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Supporting Information

Asymmetric Sequential Cu-Catalyzed 1,6/1,4-Conjugate Additions of Hard Nucleophiles to Cyclic Dienones: Determination of Absolute Configurations and Origins of Enantioselectivity

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Author Contributions

M.M. Conceptualization: Lead

C.B. Methodology: Equal.

Theoretical calculations and Vibrational Circular Dichroism

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1. Theoretical determination of the reaction mechanism of 1,6-ACA catalyzed by Cu/DiPPAM: toward a rationale of enantioselectivity.

Computational Details

The calculations were carried out with the Gaussian09 package.¹ Concerning the mechanistic investigations, all geometries and frequencies were done using the Density Functional Theory (DFT) with the hybrid B3PW91 functional.² The copper, zinc and phosphorous were represented with the quasi-relativistic effective core potential ECP^{3,4} from Stuttgart group completed by the associated basis-set.⁵ A 6-31G(d,p) basis set was used for all other atoms (H, C, N, O, P).⁶ The geometry optimizations were performed without any constraint and the nature of the extrema (minima and transition state) were verified by analytical calculations of frequencies. In particular the connection between the transition state and minima was verified by carrying out a small displacement along the reaction coordinate in each direction and optimizing geometry starting from that structure. For the enantioselectivity aspects, all calculations were performed with the hybrid B3PW91-D functional corrected with dispersion.⁷

Table S1 Energetics (in kcal/mol with respect to **Cu(L1)**) and geometric (Å) parameters along the reaction path of Me transfer from Cu to C5 position of the carbonyl compound.

	Free substrate	I1	TS1	A1
ΔE		0.0	16.9	-36.0
ΔG		0.0	17.8	-36.0
Zn...O=C		2.111	2.025	2.019
C=O	1.223	1.257	1.274	1.271
Cu-Et		1.996	2.182	3.385
Cu-C5		2.031	2.132	2.016
Et...C5		3.070	2.125	1.542
C5=C4	1.344	1.405	1.465	1.525
C4-C3	1.457	1.437	1.411	1.430

Cartesian coordinates

Cu(L1)

55
scf done: -1376.514997
C -0.759434 0.799910 -0.239490
C 0.399492 0.045548 -0.573036
C 1.094595 0.382534 -1.748115
C 0.694874 1.424793 -2.574376
C -0.443020 2.155304 -2.247120
C -1.157592 1.834533 -1.094500
H 1.973853 -0.200224 -2.012037
H 1.261941 1.655560 -3.471369
H -0.783231 2.965754 -2.885184
H -2.056290 2.396757 -0.860169
P -1.800142 0.462400 1.265301
C 0.960288 -1.105683 0.152512
N 0.611635 -1.519210 1.311981
C 1.216402 -2.728713 1.844953
C 0.108876 -3.808067 2.107779
O 0.474620 -4.972949 2.173181
O -1.112530 -3.395016 2.255877
Cu -1.463950 -1.590374 1.853931
H 1.748492 -1.638105 -0.400126
C -1.160917 1.632727 2.544479
C -0.336736 2.722569 2.243103
C -1.535656 1.400778 3.875642
C 0.101786 3.570448 3.260210
H -0.030916 2.907321 1.217739
C -1.102160 2.254502 4.886562
H -2.163177 0.547043 4.120119
C -0.281134 3.339813 4.580097
H 0.746122 4.411121 3.018198
H -1.397431 2.065254 5.914620
H 0.064481 4.000521 5.370170
C -3.466856 1.130095 0.833784
C -3.874987 2.432704 1.145502
C -4.362938 0.261036 0.196960
C -5.159164 2.861217 0.811561
H -3.194973 3.107757 1.657149
C -5.641317 0.695951 -0.143103
H -4.060340 -0.760596 -0.021293
C -6.040804 1.996615 0.164560
H -5.471128 3.871661 1.060980
H -6.329153 0.014990 -0.636153
H -7.041827 2.332596 -0.091086
H 1.906374 -3.171738 1.110412
C 2.043445 -2.416582 3.138554
C 2.850724 -3.663422 3.527743
H 2.201522 -4.523951 3.697757
H 3.560156 -3.935738 2.737866
H 3.425733 -3.459485 4.438403
C 1.122218 -2.014650 4.298273

H 1.720066 -1.761356 5.181244
H 0.518332 -1.137600 4.041825
H 0.443757 -2.828431 4.571064
C 3.022077 -1.270198 2.842689
H 2.500548 -0.332241 2.628575
H 3.673424 -1.101591 3.707456
H 3.665853 -1.506918 1.986553

Cyclic dienone

22
scf done: -425.248283
C -4.054633 -3.874938 -1.352697
C -2.721817 -3.917676 -1.184787
H -4.466429 -3.455265 -2.269776
H -2.329707 -4.353573 -0.265456
C -1.717044 -3.456979 -2.134571
C -0.401628 -3.637750 -1.850817
H -0.094389 -4.090903 -0.910838
C 0.690086 -3.296396 -2.771364
O 1.861341 -3.484192 -2.472788
C -5.050088 -4.380414 -0.361274
H -5.735701 -3.582235 -0.049836
H -5.673779 -5.170535 -0.798280
H -4.565345 -4.783044 0.532359
C 0.284835 -2.745098 -4.127690
C -1.026103 -1.966395 -4.053503
C -2.139270 -2.810001 -3.432021
H 1.111341 -2.141211 -4.512553
H 0.174007 -3.603274 -4.807185
H -0.877285 -1.068553 -3.440367
H -1.327423 -1.622031 -5.048766
H -3.024955 -2.187770 -3.262767
H -2.453215 -3.598848 -4.132235

ZnEt₂

15
scf done: -385.572413
Zn -0.172356 -0.180909 -0.109833
C -2.121870 -0.319528 -0.093557
H -2.536341 0.686789 -0.244509
H -2.429770 -0.898053 -0.975450
C -2.721803 -0.944387 1.174136
H -3.817816 -0.996086 1.126986
H -2.362454 -1.967005 1.337223
H -2.469388 -0.370634 2.073360
C 1.777167 -0.042614 -0.125037
H 2.191000 -1.059250 -0.075489
H 2.090983 0.446732 0.807320
C 2.370806 0.702659 -1.328980
H 2.011214 1.736342 -1.389818
H 3.467074 0.749494 -1.282695

H 2.113411 0.219271 -2.278477

A1
92
scf done: -2187.339915

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C 0.269885 -0.045004 -0.427994
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C 0.632227 1.150873 -2.535185
C -0.705190 1.528451 -2.546482
C -1.541423 1.144953 -1.499296
H 2.144133 0.072538 -1.463949
H 1.303896 1.450639 -3.334207
H -1.104440 2.133311 -3.355783
H -2.572653 1.476234 -1.520579
P -2.332899 -0.085808 0.898268
C 0.960188 -0.909837 0.543501
N 0.417005 -1.665301 1.416296
C 1.365018 -2.550338 2.123654
C 1.765469 -3.642250 1.107667
O 1.229945 -4.777608 1.079421
O 2.634914 -3.296029 0.238937
Cu -3.572441 -2.106169 1.121032
H 2.048742 -0.923930 0.401771
Zn 2.471532 -5.015351 -0.858709
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H 4.341823 -6.264023 -2.019591
H 3.988627 -7.005584 -0.472115
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H -5.170471 -0.566624 2.379197
H -6.049624 -1.941840 1.735141
C -4.258701 -3.828047 0.290431
C -2.870524 -3.880639 0.081083
H -4.882171 -3.448446 -0.522677
H -2.289744 -4.403911 0.841495
C -2.141579 -3.594227 -1.123773
C -0.815865 -3.958342 -1.166415
H -0.355924 -4.382754 -0.279730
C -0.001069 -3.858813 -2.328869
O 1.200830 -4.225433 -2.348506
C -4.956224 -4.783528 1.217094
H -5.884081 -4.364178 1.613379
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C -0.202216 2.187325 3.648487
H -0.077262 1.824159 1.534505
C -1.937343 1.003050 4.831854
H -3.160908 -0.307335 3.642923
C -0.870398 1.900263 4.837708
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H -2.461880 0.770791 5.754412
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C -3.696130 2.445851 0.911086
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H -2.867860 2.820750 1.504415
C -5.839570 1.504244 -0.604078
H -4.836967 -0.396382 -0.561373
C -5.814758 2.834462 -0.187957
H -4.721121 4.335246 0.905427
H -6.675494 1.129035 -1.187980
H -6.630693 3.502732 -0.448904
H 2.299945 -2.001477 2.314720
C 0.831184 -3.031823 3.491711
C 1.832272 -4.028764 4.095698
H 1.892932 -4.943312 3.500311
H 2.836778 -3.592796 4.163532
H 1.523646 -4.301314 5.110952
C -0.550500 -3.686691 3.376380
H -0.907062 -3.983349 4.369582
H -1.274104 -2.984869 2.949297
H -0.502761 -4.575290 2.743072
C 0.740862 -1.803569 4.409028
H 0.077411 -1.042535 3.990236
H 0.352139 -2.089061 5.392897
H 1.727694 -1.349131 4.560637
C -5.126302 -2.317206 3.656751
H -4.240508 -2.047997 4.245460
H -6.001749 -2.031352 4.260060
H -5.132212 -3.410680 3.597031
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H 2.247068 -7.316891 -3.006342
H 3.334641 -8.551040 -2.366458
H 1.902455 -8.074847 -1.454203
C -0.628449 -3.342096 -3.602596
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C -2.807680 -3.023760 -2.349852
H 0.149085 -2.862124 -4.204216
H -0.970487 -4.218139 -4.173807
H -1.412191 -1.474067 -2.879150
H -2.299252 -2.125545 -4.252726
H -3.562111 -2.281245 -2.064558
H -3.357670 -3.836770 -2.848372

TS1
92
scf done: -2187.313026

C -1.025698 0.652565 -0.331308
C 0.307031 0.168421 -0.419495
C 1.134057 0.677626 -1.437049
C 0.695784 1.616692 -2.360846
C -0.605521 2.092218 -2.267778

C	-1.442435	1.615936	-1.260516	H	-5.168932	4.066789	1.961110
H	2.151991	0.302581	-1.500146	H	-6.329916	1.701364	-1.435053
H	1.366652	1.973584	-3.136712	H	-6.727347	3.639201	0.074176
H	-0.977624	2.837275	-2.965156	H	2.422612	-2.037695	1.996533
H	-2.445871	2.018036	-1.201228	C	1.043297	-2.937233	3.364589
P	-2.277648	0.082686	0.932708	C	2.060601	-3.962730	3.889492
C	0.992583	-0.817067	0.434382	H	2.008685	-4.896918	3.326970
N	0.479571	-1.563318	1.332427	H	3.084648	-3.574229	3.823144
C	1.433172	-2.518046	1.928928	H	1.860458	-4.179445	4.945013
C	1.656153	-3.661075	0.903141	C	-0.369309	-3.530468	3.422633
O	1.203150	-4.814250	1.069863	H	-0.631436	-3.779710	4.457960
O	2.329399	-3.330164	-0.129674	H	-1.103636	-2.812194	3.044157
Cu	-3.243959	-1.952712	0.784481	H	-0.422864	-4.439590	2.819333
H	2.059390	-0.905216	0.194160	C	1.120815	-1.682883	4.246860
Zn	2.277717	-5.150686	-1.075452	H	0.460970	-0.894028	3.878147
C	3.578049	-6.618837	-1.261265	H	0.828066	-1.919715	5.276039
H	4.391220	-6.273402	-1.914353	H	2.142818	-1.284822	4.275376
H	4.037402	-6.794114	-0.280117	C	-5.510579	-1.756056	2.689508
C	-5.384736	-2.036367	1.199549	H	-4.907223	-0.896008	2.995188
H	-5.388750	-1.109224	0.612815	H	-6.550449	-1.530603	2.964107
H	-6.238030	-2.611980	0.842413	H	-5.204703	-2.610019	3.304992
C	-4.344143	-3.758982	0.517820	C	2.997390	-7.927531	-1.808308
C	-2.916060	-3.912239	0.230746	H	2.548373	-7.789358	-2.798695
H	-4.964766	-3.753190	-0.376927	H	3.758373	-8.715955	-1.907110
H	-2.306128	-4.324482	1.034338	H	2.210407	-8.325785	-1.156791
C	-2.309041	-3.879842	-1.042756	C	-0.993750	-3.887677	-3.661706
C	-0.987202	-4.308714	-1.184471	C	-2.136123	-2.917083	-3.366108
H	-0.458904	-4.648242	-0.299365	C	-3.068058	-3.464589	-2.283667
C	-0.289739	-4.329151	-2.397006	H	-0.249846	-3.448331	-4.333749
O	0.914407	-4.729233	-2.512022	H	-1.377184	-4.786539	-4.166836
C	-4.854379	-4.700069	1.588861	H	-1.714378	-1.964345	-3.022093
H	-5.906880	-4.540324	1.837614	H	-2.704529	-2.704212	-4.279036
H	-4.739741	-5.729492	1.229670	H	-3.838780	-2.722528	-2.041871
H	-4.266200	-4.615639	2.508157	H	-3.603257	-4.345454	-2.670789
C	-1.616653	0.638241	2.561321				
C	-0.686037	1.678945	2.660817	E1			
C	-2.148688	0.080253	3.728862	92			
C	-0.304353	2.158886	3.912627	scf done: -2187.397245			
H	-0.260284	2.116951	1.762978	C	-0.615857	1.033863	-0.308515
C	-1.776623	0.572524	4.978265	C	0.716638	0.554538	-0.389248
H	-2.849926	-0.746135	3.664563	C	1.591067	1.156865	-1.308532
C	-0.855069	1.613881	5.072135	C	1.188036	2.192402	-2.142581
H	0.422676	2.963354	3.980175	C	-0.119989	2.656832	-2.063184
H	-2.197518	0.131687	5.877308	C	-1.005192	2.080410	-1.153422
H	-0.558997	1.993379	6.045938	H	2.610518	0.784558	-1.368092
C	-3.679599	1.286600	0.676635	H	1.889852	2.629531	-2.846704
C	-3.909113	2.383984	1.514435	H	-0.459496	3.467234	-2.701795
C	-4.572401	1.050445	-0.381972	H	-2.020288	2.457725	-1.103926
C	-5.003645	3.221992	1.298153	P	-1.886186	0.291937	0.822815
H	-3.235951	2.589535	2.340059	C	1.313143	-0.530789	0.401959
C	-5.655819	1.896526	-0.605687	N	0.706667	-1.261683	1.255157
H	-4.409394	0.206214	-1.049077	C	1.529835	-2.320880	1.857145
C	-5.877130	2.983672	0.239798	C	1.614567	-3.482435	0.833518

O 1.065361 -4.595704 1.032255
O 2.279951 -3.236239 -0.218701
Cu -2.408978 -1.864963 0.572781
H 2.374774 -0.699939 0.181636
Zn 1.958656 -5.169563 -0.985448
C 3.172704 -6.704667 -1.212180
H 3.822347 -6.501307 -2.074272
H 3.838323 -6.749978 -0.340629
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H -6.417955 -3.044197 1.885361
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C -3.323774 -3.652139 0.395104
H -5.301599 -3.123141 -0.250062
H -2.788247 -4.212067 1.170584
C -2.684024 -3.738877 -0.880680
C -1.359461 -4.190698 -1.002142
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C -0.658229 -4.253031 -2.216045
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H -6.445055 -5.178453 0.586321
H -5.107401 -5.569880 -0.507961
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C -1.462111 0.883466 2.516252
C -0.516885 1.888303 2.743833
C -2.172673 0.345702 3.596663
C -0.284338 2.347724 4.039989
H 0.039918 2.308706 1.911857
C -1.943074 0.813112 4.888248
H -2.905799 -0.439287 3.428688
C -0.997548 1.813715 5.111879
H 0.455953 3.124500 4.210086
H -2.497238 0.389048 5.720700
H -0.813934 2.173079 6.120447
C -3.416511 1.276288 0.450578
C -3.715980 2.487163 1.087323
C -4.309928 0.768621 -0.502029
C -4.886085 3.176101 0.772341
H -3.037490 2.889844 1.833250
C -5.475044 1.462790 -0.822240
H -4.091845 -0.178458 -0.990855
C -5.765581 2.667138 -0.182616
H -5.110973 4.112098 1.276123
H -6.158918 1.058206 -1.563110
H -6.678148 3.205065 -0.423731
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C 1.086129 -2.680039 3.294379
C 2.010486 -3.777730 3.844990
H 1.896699 -4.709375 3.287092
H 3.062637 -3.470339 3.796854
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C -0.370203 -3.155255 3.344487

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H -1.042937 -2.383057 2.954234
H -0.495282 -4.064752 2.753559
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H 0.629728 -0.600783 3.798520
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H -3.694402 -3.525731 3.233499
H -5.199222 -3.063432 4.033397
H -5.054752 -4.653150 3.286236
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H 3.184610 -8.883014 -1.533568
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H -3.035905 -2.634257 -4.152547
H -4.212585 -2.642432 -1.941936
H -3.925418 -4.272049 -2.519572

Enantioselectivity

DFT-D3

(a) (0.0)

92

scf done: -2187.617545

C -0.870692 0.317902 -0.307220
C 0.397858 -0.299604 -0.396496
C 1.250643 0.035077 -1.459852
C 0.886658 0.973762 -2.415877
C -0.350203 1.604870 -2.311363
C -1.216335 1.272883 -1.272512
H 2.207915 -0.473432 -1.530705
H 1.563044 1.212823 -3.230710
H -0.650740 2.351859 -3.039983
H -2.180936 1.762297 -1.218998
P -2.119688 -0.185438 0.956110
C 0.930471 -1.269438 0.557507
N 0.325020 -1.642829 1.617495
C 1.029272 -2.628254 2.464886
C 1.335883 -3.859037 1.595920
O 0.588203 -4.840098 1.544376
O 2.385662 -3.698634 0.845331
Cu -3.156593 -2.221335 1.102331
H 1.916847 -1.665634 0.296500
Zn 2.409776 -4.839993 -0.712810
C 2.723957 -6.534120 -1.625125
H 3.732710 -6.533234 -2.055825
H 2.699906 -7.345143 -0.888839

C	-4.796558	-1.851318	2.164066
H	-4.925137	-0.763685	2.210965
H	-5.655542	-2.240155	1.603426
C	-3.795487	-3.926562	0.251059
C	-2.411011	-3.893267	0.012659
H	-4.462700	-3.547929	-0.525929
H	-1.775873	-4.430775	0.716908
C	-1.716153	-3.386515	-1.129126
C	-0.359100	-3.608904	-1.177570
H	0.074790	-4.150675	-0.345584
C	0.495074	-3.202504	-2.227074
O	1.738356	-3.416143	-2.187456
C	-4.399335	-4.944119	1.173767
H	-5.339873	-4.591810	1.603999
H	-4.611532	-5.868989	0.621394
H	-3.714212	-5.194020	1.988531
C	-1.584578	0.633317	2.505517
C	-0.434756	1.421401	2.576605
C	-2.400220	0.487281	3.631766
C	-0.097825	2.050490	3.773213
H	0.198914	1.534595	1.703195
C	-2.064524	1.124942	4.822256
H	-3.293579	-0.124089	3.571189
C	-0.910643	1.904187	4.896296
H	0.803243	2.654393	3.827799
H	-2.699910	1.004298	5.694588
H	-0.643346	2.393682	5.828081
C	-3.543697	0.897309	0.477369
C	-3.688382	2.208233	0.941149
C	-4.504502	0.372173	-0.393521
C	-4.773524	2.981390	0.532115
H	-2.952931	2.623184	1.623043
C	-5.583926	1.145807	-0.808557
H	-4.415114	-0.658186	-0.728366
C	-5.720052	2.453900	-0.344452
H	-4.879340	3.997675	0.900658
H	-6.324952	0.724955	-1.481904
H	-6.566419	3.057337	-0.659286
H	2.006349	-2.206154	2.735816
C	0.260436	-2.892382	3.773528
C	0.939638	-4.036139	4.535976
H	0.851539	-4.981003	3.995409
H	2.004268	-3.825177	4.693914
H	0.477252	-4.155981	5.521450
C	-1.205140	-3.242837	3.508789
H	-1.738787	-3.384124	4.453993
H	-1.700365	-2.427948	2.966222
H	-1.281353	-4.160206	2.922982
C	0.339156	-1.615253	4.615292
H	-0.051105	-0.759404	4.064643
H	-0.244021	-1.723930	5.535595
H	1.375643	-1.396146	4.897285
C	-4.753114	-2.455981	3.562757

H	-3.927688	-2.054404	4.160821
H	-5.678916	-2.267669	4.127346
H	-4.612432	-3.541576	3.539068
C	1.680391	-6.768973	-2.722017
H	1.703350	-5.971007	-3.471769
H	1.840056	-7.719491	-3.249437
H	0.663331	-6.794693	-2.313541
C	-0.124431	-2.552599	-3.437108
C	-1.444491	-1.854073	-3.107791
C	-2.400466	-2.729743	-2.295006
H	0.597753	-1.857278	-3.873846
H	-0.280519	-3.352687	-4.175551
H	-1.225391	-0.954344	-2.530879
H	-1.935012	-1.525965	-4.029937
H	-3.252870	-2.132011	-1.955070
H	-2.819704	-3.528294	-2.924934

(b) (2.1)

92

scf done: -2187.614165

C	-2.782889	1.501488	1.038526
C	-2.862580	1.853586	-0.326829
C	-3.085712	3.185328	-0.685158
C	-3.179562	4.177087	0.286750
C	-3.067348	3.835810	1.631928
C	-2.887345	2.503250	2.003132
H	-3.167058	3.441544	-1.738482
H	-3.342352	5.210157	-0.005011
H	-3.141375	4.601761	2.398177
H	-2.855874	2.240384	3.055332
P	-2.852960	-0.283652	1.503468
C	-2.672295	0.855023	-1.386112
N	-1.934117	-0.161111	-1.166706
C	-1.636650	-1.087069	-2.232139
C	-1.394958	-2.500423	-1.677778
O	-0.681074	-2.554066	-0.609074
O	-1.856642	-3.465919	-2.295107
Cu	-4.646618	-0.988438	0.227686
H	-3.142257	1.059342	-2.359148
Zn	0.155603	-4.143943	0.110081
C	1.917201	-4.999036	0.013680
H	2.637072	-4.278078	-0.393144
H	1.858305	-5.814957	-0.717817
C	-4.232743	-3.668218	0.574556
C	-3.021075	-4.311861	0.467170
C	-4.706316	-2.955237	-0.575386
H	-4.061950	-3.018066	-1.451705
C	-5.912541	-2.249762	-0.695910
H	-6.681700	-2.376187	0.066032
H	-2.510970	-4.292163	-0.490697
C	-2.321855	-4.836664	1.572617
O	-1.093560	-5.123770	1.500199
C	-5.879967	0.574369	0.281923

H	-5.853248	0.981987	-0.738363
H	-5.427287	1.332604	0.930990
C	-3.448431	-0.227898	3.253706
C	-2.583817	-0.127041	4.350590
C	-4.826842	-0.319994	3.481229
C	-3.091662	-0.128223	5.648016
H	-1.512952	-0.059409	4.188658
C	-5.333249	-0.321052	4.777767
H	-5.497307	-0.384358	2.629741
C	-4.465255	-0.229100	5.864795
H	-2.411240	-0.053129	6.491449
H	-6.404925	-0.396456	4.938050
H	-4.857147	-0.236138	6.877779
C	-1.117525	-0.821514	1.753050
C	-0.042947	-0.066641	1.284439
C	-0.873292	-2.037810	2.394243
C	1.258729	-0.539107	1.426015
H	-0.229825	0.878716	0.787702
C	0.427192	-2.516651	2.530887
H	-1.699201	-2.618263	2.784497
C	1.497686	-1.770121	2.033922
H	2.087633	0.049785	1.044969
H	0.598463	-3.470557	3.020250
H	2.510830	-2.149545	2.124288
C	2.406208	-5.540277	1.358755
H	1.699035	-6.260093	1.784542
H	3.379278	-6.045164	1.278774
H	2.525817	-4.739518	2.098565
C	-7.321241	0.320569	0.708731
H	-7.920208	1.242410	0.732051
H	-7.841390	-0.373122	0.038275
H	-7.385447	-0.113788	1.715565
C	-6.397398	-1.781397	-2.038285
H	-7.063363	-2.530953	-2.484870
H	-6.956825	-0.845896	-1.959457
H	-5.560782	-1.628189	-2.725900
C	-3.068263	-5.036078	2.868976
C	-4.118592	-3.941282	3.085087
C	-5.011390	-3.721002	1.862914
H	-3.554159	-6.020902	2.822704
H	-2.349005	-5.072624	3.692203
H	-4.734869	-4.179154	3.958008
H	-3.618827	-2.995525	3.320877
H	-5.745246	-4.535430	1.773564
H	-5.591140	-2.800855	1.999903
C	-0.373676	-0.618003	-3.043800
C	-0.730577	0.629629	-3.857993
H	0.127900	0.927596	-4.468832
H	-1.574027	0.443612	-4.532578
H	-0.979288	1.480379	-3.216359
C	0.032854	-1.736335	-4.011492
H	-0.809725	-2.060000	-4.629996
H	0.828934	-1.377235	-4.672152

H	0.406736	-2.614292	-3.478863
C	0.795540	-0.290136	-2.112726
H	1.678396	-0.031645	-2.707734
H	0.555544	0.561105	-1.470480
H	1.034819	-1.136140	-1.466534
H	-2.466260	-1.163984	-2.950899

(c) (4.1)

92

scf done: -2187.611059

C	-3.374243	1.594949	0.848085
C	-2.640230	2.101318	-0.248794
C	-2.704348	3.461741	-0.562069
C	-3.526050	4.324376	0.156547
C	-4.271415	3.825006	1.219415
C	-4.181398	2.476839	1.567969
H	-2.112443	3.836772	-1.393445
H	-3.578239	5.376083	-0.107913
H	-4.912232	4.484681	1.797017
H	-4.737226	2.116243	2.426226
P	-3.190806	-0.179754	1.380271
C	-1.799956	1.231110	-1.081660
N	-2.099564	0.004753	-1.208703
C	-1.273009	-0.888192	-1.977053
C	-1.402196	-2.273045	-1.338750
O	-0.296194	-2.907241	-1.182636
O	-2.526920	-2.706177	-1.037348
Cu	-4.377574	-1.693454	0.044702
H	-0.928106	1.692924	-1.568449
Zn	-0.293000	-4.780020	-0.627157
C	-0.229018	-6.519334	-1.526872
H	0.795648	-6.709896	-1.870180
H	-0.845310	-6.471148	-2.433217
C	-3.786117	-4.012003	1.527365
C	-2.595989	-4.635455	1.159121
C	-4.749664	-3.812991	0.508694
H	-4.519378	-4.309980	-0.432998
C	-5.892404	-2.997038	0.492866
H	-6.230317	-2.559625	1.434022
H	-2.494964	-4.919951	0.114206
C	-1.438791	-4.626321	1.946722
O	-0.279793	-4.796916	1.437597
C	-5.546959	-0.413159	-0.920678
H	-5.937223	-0.968198	-1.781610
H	-4.798991	0.302109	-1.282125
C	-3.941802	-0.107145	3.071219
C	-3.209601	0.090446	4.245758
C	-5.323981	-0.324862	3.161337
C	-3.847503	0.067243	5.484610
H	-2.137144	0.247122	4.193219
C	-5.963291	-0.331509	4.398192
H	-5.893997	-0.485680	2.251551
C	-5.223292	-0.141191	5.564771

H	-3.266014	0.212905	6.390588	C	-0.946746	0.401063	-0.565524
H	-7.035864	-0.495383	4.450954	C	0.284535	-0.269943	-0.731539
H	-5.716878	-0.157799	6.532083	C	1.091543	0.031424	-1.838586
C	-1.389527	-0.233597	1.750357	C	0.706758	0.985377	-2.771332
C	-0.661913	0.883015	2.179089	C	-0.508227	1.648630	-2.607673
C	-0.744689	-1.461303	1.600998	C	-1.325624	1.353845	-1.519317
C	0.694992	0.757137	2.465023	H	2.021203	-0.516752	-1.963496
H	-1.155336	1.844848	2.283792	H	1.344655	1.205127	-3.621902
C	0.610699	-1.589570	1.894204	H	-0.827055	2.395211	-3.328966
H	-1.307872	-2.311731	1.238175	H	-2.272209	1.870255	-1.415505
C	1.330927	-0.478771	2.326989	P	-2.083818	-0.039289	0.814192
H	1.258186	1.624547	2.798214	C	0.770258	-1.311363	0.166622
H	1.084399	-2.558386	1.774356	N	0.184560	-1.610607	1.262696
H	2.389731	-0.570588	2.551826	C	0.701375	-2.708534	2.081916
C	-0.702798	-7.653544	-0.613730	C	1.342886	-3.836460	1.260750
H	-1.734908	-7.498862	-0.277657	O	0.790481	-4.942211	1.222842
H	-0.669139	-8.633113	-1.110624	O	2.396336	-3.536205	0.559060
H	-0.087954	-7.724013	0.290005	Cu	-3.063155	-2.086890	1.032233
C	-6.655235	0.302542	-0.171770	H	1.669130	-1.829200	-0.170051
H	-7.257430	0.947970	-0.828814	Zn	2.538813	-4.748363	-0.960328
H	-7.356884	-0.392709	0.308849	C	3.222297	-6.375959	-1.790680
H	-6.253918	0.952731	0.612780	H	4.196491	-6.157159	-2.245701
C	-6.962977	-3.213482	-0.536667	H	3.405376	-7.121977	-1.009193
H	-7.667852	-3.980027	-0.187595	C	-4.489164	-1.755899	2.370173
H	-7.534143	-2.303352	-0.730511	H	-4.665993	-0.675656	2.428847
H	-6.534318	-3.559059	-1.481590	H	-5.431864	-2.212075	2.048420
C	-1.576837	-4.352748	3.422366	C	-3.790804	-3.802485	0.296335
C	-2.689099	-3.334772	3.698233	C	-2.424868	-3.821460	-0.044172
C	-3.997665	-3.646275	2.971091	H	-4.500864	-3.419023	-0.440314
H	-1.797854	-5.307076	3.920733	H	-1.766245	-4.370092	0.631746
H	-0.616284	-3.999180	3.806982	C	-1.788126	-3.371293	-1.239938
H	-2.873200	-3.255981	4.774214	C	-0.449058	-3.666204	-1.372553
H	-2.341305	-2.350836	3.376188	H	0.012345	-4.239163	-0.578689
H	-4.496048	-4.503434	3.447386	C	0.365501	-3.285136	-2.460121
H	-4.681020	-2.799181	3.067615	O	1.606442	-3.519619	-2.472393
C	-1.700060	-0.946776	-3.484387	C	-4.354411	-4.797051	1.269572
C	-3.197125	-1.226235	-3.635936	H	-5.218489	-4.398279	1.806413
H	-3.794199	-0.445015	-3.160238	H	-4.681177	-5.697803	0.733862
H	-3.457180	-1.259782	-4.699666	H	-3.601075	-5.104328	2.000127
H	-3.470677	-2.177944	-3.176649	C	-1.373320	0.809756	2.278846
C	-1.371451	0.397887	-4.140306	C	-0.154196	1.488502	2.224641
H	-1.612507	0.356603	-5.207575	C	-2.107750	0.799678	3.468517
H	-1.957495	1.213830	-3.706751	C	0.332965	2.137983	3.356754
H	-0.307708	0.644249	-4.045311	H	0.417294	1.503107	1.302956
C	-0.890010	-2.050367	-4.175032	C	-1.617863	1.450726	4.597539
H	-1.149929	-3.041022	-3.791985	H	-3.062087	0.286727	3.508035
H	-1.096285	-2.042537	-5.250334	C	-0.395180	2.118184	4.545049
H	0.186118	-1.909145	-4.031815	H	1.286451	2.655652	3.309502
H	-0.215196	-0.591811	-1.947596	H	-2.191447	1.431991	5.519456
				H	-0.010285	2.620277	5.427630
				C	-3.521464	1.069611	0.453534
				C	-3.547585	2.419788	0.817966
				C	-4.612819	0.526349	-0.231808

(d) (2.3)

92

scf done: -2187.613826

C	-4.645437	3.213081	0.492286	H	-4.325839	2.675305	1.976835
H	-2.707083	2.848082	1.355219	P	-2.831561	0.244184	1.301325
C	-5.708124	1.319544	-0.562897	C	-1.573561	1.177811	-1.483560
H	-4.610496	-0.531888	-0.483430	N	-1.033988	0.201505	-0.873304
C	-5.724882	2.665708	-0.200414	C	-0.153592	-0.655840	-1.638434
H	-4.658318	4.260230	0.780768	C	-0.805517	-2.030938	-1.794349
H	-6.551843	0.885384	-1.091365	O	-0.181745	-2.857213	-2.549875
H	-6.581196	3.285368	-0.450238	O	-1.876681	-2.313436	-1.226230
C	-4.031162	-2.324589	3.709115	Cu	-3.622305	-1.521922	0.055973
H	-3.073439	-1.898554	4.031551	H	-1.365262	1.379435	-2.546305
H	-4.753312	-2.134186	4.517926	Zn	-1.153337	-4.572774	-2.439329
H	-3.892094	-3.410256	3.662606	C	-2.426080	-5.669737	-3.442796
C	2.258626	-6.926607	-2.846463	H	-1.944349	-6.029023	-4.360785
H	2.063065	-6.190713	-3.633827	H	-3.247863	-5.020985	-3.771402
H	2.650572	-7.830611	-3.332713	C	-2.801584	-3.939040	1.452310
H	1.289486	-7.192547	-2.408770	C	-2.217369	-4.571130	0.370844
C	-0.295701	-2.628995	-3.645349	C	-4.031441	-3.225625	1.356073
C	-1.575808	-1.881328	-3.263069	H	-4.444381	-2.827015	2.282101
C	-2.515094	-2.694496	-2.368243	C	-4.824248	-3.116300	0.184954
H	0.423126	-1.962225	-4.129744	H	-4.516883	-3.692098	-0.687193
H	-0.515426	-3.432490	-4.363579	H	-2.725736	-4.548898	-0.585844
H	-1.299150	-0.969309	-2.732794	C	-0.881286	-5.015606	0.361399
H	-2.107509	-1.568566	-4.167551	O	-0.268298	-5.282865	-0.716798
H	-3.308395	-2.044870	-1.981610	C	-4.573389	-0.746710	-1.502159
H	-3.019027	-3.478700	-2.952560	H	-4.903662	-1.576951	-2.135310
H	-0.175136	-3.172141	2.546808	H	-3.727973	-0.263842	-2.005853
C	1.597871	-2.194959	3.250076	C	-4.071498	0.389342	2.670344
C	2.241038	-3.411240	3.926787	C	-3.764294	0.789600	3.974311
H	2.966308	-3.897663	3.267724	C	-5.394461	0.051865	2.355944
H	2.766363	-3.099302	4.835575	C	-4.761803	0.835069	4.948094
H	1.486413	-4.153198	4.208887	H	-2.746748	1.064190	4.231722
C	0.700312	-1.471308	4.256806	C	-6.390815	0.107809	3.325038
H	0.161193	-0.651460	3.783507	H	-5.633112	-0.248101	1.340215
H	-0.034496	-2.158989	4.690535	C	-6.074277	0.493893	4.627869
H	1.299620	-1.058721	5.075413	H	-4.510980	1.142638	5.959418
C	2.685769	-1.246014	2.745636	H	-7.412437	-0.154618	3.064854
H	2.249347	-0.330245	2.337523	H	-6.848069	0.530136	5.389228
H	3.342073	-0.962930	3.575584	C	-1.268191	0.453999	2.239855
H	3.291567	-1.721931	1.970138	C	-0.465933	1.590945	2.134630

(e) (-3.1)

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C	-3.054477	1.867731	0.443458	C	1.085548	0.656788	3.737277
C	-2.492564	2.108078	-0.830439	H	1.333747	2.570858	2.781790
C	-2.813233	3.286523	-1.515552	H	0.559061	-1.279795	4.528525
C	-3.650718	4.241527	-0.953251	H	2.003968	0.734292	4.311489
C	-4.179727	4.021304	0.315658	C	-2.968641	-6.852575	-2.635780
C	-3.886580	2.843590	1.000136	H	-3.483886	-6.524884	-1.724994
H	-2.388474	3.448196	-2.503124	H	-3.686069	-7.455429	-3.209715
H	-3.886836	5.149836	-1.499052	H	-2.164645	-7.523649	-2.314064
H	-4.830309	4.760003	0.774338	C	-5.699054	0.242574	-1.260561

H	-6.125496	0.619807	-2.202620	Zn	1.259578	-6.180138	0.154970
H	-6.533767	-0.203114	-0.705027	C	0.226530	-7.790250	0.550800
H	-5.363867	1.117800	-0.694820	H	0.530521	-8.603642	-0.117789
C	-6.302910	-2.875770	0.272648	H	0.452060	-8.120676	1.571355
H	-6.688556	-2.403021	-0.633526	C	-3.146201	-3.180225	2.117366
H	-6.828344	-3.832727	0.393806	H	-3.327045	-4.254416	2.007551
H	-6.561527	-2.251341	1.131943	H	-2.444134	-3.056444	2.950744
C	-0.145217	-5.147419	1.670344	C	-2.855085	-3.863769	-0.703188
C	-0.595389	-4.071600	2.659589	C	-2.125720	-2.979803	-1.539552
C	-2.117341	-4.036507	2.791080	H	-2.367096	-4.792461	-0.413879
H	-0.352495	-6.148034	2.076167	H	-2.655826	-2.136464	-1.980784
H	0.928695	-5.093610	1.473288	C	-0.801959	-3.200431	-2.018323
H	-0.132424	-4.236783	3.638692	C	-0.087451	-4.347055	-1.727471
H	-0.247189	-3.099529	2.296482	H	-0.538681	-5.095624	-1.084121
H	-2.464245	-4.960579	3.277216	C	1.235356	-4.587220	-2.150551
H	-2.443398	-3.216268	3.439499	O	1.918421	-5.555018	-1.698285
H	-0.011292	-0.264754	-2.661454	C	-4.351950	-3.951140	-0.760548
C	1.256180	-0.734515	-0.971147	H	-4.652493	-4.637405	-1.563828
C	1.705860	0.691538	-0.637735	H	-4.766153	-4.335537	0.174148
H	1.719515	1.320868	-1.535769	H	-4.818549	-2.984143	-0.968370
H	1.048713	1.155536	0.098899	C	-1.224082	0.501339	2.379158
H	2.720211	0.673680	-0.225465	C	-0.385088	1.617550	2.430010
C	1.176342	-1.572615	0.306318	C	-1.791338	0.013718	3.559965
H	0.407109	-1.184465	0.975749	C	-0.104892	2.227967	3.651078
H	0.946478	-2.616623	0.070332	H	0.052058	2.008932	1.517269
H	2.132886	-1.550127	0.838438	C	-1.509292	0.624940	4.778536
C	2.273626	-1.347691	-1.938446	H	-2.448710	-0.848459	3.524818
H	2.340447	-0.762083	-2.862547	C	-0.663624	1.731566	4.827641
H	3.263846	-1.346363	-1.469566	H	0.553535	3.091335	3.681725
H	2.008899	-2.370736	-2.204960	H	-1.947924	0.230933	5.690468
				H	-0.440508	2.205491	5.778931
				C	-3.341208	0.518977	0.530452
				C	-3.668612	1.758076	1.093251
				C	-4.287760	-0.136319	-0.262093
				C	-4.918796	2.326463	0.861351
				H	-2.947605	2.274971	1.718358
				C	-5.535697	0.433207	-0.500126
				H	-4.044851	-1.108090	-0.675751
				C	-5.853843	1.667110	0.063909
				H	-5.164349	3.286265	1.306941
				H	-6.262041	-0.091937	-1.113785
				H	-6.829533	2.111059	-0.111311
				C	-4.441815	-2.423608	2.355308
				H	-5.124816	-2.491987	1.501149
				H	-4.991469	-2.804619	3.229924
				H	-4.276842	-1.353320	2.522475
				C	-1.276903	-7.518821	0.410079
				H	-1.543762	-7.250584	-0.619915
				H	-1.885222	-8.394515	0.675408
				H	-1.599739	-6.692068	1.053401
				C	1.841948	-3.661148	-3.171601
				C	1.339060	-2.235031	-2.948790
				C	-0.185729	-2.165381	-2.925245

(f) (-3.3)
92
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C	-0.663088	0.573454	-0.454011
C	0.727826	0.334054	-0.553580
C	1.472330	0.984064	-1.546926
C	0.869456	1.846910	-2.452817
C	-0.503041	2.068653	-2.369062
C	-1.254932	1.442835	-1.376698
H	2.539391	0.786017	-1.610846
H	1.462391	2.336841	-3.218920
H	-0.994104	2.736179	-3.071008
H	-2.319905	1.636189	-1.319153
P	-1.701834	-0.305593	0.796515
C	1.428442	-0.639730	0.278994
N	0.857962	-1.311391	1.197704
C	1.633806	-2.375362	1.798571
C	1.075222	-3.704727	1.276696
O	-0.143729	-3.870086	1.101096
O	1.975509	-4.590465	1.051718
Cu	-2.041697	-2.572272	0.592642
H	2.487397	-0.806440	0.024121

H	2.930962	-3.728491	-3.104363
H	1.552493	-4.015607	-4.171166
H	1.720087	-1.883908	-1.984880
H	1.735588	-1.559329	-3.713492
H	-0.518394	-1.167188	-2.623180
H	-0.578519	-2.329821	-3.940215
H	2.681960	-2.324948	1.463900
C	1.642016	-2.323473	3.352016
C	2.024171	-0.902945	3.776638
H	2.983728	-0.604767	3.337506
H	1.267377	-0.179045	3.469144
H	2.121991	-0.850021	4.865839
C	2.694141	-3.311200	3.867134
H	2.477859	-4.333070	3.545522
H	3.695053	-3.052237	3.504745
H	2.715391	-3.290448	4.961901
C	0.271361	-2.686219	3.922485
H	0.255515	-2.509318	5.003244
H	-0.504930	-2.074760	3.464751
H	0.022190	-3.734512	3.739920

(g) (-7.8)

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C	-0.872376	0.567434	-0.646692
C	0.390632	-0.040142	-0.830912
C	1.182720	0.337695	-1.923836
C	0.752367	1.304443	-2.824813
C	-0.498498	1.892590	-2.650092
C	-1.302706	1.520823	-1.573713
H	2.143455	-0.151553	-2.059027
H	1.381801	1.587647	-3.662677
H	-0.854745	2.641241	-3.351384
H	-2.275325	1.984363	-1.451894
P	-1.938771	0.106899	0.783336
C	0.942929	-1.065412	0.053580
N	0.392547	-1.387246	1.160649
C	0.993916	-2.429703	1.998333
C	1.606104	-3.533219	1.136807
O	0.973402	-4.600520	0.975016
O	2.693020	-3.290137	0.493608
Cu	-2.282088	-2.087516	1.180947
H	1.860615	-1.544411	-0.298929
Zn	2.532409	-4.752914	-0.886620
C	3.215439	-6.438723	-1.606333
H	4.203631	-6.261344	-2.049353
H	3.370941	-7.143527	-0.781282
C	-2.416983	-2.311423	3.133402
H	-2.089355	-3.310585	3.440605
H	-1.712097	-1.584111	3.548930
C	-2.614124	-3.976972	0.687114
C	-2.822064	-3.242507	-0.508336
H	-1.630946	-4.423455	0.848718

H	-3.853663	-2.984705	-0.753301
C	-1.856314	-2.986915	-1.533738
C	-0.546608	-3.407644	-1.446504
H	-0.213786	-3.941580	-0.565457
C	0.417923	-3.180140	-2.452974
O	1.623722	-3.539321	-2.335321
C	-3.753349	-4.679908	1.365410
H	-3.880420	-5.682693	0.936693
H	-3.569669	-4.800815	2.435658
H	-4.697185	-4.140961	1.235318
C	-1.222180	1.086761	2.162156
C	-0.028188	1.800108	2.033326
C	-1.903000	1.096659	3.384252
C	0.485596	2.504868	3.119867
H	0.506630	1.798403	1.089820
C	-1.388072	1.803645	4.467050
H	-2.834427	0.550595	3.487452
C	-0.190248	2.505349	4.338351
H	1.419495	3.048762	3.013472
H	-1.919914	1.798862	5.413789
H	0.215941	3.049092	5.186048
C	-3.502046	1.025025	0.451915
C	-3.670122	2.382234	0.749969
C	-4.563295	0.308817	-0.111928
C	-4.881119	3.012807	0.476484
H	-2.853440	2.938499	1.200087
C	-5.772768	0.941671	-0.389802
H	-4.435076	-0.749904	-0.322185
C	-5.931825	2.294787	-0.095365
H	-5.006574	4.065753	0.711849
H	-6.592352	0.377677	-0.825534
H	-6.876392	2.788661	-0.303902
C	-3.839239	-2.033031	3.602233
H	-4.548867	-2.776192	3.221974
H	-3.931343	-2.042931	4.699129
H	-4.204987	-1.056173	3.259827
C	2.271483	-7.040586	-2.652327
H	2.100434	-6.348928	-3.484765
H	2.662693	-7.974565	-3.079952
H	1.289099	-7.271838	-2.224082
C	-0.008772	-2.522452	-3.742282
C	-1.230322	-1.623559	-3.569429
C	-2.345225	-2.305735	-2.785037
H	0.844395	-1.970468	-4.147174
H	-0.222133	-3.334097	-4.453211
H	-0.932254	-0.723347	-3.031861
H	-1.602378	-1.298809	-4.546736
H	-3.125178	-1.580438	-2.526918
H	-2.832663	-3.074246	-3.404177
H	0.161908	-2.897700	2.531934
C	1.945839	-1.834182	3.077903
C	2.653222	-3.003684	3.773025
H	3.342359	-3.512477	3.093033

H	3.229720	-2.636991	4.628882
H	1.929777	-3.737803	4.144626
C	1.095910	-1.076154	4.100845
H	0.513152	-0.289150	3.621448
H	0.402406	-1.751214	4.612898
H	1.738310	-0.612348	4.857095
C	2.983348	-0.887688	2.470674
H	2.507753	0.007252	2.058567
H	3.680084	-0.561571	3.250253
H	3.552993	-1.382533	1.680444

(h) (-3.8)

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C	-3.071448	1.878499	0.650793
C	-2.190617	2.443915	-0.299939
C	-2.257499	3.813235	-0.572425
C	-3.216595	4.620001	0.032294
C	-4.104938	4.058370	0.943803
C	-4.018906	2.702316	1.259967
H	-1.556553	4.240096	-1.285554
H	-3.265753	5.678630	-0.203614
H	-4.854951	4.675323	1.429737
H	-4.687848	2.287296	2.006245
P	-2.924112	0.098144	1.145337
C	-1.196035	1.636939	-1.023258
N	-1.419971	0.408583	-1.248535
C	-0.445074	-0.411981	-1.919706
C	-0.592821	-1.841230	-1.400992
O	0.492019	-2.497796	-1.249370
O	-1.728172	-2.325755	-1.192765
Cu	-3.799221	-1.460742	-0.252424
H	-0.279293	2.152621	-1.346155
Zn	-0.077758	-4.412555	-1.010623
C	-0.555552	-5.652801	-2.453583
H	-0.395213	-6.689751	-2.136759
H	0.116512	-5.480444	-3.303337
C	-3.409628	-3.626582	1.564528
C	-2.303685	-4.214251	0.955745
C	-4.551162	-3.179207	0.853780
H	-5.372888	-2.812368	1.467897
C	-4.772689	-3.180496	-0.548428
H	-4.028617	-3.664704	-1.183137
H	-2.320315	-4.345783	-0.119929
C	-1.084647	-4.413005	1.612555
O	0.002284	-4.658077	0.981140
C	-4.714284	-0.385178	-1.634514
H	-4.902057	-0.994771	-2.522560
H	-3.938357	0.350218	-1.866116
C	-3.887171	0.034695	2.719607
C	-3.301801	0.088268	3.987281
C	-5.265367	-0.204321	2.612722
C	-4.080015	-0.103456	5.128513

H	-2.234541	0.258861	4.082631
C	-6.043725	-0.374870	3.753409
H	-5.720633	-0.272105	1.627884
C	-5.449313	-0.333522	5.015572
H	-3.611940	-0.074758	6.108302
H	-7.110411	-0.556180	3.657394
H	-6.051939	-0.485057	5.906264
C	-1.181599	0.020812	1.718585
C	-0.536002	1.113426	2.308981
C	-0.490619	-1.176854	1.537435
C	0.790750	0.994802	2.714954
H	-1.064949	2.052955	2.439939
C	0.838626	-1.292838	1.937082
H	-0.994954	-2.007538	1.061739
C	1.478918	-0.206233	2.528065
H	1.291393	1.842982	3.173526
H	1.360525	-2.228217	1.763968
H	2.517271	-0.288279	2.836312
C	-2.010875	-5.453264	-2.894684
H	-2.204660	-4.416847	-3.192933
H	-2.284111	-6.095183	-3.744008
H	-2.712874	-5.686121	-2.084330
C	-5.974197	0.288245	-1.122762
H	-6.472266	0.887823	-1.900442
H	-6.718873	-0.432226	-0.763318
H	-5.753742	0.976322	-0.298086
C	-6.170823	-3.180106	-1.091560
H	-6.221373	-2.724591	-2.083489
H	-6.540144	-4.210589	-1.178374
H	-6.855468	-2.640736	-0.429859
C	-1.023896	-4.312962	3.115840
C	-2.038308	-3.308807	3.665806
C	-3.428798	-3.505351	3.068406
H	-1.221766	-5.315422	3.521792
H	-0.002719	-4.048510	3.403874
H	-2.087007	-3.378701	4.757496
H	-1.696523	-2.296586	3.431372
H	-3.872344	-4.432717	3.461410
H	-4.090304	-2.688940	3.372035
H	0.580672	-0.081172	-1.703479
C	-0.614190	-0.400591	-3.481634
C	0.367537	-1.409029	-4.091885
H	0.109967	-2.437663	-3.827673
H	0.342599	-1.325125	-5.183303
H	1.393470	-1.227729	-3.756573
C	-0.274883	0.998202	-4.005750
H	-0.975447	1.752284	-3.634749
H	0.741600	1.298331	-3.726051
H	-0.337491	1.007027	-5.098836
C	-2.042104	-0.760483	-3.894172
H	-2.104809	-0.816832	-4.986333
H	-2.346228	-1.721188	-3.474095
H	-2.755141	-0.009556	-3.549452

2. Vibrational Circular Dichroism (VCD) spectroscopy studies.

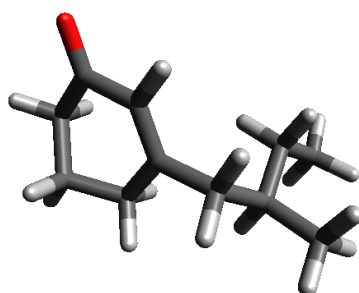
IR and VCD spectra of **P1**, **P5,6** and **P7** enantiomers were recorded on a Jasco FSV-6000 spectrometer in CD₂Cl₂ in a 200 microns cell and at respective concentrations 0.36 M, 0.41 M and 0.33 M. In the case of **P1**, the half-sum of the two enantiomers has been used as the baseline.

