Self-Assembled Ion-Pair Organocatalysis — Asymmetric Baeyer-Villiger Oxidation Mediated by Flavinium–Cinchona Alkaloid Dimer

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Supporting Information

1. Experimental Section

General

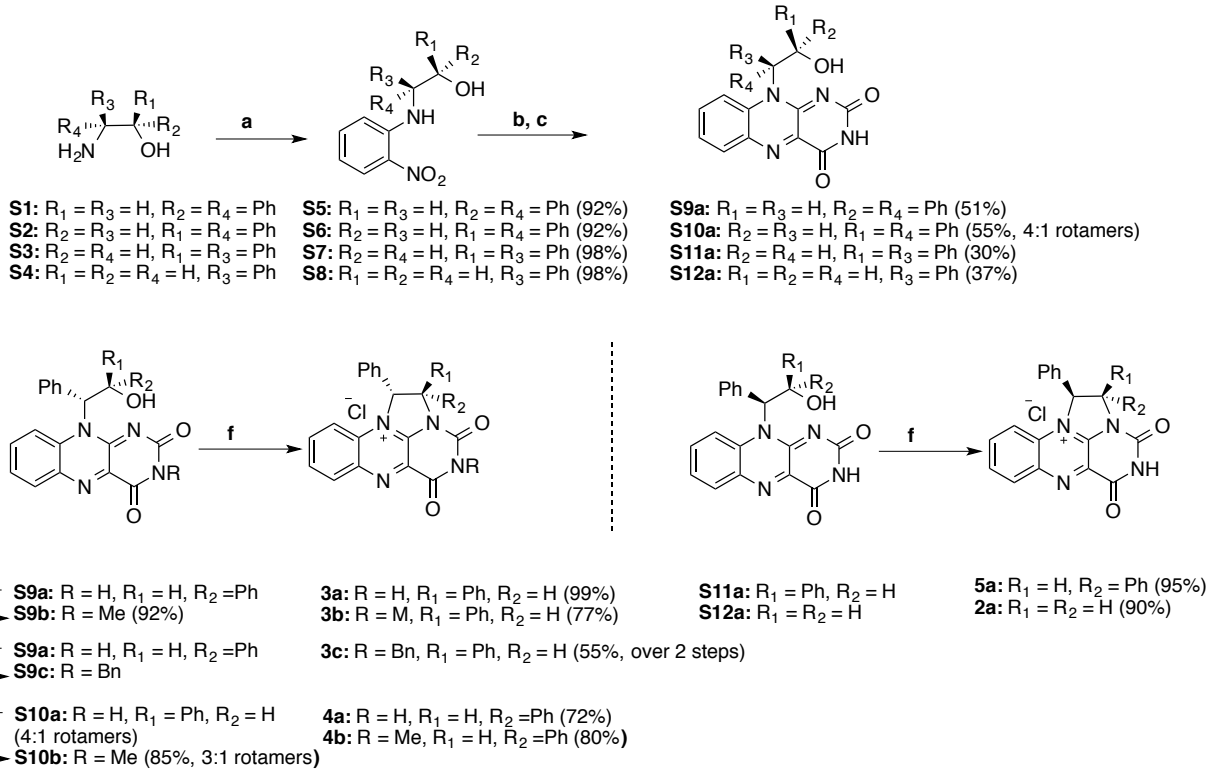
^{1}H-NMR/^{13}C-NMR spectra were run in $CDCl_3$, d_6-DMSO or CD_3CN on either Varian VXRS 400 (400 MHz), Varian Unity Inova 600 (600 MHz) or Brucker Advance 600 (600 MHz) NMR spectrometers. Chemical shifts (δ) were reported as parts per million (ppm) with reference to tetramethylsilane (TMS) or solvent unless otherwise stated. The coupling constants (*J*) are reported in Hz. Mass spectra were obtained with Hewlett-Packard Esquire Ion Trap LC-MS (electrospray). High resolution mass spectra were run on a Micromass Q-Tof II. Analytical chiral HPLC was performed with an Agilent HPLC (HP 1100) utilizing chiralcel AD or OD columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries with detection at 210 nm. GC experiments were performed with Hewlett Packard 5890 series II gas chromatograph equipped with an auto injector HP 7672A and an FID detector, utilizing Restek MXT Biodiesel TG (Siltek – treated stainless steel) capillary column. Optical rotation data were collected using a Rudolph Research Analytical Autopol (APIV/6W), automatic polarimeter. UV-Vis experiments were performed using a Nicolet Evolution 300 UV-Vis spectrophotometer (Thermo Electron Corporation).

Materials

Most reagents were purchased from commercial suppliers and used without further purification. Thin layer chromatography (TLC) was carried out on glass backed silica plates, purchased from Sorbent Technology. The plates were visualized under UV (254 nm) light, and occasionally by staining with Ceric ammonium molybdate and gentle heating. During compound separations, column chromatography was carried out using 20–60 micron dry silica purchased from Sorbent Technology. *Tert*-butyl N-(3-oxocyclobutyl)carbamate (**10**) was purchased from PharmaBlock. 3-Oxocyclobutanecarboxylic acid was purchased from AK Scientific. Benzyl ester (**8**) was prepared from 3-Oxocyclobutanecarboxylic acid by Fisher esterification. The other cyclobutanones were prepared according to the literature procedures.

1-1. Preparation of flavinium catalysts:

Unless otherwise specified, flavinium species used in this study were prepared according to the synthetic scheme illustrated in Scheme S1.



S1: $R_1 = R_3 = H$, $R_2 = R_4 = Ph$
S2: $R_2 = R_3 = H$, $R_1 = R_4 = Ph$
S3: $R_2 = R_4 = H$, $R_1 = R_3 = Ph$
S4: $R_1 = R_2 = R_4 = H$, $R_3 = Ph$

S5: $R_1 = R_3 = H$, $R_2 = R_4 = Ph$ (92%)
S6: $R_2 = R_3 = H$, $R_1 = R_4 = Ph$ (92%)
S7: $R_2 = R_4 = H$, $R_1 = R_3 = Ph$ (98%)
S8: $R_1 = R_2 = R_4 = H$, $R_3 = Ph$ (98%)

S9a: $R_1 = R_3 = H$, $R_2 = R_4 = Ph$ (51%)
S10a: $R_2 = R_3 = H$, $R_1 = R_4 = Ph$ (55%, 4:1 rotamers)
S11a: $R_2 = R_4 = H$, $R_1 = R_3 = Ph$ (30%)
S12a: $R_1 = R_2 = R_4 = H$, $R_3 = Ph$ (37%)

S9a: R = H, R_1 = H, R_2 =Ph
S9b: R = Me (92%)

3a: R = H, R_1 = Ph, R_2 = H (99%)
3b: R = M, R_1 = Ph, R_2 = H (77%)

S11a: R_1 = Ph, R_2 = H
S12a: $R_1 = R_2$ = H

5a: R_1 = H, R_2 = Ph (95%)
2a: $R_1 = R_2$ = H (90%)

S9a: R = H, R_1 = H, R_2 =Ph
S9c: R = Bn

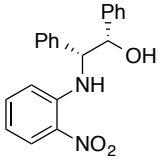
3c: R = Bn, R_1 = Ph, R_2 = H (55%, over 2 steps)

S10a: R = H, R_1 = Ph, R_2 = H (4:1 rotamers)
S10b: R = Me (85%, 3:1 rotamers)

4a: R = H, R_1 = H, R_2 =Ph (72%)
4b: R = Me, R_1 = H, R_2 =Ph (80%)

a: 2-nitrofluorobenzene, iPr_2NEt, DMF, b: H_2, Pd/C, MeOH, c: alloxan monohydrate, $B(OH)_3$, AcOH, d: MeI, K_2CO_3, DMF, e: BnBr, K_2CO_3,, DMF, f: $SOCl_2$, CH_2Cl_2

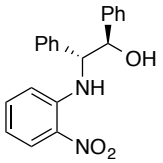
Scheme S1. General synthetic scheme for flavinium catalysts.



(1*S*, 2*R*)-1,2-Diphenyl-2-[(2-nitrophenyl)amino]ethan-1-ol (S5)

Diisopropylethyl amine (1.55 mL, 9.38 mmol) was added to a mixture of 2-nitrofluorobenzene (1.97 mL, 18.71 mmol) and (1*S*,2*R*)-(+)-2-amino-1,2-diphenylethanol (**S1**) (1.00 g, 4.69 mmol) in DMF (20 mL) and then the mixture was stirred at 50℃ for 24 h. The reaction mixture was cooled into room temperature, poured into saturated NH_4Cl aqueous solution, and extracted with ethyl acetate. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2) to obtain **7** as an orange amorphous solid (1.45 g, 92%).

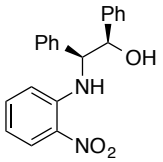
[α] = +639.4° (*c* = 0.50, MeOH); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.20 (d, *J* = 4.2 Hz, 1H), 4.83 (t, *J* = 6.0 Hz, 1H), 5.14 (t, *J* = 4.8 Hz, 1H), 6.58 (m, 2H), 7.16–7.23 (m, 4H), 7.28–7.31 (m, 7H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.85 (d, *J* = 6.0 Hz, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 63.4, 77.28, 115.1, 115.8, 126.6 (2C), 126.7, 127.8 (2C), 128.1, 128.40 (2C), 128.43, 128.5 (2C), 132.5, 135.9, 137.5, 139.3, 144.2; HRMS (ESI$^+$) *m/z* 357.1222 $(M+Na)^+$ (calcd for $C_{20}H_{18}N_2O_3Na$ 357.1215).



(1*R,* 2*R*)-1,2-Diphenyl-2-[(2-nitrophenyl)amino]ethan-1-ol (S6)

Diisopropylethyl amine (700 µL, 4.23 mmol) was added to a mixture of 2-nitrofluorobenzene (890 µL, 8.45 mmol) and (1*R*,2*R*)-(+)-2-amino-1,2-diphenylethanol (**S2**) (450.0 mg, 2.11 mmol) in DMF (10 mL). After stirring the reaction mixture at 50℃ for 20 h, it was treated in the same manner as the synthesis of **S5**. The residue was purified by silica gel column chromatography (CH_2Cl_2) to obtain **8** as an orange amorphous solid (647.8 mg, 92%).

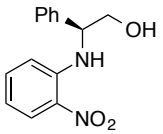
[α] = +325.1° (*c* = 0.53, MeOH); ^{1}H-NMR (600 MHz,$CDCl_3$) δ 2.23 (m, 1H), 4.75 (dd, *J* = 4.2, 6.3 Hz, 1H), 5.07 (t, *J* = 3.5 Hz, 1H), 6.49 (d, *J* = 8.8 Hz, 1H), 6.55 (t, *J* = 7.0 Hz, 1H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.27–7.36 (m, 8H), 7.40 (d, *J* = 7.2 Hz, 2H), 8.13 (dd, *J* = 1.5, 8.7 Hz, 1H), 9.08 (d, *J* = 6.3 Hz, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 63.8, 77.6, 115.1, 115.6, 126.2 (2C), 126.7, 127.0 (2C), 128.1, 128.2, 128.5 (2C), 128.9 (2C), 132.6, 135.9, 139.1, 140.2, 144.5; HRMS (ESI$^+$) *m/z* 357.1210 $(M+Na)^+$ (calcd for $C_{20}H_{18}N_2O_3Na$ 357.1215).



(1*R,* 2*S*)-1,2-Diphenyl-2-[(2-nitrophenyl)amino]ethan-1-ol (S7)

Diisopropylethyl amine (816 µL, 4.68 mmol) was added to a mixture of 2-nitrofluorobenzene (990 µL, 9.36 mmol) and (1*R*,2*S*)-2-amino-1,2-diphenylethanol (**S3**) (500.0 mg, 2.34 mmol) in DMF (10 mL). After stirring the reaction mixture at 50℃ for 22 h, it was treated in the same manner as the synthesis of **S5**. The residue was purified by silica gel column chromatography (0→100% CH_2Cl_2 / Hexanes) to obtain **S7** as an orange amorphous solid (767 mg, 2.29 mmol, 98%).

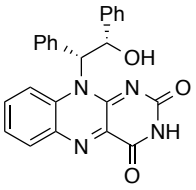
^{1}H-NMR (600 MHz,$CDCl_3$); δ 2.20 (br d, *J* = 4.1 Hz, 1H), 4.81 (t, *J* = 5.5 Hz, 1H), 5.13 (t, *J* = 4.4 Hz, 1H), 6.57 (m, 2H), 7.16–7.23 (m, 4H), 7.28–7.31 (m, 7H), 8.12 (d, *J* = 8.2 Hz, 1H), 8.83 (br d, *J* = 5.8 Hz, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 63.4 (CH), 77.2 (CH), 115.0 (CH), 115.8 (CH), 126.6 (CH, 2C), 127.7 (CH, 2C), 128.1 (CH), 128.38 (CH, 2C), 128.41 (CH), 128.5 (CH, 2C), 132.5 (C), 135.9 (CH), 137.5 (C), 139.2 (C), 144.2 (C); LRMS (ESI$^+$) *m/z* 357.6 $(M+Na)^+$ (calcd for $C_{20}H_{18}N_2O_3Na$ 357.12). The ^{1}H-NMR spectra matched those of **S5**.



(2*S*)-2-Phenyl-2-[(2-nitrophenyl)amino]ethan-1-ol (S8)

Diisopropylethyl amine (1270 µL, 7.28 mmol) was added to a mixture of 2-nitrofluorobenzene (1530 µL, 14.56 mmol) and (2*S*)-2-aminophenylethanol (**S4**) (500.0 mg, 3.64 mmol) in DMF (10 mL). After stirring the reaction mixture at 50℃ for 22 h, it was treated in the same manner as the synthesis of **S5**. The residue was purified by silica gel column chromatography (0→66% CH_2Cl_2 / Hexanes) to obtain **S8** as an orange oil still containing ~14.2% DMF (970 mg, ~95 wt%, 3.57 mmol, 98%).

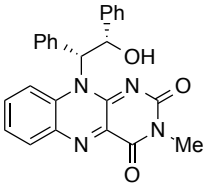
^{1}H-NMR (600 MHz,$CDCl_3$); δ 2.28 (m, 1H), 3.90 (dd, *J* = 5.3, 11.4 Hz, 1H), 4.01 (dd, *J* = 4.4, 11.4, 1H), 4.71 (dt, *J* = 4.4, 5.9 Hz, 1H), 6.61 (m, 2H), 7.24–7.36 (m, 6H), 8.15 (dd, *J* = 1.5, 3.8 Hz, 1H), 8.74 (br d, *J* = 5.9 Hz, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 59.2 (CH), 67.0 (CH_2), 115.1 (CH), 115.9 (CH), 126.5 (CH, 2C), 126.7 (CH), 128.0 (CH), 129.0 (CH, 2C), 132.5 (C), 136.0 (CH), 138.7 (C), 144.6 (C); LRMS (ESI$^+$) *m/z* 281.5 $(M+Na)^+$ (calcd for $C_{14}H_{14}N_2O_3Na$ 281.09).



10-[(1*R*,2*S*)-1,2-Diphenyl-2-hydroxy]ethyl-benzo[*g*]pteridin-2,4(3*H*,10*H*)-dione (S9a)

A catalytic amount of Pd–C (29.7 mg) was added to a solution of **S5** (296.6 mg, 0.89 mmol) in MeOH (10 mL) and the mixture was stirred for 2 h under hydrogen atmosphere. The mixture was filtered through Celite® and the filtrate was concentrated under reduced pressure. Alloxan monohydrate (141.7 mg, 0.89 mmol) and boric acid (57.8 mg, 0.93 mmol) were added to a solution of the crude in acetic acid (10 mL) and then the mixture was stirred at room temperature for 18 h. The reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. MeOH was added to the residue solidified was collected by filtration to obtain **S9a** as a yellow solid (185.3 mg, 51%).

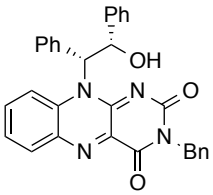
[α] = –68.9° (*c* = 0.10, MeOH); ^{1}H-NMR (600 MHz, DMSO-d_6) δ 5.91 (br, 1H), 6.44 (br, 1H), 6.97–7.06 (m, 5H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.49 (br, 1H), 7.59 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 3H), 7.93 (d, *J* = 7.9 Hz, 1H), 11.50 (s, 1H); ^{13}C-NMR (150 MHz, DMSO-d_6) δ 61.6, 73.3, 118.8, 126.0, 126.6 (2C), 127.3 (2C), 127.5 (2C), 127.8, 128.7, 131.4, 131.8 (2C), 134.0, 134.8 (2C), 136.7, 138.1, 140.4, 151.7, 155.3, 159.3; HRMS (ESI$^+$) *m/z* 433.1261 $(M+Na)^+$ (calcd for $C_{24}H_{18}N_4O_3Na$ 433.1277).



10-[(1*R*,2*S*)-1,2-Diphenyl-2-hydroxy]ethyl-3-methyl-benzo[*g*]pteridin-2,4(3*H*,10*H*)-dione (S9b)

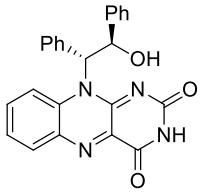
Potassium carbonate (64.1 mg, 0.46 mmol) and methyl iodide (29 μL, 0.47 mmol) were added to a solution of **S9a** (47.4 mg, 0.12 mmol) in DMF and then the mixture was stirred at room temperature for 11 h. The reaction was poured into saturated NH_4Cl aqueous solution and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 100/1) and recrystallization from CH_2Cl_2–hexanes to obtain **S9b** as a yellow solid (45.1 mg, 92%).

[α] = –71.5° (*c* = 0.42, MeOH); ^{1}H-NMR (600 MHz, DMSO-d_6) δ 3.28 (s, 3H), 5.94 (br, 1H), 6.45 (br, 1H), 6.96–7.01 (m, 3H), 7.08 (br, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.51 (br t, *J* = 7.1 Hz, 1H), 7.62 (m, 2H), 7.67 (d, *J* = 8.1 Hz, 3H), 7.99 (d, *J* = 7.9 Hz, 1H); ^{13}C-NMR (150 MHz, DMSO-d_6) δ 28.1, 61.5, 73.4, 118.9, 126.1, 126.7 (2C), 127.3 (2C), 127.6 (2C), 127.8, 128.7, 131.3, 131.9 (2C), 134.1, 135.1 (2C), 136.6, 137.2, 140.4, 150.2, 154.9, 159.0; HRMS (ESI$^+$) *m/z* 447.1421 $(M+Na)^+$ (calcd for $C_{25}H_{20}N_4O_3Na$ 447.1433)



10-[(1*R*,2*S*)-1,2-Diphenyl-2-hydroxy]ethyl-3-benzyl-benzo[*g*]pteridin-2,4(3*H*,10*H*)-dione (S9c)

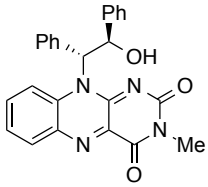
Potassium carbonate (94.6 mg, 0.7 mmol) and benzyl bromide (62 μL, 0.52 mmol) were added to a solution of **S9a** (143.6 mg, 0.35 mmol) in DMF (10 mL) and then the mixture was stirred at room temperature for 5 h. The reaction was poured into water and extracted with ethyl acetate. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes/ethyl acetate = 3:1 to 2:1) to obtain **S9c** as a yellow solid (173.2 mg). Due to the difficulty in rigorous purification, the crude material was carried to the cyclization step.



10-[(1*R*,2*R*)-1,2-Diphenyl-2-hydroxy]ethyl-benzo[*g*]pteridin-2,4(3*H*,10*H*)-dione (S10a)

A catalytic amount of Pd–C (9.3 mg) was added to a solution of **8** (92.8 mg, 0.28 mmol) in MeOH (3 mL) and the mixture was stirred for 1.5 h under hydrogen atmosphere. The mixture was filtered through Celite® and the filtrate was concentrated under reduced pressure. Alloxan monohydrate (44.4 mg, 0.28 mmol) and boric acid (17.2 mg, 0.28 mmol) were added to a solution of the crude in acetic acid (3 mL) and then stirred at room temperature for 18 h. The reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. EtOAc and hexanes were added to the residue and the yellow solid formed was collected by filtration to obtain **S10a** as a yellow solid (63.1 mg, 55%).

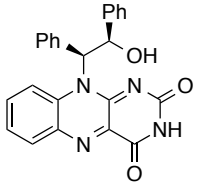
^{1}H-NMR (600 MHz, DMSO-d_6) δ 5.81 (d, *J* = 4.2 Hz, 0.8H), 6.03 (dd, *J* = 4.2, 8.7 Hz, 0.8H), 6.15 (br, 0.2H), 6.42 (m, 0.2H), 7.16–7.24 (m, 2.4H), 7.26–7.29 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 1.6H), 7.40 (d, *J* = 8.0 Hz, 0.4H), 7.50 (d, *J* = 7.5 Hz, 1.6H), 7.54 (t, *J* = 8.1 Hz, 0.8H), 7.58–7.60 (m, 2H), 7.65–7.69 (m, 1H), 7.91 (d, *J* = 8.8 Hz, 0.8H), 7.94 (m, 0.4H), 7.96 (d, *J* = 8.7 Hz, 0.8H), 8.10 (d, *J* = 8.1 Hz, 0.8H), 8.14 (d, *J* = 7.9 Hz, 0.2H), 8.38 (d, *J* = 8.8 Hz, 0.2H), 11.53 (s, 0.8H), 11.55 (s, 0.2H)



10-[(1*R*,2*R*)-1,2-diphenyl-2-hydroxy]ethyl-3-methyl-benzo[*g*]pteridin-2,4(3*H*,10*H*)-dione (S10b)

Potassium carbonate (45.6 mg, 0.33 mmol) and methyl iodide (21 μL, 0.34 mmol) were added to a solution of **S10a** (33.8 mg, 0.082 mmol) in DMF and then the mixture was stirred at room temperature for 21 h. The reaction was poured into saturated NH_4Cl aqueous solution and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 100/1) to obtain **S10b** as a yellow solid (29.9 mg, 85%).

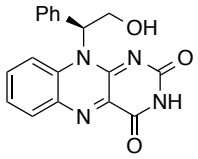
^{1}H-NMR (600 MHz, DMSO-d_6) δ 3.29 (s, 0.75H), 3.32 (s, 2.25H), 5.82 (d, *J* = 4.2 Hz, 0.75H), 6.05 (dd, *J* = 4.2, 8.8 Hz, 0.75H), 6.39 (d, *J* = 8.6 Hz, 0.25H), 6.48 (br t, *J* = 8.3 Hz, 0.25H), 7.18–7.20 (m, 2.5H), 7.23 (t, *J* = 6.6 Hz, 0.5H), 7.27 (t, *J* = 7.6 Hz, 1.5H), 7.36 (t, *J* = 7.6 Hz, 1.5H), 7.42 (d, *J* = 7.3 Hz, 0.5H), 7.50 (d, *J* = 7.6 Hz, 1.5H), 7.57 (t, *J* = 7.3 Hz, 0.75H), 7.60 (m, 0.5H), 7.63 (d, *J* = 7.9 Hz, 1.5H), 7.69 (m, 0.5H), 7.71 (t, *J* = 7.3 Hz, 0.75H), 7.95 (d, *J* = 8.6 Hz, 0.75H), 7.97 (m, 0.25H), 7.98 (d, *J* = 8.8 Hz, 0.75H), 8.16 (d, *J* = 8.1 Hz, 0.75H), 8.20 (d, *J* = 8.3 Hz, 0.25H), 8.46 (d, *J* = 8.8 Hz, 0.25H)



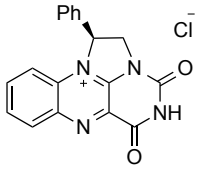
10-[(1*S*,2*R*)-1,2-Diphenyl-2-hydroxy]ethyl-benzo[*g*]pteridin-2,4(3*H*,10*H*)-dione (S11a)

A catalytic amount of Pd–C (47 mg) was added to a solution of **S7** (736 mg, 2.20 mmol) in MeOH (22 mL) and the mixture was stirred for 20 h under hydrogen atmosphere. The mixture was filtered through Celite® and the filtrate was concentrated under reduced pressure. Alloxan monohydrate (352 mg, 2.20 mmol) and boric acid (144 mg, 2.31 mmol) were added to a solution of the crude in acetic acid (22 mL) and then the mixture was stirred at 50 °C for 24.5 h. The reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced

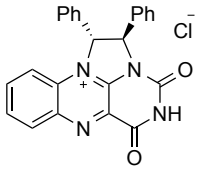
pressure. After stripping off twice with MeOH, anhydrous MeOH (2 mL) was added to the residue, and the solid was isolated by filtration to obtain **S11a** as a yellow solid (269 mg, 30%).
The ^{1}H-NMR spectra matched those of compound **S9a**. HRMS (ESI$^+$) *m/z* 433.1276 (M+Na)$^+$ (calcd for $C_{24}H_{18}N_4O_3Na$ 433.1277).



10-[(1*S*)-1-Phenyl-2-hydroxy]ethyl-benzo[*g*]pteridin-2,4(3*H*,10*H*)-dione (S12a)
A catalytic amount of Pd–C (115 mg) was added to a solution of **S8** (1157 mg, 4.48 mmol) in MeOH (10 mL) and the mixture was stirred for 4 h under hydrogen atmosphere. The mixture was filtered through Celite® and the filtrate was concentrated under reduced pressure. Alloxan monohydrate (717 mg, 4.48 mmol) and boric acid (282 mg, 4.52 mmol) were added to a solution of the crude in acetic acid (10 mL) and then the mixture was stirred at room temperature for 26 h. The reaction mixture was poured into water (200 mL) and extracted with CH_2Cl_2 (150 mL x 4). The organic layer was washed with water (50 mL x 2), dried over $MgSO_4$, and concentrated under reduced pressure. The crude mass thus obtained was washed with CH_2Cl_2 (50 mL) and dried at room temperature to give **S12a** as a yellow solid (700 mg, 37%) which contained 20% (weight) of CH_2Cl_2 as indicated by ^{1}H-NMR.
[α] = 288.7° (*c* = 0.5, MeOH); ^{1}H-NMR (600 MHz, DMSO-d_6): δ 4.33 (br, s, 1H), 4.64 (br, s, 1H), 5.35 (br, s, 1H), 7.28–7.42 (m 7H), 7.52 (br, s, 1H), 7.58 (br, s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 11.52 (s, 1H); ^{13}C-NMR (150 MHz, DMSO-d_6) δ 59.09, 60.08, 118.19, 125.72, 126.27, 127.48, 128.82, 131.40, 132.11, 133.62, 135.45, 136.60, 139.04, 152.52, 155.67, 159.82; HRMS (ESI$^+$) *m/z* 357.0960 (M+Na)$^+$ (calcd for $C_{18}H_{14}N_4O_3Na$ 357.0964)

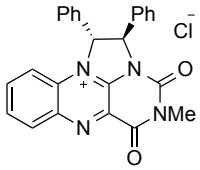


(1*S*)-1-Phenyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (2a)
Thionyl chloride (0.5 mL) was added to a suspension of **S12a** (200 mg of 80% pure sample, 20% being CH_2Cl_2, 0.48 mmol)) in CH_2Cl_2 (5 mL) at 0 ℃ and then the mixture was stirred at room temperature for 2 h. Hexanes (2 mL) was added to the reaction mixture and the precipitate formed was collected by filtration. The crude mass was washed with hexanes and small amount of CH_2Cl_2 to obtain **2a** as a yellow solid (160 mg, 90.2%) which contained 5% (weight) of CH_2Cl_2 as indicated by ^{1}H-NMR.
[α] = –173.6° (*c* = 0.5, MeOH); ^{1}H-NMR (600 MHz, DMSO-d_6) δ 4.48 (dd, *J* = 6.3, 11.2 Hz, 1H), 5.12 (dd, *J* = 11.2, 10.9 Hz 1H), 7.18 (dd, *J* = 6.3, 10.9 Hz, 1H), 7.48–7.51 (m, 3H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.73–7.75 (m, 2H), 8.02 (m, 1H), 8.15 (m, 1H), 8.58 (d, *J* = 8.3 Hz, 1H), 13.02 (s, 1H); ^{13}C-NMR (150 MHz, DMSO-d_6) δ 53.29, 66.58, 117.24, 127.47, 127.88, 129.60, 130.27, 130.89, 132.89, 135.52, 135.63, 137.98, 139.39, 144.32, 146.30, 158.05; HRMS (ESI$^+$) *m/z* 317.1031 (M-Cl)$^+$ (calcd for $C_{18}H_{13}N_4O_2$ 317.1039)



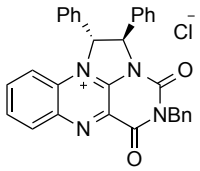
(1*R*,2*R*)-1,2-Diphenyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (3a)
Thionyl chloride (1 mL) was added to a suspension of **S9a** in CH_2Cl_2 (5 mL) at 0 ℃ and then the mixture was stirred at room temperature for 3h. Hexanes (10 mL) was added to the reaction mixture and the precipitate formed was collected by filtration to obtain **3a** as a yellow solid (148.3 mg, 99%).

