Surfactant-Accelerated Asymmetric Transfer Hydrogenation with Recyclable Water-Soluble Catalyst in Aqueous Media

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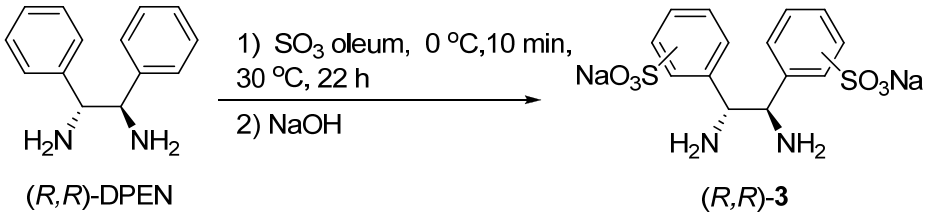
Supplementary data

Table of Contents

1. General methods.

All commercially available reagents were used as received without further purification. All solvents used in the reactions were distilled from appropriate drying agents prior to use. All reactions were performed under argon atmosphere in flame-dried glassware. Melting points were determined using electrothermal capillary apparatus without correction. NMR was referenced to the solvent unless stated otherwise. The chemical shifts were reported in ppm and the coupling constants (*J*) were given in hertz (Hz). Enantiomeric excess was determined by GC on chiral CP-cyclodex B-236 M/ CP-Chirasil-DEX columns or HPLC on Chiral OD/OJ columns.

2. Sulfonation of DPEN with SO_3 oleum



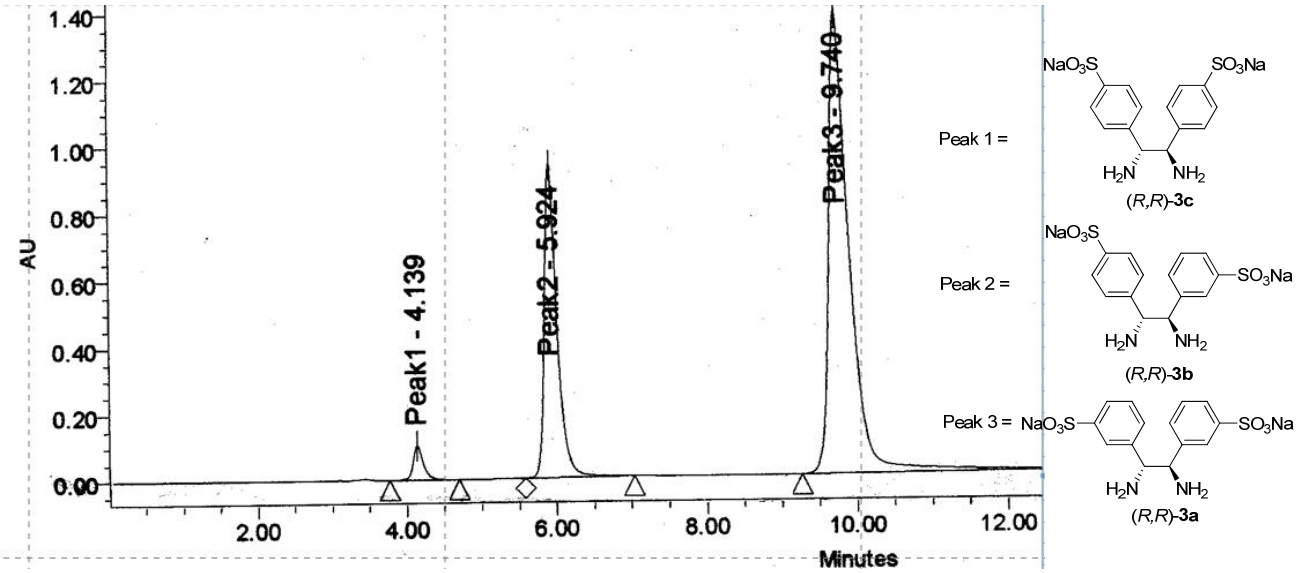


Figure S1. The mixture of (*R,R*)-**3**.

Table 1S. Influence of SO_3 oleum on sulfonation.[a]

Entry	SO_3 oleum	T (□)	Components concentration (%)			Total Yield (%)
			Peak 1	Peak 2	Peak 3	
1[b]	*Con.* H_2SO_4	90	0	0	0	0
2	20%	30	0	0	0	0
3[c]	20% : 50% = 1 : 1	23	3.55	29.96	66.49	76
4[c]	20% : 50% = 1 : 1	30	3.03	23.28	73.69	80
5	50%	23	2.64	23.12	74.24	83
6	50%	30	1.89	23.37	75.49	89

[a] Unless otherwise noted, all the reaction was conducted without solvent. The Components were determined by HPLC analysis. Total yield was isolated yield of the mixture of (*R,R*)-**3**. [b] Concentrated H_2SO_4 (98%) was used. [c] Mixture of 10 mL of 20% SO_3 oleum and 10 mL of 50% SO_3 oleum.

Three peaks were found on HPLC spectra (Figure S1). (*R,R*)-**3**(**a-b**) were separated by preparative HPLC (Varian Dynamax 250 x 10 mm column, 0.02 mol/L KCl, UV 220 nm) and (*R,R*)-**3a** was the main product.

3. Influence of pH values on ATH of acetophenone

Table 2S. Influence of pH on the conversion and enantioselectivity of ATH of acetophenone.[a]

Entry	HCOOH: HCOONa	pH (Start)	pH (End)	Conv. %	Ee %
1	5 : 0	1.7	1.8	0	-
2	3 : 1	3.3	3.5	1.3	-
3	1 : 1	3.9	4.1	7.4	91
4	1 : 3	4.8	6.9	28	96
5	1 : 4	5.5	7.5	70	96
6	1 : 5	7.1	8.4	87	96
7	0 : 5	8.1	9.3	93	96
8[b]	0 : 5	9.8	10.5	83	96

[a] Unless otherwise noted, all the reaction was conducted in 1 mL of degassed water under

argon atmosphere at 40 °C. [**2**] = 0.005 M; [**2**] : [CTAB] : [acetophenone] = 1 : 4 : 100. [HCOONa] + [HCOOH] = 2.5 M. The conversions and ee values were determined by GC analysis (CP-cyclodex B-236 M). [b] [HCOONa] = 2.5 M, [Na_2CO_3] = 0.625 M.

4. Recycle results of ATH applying surfactant

Table 3S. Recycle results of asymmetric transfer hydrogenation of acetophenone applying CTAB as surfactant.[a]

Run	1	2	3	4	5	6	7	8	9	10	11	12	13
Time (h)	4	4	4	4	5	5	7	6	6	8	14	18	22
Conv [%]	>99	>99	>99	>99	>99	>99	>99	99	95	92	78	44	20
Ee [%]	96	96	96	96	96	96	96	96	96	96	96	96	97

[a] Unless otherwise noted, all the reaction was conducted in 1 mL of degassed water under argon atmosphere at 40 °C. [**2**] = 0.005 M; [**2**] : [CTAB]: [acetophenone]: [$HCOONa \cdot 2H_2O$] = 1 : 4 : 100 : 500. The conversions and ee values were determined by GC analysis (CP-cyclodex B-236 M).

Table 4S. Recycle results of asymmetric transfer hydrogenation of acetophenone applying CPB as surfactant.[a]

Run	1	2	3	4	5	6	7	8	9	10	11	12
Time (h)	4	4	4	4	5	5	7	6	6	8	14	18
Conv [%]	>99	>99	>99	>99	>99	99	>99	>99	>99	99	99	98
Ee [%]	96	95	94	95	95	95	94	95	95	95	95	95
Run	13	14	15	16	17	18	19	20	21	22	23	24

Time (h)	22	27	24	36	36	40	46	49	60	75	130	144
Conv [%]	99	98	95	96	93	89	86	89	89	78	63	59
Ee [%]	95	94	95	94	94	94	94	94	94	94	94	96

[a] Unless otherwise noted, all the reaction was conducted in 1 mL of degassed water under argon atmosphere at 40 °C. [**2**] = 0.005 M; [**2**] : [CPB] : [acetophenone] : [$HCOONa{\cdot}2H_2O$] = 1 : 4 : 100 : 500. The conversions and ee values were determined by GC analysis (CP-cyclodex B-236 M).

5. The influence of metal precursor for ATH of α-bromoacetophenones.

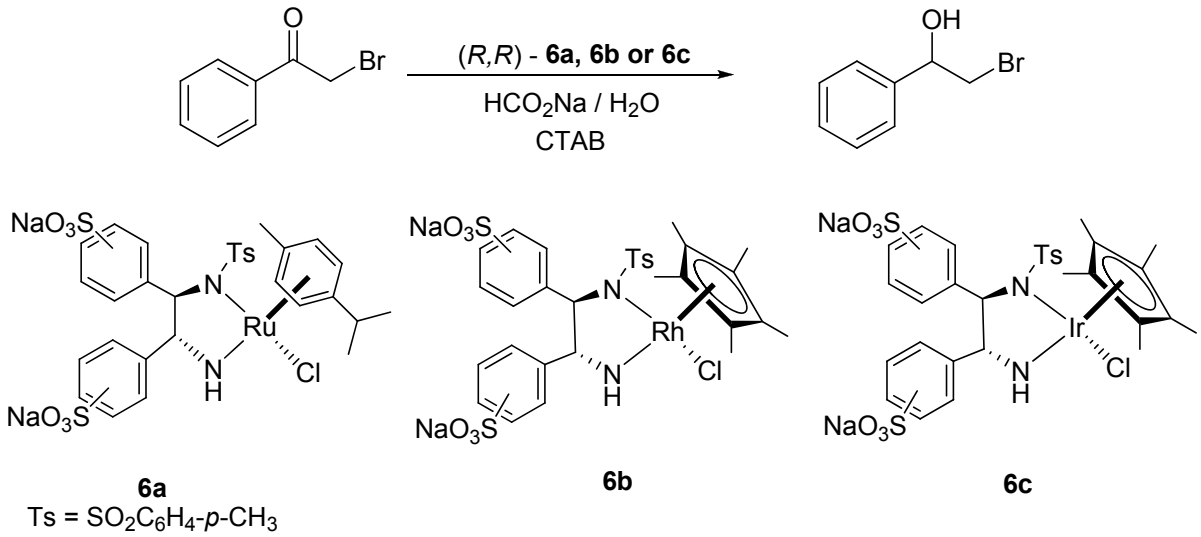
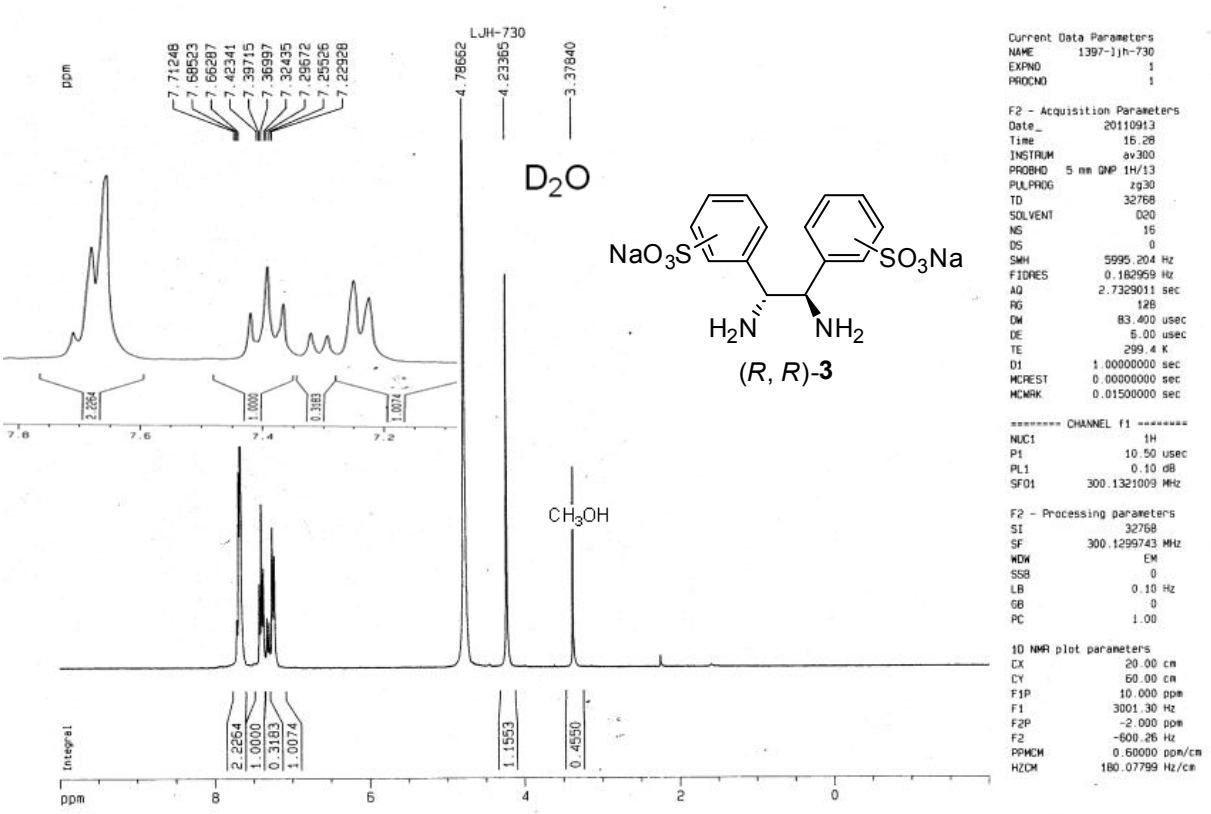


