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Supporting Information

Toward the Creation of NMR Databases in Chiral Solvents for Assignments of Relative and Absolute Stereochemistry: Proof of Concept

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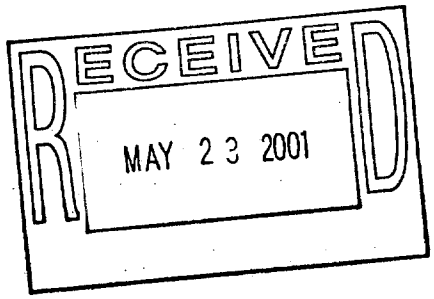


1. NMR database 1a-h (di-propionate) in DMBA

a. ^{13}C NMR chemical shifts

(*R*)-DMBA	1a	1b	1c	1d	1e	1f	1g	1h
1	61.185	61.114	61.163	61.099	61.210	61.149	61.235	61.156
2	33.259	33.224	33.332	33.180	33.269	33.185	33.298	33.202
3	23.319	22.922	23.106	22.884	21.918	23.017	22.005	23.071
4	33.600	35.727	**	35.717	34.477	35.379	34.522	35.657
5	72.156	75.543	71.168	76.251	75.298	74.934	75.127	75.215
6	39.590	38.246	38.032	37.956	41.262	38.756	41.198	38.548
7	75.942	79.575	79.152	80.118	77.471	73.973	80.204	73.864
8	37.230	37.609	37.805	37.742	37.151	37.420	37.354	37.672
9	26.826	25.526	**	25.295	27.267	25.339	21.531	25.519
10	11.707	11.015	11.521	10.950	12.071	10.810	12.140	11.063
11	11.602	5.664	11.710	4.872	12.795	11.161	13.204	10.875
12	12.871	15.104	15.837	14.764	11.835	15.420	16.935	14.752

(*S*)-DMBA	1a	1b	1c	1d	1e	1f	1g	1h	Average
1	61.187	61.115	61.160	61.101	61.230	61.160	61.222	61.159	61.165
2	33.327	33.214	33.347	33.166	33.272	33.180	33.303	33.202	33.248
3	23.366	22.923	23.100	22.887	21.943	22.998	21.991	23.040	22.781
4	33.476	35.722	**	35.706	34.550	35.365	34.432	35.651	34.999
5	72.419	75.536	71.277	76.263	75.349	74.841	75.072	75.106	74.472
6	39.560	38.245	37.979	37.946	41.274	38.816	41.188	38.654	39.203
7	76.026	79.547	79.231	80.095	77.428	73.928	80.215	73.795	77.535
8	37.275	37.579	37.841	37.699	37.138	37.435	37.368	37.666	37.499
9	26.807	25.516	**	25.262	27.262	25.345	21.520	25.547	25.326
10	11.761	11.011	11.526	10.927	12.073	10.821	12.144	11.056	11.412
11	11.701	5.673	11.766	4.879	12.825	11.118	13.167	10.843	10.241
12	12.890	15.066	15.799	14.756	11.857	15.451	16.942	14.779	14.691

b. relative (See Figure 1 in text)

(*R*)-DMBA	1a	1b	1c	1d	1e	1f	1g	1h
1	0.020	-0.051	-0.002	-0.066	0.045	-0.016	0.070	-0.009
2	0.011	-0.024	0.084	-0.068	0.021	-0.063	0.050	-0.046
3	0.538	0.141	0.325	0.103	-0.863	0.236	-0.776	0.290
4	-1.399	0.728	**	0.718	-0.522	0.380	-0.477	0.658
5	-2.316	1.071	-3.304	1.779	0.826	0.462	0.655	0.743
6	0.387	-0.957	-1.171	-1.247	2.059	-0.447	1.995	-0.655
7	-1.593	2.040	1.617	2.583	-0.064	-3.562	2.669	-3.671
8	-0.269	0.110	0.306	0.243	-0.348	-0.079	-0.145	0.173
9	1.500	0.200	**	-0.031	1.941	0.013	-3.795	0.193
10	0.295	-0.397	0.109	-0.462	0.659	-0.602	0.728	-0.349
11	1.361	-4.577	1.469	-5.369	2.554	0.920	2.963	0.634
12	-1.820	0.413	1.146	0.073	-2.856	0.729	2.244	0.061