[α] = +226.0° (*c* = 0.05, MeOH); ^{1}H-NMR (600 MHz, DMSO-d_6) δ 5.88 (d, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 7.46–7.54 (m, 7H), 7.66 (m, 2H), 7.74 (m, 2H), 8.01 (t, *J* = 7.5 Hz, 1H), 8.08 (t, *J* = 7.5 Hz, 1H), 8.59 (d, *J* = 8.2 Hz, 1H), 12.95 (s, 1H); ^{13}C-NMR (150 MHz, DMSO-d_6) δ 70.4, 74.8, 117.5, 127.7 (2C), 128.2 (2C), 129.1 (2C), 129.5, 129.8 (2C), 130.5, 130.7, 132.7, 134.8, 135.2, 135.9, 137.2, 139.7, 144.3, 145.8, 158.2; HRMS (ESI$^+$) *m/z* 393.1344 (M–Cl)$^+$ (calcd for $C_{24}H_{17}N_4O_2$ 393.1352)



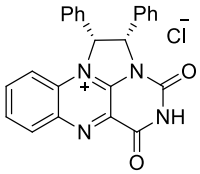
(1*R*,2*R*)-1,2-Diphenyl-3-methyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (3b)

Thionyl chloride (1 mL) was added to a suspension of **S9b** (81.2 mg, 0.19 mmol) in CH_2Cl_2 (5 mL) at 0℃ and then the mixture was stirred at room temperature for 3h. Hexanes (10 mL) was added to the reaction mixture and the precipitate formed was collected by filtration to obtain **3b** as yellow solid (65.1 mg, 77%).
[α] = +166.2° (*c* = 0.20, MeOH); ^{1}H-NMR (600 MHz, DMSO-d_6) δ 3.40 (s, 3H), 5.97 (d, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 7.49–7.52 (m, 7H), 7.67 (m, 3H), 7.71 (d, *J* = 6.4 Hz, 1H), 8.04 (t, *J* = 7.7 Hz, 1H), 8.12 (t, *J* = 7.7 Hz, 1H), 8.65 (d, *J* = 8.4 Hz, 1H); ^{13}C-NMR (150 MHz, DMSO-d_6) δ 28.8, 71.0, 74.6, 117.5, 127.5, 127.9 (2C), 128.2 (2C), 129.1 (2C), 129.6, 129.8 (2C), 130.6, 130.9, 132.9, 134.7 (2C), 135.1, 137.7, 140.1, 142.8, 146.3, 157.7; HRMS (ESI$^+$) *m/z* 407.1515 (M–Cl)$^+$ (calcd for $C_{25}H_{19}N_4O_2$ 407.1508)



(1*R*,2*R*)-1,2-Diphenyl-3-benzyl-1,2-dihydro-4,63*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (3c)

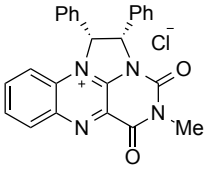
Thionyl chloride (1 mL) was added to a suspension of **S9c** (173.2 mg of dried mass from previous step without purification) in CH_2Cl_2 (5 mL) at 0℃ and then the mixture was stirred at room temperature for 3.5h. Hexanes (10 mL) was added to the reaction mixture and the precipitate formed was collected by filtration to obtain **3c** as yellow solid (100.4 mg, 55.3% over two steps).
[α] = +98.2° (*c* = 0.5, MeOH); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 5.00 (d, *J* = 14.4 Hz, 1H), 5.14 (d, *J* = 14.4 Hz, 1H), 5.87 (broad s, 1H), 6.43 (broad s, 1H), 7.15 (broad m, 4H), 7.39–7.50 (m, 8H), 7.62–7.71 (m, 6H), 8.31 (broad s, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 45.94, 73.16, 117.08, 127.75, 128.24, 128.46, 128.54, 128.73, 128.87, 129.41, 129.49, 130.05, 130.45, 131.00, 132.50, 132.86, 133.81, 133.96, 135.34, 137.29, 141.18, 143.65, 146.43, 157.41; HRMS (ESI$^+$) *m/z* 483.1819 (M–Cl)$^+$ (calcd for $C_{31}H_{23}N_4O_2$ 483.1821)



(1*R*,2*S*)-1,2-Diphenyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (4a)

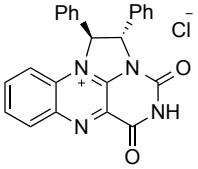
Thionyl chloride (200 μL) was added to a suspension of **S10a** (42.0 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) at 0℃ and then stirred at room temperature for 3h. Hexanes (2 mL) was added to the reaction mixture and the precipitate formed was collected by filtration to obtain **4a** as a yellow solid (31.7 mg, 72%).
[α] = +206.2° (*c* = 0.15, MeOH); ^{1}H-NMR (600 MHz, DMSO-d_6) δ 6.61 (d, *J* = 11.2 Hz, 1H), 7.00 (br, 1H), 7.07–7.14 (m, 4H), 7.22 (br, 1H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.42–7.46 (m, 2H), 7.53 (d, *J* = 11.2 Hz, 1H), 8.04 (t, *J* = 7.5 Hz, 1H), 8.10 (t, *J* = 7.5 Hz, 1H), 8.62 (d, *J* = 8.1 Hz, 1H), 12.94 (s, 1H); ^{13}C-NMR (150 MHz, DMSO-d_6) δ 66.1, 70.4, 117.7, 127.3, 127.4, 127.7 (2C), 128.2 (2C), 128.3, 128.5, 129.3 (2C),

129.5, 130.8, 131.3, 132.1, 132.8, 136.1, 137.6, 139.4, 145.6, 146.2, 158.1; HRMS (ESI^+) *m/z* 393.1360 $(M–Cl)^+$ (calcd for $C_{24}H_{17}N_4O_2$ 393.1352)



(1*R*,2*S*)-1,2-Diphenyl-3-methyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride(4b)

Thionyl chloride (600 μL) was added to a suspension of **S10b** (49.1 mg, 0.12 mmol) in CH_2Cl_2 (3 mL) at 0℃ and then stirred at room temperature for 3h. Hexanes (6 mL) was added to the reaction mixture and the precipitate formed was collected by filtration to obtain **4b** as a yellow solid (40.7 mg, 80%).
[α] = +231.5° (*c* = 0.20, MeOH); ^{1}H-NMR (600 MHz, DMSO-d_6) δ 3.43 (s, 3H), 6.67 (d, *J* = 11.2 Hz, 1H), 6.91 (br, 1H), 7.02 (br, 1H), 7.09 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 2H), 7.23 (m, 1H), 7.33 (br, 2H), 7.39 (m, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 11.2 Hz, 1H), 8.08 (t, *J* = 7.3 Hz, 1H), 8.15 (t, *J* = 7.3 Hz, 1H), 8.69 (d, *J* = 8.2 Hz, 1H); ^{13}C-NMR (150 MHz, DMSO-d_6) δ 28.9, 66.8, 70.3, 117.8, 127.2, 127.4, 127.8 (2C), 128.3 (2C), 128.6, 129.4 (2C), 129.5, 131.1 (2C), 131.9, 132.9 (2C), 134.8, 138.1, 139.8, 144.1, 146.6, 157.6; HRMS (ESI^+) *m/z* 407.1490 $(M–Cl)^+$ (calcd for $C_{25}H_{19}N_4O_2$ 407.1508).



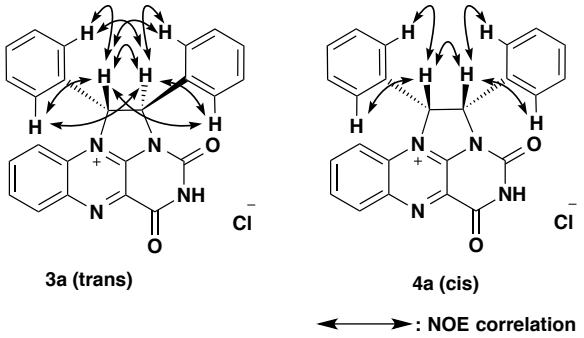
(1*S*,2*S*)-1,2-Diphenyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (5a)

The procedure to make **3a** from **S9a** was followed to make **5a** from thionyl chloride treatment of **S11a**. It was obtained as yellow solid (95%).
[α] = –243.0° (*c* = 0.05, MeOH); ^{1}H-NMR (600 MHz, DMSO-d_6) δ 5.90 (d, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 7.7, 1H), 7.47–7.52 (m, 7H), 7.65 (m, 2H), 7.70 (m, 2H), 8.02 (m, 1H), 8.09 (m, 1H), 8.60 (d, *J* = 8.3), 12.97 (s, 1H); ^{13}C-NMR (150 MHz, DMSO-d_6) δ 70.30, 74.77, 117.48, 127.31, 127.67, 128.09, 129.09, 129.58, 129.83, 130.51, 130.81, 132.76, 134.79, 135.28, 135.80, 137.44, 139.76, 144.18, 145.79, 158.19; HRMS (ESI^+) *m/z* 393.1347 $(M–Cl)^+$ (calcd for $C_{24}H_{17}N_4O_2$ 393.1352)

1-2. Relative stereochemical assignment of **3a** and **4a**

A note on relative configuration of **3a** and **4a**:The cyclization to form the flavinium salt was furnished by thionyl chloride activation of the hydroxyl group at the stereogenic center, which should undergo by S_Ni mechanism under the reaction conditions. However, we suspected that it may not be a case due to the sterics of the system. Therefore, NOESY spectra (see section 5) of flavinium **3a** and **4a** were obtained in order to confirm the relative configuration of the two phenyl groups.

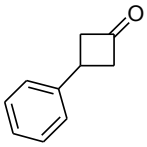
The spectral data of **3a** showed that each proton on the ethylene bridge recorded correlations to each other as well as with the four protons at the *ortho*-position of both phenyl rings (Figure S1). On the other hand, those of **4a** only showed the correlations between one of the two phenyl rings in addition to the correlations to each other. The difference can be explained by the restriction of free rotation of the phenyl rings: that of **3a** should be relatively facile while that of **4a** can be restricted. With this assumption, the stereochemistry of these compounds was assigned as shown in Figure S1. The stereochemical assignment confirmed that the mode of thionyl chloride cyclization was S_N2 rather than the S_Ni mechanism.



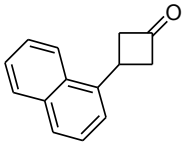
Figrue S1. The correlations recorded in the 2D-NOESY experiments.

1-3. Preparation/Characterization of cyclobutanones:

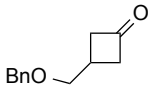
Unless otherwise specified in the materials section, cyclobutanones were prepared according to the literature procedure.[1]



3-phenylcyclobutanone (10)[1, 2]
Yield: 51%. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.26 (ddt, *J* = 3.2, 8.2, 19.9 Hz, 2H), 3.50 (ddt, *J* = 3.7, 8.2, 19.9 Hz, 2H), 3.69 (pent, *J* = 8.0, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H).

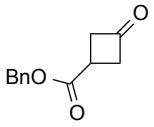


3-(1-Naphthyl)cyclobutanone (11)[3]
Yield: 20%. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.38–3.43 (m, 2H), 3.61–3.66 (m, 2H), 4.29 (pent, *J* = 8.4 Hz, 1H), 7.44–7.50 (m, 2H), 7.52-7.58 (m, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 26.03, 52.99, 122.27, 123.71, 125.29, 125.89, 126.26, 127.59, 139.01, 131.64, 133.98, 138.12, 206.55; HRMS (ESI^+) *m/z* 219.0780 $(M+Na)^+$ (calcd for $C_{14}H_{12}ONa$ 219.0786).



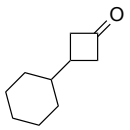
3-(Benzyloxymethyl)cyclobutanone (12)[1, 4]
Yield: 50.7%. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.66–2.69 (m, 1H), 2.85–2.89 (m, 2H), 3.10–3.15 (m, 2H), 3.59 (d, 2H, *J* = 6.2), 4.55 (s, 2H), 7.25–7.36 (m, 5H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 23.65 (CH), 50.03 (CH_2), 72.87 (CH_2), 73.19 (CH_2), 127.65 (CH), 127.76 (C), 128.45 (CH), 138.01 (C), 207.55 (C).

[1] Trost, B. M.; Xie, J. *J. Am. Chem. Soc*. **2008**, *130*, 6231–6242.
[2] Petersen, K. S.; Stoltz, B. M. *Tetrahedron,* **2011**, *67*, 4352–4357.
[3] Chai, Z.; Rainey, T. J. *J. Am. Chem. Soc.* **2012**, *134*, 3615−3618.
[4] Rammeloo, T.; Stevens, C. *Chem*. *Commun*. **2002**, *3*, 250.



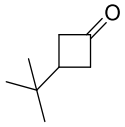
Benzyl-3-oxocyclobutanoate (13)[5]

Cyclobutanone **9** was prepared by trans-esterification of the corresponding carboxylic acid. Yield: 46.1%. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.25–3.33 (m, 3H), 3.40–3.48 (m, 2H), 5.19 (s, 2H), 7.34–7.40 (m, 5H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 17.54, 51.79, 67.26, 128.48, 128.68, 128.83, 135.54, 173.99, 203.76.



3-cyclohexylcyclobutan-1-one (15)[6]

Yield: 22.3%. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 0.90–0.96 (m, 2H), 1.14–1.28 (m, 4H), 1.67–1.70 (m, 1H), 1.74–1.79 (m, 4H), 2.01-2.09 (m, 1H), 2.73–2.77 (m, 2H), 3.02–3.06 (m, 2H);^{13}C-NMR (150 MHz, $CDCl_3$) δ 26.01, 26.18, 29.95, 30.89, 43.74, 50.80, 208.59.



3-*t*-butylclobutan-1-one[1, 2]

Yield: 7.7%. Low yield is associated with volatility of the product. Presence of some impurities (solvents and other) were indicated by ^{1}H NMR which were not removed completely as there was a decrease in compound quantity while drying the sample under reduced pressure. NMR (^{1}H & ^{13}C) data matched with the literature reported values.[1] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.27–2.33 (m, 1H), 2.82–2.89 (m, 4H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 26.41, 31.46, 34.72, 47.72, 208.32.

1-4. General procedure of Baeyer-Villiger oxidation

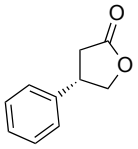
A mixture of a substrate (0.1 mmol) and a flavinium catalyst (10 mol%) in solvent (1 mL) was cooled to the indicated temperature. Cinchona alkaloid or other base (20 mol%) was added to the reaction mixture and the reaction was initiated by adding 30% H_2O_2 (0.15 mmol). After being stirred for the designated time, the reaction was quenched by addition of 1N sodium thiosulfate aqueous solution, and the mixture was extracted with methylene chloride. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes/EtOAc = 9:1 to 8:2) or by preparatory TLC (SiO_2, hexanes/EtOAc = 8:2 or 7:3) to obtain *γ*-butyrolactone. Reaction conversion was monitored by GC analyses with the following method: Oven temperature: 60 ^{o}C→370 ^{o}C (10 ^{o}C/min; 6 min hold at 370 ^{o}C; total time 37 min). Injector temp: 250 ^{o}C; Detector temp: 370 ^{o}C. Injection vol: 1 μL; Split mode: 40:3. Dry N_2 was used as a carrier gas with a column flow rate of 15 mL/min.

[5] Du, X.; Hinklin, R. J.; Xiong, Y.; Dransfield, P.; Park, P.; Kohn, T. J.; Pattaropong, V.; Lai, S.; Fu, Z.; Jiao, X.; Chow, D.; Jin, L.; Davda, J.; Veniant, M. M.; Anderson, D. A.; Baer, B. R.; Bencsik, J. R.; Boyd, S. A.; Chicarelli, M. J.; Mohr, P. J.; Wang, B.; Condroski, K. R.; DeWolf, W. E.; Conn, M.; Tran, T.; Yang, J.; Aicher, T. D.; Medina, J. C.; Coward, P.; Houze, J. B., *ACS Med. Chem. Lett.* **2014**, *5*, 1284−1289.

[6] Malkov, A. V.; Friscourt, F.; Bell, M.; Swarbrick, M. E.; Kocˇovský, P. *J. Org. Chem.* **2008**, *73,* 3996–4003.

1-5. Characterization of γ-lactone products

Stereoselectivity was determined by chiral HPLC analysis using the following method: [Daicel CHIRALCEL AD (0.46 x 25 cm); *n*-hexanes/2-propanol = 98/2, flow rate = 1.25 mL/min; Injection vol = 5 μL; detection wavelength 210 nm] for all compounds except for γ-lactones of 3-cyclohexylcyclobutanone and 3-*t*-butylcyclobutanone which were reacted with benzyl amine / Me_3Al and the corresponding γ-hydroxy-N-benzylamide derivatives[9] were analyzed by Daicel CHIRALCEL OD (0.46 x 25 cm); *n*-hexanes/2-propanol = 90/10, flow rate = 0.75 mL/min; Injection vol = 5 μL; detection wavelength 210 nm]. The absolute configuration of γ-lactone product of 3-phenylcyclobutanone (**10**) was determined by the reported retention time.[6] The configuration of the other γ-lactone products was presumed to be identical based on their structural similarity, unless otherwise noted. The structures of the major isomer are shown.



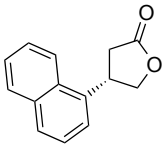
(*S*)-4-phenyldihydrofuran-2(3*H*)-one[2, 7]

A mixture of 3-phenylcyclobutanone **10** (300 mg, 2.05 mmol) and flavinium catalyst **3a** (10 mol%) in $CHCl_3$ (20 mL) was cooled to about -15℃. $(DHQ)_2PHAL$ (10 mol%) was added to the reaction mixture and the reaction was initiated by adding 1.1 equivalent of 3% H_2O_2 in CH_3CN (9): water(1). The reaction was stirred at -15℃ for 64h and then quenched by 1N sodium thiosulfate aqueous solution (1 mL). Water (5 mL) was added to the mixture and organic layer was separated. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes/EtOAc = 9:1) to obtain 4-phenyldihydrofuran-2(3*H*)-one.

Yield: 87 %, e.r.: 91.7:8.3. t_R = 34.9 (major), 42.1 (minor) min. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.69 (dd, *J* = 9.2, 17.2 Hz, 1H), 2.94 (dd, *J* = 9.0, 17.2 Hz, 1H), 3.80 (m, 1H), 4.28 (dd, *J* = 8.2, 9.0 Hz, 1H), 4.68 (dd, *J* = 8.0, 8.8 Hz, 1H), 7.23–7.40 (m, 5H).

Recrystallization of 4-phenyldihydrofuran-2(3*H*)-one[2,]

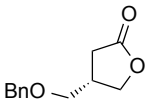
200 mg of the lactone described above (e.r.: 91.7:8.3) was dissolved in a warm mixture of Et_2O (61mL) and hexanes (25 mL) and the resultant solution was kept in a refrigerator for 4 hrs. The white crystals was filtered and washed with cold hexanes (1 mL x 3) to give 120 mg of the enantioenriched lactone (60%, e.r.: 98.5:1.5). HPLC spectrum of the recrystallized sample is given below.



(*S*)-4-(naphthalen-1-yl)dihydrofuran-2(3*H*)-one

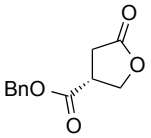
Yield: 92 %, e.r.: 96.9:3.1. t_R = 44.4 (major), 54.1 (minor). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.87 (dd, *J* = 7.3, 17.4 Hz, 1H), 3.09 (dd, *J* = 8.5, 17.4 Hz, 1H), 4.47 (dd, *J* = 6.3, 9.1 Hz, 1H), 4.58 (m, 1H), 4.85 (dd, *J* = 7.3, 9.1 Hz, 1H), 7.44 (d, *J* = 7.1 Hz, 1H), 7.49 (m, 1H, 7.55 (m, 1H), 7.59 (m, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.92 (m, 1H), 7.97 (d, *J* = 8.5 Hz, 1H); ^{13}C-NMR (600 MHz, $CDCl_3$) δ 35.34, 36.94, 73.55, 122.59, 122.67, 125.76, 126.97, 128.56, 129.53, 131.39, 134.29, 135.30, 176.61; HRMS (ESI^+) *m/z* 235.0739 $(M+Na)^+$ (calcd for $C_{14}H_{12}O_2Na$ 235.0735).

[7] Xu, Q-L.; Dai, L-X.; You, S-L. *Adv. Synth. Catal.* **2012**, *354*, 2275–2282.



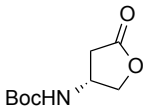
(*S*)-4-((benzyloxy)methyl)dihydrofuran-2(3*H*)-one

Yield: 85 %, e.r.: 82.0:18.0. t_R = 37.6 (major), 42.9 (minor) min. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.37 (dd, J = 6.2, 17.7 Hz, 1H), 2.60 (dd, J = 9.0, 17.7 Hz, 1H), 2.79–2.84 (m, 1H), 3.44–3.50 (m, 2H), 4.18 (dd, J = 5.5, 9.2 Hz, 1H), 4.39 (dd, J = 7.5, 9.2 Hz, 1H), 4.52 (s, 2H), 7.29-7.37 (m, 5H); ^{13}C-NMR (600 MHz, $CDCl_3$) δ 31.13, 35.39, 70.38, 70.77, 73.32, 127.67, 127.91, 128.52, 137.60, 176.90.



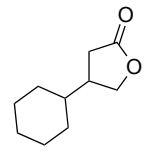
benzyl (*R*)-5-oxotetrahydrofuran-3-carboxylate

Yield: 58 %, e.r.: 89.3:10.7. t_R = 99.2 (major), 112.4 (minor) min. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.74 (dd, *J* = 9.7, 17.9 Hz, 1H), 2.87 (dd, *J* = 7.3, 17.9 Hz, 1H), 3.46–3.51 (m, 1H), 4.44 (dd, *J* = 6.5, 9.4 Hz, 1H), 4.50 (dd, *J* = 8.4, 9.4 Hz, 1H), 5.18 (s, 2H), 7.33–7.37 (m, 5H); ^{13}C-NMR (600 MHz, $CDCl_3$) δ 30.83, 39.98, 67.57, 68.97, 128.43, 128.76, 134.93, 170.97, 175.7.



***tert*-butyl (*R*)-(5-oxotetrahydrofuran-3-yl)carbamate**[8]

Yield: 92 %, e.r.: 97.8:2.2. [α] = +53.53° (*c* = 0.5, $CHCl_3$), (lit. [α] = +56.0° (*c* = 1.0, $CHCl_3$))[8]; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 1.47 (s, 9H), 2.47 (dd, J = 4.2, 17.9 Hz, 1H), 2.86 (dd, J = 7.7, 17.9 Hz, 1H), 4.24 (broad d, J = 7.7 Hz, 1H), 4.49 (broad s, 1H), 4.52 (dd, J = 6.0, 9.6 Hz, 1H), 4.87 (broad s, 1H); ^{13}C-NMR (600 MHz, $CDCl_3$) δ 28.28, 47.71, 73.66, 80.64, 154.97, 174.99.

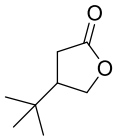


(–)-4-cyclohexyldihydrofuran-2(3*H*)-one[5]

Yield: 85 %, e.r.: 67.0:33.0. The stereoselectivity was determined by chiral HPLC analysis after conversion to hydroxyl benzylamide derivative.[9] The absolute configuration was not determined. [Daicel CHIRALCEL OD (0.46 x 25 cm); *n*-hexanes/2-propanol = 90/10, flow rate = 0.75 mL/min; Injection vol = 5 μL; detection wavelength 210 nm]: t_R = 14.8 (major), 22.0 (minor); [α] = –4.09° (*c* = 0.45, $CHCl_3$), (lit. [α] = –6.8° (*c* = 0.5, $CHCl_3$) for 61% ee); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 0.94–1.02 (m, 2H), 1.13–1.34 (m, 4H), 1.61–1.76 (m, 5H), 2.22 (dd, *J* = 9.9, 17.1 Hz, 1H), 2.32 (m, 1H), 2.56 (dd, *J* = 8.3, 17.1 Hz, 1H), 3.98 (t, *J* = 8.8 Hz), 4.42 (t, *J* = 8.4 Hz, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 25.77, 25.85, 26.15, 30.51, 31.17, 32.77, 41.43, 41.73, 72.27, 177.46.

[8] Bergman, Y.; Ciampini, M.; Jalal, S.; Lagiakos, H. L.; Aguilar, M-I.; Perlmutter, P. *Tetrahedron Asymmetry,* **2008**, *19*, 2861–2863.

[9] Uchida, T.; Katsuki, T. *Helv. Chim. Acta,* **2002**, *85*, 3078–3089.



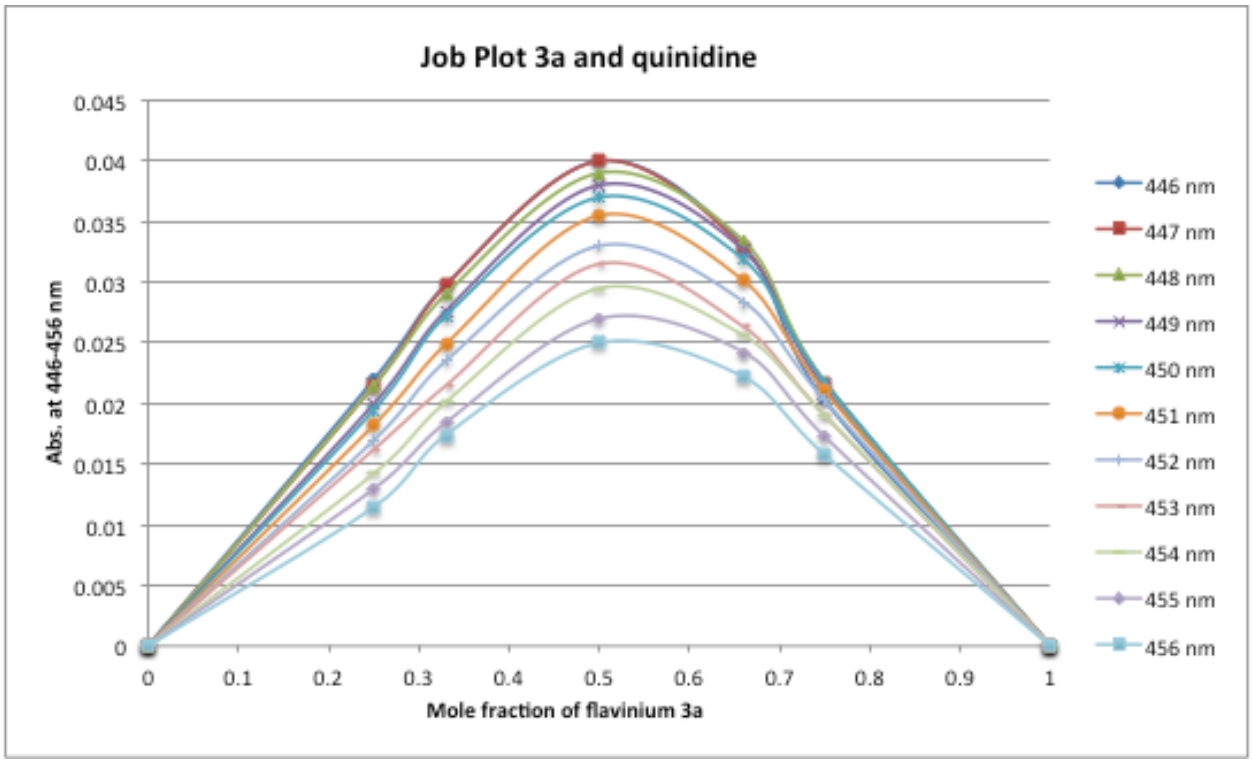
4-*t*-butyldihydrofuran-2(3*H*)-one[2]

Yield: 80.3 %, e.r.: 56.6:43.4. The stereoselectivity was determined by chiral HPLC analysis after conversion to hydroxyl benzylamide derivative.[9] The absolute configuration was not determined. [Daicel CHIRALCEL OD (0.46 x 25 cm); *n*-hexanes/2-propanol = 90/10, flow rate = 0.75 mL/min; Injection vol = 5 μL; detection wavelength 210 nm]: t_R = 10.4 (major), 14.5 (minor); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 0.93 (s, 9H), 2.32–2.38 (m, 1H), 2.41–2.48 (m, 2H), 4.08–4.11 (m, 1H), 4.31–4.34 (m, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 26.81, 30.07, 31.36, 45.88, 69.81, 177.45.

3. UV-Vis study and Jobs plot of Flavinium 3a and quinidine

The stoichiometry of the association between flavinium **3a** and quinidine was determined by using Job's method of continuous variation: The absorption (446 – 456 nm) of the samples wherein molar fractions of a solution **3a** and quinidine (1 x 10^{-4} each in CH_3CN) were varied while keeping the total concentration constant. .

Each data point was subtracted with absorption of the individual compounds at the equimolar concentrations, and plotted against the molar ratio. The stoichiometry of the complex formed was determined from the inflection point in the Job's plots of absorbance vs. mole fraction at a particular wavelength between 446–456 nm. Each colored line represents absorbance at a particular wavelength from 446–456 nm ranges.



4. Reaction screening data for Baeyer-Villiger oxidation of 3-phenylcyclobutanone

The structures of the compounds used in the screening study are shown in Figure S2. Unless otherwise specified, all the reactions were carried out using 0.1 mmol of 3-phenylcyclobutanone following the general experimental procedures described in section 1-4.

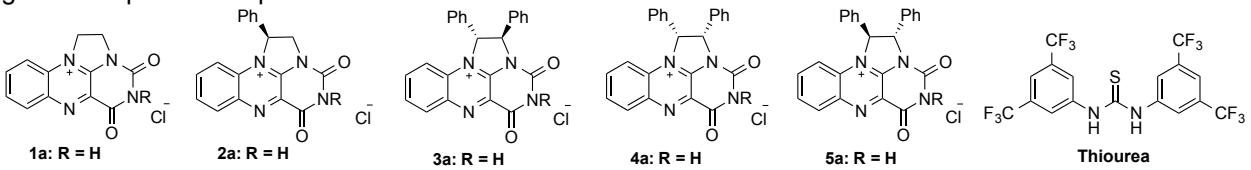


Figure S2: The structures of the compounds used in the screening study.

