Mechanistic identification and improvement of a direct enantioconvergent transformation in copper-catalyzed asymmetric allylic alkylation

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Supporting Information

1. General comments

Nuclear magnetic resonance spectra:

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded either on ARX-300, AMX-400 or AM-500 Bruker Avance spectrometers. ^{2}H NMR spectra were recorded on ARX-300 Bruker Avance spectrometers. ^{1}H, ^{2}H and ^{13}C NMR chemical shifts (δ) are given in ppm relative to $SiMe_4$. ^{19}F NMR chemical shifts (δ) are given in ppm relative to $CFCl_3$. Peaks multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet), td (triplet of doublet), qd (quartet of doublet), brs (broad signal). Coupling constants are reported in Hertz (Hz).

Optical activity:

Optical rotations were recorded on a Perkin-Elmer 241 polarimeter at 25 °C in a 10 cm cell in the stated solvent; $[\alpha]_D$ values are given in 10^{-1} deg.cm^2 g^{-1} (concentration c given as g/100 mL).

Enantiomeric excesses:

Enantiomeric excesses were determined by GC on chiral stationary phase. The measurements were recorder either on a HP6890 (H_2 as vector gas) or HP6850 (H_2 as vector gas) with stated stationary phase. Temperature programs are described as follows: initial temperature (°C) - initial time (min) - temperature gradient (°C/min) - final temperature (°C); retention times (R_T) are given in minute.

Chromatography:

Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} supported on aluminium sheets. TLC traces were visualized by UV lamp (254 nm) or with potassium permanganate ($KMnO_4$) stain. Flash chromatography was performed using silicagel 32-63 µm, 60 Å from Fluka.

IR spectra:

IR spectra measurements were recorded on a Perkin-Elmer 1650 FT-IR spectrometer using neat samples. Wavenumbers are given in cm^{-1}.

Mass spectrometry:

Mass spectrometry analyses were mainly achieved by electronic impact (EI) on a double-focusing magnetic sector mass spectrometer (geometry BE), MAT 95 from Finnigan. The measurements were performed at the University of Zürich. Few analyses were obtained by electrospray ionization (ESI) and were performed on QqTOF, QStar pulsar or XL instrument from AB/MDS Sciex. The measurements have been done at the University of Geneva by the Science Mass Spectrometry team.

Reagent and solvent:

All reactions were carried out with flame-dried glassware. Solvents were dried by filtration over alumina previously activated at 350 °C during 12 hours under nitrogen before use. CuTC was purchased from FrontierScientific and used as received. All chiral ligands were prepared according to litterature procedures.[1] Chiral amines used for the preparation of phospharamidite ligands were given by BASF.

[1] For phosphoramidite ligands **L1** and **L2**, see: A. Alexakis, D. Polet, S. Rosset, S. March, *J. Org. Chem.* **2004**, *69*, 5660.

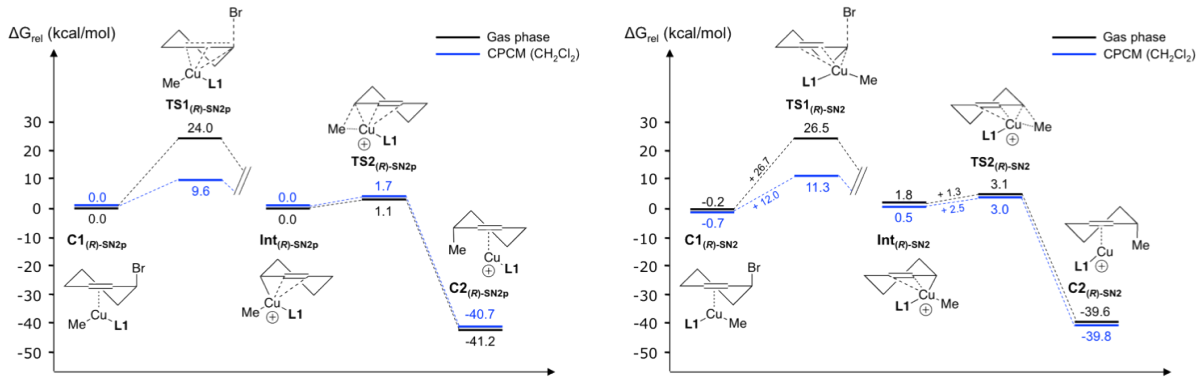
Computational investigations:

All calculations have been performed with Gaussian 03 package.[2] The density functional theory (DFT) method was employed using B3LYP hybrid functional.[3] The structures were optimized in gas phase using 6-31G(d) for C H N O P Br atoms and LanL2DZ basis sets for Cu.[4] All stationary points were characterized by vibrational analysis, and were confirmed to be part of the intrinsic reaction coordinate (IRC) of the reported pathways. Single point energy calculations have been performed in dichloromethane using the CPCM solvation model.[5] Relative energies are corrected for enthalpy and entropy factors at -78 °C and are showed in units of kcal/mol. Distances and bond lengths are given in units of angströms (Å). All depicted structures were generated using CYLview program.[6]

2. Additional data

2.1. Computational investigations

2.1.1. Alkylation of (*R*)-**1**



For *anti*-S_N2' pathway For *anti*-S_N2 pathway

Figure S1. Energy profiles corresponding to the alkylation of (*R*)-**1** by MeCu**L1** in both *anti*-S_N2' and *anti*-S_N2 pathways.

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[2] M. J. Frisch *et al*. *Gaussian 03*, revision C. 02; Gaussian, Inc.:Wallingford, CT, 2004.

[3] For B3LYP hybrid functional, see: a) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.

[4] For 6-31G(d), see: a) W. J. Hehre, L. Radom, P. v R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons Inc. New York. 1986. For LanL2DZ, see: b) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284; c) P. J. Hay, W. R: Wadt, *J. Chem. Phys.* **1985**, *82*, 299.

[5] For CPCM, see: a) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669; b) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995.

[6] C. Y. Legault, CYL*view*, 1.0b; Université de Sherbrooke, 2009; http://www.cylview.org.

Table S1. Energy values of all stationary points relative to the *anti*-S_N2' pathway in gas phase

Coordinate	E (au)	E+ZPE (au)	H (au)	G (au)	**ΔG (kcal/mol)**
C1$_{(R)\text{-SN2p}}$	-4977.210045	-4976.467738	-4976.445817	-4976.511307	**0.0**
TS1$_{(R)\text{-SN2p}}$	-4977.173301	-4976.431211	-4976.409806	-4976.472993	**24.0**
Int$_{(R)\text{-SN2p}}$	-2405.586869	-2404.844357	-2404.823780	-2404.885295	**0.0**
TS2$_{(R)\text{-SN2p}}$	-2405.585323	-2404.842676	-2404.822418	-2404.883471	**1.1**
C2$_{(R)\text{-SN2p}}$	-2405.655953	-2404.909699	-2404.889378	-2404.950933	**-41.2**

Table S2. Energy values of all stationary points relative to the *anti*-S_N2 pathway in gas phase

Coordinate	E (au)	E+ZPE (au)	H (au)	G (au)	**ΔG (kcal/mol)**
C1$_{(R)\text{-SN2}}$	-4977.209006	-4976.467053	-4976.444879	-4976.511674	**-0.2**
TS1$_{(R)\text{-SN2}}$	-4977.168410	-4976.426509	-4976.405008	-4976.469101	**26.5**
Int$_{(R)\text{-SN2}}$	-2405.582867	-2404.840654	-2404.819892	-2404.882433	**1.8**
TS2$_{(R)\text{-SN2}}$	-2405.581948	-2404.839415	-2404.819081	-2404.880391	**3.1**
C2$_{(R)\text{-SN2}}$	-2405.652006	-2404.906042	-2404.885538	-2404.948398	**-39.6**

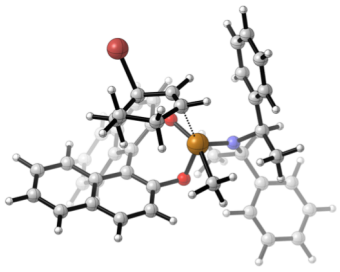
Table S3. Energy values of all stationary points relative to the *anti*-S_N2' pathway in dichloromethane (CPCM)

Coordinate	E (au)	E+ZPE (au)	H (au)	G (au)	**ΔG (kcal/mol)**
C1$_{(R)\text{-SN2p}}$	-4978.050351	-4977.308044	-4977.286123	-4977.351613	**0.0**
TS1$_{(R)\text{-SN2p}}$	-4978.036615	-4977.294525	-4977.273120	-4977.336307	**9.6**
Int$_{(R)\text{-SN2p}}$	-2406.468103	-2405.725591	-2405.705014	-2405.766529	**0.0**
TS2$_{(R)\text{-SN2p}}$	-2406.465726	-2405.723079	-2405.702821	-2405.763874	**1.7**
C2$_{(R)\text{-SN2p}}$	-2406.536391	-2405.790137	-2405.769816	-2405.831371	**-40.7**

Table S4. Energy values of all stationary points relative to the *anti*-S_N2 pathway in dichloromethane (CPCM)

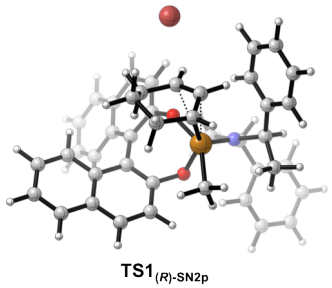
Coordinate	E (au)	E+ZPE (au)	H (au)	G (au)	**ΔG (kcal/mol)**
C1$_{(R)\text{-SN2}}$	-4978.050097	-4977.308144	-4977.285970	-4977.352765	**-0.7**
TS1$_{(R)\text{-SN2}}$	-4978.032900	-4977.290999	-4977.269498	-4977.333591	**11.3**
Int$_{(R)\text{-SN2}}$	-2406.466158	-2405.723945	-2405.703183	-2405.765724	**0.5**
TS2$_{(R)\text{-SN2}}$	-2406.463340	-2405.720807	-2405.700473	-2405.761783	**3.0**
C2$_{(R)\text{-SN2}}$	-2406.533610	-2405.787646	-2405.767142	-2405.830002	**-39.8**

Cartesian coordinates of all stationary points:



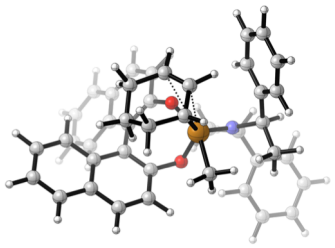
C1 $_{(R)\text{-SN2p}}$

P	-1.098758	0.019047	0.073565
O	-0.693516	1.384238	0.957622
C	0.584460	1.349685	1.513763
C	1.683401	1.661126	0.727482
C	2.991011	1.516271	1.320490
C	3.100318	1.189909	2.714665
C	4.387222	1.063074	3.304376
C	5.530133	1.211778	2.553263
C	5.427410	1.484205	1.169106
C	4.195236	1.633697	0.570673
H	4.139009	1.831601	-0.492919
H	6.328996	1.570743	0.568909
H	6.508019	1.104794	3.014397
H	4.448946	0.828488	4.364396
C	1.922099	0.961987	3.475072
C	0.685315	1.008446	2.881399
H	2.014020	0.715697	4.529689
C	1.494695	2.078938	-0.690426
C	0.744726	1.297351	-1.561647
O	0.076646	0.164287	-1.140774
C	0.690295	1.561713	-2.952215
C	1.320422	2.664379	-3.469118
C	1.990831	3.579040	-2.613839
C	2.067401	3.297920	-1.208860
C	2.679947	4.272788	-0.372214
C	3.213023	5.431180	-0.894933
C	3.170992	5.683046	-2.285842
C	2.566900	4.773352	-3.123078
H	2.508448	4.960543	-4.192757
H	3.601999	6.596513	-2.685940
H	3.665429	6.161181	-0.229165
H	2.713352	4.104015	0.697716
H	1.290123	2.864787	-4.537118
N	-2.624718	0.463667	-0.480018
C	-3.193192	1.796452	-0.865671
C	-4.146621	2.367986	0.183813
C	-3.713023	2.687508	1.479367
C	-4.594607	3.249905	2.402006
C	-5.922135	3.507503	2.046561
C	-6.361877	3.197273	0.760142
C	-5.477588	2.630672	-0.161732
H	-5.828484	2.391265	-1.163923
H	-7.391853	3.390956	0.472044
H	-6.606582	3.944621	2.768605
H	-4.244354	3.488127	3.403022
H	-2.685608	2.484102	1.764209
C	-3.652873	-0.639024	-0.488413
C	-3.175635	-1.877150	-1.255811
C	-3.344452	-3.176963	-0.759872
C	-2.971649	-4.289399	-1.522262
C	-2.421912	-4.121805	-2.792357
C	-2.248593	-2.829971	-3.299136
C	-2.625001	-1.724211	-2.539575
H	-2.482388	-0.724205	-2.940135
H	-1.821105	-2.685634	-4.287712
H	-2.129021	-4.985525	-3.382602
H	-3.114091	-5.287855	-1.117084
H	-3.770469	-3.333647	0.224704
H	-0.223021	0.781667	3.428460
H	0.147075	0.864911	-3.582592
C	-2.167133	2.851833	-1.291613
H	-1.509853	3.149798	-0.474185
H	-1.556739	2.501086	-2.126428
H	-2.717158	3.738210	-1.624609
H	-3.798856	1.586069	-1.757459
C	-4.221267	-0.930950	0.907117
H	-3.470368	-1.380764	1.564111
H	-4.565069	-0.002686	1.366372
H	-5.079114	-1.609140	0.836141
H	-4.474056	-0.220269	-1.082865
Cu	-0.802481	-1.990630	1.366290
C	-1.449397	-2.080094	3.248810
H	-2.109399	-2.946959	3.404678
H	-0.599129	-2.197628	3.938027
H	-2.004009	-1.185887	3.566959
C	0.166754	-3.989674	0.952508
C	0.454031	-3.232021	-0.151814
H	-0.237567	-3.197664	-0.988441
C	1.783488	-2.580320	-0.334120
C	2.630001	-2.559223	0.934197
C	1.178359	-4.332399	2.028258
H	0.875453	-3.865610	2.973430
H	1.139215	-5.416410	2.202886
C	2.610828	-3.916463	1.646590
H	-0.778676	-4.527863	0.979249
H	1.693776	-1.598781	-0.792347
H	3.651194	-2.245047	0.700333
H	2.200830	-1.787544	1.592263
H	3.242272	-3.882577	2.541678
H	3.046611	-4.665410	0.974607
Br	2.787127	-3.596557	-1.812281



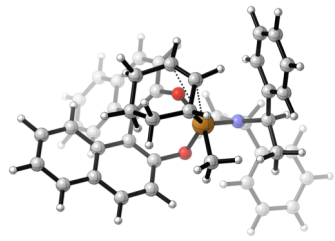
TS1 $_{(R)\text{-SN2p}}$

P	0.695446	0.583010	-0.445041
O	-0.489080	1.641758	-0.950396
C	-1.622174	1.066319	-1.531408
C	-2.590033	0.473162	-0.735167
C	-3.685399	-0.187452	-1.408323
C	-3.805246	-0.084746	-2.835701
C	-4.892538	-0.718992	-3.495303
C	-5.812197	-1.462295	-2.792452
C	-5.669657	-1.609548	-1.393220
C	-4.639141	-0.989588	-0.720538
H	-4.543059	-1.125542	0.349455
H	-6.376610	-2.222729	-0.841310
H	-6.635237	-1.948448	-3.308677
H	-4.973169	-0.616429	-4.574856
C	-2.816803	0.620327	-3.572779
C	-1.727868	1.160986	-2.937099
H	-2.919417	0.701042	-4.651745
C	-2.466037	0.462850	0.750308
C	-1.315446	-0.015270	1.361081
O	-0.186192	-0.336973	0.620960
C	-1.239349	-0.311483	2.742455
C	-2.299524	0.009484	3.551799
C	-3.443277	0.670945	3.026459
C	-3.534302	0.905614	1.613658
C	-4.669854	1.610775	1.127400
C	-5.666240	2.034791	1.980238
C	-5.589560	1.770406	3.367211
C	-4.497395	1.103728	3.874410
H	-4.416802	0.905861	4.940541
H	-6.385311	2.102692	4.027997
H	-6.516649	2.581894	1.582326
H	-4.741567	1.830553	0.068146
H	-2.266399	-0.229504	4.611384
N	1.774186	1.638410	0.269377
C	1.537113	2.828499	1.157380
C	1.848765	4.147113	0.450120
C	1.133865	4.562810	-0.683538
C	1.407731	5.792856	-1.281272
C	2.396410	6.630022	-0.755734
C	3.110313	6.227685	0.372526
C	2.836867	4.993271	0.967938
H	3.395836	4.687149	1.850202
H	3.881524	6.869472	0.790067
H	2.607053	7.587764	-1.223830
H	0.845847	6.100963	-2.159265
H	0.365732	3.917376	-1.098169
C	3.226298	1.473532	-0.094412
C	3.835059	0.152036	0.385865
C	4.973293	-0.385602	-0.238149
C	5.589953	-1.534647	0.265243
C	5.075112	-2.174950	1.394113
C	3.940211	-1.656669	2.023009
C	3.338669	-0.498695	1.526226
H	2.452266	-0.117796	2.022761
H	3.483480	-2.172640	2.862813
H	5.544547	-3.077312	1.775867
H	6.472067	-1.928871	-0.233325
H	5.395157	0.090458	-1.117032
H	-0.940770	1.670511	-3.482793
H	-0.368153	-0.848743	3.110068
C	0.164453	2.882978	1.833198
H	-0.650740	2.990202	1.116053
H	-0.016537	2.000062	2.450096
H	0.151242	3.758390	2.490345
H	2.273343	2.714024	1.963361
C	3.493167	1.810670	-1.571483
H	3.139334	1.024219	-2.246065
H	2.989724	2.745929	-1.827833
H	4.563747	1.951322	-1.749724
H	3.718730	2.263107	0.483657
Cu	1.451788	-1.158150	-1.953188
C	1.496789	-0.702637	-3.889217
H	2.439296	-1.016793	-4.348596
H	0.659602	-1.204014	-4.386356
H	1.383589	0.382089	-3.984569
C	1.943114	-3.214601	-2.271334
C	2.136059	-2.944295	-0.891177
H	3.115220	-2.647483	-0.525255
C	1.032205	-2.880442	-0.040137
C	-0.299182	-3.406406	-0.482959
C	0.715577	-3.970622	-2.750712
H	0.123520	-3.344834	-3.430688
H	1.059262	-4.819075	-3.358193
C	-0.146260	-4.473180	-1.577054
H	2.807394	-3.197100	-2.929204
H	1.127661	-2.487652	0.965343
H	-0.809134	-3.797382	0.403250
H	-0.915865	-2.565755	-0.845184
H	-1.128072	-4.791294	-1.943411
H	0.332111	-5.353861	-1.131407
Br	0.968694	-3.641149	3.047796