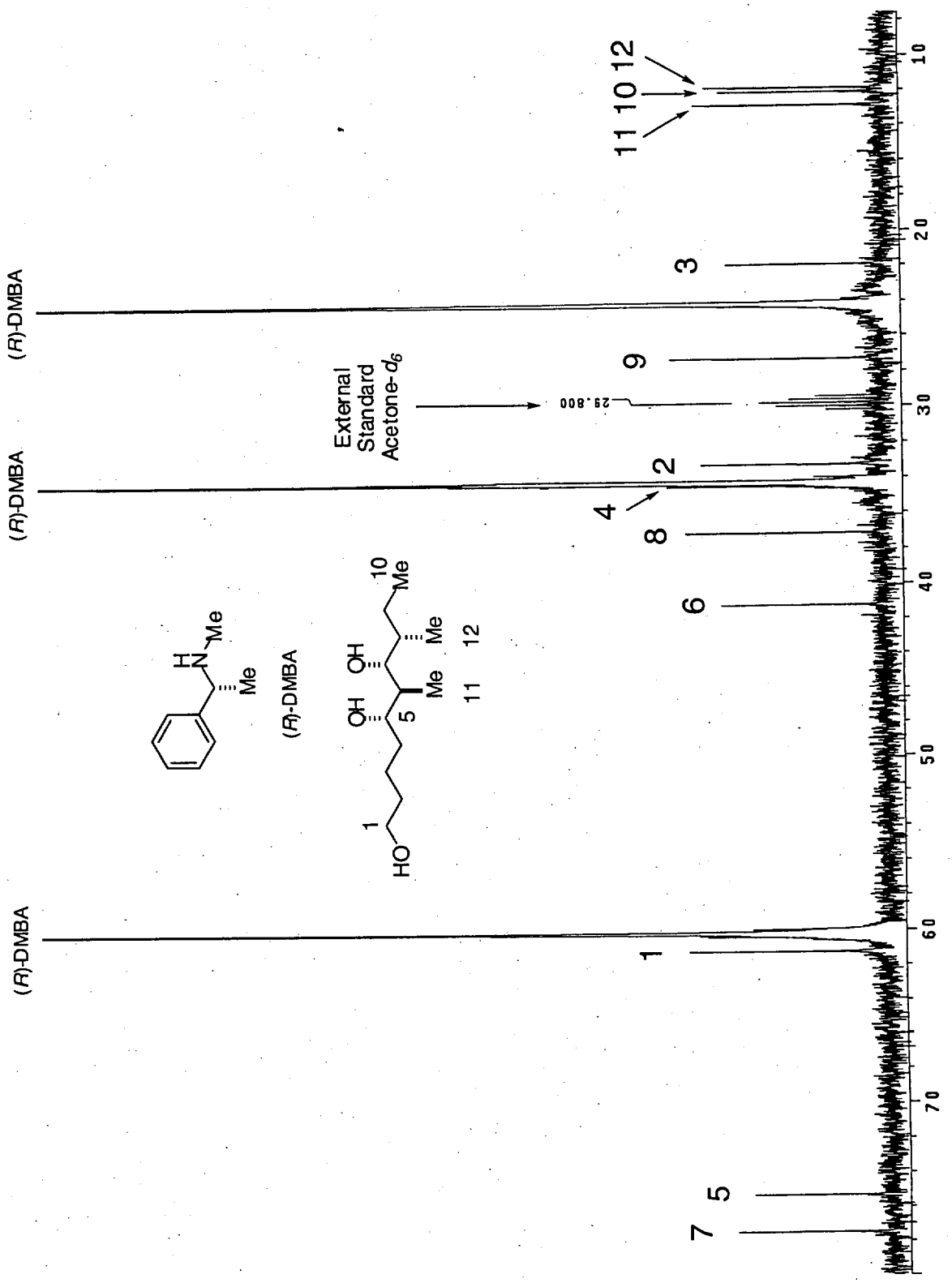
(*S*)-DMBA	1a	1b	1c	1d	1e	1f	1g	1h
1	0.022	-0.050	-0.005	-0.064	0.065	-0.005	0.057	-0.006
2	0.079	-0.034	0.099	-0.082	0.024	-0.068	0.055	-0.046
3	0.585	0.142	0.319	0.106	-0.838	0.217	-0.790	0.259
4	-1.523	0.723	**	0.707	-0.449	0.366	-0.567	0.652
5	-2.053	1.064	-3.195	1.791	0.877	0.369	0.600	0.634
6	0.357	-0.958	-1.224	-1.257	2.071	-0.387	1.985	-0.549
7	-1.509	2.012	1.696	2.560	-0.107	-3.607	2.680	-3.740
8	-0.224	0.080	0.342	0.200	-0.361	-0.064	-0.131	0.167
9	1.481	0.190	**	-0.064	1.936	0.019	-3.806	0.221
10	0.349	-0.401	0.114	-0.485	0.661	-0.591	0.732	-0.356
11	1.460	-4.568	1.525	-5.362	2.584	0.877	2.926	0.602
12	-1.801	0.375	1.108	0.065	-2.834	0.760	2.251	0.088

c. absolute (See Figure 3 in text)

(*R*)-(*S*)	1a	1b	1c	1d	1e	1f	1g	1h
1	-0.002	-0.001	0.003	-0.002	-0.020	-0.011	0.013	-0.003
2	-0.068	0.010	-0.015	0.014	-0.003	0.005	-0.005	0.000
3	-0.047	-0.001	0.006	-0.003	-0.025	0.019	0.014	0.031
4	0.124	0.005	**	0.011	-0.073	0.014	0.090	0.006
5	-0.263	0.007	-0.109	-0.012	-0.051	0.093	0.055	0.109
6	0.030	0.001	0.053	0.010	-0.012	-0.060	0.010	-0.106
7	-0.084	0.028	-0.079	0.023	0.043	0.045	-0.011	0.069
8	-0.045	0.030	-0.036	0.043	0.013	-0.015	-0.014	0.006
9	0.019	0.010	**	0.033	0.005	-0.006	0.011	-0.028
10	-0.054	0.004	-0.005	0.023	-0.002	-0.011	-0.004	0.007
11	-0.099	-0.009	-0.056	-0.007	-0.030	0.043	0.037	0.032
12	-0.019	0.038	0.038	0.008	-0.022	-0.031	-0.007	-0.027

