Supporting Information

Trans-Diastereoselective Syntheses of γ-Lactones by Visible Light-Iodine Mediated Carboesterification of Alkenes

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Figure S1. General reaction set up

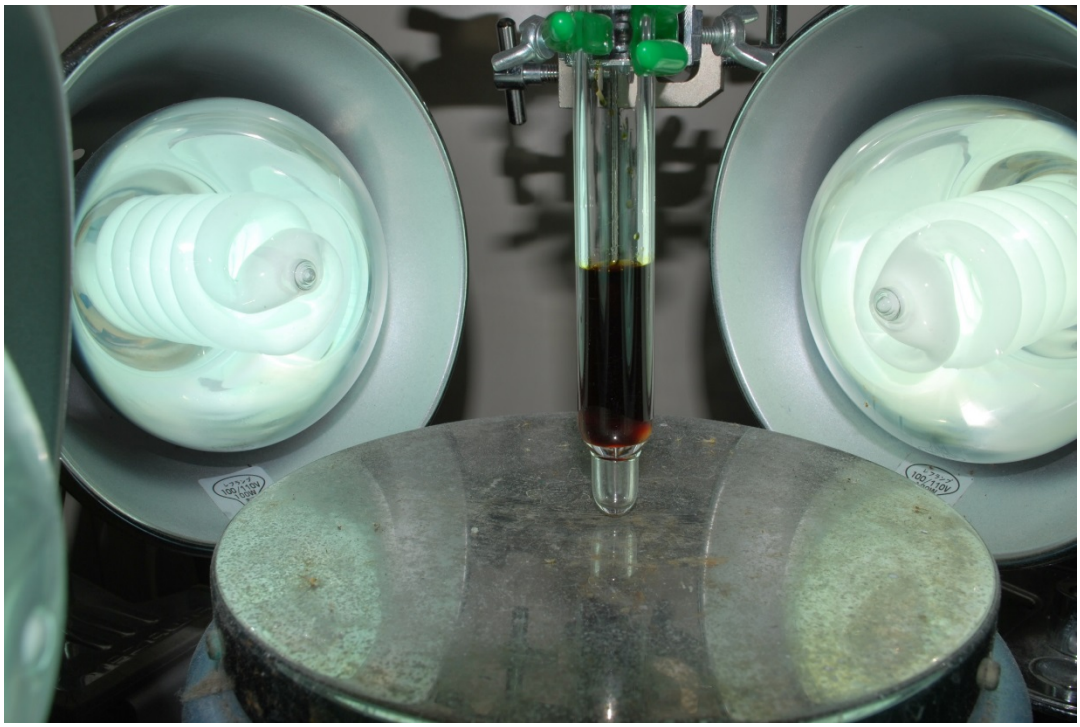


Figure S2. The wave length and spectral irradiance of fluorescent lamp (ERF25ED/22-SP-F)

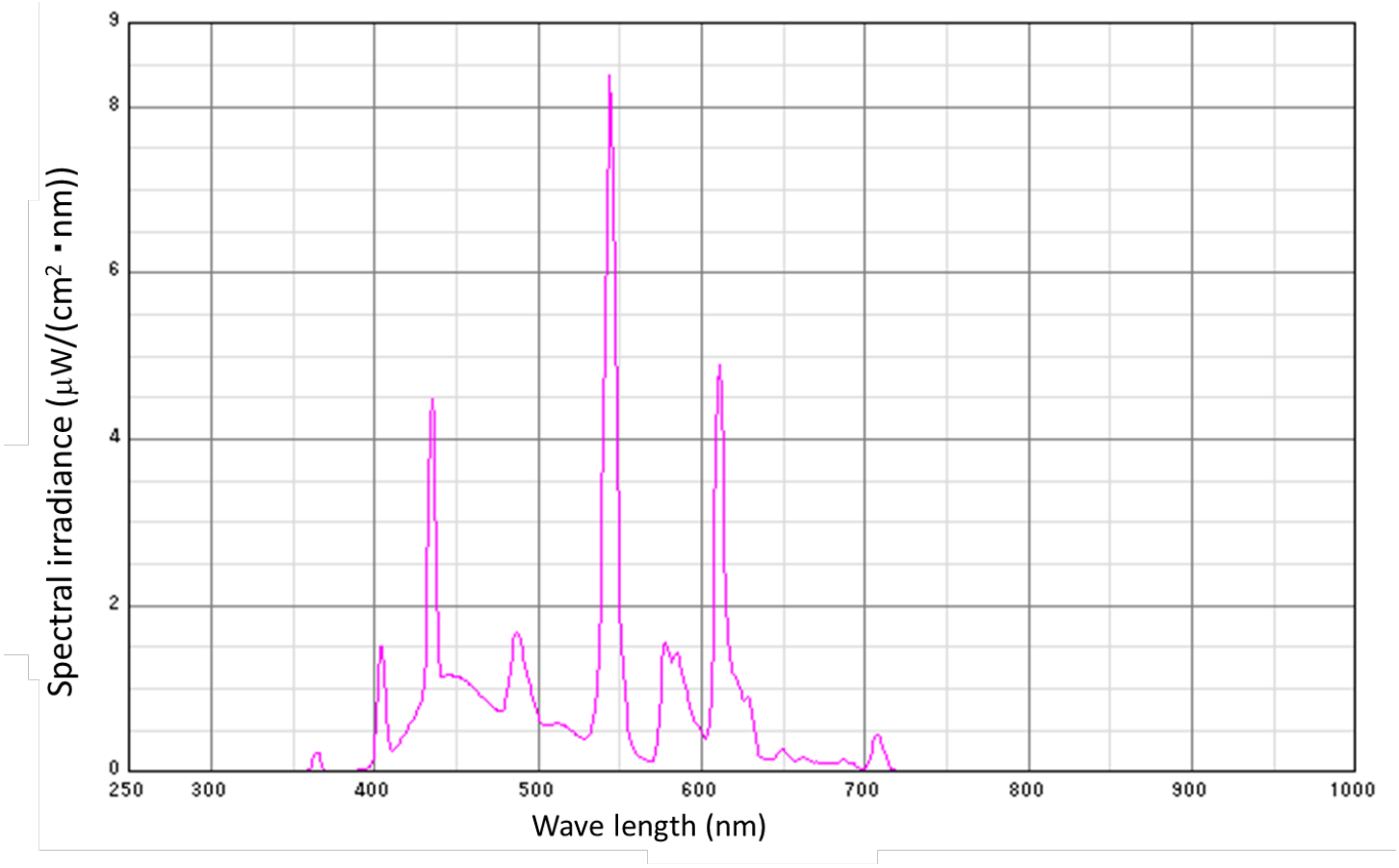
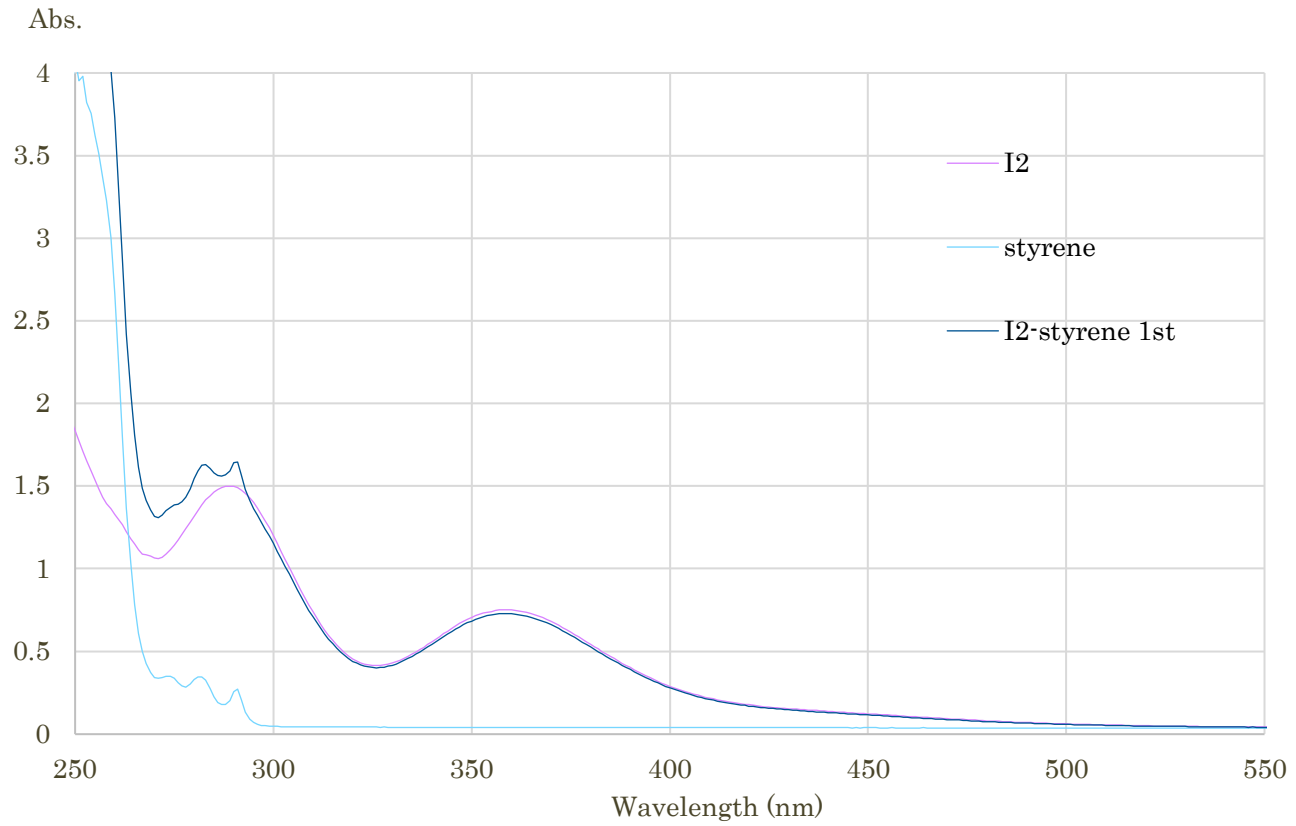


