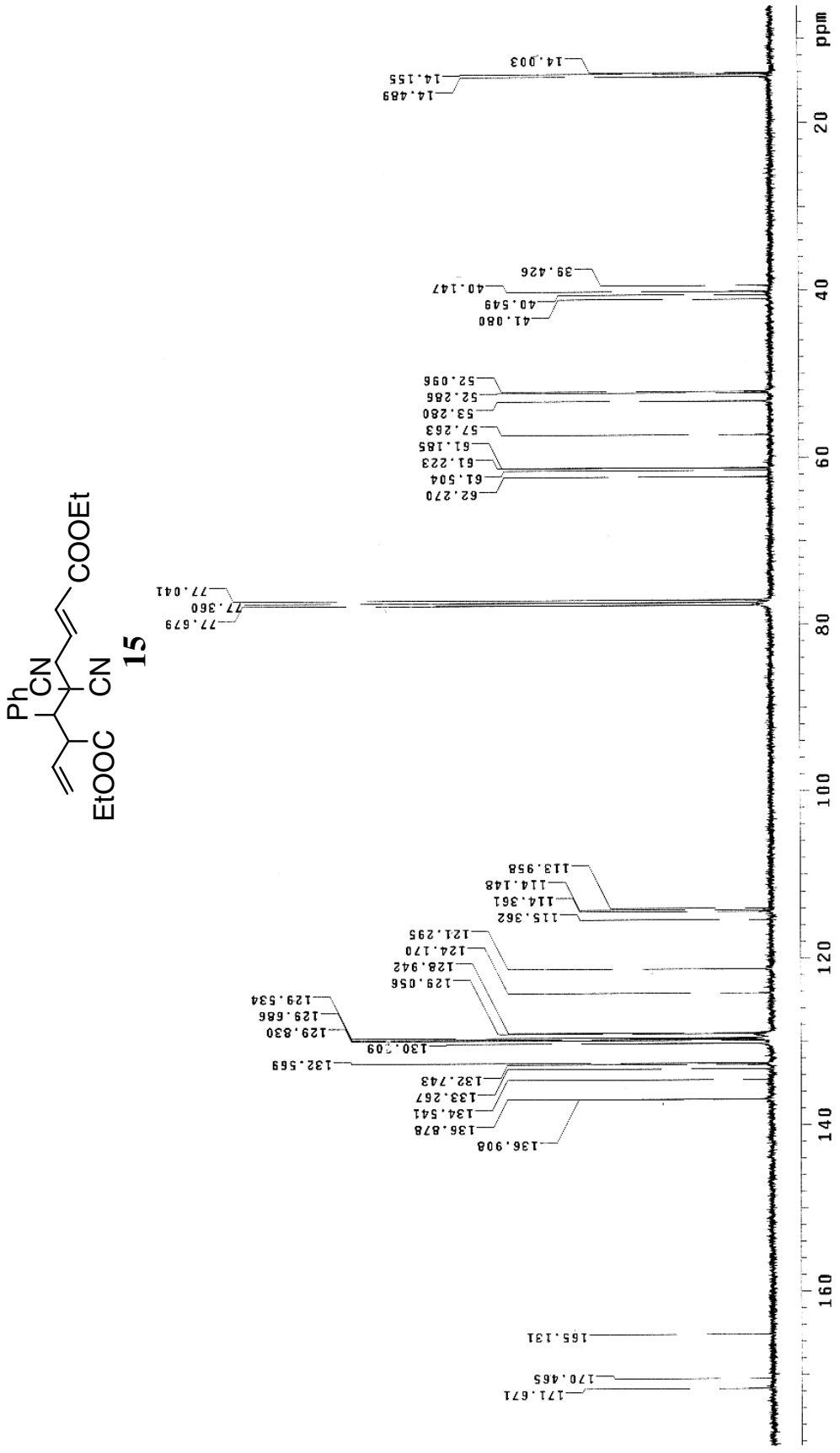

OH
Ph
O_2N
10
59.895
76.738
77.041
77.360
77.679
119.876
123.434
127.539
127.812
128.487
129.079
137.159
139.837
149.464
ppm
70
80
90
100
110
120
130
140
150

