

Supplementary Material

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

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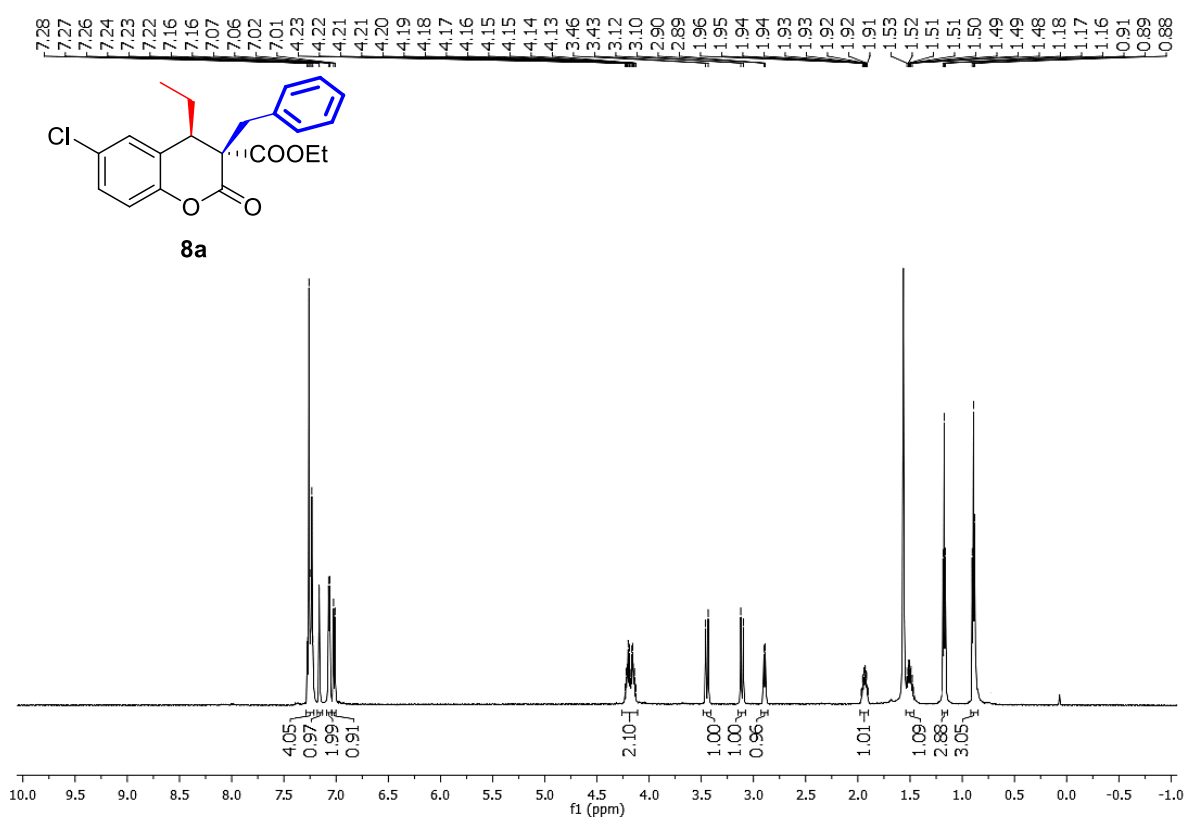
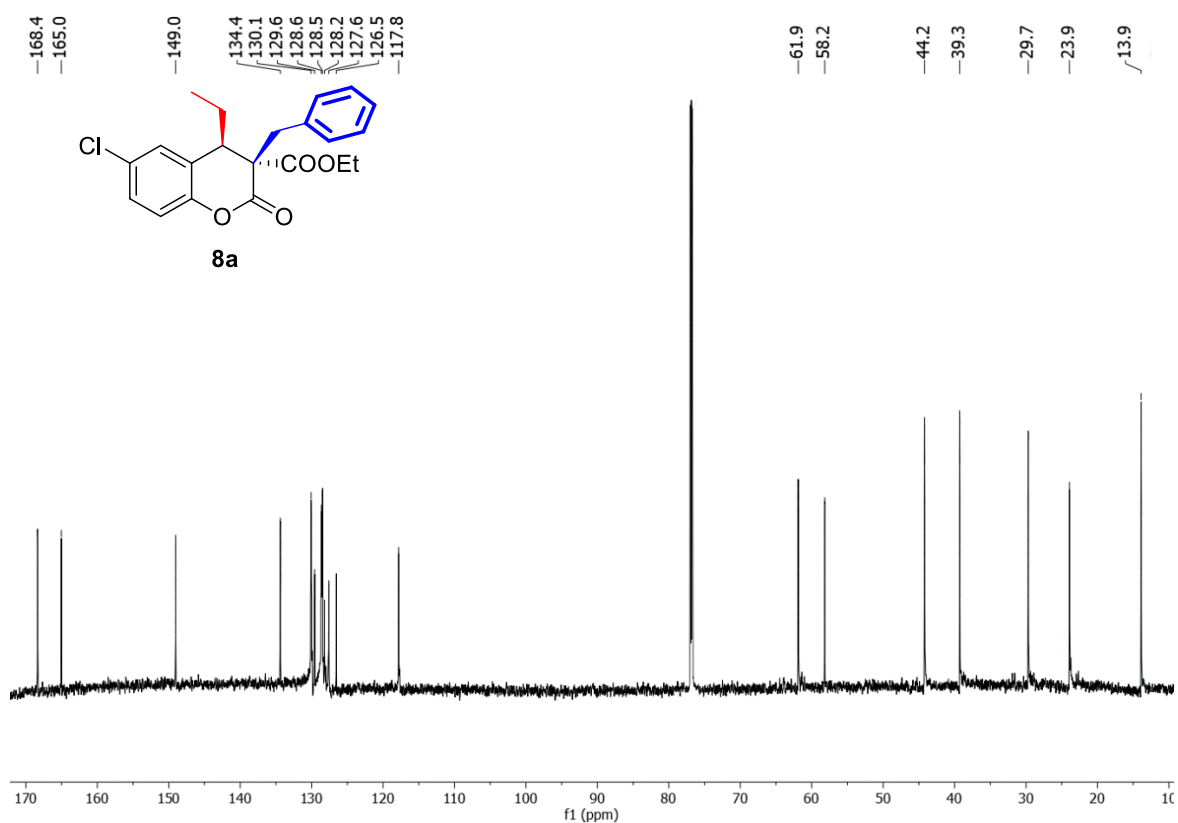