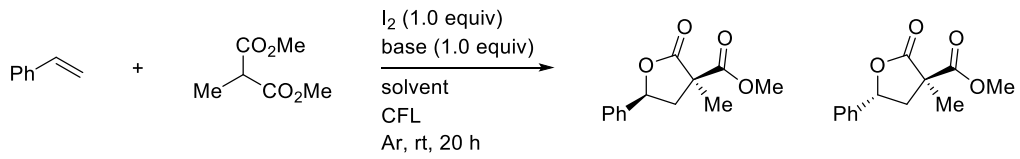
Figure S3. UV/Vis absorption spectra of the iodine and styrene



The *t*BuOH solution were prepared to 1.0×10^{-4} M, and the UV/Vis absorption spectra of I_2, styrene and I_2/styrene were measured.

	Wavelength (nm)	Abs.		Wavelength (nm)	Abs.		Wavelength (nm)	Abs.
I_2 (10^{-4} M)	359	0.75	Styrene (10^{-4} M)	291	0.26	I_2/Styrene (10^{-4} M)	359	0.727
	289	1.50		282	0.345		291	1.643

Table S1. Optimization of reaction conditions



1a **2a** **3aa-*cis*** **3aa-*trans***

entry	base	solvent	**3aa** yield (%)	*dr* (*cis* : *trans*)[a]
1	$Ca(OH)_2$	MeOH	17	33:67
2	$Ca(OH)_2$	EtOH	67[b]	48:52
3	$Ca(OH)_2$	IPA	85[b]	48:42
4	$Ca(OH)_2$	^{t}AmylOH	74	66:34
5	$Ca(OH)_2$	^{t}BuOH	83	79:21
6[c]	$Ca(OH)_2$	^{t}BuOH	23	70:30
7	$Mg(OH)_2$	^{t}BuOH	trace	-
8	$Ba(OH)_2$	^{t}BuOH	74	67:33
9	$Sr(OH)_2$	^{t}BuOH	33	50:50
10	$BaCO_3$	^{t}BuOH	trace	-
11	$SrCO_3$	^{t}BuOH	trace	-
12	$NaHCO_3$	^{t}BuOH	32	50:50
13	Na_2CO_3	^{t}BuOH	77	45:55
14	K_2CO_3	^{t}BuOH	53	40:60
15	Cs_2CO_3	^{t}BuOH	49	37:63
16	KOH	^{t}BuOH	36	33:67
17	K_3PO_4	^{t}BuOH	26	30:70
18	-	^{t}BuOH	no reaction	-
19[d]	$Ca(OH)_2$	^{t}BuOH	no reaction	-

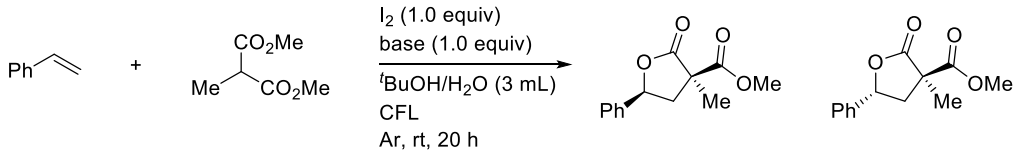
[a] Diasteremeric ratio were determined by ^{1}H NMR analysis of crude reaction mixture.

[b] Transesterification product was also included.

[c] 0.5 equiv of I_2 was used.

[d] Without iodine.

Table S2. Optimization of bases

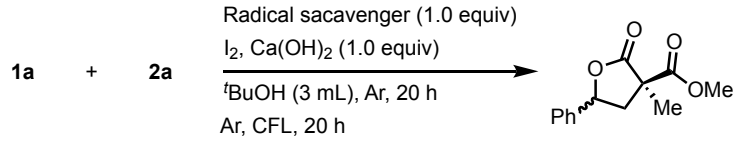


1a **2a** **3aa-*cis*** **3aa-*trans***

entry	base	**3aa** yield (%)	*dr* (*cis* : *trans*)[a]
1	$Mg(OH)_2$	65	34:66
2	$Ca(OH)_2$	61	40:60
3	$Sr(OH)_2$	29	42:58
4	$Ba(OH)_2$	7	29:71
5	$SrCO_3$	trace	-
6	$BaCO_3$	trace	-
7	NaOH	20	25:75
8	KOH	trace	-
9	$NaHCO_3$	20	25:75
10	Li_2CO_3	60	29:71
11	Na_2CO_3	69	25:75
12	K_2CO_3	60	26:74
13	Cs_2CO_3	56	28:72
14	K_3PO_4	41	27:73

[a] Diasteremeric ratio were determined by ^1H NMR analysis of crude reaction mixture.

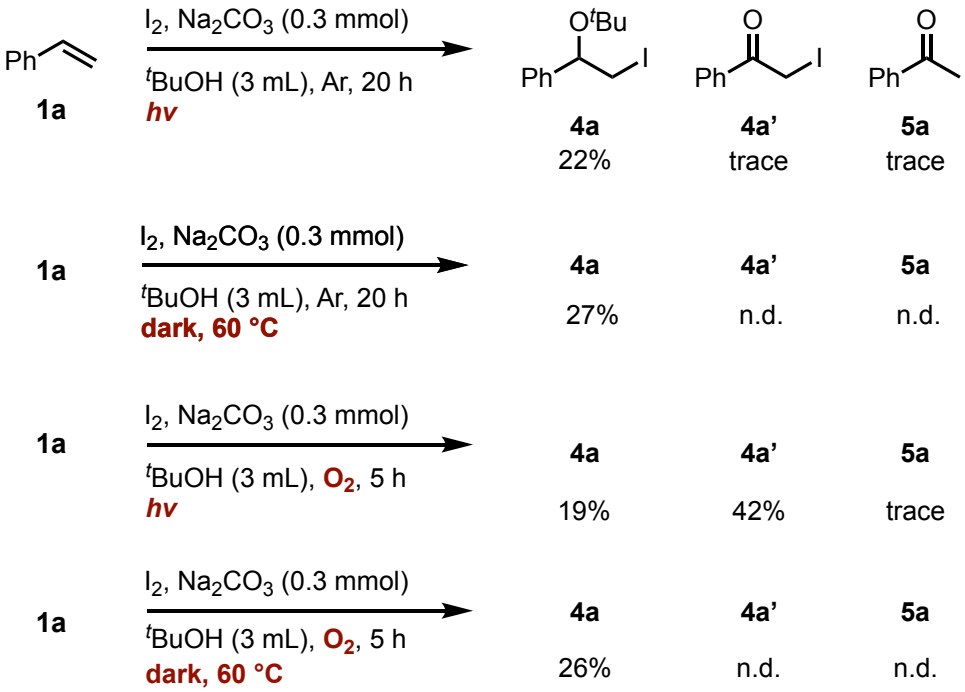
Scheme S1. Reaction with radical scavenger[S1]



