Supplementary Materials for

Enantioselective photochemistry via Lewis acid catalyzed triplet energy transfer

Travis R. Blum, Zachary D. Miller, Desiree M. Bates, Ilia A. Guzei, Tehshik P. Yoon*

correspondence to: tyoon@chem.wisc.edu

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Materials and Methods

A. General Information:

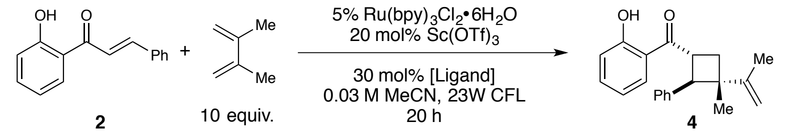
Reagent Preparation. MeCN solvent was purified by elution through alumina as described by Grubbs.(*38*) A 23 W (1200 lumens) SLI Lighting Mini-Lynx compact fluorescent light bulb (CFL) or a 15W EagleLight PAR38 blue LED flood light (500 lumens) was used for all photochemical reactions, unless otherwise noted. Flash-column chromatography was performed with Silicycle 40–63Å silica (230–40 mesh). 2,3-Dimethyl-1,3-butadiene and isoprene were purchased from Sigma Aldrich and distilled prior to use. 2,3-Butadiene (20 wt% in toluene) was purchased from TCI and *trans*-2,3-pentadiene was purchased from Aldrich, and both were used as received. Bisoxazoline ligands were prepared according to literature methods.(*39*) $Ru(bpy)_3(PF_6)_2$ was prepared according to known procedures.(*40*) Unless otherwise noted, all other compounds were purchased from Sigma Aldrich or Strem and were used without further purification. All 2'-hydroxychalcones were previously documented substrates and were synthesized according to a known procedure.(*41*)

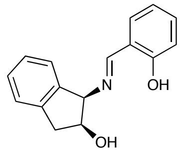
Product Characterization. Diastereomer ratios for all compounds were determined by ^1H NMR analysis of unpurified reaction mixtures. Enantiomeric excesses were determined by analysis of isolated material using chiral SFC (Waters Investigator system) or HPLC Shimadzu LC-20AB with Daicel CHIRALPAK® columns and Chromasolv®-grade methanol, *i*-PrOH, or 25% *i*-PrOH in hexanes. ^1H and ^{13}C NMR data for all previously uncharacterized compounds were obtained using a Bruker Avance 500 spectrometer with DCH cryoprobe and are referenced to tetramethyl silane (0.0 ppm) and $CDCl_3$ (77.0 ppm), respectively. These facilities are funded by the NSF (CHE-9974839, CHE-9304546) and the University of Wisconsin–Madison. IR spectral data were obtained using a Bruker Vector 22 or Alpha Platinum spectrometer (thin film). Melting points were obtained using a Stanford Research Systems DigiMelt apparatus and are uncorrected. Optical rotations were measured using a Rudolph Research Autopol III polarimeter at room temperature. UV-vis absorption spectra were obtained on a Varian Cary 50 spectrophotometer. Emission spectra were obtained on a Horiba Scientific NanoLog FluoroLog3 Spectrofluorimeter with a 1024 channel InGaAs Array NearIR detector. Cyclic voltammetry was performed on a Pine WaveNow (SN4415109) potentiostat.

B. Optimization and Control Studies:

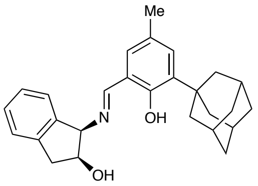
Optimization studies were conducted on small (0.1 mmol) scale. An example procedure follows. In an oven-dried 2 dram vial were combined 2'-hydroxychalcone (**2**, 22.4 mg, 0.100 mmol), $Sc(OTf)_3$ (4.9 mg, 0.10 equiv.), (*S*,*S*)-*t*-BuPyBox (5.0 mg, 0.15 equiv.), $Ru(bpy)_3(PF_6)_2$

(1.3 mg, 0.025 equiv.), and phenanthrene as an internal standard. A magnetic stir bar was added, and the contents were dissolved in 3:1 *i*-PrOAc:MeCN (3 mL). To the resulting solution was added 2,3-dimethyl-1,3-butadiene (110 μL, 9.72 equiv.) by syringe, then the vial was sealed with a Teflon-lined cap and stirred under 23W CFL irradiation for 20 h at room temperature. The reaction progress was monitored by TLC (10% EtOAc/Hexanes). At 20 h, the reaction mixture was diluted with H_2O and Et_2O (approx. 2.0 mL each), and mixed vigorously. After allowing the layers to separate, the organic layer was removed, dried by passing through a plug of $MgSO_4$, and concentrated *in vacuo*. The yield of **4** was obtained by ^{1}H NMR spectroscopic analysis of the crude reaction mixture (relative to phenanthrene internal standard), then the crude material was purified by flash-column chromatography (2.5% EtOAc/Hexanes) to afford pure material for analysis.

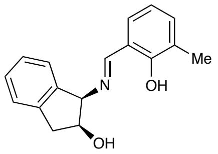




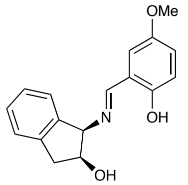
28% yield
8% RSM
3:1 d.r.
2% ee



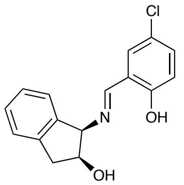
73% yield
0% RSM
3:1 d.r.
1% ee



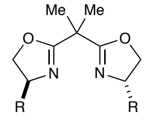
75% yield
0% RSM
3.5:1 d.r.
3% ee



41% yield
40% RSM
3.5:1 d.r.
0% ee

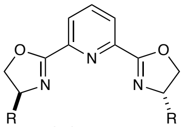


25% yield
59% RSM
4% ee



S,S-Box

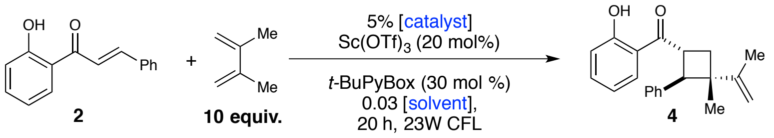
Ligand	Remaining SM	Yield	dr	ee
t-Bu-Box	33%	34%	3.5:1	0%
Indanyl-Box	0%	47%	-	2%
Ph-Box	0%	61%	3.5:1	0%
Bn-Box	0%	63%	3.5:1	2%



S,S-PyBox

Ligand	Remaining SM	Yield	dr	ee
i-Pr-PyBox	43%	43%	3:1	23%
Cyclohexyl-PyBox	27%	46%	3.5:1	11%
i-BuPyBox	43%	35%	2.5:1	51%
t-BuPyBox	0%	82%	3:1	62%

Table S1. Chiral ligand effects in the asymmetric [2+2] photocycloaddition



Entry	[catalyst]	[solvent]	Excited state potentials (vs. SCE) $2^{+*}/3^{+}$	 $2^{+*}/1^{+}$	Yield [2+2] (%ee)
1	$Ru(bpy)_3(PF_6)_2$	MeCN	–0.81 V	+0.77 V	75% (74%)
2	$Ru(CF_3bpy)_3(PF_6)_2$	MeCN	–0.35 V	+1.11	15%
3	$Ru(deeb)_3(PF_6)_2$	MeCN	–0.42 V	+1.07 V	68% (51%)
4	$Ru(dmb)_3(PF_6)_2$	MeCN	–1.16 V	+0.20 V	78% (69%)
5	$Ru(dtbbpy)_3(PF_6)_2$	MeCN	–1.05 V	+0.72	41% (72%)
6	$Ru(bpy)_3(PF_6)_2$	3:1 *i*-PrOAc:MeCN	–1.16 V	+0.20 V	93% (94%)
7	$Ru(deeb)_3(PF_6)_2$	3:1 *i*-PrOAc:MeCN	–0.42 V	+1.07 V	67% (94%)
8	$Ru(dmb)_3(PF_6)_2$	3:1 *i*-PrOAc:MeCN	–1.16 V	+0.20 V	86% (97%)

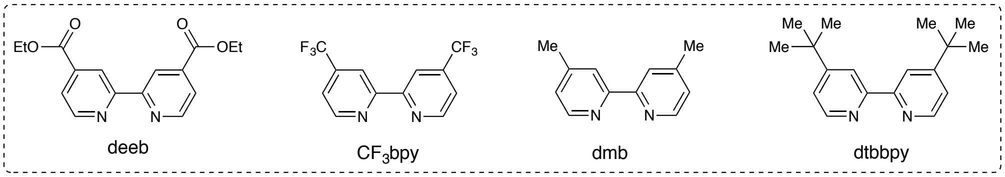
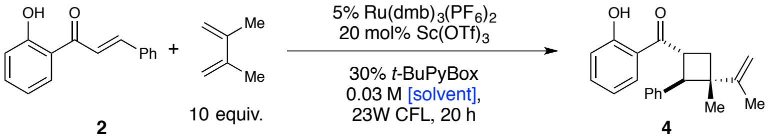
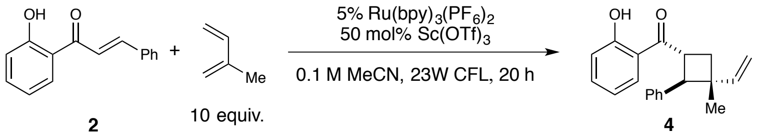


Table S2. Photocatalyst effects in the asymmetric [2+2] photocycloaddition



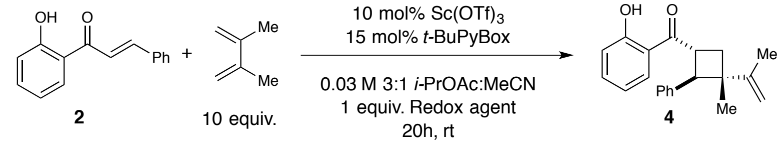
Solvent	Remaining SM	Yield	dr	ee
MeCN	0%	75%	3:1	74%
3:1 *i*-PrOAc: MeCN	0%	87%	3:1	94%
3:1 DCM: MeCN	0%	79%	3:1	91%
3:1 TBME: MeCN	0%	84%	2.5:1	91%
3:1 Et_2O: MeCN	0%	86%	2.5:1	94%

Table S3. Solvent effects in the asymmetric [2+2] photocycloaddition



Conditions	Yield (7.5 h)	Yield (22 h)
Under air	23%	72%
N_2 (sparged)	26%	66%
N_2 (degassed)	34%	62%

Table S4. Effects of degassing on the asymmetric [2+2] photocycloaddition

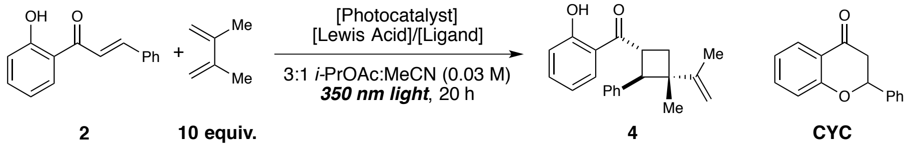


Oxidant	**Result**
CAN	0% yield, 69% RSM
Fe(acac)$_3$	0% yield, 85% RSM
K_3[Fe(CN)$_6$]	0% yield, 105% RSM
Mn(OAc)$_3$	0% yield, 104% RSM
(Ar$_3$N)·SbCl$_6$	0% yield, 96% RSM

Reductant	**Result**
TDAE	0% yield, 88% RSM
SmI$_2$	0% yield, 34% Chalcone reduction 2% RSM**
Li[Naphthalenide]	0% yield, 70% RSM**
Cobaltocene	0% yield, 54% chromanone 26% RSM

***i*-PrOAc replaced with THF due to known reactivity of esters

Table S5. Failed attempts to replicate [2+2] cycloaddition using chemical redox reagents. CAN: cerium(IV) ammonum nitrate, TDAE: Tetrakis(dimethylamino)ethylene, (Ar$_3$N)SbCl$_6$: tris(2,4-dibromophenyl)aminium hexachloroantimonate.



Entry	Photocatalyst (mol%)	Lewis Acid (mol%)	Ligand (mol %)	Result
1	none	none	none	68% yield **CYC**
2	none	$Sc(OTf)_3$ 10 mol%	none	3% yield **4**
3	none	$Sc(OTf)_3$ 10 mol%	*t*-BuPyBox (15 mol%)	1% yield **4**
4	Benzil (100 mol%)	none	none	61% yield **CYC**
5	Benzil (100 mol%)	$Sc(OTf)_3$ 10 mol%	none	8% yield **4**
6	$Ru(bpy)_3(PF_6)_2$ (2.5 mol%)	$Sc(OTf)_3$ 10 mol%	*t*-BuPyBox (15 mol%)	73% yield **4**, 89% ee
7	Benzil (100 mol%)	$Sc(OTf)_3$ 10 mol%	*t*-BuPyBox (15 mol%)	16% yield **4**, 82% ee
8	$Ru(bpy)_3(PF_6)_2$ (5 mol%)	$Sc(OTf)_3$ 50 mol%	*t*-BuPyBox (75 mol%)	96% yield **4**, 94% ee
9	Benzil (100 mol%)	$Sc(OTf)_3$ 50 mol%	*t*-BuPyBox (75 mol%)	45% yield **4**, 89% ee

Table S6. Effects of Lewis acid and sensitizer on the reactivity of 2'-hydroxychalcone under 350 nm irradiation.

Preparation of a mixture of 2'-hydroxychalcone geometric isomers (Table 1, entry 12). Geometrically pure (*E*)-2'-hydroxychalcone was photochemically isomerized as follows. Two oven-dried 6-dram vials were each charged with (*E*)-2'-hydroxychalcone (89.6 mg, 0.4 mmol, 1 equiv.) and $Gd(OTf)_3$ (72.5 mg, 0.12 mmol, 0.3 equiv.). Magnetic stir bars were added, and the contents in each vial were dissolved in MeCN (12 mL). Both vials were then sealed with Teflon-lined caps and irradiated with 23 W CFLs for 72 h with constant stirring. The reaction mixtures were then combined and filtered through a plug of silica (eluting with 5% $MeOH/Et_2O$). The filtrate was concentrated *in vacuo*, and the crude material was purified by flash-column chromatrography (2.5% EtOAc:Hex) to afford analytically pure material (150.5 mg, 84%) as a 2:1 mixture of *Z*/*E* geometric isomers.

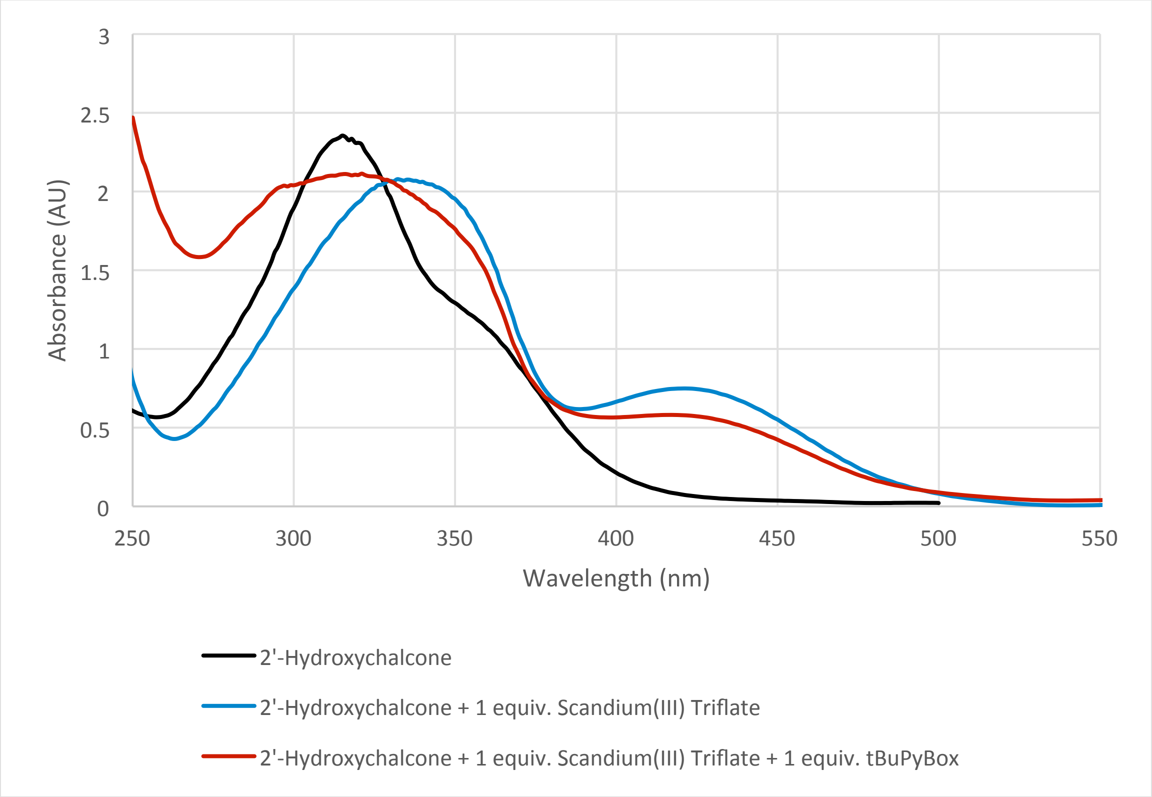
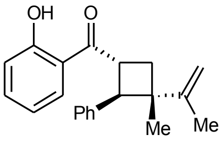


Fig. S1. Lewis acid effects on UV-Vis absorption for 2'-hydroxychalcone (**4**). All measurements obtained at ambient temperature at a concentration of 1.0x 10^{-4} M 2'-hydroxychalcone in MeCN**.** 2'-hydroxychalcone (black), 2'-hydroxychalcone + 1 equiv. Sc(OTf)$_3$ (blue), 2'-hydroxychalcone + 1 equiv. Sc(OTf)$_3$ + 1 equiv. tBuPyBox (red).

C. Isolation Scale Asymmetric [2+2] Cycloadditions (Figure 2)

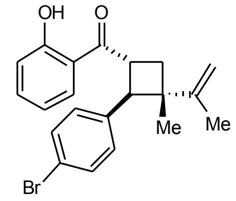
General Procedure A for Isolation Scale Asymmetric [2+2] Cycloaddition with 23 W CFLs*:* In an oven-dried 6 dram vial were combined 2'-hydroxychalcone (1.0 equiv.), Sc(OTf)$_3$ (0.10 equiv.), (*S*,*S*)-*t*-BuPyBox (0.15 equiv.), and Ru(bpy)$_3$(PF$_6$)$_2$ (0.025 equiv.). A magnetic stir bar was added, and the contents were dissolved in 3:1 *i*-PrOAc:MeCN (12 mL). To the resulting solution was added the diene (10 equiv.) by syringe, then the vial was sealed with a Teflon-lined cap and stirred under 23W CFL irradiation for 20 h at room temperature. The reaction progress was monitored by TLC, and at 20 h, the reaction mixture was filtered through a plug of silica (eluting with 5% MeOH/Et$_2$O). The filtrate was then concentrated *in vacuo* and the crude material was purified by flash-column chromatography to afford analytically pure material for analysis. The isolated yields reported in Table 2 represent the summation of both major and minor diastereomeric cycloadducts. Unless otherwise noted, characterization data and enantiomeric excesses are reported for the major isomer.

(2-Hydroxyphenyl)((1*R*,2*R*,3*S*)-3-methyl-2-phenyl-3-(prop-1-en-2-yl)methanone (Figure 2, **4**). Experiment 1: Prepared according to general procedure A using 89.6 mg (0.40 mmol) (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene, and an irradiation time of 20 h. The crude



material resulted in a 3:1 (major:minor) mixture of inseparable diastereomers that was purified by flash-column chromatography on silica gel (2.5% EtOAc:Hex). Combined yield: 108 mg (88%, 0.35 mmol) as a 3:1 (major:minor) mixture of diastereomers; Major isomer**:** 93% ee (Daicel CHIRALPAK® OD-H, gradient 5-50% *i*-PrOH, 4.0 mL/min, 241 nm; t_1 = 4.4 min, t_2 = 4.8 min). Minor isomer: 93% ee (Daicel CHIRALPAK® OD-H, gradient 5-20% MeOH, 4.0 mL/min, 245 nm; t_1 = 4.28 min, t_2 = 4.59 min Characterization data was obtained for the major diastereomer (a white solid) by flash-column chromatography (2.5% EtOAc:Hex), while data for the minor diastereomer (a white solid) was obtained by iterative prep TLC (10% acetone:Hex). Experiment 2: 89.6 mg of a clear oil (0.40 mmol) (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) $Sc(OTf)_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) $Ru(bpy)_3(PF_6)_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 μL (4.0 mmol) 2,3-dimethylbutadiene. Crude d.r.: 3:1; Combined isolated yield: 98 mg of a clear oil (80%, 0.32 mmol); 93% ee.

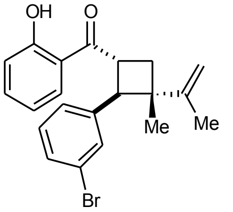
(1*R*,2*R*,3*S*) Diastereomer (major): **^{1}H NMR** (500 MHz, $CDCl_3$): δ 12.35 (s, 1H), 7.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.45 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.31 (dd, *J* = 8.8, 6.9 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 3H), 6.98 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.86 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 4.91 (s, 1H), 4.84 (m, 1H), 4.25 (q, *J* = 9.8 Hz, 1H), 4.19 (d, *J* = 10.0 Hz, 1H), 2.40 (t, *J* = 10.0 Hz, 1H), 2.23 (dd, *J* = 10.9, 8.7 Hz, 1H), 1.75 (s, 3H), 1.37 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 206.3, 162.8, 152.2, 139.5, 136.3, 130.0, 128.2, 128.0, 126.5, 118.8, 118.6, 118.5, 109.0, 47.3, 45.1, 40.7, 36.8, 21.8, 18.8; **IR** (thin film): ν 3033, 2973, 2925, 2370, 2335, 1637, 1436 cm^{-1}; **HRMS** (ESI$^-$) (m/z): [M-H]$^-$ calculated for $C_{21}H_{22}O_2$, 305.1547; found, 305.1548; **mp** = 58-60 ºC; **$[\alpha]^{22}_{D}$** −28.0 º (*c*0.5, CH_2Cl_2). **(1*R*,2*R*,3*R*) Diastereomer** (minor): **^{1}H NMR** (500 MHz, $CDCl_3$): δ 12.38 (s, 1H), 7.54 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.42 (ddd, *J* = 8.8, 7.4, 1.8 Hz, 1H), 7.26-7.30 (m, 3H), 7.20-7.25 (m, 2H), 6.97 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.79 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 5.01 (s, 1H), 4.94 (m, 1H), 4.13 (q, *J* = 8.5 Hz, 1H), 3.70 (d, *J* = 8.5 Hz, 1H), 2.80 (dd, *J* = 11.9, 9.5 Hz, 1H), 2.28 (dd, *J* = 11.9, 8.5 Hz, 1H), 1.41 (s, 3H), 1.11 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 206.4, 162.7, 148.0, 140.0, 136.2, 130.1, 128.2, 127.9, 126.8, 118.8, 118.5, 118.4, 110.9, 52.7, 46.9, 42.0, 34.1, 28.6, 20.1; **IR** (thin film): ν 3034, 2964, 2920, 2362, 2340, 1633 cm^{-1}; **HRMS** (ESI$^-$) (m/z): [M-H]$^-$ calculated for $C_{21}H_{22}O_2$, 305.1547; found, 305.1548; **mp** = 55-57 ºC; **$[\alpha]^{22}_{D}$** − 45.4 º (*c*0.5, CH_2Cl_2).



((1*R*,2*R*,3*S*)-2-(4-Bromophenyl)-3-methyl-3-(prop-1-en-2-yl)cyclobutyl)(2-hydroxyphenyl)methanone (Figure 2, **9**). Experiment 1: Prepared according to general procedure A using 121.3 mg (0.40 mmol) (*E*)-3-(4-bromophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one, 19.2 mg (0.04 mmol) $Sc(OTf)_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) $Ru(bpy)_3(PF_6)_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 μL (4.0 mmol) 2,3-dimethylbutadiene, and an irradiation time of 20 h. The crude material resulted in a 3:1 (major:minor) mixture of diastereomers that was purified by flash-column chromatography on silica gel (2.5% EtOAc:Hex). Combined yield: 130 mg of a clear oil (84%, 0.34 mmol) as a 3:1 (major:minor) mixture of diastereomers; 94% ee (Daicel CHIRALPAK® OD-H, 3% MeOH, 3 mL/min, 248 nm; t_1 = 12.4 min, t_2 = 15.2 min). Characterization data was obtained for the major diastereomer by flash-column chromatography (1-2.5% EtOAc:Hex). Experiment 2: 121.3 mg (0.40 mmol) (*E*)-3-(4-bromophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one, 19.2 mg (0.04 mmol) $Sc(OTf)_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) $Ru(bpy)_3(PF_6)_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 μL (4.0 mmol) 2,3-dimethylbutadiene. Crude d.r.: 3:1; Combined isolated yield: 124 mg of a clear oil (80%, 0.32 mmol); 94% ee.

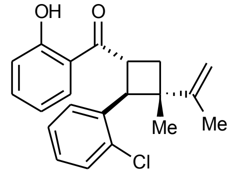
^{1}H NMR (500 MHz, $CDCl_3$): δ 12.28 (s, 1H), 7.70 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.47 (ddd, *J* = 8.3, 7.7, 1.7 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.99 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.88 (ddd, J = 8.3, 7.6, 1.3 Hz, 1H), 4.88 (s, 1H), 4.84 (m, 1H), 4.18 (q, J = 9 Hz, 1H), 4.15 (d, J = 9.5 Hz, 1H), 2.37 (dd, J = 10.9, 9.2 Hz, 1H), 2.25 (dd, J = 10.9, 8.8 Hz, 1H), 1.74 (s, 3H), 1.15 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 205.9, 162.8, 151.8, 138.6, 136.4, 131.3, 129.8, 129.7, 120.4, 118.9, 118.7, 118.3, 109.2, 46.5, 45.0, 40.8, 37.0, 21.7, 18.8; **IR** (thin film): ν 2967, 2923, 1633, 1484, 1239 cm^{-1}; **HRMS** (ESI$^-$) (m/z): [M-H]$^-$ calculated for $C_{21}H_{21}BrO_2$, 383.0652; found, 383.0657; **$[\alpha]^{22}_{D}$** −47.3 ° (*c*1.0, CH_2Cl_2).

((1*R*,2*R*,3*S*)-2-(3-Bromophenyl)-3-methyl-3-(prop-1-en-2-yl)cyclobutyl)(2-hydroxyphenyl)methanone (Figure 2, **10**). <u>Experiment 1:</u> Prepared according to general procedure A using 121.3 mg (0.40 mmol) (*E*)-3-(3-bromophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene, and an irradiation time of 20 h. The crude material resulted in a 3:1 (major:minor) mixture of diastereomers that was purified by flash-column chromatography on silica gel (1.0% EtOAc:Hex). Combined yield: 113 mg of a clear oil (73%, 0.29 mmol) as a 3:1 (major:minor) mixture of diastereomers; 93% ee (Daicel CHIRALPAK® OJ-H, 8% solvent, 3 mL/min, 245 nm; t_1 = 4.1 min, t_2 = 4.6 min). Characterization data was obtained for the major diastereomer by flash-column chromatography (1.0% EtOAc:Hex). <u>Experiment 2:</u> 121.3 mg (0.40 mmol) (*E*)-3-(3-bromophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene. Crude d.r.: 3:1; Combined isolated yield: 110 mg of a clear oil (71%, 0.28 mmol); 93% ee.



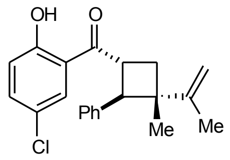
^{1}H NMR (500 MHz, $CDCl_3$): δ 12.27 (s, 1H), 7.71 (dd, J = 7.7, 1.8 Hz, 1H), 7.47 (ddd, J = 8.7, 7.9, 1.9 Hz, 1H), 7.33-7.37 (m, 2H), 7.17 (q, J = 7.5 Hz, 1H), 7.13-7.16 (m, 1H), 7.00 (dd, J = 8.3, 1.2 Hz, 1H), 6.89 (t, J = 7.7 Hz, 1H), 4.89 (s, 1H), 4.86 (m, 1H), 4.19-4.23 (m, 1H), 4.17 (d, J = 9.4 Hz, 1H), 2.32-2.38 (m, 1H), 2.24-2.29 (m, 1H), 1.75 (s, 3H), 1.15 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 205.8, 162.8, 151.7, 142.1, 136.5, 130.8, 129.9, 129.8, 129.6, 126.7, 122.5, 118.9, 118.7, 118.3, 109.4, 46.3, 45.2, 40.8, 37.2, 21.7, 18.8; **IR** (thin film): ν 2953, 2920, 2856, 2366, 1633, 1455 cm^{-1}; **HRMS** (ESI$^-$) (m/z): [M-H]$^-$ calculated for $C_{21}H_{21}BrO_2$, 383.0652; found, 383.0655; **$[\alpha]^{22}_{D}$** −21.6 ° (*c*1.0, CH_2Cl_2).

