Supporting Information

Rational Design of BINOL-Based Diimidazolyl Ligands: Homochiral Channel-like Mono-Component Organic Frameworks by Hydrogen-Bond-Directed Self-Assembly

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I. General remarks

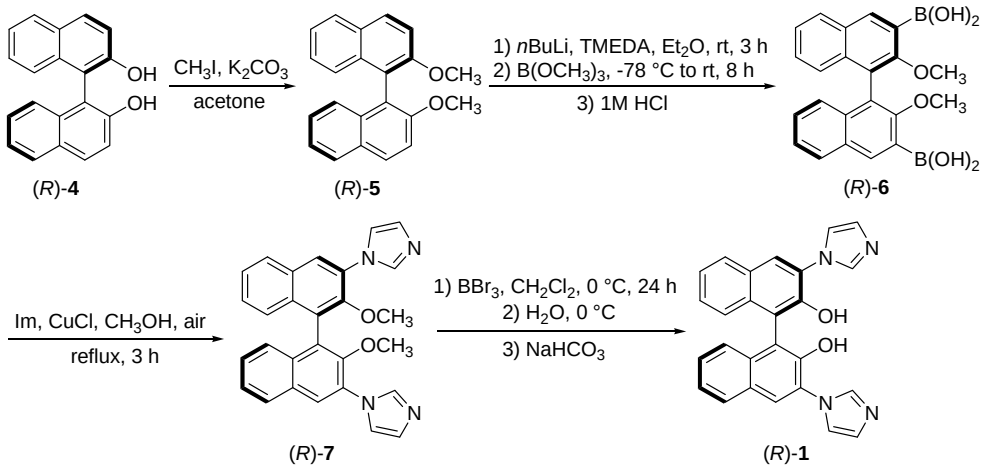
^{1}H NMR spectra were obtained with a Bruker AV-400 (400 MHz) or a Varian Inova-400 (400 MHz) spectrometer, while ^{13}C NMR spectra were also recorded with a Bruker AV-400 (100 MHz), a Bruker AV-600 (150 MHz), a Varian Inova-400 (100 MHz) or a Varian Inova-600 (150 MHz) spectrometer. The ^{1}H NMR chemical shifts were measured relative to tetramethylsilane, $CDCl_3$ or DMSO-d_6 as the internal reference, while the ^{13}C NMR chemical shifts were recorded with $CDCl_3$ or DMSO-d_6 as the internal standard. Elemental analyses were performed with a CARLO ERBA1106 instrument or a Heraeus CHN-O-RAPID instrument. The ESI-TOF mass spectra were recorded with a Waters Q-Tof premier instrument. High-resolution FAB mass spectra was obtained using a JEOL JMS-SX/SX 102A instrument. The optical rotations were determined with a WZZ-2B polarimeter. Melting points were determined with XRC-1 and are uncorrected. Powder X-ray diffraction (PXRD) patterns were collected on a Philips X'PERT Pro MPDX powder diffractometer with Cu Kα radiation (1.54056 Å). The tube voltage and amperage were set at 40 kV and 35 mA, respectively. The sample was scanned between 5° and 45° in 2 θ with a step size of 0.03°. The simulated PXRD spectra from single-crystal structures was carried out using Mercury (version 1.4.2, 2002) and were compared to confirm the composition of the crystal with the experimental PXRD pattern.

Materials: (*R*)-1,1′-Bi-2-naphthol [(*R*)-**4**] (>99% ee) was purchased from Lian YunGang Chiral Chemicals (China) Co., Ltd. Pyridine was distilled before use, while the others were used without further purification. Solvents were dried by heating at reflux for at least 24h over CaH_2 (dichloromethane and DMSO) or sodium/benzophenone (tetrahydrofuran and diethyl ether) and were freshly distilled prior to use. Unless otherwise indicated, all syntheses and manipulations were carried out under a dry nitrogen atmosphere. *n*BuLi in Et_2O was prepared according to the

literature.[1] Compounds (*R*)-**5**, (*R*)-**6** and (*R*)-**7** were synthesized according to literature methods.[2] Compound (*R*)-**8** was synthesized by following literature procedures.[3] Compounds (*R*)-**10** and (*R*)-**11** were prepared according to literature procedures.[4]

II. Procedures for the preparation of chiral ligands (*R*)-1-3

i. Synthesis of chiral ligand (*R*)-1



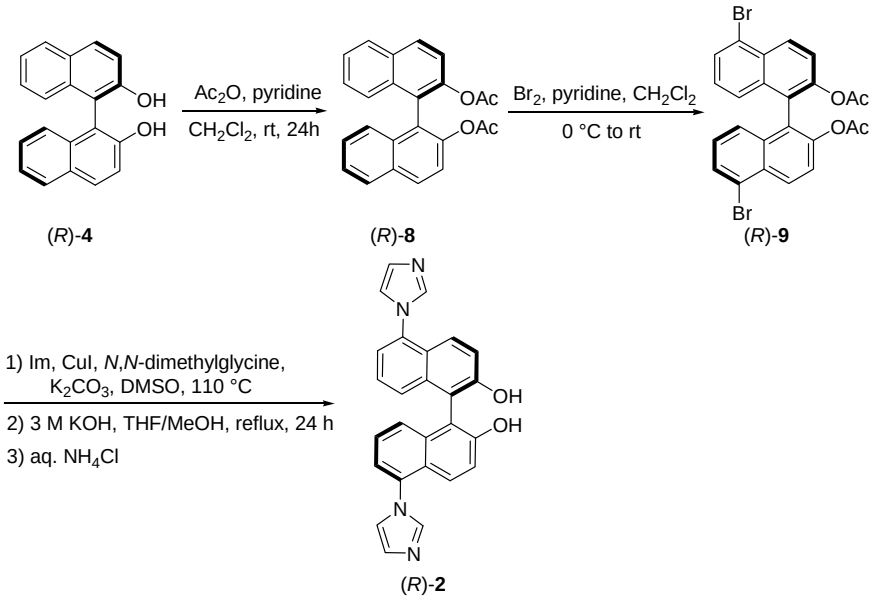
Scheme S1 Synthesis of the 3,3′-diimidazolyl-substituted BINOL (*R*)-**1**.

(*R*)-3,3′-Bis(1*H*-imidazol-1-yl)-1,1′-bi-2-naphthol ((*R*)-1)

A flame-dried Schlenk flask was charged with (*R*)-**7** (0.47 g, 1 mmol) and anhydrous CH_2Cl_2 (20 mL) under N_2. The solution was cooled to 0 ºC, and then BBr_3 (1.0 *M* in CH_2Cl_2, 4 mL, 4 mmol) was added over a period of 30 min. The mixture was allowed to warm to room temperature and stirred for 24 h. Thereafter, water (5 mL) was carefully added at 0 ºC to quench the reaction, followed by MeOH (5 mL) and solid $NaHCO_3$ to neutralize the mixture. The resulting mixture was stirred for a further 12 h at room temperature and then filtered through a pad of Celite. The filtrate was washed with saturated aqueous NaCl solution (10 mL). The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (2×10 mL). The combined organic layers were dried over Na_2SO_4

and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH (12:1 to 10:1) to give (*R*)-**1** (0.36 g, 85%) as a pale-yellow solid. M.p. > 300 ºC; $[\alpha]^{20}_D$ = +30.2 (c = 0.51, DMSO); ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.93 (d, *J* = 8.4 Hz, 2H), 7.11 (s, 2H), 7.27 (t, *J* = 6.8 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.62 (s, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 8.07 (s, 2H), 8.13 (s, 2H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6): δ 116.4, 120.8, 121.5, 123.6, 124.1, 126.7, 127.8, 127.9, 128.1, 132.9, 135.0, 137.7, 148.4 ppm; HRMS (FAB): calcd for $C_{26}H_{19}N_4O_2$ $[M+H]^+$: 419.1508, found: 419.1505; Anal. Calcd. for $C_{26}H_{18}N_4O_2$: C, 74.63; H, 4.34; N, 13.39. Found: C, 74.38; H, 4.45; N, 13.20.

ii. Synthesis of chiral ligand (*R*)-2



Scheme S2 Synthesis of the 5,5′-diimidazolyl-substituted BINOL (*R*)-**2**.