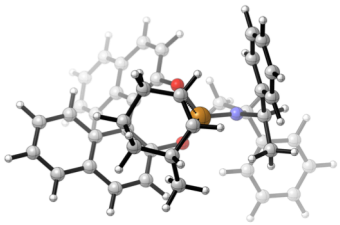
Int$_{(R)\text{-SN2p}}$

P	0.754161	0.234611	-0.103995
O	-0.320231	1.016710	-1.092817
C	-1.420040	0.229436	-1.466550
C	-2.462480	0.032492	-0.574145
C	-3.510260	-0.878946	-0.968332
C	-3.501473	-1.435834	-2.293378
C	-4.541887	-2.320518	-2.687715
C	-5.537841	-2.677736	-1.808595
C	-5.526002	-2.167049	-0.489297
C	-4.543196	-1.291863	-0.080393
H	-4.552200	-0.913204	0.934602
H	-6.300723	-2.467912	0.210050
H	-6.326406	-3.356395	-2.119711
H	-4.529761	-2.717164	-3.699763
C	-2.442106	-1.111759	-3.182840
C	-1.401746	-0.314371	-2.770509
H	-2.457604	-1.514620	-4.192060
C	-2.456555	0.718235	0.749125
C	-1.363475	0.596271	1.594360
O	-0.228609	-0.112605	1.200020
C	-1.356024	1.101390	2.913764
C	-2.441534	1.803132	3.376348
C	-3.549862	2.065945	2.528050
C	-3.558565	1.536223	1.193742
C	-4.649062	1.881630	0.348524
C	-5.681314	2.672199	0.805327
C	-5.687245	3.159696	2.132907
C	-4.638467	2.863436	2.972497
H	-4.619173	3.247249	3.989282
H	-6.511057	3.775982	2.480228
H	-6.496814	2.928775	0.135256
H	-4.660082	1.529261	-0.676192
H	-2.451796	2.188927	4.392153
N	1.894128	1.405108	0.185061
C	1.745643	2.902157	0.338309
C	2.351262	3.648605	-0.846605
C	1.812762	3.533647	-2.137493
C	2.359621	4.254750	-3.198362
C	3.449936	5.104455	-2.986433
C	3.989032	5.228902	-1.706597
C	3.441703	4.502950	-0.645009
H	3.863928	4.611356	0.352181
H	4.834064	5.888433	-1.530563
H	3.872502	5.666356	-3.814399
H	1.931592	4.159059	-4.192568
H	0.963276	2.879050	-2.310325
C	3.328363	0.946091	0.256698
C	3.565654	-0.096889	1.353929
C	4.474707	-1.151674	1.186312
C	4.764264	-2.024976	2.240227
C	4.149428	-1.859974	3.481535
C	3.240982	-0.812241	3.662109
C	2.956042	0.057688	2.611013
H	4.387526	-2.527361	4.305073
H	-0.576515	-0.064199	-3.429427
H	-0.487034	0.915793	3.536684
C	0.329812	3.398377	0.644746
H	-0.357778	3.248635	-0.188062
H	-0.082796	2.923958	1.538245
H	0.394653	4.473840	0.837265
H	2.354952	3.139796	1.219195
C	3.893786	0.582139	-1.122155
H	3.495500	-0.366979	-1.493270
H	3.644308	1.368341	-1.837521
H	4.984527	0.499281	-1.082485
H	3.864300	1.846787	0.574744
Cu	1.112822	-1.988448	-0.916689
C	1.964480	-2.354108	-2.686920
H	2.981305	-2.672492	-2.443277
H	1.475939	-3.063644	-3.351431
H	1.946010	-1.345646	-3.108896
C	0.541729	-3.966592	-1.051462
C	-0.238849	-3.470166	0.068492
C	0.228464	-3.562545	1.351459
C	1.674485	-4.917801	-0.749486
H	1.227878	-5.918290	-0.625465
H	2.354353	-4.991702	-1.603786
C	2.433075	-4.515475	0.523789
C	1.494815	-4.270000	1.719167
H	1.196134	-5.224283	2.186446
H	3.172023	-5.280728	0.781019
H	-1.206183	-3.009438	-0.120212
H	0.004360	-4.115765	-1.982913
H	2.014877	-3.713489	2.508635
H	2.998422	-3.594559	0.326939
H	-0.383854	-3.167464	2.159019
H	4.985521	-1.289342	0.239195
H	2.255910	0.872878	2.767716
H	5.485018	-2.824291	2.090277
H	2.766119	-0.663542	4.628077



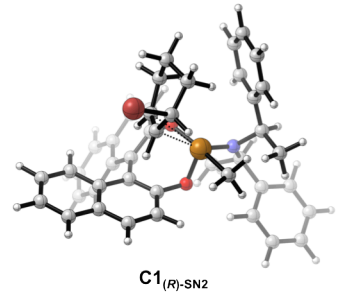
TS2$_{(R)\text{-SN2p}}$

P	0.855346	0.145139	-0.055152
O	-0.118729	1.015919	-1.071604
C	-1.282589	0.346490	-1.477611
C	-2.358648	0.245427	-0.610242
C	-3.481570	-0.554703	-1.039430
C	-3.499244	-1.090276	-2.372442
C	-4.610352	-1.866547	-2.800425
C	-5.652466	-2.142126	-1.945527
C	-5.618151	-1.654608	-0.617999
C	-4.565843	-0.881138	-0.177712
H	-4.559739	-0.517899	0.842854
H	-6.430941	-1.891596	0.062530
H	-6.495012	-2.738848	-2.282135
H	-4.615287	-2.247969	-3.818346
C	-2.395413	-0.858507	-3.236514
C	-1.290097	-0.176222	-2.790057
H	-2.429106	-1.244539	-4.251759
C	-2.323774	0.919280	0.718957
C	-1.270684	0.705192	1.596174
O	-0.171689	-0.077440	1.237296
C	-1.272956	1.183220	2.926122
C	-2.316533	1.957150	3.367469
C	-3.367623	2.325073	2.486104
C	-3.369557	1.821137	1.142057
C	-4.393678	2.274405	0.265265
C	-5.372209	3.141840	0.700858
C	-5.389224	3.602377	2.037719
C	-4.401996	3.202410	2.908388
H	-4.388787	3.564299	3.933270
H	-6.171100	4.279646	2.368000
H	-6.135683	3.480411	0.006355
H	-4.394637	1.945313	-0.767169
H	-2.333373	2.321857	4.390914
N	2.116135	1.185487	0.235442
C	2.121099	2.675030	0.479752
C	2.703717	3.453909	-0.696184
C	2.064093	3.487744	-1.945020
C	2.595153	4.242896	-2.990228
C	3.769254	4.979315	-2.803753
C	4.409241	4.955739	-1.565135
C	3.878080	4.195336	-0.519697
H	4.379625	4.187968	0.446120
H	5.320050	5.526769	-1.408933
H	4.178719	5.568649	-3.619139
H	2.089481	4.262446	-3.951829
H	1.151689	2.919021	-2.098139
C	3.498168	0.597393	0.114587
C	3.731906	-0.583399	1.064767
C	4.542745	-1.671078	0.703289
C	4.857958	-2.673222	1.627993
C	4.364082	-2.608964	2.931060
C	3.550386	-1.533414	3.303224
C	3.242096	-0.533735	2.382243
H	2.619357	0.301526	2.688378
H	3.171382	-1.464164	4.319248
H	4.619955	-3.378586	3.653635
H	5.503744	-3.494181	1.328289
H	4.961676	-1.732933	-0.295272
H	-0.429525	0.000489	-3.427835
H	-0.442869	0.920283	3.573966
C	0.774947	3.254497	0.918994
H	0.011349	3.175878	0.143357
H	0.407477	2.777676	1.830148
H	0.923508	4.317001	1.134100
H	2.809180	2.802331	1.325165
C	3.896312	0.340226	-1.346196
H	3.354964	-0.510752	-1.773990
H	3.678832	1.224555	-1.947279
H	4.968672	0.136638	-1.427508
H	4.148277	1.403817	0.471775
Cu	1.290679	-2.092094	-0.535621
C	1.806039	-2.988936	-2.314910
H	2.896642	-2.996398	-2.272209
H	1.426496	-3.885887	-2.794078
H	1.424885	-2.106694	-2.842404
C	1.304904	-3.736063	0.933428
C	0.227207	-3.421961	1.704493
H	0.400992	-3.105065	2.730508
C	-1.195845	-3.581595	1.259292
C	-1.330948	-3.780136	-0.259552
C	1.155406	-4.204985	-0.454631
C	-0.232951	-4.695467	-0.820573
H	2.306518	-3.650474	1.348283
H	-2.319098	-4.183787	-0.500399
H	-1.273183	-2.802022	-0.757673
H	-0.342073	-4.814468	-1.902177
H	-0.330629	-5.703593	-0.386554
H	-1.786334	-2.718686	1.590503
H	-1.612318	-4.445354	1.803071
H	1.984092	-4.809302	-0.809367



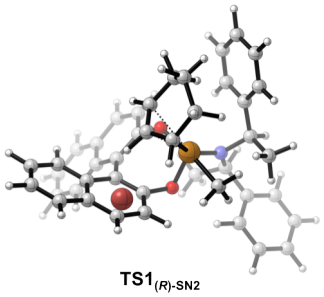
C2$_{(R)\text{-SN2p}}$

P	-0.791585	-0.345763	0.090089
O	0.206333	-0.960471	-1.069547
C	1.306352	-0.142222	-1.381629
C	2.387049	-0.079932	-0.517460
C	3.426204	0.873392	-0.827942
C	3.370510	1.601068	-2.065266
C	4.402893	2.525862	-2.380281
C	5.434577	2.760279	-1.500987
C	5.467650	2.081015	-0.260615
C	4.494365	1.161727	0.066247
H	4.536440	0.654864	1.022746
H	6.269265	2.286274	0.442993
H	6.216431	3.471585	-1.750103
H	4.355189	3.053565	-3.329512
C	2.273559	1.404068	-2.946475
C	1.239706	0.568485	-2.599688
H	2.253242	1.938550	-3.892372
C	2.447124	-0.955614	0.686899
C	1.407099	-0.981932	1.603394
O	0.229566	-0.258239	1.391854
C	1.488871	-1.663962	2.837782
C	2.608425	-2.400915	3.131694
C	3.661326	-2.525357	2.186953
C	3.579862	-1.814371	0.942873
C	4.613826	-2.025476	-0.010840
C	5.677263	-2.858011	0.264057
C	5.773935	-3.523065	1.508259
C	4.780901	-3.360391	2.446365
H	4.829702	-3.881323	3.399100
H	6.622115	-4.169441	1.712991
H	6.447110	-3.009503	-0.487142
H	4.556030	-1.536429	-0.976077
H	2.687551	-2.920792	4.082532
N	-1.988686	-1.486176	0.226297
C	-1.912519	-2.990784	0.247952
C	-2.475555	-3.622473	-1.021568
C	-1.856896	-3.445477	-2.268923
C	-2.368437	-4.070543	-3.405844
C	-3.501879	-4.884523	-3.314712
C	-4.120644	-5.069998	-2.079004
C	-3.608620	-4.440776	-0.940987
H	-4.092214	-4.597786	0.021278
H	-4.999479	-5.703150	-1.996570
H	-3.896020	-5.371949	-4.201760
H	-1.878926	-3.927391	-4.365312
H	-0.975467	-2.815904	-2.350534
C	-3.393900	-0.943505	0.212049
C	-3.621207	0.124991	1.290796
C	-4.423690	1.255545	1.057791
C	-4.710245	2.160131	2.088585
C	-4.196333	1.954678	3.368357
C	-3.395710	0.833659	3.614511
C	-3.116453	-0.069412	2.590908
H	-2.502933	-0.940560	2.799439
H	-3.001213	0.655263	4.610811
H	-4.428929	2.648481	4.170965
H	-5.351541	3.014229	1.888303
H	-4.863735	1.421906	0.080224
H	0.382946	0.414928	-3.248173
H	0.659847	-1.581855	3.533220
C	-0.523448	-3.541251	0.578787
H	0.215800	-3.298681	-0.186879
H	-0.165523	-3.180297	1.545702
H	-0.598426	-4.631272	0.635105
H	-2.573514	-3.281411	1.074625
C	-3.842029	-0.532598	-1.198442
H	-3.335200	0.380076	-1.538212
H	-3.611285	-1.331045	-1.905036
H	-4.921668	-0.355083	-1.231336
H	-4.007662	-1.804981	0.498908
Cu	-1.535423	1.801793	0.146246
C	-1.373942	3.711214	-2.518802
H	-2.357849	3.270762	-2.722618
H	-1.063312	4.256981	-3.416165
H	-0.657596	2.895041	-2.361845
C	-2.055173	3.997728	-0.094977
C	-1.414495	3.793500	1.095524
H	-2.002182	3.473386	1.958839
C	0.033612	4.157565	1.317320
C	0.777507	4.371439	-0.008218
C	-1.420039	4.658732	-1.303884
C	-0.040900	5.265207	-0.951910
H	-3.129505	3.812513	-0.144415
H	1.757992	4.819323	0.183141
H	0.969990	3.397643	-0.480329
H	0.517277	5.461143	-1.874219
H	-0.194304	6.238373	-0.467381
H	0.525359	3.392940	1.931406
H	0.054514	5.079273	1.919848
H	-2.096668	5.482919	-1.573100



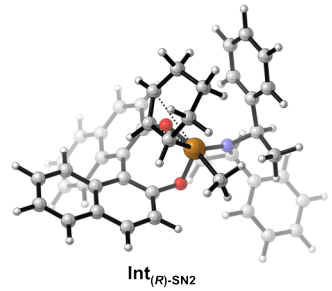
C1$_{(R)\text{-SN2}}$

P	0.597986	-0.913254	0.006702
O	1.522046	-0.013874	-1.065065
C	0.945626	1.210324	-1.402986
C	1.068034	2.286933	-0.537519
C	0.361988	3.499090	-0.876387
C	-0.325943	3.586692	-2.134190
C	-1.013553	4.783197	-2.473864
C	-1.059249	5.846911	-1.602927
C	-0.421343	5.748860	-0.344390
C	0.269826	4.610282	0.008296
H	0.742047	4.552096	0.981572
H	-0.481927	6.577692	0.355614
H	-1.595771	6.752789	-1.870557
H	-1.519530	4.833544	-3.434919
C	-0.337627	2.465083	-3.005794
C	0.262276	1.285881	-2.637807
H	-0.855266	2.542218	-3.958352
C	1.862104	2.150819	0.716967
C	1.602423	1.114267	1.606828
O	0.673145	0.131761	1.338113
C	2.216105	1.048782	2.882167
C	3.156303	1.978962	3.244224
C	3.563037	2.987431	2.330244
C	2.925816	3.068075	1.047049
C	3.411178	4.040449	0.128116
C	4.434357	4.898670	0.468338
C	5.030782	4.840933	1.749322
C	4.602069	3.899290	2.656515
H	5.063520	3.827683	3.638684
H	5.831487	5.528322	2.007363
H	4.789838	5.623813	-0.258709
H	2.974960	4.094457	-0.862432
H	3.621696	1.937053	4.225834
N	1.604502	-2.241655	0.226621
C	3.099083	-2.363895	0.217359
C	3.629347	-3.027887	-1.053564
C	3.433991	-2.455610	-2.319545
C	3.968259	-3.057674	-3.458225
C	4.710148	-4.238049	-3.352543
C	4.912758	-4.813008	-2.098375
C	4.373417	-4.209756	-0.958949
H	4.535495	-4.664544	0.016602
H	5.485625	-5.731777	-2.003496
H	5.123865	-4.705182	-4.242202
H	3.805376	-2.604050	-4.432483
H	2.854798	-1.541921	-2.408908
C	0.904562	-3.568247	0.385272
C	-0.154672	-3.539473	1.492735
C	-1.461095	-4.005311	1.296396
C	-2.374343	-4.043651	2.355622
C	-1.998155	-3.613398	3.627267
C	-0.698334	-3.141104	3.835231
C	0.210238	-3.108844	2.779548
H	-2.706547	-3.648183	4.450543
H	0.227599	0.404147	-3.268800
H	1.912469	0.250676	3.552174
C	3.875753	-1.075961	0.515803
H	3.750140	-0.321122	-0.260623
H	3.584483	-0.646824	1.476923
H	4.938674	-1.333878	0.569494
H	3.323031	-3.048286	1.046528
C	0.421141	-4.150918	-0.948637
H	-0.384801	-3.553714	-1.384426
H	1.249282	-4.180079	-1.659088
H	0.061592	-5.176328	-0.805816
H	1.695920	-4.232875	0.751993
Cu	-1.621436	-1.068930	-0.915275
C	-2.276934	-2.041595	-2.520898
H	-2.889394	-2.914821	-2.247764
H	-2.904764	-1.388607	-3.145138
H	-1.459304	-2.408199	-3.157343
C	-3.283778	0.470683	-0.447295
C	-2.509885	0.639671	0.659690
C	-2.829439	0.023083	2.002883
C	-4.541490	-0.338127	-0.434341
H	-4.672645	-0.896858	-1.358325
C	-4.685176	-1.221033	0.801669
C	-4.281362	-0.479129	2.081513
H	-4.958682	0.372308	2.220653
H	-5.706630	-1.607200	0.870262
H	-1.666510	1.322600	0.610303
H	-3.081506	1.045794	-1.347141
H	-4.403466	-1.135275	2.950765
H	-4.019437	-2.083892	0.650567
H	-2.128865	-0.796959	2.211943
H	-1.776699	-4.343395	0.315841
H	1.218805	-2.740683	2.949757
H	-3.380418	-4.415785	2.180985
H	-0.391566	-2.805590	4.822501
H	-2.645281	0.771232	2.785069
Br	-6.111209	0.971020	-0.529961



