

In situ manipulation of catalyst performance via photocontrolled aggregation/dissociation state of the catalyst

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1. General

Formation of heterochiral aggregation was performed in a test tube, a micro tube or an eppendorf tube (Watson Co. Ltd., 2.0 mL) with a Teflon-coated magnetic stirring bar unless otherwise noted. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere.

2. Instrumentation

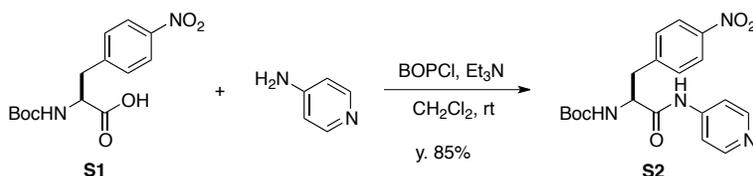
Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR was recorded on JEOL ECS-400, or ECA-600 spectrometers. Chemical shifts for proton are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CDCl₃: δ 7.24 ppm, CD₃OD: δ 3.31 ppm). For ¹³C NMR, chemical shifts were reported in the scale relative to NMR solvent (CDCl₃: 77.0 ppm, CD₃OD: δ 49.0 ppm) as an internal reference. Optical rotation was measured using a 1 mL cell with a 0.5 dm path length on a JASCO polarimeter P-1030. High-resolution mass spectra (ESI TOF (+)) were measured on ThermoFisher Scientific LTQ Orbitrap XL. HPLC analysis was conducted on a JASCO HPLC system equipped with Daicel chiral-stationary-phase columns (0.46 cm φ × 25 cm). Photoirradiation was conducted using a xenon arc lamp (150 W, equipped with a glass fiber outlet module) with a band pass filter (λ = 365 ± 10 nm) for UV irradiation or a cut filter of >422 nm for visible light irradiation.

3. Materials

Unless otherwise noted, materials were purchased from commercial suppliers and were used without purification. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM).

4. Synthesis of (S)-1c

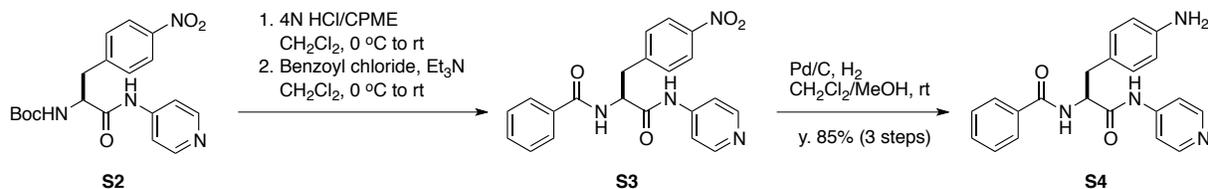
(S)-tert-Butyl(1-(4-pyridineamino)-3-(4-nitrophenyl)-1-oxopropan-2-yl)carbamate (S2)



To a stirred solution of (S)-2-((tert-butoxycarbonyl)amino)-3-(4-nitrophenyl)propanoic acid (S1) (3.5 g, 11 mmol, purchased from Watanabe Chemical Industries, Ltd.) and 4-aminopyridine (1.1 g, 12 mmol) in CH₂Cl₂ (60 mL) were added BOPCl (3.2 g, 12 mmol) and Et₃N (3.2 mL, 24 mmol) at 0 °C. After stirring the resulting mixture at room temperature for 12 h, the reaction was quenched by sat. NaHCO₃ aq., and the resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, then dried over anhydrous Na₂SO₄. The organic solvent was removed under reduced pressure and the resulting crude residue was purified by silica gel chromatography (SiO₂, CH₂Cl₂/MeOH = 20/1) to give S2 (3.66 g, 9.47 mmol, y. 85%).

Colorless solid; M.p. 124–126 °C; IR (KBr) ν 3285, 1693, 1670, 1597, 1520, 1346, 1164 cm⁻¹; ¹H NMR (CDCl₃) δ 9.46 (s, 1H), 8.38 (d, J = 5.7 Hz, 2H), 8.07 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 5.5 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 5.58–5.70 (m, 1H), 4.62 (d, J = 6.2 Hz, 1H), 3.32 (dd, J = 14.0, 6.4 Hz, 1H), 3.10 (dd, J = 14.0, 8.0 Hz, 1H), 1.36 (s, 9H); ¹³C NMR (CDCl₃) δ 170.4, 156.2, 150.3, 147.0, 144.9, 144.1, 130.2, 123.7, 113.8, 81.3, 56.1, 37.5, 28.2; [α]_D²⁴ -26.4 (c 0.5, CHCl₃); HRMS (ESI) Anal. calcd. for C₁₉H₂₃N₄O₅ m/z 387.1663 [M+H]⁺, found 387.1660.

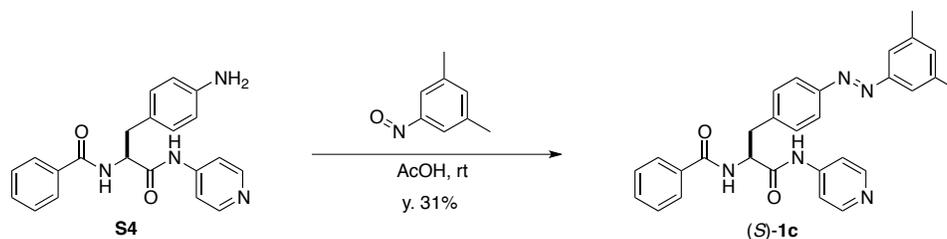
(S)-N-(3-(4-Aminophenyl)-1-(4-pyridineamino)-1-oxopropan-2-yl)-benzamide (S4)



To a stirred solution of **S2** (3.61 g, 9.34 mmol) in CH_2Cl_2 (70 mL) was added 4N HCl/CPME (10 mL) at 0 °C and the resulting solution was stirred at room temperature for 24 h. The resulting white suspension was filtered and washed with CH_2Cl_2 to give amine hydrochloride (3.24 g, 9.02 mmol, 97%). To a stirred solution of the amine hydrochloride (3.24 g, 9.02 mmol) in CH_2Cl_2 (60 mL) were added benzoyl chloride (1.24 mL, 10.8 mmol) and Et_3N (3.76 mL, 27.0 mmol) at 0 °C. After stirring the resulting solution at room temperature for 1 h, the reaction was quenched by sat. NaHCO_3 aq. and the resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, then dried over anhydrous Na_2SO_4 . The organic solvent was removed under reduced pressure and the resulting residue was washed with CH_2Cl_2 to give diamide **S3** (2.77 g, 7.10 mmol, y. 79%). To a stirred solution of the diamide **S3** (2.77 g, 7.10 mmol) in CH_2Cl_2 (27 mL) and MeOH (27 mL) was added Pd/C (10%, 277 mg) at room temperature and the resulting black suspension was stirred under H_2 atmosphere. After 19 h of stirring, Pd/C was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure to give **S4** (2.51 g, 6.96 mmol, y. 98%).

Colorless solid; M.p. 132-133 °C; IR (KBr) ν 3377, 1698, 1639, 1592, 1517, 1288, 826, 711 cm^{-1} ; ^1H NMR (CD_3OD) δ 8.35 (dd, $J = 5.0, 1.6$ Hz, 2H), 7.76-7.80 (m, 2H), 7.62 (dd, $J = 5.0, 1.6$ Hz, 2H), 7.48-7.54 (m, 1H), 7.42 (dd, $J = 8.0, 7.8$ Hz, 2H), 7.06 (d, $J = 8.5$ Hz, 2H), 6.64 (d, $J = 8.5$ Hz, 2H), 4.85 (dd, $J = 8.0, 7.1$ Hz, 1H), 3.15 (dd, $J = 13.5, 7.1$ Hz, 1H), 3.05 (dd, $J = 13.5, 8.2$ Hz, 1H); ^{13}C NMR (CD_3OD) δ 173.7, 170.3, 150.2, 148.2, 147.3, 135.0, 132.9, 131.0, 129.5, 128.5, 127.4, 116.9, 115.3, 58.2, 38.1; $[\alpha]_{\text{D}}^{23} +61.0$ (c 1.93, CH_3OH); HRMS (ESI) Anal. calcd. for $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_2\text{Na}$ m/z 383.1478 $[\text{M}+\text{Na}]^+$, found 383.1475.

(S,E)-N-(3-(4-((3,5-Dimethylphenyl)diazenyl)phenyl)-1-(4-pyridineamino)-1-oxopropan-2-yl)-benzamide ((S)-1c)



To a stirred solution of **S4** (720 mg, 2.0 mmol) in AcOH (4.0 mL) was added 3,5-dimethylnitrosobenzene¹ (330 mg, 2.4 mmol) at room temperature. After 16 h of stirring, AcOEt and sat. NaHCO_3 aq. were added and the separated organic layer was washed with brine, then dried over anhydrous Na_2SO_4 . Volatiles were removed under reduced pressure and the resulting crude residue was purified by silica gel column chromatography (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH} = 20/1$) to give **(S)-1c** (38.9 mg, 0.62 mmol, y. 31%).

Orange solid; M.p. 245-246 °C; IR (KBr) ν 3412, 1640, 1593, 1514, 1288, 825 cm^{-1} ; ^1H NMR (CDCl_3 , 0.02 M) δ 9.48 (s, 1H), 8.38 (d, $J = 5.7$ Hz, 2H), 7.78 (d, $J = 8.2$ Hz, 2H), 7.71 (d, $J = 7.6$ Hz, 2H), 7.51 (dd, $J = 7.6, 7.3$ Hz, 1H), 7.47 (s, 2H), 7.36-7.42 (m, 6H), 7.12 (d, $J = 7.8$ Hz, 1H), 7.08 (s, 1H), 5.23 (dd, $J = 14.7, 7.3$ Hz, 1H), 3.40 (dd, $J = 14.0, 7.1$ Hz, 1H), 3.33 (dd, $J = 14.0, 7.3$ Hz, 1H), 2.37 (s, 6H); ^{13}C NMR (CDCl_3) δ 170.7, 168.4, 152.7, 151.8, 150.4, 144.8, 138.9, 138.7, 132.9, 132.8, 127.2, 123.1, 120.6, 113.9, 55.9, 38.2, 21.2; $[\alpha]_{\text{D}}^{25} -15.5$ (c 0.5, CHCl_3); HRMS (ESI) Anal. calcd. for $\text{C}_{29}\text{H}_{28}\text{N}_5\text{O}_2$ m/z 478.2238 $[\text{M}+\text{H}]^+$, found 478.2233.

¹ (a) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200. (b) Dai, X.; Kapoor, P.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 4798.

Cis isomer: $^1\text{H NMR}$ (CDCl_3 , 0.02 M) δ 9.41 (s, 1H), 8.38 (d, $J = 6.0$ Hz, 2H), 7.66 (d, $J = 7.6$ Hz, 2H), 7.53 (dd, $J = 7.6, 7.4$ Hz, 1H), 7.35-7.45 (m, 4H), 7.13 (d, $J = 8.2$ Hz, 2H), 6.98 (d, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 8.3$ Hz, 2H), 6.68 (s, 1H), 6.38 (s, 2H), 5.08 (dd, $J = 14.2, 7.0$ Hz, 1H), 3.27 (dd, $J = 14.0, 6.8$ Hz, 1H), 3.18 (dd, $J = 14.0, 7.1$ Hz, 1H), 2.09 (s, 6H).