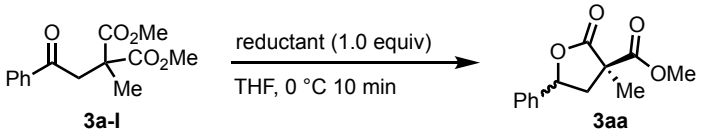
TEMPO	0% yield
Galvinoxyl	0% yield

A Pyrex® test tube (16.5 cm × 1.5 cm) containing a mixture of dimethyl 2-methylmalonate **2a** (44 mg, 0.30 mmol), I_2 (76 mg, 1.0 equiv., 0.30 mmol), calcium hydroxide (22 mg, 1.0 equiv., 0.30 mmol), styrene **1a** (63 mg, 2.0 equiv., 0.60 mmol) and radical scavenger (1.0 equiv., 0.30 mmol) in ^{t}Butylalcohol (3.0 mL) was degassed *via* FPT cycling for three times and backfilled with Ar. The resulting solution was stirred at ambient temperature for 20 h. The reaction was quenched with sat. $Na_2S_2O_3$ aq. and extracted with Et_2O (10 mL x 3). The combined organic layers were washed with brine, dried over Mg_2SO_4, filtered and concentrated *in vacuo*. The reaction was inhibited in both TEMPO and Galvinoxyl, and lactone **3aa** was not obtained.

Scheme S2. Reaction of styrene 1a with iodine



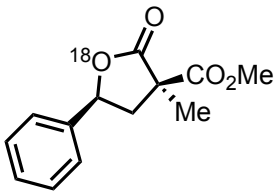
Scheme S3. Reduction of 3a-I



N-Selectride (1.0 equiv)	yield 64% *cis*:*trans*=37:63
K-Selectride (1.0 equiv)	yield 60% *cis*:*trans*=40:60

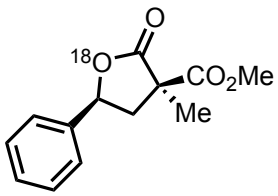
NMR spectra of lactones 3

3aa' cis 1H.esp



3aa'-*cis*

3aa' cis 13C-1.esp



3aa'-*cis*

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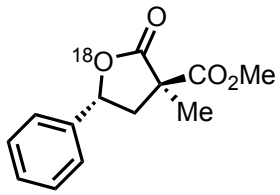
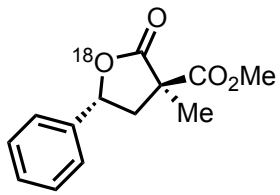


3aa'-*trans*

3aa' trans 13C-1.esp



3aa'-*trans*

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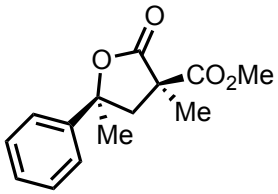

3oa-*cis*

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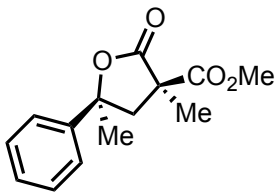
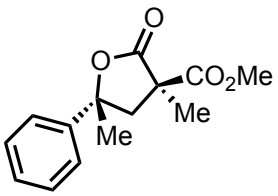


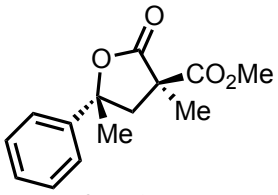
3oa-*cis*

a-methyl trans major 1H.esp



3oa-*trans*

a-methyl trans major 13C.esp



3oa-*trans*

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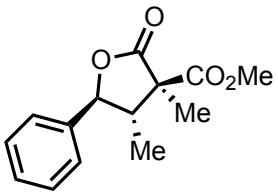

3pa-*cis*

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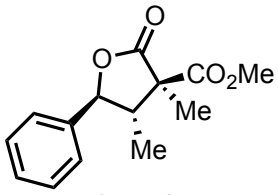

3pa-*cis*

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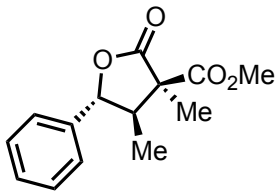
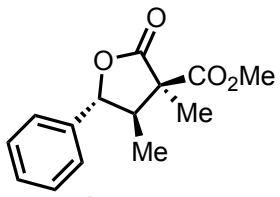


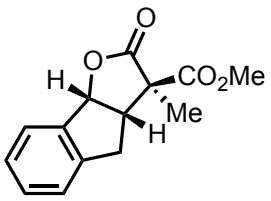
3pa-*trans*

b-methyl trans 13C.esp



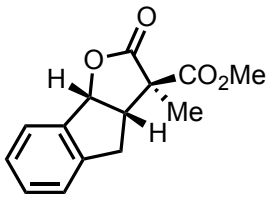
3pa-*trans*

Indene 1H.esp



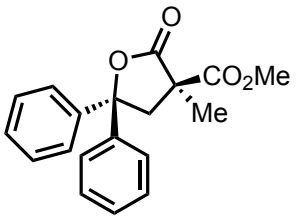
3qa-*cis*

Indene 13C.esp



3qa-*cis*

1,1-diphenylstyrene 1H.esp



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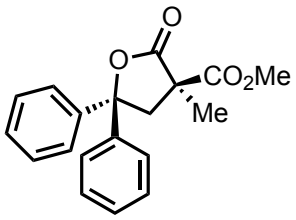

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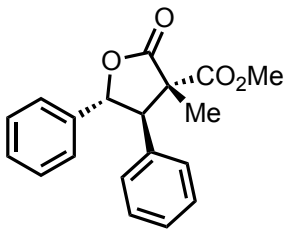

3-*A*

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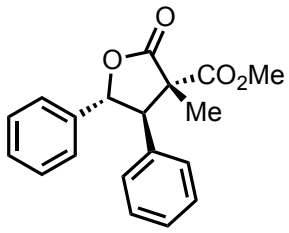

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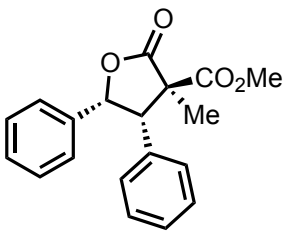

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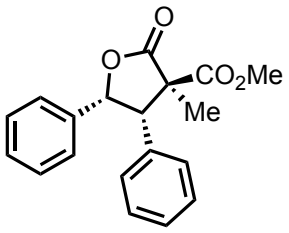

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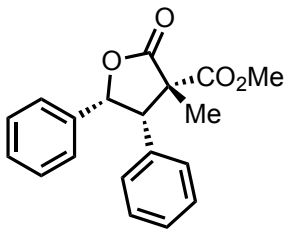

3-*C*

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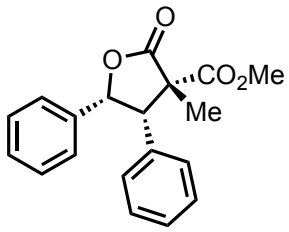

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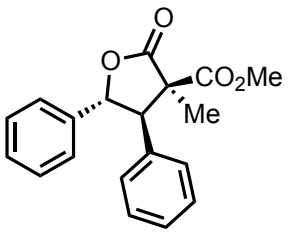

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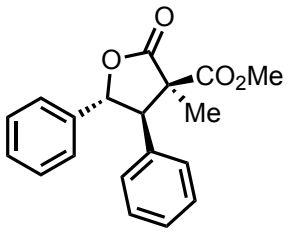


