

# **New Biphenyl Iminium Salt Catalysts for Highly Enantioselective Asymmetric Epoxidation: Role of Additional Substitution and Dihedral Angle.**

Philip C. Bulman Page,\* Christopher J. Bartlett, Yohan Chan, Steven M. Allin, Michael J. McKenzie, Jérôme Lacour, and Garth A. Jones

## **Supplementary Information**

S2 Table S1: Asymmetric epoxidation mediated by iminium salt 7a under different reaction conditions

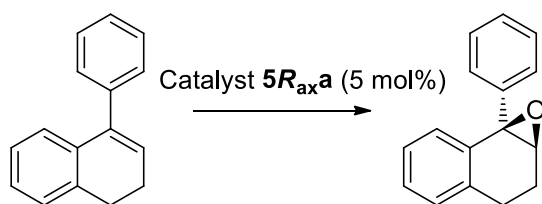
S2 Table S2: Asymmetric epoxidation mediated by iminium salt 9

S3-S4 Table S3: Computational Chemistry Data: Structures

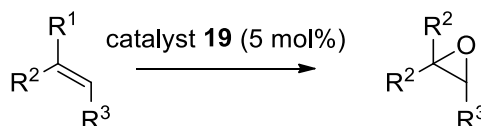
S5-S26 NMR Spectra

S27-S42 Analysis of enantiomeric excess: HPLC traces, NMR spectra and GC traces

S43-S92 Computational Chemistry Data: Cartesian coordinates

**Table S1:** Asymmetric epoxidation mediated by iminium salt **5R<sub>ax</sub>a** under different reaction conditions

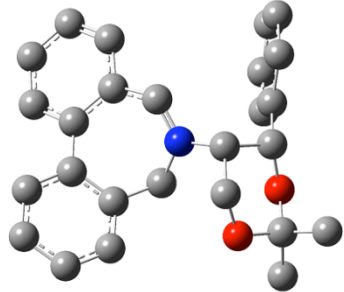
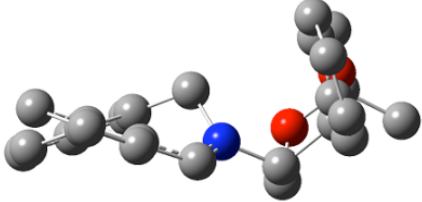
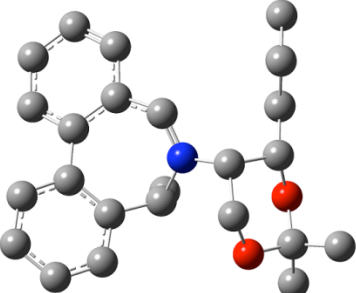
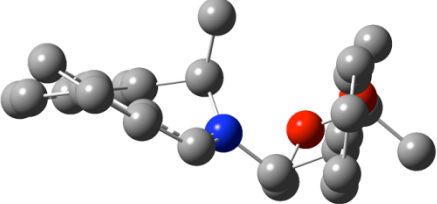
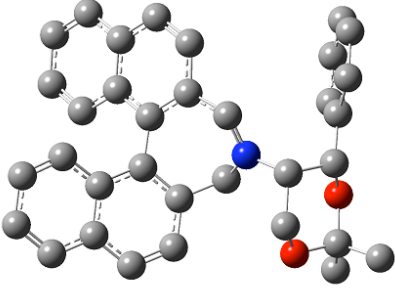
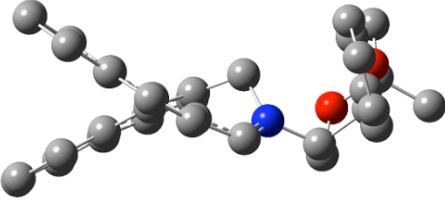
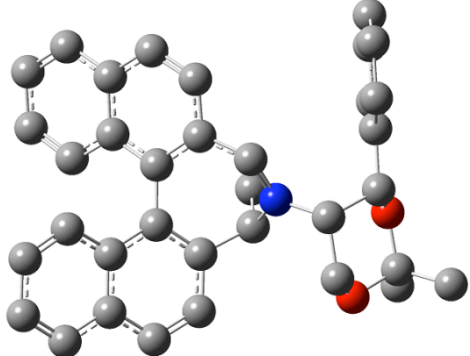
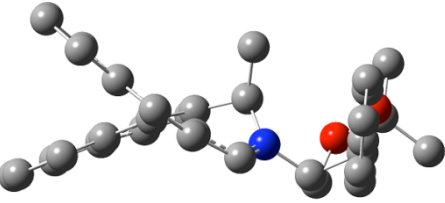
Conditions	Time	Conv. (%)	ee (%)	Config.
MeCN/H <sub>2</sub> O 10:1, Oxone, NaHCO <sub>3</sub> , 0 °C	30 min	99	89	(+)-(1 <i>R</i> ,2 <i>S</i> )
MeCN/H <sub>2</sub> O 1:1, Oxone, NaHCO <sub>3</sub> , 0 °C	20 min	98	81	(+)-(1 <i>R</i> ,2 <i>S</i> )
CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O 3:2, Oxone, 18-C-6, NaHCO <sub>3</sub> , 0 °C	2 h	80	47	(+)-(1 <i>R</i> ,2 <i>S</i> )
CHCl <sub>3</sub> , TPPP, -30 °C	72 h	47	4	-
MeCN, TPPP, -30 °C	2 h	99	77	(+)-(1 <i>R</i> ,2 <i>S</i> )

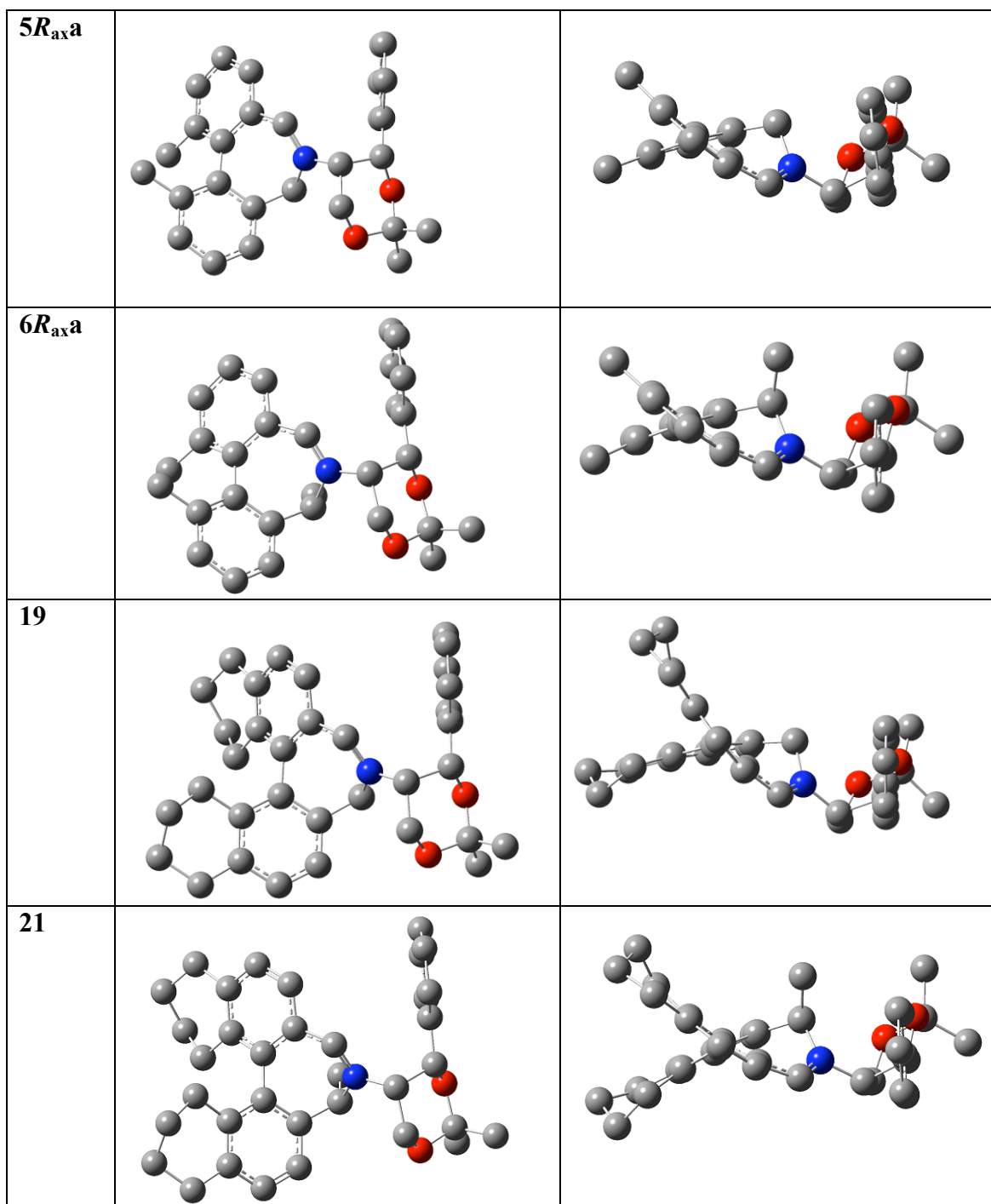
**Table S2:** Asymmetric epoxidation mediated by iminium salt **19**

Substrate	Conditions	Time	Conv. (%)	ee (%)	Config.
	<b>A</b>	0.7 h	99	93	(+)-(1 <i>R</i> ,2 <i>S</i> )
	<b>B</b>	1.3 h	99	86 (94)	(+)-(1 <i>R</i> ,2 <i>S</i> )
	<b>A</b>	0.6 h	99	90	(-)-(1 <i>S</i> ,2 <i>S</i> )
	<b>B</b>	1 h	99	80 (91)	(-)-(1 <i>S</i> ,2 <i>S</i> )
	<b>A</b>	1 h	99	60	(-)-(1 <i>S</i> ,2 <i>S</i> )
	<b>B</b>	2 h	99	63 (49)	(-)-(1 <i>S</i> ,2 <i>S</i> )

Reaction conditions: **(A)**: Oxone (2 equiv.), NaHCO<sub>3</sub> (5 equiv.), MeCN / H<sub>2</sub>O 10:1, 0 °C; **(B)** Oxone® (2 equiv.), NaHCO<sub>3</sub> (5 equiv.), MeCN / H<sub>2</sub>O 1:1, 0 °C; Enantioselectivities obtained using catalyst **2** are shown in parentheses

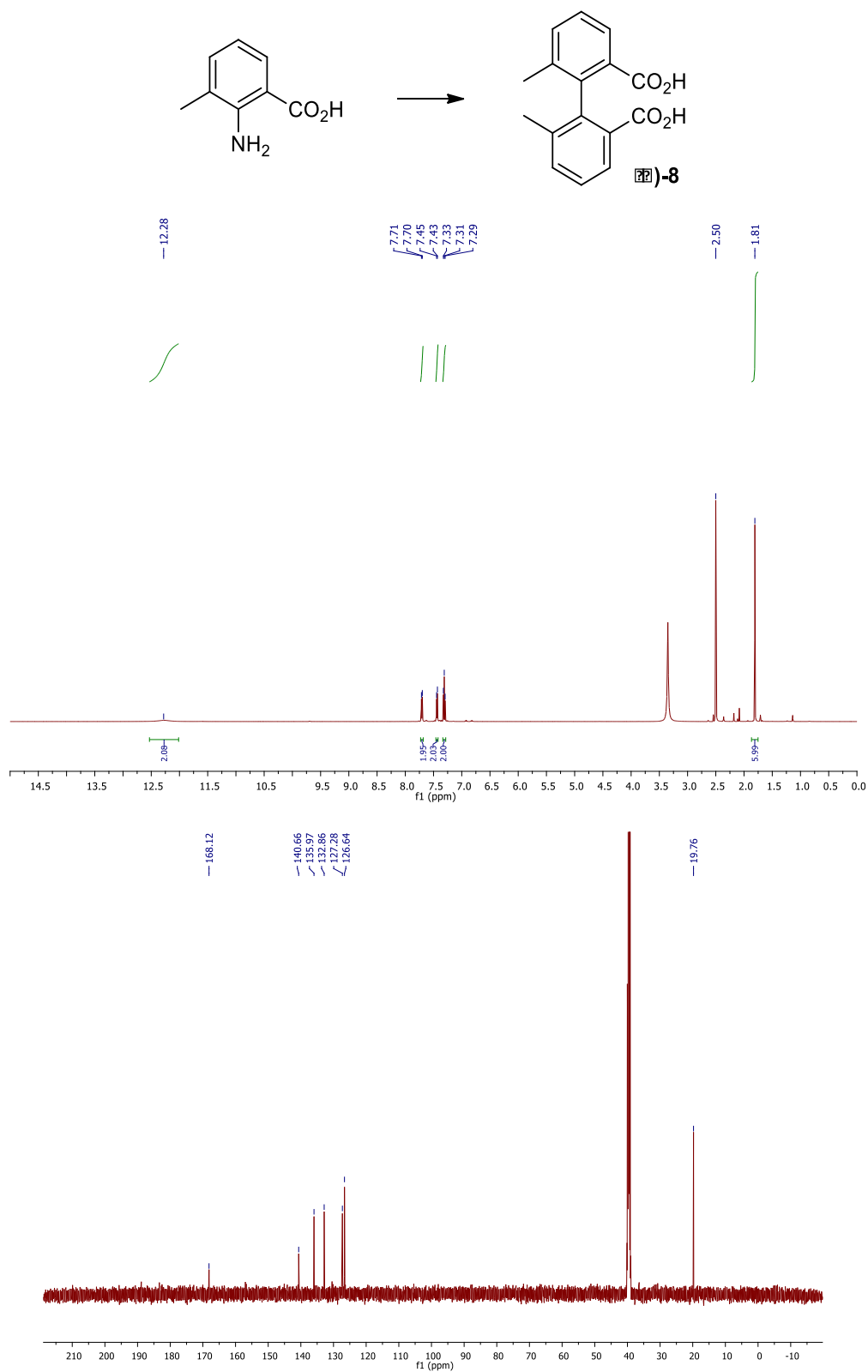
Table S3: Computational Chemistry Data: Structures

Structure	Top	Side
1		
30		
2		
31		

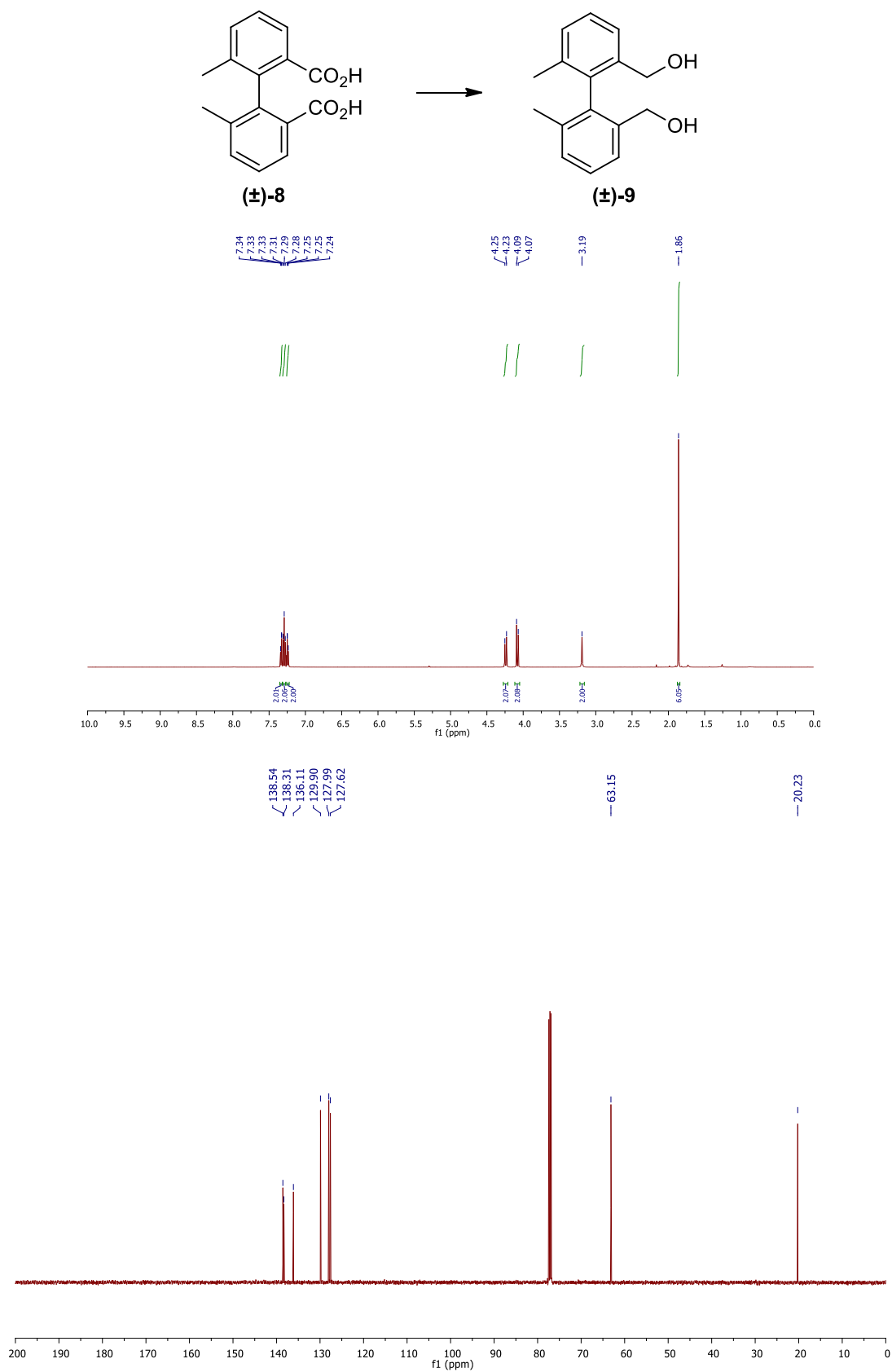


## NMR Spectra

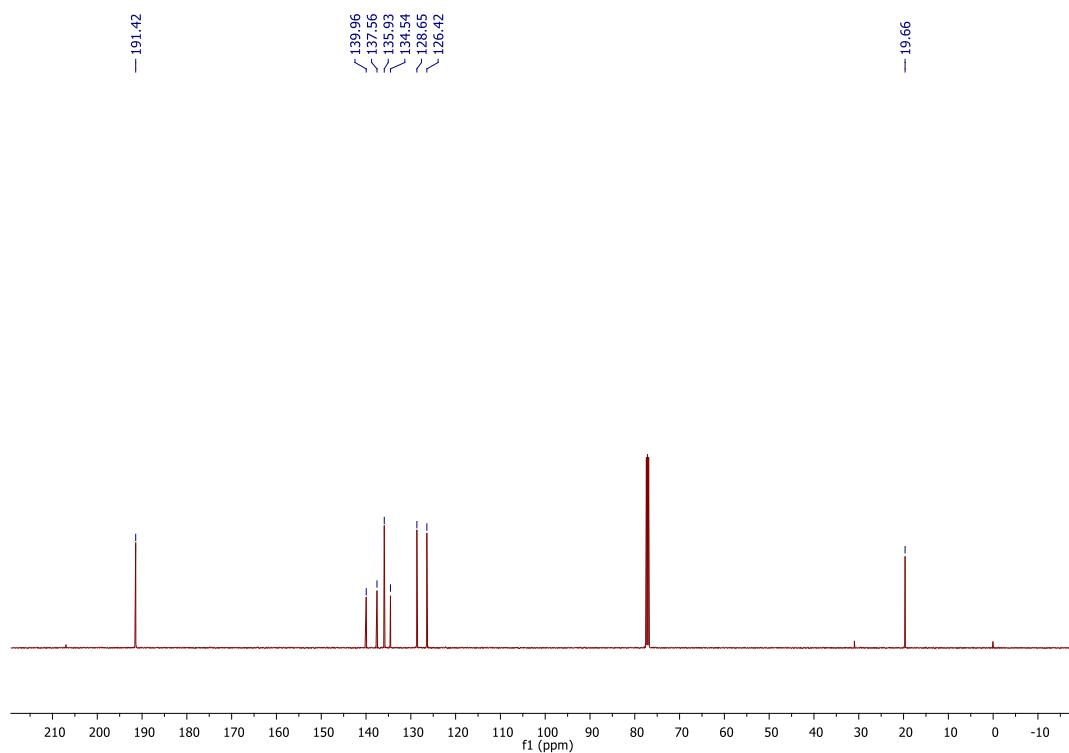
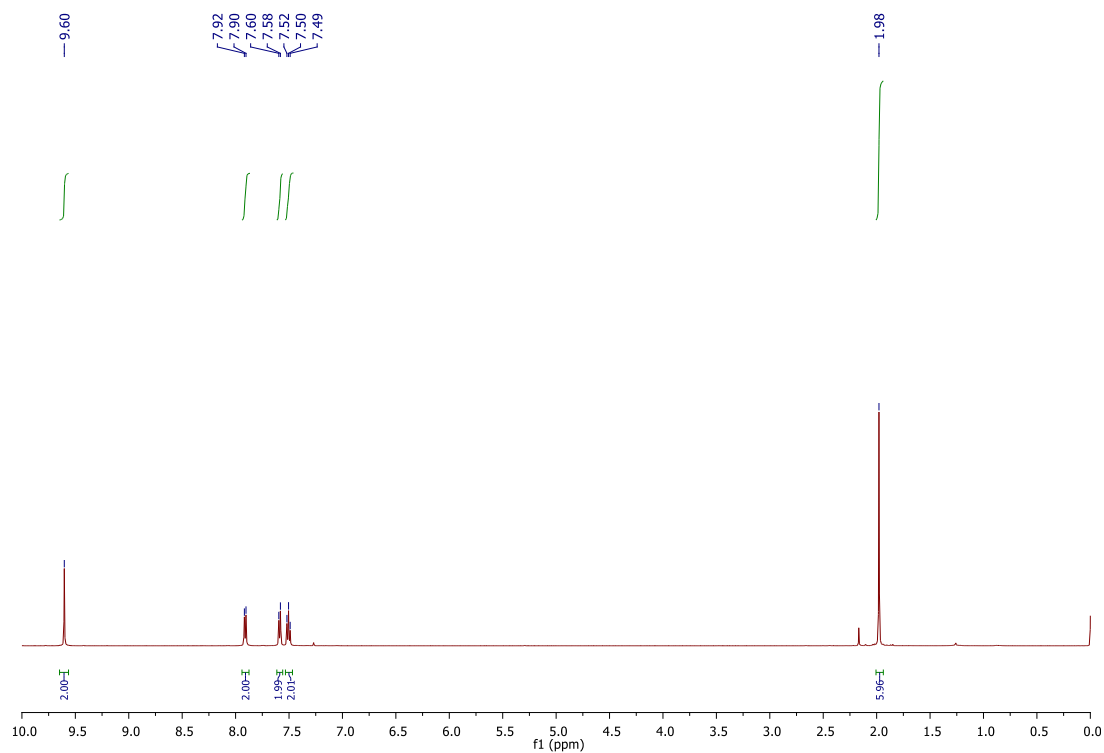
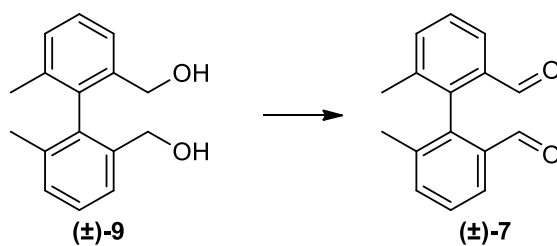
### 6,6'-Dimethylbiphenyl-2,2'-bis(carboxylic acid) ( $\pm$ )-**(8)**:



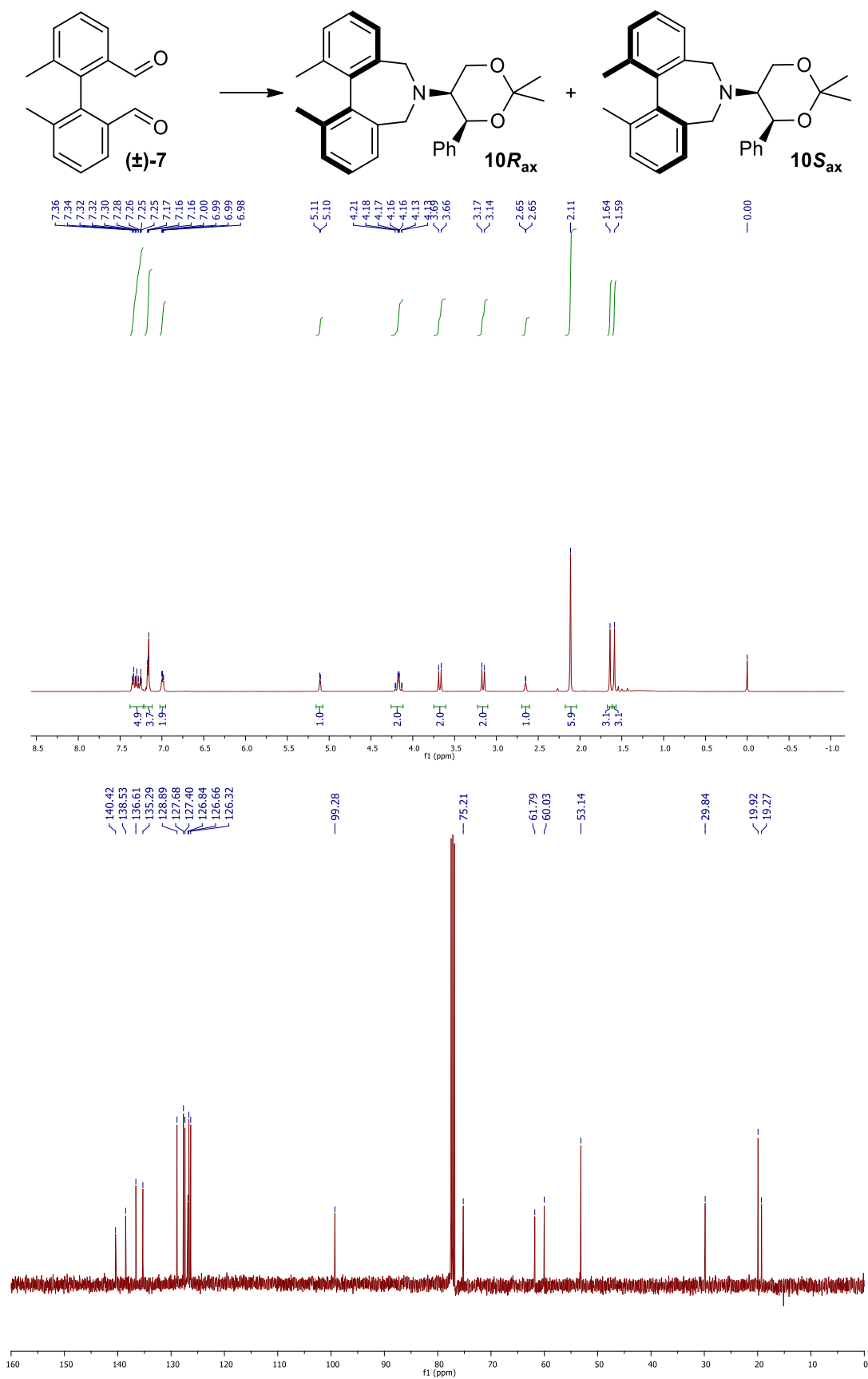
### 6,6'-Dimethyl-2,2'-bis(hydroxymethyl)biphenyl ( $\pm$ )-(9):



**6,6'-Dimethyl-1,1'-biphenyl-2,2'-bis(carboxaldehyde) ( $\pm$ )-(7):**

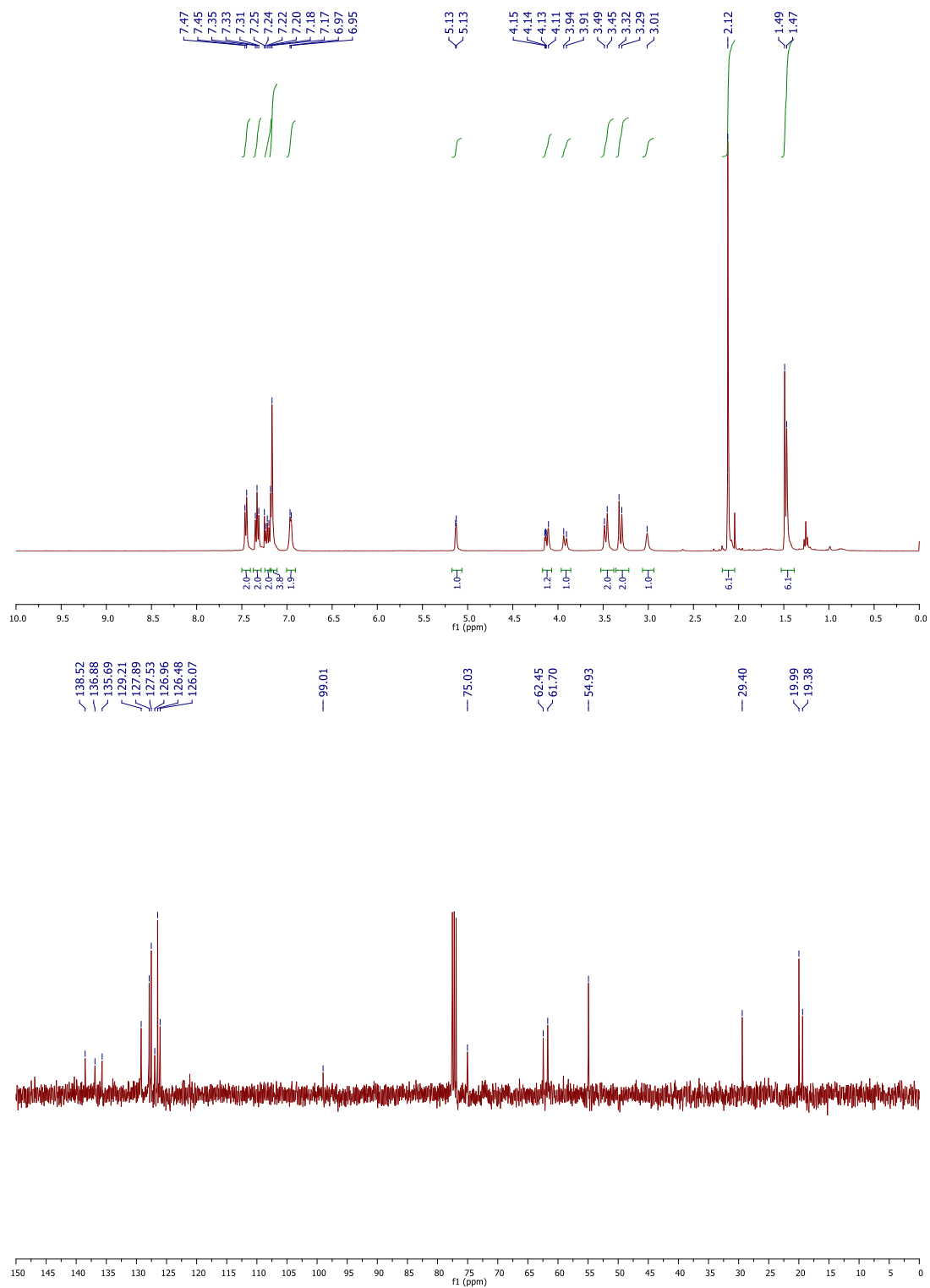


**(+)-(R<sub>ax</sub>)-6-((4S,5S)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-1,11-dimethyl-6,7-dihydro-5H-dibenzo[*c,e*]azepine (10R<sub>ax</sub>):**

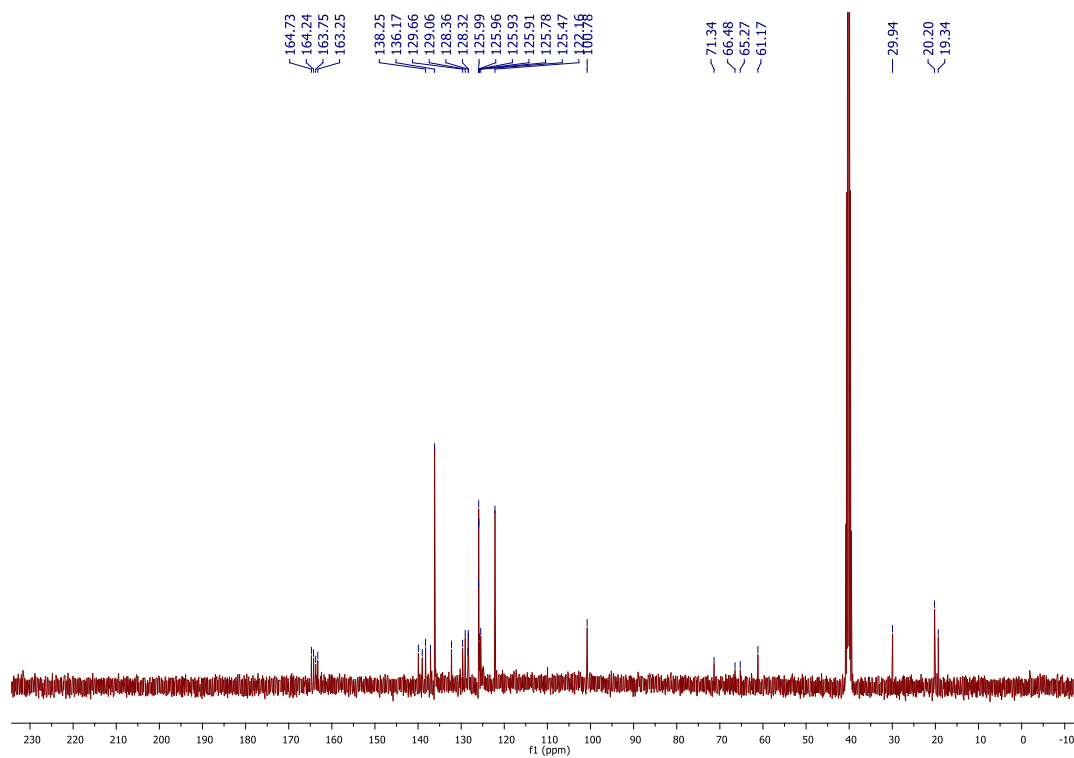
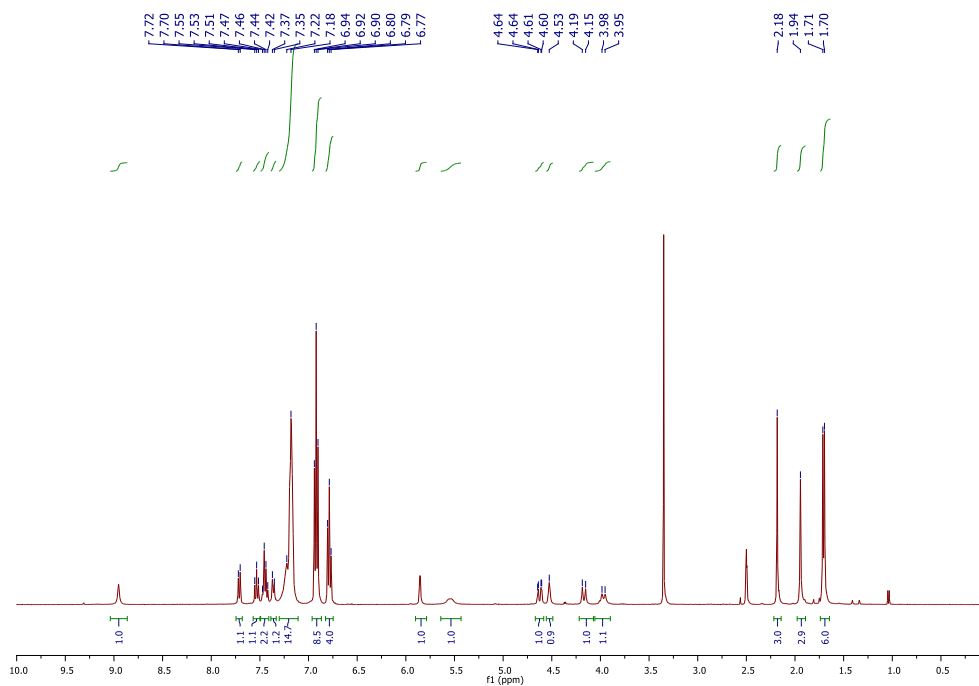
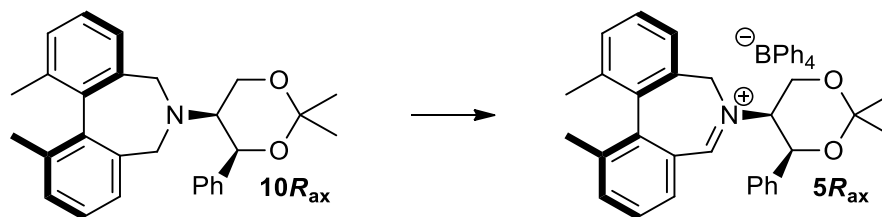




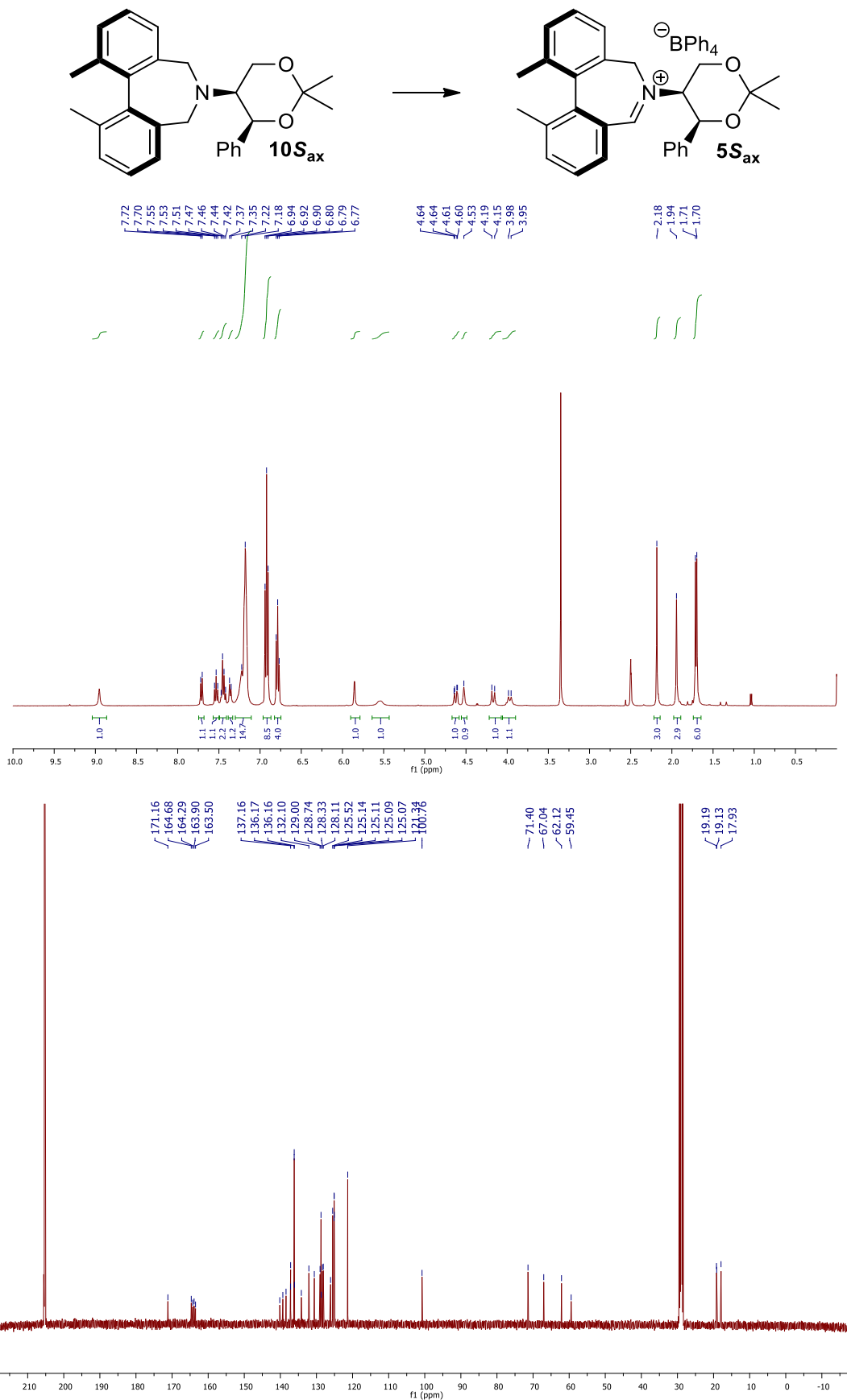
**(+)-(S<sub>ax</sub>)-6-((4S,5S)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-1,11-dimethyl-6,7-dihydro-5H-dibenzo[*c,e*]azepine (10S<sub>ax</sub>)**



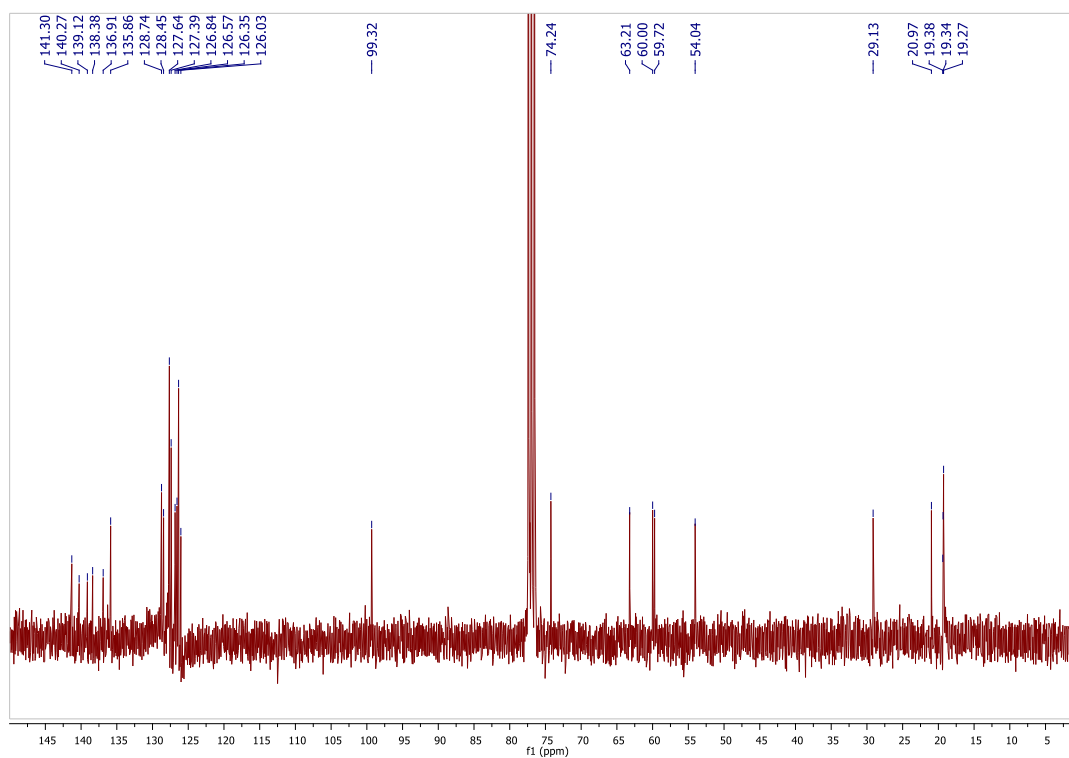
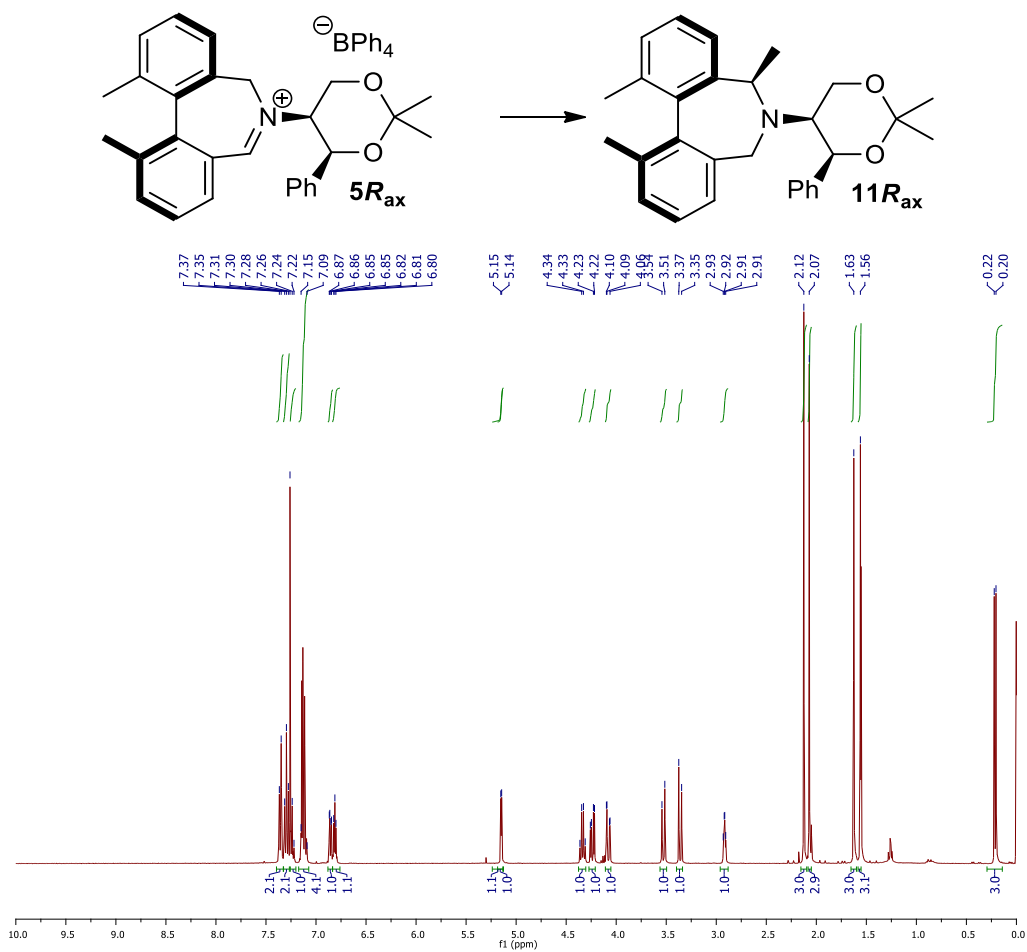
(-)-(*R<sub>ax</sub>*)-6-((4*S*,5*S*)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-1,11-dimethyl-5*H*-dibenzo[*c,e*]azepin-6-ium tetraphenylborate (*5R<sub>ax</sub>*)



