Electronic Supplementary Material (ESI) for Catalysis Science & Technology

NOBIN-based Phosphoramidite and Phosphorodiamidite Ligands and their Use in Asymmetric Nickel-Catalyzed Hydrovinylation

Mike Schmitkamp,[a] Walter Leitner,[a] Giancarlo Franciò[a]*

[a]Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Worringerweg 1, 52074 Aachen, Germany, Fax: +49-241-80 22177, francio@itmc.rwth-aachen.de

Supporting Information

Computational methods.

Conformational minima were calculated via conformational searches at the PM3 level[1] followed by DFT calculation. The geometry optimisation were carried out with the Gaussian 09 program[2] series applying the B97-D[3] functional and the def2-TZVP basis set[4].

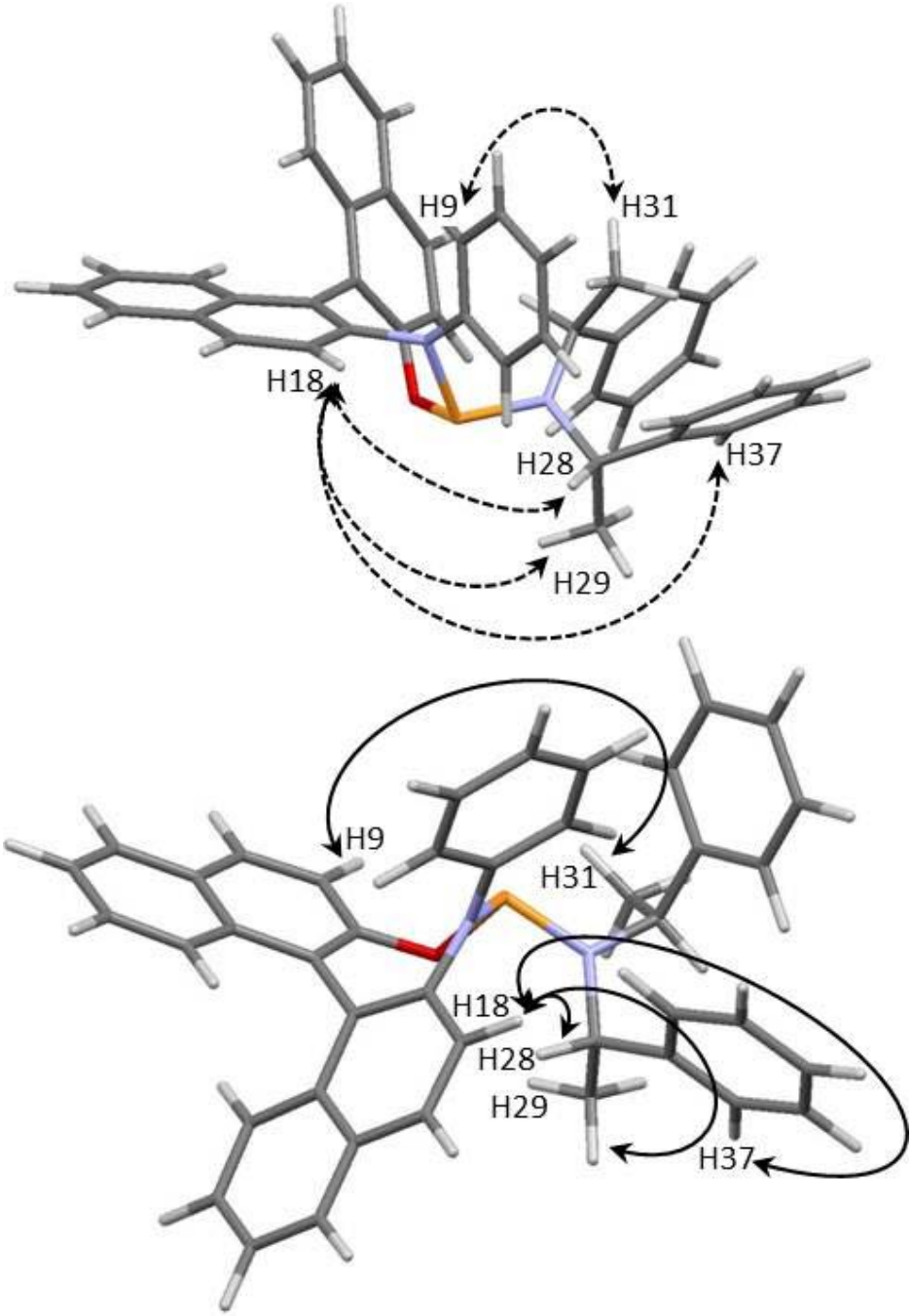

Figure 1. Calculated conformational minima of (S_a,S_C,S_C,S_P)-**L1** (top) and (S_a,S_C,S_C,R_P)-**L1** (bottom): continuous arrows highlight NOE interactions (atom distances ≤ 3.8 Å); dashed arrows not expected NOE-interactions (atom distances ≥ 5.0 Å)

DFT calculation: optimised conformer of (S_a,S_C,S_C,R_P)-**L1** (xyz)

C	1.407000	2.901000	1.638000
C	2.633000	2.983000	0.925000
C	3.050000	1.861000	0.128000
C	2.242000	0.672000	0.094000
C	0.996000	0.680000	0.726000
C	0.607000	1.792000	1.526000
C	3.440000	4.149000	0.970000
C	4.611000	4.231000	0.245000
C	5.010000	3.142000	-0.565000
C	4.251000	1.990000	-0.622000
C	1.932000	-1.074000	-1.630000
C	2.715000	-0.541000	-0.617000
C	3.942000	-1.205000	-0.281000
C	4.361000	-2.342000	-1.059000
C	3.541000	-2.801000	-2.123000
C	2.336000	-2.192000	-2.393000
C	4.751000	-0.813000	0.820000
C	5.922000	-1.480000	1.118000
C	6.350000	-2.576000	0.330000
C	5.579000	-2.997000	-0.733000
C	-3.661000	3.032000	-1.184000
C	-2.734000	2.161000	-0.603000
C	-2.905000	1.801000	0.742000
C	-3.968000	2.301000	1.491000
C	-4.894000	3.169000	0.899000
C	-4.738000	3.530000	-0.440000
C	-4.404000	-3.374000	-0.047000
C	-3.642000	-2.662000	-0.976000
C	-3.834000	-1.286000	-1.155000
C	-4.821000	-0.640000	-0.397000
C	-5.585000	-1.348000	0.533000
C	-5.376000	-2.718000	0.714000
N	0.081000	-0.407000	0.607000
O	0.711000	-0.483000	-1.913000
P	-0.554000	-1.032000	-0.923000
N	-1.744000	0.057000	-1.401000
C	-2.964000	-0.460000	-2.095000
C	-2.629000	-1.167000	-3.417000
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C	-1.349000	2.100000	-2.782000
C	-0.422000	-0.984000	1.803000
C	-1.753000	-1.427000	1.903000
C	-2.207000	-2.032000	3.079000
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C	-0.039000	-1.718000	4.089000
C	0.431000	-1.137000	2.914000
H	1.096000	3.744000	2.252000
H	-0.343000	1.745000	2.047000
H	3.108000	4.985000	1.585000
H	5.219000	5.132000	0.284000
H	5.922000	3.214000	-1.154000
H	4.569000	1.167000	-1.253000
H	3.870000	-3.658000	-2.707000
H	1.680000	-2.547000	-3.184000
H	4.435000	0.025000	1.434000
H	6.521000	-1.162000	1.969000
H	7.278000	-3.089000	0.573000
H	5.886000	-3.850000	-1.336000
H	-3.552000	3.324000	-2.226000

H	-2.221000	1.085000	1.186000
H	-4.084000	2.001000	2.530000
H	-5.731000	3.556000	1.477000
H	-5.455000	4.200000	-0.911000
H	-4.232000	-4.440000	0.089000
H	-2.875000	-3.178000	-1.547000
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H	-3.543000	0.437000	-2.342000
H	-3.551000	-1.463000	-3.933000
H	-2.027000	-2.068000	-3.245000
H	-2.053000	-0.493000	-4.061000
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H	-0.463000	1.627000	-3.215000
H	-1.192000	3.185000	-2.735000
H	-2.208000	1.908000	-3.437000
H	-2.444000	-1.289000	1.079000
H	-3.239000	-2.372000	3.128000
H	-1.721000	-2.635000	5.097000
H	0.635000	-1.827000	4.936000
H	1.462000	-0.802000	2.839000

DFT calculation: optimised conformer of (S_a,S_C,S_C,S_P)-**L1** (xyz)

C	-3.913000	-3.014000	-0.842000
C	-4.772000	-1.888000	-0.946000
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C	-2.827000	-0.425000	-0.454000
C	-2.015000	-1.555000	-0.432000
C	-2.569000	-2.852000	-0.617000
C	-6.153000	-2.036000	-1.236000
C	-6.971000	-0.934000	-1.379000
C	-6.426000	0.366000	-1.248000
C	-5.089000	0.542000	-0.955000
C	-1.186000	1.378000	-0.940000
C	-2.244000	0.907000	-0.173000
C	-2.747000	1.742000	0.882000
C	-2.239000	3.079000	1.034000
C	-1.251000	3.546000	0.128000
C	-0.730000	2.713000	-0.833000
C	-3.709000	1.283000	1.823000
C	-4.159000	2.100000	2.841000
C	-3.675000	3.424000	2.971000
C	-2.731000	3.899000	2.084000
C	5.104000	0.025000	-0.542000
C	4.202000	-1.033000	-0.718000
C	4.423000	-2.225000	-0.017000
C	5.496000	-2.355000	0.865000
C	6.375000	-1.283000	1.054000
C	6.178000	-0.097000	0.343000
C	3.093000	3.662000	-1.602000
C	2.472000	2.446000	-1.315000
C	2.567000	1.858000	-0.047000
C	3.290000	2.543000	0.940000
C	3.911000	3.764000	0.663000
C	3.822000	4.328000	-0.612000
N	-0.605000	-1.423000	-0.240000
O	-0.586000	0.578000	-1.901000
N	1.775000	-0.361000	-0.932000
C	1.856000	0.535000	0.253000
C	2.361000	-0.144000	1.546000
C	2.992000	-0.919000	-1.632000
C	3.328000	-0.215000	-2.959000
C	-0.022000	-2.354000	0.660000
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C	0.092000	-3.218000	2.928000
C	1.104000	-4.109000	2.550000
C	1.533000	-4.132000	1.222000
C	0.967000	-3.271000	0.278000
H	-4.334000	-4.010000	-0.975000
H	-1.906000	-3.711000	-0.568000
H	-6.553000	-3.042000	-1.355000
H	-8.028000	-1.060000	-1.607000
H	-7.066000	1.235000	-1.385000
H	-4.686000	1.546000	-0.863000
H	-0.893000	4.570000	0.217000
H	0.040000	3.057000	-1.512000
H	-4.088000	0.269000	1.736000
H	-4.890000	1.721000	3.552000
H	-4.041000	4.059000	3.775000
H	-2.339000	4.910000	2.178000
H	4.955000	0.959000	-1.072000
H	3.726000	-3.049000	-0.146000