(*R*)-5,5′ -Dibromo-2,2′ -diacetoxyl-1,1′ -dinaphthyl ((*R*)-9)

A solution of bromine (4.6 mL, 90 mmol) in CH_2Cl_2 (50 mL) was added dropwise to a stirred solution of (*R*)-**8** (5.56 g, 15 mmol) and pyridine (3.6 mL, 45 mmol) in CH_2Cl_2 (150 mL) at room temperature. After stirring for 81 h, 200 mL of 15% aqueous solution of sodium bisulfite was carefully added at 0 ºC to quench the reaction. The resulting mixture was stirred for an additional 2 h

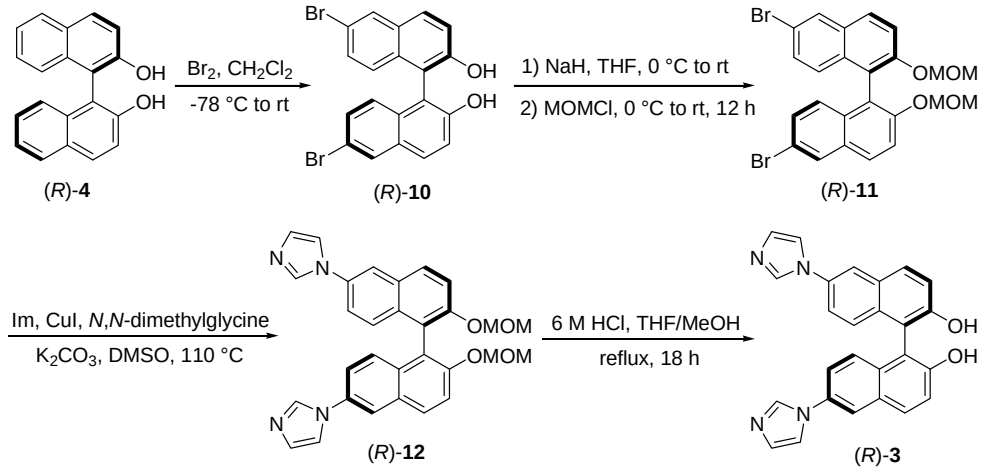
at room temperature. The organic layer was separated, washed with $NaHSO_3$ (15%, 2×100 mL) and brine (2×100 mL), and then dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (13:1) to give (*R*)-**9** (3.33 g, 42%) as a white foam. M.p. 123-124 °C; $[\alpha]^{20}_D$ = +32.0 (c = 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (s, 6H), 7.08-7.15 (m, 4H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 2H), 8.45 (d, *J* = 9.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 122.9, 123.2, 123.3, 125.9, 127.2, 129.1, 129.9, 130.0, 134.4, 147.4, 169.0 ppm; HRMS (ESI): calcd for $C_{24}H_{17}Br_2O_4$ $[M+H]^+$: 528.9473, found: 528.9456.

(*R*)-5,5′ -Bis(1*H*-imidazol-1-yl)-1,1′ -bi-2-naphthol ((*R*)-2)

A flame-dried Schlenk flask was charged with CuI (457 mg, 2.4 mmol), *N*,*N*-dimethylglycine (495 mg, 4.8 mmol), K_2CO_3 (11.59 g, 84 mmol), (*R*)-**9** (6.34 g, 12 mmol), imidazole (2.86 g, 42 mmol), and DMSO (18 mL) at room temperature under nitrogen. After being heated at 110 ºC for 60 h, the mixture was evaporated under vacuum. Thereafter, the resulting residue was partitioned with 200 mL of CH_2Cl_2 and filtered through a pad of Celite. The filtrate was removed under reduced pressure to give the crude product. Aqueous KOH (3 *M*, 15 mL) was then added to the solution of the crude product in THF (80 mL) and methanol (40 mL). The resulting solution was refluxed for 24 h until the conversion of reactant was complete. The solution was then cooled to room temperature and neutralized by addition of saturated aqueous NH_4Cl solution. The resulting mixture was stirred for a further 2 h and volatiles were then removed in *vacuo*. The aqueous phase was extracted with CH_2Cl_2 (3×120 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum. The resulting residue was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH (13:1 to 8:1) to give (*R*)-**2** (3.41 g, 68% (two steps)) as a pale-yellow solid. M.p.

>300 ºC; $[\alpha]^{20}_{D}$ = +39.0 (c = 0.50, DMSO); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.09 (d, J = 7.6 Hz, 2H), 7.23 (s, 2H), 7.32-7.37 (m, 4H), 7.41 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 9.2 Hz, 2H), 7.62 (s, 2H), 8.03 (s, 2H), 9.69 (s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 115.8, 120.0, 120.4, 122.2, 123.2, 123.8, 125.3, 125.8, 128.9, 134.2, 134.9, 138.6, 153.9 ppm; HRMS (ESI): calcd for $C_{26}H_{19}N_4O_2$ $[M+H]^+$: 419.1508, found: 419.1517; Anal. Calcd. for : C, 74.63; H, 4.34; N, 13.39. Found: C, 74.26; H, 4.36; N, 13.10.

iii. Synthesis of chiral ligand (*R*)-3



Scheme S3 Synthesis of the 6,6′-diimidazolyl-substituted BINOL (*R*)-**3**.

(*R*)-6,6′-Bis(1*H*-imidazol-1-yl)-2,2′-dimethoxymethoxy-1,1′-binaphthyl ((*R*)-12)

A flame-dried Schlenk flask was charged with CuI (381 mg, 2.0 mmol), *N*,*N*-dimethylglycine (412 mg, 4.0 mmol), K_2CO_3 (11.04 g, 80 mmol), (*R*)-**11** (5.32 g, 10 mmol), imidazole (2.72 g, 40 mmol), and DMSO (15 mL) at room temperature under nitrogen. After being heated at 110 ºC for 48 h, the mixture was concentrated under reduced pressure. The resulting residue was then partitioned between water (60 mL) and CH_2Cl_2 (120 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried over Na_2SO_4 and evaporated in *vacuo*. The crude product was purified by chromatography on a silica gel column

eluting CH_2Cl_2/MeOH (20:1 to 15:1). (*R*)-**12** was obtained in 84% yield (4.26 g) as a yellow solid. M.p. 77-78 ºC; $[\alpha]^{20}_D$ = -5.0 (c = 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.31 (s, 6H), 4.94 (dd, *J* = 6.8 Hz, 7.2 Hz, 4H), 7.14-7.22 (m, 6H), 7.60 (d, *J* = 9.2 Hz, 2H), 7.79 (d, *J* = 2.0 Hz, 2H), 7.86 (s, 2H), 7.92 (d, *J* = 9.2 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ 56.0, 95.0, 118.4, 118.5, 119.3, 120.6, 120.9, 127.4, 129.6, 129.8, 130.4, 132.8, 133.4, 135.8, 153.2 ppm; HRMS (ESI): calcd for $C_{30}H_{27}N_4O_4$ $[M+H]^+$: 507.2032, found: 507.2040.