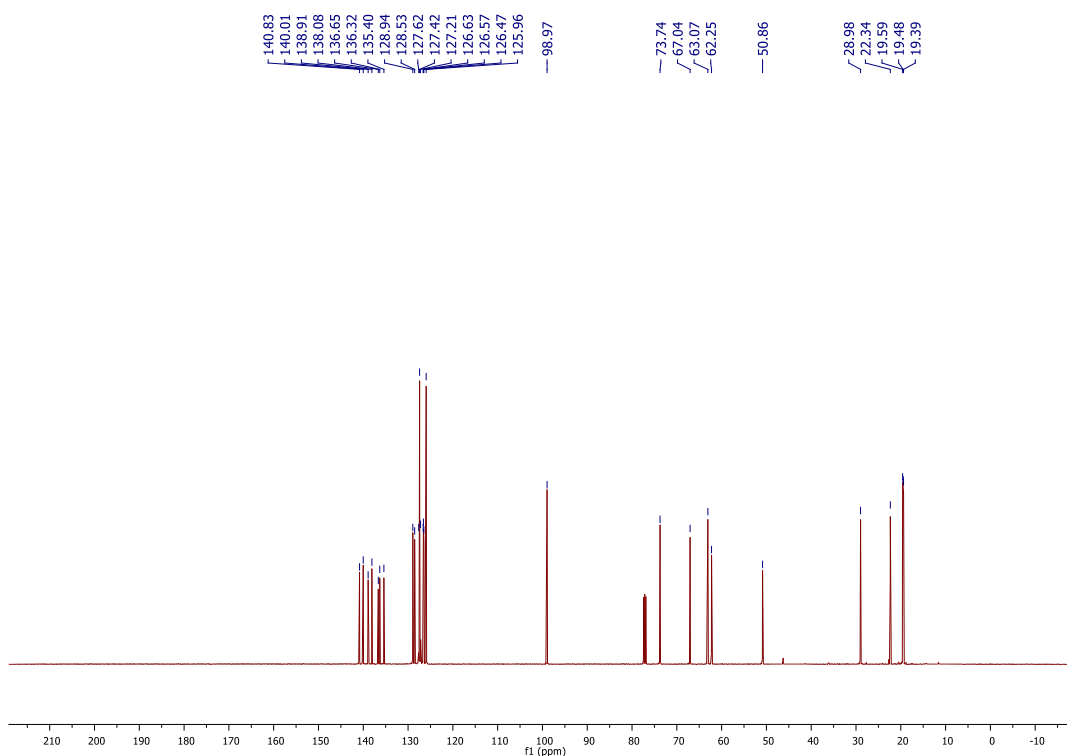
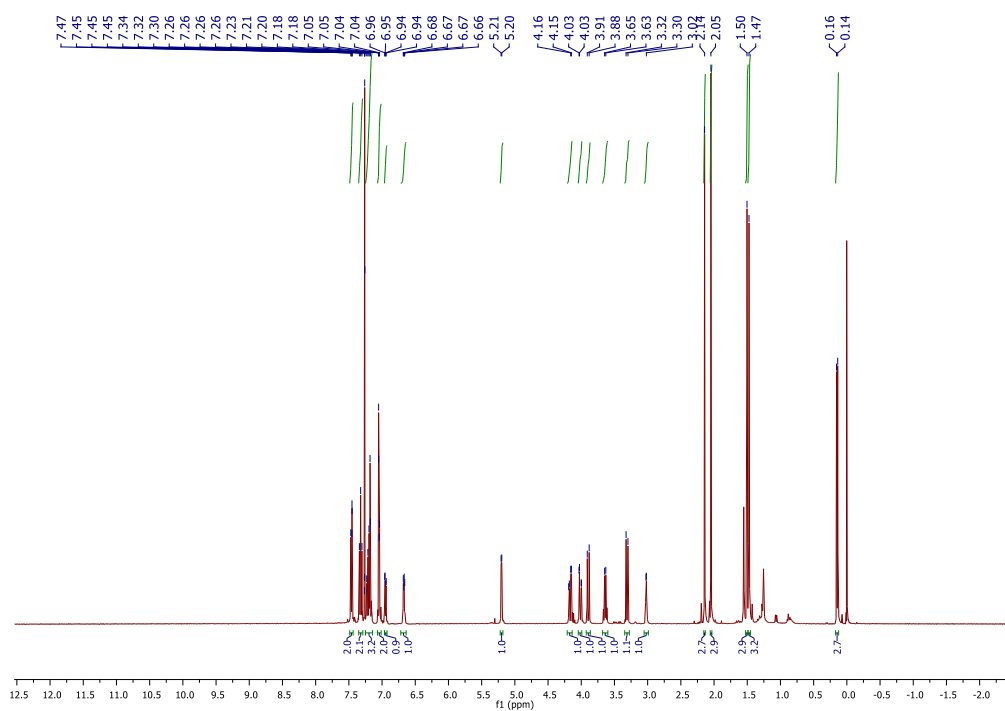
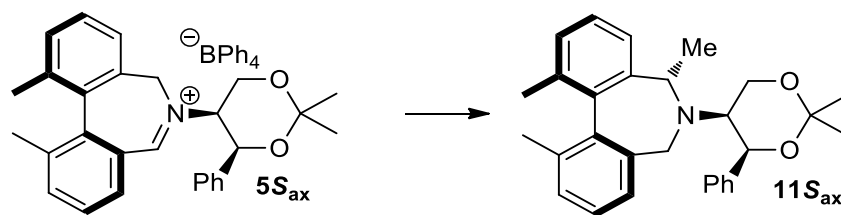
(+)-(*S*<sub>ax</sub>)-6-((4*S*,5*S*)-2,2-Dimethyl-4-phenyl-[1,3]dioxan-5-yl)-1,11-dimethyl-5*H*-dibenzo[*c,e*] azepinium tetraphenylborate (*5S*<sub>ax</sub>)



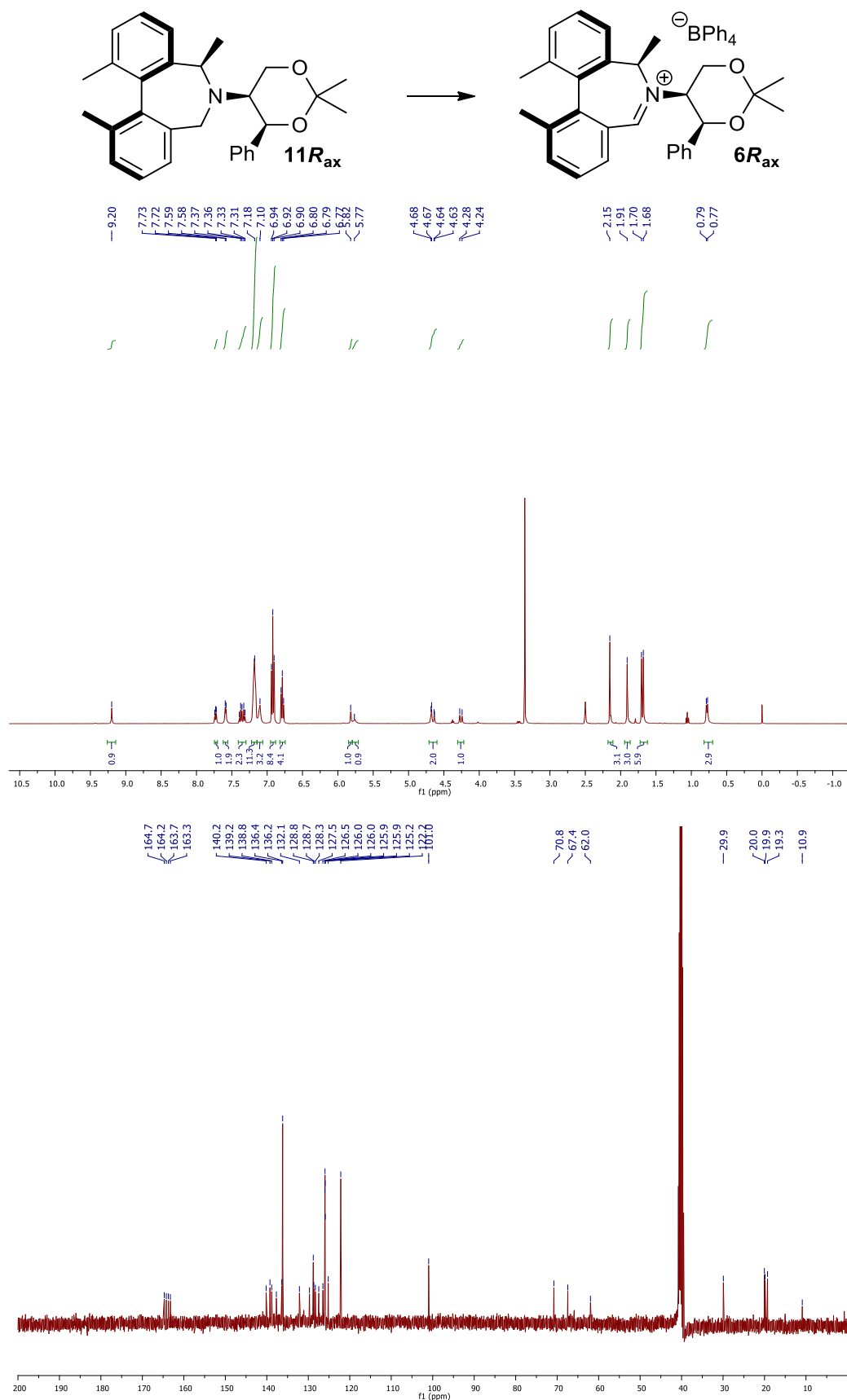
**(5*R*, 11*bR*<sub>ax</sub>)-6-((4*S*,5*S*)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-1,5,11-trimethyl-6,7-dihydro-5*H*-dibenzo[*c,e*]azepine (11*R*<sub>ax</sub>)**



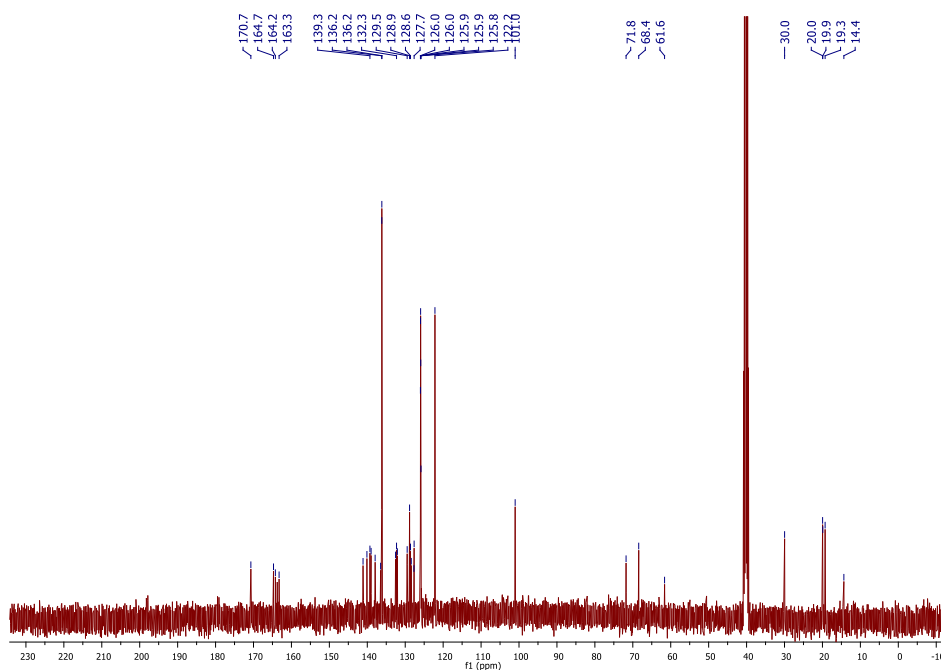
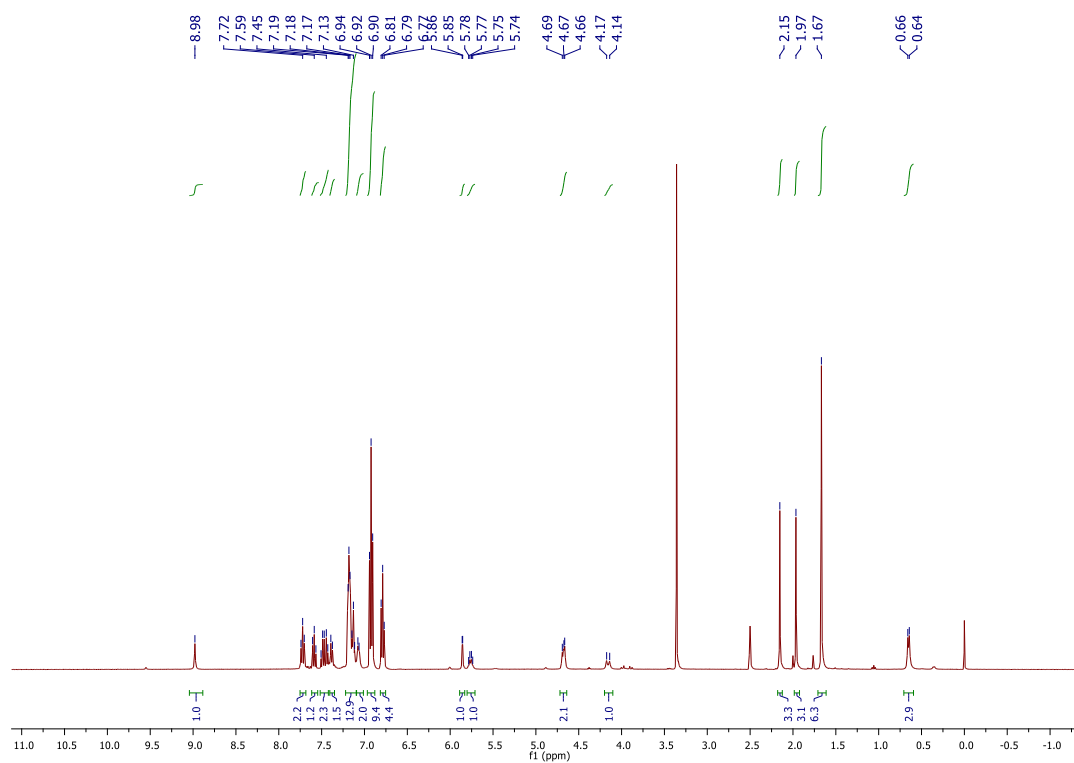
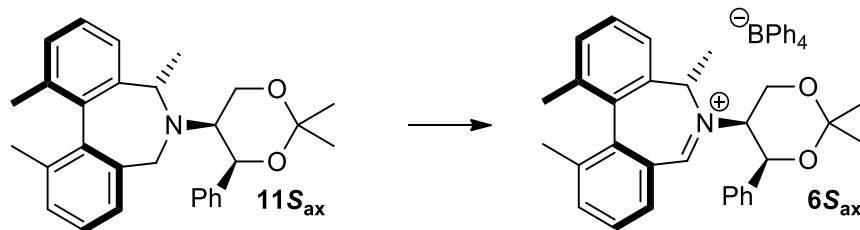
(5*S*, 11*bS*<sub>ax</sub>)-6-((4*S*,5*S*)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-1,5,11-trimethyl-6,7-dihydro-5*H*-dibenzo[*c,e*]azepine (11*S*<sub>ax</sub>)



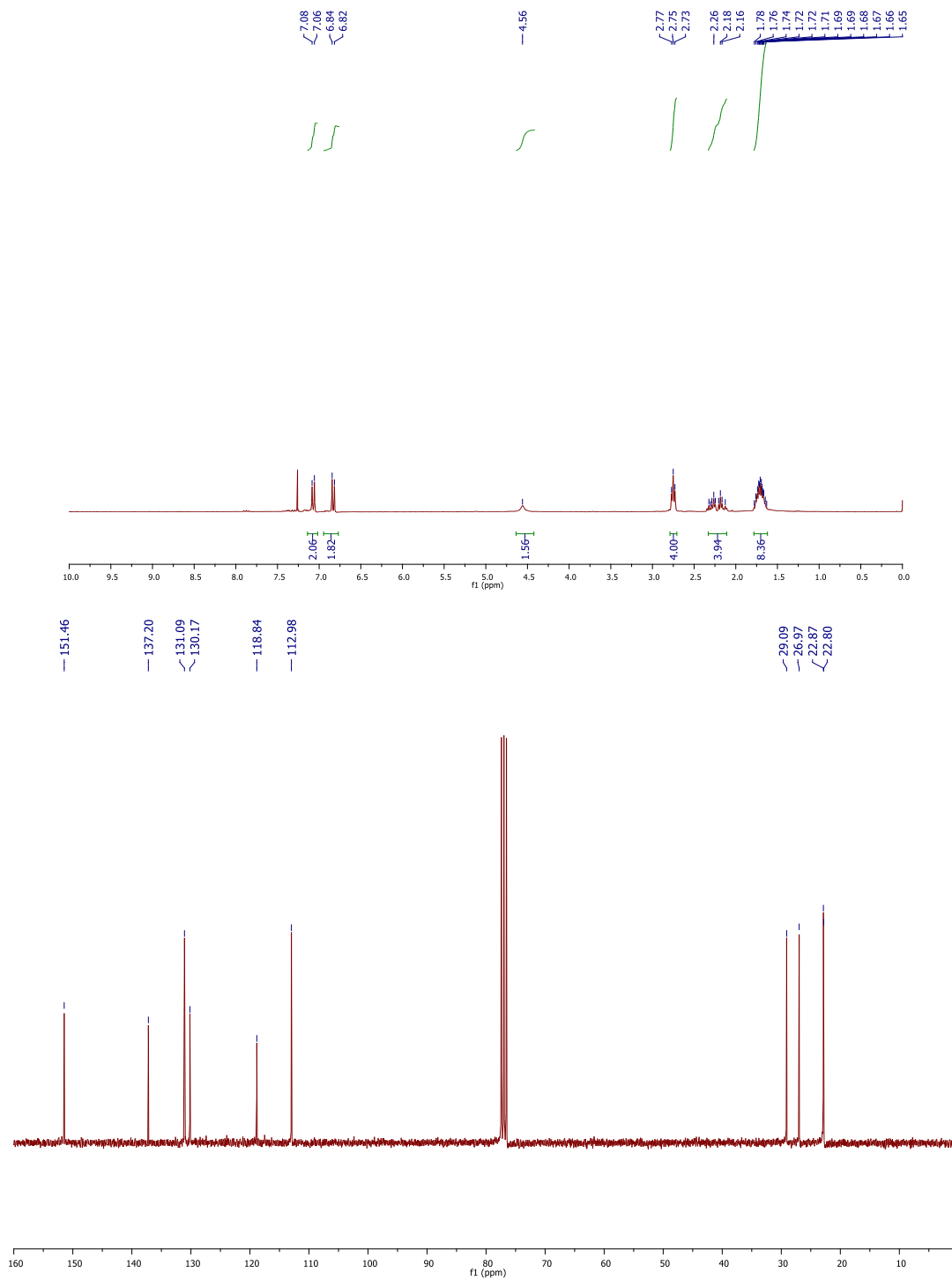
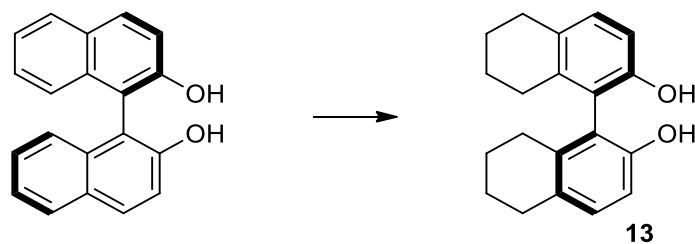
(-)-(5*R*, 11*bR*<sub>ax</sub>)-6-((4*S*,5*S*)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-1,5,11-trimethyl-5*H*-  
dibenzo[*c,e*]azepin-6-ium tetraphenylborate (6*R*<sub>ax</sub>)



(+)-(5*S*, 11*bS*<sub>ax</sub>)-6-((4*S*,5*S*)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-1,5,11-trimethyl-5*H*-  
dibenzo[*c,e*]azepin-6-ium tetraphenylborate (6*S*<sub>ax</sub>)

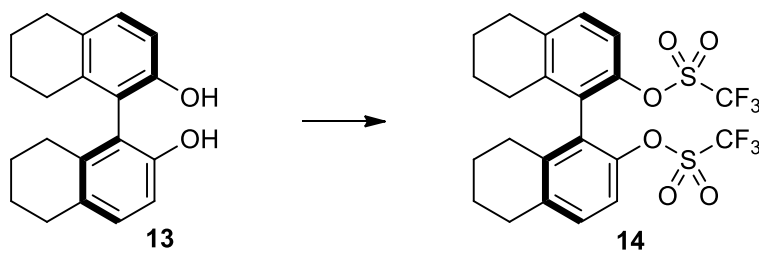


(-)-(R<sub>ax</sub>)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diol (**13**):



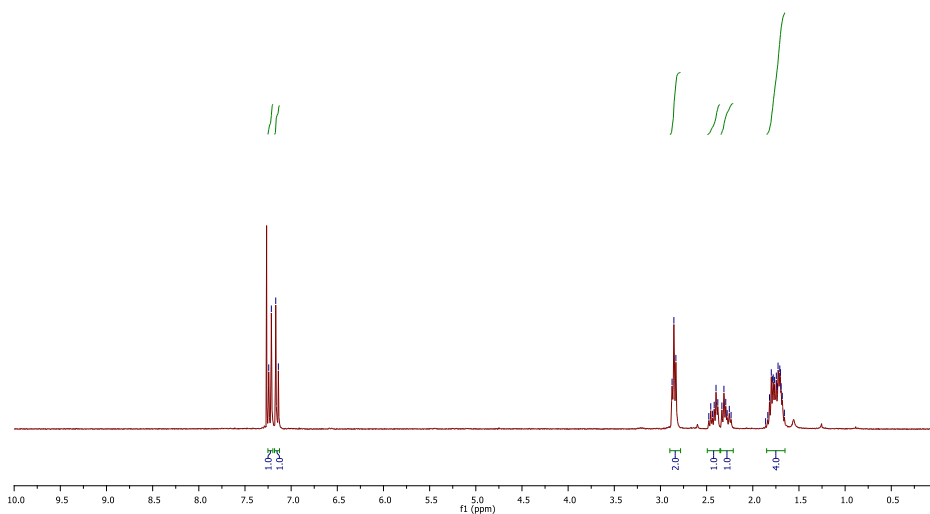


(-)-(R<sub>ax</sub>)-2,2'-Trifluoromethanesulfonyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (14):



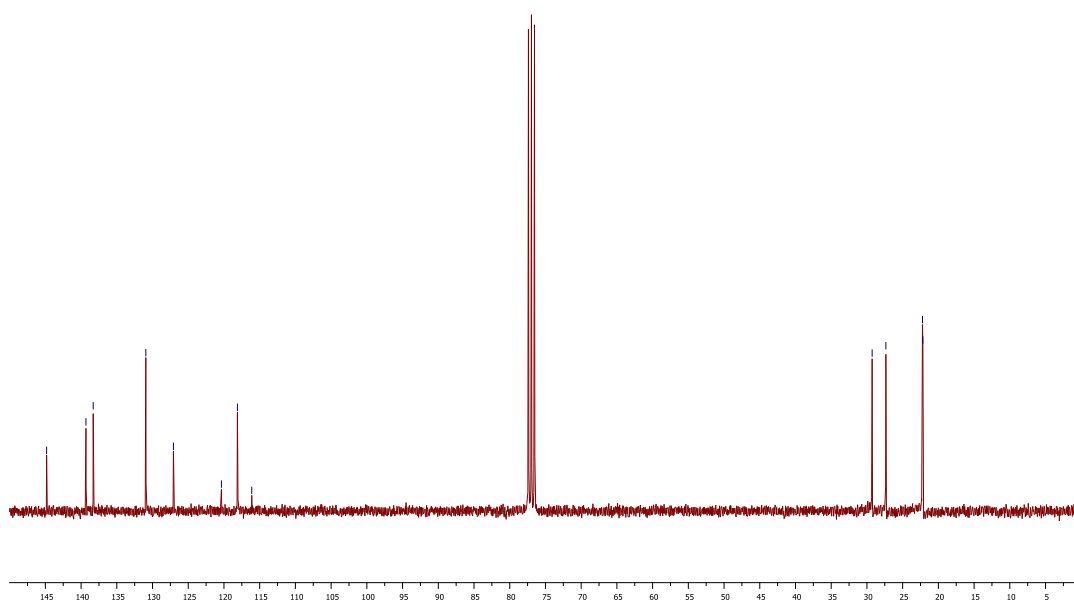
7.24  
7.21  
7.17  
7.14

2.87  
2.85  
2.83  
2.40  
2.31  
2.29  
1.82  
1.80  
1.78  
1.76  
1.74  
1.73  
1.71  
1.69  
1.68  
0.00