Table S2. Experimental specific rotation values of (+)- and (-)-P1, (+)-P5 and (-)-P6, of (+)- and (-)-P7.

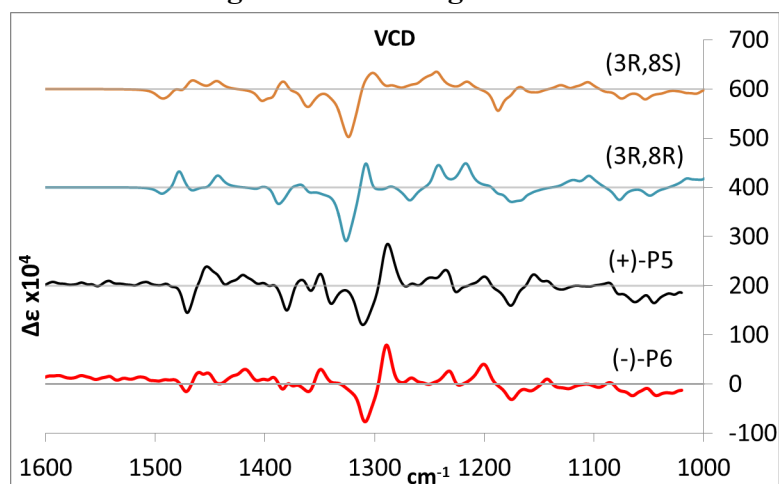
	(+)-P1	(-)-P1	(+)-P5	(-)-P6	(+)-P7	(-)-P7
ee^[a] or stereoisomer ratio	98%	98%	(3 <i>R</i> ,2' <i>S</i>)/ (3 <i>R</i> ,2' <i>R</i>)/ (3 <i>S</i> ,2' <i>S</i>) = 96.7/2.2/1.1	(3 <i>R</i> ,2' <i>R</i>)/ (3 <i>R</i> ,2' <i>S</i>)/ (3 <i>S</i> ,2' <i>R</i>) = 94.4/4.6/0.9	(3 <i>S</i> ,2' <i>S</i>)/ (3 <i>R</i> ,2' <i>S</i>)/ (3 <i>S</i> ,2' <i>R</i>) = 86.5/10.2/3.3	(3 <i>R</i> ,2' <i>R</i>)/ (3 <i>R</i> ,2' <i>S</i>)/ (3 <i>S</i> ,2' <i>R</i>) = 90.5/8.2/1.3
Conc. (in g/100 mL)^[b]	0.019	0.016	0.02	0.0017	0.016	0.015
[α]_D²³^[c,d]	+17.6	-16.6	+5.8	-12.3	+2.05	-3.9
[α]₅₇₈²³^[c]	+18.3	-17.8	+7.1	-13.2	+2.4	-3.95
[α]₅₄₆²³^[c]	+21.6	-20.8	+3.2	-15.7	+3.2	-5.35
[α]₄₃₆²³^[c]	+48.4	-46.4	-15.7	-33.4	+11.5	-18.3

^[a] Determined by GC. ^[b] In CH₂Cl₂. ^[c] In deg/(dm g/cm³). ^[d] Errors between 5-10%.

Figure S1. The lowest energy conformer of *R*-(-)-P1

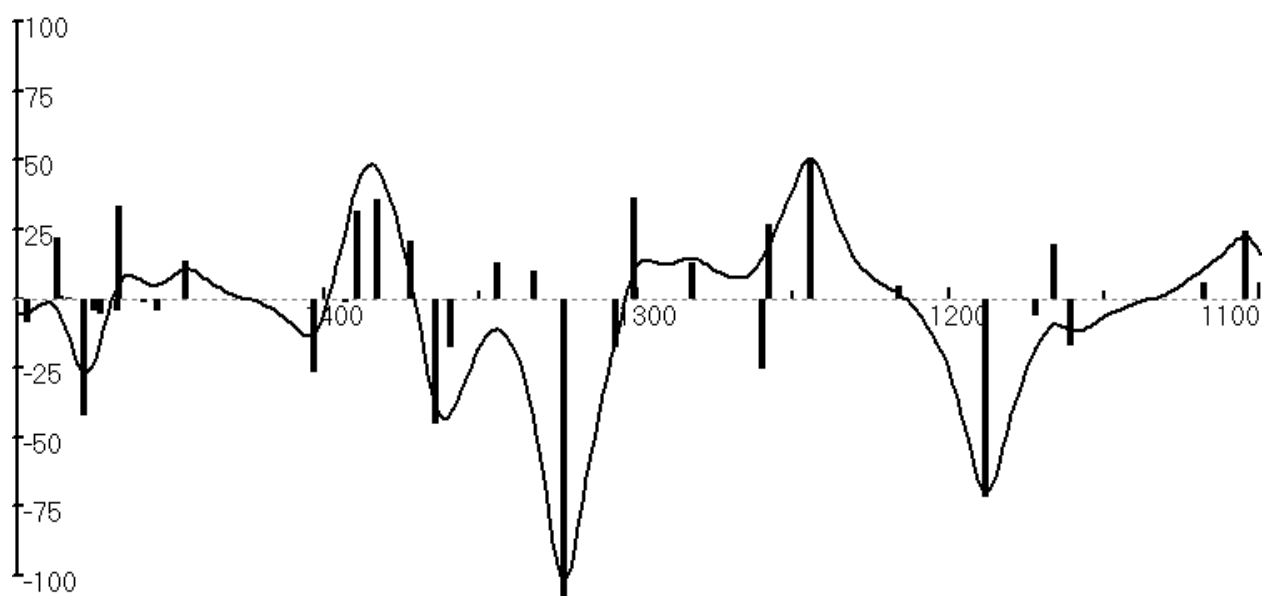


Vibrational assignments for bisignate VCD features at 1300 cm⁻¹



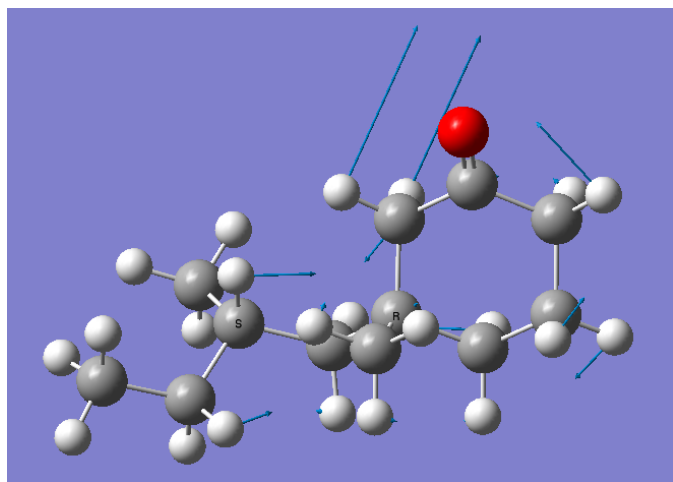
(*R,S*) Configuration

For (*R,S*) configuration, the major conformer is #4 with ~15% population (Gibbs Energy). The predicted spectrum for this conformer is given below.

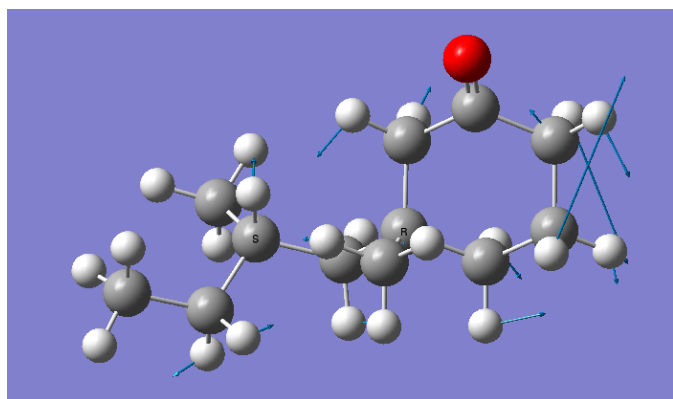


The non-conservative couplet at 1300 cm⁻¹ in calculations for conformer #4 comes from 1301 and 1323 cm⁻¹ bands. These two bands are from ring methylene bending vibrations (see pictures below):

1301 cm^{-1} vibration ; $R_+ = 20.23$

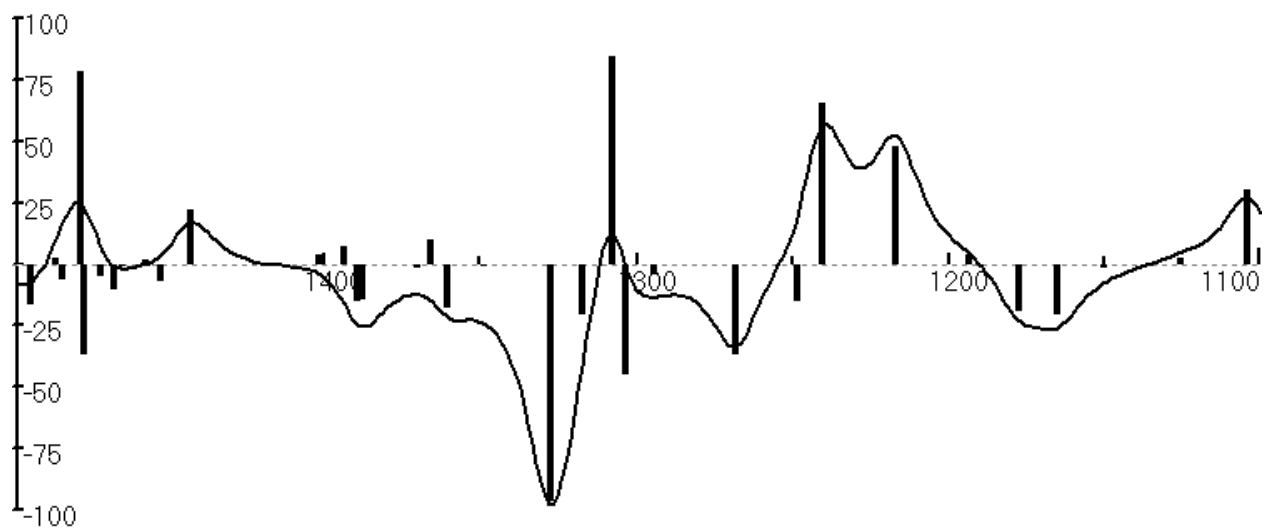


1323 cm^{-1} vibration ; $R_- = -59.6$



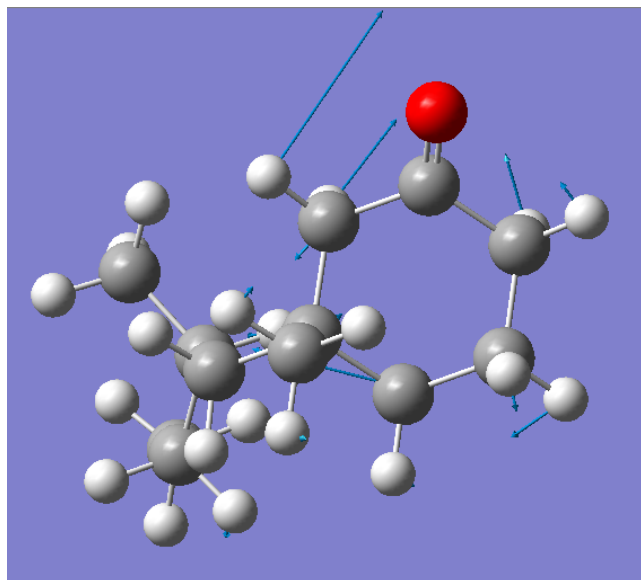
(*R,R*) Configuration

For (*R,R*) configuration, the major conformer is #17 with ~36% population. The predicted spectrum for this conformer is given below.



The non-conservative couplet for this conformer comes from 1307 and 1327 cm^{-1} bands. These two bands are from ring methylene bending vibrations (see pictures below):

1307 cm^{-1} vibration ; $R_+ = 46.8$



1327 cm^{-1} vibration ; R. = -52.6

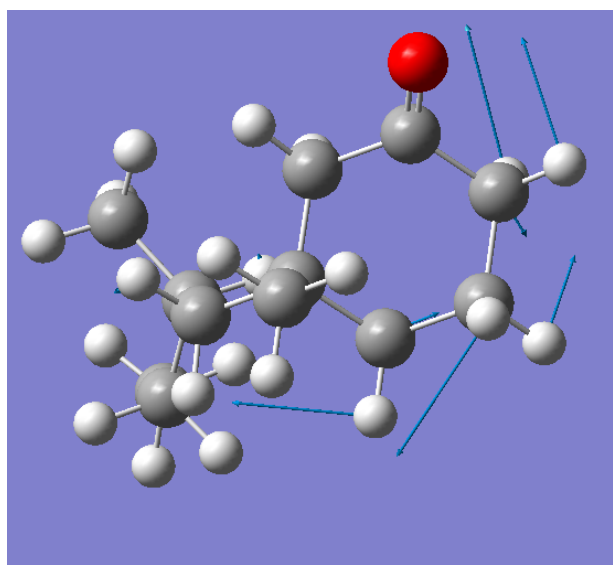
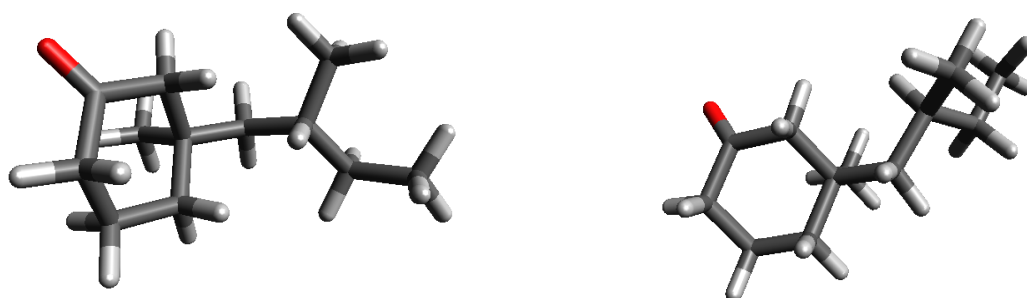
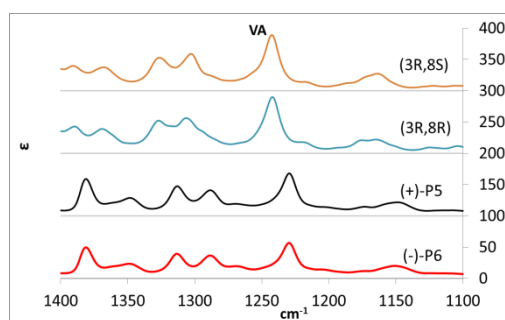
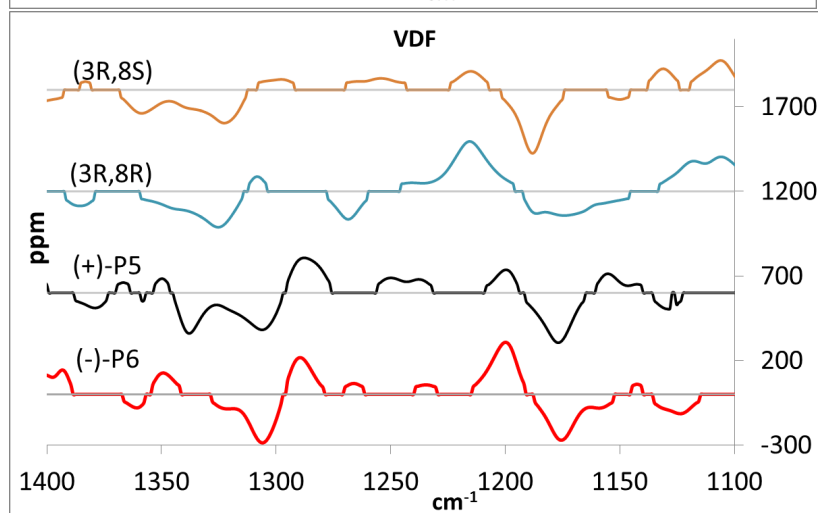
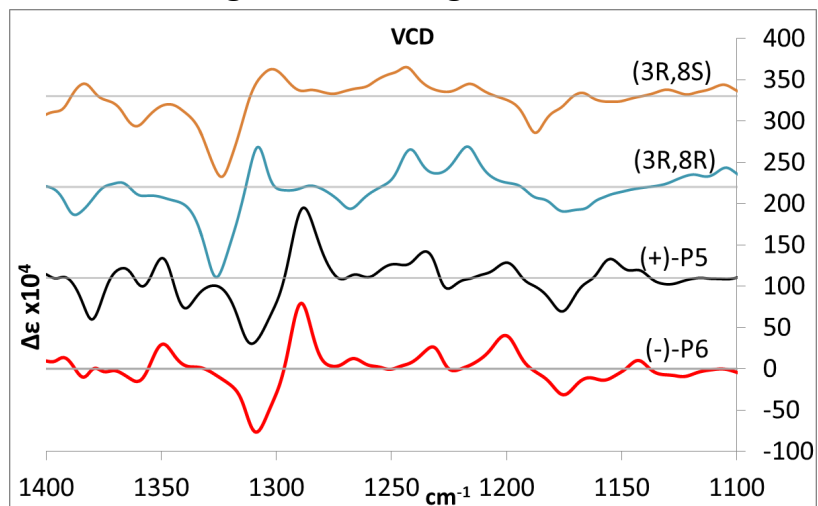


Figure S2. The lowest energy conformers in the (3*R*,2'*R*) configuration (left) and the (3*R*,2'*S*) configuration (right).

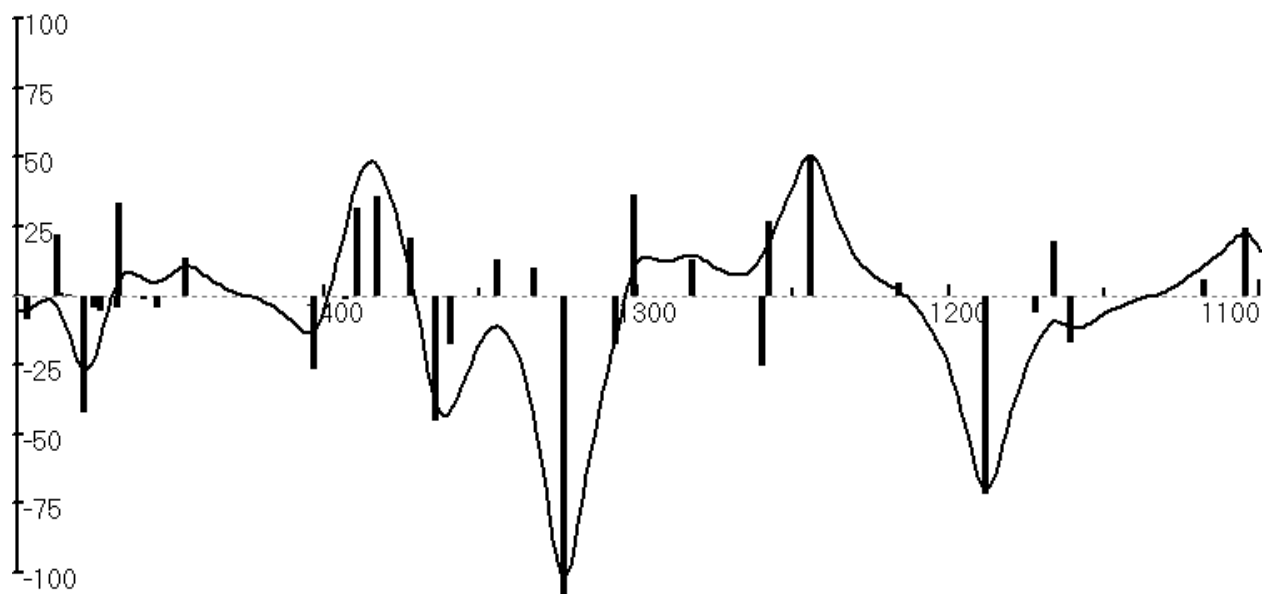


Vibrational assignments for bisignate VCD at 1200 cm⁻¹



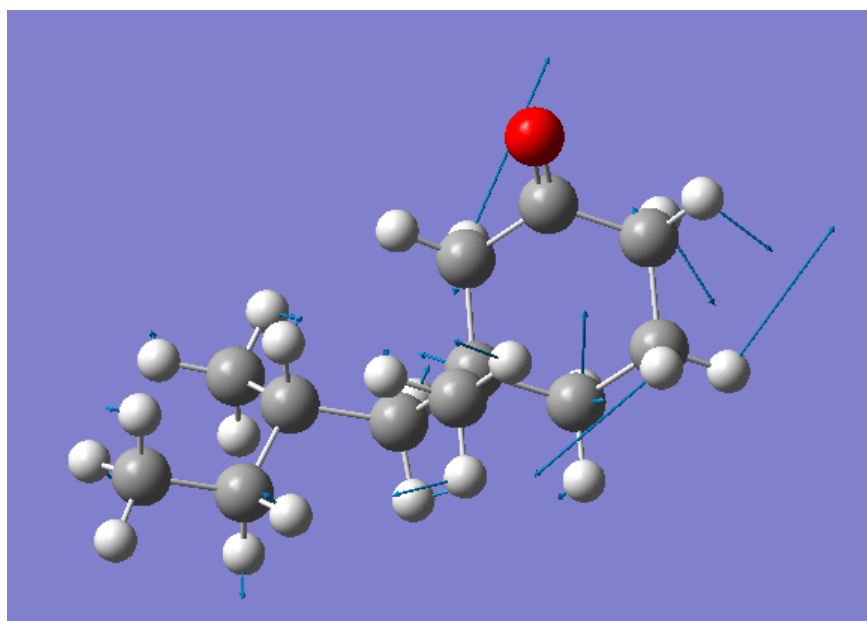
For (*R,S*) configuration:

*Major conformer #4 ~15% population (Gibbs Energy)

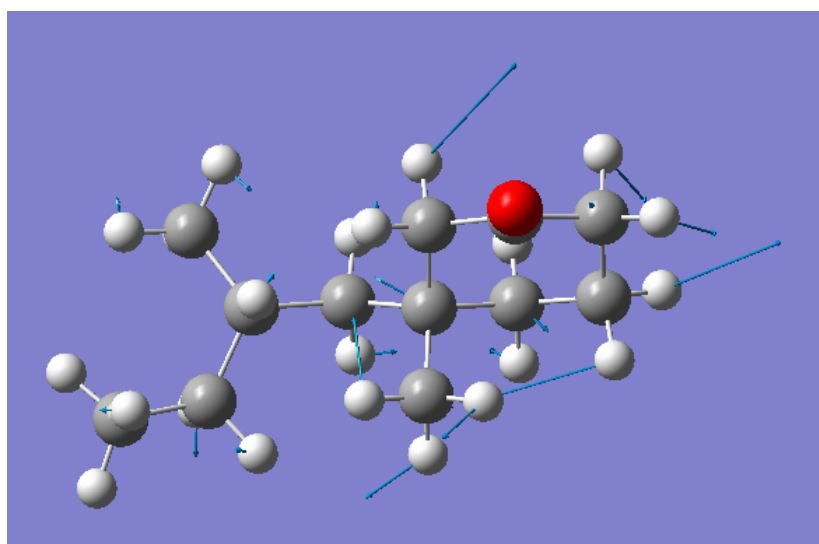


Couplet at $\sim 1220\text{ cm}^{-1}$ in calculations

1188 cm^{-1} vibration : R. = -43.53 ; Dip. Str= 12.0555

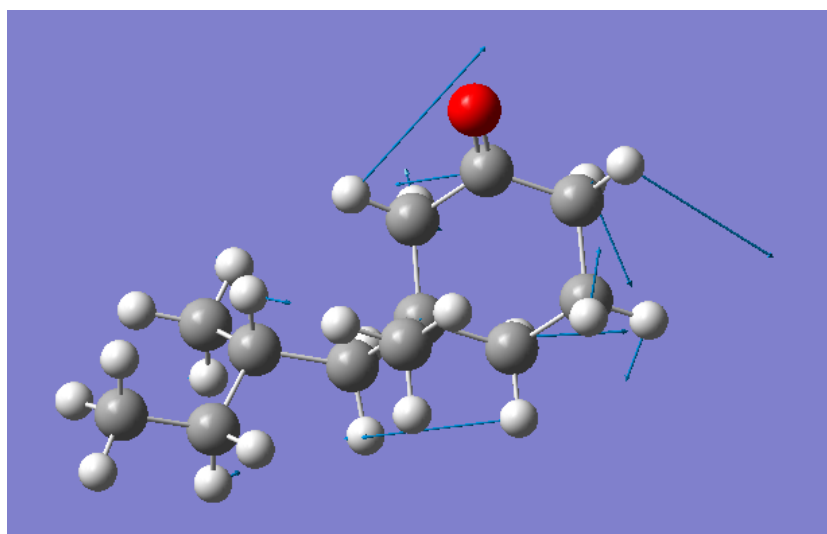


View 1

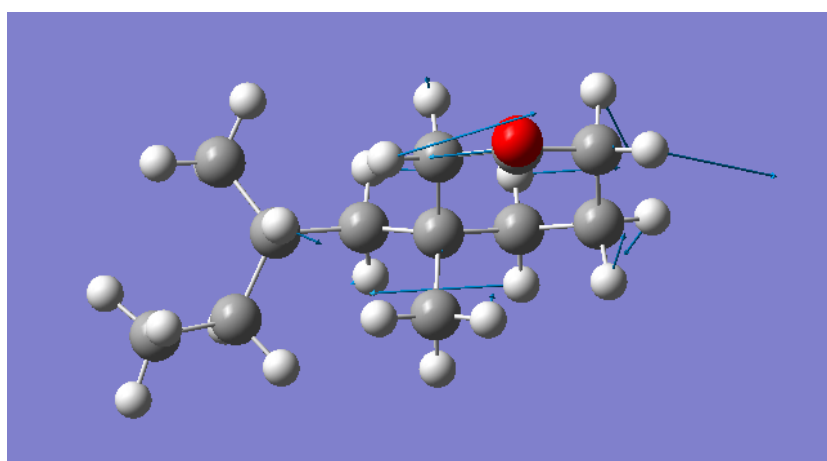


View along C=O bond

1244 cm^{-1} vibration ; $R_{\text{+}} = 29.55$; Dip. Str= 120.9057



View 1

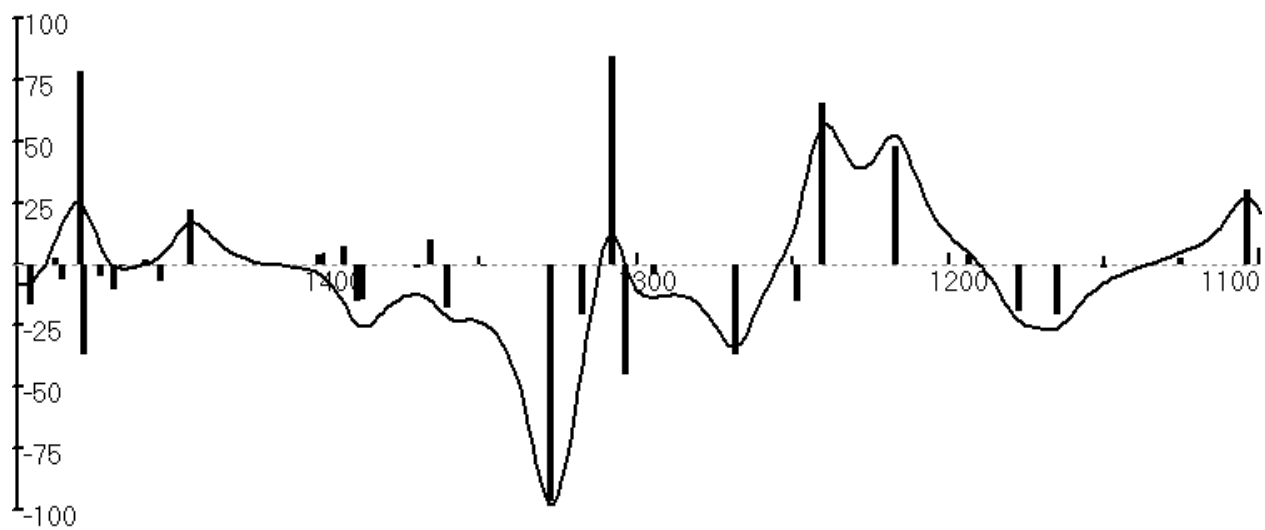


View along C=O bond

Note large Carbonyl carbon motion.

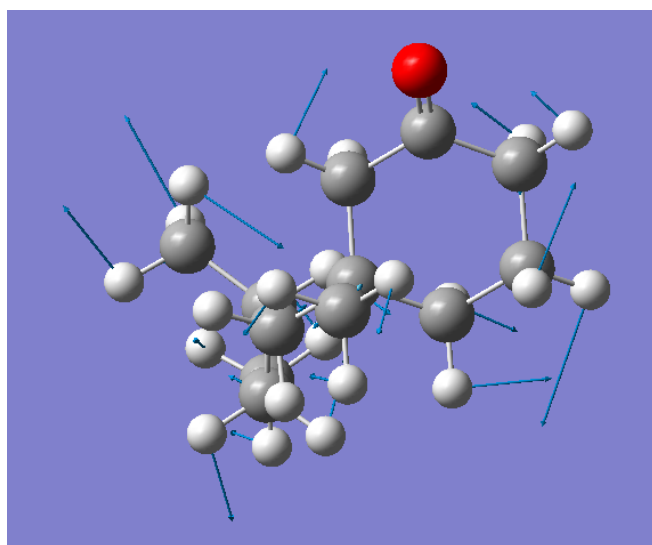
For (*R,R*) configuration:

*Major conformer #17 ~36%

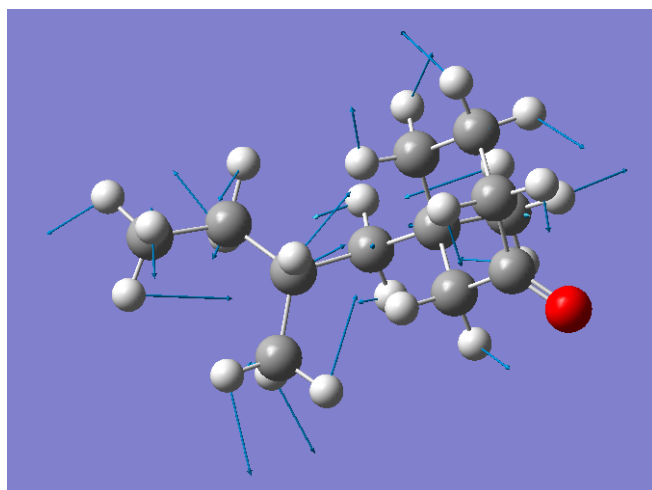


No Conservative Couplet!!!

1165 cm^{-1} vibration ; R- =-13.01 ; Dip. Str=4.0740



View1



View 3

3. References.

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Preparation of dienones, ACA, Cyclisation studies on ACA adducts and X-ray crystallography: Experimental procedures and data.

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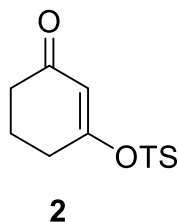
1. General

All the reactions were carried out under inert atmosphere (argon). Dichloromethane (DCM) was dried over calcium hydride overnight then distilled. Diethyl ether and THF were distilled over sodium/benzophenone. Et₂Zn (1 M in hexanes), Et₃Al (1 M in hexanes), Me₃Al (2 M in hexanes) and MeLi (1.6 M in Et₂O) were purchased from Aldrich and used without further purification. MeMgBr and EtMgBr (3 M in Et₂O) were purchased from Aldrich and when required diluted by 3 to obtain 1 M solutions in Et₂O. All commercial chemicals were used as received unless otherwise noted. ¹H and ¹³C NMR spectra were recorded on a Bruker ARX400 (400 MHz; 100 MHz), Bruker AV300 (300 MHz; 75 MHz), AV400 (400 MHz; 100 MHz) instruments. ¹H and ¹³C chemical shifts are reported in parts per million with the solvent resonance as the internal standard (CDCl₃, ¹H: δ 7.26 ppm, ¹³C: δ 77.16 ppm). Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quadruplet, quint = quintuplet, sept = septuplet, m = multiplet, br = broad. High-resolution mass spectroscopy (HMRS) analyses were performed either at the SCMB Mass Spectrometry Facility (University of Queensland) on a Bruker micrOTOF-Q or at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1, on a Waters Q-TOF 2, a Bruker Maxis 4G or an Agilent LCMS 6510. Melting points were measured on a Stuart Melting Point Apparatus SMP3 or a Digimelt MPA161 SRS apparatus and are uncorrected. Optical rotations were recorded on a Perkin Elmer 341 polarimeter. Enantiomeric excess (ee) was measured using gas chromatography (capillary column - Chiraldex Beta-dex, 30 m x 0.25 mm id, 0.25 μm or G-TA, 30 m x 0.25 mm id, 0.12 μm or G-BP column, 30 m x 0.25 mm id, 0.12 μm) or by HPLC (Chiral Technology OD-H column 250 x 4.6 mm, 5 μm).

The dienyl aryl ketones **S1** (R¹ = Me)ⁱ and **S2** (R² = Bu)ⁱⁱ were synthesized according to literature procedure. 4-Chloro-but-1-yn was prepared according to a reported procedure.ⁱⁱⁱ

2. Preparation and experimental data of dienones **S3** and **S4**

3-Oxocyclohex-1-en-1-yl 4-methylbenzenesulfonate **2**

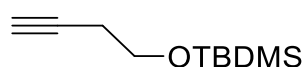


Intermediate **2**, 3-oxocyclohex-1-en-1-yl 4-methylbenzenesulfonate, was obtained using a modified procedure of Fu.^{iv} A flame dried round bottomed flask under an argon atmosphere was charged with 1,3-cyclohexanedione (2.00 g, 17.8 mmol) and anhydrous dichloromethane (85 mL) was added followed by triethylamine (3.5 mL, 25.1 mmol). The solution was cooled to 0 °C and *p*-toluenesulfonyl chloride (3.39 g, 17.8 mmol) was added. The reaction was stirred for 1 h and then allowed to return to ambient temperature for a further 3 h. The

resulting solution was concentrated under reduced pressure. The residue was dissolved in a DCM/AcOEt (9/1) mixture (50 mL) and filtered through a silica pad. The silica was rinsed with another 50 mL of the same DCM/AcOEt mixture and the filtrate was concentrated under reduced pressure to afford compound **2** (4.35 g, 92% yield) as a light yellow crystalline solid. Spectra were consistent with those previously described.^{iv}

¹H NMR (400 MHz, CDCl₃): δ 7.82 (br d, *J*=8.4 Hz, 2H), 7.38 (br d, *J*= 8.4 Hz, 2H), 5.79 (t, *J*= 1.2 Hz, 1H), 2.50 (td, *J*= 1.3, 6.3 Hz, 2H), 2.47 (s, 3H), 2.35-2.31 (m, 2H), 1.99 (quint, *J*= 6.5 Hz, 2H).

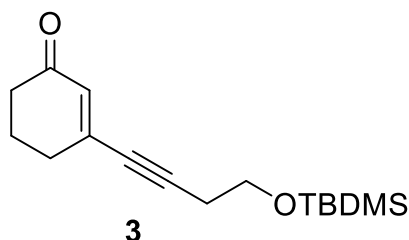
1-*t*-Butyldimethylsilyloxybut-3-yne



1-*t*-Butyldimethylsilyloxybut-3-yne was obtained using a modified procedure.^v A round bottomed flask was charged with 3-butyne-1-ol (1.01 g, 14.4 mmol) and dissolved in CH₂Cl₂ (50 mL). To this solution, imidazole (2.46 g, 36.1 mmol) was added and stirred until fully dissolved. The resulting solution was cooled to 0°C and *t*-butyldimethylsilyl chloride (2.13 g, 14.1 mmol) was added while stirring. The reaction was stirred for 1 h, then allowed to return to ambient temperature and stirred for a further 2 h. Upon completion the reaction was quenched by the addition of sat. NaHCO₃ solution (40 mL), transferred to a separatory funnel rinsing with dichloromethane (2 x 100 mL), washed with sat. NaHCO₃ (2 x 100 mL) and brine (2 x 100 mL), dried over MgSO₄, filtered and concentrated under reduced pressure to give 2.28 g of a colorless liquid. The crude material was carried forward without further purification. Spectra were consistent with those previously reported.^{vi}

¹H NMR (400 MHz CDCl₃): δ 3.74 (t, *J*= 7.1 Hz, 2H), 2.40 (td, *J*= 7.2, 2.6 Hz, 2H), 1.96 (t, *J*= 2.6 Hz, 1H), 0.90 (s, 9H), 0.07 (s, 6H).

3-(4-((*t*-Butyldimethylsilyl)oxy)but-1-yn-1-yl)cyclohex-2-en-1-one **3**



Tosylate **2** (491 mg, 1.84 mmol) was dissolved in anhydrous THF (3 mL) in a flame dried Schlenk tube and to this solution was added DIPEA (3.3 mL, 18.9 mmol), CuI (37 mg, 0.19 mmol) and PdCl₂(PPh₃)₂ (131 mg, 0.19 mmol). The resulting suspension was then degassed

for 10 minutes by argon bubbling at room temperature. During this time, a solution of 1-*t*-butyldimethylsilyloxybut-3-yne (517 mg, 2.8 mmol) in anhydrous THF (1.5 mL) was also degassed by three vacuum/argon cycles. The solution of alkyne was added dropwise to the suspension and the reaction was stirred at room temperature for 16 h. The resulting brown solution was diluted with AcOEt (20 mL), washed with sat. NH₄Cl (2 x 20 mL), brine (2 x 20 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography (pentane/AcOEt, 1/0 to 9/1) to afford compound **3** as a yellow oil (479 mg, 93% yield).

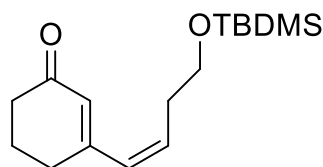
¹H NMR (400 MHz, CDCl₃): δ 6.14 (t, *J* = 1.7 Hz, 1H), 3.77 (t, *J* = 6.8 Hz, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.43-2.37 (m, 4H), 2.04-1.97 (m, 2H), 0.90 (s, 9H), 0.08 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 199.1, 144.4, 132.3, 99.4, 81.4, 61.5, 37.4, 30.9, 26.0, 24.4, 22.7, 18.5, -5.1.

LRMS (ESI): *m/z* 279.1 [M+H]⁺ 301.1 [M+Na]⁺

HRMS (ESI): *m/z* calcd for C₁₆H₂₆NaO₂Si : 301.1594 [M+Na]⁺; found 301.1591 (1 ppm)

(*Z*)-3-(4-((*t*-Butyldimethylsilyloxy)but-1-en-1-yl)cyclohex-2-en-1-one (S4)



S4

Cyclohexenyne **3** (702 mg, 2.5 mmol) was dissolved in anhydrous MeOH (6.5 mL) and placed in round bottomed flask under argon. After degassing the solution by three vacuum/argon cycles, Lindlar catalyst (815 mg, 115% w/w) was added and the atmosphere was switched to H_{2(g)} (3 vacuum/H₂ cycles followed by a 10 min H₂ bubbling). The suspension was then stirred at room temperature for 1.5 h. Lindlar catalyst was removed by filtration on a Celite® pad and the filtrate was concentrated under reduced pressure. The crude product was then purified by silica gel chromatography (Pentane/AcOEt, 1/0 to 95/5) to afford compound **S4** as a yellow oil (413 mg, 58% yield).

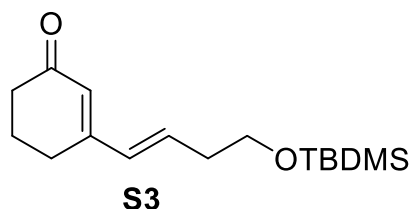
¹H NMR (400 MHz, CDCl₃): δ 6.04-5.99 (m, 1H), 5.97 (br s, 1H), 5.80 (dt, *J* = 12.0, 7.4 Hz, 1H), 3.68 (t, *J* = 6.3 Hz, 2H), 2.54-2.48 (m, 2H), 2.48-2.43 (m, 2H), 2.41-2.37 (m, 2H), 2.06-1.98 (m, 2H), 0.88 (s, 9H), 0.05 (s, 6H).

¹³C NMR (75 MHz, CDCl₃): δ 200.1, 158.4, 135.0, 130.5, 127.8, 62.6, 37.4, 33.3, 30.1, 26.0, 23.0, 18.4, -5.2.

LRMS (ESI): m/z 280.9 [M+H]⁺ 302.7 [M+Na]⁺ 318.4 [M+K]⁺

HRMS (ESI): m/z calcd for C₁₆H₂₈NaO₂Si : 303.1751 [M+Na]⁺; found 303.1748 (0.8 ppm)

(E)-3-(4-((*t*-Butyldimethylsilyl)oxy)but-1-en-1-yl)cyclohex-2-en-1-one (S3)



The (*Z*)-dienone **S4** (248 mg, 0.885 mmol) was dissolved in anhydrous DCM (2 mL) and the solution was placed in a round bottomed flask. I₂ (8.3 mg, 0.032 mmol) was dissolved in anhydrous DCM (20 mL) and 2 mL of the solution was added and stirred under a light source (60 W) for 2 h. The solution was washed with 0.1M Na₂S₂O_{3(aq)} (5 mL), water (2 x 30 mL) and brine (2 x 20 mL) before being dried over MgSO₄, filtered and concentrated under reduced pressure. The resulting crude was purified by silica gel chromatography (pentane/AcOEt, 9/1) to afford the desired compound **S3** (161 mg, 65% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 6.29-6.18 (m, 2H), 5.88 (t, *J* = 1.3 Hz, 1H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.48-2.38 (m, 6H), 2.06-1.99 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H).

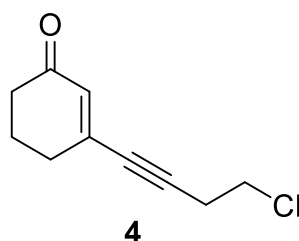
¹³C NMR (100 MHz, CDCl₃): δ 200.6, 157.4, 135.6, 133.2, 126.9, 62.4, 37.9, 36.9, 26.0, 25.1, 22.5, 18.5, -5.1.

