Supporting Information

Enantioselective Aza-Friedel-Crafts Reaction of Cyclic Ketimines with Indoles Using Chiral Imidazoline-Phosphoric Acid Catalysts

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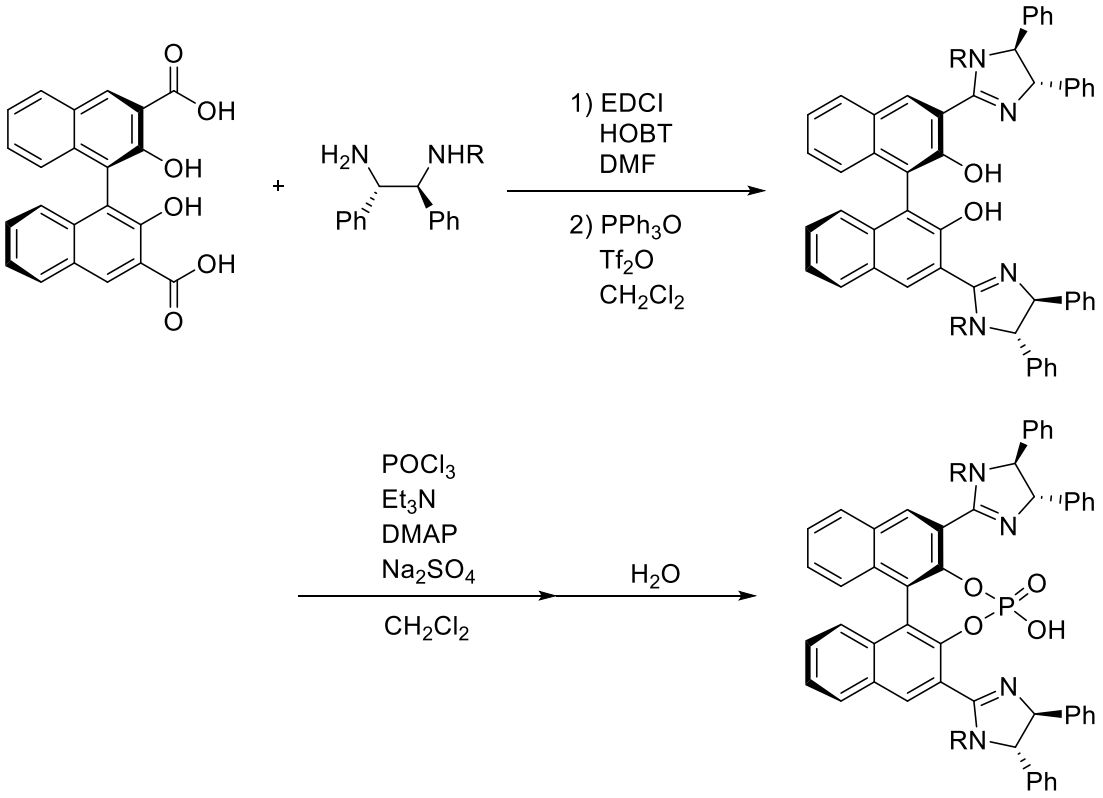
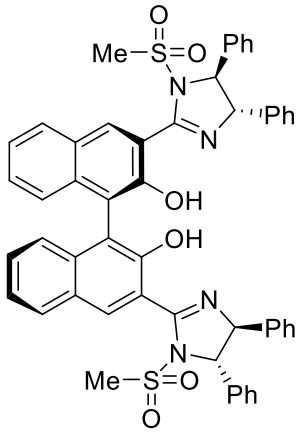
Experimental Section

General method: All reactions were performed in flame-dried glassware under a positive pressure of argon. Solvents were transferred via syringe and were introduced into the reaction vessels though a rubber septum. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel (60-F254). The TLC plates were visualized with UV light. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 63-210 μm. The ^{1}H NMR (300 MHz), ^{13}C NMR (75.5 MHz), ^{19}F NMR (282 MHz), and ^{31}P NMR (121 MHz) spectra for solution in $CDCl_3$, DMSO-d_6 or CD_3OD were recorded on a Varian Gemini-300. Chemical shifts (δ) are expressed in ppm downfield from internal TMS, $CHCl_3$, DMSO or MeOH. HPLC analyses were performed on a JASCO PU-2080 Plus using 4.6 x 250 mm DAICEL CHIRALPAK AY-3®, IA®, ID®, ID-3®, and IG® column. ESI Mass spectra were recorded on a Waters SYNAPT G2 HDMS. Optical rotations were measured on a JASCO P-2200. Infrared spectra were recorded on a JASCO FT/IR-4600 spectrometer with ZnSe ATR unit. Imidazoline phosphoric acid catalysts **3a**, **b** were synthesized by published procedures.[1)] Cyclic ketimines **1a**, **b** were prepared by published procedures.[2)]

General procedure for synthesis of bis(imidazoline) phosphoric acid catalyst



(*R*)-3,3'-Bis[1-(methanesulfonyl)-(4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl]-1,1'-binaphthol



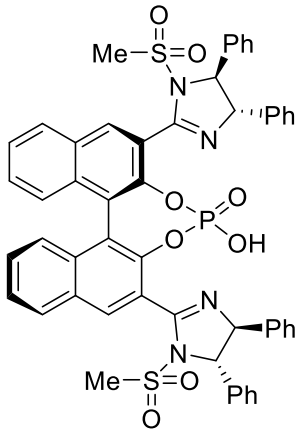
A solution of (*R*)-2,2'-dihydroxybinaphthyl-3,3'-biscarboxylic acid (187.2 mg, 0.50 mmol), (1*S*,2*S*)-*N*-methanesulfonyl-1,2-diphenylethane-1,2-diamine (300.0 mg, 1.00 mmol), and 1-hydroxybenzotriazole (202.7 mg, 1.5 mmol) in dimethylformamide (7.1 mL) was stirred for 10 min at 0 ℃, then a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (191.7 mg, 1.00 mmol) in dimethylformamide (2.5 mL) was added into the reaction mixture at 0 ℃. The reaction mixture was stirred for 18 h at room temperature. The reaction mixture was diluted by ethyl acetate, then washed

with 1 M HCl aq., sat. $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated under reduced pressure to give (*R*)-3,3'-bis{[(1*S*,2*S*)-1,2-dipheny-2-(methanesulfonylamino)ethylcarboxamide]}-1,1'-binaphthol.

Trifluoromethanesulfonic anhydride (0.24 mL, 1.41 mmol) was added to a solution of triphenylphosphine oxide (310.7 mg, 0.90 mmol) in CH_2Cl_2 (2.7 mL) at 0 ℃, and the reaction mixture was stirred for 1 h at room temperature. Then the reaction mixture was cooled to 0 ℃. (*R*)-3,3'-Bis{[(1*S*,2*S*)-1,2-dipheny-2-(methanesulfonylamino)ethylcarboxamide]}-1,1'-binaphthol (393.3 mg, 0.43 mmol) was added to the reaction mixture and stirred for 30 min at 0 ℃. Then sat. $NaHCO_3$ was added, and aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (hexane:ethyl acetate = 60:40) to afford (*R*)-3,3'-bis[1-(methanesulfonyl)-(4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl]-1,1'-binaphthol (245.2 mg, 65%).

$[\alpha]_D^{25}$ +96.2 (c 0.68, $CHCl_3$); m.p. 223.2-223.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.76 (s, 6H), 5.30 (d, *J* = 4.5 Hz, 2H), 5.39 (d, *J* = 4.5 Hz, 2H), 7.33-7.55 (m, 28H), 7.96-7.99 (m, 2H), 8.55 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.4, 71.6, 77.7, 114.3, 118.1, 124.6, 126.5, 128.1, 128.4, 128.9, 129.1, 129.3, 129.5, 129.6, 133.5, 135.0, 140.9, 141.2, 151.6, 158.0; IR (ATR) 3030, 1630, 1495, 1452, 1350, 1162, 1061, 1026, 964, 907, 756, 728, 696, 623 cm^{-1}; HRMS (ESI, positive) m/z for $C_{52}H_{43}N_4O_6S_2$ $[M+H]^+$ calcd. 883.2624, found 883.2622.

(*R*)-3,3'-Bis[1-(methanesulfonyl)-(4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl]-1,1'-binaphthalene-2,2'-diyl hydrogen phosphate (3c)

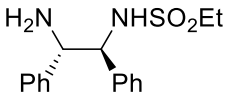


Triethylamine (0.86 mL, 6.27 mmol) was added to a solution of (*R*)-3,3'-bis[1-(methanesulfonyl)-(4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl]-1,1'-binaphthol (100.0 mg, 0.113 mmol), *N*,*N*-dimethyl-4-aminopyridine (27.6 mg, 0.226 mmol), and Na_2SO_4 (77.8 mg) in CH_2Cl_2 (3.4 mL), and the reaction mixture was stirred for 5 min at room temperature. To the reaction mixture, phosphoryl chloride (57 μL, 0.622 mmol) was dropwised at room temperature, and the mixture was stirred for 12 h.

Then water (2.0 mL) was added to the reaction mixture, and stirred for 4 h. 1M HCl aq. was added to reaction mixture, and aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (ethyl acetate:methanol = 95:5) to afford **3c** (85.3 mg, 80%). The product was diluted with CH_2Cl_2, and washed with 1M HCl aq. The organic layer was concentrated and dried at 90 ℃ under reduced pressure for 2 h.

$[\alpha]_D^{25}$ −110.7 (c 0.34, $CHCl_3$); m.p. 247.5-248.4 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.81 (s, 6H), 5.38 (d, *J* = 7.5 Hz, 2H), 5.44 (d, *J* = 7.5 Hz, 2H), 7.31-7.64 (m, 24H), 7.99 (d, *J* = 7.5 Hz, 2H), 8.30 (d, *J* = 8.1 Hz, 2H), 8.70 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 41.3, 72.7, 73.7, 121.7, 122.2, 125.9, 126.0, 126.7, 127.0, 128.6, 128.7, 129.2, 129.3, 129.5, 129.6, 132.8, 133.4, 138.6, 139.4, 146.5, 146.6, 159.6; ^{31}P NMR (121 MHz, DMSO-d_6) δ 4.13; IR (ATR) 3041, 1632, 1482, 1450, 1330, 1145, 1087, 1053, 960, 943, 923, 731, 695, 612 cm^{-1}; HRMS (ESI, positive) m/z for $C_{52}H_{42}N_4O_8PS_2$ $[M+H]^+$ calcd. 945.2182, found 945.2180.

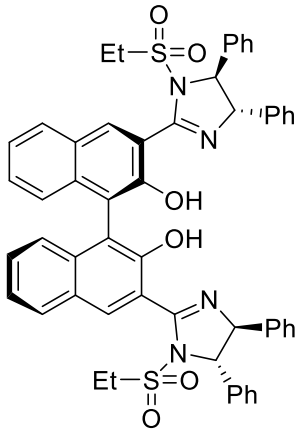
(1*S*,2*S*)-*N*-Ethanesulfonyl-1,2-diphenylethane-1,2-diamine



Triethylamine (1.38 mL, 9.9 mmol) was added to a solution of (1*S*,2*S*)-1,2-diphenylethane-1,2-diamine (700.0 mg, 3.3 mmol) in THF (46.0 mL), and cooled to 0 ℃. A solution of ethanesulfonyl chloride (0.34 mL, 3.63 mmol) in THF (13.0 mL) was dropwised to the mixture at 0 ℃, and the reaction mixture was stirred 18 h at room temperature. The solvent was removed under reduced pressure, and diluted by CH_2Cl_2, then extracted with CH_2Cl_2, and washed with brine. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (hexane:ethyl acetate = 30:70) to afford (1*S*,2*S*)-*N*-ethanesulfonyl-1,2-diphenylethane-1,2-diamine (619.5 mg, 62%).

$[\alpha]_D^{25}$ −9.6 (c 0.46, $CHCl_3$); m.p. 128.1-129.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 (t, *J* = 7.4 Hz, 3H), 1.58 (br, 2H), 2.34-2.46 (m, 2H), 4.22 (d, *J* = 5.7 Hz, 1H), 4.55 (d, *J* = 5.7 Hz, 1H), 7.25-7.31 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.0, 47.8, 60.5, 63.5, 126.8, 127.1, 127.9, 128.7, 140.0, 142.0; IR (ATR) 3354, 3174, 1604, 1452, 1318, 1137, 1054, 897, 769, 726, 695 cm^{-1}; HRMS (ESI, positive) m/z for $C_{16}H_{21}N_2O_2S$ $[M+H]^+$ calcd. 305.1324, found 305.1328.

(*R*)-3,3'-Bis[1-(ethanesulfonyl)-(4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl]-1,1'-binaphthol

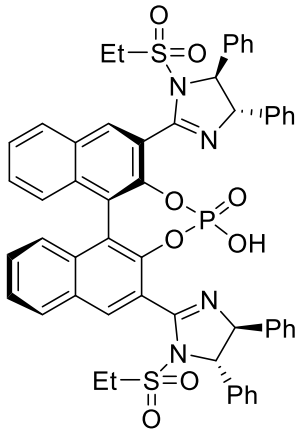


A solution of (*R*)-2,2'-dihydroxybinaphthyl-3,3'-biscarboxylic acid (243.3 mg, 0.65 mmol), (1*S*,2*S*)-*N*-ethanesulfonyl-1,2-diphenylethane-1,2-diamine (397.2 mg, 1.3 mmol), 1-hydroxybenzotriazole (263.5 mg, 1.95 mmol) in dimethylformamide (6.5 mL) was stirred for 10 min at 0 ℃, then a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (249.2 mg, 1.3 mmol) in dimethylformamide (2.5 mL) was added into the solution at 0 ℃. The reaction mixture was stirred for 18 h at room temperature. The reaction mixture was diluted by ethyl acetate, then washed with 1 M HCl aq., sat. $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated under reduced pressure to give (*R*)-3,3'-bis{[(1*S*,2*S*)-1,2-dipheny-2-(ethanesulfonylamino)ethylcarboxamide]}-1,1'-binaphthol.

Trifluoromethanesulfonic anhydride (0.34 mL, 2.0 mmol) was added to a solution of triphenylphosphine oxide (556.6 mg, 2.0 mmol) in CH_2Cl_2 (4 mL) at 0 ℃, and the reaction mixture was stirred for 1 h at room temperature. Then the reaction mixture was cooled to 0 ℃. (*R*)-3,3'-Bis{[(1*S*,2*S*)-1,2-dipheny-2-(ethanesulfonylamino)ethylcarboxamide]}-1,1'-binaphthol (640.0 mg, 0.67 mmol) was added to the reaction mixture and stirred for 30 min at 0 ℃. Then sat. $NaHCO_3$ was added, and aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (hexane:ethyl acetate = 60:40) to afford (*R*)-3,3'-bis[1-(methanesulfonyl)-(4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl]-1,1'-binaphthol (363.0 mg, 59%).

$[\alpha]_D^{25}$ +42.2 (c 0.62, $CHCl_3$); m.p. 211.9-212.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.4 Hz, 6H), 2.73-2.85 (m, 2H), 3.01-3.13 (m, 2H), 5.29 (d, *J* = 4.2 Hz, 2H), 5.39 (d, *J* = 4.2 Hz, 2H), 7.32-7.53 (m, 26H), 7.95-7.98 (m, 2H), 8.57 (s, 2H), 8.92 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.6, 49.2, 71.4, 77.9, 114.7, 117.9, 124.5, 124.7, 126.4, 127.9, 128.4, 128.8, 129.0, 129.3, 133.3, 135.1, 140.7, 141.7, 151.8, 158.5; IR (ATR) 3057, 1631, 1495, 1452, 1346, 1205, 1152, 1026, 907, 727, 696, 622 cm^{-1}; HRMS (ESI, positive) m/z for $C_{54}H_{47}N_4O_6S_2$ $[M+H]^+$ calcd. 911.2937, found 911.2927.

(*R*)-3,3'-Bis[1-(ethanesulfonyl)-(4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl]-1,1'-binaphthalene-2,2'-diyl hydrogen phosphate (3d)

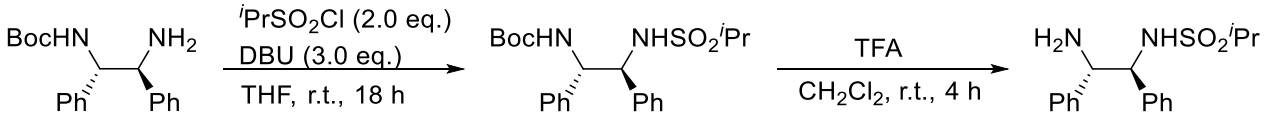


Triethylamine (3.0 mL, 22.2 mmol) was added to a solution of (*R*)-3,3'-bis[1-(ethanesulfonyl)-(4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl]-1,1'-binaphthol (360.0 mg, 0.4 mmol), *N*,*N*-dimethyl-4-aminopyridine (97.7 mg, 0.8 mmol), and Na_2SO_4 (274.6 mg) in CH_2Cl_2 (12.0 mL), and the reaction mixture was stirred for 5 min at room temperature. To the reaction mixture, phosphoryl chloride (0.2 mL, 2.2 mmol) was dropwised at room temperature, and the mixture was stirred for 12 h. Then water (7.0 mL) was added, stirred for 4 h. 1 M HCl aq. was added, and aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (ethyl acetate:methanol = 95:5) to afford **3d** (241.3 mg, 62%). The product was diluted with CH_2Cl_2, and washed with 1 M HCl aq. The organic layer was concentrated and dried at 90 °C under reduced pressure for 2 h.

$[\alpha]_D^{25}$ −140.8 (c 0.34, $CHCl_3$); m.p. 252.2-253.0 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.79-0.82 (m, 6H), 2.58-2.73 (m, 2H), 3.34-3.42 (m, 2H), 5.34-5.52 (m, 4H), 7.29-7.32 (m, 2H), 7.44-7.65 (m, 24H), 7.90 (d, *J* = 6.9 Hz, 2H), 8.31 (d, *J* = 8.1 Hz, 2H), 8.74 (s, 2H) ; ^{13}C NMR (125 MHz, DMSO-d_6) δ 6.7, 45.2, 72.3, 74.2, 121.7, 122.2, 125.8, 126.1, 126.8, 127.7, 128.1, 128.7, 129.0, 129.3, 129.5, 129.9, 132.9, 133.2, 138.8, 139.5, 146.1, 162.9; ^{31}P NMR (121 MHz, DMSO-d_6) δ 3.20; IR (ATR) 3061, 1621, 1496, 1453, 1349, 1282, 1153, 1092, 1044, 819, 751, 727, 697, 624 cm^{-1}; HRMS (ESI, positive) m/z for $C_{54}H_{46}N_4O_8PS_2$ $[M+H]^+$ calcd. 973.2495, found 973.2476.

(1*S*,2*S*)-*N*-(1-Methylethanelsulfonyl)-1,2-diphenylethane-1,2-diamine

The synthetic method for *tert*-butyl [(1*S*,2*S*)-2-amino-1,2-diphenylethyl]carbamate were reported.[3)]

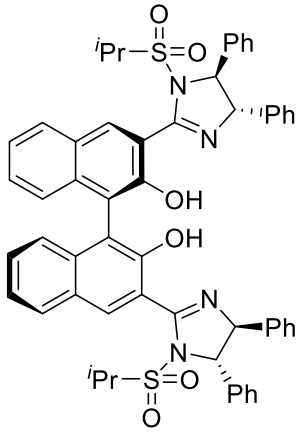


1,8-Diazabicyclo[5.4.0]undec-7-ene (1.3 mL, 9.0 mmol) and 1-methylethanesulfonyl chloride (0.67 mL, 6.0 mmol) were added to a solution of *tert*-butyl [(1*S*,2*S*)-2-amino-1,2-diphenylethyl]carbamate (924.1 mg, 3.0 mmol) in THF (15.0 mL) at 0 ℃. The reaction mixture was stirred for 18 h at room temperature. The reaction mixture was diluted by ethyl acetate, then washed with 1 M HCl aq., sat. $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated under reduced pressure to give the *tert*-butyl [(1*S*,2*S*)-1-methylethylsulfonamido-1,2-diphenylethyl]carbamate.

Trifluoroacetic acid (7.8 mL) was added to a solution of *tert*-butyl [(1*S*,2*S*)-1-methylethylsulfonamido-1,2-diphenylethyl]carbamate (1.24 g, 2.96 mmol) in CH_2Cl_2 (7.8 mL), and the reaction mixture was stirred for 4 h at room temperature. The reaction mixture was diluted by 1 M NaOH aq., then extracted with CH_2Cl_2, and washed with brine. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to give (1*S*,2*S*)-*N*-(1-methylethanesulfonyl)-1,2-diphenylethane-1,2-diamine (299.3 mg, 94%).

$[\alpha]_D^{25}$ +3.3 (c 0.50, $CHCl_3$); m.p. 118.8-119.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02-1.08 (m, 6H), 1.56 (br, 2H), 2.52-2.61 (m, 1H), 4.23 (d, *J* = 5.1 Hz, 1H), 4.57 (d, *J* = 5.1 Hz, 1H), 5.80 (br, 1H), 7.24-7.31 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.0, 16.4, 54.0, 60.6, 63.8, 126.8, 126.9, 127.7, 127.8, 128.5, 128.6, 140.4, 141.8; IR (ATR) 3351, 3295, 1604, 1452, 1308, 1127, 1052, 996, 898, 769, 695, 635 cm^{-1}; HRMS (ESI, positive) m/z for $C_{17}H_{23}N_2O_2S$ $[M+H]^+$ calcd. 319.1480, found 319.1480.

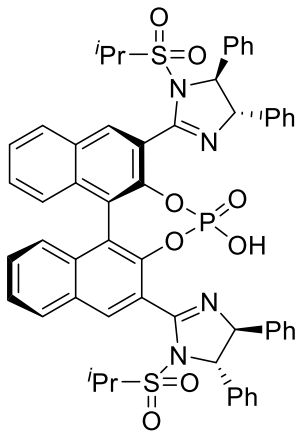
(*R*)-3,3'-Bis[1-(1-methylethanesulfonyl)-(4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl]-1,1'-binaphthol



A solution of (*R*)-2,2'-dihydroxybinaphthyl-3,3'-biscarboxylic acid (209.6 mg, 0.56 mmol), (1*S*,2*S*)-*N*-1-methylethanesulfonyl-1,2-diphenylethane-1,2-diamine (355.9 mg, 1.12 mmol), 1-hydroxybenzotriazole (227.0 mg, 1.68 mmol) in dimethylformamide (5.4 mL) was stirred for 10 min at 0 ℃, then a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (214.7 mg, 1.12 mmol) in dimethylformamide (2.2 mL) was added into the solution at 0 ℃. The reaction mixture was stirred for 18 h at room temperature. The reaction mixture was diluted by ethyl acetate, then washed with 1 M HCl aq., sat. $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated under reduced pressure to give (*R*)-3,3'-bis{[(1*S*,2*S*)-1,2-dipheny-2-(1-methylethanesulfonylamino)ethylcarboxamide]}-1,1'-binaphthol. Trifluoromethanesulfonic anhydride (0.26 mL, 1.54 mmol) was added to a solution of triphenylphosphine oxide (428.6 mg, 1.54 mmol) in CH_2Cl_2 (3.0 mL) at 0 ℃, and the reaction mixture was stirred for 1 h at room temperature, then the reaction mixture was cooled to 0 ℃. (*R*)-3,3'-Bis{[(1*S*,2*S*)-1,2-dipheny-2-(1-methylethanesulfonylamino)ethylcarboxamide]}-1,1'-binaphthol (500.0 mg, 0.513 mmol) was added to the reaction mixture and stirred for 30 min at 0 ℃. Then sat. $NaHCO_3$ was added, and aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (hexane:ethyl acetate = 60:40) to afford (*R*)-3,3'-bis[1-(1-methylethanesulfonyl)-(4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl]-1,1'-binaphthol (401.3 mg, 83%).

$[\alpha]_D^{25}$ +65.1 (c 0.51, $CHCl_3$); m.p. 198.1-198.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (d, *J* = 6.9 Hz, 6H), 1.29 (d, *J* = 6.9 Hz, 6H), 3.19-3.28 (m, 2H), 5.30 (d, *J* = 3.9 Hz, 2H), 5.39 (d, *J* = 3.9 Hz, 2H), 7.25-7.51 (m, 26H), 7.95-7.98 (m, 2H), 8.61 (s, 2H), 9.59 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.3, 16.9, 55.8, 71.4, 78.1, 115.5, 117.6, 124.3, 124.8, 126.3, 126.4, 127.6, 128.4, 128.6, 128.9, 129.2, 129.5, 132.9, 135.3, 140.4, 142.1, 152.1, 159.4; IR (ATR) 3030, 1631, 1600, 1496, 1452, 1342, 1203, 1170, 1143, 1051. 1028, 907, 728, 695, 613 cm^{-1}; HRMS (ESI, positive) m/z for $C_{56}H_{51}N_4O_6S_2$ $[M+H]^+$ calcd. 939.3250, found 939.3236.

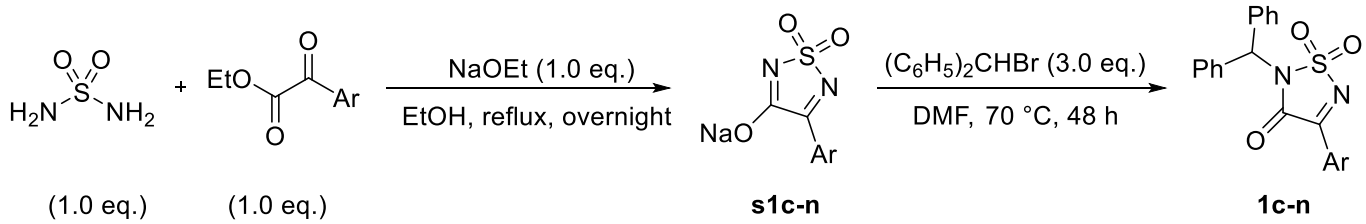
(*R*)-3,3'-Bis[1-(1-methylethanesulfonyl)-(4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl]-1,1'-binaphthalene-2,2'-diyl hydrogen phosphate (3e)



Triethylamine (2.66 mL, 17.8 mmol) was added to a solution of (*R*)-3,3'-bis[1-(1-methylethanesulfonyl)-(4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl]-1,1'-binaphthol (300.0 mg, 0.32 mmol), *N*,*N*-dimethyl-4-aminopyridine (78.2 mg, 0.64 mmol), and Na_2SO_4 (219.8 mg) in CH_2Cl_2 (9.6 mL), and the reaction mixture was stirred for 5 min at room temperature. To the reaction mixture, phosphoryl chloride (0.16 mL, 1.76 mmol) was dropwised at room temperature, and the mixture was stirred for 12 h. Then water (5.6 mL) was added, stirred for 4 h. 1M HCl aq. was added and aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (ethyl acetate:methanol = 95:5) to afford **3e** (228.2 mg, 71%) The product was diluted with CH_2Cl_2, and washed with 1M HCl aq. The organic layer was concentrated and dried at 90 °C under reduced pressure for 2 h.

$[\alpha]_D^{25}$ −191.4 (c 0.35, $CHCl_3$); m.p. 270.1-271.0 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.83 (d, *J* = 6.6 Hz, 6H), 0.90 (d, *J* = 6.6 Hz, 6H), 3.29 (br, 2H), 5.33-5.52 (m, 4H), 7.22-7.78 (m, 26H), 8.31 (d, *J* = 8.4 Hz, 2H), 8.65 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 18.1, 49.4, 69.4, 71.4, 123.2, 123.8, 126.5, 129.2, 129.3, 129.9, 130.1, 132.7, 133.7, 133.8, 134.2, 138.9, 146.0, 146.9, 162.9; ^{31}P NMR (121 MHz, DMSO-d_6) δ 5.93; IR (ATR) 3049, 1623, 1496, 1455, 1341, 1281, 1092, 1029, 818, 752, 696, 608 cm^{-1}; HRMS (ESI, positive) m/z for $C_{56}H_{50}N_4O_8PS_2$ $[M+H]^+$ calcd. 1001.2808, found 1001.2802.

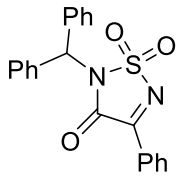
General procedure for synthesis of cyclic ketimines



A solution of sodium ethoxide (1.0 g, 15 mmol) in ethanol (3.7 mL) was dropwised to a solution of sulfamide (1.44 g, 15 mmol) in ethanol (22 mL), at room temperature. The suspension was stirred at room temperature for 15 min and then ethyl arylglyoxylate (15 mmol) in ethanol (15 mL) was added. After stirring for 15 min, the mixture was refluxed overnight and concentrated under reduced pressure. The residue was suspended in diethyl ether and stirred at room temperature for 30 min. The residue was filtered, washed with diethyl ether, and dried under vacuum to give **s1c-n**, which was used for the next reaction without further purification.

A solution of bromodiphenylmethane (6.67 g, 27 mmol) in dimethylformamide (4.5 mL) was added to a solution of **s1c-n** (9.0 mmol) in dimethylformamide (14 mL) at 70 ℃. The mixture was stirred at 70 ℃ for 48 h. Then H_2O was added, and aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (hexane:$CHCl_3$:ethyl acetate = 40:5:1) to afford the corresponding cyclic ketimines.

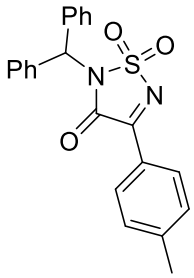
2-Benzhydryl-4-phenyl-3-oxo-1,2,5-thiadiazol 1,1-oxides (1c) (R = Ph)



According to the general procedure, the reaction with ethyl phenylglyoxylate (2.38 mL, 15 mmol) gave **s1c** (2.87 g), and the reaction of **s1c** (2.09 g, 9 mmol) gave **1c** as a white solid (1.32 g, 40%).

m.p. 164.5-165.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.49 (s, 1H), 7.36-7.46 (m, 10H), 7.49-7.55 (m, 2H), 7.68-7.73 (m, 1H), 8.53 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.7, 126.9, 128.8, 128.9, 129.0, 129.4, 132.2, 135.4, 136.3, 155.8, 163.8; IR (ATR) 1739, 1561, 1446, 1353, 1236, 1190, 1013, 809, 699, 605 cm^{-1}; HRMS (ESI, positive) m/z for $C_{21}H_{16}N_2NaO_3S$ $[M+Na]^+$ calcd. 399.0779, found 399.0771.

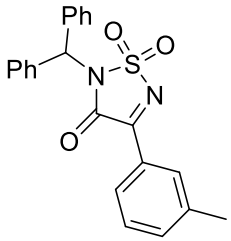
2-Benzhydryl-4-(4-tolyl)-3-oxo-1,2,5-thiadiazol 1,1-oxides (1d) (R = 4-$CH_3C_6H_4$)



According to the general procedure, the reaction with ethyl 4-methylbenzoylformate (864.5 mg, 6.2 mmol) gave **s1d** (703.0 mg), then the reaction of **s1d** (615.0 mg, 2.5 mmol) gave **1d** as a white solid (375.1 mg, 38%).

m.p. 165.0-165.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 3H), 6.48 (s, 1H), 7.32-7.45 (m, 12H), 8.45 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.3, 63.6, 124.2, 128.8, 129.0, 130.2, 132.4, 135.5, 148.3, 156.0, 163.5; IR (ATR) 1730, 1678, 1572, 1545, 1364, 1253, 1174, 1066, 762, 697, 619 cm^{-1}; HRMS (ESI, positive) m/z for $C_{22}H_{18}N_2NaO_3S$ $[M+Na]^+$ calcd. 413.0936, found 413.0931.

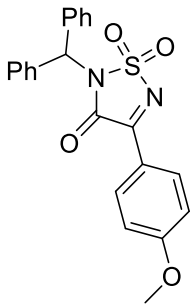
2-Benzhydryl-4-(*3'*-tolyl)-3-oxo-1,2,5-thiadiazol 1,1-oxides (1e) (R = 3-$CH_3C_6H_4$)



According to the general procedure, the reaction with ethyl 3-methylbenzoylformate (768.3 mg, 4 mmol) gave **s1e** (653.8 mg), then the reaction of **s1e** (492.0 mg, 2.0 mmol) gave **1e** as a white solid (288.7 mg, 37%).

m.p. 158.0-158.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 6.48 (s, 1H), 7.34-7.45 (m, 11H), 7.52 (d, *J* = 7.5 Hz, 1H), 8.33-8.34 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 63.6, 126.8, 128.8, 129.0, 129.3, 129.6, 132.5, 137.3, 139.3, 155.9, 163.9; IR (ATR) 1746, 1551, 1362, 1261, 1246, 1181, 882, 755, 696, 682 cm^{-1}; HRMS (ESI, positive) m/z for $C_{22}H_{18}N_2NaO_3S$ $[M+Na]^+$ calcd. 413.0936, found 413.0933

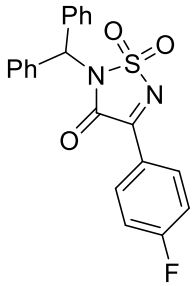
2-Benzhydryl-4-(4-methoxyphenyl)-3-oxo-1,2,5-thiadiazol 1,1-oxides (1f) (R = 4-$CH_3OC_6H_4$)



According to the general procedure, the reaction with ethyl 4-methoxylbenzoylformate (936.9 mg, 4.5 mmol) gave **s1f** (882.8 mg), then the reaction of **s1f** (524.0 mg, 2.0 mmol) gave **1f** as a yellow solid (227.4 mg, 28%).

m.p. 157.4-157.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.91 (s, 3H), 6.47 (s, 1H), 6.98 (d, J = 9.3 Hz, 2H), 7.36-7.45 (m, 10H), 8.58 (d, J = 9.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.0, 63.4, 115.1, 119.4, 128.7, 128.8, 129.0, 135.10, 135.6, 156.5, 162.3, 166.7; IR (ATR) 1724, 1603, 1547, 1511, 1368, 1255, 1189, 1160, 1013, 844, 815, 760, 697, 612 cm^{-1}; HRMS (ESI, positive) m/z for $C_{22}H_{18}N_2NaO_4S$ $[M+Na]^+$ calcd. 429.0885, found 429.0878.

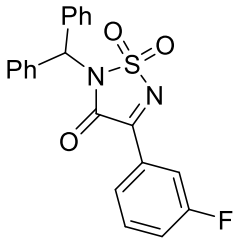
2-Benzhydryl-4-(4-fluorophenyl)-3-oxo-1,2,5-thiadiazol 1,1-oxides (1g) (R = 4-FC$_6$H$_4$)



According to the general procedure, the reaction with ethyl 4-fluorobenzoylformate (882.4 mg, 4.5 mmol) gave **s1g** (912.3 mg), then the reaction of **s1g** (500.0 mg, 2.0 mmol) gave **1g** as a white solid (236.4 mg, 30%).

m.p. 143.4-144.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48 (s, 1H), 7.17-7.23 (m, 2H), 7.37-7.42 (m, 10H), 8.59-8.63 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.7, 117.0 (d, J_{C-F} = 22.5 Hz), 123.2, 123.3, 128.8, 128.9, 129.0, 135.2, 135.3, 135.4, 155.7, 168.9 (d, J_{C-F} = 261.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −97.78; IR (ATR) 1727, 1591, 1562, 1366, 1254, 1188, 1158, 855, 812, 787, 762, 698, 618 cm^{-1}; HRMS (ESI, positive) m/z for $C_{21}H_{15}FN_2NaO_3S$ $[M+Na]^+$ calcd. 417.0685, found 417.0684.