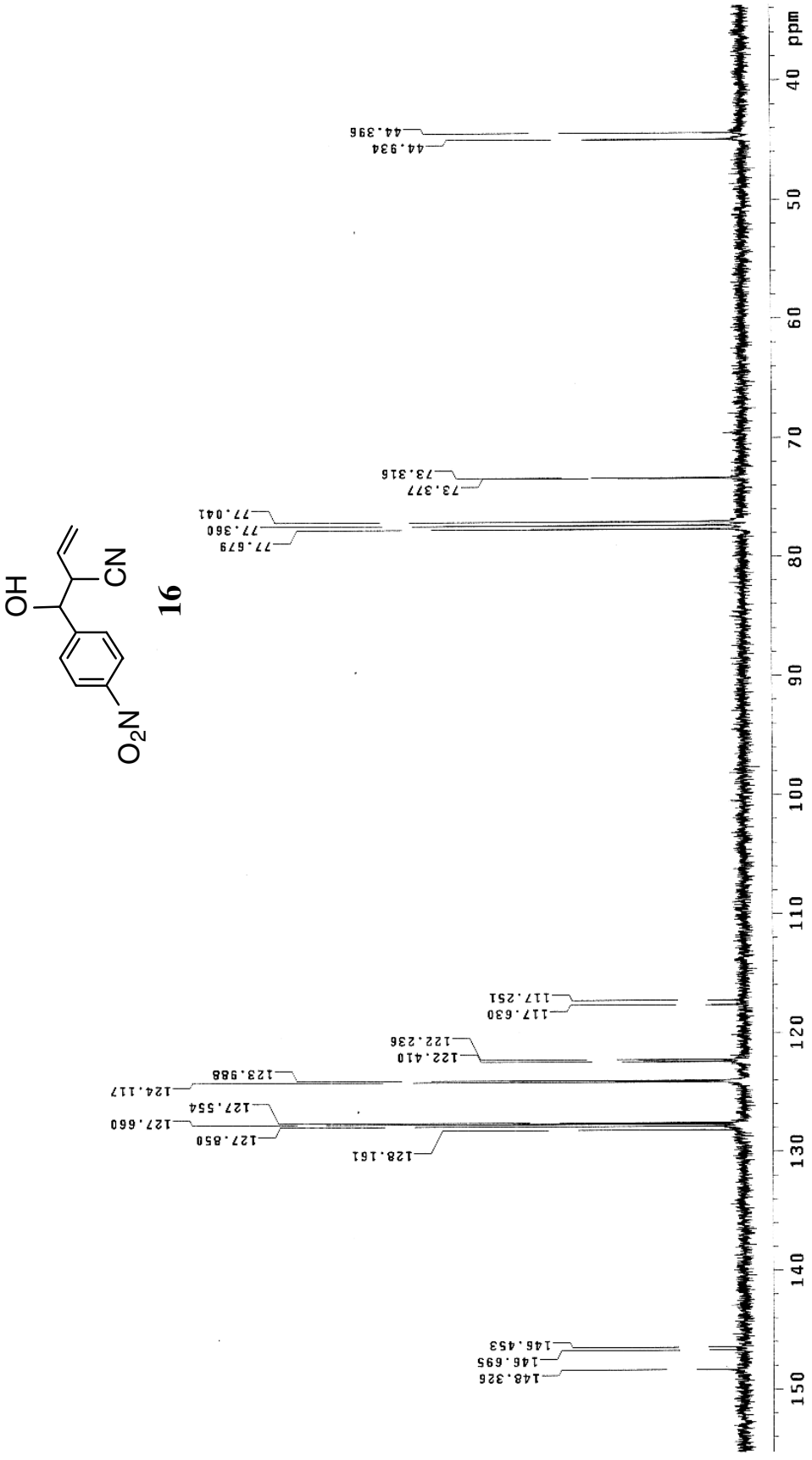

NHBs
Ph
Ph
11
ppm
60
70
80
90
100
110
120
130
140
56.754
62.020
77.041
77.360
77.679
118.541
127.326
127.653
127.736
128.055
128.168
128.684
128.851
129.109
132.417
136.666
138.494
139.313
140.413