5. Determination of the Ratio of Absorption Coefficients

—for the Determination Molecules in Solution Phase by % Area of HPLC Trace

5-1. Determination of the ratio of the absorption coefficient of *trans*-**1c** and *cis*-**1c** for Table S5, S7, S10.

Trans-(*S*)-**1c** (2.4 mg, 0.005 mmol) was dissolved in 0.05 M CH_3CN solution of *p*-cresol (100 μL , 0.025 mmol) to give a 0.050 M CH_3CN solution of *trans*-(*S*)-**1c** (100 μL , 0.005 mmol, containing 0.025 mmol *p*-cresol). A small aliquot was extracted and subjected to HPLC analysis [HPLC conditions: Daicel CHIRALPAK IB column (0.46 cm ϕ \times 25 cm): eluent *n*-hexane/2-propanol = 4/1, flow rate 1.0 mL/min, detection at 254 nm, $t_{\text{R}} = 4.4$ min (*p*-cresol), $t_{\text{R}} = 12.9$ min (*trans*-(*S*)-**1c**), $t_{\text{R}} = 20.0$ min (*cis*-(*S*)-**1c**)] (Chart S1). The %area data were collected for three times after irradiation of UV at 365 nm for arbitrary period. Absorption coefficient at 254 nm of *cis*-(*S*)-**1c** was higher than that of *trans*-(*S*)-**1c** and the %area of *p*-cresol decreased as the content of *cis*-(*S*)-**1c** increased.

$$\text{Eq. 1: } A_{\text{trans}} = \epsilon_{\text{trans}} \cdot x_{\text{trans}}$$

$$\text{Eq. 2: } A_{\text{cis}} = \epsilon_{\text{cis}} \cdot x_{\text{cis}}$$

$$\text{Eq. 3: } A_{\text{cre}} = \epsilon_{\text{cre}} \cdot x_{\text{cre}}$$

$$\text{Eq. 4: } x_{\text{trans}} + x_{\text{cis}} = \text{const}$$

A_{trans} , A_{cis} and A_{cre} are absorption of *trans*-(*S*)-**1c**, *cis*-(*S*)-**1c**, and *p*-cresol, respectively.

ϵ_{trans} , ϵ_{cis} and ϵ_{cre} are absorption coefficient of *trans*-(*S*)-**1c**, *cis*-(*S*)-**1c**, and *p*-cresol, respectively.

x_{trans} , x_{cis} and x_{cre} are moles of *trans*-(*S*)-**1c**, *cis*-(*S*)-**1c**, and *p*-cresol, respectively.

From eq. 1-4,

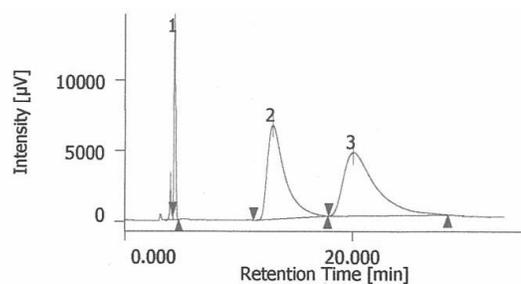
$$\begin{aligned} A_{\text{cis}}/A_{\text{cre}} &= (\epsilon_{\text{cis}} \cdot x_{\text{cis}})/(\epsilon_{\text{cre}} \cdot x_{\text{cre}}) = [\epsilon_{\text{cis}} \cdot (\text{const} - x_{\text{trans}})]/(\epsilon_{\text{cre}} \cdot x_{\text{cre}}) \\ &= (\epsilon_{\text{cis}} \cdot \text{const})/(\epsilon_{\text{cre}} \cdot x_{\text{cre}}) - \epsilon'(\epsilon_{\text{trans}} \cdot x_{\text{trans}})/(\epsilon_{\text{cre}} \cdot x_{\text{cre}}) \\ &= -\epsilon' \cdot (A_{\text{trans}}/A_{\text{cre}}) + \text{const}', \quad \text{where } \epsilon' = \epsilon_{\text{cis}}/\epsilon_{\text{trans}} \end{aligned}$$

$A_{\text{cis}}/A_{\text{cre}}$ and $A_{\text{trans}}/A_{\text{cre}}$ were calculated from Table S1 and plotted in Figure S1, affording the ratio of the absorption coefficient of *trans*-**1c** and *cis*-**1c** $\epsilon' = \epsilon_{\text{cis}}/\epsilon_{\text{trans}} = 1.57$.

Table S1. %area and %area normalized by *p*-cresol in HPLC analysis.

	%area			
	before irradiation	after irradiation		
<i>p</i> -cresol	9.33	6.86	7.07	8.13
<i>trans</i> -(<i>S</i>)- 1c	68.94	2.26	21.48	41.43
<i>cis</i> -(<i>S</i>)- 1c	21.73	90.88	71.45	50.44

	%area normalized by <i>p</i> -cresol ($A_{\text{trans}}/A_{\text{cre}}$ and $A_{\text{cis}}/A_{\text{cre}}$)			
	<i>trans</i> -(<i>S</i>)- 4	7.39	0.33	3.04
<i>cis</i> -(<i>S</i>)- 4	2.33	13.26	10.10	6.20



#	tR [min]	area%	
1	4.350	8.131	p-cresol
2	12.917	41.434	trans-(S)-1c
3	20.000	50.435	cis-(S)-1c

Chart S1. One of the HPLC traces for Table S1.

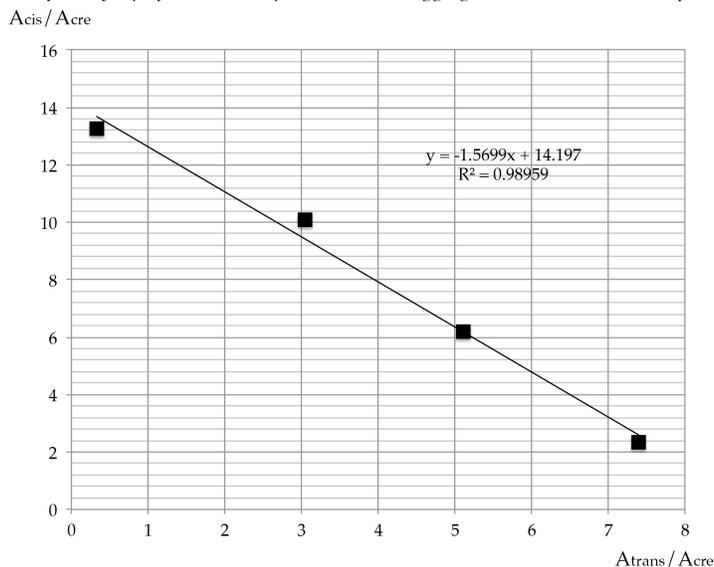


Figure S1. Plot of A_{trans}/A_{cre} vs A_{cis}/A_{cre} .

5-2. Determination of the ratio of the absorption coefficient of 1-naphthol (2) and Boc-protected 1-naphthol (4) for Table S3,S4,S6.

The sample (2/4 = 67/33) was subjected to HPLC analysis [HPLC conditions: Daicel CHIRALPAK IC column (0.46 cm ϕ x 25 cm): eluent *n*-hexane/ethanol = 80/1, flow rate 1.0 mL/min, detection at 254 nm, $t_R = 4.3$ min (3), $t_R = 13.5$ min (2)].

The %area data were shown in Chart 2. Absorption coefficient at 254 nm of 4 was higher than that of 2.

$$\text{Eq. 5: } A_2 = \varepsilon_2 \cdot x_2$$

$$\text{Eq. 6: } A_4 = \varepsilon_4 \cdot x_4$$

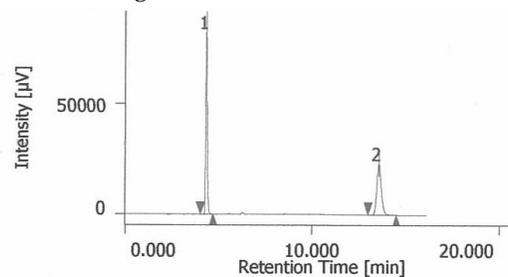
A_2 and A_4 are absorption of 2 and 4, respectively.

ε_2 and ε_4 are absorption coefficient of 2 and 4, respectively.

x_2 and x_4 are moles of 2 and 4, respectively.

From eq. 5 and 6,

$$A_2/A_4 = (\varepsilon_2 \cdot x_2)/(\varepsilon_4 \cdot x_4) = \varepsilon' \cdot (x_2/x_4), \quad \text{where } \varepsilon' = \varepsilon_2/\varepsilon_4$$



#	tR [min]	area%	
1	4.325	55.643	4
2	13.508	44.357	2

Chart S2. HPLC trace of the sample of 2/4 = 67/33.

A_2/A_4 was determined from HPLC analysis (44.357/55.643, Chart 2) and x_2/x_4 was determined by ^1H NMR analysis (67/33), respectively, affording the ratio of the absorption coefficient of 2 and 4 $\varepsilon' = \varepsilon_2/\varepsilon_4 = 0.391$.

5-3. Determination of the ratio of the absorption coefficient of 5 and 6 for Table S8,S9,S11,S12.

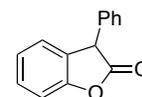
In the rearrangement of 5 promoted by 1c, small amount of byproduct benzofuranone S5 was associated. The sample (5/6 ((S)-6 + (R)-6)/S5 = 30/59/11) was subjected to HPLC analysis [HPLC conditions: Daicel CHIRALPAK IC column (0.46 cm ϕ x 25 cm): eluent *n*-hexane/dichloromethane = 1/1, flow rate 0.5 mL/min, detection at 254 nm, $t_R = 7.0$ min (5), $t_R = 10.8$ min ((S)-6), $t_R = 11.7$ min ((R)-6), $t_R = 13.8$ min (S5)]. The %area data was shown in Chart 3.

$$\text{Eq. 7: } A_5 = \varepsilon_5 \cdot x_5$$

$$\text{Eq. 8: } A_6 = \varepsilon_6 \cdot x_6$$

$$\text{Eq. 9: } A_{S5} = \varepsilon_{S5} \cdot x_{S5}$$

A_5 , A_6 , and A_{S5} are absorption of 5, 6, and S5 respectively.



S5

ϵ_5 , ϵ_6 , and ϵ_{S5} are the absorption coefficient of **5**, **6**, and **S5** respectively.

x_5 , x_6 , and x_{S5} are moles of **5**, **6**, and **S5** respectively.

From eq. 7 and 8,

$$A_5/A_6 = (\epsilon_5 \cdot x_5)/(\epsilon_6 \cdot x_6) = \epsilon' \cdot (x_5/x_6), \quad \text{where } \epsilon' = \epsilon_5/\epsilon_6$$

From eq. 7 and 9,

$$A_5/A_{S5} = (\epsilon_5 \cdot x_5)/(\epsilon_{S5} \cdot x_{S5}) = \epsilon'' \cdot (x_5/x_{S5}), \quad \text{where } \epsilon'' = \epsilon_5/\epsilon_{S5}$$

A_5/A_6 was determined from HPLC analysis (89.812/(4.78 + 3.996), Chart S3) and x_5/x_6 was determined by NMR analysis (30/59), affording the absorption coefficient of **5** and **6** $\epsilon' = \epsilon_5/\epsilon_6 = 20.1$.