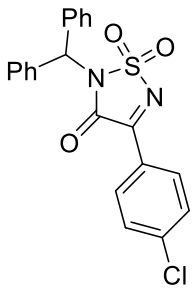
2-Benzhydryl-4-(3-fluorophenyl)-3-oxo-1,2,5-thiadiazol 1,1-oxides (1h) (R = 3-FC$_6$H$_4$)



According to the general procedure, the reaction with ethyl 3-fluorobenzoylformate (784.4 mg, 4.0 mmol) gave **s1h** (922.2 mg), then the reaction of **s1h** (500.0 mg, 2.0 mmol) gave **1h** as a white solid (244.3 mg, 31%).

m.p. 146.7-147.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.49 (s, 1H), 7.37-7.53 (m, 12H), 8.24-8.28 (m, 1H), 8.34-8.38 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.9, 118.7 (d, J_{C-F} = 25.0 Hz), 123.4 (d, J_{C-F} = 21.3 Hz), 128.1, 128.5, 128.6, 128.9, 129.0, 131.1 (d, J_{C-F} = 7.5 Hz), 135.3, 155.3, 162.6 (d, J_{C-F} = 247.5 Hz), 162.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ −109.8; IR (ATR) 1739, 1566, 1368, 1254, 1188, 1159, 1063, 889, 757, 740, 697 cm^{-1}; HRMS (ESI, positive) m/z for $C_{21}H_{15}FN_2NaO_3S$ $[M+Na]^+$ calcd. 417.0685, found 417.0677.

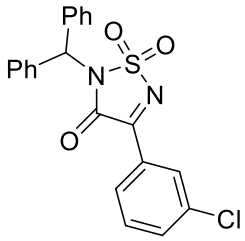
2-Benzhydryl-4-(4-chlorophenyl)-3-oxo-1,2,5-thiadiazol 1,1-oxides (1i) (R = 4-ClC$_6$H$_4$)



According to the general procedure, the reaction with ethyl 4-chlorobenzoylformate (954.0 mg, 4.5 mmol) gave **s1i** (945.9 mg), then the reaction of **s1i** (665.0 mg, 2.5 mmol) gave **1i** as a white solid (350.0 mg, 34%).

m.p. 131.8-132.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48 (s, 1H), 7.37-7.43 (m, 10H), 7.49 (d, J = 8.7 Hz, 2H), 8.49 (d, J = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.8, 125.2, 128.8, 128.9, 129.0, 129.9, 133.4, 135.3, 143.4, 155.6, 162.8; IR (ATR) 1738, 1582, 1375, 1255, 1186, 1094, 1067, 844, 815, 744, 713, 694 cm^{-1}; HRMS (ESI, positive) m/z for $C_{21}H_{15}ClN_2NaO_3S$ $[M+Na]^+$ calcd. 433.0390, found 433.0386.

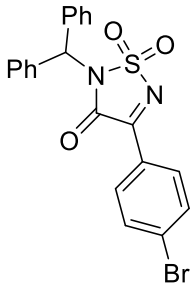
2-Benzhydryl-4-(3-chlorophenyl)-3-oxo-1,2,5-thiadiazol 1,1-oxides (1j) (R = 3-ClC$_6$H$_4$)



According to the general procedure, the reaction with ethyl 3-chlorobenzoylformate (850.5 mg, 4.0 mmol) gave **s1j** (1.0 g), then the reaction of **s1j** (532.0 mg, 2.0 mmol) gave **1j** as a white solid (287.1 mg, 35%).

m.p. 151.1-152.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.49 (s, 1H), 7.37-7.50 (m, 11H), 7.66-7.70 (m, 1H), 8.42-8.45 (m, 1H), 8.55 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.9, 128.4, 128.9, 129.0, 130.2, 130.6, 131.8, 135.2, 135.6, 136.1, 155.3, 162.9; IR (ATR) 1741, 1583, 1556, 1363, 1240, 1182, 842, 747, 696, 675, 651 cm^{-1}; HRMS (ESI, positive) m/z for $C_{21}H_{15}ClN_2NaO_3S$ $[M+Na]^+$ calcd. 433.0390, found 433.0391.

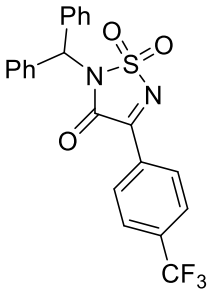
2-Benzhydryl-4-(4-bromophenyl)-3-oxo-1,2,5-thiadiazol 1,1-oxides (1k) (R = 4-BrC$_6$H$_4$)



According to the general procedure, the reaction with ethyl 4-bromobenzoylformate (1.23 g, 4.8 mmol) gave **s1k** (1.07 g), then the reaction of **s1k** (665.0 mg, 2.5 mmol) gave **1k** as a yellow solid (324.7 mg, 32%).

m.p. 144.8-145.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48 (s, 1H), 7.38-7.42 (m, 10H), 7.67 (d, J = 8.7 Hz, 2H), 8.40 (d, J = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.8, 125.7, 128.9, 129.0, 132.6, 132.9, 133.4, 135.3, 155.6, 163.1; IR (ATR) 1727, 1580, 1549, 1494, 1370, 1247, 1195, 1174, 1010, 810, 699 cm^{-1}; HRMS (ESI, positive) m/z for $C_{21}H_{15}BrN_2NaO_3S$ $[M+Na]^+$ calcd. 476.9884, found 476.9873.

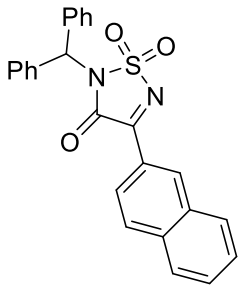
2-Benzhydryl-4-(4-trifluoromethylphenyl)-3-oxo-1,2,5-thiadiazol 1,1-oxides (1l) (R = 4-$CF_3C_6H_4$)



According to the general procedure, the reaction with ethyl [4-(trifluoromethyl)phenyl]glyoxylate (984.2 mg, 4.0 mmol) gave **s1l** (1.01 g), then the reaction of **s1l** (600.0 mg, 2.0 mmol) gave **1l** as a white solid (266.4 mg, 30%).

m.p. 139.1-139.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.51 (s, 1H), 7.39-7.44 (m, 10H), 7.79 (d, J = 6.0 Hz, 2H), 8.85 (d, J = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 64.0, 122.1, 124.2, 126.1, 126.2, 127.4, 128.8, 128.9, 129.8, 132.4, 135.1, 136.6 (q, J_{C-F} = 32.5 Hz) 136.8 (q, J_{C-F} = 32.5 Hz), 137.1 (q, J_{C-F} = 33.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.63; IR (ATR) 1738, 1592, 1564, 1378, 1319, 1250, 1177, 1129, 1069, 1015, 854, 811, 699 cm^{-1}; HRMS (ESI, positive) m/z for $C_{22}H_{15}F_3N_2NaO_3S$ $[M+Na]^+$ calcd. 467.0653, found 467.0656.

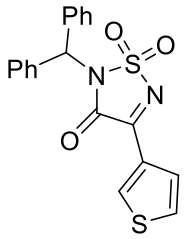
2-Benzhydryl-4-(naphthalen-2-yl)-3-oxo-1,2,5-thiadiazol 1,1-oxides (1m) (R = 2-Naphthyl)



According to the general procedure, the reaction with ethyl 2-naphthylglyoxylate (250.8 mg, 2.61 mmol) gave **s1m** (604.9 mg), then the reaction of **s1m** (564.0 mg, 2.0 mmol) gave **1m** as a yellow solid (238.6 mg, 28%).

m.p. 237.6-238.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.52 (s, 1H), 7.34-7.49 (m, 10H), 7.53-7.58 (m, 1H), 7.63-7.68 (m, 1H), 7.84-7.93 (m, 3H), 8.28 (d, J = 8.7 Hz, 1H), 9.37 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.7, 124.3, 125.1, 127.6, 128.1, 128.9, 129.1, 129.5, 130.7, 132.5, 135.5, 136.8, 137.2, 156.1, 163.3; IR (ATR) 1745, 1548, 1357, 1268, 1178, 883, 746, 697, 633, 610 cm^{-1}; HRMS (ESI, positive) m/z for $C_{25}H_{18}N_2NaO_3S$ $[M+Na]^+$ calcd. 449.0936, found 449.0936.

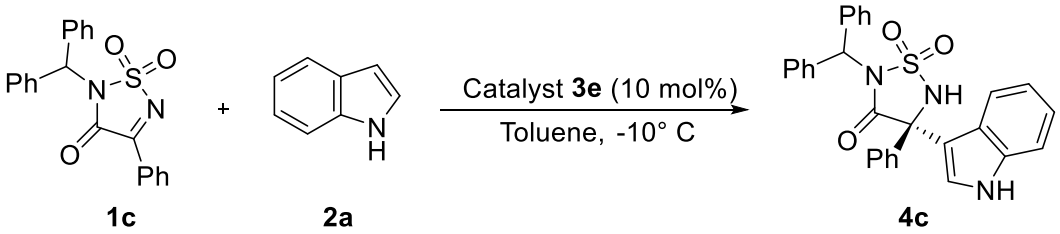
2-Benzhydryl-4-(thiophen-3-yl)-3-oxo-1,2,5-thiadiazol 1,1-oxides (1n) (R = 3-Thienyl)



According to the general procedure, the reaction with ethyl 3-thienylglyoxylate (552.0 mg, 3.0 mmol) gave **s1n** (653.2 mg), then the reaction of **s1n** (475.8 mg, 2.0 mmol) gave **1n** as a yellow solid (129.9 mg, 17%).

m.p. 148.2-149.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48 (s, 1H), 7.22-7.30 (m, 1H), 7.35-7.47 (m, 10H), 7.85-7.87 (m, 1H), 9.13-9.14 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.5, 127.7, 128.3, 128.8, 129.0, 135.5, 141.9, 155.8, 158.3; IR (ATR) 1731, 1565, 1366, 1251, 1173, 879, 820, 732, 695, 622 cm^{-1}; HRMS (ESI, positive) m/z for $C_{19}H_{14}N_2NaO_3S_2$ $[M+Na]^+$ calcd. 405.0344, found 405.0332.

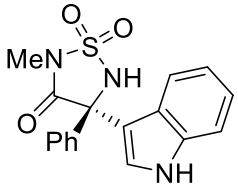
General procedure for the enantioselective aza-Friedel-Crafts reaction of cyclic ketimines with indoles:



1c **2a** **4c**

Indole **2a** (8.8 mg, 0.075 mmol) was added to a solution of bis(imidazoline)-phosphoric acid catalyst **3e** (5.0 mg, 10 mol%) and cyclic ketimine **1c** (18.8 mg, 0.05 mmol) in toluene (0.25 mL) at −10 ℃. After stirred for 40 h, the mixture was purified over silica gel column chromatography (hexane/ethyl acetate=70:30) to give **4c** (24.1 mg, 98%, 99% ee).

(*R*)-2-Methyl-4-(1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4a)

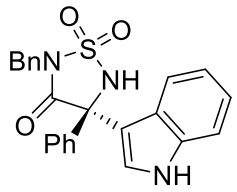


Reaction of **3a** (3.6 mg, 0.005 mmol), **1a** (11.2 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at r.t. for 72 h gave **4a** (13.0 mg, 76%, 5% ee).

$[\alpha]_D^{25}$ +0.3 (c 0.33, EtOH); m.p. 199.2-200.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.11 (s, 3H), 5.27 (s, 1H), 7.04-7.10 (m, 1H), 7.19-7.30 (m, 3H), 7.36-7.42 (m, 4H), 7.73-7.76 (m, 2H), 8.29 (s, 1H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 26.3, 72.1, 112.0, 114.2, 119.4, 121.1, 123.4, 124.1, 125.4, 127.3, 128.8, 129.1, 136.8, 136.9, 168.6; IR (ATR) 3385, 3305, 1745, 1462, 1431, 1295, 1249, 1165, 1112, 1054, 962.3, 908, 743, 697, 650 cm^{-1}; HRMS (ESI, positive) m/z for $C_{17}H_{15}N_3NaO_3S$ $[M+Na]^+$ calcd. 364.0732, found 364.0735; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 90:10, 1.0 mL/min, 254 nm), tR = 22.9 min (major), 27.5 min (minor).

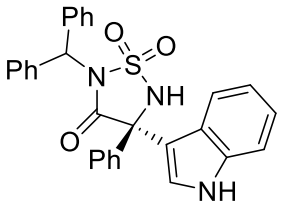
(*R*)-2-Benzyl-4-(1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4b)



Reaction of **3a** (3.6 mg, 0.005 mmol), **1b** (15.0 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at r.t. for 72 h gave **4b** (14.9 mg, 71%, 5% ee).

$[\alpha]_D^{25}$ +0.3 (c 0.35, EtOH); m.p. 204.6-205.1 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 4.75 (d, *J* = 15.3 Hz, 1H), 4.85 (d, *J* = 15.3 Hz, 1H), 5.27 (s, 1H), 6.96-6.99 (m, 1H), 7.09-7.26 (m, 4H), 7.34-7.40 (m, 6H), 7.45-7.48 (m, 2H), 7.73-7.76 (m, 2H), 8.23 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 45.5, 71.3, 111.9, 114.9, 119.3, 121.1, 123.4, 124.1, 125.5, 127.3, 128.6, 128.9, 129.0, 129.1, 134.2, 136.7, 136.9, 168.7; IR (ATR) 3368, 3316, 1727, 1431, 1369, 1327, 1290, 1247, 1174, 1109, 1053, 951, 907, 753, 726, 697, 656 cm^{-1}; HRMS (ESI, positive) m/z for $C_{23}H_{19}N_3NaO_3S$ $[M+Na]^+$ calcd. 440.1045, found 440.1053; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 11.8 min (major), 15.6 min (minor).

(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4c)

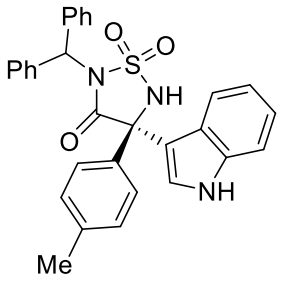


Reaction of **3e** (5.0 mg, 0.005 mmol), **1c** (18.8 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 °C for 40 h gave **4c** (24.1 mg, 98%, 99% ee).

$[\alpha]_D^{25}$ +22.5 (c 0.78, EtOH); m.p. 125.5-126.3 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 5.36 (s, 1H), 6.39 (s, 1H), 6.86-6.95 (m, 2H), 7.10-7.15 (m, 2H), 7.22-7.44 (m, 14H), 7.68-7.70 (m, 2H), 8.21 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.7, 111.9, 114.1, 119.1, 120.9, 123.2, 124.0, 125.6, 127.3, 128.3, 128.5, 128.6, 128.7, 129.0, 129.5, 135.9, 136.1, 136.5, 136.8, 168.3; IR (ATR) 3411, 3281, 1725, 1495, 1383, 1327, 1248, 1176, 1028, 907, 739, 695, 649 cm^{-1}; HRMS (ESI, positive) m/z for $C_{29}H_{23}N_3NaO_3S$

[M+Na]$^+$ calcd. 516.1358, found 516.1364; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 10.7 min (major), 14.8 min (minor).

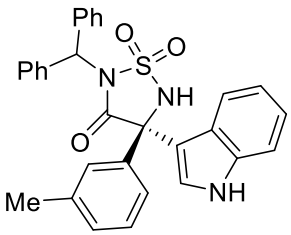
(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-4-(*p*-tolyl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4d)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1d** (19.5 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 ℃ for 72 h gave **4d** (23.7 mg, 93%, 98% ee).

$[\alpha]_D^{25}$ +0.4 (c 0.56, EtOH); m.p. 145.7-146.2 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 5.34 (s, 1H), 6.39 (s, 1H), 6.91-6.96 (m, 2H), 7.12-7.18 (m, 3H), 7.24-7.33 (m, 10H), 7.41-7.44 (m, 2H), 7.56 (d, *J* = 9.0 Hz, 2H), 8.21 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 62.7, 70.5, 111.9, 114.2, 114.3, 119.3, 120.9, 123.2, 124.0, 124.1, 125.6, 127.2, 128.3, 128.5, 128.6, 128.7, 129.5, 133.7, 136.0, 136.2, 136.8, 138.9, 168.4; IR (ATR) 3413, 3285, 1726, 1382, 1327, 1266, 1248, 1175, 1105, 1028, 908, 849, 818, 735, 696 cm^{-1}; HRMS (ESI, positive) m/z for $C_{30}H_{25}N_3NaO_3S$ [M+Na]$^+$ calcd. 530.1514, found 530.1497; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 11.4 min (major), 14.1 min (minor).

(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-3-(4-methylphenyl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4e)

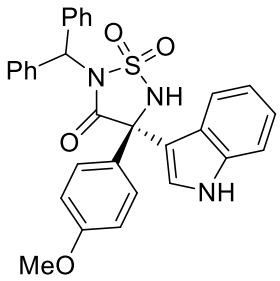


Reaction of **3e** (5.0 mg, 0.005 mmol), **1e** (19.5 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 ℃ for 120 h gave **4e** (24.7 mg, 98%, 95% ee).

$[\alpha]_D^{25}$ +33.2 (c 0.55, EtOH); m.p. 143.1-143.9 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 5.33 (s, 1H), 6.39 (s, 1H), 6.93-6.98 (m, 2H), 7.15-7.19 (m, 3H), 7.23-7.33 (m, 10H), 7.42-7.50 (m, 4H), 8.20 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7, 62.8, 70.6, 111.9, 114.2, 119.4, 120.9, 123.2, 124.1, 124.5, 125.6, 127.8, 128.3, 128.5, 128.6, 128.8, 129.5, 129.8, 136.2, 136.6, 136.8, 138.5, 168.3; IR (ATR) 3412, 3278, 1726, 1605, 1453, 1383, 1327, 1267, 1183, 1090, 1028, 905, 733, 698 cm^{-1}; HRMS (ESI, positive) m/z for $C_{30}H_{25}N_3NaO_3S$ [M+Na]$^+$ calcd. 530.1514, found 530.1494; HPLC (DAICEL

CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 10.5 min (major), 15.8 min (minor).

(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4f)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1f** (20.3 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 °C for 96 h gave **4f** (22.7 mg, 87%, 98% ee).

$[\alpha]_D^{25}$ +3.7 (c 0.36, EtOH); m.p. 208.4-209.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82 (s, 3H), 5.32 (s, 1H), 6.40 (s, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.96-7.02 (m, 2H), 7.13-7.21 (m, 2H), 7.26-7.35 (m, 9H), 7.41-7.45 (m, 2H), 7.61 (d, *J* = 9.0 Hz, 2H), 8.20 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5, 62.7, 70.3, 111.8, 114.0, 114.6, 119.4, 121.0, 123.3, 124.1, 125.5, 128.3, 128.6, 128.7, 129.5, 136.0, 136.2, 136.9, 160.1, 168.4; IR (ATR) 3412, 3281, 1732, 1611, 1509, 1237, 1173, 1091, 1028, 892, 743, 698, 631 cm^{-1}; HRMS (ESI, positive) m/z for $C_{30}H_{25}N_3NaO_4S$ $[M+Na]^+$ calcd. 546.1463, found 546.1465; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 14.3 min (major), 22.5 min (minor).

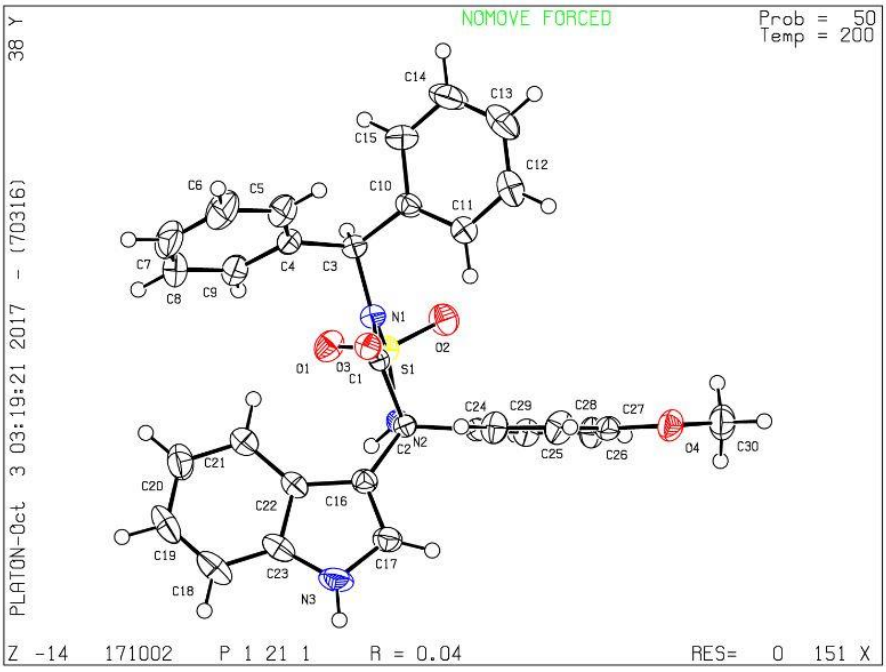
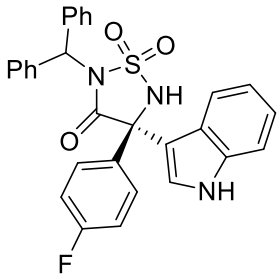


Figure S1. X-ray crystallography analysis for (*R*)-**4f** (CCDC No. 1577647).

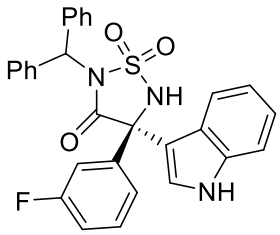
(*R*)-2-Benzhydryl-4-(4-fluorophenyl)-4-(1*H*-indol-3-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4g)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1g** (19.7 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 ℃ for 72 h gave **4g** (24.1 mg, 95%, 96% ee).

$[\alpha]_D^{25}$ +61.6 (c 0.38, EtOH); m.p. 206.2-206.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.36 (s, 1H), 6.39 (s, 1H), 6.95-7.11 (m, 5H), 7.18-7.36 (m, 10H), 7.41-7.44 (m, 2H), 7.70-7.74 (m, 2H), 8.21 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.9, 70.0, 112.0, 114.3, 115.6 (d, J_{C-F} = 21.3 Hz), 119.0, 121.1, 123.5, 123.8, 125.3, 128.3, 128.5, 128.6, 128.7, 129.3, 129.4, 129.6, 132.3, 135.9 (d, J_{C-F} = 10.0 Hz), 136.8, 163.1 (d, J_{C-F} = 246.3 Hz), 168.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ −113.2; IR (ATR) 3378, 3341, 1754, 1604, 1504, 1237, 1177, 1160, 1089, 1025, 891, 756, 699, 631 cm^{-1}; HRMS (ESI, positive) m/z for $C_{29}H_{22}FN_3NaO_3S$ $[M+Na]^+$ calcd. 534.1264, found 534.1268; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 9.2 min (major), 10.9 min (minor).

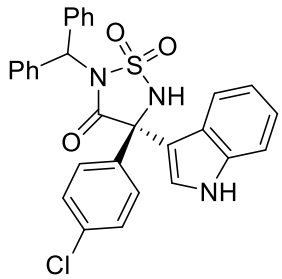
(*R*)-2-Benzhydryl-4-(4-fluorophenyl)-4-(1*H*-indol-3-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4h)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1h** (19.7 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 ℃ for 96 h gave **4h** (25.0 mg, 98%, 91% ee).

$[\alpha]_D^{25}$ +1.8 (c 0.48, EtOH); m.p. 135.3-140.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.40 (s, 1H), 6.40 (s, 1H), 6.95-7.48 (m, 16H), 7.57 (d, J = 7.8 Hz, 1H), 8.23 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.9, 70.0, 112.0, 114.0, 114.9 (d, J_{C-F} = 26.3Hz), 70.0, 112.0, 114.3, 115.6 (d, J_{C-F} = 21.3 Hz), 116.1 (d, J_{C-F} = 20.0 Hz), 119.0, 121.2, 123.0, 123.5, 123.8, 125.3, 128.4, 128.7, 128.8, 129.7, 130.2 (d, J_{C-F} = 8.8 Hz), 135.9, 136.8, 139.1 (d, J_{C-F} = 7.5 Hz), 162.9 (d, J_{C-F} = 245.0 Hz), 167.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ −111.7; IR (ATR) 3413, 3285, 1726, 1591, 1485, 1443, 1383, 1248, 1184, 1089, 1028, 908, 736, 698 cm^{-1}; HRMS (ESI, positive) m/z for $C_{29}H_{22}FN_3NaO_3S$ $[M+Na]^+$ calcd. 534.1264, found. 534.1261; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 8.6 min (major), 12.4 min (minor).

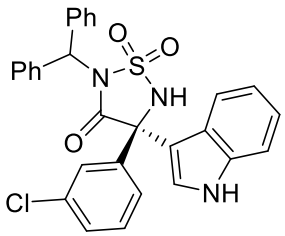
(*R*)-2-Benzhydryl-4-(4-chlorophenyl)-4-(1*H*-indol-3-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4i)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1i** (20.5 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 ℃ for 72 h gave **4i** (25.1 mg, 95%, 95% ee).

$[\alpha]_D^{25}$ +80.8 (c 0.33, EtOH); m.p. 227.4-228.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.36 (s, 1H), 6.39 (s, 1H), 6.92-6.99 (m, 2H), 7.07-7.10 (m, 1H), 7.15-7.44 (m, 14H), 7.67-7.70 (m, 2H), 8.21 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.9, 70.0, 112.0, 114.1, 118.9, 121.2, 123.5, 123.7, 125.3, 128.4, 128.5, 128.7, 128.8, 128.9, 129.6, 135.1, 135.9, 136.8, 167.9; IR (ATR) 3450, 3265, 1729, 1487, 1386, 1335, 1275, 1187, 1174, 1045, 900, 796, 740, 702, 653 cm^{-1}; HRMS (ESI, positive) m/z for $C_{29}H_{22}ClN_3NaO_3S$ $[M+Na]^+$ calcd. 550.0968, found 550.0975; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 8.1 min (major), 10.7 min (minor).

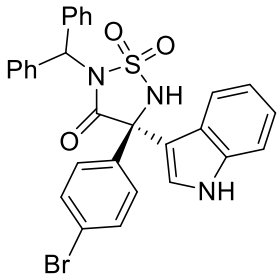
(*R*)-2-Benzhydryl-4-(3-chlorophenyl)-4-(1*H*-indol-3-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4j)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1j** (20.5 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 ℃ for 120 h gave **4j** (22.5 mg, 85%, 92% ee).

$[\alpha]_D^{25}$ +31.1 (c 0.38, EtOH); m.p. 128.1-129.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.40 (s, 1H), 6.40 (s, 1H), 6.94-7.00 (m, 2H), 7.10-7.45 (m, 15H), 7.66-7.73 (m, 2H), 8.24 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.0, 69.9, 112.0, 114.0, 118.9, 121.2, 123.5, 123.7, 125.4, 125.5, 127.6, 128.4, 128.5, 128.6, 128.7, 121026.1, 9.3, 129.9, 134.7, 135.8, 135.9, 136.8, 138.6, 167.6; IR (ATR) 3412, 3271, 1726, 1593, 1416, 1382, 1328, 1266, 1180, 1105, 907, 786, 738, 696 cm^{-1}; HRMS (ESI, positive) m/z for $C_{29}H_{22}ClN_3NaO_3S$ $[M+Na]^+$ calcd. 550.0968, found 550.0969; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 8.3 min (major), 11.9 min (minor).

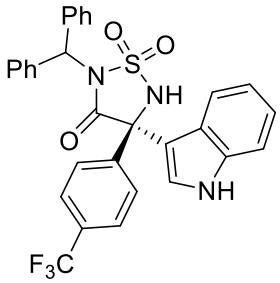
(*R*)-2-Benzhydryl-4-(4-bromophenyl)-4-(1*H*-indol-3-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4k)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1k** (22.7 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 ℃ for 72 h gave **4k** (26.8 mg, 94%, 96% ee).

$[\alpha]_D^{25}$ +40.5 (c 0.40, EtOH); m.p. 222.1-222.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.36 (s, 1H), 6.39 (s, 1H), 6.96-7.00 (m, 2H), 7.10 (d, *J* = 8.7 Hz, 1H), 7.17-7.36 (m, 10H), 7.41-7.44 (m, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 8.22 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.9, 70.0, 112.0, 114.1, 118.9, 121.2, 123.4, 123.5, 123.8, 125.3, 128.4, 128.6, 128.7, 129.1, 129.7, 131.9, 135.7, 135.9, 136.8, 167.8; IR (ATR) 3423, 3289, 1751, 1486, 1396, 1341, 1300, 1248, 1174, 1009, 939, 848, 824, 750, 700, 665 cm^{-1}; HRMS (ESI, positive) m/z for $C_{29}H_{22}BrN_3NaO_3S$ $[M+Na]^+$ calcd. 594.0463, found 594.0471; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 8.8 min (major), 13.7 min (minor).

(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-4-[4-(trifluoromethyl)phenyl]-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4l)

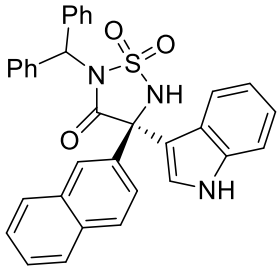


Reaction of **3e** (5.0 mg, 0.005 mmol), **1l** (22.2 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 ℃ for 40 h gave **4l** (27.4 mg, 98%, 96% ee).

$[\alpha]_D^{25}$ −12.5 (c 0.51, EtOH); m.p. 224.7-225.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.42 (s, 1H), 6.40 (s, 1H), 6.97-7.01 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 7.20-7.43 (m, 12H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.92 (d, *J* = 9.1 Hz, 2H), 8.24 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.0, 70.1, 112.1, 113.9, 118.8, 121.3, 123.6, 123.8, 125.2, 125.6 (q, $J_{C\text{-}F}$ = 3.3 Hz), 127.9, 128.4, 128.6, 128.7, 128.8, 129.7, 131.1 (q, $J_{C\text{-}F}$ = 32.5 Hz), 135.7, 135.9, 136.8, 140.4, 167.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.7; IR (ATR) 3494, 3358, 1739, 1621, 1326, 1248, 1175, 1108, 1068, 1016, 855, 832, 750, 700, 653 cm^{-1}; HRMS (ESI, positive) m/z for $C_{30}H_{22}F_3N_3NaO_3S$ $[M+Na]^+$ calcd. 584.1232, found 584.1215; HPLC (DAICEL

CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 14.1 min (major), 21.7 min (minor).

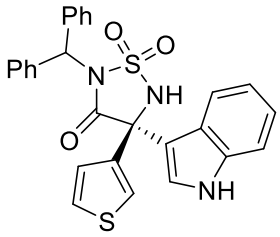
(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-4-(naphthalen-2-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4m)



Reaction of **3e** (10.0 mg, 0.01 mmol), **1m** (21.3 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at r.t. for 120 h gave **4m** (20.8 mg, 77%, 91% ee).

$[\alpha]_D^{25}$ +8.8 (c 0.56, EtOH); m.p. 232.3-233.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.44 (s, 1H), 6.41 (s, 1H), 6.90-6.95 (m, 2H), 7.13-7.32 (m, 11H), 7.42-7.46 (m, 2H), 7.50-7.54 (m, 2H), 7.70-7.74 (m, 1H), 7.79-7.86 (m, 3H), 8.21-8.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.8, 70.6, 111.9, 114.2, 119.1, 121.0, 123.3, 124.0, 124.8, 125.8, 126.6, 126.7, 127.0, 127.7, 128.3, 128.5, 128.6, 128.9, 129.6, 133.0, 133.4, 133.9, 136.0, 136.1, 136.8, 168.1; IR (ATR) 3448, 3279, 1728, 1382, 1329, 1269, 1187, 1104, 1058, 936, 903, 826, 794, 750, 707, 649 cm^{-1}; HRMS (ESI, positive) m/z for $C_{33}H_{25}N_3NaO_3S$ $[M+Na]^+$ calcd. 566.1514, found 566.1493; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 13.4 min (major), 29.2 min (minor).

(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-4-(thiophen-3-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4n)

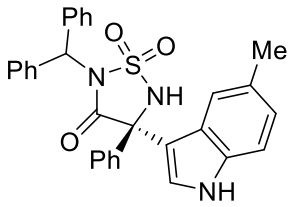


Reaction of **3e** (5.0 mg, 0.005 mmol), **1n** (19.1 mg, 0.05 mmol) and **2a** (8.8 mg, 0.075 mmol) in toluene (0.25 mL) at 0 ℃ for 120 h gave **4n** (22.7 mg, 91%, 97% ee).

$[\alpha]_D^{25}$ −85.1 (c 0.39, EtOH); m.p. 205.8-206.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.37 (s, 1H), 6.40 (s, 1H), 6.95-7.00 (m, 2H), 7.14-7.19 (m, 3H), 7.24-7.35 (m, 10H), 7.42-7.46 (m, 2H), 7.61-7.63 (m, 1H), 8.20 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.7, 68.5, 111.9, 113.5, 118.9, 121.0, 123.3, 123.9, 124.9, 125.5, 126.8, 127.0, 128.3, 128.5, 128.6, 129.5, 135.8, 136.2, 136.8, 137.8, 167.8; IR (ATR) 3414, 3343, 1739, 1495, 1452, 1377, 1325, 1249, 1175, 1081, 1025, 908, 847, 786, 736, 697.1 cm^{-1}; HRMS (ESI,

positive) m/z for $C_{27}H_{21}N_3NaO_3S_2$ $[M+Na]^+$ calcd. 522.0922, found 522.0941; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 11.7 min (major), 15.7 min (minor).

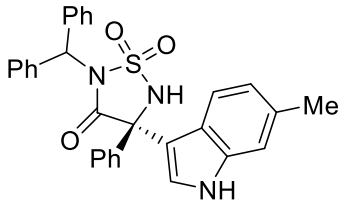
(*R*)-2-Benzhydryl-4-(5-methyl-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (5)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1c** (18.8 mg, 0.05 mmol) and **2b** (9.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 ℃ for 96 h gave **5** (25.2 mg, 99%, 96% ee).

$[\alpha]_D^{25}$ −29.5 (c 0.77, EtOH); m.p. 208.1-208.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.25 (s, 3H), 5.37 (s, 1H), 6.38 (s, 1H), 6.76 (s, 1H), 6.95-6.98 (m, 2H), 7.13-7.46 (m, 14H), 7.71-7.74 (m, 2H), 8.11(s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 63.6, 70.6, 111.7, 113.7, 118.4, 124.1, 124.9, 125.9, 127.3, 128.2, 128.5, 128.6, 128.7, 129.0, 129.6, 130.5, 135.1, 136.1, 136.3, 136.4, 168.4; IR (ATR) 3417, 3352, 1752, 1723, 1495, 1448, 1326, 1290, 1248, 1182, 1116, 1029, 822, 798, 765, 696 cm^{-1}; HRMS (ESI, positive) m/z for $C_{30}H_{25}N_3NaO_3S$ $[M+Na]^+$ calcd. 530.1514, found 530.1519.; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 9.2 min (major), 12.6 min (minor).

