Supplementary Material

Highly chemoselective conjugate addition of lithium tetraorganozincates to coumarin derivatives and functionalization with electrophiles

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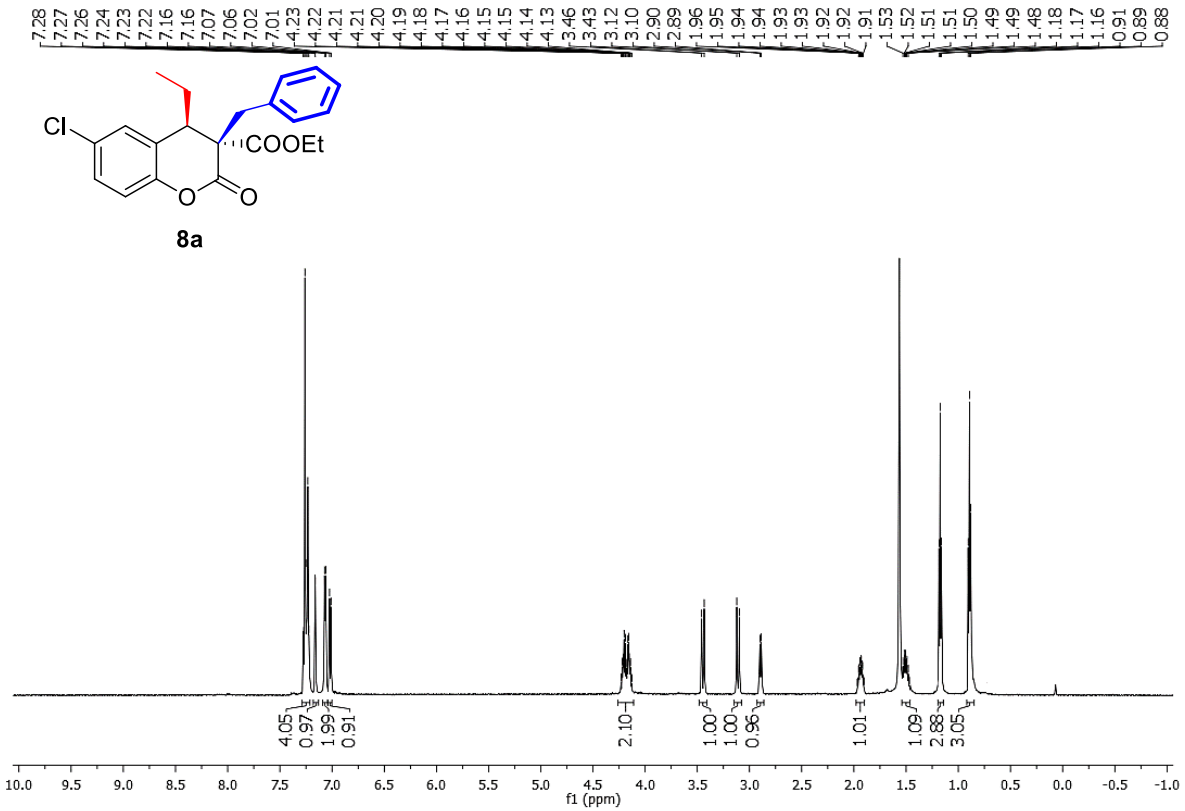
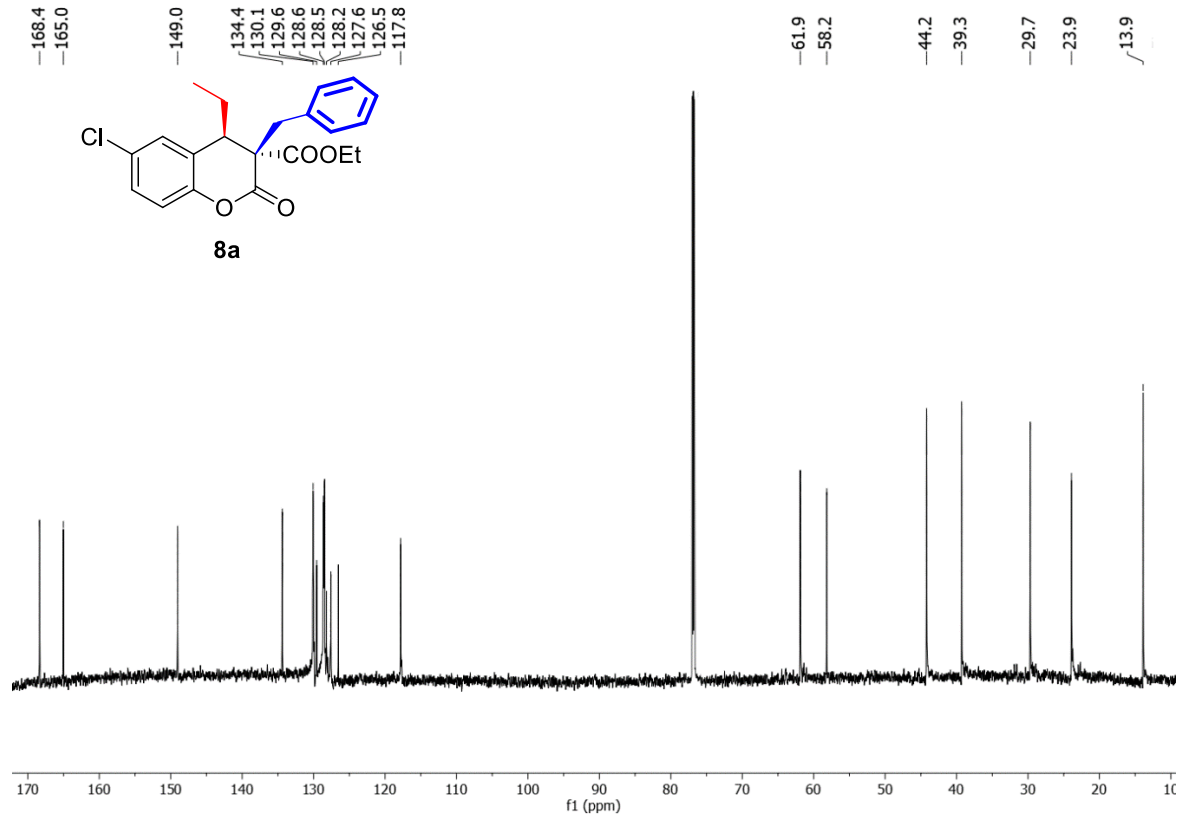
Table of Contents

^{1}H NMR and ^{13}C NMR spectra of 8a

^{1}H NMR (600 MHz, $CDCl_3$)