TS1$_{(R)\text{-SN2}}$

P	-1.083316	-0.169012	-0.046866
O	-0.634457	0.864834	1.167191
C	0.760743	1.069628	1.182817
C	1.322480	1.971681	0.294170
C	2.762803	2.030187	0.229614
C	3.536114	1.201369	1.111767
C	4.953766	1.185574	1.004662
C	5.595520	1.971175	0.075260
C	4.839714	2.790394	-0.795863
C	3.463045	2.814692	-0.729292
H	2.904801	3.427491	-1.427065
H	5.348828	3.395181	-1.541956
H	6.678276	1.945946	-0.008078
H	5.503355	0.495944	1.638289
C	2.885010	0.360463	2.054594
C	1.512304	0.289179	2.085646
H	3.486878	-0.291133	2.679690
C	0.444531	2.758904	-0.616527
C	-0.460696	2.103928	-1.440774
O	-0.613445	0.723811	-1.387448
C	-1.217232	2.779721	-2.426392
C	-1.118487	4.143563	-2.547799
C	-0.294114	4.889684	-1.664181
C	0.486701	4.197189	-0.678947
C	1.252832	4.976764	0.232258
C	1.269052	6.352199	0.154417
C	0.524313	7.028777	-0.840271
C	-0.242280	6.308186	-1.726847
H	-0.832344	6.815269	-2.486653
H	0.551631	8.113472	-0.894110
H	1.857059	6.923204	0.867632
H	1.824590	4.474311	1.003959
H	-1.689015	4.669849	-3.308833
N	-2.749951	-0.196269	0.128506
C	-3.692493	0.858481	0.644481
C	-4.234638	0.505097	2.028029
C	-3.385452	0.394043	3.139678
C	-3.905345	0.105089	4.400882
C	-5.281499	-0.073735	4.573553
C	-6.134030	0.039491	3.476007
C	-5.610475	0.325871	2.212114
H	-6.282241	0.414703	1.360325
H	-7.205140	-0.097416	3.598621
H	-5.683430	-0.299728	5.557392
H	-3.235196	0.020624	5.252236
H	-2.315625	0.531446	3.013361
C	-3.450768	-1.481271	-0.225797
C	-3.176819	-1.932933	-1.665379
C	-2.972565	-3.280015	-1.995828
C	-2.824191	-3.678901	-3.328464
C	-2.875981	-2.737033	-4.355062
C	-3.079399	-1.390656	-4.039505
C	-3.229997	-0.996797	-2.711497
H	-2.763291	-3.046522	-5.390416
H	0.992924	-0.371953	2.771318
H	-1.857684	2.193161	-3.077446
C	-3.174764	2.300749	0.610005
H	-2.354725	2.469364	1.307350
H	-2.850498	2.587938	-0.392817
H	-4.005467	2.954195	0.896520
H	-4.541339	0.825847	-0.050916
C	-3.262347	-2.573977	0.833098
H	-2.249598	-2.983503	0.819991
H	-3.454433	-2.161326	1.825321
H	-3.969197	-3.394226	0.667340
H	-4.511532	-1.207303	-0.197567
Cu	0.433617	-2.076975	0.167787
C	0.202970	-3.143670	1.837344
H	-0.104187	-4.168240	1.608270
H	1.144158	-3.140661	2.389967
H	-0.579629	-2.623768	2.399035
C	2.329477	-2.048510	-0.893962
C	1.623240	-1.741980	-2.036909
C	0.932095	-2.816730	-2.839126
C	2.132181	-3.318279	-0.254756
H	2.679091	-3.471413	0.675956
C	1.677823	-4.509000	-1.074412
C	1.575628	-4.190149	-2.577800
H	2.585866	-4.182710	-3.005226
H	2.407616	-5.312474	-0.907652
H	1.635833	-0.725788	-2.420804
H	2.938856	-1.316166	-0.368718
H	1.014165	-4.975767	-3.095177
H	0.726285	-4.897941	-0.688728
H	-0.143796	-2.846222	-2.606130
H	-2.936733	-4.033780	-1.216762
H	-3.386121	0.052211	-2.477481
H	-2.671989	-4.730153	-3.558595
H	-3.125619	-0.647023	-4.830697
H	0.986622	-2.559635	-3.904259
Br	4.732488	-2.640679	1.712376



Int$_{(R)\text{-SN2}}$

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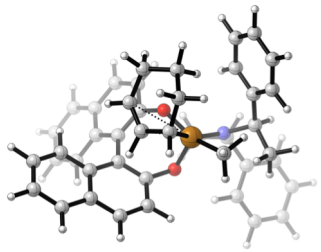
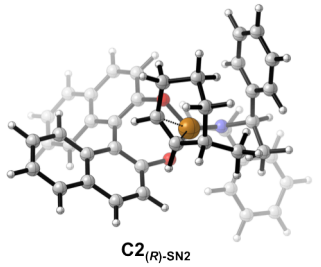
O	-0.320231	1.016710	-1.092817
C	-1.420040	0.229436	-1.466550
C	-2.462480	0.032492	-0.574145
C	-3.510260	-0.878946	-0.968332
C	-3.501473	-1.435834	-2.293378
C	-4.541887	-2.320518	-2.687715
C	-5.537841	-2.677736	-1.808595
C	-5.526002	-2.167049	-0.489297
C	-4.543196	-1.291863	-0.080393
H	-4.552200	-0.913204	0.934602
H	-6.300723	-2.467912	0.210050
H	-6.326406	-3.356395	-2.119711
H	-4.529761	-2.717164	-3.699763
C	-2.442106	-1.111759	-3.182840
C	-1.401746	-0.314371	-2.770509
H	-2.457604	-1.514620	-4.192060
C	-2.456555	0.718235	0.749125
C	-1.363475	0.596271	1.594360
O	-0.228609	-0.112605	1.200020
C	-1.356024	1.101390	2.913764
C	-2.441534	1.803132	3.376348
C	-3.549862	2.065945	2.528050
C	-3.558565	1.536223	1.193742
C	-4.649062	1.881630	0.348524
C	-5.681314	2.672199	0.805327
C	-5.687245	3.159696	2.132907
C	-4.638467	2.863436	2.972497
H	-4.619173	3.247249	3.989282
H	-6.511057	3.775982	2.480228
H	-6.496814	2.928775	0.135256
H	-4.660082	1.529261	-0.676192
H	-2.451796	2.188927	4.392153
N	1.894128	1.405108	0.185061
C	1.745643	2.902157	0.338309
C	2.351262	3.648605	-0.846605
C	1.812762	3.533647	-2.137493
C	2.359621	4.254750	-3.198362
C	3.449936	5.104455	-2.986433
C	3.989032	5.228902	-1.706597
C	3.441703	4.502950	-0.645009
H	3.863928	4.611356	0.352181
H	4.834064	5.888433	-1.530563
H	3.872502	5.666356	-3.814399
H	1.931592	4.159059	-4.192568
H	0.963276	2.879050	-2.310325
C	3.328363	0.946091	0.256698
C	3.565654	-0.096889	1.353929
C	4.474707	-1.151674	1.186312
C	4.764264	-2.024976	2.240227
C	4.149428	-1.859974	3.481535
C	3.240982	-0.812241	3.662109
C	2.956042	0.057688	2.611013
H	4.387526	-2.527361	4.305073
H	-0.576515	-0.064199	-3.429427
H	-0.487034	0.915793	3.536684
C	0.329812	3.398377	0.644746
H	-0.357778	3.248635	-0.188062
H	-0.082796	2.923958	1.538245
H	0.394653	4.473840	0.837265
H	2.354952	3.139796	1.219195
C	3.893786	0.582139	-1.122155
H	3.495500	-0.366979	-1.493270
H	3.644308	1.368341	-1.837521
H	4.984527	0.499281	-1.082485
H	3.864300	1.846787	0.574744
Cu	1.112822	-1.988448	-0.916689
C	1.964480	-2.354108	-2.686920
H	2.981305	-2.672492	-2.443277
H	1.475939	-3.063644	-3.351431
H	1.946010	-1.345646	-3.108896
C	0.541729	-3.966592	-1.051462
C	-0.238849	-3.470166	0.068492
C	0.228464	-3.562545	1.351459
C	1.674485	-4.917801	-0.749486
H	1.227878	-5.918290	-0.625465
H	2.354353	-4.991702	-1.603786
C	2.433075	-4.515475	0.523789
C	1.494815	-4.270000	1.719167
H	1.196134	-5.224283	2.186446
H	3.172023	-5.280728	0.781019
H	-1.206183	-3.009438	-0.120212
H	0.004360	-4.115765	-1.982913
H	2.014877	-3.713489	2.508635
H	2.998422	-3.594559	0.326939
H	-0.383854	-3.167464	2.159019
H	4.985521	-1.289342	0.239195
H	2.255910	0.872878	2.767716
H	5.485018	-2.824291	2.090277
H	2.766119	-0.663542	4.628077



TS2$_{(R)\text{-SN2}}$

P	0.844400	0.182282	-0.116735
O	-0.147068	1.100869	-1.074995
C	-1.299298	0.428935	-1.504004
C	-2.366349	0.266263	-0.634927
C	-3.472956	-0.542035	-1.089956
C	-3.485229	-1.028278	-2.442679
C	-4.581099	-1.813260	-2.894882
C	-5.612520	-2.144067	-2.046823
C	-5.582722	-1.706008	-0.702108
C	-4.546165	-0.925513	-0.236881
H	-4.546256	-0.596639	0.795339
H	-6.387357	-1.985696	-0.028186
H	-6.442925	-2.746749	-2.402215
H	-4.582884	-2.155850	-3.926521
C	-2.390836	-0.738942	-3.302242
C	-1.300183	-0.045826	-2.834801
H	-2.420535	-1.086935	-4.331319
C	-2.333031	0.875872	0.725038
C	-1.269201	0.636907	1.583675
O	-0.161122	-0.107441	1.181367
C	-1.269606	1.054110	2.934141
C	-2.322243	1.789592	3.417992
C	-3.386866	2.179353	2.562669
C	-3.390691	1.738378	1.196812
C	-4.429754	2.213156	0.349388
C	-5.419731	3.041986	0.831793
C	-5.433750	3.440201	2.188575
C	-4.432626	3.018116	3.032567
H	-4.417197	3.332873	4.072844
H	-6.224461	4.087748	2.555370
H	-6.194696	3.398584	0.159374
H	-4.433508	1.932054	-0.697206
H	-2.336324	2.107354	4.457027
N	2.089692	1.224546	0.222930
C	2.061941	2.707299	0.516297
C	2.675704	3.524350	-0.616780
C	2.085584	3.573952	-1.889100
C	2.641009	4.363874	-2.895113
C	3.790828	5.119653	-2.645373
C	4.381903	5.080029	-1.383098
C	3.826332	4.284819	-0.376962
H	4.290038	4.264358	0.607380
H	5.273865	5.665183	-1.178042
H	4.219618	5.735852	-3.430399
H	2.173497	4.395320	-3.875546
H	1.191648	2.990986	-2.090730
C	3.486319	0.660862	0.174859
C	3.685050	-0.523506	1.128064
C	4.556029	-1.579743	0.820328
C	4.811343	-2.595938	1.746429
C	4.203852	-2.573239	3.001897
C	3.338933	-1.524000	3.324710
C	3.085935	-0.511707	2.399546
H	4.411433	-3.355714	3.726132
H	-0.447459	0.176471	-3.468874
H	-0.430032	0.776501	3.563267
C	0.698266	3.267229	0.927779
H	-0.035104	3.224334	0.121538
H	0.296323	2.753765	1.803814
H	0.841008	4.319064	1.193787
H	2.718832	2.815567	1.388401
C	3.966497	0.434841	-1.265636
H	3.452177	-0.404154	-1.743886
H	3.781646	1.334195	-1.855715
H	5.042192	0.234931	-1.290777
H	4.100024	1.475772	0.574345
Cu	1.058533	-2.052922	-0.836769
C	2.387419	-3.016784	-2.045060
H	3.241710	-2.735294	-1.423014
H	2.475379	-4.052679	-2.355074
H	2.266528	-2.365139	-2.915606
C	0.442146	-4.045664	-1.135129
C	-0.772466	-3.347989	-0.688013
C	-1.123835	-3.288916	0.625840
C	1.072755	-4.976646	-0.119307
H	0.475003	-5.902359	-0.125819
H	2.085549	-5.261336	-0.418534
C	1.071194	-4.365416	1.289777
C	-0.337794	-3.932142	1.727984
H	-0.920254	-4.799039	2.080935
H	1.485563	-5.078853	2.008924
H	-1.424361	-2.908242	-1.439237
H	0.386636	-4.411057	-2.154891
H	-0.284845	-3.251454	2.587066
H	1.741722	-3.494222	1.306905
H	-2.061809	-2.804689	0.888963
H	5.064062	-1.608320	-0.137853
H	2.419440	0.301802	2.668831
H	5.498545	-3.396476	1.486555
H	2.871265	-1.485520	4.304784



C2$_{(R)\text{-SN2}}$

P	0.547790	0.556721	0.051576
O	-0.580055	1.003427	-1.071063
C	-1.423117	-0.063353	-1.425175
C	-2.453173	-0.434828	-0.576343
C	-3.198978	-1.622140	-0.920740
C	-2.932930	-2.287362	-2.166670
C	-3.676345	-3.448387	-2.512709
C	-4.622219	-3.963179	-1.656572
C	-4.855702	-3.337296	-0.409602
C	-4.166961	-2.198453	-0.051787
H	-4.359380	-1.735808	0.908608
H	-5.586332	-3.759091	0.274483
H	-5.182570	-4.852402	-1.929529
H	-3.476188	-3.927979	-3.467510
C	-1.916125	-1.789344	-3.025629
C	-1.150598	-0.710742	-2.651425
H	-1.743203	-2.280956	-3.979392
C	-2.736217	0.359246	0.652380
C	-1.733416	0.618223	1.575191
O	-0.415753	0.207706	1.356353
C	-1.981035	1.230288	2.824049
C	-3.248723	1.658169	3.129074
C	-4.301555	1.536444	2.183960
C	-4.047671	0.898320	0.923704
C	-5.103608	0.864256	-0.028401
C	-6.341527	1.396149	0.261957
C	-6.598526	1.987588	1.520530
C	-5.594291	2.057710	2.458215
H	-5.770172	2.527614	3.422439
H	-7.581169	2.395776	1.737067
H	-7.126940	1.366053	-0.487771
H	-4.926474	0.427911	-1.004452
H	-3.453400	2.120319	4.090911
N	1.490720	1.901418	0.240480
C	1.097983	3.354763	0.329435
C	1.547514	4.140719	-0.898220
C	1.017277	3.878687	-2.171032
C	1.411766	4.639936	-3.270808
C	2.337859	5.676282	-3.115992
C	2.867143	5.946486	-1.854615
C	2.473686	5.180418	-0.753851
H	2.885453	5.402407	0.228709
H	3.584691	6.751425	-1.723452
H	2.640944	6.269354	-3.974028
H	0.991813	4.429284	-4.250600
H	0.295097	3.077463	-2.300146
C	2.979879	1.668978	0.261064
C	3.412100	0.710628	1.376670
C	4.490174	-0.172427	1.211026
C	4.936618	-0.969626	2.270691
C	4.313237	-0.898727	3.516216
C	3.242837	-0.018535	3.696984
C	2.801769	0.777973	2.641327
H	4.664786	-1.511012	4.341517
H	-0.362135	-0.317686	-3.286070
H	-1.157214	1.339722	3.521721
C	-0.382532	3.591712	0.638114
H	-1.038017	3.247649	-0.163957
H	-0.682883	3.112558	1.572932
H	-0.532156	4.669526	0.751623
H	1.665982	3.735127	1.187840
C	3.525639	1.330029	-1.133433
H	3.241176	0.318384	-1.448037
H	3.134127	2.041355	-1.863100
H	4.617943	1.394378	-1.153440
H	3.386017	2.652977	0.520179
Cu	1.367108	-1.535692	-0.288535
C	3.999256	-2.973746	-1.683891
H	4.126252	-2.289139	-0.836108
H	4.983985	-3.387057	-1.926569
H	3.661595	-2.390271	-2.549326
C	3.009528	-4.104386	-1.342863
C	1.589167	-3.590704	-1.201219
C	0.849790	-3.682601	-0.054046
C	3.431918	-4.932415	-0.106177
H	3.024166	-5.947166	-0.202860
H	4.522603	-5.036208	-0.091613
C	2.931722	-4.327123	1.213926
C	1.399014	-4.249841	1.231124
H	0.965709	-5.254362	1.357775
H	3.281722	-4.926661	2.060797
H	1.085878	-3.274380	-2.117796
H	2.988797	-4.776897	-2.212730
H	1.037861	-3.665720	2.086922
H	3.349679	-3.320553	1.354800
H	-0.219646	-3.465162	-0.097353
H	5.011484	-0.227262	0.261447
H	1.973982	1.462071	2.800946
H	5.783271	-1.634004	2.120655
H	2.757545	0.056968	4.666036

2.1.2. Alkylation of (*S*)-**1**

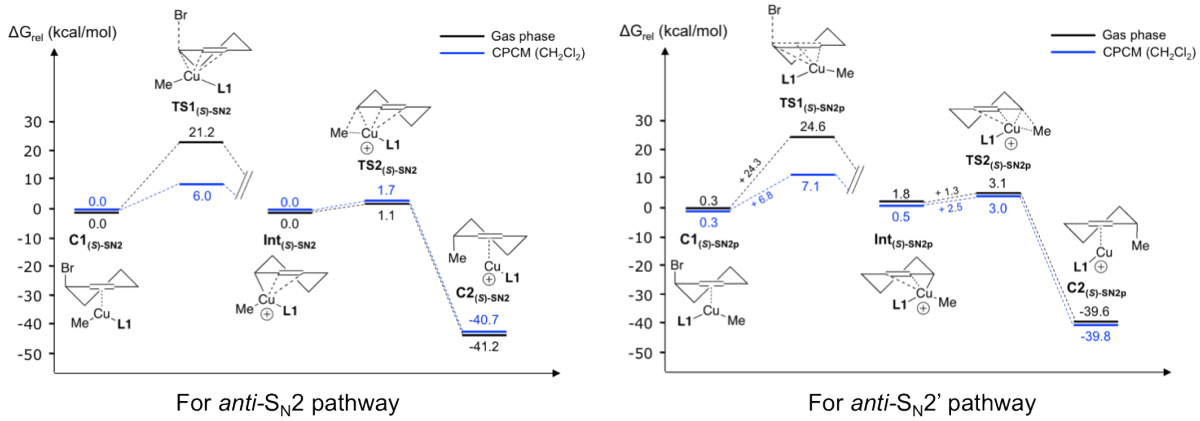


Figure S2. Energy profiles corresponding to the alkylation of (*S*)-**1** by MeCu**L1** in both *anti*-S_N2 and *anti*-S_N2' pathways.