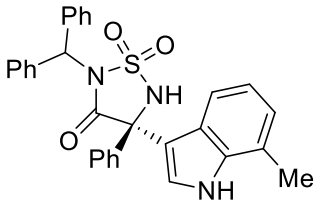
(*R*)-2-Benzhydryl-4-(6-methyl-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (6)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1c** (18.8 mg, 0.05 mmol) and **2c** (9.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 ℃ for 96 h gave **6** (25.0 mg, 98%, 93% ee).

$[\alpha]_D^{25}$ +16.2 (c 0.48, EtOH); m.p. 204.5-205.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 5.34 (s, 1H), 6.38 (s, 1H), 6.74-6.78 (m, 2H), 6.99-7.02 (m, 2H), 7.22-7.44 (m, 13H), 7.67-7.71 (m, 2H), 8.08 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7, 62.8, 70.6, 111.8, 114.0, 118.7, 121.8, 122.6, 125.0, 127.3, 128.3, 128.5, 128.6, 129.0, 129.5, 133.2, 136.0, 136.2, 136.6, 137.3, 168.3; IR (ATR) 3343, 3281, 1714, 1449, 1386, 1339, 1318, 1286, 1179, 1025, 952, 907, 803, 763, 730, 696 cm^{-1}; HRMS (ESI, positive) m/z for $C_{30}H_{25}N_3NaO_3S$ $[M+Na]^+$ calcd. 530.1514, found 530.1516.; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 13.5 min (major), 24.2 min (minor).

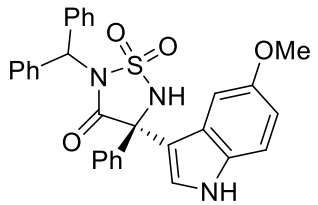
(*R*)-2-Benzhydryl-4-(7-methyl-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (7)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1c** (18.8 mg, 0.05 mmol) and **2d** (9.8 mg, 0.075 mmol) in toluene (0.25 mL) at −10 ℃ for 96 h gave **7** (24.6 mg, 97%, 97% ee).

$[\alpha]_D^{25}$ +11.1 (c 0.55, EtOH); m.p. 135.1-135.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.25 (s, 3H), 5.38 (s, 1H), 6.39 (s, 1H), 6.78-6.97 (m, 4H), 7.22-7.45 (m, 13H), 7.68-7.71 (m, 2H), 8.17 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.5, 62.7, 70.6, 114.5, 116.5, 121.2, 121.3, 123.4, 125.6, 127.2, 128.3, 128.5, 128.6, 128.7, 129.0, 129.6, 135.9, 136.1, 136.4, 168.5; IR (ATR) 3340, 3281, 1721, 1495, 1447, 3174, 1345, 1321, 1280, 1241, 1179, 1111, 1026, 908, 728, 697 cm^{-1}; HRMS (ESI, positive) m/z for $C_{30}H_{25}N_3NaO_3S$ $[M+Na]^+$ calcd. 530.1514, found 530.1508; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 10.5 min (major), 15.5 min (minor).

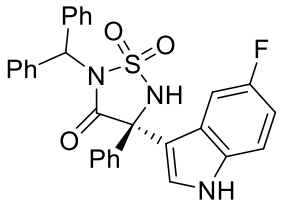
(*R*)-2-Benzhydryl-4-(5-methoxy-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (8)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1c** (18.8 mg, 0.05 mmol) and **2e** (11.0 mg, 0.075 mmol) in toluene (0.25 mL) at −20 ℃ for 48 h gave **8** (25.8 mg, 99%, 98% ee).

$[\alpha]_D^{25}$ −52.3 (c 0.70, EtOH); m.p. 122.2-122.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.49 (s, 3H), 5.41 (s, 1H), 6.36 (s, 1H), 6.63 (s, 1H), 6.77-6.84 (m, 2H), 7.12-7.45 (m, 14H), 7.70-7.73 (m, 2H), 8.15 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.6, 62.6, 70.7, 100.2, 112.8, 113.8, 124.5, 126.2, 127.4, 128.2, 128.5, 128.6, 128.7, 129.0, 129.5, 131.7, 136.0, 126.3, 126.5, 154.8, 168.2; IR (ATR) 3410, 3293, 1726, 1586, 1486, 1449, 1383, 1330, 1265, 1218, 1175, 1078, 1027, 911, 803, 768, 729, 695 cm^{-1}; HRMS (ESI, positive) m/z for $C_{30}H_{25}N_3NaO_4S$ $[M+Na]^+$ calcd. 546.1463, found 546.1457; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 11.3 min (major), 16.8 min (minor).

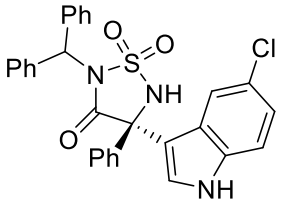
(*R*)-2-Benzhydryl-4-(5-fluoro-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (9)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1c** (18.8 mg, 0.05 mmol) and **2f** (10.1 mg, 0.075 mmol) in toluene (0.25 mL) at 0 ℃ for 168 h gave **9** (22.9 mg, 90%, 95% ee).

$[\alpha]_D^{25}$ +25.7 (c 0.39, EtOH); m.p. 137.6-138.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.30 (s, 1H), 6.40 (s, 1H), 6.79-6.94 (m, 2H), 7.10 (s, 1H), 7.19-7.39 (m, 14H), 7.63-7.66 (m, 2H), 8.27 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.9, 70.4, 104.8 (d, $J_{C\text{-}F}$ = 25.5 Hz), 111.9 (d, $J_{C\text{-}F}$ = 26.3 Hz), 112.6, 114.2 (d, $J_{C\text{-}F}$ = 5.0 Hz), 124.5, 124.6, 127.0, 127.3, 128.4, 128.6, 128.7, 128.9, 129.2, 129.3, 133.3, 135.8, 136.1, 136.4, 158.1 (d, $J_{C\text{-}F}$ = 236.3 Hz), 168.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ −121.8; IR (ATR) 3410, 3288, 1720, 1584, 1487, 1450, 1384, 1329, 1267, 1107, 1027, 908, 846, 803, 730, 623 cm^{-1}; HRMS (ESI, positive) m/z for $C_{29}H_{22}FN_3NaO_3S$ $[M+Na]^+$ calcd. 534.1264, found 534.1273; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 90:10, 1.0 mL/min, 254 nm), tR = 25.0 min (major), 38.9 min (minor).

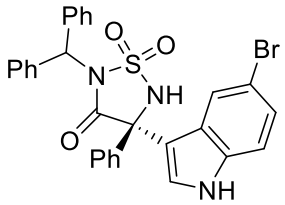
(*R*)-2-Benzhydryl-4-(5-chloro-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (10)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1c** (18.8 mg, 0.05 mmol) and **2g** (15.2 mg, 0.10 mmol) in toluene (0.25 mL) at 0 ℃ for 168 h gave **10** (22.7 mg, 86%, 93% ee).

$[\alpha]_D^{25}$ +11.7 (c 0.52, EtOH); m.p. 133.8-134.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.25 (br, 1H), 6.39 (s, 1H), 6.97 (s, 1H), 7.06-7.50 (m, 16H), 7.60-7.63 (m, 2H), 8.31 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.9, 70.3, 112.9, 113.6, 118.9, 123.7, 125.1, 126.7, 126.8, 127.3 ,128.4, 128.6, 128.7, 128.9, 129.2, 129.3, 135.2, 135.8, 136.2, 136.4, 168.2; IR (ATR) 3411, 3300, 1724, 1295, 1449, 1329, 1268, 1176, 1109, 1028, 894, 800, 695, 649 cm^{-1}; HRMS (ESI, positive) m/z for $C_{29}H_{22}ClN_3NaO_3S$ $[M+Na]^+$ calcd. 550.0968, found 550.0960; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 90:10, 1.0 mL/min, 254 nm), tR = 21.1 min (major), 33.8 min (minor).

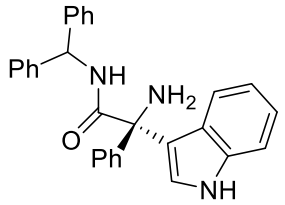
(*R*)-2-Benzhydryl-4-(5-bromo-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (11)



Reaction of **3e** (5.0 mg, 0.005 mmol), **1c** (18.8 mg, 0.05 mmol) and **2h** (19.6 mg, 0.10 mmol) in toluene (0.25 mL) at 0 ℃ for 168 h gave **11** (22.8 mg, 80%, 94% ee).

$[\alpha]_D^{25}$ −50.6 (c 0.42, EtOH); m.p. 124.0-126.3 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.33 (s, 1H), 6.39 (s, 1H), 6.99 (s, 1H), 7.08-7.11 (m, 1H), 7.20-7.39 (m, 15H), 7.60-7.63 (m, 2H), 8.31 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.8, 70.2, 113.2, 113.4, 114.2, 121.8, 125.7, 126.2, 126.5, 127.1, 128.3, 128.5, 128.6, 128.9, 129.1, 129.2, 135.4, 135.7, 136.1, 136.3, 169.1; IR (ATR) 3412, 3294, 1721, 1449, 1328, 1269, 1176, 1106, 1028, 907, 885, 799, 731, 695, 622 cm^{-1}; HRMS (ESI, positive) m/z for $C_{29}H_{22}BrN_3NaO_3S$ $[M+Na]^+$ calcd. 594.0463, found 594.0461; HPLC (DAICEL CHIRALPAK IG®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 7.6 min (major), 10.9 min (minor).

(*R*)-2-Amino-*N*-benzhydryl-2-(1*H*-indol-3-yl)-2-phenylacetamide (13)[4)]

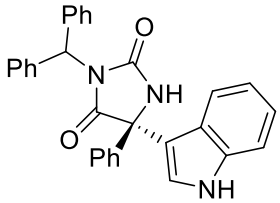


A solution of **4c** (300 mg, 0.608 mmol) in THF (0.9 mL) was dropwised to the solution of lithium aluminium hydride (69.1 mg, 1.82 mmol) in THF (0.3 mL) at 0 ℃. Then the reaction mixture was stirred 12 h at 70 ℃. The mixture was cooled to 0 ℃, H_2O and 15% NaOH aq. were added. Then, aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (hexane:ethyl acetate = 30:70) to afford (*R*)-2-Amino-*N*-benzhydryl-2-(1*H*-indol-3-yl)-2-phenylacetamide (232.4 mg, 89%, 97% ee).

$[\alpha]_D^{25}$ −29.7 (c 0.50, EtOH); m.p. 163.1-163.7 ℃; ^{1}H NMR (300 MHz, CD_3OD) δ 6.17 (s, 1H), 6.86-6.89 (m, 1H), 7.03-7.11 (m, 4H), 7.14-7.16 (m, 3H), 7.18-7.31 (m, 9H), 7.35-7.38 (m, 1H), 7.46-7.49

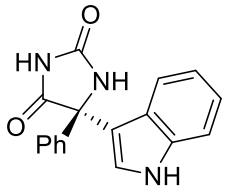
(m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 58.6, 65.5, 112.6, 119.4, 120.1, 121.6, 122.7, 125.6, 128.3, 128.4, 128.5, 129.2, 129.5, 129.6, 138.8, 142.9, 145.4, 175.9; IR (ATR) 3391, 3352, 3281, 1661, 1587, 1489, 1446, 1342, 1243, 1117, 1928, 936, 868, 819, 755, 741, 697 cm^{-1}; HRMS (ESI, positive) m/z for $C_{29}H_{25}N_3NaO$ $[M+Na]^+$ calcd. 454.1895, found 454.1888; HPLC (of its *N*-Boc protected derivative, DAICEL CHIRALPAK ID®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 10.5 min (minor), 29.6 min (major).

(*R*)-3-Benzhydryl-5-(1*H*-indol-3-yl)-5-phenylimidazolidine-2,4-dione (14)[4)]



To a solution of **13** (30 mg, 0.07 mmol) in dry THF, triphosgene (20.8 mg, 0.07 mmol) was added at 0 ℃ slowly, then triethylamine (49 μL, 0.35 mmol) was added dropwise. The mixture was stirred for 18 h, then H_2O was added, and aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (hexane:ethyl acetate = 60:40) to afford (*R*)-3-Benzhydryl-5-(1*H*-indol-3-yl)-5-phenylimidazolidine-2,4-dione (24.1 mg, 75%, 97% ee).
$[\alpha]_D^{25}$ −58.7 (c 0.33, EtOH); m.p. 235.3-236.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32 (s, 1H), 6.58 (s, 1H), 6.86-6.92 (m, 3H), 7.11-7.19 (m, 1H), 7.25-7.35 (m, 14H), 7.46-7.49 (m, 2H), 8.17 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 58.6, 66.3, 111.7, 114.6, 119.6, 120.5, 122.9, 123.8, 124.7, 126.7, 127.8, 128.0, 128.5, 128.6, 128.7, 128.8, 136.9, 137.7, 138.0, 138.3, 156.4, 173.2; IR (ATR) 3318, 3222, 1619, 1495, 1449, 1415, 1362, 1335, 1247, 1119, 1076, 1029, 912, 871, 833, 741, 728, 647, 615 cm^{-1}; HRMS (ESI, positive) m/z for $C_{30}H_{23}N_3NaO_2$ $[M+Na]^+$ calcd. 480.1688, found 480.1672; HPLC (DAICEL CHIRALPAK ID-3®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 25.2 min (major), 33.7 min (minor).

(*R*)-5-(1*H*-indol-3-yl)-5-phenylimidazolidine-2,4-dione (15)

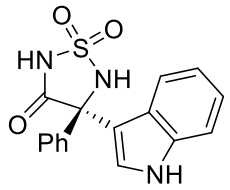


Pd/C (20 wt% on carbon, 6.9 mg) was added to a solution of **14** (32.0 mg, 0.07 mmol) in THF/methanol (0.35/0.35 mL). The reaction mixture was degassed in vacuo, placed under H_2 (balloon), stirred at 50 ℃

for 48 h. The mixture was filtered and washed with methanol, then the solvent was removed under reduced pressure to give the crude product, which was purified by silica gel column chromatography (hexane:ethyl acetate = 30:70) to afford (*R*)-5-(1*H*-indol-3-yl)-5-phenylimidazolidine-2,4-dione (18.5 mg, 91%, 97% ee)

$[\alpha]_D^{25}$ +37.5 (c 0.33, EtOH); m.p. 282.3-283.1 °C; ^{1}H NMR (300 MHz, CD_3OD) δ 6.91-6.94 (m, 1H), 7.03 (s, 1H), 7.09-7.12 (m, 1H), 7.20-7.22 (m, 1H), 7.36-7.39 (m, 4H), 7.54-7.56 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 69.4, 112.6, 115.3, 120.3, 120.7, 123.0, 125.6, 127.9, 129.3, 129.4, 138.7, 140.3, 158.9, 177.7; IR (ATR) 3140, 3054, 2924, 1698, 1456, 1389, 1233, 1199, 1013, 922, 763, 744, 696, 643 cm^{-1}; HRMS (ESI, negative) m/z for $C_{17}H_{11}N_3O_2$ $[M-H]^-$ calcd. 290.0930, found 290.0918; HPLC (DAICEL CHIRALPAK IA®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 254 nm), tR = 17.6 min (major), 19.8 min (minor).

(*R*)-4-(1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (16)



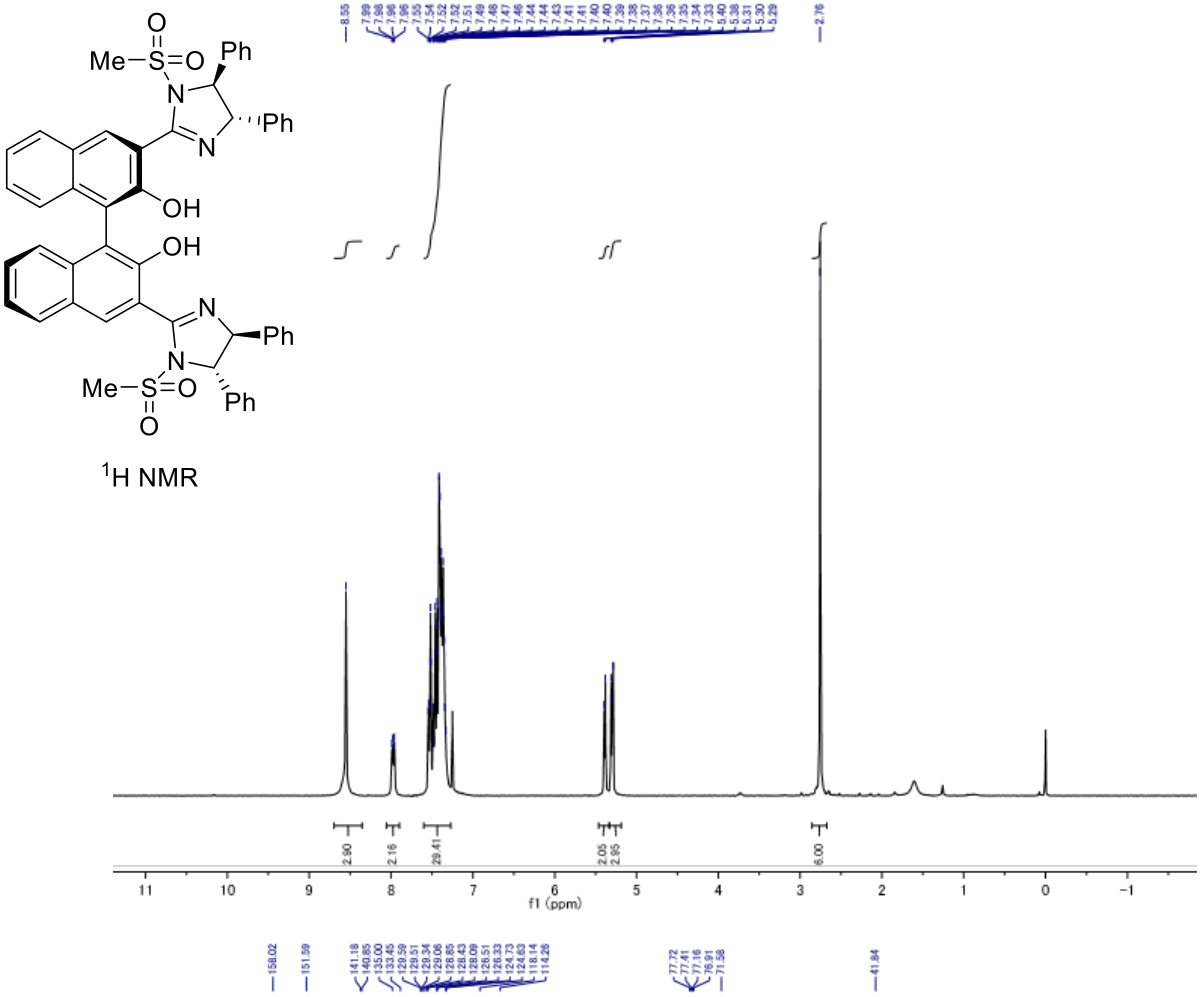
Pd/C (20 wt% on carbon, 9.9 mg) was added to a solution of **4c** (43.9 mg, 0.10 mmol) in THF/methanol (0.5/0.5 mL). The reaction mixture was degassed in vacuo, placed under H_2 (balloon), stirred at r.t. for 12 h. The mixture was filtered and washed with methanol, then the solvent was removed under reduced pressure to give the crude product, which was purified by silica gel column chromatography (ethyl acetate:methanol = 80:20) to afford (*R*)-4-(1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (31.2 mg, 95%, 97% ee)

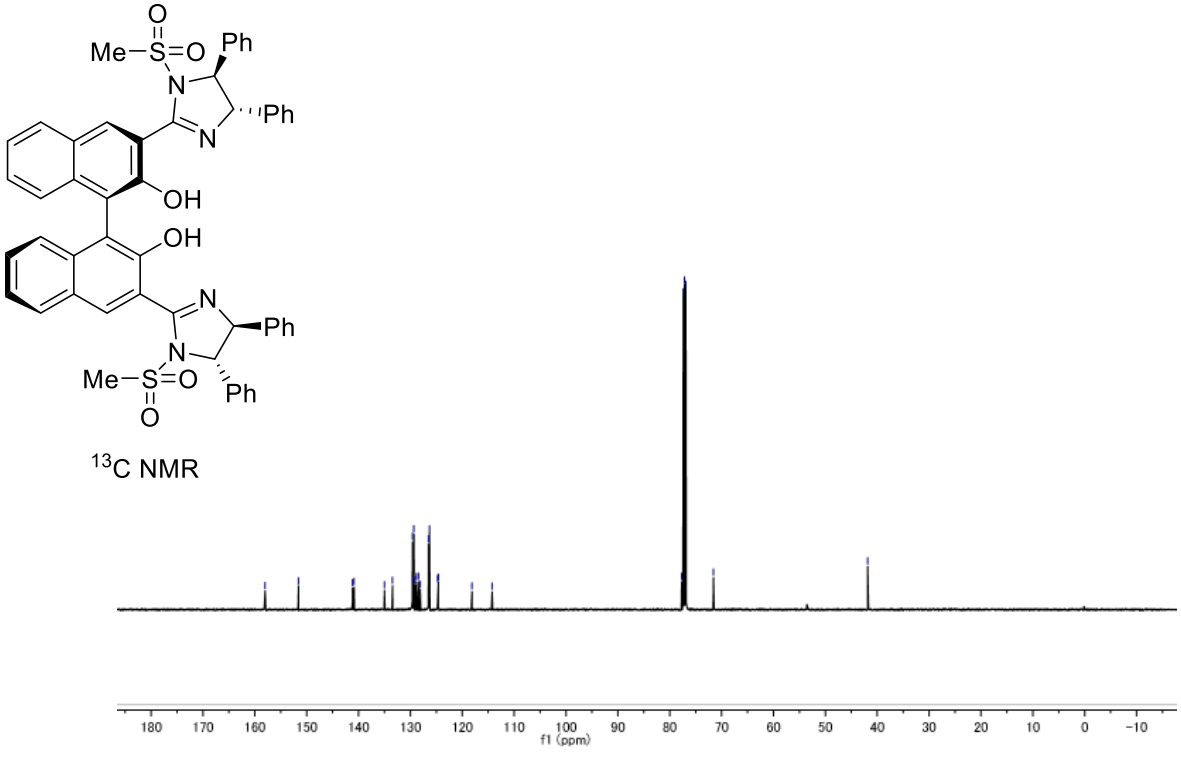
$[\alpha]_D^{25}$ +66.0 (c 0.79, EtOH); m.p. 255.6-256.4 °C; ^{1}H NMR (300 MHz, CD_3OD) δ 6.83-6.88 (m, 1H), 7.01-7.09 (m, 2H), 7.22-7.31 (m, 5H), 7.67-7.70 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 75.8, 112.4, 117.4, 120.1, 121.3, 122.7, 126.2, 126.7, 127.0, 128.4, 128.7, 128.8, 129.4, 129.9, 138.6, 142.7, 181.5; IR (ATR) 3410, 3321, 3059, 1619, 1454, 1330, 1265, 1246, 1145, 1112, 1047, 1030, 987, 915, 846, 741, 698, 544, 616 cm^{-1}; HRMS (ESI, negative) m/z for $C_{16}H_{12}N_3O_3S$ $[M-H]^-$ calcd. 326.0599, found 326.0606; HPLC (DAICEL CHIRALPAK AY-3®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 215 nm, 40 °C), tR = 22.3 min (major), 34.5 min (minor).

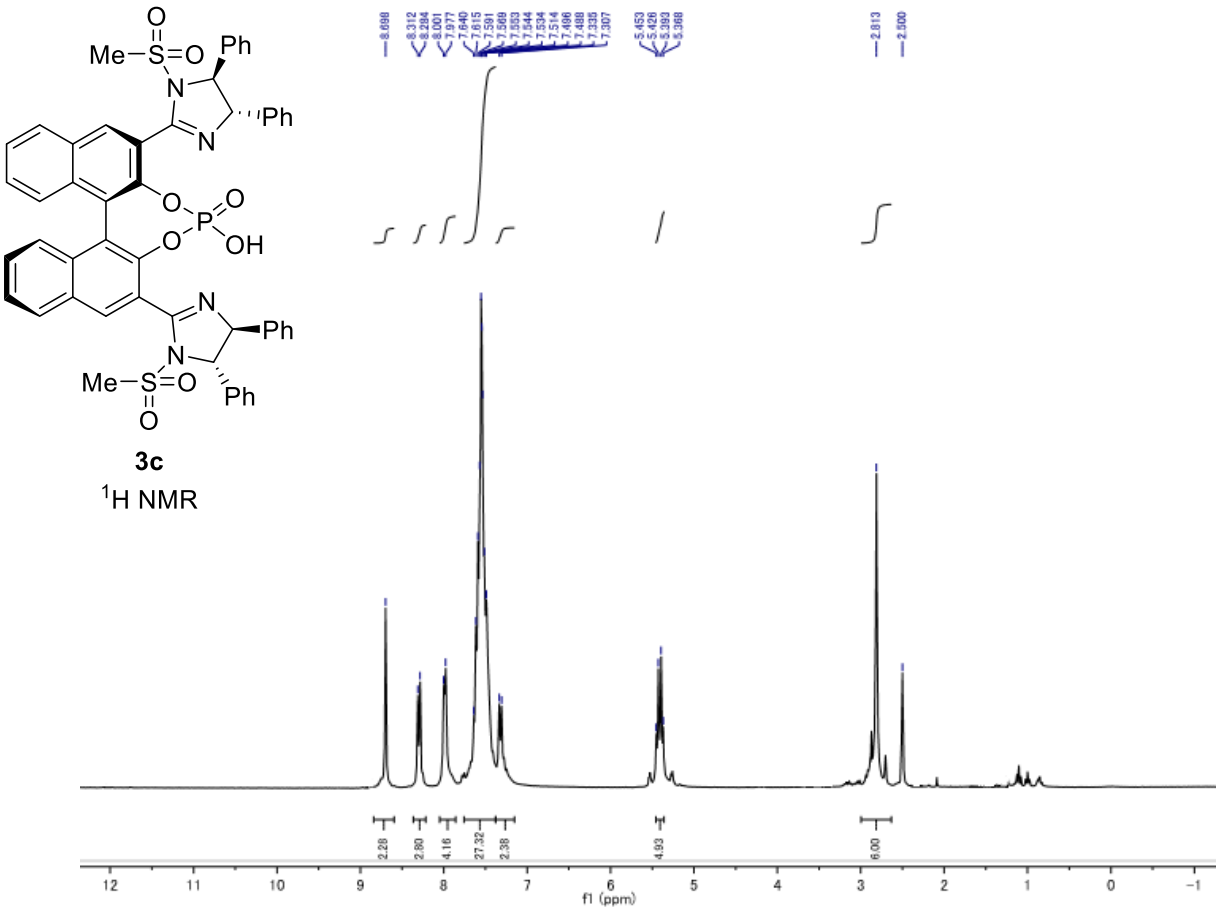
References

1. a) S. Nakamura, M. Ohara, M. Koyari, M. Hayashi, K. Hyodo, N. R. Nabisaheb, Y. Funahashi, *Org. Lett*. **2014**, *16*, 4452–4455. b) S. Nakamura, N. Matsuda. M. Ohara, *Chem. Eur. J.* **2016**, *22*, 9478−9482.
2. a) T. Nishimura, Y. Ebe, H. Fujimoto, T. Hayashi, *Chem. Commun.* **2013**, *49*, 5504−5506. b) Z.-H. Zhu, M.-L. Chen, G.-F. Jiang, *Org. Biomol. Chem*. **2017**, *15*, 1325–1328.
3. T. Takeda, M. Terada, *J. Am. Chem. Soc*. **2013**, *135*, 15306–15309.
4. Y. Li, Y.-N. Yu, M.-H. Xu, *ACS Catal*. **2016**, *6*, 661–665.

