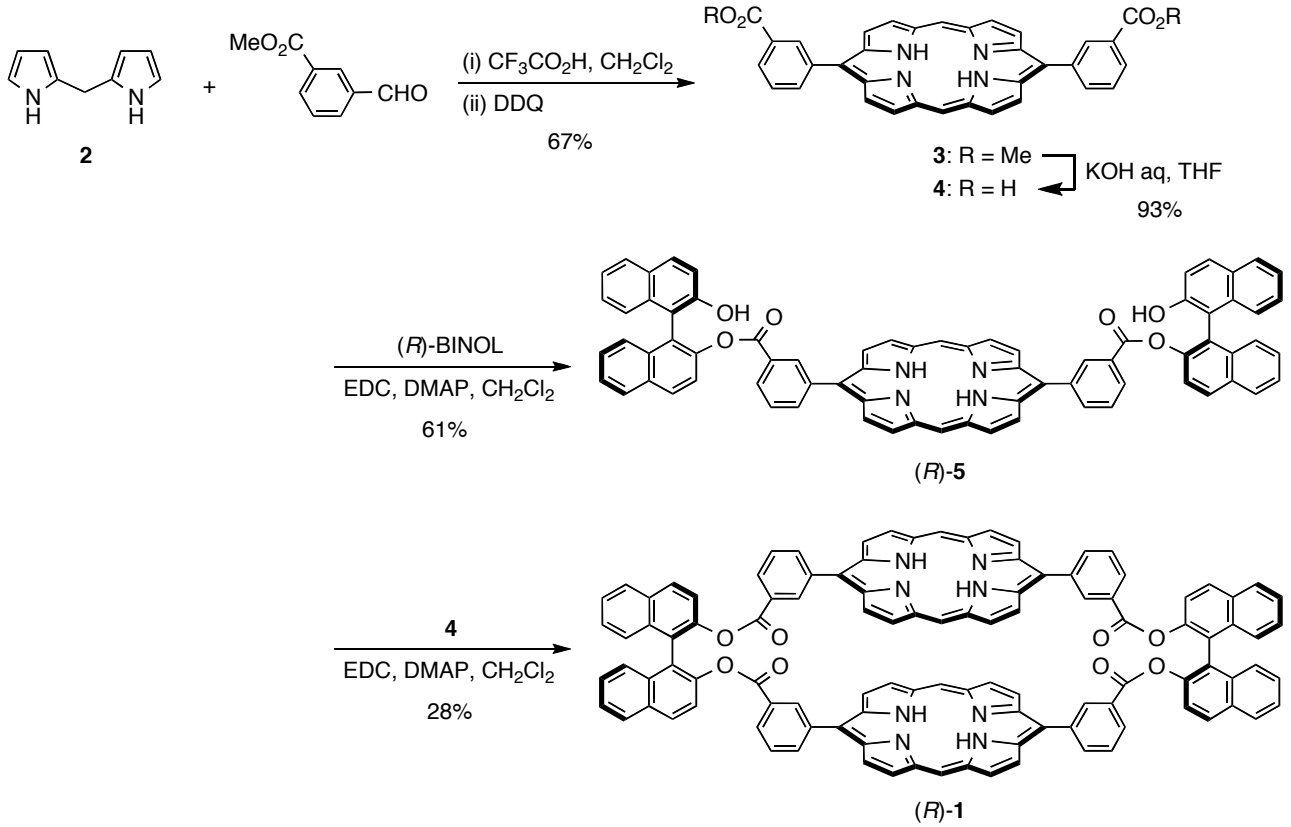
Supplementary Information

Chiral porphyrin dimer with a macrocyclic cavity for intercalation of aromatic guests

Tadashi Ema,* Norichika Ura, Katsuya Eguchi, Yuhei Ise and Takashi Sakai*
Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan

[1] Synthesis of Host Compound (*R*)-1.



5,15-Bis(3-methoxycarbonylphenyl)porphyrin (3).

A solution of dipyrromethane **2**[1] (914 mg, 6.25 mmol) and methyl 3-formylbenzoate (1.03 g, 6.27 mmol) in dry CH_2Cl_2 (1.2 L) was degassed with Ar for 15 min, and CF_3CO_2H (320 μL, 4.31 mmol) was then added. The mixture was vigorously stirred in the dark at room temperature for 14 h. DDQ (1.92 g, 8.44 mmol) was added, and the mixture was further stirred for 30 min. The solvent was removed under reduced pressure. Purification by a short pad of basic alumina ($CHCl_3$) twice gave **3** in 67%. Recrystallization from $CHCl_3$/hexane afforded **3** as reddish purple crystals (666 mg, 37%): mp >300 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ –3.14 (br s, 2H), 4.02 (s, 6H), 7.91 (t, J = 7.7 Hz, 2H), 8.46 (d, J = 7.7 Hz, 2H), 8.53 (d, J = 7.7 Hz, 2H), 8.96 (s, 2H), 9.02 (d, J = 4.2 Hz, 4H), 9.43 (d, J = 4.2 Hz, 4H), 10.36 (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 52.4, 105.5, 117.7, 127.1, 129.0, 130.7, 131.9, 135.1, 138.7, 141.6, 145.3, 146.9, 167.3; IR (KBr) 3287, 3132, 3023, 2953, 1725, 1577, 1435, 1409, 1300, 1272, 1241, 1196, 1104, 1079, 1065, 957, 854 cm^{-1}; Anal. Calcd for $C_{36}H_{26}N_4O_4$: C, 74.73; H, 4.53; N, 9.68. Found: C, 74.45; H, 4.57; N, 9.29; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{36}H_{27}N_4O_4$ 579.2032, found 579.2031 (M + H).

(*R*)-5,15-Bis[3-(2'-hydroxy-1,1'-binaphthyl-2-oxycarbonyl)phenyl]porphyrin ((*R*)-5).

To a solution of **3** (1.38 g, 2.38 mmol) in THF (480 mL) was added aqueous 2N KOH (100 mL), and the solution was heated at reflux for 14 h. After removal of THF, the mixture was acidified with conc. HCl. The resulting purple precipitate was filtered, washed with water and CH_2Cl_2, and dried in vacuo to give diacid **4**[2] (1.22 g, 93%). To a solution of **4** (660 mg, 1.20 mmol) and (*R*)-1,1'-bi-2-naphthol (1.72 g, 6.00 mmol) in dry CH_2Cl_2 (28 mL) under Ar were added

1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) (1.38 g, 7.20 mmol) and DMAP (1.76 g, 14.4 mmol), and the mixture was stirred at 40 °C for 23 h. The reaction was quenched with dil. HCl at 0 °C, and the product was extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography ($CHCl_3$/EtOAc (15:1)) afforded (*R*)-**5** in 61%. Recrystallization from $CHCl_3$/hexane afforded (*R*)-**5** as purple crystals (619 mg, 47%): mp >300 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ –3.17 (br s, 2H), 5.26 (br s, 2H), 6.46–6.50 (m, 2H), 6.91–6.94 (m, 2H), 7.04 (dd, *J* = 8.1, 11.7 Hz, 2H), 7.09 (dd, *J* = 2.1, 8.1 Hz, 2H), 7.19 (dd, *J* = 5.1, 9.0 Hz, 2H), 7.35–7.36 (m, 4H), 7.48–7.53 (m, 4H), 7.70–7.74 (m, 4H), 8.00 (dd, *J* = 3.0, 8.4 Hz, 2H), 8.13–8.16 (m, 4H), 8.30–8.34 (m, 4H), 8.70 (t, *J* = 4.2 Hz, 2H), 8.84 (t, *J* = 4.2 Hz, 2H), 9.40–9.43 (m, 4H), 10.38 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 105.5, 113.8, 117.4, 117.9, 121.8, 122.9, 123.0, 124.3, 125.7, 126.3, 126.5, 127.0, 127.51, 127.54, 127.6, 127.76, 127.77, 128.4, 128.7, 129.2, 130.3, 130.78, 130.81, 131.9, 132.2, 133.3, 135.1, 135.2, 139.1, 139.2, 141.5, 145.3, 146.8, 148.3, 151.6, 165.9; IR (KBr) 3466, 3063, 1715, 1622, 1578, 1508, 1412, 1344, 1271, 1246, 1200, 1146, 1055, 974, 928, 897, 849, 737 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{74}H_{47}N_4O_6$ 1087.3496, found 1087.3511 (M + H).

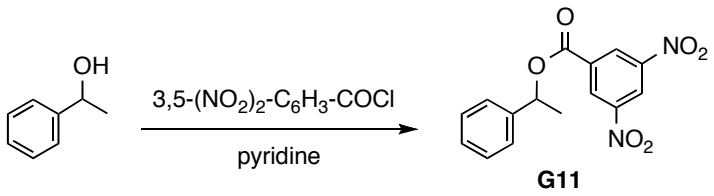
Macrocyclic Chiral Diporphyrin (*R*)-1.

To a solution of diacid **4** (421 mg, 0.764 mmol) and (*R*)-**5** (754 mg, 0.693 mmol) in dry CH_2Cl_2 (71 mL) under Ar were added EDC (797 mg, 4.16 mmol) and DMAP (1.02 g, 8.32 mmol), and the mixture was stirred at 40 °C for 14 h. The reaction was quenched with water at 0 °C, and the product was extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography ($CHCl_3$) afforded (*R*)-**1** as purple crystals (308 mg, 28%): mp >300 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ –6.92 (br s, 4H), 7.44 (t, *J* = 7.2 Hz, 4H), 7.48 (d, *J* = 7.2 Hz, 4H), 7.56 (dt, *J* = 1.2, 8.1 Hz, 4H), 7.62–7.66 (m, 8H), 7.96 (d, *J* = 8.1 Hz, 4H), 8.02 (dt, *J* = 1.2, 7.2 Hz, 4H), 8.08 (d, *J* = 8.1 Hz, 4H), 8.20 (d, *J* = 8.1 Hz, 4H), 8.55 (d, *J* = 4.2 Hz, 4H), 8.75 (d, *J* = 4.2 Hz, 4H), 8.80 (d, *J* = 4.2 Hz, 4H), 8.81 (d, *J* = 4.2 Hz, 4H), 8.83 (s, 4H), 9.84 (s, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 103.5, 115.4, 121.7, 124.6, 125.9, 126.9, 127.0, 127.1, 127.8, 128.1, 128.2, 128.7, 129.7, 130.1, 130.7, 132.0, 132.3, 133.9, 135.7, 140.1, 140.9, 141.0, 142.1, 145.7, 147.5, 147.6, 165.4; IR (KBr) 3279, 3063, 1738, 1732, 1580, 1510, 1472, 1412, 1292, 1242, 1219, 1188, 1169, 1063, 1011, 961, 943, 895, 849, 791, 723 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{108}H_{65}N_8O_8$ 1601.4925, found 1601.4933 (M + H).

[2] Synthesis of Guest Compounds.

Typical Procedure for G11 and G12. To a solution of 3,5-dinitrobenzoyl chloride (553 mg, 2.40 mmol) in pyridine (1.6 mL) under N_2 in an ice bath was added alcohol (2.10 mmol). The mixture was stirred at room temperature overnight. The reaction was quenched with water, and the product was extracted with EtOAc. The organic layer was dried over $MgSO_4$, and concentrated.

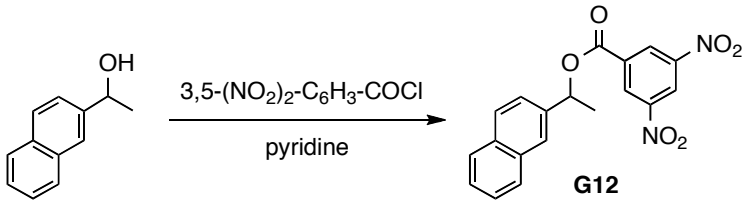
Preparation of G11.



