Electronic Supplementary Information

Unveiling Abnormal Effect of Temperature on Enantioselectivity in Palladium-mediated Decabonylative Alkylation of MBH Acatate

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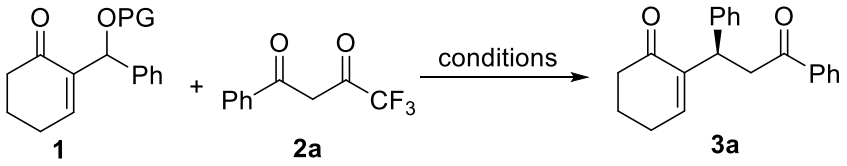
1. General Information

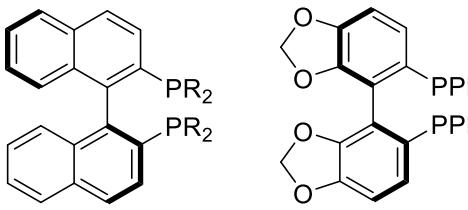
Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in *ppm* relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. Chemical shifts were reported in *ppm* from the tetramethylsilane with the solvent resonance as internal standard. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS mass spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200-300 mesh). All solvents and commercially available reagents were either purified via literature procedures or used without further purification. 4,4,4-Trifluoro-1-phenyl-1,3-butanedione[1] and *β-oxo*-benzenepropanoic acid[2] were synthesized according to the references.

2. Screening of the reaction conditions

Table S1. Optimization of Reaction Conditions.[a]

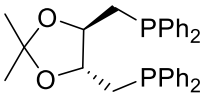


1 **2a** **3a**

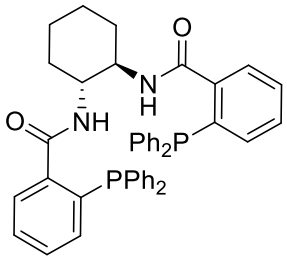


R = Ph, (*S*)-BINAP
R = Tol, (*S*)-*tol*-BINAP
R = 2,6-Dimethylphenyl, (*R*)-DM-BINAP

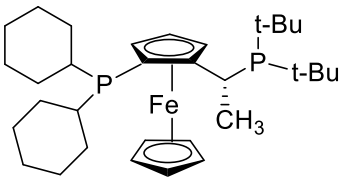
(*S*)-SegPhos



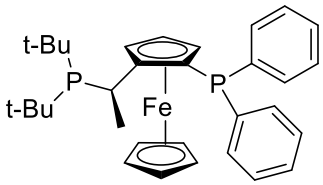
DIOP



Trost's Ligand



C1

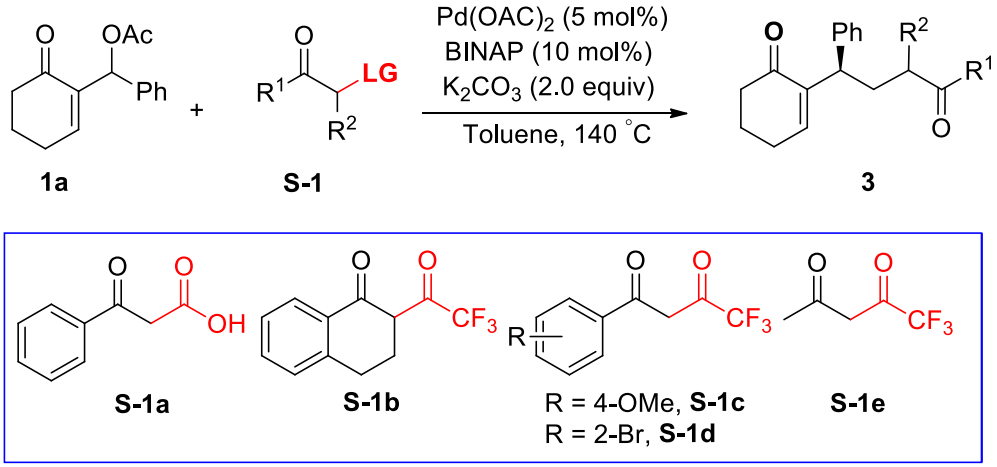


C2

Entry	**1a**:**2a**	Pd source (5 mol%)	ligand (10 mol%)	base (2.0 equiv)	yield (%)	*er*
1	1.2:1	$Pd(OAc)_2$	(*S*)-BINAP	K_2CO_3	47	82.5:17.5
2	1.5:1	$Pd(OAc)_2$	(*S*)-BINAP	K_2CO_3	62	82.5:17.5
3	2:1	$Pd(OAc)_2$	(*S*)-BINAP	K_2CO_3	64	87:13
4	1:1.5	$Pd(OAc)_2$	(*S*)-BINAP	K_2CO_3	47	80:20
5	1:2	$Pd(OAc)_2$	(*S*)-BINAP	K_2CO_3	48	81.5:18.5
6	2:1	$Pd(OAc)_2$	(*S*)-BINAP	Et_3N	decomposed	-
7	2:1	$Pd(OAc)_2$	(*S*)-BINAP	DIPEA	decomposed	-
8	2:1	$Pd(OAc)_2$	(*S*)-BINAP	$CsCO_3$	54	85.5:14.5
9	2:1	$Pd(OAc)_2$	(*S*)-BINAP	KOH	51	81.5:18.5
10	**2:1**	**$Pd(OAc)_2$**	**(*S*)-BINAP**	**K_3PO_4**	**65**	**88.5:11.5**
11	2:1	$Pd(OAc)_2$	(*S*)-BINAP	K_2HPO_4	54	84:16
12	2:1	$Pd_2(dba)_3$	(*S*)-BINAP	K_3PO_4	67	78:22
13	2:1	$PdCl_2$	(*S*)-BINAP	K_3PO_4	52	77:23
14	2:1	$PdCl_2(PPh_3)_2$	(*S*)-BINAP	K_3PO_4	41	80:20
15	2:1	$Pd(OAc)_2$	(*S*)-Tol-BINAP	K_3PO_4	59	87:13
16	2:1	$Pd(OAc)_2$	(*R*)-DM-BINAP	K_3PO_4	44	12.5:87.5
17	2:1	$Pd(OAc)_2$	(*S*)-SegPhos	K_3PO_4	36	84:16
18	2:1	$Pd(OAc)_2$	DIOP	K_3PO_4	62	50:50
19	2:1	$Pd(OAc)_2$	Trost's ligand	K_3PO_4	nr	-
20	2:1	$Pd(OAc)_2$	**C1**	K_3PO_4	13	47:53
21	2:1	$Pd(OAc)_2$	**C2**	K_3PO_4	20	18.5:81.5
22[b]	2:1	$Pd(OAc)_2$	(*S*)-BINAP	K_3PO_4	49	68.5:31.5
23[c]	2:1	$Pd(OAc)_2$	(*S*)-BINAP	K_3PO_4	61	83:17
24[d]	2:1	$Pd(OAc)_2$	(*S*)-BINAP	K_3PO_4	9	82:18
25[e]	2:1	$Pd(OAc)_2$	(*S*)-BINAP	K_3PO_4	trace	-

[a] Unless otherwise noted, the reaction was performed on 0.2 mmol scale with 0.4 mmol of MBH ester **1a** and 0.2 mmol of 1,3-diketones **2a** in toluene (2.0 mL) at 140 ℃ for three minutes under the given conditions, PG = Ac. [b]PG = CO_2Et. [c]PG = Boc. [d] Slow addition of MBH acetate **1a** within three minutes. [e] Slow addition of 1,3-diketones **2a** within three minutes.

Table S2. Screening of Reaction Partners.

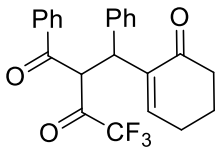


Entry	***S*-1**	**LG**	T (℃)	time	yield (%)	*er*
1	***S*-1a**	COOH	60	24 h	8	72:28
2	***S*-1a**	COOH	90	6 h	14	75.5:24.5
3	***S*-1a**	COOH	140	5 min	31	72.5:27.5
4	***S*-1b**	CF_3	140	10 min	NR	-
6	***S*-1c**	CF_3	140	30 min	NR	-
7	***S*-1d**	CF_3	140	30 min	NR	-
5	***S*-1e**	CF_3	140	5 min	complex	-

[a] Unless otherwise noted, the reaction was performed on 0.2 mmol of MBH ester **1a** and 0.2 mmol of *β*-oxo-benzenepropanoic acid (***S*-1a**) or 1,3-diones (***S*-1b-1e**) in presence of 5 mol% of Pd(OAc), 10 mol% of *S*-BINAP and 2.0 equiv of K_2CO_3 in toluene (2 mL) at 140 ℃.

In order to identify the activator in the reactant, *β-oxo*-benzenepropanoic acid[3] was evaluated in the reaction. Compared with the reaction using 1-phenyl-4,4,4-trifluoro-1,3-butanedione, the corresponding product **3** was obtained with relatively lower yield and *e*r (entry 1-3). Furthermore, 3,4-dihydro-2-(2,2,2-trifluoroacetyl)-1(2*H*)-naphthalenone,[4] 4,4,4-trifluoro-1-(4-methoxyphenyl)-1,3-butanedione[5] and 1-(2-bromophenyl)-4,4,4-trifluoro-1,3-butanedione[6] were inactive in the reaction. The employment of 1,1,1-trifluoro-2,4-pentanedione[7] gave a complicated reaction, which was extremely difficult to isolate the corresponding product.

3. Mechanistic studies on the reaction



IV

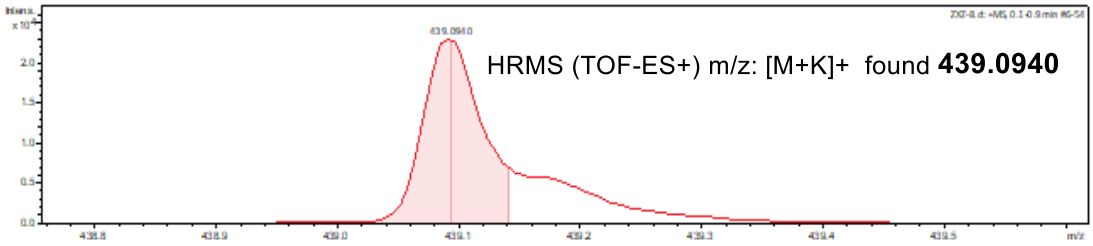


Figure S1 Experimental support of key intermediate from HRMS analysis

The allylic alkylation adduct **IV** was found by HRMS analysis HRMS (TOF-ES$^+$) m/z: [M+K]$^+$ calcd for $C_{23}H_{17}O_3K$ 439.0918, found 439.0940.

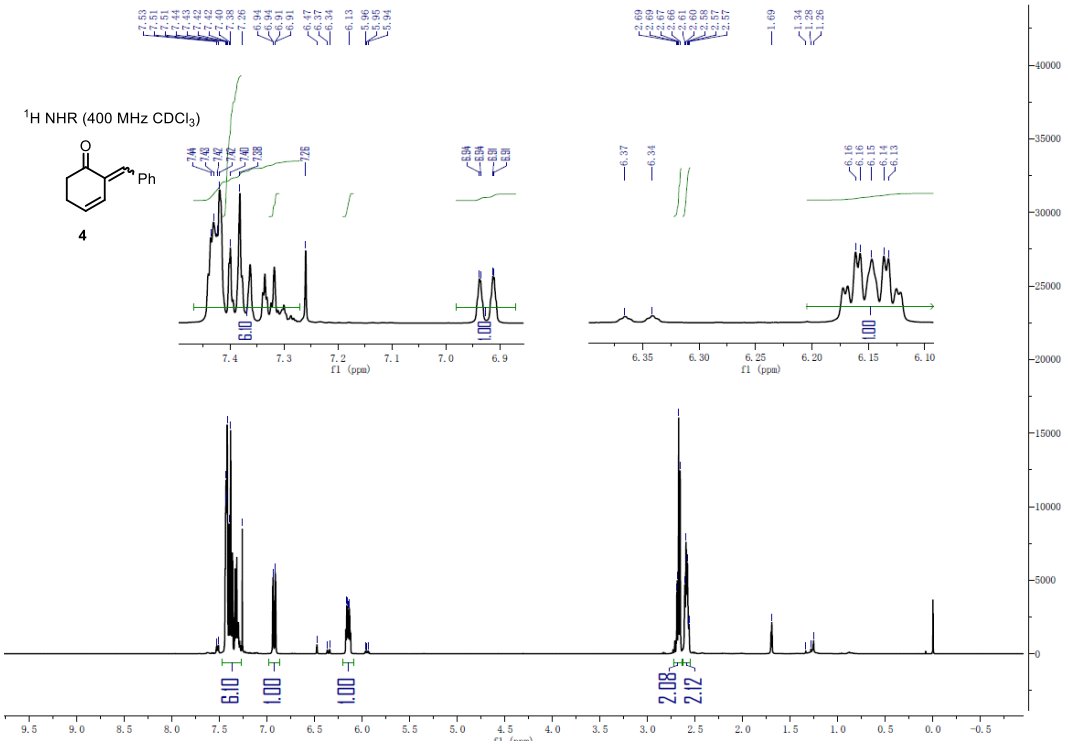


Figure S2. Evidence of the side product from ^{1}H NMR analysis

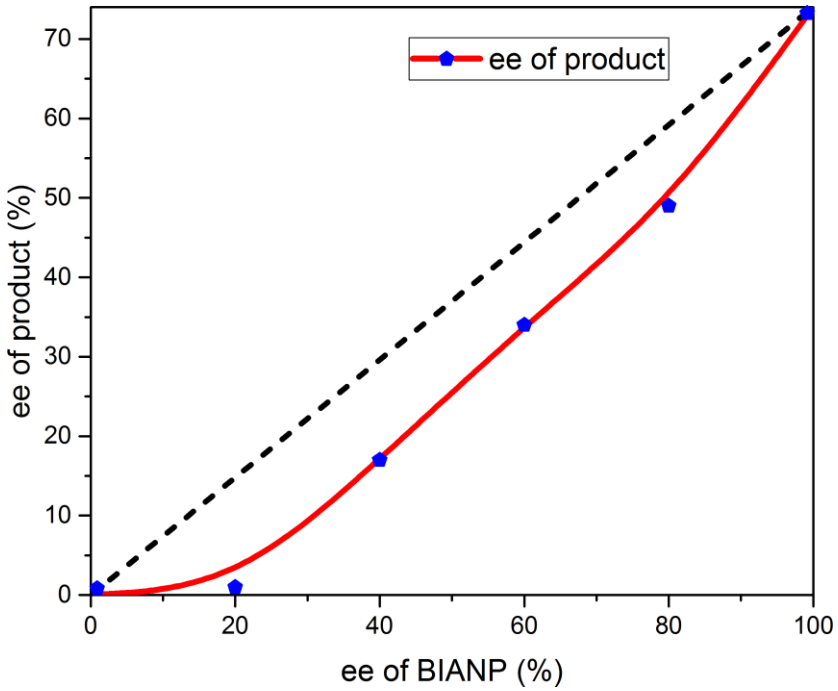
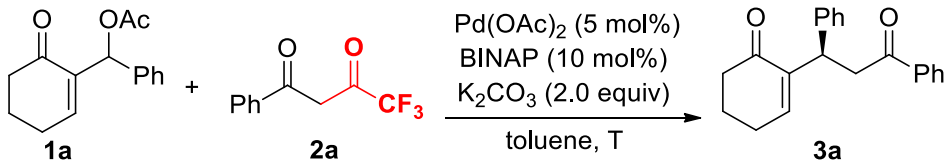


Figure S3. Nonlinear relationship of *S*-BINAP and product.

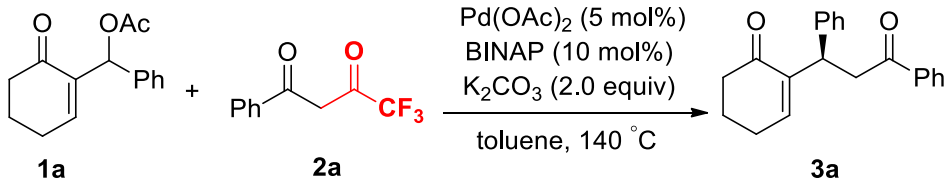
Table S3. Relationship of Enantioselectivity and Reaction Temperature.[a]



Entry	T (℃)	time	yield (%)	er
1	rt	120 h	-	-
2	40	72 h	21	57.5:42.5
3	60	12 h	25	62:38
4	70	9 h	28	64.5:35.5
5	80	6 h	31	73:27
6	90	3 h	34	77:23
7	100	1 h	44	78.5:21.5
8	110	30 min	43	80:20
9	120	20 min	44	83:17
10	130	10 min	35	84:16
11	140	5 min	37	86:14
12	150	3 min	23	85.5:14.5[b]
13	160	2 min	24	84.5:15.5[b]

[a] Unless otherwise noted, the reaction was performed on 0.2 mmol scale with 0.2 mmol of MBH ester **1a** and 0.2 mmol of 1,3-diketones **2a** in toluene (2.0mL) under given conditions. [b] The reaction was performed in mesitylene.

Table S4. Relationship of Enantioselectivity and *ee* of *S*-BINAP.[a]

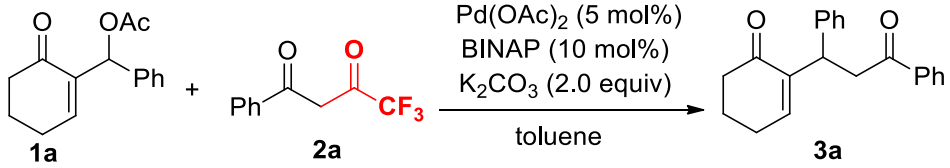


1a 2a 3a

Entry	*ee* of *S*-BINAP (%)	er	yield (%)
1	100	87:13	62
2	80	74.5:25.5	48
3	60	67:33	42
4	40	58.5:41.5	47
5	20	50.5:49.5	43
6	0	50:50	53

[a] Unless otherwise noted, the reaction was performed on 0.2 mmol of MBH ester **1a** and 0.2 mmol of 1,3-diketone **2a** in presence of 5 mol% of $Pd(OAc)_2$, 10 mol% of *S*-BINAP and 2.0 equiv of K_2CO_3 in toluene (2 mL) at 140 ℃.

Table S5. Monitoring the Progress of Reaction.



1a 2a 3a

Entry	Time (min)	er
1	60	84.5:15.5
2	120	78.5:11.5
3	180	63:37
4	240	65:35
5	300	65:35
6	360	63.5:36.5
7	420	65:35

The reaction was performed on 0.2 mmol scale with 0.2 mmol of MBH ester **1a** and 0.2 mmol of 1,3-diketones **2a** in toluene (2.0 mL) at **70 ℃.**

Entry	Time (min)	er
1	40	86:14
2	70	81.5:18.5
3	90	79:21
4	110	77.5:22.5
5	140	77:23
6	180	77:23
7	240	77:23

The reaction was performed on 0.2 mmolscale with 0.2 mmol of MBH ester **1a** and 0.2 mmol of 1,3-diketones **2a** in toluene (2.0 mL) at **90 ℃.**

Entry	Time (min)	er
1	6	84:16
2	10	82:18
3	15	78.5:21.5
4	20	78.5:21.5
5	25	78.5:21.5
6	30	78.5:21.5

The reaction was performed on 0.2 mmolscale with 0.2 mmol of MBH ester **1a** and 0.2 mmol of 1,3-diketones **2a** in toluene (2.0 mL) at **110 ℃**.

Entry	Time (min)	er
1	0.5	85.5:14.5
2	1	86:14
3	1.5	86:14
4	2	86:14
5	2.5	85.5:14.5
6	3	86:14

The reaction was performed on 0.2 mmol scale with 0.2 mmol of MBH ester **1a** and 0.2 mmol of 1,3-diketones **2a** in toluene (2.0 mL) at **140 ℃.**

Studies on the effects of addition mode.

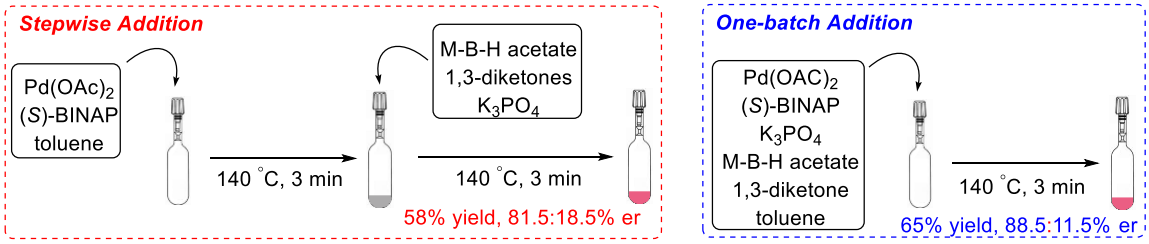


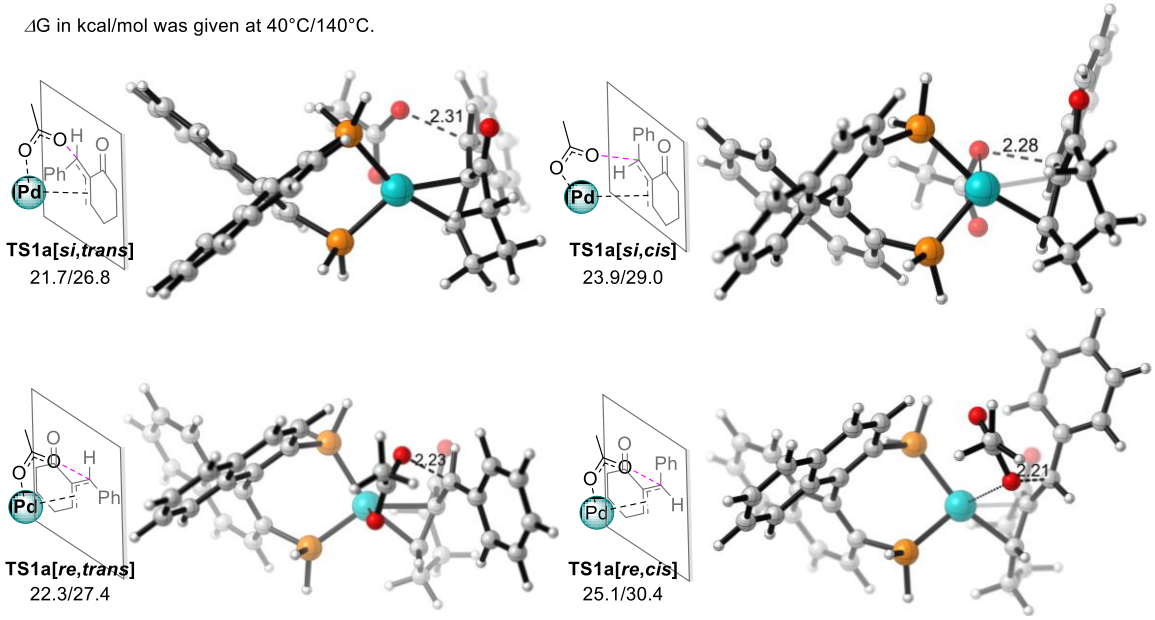
Figure S4. Different Modes for Addition of Reagents

The addition modes of reaction reagents were investigated.[8] **Stepwise mode**: $Pd(OAc)_2$ and (*S*)-BINAP and toluene were added to the seal tube firstly. And MBH acetate, 1,3-diketones and K_3PO_4 were then added to the reaction system. **One-batch Addition**: $Pd(OAc)_2$, (*S*)-BINAP, MBH acetate, 1,3-diketones, K_3PO_4 and toluene were added to the seal tube sequentially.The resulting mixture was then stirred at the given temperature.