^{1}H NMR and ^{13}C NMR

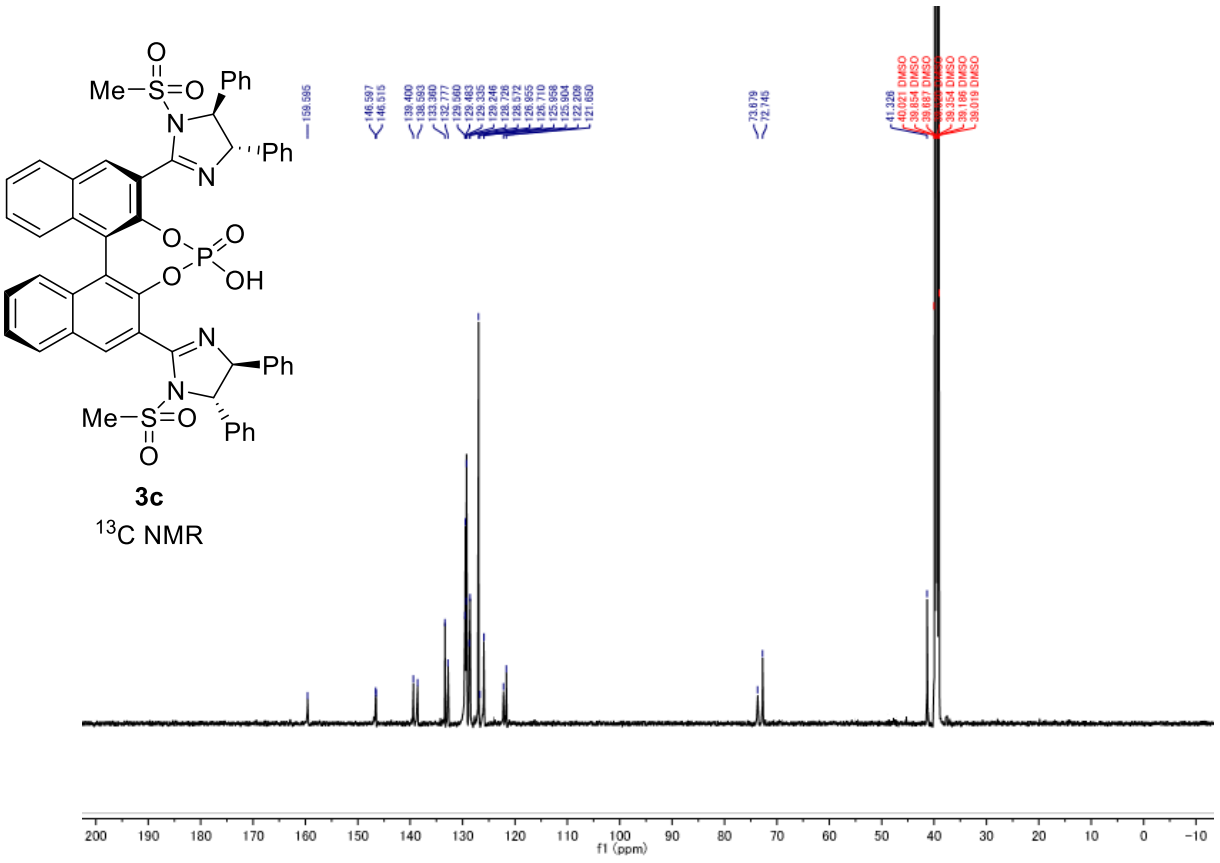






3c

^{1}H NMR



3c

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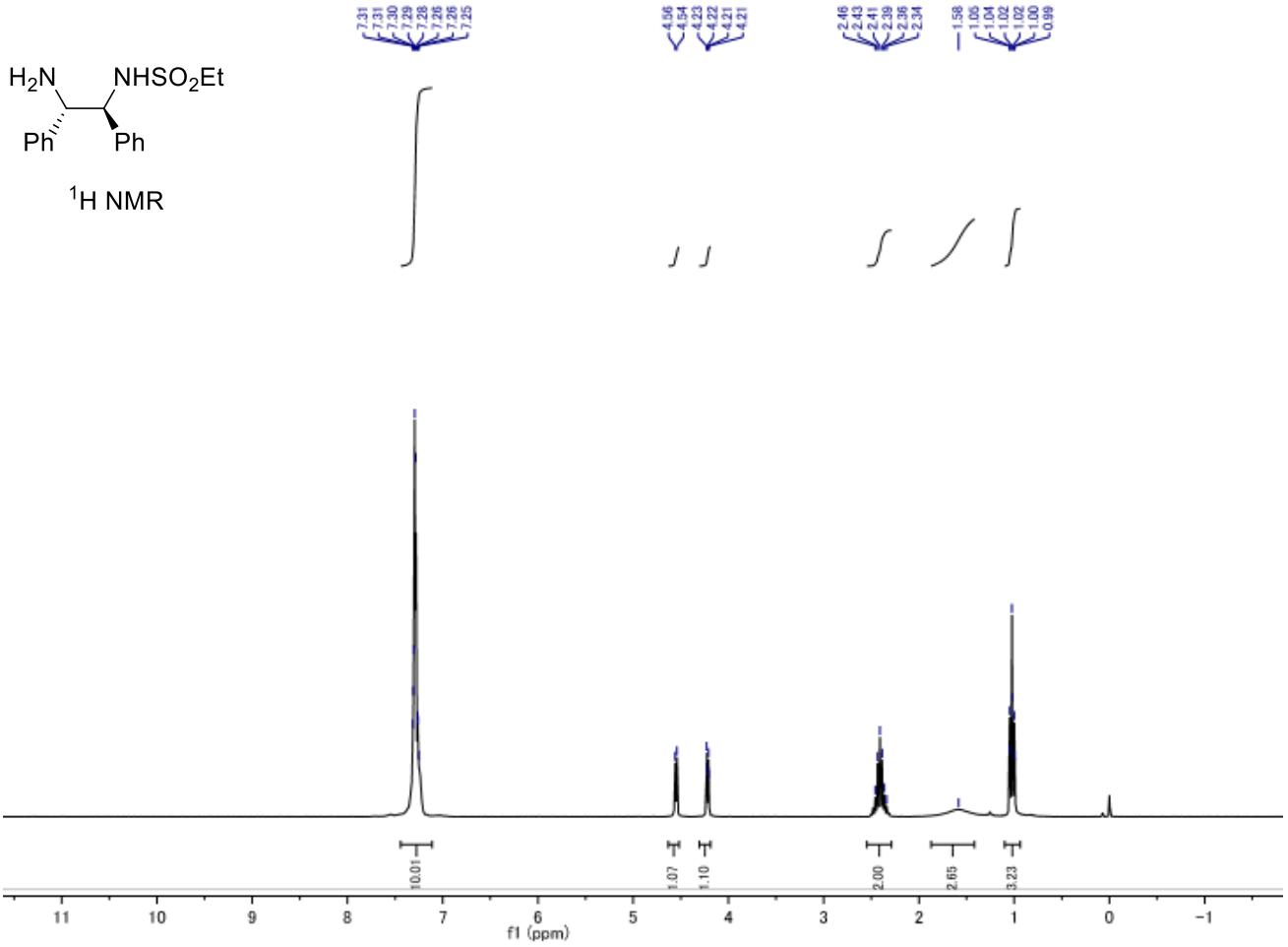
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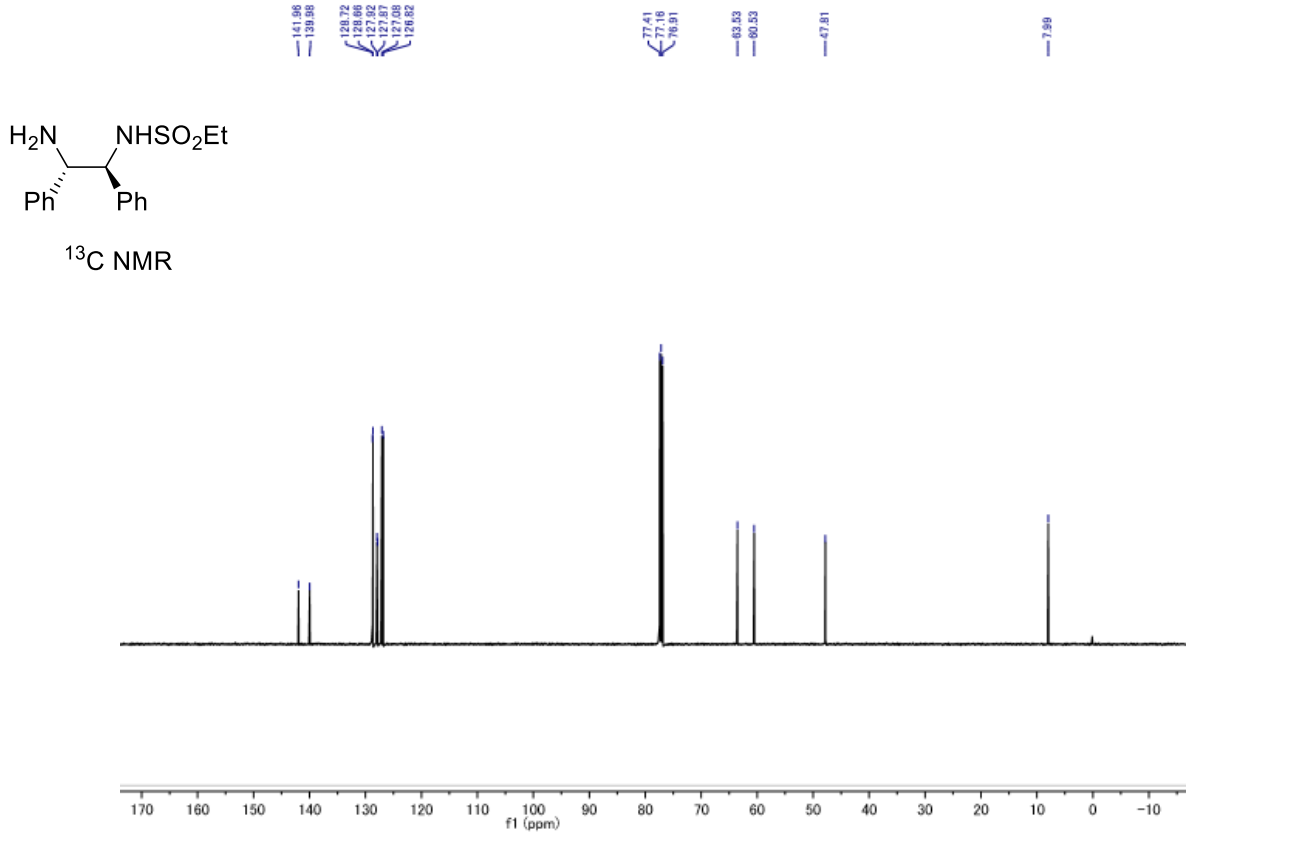
Ph
Ph
1H NMR
7.31
7.31
7.30
7.29
7.28
7.26
7.26
7.25
4.56
4.54
4.23
4.22
4.21
4.21
2.46
2.43
2.41
2.39
2.36
2.34
1.58
1.05
1.04
1.02
1.02
1.00
0.99
10.01
1.07
1.10
2.00
2.65
3.23
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)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Ph
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127.87
127.08
126.82
77.41
77.16
76.91
63.53
60.53
47.81
7.99
170
160
150
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110
100
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80
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60
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40
30
20
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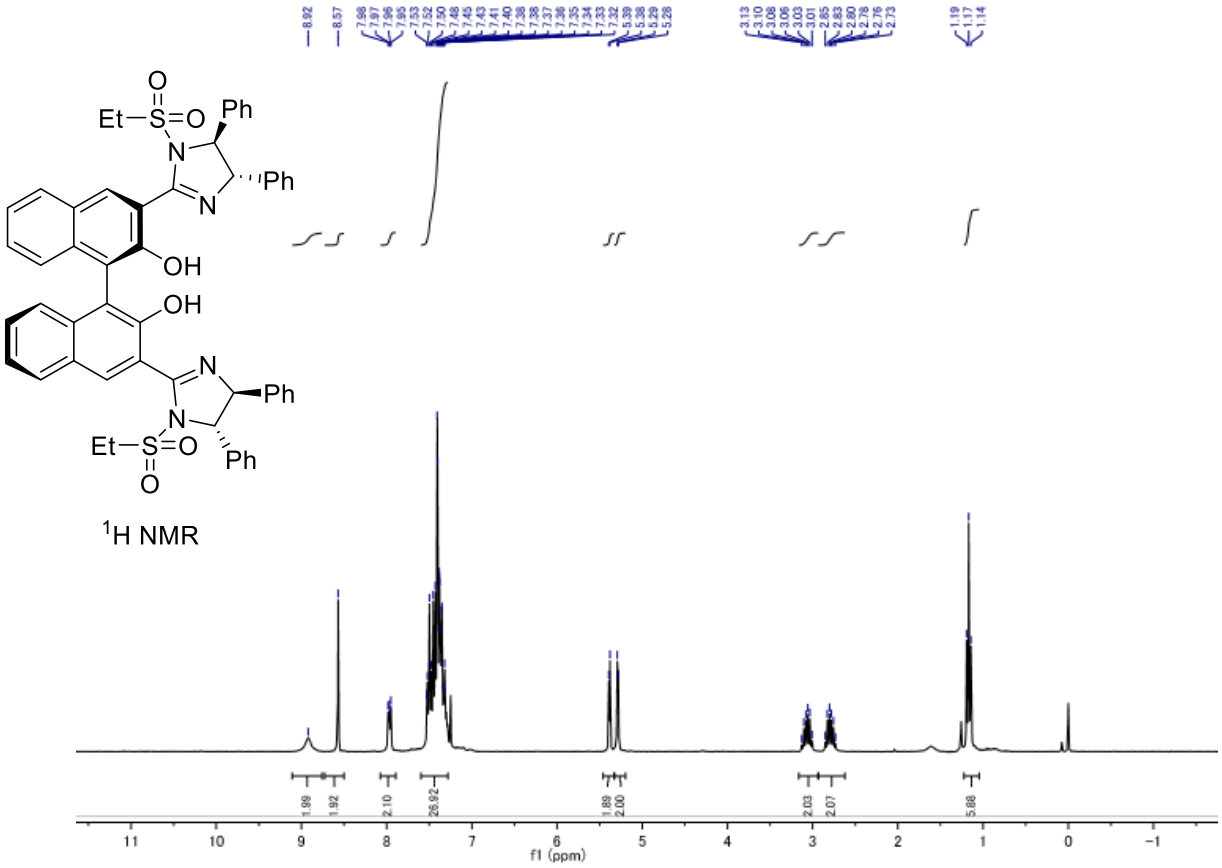
0
−10
f1 (ppm)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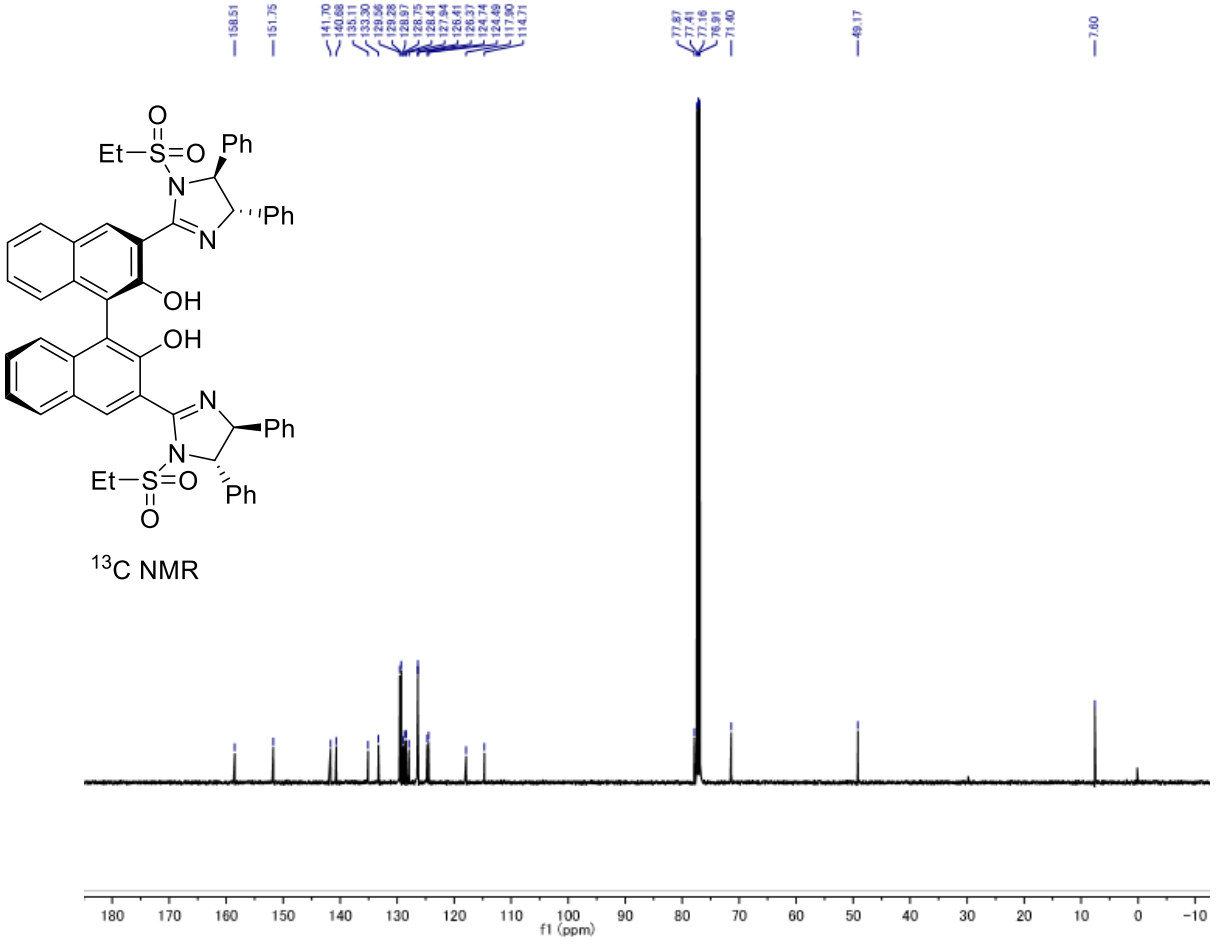
OH
OH
N
Ph
Et—S=O
Ph
O
1H NMR
f1 (ppm)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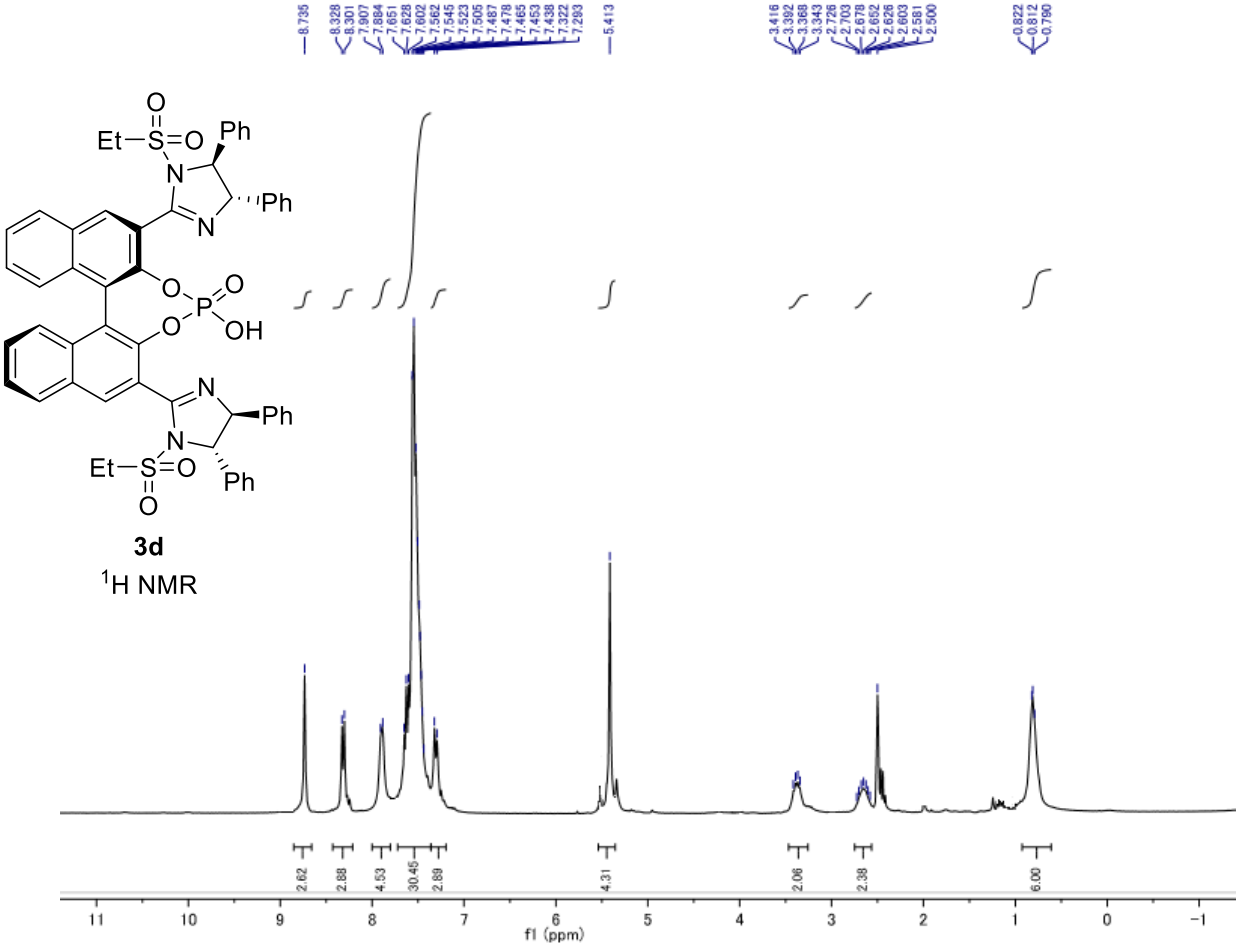
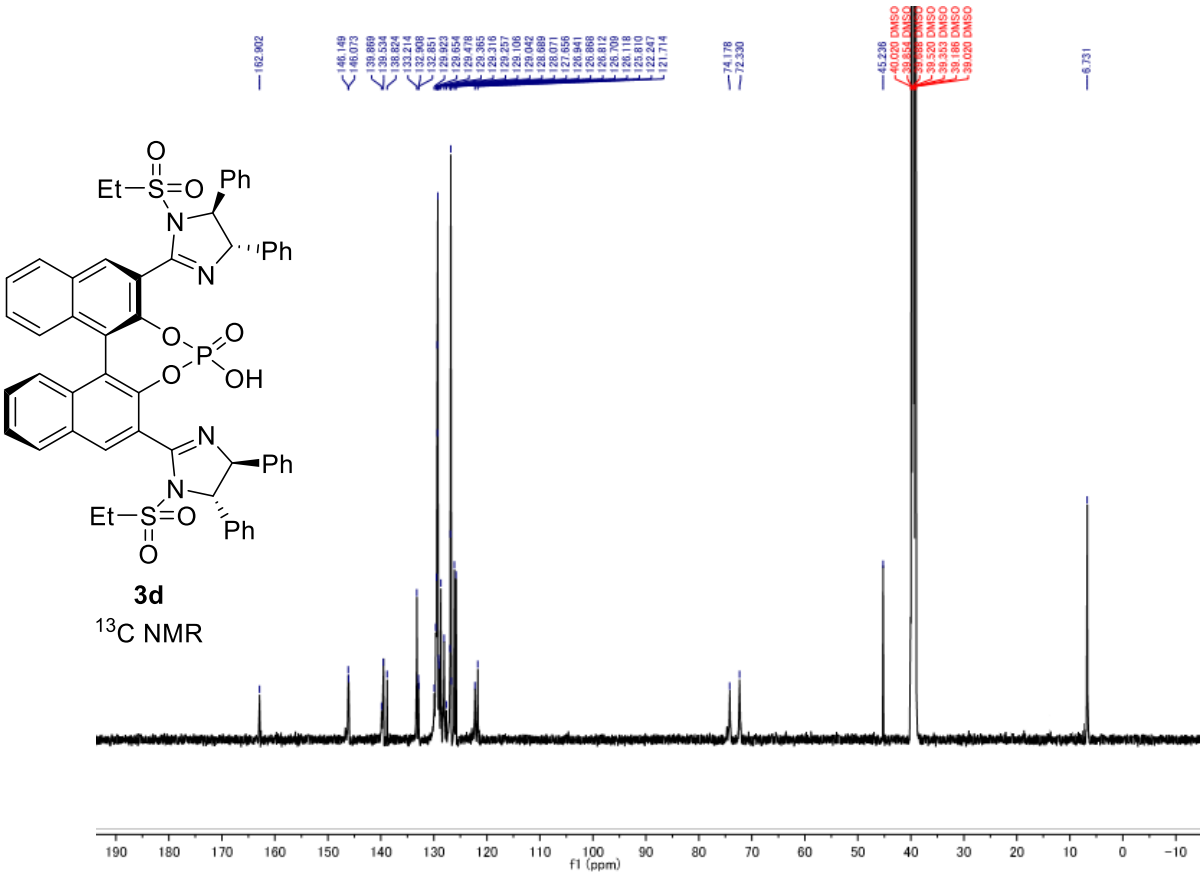
Ph
N
Ph
OH
OH
N
Ph
Et—S=O
Ph
O
13C NMR
f1 (ppm)


3d
1H NMR
f1 (ppm)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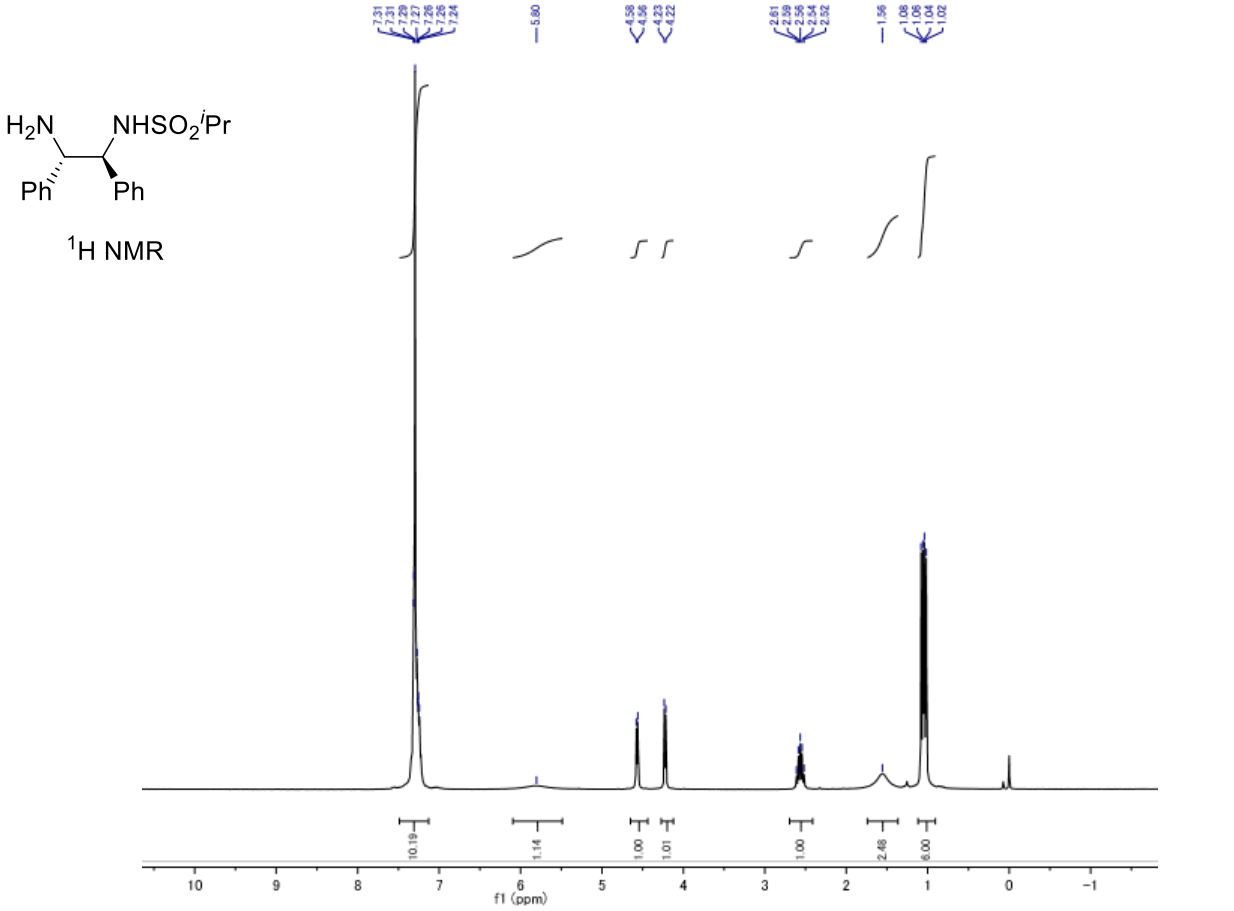
13C NMR
f1 (ppm)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Ph
Ph
^{1}H NMR
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7.31
7.29
7.27
7.26
7.26
7.24
5.80
4.58
4.56
4.23
4.22
2.61
2.59
2.56
2.54
2.52
1.56
1.06
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1.02
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1.14
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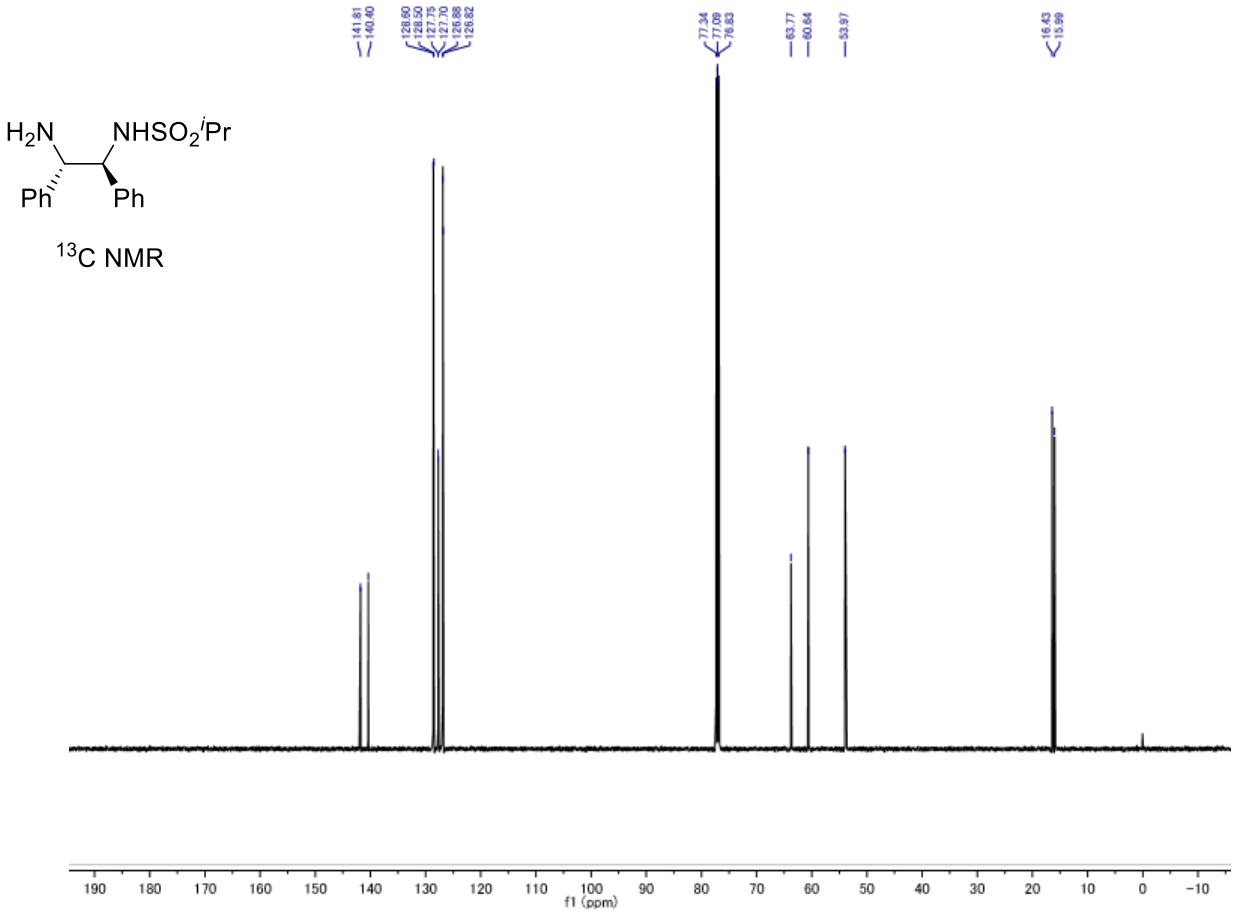
1.00
2.48
6.00
f1 (ppm)


H_2N
$NHSO_2{}^iPr$
Ph
Ph
^{13}C NMR
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140.40
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128.50
127.75
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60.64
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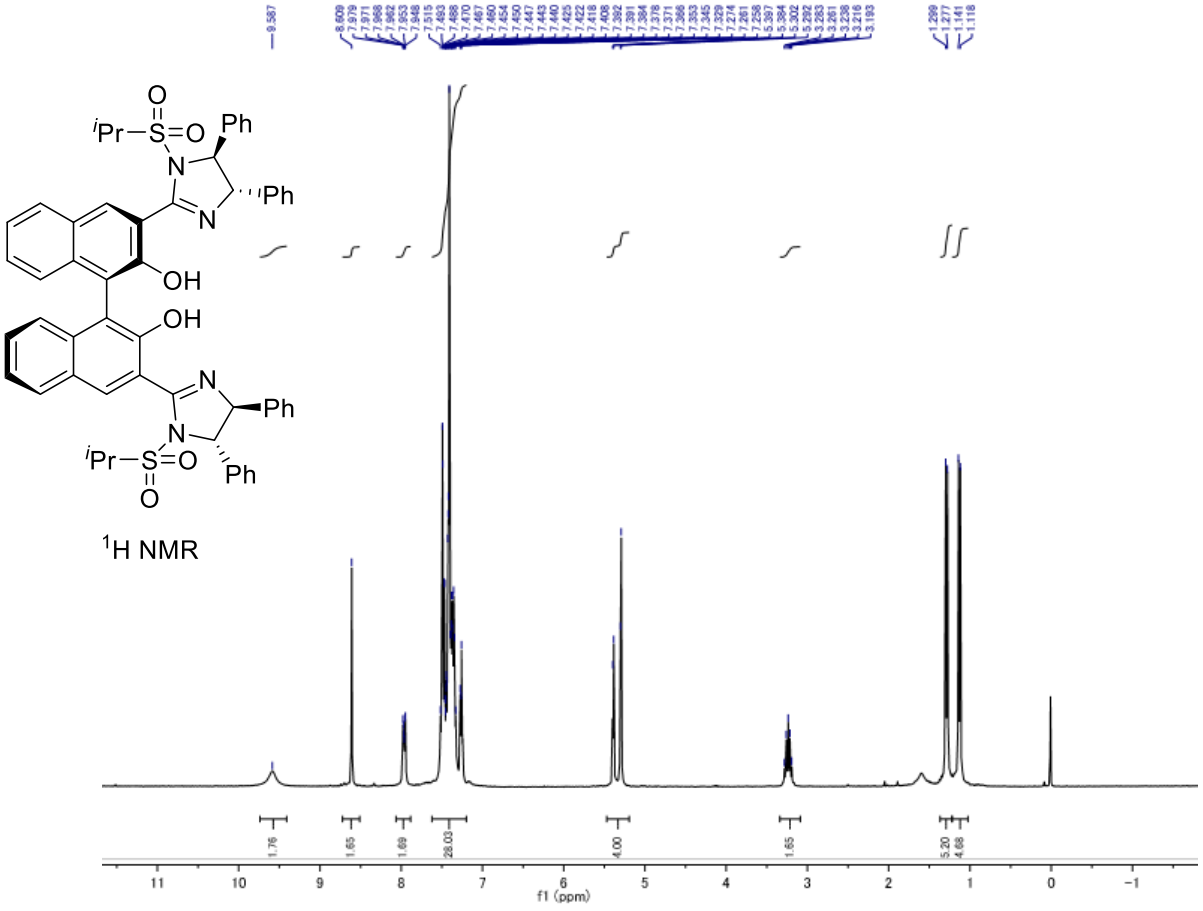
15.99
f1 (ppm)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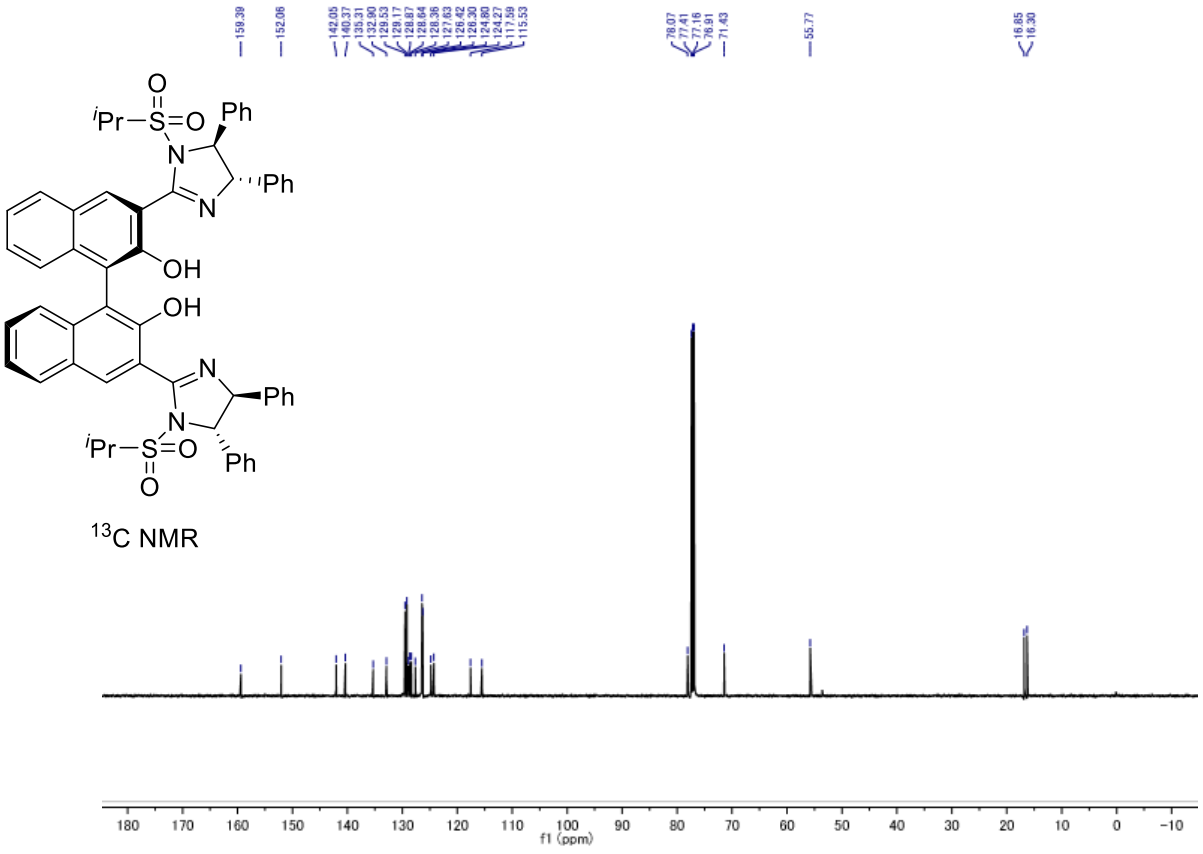
S
O
Ph
N
OH
^{i}Ph
^{1}H NMR
f1 (ppm)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O
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N
OH
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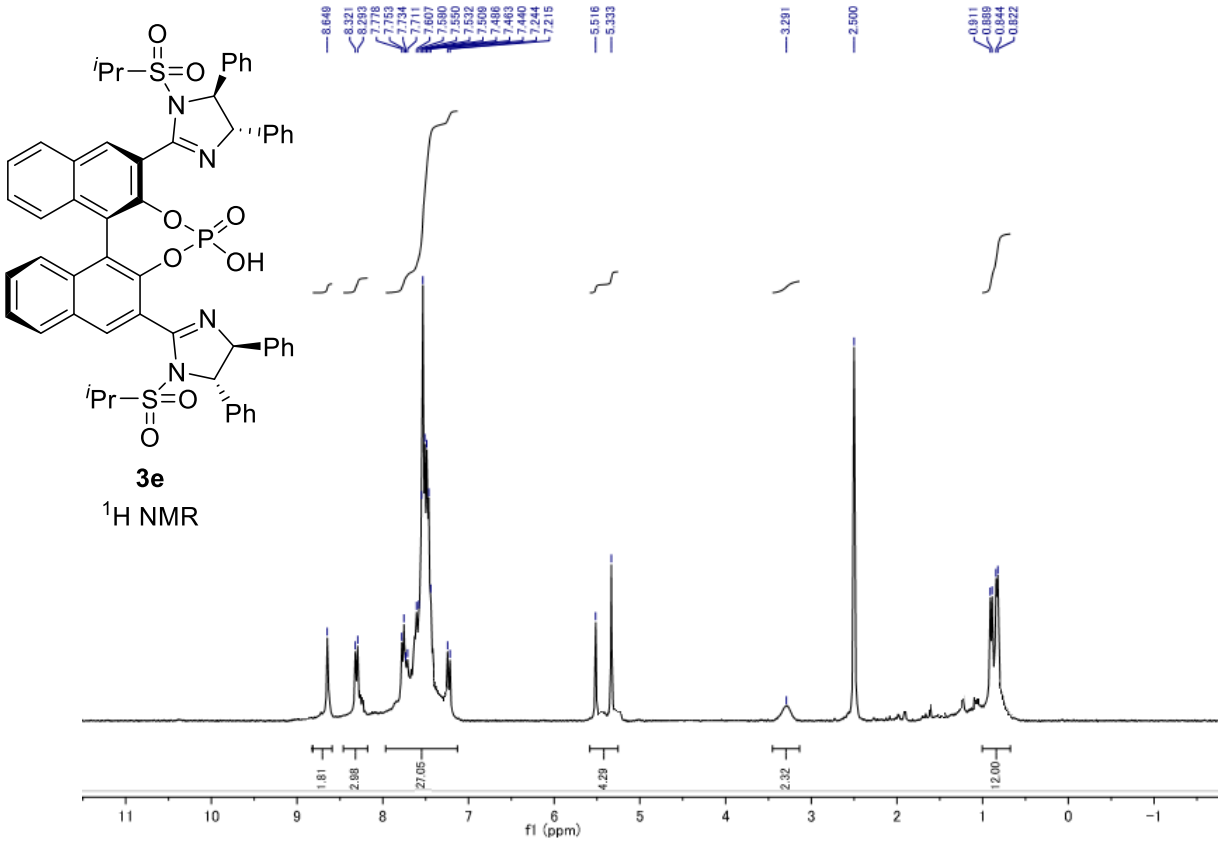
f1 (ppm)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1H NMR
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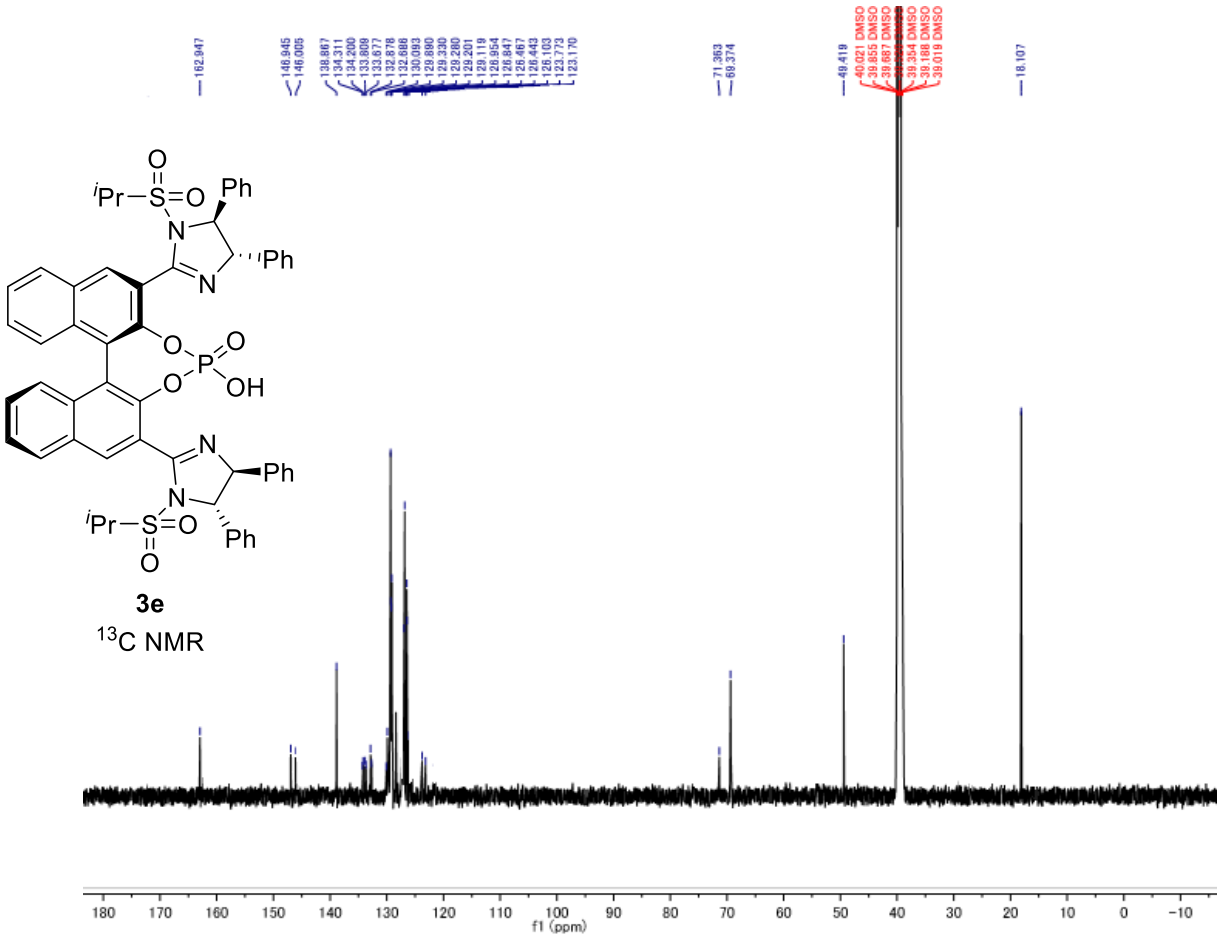
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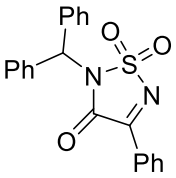
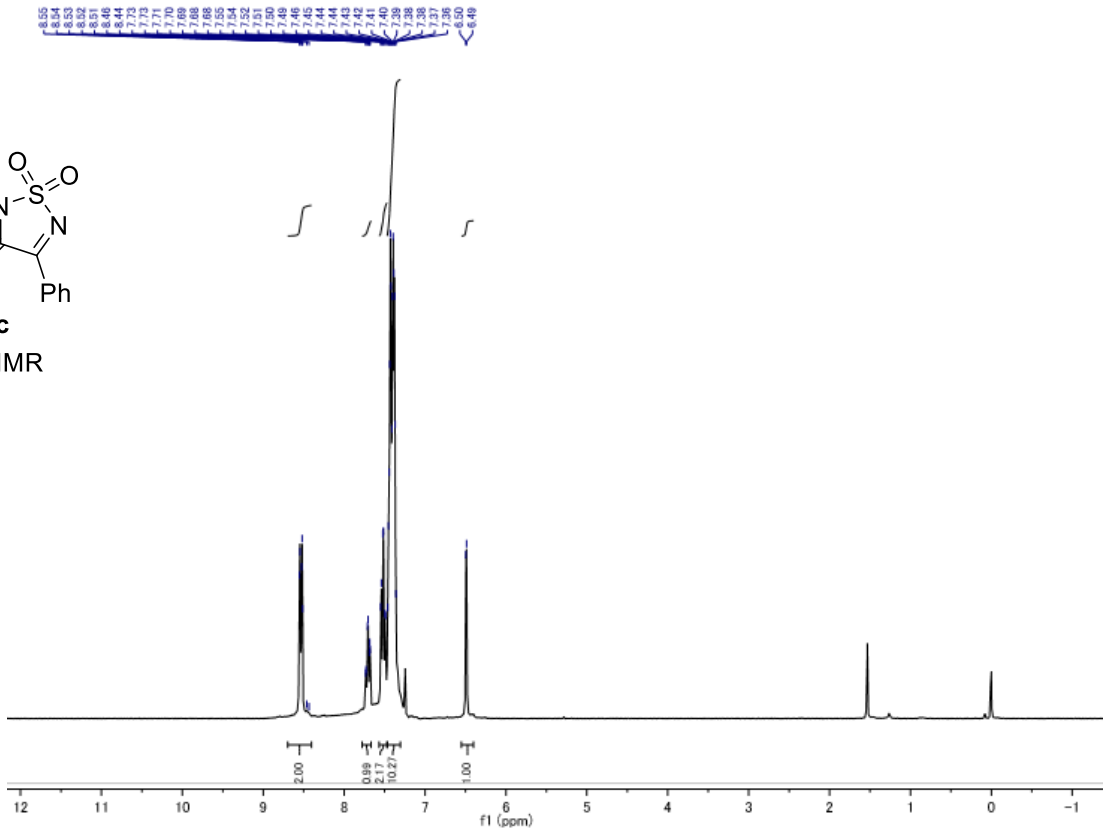
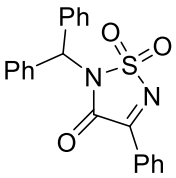
13C NMR
f1 (ppm)