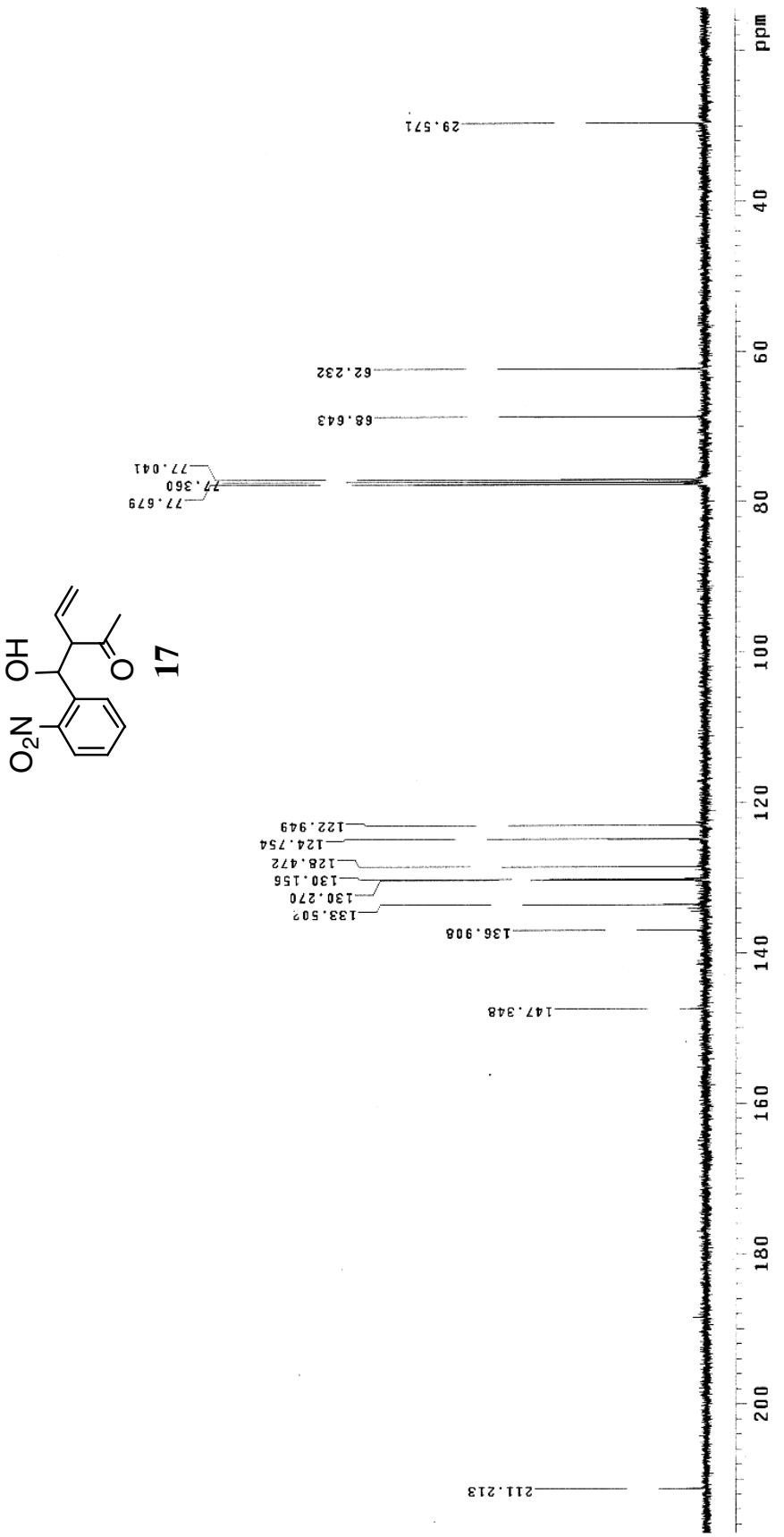

Ph
CN
Ph
CN
12
77.679
77.360
77.041
57.134
56.185
42.241
41.224
141.172
138.577
138.046
136.248
135.899
129.208
128.980
128.920
128.791
128.639
127.911
127.038
126.985
120.225
119.633
116.811
115.127
ppm