3-*D*

Figure S4. Key NOE of 3pa-cis

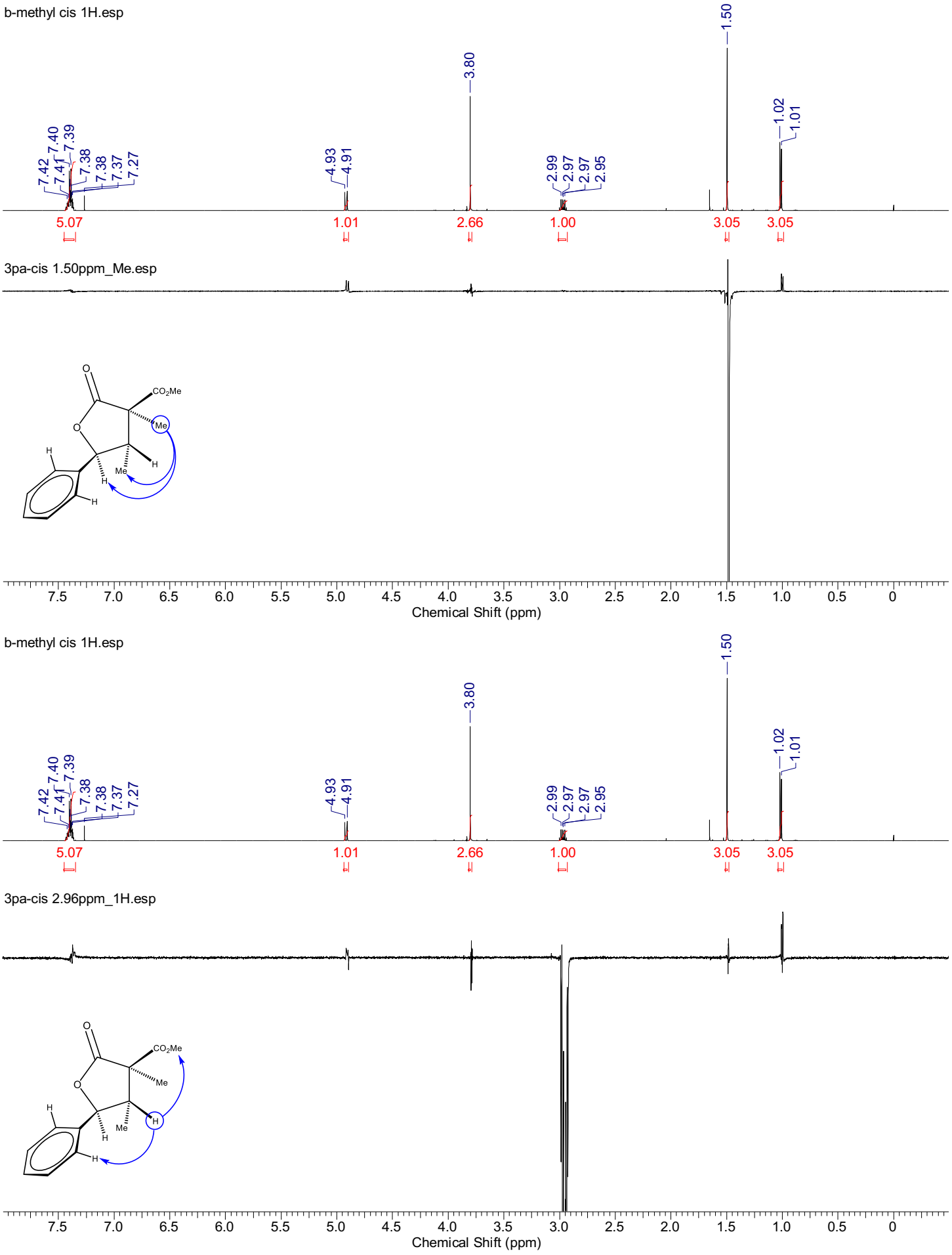
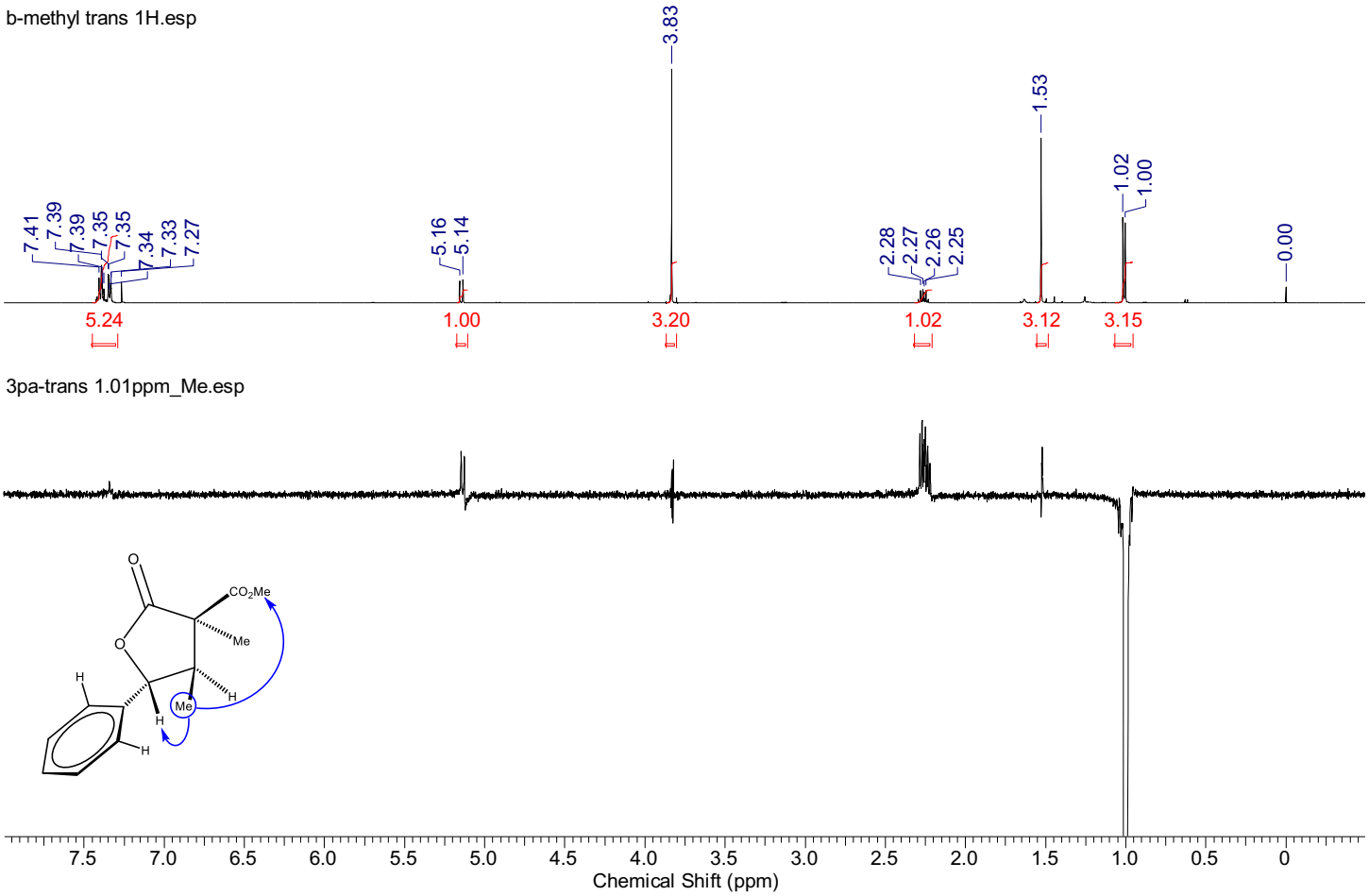