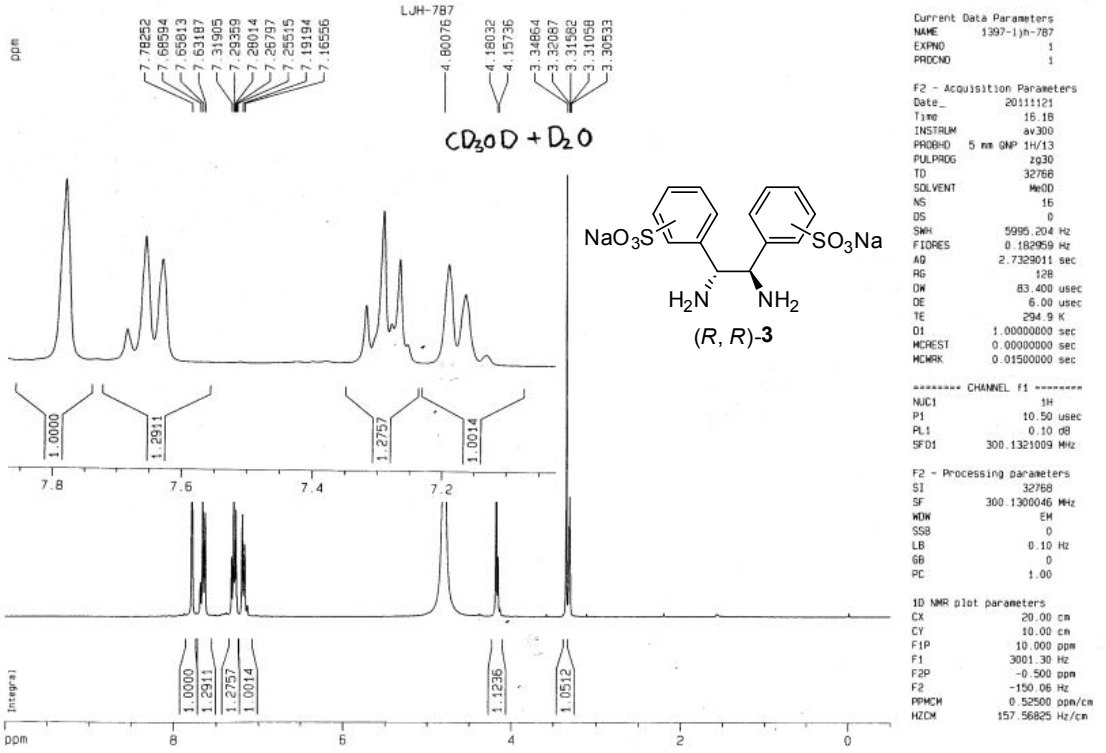
Table 5S. The catalytical effect of different metal complex for ATH of α-bromoacetophenones.[a]

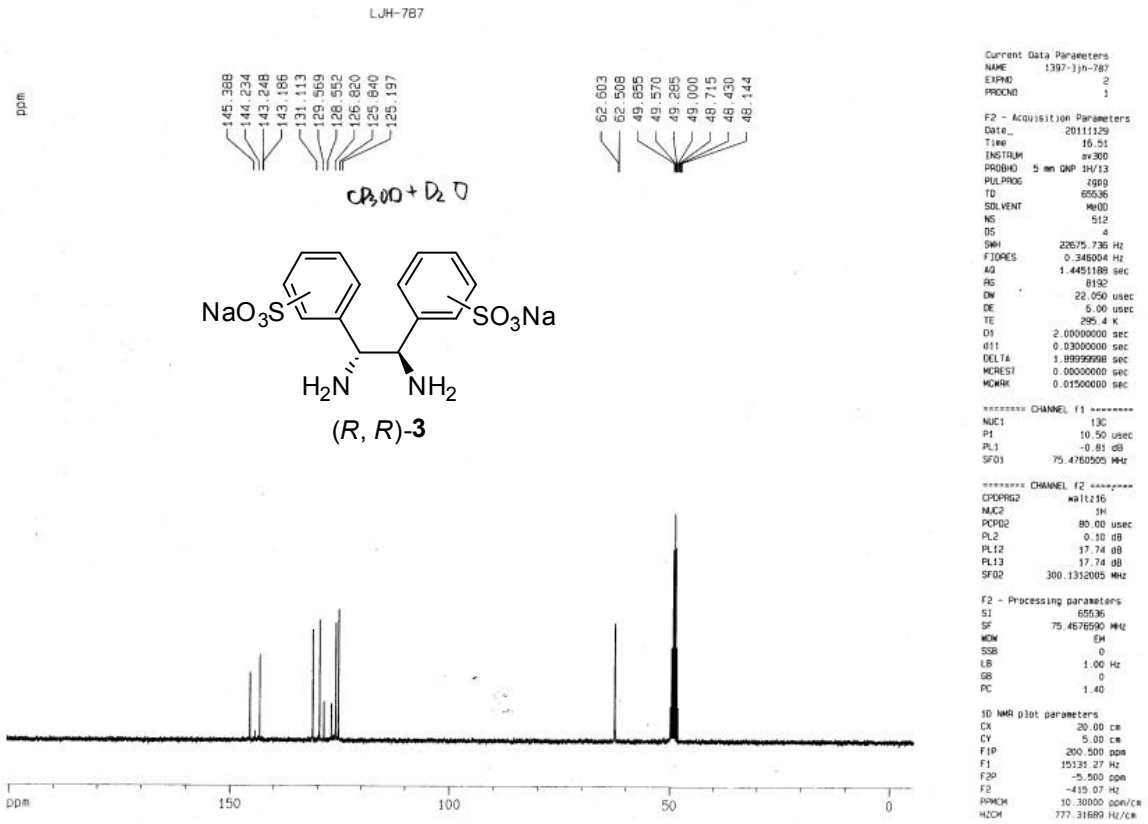
Entry	Catalyst	Conversion (%)	Yield (%)	Ee (%)
1	**6a**	81	78	93
2	**6b**	97	95	95
3	**6c**	88	82	94

[a] Unless otherwise noted, the reaction was carried out in 1 mL of degassed water under argon atmosphere at 40 °C for certain time using 0.5 mmol substrate, 5 equivalents of HCO_2Na as hydrogen donor, 0.02 mmol CTAB, S/C = 100:1. All the yields were isolated yields and the ee values were determined by GC analysis : GC analysis: CP-Chirasil-DEX CB, 0.25 mm × 25 m, column temperature = 100 °C (isothermal), inject temperature = 240 °C, detector temperature = 260 °C, inlet pressure = 12.1 psi; t_{major} = 7.9 min, t_{minor} =8.3 min.).