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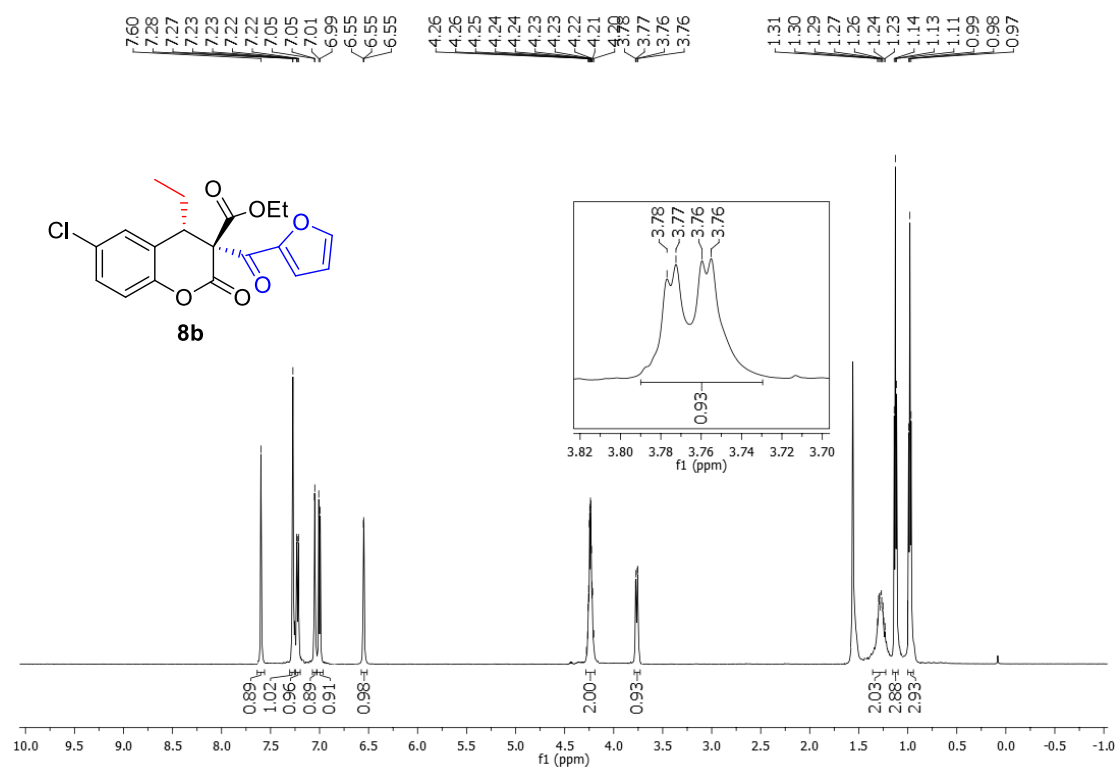
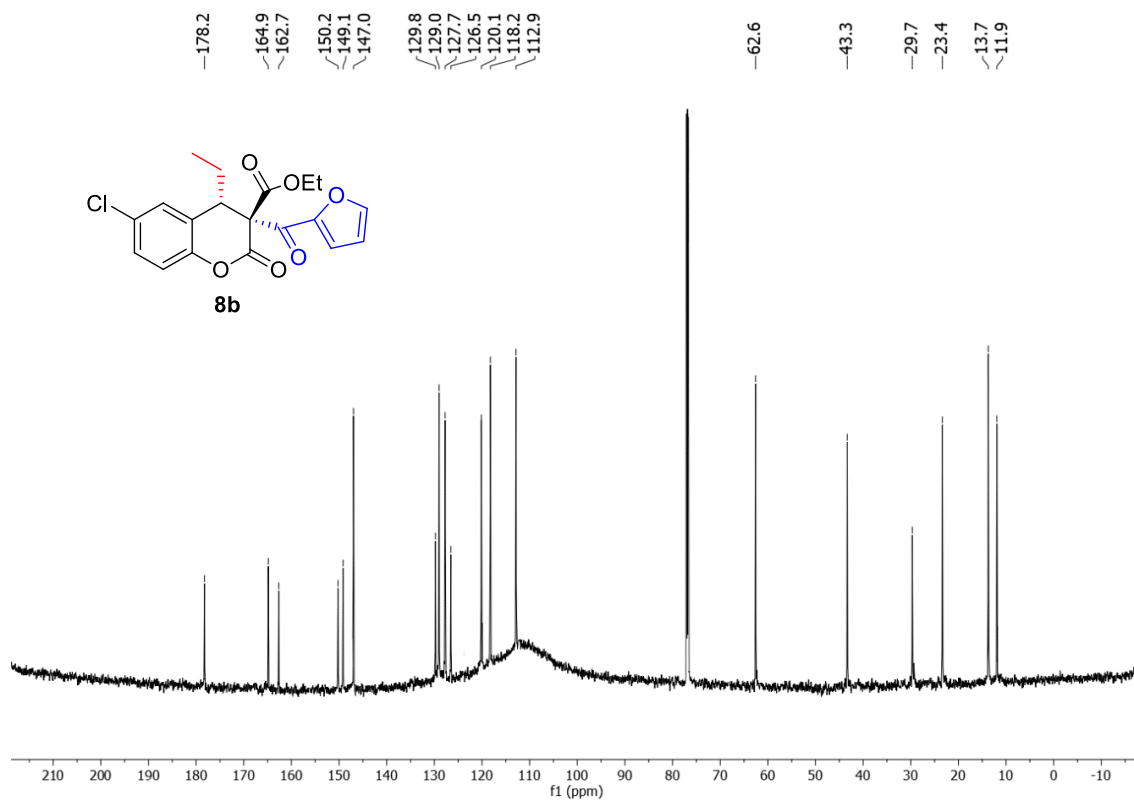
^c *Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Consorzio C.I.N.M.P.I.S., Via E. Orabona 4, 70125, Bari, Italy*