(*R*)-6,6′ -Bis(1*H*-imidazol-1-yl)-1,1′ -bi-2-naphthol ((*R*)-3)

Aqueous HCl (6 *M*, 10 mL) was added to a solution of (*R*)-**12** (3.04 g, 6.0 mmol) in THF (40 mL) and methanol (20 mL). The resulting solution was refluxed for 18 h until the conversion of (*R*)-**12** was complete. The solution was then cooled to room temperature and neutralized by addition of saturated aqueous Na_2CO_3 solution. After the resulting mixture was stirred for a further 12 h and volatiles were removed under reduced pressure. The aqueous phase was extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. The resulting residue was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH (18:1 to 10:1) to give (*R*)-**3** (2.23 g, 89%) as a pale-yellow solid. M.p. >300 ºC; $[\alpha]^{20}_D$ = +15.0 (c = 0.50, DMSO); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.06 (d, *J* = 9.2 Hz, 2H), 7.13 (s, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.49 (dd, *J* = 2.0 Hz, 2.4 Hz, 2H), 7.74 (s, 2H), 7.95 (d, *J* = 9.2 Hz, 2H), 8.13 (d, *J* = 2.4 Hz, 2H), 8.24 (s, 2H), 9.47(s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 115.8, 118.9, 119.0, 120.4, 120.6, 126.7, 128.6, 129.4, 130.1, 132.3, 133.2, 136.2, 154.0 ppm; HRMS (ESI): calcd for $C_{26}H_{19}N_4O_2$ $[M+H]^+$: 419.1508, found: 419.1510; Anal. Calcd. for : C, 74.63; H, 4.34; N, 13.39. Found: C, 74.32; H, 4.31; N, 13.12

III. General procedure for the preparation of organic crystals (*R*)-1-3

At elevated temperature, (*R*)-**1**-**3** (50 mg) was dissolved in a DMF solution (2 mL) with constant stirring to give a light yellow solution. Then the mixture was filtered to remove a trace amount of undissolved substance. Colorless block crystals (*R*)-**1**-**3** suitable for X-ray analysis were obtained by slow diffusion of 1,4-dioxane into the corresponding DMF solution at ambient temperature after several days (yields: 70-75%).

IV. Single-crystal X-ray diffraction determination and refinement

X-Ray single-crystal diffraction data for (*R*)-**1**-**3** were collected on a Bruker SMART 1000 CCD areadetector diffractometer at 100 K with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) with ω scan mode. All the structures were solved by direct methods using the SHELXS program and refined by full-matrix least-squares methods with SHELXL.[5] All non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. Hydrogen atoms were included in calculated positions and refined with constrained thermal parameters riding on their parent atoms. The guest molecules of (*R*)-**3** could not be located in the difference map because of disorder. The crystal parameters, data collection and refinement results for the three compounds are summarized in Table S1.

Table S1 Crystallographic Data for Crystals (*R*)-**1**-**3**

	(*R*)-**1**	(*R*)-**2**	(*R*)-**3**
Chemical formula	$C_{26}H_{18}N_4O_2$	$C_{33}H_{33}N_5O_5$	$C_{26}H_{18}N_4O_2$
Formula weight (M)	418.44	579.64	418.44
Temperature (K)	297(2)	100(2)	297(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Tetragonal
Space group	*P* 21 21 2	*P* 21 21 21	*P* 43
Crystal size (mm^3)	0.75×0.50×0.17	0.44×0.42×0.38	0.60×0.58×0.48

a (Å)	27.513(3)	9.2610(3)	11.950(2)
b (Å)	12.2721(11)	16.4271(5)	11.950(2)
c (Å)	12.3143(11)	19.8316(4)	21.080(6)
α (º)	90	90	90
β (º)	90	90	90
γ (º)	90	90	90
Volume ($Å^3$)	4157.8(7)	3017.01(15)	3010.3(12)
Z	6	4	4
Calculated density (g cm^{-3})	1.003	1.276	0.923
μ (mm^{-1})	0.065	0.088	0.060
Reflections collected	23774	22393	13487
Independent reflections	4556	5247	5400
R_{int}	0.0722	0.1015	0.1045
F(000)	1308	1224	872
GOF	1.125	1.090	1.101
R_1, wR_2 [I >2 σ (I)]	0.0844, 0.2112	0.0624, 0.1703	0.0770, 0.2107
R_1, wR_2 (all data)	0.1438, 0.2554	0.0694, 0.1774	0.0838, 0.2197

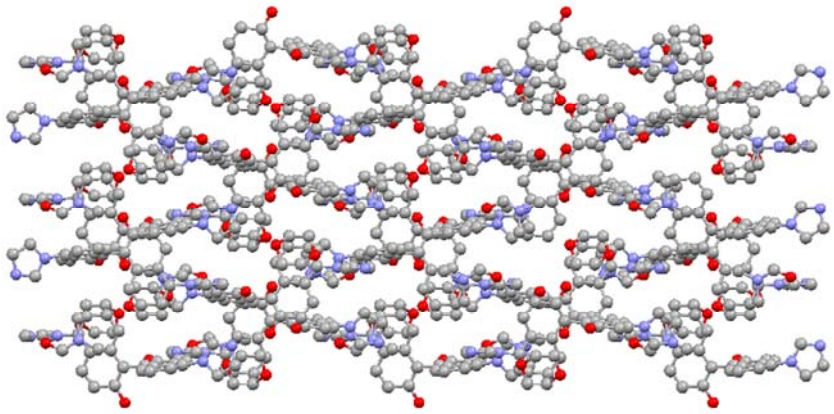


Fig. S1 2-D network layer of (*R*)-**2** viewed along the *b*-axis. Color code: C, dark gray; N, blue; O, red; H atoms were omitted for clarity. DMF and 1,4-dioxane molecules were positioned in the network.

V. Powder X-ray diffraction analysis of (*R*)-1-3

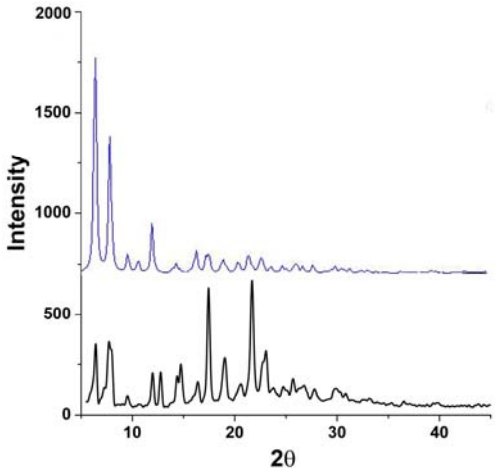


Fig. S2 Comparison of powder X-ray diffraction patterns of (*R*)-**1**: the top and bottom patterns correspond to the simulated and experimental results, respectively.