Base screening:

Catalyst	Additive	Solvent	Temp (°C)	Time (h)	GC Conv. (%)	ee (%)	e.r.		Yield (%)
							RT = 34.9	RT = 42.1	
		MeOH	-40	18	N/A	**2.8**	51.4	48.6	
		MeCN	-20	18	N/A	**0.4**	50.2	49.8	
3a		MeCN	-25	18	10.4	**0.4**	50.2	49.8	
3a		MeCN	-40	18	4.7	**3.8**	51.9	48.1	
3b		MeCN	-40	24	N/A	**2.4**	51.2	48.8	13
3a		MeOH	-40	18	N/A	**4.9**	52.5	47.6	
3a		CF3CH2OH	-40	24	N/A				3
3b		MeCN	0	24	N/A	**4.2**	52.1	47.9	83
3b	LiCl	MeCN	0	24	N/A	**3.8**	51.9	48.1	91
3b		DCM	RT	24	N/A	**1.8**	50.9	49.1	38
3b		MeOH	RT	24	N/A	**4.6**	52.3	47.7	37
3b		MeCN	RT	22	N/A	**3.8**	51.9	48.1	91
3a	20 mol% quinidine	DCM	-79	18	N/A	**18**	59.0	41.0	
3a	20 mol% 1,2,2,6,6-pentamethyl-4-hydroxypiperidine	DCM	-79	18	N/A	**18.6**	59.3	40.7	
3a	15 mol% NaHCO3	MeOH	-40	24	N/A	**5.4**	52.7	47.3	18
3a	100 mol% NaHCO3	MeOH	-40	24	N/A				
3a	20 mol% (-)-sparteine	MeCN	-42	18	23	**4.8**	47.6	52.4	
3a	20 mol% 1,2,2,6,6-pentamethyl-4-hydroxypiperidine	MeCN	-42	18	12	**23.4**	61.7	38.3	
3a	TBS-protected quinidine	MeCN	-42	18	4.8	**12.4**	56.2	43.8	
3a	100 mol% thiourea	MeCN	-40	18	N/A	**1.6**	50.8	49.2	
3a	20 mol% Proton sponge	MeCN	-40	18	7.6	**4.4**	52.2	47.8	
3a	20 mol% 4-methylmorpholine	MeCN	-40	18	9.7	**10**	55.0	45.0	
3a	20 mol% 4-methylmorpholine N-oxide	MeCN	-40	18	5.2	**4.8**	52.4	47.6	
3a	20 mol% quinidine + 40 mol% [BMIM]Cl	MeCN	-40	18	11.1	**15.9**	58.0	42.1	
3a	20 mol% quinidine + 40 mol% [BMIM]Cl	MeCN	-40	18	30	**22.2**	61.1	38.9	
3a	20 mol% TMEDA	MeCN	-40	18	1.2	**8**	54.0	46.0	
3a	20 mol% 1,1,1,3,3,3-hexamethyldisilazine	MeCN	-40	18	6	**4.4**	52.2	47.8	
3a	20 mol% (-)-sparteine	MeCN	-40	18	30.4	**1.6**	49.2	50.8	
3a	20 mol% D(+)-10-CSA	DCM	-40	45	17.3	**13**	56.5	43.5	
3a	120 mol% MeSO2NH2	DCM	-38	24	2.1	**21.8**	60.9	39.1	
3a	100 mol% Boc-L-isolucinol	MeCN	-25	18	N/A	**6**	53.0	47.0	
3a	100 mol%R-(+)-2,2'-diamino-1,1'-binaphthalene	MeCN	-25	18	N/A	**13**	56.5	43.5	
3a	100 mol% C6F6	MeCN	-25	18	N/A	**6.8**	53.4	46.6	
3a	100 mol% R-(+)-2,2'-diamino-1,1'-binaphthalene	MeCN	-25	18	1.5	**0**	50.0	50.0	
3a	100 mol% HMPA	MeCN	-25	18	1.2	**6.2**	53.1	46.9	
3a	100 mol% (S)-(-)-N,N'-dimethyl-1-phenylethylamine	MeCN	-25	18	10	**25.2**	62.6	37.4	
3a	100 mol% thiourea	MeCN	-20	18	N/A	**0.8**	50.4	49.6	
3a	1.2 equiv. of MeSO2NH2	DCM	-38	24	2.1	**21.8**	60.9	39.1	
3a	100 mol% Et3N	MeCN	-40	18	60.5	**24.4**	62.2	37.8	

Base screening (cont.):

Catalyst	Additive	Solvent	Temp (°C)	Time (h)	GC Conv. (%)	ee (%)	e.r.		Yield (%)
							RT = 34.9	RT = 42.1	
3a	100 mol% DIPEA	DCM	-40	18	33	**15.4**	57.7	42.3	
3a	100 mol% DABCO	MeCN	-35	18	21.2	**28.6**	64.3	35.7	
	100 mol% DABCO	MeCN	-35	18	7.9	**1.4**	50.7	49.3	
3a	20 mol % 3-quinuclidinol	MeCN	-35	18	38.3	**36.2**	68.1	31.9	
3a	100 mol% quinine	MeCN	-40	18	16.9	**53.8**	76.9	23.1	
3a	100 mol% quinidine	MeCN	-35	18	49.2	**48.8**	74.4	25.6	
	100 mol% quinidine	MeCN	-35	18	12.4	**4.8**	52.4	47.6	
3a	20 mol% quinidine	MeCN	-35	18	21.3	**48.4**	74.2	25.8	
3a	20 mol% (DHQ)2 PHAL	DCM	(-79 to -38)	18	N/A	**56.6**	78.3	21.7	

Solvent effects (earlier studies):

Catalyst	Additive	Solvent	Temp (°C)	Time (h)	GC Conv. (%)	ee (%)	e.r.		Yield (%)
							RT = 34.9	RT = 42.1	
		MeOH	-40	18	N/A	**2.8**	51.4	48.6	
		MeCN	-20	18	N/A	**0.4**	50.2	49.8	
3a		MeCN	-40	18	4.7	**3.8**	51.9	48.1	
3b		MeCN	-40	24	N/A	**2.4**	51.2	48.8	13
3a		MeOH	-40	18	N/A	**4.9**	52.5	47.6	
3a		CF3CH2OH	-40	24	N/A				3
3a		CF3CH2OH	-35	15	21	**3.6**	51.8	48.2	
3a	100 mol% quinidine	DCM	-40	18	22.7	**34**	67.0	33.0	
3a	100 mol% quinidine	MeCN	-35	18	49.2	**48.8**	74.4	25.6	
3a	100 mol% quinidine	CF3CH2OH	-35	15	94.6	**2.4**	51.2	48.8	
3a	20 mol % quinidine	MeOH	-40	18	6.2	**2.6**	51.3	48.7	
3a	100 mol% quinidine	MeCN	-25	18	37.3	**39.4**	69.7	30.3	
3a	170 mol% quinidine	EtOAc	-37	50	22.4	**28**	64.0	36.0	
3a	170 mol% quinidine	DMF	-37	50	10.2	**N/A**			
3a	20 mol% (DHQ)2 PHAL	MeOH	-40	18	7.6	**35.6**	67.8	32.2	
3a	20 mol% (DHQD)2PHAL	EtOAc	-38	24	24.7	**7.8**	53.9	46.1	
3a	10 mol % (DHQ)2 PHAL	Et2O	-38	24	3.9	**N/A**			
3a	10 mol % (DHQ)2 PHAL	THF	-38	24	2.2	**N/A**			

Stoichiometry of the base (cinchona alkaloid monomer):

Catalyst	Additive	Solvent	Temp (°C)	Time (h)	GC Conv. (%)	ee (%)	e.r.		Yield (%)
							RT = 34.9	RT = 42.1	
3a	100 mol% quinine	MeCN	-40	18	16.9	**53.8**	76.9	23.1	
3a	100 mol% quinidine	MeCN	-35	18	49.2	**48.8**	74.4	25.6	
3a	170 mol% quinidine	MeCN	-37	50	83	**51.2**	75.6	24.4	
3a	10 mol % quinidine	MeCN	-35	18	3.7	**10.2**	55.1	44.9	
3a	20 mol% quinidine	MeCN	-35	18	21.3	**48.4**	74.2	25.8	
3a	30 mol% quinidine	MeCN	-35	18	25.3	**50.4**	75.2	24.8	
3a	40 mol% quinidine	MeCN	-35	18	29.5	**49.6**	74.8	25.2	
3a	50 mol % quinidine	MeCN	-35	18	28	**49.2**	74.6	25.4	
3a	20 mol% quinidine	MeCN	-35	18	13.1	**50**	75.0	25.0	

Structure-activity relationship (monomer):

Catalyst	Additive	Solvent	Temp (°C)	Time (h)	GC Conv. (%)	ee (%)	e.r.		Yield (%)
							RT = 34.9	RT = 42.1	
3a	100 mol% quinine	MeCN	-40	18	16.9	**53.8**	76.9	23.1	
3a	100 mol% quinidine	MeCN	-35	18	49.2	**48.8**	74.4	25.6	
	100 mol% quinidine	MeCN	-35	18	12.4	**4.8**	52.4	47.6	
3a	20 mol% quinidine	MeCN	-35	18	21.3	**48.4**	74.2	25.8	
3a	TBS-protected quinidine	MeCN	-42	18	4.8	**12.4**	56.2	43.8	
3c	10 mol % quinidine	MeCN	-40	18	3.1	**2.5**	48.8	51.3	
3c	20 mol % quinidine	MeCN	-40	18	6.8	**3.8**	48.1	51.9	
4a	20 mol % quinidine	MeCN	-40	18	3.1	**6.8**	53.4	46.6	
4b	20 mol % quinidine	MeCN	-40	18	3.3	**0.8**	50.4	49.6	
1a	20 mol% quinidine	MeCN	-40	18	13.6	**18.8**	59.4	40.6	
5a	20 mol% quinidine	MeCN	-40	18	12	**13.8**	43.1	56.9	
5a	20 mol% quinine	MeCN	-40	18	13.3	**21**	39.5	60.5	
5a	20 mol% N-Bn quinidine	MeCN	-40	18	1.7	**4.8**	47.6	52.4	

Stoichiometry of the base (cinchona alkaloid dimer) and *solvent effects:*

Catalyst	Additive	Solvent	Temp (°C)	Time (h)	GC Conv. (%)	ee (%)	e.r.		Yield (%)
							RT = 34.9	RT = 42.1	
3a	20 mol% (DHQD)2 PHAL	MeCN	-40	18	28.5	**6**	53.0	47.0	
3a	20 mol% (DHQD)2AQN	MeCN	-38	24	42.7	**8.6**	54.3	45.7	
3a	20 mol% (DHQD)2Pyr	MeCN	-38	24	33.8	**10.2**	44.9	55.1	
3a	20 mol% (DHQ)2PHAL	MeCN	-38	24	33.7	**43.8**	71.9	28.1	
3a	20 mol% (DHQ)2AQN	MeCN	-38	24	25	**33.6**	66.8	33.2	
3a	20 mol% (DHQ)2Pyr	MeCN	-38	24	29.3	**33.4**	66.7	33.3	
3a	20 mol% (DHQD)2AQN	EtOAc	-38	24	22.5	**11.4**	55.7	44.3	
3a	20 mol% (DHQD)2Pyr	EtOAc	-38	24	22.1	**8.6**	45.7	54.3	
3a	20 mol% (DHQ)2PHAL	EtOAc	-38	24	27.6	**48.2**	74.1	25.9	
3a	20 mol% (DHQ)2PHAL	EtOAc	-35	20	10.4	**60.5**	80.3	19.8	
3a	20 mol% (DHQ)2AQN	EtOAc	-38	24	21.5	**26.2**	63.1	36.9	
3a	20 mol% (DHQ)2Pyr	EtOAc	-38	24	25.3	**38.6**	69.3	30.7	
3a	20 mol% (DHQD)2PHAL	DCM	-38	24	15.5	**15.2**	57.6	42.4	
3a	20 mol% (DHQD)2AQN	DCM	-38	24	16.7	**17.8**	58.9	41.1	
3a	20 mol% (DHQD)2Pyr	DCM	-38	24	18.5	**21.2**	39.4	60.6	
3a	20 mol% (DHQ)2PHAL	DCM	-38	24	21.5	**59.8**	79.9	20.1	
3a	20 mol% (DHQ)2AQN	DCM	-38	24	14.9	**43.4**	71.7	28.3	
3a	20 mol% (DHQ)2Pyr	DCM	-38	24	22	**67**	83.5	16.5	
3a	10 mol % (DHQ)2 PHAL	CHCl3	-38	24	17.6	**87.2**	93.6	6.4	
3a	20 mol % (DHQ)2 PHAL	CHCl3	-38	24	16.6	**84**	92.0	8.0	
3a	30 mol % (DHQ)2 PHAL	CHCl3	-38	24	12.5	**87**	93.5	6.5	

Structure-activity relationship (dimer):

Catalyst	Additive	Solvent	Temp (°C)	Time (h)	GC Conv. (%)	ee (%)	e.r.		Yield (%)
							RT = 34.9	RT = 42.1	
3a	10 mol% (DHQ)2 PHAL	DCM	-38	24	33.6	**58**	79.0	21.0	
3a	20 mol% (DHQ)2PHAL	DCM	-38	24	21.5	**59.8**	79.9	20.1	
3a	20 mol% (DHQD)2PHAL	MeCN	-38	24	33.9	**6**	53.0	47.0	
3b	20 mol% (DHQ)2PHAL	DCM	-38	24	18.9	**36.6**	68.3	31.7	
5a	20 mol% (DHQ)2PHAL	DCM	-38	24	7.4	**2.6**	48.7	51.3	
5a	10 mol% (DHQD)2PHAL	DCM	-38	24	9.7	**34.6**	32.7	67.3	
5a	20 mol% (DHQD)2PHAL	DCM	-38	24	18	**52.2**	23.9	76.1	
1a	20 mol% (DHQ)2PHAL	DCM	-38	24	8.1	**39.4**	69.7	30.3	
1a	20 mol% (DHQD)2PHAL	DCM	-38	24	5.6	**4.4**	47.8	52.2	
2a	20 mol% (DHQ)2 PHAL	DCM	-38	24	16.4	**31**	65.5	34.5	
2a	20 mol% (DHQD)2 PHAL	DCM	-38	24	42.1	**13.6**	43.2	56.8	
5a (10 mol%)	20 mol% (DHQD)2 PHAL	EtOAc	-35	20	9.4	**49.4**	25.3	74.7	
2a (10 mol%)	20 mol% (DHQD)2 PHAL	EtOAc	-35	20	12.8	**35.6**	32.2	67.8	

Reaction optimization (reaction conversion) – combination of other bases:

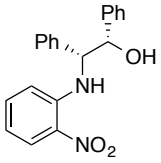
Catalyst	Additive	Solvent	Temp (°C)	Time (h)	GC Conv. (%)	ee (%)	e.r.		Yield (%)
							RT = 34.9	RT = 42.1	
3a	20 mol% (DHQ)2PHAL	DCM	-38	24	**21.5**	**59.8**	79.9	20.1	
3a	20 mol% (DHQ)2PHAL, 80 mol% quinine	DCM	-38	24	**67.9**	**57.8**	78.9	21.1	
3a	20 mol% (DHQ)2PHAL, 80 mol% Et3N	DCM	-38	24	**59.7**	**42.7**	71.4	28.7	
3a	20 mol% (DHQ)2PHAL, 80 mol% DMAP	DCM	-38	24	**43.3**	**44.8**	72.4	27.6	
3a	120 mol% MeSO2NH2	DCM	-38	24	**2.1**	**21.8**	60.9	39.1	
3a	20 mol % (DHQ)2 PHAL, 100 mol% MeSO2NH2	DCM	-38	24	**29.5**	**65.9**	83.0	17.1	
3a	20 mol% (DHQ)2 PHAL, 80 mol% quinine	DCM	-38	24	**67.9**	**57.8**	78.9	21.1	
3a	20 mol% (DHQ)2 PHAL, 80 mol% Et3N	DCM	-38	24	**59.7**	**42.7**	71.4	28.7	
3a	20 mol% (DHQ)2 PHAL, 80 mol% DMAP	DCM	-38	24	**43.3**	**44.8**	72.4	27.6	
3a	1.2 equiv. of MeSO2NH2	DCM	-38	24	**2.1**	**21.8**	60.9	39.1	
3a	1 equiv. of MeSO2NH2 + 0.2 equiv. of (DHQ)2 PHAL	DCM	-38	24	**29.5**	**65.9**	83.0	17.1	

Reaction optimization (reaction conversion) – temperature effect:

Catalyst	Additive	Solvent	Temp (°C)	Time (h)	GC Conv. (%)	ee (%)	e.r.		Yield (%)
							RT = 34.9	RT = 42.1	
3a	10 mol % (DHQ)2 PHAL	CHCl3	-38	5d	**46.4**	**87.2**	93.6	6.4	
3a	20 mol % (DHQ)2 PHAL	CHCl3	-38	5d	**38.2**	**84**	92.0	8.0	
3a	30 mol % (DHQ)2 PHAL	CHCl3	-38	5d	**27.6**	**87**	93.5	6.5	
3a	20 mol % (DHQ)2 PHAL, 2 mL solvent	CHCl3	-38	5d	**35.3**	**82.6**	91.3	8.7	
3a	20 mol % (DHQ)2 PHAL, 2 mL solvent, 2 equiv. of H2O2	CHCl3	-38	5d	**41.8**	**78.8**	89.4	10.6	
3a	20 mol % (DHQ)2 PHAL, 2 mL solvent, 2 equiv. of urea.H2O2	CHCl3	-38	5d	**14.9**	48.6	74.3	25.7	
3a	5 mol % (DHQ)2 PHAL	CHCl3	-38 to -29	24	**26.2**	**61**	80.5	19.5	
3a	***20 mol % (DHQ)2 PHAL***	***CHCl3***	***-38 to -29***	24	***34.6***	***83.8***	91.9	8.1	
3a	50 mol % (DHQ)2 PHAL	CHCl3	-38 to -29	24	**23.1**	**66.6**	83.3	16.7	
3a	5 mol % (DHQ)2 PHAL	CHCl3	-38 to -29	24	**26.2**	**61**	80.5	19.5	
3a	20 mol % (DHQ)2 PHAL	CHCl3	-38 to -29	24	**34.6**	**83.8**	91.9	8.1	
3a	50 mol % (DHQ)2 PHAL	CHCl3	-38 to -29	24	**23.1**	**66.6**	83.3	16.7	
3a	***10 mol% of (DHQ)2 PHAL***	***CHCl3***	***-15 to -20***	24	***70***	***87.6***	93.8	6.2	
3a	***10 mol% of (DHQ)2 PHAL + 5 mol% of quinine sulfate***	***CHCl3***	***-20 to -15***	24	***71.2***	***85.2***	92.6	7.4	
3a (20 mol%)	***20 mol% of (DHQ)2 PHAL***	***CHCl3***	***-20 to -15***	24	***92***	***88.8***	94.4	5.6	
3a	10 mol% of (DHQ)2 PHAL	CHCl3	-10 to -8	42	**86.2**	**84.2**	92.1	7.9	
3a	20 mol% of (DHQ)2 PHAL	CHCl3	-10 to -8	42	**97.2**	**85.4**	92.7	7.3	
3a	10 mol% of (DHQ)2 PHAL	CHCl3	-4 to 2	24	**81.4**	**81.8**	90.9	9.1	
3a	20 mol% of (DHQ)2 PHAL	CHCl3	-4 to 2	24	**91.6**	**83.8**	91.9	8.1	
3a	20 mol% quinidine	DCM	-77 to RT	18	**0.6**	**23.4**	61.7	38.3	
3a	20 mol% (DHQD)2 PHAL	DCM	-77 to RT	18	**0.5**	**11.6**	44.2	55.8	
3a	20 mol% (DHQ)2 AQN	DCM	-77 to RT	18	**0.4**	**37.8**	68.9	31.1	
3a	20 mol% (DHQ)2 AQN	MeCN	RT	20.5	**8.7**	**13.5**	56.8	43.3	
3a	20 mol% (DHQ)2 PHAL	MeCN + DCM	RT	18	**2.9**	**34.6**	67.3	32.7	

5. NMR spectral data:

(1*S*, 2*R*)-1,2-Diphenyl-2-[(2-nitrophenyl)amino]ethan-1-ol (S5)



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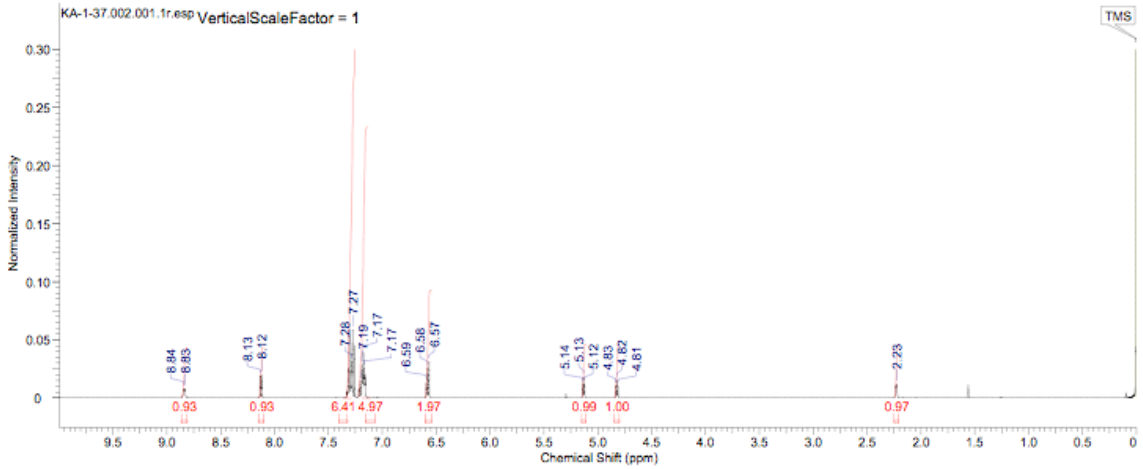

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2	4.81	2888.9	0.0099	7	5.14	3084.8	0.0111	12	7.17	4305.7	0.0389	17	8.12	4873.1	0.0206
3	4.82	2894.6	0.0150	8	6.57	3940.9	0.0309	13	7.19	4314.1	0.0288	18	8.13	4880.2	0.0186
4	4.83	2900.5	0.0106	9	6.58	3949.7	0.0259	14	7.20	4323.3	0.0146	19	8.83	5301.3	0.0080
5	5.12	3075.4	0.0118	10	6.59	3955.4	0.0137	15	7.27	4365.8	0.0588	20	8.84	5307.6	0.0080

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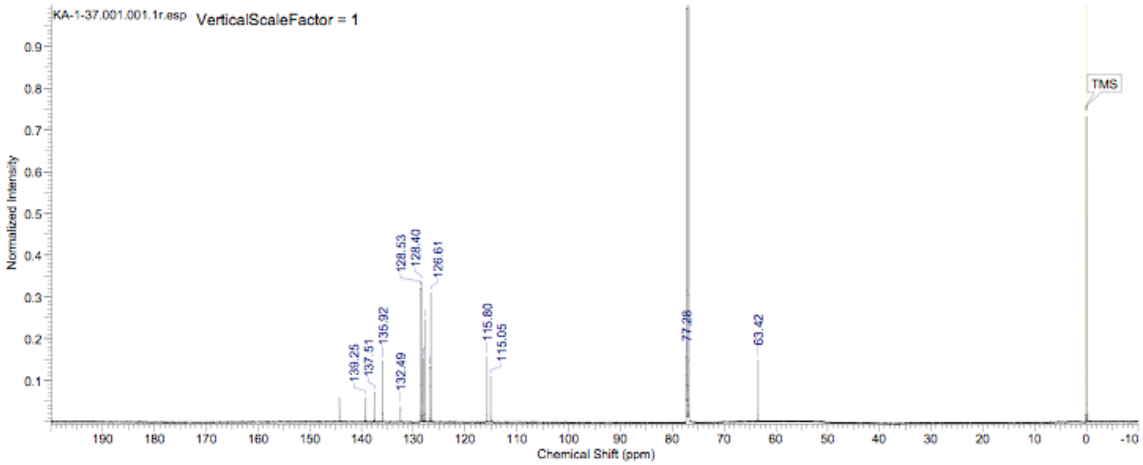

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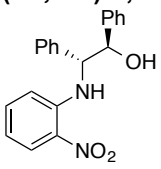
2	77.28	11662.7	0.1574	6	126.70	19122.3	0.1316	10	128.43	19383.0	0.1604	14	137.51	20753.0	0.0713
3	115.05	17362.7	0.1084	7	127.75	19280.7	0.2439	11	128.53	19397.4	0.3207	15	139.25	21016.0	0.0588
4	115.80	17476.1	0.1566	8	128.08	19330.2	0.1531	12	132.49	19996.0	0.0385				

(1*R*, 2*R*)-1,2-Diphenyl-2-[(2-nitrophenyl)amino]ethan-1-ol (S6)



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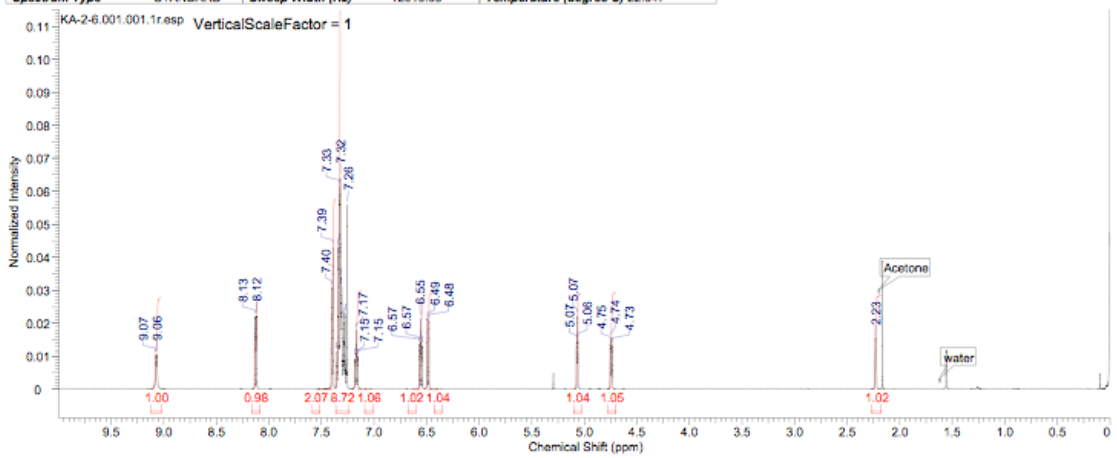

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3	[5.0303 .. 5.09	1.03787732	1.52834230e+7	1.03787732
4	[6.4513 .. 6.51	1.04009843	1.53161310e+7	1.04009843
5	[6.5221 .. 6.59	1.02017236	1.50227060e+7	1.02017236
6	[7.1224 .. 7.20	1.06464612	1.56776110e+7	1.06464612
7	[7.2358 .. 7.36	8.71718979	1.28366336e+8	8.71718979
8	[7.3658 .. 7.43	2.06572008	3.04190620e+7	2.06572008
9	[8.0836 .. 8.16	0.97711331	1.43866340e+7	0.97711331
10	[9.0241 .. 9.11	1.00047028	1.47325810e+7	1.00047028

7/26/2013 8:53:17 PM

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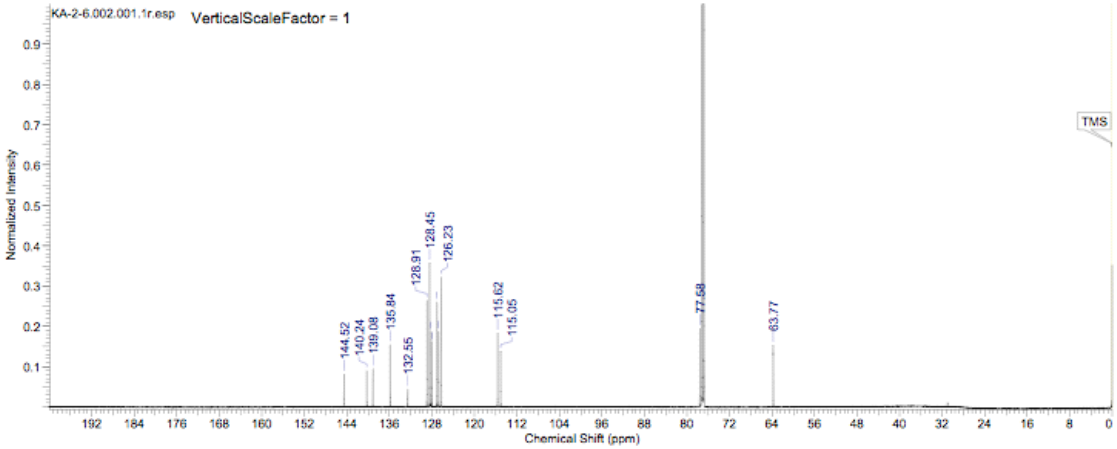

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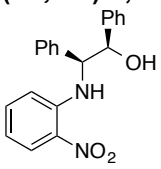
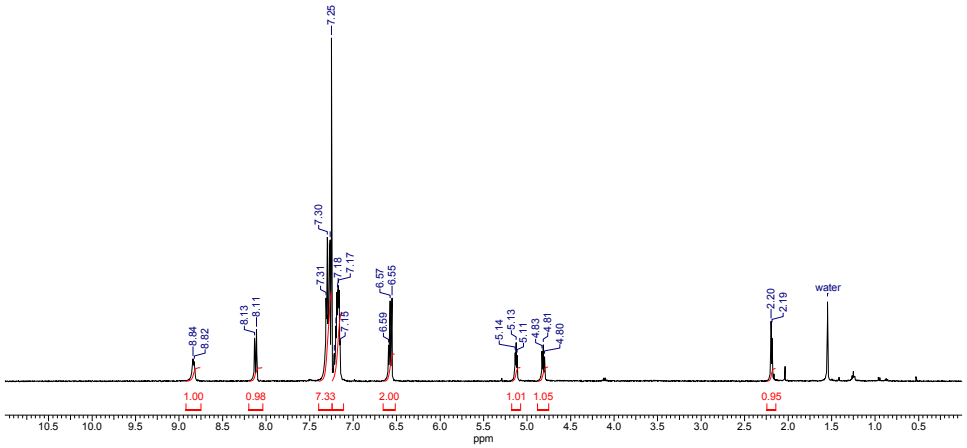
1	63.77	9624.8	0.1528	5	126.23	19050.7	0.3216	9	128.16	19341.2	0.1863	13	135.84	20501.0	0.1544
2	77.58	11708.9	0.1953	6	126.73	19125.6	0.1882	10	128.45	19385.2	0.3573	14	139.08	20990.7	0.0944
3	115.05	17363.8	0.1385	7	127.03	19171.8	0.2611	11	128.91	19455.7	0.2646	15	140.24	21164.6	0.0904
4	115.62	17449.7	0.1824	8	128.05	19324.7	0.1599	12	132.55	20004.8	0.0448	16	144.52	21810.5	0.0821

(1*R*, 2*S*)-1,2-Diphenyl-2-[(2-nitrophenyl)amino]ethan-1-ol (S7)





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4	4.81	1925.3
5	4.83	1930.8
6	5.11	2045.5
7	5.13	2050.2
8	5.14	2054.6
9	6.55	2620.8
10	6.57	2629.2
11	6.59	2636.2
12	7.15	2858.1

No.	(ppm)	(Hz)
13	7.17	2866.5
14	7.18	2871.3
15	7.20	2878.6
16	7.22	2885.9
17	7.25	2899.5
18	7.27	2905.7
19	7.30	2918.9
20	7.31	2924.4
21	8.11	3243.7
22	8.13	3252.9
23	8.82	3529.4
24	8.84	3535.2