1c

^{1}H NMR





1c

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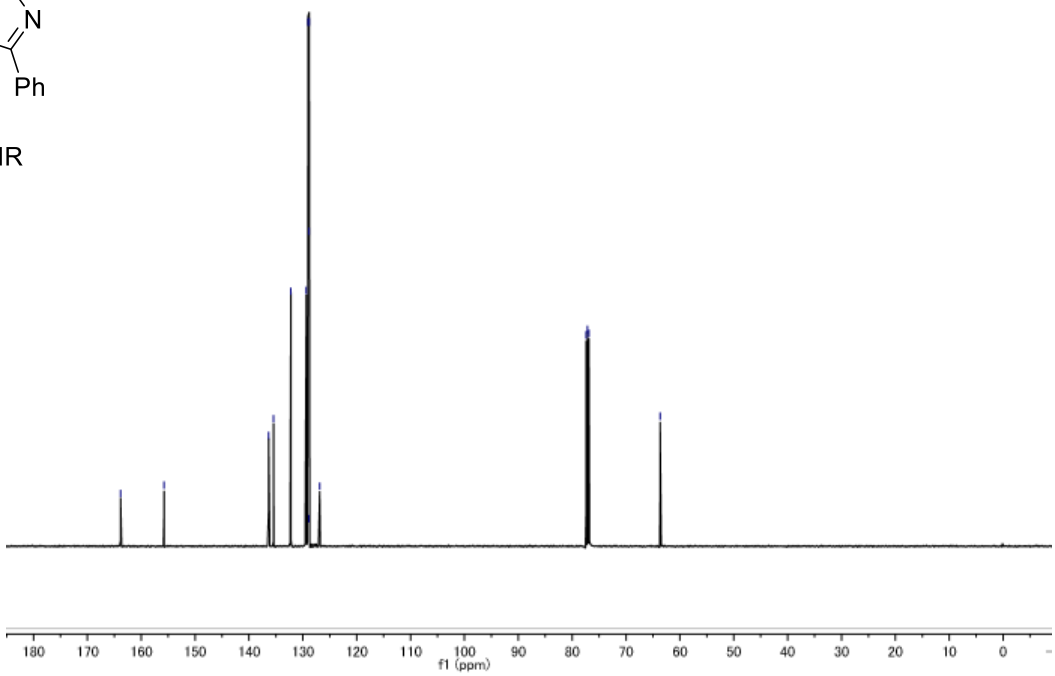

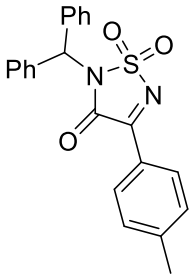

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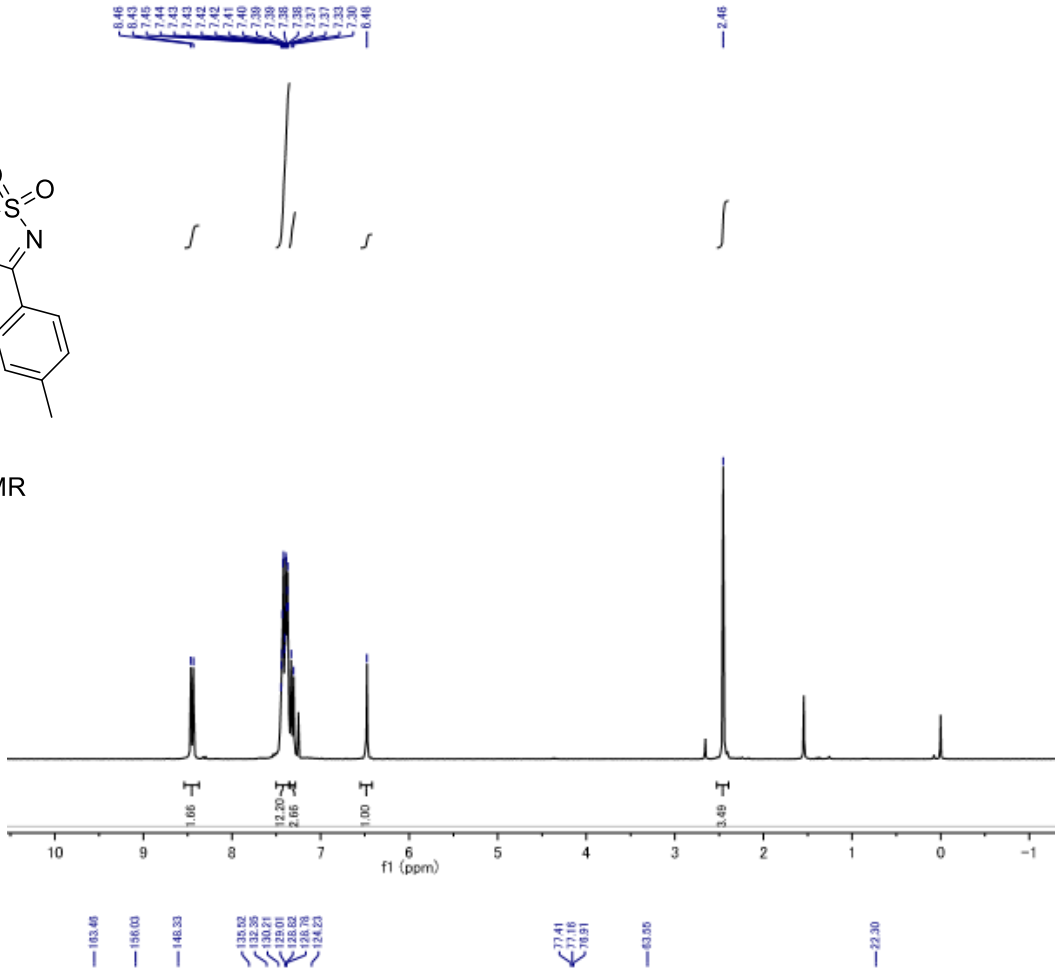
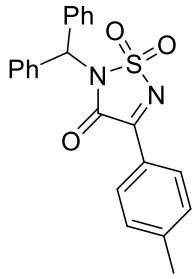
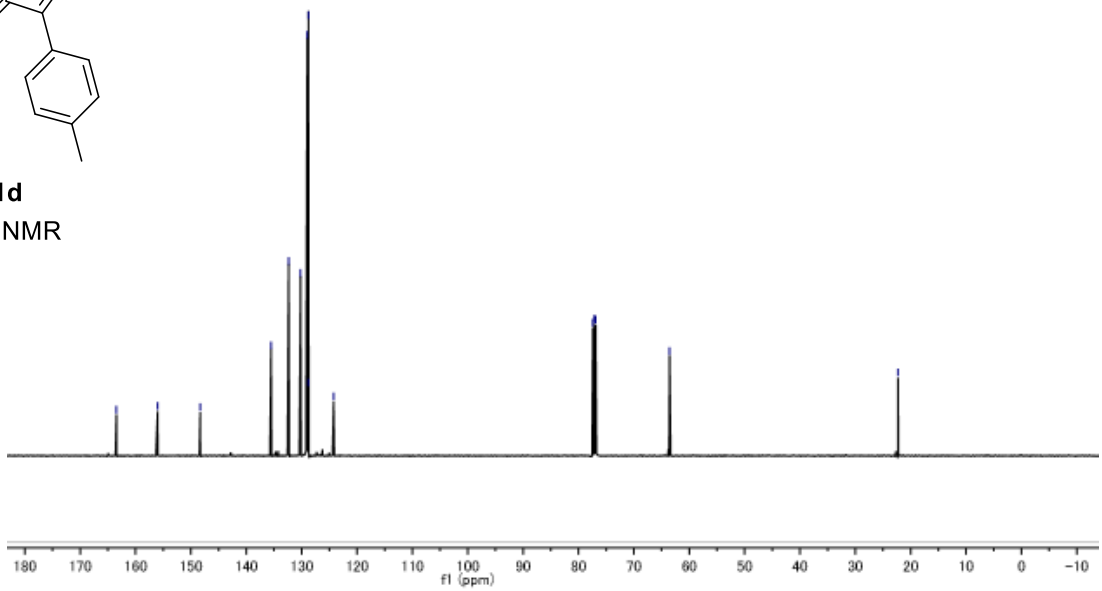
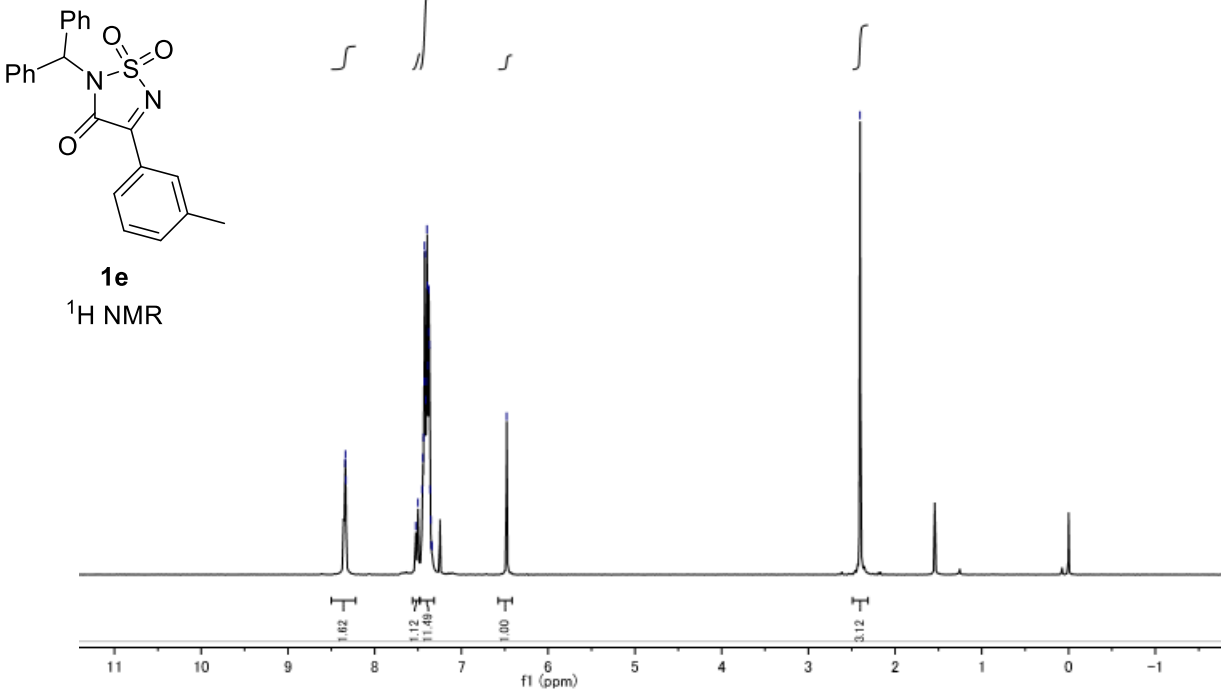




1d

^{13}C NMR





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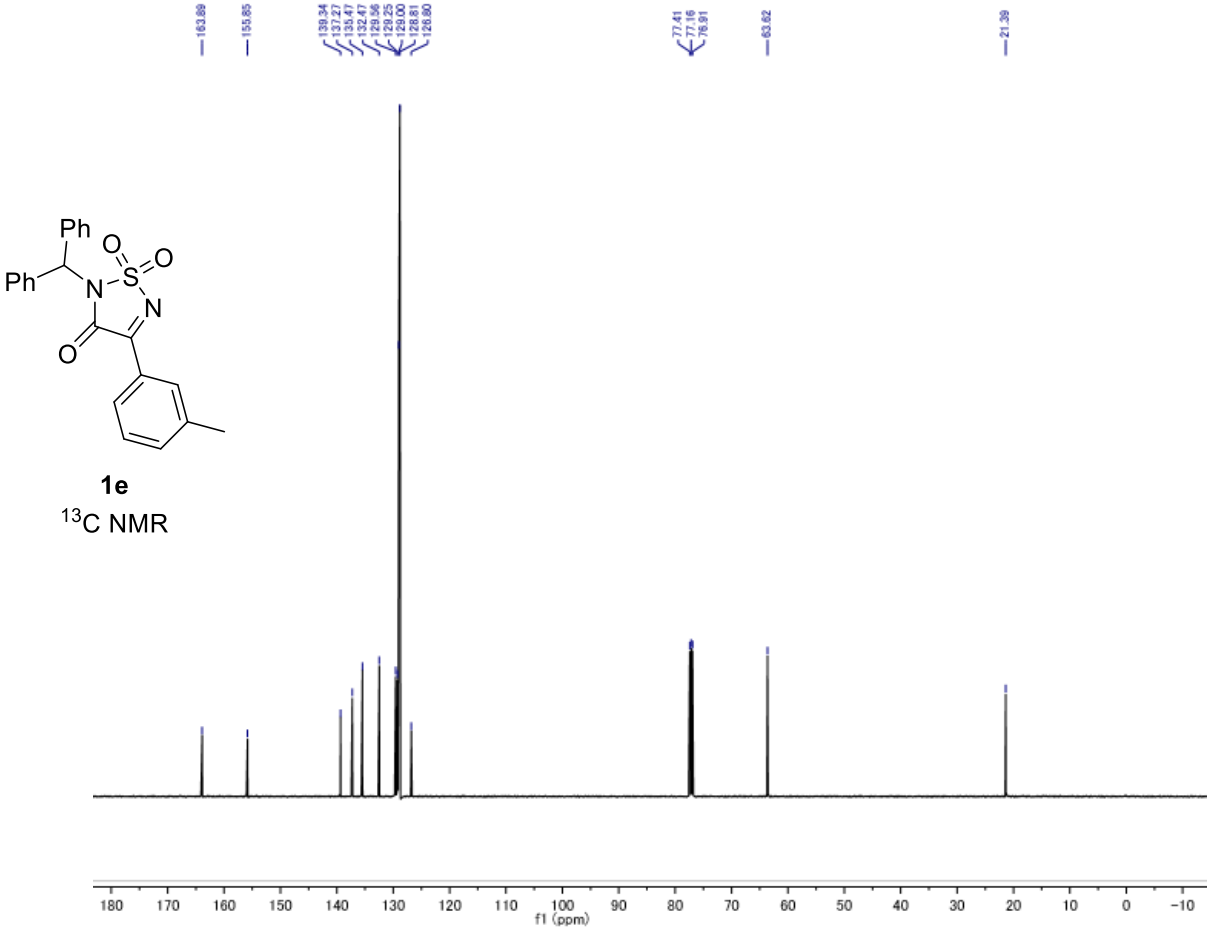

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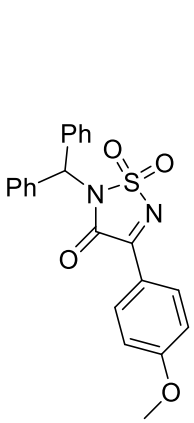
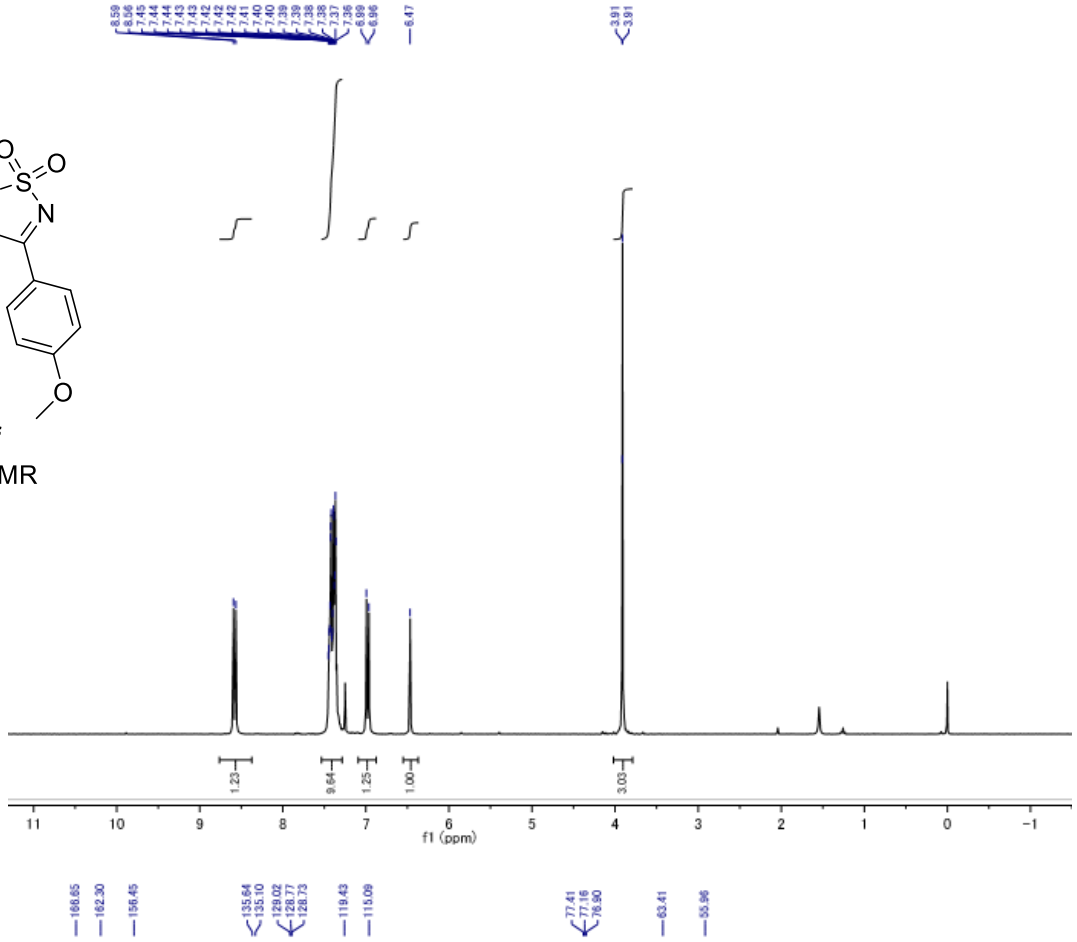
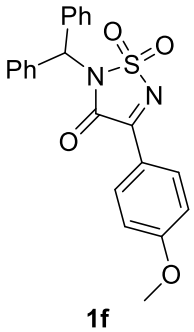


1f

^{1}H NMR





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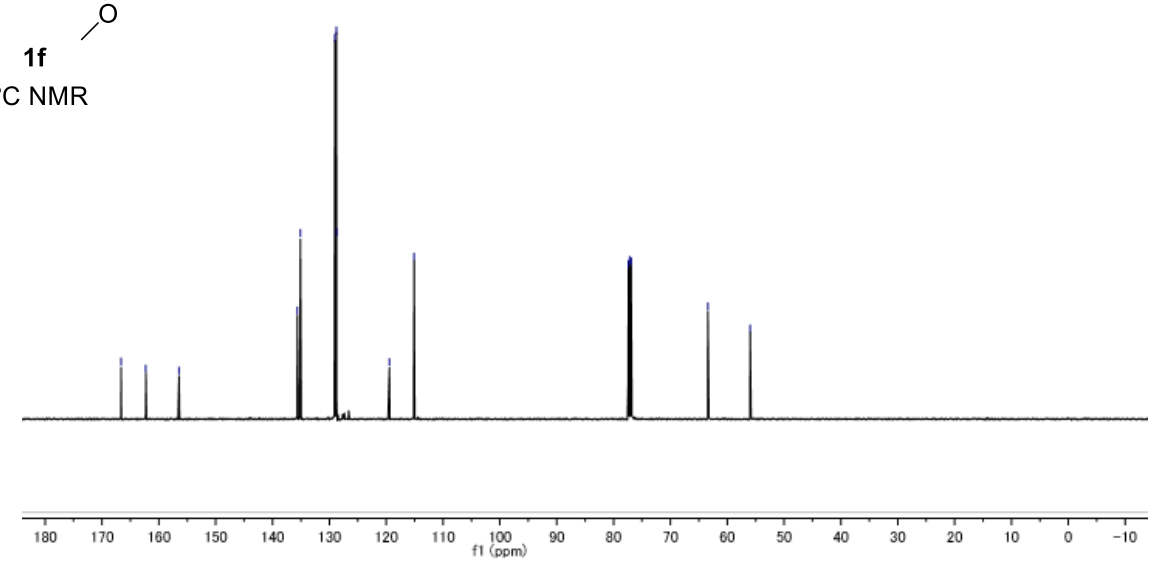
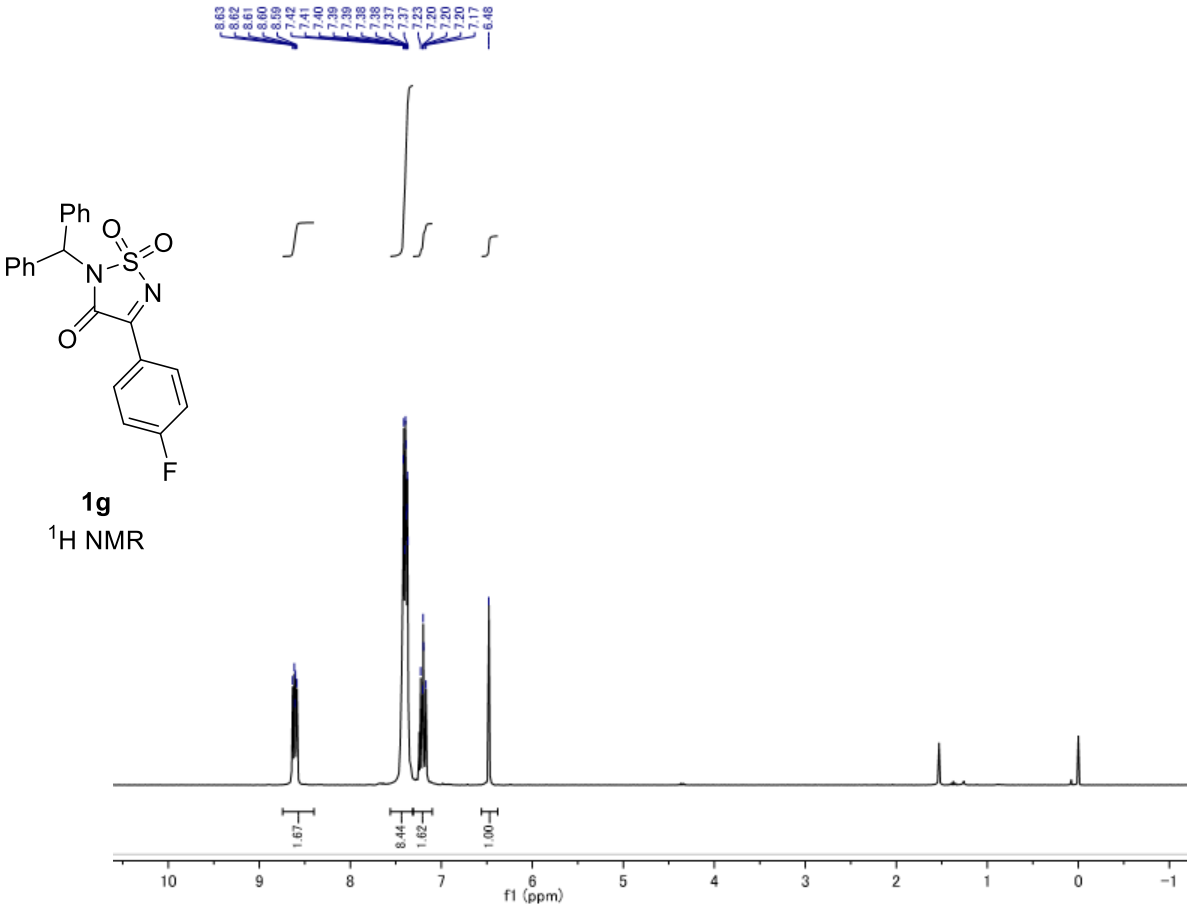
^{13}C NMR

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S
N
N
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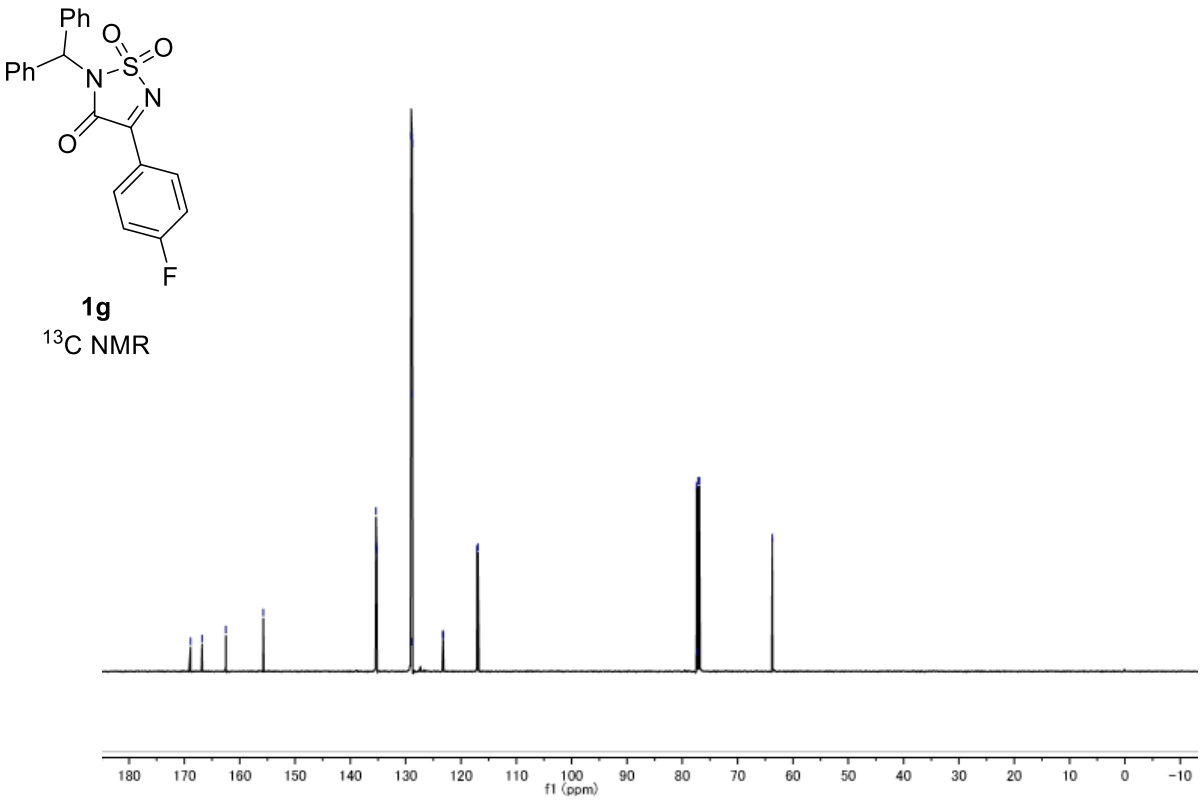
F
1g
1H NMR
f1 (ppm)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O
S
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N
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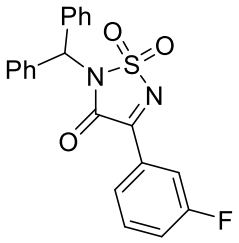
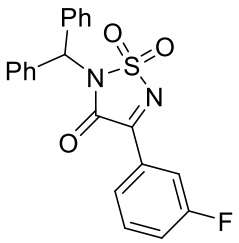
F
1g
13C NMR
f1 (ppm)