H	5.644000	-3.286000	1.407000
H	7.210000	-1.376000	1.746000
H	6.859000	0.741000	0.478000
H	3.009000	4.089000	-2.600000
H	1.909000	1.932000	-2.087000
H	3.389000	2.118000	1.934000
H	4.473000	4.270000	1.446000
H	4.313000	5.274000	-0.832000
H	0.809000	0.796000	0.456000
H	3.451000	-0.172000	1.601000
H	1.986000	0.418000	2.411000
H	1.978000	-1.161000	1.612000
H	2.723000	-1.951000	-1.896000
H	2.431000	-0.155000	-3.587000
H	3.718000	0.793000	-2.808000
H	4.089000	-0.804000	-3.489000
H	-1.235000	-1.637000	2.284000
H	-0.255000	-3.192000	3.959000
H	1.546000	-4.782000	3.281000
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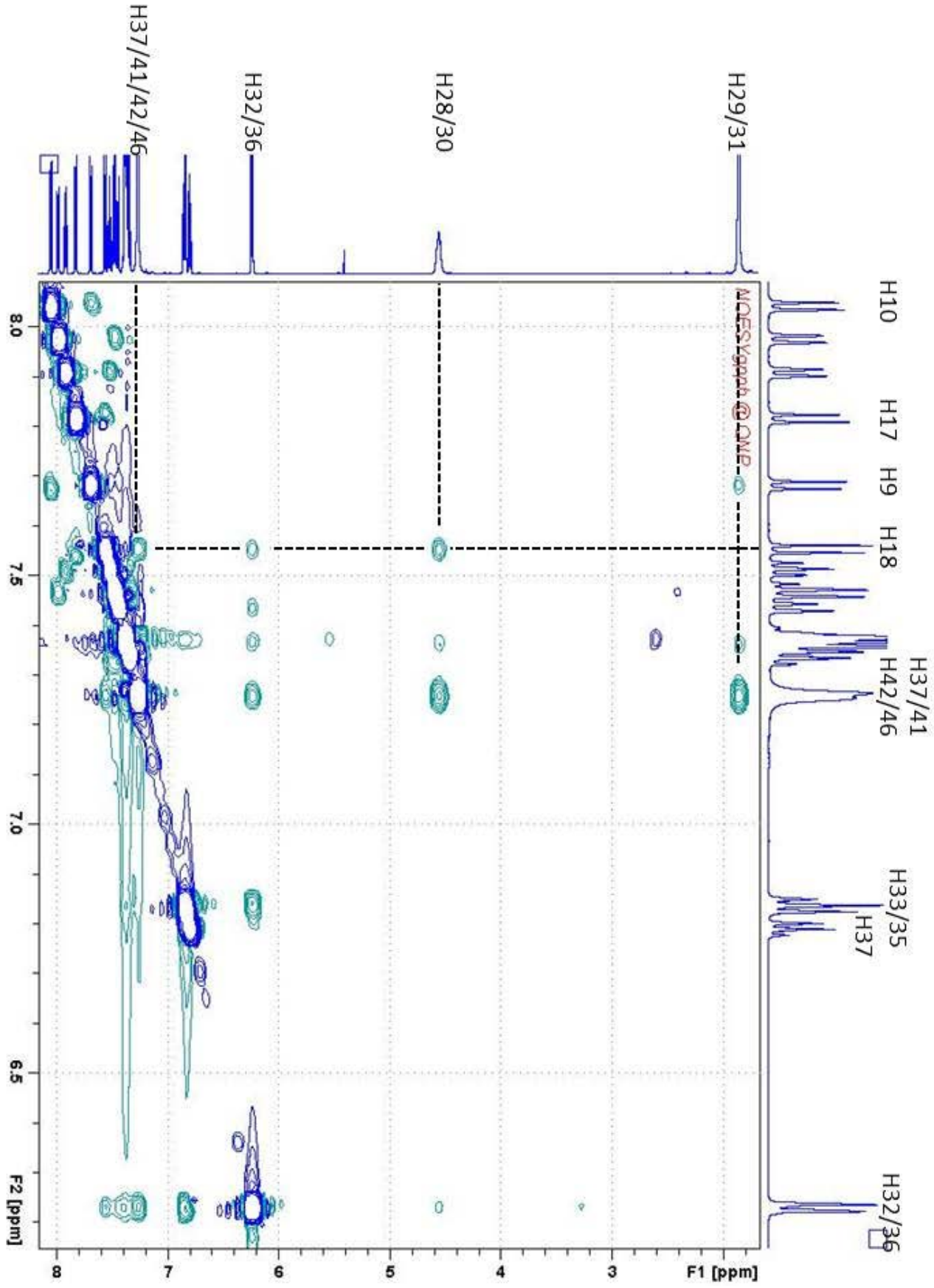