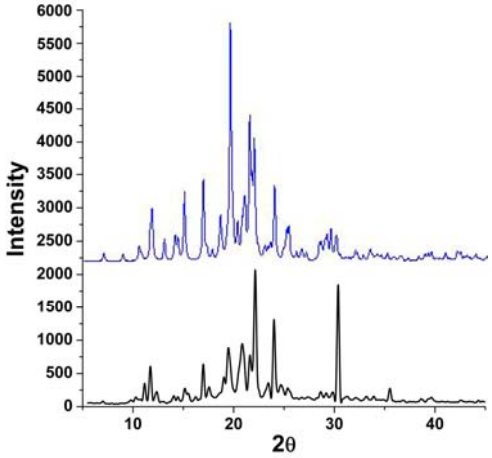


Fig. S3 Comparison of powder X-ray diffraction patterns of (*R*)-**2**: the top and bottom patterns correspond to the simulated and experimental results, respectively.

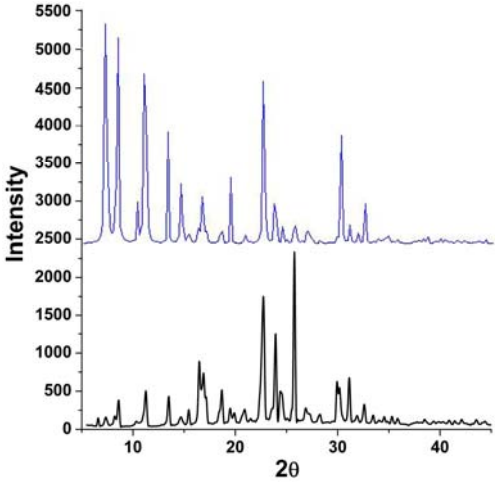


Fig. S4 Comparison of powder X-ray diffraction patterns of (*R*)-**3**: the top and bottom patterns correspond to the simulated and experimental results, respectively.

VI. References

(1) (a) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *J. Am. Chem. Soc.* 1949, **71**, 1499; (b) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.* 1944, **66**, 1515.

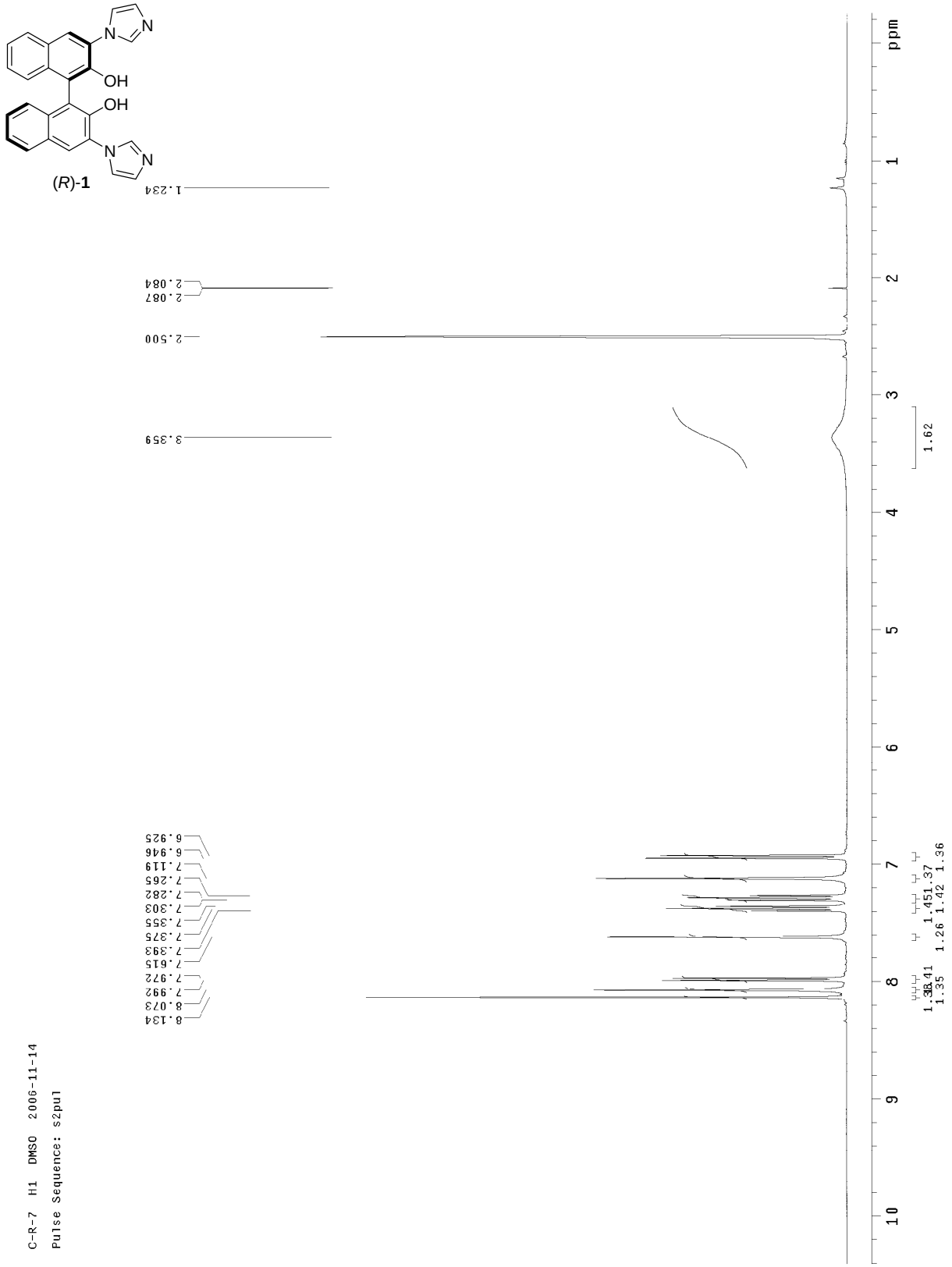
(2) Q.-S. Lu, L. Dong, J. Zhang, J. Li, L. Jiang, Y. Huang, S. Qin, C.-W. Hu and X.-Q. Yu, *Org. Lett.* 2009, **11**, 669.

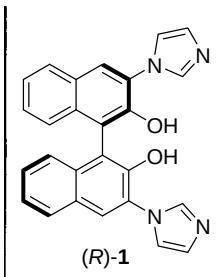
(3) (a) Q.-S. Hu, V. Pugh, M. Sabat and L. Pu, *J. Org. Chem.* 1999, **64**, 7528; (b) P. Saravanan and V. K. Singh, *Tetrahedron Lett.* 1999, **40**, 2611.

(4) M.-H. Xu, J. Lin, Q.-S. Hu and L. Pu, *J. Am. Chem. Soc.* 2002, **124**, 14239.

(5) G. M. Scheldrick, *SHELX-97 and SHELXL-97, Program for Solution and Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.