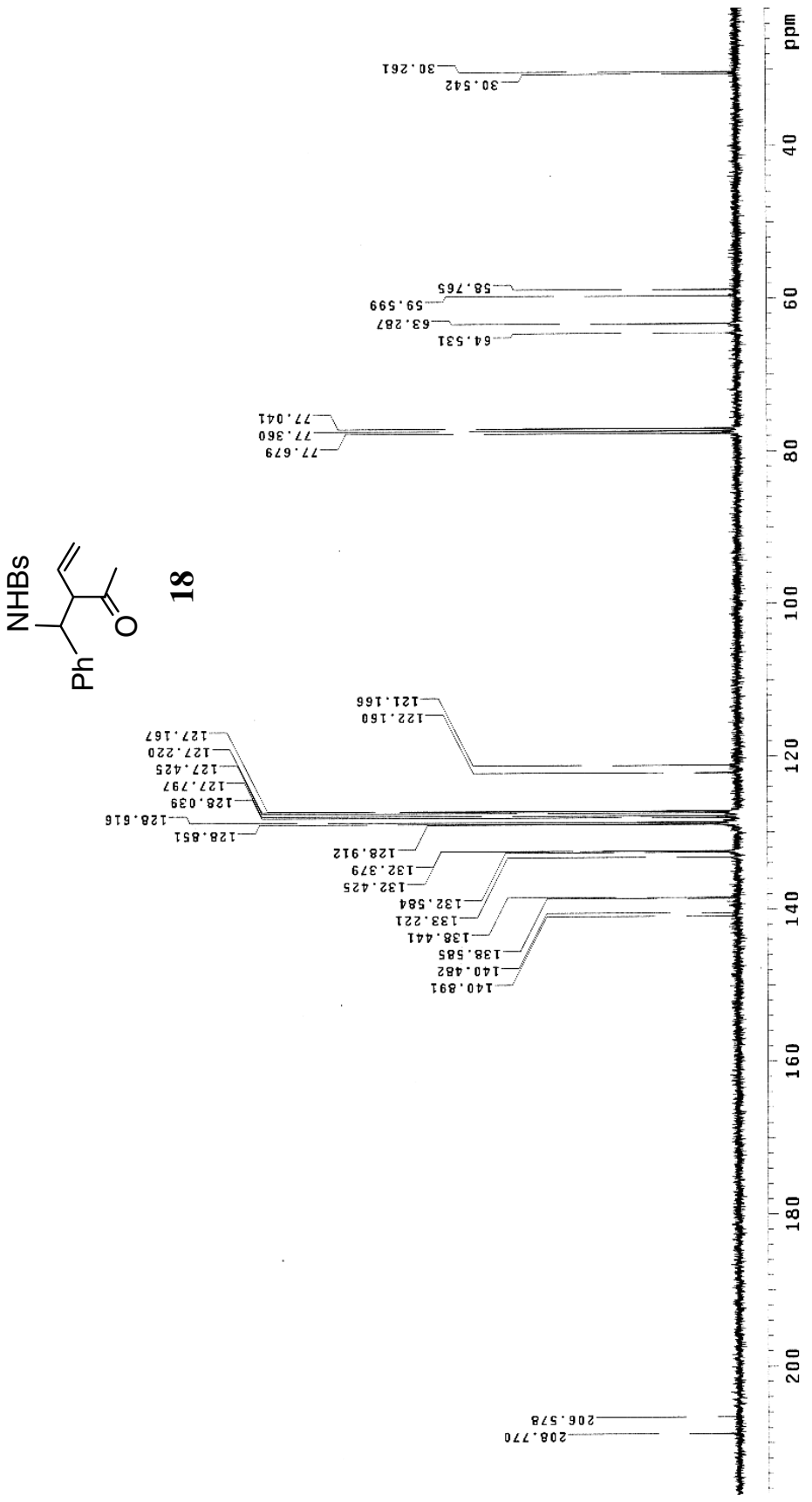

OH
COOEt
O2N
13
172.748
148.812
148.342
147.811
147.697
131.711
130.672
127.842
127.562
123.738
123.670
121.742
120.741
77.671
77.360
77.041
74.523
73.104
61.678
57.983
57.763
14.322
14.276
ppm
160
140
120
100
80
60
40
20


NHBs
COOEt
Ph
14
14.253
56.595
59.622
61.519
77.041
77.360
77.671
120.347
127.023
127.190
127.888
128.548
128.844
132.174
132.394
138.213
141.043
171.974
ppm
20
40
60
80
100
120
140
160


Ph
CN
COOEt
EtOOC
CN
15
14.003
14.155
14.489
39.426
40.147
40.549
41.080
52.096
52.286
53.280
57.263
61.185
61.223
61.504
62.270
77.041
77.360
77.679
113.958
114.148
114.361
115.362
121.295
124.170
128.942
129.056
129.534
129.686
129.830
130.309
132.569
132.743
133.267
134.541
136.878
136.908
165.131
170.465
171.671
ppm
20
40
60
80
100
120
140
160


OH
CN
O_2N
16
44.396
44.934
73.316
73.377
77.041
77.360
77.679
117.251
117.630
122.236
122.410
123.988
124.117
127.554
127.660
127.850
128.161
146.326
146.695
146.453
40 ppm
50
60
70
80
90
100
110
120
130
140
150


ppm
40
60
80
100
120
140
160
180
200
29.571
62.232
68.643
77.041
77.360
77.679
122.949
124.754
128.472
130.156
130.270
133.502
136.908
147.348
211.213
OH
O
O_2N
17


NHBs
Ph
O
18
ppm
40
60
80
100
120
140
160
180
200
30.261
30.542
58.765
59.599
63.287
64.531
77.041
77.360
77.679
121.166
122.160
127.167
127.220
127.425
127.797
128.039
128.516
128.851
128.912
132.379
132.425
132.584
133.221
138.441
138.585
140.482
140.891
206.578
206.770