G11

Recrystallization from EtOAc afforded (*R*)-**G11** as slightly yellow crystals (92%).[3] The opposite enantiomer was also prepared in the same way: mp 117–118 °C; $[\alpha]^{22}_{D}$ = –32.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.76 (d, *J* = 6.6 Hz, 3H), 6.22 (q, *J* = 6.6 Hz, 1H), 7.34–7.37 (m, 1H), 7.40–7.43 (m, 2H), 7.46–7.48 (m, 2H), 9.17 (d, *J* = 2.2 Hz, 2H), 9.22 (t, *J* = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.9, 75.5, 122.3, 126.3, 128.6, 128.8, 129.4, 134.1, 140.1, 148.6, 161.8; IR (KBr) 3094, 3032, 2976, 2922, 2883, 1728, 1630, 1539, 1497, 1456, 1383, 1346, 1277, 1215, 1167, 1072, 1055, 1026, 1009, 993, 937, 922, 864, 835, 761, 738, 719 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{12}N_2O_6$ 316.0695, found 316.0689 (M^+).

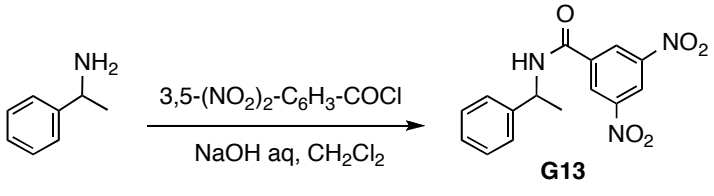
Preparation of G12.



G12

Purification by silica gel column chromatography (CH_2Cl_2) afforded **G12** as a slightly yellow powder (97%):[4] mp 150–150.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.86 (d, *J* = 6.8 Hz, 3H), 6.39 (q, *J* = 6.8 Hz, 1H), 7.49–7.53 (m, 2H), 7.59 (dd, *J* = 1.6, 8.8 Hz, 1H), 7.84–7.91 (m, 4H), 9.18 (d, *J* = 2.0 Hz, 2H), 9.22 (t, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 75.6, 122.2, 123.8, 125.6, 126.50, 126.53, 127.7, 128.0, 128.7, 129.3, 133.0, 133.2, 134.0, 137.4, 148.5, 161.8; IR (KBr) 3109, 2982, 2935, 2878, 1732, 1628, 1535, 1460, 1346, 1273, 1167, 1126, 1063, 1024, 914, 862, 822, 756, 731, 720 cm^{-1}; Anal. Calcd for $C_{19}H_{14}N_2O_6$: C, 62.30; H, 3.85; N, 7.65. Found: C, 62.24; H, 3.82; N, 7.45; HRMS (EI) calcd for $C_{19}H_{14}N_2O_6$ 366.0852, found 366.0852 (M^+).

Preparation of G13.

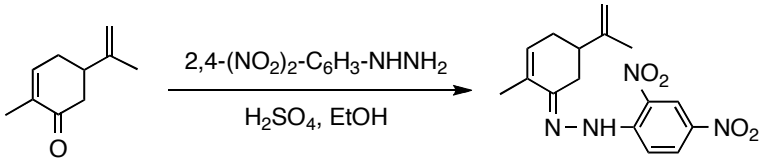


G13

Amide (*R*)-**G13** was obtained in 73% yield as white crystals according to the literature.[5] The

opposite enantiomer was also prepared in the same way: mp 154–156 °C; $[\alpha]^{22}_{D}$ = –5.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.69 (d, *J* = 7.0 Hz, 3H), 5.36 (quint, *J* = 7.0 Hz, 1H), 6.57 (d, *J* = 7.0 Hz, 1H), 7.30–7.34 (m, 1H), 7.37–7.42 (m, 4H), 8.93 (d, *J* = 2.1 Hz, 2H), 9.16 (t, *J* = 2.1 Hz, 1H); IR (KBr) 3341, 3096, 2980, 2876, 1634, 1539, 1456, 1346, 1277, 1211, 1186, 1124, 1090, 1015, 918, 833, 764, 704, 662 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{13}N_3O_5$ 315.0855, found 315.0864 (M^+).

Preparation of G14.



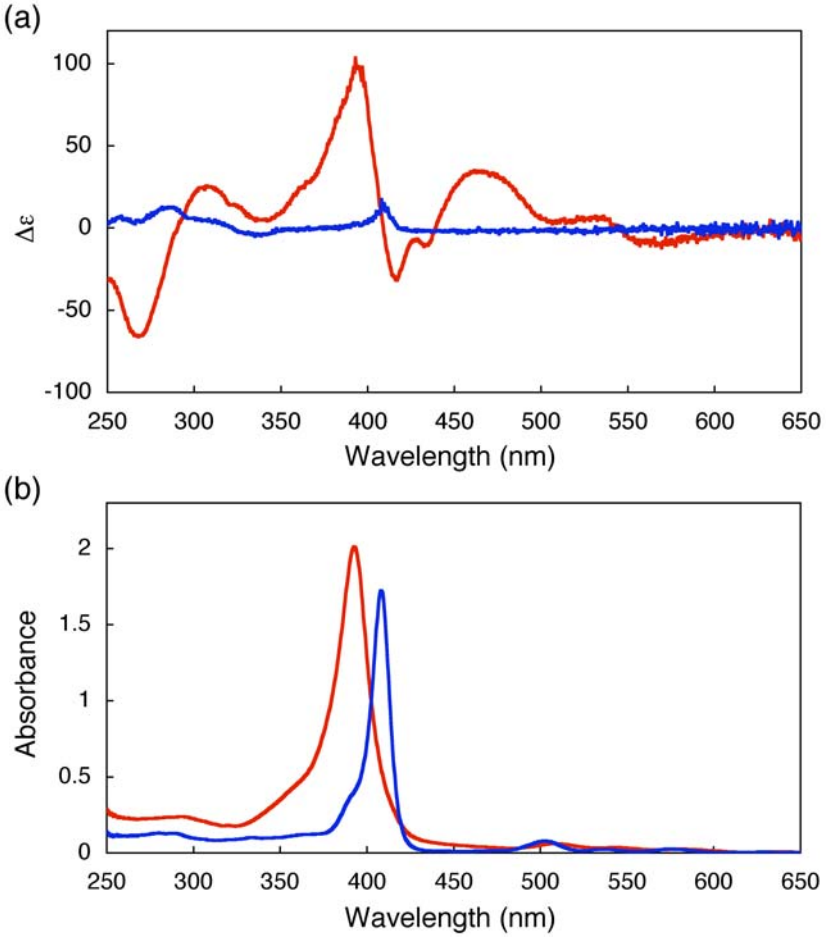
G14

To a solution of 2,4-dinitrophenylhydrazine (170 mg, 0.86 mmol) in EtOH (30 mL) was added 5 drops of H_2SO_4, and the mixture was heated until 2,4-dinitrophenylhydrazine was dissolved. After cooling, a solution of ketone (0.86 mmol) in EtOH (4 mL) and H_2O (2 mL) was added, and the mixture was stirred at room temperature. The reaction was monitored by TLC. Saturated aqueous $NaHCO_3$ was added to neutralize the solution, and the product was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, and concentrated. Recrystallization from CH_2Cl_2 afforded (*R*)-**G14** as orange crystals (74%).[6] The opposite enantiomer was also prepared in the same way: mp 194–196 °C; $[\alpha]^{22}_{D}$ = –116 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.81 (s, 3H), 2.00 (s, 3H), 2.19–2.25 (m, 1H), 2.30 (dd, *J* = 12.3, 15.6 Hz, 1H), 2.36–2.41 (m, 1H), 2.52–2.56 (m, 1H), 2.87 (dd, *J* = 3.6, 15.6 Hz, 1H), 4.84 (s, 1H), 4.88 (s, 1H), 6.27–6.28 (m, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 8.32–8.34 (m, 1H), 9.15 (d, *J* = 2.4 Hz, 1H), 11.31 (s, 1H); IR (KBr) 3294, 3109, 2968, 2916, 1614, 1591, 1539, 1497, 1420, 1333, 1250, 1217, 1128, 1088, 1045, 891, 849, 833, 741 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{18}N_4O_4$ 330.1328, found 330.1313 (M^+).

References

1 B. J. Littler, M. A. Miller, C.-H. Hung, R. W. Wagner, D. F. O'Shea, P. D. Boyle and J. S. Lindsey, *J. Org. Chem.*, 1999, **64**, 1391–1396.
2 T. B. Norsten, K. Chichak and N. R. Branda, *Tetrahedron*, 2002, **58**, 639–651.
3 M.-J. Brienne, A. Collet and J. Jacques, *Synthesis*, 1983, 704–705.
4 C. Minguillón, P. Franco and L. Oliveros, *J. Chromatogr. A*, 1996, **728**, 415–422.
5 Z.-Y. Chang and R. M. Coates, *J. Org. Chem.*, 1990, **55**, 3475–3483.
6 A. J. Mancuso, D. S. Brownfain and D. Swern, *J. Org. Chem.*, 1979, **44**, 4148–4150.

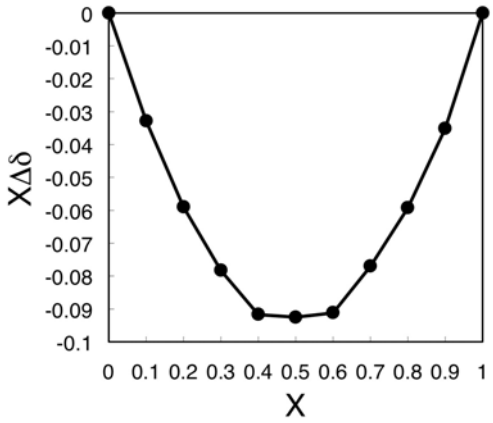
[3] UV–Vis and CD Spectra of (*R*)-1 and (*R*)-5.



(a) CD and (b) UV–Vis spectra of (*R*)-**1** (red) and (*R*)-**5** (blue) in $CHCl_3$.

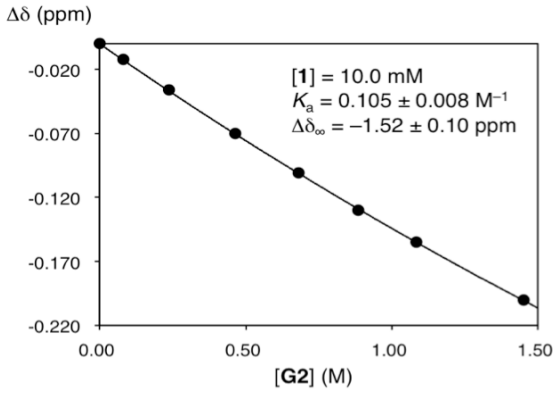
[4] Job Plots.

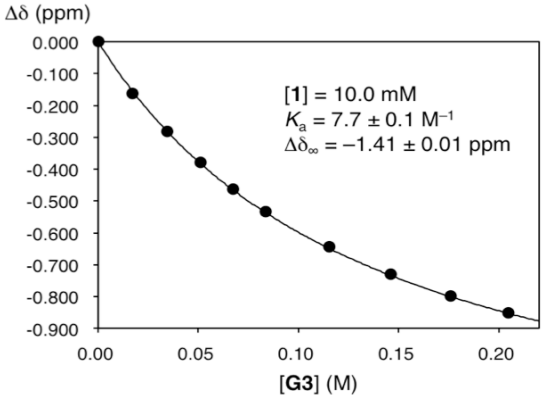
The stoichiometry of the host–guest complex was investigated by Job plots. The plots for the complexation between **1** and **G6** are shown, where X is the mole fraction of **1** (X = [**1**]/([**1**] + [**G6**])) with the total concentration of the two compounds being kept constant (10 mM) while $\Delta\delta$ is the chemical-shift change of the H_a protons of **1** upon complexation. The plots exhibit a minimum at X = 0.5, indicating 1:1 complexation.