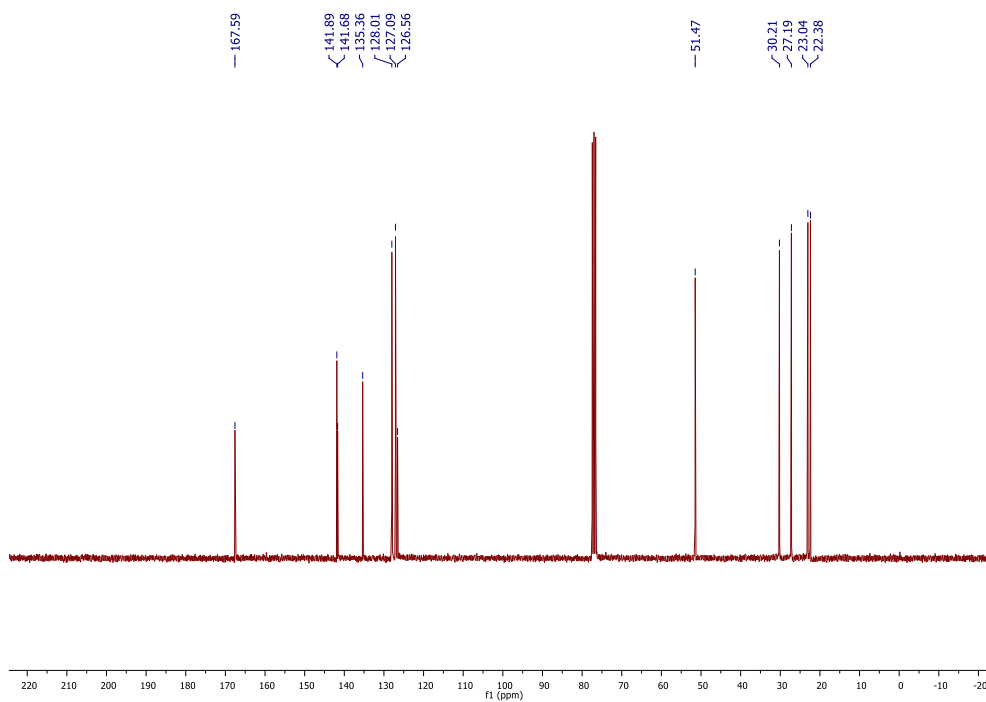
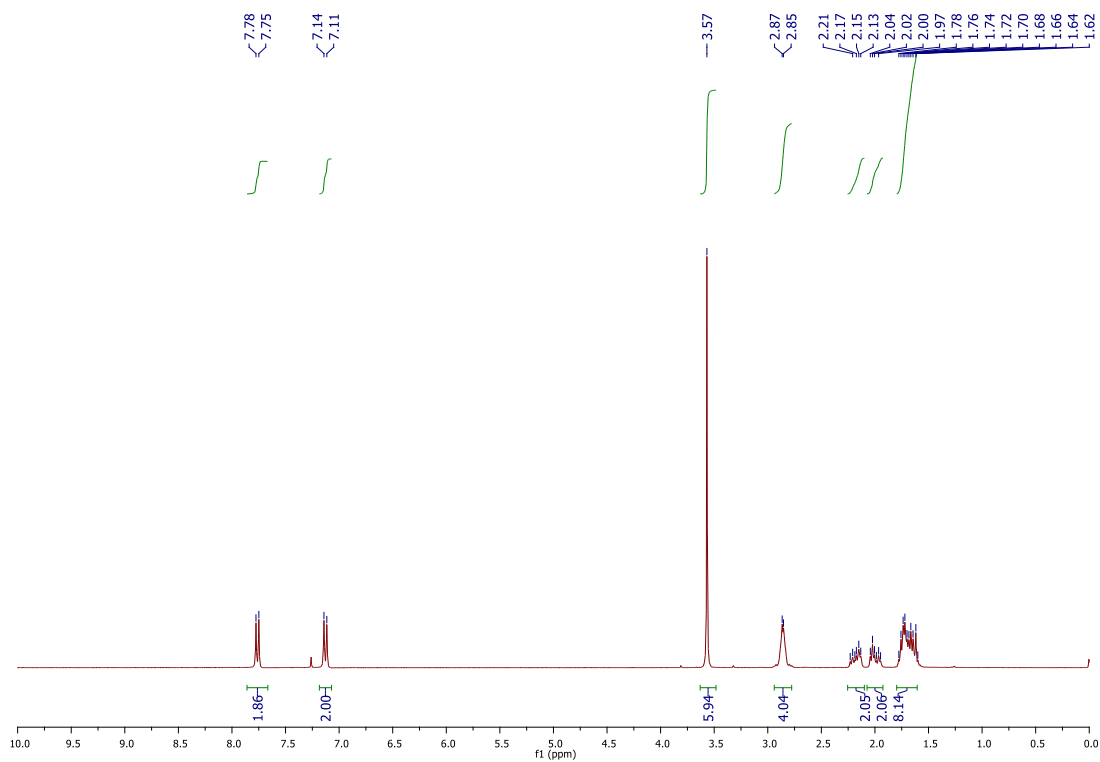
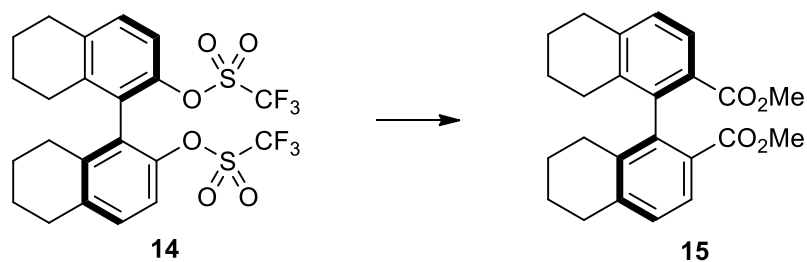


144.82  
139.32  
138.30  
130.94  
127.07  
120.36  
118.12  
116.11

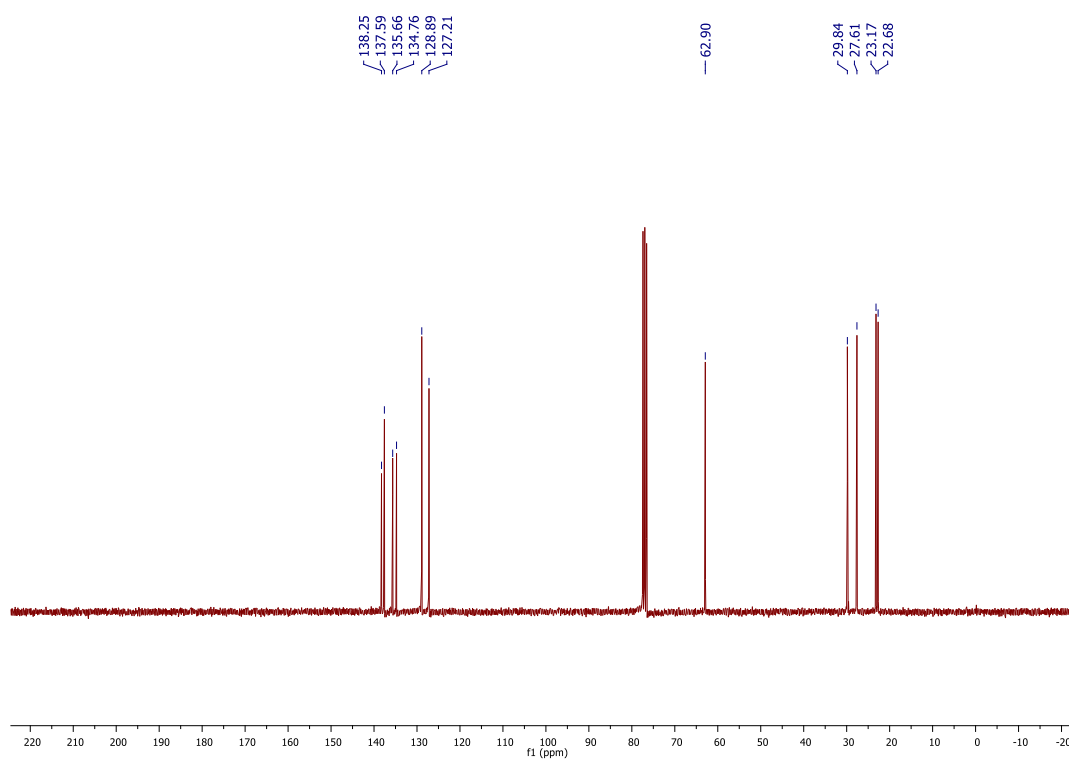
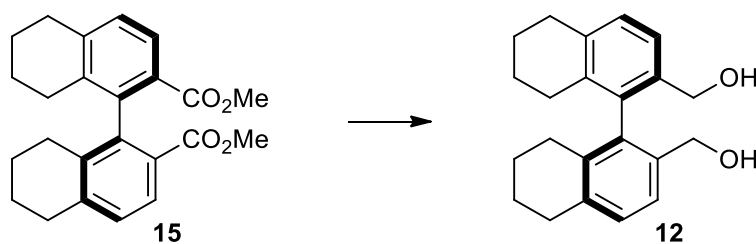
29.27  
27.35  
22.22  
22.17



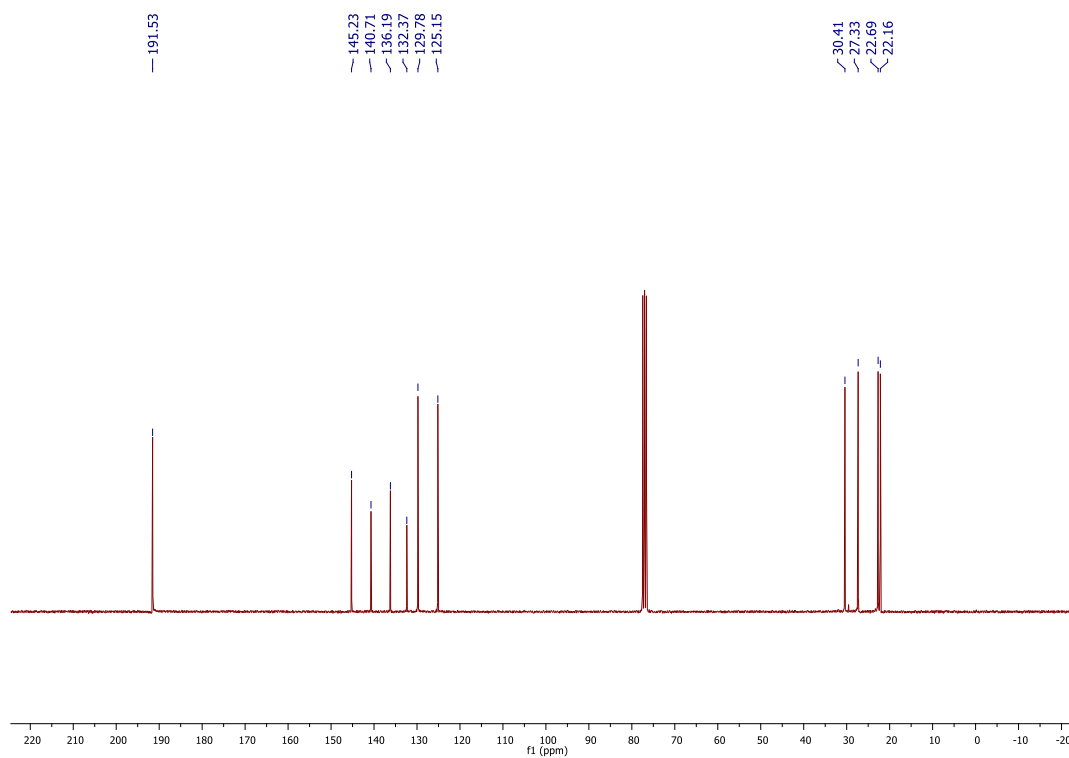
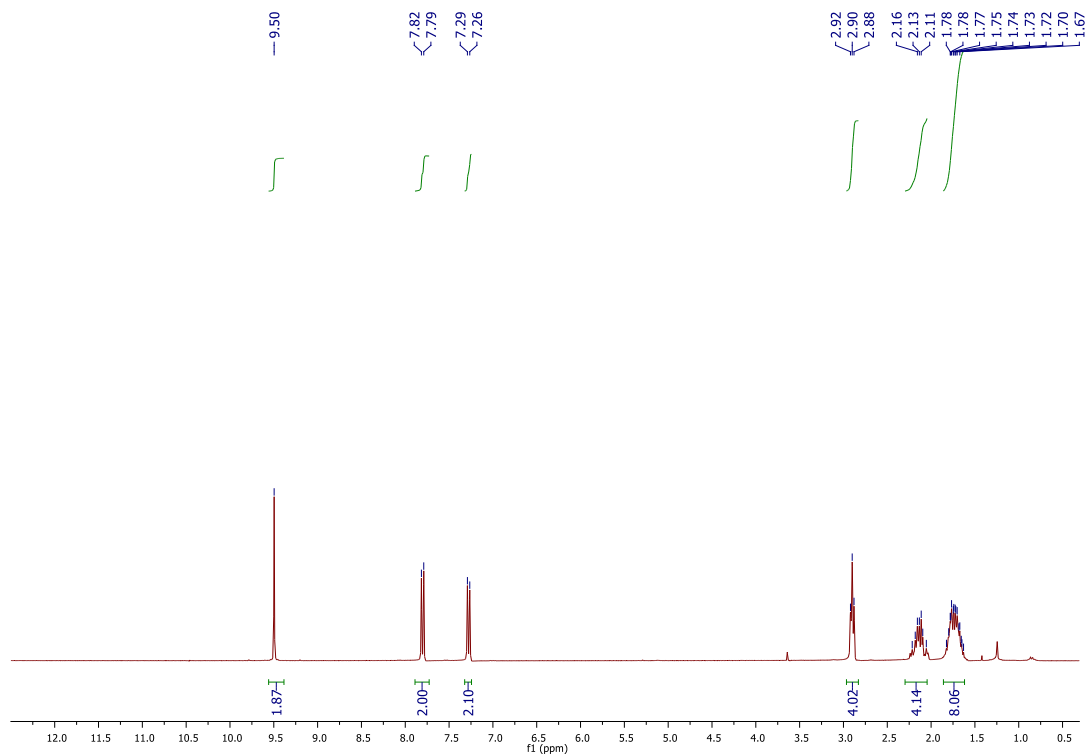
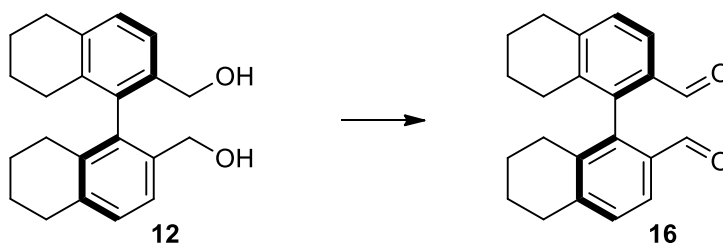
(-)-(R<sub>ax</sub>)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-bis(carboxylate) 15:



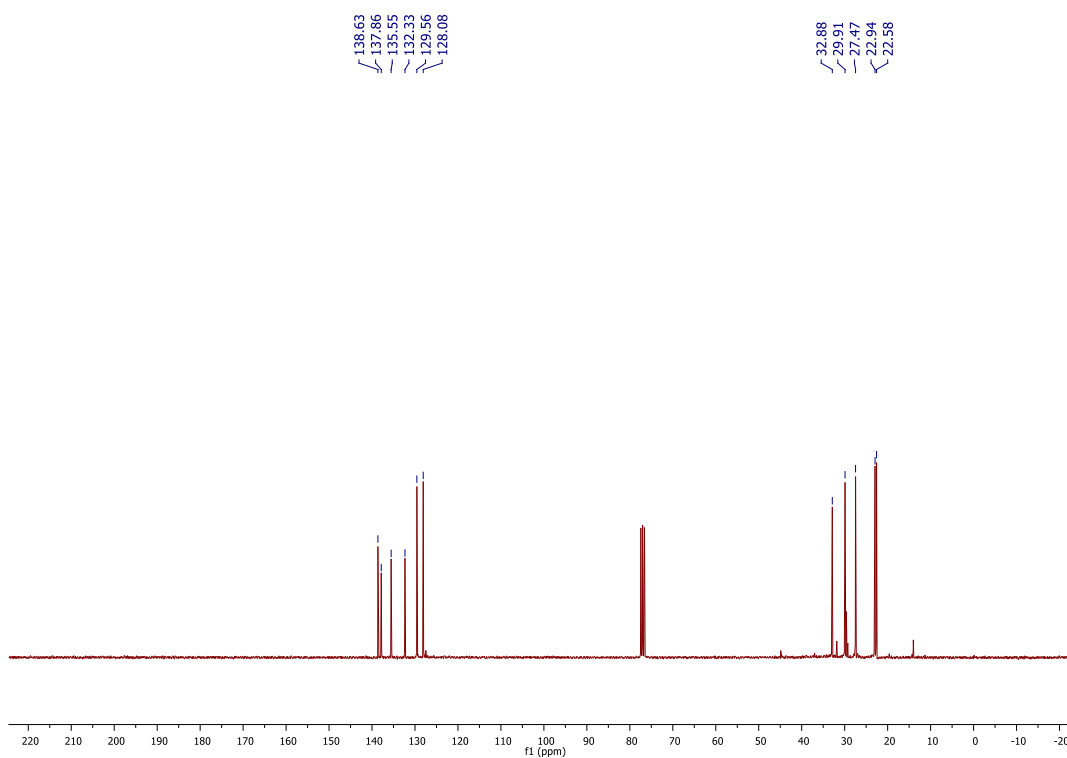
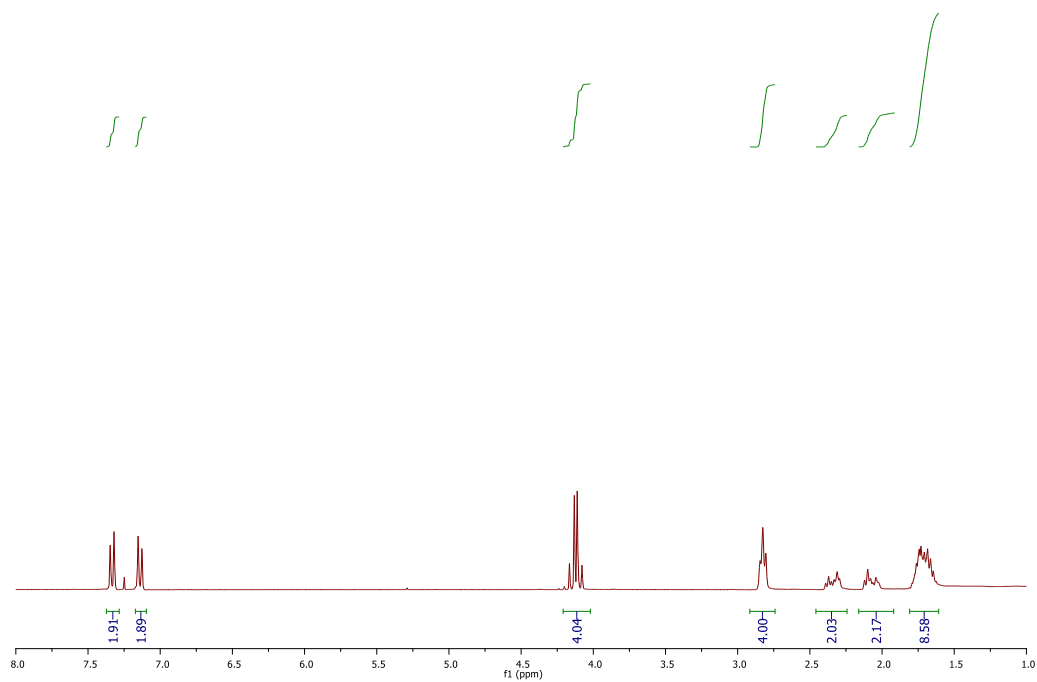
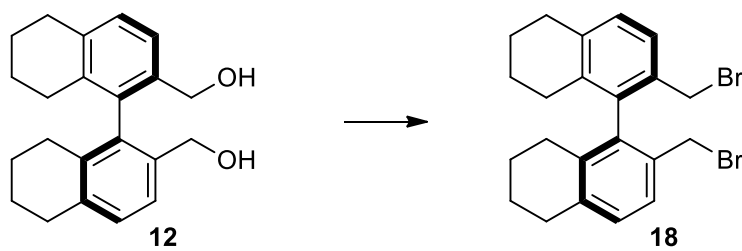
**(-)-(R<sub>ax</sub>)-5,5',6,6',7,7',8,8'-Octahydro-1,1'-binaphthyl-2,2'-dimethanol (12)**



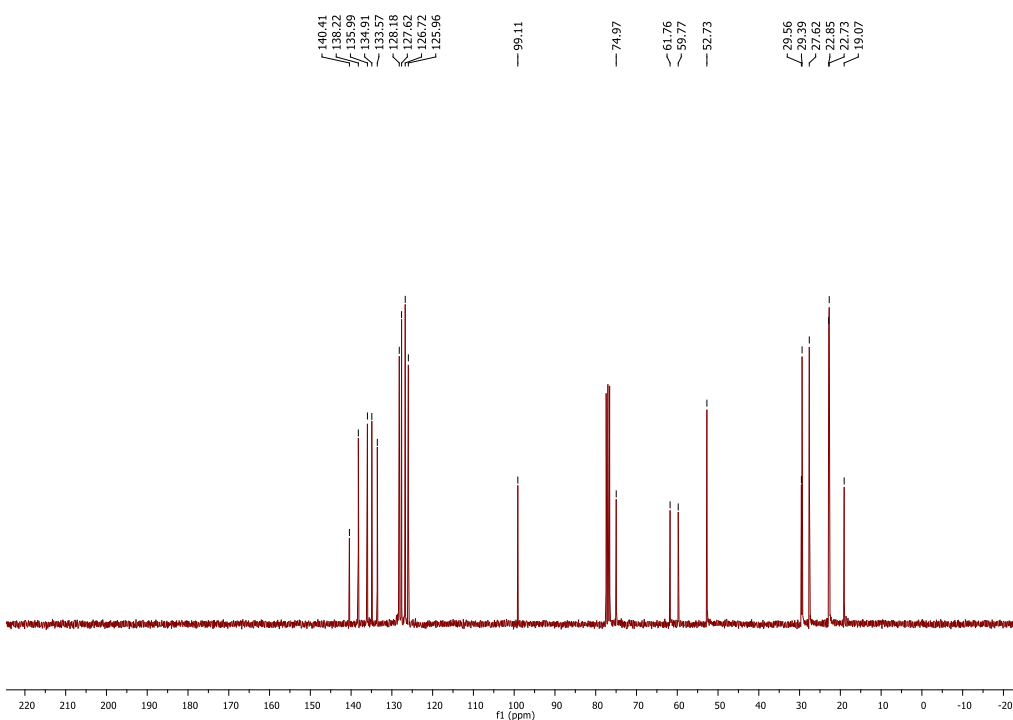
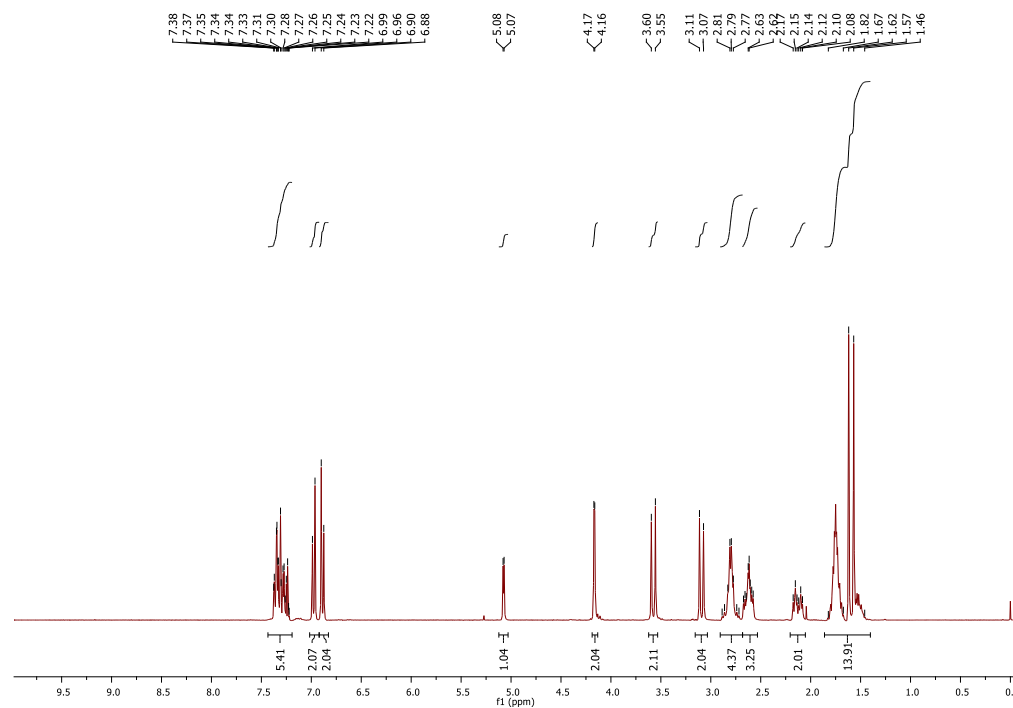
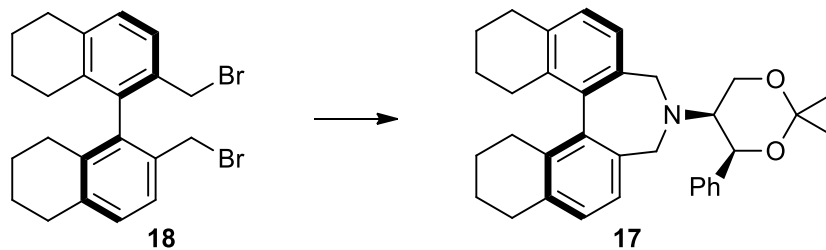
**(+)-(R<sub>ax</sub>)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-bis(carbaldehyde) 16:**