((1*R*,2*S*,3*S*)-2-(2-Chlorophenyl)-3-methyl-3-(prop-1-en-2-yl)cyclobutyl)(2-hydroxyphenyl)methanone (Figure 2, **11**). <u>Experiment 1:</u> Prepared according to general procedure A using 103.5 mg (0.40 mmol) (*E*)-3-(2-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene, and an irradiation time of 20 h. The crude material resulted in a 2:1 (major:minor) mixture of inseparable diastereomers that was purified by flash-column chromatography on silica gel (1-2.5% EtOAc:Hex). Combined yield: 88.0 mg of a clear oil (64%, 0.26 mmol) as a 2:1 (major:minor) mixture of diastereomers; 98% ee (Daicel CHIRALPAK® OJ-H, 8% *i*-PrOH, 4 mL/min, 250 nm; t_1 = 3.2 min, t_2 = 3.4 min). Characterization data was obtained for the major diastereomer by flash-column chromatography (1.0 - 2.5% EtOAc:Hex), while data for the minor diastereomer was obtained by iterative prep TLC (20% acetone:Hex). <u>Experiment 2:</u> 103.5 mg (0.40 mmol) (*E*)-3-(2-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol)



$Ru(bpy)_3(PF_6)_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene. Crude d.r.: 2:1; Combined isolated yield: 84.5 mg of a clear oil (62%, 0.25 mmol); 98% ee.

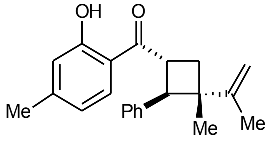
(1*R*,2*S*,3*S*) Diastereomer (major): **^{1}H NMR** (500 MHz, $CDCl_3$): δ 12.29 (s, 1H), 7.65 (dd *J* = 8.0, 1.9 Hz, 1H), 7.44 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.41 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.36 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.26 (td, *J* = 7.5, 1.3 Hz, 1H), 7.17 (td, *J* = 7.5, 1.8 Hz, 1H), 6.97 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.84 (ddd, *J* = 8.4, 7.5, 1.1 Hz, 1H), 4.81 (s, 1H), 4.80 (m, 1H), 4.60 (d, *J* = 9.8 Hz, 1H), 4.29 (q, *J* = 9.6 Hz, 1H), 2.59 (t, *J* = 10.4 Hz, 1H), 2.16 (dd, *J* = 11.1, 9.8 Hz, 1H), 1.83 (s, 3H), 1.22 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 205.6, 162.7, 151.0, 136.6, 136.3, 134.7, 130.0, 129.8, 129.3, 127.9, 126.3, 118.8, 118.6, 118.4, 109.5, 45.4, 44.3, 41.2, 35.4, 21.8, 19.2; **IR** (thin film): ν 2964, 2920, 2361, 2336, 1633 cm^{-1}; **HRMS** (ESI^-) (m/z): $[M-H]^-$ calculated for $C_{21}H_{21}ClO_2$, 339.1157; found, 339.1159; **$[\alpha]^{22}_D$** − 52.1 ° (*c*1.0, CH_2Cl_2). **(1*R*,2*S*,3*R*) Diastereomer** (minor): **^{1}H NMR** (500 MHz, $CDCl_3$): δ 12.32 (s, 1H), 7.59 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.45 (ddd, *J* = 8.8, 7.7, 2.3 Hz, 1H), 7.35 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.29 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.21 (td, *J* = 7.5, 1.7 Hz, 1H), 7.15 (td, *J* = 8.2, 1.7 Hz, 1H), 6.97 (dd, *J* = 8.5, 1.2 Hz, 1H), 6.84 (ddd, *J* = 8.2, 7.7, 1.2 Hz, 1H), 5.04 (s, 1H), 4.94 (m, 1H), 4.40 (d, *J* = 8.7 Hz, 1H), 4.15 (q, *J* = 9.1 Hz, 1H), 2.82 (dd, *J* = 11.3, 9.5 Hz, 1H), 2.25 (dd, *J* = 11.3, 9.1 Hz, 1H), 1.51 (s, 3H), 1.11 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 205.8, 162.8, 147.5, 137.5, 136.3, 134.7, 129.8, 129.3, 128.3, 127.8, 126.6, 118.8, 118.6, 118.3, 110.6, 48.0, 47.1, 41.0, 34.5, 28.8, 19.8; **IR** (thin film): ν 2968, 2924, 2357, 2340, 1629 cm^{-1}; **HRMS** (ESI^-) (m/z): $[M-H]^-$ calculated for $C_{21}H_{21}ClO_2$, 339.1157; found, 339.1158; **$[\alpha]^{22}_D$** −32.8 ° (*c*1.0, CH_2Cl_2).



(5-Chloro-2-hydroxyphenyl)((1*R*,2*R*,3*S*)-3-methyl-2-phenyl-3-(prop-1-en-2-yl)cyclobutyl)methanone (Figure 2, **15**). Experiment 1: Prepared according to general procedure A using 103.5 mg (0.40 mmol) (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) $Sc(OTf)_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) $Ru(bpy)_3(PF_6)_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene, and an irradiation time of 20 h. The crude material resulted in a 2.2:1 (major:minor) mixture of inseparable diastereomers that was purified by flash-column chromatography on silica gel (2.5% EtOAc:Hex). Combined yield: 120 mg of a clear oil (88%, 0.35 mmol) as a 2:1 (major:minor) mixture of diastereomers; 88% ee (Daicel CHIRALPAK® OD-H, gradient 5 - 50% MeOH, 3 mL/min, 248 nm; t_1 = 4.5 min, t_2 = 4.9 min). Characterization data was obtained for the major diastereomer by flash-column chromatography (2.5% EtOAc:Hex). Experiment 2: 103.5 mg (0.40 mmol) (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) $Sc(OTf)_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) $Ru(bpy)_3(PF_6)_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene. Crude d.r.: 2:1; Combined isolated yield: 113.0 mg of a clear oil (83%, 0.33 mmol); 89% ee.

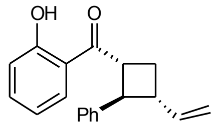
^{1}H NMR (500 MHz, $CDCl_3$): δ 12.23 (s, 1H), 7.62 (d, *J* = 2.7 Hz, 1H), 7.39 (dd, *J* = 8.7, 7.5 Hz, 1H), 7.31-7.34 (m, 2H), 7.22-7.26 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 1H), 4.90 (s, 1H), 4.84 (p, *J* = 1.4 Hz, 1H), 4.17 (q, *J* = 9.4 Hz, 1H), 4.14 (d, *J* = 9.4 Hz, 1H), 2.41 (t, *J* = 9.4 Hz, 1H), 2.24 (dd, *J* = 10.5, 8.1 Hz, 1H), 1.74 (s, 3H), 1.18 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 205.5, 161.2, 152.2, 139.1, 136.2, 129.2, 128.3, 128.1, 126.7, 123.5, 120.2, 119.0, 109.0, 47.7, 45.2, 40.1, 36.5, 21.8, 18.8; **IR** (thin film): ν 3029, 2925, 2366, 2336, 1633, 1607, 1275 cm^{-1}; **HRMS** (ESI^-) (m/z): $[M-H]^-$ calculated for $C_{21}H_{21}ClO_2$, 339.1157; found, 339.1158; **$[\alpha]^{22}_D$** −15.9 ° (*c*0.9, CH_2Cl_2).

(2-Hydroxy-4-methylphenyl)((1*R*,2*R*,3*S*)-3-methyl-2-phenyl-3-(prop-1-en-2-yl)cyclobutyl)methanone (Figure 2, **16**). Experiment 1: Prepared according to general procedure A using 95.3 mg (0.40 mmol) (*E*)-1-(2-hydroxy-4-methylphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene, and an irradiation time of 20 h. The crude material resulted in a 2:1 (major:minor) mixture of inseparable diastereomers that was purified by flash-column chromatography on silica gel (conditions). Combined yield: 112 mg of a clear oil (88%, 0.34 mmol) as a 2:1 (major:minor) mixture of diastereomers; 83% ee (Daicel CHIRALPAK® OD-H, 4% *i*-PrOH, 5 mL/min, 255 nm; t$_1$ = 4.2 min, t$_2$ = 4.9 min). Characterization data was obtained for the major diastereomer (white solid) by flash-column chromatography (conditions). Experiment 2: 95.3 mg (0.40 mmol) (*E*)-1-(2-hydroxy-4-methylphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene. Crude d.r.: 2:1; Combined isolated yield: 106.5 mg of a clear oil (83%, 0.33 mmol); 83% ee.



^{1}H NMR (500 MHz, CDCl$_3$): δ 12.38 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.28-7.32 (m, 2H), 7.22 (d, *J* = 7.7 Hz, 3H), 6.78 (s, 1H), 6.66 (dd, *J* = 8.0, 1.5 Hz, 1H), 4.9 (s, 1H), 4.83 (p, *J* = 1.4 Hz, 1H), 4.22 (q, *J* = 9.2 Hz, 1H), 4.17 (d, *J* = 10.0 Hz, 1H), 2.38 (t, *J* = 9.7 Hz, 1H), 2.33 (s, 3H), 2.20 (dd, *J* = 10.5, 8.3 Hz, 1H), 1.75 (s, 3H), 1.16 (s, 3H); **^{13}C NMR** (126 MHz, CDCl$_3$): δ 205.6, 162.9, 152.3, 147.9, 139.6, 129.8, 128.2, 128.0, 126.5, 120.1, 118.6, 116.3, 109.0, 47.4, 45.1, 40.5, 36.7, 22.0, 21.8, 18.8; **IR** (thin film): ν 2962, 1635, 1503, 1448, 1242 cm^{-1}; **HRMS** (ESI$^-$) (m/z): [M-H]$^-$ calculated for $C_{22}H_{24}O_2$, 319.1704; found, 319.1705; **mp** = 63-65 ºC; **[α]$^{22}_{D}$** −49.1 º (*c*1.0, CH$_2$Cl$_2$).

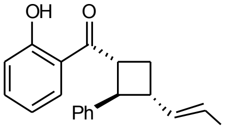
(2-Hydroxyphenyl)((1*R*,2*R*,3*R*)-2-phenyl-3-vinylcyclobutyl)methanone (Figure 2, **17**). Experiment 1: Prepared according to general procedure A using 89.6 mg (0.400 mmol) (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 268 µL (4.0 mmol) 2,3-butadiene, and an irradiation time of 20 h. The crude material resulted in a 1.5:1 (major:minor) mixture of inseparable diastereomers that was purified by flash-column chromatography on silica gel (1-2.5% EtOAc:Hex). Combined yield: 57.0 mg of a clear oil (51%, 0.20 mmol) as a 2:1 (major:minor) mixture of diastereomers; 91% ee (Daicel CHIRALPAK® OJ-H, 5% MeOH, 5 mL/min, 245 nm; t$_1$ = 2.5 min, t$_2$ = 3.1 min). Experiment 2: 89.6 mg (0.400 mmol) (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 268 µL (4.0 mmol) 2,3-butadiene. Crude d.r.: 2:1; Combined isolated yield: 48.0 mg of a clear oil (43%, 0.17 mmol); 91% ee. Experiment 3: 89.6 mg (0.400 mmol) (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 268 µL (4.0 mmol) 2,3-butadiene, and an irradiation time of 40 h. Crude d.r.: 2:1; Combined isolated yield: 89.1 mg of a clear oil (80%, 0.32 mmol); 92% ee. Experiment 4: 89.6 mg (0.400 mmol) (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 268 µL (4.0 mmol) 2,3-butadiene, and an irradiation time of 40 h. Crude d.r.: 2:1; Combined isolated yield: 90.0 mg of a clear oil (81%, 0.32 mmol); 92% ee.



(1*R*,2*R*,3*R*) Diastereomer (major) and **(1*R*,2*R*,3*S*) diastereomer** (minor) as a mixture: **^{1}H NMR** (500 MHz, CDCl$_3$): δ 12.38 (s, 0.54H), 12.36 (s, 0.34H), 7.60 (dd, *J* = 8.0, 1.6 Hz, 0.40H), 7.50

(dd, *J* = 8.0, 1.6 Hz, 0.66H), 7.46 (ddd, *J* = 8.5, 0.46H), 7.43 (ddd, J = 8.5, 7.6, 1.6 Hz, 0.66H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.19-7.25 (m, 1.5H), 7.16 (d, *J* = 7.9 Hz, 0.78H), 6.98 (ddd, *J* = 9.7, 8.4, 1.1 Hz, 1H) 6.83(ddd, *J* = 8.2, 7.3, 1.1 Hz, 0.44H), 6.77(ddd, *J* = 8.2, 7.1, 1.1 Hz, 0.6H), 5.98 (ddd, *J* = 17.1, 10.3, 6.8 Hz, 0.66H), 5.73 (ddd, *J* = 17.1, 10.3, 7.8 Hz, 0.40Hz), 5.13 (m, 0.29H), 5.09 (s, 0.48H), 5.05 (dt, *J* = 10.2, 1.5 Hz, 0.74H), 5.02 (dt, *J* = 10.2, 1.5 Hz, 0.40H), 4.36 (q, *J* = 8.4 Hz, 0.44H), 4.23 (t, *J* = 8.8 Hz, 0.43H), 3.95 (q, J = 8.7 Hz, 0.65H), 3.78 (t, *J* = 9.6 Hz, 0.60H), 3.33-3.40 (qdd, *J* = 4.3, 3.8, 1.2 Hz, 0.40H), 3.16 (tddt, *J* = 9.4, 7.9, 6.7, 1.2 Hz, 0.64H), 2.67 (dt, *J* = 11.5, 8.4 Hz, 0.43H), 2.57 (dt, *J* = 10.9, 8.5 Hz, 0.69H), 2.39 (ddd, *J* = 11.4, 9.2, 4.0 Hz, 0.46H), 2.22 (q, *J* = 10.2 Hz, 0.69H); **^{13}C NMR** (126 MHz, CDCl$_3$): δ 206.1, 205.6, 162.81, 162.80, 142.1, 140.2, 139.5, 138.5, 136.33, 136.31, 130.1, 130.0, 128.2, 127.8, 126.9, 126.8, 126.7, 126.5, 118.9, 118.8, 118.6, 118.4, 115.5, 115.0, 47.5, 46.0, 44.4, 44.2, 41.8, 39.9, 29.9, 28.7; **IR** (thin film): ν 2950, 2361, 2335, 1646, 1607, 1493, 1441, 1280 cm^{-1}; **HRMS** (ESI$^-$) (m/z): [M-H]$^-$ calculated for $C_{19}H_{18}O_2$, 277.1234; found, 277.1232; $[\alpha]^{22}_{D}$ −36.4 ° (*c*0.5, CH$_2$Cl$_2$).

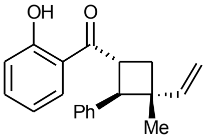
(2-Hydroxyphenyl)((1*R*,2*R*,3*R*)-2-phenyl-3-((*E*)-prop-1-en-1-yl)cyclobutyl)methanone



(Figure 2, **18**). Experiment 1: Prepared according to general procedure A using 89.6 mg (0.400 mmol) (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 399 µL (4.0 mmol) 2,3-*trans*-pentadiene, and an irradiation time of 20 h. The crude material resulted in a 2:1 (major:minor) mixture of inseparable diastereomers that was purified by flash-column chromatography on silica gel (1-2.5% EtOAc:Hex). Combined yield: 100 mg of a clear oil (86%, 0.34 mmol) as a 2:1 (major:minor) mixture of diastereomers; 92% ee (Daicel CHIRALPAK® AD-H, gradient 1-6% (*i*-PrOH:Hex), Shimadzu HPLC, 0.4 mL/min, 265 nm; t_1 = 15.5 min, t_2 = 17.4 min). Experiment 2: 89.6 mg (0.400 mmol) (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 399 µL (4.0 mmol) 2,3-*trans*-pentadiene. Crude d.r.: 2:1; Combined isolated yield: 95.0 mg of a clear oil (81%, 0.32 mmol); 92% ee.

(1*R*,2*R*,3*R*) Diastereomer (major) and **(1*R*,2*R*,3*S*) diastereomer** (minor) as a mixture: **^{1}H NMR** (500 MHz, CDCl$_3$): δ 12.41 (s, 0.60H), 12.39 (s, 0.42H), 7.60 (dd, *J* = 8.1, 1.5 Hz, 0.43H), 7.49 (dd, *J* = 8.1, 1.5 Hz, 0.64H), 7.45 (ddd, *J* = 8.7, 7.9, 1.9 Hz, 0.40H), 7.42 (ddd, *J* = 8.7, 7.9, 1.9 Hz, 0.72H), 7.28-7.32 (m, 2H), 7.19-7.24 (m, 1.6H), 7.15 (d, *J* = 7.2 Hz, 0.87H), 6.98 (ddd, *J* = 10.1, 8.8, 1.0 Hz, 1H), 6.83 (ddd, *J* = 8.1, 7.4, 1.1 Hz, 0.42H), 6.77 (ddd, *J* = 8.1, 7.4, 1.1 Hz, 0.62H), 5.59 (ddq, *J* = 15.4, 1.3, 1.2 Hz, 0.62H), 5.52 (dq, *J* = 15.4, 6.1 Hz, 0.54H), 5.47 (dqd, *J* = 15.4, 6.3, 1.1 Hz, 0.53H), 5.35 (ddq, *J* = 15.5, 8.0, 1.2 Hz, 0.43H), 4.33 (q, *J* = 8.8 Hz, 0.44H), 4.17 (t, *J* = 8.8 Hz, 0.42H), 3.91 (q, *J* = 9.4 Hz, 0.62H), 3.73 (t, *J* = 9.4 Hz, 0.62H), 3.31 (qdd, *J* = 4.6, 4.0, 1.3 Hz, 0.42H), 3.10 (quint, *J* = 8.1 Hz, 0.62H), 2.64 (dt, *J* = 11.4, 8.0 Hz, 0.42H), 2.53 (dt, *J* =10.7, 8.4 Hz, 0.62H), 2.31 (ddd, *J* = 11.2, 9.3, 4 Hz, 0.44H), 2.16 (q, *J* = 10.5 Hz, 0.66H), 1.67 (d, *J* = 6.2 H, 1.82H), 1.58 (d, *J* = 6.3 Hz, 1.25H); **^{13}C NMR** (126 MHz, CDCl$_3$) 206.3, 205.8, 162.79, 162.76, 142.3, 139.9, 136.3, 133.3, 131.2, 130.1, 130.0, 128.52, 128.50, 128.1, 127.8, 126.8, 126.6, 126.27, 126.26, 125.7, 118.9, 118.5, 118.5, 118.4, 118.3, 47.9, 46.0, 44.7, 44.4, 41.0, 39.1, 30.1, 29.6, 17.91, 17.90**, IR** (thin film): ν 3038, 2938, 2362, 2331, 1633, 1480, 1210 cm^{-1}; **HRMS** (ESI$^-$) (m/z): [M-H]$^-$ calculated for $C_{20}H_{20}O_2$, 291.1391; found, 291.1393; $[\alpha]^{22}_{D}$ −39.0 ° (*c*0.5, CH$_2$Cl$_2$).

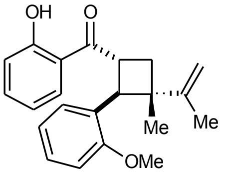
(2-Hydroxyphenyl)((1*R*,2*S*,3*R*)-3-methyl-2-phenyl-3-vinylcyclobutyl)methanone (Figure 2, **19**). <u>Experiment 1:</u> Prepared according to general procedure A using 89.6 mg (0.400 mmol) (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 400 µL (4.0 mmol) isoprene, and an irradiation time of 20 h. The crude material resulted in a 2:1 (major:minor) mixture of inseparable diastereomers that was purified by flash-column chromatography on silica gel (1.0-2.5% EtOAc:Hex). Combined yield: 103 mg of a clear oil (88%, 0.35 mmol) as a 2:1 (major:minor) mixture of diastereomers and in 86:14 regioselectivity; 92% ee (Daicel CHIRALPAK® OJ-H, gradient 5-50% (25% *i*-PrOH:Hex), 3 mL/min, 243 nm; t$_1$ = 4.8 min, t$_2$ = 5.5 min). Characterization data was obtained for the major diastereomer and regioisomer by flash-column chromatography (1.0-2.5 % EtOAc:Hex). <u>Experiment 2:</u> 89.6 mg (0.400 mmol) (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 400 µL (4.0 mmol) isoprene. Crude d.r.: 2:1; crude r.r.: 86:14); Combined isolated yield: 102 mg of a clear oil (84%, 0.34 mmol); 92% ee.



^{1}H NMR (500 MHz, CDCl$_3$): δ 12.35 (s, 1H), 7.78 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.48 (ddd, *J* = 7.9, 7.0, 1.5 Hz, 1H), 7.27-7.32 (m, 2H), 7.19-7.23 (m, 1H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.00 (dd, J = 8.4, 1.2 Hz, 1H), 6.90 (ddd, *J* = 8.4, 7.2, 1.1 Hz, 1H), 6.12 (dd, *J* = 17.6, 10.3 Hz, 1H), 5.08 (m, 1H), 5.05 (dd, *J* = 5.3, 1.1 Hz, 1H), 4.33 (q, *J* = 9.6Hz, 1H), 4.08 (d, *J* = 9.9 Hz, 1H), 2.35 (t, *J* = 10.6 Hz 1H), 2.24 (dd, *J* = 10.6, 9.2 Hz, 1H), 1.05 (s, 3H); **^{13}C NMR** (500 MHz, CDCl$_3$): δ 206.2, 162.8, 146.8, 139.0, 136.4, 129.9, 128.2, 127.1, 126.5, 118.9, 118.6, 118.5, 111.8, 48.1, 41.9, 40.33, 37.5, 20.5; **IR** (thin film): ν 2929, 2353, 2336, 1611, 1589 cm^{-1}; **HRMS** (ESI$^+$) (m/z): [M+H]$^+$ calculated for C$_{20}$H$_{20}$O$_2$, 293.1536; found, 293.1532; **[α]$^{22}_{D}$** −31.8 º (*c*0.5, CH$_2$Cl$_2$).

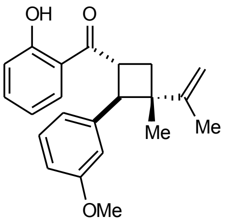
General Procedure B for Isolation Scale Asymmetric [2+2] Cycloaddition with Blue LEDs: In an oven-dried 6 dram vial were combined the 2'-hydroxychalcone (1.0 equiv.), Sc(OTf)$_3$ (0.10 equiv.), (S,S)-t-BuPyBox (0.15 equiv.), and Ru(bpy)$_3$(PF$_6$)$_2$ (0.025 equiv.). A magnetic stir bar was added, and the contents were dissolved in 3:1 ^{i}PrOAc:MeCN (12 mL). To the resulting solution was added the diene (10 equiv.) neat by syringe, then the vial was sealed with a Teflon-lined cap and stirred under high-intensity blue LED irradiation for 2 h, when the starting material was consumed as judged by TLC. The reaction mixture was then filtered through a plug of silica (eluting with 5% MeOH/Et$_2$O). The filtrate was then concentrated *in vacuo* and the crude material was purified by flash-column chromatography to afford analytically pure material for analysis. The isolated yields reported in Table **2** represent the summation of both major and minor diastereomeric cycloadduct products. Characterization data and enantiomeric excesses are reported for the major isomer.

(2-Hydroxyphenyl)((1*R*,2*S*,3*S*)-2-(2-methoxyphenyl)-3-methyl-3-(prop-1-en-2-yl)cyclobutyl)methanone (Figure 2, **12**). <u>Experiment 1:</u> Prepared according to general procedure B using 101.7 mg (0.40 mmol) (*E*)-1-(2-hydroxyphenyl)-3-(2-methoxyphenyl)prop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene, and an irradiation time of 2 h. The crude material resulted in a 4:1 (major:minor) mixture of inseparable diastereomers that was purified by flash-column chromatography on silica gel (2.5% EtOAc:Hex). Combined yield: 92.1 mg of a clear oil (68%, 0.27 mmol) as a 4:1 (major:minor) mixture of diastereomers; 85% ee (Daicel



CHIRALPAK® OJ-H, 5% MeOH, 3 mL/min, 255 nm; t_1 = 4.2 min, t_2 = 4.9 min). <u>Experiment 2:</u> 101.7 mg (0.40 mmol) (*E*)-1-(2-hydroxyphenyl)-3-(2-methoxyphenyl)prop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene. Crude d.r.: 4:1; Combined isolated yield: 87.5 mg of a clear oil (65%, 0.26 mmol); 85% ee.

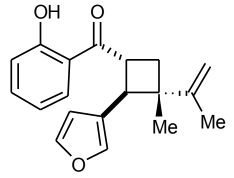
(1*R*,2*R*,3*S*) Diastereomer (major) and **(1*R*,2*R*,3*R*) diastereomer** (minor) as a mixture: **^{1}H NMR** (500 MHz, CDCl$_3$): δ 12.46 (s, 0.68H), 12.43 (s, 0.23H), 7.71 (dd, *J* = 8.0, 1.0 Hz, 0.76H), 7.65 (dd, *J* = 8.0, 1.0 Hz, 0.27H), 7.44 (ddd, *J* = 8.6, 7.8, 1.5 Hz, 1H), 7.24 (m, 0.38H), 7.19 (qd, *J* = 7.6, 1.7 Hz, 1H), 7.13 (dd, *J* = 7.5, 1.6 Hz, 0.27H), 6.98 (dd, *J* = 8.5, 1.2 Hz, 0.75H), 6.96 (dd, *J* = 8.5, 1.2 Hz, 0.25H), 6.93 (td, *J* = 7.5, 1.1 Hz, 0.74H), 6.88 (td, *J* = 7.5, 1.1 Hz, 0.27H), 6.80-6.86 (m, 2H), 4.95 (s, 0.26H), 4.86 (m, 1H), 4.78 (quint, *J* = 1.4 Hz, 0.73H), 4.48 (d, *J* = 9.8 Hz, 0.71H), 4.32 (q, *J* = 9.4 Hz, 0.75H), 4.25 (d, *J* = 9.0 Hz, 0.27H), 4.20 (q, *J* = 9.4 Hz, 0.28H), 3.80 (s, 0.74H), 3.65 (s, 2.19H), 2.76 (dd, *J* = 11.1, 8.9 Hz, 0.27H), 2.46 (t, *J* = 10.0 Hz, 0.74H), 2.20 (dd, *J* = 11.5, 8.7 Hz, 0.30H), 2.12 (dd, *J* = 11.2, 9.4 Hz, 0.74H), 1.79 (s, 2.21H), 1.46 (s, 0.79H), 1.20 (s, 2.18H), 1.17 (s, 0.81H); **^{13}C NMR** (126 MHz, CDCl$_3$): δ 206.7, 206.6, 162.73, 162.71, 157.62, 157.57, 152.1, 148.2, 138.4, 136.1, 136.0, 130.03, 130.00, 128.6, 128.4, 127.7, 127.6, 127.5, 127.4, 120.2, 120.0, 118.8, 118.7, 118.6, 118.44, 118.42, 110.5, 109.96, 109.87, 108.5, 55.2, 54.9, 47.1, 45.1, 45.0, 42.0, 40.5, 40.3, 36.3, 34.9, 28.7, 21.8, 20.0, 18.79; **IR** (thin film): ν 3069, 2964, 2366, 1629, 1581, 1445, 1245 cm^{-1}; **HRMS** (ESI$^-$) (m/z): [M-H]$^-$ calculated for $C_{22}H_{24}O_3$, 335.1653; found, 335.1652; **$[\alpha]^{22}_D$** −61.2 ° (*c*1.0, CH$_2$Cl$_2$).