No.	Annotation	(ppm)
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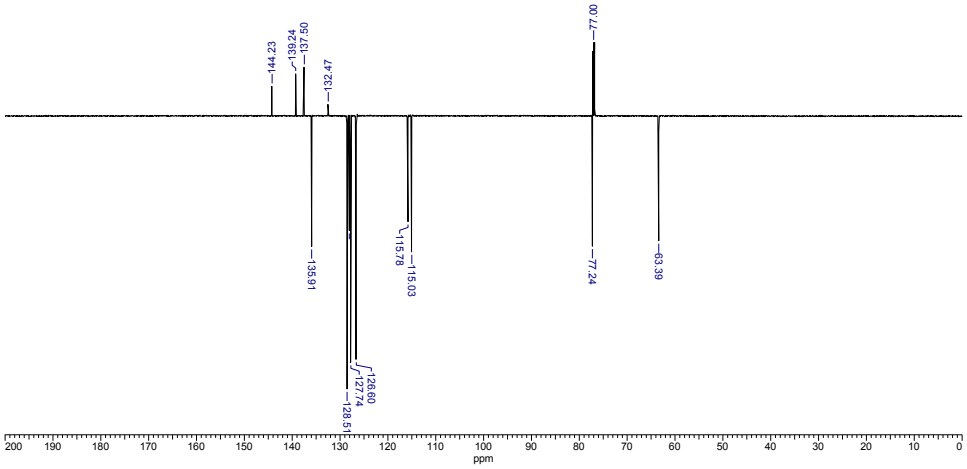

No.	(ppm)	(Hz)
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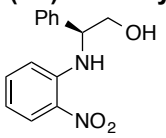
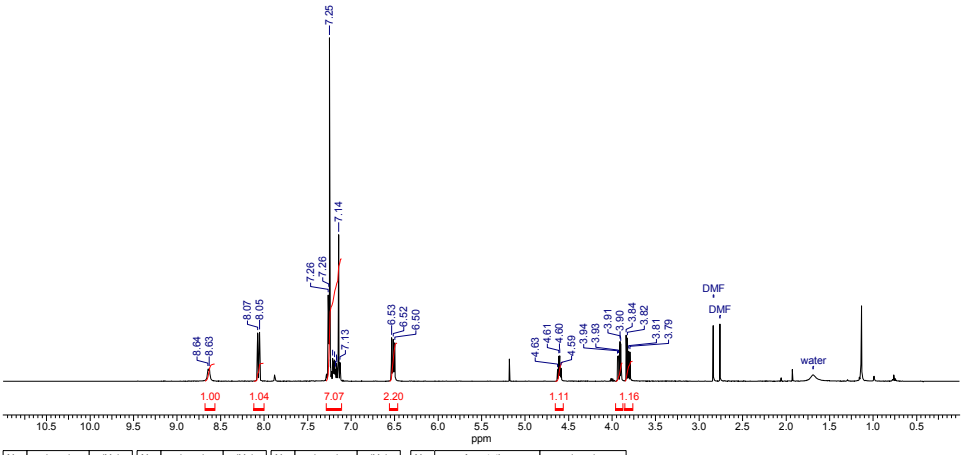
2	77.00	11620.8
3	77.24	11657.2
4	115.03	17360.7
5	115.78	17474.0
6	126.60	19105.9
7	126.68	19119.1
8	127.74	19278.7
9	128.06	19327.1

No.	(ppm)	(Hz)
10	128.38	19375.5
11	128.41	19380.0
12	128.51	19394.3
13	132.47	19991.8
14	135.91	20512.3
15	137.50	20751.1
16	139.24	21014.1
17	144.23	21766.8

Avance600\nmrdata\kanay\KY-2-22_001001r

(2*S*)-2-Phenyl-2-[(2-nitrophenyl)amino]ethan-1-ol (S8)





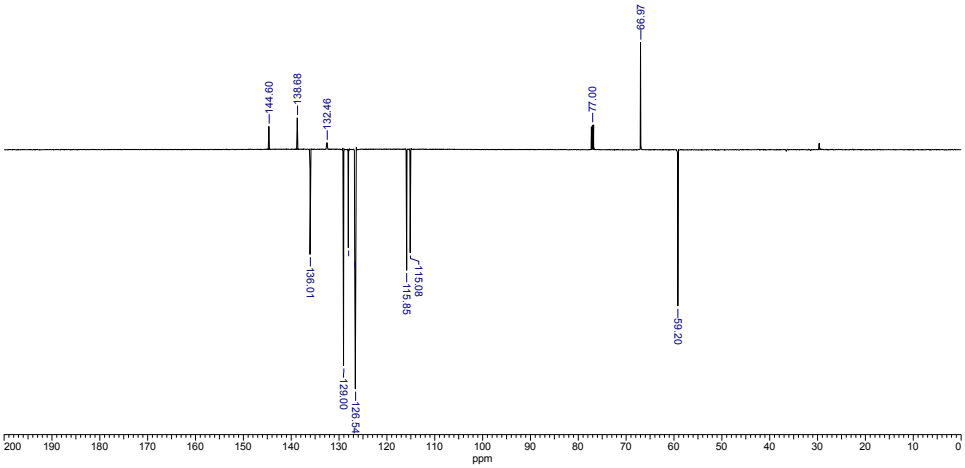
No.	(ppm)	(Hz)
1	3.79	1517.8
2	3.81	1524.0
3	3.82	1529.1
4	3.84	1535.4
5	3.90	1559.9
6	3.91	1563.9
7	3.93	1570.9
8	3.94	1575.3
9	4.59	1834.9
10	4.60	1839.3
11	4.60	1840.8
12	4.61	1845.2

No.	(ppm)	(Hz)
13	4.62	1847.0
14	4.63	1851.4
15	6.50	2597.8
16	6.50	2598.9
17	6.52	2605.8
18	6.53	2613.5
19	6.54	2614.6
20	7.13	2850.1
21	7.13	2851.2
22	7.14	2857.0
23	7.16	2865.1
24	7.17	2867.3

No.	(ppm)	(Hz)
25	7.18	2871.0
26	7.19	2876.4
27	7.21	2884.9
28	7.25	2899.5
29	7.26	2902.8
30	7.26	2904.6
31	8.05	3220.3
32	8.06	3221.8
33	8.07	3229.1
34	8.08	3230.6
35	8.63	3451.4
36	8.64	3457.3

No.	Annotation	(ppm)
1	water	1.69
2	DMF	2.76
3	DMF	[2.83 .. 2.84]

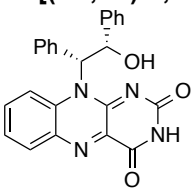
Neptune\data1\kana\vxrs400\KY-2-23p



No.	(ppm)	(Hz)
1	59.20	8934.7
2	66.97	10106.6
3	77.00	11620.8
4	115.08	17368.3
5	115.85	17483.9
6	126.54	19098.2
7	126.68	19119.1
8	128.00	19318.3
9	129.00	19469.0
10	132.46	19990.6
11	136.01	20526.6
12	138.68	20929.3
13	144.60	21822.9

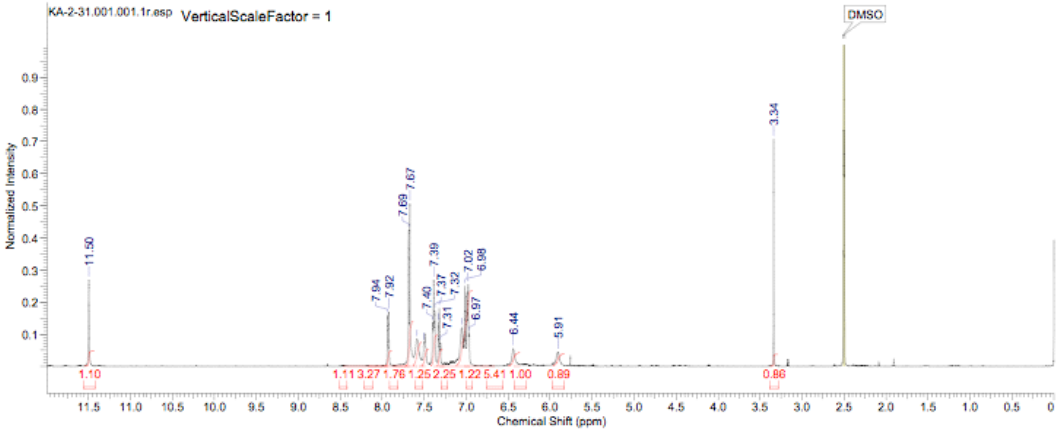
Avance600\nmrdata\kanay\KY-2-23_002001r

10-[(1*R*,2*S*)-1,2-Diphenyl-2-hydroxy]ethyl-benzo[*g*]pteridin-2,4(3*H*,10*H*)-dione (S9a)



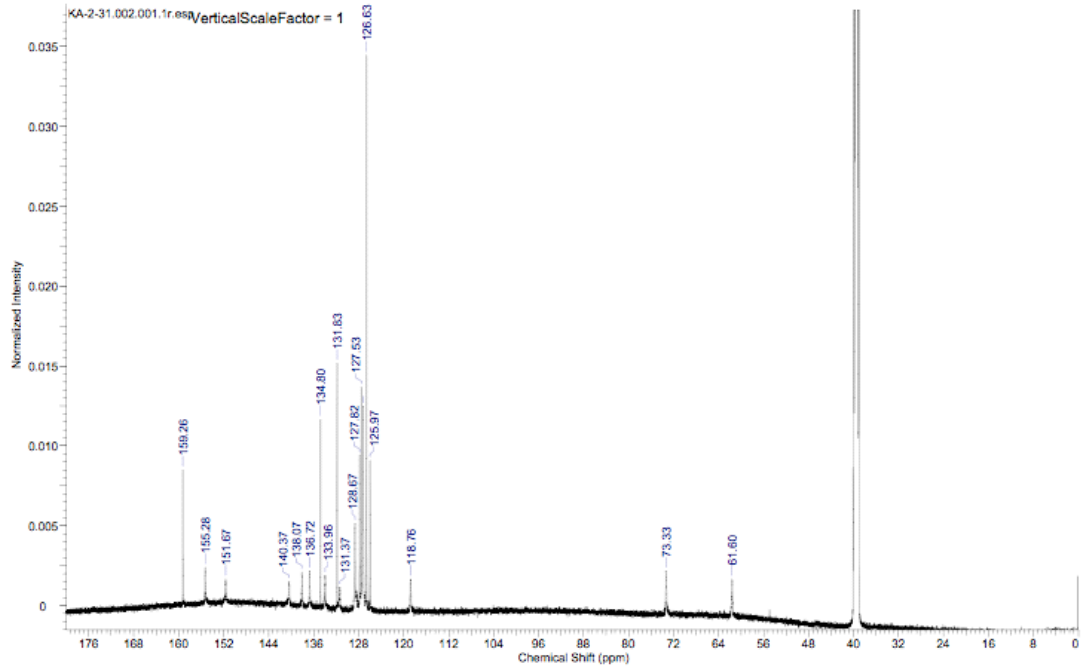
7/26/2013 8:04:12 PM

Acquisition Time (sec)	2.7263	*Comment*	1H	*Date*	04 Mar 2013 16:09:20		
Date Stamp	04 Mar 2013 16:09:20						
File Name	C:\Users\Kana Yamamoto\Desktop\Chiral flavinium salts\sample data\NMR\KA-2-31\1\pdata\1\1r					*Frequency (MHz)*	600.20
Nucleus	1H	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	32768
Owner	kenji	*Points Count*	65536	*Pulse Sequence*	zg30	*Receiver Gain*	10.73
SW(cyclical) (Hz)	12019.23	*Solvent*	DMSO-d6	*Spectrum Offset (Hz)*	3703.6492	*Spectrum Type*	STANDARD
Sweep Width (Hz)	12019.05	*Temperature (degree C)*	22.150				

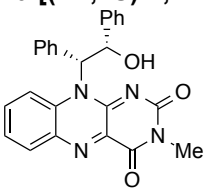


No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	3.34	2003.6	0.7071	7	7.02	4211.9	0.2493	13	7.39	4433.9	0.2692	19	7.92	4755.7	0.1695
2	5.91	3545.5	0.0432	8	7.06	4234.9	0.1203	14	7.40	4441.4	0.1363	20	7.94	4763.6	0.1579
3	6.44	3865.1	0.0557	9	7.31	4385.8	0.0731	15	7.50	4502.8	0.0739	21	11.50	6899.5	0.2687
4	6.97	4180.6	0.1014	10	7.32	4393.0	0.1793	16	7.58	4552.1	0.0844				
5	6.98	4187.5	0.2542	11	7.33	4400.3	0.1346	17	7.67	4605.0	0.5054				
6	7.01	4209.7	0.1078	12	7.37	4426.3	0.1746	18	7.69	4613.2	0.4235				

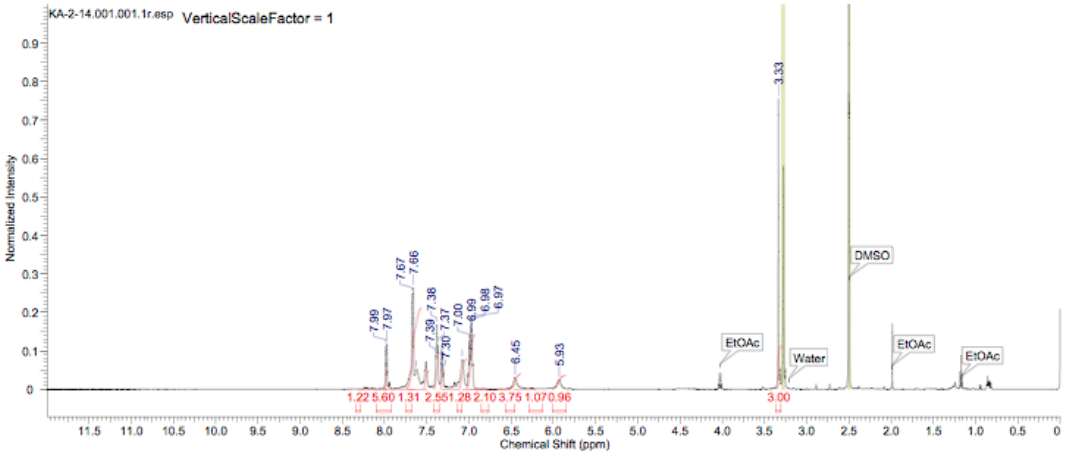
Acquisition Time (sec)	0.9088	*Comment*	13C	*Date*	04 Mar 2013 16:58:24		
Date Stamp	04 Mar 2013 16:58:24			*File Name*	C:\Users\Kana Yamamoto\Desktop\NMR\KA-2-31\2\pdata\1\1r		
Frequency (MHz)	150.92	*Nucleus*	13C	*Number of Transients*	918	*Origin*	spect
Original Points Count	32768	*Owner*	kenji	*Points Count*	32768	*Pulse Sequence*	zgpg30
Receiver Gain	173.95	*SW(cyclical) (Hz)*	36057.69	*Solvent*	DMSO-d6	*Spectrum Offset (Hz)*	15021.8535
Spectrum Type	STANDARD	*Sweep Width (Hz)*	36056.59	*Temperature (degree C)*	22.150		



10-[(1*R*,2*S*)-1,2-Diphenyl-2-hydroxy]ethyl-3-methyl-benzo[*g*]pteridin-2,4(3*H*,10*H*)-dione (S9b)

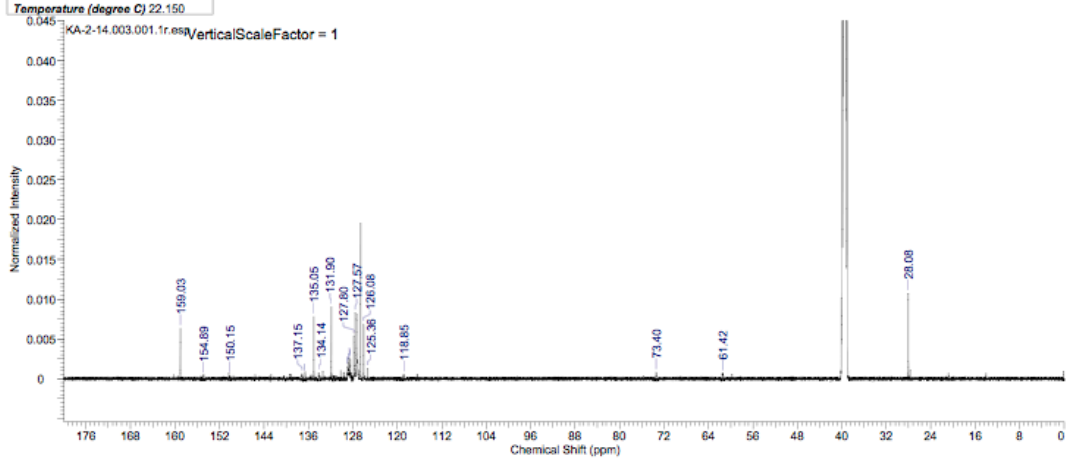


Acquisition Time (sec)	2.7263	*Comment*	1H	*Date*	21 Feb 2013 22:50:24				
Date Stamp	21 Feb 2013 22:50:24			*File Name*	H:\KA-2-14\1\pdata\1\1r			*Frequency (MHz)*	600.20
Nucleus	1H	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	32768	*Owner*	kenji
Points Count	65536	*Pulse Sequence*	zg30	*Receiver Gain*	9.93	*SW(cyclical) (Hz)*	12019.23	*Solvent*	DMSO-d6
Spectrum Offset (Hz)	3701.0117	*Spectrum Type*	STANDARD			*Sweep Width (Hz)*	12019.05	*Temperature (degree C)*	22.050



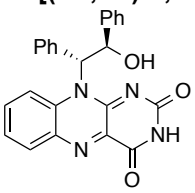
No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	3.3049 .. 3.363	3.00000000	1.49394860e+7	3.00000000
2	5.8480 .. 6.010	0.95807481	4.77104850e+6	0.95807481
3	6.3844 .. 6.531	1.06862330	5.32156100e+6	1.06862330
4	6.9255 .. 7.033	3.75067925	1.86777400e+7	3.75067925
5	7.0323 .. 7.122	2.10106421	1.04629400e+7	2.10106421
6	7.2848 .. 7.331	1.28482831	6.39822500e+6	1.28482831
7	7.3528 .. 7.412	2.54945183	1.26958330e+7	2.54945183
8	7.4710 .. 7.521	1.30715954	6.50943050e+6	1.30715954
9	7.5665 .. 7.735	5.60272360	2.79006040e+7	5.60272360
10	7.9506 .. 8.001	2.16833300	6.05962000e+6	1.21683300

Acquisition Time (sec)	0.9088	*Comment*	13C	*Date*	15 Mar 2013 19:51:28				
Date Stamp	15 Mar 2013 19:51:28			*File Name*	H:\KA-2-14\3\pdata\1\1r			*Frequency (MHz)*	150.92
Nucleus	13C	*Number of Transients*	886	*Origin*	spect	*Original Points Count*	32768	*Owner*	kenji
Points Count	32768	*Pulse Sequence*	zgpg30	*Receiver Gain*	173.95	*SW(cyclical) (Hz)*	36057.69	*Solvent*	DMSO-d6
Spectrum Offset (Hz)	15021.8535			*Spectrum Type*	STANDARD			*Sweep Width (Hz)*	36056.59
Temperature (degree C)	22.150								

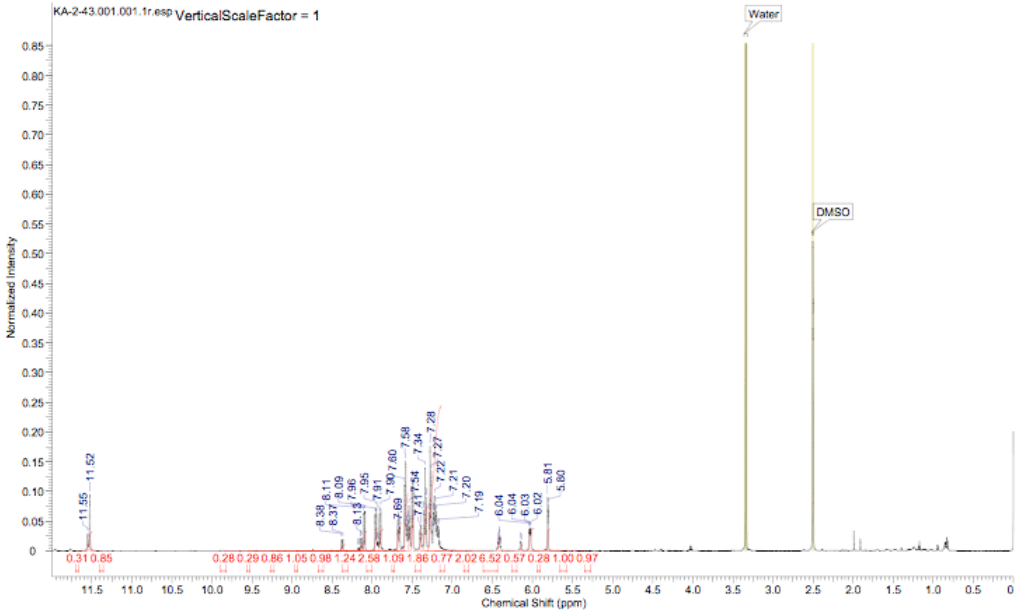


No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	28.08	4237.4	0.0108	6	126.08	19027.8	0.0069	11	128.85	19446.0	0.0020	16	136.61	20617.9	0.0006
2	61.42	9269.5	0.0007	7	127.57	19253.4	0.0083	12	128.95	19461.4	0.0015	17	137.15	20698.2	0.0007
3	73.40	11077.5	0.0009	8	127.80	19287.5	0.0054	13	131.90	19905.9	0.0090	18	150.15	22661.3	0.0004
4	118.85	17936.2	0.0005	9	128.46	19386.6	0.0025	14	134.14	20243.8	0.0008	19	154.89	23376.6	0.0004
5	125.36	18918.9	0.0013	10	128.67	19419.6	0.0027	15	135.05	20382.4	0.0078	20	159.03	24001.6	0.0064

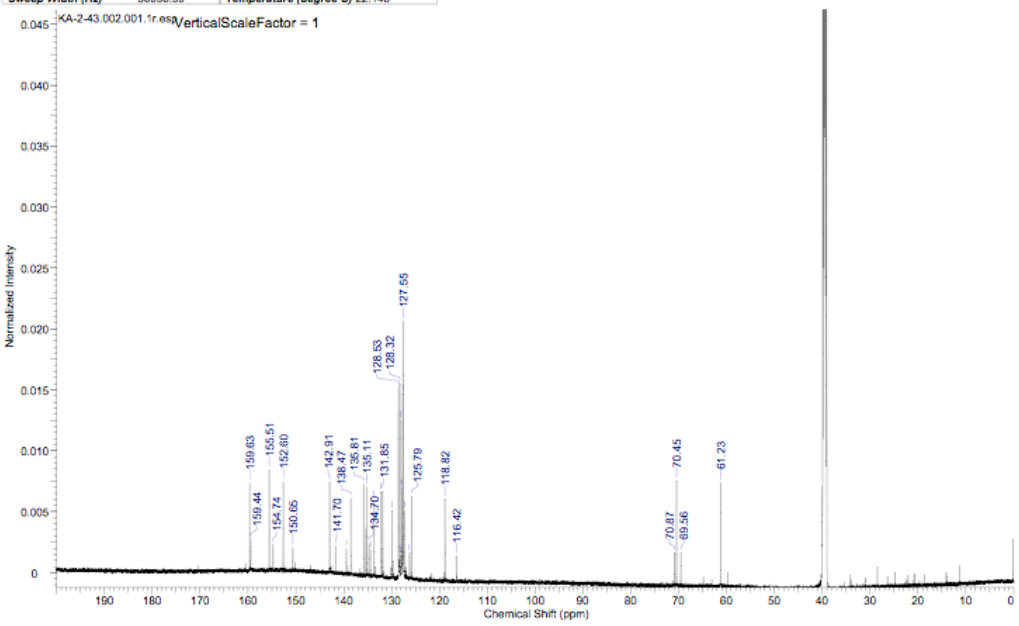
10-[(1*R*,2*R*)-1,2-Diphenyl-2-hydroxy]ethyl-benzo[*g*]pteridin-2,4(3*H*,10*H*)-dione (S10a)



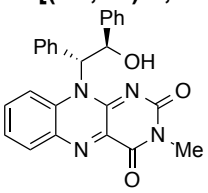
Acquisition Time (sec)	2.7263	*Comment*	1H	*Date*	15 Mar 2013 13:10:24		
Date Stamp	15 Mar 2013 13:10:24						
File Name	C:\Users\Kana Yamamoto\Desktop\Chiral flavinium salts\sample data\NMR\KA-2-43\1\pdata\1\1r					*Frequency (MHz)*	600.20
Nucleus	1H	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	32768
Owner	kenji	*Points Count*	65536	*Pulse Sequence*	zg30	*Receiver Gain*	10.73
SW(cyclical) (Hz)	12019.23	*Solvent*	DMSO-d6	*Spectrum Offset (Hz)*	3703.6492	*Spectrum Type*	STANDARD
Sweep Width (Hz)	12019.05	*Temperature (degree C)*	22.148				



Acquisition Time (sec)	0.9088	*Comment*	13C	*Date*	15 Mar 2013 13:50:56		
Date Stamp	15 Mar 2013 13:50:56						
File Name	C:\Users\Kana Yamamoto\Desktop\Chiral flavinium salts\sample data\NMR\KA-2-43\2\pdata\1\1r					*Frequency (MHz)*	150.92
Nucleus	13C	*Number of Transients*	777	*Origin*	spect	*Original Points Count*	32768
Owner	kenji	*Points Count*	32768	*Pulse Sequence*	zgpg30	*Receiver Gain*	173.95
SW(cyclical) (Hz)	36057.69	*Solvent*	DMSO-d6	*Spectrum Offset (Hz)*	15021.8535	*Spectrum Type*	STANDARD
Sweep Width (Hz)	36056.59	*Temperature (degree C)*	22.148				



10-[(1*R*,2*R*)-1,2-diphenyl-2-hydroxy]ethyl-3-methyl-benzo[*g*]pteridin-2,4(3*H*,10*H*)-dione (S10b)



Acquisition Time (sec)	2.7263	*Comment*	1H	*Date*	15 Mar 2013 13:10:24		
Date Stamp	15 Mar 2013 13:10:24						
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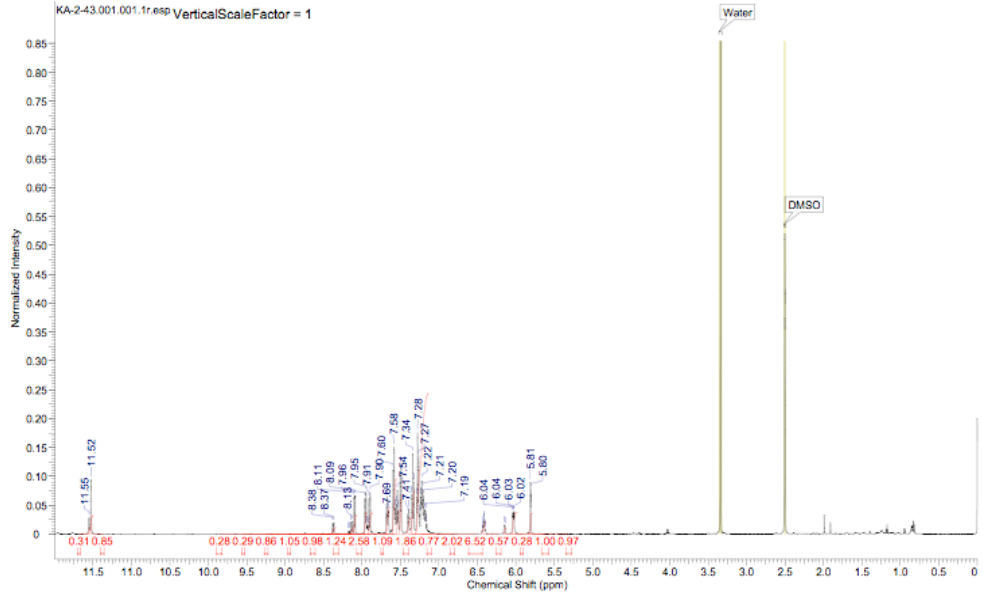
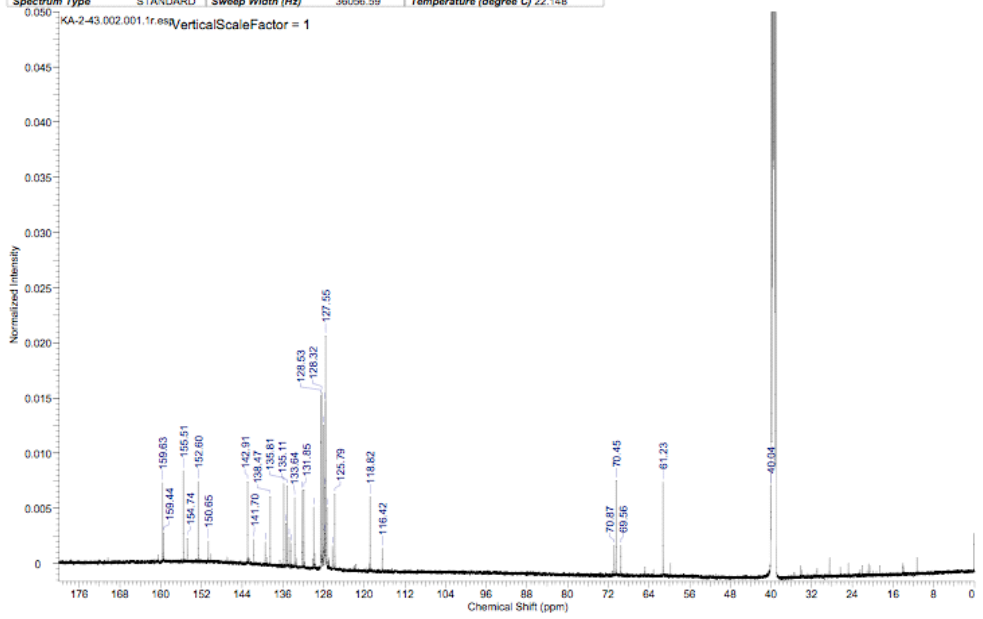
Nucleus	1H	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	32768
Owner	kenji	*Points Count*	65536	*Pulse Sequence*	zg30	*Receiver Gain*	10.73
SW(cyclical) (Hz)	12019.23	*Solvent*	DMSO-d6	*Spectrum Offset (Hz)*	3703.6492	*Spectrum Type*	STANDARD
Sweep Width (Hz)	12019.05	*Temperature (degree C)*	22.148				

