Supporting Information

Sulfoxonium Ylides in Aminocatalysis: An Enantioselective Entry to Cyclopropane-Fused Chromanol Structures

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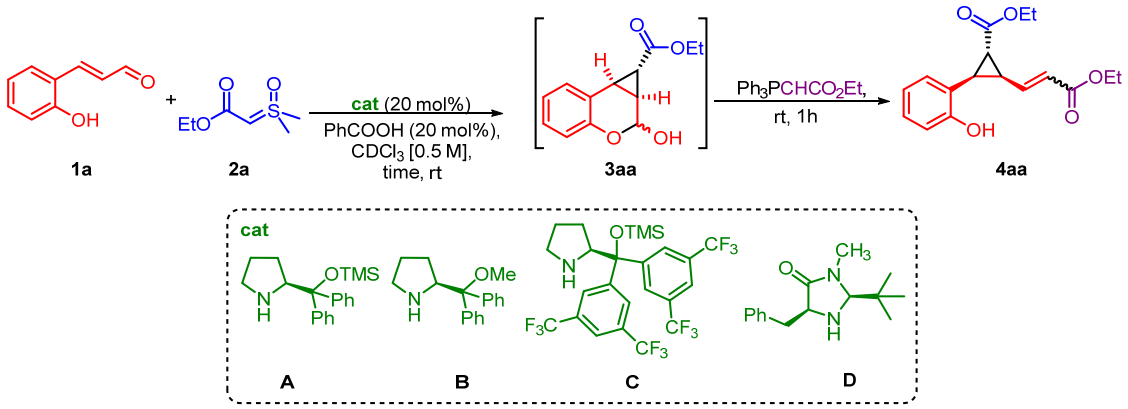
Optimization of reaction conditions for product 4aa: additional results

Different catalysts were tested in the reaction between 2'-hydroxy cinnamaldehyde **1a** and stabilized sulfoxonium ylide **2a** and the results are reported in Table S1. Only the reaction performed with catalyst **A** gives product **4aa** with promising results in terms of yield and enantioselectivity (entry 1). Indeed, a little change on the catalyst's backbone such as a methyl as O-protecting group or 3,5-CF_3 as substituents on the two aromatic rings leads to obtaining product **4aa** with a lower value of yield and enantioselection (entries 2 and 3). While, performing the reaction with imidazolidinone **D** as catalyst, product **4aa** was present in the reaction mixture only in traces and in a racemic form.

Table S1. Catalyst screening[a]

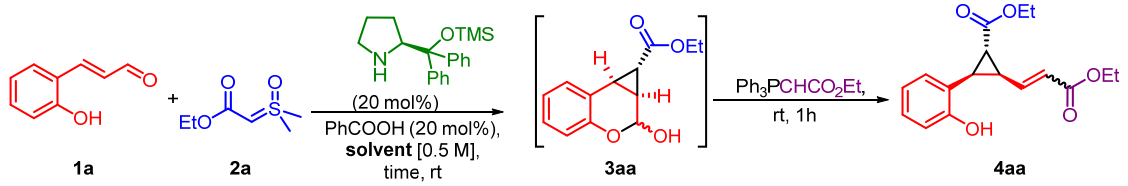


entry	cat	ee [%][b]	Yield [%][c]	Time [h]
1	**A**	88	50	1
2	**B**	7	27	12
3	**C**	52	22	12
4	**D**	*rac*	9	12

[a] Reaction conditions: **1a** (0.1 mmol, 1 equiv.), **2a** (0.15 mmol, 1.5 equiv.), PhCOOH (0.02 mmol, 20 mol%) catalyst **A-D** (0.02 mmol, 20 mol%) and $CDCl_3$ (200 µL), rt, 1-12 h. [b] Enantiomeric excess determined by CSP-HPLC. [c] Yield determined after chromatographic column on silica gel.

Once the right catalyst for the reaction was identified, a solvent screening was performed and the results are reported in Table S2. Numerous solvents were tested, but product **4aa** was obtained only by performing the reaction in toluene or in halogenated solvents (entries 1-3). Indeed, performing the reaction in THF, MTBE or EtOAc only starting materials were present in the reaction mixture without traces of product **4aa** (entries 4-6). Performing the reaction in toluene (entry 2) product **4aa** was obtained with a lower value of yield and enantiomeric excess, compared to $CDCl_3$. While using dichloromethane, comparable results in terms of yield and enantio-selection were obtained (entry 3). Given the convenience of using a deuterated solvent during the optimization process, and the good results obtained, we decided to use deuterated chloroform as solvent for the next screening.

Table S2. Solvent screening[a]

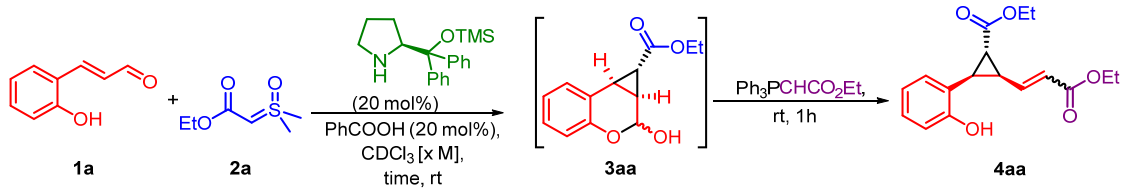


entry	solvent	ee [%][b]	Yield [%][c]	Time [h]
1	$CDCl_3$	88	50	1
2	PhMe	63	37	12
3	DCM	85	50	1.5.
4	THF	/	/	12
5	MTBE	/	/	12
6	EtOAc	/	/	12

[a] Reaction conditions: **1a** (0.1 mmol, 1 equiv.), **2a** (0.15 mmol, 1.5 equiv.), PhCOOH (0.02 mmol, 20 mol%) catalyst **A** (0.02 mmol, 20 mol%) and solvent (200 µL), rt, 1-12 h. [b] Enantiomeric excess determined by CSP-HPLC. [c] Yield determined after chromatographic column on silica gel.

To improve both the enantiomeric excess and the yield of the product **4aa** we investigated the dilution of the reaction (Table S3). We found that performing a more diluted reaction (0.1 M, entry 2 instead of 0.5 M entry 1), product **4aa** can be obtained with higher values of both yield and enantio-selection.

Table S3. Concentration[a]



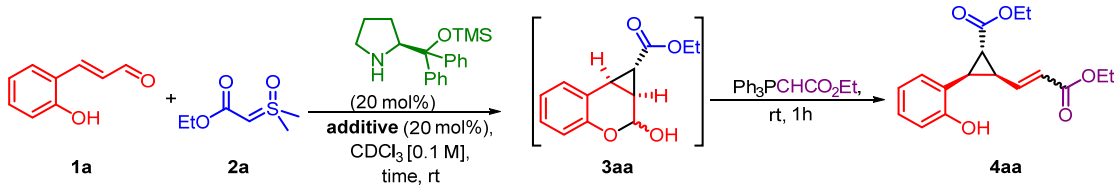
entry	Concentration [M]	ee [%][b]	Yield [%][c]	Time [h]
1	0.5	88	50	1
2	0.1	95	57	2

[a] Reaction conditions: **1a** (0.1 mmol, 1 equiv.), **2a** (0.15 mmol, 1.5 equiv.), PhCOOH (0.02 mmol, 20 mol%) catalyst **A** (0.02 mmol, 20 mol%) and $CDCl_3$ (200 or 1000 µL), rt, 1-2 h. [b] Enantiomeric excess determined by CSP-HPLC. [c] Yield determined after chromatographic column on silica gel.

In the end, we moved to evaluate the influence of the additives as co-catalysts in the reaction between aldehyde **1a** and sulfoxonium ylide **2a**. We found that performing the reaction with CSA as additive, product **4aa** can be obtained with a very high value of enantiomeric excess but a lower yield (entry 2). Moving on to evaluate the different acidity of benzoic acid derivatives, we understood that performing the reaction with a rather acidic benzoic acid, *p*-NO_2-benzoic acid, it is possible to improve the yield of product **4aa**, compared to the simple benzoic acid, while the enantiomeric excess experiences a considerable decrease (entry 3). Performing the reaction with a less acidic benzoic acid, *p*-MeO-benzoic acid, both the value of yield and enantioselectivity remain unchanged (entry 4). In the end, we decided to test an aliphatic acid (AcOH) but no variation of the yield or enantiomeric excess was verified (entry 5). Taking into consideration the achieved result, but considering that the

acidity of the additive could compromise the stability of the sulfoxonium ylide **2a** we decided to perform the same experiment but using sodium acetate as additive. In this case, an increase of yield was observed (entry 6). The beneficial effect of sodium acetate on the yield of the reaction was confirmed by an experiment performed without additives (entry 7). We then tried alternative bases, such as tertiary amines, as additives in the reaction. As shown in entries 8-11, use of these bases in either catalytic or stoichiometric amounts led to poorer results, so sodium acetate was chosen as co-catalyst for the reaction.

Table S4. Additives screening[a]



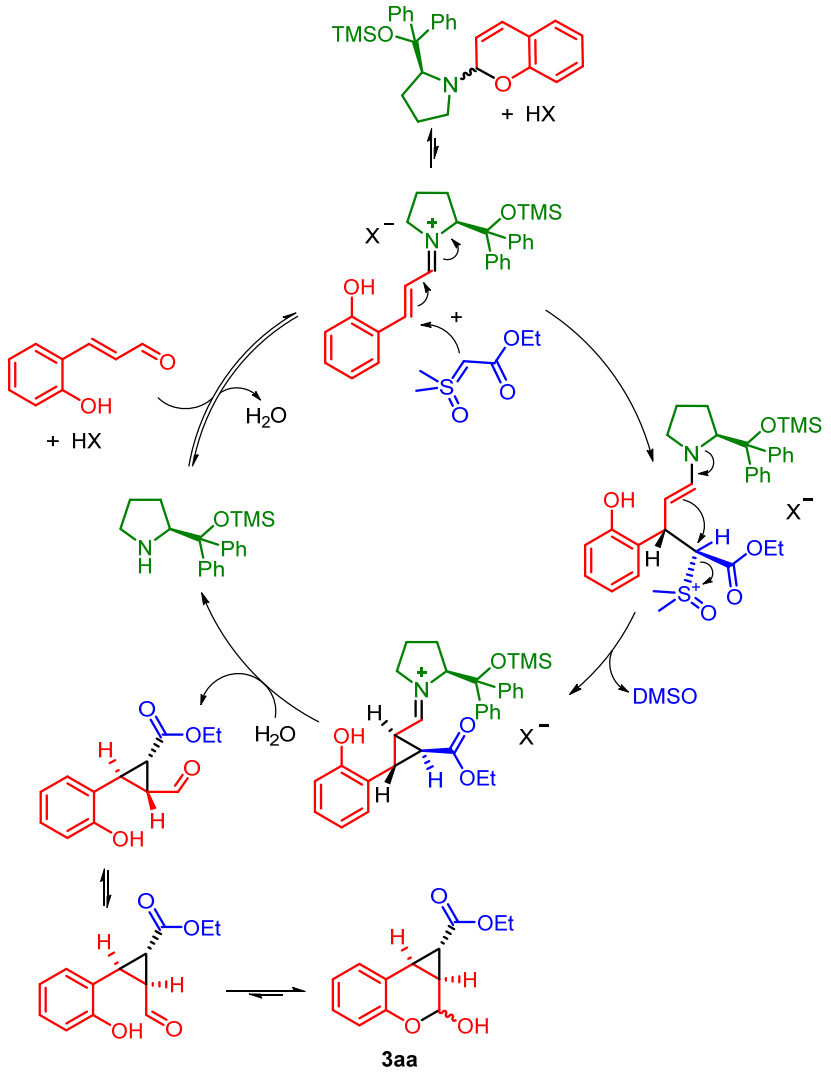
1a 2a 3aa 4aa

entry	additive	ee [%][b]	Yield [%][c]	Time [h]
1	PhCOOH	95	57	2
2	CSA	98	36	1
3	p-NO_2 benzoic acid	*72*	63	2
4	p-MeO benzoic acid	96	50	12
5	AcOH	96	52	12
6	AcONa	96	67	12
7	-	96	41	12
8	Et_3N	97	42	12
9	Et_3N (1 equiv.)	97	29	12
10	*i*-Pr_2EtN	93	40	12
11	*i*-Pr_2EtN (1 equiv.)	94	25	12

[a] Reaction conditions: **1a** (0.1 mmol, 1 equiv.), **2a** (0.15 mmol, 1.5 equiv.), additive (0.02 mmol, 20 mol%) catalyst **A** (0.02 mmol, 20 mol%) and $CDCl_3$ (1000 µL), rt, 1-12 h. [b] Enantiomeric excess determined by CSP-HPLC. [c] Yield determined after chromatographic column on silica gel.

Proposed reaction pathway for the catalytic reaction

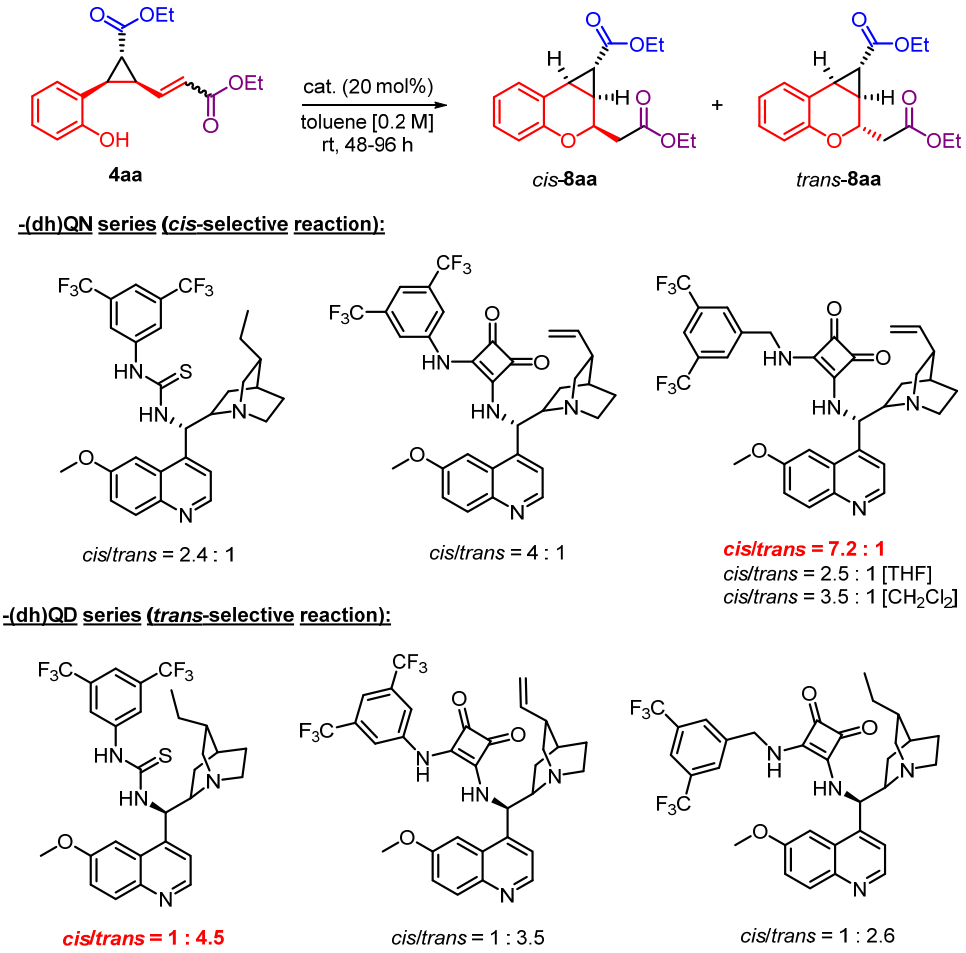
Scheme S1 summarizes our current hypothesis on the reaction pathway. Condensation of the cinnamaldehyde with the catalyst, under acidic conditions, affords a reactive iminium ion in equilibrium with its more stable (and unreactive) hemiaminal form. Attack of the sulfoxonium ylide on the less hindered rear face of the iminium ion results in an enamine intermediate. The enamine can displace DMSO by attacking with its rear face in a S$_N$2-like reaction. The perfect diastereoselectivity observed in all cases can be ascribed either to a highly diastereoselective attack of the ylide to the imium ion, or to a reversible attack to the iminium ion followed by a selectivity determining DMSO displacement step. Hydrolysis releases the catalyst and an aldehyde product with 2,3-*trans* configuration. Epimerization α to the aldehyde function can be expected to be facile in this species. Hemiacetalization traps the *cis*-isomer giving stable compound **3aa**.



Scheme S1

Additional experiments for the diastereodivergent oxa-Michael reaction 4aa → 8aa

The intramolecular oxa-Michael reaction delivering **8aa** from **4aa** was found to proceed smoothly under basic promotion. Since an achiral catalyst/promoter such as Et_3N delivered the product with low diastereomeric ratio (1.5 : 1 favoring *trans*-**8aa**), few chiral bifunctional catalysts derived from *Cinchona* alkaloids were tried in the reaction in toluene at RT (Scheme S2), in order to develop a selective, and possibly diastereo-divergent, process. This class of catalysts is known to be very effective in a related oxa-Michael reaction.[1]



Scheme S2

Catalysts from the quinine series were found to promote the selective formation of the *cis*-**8aa** isomer, with a benzylic squaramide derivative outperforming other structures. Solvents other than toluene did not provide any improvement. Quinidine derived catalysts were indeed able to steer the reaction towards the *trans*-**8aa** isomer. However, in this case the catalyst providing the best result was found to be a thiourea derivative. The requirement of non-pseudoenantiomeric catalysts for a diastereo-

[1] Zhu, D.-X.; Liu, J.-G.; Xu, M.-H. *J. Am. Chem. Soc.* **2021**, *143*, 8583.

divergent process of this type can be rationalized considering that the transition states leading to *cis*-**8aa** and *trans*-**8aa** are intrinsically diastereomeric, and thus do not necessarily require enantiomeric catalysts for their stabilization/promotion.[2]

[2] a) Lotter, D.; Castrogiovanni, A.; Neuburger, M.; Sparr, C. *ACS Cent. Sci.* **2018**, *4*, 656. b) Corti, V.; Riccioli, R.; Martinelli, A.; Sandri, S.; Fochi, M.; Bernardi, L. *Chem. Sci.* **2021**, *12*, 10233.

General methods and materials

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300, 400 or Inova 600 spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvents signals for ^{1}H and ^{13}C NMR.[3] ^{13}C NMR were acquired with ^{1}H broad-band decoupled mode. NOE spectra were recorded using the DPFGSE-NOE sequence,[4] using a mixing time of 2.80 s and "rsnob" 50 Hz wide selective pulses. ECD spectra were recorded on a Jasco J-810 instrument. High Resolution Mass Spectra (HRMS) were recorded on a Waters Xevo Q-TOF spectrometer. ESI spectra were recorded on a micromass LCT spectrometer using electrospray (ESI) ionization technique. Compounds **4ba-ga** are rather unstable and could not be subjected to HRMS analysis, but only to low resolution ESI-MS (faster access). Optical rotations were measured on a Perkin Elmer 241 Polarimeter provided with a sodium lamp and are reported as follows: $[\alpha]_{\lambda}^{T\ (^{\circ}C)}$ (c = g/100 mL, solvent). The enantiomeric excess of the products (ee) were determined by chiral stationary phase HPLC (Daicel Chiralpak OJ-H or AD-H or IC columns), using a UV detector operating at 254 nm. Infrared (ATR) spectra were recorded on a Perkin Elmer Spectrum Two FT-IR spectrometer equipped with an ATR probe. Signals are reported as strong (s), medium (m), and weak (w). Melting points (uncorrected) were determined with a Stuart Scientific SMP3 apparatus. Purification of reaction products was carried out by flash chromatography (FC) on silica gel (230-400 mesh) or by gravimetric chromatography using 70-230 mesh silica. The absolute and relative configuration of the products was determined on compounds **4'ab** and **3ab** (see dedicated section), and assigned by analogy to the remaining compounds. The relative configuration at the cyclopropane of known compound **6aa**, derived from **3aa**, is in line with this assignment.

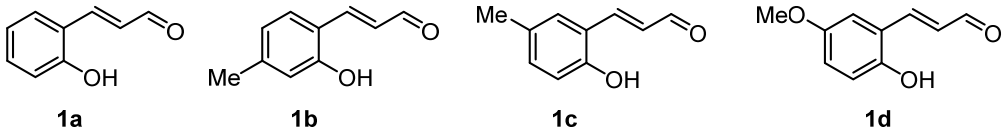
Materials. Analytical grade solvents and commercially available reagents were used as received, unless otherwise stated. Catalyst **A** was purchased from Fluorochem and used as received. Reference racemic products **4** for CSP HPLC analysis were prepared using an equimolar mixture of (*R*)-**A** and (*S*)-**A** as catalyst. Catalysts **QN-1** and **dhQD-1** were prepared according to the literature.[5]

[3] Gottlieb, H. E.; Kottlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.
[4] (a) Stonehouse, J.; Adell, P.; Keeler, J.; Shaka, A. J. *J. Am. Chem. Soc.* **1994**, *116*, 6037. (b) Stott, K.; Stonehouse, J.; Keeler, J.; Hwang, T. L.; Shaka, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 4199. (c) Stott, K.; Keeler, J.; Van, Q. N.; Shaka, A. J. *J. Magn. Reson.* **1997**, *125*, 302. (d) Van, Q. N.; Smith, E. M.; Shaka, A. J. *J. Magn. Reson.* **1999**, *141*, 191.
[5] Wang, Y.; Milikiewicz, K. L.; Kaufman, M. L.; He, L.; Landmesser, N. G.; Levy, D. V.; Allwein, S. P.; Christie, M. A.; Olsen, M. A.; Nelville, C. J.; Muthukumaran, K. *Org. Process Res. Dev.* **2017**, *21*, 408; Cassani, C; Martín-Rapún, R.; Arceo, E.; Bravo, F.; Melchiorre, P. *Nat. Protoc.* **2013**, *8*, 325; Malerich, J. P.; Hagihara, K.; Rawal, V. H. *J. Am. Chem. Soc.* **2008**, *130*, 14416.

Starting Materials

2'-hydroxycinnamaldehydes 1

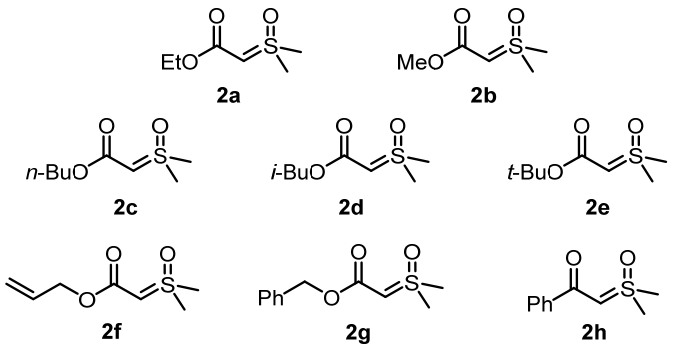
2'-hydroxycinnamaldehydes **1**, reported below, were prepared according to literature procedure.[6]



1a **1b** **1c** **1d** **1e** **1f** **1g**

Sulfoxonium ylides 2

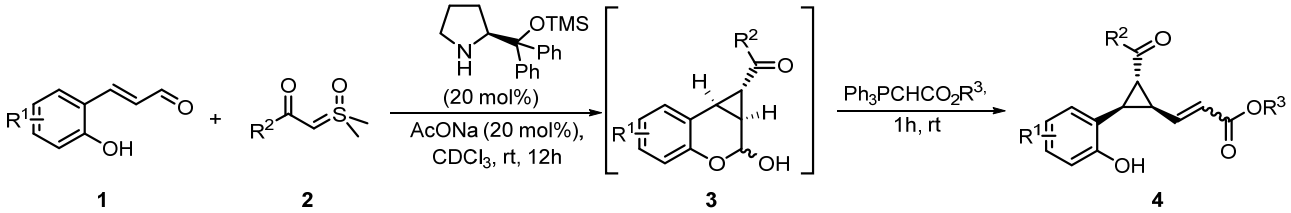
Sulfoxonium ylides **2**, reported below, were prepared according to literature procedure.[7]



2a **2b** **2c** **2d** **2e** **2f** **2g** **2h**

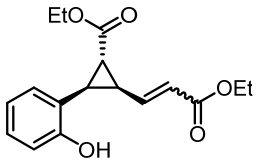
[6] Ackrill, T. D.; Sparkes, H. A.; Wills, C. L. *Org. Lett.* **2015**, *17*, 3884-3887.
[7] Bisag, G. D.; Ruggieri, S.; Fochi, M.; Bernardi, L. *Adv. Synth. Catal.* **2021**, *363*, 3053-3059.

Synthesis of products 4: general procedure and characterization



In a small vial equipped with a magnetic stirring bar, aldehyde **1** (0.1 mmol, 1 equiv.) and sulfoxonium ylide **2** (0.15 mmol, 1.5 equiv.) were added to a $CDCl_3$ (1 mL) solution of catalyst (*S*)-**A** (0.02 mmol, 0.20 equiv., 6.5 mg) and AcONa (0.02 mmol, 0.20 equiv., 1.6 mg). The resulting mixture was stirred at room temperature for 12 h. Subsequently, the appropriate phosphorous ylide (0.3 mmol, 3 equiv.) was added and the resulting mixture was stirred at room temperature for 1 h. Next, the solvent was eliminated under vacuum and directly purified by flash column chromatography on silica gel affording compounds **4** as E/Z mixtures. In some cases, a fraction containing compounds **4** as single E-isomers was collected and used for the characterization. In all cases, the E-**4** isomer was highly prevalent over its Z-**4** counterpart (estimated ratio >9:1).

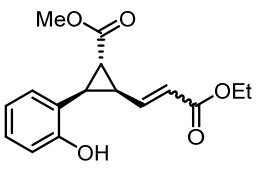
Ethyl (1*R*,2*S*,3*R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4aa



4aa

The general procedure was followed using aldehyde **1a**, sulfoxonium ylide **2a**, and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing **4aa** as E/Z mixture, and a fraction containing pure E-**4aa** as colorless oils (overall 67% yield, 20.4 mg). Performing the reaction on 1 mmol scale, that is, using 148.2 mg of substrate **1a** (1.0 mmol), 246.3 mg of ylide **2a** (1.5 mmol), 65.1 mg of catalyst (*S*)-**A** (0.20 mmol), 16.4 mg of sodium acetate (0.20 mmol) in 10 mL of $CDCl_3$ as solvent for the catalytic reaction, and 1.045 g of phosphorous ylide (3 mmol) for the Wittig reaction, product **4aa** was obtained in 69% overall yield (210.0 mg, 0.69 mmol) and 97% ee. E-**4aa** isomer: $[\alpha]_D^{25}$ = +20 (c = 0.5, CH_2Cl_2) for 97% ee. **IR** (ATR) ν(max) =3390 (br, m) 1714 (s) 1687 (s) 1176 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, +25 °C) δ = 7.18 – 7.07 (m, 2H), 6.88 (t, J = 7.5 Hz, 1H), 6.78 (dd, J = 8.0, 1.2 Hz, 1H), 6.22 (dd, J = 15.5, 10.3 Hz, 1H), 6.02 (d, J = 15.5 Hz, 1H), 5.35 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 4.10 (q, J = 7.1 Hz, 2H), 2.98 (dd, J = 9.2, 5.7 Hz, 1H), 2.61 (ddd, J = 10.4, 9.2, 4.4 Hz, 1H), 2.37 (dd, J = 5.7, 4.3 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, +25 °C) δ = 172.0, 166.0, 155.0, 144.9, 129.8, 128.9, 122.7, 120.9, 120.7, 115.5, 61.3, 60.3, 30.4, 28.4, 27.8, 14.25, 14.21. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}O_5Na$ 327.1203; Found 327.1196. **HPLC**: OJ-H (*n*-hexane/*i*-PrOH 90:10, 0.75 mL/min) t_{min} = 15.1, min, t_{maj} = 17.9 min.

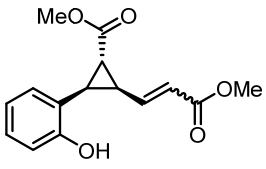
Methyl (1*R*,2*S*,3*R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ab



4ab

The general procedure was followed using aldehyde **1a**, sulfoxonium ylide **2b**, and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing E/Z mixture of **4ab** as colorless oil (64% yield, 18.6 mg) with 96% ee. E/Z-**4ab**: **IR** (ATR) ν(max) =3392 (br, m) 1710 (s) 1691 (s) 1248 (s) 1167 (s) 1139 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 7.14 (ddd, J = 8.1, 7.4, 1.7, Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 6.87 (t, J = 7.5 Hz, 1H), 6.77 (dd, J = 8.0, 1.1 Hz, 1H), 6.20 (dd, J = 15.5, 10.4 Hz, 1H), 6.01 (d, J = 15.5 Hz, 1H), 5.12 (s, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 2.97 (dd, J = 9.1, 5.7 Hz, 1H), 2.61 (ddd, J = 10.3, 9.2, 4.3 Hz, 1H), 2.36 (dd, J = 5.7, 4.4 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 172.4, 165.9, 154.9, 144.7, 129.8, 128.9, 122.8, 120.8, 120.7, 115.5, 60.3, 52.3, 30.4, 28.4, 27.5, 14.2 **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{18}O_5Na$ 313.1046; Found 313.1043; $[M + K]^+$ Calcd for $C_{16}H_{18}KO_5$ 329.0786; Found 329.0780. **HPLC**: IC (*n*-hexane/*i*-PrOH 80:20, 1 mL/min) E-isomer: t_{min} = 7.7 min, t_{maj} = 9.4 min.

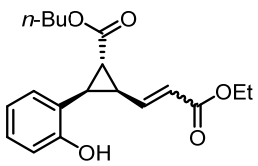
Methyl (1*R*,2*R*,3*S*)-2-(2-hydroxyphenyl)-3-(3-methoxy-3-oxoprop-1-en-1-yl)cyclopropane-1-carboxylate 4'ab



4'ab

The general procedure was followed using aldehyde **1a**, sulfoxonium ylide **2b,** and methyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing E/Z mixture of **4'ab** as colorless oil in 62% yield (17.1 mg) with 94% ee. E/Z-**4'ab**: **IR** (ATR) ν(max) =3400 (br, m) 1719 (s) 1694 (s) 1251 (s) 1160 (s) 1139 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 7.15 (td, *J* = 7.8, 1.6 Hz, 1H), 7.10 (dd, *J* = 6.3, 4.8 Hz, 1H), 6.90 – 6.85 (m, 1H), 6.78 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.20 (dd, *J* = 15.5, 10.4 Hz, 1H), 6.01 (d, *J* = 15.4 Hz, 1H), 5.09 (s, 1H), 3.76 (s, 3H), 3.63 (s, 3H), 3.01 – 2.94 (m, 1H), 2.61 (ddd, *J* = 10.2, 9.1, 4.3 Hz, 1H), 2.36 (dd, *J* = 5.7, 4.4 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 172.3, 166.3, 154.9, 145.0, 129.9, 128.9, 122.4, 120.83, 120.81, 115.5, 52.3, 51.5, 30.4, 28.5, 27.6. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{16}O_5Na$ 299.0890; Found 299.0886; $[M + K]^+$ Calcd for $C_{15}H_{16}KO_5$ 315.0629; Found 315.0637. **HPLC**: ADH (*n*-hexane/*i*-PrOH 90:10, 0.75 mL/min) E-isomer: t_{maj} = 18.2 min, t_{min} = 19.6 min.

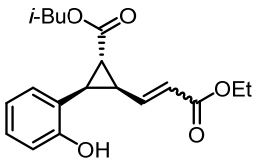
Butyl (1*R*,2*S*,3*R*)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylatecarboxylate 4ac



4ac

The general procedure was followed using aldehyde **1a**, sulfoxonium ylide **2c,** and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing **4ac** as E/Z mixture, and a fraction containing pure E-**4ac** as colorless oils (overall 60% yield, 19.9 mg) with 95% ee. E-**4ac** isomer: $[\alpha]_D^{25}$ = +28 (c = 0.5, CH_2Cl_2) for 95% ee. **IR** (ATR) ν(max) =3398 (br, m) 1718 (s) 1693 (s) 1248 (s) 1168 (s) 1139 (s) cm^{-1}.**^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) δ = 7.17 – 7.06 (m, 2H), 6.87 (td, J = 7.5, 1.2 Hz, 1H), 6.77 (dd, J = 8.1, 1.2 Hz, 1H), 6.21 (dd, J = 15.5, 10.4 Hz, 1H), 6.01 (d, J = 15.4 Hz, 1H), 5.29 (s, 1H), 4.15 (t, J = 6.7 Hz, 2H), 4.09 (q, J = 7.1 Hz, 2H), 2.96 (dd, J = 9.1, 5.7 Hz, 1H), 2.60 (ddd, J = 10.3, 9.1, 4.3 Hz, 1H), 2.36 (dd, J = 5.7, 4.3 Hz, 1H), 1.72 – 1.56 (m, 2H), 1.46 – 1.34 (m, 2H), 1.20 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, +25 °C) δ = 172.1, 166.0, 155.0, 144.9, 129.8, 128.9, 122.7, 120.9, 120.7, 115.5, 65.2, 60.3, 30.6, 30.3, 28.4, 27.8, 19.1, 14.1, 13.7. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{24}O_5Na$ 355.1516; Found 355.1508. **HPLC**: OJ-H (*n*-hexane/*i*-PrOH 90:10, 0.75 mL/min) t_{min} = 10.6 min, t_{maj} = 12.4 min.

Isobutyl (1*R*,2*S*,3*R*)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ad

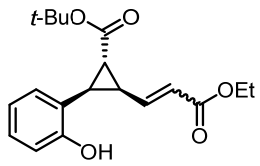


4ad

The general procedure was followed using aldehyde **1a**, sulfoxonium ylide **2d**, and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing **4ad** as E/Z mixture, and a fraction containing pure E-**4ad** as colorless oils (overall 70% yield, 23.2 mg) with 95% ee. E-**4ad** isomer: $[\alpha]_D^{25}$ = +27 (c = 0.5, CH_2Cl_2) for 95% ee. **IR** (ATR) ν(max) =3396 (br, m) 1718 (s) 1693 (s) 1247 (s) 1163 (s) 1139 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) δ = 7.17 – 7.05 (m, 2H), 6.87 (td, J = 7.5, 1.2 Hz, 1H), 6.77 (dd, J = 8.1, 1.2 Hz, 1H), 6.22 (dd, J = 15.5, 10.4 Hz, 1H), 6.01 (d, J = 15.4 Hz, 1H), 5.30 (s, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.93 (d, J = 6.6 Hz, 2H), 2.97 (dd, J = 9.2, 5.7 Hz, 1H), 2.61 (ddd, J = 10.4, 9.1, 4.4 Hz, 1H), 2.37 (dd, J = 5.7, 4.4 Hz, 1H), 2.01-1.97 (m, 1H), 1.20 (t, J = 7.1 Hz, 3H), 0.95 (d, J = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$, +25 °C) δ = 172.0, 166.0, 155.0, 144.9, 129.8, 128.9, 122.7, 120.9, 120.7, 115.5, 71.4, 60.3, 30.3, 28.4, 27.8, 27.7, 19.1, 14.1. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd

for $C_{19}H_{24}O_5Na$ 355.1516; Found 355.1515. **HPLC**: OJ-H (*n*-hexane/*i*-PrOH 90:10, 0.75 mL/min) t_{min} = 8.9 min, t_{maj} = 10.0 min.

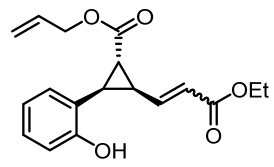
***tert*-Butyl (1*R*,2*S*,3*R*)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ae**



4ae

The general procedure was followed using aldehyde **1a**, sulfoxonium ylide **2e**, and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing **4ae** as E/Z mixture, and a fraction containing pure E-**4ae** as colorless oils (overall 57% yield, 19.0 mg) with 95% ee. E-**4ae** isomer: $[\alpha]_D^{25}$ = +25 (c = 0.4, CH_2Cl_2) for 95% ee. **IR** (ATR) ν(max) =3423 (br, m) 1710 (s) 1698 (s) 1254 (s) 1141 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) δ = 7.17 – 7.06 (m, 2H), 6.87 (td, *J* = 7.5, 1.2 Hz, 1H), 6.78 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.20 (dd, *J* = 15.5, 10.4 Hz, 1H), 6.00 (d, *J* = 15.5 Hz, 1H), 5.29 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.89 (dd, *J* = 9.1, 5.7 Hz, 1H), 2.53 (ddd, *J* = 10.4, 9.2, 4.4 Hz, 1H), 2.28 (dd, *J* = 5.8, 4.4 Hz, 1H), 1.48 (s, 9H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, +25 °C) δ = 171.0, 166.0, 155.0, 145.1, 129.8, 128.8, 122.6, 121.0, 120.6, 115.5, 81.6, 60.2, 30.0, 28.8, 28.1, 28.0, 14.2. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{24}O_5Na$ 355.1516; Found 355.1514. **HPLC**: OJ-H (*n*-hexane/*i*-PrOH 90:10, 0.75 mL/min) t_{min} = 7.1 min, t_{maj} = 7.8 min.

Allyl (1*R*,2*S*,3*R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4af

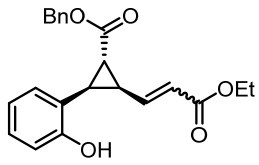


4af

The general procedure was followed using aldehyde **1a**, sulfoxonium ylide **2f**, and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing **4af** as E/Z mixture, and a fraction containing pure E-**4af** as colorless oils (overall 65% yield, 20.5 mg) with 90% ee. E-**4af** isomer: $[\alpha]_D^{25}$ +31 (c = 0.3, CH_2Cl_2) for 90% ee. **IR** (ATR) ν(max) =3393 (br, m) 1715 (s) 1691 (s) 1249 (s) 1160 (s) 1139 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) δ = 7.19 – 7.06 (m, 2H), 6.87 (td, *J* = 7.5, 1.2 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.21 (dd, *J* = 15.5, 10.3 Hz, 1H), 6.01 (d, *J* = 15.5 Hz, 1H), 5.94 (ddt, *J* = 17.1, 10.4, 5.8 Hz, 1H), 5.39 – 5.31 (m, 1H), 5.27 (dq, *J* = 10.4, 1.2 Hz, 1H), 5.23 (s, 1H), 4.65 (dt, *J* = 5.9, 1.4 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.99 (dd, *J* = 9.2, 5.7 Hz, 1H), 2.62 (ddd, *J* = 10.3, 9.1, 4.3 Hz, 1H), 2.39 (dd, *J* = 5.7, 4.4 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, +25 °C) δ = 171.7, 165.9, 154.9, 144.7, 131.8, 129.8, 128.9, 122.8, 120.8, 120.7, 118.7, 115.5, 65.9, 60.3, 30.5,

28.5, 27.7, 14.1. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{20}O_5Na$ 339.1203; Found 339.1210. **HPLC**: OJ-H (*n*-hexane/*i*-PrOH 90:10, 0.75 mL/min) t_{min} = 15.3 min, t_{maj} = 19.1 min.

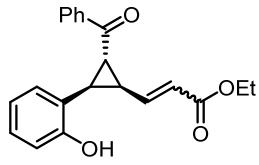
Benzyl (1*R*,2*S*,3*R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ag



4ag

The general procedure was followed using aldehyde **1a**, sulfoxonium ylide **2g** and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing **4ag** as E/Z mixture, and a fraction containing pure E-**4ag** as colorless oils (overall 56% yield, 10.5 mg) with 97% ee. E-**4ag** isomer: $[\alpha]_D^{25}$ = +11 (c = 0.4, CH_2Cl_2) for 97% ee. **IR** (ATR) ν(max) =3388 (br, m) 1714 (s) 1690 (s) 1248 (s) 1161 (s) 1138 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) δ = 7.41 – 7.29 (m, 5H), 7.17 – 7.06 (m, 2H), 6.86 (td, *J* = 7.5, 1.2 Hz, 1H), 6.76 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.20 (dd, *J* = 15.5, 10.3 Hz, 1H), 6.00 (d, *J* = 15.5 Hz, 1H), 5.19 (br s, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.00 (dd, *J* = 9.2, 5.7 Hz, 1H), 2.63 (ddd, *J* = 10.4, 9.2, 4.3 Hz, 1H), 2.42 (dd, *J* = 5.7, 4.3 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, +25 °C) δ = 171.8, 165.9, 154.9, 144.7, 135.5, 129.8, 128.9, 128.6, 128.4, 128.3, 122.9, 120.8, 120.7, 115.5, 67.1, 60.3, 30.5, 28.6, 27.7, 14.1. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{22}O_5Na$ 389.1359; Found 389.1357. **HPLC**: OJ-H (*n*-hexane/*i*-PrOH 90:10, 0.75 mL/min) t_{min} = 27.3 min, t_{maj} = 38.7 min.

Ethyl 3-((1*S*,2*R*,3*R*)-2-benzoyl-3-(2-hydroxyphenyl)cyclopropyl)acrylateacrylate 4ah

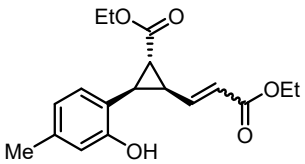


4ah

The general procedure was followed using aldehyde **1a**, sulfoxonium ylide **2h**, and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing **4ah** as E/Z mixture as colorless oil (35% yield, 12.4 mg) with 93% ee. E/Z-**4ah** mixture: **IR** (ATR) ν(max) =3431 (br, m) 1700 (s) 1661 (s) 1253 (s) 1140 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 8.09 – 8.05 (m, 2H), 7.65 – 7.57 (m, 1H), 7.55 – 7.48 (m, 2H), 7.20-7.17 (m, 2H), 6.91 (td, *J* = 7.5, 1.2 Hz, 1H), 6.82 (dd, *J* = 8.5, 1.2 Hz, 1H), 6.41 (dd, *J* = 15.5, 10.5 Hz, 1H), 6.06 (d, *J* = 15.5 Hz, 1H), 5.24 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.38 (dd, *J* = 5.6, 4.2 Hz, 1H), 3.23 (dd, *J* = 8.9, 5.6 Hz, 1H), 2.81 (ddd, *J* = 10.6, 8.9, 4.2 Hz, 1H), 1.29 – 1.15 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 197.1, 166.1, 155.0, 145.2, 137.3, 133.4, 130.0, 129.0, 128.8, 128.3, 122.7, 121.3, 120.8, 115.7, 60.3, 33.5, 32.2, 30.7, 14.2. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}O_4Na$ 359.1254; Found

359.1253. **HPLC**: OJ-H (*n*-hexane/*i*-PrOH 90:10, 0.75 mL/min, E-isomer) t_{min} = 30.7 min, t_{maj} = 42.6 min.