(2-Hydroxyphenyl)((1*R*,2*R*,3*S*)-2-(3-methoxyphenyl)-3-methyl-3-(prop-1-en-2-yl)cyclobutyl)methanone (Figure 2, **13**). <u>Experiment 1:</u> Prepared according to general procedure B using 101.7 mg (0.40 mmol) (*E*)-1-(2-hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene, and an irradiation time of 2 h. The crude material resulted in a 2:1 (major:minor) mixture of inseparable diastereomers that was purified by flash-column chromatography on silica gel (2.5% EtOAc:Hex). Combined yield: 108 mg of a clear oil (80%, 0.32 mmol) as a 2:1 (major:minor) mixture of diastereomers; 88% ee (Daicel CHIRALPAK® OJ-H, 3% (25% *i*-PrOH:Hex), 3 mL/min, 245 nm; t_1 = 6.9 min, t_2 = 8.6 min). Characterization data was obtained for the major diastereomer by flash-column chromatography (2.5 - 5% EtOAc:Hex). <u>Experiment 2:</u> 101.7 mg (0.40 mmol) (*E*)-1-(2-hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene. Crude d.r.: 2:1; Combined isolated yield: 102 mg of a clear oil (76%, 0.30 mmol); 88% ee.

^{1}H NMR (500 MHz, CDCl$_3$): δ 12.35 (s, 1H), 7.73 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.46 (ddd, *J* = 8.9, 7.9, 1.7 Hz, 1H), 7.23 (dd, *J* = 8.9, 7.7 Hz, 1H), 6.98 (dd, *J* = 8.5, 1.1 Hz, 1H), 6.87 (ddd, *J* = 8.5, 7.6, 1.1 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.75-6.78 (m, 2H), 4.91 (s, 1H), 4.84 (m, 1H), 4.23 (q, *J* = 9.0 Hz, 1H), 4.17 (d, *J* = 9.4 Hz, 1H), 3.77 (s, 3H), 2.37 (dd, *J* = 10.6, 9.4 Hz, 1H), 2.23 (dd, *J* = 10.6, 8.2 Hz, 1H), 1.76 (s, 3H), 1.18 (s, 3H); **^{13}C NMR** (126 MHz, CDCl$_3$): δ 206.2, 162.8, 159.5, 152.1, 141.3, 136.3, 130.0, 129.2, 120.4, 118.8, 118.6, 118.56, 118.47, 114.3, 111.3, 109.1, 55.2, 47.1, 45.1, 40.7, 36.9, 21.7, 18.9; **IR** (thin film): ν 2960, 2933, 2859, 2366, 2335, 1633, 1240 cm^{-1}; **HRMS** (ESI$^-$) (m/z): [M-H]$^-$ calculated for $C_{22}H_{24}O_3$, 335.1653; found, 335.1653; **$[\alpha]^{22}_D$** −44.4 ° (*c*1.0, CH$_2$Cl$_2$).

(1*R*,2*S*,3*S*)-2-(Furan-3-yl)-3-methyl-3-(prop-1-en-2-yl)cyclobutyl)(2-hydroxyphenyl)methanone (Figure 2, **14**).



Experiment 1: Prepared according to general procedure B using 85.7 mg (0.40 mmol) (*E*)-3-(furan-3-yl)-1-(2-hydroxyphenyl)prop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene, and an irradiation time of 1.5 h. The crude material resulted in a 3.5:1 (major:minor) mixture of inseparable diastereomers that was purified by flash-column chromatography on silica gel (2.5% EtOAc:Hex). Combined yield: 97.8 mg of a clear oil (83%, 0.33 mmol) as a 4:1 (major:minor) mixture of diastereomers; 85% ee (Daicel CHIRALPAK® OJ-H, Shimadzu HPLC, gradient 1-10% (*i*-PrOH:Hex), 0.7 mL/min, 265 nm; t_1 = 10.1 min, t_2 = 15.5 min). Characterization data was obtained for the major diastereomer by flash-column chromatography (2.5% EtOAc:Hex). Experiment 2: 85.7 mg (0.40 mmol) (*E*)-3-(furan-3-yl)-1-(2-hydroxyphenyl)prop-2-en-1-one, 19.2 mg (0.04 mmol) Sc(OTf)$_3$, 20.0 mg (0.06 mmol) (*S*,*S*)-*t*-BuPyBox, 8.7 mg (0.01 mmol) Ru(bpy)$_3$(PF$_6$)$_2$, 12 mL (3:1) *i*-PrOAc:MeCN, 450 µL (4.0 mmol) 2,3-dimethylbutadiene. Crude d.r.: 4:1; Combined isolated yield: 95.0 mg of a clear oil (80%, 0.32 mmol); 85% ee.

^{1}H NMR (500 MHz, CDCl$_3$): δ 12.33 (s, 1H), 7.65 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.45 (ddd, *J* = 8.6, 7.6, 1.5 Hz, 1H), 7.38 (t, *J* = 1.7 Hz, 1H), 7.29 (m, 1H), 6.97 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.85 (ddd, *J* = 8.5, 7.5, 1.1 Hz, 1H), 6.37 (m, 1H), 4.77 (s, 2H), 3.99 (q, *J* = 9.1 Hz, 1H), 3.87 (d, *J* = 9.8 Hz, 1H), 2.41 (t, *J* = 10.3 Hz, 1H), 2.20 (dd, *J* = 11.5, 9.0 Hz, 1H), 1.70 (s, 3H), 1.24 (s, 3H); **^{13}C NMR** (126 MHz, CDCl$_3$): δ 206.0, 162.7, 157.0, 152.6, 143.0, 140.0, 136.3, 130.0, 123.9, 118.8, 118.5, 110.8, 108.3, 44.5, 41.9, 39.9, 36.4, 22.4, 18.3; **IR** (thin film): ν 2968, 2929, 2366, 2331, 1760, 1633, 1484, 1450, 1235 cm^{-1}; **HRMS** (ESI$^-$) (m/z): [M-H]$^-$ calculated for $C_{19}H_{20}O_3$, 295.1340; found, 295.1339; **[α]$^{22}_{D}$** −77.2° (*c*0.8, CH$_2$Cl$_2$).

D. Stereochemical Assignment of Minor Diastereomer by 1D NOESY

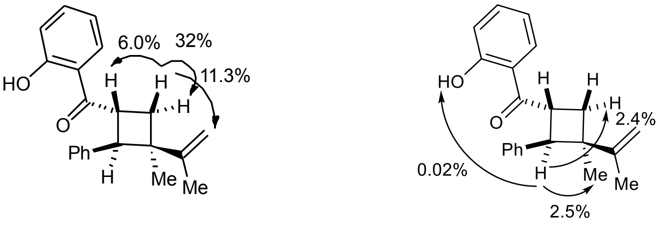
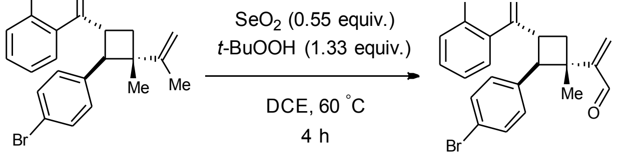


Fig. S2. 1D NOESY correlations for **8** (minor diastereomer).

E. Procedure for Derivitization of **9** for X-Ray Analysis



9
3:1 d.r.
94% ee

S1
86%, 3:1 d.r.

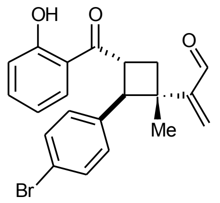
Fig. S3. Riley oxidation of enantioenriched vinylcyclobutane **9**

2-((1*S*,2*R*,3*R*)-2-(4-Bromophenyl)-3-(2-hydroxybenzoyl)-1-methylcyclobutyl)acrylaldehyde (SX). Riley oxidation of **9** was conducted using a variation of a known procedure.(*42*) An oven-dried 6 dram vial equipped with a magnetic stir bar was charged with SeO$_2$ (40.0 mg, 0.36 mmol) and 1 mL of DCE. To the white slurry was added *t*-BuOOH (97 µL, 0.86 mmol, 18 wt % in H$_2$O) dropwise followed by 10 min of stirring at rt. To the solution was then added **9** (250 mg, 0.65 mmol) as a solution in 5.5 mL of DCE. The vial was then sealed with a Teflon-lined cap and the reaction vessel was heated at 60 ºC for 4 h. Upon completion of the reaction, as monitored by TLC, the reaction was diluted with 10 mL of DCM and washed with H$_2$O (3 X 5 mL). The organic layer was then dried over MgSO$_4$ and filtered. The solvent was removed *in vacuo* and the crude oil was then subjected to flash column chromatography (10% - 20% acetone:hexane) to afford title compound **S1** in 3.3:1 d.r. (200 mg, 86% yield) as a white foam. An analytically pure sample of the major isomer of **S1** was isolated for characterization purposes by flash column chromatography (10% to 20% acetone:hexane) affording a white solid that was recrystallized from 5% acetone:hexane to afford X-ray quality crystals.

^{1}H NMR (500 MHz, CDCl$_3$): δ 12.19 (s, 1H), 9.54 (s, 1H), 7.65 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.48 (dd, *J* = 6.9, 1.5 Hz, 1H), 7.46 (d, *J* = 8.33, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.98 (dd, *J* = 8.5, 1.2 Hz, 1H), 6.88 (ddd, *J* = 7.4, 7.0, 1.2 Hz, 1H), 6.48 (s, 1H), 6.08 (s, 1H), 4.27 (q, *J* = 9.0 Hz, 1H), 4.24 (d, *J* = 8.0 Hz, 1H), 2.55-2.60 (m, 1H), 2.41-2.46 (m, 1H), 1.27 (s, 3H); **^{13}C NMR** (126 MHz, CDCl$_3$): δ 205.5, 193.8, 162.7, 156.9, 137.9, 136.6, 133.1, 131.5, 129.9, 129.7, 120.8, 119.0, 118.6, 118.1, 46.8, 42.7, 41.6, 37.6, 21.9; **IR** (thin film): ν 2971, 2929, 2363, 2333, 1687, 1630, 1487, 1445, 1244, 1159, 1010, 757 cm^{-1}; **mp** = 115-117 ºC; **HRMS** (ESI$^-$) (m/z): [M-H]$^-$ calculated for C$_{21}$H$_{19}$BrO$_3$, 397.0445; found, 397.0446; **[α]^{22}$_D$** −49.4º (*c*1.6, CH$_2$Cl$_2$).

F. X-Ray Crystallographic Data for **S1**

Data Collection for S1



A colorless crystal with approximate dimensions 0.23 x 0.05 x 0.02 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm.(*43*)

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite.

The final cell constants were calculated from a set of 9964 strong reflections from the actual data collection. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.70 Å. A total of 42386 data were harvested by collecting 5 sets of frames with 0.5º scans in ω and φ with exposure times of 30 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.(*44*)

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_12_12_1$ that yielded chemically reasonable and computationally stable results of refinement.(*45–50*) A successful solution by the direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydroxyl H atom was located in the difference Fourier map and refined independently. All other hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The absolute configuration of the chiral centers was unequivocally established by resonant scattering as follows: C1 – *R*, C2 – *R*, C4 – *S*. The final least-squares refinement of 231 parameters against 5363 data resulted in residuals R (based on F2 for $I \geq 2\sigma$) and wR (based on F2 for all data) of 0.0253 and 0.0626, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{21}H_{19}BrO_3$ (M =399.27 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 6.035(2) Å, b = 9.961(3) Å, c = 29.033(9) Å, V = 1745.2(10) Å^3, Z = 4, T = 99.99 K, $\mu(\mathrm{MoK}\alpha)$ = 2.372 mm^{-1}, $Dcalc$ = 1.520 g/cm^3, 42386 reflections measured ($2.806° \leq 2\Theta \leq 61.146°$), 5363 unique ($R_{\mathrm{int}}$ = 0.0414, R_{sigma} = 0.0272) which were used in all calculations. The final R_1 was 0.0253 ($I > 2\sigma(I)$) and wR_2 was 0.0626 (all data).

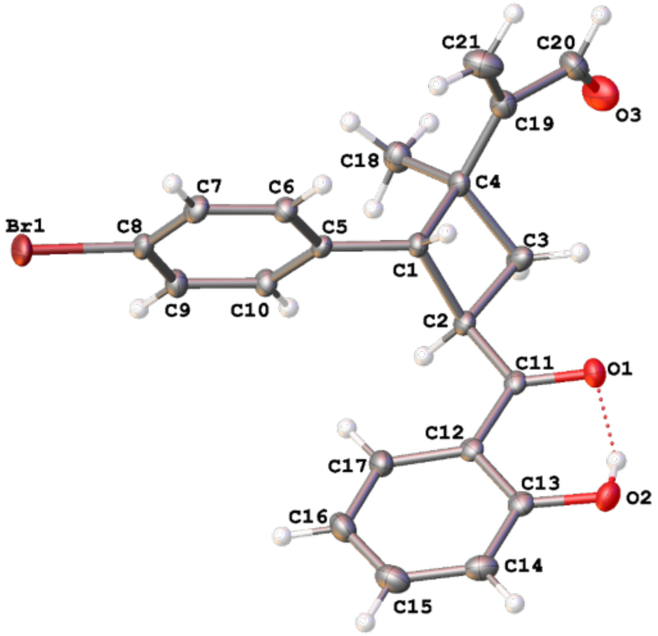


Fig. S4. A molecular drawing of **S1** shown with 50% probability ellipsoids.

Table S7. Crystal data and structure refinement for **S1**.

Identification code	**S1**
Empirical formula	$C_{21}H_{19}BrO_3$
Formula weight	399.27
Temperature/K	99.99
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.035(2)
b/Å	9.961(3)
c/Å	29.033(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1745.2(10)
Z	4
ρ_{calc}g/cm^3	1.520
μ/mm^{-1}	2.372
F(000)	816.0
Crystal size/mm^3	0.227 × 0.05 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.806 to 61.146
Index ranges	$-8 \leq h \leq 8$, $-14 \leq k \leq 14$, $-41 \leq l \leq 41$
Reflections collected	42386
Independent reflections	5363 [R_{int} = 0.0414, R_{sigma} = 0.0272]
Data/restraints/parameters	5363/0/231
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0253, wR_2 = 0.0616
Final R indexes [all data]	R_1 = 0.0298, wR_2 = 0.0626
Largest diff. peak/hole / e Å^{-3}	0.39/-0.28
Flack parameter	-0.013(3)

Table S8. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **S1**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	8712.7(4)	616.6(2)	3711.5(2)	24.95(7)
O1	-455(3)	7698.5(16)	4189.1(6)	20.2(3)
O2	-2942(3)	6791.4(18)	4817.2(6)	21.6(3)
O3	3315(4)	9509.8(19)	2737.9(7)	36.7(5)
C1	3128(4)	5812(2)	3568.9(7)	14.9(4)
C2	3065(4)	6844(2)	3979.4(8)	15.8(4)
C3	3255(4)	8009(2)	3631.6(8)	20.9(5)
C4	3905(4)	7006(2)	3244.8(7)	17.1(4)
C5	4492(4)	4555(2)	3605.3(7)	14.5(4)
C6	3755(4)	3358(2)	3405.8(7)	17.1(4)
C7	5006(4)	2183(2)	3428.4(8)	18.8(5)
C8	7018(4)	2211(2)	3656.3(8)	18.0(4)
C9	7800(4)	3374(2)	3859.0(8)	18.5(4)
C10	6531(3)	4539(2)	3830.1(7)	17.1(4)
C11	970(3)	6841(2)	4266.8(7)	14.2(4)
C12	612(4)	5820(2)	4626.1(7)	15.2(4)
C13	-1362(4)	5851(2)	4886.1(7)	17.5(4)
C14	-1755(4)	4896(3)	5229.5(8)	22.5(5)
C15	-173(5)	3928(3)	5318.3(9)	25.8(5)
C16	1798(4)	3893(2)	5070.5(9)	23.5(5)
C17	2189(4)	4823(2)	4728.8(8)	19.7(4)
C18	6398(4)	7040(2)	3140.4(8)	22.1(4)
C19	2641(4)	7141(2)	2801.3(9)	21.9(5)
C20	2498(5)	8484(3)	2585.0(9)	27.9(6)
C21	1659(5)	6144(3)	2578.0(9)	31.3(6)

Table S9. Anisotropic Displacement Parameters ($Å^2×10^3$) for **S1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	33.27(12)	15.00(9)	26.59(12)	-0.50(9)	-1.83(11)	11.39(9)
O1	21.9(8)	16.9(8)	21.8(8)	2.0(7)	-1.2(7)	5.5(6)
O2	20.0(8)	20.1(8)	24.8(9)	-1.7(7)	3.8(7)	4.6(7)
O3	57.6(13)	20.3(9)	32.2(10)	3.9(8)	-0.9(9)	1.6(10)
C1	16.8(9)	12.7(9)	15.2(9)	-0.8(7)	-0.7(7)	2.9(7)
C2	19.8(10)	11.8(8)	15.7(10)	-2.0(8)	-0.4(8)	2.5(8)
C3	30.5(12)	13.9(9)	18.2(11)	-0.1(8)	4.6(9)	2.1(8)
C4	21.1(10)	12.3(9)	17.7(10)	1.3(8)	0.6(9)	2.8(8)
C5	18.4(9)	11.5(9)	13.7(10)	-0.6(7)	1.7(7)	3.2(7)
C6	19.2(9)	14.5(9)	17.6(10)	-1.8(8)	-1.2(9)	0.9(9)
C7	23.9(11)	11.8(10)	20.9(11)	-3.1(8)	1.3(9)	0.7(8)
C8	22.9(10)	12.9(8)	18.3(11)	1.6(8)	2.9(8)	5.1(8)
C9	19(1)	16.4(10)	20.2(11)	1.1(8)	-1.1(8)	3.3(8)
C10	20(1)	11.8(9)	19.3(10)	-1.5(7)	-1.5(8)	1.4(8)
C11	16.8(10)	11.9(8)	14.0(9)	-4.2(7)	-2.7(8)	0.4(8)
C12	21.2(9)	11.3(9)	13.0(9)	-3.2(7)	-1.7(7)	-0.1(7)
C13	21.0(9)	14.9(9)	16.7(9)	-4.6(7)	-2.2(9)	-0.4(9)
C14	25.9(13)	23.5(11)	18.3(11)	-1.3(9)	2.1(9)	-5.4(9)
C15	34.6(13)	24.0(12)	18.9(12)	3.6(9)	-3.3(10)	-4.4(10)
C16	29.5(13)	19.5(10)	21.6(12)	2.9(9)	-5.1(9)	3.8(9)
C17	24.2(11)	16.9(10)	18.1(11)	-1.0(8)	-1.7(9)	4.2(9)
C18	22.9(11)	18.7(10)	24.8(11)	2.8(9)	2.1(10)	0.0(9)
C19	24.1(12)	20.5(11)	21.0(12)	2.0(9)	0.6(9)	3.2(9)
C20	35.3(15)	26.5(13)	21.8(12)	6(1)	-2.4(10)	7.7(11)
C21	37.6(16)	34.9(14)	21.5(12)	3.1(10)	-3.2(11)	-6.8(12)

Table S10. Bond Lengths for **S1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C8	1.896(2)	C6	C7	1.395(3)
O1	C11	1.233(3)	C7	C8	1.383(3)
O2	C13	1.352(3)	C8	C9	1.382(3)
O3	C20	1.218(3)	C9	C10	1.393(3)
C1	C2	1.574(3)	C11	C12	1.472(3)
C1	C4	1.588(3)	C12	C13	1.410(3)
C1	C5	1.502(3)	C12	C17	1.408(3)
C2	C3	1.543(3)	C13	C14	1.398(3)
C2	C11	1.515(3)	C14	C15	1.381(4)
C3	C4	1.553(3)	C15	C16	1.391(4)
C4	C18	1.535(3)	C16	C17	1.378(3)
C4	C19	1.503(3)	C19	C20	1.480(4)
C5	C6	1.397(3)	C19	C21	1.326(4)
C5	C10	1.393(3)			

Table S11. Bond Angles for **S1**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	C1	C4	88.07(15)	C9	C8	C7	121.3(2)
C5	C1	C2	120.28(18)	C8	C9	C10	119.0(2)
C5	C1	C4	120.32(18)	C5	C10	C9	121.54(19)
C3	C2	C1	89.66(16)	O1	C11	C2	118.7(2)
C11	C2	C1	115.83(17)	O1	C11	C12	120.4(2)
C11	C2	C3	115.06(18)	C12	C11	C2	120.93(18)
C2	C3	C4	90.45(15)	C13	C12	C11	119.22(19)
C3	C4	C1	88.80(16)	C17	C12	C11	122.5(2)
C18	C4	C1	115.02(18)	C17	C12	C13	118.2(2)
C18	C4	C3	112.11(19)	O2	C13	C12	122.1(2)
C19	C4	C1	115.14(19)	O2	C13	C14	117.2(2)
C19	C4	C3	115.72(19)	C14	C13	C12	120.7(2)
C19	C4	C18	109.03(19)	C15	C14	C13	119.4(2)
C6	C5	C1	120.50(19)	C14	C15	C16	120.8(2)
C10	C5	C1	121.75(18)	C17	C16	C15	120.2(2)
C10	C5	C6	117.75(19)	C16	C17	C12	120.7(2)
C7	C6	C5	121.6(2)	C20	C19	C4	118.3(2)
C8	C7	C6	118.7(2)	C21	C19	C4	125.4(2)
C7	C8	Br1	119.80(17)	C21	C19	C20	116.3(2)
C9	C8	Br1	118.83(17)	O3	C20	C19	125.4(2)

Table S12. Hydrogen Bonds for **S1**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	H2	O1	0.80(4)	1.77(4)	2.529(3)	157(4)

Table S13. Torsion Angles for **S1**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
Br1	C8	C9	C10	-178.25(17)	C4	C1	C5	C10	70.9(3)
O1	C11	C12	C13	-1.2(3)	C4	C19	C20	O3	-0.4(4)
O1	C11	C12	C17	-179.8(2)	C5	C1	C2	C3	137.4(2)
O2	C13	C14	C15	-178.9(2)	C5	C1	C2	C11	-104.7(2)
C1	C2	C3	C4	-13.28(16)	C5	C1	C4	C3	-137.3(2)
C1	C2	C11	O1	-98.9(2)	C5	C1	C4	C18	-23.4(3)
C1	C2	C11	C12	79.9(2)	C5	C1	C4	C19	104.7(2)
C1	C4	C19	C20	153.0(2)	C5	C6	C7	C8	0.3(3)
C1	C4	C19	C21	-28.3(3)	C6	C5	C10	C9	-0.3(3)
C1	C5	C6	C7	179.0(2)	C6	C7	C8	Br1	177.85(18)
C1	C5	C10	C9	-179.3(2)	C6	C7	C8	C9	-0.1(3)
C2	C1	C4	C3	-12.91(16)	C7	C8	C9	C10	-0.3(4)
C2	C1	C4	C18	101.02(19)	C8	C9	C10	C5	0.5(3)
C2	C1	C4	C19	-130.93(19)	C10	C5	C6	C7	-0.1(3)
C2	C1	C5	C6	144.6(2)	C11	C2	C3	C4	-131.85(19)
C2	C1	C5	C10	-36.3(3)	C11	C12	C13	O2	-0.2(3)
C2	C3	C4	C1	13.17(16)	C11	C12	C13	C14	180.0(2)
C2	C3	C4	C18	-103.45(19)	C11	C12	C17	C16	179.4(2)
C2	C3	C4	C19	130.7(2)	C12	C13	C14	C15	1.0(3)
C2	C11	C12	C13	-179.96(19)	C13	C12	C17	C16	0.8(3)
C2	C11	C12	C17	1.4(3)	C13	C14	C15	C16	0.0(4)
C3	C2	C11	O1	3.8(3)	C14	C15	C16	C17	-0.6(4)
C3	C2	C11	C12	-177.40(19)	C15	C16	C17	C12	0.1(4)
C3	C4	C19	C20	51.4(3)	C17	C12	C13	O2	178.5(2)
C3	C4	C19	C21	-129.9(3)	C17	C12	C13	C14	-1.4(3)
C4	C1	C2	C3	13.00(16)	C18	C4	C19	C20	-76.0(3)
C4	C1	C2	C11	130.89(19)	C18	C4	C19	C21	102.7(3)
C4	C1	C5	C6	-108.1(2)	C21	C19	C20	O3	-179.3(3)

Table S14. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **S1.**

Atom	***x***	***y***	***z***	**U(eq)**
H2	-2310(70)	7270(40)	4638(15)	52(12)
H1	1574	5560	3486	18
H2A	4420	6772	4176	19
H3A	4440	8660	3708	25
H3B	1833	8477	3574	25
H6	2368	3345	3251	21
H7	4486	1378	3290	23
H9	9182	3379	4016	22
H10	7069	5342	3967	20
H14	-3097	4914	5400	27
H15	-436	3278	5551	31
H16	2878	3227	5137	28
H17	3539	4792	4561	24
H18A	7231	7059	3430	33
H18B	6746	7845	2960	33
H18C	6809	6239	2964	33
H20	1702	8552	2304	33
H21A	917	6314	2295	38
H21B	1697	5260	2701	38

G. Procedure for [2+2] Cycloaddition under 350 nm irradiation (Figure S6)

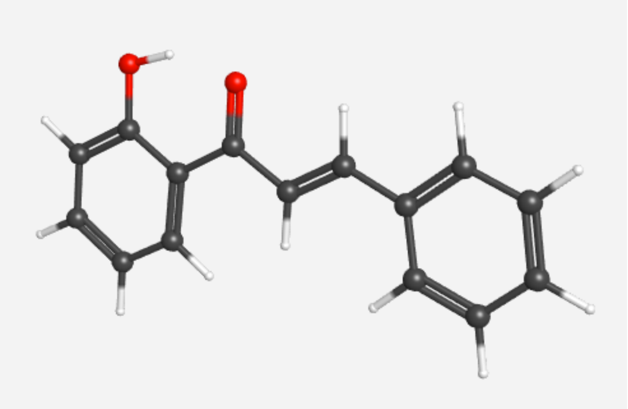
In a 25 mL Schlenck flask were combined 2'-hydroxychalcone (22.5 mg, 0.100 mmol), Sc(OTf)$_3$ (24.1 mg, 0.49 equiv.), ^{t}BuPyBox (24.5 mg, 0.74 equiv.), and sensitizer (2.5 mol% – 50 mol% as indicated). Solvent (3:1 iPrOAc:MeCN, 3 mL) was then added to the flask, and the mixture stirred to dissolve. After addition of 2,3-dimethyl-1,2-butadiene (110 µL, 9.72 equiv.) by syringe, the flask was sealed, and degassed by three freeze-pump-thaw cycles. After the final thaw, the flask was backfilled with nitrogen gas, and sealed. The resulting solution was then stirred in a Rayonet photoreactor (bulb emission λ_{max} = 350 nm) for 18 hours. At 18 hours, irradiation was ceased, phenanthrene was added as an internal standard and allowed to dissolve. The reaction mixture was diluted with H_2O and Et_2O (approx. 2.0 mL each), and mixed vigorously. After allowing the layers to separate, the organic layer was removed by pipette, dried by passing through a plug of $MgSO_4$, and concentrated *in vacuo*. The yield of **8** was obtained by ^{1}H NMR spectroscopic analysis of the crude reaction mixture (relative to phenanthrene internal standard), and the crude material was purified by flash-column chromatography (2.5% EtOAc/Hexanes) to afford pure material for SFC analysis.

H. Computational Experiments Modeling the Excited States of 2’-Hydroxychalcone **2.**

The adiabatic S_0–T_1 gap for 2’-hydroxychalcone and the Sc(2’-hydroxychalcone)$^{2+}$ complex were determined via the energy difference of the optimized singlet ground state structure and the first excited triplet structure. All ground state and triplet state geometries were optimized using the B3LYP density functional with 6-311+G(2d,p) basis set. All calculations were performed using the Gaussian09 software package.(*51*) Structures were confirmed to be a minimum on the potential energy surface via harmonic frequency calculations.