A_5/A_{S5} was determined from HPLC analysis (89.812/1.412, Chart S3) and x_5/x_{S5} was determined by NMR analysis (30/11), affording the absorption coefficient of **5** and **S5** $\epsilon'' = \epsilon_5/\epsilon_{S5} = 23.3$.

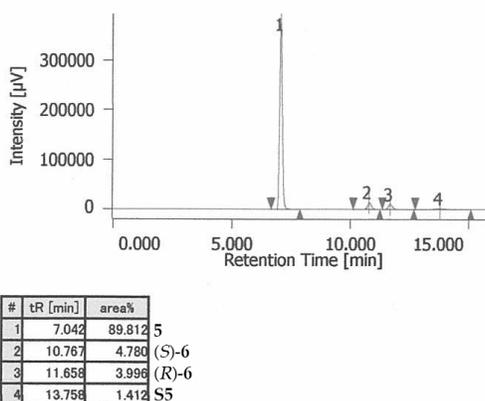


Chart S3. HPLC trace of the sample of **5/6** ((S)-**6** + (R)-**6**)/**S5** = 30/59/11.

6. Reversible Aggregation/Dissociation of (S)-**1c** (For Fig. 2)

To an eppendorf tube with a Teflon-coated magnetic stirring bar were added *trans*-(S)-**1c** (4.8 mg, 0.010 mmol), *n*-hexane (800 μ L), and propionitrile (200 μ L) successively at 21 °C. The resulting suspension was irradiated with UV at 365 nm for 150 min at the same temperature. After the irradiation, the suspension became clear orange solution. At 165 min, the tube was centrifuged for 15 sec (ca. 10^4 rpm) to separate the insoluble material and supernatant in the tube. A small aliquot of the supernatant (10 μ L) was extracted and was mixed with 0.005 M CHCl₃ solutions of salicylamide (300 μ L, 0.0015 mmol). The resulting mixture was subjected to HPLC analysis to determined the content of the solution phase [HPLC conditions: Daicel CHIRALPAK IC column (0.46 cm ϕ x 25 cm): eluent *n*-hexane/2-propanol = 4/1, flow rate 1.0 mL/min, detection at 254 nm, $t_R = 6.9$ min (salicylamide), $t_R = 12.1$ min (*trans*-(S)-**1c**), $t_R = 17.9$ min (*cis*-(S)-**1c**)]. Visible light (>422 nm) was irradiated during the period of 165-180 min, and at 195 min, the tube was centrifuged for 15 sec (ca. 10^4 rpm) to separate the insoluble material and supernatant in the tube. A small aliquot of the supernatant (10 μ L) was extracted and was mixed with 0.005 M CHCl₃ solutions of salicylamide (300 μ L, 0.0015 mmol). The identical procedure for HPLC analysis was followed. The summary of the time that irradiation was applied is as follows,

UV (365 nm)	0–150 min, 195–325 min,
Visible light (>422 nm)	165–180 min, 340–355 min

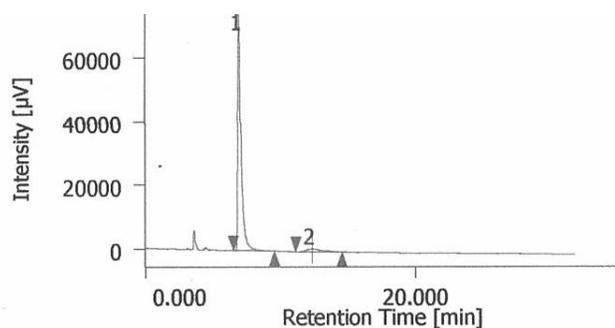
Table S2. %area, %area normalized by salicylamide, and %content of **1c** in the solution phase at specified period in HPLC analysis.

	%area				
	0 min	165 min	195 min	340 min	370 min
salicylamide	94.549	30.613	84.841	30.376	84.913
<i>trans</i> -(S)- 1c	5.451	1.492	9.506	1.719	9.106
<i>cis</i> -(S)- 1c	0	67.896	5.653	67.904	5.982

	%area normalized by salicylamide ^a				
	0 min	165 min	195 min	340 min	370 min
<i>trans</i> -(S)- 1c	0.058	0.048	0.110	0.055	0.103
<i>cis</i> -(S)- 1c	0.000	1.399	0.042	1.381	0.043
total (S)- 1c	0.058	1.447	0.151	1.436	0.146

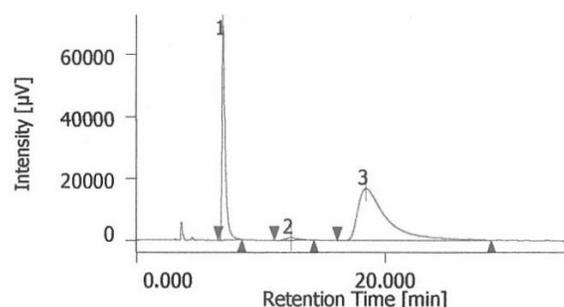
	%content in solution ^b				
	0 min	165 min	195 min	340 min	370 min
<i>trans</i> -(S)- 1c	4.0	3.3	7.6	3.8	7.1
<i>cis</i> -(S)- 1c	0.0	96.7	2.9	95.5	3.0
total (S)- 1c	4.0	100.0	10.5	99.3	10.1

^aValues for *cis*-(S)-**1c** was normalized by using $\epsilon_{cis}/\epsilon_{trans} = 1.57$ determined in section 5-1. Data were corrected by considering the reduced entire solvent volume by each sampling. ^bAt 165 min, the mixture is homogeneous and all **1c** existed in the solution phase. %content was calculated based on the relative to 1.447.



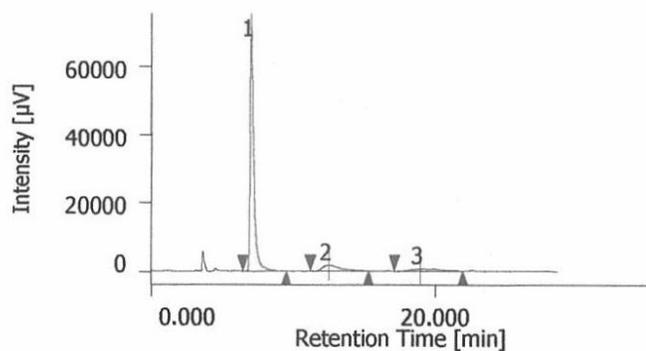
#	tR [min]	area%	
1	6.908	94.549	salicylamide
2	12.317	5.451	<i>trans</i> -(S)- 1c

Chart S4. HPLC trace at 0 min.



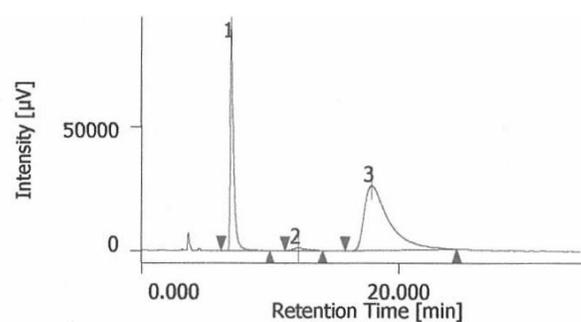
#	tR [min]	area%	
1	6.925	30.613	salicylamide
2	12.392	1.492	<i>trans</i> -(S)- 1c
3	18.400	67.896	<i>cis</i> -(S)- 1c

Chart S5. HPLC trace at 165 min.



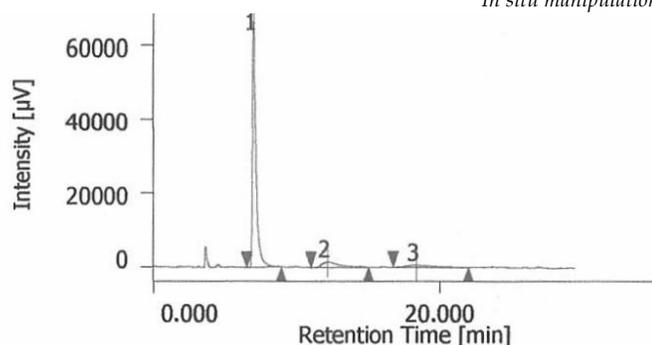
#	tR [min]	area%	
1	6.983	84.841	salicylamide
2	12.475	9.506	<i>trans</i> -(S)- 1c
3	18.875	5.653	<i>cis</i> -(S)- 1c

Chart S6. HPLC trace at 195 min.



#	tR [min]	area%	
1	6.933	30.376	salicylamide
2	12.156	1.719	<i>trans</i> -(S)- 1c
3	17.817	67.904	<i>cis</i> -(S)- 1c

Chart S7. HPLC trace at 340 min.



#	tR [min]	area%	
1	6.958	84.913	salicylamide
2	12.150	9.106	<i>trans</i> -(S)-1c
3	18.317	5.982	<i>cis</i> -(S)-1c

Chart S8. HPLC trace at 370 min.

7. General Procedure for the Reaction of 1-Naphthol (2) and Boc₂O (3) (For Fig. 3)

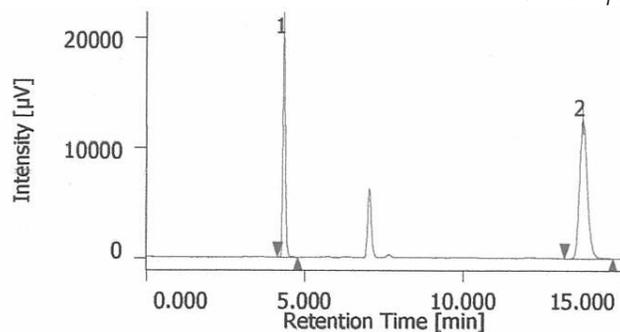
7-1. The reaction promoted by *cis*-(S)-1c (For Fig. 3).

To an eppendorf tube with a Teflon-coated magnetic stirring bar were added *trans*-(S)-1c (7.2 mg, 0.015 mmol), 1-naphthol (2, 14.4 mg, 0.10 mmol), *n*-hexane (1200 µL) and propionitrile (300 µL) successively at the room temperature. The resulting suspension was irradiated with UV at 365 nm for 105 min at the same temperature. After the irradiation, the suspension became clear orange solution of *cis*-(S)-1c (*trans*/*cis* = 4/96 at the photostationary state). To the solution was added Boc₂O (3, 27.5 µL, 0.12 mmol) at 21 °C to run the reaction. At the specified period (6, 30, 60, 90, 120, 150, 180 min), a small aliquot of the supernatant (ca. 2 µL) was extracted and (S)-1c was removed by a short path silica gel column chromatography (SiO₂, AcOEt as eluent). Volatiles were removed under reduced pressure and the resulting crude residue was subjected to HPLC analysis to determined the conversion (no reaction proceeded under concentrated conditions in the absence of 1c) [HPLC conditions: Daicel CHIRALPAK IB column (0.46 cm φ x 25 cm): eluent *n*-hexane/ethanol = 80/1, flow rate 1.0 mL/min, detection at 254 nm, t_R = 4.3 min (4), t_R = 13.5 min (2), selected HPLC traces are in Chart S9,S10]. HPLC data and calculated conversion are summarized in Table S3. At the specified period (3, 180 min), the tube was centrifuged for 15 sec (ca. 10⁴ rpm) to separate the insoluble material and supernatant in the tube. A small aliquot of the supernatant (10 µL) was extracted and was mixed with 0.005 M CHCl₃ solutions of salicylamide (300 µL, 0.0015 mmol). The resulting mixture was subjected to HPLC analysis to determined the content of the solution phase [HPLC conditions: Daicel CHIRALPAK IC column (0.46 cm φ x 25 cm): eluent *n*-hexane/2-propanol = 4/1, flow rate 1.0 mL/min, detection at 254 nm, t_R = 8.9 min (salicylamide), t_R = 12.1 min (*trans*-(S)-1c), t_R = 17.9 min (*cis*-(S)-1c), HPLC traces are in Chart S13,S14]. The data are summarized in Table S5 (in section 7-2).