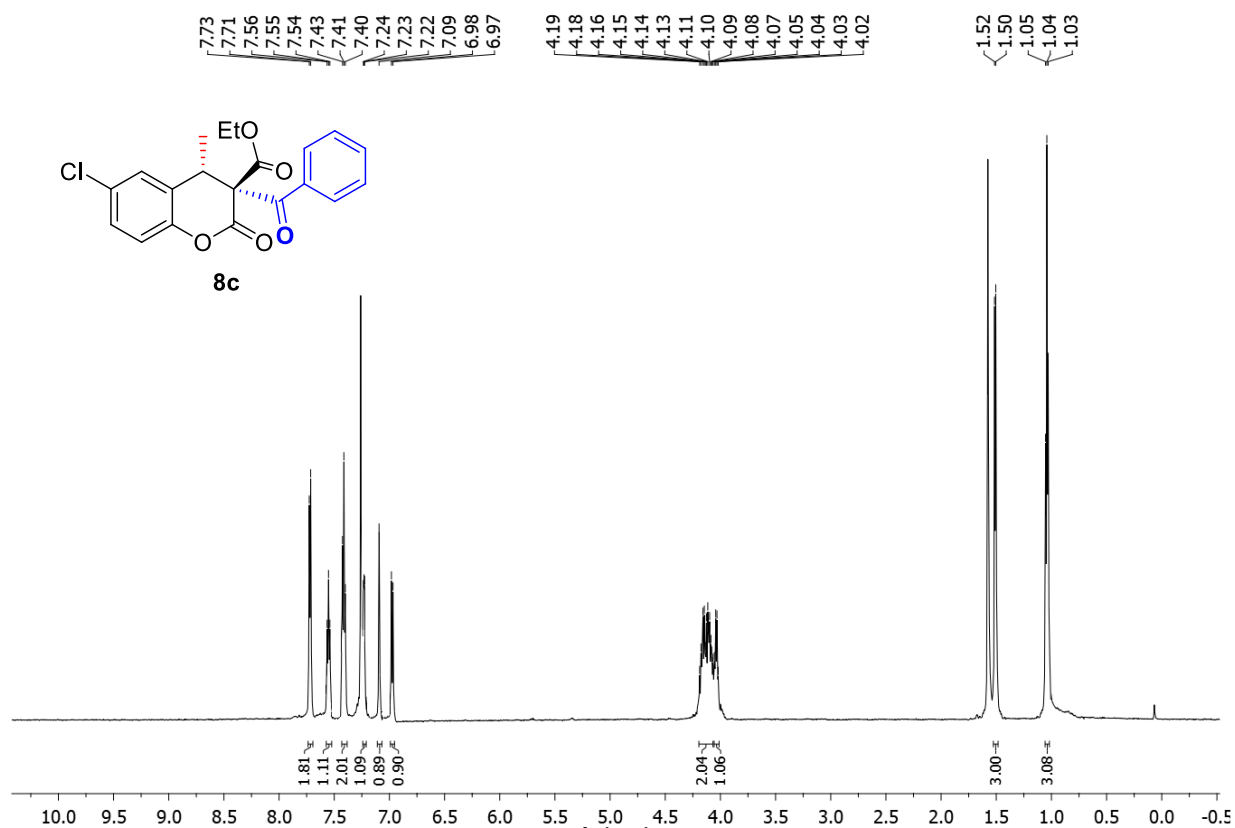
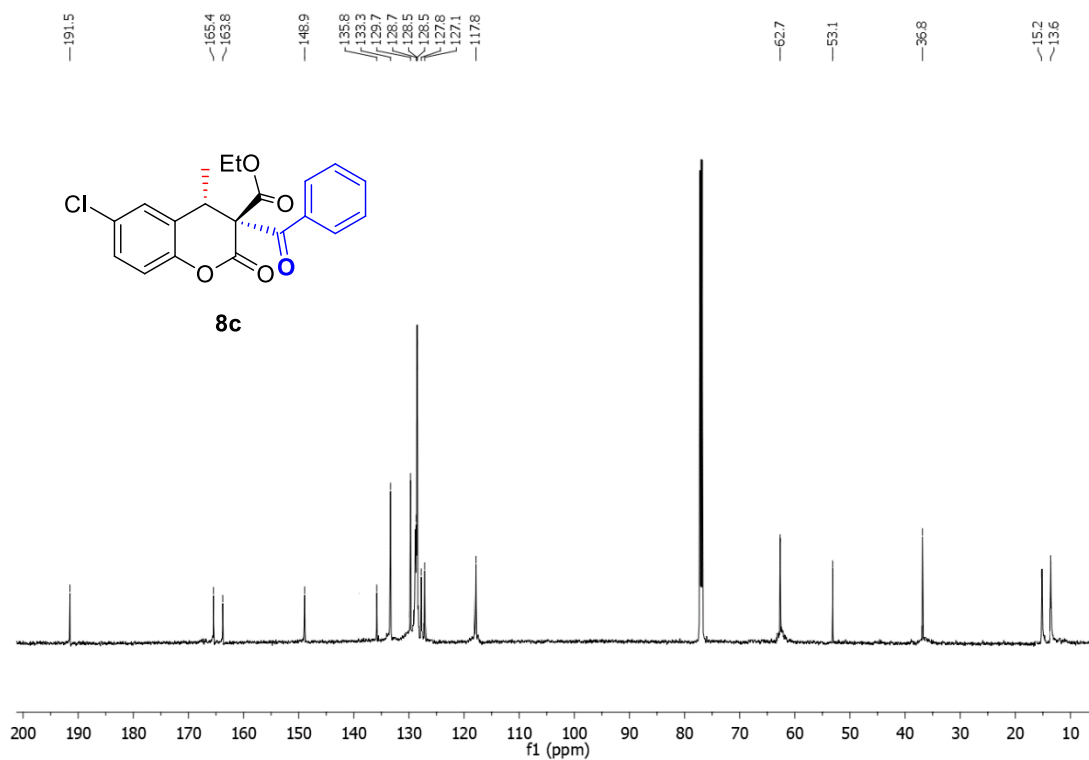
Email: vito.capriati@uniba.it