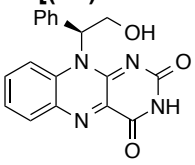


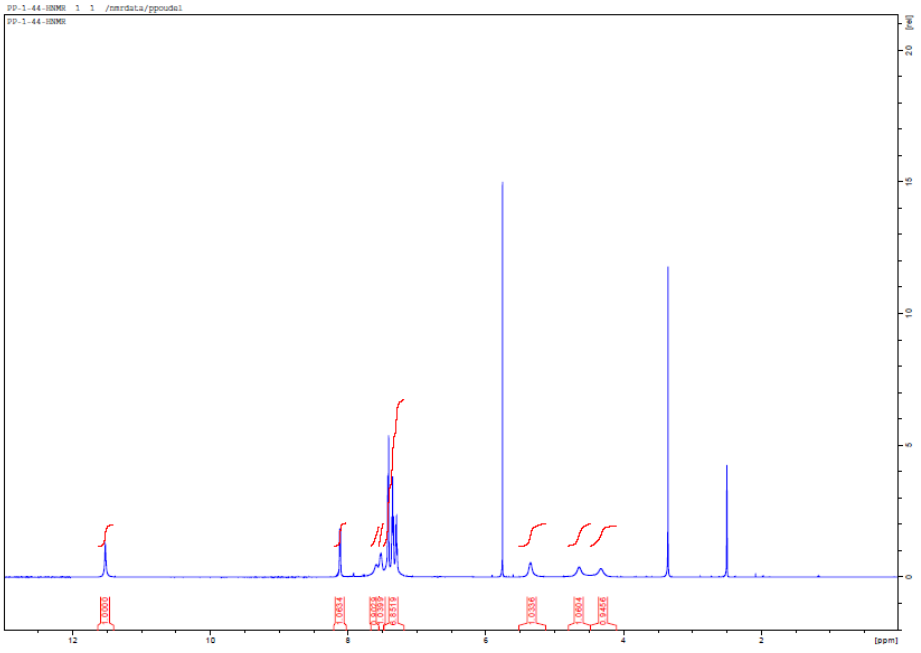
7/27/2013 7:00:08 PM

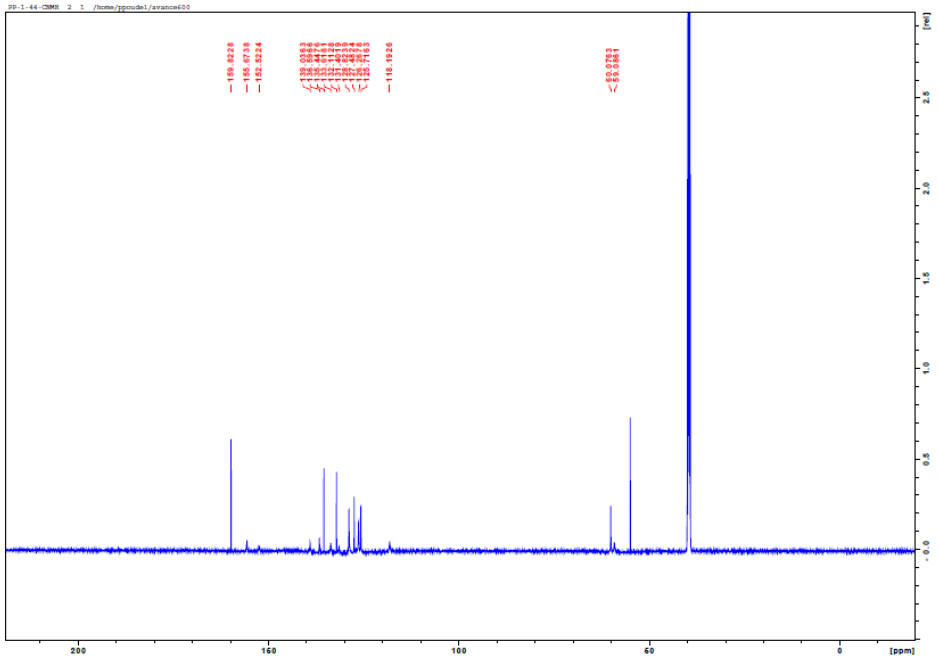
Acquisition Time (sec)	0.9088	*Comment*	13C	*Date*	15 Mar 2013 13:50:56		
Date Stamp	15 Mar 2013 13:50:56			*File Name*	C:\Users\Kana Yamamoto\Desktop\NMR\KA-2-43\2\pdata\1\1r		
Frequency (MHz)	150.92	*Nucleus*	13C	*Number of Transients*	777	*Origin*	spect
Original Points Count	32768	*Owner*	kenji	*Points Count*	32768	*Pulse Sequence*	zgpg30
Receiver Gain	173.95	*SW(cyclical) (Hz)*	36057.69	*Solvent*	DMSO-d6	*Spectrum Offset (Hz)*	15021.8535
Spectrum Type	STANDARD	*Sweep Width (Hz)*	36056.59	*Temperature (degree C)*	22.148		



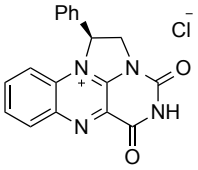
10-[(1*S*)-1-Phenyl-2-hydroxy]ethyl-benzo[*g*]pteridin-2,4(3*H*,10*H*)-dione (S12a)

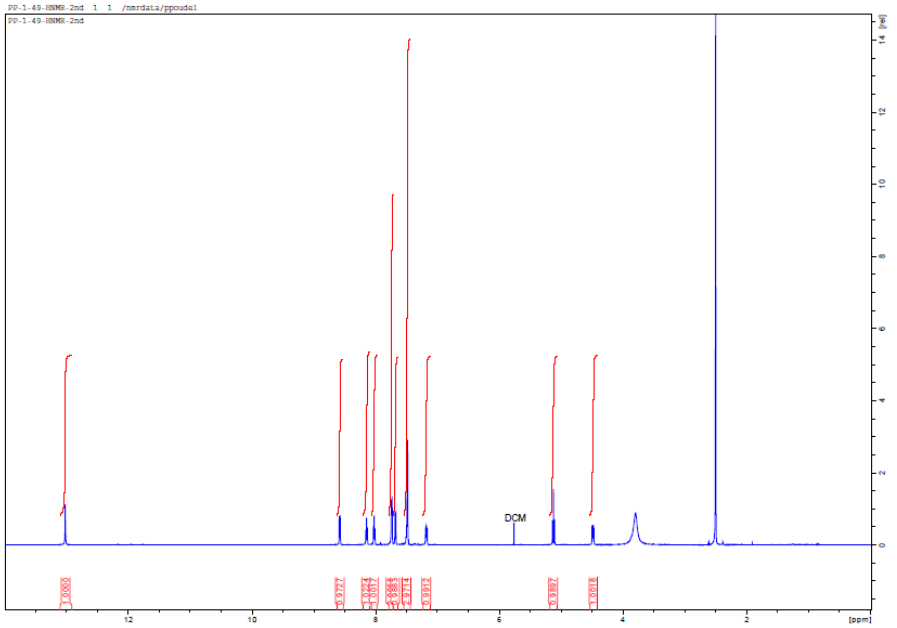


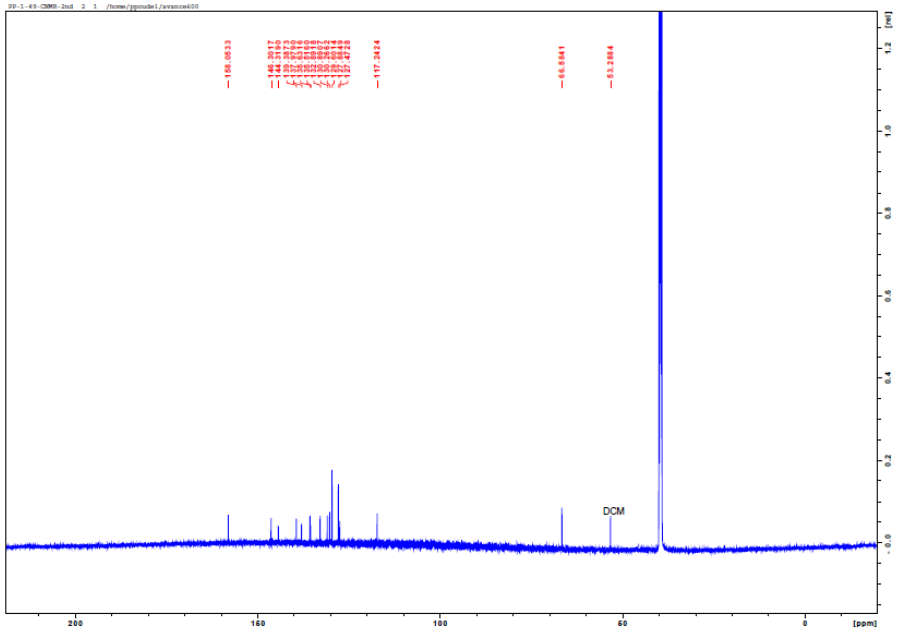




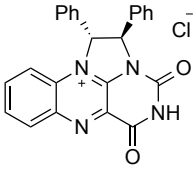
(1*S*)-1-Phenyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (2a)

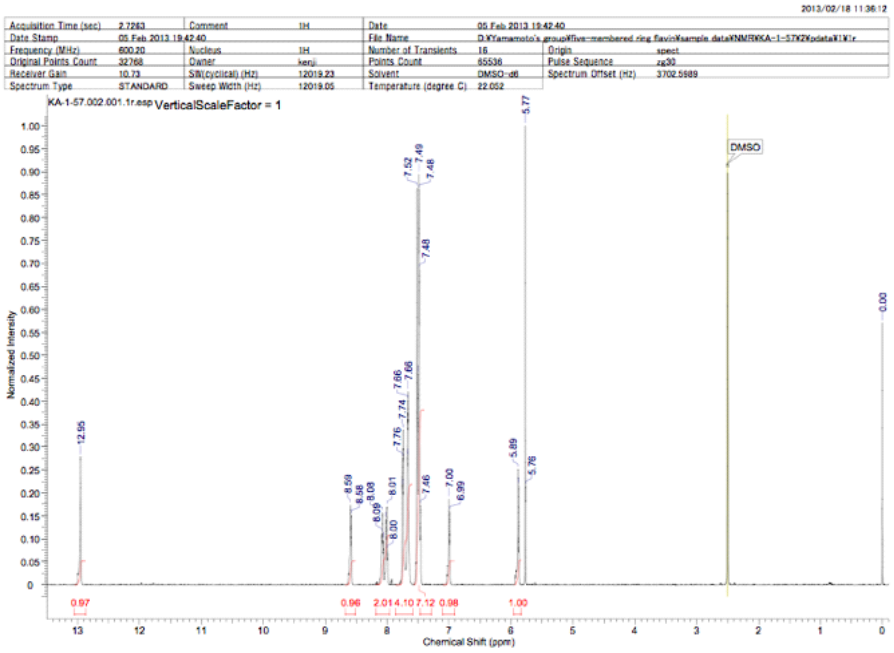




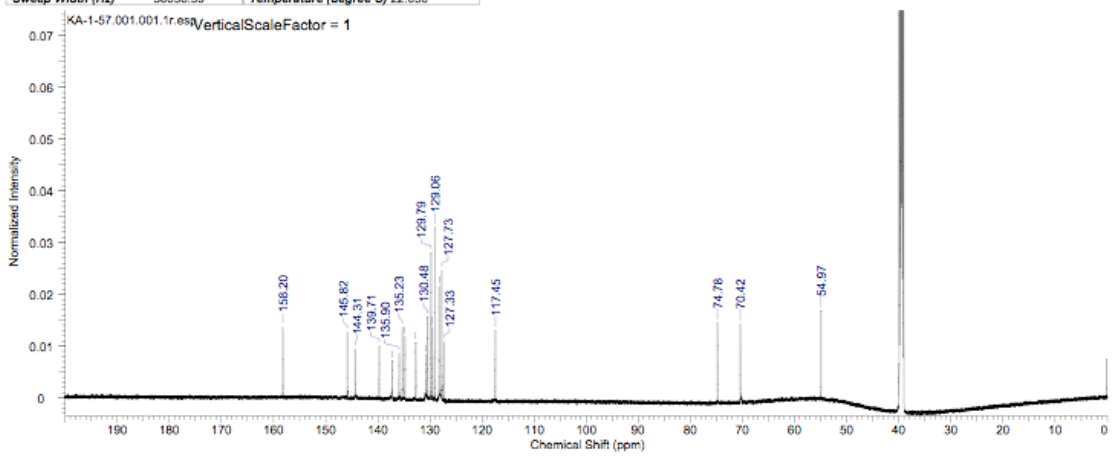


(1*R*,2*R*)-1,2-Diphenyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (3a)



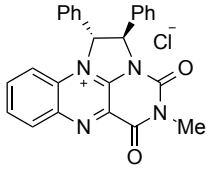


Acquisition Time (sec)	0.9086	Comment	C13	Date	05 Feb 2013 19:29:52		
Date Stamp	05 Feb 2013 19:29:52						
File Name	C:\Users\Kana Yamamoto\Desktop\Chiral flavinium salts\sample data\NMR\KA-1-57\1\pdata\1\1r					Frequency (MHz)	150.92
Nucleus	13C	Number of Transients	256	Origin	spect	Original Points Count	32768
Owner	kenji	Points Count	32768	Pulse Sequence	zgpg30	Receiver Gain	173.95
SW(cyclical) (Hz)	36057.69	Solvent	DMSO-d6	Spectrum Offset (Hz)	15020.7539	Spectrum Type	STANDARD
Sweep Width (Hz)	36056.59	Temperature (degree C)	22.050				

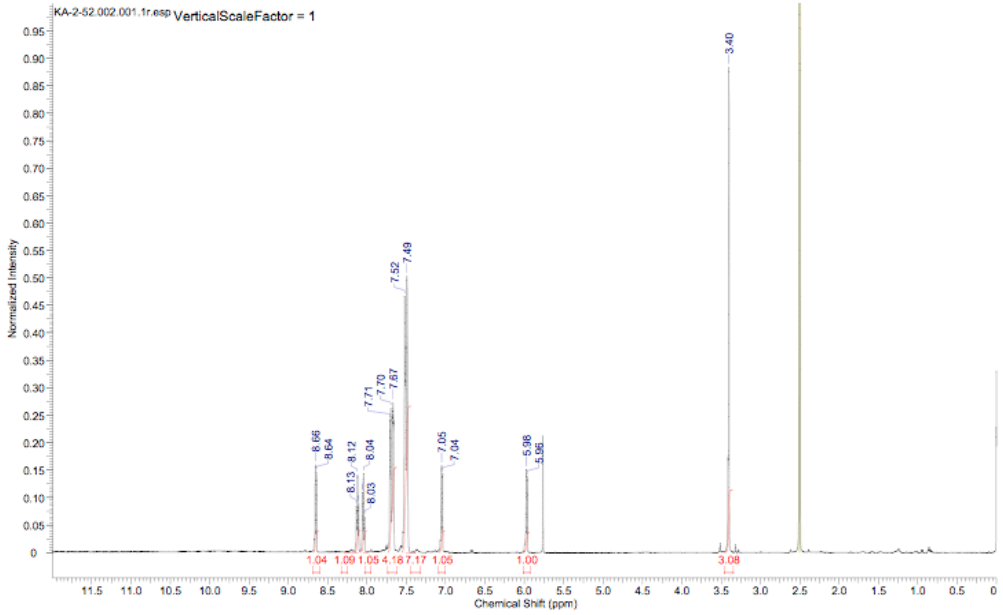


No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	54.97	8295.7	0.0169	7	128.22	19351.4	0.0215	13	132.71	20028.1	0.0108	19	144.31	21779.9	0.0094
2	70.42	10627.4	0.0144	8	129.06	19477.9	0.0330	14	134.77	20339.5	0.0118	20	145.82	22007.7	0.0127
3	74.76	11286.6	0.0145	9	129.53	19549.4	0.0137	15	135.23	20408.6	0.0136	21	158.20	23875.1	0.0138
4	117.45	17726.1	0.0131	10	129.79	19587.9	0.0281	16	135.90	20510.1	0.0086				
5	127.33	19216.0	0.0109	11	130.48	19692.5	0.0157	17	137.23	20711.4	0.0073				
6	127.73	19276.5	0.0247	12	130.69	19723.3	0.0083	18	139.71	21085.6	0.0101				

(1*R*,2*R*)-1,2-Diphenyl-3-methyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (3b)

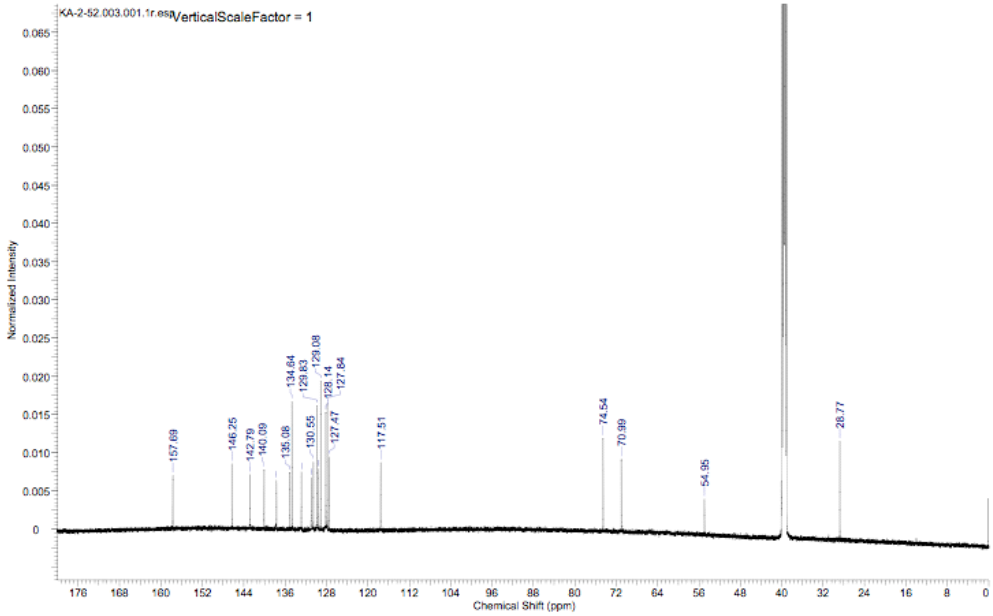


Acquisition Time (sec)	2.7263	Comment	1H	Date	23 Mar 2013 17:54:08		
Date Stamp	23 Mar 2013 17:54:08			File Name	C:\Users\Kana Yamamoto\Desktop\NMR\KA-2-52\2\pdata\1\1r		
Frequency (MHz)	600.20	Nucleus	1H	Number of Transients	16	Origin	spect
Original Points Count	32768	Owner	kenji	Points Count	65536	Pulse Sequence	zg30
Receiver Gain	10.73	SW(cyclical) (Hz)	12019.23	Solvent	DMSO-d6	Spectrum Offset (Hz)	3704.5662
Spectrum Type	STANDARD	Sweep Width (Hz)	12019.05	Temperature (degree C)	22.146		

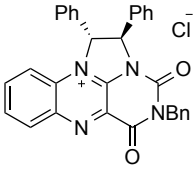


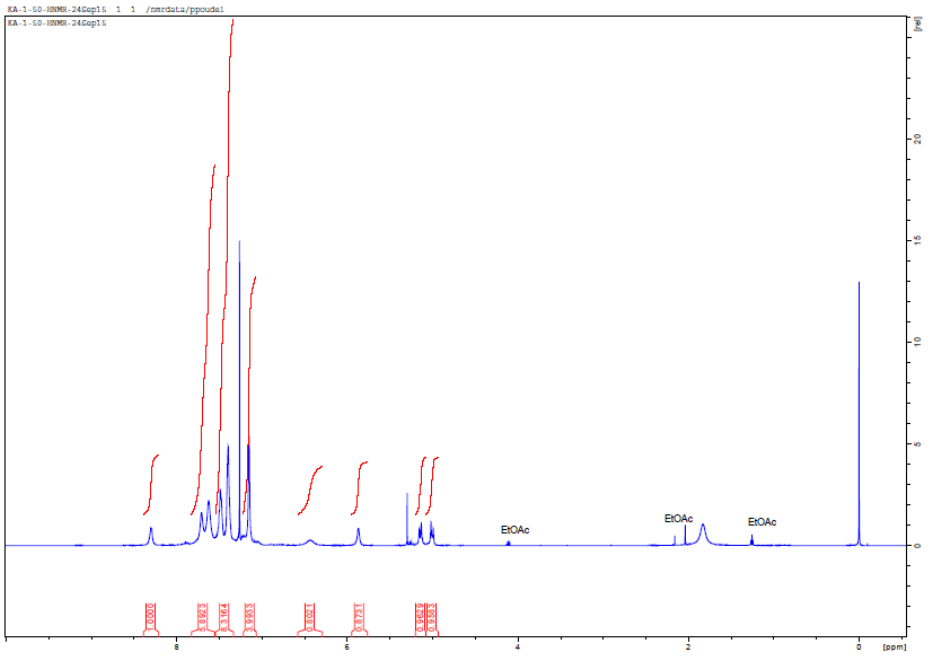
7/27/2013 8:29:12 PM

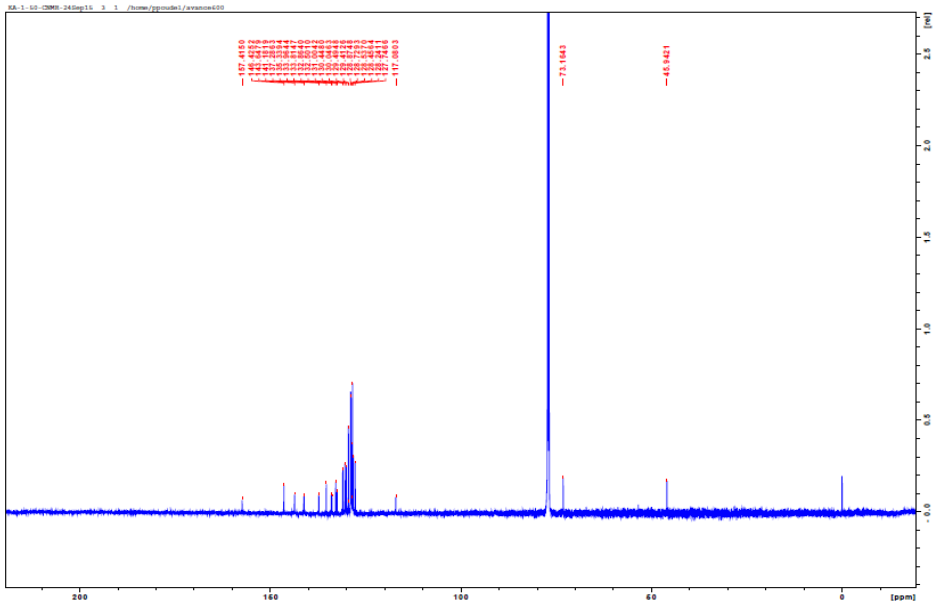
Acquisition Time (sec)	0.9088	Comment	13C	Date	23 Mar 2013 18:09:04		
Date Stamp	23 Mar 2013 18:09:04			File Name	C:\Users\Kana Yamamoto\Desktop\NMR\KA-2-52\3\pdata\1\1r		
Frequency (MHz)	150.92	Nucleus	13C	Number of Transients	256	Origin	spect
Original Points Count	32768	Owner	kenji	Points Count	32768	Pulse Sequence	zgpg30
Receiver Gain	173.95	SW(cyclical) (Hz)	36057.69	Solvent	DMSO-d6	Spectrum Offset (Hz)	15021.8535
Spectrum Type	STANDARD	Sweep Width (Hz)	36056.59	Temperature (degree C)	22.147		



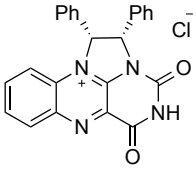
(1*R*,2*R*)-1,2-Diphenyl-3-benzyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (3c)



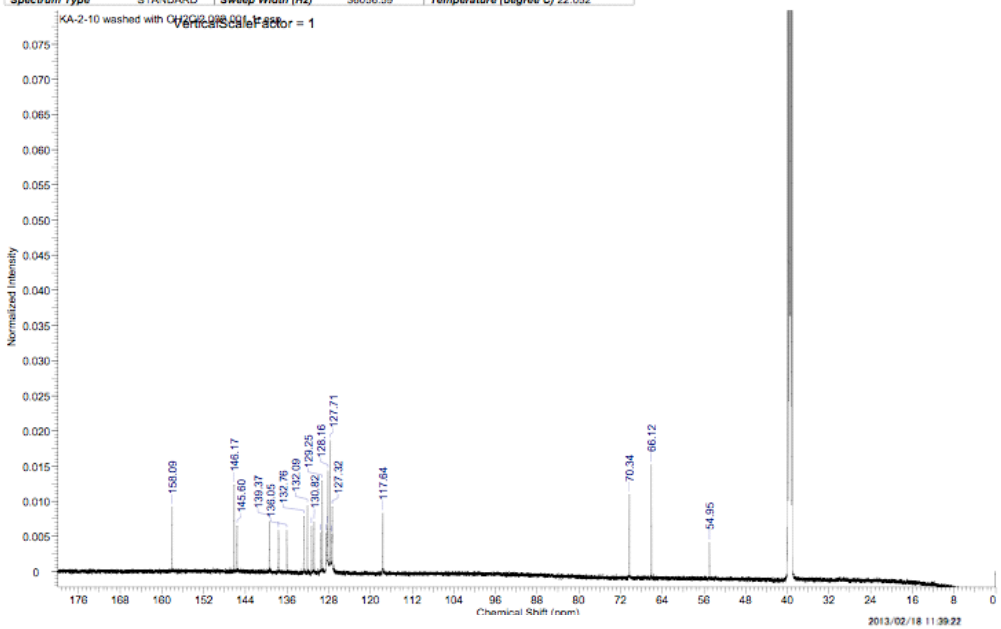




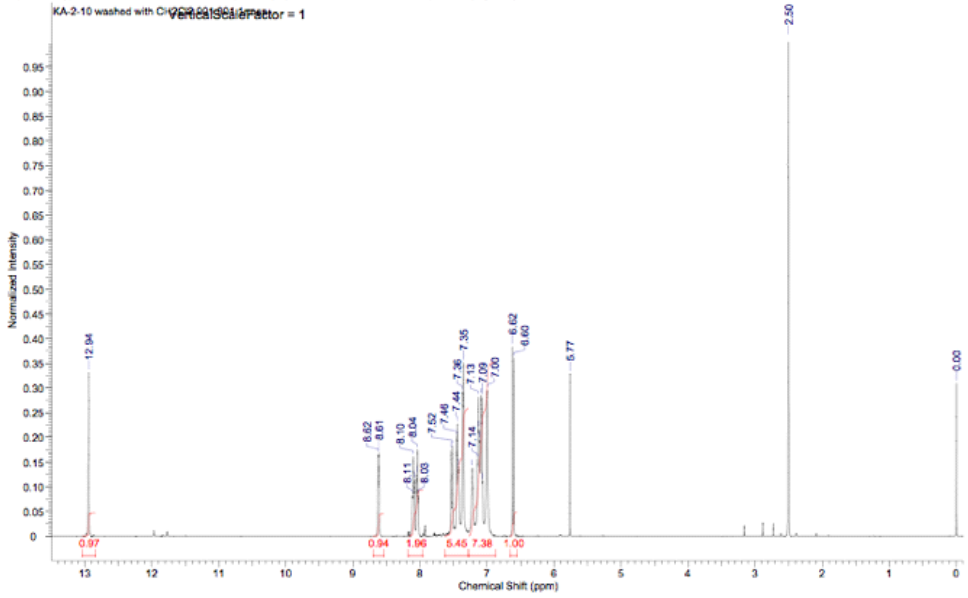
(1*R*,2*S*)-1,2-Diphenyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (4a)



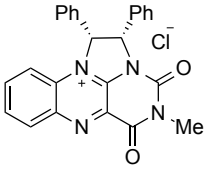
Acquisition Time (sec)	0.9088	*Comment*	13C	*Date*	17 Feb 2013 18:53:36		
Date Stamp	17 Feb 2013 18:53:36			*File Name*	C:\Users\Kana Yamamoto\Desktop\NMR\KA-2-10 washed with CH2Cl2\2\pdata\1\1r		
Frequency (MHz)	150.92	*Nucleus*	13C	*Number of Transients*	256	*Origin*	spect
Original Points Count	32768	*Owner*	kenji	*Points Count*	32768	*Pulse Sequence*	zgpg30
Receiver Gain	173.95	*SW(cyclical) (Hz)*	36057.69	*Solvent*	DMSO-d6	*Spectrum Offset (Hz)*	15020.7539
Spectrum Type	STANDARD	*Sweep Width (Hz)*	36056.59	*Temperature (degree C)*	22.052		