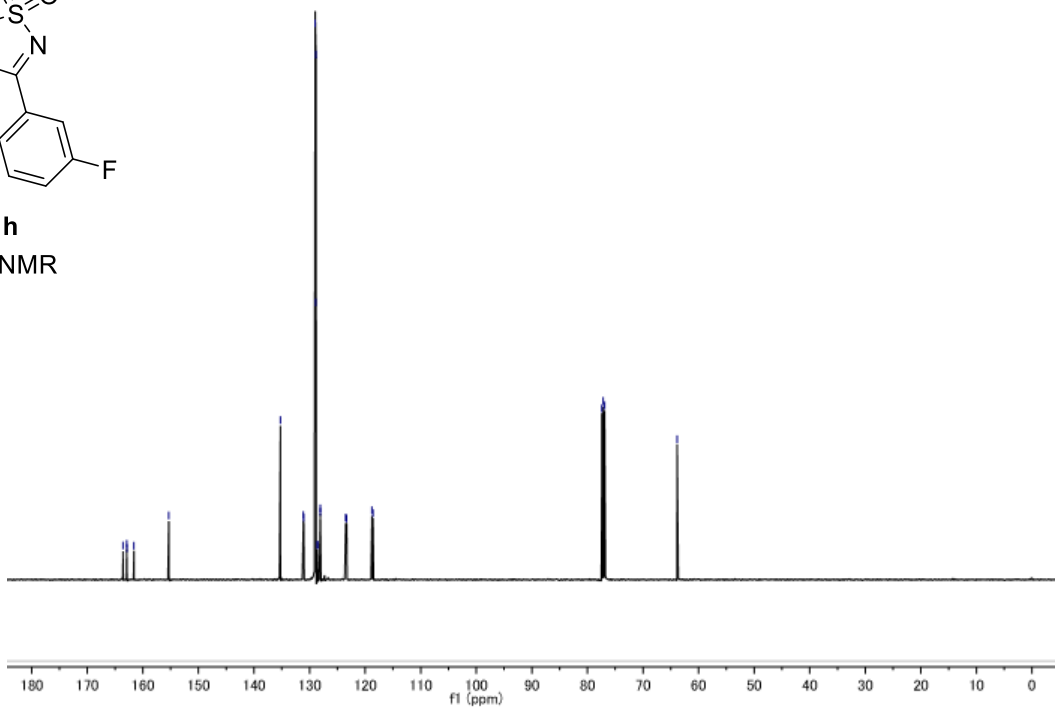
1h

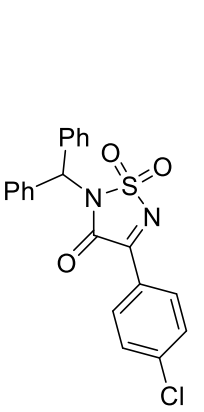
^{1}H NMR



1h

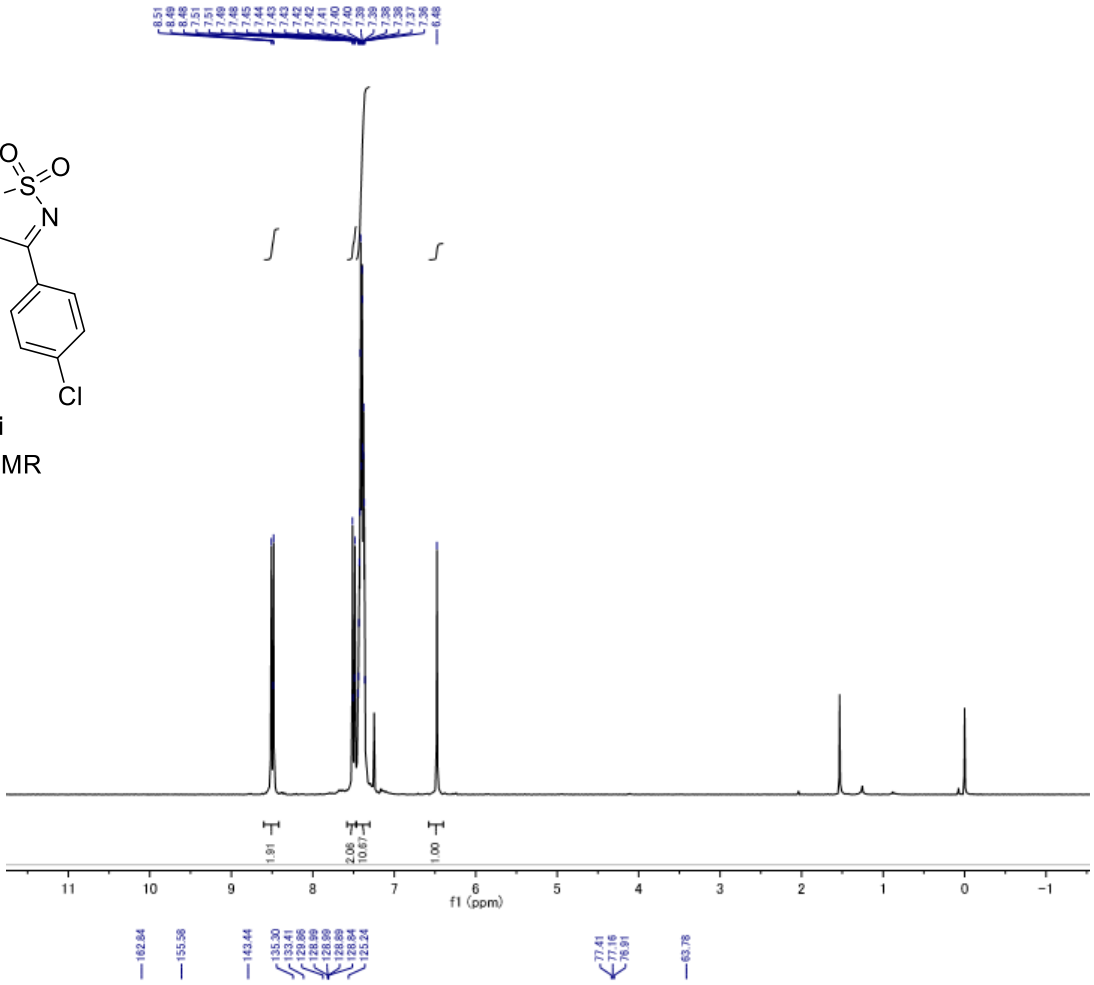
^{13}C NMR

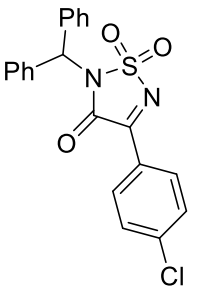




1i

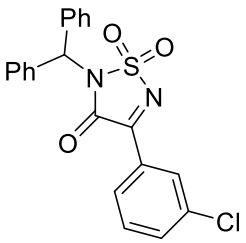
^{1}H NMR





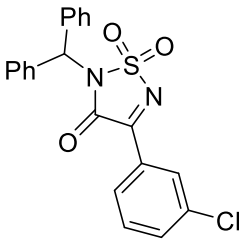
1i

^{13}C NMR



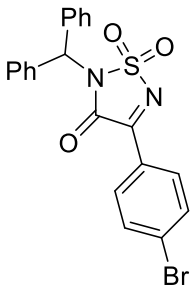
1j

^{1}H NMR



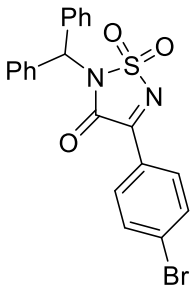
1j

^{13}C NMR



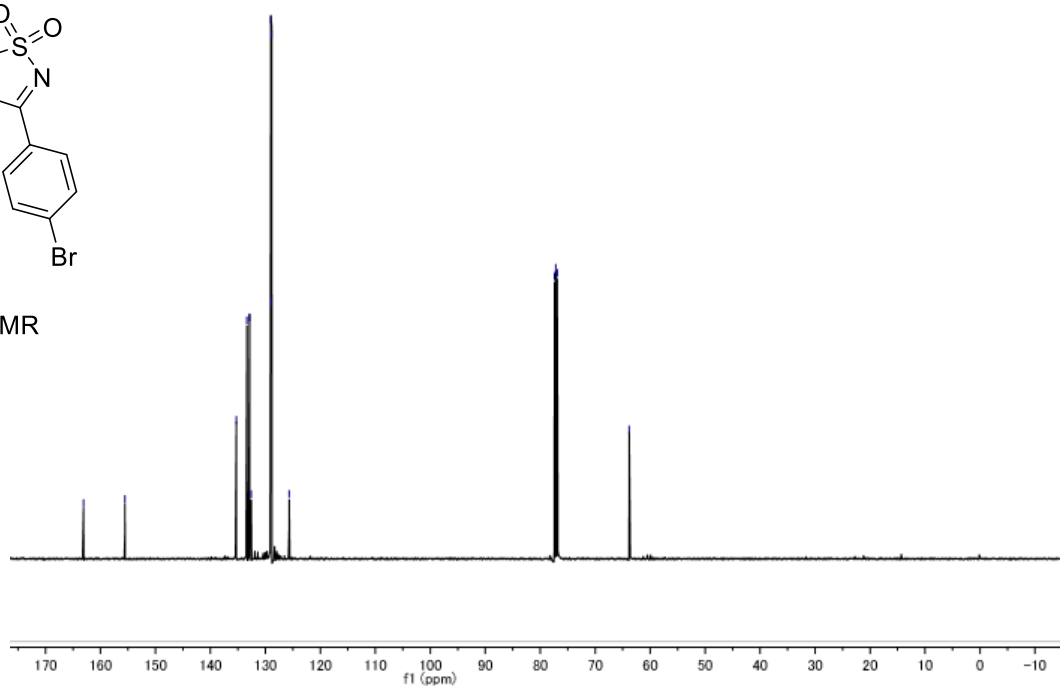
1k

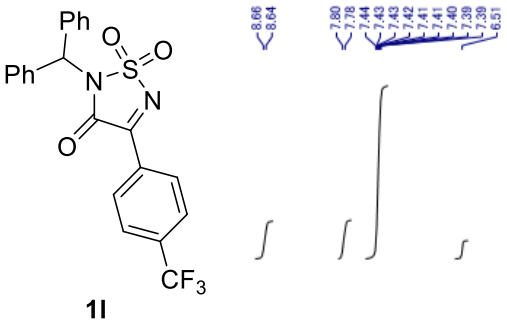
^{1}H NMR



1k

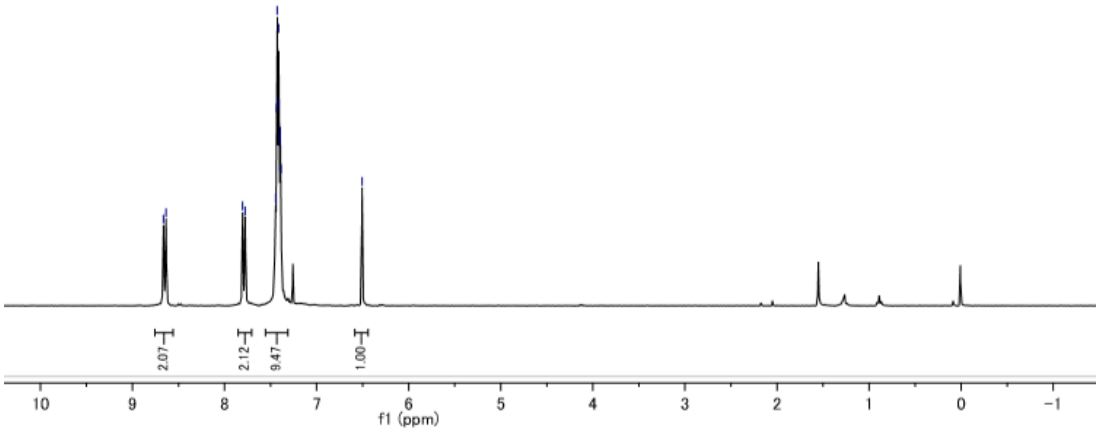
^{13}C NMR

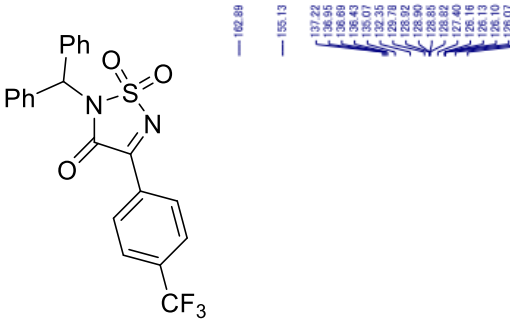




1l

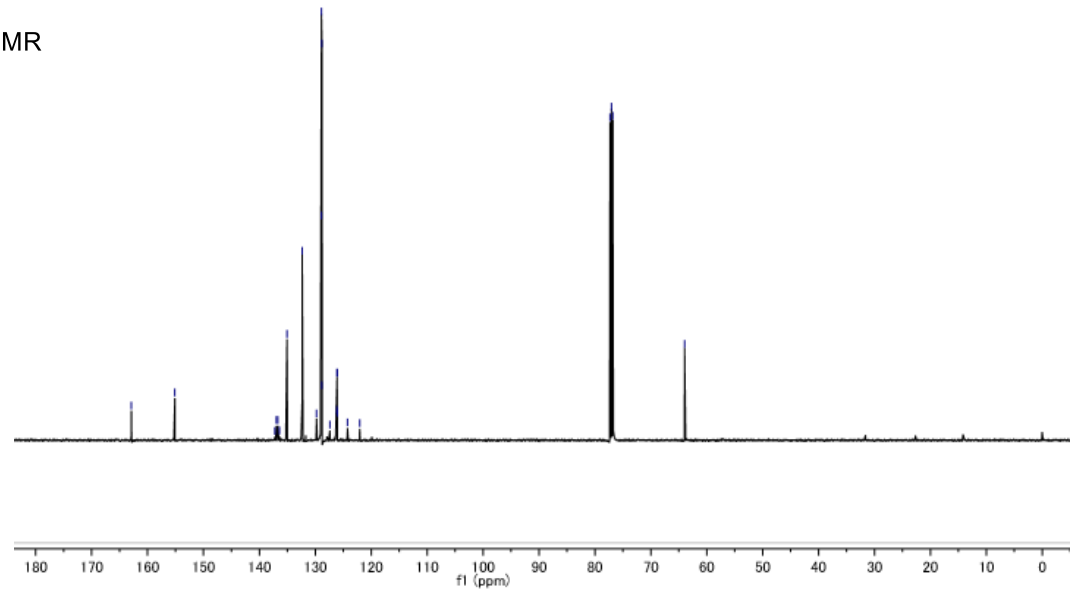
^{1}H NMR

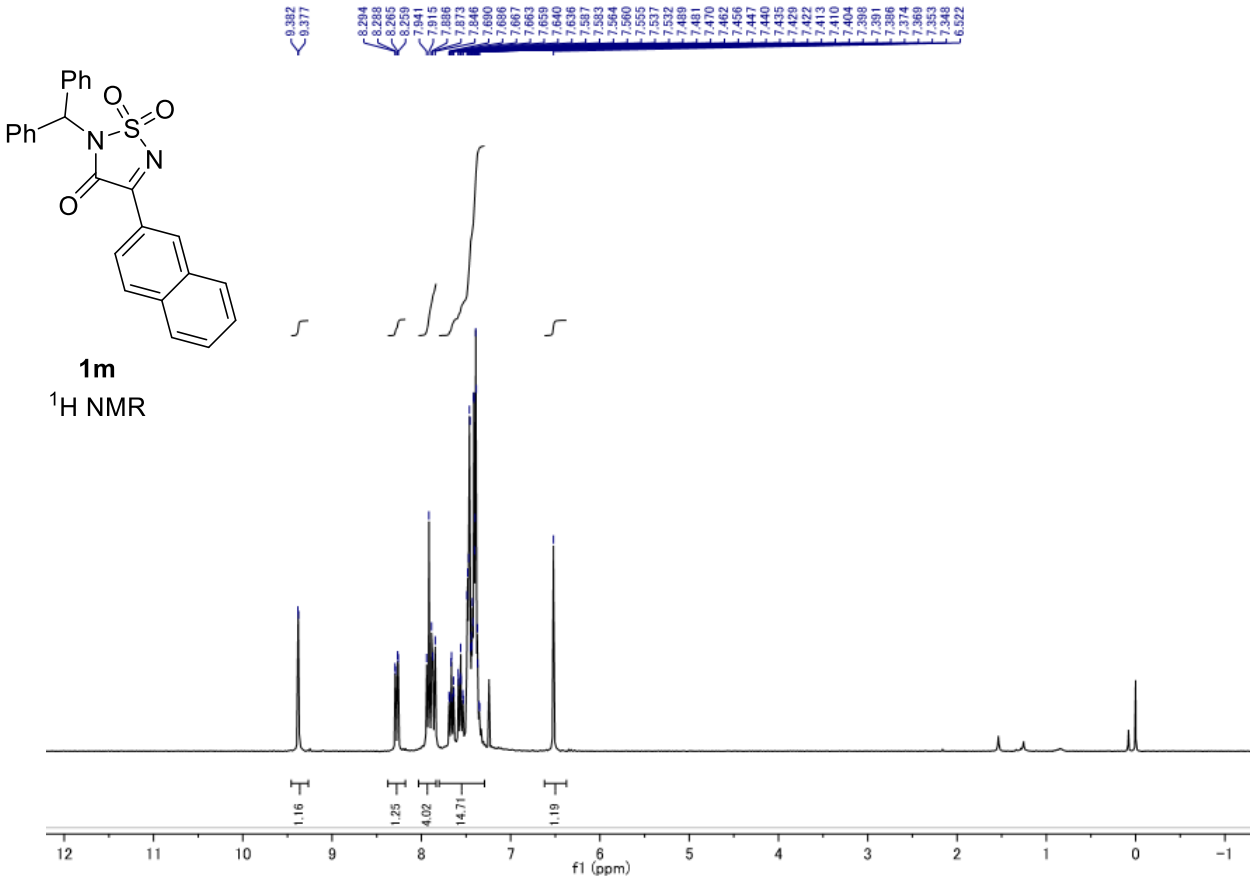


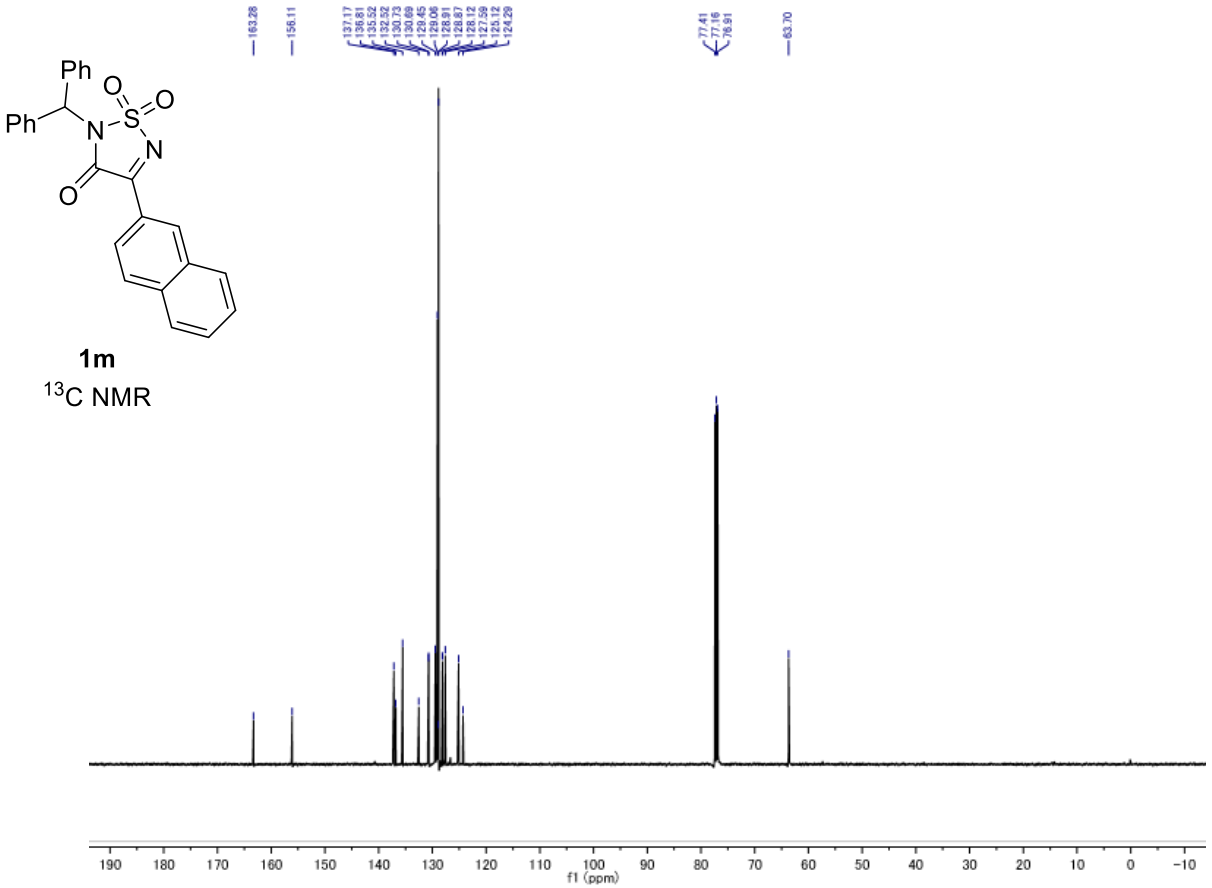


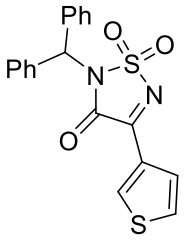
1l

^{13}C NMR



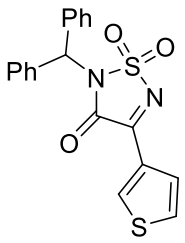

Ph
Ph
O
O
N
S
N
O
1m
1H NMR
f1 (ppm)


Ph
Ph
O
O
N
S
N
O
1m
13C NMR
f1 (ppm)