4. Computational details

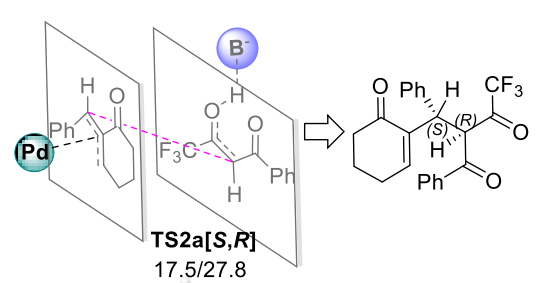
DFT calculations were performed with Gaussian 16 program.[9] The hybrid B3LYP functional[10,11] in conjunction with the def2-SVP basis set[12,13] was applied for the optimization of all stationary points. Empirical dispersion was included using the D3 version of Grimme's dispersion with Becke-Johnson damping.[14] Frequency calculations were performed at the same level to confirm whether each stationary point was either a minimum or a transition structure. Single point energy calculations were carried out with Truhlar's M06 functional[15] with def2-TZVPP basis set.[12, 13] Solvent effect of toluene was considered with SMD solvent model for all calculations with solvent accessible surface (SAS) for optimizations and solvent excluding surface (SES) for single point energy calculations.[16] For each stationary point, the free energy corrections were calculated using Grimme's quasiharmonic approximation[17] with GoodVibes.[18] Computed structures were illustrated using CYLView.[19]

4.1 Transition state structures of the acetate dissociation steps.

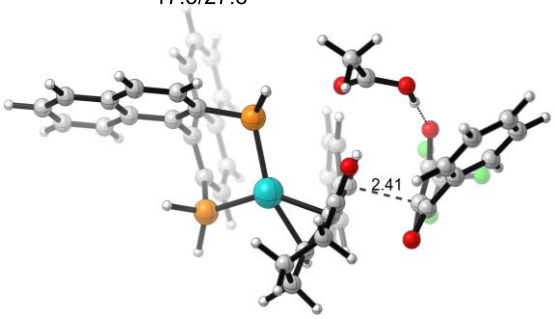


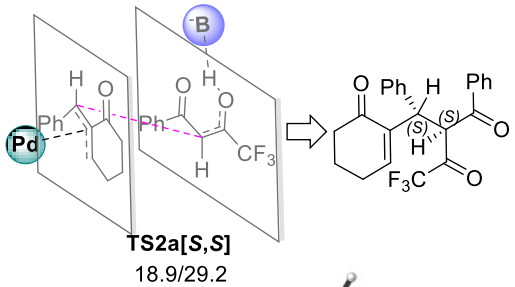
4.2 Transition state structures of the nucleophilic attacking steps.

⊿G in kcal/mol was given at 40°C/140°C.

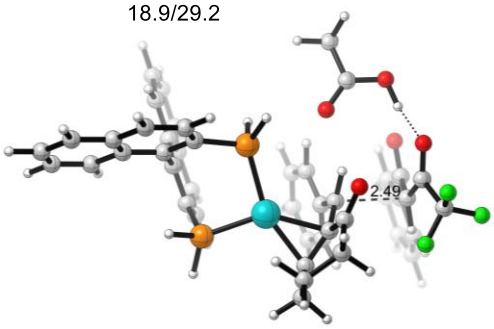


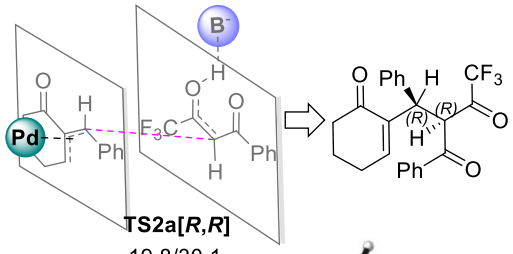
TS2a[*S*,*R*]
17.5/27.8





TS2a[*S*,*S*]
18.9/29.2





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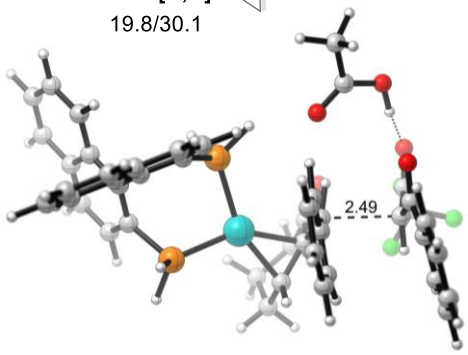
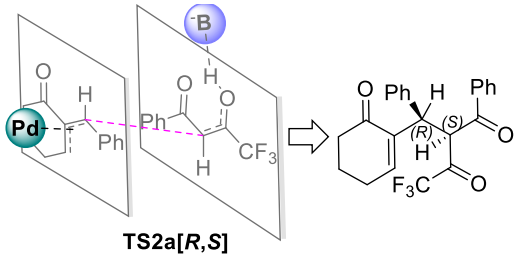
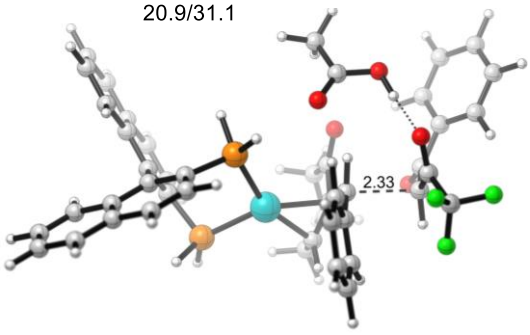
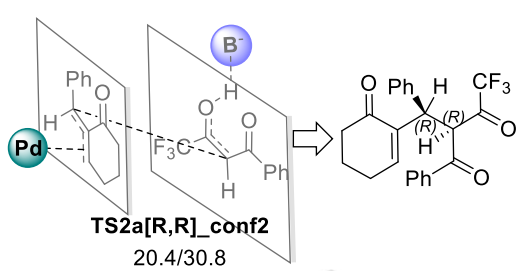
19.8/30.1





TS2a[*R*,*S*]
20.9/31.1





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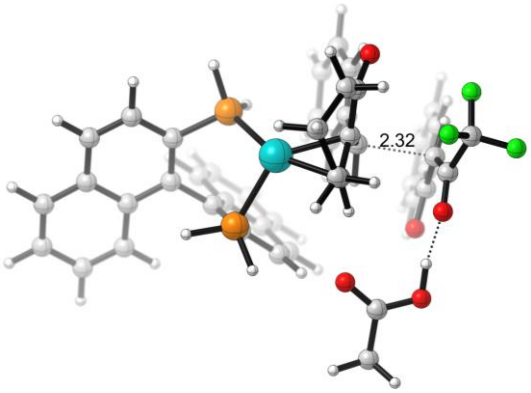
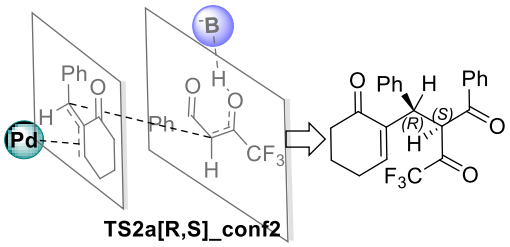
20.4/30.8





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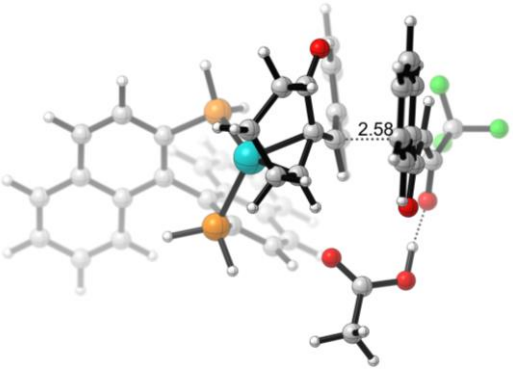
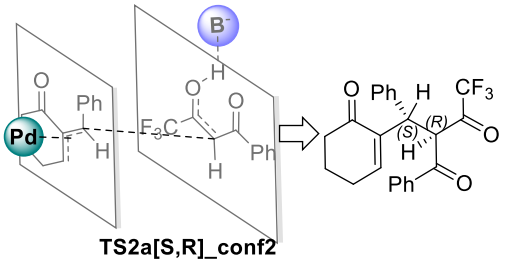
18.0/28.3





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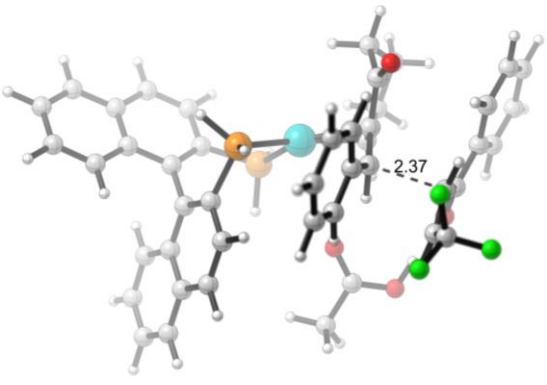
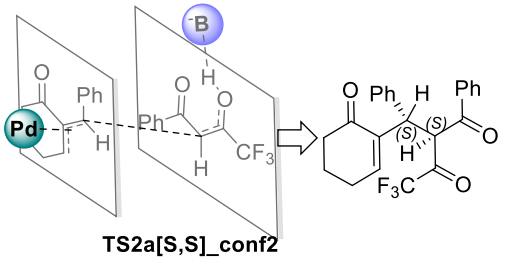
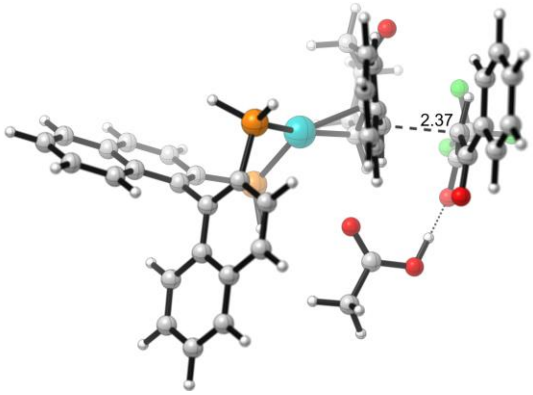
20.3/30.5





TS2a[S,S]_conf2
21.2/31.4



4.3 Potential energy surfaces of the favorable pathways to deliver **(*R*)-** and **(*S*)-3a** at low (40 ℃) and high (140 ℃) temperatures.

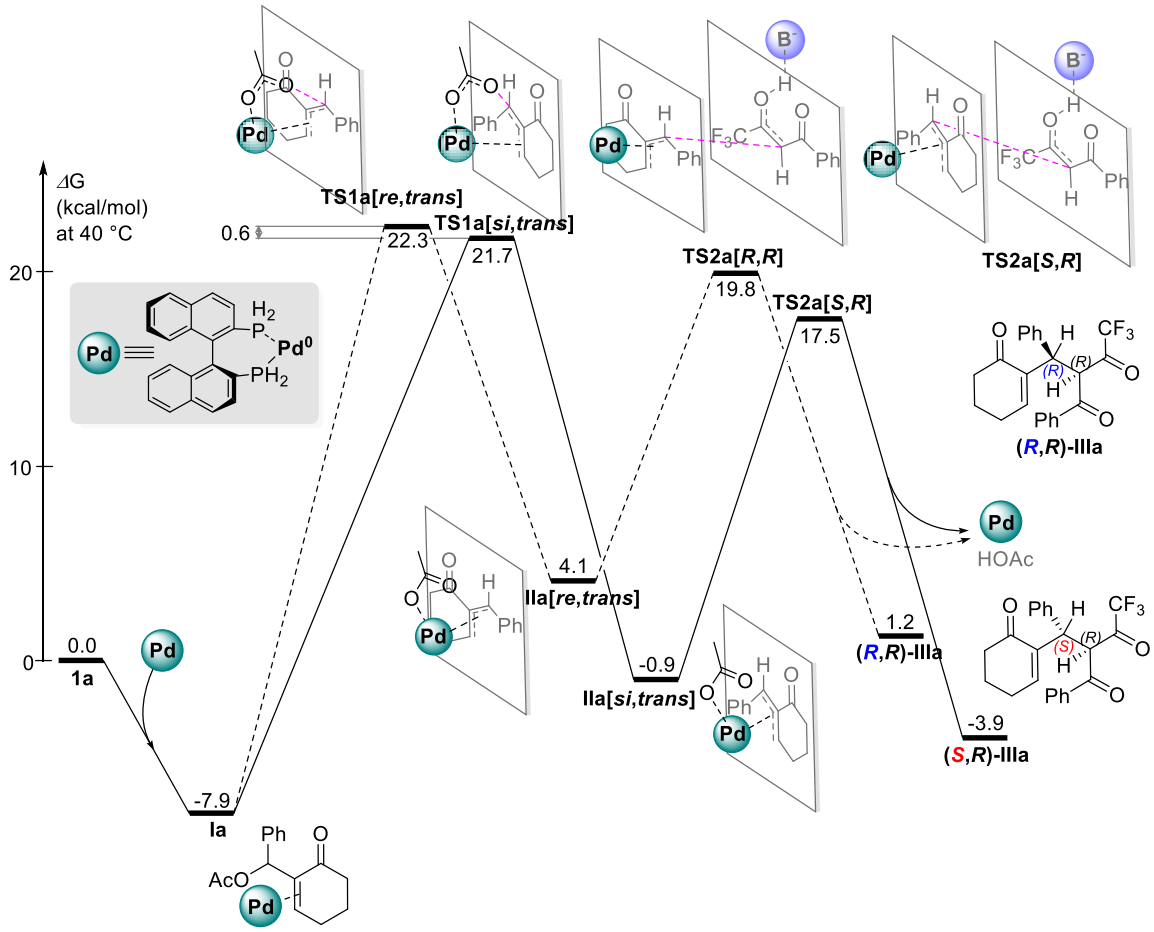


Figure S5. Free energy profiles of the favorable pathways to deliver **(*R*)-** and **(*S*)-3a** at 40 ℃.

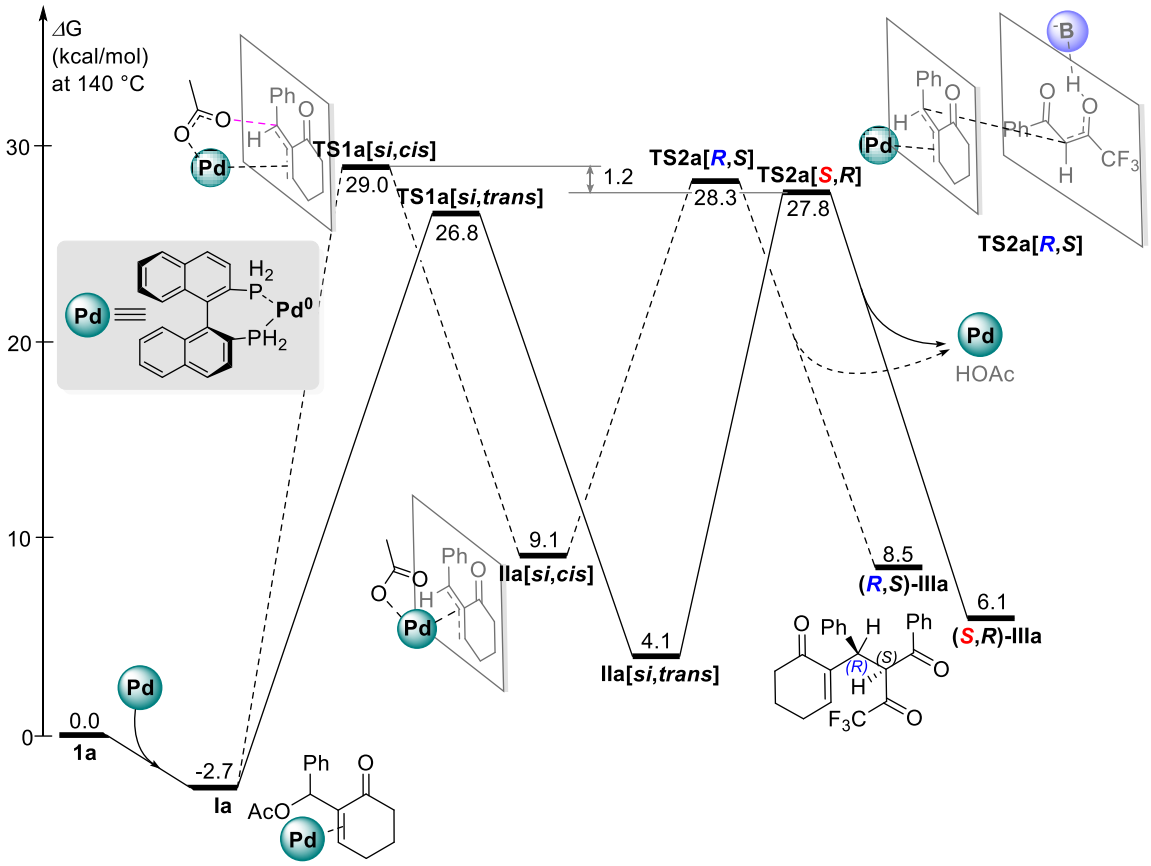
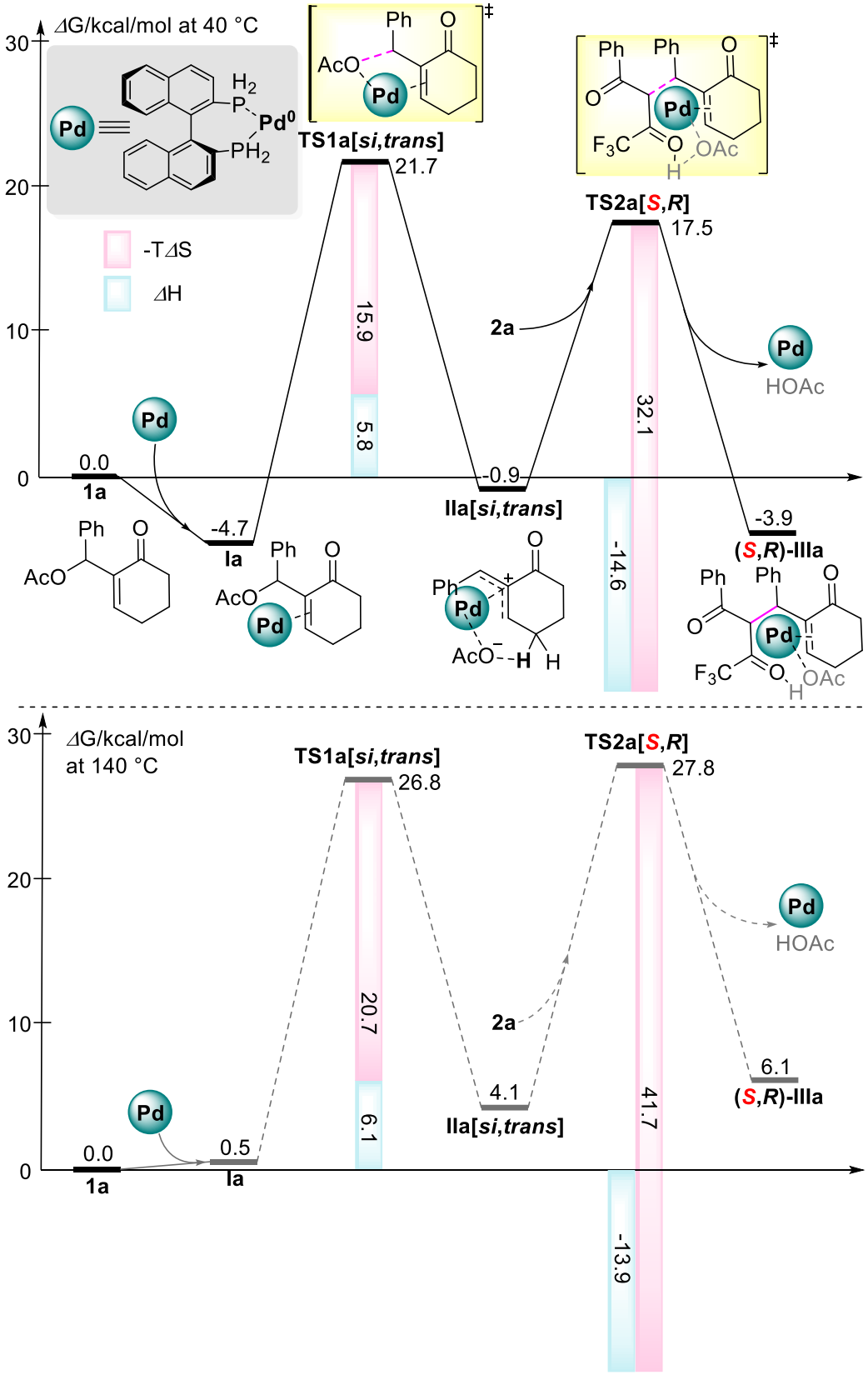


Figure S6. Free energy profiles of the favorable pathways to deliver **(*R*)-** and **(*S*)-3a** at 140 ℃.