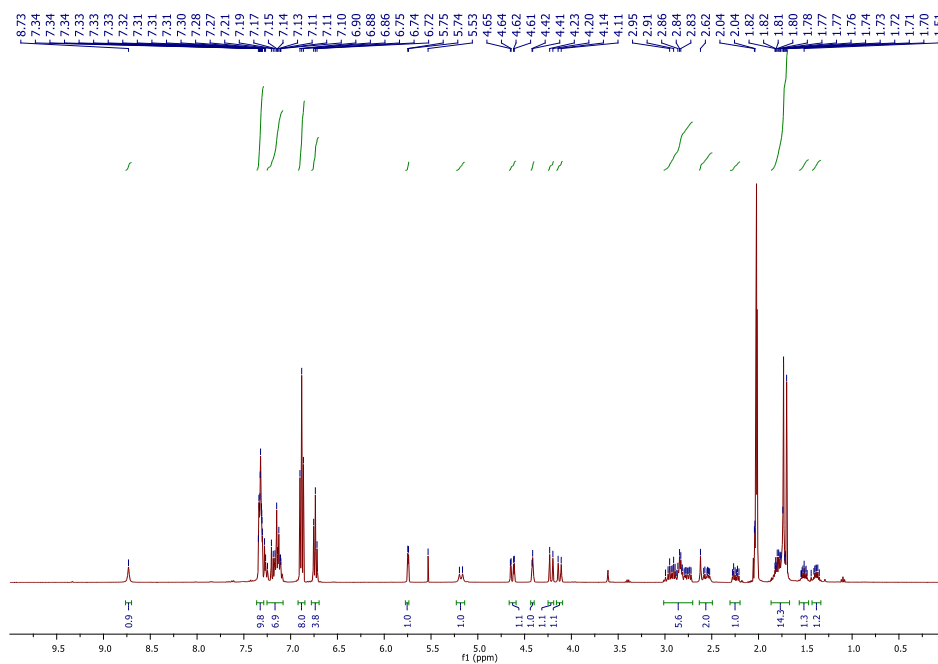
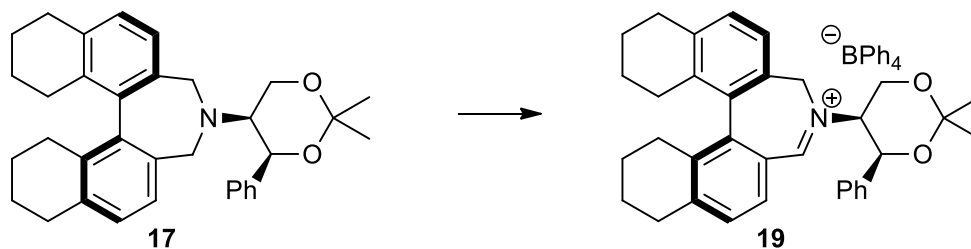
**(*R*<sub>ax</sub>)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-bis(bromomethyl) (18):**



(-)-(R<sub>ax</sub>)-4-((4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-4,5,8,9,10,11,12,13,14,15-decahydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]azepine (17)



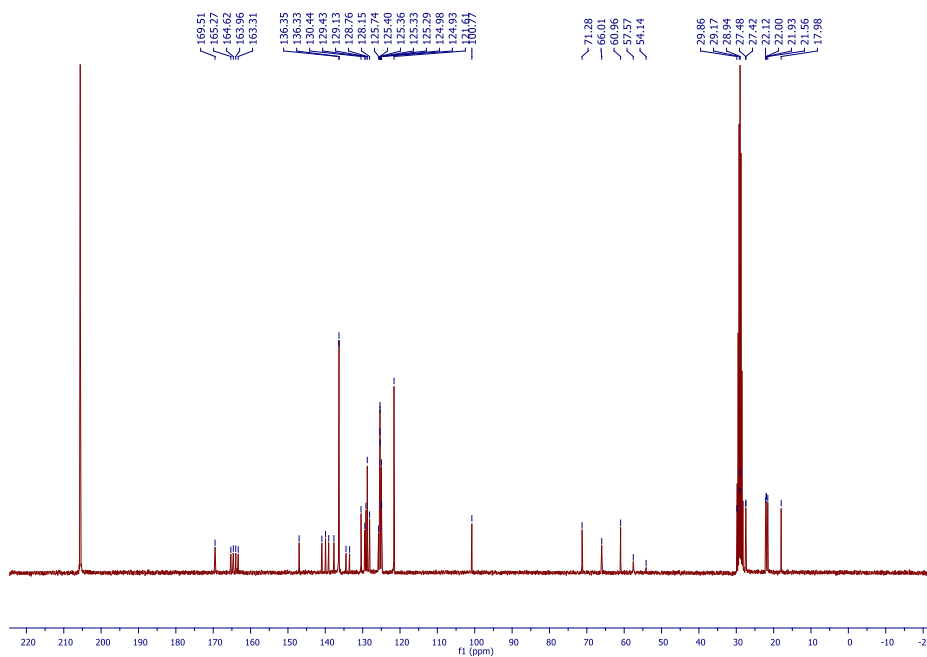
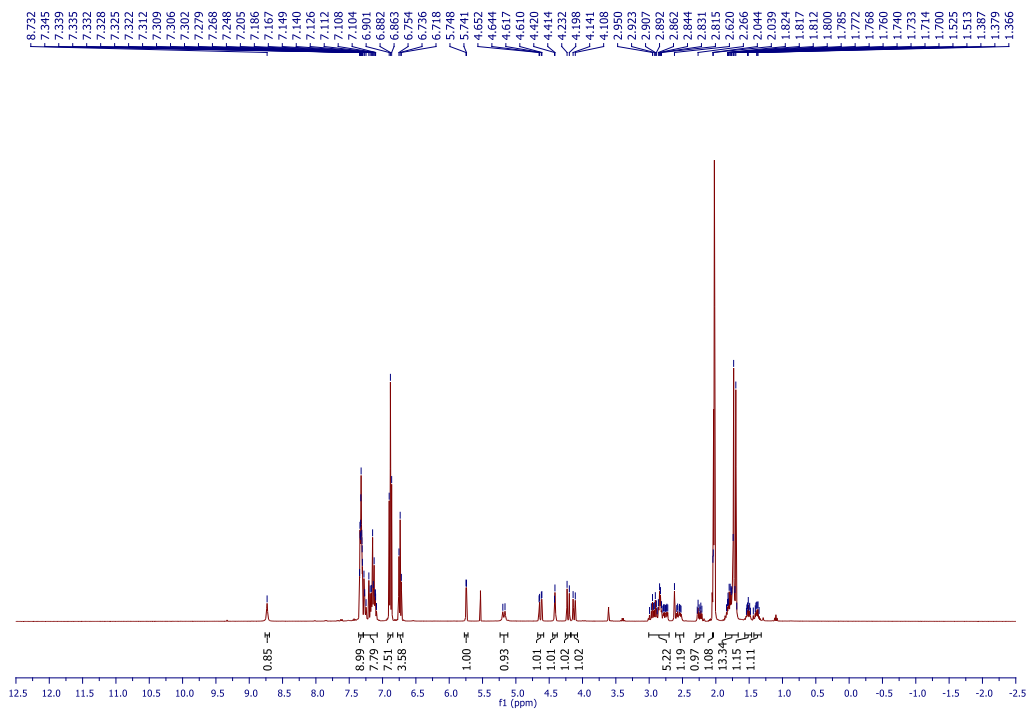
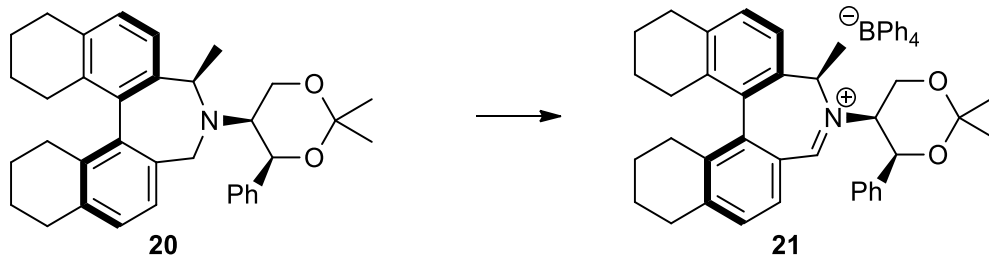
(-)-(R<sub>ax</sub>)-4-((4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-8,9,10,11,12,13,14,15-octahydro-3*H*-  
dinaphtho[2,1-*c*:1',2'-*e*]azepin-4-ium tetraphenylborate (19)







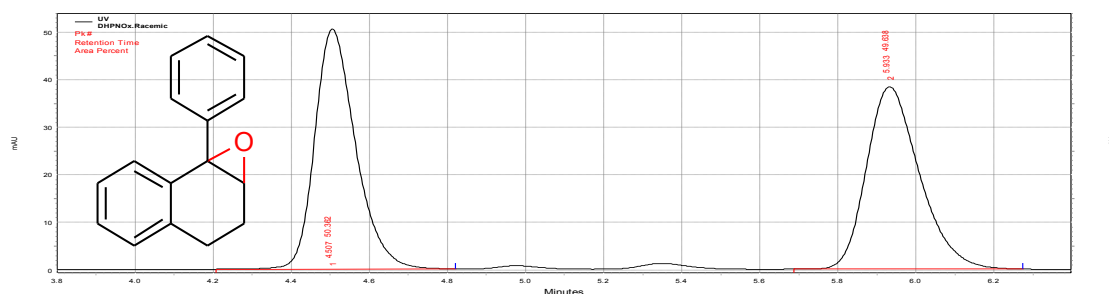
(-)-(3*R*,11*cR*<sub>ax</sub>)-4-((4*S*,5*S*)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-3-methyl-8,9,10,11,12,13,14,15-octahydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]azepin-4-ium tetraphenylborate (21)



## Supporting Chiral Separation Data

### Area % report of racemic 1-phenyl-3,4-dihydronaphthalene oxide

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\DHPNOx.Racemic.dat



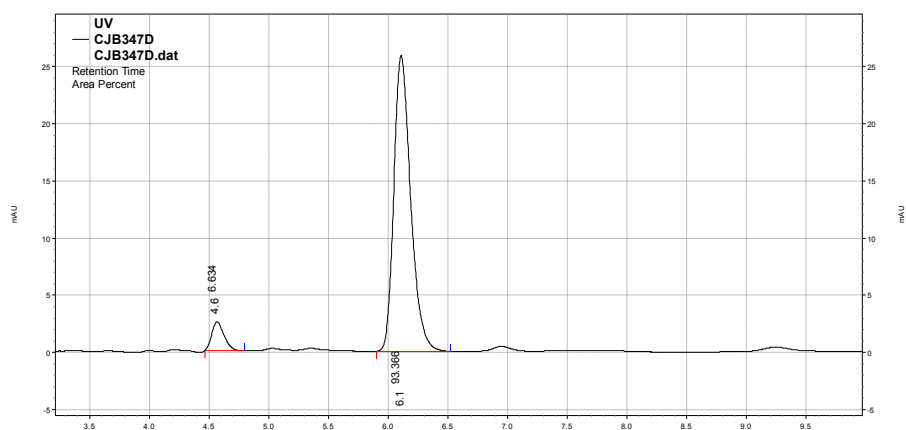
#### UV Results

Retention Time	Area	Area %	Height	Height %
4.507	1467968	50.36	201731	56.82
5.933	1446888	49.64	153330	43.18
<b>Totals</b>	<b>2914856</b>	<b>100.00</b>	<b>355061</b>	<b>100.00</b>

### Area % Report Cat 19 + 1-phenyl-3,4-dihydronaphthalene

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\CJB347D.dat

Method: C:\EZChrom Elite\Enterprise\Projects\ben\Method\untitled.met



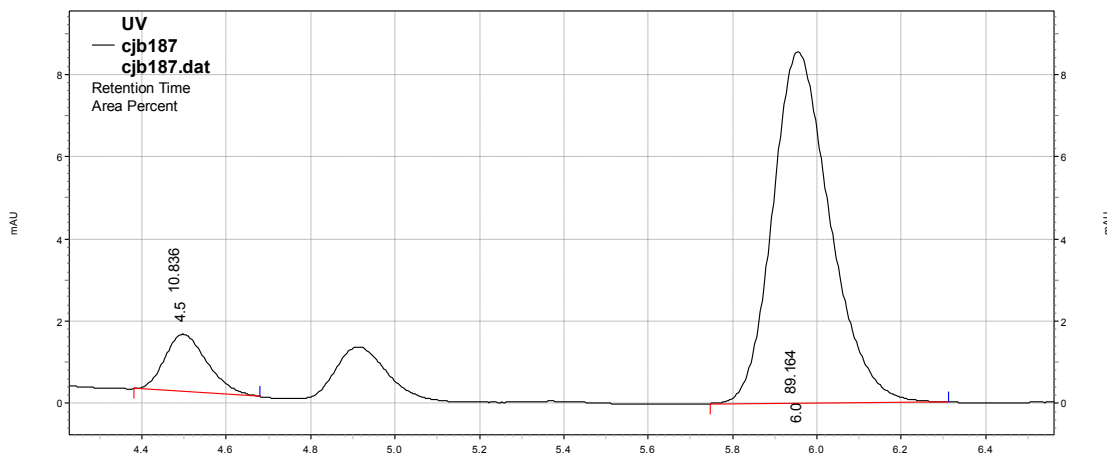
#### UV Results

Retention Time	Area	Area %	Height	Height %
4.567	71884	6.63	10020	8.82
6.110	1011733	93.37	103561	91.18
<b>Totals</b>	<b>1083617</b>	<b>100.00</b>	<b>113581</b>	<b>100.00</b>

### Area % Report Cat 6S<sub>ax</sub> + 1-Phenyl-3,4-dihydronaphthalene

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\cjb187.dat

Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10 30min.met



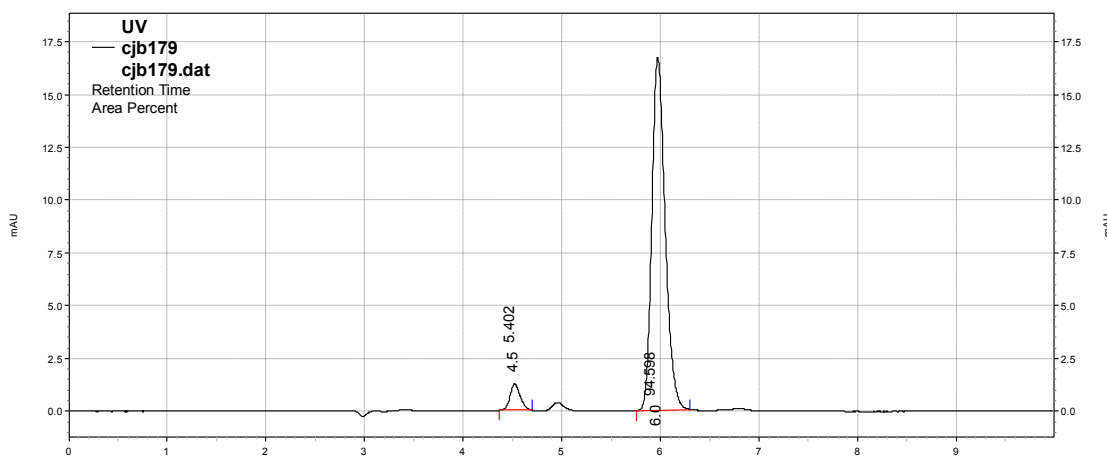
#### UV Results

Retention Time	Area	Area %	Height	Height %
4.497	39295	10.84	5608	14.11
5.957	323340	89.16	34141	85.89
<b>Totals</b>	<b>362635</b>	<b>100.00</b>	<b>39749</b>	<b>100.00</b>

### Area % Report Cat 5R<sub>ax</sub> + 1-Phenyl-3,4-dihydronaphthalene

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\cjb179.dat

Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10 30min.met

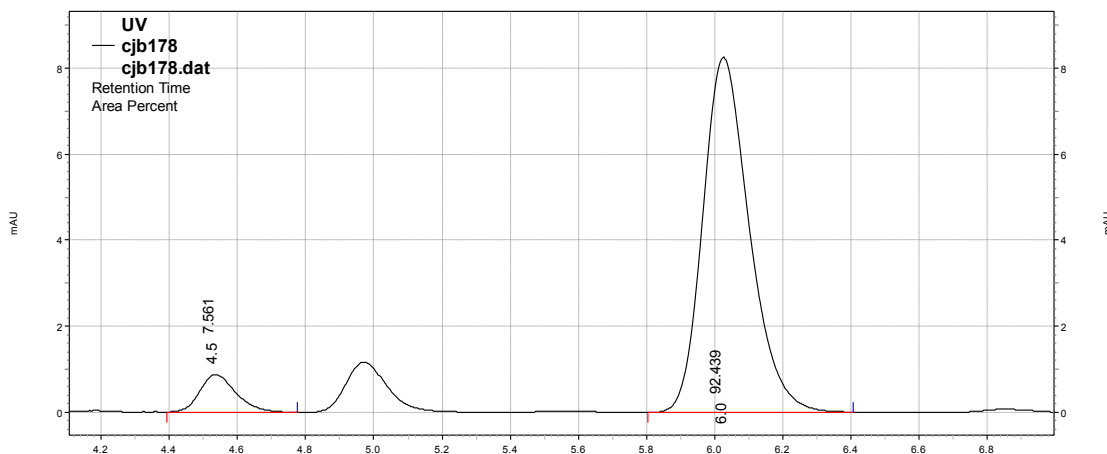


#### UV Results

Retention Time	Area	Area %	Height	Height %
4.523	35789	5.40	4970	6.92
5.973	626688	94.60	66811	93.08

### Area % Report Cat 6R<sub>ax</sub> + 1-Phenyl-3,4-dihydronaphthalene

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\cjb178.dat  
 Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10 30min.met



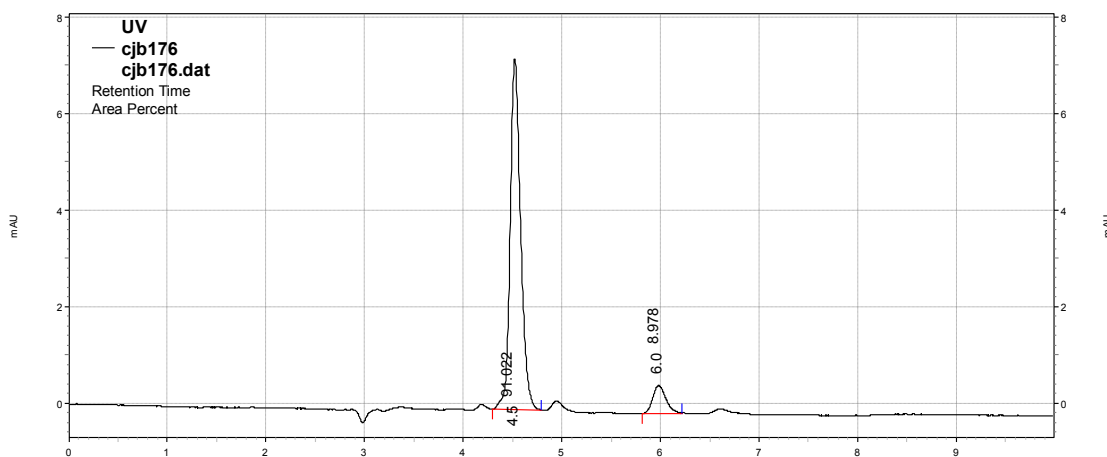
#### UV Results

Retention Time	Area	Area %	Height	Height %
4.533	25720	7.56	3496	9.57
6.027	314440	92.44	33035	90.43

Totals	Area	Area %	Height	Height %
	340160	100.00	36531	100.00

### Area % Report Cat 5S<sub>ax</sub> + 1-Phenyl-3,4-dihydronaphthalene

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\cjb176.dat  
 Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10 30min.met



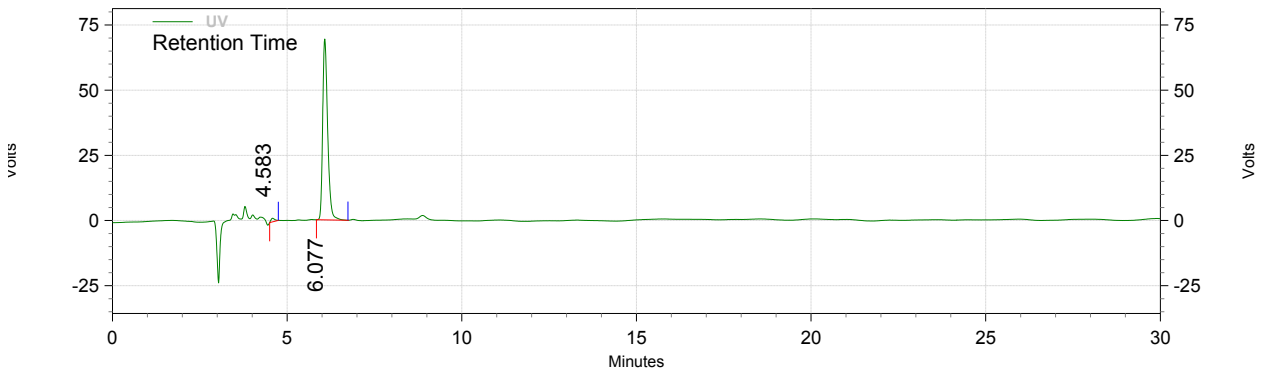
#### UV Results

Retention Time	Area	Area %	Height	Height %
4.523	215011	91.02	29076	92.69
5.983	21208	8.98	2292	7.31