VII. Copies of ^{1}H and ^{13}C NMR spectra of (*R*)-1-3, 9 and 12

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N
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(*R*)-**1**

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116.380
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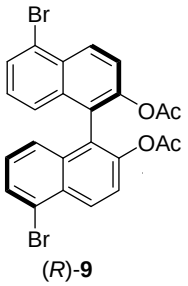
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OAc
OAc
Br

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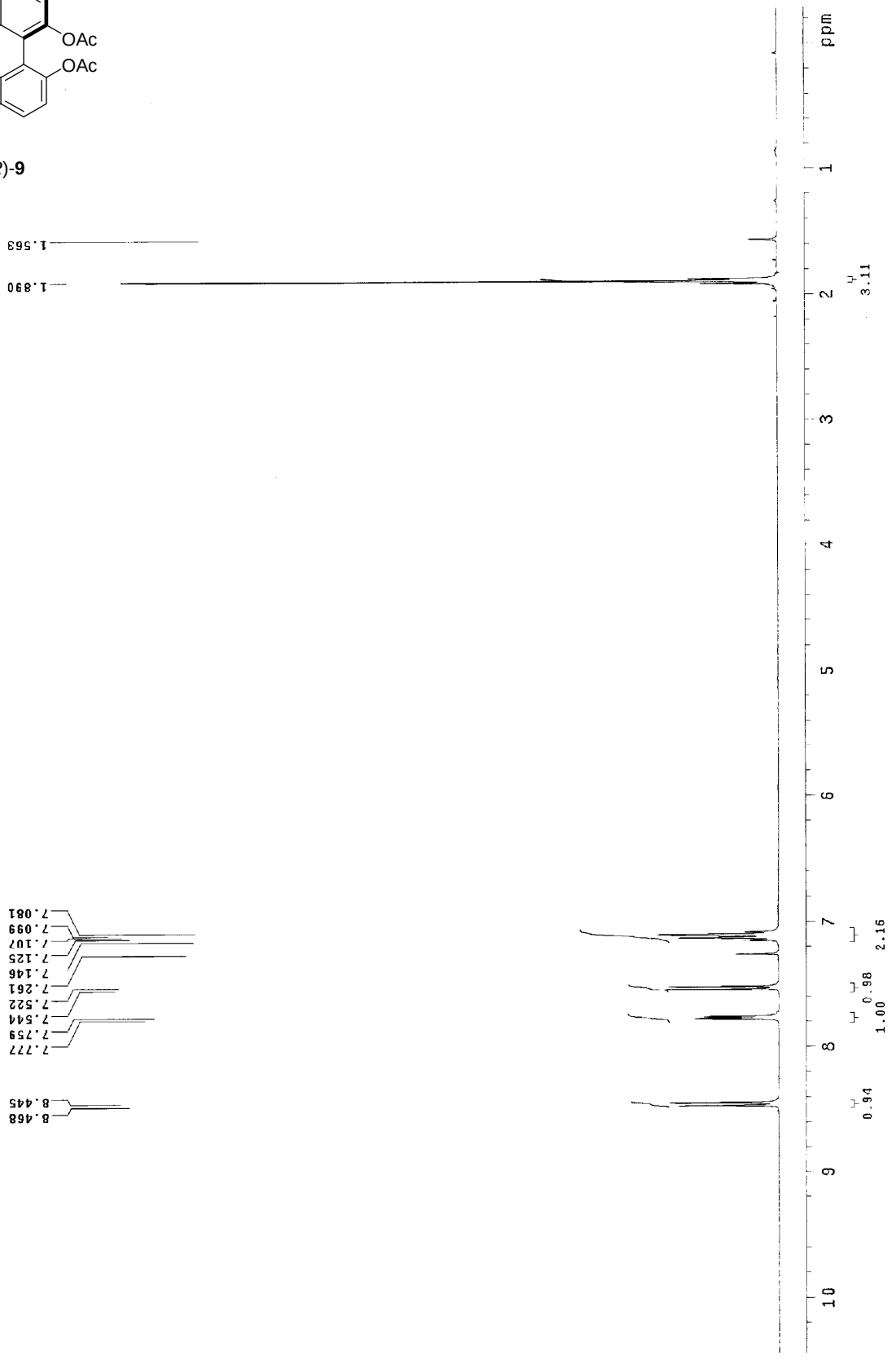
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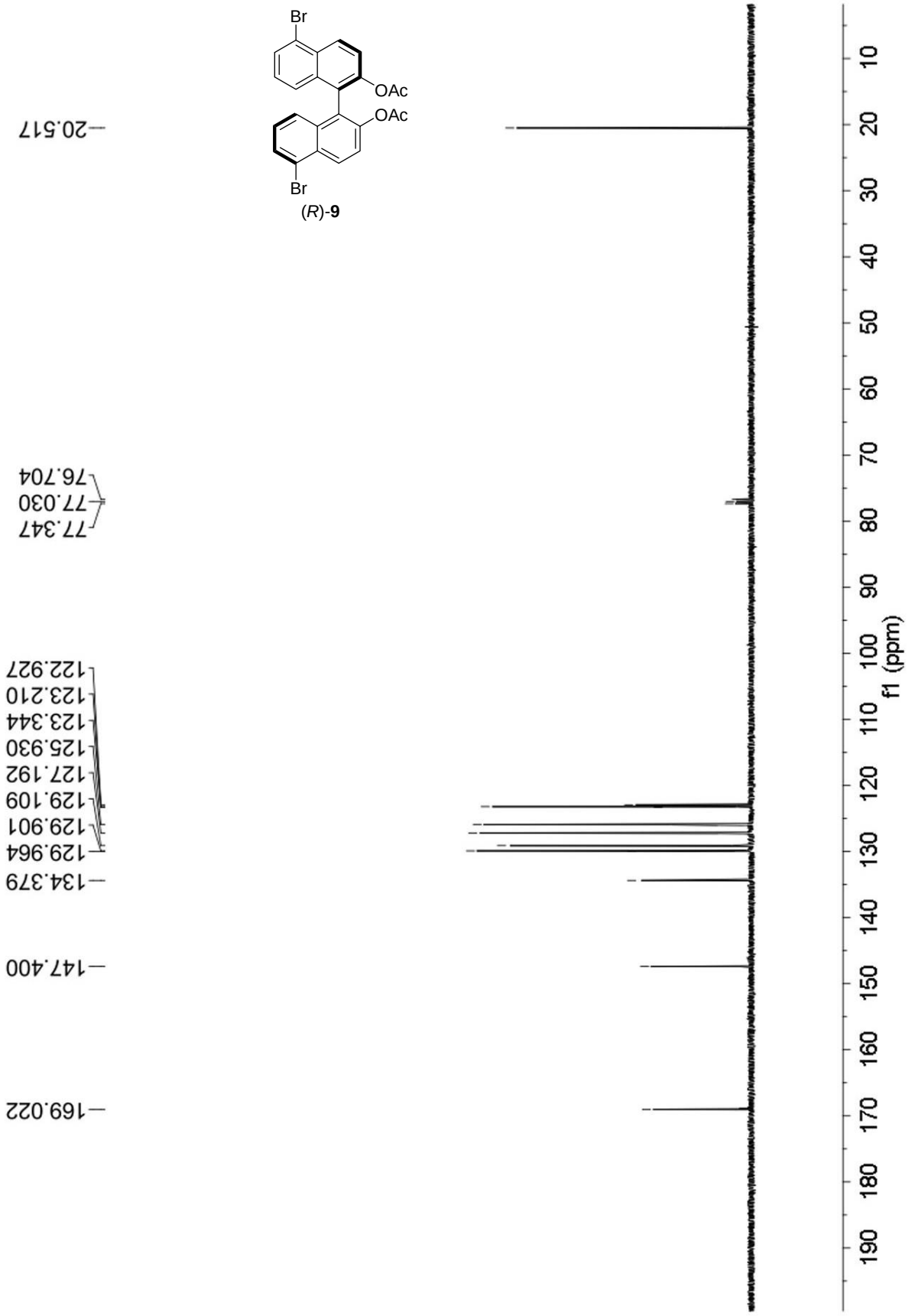
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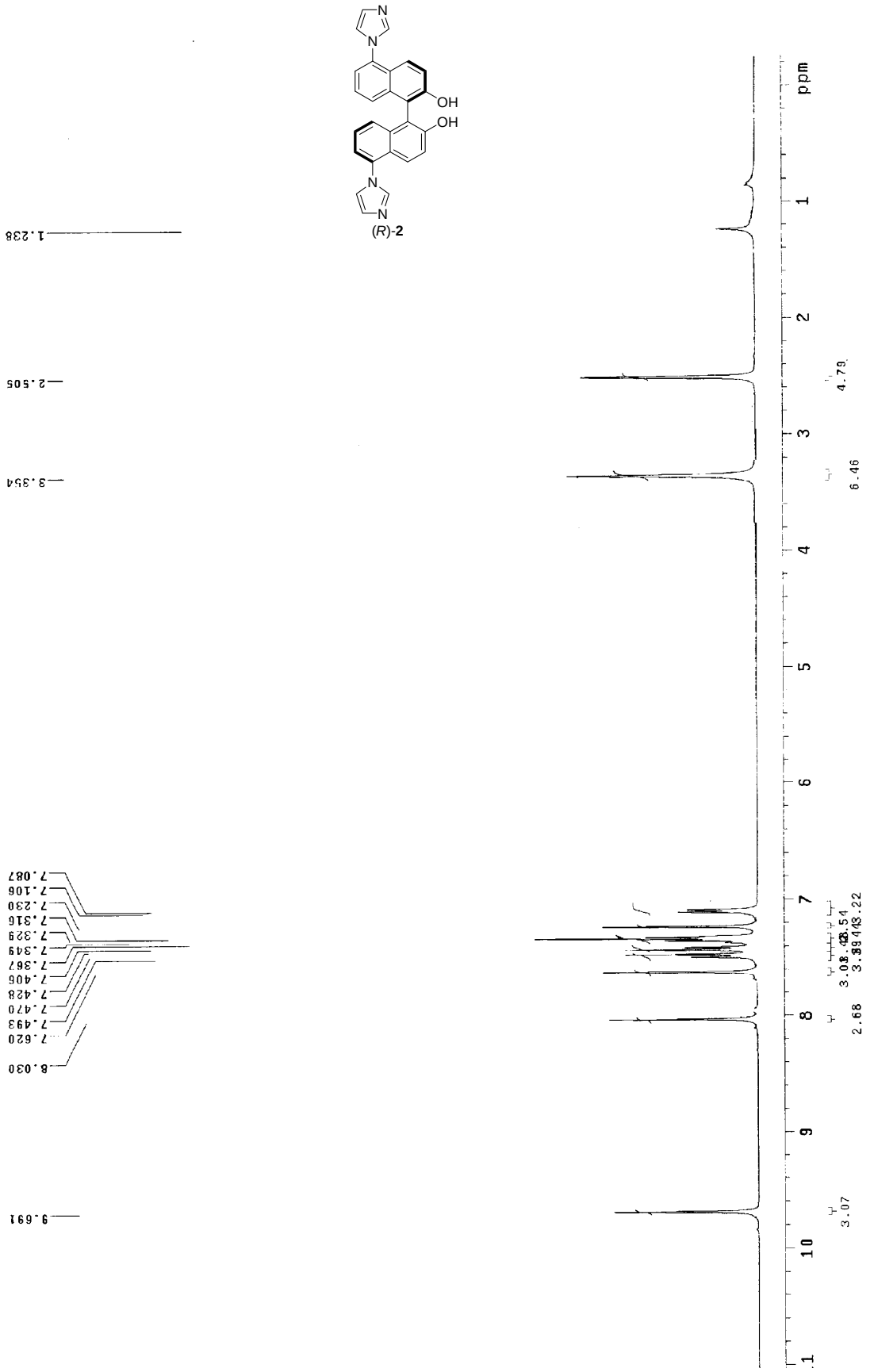
f1 (ppm)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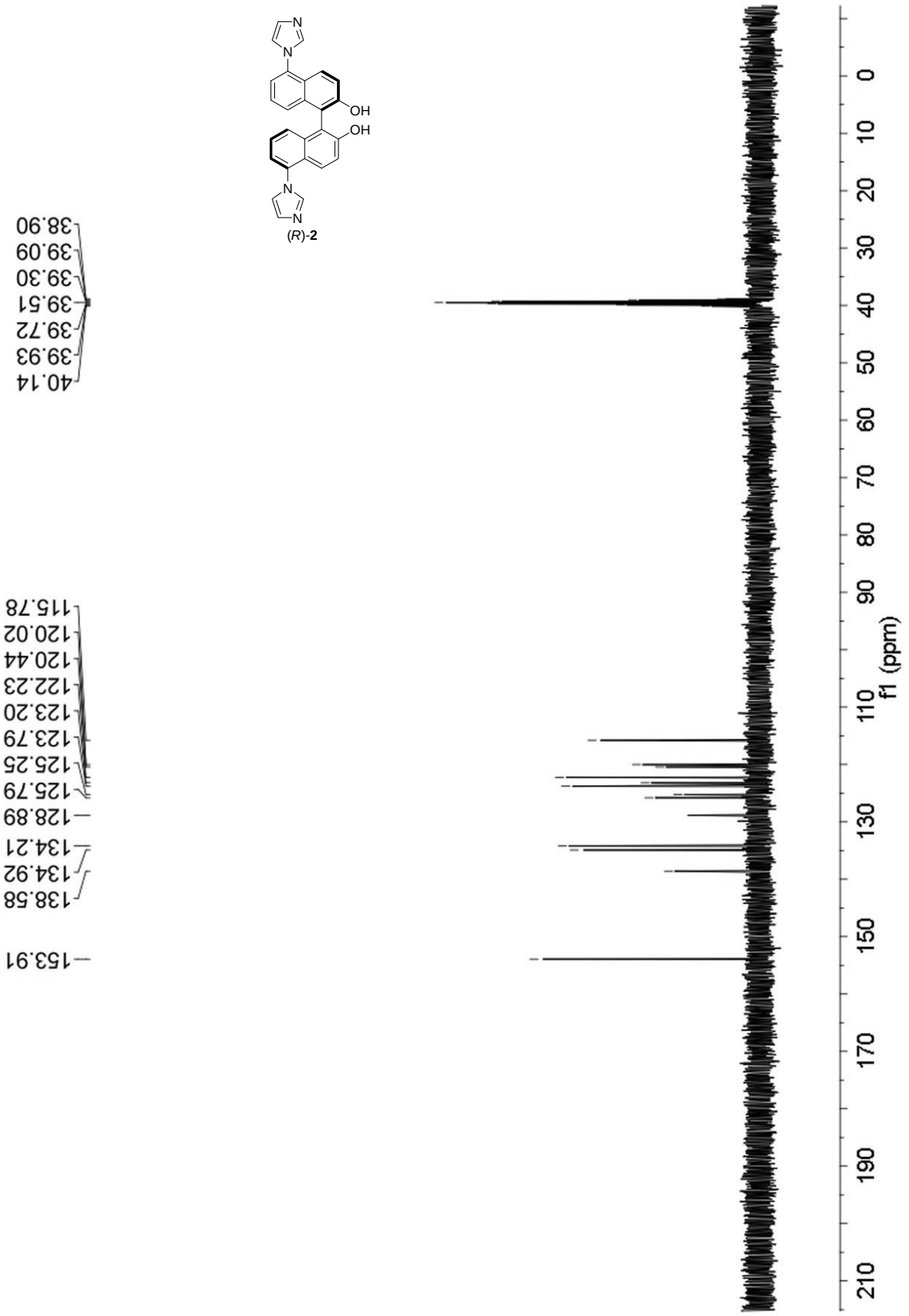