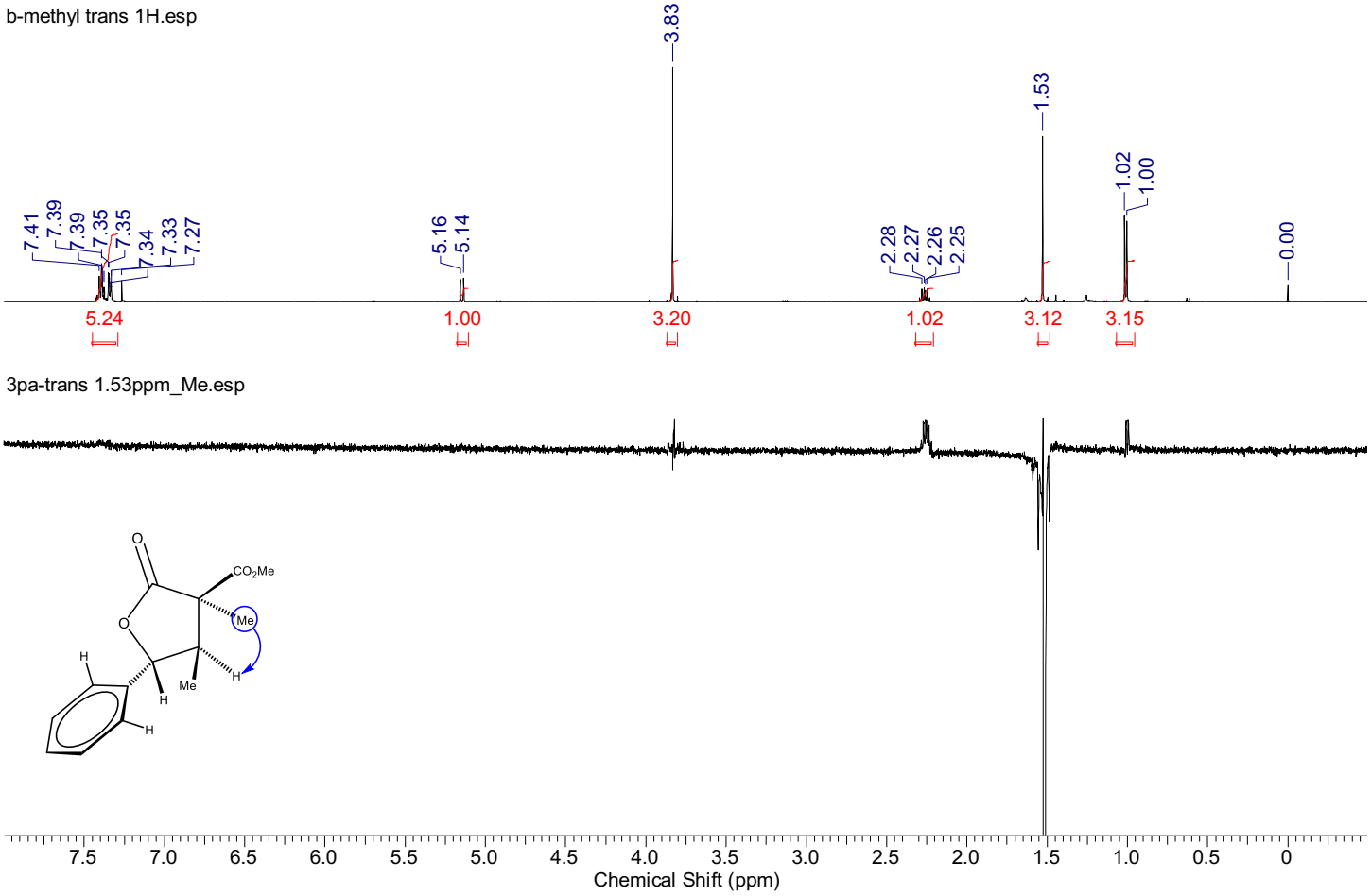
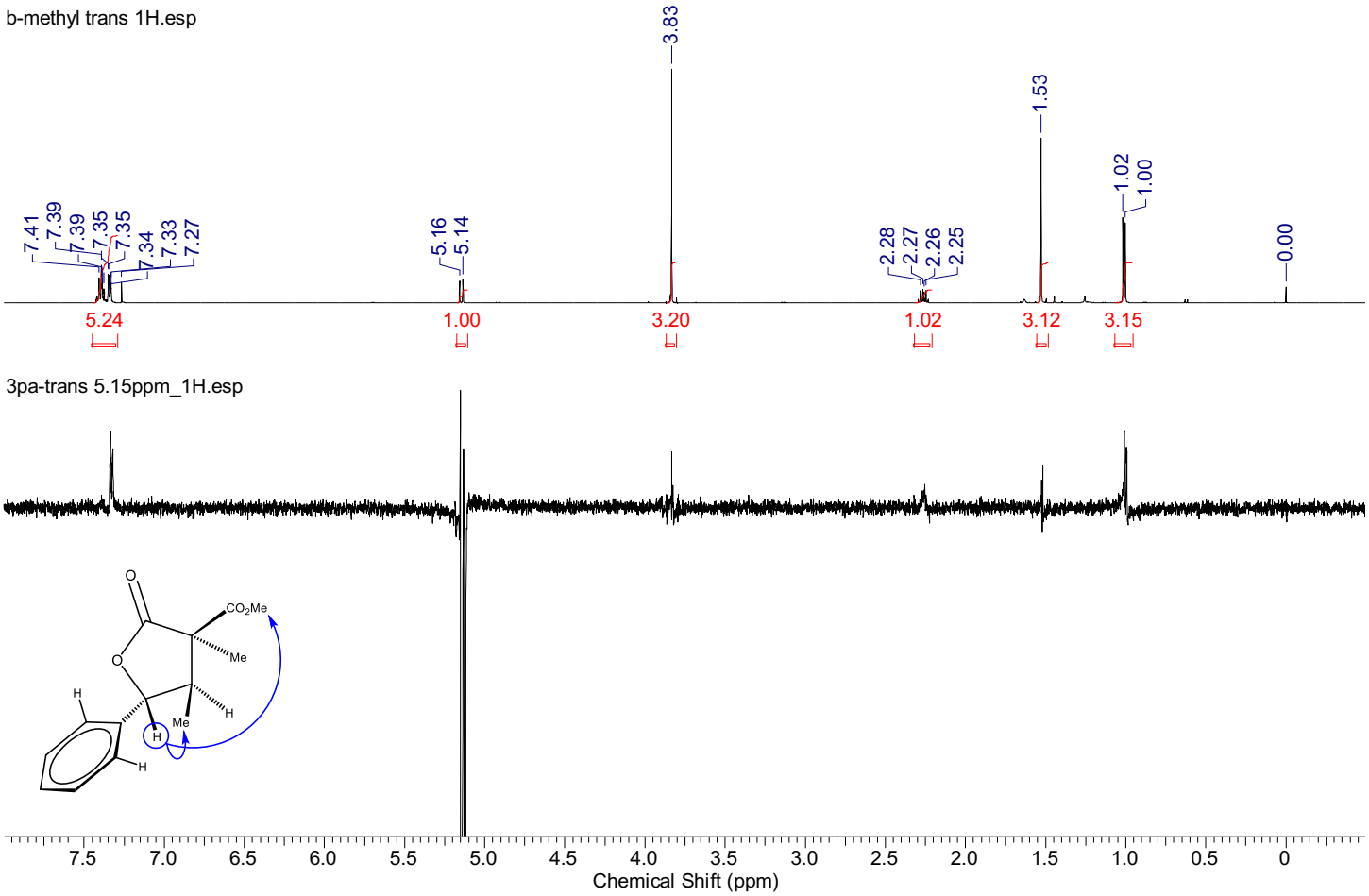