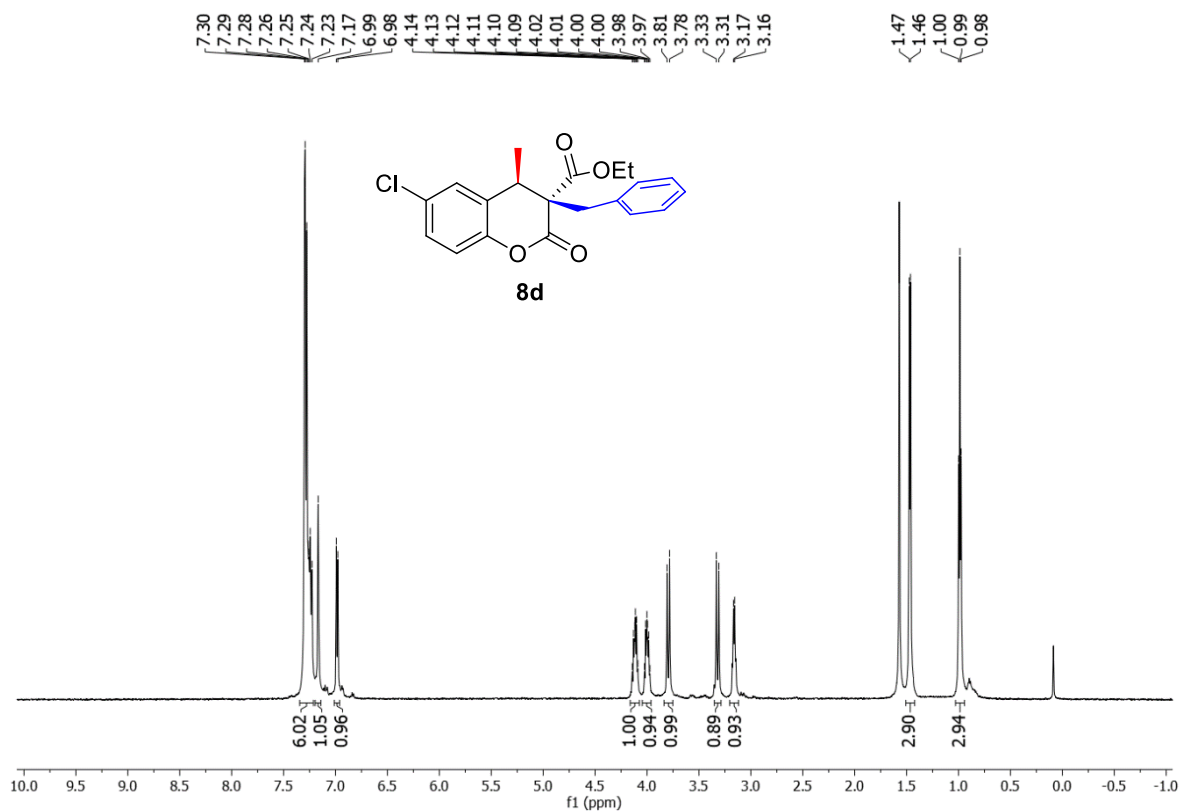
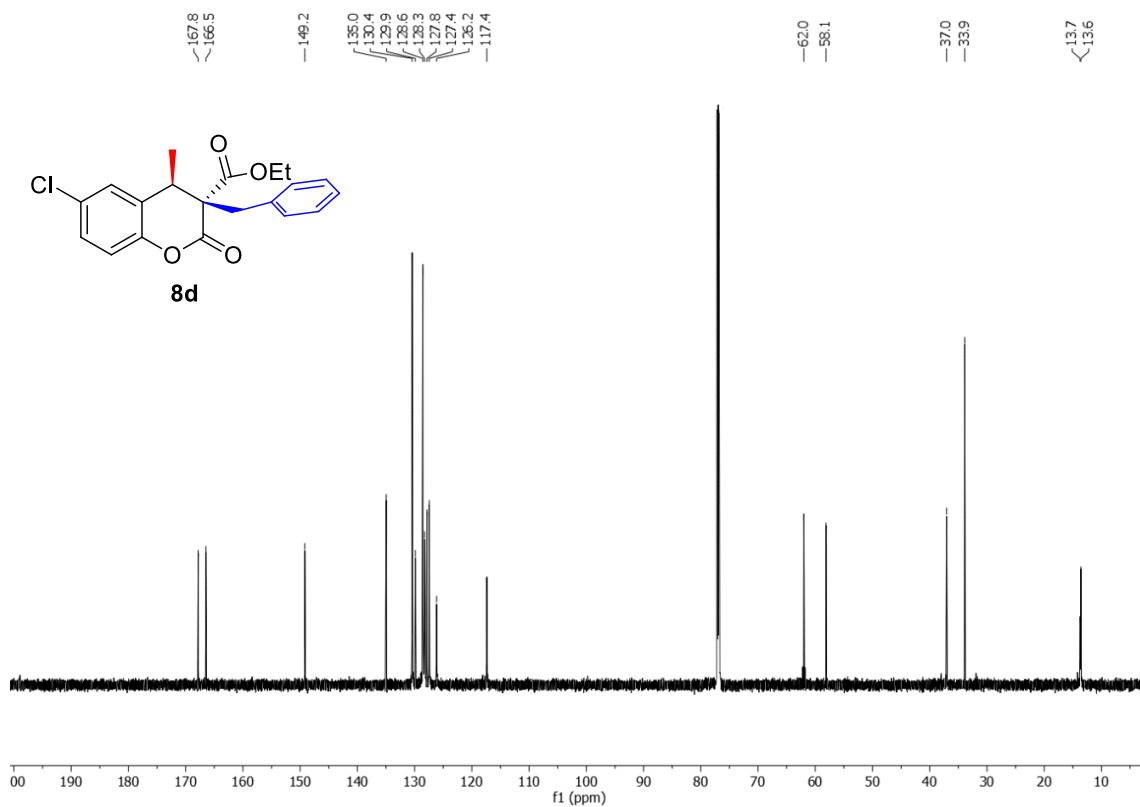
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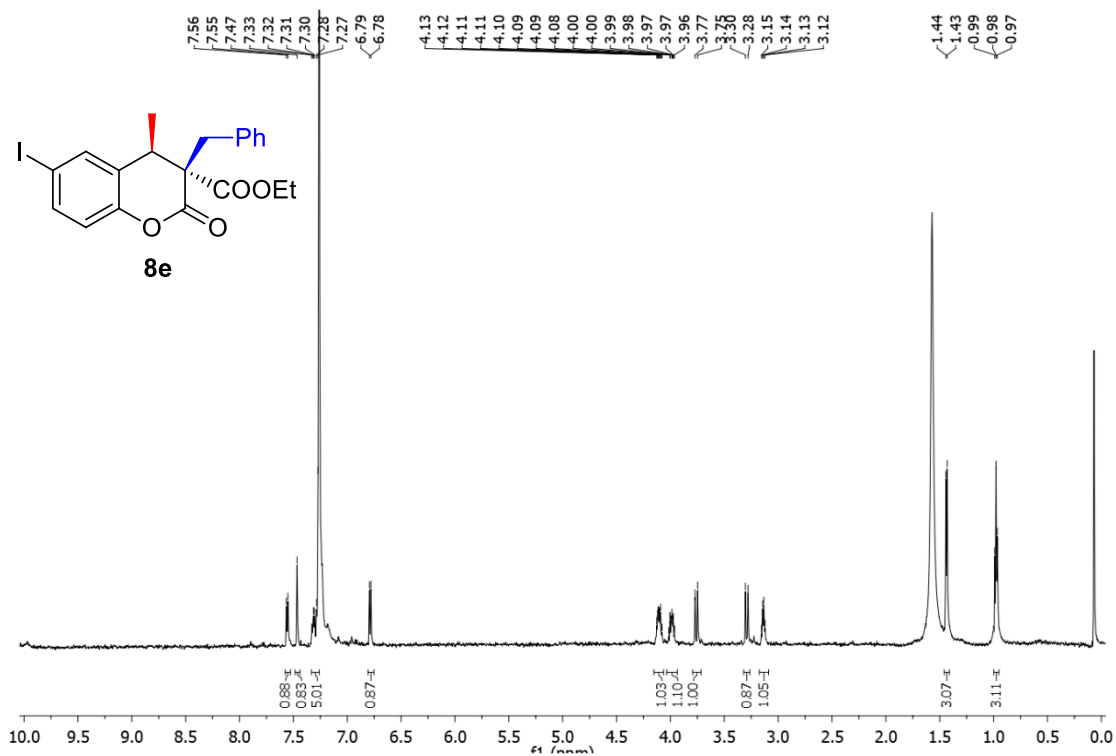
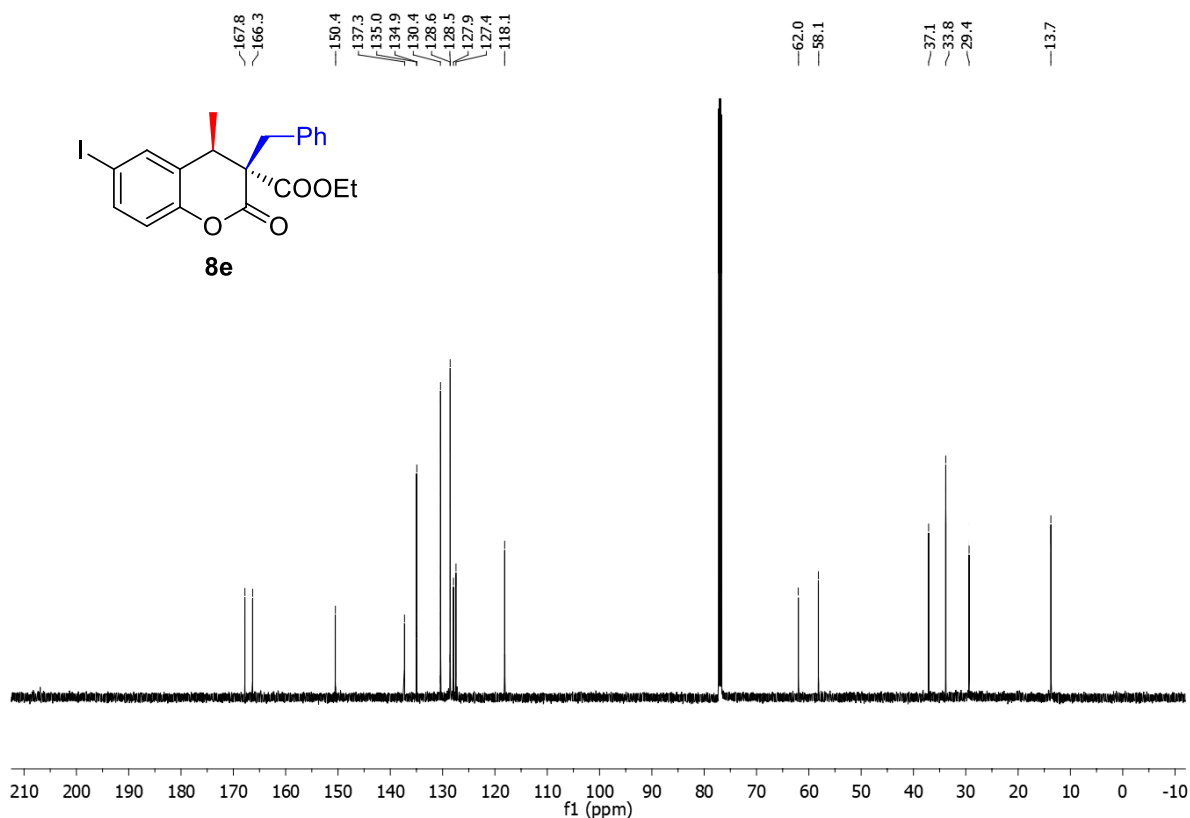
Copies of ¹ H and ¹³ C NMR spectra of compounds 8a–h	S2