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50
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70
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130
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170
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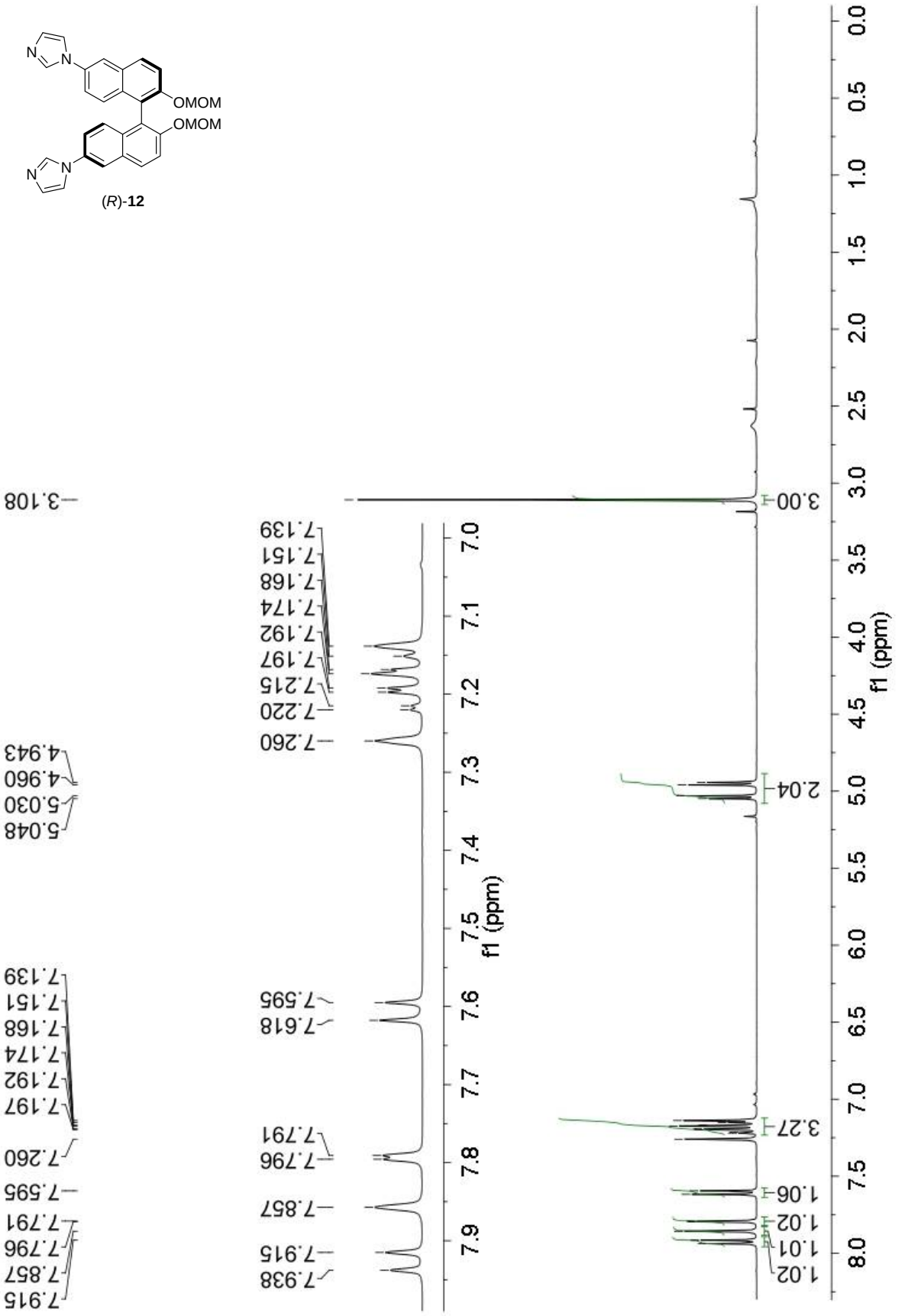
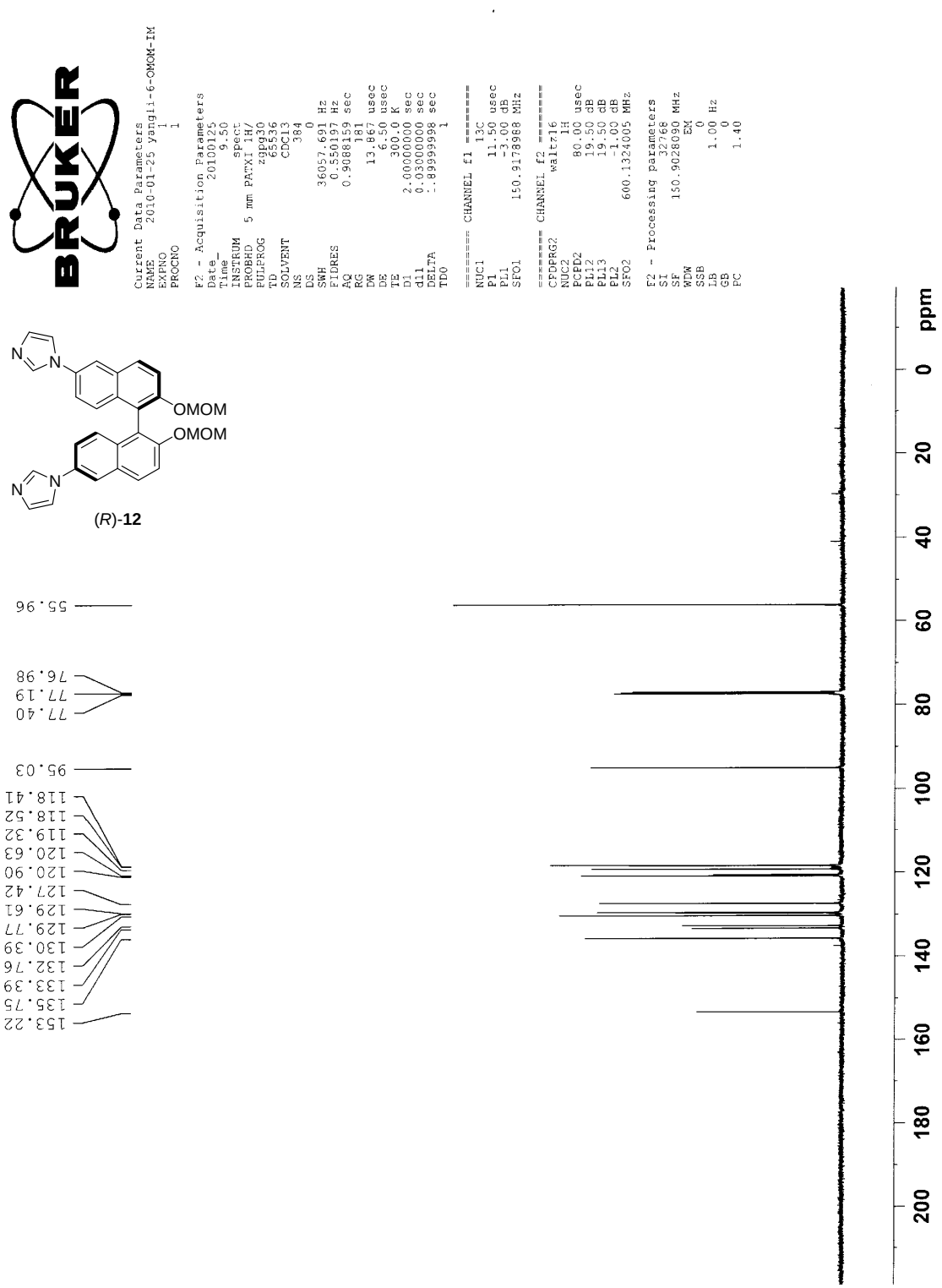
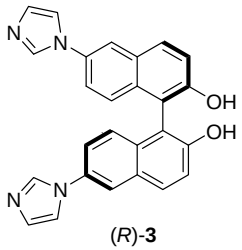
210
f1 (ppm)