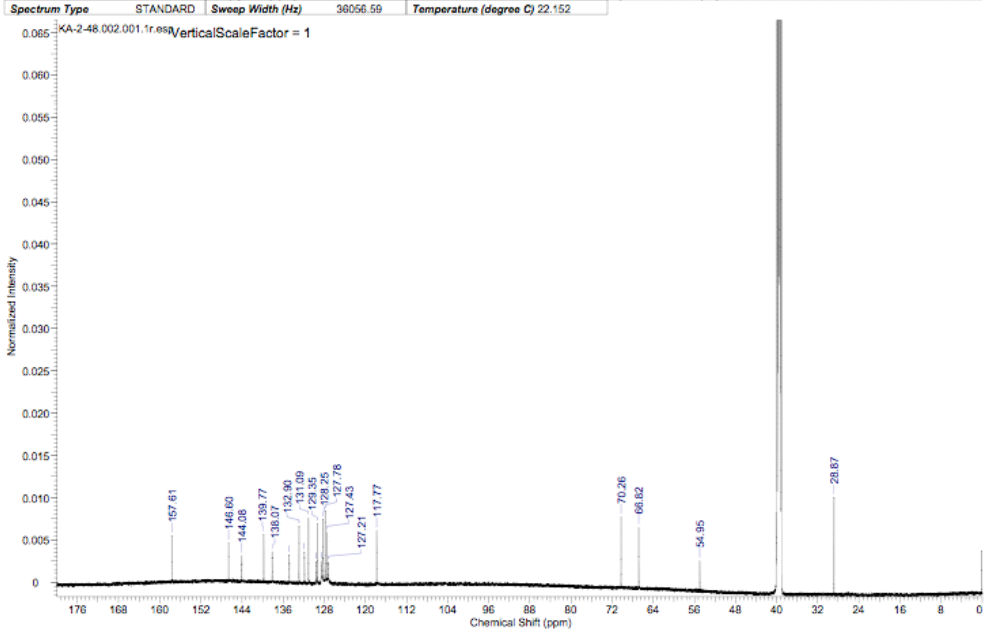
Acquisition Time (sec)	2.7263	Comment	1H	Date	17 Feb 2013 18:38:40		
Date Stamp	17 Feb 2013 18:38:40						
File Name	D:¥Yamamoto's group¥five-membered ring flavin¥sample data¥NMR¥KA-2-10 washed with CH2Cl2¥1¥pdata¥1¥1r						
Frequency (MHz)	600.20	Nucleus	1H	Number of Transients	16	Origin	spect
Original Points Count	32768	Owner	kenji	Points Count	65536	Pulse Sequence	zg30
Receiver Gain	9.93	SW(cyclical) (Hz)	12019.23	Solvent	DMSO-d6	Spectrum Offset (Hz)	3703.1333
Spectrum Type	STANDARD	Sweep Width (Hz)	12019.05	Temperature (degree C)	22.048		



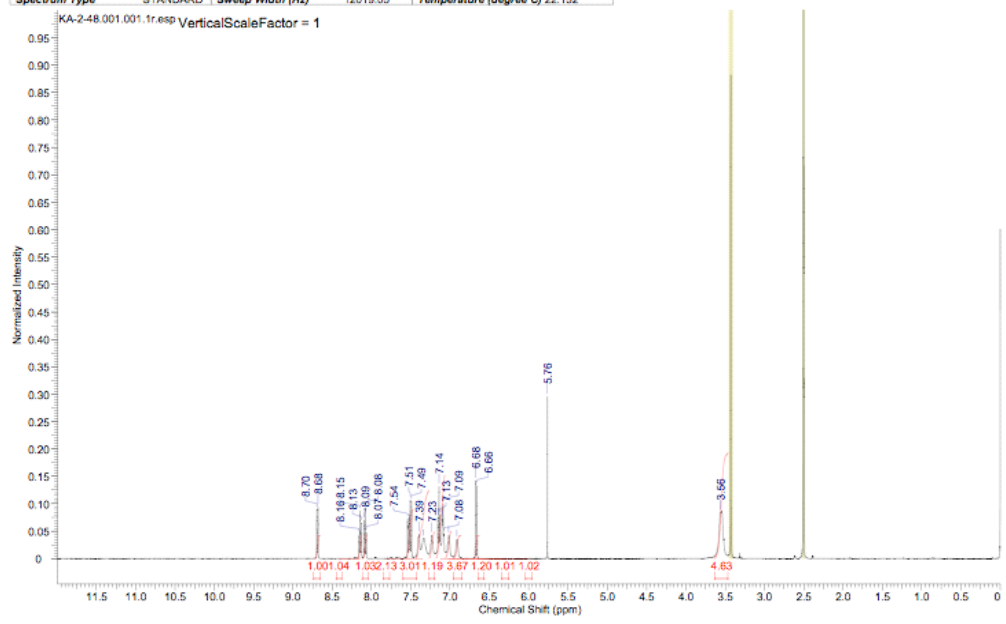
(1*R*,2*S*)-1,2-Diphenyl-3-methyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (4b)



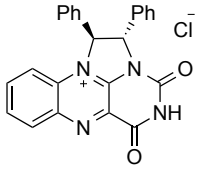
Acquisition Time (sec)	0.9088	Comment	13C	Date	19 Mar 2013 00:03:12		
Date Stamp	19 Mar 2013 00:03:12			File Name	C:\Users\Kana Yamamoto\Desktop\NMR\KA-2-48\2\pdata\1\1r		
Frequency (MHz)	150.92	Nucleus	13C	Number of Transients	756	Origin	spect
Original Points Count	32768	Owner	kenji	Points Count	32768	Pulse Sequence	zgpg30
Receiver Gain	173.95	SW(cyclical) (Hz)	38057.69	Solvent	DMSO-d6	Spectrum Offset (Hz)	15021.8535
Spectrum Type	STANDARD	Sweep Width (Hz)	38056.59	Temperature (degree C)	22.152		

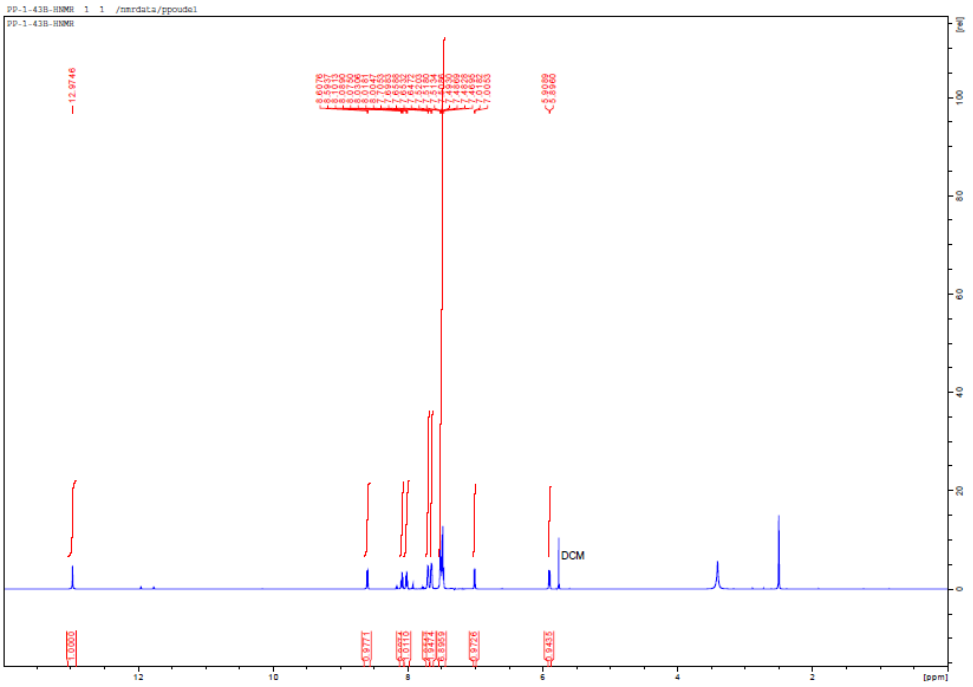


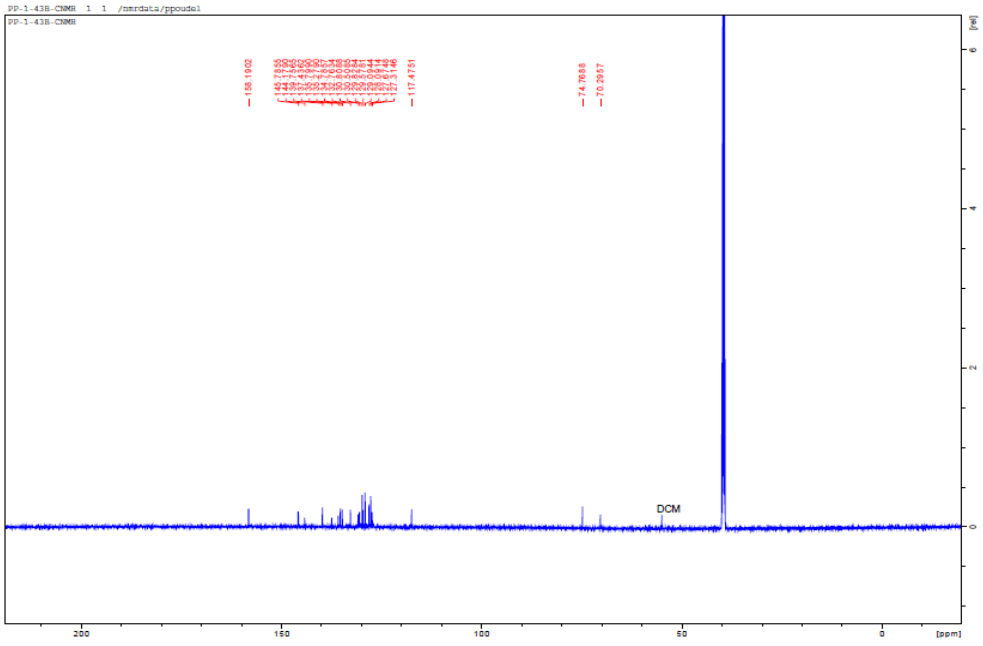
Acquisition Time (sec)	2.7263	Comment	1H	Date	18 Mar 2013 23:22:40		
Date Stamp	18 Mar 2013 23:22:40			File Name	C:\Users\Kana Yamamoto\Desktop\NMR\KA-2-48\1\pdata\1\1r		
Frequency (MHz)	600.20	Nucleus	1H	Number of Transients	16	Origin	spect
Original Points Count	32768	Owner	kenji	Points Count	65536	Pulse Sequence	zg30
Receiver Gain	12.09	SW(cyclical) (Hz)	12019.23	Solvent	DMSO-d6	Spectrum Offset (Hz)	3704.1992
Spectrum Type	STANDARD	Sweep Width (Hz)	12019.05	Temperature (degree C)	22.152		



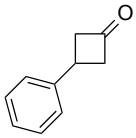
(1*S*,2*S*)-1,2-Diphenyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (5a)





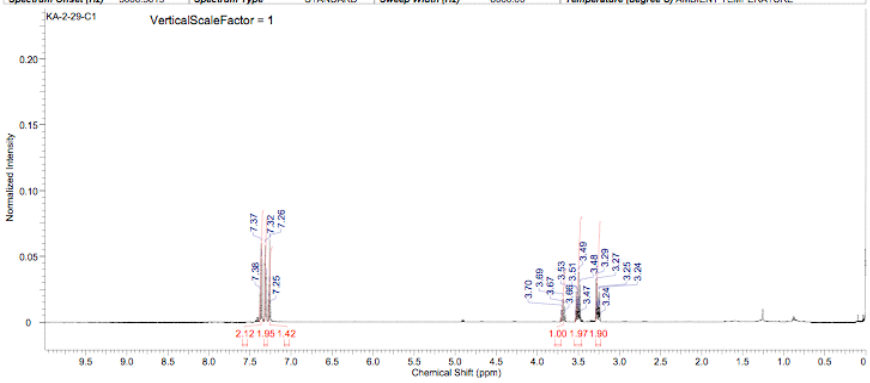


3-Phenylcyclobutanone (10)



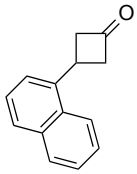
7/27/2013 10:37:40 PM

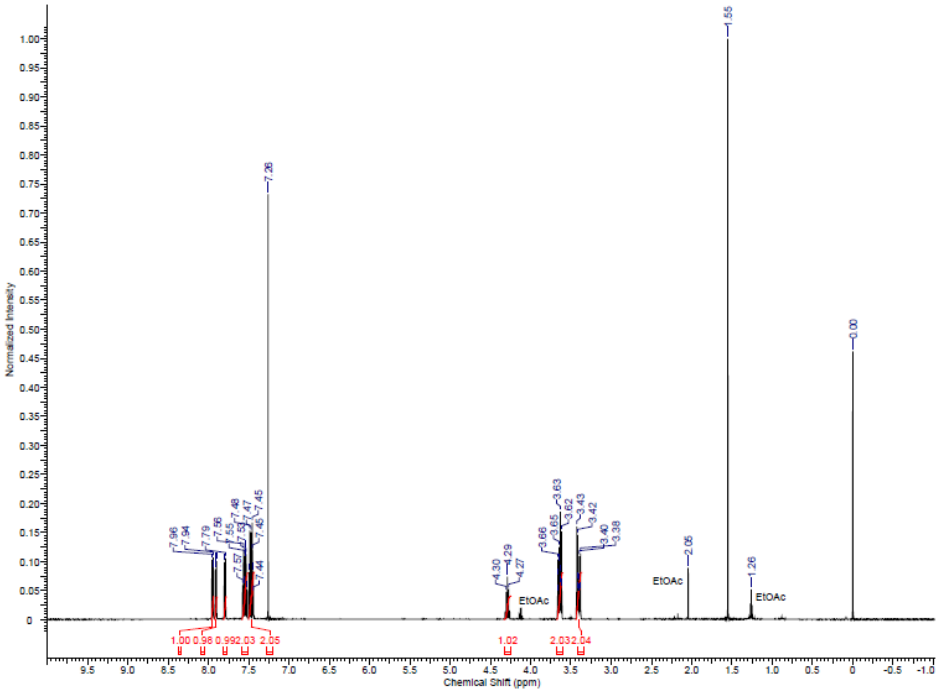
Acquisition Time (sec)	3.0000	***Comment***	KA-2-29-C1	***Date***	Mar 1 2013	***Date Stamp***	Mar 1 2013
File Name	C:\Users\Kana Yamamoto\Desktop\NMR others\KA-2-29-C1.fid\fid					***Frequency (MHz)***	599.88
Nucleus	1H	***Number of Transients***	16	***Original Points Count***	24000	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	42.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	3008.5615	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	8000.00	***Temperature (degree C)***	AMBIENT TEMPERATURE

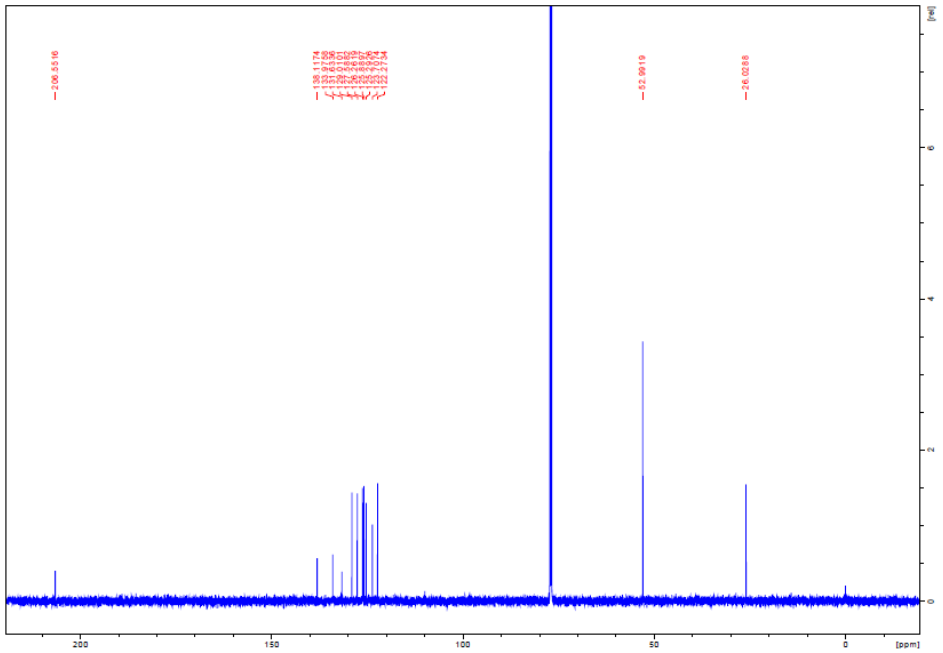


No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	3.24	1940.7	0.0035	12	3.27	1963.9	0.0296	23	3.50	2101.9	0.0192	34	3.70	2220.8	0.0091
2	3.24	1943.9	0.0226	13	3.28	1967.8	0.0104	24	3.51	2103.8	0.0083	35	3.72	2228.8	0.0034
3	3.24	1945.9	0.0072	14	3.29	1971.5	0.0330	25	3.51	2106.0	0.0074	36	7.25	4349.7	0.0121
4	3.25	1947.6	0.0107	15	3.29	1974.9	0.0041	26	3.51	2107.7	0.0225	37	7.26	4354.9	0.0626
5	3.25	1949.5	0.0112	16	3.47	2084.3	0.0047	27	3.52	2110.9	0.0135	38	7.26	4357.1	0.0264
6	3.25	1951.0	0.0230	17	3.48	2087.0	0.0283	28	3.52	2113.1	0.0094	39	7.28	4364.4	0.0173
7	3.26	1952.7	0.0072	18	3.49	2090.9	0.0099	29	3.53	2116.3	0.0231	40	7.30	4381.2	0.0351
8	3.26	1955.1	0.0086	19	3.49	2093.1	0.0139	30	3.53	2120.4	0.0031	41	7.32	4388.8	0.0586
9	3.26	1957.1	0.0125	20	3.49	2096.5	0.0379	31	3.66	2195.9	0.0054	42	7.35	4410.8	0.0483
10	3.26	1958.3	0.0117	21	3.50	2097.7	0.0098	32	3.67	2203.7	0.0119	43	7.37	4418.3	0.0598
11	3.27	1961.0	0.0100	22	3.50	2099.9	0.0114	33	3.69	2212.5	0.0176	44	7.38	4426.2	0.0226

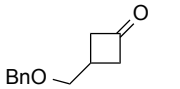
3-(1-naphthyl)cyclobutanone (11)

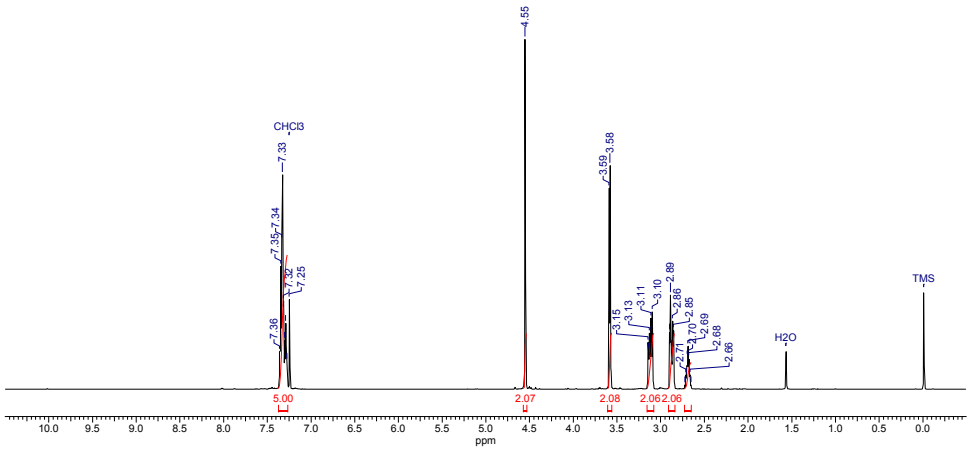






3-(Benzyloxymethyl)cyclobutanone (12)

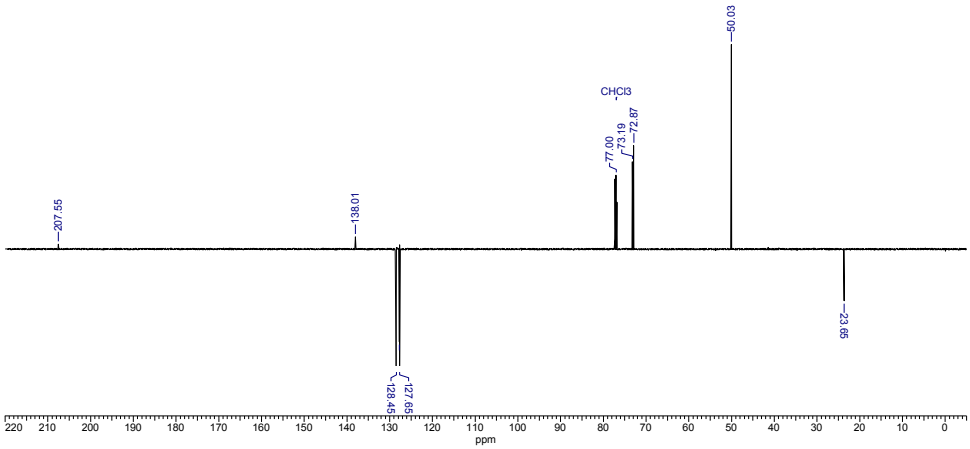




No.	(ppm)	No.	(ppm)	No.	(ppm)
1	2.65	16	2.88	31	3.15
2	2.66	17	2.88	32	3.58
3	2.67	18	2.89	33	3.59
4	2.68	19	2.89	34	4.55
5	2.69	20	2.90	35	7.25
6	2.69	21	3.10	36	7.28
7	2.70	22	3.10	37	7.29
8	2.71	23	3.11	38	7.30
9	2.71	24	3.11	39	7.32
10	2.72	25	3.12	40	7.33
11	2.85	26	3.12	41	7.34
12	2.86	27	3.13	42	7.35
13	2.86	28	3.13	43	7.36
14	2.87	29	3.14		
15	2.87	30	3.14		

No.	Annotation	(ppm)
1	TMS	-0.01
2	H2O	1.57
3	CHCl3	7.25

2-27_004000fid



No.	(ppm)
1	23.65
2	50.03
3	72.87
4	73.19
5	77.00
6	127.65
7	127.76
8	128.45
9	138.01
10	207.55

No.	Annotation	(ppm)
1	CHCl3	77.00

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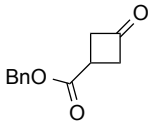
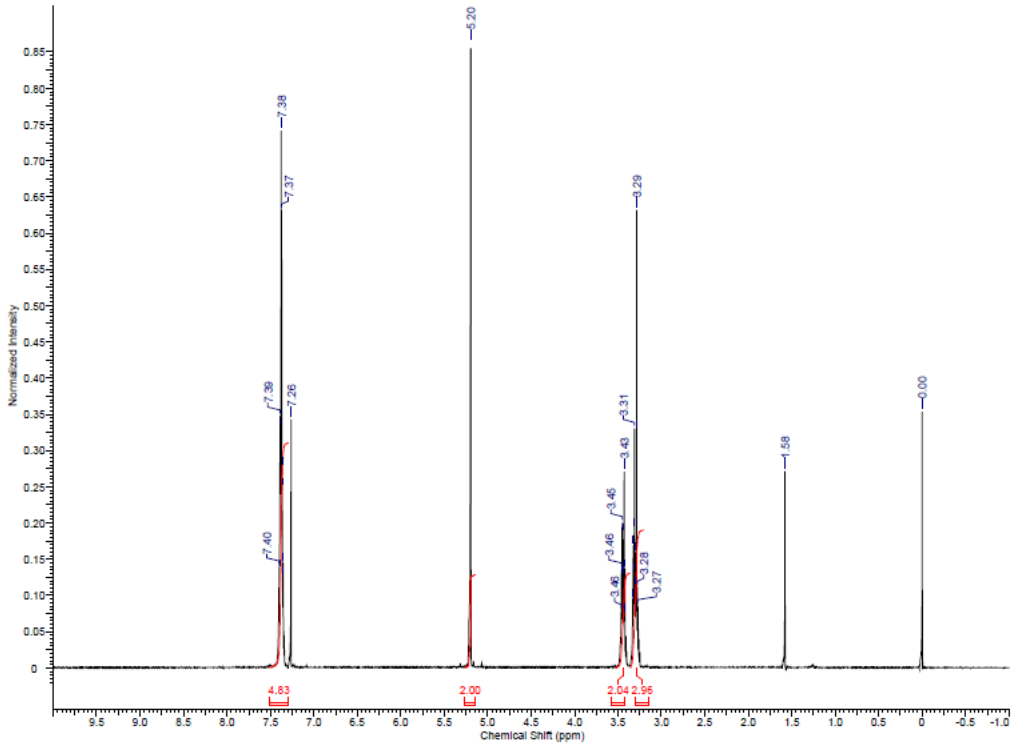
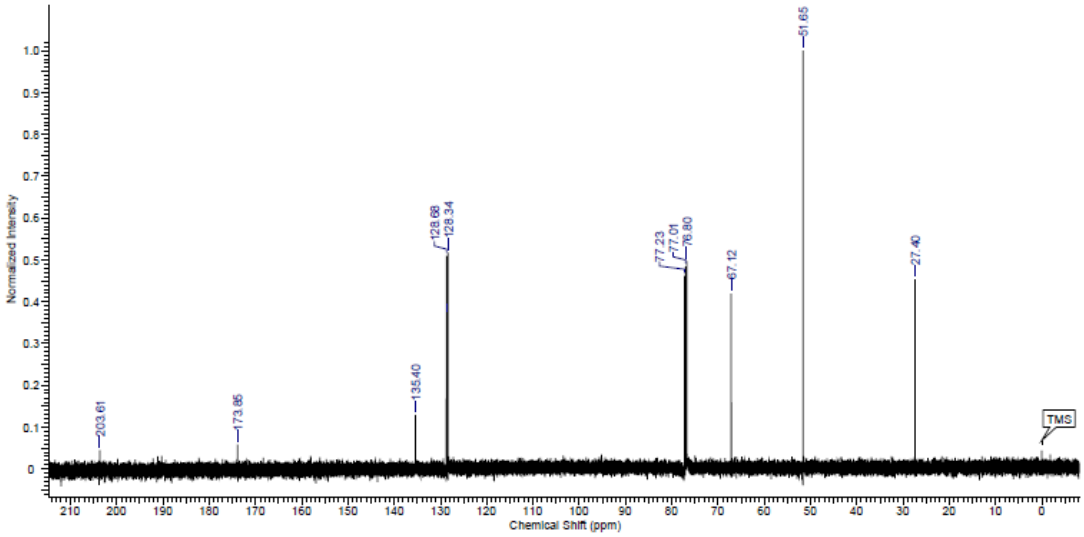
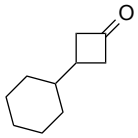
Benzyl-3-oxocyclobutanoate (13)

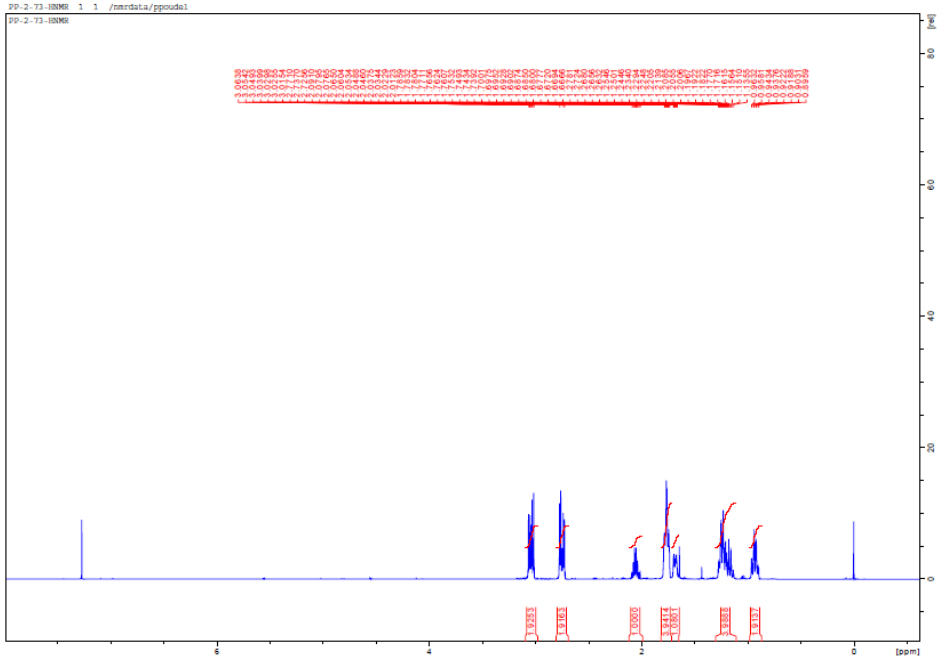


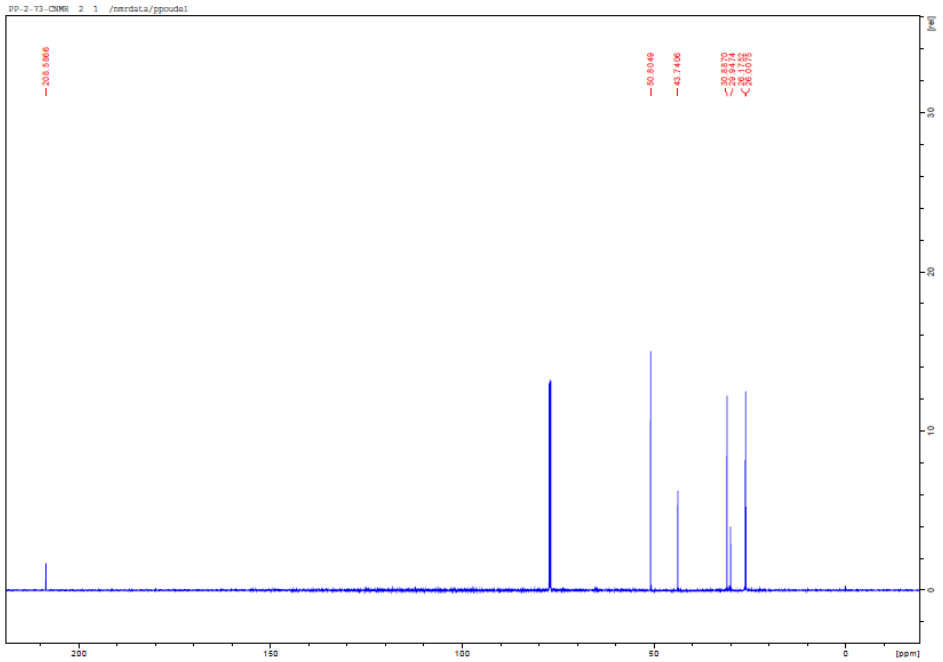


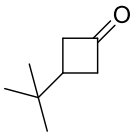


3-cyclohexylcyclobutanone (15)