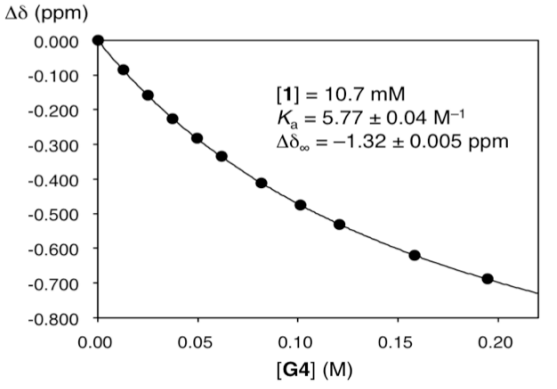


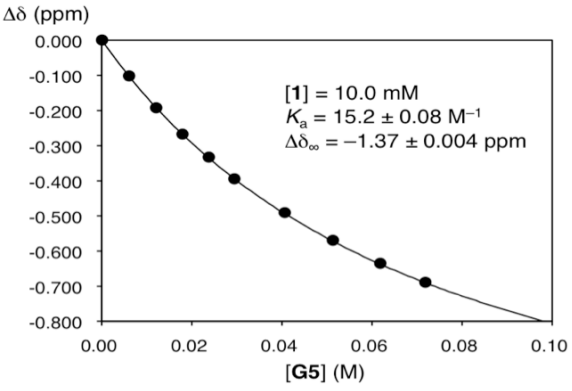
[5] Determination of Binding Constants by NMR Titration.

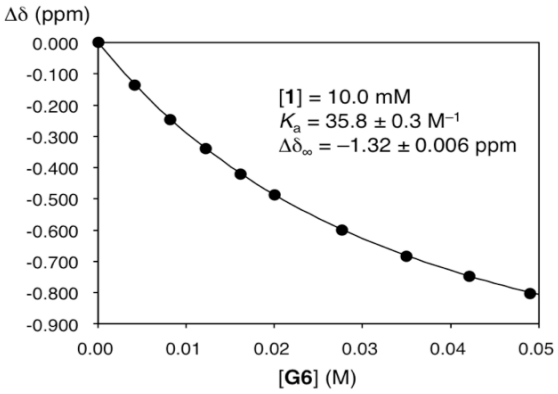
To a solution of **1** (10 mM) in $CDCl_3$ (0.6 mL) was added a small amount of $CDCl_3$ containing guest, and ^1H NMR was then measured at 25 °C. The change in the H_a signal of **1** was monitored at several different concentrations of guest. Assuming 1:1 complexation, the binding constant was calculated by the nonlinear least-squares curve-fitting method.

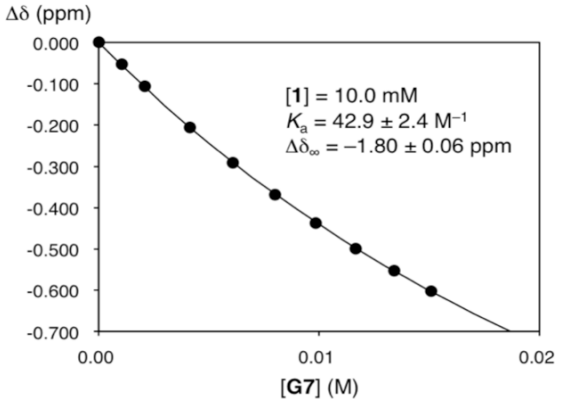


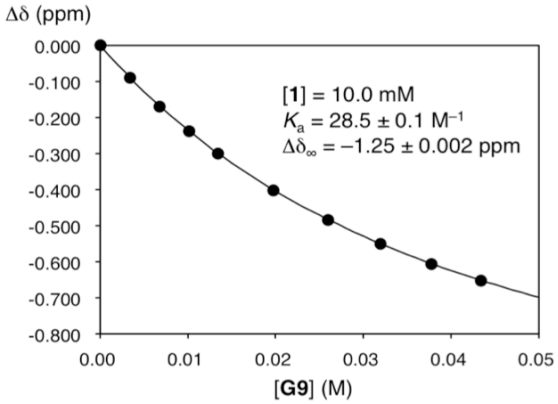


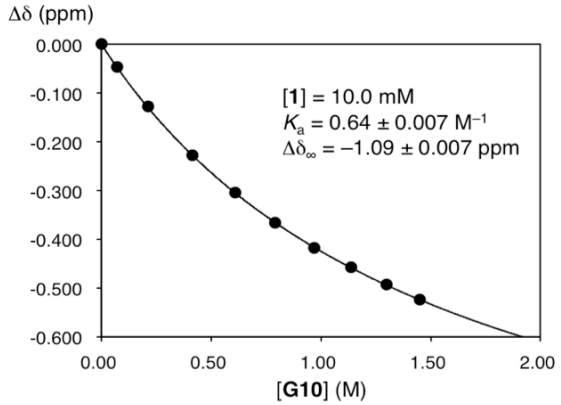





Δδ (ppm)
0.000
-0.100
-0.200
-0.300
-0.400
-0.500
-0.600
-0.700
-0.800
-0.900
0.00
0.01
0.02
0.03
0.04
0.05
[G6] (M)
[1] = 10.0 mM
Ka = 35.8 ± 0.3 M–1
Δδ∞ = –1.32 ± 0.006 ppm

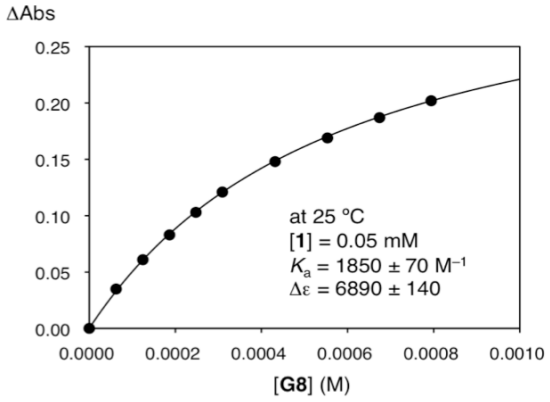

Δδ (ppm)
0.000
-0.100
-0.200
-0.300
-0.400
-0.500
-0.600
-0.700
0.00
0.01
0.02
[G7] (M)
[1] = 10.0 mM
Ka = 42.9 ± 2.4 M–1
Δδ∞ = –1.80 ± 0.06 ppm

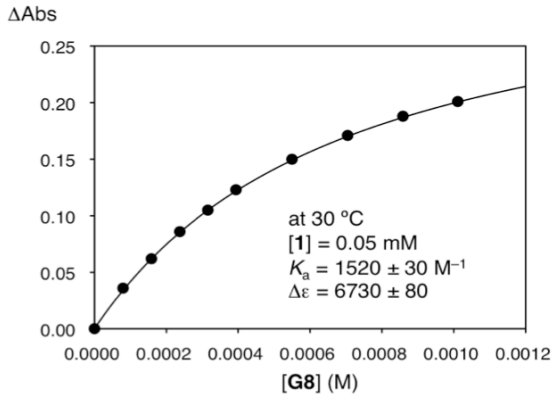

Δδ (ppm)
0.000
-0.100
-0.200
-0.300
-0.400
-0.500
-0.600
-0.700
-0.800
0.00
0.01
0.02
0.03
0.04
0.05
[G9] (M)
[1] = 10.0 mM
Ka = 28.5 ± 0.1 M–1
Δδ∞ = –1.25 ± 0.002 ppm

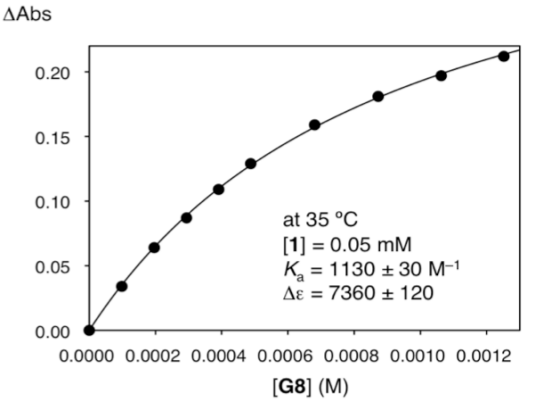

Δδ (ppm)
0.000
-0.100
-0.200
-0.300
-0.400
-0.500
-0.600
0.00
0.50
1.00
1.50
2.00
[G10] (M)
[1] = 10.0 mM
Ka = 0.64 ± 0.007 M–1
Δδ∞ = –1.09 ± 0.007 ppm

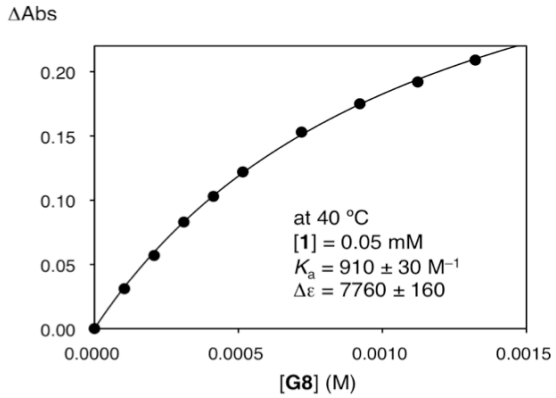
[6] Determination of Binding Constants by UV–Vis Titration.

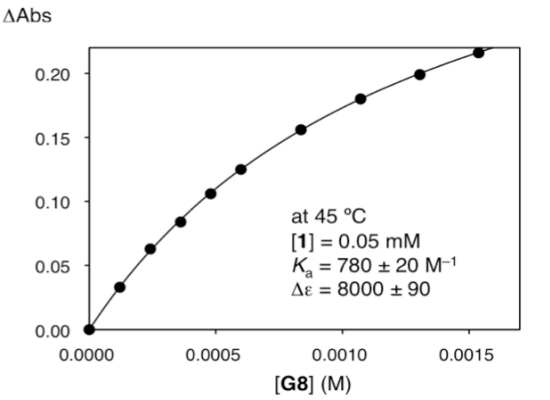
To a solution of **1** (50 μM) in $CHCl_3$ (3.0 mL) was added a small amount of $CHCl_3$ containing **G8**, and UV–Vis spectrum was then measured at a constant temperature. The absorbance change at 505 nm was monitored at several different concentrations of **G8**. Several isosbestic points were observed, indicating 1:1 complexation. The binding constant was calculated by the nonlinear least-squares curve-fitting method. The thermodynamic parameters were obtained by the van't Hoff plots.