Figure 2. Selected NOE interactions for (S_a,S_C,S_C)-**L1**

Figure 3. ^{1}**H-NMR** of (S_a,S_C,S_C,R_P)-**L1**

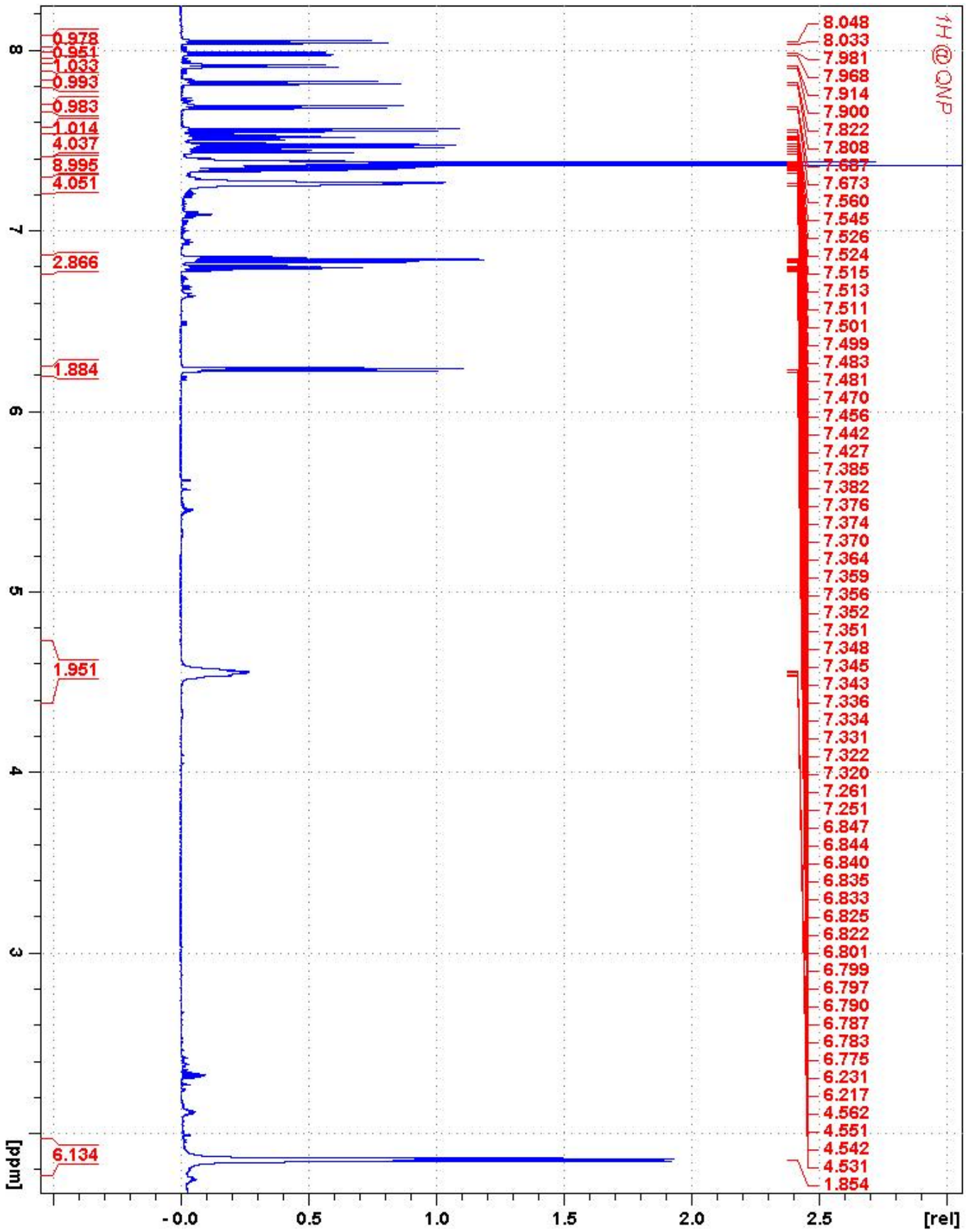


Figure 4. ^{13}**C NMR (apt)** of (S_a,S_C,S_C,R_P)-**L1**

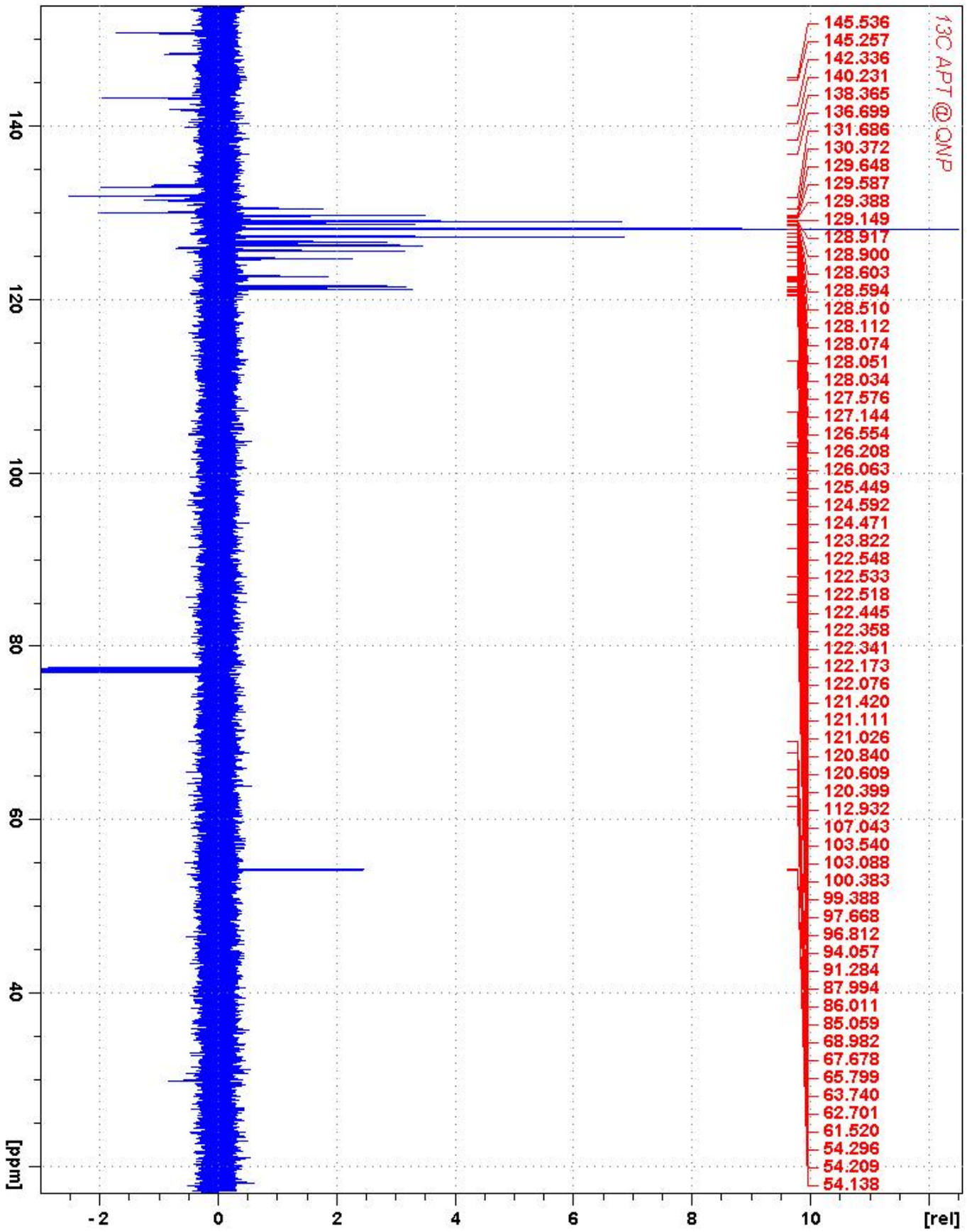
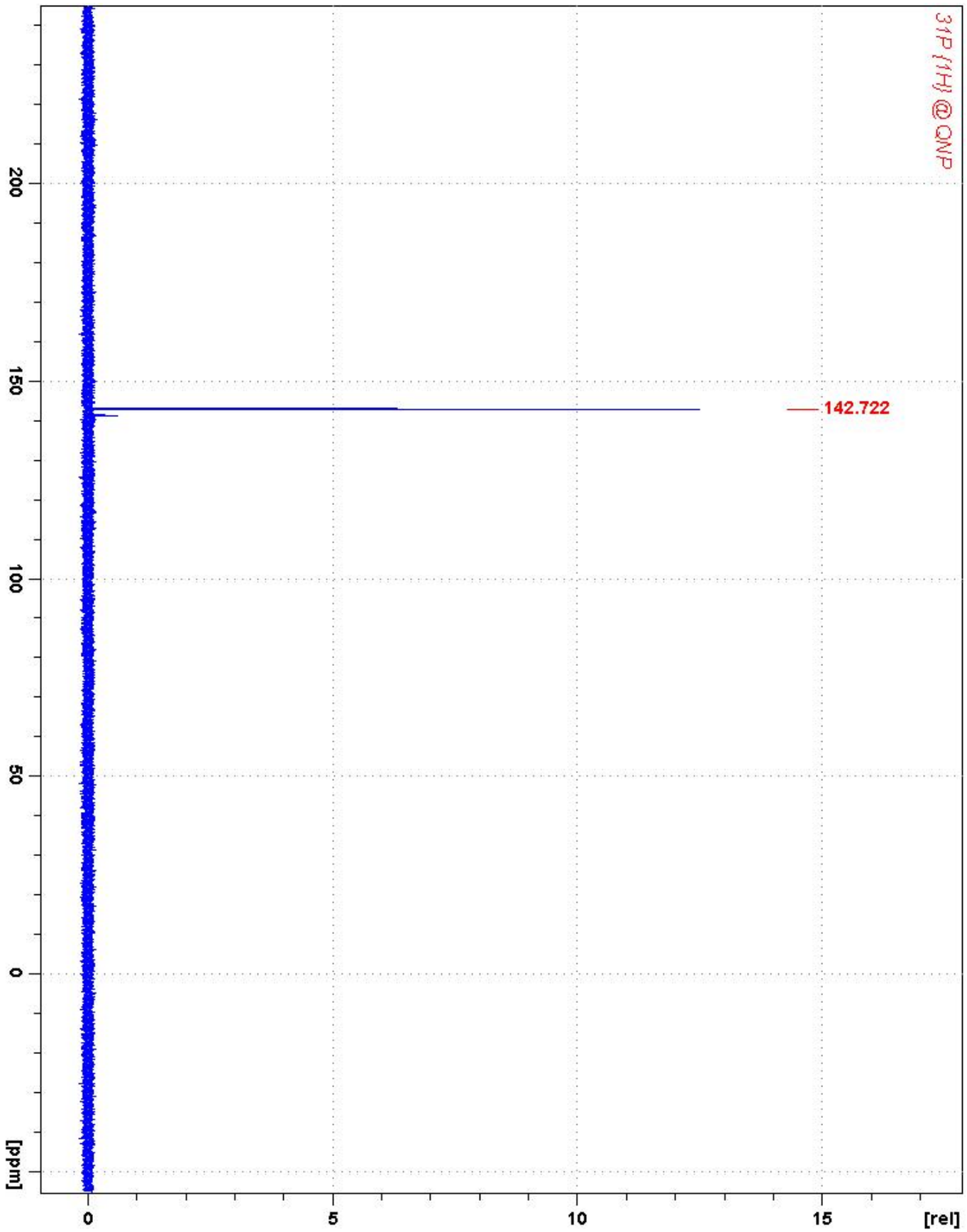
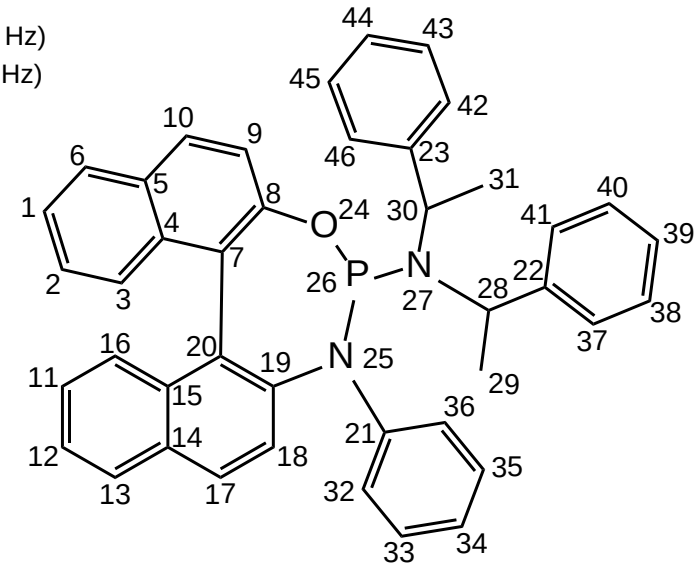


Figure 5. ^{31}**P NMR** of (S_a,S_C,S_C,R_P)-**L1**



NMR signal assignment for (S_a,S_C,S_C,R_P)-**L1**

Atom number	Type	^{13}C	^{1}H
1	CH	124,59	7,46
2	CH	126,21	7,33 (m)
3	CH	126,55	7,43(m)
4	Cq	133,12 (d, 2.4 Hz)	
5	Cq	131,32	
6	CH	128,51	7,97 (d, 8.2 Hz)
7	Cq	125,84 (d, 5.5 Hz)	
8	Cq	150,60	
9	CH	122,52	7,68 (d, 8.8 Hz)
10	CH	130,37	8,04 (d, 8.8 Hz)
11	CH	126,06	7,34 m
12	CH	125,45	7,51 m
13	CH	128,11	7,90 (d, 7.9 Hz)
14	Cq	131,83	
15	Cq	132,83	
16	CH	128,05	7,46 m
17	CH	129,59	7,81 (d, 8.8 Hz)
18	CH	128,11	7,54 (d, 8.8 Hz)
19	Cq	141,84 (d, 5.4 Hz)	
20	Cq	129,88	
21	Cq	148,2 (d, 26.2 Hz)	
22	Cq	143,10	
23	Cq	143,09	
24	O		
25	N		
26	P		
27	N		
28	CHaliph	54,21	4,54
29	CH3	22,66	1,84
30	CHaliph	54,14	4,54
31	CH3	22,16	1,84
32	CH	121,07 (d, 12.7 Hz)	6,22 (d, 7.9 Hz)
33	CH	128,6 (d, 1.4 Hz)	6,80 m
34	CH	121,42	6,80 m
35	CH	128,60 (d, 1.4 Hz)	6,80 m
36	CH	121,07 (d, 12.7 Hz)	6,22 (d, 7.9 Hz)
37	CH	128,92	7,24
38	CH	128,03	7,36
39	CH	127,14	7,37
40	CH	128,03	7,36
41	CH	128,92	7,24
42	CH	128,90	7,24
43	CH	128,03	7,36
44	CH	127,14	7,37
45	CH	128,03	7,36
46	CH	128,90	7,24