4.4 Enthalpy and entropy contributions to deliver **(*S*,*R*)-IIIa** at different temperatures.



4.5 Tables of energies and other thermodynamic parameters.

Structure	E_{ele}	E_{ele}(SP)	ZPE	H(40 ℃)	T•S_{qh}(40 ℃)	H(140 ℃)	T•S_{qh}(140 ℃)
HOAc	-228.92703	-229.06514	0.06188	-228.85929	0.03336	-228.85634	0.04690
CF3CO2H	-526.40654	-526.82604	0.03958	-526.35929	0.03914	-526.35525	0.05570
H2O	-76.36042	-76.43036	0.02123	-76.33521	0.02247	-76.33393	0.03076
OAc-	-228.36796	-228.54325	0.04805	-228.31424	0.03304	-228.31152	0.04621
1a	-806.40911	-806.68380	0.27906	-806.11094	0.06418	-806.09868	0.09710
2a	-834.69188	-835.15365	0.15452	-834.52291	0.05492	-834.51386	0.08175
Pd-cat	-1581.85094	-1582.14198	0.29361	-1581.53489	0.07063	-1581.51954	0.10927
Ia	-2388.31949	-2388.86684	0.57479	-2387.70292	0.10874	-2387.67478	0.17250
TS1a[*si,trans*]	-2388.27071	-2388.81583	0.57151	-2387.65722	0.10945	-2387.62908	0.17335
IIa[*si,trans*]	-2388.30938	-2388.85276	0.57259	-2387.69419	0.11020	-2387.66581	0.17456
TS2a[*S,R*]	-3223.01203	-3224.00497	0.72833	-3222.22655	0.13856	-3222.18873	0.22168
TS2a[*S,S*]	-3223.00785	-3224.00201	0.72787	-3222.22266	0.13904	-3222.18484	0.22215
(*S,R*)-IIIa	-3223.04176	-3224.03996	0.73110	-3222.25277	0.14126	-3222.21490	0.22495
(*S,S*)-IIIa	-3223.02607	-3224.02509	0.73103	-3222.23748	0.14040	-3222.19960	0.22396
TS1a[*re,trans*]	-2388.27024	-2388.81530	0.57169	-2387.65670	0.10914	-2387.62858	0.17300
IIa[*re,trans*]	-2388.30171	-2388.84563	0.57300	-2387.68647	0.10943	-2387.65811	0.17362
TS2a[*R,R*]	-3223.00632	-3223.99986	0.72785	-3222.22113	0.13960	-3222.18333	0.22282
TS2a[*R,S*]	-3223.00512	-3223.99889	0.72834	-3222.21945	0.13937	-3222.18162	0.22267
(*R,R*)-IIIa	-3223.03863	-3224.03380	0.73135	-3222.24991	0.13890	-3222.21205	0.22201
(*R,S*)-IIIa	-3223.03089	-3224.03448	0.73019	-3222.24277	0.14174	-3222.20483	0.22567
TS1a[*si,cis*]	-2388.26766	-2388.81276	0.57206	-2387.65364	0.10958	-2387.62556	0.17349
IIa[*si,cis*]	-2388.30011	-2388.84347	0.57192	-2387.68547	0.11079	-2387.65703	0.17541
TS2a[*R,R*]_conf2	-3223.01455	-3224.00064	0.72871	-3222.22844	0.13891	-3222.19066	0.22187
TS2a[*R,S*]_conf2	-3223.01376	-3224.00329	0.72799	-3222.22821	0.13950	-3222.19040	0.22264
TS1a[*re,cis*]	-2388.26691	-2388.81103	0.57179	-2387.65326	0.10897	-2387.62515	0.17265
IIa[*re,cis*]	-2388.30574	-2388.84583	0.57240	-2387.69073	0.11000	-2387.66231	0.17438
TS2a[*S,R*]_conf2	-3223.00939	-3224.00000	0.72854	-3222.22323	0.13982	-3222.18545	0.22296
TS2a[*S,S*]_conf2	-3223.00859	-3223.99820	0.72844	-3222.22249	0.14009	-3222.18469	0.22332

Notes: E_{ele}, ZPE, H(T), and T•S_{qh} were the electronic energies, zero-point energies, sum of electronic and thermal ethalpies, and product of temperature and entropies using Grimme's quasiharmonic approximation, respectively, which were given at the B3LYP-D3(BJ)/def2-SVP-SMD(toluene) level. E_{ele}(SP) were electronic energies from single point energy calculations at the M06/def2-TZVPP-SMD(toluene) level.

4.6 Coordinates of all stationary points.

1a

C	-3.654039	0.986516	2.098953
C	-3.951768	2.205801	1.607506
C	-4.921208	3.098834	2.302044
C	-5.404701	2.638566	3.665729
C	-5.562198	1.119436	3.737611
C	-4.260349	0.417230	3.347506
H	-2.925504	0.373971	1.560393
H	-4.647727	2.974202	4.400378
H	-6.336235	3.174891	3.896539
H	-5.881389	0.810232	4.745064
H	-6.360410	0.806738	3.042189
H	-3.518083	0.507433	4.165943
H	-4.420665	-0.666572	3.221315
O	-5.278696	4.152157	1.807697
C	-3.336071	2.782736	0.355846
H	-4.130276	3.202915	-0.274356
C	-2.334728	3.883189	0.667121
C	-1.162233	3.581889	1.372339
C	-2.566312	5.197180	0.250510
C	-0.230139	4.581742	1.652986
H	-0.979811	2.555884	1.700831
C	-1.638127	6.200419	0.537681
H	-3.480651	5.430774	-0.297021
C	-0.468305	5.895344	1.237461
H	0.683426	4.337278	2.200707
H	-1.828162	7.225158	0.209457
H	0.258674	6.680478	1.459485
O	-2.684133	1.715925	-0.358439
C	-2.508290	1.887769	-1.688254
O	-2.929336	2.835538	-2.299480
C	-1.716492	0.747029	-2.270415
H	-0.690816	0.774157	-1.869056
H	-2.157390	-0.217505	-1.977299
H	-1.686267	0.836483	-3.362817

2a

C	-3.141149	0.870434	0.297186
C	-4.489269	1.328502	0.010039
H	-5.230604	0.695469	-0.465881
C	-4.825518	2.606984	0.356431
C	-6.209973	3.180857	0.098361
C	-2.710803	-0.510219	-0.054515
C	-3.562891	-1.441875	-0.671822
C	-1.390724	-0.887829	0.249324
C	-3.103275	-2.722481	-0.977793
H	-4.591072	-1.176591	-0.918577
C	-0.933672	-2.166549	-0.056936
H	-0.741579	-0.153868	0.728329
C	-1.789502	-3.086986	-0.671462
H	-3.773368	-3.439233	-1.457462
H	0.093520	-2.450420	0.182983
H	-1.431614	-4.090891	-0.912191
F	-6.784441	3.556982	1.246653
F	-6.133154	4.254173	-0.696729
F	-7.012047	2.284135	-0.492117
O	-4.016999	3.458742	0.933309
O	-2.327885	1.643888	0.847238
H	-3.142485	2.939839	1.039936

CF_3CO_2H

C	-0.675120	-2.664337	-1.022363
C	-1.138878	-4.136464	-1.084310
F	-0.385633	-4.820229	-1.936136
F	-1.045487	-4.702746	0.124286
F	-2.413327	-4.204086	-1.485762
O	-1.433309	-1.982236	-0.165858
O	0.236750	-2.228142	-1.663037
H	-1.114269	-1.062585	-0.153047

HOAc

O	2.700851	5.420926	3.120110
C	1.399063	5.692645	3.348028
O	0.572679	4.827255	3.490323
C	1.142739	7.174753	3.396152
H	1.751894	7.635144	4.189569
H	1.446576	7.638910	2.444942
H	0.078770	7.361184	3.582709
H	2.781884	4.451837	3.103703

H_2O

O	1.737413	0.475795	0.000000
H	2.702538	0.530255	0.000000
H	1.466585	1.403740	0.000000

OAc^-

C	-1.602190	0.765786	-0.000635
C	-3.176608	0.772147	-0.003043
H	-3.549918	1.342629	-0.873411
H	-3.600538	-0.246453	-0.022330
H	-3.548308	1.301511	0.894072
O	-1.081442	1.902460	-0.030313
O	-1.061655	-0.360156	0.035948

Pd-cat

C	-7.039420	0.709606	0.728940
C	-5.680581	0.663185	0.500865
C	-4.946430	1.846681	0.203446
C	-5.657159	3.091794	0.146057
C	-7.058207	3.103815	0.382746
C	-7.738001	1.939703	0.668594
H	-7.583019	-0.210132	0.957741
H	-5.150331	-0.288350	0.549479
C	-3.531252	1.826818	-0.030428
C	-4.935378	4.279412	-0.146961
H	-7.588507	4.058451	0.335266
H	-8.815118	1.962227	0.849745
C	-3.578996	4.242348	-0.363336
C	-2.859205	3.015859	-0.307947
H	-5.475410	5.228421	-0.195718
H	-3.039514	5.168061	-0.578735
C	-2.816333	0.510124	0.010628
C	-2.799546	-0.298571	-1.174055
C	-2.191997	0.052390	1.169626
C	-3.412508	0.125078	-2.387701
C	-2.142297	-1.573847	-1.152812
C	-1.546092	-1.215746	1.174942
C	-3.376253	-0.667357	-3.515222
H	-3.912769	1.093527	-2.416049
C	-2.126582	-2.367271	-2.331529
C	-1.524758	-2.005919	0.051013
H	-1.057566	-1.561568	2.089344
C	-2.729301	-1.926572	-3.489753
H	-3.850966	-0.322025	-4.436723
H	-1.623570	-3.337290	-2.302466
H	-1.027495	-2.979037	0.070971
H	-2.709378	-2.545401	-4.389843
P	-1.014826	3.094008	-0.388039
P	-1.976170	1.136699	2.650080
H	-0.903492	4.179531	-1.311037
H	-0.735847	2.071196	-1.336166
H	-1.978148	0.112244	3.646636
H	-3.314164	1.561288	2.879061
Pd	-0.517538	2.667964	1.796483

Ia

C	-5.564866	1.693790	0.917936
C	-4.410062	1.253697	0.306956
C	-3.402299	2.172690	-0.101875
C	-3.614217	3.570835	0.141278
C	-4.817795	3.990513	0.769827
C	-5.774441	3.074718	1.150517
H	-6.325380	0.972164	1.225336
H	-4.256923	0.188356	0.132001

C	-2.189204	1.744464	-0.736062
C	-2.609180	4.495600	-0.249673
H	-4.970017	5.058126	0.947863
H	-6.695160	3.410256	1.633352
C	-1.445816	4.068995	-0.845066
C	-1.226943	2.685415	-1.098832
H	-2.770718	5.560566	-0.063377
H	-0.664987	4.785464	-1.104653
C	-1.978698	0.285194	-1.002349
C	-2.616939	-0.319820	-2.136160
C	-1.175066	-0.489360	-0.168755
C	-3.433478	0.426861	-3.031724
C	-2.425395	-1.718438	-2.392213
C	-0.989625	-1.874285	-0.437722
C	-4.031137	-0.178064	-4.116830
H	-3.579522	1.492031	-2.850630
C	-3.059430	-2.311402	-3.517238
C	-1.601548	-2.471645	-1.513372
H	-0.352032	-2.467989	0.222125
C	-3.846445	-1.560088	-4.362725
H	-4.652100	0.413188	-4.793829
H	-2.908170	-3.378002	-3.701639
H	-1.457452	-3.537520	-1.706979
H	-4.327406	-2.026941	-5.225320
P	0.428369	2.148879	-1.694882
P	-0.143087	0.284125	1.141265
Pd	1.680897	1.335148	0.139995
C	3.527192	1.131960	1.253616
C	3.760544	1.989961	0.148134
C	4.242541	1.446457	-1.142340
C	4.393563	-0.070224	-1.211230
C	4.968304	-0.609095	0.100876
C	4.047892	-0.300635	1.285860
H	3.401049	1.613567	2.227884
H	3.401920	-0.517472	-1.406964
H	5.035360	-0.297719	-2.074494
H	5.150724	-1.693368	0.027667
H	5.949646	-0.133010	0.272853
H	3.212015	-1.020747	1.301979
H	4.594418	-0.458172	2.231729
O	4.529044	2.160202	-2.095317
C	3.886873	3.500990	0.308117
H	3.698141	3.963652	-0.666636
C	5.262318	3.893240	0.808519
C	5.518246	4.097506	2.170786
C	6.318373	3.997684	-0.108496
C	6.809145	4.401372	2.609312
H	4.697695	4.029110	2.886150
C	7.608588	4.296744	0.333298
H	6.118050	3.829723	-1.168221
C	7.859205	4.499551	1.693121
H	6.995131	4.563822	3.674180
H	8.422935	4.377045	-0.391278
H	8.868833	4.737373	2.037250
O	2.901244	3.973264	1.250560
C	1.804591	4.589816	0.783930
O	1.638286	4.902309	-0.373097
C	0.798491	4.799712	1.882918
H	0.205408	3.875364	1.977306
H	1.292548	4.984941	2.846157
H	0.121900	5.623435	1.625896
H	0.811517	3.278250	-2.457544
H	0.069231	1.286545	-2.765108
H	-0.099034	-0.796881	2.066827
H	-1.103502	1.066411	1.836888

TS1a[*si,trans*]

C	-4.201545	-2.511184	0.360170
C	-3.717665	-1.224621	0.466646
C	-2.986796	-0.810848	1.616005
C	-2.758989	-1.765889	2.661983
C	-3.273878	-3.082865	2.521031
C	-3.980772	-3.450110	1.396536
H	-4.758570	-2.809874	-0.530913

H	-3.890323	-0.508410	-0.337098
C	-2.465573	0.518837	1.752262
C	-2.006690	-1.373320	3.801570
H	-3.093829	-3.803076	3.323080
H	-4.369634	-4.466443	1.299886
C	-1.501078	-0.101356	3.911575
C	-1.742270	0.861183	2.892507
H	-1.815247	-2.108465	4.586808
H	-0.879854	0.167408	4.765829
C	-2.682507	1.507032	0.646935
C	-3.943800	2.178588	0.530073
C	-1.667890	1.770577	-0.271925
C	-5.007852	1.956331	1.449080
C	-4.147763	3.113569	-0.539018
C	-1.882867	2.704651	-1.323275
C	-6.208916	2.619755	1.315261
H	-4.860266	1.250697	2.267311
C	-5.399488	3.777342	-0.649868
C	-3.088618	3.351332	-1.455836
H	-1.076250	2.908045	-2.031892
C	-6.410045	3.537369	0.255701
H	-7.013220	2.436444	2.031553
H	-5.545530	4.486024	-1.469028
H	-3.245525	4.061540	-2.271583
H	-7.367581	4.054449	0.160106
P	-0.886343	2.478665	3.009831
P	0.029543	1.129611	0.013289
Pd	1.046982	2.367989	1.773506
C	2.461700	3.470270	2.880656
C	3.164096	2.944482	1.728114
C	3.101012	3.707589	0.430969
C	2.533712	5.120002	0.526352
C	2.846405	5.768490	1.874929
C	2.253672	4.968651	3.039058
H	2.550833	2.900886	3.807199
H	2.942029	5.693216	-0.318872
H	1.440701	5.052907	0.378800
H	3.943125	5.820507	1.992956
H	2.479782	6.807072	1.896964
H	2.715262	5.297886	3.987008
H	1.179107	5.194664	3.139085
O	3.508042	3.254941	-0.624836
C	3.841437	1.699329	1.678966
H	4.066605	1.367581	0.665477
C	4.637190	1.094521	2.743433
C	5.179069	-0.194606	2.542789
C	4.979767	1.784991	3.922609
C	5.995688	-0.781927	3.501140
H	4.905138	-0.735611	1.637334
C	5.804494	1.195903	4.880363
H	4.625309	2.802480	4.076302
C	6.307127	-0.090825	4.678859
H	6.394169	-1.785446	3.334505
H	6.061141	1.749090	5.786793
H	6.950030	-0.552704	5.432237
O	2.513392	-0.183502	1.480892
C	1.881342	-0.493901	2.544166
O	1.555884	0.289500	3.457143
C	1.447354	-1.956816	2.649185
H	0.446563	-2.059469	2.197299
H	2.134713	-2.620750	2.106379
H	1.369894	-2.258750	3.703338
H	-0.828666	2.647626	4.416619
H	-1.936403	3.394494	2.734886
H	0.539503	1.133883	-1.310439
H	-0.181593	-0.262042	0.160423

IIa[*si,trans*]

C	-4.974297	2.294450	1.473037
C	-3.941473	1.949856	0.627417
C	-3.007727	2.925636	0.176940
C	-3.176167	4.282529	0.608104
C	-4.253334	4.604183	1.478203
C	-5.132044	3.633262	1.907053

H	-5.677992	1.530244	1.811164
H	-3.827005	0.916498	0.296597
C	-1.891726	2.589548	-0.656853
C	-2.249500	5.262521	0.166951
H	-4.369907	5.640757	1.804485
H	-5.952313	3.892299	2.580290
C	-1.213253	4.927633	-0.670271
C	-1.019715	3.584675	-1.094408
H	-2.369481	6.293841	0.507342
H	-0.507989	5.692316	-0.996108
C	-1.612233	1.154916	-0.985027
C	-1.992924	0.599992	-2.247189
C	-0.955713	0.361020	-0.044571
C	-2.692908	1.360705	-3.225801
C	-1.658288	-0.763486	-2.545490
C	-0.641586	-0.991308	-0.347523
C	-3.033768	0.805683	-4.440257
H	-2.956768	2.394387	-2.997137
C	-2.024824	-1.303717	-3.808489
C	-0.976987	-1.534981	-1.566919
H	-0.134486	-1.606386	0.399793
C	-2.695106	-0.537800	-4.736980
H	-3.570804	1.403409	-5.180398
H	-1.765790	-2.342240	-4.029643
H	-0.730003	-2.575401	-1.792618
H	-2.970694	-0.964715	-5.704053
P	0.457377	3.127776	-2.110567
P	-0.427918	1.125721	1.539740
Pd	1.360146	2.637976	1.489576
C	2.832377	1.568579	0.305133
C	3.479166	2.402343	1.266110
C	4.138188	1.788475	2.485331
C	4.296364	0.279846	2.478906
C	3.145441	-0.449755	1.784981
C	2.961351	0.068678	0.360062
H	2.594377	1.982996	-0.677856
H	5.241325	0.073062	1.939628
H	4.446442	-0.045572	3.518080
H	3.332675	-1.534929	1.781282
H	2.218420	-0.284599	2.358661
H	3.831374	-0.231495	-0.257136
H	2.084891	-0.388591	-0.124422
O	4.564755	2.480548	3.383700
C	3.205282	3.795257	1.299429
H	3.456574	4.285846	2.244606
C	3.031196	4.689382	0.136744
C	2.218364	5.832857	0.265185
C	3.699972	4.472026	-1.081782
C	2.082742	6.727762	-0.794971
H	1.672306	5.986314	1.198480
C	3.564111	5.372176	-2.139286
H	4.352114	3.603530	-1.188941
C	2.755145	6.503032	-2.001646
H	1.448008	7.610011	-0.679865
H	4.098704	5.191873	-3.075053
H	2.651705	7.209027	-2.828945
O	-0.435239	2.546684	3.943879
C	-0.404843	3.709591	3.527384
O	0.273706	4.116269	2.507453
C	-1.261097	4.781208	4.183732
H	-1.447662	4.528848	5.236366
H	-0.798083	5.774341	4.100499
H	-2.231816	4.812361	3.661103
H	0.830184	4.453044	-2.464231
H	-0.221839	2.869271	-3.340806
H	-1.652239	1.573819	2.063147
H	-0.226919	-0.030222	2.328850

TS2a[*S*,*R*]

C	-4.023709	2.076980	-0.243618
C	-4.360449	0.818688	0.351199
C	-5.744018	0.619745	0.919445
C	-6.810296	1.598506	0.479350
C	-6.294068	3.027087	0.306016

C	-5.100087	3.054006	-0.644787
H	-3.110691	2.137058	-0.835745
H	-7.171622	1.204100	-0.486757
H	-7.641080	1.535621	1.196642
H	-7.099752	3.678140	-0.068443
H	-5.984681	3.430818	1.287049
H	-5.439038	2.787562	-1.665270
H	-4.674772	4.067893	-0.715839
O	-5.990091	-0.288692	1.694665
C	-3.419170	-0.222732	0.619827
H	-3.760440	-0.935906	1.366596
C	-1.957689	-0.206484	0.422873
C	-1.178282	-0.826745	1.422668
C	-1.302055	0.349732	-0.692469
C	0.211292	-0.843059	1.330391
H	-1.692564	-1.297919	2.261709
C	0.087216	0.315911	-0.786891
H	-1.882704	0.756953	-1.519669
C	0.849356	-0.270647	0.228036
H	0.798739	-1.320009	2.117934
H	0.578185	0.731711	-1.669926
H	1.938550	-0.300062	0.147191
C	-5.404778	-1.848370	-0.911191
C	-3.948314	-1.906895	-1.014841
H	-3.559021	-1.335502	-1.856841
C	-3.078705	-2.866780	-0.435673
C	-1.795347	-3.216879	-1.227236
C	-6.184948	-3.005800	-0.360620
C	-5.812871	-4.335156	-0.609350
C	-7.360275	-2.749057	0.360440
C	-6.591903	-5.387746	-0.129009
H	-4.916291	-4.550998	-1.191582
C	-8.127881	-3.800989	0.856067
H	-7.643140	-1.714858	0.550004
C	-7.745350	-5.123396	0.613628
H	-6.294920	-6.419238	-0.333512
H	-9.029572	-3.589873	1.436561
H	-8.348065	-5.948984	1.000939
F	-0.738064	-3.368992	-0.427359
F	-1.997586	-4.388557	-1.865092
F	-1.470553	-2.309269	-2.165922
O	-3.198680	-3.487725	0.630886
O	-6.003933	-0.851335	-1.323321
C	2.021484	1.225858	6.268546
C	0.898028	1.929773	5.890972
C	0.722265	2.355476	4.544275
C	1.743450	2.039959	3.586835
C	2.890425	1.316469	4.010999
C	3.028348	0.915852	5.322224
H	2.136587	0.902222	7.305511
H	0.125427	2.162739	6.624545
C	-0.444338	3.069588	4.118037
C	1.572579	2.445962	2.236921
H	3.661881	1.079298	3.274185
H	3.912971	0.356849	5.635473
C	0.440581	3.114560	1.839294
C	-0.576254	3.433633	2.779967
H	2.348875	2.202163	1.509170
H	0.311338	3.386630	0.789616
C	-1.512164	3.417434	5.109048
C	-1.339971	4.567866	5.948074
C	-2.671185	2.650886	5.208282
C	-0.179161	5.389158	5.879733
C	-2.370703	4.917739	6.882905
C	-3.685259	3.013200	6.138693
C	-0.044153	6.492449	6.695067
H	0.608564	5.134717	5.170058
C	-2.197917	6.060087	7.710647
C	-3.538391	4.111940	6.951700
H	-4.590424	2.405138	6.206412
C	-1.060219	6.832018	7.621117
H	0.854175	7.110444	6.627865
H	-2.987977	6.316526	8.420849
H	-4.322511	4.377168	7.665189

H	-0.938857	7.707883	8.262491
P	-2.176276	4.055258	2.138787
P	-2.999795	1.273642	4.035208
Pd	-3.359543	2.093428	1.817188
H	-4.020633	0.594342	4.731311
H	-1.919598	0.394993	4.274551
H	-2.544825	5.052395	3.076330
H	-1.744543	4.905416	1.086689
H	-4.220866	-3.336655	1.877399
C	-4.641052	-2.311903	3.464207
C	-5.769661	-2.063852	4.430158
H	-5.391106	-1.612808	5.357068
H	-6.459969	-1.360122	3.938344
H	-6.320567	-2.989233	4.646191
O	-4.904426	-3.276617	2.612443
O	-3.608263	-1.655462	3.465202

TS2a[*S,S*]