Computational Details for 27a-d

Computational Methods. All geometries were fully optimized employing a Becke-type[5] three-parameter density functional model, B3PW91. This so called hybrid functional includes the exact (Hartree-Fock) exchange, the gradient corrected exchange functional introduced by Becke[5] and the more recent correlation functional of Perdew and Wang[6]. All calculations have been carried out using a valence double-ζ(DZ)+P basis constructed from the LANL2DZ basis[7-9] by adding one set of d-polarization functions to the heavy atoms (exponents: C, 0.63; P, 0.34) and one set of diffuse d-functions for palladium (exponent: 0.0628). All calculations have been conducted by employing the Gaussian 98 program package.[10] In the theoretical calculations the PPh_3 ligand (employed for example in entry 3) is approximated by PH_3 to reduce the computational burden of the study.

Calculated geometries.

Complex **27a**. E(RB+HF-PW91) = -831.646475889

C1	-1.177915	-2.317037	.233723
C2	-2.177779	-1.277267	.508118
C3	-3.084731	-.789313	-.381100
C4	-4.071425	.268100	-.155009
Pd5	.667342	-1.316167	-.049779
C6	2.614493	-.442372	-1.093099
C7	3.361424	.728797	-.611123
P8	1.133947	-.953580	2.210491
C9	.702564	-1.578628	-2.178612
C10	1.456574	-.402547	-1.890306
H11	-1.397154	-2.895464	-.669667
H12	-.229532	-1.476861	-2.731803
H13	3.151550	-1.393483	-1.043343
H14	1.213392	-2.538692	-2.283501
H15	1.007729	.564329	-2.124977
H16	1.200648	.387285	2.699941