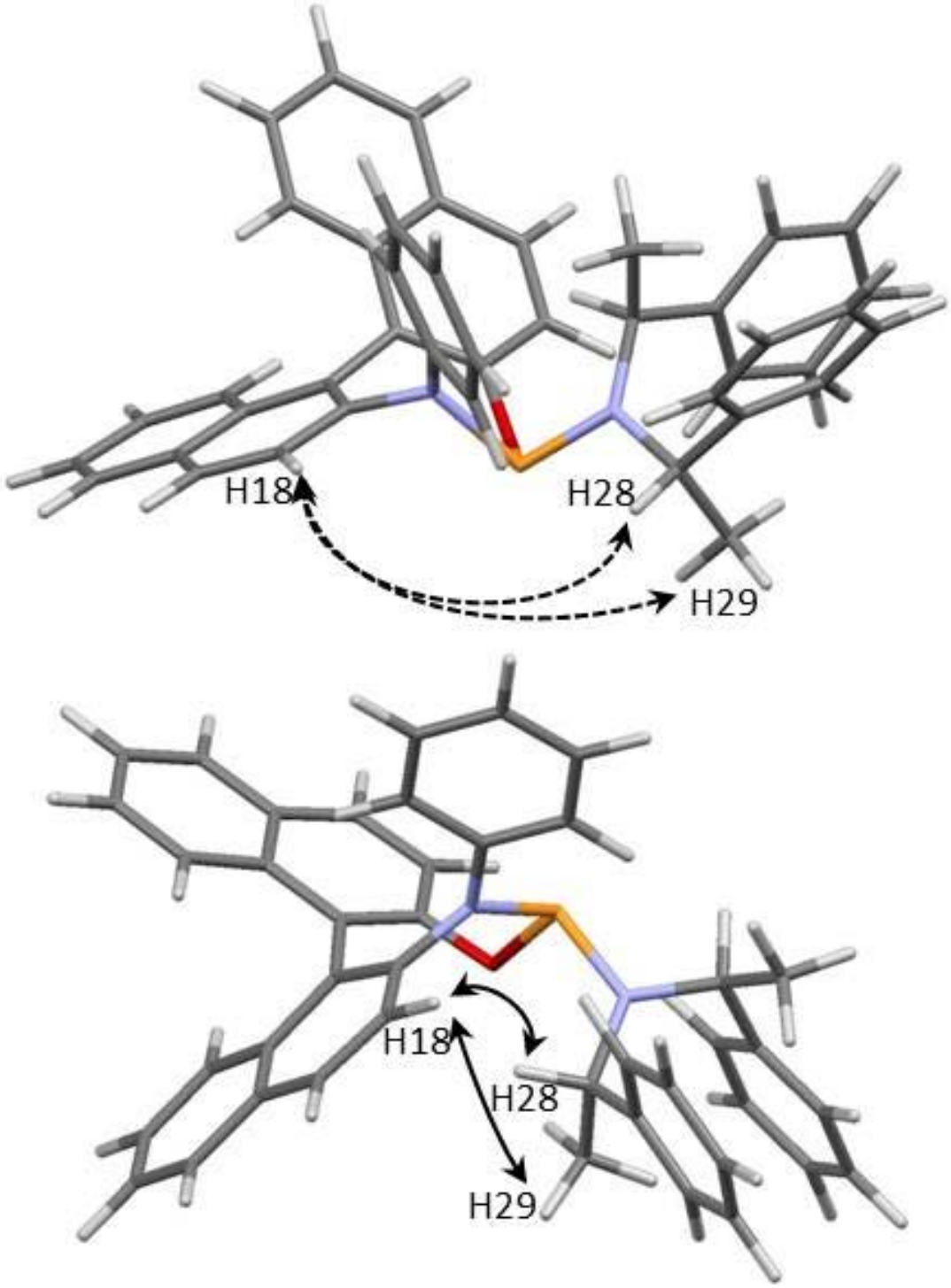


Figure 6. Calculated conformational minima of (S_a,R_C,R_C,S_P)-**L1** (top) and (S_a,R_C,R_C,R_P)-**L1** (bottom): continuous arrows highlight NOE interactions (atom distances ≤ 3.0 Å); dashed arrows not expected NOE-interactions (atom distances ≥ 5.0 Å).

DFT calculation: optimised conformer of (S_a,R_C,R_C,R_P)-**L1** (xyz)

C	-1.303000	-0.623000	3.264000
C	-2.309000	-1.502000	2.761000
C	-2.720000	-1.379000	1.381000
C	-2.136000	-0.352000	0.549000
C	-1.080000	0.421000	1.061000
C	-0.694000	0.296000	2.434000
C	-2.902000	-2.504000	3.585000
C	-3.856000	-3.375000	3.075000
C	-4.243000	-3.277000	1.711000
C	-3.690000	-2.305000	0.886000
C	-1.739000	-0.211000	-1.900000
C	-2.637000	-0.118000	-0.833000
C	-4.009000	0.224000	-1.111000
C	-4.433000	0.378000	-2.487000
C	-3.479000	0.217000	-3.537000
C	-2.152000	-0.053000	-3.251000
C	-4.971000	0.454000	-0.080000
C	-6.285000	0.785000	-0.385000
C	-6.707000	0.904000	-1.738000
C	-5.795000	0.708000	-2.765000
C	4.555000	1.997000	-0.463000
C	4.406000	0.683000	-0.954000
C	5.449000	-0.236000	-0.737000
C	6.593000	0.136000	-0.009000
C	6.716000	1.439000	0.502000
C	5.695000	2.376000	0.262000
C	2.052000	-4.260000	-0.998000
C	1.654000	-2.962000	-0.650000
C	2.486000	-2.139000	0.140000
C	3.711000	-2.658000	0.599000
C	4.115000	-3.959000	0.248000
C	3.291000	-4.762000	-0.557000
N	-0.358000	1.348000	0.253000
O	-0.409000	-0.464000	-1.633000
P	0.530000	0.937000	-1.242000
N	1.966000	0.172000	-0.727000
C	2.010000	-0.722000	0.465000
C	2.718000	-0.060000	1.658000
C	3.110000	0.309000	-1.673000
C	3.247000	-0.864000	-2.662000
C	-0.216000	2.675000	0.740000
C	1.028000	3.344000	0.695000
C	1.136000	4.671000	1.144000
C	0.019000	5.337000	1.675000
C	-1.216000	4.663000	1.746000
C	-1.339000	3.349000	1.276000
H	-0.998000	-0.710000	4.315000
H	0.106000	0.945000	2.805000
H	-2.580000	-2.577000	4.632000
H	-4.302000	-4.144000	3.718000
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H	-3.813000	0.331000	-4.576000
H	-1.399000	-0.155000	-4.041000
H	-4.658000	0.367000	0.966000
H	-7.003000	0.960000	0.427000
H	-7.749000	1.161000	-1.966000
H	-6.103000	0.813000	-3.814000
H	3.763000	2.731000	-0.658000

H	5.362000	-1.257000	-1.120000
H	7.392000	-0.599000	0.160000
H	7.608000	1.727000	1.072000
H	5.789000	3.403000	0.638000
H	1.395000	-4.885000	-1.617000
H	0.700000	-2.557000	-1.007000
H	4.364000	-2.041000	1.224000
H	5.078000	-4.345000	0.609000
H	3.607000	-5.777000	-0.831000
H	0.957000	-0.851000	0.762000
H	2.570000	-0.678000	2.564000
H	3.800000	0.068000	1.493000
H	2.278000	0.937000	1.834000
H	2.844000	1.195000	-2.287000
H	2.269000	-1.051000	-3.141000
H	3.566000	-1.800000	-2.176000
H	3.988000	-0.604000	-3.442000
H	1.910000	2.806000	0.335000
H	2.110000	5.177000	1.099000
H	0.109000	6.368000	2.037000
H	-2.096000	5.173000	2.158000
H	-2.304000	2.829000	1.310000

DFT calculation: optimised conformer of (S_a,R_C,R_C,S_P)-**L1** (xyz)

C	4.007000	2.709000	-1.242000
C	4.821000	1.557000	-1.035000
C	4.188000	0.311000	-0.665000
C	2.758000	0.273000	-0.439000
C	1.994000	1.418000	-0.714000
C	2.636000	2.634000	-1.116000
C	6.235000	1.608000	-1.217000
C	7.016000	0.470000	-1.072000
C	6.395000	-0.769000	-0.753000
C	5.023000	-0.847000	-0.557000
C	1.167000	-1.610000	-0.805000
C	2.124000	-0.998000	0.009000
C	2.551000	-1.686000	1.202000
C	2.110000	-3.043000	1.440000
C	1.256000	-3.671000	0.484000
C	0.777000	-2.965000	-0.605000
C	3.395000	-1.068000	2.176000
C	3.786000	-1.751000	3.319000
C	3.363000	-3.091000	3.544000
C	2.541000	-3.720000	2.620000
C	-3.231000	2.045000	1.338000
C	-3.153000	0.642000	1.229000
C	-4.260000	-0.123000	1.648000
C	-5.428000	0.499000	2.122000
C	-5.503000	1.900000	2.200000
C	-4.392000	2.671000	1.816000
C	-2.979000	-3.931000	-1.836000
C	-2.604000	-2.587000	-1.968000
C	-3.477000	-1.548000	-1.581000
C	-4.749000	-1.885000	-1.085000
C	-5.129000	-3.233000	-0.947000
C	-4.245000	-4.260000	-1.314000
N	0.567000	1.409000	-0.598000
O	0.606000	-0.935000	-1.861000
P	-0.397000	0.466000	-1.782000
N	-1.803000	0.165000	-0.837000
C	-2.983000	-0.107000	-1.715000
C	-4.081000	0.972000	-1.674000
C	-1.889000	-0.004000	0.652000
C	-1.700000	-1.447000	1.147000
C	-0.010000	2.621000	-0.106000
C	0.286000	3.010000	1.220000
C	-0.233000	4.202000	1.742000
C	-1.066000	5.020000	0.956000
C	-1.362000	4.638000	-0.364000
C	-0.831000	3.453000	-0.898000
H	4.486000	3.652000	-1.536000
H	2.016000	3.515000	-1.314000
H	7.005000	-1.677000	-0.667000
H	4.569000	-1.815000	-0.327000
H	6.691000	2.569000	-1.489000
H	8.102000	0.519000	-1.218000
H	0.953000	-4.713000	0.647000
H	0.072000	-3.415000	-1.310000
H	3.726000	-0.038000	2.008000
H	4.427000	-1.251000	4.058000
H	3.684000	-3.621000	4.451000
H	2.201000	-4.751000	2.785000
H	-4.225000	-1.214000	1.586000

H	-6.283000	-0.116000	2.433000
H	-2.286000	-4.726000	-2.140000
H	-1.611000	-2.325000	-2.354000
H	-5.445000	-1.094000	-0.788000
H	-2.562000	-0.045000	-2.741000
H	-3.614000	1.969000	-1.756000
H	-4.758000	0.821000	-2.536000
H	-4.684000	0.955000	-0.754000
H	-1.036000	0.576000	1.043000
H	-2.453000	-2.139000	0.736000
H	-0.705000	-1.818000	0.874000
H	-1.778000	-1.458000	2.251000
H	0.001000	4.488000	2.776000
H	-2.005000	5.271000	-0.989000
H	-1.044000	3.177000	-1.937000
H	-2.377000	2.652000	1.035000
H	-4.542000	-5.311000	-1.205000
H	-6.123000	-3.479000	-0.549000
H	-1.481000	5.948000	1.369000
H	-6.416000	2.386000	2.569000
H	-4.426000	3.766000	1.886000
H	0.928000	2.360000	1.826000