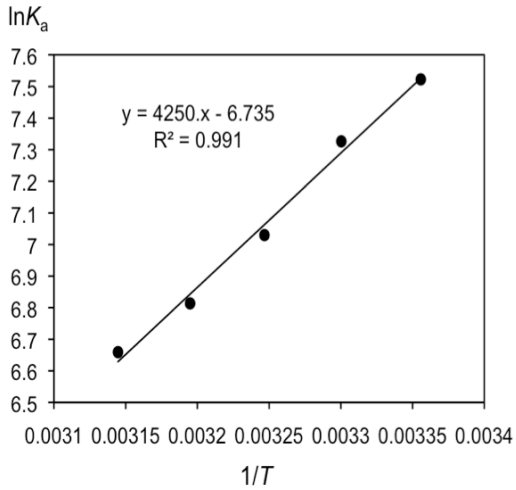




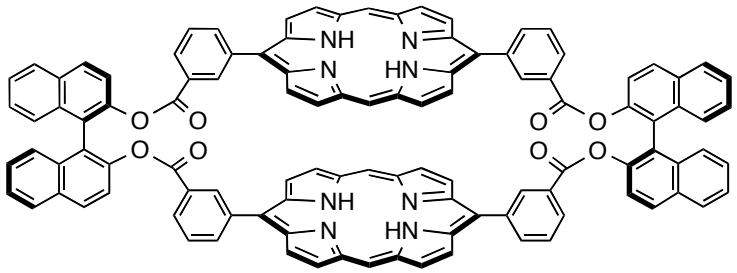




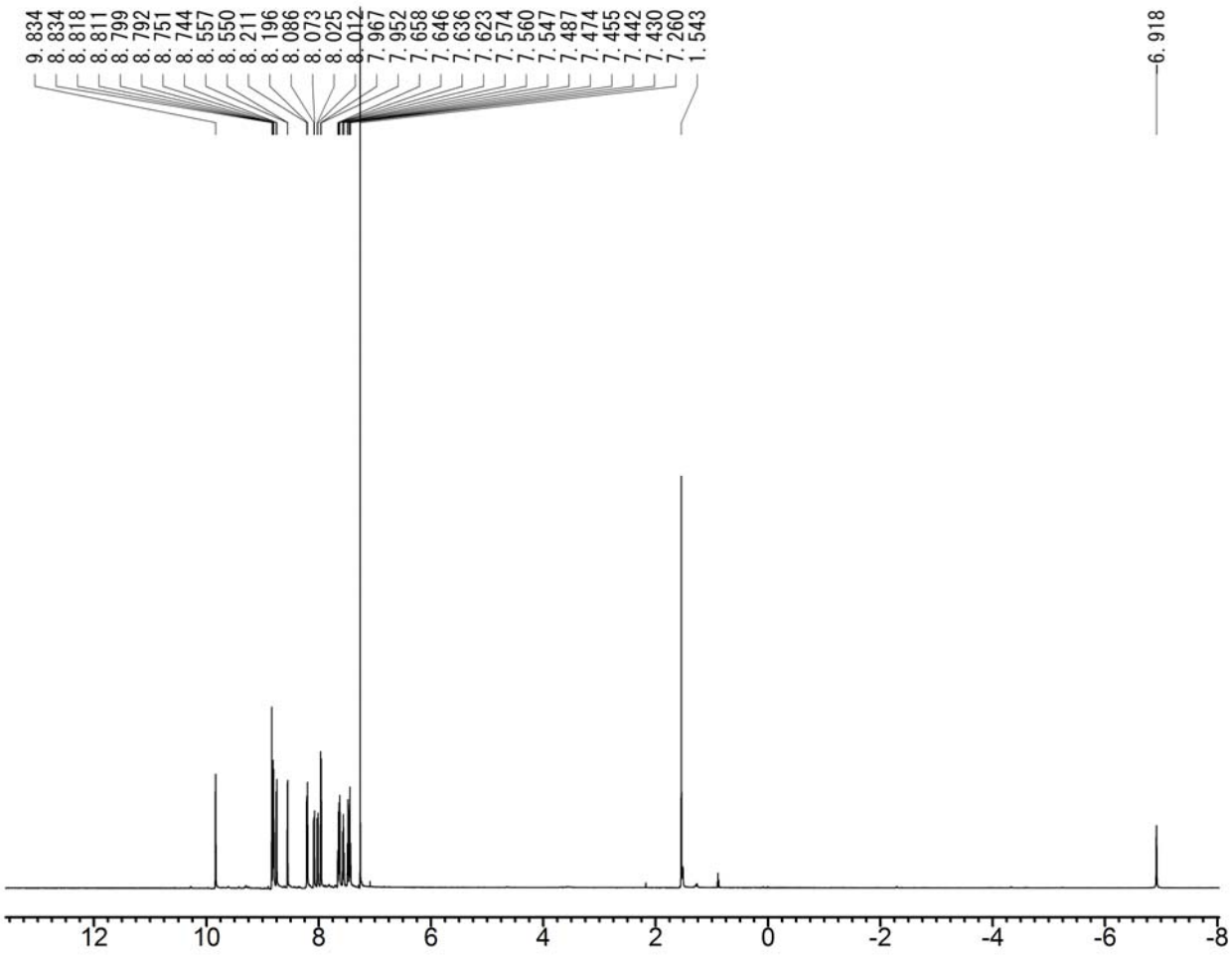




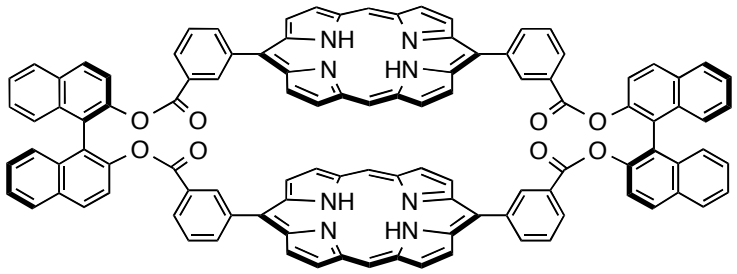
[7] ^{1}H and ^{13}C NMR Spectra.



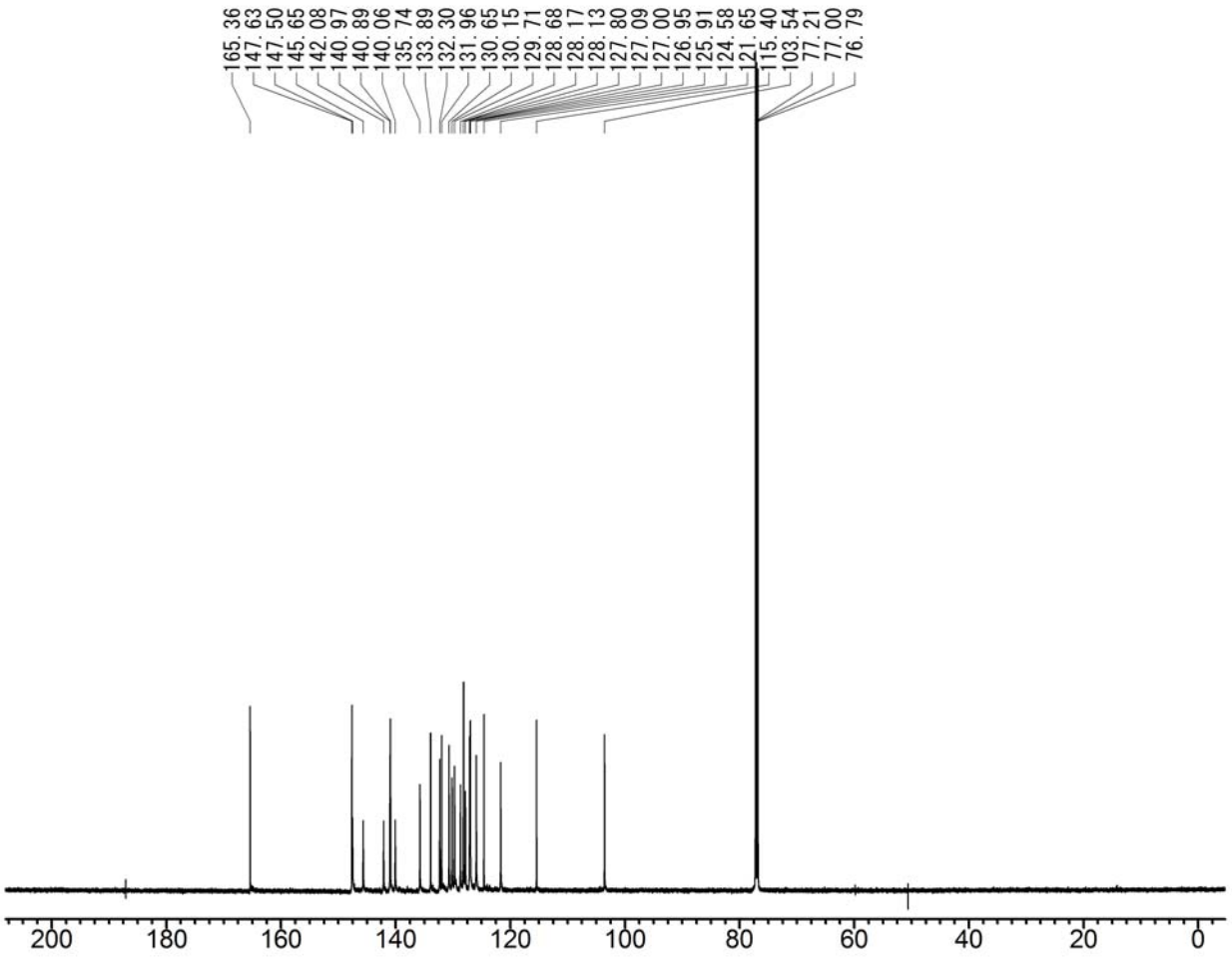
(*R*)-**1**



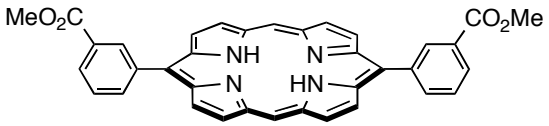
600 MHz ^{1}H NMR of (*R*)-**1** in $CDCl_3$.



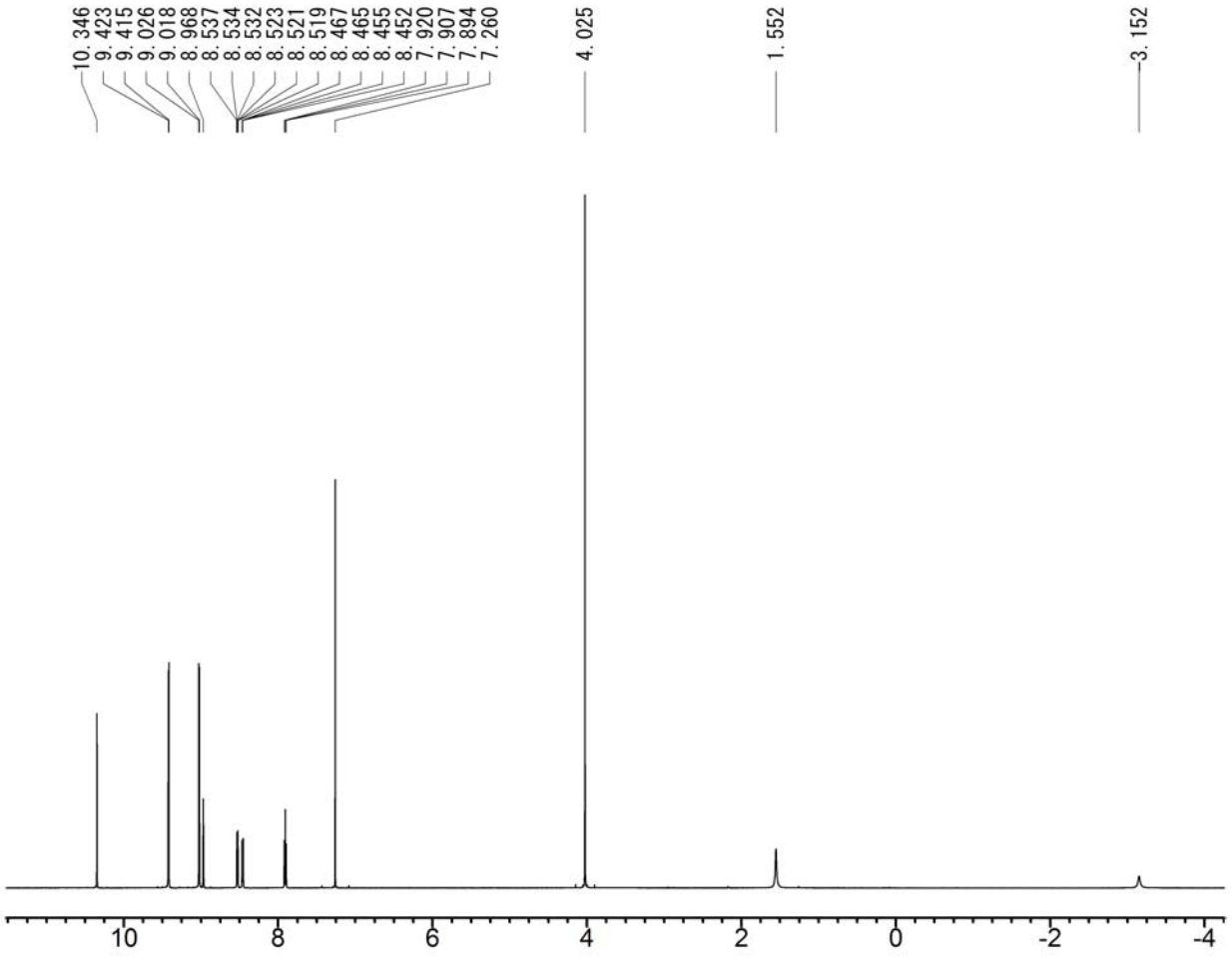
(*R*)-**1**



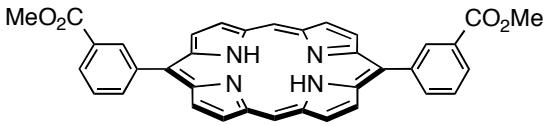
150 MHz ^{13}C NMR of (*R*)-**1** in $CDCl_3$.