LRMS (ESI): m/z 281.0 [M+H]⁺ 302.8 [M+Na]⁺ 318.5 [M+K]⁺

HRMS (ESI): m/z calcd for C₁₆H₂₉O₂Si : 281.1931 [M+H]⁺; found 281.1925 (2.1 ppm)

3. Preparation and experimental data of dienones S5

3-(4-Chlorobut-1-yn-1-yl)cyclohex-2-en-1-one (4)



Substrate **2** (1.49 g, 5.6 mmol) was dissolved in anhydrous THF (8.5 mL) in a flame dried Schlenk tube and to this solution was added DIPEA (9.7 mL, 55.6 mmol), CuI (106 mg, 0.56 mmol), and PdCl₂(PPh₃)₂ (390 mg, 0.56 mmol). The resulting suspension was then degassed

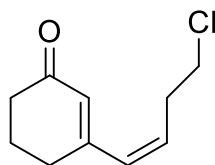
for 10 minutes by argon bubbling at ambient temperature. During this time, a solution of 4-chloro-1-butyne (1.0 mL, 11.1 mmol) in anhydrous THF (4.5 mL) was also degassed by three vacuum/argon cycles. The solution of alkyne was added dropwise to the suspension and the reaction was stirred at room temperature for 16 h. The resulting brown solution was diluted with AcOEt (80 mL), washed with sat. NH₄Cl (2 x 40 mL), brine (2 x 40 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was then dissolved in Et₂O to precipitate out the tosylated side product. After filtration and concentration of the filtrate, the product was purified by silica gel chromatography (pentane/Et₂O, 8/2 to 6/4) to afford compound **3** as a yellow oil (724 mg, 71% yield).

¹H NMR (400 MHz, CDCl₃): δ 6.17 (t, *J* = 1.7 Hz, 1H), 3.63 (t, *J* = 7.0 Hz, 2H), 2.88 (t, *J* = 7.0 Hz, 2H), 2.45-2.38 (m, 4H), 2.06-1.98 (m, 2H).

¹³C NMR: (100 MHz, CDCl₃): δ 198.8, 143.5, 132.7, 96.9, 82.0, 41.7, 37.4, 30.6, 24.2, 22.6.

HRMS (ESI): *m/z* calcd for C₁₀H₁₁ClONa: 205.03961 [M+Na]⁺; found 205.0397 (0 ppm).

(*Z*)-3-(4-Chlorobut-1-en-1-yl)cyclohex-2-en-1-one (**5**)



5

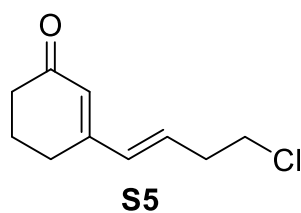
Alkyne **4** (911 mg, 5.0 mmol) was dissolved in anhydrous MeOH (11 mL) and placed in round bottomed flask under argon. After degassing the solution by three vacuum/argon cycles, Lindlar catalyst (1.05 g, 115% w/w) was added and the atmosphere was switched to H_{2(g)} (3 purges). The suspension was then stirred for 6 h. Lindlar catalyst was removed by filtration on a Celite® pad and the filtrate was concentrated under reduced pressure to afford a 89/7/4 mixture of compound **5**, over-reduced compound **5'** and (*E*)-isomer **S5** (917 mg, 99% yield) as a yellow oil. Compound **5'** was separated at the 1,6-ACA stage.

¹H NMR (400 MHz, CDCl₃): δ 6.09 (br d, *J* = ~12 Hz, 1H), 5.93 (br s, 1H), 5.77 (dt, *J* = 12.0, 7.2 Hz, 1H), 3.58 (t, *J* = 6.5 Hz, 2H), 2.76 (qd, *J* = 6.6, 1.8 Hz, 2H), 2.45-2.37 (m, 4H), 2.08-2.00 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 199.9, 157.8, 132.8, 131.6, 128.0, 43.9, 37.4, 32.5, 30.0, 22.9.

HRMS (ESI): *m/z* calcd for C₁₀H₁₃ClONa: 207.05526 [M+Na]⁺; found 207.0556 (2 ppm).

(*Z*)-3-(4-Chlorobut-1-en-1-yl)cyclohex-2-en-1-one (S5)



The 93/7 mixture of compounds **5**+**S5** and **5'** (917 mg, 4.64 mmol of **5**+**S5**) was dissolved in anhydrous DCM (10 mL) and the solution was placed in a round bottomed flask. I₂ (4 mg, 0.016 mmol) was added and the solution was stirred under a light source (60 W) for 6 h. The solution was diluted with DCM (30 mL), washed with 0.1M Na₂S₂O_{3(aq)} (15 mL), water (15 mL) and brine (15 mL) before being dried over MgSO₄, filtered and concentrated under reduced pressure. The resulting crude was purified by silica gel chromatography (pentane/Et₂O, 7/3 to 1/1) to afford a 93/7 mixture of compound **S5** and compound **5'** (840 mg, 92% yield of **S5**) as a light yellow crystalline solid.

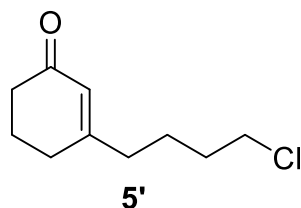
MP = 28°C

¹H NMR (400 MHz, CDCl₃): δ 6.29 (d, *J* = 15.9 Hz, 1H), 6.18 (dt, *J* = 15.6, 6.7 Hz, 1H), 5.91 (br s, 1H), 3.61 (t, *J* = 6.6 Hz, 2H), 2.67 (qd, *J* = 6.6, ~ 0.7 Hz, 2H), 2.47 (br t, *J* ~ 6.0 Hz, 2H), 2.43-2.38 (m, 2H), 2.08-2.00 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 200.4, 156.6, 134.3, 133.5, 127.7, 43.5, 37.8, 36.2, 25.1, 22.4.

HRMS (ESI): *m/z* calcd for C₁₀H₁₄OCl: 185.0728 [M+H]⁺; found 185.0727 (0.5 ppm).

3-(Chlorobutyl)cyclohex-2-en-1-one (**5'**)



¹H NMR (400 MHz, CDCl₃): δ 5.87 (quint, *J* = 1.3 Hz, 1H), 3.55 (t, *J* = 6.3 Hz, 2H), 2.38-2.33 (m, 2H), 2.28 (t, *J* = 6.1 Hz, 2H), 2.24 (t, *J* = 7.6 Hz, 2H), 2.03-1.95 (m, 2H), 1.83-1.74 (m, 2H), 1.71-1.64 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 199.9, 165.6, 126.1, 44.7, 37.5, 37.3, 32.1, 29.7, 24.2, 22.8.

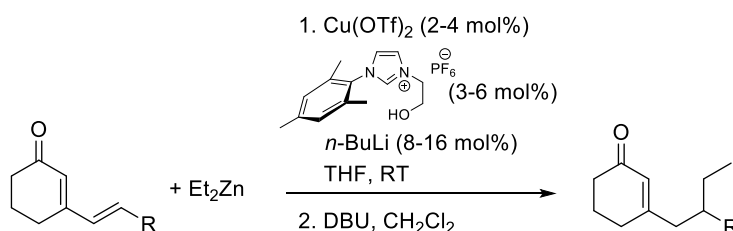
HRMS (ESI): *m/z* calcd for C₁₀H₁₅OClNa: 209.07091[M+Na]⁺; found 209.0711 (1 ppm)

4. General experimental procedure for 1,6-ACA on dienones S1-S5

General experimental procedure for Cu/DiPPAM catalyzed 1,6-ACA on dienones S1-S5

The 1,6-asymmetric conjugate addition was performed using a modified procedure of the one previously described.ⁱⁱ A flame dried Schlenk, under an argon atmosphere, was charged with DiPPAM ligand (21.3 mg, 0.05 mmol, 10 mol%), Cu(OTf)₂ (9.0 mg, 0.025 mmol, 5 mol%) and anhydrous THF (1 mL). The resulting mixture was stirred for 10 min. A 1 M solution of diethylzinc in hexanes (1.5 mL, 1.5 mmol, 3 equiv.) was added and the reaction mixture was stirred for 10 min. Finally, a solution of substrate (0.5 mmol, 1 equiv.) in 0.5 mL of THF was added. The reaction mixture was stirred for 16-40 h at the required temperature. The reaction was quenched by the addition of solid NH₄Cl (500 mg) and the mixture was stirred for 1h. Then, anhydrous CH₂Cl₂ (4 mL) and DBU (100 μL, 0.7 mmol, 1.4 equiv.) were added. The mixture was stirred for 5 h. The solution was filtered on a small pad of silica, washed with EtOAc, and concentrated under vacuo. The crude product was purified by flash chromatography on silica gel (pentane/Et₂O 85/15 for **P1** and **P2**, pentane/Et₂O 90/10 to 85/15 for **P3**, pentane/Et₂O 80/20 to 60/40 for **P4**). The enantiomeric excess was determined by GC or HPLC analysis of the purified compound.

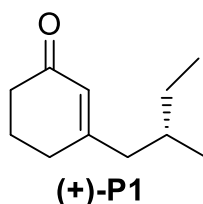
Preparation of racemic compounds



A flame-dried test tube was charged with Cu(OTf)₂ (4-8 mol%), and the ligand imidazolium^{vii} (6-12 mol%). The system was flushed with argon, and 1 mL of anhydrous THF was added. The solution was stirred for 10 min and *n*BuLi (1.6 M in hexanes, 16-32 mol%) was added and stirred again for 10 min. 0.5 mL of this solution was transferred to a flame-dried Schlenk tube (to weigh more accurately the small amounts of copper and ligand, a stock solution was prepared with twice the amount of catalyst). A 1 M solution of diethylzinc in hexanes (3-4 equiv.) was added dropwise and the reaction mixture was stirred 10 min at rt and 10 min at 0 °C. A solution of dienone (1 equiv.) in 0.3-0.5 mL of THF (for 0.5 mmol of substrate) was added to the reaction and the solution was stirred at room temperature until full conversion was attained. The reaction was quenched with NH₄Cl solid (500 mg/0.5 mmol substrate). The solution was stirred for 1 h and then 3-5 mL (for 0.5 mmol substrate) of anhydrous CH₂Cl₂ and DBU (1.4-1.9 equiv.) were added to the solution. The reaction was stirred until full conversion was reached and then filtered on a small pad of silica, washed with EtOAc, and concentrated under vacuo. The crude product was purified by flash chromatography on silica gel (pentane/Et₂O).

5. Experimental data for 1,6-adducts P1-P4

(S)-3-(2-Methylbutyl)cyclohex-2-enone (+)-P1



Known compound.¹

The reaction was performed with dienone **S1** (143 mg, 1.05 mmol) and L-DiPPAM for 16 h at 0 °C. The desired product was obtained as a colorless oil in 50% yield (82 mg).

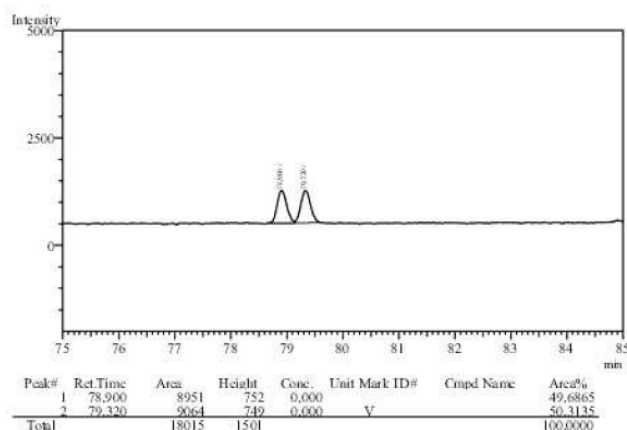
¹H NMR (400 MHz, CDCl₃): δ 5.86-5.84 (m, 1H), 2.38-2.33 (m, 2H), 2.29-2.20 (m, 3H), 2.01-1.94 (m, 3H), 1.70-1.57 (m, 1H), 1.41-1.29 (m, 1H), 1.23-1.11 (m, 1H), 0.91-0.84 (m, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 200.0, 165.9, 127.2, 45.8, 37.5, 32.8, 29.8, 29.6, 22.9, 19.2, 11.5.

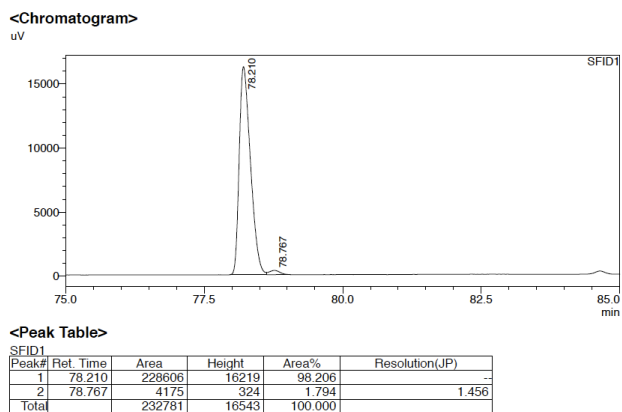
$[\alpha]_D^{20} = +18.2$ (*c* = 1, CHCl₃), ee = 96%. {Lit. $[\alpha]_D^{20} = +14.0$ (*c* = 1, CHCl₃)^{vii}, e.r. = 95:5}

Determination of ee: GC, Beta-dex column, helium (40 cm/sec), 100 °C-45 min-1 °C/min-150 °C-5 min-10 °C/min-170 °C-10 min, $R_{T1}(\text{major}) = 78.2$ min, $R_{T2}(\text{minor}) = 78.8$ min.

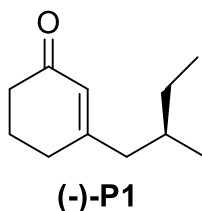
Racemic mixture:



Compound (+)-P1 (ee = 96%)



(R)-3-(2-Methylbutyl)cyclohex-2-enone (-)-P1



Known compound.ⁱ

The reaction was performed with dienone **S1** (204 mg, 1.5 mmol) and D-DiPPAM, for 16 h at 0 °C. The desired product was obtained as a colorless oil in 68% yield (170 mg).

¹H NMR (400 MHz, CDCl₃): δ 5.86-5.84 (m, 1H), 2.38-2.33 (m, 2H), 2.29-2.19 (m, 3H), 2.01-1.93 (m, 3H), 1.70-1.57 (m, 1H), 1.41-1.29 (m, 1H), 1.23-1.11 (m, 1H), 0.91-0.84 (m, 6H).

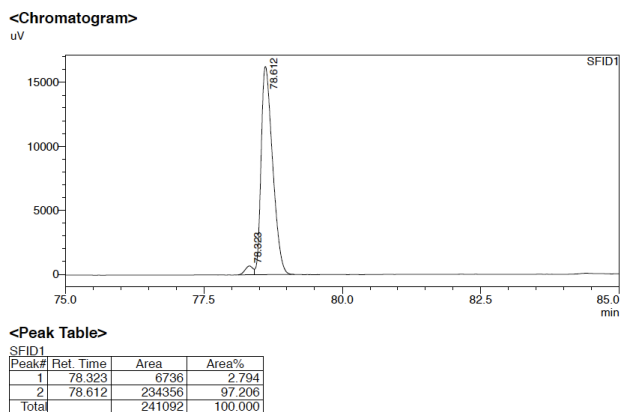
¹³C NMR (100 MHz, CDCl₃): δ 200.0, 165.9, 127.2, 45.8, 37.5, 32.8, 29.8, 29.6, 22.9, 19.2, 11.5.

HRMS (ESI): m/z calcd for C₁₁H₁₈ONa: 189.12499 [M+Na]⁺; found 189.1249 (0 ppm).

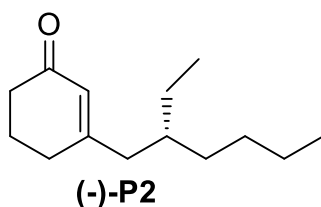
[α]_D²⁰ = - 18.6 (c = 1, CHCl₃); ee = -94% (with D-DiPPAM)

Determination of ee: GC, Beta-dex column, helium (40 cm/sec), 100 °C-45 min-1 °C/min-150 °C-5 min-10 °C/min-170 °C-10 min, R_{T1}(minor) = 78.3 min, R_{T2}(major) = 78.6 min.

Compound (-)-**P1** (94% ee)



(R)-3-(2-Ethylhexyl)cyclohex-2-enone (-)-P2



Known compound.ⁱⁱ

The reaction was performed with dienone **S2** (89 mg, 0.5 mmol) and L-DiPPAM, for 40 h at room temperature. The desired product was obtained as a slightly yellow oil in 56% yield (58 mg).

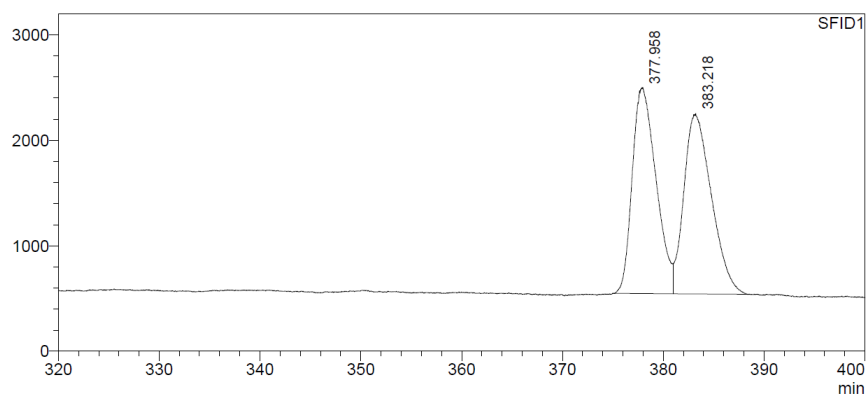
¹H NMR (400 MHz, CDCl₃): δ 5.88-5.86 (m, 1H), 2.39-2.33 (m, 2H), 2.26 (t, *J* = 6.4 Hz, 2H), 2.13 (d, *J* = 7.3 Hz, 2H), 1.98 (quint, *J* = 6.4 Hz, 2H), 1.58-1.49 (m, 1H), 1.33-1.19 (m, 8H), 0.91-0.83 (m, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 200.0, 166.4, 127.2, 43.1, 37.5, 37.2, 32.8, 29.9, 28.9, 26.0, 23.1, 22.9, 14.2, 10.8.

$[\alpha]_D^{20} = -2.0$ (*c* = 1, CHCl₃), ee = 98% {Lit. $[\alpha]_D^{20} = -3.3$ (*c* = 1, CHCl₃)⁷, e.r. = 95.5:4.5}

Enantiomeric excess was measured by chiral GC: Beta-dex column, helium (40 cm/sec), 100 °C-400 min-5 °C/min-170 °C-10 min, *Rt*_{1(minor)} = 378.3 min, *Rt*_{2(major)} = 381.6 min.

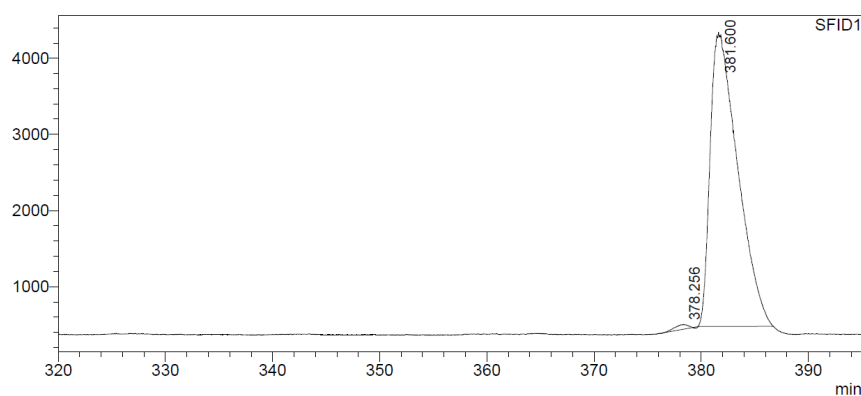
Racemic mixture:



<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	377.958	321439	1951	49.762			
2	383.218	324508	1706	50.238		V	
Total		645947	3656				

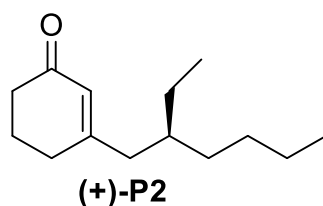
Compound (-)-P2 (98% ee)



<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	378.256	5496	65	0.790		M	
2	381.600	690673	3865	99.210		M	
Total		696169	3930				

(S)-3-(2-Ethylhexyl)cyclohex-2-enone (+)-P2



The reaction was performed following with dienone **S2** (178 mg, 1.0 mmol) and D-DiPPAM, for 40 h at room temperature. The desired product was obtained as a slightly yellow oil in 56% yield (117 mg).

¹H NMR (400 MHz, CDCl₃): δ 5.87-5.85 (m, 1H), 2.38-2.33 (m, 2H), 2.26 (t, *J* = 6.4 Hz, 2H), 2.13 (d, *J* = 7.3 Hz, 2H), 1.98 (quint, *J* = 6.4 Hz, 2H), 1.59-1.49 (m, 1H), 1.33-1.20 (m, 8H), 0.91-0.83 (m, 6H).

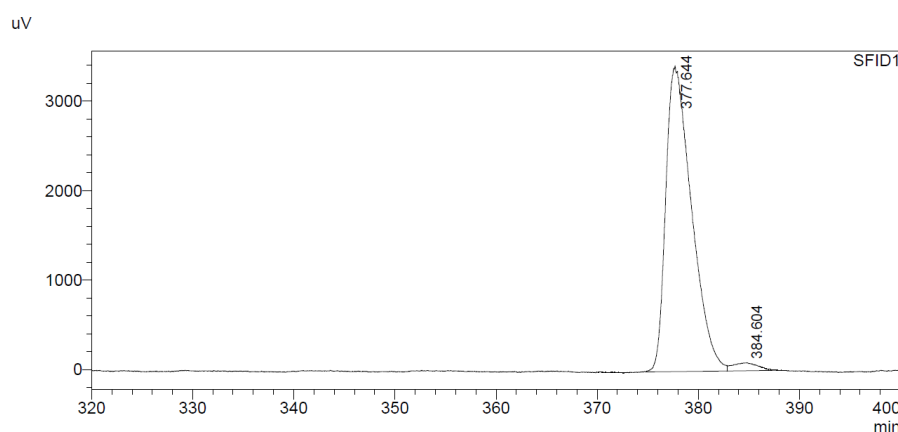
^{13}C NMR (100 MHz, CDCl_3): δ 200.0, 166.4, 127.2, 43.1, 37.5, 37.2, 32.8, 29.9, 28.9, 26.0, 23.1, 22.9, 14.2, 10.8.

HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{24}\text{ONa}$: 231.17194 $[\text{M}+\text{Na}]^+$; found 231.1721 (1 ppm).

$[\alpha]_{\text{D}}^{20} = +2.0$ ($c = 1$, CHCl_3), ee = 95%

Enantiomeric excess was measured by chiral GC: Beta-dex column, helium (40 cm/sec), 100 °C-400 min-5 °C/min-170 °C-10 min, $\text{Rt}_{1(\text{major})} = 377.7$ min, $\text{Rt}_{2(\text{minor})} = 384.6$ min.

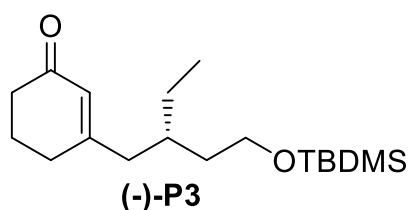
Compound (+)-P2 (95% ee)



<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	377.644	605004	3390	97.486			
2	384.604	15600	84	2.514		V	
Total		620604	3475				

(S)-3-(4-((*t*-Butyldimethylsilyloxy)-2-ethylbutyl)cyclohex-2-enone (-)-P3



The reaction was performed with (*E*)-dienone S3 (140 mg, 0.5 mmol) and L-DiPPAM, for 24 h at room temperature. The desired product was obtained as a slightly yellow oil in 42% yield (66 mg).

^1H NMR (400 MHz CDCl_3): δ 5.89-5.86 (m, 1H), 3.67-3.58 (m, 2H), 2.38-2.33 (m, 2H), 2.27 (t, $J = 6.2$ Hz, 2H), 2.23-2.11 (m, 2H), 1.98 (quint, $J = 6.4$ Hz, 2H), 1.74 (sept., $J = 6.7$ Hz, 1H), 1.53-1.38 (m, 2H), 1.36-1.24 (m, 2H), 0.90-0.85 (m, 3H), 0.88 (s, 9H), 0.04 (s, 6H).

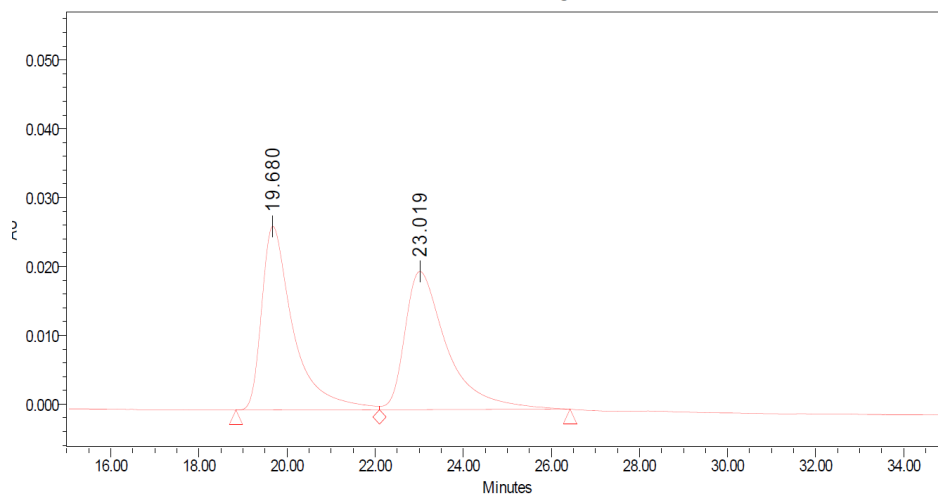
^{13}C NMR (100 MHz, CDCl_3): δ 199.9, 166.0, 127.4, 61.0, 43.1, 37.5, 36.2, 33.9, 29.7, 26.2, 26.1, 22.9, 18.4, 10.8, -5.2, -5.2.

$[\alpha]_{\text{D}}^{20} = -5.3$ ($c = 1$, CHCl_3), ee = 95%

HRMS (ESI): m/z calcd for $C_{18}H_{34}O_2SiNa$: 333.22203 $[M+Na]^+$; found 333.2220 (0 ppm).

The ee was determined by chiral HPLC: Chiralcel OD-H column, *n*-Hexane/*i*-PrOH 99.9/0.1, 1 mL/min, $R_{T1(\text{minor})} = 19.6$ min, $R_{T2(\text{major})} = 23.2$ min.

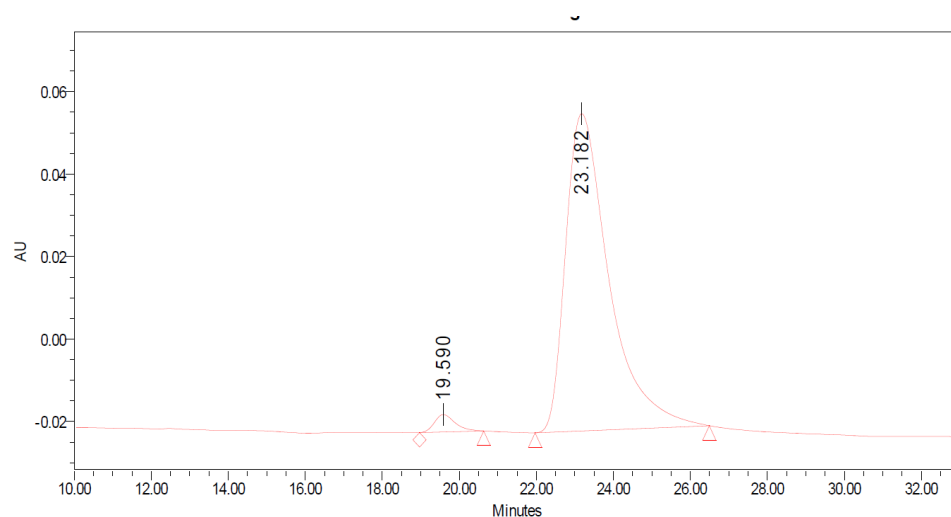
Racemic mixture:



Peak Results

Name	RT	Area	Height	% Area	% Height
1	19.680	1336495	26696	50.02	57.08
2	23.019	1335679	20076	49.98	42.92

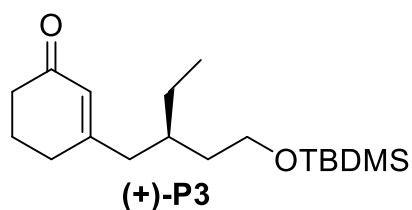
Chromatogram obtained starting from (*E*)-isomer (**S3**); (95% ee)



Peak Results

Name	RT	Area	Height	% Area	% Height
1	19.590	157995	4227	2.55	5.21
2	23.182	6039029	76920	97.45	94.79

(R)-3-(4-((*t*-Butyldimethylsilyl)oxy)-2-ethylbutyl)cyclohex-2-enone (+)-P3



The reaction was performed with (*Z*)-dienone **S4** (140 mg, 0.5 mmol) and L-DiPPAM, for 24 h at room temperature. The desired product was obtained as a slightly yellow oil in 31% yield (48 mg).

¹H NMR (400 MHz, CDCl₃): δ 5.88-5.86 (m, 1H), 3.68-3.58 (m, 2H), 2.38-2.33 (m, 2H), 2.27 (br t, *J* = 6.2 Hz, 2H), 2.23-2.11 (m, 2H), 1.98 (quint, *J* = 6.4 Hz, 2H), 1.74 (sept, *J* = 6.6 Hz, 1H), 1.53-1.38 (m, 2H), 1.36-1.24 (m, 2H), 0.90-0.84 (m, 3H), 0.88 (s, 9H), 0.04 (s, 6H).

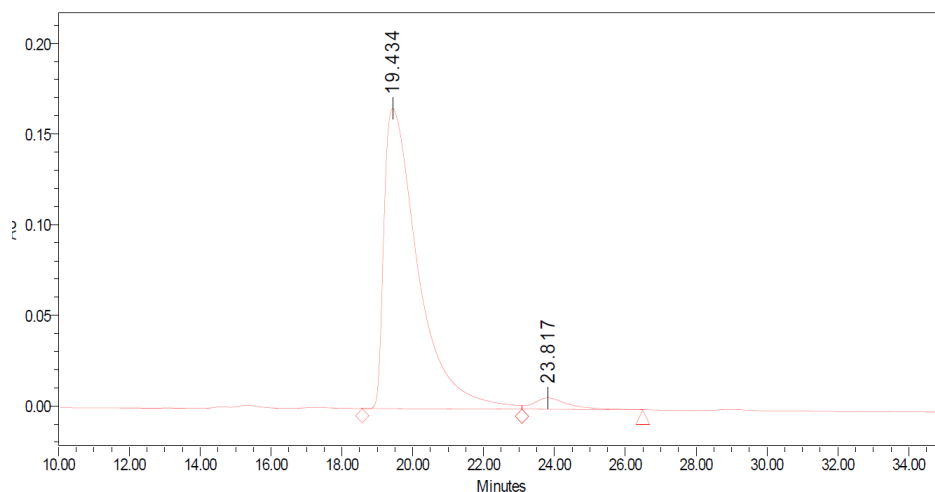
¹³C NMR (100 MHz, CDCl₃): δ 199.9, 166.0, 127.4, 61.0, 43.1, 37.5, 36.2, 33.9, 29.7, 26.2, 26.1, 22.9, 18.4, 10.8, -5.1, -5.2.

[α]_D²⁰ = + 5.5 (*c* = 1, CHCl₃), ee = 93%

HRMS (ESI): *m/z* calcd for C₁₈H₃₄O₂SiNa: 333.22203 [M+Na]⁺; found 333.2223 (1 ppm).

The ee was determined by chiral HPLC: Chiralcel OD-H column, *n*-Hexane/*i*-PrOH 99.9/0.1, 1 mL/min, R_{T1}(major) = 19.4 min, R_{T2}(minor) = 23.8 min.

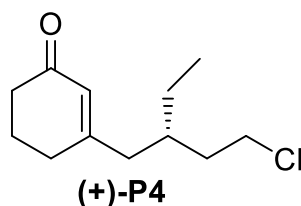
Chromatogram obtained starting from (*Z*)-isomer (**S4**); (93% ee).



Peak Results

Name	RT	Area	Height	% Area	% Height
1	19.434	11074368	166577	96.25	96.33
2	23.817	430949	6301	3.75	3.67

(S)-3-(4-Chloro-2-ethylbutyl)cyclohex-2-enone (+)-P4



The reaction was performed with a 93:7 mixture of dienone **S5** and compound **5'** (99 mg, 0.5 mmol of **S5**) and L-DiPPAM, for 40 h at 0 °C. The desired product was obtained in 58% of yield (62 mg) as a light yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 5.88 (br s, 1H), 3.61-3.51 (m, 2H), 2.39-2.35 (m, 2H), 2.31-2.26 (m, 2H), 2.22 (dd, *J* = 13.9, 7.2 Hz, 1H), 2.12 (dd, *J* = 13.7, 7.2 Hz, 1H), 2.00 (quint, *J* = 6.2 Hz, 2H), 1.90-1.80 (m, 1H), 1.80-1.64 (m, 2H), 1.41-1.28 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 199.7, 165.0, 127.5, 42.8, 42.4, 37.4, 36.0, 34.2, 29.5, 25.5, 22.8, 10.4.

HRMS (ESI): *m/z* calcd for C₁₂H₁₉O³⁵ClNa: 237.10221 [M+Na]⁺; found 237.1021 (0 ppm).

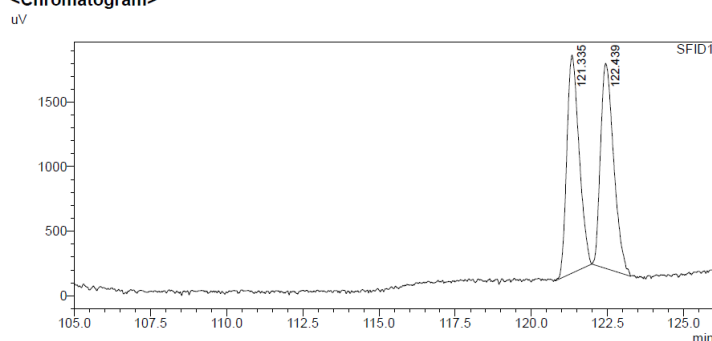
[α]_D²⁰ = + 7.9 (*c* = 1.5, CHCl₃), ee = 90%.

[α]_D²⁰ = + 8.0 (*c* = 1.0, CHCl₃), ee = 95%.

Enantiomeric excess was measured by chiral GC: G-TA column, helium (35 cm/sec), 130 °C-100 min-5 °C/min-150 °C-10 min, 5 °C/min-160 °C-10 min, Rt_{1(minor)} = 121.8 min, Rt_{2(major)} = 122.8 min.

Racemic mixture:

<Chromatogram>

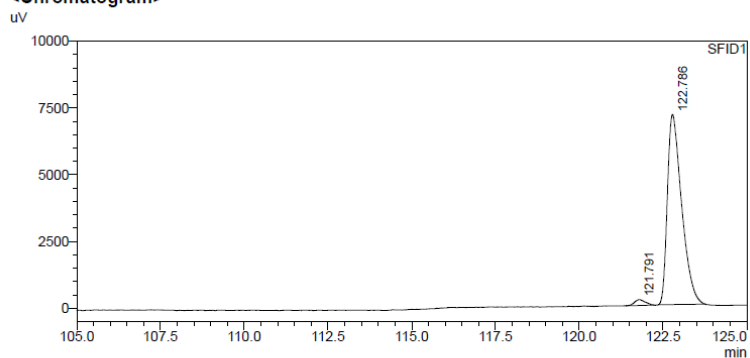


<Peak Table>

Peak#	Name	Ret. Time	Area	Area%	Resolution(USP)
1		121.34	47310	49.7	-
2		122.44	47882	50.3	1.39
Total			95191	100.0	

Compound **P4** chromatogram (ee = 95%):

<Chromatogram>



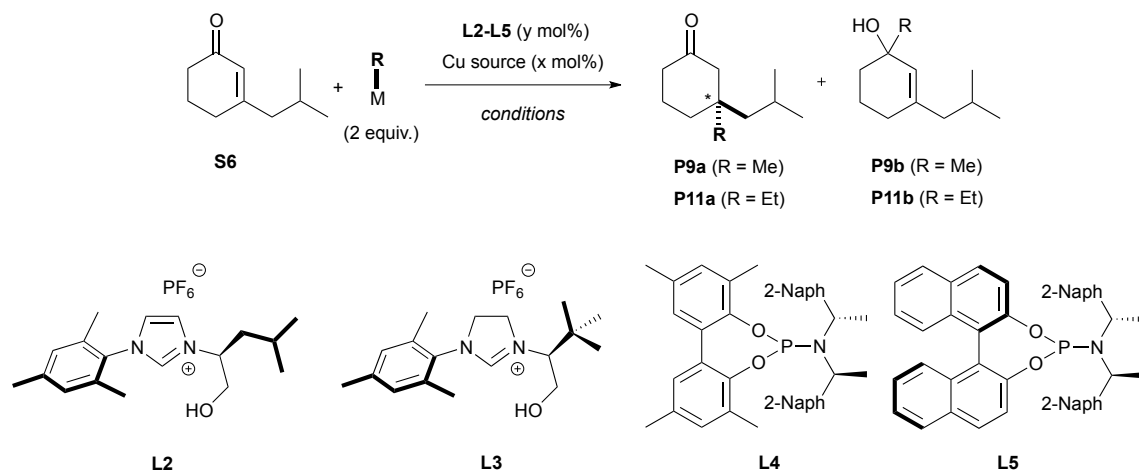
<Peak Table>

SFID1

Peak#	Name	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1		121.79	4890	217	2.3	3.0	--
2		122.79	211072	7118	97.7	97.0	1.44
Total			215961	7334	100.0	100.0	

6. Reactions condition screening for 1,4 ACA on the model substrate **S6**

Table S1:



Entry	Cu source (x)	Ligand (y)	R-M	Conditions ^a	PXa/PXb Selectivity ^{b,c}	ee (%) ^d
1	Cu(OTf) ₂ (4)	L2 (6)/ <i>n</i> BuLi ^g	Et ₂ Zn	THF, RT, 2 d	Degradation	—
2	Cu(OTf) ₂ (3)	L3 (4)	EtMgBr	Et ₂ O, 0°C, 4 h	40%/23%	86
3	Cu(OTf) ₂ (3)	L3 (4)	EtMgBr	Et ₂ O, 0°C, 16 h	22%/Nd ^e	83
4	Cu(OTf) ₂ (3)	L3 (4)	MeMgBr	Et ₂ O, 0°C, 2 h	24%/37% ^f	52
5	Cu(OTf) ₂ (4)	L2 (6)/ <i>n</i> BuLi ^g	Et ₃ Al	THF, RT, 3 d	23%/16%	29
6	Cu(OTf) ₂ (4)	L2 (6)/ <i>n</i> BuLi ^g	Me ₃ Al	THF, RT, 2 h 30	58%/11%	9
7	(CuOTf) ₂ .C ₆ H ₆ (2.5) ^h	L4 (10)	Et ₃ Al	Et ₂ O, -10 °C, 14 h	54%/-	98
8	(CuOTf) ₂ .C ₆ H ₆ (2.5) ^h	L4 (10)	Me ₃ Al	Et ₂ O, -10 °C, 15 h	83%/-	97
9	(CuOTf) ₂ .C ₆ H ₆ (2.5) ^h	L5 (10)	Me ₃ Al	Et ₂ O, -10 °C, 15 h	50%/-	95

^aAll reactions were performed on a 0.5 mmol scale. ^bNMR yields based on mesitylene (0.33 equiv.) used as an internal standard. ^cFor a better accuracy, yields were calculated after treatment of the spectra using line fitting deconvolution tool of Mnova. ^dee on product **P9a** or **P11a** was determined by GC on chiral column. ^e14% of **S6** remaining. ^f18% of **S6** remaining. ^g16 mol% of *n*BuLi was used to convert the imidazolium salt into the corresponding NHC. ^h[Cu] = 5.0 mol%. Nd: not determined.

Experimental procedures:

Cu/NHC (L2)-catalyzed 1,4-ACA of Et₂Zn to enone S6 (Table S1, entry 1)

The 1,4-asymmetric conjugate addition was performed using a modified literature procedure.^{vii}

A flame-dried Schlenk tube was charged with Cu(OTf)₂ (7.23 mg, 0.02 mmol, 4 mol%), and chiral imidazolium salt (0.03 mmol, 6 mol%). The system was flushed with argon, and 1 mL of anhydrous THF was added. The solution was stirred for 10 min and *n*BuLi (1.6 M in hexanes) (50.0 μL, 0.08 mmol, 16 mol%) was added and stirred again for 10 min. A solution of Et₂Zn (1.5 mL, 1.5 mmol, 3 equiv.) was added dropwise and the reaction mixture was stirred 10 min at room temperature and 10 min at 0 °C. A solution of enone (76 mg, 0.5 mmol, 1 equiv.) in 0.3 mL of anhydrous THF was added to the reaction at 0 °C and the solution was stirred at room temperature for 2 days. The reaction was quenched with NH₄Cl solid (500 mg) and then filtered on a small pad of silica, washed with ethyl acetate, and concentrated under vacuo. The crude product was analyzed by ¹H NMR and no product of 1,4-addition was observed.

Cu/NHC (L2/L3)-catalyzed 1,4-ACA of Grignard Reagents to enone S6 (Table S1, entries 2-4)

The 1,4-asymmetric conjugate addition was performed using a modified procedure from literature.^{viii}

A flame-dried Schlenk tube was charged with Cu(OTf)₂ (5.4 mg, 3.0 mol%) and the chiral imidazolium salt (4.0 mol%). The system was flushed under argon and anhydrous Et₂O (2 mL for entry 3; 1 mL for entry 2) was added. The mixture was cooled down to 0 °C. The Grignard reagent (600 μL, 1 M, 1.2 equiv) in Et₂O was added dropwise to the solution for 10 min. The mixture was stirred 15 min (entry 2) or 5 min (entry 3) at 0 °C. A solution of the cyclohexenone (76 mg, 0.5 mmol, 1 equiv.) in Et₂O (5 mL for entry 3, 2.5 mL for entry 2) was then added dropwise during ~30 min with a syringe pump. The solution was stirred at 0 °C for 2-4 h. The reaction was quenched with NH₄Cl solid (500 mg) and then filtered on a small pad of silica, washed with ethyl acetate, and concentrated *in vacuo*. The crude product was analyzed by ¹H NMR using 0.33 equiv. of mesitylene as internal standard.

Cu/NHC (L2)-catalyzed 1,4-ACA of trialkylaluminum to enone S6 (Table S1, entries 5-6)

A flame-dried Schlenk tube was charged with Cu(OTf)₂ (7.23 mg, 0.02 mmol, 4 mol%), and chiral imidazolium salt (0.03 mmol, 6 mol%). The system was flushed with argon, and 1 mL of anhydrous THF was added. The solution was stirred for 10 min and *n*BuLi (1.6 M in hexanes) (50.0 μL, 0.08 mmol, 16 mol%) was added and the mixture was stirred again for 10 min. A solution of enone (76 mg, 0.5 mmol, 1 equiv.) in 0.5 mL of anhydrous THF was added. A solution of R₃Al (1 M in hexanes for Et₃Al and 2 M in hexanes for Me₃Al, 3 equiv.) was added dropwise (at rt for entry 5 or 0 °C for entry 4). The solution was stirred at room temperature for 2.5h to 3 days. The reaction was quenched with NH₄Cl solid (500 mg) and then filtered on a small pad of silica, washed with ethyl acetate, and concentrated under vacuo. The crude product was analyzed by ¹H NMR using 0.33 equiv. of mesitylene as internal standard.

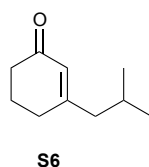
Cu/Phosphoramidite (L4/L5)-catalyzed 1,4-ACA of trialkylaluminum to enone S6 (Table S1, entries 7-9)

The 1,4-conjugate addition was performed using Alexakis' procedure.^{ix}

A flame-dried Schlenk tube was charged with [Cu] (5 mol%) and the chiral phosphoramidite (10 mol%). Anhydrous Et₂O (1 mL) was added and the mixture was stirred at room temperature for 30 min. Then a solution of enone (76 mg, 0.5 mmol, 1 equiv.) in Et₂O (1 mL) was added dropwise at room temperature and the reaction mixture was stirred for further 5 min before being cooled to -10 °C. Then, trialkylaluminum (2.0 equiv.) was introduced dropwise. Once the addition was complete the reaction mixture was left at -10 °C for 14-15 h. The reaction was hydrolyzed by the addition of solid NH₄Cl (500 mg) at -10 °C, and stirred for 1 h at rt. The solution was filtered on a pad of silica gel, washed with EtOAc, and concentrated in vacuo. The crude product was analyzed by ¹H NMR using 0.33 equiv. of mesitylene as internal standard.

Experimental data concerning enone S6 and 1,4-ACA adducts P9a-b and P11a-b:

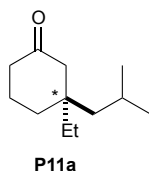
3-(2-Methylpropyl)-2-cyclohexen-1-one S6



3-Isobutylcyclohex-2-enone was prepared using known procedure and spectra were consistent with those previously reported.^x

¹H NMR (400 MHz, CDCl₃): δ 5.85 (quint, *J* = 1.2 Hz, 1H), 2.38-2.33 (m, 2H), 2.26 (br t, *J* = 5.9 Hz, 2H), 2.08 (d, *J* = 7.3 Hz, 2H), 2.01-1.94 (m, 2H), 1.92-1.81 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 6H).

3-Ethyl-3-(2-methylpropyl)cyclohexanone P11a



Spectra were consistent with those previously reported.^{viii}

¹H NMR (400 MHz, CDCl₃): δ 2.27 (t, *J* = 6.8 Hz, 2H), 2.19 (d, *J* = 13.7 Hz, 1H), 2.15 (d, *J* = 13.7 Hz, 1H), 1.92-1.75 (m, 2H), 1.70-1.62 (m, 1H), 1.60 (t, *J* = 6.2 Hz, 2H), 1.35 (q, *J* = 7.5 Hz, 2H), 1.22 (dd, *J* = 14.5, 5.2 Hz, 1H), 1.18 (dd, *J* = 14.4, 5.5 Hz, 1H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.80 (t, *J* = 7.5 Hz, 3H).

Enantiomeric excess was measured by chiral GC: Beta-dex column, helium (40 cm/sec), 80 °C-90 min-2 °C/min-160 °C-10 min, $R_{t1(\text{minor})} = 110.9$ min, $R_{t2(\text{major})} = 111.6$ min.