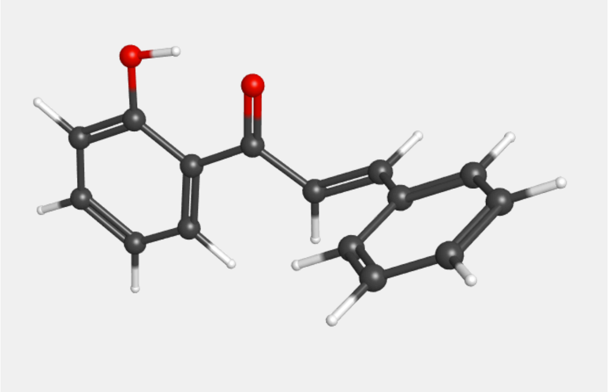
2’-Hydroxychalcone

Optimized structure for S_0:



B3LYP/6−311+G(2d,p) energy: -729.4879467 Hartree

Optimized structure for T_1:



B3LYP/6−311+G(2d,p) energy: -729.4064396 Hartree

S_0–T_1 Energy (B3LYP/6−311+G(2d,p)): 0.081507106 Hartree (51.1 kcal/mol)

Table S15. 2’-Hydroxychalcone standard orientation S_0 (coordinates)

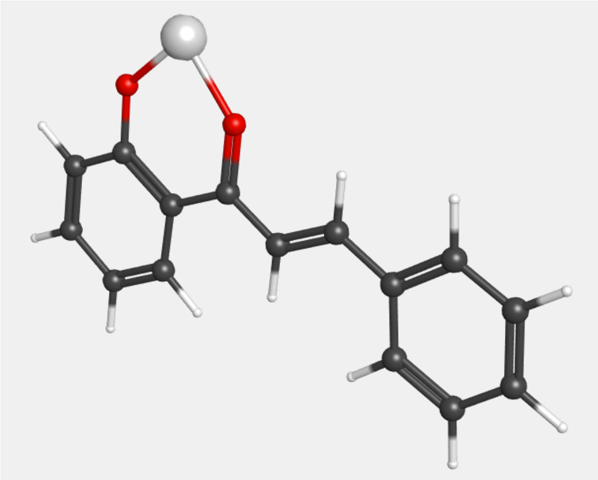
Atom	**X**	**Y**	**Z**
C	0.00000000	0.00000000	0.00000000
C	-1.37421500	-0.12724300	0.00000000
C	-2.19629900	1.00526900	0.00000000
C	-1.62073500	2.25928000	0.00000000
C	-0.22321700	2.43488700	0.00000000
C	0.59253400	1.26917100	0.00000000
O	1.92726700	1.33382400	0.00000000
H	2.15653100	2.30331100	0.00000000
C	0.42343100	3.75958600	0.00000000
C	-0.38999300	4.98934000	0.00000000
C	0.19888600	6.19678000	0.00000000
C	-0.44549300	7.50548300	0.00000000
C	-1.83877800	7.68215000	0.00000000
C	-2.39233200	8.95201200	0.00000000
C	-1.57018500	10.0785320	0.00000000
C	-0.18877900	9.92311500	0.00000000
C	0.36578900	8.64980900	0.00000000
H	1.44333800	8.53055600	0.00000000
H	0.45701300	10.7929320	0.00000000
H	-2.00724700	11.0698230	0.00000000
H	-3.46948100	9.06893200	0.00000000
H	-2.49455100	6.82043700	0.00000000
H	1.28511600	6.20363400	0.00000000
H	-1.46604500	4.90066200	0.00000000
O	1.66567400	3.84553600	0.00000000
H	-2.26981000	3.12345100	0.00000000
H	-3.27355300	0.90007000	0.00000000
H	-1.81818900	-1.11604300	0.00000000
H	0.65048900	-0.86541500	0.00000000

Table S16. 2'-Hydroxychalcone standard orientation T_1 (coordinates)

Atom	**X**	**Y**	**Z**
C	0.00000000	0.00000000	0.00000000
C	-0.32914000	1.28702700	0.37368900
C	0.61753300	2.11661700	0.98634700
C	1.88991000	1.63647100	1.21805200
C	2.26656300	0.32933000	0.85359300
C	1.29014600	-0.49472000	0.22958500
O	1.55684200	-1.74673000	-0.15584600
H	2.51041300	-1.91488900	0.07873200
C	3.61963200	-0.21732000	1.08135700
C	4.64208200	0.56998000	1.73412900
C	5.98259900	0.05196000	1.97951500
C	7.11052400	0.29382400	1.16883000
C	7.04084600	1.07332500	-0.01731600
C	8.16637400	1.29779700	-0.78625400
C	9.40042600	0.76003000	-0.41319300
C	9.49354100	-0.01286500	0.74792100
C	8.37694400	-0.24465600	1.52533000
H	8.45476500	-0.84793500	2.42270000
H	10.4480960	-0.43505400	1.03951400
H	10.2789430	0.93891900	-1.02072400
H	8.08920000	1.89438100	-1.68773300
H	6.08782700	1.49031500	-0.32123800
H	6.11360600	-0.56910700	2.86319400
H	4.39274300	1.55828100	2.10657500
O	3.90350400	-1.38392800	0.71912100
H	2.60985900	2.29064400	1.69072600
H	0.35494100	3.12568600	1.27676500
H	-1.33108600	1.65671100	0.18905600
H	-0.71899700	-0.65458500	-0.47604300

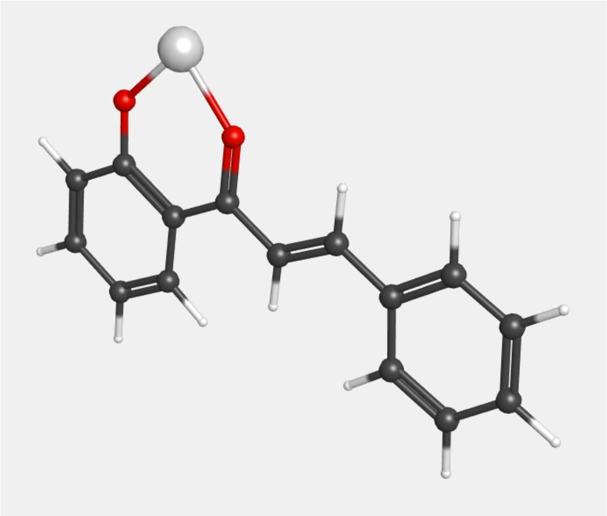
Sc(2'-hydroxychalcone)$^{2+}$ complex

Optimized structure for S_0:



B3LYP/6−311+G(2d,p) energy: –1489.102955 Hartree

Optimized structure for T_1:



B3LYP/6−311+G(2d,p) energy: –1489.052643 Hartree

S_0–T_1 Energy (B3LYP/6−311+G(2d,p)): 0.0503119 Hartree (31.6 kcal/mol)

Table S17. Sc(2'-hydroxychalcone) complex standard orientation S_0 (coordinates)

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	1.32219600	0.42995600	0.00000000
C	1.61343000	1.79299400	0.00000000
C	0.58978500	2.72080700	0.00000000
C	-0.76942300	2.33331100	0.00000000
C	-1.02168000	0.93305400	0.00000000
O	-2.30884200	0.45229000	0.00000000
Sc	-3.93321100	1.22761800	0.00000000
O	-3.11151000	2.89461900	0.00000000
C	-1.83065400	3.33054400	0.00000000
C	-1.61990300	4.70487000	0.00000000
C	-2.65044600	5.63943500	0.00000000
C	-2.52854300	7.04655200	0.00000000
C	-1.27886400	7.72730900	0.00000000
C	-1.23920200	9.10149600	0.00000000
C	-2.43358500	9.83729000	0.00000000
C	-3.67471100	9.19426800	0.00000000
C	-3.72424400	7.81763000	0.00000000
H	-4.68115000	7.30903500	0.00000000
H	-4.58714100	9.77609900	0.00000000
H	-2.39184400	10.9200450	0.00000000
H	-0.28911400	9.61977000	0.00000000
H	-0.35017300	7.17242800	0.00000000
H	-3.66523000	5.25595600	0.00000000
H	-0.59870100	5.05025000	0.00000000
H	0.85345800	3.76792000	0.00000000
H	2.64176800	2.12951000	0.00000000
H	2.12199200	-0.29998200	0.00000000
H	-0.24880700	-1.05324700	0.00000000

Table S18. Sc(2’-hydroxychalcone) complex standard orientation T_1 (coordinates)

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.22993500	1.35718900	0.01197800
C	1.55455300	1.85876400	0.02202000
C	2.62315700	1.00354600	0.01965600
C	2.45011500	-0.40905800	0.00757900
C	1.07579600	-0.89053900	-0.00303200
O	0.81017600	-2.19463400	-0.02091300
Sc	1.83997800	-3.75926100	-0.00317300
O	3.36551600	-2.62296100	0.02190800
C	3.56212000	-1.31518200	0.00881800
C	4.92634800	-0.86133000	-0.00003700
C	6.02034200	-1.70043000	0.01287500
C	7.38419900	-1.29125100	0.00547900
C	7.80081000	0.07945700	-0.02111400
C	9.13239500	0.40107200	-0.02517900
C	10.1037760	-0.61948100	-0.00323700
C	9.72183200	-1.97577100	0.02265900
C	8.39109300	-2.30591800	0.02683600
H	8.08724500	-3.34538300	0.04704800
H	10.4804090	-2.74764300	0.03919800
H	11.1553200	-0.35837500	-0.00642400
H	9.44530200	1.43698600	-0.04531100
H	7.06697100	0.87348700	-0.03849400
H	5.83812400	-2.76851700	0.03256200
H	5.08514400	0.20519300	-0.01868200
H	3.61485400	1.42915700	0.03130200
H	1.72020100	2.92816100	0.03266300
H	-0.60503700	2.04678200	0.01325400
H	-1.00337800	-0.40518300	-0.00895400

I. Procedure for Spectrofluorimetry of 2’-Hydroxychalcone **2**

General Procedure for Spectrofluorimetry: Solutions of 2’-hydroxychalcone **2** (1.0×10^{-4} M) and Sc(III) triflate (1.0×10^{-4} M) were prepared in acetonitrile, and were combined in a quartz cuvette according to the table below. The samples were then diluted to a final volume of 2 mL, sealed with a rubber septum, sparged for 15 minutes with gas (either N_2 or O_2), then sealed with parafilm. Emission spectra were obtained upon excitation at 380 nm (to avoid harmonic contamination at >800 nm), and the photon counts were integrated over 10 s with a slit width of 16 nm for all apertures. All data was obtained as background-corrected spectra, then exported and worked up with Microsoft Excel.

Sample	Components (amount, final conc.)	Sparge gas
A	2’-hydroxychalcone (1.0 mL, 5.0×10^{-5} M)	N_2
B	2’-hydroxychalcone (1.0 mL, 5.0×10^{-5} M) Sc(III) triflate (500 μL, 2.5×10^{-5} M)	N_2
C	2’-hydroxychalcone (1.0 mL, 5.0×10^{-5} M) Sc(III) triflate (500 μL, 2.5×10^{-5} M)	O_2

J. Cyclic Voltammetry

Cyclic voltammetry was performed on a Pine WaveNow (SN4415109) potentiostat and the data was analyzed on a PC using Pine WaveNow software. All data was obtained at a sweep rate of 50 mV/s using a three electrode setup: Pt wire counter electrode, glassy carbon working electrode, and a Ag/$AgNO_3$ (0.01 M $AgNO_3$, 0.1 M Bu_4NPF_6 in CH_3CN) quasi reference electrode containing a polished silver wire immersed in the electrolyte solution in a glass cuvette. Solutions of 2’-hydroxychalcone with or without Sc(III) (1 mM in CH_3CN, 5 mL total volume) with 0.1 M Bu_4NPF_6 of supporting electrolyte. The solutions were sparged with nitrogen for ten minutes prior to acquiring all CV data. All electrochemical potentials were obtained relative to Ag/$AgNO_3$, and referenced to ferrocene as an internal standard by addition of ferrocene and obtaining a CV. The data was subsequently adjusted to the saturated calomel electrode (SCE) by addition of +0.40 V.

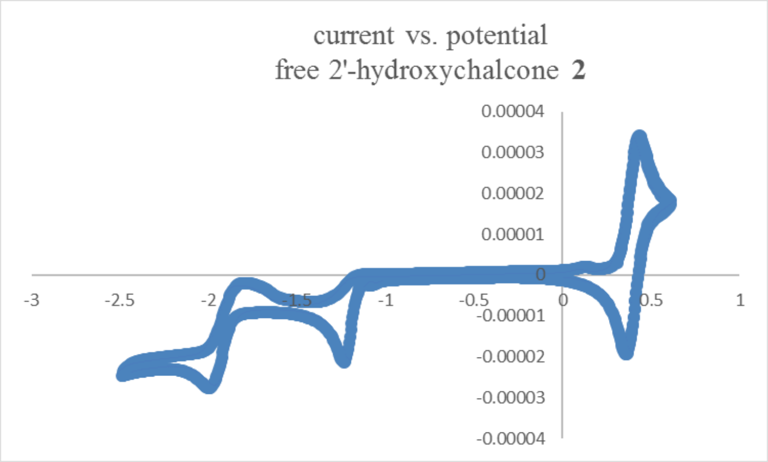


Fig. S5. CV of 2’-hydroxychalcone 2 (1mM in MeCN).

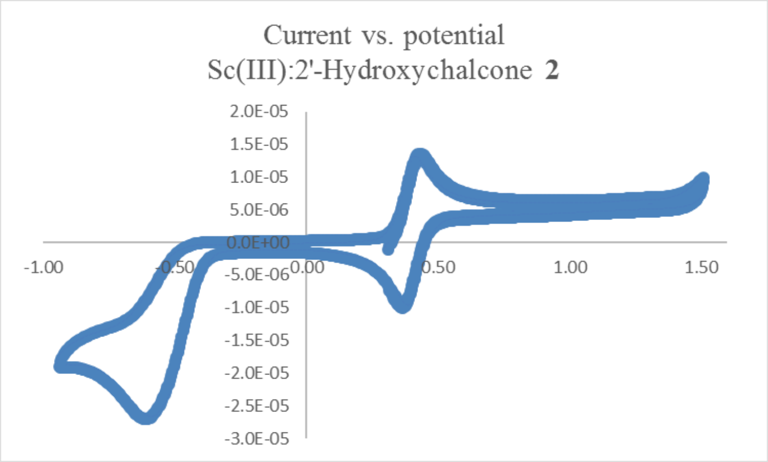


Fig. S6. CV of 2’-hydroxychalcone (1mM in MeCN) and Sc(OTf)$_3$ (1mM in MeCN)

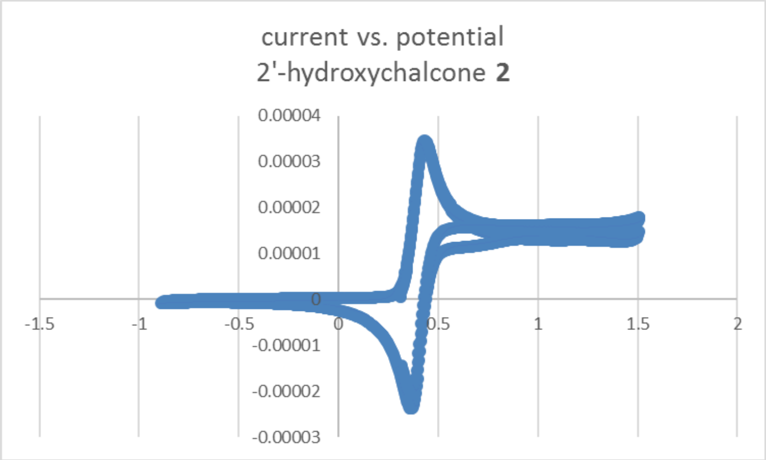


Fig. S7. CV of 2’-hydroxychalcone 2 (1mM in MeCN).

K. <u>SFC and HPLC Chromatograms</u>

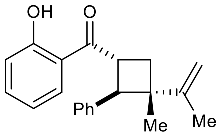
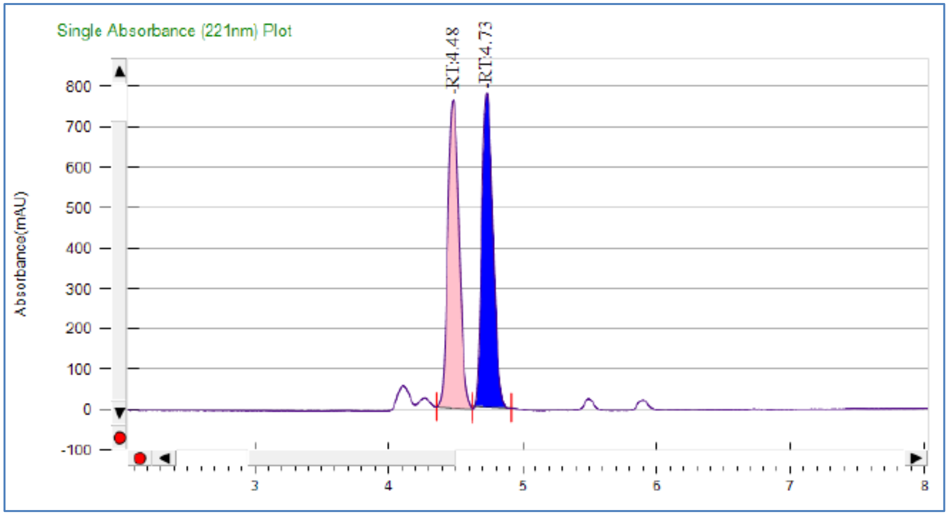


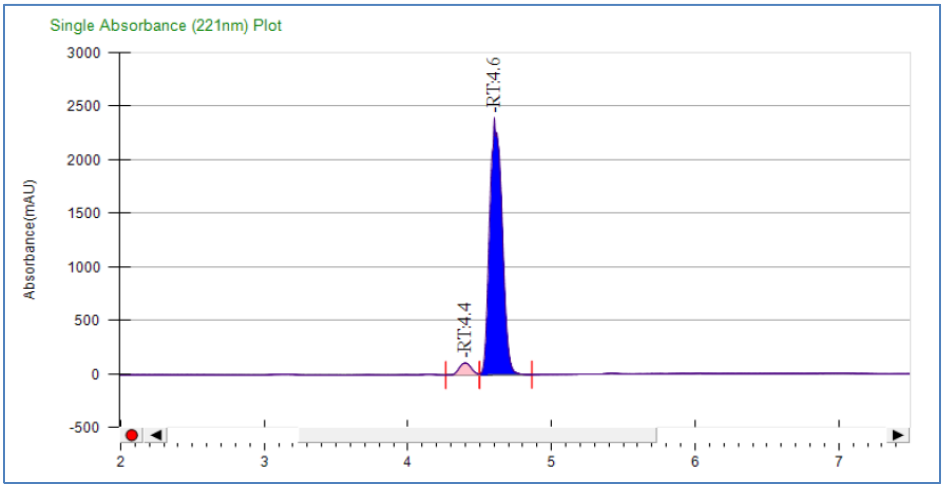
Figure 2, **4**

Racemic (Daicel CHIRALPAK® OD-H, gradient 5-50% *i*-PrOH, 4.0 mL/min, 241 nm)



Peak No	% Area	Area	RT (min)	Height (mV)
1	49.3847	5049.7432	4.48	762.6925
2	50.6153	5175.5703	4.73	776.1804
Total:	100	10225.3162		

Enantioenriched



Peak No	% Area	Area	RT (min)	Height (mV)
1	3.3917	449.3238	4.40	85.0888
2	96.6083	12798.5527	4.61	2131.6588
Total:	100	13247.8765		

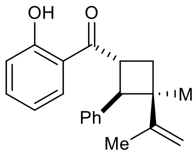
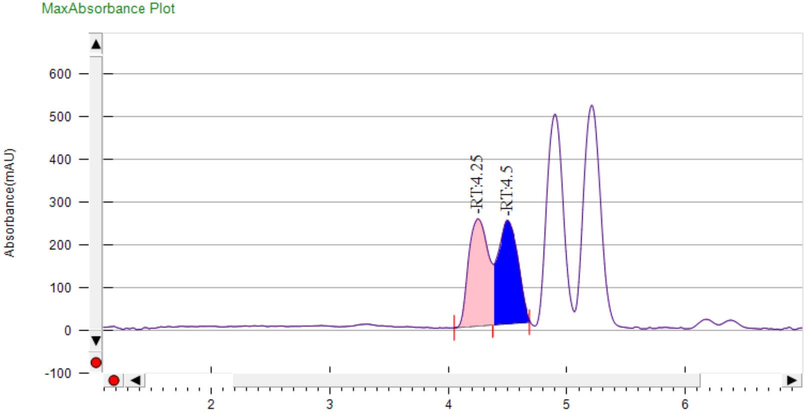


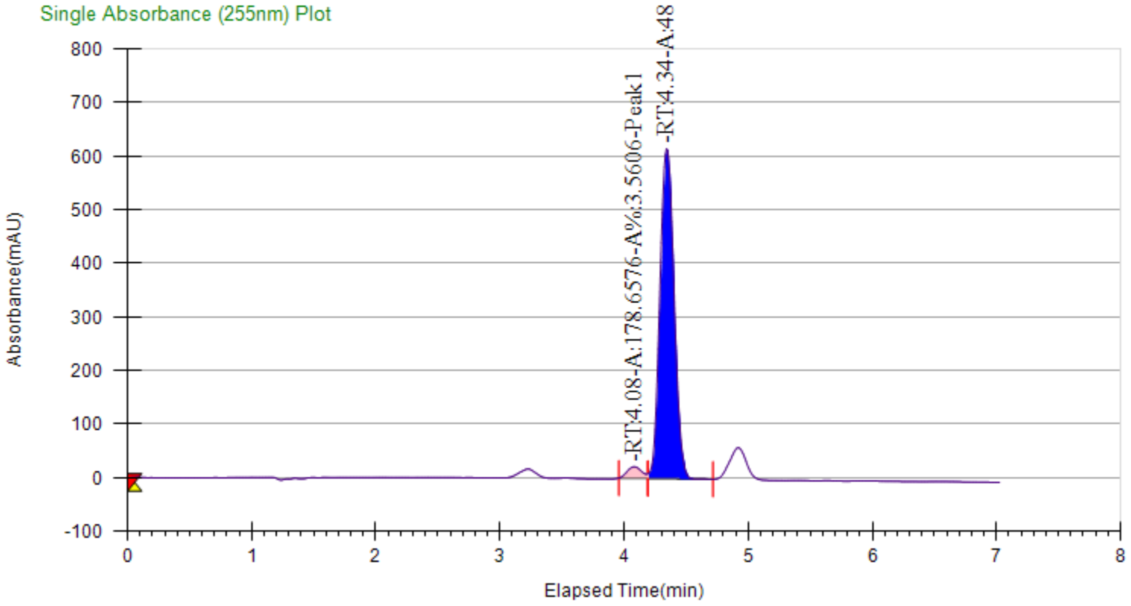
Figure 2, **4**
minor diastereomer

Racemic ((Daicel CHIRALPAK® OD-H, gradient 5-20% MeOH, 3.0 mL/min, 245 nm)



Peak No	% Area	Area	RT (min)	Height (mV)
1	50.7708	2836.4415	4.25	251.423
2	49.2292	2750.3108	4.50	242.9719
Total:	100	5586.7523		

Enantioenriched



Peak No	% Area	Area	RT (min)	Height (mV)
1	3.5606	178.6576	4.08	21.3836
2	96.4394	4838.9782	4.34	615.7895
Total:	100	5017.6358		

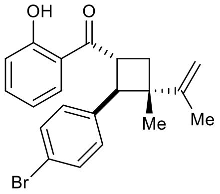
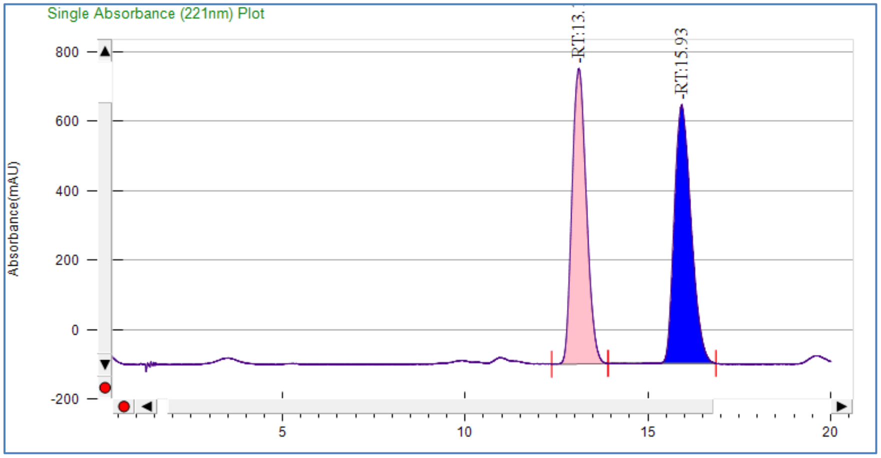


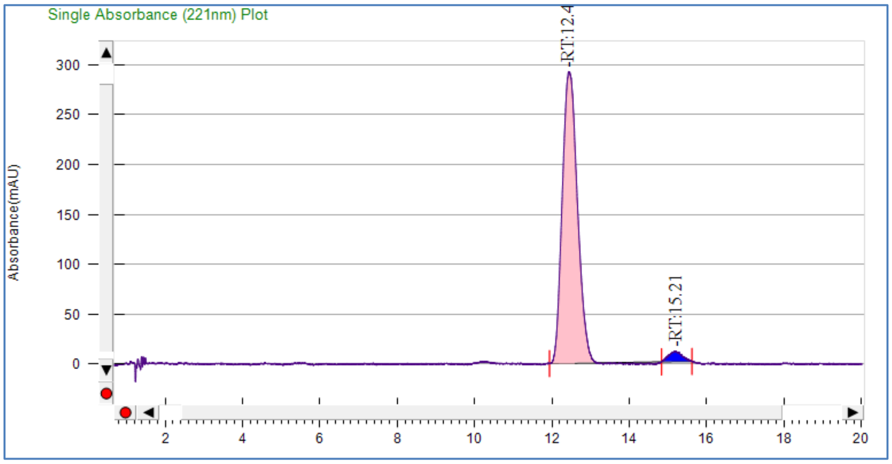
Figure 2, **9**

Racemic (Daicel CHIRALPAK® OD-H, 3% MeOH, 3 mL/min, 248 nm)



Peak No	% Area	Area	RT (min)	Height (mV)
1	49.6479	23968.7255	13.11	881.1843
2	50.3521	24308.6467	15.92	769.6972
Total:	100	48277.3722		

Enantioenriched



Peak No	% Area	Area	RT (min)	Height (mV)
1	96.9448	7966.602	12.44	292.086
2	3.0522	251.0631	15.21	10.2578
Total:	100	8217.6651		

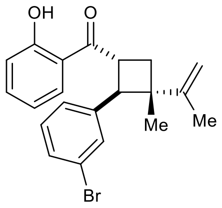
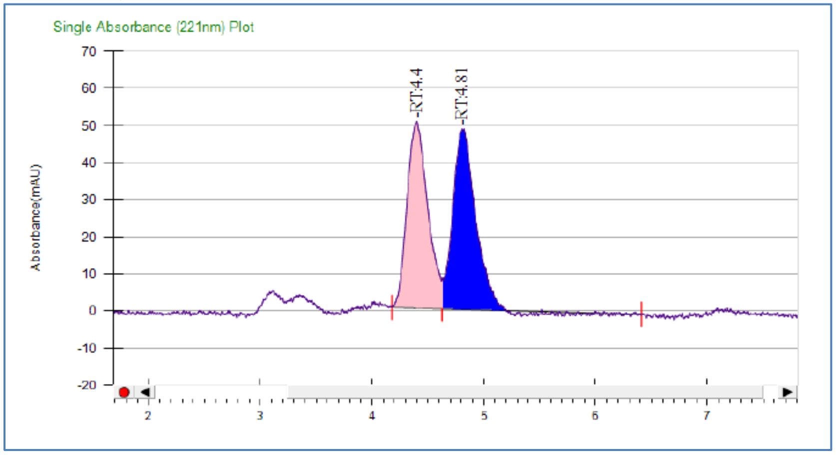


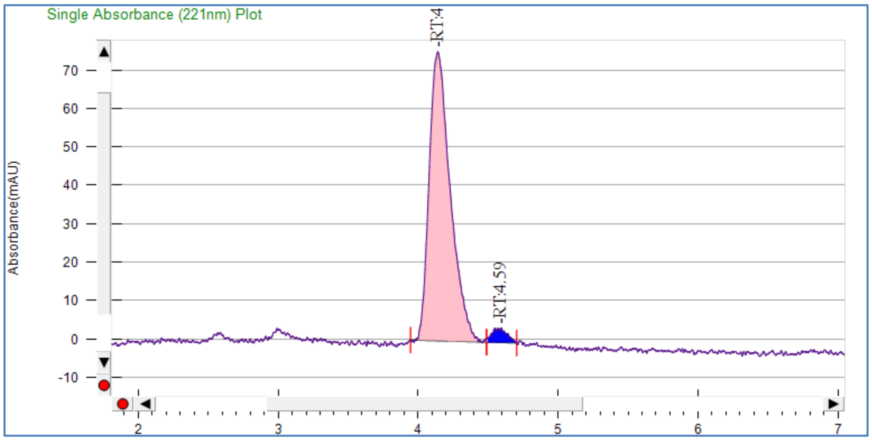
Figure 2, **10**

Racemic (Daicel CHIRALPAK® OJ-H, 8% solvent, 3 mL/min, 245 nm)



Peak No	% Area	Area	RT (min)	Height (mV)
1	50.2241	356.1117	4.40	50.2729
2	49.7759	352.9341	4.81	48.5393
Total:	100	709.0458		