**Area % Report Cat 21 + 1-Phenyl-3,4-dihydronaphthalene**

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\CJB431Dfilter.dat

Method: C:\EZChrom Elite\Enterprise\Projects\ben\Method\90.10 30min.met



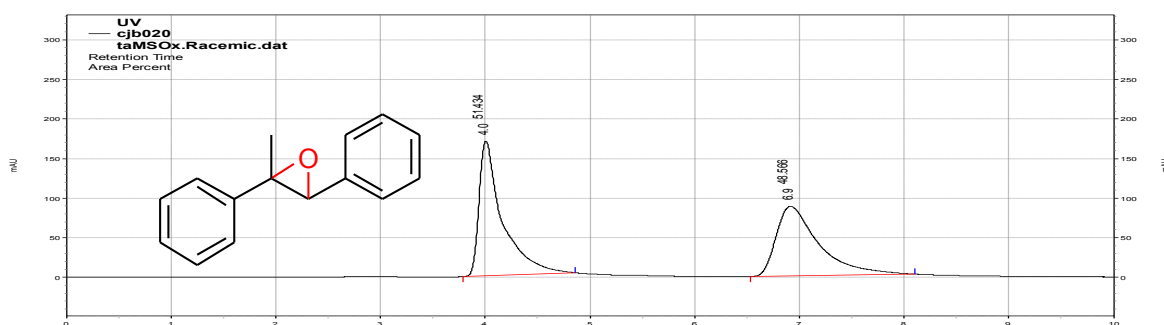
**UV Results**

Retention Time	Area	Area %	Height	Height %
4.583	40747	1.47	5472	1.93
6.077	2740028	98.53	277404	98.07
Totals	2780775	100.00	282876	100.00

### Area % Report of racemic *trans*- $\alpha$ -methylstilbene oxide

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\taMSOx.Racemic.dat

Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\Trans-Stilbene2.met



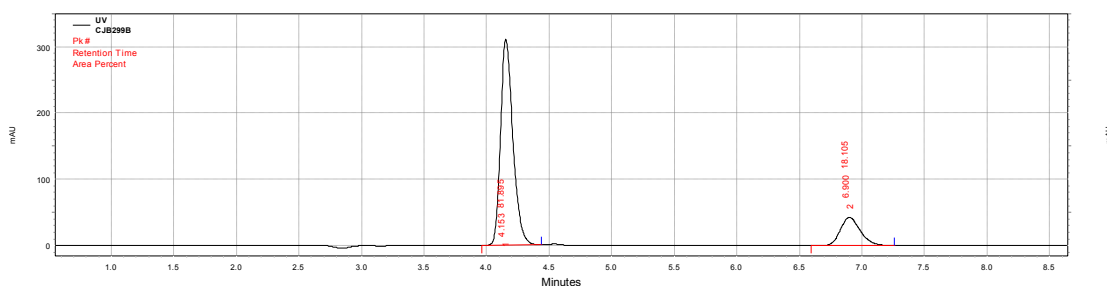
#### UV Results

Retention Time	Area	Area %	Height	Height %
4.007	10514211	51.43	680756	65.88
6.917	9928030	48.57	352506	34.12
<b>Totals</b>	<b>20442241</b>	<b>100.00</b>	<b>1033262</b>	<b>100.00</b>

### Area % Report Cat 19+ *trans*- $\alpha$ -methylstilbene

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\CJB299B.dat

Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\lactoneacidBn.met

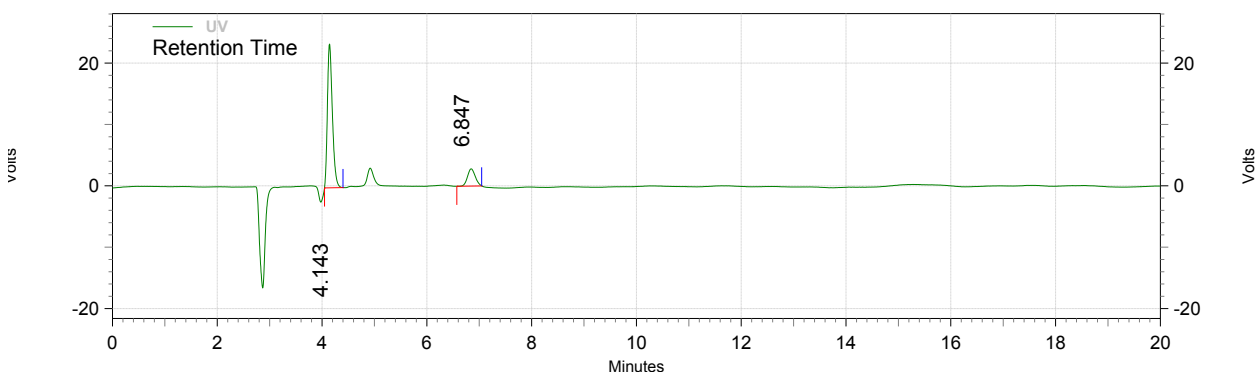


#### UV Results

Retention Time	Area	Area %	Height	Height %
4.153	8556166	81.89	1242459	87.98
6.900	1891579	18.11	169811	12.02
<b>Totals</b>	<b>10447745</b>	<b>100.00</b>	<b>1412270</b>	<b>100.00</b>

### Area % Report Cat 21 + *trans*- $\alpha$ -methylstilbene

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\CJB431B.dat  
 Method: C:\EZChrom Elite\Enterprise\Projects\ben\Method\Trans-Stilbene2.met

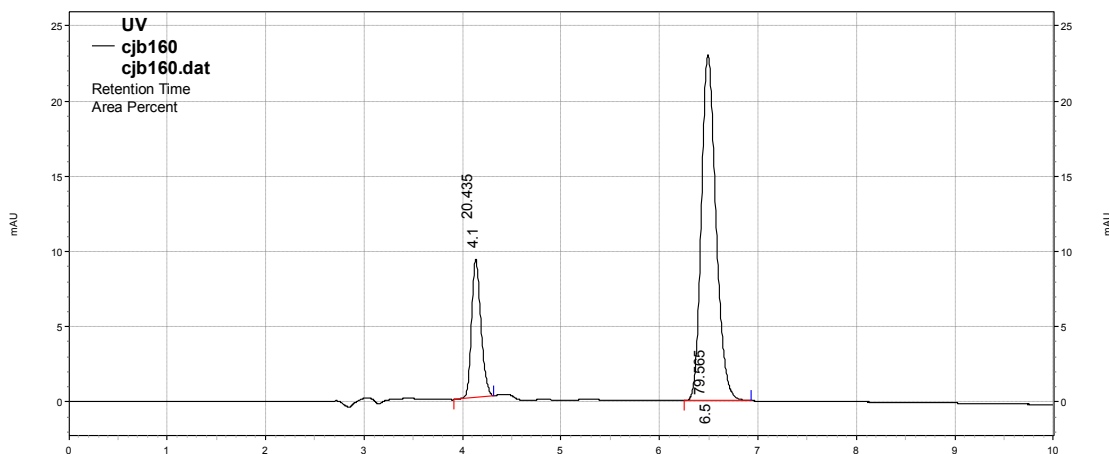


#### UV Results

Retention Time	Area	Area %	Height	Height %
4.143	616239	84.27	93730	89.30
6.847	115062	15.73	11231	10.70
<b>Totals</b>	<b>731301</b>	<b>100.00</b>	<b>104961</b>	<b>100.00</b>

### Area % Report Cat 5S<sub>ax</sub> + *trans*- $\alpha$ -methylstilbene

Data File: C:\Documents and Settings\Ben\Desktop\hplc 17.11.08\cjb160.dat  
 Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\20 min 80.20 1ml.met



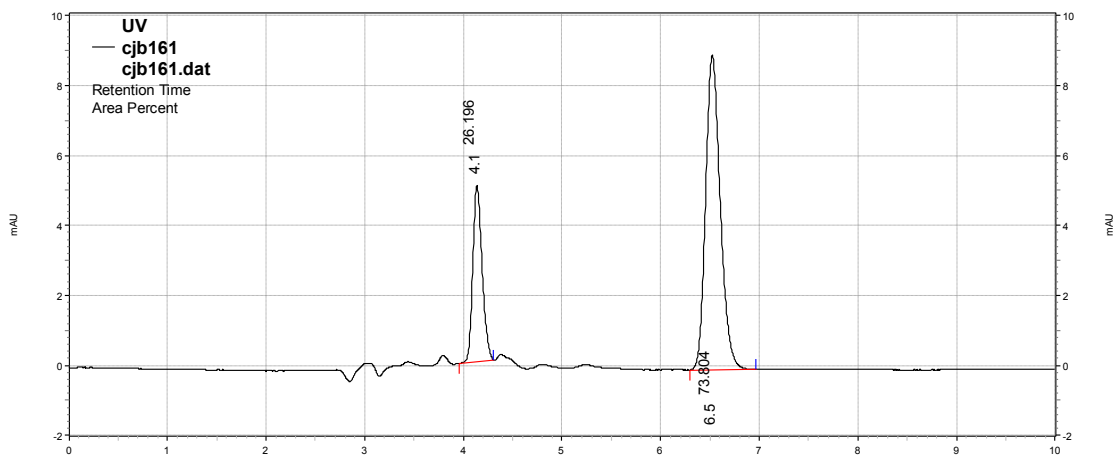
#### UV Results

Retention Time	Area	Area %	Height	Height %
4.133	243729	20.43	36758	28.58
6.490	949003	79.57	91866	71.42
<b>Totals</b>	<b>1192732</b>	<b>100.00</b>	<b>128624</b>	<b>100.00</b>

### Area % Report Cat 6S<sub>ax</sub> + *trans*- $\alpha$ -methylstilbene

Data File: C:\Documents and Settings\Ben\Desktop\hplc 17.11.08\cjb161.dat

Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\60 min 98.02 1ml.met



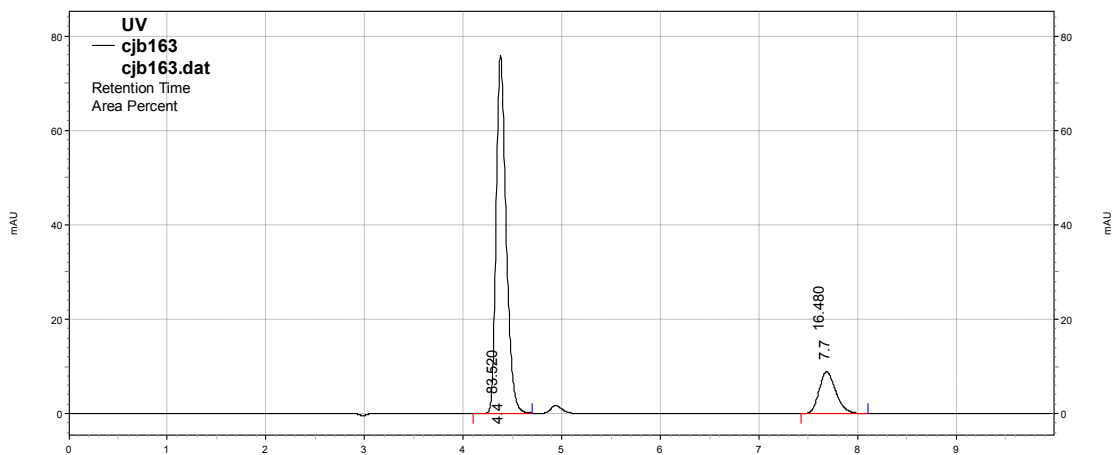
#### UV Results

Retention Time	Area	Area %	Height	Height %
4.137	131529	26.20	20126	35.90
6.523	370559	73.80	35932	64.10

### Area % Report Cat 5R<sub>ax</sub> + *trans*- $\alpha$ -methylstilbene

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\cjb163.dat

Method: C:\EZChrom Elite\Enterprise\Projects\farah\Method\1-phenyldihydro.met



#### UV Results

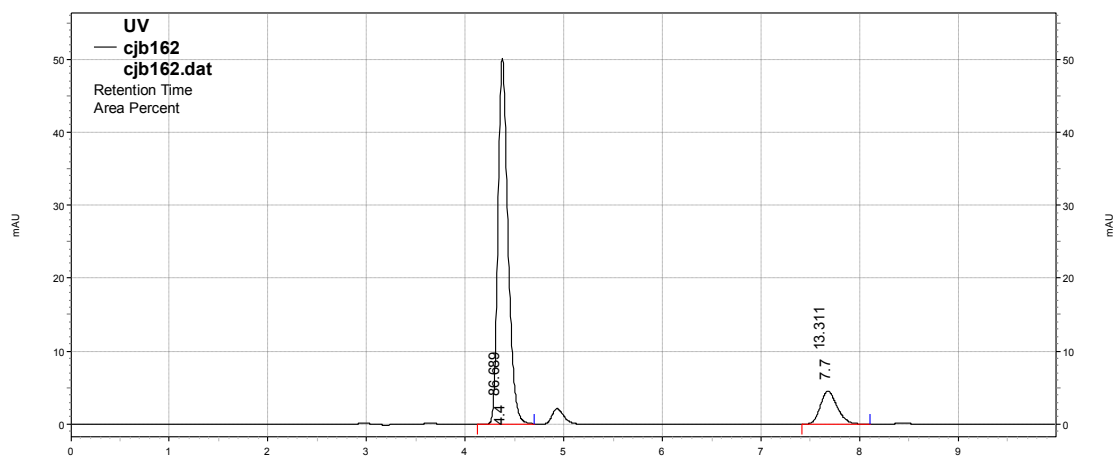
Retention Time	Area	Area %	Height	Height %
4.377	2126174	83.52	303041	89.50
7.687	419522	16.48	35549	10.50



**Area % Report Cat 6R<sub>ax</sub> + *trans*- $\alpha$ -methylstilbene**

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\cjb162.dat

Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\60 min 98.02 1ml.met



**UV Results**

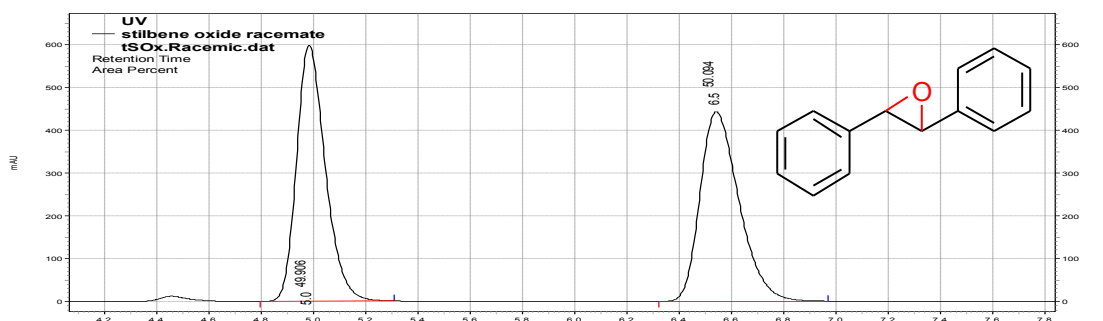
Retention Time	Area	Area %	Height	Height %
4.377	1415251	86.69	200469	91.67
7.680	217311	13.31	18210	8.33

Totals	1632562	100.00	218679	100.00
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### Area % Report of racemic *trans*-stilbene oxide

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\tSOx.Racemic.dat

Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\Trans-Stilbene2.met



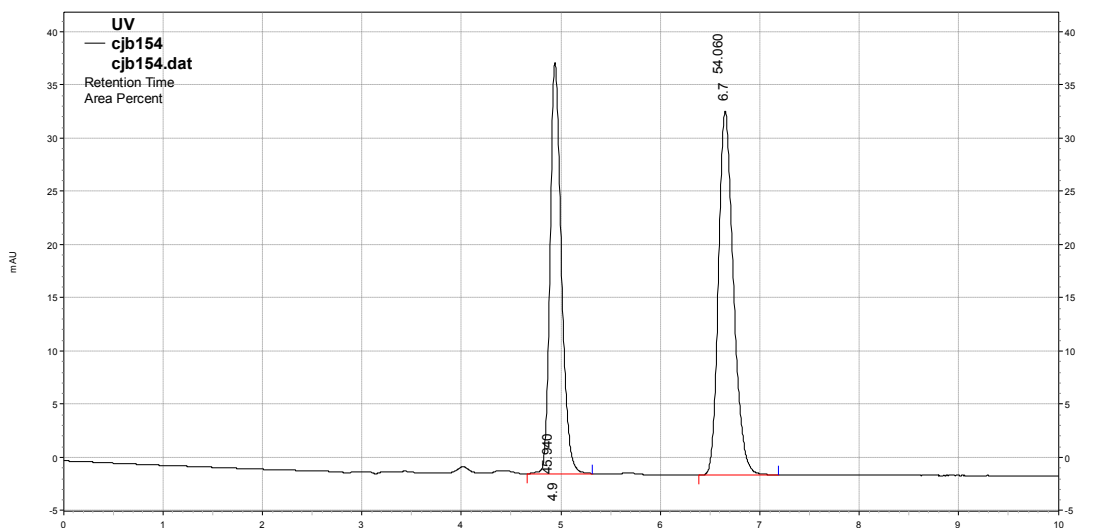
### UV Results

Retention Time	Area	Area %	Height	Height %
4.983	18312411	49.91	2394160	57.45
6.543	18381757	50.09	1773413	42.55
<b>Totals</b>	<b>36694168</b>	<b>100.00</b>	<b>4167573</b>	<b>100.00</b>

### Area % Report Cat 5S<sub>ax</sub> + *trans*-stilbene

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\cjb154.dat

Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\99.1 80min.met

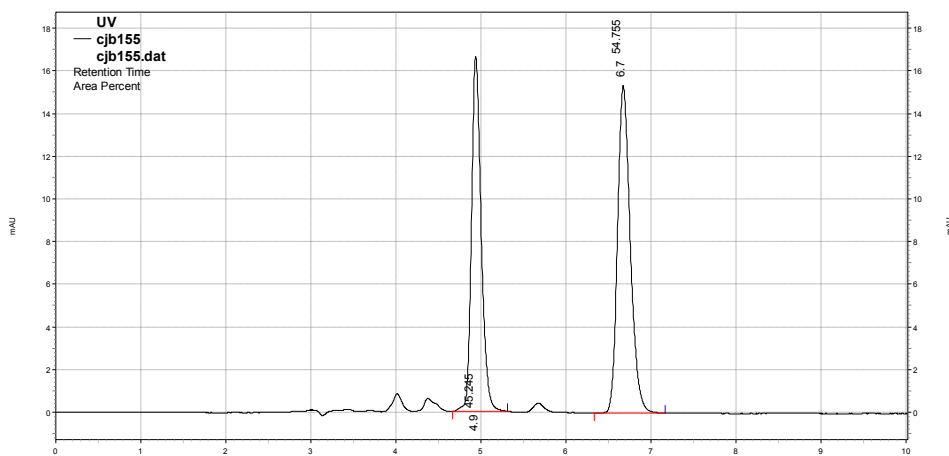


### UV Results

Retention Time	Area	Area %	Height	Height %
4.943	1214539	45.94	154301	53.00
6.653	1429185	54.06	136840	47.00

### Area % Report Cat 6S<sub>ax</sub> + *trans*-stilbene

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\cjb155.dat  
 Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\99.1 80min.met



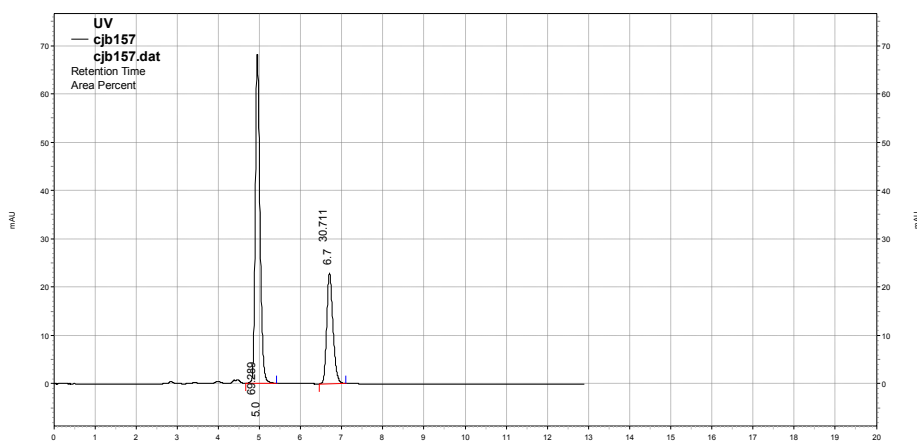
#### UV Results

Retention Time	Area	Area %	Height	Height %
4.943	527868	45.25	66537	52.04
6.677	638808	54.75	61328	47.96

Totals	Area	Area %	Height	Height %
	1166676	100.00	127865	100.00

### Area % Report cat 6R<sub>ax</sub> + *trans*-stilbene

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\cjb157.dat  
 Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\99.1 80min.met



#### UV Results

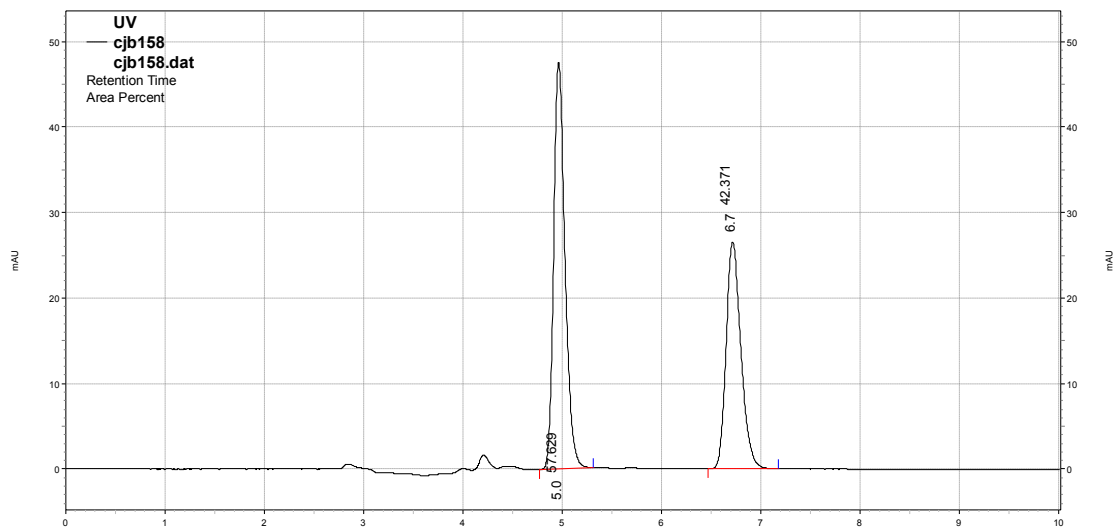
Retention Time	Area	Area %	Height	Height %
4.950	2166187	69.29	272461	74.85
6.703	960101	30.71	91528	25.15

Totals	Area	Area %	Height	Height %
	3126288	100.00	363989	100.00

## Area % Report Cat 5R<sub>ax</sub> + *trans*-stilbene

Data File: C:\EZChrom Elite\Enterprise\Projects\Chris\cjb158.dat

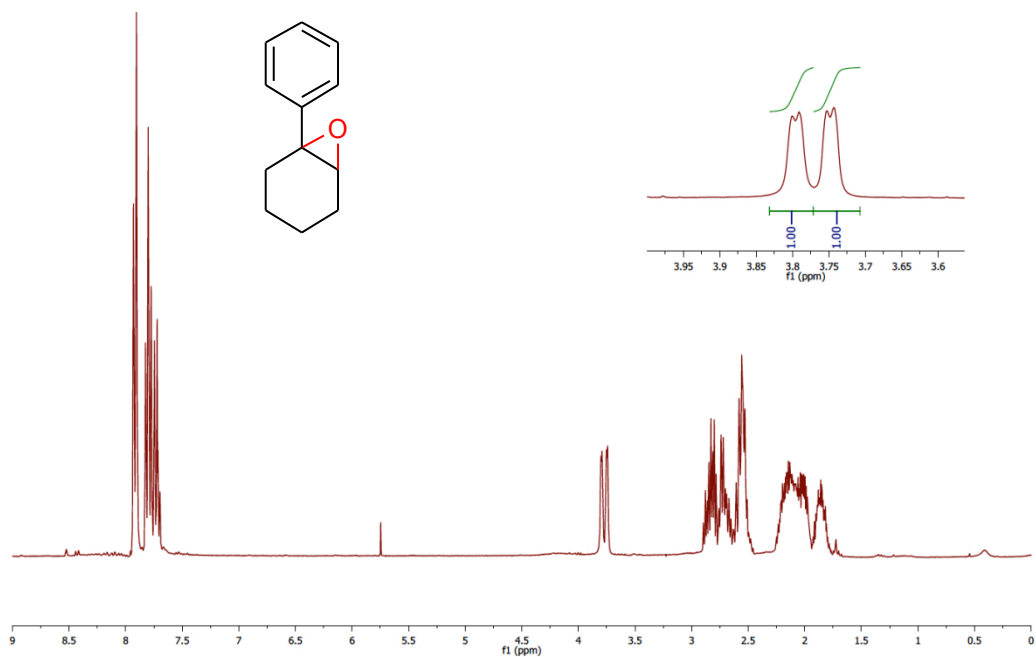
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\99.1 80min.met