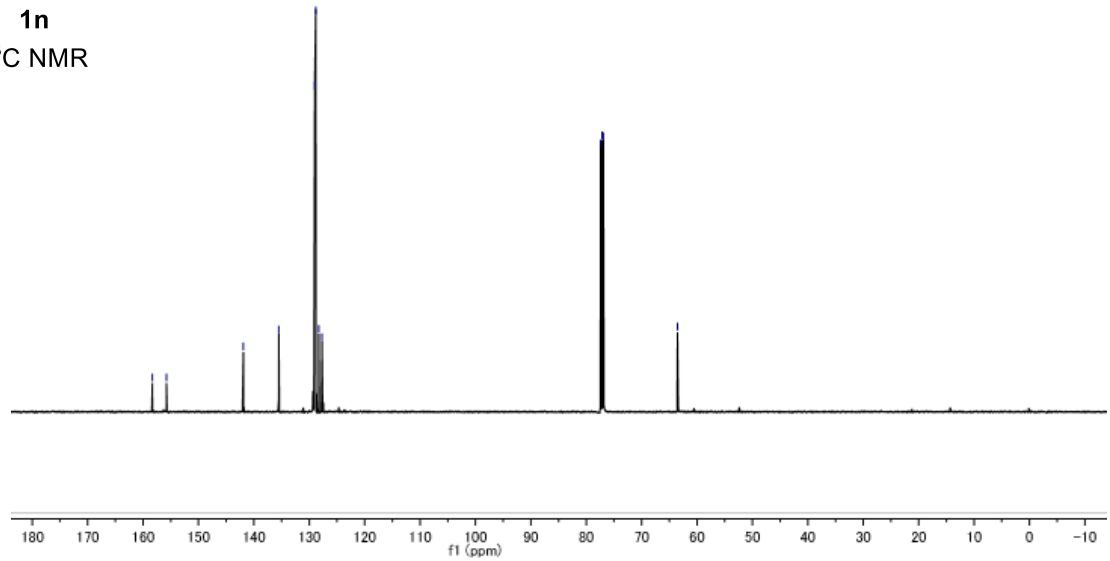
1n

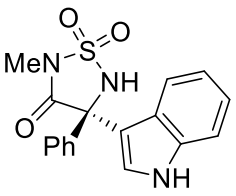
^{1}H NMR



1n

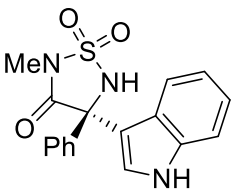
^{13}C NMR





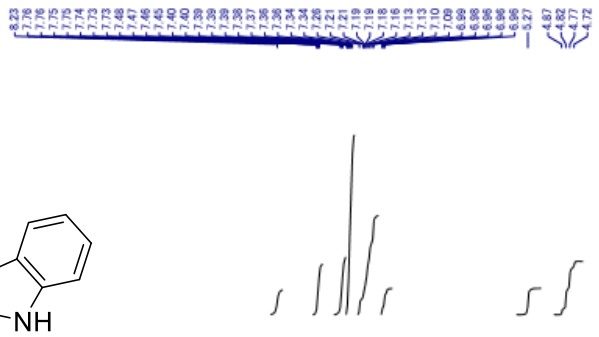
4a

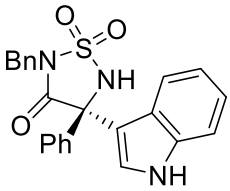
^{1}H NMR



4a

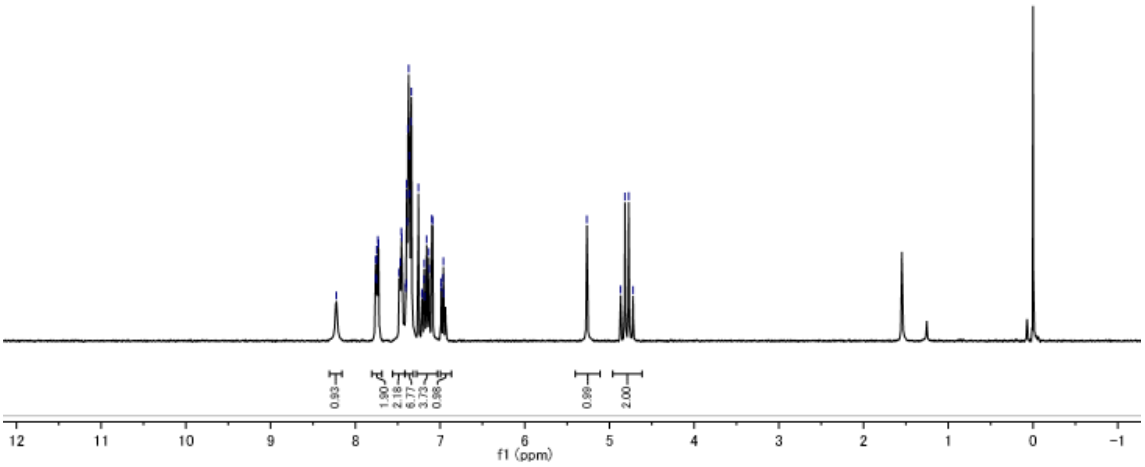
^{13}C NMR

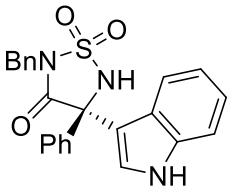




4b

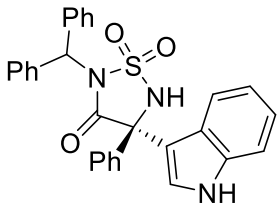
^{13}C NMR





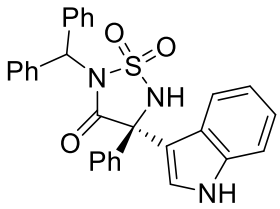
4b

^{13}C NMR



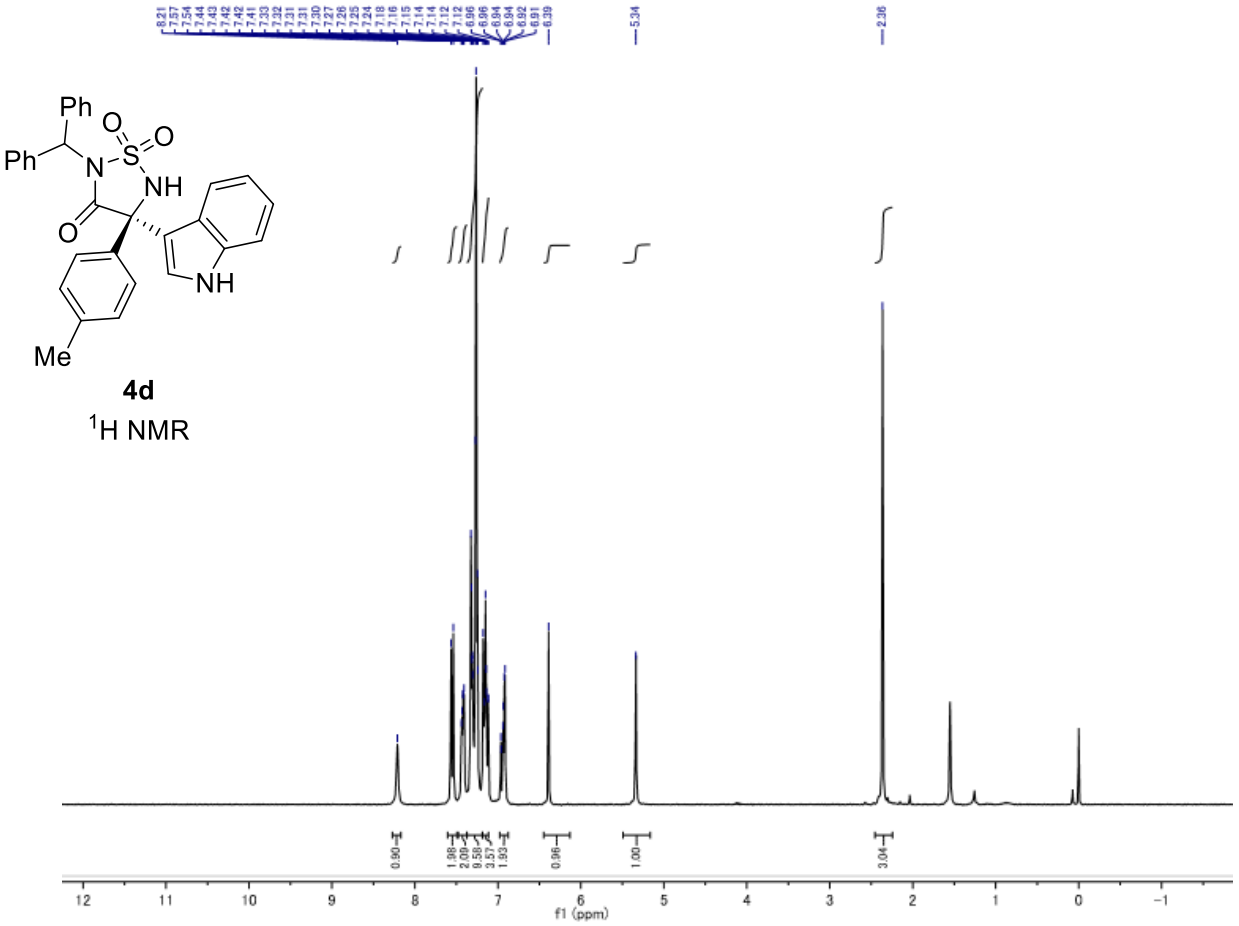
4c

^{1}H NMR



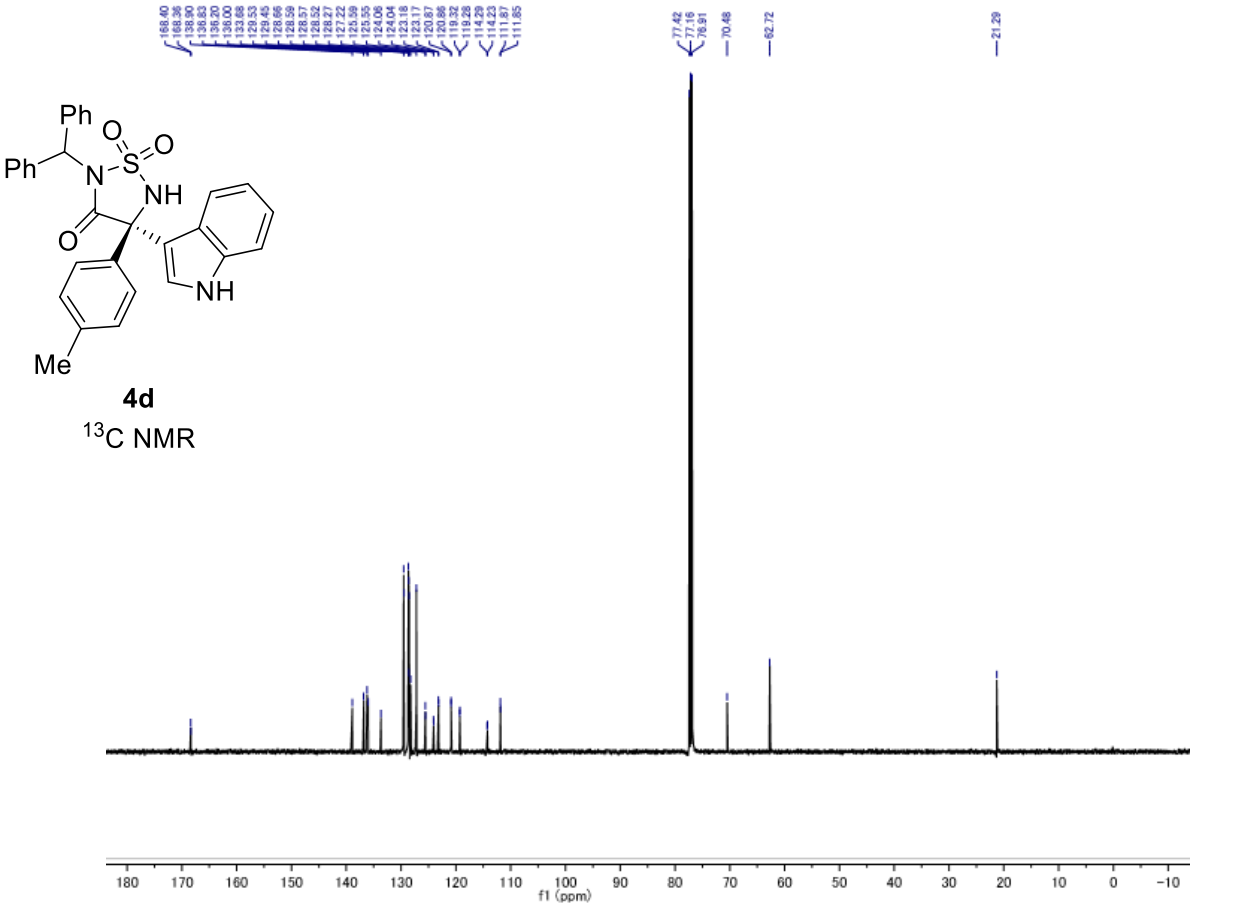
4c

^{13}C NMR



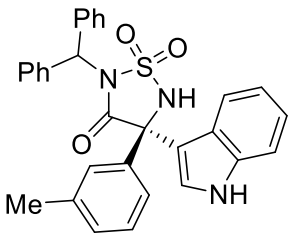
4d

^{1}H NMR



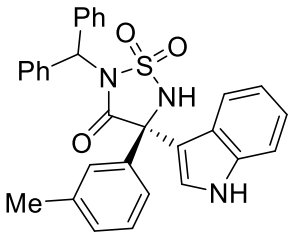
4d

^{13}C NMR



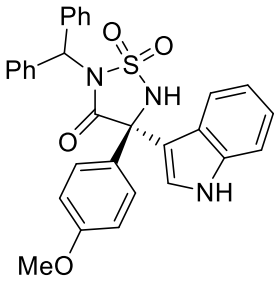
4e

^{1}H NMR



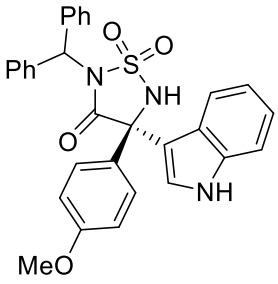
4e

^{13}C NMR



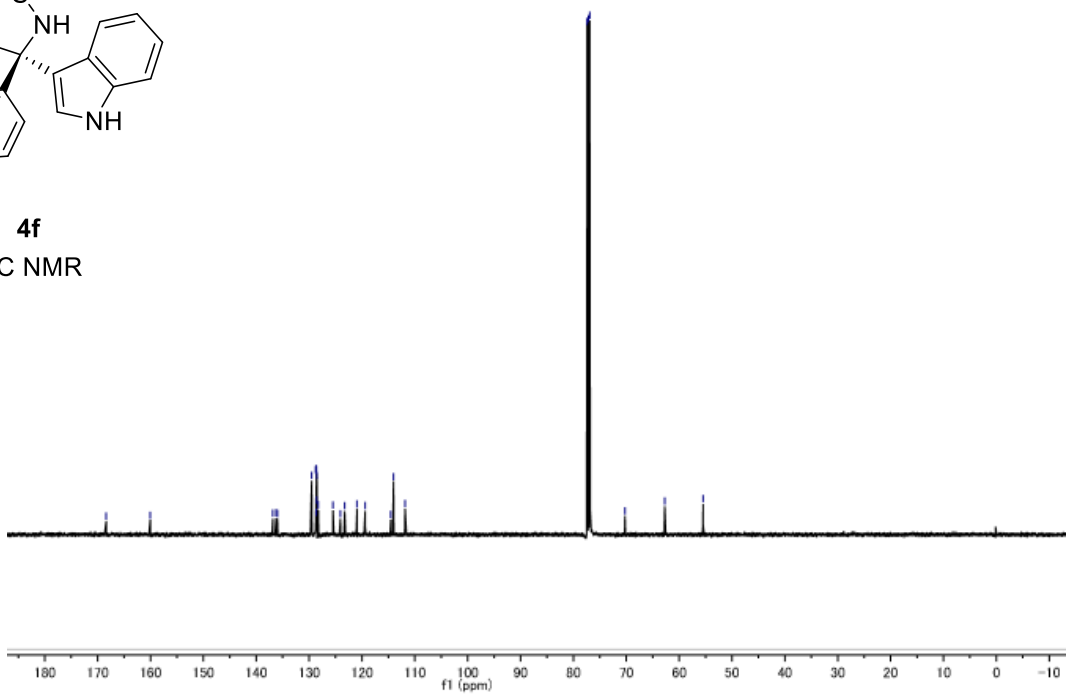
4f

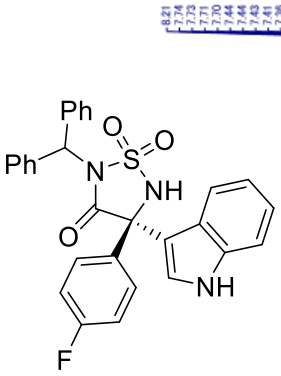
^{1}H NMR



4f

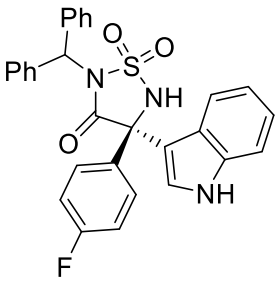
^{13}C NMR





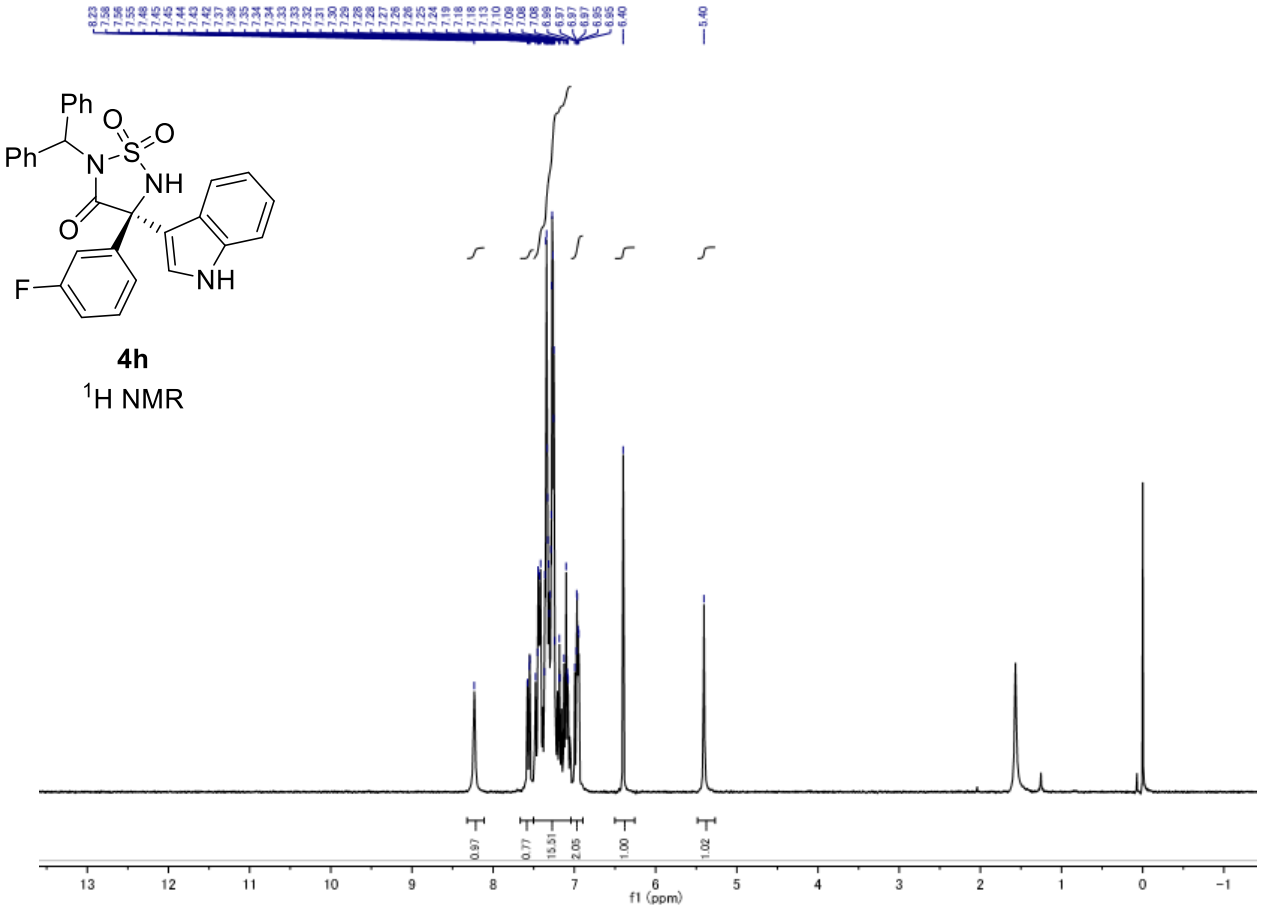
4g

^{1}H NMR



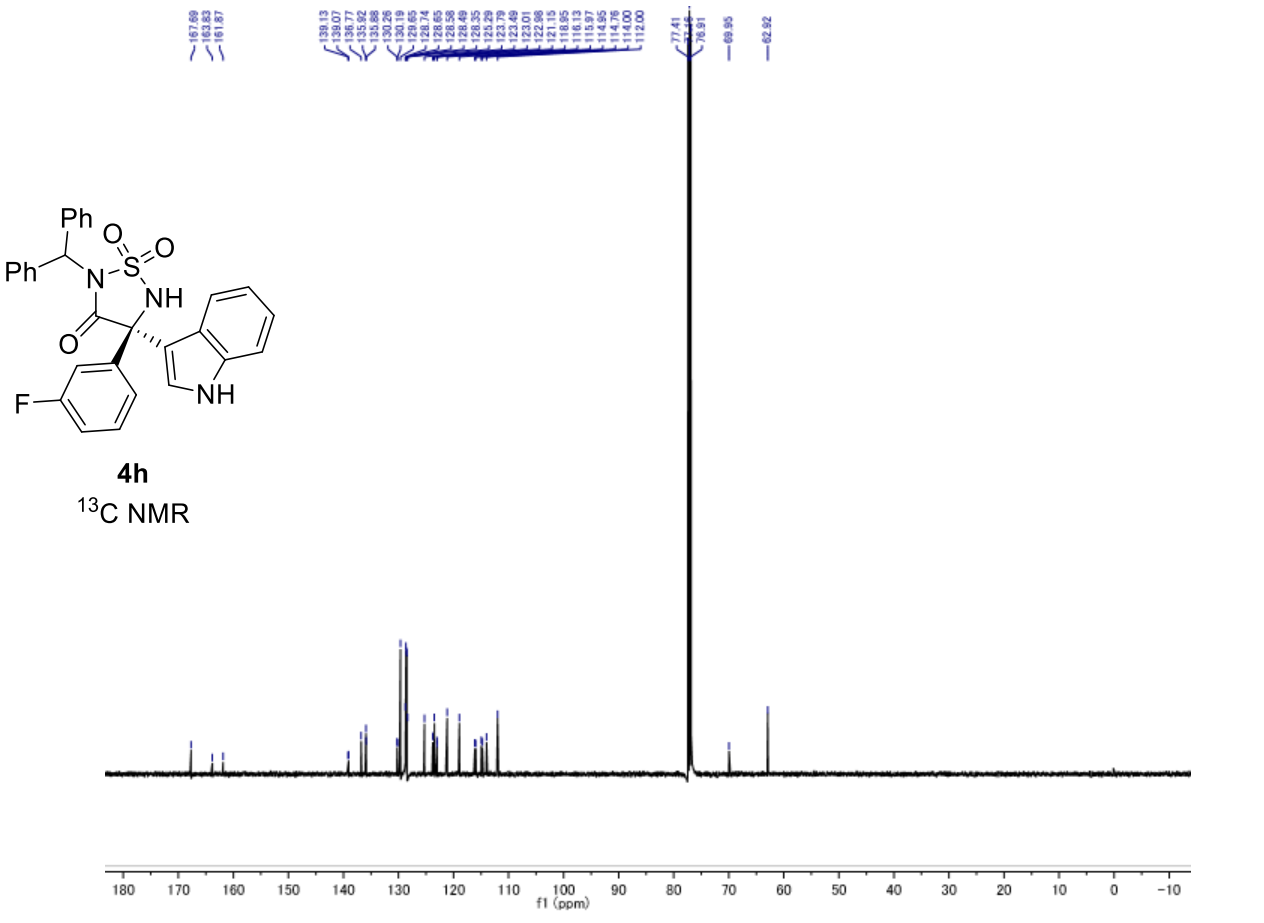
4g

^{13}C NMR



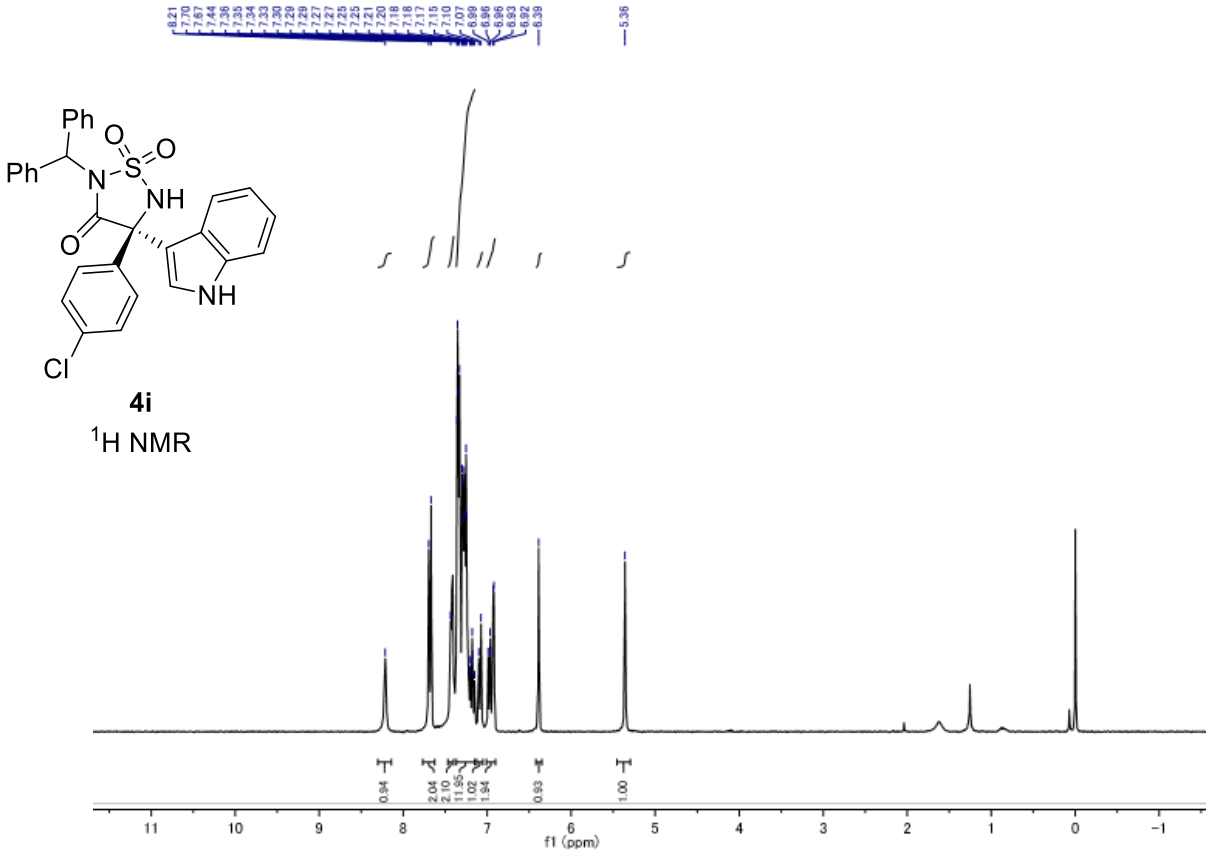
4h

^{1}H NMR



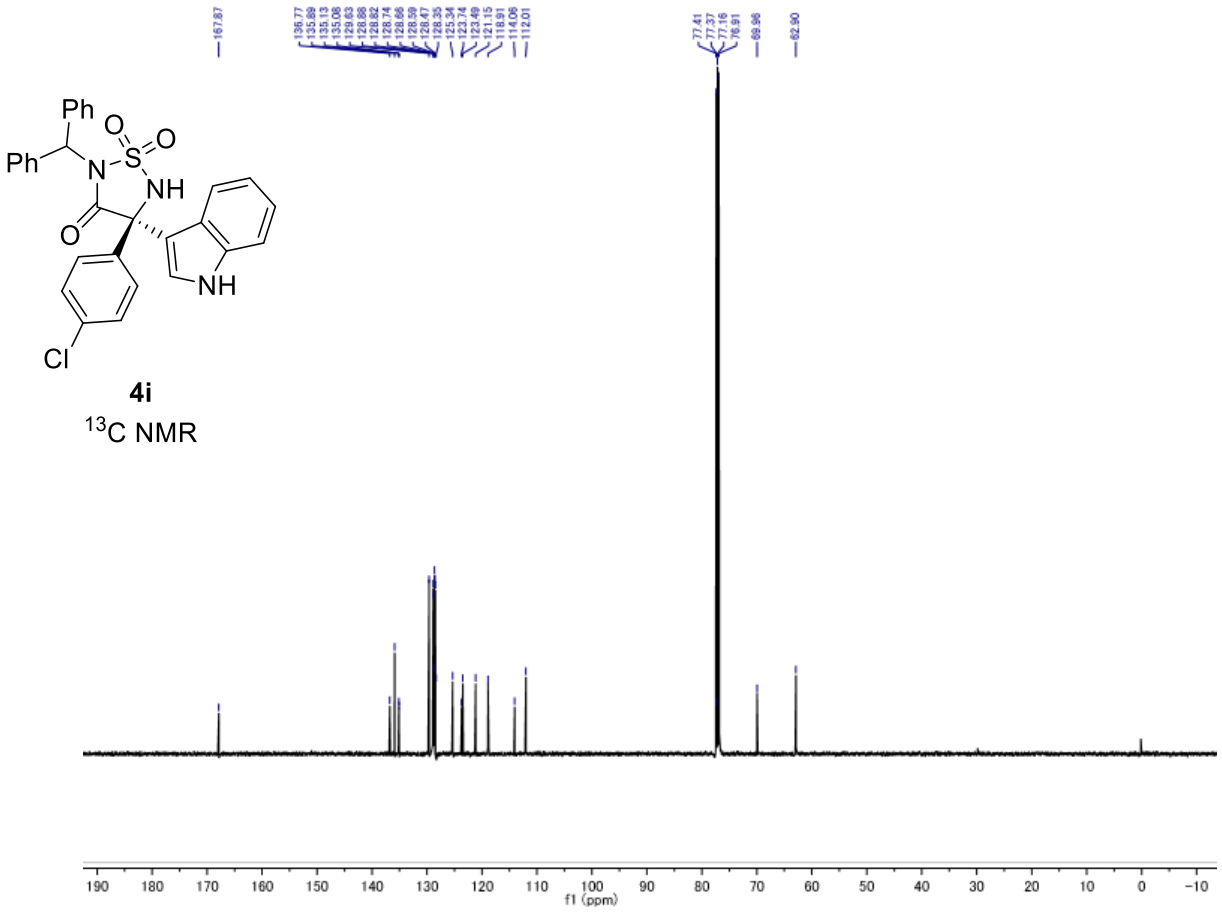
4h

^{13}C NMR



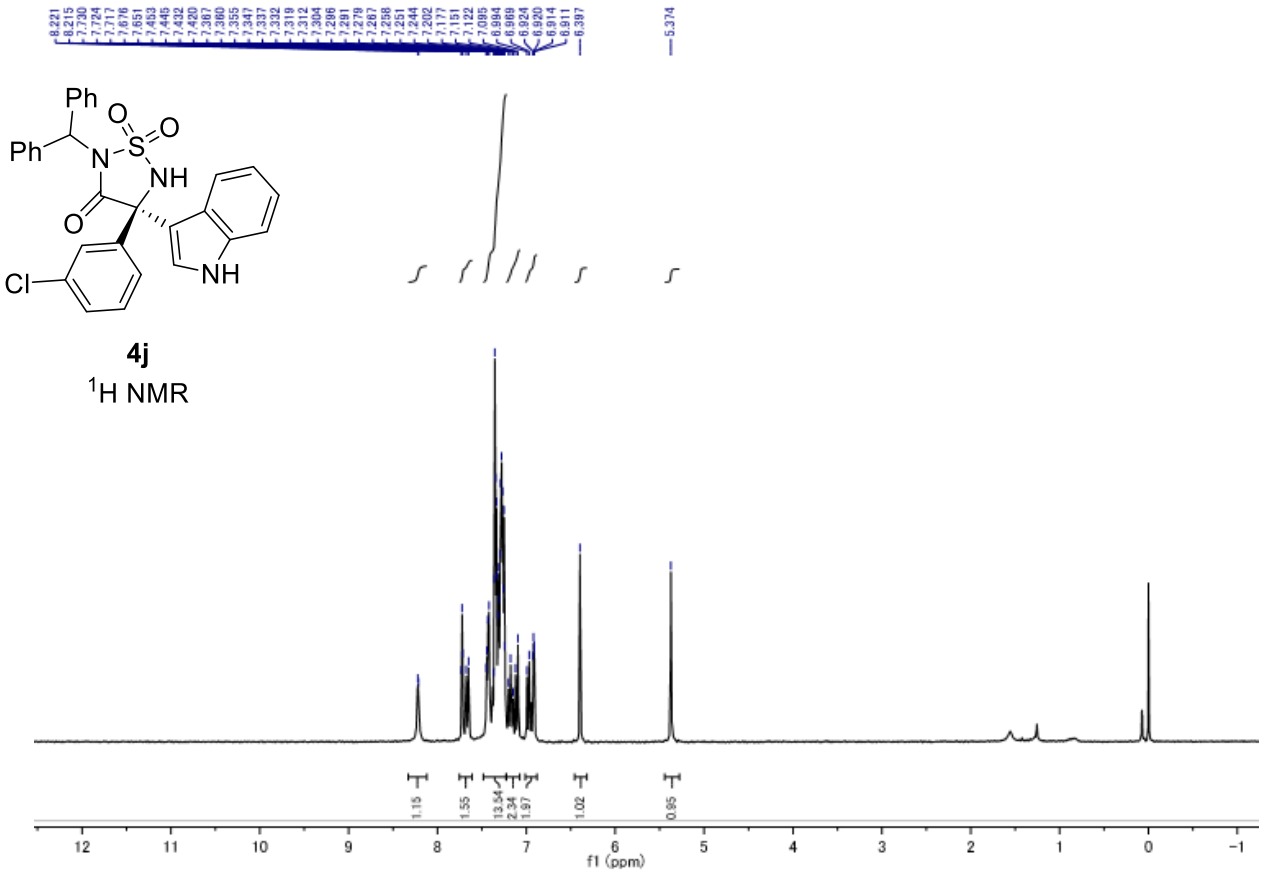
4i

^{1}H NMR



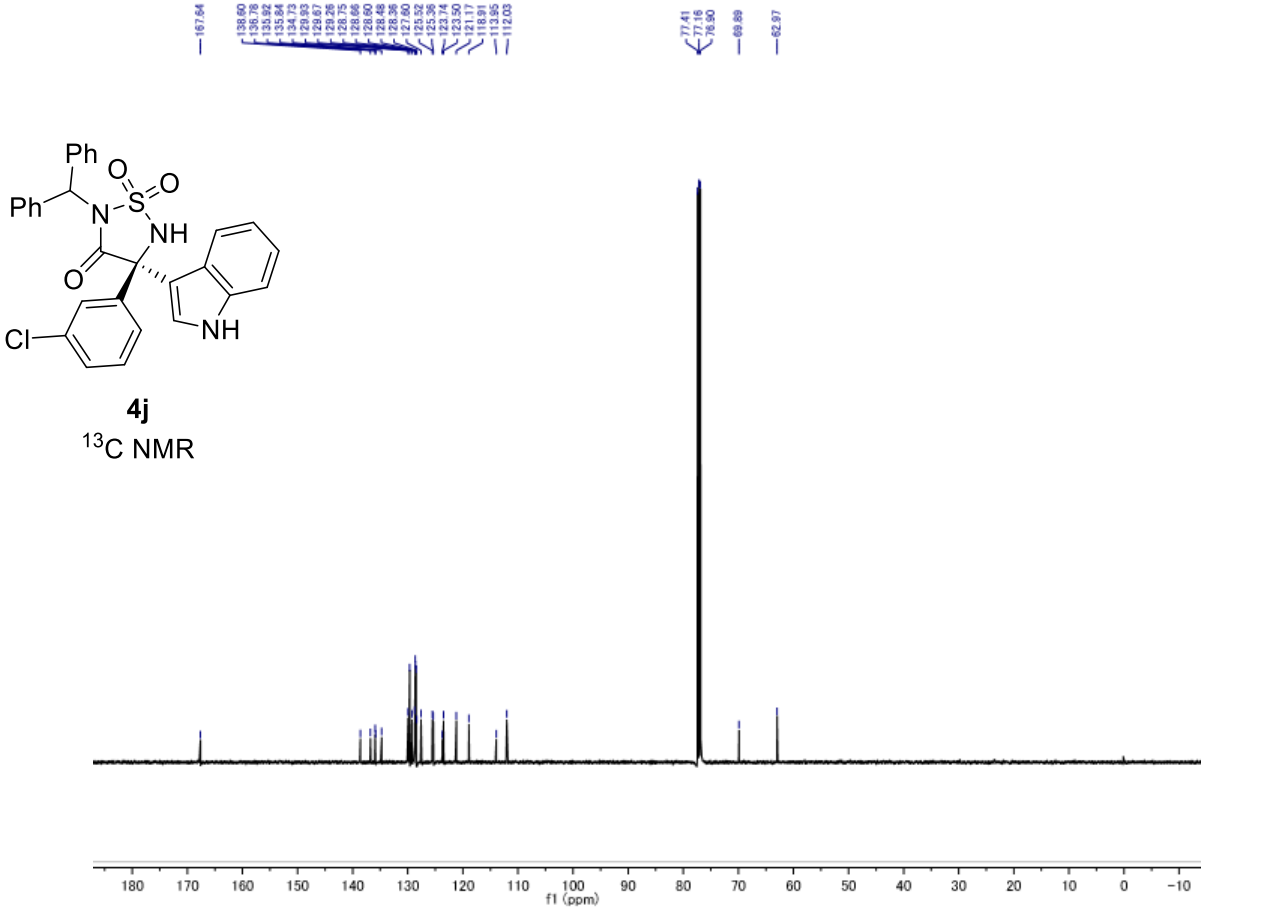
4i

^{13}C NMR



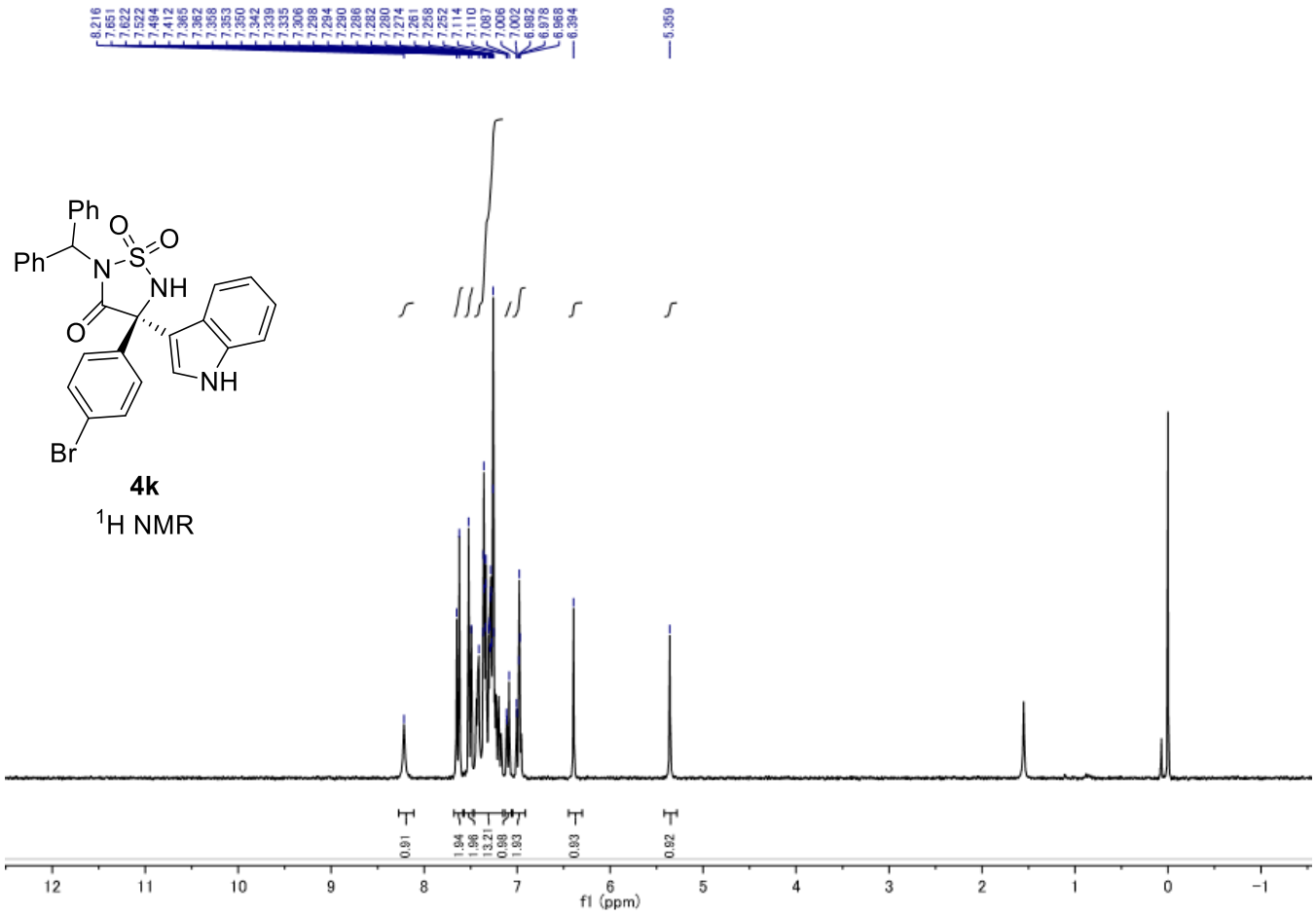
4j

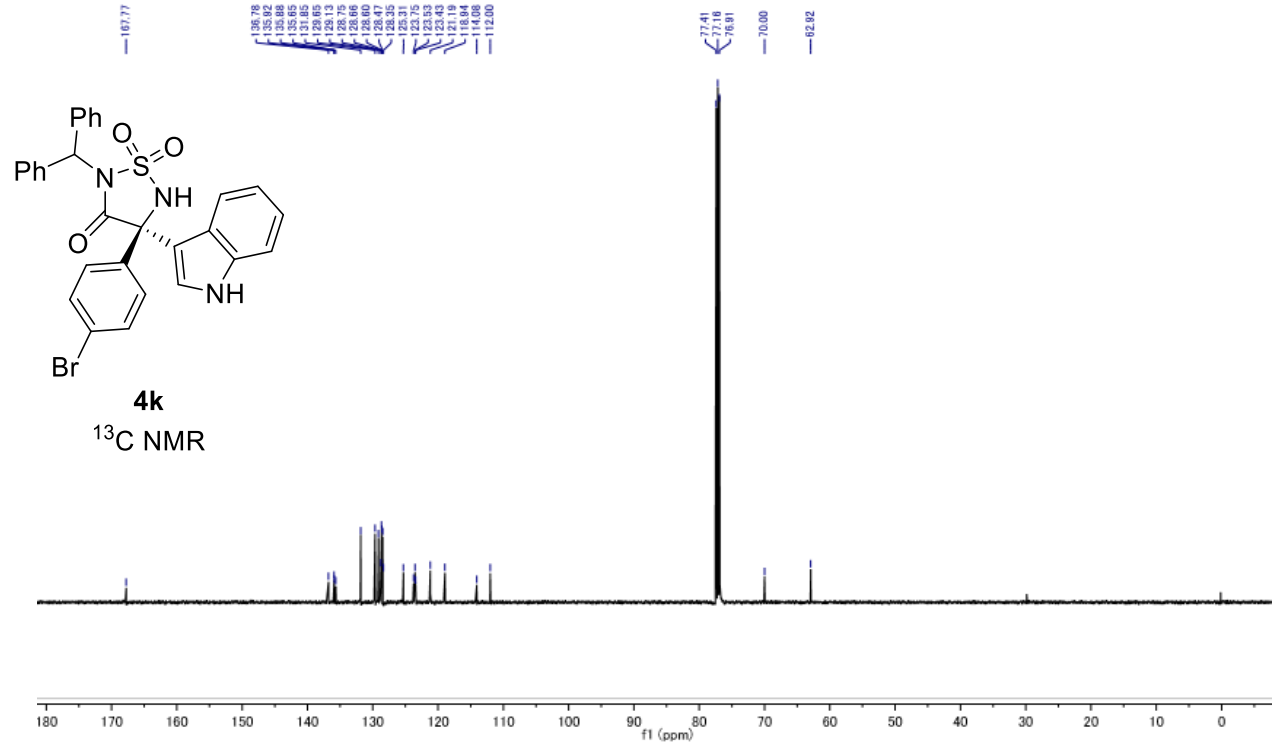
^{1}H NMR

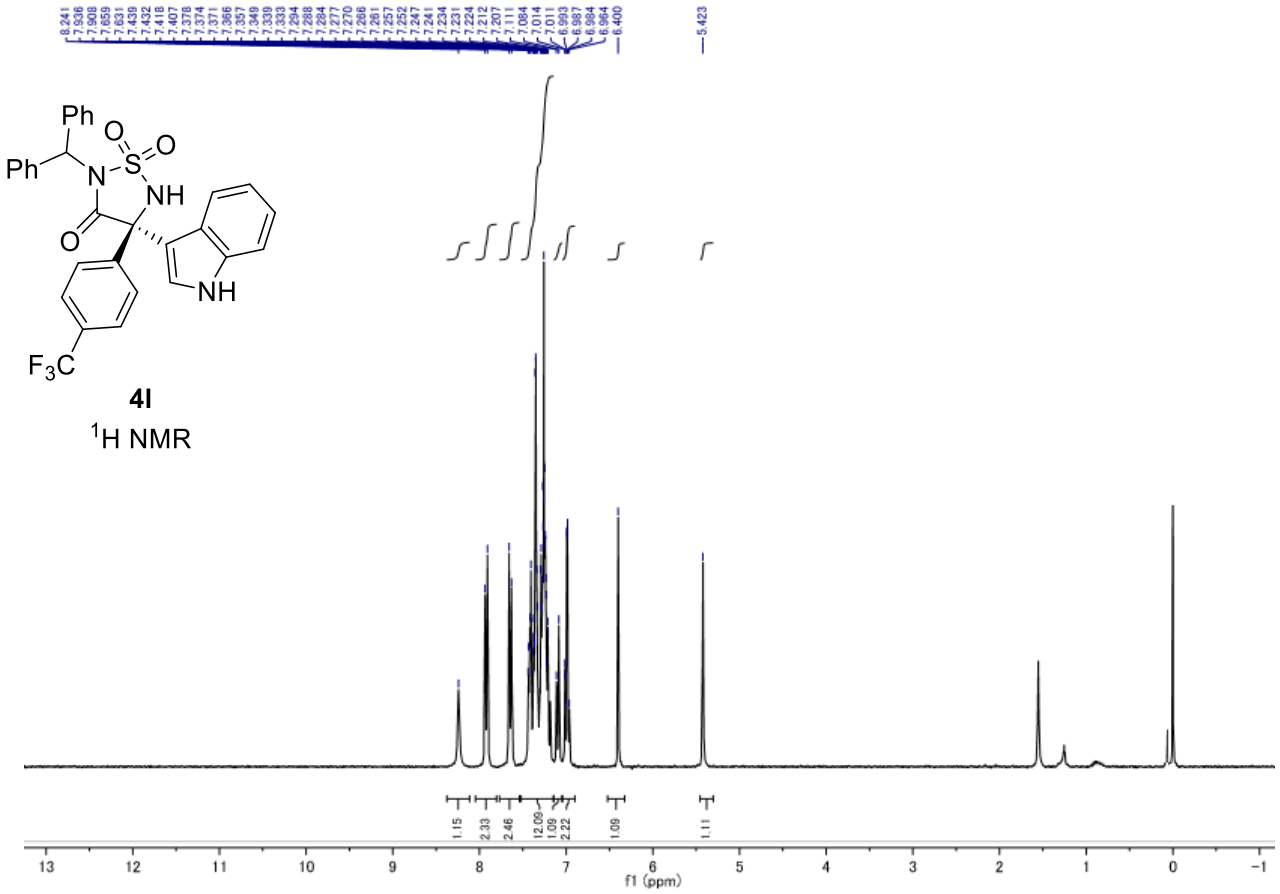


4j

^{13}C NMR

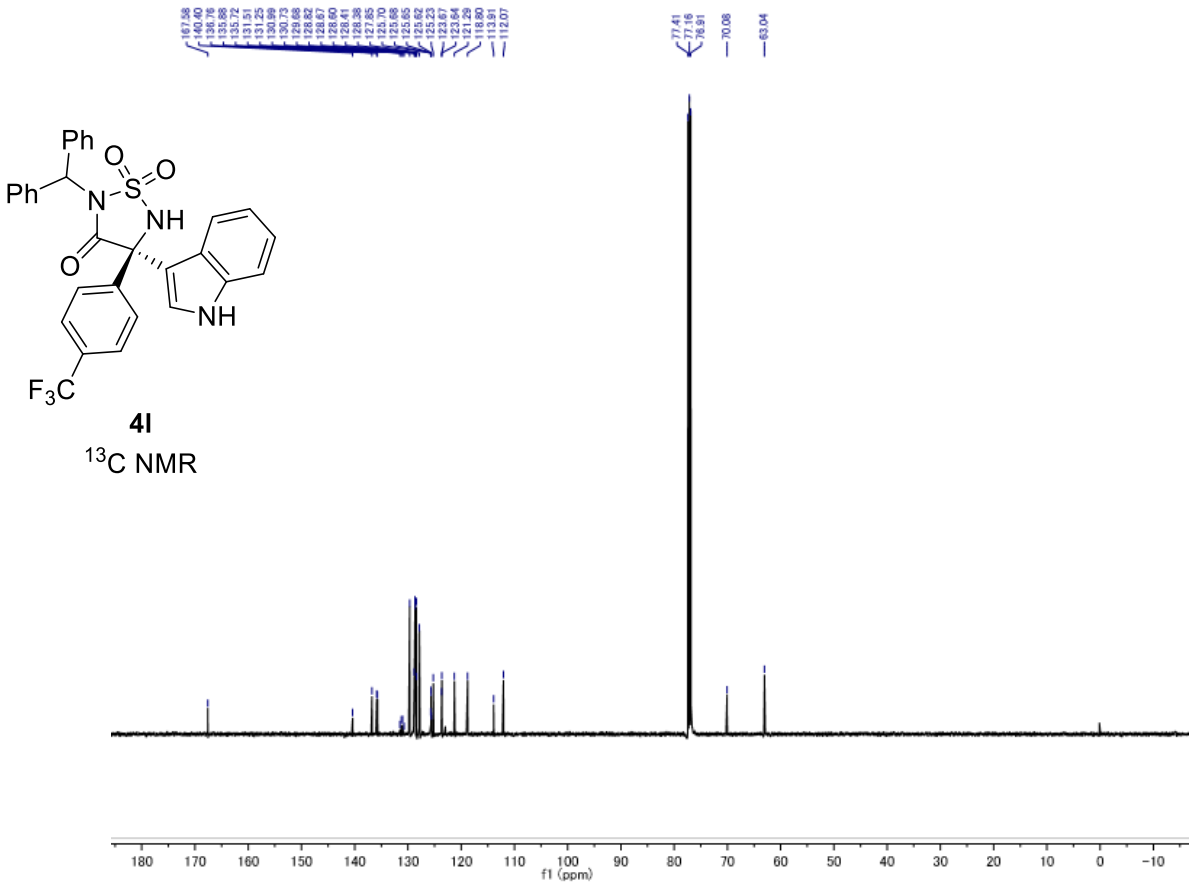

Ph
Ph
N
S
O
O
O
NH
O
NH
Br
4k
1H NMR
f1 (ppm)