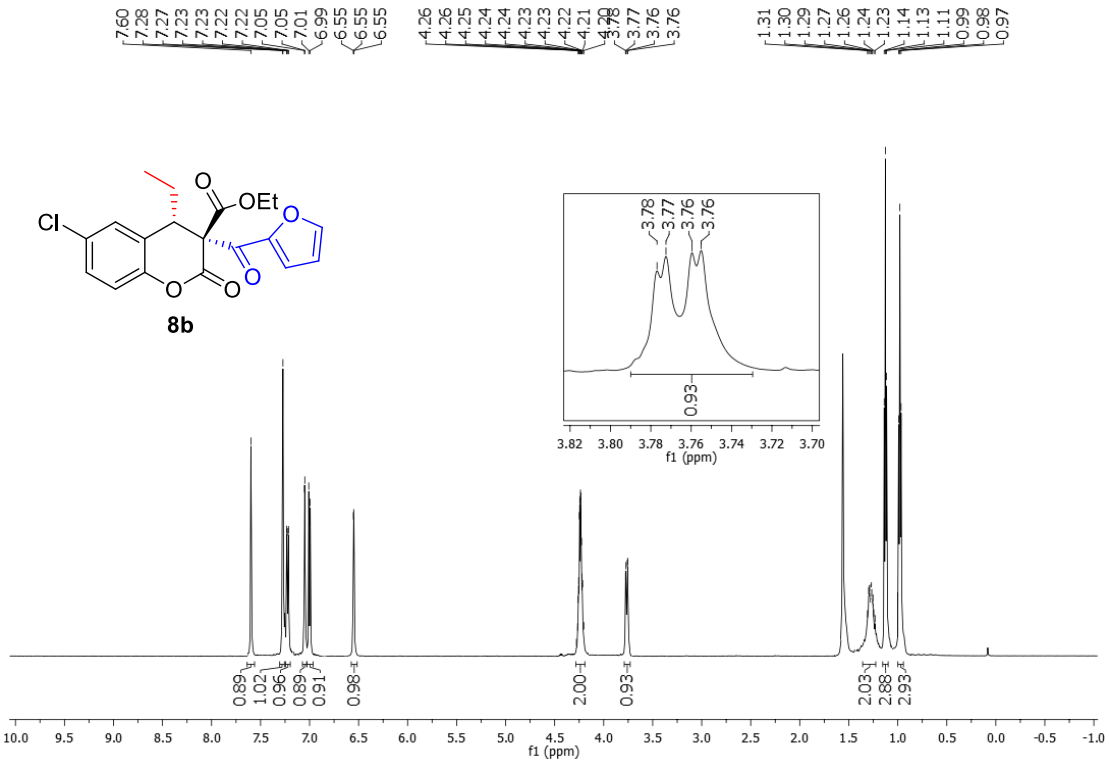


^{13}C NMR (150 MHz, $CDCl_3$)

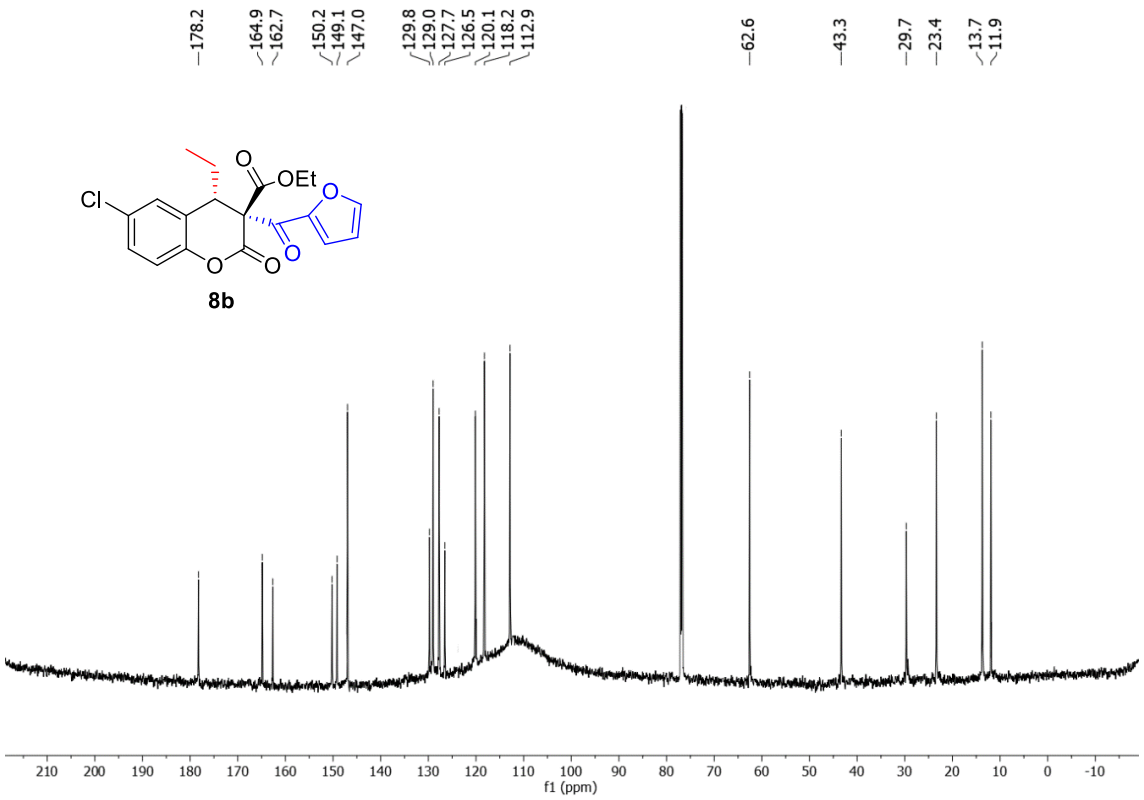


^{1}H NMR and ^{13}C NMR spectra of 8b

^{1}H NMR (600 MHz, $CDCl_3$)