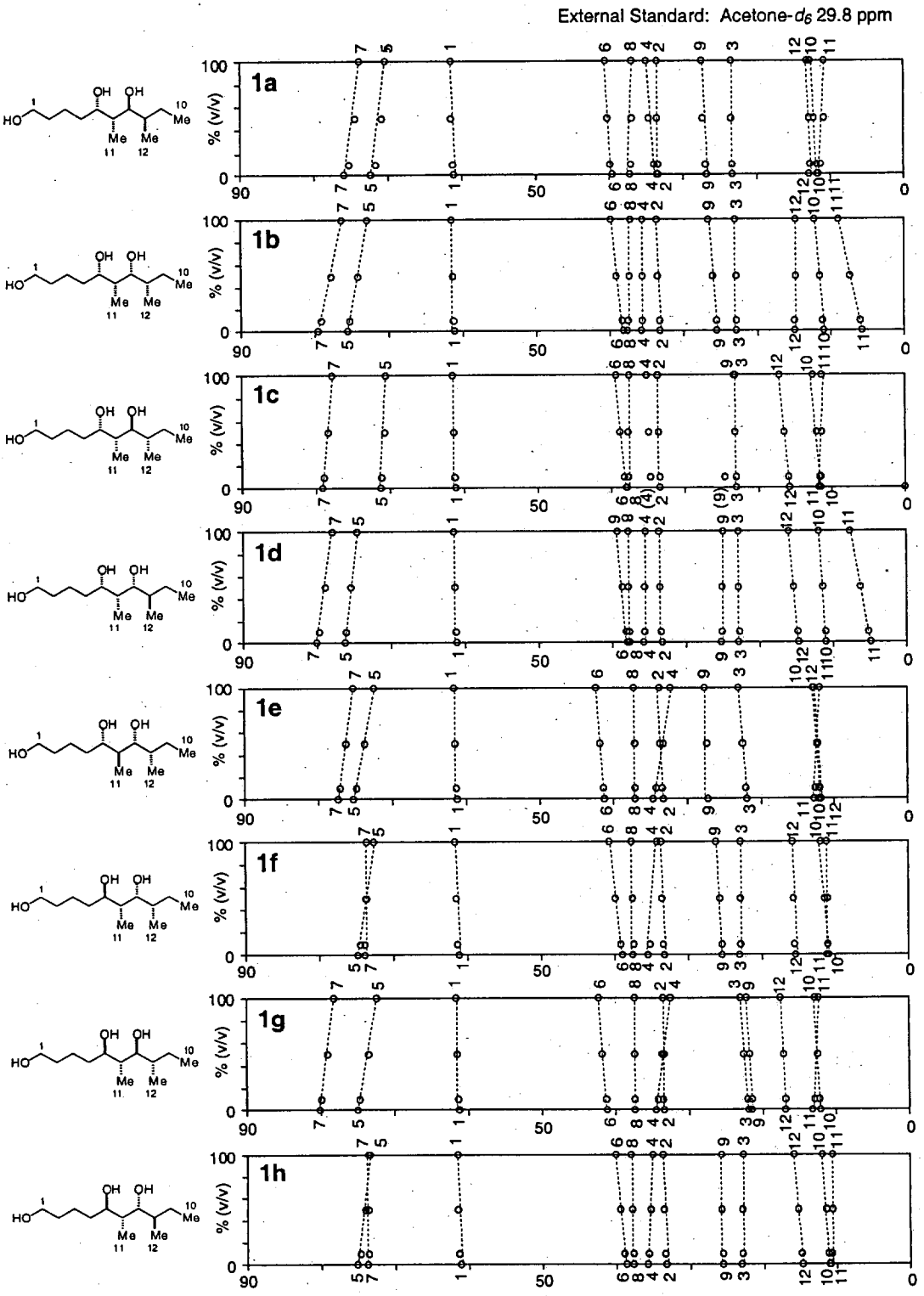
** Those peaks are hidden under the solvent peaks.

d. ^{13}C NMR spectrum of **1e** in (*R*)-DMBA



e. Assignment of ^{13}C NMR chemical shifts

Correlation of carbon chemical shifts of **1a~h** in between DMSO-d_6 and (*S*)-DMBA. The *x*- and *y*-axes represent the region of 0~90 ppm and DMSO-d_6 contents (v/v%) in (*S*)-DMBA, respectively (See ref.1a in text for assignment of ^{13}C NMR chemical shifts of **1a~h** in DMSO-d_6).



2. NMR database 1a-h (di-propionate) in DMBA containing 9.1% DMSO-d_6 (DMBA/DMSO=10:1)

a. ^{13}C NMR chemical shifts

9.1%-(*R*)	1a	1b	1c	1d	1e	1f	1g	1h
1	61.360	61.256	61.291	61.230	61.381	61.344	61.379	61.330
2	33.427	33.266	33.378	33.254	33.403	33.357	33.414	33.338
3	23.377	22.840	23.084	22.803	22.055	22.965	22.115	22.953
4	34.024	35.584	34.624	35.576	34.104	35.201	34.165	35.522
5	71.554	75.193	70.992	76.087	74.905	74.454	74.713	74.739
6	39.871	38.410	38.223	38.041	41.393	39.098	41.310	38.801
7	75.244	79.064	78.776	79.777	77.115	73.868	79.861	73.714
8	37.120	37.470	37.656	37.671	37.122	37.431	37.328	37.635
9	27.051	25.623	**	25.193	27.280	25.425	21.593	25.563
10	11.895	11.112	11.644	10.992	12.146	10.933	12.201	11.125
11	11.197	6.072	11.461	5.149	12.585	11.000	12.976	10.663
12	12.817	14.996	16.051	14.859	11.956	15.525	16.979	14.856
9.1%-(*S*)	1a	1b	1c	1d	1e	1f	1g	1h	Average
1	61.322	61.249	61.286	61.249	61.381	61.341	61.378	61.338	61.320
2	33.405	33.269	33.420	33.303	33.418	33.351	33.448	33.375	33.364
3	23.365	22.860	23.114	22.857	22.065	22.956	22.127	22.971	22.782
4	33.887	35.614	34.602	35.637	34.173	35.211	34.138	35.547	34.851
5	71.695	75.245	71.084	76.123	74.944	74.430	74.683	74.690	74.096
6	39.812	38.399	38.184	38.070	41.397	39.124	41.323	38.887	39.396
7	75.325	79.123	78.887	79.809	77.081	73.839	79.867	73.668	77.189
8	37.126	37.479	37.717	37.682	37.111	37.443	37.350	37.649	37.437
9	27.007	25.610	**	25.213	27.273	25.426	21.593	25.607	25.390
10	11.855	11.101	11.644	11.012	12.140	10.936	12.211	11.141	11.506
11	11.284	6.027	11.553	5.176	12.612	10.989	12.966	10.668	10.149
12	12.797	14.993	16.023	14.889	11.971	15.551	16.994	14.885	14.759