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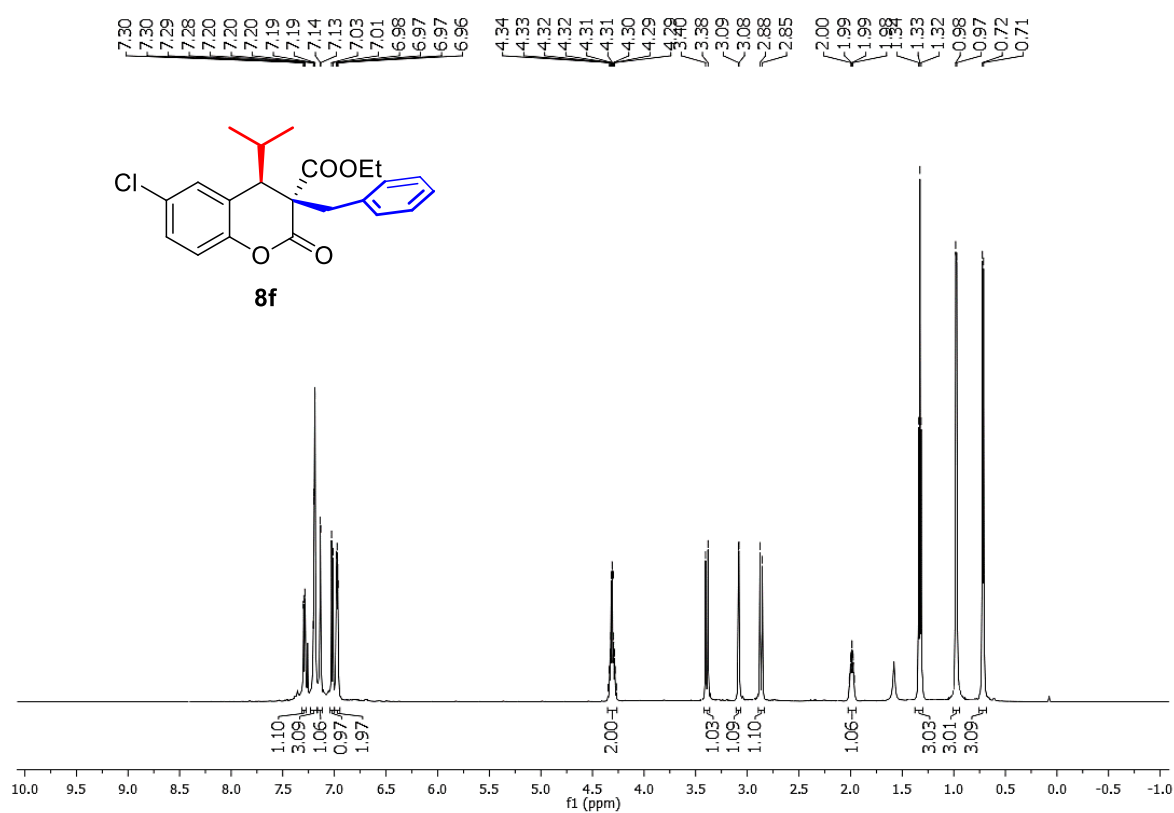
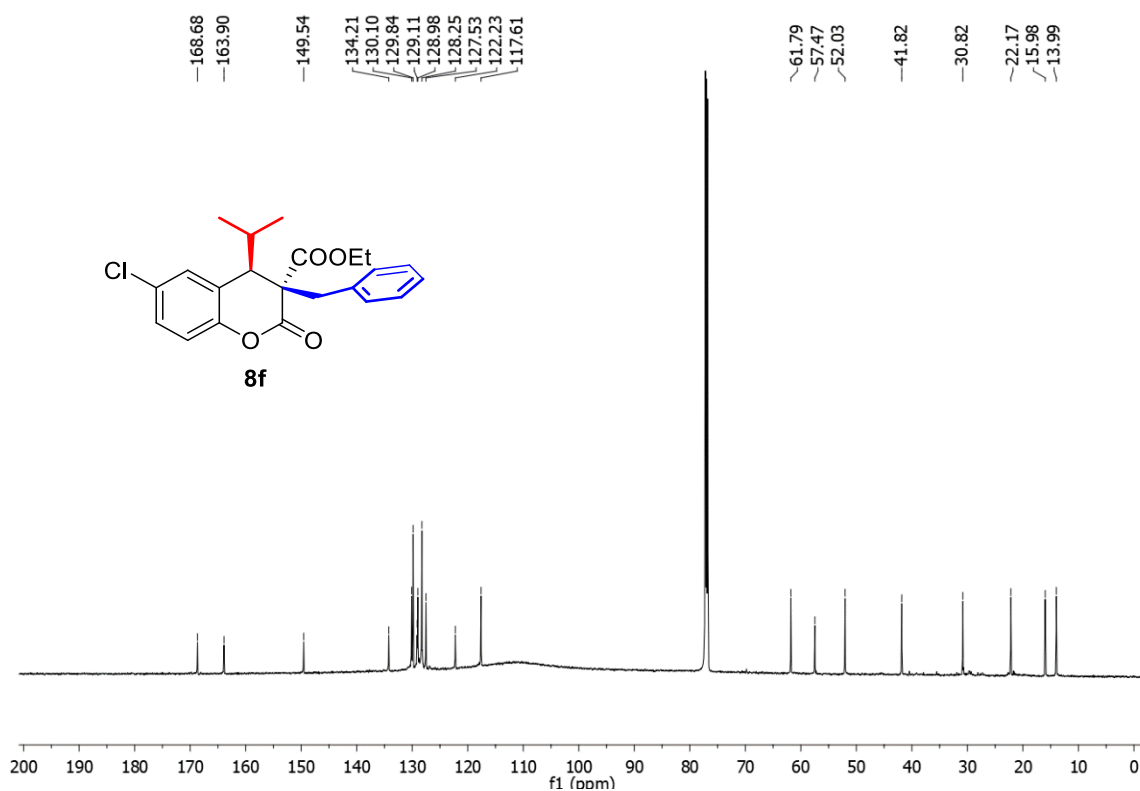
^1H NMR and ^{13}C NMR spectra of 8a **^1H NMR (600 MHz, CDCl_3)** **^{13}C NMR (150 MHz, CDCl_3)**