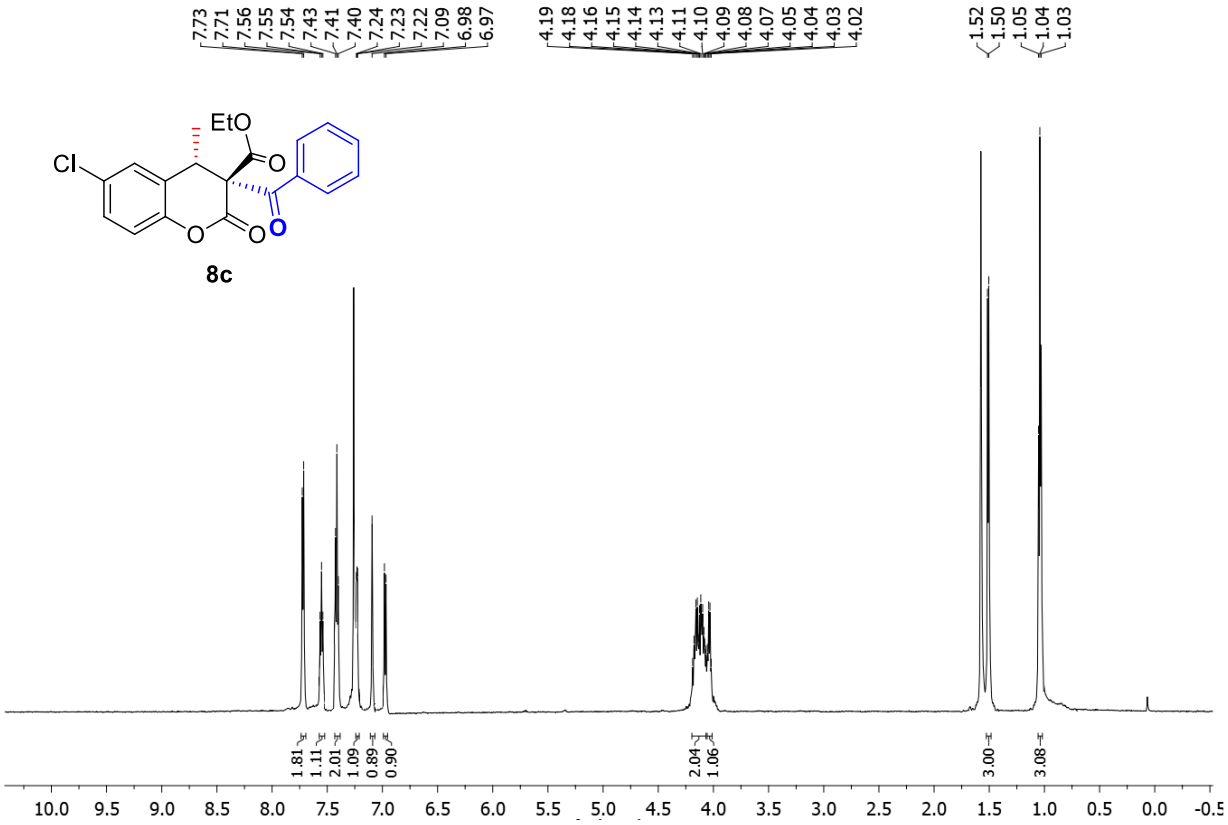


^{13}C NMR (150 MHz, $CDCl_3$)

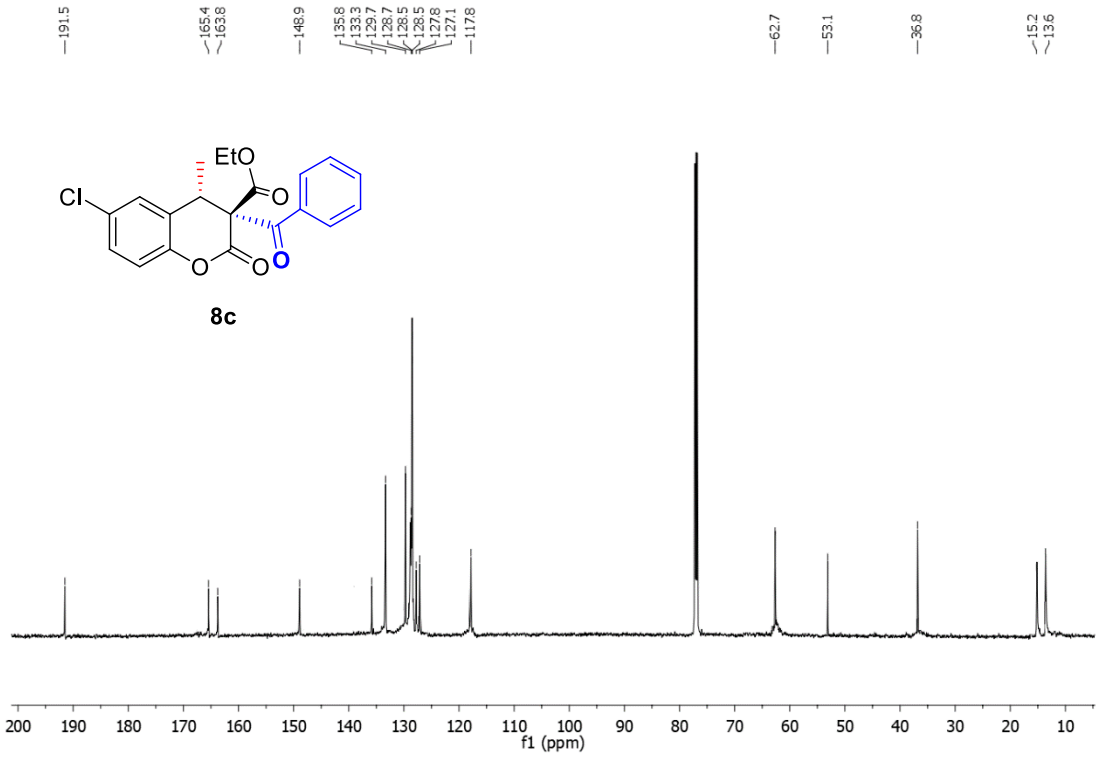


^{1}H NMR and ^{13}C NMR spectra of 8c

^{1}H NMR (600 MHz, $CDCl_3$)

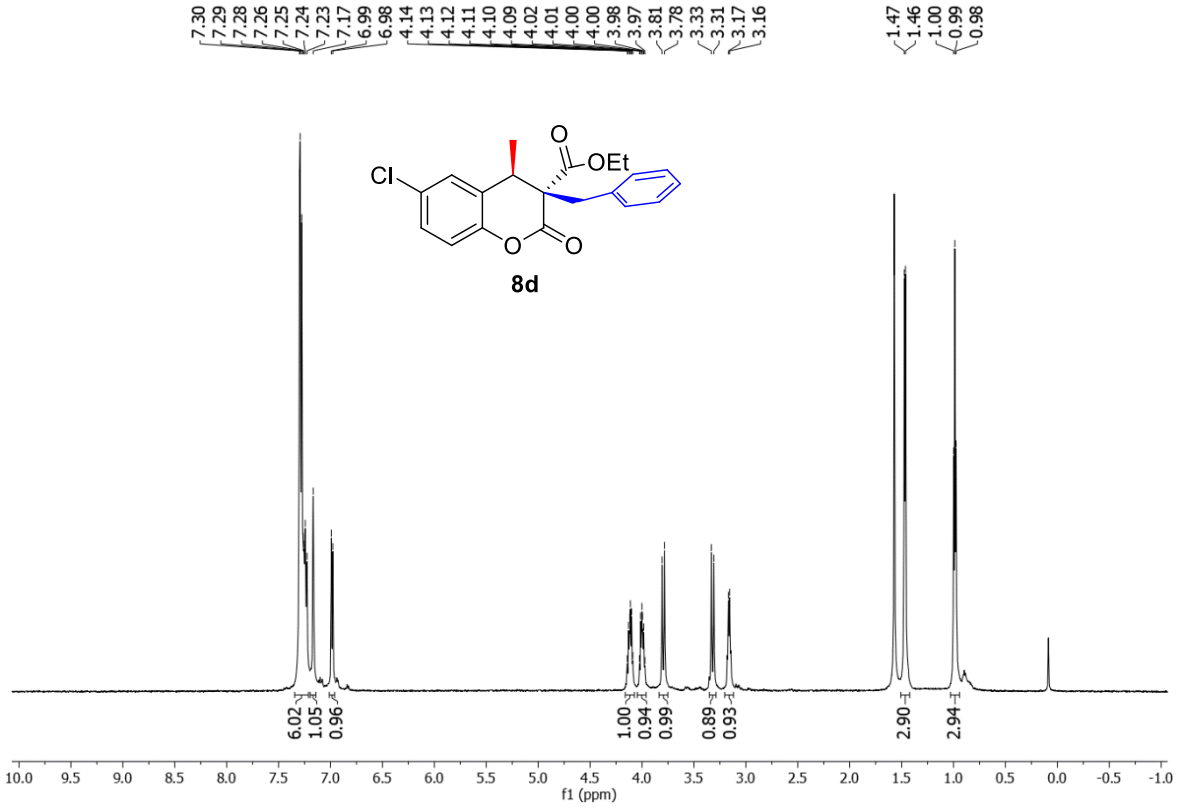


^{13}C NMR (150 MHz, $CDCl_3$)