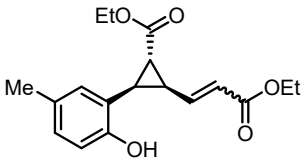
Ethyl (1*R*,2*S*,3*R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-4-methylphenyl)cyclopropane-1-carboxylate 4ba



4ba

The general procedure was followed using aldehyde **1b**, sulfoxonium ylide **2a**, and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing **4ba** as E/Z mixture, and a fraction containing pure E-**4ba** as colorless oils (overall 52% yield, 16.5 mg) with 92% ee. E-**4ba** isomer: $[\alpha]_D^{25}$ +38 (c = 0.3, CH_2Cl_2) for 92% ee. **IR** (ATR) ν(max) =3396 (br, m) 1715 (s) 1693 (s) 1251 (s) 1173 (s) 1139 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, +25 °C) δ = 7.02 – 6.93 (m, 1H), 6.69 (dt, *J* = 7.7, 1.1 Hz, 1H), 6.61 (s, 1H), 6.22 (dd, *J* = 15.5, 10.4 Hz, 1H), 6.02 (d, *J* = 15.5 Hz, 1H), 5.06 (s, 1H), 4.28 – 4.18 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.93 (dd, *J* = 9.1, 5.6 Hz, 1H), 2.58 (ddd, *J* = 10.4, 9.1, 4.3 Hz, 1H), 2.33 (dd, *J* = 5.7, 4.3 Hz, 1H), 2.28 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, +25 °C) δ = 172.0, 166.0, 154.7, 145.0, 139.1, 129.6, 122.7, 121.5, 117.7, 116.2, 61.3, 60.2, 30.4, 28.2, 27.8, 21.1, 14.25, 14.22. **MS** (ESI) m/z: $[M + Na]^+$ 341. **HPLC**: IC (*n*-hexane/*i*-PrOH 80:20, 1 mL/min) t_{min} = 7.1 min, t_{maj} = 8.8 min.

Ethyl (1*R*,2*S*,3*R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-5-methylphenyl)cyclopropane-1-carboxylate 4ca

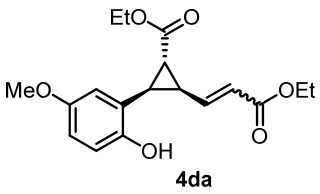


4ca

The general procedure was followed using aldehyde **1c**, sulfoxonium ylide **2a**, and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing E/Z mixture of **4ca** as colorless oil (overall 45% yield, 14.3 mg) and 95% ee. E/Z-**4ca**: **IR** (ATR) ν(max) =3433 (br, m) 1703 (s) 1700 (s) 1251 (s) 1180 (s) 1138 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 6.98 – 6.86 (m, 2H), 6.67 (d, *J* = 8.1 Hz, 1H), 6.20 (dd, *J* = 15.5, 10.4 Hz, 1H), 6.03 (dd, *J* = 23.6, 15.5 Hz, 1H), 4.94 (s, 1H), 4.26 – 4.15 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.00 – 2.89 (m, 1H), 2.58 (ddd, *J* = 10.5, 9.1, 4.3 Hz, 1H), 2.35 (dd, *J* = 5.7, 4.3 Hz, 1H), 2.24 (s, 3H), 1.33 – 1.26 (m, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 172.0, 165.9, 152.6, 144.9, 130.3, 129.9, 129.3, 122.7, 115.4, 61.3, 60.2, 30.4, 28.5, 27.7, 20.5, 14.27, 14.23. **MS** (ESI)

m/z: $[M + Na]^+$ 341. **HPLC**: IC (*n*-hexane/*i*-PrOH 80:20, 1 mL/min) E-isomer: t_{min} = 6.9 min, t_{maj} = 8.6 min.

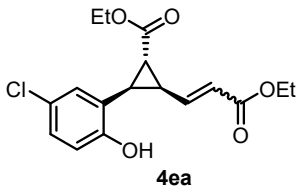
Ethyl (1*R*,2*S*,3*R*)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-5-methoxyphenyl)cyclopropane-1-carboxylate 4da



4da

The general procedure was followed using aldehyde **1d**, sulfoxonium ylide **2a**, and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing E/Z mixture of **4da** as colorless oil (overall 63% yield, 21.1 mg), and 97% ee. E/Z-**4da**: **IR** (ATR) ν(max) =3409 (br, m) 1714 (s) 1695 (s) 1251 (s) 1199 (s) 1176 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 6.80 – 6.60 (m, 3H), 6.23 (dd, *J* = 15.5, 10.3 Hz, 1H), 6.03 (d, *J* = 15.5 Hz, 1H), 4.82 (s, 1H), 4.22 (qd, *J* = 7.2, 0.6 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 2.99 – 2.93 (m, 1H), 2.60 (ddd, *J* = 10.4, 9.2, 4.3 Hz, 1H), 2.34 (dd, *J* = 5.7, 4.4 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 171.8, 165.9, 153.5, 148.9, 144.7, 122.9, 121.9, 116.3, 115.6, 113.8, 61.3, 60.3, 55.8, 30.3, 28.6, 27.8, 14.25, 14.22. **MS** (ESI) m/z: $[M + Na]^+$ 357. **HPLC**: IC (*n*-hexane/*i*-PrOH 80:20, 1 mL/min) E-isomer: t_{min} = 10.2 min, t_{maj} = 11.7 min.

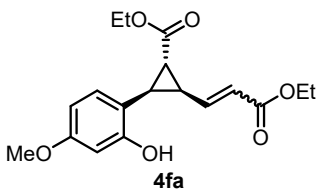
Ethyl (1*R*,2*R*,3*S*)-2-(5-chloro-2-hydroxyphenyl)-3-(-3-ethoxy-3-oxoprop-1-en-1-yl)cyclopropane-1-carboxylate 4ea



4ea

The general procedure was followed using aldehyde **1e**, sulfoxonium ylide **2a**, and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing **4ea** as E/Z mixture, and a fraction containing pure E-**4ea** as pale yellow oils (overall 57% yield, 19.3 mg) with 90% ee. E-**4ea**: $[\alpha]_D^{25}$ = +38 (c = 0.3, CH_2Cl_2) for 90% ee. **IR** (ATR) ν(max) = 3418 (br, m) 1704 (s) 1249 (s) 1179 (s) 1140 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 7.15 – 7.04 (m, 2H), 6.73 – 6.66 (m, 1H), 6.17 (dd, *J* = 15.4, 10.3 Hz, 1H), 6.01 (d, *J* = 15.5 Hz, 1H), 5.50 (s, 1H), 4.25-4.19 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.92 (dd, *J* = 9.2, 5.7 Hz, 1H), 2.59 (ddd, *J* = 10.3, 9.1, 4.4 Hz, 1H), 2.34 (dd, *J* = 5.7, 4.4 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 171.7, 166.0, 153.7, 144.2, 129.7, 128.7, 125.3, 123.2, 122.8, 116.8, 61.5, 60.4, 30.2, 28.1, 27.5, 14.2, 14.1. **MS** (ESI) m/z: $[M(^{35}Cl) + Na]^+$ 361, $[M(^{37}Cl) + Na]^+$ 363. **HPLC**: IC (*n*-hexane/*i*-PrOH 80:20, 1 mL/min) E-isomer: t_{min} = 5.1 min, t_{maj} = 5.9 min.

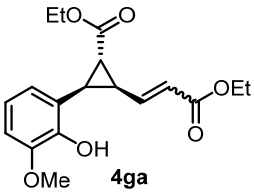
Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-4-methoxyphenyl)cyclopropane-1-carboxylate 4fa



4fa

The general procedure was followed using aldehyde **1f**, sulfoxonium ylide **2b** and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate and 1 equiv. of NaOAc (8.2 mg). Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing E/Z mixture of **4fa** as yellow oil (43% yield, 14.4 mg), and 85% ee . E-**4fa**: $[\alpha]_D^{25}$ = +23 (c = 0.4, CH_2Cl_2) for 85% ee. **IR** (ATR) ν(max) = 3393 (br, m) 1715 (s) 1695 (s) 1162 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 7.01 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.44 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.38 (d, *J* = 2.5 Hz, 1H), 6.23 (dd, *J* = 15.5, 10.3 Hz, 1H), 6.02 (d, *J* = 15.5 Hz, 1H), 5.75 (s, 1H), 4.26 – 4.16 (m, 2H), 4.16 – 4.06 (m, 2H), 3.76 (s, 3H), 2.88 (dd, *J* = 8.9, 5.5 Hz, 1H), 2.57 (ddd, *J* = 10.4, 9.0, 4.3 Hz, 1H), 2.31 (dd, *J* = 5.6, 4.3 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 171.9, 165.9, 160.3, 155.8, 144.8, 130.6, 122.7, 113.0, 106.2, 101.7, 61.3, 60.2, 55.3, 30.2, 27.9, 27.8, 14.24, 14.20. **MS** (ESI) m/z: $[M + Na]^+$ 357. **HPLC**: AD-H (*n*-hexane/*i*-PrOH 90:10, 1 mL/min) E-isomer: t_{maj} = 16.7 min, t_{min} = 22.8 min.

Ethyl (1*R*,2*S*,3*R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-3-methoxyphenyl)cyclopropane-1-carboxylate 4ga



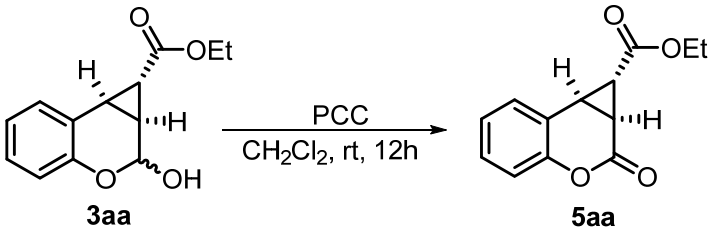
4ga

The general procedure was followed using aldehyde **1g**, sulfoxonium ylide **2a**, and ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate. Flash column chromatography (CH_2Cl_2/Acetone = 200:1) afforded a fraction containing E/Z mixture of **4ga** as colorless oil (overall 43% yield 14.4 mg) and 88% ee. E/Z-**4ga**: **IR** (ATR) ν(max) = 3427 (br, m) 1711 (s) 1272 (s) 1176 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 6.81 – 6.73 (m, 2H), 6.73 – 6.66 (m, 1H), 6.26 (dd, *J* = 15.5, 10.4 Hz, 1H), 5.99 (d, *J* = 15.4 Hz, 1H), 5.74 (s, 1H), 4.21 – 4.15 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 3.06 (dd, *J* = 9.3, 5.8 Hz, 1H), 2.58 (ddd, *J* = 10.5, 9.4, 4.4 Hz, 1H), 2.38 (dd, *J* = 5.8, 4.4 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, +25 °C) [signals of the E-isomer] δ = 172.1, 166.1, 146.4, 145.6, 145.0, 122.3, 121.4, 120.7, 119.3, 109.8, 61.1, 60.1, 56.0, 30.7, 28.6, 27.7, 14.22, 14.20. **MS** (ESI) m/z: $[M + Na]^+$ 357. **HPLC**: IC (*n*-hexane/*i*-PrOH 80:20, 1 mL/min) E-isomer: t_{maj} = 12.5 min, t_{min} = 15.2 min.

Synthetic elaborations

Synthetic elaboration on **3aa** were performed using freshly prepared **3aa**, isolated by a fast flash column chromatography using 3:1 hexane/acetone from catalytic crude, or using the one pot protocols detailed below.

Ethyl (1*S*,1a*S*,7b*S*)-2-oxo-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate 5aa



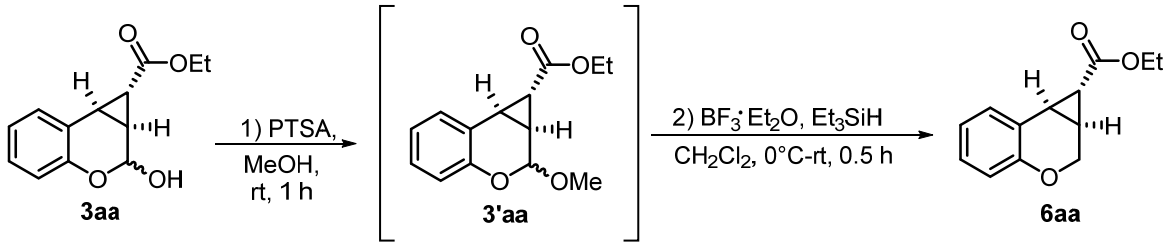
3aa **5aa**

In a small vial equipped with a magnetic stirring bar, PCC (0.2 mmol, 2 equiv., 43 mg) was added to a solution of cyclopropanchromanol **3aa** (0.1 mmol, 1 equiv., 23 mg), in CH_2Cl_2 (0.5 mL). The resulting solution was stirred at room temperature for 12 h and then poured into an aq. solution of Na_2SO_3 (3 M), and extracted with DCM (3 x). The combined organic phases were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude residue was then purified by flash column chromatography on silica gel (*n*-hexane/Et_2O = 3:1) affording product **5aa** as a white solid in 37% yield (8.6 mg)

One pot protocol: In a small vial equipped with a magnetic stirring bar, aldehyde **1a** (0.1 mmol, 1 equiv., 14.8 mg) and sulfoxonium ylide **2a** (0.15 mmol, 1.5 equiv., 25.2 mg) were added to a $CDCl_3$ (1 mL) solution of catalyst (*S*)-**A** (0.02 mmol, 0.20 equiv., 6.5 mg) and AcONa (0.02 mmol, 0.20 equiv., 1.6 mg). The resulting mixture was stirred at room temperature for 12 h, then treated directly with PCC (0.3 mmol, 3 equiv., 65 mg). Work-up and purification as above afforded compound **5aa** as a white solid in 35% yield (8.1 mg).

m.p. = 77-80 °C. $[\alpha]_D^{25}$ +7.2 (c = 0.25, CH_2Cl_2) for 96% ee. **IR** (ATR) ν(max) =1754 (s) 1722 (s) 1172 (s) 1076 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, +25 °C) δ = 7.39 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.30 – 7.22 (m, 1H), 7.13 (td, *J* = 7.5, 1.2 Hz, 1H), 7.05 – 6.98 (m, 1H), 4.26-4.21 (m, 2H), 3.04 (dd, *J* = 8.1, 4.2 Hz, 1H), 2.85 (dd, *J* = 8.1, 4.1 Hz, 1H), 2.07 (t, *J* = 4.1 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, +25 °C) δ = 169.9, 163.9, 150.0, 128.7, 128.2, 124.7, 119.0, 117.4, 62.0, 27.5, 27.0, 25.2, 14.1. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{12}O_4Na$ 255.0628; Found 255.0633. **HPLC**: AD-H (*n*-hexane/*i*-PrOH 90:10, 0.75 mL/min) t_{maj} = 11.4 min, t_{min} = 15.7 min.

Ethyl (1*S*,1a*S*,7b*R*)-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate 6aa



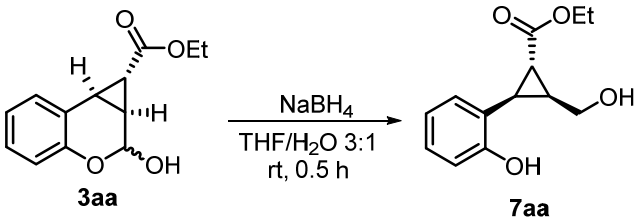
In a small vial equipped with a magnetic stirring bar, PTSA·H_2O (0.1 mmol, 1 equiv., 95.1 mg) was added to a solution of cyclopropanchromanol **3aa** (0.1 mmol, 1 equiv., 23 mg) in 2.5 mL of MeOH. The reaction was stirred at rt for 1 h and then the desired intermediate **3'aa** was purified by a short plug on silica gel using DCM as eluent. Intermediate **3'aa** was then dissolved in 1 mL of DCM and cooled to 0 °C, then BF_3·Et_2O (0.3 mmol, 3 equiv., 42.5 mg, 37 µL) and Et_3SiH (0.3 mmol, 3 equiv., 34.9 mg, 48 µL) were added and the reaction was stirred at rt for 30 min. The mixture was then poured into a solution of $NaHCO_{3(sat)}$ and extracted with DCM (3x). The combined organic phases were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (DCM/*n*-hexane = 1:1) affording product **6aa**[8] as an oil in 67% yield (14.6 mg).

One pot protocol: In a small vial equipped with a magnetic stirring bar, aldehyde **1a** (0.1 mmol, 1 equiv., 14.8 mg) and sulfoxonium ylide **2a** (0.15 mmol, 1.5 equiv., 25.2 mg) were added to a $CDCl_3$ (1 mL) solution of catalyst (*S*)-**A** (0.02 mmol, 0.20 equiv., 6.5 mg) and AcONa (0.02 mmol, 0.20 equiv., 1.6 mg). The resulting mixture was stirred at room temperature for 12 h, then evaporated to dryness (replacing residual $CDCl_3$ with MeOH portions). The residue was dissolved in MeOH (1 mL), and treated with PTSA·H_2O (0.1 mmol, 1 equiv., 95.1 mg). The reaction was stirred at rt for 1 h, then evaporated to dryness. The mixture containing intermediate **3'aa** was then dissolved in 1 mL of DCM and cooled to 0 °C, then BF_3·Et_2O (0.3 mmol, 3 equiv., 42.5 mg, 37 µL) and Et_3SiH (0.3 mmol, 3 equiv., 34.9 mg, 48 µL) were added and the reaction was stirred at rt for 30 min. Work-up and purification as above afforded compound **6aa** as an oil in 17% yield (3.7 mg). $[\alpha]_D^{25}$ -104.5 (c = 0.32, CH_2Cl_2) **IR** (ATR) ν(max) =1723 (m) 1253 (m) 1029 (s) cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$, +25 °C) δ = 7.24 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.10 (ddd, *J* = 1.6, 7.5, 8.0 Hz, 1H), 6.91 (ddd, *J* = 1.2, 7.5, 8.0 Hz, 1H), 6.8 (dd, *J* = 1.0, 8.1 Hz, 1H), 4.37 (d, *J* = 11.1 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.91 (dd, *J* = 10.7, 0.8 Hz, 1H), 2.57 (dd, *J* = 4.4, 8.4 Hz, 1H), 2.37-2.28 (m, 2H) 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, +25 °C) δ = 172.2, 152.7, 128.7, 127.3, 124.0, 121.8, 117.3, 61.6,

[8] Racemic **6aa**: Ye, L.-W.; Sun, X.-L.; Li, C.-Y.; Tang, Y. *J. Org. Chem.* **2007**, *72*, 1335.

60.8, 26.9, 24.4, 22.7, 14.2. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{14}O_3Na$ 241.0835; Found 241.0841.

Ethyl (1*S*,2*S*,3*R*)-2-(hydroxymethyl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 7aa

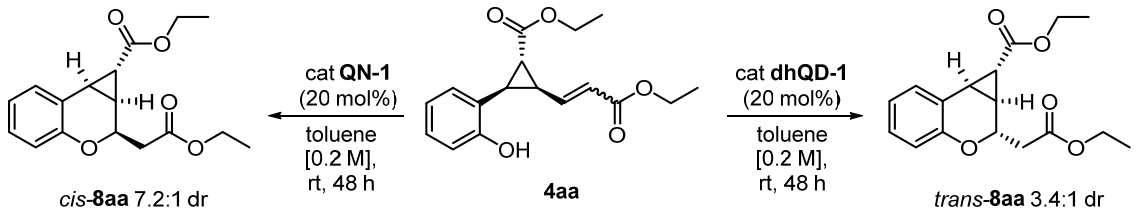


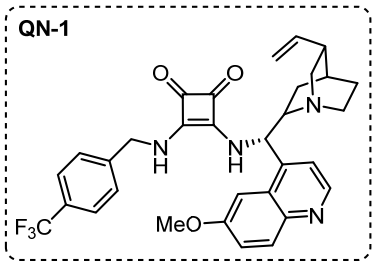
In a small vial equipped with a magnetic stirring bar $NaBH_4$ (0.225 mmol, 1.5 equiv., 8.5 mg) was added to a cooled (0 °C) solution of cyclopropanchromanol **3aa** (0.15 mmol, 35.1 mg) in a 3:1 THF/H_2O mixture (1.5 mL). After 30 minutes stirring at 0 °C, the mixture was poured into a solution of $NH_4Cl_{(sat)}$ and extracted with DCM. The combined organic phases were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (*n*-hexane/acetone = 5:1) affording product **7aa** as a yellow oil in 91% yield (32.5 mg).

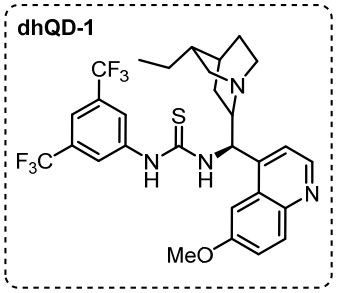
One pot protocol: In a small vial equipped with a magnetic stirring bar, aldehyde **1a** (0.1 mmol, 1 equiv., 14.8 mg) and sulfoxonium ylide **2a** (0.15 mmol, 1.5 equiv., 25.2 mg) were added to a $CDCl_3$ (1 mL) solution of catalyst (*S*)-**A** (0.02 mmol, 0.20 equiv., 6.5 mg) and AcONa (0.02 mmol, 0.20 equiv., 1.6 mg). The resulting mixture was stirred at room temperature for 12 h, then evaporated to dryness (replacing residual $CDCl_3$ with THF portions). The residue was dissolved in a 3:1 THF/H_2O mixture (1.5 mL), cooled to 0 °C, and treated with $NaBH_4$ (0.225 mmol, 1.5 equiv., 8.5 mg). After 1.5 h, additional $NaBH_4$ (0.225 mmol, 1.5 equiv., 8.5 mg) was added. The mixture was stirred at 0 °C for an additional 30 minutes. Work-up and purification as described above afforded compound **7aa** as a yellow oil in 50% yield (11.8 mg).

$[\alpha]_D^{25}$ -18.0 (c = 0.5, CH_2Cl_2). **IR** (ATR) ν(max) =3452 (w, br) 3165 (w, br) 1701 (s) 1219 (s) 1188 (s) 1018 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, +25 °C) δ = 7.20-7.15 (m, 2H), 6.90-6.85 (m, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.90 (dd, *J* = 11.2, 4.3 Hz, 1H), 2.85 (t, *J* = 10.6 Hz, 1H), 2.7 (dd, *J* = 5.0, 9.1 Hz, 1H), 2.25-2.20 (m, 1H), 1.91 (t, *J* = 4.9 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, +25 °C) δ = 173.1, 154.9, 131.3, 128.8, 122.8, 121.1, 116.7, 61.5, 61.1, 29.1, 26.6, 22.9, 14.2. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{16}O_4Na$ 259.0941; Found 259.0946.

Ethyl (1*S*,1a*S*,2*R*,7b*R*)-2-(2-ethoxy-2-oxoethyl)-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate and Ethyl (1*S*,1a*S*,2*S*,7b*R*)-2-(2-ethoxy-2-oxoethyl)-1,1a,2,7b-tetrahydro cyclopropa[*c*]chromene-1-carboxylate 8aa







***cis*-8aa-selective reaction (QN-1 catalyzed):**

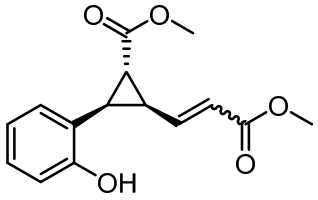
In a small vial equipped with a magnetic stirring bar catalyst **QN-1** (0.02 mmol, 0.2 equiv., 11.3 mg) was added to a solution of **4aa** (0.1 mmol, 1 equiv., 30.4 mg) in toluene (0.5 mL). The reaction was stirred 48 h at rt, then the catalyst was removed by a short plug of silica gel using Et_2O as eluent. After evaporation of the solvents, the residue was analyzed by ^1H NMR spectroscopy indicating a 7.2:1 diastereomeric ratio favoring the *cis*-**8aa** isomer. Subsequently, the crude residue was purified by flash column chromatography on silica gel (*n*-hexane/AcOEt = 14:1) affording product **8aa** as a diastereomeric mixture in 58% yield (17.6 mg) and 99% ee for the *cis*-**8aa** isomer. *Cis*/*trans*-**8aa** (*cis*-enriched): **IR** (ATR) ν(max) =1720 (s) 1263 (s) 1172 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) [signals of the *cis*-isomer] δ = 7.25 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.10 (td, *J* = 7.7, 1.6 Hz, 1H), 6.92 (td, *J* = 7.4, 1.0 Hz, 1H), 6.78 (br d, *J* = 8.1 Hz, 1H), 4.39 (br t, *J* = 6.5 Hz, 1H), 4.26-4.19 (m, 2H), 4.19-4.12 (m, 2H), 2.83 (dd, *J* = 15.5, 7.5 Hz, 1H), 2.75 (dd, *J* = 15.5, 5.5 Hz, 1H), 2.61 (dd, *J* = 9.2, 3.5 Hz, 1H), 2.38 (ddd, *J* = 9.2, 4.4, 1.4 Hz, 1H), 2.25 (br t, *J* = 4.0 Hz, 1H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, +25 °C) [signals of the *cis*-isomer] δ = 171.9, 170.2, 152.5, 128.4, 127.4, 123.6, 122.0, 117.4, 68.0, 60.9, 60.8, 40.4, 30.6, 23.7, 23.1, 14.23, 14.21. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}O_5$ 305.1389; Found 305.1389. **HPLC**: IC (*n*-hexane/*i*-PrOH 95:5, 0.75 mL/min) *cis*-**8aa** isomer: t_{min} = 18.5 min, t_{maj} = 30.8 min.

***trans*-8aa-selective reaction (dhQD-1 catalyzed):**

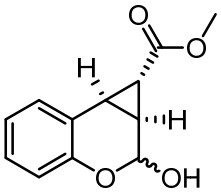
In a small vial equipped with a magnetic stirring bar catalyst **dhQD-1** (0.02 mmol, 0.2 equiv., 12.0 mg) was added to a solution of **4aa** (0.1 mmol, 1 equiv., 30.4 mg) in toluene (0.5 mL). The reaction

was stirred 48 h at rt, then the catalyst was removed by a short plug of silica gel using Et_2O as eluent. After evaporation of the solvents, the residue was analyzed by ^1H NMR spectroscopy indicating a 3.4:1 diastereomeric ratio favoring the *trans*-**8aa** isomer. Subsequently the crude residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 14:1) affording product **8aa** as a diastereomeric mixture in 58% yield (17.5 mg) and 99% ee for the *trans*-**8aa** isomer. *Cis*/*trans*-**8aa** (*trans*-enriched): **IR** (ATR) ν(max) =1726 (s) 1704 (s) 1261 (s) 1186 (s) 1029 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$, +25 °C) [signals of the *trans*-isomer] δ = 7.22 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.11 (td, *J* = 7.8, 1.6 Hz, 1H), 6.92 (td, *J* = 7.4, 1.0 Hz, 1H), 6.75 (br d, *J* = 8.1 Hz, 1H), 4.91 (br t, *J* = 6.9 Hz, 1H), 4.19-4.13 (m, 4H), 2.59 (d, *J* = 15.4, 7.9 Hz, 1H), 2.56 (dd, *J* = 8.8, 5.2 Hz, 1H), 2.49 (dd, *J* = 15.4, 5.8 Hz, 1H), 2.28 (br t, *J* = 4.0 Hz, 1H), 2.27-2.24 (m, 1H), 1.27 (t, *J* = 7.3 Hz, 3H), 1.26 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, +25 °C) [signals of the *trans*-isomer] δ = 171.9, 170.3, 149.5, 128.5, 127.8, 123.7, 122.1, 118.4, 67.6, 60.9, 60.8, 38.4, 29.6, 25.5, 22.2, 14.23, 14.18. **HPLC**: IC (*n*-hexane/*i*-PrOH 95:5, 0.75 mL/min) *trans*-**8aa** isomer: t_{min} = 23.2 min t_{maj} = 34.1 min.

Determination of the relative configuration of compounds 4'ab and 3ab



4'ab



3ab

Compound **4'ab** was selected for the assignment of the relative disposition of cyclopropane protons. Full assignment of ^{1}H NMR signals was preliminarily determined by J-coupling and HSQC and HMBC bidimensional sequences. The ^{1}H NMR spectrum shows that the H_3 signal is coupled with the H_1, H_2 and H_{1E} giving a ddd signal. The J constant H_3-H_{1E} (J = 9.5 Hz) is easily confirmed by the H_{1E} signal at 6.22 ppm. The large value of J coupling constant with the cyclopropane H_2 (J = 9.7 Hz) and the smaller J constant with the last cyclopropane H_1 (J = 4.3 Hz) suggests that H_3 is cis and trans, respectively, to these protons. To confirm the 1R*,2R*,3S* relative configuration, NOESY-1D spectra were acquired (Figure S1).

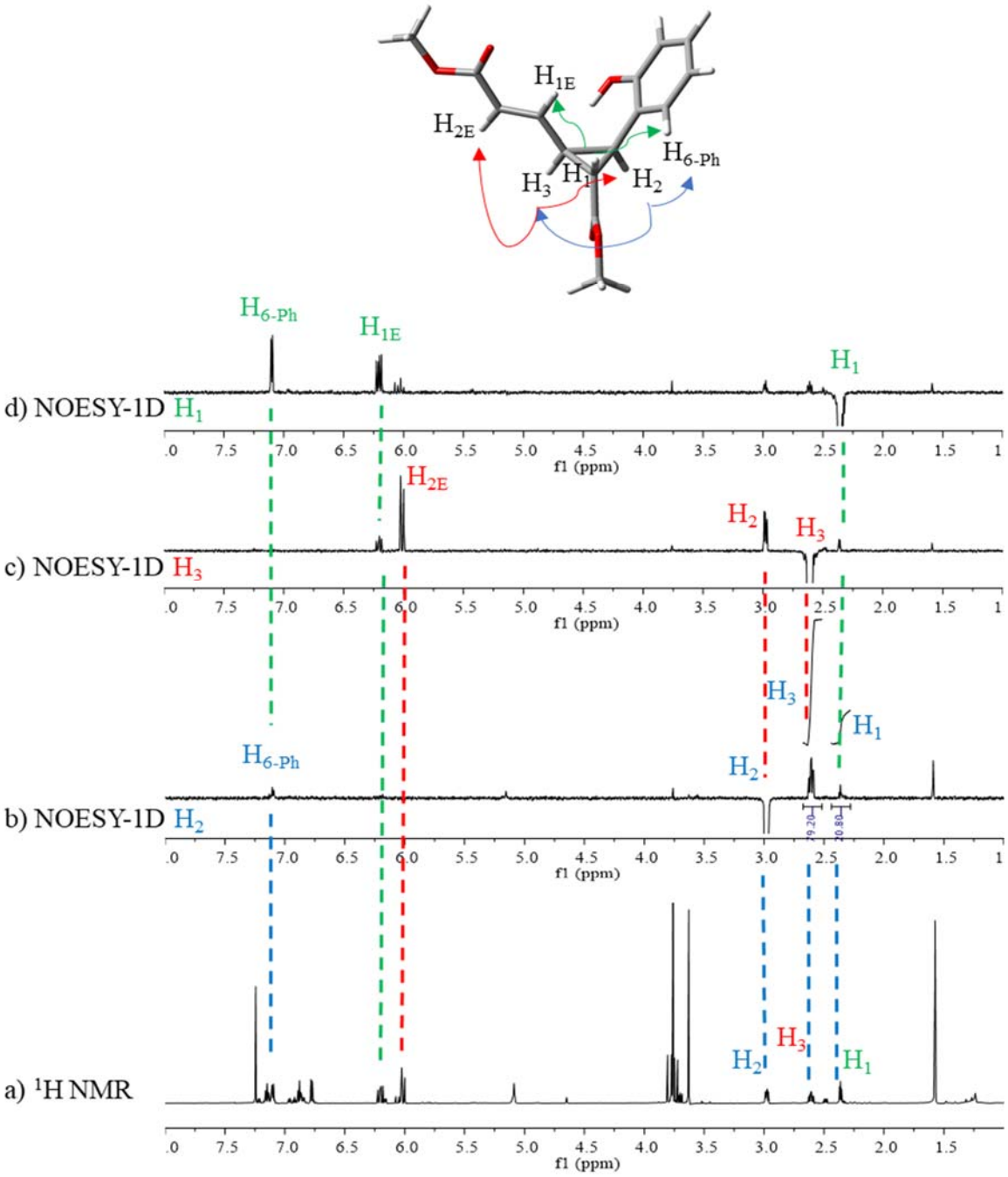
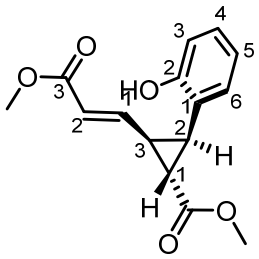


Figure S1. DPFGSE-NOE spectra of **4'ab** (600 MHz in $CDCl_3$, T = 25 °C); a) control ^{1}H-NMR spectrum; b) saturation of cyclopropane H_2 signal; c) saturation of cyclopropane H_3 signal; d) saturation of cyclopropane H_1 signal.

On saturation of the proton in position 2 of the cyclopropane (H_2), strong NOE effect is generated on the H_3 hydrogen (79.2%), smaller on the H_1 (20.8%) and $H_{6\text{-Ph}}$ signals (Fig. S1 trace b). If the protons were in the same side, a 50% of NOE effect should occur. When H_3 is saturated only H_2 and H_{2E} give strong NOE effect. Finally, on saturation of the H_1, strong NOE effect is generated on the H_{1E} and $H_{6\text{-Ph}}$ signals confirming that the substituents of the cyclopropane are in the same side of H_1.

These results indicate that cyclopropane has a 1R*,2R*,3S* relative configuration.



methyl (1*R*,2*R*,3*S*)-2-(2-hydroxyphenyl)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)cyclopropane-1-carboxylate

Having in hand the relative configuration of compound **4'ab**, the relative assignment of the cyclopropyl ring in both major and minor products of compound **3ab** was done. The two diastereoisomers differ for the configuration of the hemiacetal carbon 2. Keeping in mind the C.I.P. priority groups, the relative configuration is 1S*,1aS*,2*,7bR*. To assign the relative configuration of the two isomers, NOESY-1D experiments were acquired (Figure S2).

On saturation of the aromatic proton H_7, NOE effect is generated on the H_{7b} cyclopropane proton (Figure 2, trace b). When hemiacetal proton of major diastereosiomer (H_{2maj}) is saturated, both H_1 and H_{1a} give strong NOE effect (Figure S2, trace c), suggesting its disposition in the same side (3D structure in Figure S2, major). Vice versa, H_1 does not give NOE effect on saturation of hemiacetal proton of minor diastereosiomer (H_{2min}) (trace d) confirming their opposite side (3D structure in Figure S2, minor).

In conclusion, the relative configuration of the major diastereoisomer of **3ab** is 1S*,1aS*,2R*,7bR* and the minor diastereoisomer of **3ab** is 1S*,1aS*,2S*,7bR*.

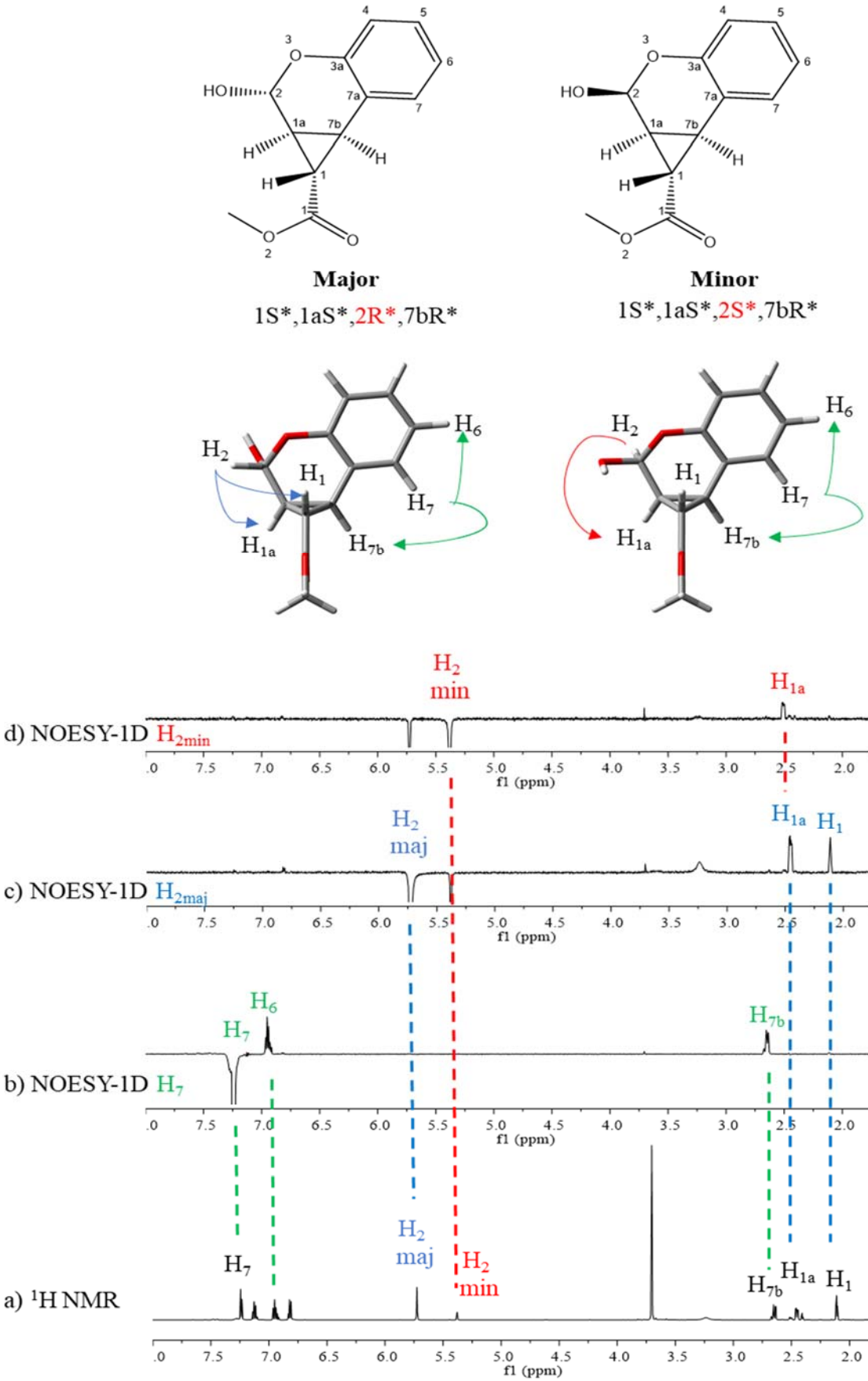
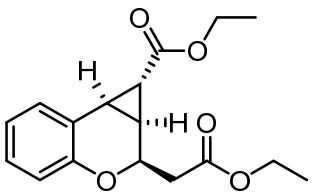
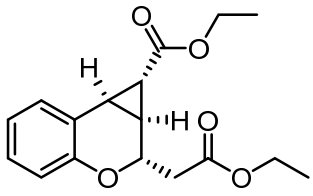


Figure S2. DPFGSE-NOE spectra of **3ab** (600 MHz in $CDCl_3$, T = 25 °C); a) control ^{1}H-NMR spectrum; b) saturation of H_7 aromatic signal; c) saturation of H_{2maj} major signal of hemiacetal; d) saturation of H_{2min} minor signal of hemiacetal.

Determination of the relative configuration of compounds *cis*-8aa and *trans*-8aa



1a,2-*cis*-**8aa**



1a,2-*trans*-**8aa**

To determine the relative configuration between the C1a and C2 chirality centers of compounds *cis*- and *trans*-**8aa**, NOESY-1D experiments were performed on a mixture enriched in the *trans*-**8aa** isomer (Figure S3). Irradiation of the aromatic signal corresponding to H_7 at 7.22 ppm (dd, J = 7.5, 1.5 Hz, 1H) gave a NOE effect on the signal at 6.92 ppm (td, J = 7.4, 1.0 Hz, 1H), assigned to H_6, and on the signal at 2.56 ppm (dd, J = 8.8, 5.2 Hz, 1H) (Figure S3, trace b). The latter signal could thus be assigned to H_{7b}. Such assignment was confirmed by irradiating the signal at 6.75 ppm (br d, J = 8.1 Hz, 1H, H_4), which gave NOE effect only on the aromatic signal at 7.11 ppm (td, J = 7.8, 1.6 Hz, 1H, H_5) (not shown). Irradiating the signal at 4.91 ppm (br t, J = 6.9 Hz, 1H), assigned to H_2 based on its chemical shift, gave NOE effect on the two cyclopropanic proton signals at 2.28 ppm (br t, J = 4.0 Hz, 1H), and 2.27-2.24 ppm (m, 1H) (Figure S3, trace c). Irrespective of the assignment of these signals to H_1 and H_{1a}, this result indicates a *cis*-relationship between H_2 and H_1 and thus, ultimately, a 1a,2-*trans* relationship.

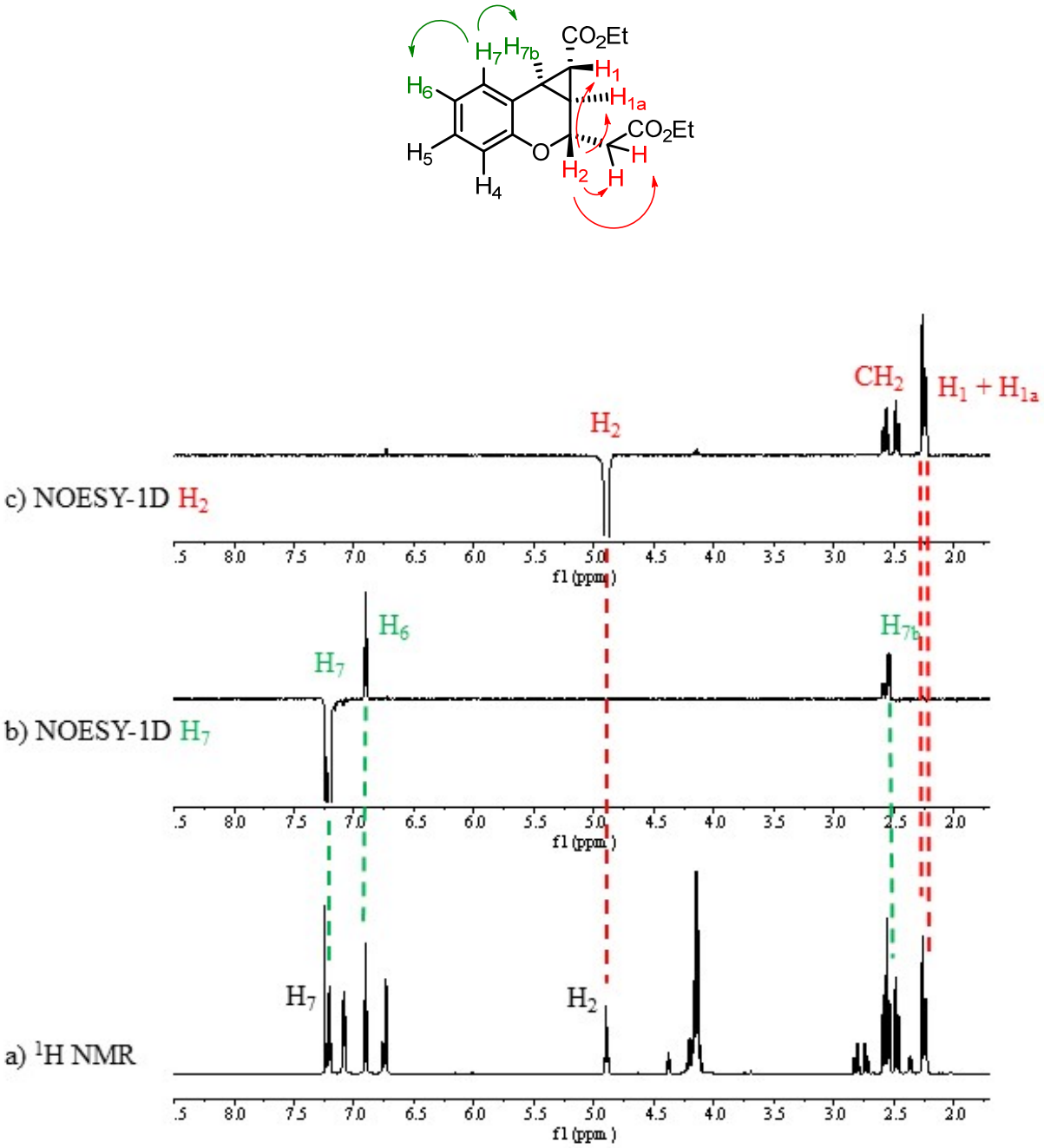


Figure S3. DPFGSE-NOE spectra of **8aa**, predominantly 1a,2-*trans* (600 MHz in $CDCl_3$, T = 25 °C); a) control ^{1}H-NMR spectrum; b) saturation of H_7 aromatic signal; c) saturation of H_2.