Enantioenriched



Peak No	% Area	Area	RT (min)	Height (mV)
1	96.5757	788.8854	4.14	75.2966
2	3.4243	27.9717	4.59	3.808
Total:	100	816.8571		

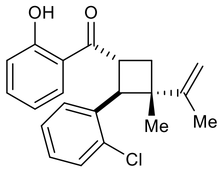
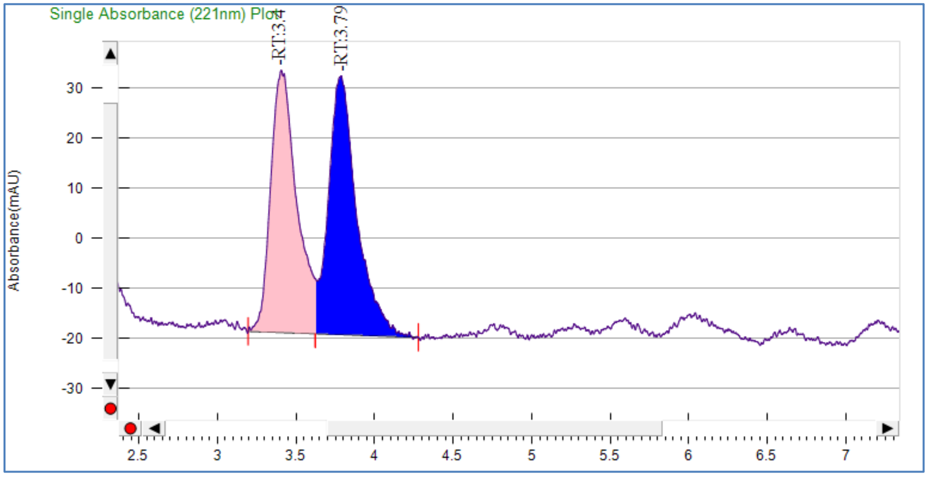


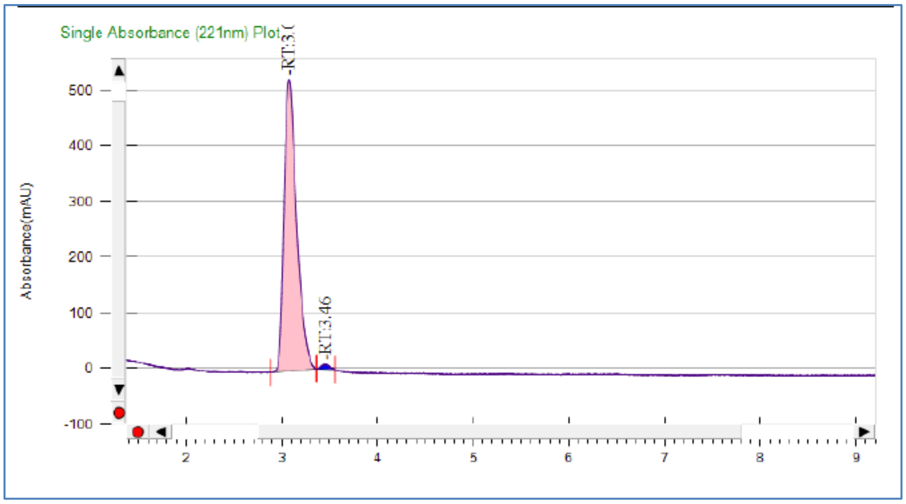
Figure 2, **11**

Racemic (Daicel CHIRALPAK® OJ-H, 8% *i*-PrOH, 4 mL/min, 250 nm)



Peak No	% Area	Area	RT (min)	Height (mV)
1	49.9313	626.8762	3.40	52.2733
2	50.0687	628.6011	3.79	51.6351
Total:	100	1255.4773		

Enantioenriched



Peak No	% Area	Area	RT (min)	Height (mV)
1	98.9005	4820.0261	3.08	523.0884
2	1.0995	53.586	3.46	8.539
Total:	100	4873.6121		

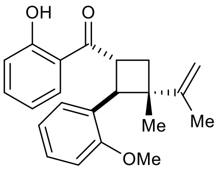
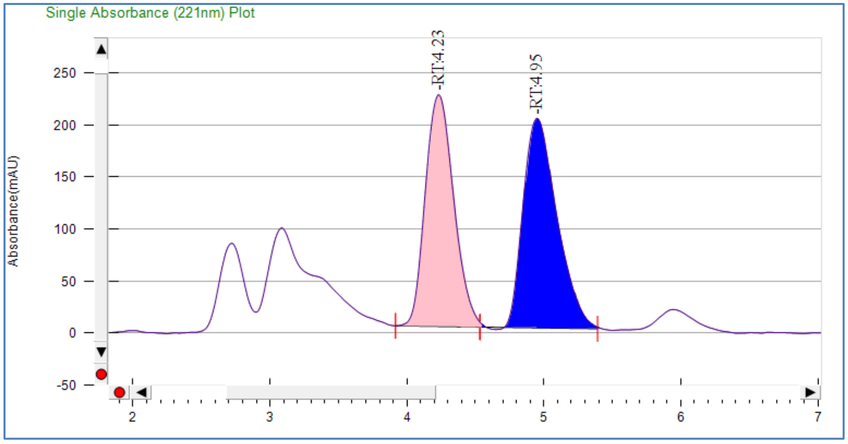


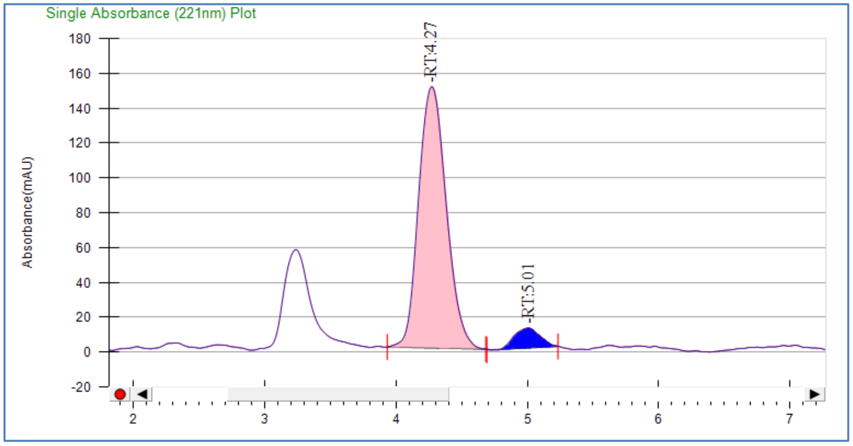
Figure 2, **12**

Racemic (Daicel CHIRALPAK® OJ-H, 5% MeOH, 3 mL/min, 255 nm)



Peak No	% Area	Area	RT (min)	Height (mV)
1	48.6411	3699.6364	4.23	267.2962
2	51.3589	3906.3558	4.96	237.2921
Total:	100	7605.9922		

Enantioenriched (Blue LED Conditions)



Peak No	% Area	Area	RT (min)	Height (mV)
1	92.291	2195.8546	4.27	149.9284
2	7.709	183.4169	5.01	11.5605
Total:	100	2379.2715		

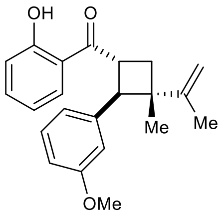
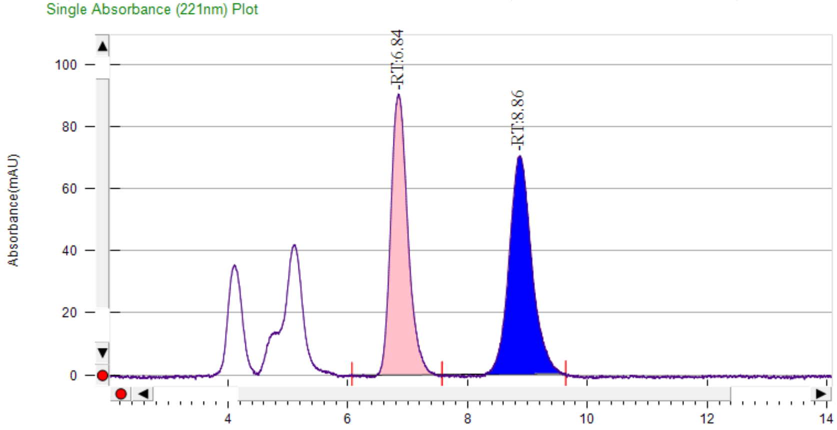


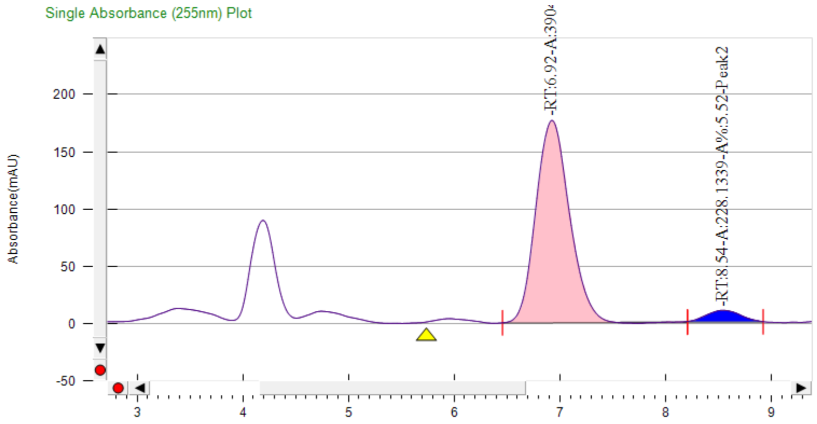
Figure 2, **13**

Racemic (Daicel CHIRALPAK® OJ-H, 3% (25% i-PrOH:Hex), 3 mL/min, 245 nm)



Peak No	% Area	Area	RT (min)	Height (mV)
1	49.1343	1777.6199	6.84	90.3663
2	50.8657	1840.2607	8.86	70.2086
Total:	100	3617.8806		

Enantioenriched (Blue LED conditions)



Peak No	% Area	Area	RT (min)	Height (mV)
1	93.7763	5103.1986	6.92	84.1899
2	6.2237	221.7657	8.52	5.2224
Total:	100	5324.9643		

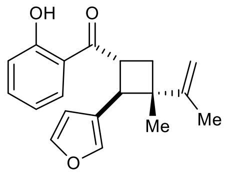
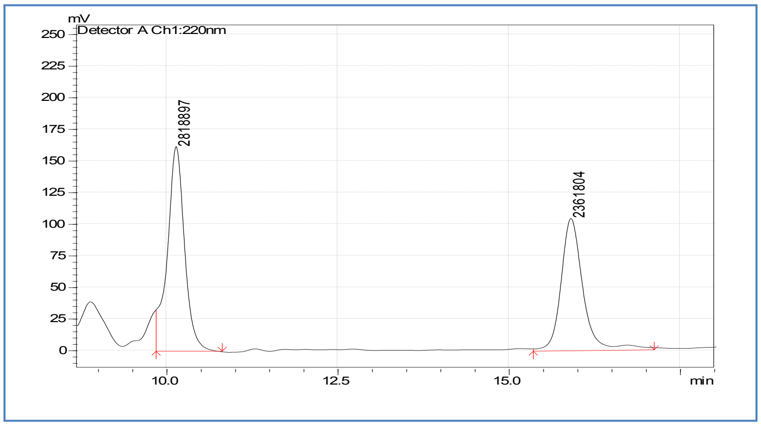


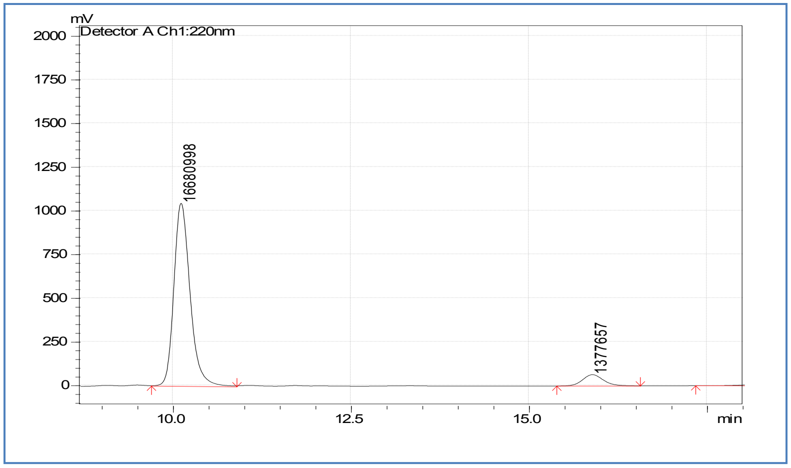
Figure 2, **14**

Racemic (Daicel CHIRALPAK® OJ-H, Shimadzu HPLC, gradient 1-10% (*i*-PrOH:Hex), 0.7 mL/min, 265 nm)



Peak No	% Area	Area	RT (min)	Height (mV)
1	54.4115	2818897	10.05	165.1934
2	45.5885	2361804	15.19	108.2456
Total:	100	5180701		

Enantioenriched (Blue LED conditions)



Peak No	% Area	Area	RT (min)	Height (mV)
1	92.3712	16680998	10.06	1050.3465
2	7.6288	1377657	15.18	100.2873
Total:	100	18058655		

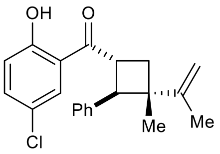
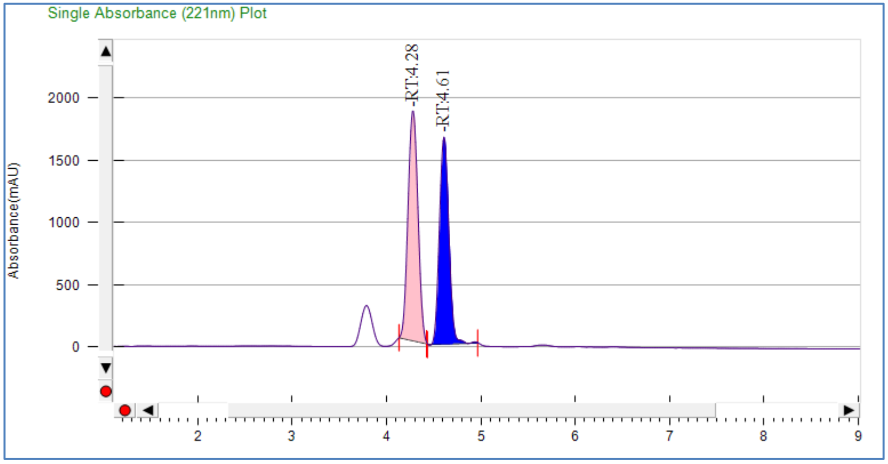


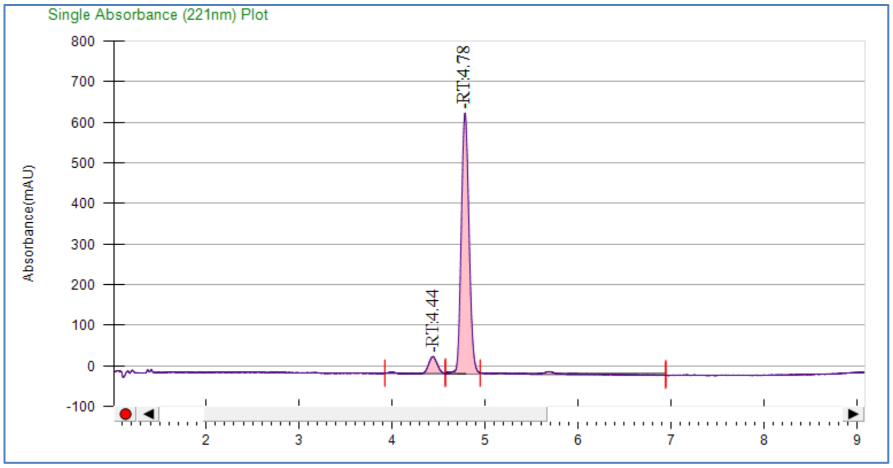
Figure 2, **15**

Racemic (Daicel CHIRALPAK® OD-H, gradient 5 - 50% MeOH, 3 mL/min, 248 nm)



Peak No	% Area	Area	RT (min)	Height (mV)
1	51.9812	13494.8102	4.28	1843.2347
2	48.0188	12466.1425	4.61	1661.4423
Total:	100	25960.9527		

Enantioenriched



Peak No	% Area	Area	RT (min)	Height (mV)
1	5.8109	67.6433	4.41	11.6444
2	94.1891	1096.4349	4.78	189.7383
Total:	100	1164.0782		

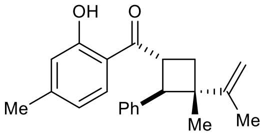
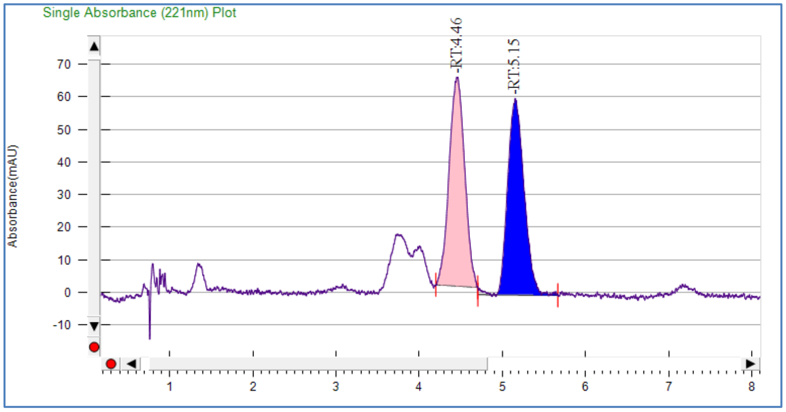


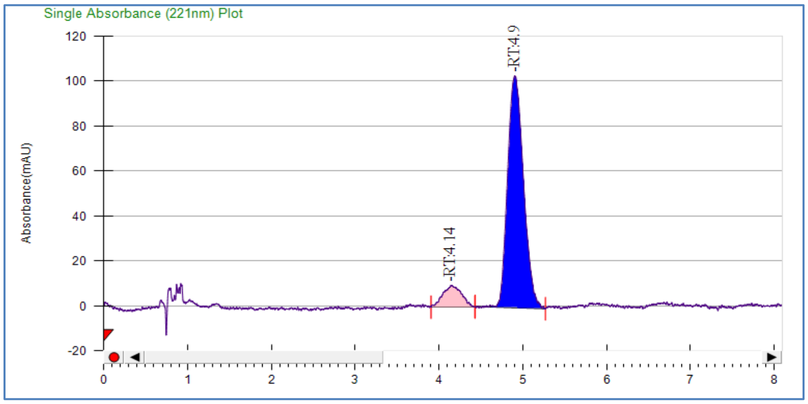
Figure 2, **16**

Racemic (Daicel CHIRALPAK® OD-H, 4% *i*-PrOH, 5 mL/min, 255 nm)



Peak No	% Area	Area	RT (min)	Height (mV)
1	51.5668	923.8581	4.46	71.3989
2	48.4332	867.7179	5.15	65.109
Total:	100	1791.576		

Enantioenriched



Peak No	% Area	Area	RT (min)	Height (mV)
1	8.6435	149.9704	4.14	9.7192
2	91.3565	1585.0979	4.90	103.2002
Total:	100	1735.0683		

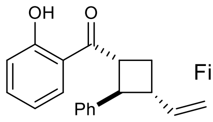
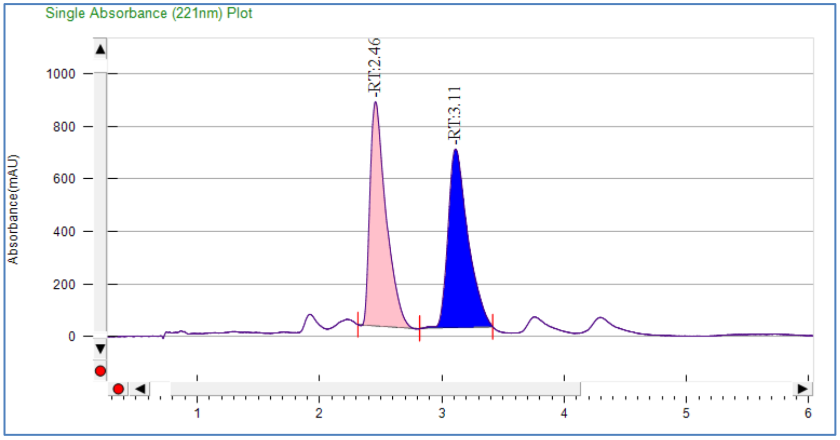


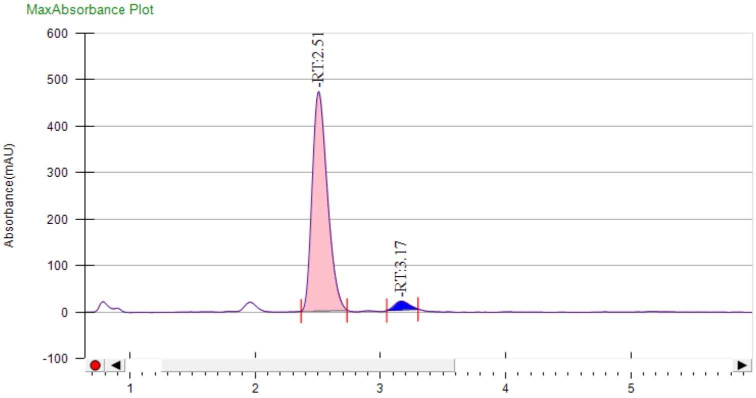
Figure 2, **17**

Racemic (Daicel CHIRALPAK® OJ-H, 5% MeOH, 5 mL/min, 245 nm)



Peak No	% Area	Area	RT (min)	Height (mV)
1	50.0337	8987.9841	2.46	990.8456
2	49.9663	8975.8691	3.11	785.2963
Total:	100	17963.8532		

Enantioenriched



Peak No	% Area	Area	RT (min)	Height (mV)
1	96.2704	3904.6574	2.51	472.3205
2	3.7296	151.2699	3.17	19.1053
Total:	100	4055.9273		

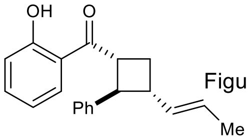
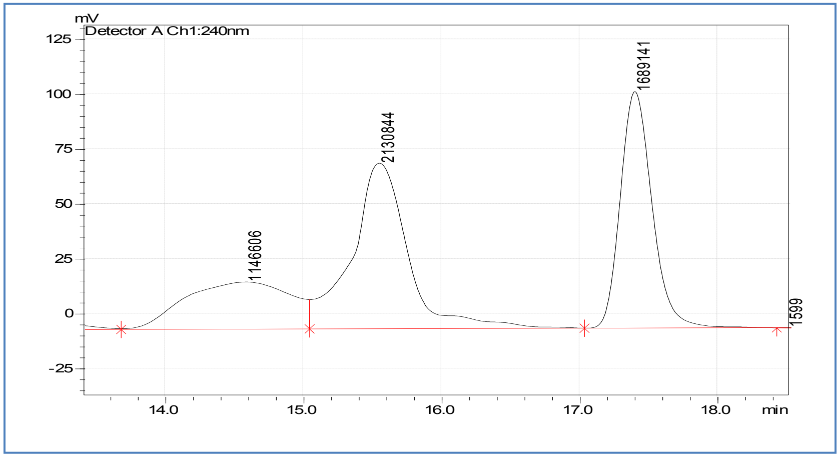


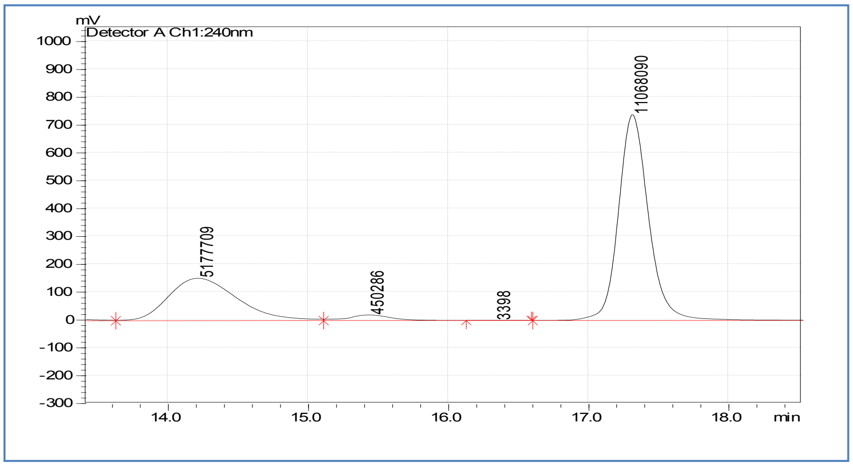
Figure 2, **18**

Racemic (Daicel CHIRALPAK® AD-H, gradient 1-6% (*i*-PrOH:Hex), Shimadzu HPLC, 0.4 mL/min, 265 nm)



Peak No	% Area	Area	RT (min)	Height (mV)
1	55.7815	2130844	15.67	65.9856
2	44.2185	1689141	17.46	103.4762
Total:	100	3819985		

Enantioenriched



Peak No	% Area	Area	RT (min)	Height (mV)
1	3.9093	450286	15.67	39.6521
2	96.0910	11068090	17.46	741.9541
Total:	100	11518376		

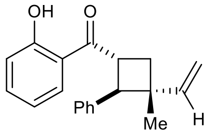
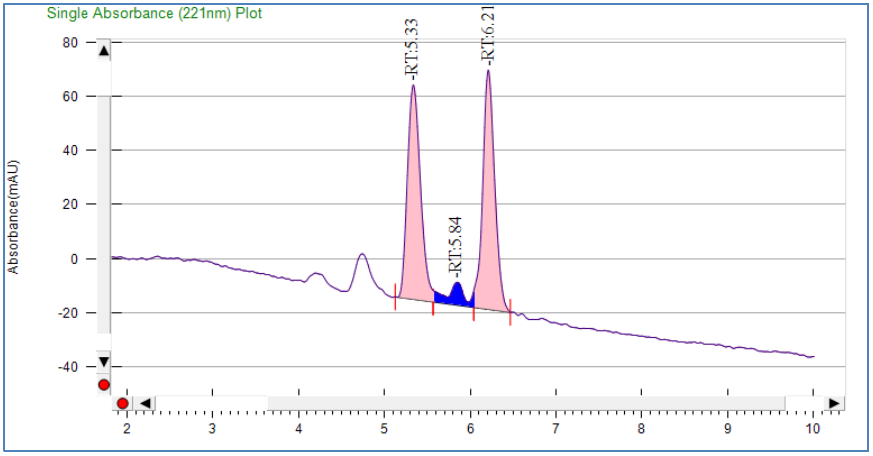


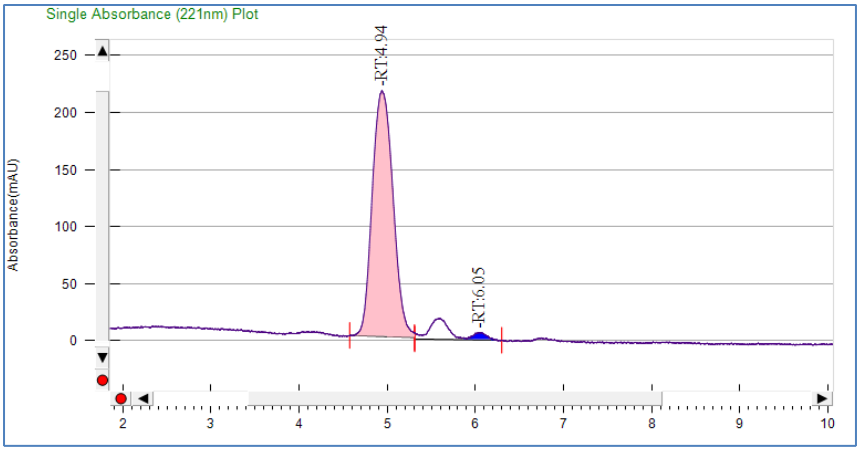
Figure 2, **19**

Racemic (Daicel CHIRALPAK® OJ-H, gradient 5-50% (25% *i*-PrOH:Hex), 3 mL/min, 243 nm)