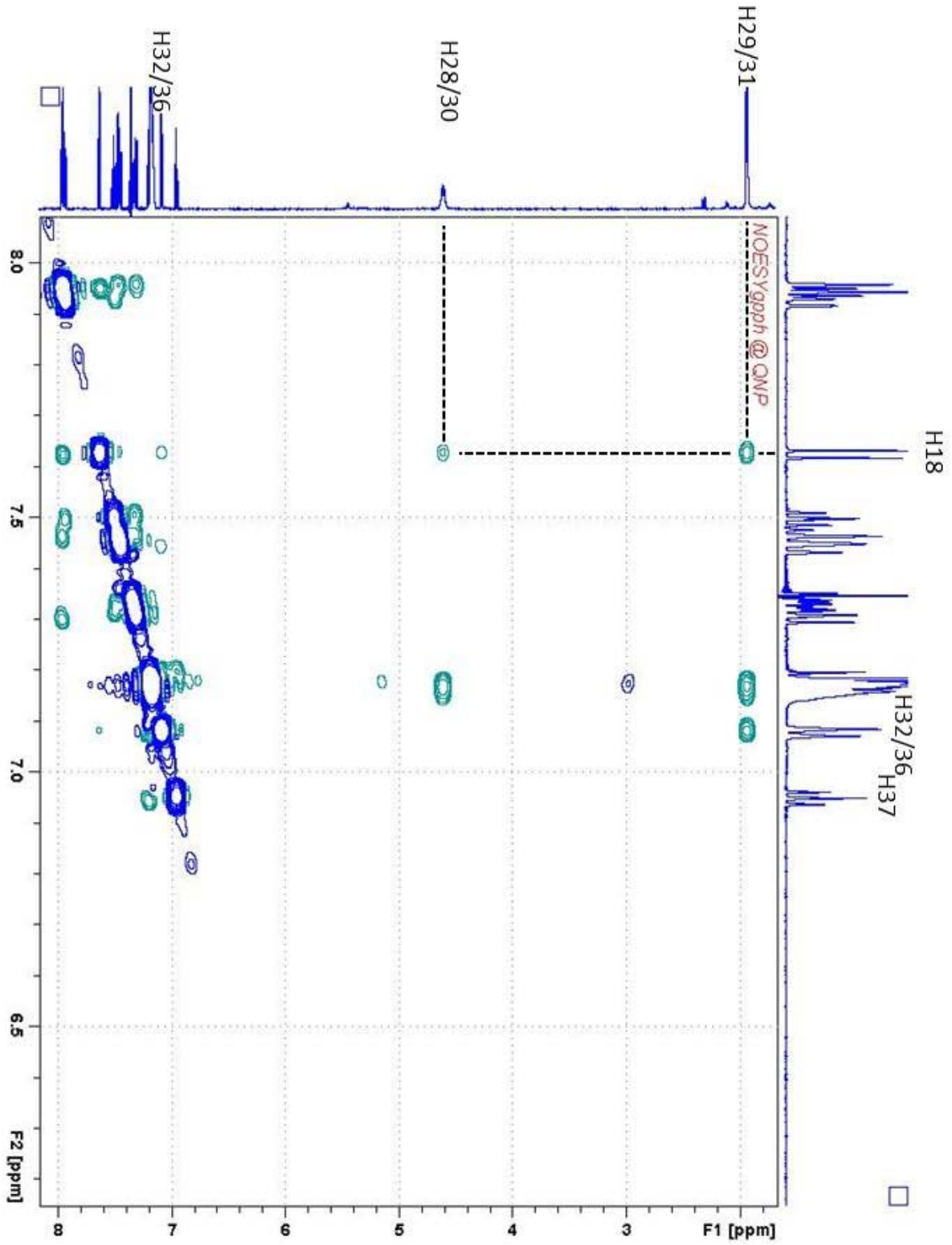


Figure 7. Selected NOE interactions for (S_a,R_C,R_C)-**L1**

Figure 8. 1H-NMR of (S_a,R_C,R_C,R_P)-**L1**

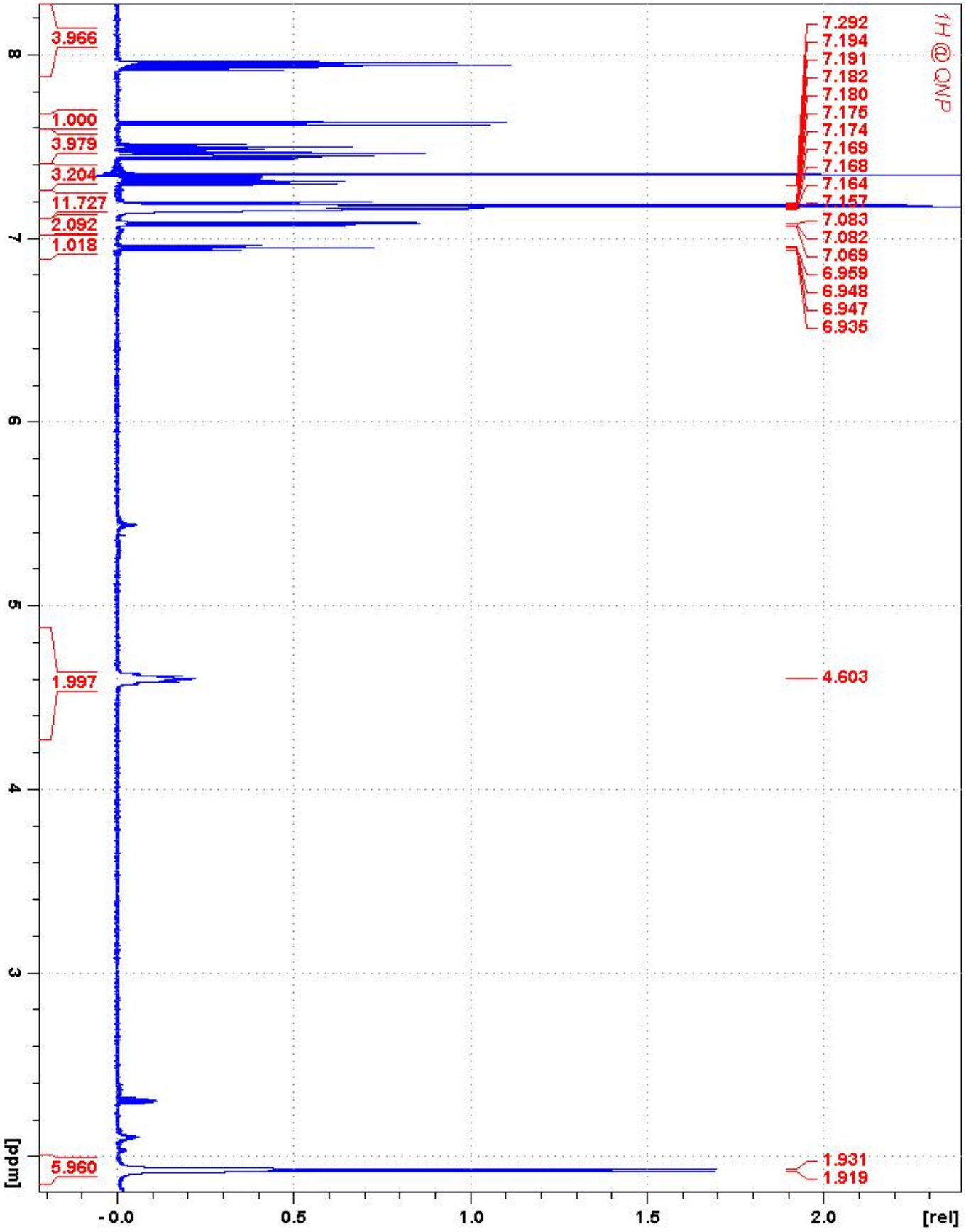


Figure 10. ^{13}**C-NMR (apt)** of (S_a,R_C,R_C,R_P)-**L1**

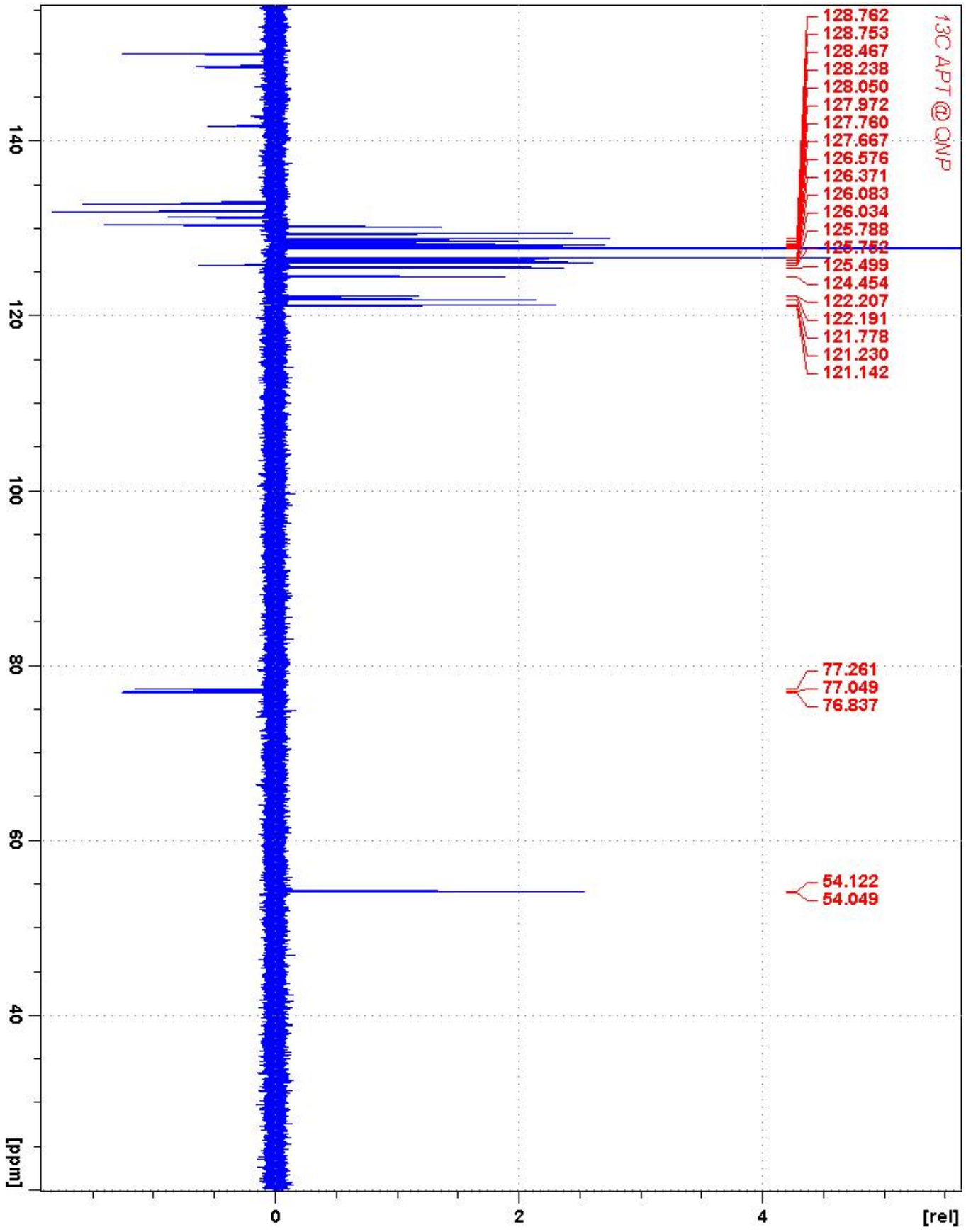
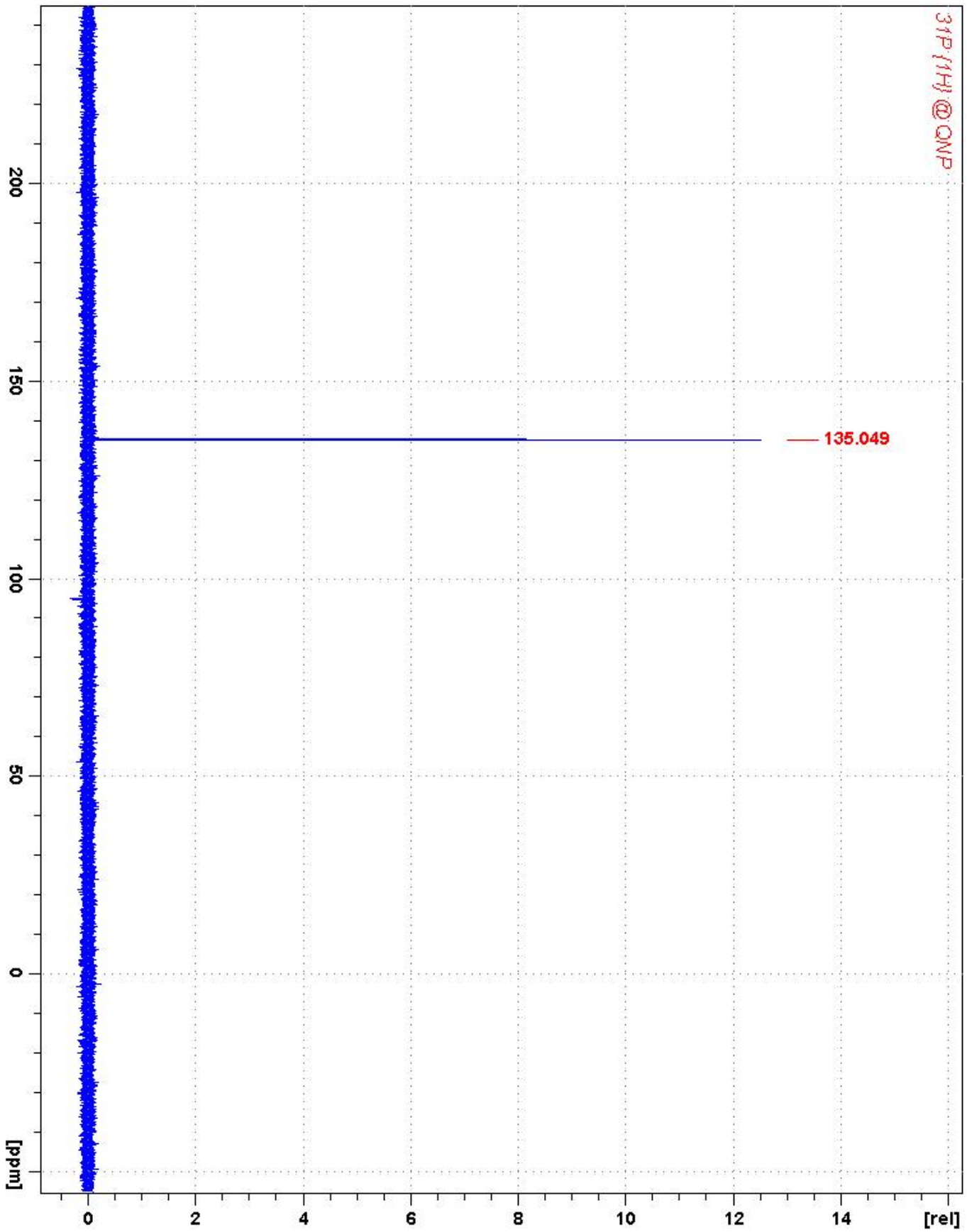


Figure 11. ^{31}P-NMR (apt) of (S_a,R_C,R_C,R_P)-**L1**



NMR signal assignment for (S_a,R_C,R_C,R_P)-**L1**

Atom number	Type	^{13}C	^{1}H
1	CH	124,45	7,45
2	CH	122,17	7,29
3	CH	126,37	7,45
4	Cq	132,93 (d, 2.2 Hz)	
5	Cq	131,22 (d, 1.2 Hz)	
6	CH	128,48	7,94
7	Cq	125,77	
8	Cq	149,89	
9	CH	122,20	7,30
10	CH	130,15	7,95
11	CH	126,08	7,31