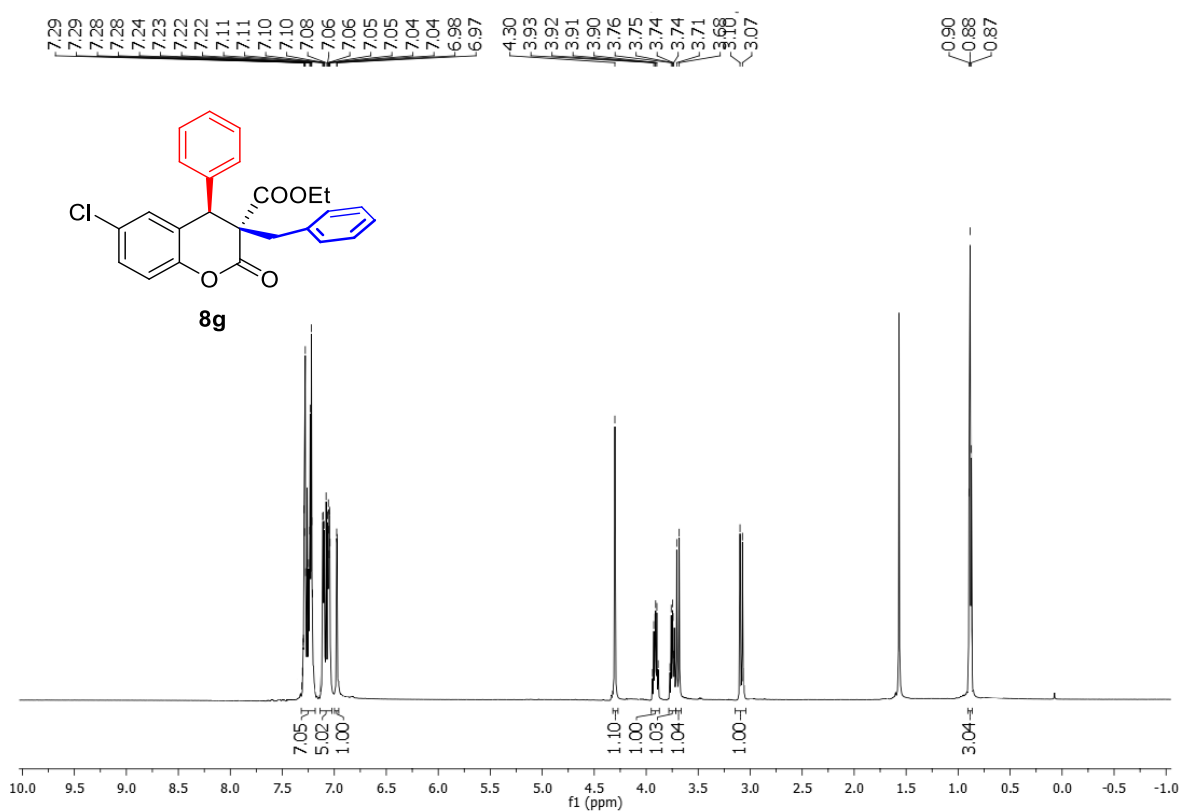
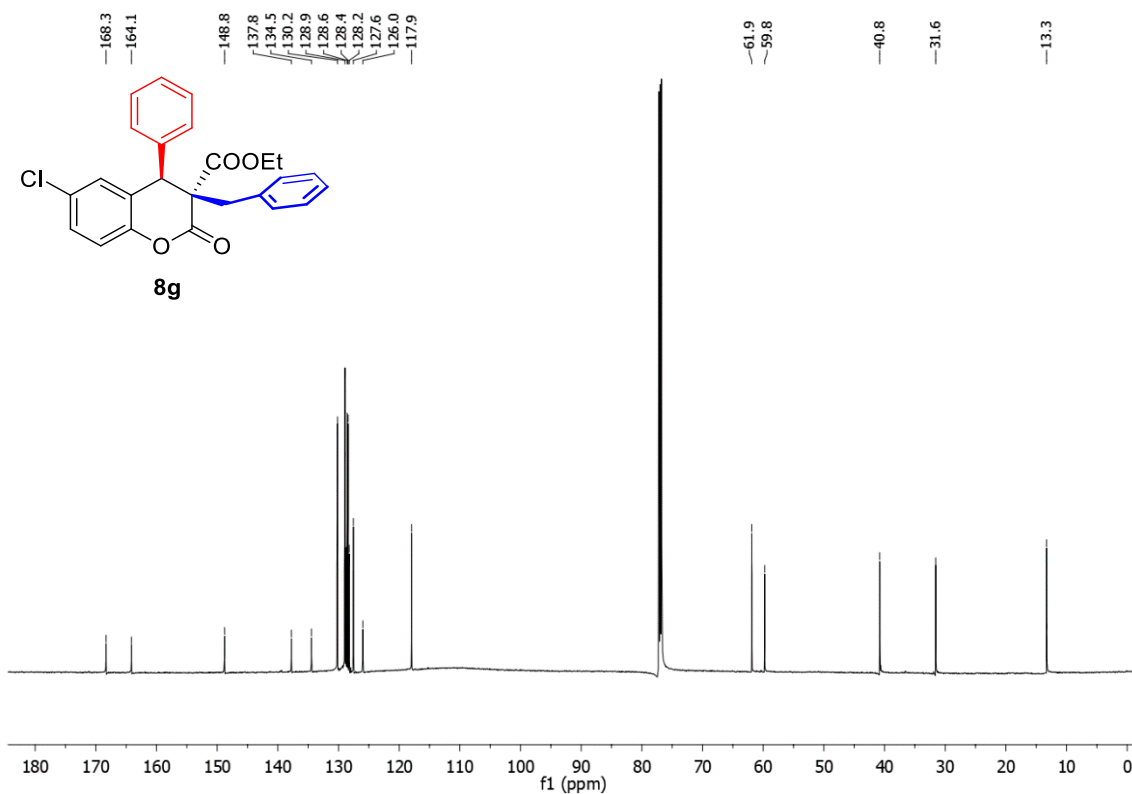
^1H NMR and ^{13}C NMR spectra of 8b **^1H NMR (600 MHz, CDCl_3)** **^{13}C NMR (150 MHz, CDCl_3)**