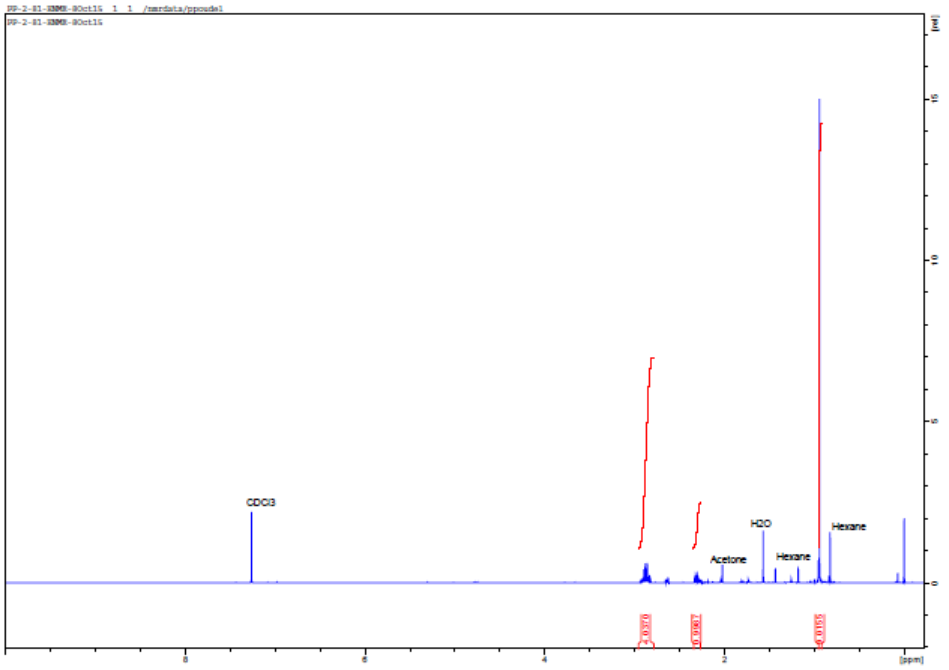


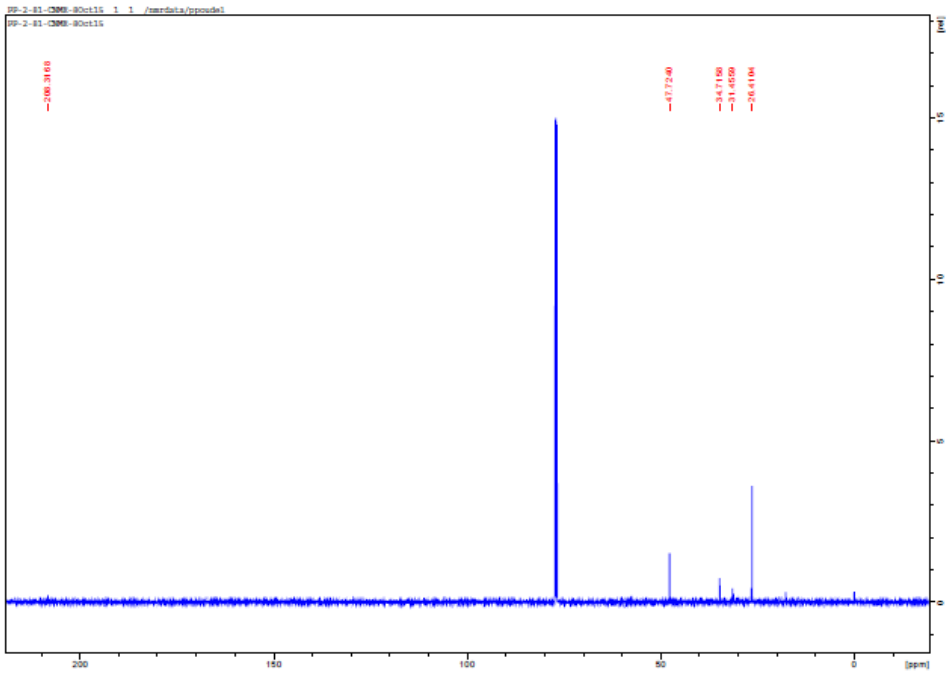




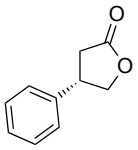


3-*t*-butylclobutan-1-one



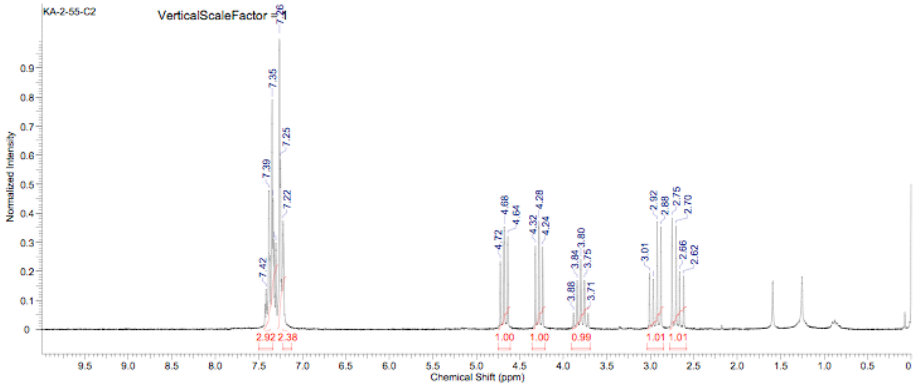


4-phenyldihydrofuran-2(3*H*)-one



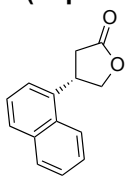
7/27/2013 10:41:57 PM

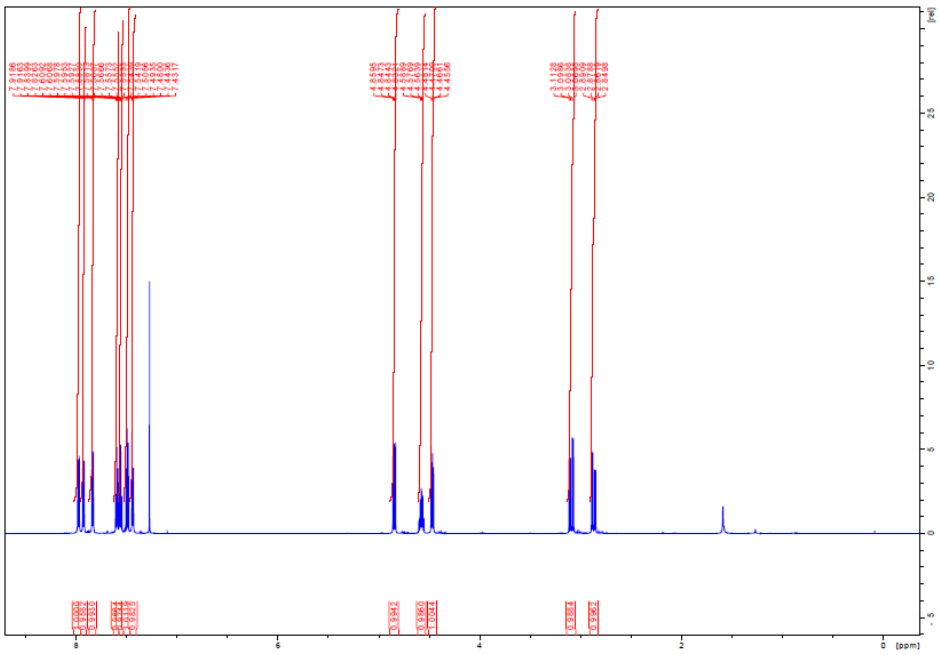
Acquisition Time (sec)	2.5001	***Comment***	KA-2-55-C2	***Date***	Mar 27 2013	***Date Stamp***	Mar 27 2013
File Name	C:\Users\Kana Yamamoto\Desktop\NMR others\KA-2-55-C2.fid\fid					***Frequency (MHz)***	199.98
Nucleus	1H	***Number of Transients***	32	***Original Points Count***	7501	***Points Count***	8192
Pulse Sequence	s2pul	***Receiver Gain***	22.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	1000.1611	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	3000.30	***Temperature (degree C)***	AMBIENT TEMPERATURE

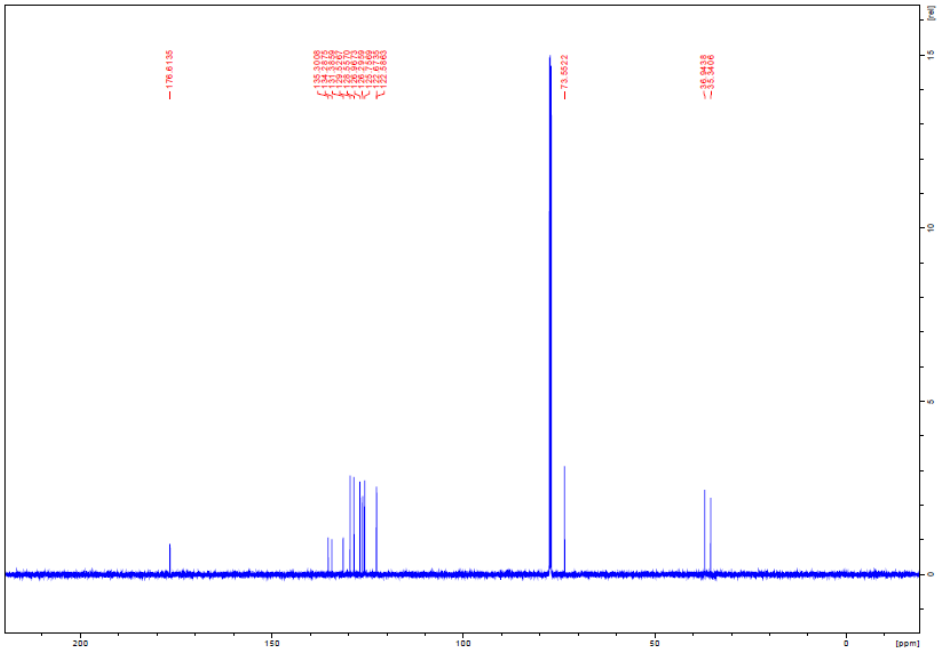


No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.62	523.1	0.1829	8	3.01	601.5	0.1925	15	4.28	855.7	0.3729	22	7.26	1452.3	1.0000
2	2.66	532.2	0.1983	9	3.71	742.8	0.0575	16	4.32	864.1	0.2878	23	7.30	1460.4	0.2973
3	2.70	540.6	0.3553	10	3.75	750.9	0.1689	17	4.64	927.5	0.3204	24	7.33	1465.5	0.3077
4	2.75	549.8	0.3847	11	3.80	759.3	0.2412	18	4.68	935.5	0.3538	25	7.34	1467.4	0.4510
5	2.88	575.4	0.3530	12	3.84	767.7	0.1682	19	4.72	944.3	0.2350	26	7.35	1469.2	0.7906
6	2.92	584.2	0.3697	13	3.86	776.2	0.0561	20	7.22	1443.9	0.3731	27	7.39	1476.9	0.4785
7	2.97	593.0	0.1729	14	4.24	847.2	0.2835	21	7.25	1450.2	0.5877	28	7.42	1483.1	0.1381

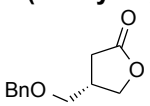
4-(naphthalen-1-yl)dihydrofuran-2(3*H*)-one

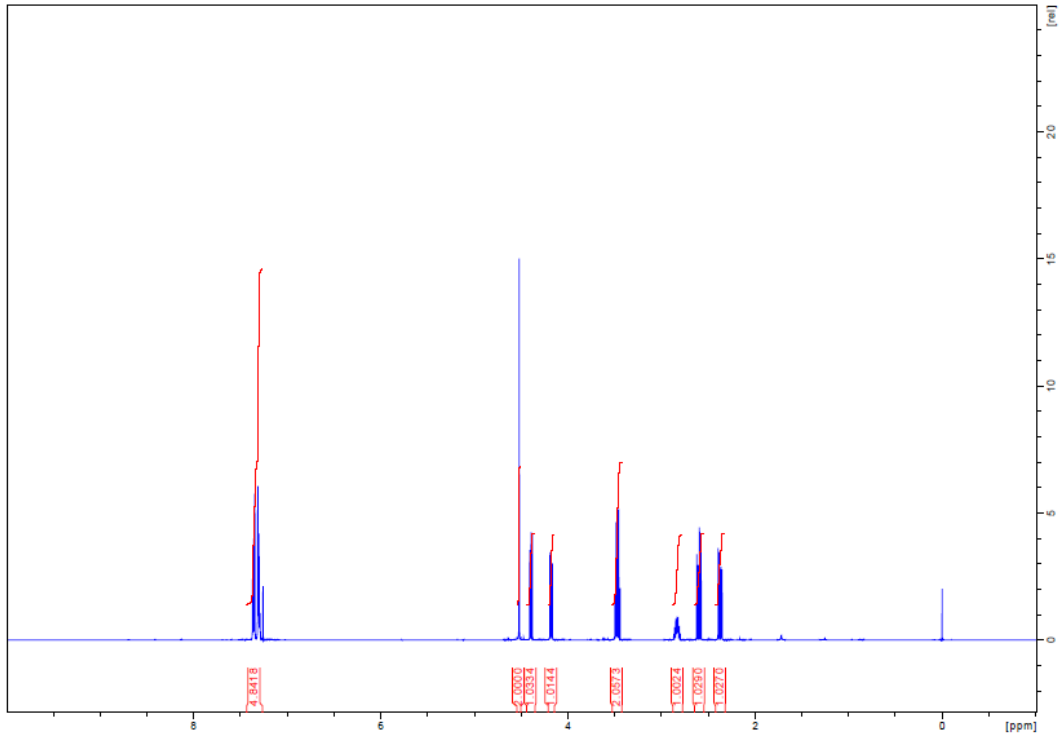


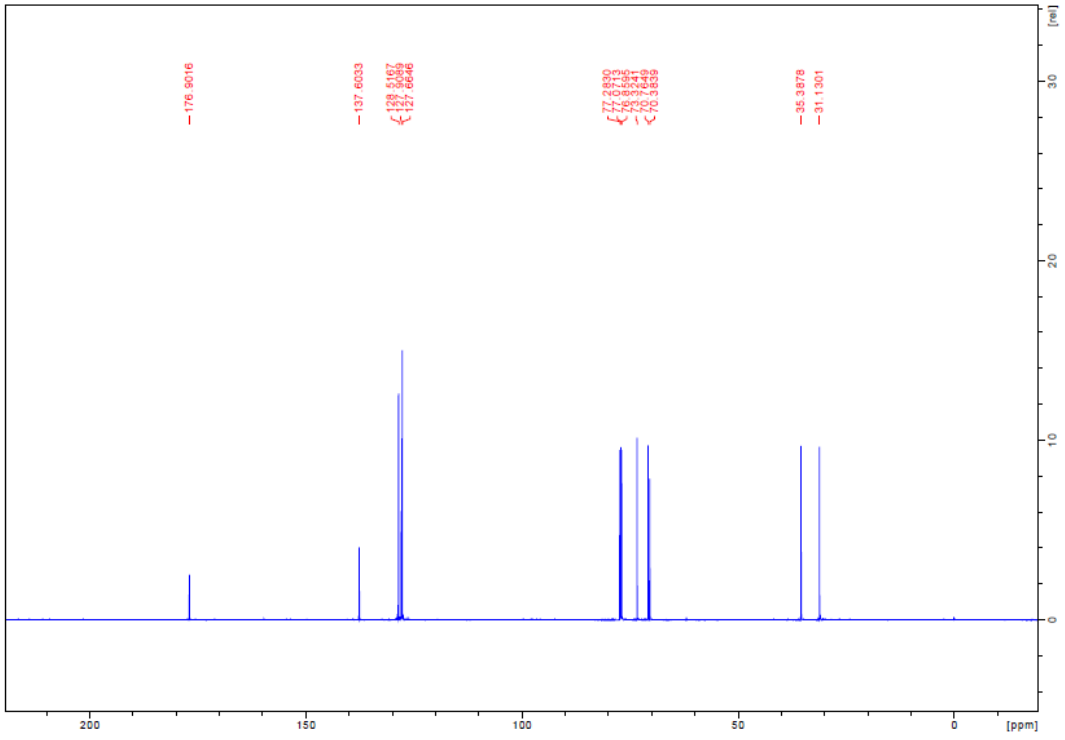




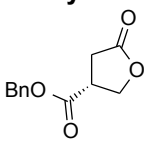
3-(benzyloxymethyl)-*γ*-butyrolactone

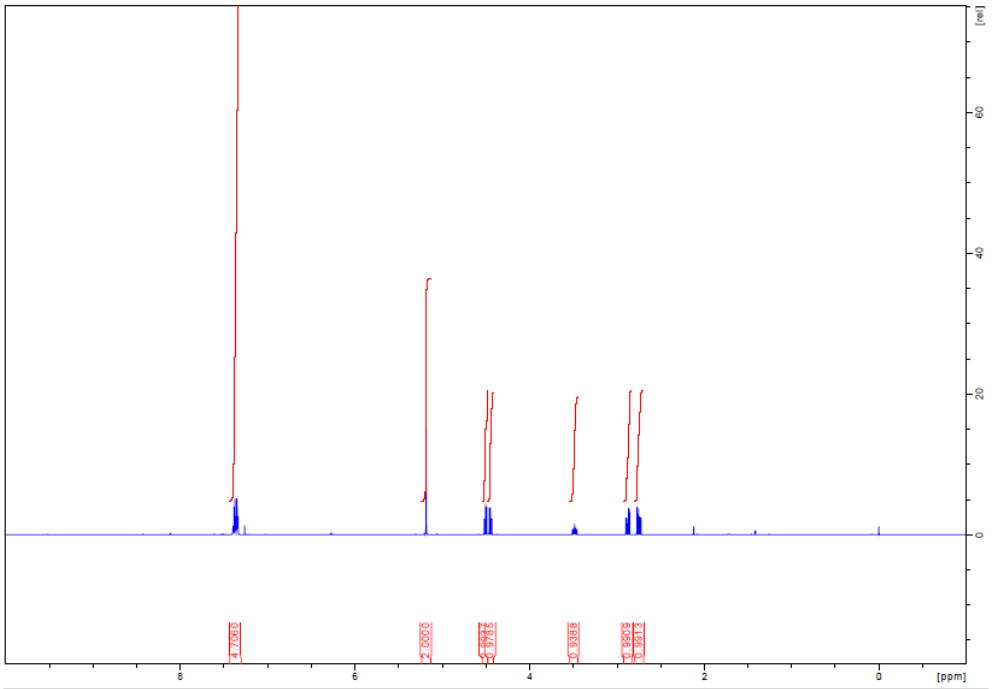


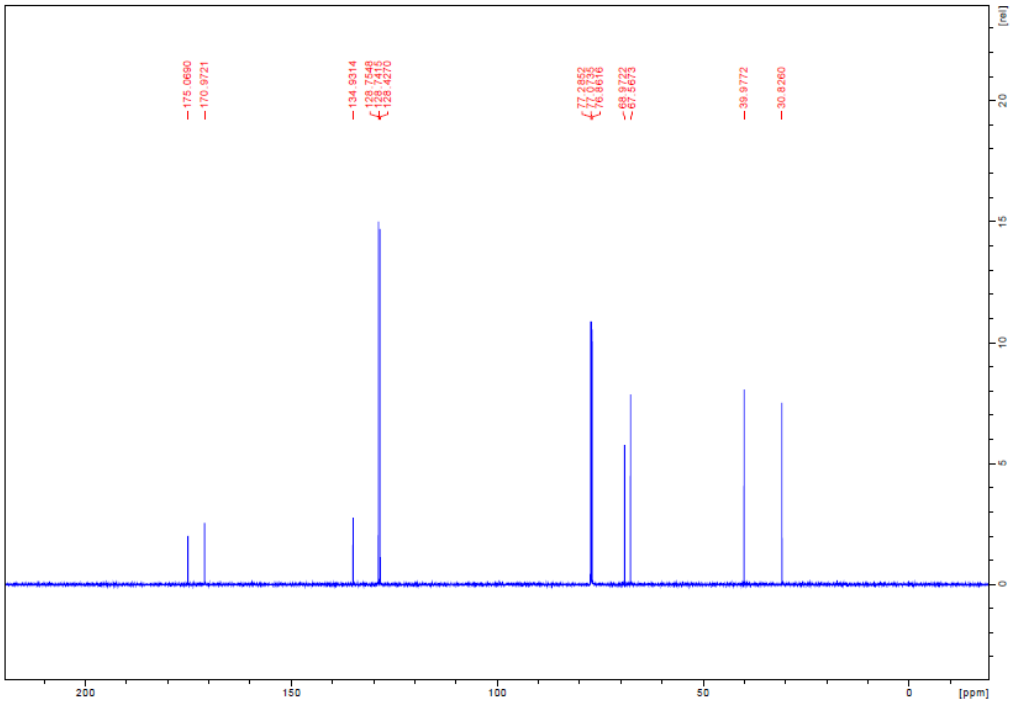




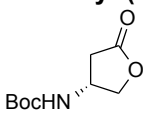
Benzyl-5-oxotetrahydrofuran-3-carboxylate

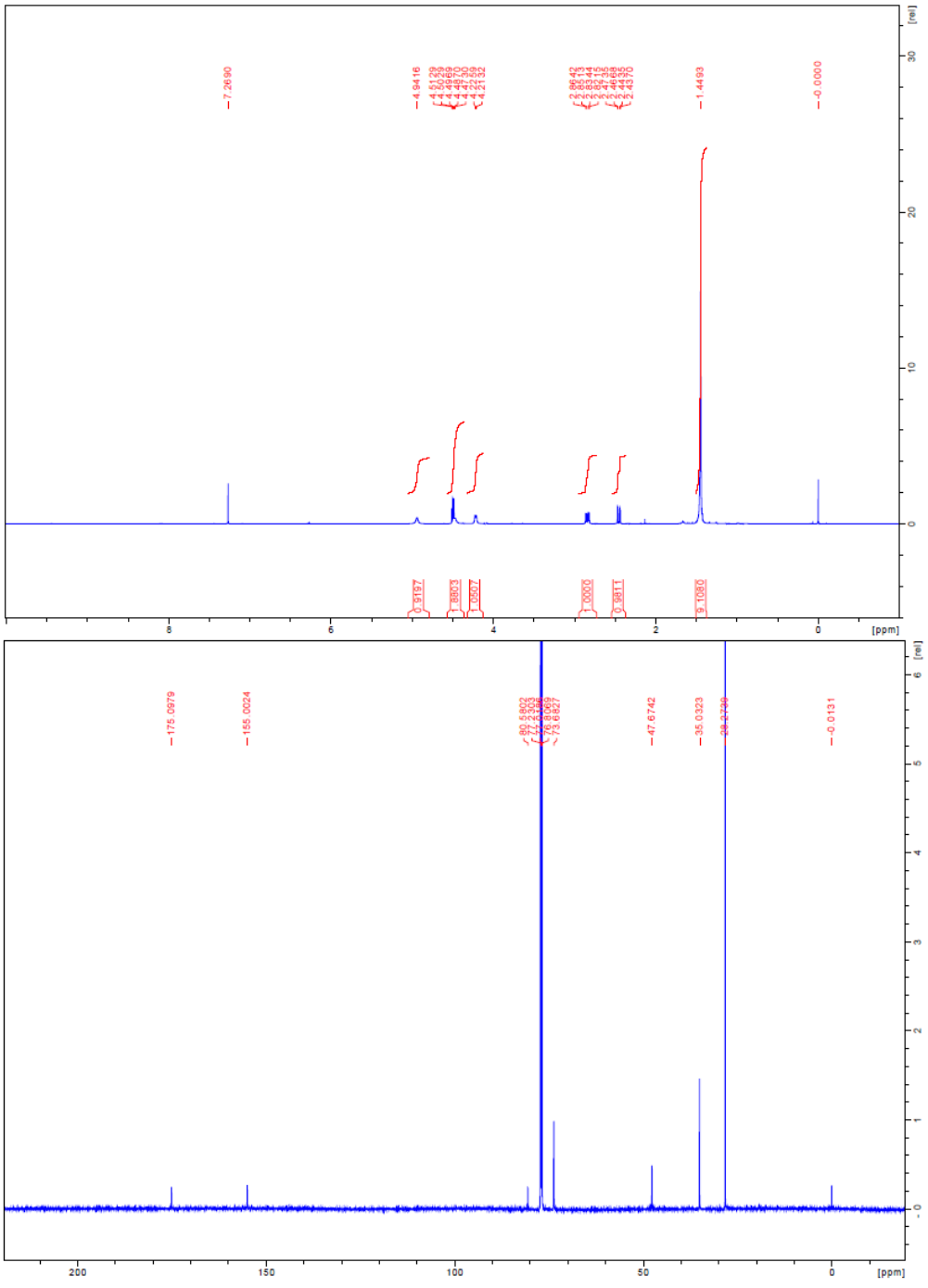




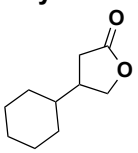


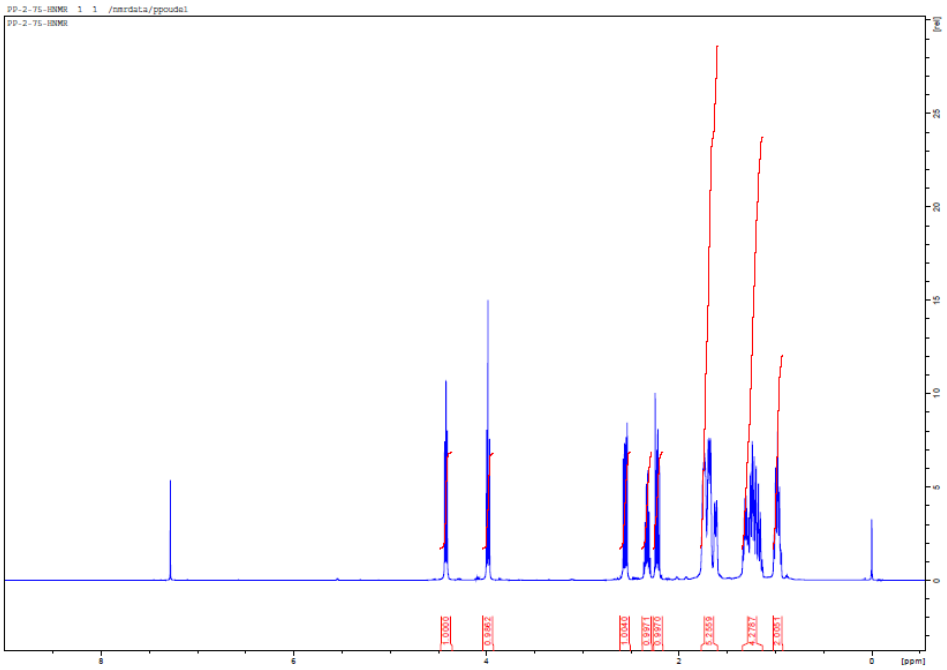
***tert*-butyl-(5-oxotetrahydrofuran-3-yl)carbamate**

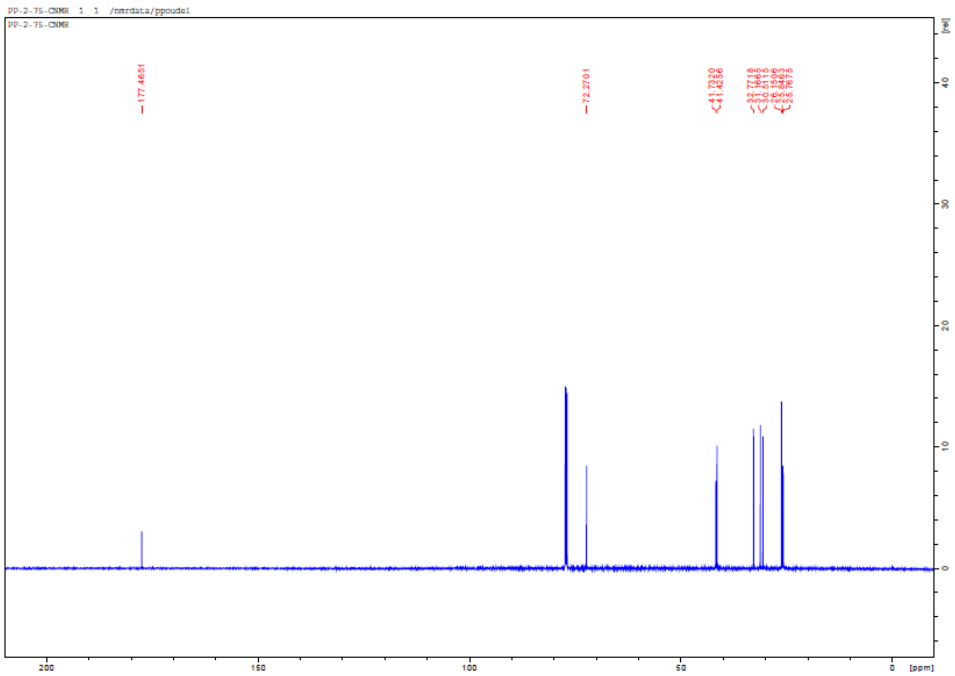


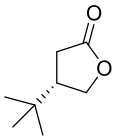


3-cyclohexyl-*γ*-butyrolactone

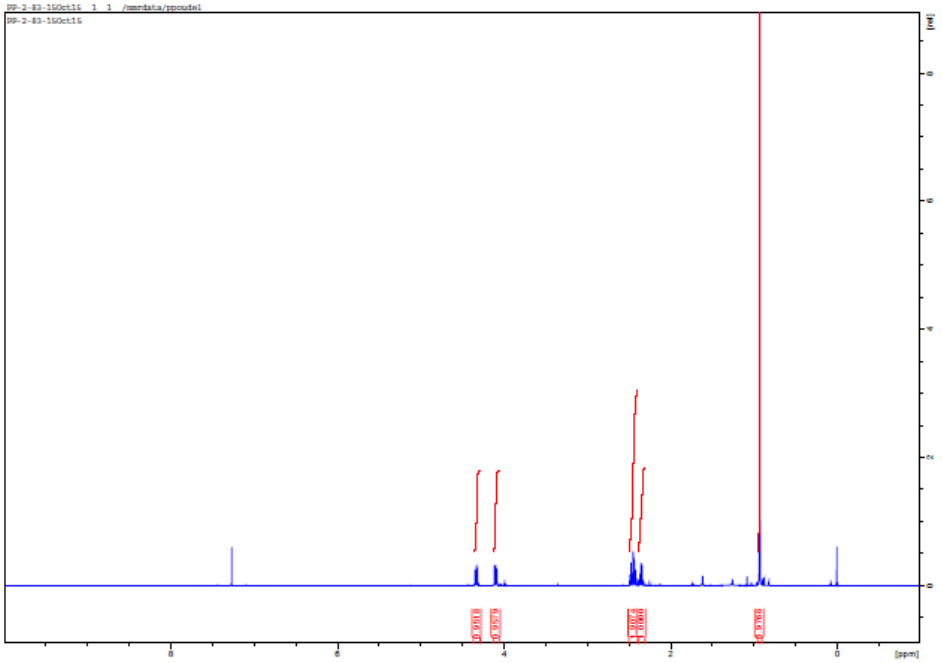


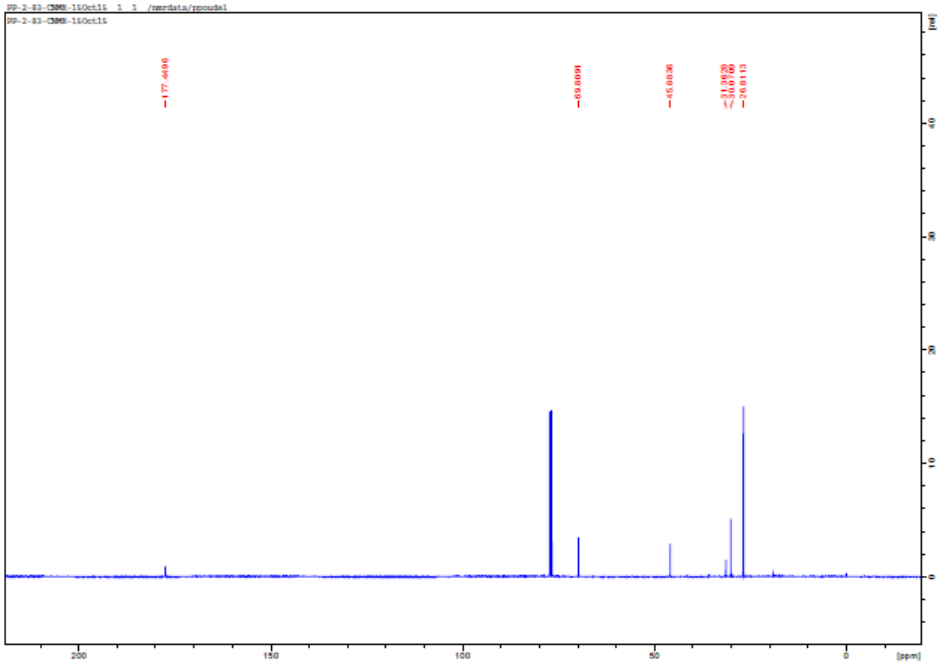






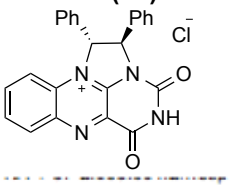
(*S*)-4-*t*-butyldihydrofuran-2(3*H*)-one