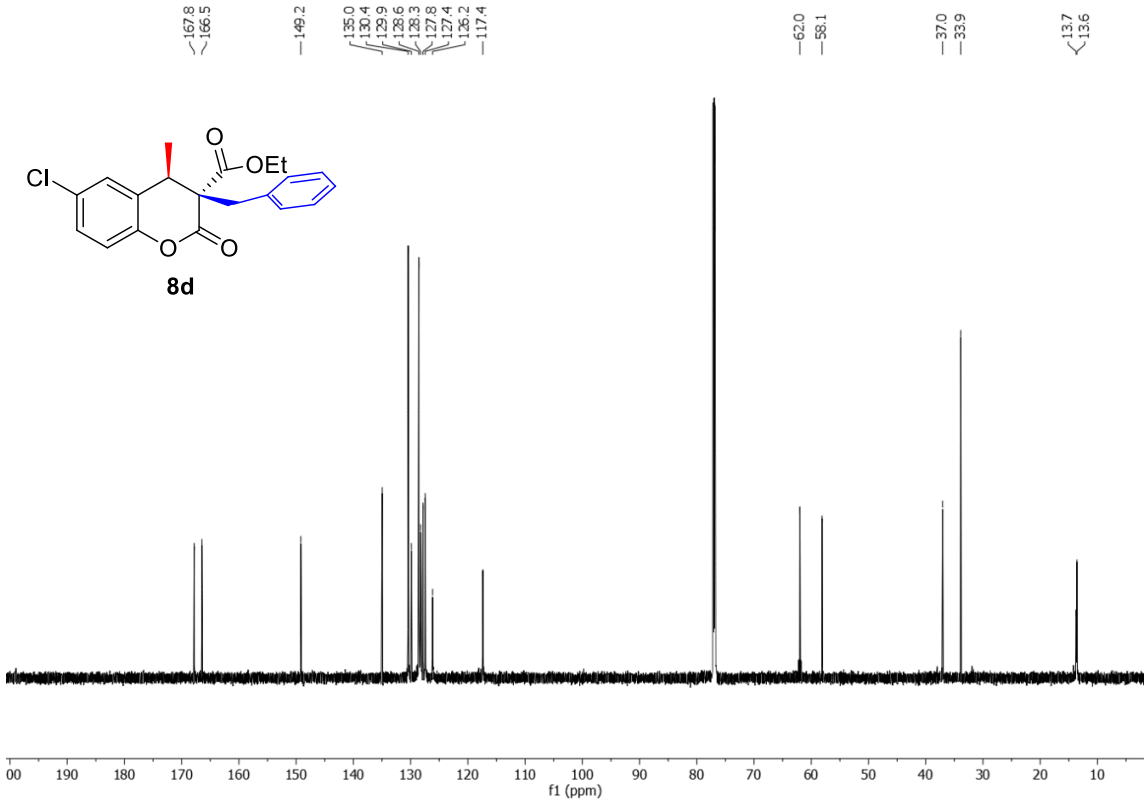


^{1}H NMR and ^{13}C NMR spectra of 8d

^{1}H NMR (600 MHz, $CDCl_3$)

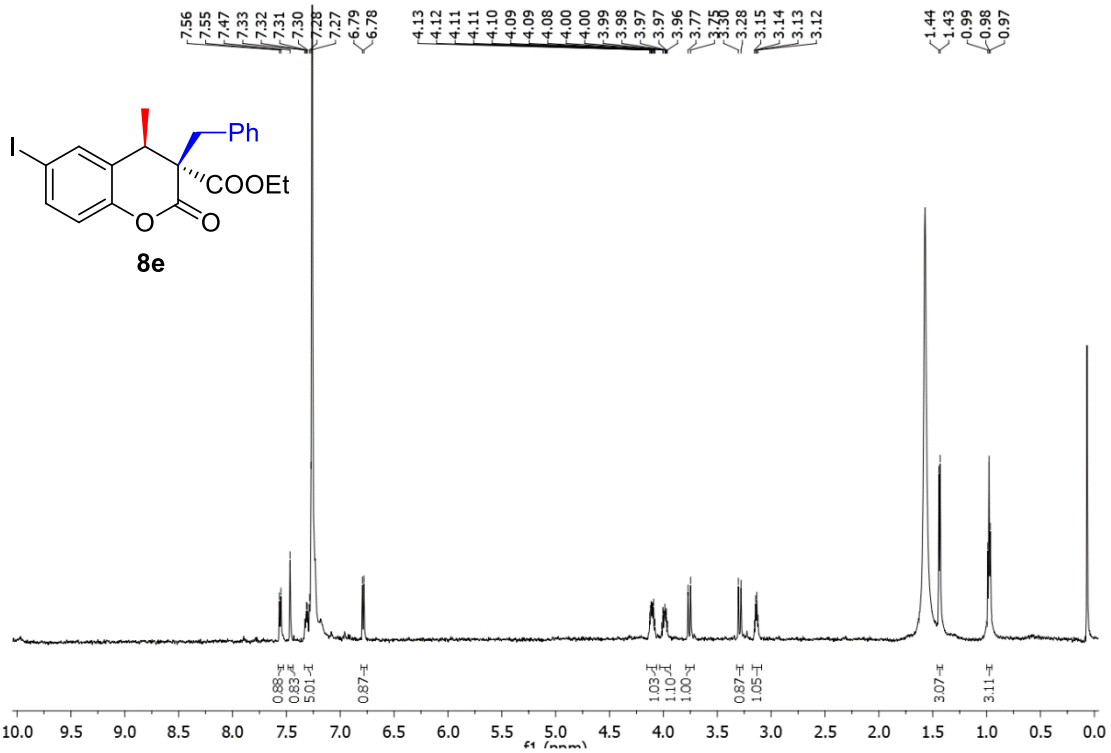


^{13}C NMR (150 MHz, $CDCl_3$)