C	-4.162707	2.562388	-0.499178
C	-4.769685	1.410337	0.101951
C	-6.192945	1.503255	0.590054
C	-7.008614	2.690769	0.114551
C	-6.197017	3.976552	-0.030492
C	-4.992241	3.743839	-0.938590
H	-3.228544	2.430792	-1.044528
H	-7.417262	2.390655	-0.868245
H	-7.864451	2.799676	0.795559
H	-6.830365	4.785905	-0.426624
H	-5.842018	4.302620	0.963676
H	-5.343407	3.560993	-1.973903
H	-4.356174	4.641934	-0.988804
O	-6.676680	0.642782	1.297023
C	-4.047327	0.224302	0.463008
H	-4.482876	-0.362614	1.273557
C	-2.629975	-0.035549	0.164000
C	-1.852419	-0.667755	1.156844
C	-2.014309	0.286445	-1.062251
C	-0.494941	-0.901924	0.952411
H	-2.339992	-0.967060	2.083958
C	-0.659132	0.039413	-1.267292
H	-2.613474	0.683325	-1.881211
C	0.108840	-0.543187	-0.255416
H	0.093004	-1.380875	1.738458
H	-0.207481	0.272030	-2.233756
H	1.169483	-0.745495	-0.422166
C	-3.896610	-2.580440	-0.515751
C	-4.997478	-1.684501	-0.816784
H	-5.016012	-1.182434	-1.780758
C	-6.257252	-1.824962	-0.164790
C	-7.459956	-1.259468	-0.964726
C	-2.825681	-2.770410	-1.566436
C	-2.940248	-2.337713	-2.896977
C	-1.643751	-3.412341	-1.167805
C	-1.890720	-2.522927	-3.798605
H	-3.856973	-1.858785	-3.242345
C	-0.592216	-3.593216	-2.063470
H	-1.579428	-3.750333	-0.133133
C	-0.710085	-3.143786	-3.382466
H	-1.996286	-2.183522	-4.832135
H	0.327043	-4.084116	-1.733677
H	0.113494	-3.284200	-4.087293
F	-7.819677	-2.137164	-1.923546
F	-8.523196	-1.029785	-0.206446
F	-7.153081	-0.100221	-1.607353
O	-6.538539	-2.413531	0.881180
O	-3.776829	-3.165272	0.561003
C	1.361627	0.748242	6.345113
C	0.410436	1.636258	5.890110
C	0.379448	2.035745	4.524417
C	1.362122	1.494895	3.629199
C	2.330624	0.585130	4.132722
C	2.332014	0.217512	5.460823
H	1.367473	0.449744	7.395906
H	-0.335060	2.039812	6.576172

C	-0.609805	2.940382	4.018804
C	1.330044	1.871588	2.260101
H	3.074986	0.178369	3.443665
H	3.079930	-0.485056	5.835242
C	0.368122	2.730572	1.787338
C	-0.607829	3.274471	2.666559
H	2.073214	1.452674	1.578458
H	0.339399	2.981191	0.724701
C	-1.650555	3.502364	4.938168
C	-1.329206	4.630860	5.761874
C	-2.928943	2.949700	4.981960
C	-0.041203	5.236882	5.748717
C	-2.335743	5.181145	6.623931
C	-3.916998	3.508689	5.839597
C	0.236522	6.324919	6.548334
H	0.729508	4.828210	5.094378
C	-2.014635	6.301604	7.437170
C	-3.627680	4.590495	6.637248
H	-4.916439	3.067823	5.863423
C	-0.756739	6.862823	7.402412
H	1.230983	6.776490	6.524647
H	-2.787374	6.712141	8.091901
H	-4.393179	5.008812	7.295477
H	-0.522063	7.724018	8.032079
P	-2.026382	4.170486	1.929955
P	-3.414036	1.616485	3.814069
Pd	-3.570794	2.476552	1.584975
H	-4.534285	1.076554	4.481283
H	-2.460675	0.612169	4.085685
H	-2.230108	5.254474	2.820202
H	-1.389485	4.881011	0.878444
H	-5.634711	-2.854096	2.133405
C	-4.488430	-2.353207	3.613054
C	-3.842274	-2.934797	4.849461
H	-3.410460	-2.138400	5.469115
H	-4.564567	-3.527783	5.428601
H	-3.037175	-3.617665	4.531024
O	-5.298885	-3.189744	3.027058
O	-4.235167	-1.219853	3.220031

(*S*,*R*)-IIIa

C	-0.767092	-0.806975	0.410312
C	-2.147151	-0.623873	0.714283
C	-2.706006	-1.183737	1.955886
C	-1.707439	-1.807346	2.927768
C	-0.673323	-2.644921	2.171955
C	0.108641	-1.807218	1.153701
H	-0.467786	-0.579991	-0.616890
H	-1.208565	-1.001956	3.495575
H	-2.283505	-2.412216	3.642692
H	0.017536	-3.131981	2.878903
H	-1.201604	-3.454679	1.644137
H	0.941066	-1.286947	1.657145
H	0.584325	-2.475803	0.414978
O	-3.911652	-1.204090	2.202442
C	-3.082471	-0.140314	-0.396274
H	-2.434214	0.081135	-1.249570
C	-3.845574	1.144624	-0.108870
C	-3.371314	2.331191	-0.691636
C	-4.999932	1.198610	0.684274
C	-4.034346	3.542396	-0.487418
H	-2.480448	2.288952	-1.322069
C	-5.666722	2.411698	0.884607
H	-5.360426	0.292152	1.168047
C	-5.189510	3.587376	0.299933
H	-3.652877	4.452597	-0.956791
H	-6.566979	2.435247	1.503976
H	-5.717460	4.532282	0.452429
C	-3.165605	-2.471512	-1.315159
C	-4.025420	-1.284272	-0.863308
H	-4.676170	-1.576680	-0.035903
C	-4.880737	-0.842859	-2.034359
C	-6.270619	-1.522716	-2.083520
C	-3.095769	-3.704837	-0.489577

C	-3.935189	-3.947830	0.610393
C	-2.116647	-4.657625	-0.832158
C	-3.788509	-5.117420	1.356992
H	-4.688065	-3.223215	0.912009
C	-1.970189	-5.819278	-0.082344
H	-1.474552	-4.452801	-1.689526
C	-2.806893	-6.050393	1.016687
H	-4.440942	-5.293874	2.214539
H	-1.201702	-6.548369	-0.348684
H	-2.690533	-6.960961	1.609407
F	-6.944283	-1.217849	-3.182709
F	-6.113405	-2.861258	-2.031033
F	-6.998858	-1.157448	-1.015211
O	-4.559955	-0.061754	-2.886641
O	-2.498056	-2.376368	-2.336398
C	2.339450	7.333252	3.416817
C	1.759852	6.100515	3.628472
C	0.463700	5.803756	3.119306
C	-0.225554	6.818801	2.375455
C	0.399307	8.080074	2.178939
C	1.654162	8.335123	2.687638
H	3.335820	7.540101	3.814438
H	2.295404	5.334705	4.190268
C	-0.161625	4.528225	3.318789
C	-1.515210	6.531060	1.854661
H	-0.135897	8.846323	1.612314
H	2.124196	9.308441	2.528980
C	-2.095728	5.300379	2.048228
C	-1.425046	4.283597	2.783692
H	-2.043033	7.305504	1.292251
H	-3.081378	5.089062	1.631572
C	0.559229	3.479555	4.109519
C	0.543110	3.546511	5.542528
C	1.245297	2.446953	3.474333
C	-0.156801	4.568351	6.244199
C	1.242678	2.552150	6.304400
C	1.931802	1.465454	4.242846
C	-0.160800	4.606307	7.622365
H	-0.696954	5.325256	5.674838
C	1.221503	2.623023	7.723388
C	1.935798	1.520477	5.615741
H	2.460699	0.657739	3.730657
C	0.535900	3.627554	8.371399
H	-0.706251	5.397612	8.141883
H	1.759423	1.861396	8.293630
H	2.471605	0.765005	6.195916
H	0.526006	3.670522	9.462928
P	-2.158907	2.596934	2.826148
P	1.060923	2.154271	1.669033
Pd	-0.980512	1.064932	1.461566
H	2.342177	1.602149	1.386374
H	1.297598	3.447781	1.133924
H	-2.219692	2.358517	4.225884
H	-3.522717	2.919192	2.620912
H	-2.095601	-1.159919	-3.512571
C	-1.361258	0.568051	-3.863876
C	-1.257018	1.593926	-4.962382
H	-0.583722	2.405132	-4.659989
H	-0.914132	1.131408	-5.899295
H	-2.262685	2.005809	-5.148110
O	-1.918354	-0.559285	-4.279178
O	-0.995981	0.765884	-2.719733

(*S*,*S*)-IIIa

C	-3.585068	-3.796401	1.692777
C	-4.766302	-3.312504	1.067690
C	-5.933461	-4.207159	0.905902
C	-5.788534	-5.615684	1.473298
C	-4.380364	-6.155137	1.217471
C	-3.315839	-5.281507	1.887902
H	-2.692005	-3.170418	1.602900
H	-6.002813	-5.588670	2.557419
H	-6.563552	-6.233574	0.997865
H	-4.296175	-7.197322	1.565364

H	-4.207145	-6.156506	0.129836
H	-3.248349	-5.526195	2.961931
H	-2.324396	-5.514252	1.463242
O	-6.957371	-3.858703	0.331496
C	-4.711725	-1.982660	0.327702
H	-3.781112	-1.525148	0.688135
C	-5.775278	-0.946522	0.667965
C	-5.424094	0.069201	1.572576
C	-7.065183	-0.932782	0.120032
C	-6.331128	1.069605	1.927625
H	-4.420669	0.072841	2.006283
C	-7.975517	0.066830	0.475381
H	-7.370782	-1.721702	-0.561958
C	-7.616123	1.071178	1.378354
H	-6.028099	1.851034	2.628602
H	-8.977504	0.056763	0.039566
H	-8.330876	1.852851	1.647513
C	-2.963939	-2.170368	-1.402295
C	-4.485648	-2.125468	-1.241995
H	-4.858054	-1.214135	-1.713167
C	-5.137854	-3.306682	-1.926907
C	-6.249545	-3.008358	-2.981605
C	-2.237529	-0.862534	-1.436947
C	-2.872217	0.384074	-1.302303
C	-0.841568	-0.904524	-1.597836
C	-2.123326	1.560852	-1.327305
H	-3.950857	0.452520	-1.161834
C	-0.097321	0.271085	-1.632022
H	-0.364515	-1.880304	-1.697055
C	-0.737576	1.507611	-1.495500
H	-2.626717	2.523733	-1.216298
H	0.986146	0.227277	-1.764836
H	-0.154567	2.431484	-1.520378
F	-6.192081	-3.889812	-3.982357
F	-7.462083	-3.120906	-2.414754
F	-6.164572	-1.773320	-3.494341
O	-4.852855	-4.459489	-1.733487
O	-2.338491	-3.217429	-1.403910
C	-6.182828	-0.942469	10.170017
C	-6.315056	-1.721200	9.040255
C	-6.660228	-1.140129	7.787067
C	-6.864836	0.278864	7.726279
C	-6.724059	1.051573	8.910750
C	-6.390817	0.456867	10.108144
H	-5.915698	-1.407655	11.121777
H	-6.152602	-2.797939	9.096847
C	-6.798975	-1.924291	6.594336
C	-7.203346	0.870635	6.480188
H	-6.884349	2.131223	8.853282
H	-6.285064	1.061816	11.011614
C	-7.324971	0.104645	5.345289
C	-7.123514	-1.303298	5.389279
H	-7.367137	1.950383	6.435246
H	-7.577904	0.573874	4.393233
C	-6.605722	-3.408386	6.669035
C	-7.679153	-4.228940	7.152786
C	-5.407611	-4.001421	6.277712
C	-8.931833	-3.680167	7.547621
C	-7.500740	-5.650129	7.235398
C	-5.246220	-5.412956	6.360583
C	-9.949114	-4.491860	8.002761
H	-9.080991	-2.602101	7.482208
C	-8.568201	-6.457251	7.712830
C	-6.259668	-6.211998	6.831652
H	-4.303292	-5.863946	6.041227
C	-9.767663	-5.893162	8.089727
H	-10.904053	-4.051035	8.298215
H	-8.420507	-7.538496	7.772915
H	-6.123206	-7.294370	6.896098
H	-10.581558	-6.524487	8.453484
P	-7.080304	-2.243904	3.810745
P	-4.110848	-3.044826	5.392537
Pd	-4.899941	-2.953598	3.206272
H	-2.951592	-3.714904	5.877552

H	-3.997186	-1.884652	6.203403
H	-8.056128	-3.247129	4.053316
H	-7.862840	-1.396683	2.988702
H	-2.582026	-4.381592	-2.708340
C	-3.157425	-3.901669	-4.447480
C	-3.327671	-4.451378	-5.837517
H	-3.507108	-3.632041	-6.544099
H	-2.455410	-5.048315	-6.139451
H	-4.205936	-5.117617	-5.835055
O	-2.607028	-4.775715	-3.614151
O	-3.522019	-2.788921	-4.113610

TS1a[*re,trans*]

C	-5.552436	0.481614	2.863515
C	-4.428740	0.570014	2.069687
C	-3.860303	1.833908	1.744419
C	-4.482026	3.015970	2.268264
C	-5.641347	2.889681	3.080066
C	-6.168130	1.650419	3.372496
H	-5.971874	-0.498349	3.102782
H	-3.960374	-0.335315	1.683129
C	-2.688892	1.954406	0.923179
C	-3.916647	4.283325	1.963341
H	-6.107587	3.797288	3.471723
H	-7.059266	1.565997	3.998696
C	-2.789534	4.380860	1.184262
C	-2.166637	3.217457	0.650653
H	-4.391204	5.183813	2.361127
H	-2.363290	5.363572	0.967740
C	-2.052723	0.711695	0.377501
C	-2.632064	0.071061	-0.767028
C	-0.920830	0.162281	0.976180
C	-3.773141	0.598509	-1.435273
C	-2.044221	-1.137485	-1.269742
C	-0.347192	-1.034981	0.467811
C	-4.304504	-0.035222	-2.538194
H	-4.224549	1.519529	-1.064996
C	-2.619647	-1.766820	-2.406634
C	-0.899688	-1.669258	-0.618296
H	0.554807	-1.429810	0.936759
C	-3.725519	-1.230405	-3.029343
H	-5.178833	0.387609	-3.038628
H	-2.163749	-2.686860	-2.781076
H	-0.451230	-2.588034	-1.003576
H	-4.156955	-1.723151	-3.903723
P	-0.550540	3.409783	-0.193657
P	-0.000676	1.090377	2.263437
Pd	1.214843	2.796963	1.136996
C	2.808100	4.063581	0.570187
C	3.331734	3.176435	1.585711
C	3.128206	3.531667	3.035118
C	2.618778	4.944731	3.300243
C	3.123193	5.937006	2.252407
C	2.666185	5.552776	0.842002
H	2.991473	3.781818	-0.467098
H	1.514569	4.910017	3.295072
H	2.931602	5.216906	4.318923
H	2.792034	6.958517	2.498487
H	4.226935	5.949063	2.284047
H	1.621362	5.870004	0.686555
H	3.258123	6.112135	0.095712
O	3.390588	2.768634	3.949105
C	3.992237	1.937593	1.353170
H	4.067626	1.323747	2.251208
C	4.974718	1.644954	0.311703
C	5.565113	0.361114	0.290851
C	5.418227	2.597225	-0.625099
C	6.540347	0.038111	-0.644804
H	5.211258	-0.384742	1.002985
C	6.398157	2.271673	-1.562898
H	5.014013	3.606923	-0.603287
C	6.957810	0.992948	-1.580868
H	6.979685	-0.962123	-0.649984
H	6.730371	3.025164	-2.280674

H	7.724665	0.740160	-2.317178
O	2.710542	0.245368	0.681520
C	2.367149	0.366187	-0.549052
O	1.971433	1.410361	-1.088984
C	2.537455	-0.884537	-1.407807
H	3.538211	-0.830742	-1.870181
H	2.496981	-1.805402	-0.809463
H	1.791042	-0.909807	-2.213623
H	-0.724425	4.700886	-0.764400
H	-0.701038	2.628551	-1.363479
H	0.639587	0.035311	2.956855
H	-1.028380	1.372417	3.202438

IIa[*re,trans*]

C	-4.724655	0.295332	3.351286
C	-3.833138	0.395184	2.304585
C	-3.238634	1.643569	1.968212
C	-3.586151	2.797574	2.746487
C	-4.512704	2.660869	3.815013
C	-5.071684	1.437221	4.113019
H	-5.167164	-0.672885	3.596523
H	-3.569448	-0.489051	1.723971
C	-2.301737	1.774283	0.889315
C	-2.993315	4.048699	2.426539
H	-4.771502	3.546621	4.400494
H	-5.781025	1.343846	4.938482
C	-2.084808	4.153918	1.401433
C	-1.727851	3.015246	0.625645
H	-3.268048	4.929741	3.011561
H	-1.637066	5.123714	1.171592
C	-1.975063	0.583709	0.040697
C	-2.937642	0.157364	-0.936577
C	-0.768008	-0.102617	0.170222
C	-4.169391	0.841977	-1.141774
C	-2.656151	-0.994437	-1.742844
C	-0.494326	-1.233370	-0.649584
C	-5.075752	0.405243	-2.084300
H	-4.392641	1.725630	-0.543718
C	-3.614255	-1.420626	-2.702218
C	-1.420278	-1.670869	-1.565016
H	0.478097	-1.715244	-0.564114
C	-4.799773	-0.739112	-2.870771
H	-6.014216	0.946283	-2.226293
H	-3.389118	-2.301307	-3.309032
H	-1.203688	-2.544572	-2.184999
H	-5.527375	-1.076560	-3.612586
P	-0.307459	3.162254	-0.518254
P	0.530796	0.522639	1.312442
Pd	1.651134	2.450690	0.558401
C	2.971035	4.236623	0.430601
C	2.996475	3.655442	1.727669
C	2.240947	4.290074	2.863724
C	1.542142	5.603591	2.552511
C	2.298116	6.425114	1.508208
C	2.477247	5.647055	0.201421
H	3.612210	3.812000	-0.343464
H	0.530703	5.351258	2.187169
H	1.410675	6.144099	3.500847
H	1.779122	7.377861	1.318345
H	3.292265	6.685348	1.912090
H	1.526950	5.632034	-0.359576
H	3.190468	6.170459	-0.456596
O	2.190400	3.775836	3.963012
C	3.410871	2.294690	1.878962
H	3.116410	1.851849	2.835041
C	4.555007	1.636773	1.220451
C	4.632018	0.232108	1.243339
C	5.603758	2.351444	0.612884
C	5.701958	-0.435846	0.654116
H	3.821269	-0.338067	1.696235
C	6.679055	1.682448	0.029062
H	5.591185	3.441802	0.620442
C	6.729759	0.286059	0.040110
H	5.727704	-1.527715	0.664563

H	7.485882	2.256606	-0.432909
H	7.569452	-0.237483	-0.423199
O	2.252498	-0.461378	-0.517276
C	2.756099	0.313682	-1.362592
O	2.600807	1.571446	-1.398837
C	3.668421	-0.274083	-2.435347
H	4.699626	0.060200	-2.239674
H	3.638846	-1.372029	-2.428560
H	3.383914	0.108201	-3.427775
H	-0.457073	4.504331	-0.962096
H	-0.731760	2.483487	-1.685272
H	1.200762	-0.637436	1.743267
H	-0.280211	0.746234	2.464278

TS2a[*R*,*R*]

C	-5.353600	0.623592	2.151407
C	-5.204765	0.737268	0.728155
C	-6.177435	1.591699	-0.045259
C	-7.441908	2.025469	0.672243
C	-7.249182	2.287579	2.164521
C	-6.619772	1.071953	2.840348
H	-4.806356	-0.161788	2.670664
H	-7.846969	2.894236	0.134354
H	-8.158490	1.196261	0.525919
H	-6.586898	3.161407	2.302310
H	-8.213001	2.537538	2.635541
H	-6.407307	1.276575	3.901997
H	-7.343542	0.232613	2.831778
O	-5.976766	1.882308	-1.207419
C	-4.076447	0.246447	-0.009764
H	-3.897844	0.737826	-0.968309
C	-2.943019	-0.506562	0.544306
C	-1.662064	-0.232808	0.020740
C	-3.058556	-1.494424	1.543887
C	-0.534214	-0.866246	0.538435
H	-1.581994	0.476901	-0.802903
C	-1.930037	-2.132601	2.049898
H	-4.043464	-1.803577	1.890748
C	-0.660971	-1.808318	1.561752
H	0.451196	-0.635911	0.126852
H	-2.043210	-2.909156	2.808880
H	0.222715	-2.314705	1.956686
C	-3.597784	-2.066042	-1.847954
C	-4.909123	-1.520784	-1.550206
H	-5.525436	-2.019060	-0.806497
C	-5.609161	-0.723543	-2.502077
C	-7.151465	-0.731293	-2.337646
C	-3.149318	-3.294302	-1.088229
C	-3.995791	-4.085362	-0.295431
C	-1.794328	-3.645326	-1.181865
C	-3.494401	-5.185284	0.402820
H	-5.058537	-3.852224	-0.223276
C	-1.289565	-4.738230	-0.480991
H	-1.156267	-3.024314	-1.811245
C	-2.137955	-5.510042	0.319148
H	-4.166614	-5.793399	1.013407
H	-0.228553	-4.990503	-0.554024
H	-1.744481	-6.367902	0.870495
F	-7.738316	0.309330	-2.913123
F	-7.659008	-1.850132	-2.893195
F	-7.532925	-0.749124	-1.031678
O	-5.181987	-0.119316	-3.487987
O	-2.824272	-1.562096	-2.662156
C	1.915886	4.997899	5.046489
C	0.733971	5.100579	4.344540
C	0.529780	4.362079	3.144591
C	1.584084	3.505331	2.681233
C	2.791116	3.426578	3.427423
C	2.956325	4.155505	4.584851
H	2.052551	5.571117	5.966374
H	-0.061543	5.752152	4.707576
C	-0.691414	4.440475	2.397524
C	1.391874	2.760234	1.487279
H	3.588414	2.772854	3.065071

H	3.888593	4.085514	5.149810
C	0.211419	2.840059	0.787953
C	-0.844122	3.679809	1.239859
H	2.198528	2.114717	1.131315
H	0.073081	2.255963	-0.123228
C	-1.781476	5.358730	2.860952
C	-1.679234	6.762093	2.578602
C	-2.890910	4.877681	3.552435
C	-0.578722	7.310259	1.861267
C	-2.717932	7.649007	3.018537
C	-3.917867	5.765964	3.977290
C	-0.507826	8.661729	1.599289
H	0.212441	6.644817	1.515383
C	-2.611383	9.037419	2.735167
C	-3.829407	7.113295	3.722549
H	-4.784522	5.370584	4.512696
C	-1.530326	9.535602	2.041391
H	0.343700	9.062950	1.045054
H	-3.407066	9.704283	3.076278
H	-4.619190	7.789703	4.058193
H	-1.460096	10.604545	1.827942
P	-2.470366	3.542904	0.406879
P	-3.179905	3.077851	3.734844
Pd	-3.873439	2.148214	1.733152
H	-3.946563	3.059795	4.930201
H	-1.952738	2.610972	4.270318
H	-2.833386	4.896134	0.193256
H	-2.114738	3.141998	-0.902918
H	-3.705114	0.336485	-3.918573
C	-2.125479	1.408461	-3.598670
C	-0.834595	1.828931	-4.262202
H	-0.354471	2.637842	-3.696621
H	-0.159174	0.957505	-4.285548
H	-1.009556	2.135722	-5.303244
O	-2.904909	0.732632	-4.394744
O	-2.371364	1.671709	-2.425866

TS2a[*R*,*S*]