Table S3. %area of 4 and 2 and calculated conversion in the reaction promoted by *cis*-(S)-1c.^a

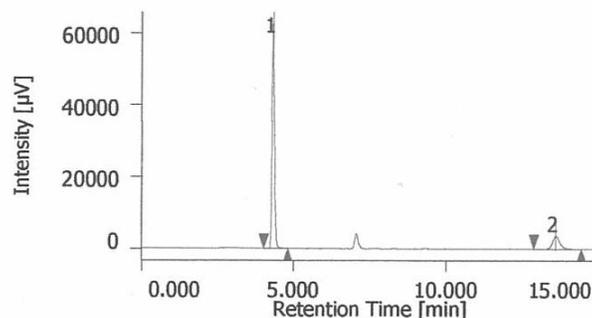
	time (min)						
	6	30	60	90	120	150	180
%area (4)	11.872	35.573	54.375	67.281	74.725	81.991	85.297
%area (2)	88.128	64.644	45.625	32.719	25.275	18.009	14.703
conversion (%)	5.0	17.7	31.8	44.6	53.6	64.0	69.4

^aε₂/ε₄ = 0.391 was used.



#	tR [min]	area%
1	4.333	35.356
2	13.742	64.644

Chart S9. HPLC trace at 30 min.



#	tR [min]	area%
1	4.325	85.297
2	13.600	14.703

Chart S10. HPLC trace at 180 min.

7-2. The reaction promoted by *trans*-(*S*)-**1c** (For Fig. 3).

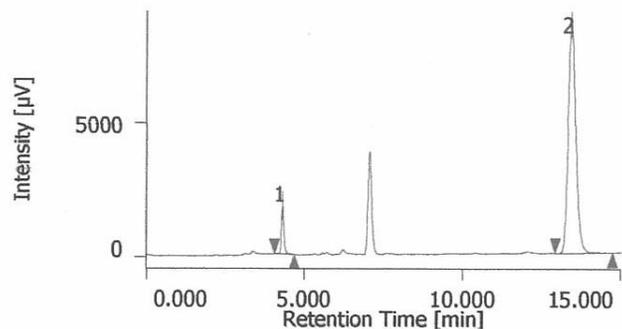
To an eppendorf tube with a Teflon-coated magnetic stirring bar were added *trans*-(*S*)-**1c** (7.2 mg, 0.015 mmol), 1-naphthol (**2**, 14.4 mg, 0.10 mmol), hexane (1200 µL) and propionitrile (300 µL) successively at the room temperature. The resulting suspension was stirred for 1 h at the same temperature. To the suspension was added Boc₂O (**3**, 27.5 µL, 0.12 mmol) at the room temperature to run the reaction. At the specified period (6, 30, 60, 90, 120, 150, 180 min), the tube was centrifuged for 15 sec (ca. 10⁴ rpm) to separate the insoluble material and supernatant in the tube. A small aliquot of the supernatant (ca. 2 µL) was extracted and (*S*)-**1c** was removed by a short path silica gel column chromatography (SiO₂, AcOEt as eluent). Volatiles were removed under reduced pressure and the resulting crude residue was subjected to HPLC analysis to determine the conversion (no reaction proceeded under concentrated conditions in the absence of **1c**) [HPLC conditions: Daicel CHIRALPAK IB column (0.46 cm φ x 25 cm): eluent *n*-hexane/ethanol = 80/1, flow rate 1.0 mL/min, detection at 254 nm, t_R = 4.3 min (**4**), t_R = 13.5 min (**2**), selected HPLC traces are in Chart S11,S12]. At the specified period (0, 180 min), the tube was centrifuged for 15 sec (ca. 10⁴ rpm) to separate the insoluble material and supernatant in the tube. A small aliquot of the supernatant (10 µL) was extracted and was mixed with 0.005 M CHCl₃ solutions of salicylamide (300 µL, 0.0015 mmol). The resulting mixture was subjected to HPLC analysis to determine the catalyst content of the solution phase [HPLC conditions: Daicel CHIRALPAK IC column (0.46 cm φ x 25 cm): eluent *n*-hexane/2-propanol = 4/1, flow rate 1.0 mL/min, detection at 254 nm, t_R = 8.9 min (salicylamide), t_R = 12.1 min (*trans*-(*S*)-**1c**), t_R = 17.9 min (*cis*-(*S*)-**1c**), HPLC traces are in Chart S15,S16]. The data are summarized in Table S5.

Table S4. %area of **4**, **2**, and calculated conversion in the reaction promoted by *trans*-(*S*)-**1c**.^a

	time (min)						
	6	30	60	90	120	150	180
% area (4)	3.059	6.386	10.433	13.908	18.219	22.458	24.859
% area (2)	96.941	93.614	89.567	86.092	81.781	77.542	75.141
conversion (%)	1.2	2.6	4.4	5.9	8.0	10.2	11.5

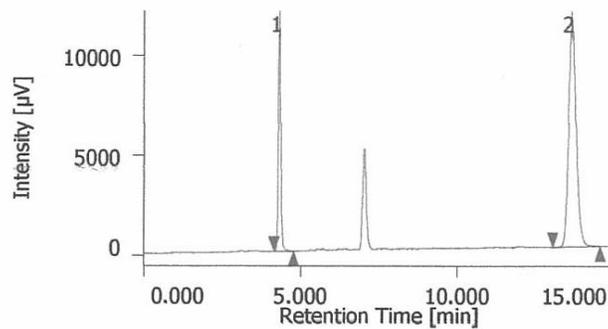
^a ε₂/ε₄ = 0.391 was used.

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#	tR [min]	area%
1	4.317	6.386
2	13.433	93.614

Chart S11. HPLC trace at 30 min.



#	tR [min]	area%
1	4.317	24.859
2	13.650	75.141

Chart S12. HPLC trace at 180 min.

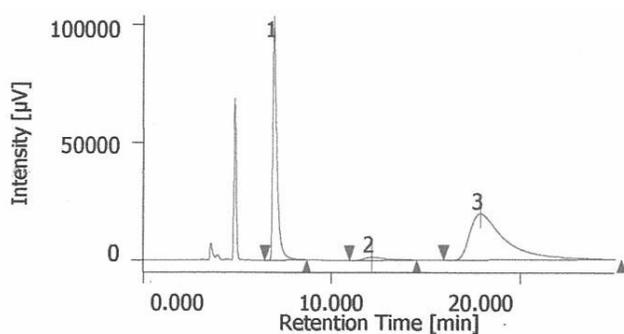
Table S5. %area, %area normalized by salicylamide, and %content of **1c** in the solution phase at specified period in HPLC analysis.

	%area			
	<i>cis</i> -cat at 3 min	<i>cis</i> -cat at 180 min	<i>trans</i> -cat at 3 min	<i>trans</i> -cat at 180 min
salicylamide	36.561	36.895	89.216	90.445
<i>trans</i> -(S)- 1c	2.371	4.333	10.783	9.555
<i>cis</i> -(S)- 1c	61.069	58.773	0	0

	%area normalized by salicylamide ^a			
	<i>cis</i> -cat at 3 min	<i>cis</i> -cat at 180 min	<i>trans</i> -cat at 3 min	<i>trans</i> -cat at 180 min
<i>trans</i> -(S)- 1c	0.065	0.117	0.121	0.106
<i>cis</i> -(S)- 1c	1.064	1.015	0.000	0.000
total 1c	1.129	1.132	0.121	0.106

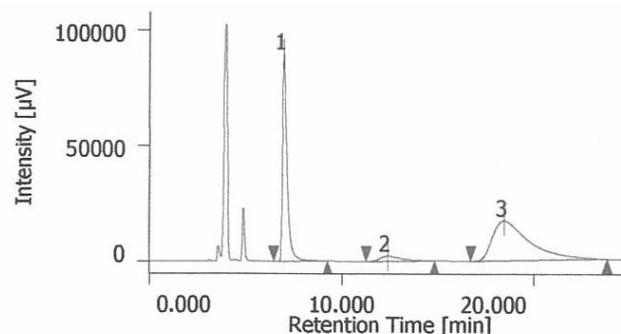
	%content in solution ^b			
	<i>cis</i> -cat at 3 min	<i>cis</i> -cat at 180 min	<i>trans</i> -cat at 3 min	<i>trans</i> -cat at 180 min
<i>trans</i> -(S)- 1c	5.7	10.4	10.7	9.4
<i>cis</i> -(S)- 1c	94.3	89.9	0.0	0.0
total 1c	100.0	100.3	10.7	9.4

^aValues for *cis*-(S)-**1c** was normalized by using $\epsilon_{cis}/\epsilon_{trans} = 1.57$ determined in section 5-1. ^bWith *cis*-catalyst at 3 min, the mixture is homogeneous and all **1c** existed in the solution phase. %content was calculated based on the relative to 1.129.



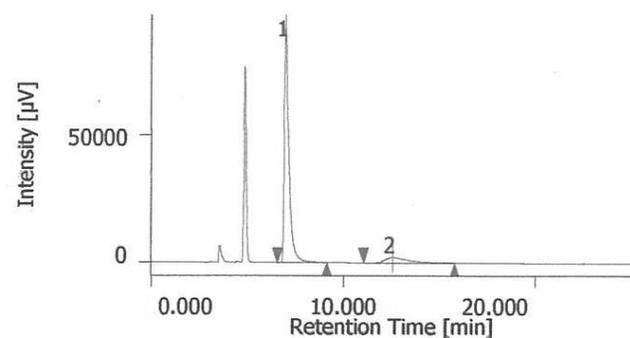
#	tR [min]	area%
1	6.917	36.561
2	12.125	2.371
3	17.850	61.069

Chart S13. HPLC trace for **1c** at 3 min with *cis* catalyst.



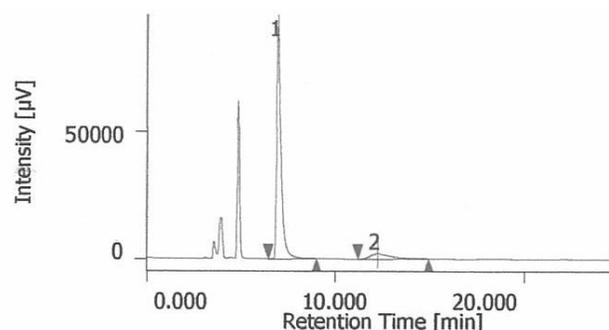
#	tR [min]	area%
1	6.950	36.895
2	12.367	4.332
3	18.433	58.773

Chart S14. HPLC trace for **1c** at 180 min with *cis* catalyst.