Racemic mixture:

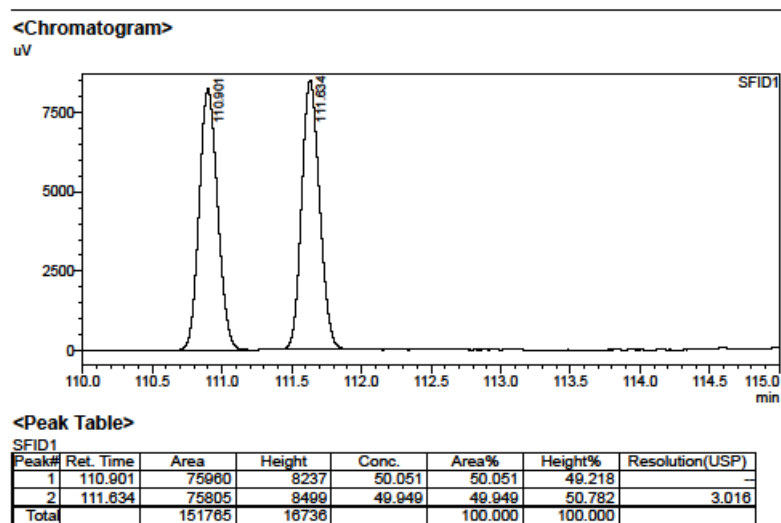
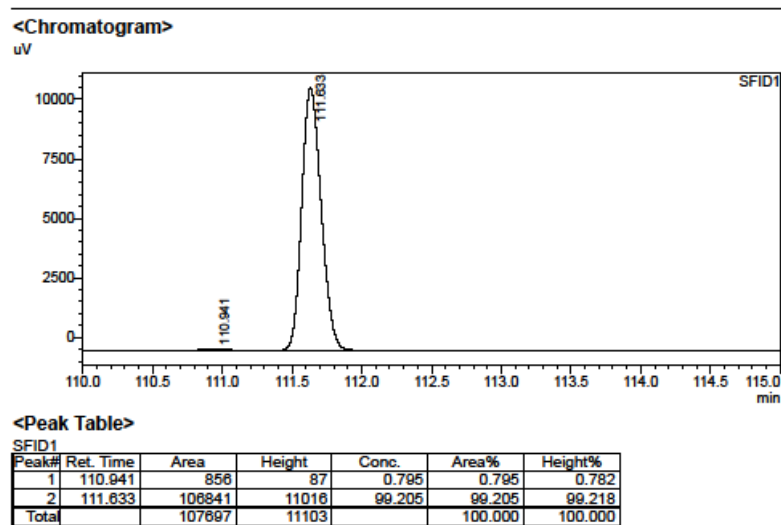
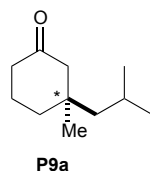


Table S1, entry 7 :



3-Methyl-3-(2-methylpropyl)-cyclohexanone **P9a**



Spectra were consistent with those previously reported.^x

¹H NMR (400 MHz, CDCl₃): δ 2.29-2.23 (m, 2H), 2.21 (d, $J = 13.3$ Hz, 1H), 2.11 (dt, $J = 13.3, 1.3$ Hz, 1H), 1.93-1.51 (m, 5H), 1.23 (dd, $J = 14.1, 5.1$, 1H), 1.19 (dd, $J = 14.1, 5.5$, 1H), 0.94 (s, 3H), 0.93 (d, $J = 6.8$ Hz, 3H), 0.92 (d, $J = 6.8$ Hz, 3H).

Enantiomeric excess was measured by chiral GC: Beta-dex column, helium (40 cm/sec), 80 °C-90 min-2 °C/min-160 °C-10 min, $R_{t1}(\text{minor}) = 87.1 \text{ min}$, $R_{t2}(\text{major}) = 92.9 \text{ min}$.

Racemic mixture:

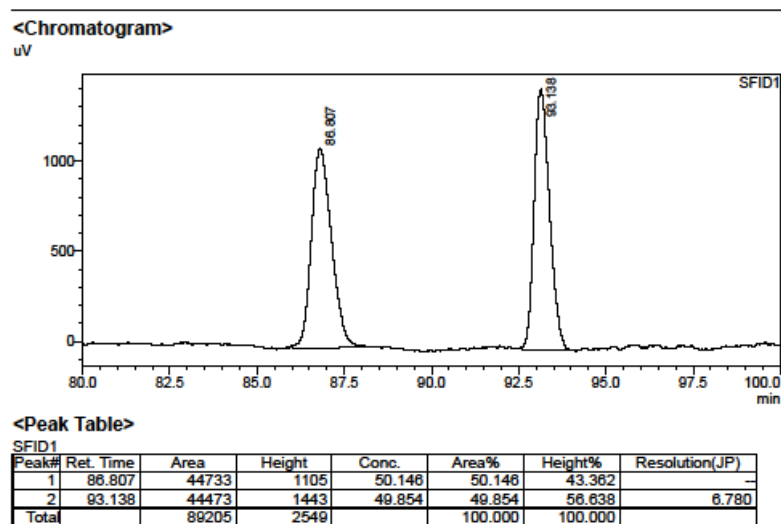
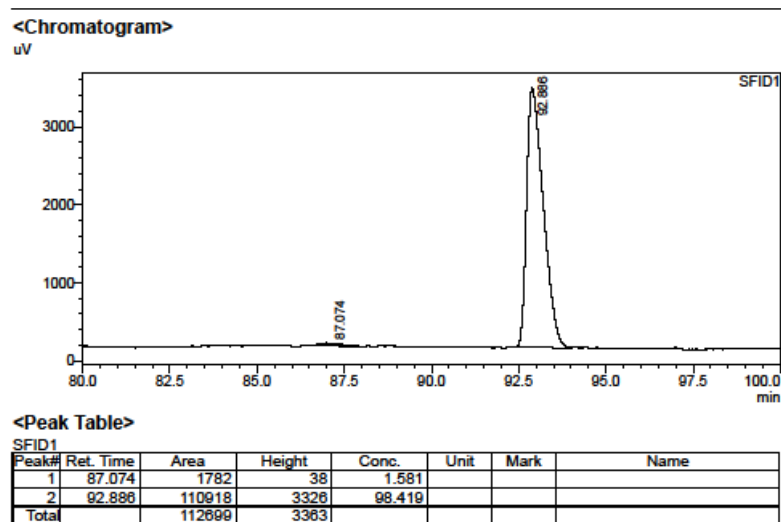
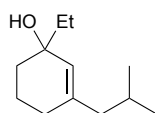


Table S1, entry 8 :



Synthesis and characterization of previously unknown 1,2-adducts P9b and P11b:

1-Ethyl-3-(2-methylpropyl)-cyclohex-2-en-1-ol **P11b**



P11b

A solution of ethylmagnesium bromide in anhydrous Et_2O ($C = 1.77 \text{ M}$, 0.65 mL , 1.15 mmol) was added dropwise to a stirred solution of enone **S6** (114.6 mg , 0.75 mmol) in anhydrous

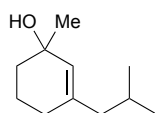
THF (3 mL) at 0 °C under argon. The resulting solution was allowed to warm to room temperature and stirred at room temperature for 12 h. Saturated NH₄Cl_(aq) (3 mL) was added at 0 °C, and the layers were separated. The aqueous layer was extracted with Et₂O (3 x 10 mL) and the combined organic layers were dried (MgSO₄) and evaporated under reduced pressure to give the crude product **P11b** in a nearly pure form (92.2 mg, 67%).

¹H NMR (400 MHz, CDCl₃): δ 5.31 (br s, 1H), 1.89-1.49 (m, 11H), 1.40 (br s, 1H), 0.90 (t, *J* = 7.5 Hz, 3H), 0.87 (d, *J* = 6.4 Hz, 3H), 0.82 (d, *J* = 6.3 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 140.8, 128.1, 70.6, 47.7, 35.2, 34.7, 28.8, 26.0, 22.9, 22.1, 19.5, 8.2.

HRMS (ESI): *m/z* calcd for C₁₂H₂₂ONa: 205.15629 [M+Na]⁺; found 205.1563 (0 ppm).

1-Methyl-3-(2-methylpropyl)-cyclohex-2-en-1-ol **9b**



P9b

Methylolithium (1.06 M in Et₂O, 1 mL, 1.06 mmol) was added dropwise to a stirred solution of enone **S6** (146.3 mg, 0.96 mmol) in anhydrous Et₂O (2.5 mL) at -78 °C under argon. The resulting solution was stirred at -78 °C for 15 min, then water (1 mL) was added, and the reaction mixture was allowed to warm to rt. Saturated NH₄Cl_(aq) (3 mL) was added, and the layers were separated. The aqueous layer was extracted with Et₂O (3 x 10 mL) and the combined layers were dried (MgSO₄) and evaporated under reduced pressure to give the crude product. The crude product was purified by filtration on a small pad of silica gel (pentane/AcOEt, 100/0 to 95/5) to give compound **P9b** as a colorless oil (102.8 mg, 64%).

¹H NMR (400 MHz, CDCl₃): δ 5.33-5.30 (m, 1H), 1.93-1.60 (m, 8H), 1.59 (br s, 1H), 1.56-1.48 (m, 1H), 1.25 (s, 3H), 0.84 (d, *J* = 6.4 Hz, 3H), 0.80 (d, *J* = 6.3 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 139.8, 129.4, 68.6, 47.4, 37.9, 29.9, 28.6, 26.1, 22.8, 22.3, 20.0.

HRMS (ESI): *m/z* calcd for C₁₁H₂₀ONa: 191.14064 [M+Na]⁺; found 191.1405 (1 ppm).

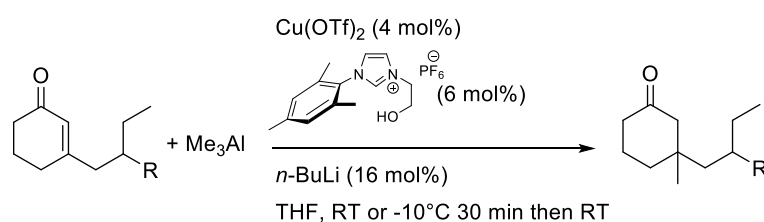
7. General experimental procedure for the 1,4-ACA on compounds (+)-P1, (-)-P1, (+)-P2, (-)-P2, (+)-P4

General experimental procedure for Cu/L4 (or L6) catalyzed 1,4-ACA on enones (+)-P1, (-)-P1, (+)-P2, (-)-P2, (+)-P4

The 1,4-conjugate addition was performed using Alexakis' procedure.^{ix}

A flame-dried Schlenk tube was charged with $(\text{CuOTf})_2 \cdot \text{C}_6\text{H}_6$ (6.3 mg, 2.5 mol%) and the chiral phosphoramidite **L4** (29.8 mg, 10 mol%). Anhydrous Et_2O (1 mL) was added and the mixture was stirred at room temperature for 30 min. Then the Michael acceptor (1.0 equiv., 0.5 mmol) in Et_2O (1 mL) was added dropwise at room temperature and the reaction mixture was stirred for further 5 min before being cooled to -10°C . Then, trimethylaluminium (0.5 mL of 2 M solution in hexanes, 2.0 equiv.) was introduced dropwise. Once the addition was complete the reaction mixture was left at -10°C for 14 h. The reaction was hydrolyzed by the addition of solid NH_4Cl (500 mg) at -10°C , and stirred for 1 h at rt. The solution was filtered on a pad of silica gel, washed with EtOAc , and concentrated in vacuo. GC analysis was performed on the crude product to determine the diastereomeric excess. The oily residue was purified by flash column chromatography (pentane/ Et_2O 97/3 to 90/10 for **P5** and **P6**, toluene/ Et_2O , 97/3 for **P7** or pentane/ Et_2O 90/10 to 80/20 for **P8**) to yield the 1,4-adduct.

Procedure using non chiral ligand

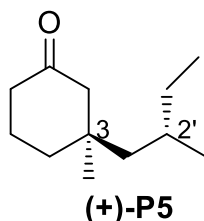


A flame dried Schlenk was charged with $\text{Cu}(\text{OTf})_2$ (7.23 mg, 0.02 mmol, 4 mol%), and the ligand imidazolium⁷ (11.3 mg, 0.03 mmol, 6 mol%). The system was flushed with argon, and 1 mL of anhydrous THF was added. The solution was stirred for 10 min and $n\text{BuLi}$ (1.6 M in hexanes) (50.0 μL , 0.08 mmol, 16 mol%) was added and stirred again for 10 min. At this stage two alternative routes were used. In the first one, the solution was cooled down to -10°C and a 2 M solution of trimethylaluminium in hexanes (0.75 mL, 1.5 mmol, 3 equiv.) was added dropwise. After 10 min, a solution of enone (0.5 mmol, 1 equiv.) in 0.5 mL of anhydrous THF was added to the reaction and the solution was stirred at -10°C for 30 min then at rt until full conversion was reached. In the second option, the solution was cooled down to 0°C before the 2 M solution of trimethylaluminium in hexanes was added dropwise. After 10 min at rt and 5 min at 0°C , the solution of enone in THF was added and the solution was stirred at rt until full conversion was reached. In all experiments, the reaction was quenched with NH_4Cl solid (500 mg) and stirred for 1 h. The reaction was filtered on a small pad of silica, washed with EtOAc , and concentrated under vacuo. Diastereomeric excess was determined by GC analysis on the crude product. The product may be possibly purified by flash chromatography on silica gel (pentane/ Et_2O 97/3 to 90/10 for **P5** and **P6**, toluene/ Et_2O , 97/3 for **P7** or pentane/ Et_2O 90/10 to 80/20 for **P8**).

Procedure for the Cu/chiral ligand L2 catalyzed 1,6-ACA of Et₂Zn to dienones was followed in an identical manner to that previously reported by our group (see reference vii).

8. Experimental data for products P5-P8

(R)-3-Methyl-3-((S)-2-methylbutyl)cyclohexanone (+)-P5



The reaction was performed with (+)-P1 (83 mg, 0.5 mmol) and the desired product (+)-P5 was obtained, as a colorless oil in 81% yield (74 mg).

¹H NMR (400 MHz, CDCl₃): δ 2.31-2.22 (m, 2H), 2.22 (d, *J* = 13.5 Hz, 1H), 2.09 (dt, *J* = 13.4, 1.4 Hz, 1H), 1.95-1.78 (m, 2H), 1.67-1.59 (m, 1H), 1.59-1.51 (m, 1H), 1.46-1.37 (m, 1H), 1.34-1.24 (m, 2H), 1.23-1.07 (m, 2H), 0.93 (s, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 212.6, 54.3, 49.3, 41.2, 39.5, 36.5, 32.1, 30.2, 25.3, 22.3, 22.2, 11.7.

$[\alpha]_D^{20} = +2.0$ (*c* = 1, CHCl₃), [(2'*S*,3*R*)/(2'*R*,3*R*)/(2'*S*,3*S*)] = 94.9/4.1/1.0

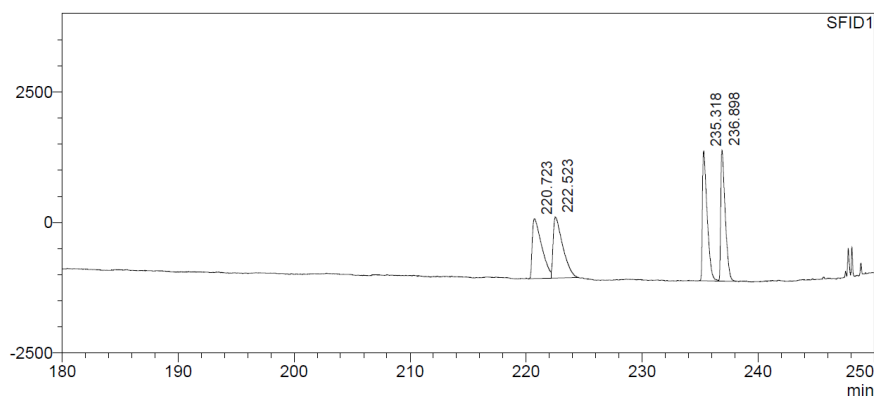
HRMS (ESI): *m/z* calcd for C₁₂H₂₂ONa: 205.15684 [M+Na]⁺; found 205.1568 (0 ppm).

Diastereomeric excess were measured by chiral GC: G-BP column, helium (30 cm/sec), 75 °C - 210 min - 1.0 °C/min - 105 °C - 5 °C/min - 160 °C - 9 min.

Mixture of 4 stereoisomers:

<Chromatogram>

uV

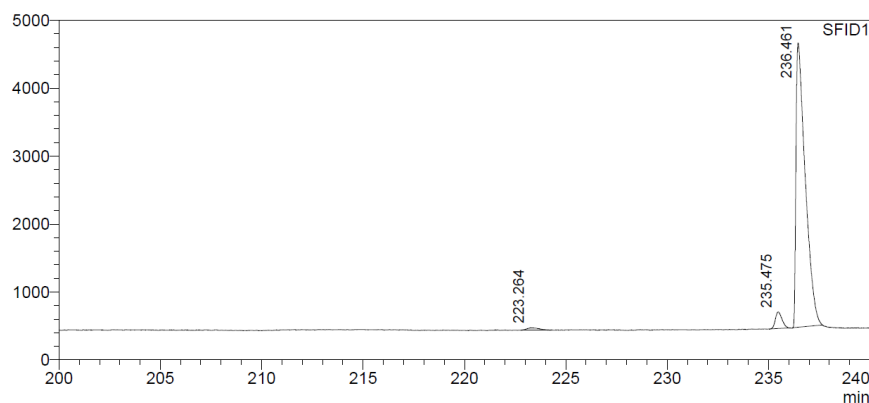


<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	220.723	64381	1147	23.956			
2	222.523	66990	1169	24.927		V	
3	235.318	70312	2479	26.163			
4	236.898	67062	2507	24.954		V	
Total		268745	7302				

Compound (+)-**P5**, $R_T(2'S,3R) = 236.5$ min, $R_T(2'S,3S) = 223.3$ min; 98% de

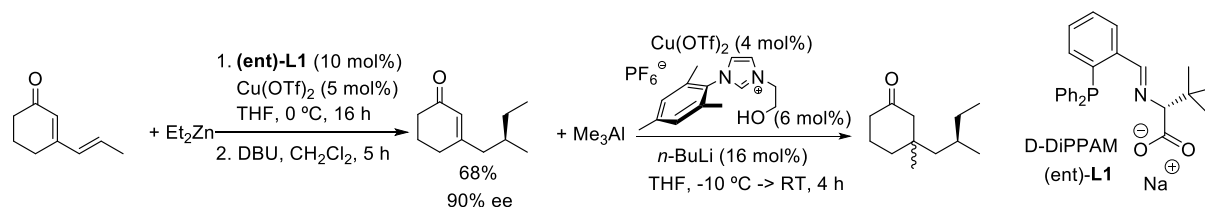
uV

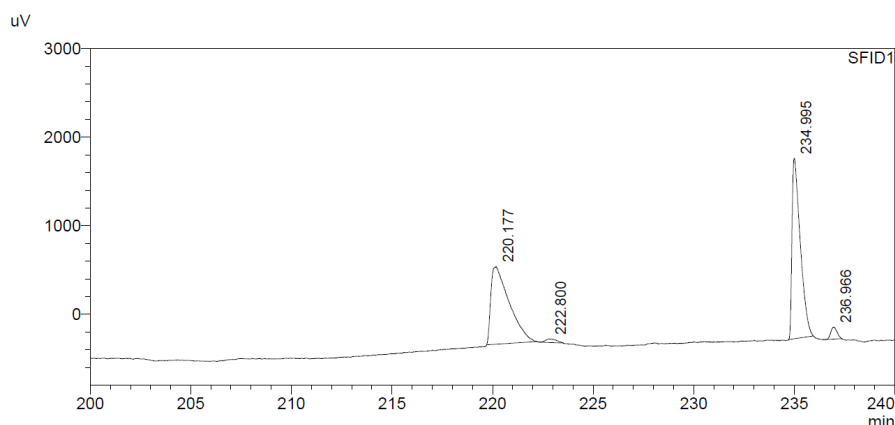


<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	223.264	1416	36	1.012		M	
2	235.475	5573	245	3.983		M	
3	236.461	132944	4181	95.005			
Total		139933	4461				

Complementary experiment and related chromatogram undertaken to identify an authentic the different stereoisomers observed on the chromatogram:



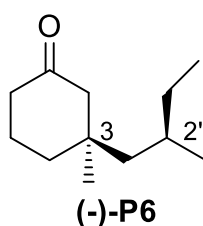


<Peak Table>

SFID1

Peak#	Name	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1		220.18	55476	877	47.0	28.3	--
2		222.80	1500	42	1.3	1.3	1.91
3		235.00	58073	2039	49.2	65.9	13.36
4		236.97	2923	136	2.5	4.4	2.94
Total			117971	3094	100.0	100.0	

(R)-3-Methyl-3-((R)-2-methylbutyl)cyclohexanone (-)-P6



The reaction was performed with (-)-P1 (83 mg, 0.5 mmol) and the desired product (-)-P6 was obtained, as a colorless oil in 57% yield (52 mg).

¹H NMR (400 MHz, CDCl₃): δ 2.32-2.23 (m, 2H), 2.20 (d, *J* = 13.2 Hz, 1H), 2.10 (dt, *J* = 13.4, 1.5 Hz, 1H), 1.96-1.79 (m, 2H), 1.70-1.62 (m, 1H), 1.59-1.51 (m, 1H), 1.47-1.38 (m, 1H), 1.33-1.25 (m, 2H), 1.22-1.08 (m, 2H), 0.93 (s, 3H), 0.91 (d, *J* = 6.6 Hz, 6H), 0.85 (t, *J* = 7.4 Hz, 3H).

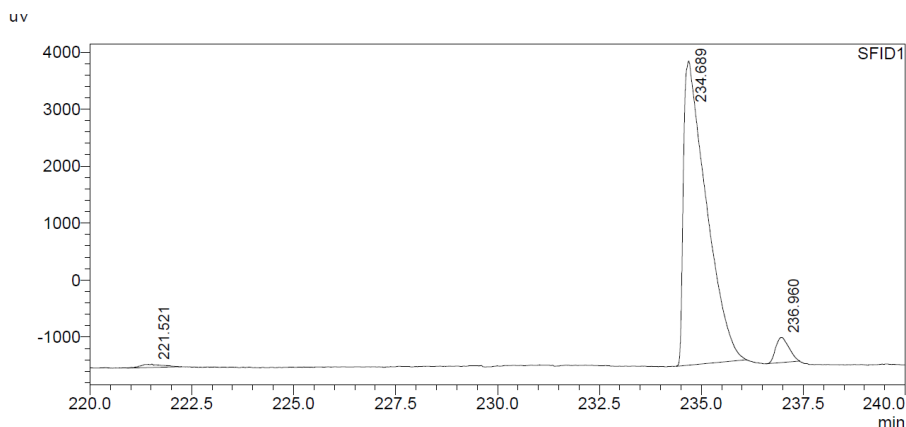
¹³C NMR (101 MHz, CDCl₃): δ 212.6, 54.3, 49.2, 41.2, 39.6, 36.6, 32.0, 30.2, 25.3, 22.4, 22.3, 11.7.

$[\alpha]_D^{20} = -17.5$ (*c* = 1, CHCl₃), [(2'*R*,3*R*)/(2'*S*,3*R*)/(2'*R*,3*S*)] = 94.2/4.8/1.0

HRMS (ESI): *m/z* calcd for C₁₂H₂₂ONa: 205.15629 [M+Na]⁺; found 205.1561 (1 ppm).

Diastereomeric excess were measured by chiral GC: G-BP column, helium (30 cm/sec), 75 °C - 210 min - 1.0 °C/min - 105 °C - 5 °C/min - 160 °C - 9 min.

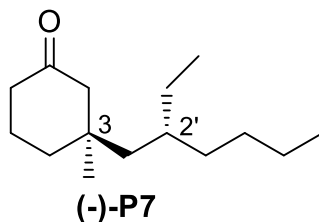
Compound (-)-P6, *R*_T (2'*R*,3*R*) = 234.7 min, *R*_T (2'*R*,3*S*) = 221.5 min; 98% de



<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	221.521	2099	59	0.955		M	
2	234.689	207693	5338	94.521		M	
3	236.960	9939	442	4.523		M	
Total		219731	5839				

(R)-3-((R)-2-Ethylhexyl)-3-methylcyclohexanone (-)-P7



The reaction was performed with (-)-P2 (92 mg, 0.44 mmol) and the desired product (-)-P7 was obtained, as a colorless oil, in 75% of yield (74 mg).

¹H NMR (400 MHz, CDCl₃): δ 2.31-2.19 (m, 2H), 2.20 (d, *J* = 13.3 Hz, 1H), 2.07 (dt, *J* = 13.3, 1.6 Hz, 1H), 1.95-1.76 (m, 2H), 1.66-1.57 (m, 1H), 1.56-1.48 (m, 1H), 1.31-1.16 (m, 11H), 0.89 (s, 3H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.82 (t, *J* = 7.1 Hz, 3H).

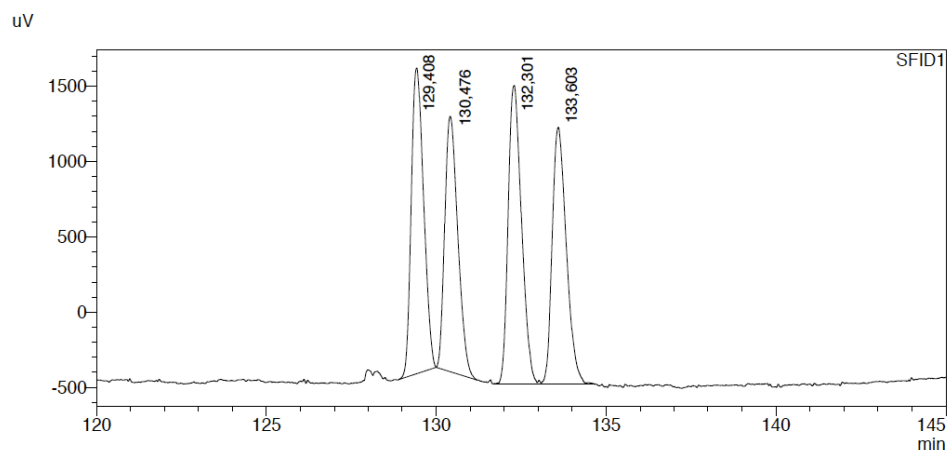
¹³C NMR (100 MHz, CDCl₃): δ 212.7, 54.1, 47.0, 41.2, 39.6, 36.4, 35.2, 34.5, 29.1, 28.2, 25.0, 23.2, 22.3, 14.3, 11.0.

$[\alpha]_D^{20} = -6.6$ (*c* = 1, CHCl₃), [(2'*R*,3*R*)/(2'*S*,3*R*)/(2'*R*,3*S*)] = 96.7/1.9/1.4

HRMS (ESI): *m/z* calcd for C₁₅H₂₈ONa: 247.20379 [M+Na]⁺; found 247.2040 (1 ppm).

Diastereomeric excess were measured by chiral GC: G-BP column, helium (36 cm/sec), 100 °C - 100 min - 1.0 °C/min - 120 °C - 20 min - 4 °C/min - 160 °C - 10 min.

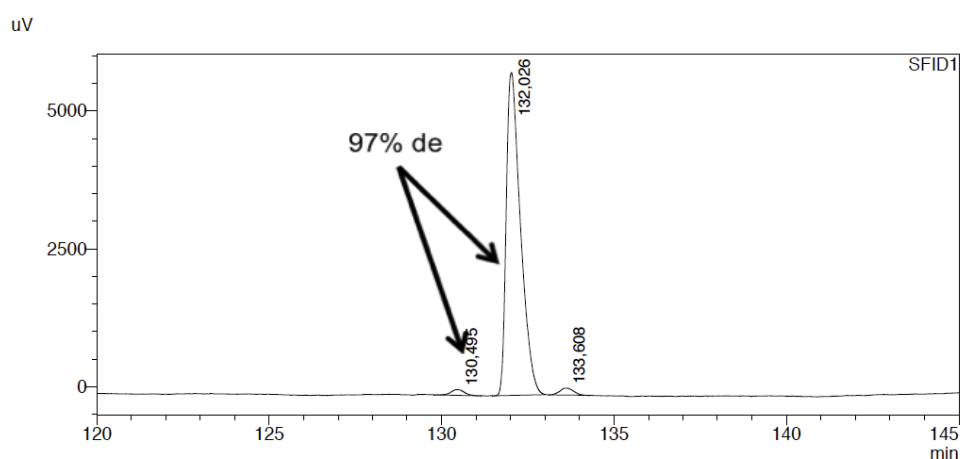
Mixture of 4 stereoisomers:



<Peak Table>

Peak#	Ret. Time	Name	Area%	Resolution(JP)
1	129.408		25.514	--
2	130.476		22.687	1,508
3	132.301		27.095	2,493
4	133.603		24.704	1,740
Total			100.000	

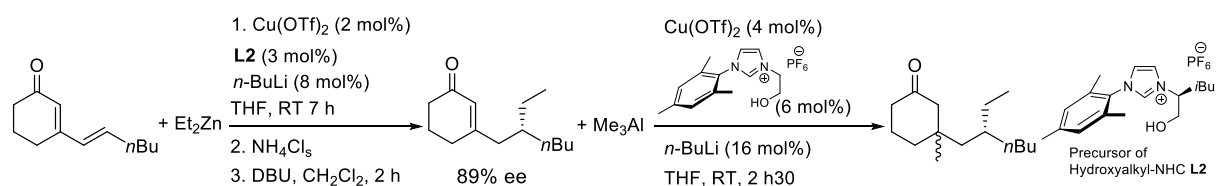
Compound (-)-**P7**, R_T ($2'R,3R$) = 132.0 min, R_T ($2'R,3S$) = 130.5 min; 97% de

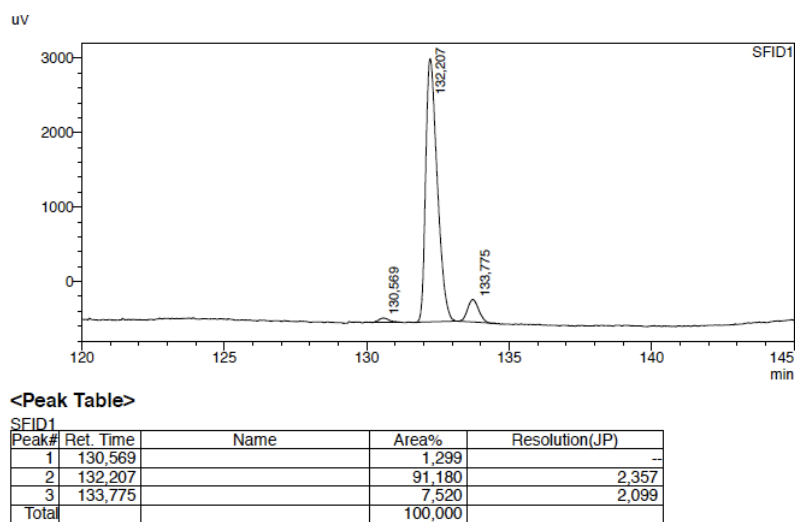
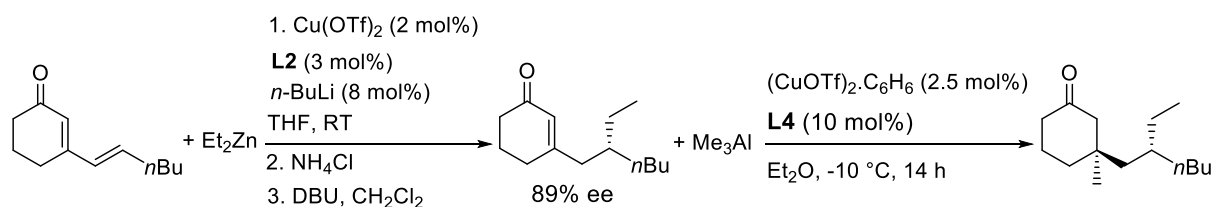
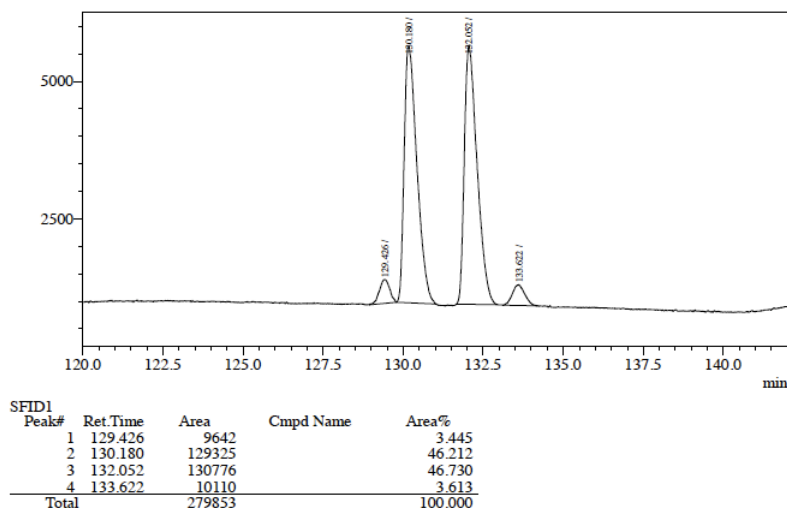


<Peak Table>

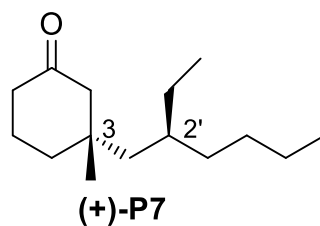
Peak#	Ret. Time	Area	Unit	Area%	Resolution(JP)
1	130.495	2799		1.598	--
2	132.026	168802		96.418	2,089
3	133.608	3473		1.984	2,121
Total		175074		100.000	

Complementary experiments and related chromatogram undertaken to identify an authentic the different stereoisomers on the chromatogram. Note: Cu/L-DiPPAM and Cu/L2 catalyzed 1,6-ACA of Et_2Zn to cyclic dienones lead to the same enantiomer (see for instance reference ii and vi, and also the following experiments):





(S)-3-((S)-2-Ethylhexyl)-3-methylcyclohexanone (+)-P7



The reaction was performed with (+)-**P2** (104 mg, 0.5 mmol) and Ligand **L6** (22 mg). The desired product (+)-**P7** was obtained in 66% yield (74 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 2.33-2.20 (m, 2H), 2.20 (d, *J* = 13.3 Hz, 1H), 2.08 (dt, *J* = 13.3, 1.6 Hz, 1H), 1.96-1.77 (m, 2H), 1.67-1.58 (m, 1H), 1.57-1.50 (m, 1H), 1.33-1.17 (m, 11H), 0.92-0.86 (m, 6H), 0.83 (t, *J* = 7.2 Hz, 3H).

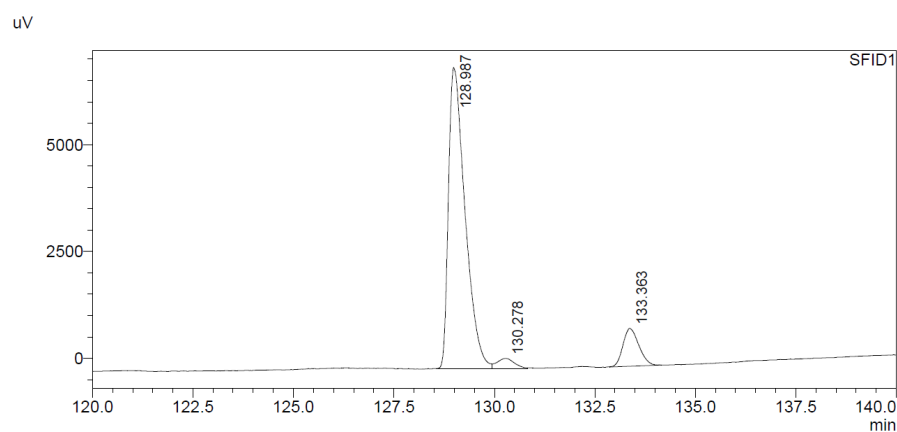
¹³C NMR (100 MHz, CDCl₃): δ 212.6, 54.2, 47.0, 41.2, 39.6, 36.5, 35.3, 34.6, 29.1, 28.3, 25.0, 23.3, 22.3, 14.3, 11.0.

$[\alpha]_D^{20} = +1.0$ (*c* 1, CHCl₃), [(2'*S*,3*S*)/(2'*S*,3*R*)/(2'*R*,3*S*)] = 88.4/10.1/1.4.

HRMS (ESI): *m/z* calcd for C₁₅H₂₈ONa: 247.20324 [M+Na]⁺; found 247.2031 (1 ppm).

Diastereomeric excess were measured by chiral GC: G-BP column, helium (36 cm/sec), 100 °C - 100 min - 1.0 °C/min - 120 °C - 20 min - 4 °C/min - 160 °C - 10 min.

Compound (+)-**P7**, R_T (2'*S*,3*S*) = 129.0 min, R_T (2'*S*,3*R*) = 133.4 min; 79% de

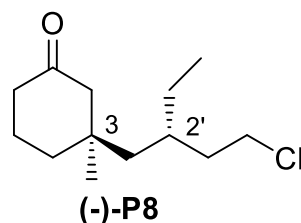


<Peak Table>

SFID1

Peak#	Name	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1		128.99	202995	7055	86.4	86.1	--
2		130.28	7729	248	3.3	3.0	1.57
3		133.36	24315	888	10.3	10.8	3.79
Total			235039	8191	100.0	100.0	

(*R*)-3-((*S*)-4-Chloro-2-ethylbutyl)-3-methylcyclohexanone (-)-P8



The reaction was performed with enone (+)-**P4** (107 mg, 0.5 mmol) and the desired product (-)-**P8** was obtained in 58% yield (67 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 3.53 (t, *J* = 6.9 Hz, 2H), 2.34-2.18 (m, 3H), 2.10 (dt, *J* = 13.3, 1.5 Hz, 1H), 1.97-1.79 (m, 2H), 1.74 (q, *J* = 6.8 Hz, 2H), 1.70-1.52 (m, 3H), 1.36-1.27 (m, 3H), 1.15 (dd, *J* = 14.4, 4.8 Hz, 1H), 0.94 (s, 3H), 0.86 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 212.2, 54.0, 46.2, 43.2, 41.1, 39.6, 38.4, 36.3, 32.0, 27.8, 25.2, 22.3, 10.7

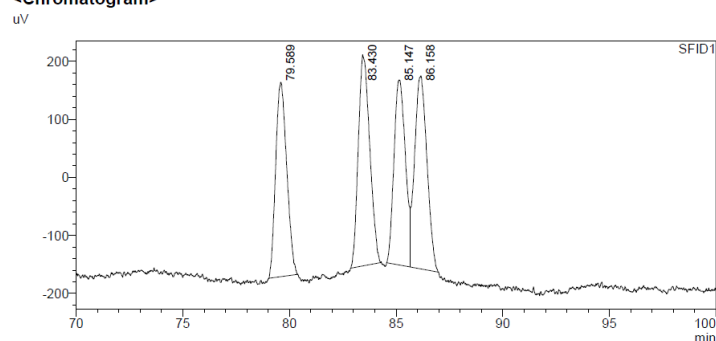
[α]_D²⁰ = - 11.5 (*c* = 0.8, CHCl₃), [(2'*S*,3*R*)/(2'*R*,3*R*)/(2'*R*,3*S*)/(2'*S*,3*S*)] : 96.1/2.4/-/1.5

HRMS (ESI): *m/z* calcd for C₁₃H₂₃ClONa: 253.13351 [M+Na]⁺; found 253.1337 (1 ppm).

Diastereomeric excess was measured by chiral GC: G-BP column, helium (35 cm/sec), 130 °C – 100 min - 5.0 °C/min - 150 °C - 10 min - 5 °C/min - 160 °C - 10 min.

Statistical mixture of the 4 diastereoisomers:

<Chromatogram>

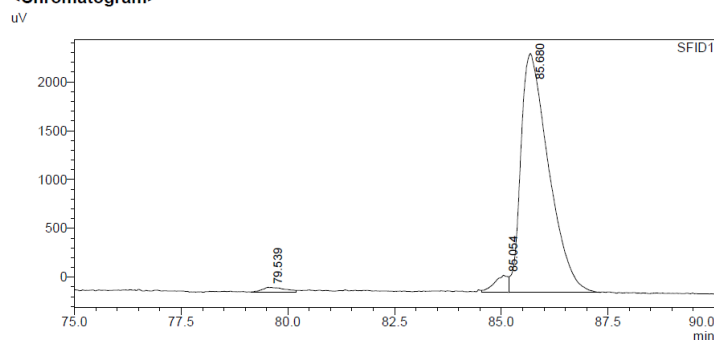


<Peak Table>

Peak#	Ret. Time	Height	Name	Area%	Resolution(USP)
1	79.589	335		23.666	--
2	83.430	364		26.605	3.880
3	85.147	319		23.297	1.719
4	86.158	333		26.432	0.989
Total		1351		100.000	

Compound (-)-**P8**, *R_T* (2'*S*,3*S*) = 79.5 min, *R_T* (2'*S*,3*R*) = 85.7 min.; *de* = 97%

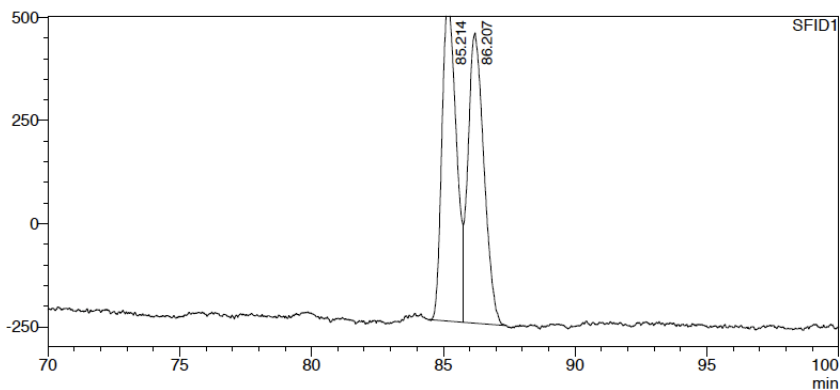
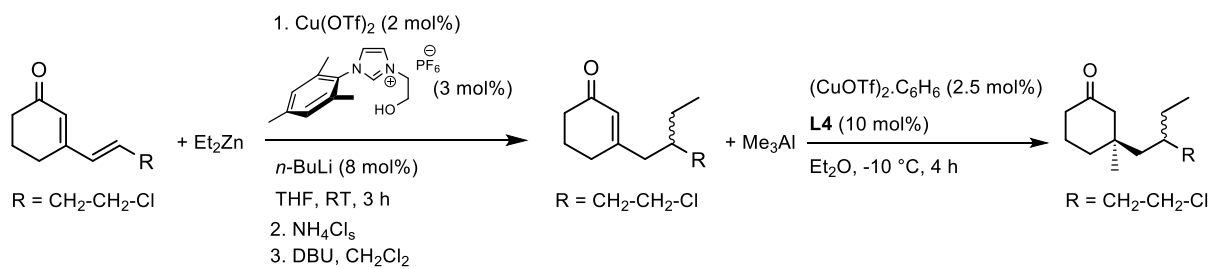
<Chromatogram>



<Peak Table>

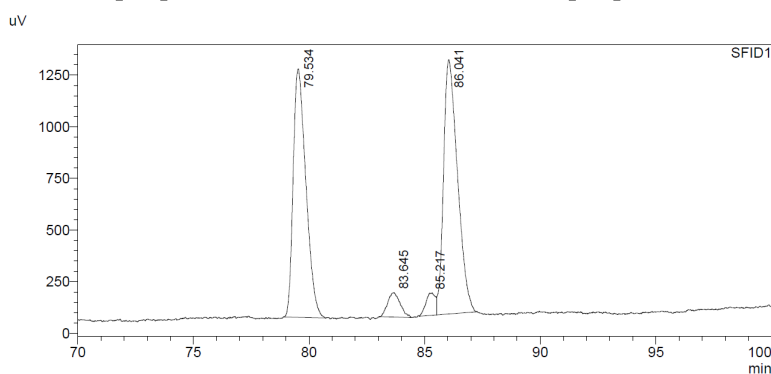
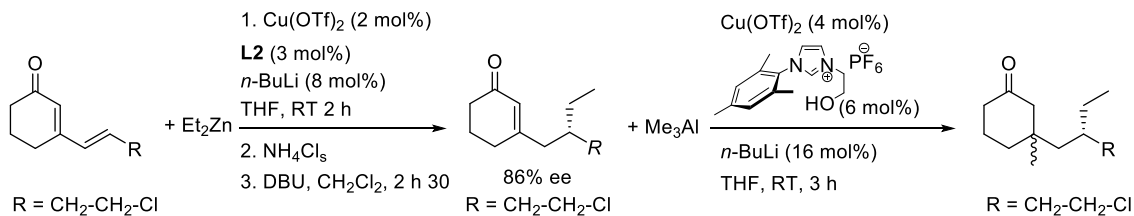
Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(USP)
1	79.539	1785	48	1.533	1.819	--
2	85.054	3921	173	3.368	6.478	3.905
3	85.680	110708	2443	95.098	91.703	0.403
Total		116414	2664	100.000	100.000	

Complementary experiment undertaken to identify and authenticate diastereoisomers:



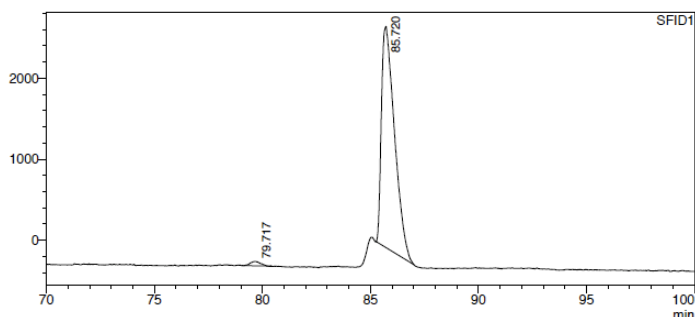
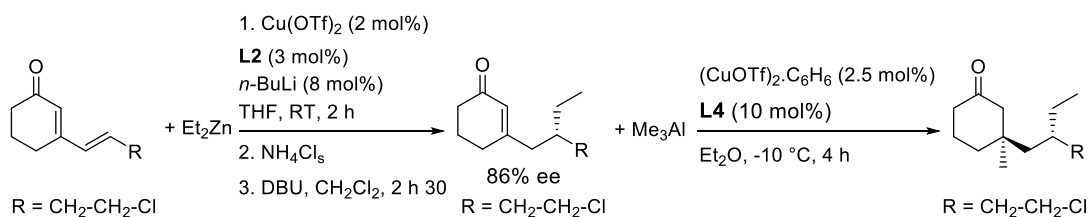
<Peak Table>

Peak#	Ret. Time	Name	Area%
1	85.214		49.445
2	86.207		50.555
Total			100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	79.534	45993	1202	43.688			
2	83.645	4457	118	4.234			
3	85.217	3115	107	2.959			
4	86.041	51711	1231	49.120		V	
Total		105277	2658				



<Peak Table>

Peak#	Ret. Time	Name	Area%	Resolution(JP)
1	79.717		1.526	-
2	85.720		98.474	5.741
Total			100.000	

9. Synthesis of cyclized compound P10

Experimental procedure for the tandem 1,4-ACA/trapping of the Aluminum enolate (Scheme 6 of the manuscript)

Without additive (conditions A): A flame-dried Schlenk tube was charged with CuTC (2.1 mg, 5 mol%) and the chiral phosphoramidite (13.1 mg, 10 mol%). Anhydrous Et2O (1 mL) was added and the mixture was stirred at room temperature for 30 min. Then the Michael acceptor **P4** (47 mg, 1.0 equiv, 0.22 mmol) in Et2O (0.5 mL) was added dropwise at room temperature and the reaction mixture was stirred for further 5 min before being cooled to -10 °C. Then, trimethylaluminium (0.220 mL of 2 M solution in heptane, 2.0 equiv) was introduced dropwise. Once the addition was complete the reaction mixture was left at -10 °C for 1 h and 16 h at room temperature. The reaction was hydrolyzed by the addition of solid NH4Cl (230 mg), and stirred for 30 min at rt. The solution was filtered on a pad of silica gel, washed with EtOAc, and concentrated in vacuo. The crude was analyzed by ¹H NMR and only the 1,4-adduct **P8** was observed with no formation of the cyclized product **P10**. The crude was purified by flash column chromatography (petroleum ether/Et2O 9/1 to 8/2) and product **P8** was collected in 72% of yield (36 mg).