C	-4.879536	0.407143	1.586722
C	-4.429982	0.494732	0.232174
C	-5.044257	1.540270	-0.662485
C	-6.277491	2.250542	-0.136294
C	-7.086010	1.378653	0.818065
C	-6.232279	0.953087	2.013120
H	-4.516049	-0.426951	2.186557
H	-5.927285	3.168908	0.372840
H	-6.862904	2.575303	-1.008023
H	-7.986488	1.912152	1.161721
H	-7.414508	0.484593	0.267042
H	-6.105475	1.803953	2.705119
H	-6.756570	0.176274	2.594574
O	-4.547312	1.841928	-1.733347
C	-3.313685	-0.210125	-0.323452
H	-2.924351	0.257480	-1.225309
C	-2.330301	-1.055868	0.380691
C	-0.987702	-0.943856	-0.038093
C	-2.640048	-1.968284	1.406515
C	0.014873	-1.681508	0.588245
H	-0.759421	-0.273806	-0.868567
C	-1.634243	-2.707755	2.025124
H	-3.678119	-2.138317	1.691057
C	-0.302011	-2.558529	1.628504
H	1.048667	-1.584789	0.247915
H	-1.894035	-3.419075	2.812529
H	0.482836	-3.142894	2.114560
C	-5.343709	-1.040650	-2.313135
C	-4.277004	-1.829643	-1.691911
H	-4.632748	-2.448318	-0.868332
C	-3.043073	-2.210606	-2.292083
C	-2.474456	-3.599138	-1.909981
C	-5.321451	-0.736579	-3.782061
C	-4.876195	-1.672539	-4.727118
C	-5.836073	0.490366	-4.225709
C	-4.926820	-1.378099	-6.089650

H	-4.499515	-2.642513	-4.400206
C	-5.868386	0.791559	-5.585591
H	-6.181469	1.210372	-3.485727
C	-5.412904	-0.141521	-6.521425
H	-4.582516	-2.117225	-6.817049
H	-6.249334	1.760045	-5.919345
H	-5.439646	0.093517	-7.588592
F	-2.792643	-4.470237	-2.890847
F	-1.145688	-3.582816	-1.797749
F	-2.977745	-4.093788	-0.765404
O	-2.346598	-1.576763	-3.094521
O	-6.295583	-0.657342	-1.629683
C	0.853210	5.771348	6.136784
C	0.073510	5.555670	5.020519
C	0.384211	4.512876	4.102579
C	1.525850	3.685439	4.368843
C	2.309768	3.937387	5.527194
C	1.983409	4.957852	6.393558
H	0.598472	6.576742	6.829526
H	-0.794624	6.187615	4.830785
C	-0.409672	4.259858	2.935383
C	1.836937	2.632259	3.467724
H	3.178494	3.302823	5.719529
H	2.593591	5.141437	7.280796
C	1.062803	2.404139	2.355093
C	-0.068472	3.220623	2.073204
H	2.705127	2.000884	3.672234
H	1.311859	1.584114	1.677801
C	-1.618265	5.103779	2.671607
C	-1.471547	6.399033	2.076018
C	-2.888712	4.635473	2.997456
C	-0.199785	6.921182	1.707976
C	-2.638259	7.197141	1.828683
C	-4.038933	5.432726	2.743257
C	-0.088518	8.167433	1.129435
H	0.691215	6.318645	1.887272
C	-2.486941	8.478986	1.234447
C	-3.914325	6.680623	2.180792
H	-5.029403	5.046963	2.996894
C	-1.240405	8.955941	0.891771
H	0.895685	8.550923	0.850923
H	-3.380697	9.080381	1.050770
H	-4.801469	7.290366	1.993250
H	-1.137056	9.942203	0.433772
P	-1.159684	2.730172	0.677064
P	-3.133965	2.891122	3.505869
Pd	-3.125591	1.678646	1.535576
H	-4.298683	3.011162	4.310977
H	-2.179993	2.720965	4.541870
H	-1.268395	3.928793	-0.069322
H	-0.238990	2.034594	-0.128941
H	-2.404845	-0.028319	-3.652431
C	-2.025083	1.814654	-3.221624
C	-2.363716	3.211326	-3.668304
H	-1.688889	3.937763	-3.197460
H	-2.329536	3.297826	-4.763260
H	-3.396293	3.409395	-3.340370
O	-2.496835	0.893314	-4.033995
O	-1.401234	1.573160	-2.197961

(*R*,*R*)-IIIa

C	-4.064946	0.494608	3.164160
C	-4.251099	0.624050	1.761107
C	-5.592056	0.904205	1.239497
C	-6.734916	1.010458	2.243933
C	-6.545552	0.034946	3.403284
C	-5.226194	0.301564	4.128814
H	-3.106337	0.103228	3.504384
H	-6.778756	2.048540	2.619263
H	-7.666270	0.826691	1.689340
H	-7.393059	0.097028	4.104380
H	-6.539052	-0.994056	3.002556
H	-5.336565	1.186774	4.779378
H	-4.988009	-0.535797	4.806540

O	-5.843480	1.017788	0.033685
C	-3.099245	0.370980	0.767863
H	-2.808198	1.322237	0.308782
C	-1.860989	-0.156062	1.468677
C	-0.818295	0.727101	1.772438
C	-1.736869	-1.497667	1.856425
C	0.324550	0.285241	2.442618
H	-0.900144	1.769188	1.467678
C	-0.588953	-1.947976	2.511431
H	-2.542588	-2.203363	1.641763
C	0.446199	-1.057278	2.807726
H	1.125990	0.994282	2.664419
H	-0.499873	-3.001666	2.785344
H	1.347280	-1.412350	3.312939
C	-2.350530	-1.151191	-1.117002
C	-3.564937	-0.498277	-0.442033
H	-4.274355	-1.262987	-0.115016
C	-4.231953	0.410063	-1.480478
C	-5.354638	-0.241297	-2.322600
C	-2.328901	-2.624589	-1.312052
C	-3.505068	-3.389979	-1.408442
C	-1.076961	-3.259428	-1.408674
C	-3.428187	-4.766809	-1.616156
H	-4.485446	-2.918093	-1.351237
C	-1.009475	-4.638824	-1.591194
H	-0.165170	-2.671300	-1.289859
C	-2.181782	-5.393543	-1.702627
H	-4.345354	-5.352760	-1.708815
H	-0.034201	-5.128259	-1.642914
H	-2.124948	-6.474624	-1.852891
F	-6.156601	0.655873	-2.872550
F	-4.749463	-0.935925	-3.316248
F	-6.100676	-1.127366	-1.639062
O	-3.764626	1.455121	-1.858555
O	-1.410615	-0.444894	-1.445795
C	2.578971	4.833514	2.047034
C	1.246733	5.141650	2.223097
C	0.257779	4.646546	1.325651
C	0.682388	3.832639	0.222415
C	2.063688	3.536423	0.068439
C	2.993884	4.023061	0.961250
H	3.322120	5.216460	2.750520
H	0.934980	5.764370	3.062716
C	-1.138918	4.911484	1.506271
C	-0.290380	3.321634	-0.676054
H	2.362843	2.900924	-0.766430
H	4.052928	3.785343	0.835894
C	-1.629149	3.563407	-0.477682
C	-2.063318	4.351454	0.624692
H	0.035793	2.694189	-1.506026
H	-2.362412	3.111610	-1.147622
C	-1.581312	5.825235	2.609939
C	-1.531494	7.241918	2.378912
C	-2.036718	5.343819	3.835837
C	-1.081758	7.791069	1.144642
C	-1.953946	8.143663	3.411707
C	-2.457282	6.250964	4.849029
C	-1.048761	9.154852	0.946135
H	-0.763353	7.116163	0.350043
C	-1.904398	9.544081	3.175347
C	-2.414408	7.608882	4.644216
H	-2.816541	5.858708	5.803413
C	-1.461247	10.041986	1.969534
H	-0.701531	9.555490	-0.009057
H	-2.227400	10.220916	3.970383
H	-2.735020	8.294932	5.432192
H	-1.428292	11.120507	1.799017
P	-3.852746	4.336608	1.038987
P	-2.291841	3.544323	4.105057
Pd	-3.834607	2.591036	2.644975
H	-2.300596	3.531608	5.527562
H	-0.977623	3.034910	3.933712
H	-4.138731	5.711375	1.254506
H	-4.423791	4.200621	-0.253198

H	0.244725	-0.026688	-1.232697
C	1.917358	-0.573835	-0.485651
C	3.219516	-0.005931	0.018965
H	3.834475	-0.809115	0.441704
H	3.761452	0.481330	-0.807002
H	3.023884	0.763686	0.780043
O	1.120938	0.366137	-0.995938
O	1.630586	-1.749842	-0.443073

(*R*,*S*)-IIIa

C	-3.387308	-3.035034	1.691505
C	-4.656192	-3.162962	1.066635
C	-5.395709	-4.449088	1.148822
C	-4.717485	-5.568180	1.936278
C	-3.208762	-5.568015	1.687163
C	-2.559439	-4.246031	2.107309
H	-2.793736	-2.149391	1.451530
H	-4.930709	-5.425249	3.010697
H	-5.189863	-6.512742	1.630039
H	-2.728229	-6.412602	2.206851
H	-3.035071	-5.722907	0.608901
H	-2.384039	-4.243841	3.196021
H	-1.562417	-4.162219	1.642055
O	-6.480957	-4.618301	0.611211
C	-5.204550	-2.165308	0.040874
H	-5.881411	-2.746209	-0.596804
C	-6.014121	-1.029044	0.640012
C	-7.399059	-0.984147	0.441096
C	-5.411816	-0.019706	1.409567
C	-8.168975	0.040033	1.000202
H	-7.871662	-1.767983	-0.153811
C	-6.178029	1.000773	1.974208
H	-4.331878	-0.024461	1.570403
C	-7.560955	1.034788	1.769463
H	-9.248322	0.061483	0.829906
H	-5.693257	1.775070	2.573254
H	-8.159193	1.840861	2.201257
C	-3.383774	-2.850561	-1.525957
C	-4.085334	-1.633641	-0.898383
H	-3.367013	-1.033801	-0.334153
C	-4.707561	-0.773012	-1.987756
C	-4.097445	0.639133	-2.192685
C	-1.936993	-3.081096	-1.269673
C	-1.055131	-2.058850	-0.885912
C	-1.446116	-4.386380	-1.440077
C	0.290644	-2.344801	-0.656930
H	-1.407222	-1.031446	-0.800652
C	-0.105780	-4.673245	-1.194708
H	-2.142066	-5.162795	-1.760679
C	0.764922	-3.652058	-0.799134
H	0.974007	-1.542515	-0.370010
H	0.264671	-5.694050	-1.313067
H	1.817534	-3.874472	-0.608024
F	-4.320191	1.099627	-3.419121
F	-4.686148	1.476784	-1.316777
F	-2.778576	0.678350	-1.948026
O	-5.683894	-1.080229	-2.616776
O	-4.043008	-3.657452	-2.161435
C	-6.335027	-0.050297	9.932653
C	-6.264288	-0.988551	8.925103
C	-6.861199	-0.745511	7.655599
C	-7.536111	0.503327	7.446639
C	-7.593446	1.446861	8.507861
C	-7.007216	1.178657	9.725676
H	-5.869276	-0.255608	10.899363
H	-5.744240	-1.932120	9.092991
C	-6.799142	-1.700463	6.587197
C	-8.126264	0.760977	6.180497
H	-8.112022	2.393966	8.338459
H	-7.057800	1.912425	10.533415
C	-8.050325	-0.162698	5.165699
C	-7.386997	-1.406476	5.358388
H	-8.642977	1.710956	6.021710
H	-8.493960	0.057328	4.193633

C	-6.099636	-3.005778	6.812935
C	-6.783094	-4.059683	7.505889
C	-4.798515	-3.208499	6.358999
C	-8.118745	-3.913882	7.975833
C	-6.113307	-5.308660	7.729370
C	-4.147358	-4.453448	6.584767
C	-8.754564	-4.945222	8.633775
H	-8.638929	-2.970854	7.805576
C	-6.796302	-6.349500	8.414266
C	-4.783676	-5.470221	7.254985
H	-3.128591	-4.599938	6.217500
C	-8.088949	-6.174361	8.858582
H	-9.780916	-4.814275	8.984450
H	-6.276143	-7.296263	8.580408
H	-4.272498	-6.420591	7.427736
H	-8.604073	-6.982704	9.382556
P	-7.130819	-2.506722	3.907614
P	-3.986457	-2.002990	5.232806
Pd	-4.887794	-2.495641	3.148172
H	-2.631704	-2.189674	5.630368
H	-4.202443	-0.775691	5.914606
H	-7.685407	-3.727222	4.377461
H	-8.217057	-2.095991	3.095462
H	-4.484196	-3.139079	-3.825870
C	-3.591687	-1.783329	-4.809207
C	-3.576418	-1.108543	-6.152635
H	-2.649295	-0.534811	-6.271858
H	-3.700160	-1.834813	-6.967978
H	-4.430037	-0.411415	-6.188250
O	-4.462102	-2.781541	-4.744573
O	-2.909299	-1.419997	-3.867301

TS1a[*si,cis*]

C	-3.101315	-1.233635	-4.379847
C	-2.921263	0.006366	-3.805261
C	-2.753080	0.142942	-2.398202
C	-2.768646	-1.042107	-1.589337
C	-2.959127	-2.304273	-2.214171
C	-3.123343	-2.400994	-3.578786
H	-3.226444	-1.317680	-5.461876
H	-2.903039	0.899789	-4.429910
C	-2.561695	1.418976	-1.771866
C	-2.570347	-0.923556	-0.187856
H	-2.967782	-3.200680	-1.589139
H	-3.266930	-3.377575	-4.046874
C	-2.365553	0.302032	0.397254
C	-2.380191	1.485220	-0.391898
H	-2.557492	-1.829683	0.422084
H	-2.144451	0.368284	1.463112
C	-2.551297	2.656862	-2.616396
C	-3.795270	3.205057	-3.076258
C	-1.351110	3.274482	-2.965291
C	-5.050174	2.626820	-2.733953
C	-3.787368	4.379309	-3.900398
C	-1.360689	4.442199	-3.778693
C	-6.230651	3.176630	-3.186728
H	-5.068283	1.737822	-2.102935
C	-5.021932	4.917864	-4.353454
C	-2.541811	4.973653	-4.237933
H	-0.413237	4.919866	-4.040394
C	-6.219385	4.330965	-4.006427
H	-7.183394	2.718336	-2.911440
H	-5.003750	5.811182	-4.982888
H	-2.535626	5.866089	-4.868741
H	-7.162016	4.754748	-4.360255
P	-1.942667	3.068338	0.418156
P	0.233005	2.765870	-2.185163
Pd	0.275125	3.498193	0.092243
C	0.827870	4.181559	1.994671
C	2.091688	4.067538	1.270493
C	2.546991	5.243648	0.474480
C	1.777250	6.542964	0.710823
C	1.255512	6.670388	2.137779
C	0.291969	5.527628	2.458517

H	0.609974	3.342166	2.661580
H	2.454152	7.363312	0.431557
H	0.934539	6.565021	-0.004630
H	2.110153	6.637326	2.836127
H	0.763957	7.645068	2.286425
H	0.101581	5.482001	3.544263
H	-0.685806	5.733337	1.991396
O	3.461217	5.236772	-0.336395
C	2.740007	2.800636	1.414049
H	2.215570	2.179151	2.139665
C	4.070722	2.291398	1.123610
C	4.425297	1.107736	1.816572
C	5.013909	2.856872	0.241891
C	5.677063	0.527907	1.658162
H	3.689368	0.645047	2.478284
C	6.267970	2.267707	0.083619
H	4.740250	3.753755	-0.308369
C	6.606782	1.109907	0.787775
H	5.930687	-0.383031	2.205276
H	6.988185	2.717756	-0.603974
H	7.591658	0.654658	0.655159
O	1.791182	1.200352	0.087444
C	1.049292	0.429722	0.789217
O	0.482721	0.734501	1.853849
C	0.887001	-0.981067	0.218683
H	0.360454	-0.933446	-0.747381
H	1.879975	-1.415407	0.023622
H	0.322407	-1.623756	0.907066
H	-2.447573	2.855258	1.725336
H	-2.951945	3.945434	-0.058481
H	1.147304	3.133811	-3.208135
H	0.245410	1.365871	-2.381853

IIa[*si,cis*]

C	-5.444274	2.099649	0.926583
C	-4.190587	1.788178	0.444055
C	-3.281663	2.811995	0.055169
C	-3.695574	4.178970	0.185740
C	-4.994838	4.464772	0.684082
C	-5.853404	3.449355	1.046540
H	-6.127544	1.299160	1.219757
H	-3.883434	0.745573	0.356789
C	-1.967102	2.520886	-0.440857
C	-2.786652	5.210145	-0.176151
H	-5.300451	5.509821	0.778964
H	-6.849297	3.682702	1.430181
C	-1.532308	4.912159	-0.649080
C	-1.115178	3.560376	-0.800232
H	-3.098534	6.251665	-0.065149
H	-0.837942	5.715759	-0.897596
C	-1.513604	1.094414	-0.505887
C	-1.886124	0.272553	-1.618782
C	-0.754236	0.556142	0.532759
C	-2.644889	0.780181	-2.710516
C	-1.480173	-1.103431	-1.646544
C	-0.366972	-0.812301	0.495312
C	-2.984272	-0.030292	-3.772808
H	-2.953592	1.826197	-2.695962
C	-1.850136	-1.911767	-2.755288
C	-0.723628	-1.618883	-0.559718
H	0.209528	-1.229131	1.324550
C	-2.585770	-1.389041	-3.796809
H	-3.565310	0.377134	-4.603416
H	-1.538631	-2.959327	-2.767377
H	-0.429088	-2.671268	-0.573037
H	-2.863092	-2.020454	-4.644032
P	0.625618	3.204914	-1.267209
P	-0.067108	1.662083	1.827028
Pd	1.846308	2.830018	1.047217
C	3.362529	1.345218	0.793091
C	3.931382	2.497590	1.442364
C	4.432980	2.403797	2.854937
C	4.345309	1.034795	3.515976
C	3.210288	0.152397	3.005105

C	3.291062	0.009637	1.487262
H	3.461702	1.292510	-0.297214
H	5.317714	0.542787	3.320589
H	4.296231	1.203199	4.601407
H	3.250074	-0.836635	3.488114
H	2.249218	0.609988	3.285612
H	4.195617	-0.572789	1.221608
H	2.441874	-0.566648	1.088096
O	4.976716	3.329573	3.419895
C	3.847088	3.689217	0.655927
H	3.940971	3.517598	-0.421818
C	4.032787	5.097073	1.029146
C	4.527791	5.976083	0.047643
C	3.660339	5.632824	2.277835
C	4.686517	7.337075	0.309461
H	4.796340	5.579796	-0.935524
C	3.813044	6.991152	2.535822
H	3.237933	4.984381	3.041558
C	4.331131	7.849270	1.558404
H	5.082789	7.998188	-0.465069
H	3.517961	7.387884	3.510138
H	4.448205	8.915189	1.769144
O	0.427450	3.916714	3.523507
C	0.404056	4.803368	2.662011
O	0.848449	4.682721	1.457638
C	-0.193743	6.168546	2.966455
H	-0.506526	6.231967	4.016824
H	0.542376	6.955512	2.741307
H	-1.063129	6.338931	2.311091
H	0.919798	4.410730	-1.957876
H	0.420013	2.399683	-2.425692
H	-1.184913	2.441568	2.175444
H	-0.018521	0.786028	2.938053

TS2a[*R*,*R*]_conf2

C	-4.658877	1.855377	-0.155498
C	-5.060303	0.699047	0.602720
C	-6.501973	0.480979	0.905542
C	-7.482096	1.571435	0.486436
C	-6.880842	2.945015	0.204671
C	-5.673239	2.810339	-0.719697
H	-3.706008	1.805737	-0.689093
H	-7.958801	1.178040	-0.428579
H	-8.271398	1.603324	1.252675
H	-7.643054	3.608565	-0.233721
H	-6.556747	3.415301	1.151761
H	-5.990410	2.426009	-1.707990
H	-5.195812	3.785237	-0.904362
O	-6.938556	-0.547240	1.397189
C	-3.977637	-0.223947	0.904667
H	-3.042706	0.131288	0.468357
C	-3.740326	-1.094078	2.068442
C	-2.397908	-1.180787	2.497767
C	-4.718538	-1.806667	2.787845
C	-2.042819	-1.922657	3.620541
H	-1.631740	-0.635227	1.950115
C	-4.356242	-2.559158	3.905324
H	-5.752318	-1.754562	2.454168
C	-3.024906	-2.618836	4.329598
H	-0.998661	-1.957909	3.933875
H	-5.127417	-3.108110	4.451418
H	-2.752647	-3.209635	5.207505
C	-2.377682	-1.964452	-0.651889
C	-3.828544	-1.824575	-0.762561
H	-4.462448	-2.587871	-0.322854
C	-4.429188	-1.054701	-1.799748
C	-5.929795	-1.321657	-2.087067
C	-1.828855	-3.102890	0.168924
C	-0.437142	-3.139161	0.360379
C	-2.622701	-4.067280	0.808453
C	0.145088	-4.097460	1.184956
H	0.161985	-2.381833	-0.146921
C	-2.041039	-5.026351	1.638318
H	-3.704939	-4.066721	0.686285

C	-0.658443	-5.041418	1.834113
H	1.228464	-4.109966	1.329115
H	-2.674166	-5.759746	2.142622
H	-0.206292	-5.789305	2.490226
F	-6.623613	-0.166450	-2.065000
F	-6.069683	-1.850470	-3.310070
F	-6.514549	-2.154122	-1.214058
O	-3.938212	-0.174965	-2.510906
O	-1.596470	-1.148027	-1.139232
C	0.946396	-0.184467	5.844866
C	0.152498	0.881395	5.477541
C	-0.014019	1.231533	4.108089
C	0.672937	0.454798	3.115872
C	1.487474	-0.633782	3.528800
C	1.622089	-0.950236	4.863706
H	1.054417	-0.442499	6.900883
H	-0.367548	1.463905	6.238995
C	-0.862498	2.311385	3.695218
C	0.491594	0.775561	1.744099
H	1.996410	-1.224534	2.763429
H	2.246473	-1.793233	5.168330
C	-0.352050	1.790245	1.360259
C	-1.036819	2.567390	2.336226
H	1.005324	0.179622	0.986385
H	-0.534383	1.989211	0.303442
C	-1.526095	3.167829	4.730919
C	-0.770874	4.229488	5.332767
C	-2.850229	2.960551	5.111240
C	0.582413	4.491760	4.976639
C	-1.391851	5.067244	6.318196
C	-3.453544	3.801531	6.087614
C	1.282262	5.522899	5.565732
H	1.063067	3.864716	4.225424
C	-0.640541	6.119644	6.908140
C	-2.744573	4.822346	6.674575
H	-4.493558	3.629487	6.374293
C	0.668414	6.344578	6.542022
H	2.319619	5.708610	5.277902
H	-1.123138	6.750476	7.658845
H	-3.217202	5.458882	7.426712
H	1.235657	7.157008	7.001908
P	-2.352669	3.710971	1.746837
P	-3.883644	1.726057	4.226235
Pd	-4.155720	2.216186	1.907252
H	-4.957532	1.619804	5.148913
H	-3.230454	0.506973	4.536028
H	-2.116122	4.877431	2.521451
H	-1.809988	4.136837	0.510938
H	-2.424591	0.442578	-2.789533
C	-1.179665	1.863352	-2.445545
C	0.142808	2.412904	-2.922666
H	0.326917	3.401845	-2.484594
H	0.941775	1.723748	-2.601779
H	0.175350	2.462248	-4.020385
O	-1.621671	0.884887	-3.195059
O	-1.746177	2.286508	-1.446238