#	tR [min]	area%
1	6.975	89.216
2	12.533	10.784

salicylamide
trans-(S)-1c



#	tR [min]	area%
1	6.933	90.445
2	12.242	9.555

salicylamide
trans-(S)-1c

Chart S15. HPLC trace for **1c** at 3 min with *trans* catalyst.

Chart S16. HPLC trace for **1c** at 180 min with *trans* catalyst.

According to Table S5, *cis/trans* ratio of *cis*-catalyst slightly changed due to thermal isomerization to *trans* isomer. For *trans*-catalyst *cis/trans* ratio in the solution phase was consistent during the course of the reaction.

8. In Situ Manipulation of the Catalytic Performance in the Reaction of **2** and **3** (For Fig 4)

To an eppendorf tube with a Teflon-coated magnetic stirring bar were added *trans*-(S)-**1c** (7.2 mg, 0.015 mmol), 1-naphthol (**2**, 14.4 mg, 0.10 mmol), *n*-hexane (1200 µL) and propionitrile (300 µL) successively at the room temperature. The resulting suspension was irradiated with UV at 365 nm for 120 min at the same temperature. After the irradiation, the suspension became clear orange solution. To the solution was added Boc₂O (**3**, 27.5 µL, 0.12 mmol) at 21 °C to run the reaction. At the specified period (0, 30, 60, 90, 150, 210, 280, 350, 420, 510 min), the tube was centrifuged for 15 sec (ca. 10⁴ rpm) to separate the insoluble material and supernatant in the tube. A small aliquot of the supernatant (ca. 2 µL) was extracted and (S)-**1c** was removed by a short path silica gel column chromatography (SiO₂, AcOEt as eluent). Volatiles were removed under reduced pressure and the resulting crude residue was subjected to HPLC analysis to determined the conversion (no reaction proceeded in the absence of **1c**) [HPLC conditions: Daicel CHIRALPAK IB column (0.46 cm φ x 25 cm): eluent *n*-hexane/ethanol = 80/1, flow rate 1.0 mL/min, detection at 254 nm, t_R = 4.3 min (**4**), t_R = 13.5 min (**2**)]. Data are summarized in Table S6. At the specified period (30, 90, 210, 300, 510 min), the tube was centrifuged for 15 sec (ca. 10⁴ rpm) to separate the insoluble material and supernatant in the tube. A small aliquot of the supernatant (10 µL) was extracted and was mixed with 0.005 M CHCl₃ solutions of salicylamide (300 µL, 0.0015 mmol). The resulting mixture was subjected to HPLC analysis to determine the catalyst content of the solution phase [HPLC conditions: Daicel CHIRALPAK IC column (0.46 cm φ x 25 cm): eluent *n*-hexane/2-propanol = 4/1, flow rate 1.0 mL/min, detection at 254 nm, t_R = 8.9 min (salicylamide), t_R = 12.1 min (*trans*-(S)-**1c**), t_R = 17.9 min (*cis*-(S)-**1c**)]. Data are summarized in Table S7.

Table S6. %area of **4**, **2**, and calculated conversion in the reaction promoted by *trans*-(S)-**1c**.^a

	time (min)									
	0	30	60	90	150	210	280	350	420	510
%area (4)	1.897	36.98	47.36	53.717	56.633	60.682	65.43	74.072	81.297	88.089
%area (2)	98.103	63.02	52.64	46.283	43.367	39.318	34.57	25.928	18.703	11.911
conversion (%)	0.8	18.7	26.0	31.2	33.8	37.6	42.5	52.8	63.0	74.3

^aε₂/ε₄ = 0.391 was used.

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Table S7. %area, %area normalized by salicylamide, and %content of **1c** in the solution phase at specified period in HPLC analysis.

	%area				
	30 min	90 min	210 min	300 min	510 min
salicylamide	33.651	82.157	84.682	55.809	39.416
<i>trans</i> -(S)- 1c	2.425	13.37	10.243	7.454	5.103
<i>cis</i> -(S)- 1c	63.925	4.473	5.074	36.737	55.481

	%area normalized by salicylamide ^a				
	30 min	90 min	210 min	300 min	510 min
<i>trans</i> -(S)- 1c	0.072	0.163	0.121	0.134	0.129
<i>cis</i> -(S)- 1c	1.210	0.035	0.038	0.419	0.897
total 1c	1.282	0.197	0.159	0.553	1.026

	%content in solution ^b				
	30 min	90 min	210 min	300 min	510 min
<i>trans</i> -(S)- 1c	5.6	12.7	9.4	10.4	10.1
<i>cis</i> -(S)- 1c	94.4	2.7	3.0	32.7	69.9
total 1c	100.0	15.4	12.4	43.1	80.0

^aValues for *cis*-(S)-**1c** was normalized by using $\epsilon_{\text{cis}}/\epsilon_{\text{trans}} = 1.57$ determined in section 5-1. ^bAt 30 min, the mixture is homogeneous and all **1c** existed in the solution phase. %content was calculated based on the relative to 1.282.

9. Control Experiment in CHCl₃ Solvent for the Reaction of **2** and **3**

To a micro tube with a Teflon-coated magnetic stirring bar were added *trans*-(S)-**1c** (2.4 mg, 0.005 mmol), 1-naphthol (**2**, 4.8 mg, 0.033 mmol) and chloroform (500 μL) successively at room temperature. To the clear orange solution was irradiated UV (365 nm) for 30 min and *cis/trans* ratio was confirmed by HPLC analysis (*cis/trans* = 96/4). To the *cis*-(S)-**1c** solution was added Boc₂O (**3**, 9.2 μL , 0.04 mmol) at room temperature to run the reaction. After stirring the resulting solution at the same temperature for 87 min, (S)-**1c** was removed by silica gel column chromatography (SiO₂, AcOEt as eluent). Volatiles were removed under reduced pressure and conversion was confirmed by NMR analysis (**2/4** = 85/15). The identical procedure was performed without photoirradiation, in which *trans*-(S)-**1c** (2.4 mg, 0.005 mmol) functioned as catalyst, which is soluble in CHCl₃ at the identical concentration, giving **2/4** ratio of 83/17. Nearly identical catalytic performance was observed in the reaction media in which both *trans*-(S)-**1c** and *cis*-(S)-**1c** were soluble.

10. Procedure for rearrangement of **5** (For Fig. 5)

10-1. The reaction promoted by *cis*-(S)-**1c**.

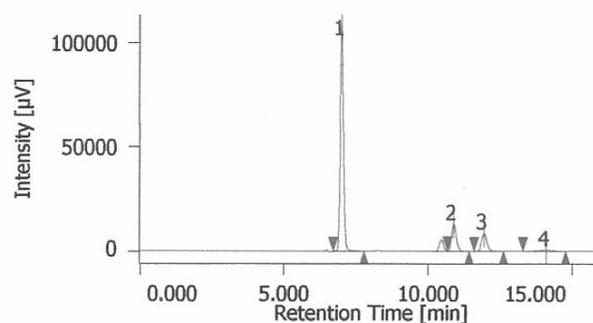
To a test tube with a Teflon-coated magnetic stirring bar were added *trans*-(S)-**1c** (7.2 mg, 0.015 mmol), *n*-hexane (750 μL) and ethyl acetate (750 μL) successively at the room temperature. The resulting suspension was irradiated with UV at 365 nm for 120 min at the same temperature. After the irradiation, the suspension became clear orange solution and the solution was cooled to -20 °C. To the solution was added acyloxybenzofuran **5** (24.8 mg, 0.06 mmol) at the same temperature to run the reaction. At the specified period (20, 40, 60, 80, 100 min), a small aliquot of the supernatant (ca. 2 μL) was extracted and (S)-**1c** was removed by a short path silica gel column chromatography (SiO₂, AcOEt as eluent). Volatiles were removed under reduced pressure and the resulting crude residue was subjected to HPLC analysis to determine the conversion [HPLC conditions: Daicel CHIRALPAK IB column (0.46 cm ϕ x 25 cm): eluent *n*-hexane/dichloromethane = 1/1, flow rate 0.5 mL/min, detection at 254 nm, t_{R} = 7.0 min (**5**), t_{R} = 10.7 min ((S)-**6**), t_{R} = 11.9 min ((R)-**6**), t_{R} = 14.0 min (**S5**), a selected HPLC trace is in Chart S17]. The data are summarized in Table S8. At 100 min, a small aliquot of the supernatant (10 μL) was extracted and was mixed with 0.005 M CHCl₃ solutions of salicylamide (300 μL , 0.0015 mmol). The resulting mixture was subjected to HPLC analysis to determine the catalyst content in the solution phase [HPLC conditions: Daicel CHIRALPAK IC column (0.46 cm ϕ x 25 cm): eluent *n*-hexane/2-propanol = 4/1, flow rate 1.0 mL/min, detection at 254 nm, t_{R} = 8.9 min (salicylamide), t_{R} = 12.1 min (*trans*-(S)-**1c**), t_{R} = 17.9 min (*cis*-(S)-**1c**)]. The data are summarized in Table S10 (section 10-2).

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Table S8. %area of **5**, **6** ((S)-**6** + (R)-**6**), **S5**, and calculated conversion in the reaction promoted by *cis*-(S)-**1c**.^a

	time (min)				
	20	40	60	80	100
%area (5)	96.971	94	87.616	78.151	75.075
%area ((S)- 6)	1.3	2.82	6.263	11.263	13.324
%area ((R)- 6)	1	2.233	4.763	8.502	9.949
%area (S5)	0.729	0.947	1.358	2.037	1.652
6 ((S)- 6 + (R)- 6)	28.7	46.5	64.8	75.8	80.3
S5	10.8	10.3	9.5	9.3	6.8

^a $\epsilon_5/\epsilon_6 = 20.1$ and $\epsilon_5/\epsilon_{S5} = 23.3$ were used.



#	tR [min]	area%
1	6.992	75.075
2	10.867	13.324
3	11.917	9.949
4	14.067	1.652

Chart S17. HPLC trace at 100 min.

10-1. The reaction promoted by *trans*-(S)-**1c**.