6. Spectra for ligands



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(R, R)-3
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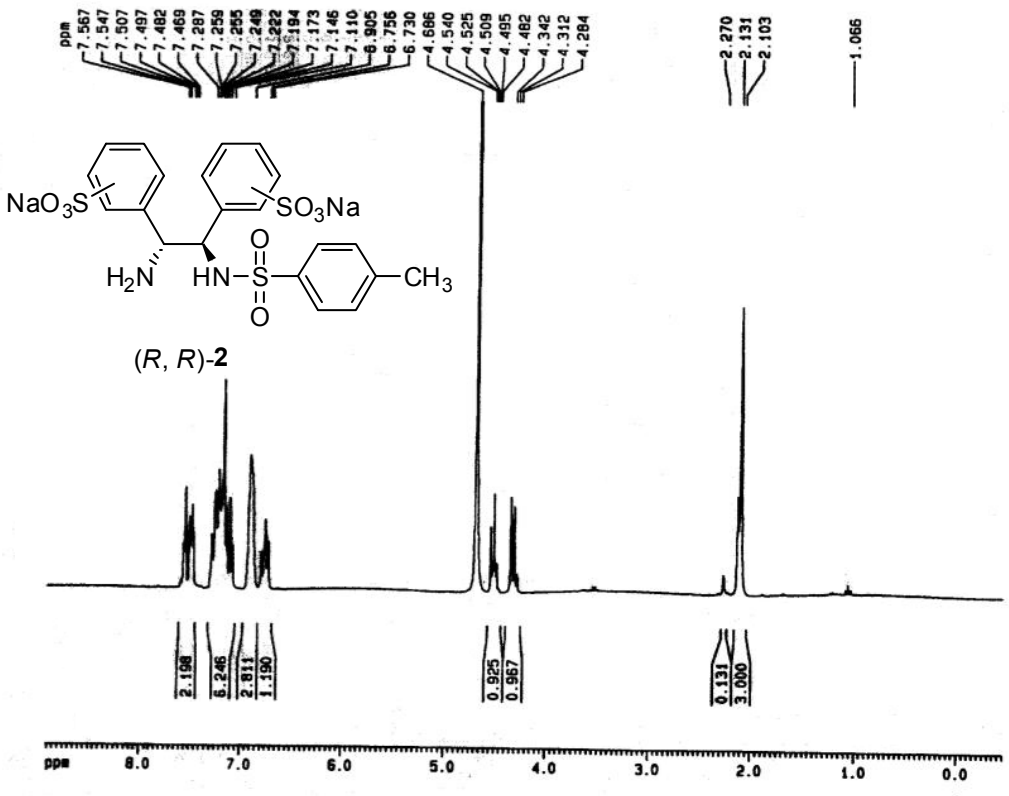
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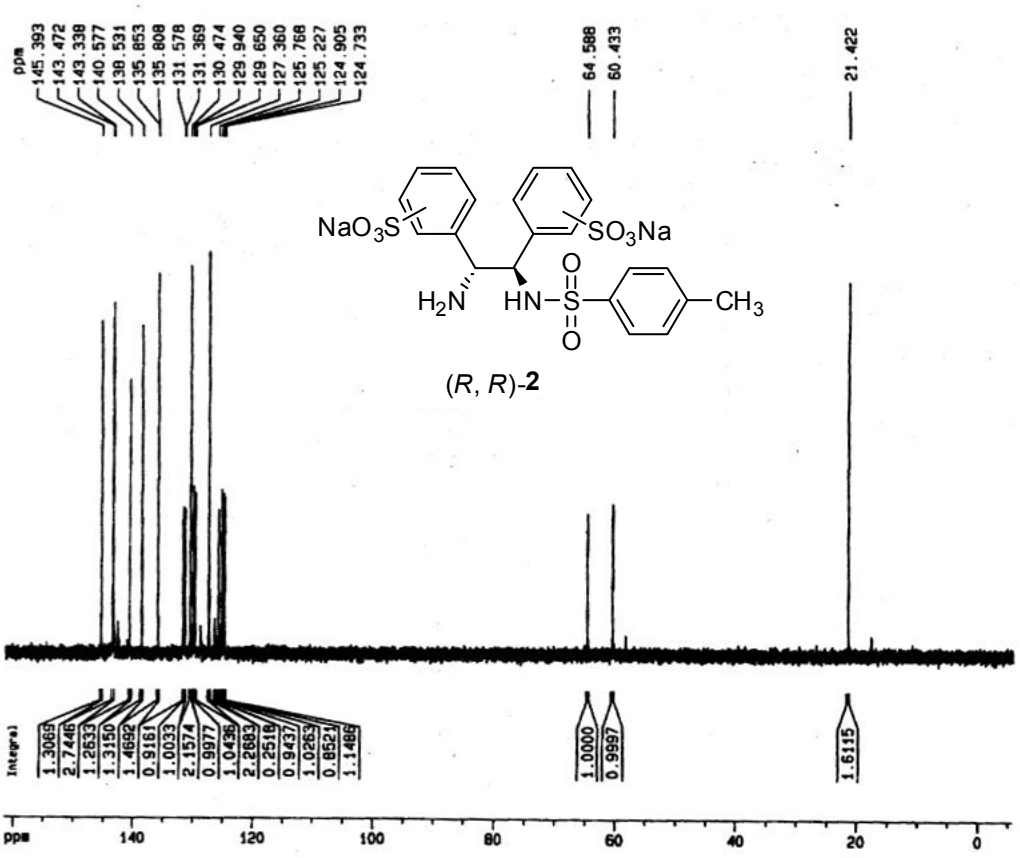