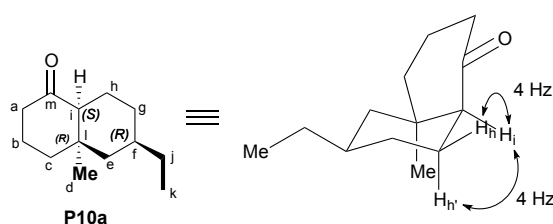
With additives (conditions B): A flame-dried Schlenk tube was charged with CuTC (1.1 mg, 5 mol%) and the chiral phosphoramidite (7 mg, 10 mol%). Anhydrous Et2O (0.8 mL) was added and the mixture was stirred at room temperature for 30 min. Then the Michael acceptor **P4** (25 mg, 1.0 equiv, 0.12 mmol) in Et2O (0.4 mL) was added dropwise at room temperature and the reaction mixture was stirred for further 5 min before being cooled to -10 °C. Then, trimethylaluminium (0.120 mL of 2 M solution in heptane, 2.0 equiv) was introduced

dropwise. Once the addition was complete the reaction mixture was left at -10 °C for 1 h and 16 h at room temperature. The solution was concentrated *in vacuo*, diluted with anhydrous HMPA (0.3 mL), stirred for 10 min and cooled down to 0 °C. MeLi (0.110 mL of 1.6 M solution in Et₂O, 1.4 eq) was injected and the solution was warmed up to rt and stirred for 1 day. The reaction was hydrolyzed by the addition of solid NH₄Cl (150 mg), and stirred for 30 min at rt. The solution was filtered on a pad of silica gel, washed with EtOAc, and concentrated *in vacuo*. Crude ¹H NMR shows the formation of product **P8** and no formation of **P10**. The crude was purified by flash column chromatography (petroleum ether/Et₂O 9/1 to 8/2) affording **P8** in trace quantity (8 mg) along with decomposition.

Cyclisation starting from isolated **P8**

In a flame dried flask, a 30% KH solution in mineral oil (87 mg, 0.65 mmol, 2.5 equiv.) was dissolved in anhydrous THF (0.6 mL). A solution of **P8** (60 mg, 0.26 mmol, e.e. of the major diastereoisomer > 98%) in THF (0.6 mL) was then added dropwise and the resulting mixture was stirred for 2 h at room temperature. Saturated NH₄Cl_s (4 mL) was slowly added, followed by Et₂O (20 mL). The aqueous phase was extracted with Et₂O (2x20 mL) and combined organic layers were washed with brine, dried over MgSO₄, filtrated and evaporated under reduced pressure. The diastereomeric ratio was determined to be 50/50 by ¹H NMR of the crude mixture. The crude product was purified by silica gel column chromatography (pentane then pentane/Et₂O 80/20) to give both diastereoisomers as colourless oil (47 mg, 93% yield). The diastereoisomers were further separated by chromatography on silica gel by eluting with a pentane/Et₂O gradient (100:0 to 96:4). The first diastereomer **10a** (R_f ~ 0.40 in pentane/Et₂O 98:2) was isolated as a colorless oil (26.2 mg, 44% yield). The second diastereomer **10b** (R_f 0.32 in pentane/Et₂O 98:2) was isolated with a small impurity (<5%) but could be obtained pure in 33 % yield (19.5 mg) as a colorless oil after a further chromatography on silica gel by eluting with a gradient pentane/Et₂O (100:0 to 98:2).

(4a*R*,6*R*,8a*S*)-6-ethyl-4a-methyloctahydronaphthalen-1(2*H*)-one **10a**



(R_f = 0.4, 26.2 mg, 44% yield)

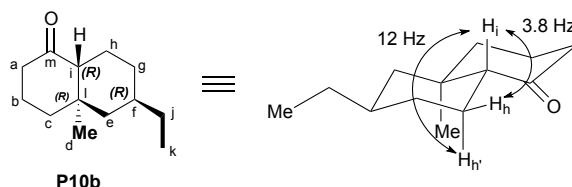
¹H NMR (400 MHz, CDCl₃): δ 2.34 (dddd, *J* = 14.1, 4.4, 2.8, 1.9 Hz, 1H, *H*_a), 2.23 (dddd, *J* = 14.3, 12.2, 7.2, 1.2 Hz, 1H, *H*_a), 2.17 – 2.09 (m, 2H, *H*_i + *H*_g), 1.95 – 1.79 (m, 2H, *H*_b), 1.73 (ddd, *J* = 13.0, 13.0, 4.7 Hz, 1H, *H*_c), 1.60 – 1.51 (m, 2H, *H*_c + *H*_h), 1.51 – 1.37 (m, 2H, *H*_g + *H*_f), 1.20 – 1.07 (m, 6H, *H*_d + *H*_e + *H*_j), 1.05 – 0.91 (m, 2H, *H*_e + *H*_h), 0.84 (t, *J* = 7.4 Hz, 3H, *H*_k).

¹³C NMR (100 MHz, CDCl₃): δ 212.7(*C*_m), 54.6(*C*_i), 41.8(*C*_a), 40.3(*C*_c), 40.1(*C*_e), 39.2(*C*_l), 34.5(*C*_f), 30.4(*C*_j), 28.6(*C*_d), 28.4(*C*_h), 21.5(*C*_b), 20.7(*C*_g), 11.5(*C*_k).

$[\alpha]_{\text{D}}^{20} = +15.5$ ($c = 0.2$, CH_2Cl_2).

HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{22}\text{O Na}$: 217.15684 $[\text{M}+\text{Na}]^+$; Found : 217.1570 (1 ppm).

(4*aR*,6*R*,8*aR*)-6-ethyl-4*a*-methyloctahydronaphthalen-1(2*H*)-one P10b



($R_f = 0.32$, 19.5 mg, 33% yield)

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 2.31 (tdd, $J = 6.6, 2.2, 1.1$ Hz, 2H, H_a), 2.13 (dd, $J = 12.2, 3.3$ Hz, 1H, H_i), 2.00 – 1.88 (m, 2H, H_b), 1.88 – 1.80 (m, 1H, H_g), 1.69 – 1.50 (m, 4H, $H_c + H_e + H_h$), 1.47 – 1.32 (m, 2H, $H_h + H_f$), 1.19 (quint, $J = 7.3$ Hz, 2H, H_j), 0.95 (t, $J = 12.5$ Hz, 1H, H_e), 0.87 (t, $J = 7.4$ Hz, 3H, H_k), 0.84 – 0.72 (m, 4H, $H_d + H_g$).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 213.4(C_m), 58.0(C_i), 47.8(C_e), 41.5(C_a), 40.9(C_c), 40.2(C_l), 34.0(C_f), 32.1(C_g), 30.1(C_j), 22.8(C_b), 20.7(C_h), 17.9(C_d), 11.6(C_k).

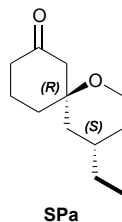
$[\alpha]_{\text{D}}^{20} = +52.0$ ($c = 0.2$, CH_2Cl_2).

HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{22}\text{O Na}$: 217.15684 $[\text{M}+\text{Na}]^+$; Found : 217.1565 (2 ppm).

10. Formation of the spiro compounds SPa and SPb

The substrate (+)-**P3** (140 mg, 0.45 mmol, 94% ee) was dissolved in methanol (15 mL) and Amberlyst® resin (70 mg) added. The solution was then stirred at ambient temperature for 7 hours. The reaction was filtered through a sintered funnel, eluting with methanol (20 mL) and the filtrate concentrated *in vacuo*. The obtained crude pale yellow oil was purified by chromatography on silica gel (1:99 ethyl acetate: pentane – 1:4 ethyl acetate: pentane) affording the (4*S*,6*S*)-**SPb** diastereomer (29 mg, 33%) and then the (4*S*,6*R*)-**SPa** diastereomer (26 mg, 30%). The (4*S*,6*R*)-**SPa** diastereomer solidified as a white powder. An X-ray quality sample was obtained by crystallisation from *n*-pentane and diethyl ether followed by slow evaporation to afford fine colourless needles. The other (4*S*,6*S*)-**SPb** diastereomer remained as a clear oil.

(4*S*,6*R*)-4-Ethyl-1-oxaspiro[5.5]undecan-8-one SPa



M.P. 74.5 °C – 75.6 °C.

¹H NMR (400 MHz, CDCl₃): δ 3.70 (ddd, *J* = 11.8, 5.1, 1.3 Hz, 1H), 3.47 (td, *J* = 12.4, 2.2 Hz, 1H), 2.42 – 2.34 (m, 2H), 2.33 (s, 2H), 2.23 (ddd, *J* = 14.5, 11.1, 7.1 Hz, 1H), 1.92– 1.75 (m, 2H), 1.67 – 1.53 (m, 3H), 1.48 (ddd, *J* = 14.2, 11.5, 4.5 Hz, 1H), 1.28-1.17 (m, 2H), 1.16-1.06 (m, 1H), 1.01 (t, *J* = 12.3 Hz, 1H), 0.89 (t, *J* = 7.4, Hz, 3H).

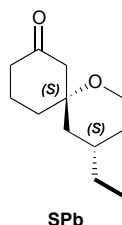
¹³C NMR (100 MHz, CDCl₃): δ 210.2, 76.7, 61.3, 55.7, 42.3, 41.1, 32.4, 31.9, 30.0, 28.7, 20.4, 11.0.

[α]_D²⁰ = +29.8 (*c* = 1, CHCl₃)

LRMS (ESI): *m/z* 197.2 [M+H]⁺ 219.1 [M+Na]⁺

HRMS (ESI): *m/z* calcd for C₁₂H₂₀O₂Na : 219.1356 [M+Na]⁺; found 219.1361 (2 ppm).

(4*S*,6*S*)-4-Ethyl-1-oxaspiro[5.5]undecan-8-one SPb



¹H NMR (400 MHz, CDCl₃): δ 3.72 (ddd, *J* = 12.0, 5.2, 1.6 Hz, 1H), 3.61 (td, *J* = 12.4, 2.3 Hz, 1H), 2.93 (dt, *J* = 14.0, 1.9 Hz, 1H), 2.39 – 2.22 (m, 3H), 2.14 – 2.02 (m, 1H), 1.86 – 1.71 (m, 3H), 1.65 – 1.58 (m, 2H), 1.57-1.45 (m, 1H), 1.26-1.17 (m, 2H), 1.17 – 1.02 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

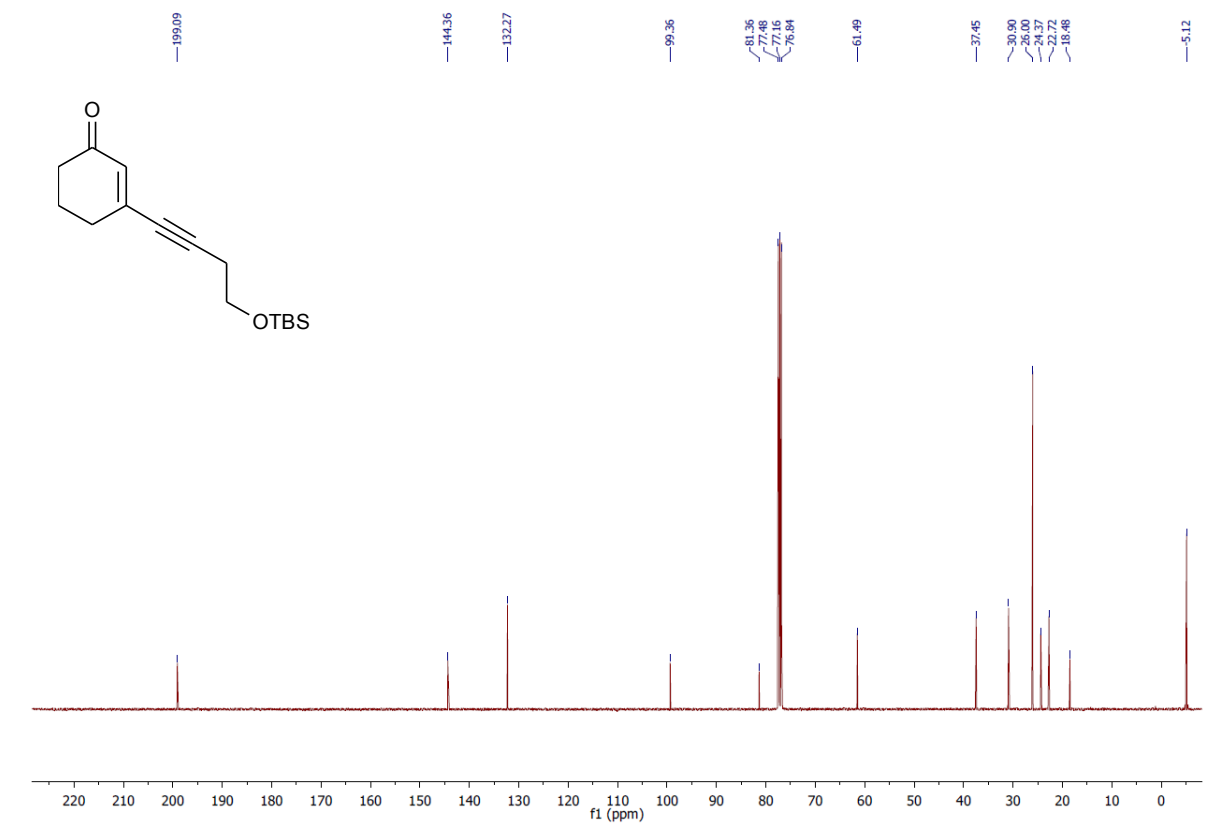
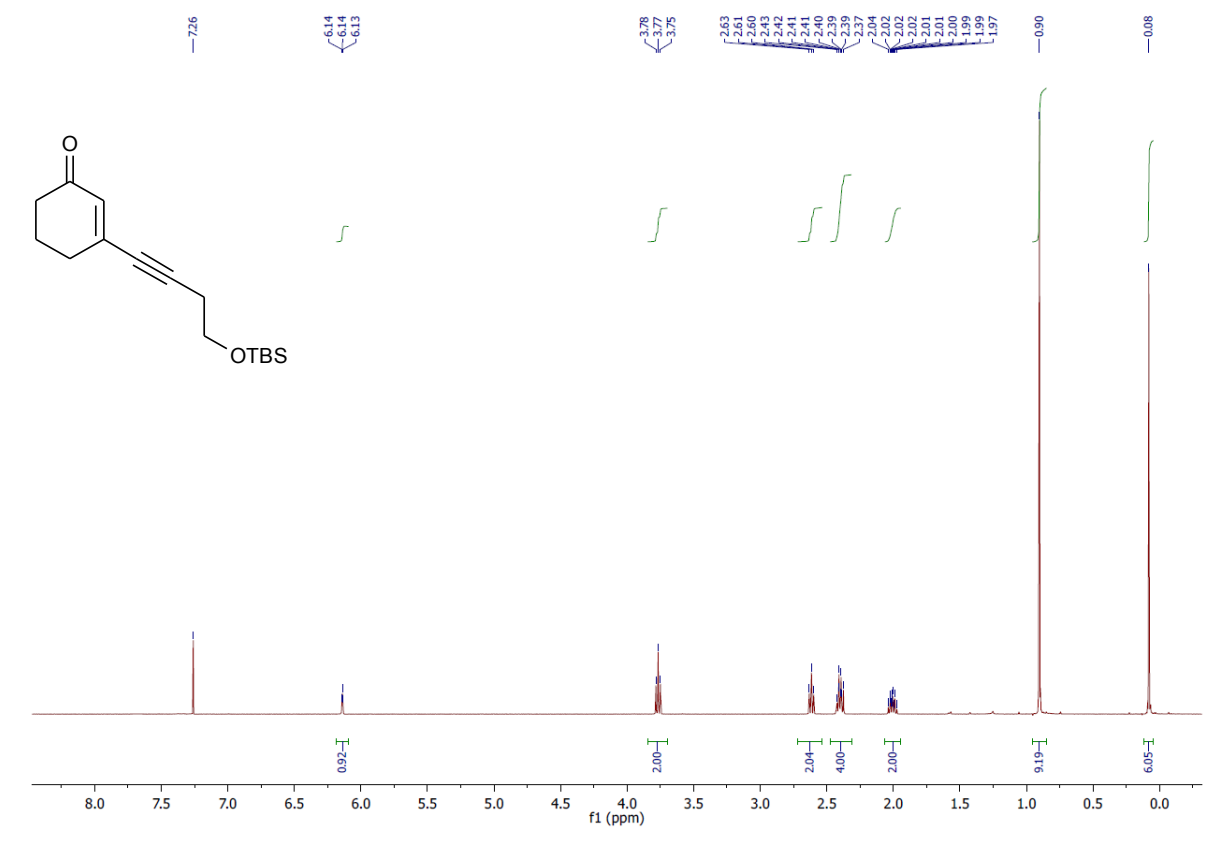
¹³C NMR (100 MHz, CDCl₃): δ 210.3, 76.8, 61.5, 46.6, 42.4, 41.0, 39.0, 32.3, 31.8, 29.9, 20.8, 11.0.

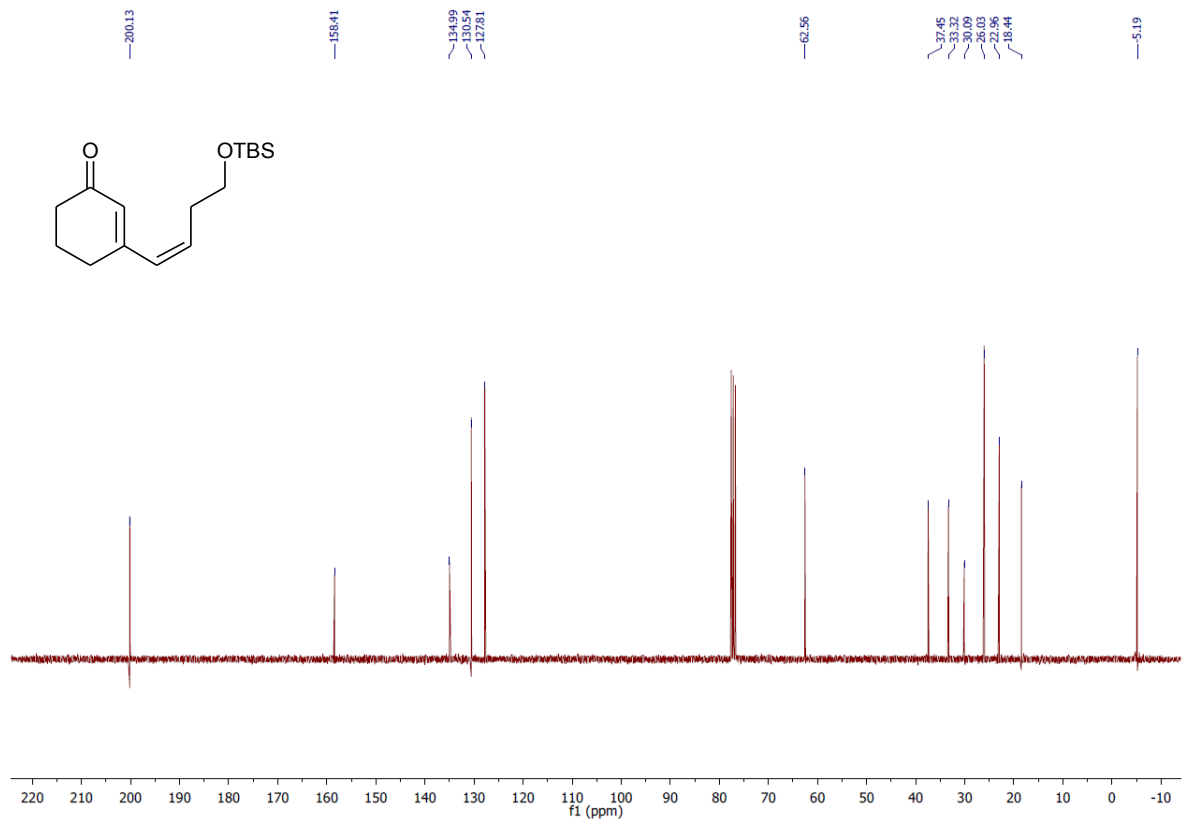
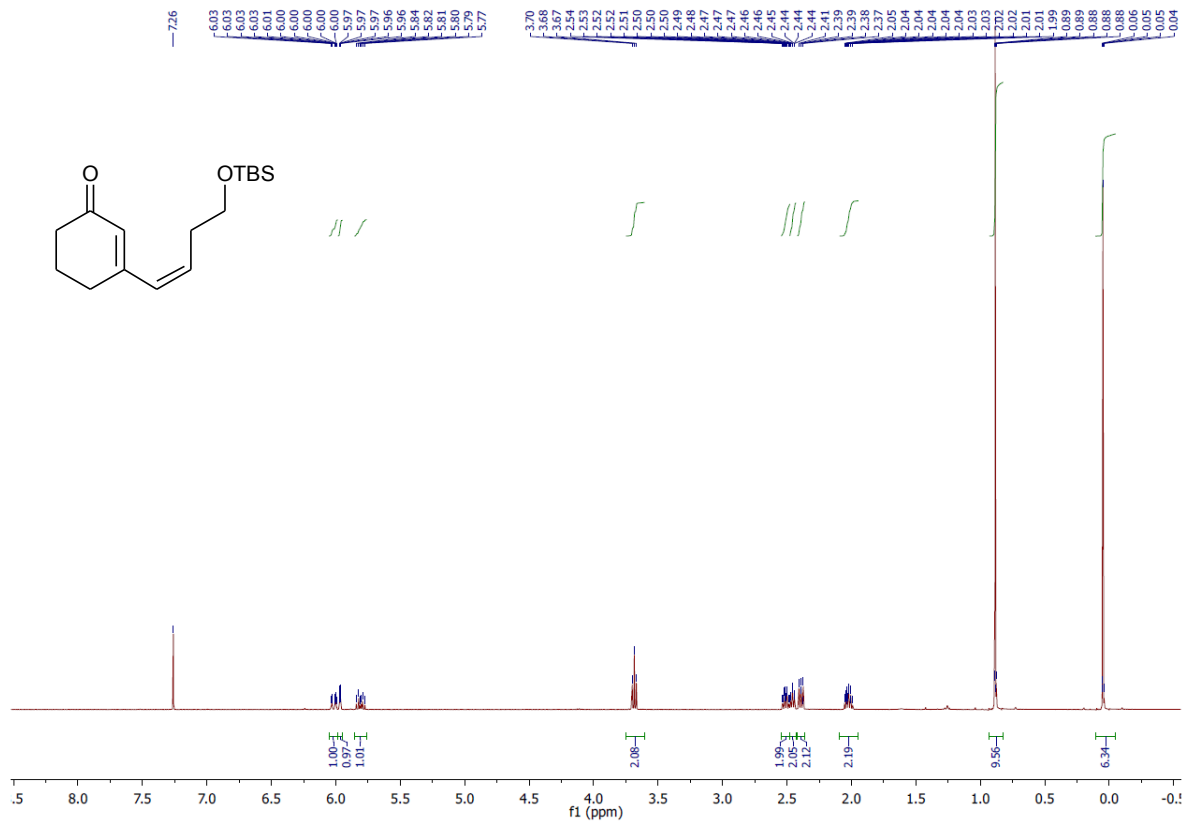
[α]_D²⁰ = +19.0 (*c* = 1, CHCl₃)

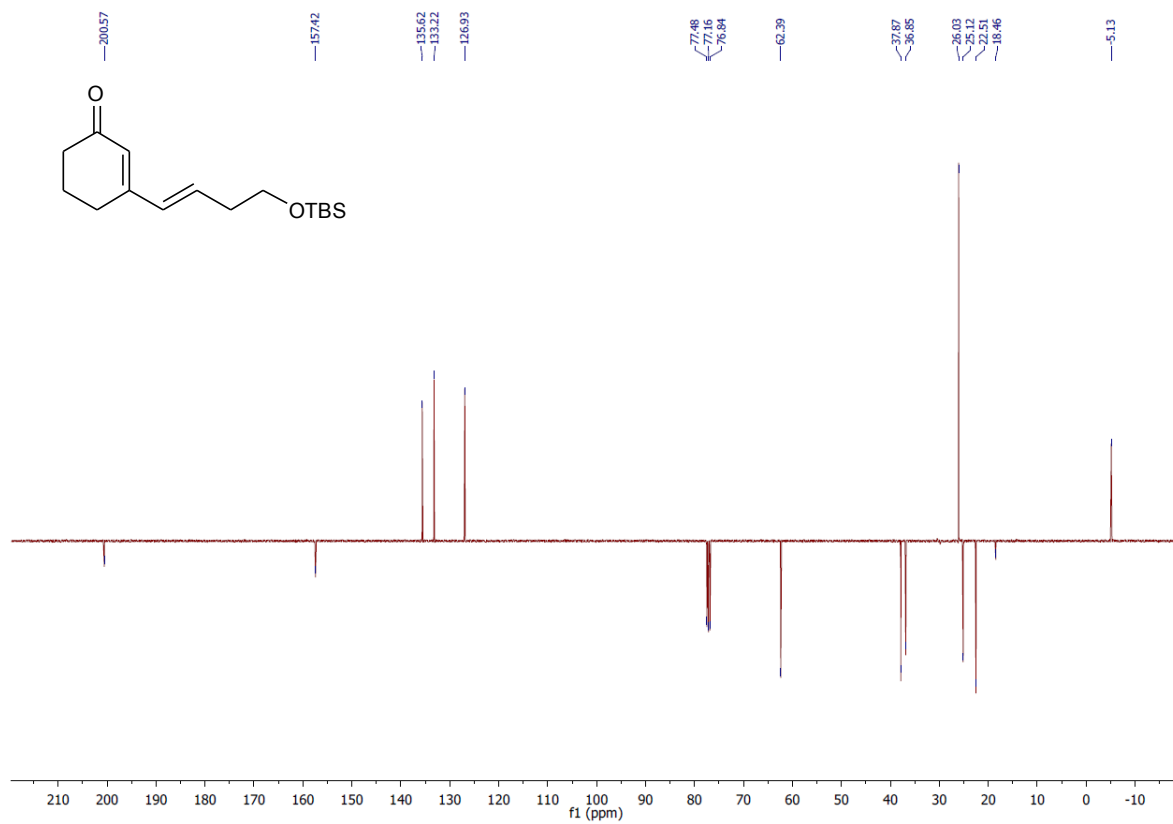
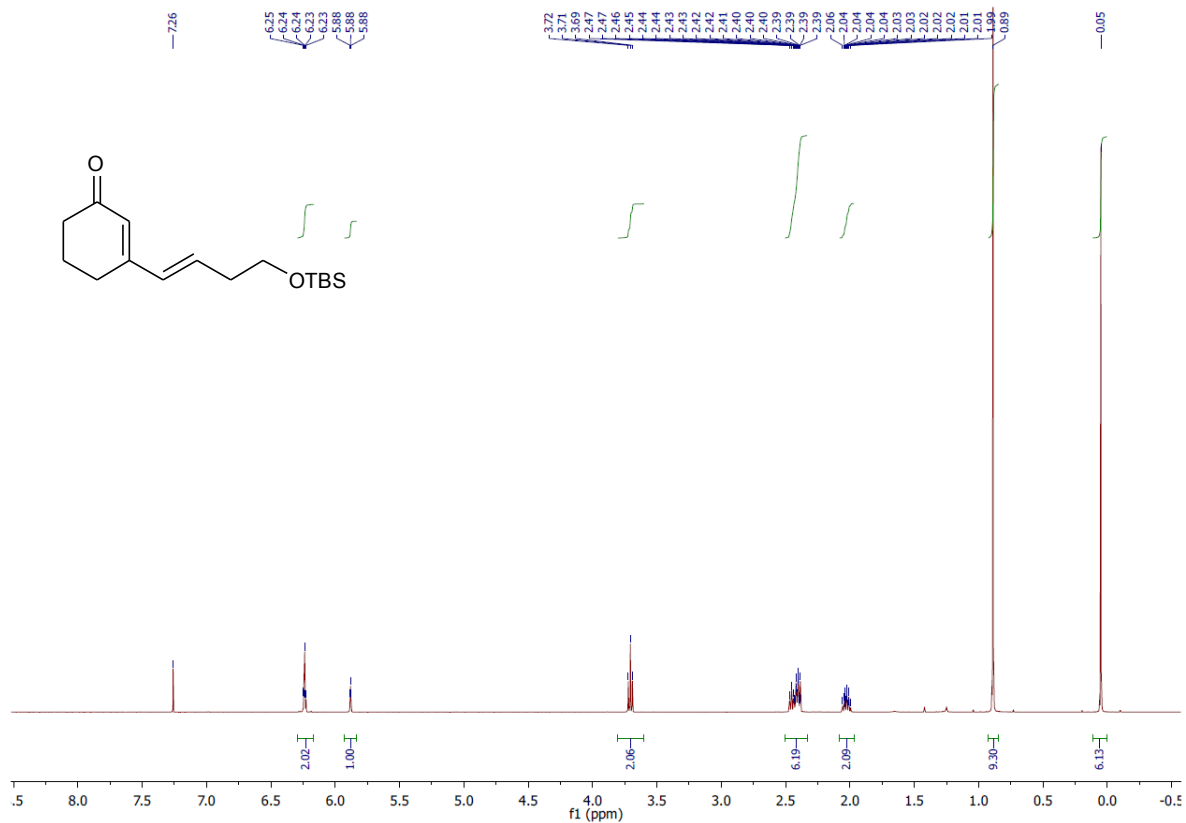
LRMS (ESI): *m/z* 197.2 [M+H]⁺, 219.1 [M+Na]⁺

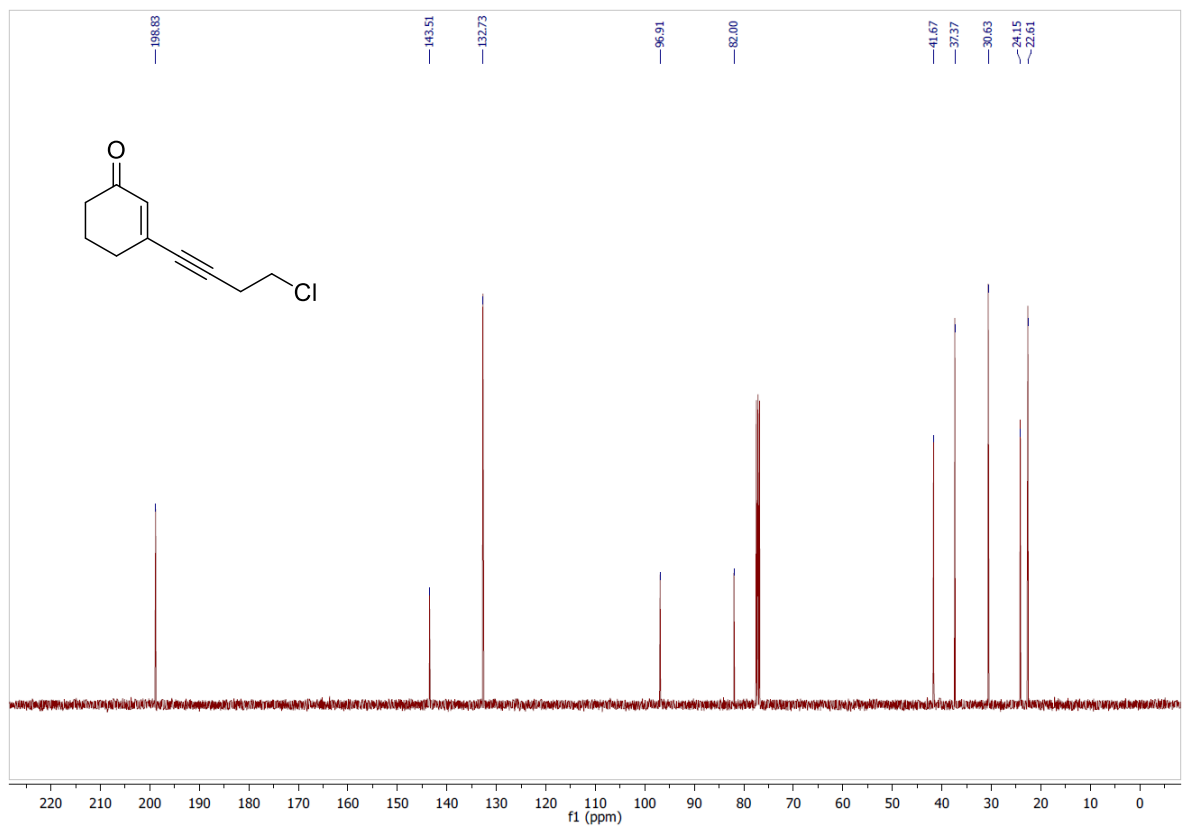
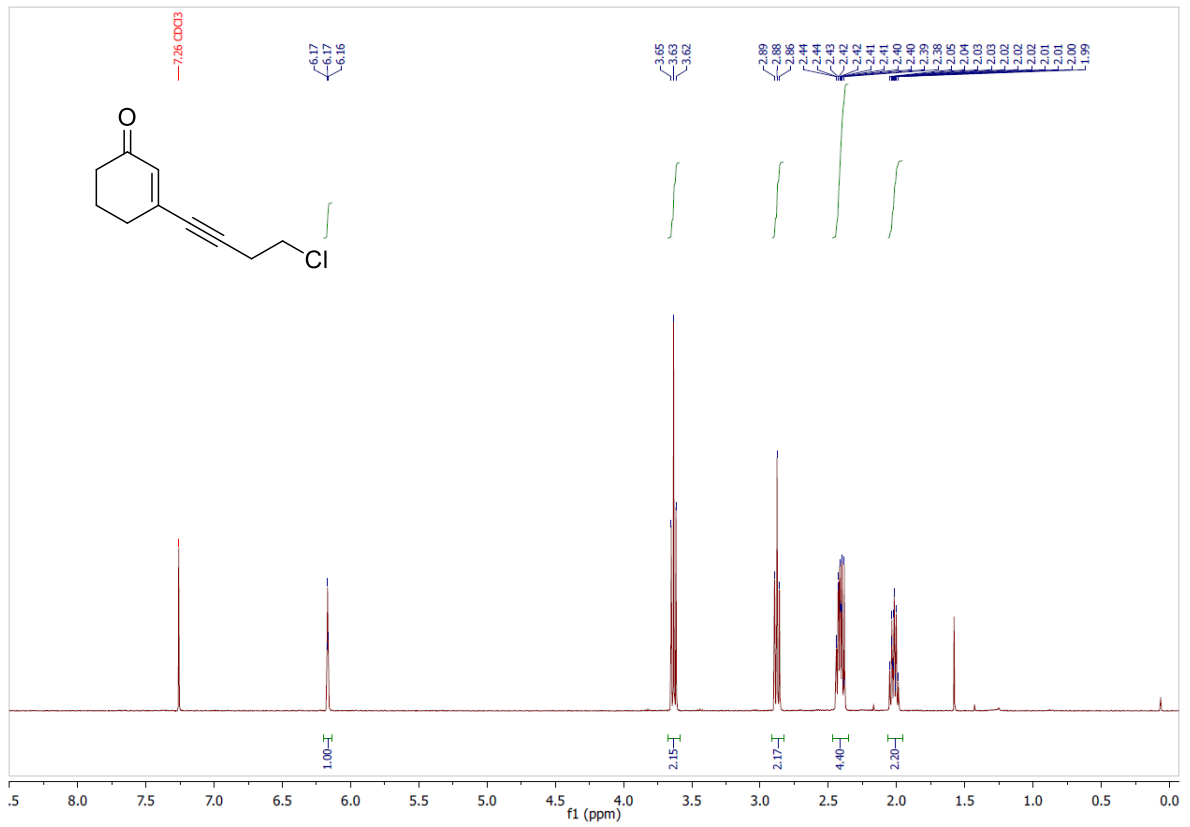
HRMS (ESI): *m/z* calcd for C₁₂H₂₀O₂Na : 219.1356 [M+Na]⁺ ; found 219.1361 (2 ppm)

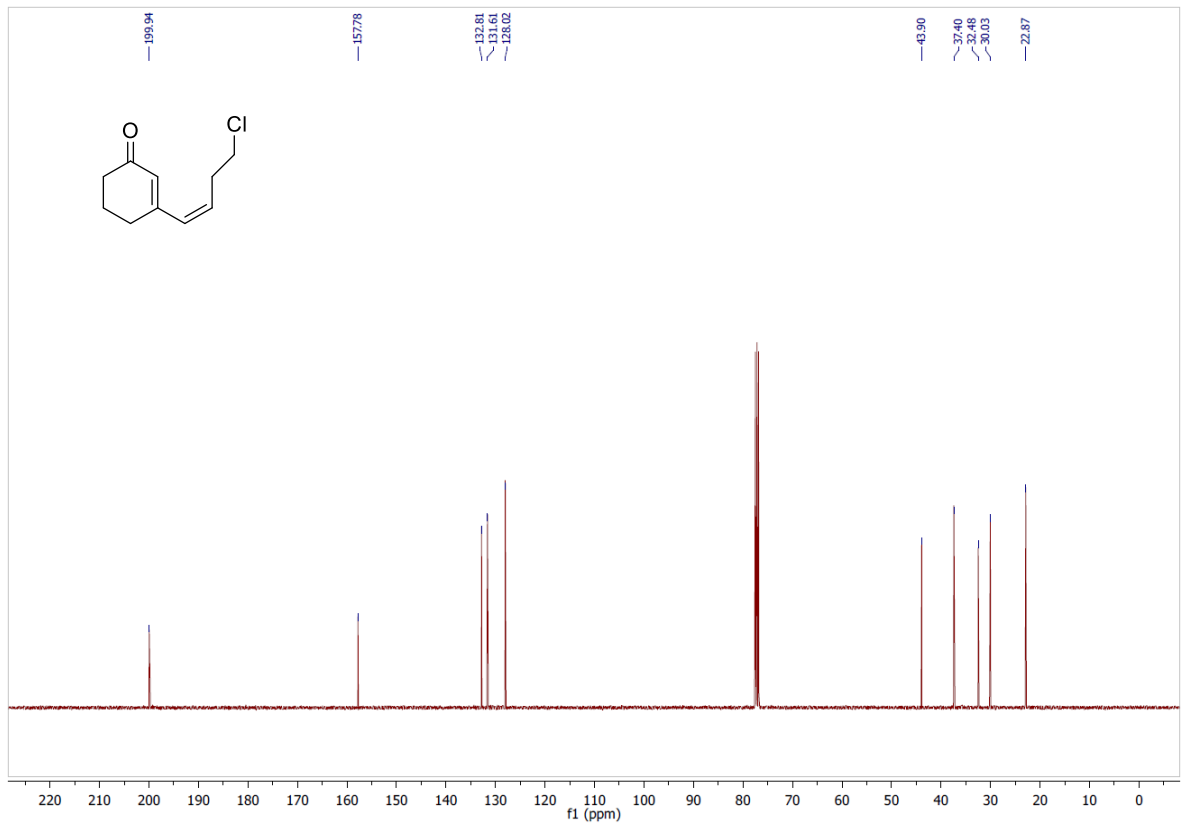
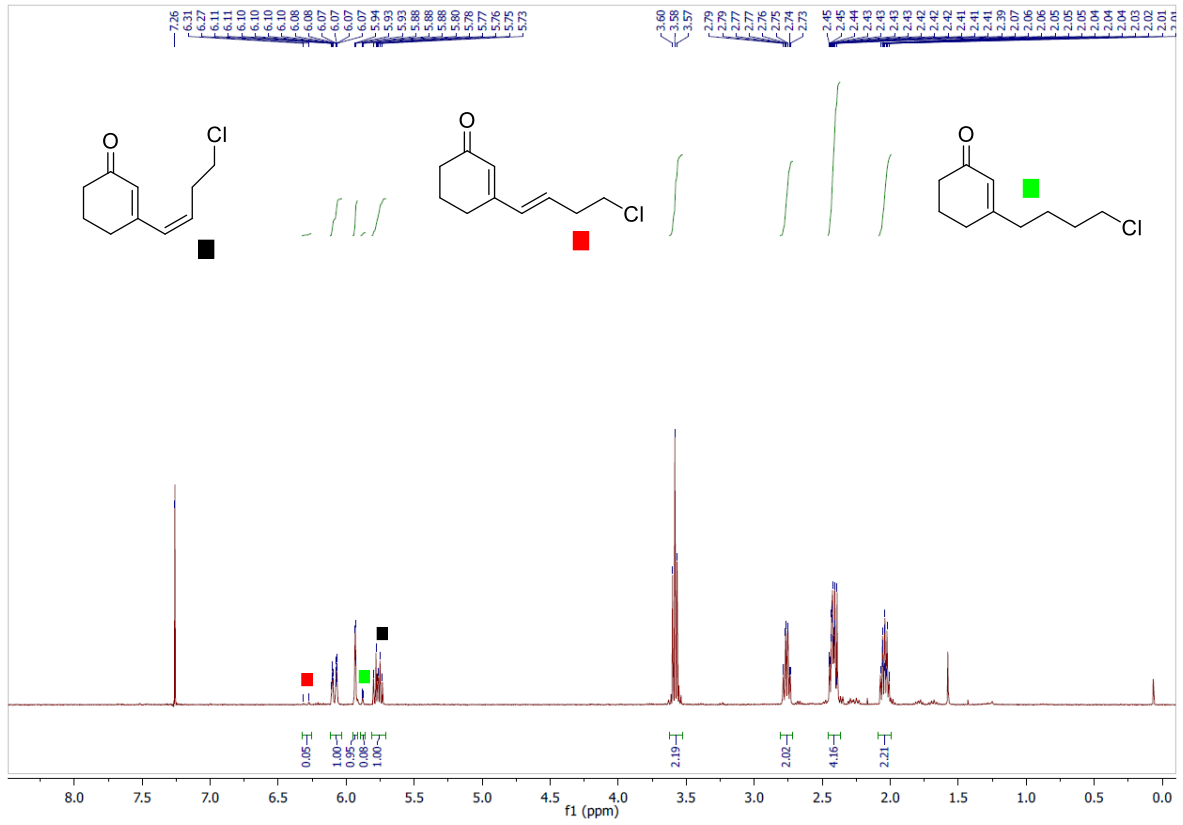
11. NMR spectra

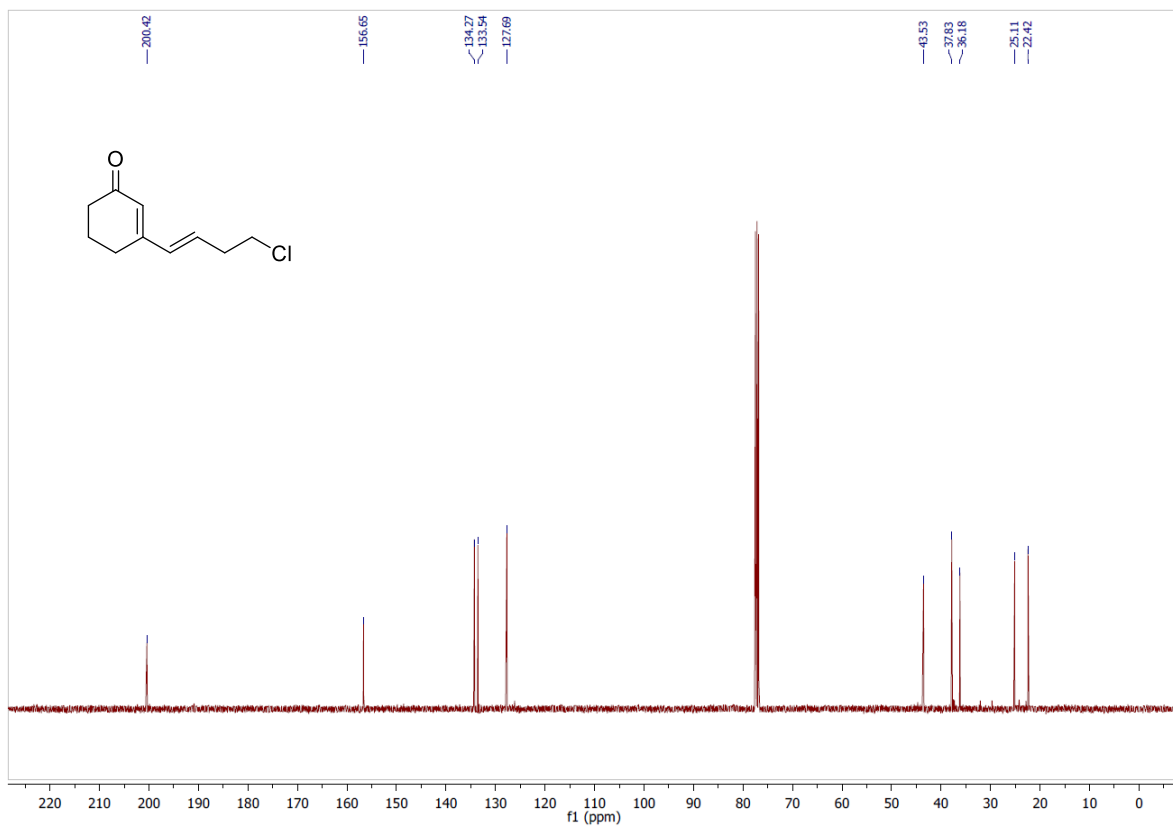
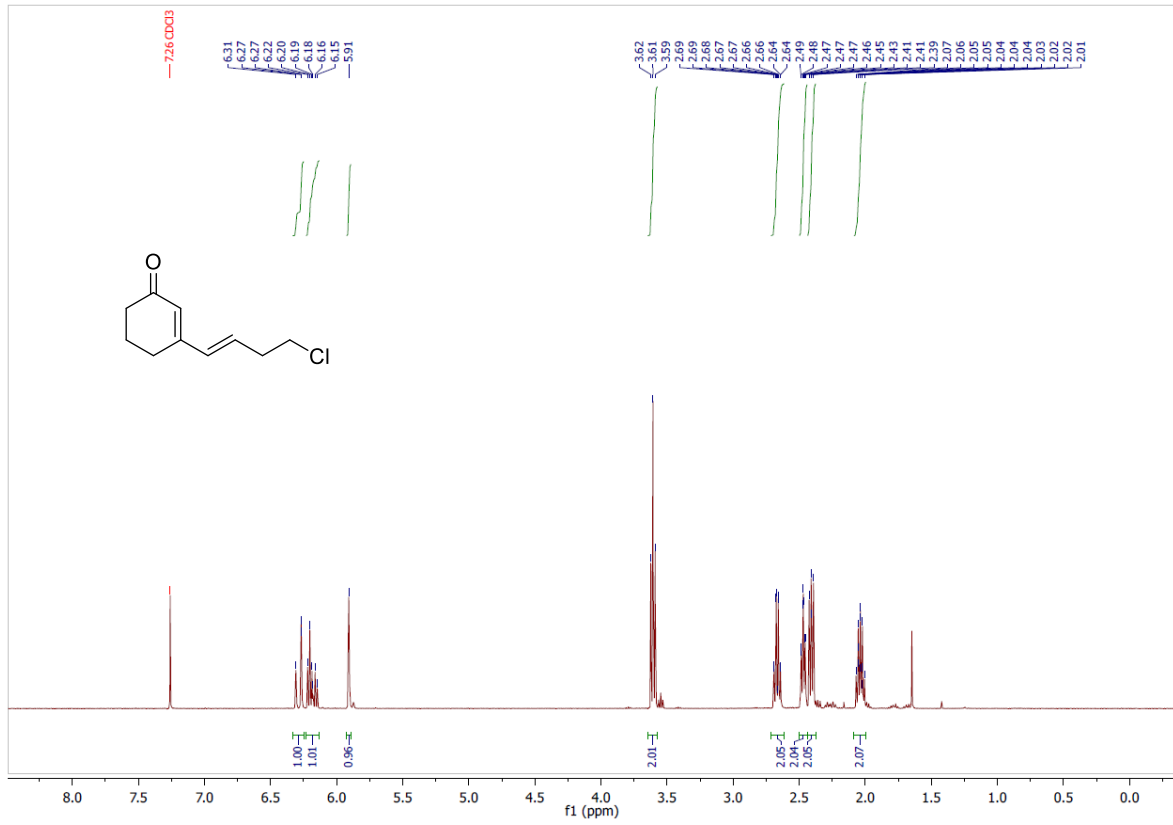