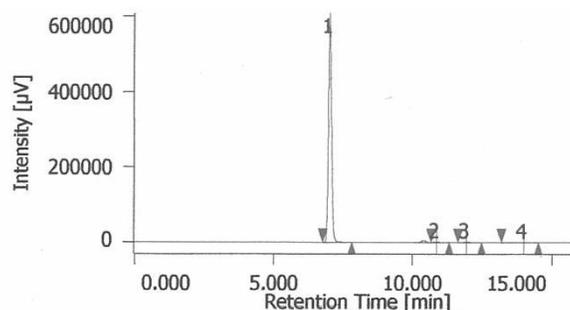
To a test tube with a Teflon-coated magnetic stirring bar were added *trans*-(S)-**1c** (7.2 mg, 0.015 mmol), *n*-hexane (750 μ L) and ethyl acetate (750 μ L) successively at the room temperature. The resulting suspension was cooled to -20 °C. To the suspension was added acyloxybenzofuran **5** (24.8 mg, 0.06 mmol) at the same temperature to run the reaction. At the specified period (20, 40, 60, 80, 100 min), the tube was centrifuged for 15 sec (ca. 10^4 rpm) to separate the insoluble material and supernatant in the tube. A small aliquot of the supernatant (ca. 2 μ L) was extracted and (S)-**1c** was removed by a short path silica gel column chromatography (SiO_2 , AcOEt as eluent). Volatiles were removed under reduced pressure and the resulting crude residue was subjected to HPLC analysis to determined the conversion [HPLC conditions: Daicel CHIRALPAK IB column (0.46 cm ϕ x 25 cm): eluent *n*-hexane/dichloromethane = 1/1, flow rate 0.5 mL/min, detection at 254 nm, $t_R = 7.0$ min (**5**), $t_R = 10.7$ min ((S)-**6**), $t_R = 11.9$ min ((R)-**6**), $t_R = 14.0$ min (**S5**), a selected HPLC trace is in Chart S18]. The data are summarized in Table S9. At 100 min, the tube was centrifuged for 15 sec (ca. 10^4 rpm) to separate the insoluble material and supernatant in the tube. A small aliquot of the supernatant (10 μ L) was extracted and was mixed with 0.005 M CHCl_3 solutions of salicylamide (300 μ L, 0.0015 mmol). The resulting mixture was subjected to HPLC analysis to determine the catalyst content in the solution phase [HPLC conditions: Daicel CHIRALPAK IC column (0.46 cm ϕ x 25 cm): eluent *n*-hexane/2-propanol = 4/1, flow rate 1.0 mL/min, detection at 254 nm, $t_R = 8.9$ min (salicylamide), $t_R = 12.1$ min (*trans*-(S)-**1c**), $t_R = 17.9$ min (*cis*-(S)-**1c**)]. The data are summarized in Table S10.

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Table S9. %area of **5**, **6** ((*S*)-**6** + (*R*)-**6**), **S5**, and calculated conversion in the reaction promoted by *cis*-(*S*)-**1c**.^a

	time (min)				
	20	40	60	80	100
%area (5)	99.638	99.545	99.362	99.049	98.947
%area ((<i>S</i>)- 6)	0.11	0.168	0.249	0.389	0.454
%area ((<i>R</i>)- 6)	0.096	0.154	0.235	0.341	0.388
%area (S5)	0.157	0.132	0.154	0.221	0.212
6 ((<i>S</i>)- 6 + (<i>R</i>)- 6)	3.8	5.9	8.6	12.3	13.9
S5	3.5	2.9	3.2	4.4	4.2

^a $\epsilon_5/\epsilon_6 = 20.1$ and $\epsilon_5/\epsilon_{S5} = 23.3$ were used.



#	tR [min]	area%	
1	7.008	98.947	5
2	10.850	0.454	(<i>S</i>)- 6
3	11.908	0.388	(<i>R</i>)- 6
4	13.950	0.212	S5

Chart S17. HPLC trace at 100 min.

Table S10. %area, %area normalized by salicylamide, and %content of **1c** in the solution phase at specified period in HPLC analysis.

	%area	
	<i>cis</i> -cat at 100 min	<i>trans</i> -cat at 100 min
salicylamide	43.165	91.804
<i>trans</i> -(<i>S</i>)- 1c	2.024	8.196
<i>cis</i> -(<i>S</i>)- 1c	54.811	0

	%area normalized by salicylamide ^a	
	<i>cis</i> -cat at 100 min	<i>trans</i> -cat at 100 min
<i>trans</i> -(<i>S</i>)- 1c	0.047	0.089
<i>cis</i> -(<i>S</i>)- 1c	0.809	0.000
total 1c	0.856	0.089

	%content in solution ^b	
	<i>cis</i> -cat at 100 min	<i>trans</i> -cat at 100 min
<i>trans</i> -(<i>S</i>)- 1c	5.5	10.4
<i>cis</i> -(<i>S</i>)- 1c	94.5	0.0
total 1c	100.0	10.4

^aValues for *cis*-(*S*)-**1c** was normalized by using $\epsilon_{cis}/\epsilon_{trans} = 1.57$ determined in section 5-1. ^bWith *cis*-catalyst, the mixture is homogeneous and all **1c** existed in the solution phase. %content was calculated based on the relative to 0.856.

11. Control Experiment in CHCl₃ Solvent for the Rearrangement of **5**

To a test tube with a Teflon-coated magnetic stirring bar were added *trans*-(*S*)-**1c** (7.2 mg, 0.015 mmol) and chloroform (1500 µL) successively at the room temperature. To the clear orange solution was irradiated UV (365 nm) for 30 min and *cis/trans* ratio was confirmed by HPLC analysis (*cis/trans* = 96/4). To the *cis*-(*S*)-**1c** solution was added **5** (24.8 mg, 0.06

In situ manipulation of catalyst performance via photocontrolled aggregation/dissociation state of the catalyst

mmol) at the same temperature to run the reaction. At the specified period (60, 120, 180, 240 min), a small aliquot of the supernatant (ca. 2 μ L) was extracted and (S)-**1c** was removed by a short path silica gel column chromatography (SiO₂, AcOEt as eluent). Volatiles were removed under reduced pressure and the resulting crude residue was subjected to HPLC analysis to determine the conversion (no reaction proceeded in the absence of **1c**) [HPLC conditions: Daicel CHIRALPAK IB column (0.46 cm ϕ x 25 cm): eluent *n*-hexane/dichloromethane = 1/1, flow rate 0.5 mL/min, detection at 254 nm, t_R = 7.0 min (**5**), t_R = 10.7 min ((S)-**6**), t_R = 11.9 min ((R)-**6**), t_R = 14.0 min (**S5**). The data are summarized in Table S11.

The identical procedure was performed without photoirradiation, in which *trans*-(S)-**1c** (7.2 mg, 0.015 mmol) functioned as catalyst, which is soluble in CHCl₃ at the identical concentration. The data are summarized in Table S12.

Table S11. %area of **5**, **6** ((S)-**6** + (R)-**6**), **S5**, and calculated conversion in the reaction promoted by *cis*-(S)-**1c** in CHCl₃.^a

	time (min)			
	60	120	180	240
%area (5)	97.963	96.87	95.147	90.34
%area ((S)- 6)	0.306	0.627	1.236	2.998
%area ((R)- 6)	0.338	0.686	1.308	3.007
%area (S5)	1.393	1.818	2.309	3.69
6 ((S)- 6 + (R)- 6)	9.0	15.8	25.3	40.3
S5	22.9	25.9	27.3	29.4

^a $\epsilon_5/\epsilon_6 = 20.1$ and $\epsilon_5/\epsilon_{S5} = 23.3$ were used.

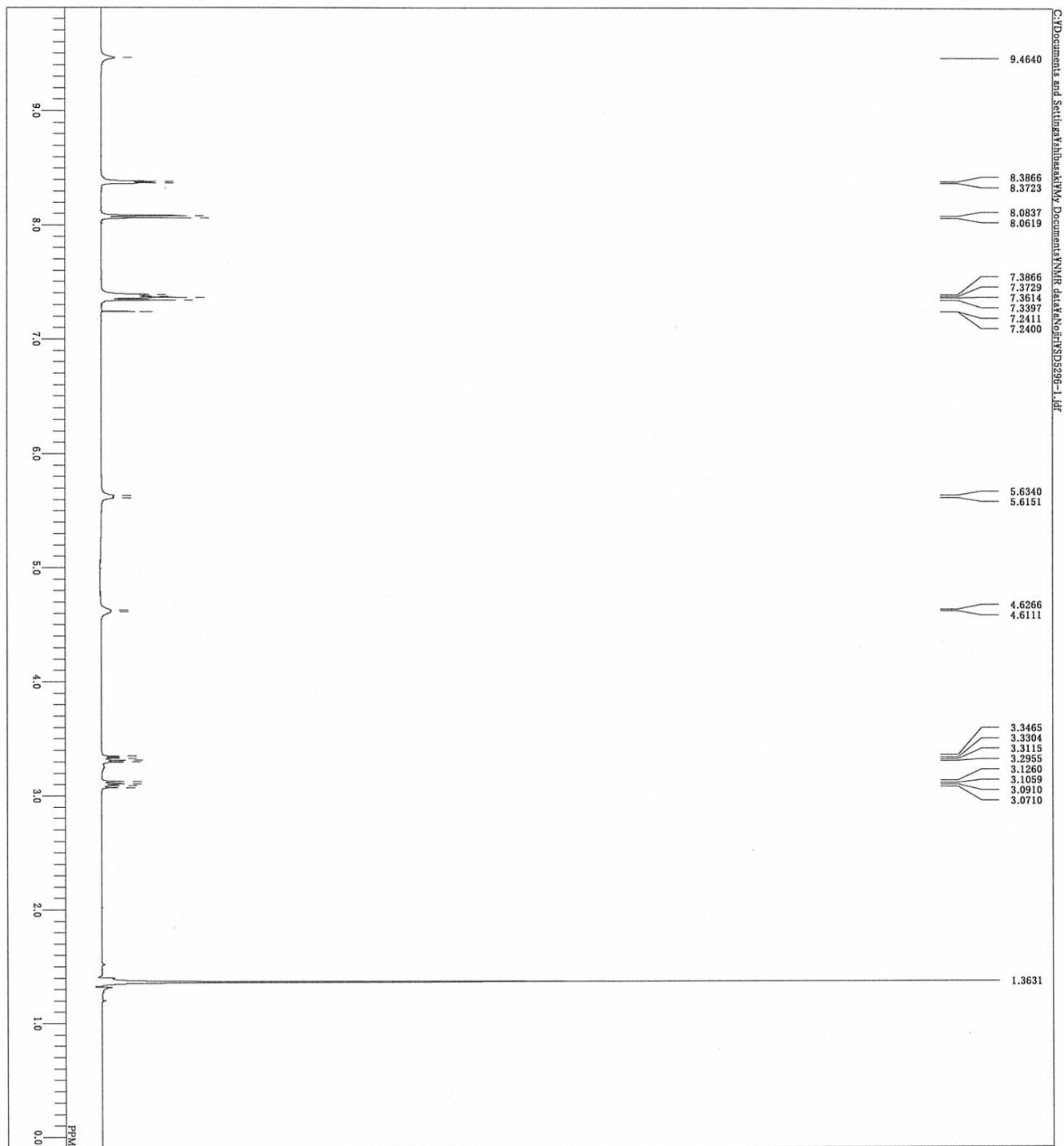
Table S12. %area of **5**, **6** ((S)-**6** + (R)-**6**), **S5**, and calculated conversion in the reaction promoted by *trans*-(S)-**1c** in CHCl₃.^a

	time (min)			
	60	120	180	240
%area (5)	97.565	96.184	93.724	87.739
%area ((S)- 6)	0.44	0.888	1.782	3.644
%area ((R)- 6)	0.483	0.922	1.735	3.492
%area (S5)	1.512	2.006	2.759	5.125
6 ((S)- 6 + (R)- 6)	12.2	20.1	30.7	40.6
S5	23.6	26.4	28.5	34.5

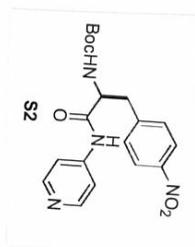
^a $\epsilon_5/\epsilon_6 = 20.1$ and $\epsilon_5/\epsilon_{S5} = 23.3$ were used.