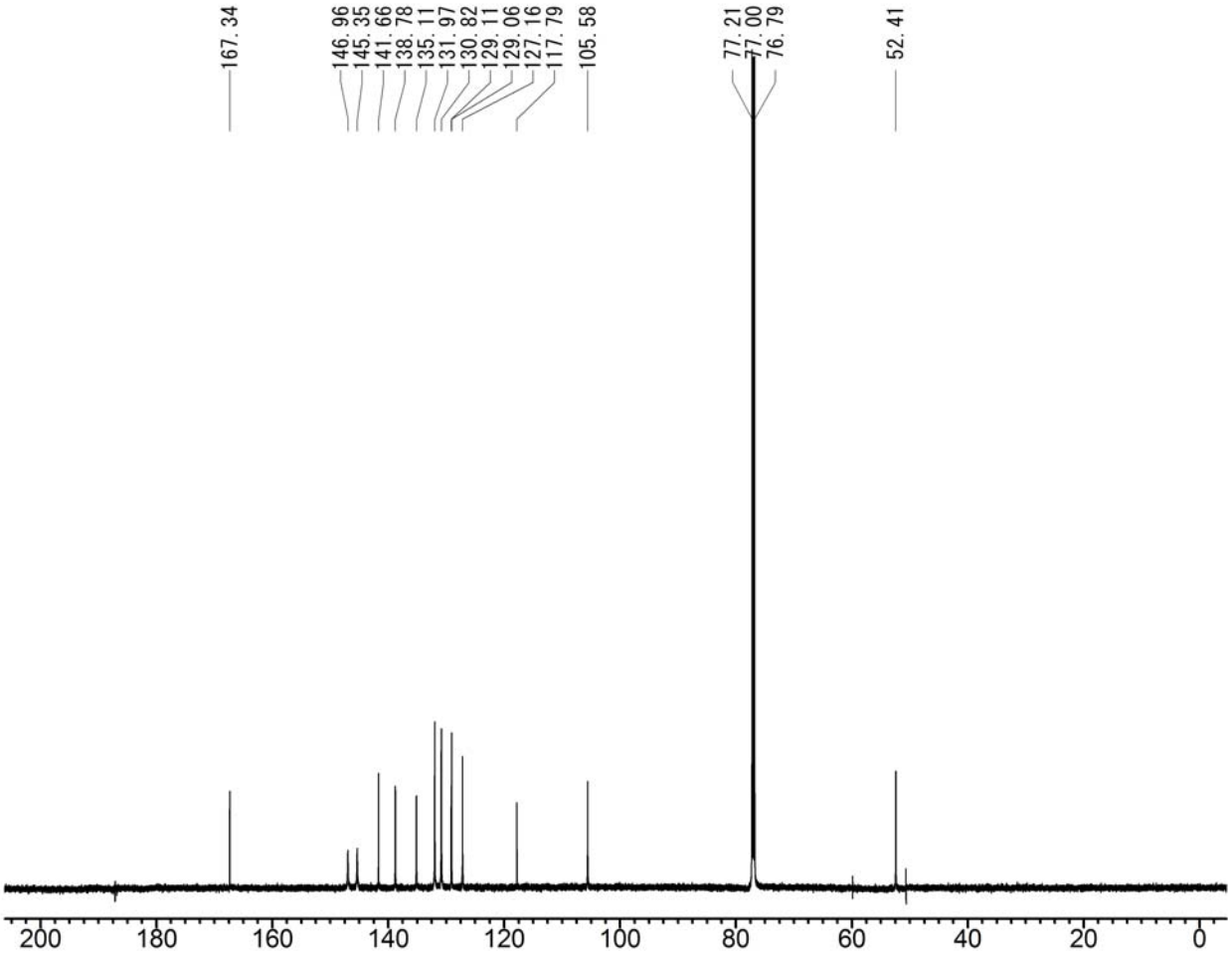
3



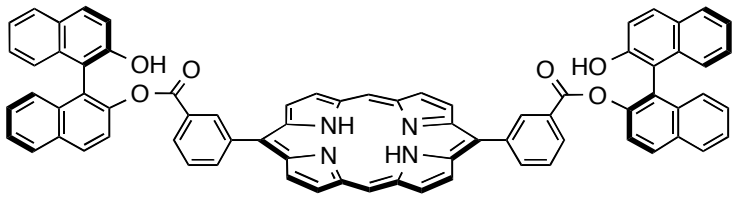
600 MHz ^{1}H NMR of **3** in $CDCl_3$.



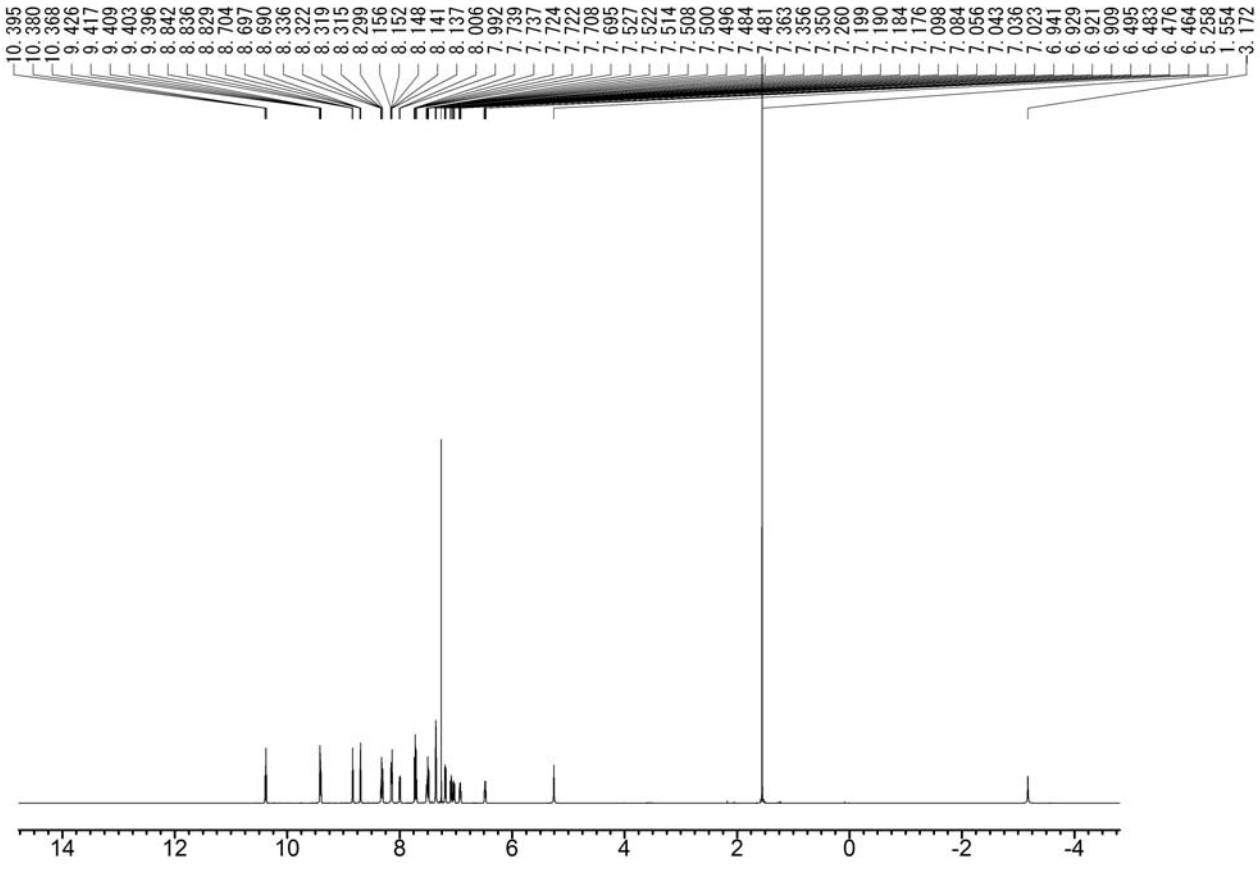
3



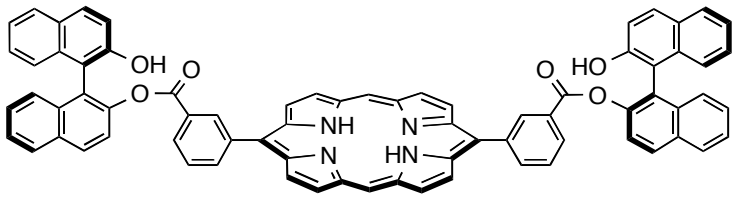
150 MHz ^{13}C NMR of **3** in $CDCl_3$.



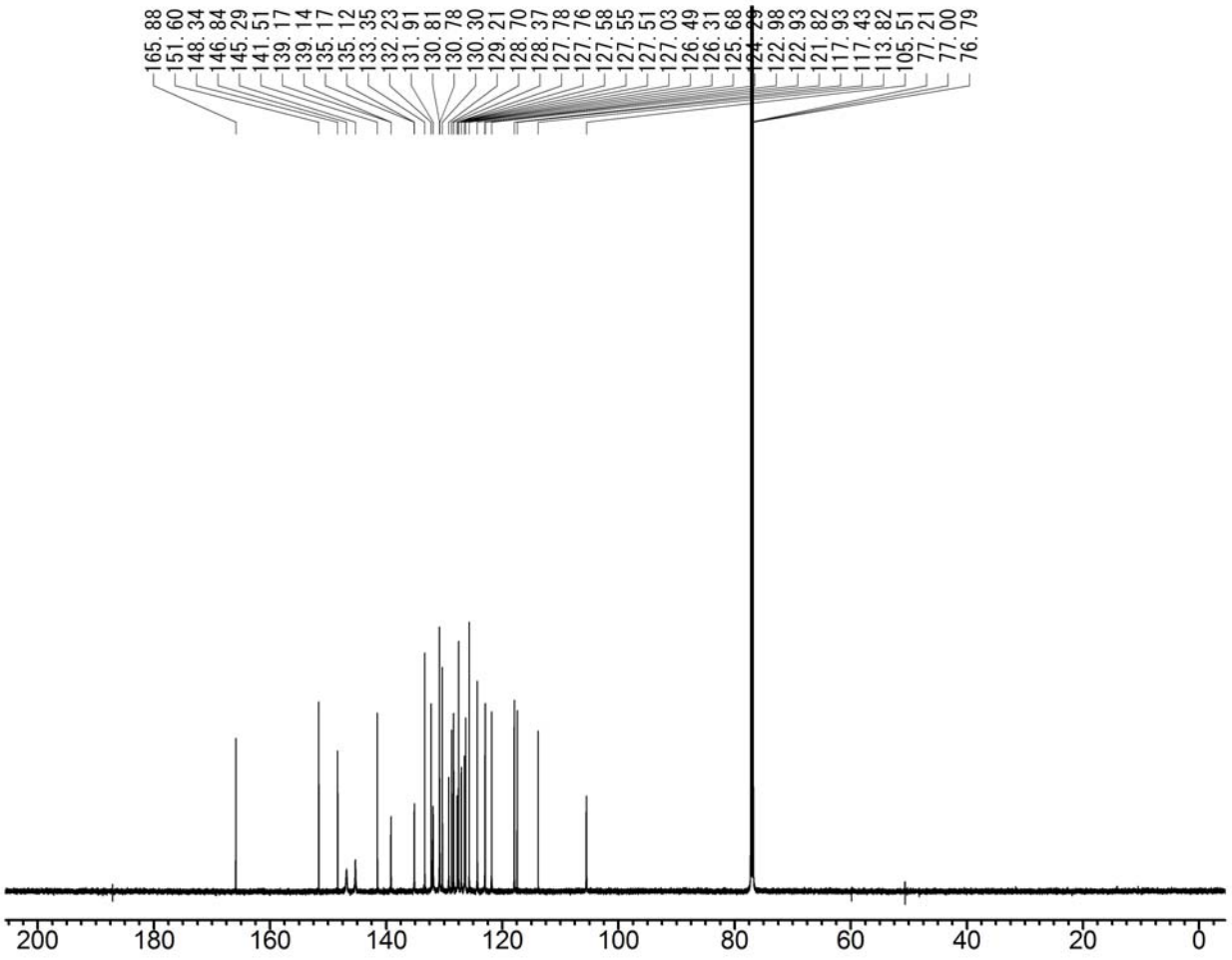
(*R*)-**5**



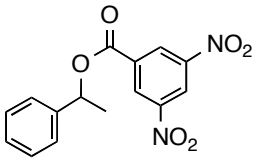
600 MHz ^{1}H NMR of (*R*)-**5** in $CDCl_3$.