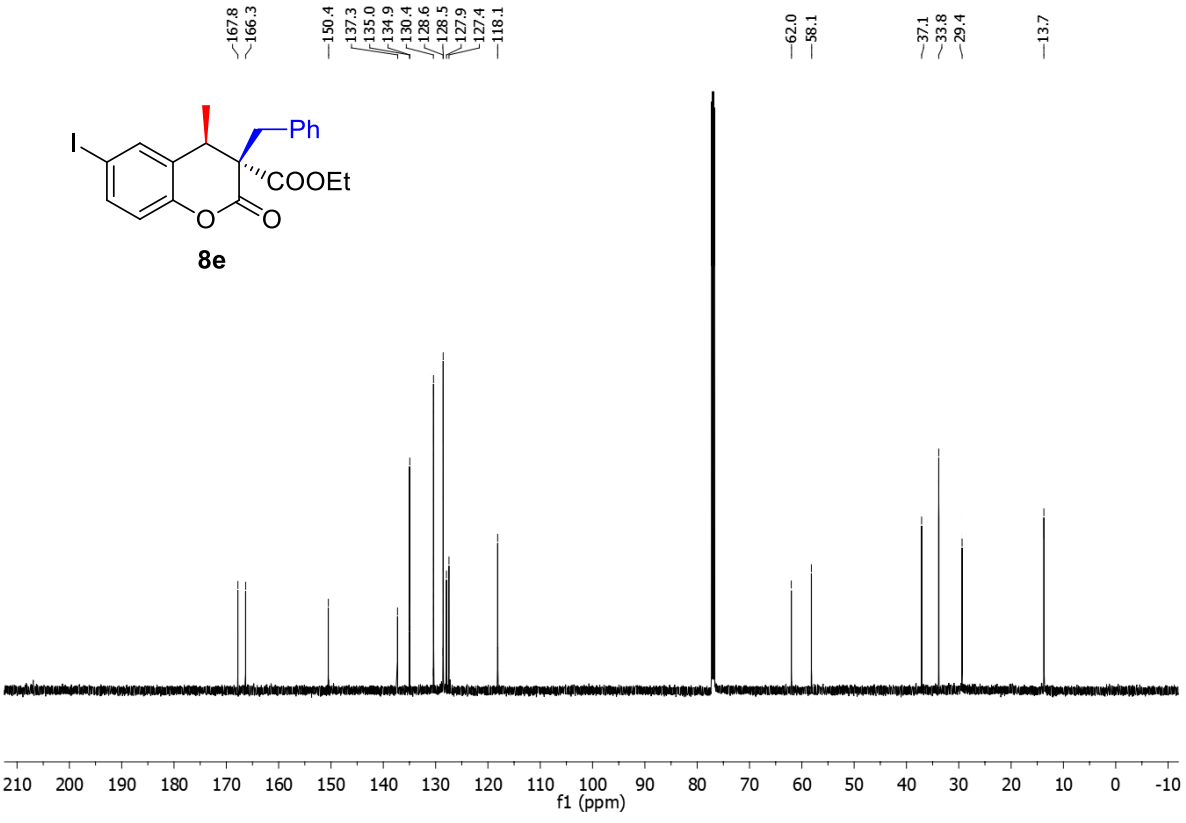


^{1}H NMR and ^{13}C NMR spectra of 8e

^{1}H NMR (600 MHz, $CDCl_3$)

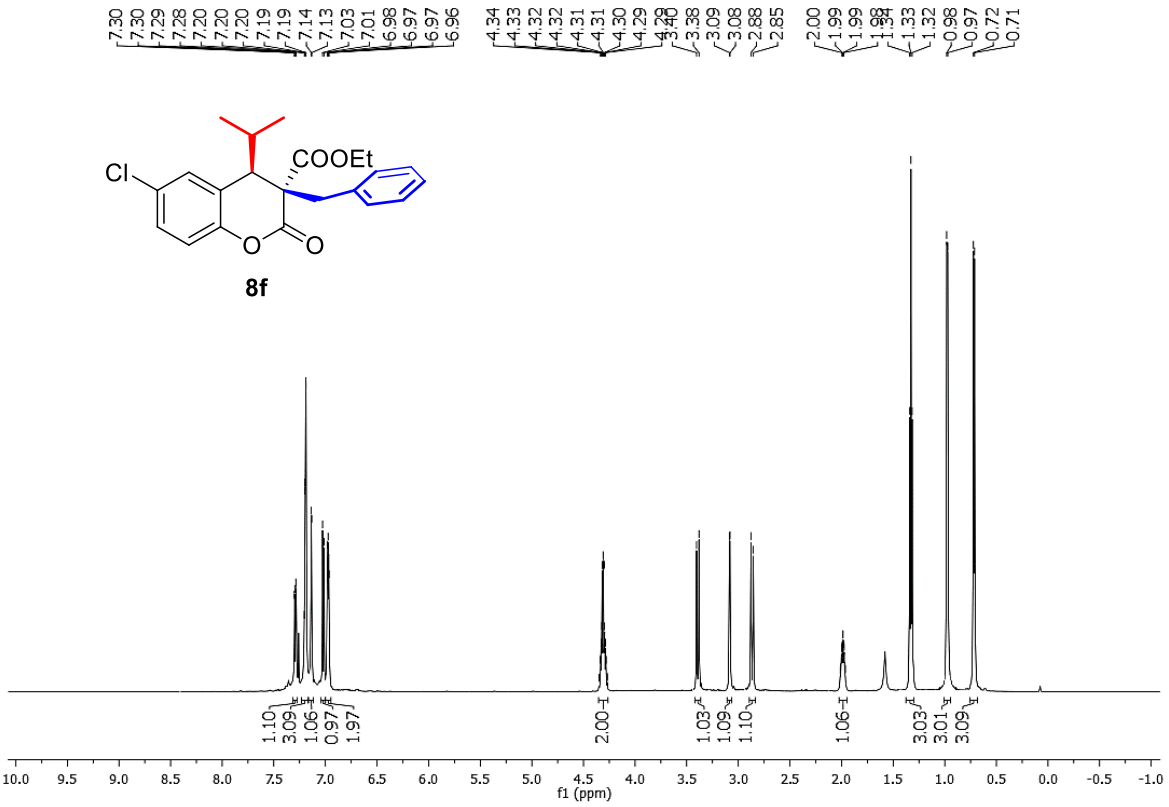


^{13}C NMR (150 MHz, $CDCl_3$)