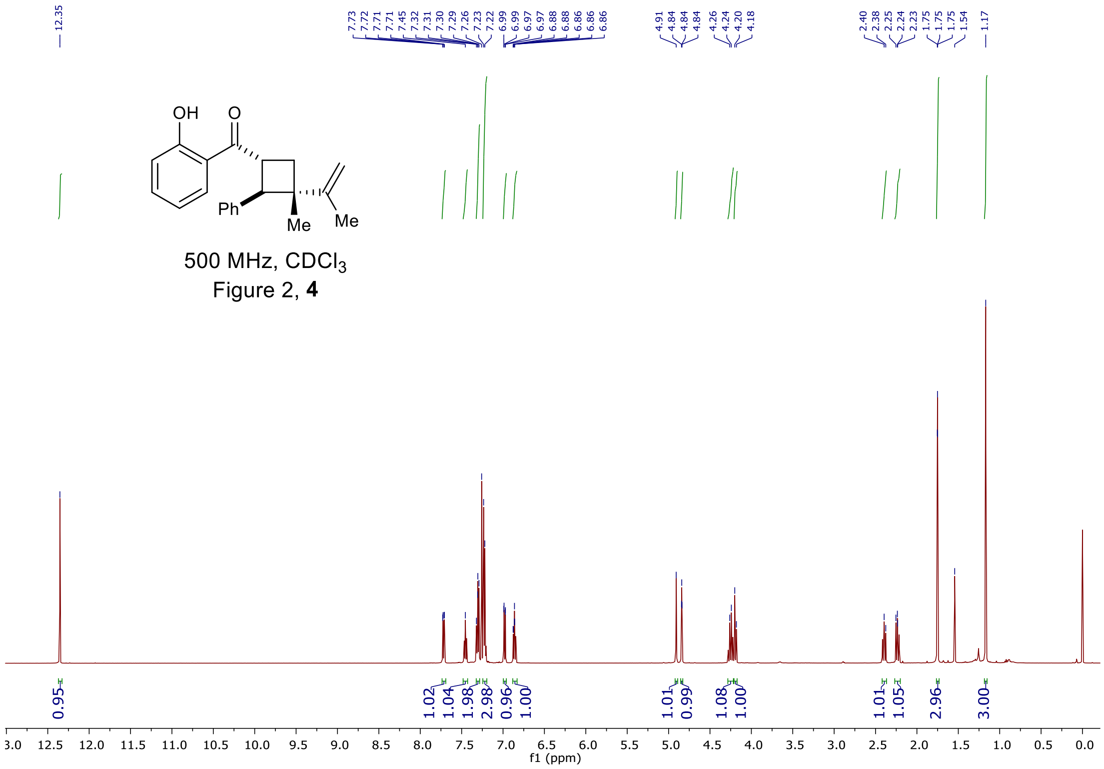
Peak No	% Area	Area	RT (min)	Height (mV)
1	49.7649	840.1165	5.33	79.1538
2	50.2351	848.0568	6.21	88.3866
Total:	100	1688.1733		

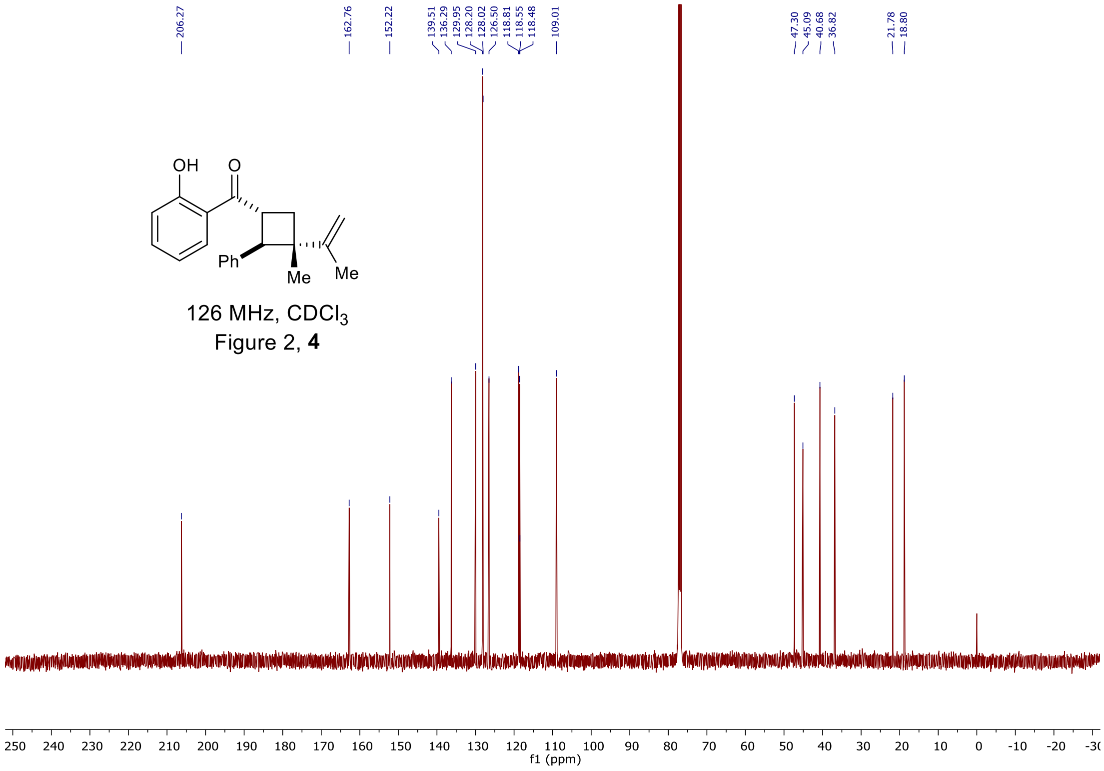
Enantioenriched

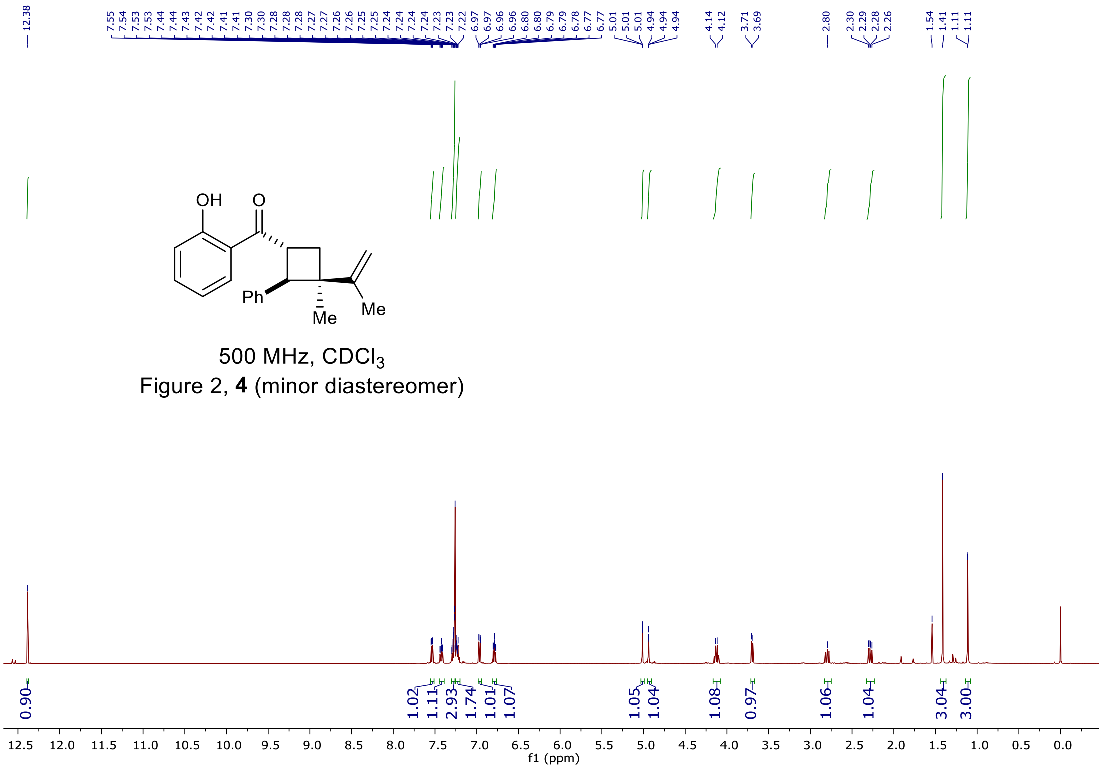


Peak No	% Area	Area	RT (min)	Height (mV)
1	95.9786	3520.4287	4.94	215.3677
2	4.0214	147.5009	6.05	6.132
Total:	100	3667.9377		

L. NMR Spectra

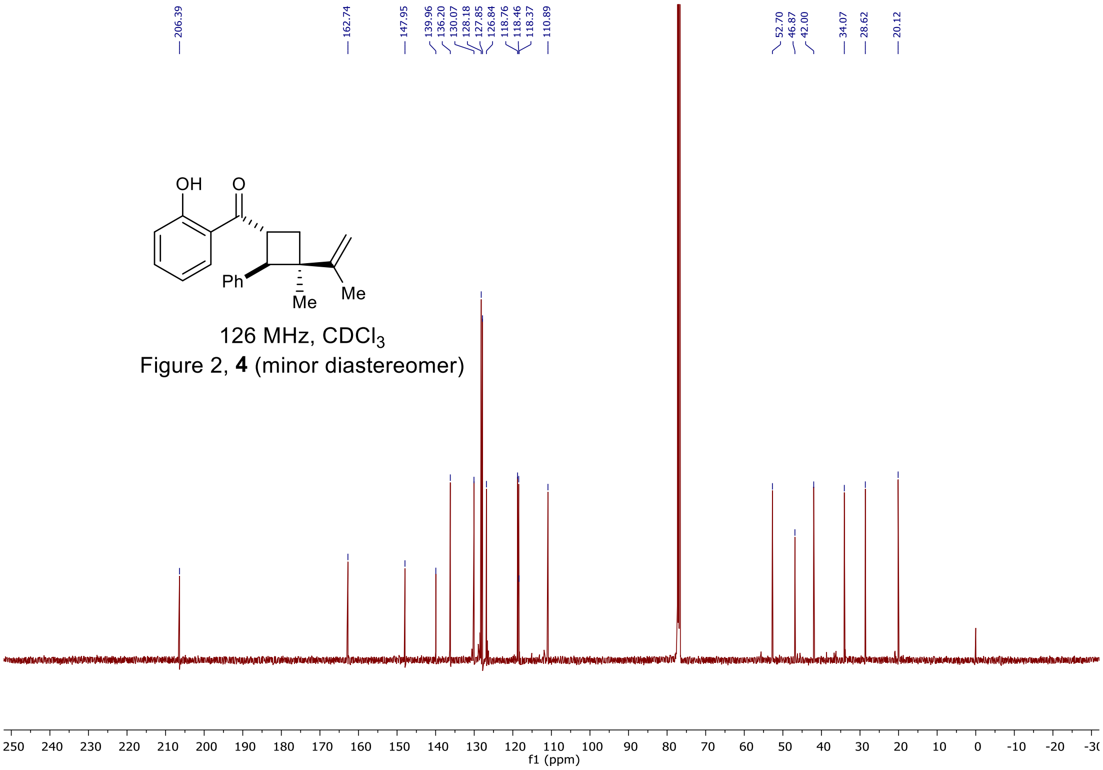

500 MHz, $CDCl_3$
Figure 2, **4**


126 MHz, $CDCl_3$
Figure 2, **4**



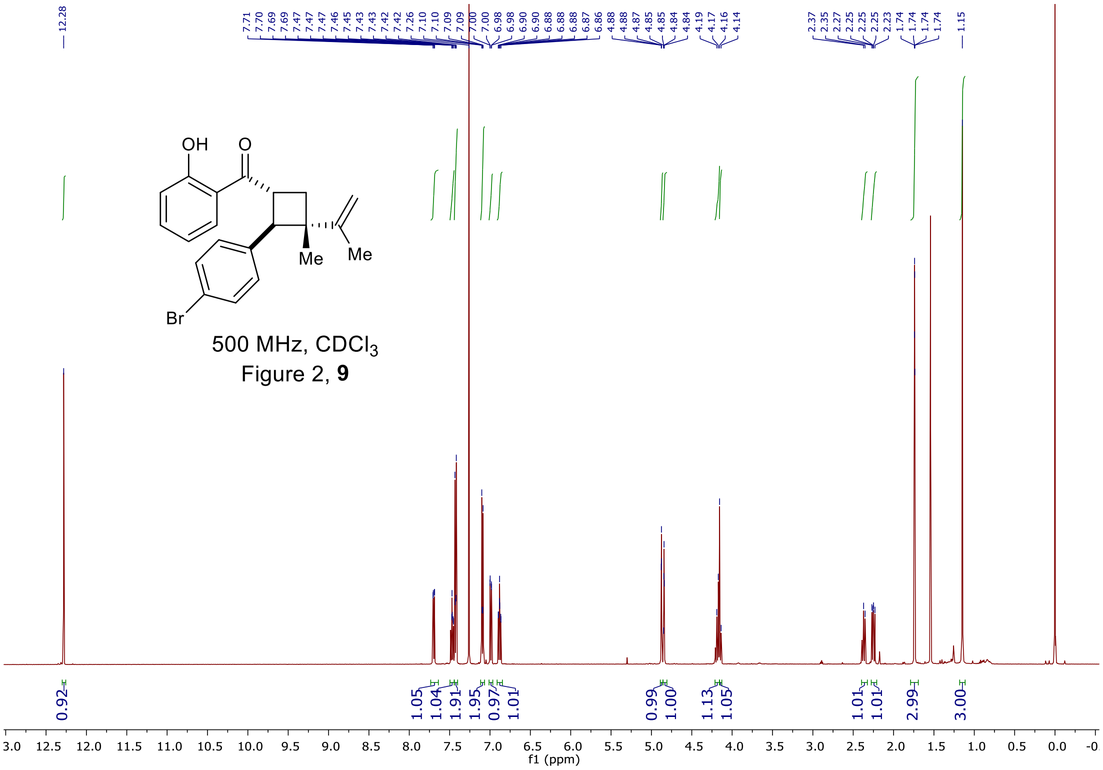
500 MHz, $CDCl_3$

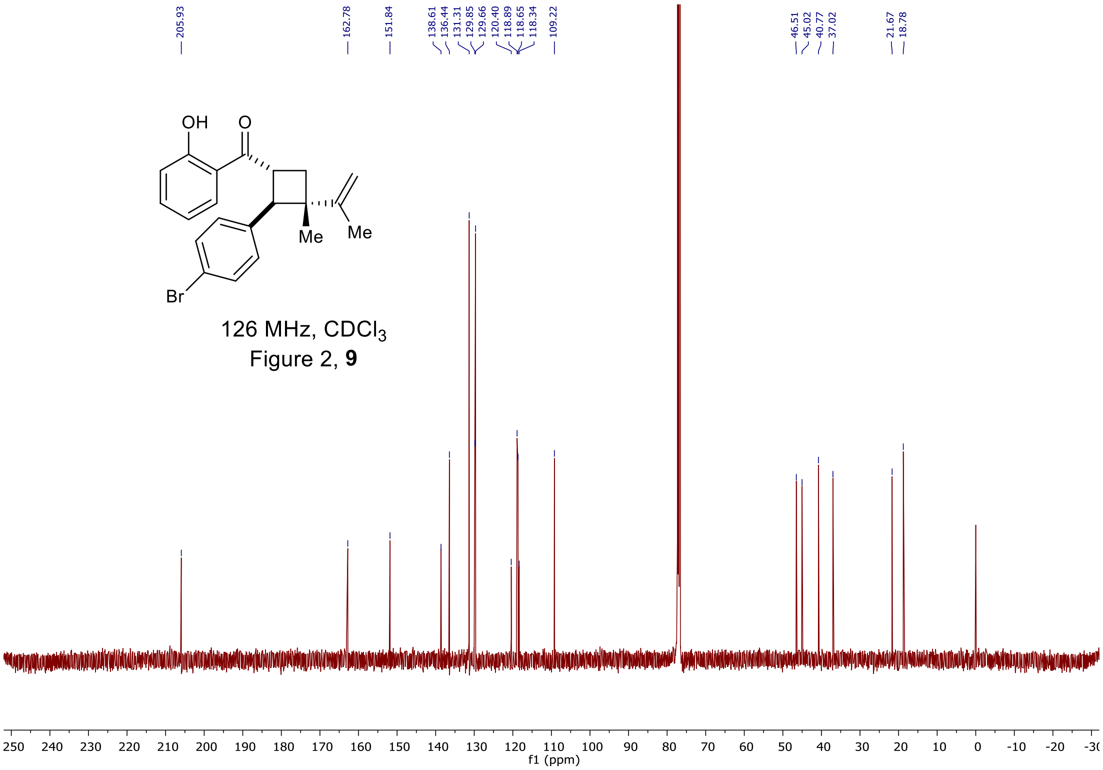
Figure 2, **4** (minor diastereomer)

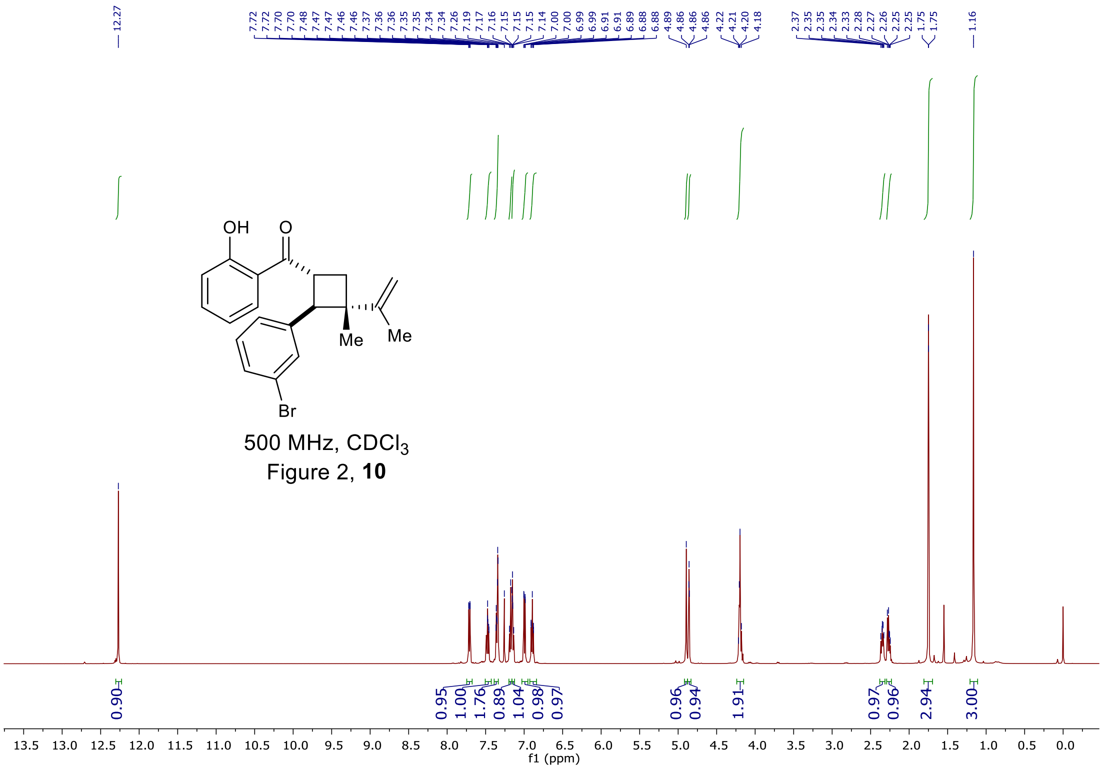


126 MHz, $CDCl_3$

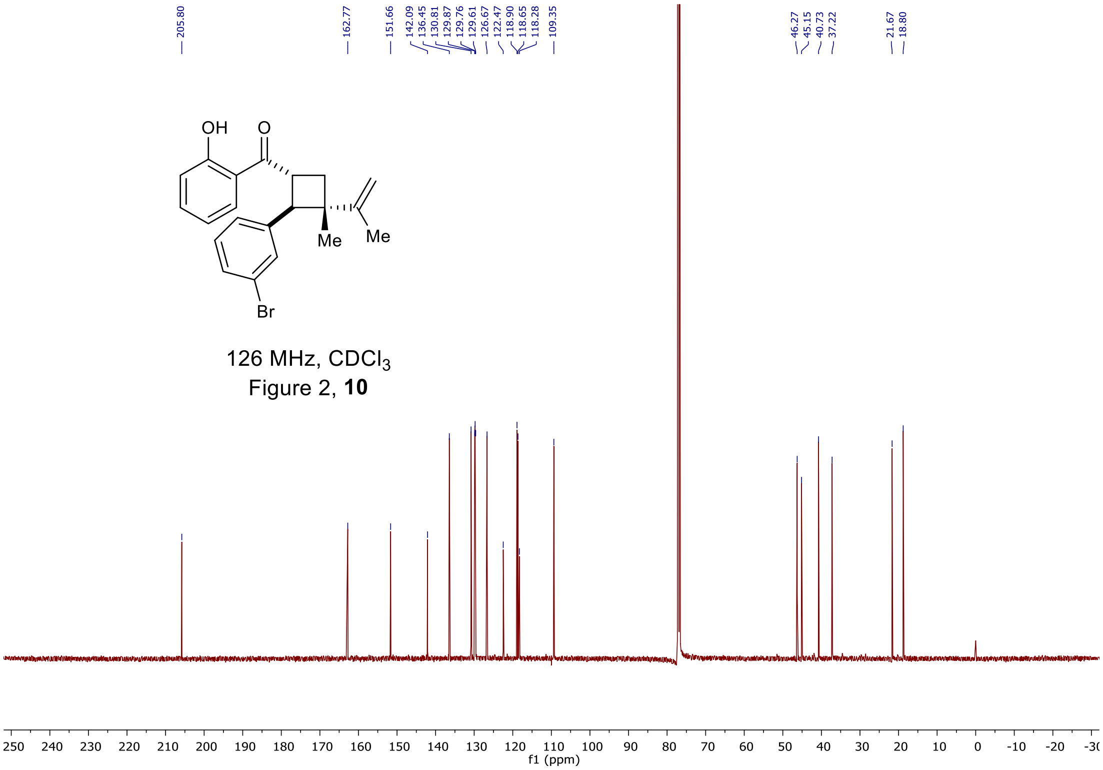
Figure 2, **4** (minor diastereomer)


12.28
7.71 7.70 7.69 7.69 7.47 7.47 7.47 7.46 7.45 7.43 7.43 7.42 7.42 7.26 7.10 7.10 7.09 7.09 7.00 7.00 6.98 6.98 6.90 6.90 6.88 6.88 6.88 6.87 6.86 4.88 4.88 4.87 4.85 4.85 4.84 4.84 4.19 4.17 4.16 4.14
2.37 2.35 2.27 2.25 2.25 2.25 2.23 1.74 1.74 1.74 1.74
1.15
OH
O
Me
Me
Br
500 MHz, CDCl$_3$
Figure 2, 9
0.92
1.05 1.04 1.91 1.95 0.97 1.01
0.99 1.00
1.13 1.05
1.01 1.01
2.99
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

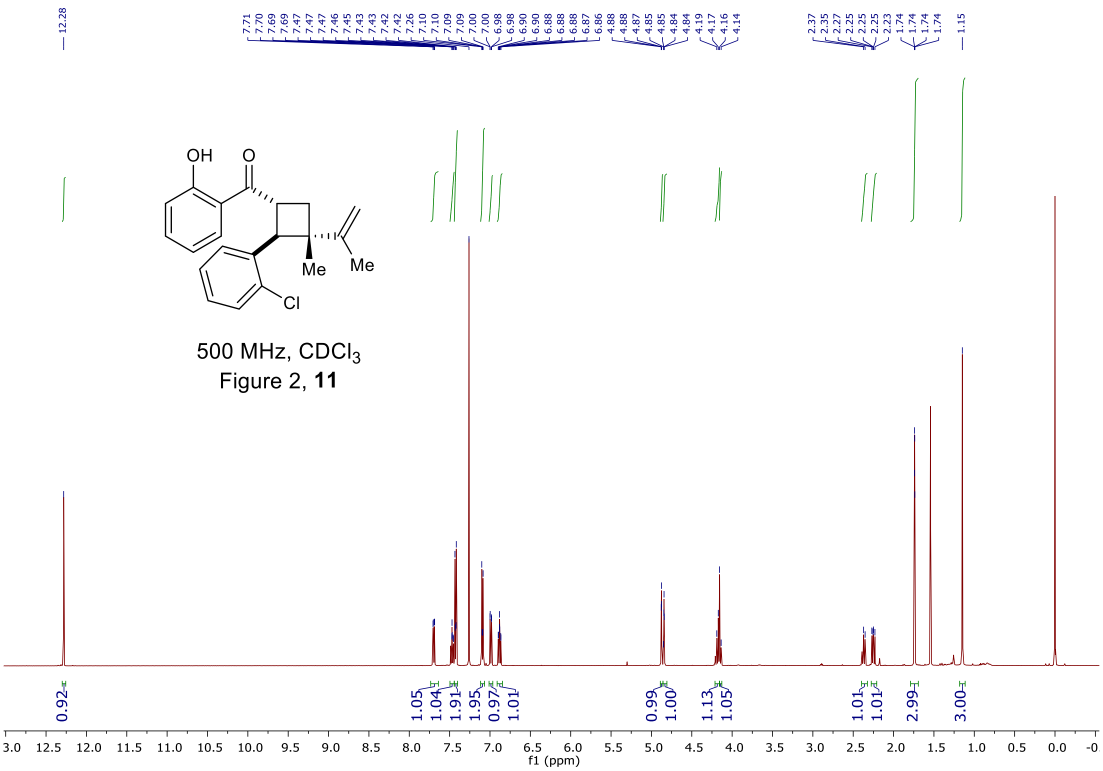

205.93
162.78
151.84
138.61 136.44 131.31 129.85 129.66 120.40 118.89 118.65 118.34
109.22
46.51 45.02 40.77 37.02
21.67 18.78
OH
O
Me
Me
Br
126 MHz, CDCl$_3$
Figure 2, 9
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)