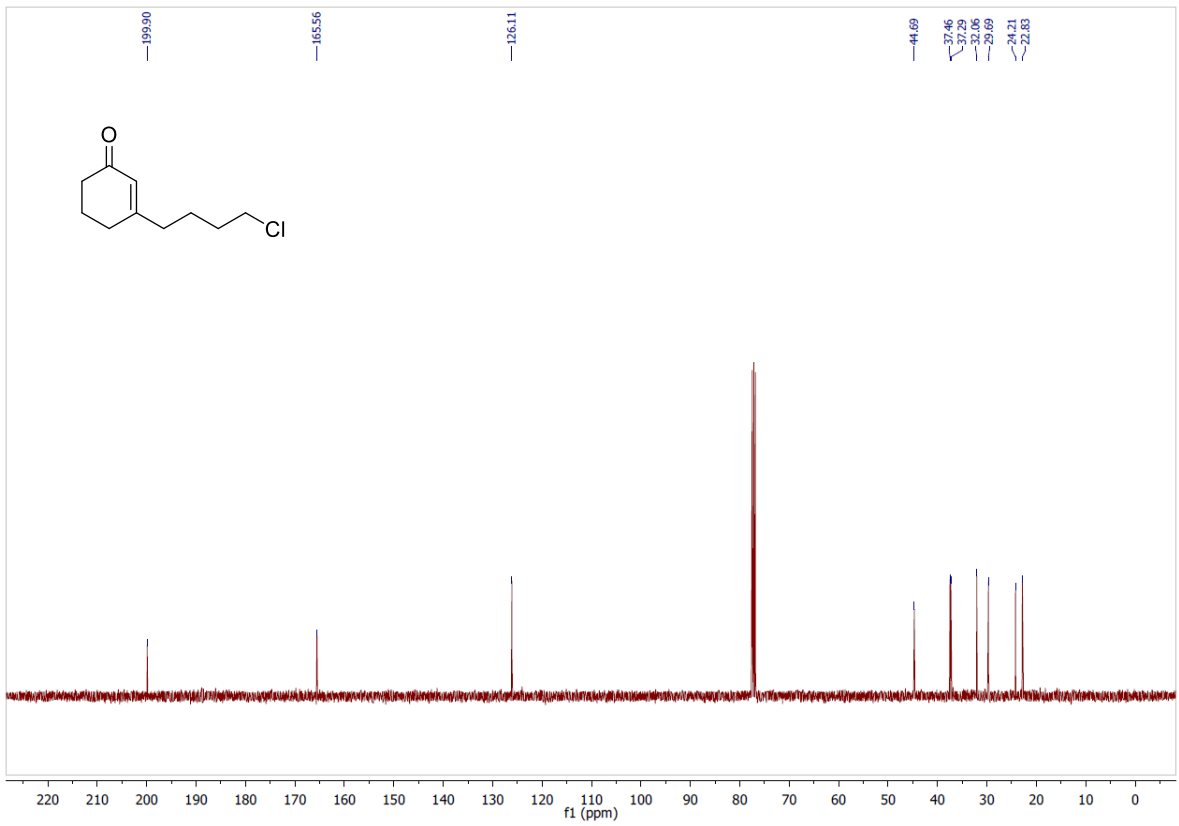
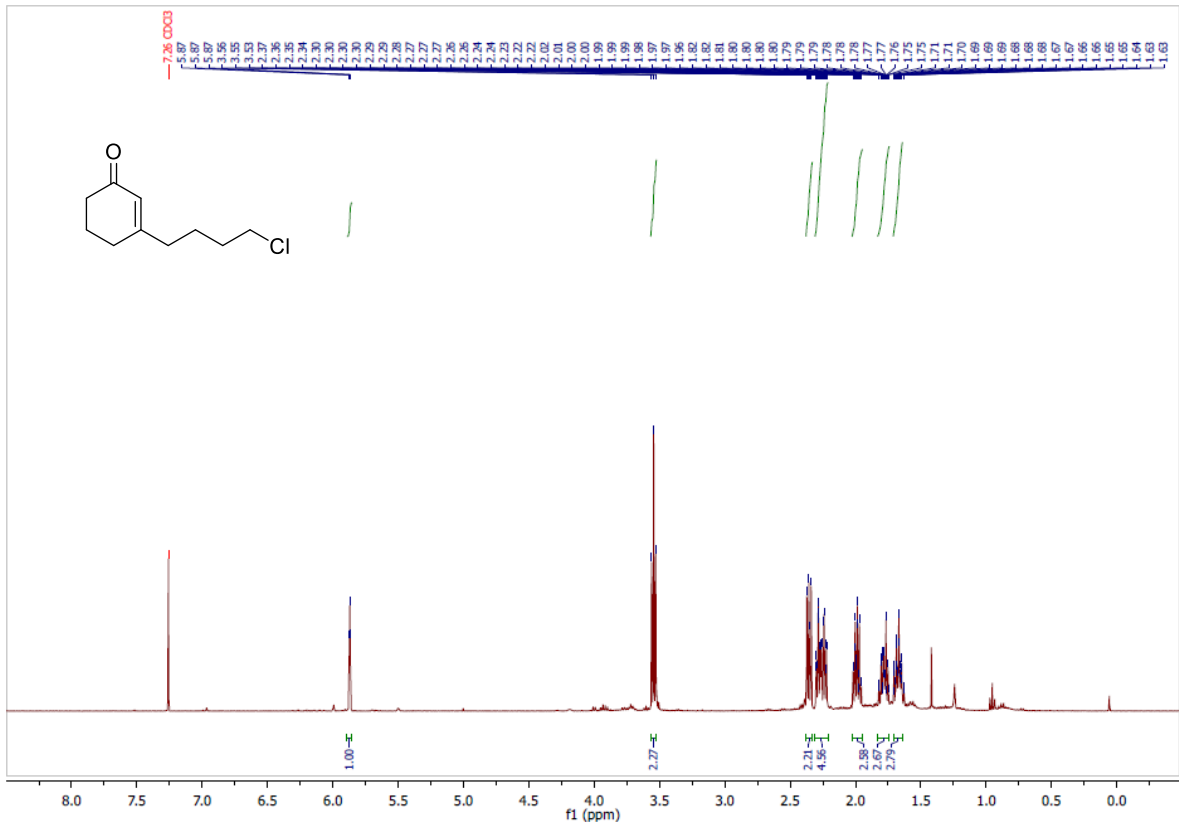


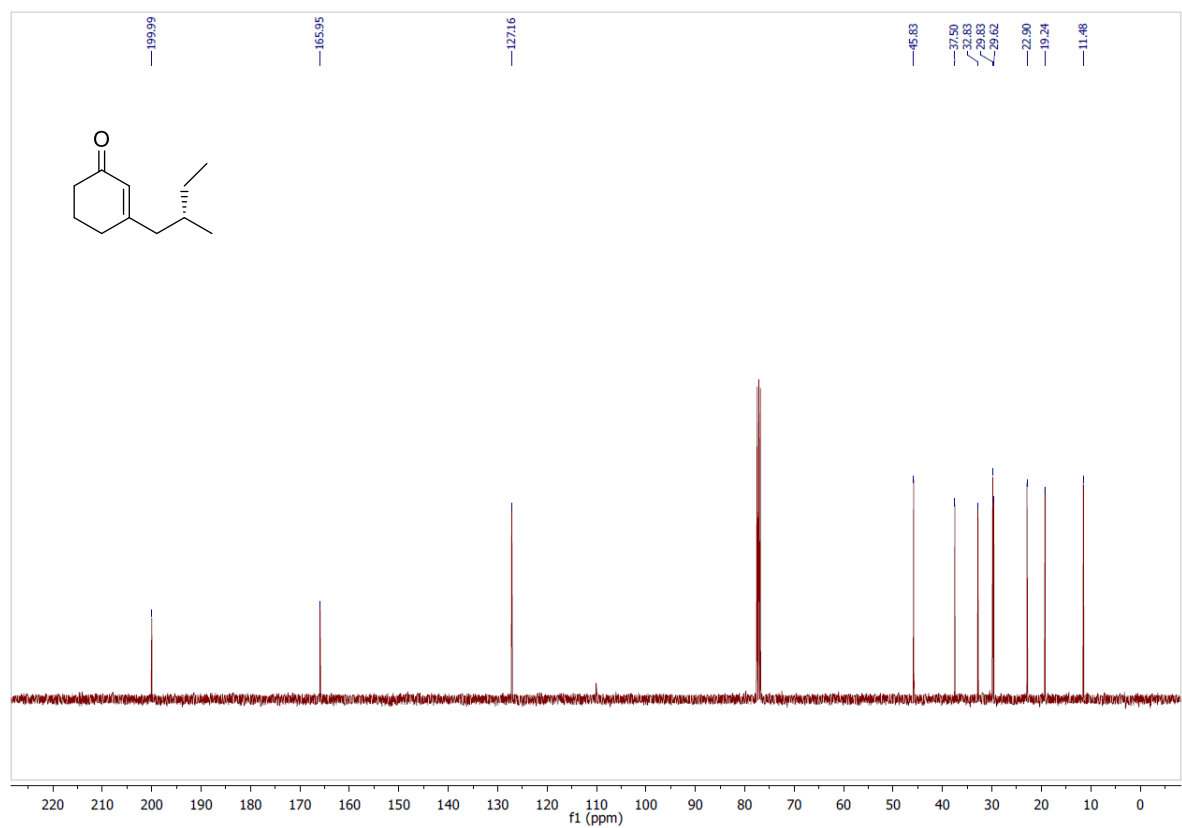
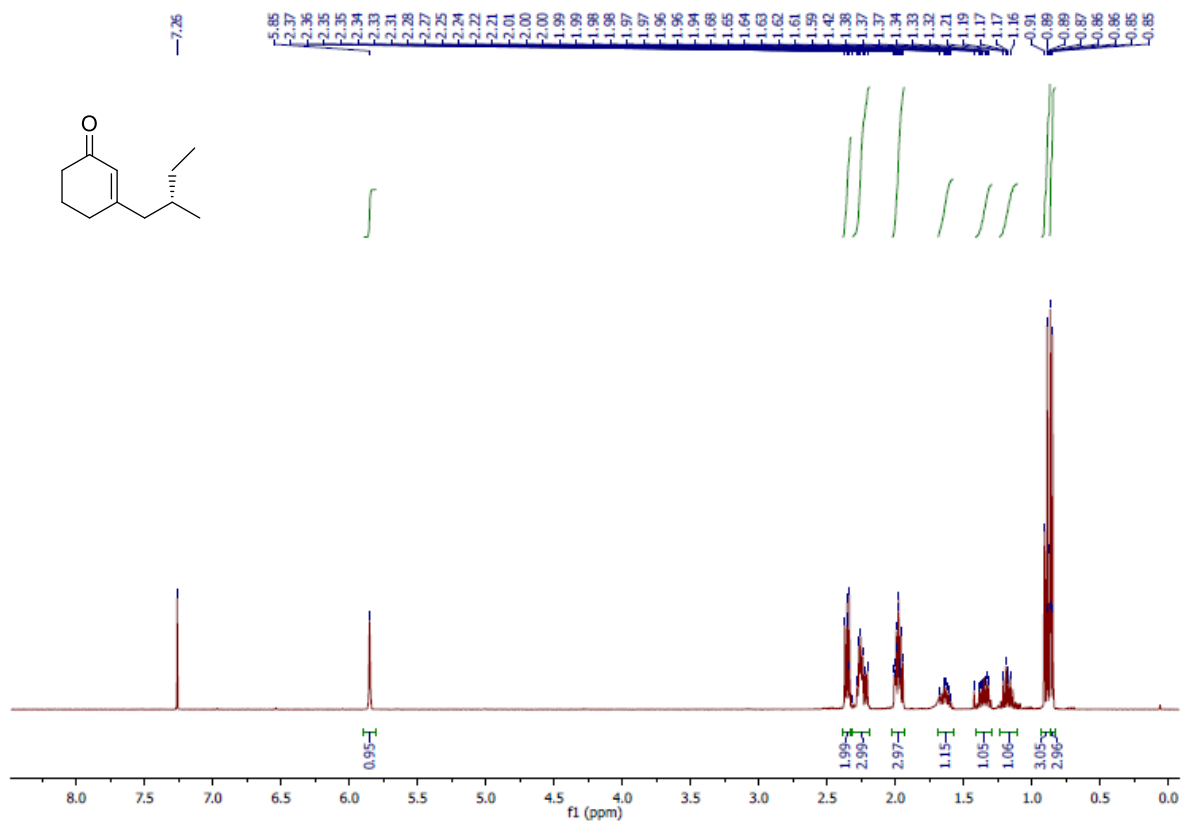


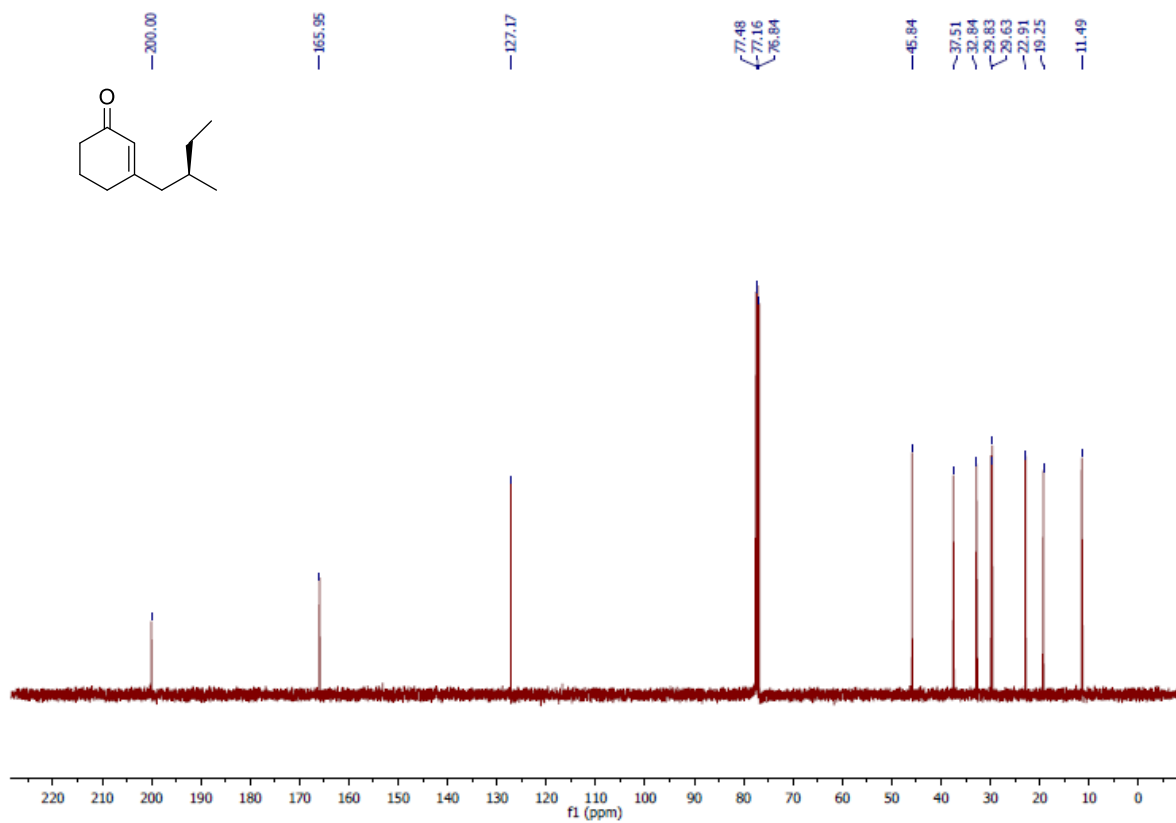
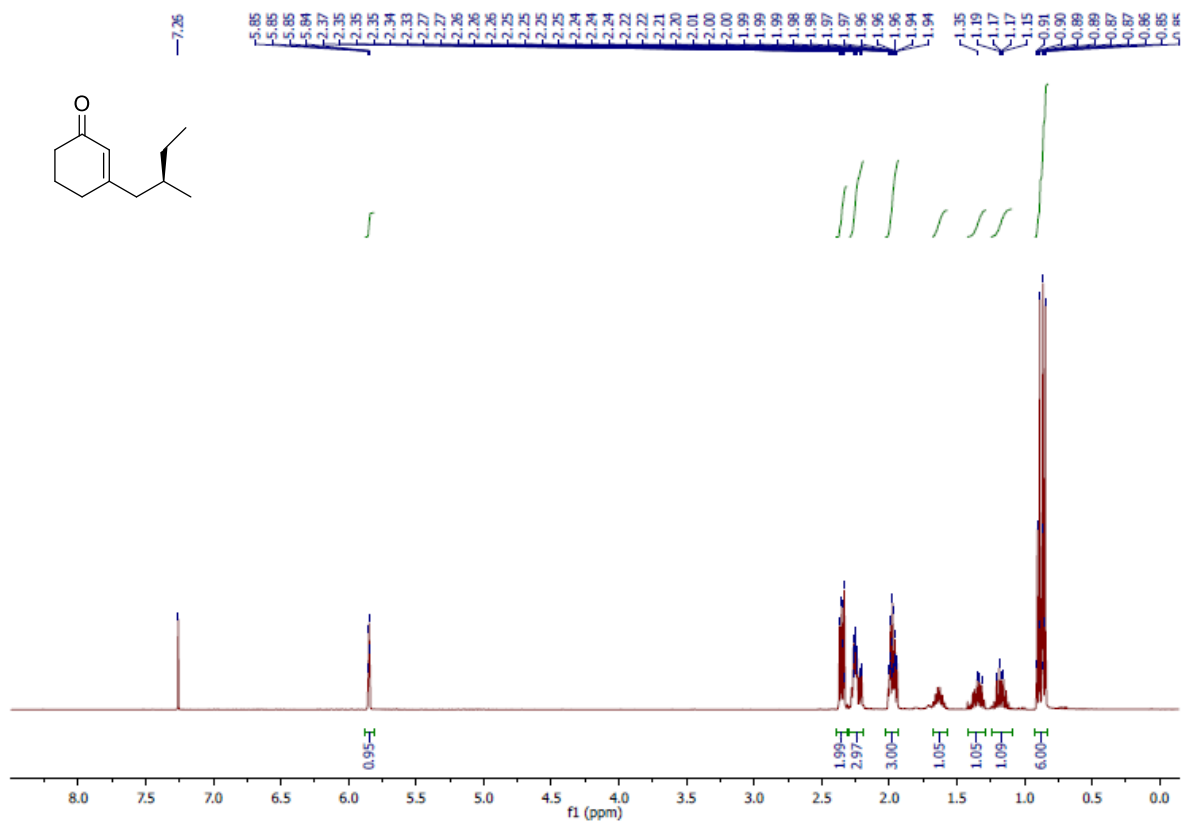


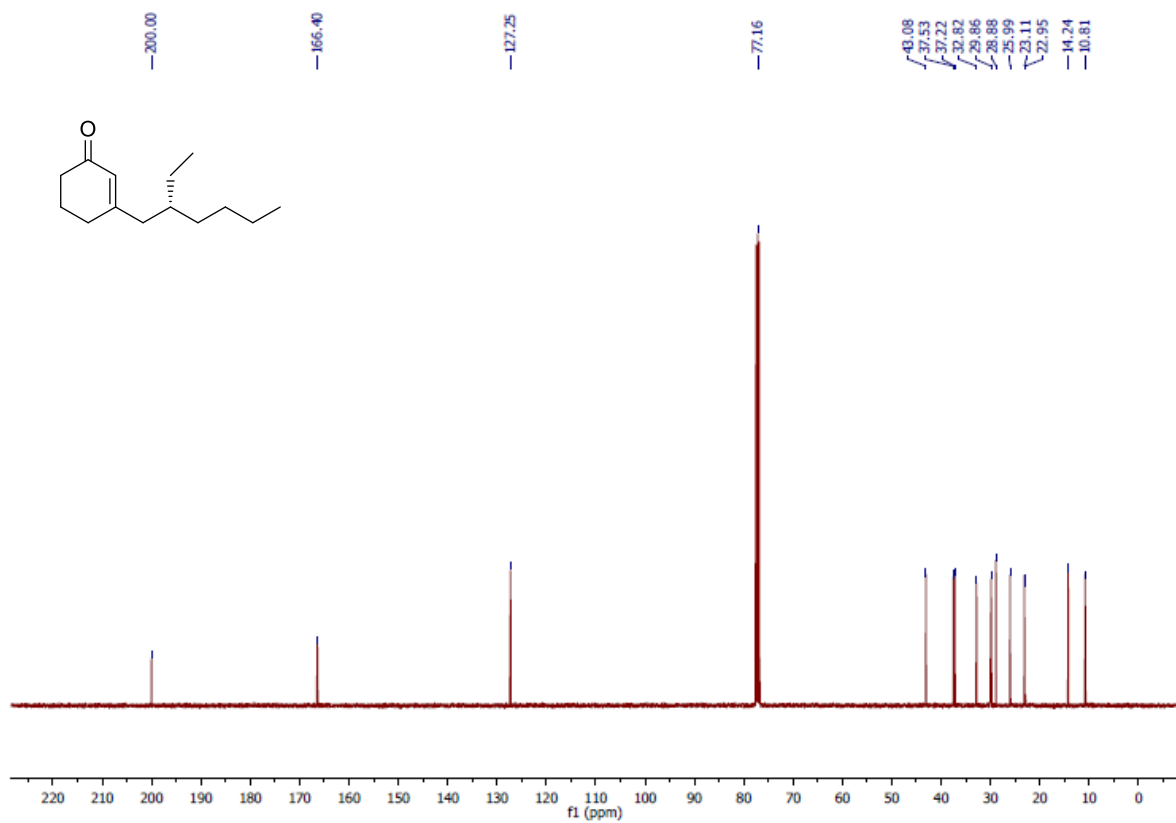
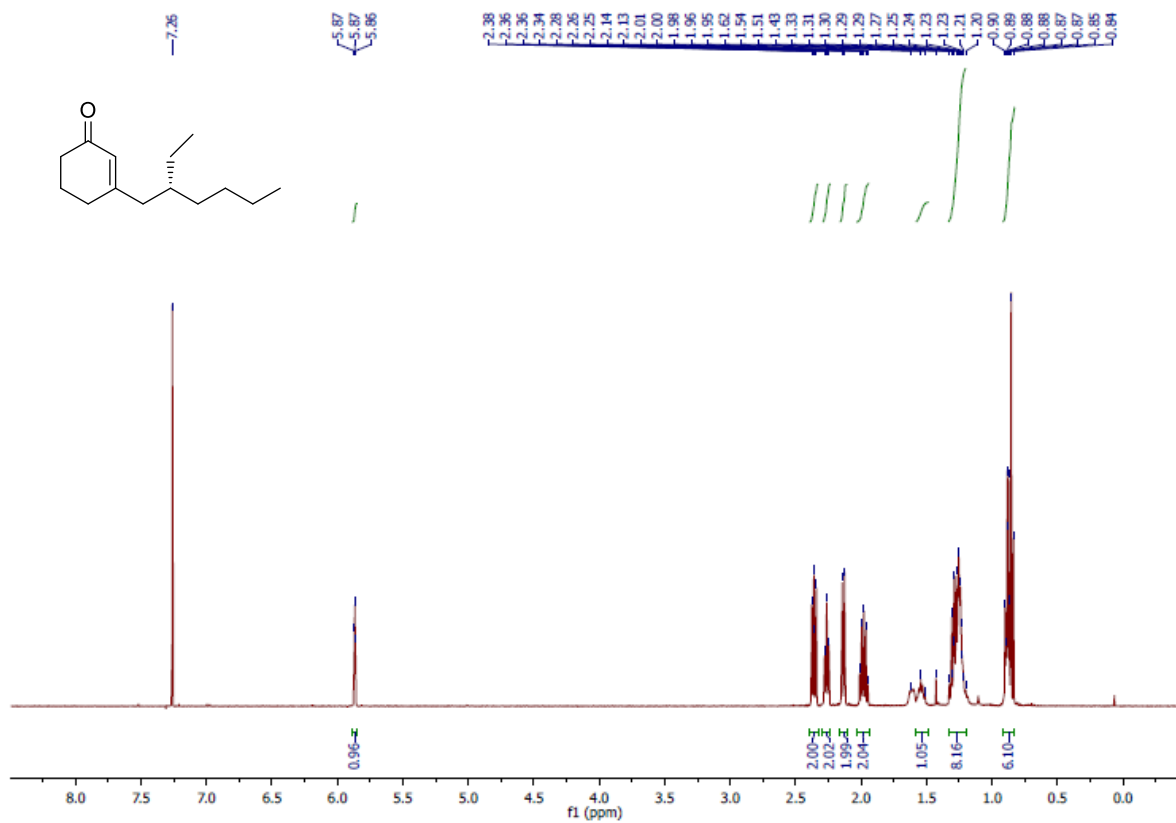


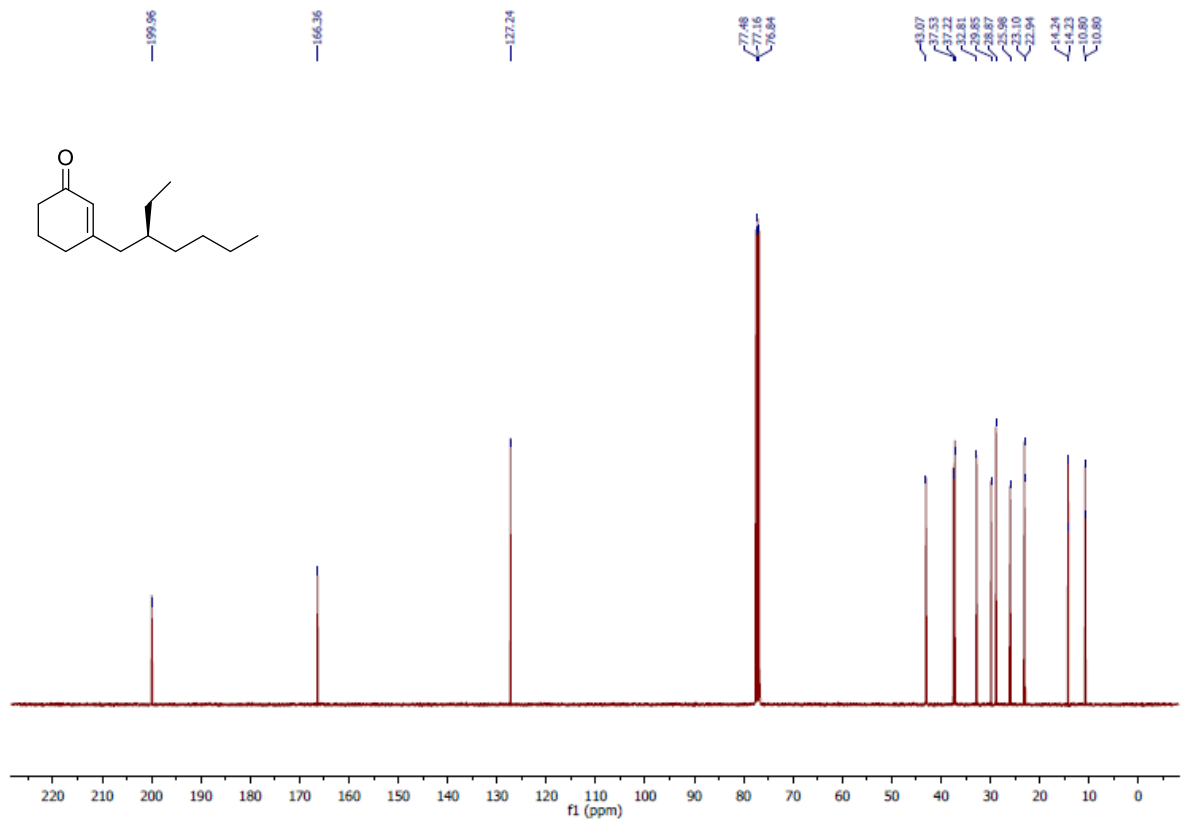
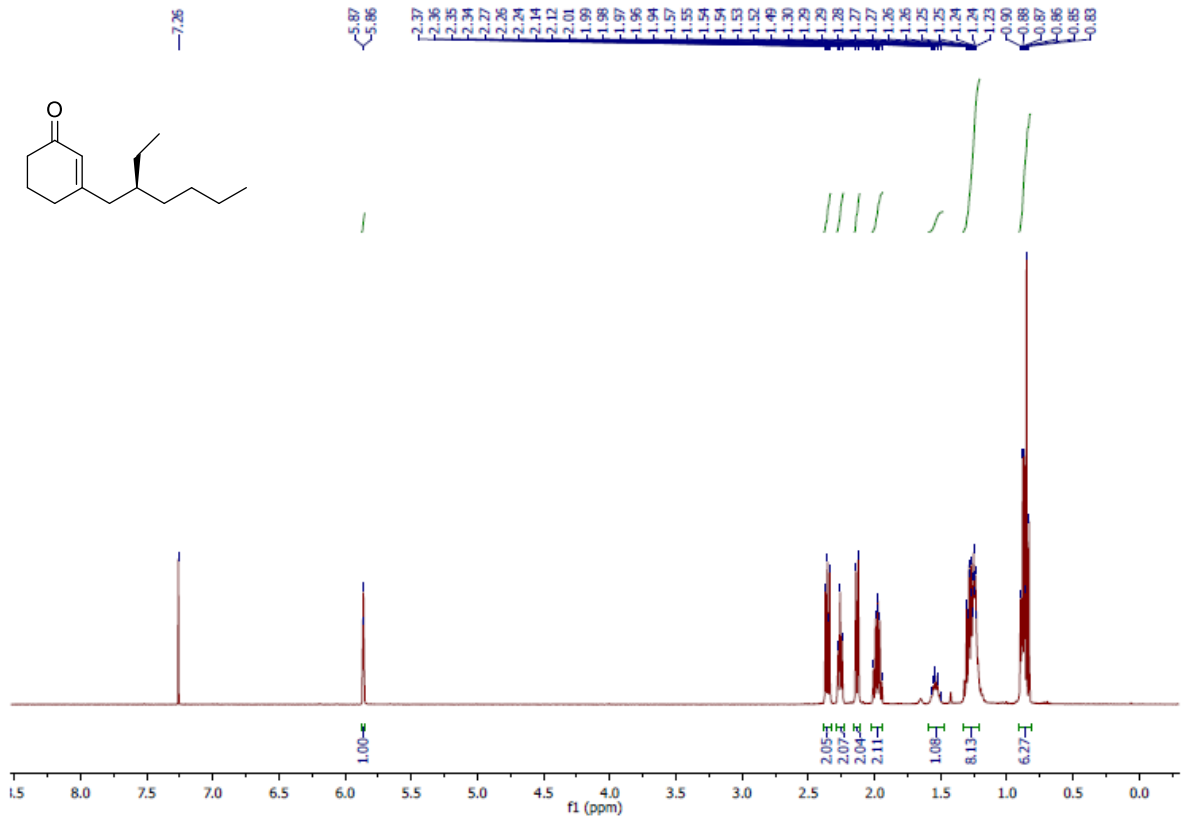


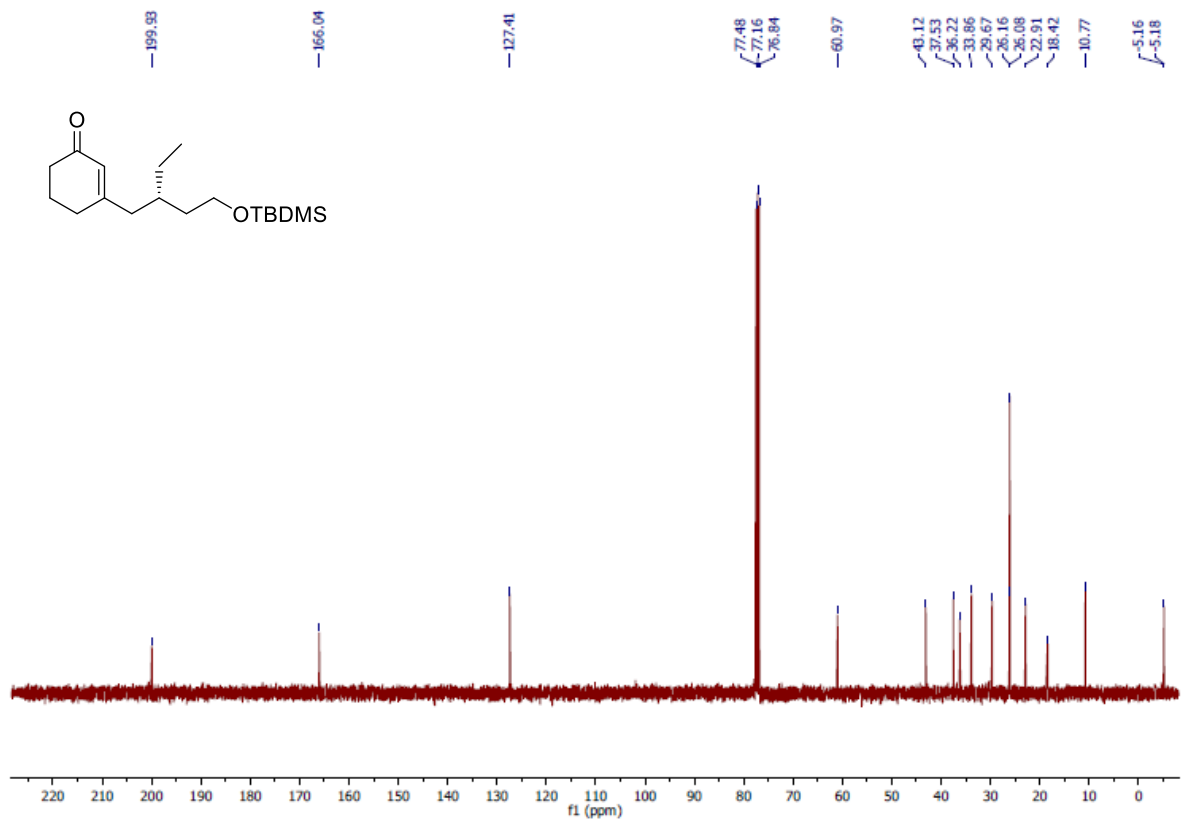
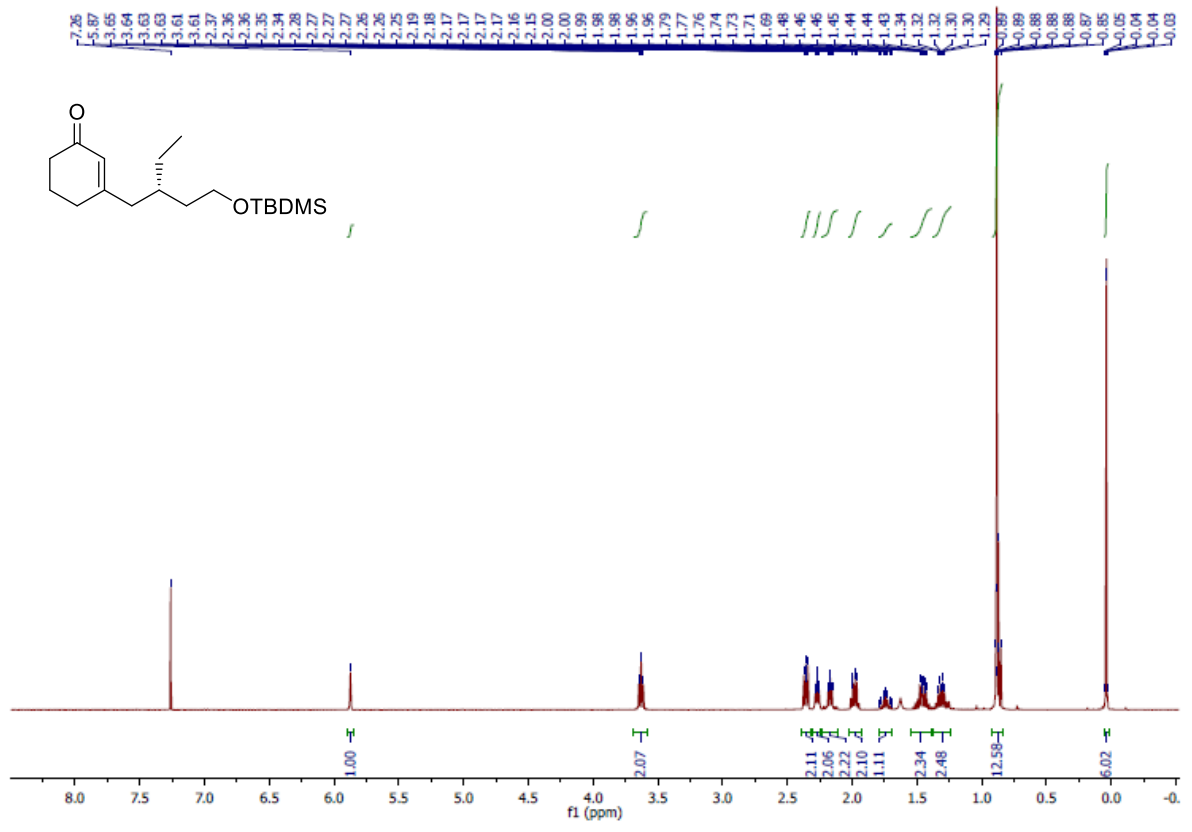


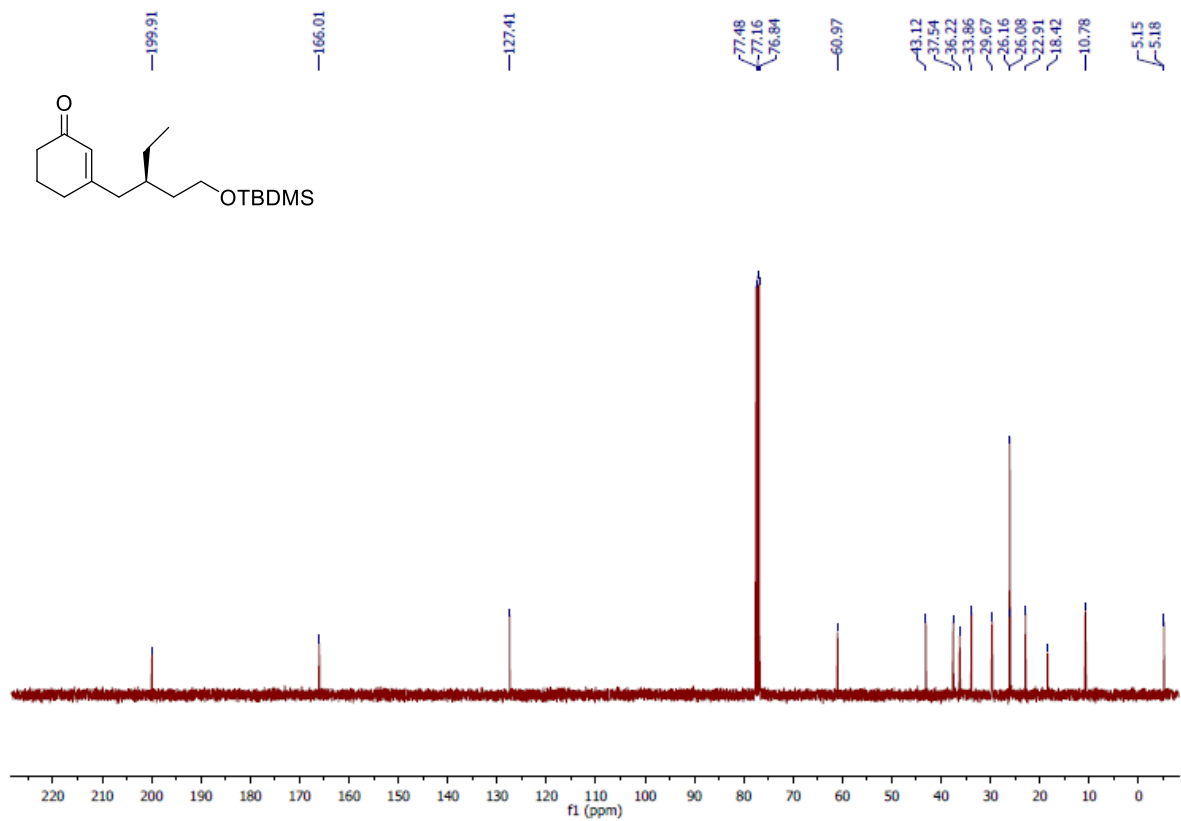
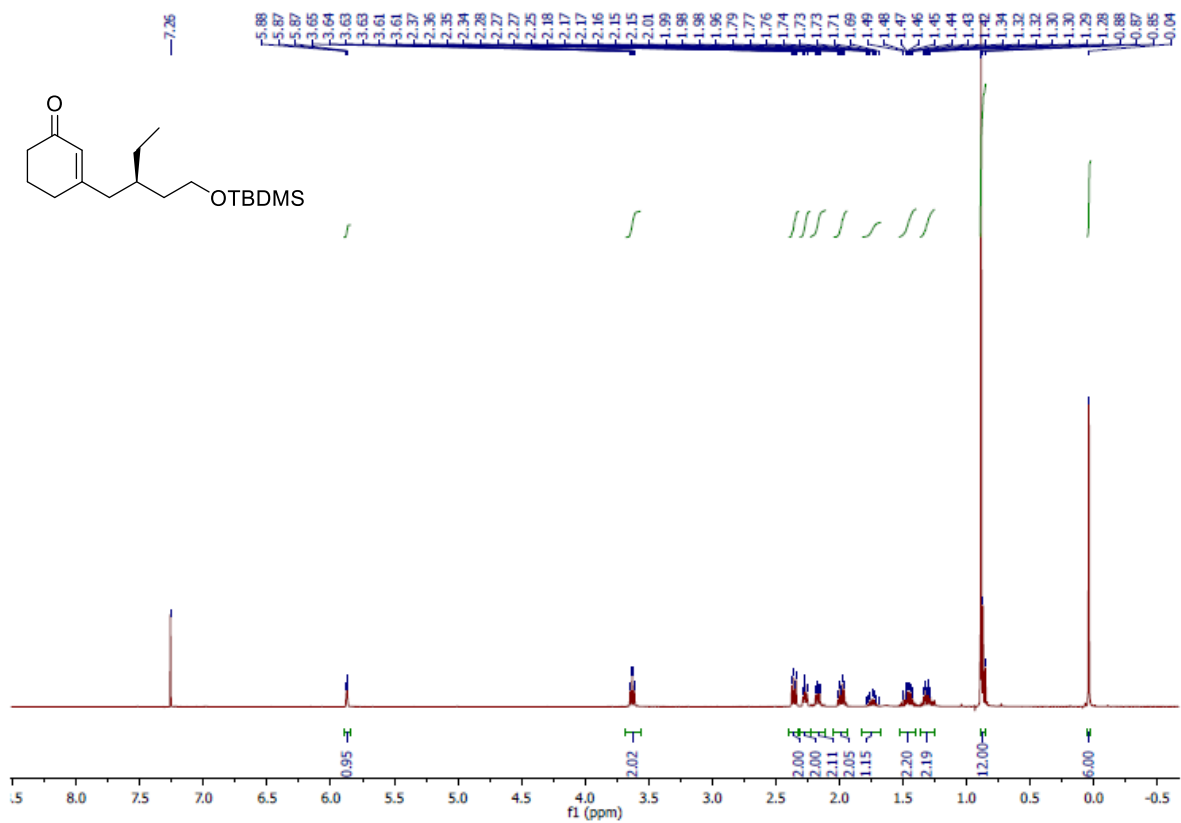