Determination of the absolute configuration of compounds 4'ab and 3ab

The determination of the absolute configuration (AC) of these products using X-Ray diffractometer was unfeasible because good crystals were not obtained. Therefore, the electronic circular dichroism (ECD) method was selected for the absolute configuration assignment.

Absolute Configuration of Compound 4'ab

The experimental ECD spectrum of compound **4'ab** was acquired in the 195-400 nm region using a JASCO J-810 spectropolarimeter in HPLC-grade acetonitrile solution. Concentration was about $2 \cdot 10^{-4}$ M, optimized in order to have a maximum absorbance less than 1, with a cell path of 0.1 cm. The spectrum was obtained by the average of 6 scans at 50 $nm \cdot min^{-1}$ scan rate.

The ECD spectrum for compound **4'ab** shows a large negative band at 280 nm and a positive one at 220 nm (vide infra).

For compound **4'ab**, two ground state geometries, within less than 1 kcal/mol, were found and optimized at the B3LYP/6-31G(d,p) level of theory (Figure S4), and validated by frequency analysis (no imaginary frequency was observed). The two geometries differ in the dihedral angle of the *o*-phenol, which can be -145.4° (73.3%) or +58.7° (26.7%).

The ECD spectra have been calculated in the gas phase for the two conformations with 1*R*,2*R*,2*S* absolute configuration using TD-DFT. Four different hybrid functionals (BH&HLYP[9] and M06-2X,[10] ωB97-XD[11] and CAM-B3LYP[12]) and the basis set (6-311++G(2d,p) were employed (Figure S4).

[9] In Gaussian 16 the BH&HLYP functional has the form: $0.5*E^{XHF} + 0.5*E^{XLSDA} + 0.5*\Delta E X^{Becke88} + E C^{LYP}$

[10] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

[11] Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615. Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. *J. Chem. Phys.* **2001**, *115*, 3540.

[12] Yanai, T.; Tew, D.; Handy, N. *Chem. Phys. Lett.* **2004**, *393*, 51.

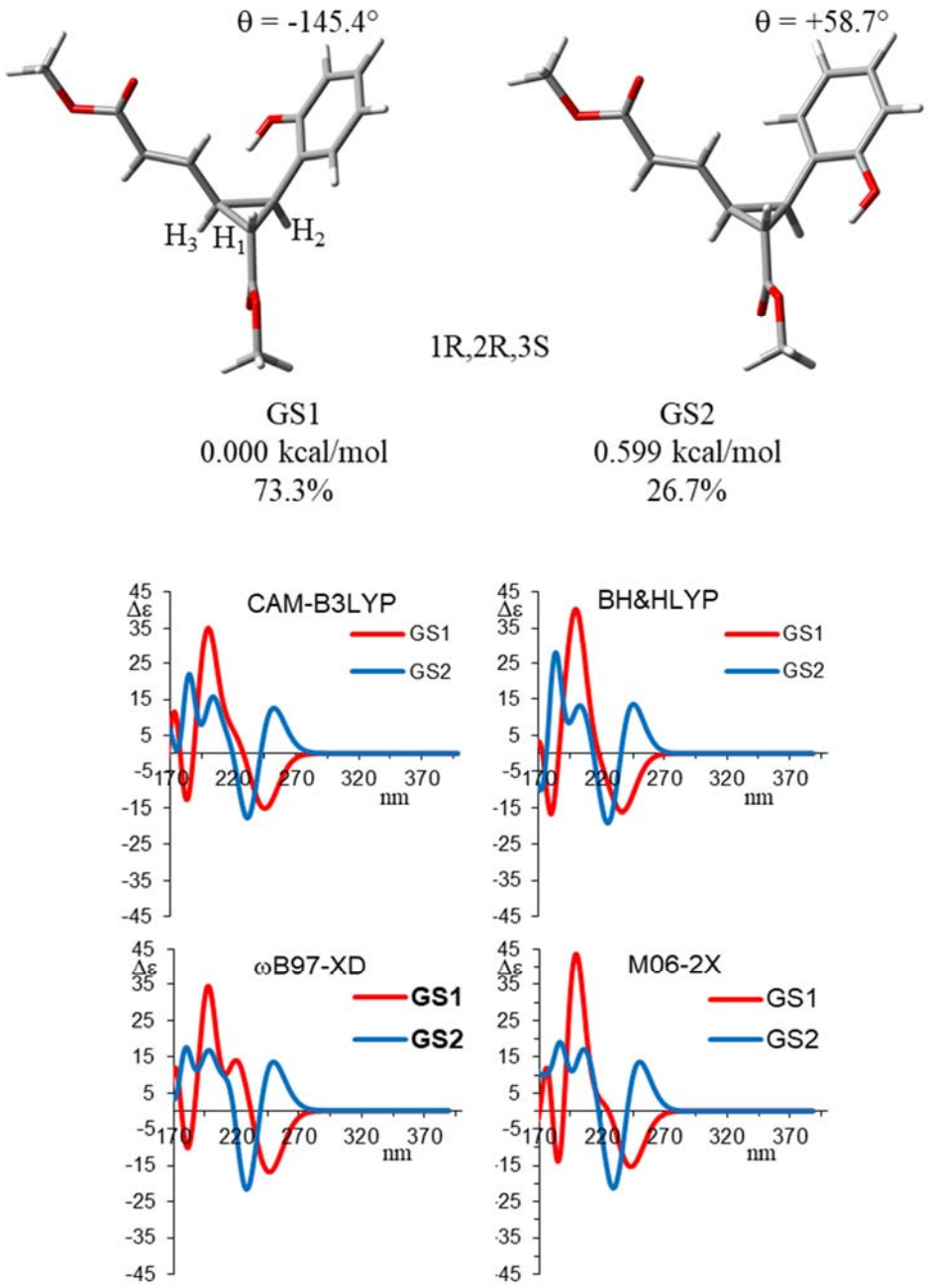


Figure S4. Top: Ground state geometries of **4'ab** with 1*R*,2*R*,3*S* absolute configuration. Bottom: calculated ECD spectra.

The calculated spectra for the two geometries are quite different (Figure S4), therefore the weighted sum was done and compared with the experimental ECD spectrum (Figure S5). The simulated spectra were vertically scaled and red-shifted to get the best match with the experimental spectrum. A very good overlap with the experimental ECD spectrum permits to assign the 1*R*,2*R*,2*S* absolute configuration to compound **4'ab**.

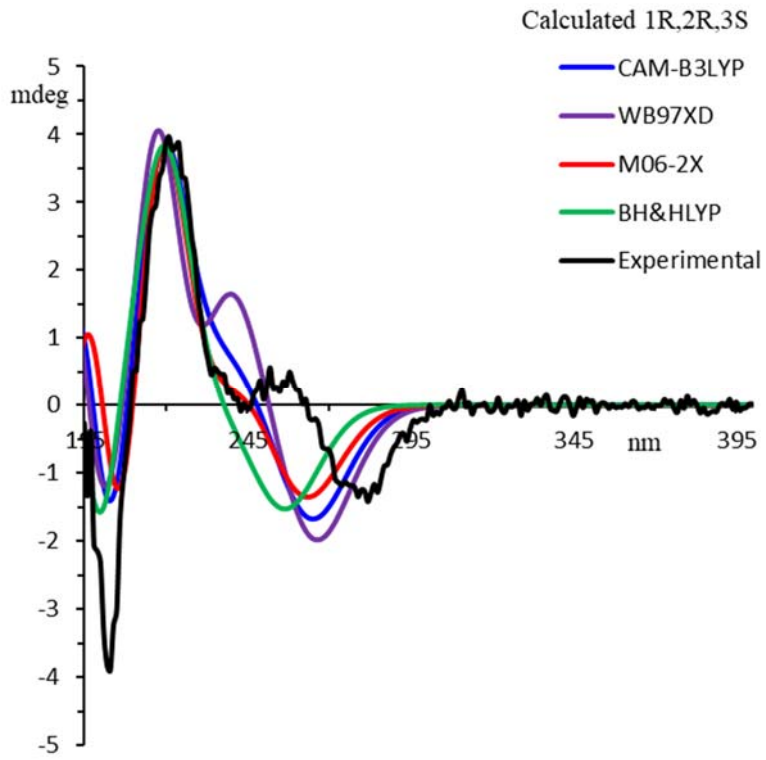


Figure S5 Overlap of calculated and experimental (black line) ECD spectra for compound (1*R*,2*R*,2*S*)-**4'ab**.

Absolute Configuration of Compound 3ab

For compound **3ab**, two diastereomeric geometries were found. Starting from relative configuration, 1*S*,1a*S*,2*R*,7b*R* geometry was calculated for the major diastereoisomer (78% by NMR) and 1*S*,1a*S*,2*S*,7b*R* geometry was calculated for the minor diastereoisomer (22% by NMR).

The ECD spectra have been calculated in the gas phase using TD-DFT, such as for compound **4'ab**. Both calculated spectra for the two diastereoisomers have a good overlap with the experimental ECD of the mixture, meaning that the hemiacetal chiral carbon does not influence the biggest band at 230 nm, that is mainly due to the chromophores tetrahydrocyclopropa[*c*]chromene (Figures S6 and S7). However, the weighted sum of the two diastereoisomers was done and compared with the experimental ECD spectrum (Figure S8). The simulated spectra were vertically scaled and red-shifted to get the best match with the experimental spectrum. A very good overlap with the experimental ECD spectrum permits to assign the 1*S*,1a*S*,2*R*,7b*R* A.C. to the major diastereosiomer and 1*S*,1a*S*,2*S*,7b*R* A.C. to the minor diastereoisomer, thus confirming the correctness of the assignment previously done on **4'ab**.

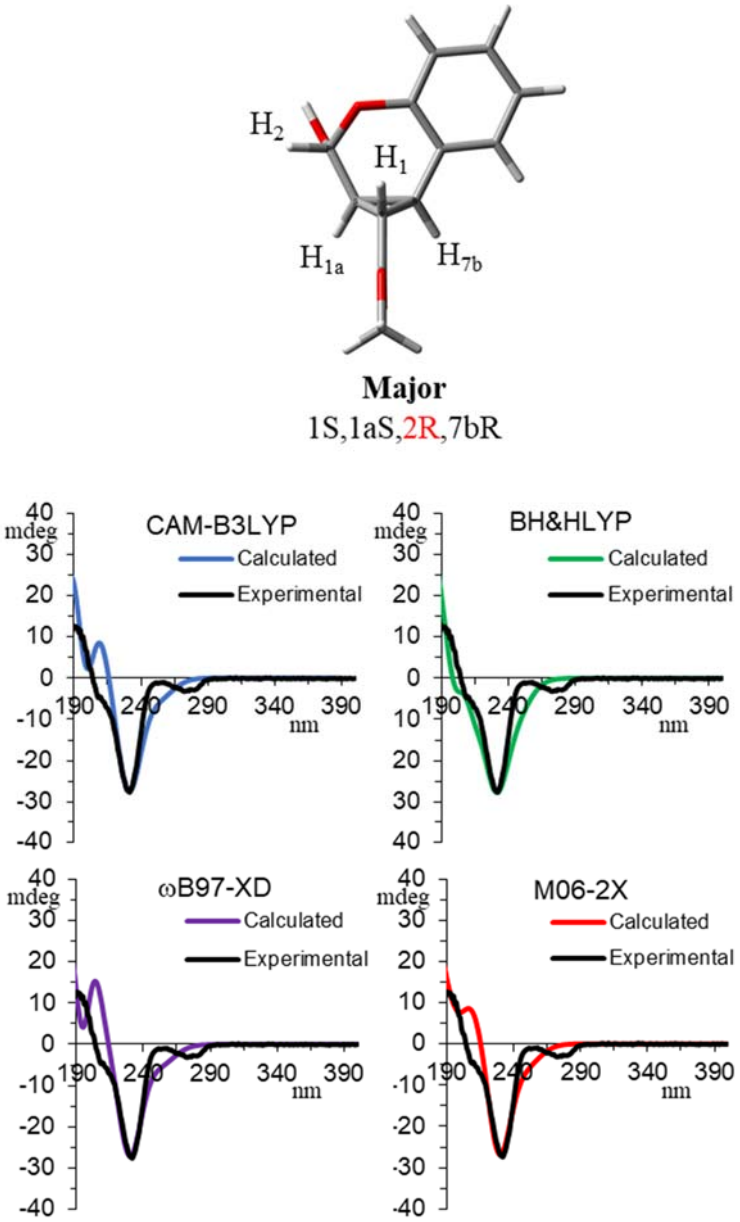


Figure S6. Overlap of calculated ECD spectra for the major diastereoisomer of **3ab**, and the experimental ECD of the diastereomeric mixture.

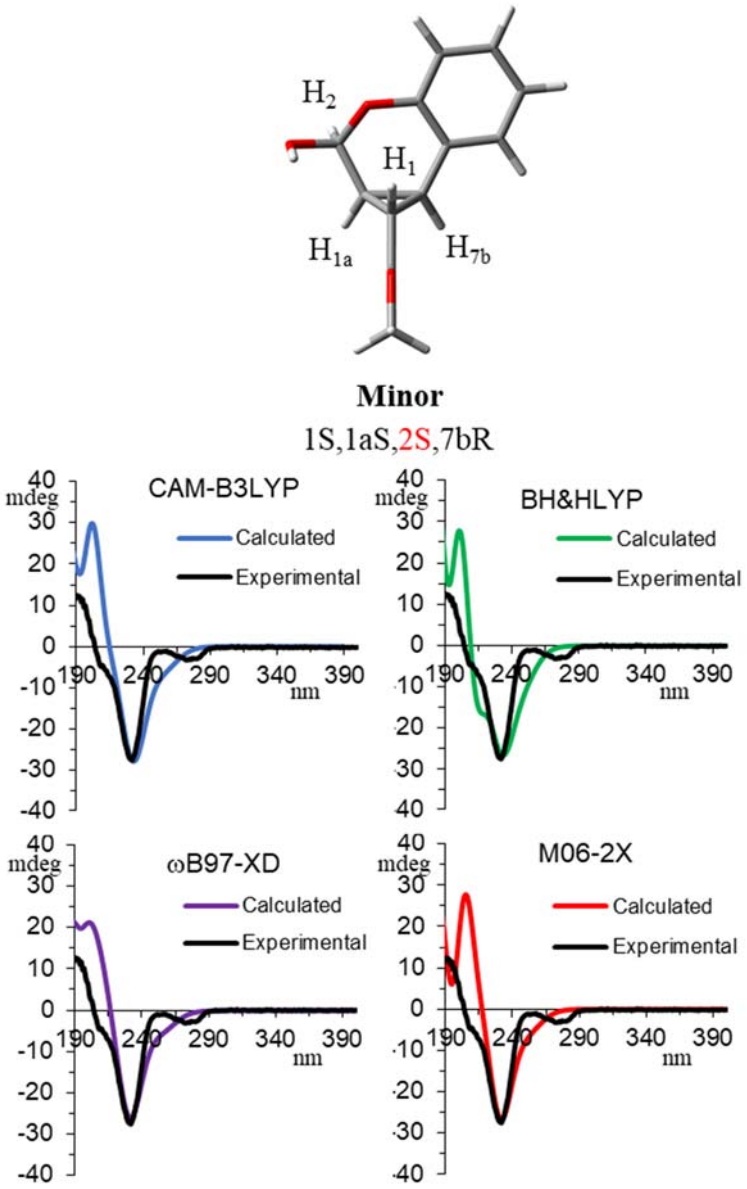


Figure S7. Overlap of calculated ECD spectra for the minor diastereoisomer of **3ab**, and the experimental ECD of the diastereomeric mixture.

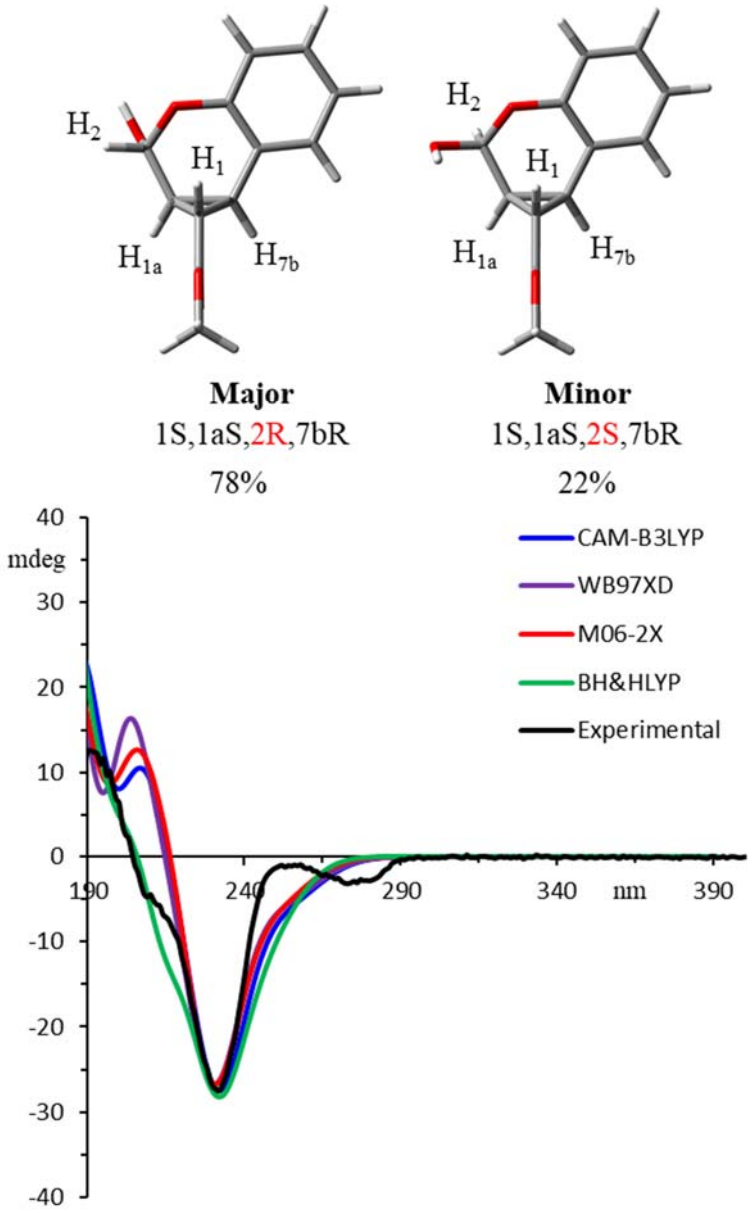
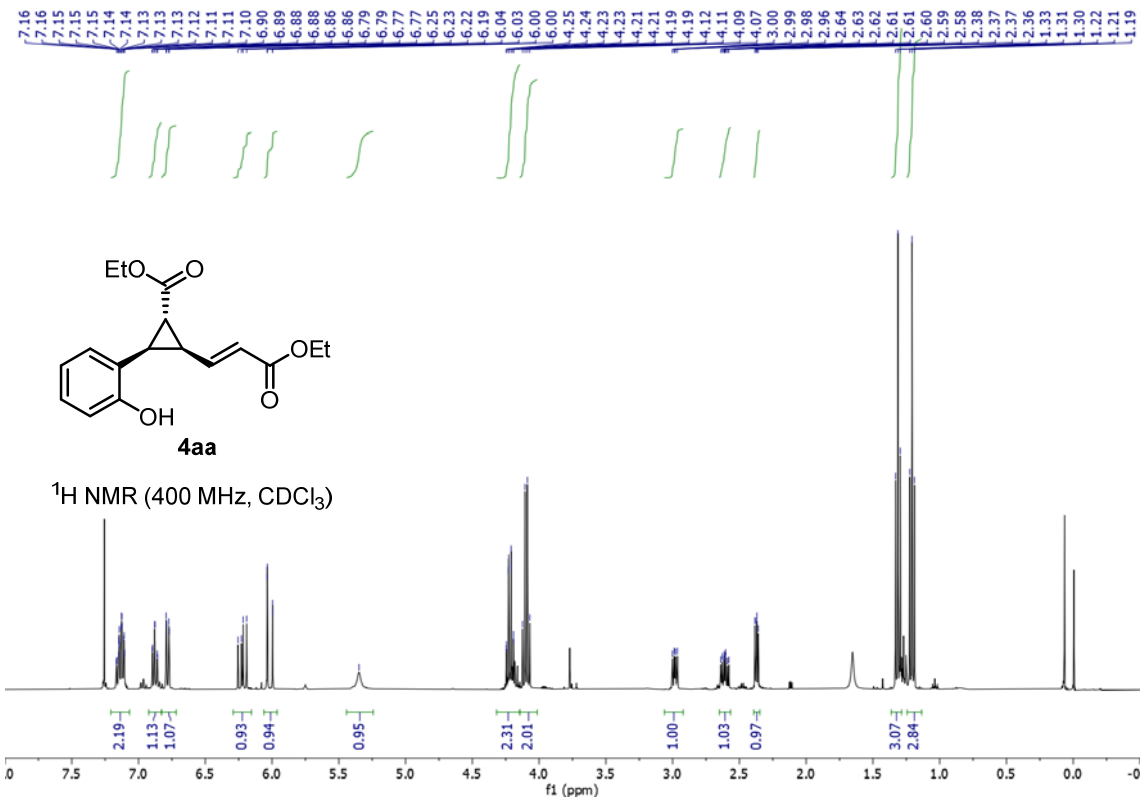
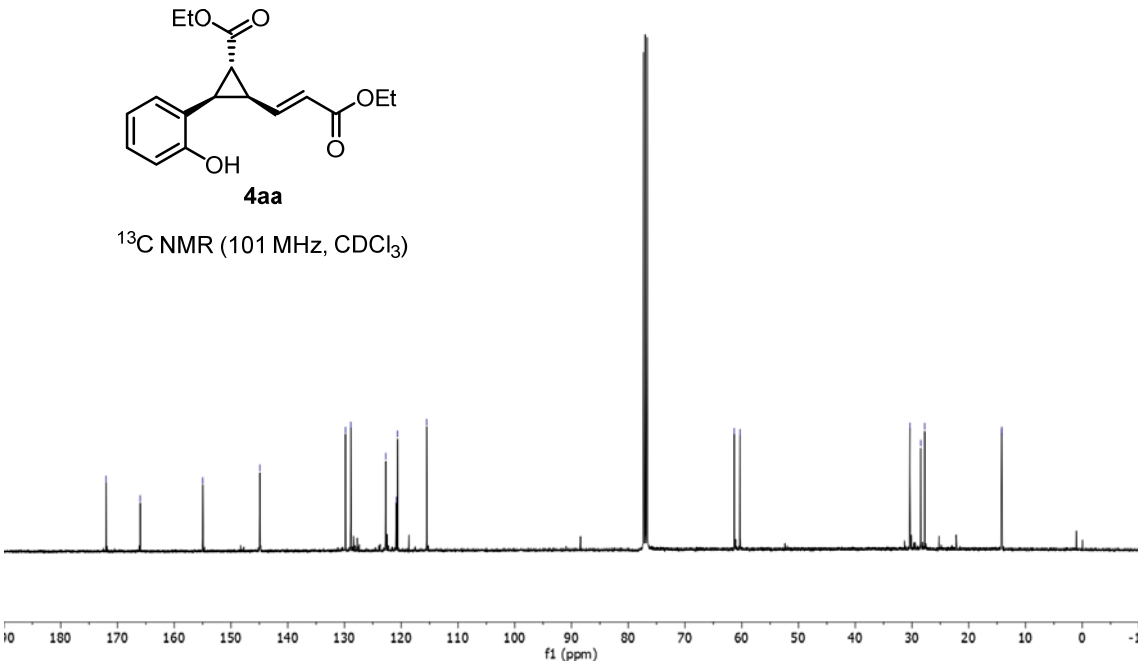


Figure S8 Overlap of calculated, the weighted sum of the two diastereoisomers of **3ab**, and experimental (black line) ECD spectra.

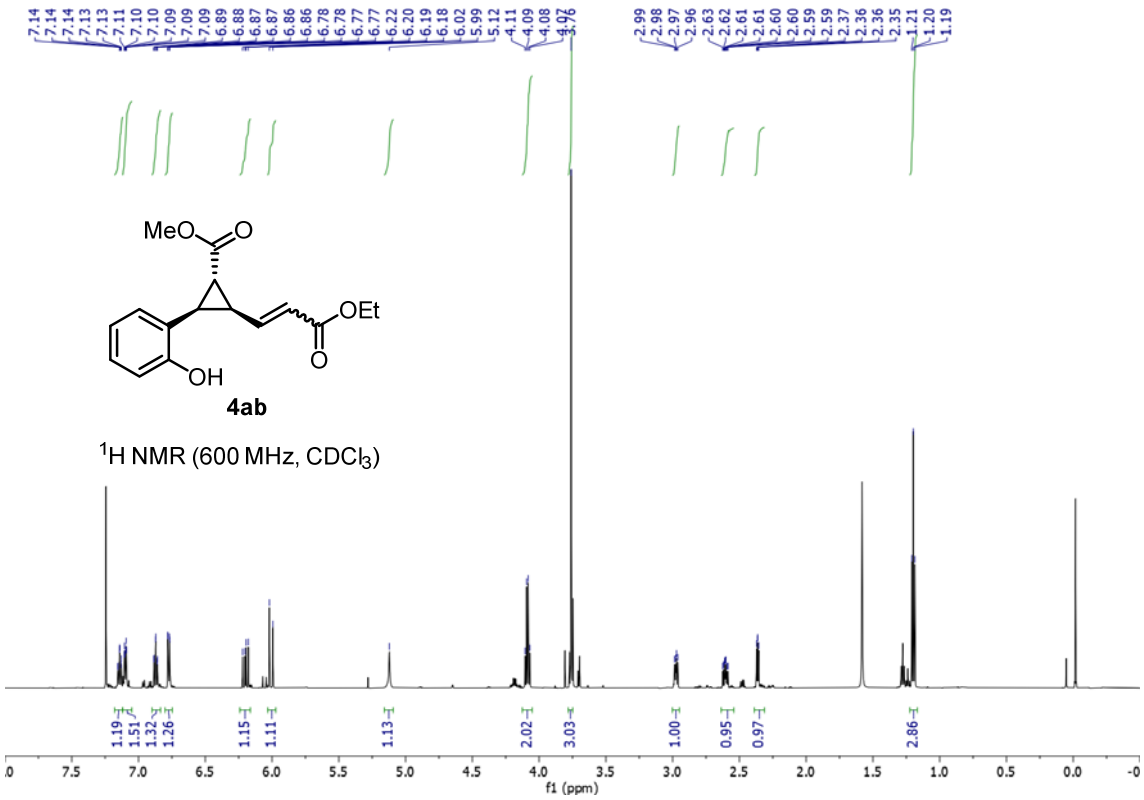
Copies of ^{1}H and ^{13}C NMR spectra of products 4-8

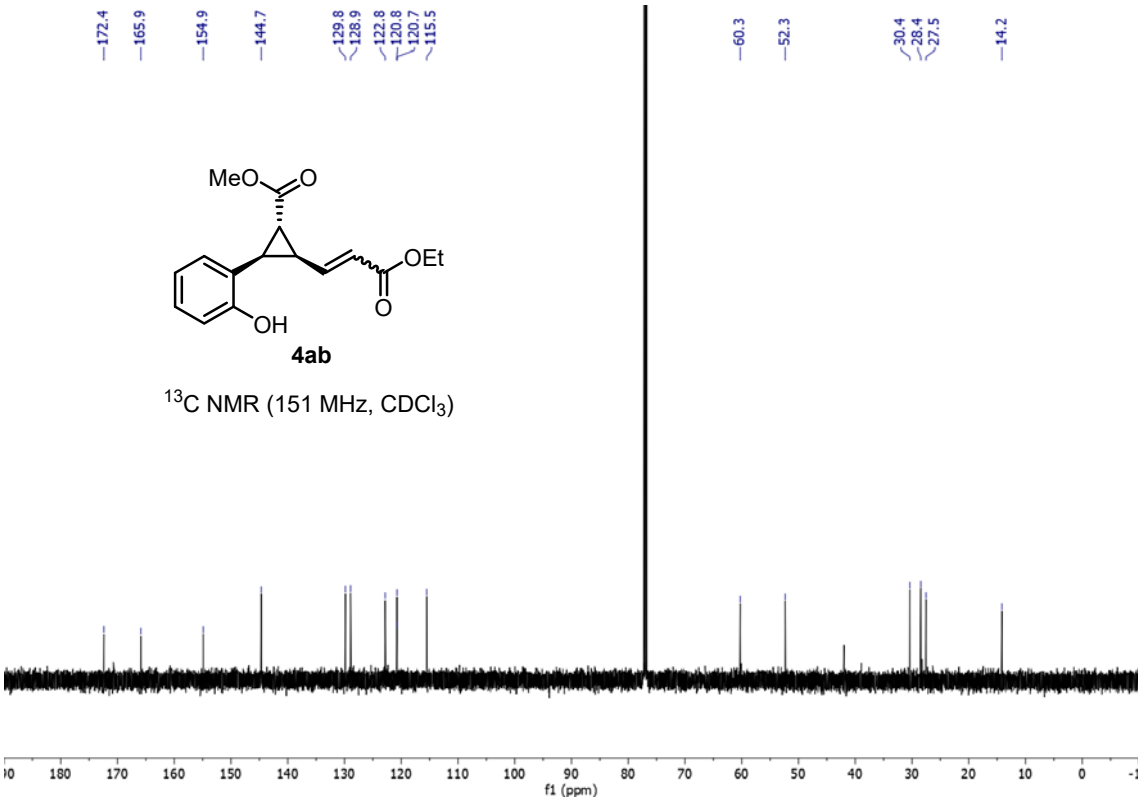
Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4aa



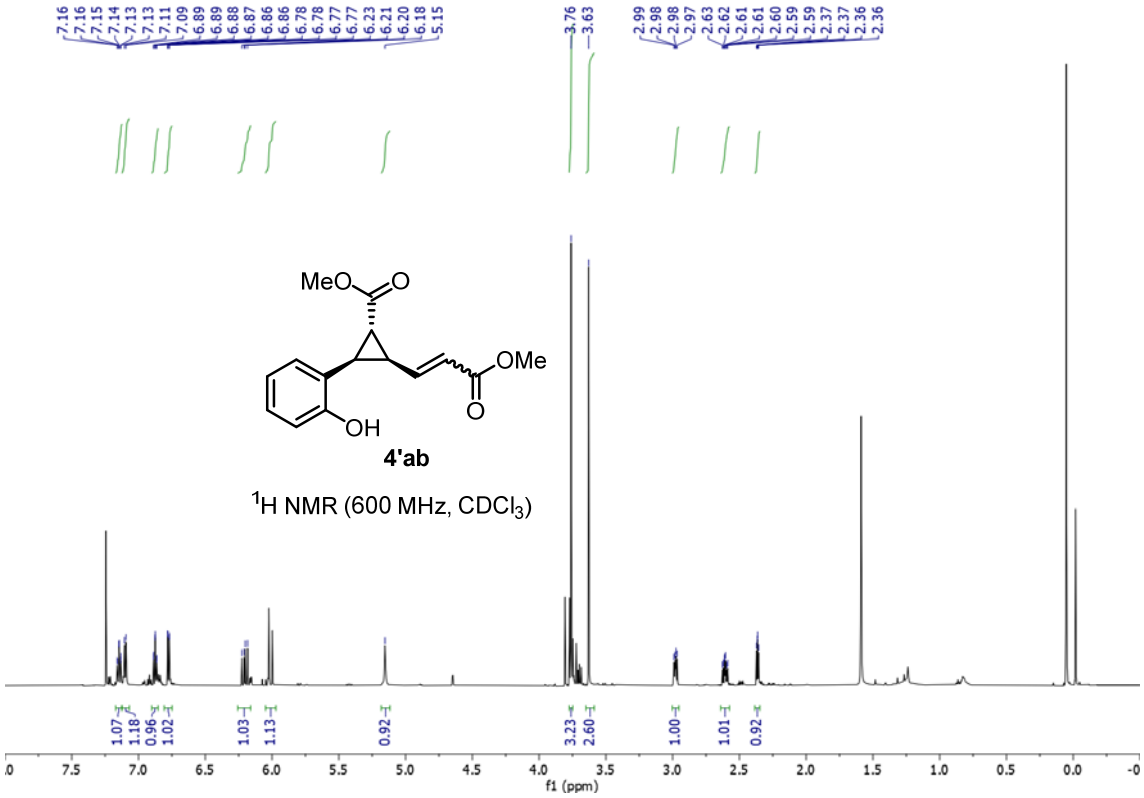


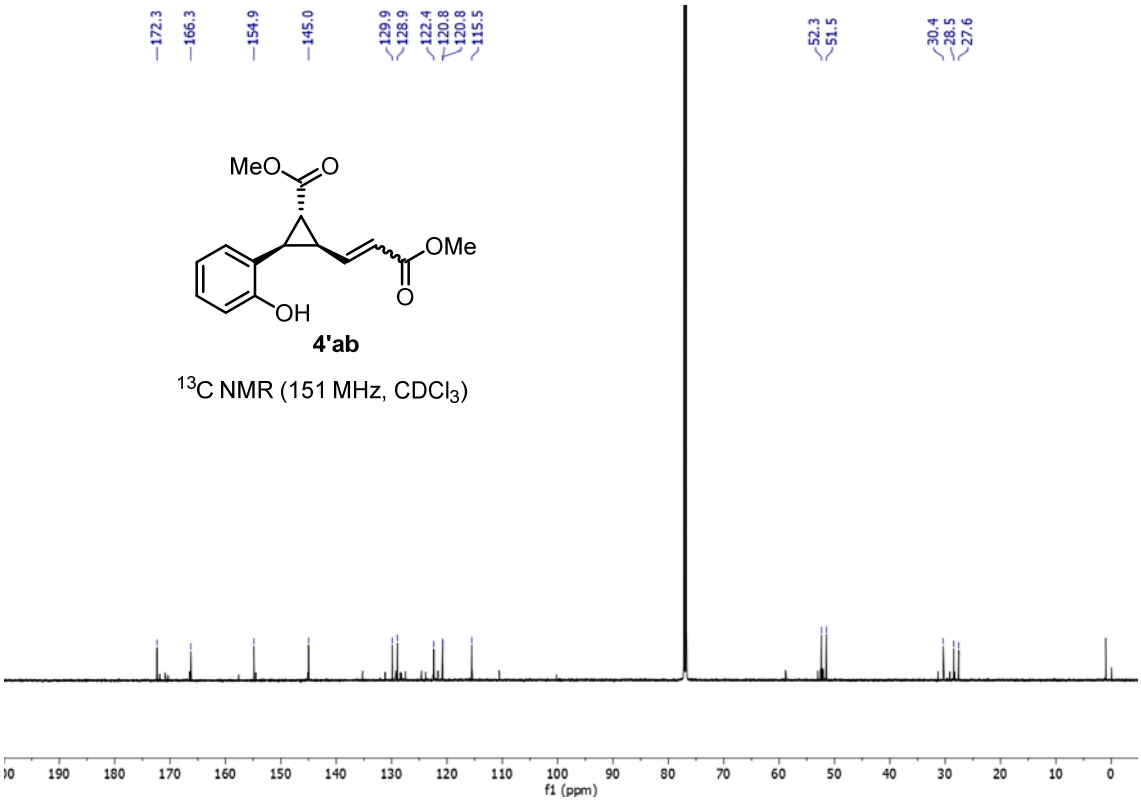
Methyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ab



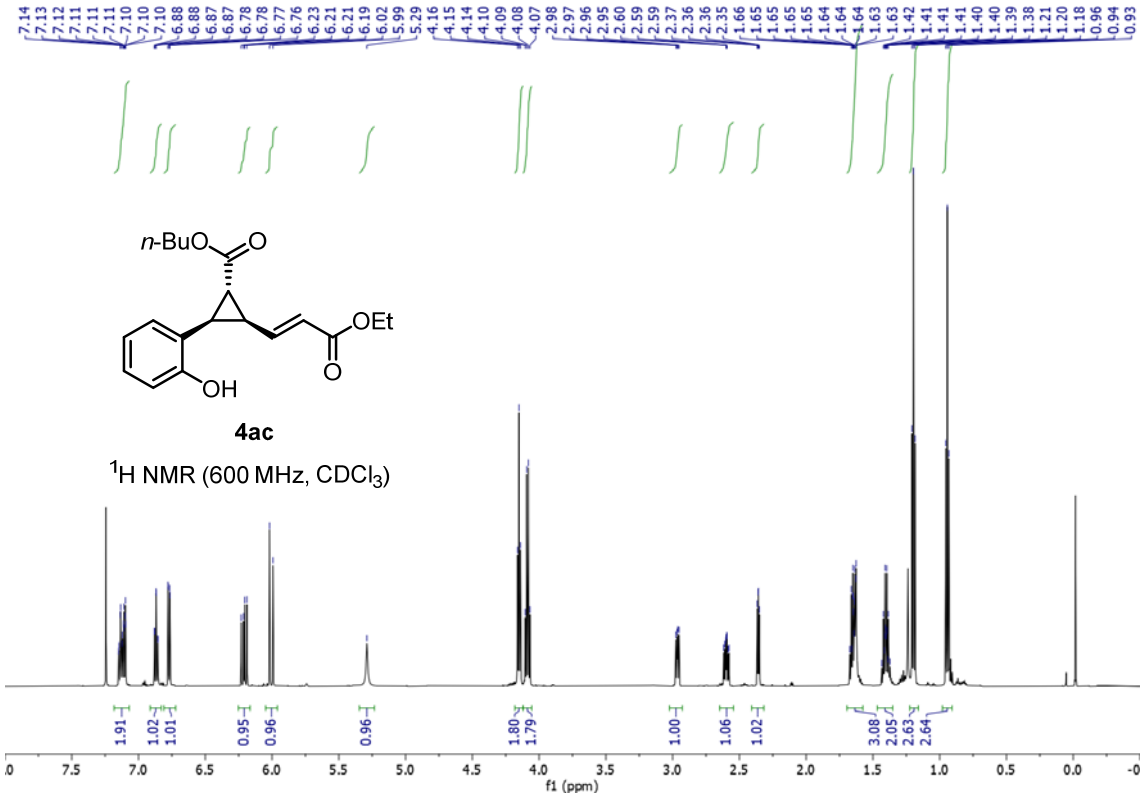


Methyl (1R,2R,3S)-2-(2-hydroxyphenyl)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)cyclopropane-1-carboxylate 4'ab



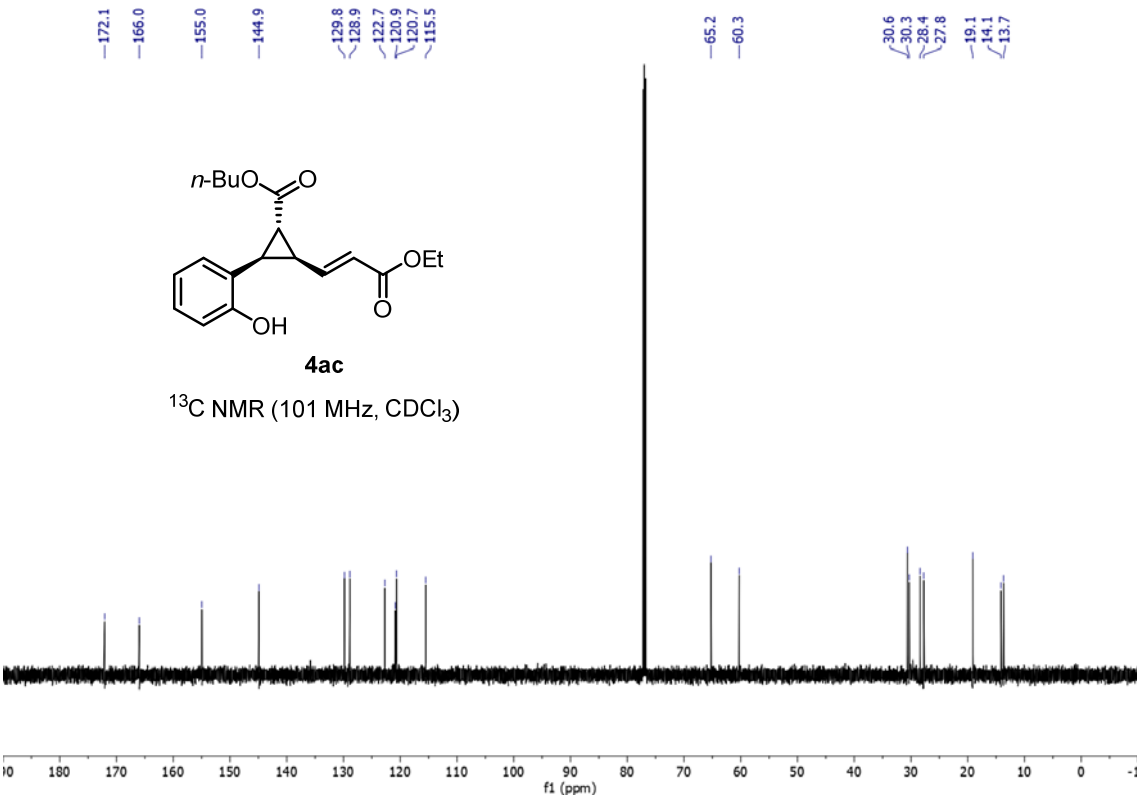


Butyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylatecarboxylate 4ac



4ac

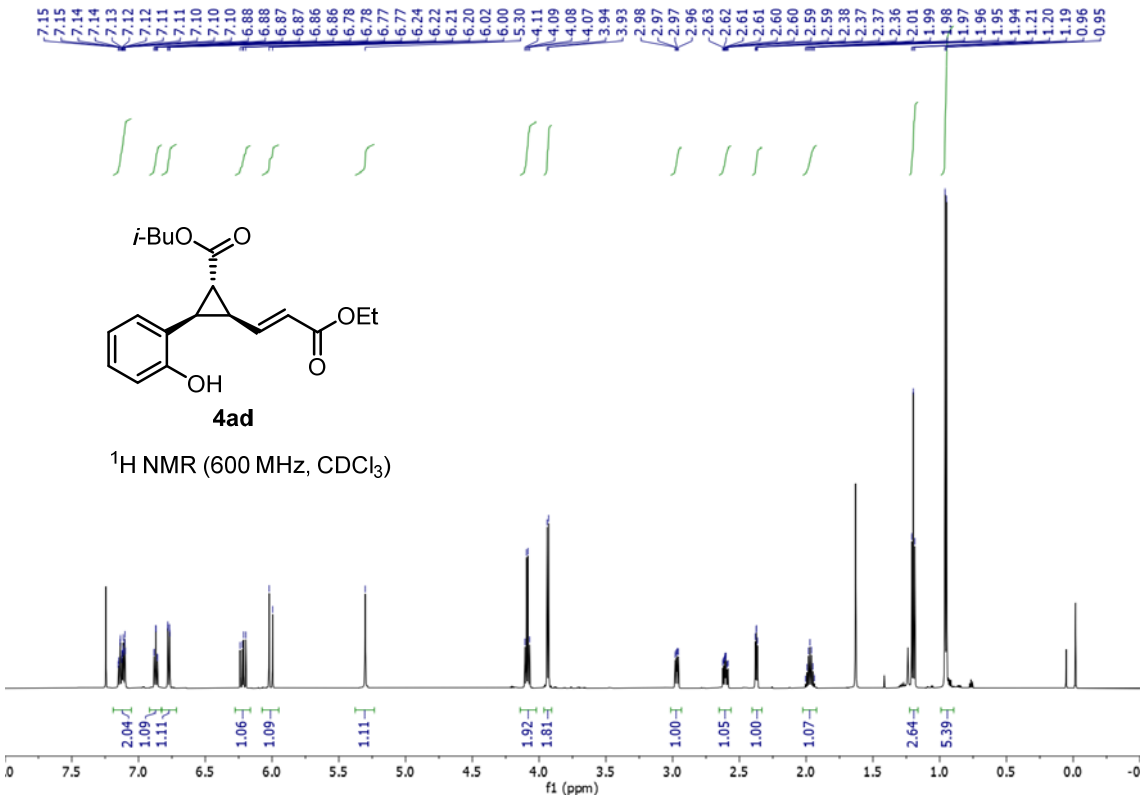
^{1}H NMR (600 MHz, $CDCl_3$)