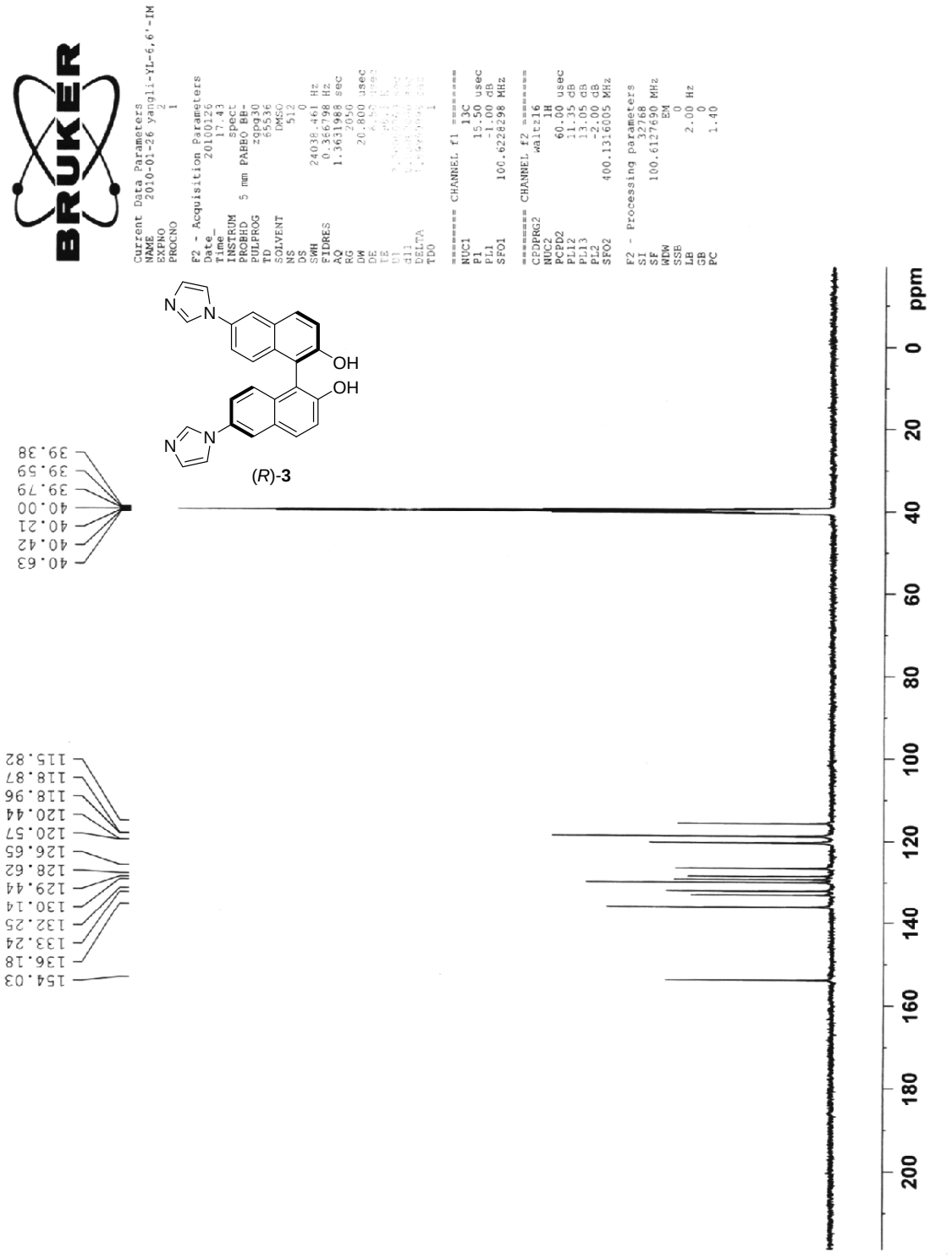

OMOM
OMOM
(R)-12
f1 (ppm)


Current Data Parameters
NAME 2010-01-25 yangli-6-OMOM-IM
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100125
Time 9.50
INSTRUM spect
PROBHD 5 mm PATX1 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 384
DS 0
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 181
DW 13.867 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA -.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.50 usec
PL1 -3.00 dB
SFO1 150.9178988 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 19.50 dB
PL13 19.50 dB
PL2 -1.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 32768
SF 150.9028090 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OMOM
OMOM
(R)-12
55.96
76.98
77.19
77.40
95.03
118.41
118.52
119.32
120.63
120.90
127.42
129.61
129.77
130.39
132.76
133.39
135.75
153.22
ppm


N
N
OH
OH
N
N

(*R*)-**3**

2.504
2.508
3.357
7.058
7.081
7.127
7.425
7.447
7.493
7.498
7.515
7.521
7.742
7.945
7.968
8.132
8.138
8.243
9.470
5.49
5.94 5.48 6.05 5.82
5.43 5.96 5.99 5.37
ppm


Current Data Parameters
NAME 2010-01-26 yangli-YL-6,6'-IM
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100126
Time_ 17.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 512
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE [illegible]
D1 [illegible]
d11 [illegible]
DELTA [illegible]
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 15.50 usec
PL1 -1.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 11.35 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
OH
OH
(R)-3
39.38
39.59
39.79
40.00
40.21
40.42
40.63
115.82
118.87
118.96
120.44
120.57
126.65
128.62
129.44
130.14
132.25
133.24
136.18
154.03
ppm
0
20
40
60
80
100
120
140
160
180
200