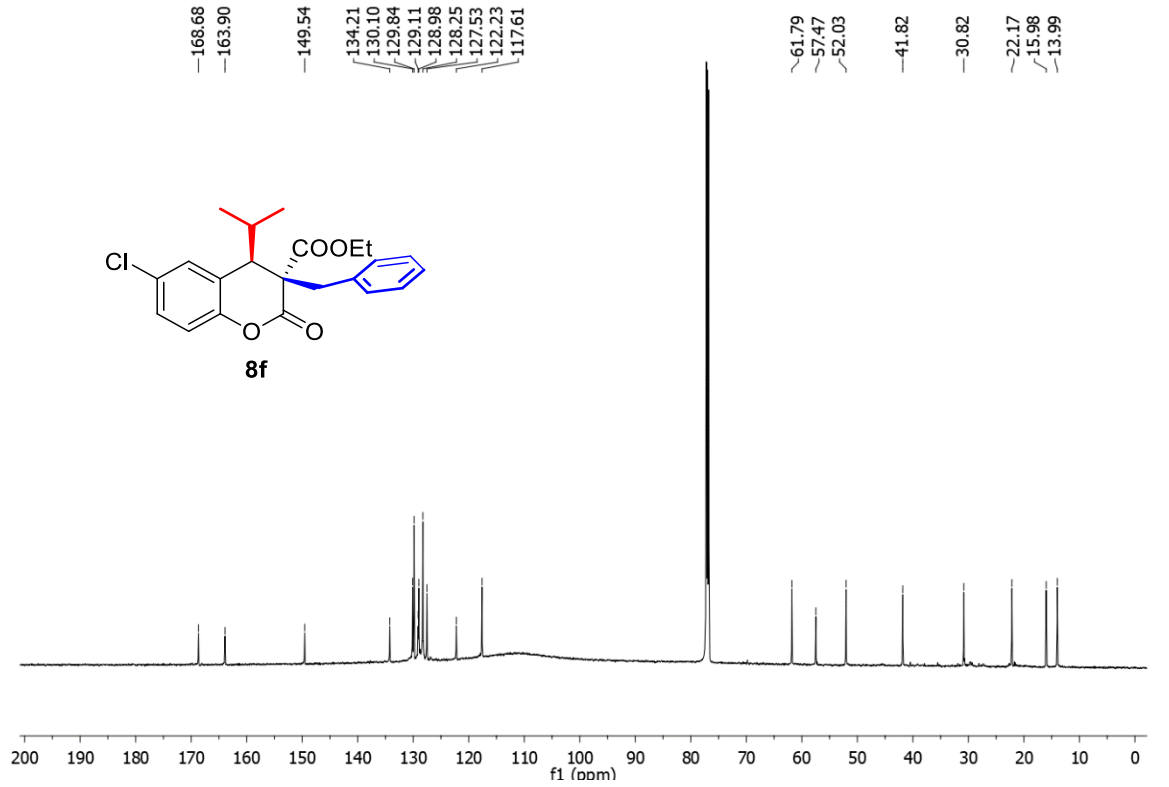


^{1}H NMR and ^{13}C NMR spectra of 8f

^{1}H NMR (600 MHz, $CDCl_3$)

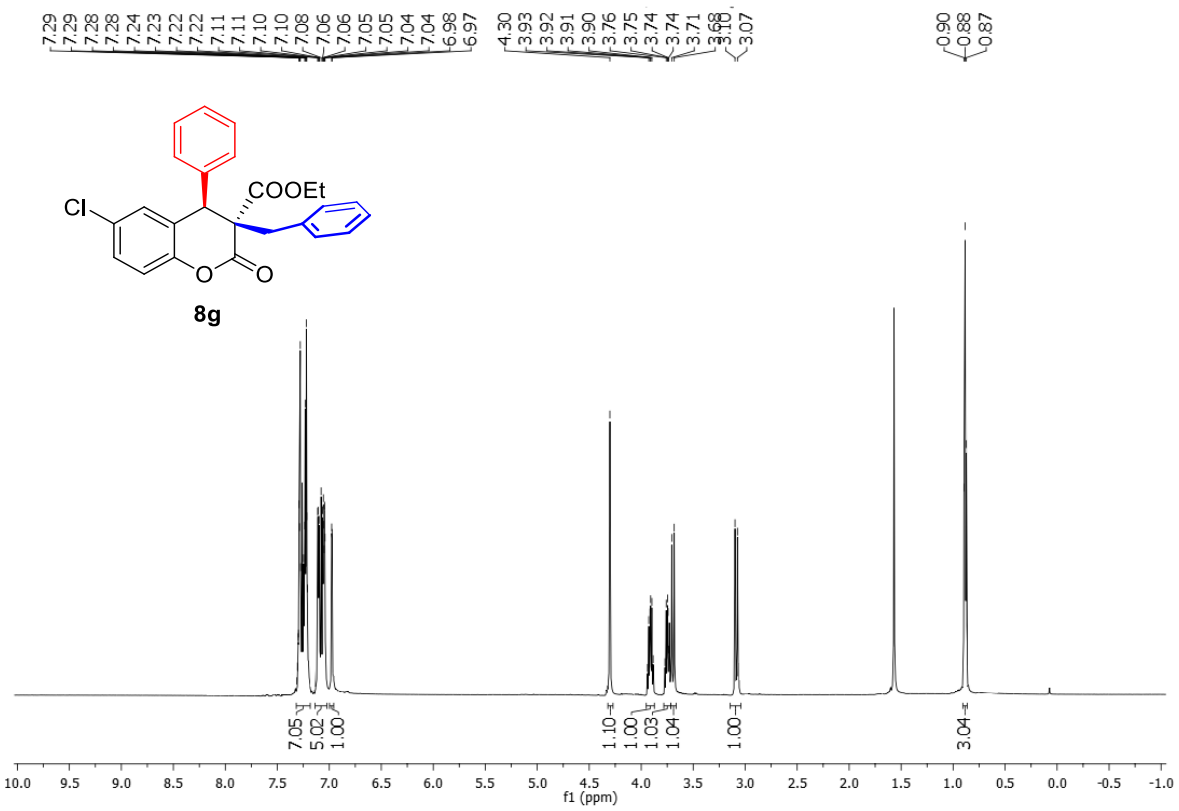


^{13}C NMR (150 MHz, $CDCl_3$)