12. NMR Spectra of New Compounds

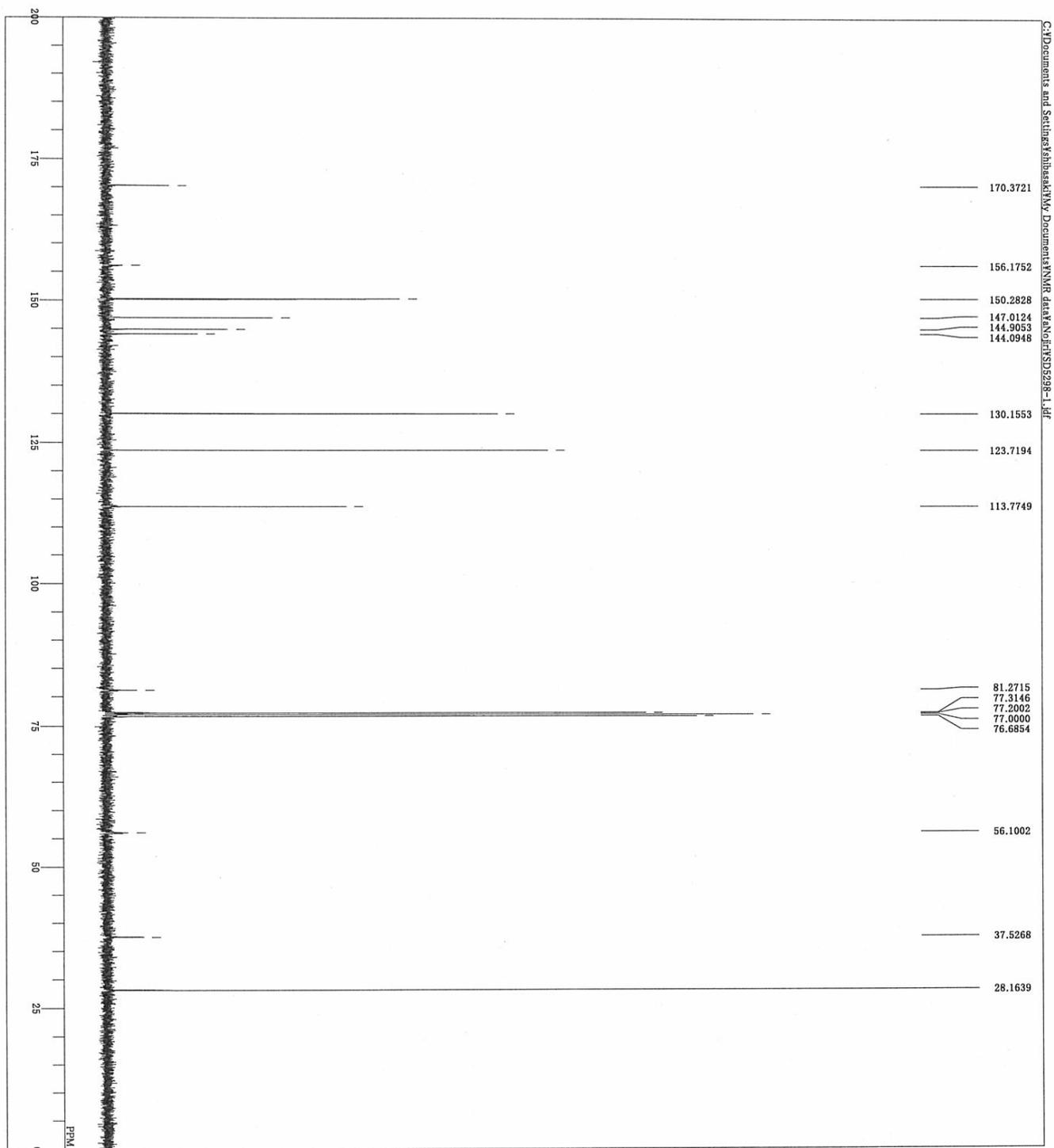
bopd pyr 1H



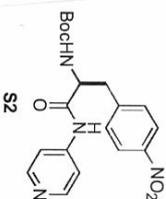
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 E1/MOD singlepulse.exe2
 O1/PRQ 393.78 MHz
 O1/PRN 14.0 Hz
 O1/PRF 7.28 Hz
 O1/PRW 32768 Hz
 POINT 7503.00 Hz
 FREQU 7503.00 Hz
 SCANS 6
 ACQTM 4.000 sec
 F1/D0 5.100 sec
 P1/W 5.49 usec
 I1/RNUC 1H
 C1/TEMP 21.5 c
 S1/VNT CDCl3 94 ppm
 BR/RF 0.12 Hz
 RC/GN 30



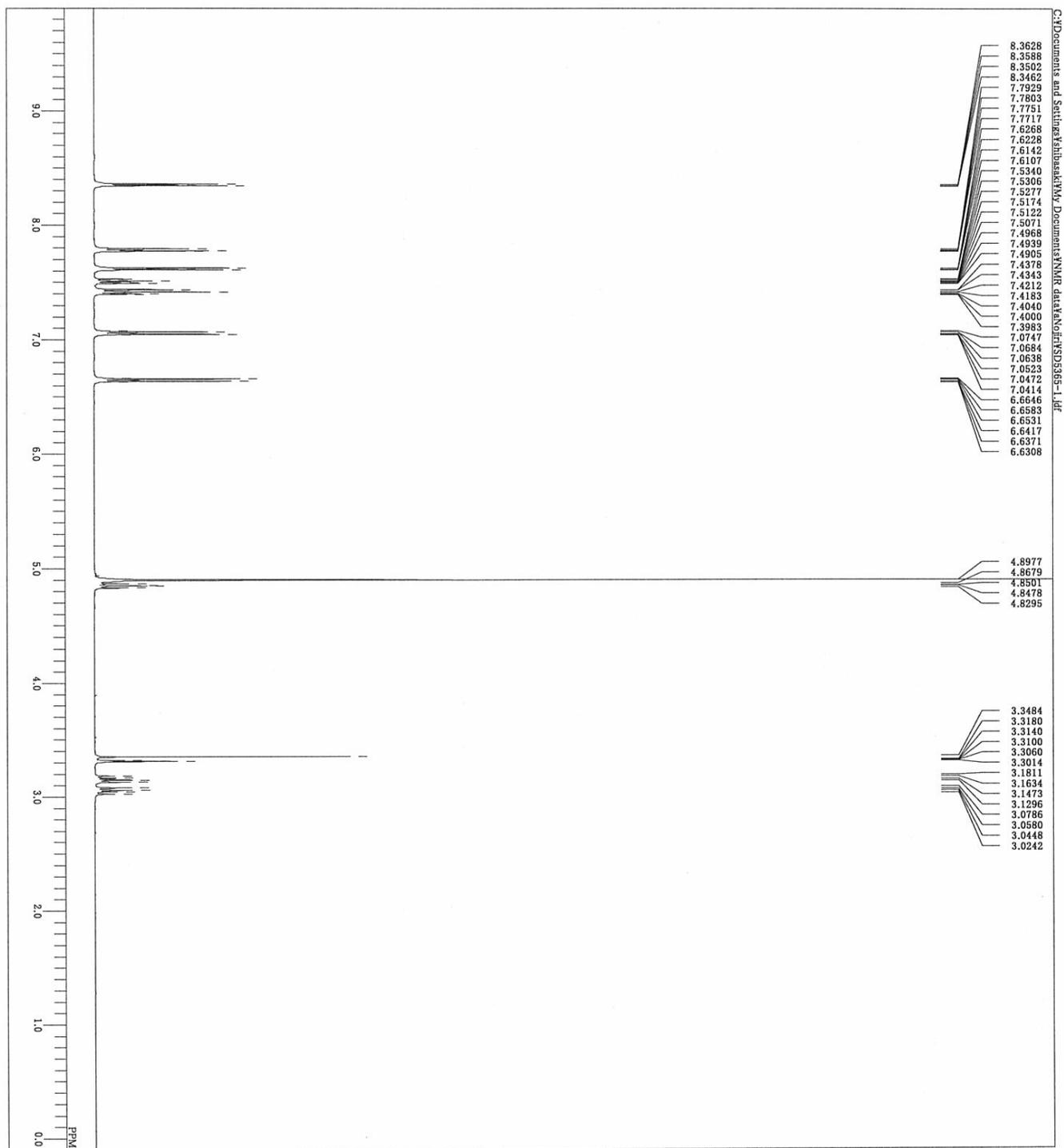
C13 bop el C13



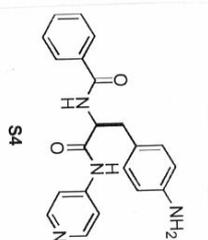
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 OBNUC singlepulse,dec
 EXMOD 100.53 MHz
 OBSFRQ 100.53 MHz
 OBSRES 5.38 kHz
 OBSSET 32758 Hz
 POINT 31407.03 Hz
 FREQU 31407.03 Hz
 SCANS 340
 ACQTM 1.0033 sec
 FWH 1.0033 sec
 PVI 2.73 usec
 IRNUC 1H
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 SLVNT CDCl3
 ERBER 71.00 ppm
 F2 0.02 Hz
 RGAIN 60