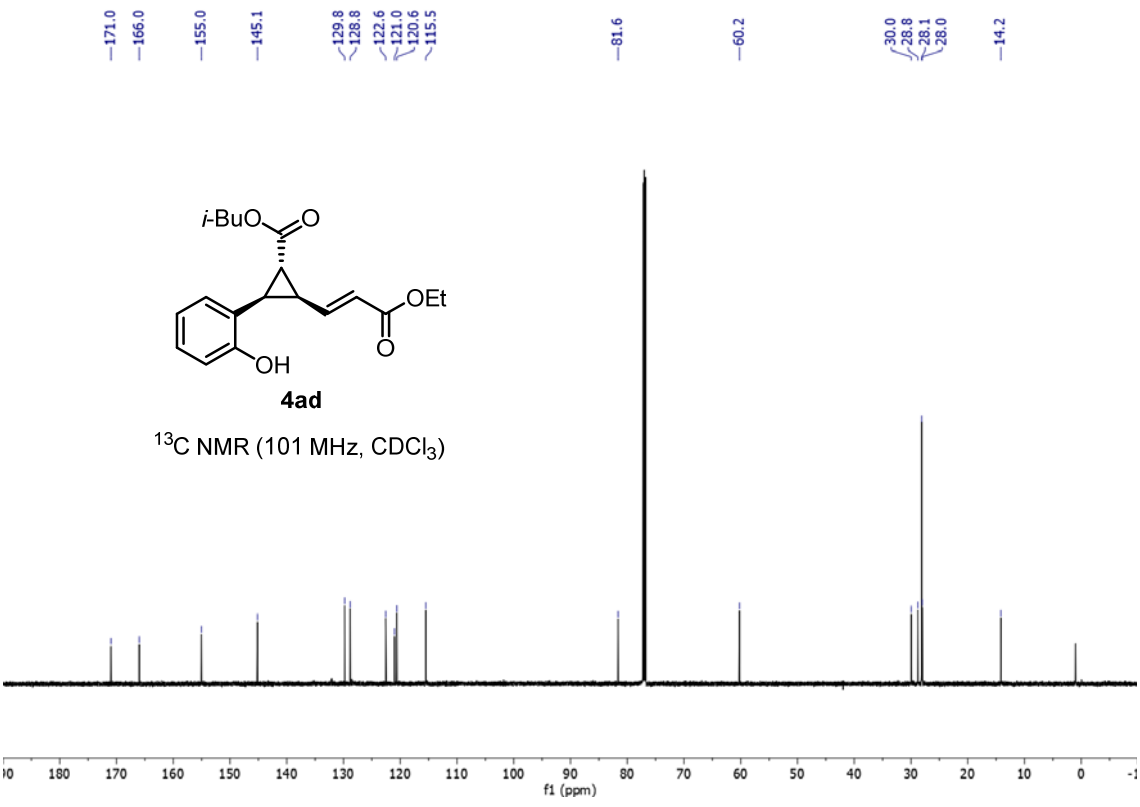


4ac

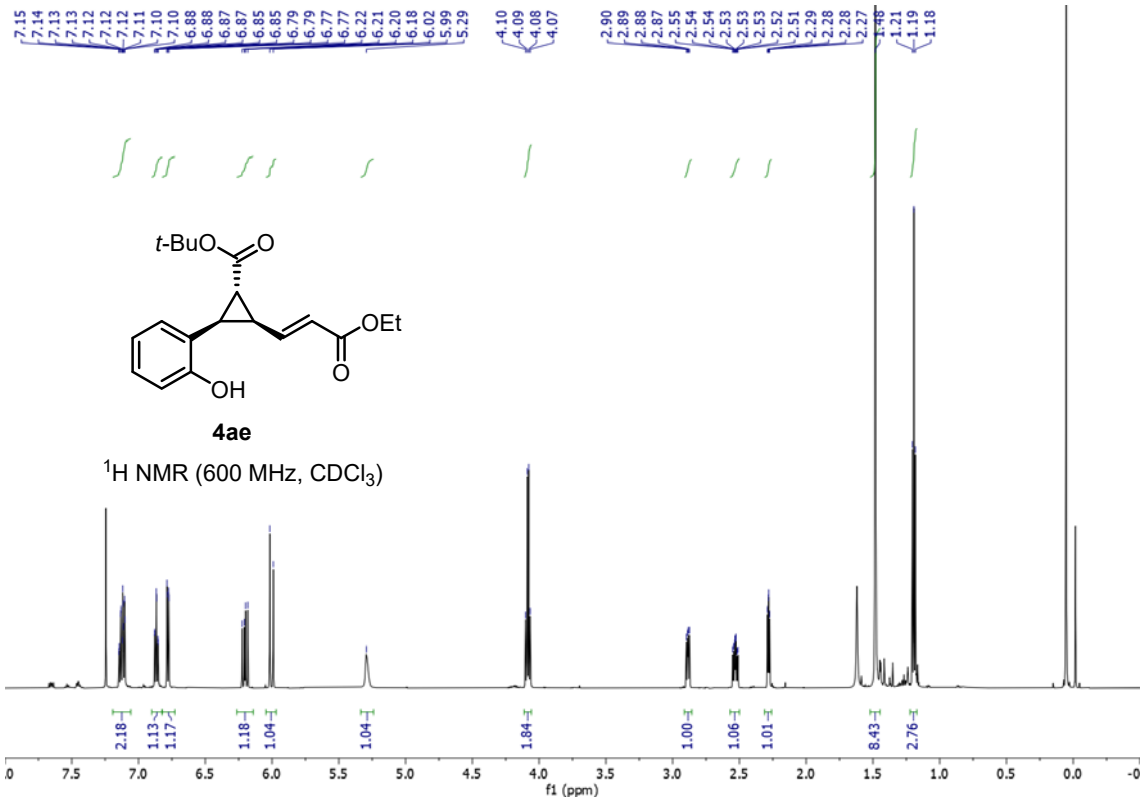
^{13}C NMR (101 MHz, $CDCl_3$)

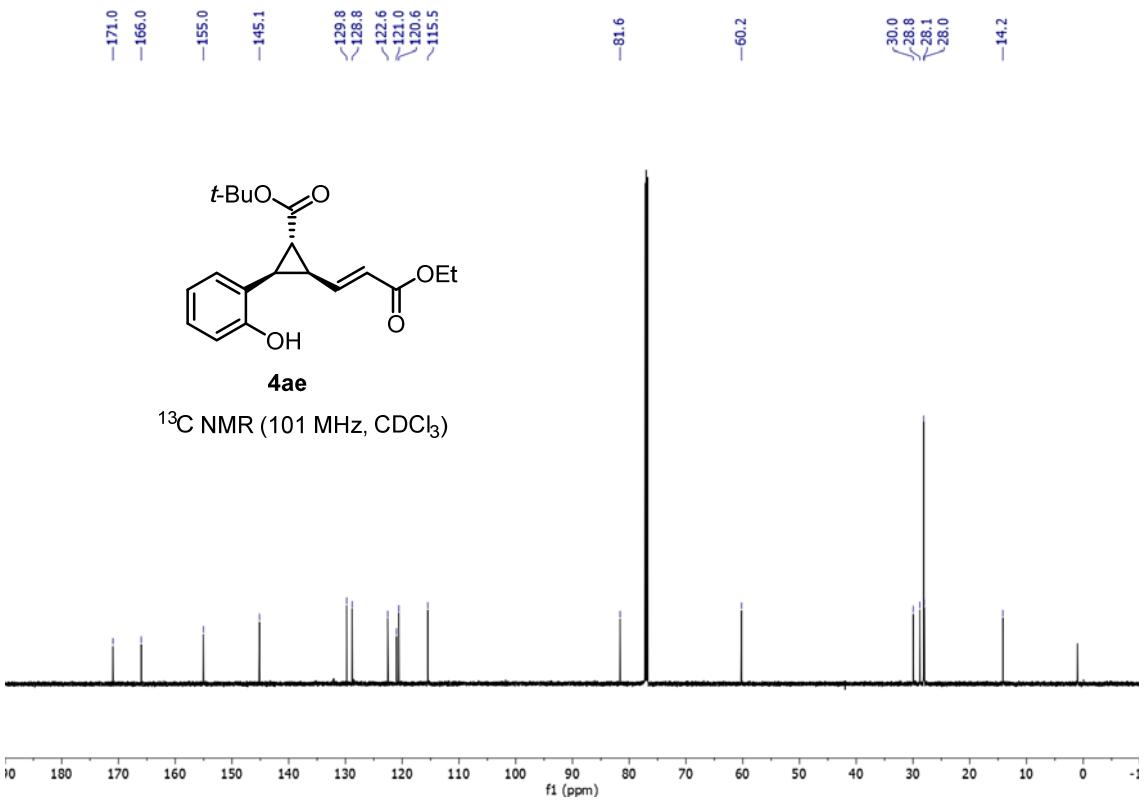
Isobutyl (1R,2S,3R)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ad



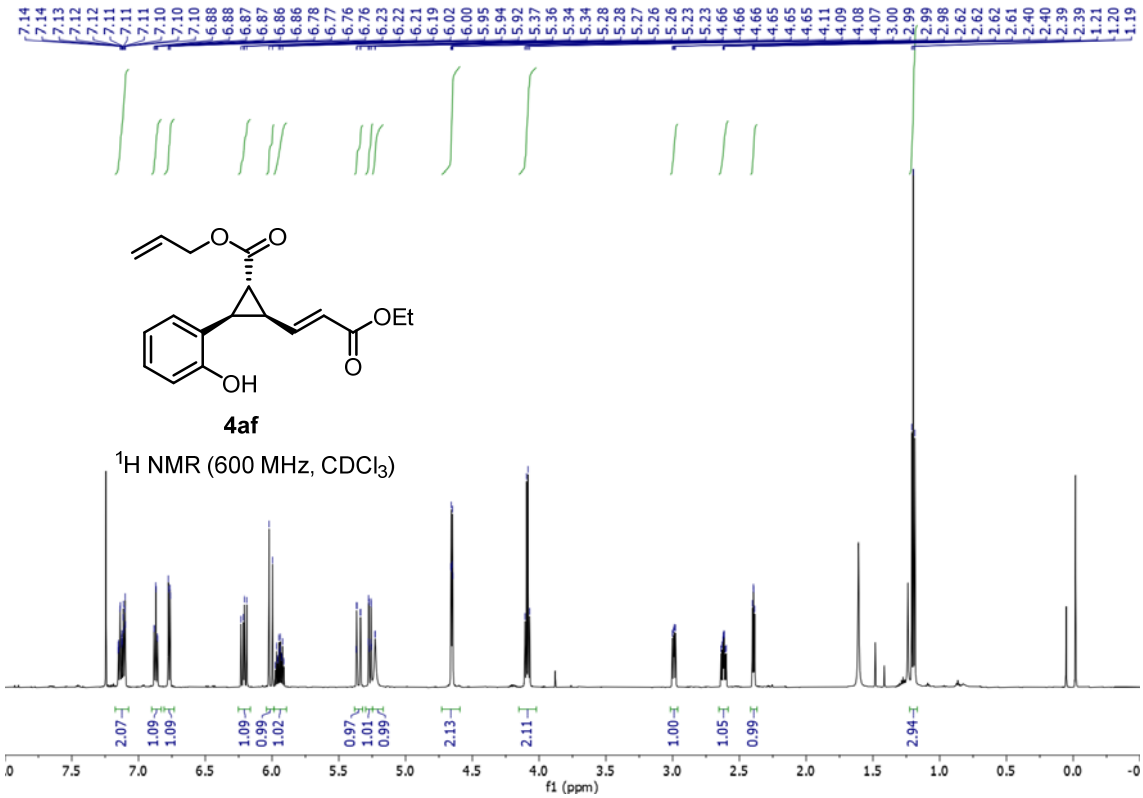


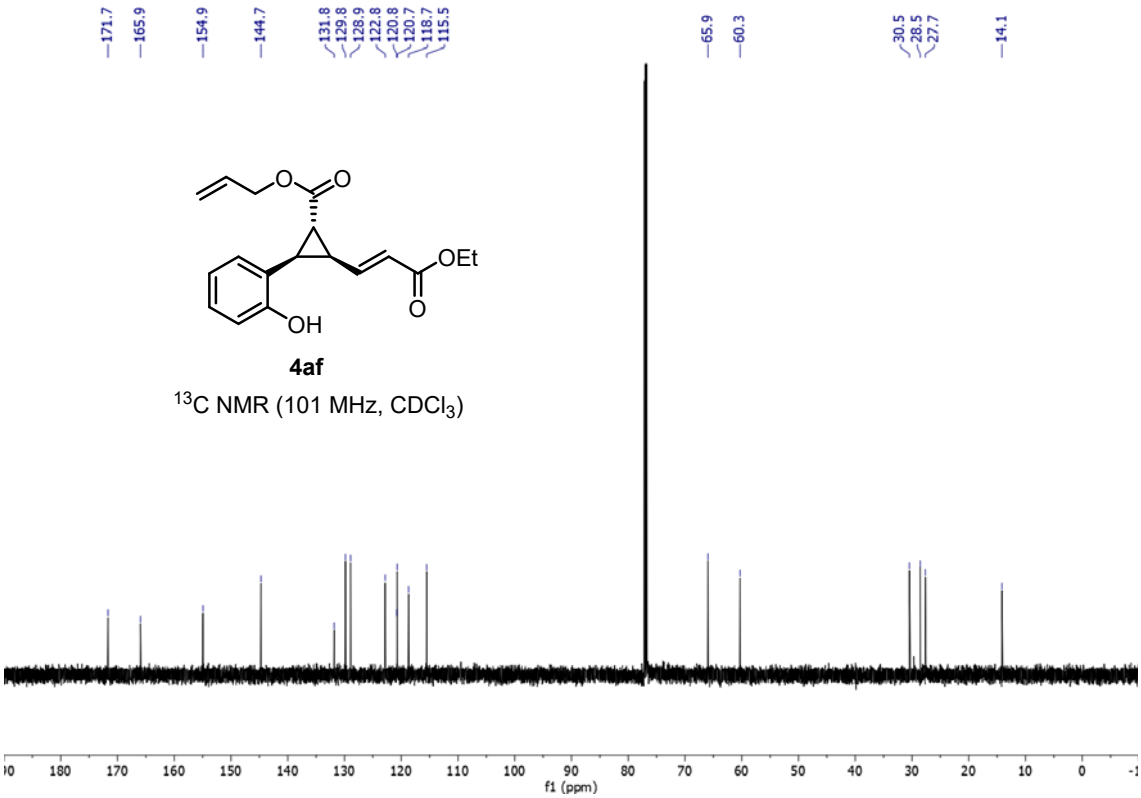
Tert-butyl (1R,2S,3R)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ae



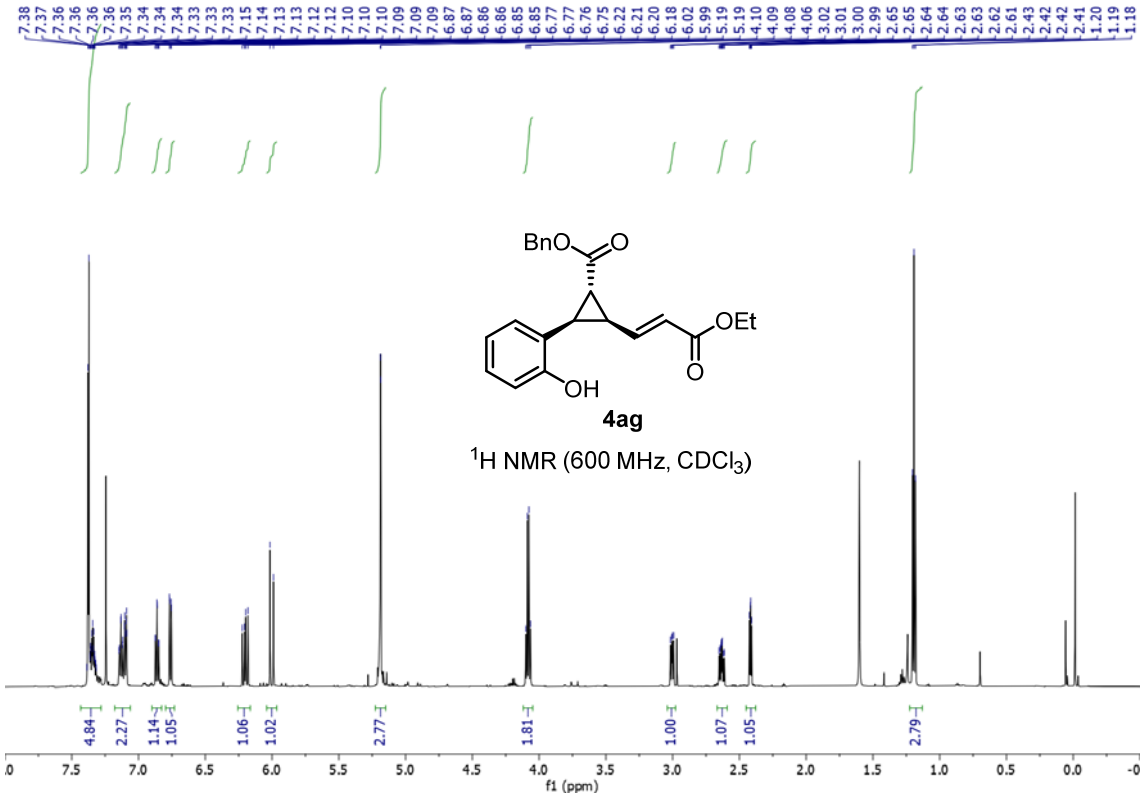


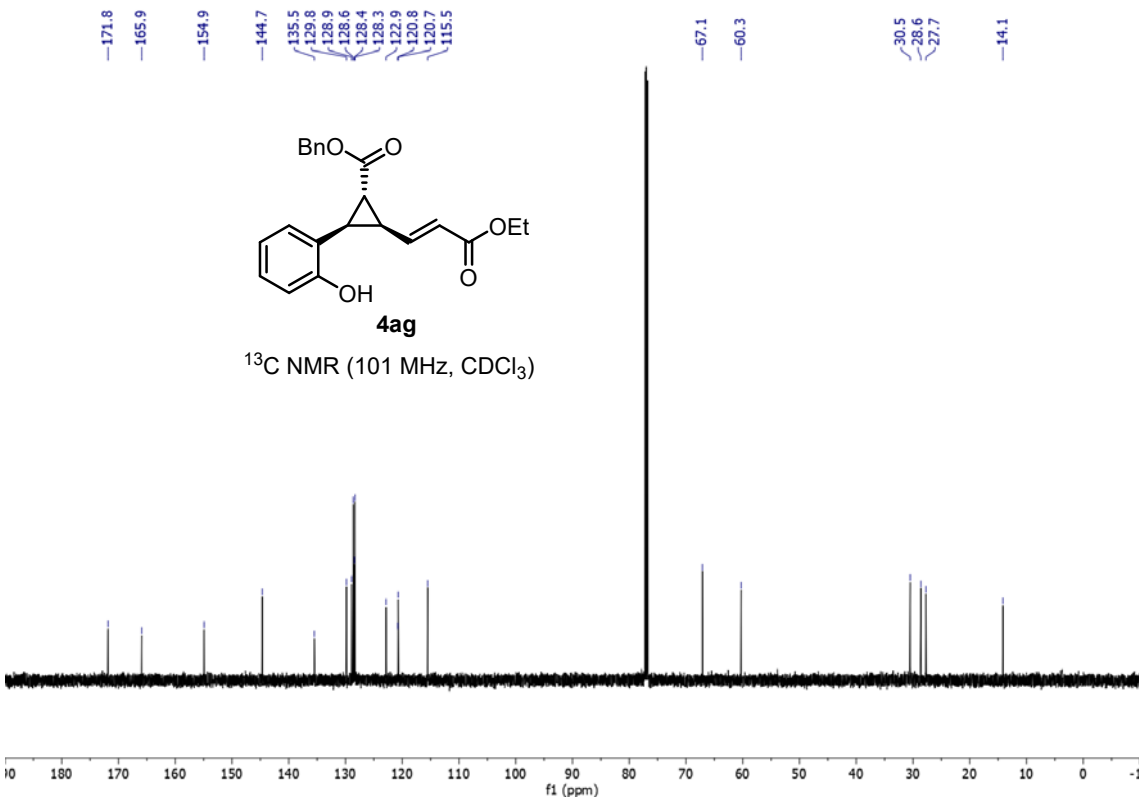
Allyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4af



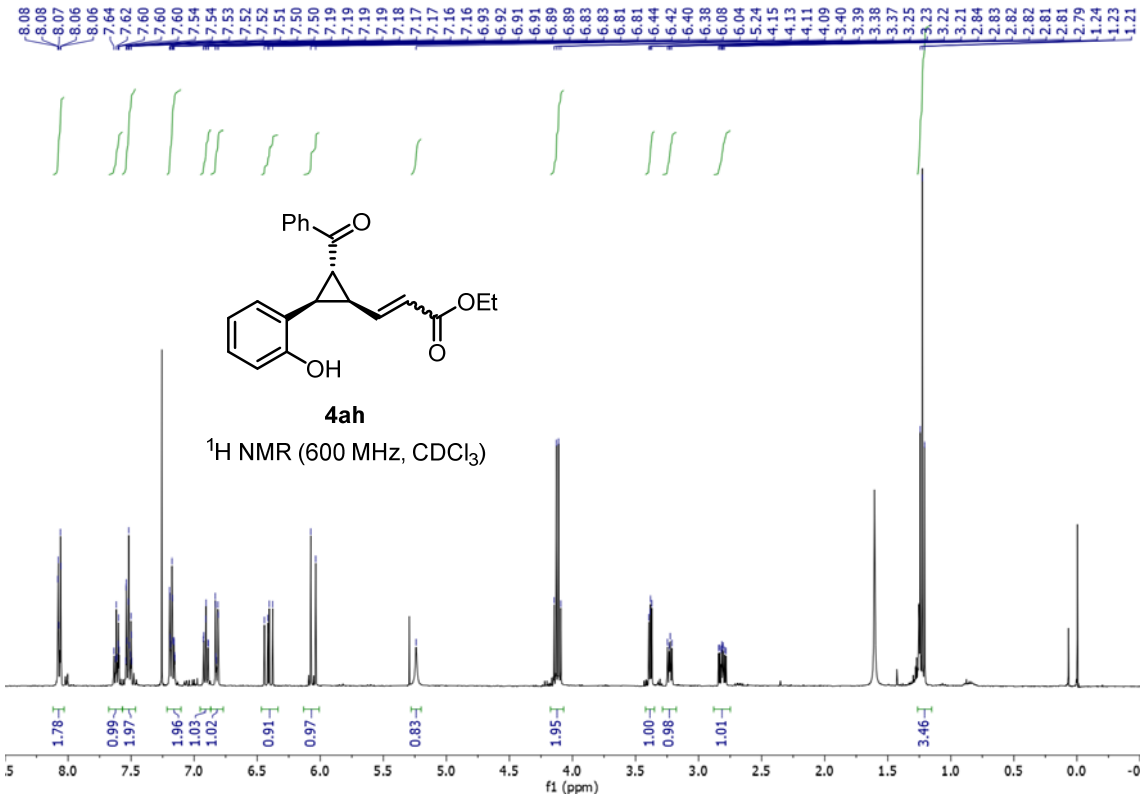


Benzyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ag



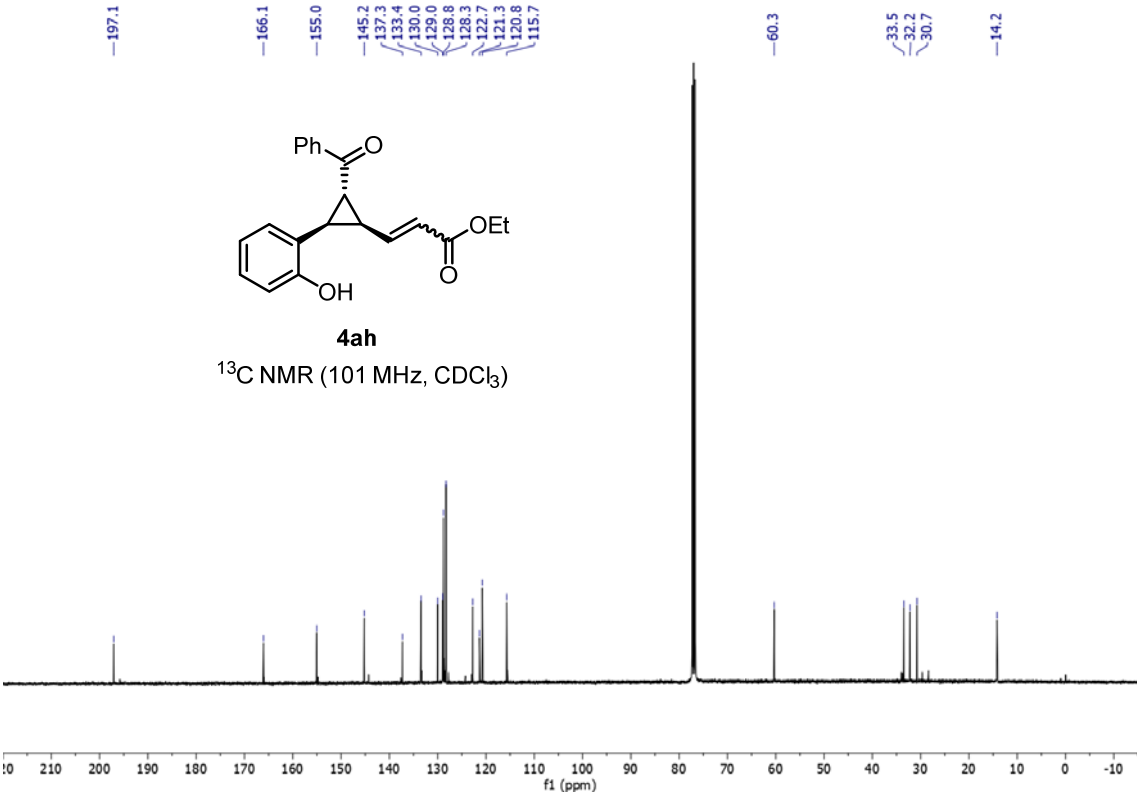


Ethyl--3-((1S,2R,3R)-2-benzoyl-3-(2-hydroxyphenyl)cyclopropyl)acrylate 4ah



4ah

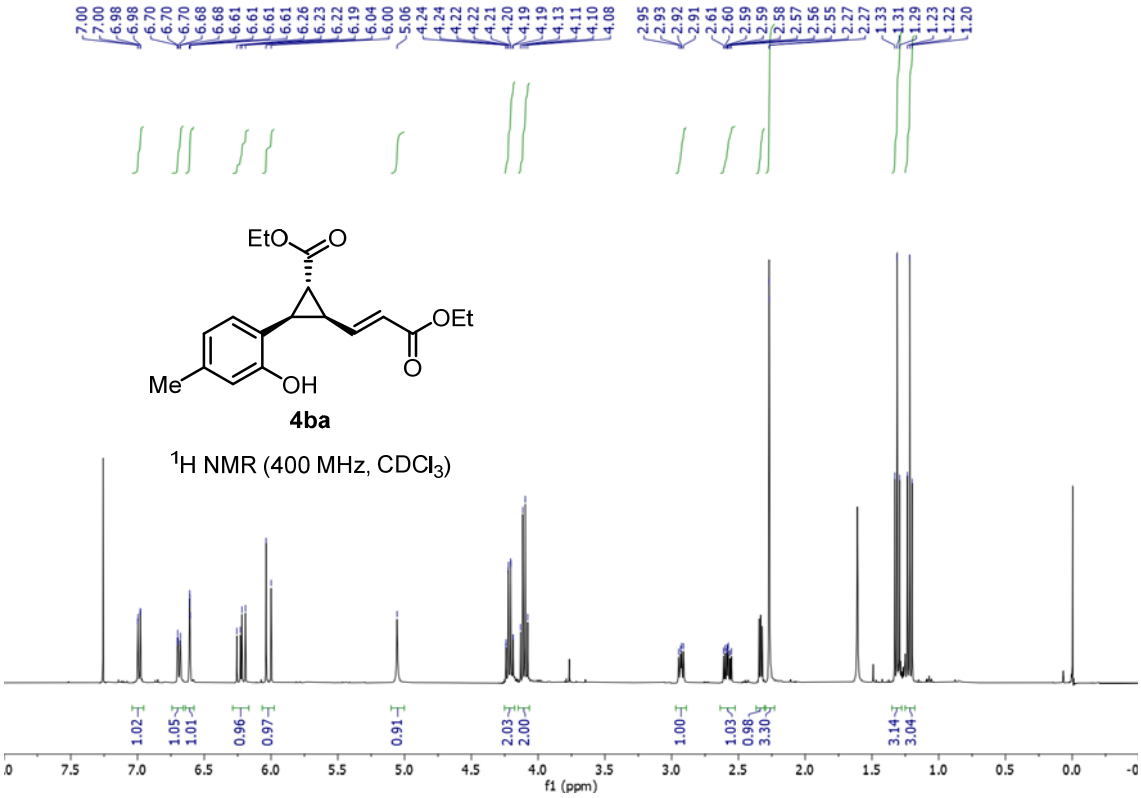
^{1}H NMR (600 MHz, $CDCl_3$)

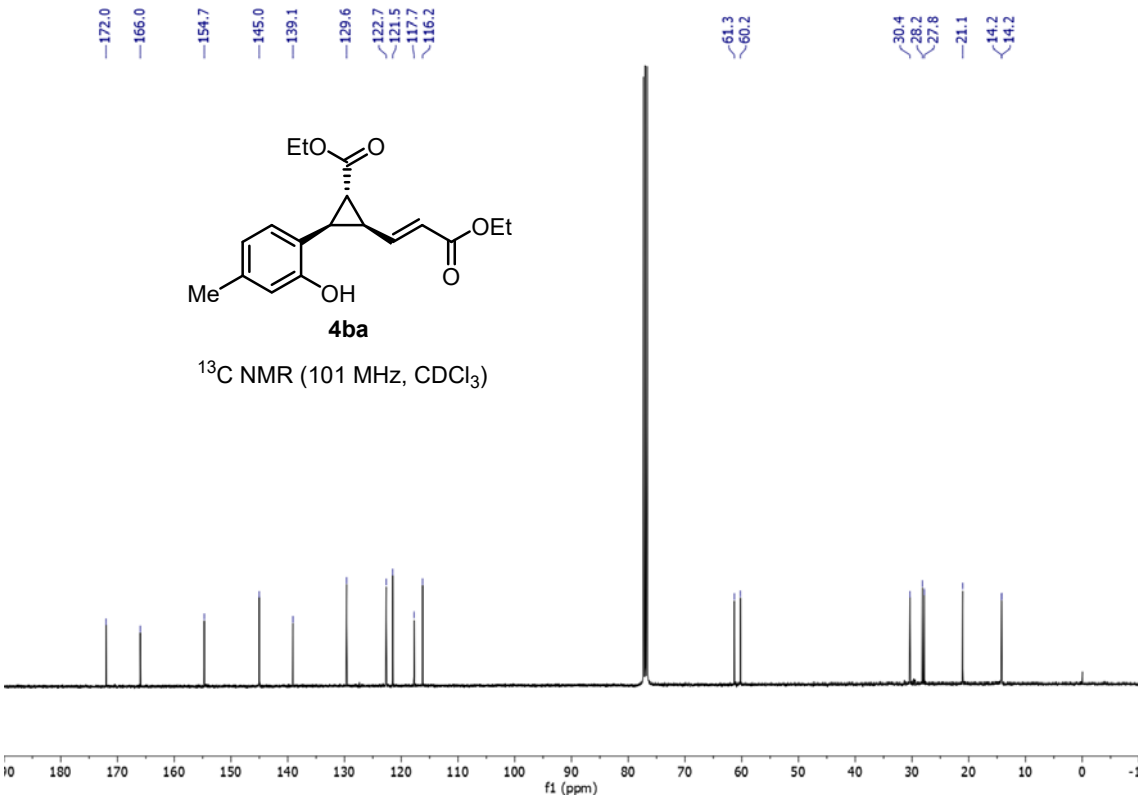


4ah

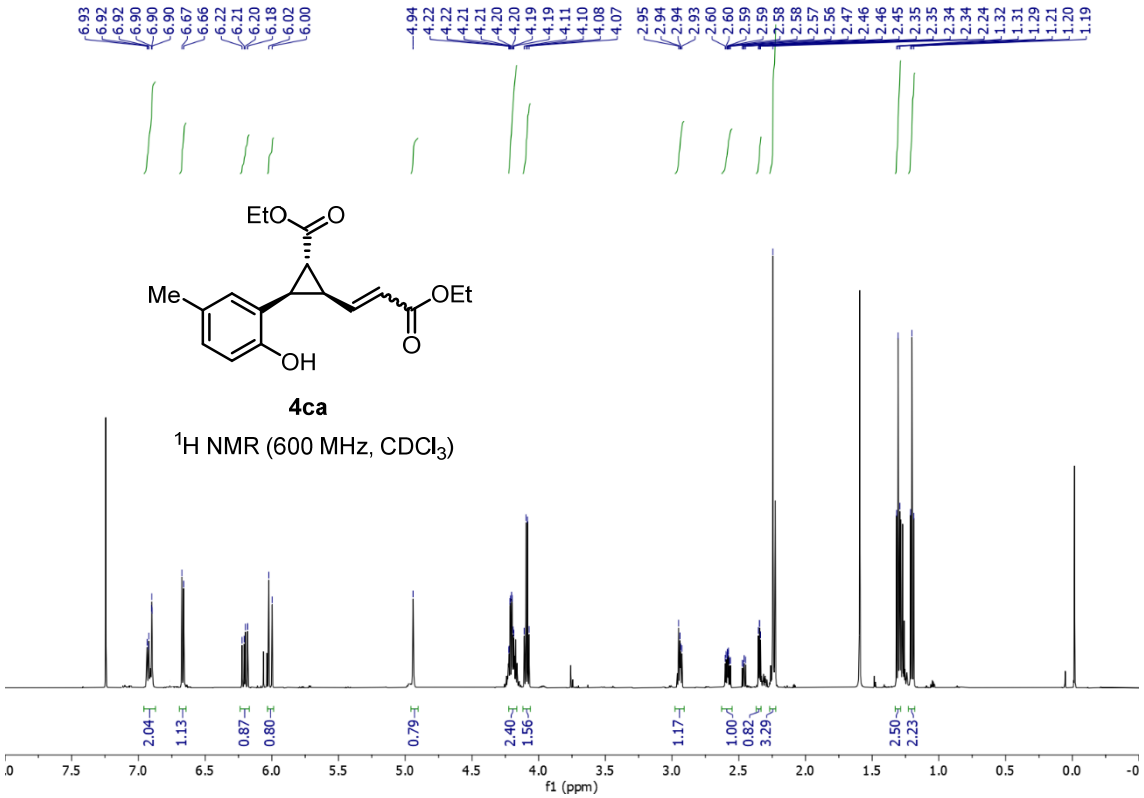
^{13}C NMR (101 MHz, $CDCl_3$)

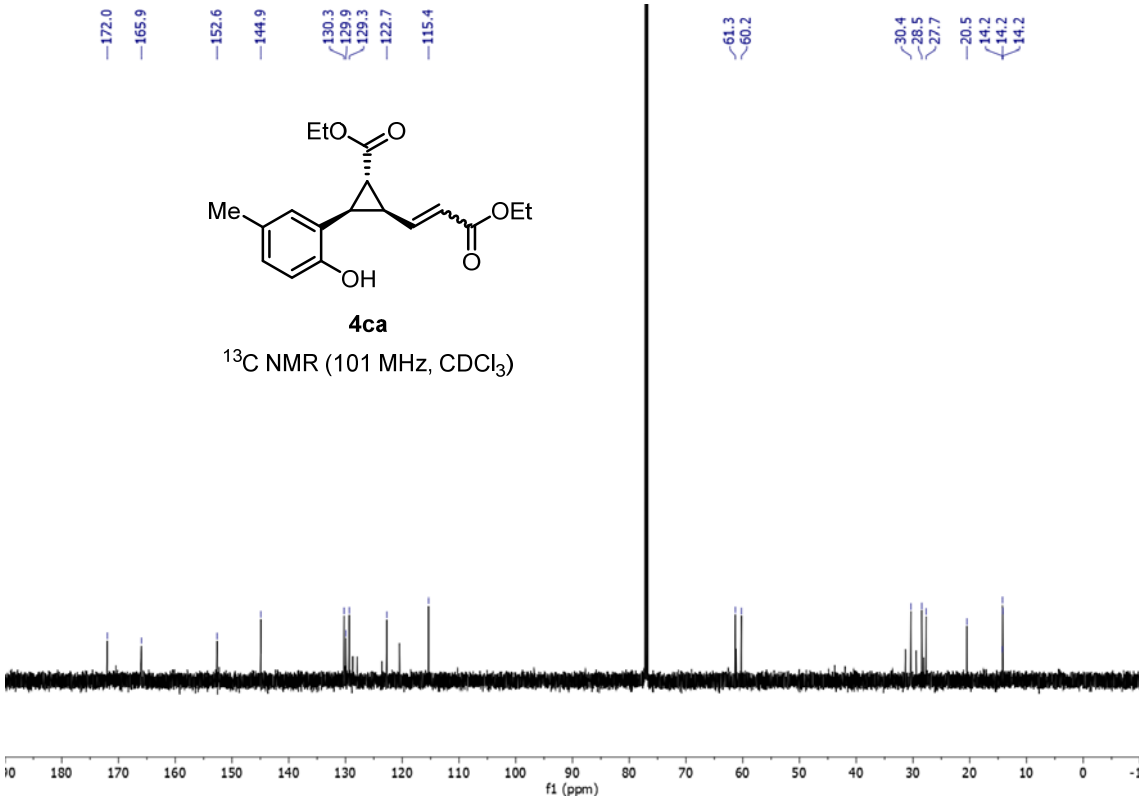
Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-4-methylphenyl)cyclopropane-1-carboxylate 4ba