Table S5. Energy values of all stationary points relative to the *anti*-S_N2 pathway in gas phase

Coordinate	E (au)	E+ZPE (au)	H (au)	G (au)	**ΔG (kcal/mol)**
$C1_{(S)\text{-}SN2}$	-4977.208413	-4976.466582	-4976.444475	-4976.510908	**0.0**
$TS1_{(S)\text{-}SN2}$	-4977.175017	-4976.433692	-4976.411940	-4976.477124	**21.2**
$Int_{(S)\text{-}SN2}$	-2405.586869	-2404.844357	-2404.823780	-2404.885295	**0.0**
$TS2_{(S)\text{-}SN2}$	-2405.585323	-2404.842676	-2404.822418	-2404.883471	**1.1**
$C2_{(S)\text{-}SN2}$	-2405.655953	-2404.909699	-2404.889378	-2404.950933	**-41.2**

Table S6. Energy values of all stationary points relative to the *anti*-S_N2' pathway in gas phase

Coordinate	E (au)	E+ZPE (au)	H (au)	G (au)	**ΔG (kcal/mol)**
$C1_{(S)\text{-}SN2p}$	-4977.208941	-4976.467091	-4976.445511	-4976.510417	**0.3**
$TS1_{(S)\text{-}SN2p}$	-4977.166776	-4976.427243	-4976.405179	-4976.471653	**24.6**
$Int_{(S)\text{-}SN2p}$	-2405.582867	-2404.840654	-2404.819892	-2404.882433	**1.8**
$TS2_{(S)\text{-}SN2p}$	-2405.581948	-2404.839415	-2404.819081	-2404.880391	**3.1**
$C2_{(S)\text{-}SN2p}$	-2405.652006	-2404.906042	-2404.885538	-2404.948398	**-39.6**

Table S7. Energy values of all stationary points relative to the *anti*-S_N2 pathway in dichloromethane (CPCM)

Coordinate	E (au)	E+ZPE (au)	H (au)	G (au)	**ΔG (kcal/mol)**
$C1_{(S)\text{-}SN2}$	-4978.048925	-4977.307094	-4977.284987	-4977.351420	**0.0**
$TS1_{(S)\text{-}SN2}$	-4978.039823	-4977.298498	-4977.276746	-4977.341930	**6.0**
$Int_{(S)\text{-}SN2}$	-2406.468103	-2405.725591	-2405.705014	-2405.766529	**0.0**
$TS2_{(S)\text{-}SN2}$	-2406.465726	-2405.723079	-2405.702821	-2405.763874	**1.7**
$C2_{(S)\text{-}SN2}$	-2406.536391	-2405.790137	-2405.769816	-2405.831371	**-40.7**

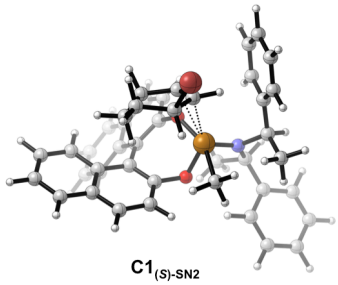
Table S8. Energy values of all stationary points relative to the *anti*-S_N2' pathway in dichloromethane (CPCM)

Coordinate	E (au)	E+ZPE (au)	H (au)	G (au)	**ΔG (kcal/mol)**
C1$_{(S)\text{-SN2p}}$	-4978.049384	-4977.307534	-4977.285954	-4977.350860	**0.3**
TS1$_{(S)\text{-SN2p}}$	-4978.035214	-4977.295681	-4977.273617	-4977.340091	**7.1**
Int$_{(S)\text{-SN2p}}$	-2406.466158	-2405.723945	-2405.703183	-2405.765724	**0.5**
TS2$_{(S)\text{-SN2p}}$	-2406.463340	-2405.720807	-2405.700473	-2405.761783	**3.0**
C2$_{(S)\text{-SN2p}}$	-2406.533610	-2405.787646	-2405.767142	-2405.830002	**-39.8**

Cartesian coordinates of all stationary points:

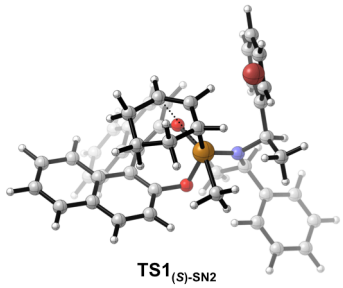
Int$_{(S)\text{-SN2}}$, **TS2$_{(S)\text{-SN2}}$** and **C2$_{(S)\text{-SN2}}$** are respectively identical to **Int$_{(R)\text{-SN2p}}$**, **TS2$_{(R)\text{-SN2p}}$** and **C2$_{(R)\text{-SN2p}}$**.

Int$_{(S)\text{-SN2p}}$, **TS2$_{(S)\text{-SN2p}}$** and **C2$_{(S)\text{-SN2p}}$** are respectively identical to **Int$_{(R)\text{-SN2}}$**, **TS2$_{(R)\text{-SN2}}$** and **C2$_{(R)\text{-SN2}}$**.



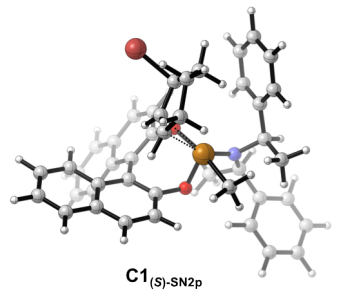
C1$_{(S)\text{-SN2}}$

P	-0.208286	0.946205	0.028197
O	-1.401397	0.499201	-1.060270
C	-1.398959	-0.852933	-1.398402
C	-1.986057	-1.774552	-0.544335
C	-1.876548	-3.170740	-0.890529
C	-1.284663	-3.541198	-2.145453
C	-1.187549	-4.915603	-2.493900
C	-1.620177	-5.898564	-1.634085
C	-2.162119	-5.540335	-0.377579
C	-2.287937	-4.216375	-0.016907
H	-2.696393	-3.963450	0.954151
H	-2.478356	-6.316963	0.313527
H	-1.534195	-6.945948	-1.909651
H	-0.747904	-5.175390	-3.453936
C	-0.774597	-2.531460	-3.004599
C	-0.802489	-1.211497	-2.628432
H	-0.331259	-2.820618	-3.953897
C	-2.651569	-1.311646	0.706614
C	-1.968936	-0.493861	1.599747
O	-0.699874	-0.023630	1.330797
C	-2.499115	-0.160046	2.869900
C	-3.755752	-0.580613	3.224056
C	-4.557045	-1.311942	2.306923
C	-4.011136	-1.669622	1.028744
C	-4.867184	-2.334572	0.106370
C	-6.165468	-2.655522	0.438848
C	-6.685159	-2.335846	1.714731
C	-5.893447	-1.673886	2.624854
H	-6.284069	-1.403037	3.603013
H	-7.708185	-2.600929	1.966558
H	-6.798009	-3.154442	-0.290381
H	-4.491534	-2.578362	-0.880520
H	-4.163345	-0.334471	4.201412
N	-0.616688	2.563188	0.255535
C	-1.932592	3.280285	0.203370
C	-2.098301	4.115366	-1.066594
C	-2.090678	3.527336	-2.340422
C	-2.287067	4.306238	-3.480335
C	-2.498880	5.683771	-3.368116
C	-2.512369	6.277050	-2.106231
C	-2.311792	5.495024	-0.965451
H	-2.323294	5.965107	0.016229
H	-2.673697	7.347235	-2.006149
H	-2.649576	6.287955	-4.258683
H	-2.273955	3.836778	-4.460563
H	-1.920014	2.459445	-2.434888
C	0.553943	3.494244	0.444425
C	1.465543	3.050135	1.593574
C	2.861105	3.014507	1.474526
C	3.665857	2.667123	2.565060
C	3.088742	2.352052	3.794340
C	1.697280	2.389718	3.928389
C	0.898921	2.736327	2.840461
H	-0.181906	2.757379	2.951962
H	1.235104	2.152080	4.883083
H	3.714137	2.082339	4.640875
H	4.746079	2.645183	2.447748
H	3.334194	3.257531	0.529434
H	-0.371879	-0.430689	-3.245504
H	-1.880412	0.425979	3.542212
C	-3.175461	2.415695	0.444984
H	-3.339023	1.687213	-0.349099
H	-3.118016	1.890092	1.400685
H	-4.042868	3.083420	0.478410
H	-1.891243	3.988449	1.041968
C	1.282085	3.806487	-0.869975
H	1.800007	2.927989	-1.269042
H	0.561384	4.142499	-1.617592
H	2.014061	4.608397	-0.721465
H	0.088144	4.430109	0.775899
Cu	1.950740	0.315340	-0.791501
C	2.589046	0.574618	-2.654795
H	3.570176	1.072279	-2.681150
H	2.705739	-0.395151	-3.163427
H	1.902037	1.178283	-3.264731
C	3.665592	-0.630588	0.453519
C	2.574542	-0.958193	1.198488
H	2.207751	-0.254154	1.941191
C	1.911218	-2.312745	1.124584
C	2.368762	-3.107549	-0.107815
C	4.371175	-1.615092	-0.439478
H	4.339126	-1.302326	-1.482125
C	3.899559	-3.057377	-0.244557
H	4.148654	0.331686	0.597619
H	2.037506	-4.149609	-0.030649
H	1.898394	-2.692602	-1.008620
H	4.247977	-3.676605	-1.077639
H	4.351915	-3.461388	0.669012
H	0.822723	-2.189948	1.127568
H	2.155189	-2.872161	2.042060
Br	6.354192	-1.510450	-0.041097



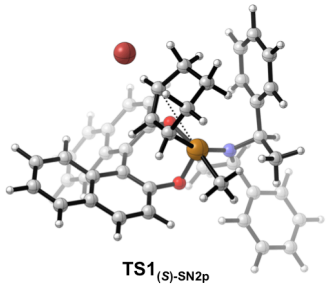
TS1$_{(S)\text{-}SN2}$

P	0.129909	0.675972	-0.172570
O	-1.197563	0.751754	-1.178347
C	-1.843025	-0.462646	-1.415049
C	-2.697562	-0.992374	-0.459085
C	-3.267432	-2.290865	-0.720456
C	-3.039021	-2.920585	-1.990978
C	-3.614129	-4.193461	-2.254053
C	-4.356687	-4.847223	-1.298233
C	-4.545482	-4.251670	-0.028936
C	-4.018338	-3.009948	0.251620
H	-4.166926	-2.574023	1.232245
H	-5.108742	-4.780479	0.734991
H	-4.785764	-5.822677	-1.509083
H	-3.442091	-4.647878	-3.226806
C	-2.217746	-2.275571	-2.953772
C	-1.606638	-1.080603	-2.663463
H	-2.059432	-2.752654	-3.917429
C	-2.955691	-0.246869	0.805703
C	-1.887716	0.177164	1.584991
O	-0.583710	-0.033341	1.169590
C	-2.058854	0.775066	2.854875
C	-3.325477	1.010530	3.328262
C	-4.464327	0.701577	2.536571
C	-4.285204	0.081901	1.253827
C	-5.442700	-0.140774	0.456400
C	-6.698975	0.194678	0.912383
C	-6.873821	0.768407	2.193427
C	-5.775360	1.018357	2.983258
H	-5.891675	1.477058	3.962283
H	-7.870668	1.021450	2.543160
H	-7.563879	0.021624	0.277861
H	-5.328599	-0.569038	-0.532664
H	-3.471134	1.461091	4.306727
N	0.467931	2.299954	0.002270
C	-0.408655	3.518692	-0.057151
C	-0.116337	4.347974	-1.306265
C	-0.278856	3.810378	-2.591661
C	-0.047238	4.594048	-3.721415
C	0.347852	5.928558	-3.585461
C	0.509811	6.472799	-2.311942
C	0.280141	5.684159	-1.181187
H	0.409773	6.114905	-0.190149
H	0.820259	7.507590	-2.194613
H	0.530277	6.536557	-4.467313
H	-0.174923	4.163527	-4.711201
H	-0.584425	2.773849	-2.702359
C	1.920455	2.636767	0.290604
C	2.418949	1.991257	1.585454
C	3.520783	1.129859	1.630110
C	3.959249	0.584001	2.843518
C	3.304292	0.905357	4.030554
C	2.208974	1.776542	4.003205
C	1.773855	2.311826	2.793445
H	0.922651	2.989721	2.783062
H	1.700741	2.044556	4.926490
H	3.645468	0.487413	4.974033
H	4.804014	-0.100021	2.819794
H	4.069421	0.857046	0.733660
H	-0.948245	-0.587323	-3.370457
H	-1.170842	1.029052	3.424723
C	-1.917541	3.294233	0.102618
H	-2.355792	2.769027	-0.745438
H	-2.148799	2.747901	1.019734
H	-2.387486	4.281264	0.170153
H	-0.102553	4.120127	0.808037
C	2.823457	2.434635	-0.930843
H	2.921157	1.382949	-1.217357
H	2.414537	2.980559	-1.784673
H	3.828255	2.815972	-0.721661
H	1.893709	3.715562	0.473040
Cu	1.735874	-0.924793	-0.990602
C	2.190906	-0.850889	-2.927433
H	3.267952	-0.849174	-3.105995
H	1.723971	-1.702658	-3.430816
H	1.749645	0.088829	-3.277997
C	2.598365	-2.252390	0.565784
C	1.537066	-2.982557	1.031119
H	1.136909	-2.756666	2.017202
C	0.970974	-4.164015	0.299938
C	1.324616	-4.175018	-1.198406
C	3.145664	-2.481417	-0.751477
H	4.087037	-1.991816	-0.980678
C	2.779745	-3.753614	-1.463979
H	3.072332	-1.502786	1.192463
H	1.133252	-5.168477	-1.619457
H	0.657677	-3.476702	-1.721687
H	2.969310	-3.662184	-2.538368
H	3.474205	-4.525254	-1.093554
H	-0.116506	-4.210162	0.440164
H	1.367788	-5.068152	0.793913
Br	5.900850	-1.841849	0.732505



C1$_{(S)\text{-}SN2p}$

P	0.842322	0.569507	-0.155146
O	-0.216595	1.572237	-0.980565
C	-1.324948	0.921095	-1.520997
C	-2.406724	0.617867	-0.707768
C	-3.488497	-0.138892	-1.289423
C	-3.465282	-0.435909	-2.694400
C	-4.537768	-1.168168	-3.271920
C	-5.579794	-1.627475	-2.500197
C	-5.582918	-1.378568	-1.107777
C	-4.568924	-0.654607	-0.519638
H	-4.583627	-0.485693	0.550334
H	-6.389769	-1.768208	-0.493196
H	-6.389829	-2.193116	-2.952073
H	-4.508601	-1.372157	-4.339643
C	-2.355540	-0.023309	-3.479284
C	-1.288002	0.618676	-2.901168
H	-2.348475	-0.248490	-4.542655
C	-2.398665	1.023032	0.726769
C	-1.331797	0.672163	1.545932
O	-0.219587	0.024264	1.048219
C	-1.354535	0.889342	2.945083
C	-2.417327	1.535341	3.523615
C	-3.480870	2.034344	2.725115
C	-3.469547	1.791796	1.310678
C	-4.511662	2.368639	0.531697
C	-5.516753	3.107602	1.117092
C	-5.543955	3.310141	2.516642
C	-4.541492	2.784927	3.299296
H	-4.537097	2.947688	4.374559
H	-6.346206	3.888544	2.966227
H	-6.293664	3.543858	0.495064
H	-4.502952	2.233903	-0.543645
H	-2.444594	1.695025	4.598595
N	1.916890	1.719711	0.438940
C	1.734447	3.162011	0.811868
C	2.343985	4.107601	-0.223067
C	1.884338	4.139776	-1.548349
C	2.428410	5.039402	-2.464370
C	3.437917	5.923955	-2.072421
C	3.899371	5.902117	-0.756779
C	3.354376	4.997816	0.158928
H	3.719310	4.986488	1.184347
H	4.685153	6.583441	-0.441050
H	3.861243	6.622353	-2.789328
H	2.064179	5.050114	-3.488402
H	1.104861	3.451366	-1.859779
C	3.350623	1.268534	0.539213
C	3.513238	0.033855	1.433238
C	4.375641	-1.019639	1.102955
C	4.572776	-2.088657	1.983174
C	3.908543	-2.125770	3.208184
C	3.044567	-1.081120	3.550122
C	2.854277	-0.014986	2.673432
H	4.060675	-2.957019	3.891058
H	-0.409486	0.899765	-3.471741
H	-0.519108	0.521888	3.532285
C	0.306086	3.593389	1.165235
H	-0.369491	3.544566	0.311636
H	-0.105362	2.989805	1.977501
H	0.350146	4.633096	1.506652
H	2.319975	3.282337	1.733004
C	4.042343	1.173069	-0.827366
H	3.654199	0.346509	-1.429710
H	3.883374	2.100649	-1.381004
H	5.122379	1.038797	-0.700029
H	3.840845	2.089241	1.075933
Cu	1.356335	-1.219390	-1.727515
C	2.306560	-0.937544	-3.448184
H	3.315554	-1.377413	-3.426075
H	1.763999	-1.418312	-4.275489
H	2.423904	0.125610	-3.701464
C	0.293464	-3.238662	-1.892078
C	0.037840	-2.828176	-0.613171
C	0.801688	-3.354215	0.555126
C	1.280006	-4.332991	-2.245773
H	0.784177	-5.034005	-2.930984
H	2.115272	-3.901609	-2.812035
C	1.788392	-5.085438	-1.003611
C	2.058112	-4.123446	0.158694
H	2.465673	-4.648798	1.026993
H	1.036894	-5.816075	-0.681406
H	-0.813920	-2.189648	-0.400723
H	-0.356668	-2.885892	-2.690167
H	2.807025	-3.374652	-0.141055
H	2.697126	-5.646481	-1.249744
H	1.001446	-2.583878	1.297673
Br	-0.446353	-4.588698	1.621519
H	4.904585	-1.014241	0.156227
H	2.179162	0.790642	2.947771
H	5.248710	-2.892869	1.704603
H	2.522032	-1.096483	4.503006