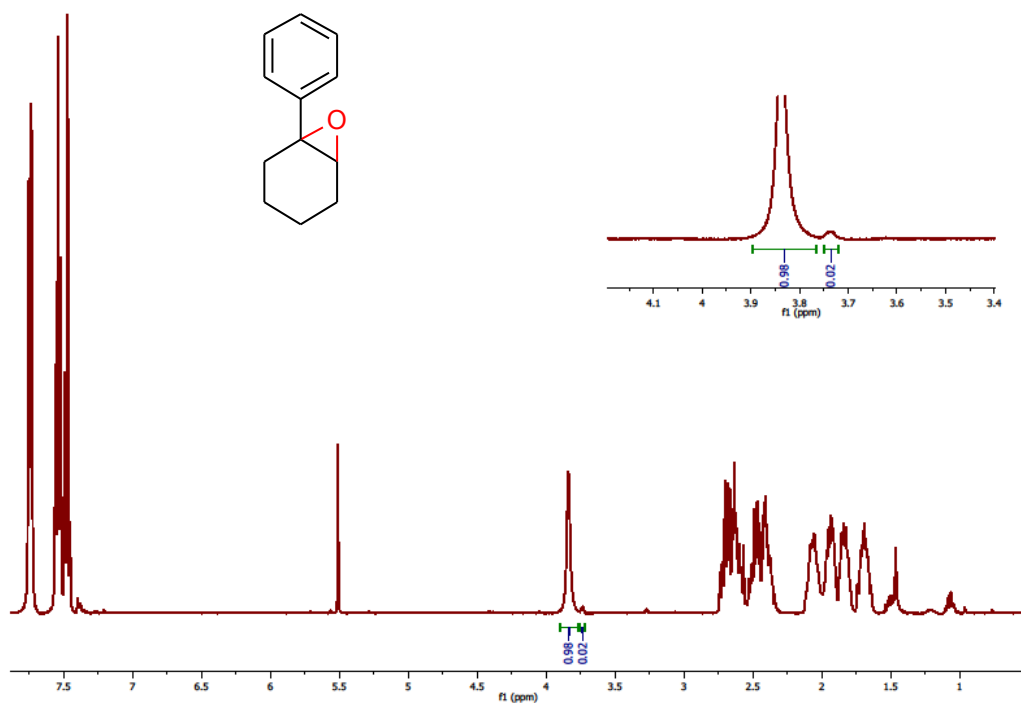
### UV Results

Retention Time	Area	Area %	Height	Height %
4.970	1494697	57.63	190251	64.20
6.720	1098946	42.37	106078	35.80

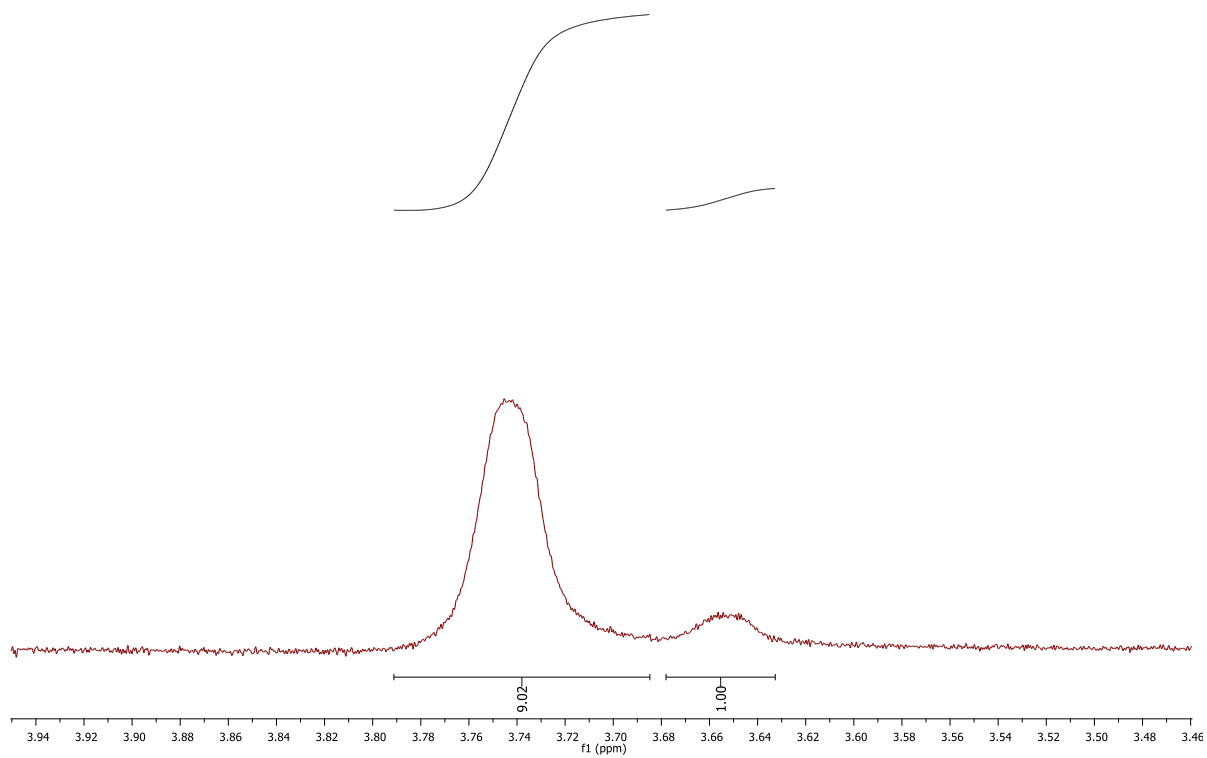
## NMR of racemic 1-phenyl-3,4-cyclohexene oxide



## NMR sample of enantioenriched 1-phenylcyclohexene oxide in the presence of chiral shift reagent Catalyst 21 + 1-phenylcyclohexene

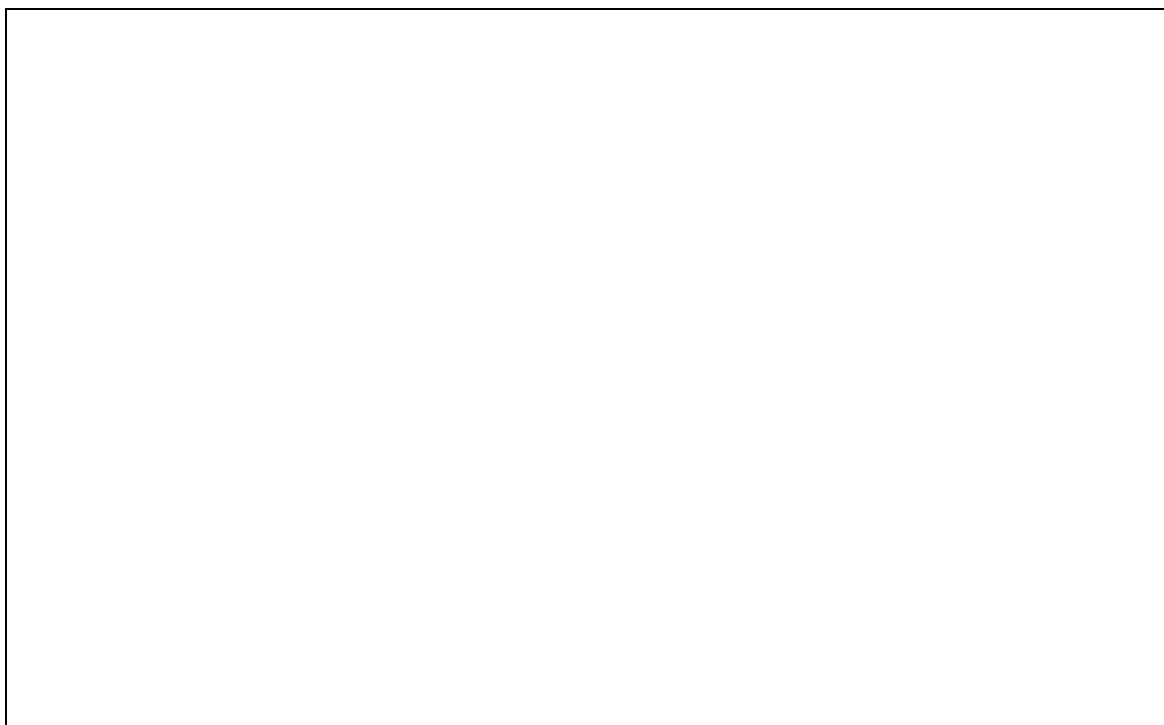


Cat 19+ 1-phenylcyclohexene

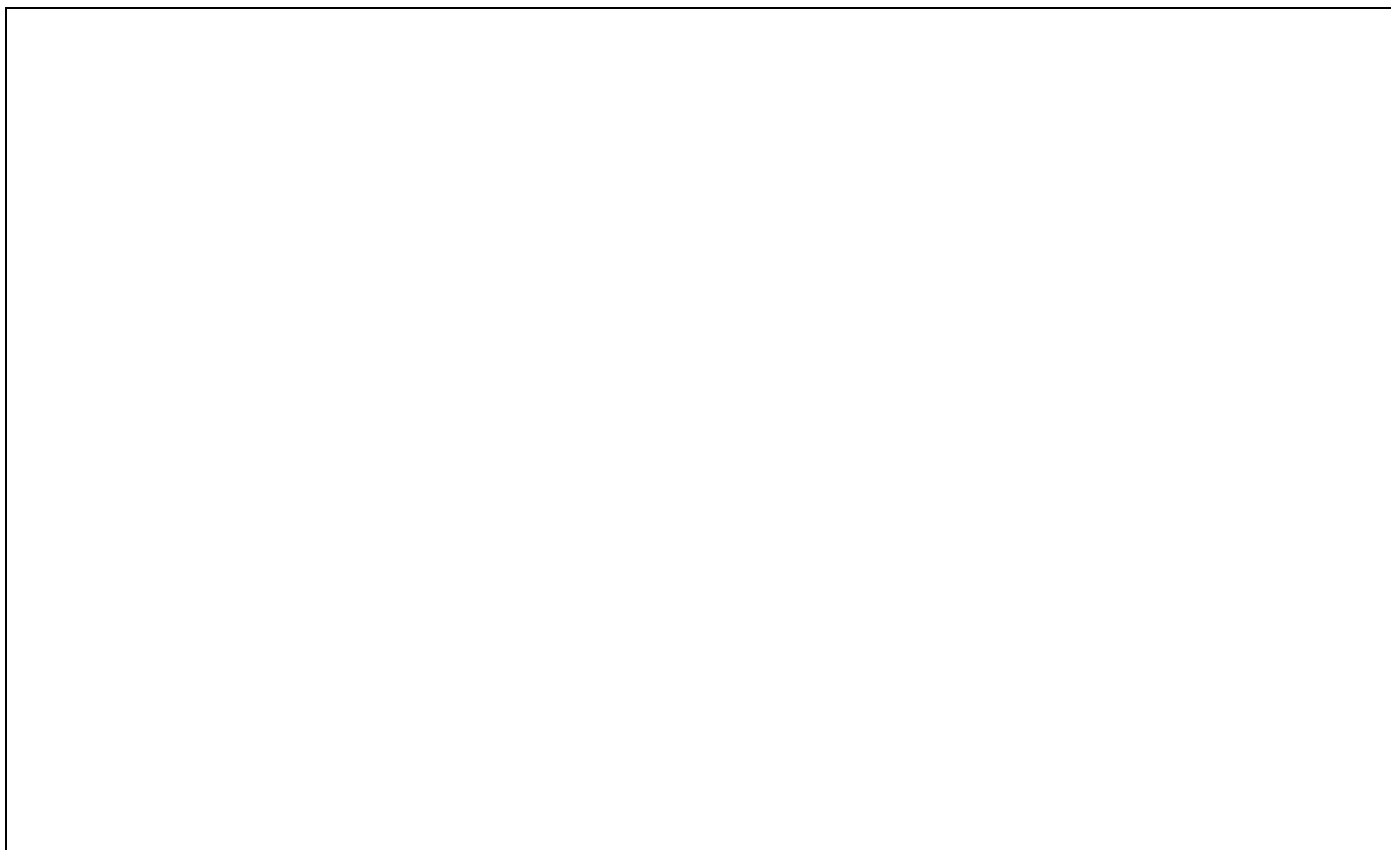


**Chiral stationary phase GC:**

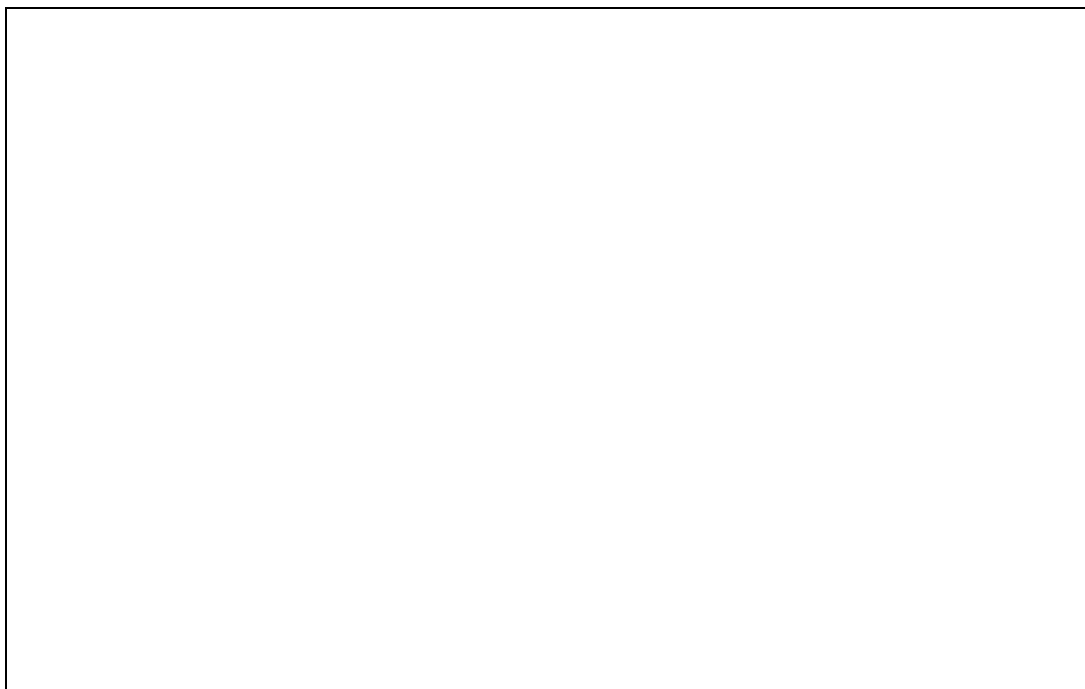
Racemic 1-phenylcyclohexene oxide



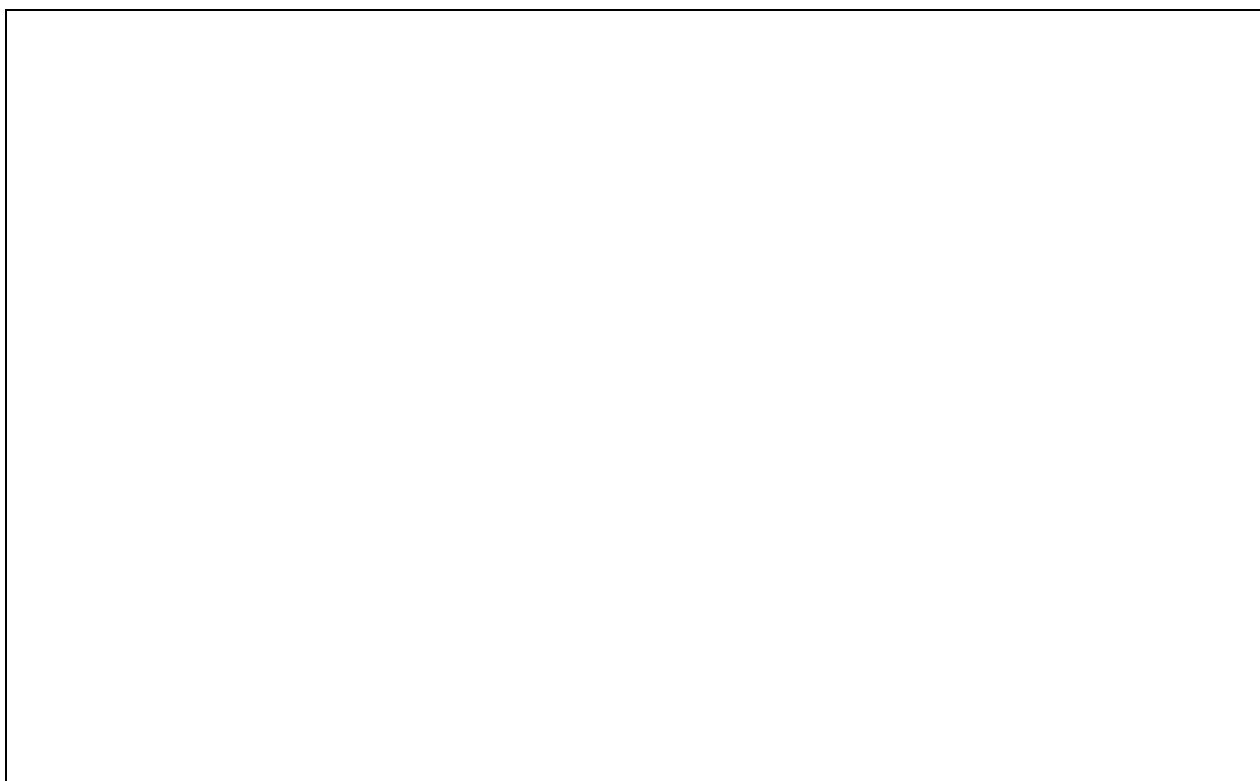
Cat **5R<sub>ax</sub>** + 1-phenylcyclohexene



Cat **5S<sub>ax</sub>** + 1-phenylcyclohexene

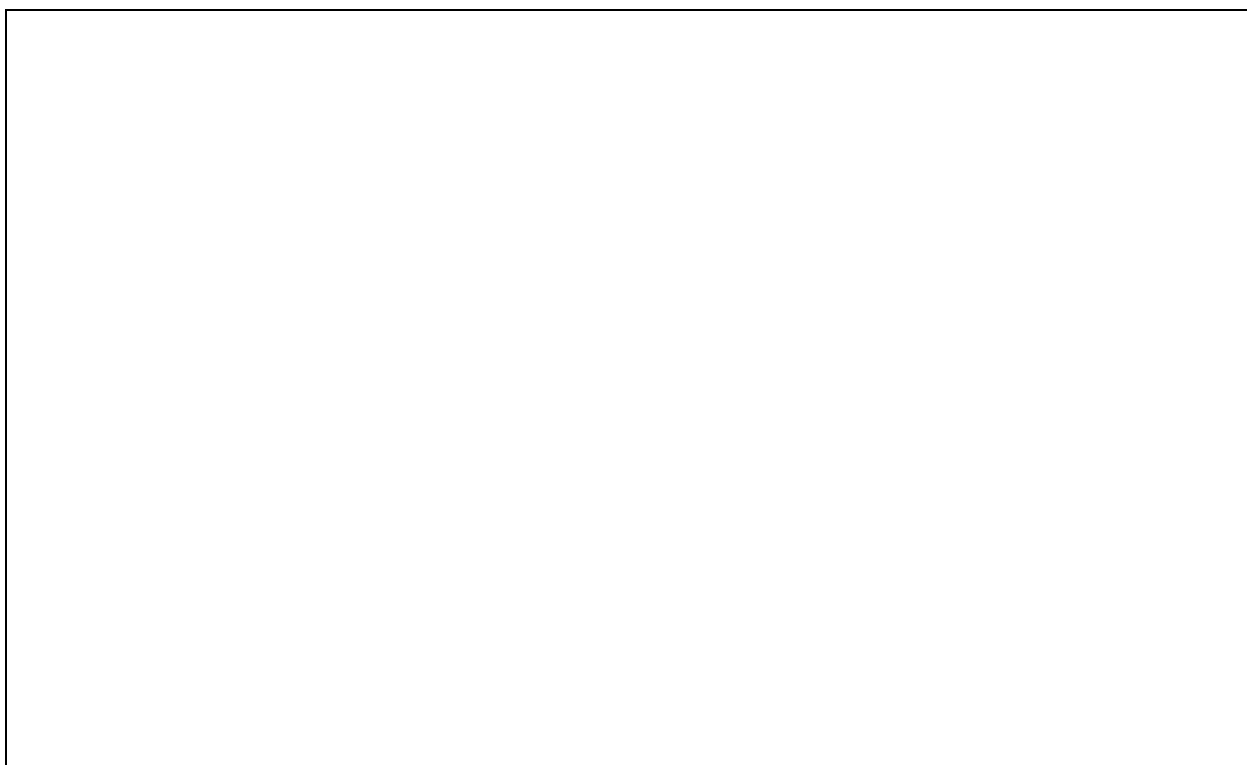


Cat **6R<sub>ax</sub>** + 1-phenylcyclohexene

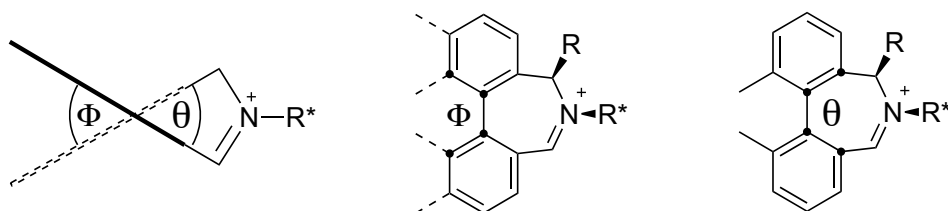


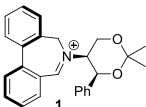
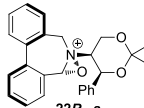
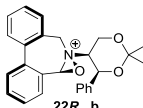
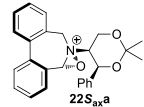
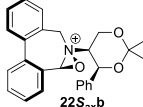
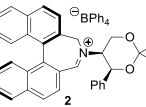
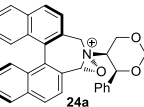
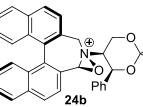
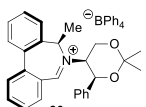
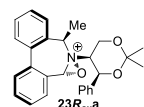
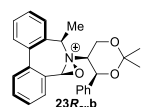
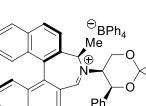
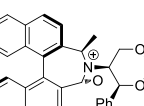
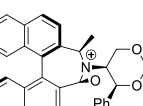
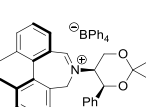
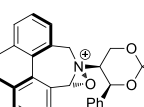
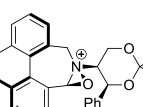
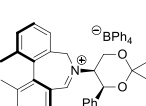
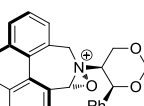
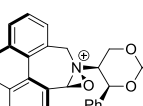
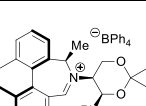
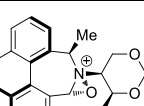
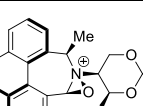
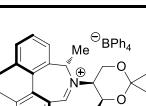
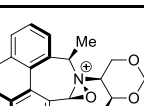
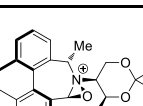