Figure S5. Key NOE of 3pa-trans



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5.14
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2.27
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3.20
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3.15
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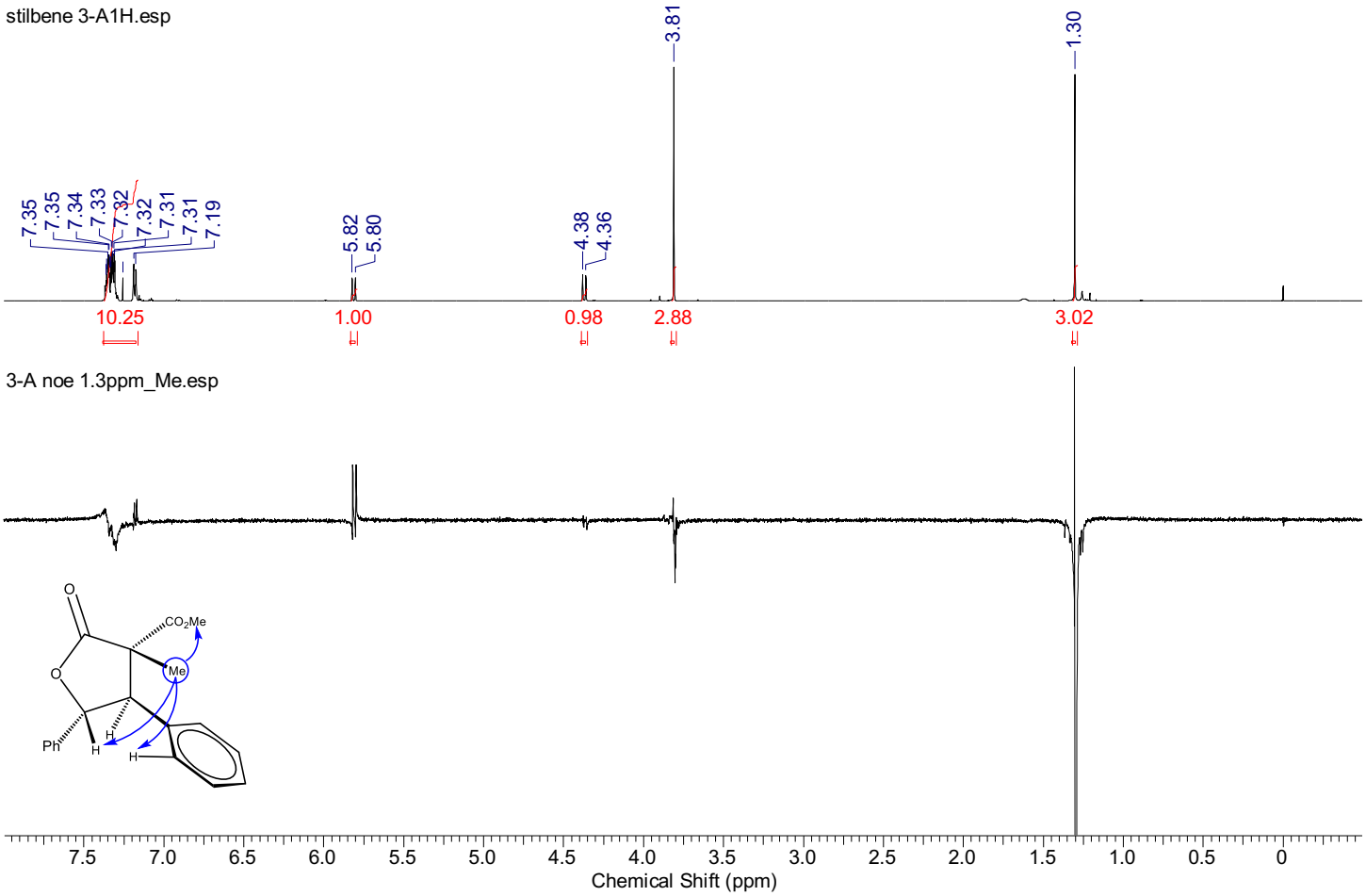
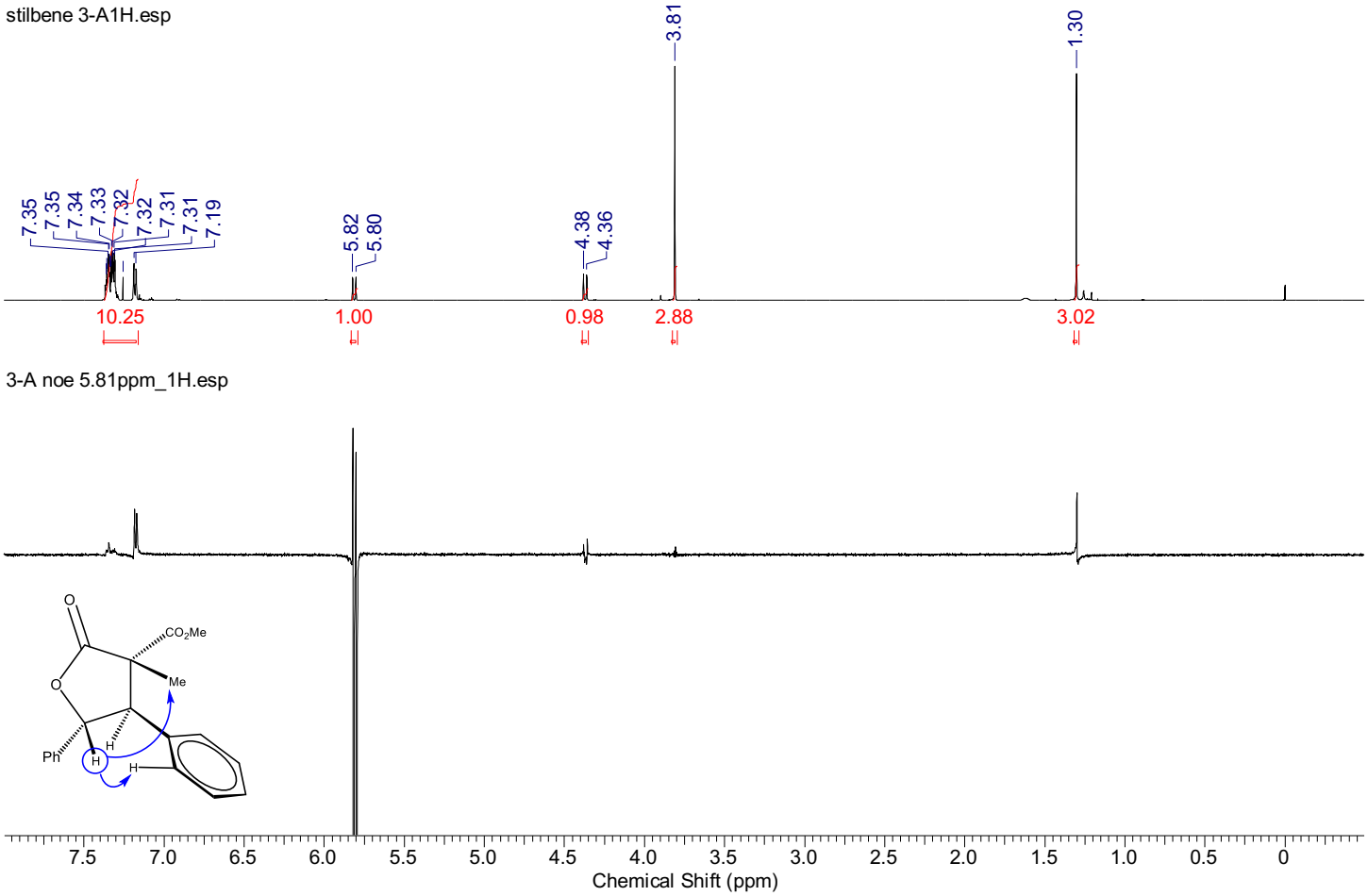
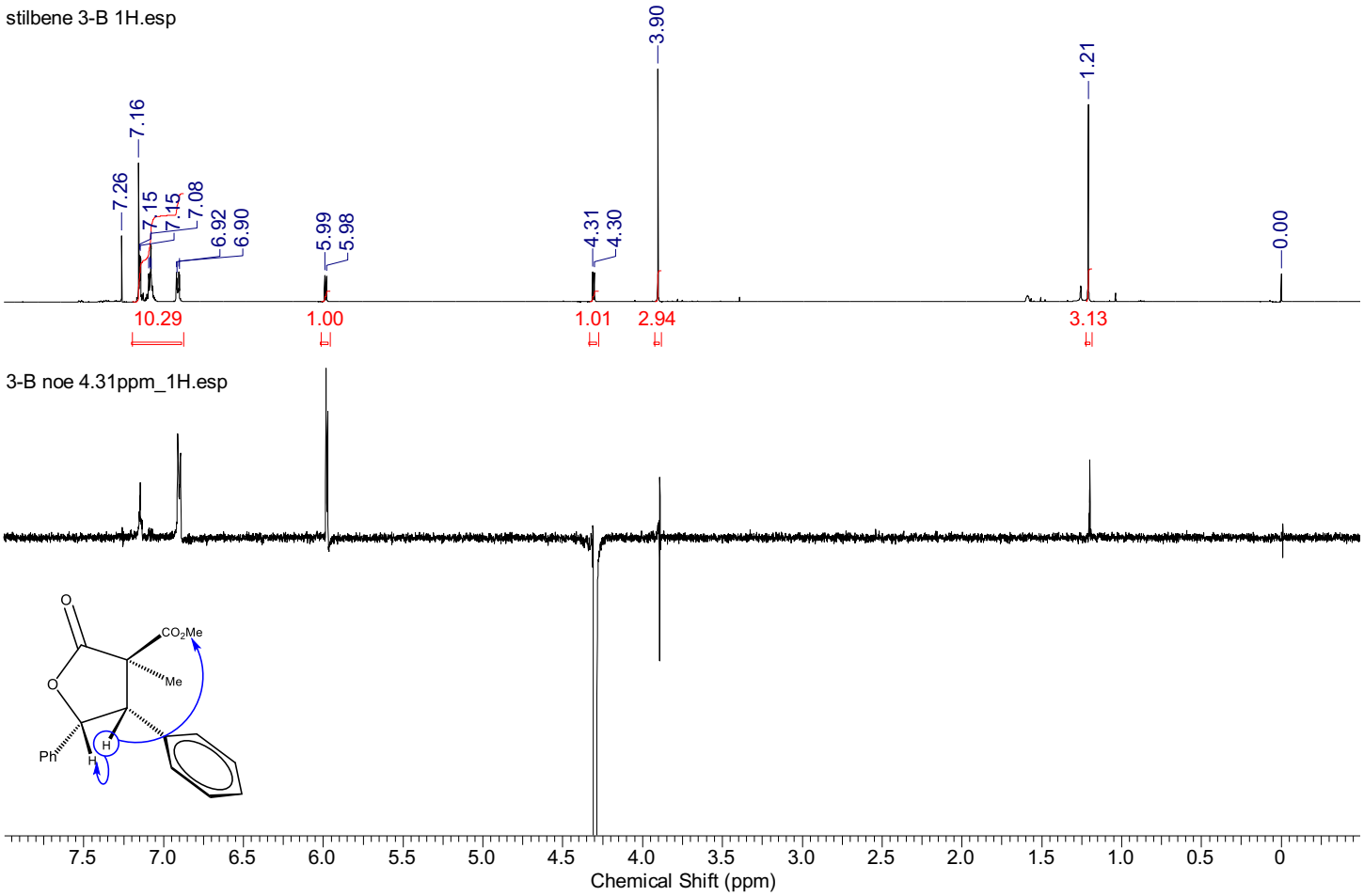
0
Chemical Shift (ppm)