12	CH	125,50	7,49
13	CH	128,05	7,92 (d, 8.1 Hz)
14	Cq	131,85	
15	Cq	132,74	
16	CH	127,76	7,45
17	CH	129,36	7,94
18	CH	127,97	7,62 (d, 8.8 Hz)
19	Cq	141,62 (d, 4.2 Hz)	
20	Cq	130,32	
21	Cq	148,44 (d, 26.2 Hz)	
22	Cq	142,73	
23	Cq	142,73	
24	O		
25	N		
26	P		
27	N		
28	CHaliph	54,05	4,60
29	CH3	22,15	1,93 (d, 7.0 Hz)
30	CHaliph	54,09	4,60
31	CH3	22,15	1,93 (d, 7.0 Hz)
32	CH	121,18 (d, 13.2 Hz)	7,08 (d, 8.1 Hz)
33	CH	128,76	7,18
34	CH	121,78	6,94 (d, 7.3 Hz)
35	CH	128,76	7,18
36	CH	121,18 (d, 13.2 Hz)	7,08
37	CH	128,24	7,17
38	CH	127,67	7,17
39	CH	126,58	7,17
40	CH	127,67	7,17
41	CH	128,24	7,17
42	CH	128,24	7,17
43	CH	127,67	7,17
44	CH	126,58	7,17
45	CH	127,67	7,17
46	CH	128,24	7,17