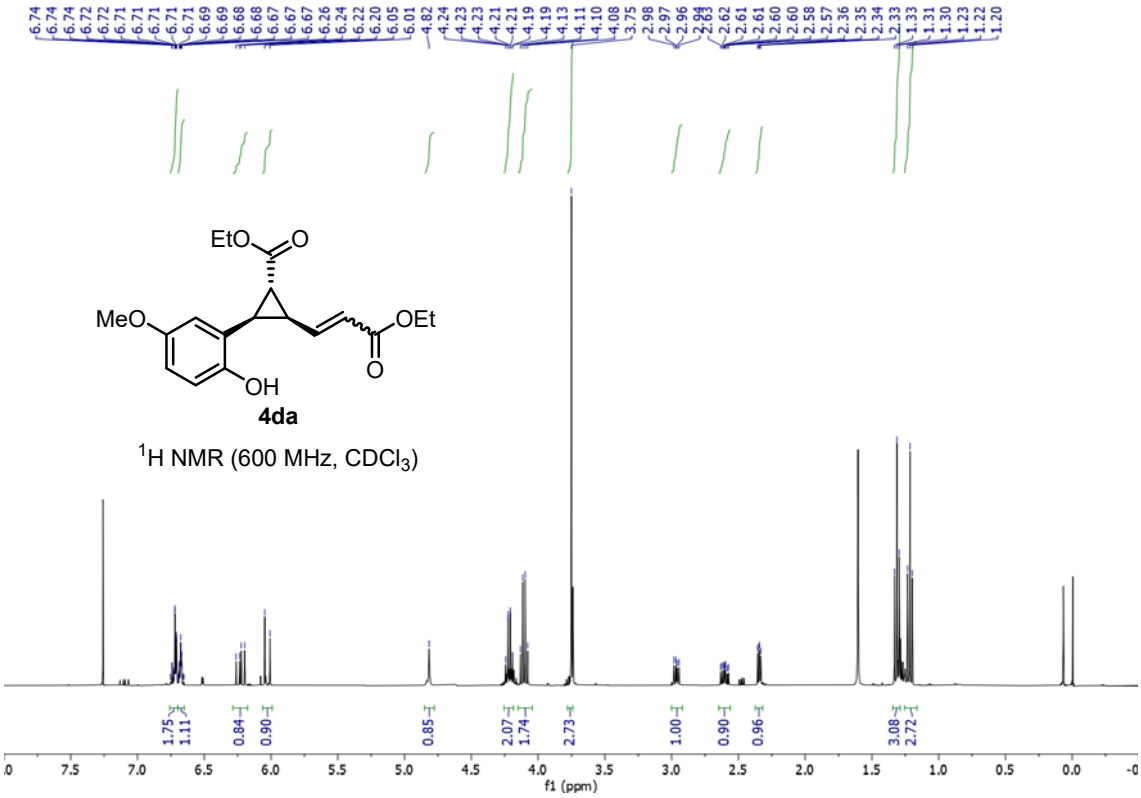


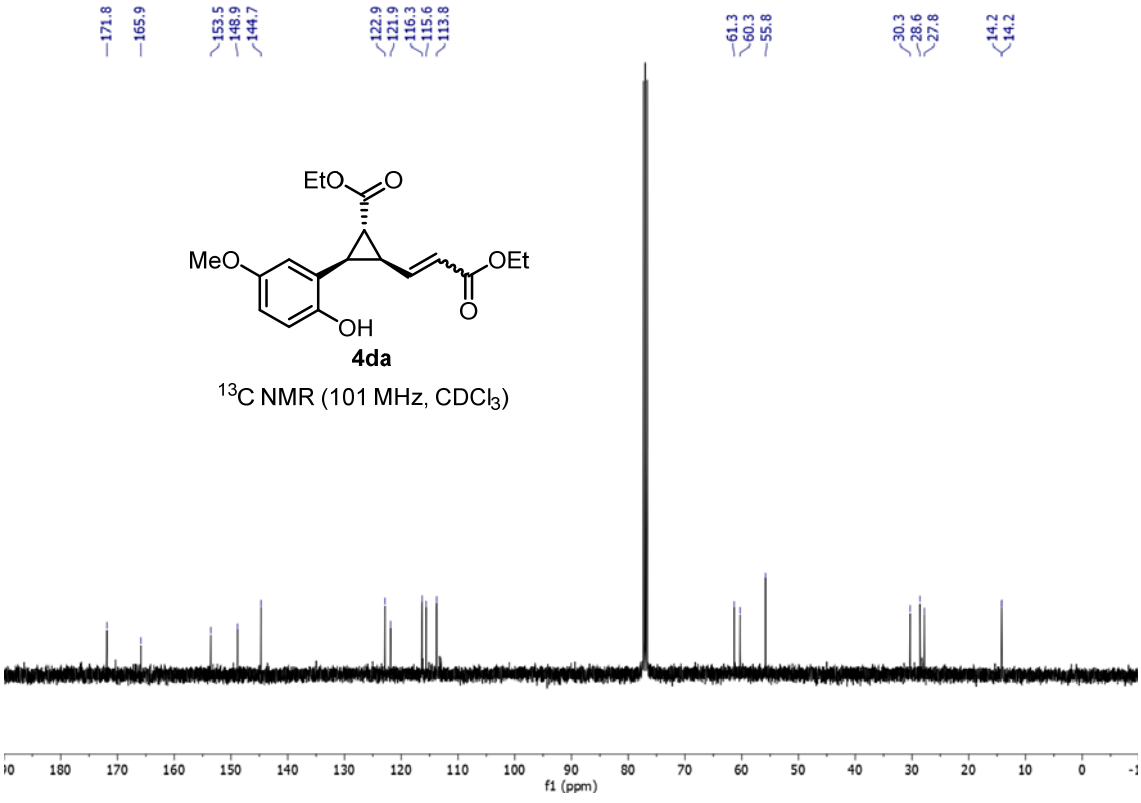
Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-5-methylphenyl)cyclopropane-1-carboxylate 4ca



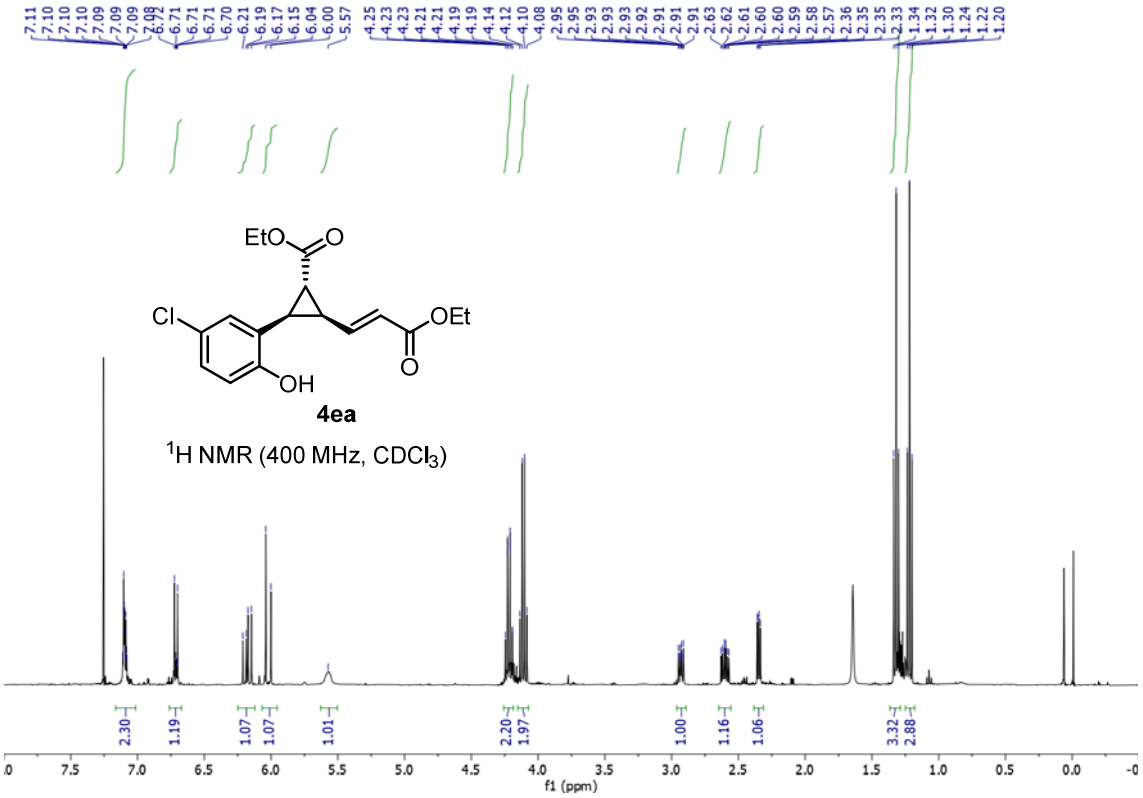


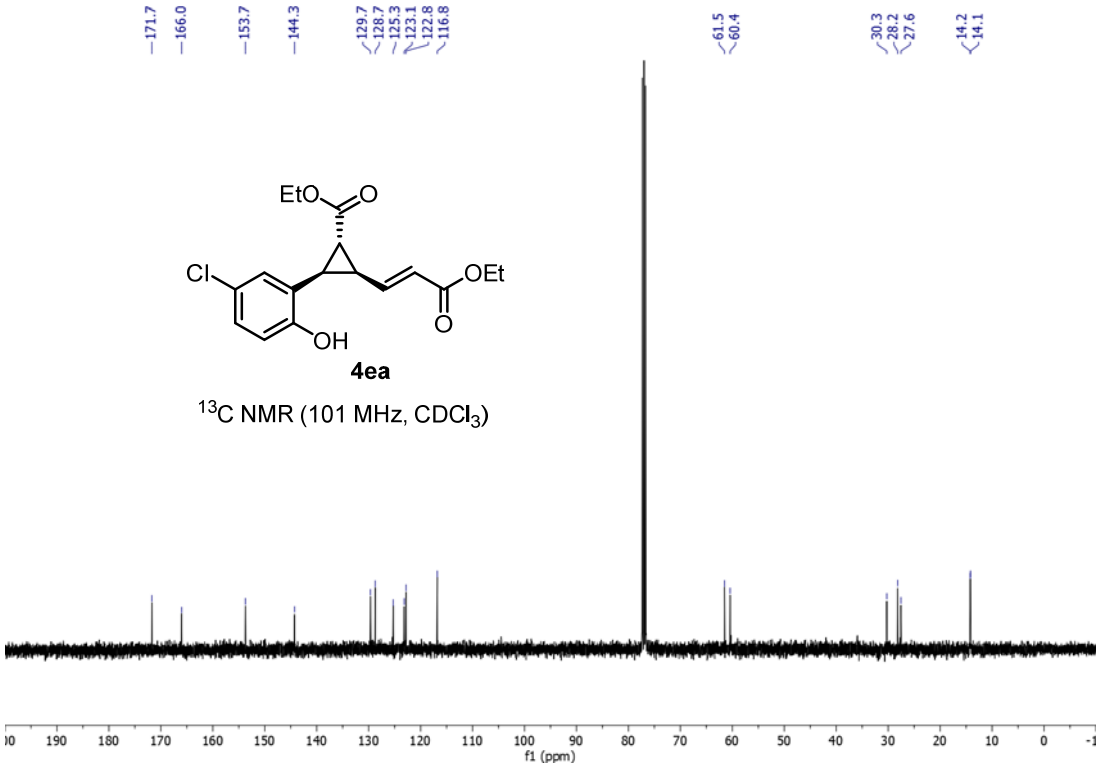
Ethyl (1R,2S,3R)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-5-methoxyphenyl)cyclopropane -1-carboxylate 4da



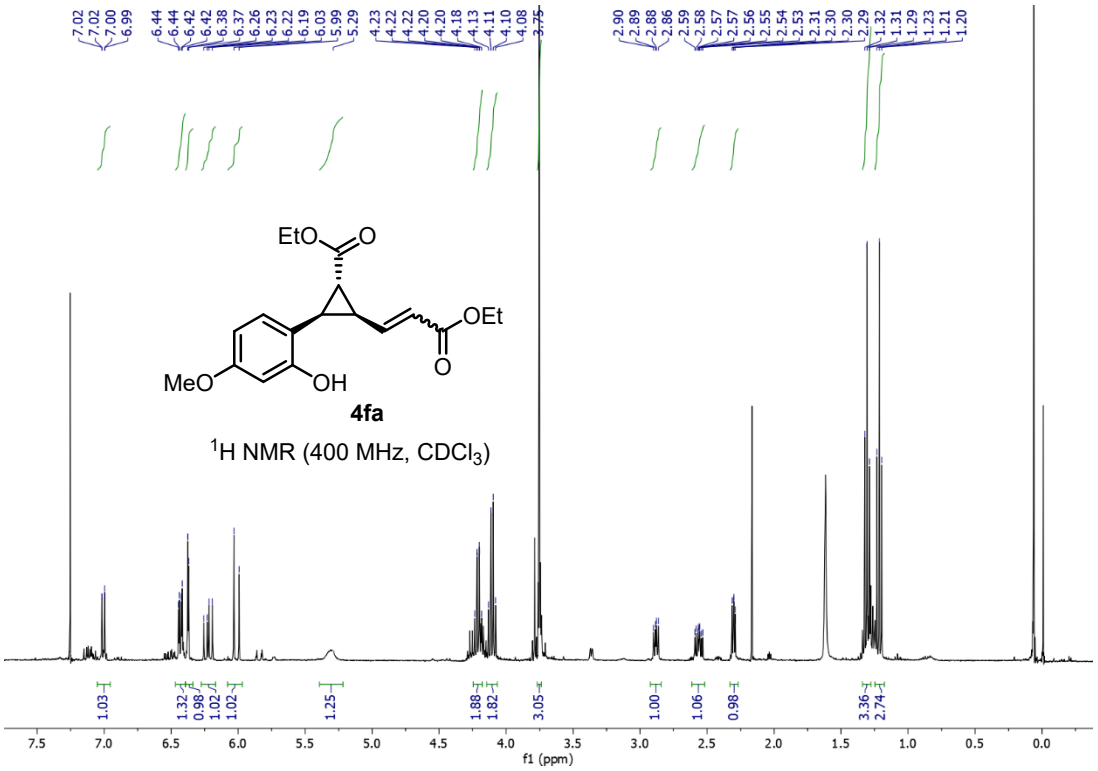


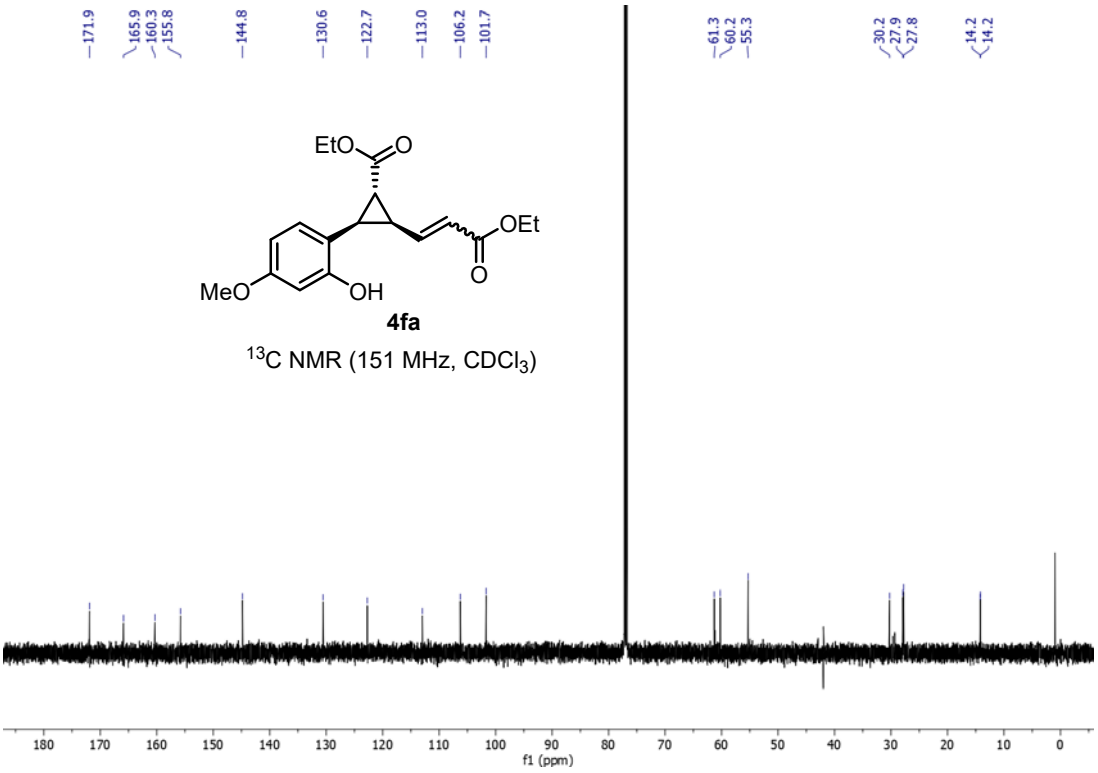
Ethyl (1R,2R,3S)-2-(5-chloro-2-hydroxyphenyl)-3-(-3-ethoxy-3-oxoprop-1-en-1-yl)cyclopropane-1-carboxylate 4ea



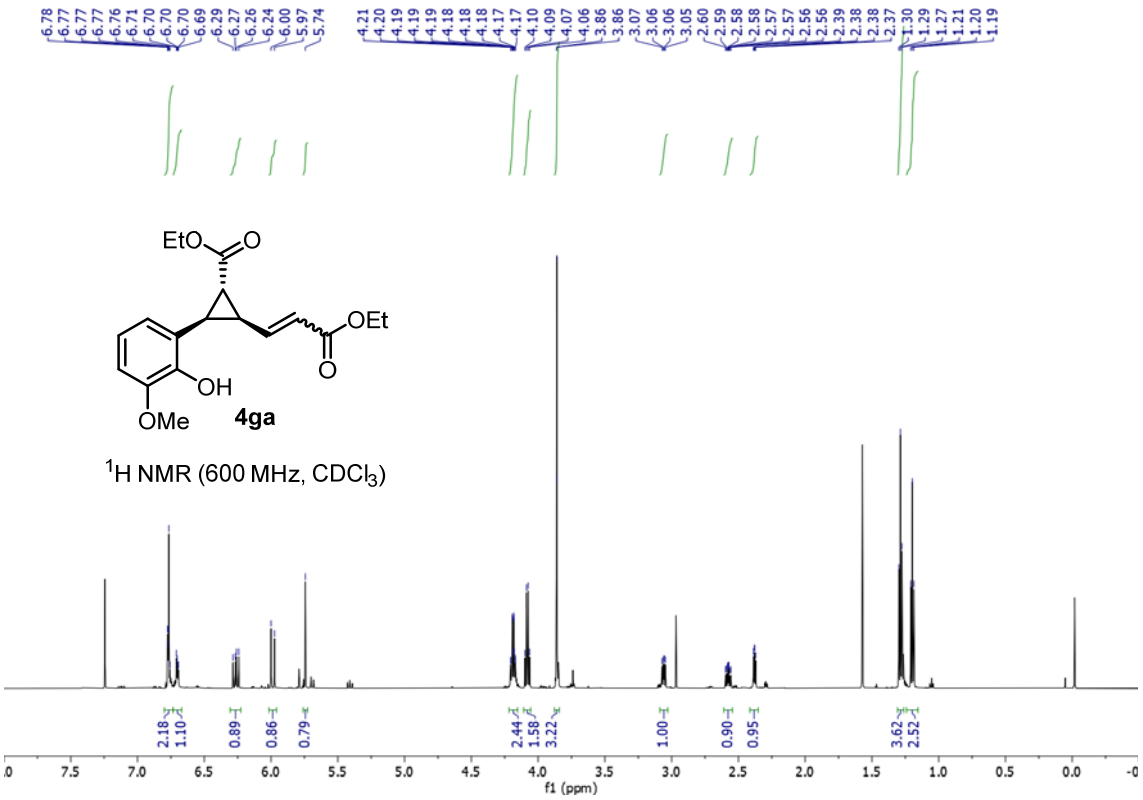


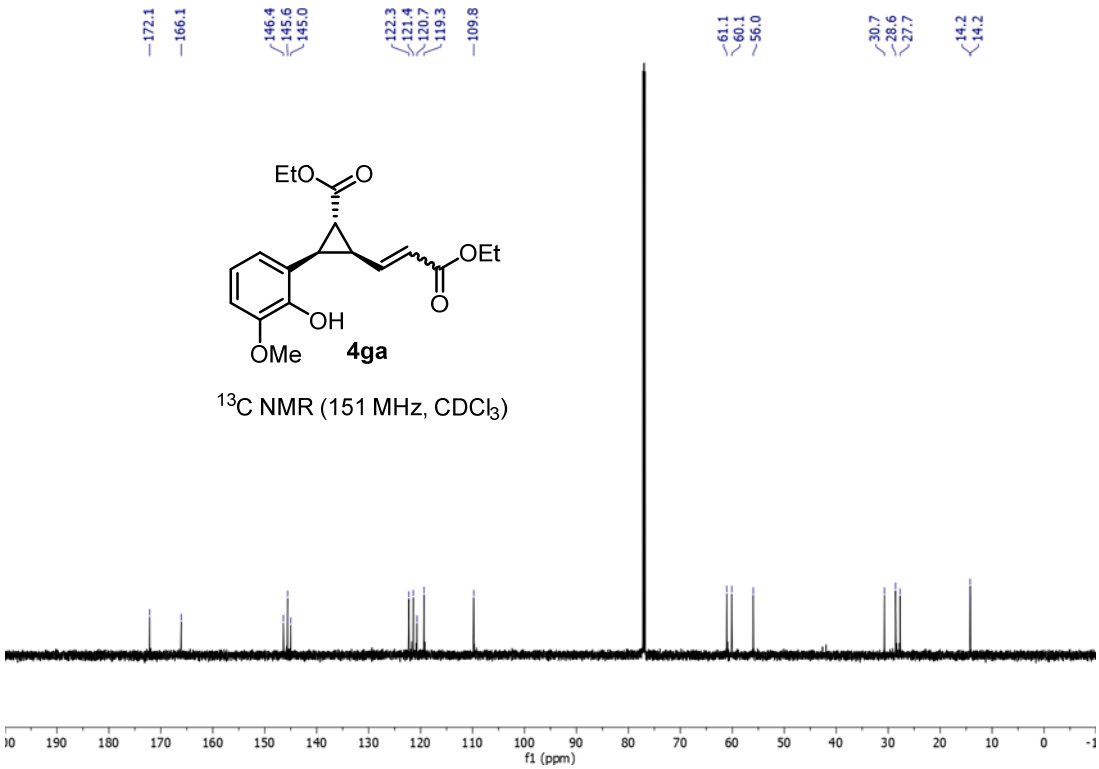
Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-4-methoxyphenyl)cyclopropane-1-carboxylate 4fa



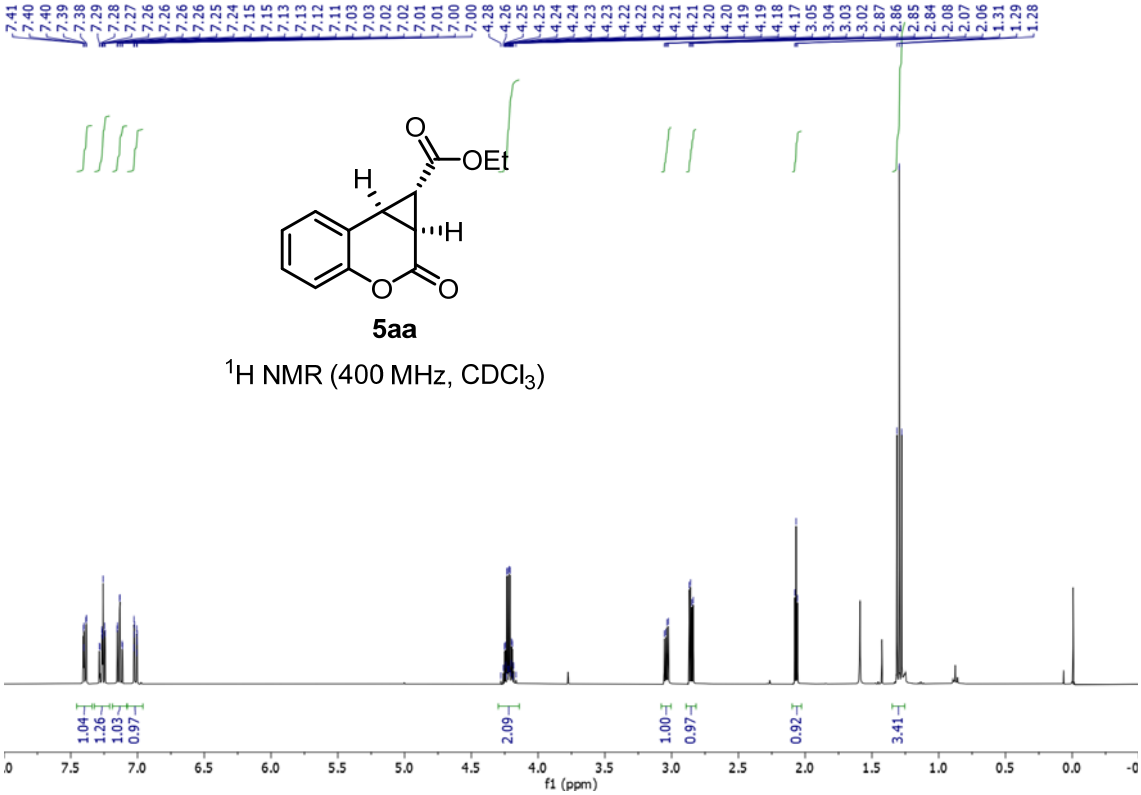


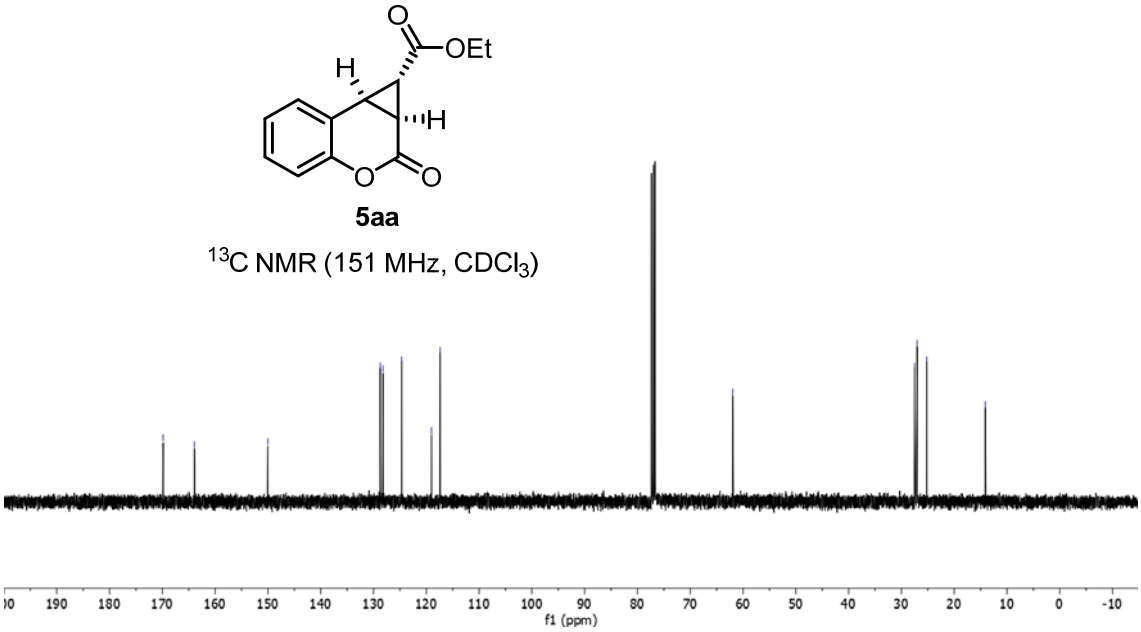
Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-3-methoxyphenyl)cyclopropane-1-carboxylate 4ga



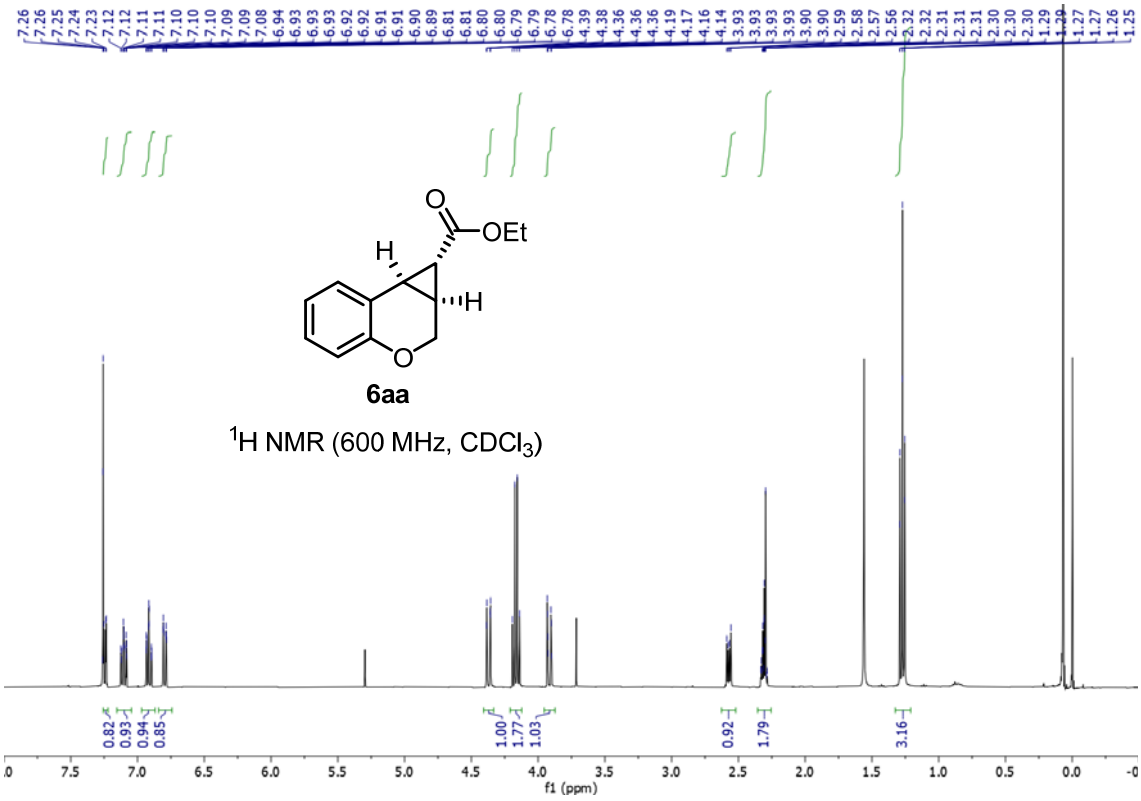


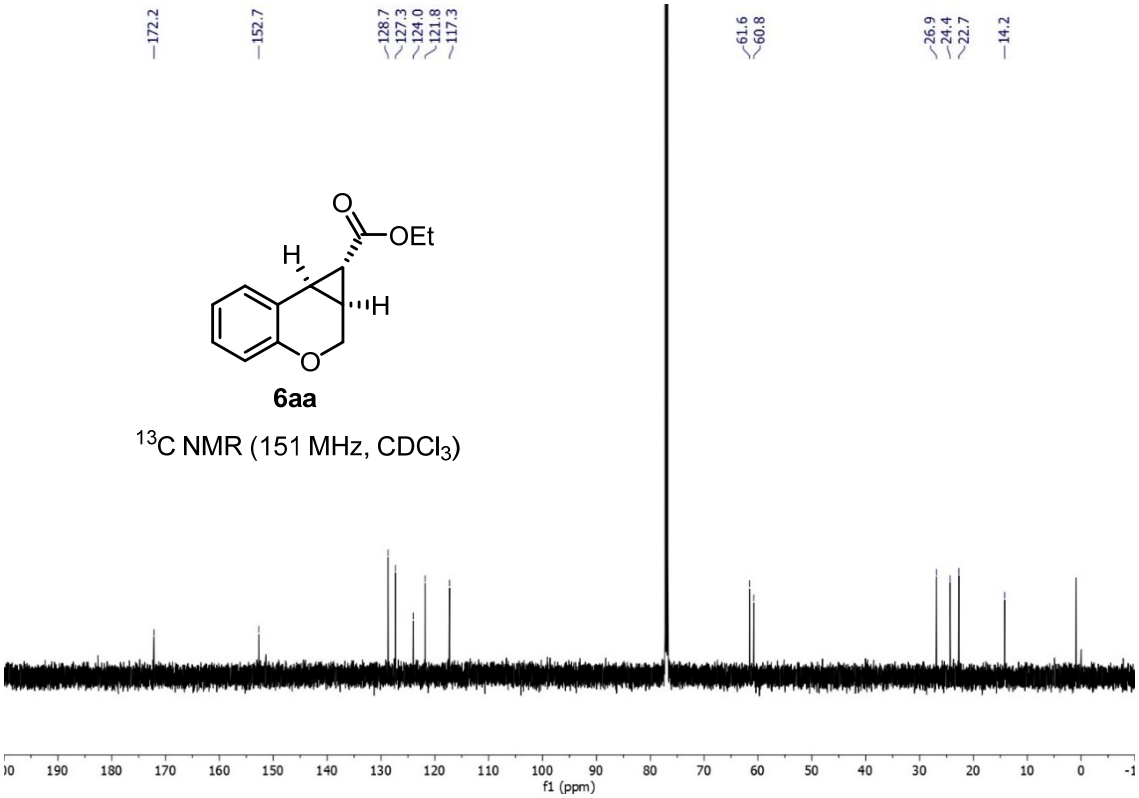
Ethyl (1S,1aS,7bS)-2-oxo-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate 5aa





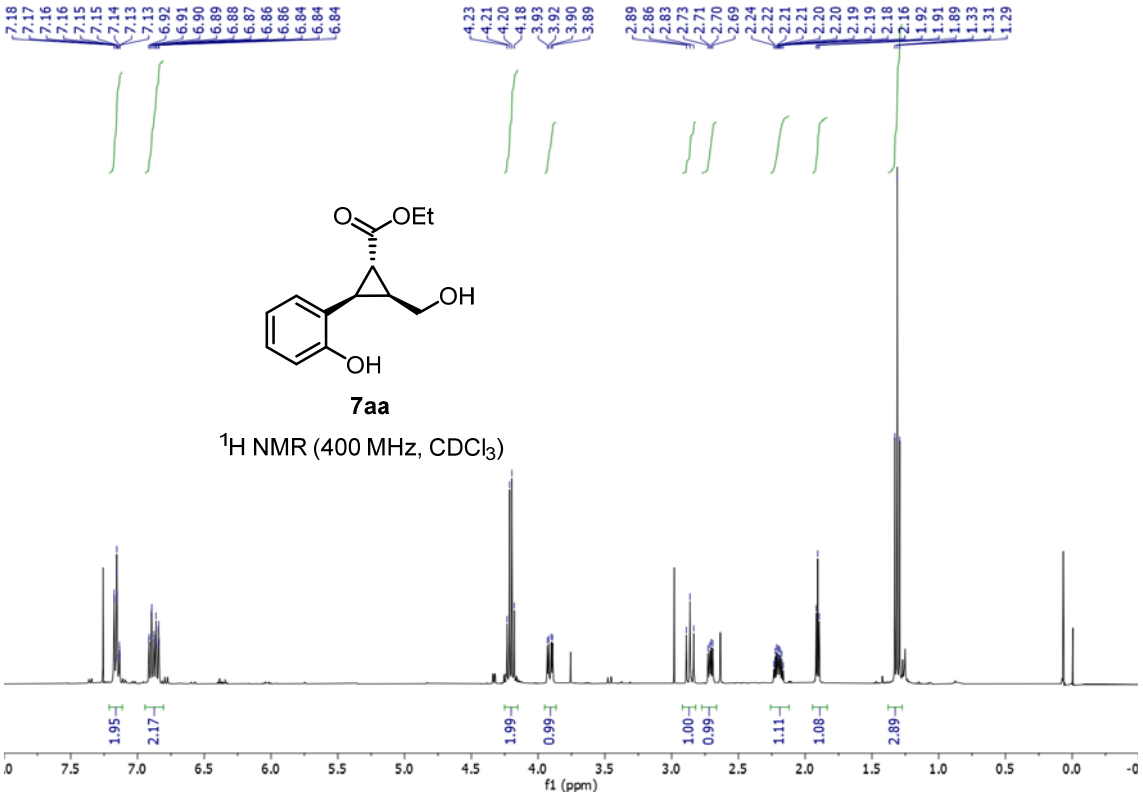
Ethyl (1S,1aS,7bR)-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate 6aa[13]

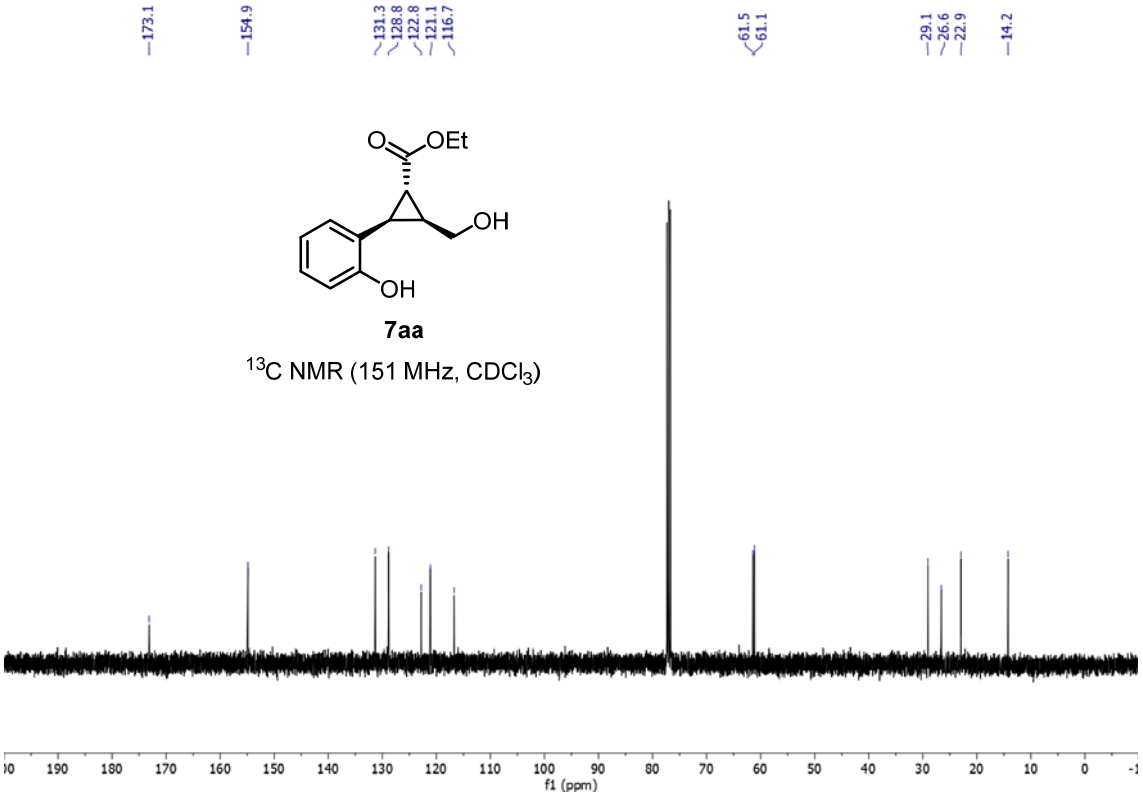




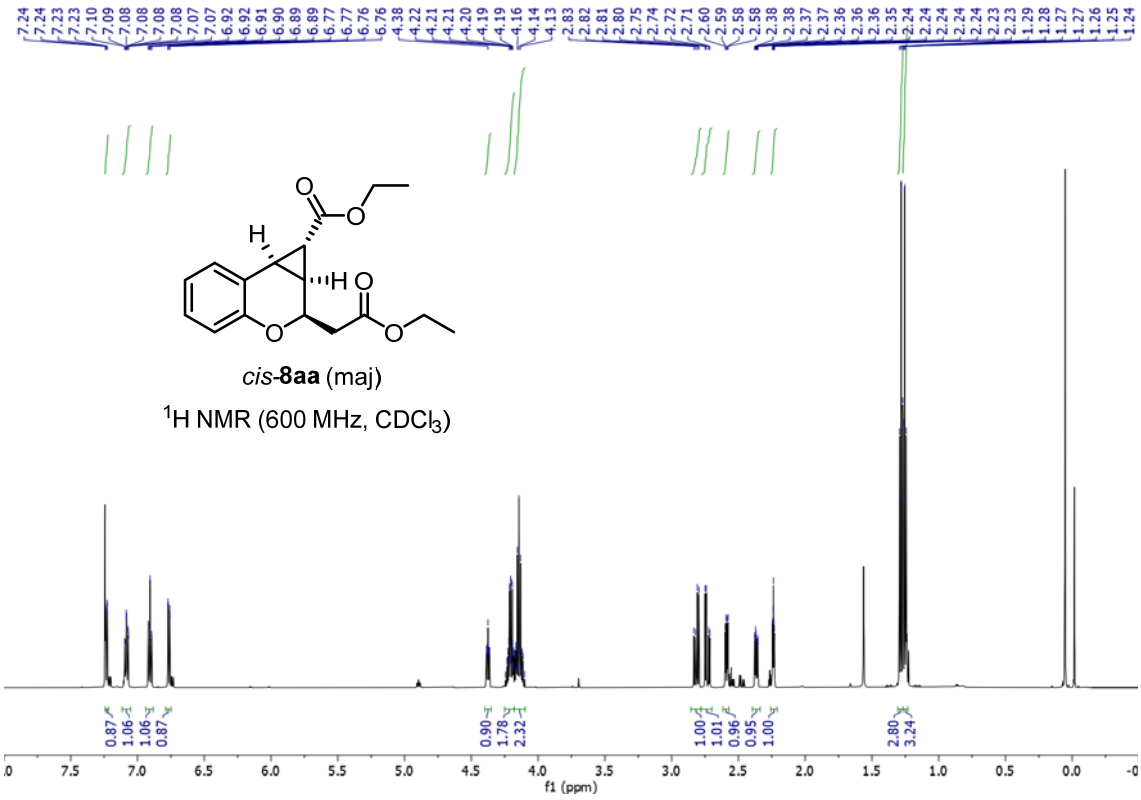
[13] Racemic **6aa**: Ye, L.-W.; Sun, X.-L.; Li, C.-Y.; Tang, Y. *J. Org. Chem.* **2007**, *72*, 1335.