b. relative

9.1%-(*R*)	1a	1d	1c	1b	1e	1g	1h	1f
1	0.040	-0.064	-0.029	-0.090	0.061	0.024	0.059	0.010
2	0.063	-0.098	0.014	-0.110	0.039	-0.007	0.050	-0.026
3	0.595	0.058	0.302	0.021	-0.727	0.183	-0.667	0.171
4	-0.827	0.733	-0.227	0.725	-0.747	0.350	-0.686	0.671
5	-2.542	1.097	-3.104	1.991	0.809	0.358	0.617	0.643
6	0.475	-0.986	-1.173	-1.355	1.997	-0.298	1.914	-0.595
7	-1.945	1.875	1.587	2.588	-0.074	-3.321	2.672	-3.475
8	-0.317	0.033	0.219	0.234	-0.315	-0.006	-0.109	0.198
9	1.661	0.233	**	-0.197	1.890	0.035	-3.797	0.173
10	0.389	-0.394	0.138	-0.514	0.640	-0.573	0.695	-0.381
11	1.048	-4.077	1.312	-5.000	2.436	0.851	2.827	0.514
12	-1.942	0.237	1.292	0.100	-2.803	0.766	2.220	0.097
9.1%-(*S*)	1a	1d	1c	1b	1e	1g	1h	1f
1	0.002	-0.071	-0.034	-0.071	0.061	0.021	0.058	0.018
2	0.041	-0.095	0.056	-0.061	0.054	-0.013	0.084	0.011
3	0.583	0.078	0.332	0.075	-0.717	0.174	-0.655	0.189
4	-0.964	0.763	-0.249	0.786	-0.678	0.360	-0.713	0.696
5	-2.401	1.149	-3.012	2.027	0.848	0.334	0.587	0.594
6	0.416	-0.997	-1.212	-1.326	2.001	-0.272	1.927	-0.509
7	-1.864	1.934	1.698	2.620	-0.108	-3.350	2.678	-3.521
8	-0.311	0.042	0.280	0.245	-0.326	0.006	-0.087	0.212
9	1.617	0.220	**	-0.177	1.883	0.036	-3.797	0.217
10	0.349	-0.405	0.138	-0.494	0.634	-0.570	0.705	-0.365
11	1.135	-4.122	1.404	-4.973	2.463	0.840	2.817	0.519
12	-1.962	0.234	1.264	0.130	-2.788	0.792	2.235	0.126

c. absolute

9.1%(*R*)-(*S*)	1a	1d	1c	1b	1e	1g	1h	1f
1	0.038	0.007	0.005	-0.019	0.000	0.003	0.001	-0.008
2	0.022	-0.003	-0.042	-0.049	-0.015	0.006	-0.034	-0.037
3	0.012	-0.020	-0.030	-0.054	-0.010	0.009	-0.012	-0.018
4	0.137	-0.030	0.022	-0.061	-0.069	-0.010	0.027	-0.025
5	-0.141	-0.052	-0.092	-0.036	-0.039	0.024	0.030	0.049
6	0.059	0.011	0.039	-0.029	-0.004	-0.026	-0.013	-0.086
7	-0.081	-0.059	-0.111	-0.032	0.034	0.029	-0.006	0.046
8	-0.006	-0.009	-0.061	-0.011	0.011	-0.012	-0.022	-0.014
9	0.044	0.013	**	-0.020	0.007	-0.001	0.000	-0.044
10	0.040	0.011	0.000	-0.020	0.006	-0.003	-0.010	-0.016
11	-0.087	0.045	-0.092	-0.027	-0.027	0.011	0.010	-0.005
12	0.020	0.003	0.028	-0.030	-0.015	-0.026	-0.015	-0.029

** Those peaks are hidden under the solvent peaks.

3. NMR studies on oasomycin A in DMBA

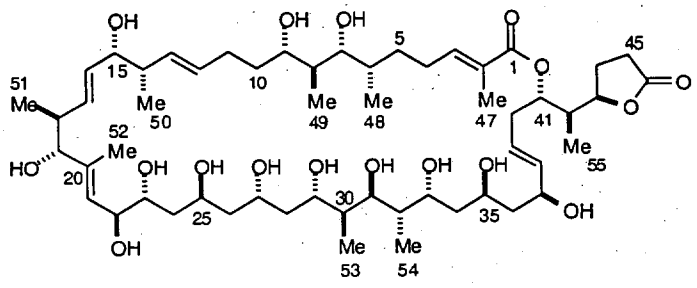
a. ^{13}C NMR chemical shifts in (*R*)- and (*S*)-DMBA-d_{13} containing 9.1% DMSO-d_6

(See Figure 7 in text)