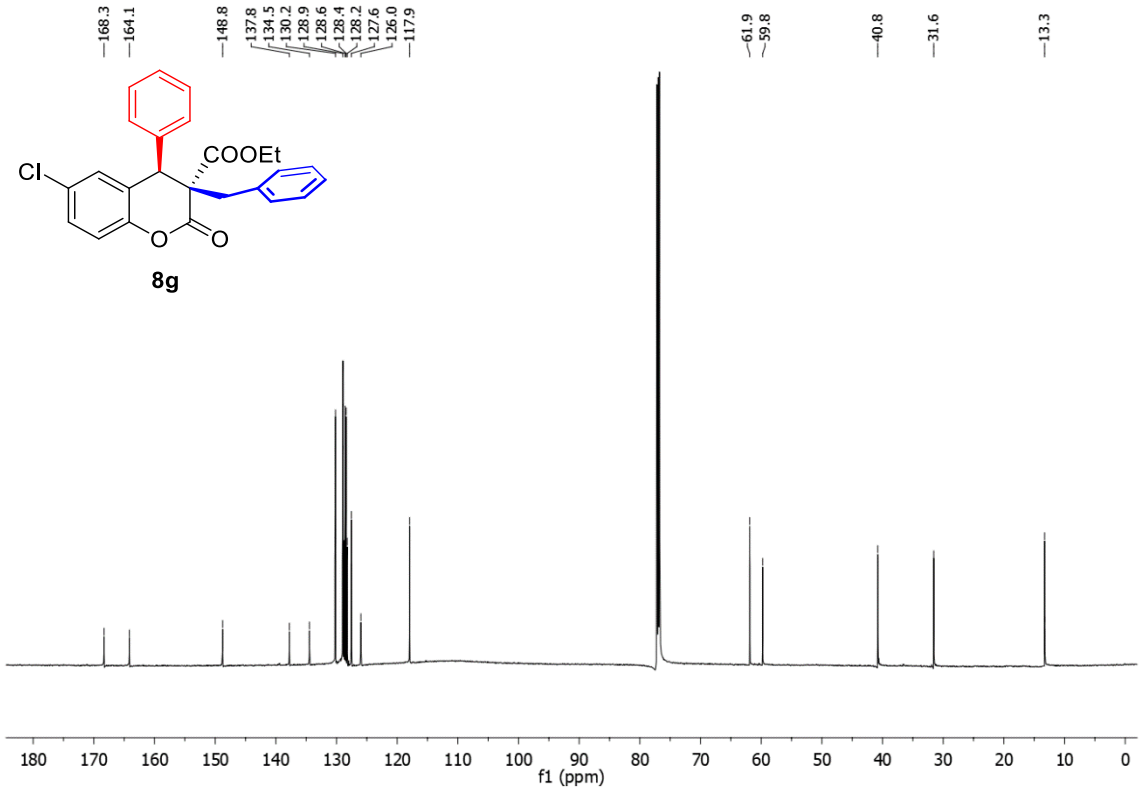


^{1}H NMR and ^{13}C NMR spectra of 8g

^{1}H NMR (600 MHz, $CDCl_3$)

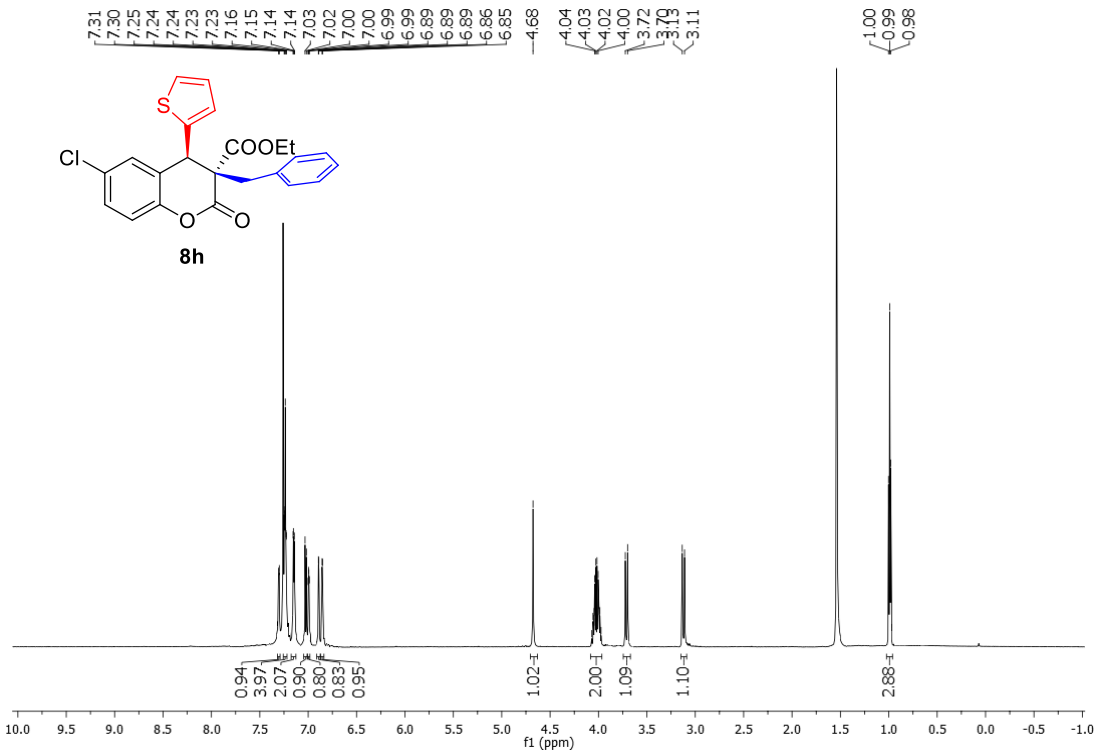


^{13}C NMR (150 MHz, $CDCl_3$)

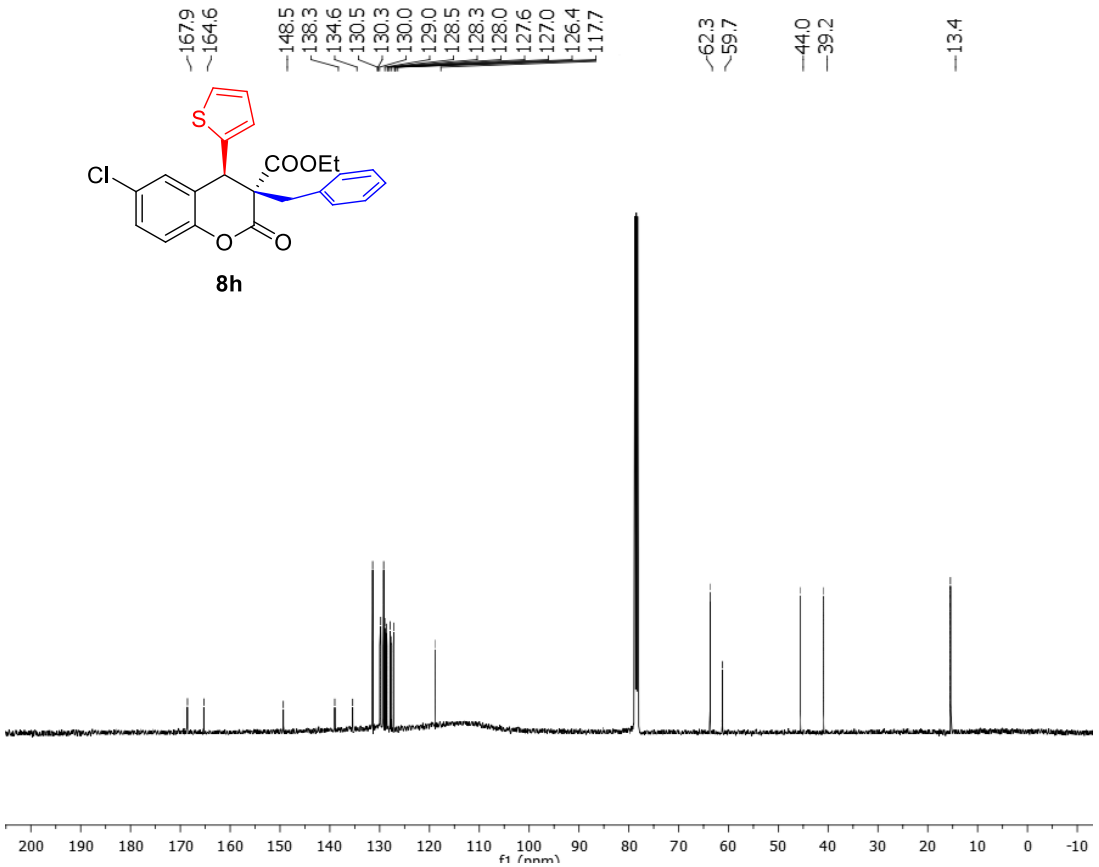


^{1}H NMR and ^{13}C NMR spectra of 8h

^{1}H NMR (600 MHz, $CDCl_3$)