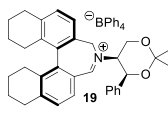
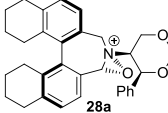
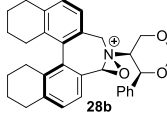
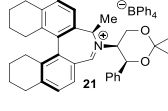
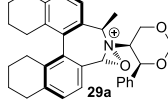
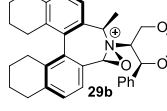
cat  $6S_{ax}$  + 1-phenylcyclohexene



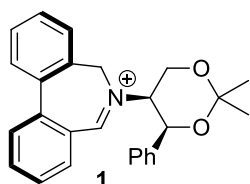
### Dihedral angles calculated for oxaziridinium species



Structure	$\phi/\theta$	Structure	$\phi/\theta$	Structure	$\phi/\theta^1$
	$\phi = -34.9$ $\theta = -39.6$		$\phi = -40.3$ $\theta = -41.3$		$\phi = -37.9$ $\theta = -40.4$
			$\phi = 38.9$ $\theta = 41.7$		$\phi = 39.4$ $\theta = 40.8$
	$\phi = -52.2$ $\theta = -53.0$		$\phi = -58.5$ $\theta = -54.8$		$\phi = -56.4$ $\theta = -54.0$
	$\phi = -33.8$ $\theta = -37.6$		$\phi = -38.7$ $\theta = -39.2$		$\phi = -37.7$ $\theta = -39.7$
	$\phi = -52.2$ $\theta = -52.2$		$\phi = -58.1$ $\theta = -54.0$		$\phi = -56.0$ $\theta = -53.9$
	$\phi = -53.1$ $\theta = -53.7$		$\phi = -57.8$ $\theta = -54.7$		$\phi = -56.3$ $\theta = -54.4$
	$\phi = 52.4$ $\theta = 53.7$		$\phi = 56.3$ $\theta = 55.0$		$\phi = 57.5$ $\theta = 54.7$
	$\phi = -52.7$ $\theta = -52.5$		$\phi = -57.7$ $\theta = -53.9$		$\phi = -55.6$ $\theta = -54.3$
	$\phi = 52.7$ $\theta = 53.3$		$\phi = 57.2$ $\theta = 54.9$		$\phi = 57.5$ $\theta = 54.3$

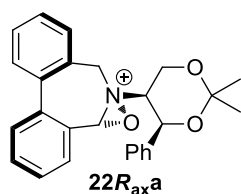
 19	$\phi = -58.2$ $\theta = -57.3$	 28a	$\phi = -63.0$ $\theta = -58.3$	 28b	$\phi = -57.3$ $\theta = -54.6$
 21	$\phi = -57.8$ $\theta = -56.2$	 29a	$\phi = -63.8$ $\theta = -57.6$	 29b	$\phi = -57.0$ $\theta = -54.9$

## Optimized Cartesian Coordinates



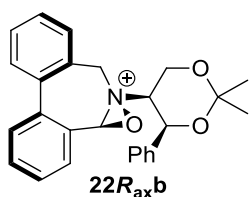
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3	6	0	0.406638	-0.829071	0.636201
4	6	0	0.744613	0.892867	-1.016696
5	1	0	0.608009	-0.065075	1.394421
6	1	0	-0.441709	-1.426579	0.948767
7	1	0	0.329699	1.485214	-1.828164
8	6	0	3.982234	-1.853777	-0.115436
9	6	0	1.523707	-3.070018	0.370959
10	6	0	3.882834	-3.242192	-0.099961
11	6	0	2.653580	-3.855382	0.146894
12	1	0	4.936420	-1.391929	-0.345265
13	1	0	4.764926	-3.845018	-0.289911
14	1	0	2.574730	-4.937472	0.164215
15	1	0	0.560984	-3.534881	0.561690
16	6	0	2.019262	1.304521	-0.484997
17	6	0	2.991848	0.431109	0.096292
18	6	0	2.301924	2.684198	-0.633510
19	1	0	1.564179	3.322999	-1.110390
20	6	0	4.176517	1.020402	0.568990
21	1	0	4.921200	0.388942	1.039992
22	6	0	3.475371	3.229603	-0.143904
23	1	0	3.666531	4.292908	-0.237263
24	6	0	4.411259	2.388175	0.468977

25	1	0	5.334849	2.800778	0.862617
26	7	0	0.000186	-0.091634	-0.596007
27	6	0	-1.289036	-0.387301	-1.271709
28	1	0	-1.230584	0.100766	-2.247790
29	6	0	-1.517210	-1.894510	-1.501366
30	1	0	-2.256967	-1.992323	-2.307077
31	1	0	-0.599890	-2.388904	-1.829367
32	6	0	-2.520072	0.196633	-0.506534
33	1	0	-3.339844	0.170258	-1.239788
34	8	0	-1.936604	-2.566211	-0.325370
35	8	0	-2.826555	-0.618830	0.611270
36	6	0	-3.087847	-2.002034	0.325215
37	6	0	-4.362663	-2.194090	-0.501130
38	1	0	-4.552450	-3.262319	-0.627204
39	1	0	-5.208470	-1.747799	0.026682
40	1	0	-4.314883	-1.747072	-1.496280
41	6	0	-3.185818	-2.692193	1.675445
42	1	0	-4.037753	-2.299173	2.233841
43	1	0	-3.316079	-3.767191	1.535864
44	1	0	-2.277003	-2.518201	2.255915
45	6	0	-2.322102	1.631040	-0.062335
46	6	0	-2.386440	2.655664	-1.017221
47	6	0	-2.046467	1.953534	1.270821
48	6	0	-2.164849	3.982640	-0.647172
49	1	0	-2.636218	2.422720	-2.050619
50	6	0	-1.831823	3.283097	1.640270
51	1	0	-2.031877	1.167185	2.016933
52	6	0	-1.883962	4.298271	0.684267
53	1	0	-2.232810	4.769332	-1.392321
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55	1	0	-1.724385	5.331440	0.976459



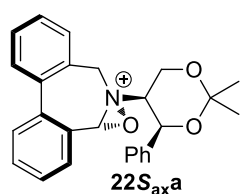
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4	7	0	-0.411170	-0.612770	-0.051247
5	1	0	0.100653	1.372632	0.600706
6	8	0	-0.858462	-0.355627	1.305731
7	1	0	-1.559408	-0.730114	-1.797497
8	6	0	-2.756476	-1.550452	-0.172354
9	6	0	-3.605087	-0.464950	0.129021
10	6	0	-3.126293	-2.851681	0.179718

11	1	0	-2.468167	-3.682062	-0.063575
12	6	0	-4.815744	-0.729133	0.786767
13	1	0	-5.465704	0.097143	1.056677
14	6	0	-4.337879	-3.097793	0.823752
15	6	0	-5.180636	-2.029981	1.130177
16	1	0	-4.616946	-4.113255	1.086393
17	1	0	-6.120823	-2.205991	1.643848
18	6	0	-1.947924	1.469927	-0.112636
19	6	0	-3.253432	0.928937	-0.241262
20	6	0	-1.695348	2.807428	-0.466283
21	1	0	-0.693532	3.210399	-0.341063
22	6	0	-4.257127	1.776561	-0.737033
23	1	0	-5.258308	1.379212	-0.867995
24	6	0	-3.995339	3.098484	-1.091588
25	6	0	-2.708806	3.622095	-0.957283
26	1	0	-4.798894	3.718536	-1.477484
27	1	0	-2.498833	4.652004	-1.226889
28	6	0	0.979804	-1.200145	-0.095902
29	6	0	1.549778	-1.402943	-1.519298
30	6	0	2.054167	-0.570797	0.827355
31	1	0	0.821701	-2.206483	0.306078
32	1	0	1.854428	-0.457313	-1.979519
33	1	0	0.835793	-1.888333	-2.189082
34	6	0	3.688957	-1.888157	-0.511461
35	8	0	2.624177	-2.305521	-1.385816
36	8	0	3.153250	-1.491330	0.765148
37	6	0	4.487171	-3.150458	-0.218411
38	1	0	4.886195	-3.562944	-1.148640
39	1	0	5.317128	-2.919628	0.454374
40	1	0	3.841062	-3.893590	0.254761
41	6	0	4.554044	-0.809581	-1.167197
42	1	0	5.320574	-0.475684	-0.462796
43	1	0	5.045872	-1.233615	-2.047352
44	1	0	3.987274	0.067688	-1.482485
45	1	0	1.699134	-0.687920	1.855096
46	6	0	2.497539	0.888993	0.681063
47	6	0	3.262901	1.386922	1.747727
48	6	0	2.240538	1.744670	-0.402034
49	6	0	3.762253	2.687707	1.733163
50	1	0	3.478690	0.738058	2.592562
51	6	0	2.734653	3.052535	-0.416936
52	1	0	1.656306	1.411373	-1.254867
53	6	0	3.499079	3.527029	0.648556
54	1	0	4.353809	3.046474	2.570159
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56	1	0	3.886341	4.541341	0.634125



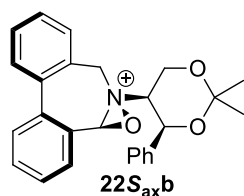
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5	6	0	2.838069	1.878381	1.221074
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7	1	0	1.122863	4.809661	0.964412
8	1	0	0.281972	3.665215	-1.067170
9	1	0	3.541740	1.378870	1.879058
10	1	0	2.756428	3.643975	2.443274
11	6	0	2.953680	-0.114932	-0.288840
12	6	0	2.208022	-1.179887	-0.845324
13	6	0	4.325762	-0.339705	-0.069161
14	6	0	2.818004	-2.409731	-1.132890
15	6	0	4.930582	-1.556457	-0.368187
16	1	0	4.931636	0.471479	0.320692
17	6	0	4.175630	-2.601977	-0.901903
18	1	0	2.221864	-3.220014	-1.545237
19	1	0	5.993859	-1.685205	-0.190528
20	1	0	4.637966	-3.554558	-1.139541
21	6	0	0.740745	-1.158315	-1.111285
22	1	0	0.108900	-1.781844	-0.481292
23	6	0	0.929666	1.202950	-1.984320
24	1	0	0.315864	1.856980	-2.605262
25	7	0	0.055223	0.021502	-1.608857
26	6	0	-1.410078	0.308133	-1.298937
27	6	0	-2.366216	-0.799146	-1.812361
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29	1	0	-1.598476	1.228154	-1.854453
30	1	0	-1.860285	-1.760496	-1.906815
31	1	0	-2.739809	-0.527239	-2.807259
32	1	0	-1.194097	1.601809	0.403019
33	6	0	-4.064280	0.139497	-0.365090
34	8	0	-3.079097	1.048617	0.183767
35	8	0	-3.418631	-1.016152	-0.895994
36	6	0	-4.835223	0.911794	-1.435305
37	1	0	-4.179882	1.254931	-2.242777
38	6	0	-4.967152	-0.354210	0.756824
39	1	0	-5.461200	0.499334	1.228293
40	1	0	-5.729892	-1.030684	0.360484
41	1	0	-4.380735	-0.880020	1.513290
42	6	0	-1.260243	-0.307385	1.289729
43	6	0	-1.631617	-1.661975	1.384067
44	6	0	-0.421500	0.219431	2.284215

45	6	0	-1.166068	-2.453752	2.435241
46	1	0	-2.311378	-2.088390	0.656049
47	6	0	0.039240	-0.571857	3.337845
48	1	0	-0.132567	1.266477	2.243379
49	6	0	-0.329193	-1.914025	3.414724
50	1	0	-1.471139	-3.494766	2.494253
51	1	0	0.679070	-0.135493	4.099440
52	1	0	0.023474	-2.533220	4.234338
53	8	0	0.297609	-1.119687	-2.483229
54	1	0	-5.620224	0.281735	-1.863085
55	1	0	-5.297667	1.795574	-0.987902
56	1	0	1.725226	0.773715	-2.595842



1	6	0	-3.101939	3.565862	-0.700112
2	6	0	-3.647855	2.363111	-0.244824
3	6	0	-2.961618	1.144013	-0.401782
4	6	0	-1.682083	1.170274	-1.014770
5	6	0	-1.149376	2.381177	-1.483289
6	6	0	-1.855500	3.577313	-1.334893
7	1	0	-3.650690	4.490776	-0.561965
8	1	0	-0.188630	2.385535	-1.988901
9	1	0	-1.436242	4.505249	-1.706240
10	6	0	-3.618240	-0.130675	0.003384
11	6	0	-2.939482	-1.208397	0.625983
12	6	0	-4.995466	-0.295578	-0.253861
13	6	0	-3.627567	-2.383239	0.981377
14	6	0	-5.672676	-1.464588	0.093116
15	6	0	-4.988615	-2.517010	0.712902
16	1	0	-3.092120	-3.194083	1.465748
17	1	0	-6.730121	-1.557720	-0.127415
18	1	0	-5.507144	-3.430112	0.980590
19	6	0	-1.518688	-1.160264	1.048338
20	1	0	-1.317171	-1.063672	2.111407
21	6	0	-0.904541	-0.108432	-1.177229
22	1	0	-0.008470	-0.003259	-1.785410
23	7	0	-0.462828	-0.570869	0.207440
24	8	0	-0.543962	-2.094964	0.387687
25	6	0	0.730374	0.085757	0.888435
26	6	0	1.388517	-0.796264	1.975987
27	6	0	1.809899	0.652676	-0.071203
28	1	0	0.293272	0.953615	1.396123
29	1	0	1.939910	-1.629165	1.534572
30	1	0	0.674975	-1.192153	2.699199

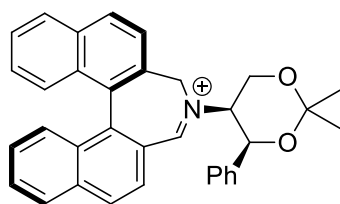
31	1	0	1.359961	1.472942	-0.637075
32	6	0	3.323884	0.730817	1.976938
33	8	0	2.245720	0.082492	2.742782
34	8	0	2.727877	1.402534	0.805423
35	6	0	4.414302	-0.269082	1.601855
36	1	0	5.187644	0.235680	1.017434
37	1	0	4.865297	-0.661570	2.517488
38	1	0	4.044644	-1.107874	1.009785
39	6	0	3.820504	1.860573	2.859802
40	1	0	4.224420	1.452784	3.789769
41	1	0	4.603921	2.420867	2.343728
42	1	0	2.994191	2.534209	3.094302
43	1	0	-1.504366	-0.932819	-1.568115
44	1	0	-5.530894	0.499607	-0.759250
45	1	0	-4.612980	2.369182	0.249034
46	6	0	2.527453	-0.263666	-1.056458
47	6	0	3.512797	0.346439	-1.858007
48	6	0	2.265411	-1.632797	-1.235345
49	6	0	4.221817	-0.392681	-2.805831
50	1	0	3.732083	1.399965	-1.716710
51	6	0	2.976078	-2.373002	-2.191246
52	1	0	1.519788	-2.147314	-0.640820
53	6	0	3.954786	-1.758085	-2.975828
54	1	0	4.980070	0.092906	-3.410611
55	1	0	2.763557	-3.429663	-2.314369
56	1	0	4.504752	-2.333850	-3.712154



1	6	0	5.027314	-1.802437	-0.760632
2	6	0	4.453166	-0.952553	0.188309
3	6	0	3.140982	-0.468440	0.033800
4	6	0	2.407528	-0.873485	-1.105817
5	6	0	2.988085	-1.730014	-2.050422
6	6	0	4.296967	-2.191570	-1.887307
7	1	0	6.038773	-2.164899	-0.614695
8	1	0	2.417623	-2.028781	-2.924850
9	1	0	4.737536	-2.849289	-2.627797
10	6	0	2.572750	0.449920	1.057686
11	6	0	1.232686	0.380829	1.534138
12	6	0	3.407735	1.438837	1.613245
13	6	0	0.793153	1.266332	2.540796
14	6	0	2.957601	2.316601	2.601507
15	6	0	1.643174	2.231854	3.073634
16	1	0	-0.224391	1.185257	2.910963



17	1	0	3.632103	3.066168	3.000481
18	1	0	1.288985	2.904001	3.846322
19	6	0	0.225817	-0.600353	1.105451
20	6	0	1.012662	-0.373626	-1.338910
21	1	0	0.649023	-0.659477	-2.324900
22	7	0	0.002217	-0.941715	-0.334155
23	1	0	-0.705578	-0.596388	1.659321
24	8	0	0.614839	-1.961065	0.630208
25	1	0	5.018828	-0.683285	1.073141
26	1	0	4.423338	1.529373	1.246259
27	1	0	0.919013	0.710649	-1.226994
28	6	0	-1.377923	-1.321427	-0.850977
29	6	0	-2.020512	-2.500135	-0.049592
30	6	0	-2.360693	-0.110227	-0.783475
31	1	0	-1.207790	-1.607822	-1.891301
32	1	0	-1.545210	-2.627558	0.924219
33	1	0	-1.926473	-3.437707	-0.595751
34	1	0	-3.195240	-0.402390	-1.431486
35	6	0	-3.805436	-1.114498	0.910499
36	8	0	-3.448182	-2.273844	0.082173
37	8	0	-2.819453	-0.041675	0.599466
38	6	0	-3.672715	-1.403063	2.396292
39	1	0	-4.404129	-2.159862	2.690523
40	1	0	-2.674992	-1.772087	2.652205
41	1	0	-3.859924	-0.491198	2.969894
42	6	0	-5.204079	-0.707191	0.484695
43	1	0	-5.895473	-1.537832	0.649402
44	1	0	-5.534496	0.155061	1.069180
45	1	0	-5.234102	-0.447908	-0.576865
46	6	0	-1.827017	1.228304	-1.244721
47	6	0	-1.653828	1.453274	-2.622710
48	6	0	-1.517145	2.250333	-0.336007
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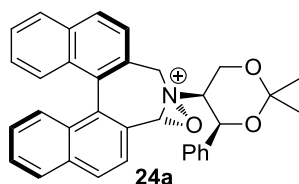


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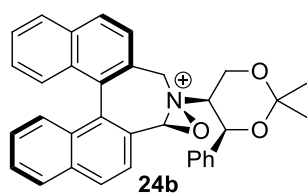
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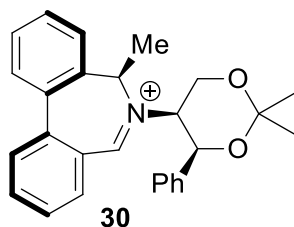
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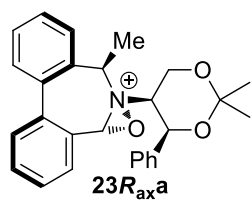
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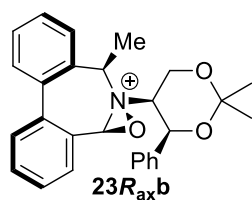
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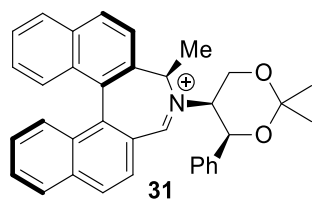
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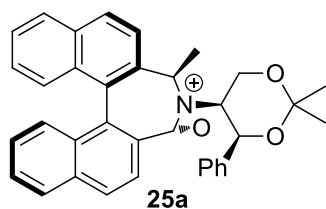
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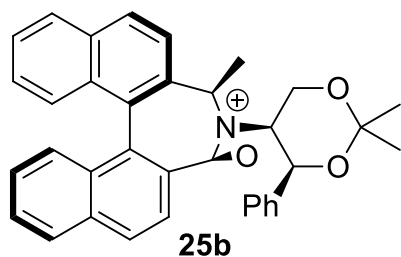


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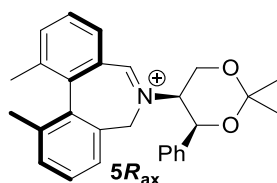
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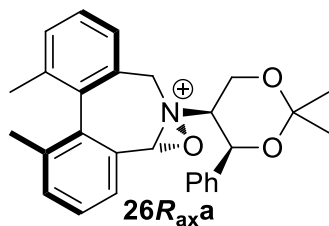


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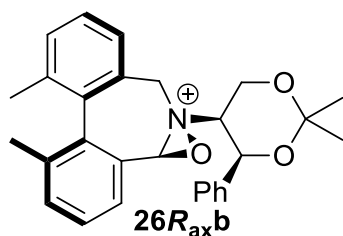


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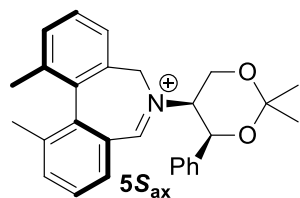
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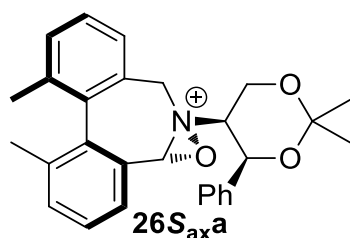
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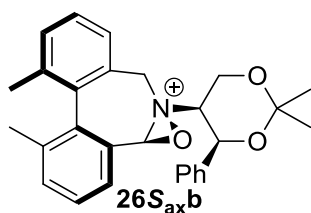
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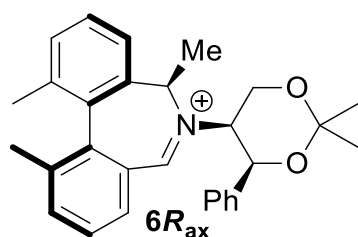
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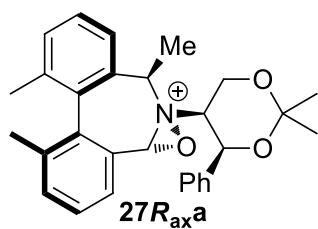


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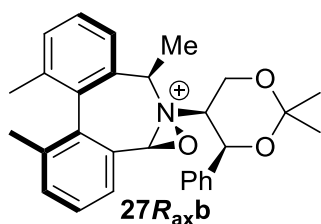
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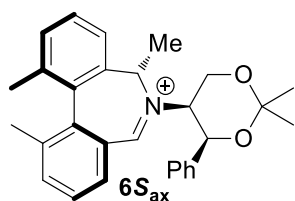
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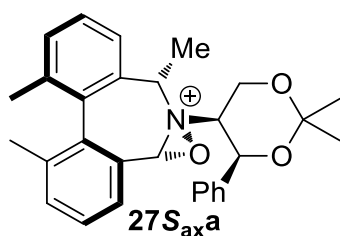
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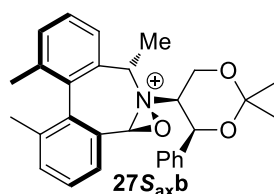
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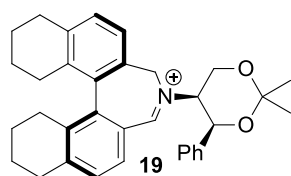
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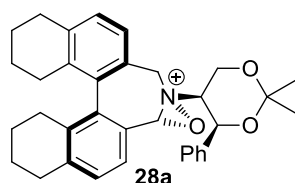
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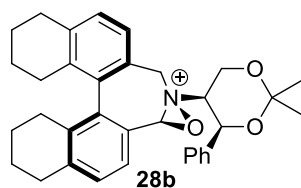
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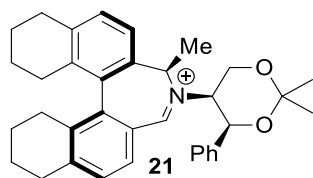
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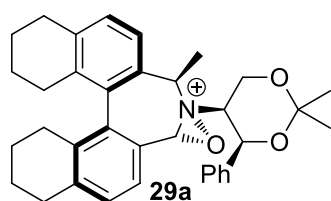
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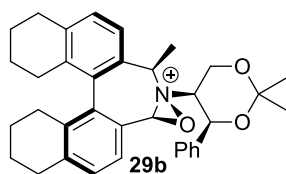
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