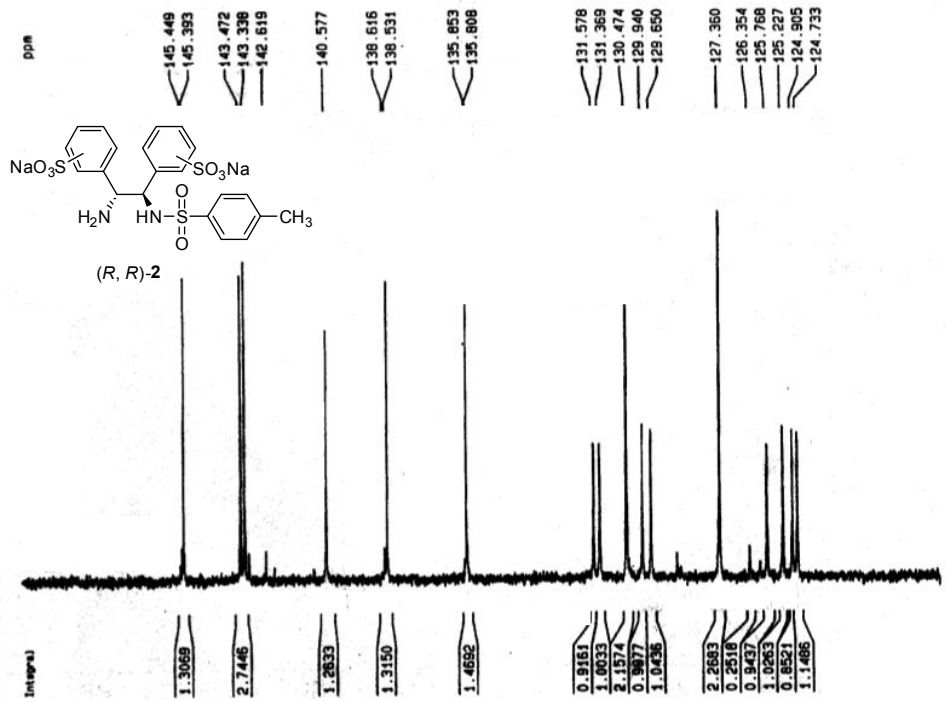

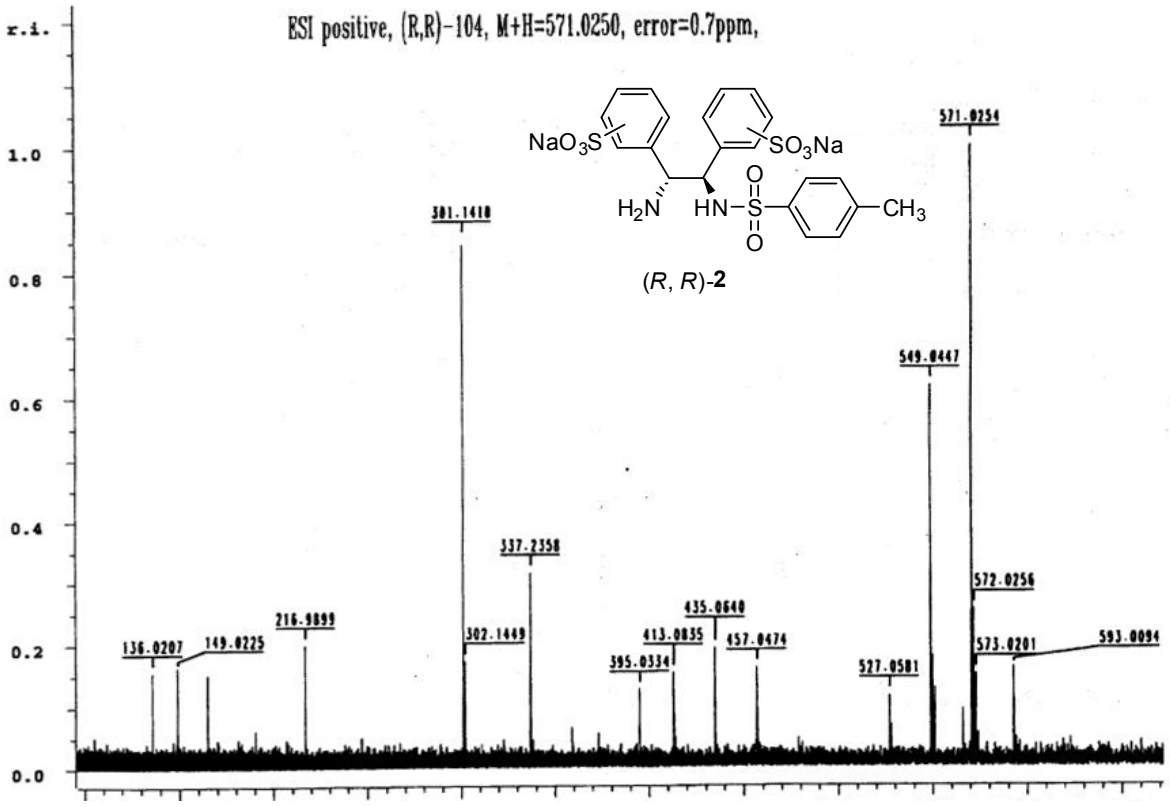
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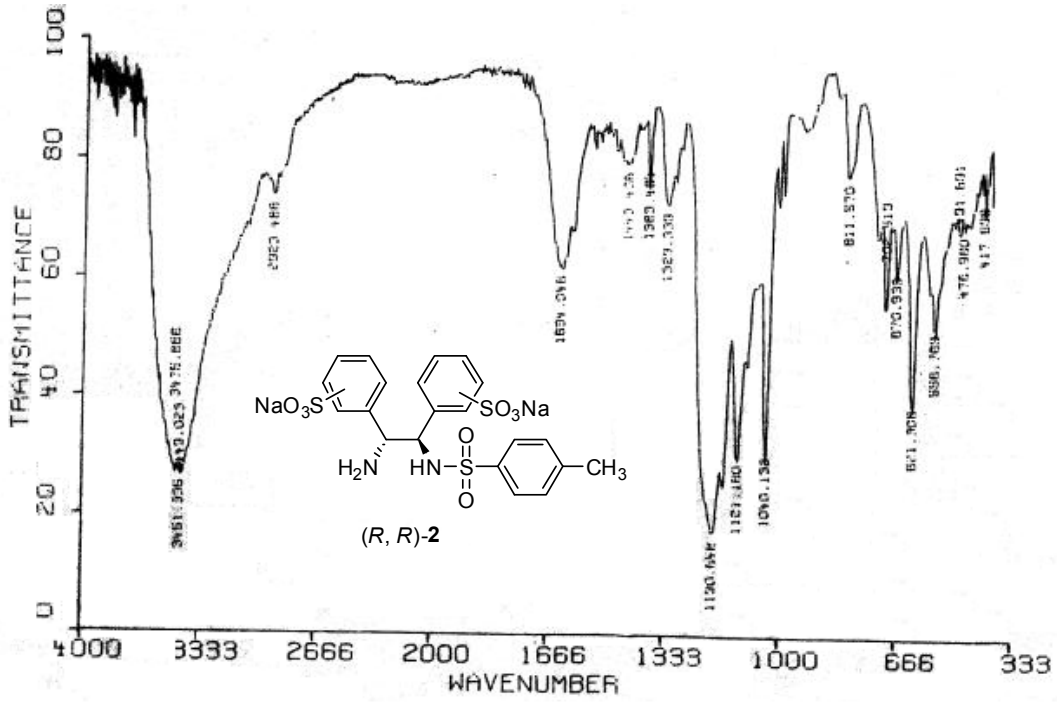
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O
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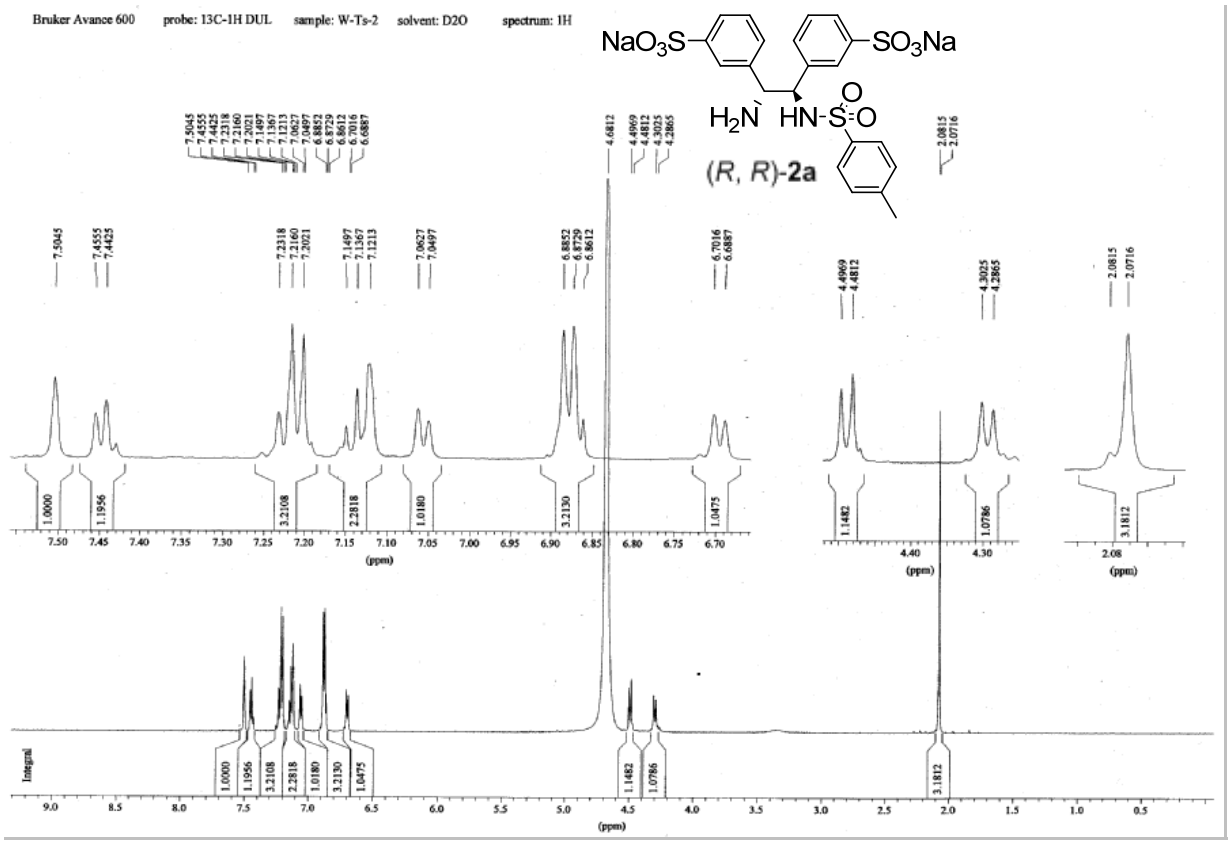
(R, R)-2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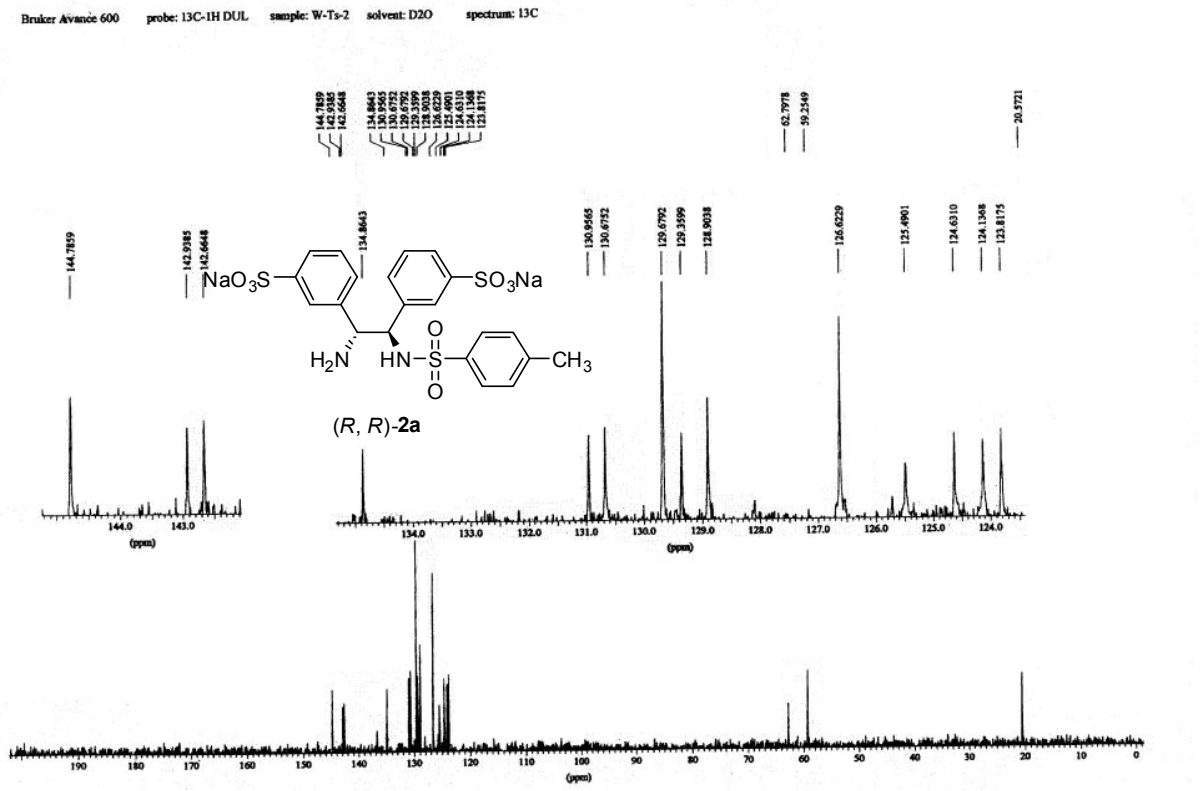
Integral
(ppm)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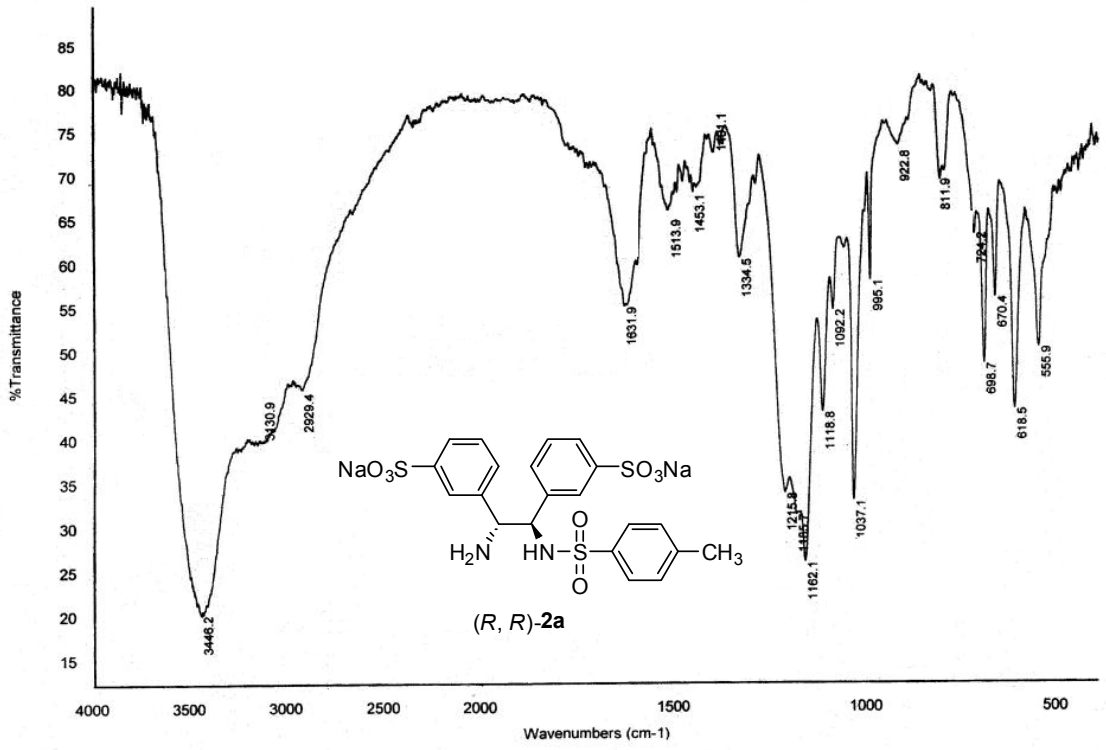
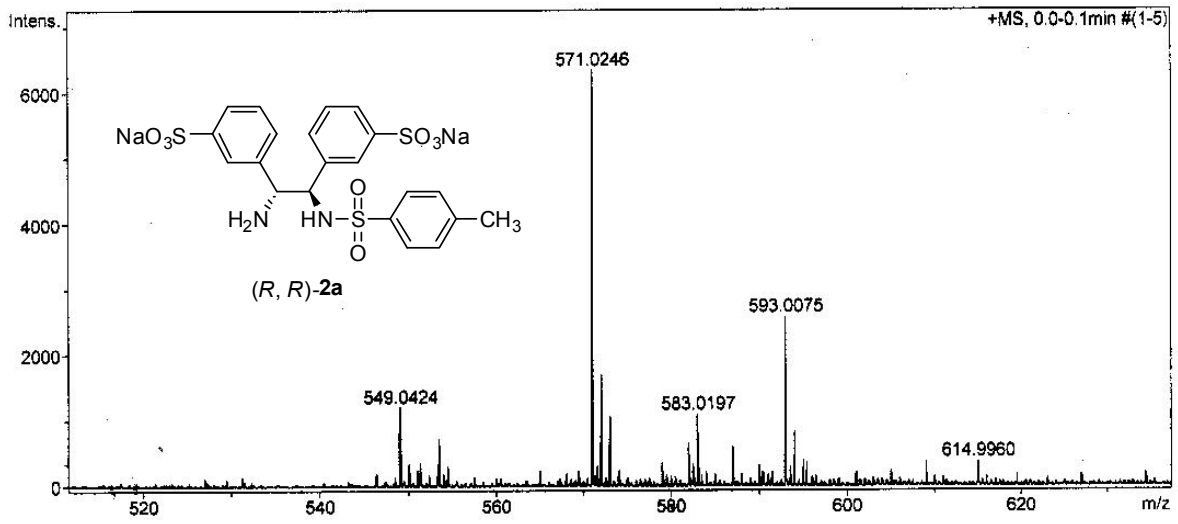
(ppm)