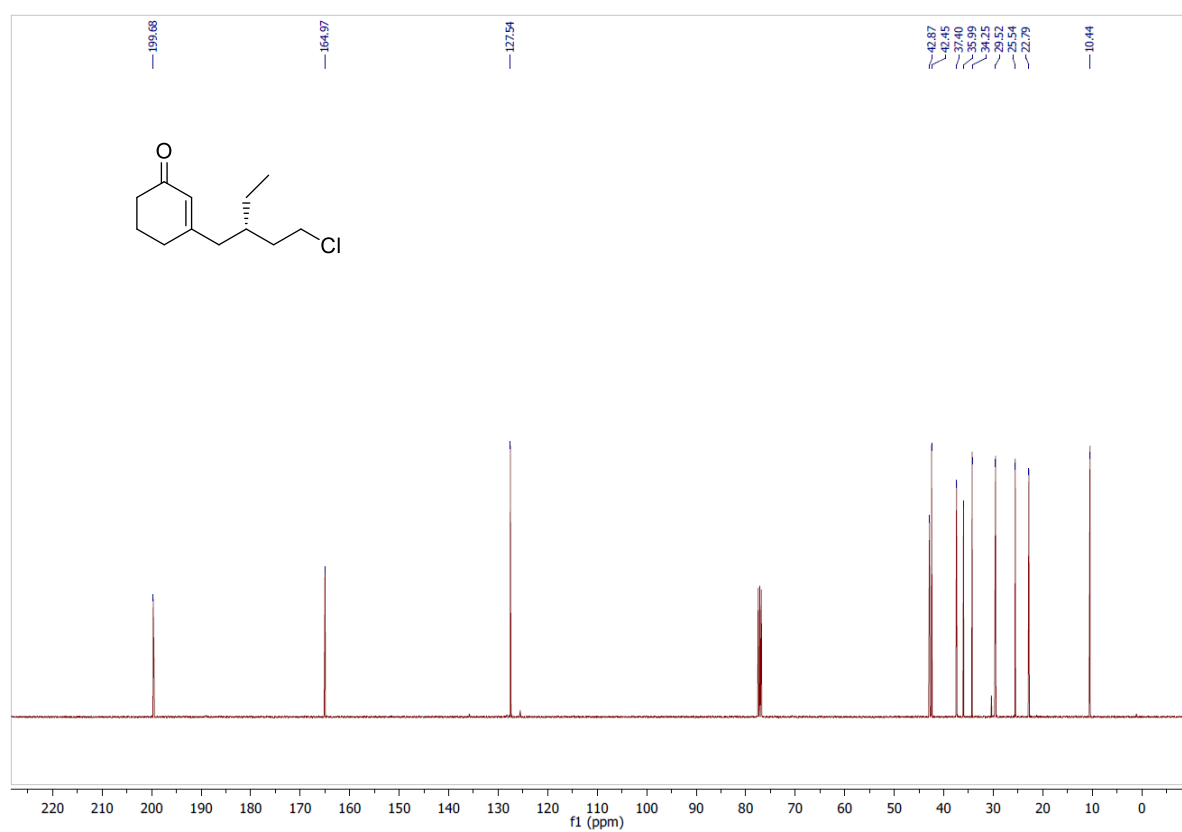
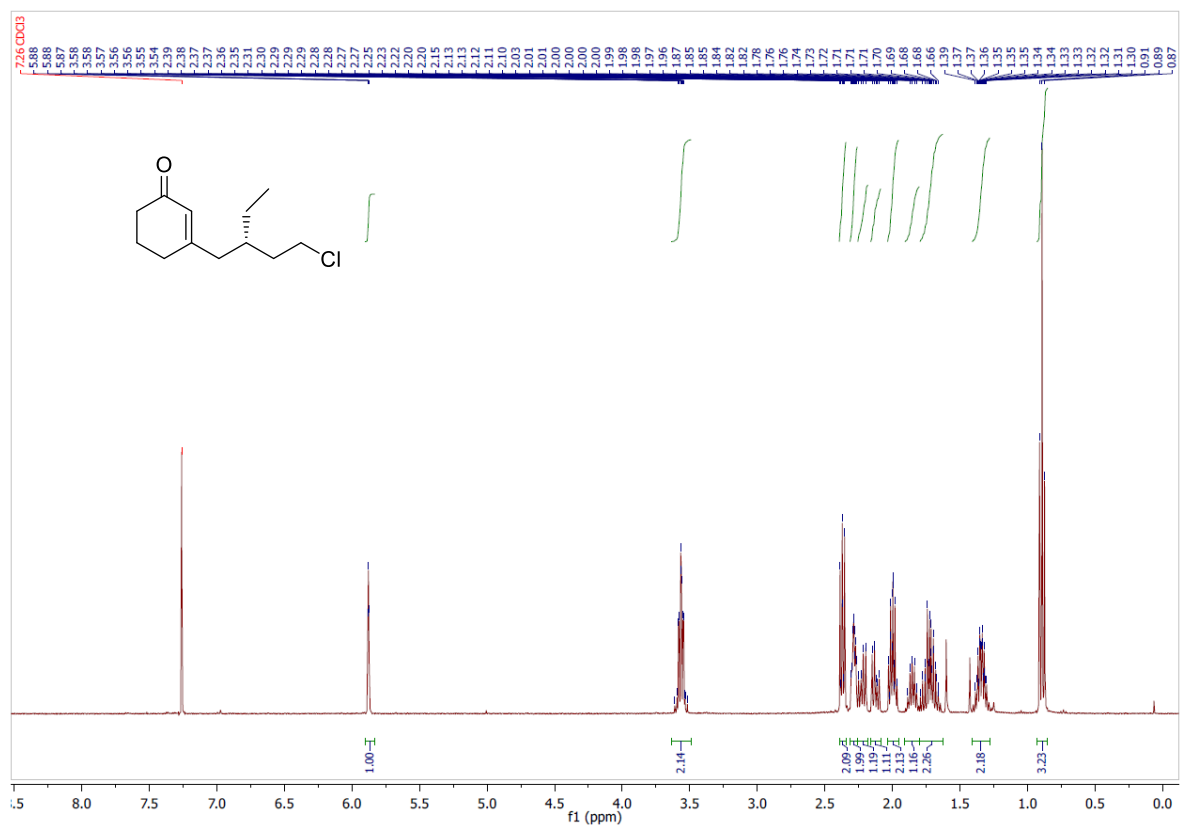


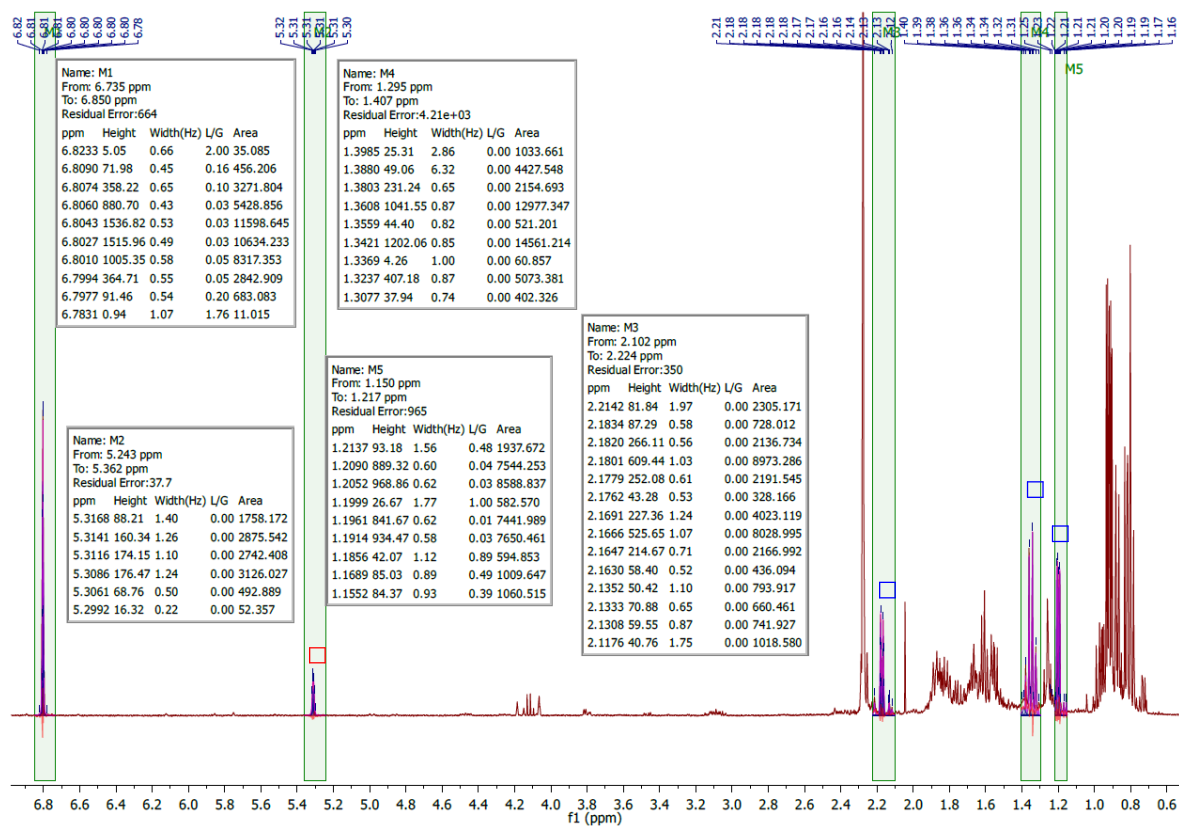
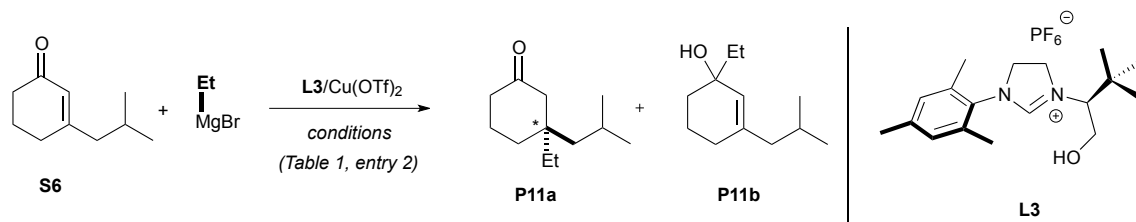


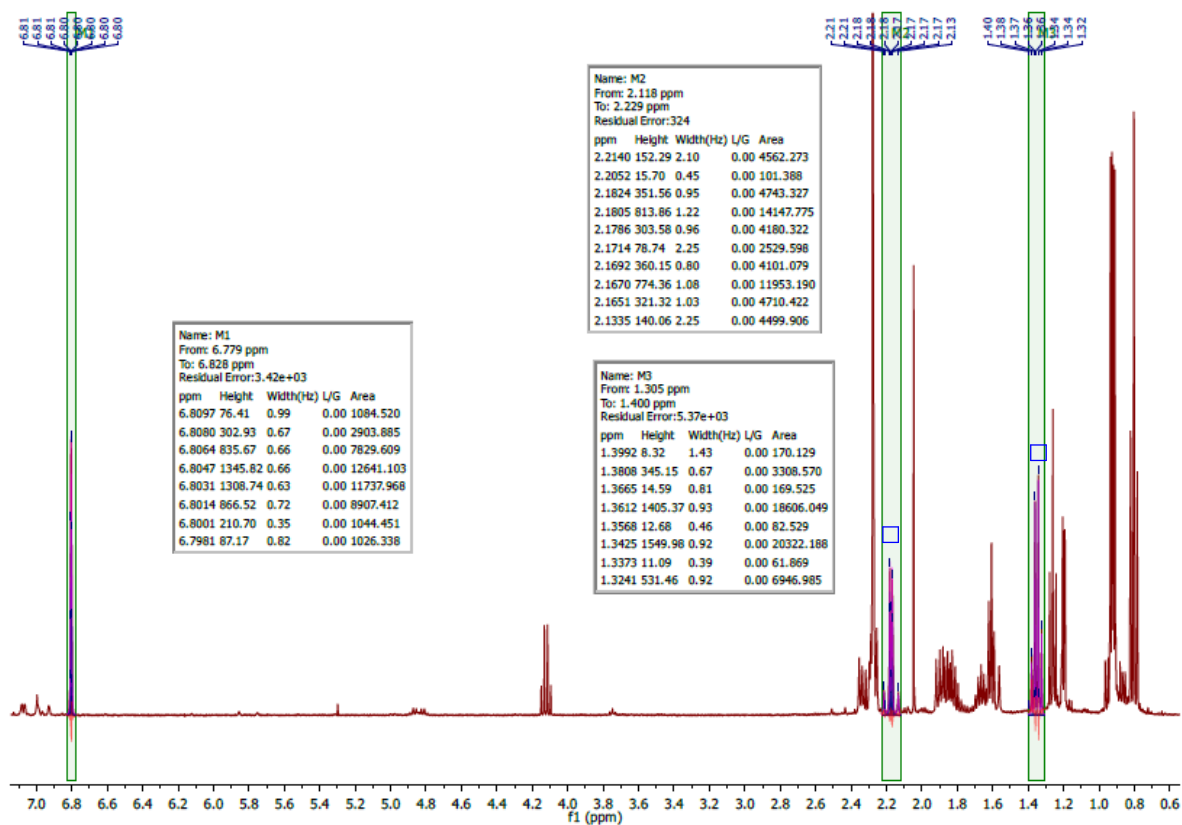
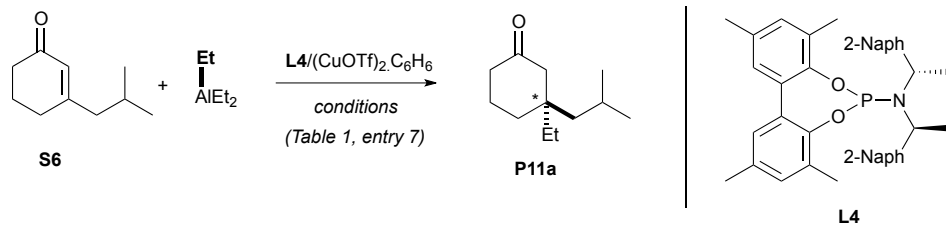


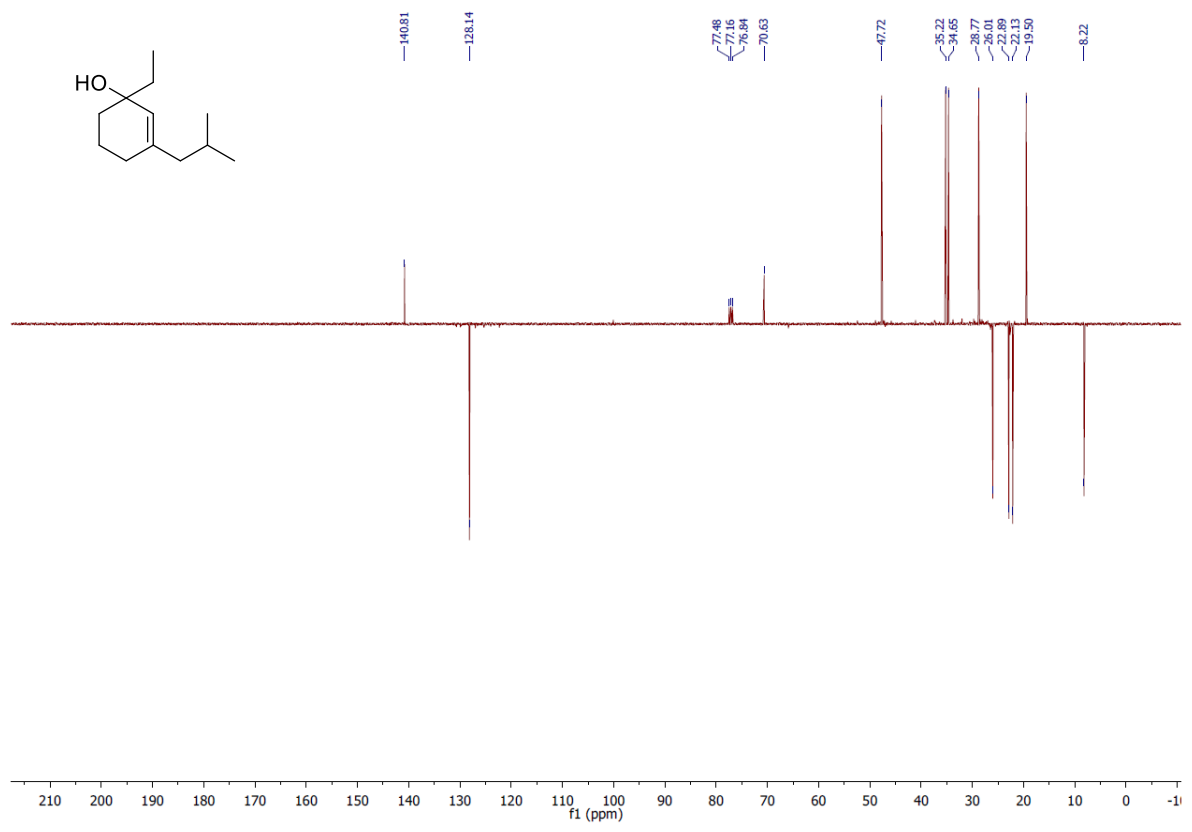


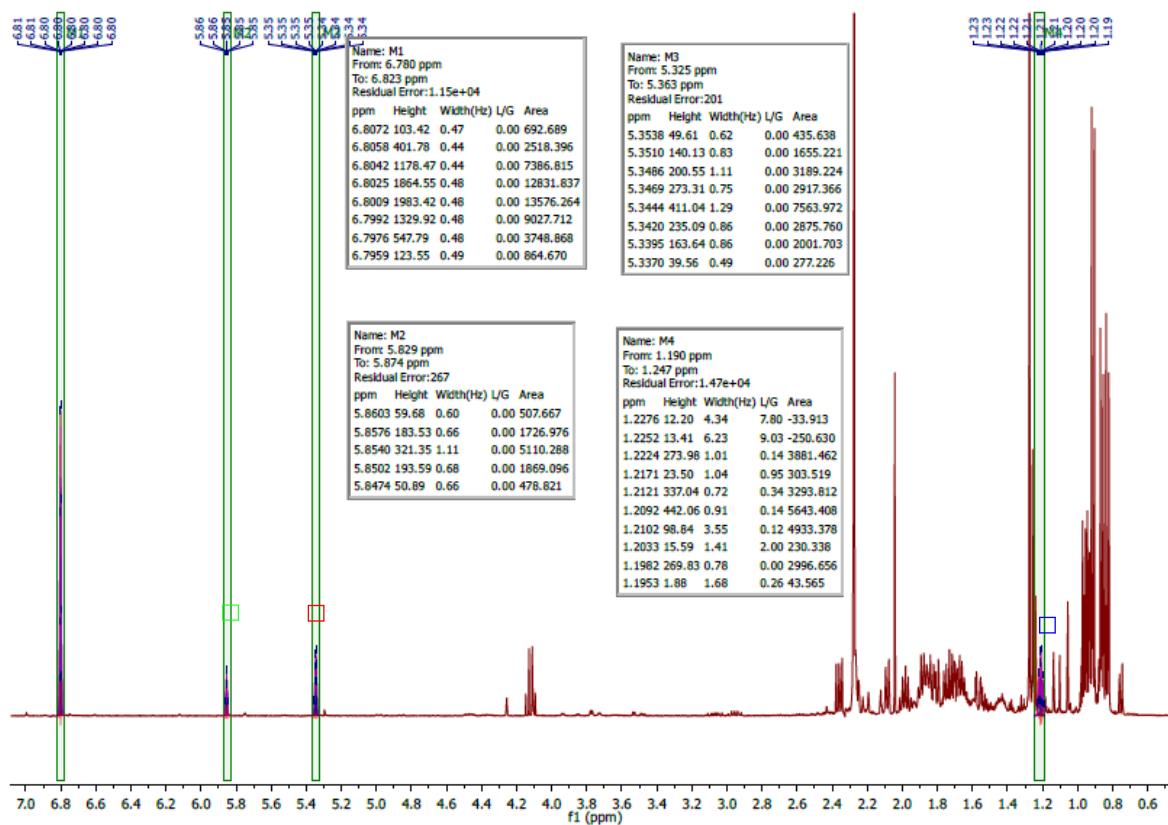
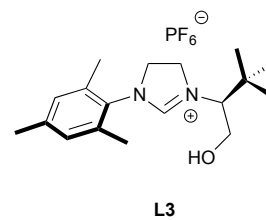
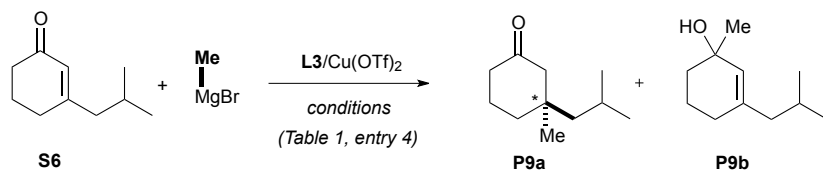


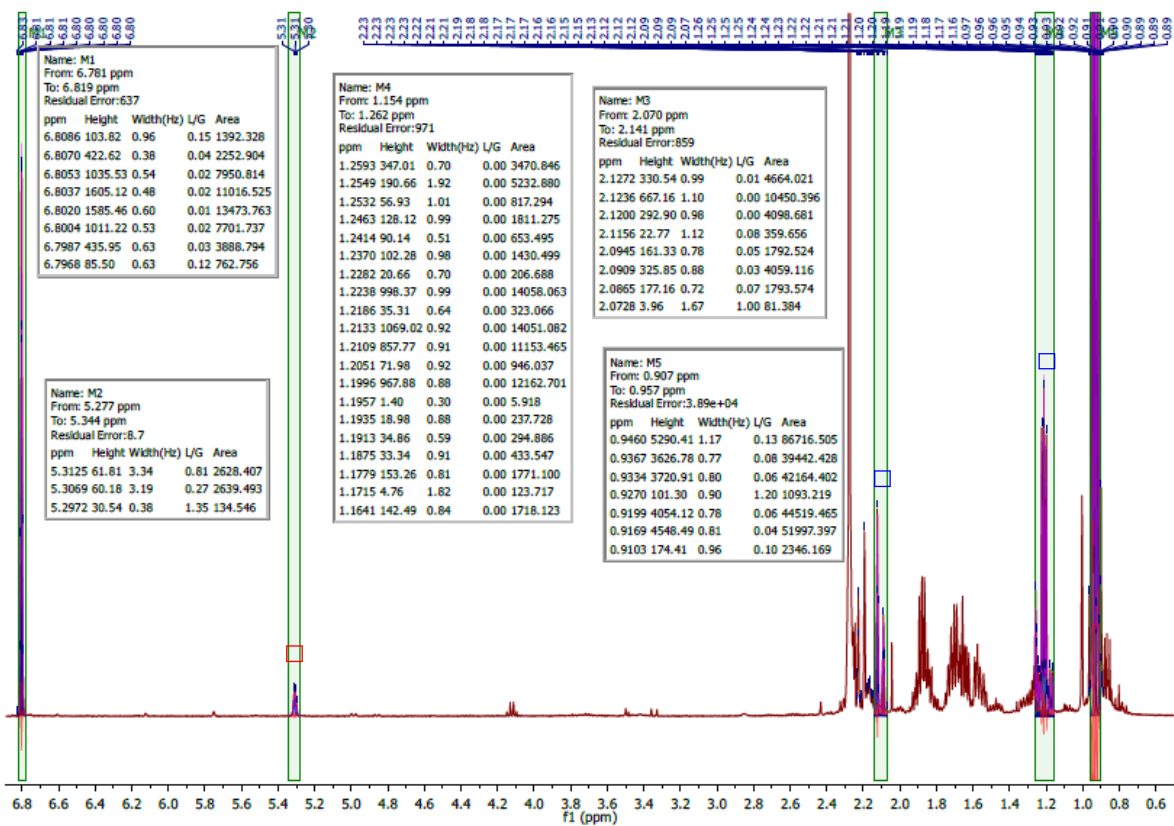
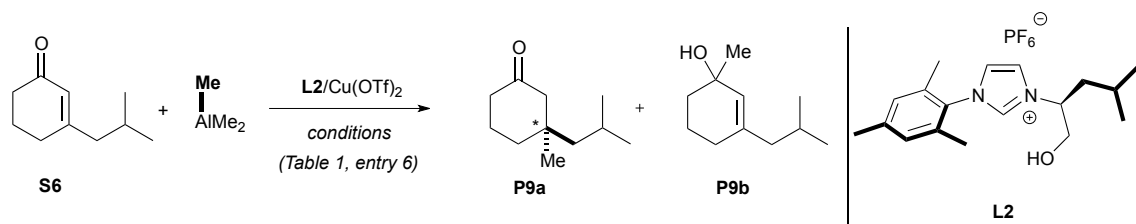


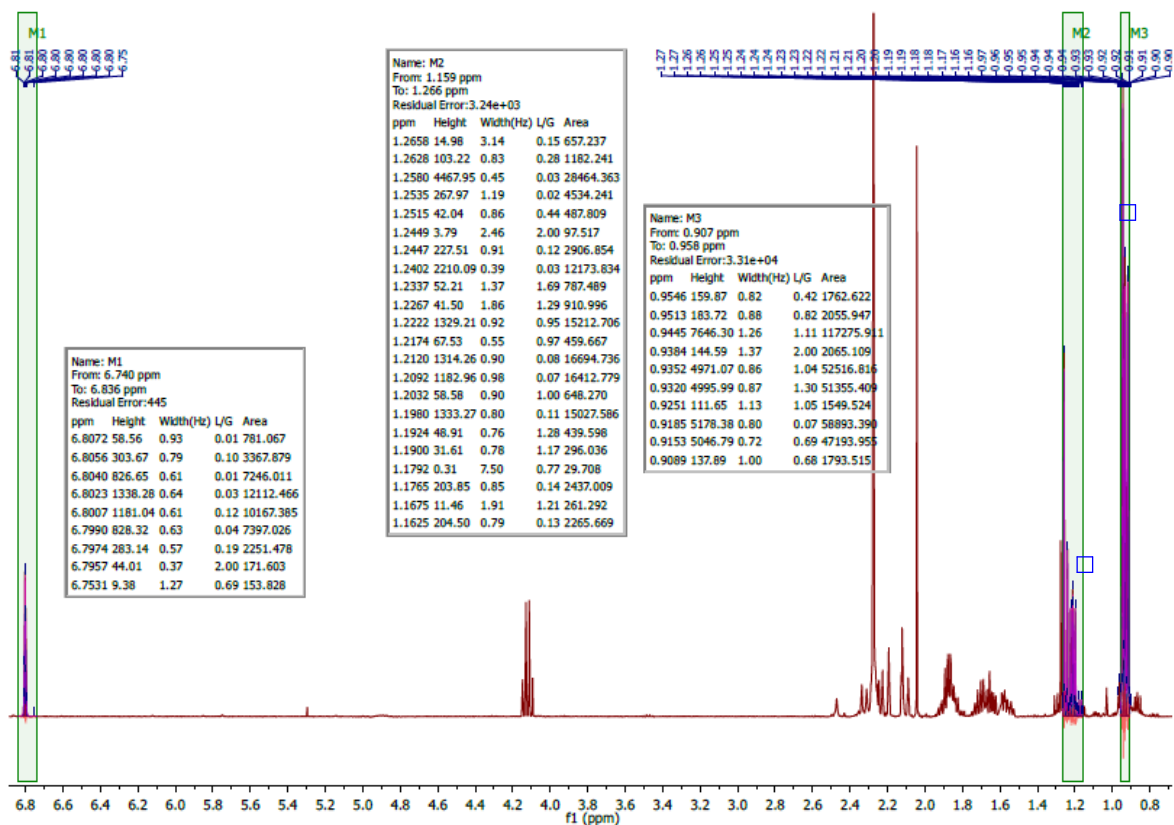
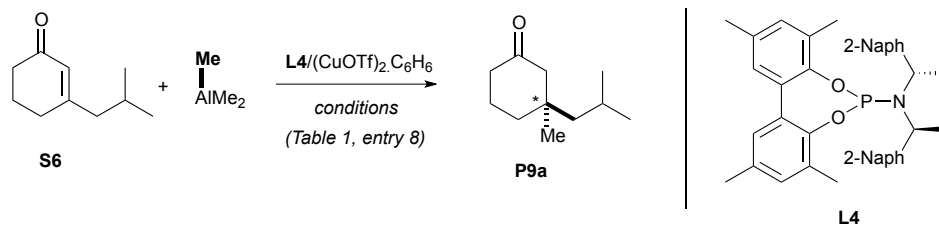


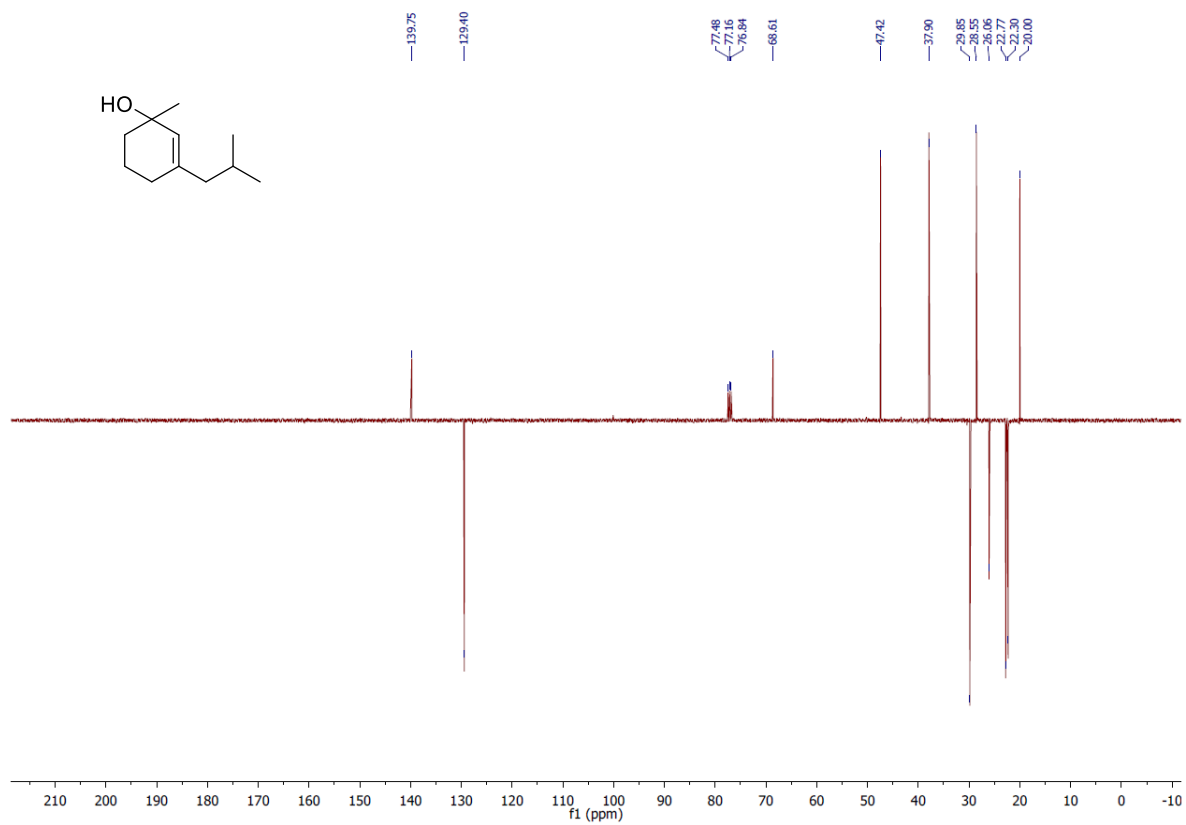


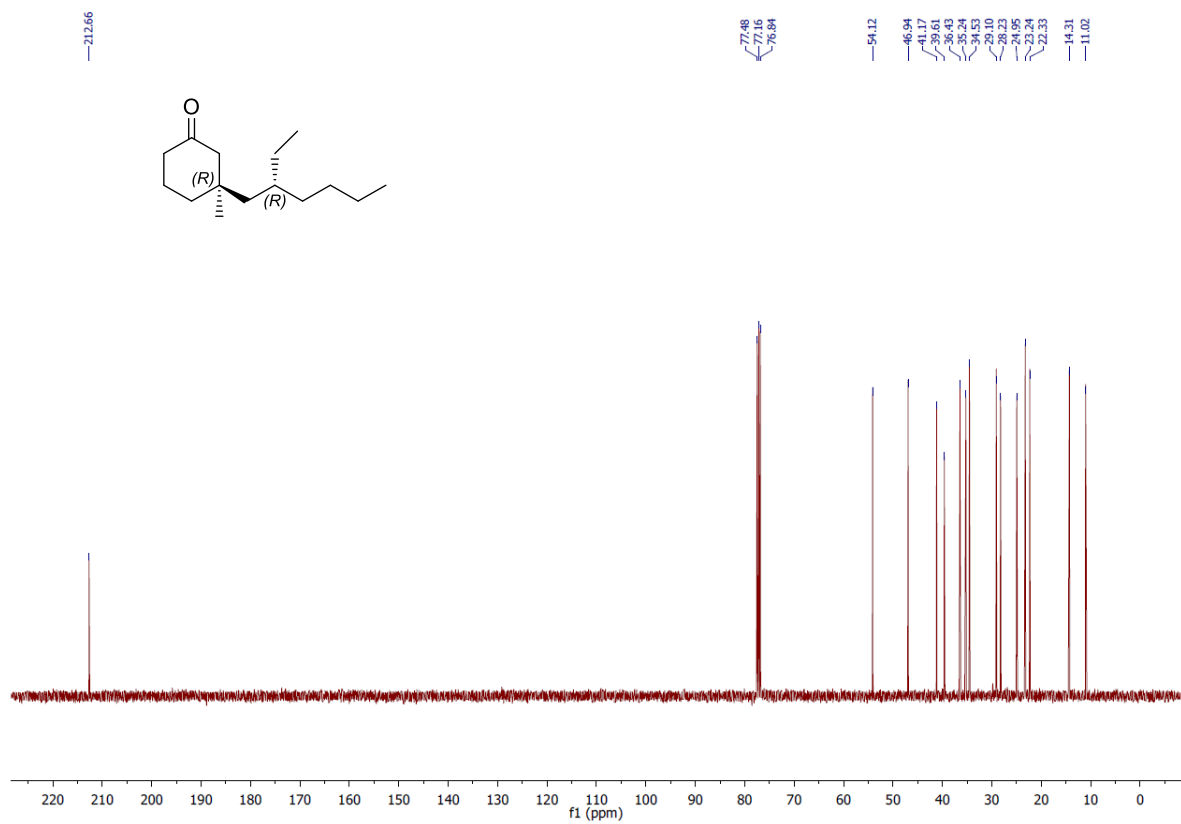
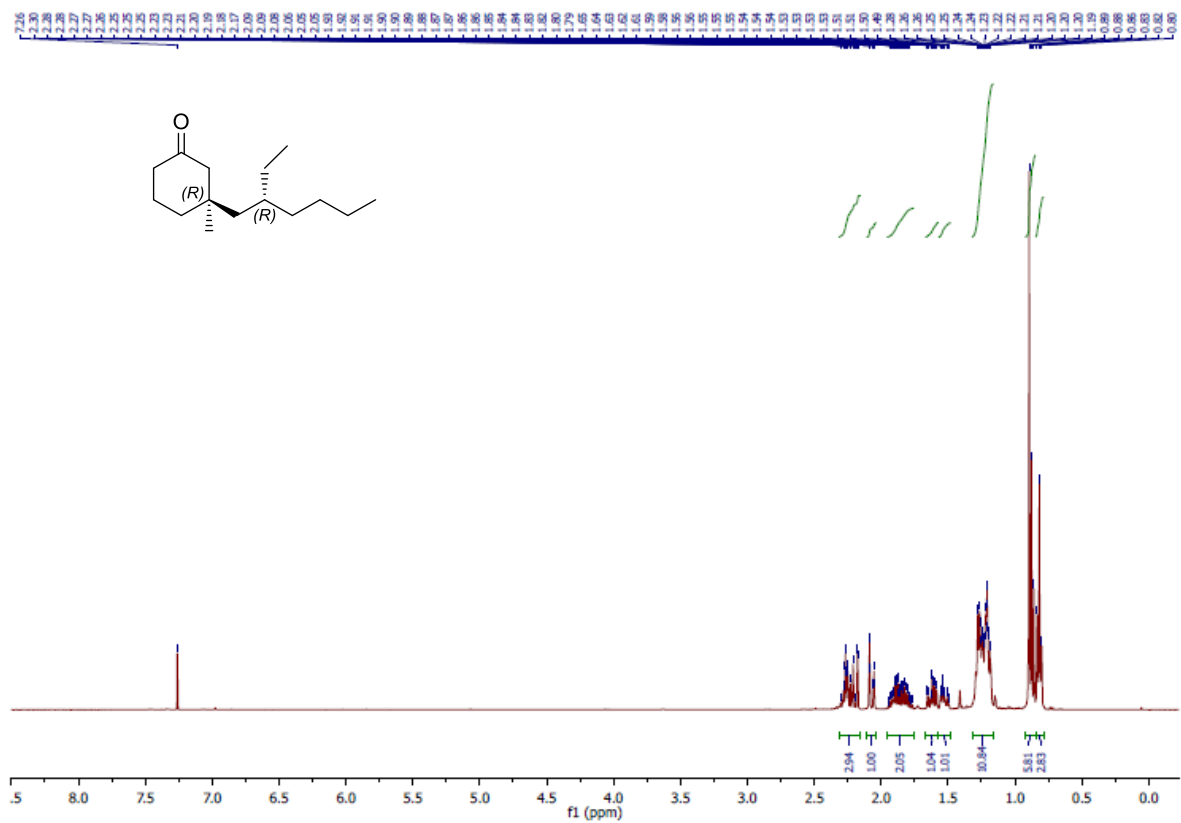


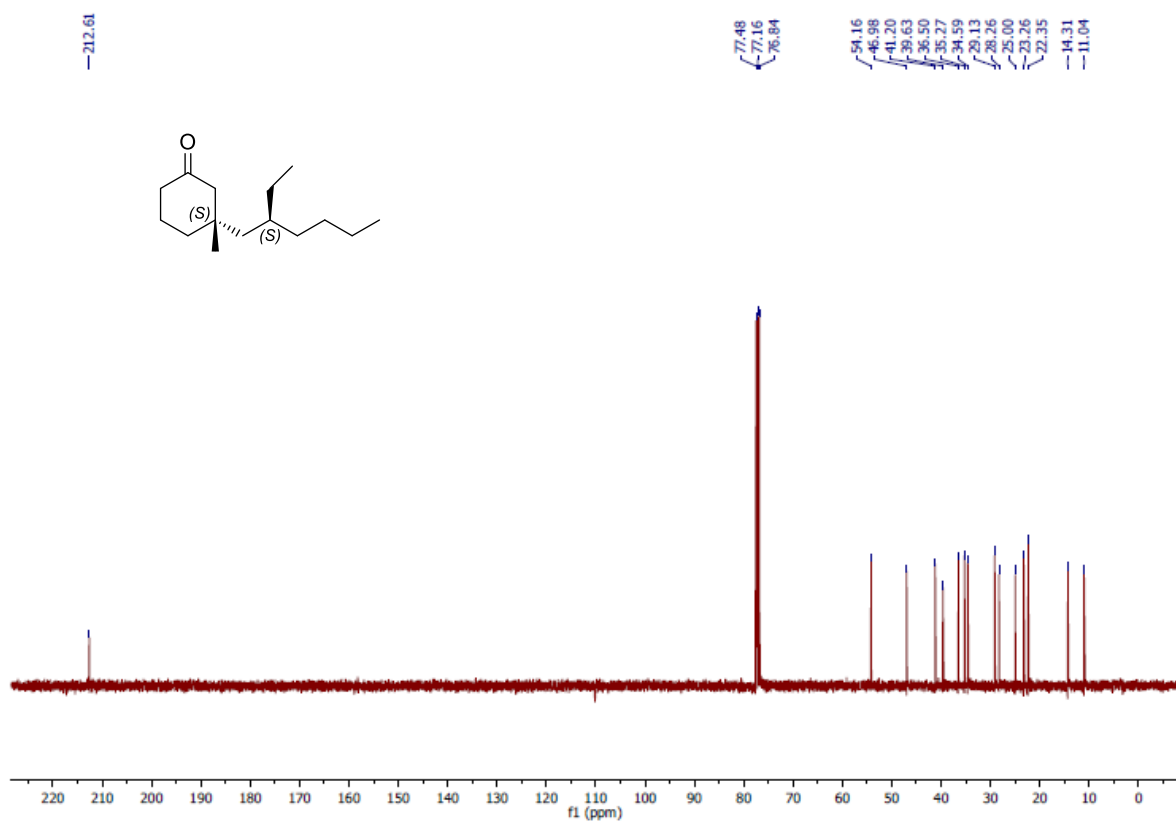
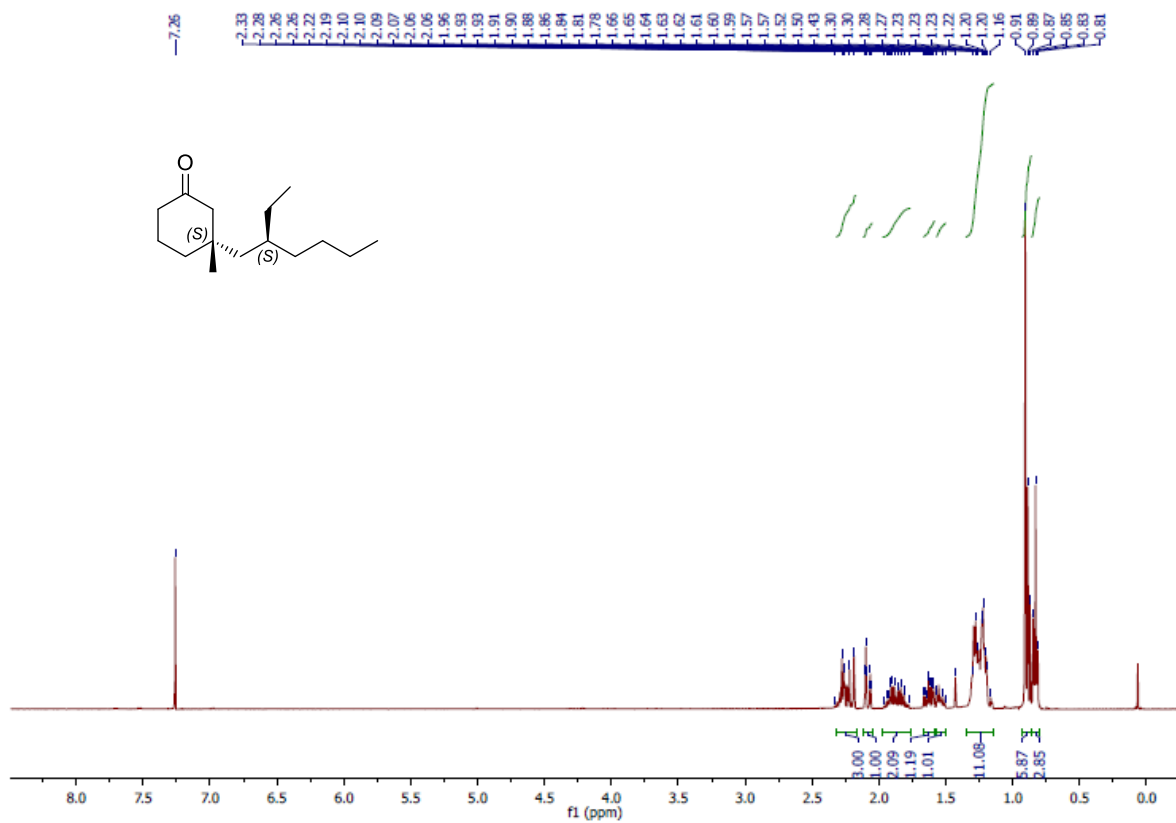


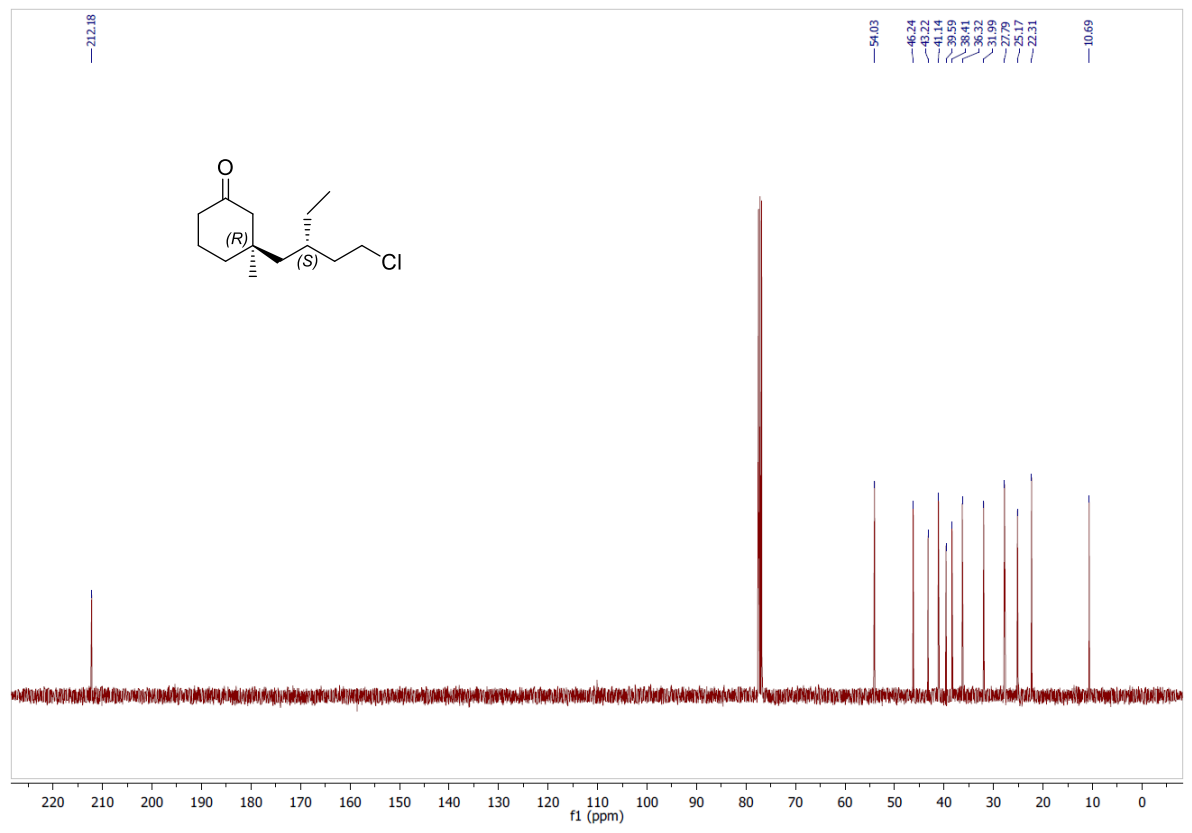
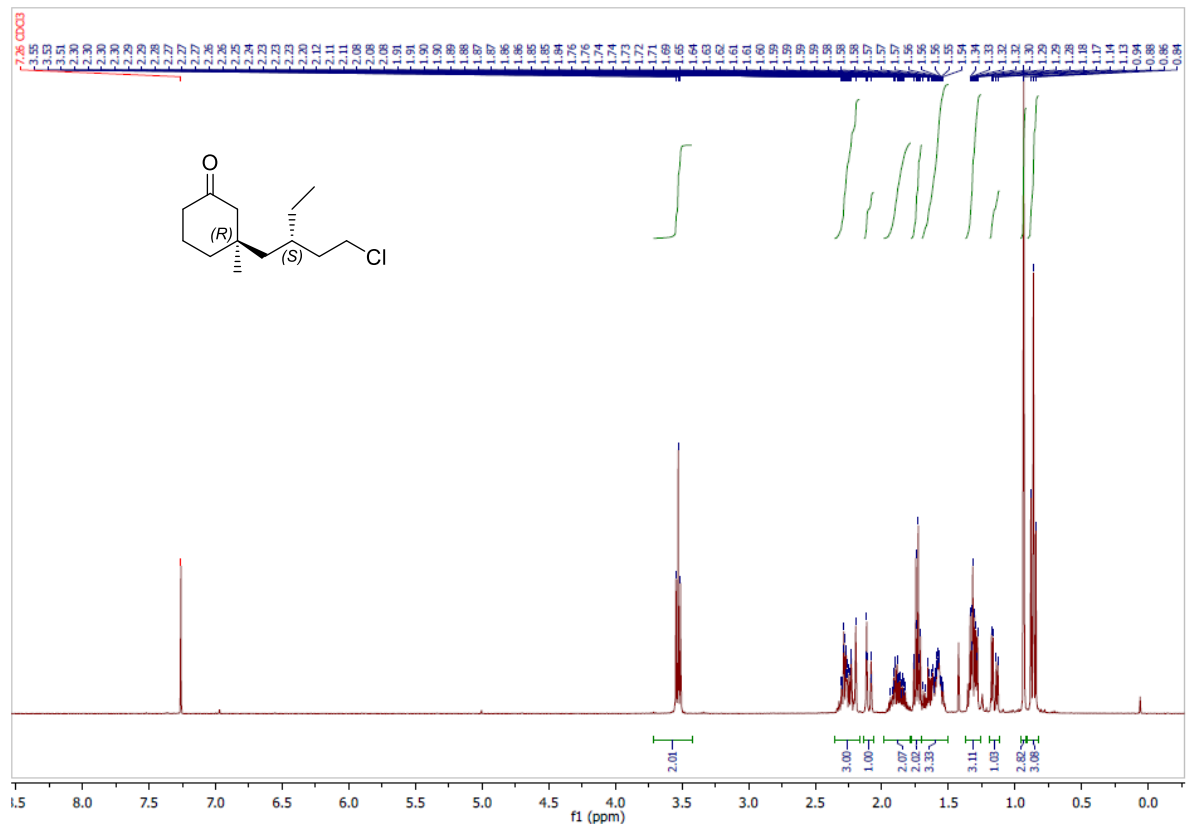