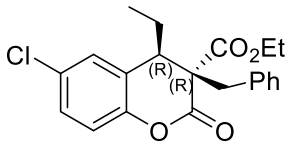
^{13}C NMR (150 MHz, $CDCl_3$)



Computational details

All the quantum mechanical calculations were performed using the ORCA 4.2.0 software.[1] Conformational search was done in the gas phase using the PM3 force field and the Monte-Carlo algorithm, implemented in Spartan '14 software[2]: The conformer with the lowest energy was subjected to further optimization with DFT method using the B3LYP functional and the standard 6-31G(d) basis set. The nature of stationary points was defined on the basis of calculations of normal vibrational frequencies (force constant Hessian matrix).

Cartesian coordinates, Electronic Energies and Gibbs Free Energies of (*R*,R**)-8a and (*R*,S**)-8a isomers at B3LYP/6-31G(d) level of theory



(*R*,R**)-**8a**

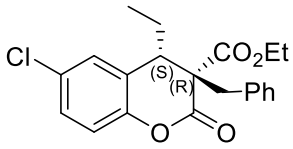
C	-1.302447000	1.792406000	1.902342000
C	0.078780000	0.833517000	4.137714000
C	-1.137584000	2.590234000	3.034271000
C	-0.786092000	0.493869000	1.879606000
C	-0.091985000	0.038014000	3.006431000
C	-0.452445000	2.121895000	4.156568000
O	0.423909000	-1.247618000	3.060583000
C	0.663082000	-1.967486000	1.912929000
C	0.434246000	-1.215752000	0.587912000
C	-0.920515000	-0.451404000	0.701518000
O	0.999039000	-3.116170000	2.016560000
Cl	-1.797973000	4.220939000	3.041344000
C	1.624468000	-0.244305000	0.421466000
O	2.744484000	-0.495205000	0.814782000
O	1.293821000	0.860918000	-0.261040000
C	2.373610000	1.786812000	-0.545113000
C	1.796815000	2.906266000	-1.390626000
C	0.529888000	-2.257813000	-0.576045000
C	0.497809000	-1.682152000	-1.977948000
C	0.477446000	-0.616215000	-4.589104000
C	-0.709819000	-1.458097000	-2.654950000
C	1.696354000	-1.378868000	-2.642223000
C	1.688966000	-0.848191000	-3.933265000
C	-0.722539000	-0.927310000	-3.946675000
H	-1.826884000	2.181474000	1.035396000
H	0.624874000	0.437031000	4.987511000
H	-0.330416000	2.756829000	5.027447000
H	2.778350000	2.147294000	0.405943000

[1] a) F. Neese, The ORCA program system. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, *2*, 73−78; b) F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2018**, *8*, e1327.
[2] W. J. Hehre, Spartan '14; Wavefunction, Inc.: Irvine, CA, 2014.

H	3.168107000	1.242912000	-1.064735000
H	0.995378000	3.427809000	-0.857009000
H	1.393597000	2.513367000	-2.329689000
H	2.582269000	3.632869000	-1.626971000
H	-0.271516000	-2.990237000	-0.443430000
H	1.463411000	-2.805283000	-0.421246000
H	0.469226000	-0.208467000	-5.596648000
H	-1.651638000	-1.713704000	-2.174771000
H	2.643967000	-1.567650000	-2.141906000
H	2.629927000	-0.626654000	-4.430889000
H	-1.670525000	-0.765283000	-4.453705000
C	-2.144888000	-1.389652000	0.878286000
H	-2.140423000	-2.141102000	0.080989000
H	-2.053265000	-1.943846000	1.821973000
C	-3.488918000	-0.652477000	0.848378000
H	-3.624331000	-0.111698000	-0.097041000
H	-3.573851000	0.072197000	1.664767000
H	-4.316871000	-1.363393000	0.946055000
H	-1.056901000	0.129375000	-0.215741000

Number of imaginary frequencies = 0

Electronic Energy	-1573.252267 Hartree
Gibbs Free Energy	**-1572.923892 Hartree**



(*R*,S**)-**8a**

C	-0.864518000	2.875488000	1.297521000
C	0.747852000	2.191623000	3.478261000
C	-1.049849000	3.484592000	2.540030000
C	0.139686000	1.917821000	1.128753000
C	0.930695000	1.589791000	2.235507000
C	-0.250443000	3.152912000	3.634165000
O	1.954641000	0.660691000	2.134732000
C	2.057540000	-0.207928000	1.066460000
C	0.833827000	-0.246185000	0.135897000
C	0.453192000	1.234203000	-0.185223000
O	3.063941000	-0.856022000	0.963570000
Cl	-2.318209000	4.688278000	2.726985000
C	1.581059000	2.016045000	-0.924321000
C	1.132818000	3.389591000	-1.435351000
C	1.153641000	-1.038522000	-1.146623000
O	1.047269000	-0.603685000	-2.273902000
O	1.511752000	-2.303054000	-0.872936000

C	1.886363000	-3.119886000	-2.009722000
C	2.366892000	-4.453471000	-1.468812000
C	-0.310927000	-1.030323000	0.900160000
C	-1.608919000	-1.196388000	0.130986000
C	-4.032081000	-1.521016000	-1.273287000
C	-2.653950000	-0.271038000	0.274619000
C	-1.808189000	-2.296881000	-0.716612000
C	-3.006109000	-2.457586000	-1.414444000
C	-3.853483000	-0.428651000	-0.422418000
H	-1.501011000	3.145655000	0.460852000
H	1.385983000	1.903944000	4.307623000
H	-0.408343000	3.634146000	4.593266000
H	-0.433859000	1.219913000	-0.826835000
H	2.438429000	2.141223000	-0.248577000
H	1.918831000	1.416535000	-1.770994000
H	1.954595000	3.881999000	-1.967359000
H	0.819852000	4.054002000	-0.622450000
H	0.295240000	3.293519000	-2.137664000
H	1.016978000	-3.224341000	-2.667537000
H	2.667211000	-2.595891000	-2.569166000
H	1.573343000	-4.963787000	-0.912211000
H	3.222211000	-4.313806000	-0.800299000
H	2.674702000	-5.099810000	-2.298454000
H	-0.514155000	-0.515818000	1.842911000
H	0.097455000	-2.013169000	1.151791000
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Number of imaginary frequencies = 0

Electronic Energy	-1573.249909 Hartree
Gibbs Free Energy	**-1572.921347 Hartree**