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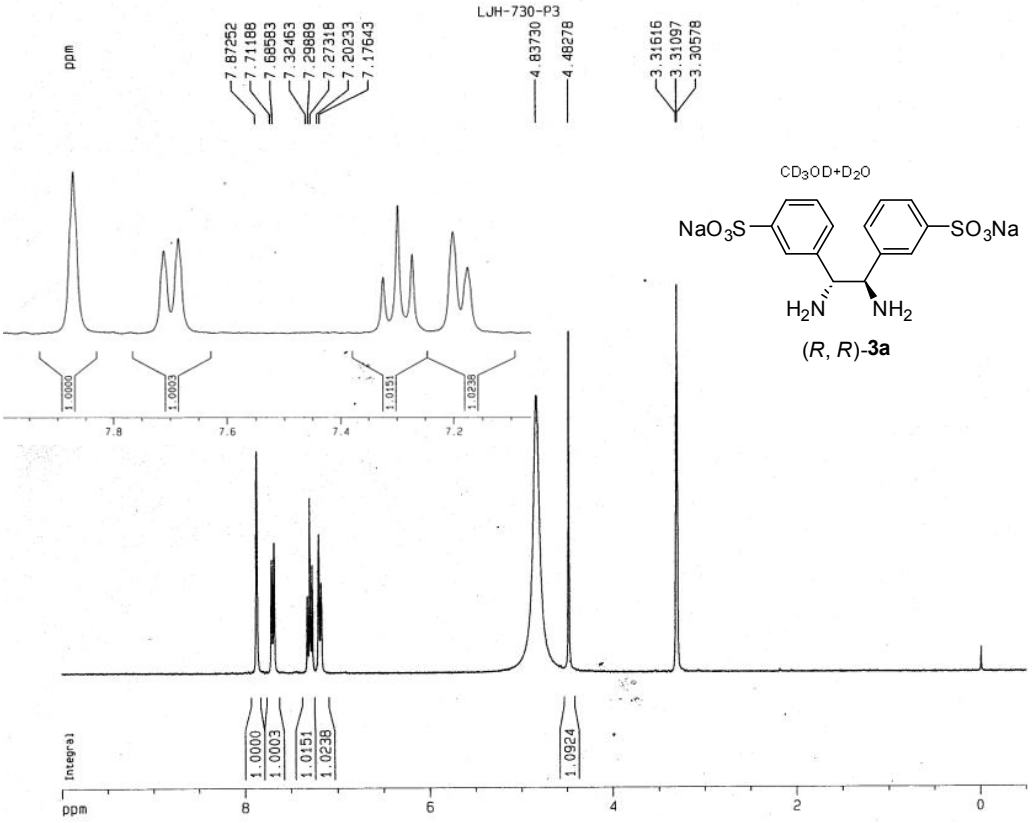


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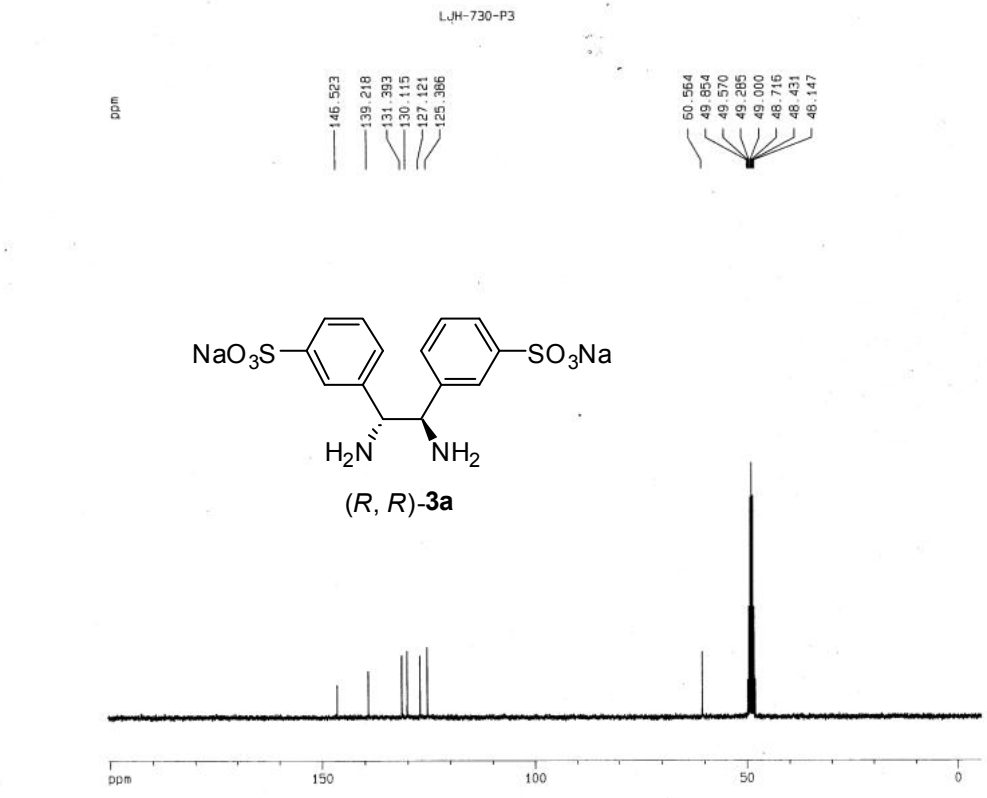


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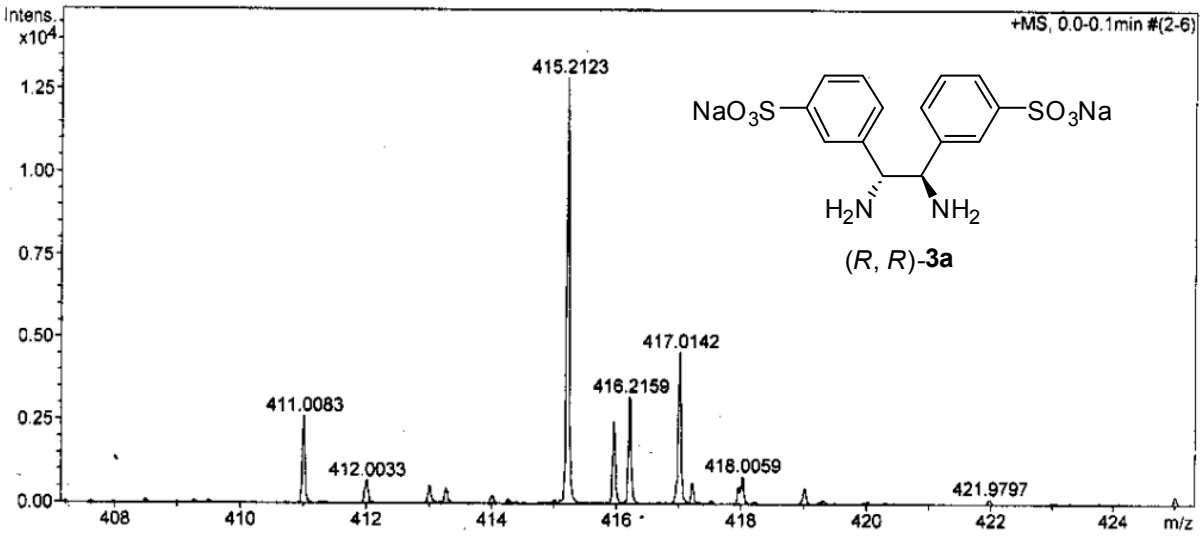

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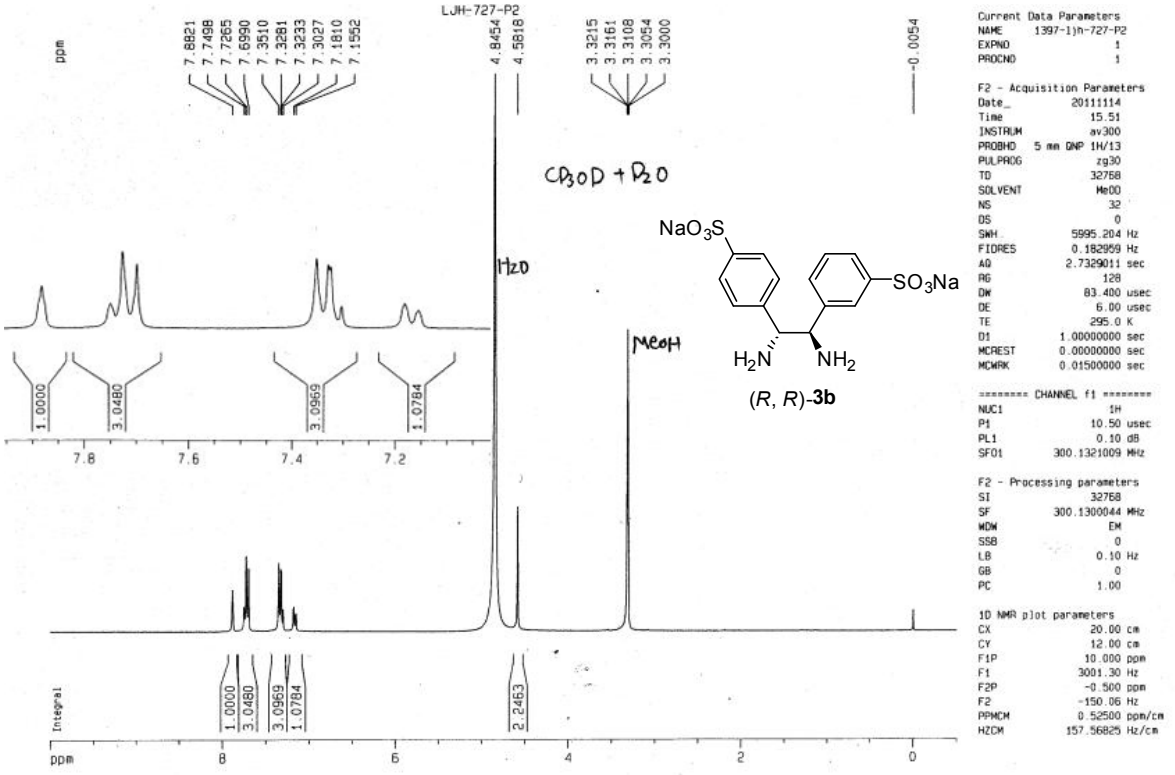