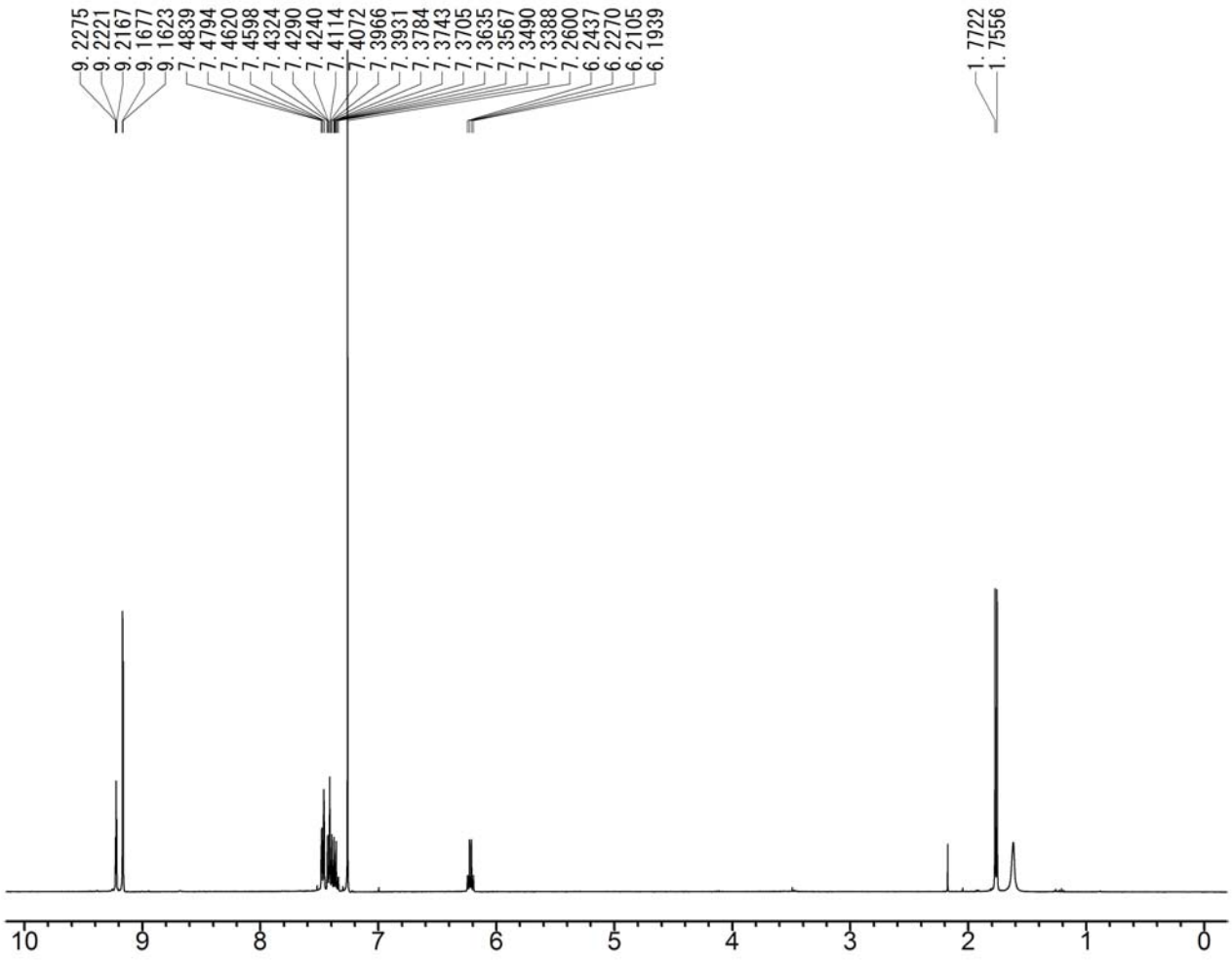
(*R*)-**5**



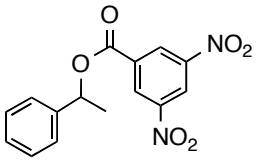
150 MHz ^{13}C NMR of (*R*)-**5** in $CDCl_3$.



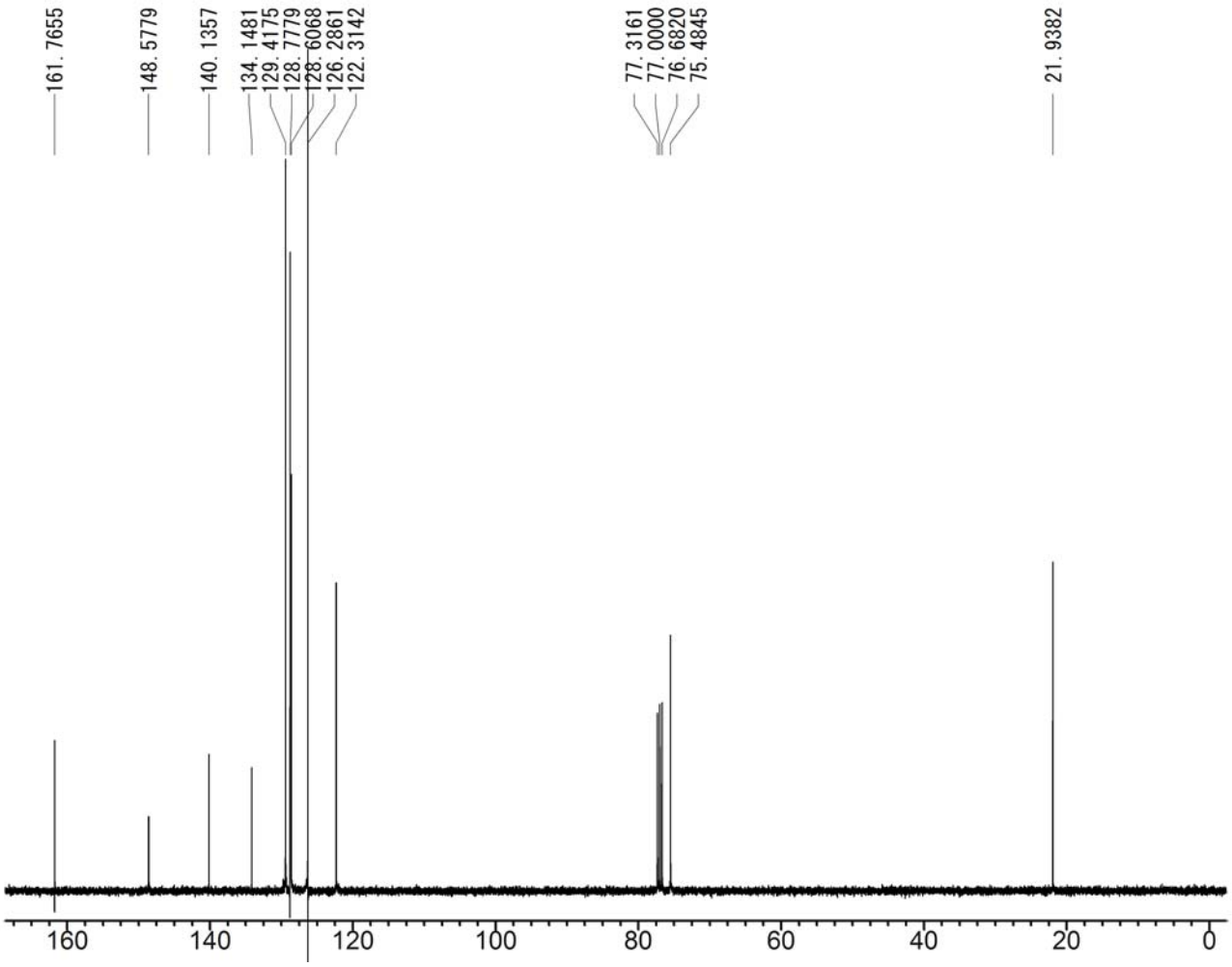
G11



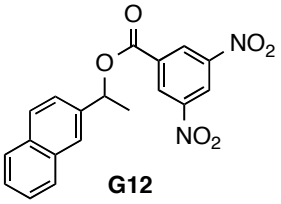
400 MHz ^{1}H NMR of **G11** in $CDCl_3$.



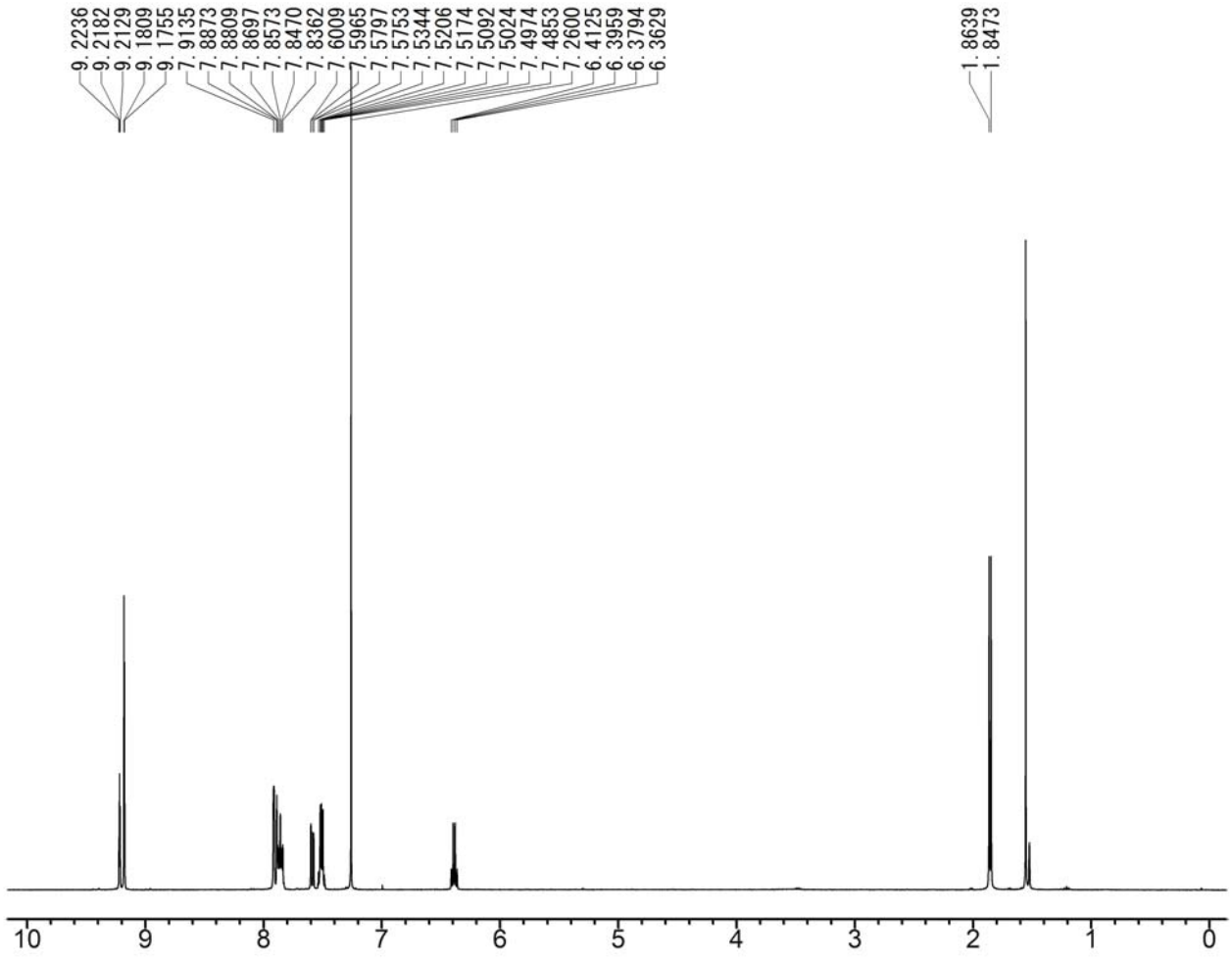
G11



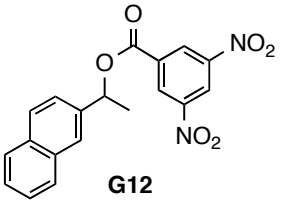
100 MHz ^{13}C NMR of **G11** in $CDCl_3$.