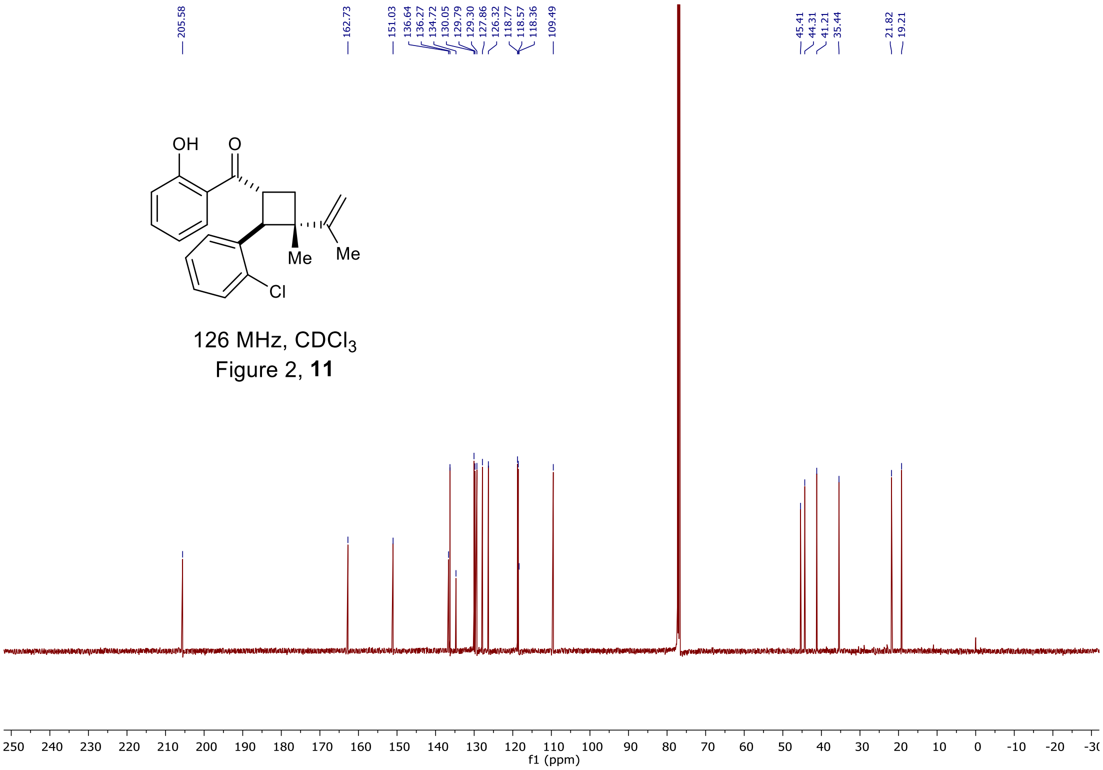
500 MHz, $CDCl_3$
Figure 2, **10**



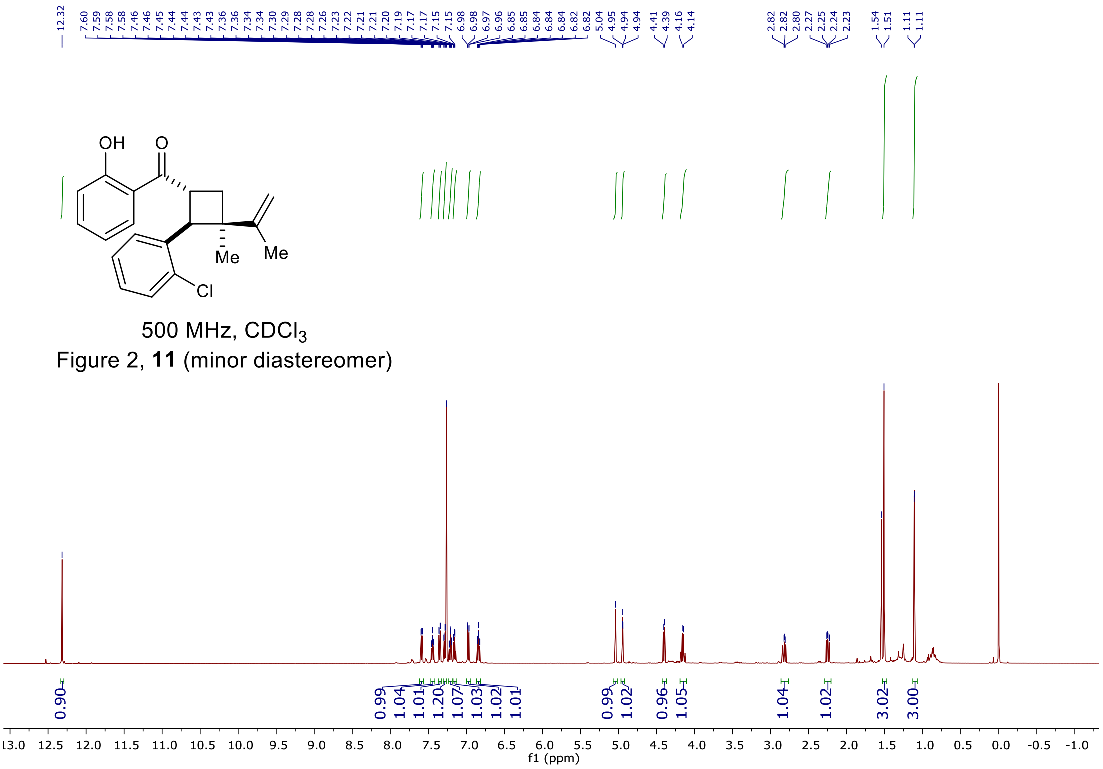
126 MHz, $CDCl_3$
Figure 2, **10**



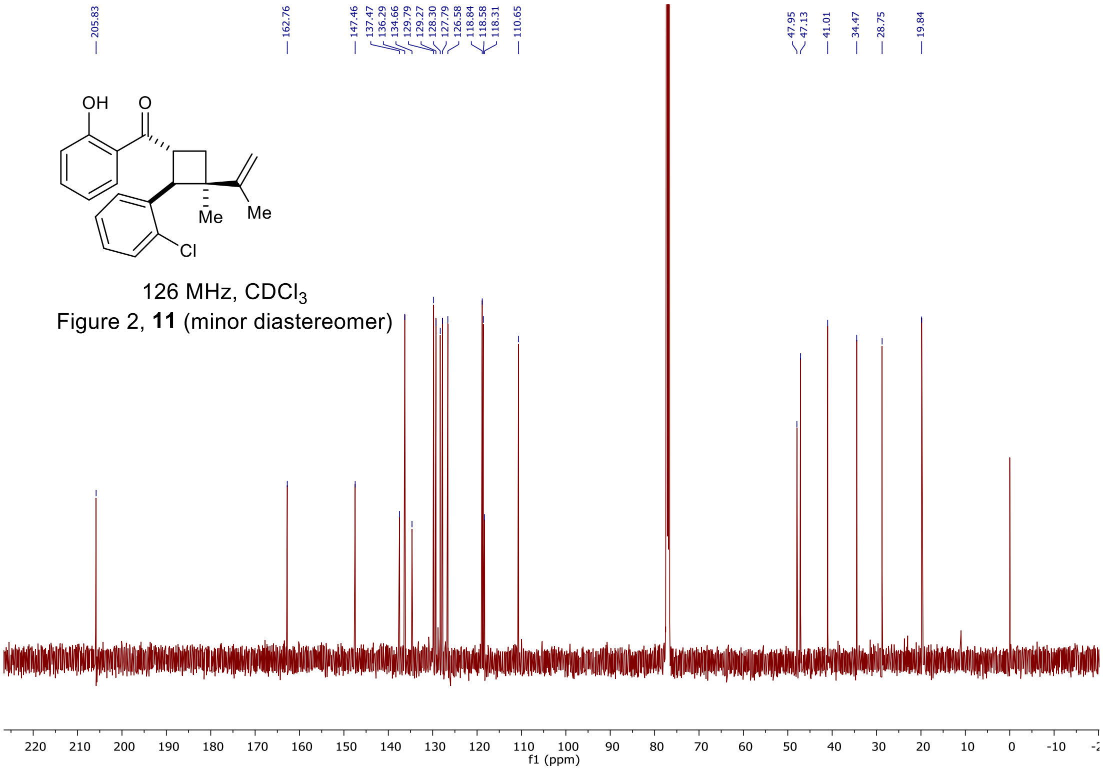
500 MHz, $CDCl_3$
Figure 2, **11**



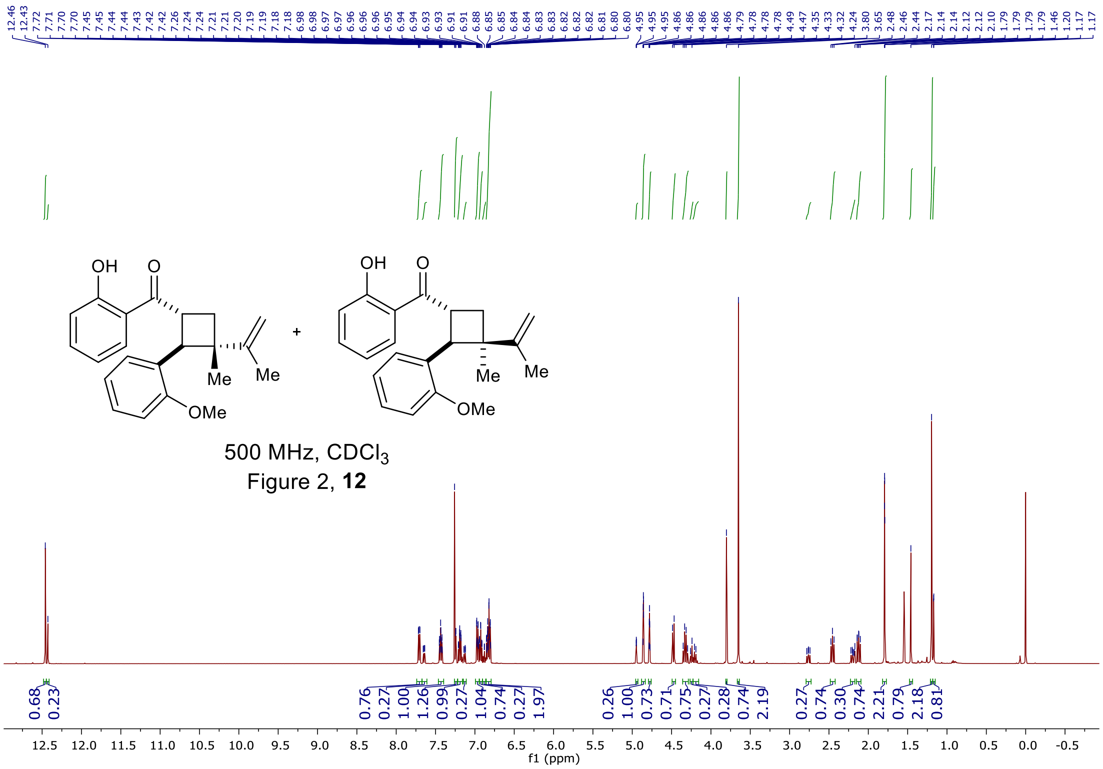
126 MHz, $CDCl_3$
Figure 2, **11**



500 MHz, $CDCl_3$
Figure 2, **11** (minor diastereomer)

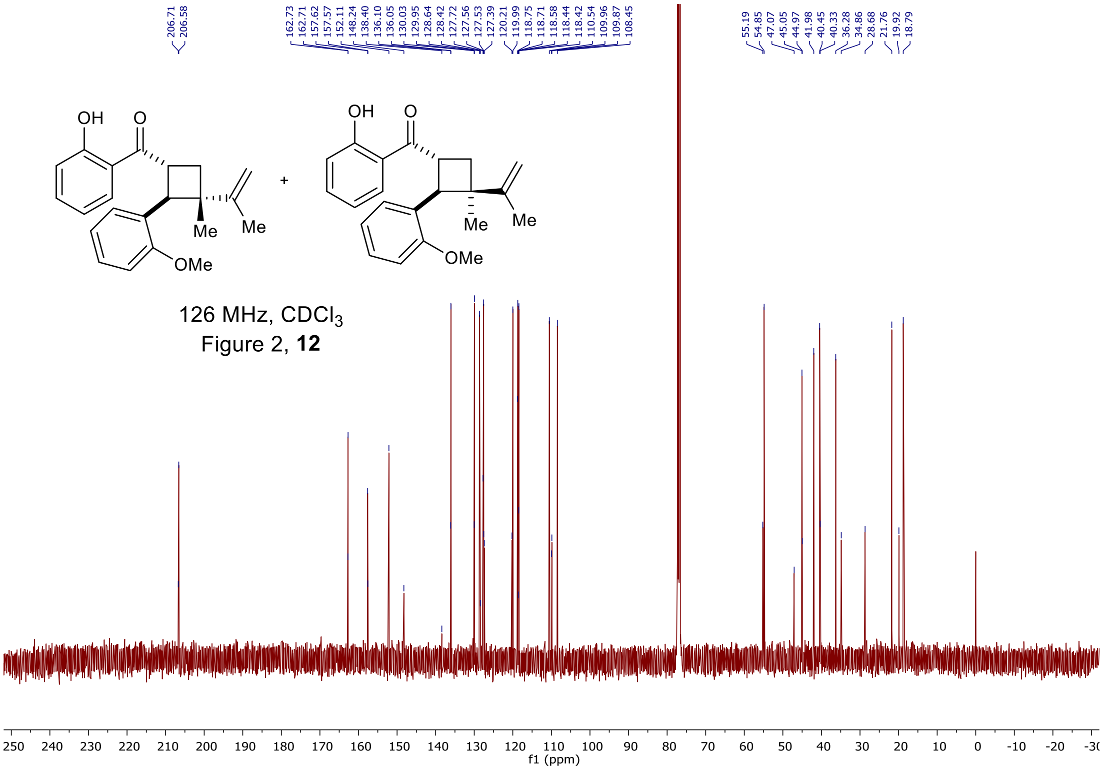


126 MHz, $CDCl_3$
Figure 2, **11** (minor diastereomer)



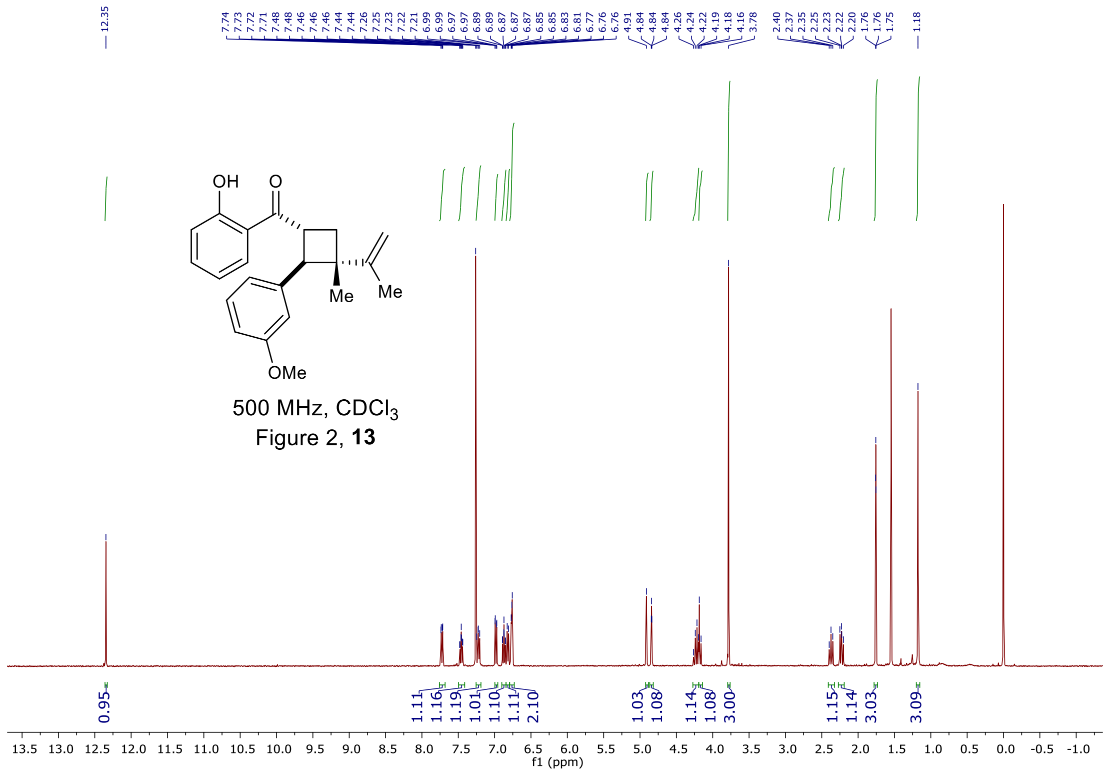
500 MHz, $CDCl_3$

Figure 2, **12**

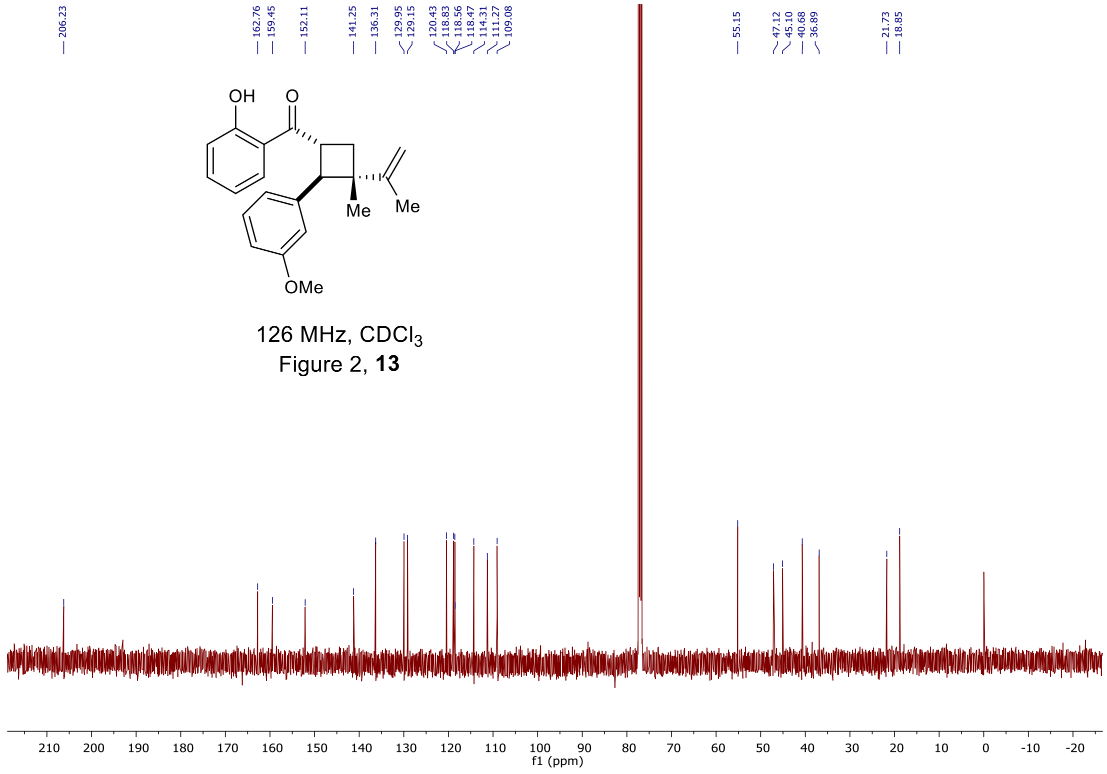


126 MHz, $CDCl_3$

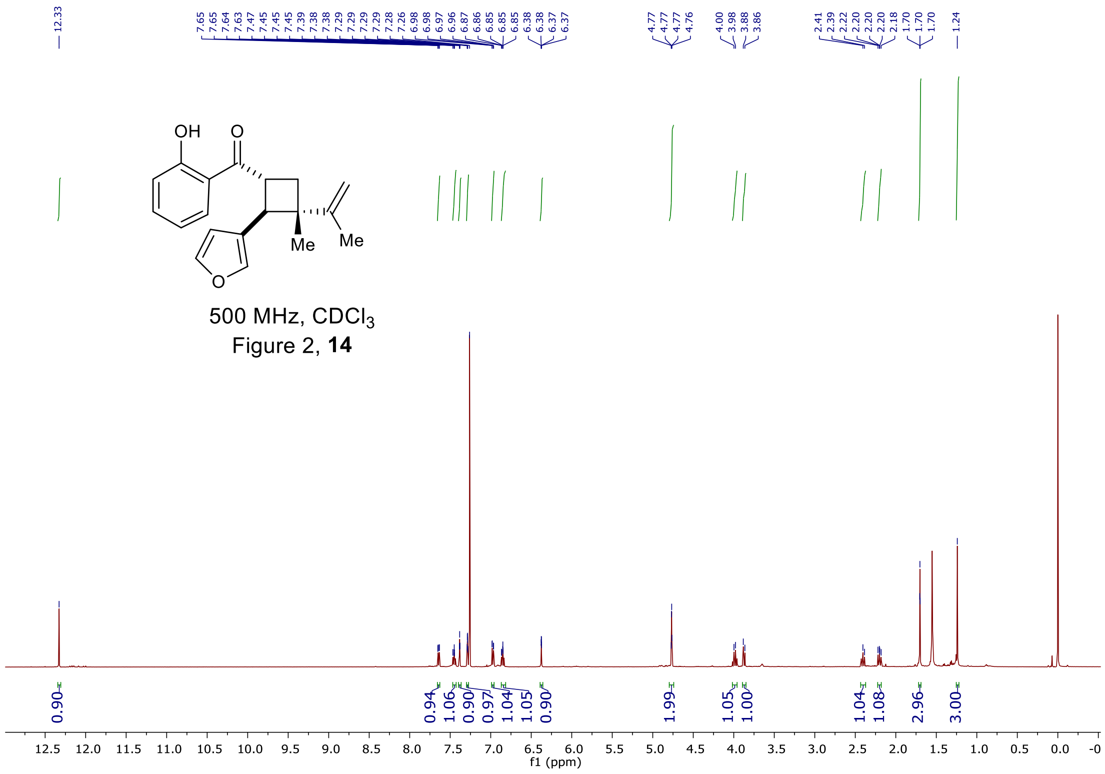
Figure 2, **12**

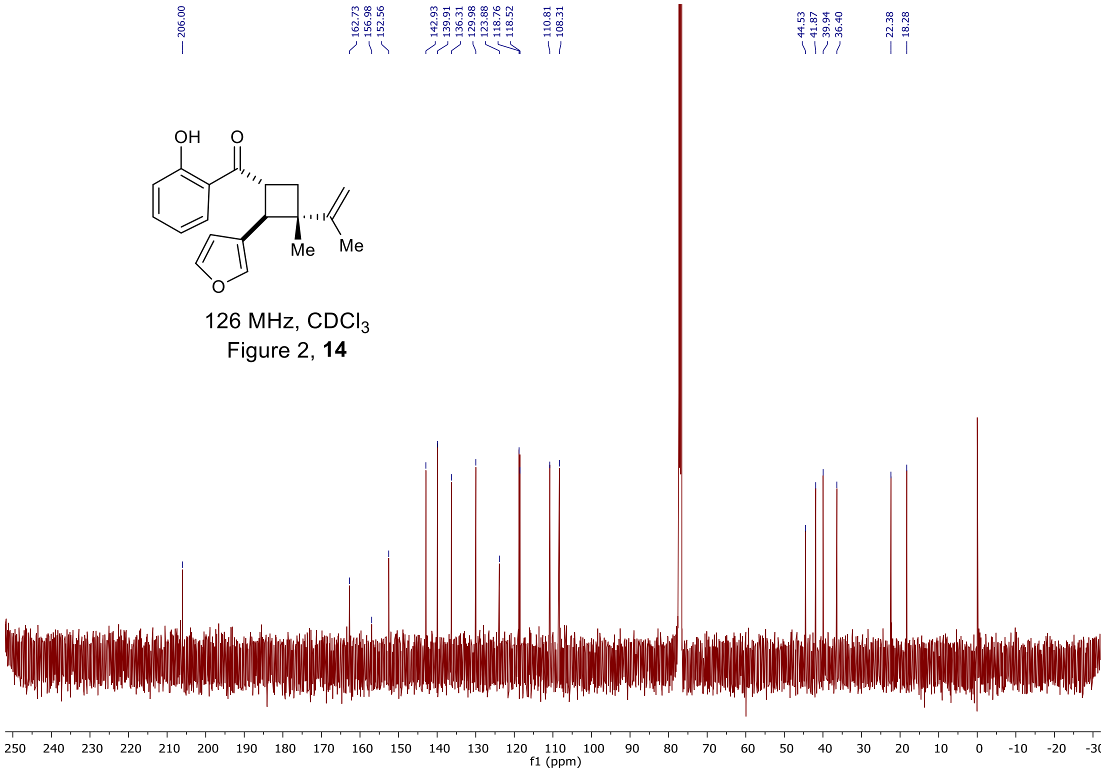


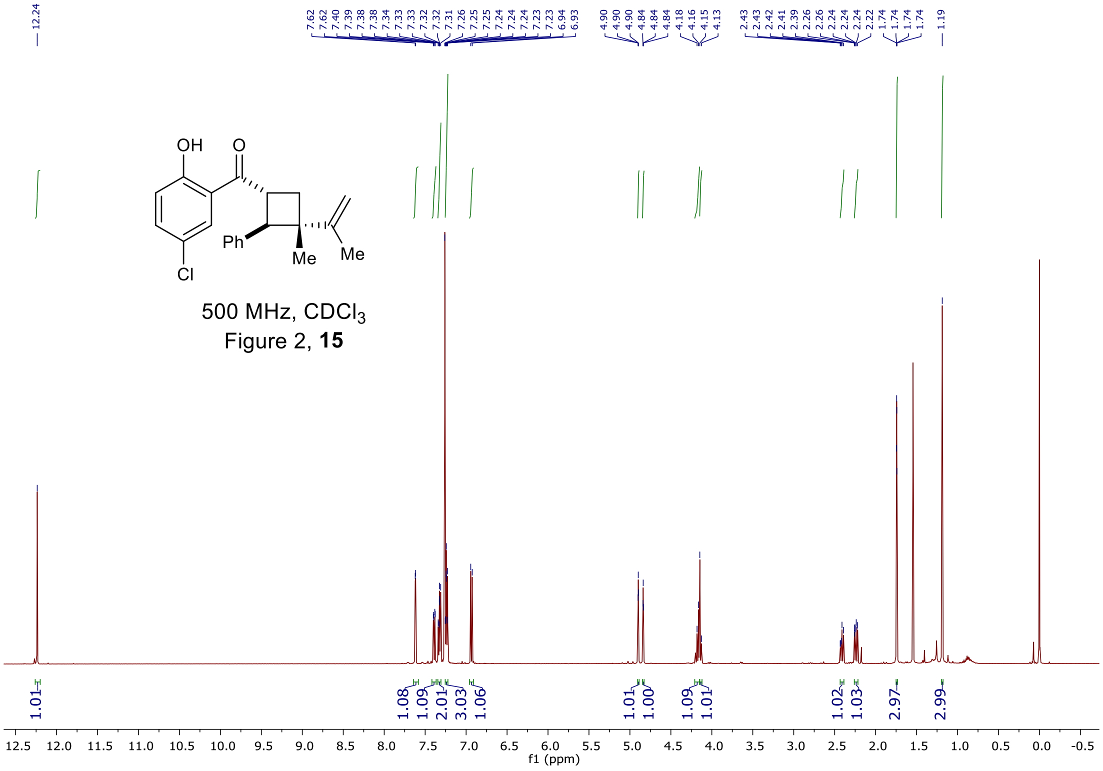
500 MHz, $CDCl_3$
Figure 2, **13**

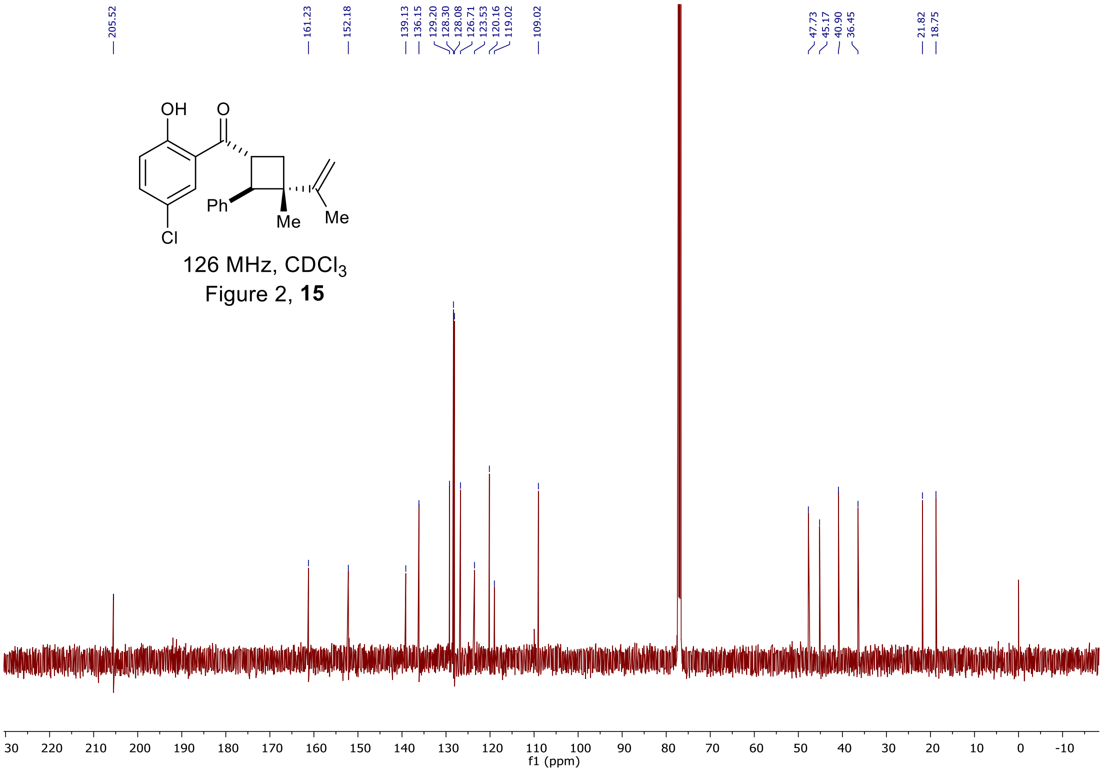


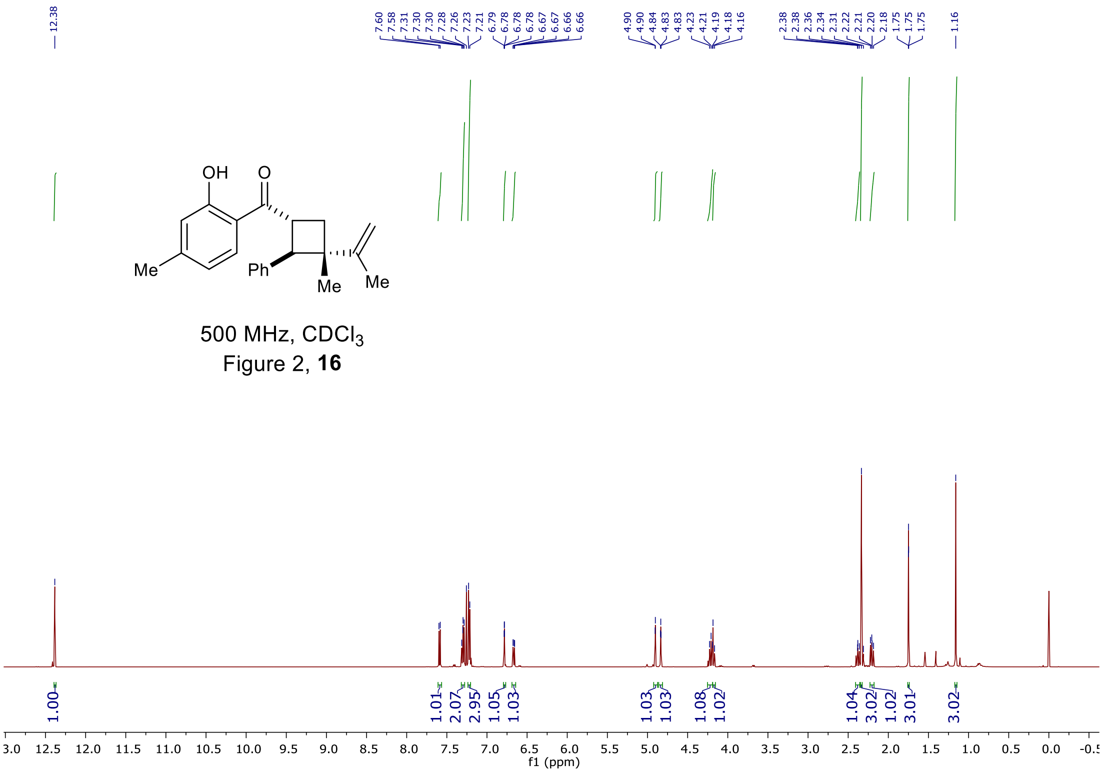
126 MHz, $CDCl_3$
Figure 2, **13**


500 MHz, $CDCl_3$
Figure 2, **14**

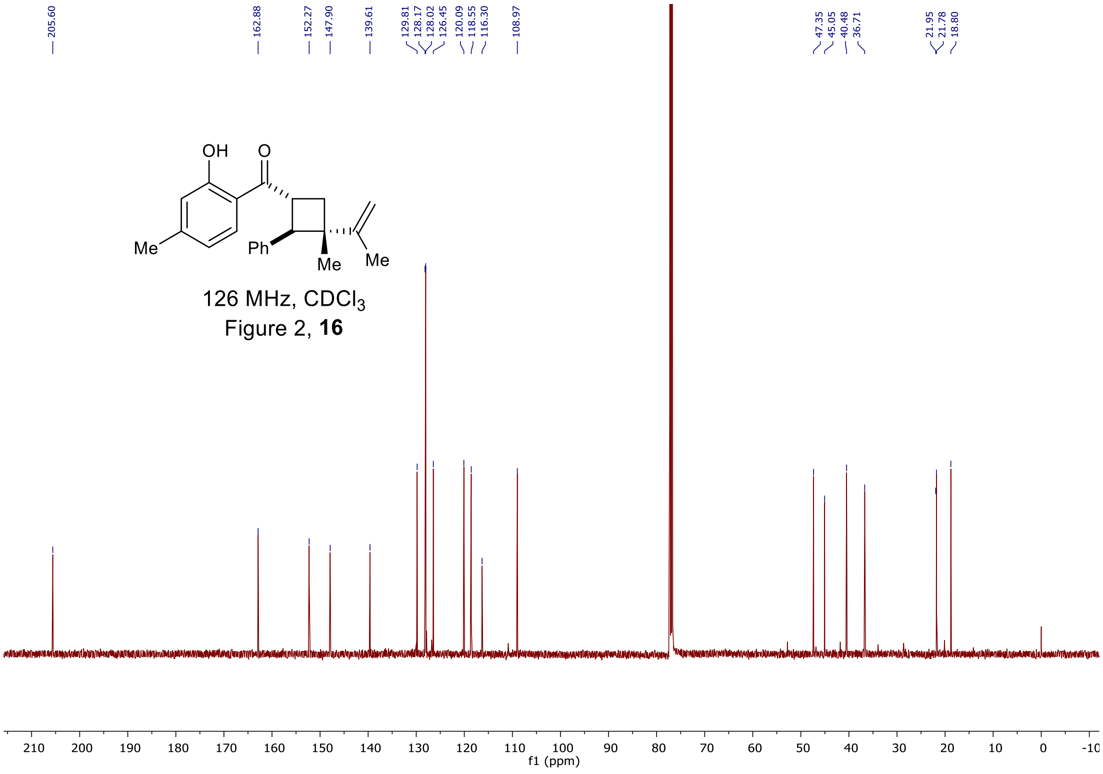

126 MHz, $CDCl_3$
Figure 2, **14**


12.24
7.62
7.62
7.40
7.39
7.38
7.38
7.34
7.33
7.33
7.32
7.32
7.31
7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.23
6.94
6.93
4.90
4.90
4.84
4.84
4.18
4.16
4.15
4.13
2.43
2.43
2.42
2.41
2.39
2.26
2.26
2.24
2.24
2.22
1.74
1.74
1.74
1.19
OH
O
Ph
Me
Me
Cl
500 MHz, CDCl3
Figure 2, 15
1.01
1.08
1.09
2.01
3.03
1.06
1.01
1.00
1.09
1.01
1.02
1.03
2.97
2.99
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

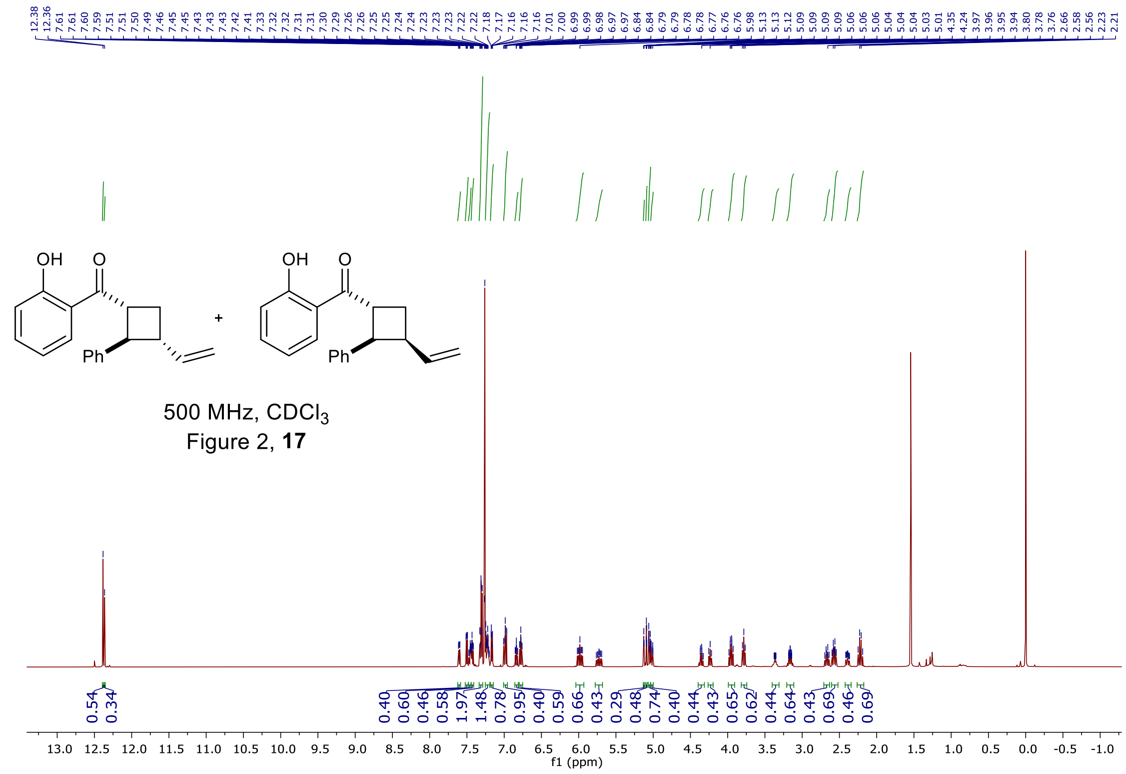

205.52
161.23