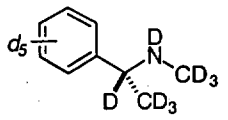
Oasomycin A	(*R*)-DMBA	(*S*) -DMBA	*R-S*
53	9.375	9.383	-0.01
55	9.853	9.888	-0.04
54	11.323	11.313	0.01
52	11.510	11.539	-0.03
48	12.119	12.148	-0.03
47	12.184	12.196	-0.01
49	12.378	12.408	-0.03
50	14.807	14.802	0.01
51	17.464	17.485	-0.02
44	24.528	24.493	0.04
4	26.662	26.671	-0.01
45	28.251	28.261	-0.01
11	29.076	29.087	-0.01
10	34.073	34.126	-0.05
40	**	**	**
5	**	**	**
6	34.964	34.963	0.00
18	**	**	**
30	**	**	**
42	**	**	**
32	**	**	**
24	40.694	40.717	-0.02
8	41.296	41.303	-0.01
14	41.635	41.648	-0.01
28	42.074	42.057	0.02
34	42.728	42.727	0.00
36	45.556	45.591	-0.04
26	45.835	45.920	-0.09

Oasomycin A	(*R*)-DMBA	(*S*) -DMBA	*R-S*
25	64.254	64.234	0.02
35	64.548	64.564	-0.02
37	67.670	67.686	-0.02
27	68.287	68.245	0.04
33	68.494	68.483	0.01
23	71.431	71.462	-0.03
31	71.512	71.504	0.01
22	71.631	71.683	-0.05
41	73.081	73.100	-0.02
29	74.203	74.197	0.01
9	74.203	74.313	-0.11
15	74.356	74.386	-0.03
7	76.655	76.653	0.00
43	80.126	80.129	0.00
19	81.904	81.906	0.00
39	122.461	122.490	-0.03
21	**	**	**
2	**	**	**
12	129.672	129.674	0.00
16	131.527	131.533	-0.01
13	132.657	132.685	-0.03
17	133.722	133.747	-0.03
38	138.991	138.988	0.00
20	138.991	138.988	0.00
3	142.951	142.965	-0.01
1	166.737	166.750	-0.01
46	175.847	175.864	-0.02

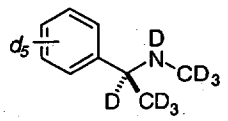
** Those peaks are hidden under the solvent peaks.



Oasomycin A



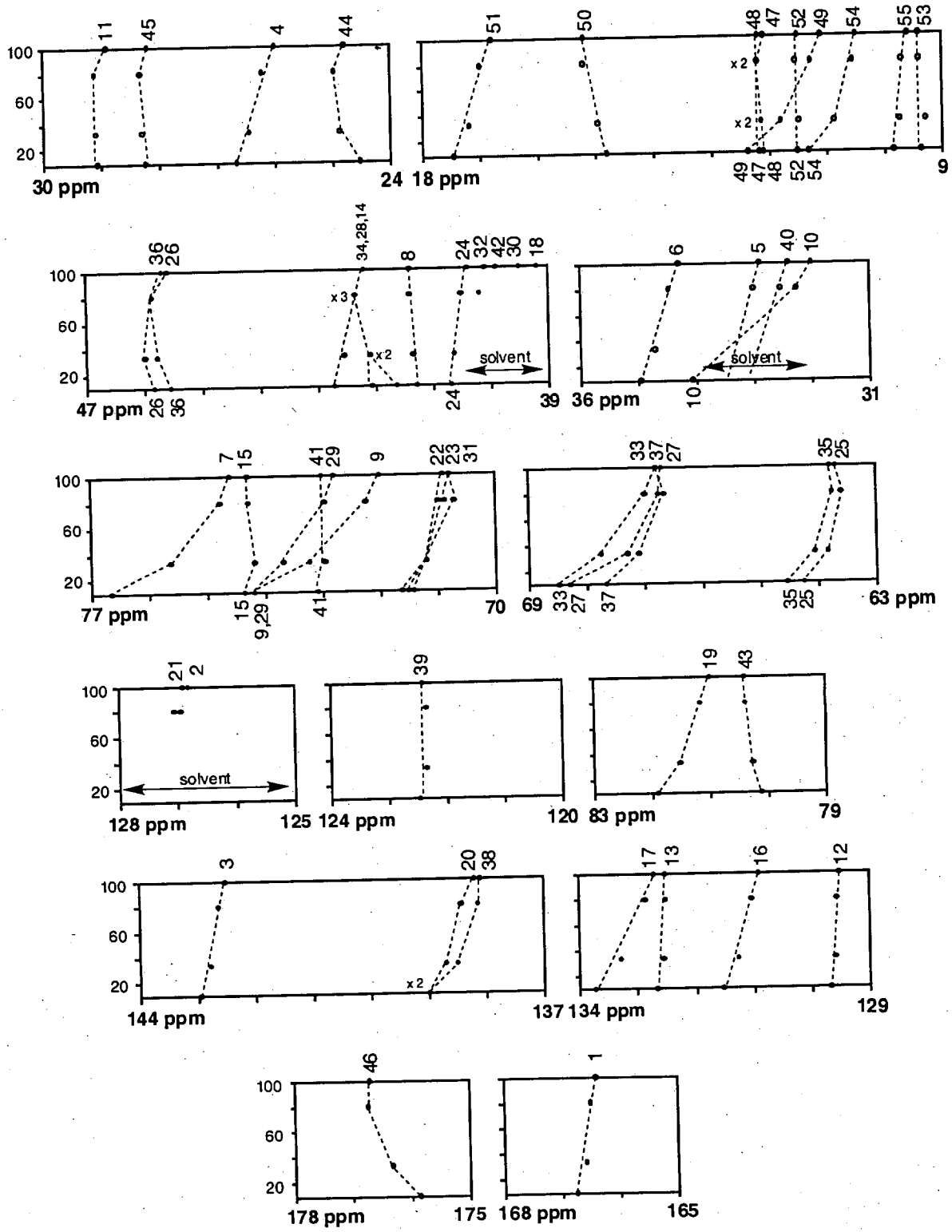
(*R*)-DMBA-d_{13}



(*S*)-DMBA-d_{13}

b. Assignment of ^{13}C NMR chemical shifts

Correlation of carbon chemical shifts of oasomycin A in between DMSO-d_6 and (*R*)-DMBA-d_{13}. The *x*- and *y*-axes represent the region of 0~90 ppm and DMSO-d_6 cotents (v/v%) in (*R*)-DMBA-d_{13}, respectively.