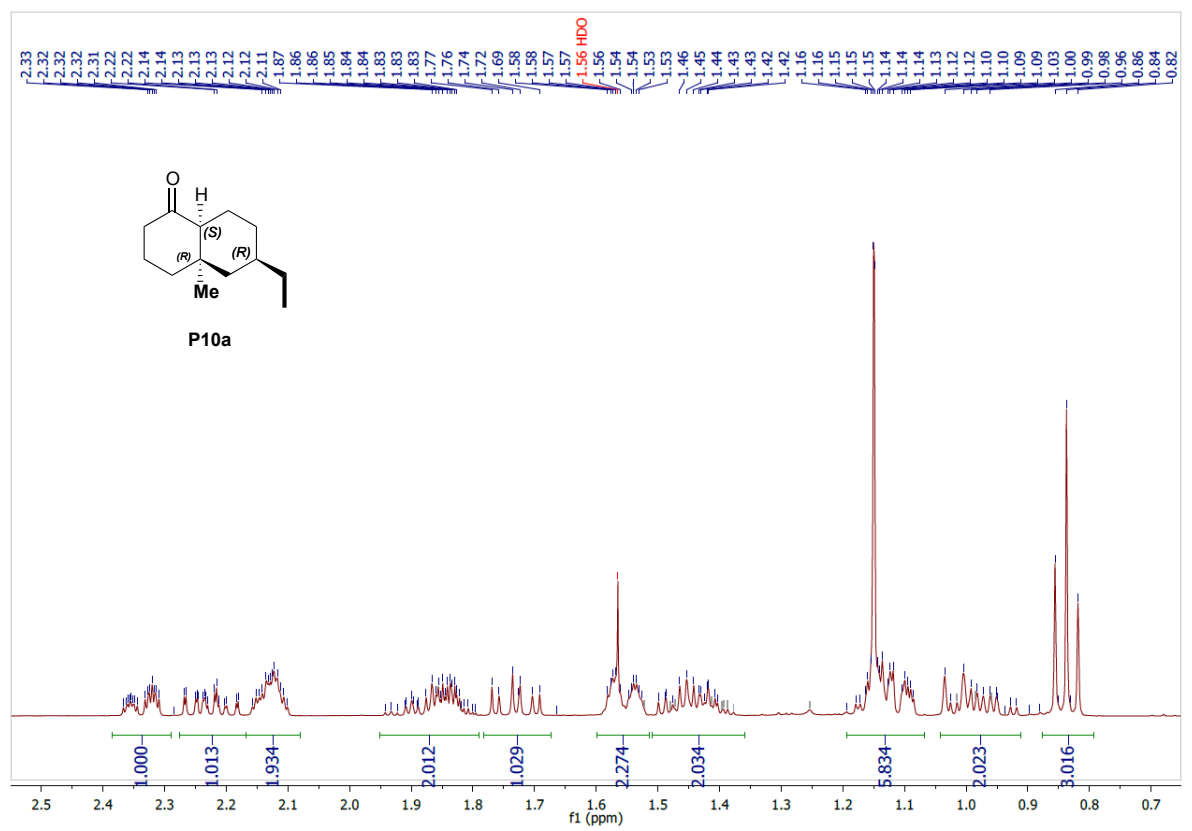
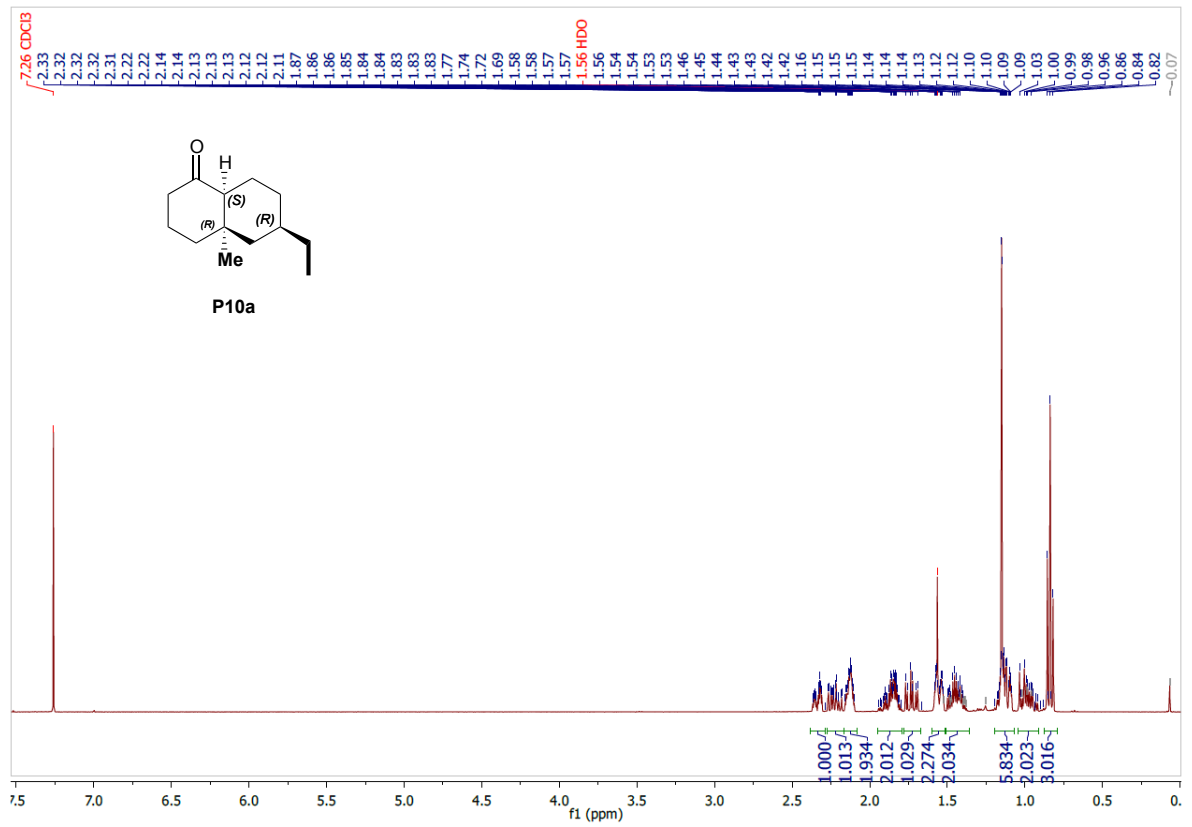


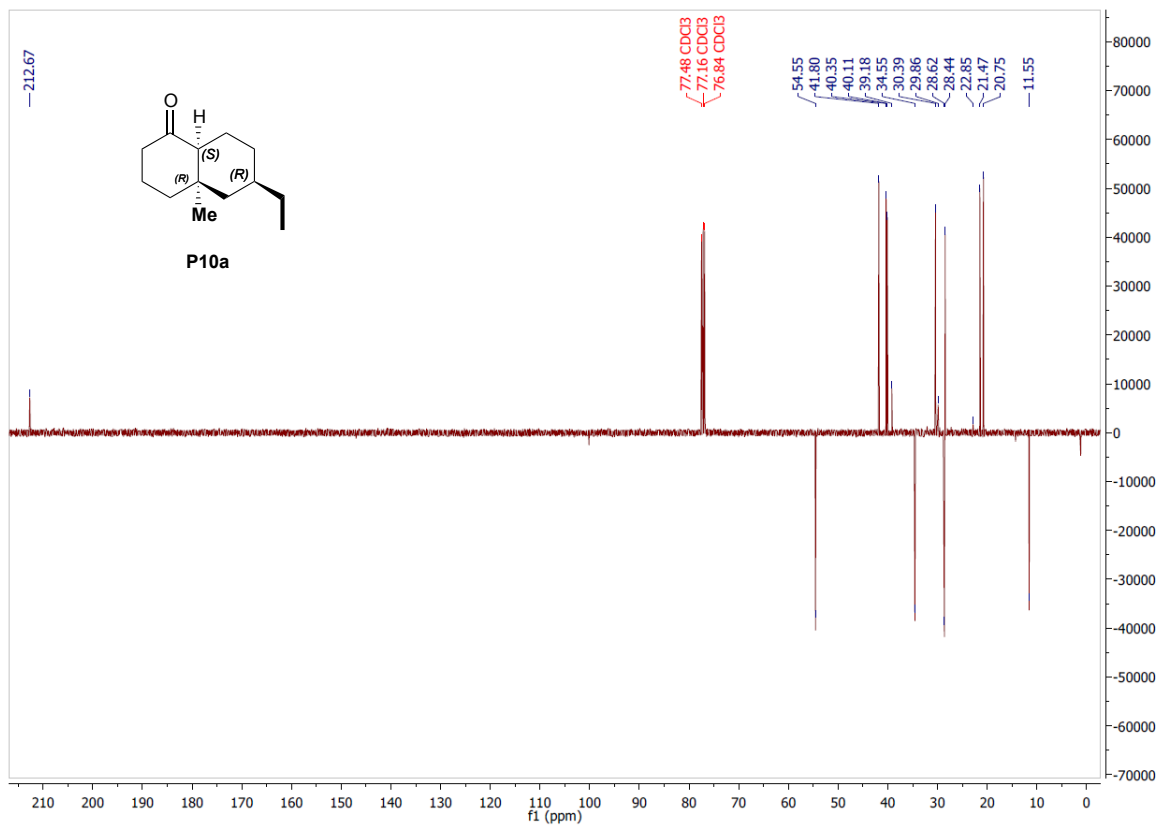
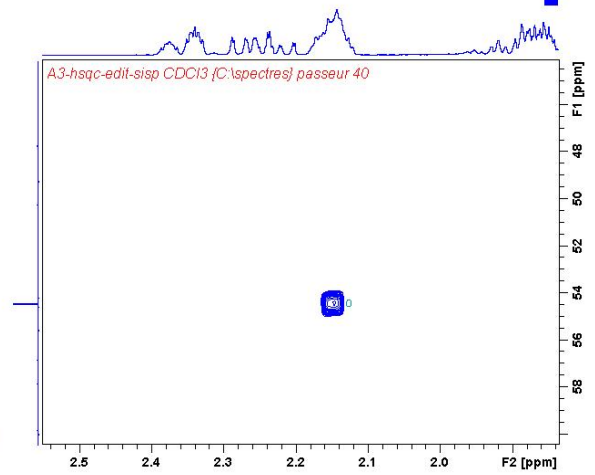
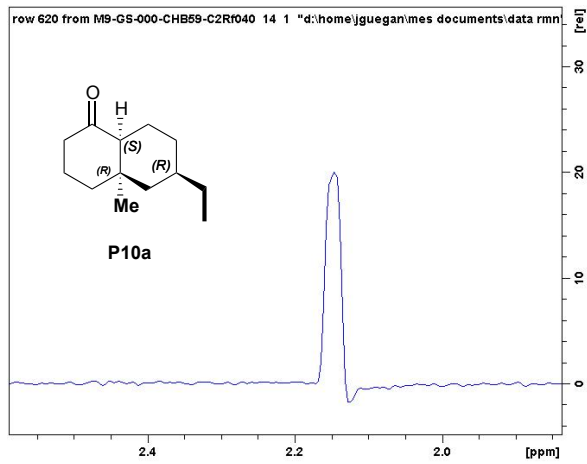


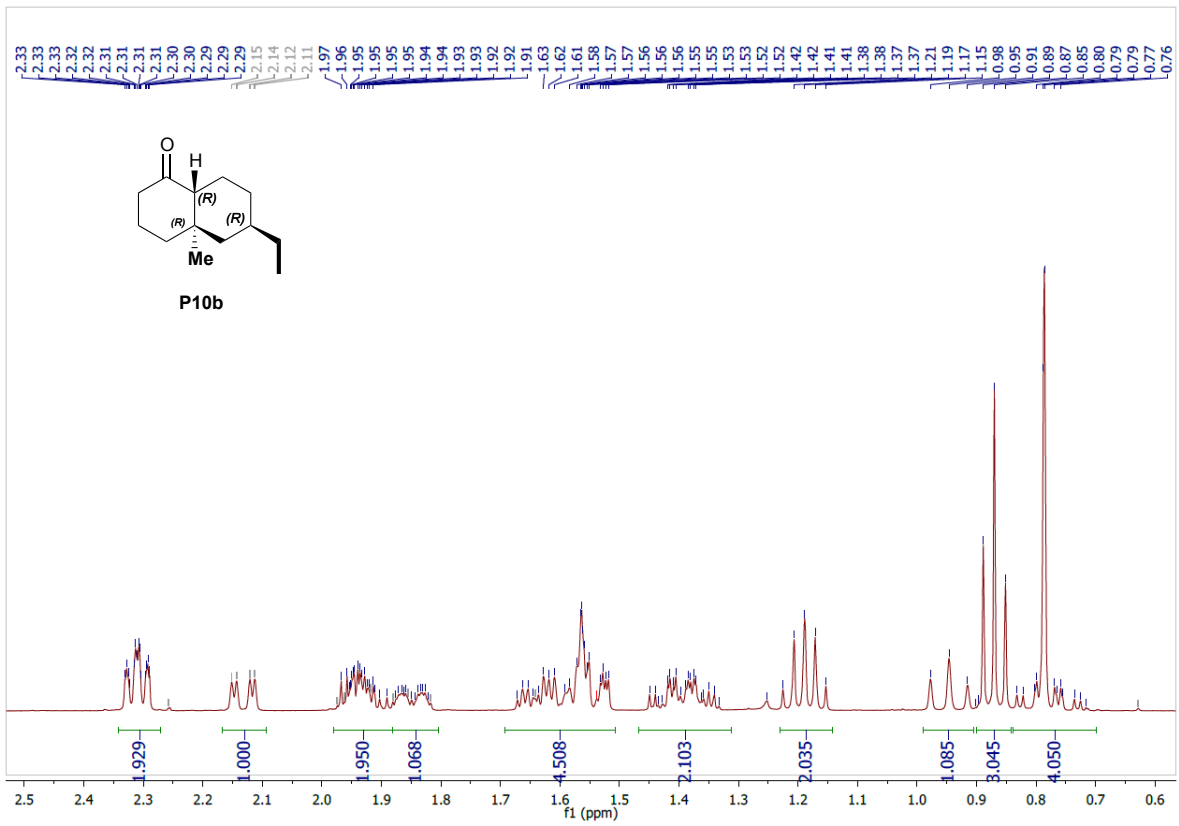
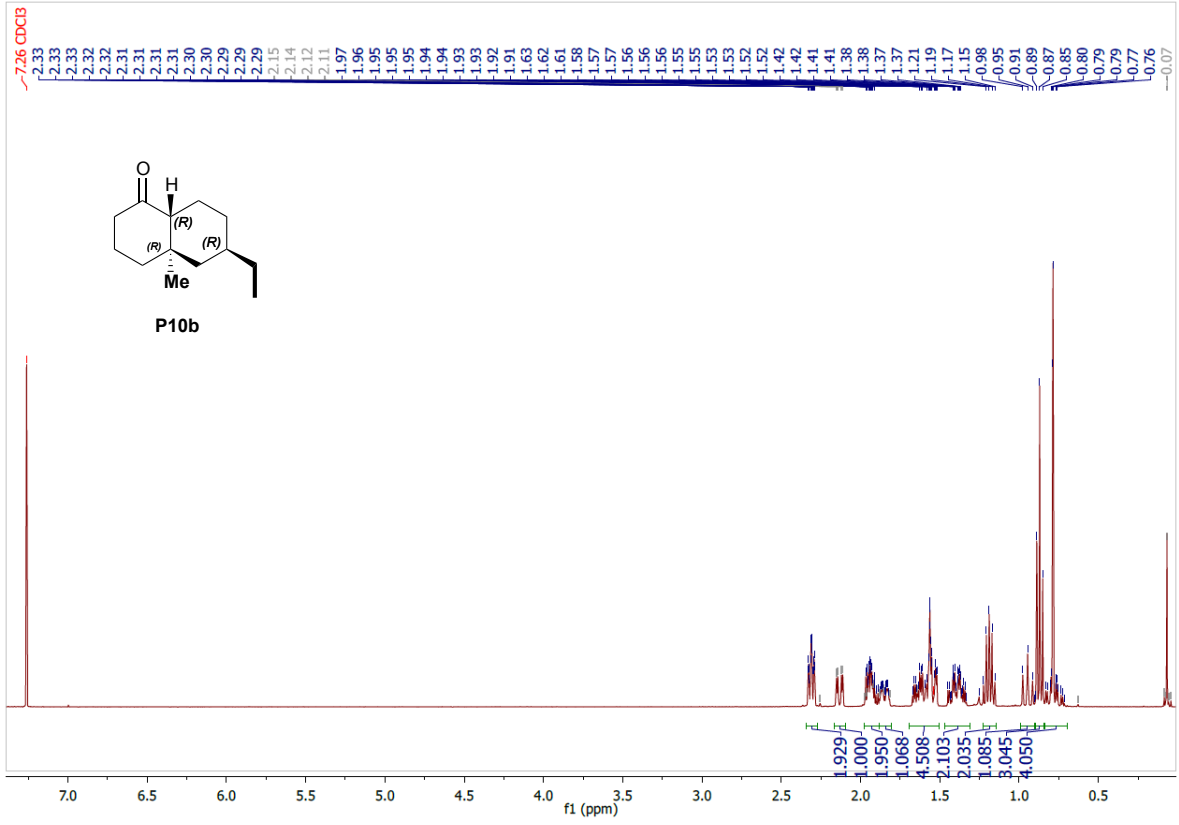


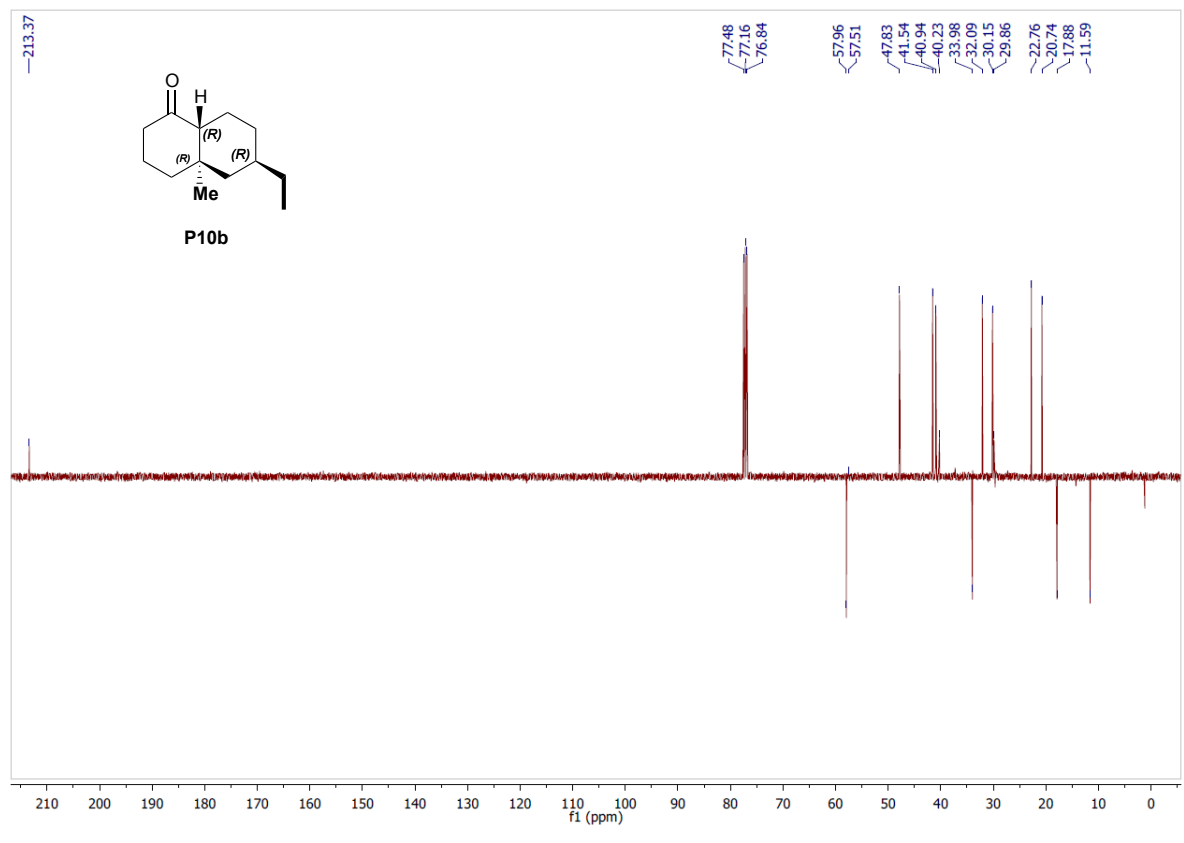
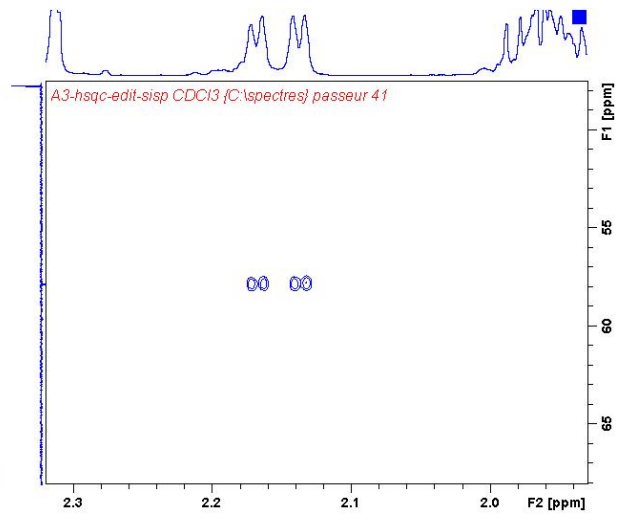
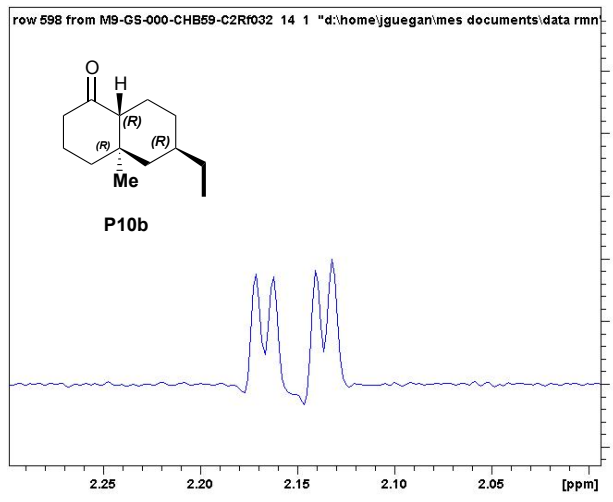


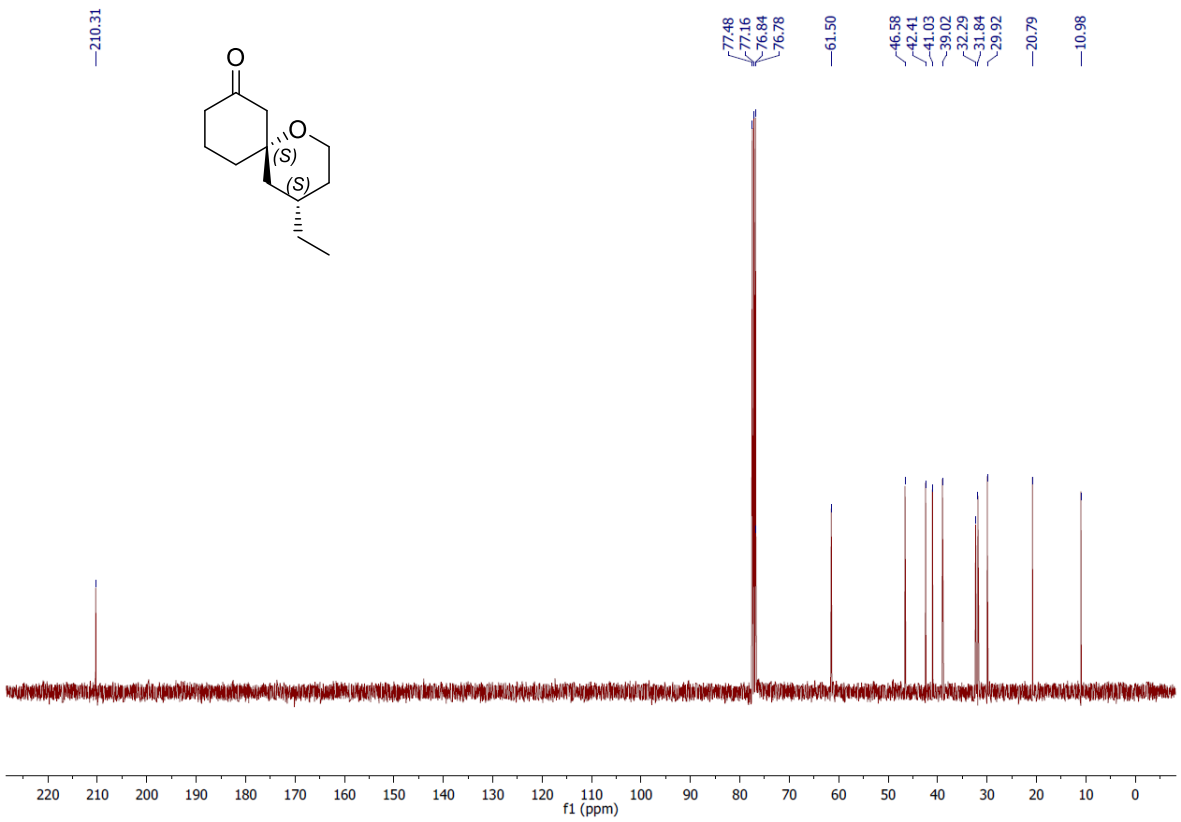
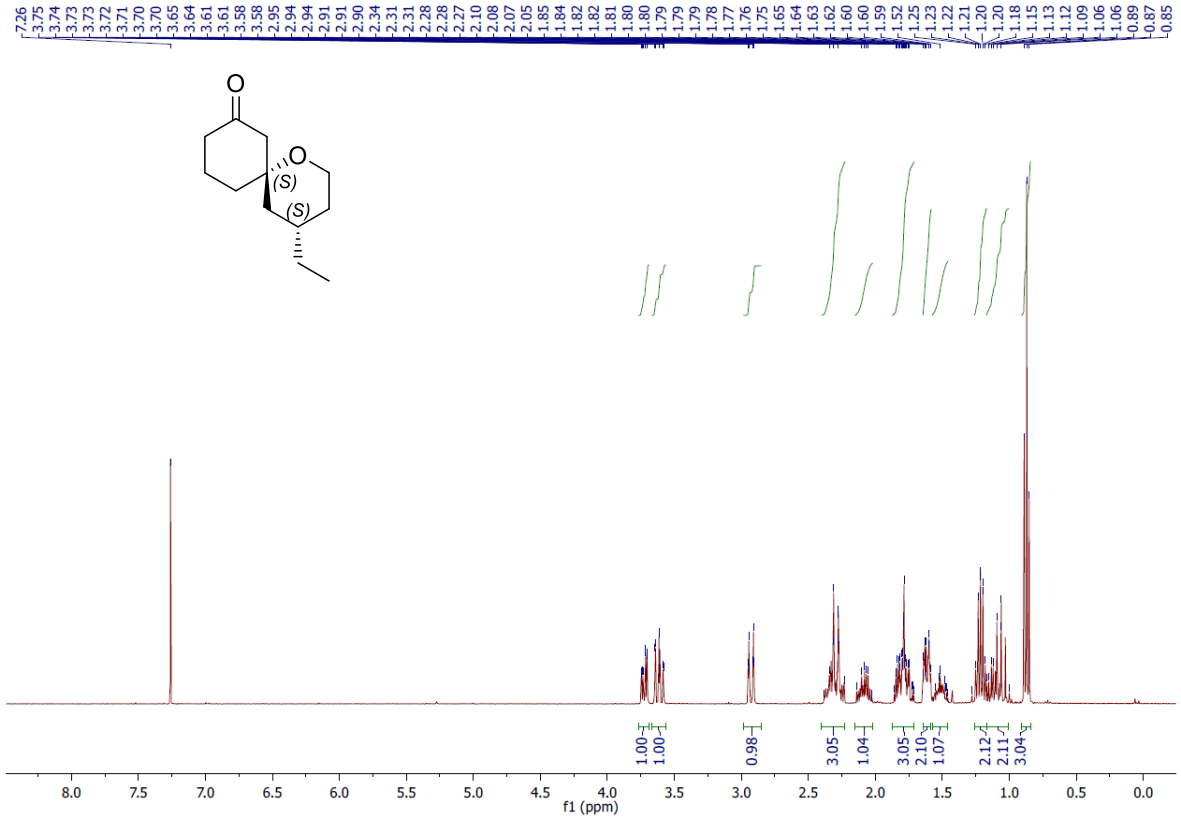


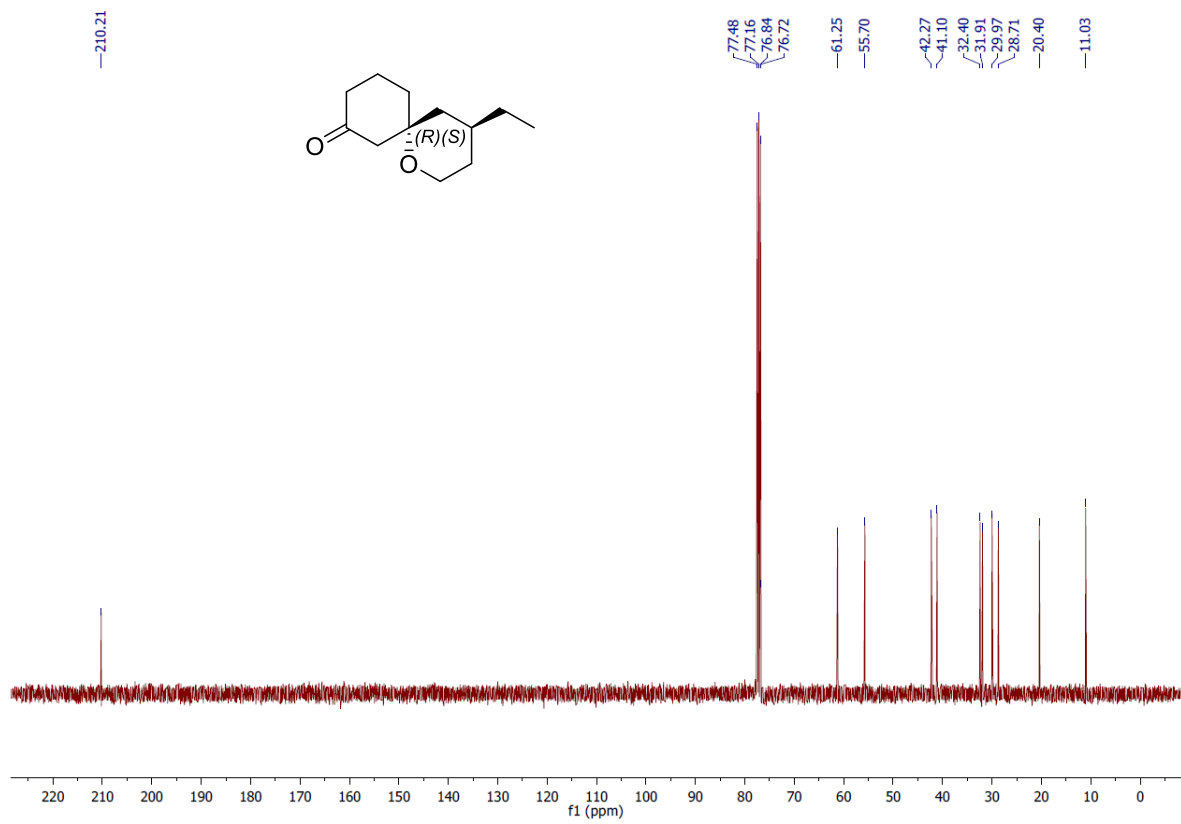
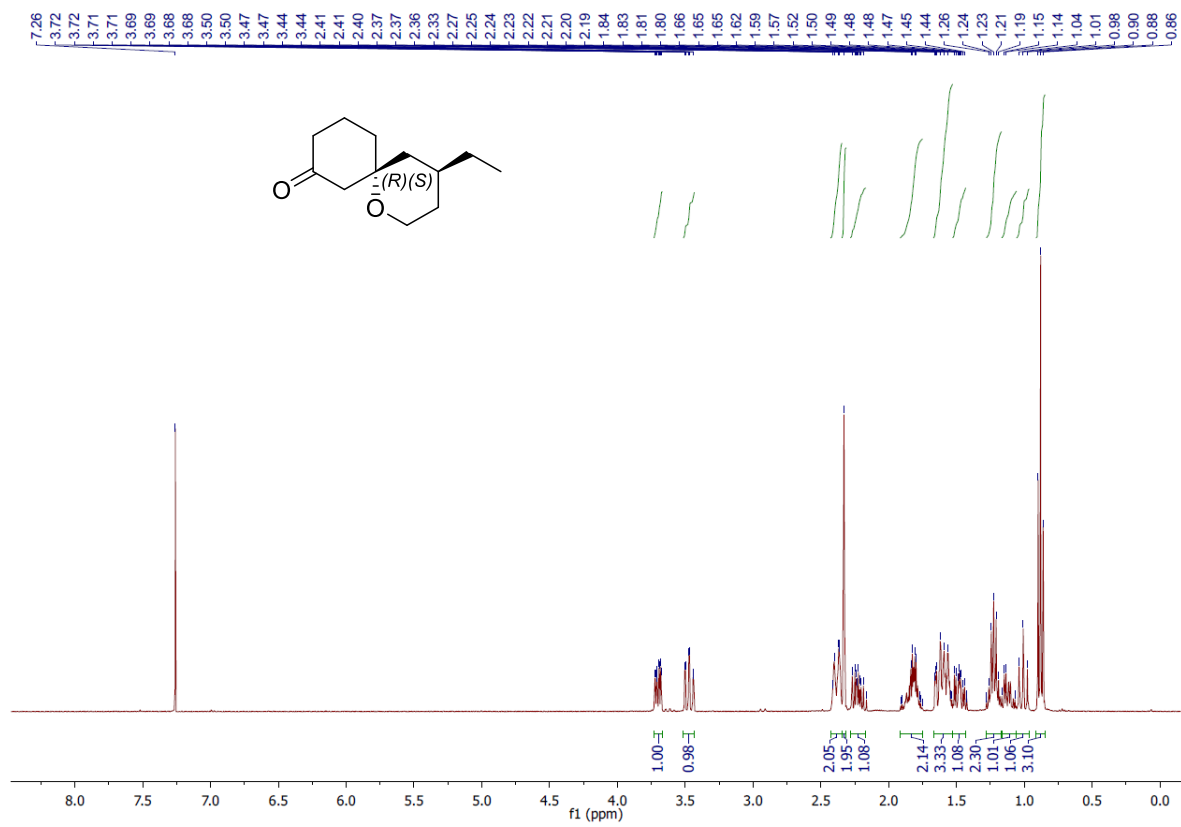












12. X-ray crystallography

An entire sphere of CuK α data ($2\theta_{\max} = 125^\circ$) was collected on an Oxford Diffraction Gemini S Ultra CCD diffractometer with the crystal cooled to 190 K using an Oxford Cryosystems Desktop Cooler. Data reduction and empirical absorption corrections were carried out with the CrysAlis Pro program (Oxford Diffraction vers. 171.37.35). The structure was solved by direct methods with SHELXS86 and refined with SHELXL97^{xi}. All crystallographic calculations were carried out within the WinGX graphical user interface^{xii} and the thermal ellipsoid plot below was produced with ORTEP3^{xiii}.

The absolute structure of (P10a) was established by the Bijvoet analysis of Hooft and co-workers^{xiv} implemented within the PLATON program^{xv}. From an analysis of 1508 pairs, the $P2$ probability parameter was 1.000 for the correct enantiomorph, the Hooft y parameter was 0.0(1) and $\nu = 15$ using Student's t -statistics. The structure comprised two molecules in the asymmetric unit with essentially the same conformations as shown below.

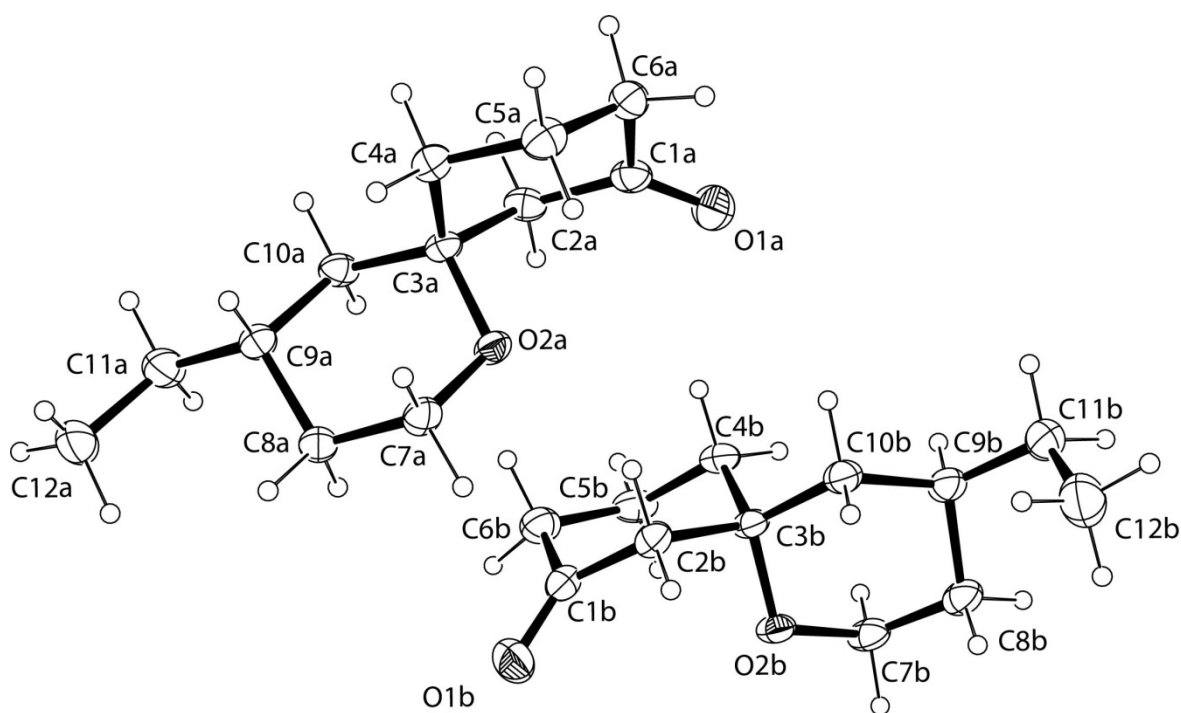


Figure S1. ORTEP view of the asymmetric unit of compound P10a.

Table S1. Crystal data and structure refinement for P10a.

Identification code	1340snc-3-41-bp
Empirical formula	C ₁₂ H ₂₀ O ₂
Formula weight	196.28
Temperature	190(2) K
Wavelength	1.54184 Å
Crystal system	Orthorhombic

Space group	$P 2_1 2_1 2_1$
Unit cell dimensions	$a = 8.8444(2) \text{ \AA}$ $b = 10.9867(3) \text{ \AA}$ $c = 23.0821(7) \text{ \AA}$
Volume	$2242.91(10) \text{ \AA}^3$
Z	8
Density (calculated)	1.163 Mg/m^3
Absorption coefficient	0.606 mm^{-1}
F(000)	864
Crystal size	$0.3 \times 0.2 \times 0.2 \text{ mm}^3$
Theta range for data collection	$3.83 \text{ to } 62.50^\circ$
Index ranges	$-10 \leq h \leq 10, -12 \leq k \leq 12, -26 \leq l \leq 26$
Reflections collected	32636
Independent reflections	3577 [R(int) = 0.0829]
Completeness to theta = 62.50°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.44756
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3577 / 0 / 256
Goodness-of-fit on F^2	1.107
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0373, wR2 = 0.0883
R indices (all data)	R1 = 0.0406, wR2 = 0.0901
Absolute structure parameter	-0.1(2)
Extinction coefficient	0.0039(4)
Largest diff. peak and hole	0.141 and -0.147 e. \AA^{-3}

Table S2. Bond lengths [\AA] and angles [$^\circ$] for P10a

C(1A)-O(1A)	1.210(2)
C(1A)-C(2A)	1.500(3)
C(1A)-C(6A)	1.500(3)
C(2A)-C(3A)	1.529(2)
C(3A)-O(2A)	1.450(2)
C(3A)-C(10A)	1.516(2)
C(3A)-C(4A)	1.533(2)
C(4A)-C(5A)	1.521(2)
C(5A)-C(6A)	1.528(3)
C(7A)-O(2A)	1.427(2)
C(7A)-C(8A)	1.503(3)
C(8A)-C(9A)	1.527(2)
C(9A)-C(11A)	1.522(3)
C(9A)-C(10A)	1.534(2)
C(11A)-C(12A)	1.518(3)
C(1B)-O(1B)	1.216(2)
C(1B)-C(6B)	1.500(3)
C(1B)-C(2B)	1.500(3)
C(2B)-C(3B)	1.526(2)
C(3B)-O(2B)	1.453(2)
C(3B)-C(10B)	1.523(3)
C(3B)-C(4B)	1.538(3)
C(4B)-C(5B)	1.524(3)
C(5B)-C(6B)	1.526(3)
C(7B)-O(2B)	1.434(2)
C(7B)-C(8B)	1.506(3)
C(8B)-C(9B)	1.526(3)
C(9B)-C(10B)	1.523(2)
C(9B)-C(11B)	1.537(3)
C(11B)-C(12B)	1.507(3)
O(1A)-C(1A)-C(2A)	122.41(17)
O(1A)-C(1A)-C(6A)	122.33(17)
C(2A)-C(1A)-C(6A)	115.26(16)
C(1A)-C(2A)-C(3A)	112.97(15)
O(2A)-C(3A)-C(10A)	110.06(13)
O(2A)-C(3A)-C(2A)	103.29(13)
C(10A)-C(3A)-C(2A)	110.77(14)
O(2A)-C(3A)-C(4A)	110.35(13)
C(10A)-C(3A)-C(4A)	113.19(14)
C(2A)-C(3A)-C(4A)	108.73(13)

C(5A)-C(4A)-C(3A)	112.46(15)
C(4A)-C(5A)-C(6A)	111.47(15)
C(1A)-C(6A)-C(5A)	111.93(15)
O(2A)-C(7A)-C(8A)	112.37(15)
C(7A)-C(8A)-C(9A)	111.25(15)
C(11A)-C(9A)-C(8A)	112.45(15)
C(11A)-C(9A)-C(10A)	110.83(15)
C(8A)-C(9A)-C(10A)	108.42(14)
C(3A)-C(10A)-C(9A)	114.67(14)
C(12A)-C(11A)-C(9A)	114.45(18)
C(7A)-O(2A)-C(3A)	114.40(13)
O(1B)-C(1B)-C(6B)	122.81(18)
O(1B)-C(1B)-C(2B)	121.77(18)
C(6B)-C(1B)-C(2B)	115.42(16)
C(1B)-C(2B)-C(3B)	112.44(15)
O(2B)-C(3B)-C(10B)	109.94(14)
O(2B)-C(3B)-C(2B)	103.09(13)
C(10B)-C(3B)-C(2B)	110.49(14)
O(2B)-C(3B)-C(4B)	110.67(14)
C(10B)-C(3B)-C(4B)	113.34(14)
C(2B)-C(3B)-C(4B)	108.83(14)
C(5B)-C(4B)-C(3B)	111.89(15)
C(4B)-C(5B)-C(6B)	111.88(16)
C(1B)-C(6B)-C(5B)	111.65(16)
O(2B)-C(7B)-C(8B)	111.41(16)
C(7B)-C(8B)-C(9B)	111.36(16)
C(10B)-C(9B)-C(8B)	109.00(15)
C(10B)-C(9B)-C(11B)	113.23(16)
C(8B)-C(9B)-C(11B)	113.18(17)
C(9B)-C(10B)-C(3B)	113.71(15)
C(12B)-C(11B)-C(9B)	115.98(17)
C(7B)-O(2B)-C(3B)	113.95(13)

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