152.18
139.13
136.15
129.20
128.30
128.08
126.71
123.53
120.16
119.02
109.02
47.73
45.17
40.90
36.45
21.82
18.75
OH
O
Ph
Me
Me
Cl
126 MHz, CDCl3
Figure 2, 15
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



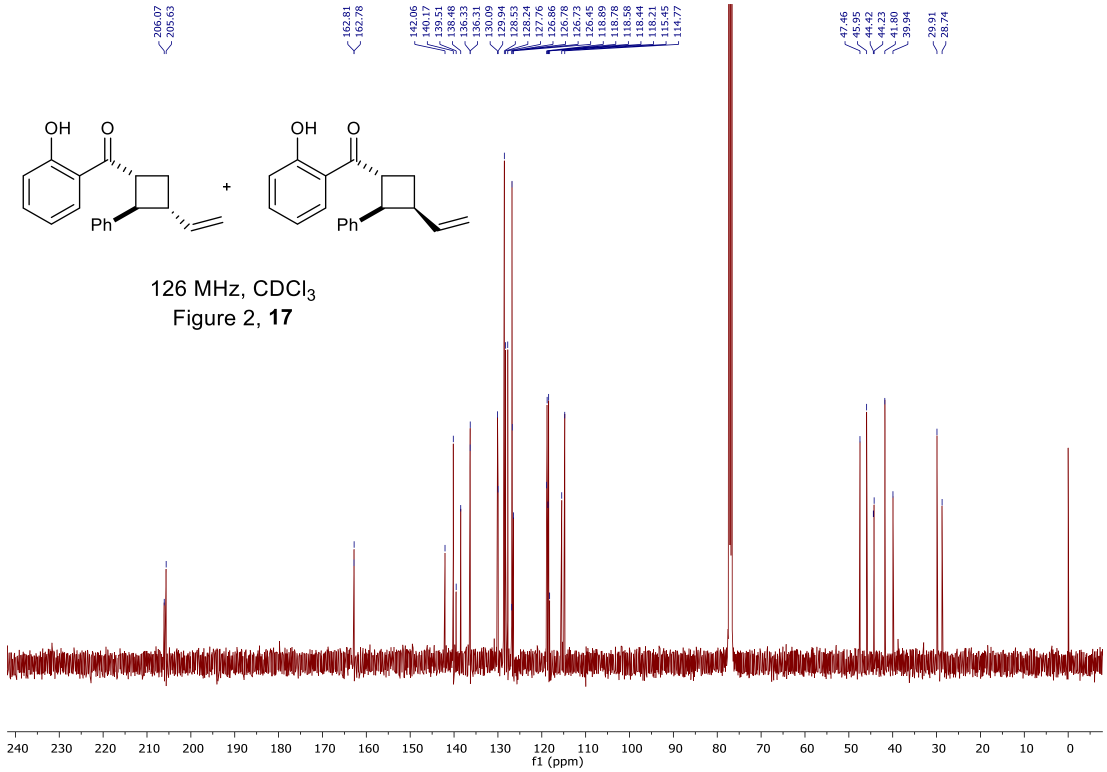
500 MHz, $CDCl_3$
Figure 2, **16**



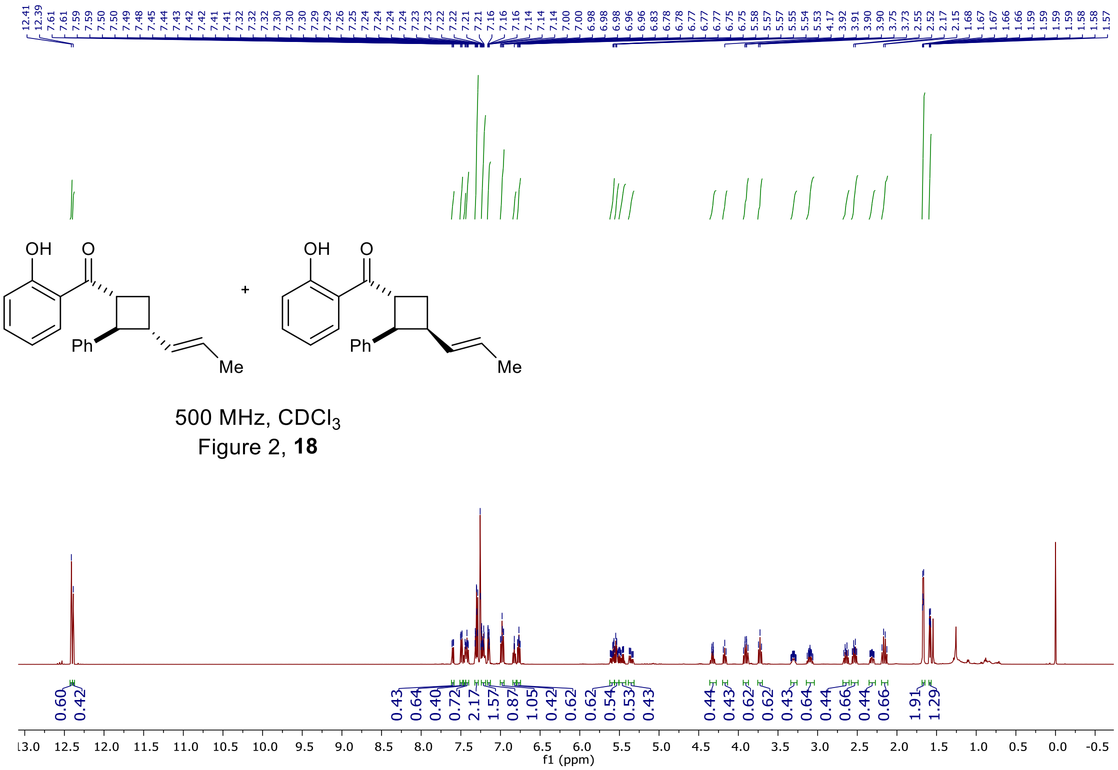
126 MHz, $CDCl_3$
Figure 2, **16**



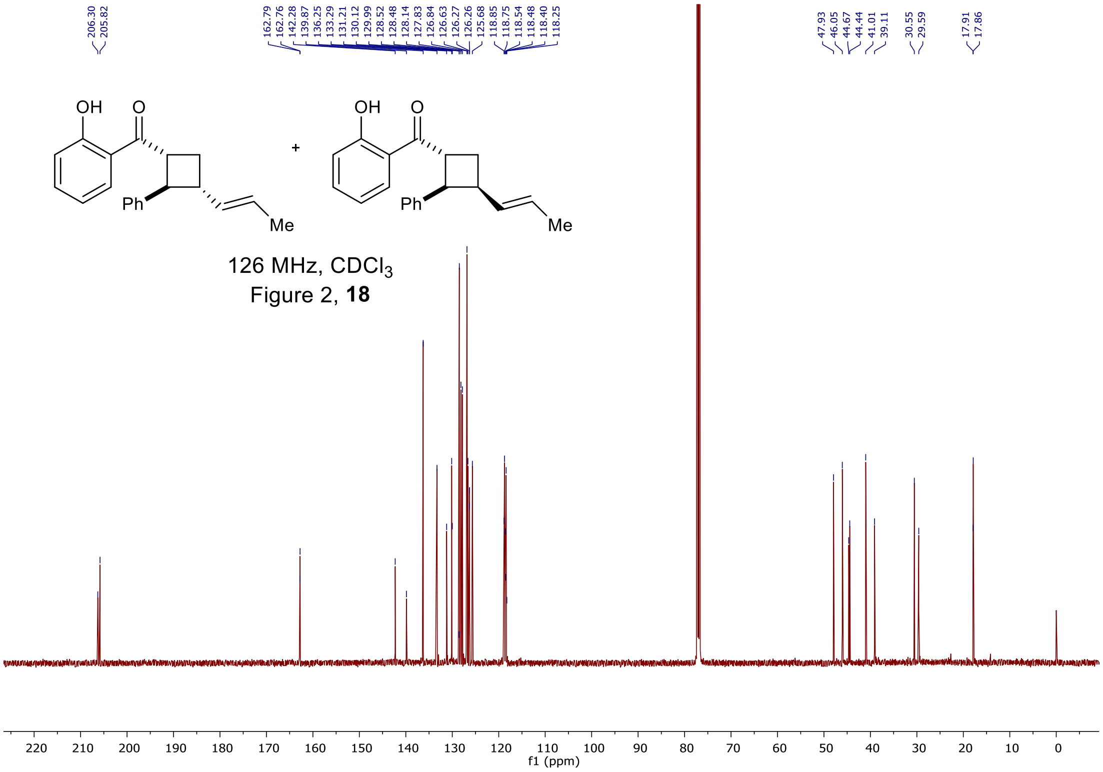
500 MHz, $CDCl_3$
Figure 2, **17**



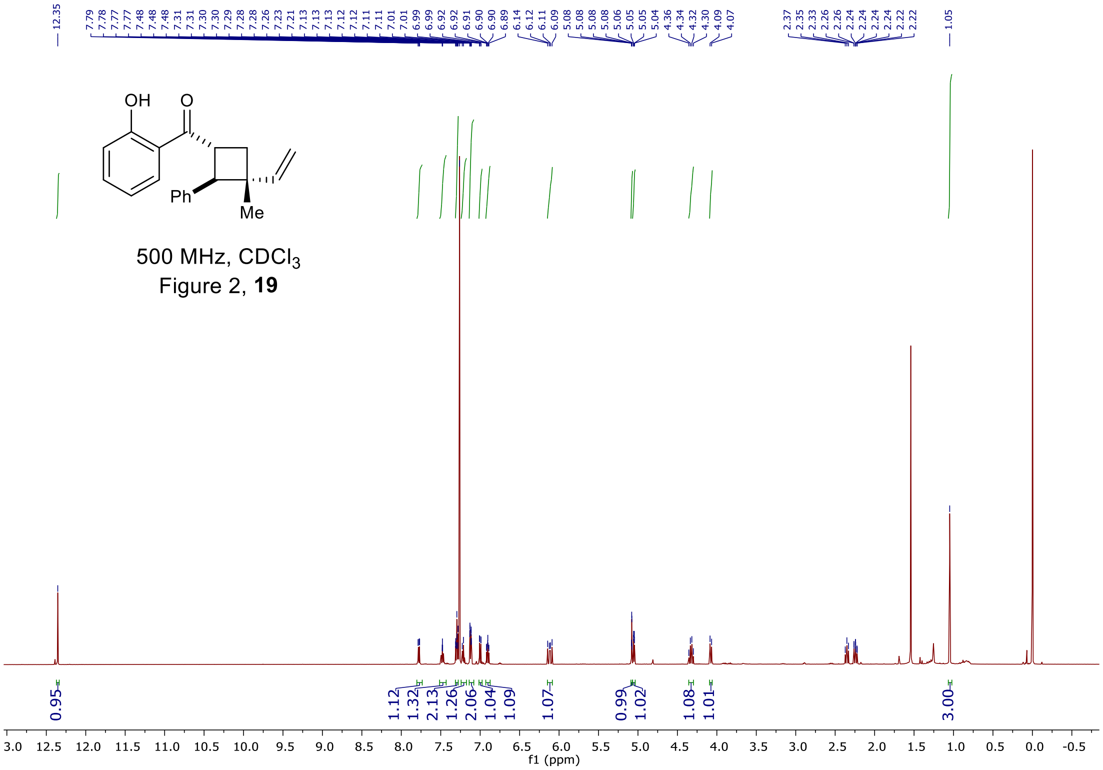
126 MHz, $CDCl_3$
Figure 2, **17**



500 MHz, $CDCl_3$
Figure 2, **18**

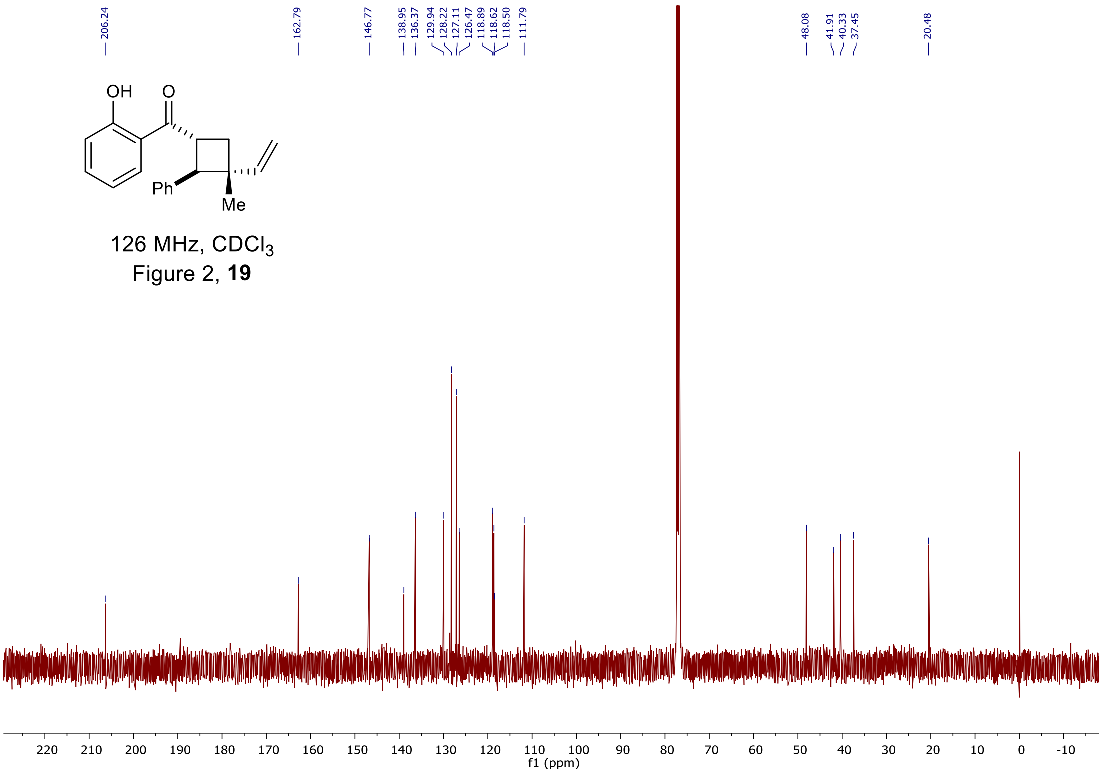


126 MHz, $CDCl_3$
Figure 2, **18**



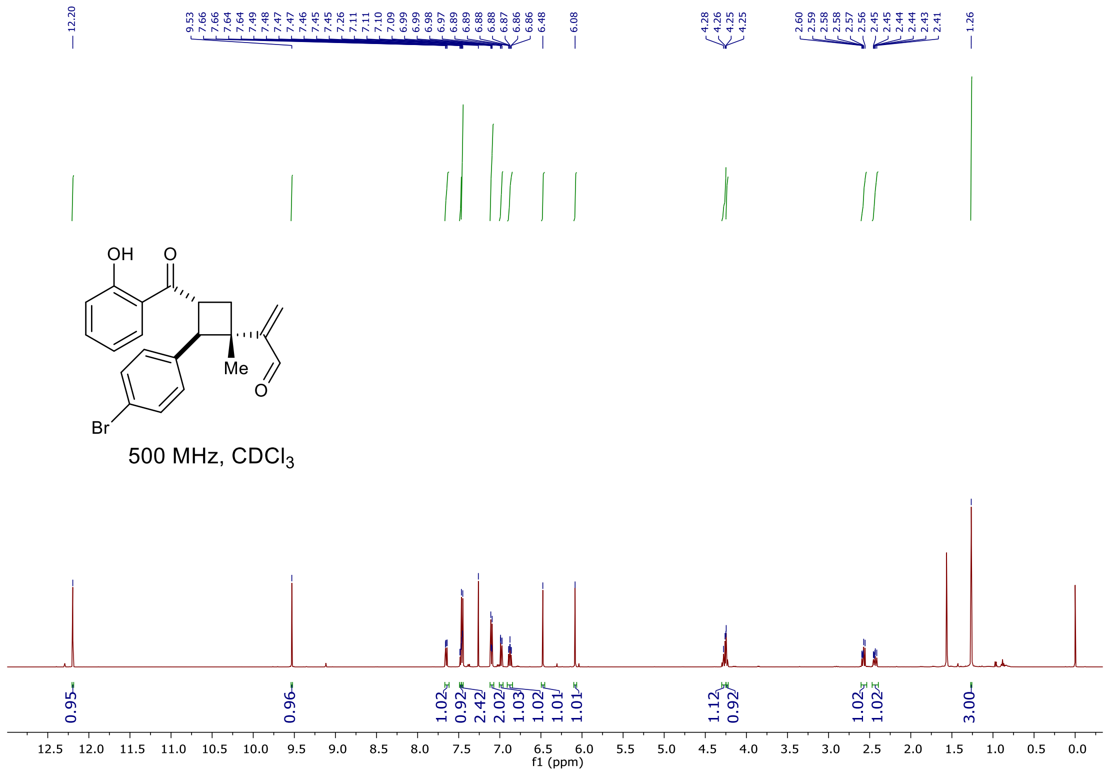
500 MHz, $CDCl_3$

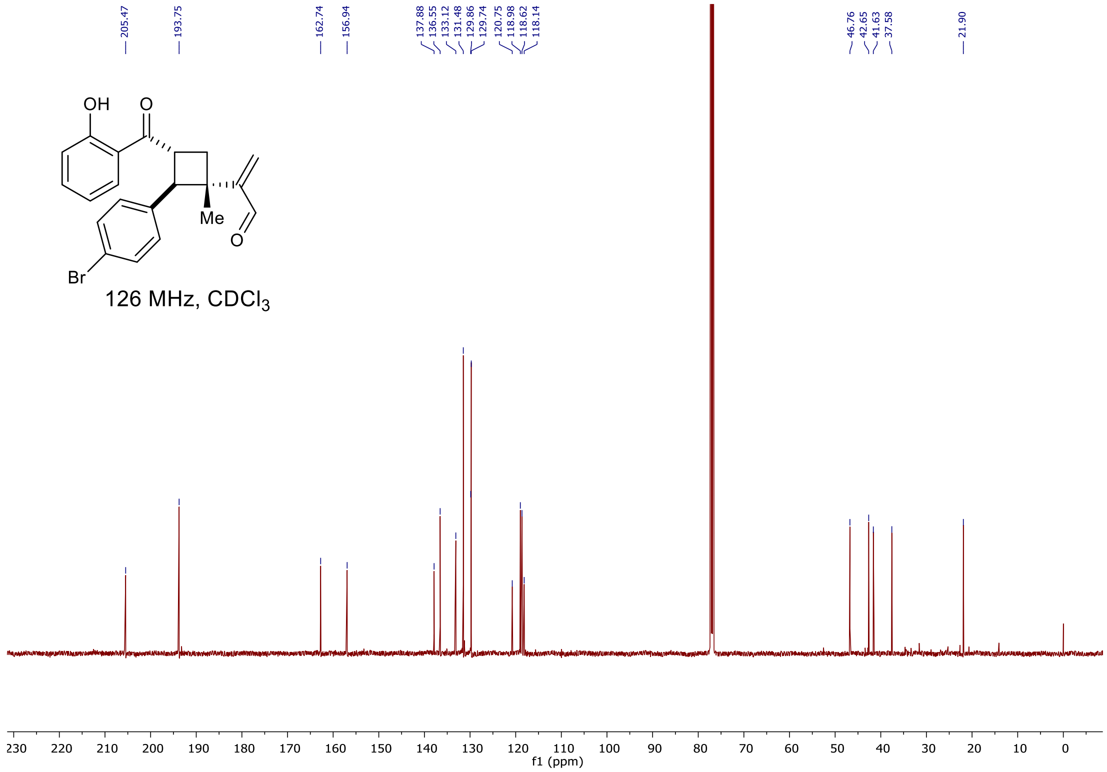
Figure 2, **19**



126 MHz, $CDCl_3$

Figure 2, **19**


12.20
9.53
7.66
7.66
7.64
7.64
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.26
7.11
7.11
7.10
7.09
6.99
6.99
6.98
6.97
6.89
6.89
6.88
6.88
6.87
6.86
6.86
6.48
6.08
4.28
4.26
4.25
4.25
2.60
2.59
2.58
2.58
2.57
2.56
2.45
2.45
2.44
2.44
2.43
2.41
1.26
OH
O
Me
O
Br
500 MHz, CDCl$_3$
0.95
0.96
1.02
0.92
2.42
2.02
1.03
1.02
1.01
1.01
1.12
0.92
1.02
1.02
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


205.47
193.75
162.74
156.94
137.88
136.55
133.12
131.48
129.86
129.74
120.75
118.98
118.62
118.14
46.76
42.65
41.63
37.58
21.90
OH
O
Me
O
Br
126 MHz, CDCl$_3$
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

M. References

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