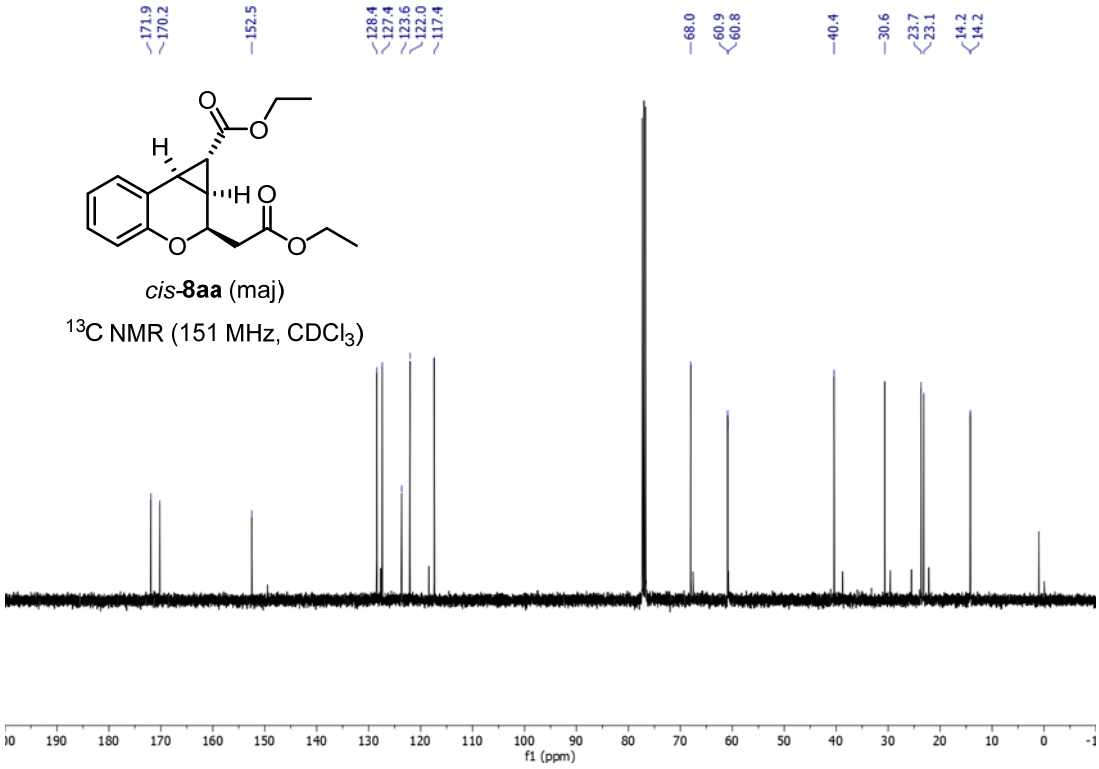
Ethyl (1S,2S,3R)-2-(hydroxymethyl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 7aa



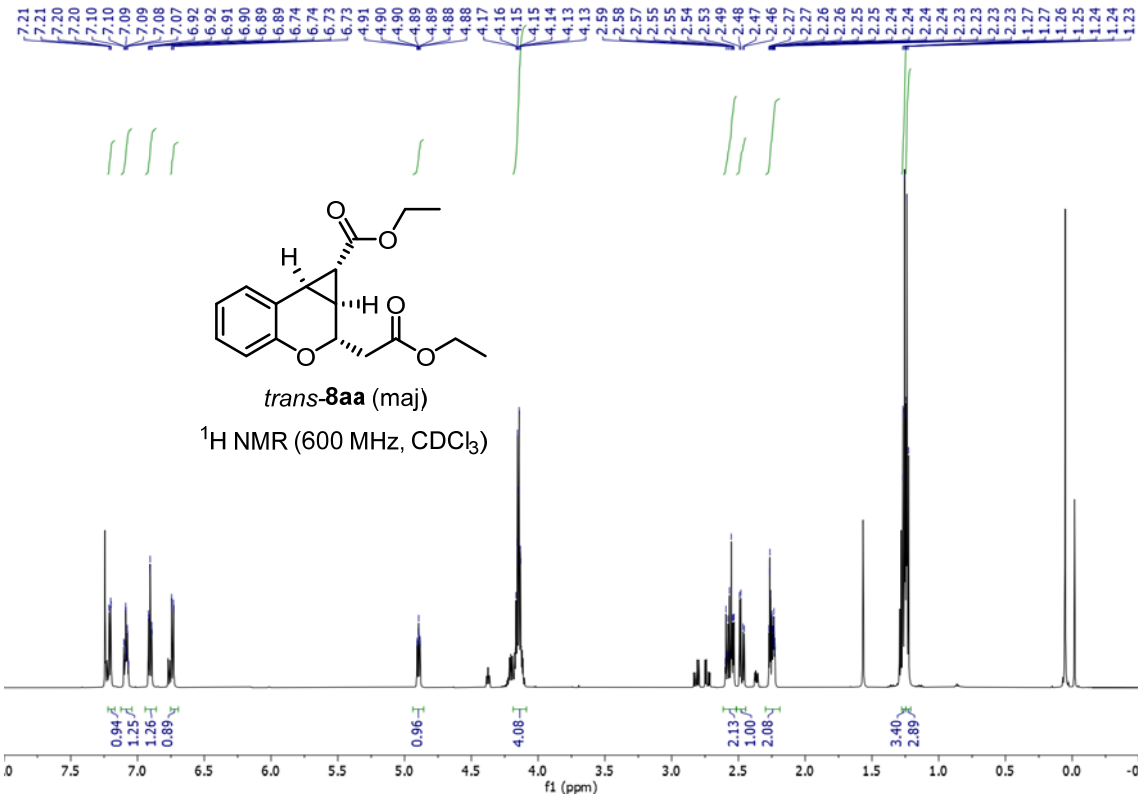


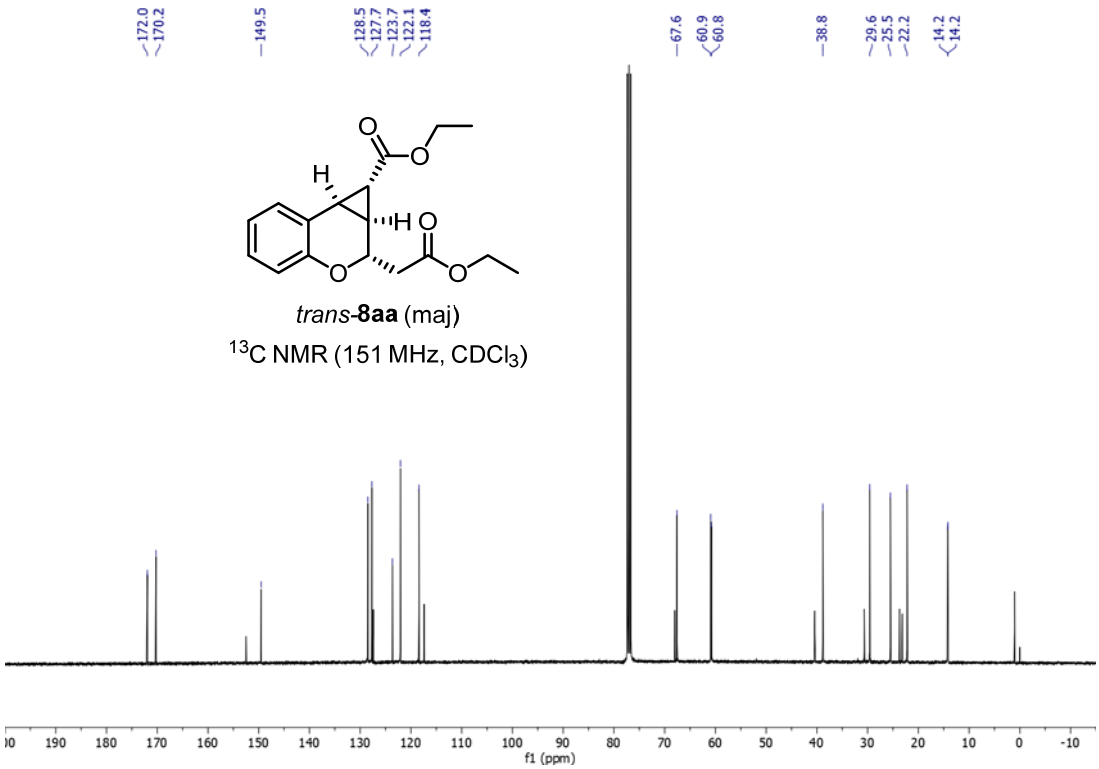
Ethyl (1S,1aS,2R,7bR)-2-(2-ethoxy-2-oxoethyl)-1,1a,2,7b-tetrahydrocyclopropa[c]chromene-1-carboxylate *cis*-8aa





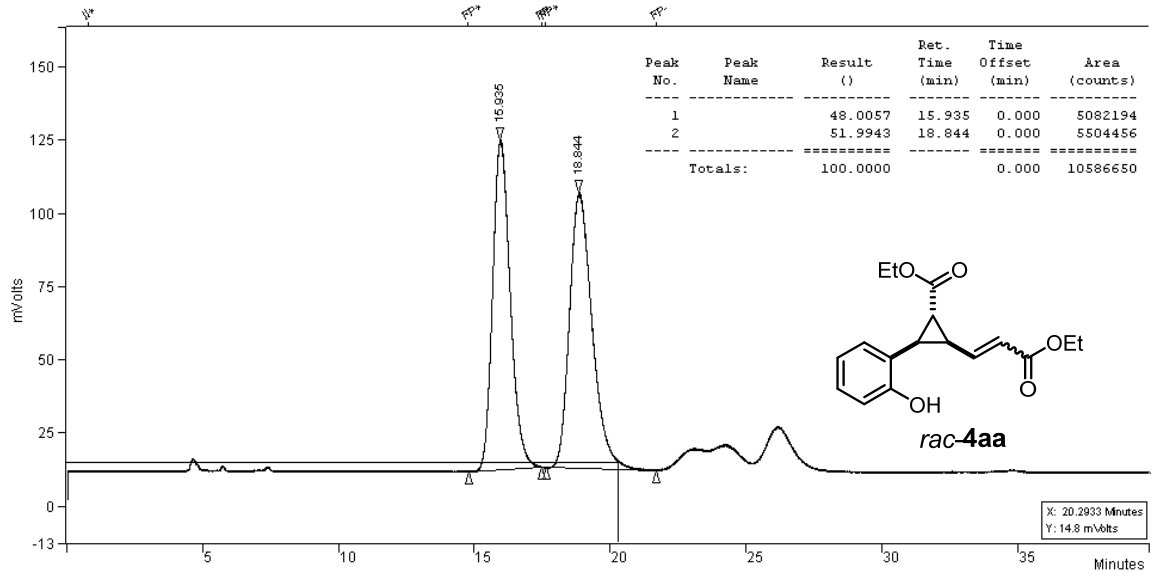
Ethyl (1S,1aS,2S,7bR)-2-(2-ethoxy-2-oxoethyl)-1,1a,2,7b-tetrahydrocyclopropa[c]chromene-1-carboxylate *trans*-8aa



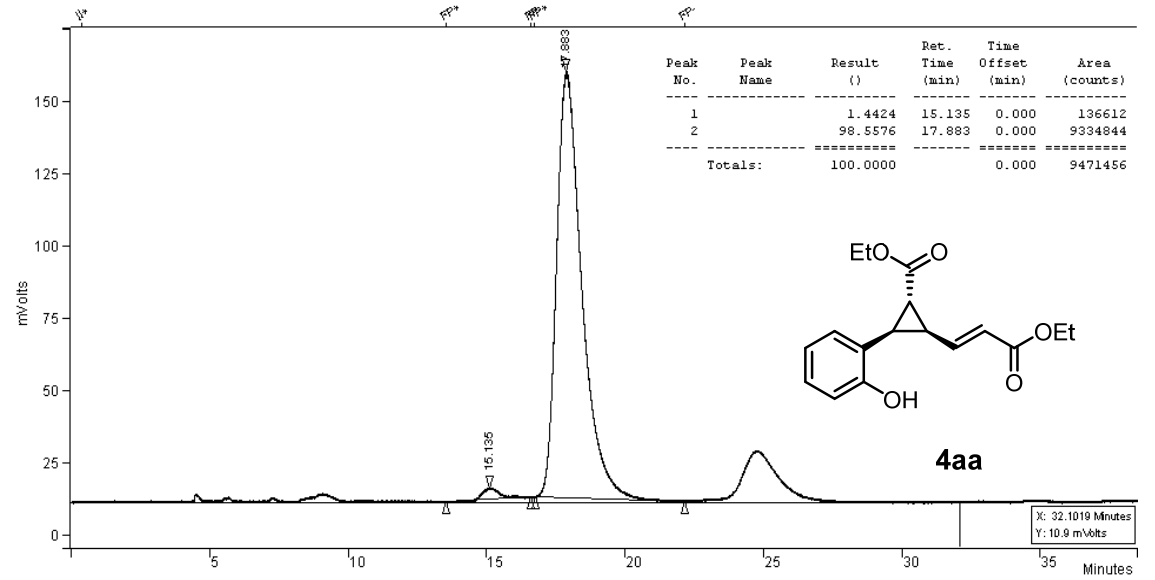


Copies of HPLC traces of products 4-8

Ethyl (1R*,2S*,3R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate *rac*-4aa

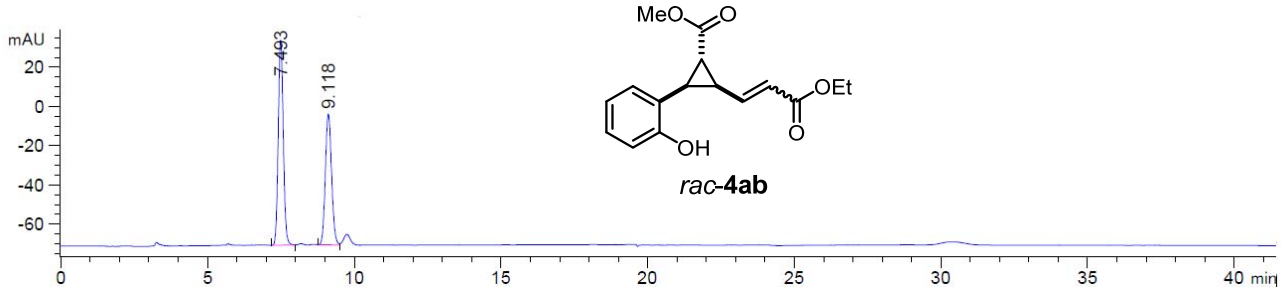


Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4aa



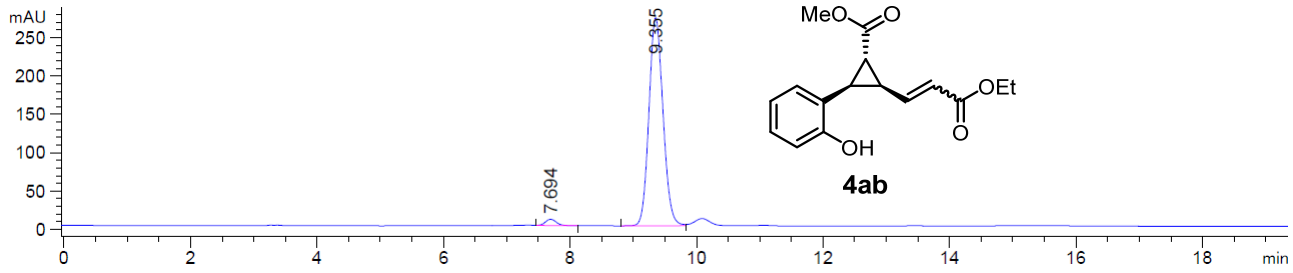
Methyl (1R*,2S*,3R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate *rac*-4ab

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.493	BB	0.1851	1246.63782	104.53787	55.8733
2	9.118	BV	0.2300	984.54730	66.77629	44.1267

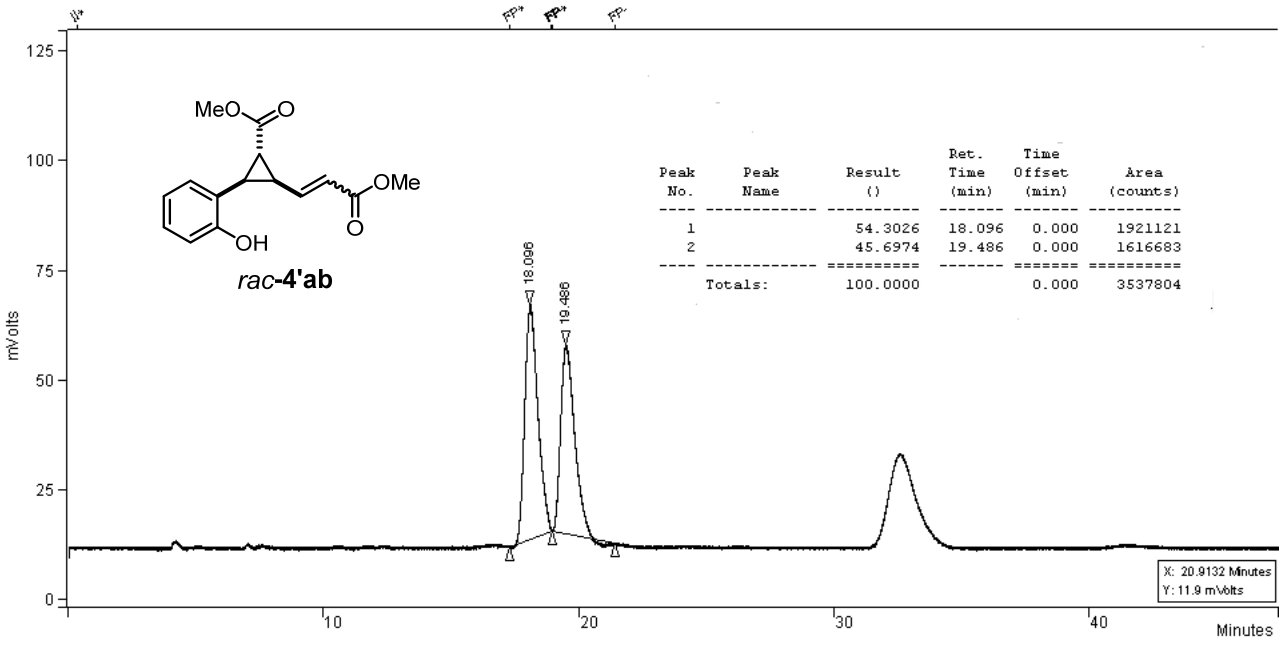


Methyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ab

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.694	BB	0.1860	96.50211	8.15624	2.2479
2	9.355	BV	0.2402	4196.45410	271.73581	97.7521

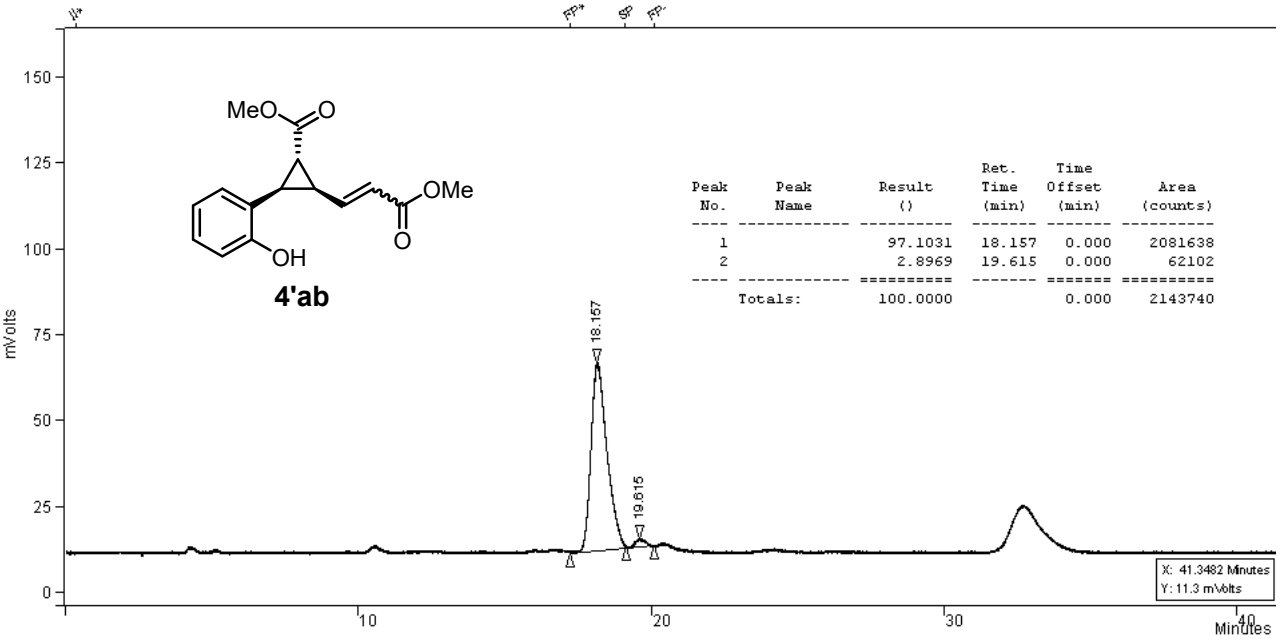


Methyl (1R*,2R*,3S*)-2-(2-hydroxyphenyl)-3-(3-methoxy-3-oxoprop-1-en-1-yl)cyclopropane-1-carboxylate 4'ab



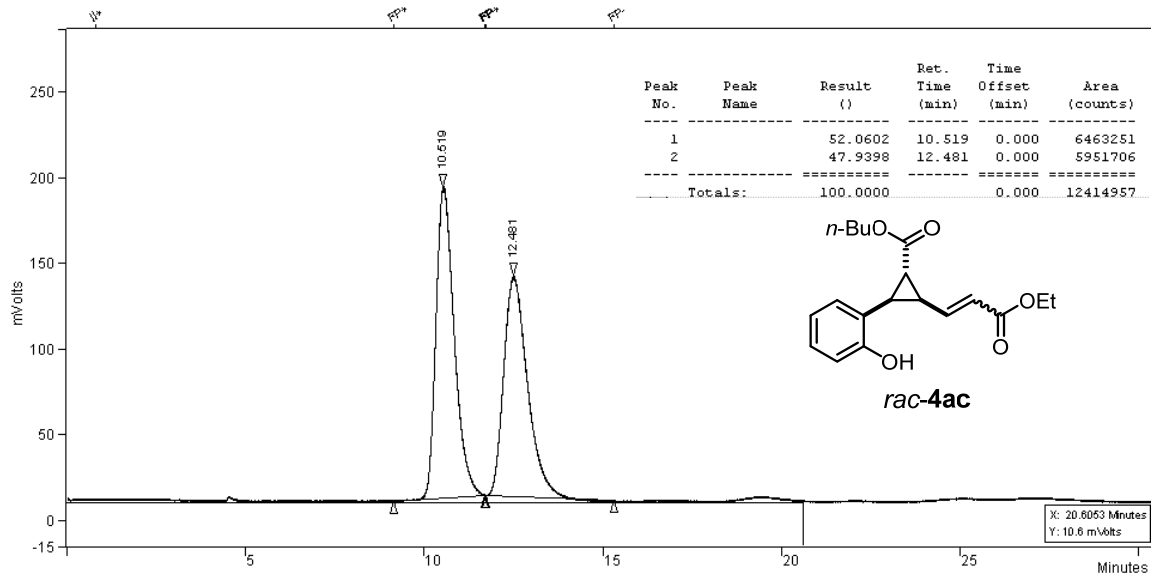
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		54.3026	18.096	0.000	1921121
2		45.6974	19.486	0.000	1616683
Totals:		100.0000		0.000	3537804

Methyl (1R,2R,3S)-2-(2-hydroxyphenyl)-3-(3-methoxy-3-oxoprop-1-en-1-yl)cyclopropane-1-carboxylate 4'ab

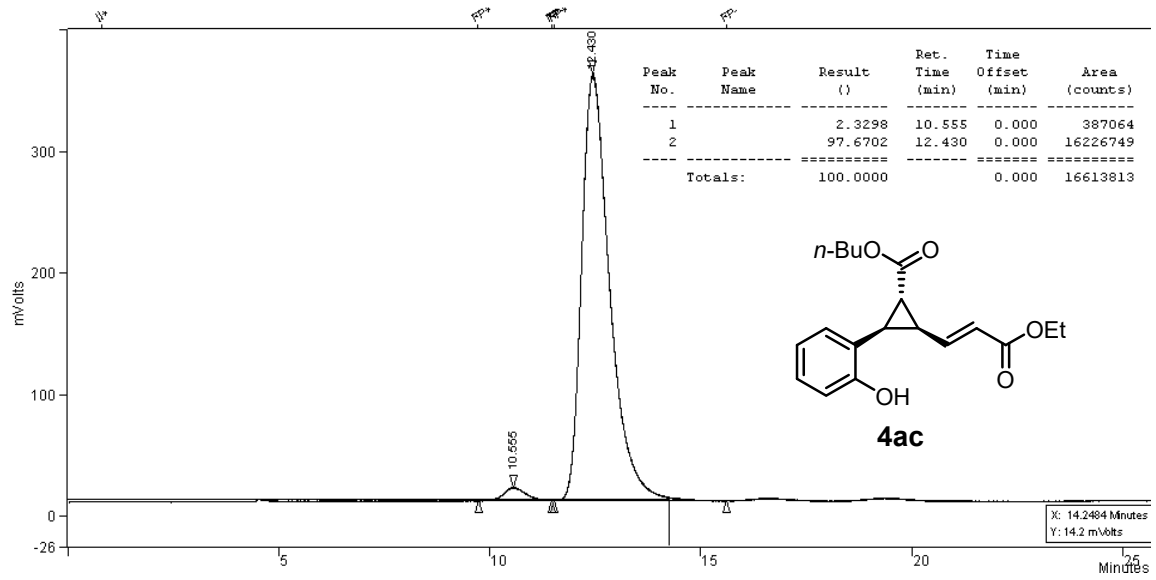


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		97.1031	18.157	0.000	2081638
2		2.8969	19.615	0.000	62102
Totals:		100.0000		0.000	2143740

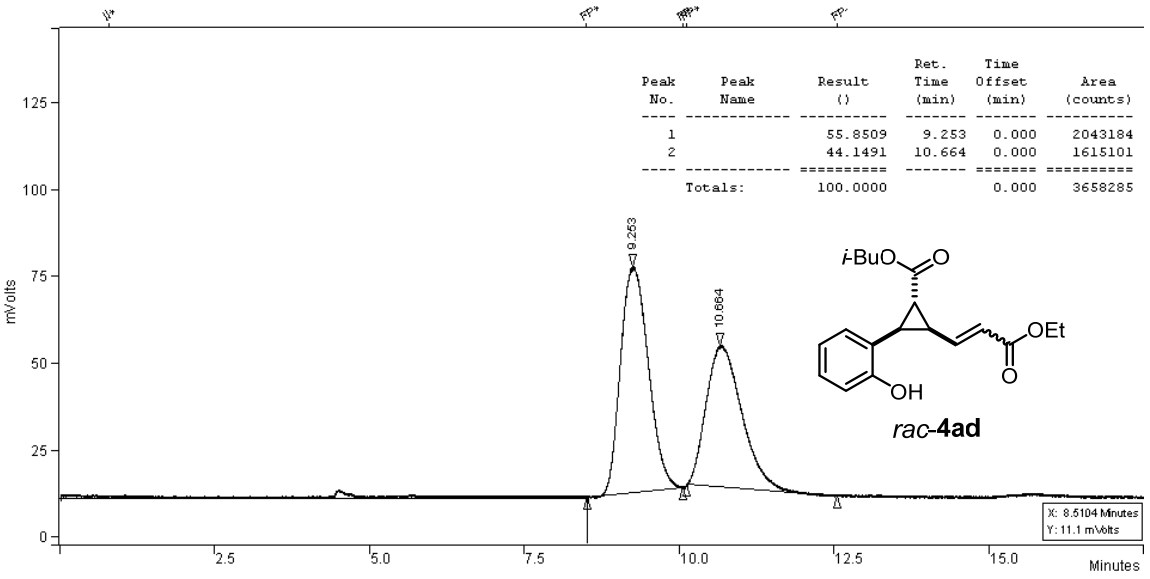
Butyl (1R*,2S*,3R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylatecarboxylate 4ac



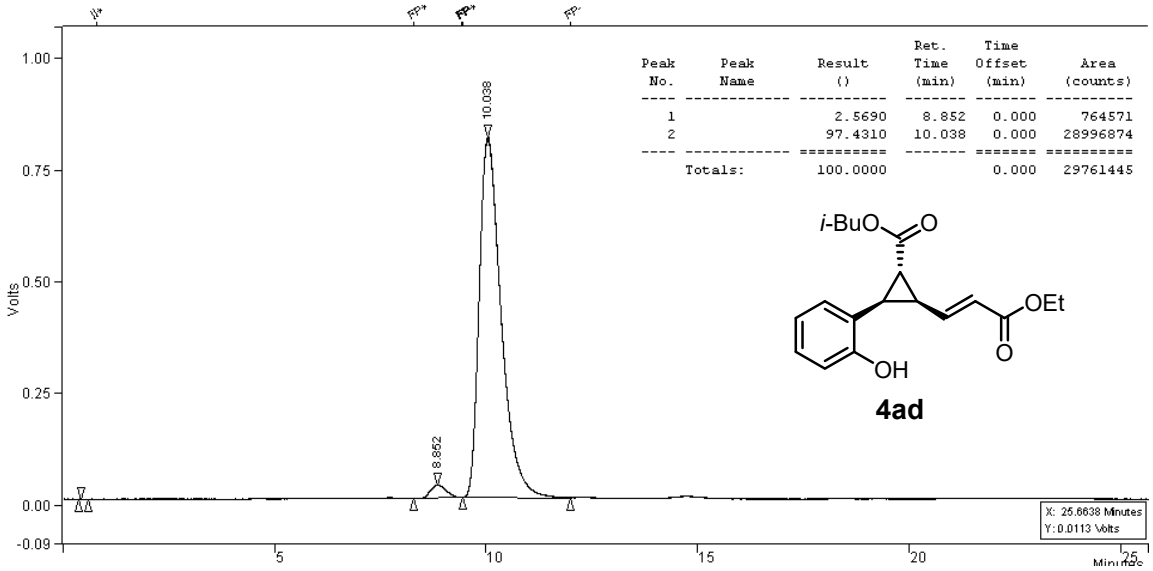
Butyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylatecarboxylate 4ac



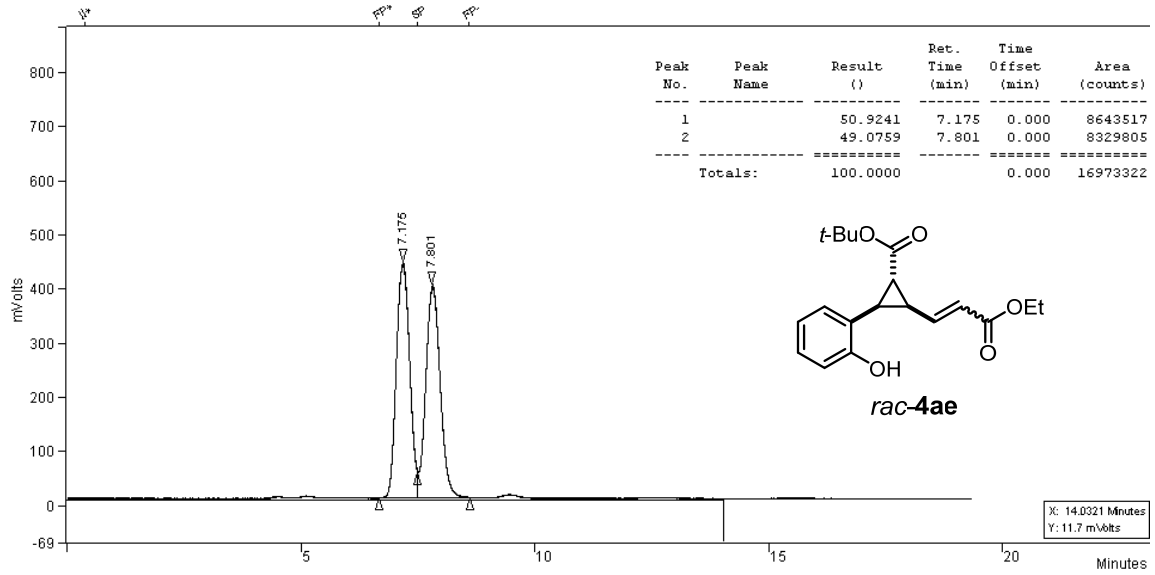
Isobutyl (1R*,2S*,3R*)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ad



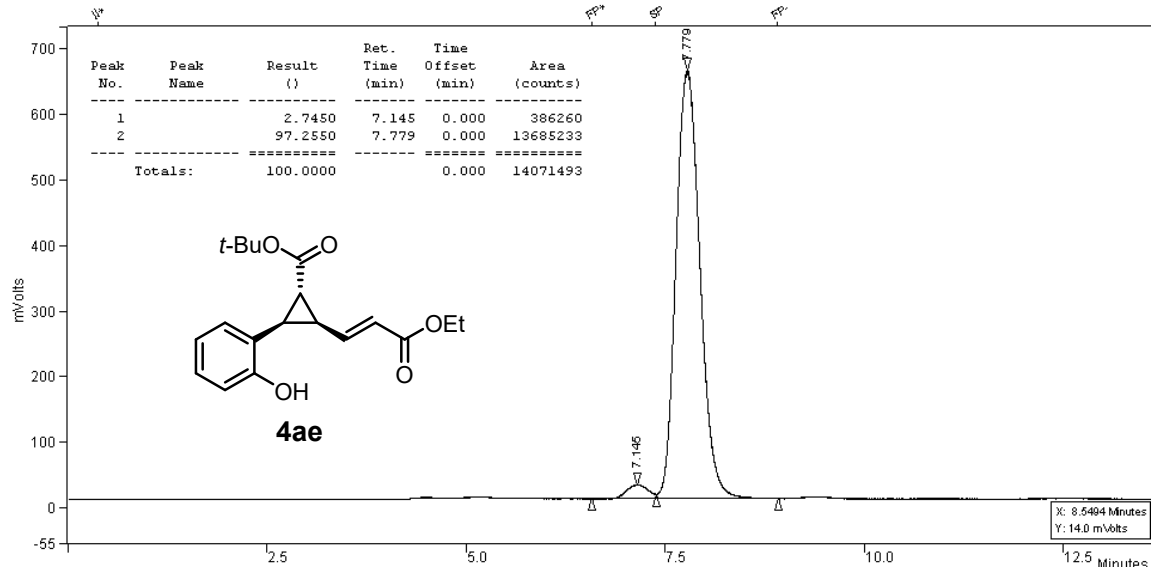
Isobutyl (1R,2S,3R)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ad



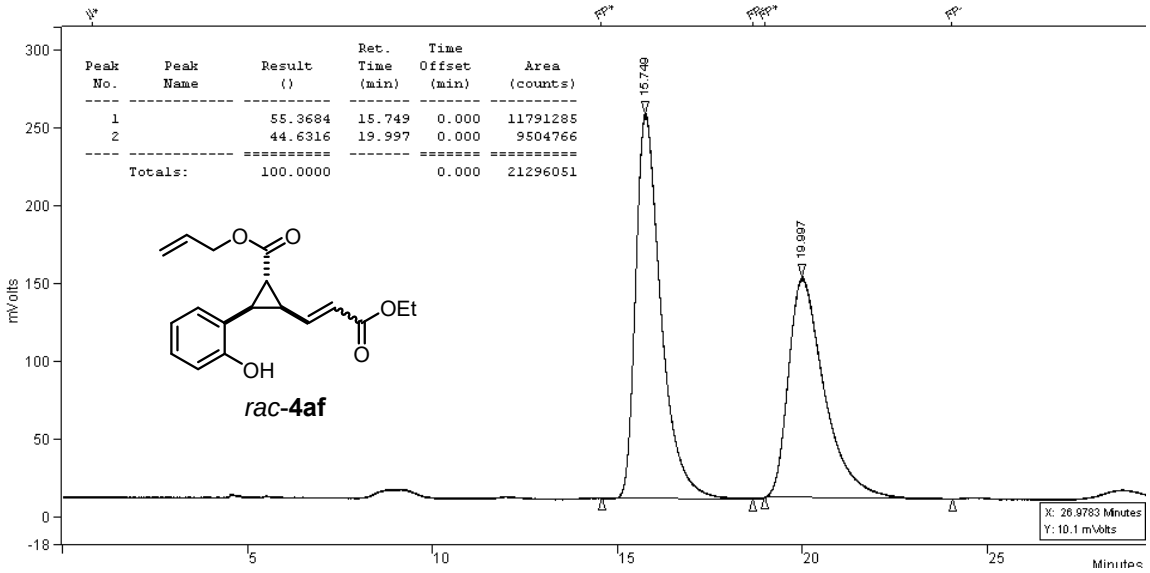
Tert-butyl (1R*,2S*,3R*)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ae



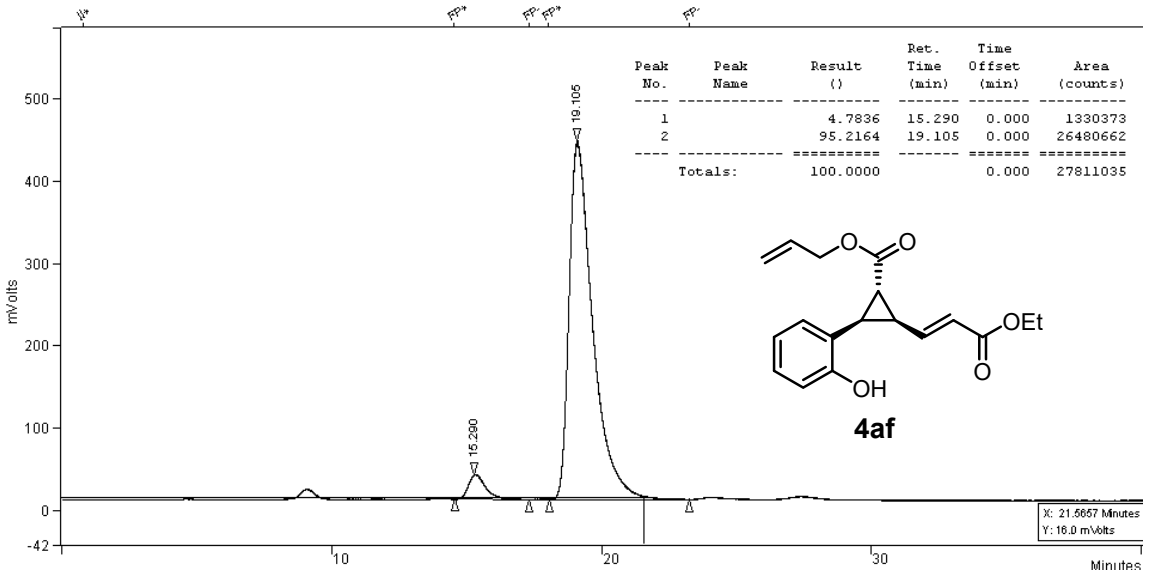
Tert-butyl (1R,2S,3R)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ae



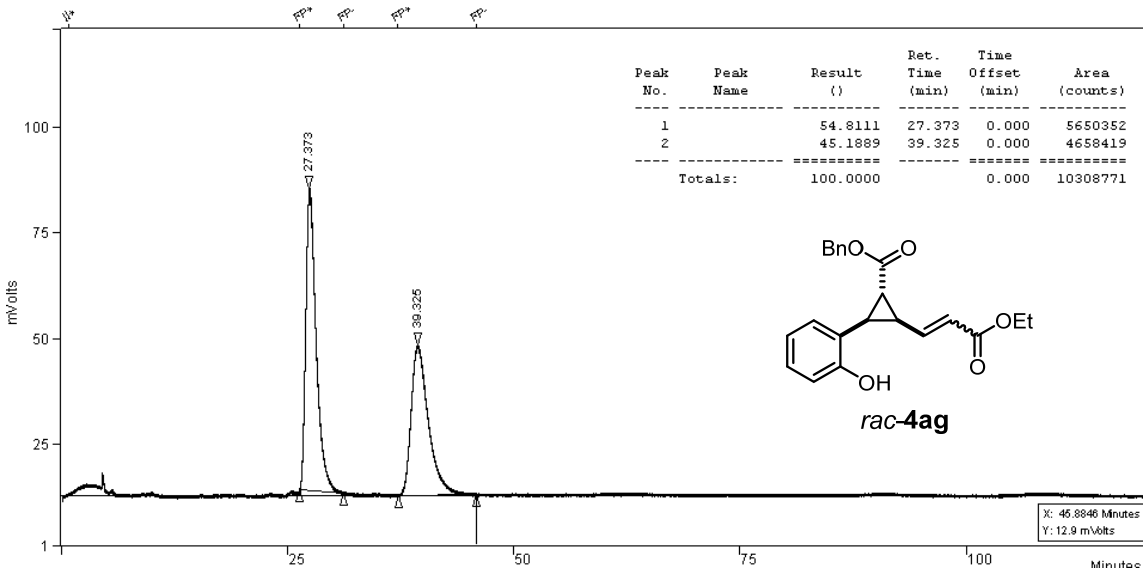
Allyl (1R*,2S*,3R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4af



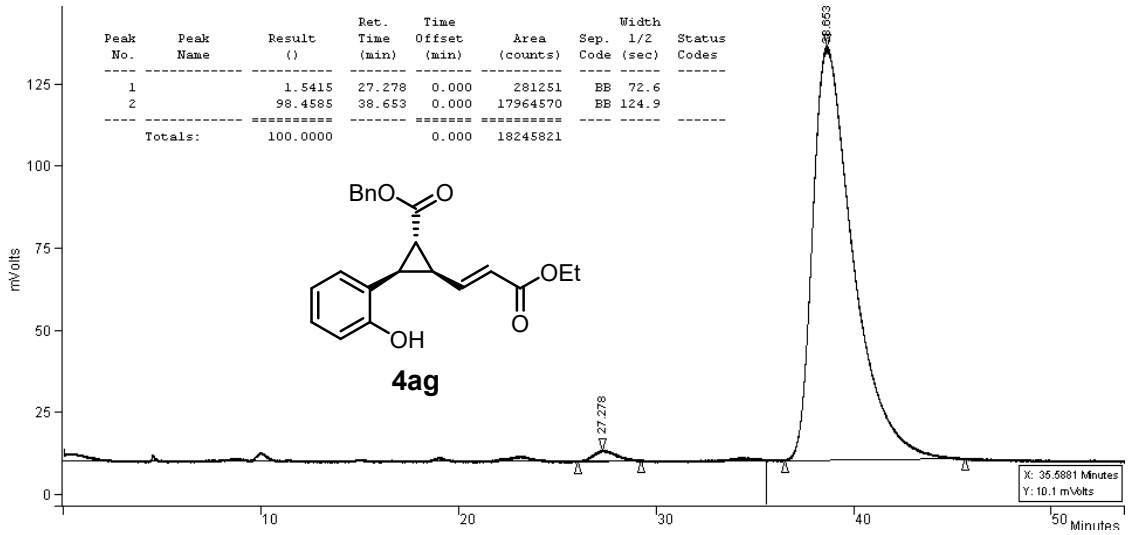
Allyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4af



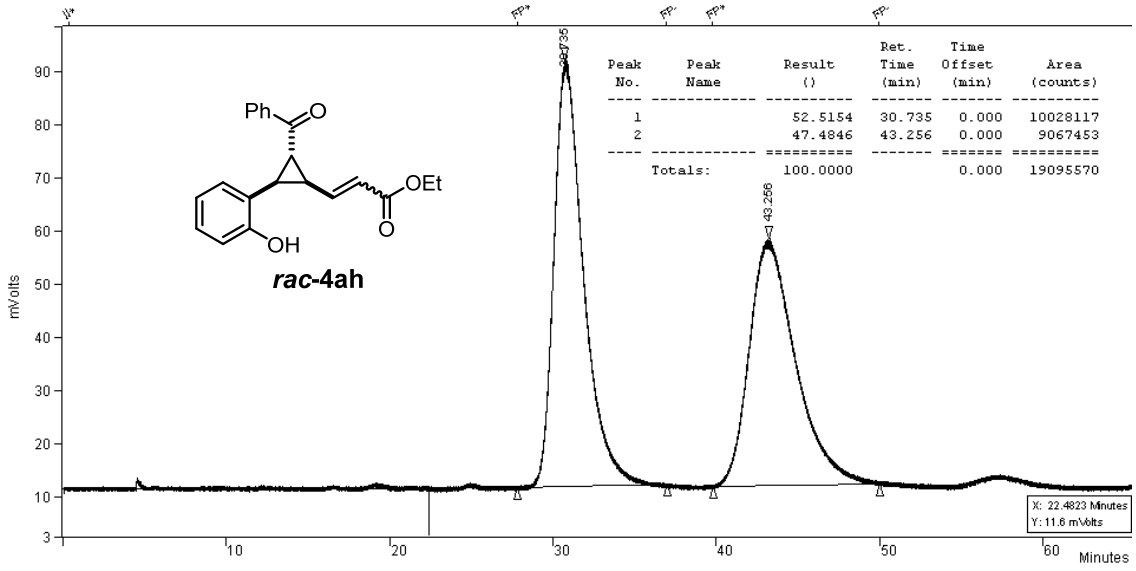
Benzyl (1R*,2S*,3R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ag