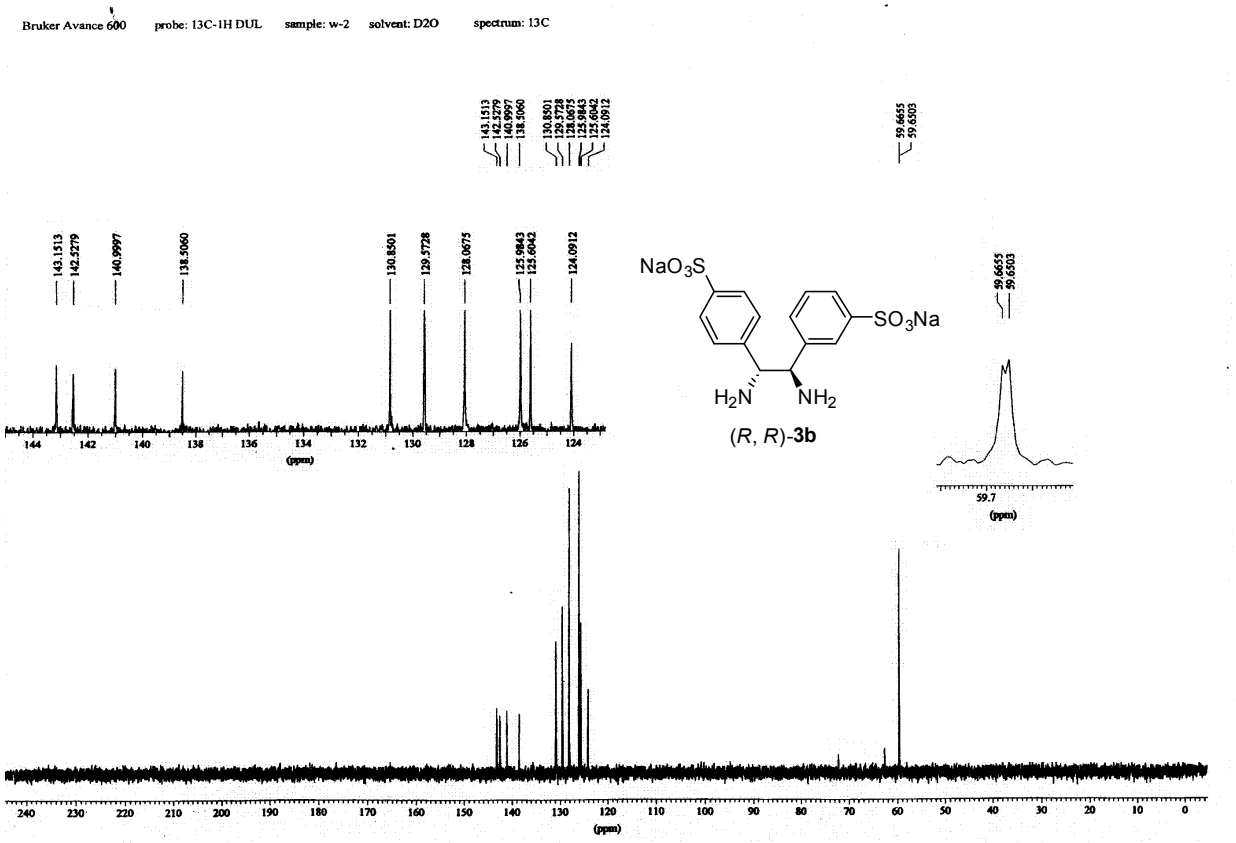

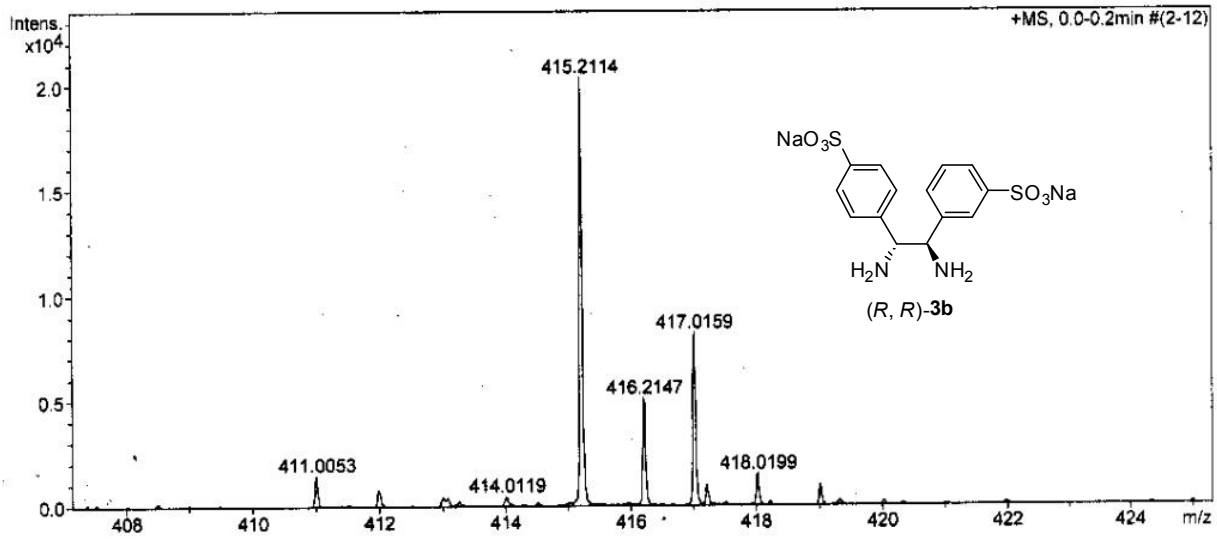

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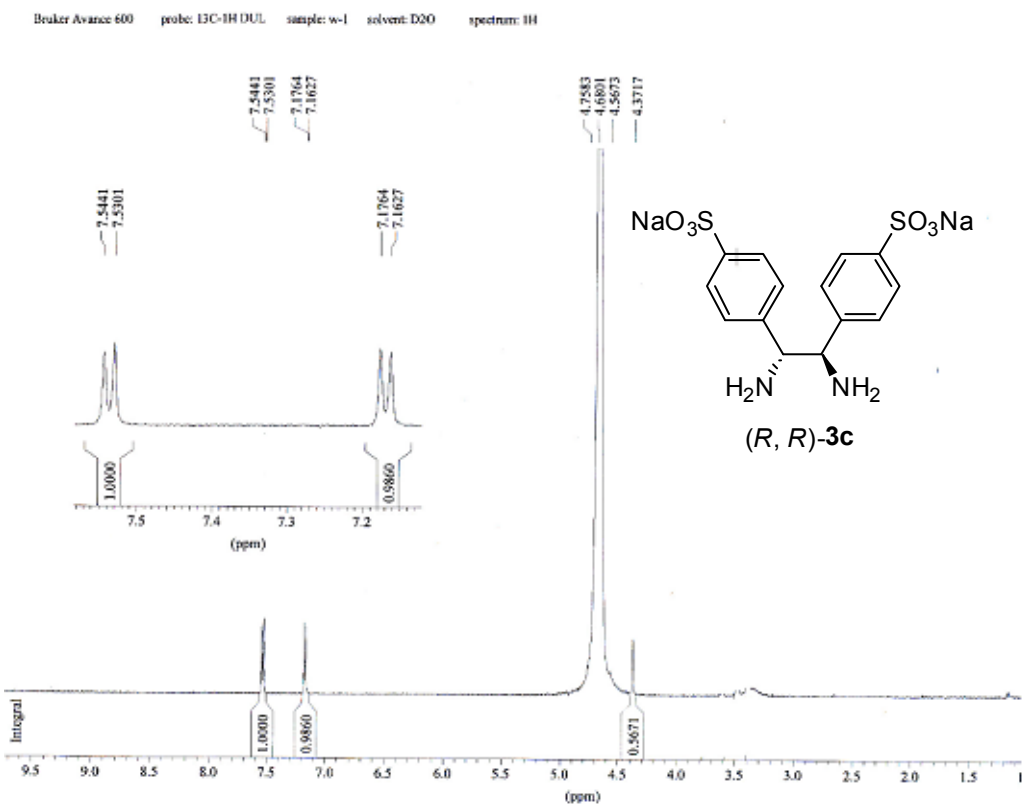