Figure S6. Key NOE of Diastereomer 3






stilbene 3-B 1H.esp
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7.15
7.15
7.08
6.92
6.90
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5.98
4.31
4.30
3.90
1.21
0.00
10.29
1.00
1.01
2.94
3.13
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CO2Me
Me
O
O
Ph
H
H
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6.0
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1.5
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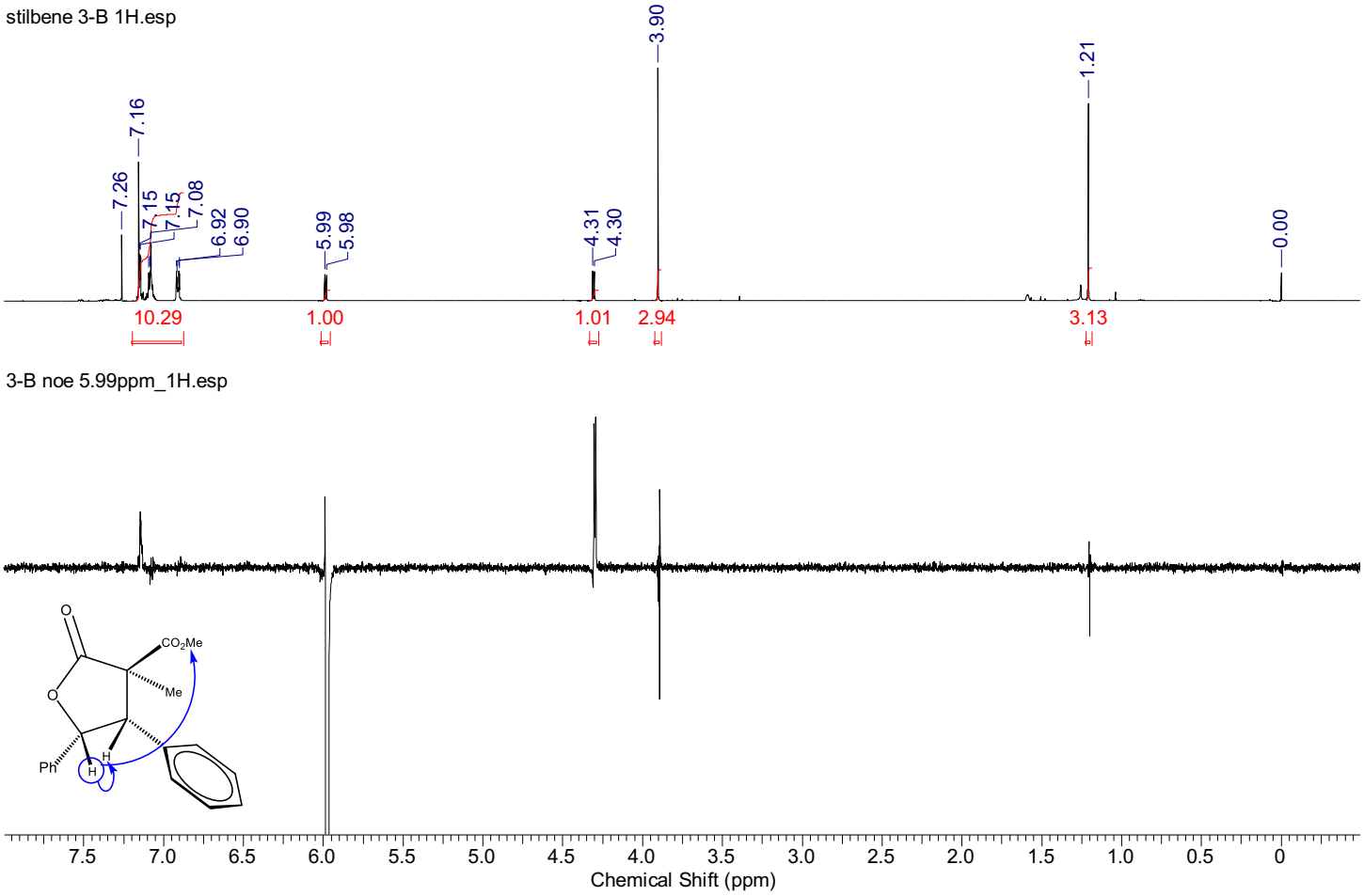
Chemical Shift (ppm)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6.5
6.0
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5.0
4.5
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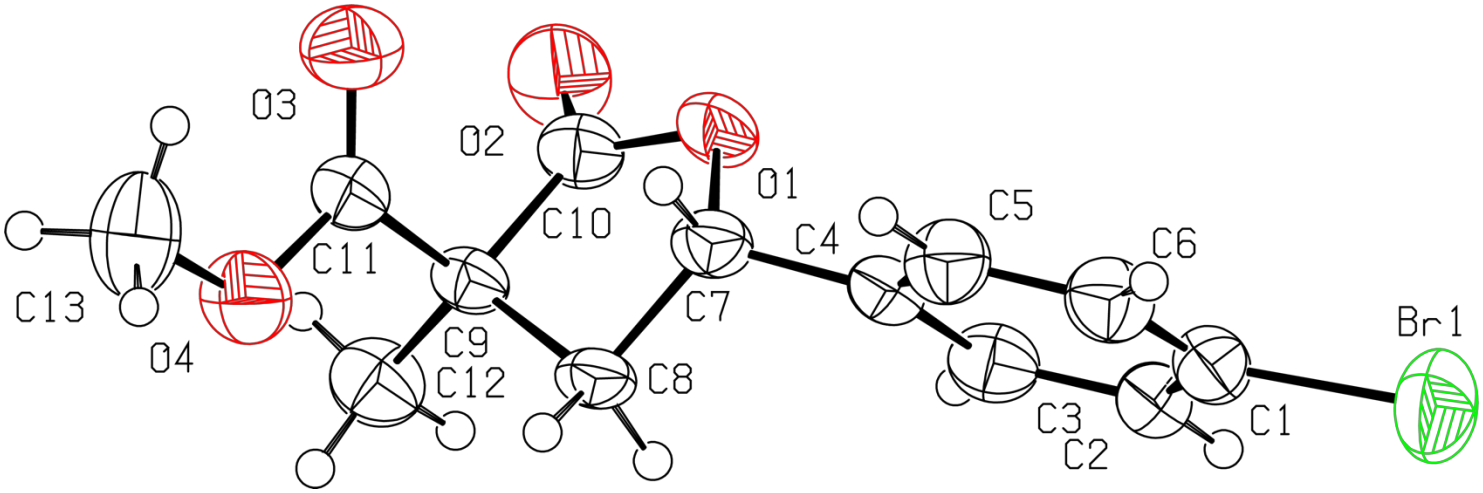
0
Chemical Shift (ppm)

Figure S7. Molecular structure of 3ha



Molecular structure of **3ha** (ORTEP drawing; thermal ellipsoids set to 50% probability).