H17	.310965	-1.479394	3.255909
H18	2.385051	-1.387074	2.747462
H19	-1.014983	-2.991140	1.084254
H20	-2.168208	-.857959	1.519362
H21	-3.092796	-1.229527	-1.382830
C22	4.684033	.554586	-.151548
C23	5.440918	1.634815	.311933
C24	4.893455	2.923751	.329088
C25	3.577118	3.112774	-.117674
C26	2.820094	2.033241	-.576408
H27	5.125754	-.443568	-.168321
H28	6.462480	1.470282	.656024
H29	5.480692	3.768847	.688053
H30	3.136350	4.110141	-.102447
H31	1.792153	2.206023	-.895908
C32	-4.975624	.590174	-1.191292
C33	-5.942904	1.587254	-1.035263
C34	-6.036220	2.297542	.168033
C35	-5.145166	1.993636	1.208837
C36	-4.179382	.998643	1.051315
H37	-4.915786	.042354	-2.133558
H38	-6.626623	1.810339	-1.855228
H39	-6.788722	3.075951	.294831
H40	-5.205384	2.541037	2.150503
H41	-3.498493	.789210	1.876213

Complex **27b**. E(RB+HF-PW91) = -831.645255817

C1	-3.043375	-2.501564	.026436
C2	-2.912258	-1.116570	-.228893
C3	-4.026726	-.296685	.057417
C4	-5.214827	-.828222	.567094
C5	-5.326753	-2.203316	.809013
C6	-4.229597	-3.034006	.533818
C7	-1.699601	-.496368	-.765542

C8	-.570864	-1.132331	-1.187553
C9	.649264	-.482566	-1.675823
Pd10	1.991056	-.516479	-.027260
C11	2.270194	.975035	1.559102
C12	1.982312	1.685792	.356788
C13	3.376987	.115539	1.665843
H14	3.503969	-.481269	2.567882
P15	2.530189	-2.753736	-.267724
H16	.501269	.567331	-1.948428
C17	.800113	2.532054	.139997
H18	4.274301	.287414	1.068961
H19	2.836547	1.920225	-.285039
H20	1.511418	.929826	2.341867
H21	2.088110	-3.692622	.715162
H22	2.123894	-3.507568	-1.414306
H23	3.900839	-3.157994	-.277409
H24	1.137934	-1.030825	-2.491416
H25	-.550142	-2.226826	-1.148639
H26	-1.721207	.593192	-.841400
H27	-3.952732	.775683	-.131088
H28	-6.057269	-.167457	.775386
H29	-6.250982	-2.622642	1.206779
H30	-4.301691	-4.106287	.721112
H31	-2.206197	-3.171611	-.168854
C32	-.332425	2.522917	.982798
C33	-1.418488	3.365616	.734942
C34	-1.414019	4.231526	-.367993
C35	-.304275	4.241347	-1.222857
C36	.785889	3.404795	-.968825
H37	-.376734	1.847181	1.836413
H38	-2.278028	3.343139	1.405684
H39	-2.264459	4.885970	-.559033
H40	-.286002	4.905267	-2.087571
H41	1.648046	3.427572	-1.637863

Complex **27c**. E(RB+HF-PW91) = -831.639249423

C1	-.955600	-1.940887	-3.536087
C2	-.965121	-1.975789	-2.185819
C3	.221544	-2.022392	-1.308393
C4	.223149	-2.953480	-.143460
Pd5	.354091	-.024568	-.534378
C6	1.104719	2.189947	-.170645
C7	.251791	3.260538	.361696
P8	-1.165307	-.281683	1.239389
C9	1.881955	.610359	-1.905475
C10	1.152804	1.769770	-1.513279
H11	1.142786	-2.134076	-1.890988
H12	-1.879833	-1.864538	-4.107858
H13	1.817715	.278260	-2.940384
H14	1.930583	1.882595	.476464
H15	2.798389	.341473	-1.374987
H16	.464522	2.211943	-2.235599
H17	-1.654332	.876403	1.920335
H18	-2.422971	-.929067	1.047370
H19	-.759320	-1.024348	2.387375
H20	-1.941939	-1.934689	-1.693547
H21	-.023770	-1.982488	-4.103168
C22	1.430649	-3.181014	.558145
C23	1.486944	-4.025785	1.666574
C24	.330739	-4.680873	2.120889
C25	-.870209	-4.483970	1.430408
C26	-.923811	-3.640161	.312678
H27	2.336060	-2.671610	.222452
H28	2.437054	-4.177761	2.180758
H29	.371345	-5.341922	2.986621
H30	-1.773791	-5.003975	1.752276
H31	-1.865546	-3.543234	-.226571
C32	.531515	3.784230	1.641966
C33	-.246622	4.805080	2.195889
C34	-1.330457	5.332089	1.482472