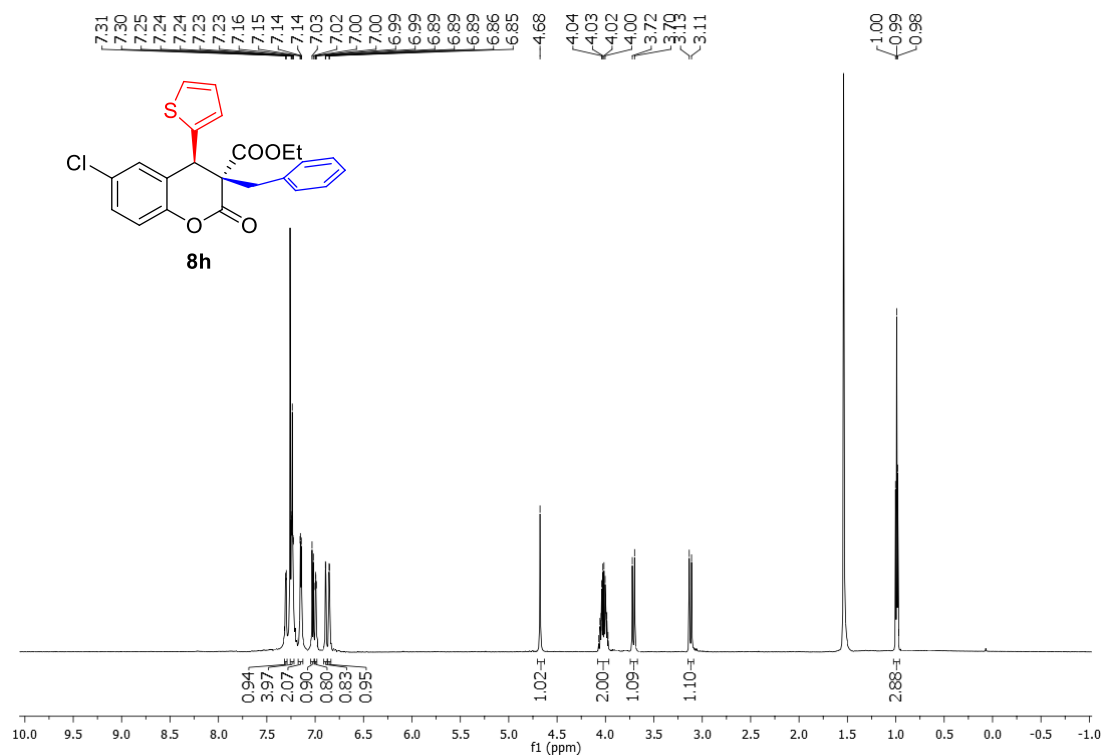
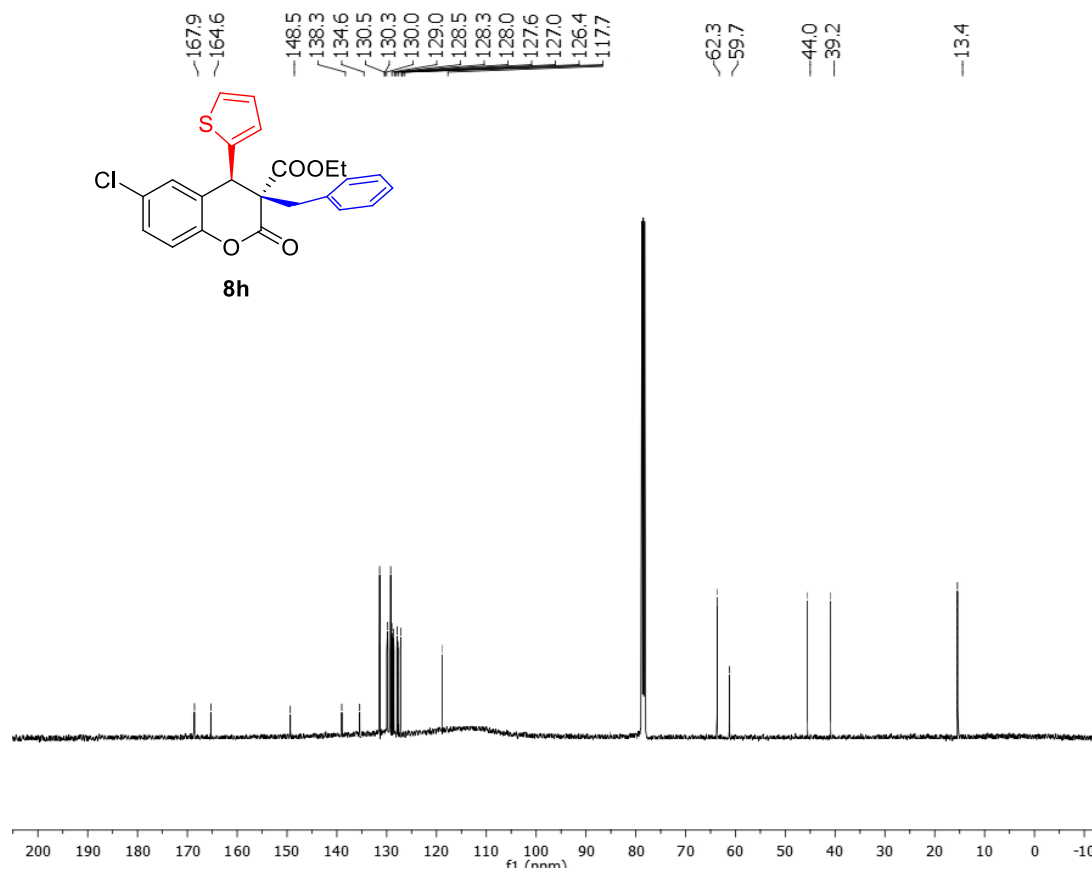
^1H NMR and ^{13}C NMR spectra of **8c** ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (150 MHz, CDCl_3)