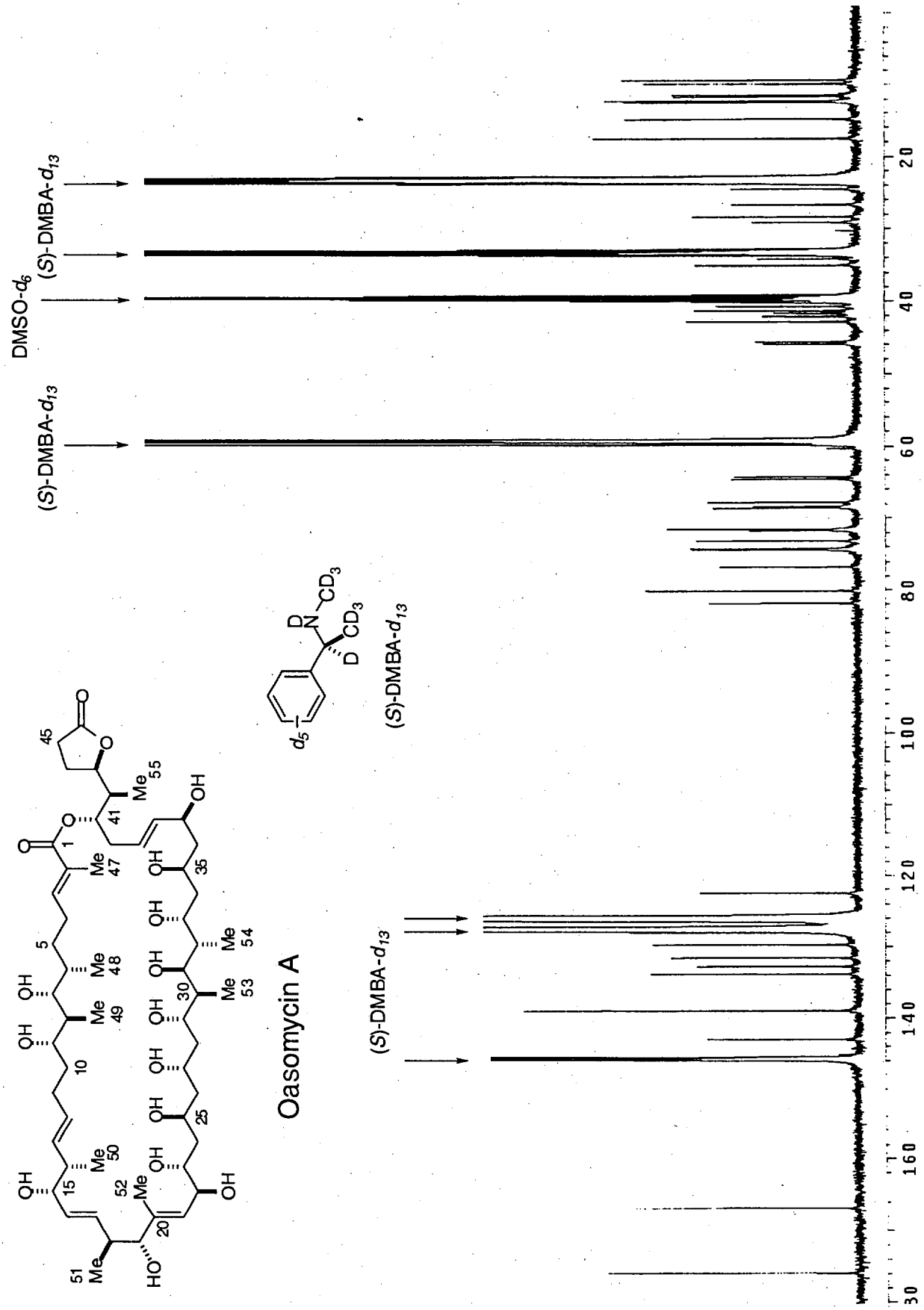


c. Correlation of relative stereochemistry of C.5-10 portion (See Figure 6 in text)

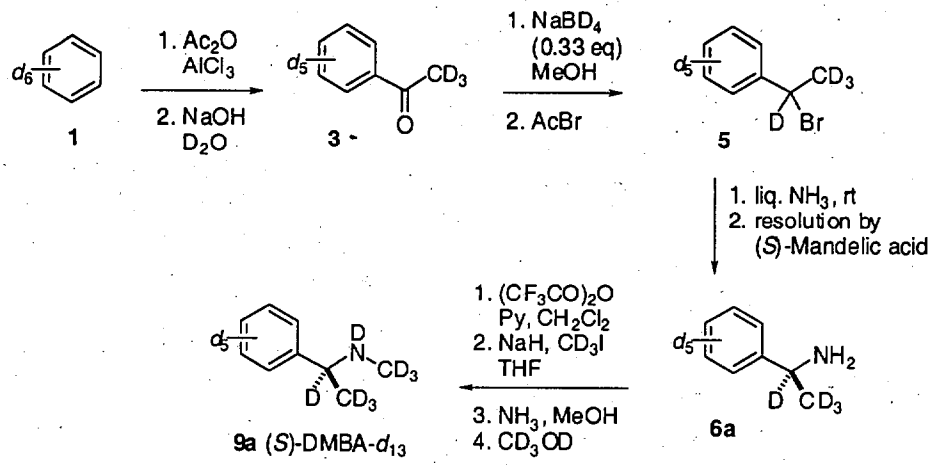
First, Increments are calculated according to a method reported previously (See ref.1b in text, oasomycin A: C.9=-0.1, C.8=-0.1, C.7=-0.4, C.6=+2.1, C.49=0, C.48=-0.4). Second, adjusted chemical shifts of C.5-10 portion of oasomycin A are calculated by addition of the increment to chemical shifts in (*R*)-DMDA-d_{13} containing DMSO-d_6 (C.9=74.103, C.8=41.196, C.7=76.255, C.6=37.064, C.49=12.378, C.48=11.719). Third, chemical shifts are compared with those of corresponding carbons of **1a-h** (See table shown below).