Table S3. Experimental details

Crystal data	
Chemical formula	$C_{13}H_{13}BrO_4$
M_r	313.14
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
a, b, c (Å)	8.848 (4), 12.172 (6), 12.759 (6)
α, β, γ (°)	103.682 (7), 98.765 (5), 90.185 (7)
V (Å^3)	1318.4 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.12
Crystal size (mm)	0.29 × 0.29 × 0.03
Data collection	
Diffractometer	Mercury CCD (2x2 bin mode)
Absorption correction	Numerical
T_{min}, T_{max}	0.465, 0.766
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11070, 6015, 3110
R_{int}	0.044
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.069, 0.176, 1.06
No. of reflections	6015
No. of parameters	329
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.46, -0.52

Computer programs: *SHELXL2014*/7 (Sheldrick, 2014).

Table S4. Selected geometric parameters (Å, º)

Br1—C1	1.891 (5)	C4—C7	1.490 (7)
Br2—C14	1.893 (5)	C5—C6	1.383 (7)
O1—C10	1.356 (6)	C7—C8	1.507 (7)
O1—C7	1.480 (5)	C8—C9	1.537 (6)
O2—C10	1.193 (5)	C9—C11	1.504 (6)
O3—C11	1.197 (6)	C9—C10	1.512 (6)
O4—C11	1.325 (6)	C9—C12	1.533 (7)
O4—C13	1.447 (6)	C14—C19	1.364 (8)
O5—C23	1.344 (6)	C14—C15	1.376 (7)
O5—C20	1.474 (5)	C15—C16	1.388 (7)
O6—C23	1.200 (5)	C16—C17	1.388 (7)
O7—C24	1.191 (6)	C17—C18	1.386 (7)
O8—C24	1.320 (5)	C17—C20	1.495 (7)
O8—C26	1.444 (6)	C18—C19	1.384 (8)
C1—C6	1.365 (7)	C20—C21	1.523 (7)
C1—C2	1.367 (6)	C21—C22	1.534 (6)
C2—C3	1.368 (7)	C22—C24	1.524 (7)
C3—C4	1.399 (6)	C22—C25	1.524 (7)
C4—C5	1.395 (7)	C22—C23	1.527 (6)
C10—O1—C7	109.9 (4)	O3—C11—C9	124.9 (5)
C11—O4—C13	118.4 (4)	O4—C11—C9	111.9 (4)
C23—O5—C20	109.9 (3)	C19—C14—C15	121.4 (5)
C24—O8—C26	117.2 (4)	C19—C14—Br2	118.9 (4)
C6—C1—C2	121.0 (5)	C15—C14—Br2	119.7 (5)
C6—C1—Br1	119.0 (4)	C14—C15—C16	118.7 (5)
C2—C1—Br1	120.1 (4)	C15—C16—C17	121.3 (5)
C1—C2—C3	119.7 (4)	C18—C17—C16	118.1 (5)
C2—C3—C4	121.5 (5)	C18—C17—C20	119.4 (5)
C5—C4—C3	117.2 (5)	C16—C17—C20	122.4 (5)
C5—C4—C7	119.8 (4)	C19—C18—C17	121.0 (5)
C3—C4—C7	123.0 (4)	C14—C19—C18	119.5 (5)
C6—C5—C4	120.9 (4)	O5—C20—C17	108.5 (4)
C1—C6—C5	119.6 (5)	O5—C20—C21	103.2 (4)
O1—C7—C4	107.6 (4)	C17—C20—C21	117.6 (4)
O1—C7—C8	103.3 (3)	C20—C21—C22	102.2 (4)
C4—C7—C8	118.1 (4)	C24—C22—C25	111.1 (4)

C7—C8—C9	101.9 (4)	C24—C22—C23	106.3 (4)
C11—C9—C10	107.9 (4)	C25—C22—C23	112.3 (4)
C11—C9—C12	111.0 (4)	C24—C22—C21	109.9 (4)
C10—C9—C12	111.8 (4)	C25—C22—C21	116.0 (4)
C11—C9—C8	109.3 (3)	C23—C22—C21	100.4 (4)
C10—C9—C8	101.1 (4)	O6—C23—O5	121.9 (4)
C12—C9—C8	115.1 (4)	O6—C23—C22	127.7 (5)
O2—C10—O1	122.3 (5)	O5—C23—C22	110.4 (4)
O2—C10—C9	128.2 (5)	O7—C24—O8	124.0 (5)
O1—C10—C9	109.5 (4)	O7—C24—C22	125.2 (5)
O3—C11—O4	123.2 (5)	O8—C24—C22	110.7 (4)
C6—C1—C2—C3	3.0 (8)	C19—C14—C15—C16	1.5 (7)
Br1—C1—C2—C3	-176.9 (4)	Br2—C14—C15—C16	-178.4 (3)
C1—C2—C3—C4	-0.6 (8)	C14—C15—C16—C17	0.6 (7)
C2—C3—C4—C5	-1.7 (8)	C15—C16—C17—C18	-2.3 (7)
C2—C3—C4—C7	178.2 (5)	C15—C16—C17—C20	177.5 (4)
C3—C4—C5—C6	1.6 (8)	C16—C17—C18—C19	1.9 (7)
C7—C4—C5—C6	-178.3 (5)	C20—C17—C18—C19	-177.9 (4)
C2—C1—C6—C5	-3.0 (8)	C15—C14—C19—C18	-1.8 (7)
Br1—C1—C6—C5	176.9 (4)	Br2—C14—C19—C18	178.0 (4)
C4—C5—C6—C1	0.7 (8)	C17—C18—C19—C14	0.1 (7)
C10—O1—C7—C4	147.7 (4)	C23—O5—C20—C17	148.0 (4)
C10—O1—C7—C8	22.1 (5)	C23—O5—C20—C21	22.5 (5)
C5—C4—C7—O1	123.6 (5)	C18—C17—C20—O5	124.4 (4)
C3—C4—C7—O1	-56.3 (6)	C16—C17—C20—O5	-55.4 (6)
C5—C4—C7—C8	-120.2 (5)	C18—C17—C20—C21	-119.1 (5)
C3—C4—C7—C8	60.0 (6)	C16—C17—C20—C21	61.1 (6)
O1—C7—C8—C9	-35.5 (4)	O5—C20—C21—C22	-35.4 (5)
C4—C7—C8—C9	-154.0 (4)	C17—C20—C21—C22	-154.8 (4)
C7—C8—C9—C11	-78.0 (4)	C20—C21—C22—C24	-77.1 (5)
C7—C8—C9—C10	35.6 (4)	C20—C21—C22—C25	155.8 (4)
C7—C8—C9—C12	156.3 (4)	C20—C21—C22—C23	34.5 (5)
C7—O1—C10—O2	-177.8 (5)	C20—O5—C23—O6	-177.7 (5)
C7—O1—C10—C9	1.5 (5)	C20—O5—C23—C22	0.3 (6)
C11—C9—C10—O2	-89.8 (6)	C24—C22—C23—O6	-90.3 (6)
C12—C9—C10—O2	32.5 (7)	C25—C22—C23—O6	31.4 (8)
C8—C9—C10—O2	155.4 (5)	C21—C22—C23—O6	155.3 (6)
C11—C9—C10—O1	91.0 (5)	C24—C22—C23—O5	91.8 (5)

C12—C9—C10—O1	-146.7 (4)	C25—C22—C23—O5	-146.5 (5)
C8—C9—C10—O1	-23.7 (5)	C21—C22—C23—O5	-22.6 (5)
C13—O4—C11—O3	-4.8 (8)	C26—O8—C24—O7	-1.9 (8)
C13—O4—C11—C9	173.0 (4)	C26—O8—C24—C22	175.7 (4)
C10—C9—C11—O3	-3.7 (7)	C25—C22—C24—O7	-123.5 (6)
C12—C9—C11—O3	-126.6 (6)	C23—C22—C24—O7	-1.1 (7)
C8—C9—C11—O3	105.4 (6)	C21—C22—C24—O7	106.8 (6)
C10—C9—C11—O4	178.5 (4)	C25—C22—C24—O8	59.0 (5)
C12—C9—C11—O4	55.6 (5)	C23—C22—C24—O8	-178.6 (4)
C8—C9—C11—O4	-72.4 (5)	C21—C22—C24—O8	-70.8 (5)

Reference

S1 S. Maejima, E. Yamaguchi, A. Itoh, *Adv. Synth. Catal*. **2017**, *359*, 3883-3887.