TS2a[*R*,*S*]_conf2

C	-4.646104	1.163740	-0.237691
C	-4.807960	-0.017649	0.578076
C	-6.164634	-0.413903	1.056944
C	-7.325070	0.471151	0.628950
C	-6.964041	1.924206	0.335781
C	-5.826670	1.980701	-0.680559
H	-3.759255	1.200989	-0.873338
H	-7.725721	-0.002213	-0.286043
H	-8.106798	0.370460	1.396066
H	-7.848183	2.466482	-0.034406
H	-6.647858	2.429108	1.267479
H	-6.176184	1.579255	-1.650852
H	-5.506326	3.016966	-0.872437
O	-6.383506	-1.429668	1.696598
C	-3.565582	-0.703581	0.828705
H	-2.765238	-0.338294	0.178322

C	-3.049504	-1.481633	1.953931
C	-1.644421	-1.440041	2.110405
C	-3.815596	-2.167311	2.919187
C	-1.028409	-2.033975	3.207645
H	-1.043216	-0.920831	1.363925
C	-3.189584	-2.767983	4.008547
H	-4.893835	-2.219764	2.787737
C	-1.800089	-2.699764	4.163502
H	0.055855	-1.975537	3.316494
H	-3.794072	-3.300306	4.746909
H	-1.319698	-3.168887	5.025470
C	-4.159089	-1.653531	-1.909862
C	-3.575702	-2.565229	-0.951437
H	-4.215967	-3.295779	-0.465988
C	-2.185485	-2.773390	-0.808071
C	-1.780694	-4.060238	-0.042653
C	-5.660351	-1.695009	-2.104229
C	-6.203633	-0.830362	-3.069713
C	-6.532294	-2.513769	-1.370096
C	-7.577489	-0.781409	-3.296209
H	-5.508197	-0.203529	-3.629874
C	-7.910560	-2.463145	-1.591424
H	-6.151713	-3.177386	-0.595477
C	-8.437775	-1.598718	-2.553880
H	-7.983019	-0.104730	-4.052670
H	-8.574854	-3.096643	-0.999365
H	-9.516458	-1.560797	-2.725168
F	-1.662471	-5.083046	-0.910694
F	-0.604017	-3.918225	0.574290
F	-2.683021	-4.432272	0.886183
O	-1.228308	-2.097009	-1.217159
O	-3.510129	-0.826059	-2.553023
C	1.398757	0.823879	6.241477
C	0.411524	1.625479	5.709176
C	0.256162	1.755237	4.300091
C	1.155851	1.037723	3.443545
C	2.166950	0.226026	4.025322
C	2.286276	0.117217	5.394035
H	1.498277	0.732138	7.325502
H	-0.268554	2.165324	6.369025
C	-0.783212	2.553174	3.718141
C	0.994761	1.141170	2.036469
H	2.846898	-0.316498	3.363667
H	3.064926	-0.513462	5.829096
C	-0.016454	1.895596	1.492195
C	-0.916913	2.608392	2.332036
H	1.675263	0.589429	1.383123
H	-0.168950	1.916674	0.413396
C	-1.728200	3.290982	4.615518
C	-1.351686	4.566035	5.149699
C	-2.967229	2.742966	4.938018
C	-0.099207	5.171573	4.848937
C	-2.263271	5.265631	6.009254
C	-3.863142	3.447188	5.788872
C	0.233726	6.402593	5.372151
H	0.597676	4.646623	4.194672
C	-1.886645	6.531835	6.533535
C	-3.518161	4.671749	6.310768
H	-4.833656	3.007423	6.030616
C	-0.665664	7.089937	6.223302
H	1.199195	6.852698	5.129944
H	-2.586268	7.057040	7.188557
H	-4.210138	5.203761	6.968307
H	-0.387708	8.064026	6.632141
P	-2.403310	3.363101	1.553883
P	-3.529342	1.218241	4.088091
Pd	-3.947730	1.596855	1.751517
H	-4.541195	0.785680	4.983752
H	-2.528567	0.275186	4.426594
H	-2.478253	4.625569	2.198490
H	-1.884400	3.777172	0.304463
H	-1.086240	-0.807409	-2.139790
C	-1.141628	1.110220	-2.262628
C	-0.962387	2.236094	-3.252267

H	-0.969226	3.207284	-2.741429
H	-0.036594	2.107356	-3.831113
H	-1.803059	2.200074	-3.964865
O	-0.792609	-0.050280	-2.744209
O	-1.588279	1.295204	-1.133975

TS1a[*re*,*cis*]

C	-5.465329	-0.849413	2.097981
C	-4.193726	-1.078454	1.616874
C	-3.486049	-0.067402	0.906694
C	-4.124895	1.201506	0.708521
C	-5.437656	1.402719	1.214491
C	-6.096788	0.401223	1.893742
H	-5.990507	-1.638441	2.641408
H	-3.715734	-2.044781	1.780414
C	-2.161501	-0.274862	0.394878
C	-3.420671	2.224148	0.018341
H	-5.915269	2.373008	1.056131
H	-7.105442	0.569402	2.278291
C	-2.145409	2.017887	-0.451168
C	-1.505661	0.759166	-0.272101
H	-3.905466	3.193148	-0.126286
H	-1.586032	2.823186	-0.929617
C	-1.505542	-1.606567	0.595827
C	-1.870430	-2.709985	-0.245285
C	-0.544252	-1.787601	1.587112
C	-2.832133	-2.579675	-1.286357
C	-1.245585	-3.986361	-0.047888
C	0.074510	-3.056102	1.767946
C	-3.162568	-3.655039	-2.083127
H	-3.305942	-1.611394	-1.449175
C	-1.612347	-5.075014	-0.884247
C	-0.271835	-4.125341	0.977644
H	0.832159	-3.178528	2.545943
C	-2.551017	-4.915815	-1.880414
H	-3.901899	-3.534455	-2.878295
H	-1.132206	-6.043644	-0.723967
H	0.202474	-5.098250	1.128353
H	-2.823839	-5.759996	-2.517830
P	0.264616	0.586880	-0.749325
P	0.124944	-0.356498	2.516945
Pd	1.608409	0.808158	1.220338
C	3.258719	1.152252	2.500992
C	3.643442	1.650205	1.196129
C	4.355885	0.732331	0.248499
C	4.685683	-0.649786	0.810166
C	5.075811	-0.597302	2.285140
C	3.923224	-0.060681	3.135477
H	2.931356	1.921853	3.207288
H	3.793119	-1.287901	0.675289
H	5.484277	-1.065049	0.179156
H	5.386651	-1.593284	2.639406
H	5.953053	0.064081	2.396439
H	3.187224	-0.865068	3.303393
H	4.291323	0.215996	4.138335
O	4.706618	1.030653	-0.878648
C	3.456022	3.053758	0.958621
H	3.536549	3.669226	1.853146
C	3.563393	3.805286	-0.270710
C	3.969679	5.154457	-0.174920
C	3.209550	3.293940	-1.536167
C	4.084729	5.948706	-1.310515
H	4.201811	5.570181	0.808643
C	3.314406	4.093447	-2.668762
H	2.834538	2.279590	-1.612940
C	3.759623	5.414572	-2.562333
H	4.416821	6.985596	-1.223547
H	3.033773	3.688514	-3.643322
H	3.837733	6.037515	-3.457086
O	1.385110	3.541436	1.565297
C	0.549195	3.928941	0.678115
O	0.466819	3.493941	-0.483307
C	-0.456867	4.980648	1.144719
H	-0.042135	5.604909	1.948475

H	-0.779186	5.603721	0.297844
H	-1.345732	4.461394	1.542050
H	0.344147	1.406579	-1.895050
H	0.225268	-0.685106	-1.384672
H	-1.047342	0.279489	3.001476
H	0.523017	-1.002404	3.719295

IIa[*re,cis*]

C	-5.579598	1.957913	0.748997
C	-4.323053	1.683857	0.251544
C	-3.387322	2.729401	0.013827
C	-3.776818	4.076940	0.312492
C	-5.079832	4.324631	0.821457
C	-5.964626	3.289678	1.035214
H	-6.284003	1.141541	0.924839
H	-4.033285	0.655191	0.034890
C	-2.070235	2.474479	-0.494448
C	-2.840710	5.125501	0.100706
H	-5.367377	5.355157	1.044903
H	-6.963190	3.493271	1.428760
C	-1.583207	4.862358	-0.384992
C	-1.190013	3.532147	-0.701961
H	-3.134637	6.151269	0.337043
H	-0.869285	5.676379	-0.517689
C	-1.639872	1.061291	-0.739519
C	-1.998643	0.398874	-1.957243
C	-0.896655	0.384201	0.226835
C	-2.745286	1.049003	-2.979945
C	-1.586877	-0.960083	-2.165650
C	-0.493444	-0.962009	0.008165
C	-3.070103	0.389455	-4.146018
H	-3.057287	2.083142	-2.828130
C	-1.941570	-1.610579	-3.378656
C	-0.834897	-1.613901	-1.153109
H	0.094025	-1.479095	0.767215
C	-2.666936	-0.953176	-4.348516
H	-3.642738	0.904611	-4.920812
H	-1.625776	-2.646132	-3.528871
H	-0.521109	-2.648791	-1.309989
H	-2.932339	-1.464665	-5.276667
P	0.555347	3.208669	-1.179158
P	-0.240230	1.298360	1.673210
Pd	1.690807	2.555909	1.109408
C	3.735421	3.350307	1.023599
C	3.695113	2.077213	1.663478
C	3.983920	1.985035	3.137412
C	3.882094	3.289103	3.900792
C	4.596551	4.419818	3.152413
C	3.998561	4.640559	1.759578
H	3.897599	3.360679	-0.058659
H	2.807396	3.518857	4.019239
H	4.307625	3.122603	4.900222
H	4.544930	5.351896	3.736709
H	5.667380	4.165867	3.059538
H	3.038296	5.178740	1.848236
H	4.659319	5.281860	1.153954
O	4.315419	0.941787	3.662282
C	3.190173	1.026534	0.813352
H	3.444947	1.161761	-0.243412
C	2.879490	-0.384381	1.120084
C	2.984496	-1.312476	0.066789
C	2.425469	-0.855648	2.368379
C	2.675352	-2.660959	0.249458
H	3.313513	-0.964524	-0.915591
C	2.111269	-2.200502	2.549508
H	2.318187	-0.167014	3.202501
C	2.236530	-3.113076	1.494858
H	2.772269	-3.357396	-0.586845
H	1.764340	-2.541714	3.527828
H	1.990623	-4.166801	1.645649
O	0.280493	3.419804	3.679332
C	0.268374	4.386713	2.911325
O	0.781787	4.403018	1.725882
C	-0.419581	5.684235	3.310967

H	-0.622676	5.698442	4.389820
H	0.186323	6.555885	3.022206
H	-1.375455	5.754809	2.765850
H	0.844509	4.456548	-1.795998
H	0.361796	2.474984	-2.384181
H	-1.371829	1.994789	2.142868
H	-0.146446	0.272142	2.640646

TS2a[*S,R*]_conf2

C	-5.256606	1.256385	1.255886
C	-4.886602	1.357090	-0.137011
C	-5.825366	2.049964	-1.064300
C	-6.927863	2.854814	-0.395091
C	-7.622025	2.016979	0.681125
C	-6.641823	1.588700	1.776160
H	-4.715418	0.500442	1.828456
H	-6.478012	3.759193	0.055192
H	-7.623651	3.176362	-1.182156
H	-8.465241	2.576044	1.116423
H	-8.050643	1.122723	0.205644
H	-6.564131	2.379038	2.541805
H	-7.035882	0.703042	2.300927
O	-5.771112	1.956505	-2.279727
C	-3.649586	0.708265	-0.503866
H	-3.195240	0.207913	0.353656
C	-2.649272	1.023800	-1.534685
C	-1.317423	0.682346	-1.204189
C	-2.892344	1.640792	-2.776825
C	-0.269227	0.950380	-2.081431
H	-1.122422	0.198497	-0.246643
C	-1.836289	1.916863	-3.643670
H	-3.916344	1.877050	-3.054574
C	-0.523515	1.574105	-3.305499
H	0.748866	0.659028	-1.812867
H	-2.044373	2.392506	-4.605173
H	0.295783	1.782273	-3.997864
C	-5.090554	-1.696532	-0.048599
C	-4.181947	-1.513142	-1.147610
H	-4.602871	-1.352433	-2.136021
C	-2.836094	-2.020010	-1.115089
C	-2.207302	-2.308765	-2.507465
C	-6.562249	-1.511519	-0.306507
C	-7.084745	-1.005739	-1.508366
C	-7.452366	-1.847016	0.727965
C	-8.462480	-0.851384	-1.673341
H	-6.423269	-0.694193	-2.314990
C	-8.827751	-1.699117	0.561588
H	-7.029072	-2.226538	1.658807
C	-9.338165	-1.202447	-0.643072
H	-8.849982	-0.444643	-2.610086
H	-9.507612	-1.970993	1.372798
H	-10.416345	-1.083047	-0.775032
F	-0.875049	-2.245370	-2.465804
F	-2.547004	-3.549920	-2.906368
F	-2.628520	-1.457410	-3.462994
O	-2.145893	-2.267512	-0.137979
O	-4.741932	-1.970240	1.114203
C	1.291200	4.109945	6.010124
C	0.377294	4.542382	5.072995
C	0.351961	3.983132	3.764003
C	1.303026	2.958723	3.440067
C	2.233527	2.538818	4.429022
C	2.229546	3.099747	5.687544
H	1.292046	4.548928	7.010496
H	-0.342669	5.319570	5.331231
C	-0.599000	4.399145	2.774416
C	1.283308	2.388688	2.139698
H	2.953113	1.757524	4.171902
H	2.948389	2.766818	6.439657
C	0.359504	2.792169	1.206433
C	-0.595385	3.798359	1.517485
H	2.011077	1.612491	1.890935
H	0.344443	2.332262	0.218460
C	-1.581954	5.477169	3.114484

C	-1.168005	6.849252	3.060100
C	-2.886608	5.164629	3.489298
C	0.148558	7.227001	2.672773
C	-2.104897	7.882539	3.397013
C	-3.807420	6.198823	3.816303
C	0.518132	8.554213	2.624927
H	0.866383	6.449302	2.410572
C	-1.689791	9.240395	3.340450
C	-3.424733	7.518178	3.776413
H	-4.828850	5.938379	4.104182
C	-0.406579	9.571711	2.963309
H	1.532792	8.824586	2.323711
H	-2.410303	10.019788	3.600712
H	-4.136506	8.305529	4.036426
H	-0.099324	10.619167	2.922786
P	-1.962968	4.096035	0.326120
P	-3.508573	3.447820	3.337030
Pd	-3.796705	2.809917	1.119833
H	-4.556147	3.470204	4.296750
H	-2.561185	2.691183	4.068241
H	-1.977770	5.512381	0.230663
H	-1.317391	3.800378	-0.900963
H	-3.340198	-2.010339	1.966797
C	-1.991716	-0.943712	2.840301
C	-0.813515	-1.067590	3.776318
H	-0.500698	-0.078597	4.133601
H	-1.049001	-1.731744	4.620083
H	0.021772	-1.525238	3.220617
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O	-2.273309	0.105722	2.276026

TS2a[*S*,*S*]_conf2

C	-5.288052	1.269129	1.141914
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C	-6.907999	2.688848	-0.734716
C	-7.630446	1.901334	0.360702
C	-6.704235	1.639843	1.550906
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H	-2.660253	-1.137882	-5.913185
H	0.723078	-3.195361	-4.199594

H	-0.427407	-2.212661	-6.183927
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F	-6.758995	-3.080364	-0.341647
O	-4.359787	-2.095414	1.220749
O	-1.981046	-2.366048	-0.328744
C	1.027505	3.973017	6.183507
C	0.172908	4.439829	5.207679
C	0.203410	3.901155	3.890225
C	1.150259	2.863441	3.598152
C	2.018919	2.407834	4.626596
C	1.960136	2.947895	5.892919
H	0.985004	4.395646	7.189974
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C	-0.690491	4.348902	2.861997
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C	0.312467	2.744440	1.320213
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H	0.336676	2.297847	0.326625
C	-1.664004	5.445507	3.167714
C	-1.217099	6.808086	3.142294
C	-2.990607	5.159939	3.481690
C	0.123729	7.158332	2.817334
C	-2.144783	7.860203	3.444520
C	-3.901685	6.212821	3.774788
C	0.524766	8.477092	2.796027
H	0.835091	6.366305	2.581747
C	-1.697223	9.208613	3.416663
C	-3.488173	7.523381	3.761654
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H	1.557802	8.726250	2.542770
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P	-1.949962	4.091129	0.352481
P	-3.641624	3.458168	3.289349
Pd	-3.829598	2.820868	1.056674
H	-4.732402	3.499826	4.198831
H	-2.746023	2.675760	4.057235
H	-1.934119	5.507950	0.262013
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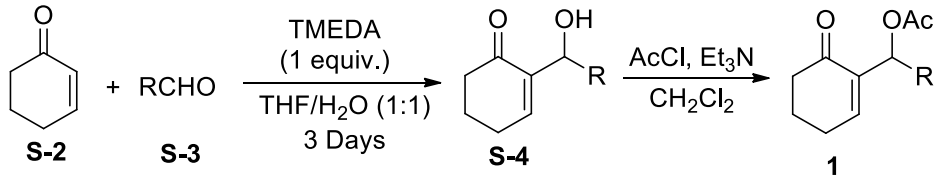
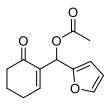
H	-2.821788	-2.043439	1.905973
C	-1.707549	-0.779406	2.834497
C	-0.543814	-0.706278	3.793863
H	-0.401601	0.321549	4.147661
H	-0.695992	-1.392262	4.639966
H	0.367952	-1.035727	3.269270
O	-2.085491	-2.010527	2.586603
O	-2.214650	0.217077	2.336997

5. Experimental procedures and characterization data

5.1 General procedure for the synthesis of Morita-Baylis-Hillman acetate 1

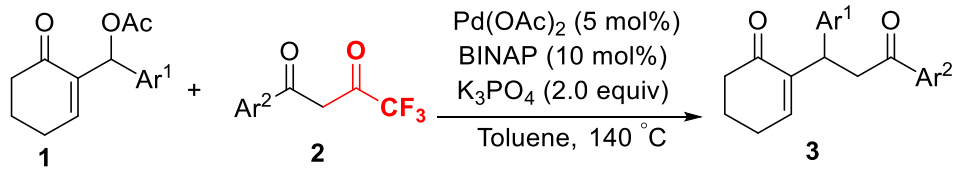


Morita-Baylis-Hillman acetates **1** were synthesized according to the reported procedure. Cyclohexenone **S-2** (30 mmol), benzylaldehyde (15 mmol) and *N*,*N*,*N'*,*N'*-tetramethyl-1,3-propanediamine (15 mmol) were dissolved in THF/H_2O (30 mL, V/V = 1:1). The mixture was then stirred at room temperature for three days before saturated NH_4Cl (aq) solution was added. The resulting mixture was extracted with EtOAc twice. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified *via* flash column chromatography (Petroleum Ether/EtOAc = 1:5-1:3) over silica gel to give Morita-Baylis-Hillman alcohol **S-4** as yellow oil. To a solution of Morita-Baylis-Hillman alcohol **S-4** (1.0 equiv.) in CH_2Cl_2 was added Et_3N (2.0 equiv.). Then acetyl chloride (1.5 equiv.) was added dropwise under ice bath over 30 minutes. The mixture was stirred at room temperature for 12 h.Then the reaction solution was filtered and concentrated under reduced pressure. The residue was purified through silica gel flash column chromatography (Petroleum Ether/EtOAc = 1:9-1:5) to yield Morita-Baylis-Hillman acetate **1**.



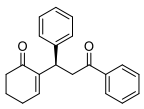
2-[(acetyloxy)(2-furyl)methyl]-2-cyclohexen-1-one **1e**: Colorless oil (1.7 g, 7.4 mmol, 49% yield over two steps); IR (KBr) ν 3121, 2947, 1742, 1675, 1370, 1227, 1017, 920, 749 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.37 (m, 1H), 7.12 (t, *J* = 4.2 Hz, 1H), 6.79 (s, 1H), 6.28-6.32 (m, 2H), 2.44-2.49 (m, 4H), 2.08 (s, 3H), 1.99-2.06 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.6, 169.4, 151.1, 147.1, 142.8, 136.1, 110.4, 109.3, 64.8, 38.1, 29.7, 25.8, 22.5, 21.0; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{13}H_{14}O_4Na$ 257.0790, found 257.0796.

5.2 Experimental procedure for the synthesis of 3

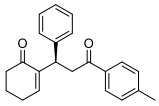


1 2 3

To a solution of Morita-Baylis-Hillman acetate **1** (0.4 mmol, 2.0 equiv.) and 1,3-dione **2** (0.2 mmol, 1.0 equiv.) in toluene was added $Pd(OAc)_2$ (0.01 mmol, 2.2 mg, 5 mol%), *S*-BINAP (0.02 mmol, 12.5 mg, 10 mol%) and K_3PO_4 or K_2CO_3 (0.4 mmol, 2.0 equiv.) respectively. The mixture was sequentially stirred at room temperature for five minutes and then at the given temperature for the specified time. After the reaction was completed, the mixture was cooled to room temperature, evaporated and purified by flash column chromatography (Petroleum Ether/EtOAc = 1:19-1:9) over silica gel to give the product **3**.

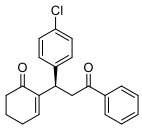


2-[(2-*oxo*-2-phenylethyl)(phenyl)methyl]-2-cyclohexen-1-one **3a**: Colorless oil (39.5 mg, 0.13 mmol, 65% yield, 88.5:11.5 er); $[\alpha]_D^{20}$= +43.4 (c=0.05 in CH_2Cl_2) (*R*-**3a,** 88.5:11.5 er); $[\alpha]_D^{20}$= -26.1 (c=0.04 in CH_2Cl_2) (*S*-**3a,** 23:77 er); IR (KBr) ν 3060, 2923, 1739, 1674, 1449, 1245, 983, 751 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.94-7.96 (m, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.24-7.29 (m, 4H), 7.15-7.20 (m, 1H), 6.71 (t, *J* = 4.2 Hz, 1H), 4.64 (t, *J* = 7.4 Hz, 1H), 3.62 (dd, *J* = 16.8, 7.2 Hz, 1H), 3.45 (dd, *J* = 16.8, 7.6 Hz, 1H), 2.33-2.47 (m, 4H), 1.90-1.99 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.5, 198.3, 146.0, 145.9, 142.4, 141.7, 136.9, 133.1, 128.6, 128.4, 128.2, 128.0, 126.5, 43.0, 40.5, 38.8, 26.2, 22.7; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{21}H_{20}O_2Na$ 327.1361, found 327.1349; HPLC analysis: (CHIRALCEL OD-H, 10% *i*-propanol/hexane, 1 mL/min, UV: 254 nm), t_R = 8.5 min (major), 9.2 min (minor).