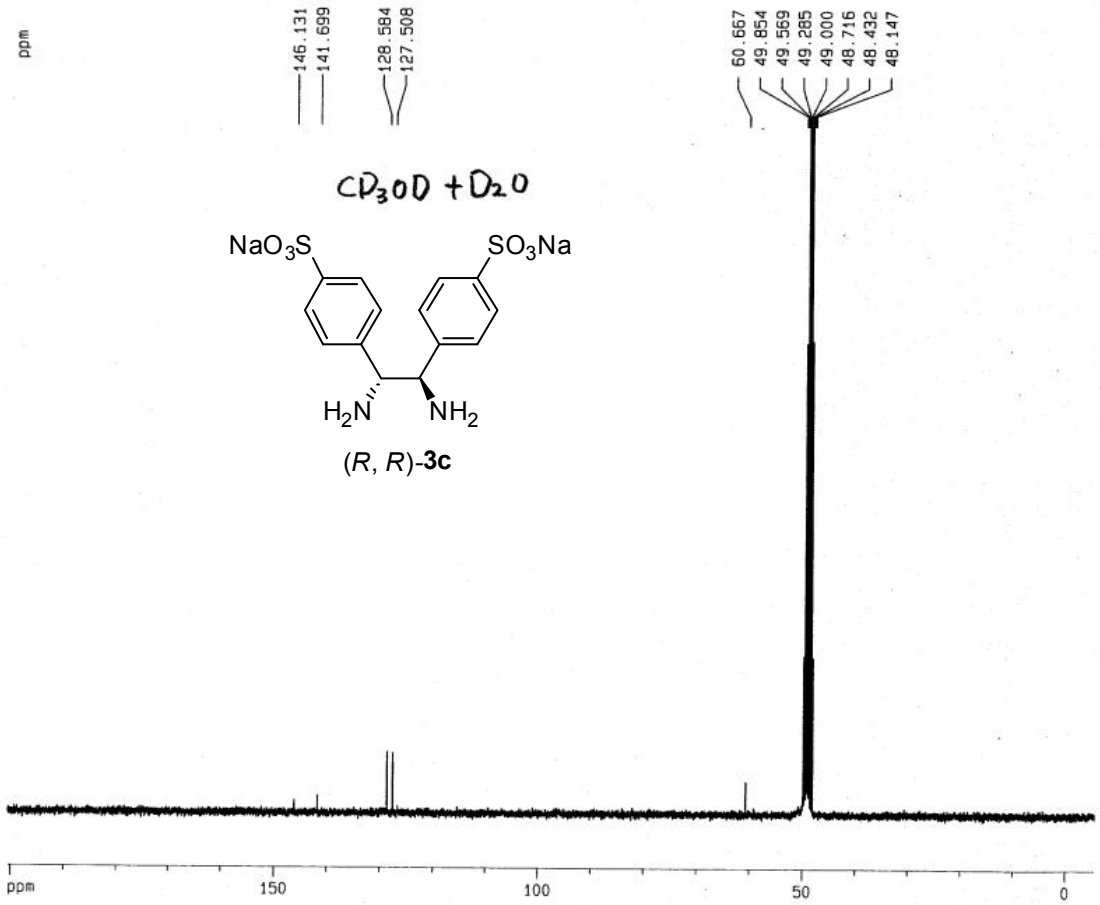

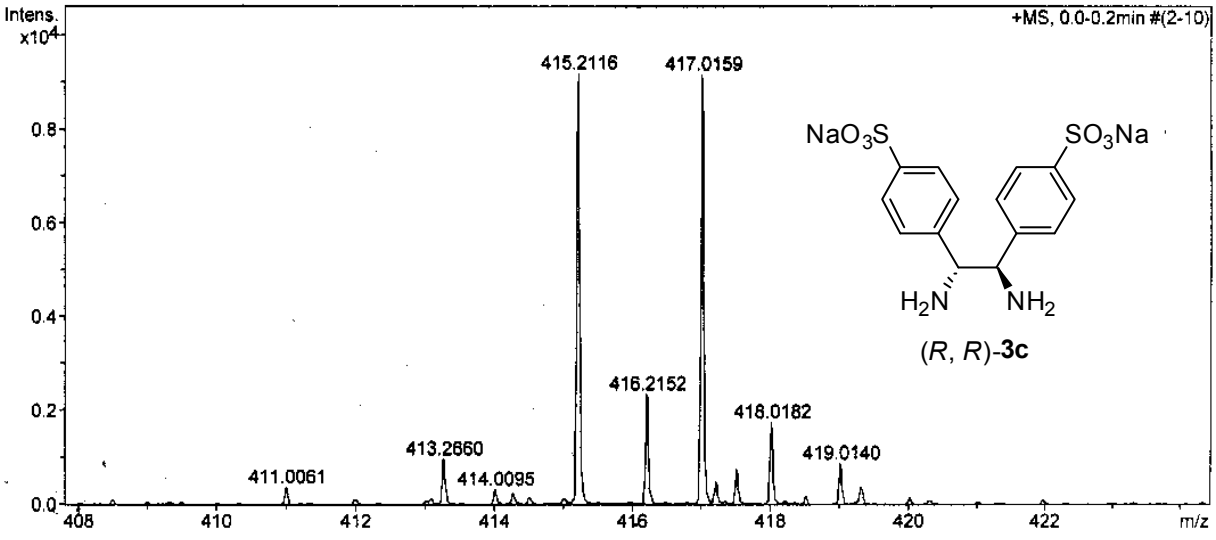

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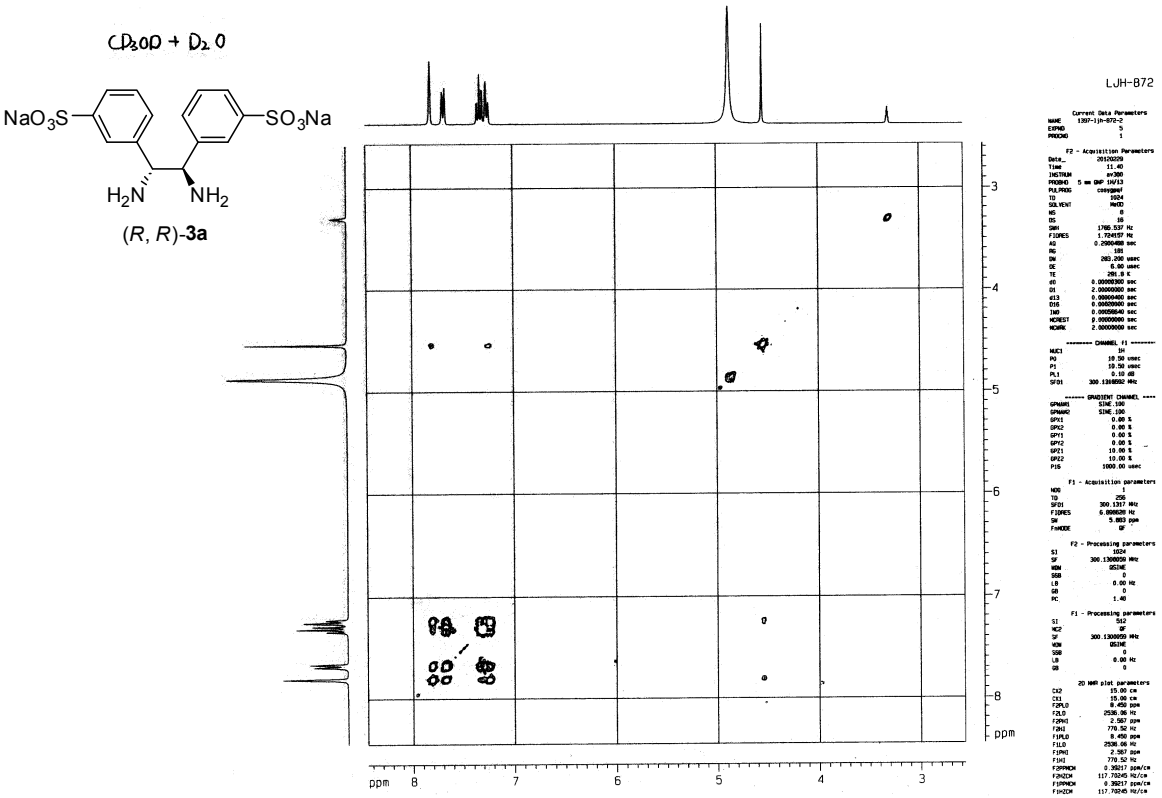