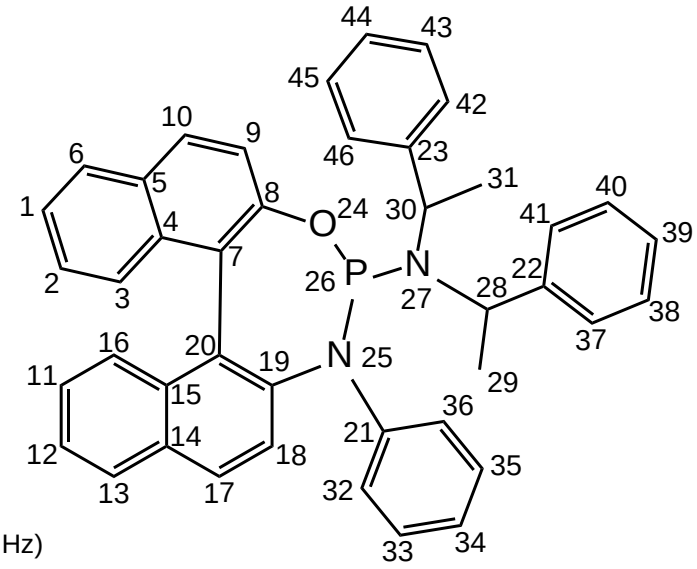


Figure 12. ^{1}**H-NMR** of (S_a,S_a,R_C,R_C)-**L2**

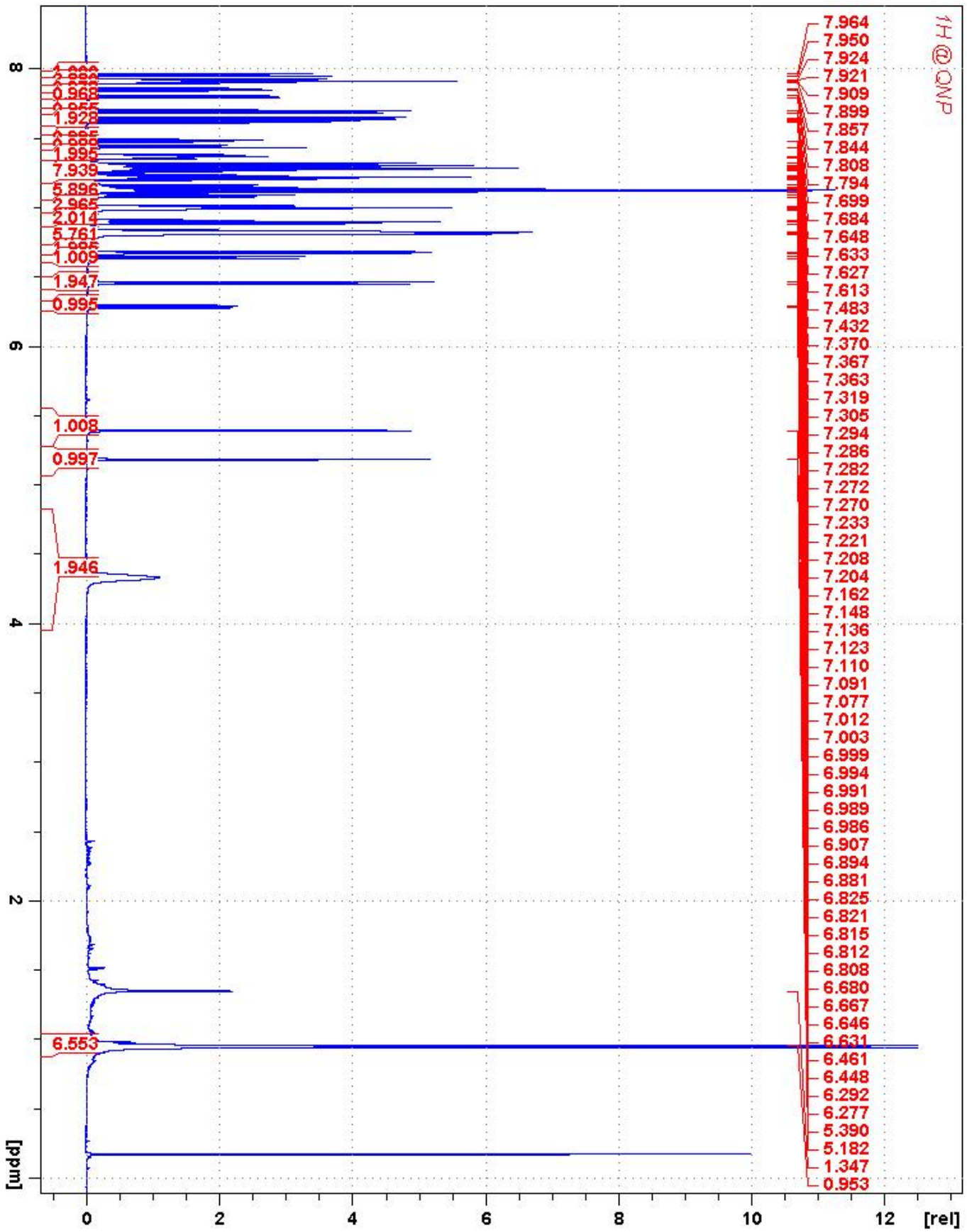


Figure 13. ^{13}**C-NMR** (apt) of (S_a,S_a,R_C,R_C)-**L2**

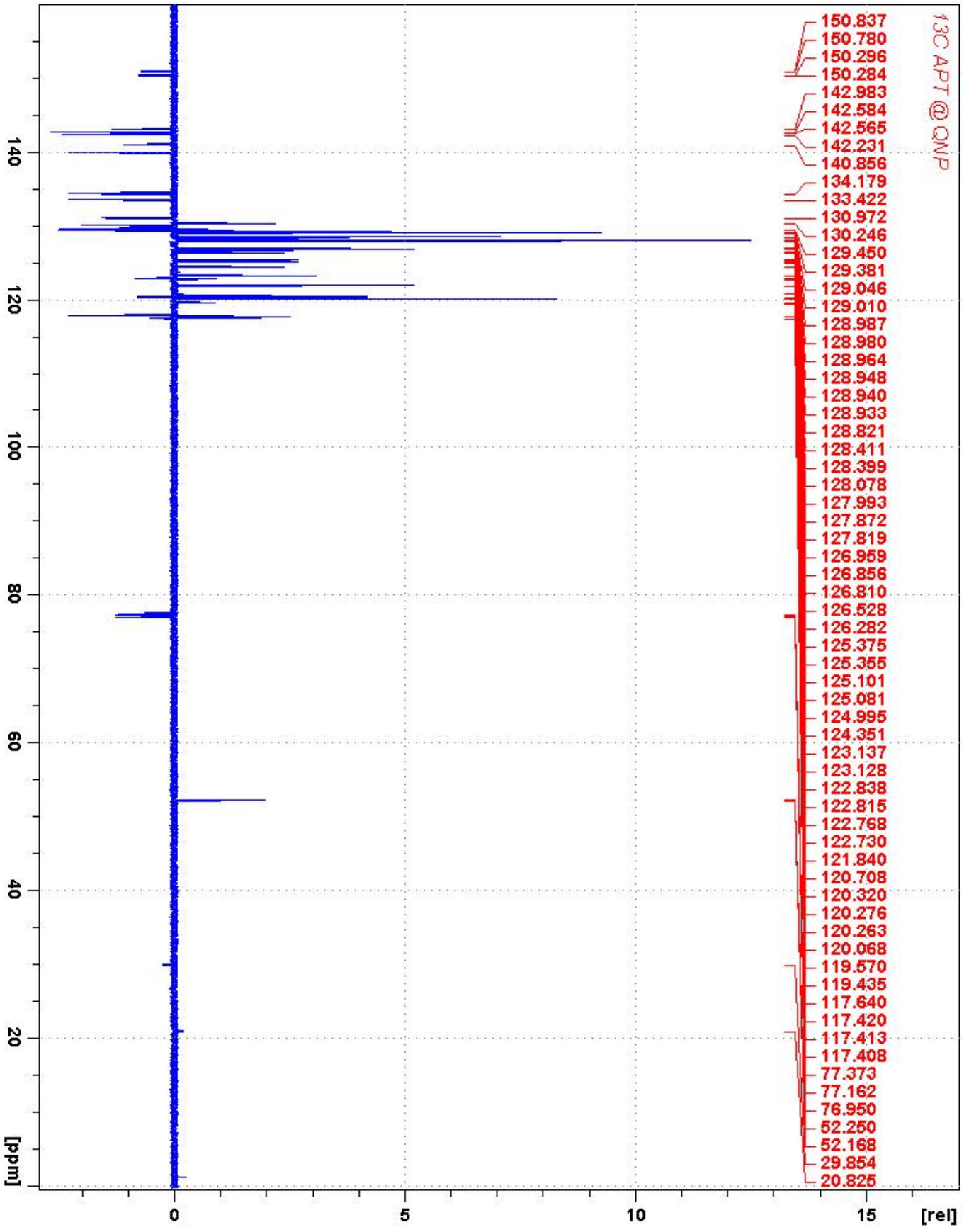


Figure 14. ^{31}**P-NMR** of (S_a,S_a,R_C,R_C)-**L2**

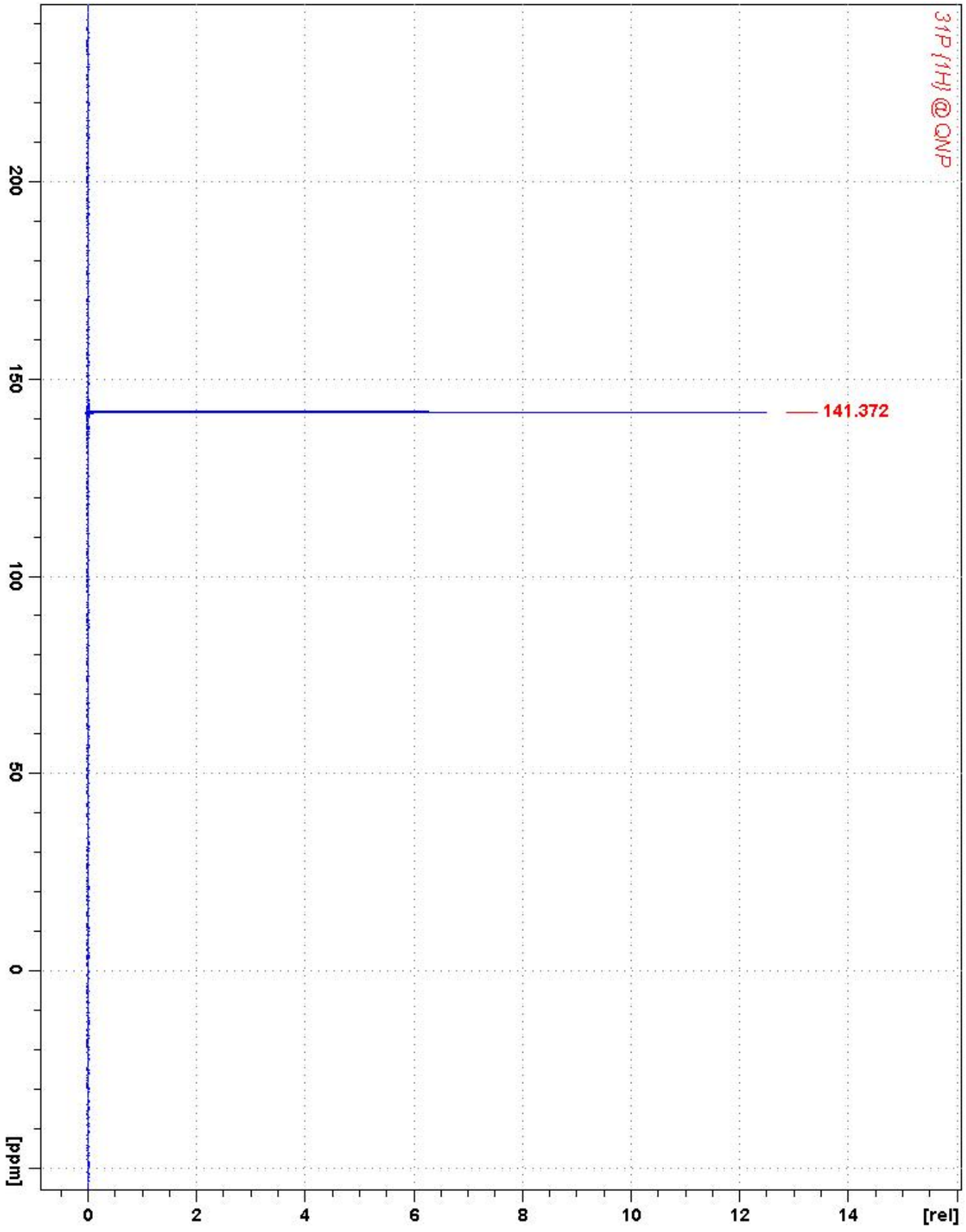