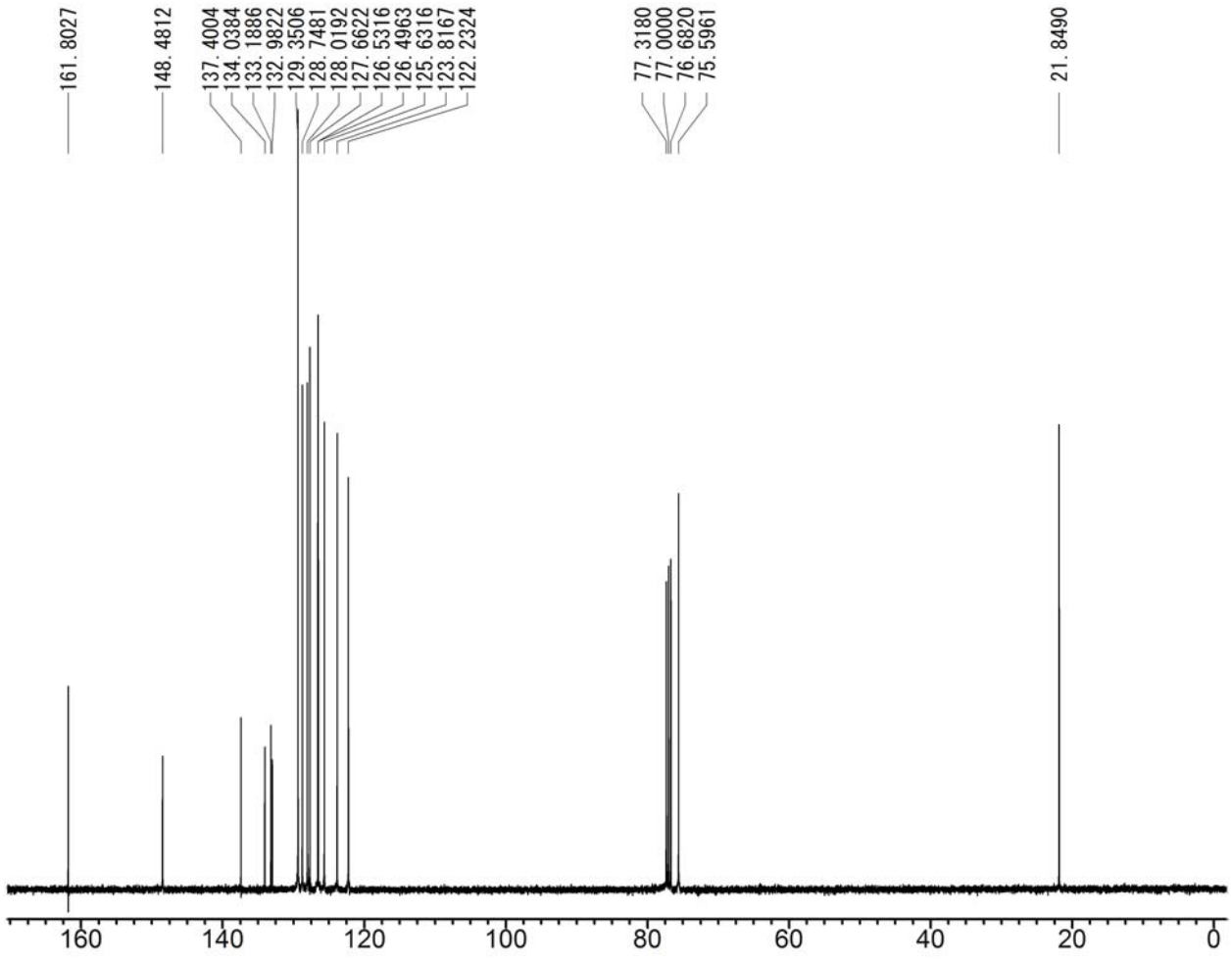
G12



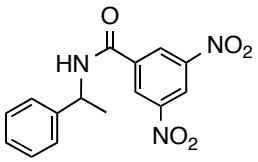
400 MHz ^{1}H NMR of **G12** in $CDCl_3$.



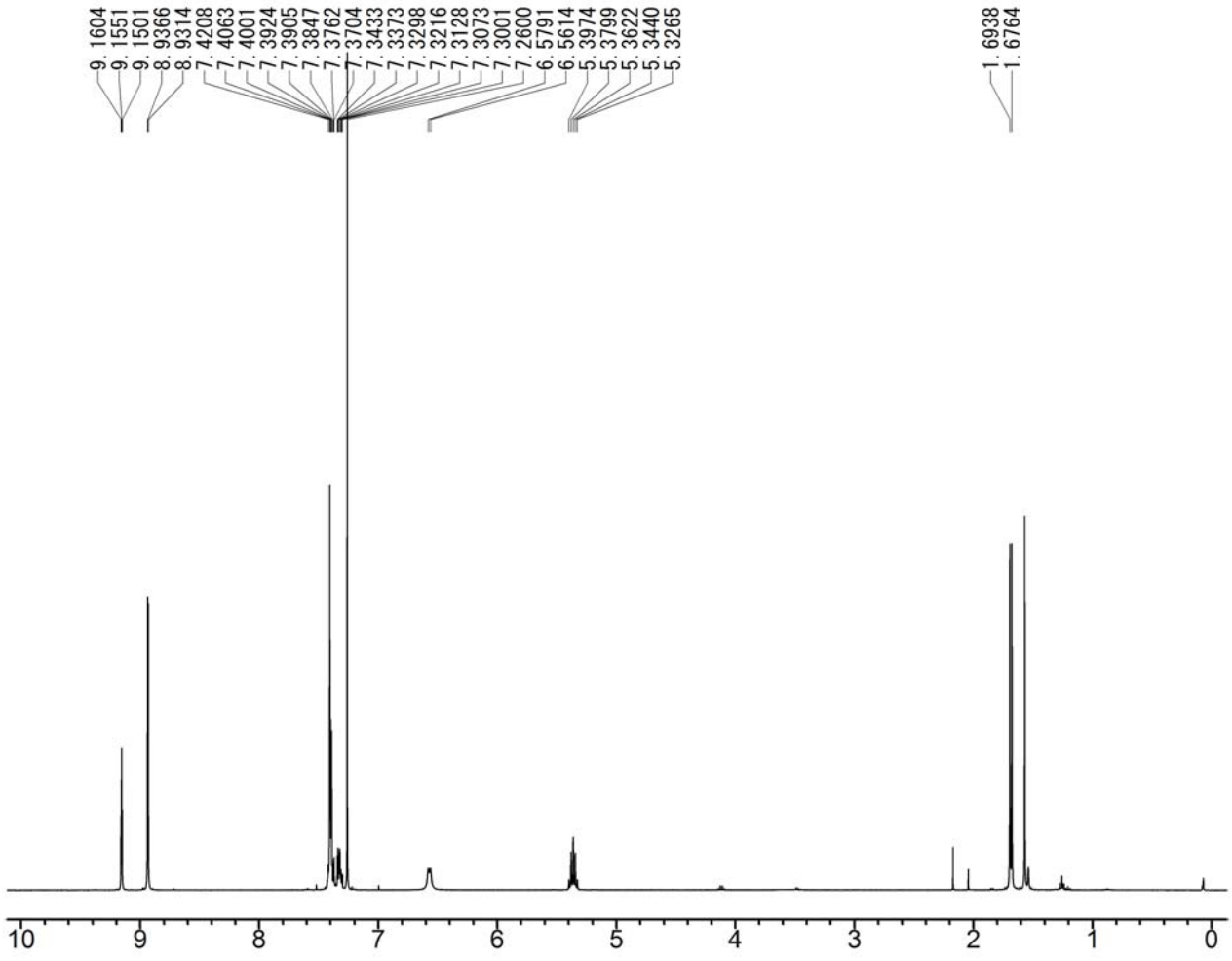
G12



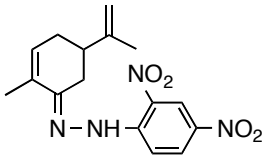
100 MHz ^{13}C NMR of **G12** in $CDCl_3$.



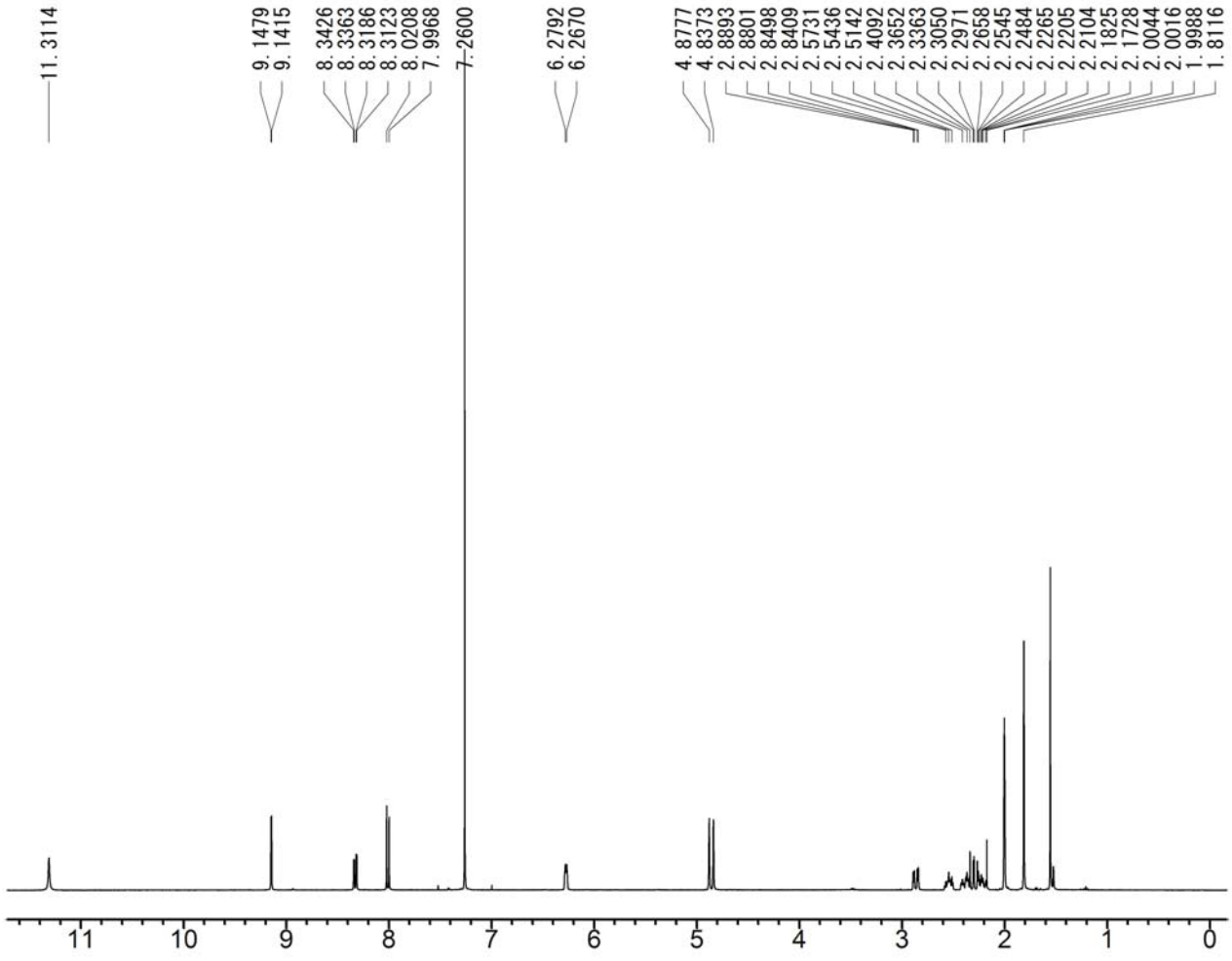
G13



400 MHz ^{1}H NMR of **G13** in $CDCl_3$.



G14



400 MHz ^{1}H NMR of **G14** in $CDCl_3$.

[8] MM Calculations.