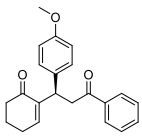


2-[(2-*oxo*-2-(4-methylphenyl)ethyl)(phenyl)methyl]-2-cyclohexen-1-one **3b**: Colorless oil (45.2 mg, 0.14 mmol, 71% yield, 87.5:12.5 er); $[\alpha]_D^{20}$= +21.2 (c=0.06 in CH_2Cl_2); IR (KBr) ν 3029, 2924, 1674, 1605, 1493, 1249, 1177, 977, 814 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, *J* = 8.4 Hz, 2H),7.22-7.29 (m, 6H), 7.15-7.19 (m, 1H), 6.71 (t, *J* = 3.6 Hz, 1H), 4.62 (t, *J* = 7.2 Hz, 1H), 3.59 (dd, *J* = 16.4,

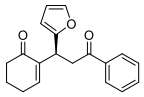
7.2 Hz, 1H), 3.41 (dd, *J* = 16.8, 7.6 Hz, 1H), 2.34-2.44 (m, 7H), 1.89-1.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.4, 197.9, 145.8, 143.8, 142.6, 141.7, 134.5, 129.3, 128.4, 128.3, 128.0, 126.4, 42.8, 40.6, 38.8, 25.2, 22.7, 21.7; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{22}H_{22}O_2Na$ 341.1517, found 341.1508; HPLC analysis: (CHIRALCEL OD-H, 5% *i*-propanol/hexane, 1 mL/min, UV: 254 nm), t_R = 17.9 min (major), 19.8 min (minor).



2-[(2-*oxo*-2-phenylethyl)(4-chlorophenyl)methyl]-2-cyclohexen-1-one **3c**: White solid (49.4 mg, 0.15 mmol, 73% yield, 82:18 er); m.p. 85-86 ℃; $[\alpha]_D^{20}$= +8.2 (c=0.06 in CH_2Cl_2); IR (KBr) ν 3065, 2925, 1673, 1478, 1351, 1248, 1048, 919, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92-7.95 (m, 2H), 7.53-7.57 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.18-7.23 (m, 4H), 6.72 (t, *J* = 4.2 Hz, 1H), 4.59 (t, *J* = 7.4 Hz, 1H), 3.60 (dd, *J* = 16.8, 6.8 Hz, 1H), 3.43 (dd, *J* = 16.8, 8.0 Hz, 1H), 2.34-2.47 (m, 4H), 1.90-1.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.4, 198.0, 146.1, 141.4, 140.9, 136.8, 133.2, 132.1, 129.4, 128.6, 128.5, 128.1, 58.4, 42.6, 40.1, 38.8, 26.1, 22.6, 18.4; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{21}H_{19}O_2ClNa$ 361.0971, found 361.0954; HPLC analysis: (CHIRALCEL OD-H, 10% *i*-propanol/hexane, 1 mL/min, UV: 254 nm), t_R = 10.4 min (major), 13.2 min (minor).

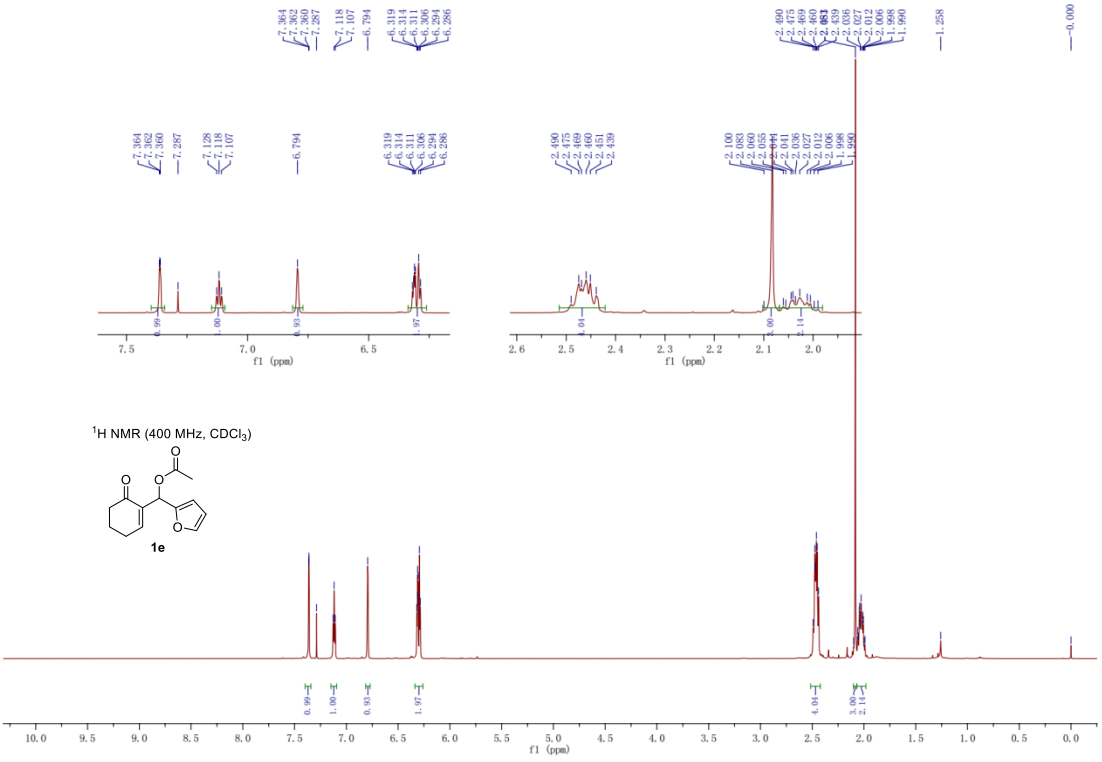


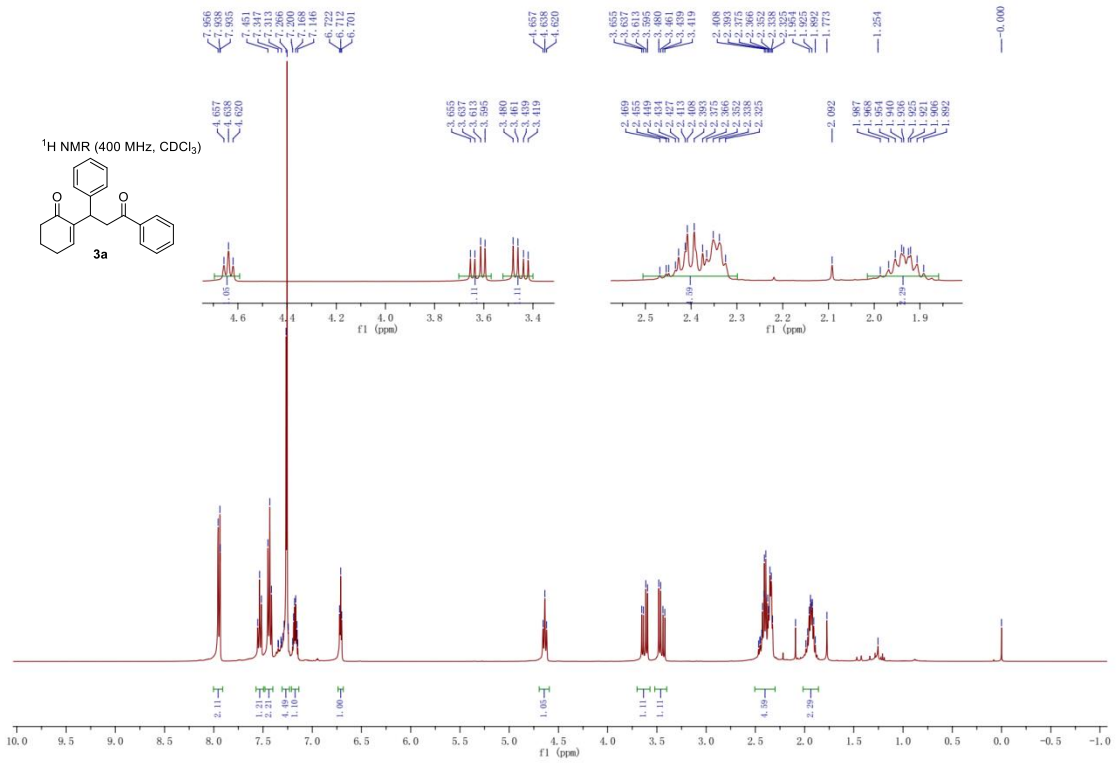
2-[(2-*oxo*-2-phenylethyl)(4-methoxylchlorophenyl)methyl]-2-cyclohexen-1-one **3d**: White solid (52.1 mg, 0.16 mmol, 78% yield, 85:15 er); m.p. 119-120 ℃; $[\alpha]_D^{20}$= +143.0 (c=0.04 in CH_2Cl_2) (*R*-**3l,** 98.5:1.5 er); $[\alpha]_D^{20}$= -131.4 (c=0.03 in CH_2Cl_2) (*S*-**3l,** 3:97% er); IR (KBr) ν 3449, 2925, 1662, 1511, 1323, 1244, 1029, 913, 824 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.70 (t, *J* = 4.0 Hz, 1H), 4.57 (t, *J* = 7.4 Hz, 1H), 3.76 (s, 3H), 3.60 (dd, *J* = 16.4, 6.8 Hz, 1H), 3.40 (dd, *J* = 16.4, 8.0 Hz, 1H), 2.33-2.43 (m, 4H), 1.90-1.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.6, 198.5, 158.1, 145.7, 141.9, 136.9, 134.3, 133.0, 129.0, 128.6, 128.2, 113.8, 43.1,40.0, 38.8, 26.1, 22.7, 18.4; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{22}H_{22}O_3Na$ 357.1467, found 357.1444; HPLC analysis: (CHIRALCEL OD-H, 10% *i*-propanol/hexane, 1 mL/min, UV: 254 nm), t_R = 14.2 min (major), 18.0 min (minor).

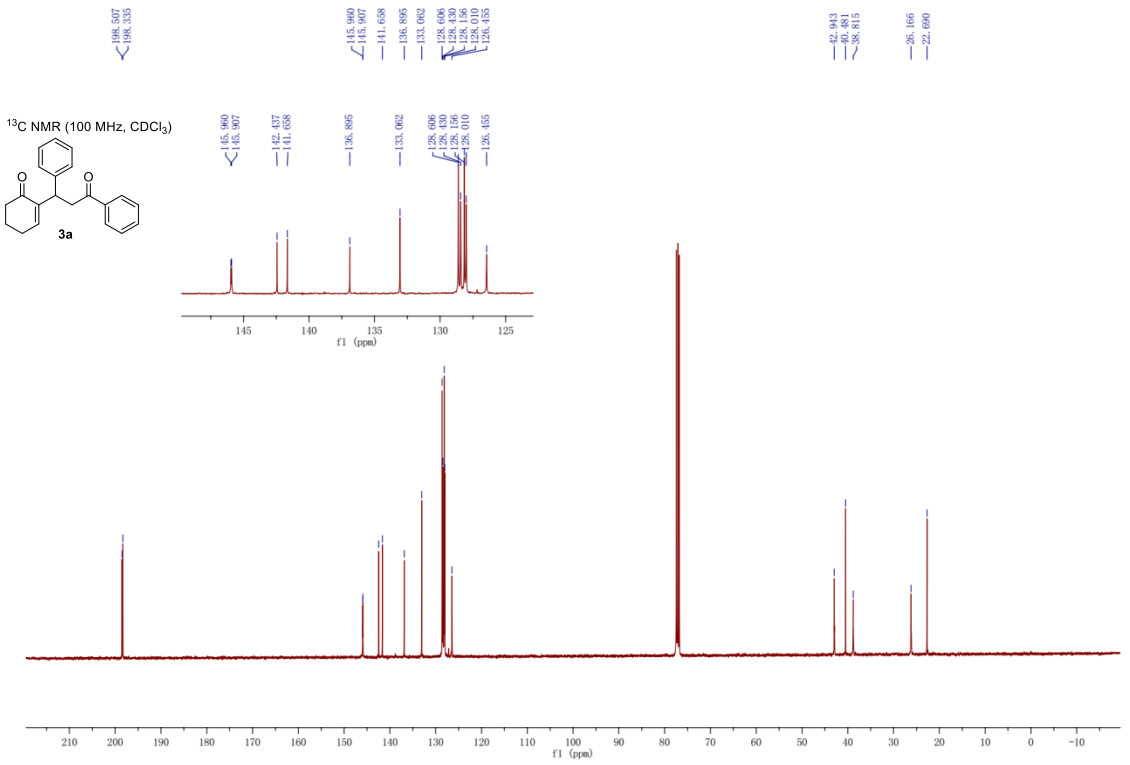


2-[(2-*oxo*-2-phenylethyl)(2-pyrrolyl)methyl]-2-cyclohexen-1-one **3e**: Colorless oil (28.8 mg, 0.098 mmol, 49% yield, 92:8 er); $[\alpha]_D^{20}$= +46.2 (c=0.04 in CH_2Cl_2); IR (KBr) ν 3357, 2923, 1674, 1448, 1371, 1246, 1011, 909, 759 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96-7.99 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 1.2 Hz, 1H), 6.73 (t, *J* = 4.0 Hz, 1H), 6.26 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.07 (d, *J* = 3.2 Hz, 1H), 4.70 (t, *J* = 7.2 Hz, 1H), 3.43-3.54 (m, 2H), 2.43-2.51 (m, 2H), 2.36 (dd, *J* = 10.8, 6.0 Hz, 2H), 1.94-2.03 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.1, 197.9, 155.3, 147.0, 141.3, 139.7, 136.8, 133.0, 128.6, 128.2, 110.3, 106.2, 41.7, 38.6, 34.7, 26.1, 22.7; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}O_3Na$ 317.1154, found 317.1149; HPLC analysis: (CHIRALCEL OD-H, 10% *i*-propanol/hexane, 1 mL/min, UV: 254 nm), t_R = 9.9 min (major), 10.8 min (minor).

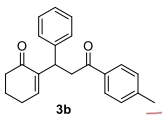
5.2 NMR Spectra




^{1}H NMR (400 MHz, CDCl$_3$)
3a
f1 (ppm)

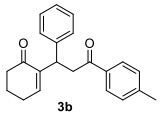

^{13}C NMR (100 MHz, CDCl$_3$)
3a
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$)

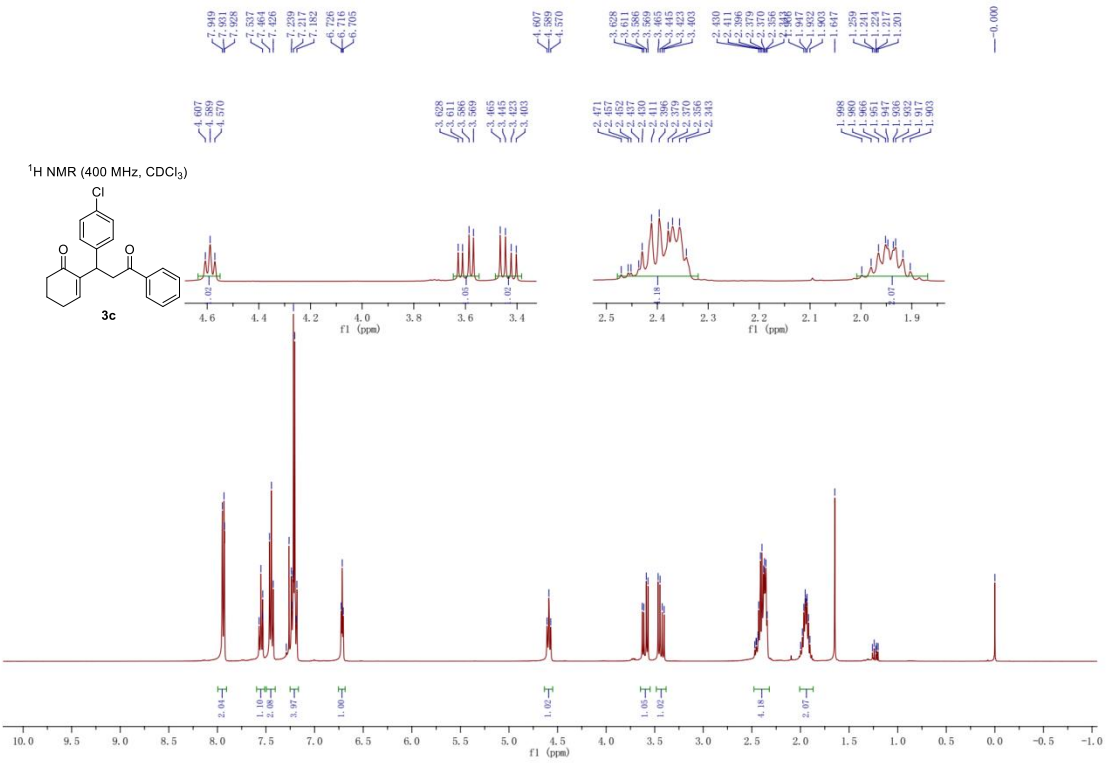


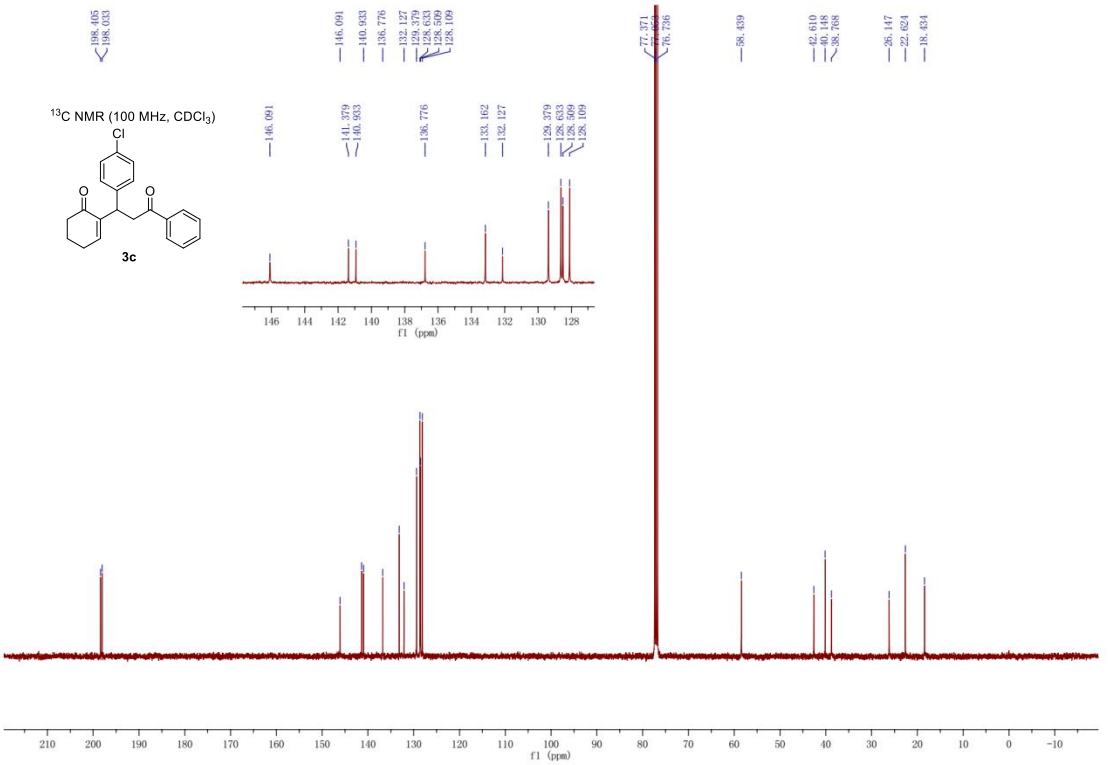
3b

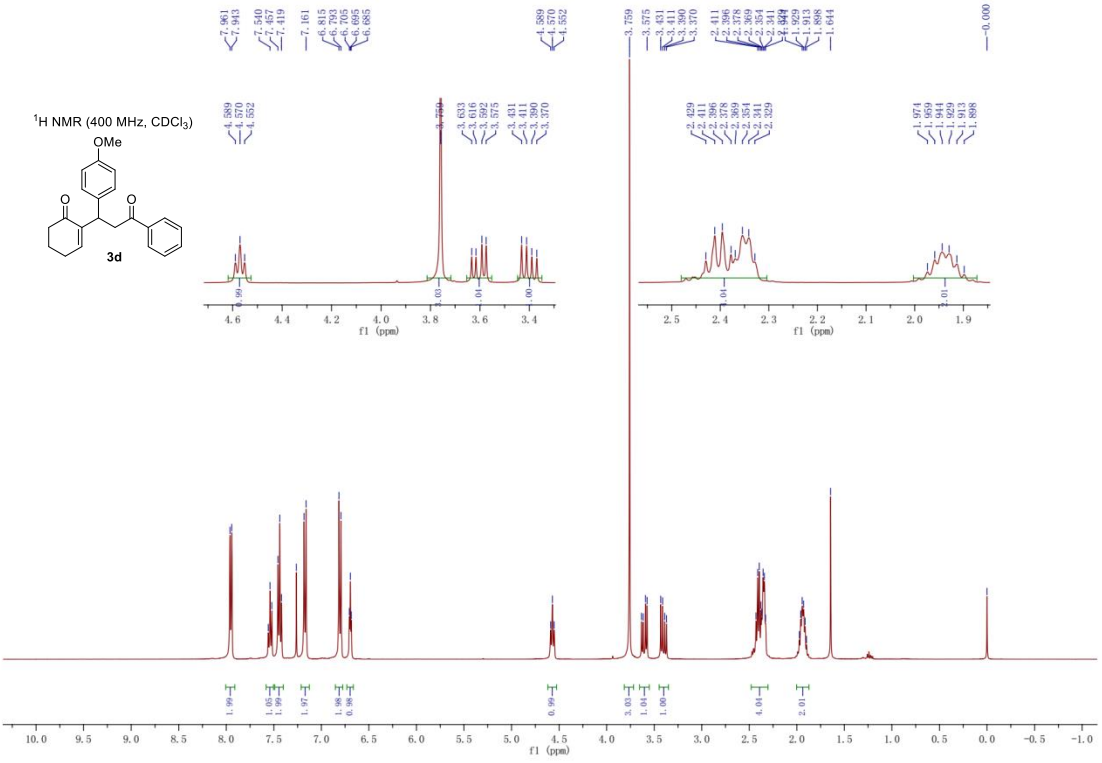
^{13}C NMR (100 MHz, $CDCl_3$)