TS1$_{(S)\text{-SN2p}}$

P	0.847239	-0.747695	-0.122116
O	1.638514	0.393163	-1.047404
C	0.825504	1.447272	-1.475980
C	0.515406	2.477328	-0.601102
C	-0.416948	3.480171	-1.055442
C	-0.882232	3.446686	-2.414297
C	-1.795283	4.437639	-2.866093
C	-2.266864	5.407529	-2.012542
C	-1.845572	5.418418	-0.662310
C	-0.945499	4.484921	-0.197015
H	-0.645156	4.503864	0.843686
H	-2.243076	6.165737	0.018535
H	-2.974087	6.152365	-2.365568
H	-2.128941	4.401233	-3.900135
C	-0.448928	2.405228	-3.277535
C	0.368890	1.404728	-2.812174
H	-0.796413	2.394595	-4.307248
C	1.099144	2.493333	0.770430
C	0.966284	1.386767	1.598992
O	0.354588	0.225810	1.155869
C	1.369428	1.402026	2.955115
C	1.979158	2.516272	3.474193
C	2.252594	3.640837	2.650636
C	1.826018	3.629426	1.280305
C	2.182143	4.740371	0.465544
C	2.883077	5.808638	0.981532
C	3.265938	5.832694	2.342856
C	2.958209	4.765878	3.155369
H	3.261957	4.760608	4.199439
H	3.811097	6.684941	2.738386
H	3.148288	6.639343	0.333358
H	1.906615	4.737236	-0.582558
H	2.282042	2.540669	4.517826
N	2.125458	-1.753130	0.276979
C	3.587657	-1.468769	0.480849
C	4.435128	-2.011802	-0.668580
C	4.278779	-1.539323	-1.980474
C	5.089925	-2.021035	-3.007314
C	6.072762	-2.979439	-2.741087
C	6.238356	-3.452723	-1.440028
C	5.422023	-2.970882	-0.412930
H	5.558403	-3.343604	0.600544
H	6.998087	-4.198333	-1.221321
H	6.702682	-3.353219	-3.543630
H	4.956671	-1.646544	-4.018907
H	3.516817	-0.795676	-2.193812
C	1.791138	-3.218074	0.404234
C	0.749528	-3.489384	1.494831
C	-0.299283	-4.400624	1.316626
C	-1.183846	-4.689657	2.361041
C	-1.032859	-4.074300	3.602824
C	0.011733	-3.164803	3.794915
C	0.890146	-2.878395	2.752451
H	-1.719034	-4.300553	4.414091
H	0.682283	0.580861	-3.444613
H	1.173460	0.521348	3.558205
C	3.954546	-0.013706	0.792763
H	3.775581	0.654094	-0.049625
H	3.410361	0.360125	1.663088
H	5.024008	0.013171	1.026490
H	3.855132	-2.046340	1.375230
C	1.499990	-3.876264	-0.950268
H	0.544100	-3.551462	-1.371082
H	2.291714	-3.619201	-1.657554
H	1.477458	-4.966648	-0.849003
H	2.726336	-3.662072	0.763091
Cu	-1.205349	-1.354330	-1.326052
C	-1.212031	-2.235887	-3.107425
H	-1.755874	-3.183614	-3.031226
H	-1.683104	-1.609473	-3.870062
H	-0.168320	-2.425806	-3.383066
C	-3.293985	-0.841031	-1.527239
C	-2.814274	-0.001693	-0.463848
C	-2.941365	-0.405514	0.843441
C	-4.198633	-1.942158	-1.168820
H	-5.174043	-1.411109	-0.902513
H	-4.398715	-2.615528	-2.007536
C	-3.757251	-2.690708	0.097912
C	-3.493516	-1.725634	1.270967
H	-4.436710	-1.493452	1.786964
H	-4.529757	-3.410346	0.386191
H	-2.430803	0.990436	-0.688900
H	-3.375618	-0.403111	-2.517603
H	-2.823219	-2.178187	2.014745
H	-2.844684	-3.265064	-0.124147
H	-2.649377	0.288221	1.628408
Br	-6.583607	-0.261661	0.489683
H	-0.434602	-4.899473	0.363054
H	1.695887	-2.166700	2.910951
H	-1.990838	-5.398743	2.198097
H	0.142343	-2.681487	4.759550

2.1.3. Quadrant diagrams

The elaboration of a quadrant diagram was attempted to correlate the geometrical properties of the chiral catalyst and the observed discrimination of the system. Indeed, even though the approach of the substrate was not the enantiodetermining step, we were convinced that this modelization would help us to apprehend the steric interactions at play during the key oxidative addition step. Thus, a rational model was designed from **C1**$_{(R)\text{-SN2p}}$ and all potential approaches were subsequently implemented (figure 3). As mentioned in the manuscript, the rigid binaphthyl core and the upper phenyl part of the amine moiety were the most encumbering elements of the chiral catalyst and hence, logically shielded the quadrants II and IV of the model. In addition, the position of the transferable methyl group appeared to block the window III. Consequently, a single quadrant remained open to allow for the approach of both enantiomers of the racemic substrate, namely the quadrant I. With this model in hand, the substrate was superimposed in a way that facilitates the displacement of the leaving group in *anti*-S_N2' or in *anti*-S_N2. Among the four possible routes, only two pathways allowed for the approach of the substrate by the open quadrant I. These possibilities were an *anti*-S_N2' for

the *R*-enantiomer of the substrate and an *anti*-S_N2 for its *S* antipode. Finally, such model conveniently explained the selectivity at play in the present process but we are confident with the fact that it could also provide an interesting tool for the rationalization of related reactions using a similar chiral catalyst.

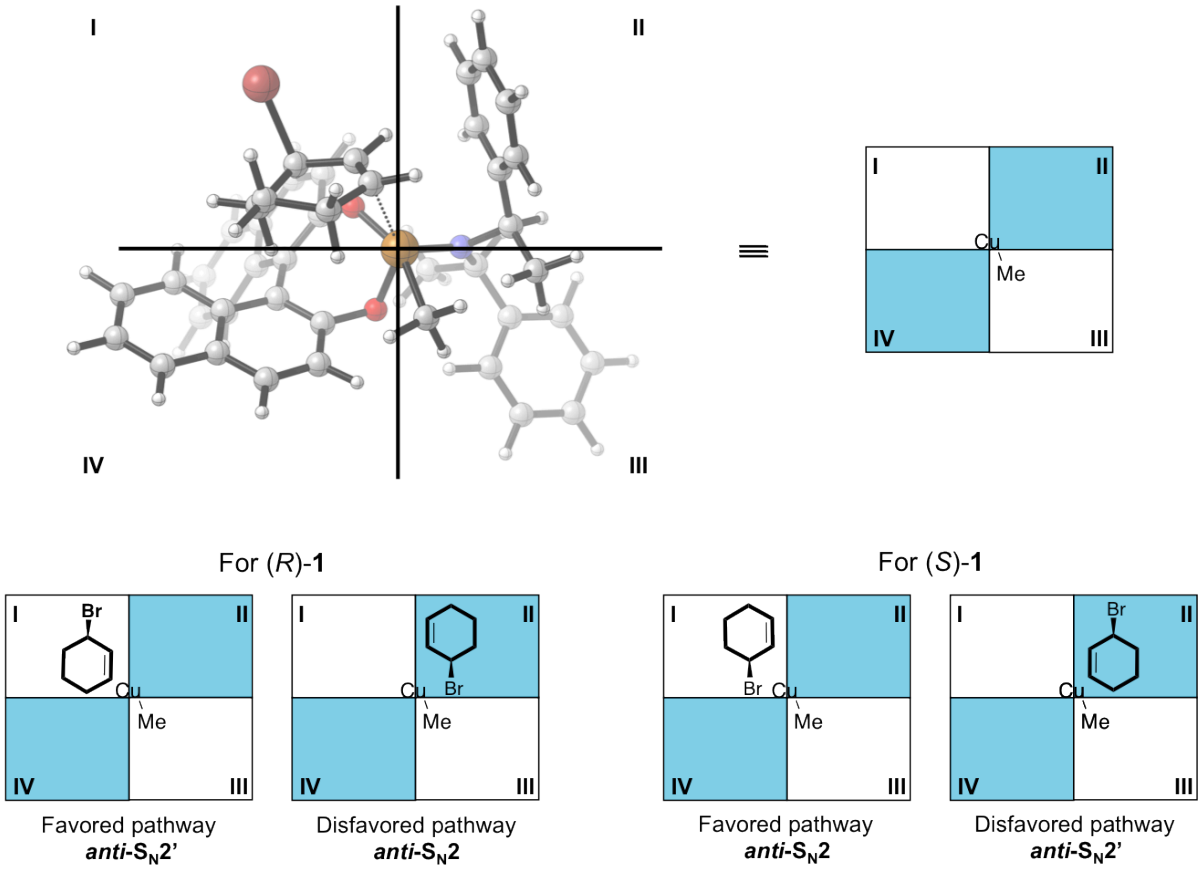
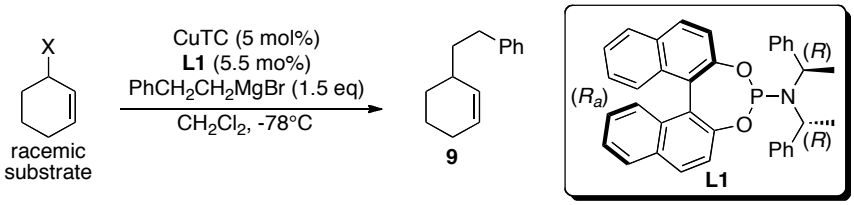


Figure S3. Rationalization of the system by means of steric quadrant diagrams

2.2. Additional chemical experiments

2.2.1. Screening of various allylic derivatives

Table S9. Influence of the leaving group[(a)]



Entry	X	Time (h)	Conversion (%)[(b)]	*ee* (%)[(c)]
1	OAc	15	70	0
2	OCO_2Me	15	83	4
3	$OP(O)Ph_2$	3	> 99	8
4	$OP(O)(OEt)_2$	3	> 99	14 (*S*)
5	Cl	2	> 99	53 (*S*)
6	Br	1	> 99	78 (*S*)
7	OTf	1	-[(d)]	-[(d)]

(a) Reaction conditions: the racemic substrate (0.5 mmol) was added to a solution of CuTC (5 mol%) and **L1** (5.5 mol%) in CH_2Cl_2 (2 ml). The reaction mixture was cooled to -78 °C, stirred for 10 min, and the Grignard reagent (1M in Et_2O, 1.5 eq) was added dropwise. The reaction mixture was stirred for the indicated period of time. (b) Conversion relative to the formation of **9**, determined by ^{1}H NMR and GC-MS. (c) Determined by GC on chiral stationary phase after derivatization in corresponding diastereomeric mixture of epoxides. (d) The formation of **9** was not observed.

2.2.2. Evolution of the *ee* throughout the reaction

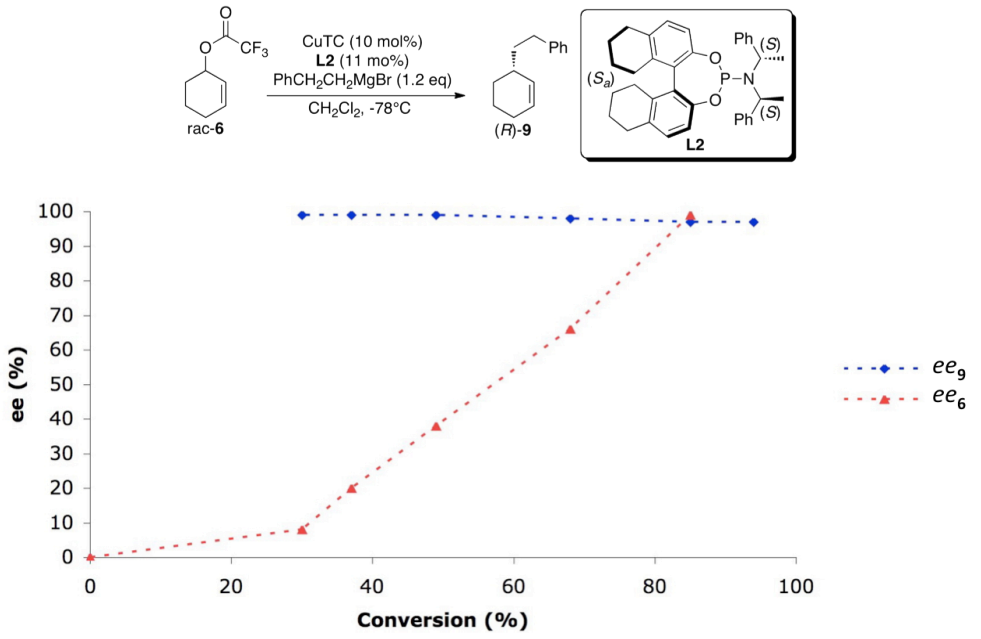


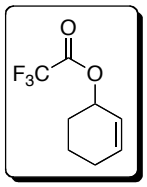
Figure S4. Monitoring of the *ee* of **6** and **9** during the course of the reaction (^{1}H NMR and GC on chiral stationary phase)

3. Experimental part

3.1. Preparation of allylic trifluoroacetates

General procedure for the preparation of various cycloalk-2-en-1-yl 2',2',2'-trifluoroacetates:

In a round-bottomed flask, a solution of cycloalkenol (1 eq) and triethylamine (2 eq) in dry diethylether (5 ml/mmol) was prepared and cooled to 0 °C. 2,2,2-trifluoroacetic anhydride (1.2 eq) was added followed by dimethylaminopyridine (0.05 eq), and the reaction mixture was stirred for 30 min at 0 °C. Then, the reaction mixture was warmed to room temperature and stirred for 2 h. The reaction was quenched with a solution of HCl_{aq} 1M (5 ml/mmol) and extracted with diethylether (3x 5 ml/mmol). The organic layer was washed with a saturated solution of $NaHCO_{3aq}$ (20 ml/mmol), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude mixture was distilled bulb-to-bulb to recover the desired allylic trifluoroacetate.

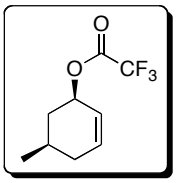


Cyclohex-2-en-1-yl 2',2',2'-trifluoroacetate (6): prepared from cyclohex-2-en-1-ol. Purified by bulb-to-bulb distillation (50-60 °C, 0.5-1 mmHg). Yield = 46 %. Slightly yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.67-1.71 (M, 1H, CH_2), 1.75-1.80 (m, 1H, CH_2), 1.88-1.92 (m, 2H, CH_2), 2.01-2.05 (m, 1H, CH_2), 2.12-2.18 (m, 1H, CH_2), 5.43 (brs, 1H, CH), 5.74-5.77 (m, 1H, CH), 6.08-6.10 (m, 1H, CH) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 18.3 (CH_2), 24.9 (CH_2), 27.9 (CH_2), 73.0 (CH), 110.5-119.0 (q, J = 284.4 Hz, CF_3), 123.2 (CH), 135.5 (CH), 156.9-158.0 (q, J = 35 Hz, C) ppm.

^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = -75.3 (s, 3F, CF_3) ppm.



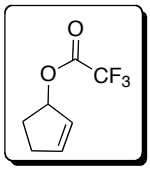
***cis*-5-methylcyclohex-2-en-1-yl 2',2',2'-trifluoroacetate (11):** prepared from *cis*-5-methylcyclohex-2-enol (prepared from crotonaldehyde according to a reported procedure. *cis*/*trans* 12/1)[7]. Purified by bulb-to-bulb distillation (50-60 °C, 0.5-1 mmHg). Yield = 38 %. cis/trans = 12/1. Colorless liquid. The product was stored at -5 °C in the absence of light.

For *cis*-**11** isomer:

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.02 (d, 3H, J = 6.6 Hz, CH_3), 1.43-1.49 (m, 1H, CH_2), 1.68-1.80 (m, 1H, CH_2), 1.82-1.95 (m, 1H, CH), 2.11-2.18 (m, 2H, CH_2), 5.56-5.63 (m, 2H, CH), 5.93-5.97 (m, 1H, CH) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.7 (CH_3), 27.8 (CH), 33.3 (CH_2), 36.0 (CH_2), 75.7 (CH), 110.4-118.9 (q, 1C, J = 286.0 Hz, CF_3), 124.5 (CH), 132.8 (CH), 156.9-158.1 (q, 1C, J = 41.9 Hz, C) ppm.