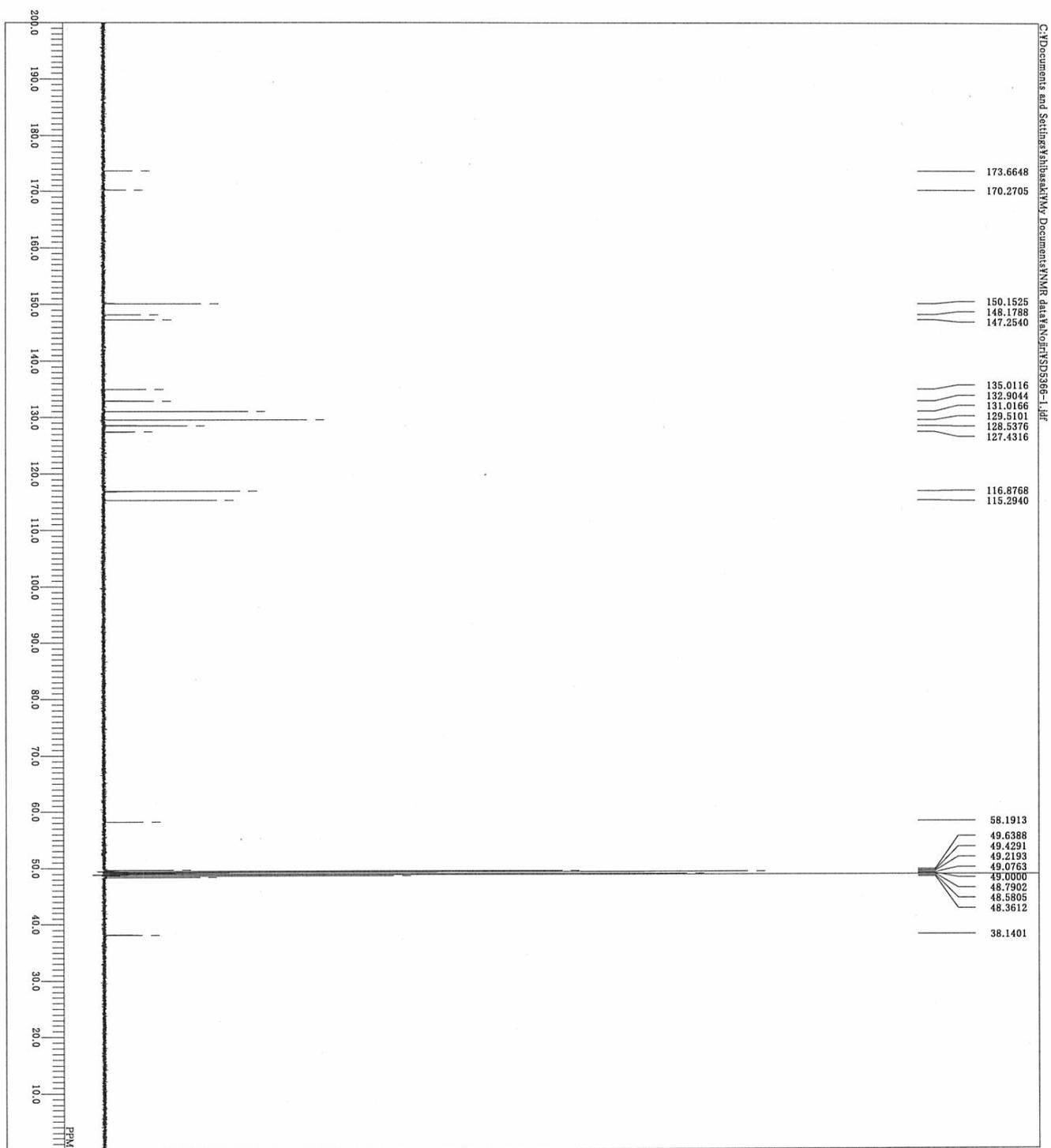
aniline 1H



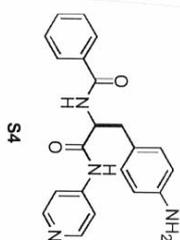
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 7.28 Hz
 32768
 7503.00 Hz
 4.000 sec
 5.49 usec
 30.000
 PVI
 IRNUC
 CTEMP
 SIVNT
 SLEW
 RF
 RCALN
 1H
 20.9 c
 CD3OD
 0.12 ppm
 30



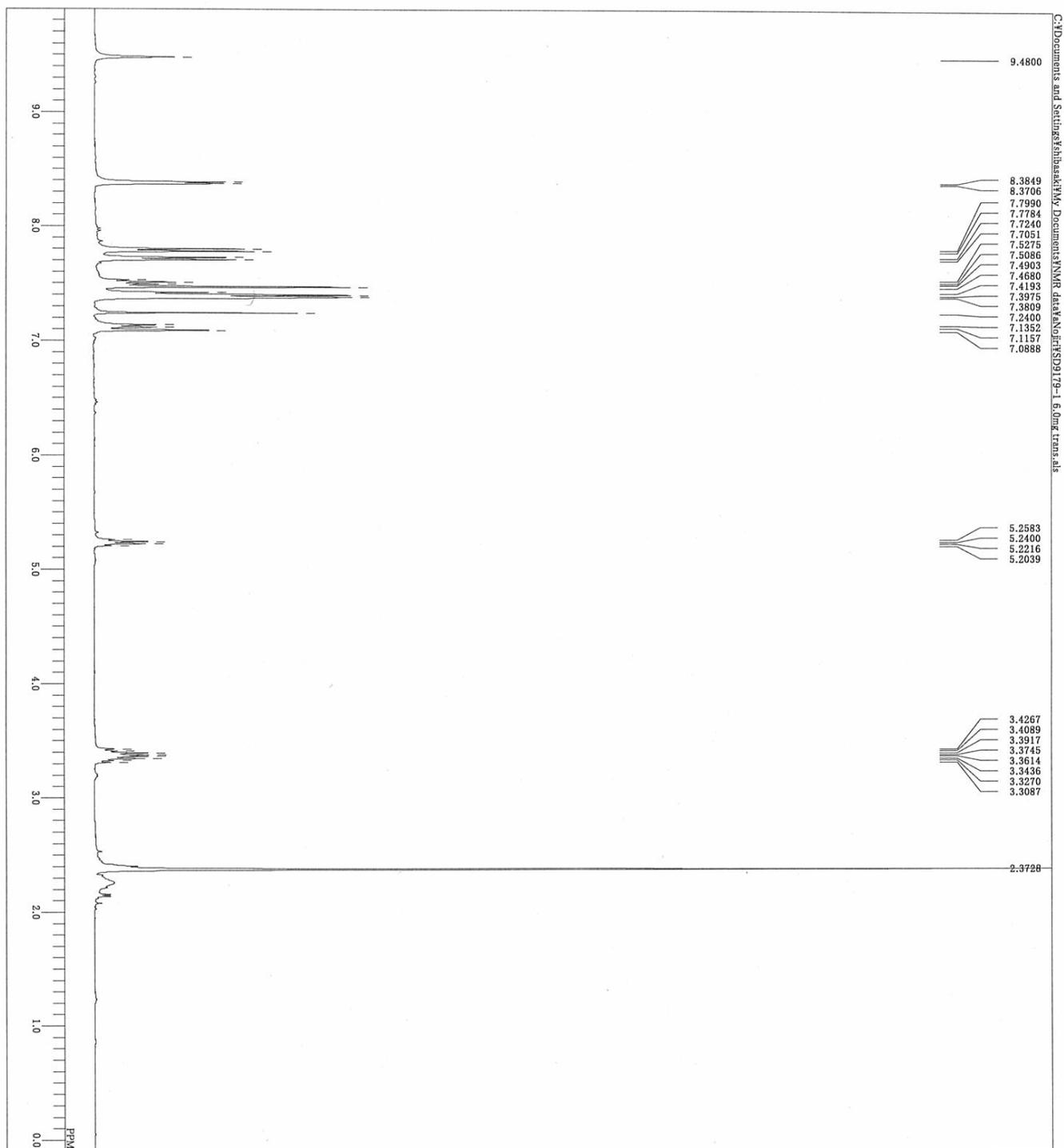
C13 aniline



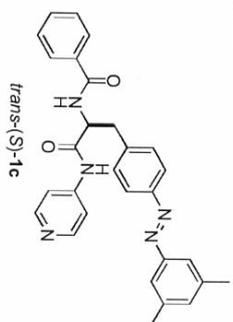
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 CPMPT 2013 aniline
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 OBFRQ 100.63 MHz
 OBSFT 5.38 kHz
 C 12
 POINT 32768 Hz
 PREQU 31407.03 Hz
 SCANS 260
 ACQTM 1.0433 sec
 PUL 2.000 sec
 Pw 21.9 usec
 IRNUC 21.5 c
 CTBMP CD3OD
 SILVNT 49.00 ppm
 EXREF 0 Hz
 RGAIN 58



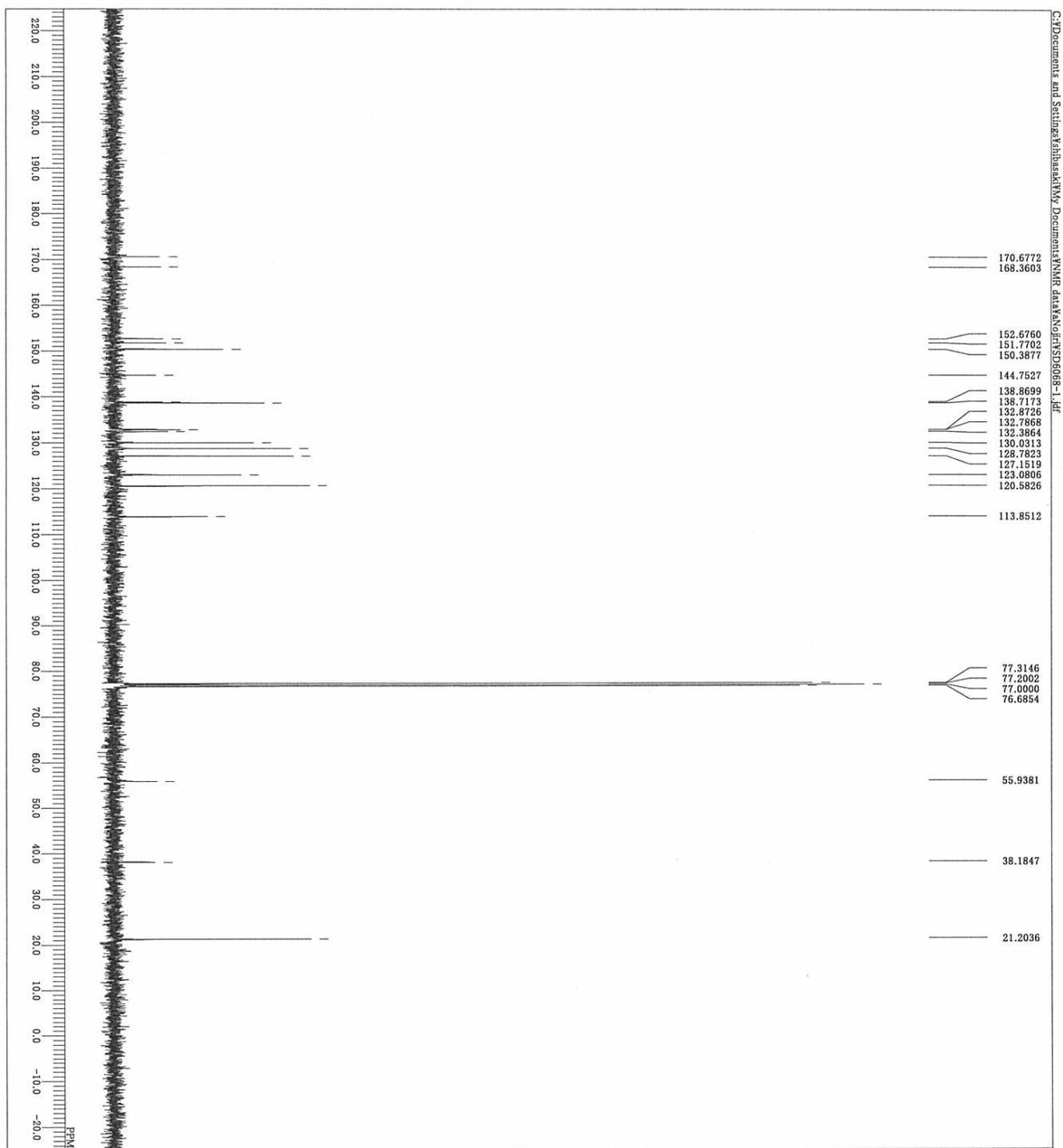
6.0mg trans



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 OBRFQ
 4.19 KHz
 7.49 Hz
 262.14
 POINT
 FREQQU
 6002.31 Hz
 SCANS
 8
 ACQTM
 4.3673 sec
 FID
 3.99 sec
 1H
 20.9 °C
 CDCl3
 1.24 ppm
 146
 RGAIN



xy1 13C



DP1LE SDB008-1.jdt
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 ORNUC 13C
 EXMOD single pulse dec
 OBPRG 100.53 MHz
 OBSF1 5.35 MHz
 OBSF2 5.35 MHz
 POINT 32768
 PREQU 31407.03 Hz
 SCANS 146
 ACQTM 1.0483 sec
 FID 2.070 sec
 PULP 2.773 usec
 IRNUC 1H
 CTEMP 21.1 c
 SLVNT CDCl3
 EXREF 77.00 ppm
 RGAIN 1.00 Hz
 BCAN 60