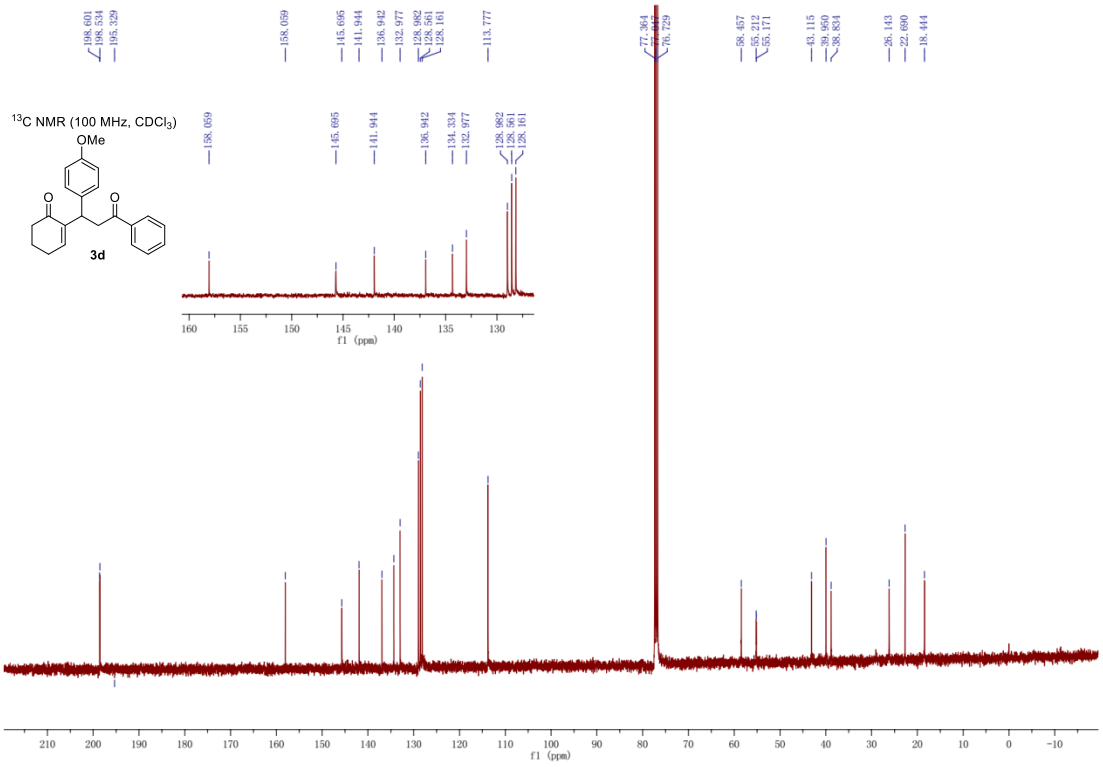


3b

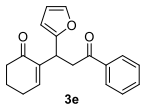

^{1}H NMR (400 MHz, CDCl$_3$)
Cl
O
O
3c
f1 (ppm)


^{13}C NMR (100 MHz, CDCl$_3$)
Cl
O
O
3c
f1 (ppm)

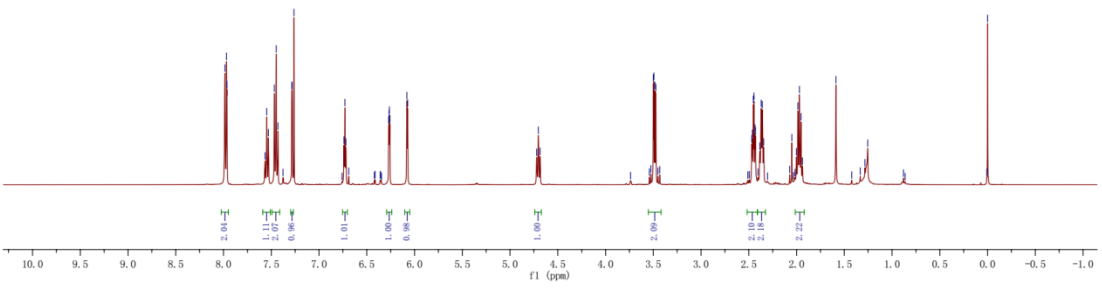

^{1}H NMR (400 MHz, CDCl$_3$)
OMe
O
O
3d
f1 (ppm)

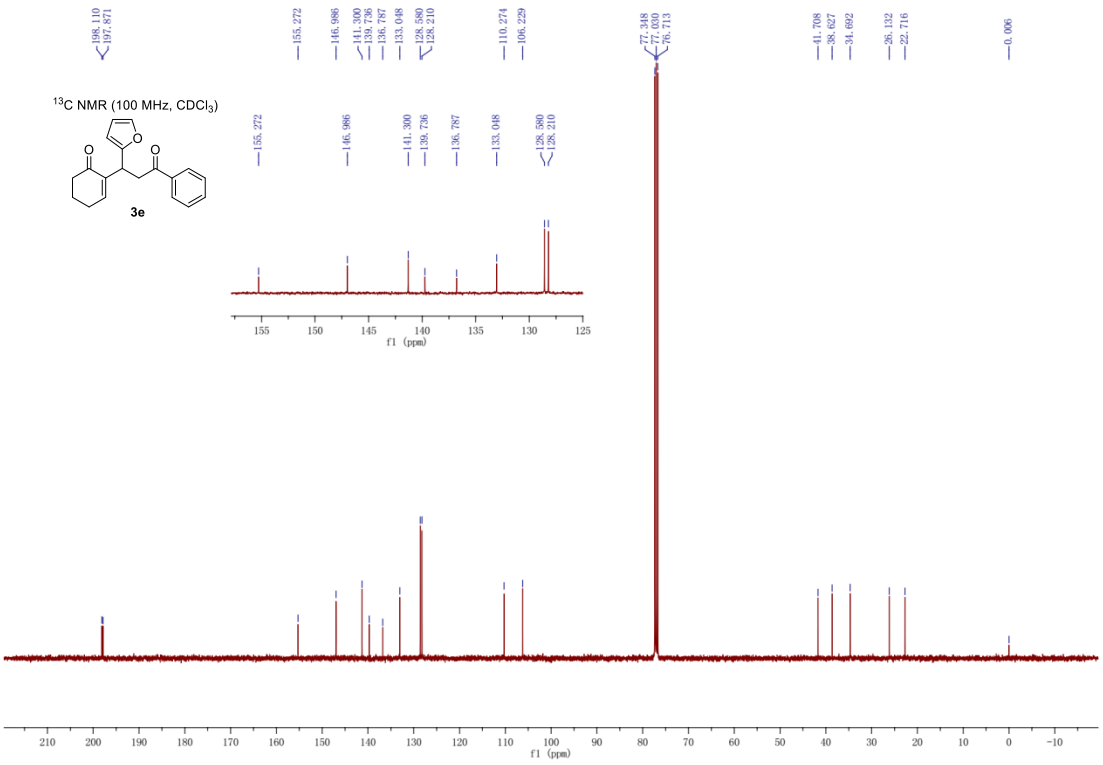

^{13}C NMR (100 MHz, CDCl$_3$)
OMe
O
O
3d
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$)



3e



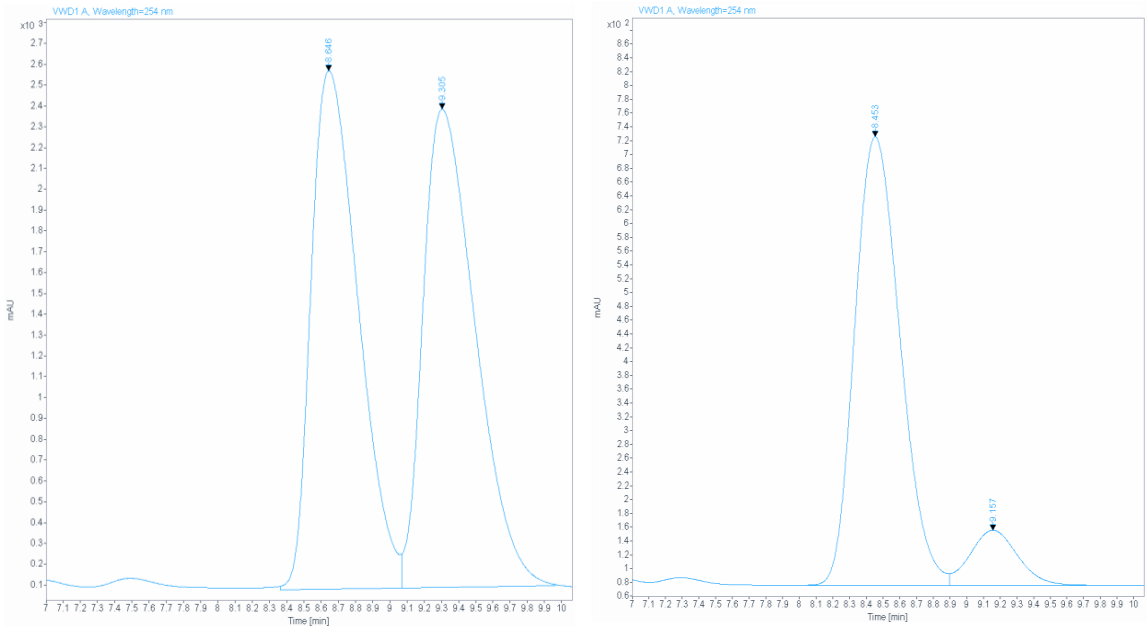


^{13}C NMR (100 MHz, $CDCl_3$)

3e

5.3 HPLC spectra

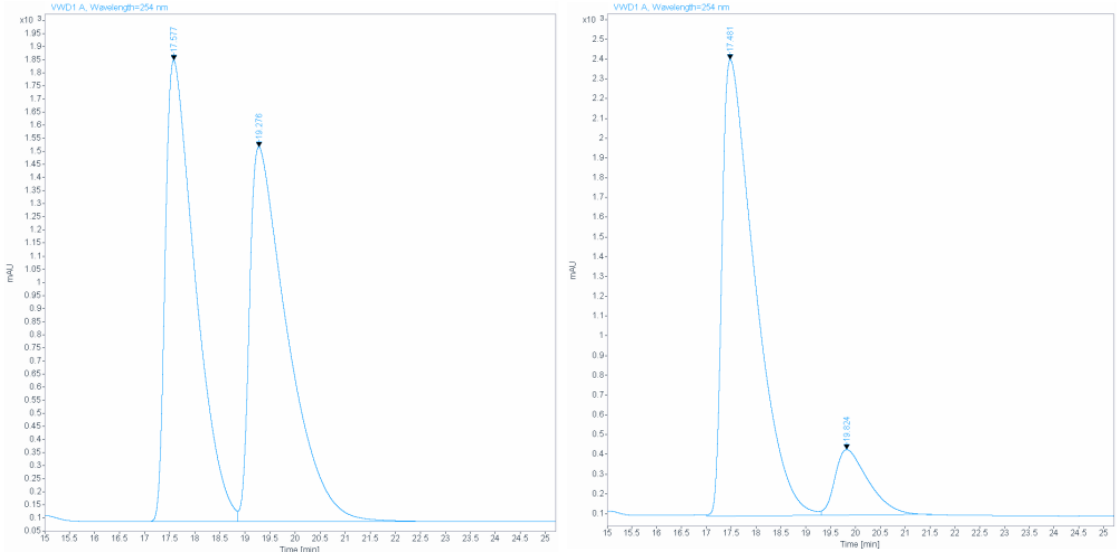
HPLC spectra of **3a**



RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.646	MF	0.3169	47325.2578	2489.0149	49.3257	
9.305	FM	0.3528	48619.1094	2296.7419	50.6743	

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.453	MF	0.3141	12247.6631	649.8004	88.5786	
9.157	FM	0.3295	1579.2275	79.8854	11.4214	

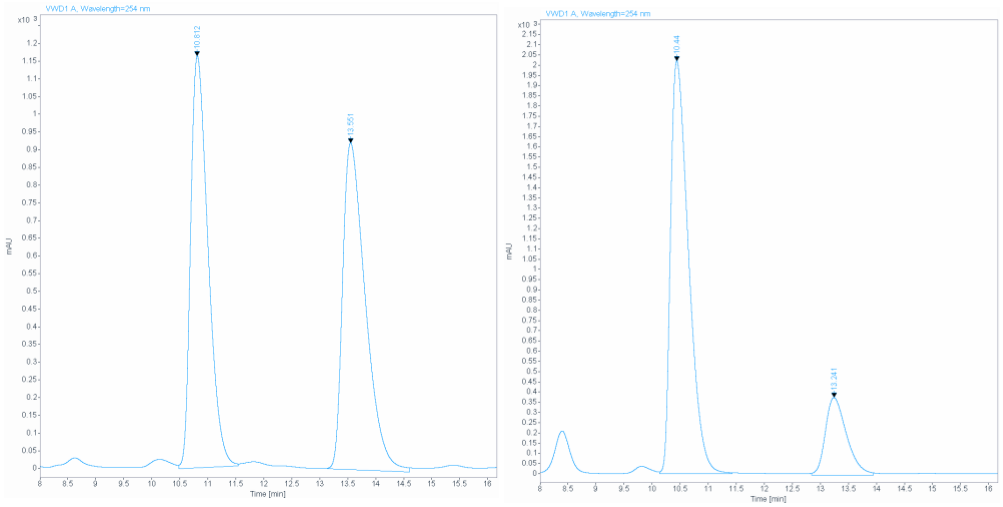
HPLC spectra of **3b**



RT [min]	Type	Width [min]	Area	Height	Area%	Name
17.577	BV	0.6167	73129.1875	1762.0511	49.3856	
19.276	VB	0.7517	74948.8047	1430.5408	50.6144	

RT [min]	Type	Width [min]	Area	Height	Area%	Name
17.481	MF	0.7655	106064.8359	2309.2971	87.2996	
19.824	FM	0.7775	15430.3506	330.7573	12.7004	

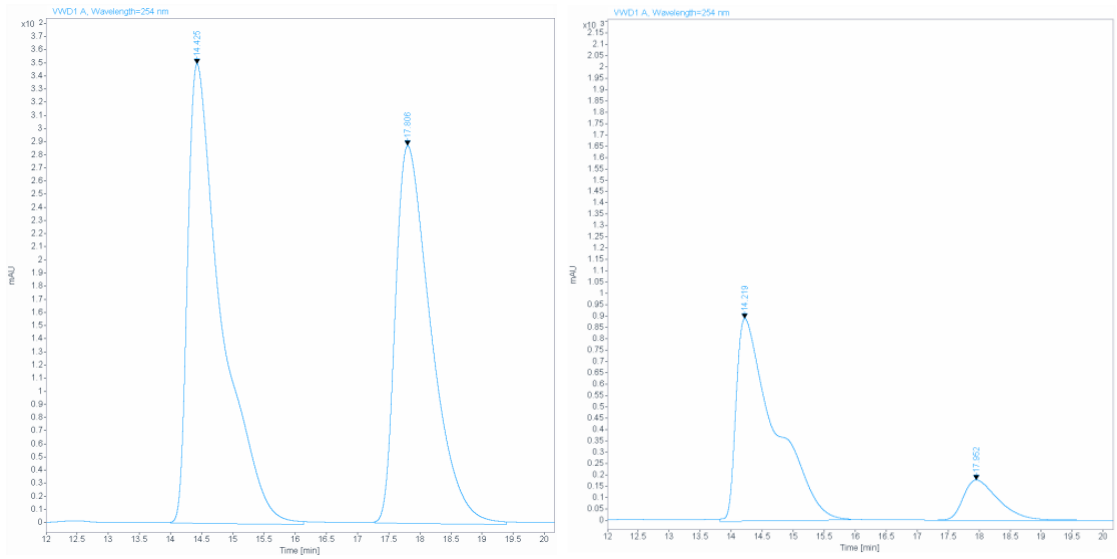
HPLC spectra of **3c**



RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.812	MM	0.3602	25143.4453	1163.3221	49.1660	
13.551	MM	0.4696	25996.4746	922.7299	50.8340	

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.440	MM	0.3727	45161.7266	2019.6235	81.8652	
13.241	MM	0.4393	10004.2529	379.5688	18.1348	

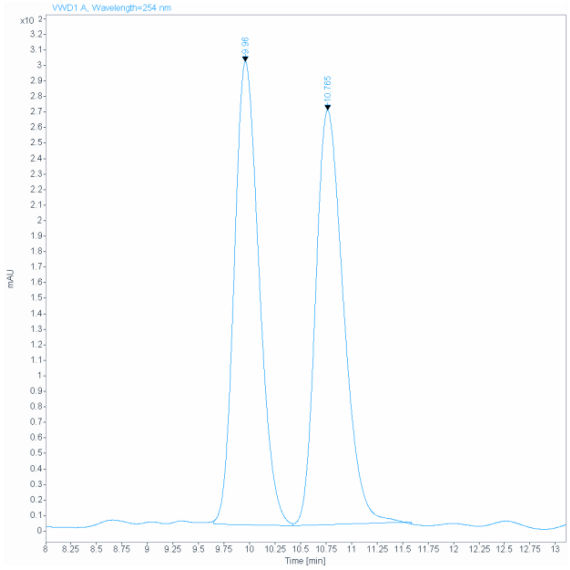
HPLC spectra of **3d**

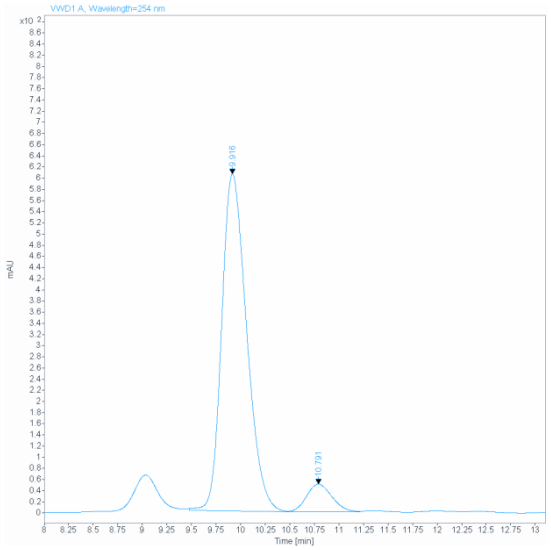


RT [min]	Type	Width [min]	Area	Height	Area%	Name
14.425	MM	0.6256	13118.5762	349.5035	53.6075	
17.806	MM	0.6586	11352.9648	287.2884	46.3925	

RT [min]	Type	Width [min]	Area	Height	Area%	Name
14.219	MM	0.7219	38677.9727	893.0164	84.9088	
17.952	BB	0.5909	6874.4077	176.6926	15.0912	

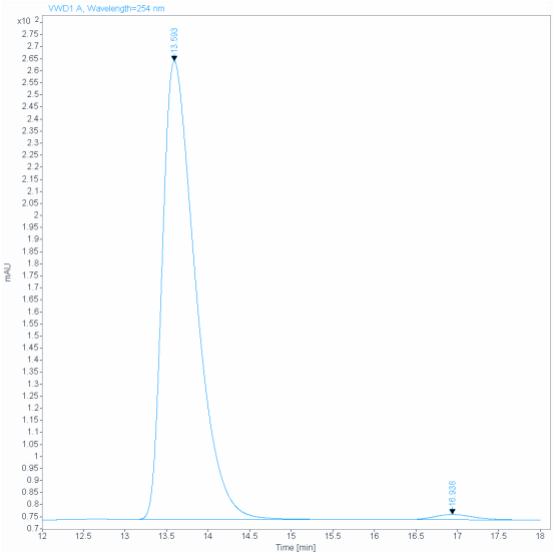
HPLC spectra of **3e**

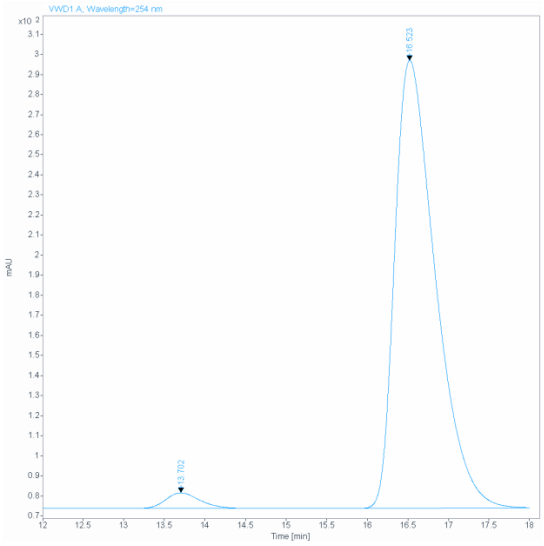




RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.960	MM	0.2813	5035.7583	298.3152	49.8474	
10.765	MM	0.3163	5066.5957	266.9731	50.1526	

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.916	MM	0.2945	10667.3643	603.7795	92.1847	
10.791	MM	0.3018	904.3615	49.9488	7.8153	

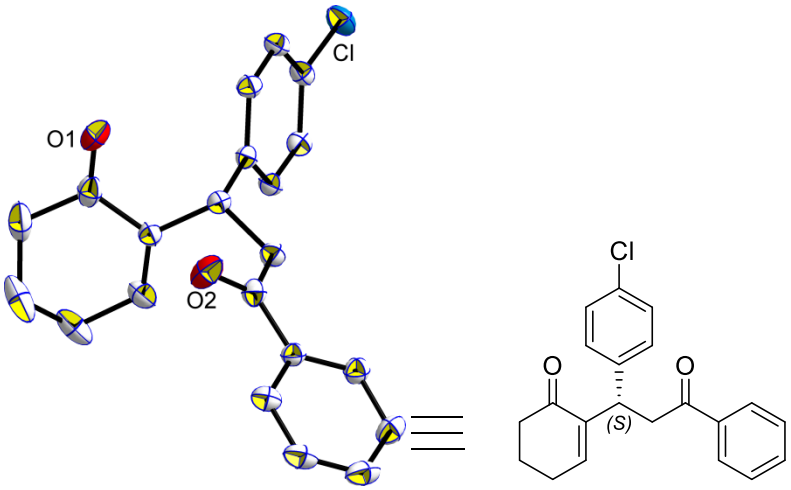




RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.593	BB	0.4217	5279.7661	190.3111	98.6220	
16.938	BB	0.4536	73.7724	2.2091	1.3780	

RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.702	BB	0.4323	227.8969	7.7778	2.8663	
16.523	BBA	0.5269	7722.8813	223.0584	97.1337	

6. X-ray single crystal structure for 3c



Single crystal structure of compound (*S*)-3c (20% probability level)

Compound 3c （CCDC 1558121）		**Flack parameter: 0.05**
Bond precision: C-C = 0.0065 A		Wavelength= 0.71073
a = 10.724(1)	b = 10.837(1)	c = 15.1156(15)
alpha = 90	beta = 90	gamma = 90
Cell setting: Orthorhombic		Moiety formula: $C_{21}H_{19}ClO_2$
Cell volume = 1756.7(3)		Space group: P2(1)2(1)2(1)
Data completeness= 0.99		Theta(max)= 25.010
R(reflections)= 0.0530(1547)		WR2(reflections)= 0.1089(3083)
S = 0.894		Radiation type: MoK\a
Measurement device type: CCD area detector		Measurement method: phi and omega scans
Structure solution: SHELXS-97		Structure refinement: SHELXL-97
Solution primary: direct		Solution secondary: difmap
Solution hydrogens: geom		Hydrogen treatment: mixed

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