Figure 15. ^{1}**H-NMR** of (S_a,S_a,S_C,S_C)-**L2**

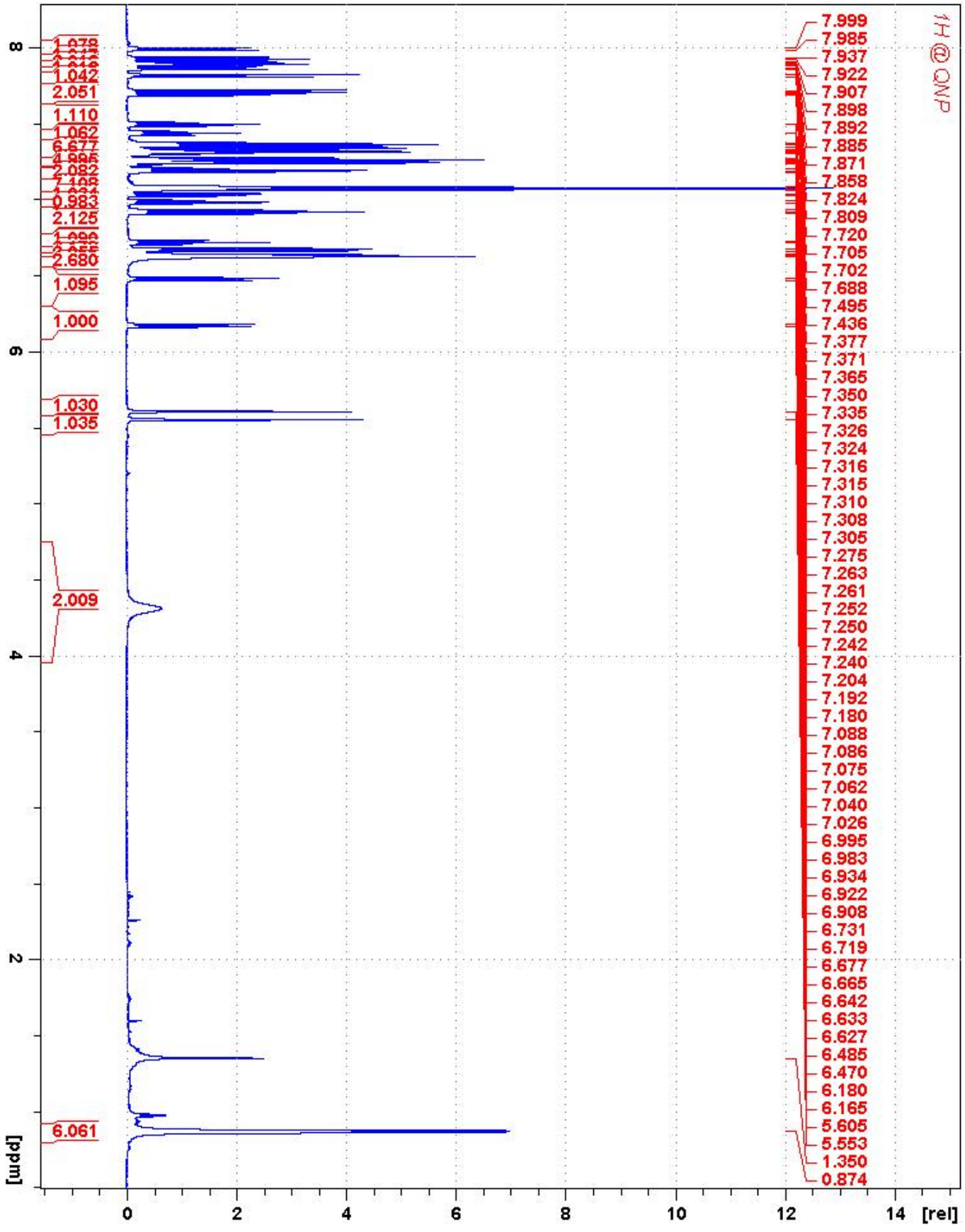


Figure 16. ^{13}C-NMR (apt) of (S_a,S_a,S_C,S_C)-**L2**

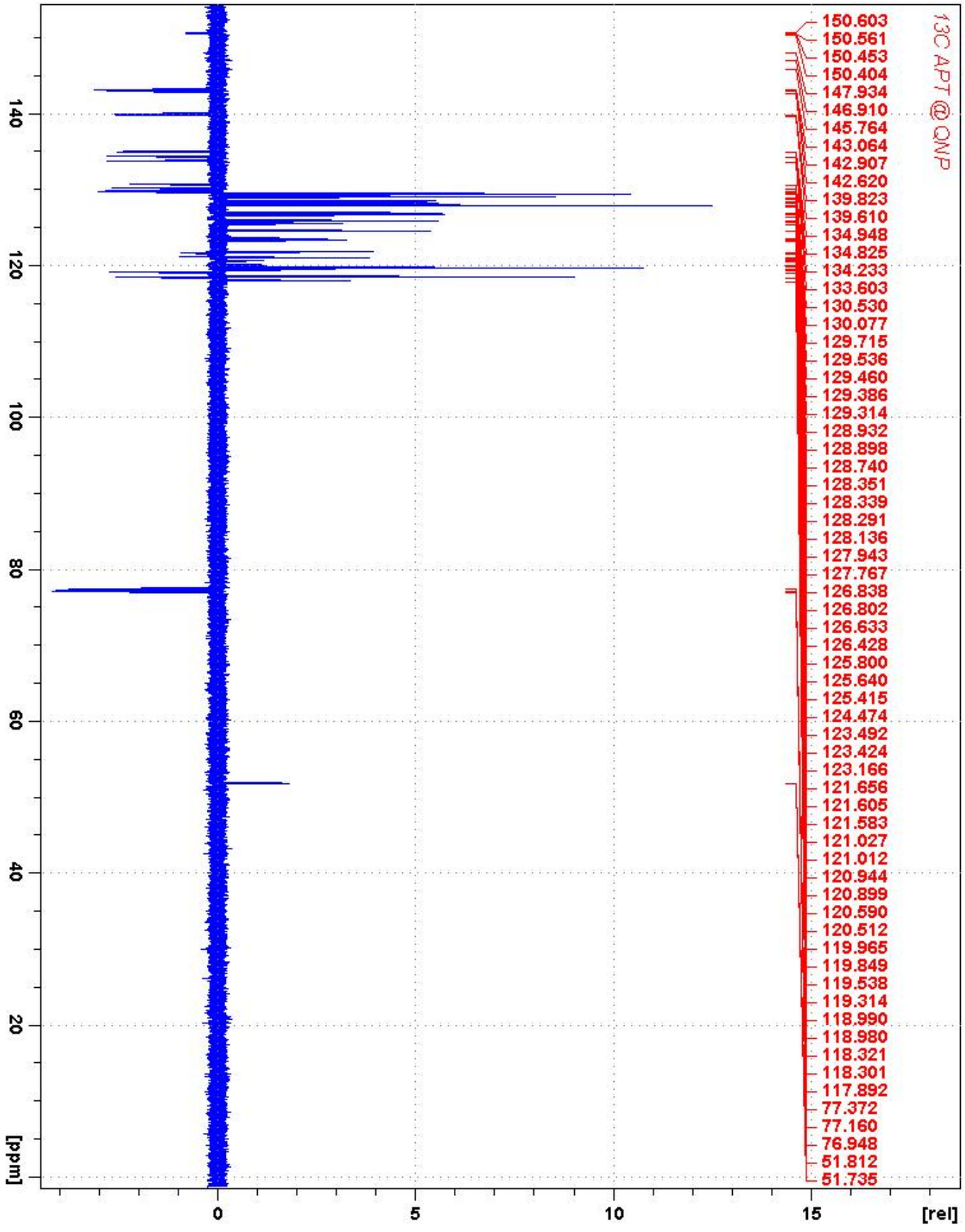
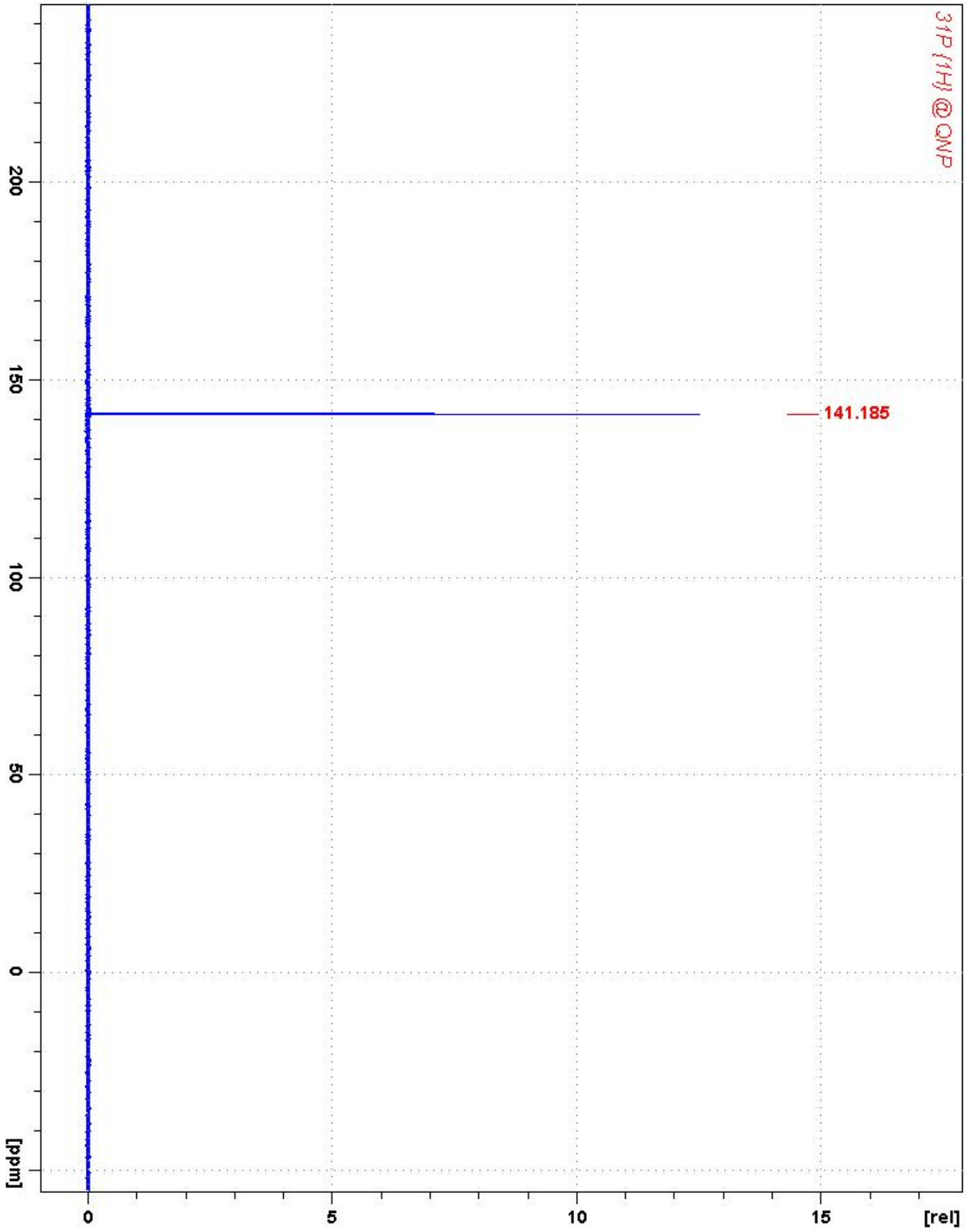


Figure 17. ^{31}**P-NMR** of (S_a,S_a,S_C,S_C)-**L2**



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