^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = -75.3 (s, 3F, CF_3) ppm.



Cyclopent-2-en-1-yl 2',2',2'-trifluoroacetate (12): prepared from cyclopent-2-en-1-ol. Purified by bulb-to-bulb distillation (30-40 °C, 0.5-1 mmHg). Yield = 28 %. Slightly yellow liquid. The product was stored at -25 °C in the absence of light.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.94-2.04 (m, 1H, CH_2), 2.32-2.45 (m, 2H, CH_2), 2.55-2.66 (m, 1H, CH_2), 5.87-5.89 (m, 2H, CH), 6.25-6.27 (m, 1H, CH) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 29.5 (CH_2), 31.3 (CH_2), 85.5 (CH), 110.4-118.9 (q, 1C, J = 286.1 Hz, CF_3), 127.3 (CH), 140.7 (CH), 157.0-158.2 (q, 1C, J = 41.8 Hz, C) ppm.

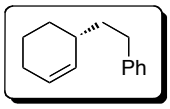
^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = -75 2 (s, 3F, CF_3) ppm.

[7] I. D. G. Watson, A. K. Yudin, *J. Am. Chem. Soc.* **2005**, *127*, 17516.

3.2. Alkylation products

General procedure for the copper-catalyzed AAA of various cycloalk-2-en-1-yl 2',2',2'-trifluoroacetates:

In a flame-dried Schlenk tube under argon atmosphere, CuTC (4.8 mg, 0.25 mmol, 0.10 eq) and **L2** (15.1 mg, 0.028 mmol, 0.11 eq) were dissolved in dry dichloromethane (2 ml) and the solution was stirred for 10 min at room temperature. Then, the trifluoroacetate derivative (0.25 mmol) was added and the solution was cooled to -78 °C. After 10 min at this temperature, the organomagnesium reagent solution (1M in diethylether, 0.3 ml, 0.3 mmol, 1.2 eq) was added at a 0.6 ml/h rate and the reaction mixture was stirred for 3 h. The reaction was quenched with a solution of HCl_{aq} 1M (8 ml) and extracted with diethylether (3x10 ml). The organic layer dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude mixture was purified by chromatography on silica gel (pentane, R_f = 0.7) affording the desired alkylation product.



(*R*)-(2-(cyclohex-2-enyl)ethyl)benzene (9): prepared from cyclohex-2-en-1-yl 2',2',2'-trifluoroacetate (**6**). Yield = 85 %. ee_9 = 97 %. Colorless liquid. The enantiomeric excess was determined by GC on a chiral stationary phase using Hydrodex B3P column, Method: 60-30-1-140-20-170-5, R_T = 102.17 (*S*), 102.76 (*R*) min. The enantiomeric excess was also determined after derivatization in corresponding mixture of diastereoisomeric epoxides using Hydrodex TBDM column, Method: 90-0-1-170-5, R_T = 71.97, 73.05, 76.61, 77.96 min.

^{1}H NMR (400 MHZ, $CDCl_3$, 25 °C): δ = 1.27-1.36 (m, 1H, CH_2), 1.50-1.81 (m, 4H, CH_2), 1.84-1.90 (m, 1H, CH_2), 1.99-2.04 (m, 2H, CH_2), 2.08-2.18 (m, 1H, CH), 2.64-2.75 (m, 2H, CH_2), 5.64-5.68 (m, 1H, CH), 5.70-5.75 (m, 1H, CH), 7.18-7.23 (m, 3H, CH), 7.29-7.33 (m, 2H, CH) ppm.

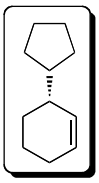
^{13}C NMR (100 MHZ, $CDCl_3$, 25 °C): δ = 21.6 (CH_2), 25.5 (CH_2), 29.2 (CH_2), 33.4 (CH_2), 34.9 (CH), 38.4 (CH_2), 125.8 (CH), 127.3 (C), 128.4 (2C, CH), 128.5 (2C, CH), 131.9 (CH), 143.0 (C) ppm.

IR ($CHCl_3$): 71.9, 1453, 1493, 2856, 2923, 3023 cm^{-1}.

MS (EI mode) *m*/z (%): 186 (28), 143 (4), 129 (4), 104 (26), 91 (100), 65 (34), 53 (22).

HRMS (EI): calculated for $C_{14}H_{18}$ [M^+] 186.1407, found 186.1409.

Optical activity: $[\alpha]^{25}_D$ = -72.5 (c = 1.2 in $CHCl_3$, 92 % *ee*).



(*R*)-3-cyclopentylcyclohex-1-ene (**13**)**:** prepared from cyclohex-2-en-1-yl 2',2',2'-trifluoroacetate (**6**). Yield = 86 %. $ee_{\mathbf{13}}$ = 90 %. Colorless liquid. The enantiomeric excess was determined by GC on a chiral stationary phase after derivatization in corresponding mixture of diastereoisomeric epoxides using Hydrodex TBDM column, Method: 60-0-1-170-5, R_T = 63.11, 63.21, 69.09, 70.73 min

^{1}H NMR (400 MHZ, $CDCl_3$, 25 °C): δ = 1.14-1.28 (m, 3H, CH_2), 1.46-1.62 (m, 6H, CH_2), 1.65-1.79 (m, 4H, CH_2), 1.86-1.90 (m, 1H, CH), 1.91-1.97 (m, 2H, CH_2), 5.67 (brs, 2H, CH) ppm.

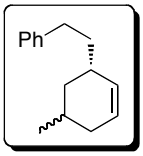
^{13}C NMR (100 MHZ, $CDCl_3$, 25 °C): δ = 21.9 (CH_2), 25.4 (CH_2), 25.5 (CH_2), 25.6 (CH_2), 28.6 (CH_2), 30.3 (CH_2), 30.8 (CH_2), 41.1 (CH), 45.8 (CH), 127.2 (CH), 131.5 (CH) ppm.

IR ($CHCl_3$): 720.9, 1217, 1228.9, 1365.8, 1447.7, 1738.8, 2865.6, 2947.2, 3021.2 cm^{-1}.

MS (EI mode) *m*/z (%): 150 (22), 135 (13), 121 (10), 108 (8), 93 (27), 79 (78), 67 (100).

HRMS (EI): calculated for $C_{11}H_{18}$ [M^+] 150.1409, found 150.1391.

Optical activity: $[\alpha]^{25}_D$ = -80.6 (c = 1.0 in $CHCl_3$, 64 % *ee*).



(2-((*1S*,5*S* or *R*)-5-methylcyclohex-2-en-1-yl)ethyl)benzene (**14**)**:** prepared from cis-5-methylcyclohex-2-en-1-yl 2',2',2'-trifluoroacetate (**11**). Yield = 80 %. $ee_{trans\text{-}\mathbf{14}}$ = 93 %. *trans/cis* = 11.5/1. Colorless liquid. The enantiomeric excess was determined by GC on a chiral stationary phase after derivatization in corresponding mixture of diastereoisomeric epoxides using Hydrodex TBDM column, Method: 60-0-1-170-5, $R_{T\textit{cis}\text{-}\mathbf{85}}$ = 103.85, 104.68, 105.12, 105.87 min; $R_{T\textit{trans}\text{-}\mathbf{85}}$ = 106.98, 107.43, 108.07, 108.94 min.

For *trans*-**14**:

^{1}H NMR (400 MHZ, $CDCl_3$, 25 °C): δ = 0.97 (d, 3H, J = 6.7 Hz, CH_3), 1.36-1.41 (m, 1H, CH_2), 1.53-1.57 (m, 1H, CH_2), 1.60-1.73 (m, 3H, CH_2), 1.79-1.88 (m, 1H, CH), 2.09-2.18 (m, 2H, CH_2 and CH), 2.65-2.71 (m, 2H, CH_2), 5.66-5.72 (brs, 2H, CH), 7.18-7.24 (m, 3H, CH), 7.28-7.32 (m, 2H, CH) ppm.

^{13}C NMR (100 MHZ, $CDCl_3$, 25 °C): δ = 21.6 (CH_3), 24.8 (CH), 33.4 (CH), 33.8 (CH_2), 33.9 (CH_2), 35.8 (CH_2), 38.1 (CH_2), 125.7 (CH), 126.4 (CH), 128.4 (2C, CH), 128.5 (2C, CH), 131.0 (CH), 143.0 (C) ppm.

For *cis*-**14**:

^{1}H NMR (400 MHZ, $CDCl_3$, 25 °C): δ = 0.98 (m, 1H, CH_2), 1.01 (d, 3H, J = 6.3 Hz, CH_3), 1.55-1.68 (m, 4H, CH_2), 1.81-1.87 (brs, 1H, CH_2), 2.04-2.11 (brs, 1H, CH_2), 2.18-2.26 (m, 1H, CH), 2.64-2.74 (m, 2H, CH_2), 5.61-5.65 (m, 1H, CH), 5.71-5.75 (m, 1H, CH), 7.18-7.24 (m, 3H, CH), 7.28-7.33 (m, 2H, CH) ppm.

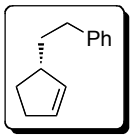
^{13}C NMR (100 MHZ, $CDCl_3$, 25 °C): δ = 22.6 (CH_3), 29.2 (CH), 33.2 (CH_2), 34.4 (CH_2), 36.3 (CH), 38.6 (CH_2), 38.7 (CH_2), 125.7 (CH), 126.9 (CH), 128.4 (2C, CH), 128.5 (2C, CH), 131.7 (CH), 143.0 (C) ppm.

For the mixture of isomers:

IR ($CHCl_3$): 700, 746.7, 1216.9, 1229, 1374.5, 1454.7, 1496.3, 1739, 2906, 2947.3 cm^{-1}.

MS (EI mode) *m*/z (%): 200 (29), 172 (5), 143 (8), 122 (50), 109 (27), 104 (52), 91 (100), 79 (30), 67 (73).

HRMS (EI): calculated for $C_{15}H_{20}$ [M^+] 200.1565, found 200.1568.



(*R*)-(2-(cyclopent-2-enyl)ethyl)benzene (**15**)**:** prepared from cyclopent-2-en-1-yl 2',2',2'-trifluoroacetate (**12**) directly after distillation. Yield = 78 %. ee_{15} = 62 %. Colorless liquid. The enantiomeric excess was determined by GC on a chiral stationary phase after derivatization in corresponding mixture of diastereoisomeric epoxides using Hydrodex TBDM column, Method: 60-0-1-170-5, R_T = 90.41, 90.93, 97.62, 99.06 min.

^{1}H NMR (400 MHZ, $CDCl_3$, 25 °C): δ = 1.44-1.53 (m, 1H, CH_2), 1.58-1.67 (m, 1H, CH_2), 1.72-1.81 (m, 1H, CH_2), 2.06-2.15 (m, 1H, CH_2), 2.26-2.45 (m, 2H, CH_2), 2.63-2.73 (m, 3H, CH_2), 5.72-5.78 (m, 2H, CH), 7.18-7.24 (m, 3H, CH), 7.28-7.33 (m, 2H, CH) ppm.

^{13}C NMR (100 MHZ, $CDCl_3$, 25 °C): δ = 29.9 (CH_2), 32.1 (CH_2), 34.5 (CH_2), 38.1 (CH_2), 45.3 (CH), 125.7 (CH), 128.4 (2C, CH), 128.5 (2C, CH), 130.0 (CH), 135.0 (CH), 142.9 (C) ppm.

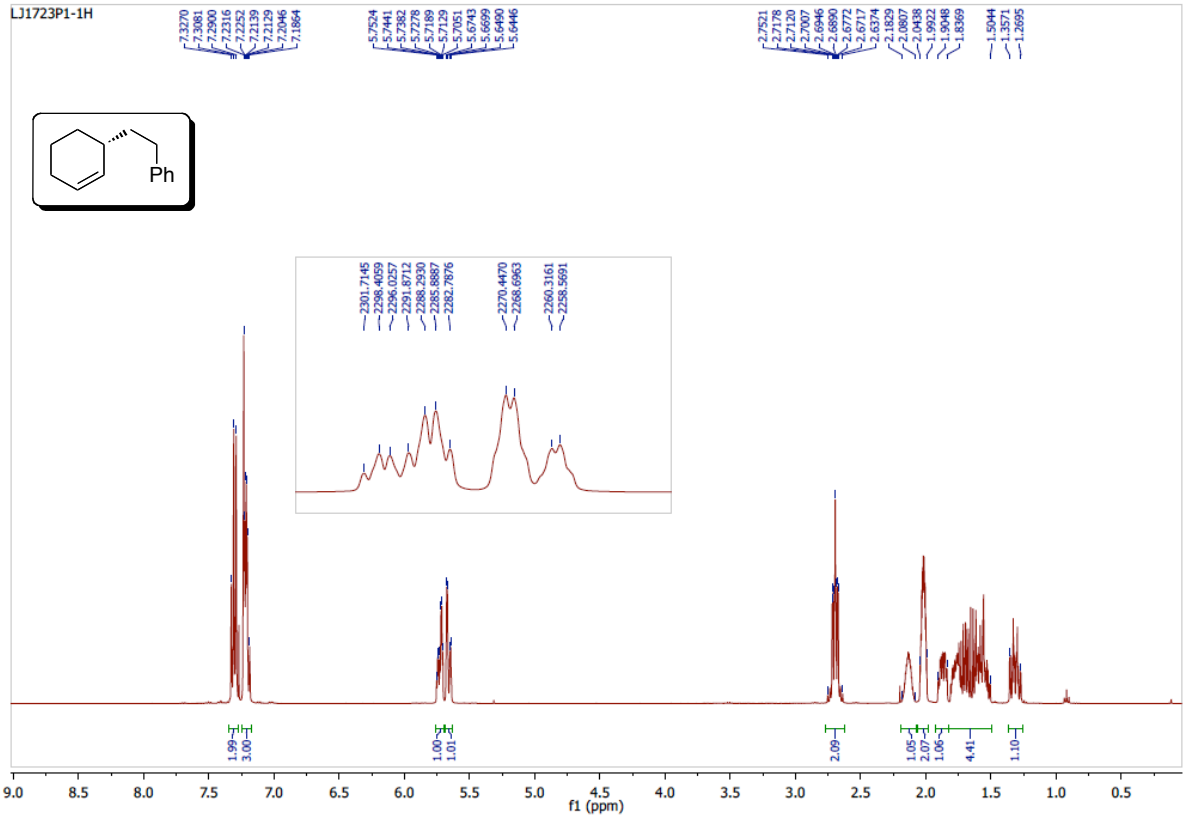
IR ($CHCl_3$): 697.7, 717.5, 748.6, 772.2, 1362.2, 1454.2, 1496, 1739.1, 2850.5, 2929.9, 30.26.9, 3050.9 cm^{-1}.

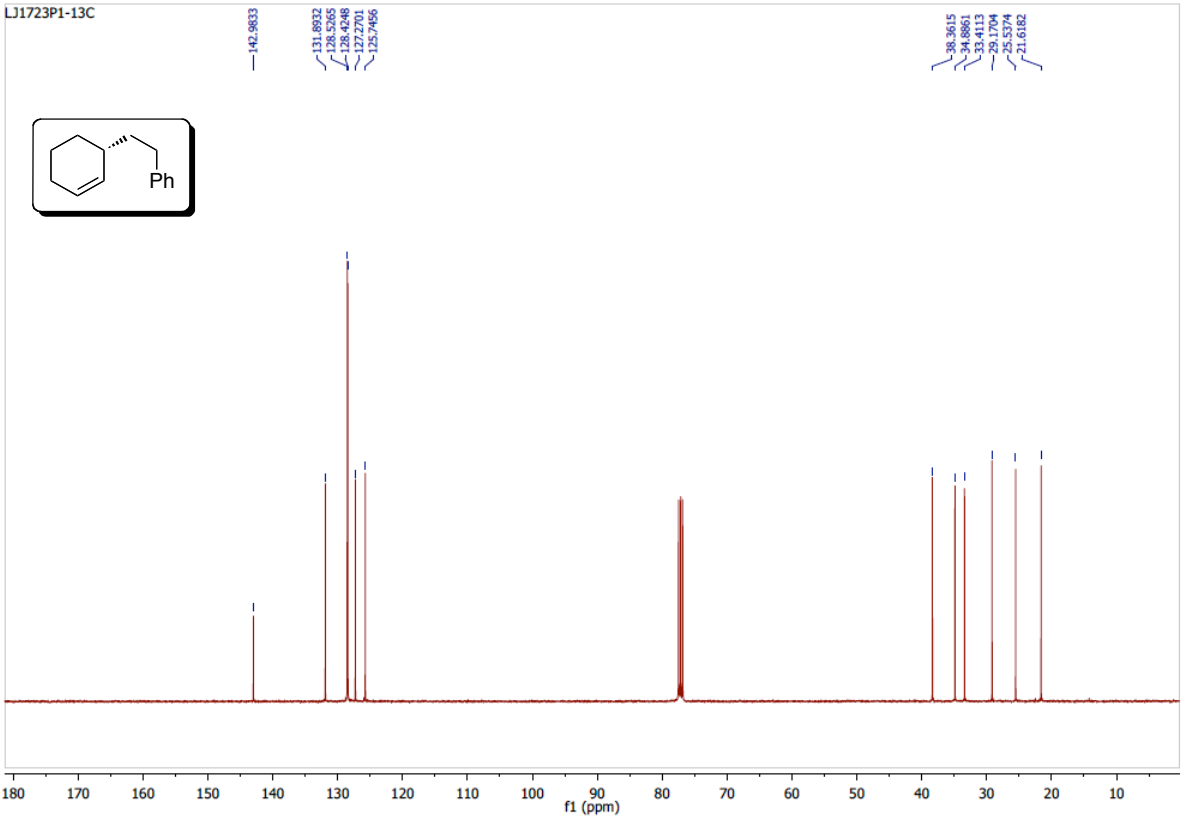
MS (EI mode) *m*/z (%): 172 (28), 152 (2), 144 (8), 129 (4), 115 (4), 104 (36), 92 (88), 81 (44), 67 (100), 53 (14), 51 (18).