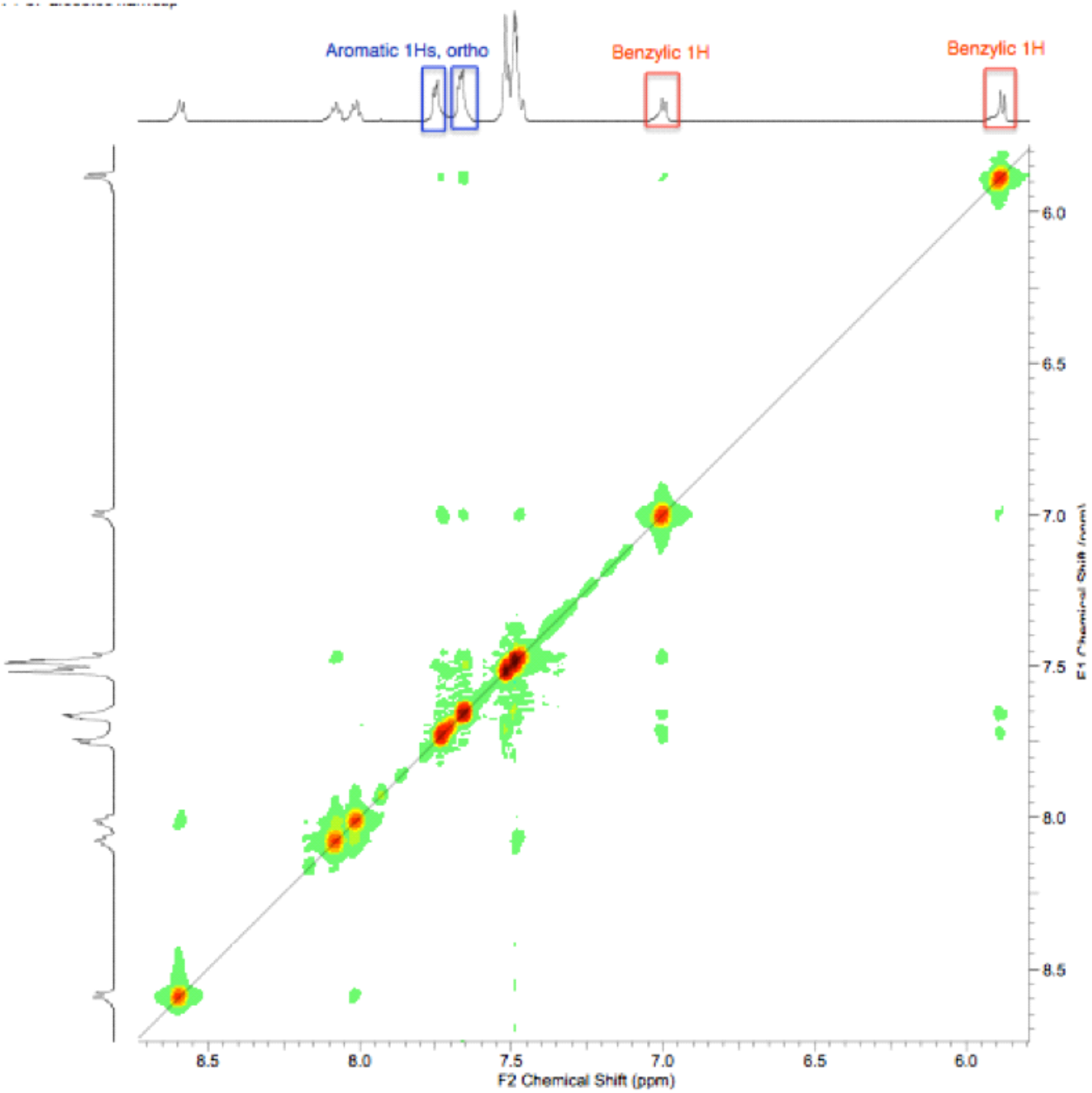




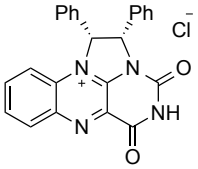
NOESY spectra of 3a and 4a and determination of relative configuration.

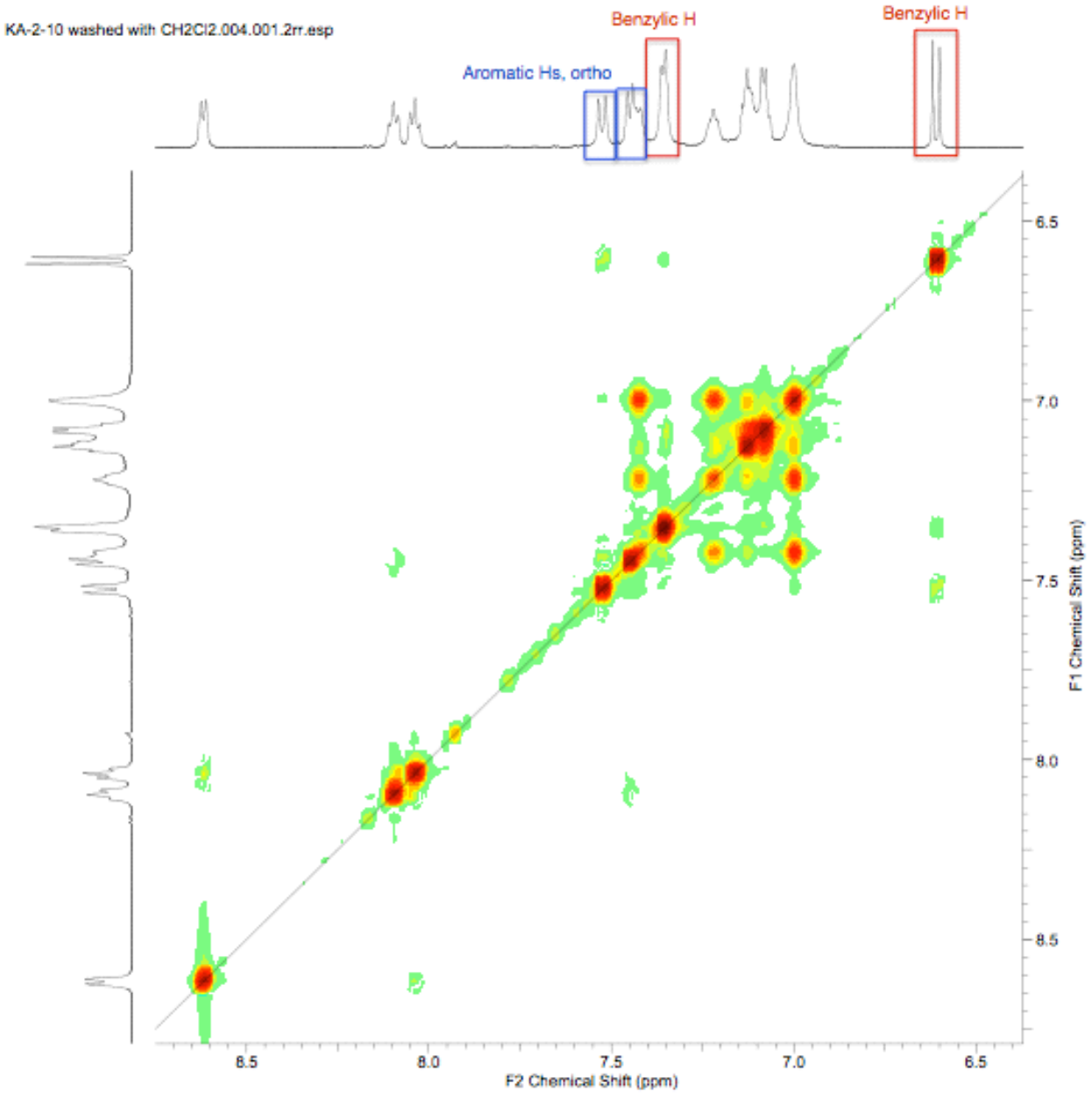
(1*R*,2*R*)-1,2-Diphenyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (3a)





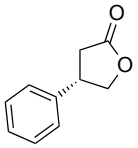
(1*R*,2*S*)-1,2-Diphenyl-1,2-dihydro-4,6(3*H*,5*H*)-dioxo-benzo[*g*]imidazo[1,2,3-*i*,*j*]pteridin-12-ium chloride (4a)

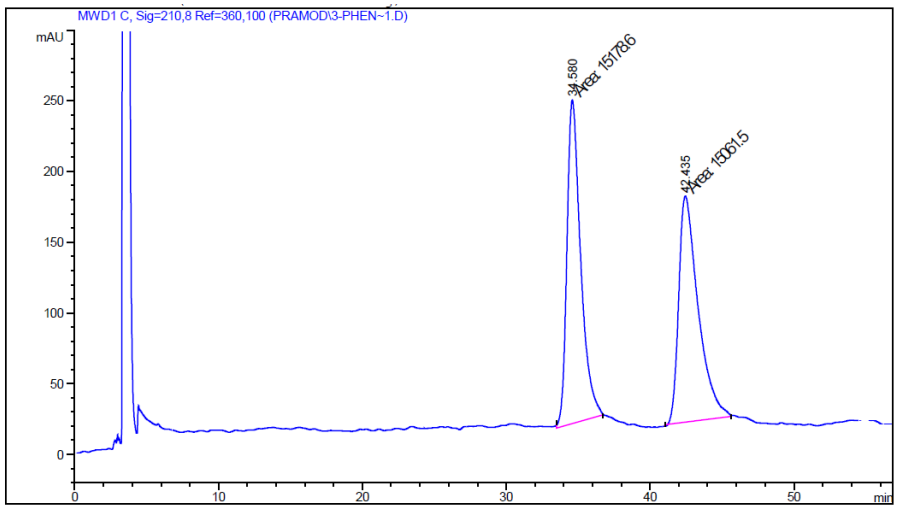




6. HPLC data for γ-lactone products:

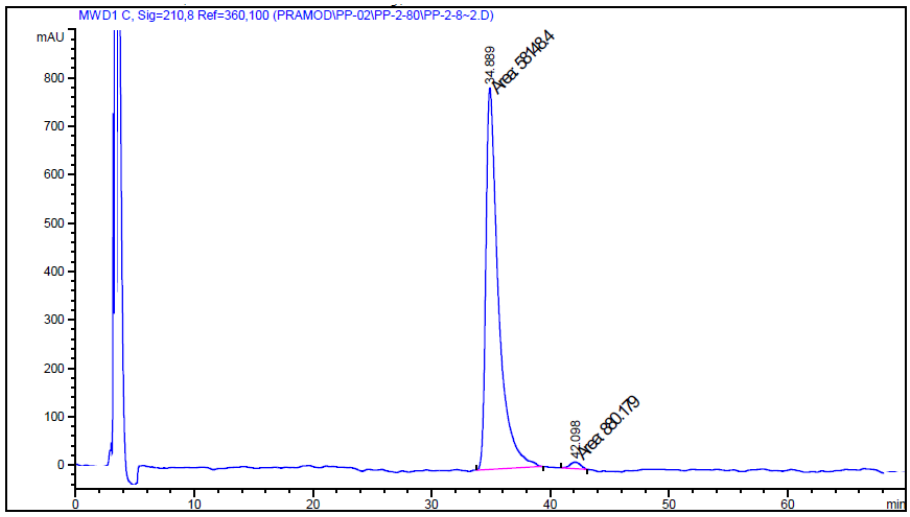
4-phenyldihydrofuran-2(3*H*)-one (after recrystallization)





Racemic compound

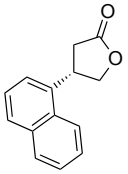
S.N.	Retention Time (minutes)	% Area
1	34.6	50.2
2	42.4	49.8

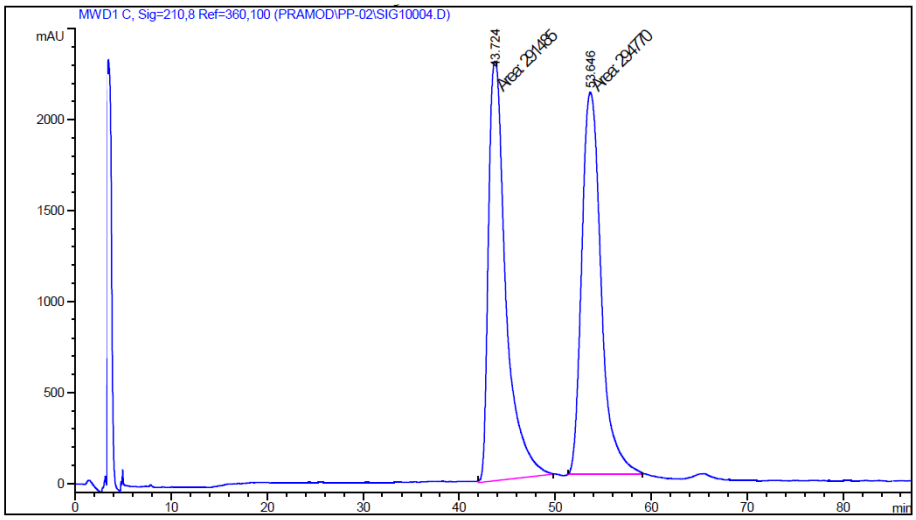


Asymmetric compound

S.N.	Retention Time (minutes)	% Area
1	34.9	98.5
2	42.1	1.5

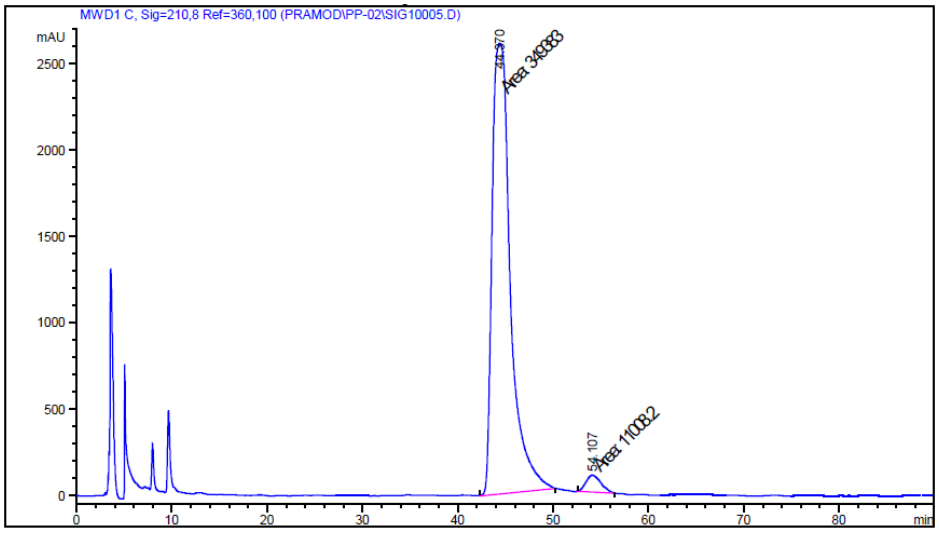
4-(naphthalen-1-yl)dihydrofuran-2(3*H*)-one





Racemic compound

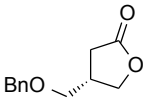
S.N.	Retention Time (minutes)	% Area
1	43.7	49.7
2	53.6	50.3

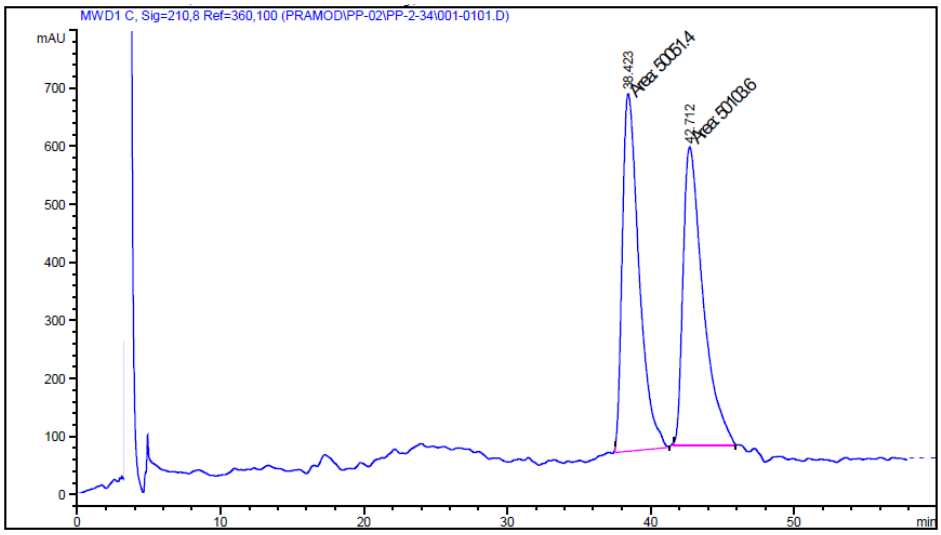


Asymmetric compound

S.N.	Retention Time (minutes)	% Area
1	44.4	96.9
2	54.1	3.1

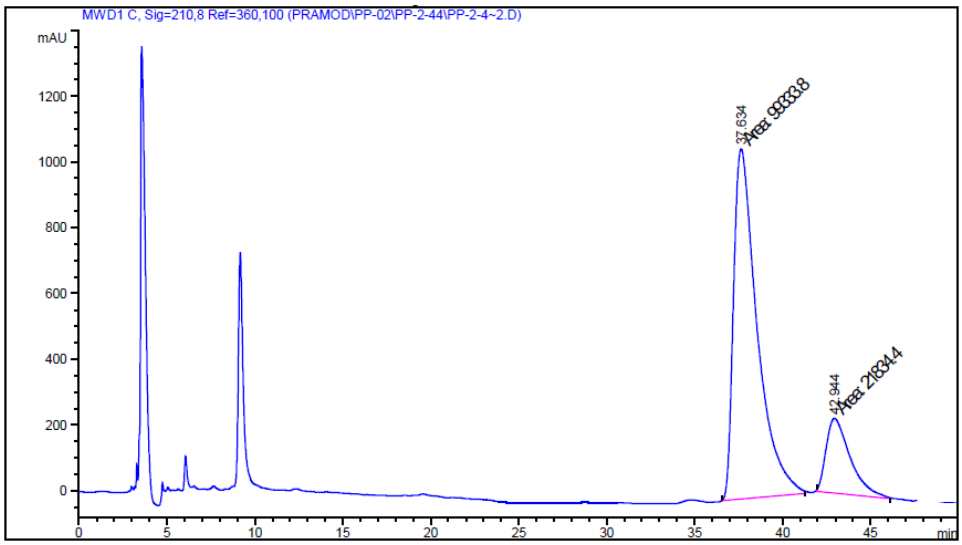
3-(benzyloxymethyl)-*γ*-butyrolactone





Racemic compound

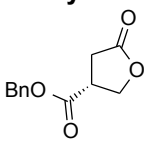
S.N.	Retention Time (minutes)	% Area
1	38.4	50.0
2	42.7	50.0

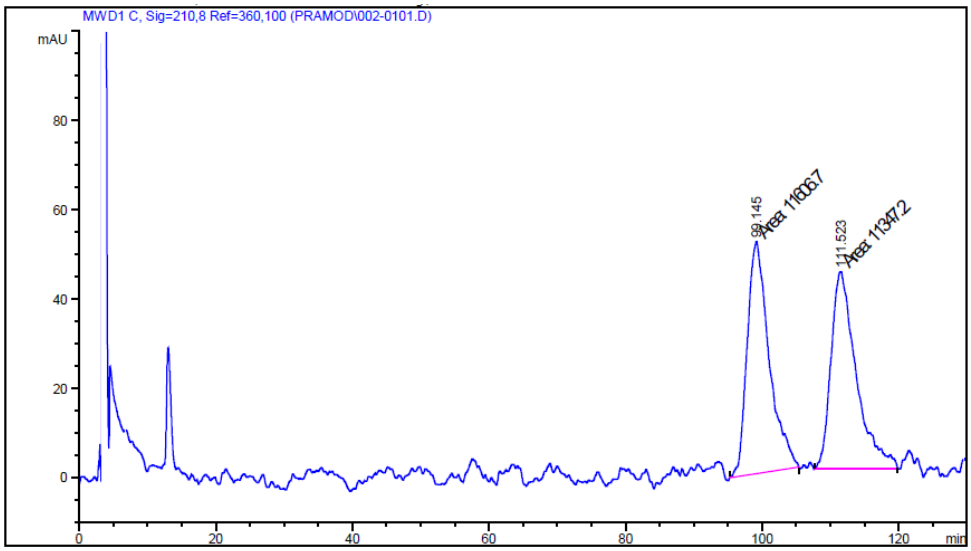


Asymmetric compound

S.N.	Retention Time (minutes)	% Area
1	37.6	82.0
2	42.9	18.0

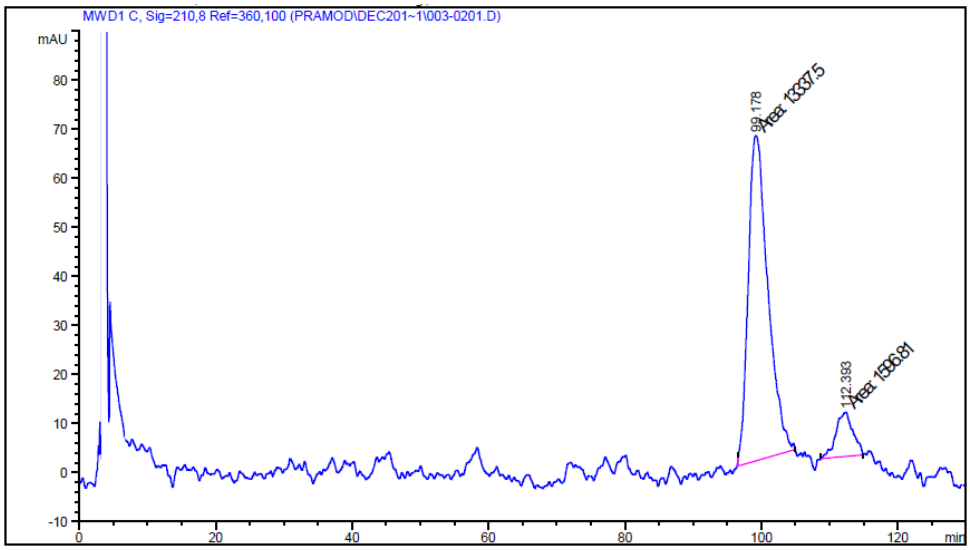
Benzyl-5-oxotetrahydrofuran-3-carboxylate





Racemic compound

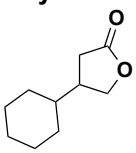
S.N.	Retention Time (minutes)	% Area
1	99.1	50.6
2	111.5	49.4

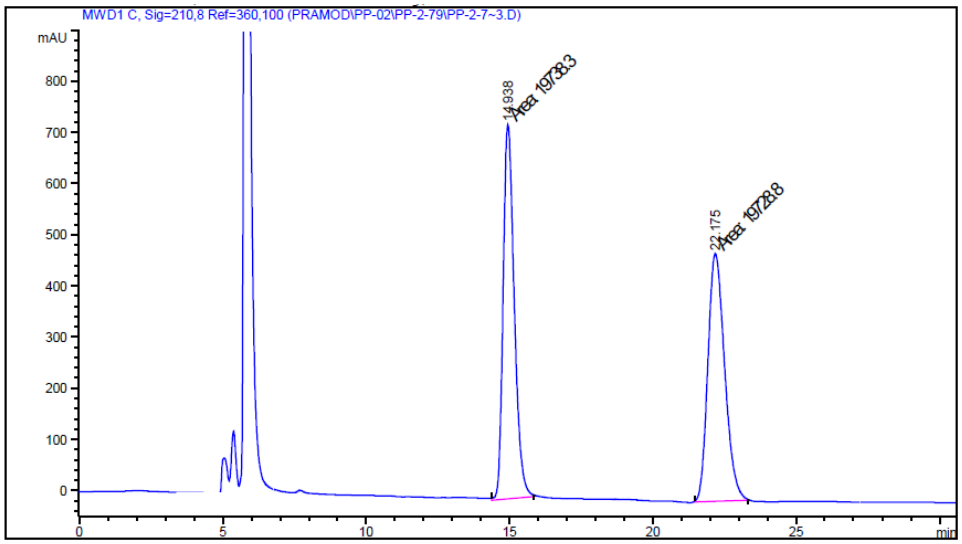


Asymmetric compound

S.N.	Retention Time (minutes)	% Area
1	99.2	89.3
2	112.4	10.7

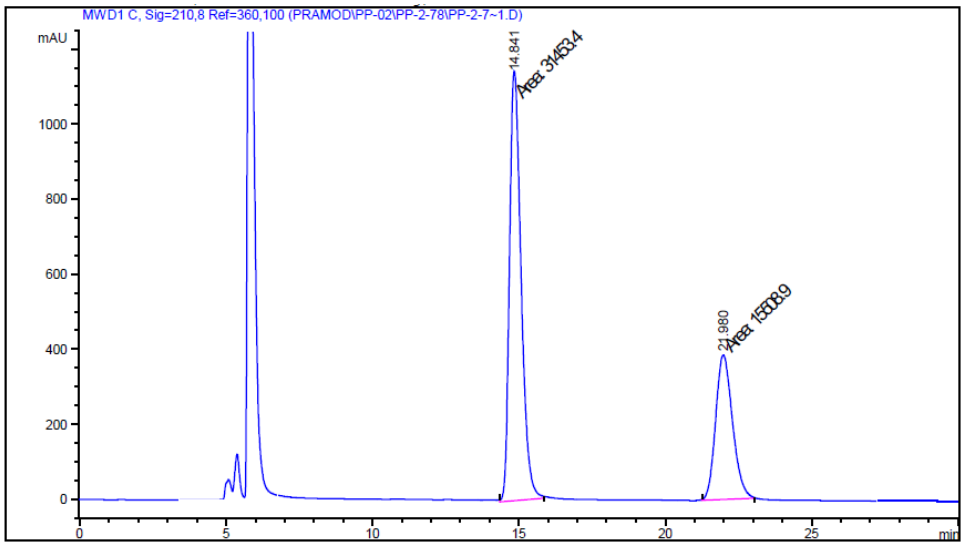
3-cyclohexyl-*γ*-butyrolactone (after converting into hydroxy benzylamide derivative[9])





Racemic compound

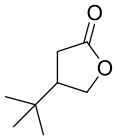
S.N.	Retention Time (minutes)	% Area
1	14.9	50.0
2	22.2	50.0

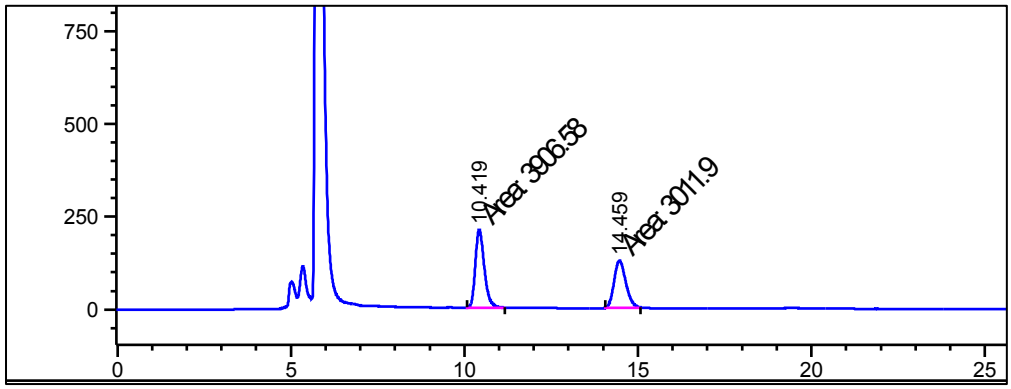


Asymmetric compound

S.N.	Retention Time (minutes)	% Area
1	14.8	67.0
2	22.0	33.0

4-*t*-butyldihydrofuran-2(3*H*)-one[2] **((after converting into hydroxy benzylamide derivative**[9]**))**





Asymmetric compound

S.N.	Retention Time (minutes)	% Area
1	10.4	56.6
2	14.5	43.4