C35	-1.626737	4.817187	.211444
C36	-.852248	3.794991	-.339610
H37	1.378312	3.387333	2.205114
H38	-.003451	5.192925	3.185574
H39	-1.938298	6.129325	1.910060
H40	-2.472490	5.213795	-.351313
H41	-1.117944	3.400262	-1.320397

Complex **27d**. E(RB+HF-PW91) = -831.637515832

C1	2.965087	-1.480366	.990078
C2	1.919117	-1.220376	.077218
C3	2.233777	-1.302852	-1.300038
C4	3.521416	-1.605891	-1.742467
C5	4.554158	-1.838563	-.819290
C6	4.261746	-1.777467	.547326
C7	.528200	-.877586	.490384
Pd8	.164534	1.207828	.068626
C9	-1.700814	2.213987	-.502527
C10	-1.733832	.923293	-1.103551
C11	.157760	-.983844	1.913069
C12	-.993375	-1.500539	2.400233
C13	-.673341	3.131845	-.783704
H14	-.626528	4.068809	-.230782
P15	2.203275	1.944262	.908327
H16	-.206641	-1.373166	-.153773
H17	-1.204339	-1.493453	3.469559
C18	-2.718981	-.123745	-.803599
H19	-.158637	3.111315	-1.745808
H20	-1.250027	.832553	-2.080485
H21	-2.360656	2.425137	.340400
H22	2.429444	3.323532	1.210341
H23	2.733616	1.406467	2.119850
H24	3.360598	1.739950	.099996
H25	.866513	-.574907	2.640838
H26	-1.746069	-1.939087	1.745717

H27	1.443346	-1.116931	-2.029710
H28	3.724190	-1.663711	-2.812843
H29	5.561248	-2.076698	-1.161540
H30	5.044172	-1.980300	1.280189
H31	2.761475	-1.489308	2.060299
C32	-3.583449	-.084571	.312016
C33	-4.516955	-1.099811	.533081
C34	-4.604827	-2.192019	-.341277
C35	-3.742696	-2.254626	-1.443987
C36	-2.816533	-1.233358	-1.670561
H37	-3.526133	.740229	1.021482
H38	-5.175800	-1.043371	1.400134
H39	-5.331395	-2.984543	-.162645
H40	-3.794726	-3.099314	-2.131394
H41	-2.158437	-1.288761	-2.539648

References:

1) Fujita, M.; Ota, A.; Ito, S.; Yamamoto, K.; Kawashima, Y. *Synthesis* **1988**, 599.

2) Nudelman, A.; Keinan, E. *Synthesis* 1982, 687.

3) Oppolzer, W.; Gaudin, J.-M.; Birkinshaw, T. N. *Tetrahedron Lett.* 1988, *29*, 4705.

4) Kulinkovich, O. G.; Tischenko, I. G.; Sorokin, V. L. *Synthesis* **1985**, 1058.

5) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

6) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

7) Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*; Plenum: New York, 1977; Vol. 3; 1.

8) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

9) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Q. Cui; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; G. Liu;

Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; A. Nanayakkara; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; W. Chen; Wong, M. W.; Andres, J. L.; Gonzalez, C.; M. Head-Gordon; Replogle, E. S.; J. A. Pople *Gaussian 98* **1998**, Gaussian, Inc., Pittsburgh PA.