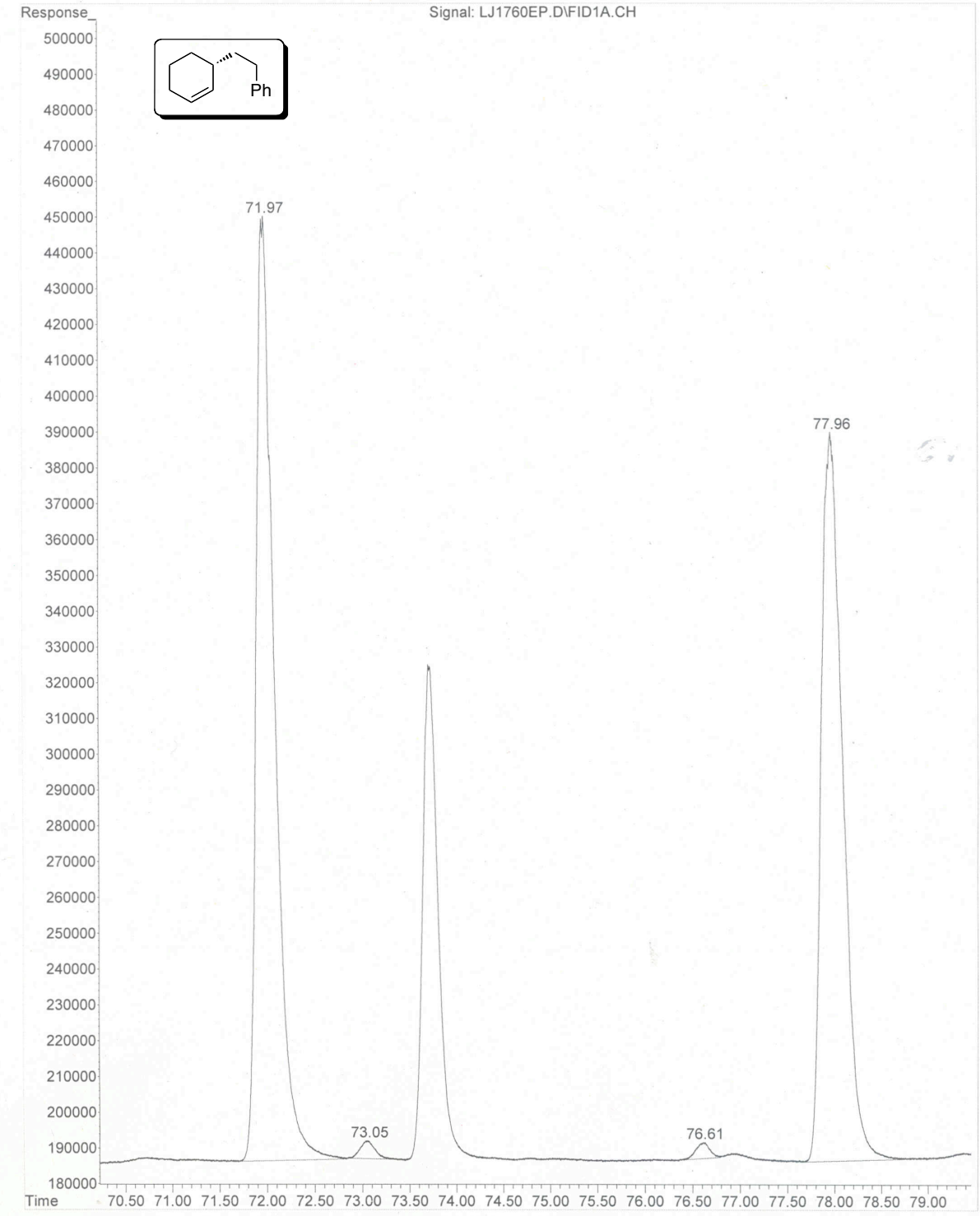
HRMS (EI): calculated for $C_{13}H_{16}$ [M^+] 172.1249, found 172.1252.

Optical activity: $[\alpha]^{25}_D$ = -52 (c = 1.5 in $CHCl_3$, 44 % *ee*).

4. Spectroscopic and chromatographic data

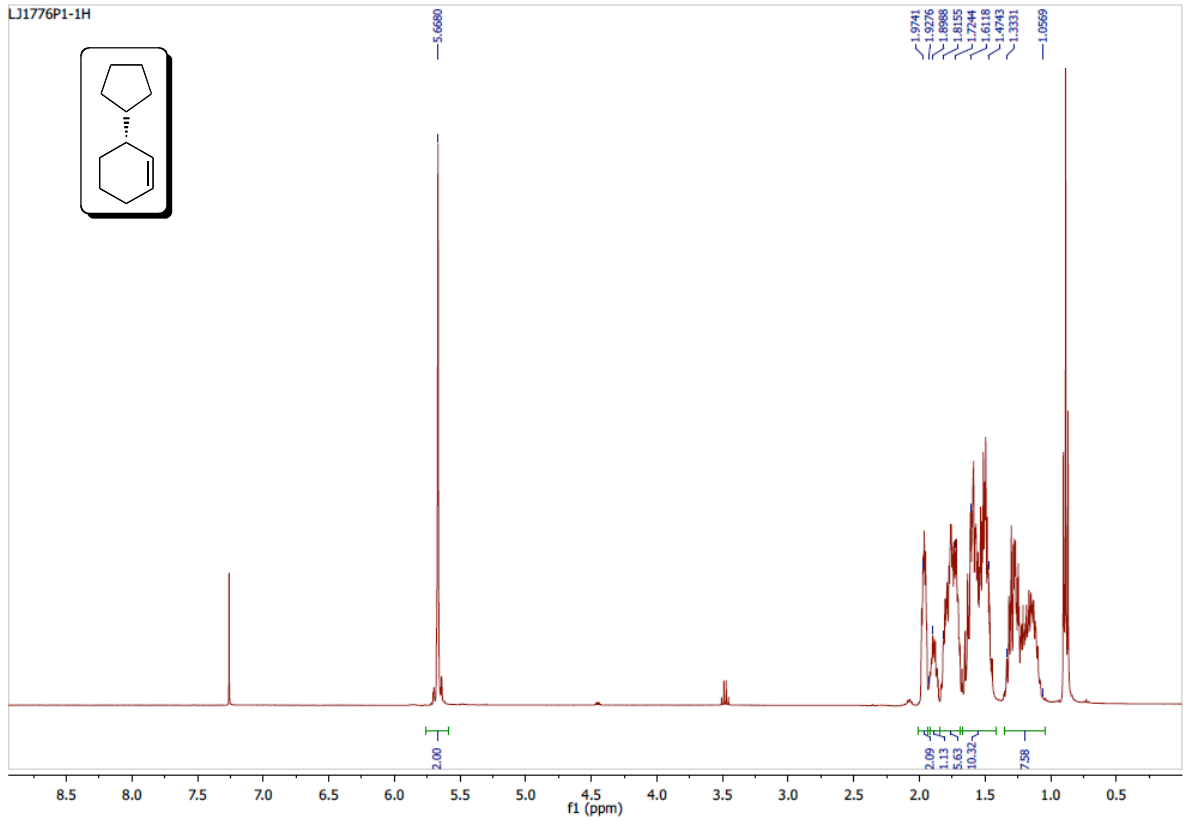


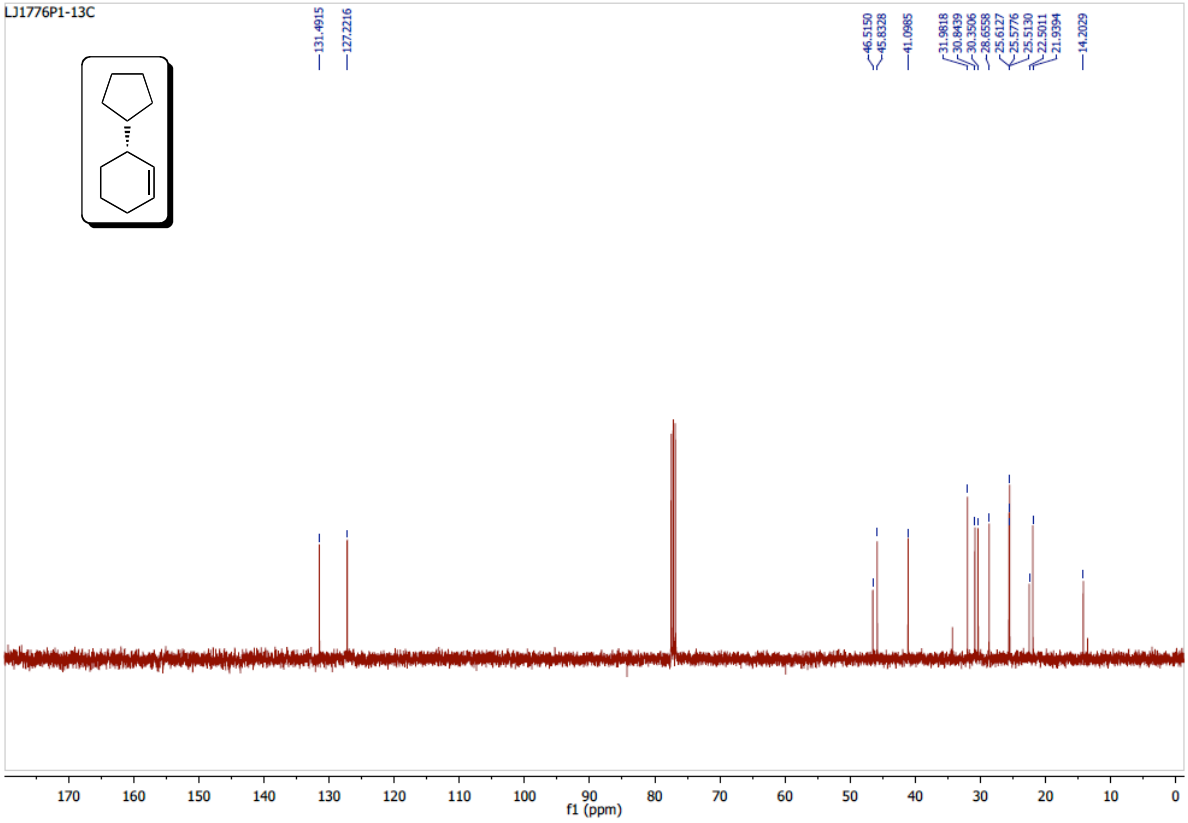


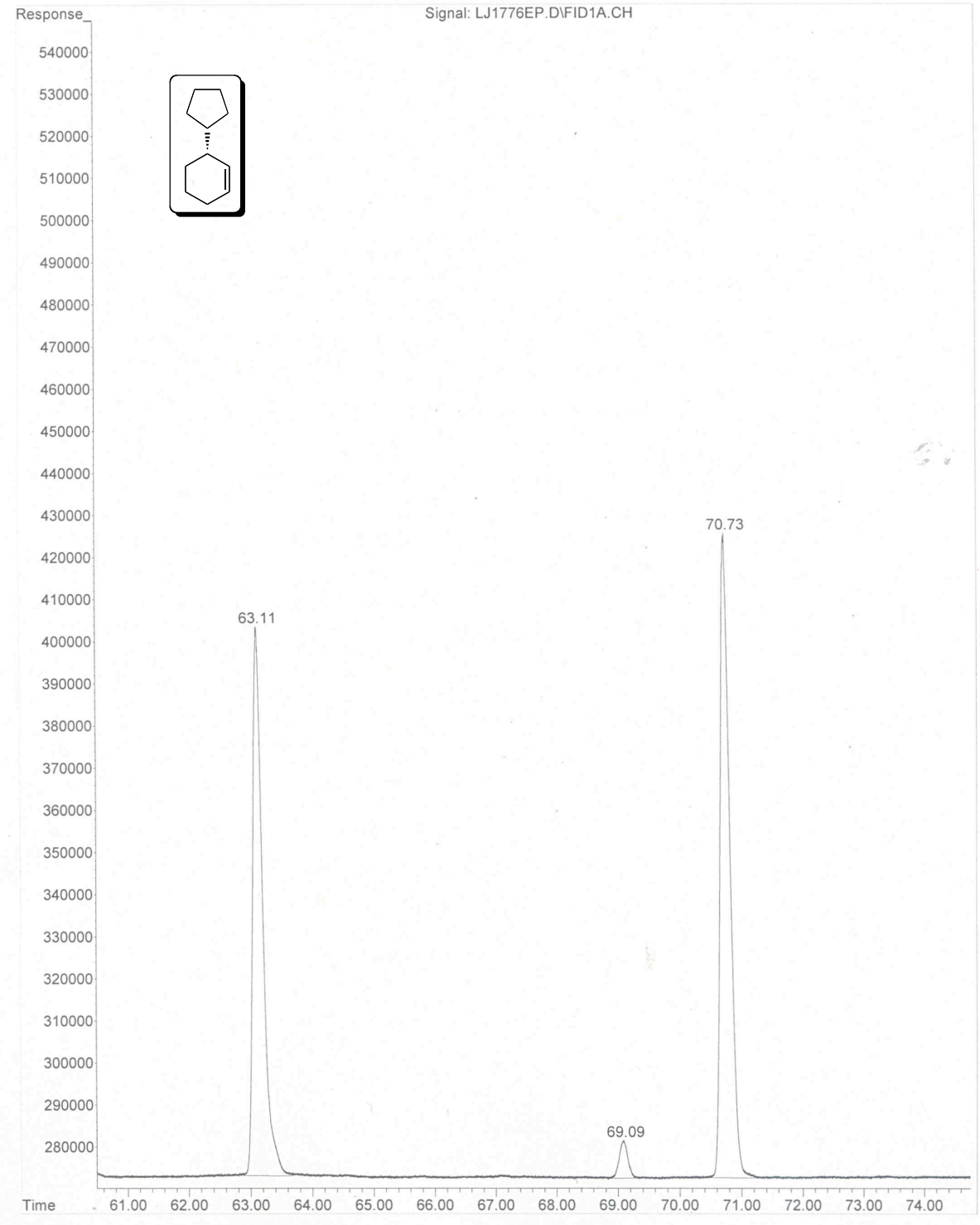


peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	71.971	71.690	72.794	M	263854	35277428	100.00%	51.377%
2	73.053	72.855	73.328	M	5073	547976	1.55%	0.798%
3	76.609	76.390	76.782	M	4597	463568	1.31%	0.675%
4	77.955	77.673	78.747	M	203455	32374577	91.77%	47.150%