MM calculations on (*R*)-**1** were done with CAChe WorkSystem Pro ver. 5.02 (Fujitsu), where the structures were optimized by the MM3 method.

The coordinates for the optimized structure of (*R*)-**1**.

E = 181.3110 kcal/mol

1	C	0.00000000	0.00000000	0.00000000
2	C	-1.08078075	-0.42942790	-0.90620780
3	N	1.17200990	-0.20535798	-0.62918596
4	C	0.95372896	-0.72042786	-1.85555671
5	C	-0.50568893	-0.86426873	-2.02698144
6	C	-0.19166403	0.52103509	1.27959928
7	H	-2.16191891	-0.39011390	-0.69829578
8	C	4.25960474	1.52362501	3.33829120
9	C	0.83210325	0.91765619	2.14454251
10	H	-1.02854490	-1.24930371	-2.91737840
11	N	2.20376473	0.91064718	1.98710443
12	C	0.62749825	1.42703619	3.43169754
13	C	2.88225750	1.37816001	3.09892503
14	C	1.86592361	1.70418525	4.00967671
15	C	5.22740877	1.19351101	2.38050917
16	N	5.01077083	0.70926219	1.14184255
17	C	6.18378789	0.50561117	0.51425449
18	C	6.68846128	1.31384197	2.56152011
19	C	7.26524937	0.90138193	1.43382396
20	C	1.92595701	-1.05836286	-2.80544876
21	C	3.30106645	-0.88544679	-2.57081267
22	N	3.97984264	-0.39208466	-1.47098835
23	C	5.35106156	-0.39581166	-1.63274633
24	C	4.31783374	-1.21490386	-3.48112591
25	C	5.55581574	-0.91738686	-2.91418389
26	C	6.37626681	0.00043837	-0.77064907
27	H	2.67446069	0.57632120	1.10709946
28	H	3.50719676	-0.05118976	-0.59441060
29	H	3.00811151	7.60830223	1.63438995
30	C	4.67618177	1.97139103	4.53194333
31	C	5.02286674	3.31544894	4.71537033
32	C	5.49717166	3.76017486	5.95562814
33	C	5.59282264	2.86512800	7.02710095
34	C	5.24131265	1.52759496	6.85146894

35	C	4.79156072	1.08340803	5.60850611
36	C	1.53937511	-1.58179370	-3.97804945
37	C	1.43490507	-0.77698647	-5.11865672
38	C	1.27950120	-2.95393133	-4.08486444
39	C	1.10604300	-1.34853954	-6.35131394
40	C	0.87940401	-2.72364152	-6.45645298
41	C	0.94578903	-3.52246368	-5.31501082
42	O	1.98774688	-0.54664160	-8.22524371
43	H	1.64454404	0.30413131	-5.04861272
44	C	1.05069151	-0.56017061	-7.45894939
45	H	0.76087609	-4.60748736	-5.38825583
46	H	1.36434821	-3.59908627	-3.19372256
47	O	-0.51799183	2.34501671	-2.33129253
48	C	5.84110678	5.07020233	6.11582922
49	H	4.93467576	4.02213180	3.87160353
50	H	4.52645078	0.02064221	5.47498613
51	H	5.31938969	0.82056066	7.69466231
52	H	5.93300865	3.20702802	8.01710802
53	H	0.64871405	-3.17887837	-7.43428475
54	H	-0.35064555	1.58288415	3.91385445
55	H	2.01056658	2.11699414	5.02097549
56	H	7.21215945	1.67567709	3.46084142
57	H	8.34697927	0.85775393	1.22871398
58	H	4.17630376	-1.64407679	-4.48613477
59	H	6.53318907	-1.07404590	-3.39773205
60	C	-1.19303309	0.31557226	-7.09729344
61	C	-1.65366602	1.56342414	-6.65627046
62	C	-1.96763489	-0.82747941	-6.89316452
63	C	-3.18611861	-0.73749643	-6.22545066
64	C	-3.66479357	0.50117152	-5.79024066
65	C	-2.90781830	1.66268992	-6.02648872
66	C	-3.44342321	2.90510975	-5.65867875
67	C	-4.67279536	2.99102377	-5.00630467
68	C	-5.39761237	1.83323576	-4.73482769
69	C	-4.89697221	0.59435637	-5.13239585
70	O	0.00410175	0.24022223	-7.74720932
71	O	-0.33677482	2.63137676	-4.48387547
72	H	-1.62524088	-1.80821647	-7.26063458
73	H	-3.77942680	-1.65197471	-6.05912462
74	H	-2.91446230	3.83762059	-5.90995069

75	H	-5.07852738	3.97580785	-4.71980764
76	H	-6.37177475	1.89810379	-4.22170148
77	H	-5.48573012	-0.31470550	-4.92616291
78	C	0.80595995	4.28980747	-5.81908616
79	C	1.01533697	4.88036050	-7.06251215
80	C	-0.11403274	3.24771001	-5.68288689
81	C	-0.77696571	2.74955804	-6.81431190
82	C	-0.57575668	3.35186515	-8.06961805
83	C	0.32630198	4.42456653	-8.18974619
84	C	0.54264707	5.01736776	-9.43934560
85	C	-0.13566371	4.56114693	-10.56837928
86	C	-1.04252976	3.51057589	-10.45243230
87	C	-1.26447876	2.91481196	-9.21093945
88	H	1.38750018	4.64515660	-4.95312481
89	H	1.74095406	5.70597163	-7.15158812
90	H	1.25821430	5.84990201	-9.54201860
91	H	0.04323527	5.03186586	-11.54971909
92	H	-1.58715367	3.15174996	-11.34192419
93	H	-1.99989009	2.09668360	-9.14546843
94	C	8.85058768	7.66296426	8.69040323
95	C	8.24560270	6.42855531	8.95819419
96	C	8.36077182	8.82459591	9.28963706
97	C	7.25289098	8.76442190	10.13129891
98	C	6.64520879	7.53836953	10.41566696
99	C	7.15388273	6.35949770	9.84204702
100	C	6.57743064	5.13094752	10.19449704
101	C	5.48384852	5.07455050	11.05788810
102	C	4.96162040	6.24835773	11.59559522
103	C	5.54414123	7.47448035	11.27782536
104	O	9.93700138	7.70052925	7.86639847
105	O	6.99166802	5.49445042	6.68750435
106	H	8.84870086	9.79585797	9.10964407
107	H	6.87102885	9.69260225	10.58802510
108	H	7.00059677	4.18612022	9.81861791
109	H	5.04165238	4.10033219	11.32606216
110	H	4.09877719	6.20641870	12.28138336
111	H	5.13081004	8.39653275	11.71887256
112	C	8.57227132	3.69354113	6.39046228
113	C	9.69192518	3.00296423	6.84779820
114	C	8.07813221	4.78308928	7.11113742

115	C	8.74582924	5.21799428	8.26443147
116	C	9.87575903	4.52215341	8.72936338
117	C	10.34631405	3.40508712	8.01577100
118	C	11.47553232	2.71345796	8.46997009
119	C	12.13860146	3.11926404	9.62713136
120	C	11.67256638	4.22049315	10.34127447
121	C	10.54746343	4.91460910	9.89647149
122	H	8.09360539	3.37803318	5.44898636
123	H	10.06635033	2.14106093	6.27076595
124	H	11.85402520	1.84148728	7.91132126
125	H	13.02939166	2.57038993	9.97621742
126	H	12.19288350	4.54300921	11.25880271
127	H	10.19530448	5.77754990	10.48468639
128	O	11.20716931	8.42238819	6.23965563
129	O	5.08018699	5.93160509	5.73876933
130	C	2.82509356	8.37541911	4.47677653
131	C	3.17704854	8.84586706	5.82883541
132	N	3.93724935	8.42603109	3.72013867
133	C	4.97391307	8.88366797	4.45076149
134	C	4.47337301	9.15399717	5.81350940
135	C	1.55183384	7.96371320	4.08283762
136	H	2.49602260	8.92469406	6.69116335
137	C	1.66381332	6.65835509	-0.74705730
138	C	1.21242385	7.52838922	2.79887062
139	H	5.06056015	9.53046626	6.66656860
140	N	1.97952264	7.38623327	1.65994095
141	C	-0.07261935	7.13349517	2.41040455
142	C	1.25835679	6.92911737	0.57103422
143	C	-0.04607335	6.77262312	1.06362437
144	C	2.98844850	6.81912410	-1.17399237
145	N	4.03420043	7.23922107	-0.43565543
146	C	5.14735821	7.27428506	-1.19117629
147	C	3.48549044	6.55636211	-2.54001124
148	C	4.78938522	6.82809905	-2.54919125
149	C	6.29229509	9.06570396	4.01218948
150	C	6.69672422	8.76460385	2.69964106
151	N	5.98616807	8.26578576	1.62245386
152	C	6.75567734	8.11910569	0.48547546
153	C	7.99787595	8.93645980	2.20050117
154	C	8.03339696	8.54267782	0.86420127

155	C	6.42309682	7.67190894	-0.79515443
156	C	0.75720057	6.24479321	-1.64440702
157	C	0.62928255	4.88645107	-1.95706803
158	C	-0.28307640	4.46841509	-2.93293293
159	C	-1.09589944	5.40835311	-3.57642996
160	C	-0.97976647	6.76145980	-3.26038707
161	C	-0.05316356	7.17676776	-2.30420622
162	C	7.20186141	9.56544212	4.86257176
163	C	8.17212969	8.73879989	5.44177094
164	C	7.22261842	10.93820488	5.14134270
165	C	9.16244465	9.28758187	6.26185690
166	C	9.19483265	10.66276174	6.50923387
167	C	8.20841644	11.48441992	5.96442174
168	H	8.17336269	7.65764134	5.22206505
169	C	10.12557523	8.47822720	6.78034865
170	H	8.22350944	12.57003234	6.15945680
171	H	6.46990655	11.60229877	4.68315078
172	C	-0.37804386	3.14125456	-3.23088632
173	H	1.26624031	4.14566238	-1.44250125
174	H	0.04368049	8.25118411	-2.07201617
175	H	-1.61671176	7.50431612	-3.76978331
176	H	-1.83663514	5.09175423	-4.32728060
177	H	9.99475861	11.10042571	7.12985185
178	H	-0.96266044	7.11194218	3.05912361
179	H	-0.91705303	6.41835727	0.48918259
180	H	2.89342632	6.20247104	-3.39903138
181	H	5.47087930	6.74295302	-3.41082936
182	H	8.86439929	9.32309594	2.76047740
183	H	8.92246232	8.57013983	0.21424301
184	H	-1.22846644	0.62181613	1.63487343
185	H	7.41285146	-0.10197660	-1.12653696
186	H	0.75397771	7.99043021	4.84053175
187	H	7.22241699	7.64279692	-1.55135961
188	H	4.96197220	8.02501579	1.65608386