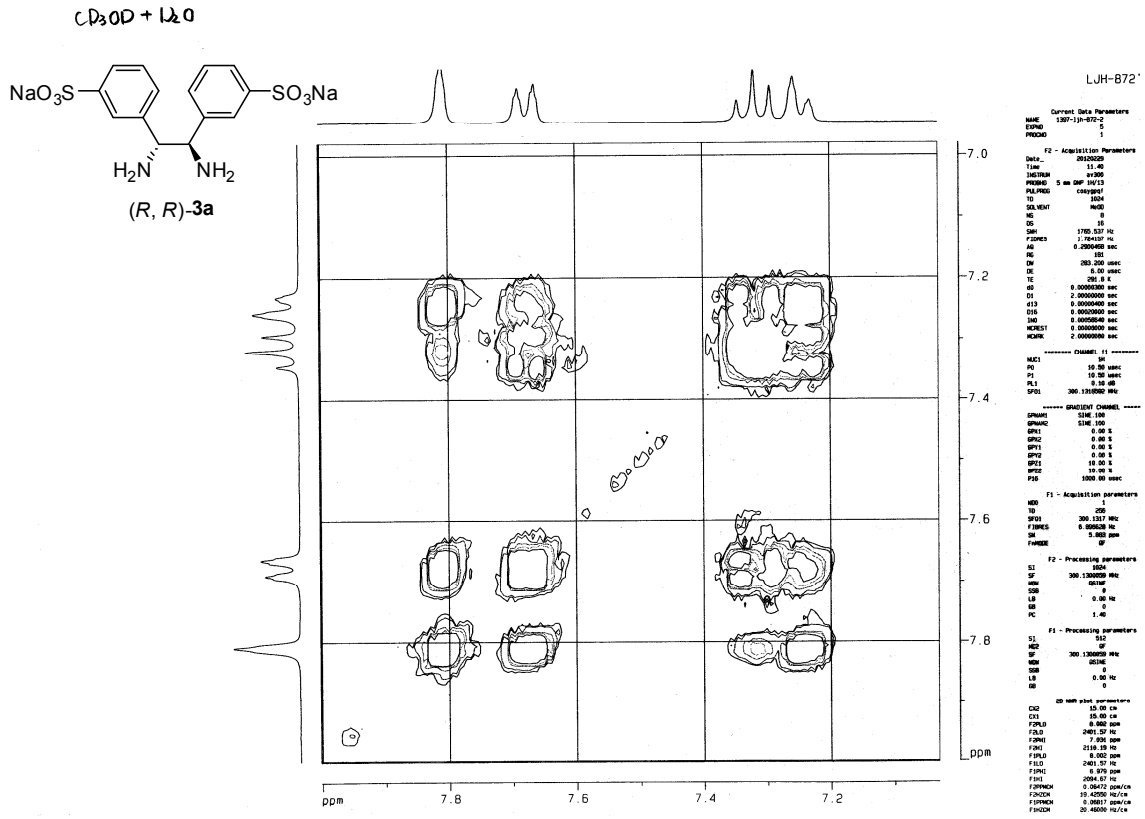
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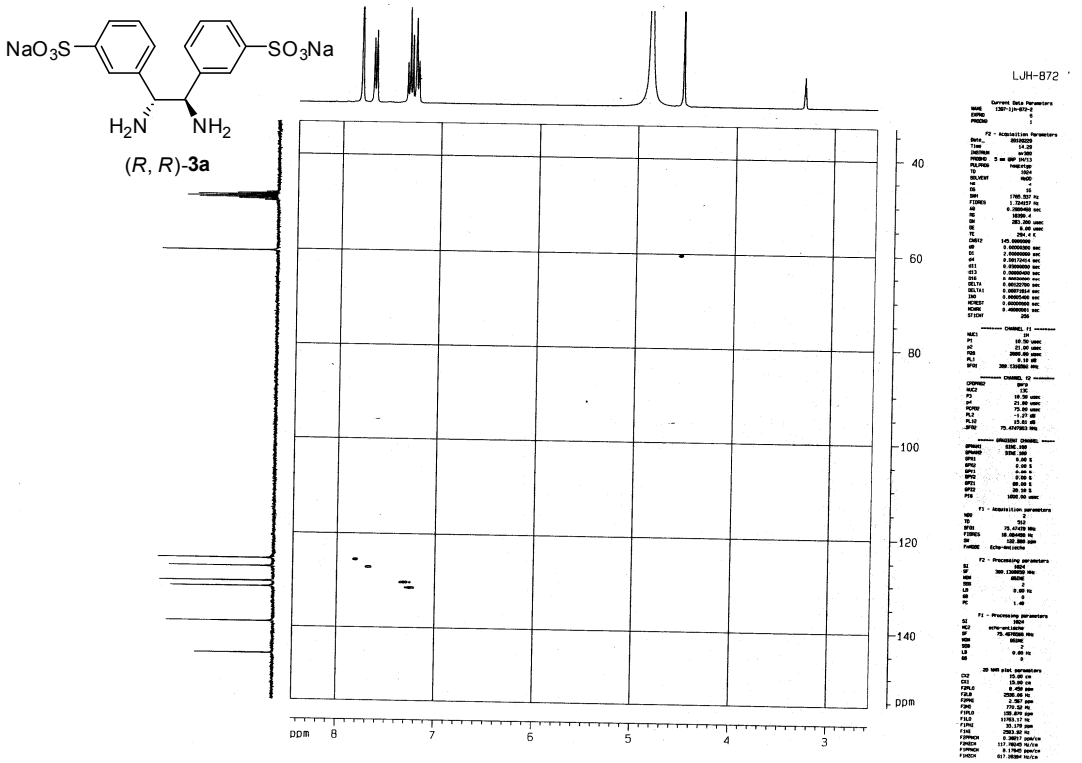
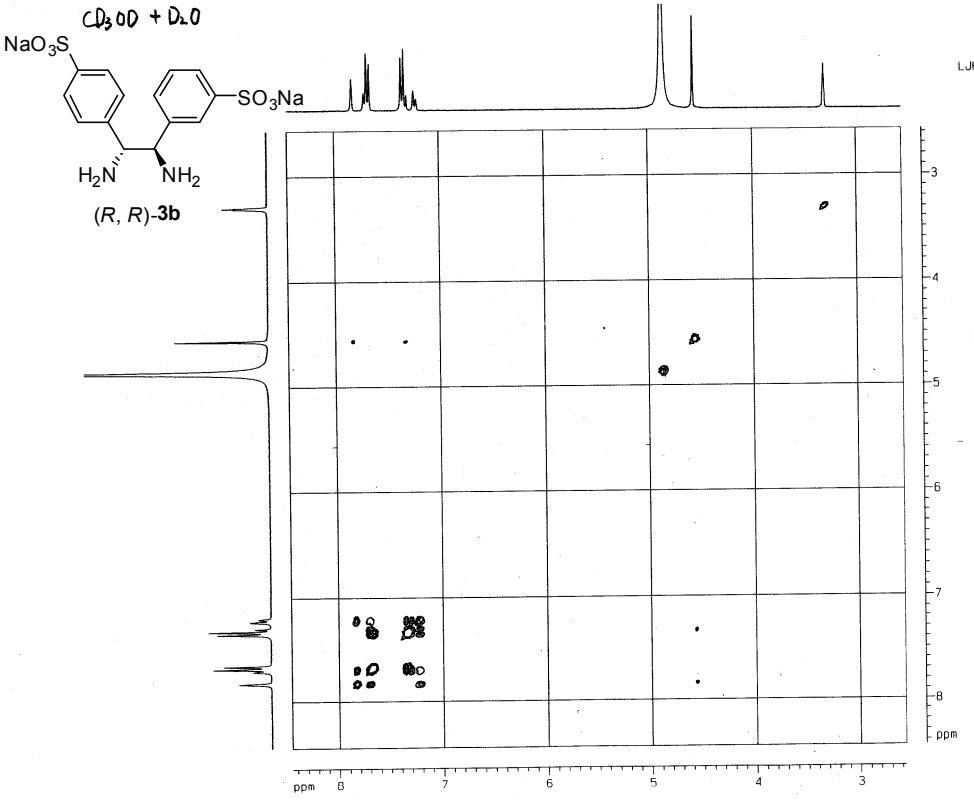
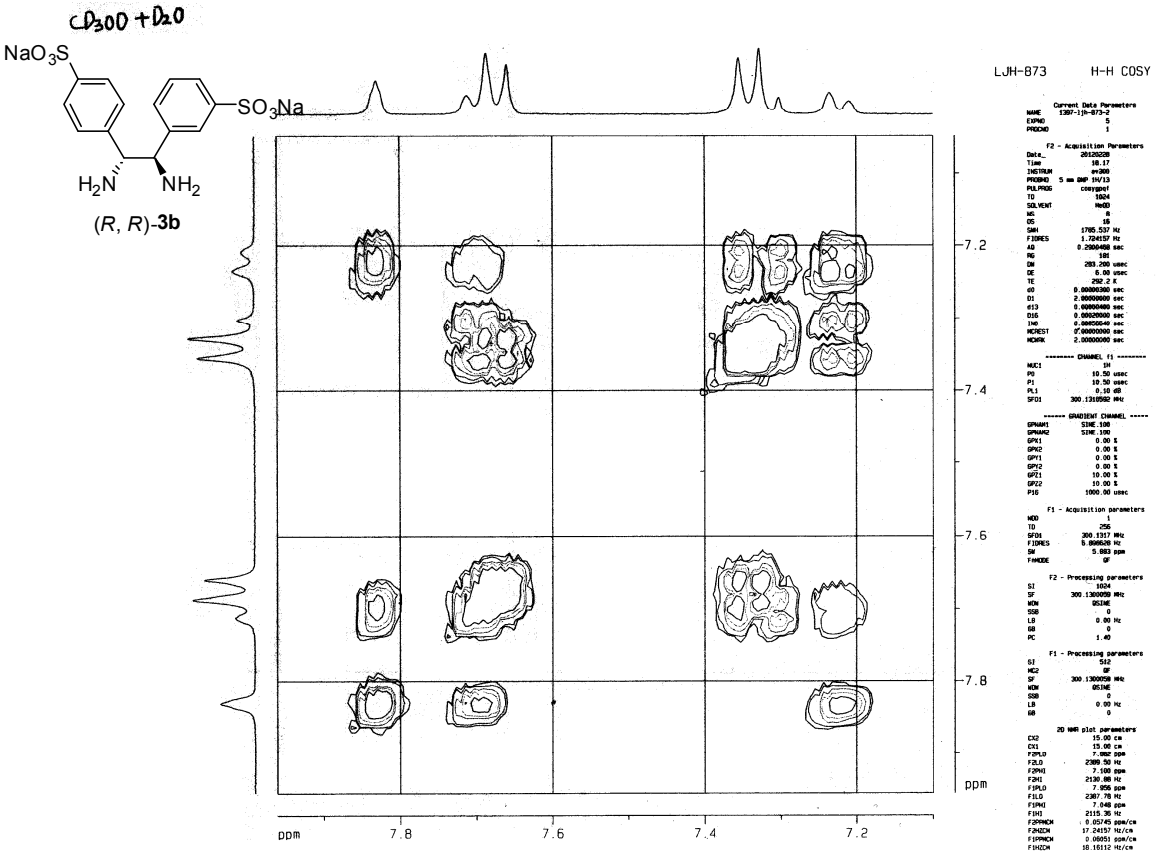
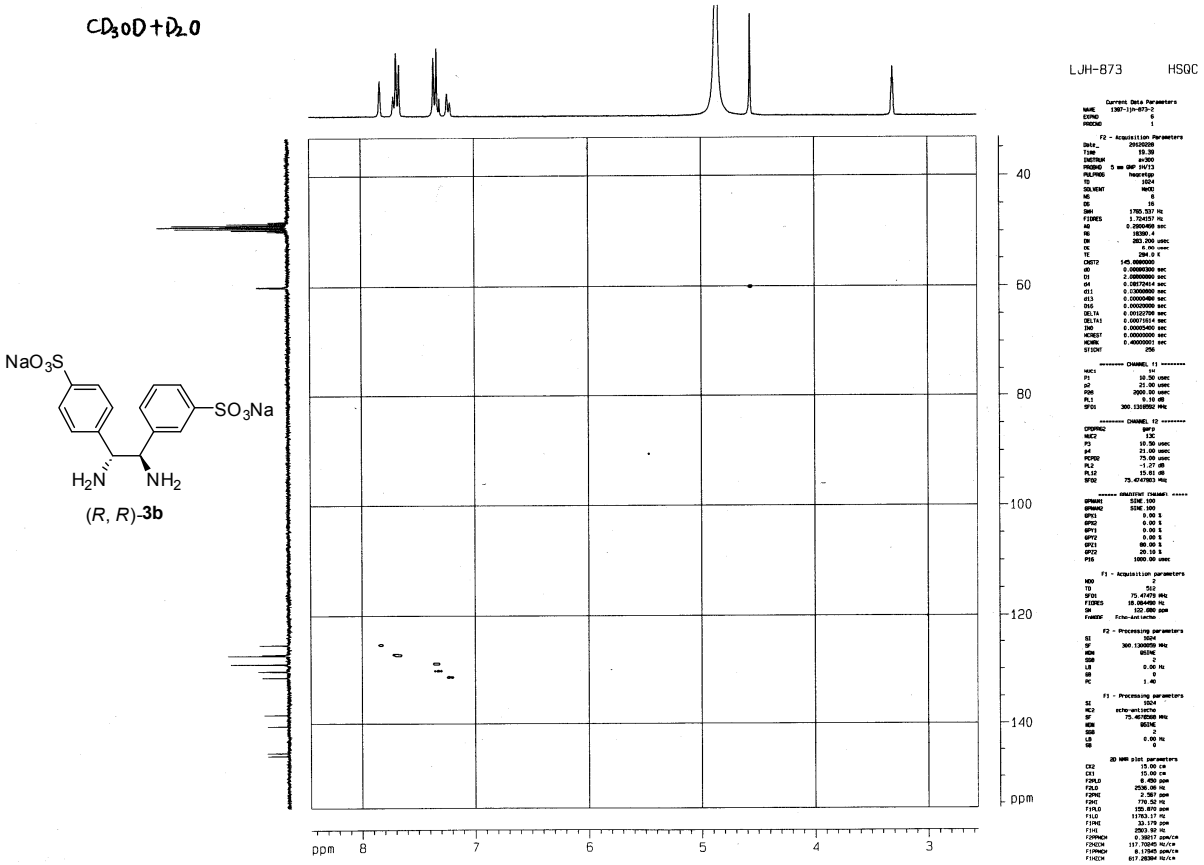
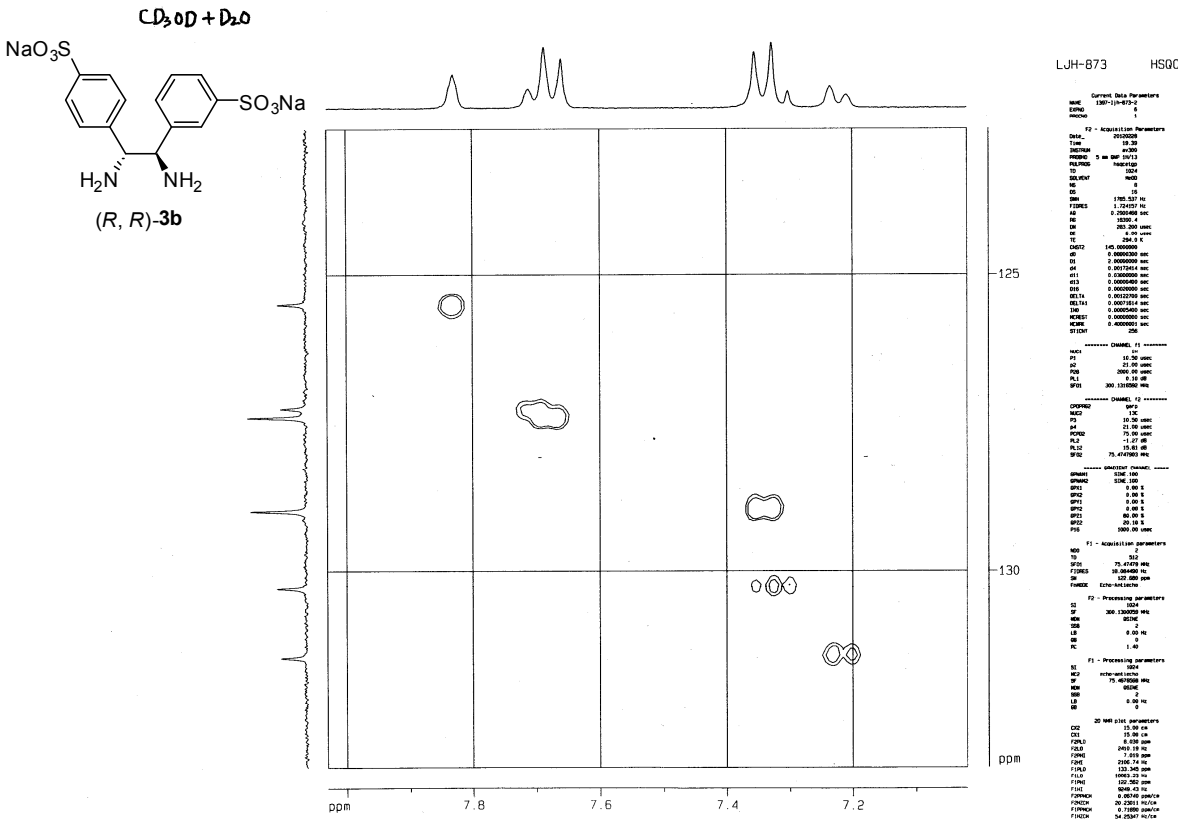
ppm
7.8
7.6
7.4
7.2


NaO3S
SO3Na
H2N
NH2
(R, R)-3a
LJH-872'
40
60
80
100
120
140
ppm
ppm
8
7
6
5
4
3


CD3OD + D2O
NaO3S
SO3Na
H2N
NH2
(R, R)-3b
LJH-873
H-H COSY
ppm
8
7
6
5
4
3


CD3OD + D2O
NaO3S
SO3Na
H2N
NH2
(R, R)-3b
LJH-873
H-H COSY
ppm
7.8
7.6
7.4
7.2


CD3OD + D2O
NaO3S
SO3Na
H2N
NH2
(R, R)-3b
LJH-873
HSQC
ppm
8
7
6
5
4
3
40
60
80
100
120
140


CD3OD + D2O
NaO3S
SO3Na
H2N
NH2
(R, R)-3b
LJH-873
HSQC
ppm
7.8
7.6
7.4
7.2
125
130