Sum of corrected areas: 68663549

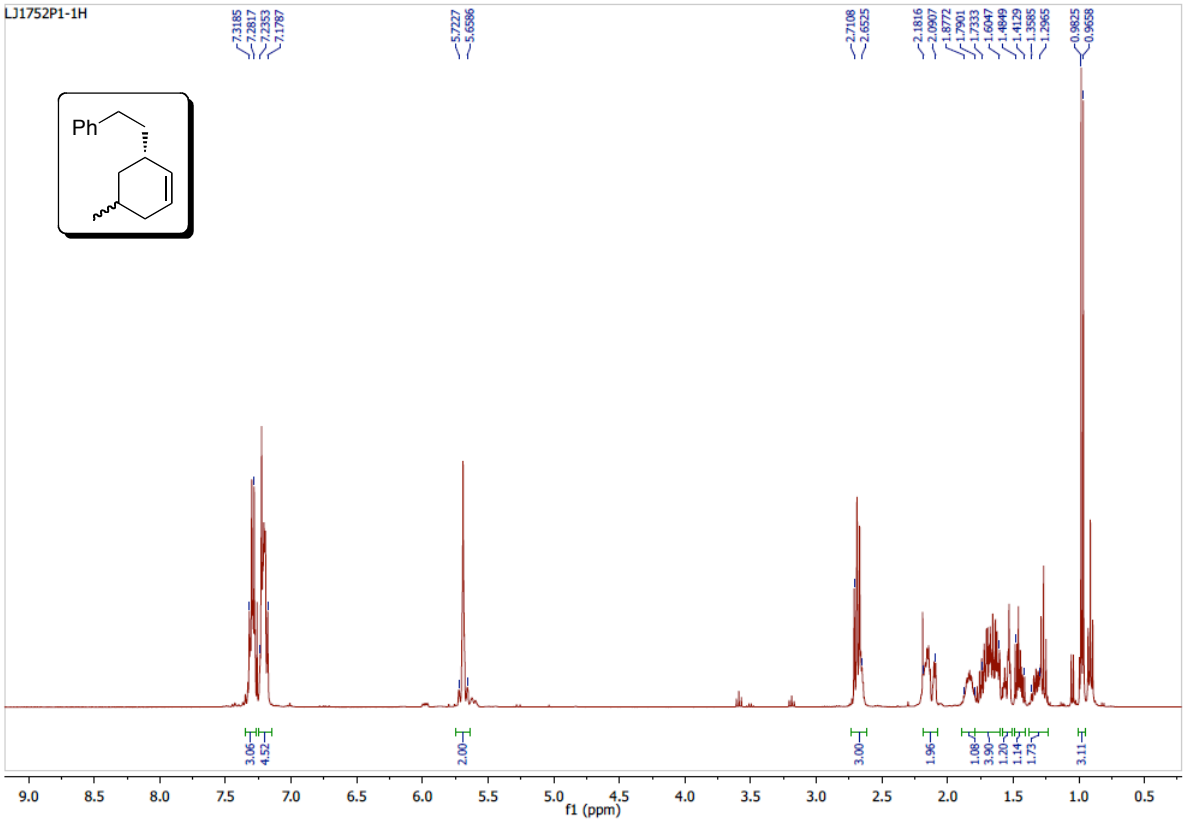


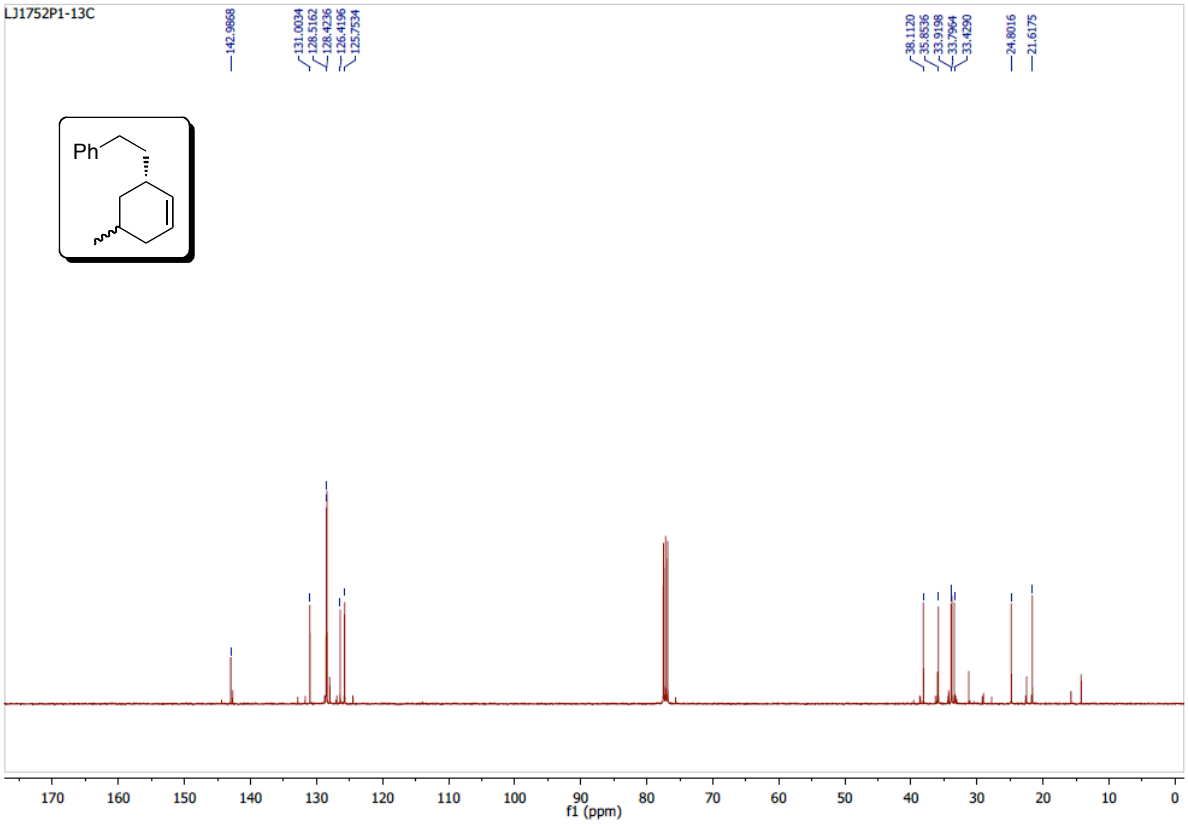


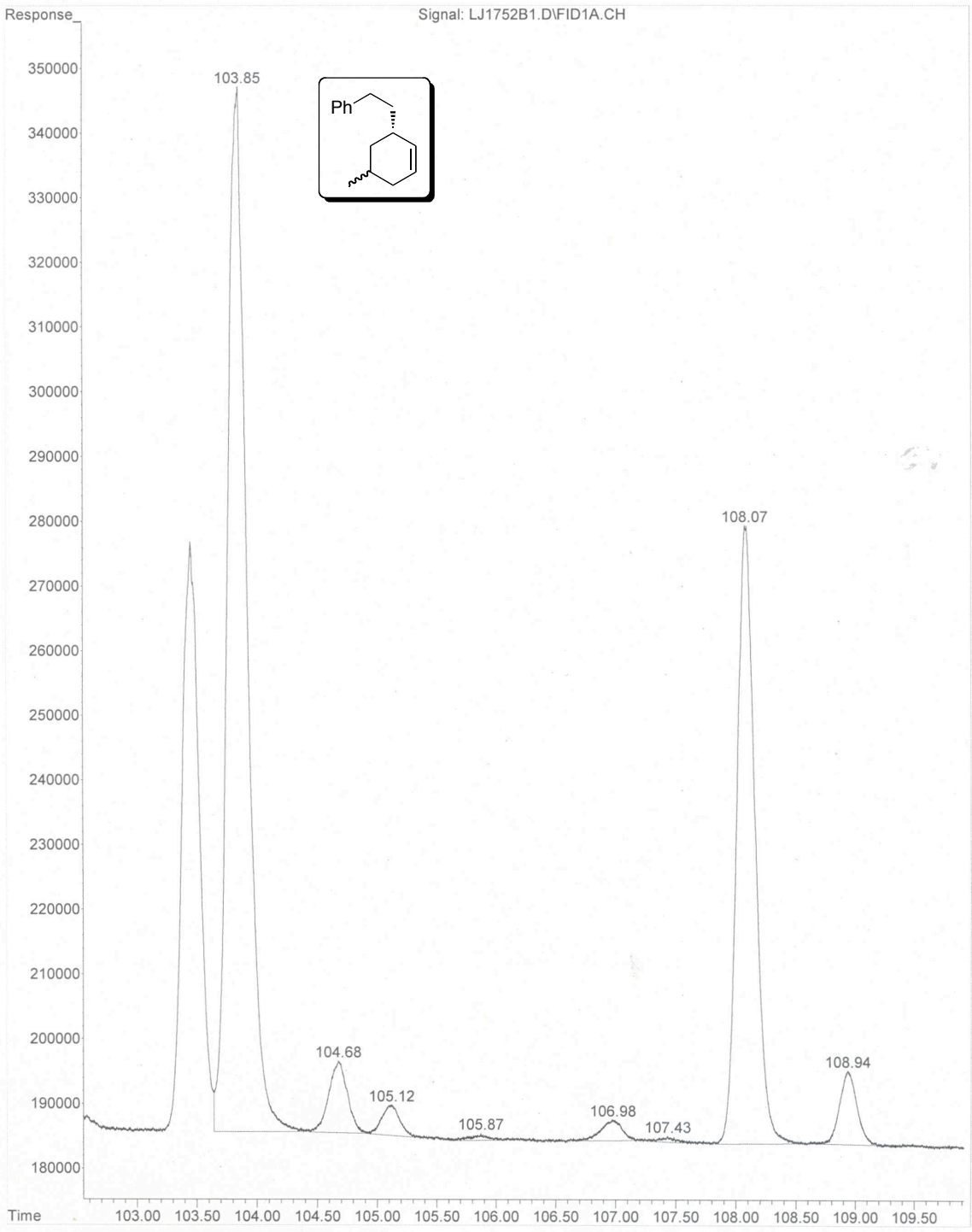


peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	63.109	62.931	63.543	M	129925	14243482	86.06%	44.950%
2	69.089	68.879	69.297	M	9115	893945	5.40%	2.821%
3	70.730	70.475	71.285	M	153076	16550013	100.00%	52.229%

Sum of corrected areas: 31687440

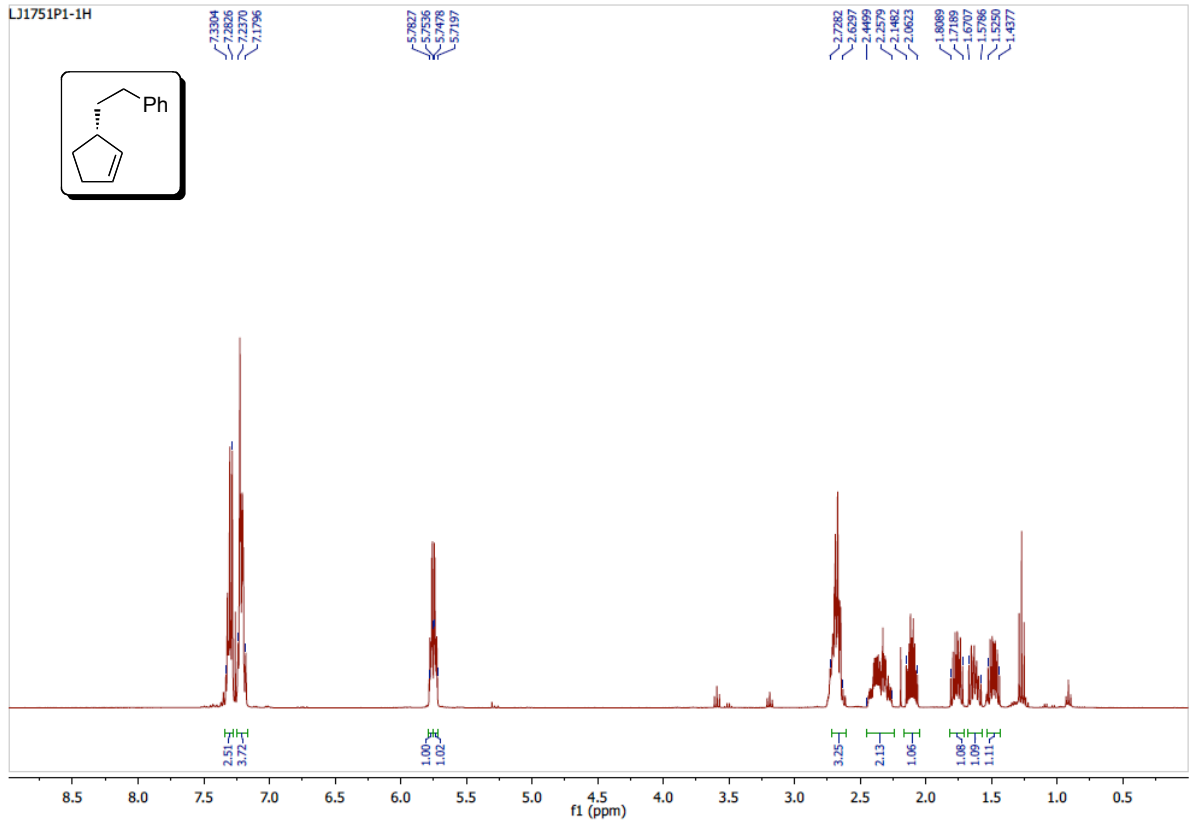


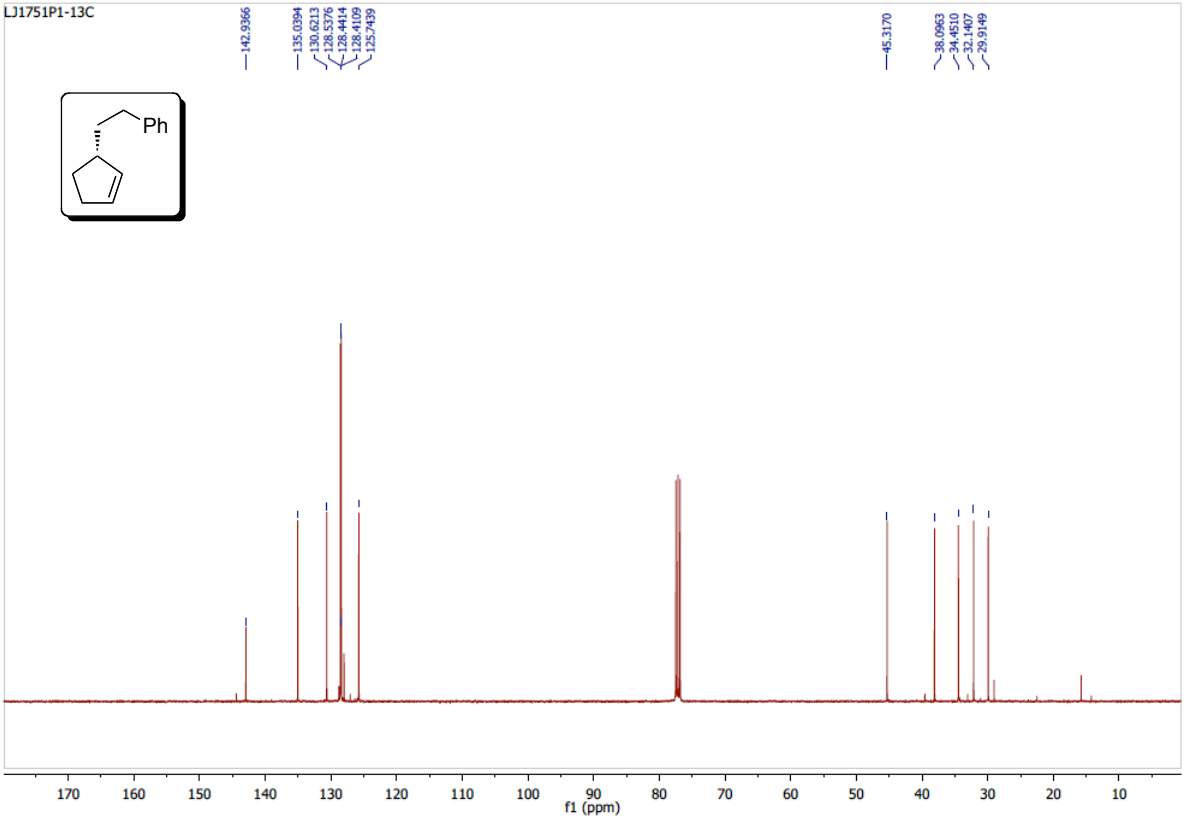


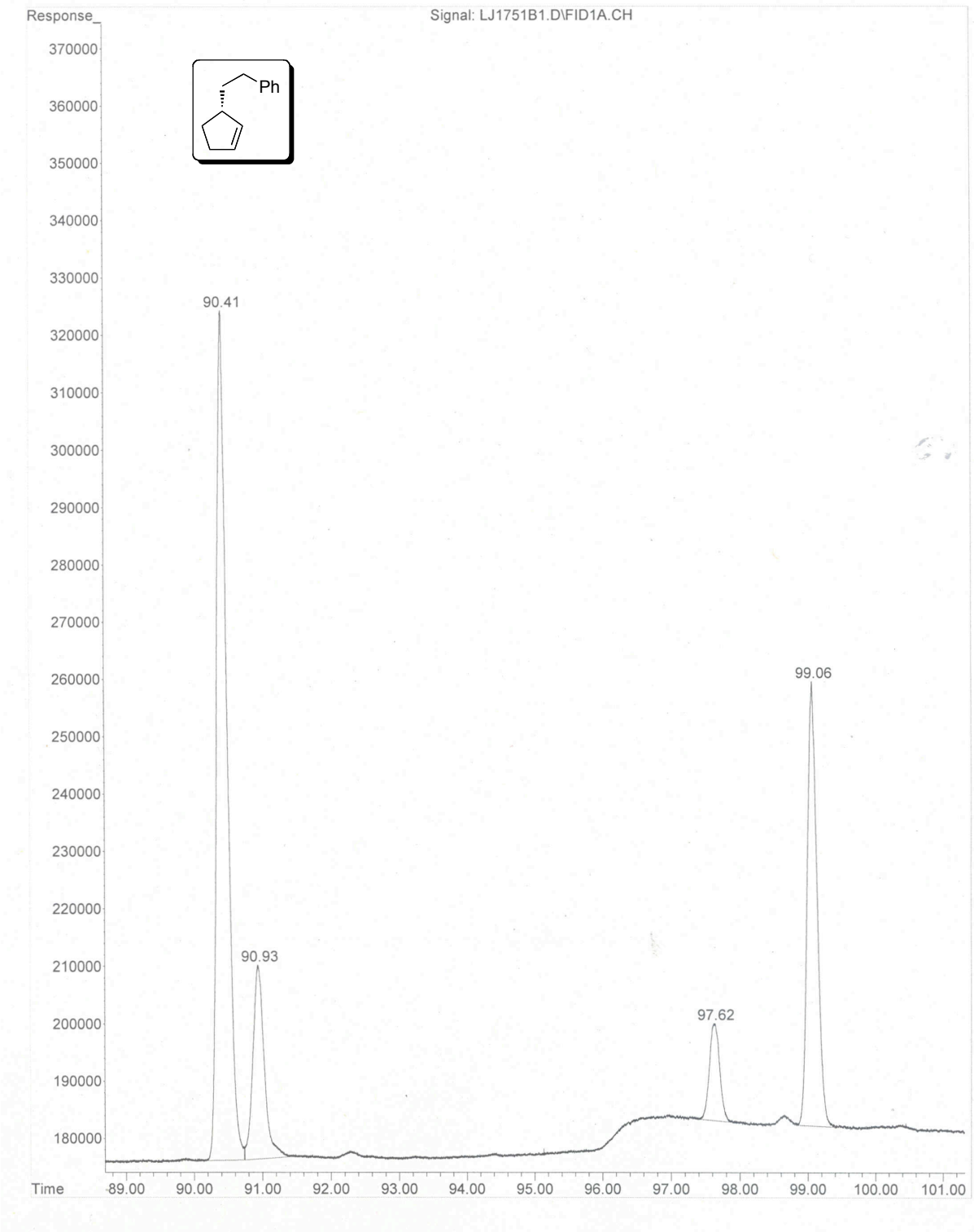


peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	103.850	103.641	104.373	M	161562	18213215	100.00%	57.664%
2	104.676	104.433	104.883	M	11120	1184793	6.51%	3.751%
3	105.120	104.924	105.316	M	4756	482335	2.65%	1.527%
4	105.870	105.651	106.019	M	1124	91518	0.50%	0.290%
5	106.977	106.697	107.163	M	3241	390674	2.15%	1.237%
6	107.432	107.261	107.564	M	937	68114	0.37%	0.216%
7	108.073	107.849	108.569	M	95575	9999180	54.90%	31.658%
8	108.936	108.659	109.215	M	11365	1155003	6.34%	3.657%

Sum of corrected areas: 31584830







peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	90.415	90.178	90.737	M	148384	15536832	100.00%	53.768%
2	90.934	90.764	91.350	M	33993	3903470	25.12%	13.509%
3	97.622	97.417	97.869	M	17050	1780038	11.46%	6.160%
4	99.060	98.854	99.413	M	77449	7675465	49.40%	26.563%

Sum of corrected areas: 28895805