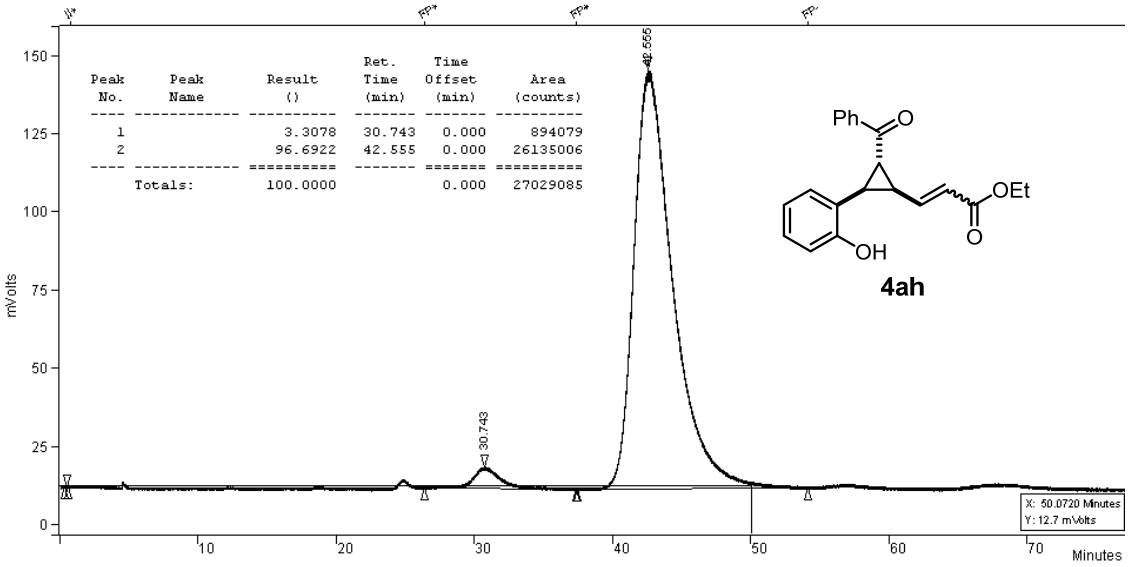
Benzyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4af



Ethyl 3-((1S*,2R*,3R*)-2-benzoyl-3-(2-hydroxyphenyl)cyclopropyl)acrylate *rac*-4ah

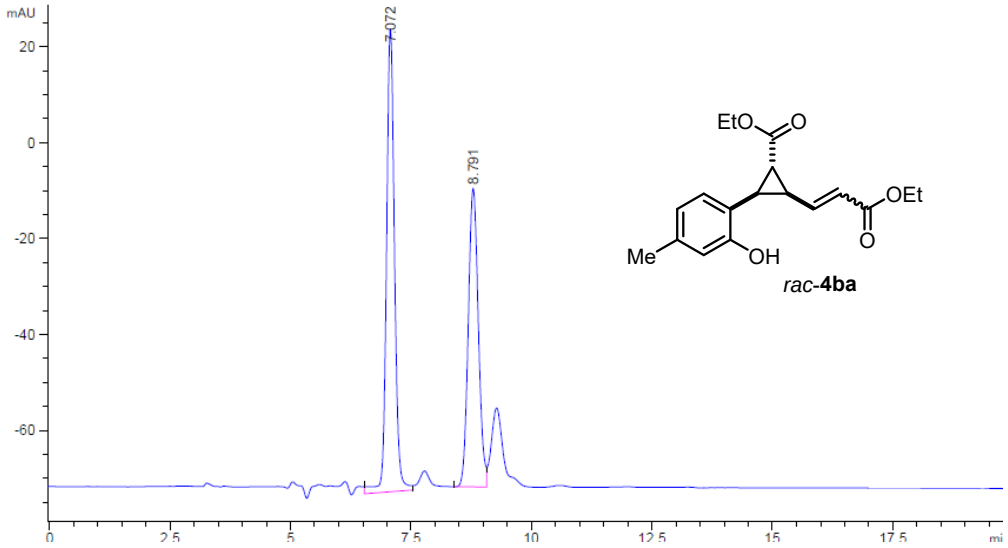


Ethyl 3-((1S,2R,3R)-2-benzoyl-3-(2-hydroxyphenyl)cyclopropyl)acrylate 4ah



Ethyl (1R*,2S*,3R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-4-methylphenyl)cyclopropane-1-carboxylate 4ba

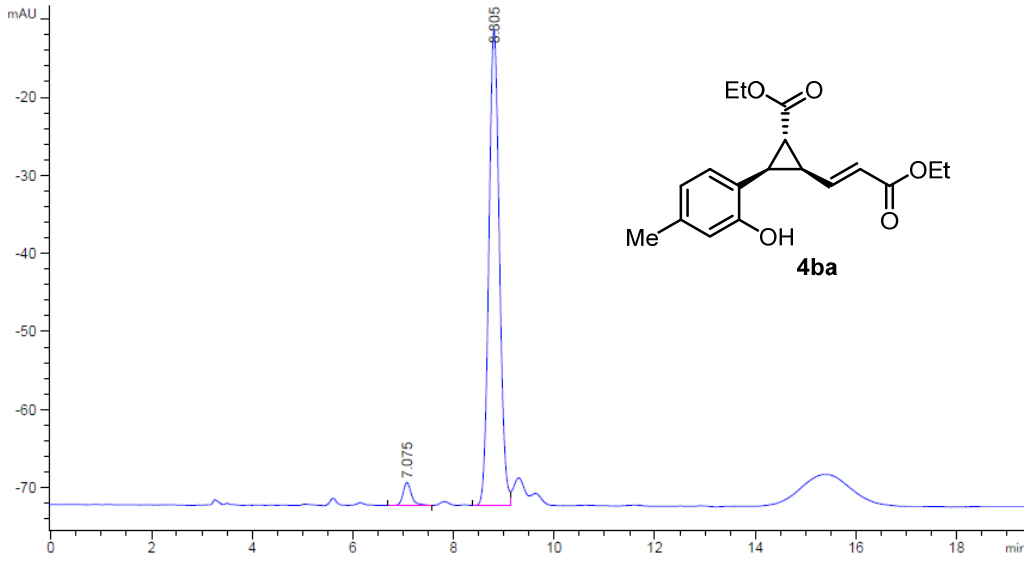
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.072	VV	0.1755	1119.23657	96.39005	55.3514
2	8.791	BV	0.2252	902.81921	62.24410	44.6486
Totals :				2022.05579	158.63414	



rac-**4ba**

Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-4-methylphenyl)cyclopropane-1-carboxylate 4da

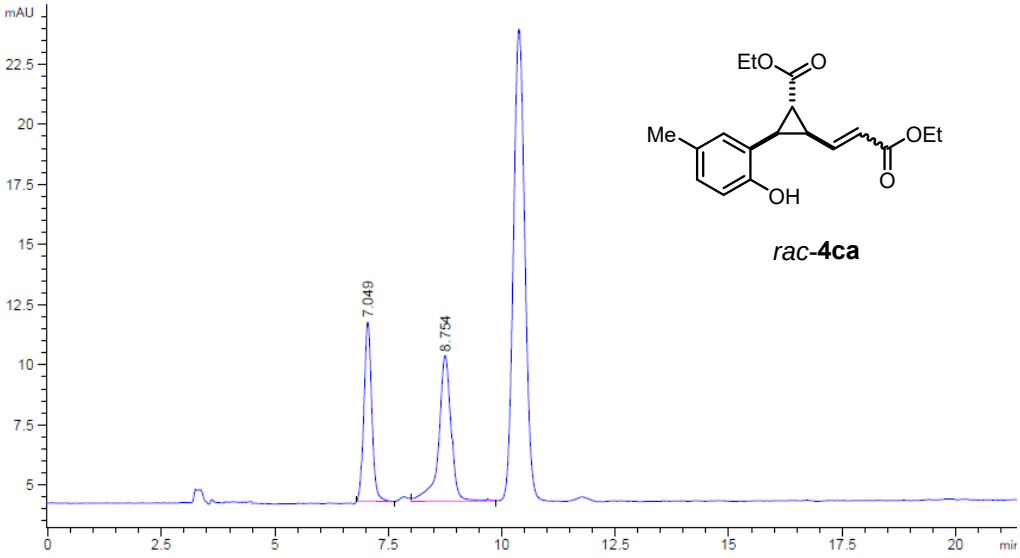
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.075	BB	0.1790	34.59105	2.94582	3.7611
2	8.805	BV	0.2255	885.12604	60.93709	96.2389
Totals :				919.71708	63.88291	



4ba

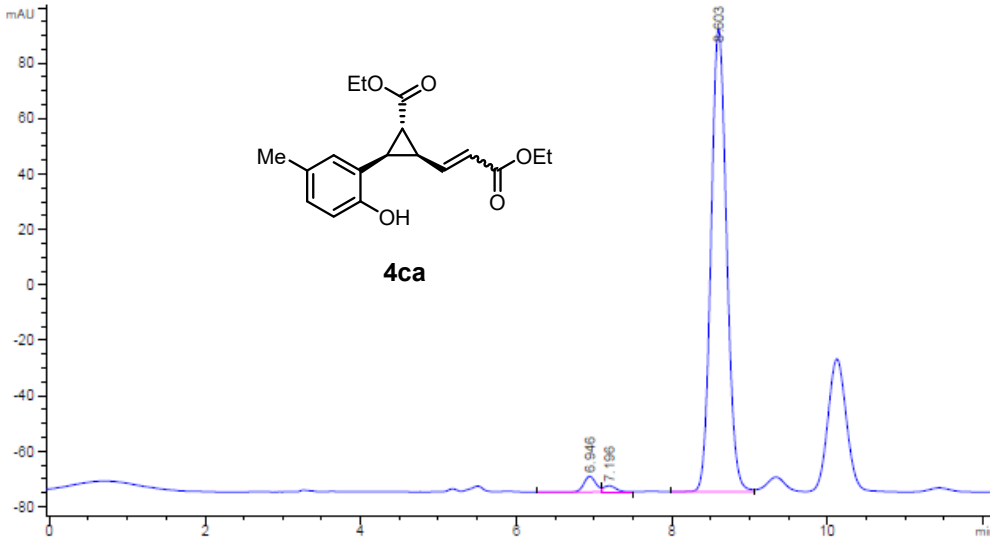
Ethyl (1R*,2S*,3R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-5-methylphenyl)cyclopropane-1-carboxylate 4ca

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.049	VB	0.1841	91.06892	7.47739	40.9751
2	8.754	VB	0.3107	131.18553	6.05758	59.0249
Totals :				222.25446	13.53497	



Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-5-methylphenyl)cyclopropane-1-carboxylate 4ca

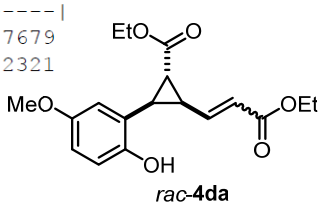
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.946	BV	0.1662	60.97028	5.63460	2.5248
2	7.196	VB	0.1635	23.43864	2.21344	0.9706
3	8.603	BV	0.2189	2330.41064	166.94904	96.5045
Totals :				2414.81957	174.79707	



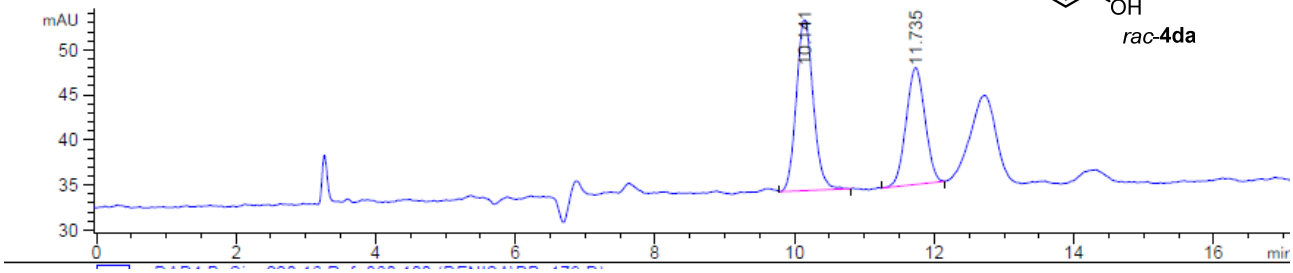
Ethyl(1R*,2S*,3R)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-5-methoxyphenyl)cyclopropane -1-carboxylate 4da

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.141	BB	0.2583	319.48050	18.98366	56.7679
2	11.735	BB	0.2929	243.30342	12.96890	43.2321
Totals :				562.78392	31.95257	

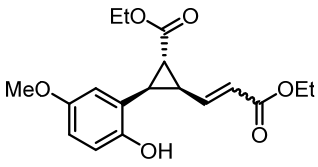


rac-**4da**



Ethyl(1R,2S,3R)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-5-methoxyphenyl)cyclopropane -1-carboxylate 4ba

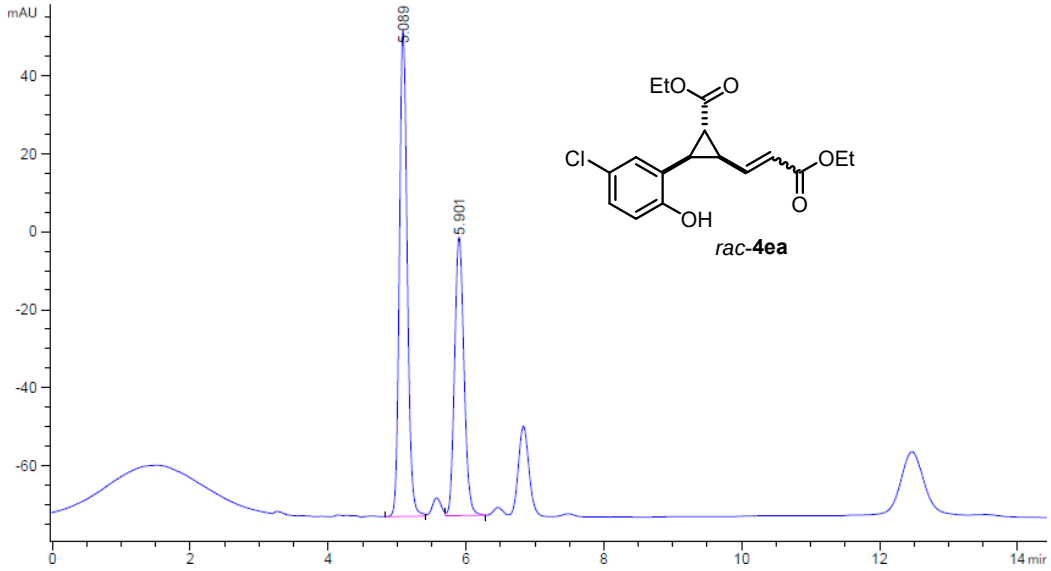
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.164	BB	0.2538	22.87235	1.30941	1.6635
2	11.723	BV	0.3108	1170.94824	58.19378	98.3364



4da

Ethyl (1R*,2R*,3S*)-2-(5-chloro-2-hydroxyphenyl)-3-(-3-ethoxy-3-oxoprop-1-en-1-yl)cyclopropane-1-carboxylate 4ea

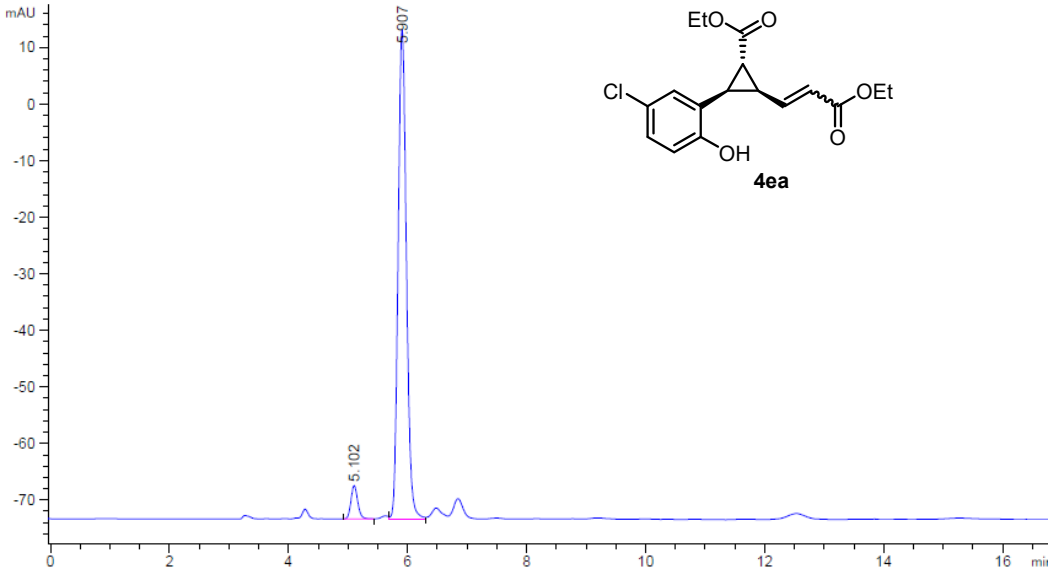
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.089	BV	0.1245	969.53308	122.26378	58.7465
2	5.901	VB	0.1518	680.83551	71.04188	41.2535
Totals :				1650.36859	193.30566	



rac-**4ea**

Ethyl (1R,2R,3S)-2-(5-chloro-2-hydroxyphenyl)-3-(-3-ethoxy-3-oxoprop-1-en-1-yl)cyclopropane-1-carboxylate 4fa

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.102	BB	0.1221	46.74147	5.91772	5.2954
2	5.907	VV	0.1508	835.93378	86.48706	94.7046
Totals :				882.67525	92.40478	

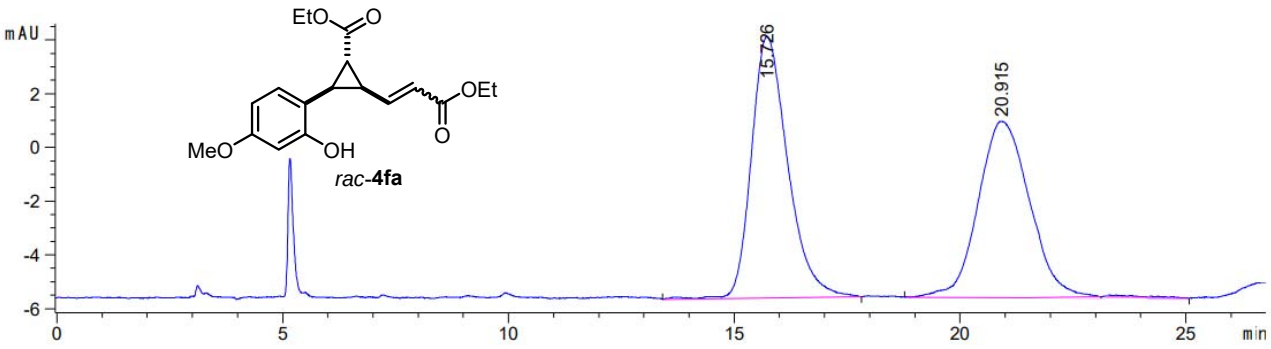


4ea

Ethyl (1R*,2S*,3R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-4-methoxyphenyl)cyclopropane-1-carboxylate 4fa

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

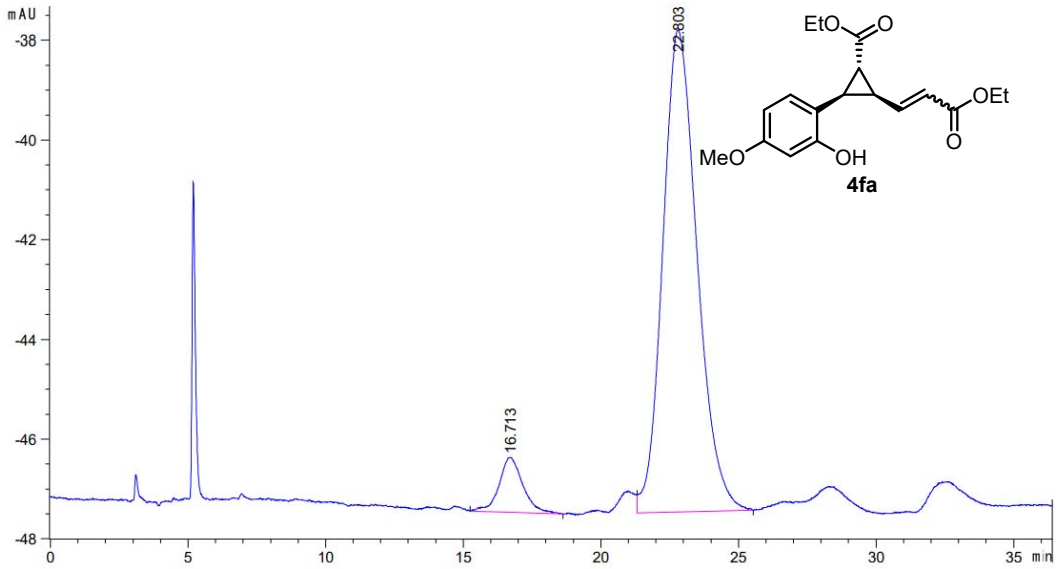
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.726	BB	0.8584	545.57031	9.72621	48.1374
2	20.915	BB	1.3468	587.78912	6.55085	51.8626
Totals :				1133.35944	16.27706	



Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-4-methoxyphenyl)cyclopropane-1-carboxylate 4fa

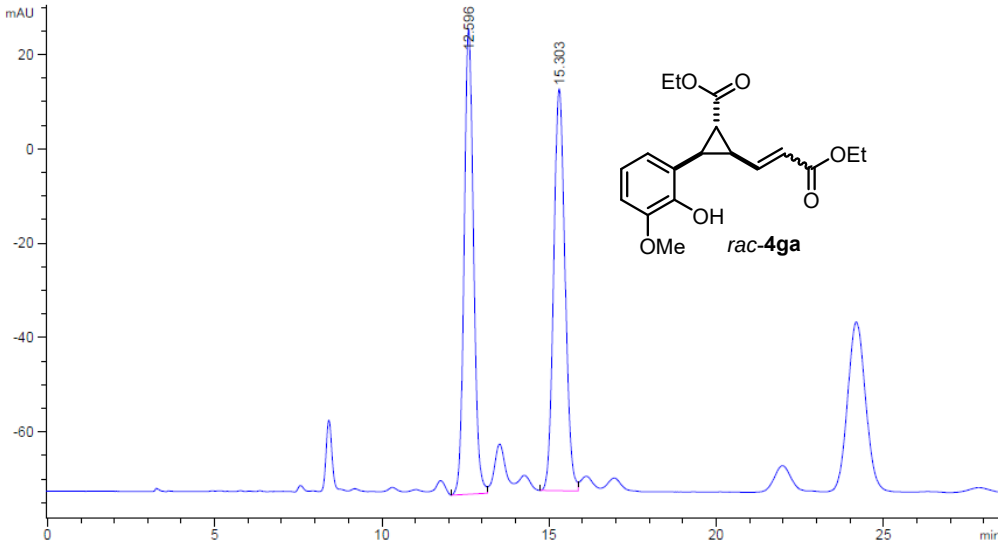
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.713	BB	0.8369	66.84313	1.10624	7.3784
2	22.803	VB	1.3048	839.09265	9.66531	92.6216
Totals :				905.93578	10.77155	



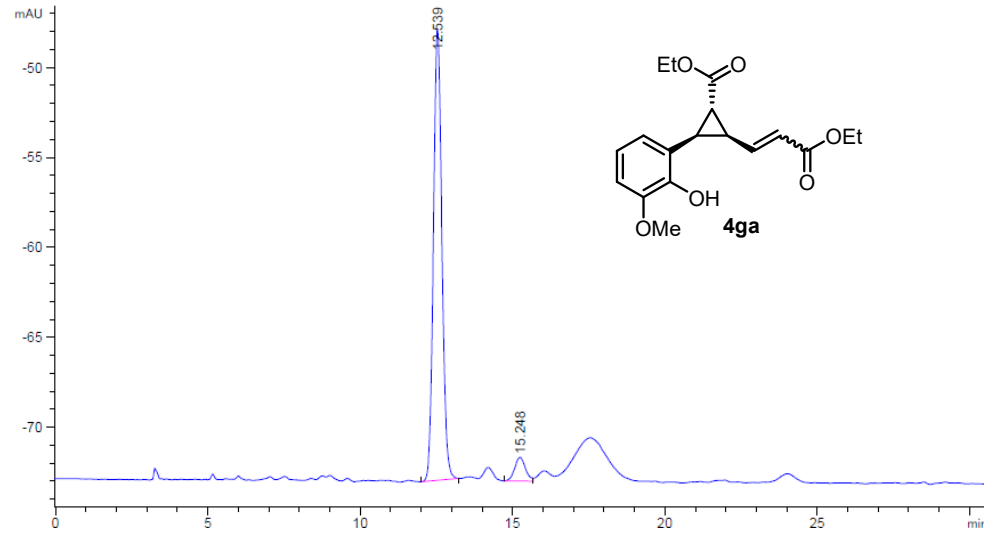
Ethyl (1R*,2S*,3R*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-3-methoxyphenyl)cyclopropane-1-carboxylate 4ga

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.596	BV	0.3021	1928.07642	98.59661	48.9097
2	15.303	BV	0.3678	2014.03845	85.19571	51.0903
Totals :				3942.11487	183.79232	

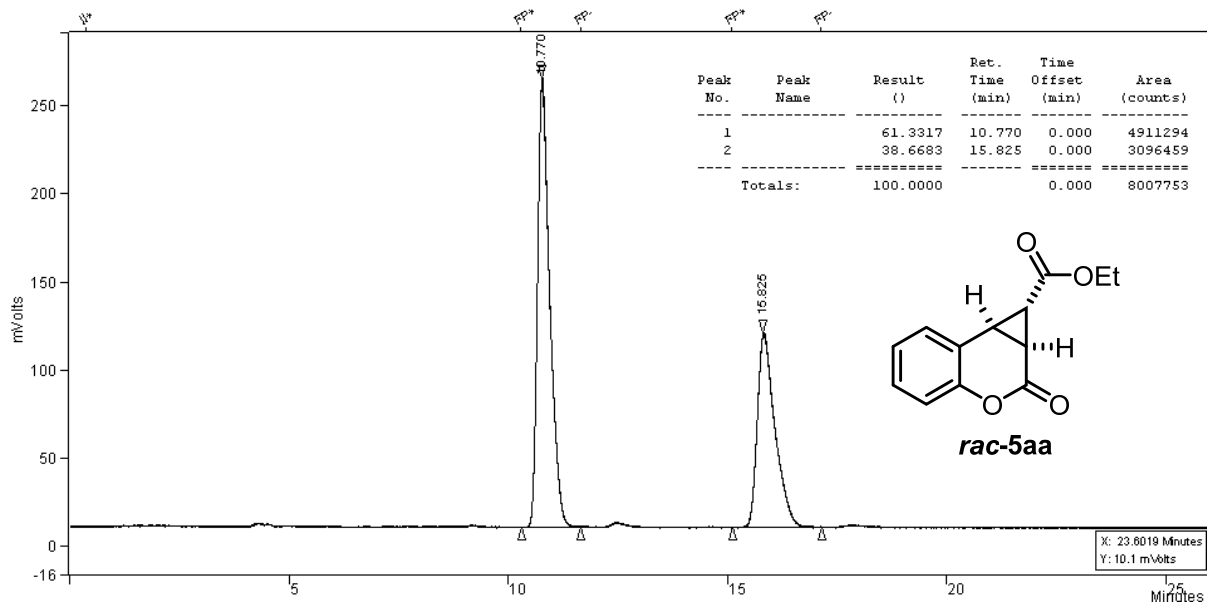


Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-3-methoxyphenyl)cyclopropane-1-carboxylate 4ea

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.539	BB	0.2985	482.45602	25.07698	93.7354
2	15.248	BV	0.3654	32.24416	1.31818	6.2646
Totals :				514.70019	26.39517	

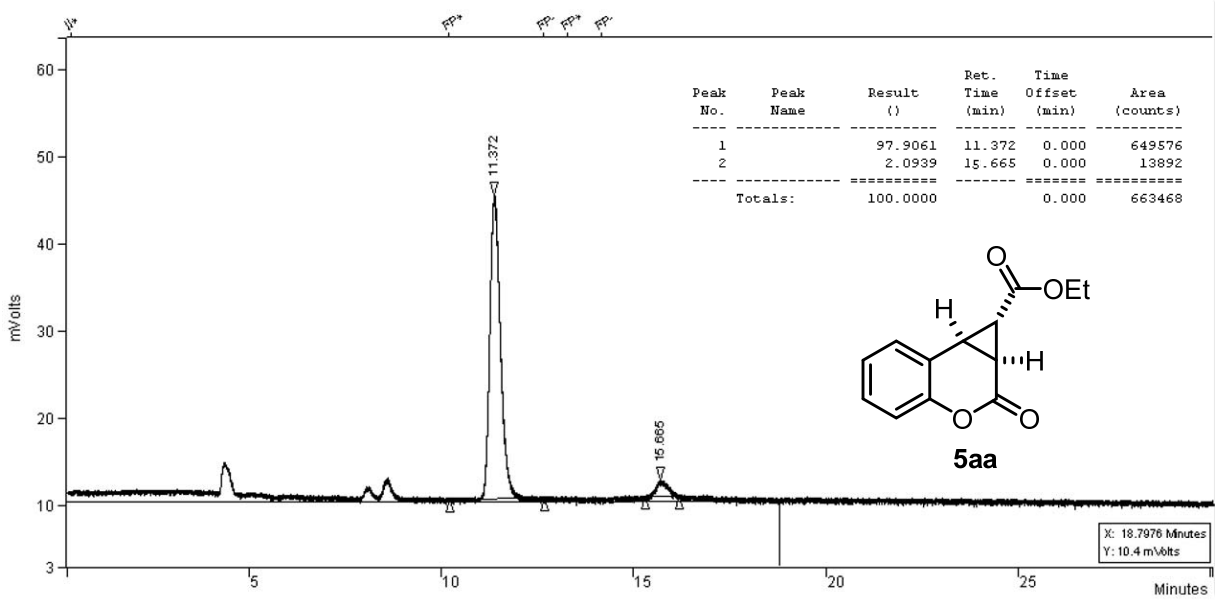


Ethyl (1S*,1aS*,7bS*)-2-oxo-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate 5aa



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		61.3317	10.770	0.000	4911294
2		38.6683	15.825	0.000	3096459
	Totals:	100.0000		0.000	8007753

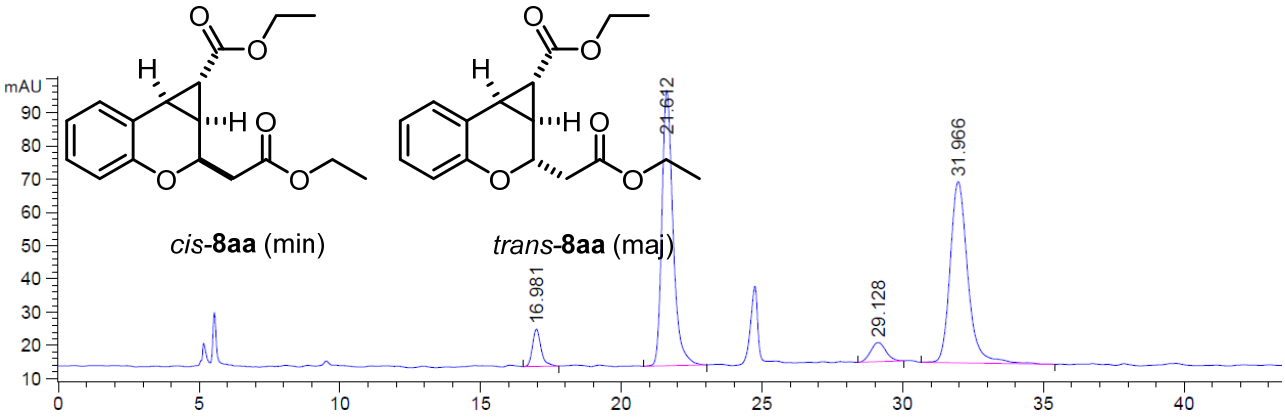
Ethyl (1S*,1aS*,7bS*)-2-oxo-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate 5aa



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		97.9061	11.372	0.000	649576
2		2.0939	15.665	0.000	13892
	Totals:	100.0000		0.000	663468

Ethyl (1S*,1aS*,2R*,7bR*)-2-(2-ethoxy-2-oxoethyl)-1,1a,2,7b-tetrahydrocyclopropa[*c*] chromene-1-carboxylate *cis*-8aa and Ethyl (1S*,1aS*,2S*,7bR*)-2-(2-ethoxy-2-oxoethyl)-1,1a,2,7b-tetrahydro cyclopropa[*c*]chromene-1-carboxylate *trans*-8aa (*trans*:*cis* ca. 9:1 favoring the *trans*-8aa isomer).

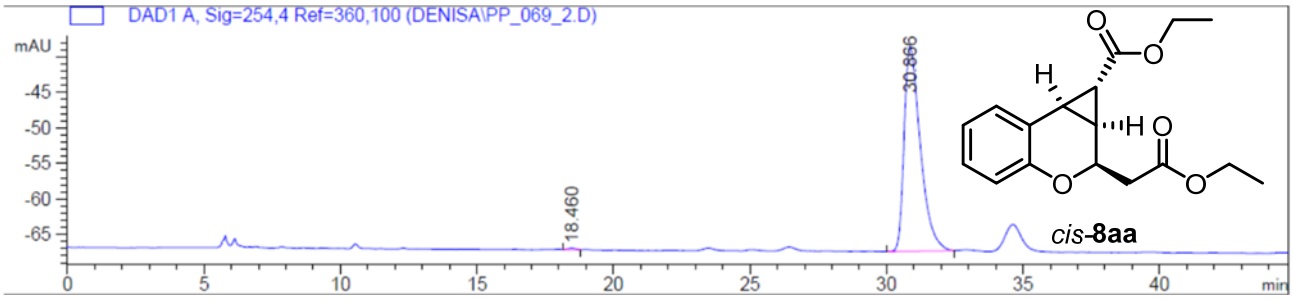
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.981	BB	0.3233	237.06837	11.18567	4.6550
2	21.612	BB	0.4197	2269.65967	82.83414	44.5668
3	29.128	BB	0.5896	215.58414	5.74745	4.2332
4	31.966	BB	0.6643	2370.40747	54.40604	46.5450



Ethyl (1S,1aS,2R,7bR)-2-(2-ethoxy-2-oxoethyl)-1,1a,2,7b-tetrahydrocyclopropa[*c*] chromene-1-carboxylate *cis*-8aa

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

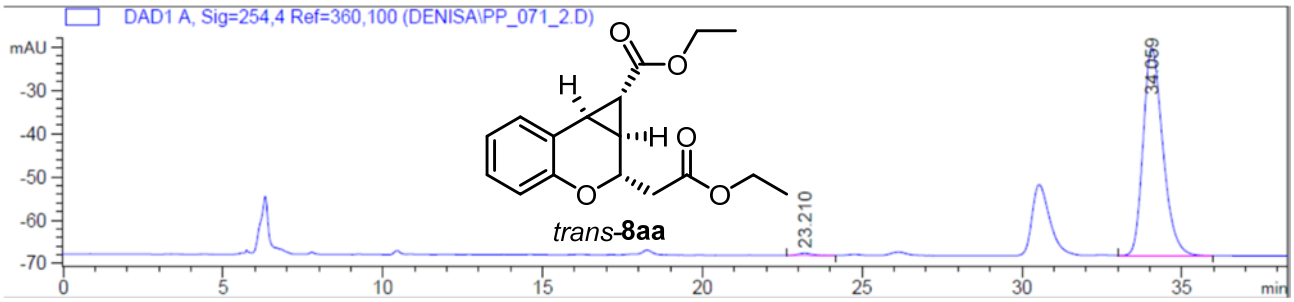
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.460	BB	0.2603	4.11539	2.32698e-1	0.3436
2	30.866	BB	0.6321	1193.65674	28.88521	99.6564



Ethyl (1S,1aS,2S,7bR)-2-(2-ethoxy-2-oxoethyl)-1,1a,2,7b-tetrahydro cyclopropa[*c*]chromene-1-carboxylate *trans*-8aa

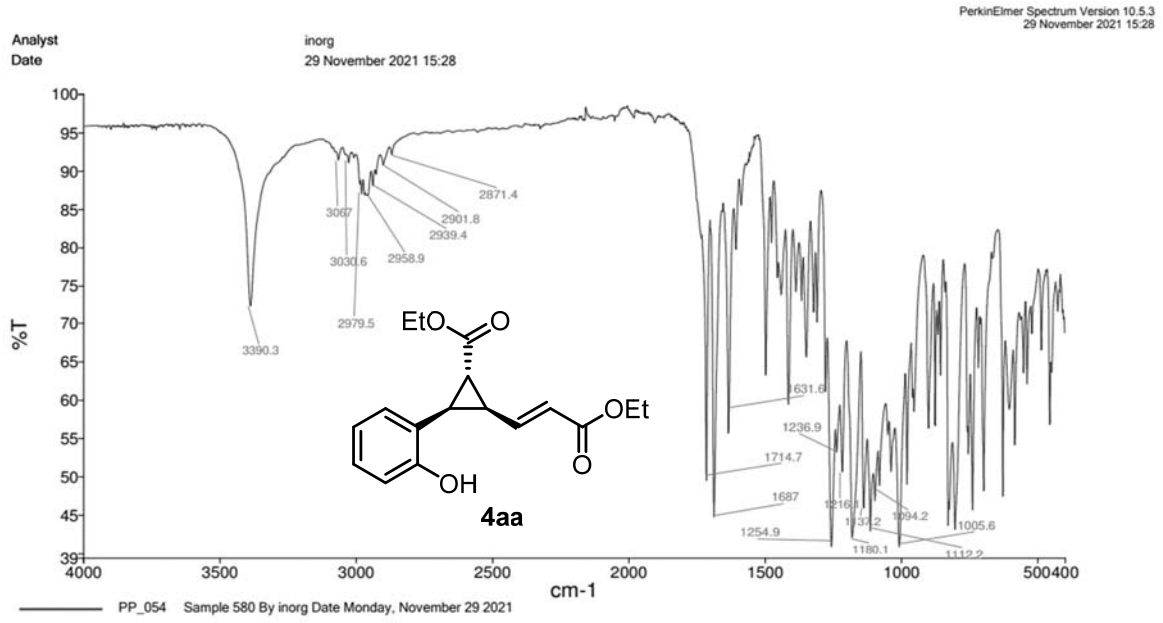
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.210	BB	0.4817	14.20832	4.53328e-1	0.6869
2	34.059	BB	0.6599	2054.15625	47.94344	99.3131
Totals :				2068.36457	48.39677	

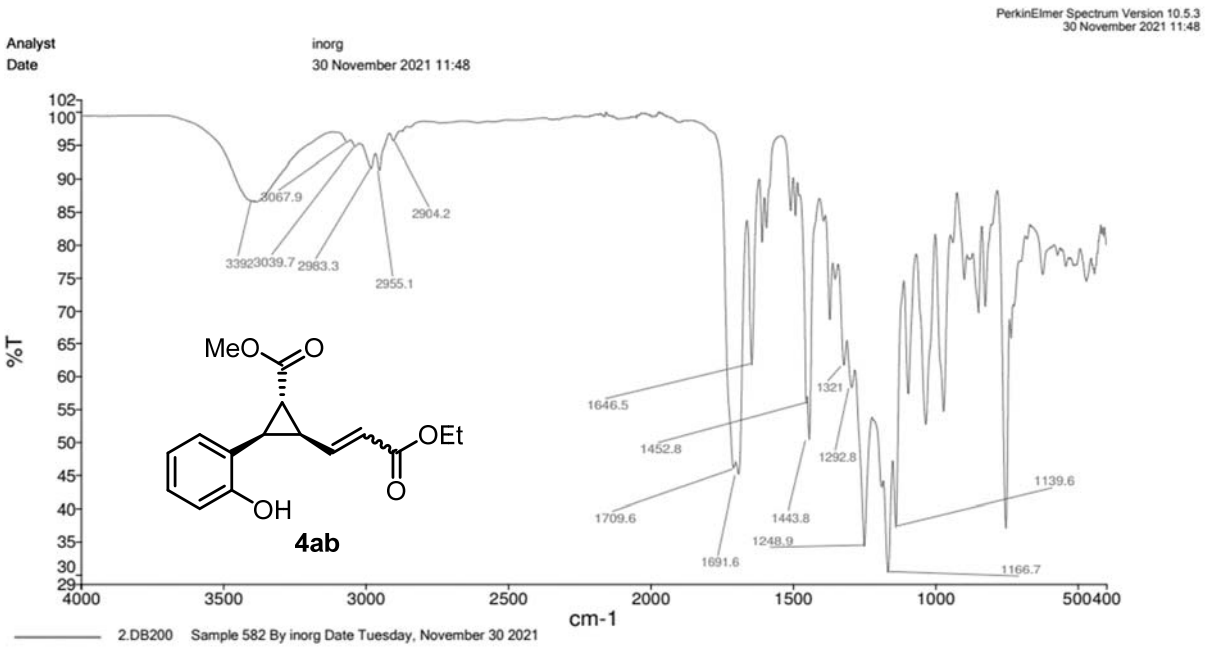


Copies of IR spectra of products 4-8

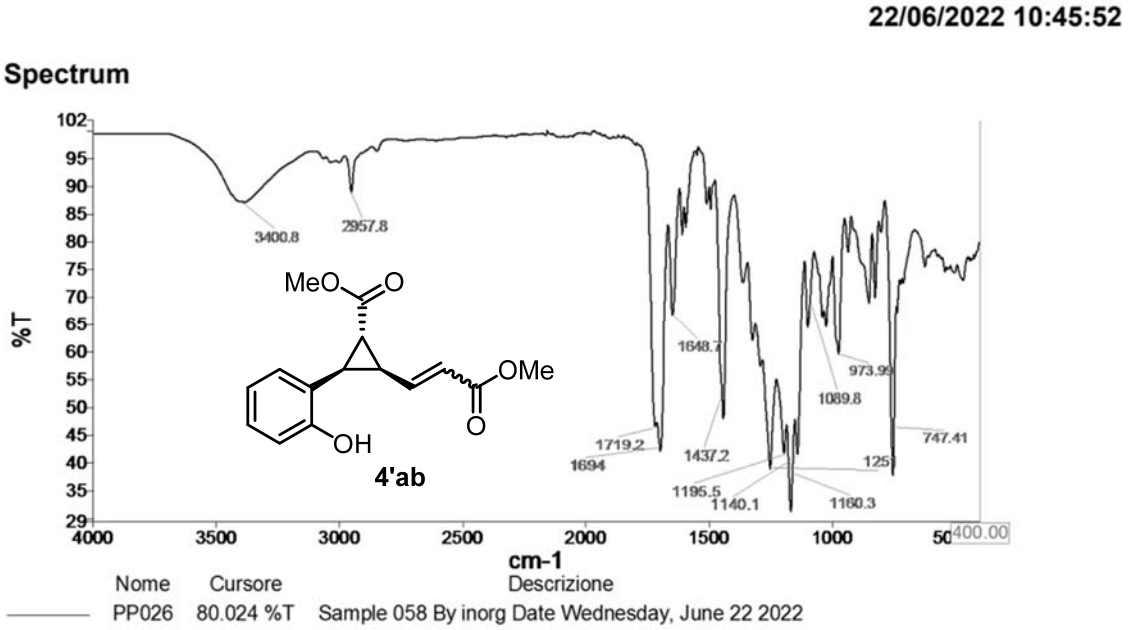
Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4aa