^1H NMR and ^{13}C NMR spectra of 8d **^1H NMR (600 MHz, CDCl_3)** **^{13}C NMR (150 MHz, CDCl_3)**

^1H NMR and ^{13}C NMR spectra of **8e** ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (150 MHz, CDCl_3)

¹H NMR and ¹³C NMR spectra of 8f**¹H NMR (600 MHz, CDCl₃)****¹³C NMR (150 MHz, CDCl₃)**

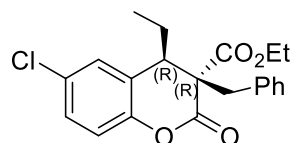
^1H NMR and ^{13}C NMR spectra of **8g** ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (150 MHz, CDCl_3)

^1H NMR and ^{13}C NMR spectra of 8h **^1H 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 software²: 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

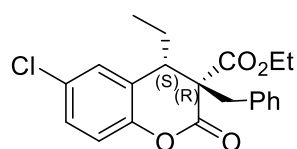
¹ a) F. Neese, The ORCA program system. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, 2, 73–78; b) F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2018**, 8, e1327.

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
H	-4.966400000	-1.646775000	-1.814202000
H	-2.532635000	0.572735000	0.949122000
H	-1.021797000	-3.039692000	-0.818004000
H	-3.140166000	-3.319724000	-2.062974000
H	-4.650956000	0.298741000	-0.292838000

Number of imaginary frequencies = 0

Electronic Energy	-1573.249909	Hartree
Gibbs Free Energy	-1572.921347	Hartree