1a-h	Oasomycin A	1a	1b	1c	1d	1e	1f	1g	1h
5	9	-2.549	1.090	-3.111	1.984	0.802	0.351	0.610	0.636
6	8	-1.325	-2.786	-2.973	-3.155	0.197	-2.098	0.114	-2.395
7	7	-1.011	2.809	2.521	3.522	0.860	-2.387	3.606	-2.541
8	6	0.056	0.406	0.592	0.607	0.058	0.367	0.264	0.571
11	49	-1.181	-6.306	-0.917	-7.229	0.207	-1.378	0.598	-1.715
12	48	1.098	3.277	4.332	3.140	0.237	3.806	5.260	3.137

d. ^{13}C NMR spectrum of oasomycin A in (*S*)-DMBA-d_{13} containing 9.1% DMSO-d_6



4. Experimental procedure of synthesis of (*R*)- and (*S*)-DMBA-d_{13}'s



Scheme Chromatography-Free Synthesis of (*S*)-DMBA-d_{13}

Acetophenone-*2',3',4',5',6'*-d_5 (2). (Reference: Challacombe, K.; Leach, S. E.; Plackett, S. J.; Meakins, G. D. *J. Chem. Soc. Perkin Trans. 1* **1988**, 2213-2218.) In a 2-L round-bottomed, three-necked flask, fitted with a mechanical stirrer, dropping funnel, and reflux condenser connected with a gas absorption trap for disposing of the evolved hydrogen chloride, was placed benzene-d_6 (**1**) (100 g, 1.19 mol, 99.6 atm % D) in carbon disulfide (476 mL). To this solution was added $AlCl_3$ (356 g, 2.67 mol) at rt under nitrogen. The mixture was heated in an oil bath until gentle refluxing started, and acetic anhydride (89.8 mL, 0.952 mol) was added over 1 h through the dropping funnel. The reaction mixture was stirred for 1 h at the same temperature, and then poured into conc. hydrochloric acid (400 mL) with ice. The organic layer was separated. The aqueous layer was extracted with diethyl ether (400 mL X 2). The combined organic layer was washed with water (400 mL X 2), satd. aq. $NaHCO_3$ (400 mL X 2), and brine (400 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by distillation under reduced pressure to give **2** (103 g, 87% based on acetic anhydride).

Acetophenone-d_8 (3) To a solution of acetophenone **2** (104 g, 0.829 mol) in 1,4-dioxane (99 mL) was added a solution of sodium hydroxide (one pellet) in deuterium oxide (248 mL). After stirring for 24 h at rt, the mixture was extracted with diethyl ether (300 mL X 3). The organic layer

was dried over $MgSO_4$, and concentrated *in vacuo* to give a crude product. The same operations were further repeated two times. The final crude product was purified by distillation under reduced pressure to give **3** (90.1 g, 85%).

(±)-α-Methylbenzylamine-d_9 (6). To a solution of acetophenone **3** (50.0 g, 0.390 mol) in methanol (390 mL) was added portionwise (five times) sodium borodeuteride (5.73 g, 0.137 mol, 99 atm % D) at 0 °C. After stirring for 1 h at 0 °C, the reaction was quenched by the addition of 1N HCl (100 mL). Furthermore, 1N HCl (100 mL) was added after removal of methanol *in vacuo*. The product was extracted with ethyl acetate (200 mL X 3). The organic layer was washed with satd aq. $NaHCO_3$ (150 mL) and brine (100 mL), dried over $MgSO_4$, and concentrated *in vacuo* to give (±)-1-phenylethanol-d_9 (**4**) as a crude product (56.7 g).

To the above **4** in a 500-mL round-bottomed flask fitted with dropping funnel was added dropwise acetyl bromide (120 g, 72 mL, 0.975 mol) over 30 min at rt. After stirring for 1 h at rt, the resulting acetic acid and excess reagent were removed by using a rotary evaporator. The residue was dissolved in diethyl ether (600 mL). The solution was washed with satd aq. $NaHCO_3$ (300 mL) and brine (300 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by distillation under reduced pressure to give (±)-1-phenylethyl bromide-d_9 (**5**) (70.7 g) (Reference: Smith, P. J.; Amin, M. *Can. J. Chem.* **1989**, *67*, 1457.).

The bromide **5** (70.7 g) was added dropwise into liquid ammonia (*ca.* 300 mL) in autoclave at -78 °C. The mixture was stirred for 14 h at rt. After removal of liquid ammonia, the resulting residue was dissolved in 3N HCl (450 mL). The mixture was washed with diethyl ether (300 mL X 3) to remove neutral compounds, basified with sodium hydroxide, and extracted with diethyl ether (300 mL X 3). The organic layer was washed with brine (300 mL), dried over $MgSO_4$, and concentrated *in vacuo* to give **6** as a crude product. A crude product was purified by distillation under reduced pressure to give **6** (35.2 g, 69% for 3 steps).