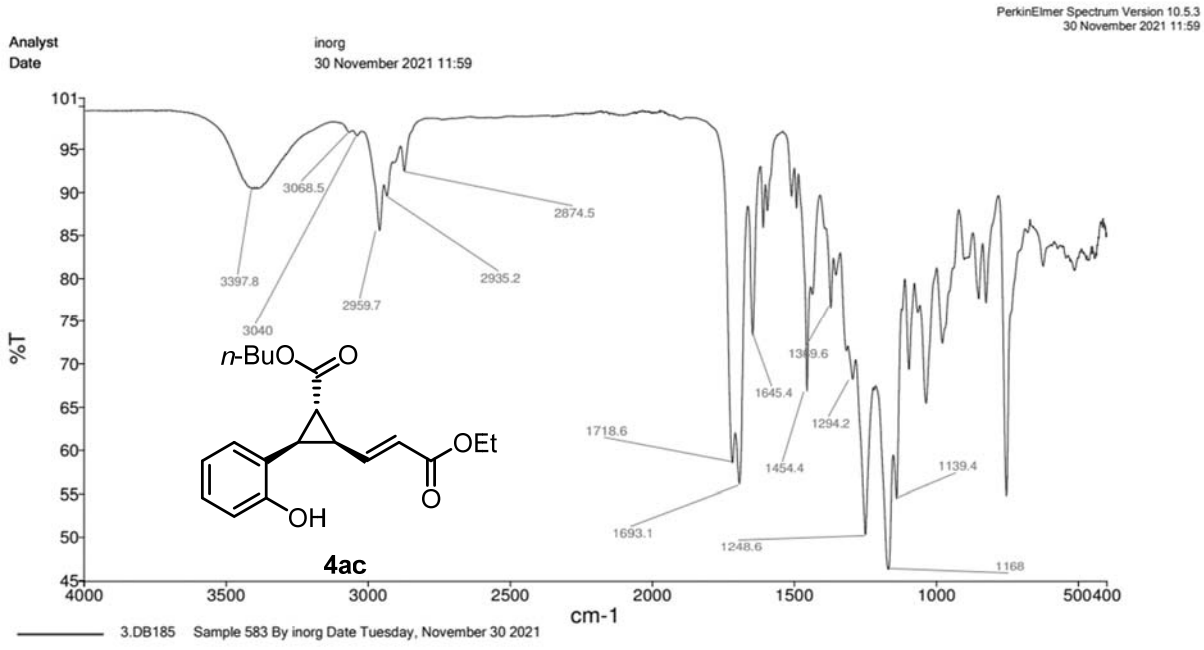
Methyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ab



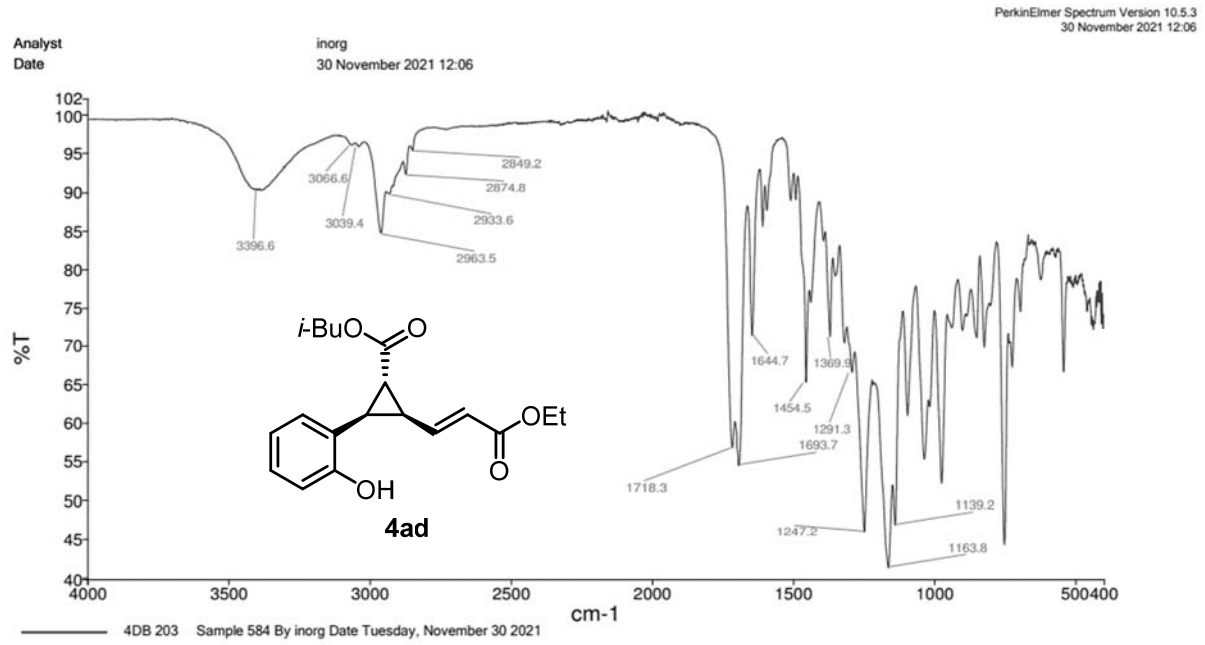
Methyl (1R,2R,3S)-2-(2-hydroxyphenyl)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)cyclopropane-1-carboxylate 4'ab



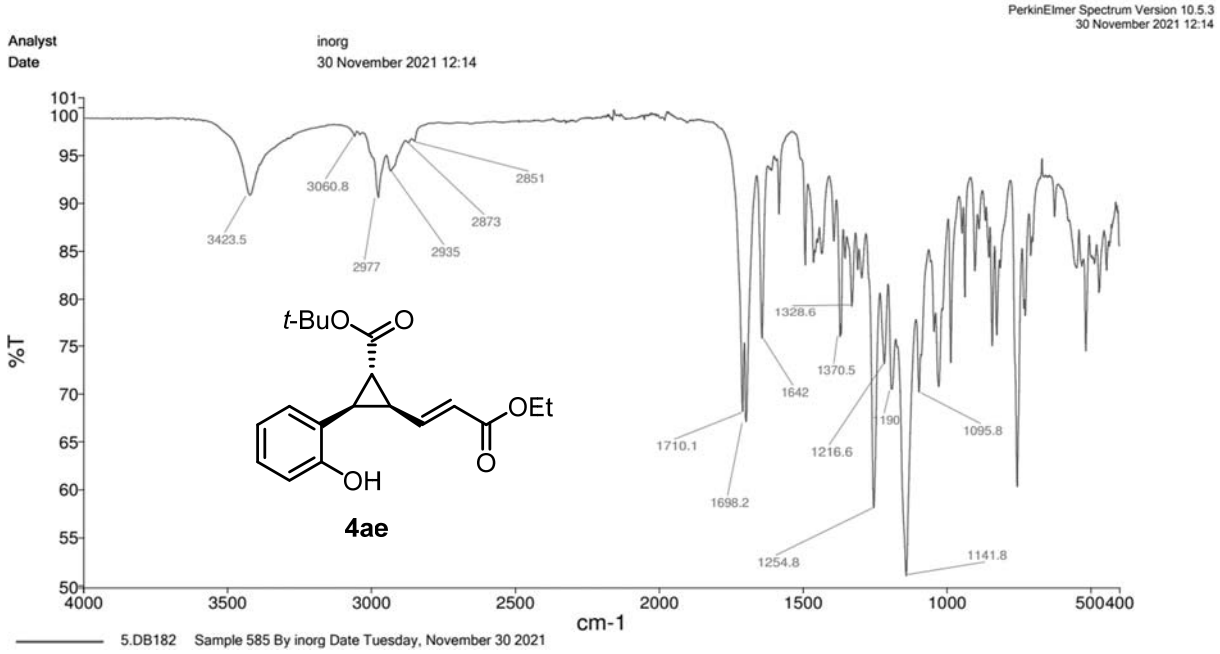
Butyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylatecarboxylate 4ac



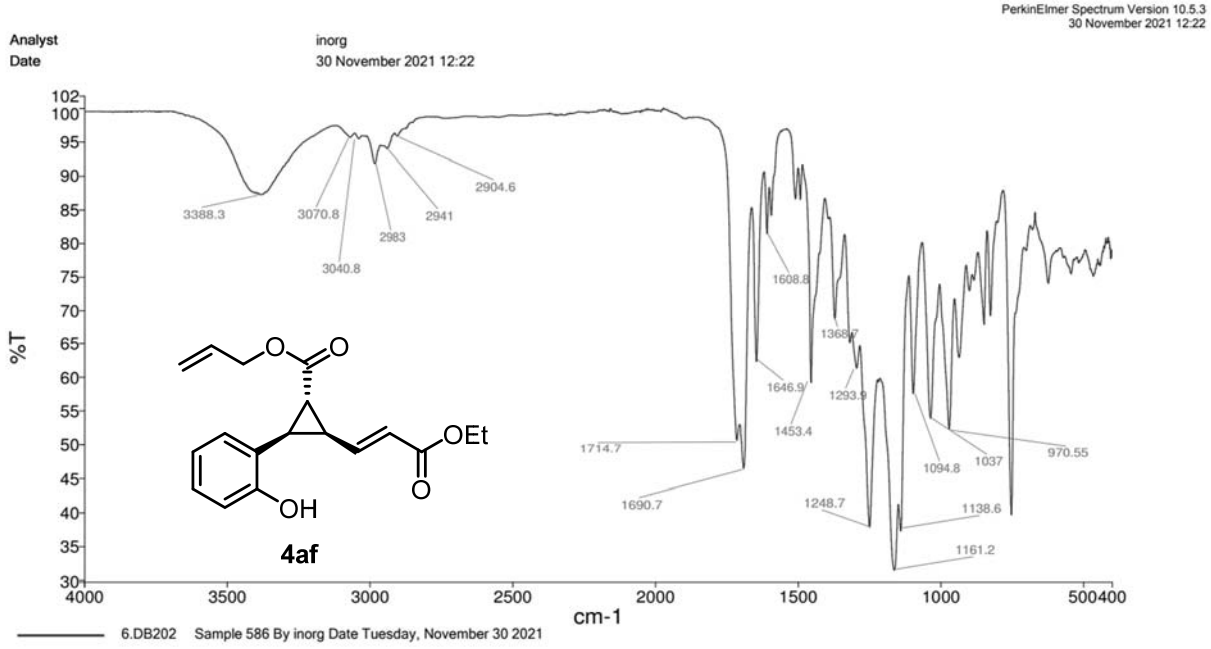
Isobutyl (1R,2S,3R)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ad



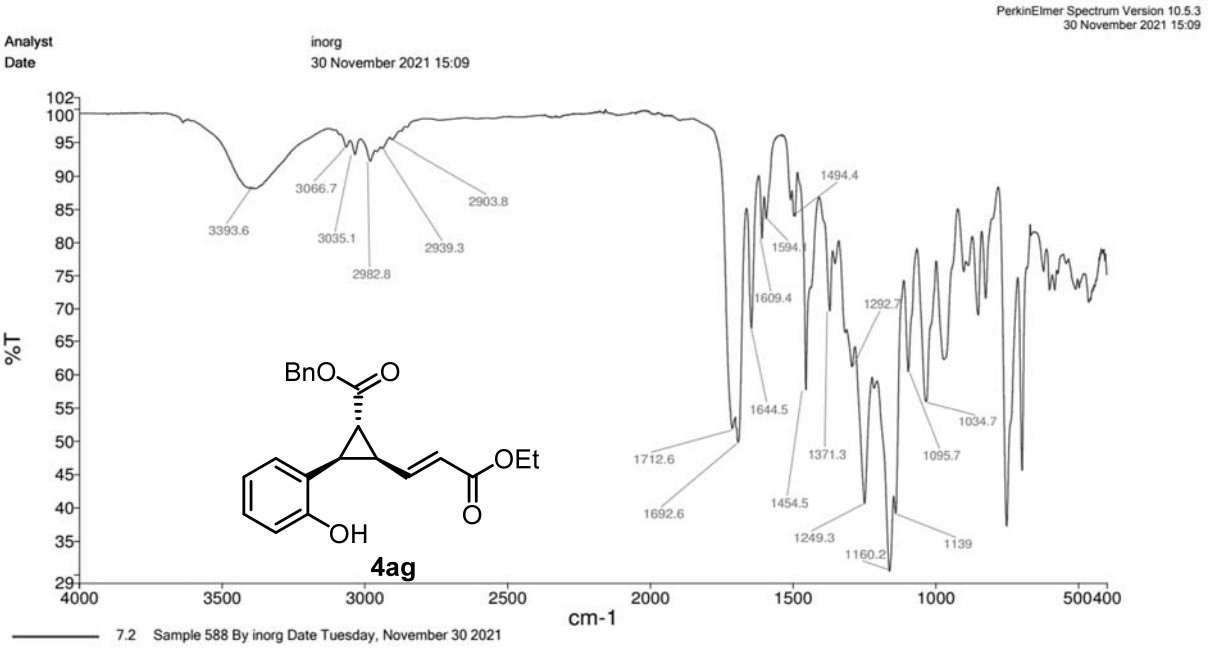
Tert-butyl (1R,2S,3R)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ae



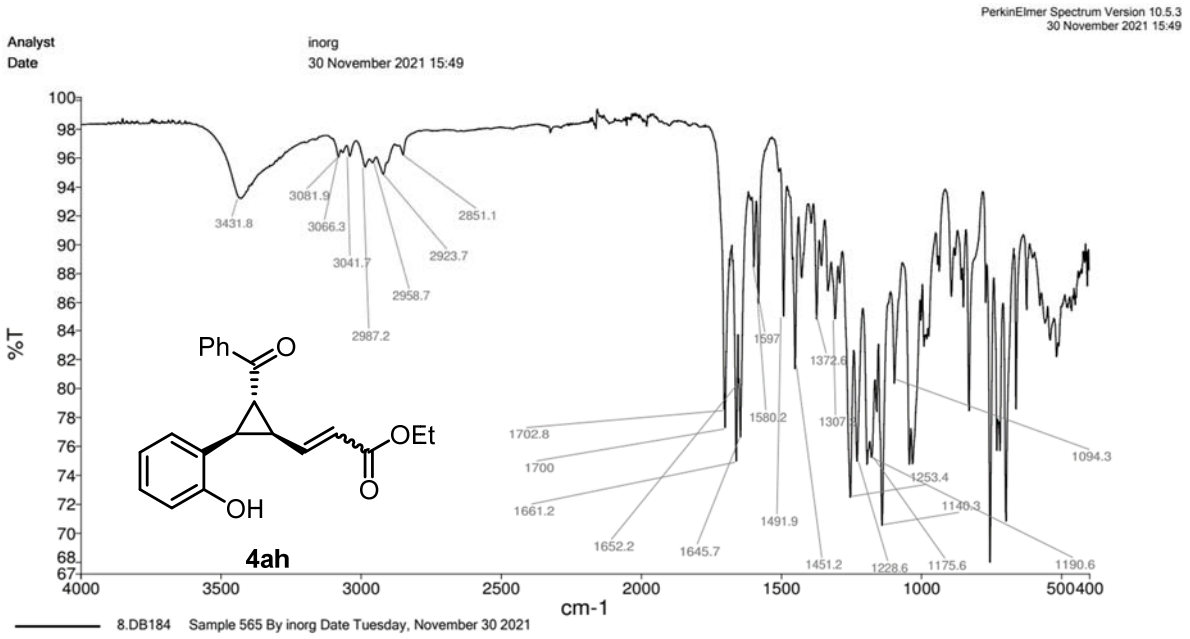
Allyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4af



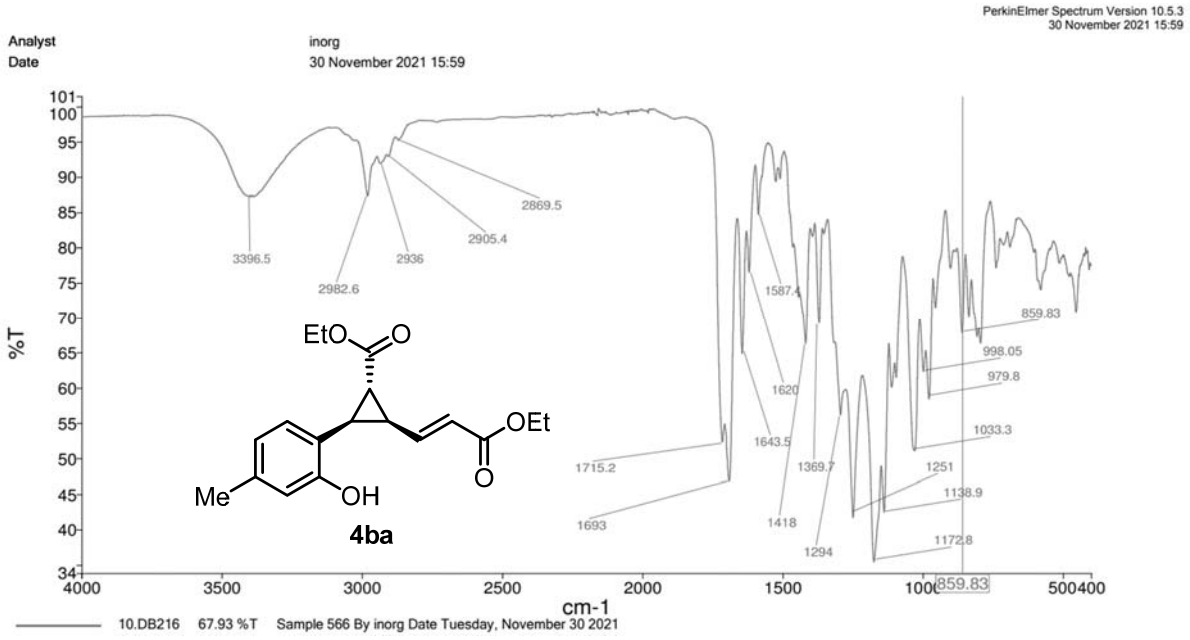
Benzyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 4ag



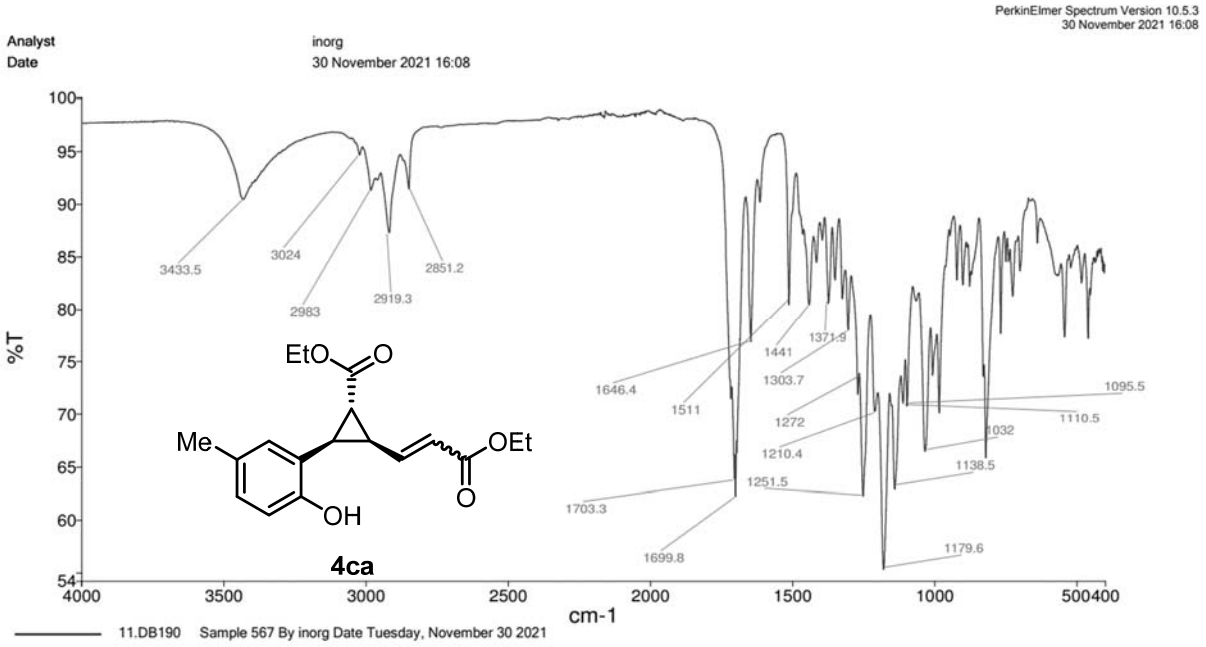
Ethyl--3-((1S,2R,3R)-2-benzoyl-3-(2-hydroxyphenyl)cyclopropyl)acrylate 4ah



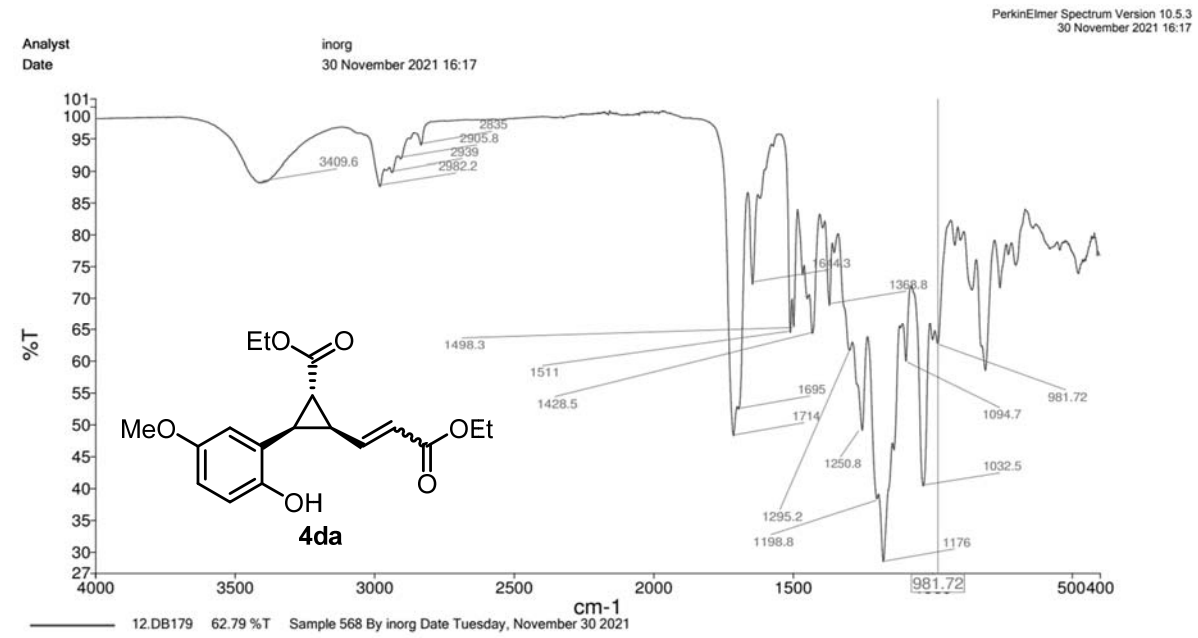
Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-4-methylphenyl)cyclopropane-1-carboxylate 4ba



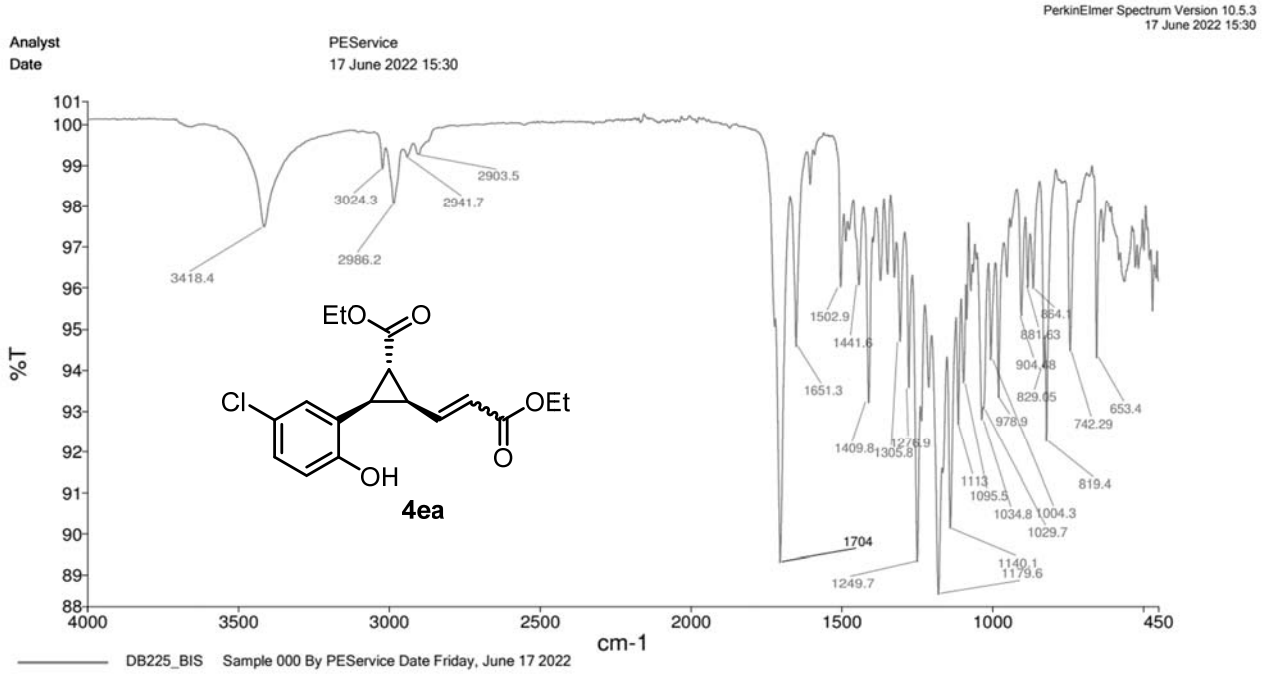
Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-5-methylphenyl)cyclopropane-1-carboxylate 4ca



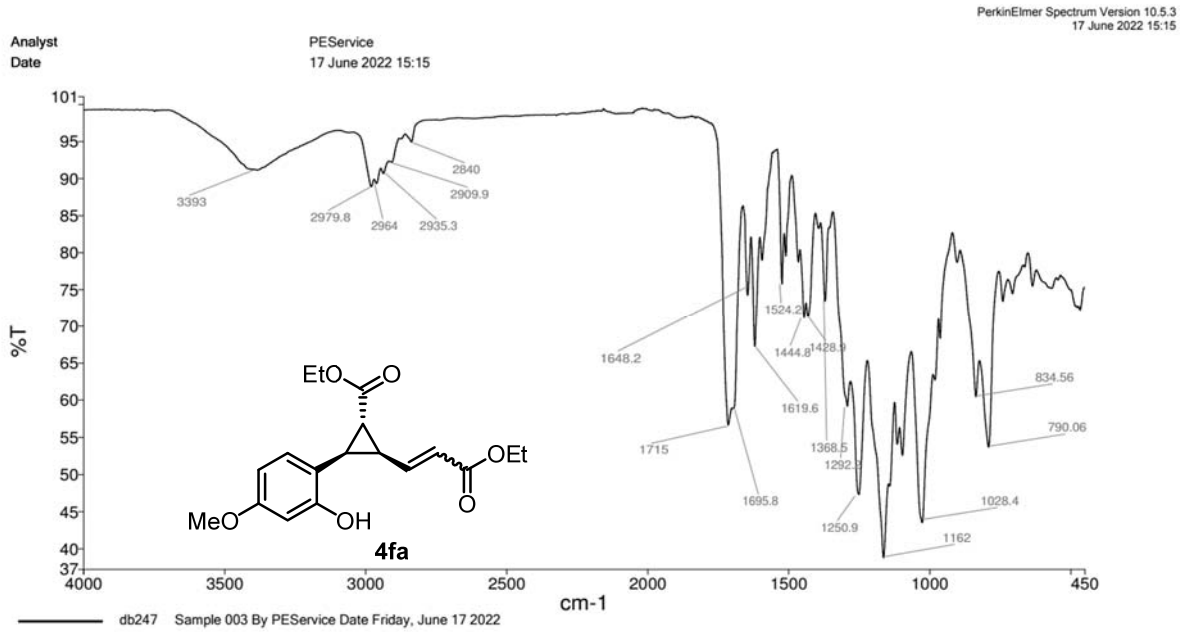
Ethyl (1R,2S,3R)-2-(-3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-5-methoxyphenyl)cyclopropane -1-carboxylate 4da



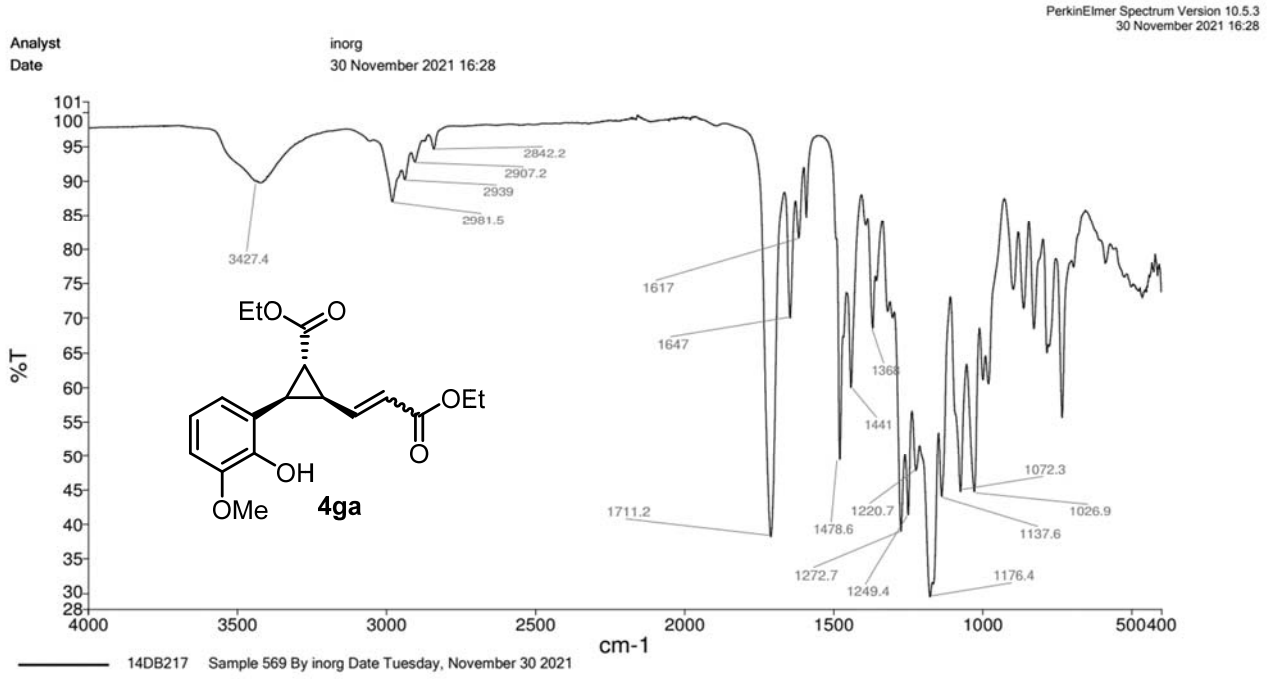
Ethyl (1R,2R,3S)-2-(5-chloro-2-hydroxyphenyl)-3-(-3-ethoxy-3-oxoprop-1-en-1-yl)cyclopropane-1-carboxylate 4ea



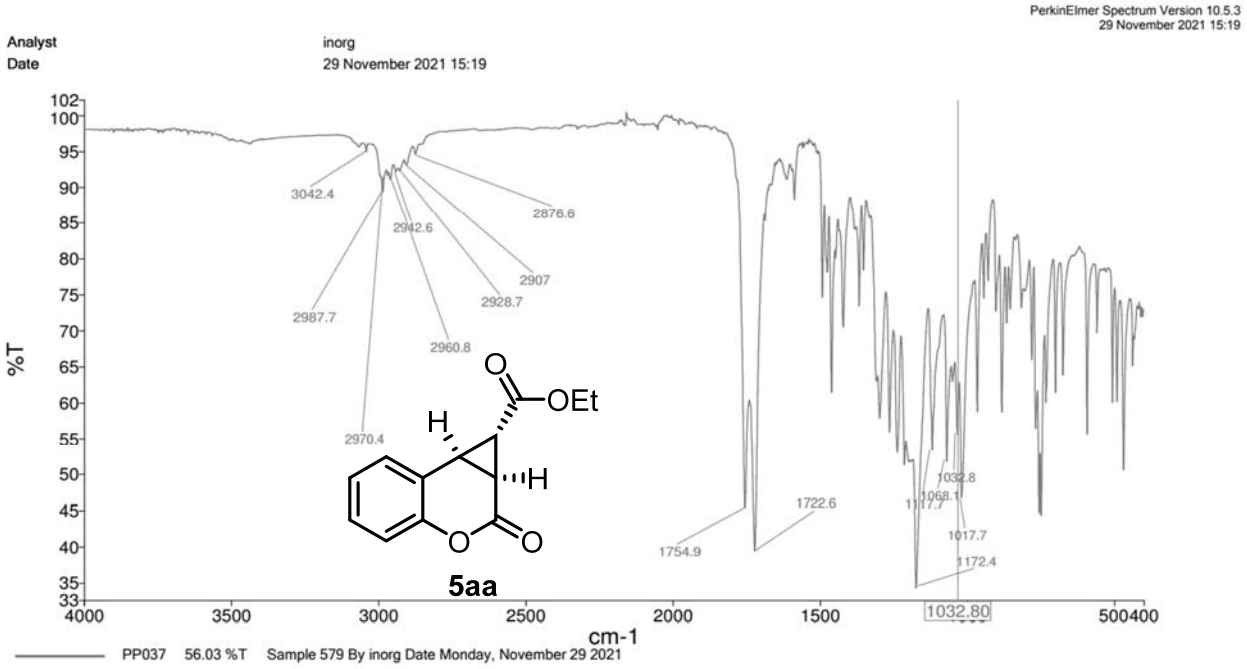
ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-4-methoxyphenyl)cyclopropane-1-carboxylate 4fa



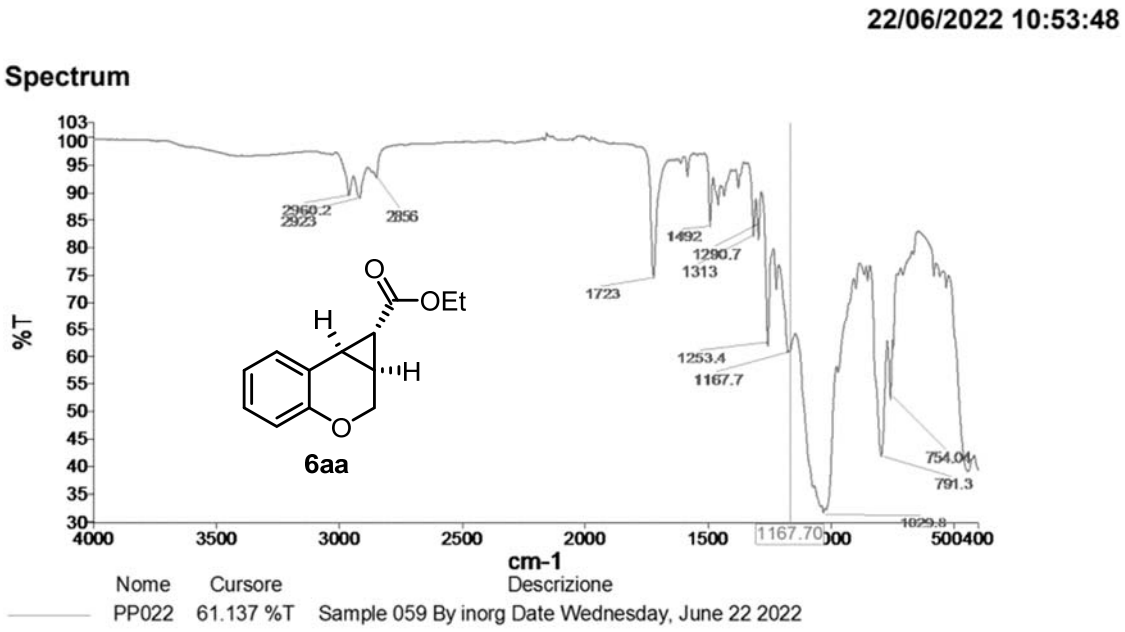
Ethyl (1R,2S,3R)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(2-hydroxy-3-methoxyphenyl)cyclopropane-1-carboxylate 4ga



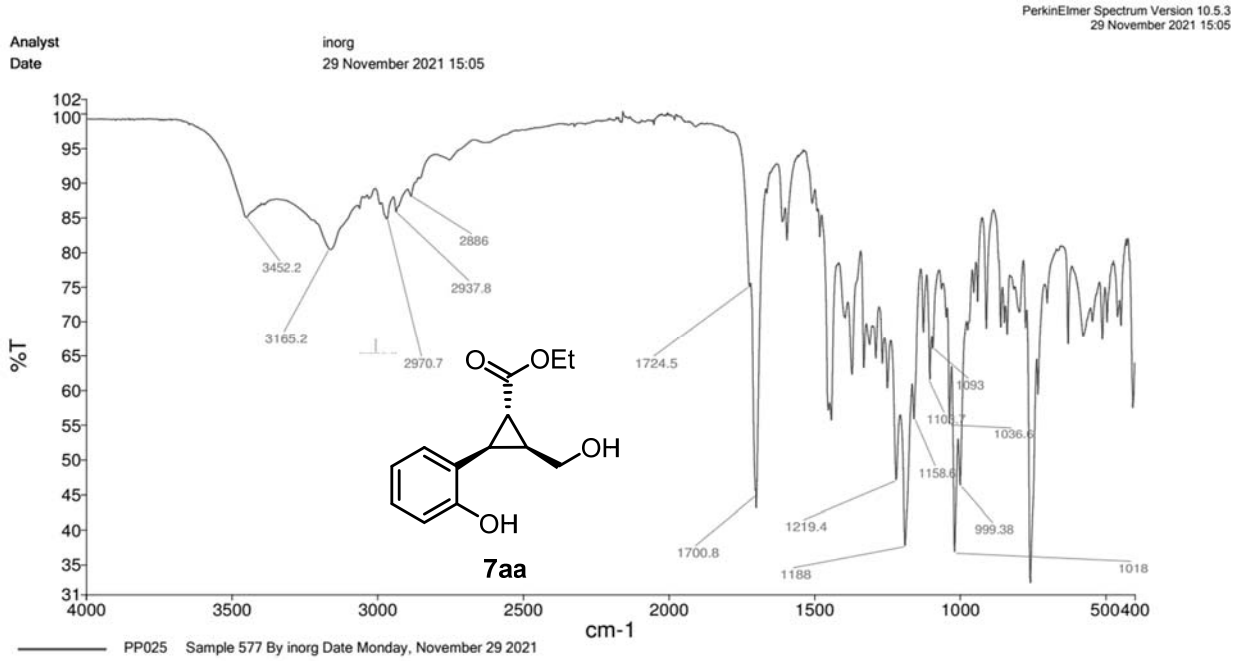
Ethyl (1S,1aS,7bS)-2-oxo-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate 5aa



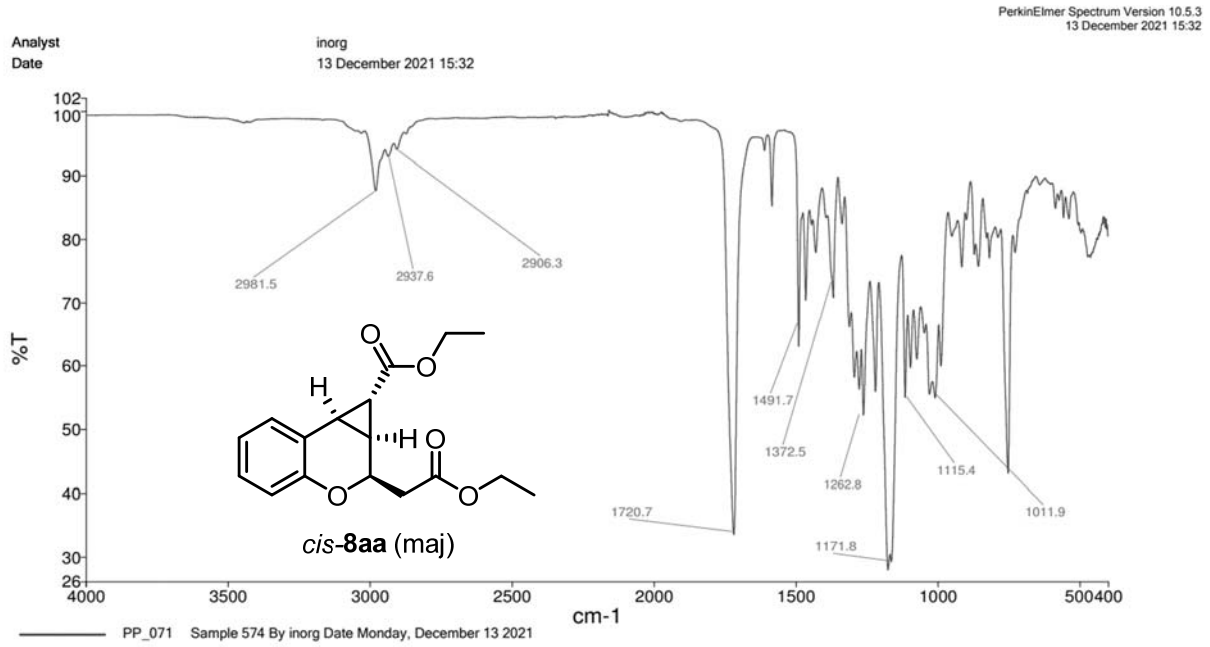
Ethyl (1S,1aS,7bR)-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate 6aa



Ethyl (1S,2S,3R)-2-(hydroxymethyl)-3-(2-hydroxyphenyl)cyclopropane-1-carboxylate 7aa



Ethyl (1S,1aS,2R,7bR)-2-(2-ethoxy-2-oxoethyl)-1,1a,2,7b-tetrahydrocyclopropa[c]chromene-1-carboxylate *cis*-8aa



Ethyl (1S,1aS,2S,7bR)-2-(2-ethoxy-2-oxoethyl)-1,1a,2,7b-tetrahydrocyclopropa[c]chromene-1-carboxylate *trans*-8aa