Optical Resolution of (±)-α-methylbenzylamine-d_9 (6). (Reference: Hagitani, H. (Sumitomo Chemical Co., Ltd., Japan) *Jpn. Kokai Tokkyo Koho* **1997**, 5pp.) To a solution of (±)-α-

methylbenzylamine-d_9 (**6**) (35.4 g, 0.272 mol) in *t*-butyl methyl ether (242 mL) was added a solution of (*S*)-(+)-mandelic acid (18.6 g, 0.122 mol) in *t*-butyl methyl ether (345 mL) at rt. The mixture was stirred for 3 h at 45 °C, and then cooled to rt. Glass-filtration gave a diastereomer salt [(*S*)-α-d_9-methylbenzylammonium (*S*)-(+)-mandelate], which was treated with 1N NaOH (490 mL) at rt for 30 min. After the mixture was extracted with diethyl ether (300 mL X 3), the organic layer was washed with brine (300 mL), dried over $MgSO_4$, and concentrated *in vacuo* to afford (*S*)-α-methylbenzylamine-d_9 (**6a**) (16.7 g, 90% ee) as a crude product. Further resolution by the same acid (16.6 g, 0.9 eq based on containing amount of (*S*)-isomer) gave enantiomerically pure **6a** (15.0 g, >99% ee). On the other hand, the mother liquor was washed with 1N NaOH (300 mL) and brine (300 mL), dried over $MgSO_4$, and concentrated *in vacuo* to afford (*R*)-α-methylbenzylamine-d_9 (**6b**) (18.2 g, 75% ee) as a crude product. Resolution by (*R*)-(-)-mandelic acid (16.7 g, 0.9 eq based on containing amount of (*R*)-isomer) gave enantiomerically enriched **6b** (14.7 g, >95% ee) and the following resolution by the same acid (15.1 g) afforded enantiomerically pure **6b** (14.1 g, >99% ee).

(*1S*)-*N*-Trifluoroacetyl-α-methylbenzylamine-d_9 (7a). To a solution of (*1S*)-α-methylbenzylamine-d_9 (**6a**) (15.0 g) and pyridine (14.0 mL, 173 mmol) in dichloromethane (150 mL) was added dropwise trifluoroacetic anhydride (21.2 mL, 150 mmol) over 10 min at -78 °C under Ar. The mixture was stirred for 2 h at rt. The reaction was quenched by the addition of 1N HCl at 0 °C. This mixture was diluted with diethyl ether (400 mL), washed with 1N HCl (300 mL X 2), satd aq. $NaHCO_3$ (300 mL) and brine (200 mL), dried over $MgSO_4$, and concentrated *in vacuo* to furnish a white solid. Recrystallization of the product from toluene gave **7a** (19.3 g, 63% from **6**).

(*1S*)-*N*,α-Dimethylbenzylamine-d_{13} (9a). To a suspension of sodium hydride (6.82 g, 170 mmol, 60% in oil dispersion) in THF (100 mL) was added a solution of **7a** (19.3 g, 85.2 mmol) in THF (50 mL) at 0 °C under Ar. The mixture was stirred for 30 min at rt, and cooled to 0 °C. Methyl iodide-*methyl*-d_3 (6.35 mL, 102 mmol, >99.5 atm % D) was added at 0 °C. The mixture was stirred for 11 h at rt, and then poured into 1N HCl (300 mL) with crushed ice. After addition of diethyl ether (500 mL) into the mixture, the organic layer was separated, washed with satd aq. $Na_2S_2O_3$ (200 mL),

satd aq. $NaHCO_3$ (200 mL) and brine (200 mL), dried over $MgSO_4$, and concentrated *in vacuo* to give **8a**.

Amide **8a** was treated in satd NH_3-MeOH (150 mL) for 63 h at rt. After the methanol was removed *in vacuo*, the residue was dissolved in 1N HCl (200 mL). The solution was washed with diethyl ether (150 mL X 2), basified with NaOH, and extracted with diethyl ether (250 mL X 3). The ether solution was washed with satd NaCl-D_2O (50 mL X 2), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by distillation under reduced pressure to give (*1S*)-*N*,α-dimethylbenzylamine-d_{13} (**9a**) (10.7 g, 85% for 2 steps, >99 atm % D based on MS): ^{13}C NMR (neat, acetone-d_6 as an external standard, 100 MHz) δ 145.7 (singlet), 127.5 (triplet, $J_{C\text{-}D}$ = 24 Hz), 126.0 (triplet, $J_{C\text{-}D}$ = 24 Hz), 125.9 (triplet, $J_{C\text{-}D}$ = 24 Hz), 59.2 (triplet, $J_{C\text{-}D}$ = 20.5 Hz), 33.2 (septet, $J_{C\text{-}D}$ = 20 Hz), 23.1 (septet, $J_{C\text{-}D}$ = 20 Hz); IR (neat) 3286, 2287, 2272, 2223, 2185, 2054, 1437, 1327, 1171, 1050 cm^{-1}; (*S*)-DMBA-d_{13}: $[\alpha]_D^{23}$ -64 (*c* 2.2, $CHCl_3$). (*1R*)-*N*,α-dimethylbenzylamine-d_{13} (**9b**) (9.77g from **6b** (12.0 g)) was obtained by the same procedure: (*R*)-DMBA-d_{13}: $[\alpha]_D^{23}$ +66 (*c* 2.3, $CHCl_3$).