Ph
Ph
N
S
O
O
O
NH
O
NH
Br
4k
13C NMR
f1 (ppm)



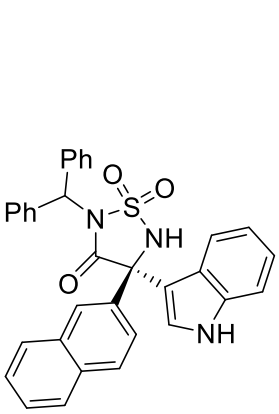
4l

^{1}H NMR



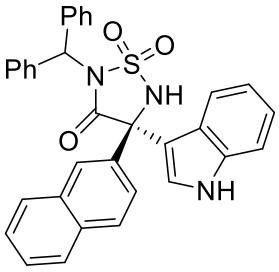
4l

^{13}C NMR



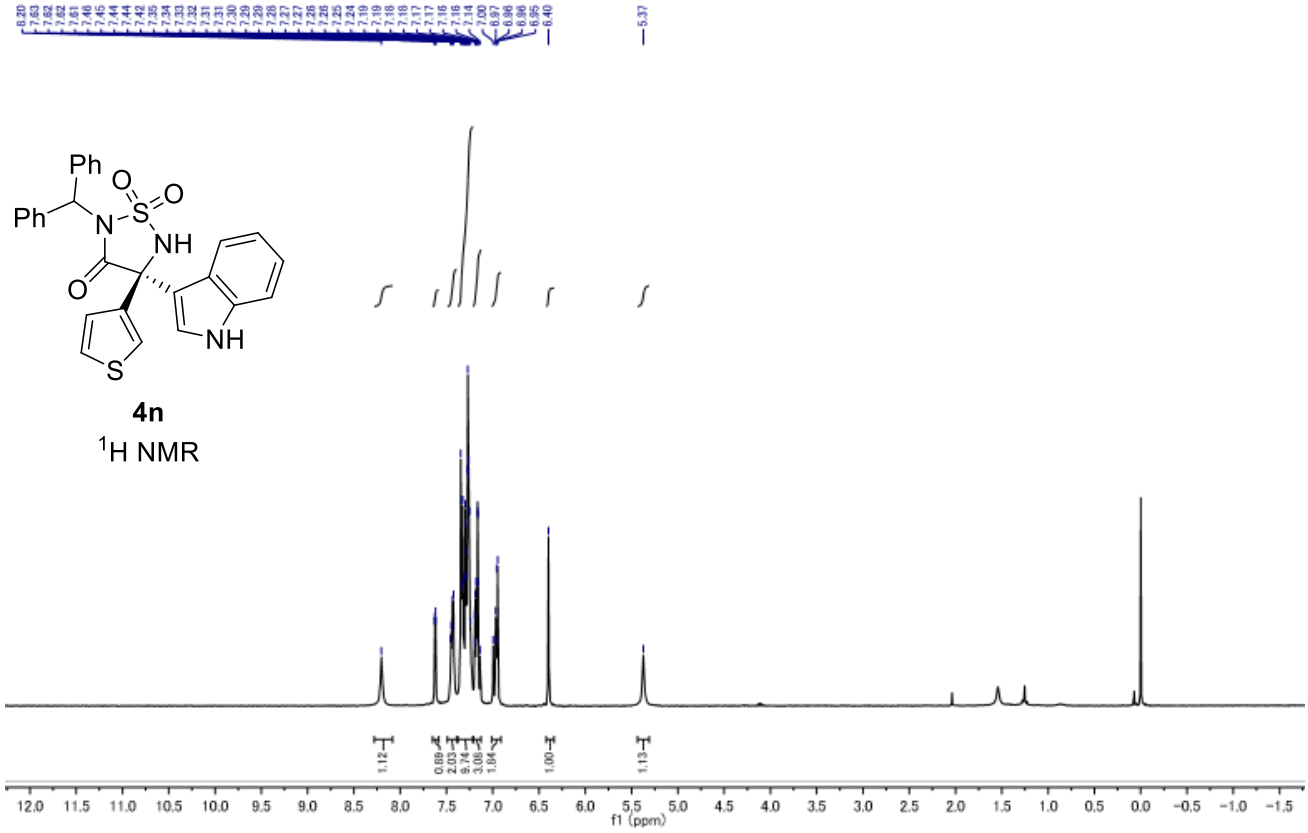
4m

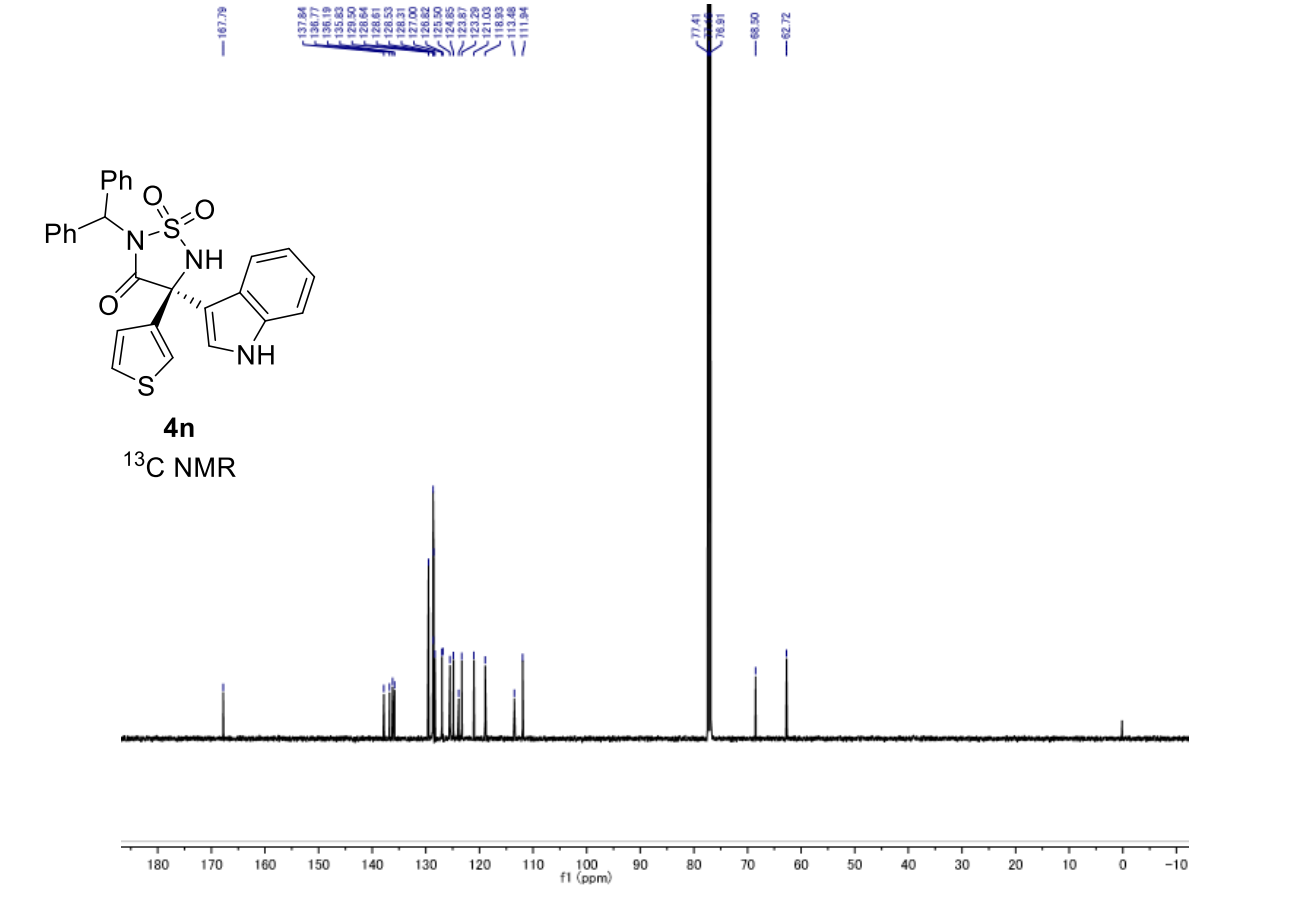
^{1}H NMR

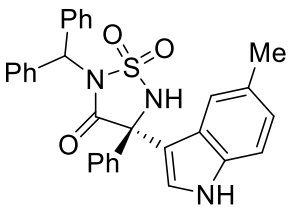


4m

^{13}C NMR

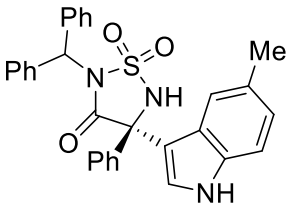

Ph
Ph
N
S
O
O
O
NH
NH
S
4n
1H NMR
f1 (ppm)


Ph
Ph
N
S
O
O
O
NH
NH
S
4n
13C NMR
f1 (ppm)



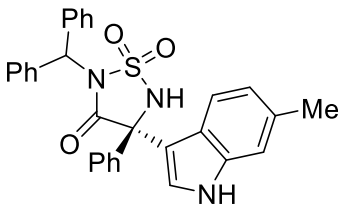
5

^{1}H NMR



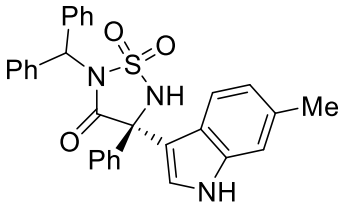
5

^{13}C NMR



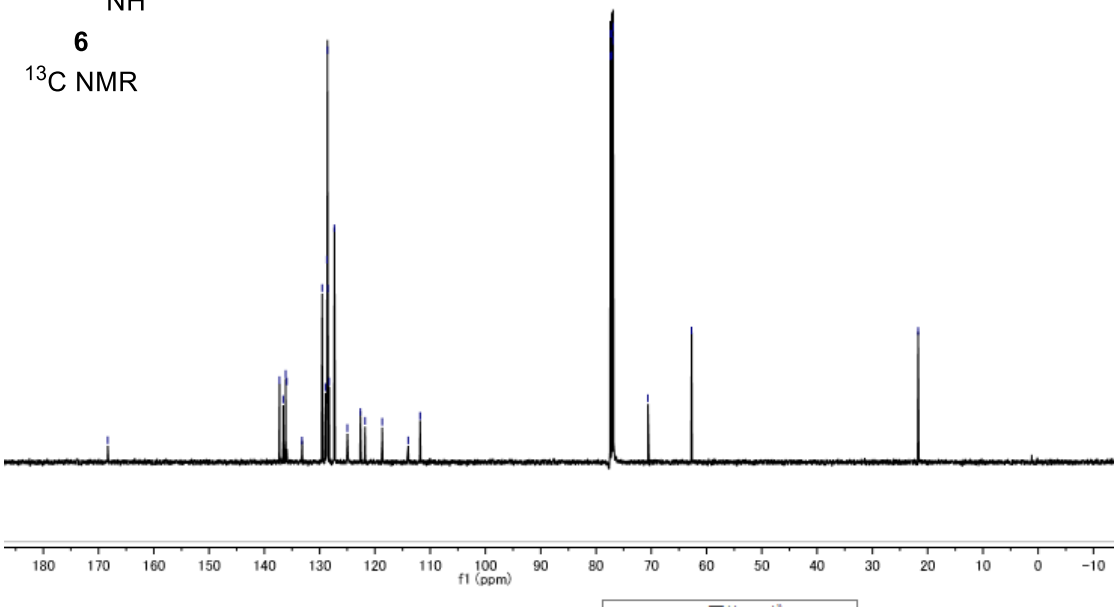
6

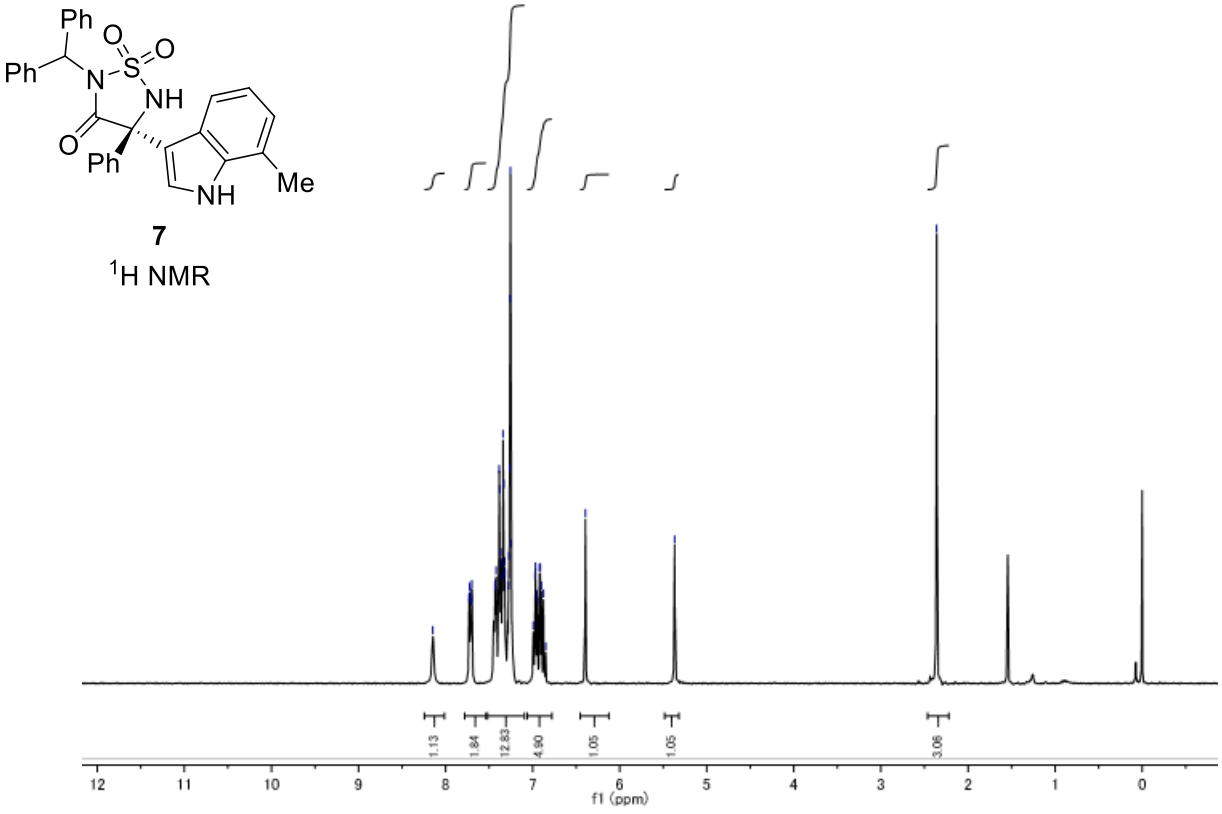
^{1}H NMR



6

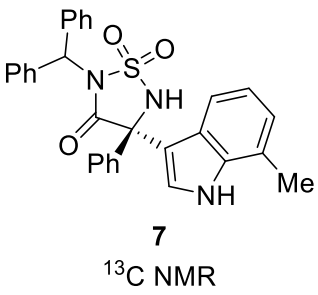
^{13}C NMR





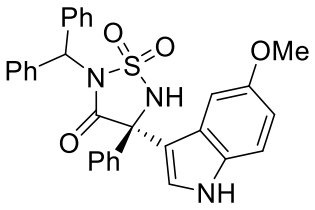
7

^{1}H NMR



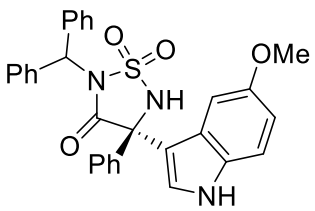
7

^{13}C NMR



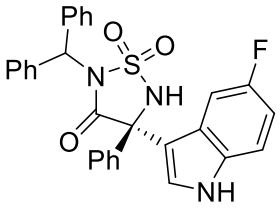
8

^{1}H NMR



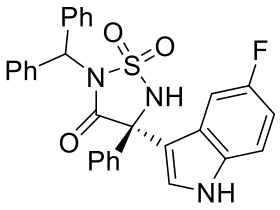
8

^{13}C NMR



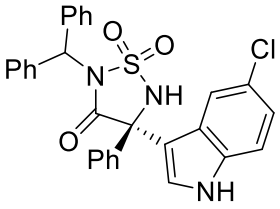
9

^{1}H NMR



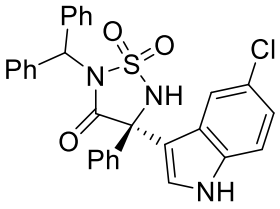
9

^{13}C NMR



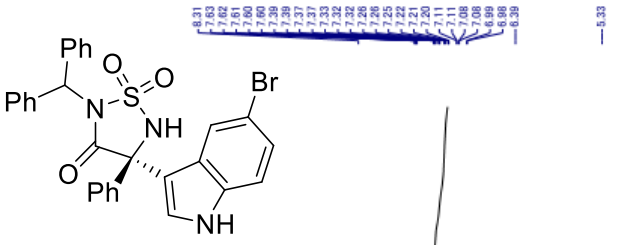
10

^{1}H NMR



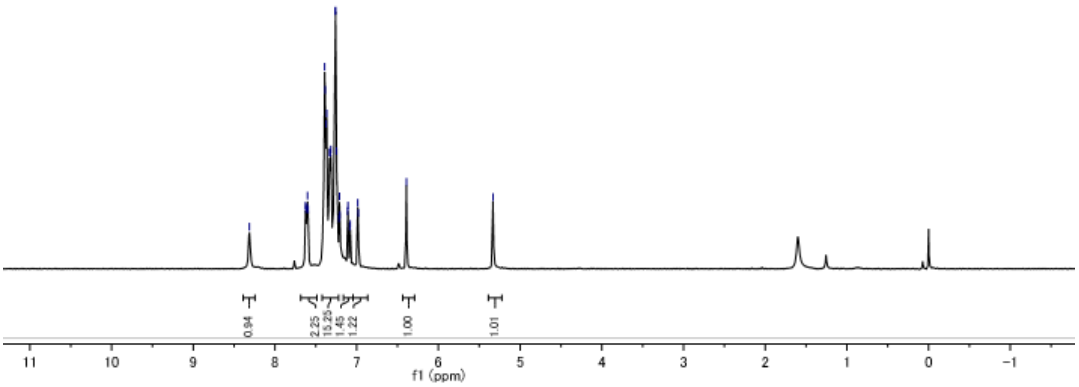
10

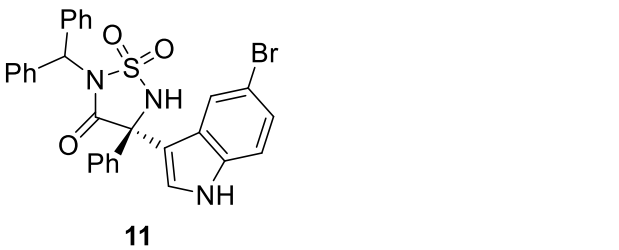
^{13}C NMR



11

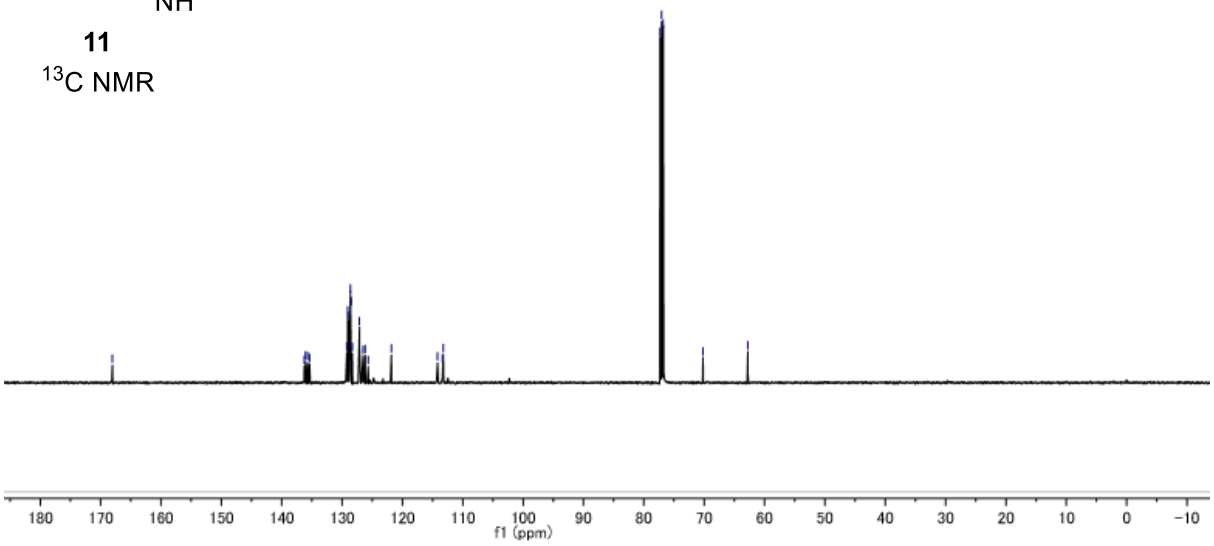
^{1}H NMR

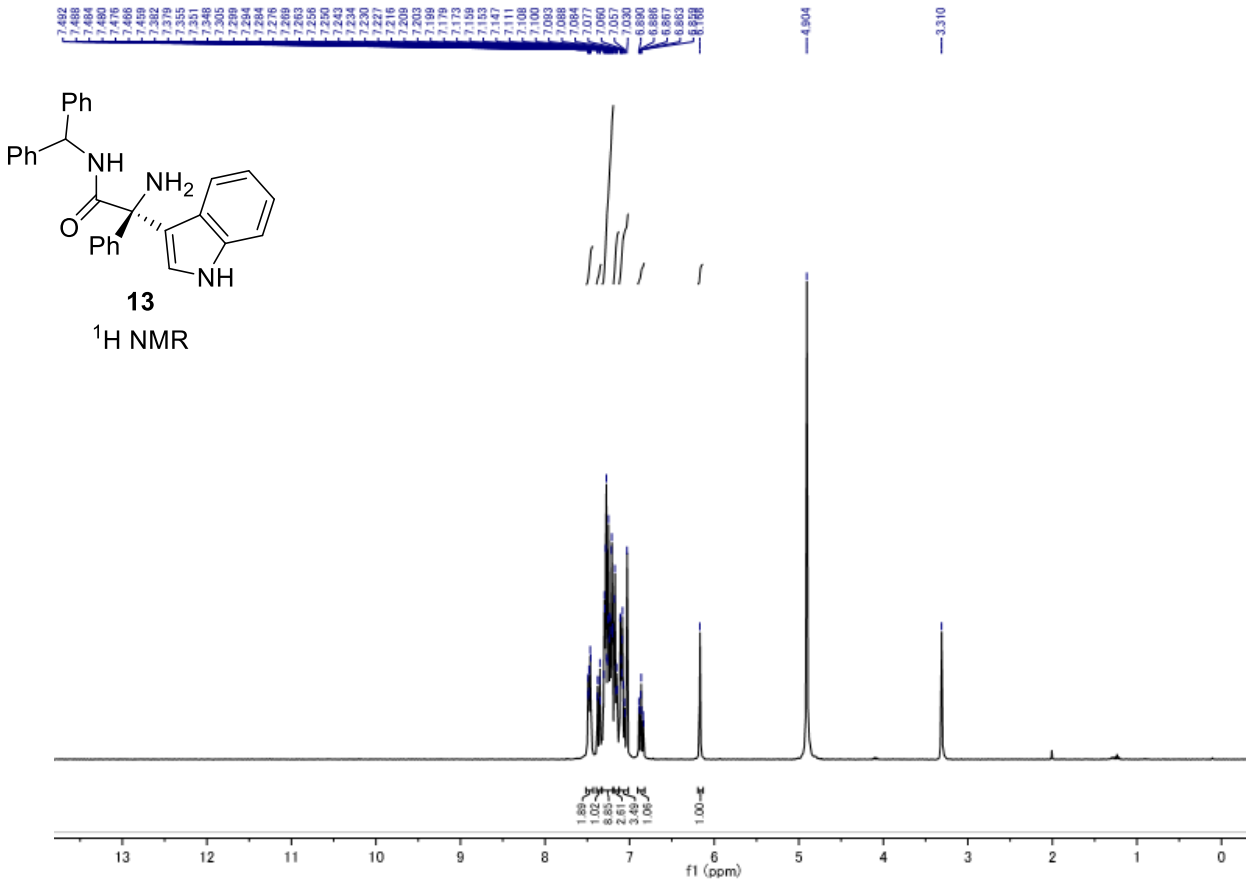


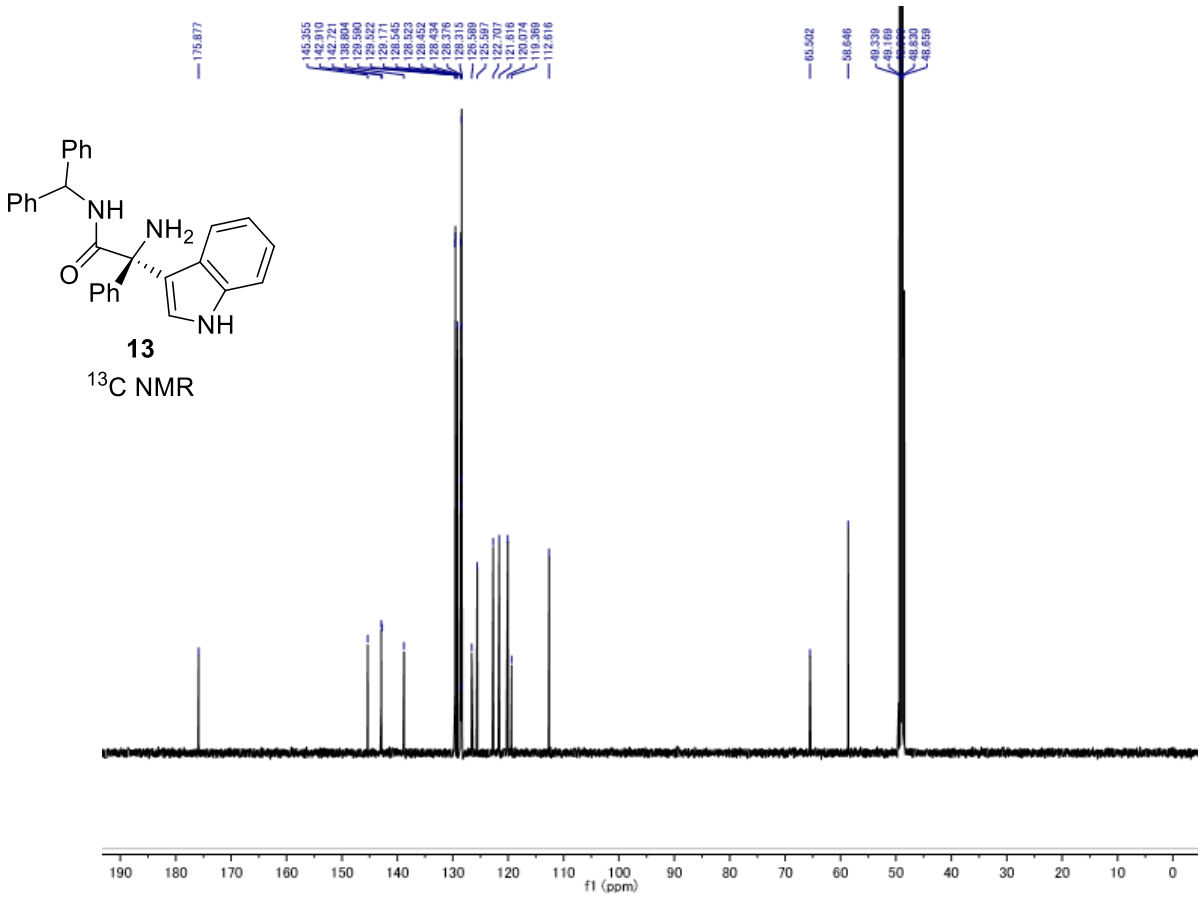


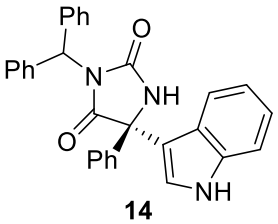
11

^{13}C NMR



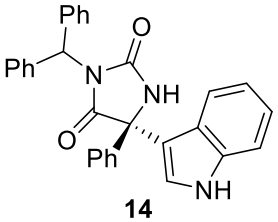

Ph
Ph
NH
NH2
O
Ph
NH
13
1H NMR
4.904
3.310
1.00
f1 (ppm)


Ph
Ph
NH
NH2
O
Ph
NH
13
13C NMR
175.877
65.502
58.646
f1 (ppm)



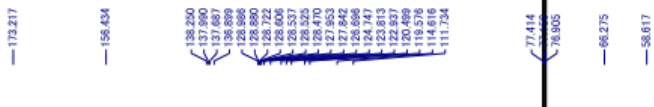
14

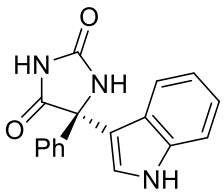
^{1}H NMR



14

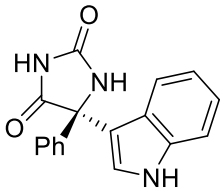
^{13}C NMR





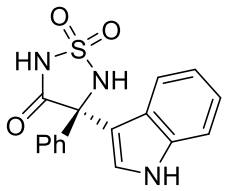
15

^{1}H NMR



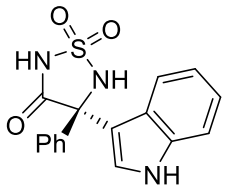
15

^{13}C NMR



16

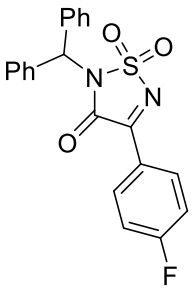
^{1}H NMR



16

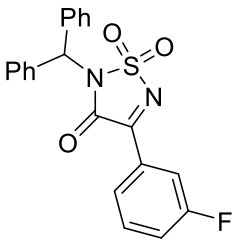
^{1}H NMR

^{19}F NMR



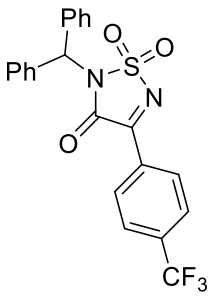
1g

^{19}F NMR



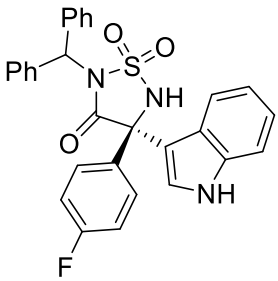
1h

^{19}F NMR



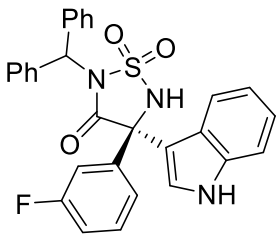
1l

^{19}F NMR



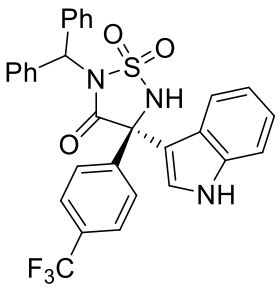
4g

^{19}F NMR



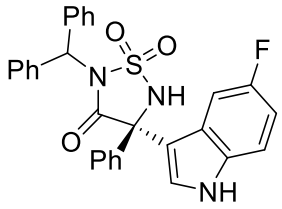
4h

^{19}F NMR



4l

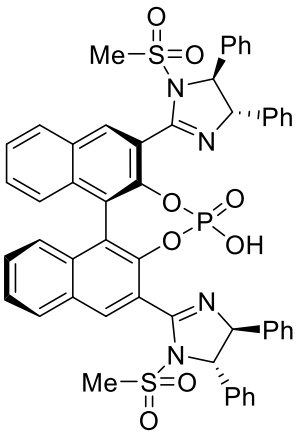
^{19}F NMR



9

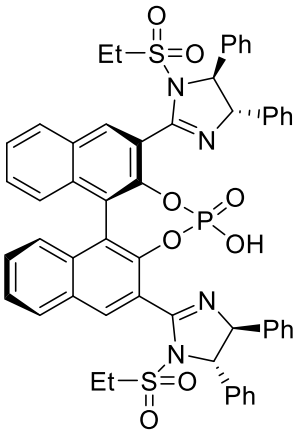
^{19}F NMR

^{31}P NMR



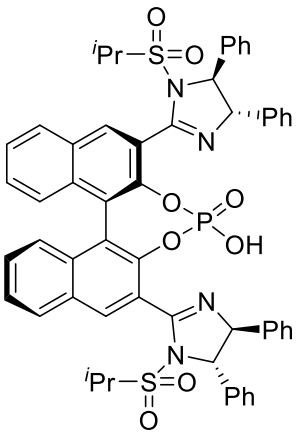
3c

^{31}P NMR



3d

^{31}P NMR

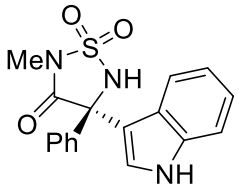


3e

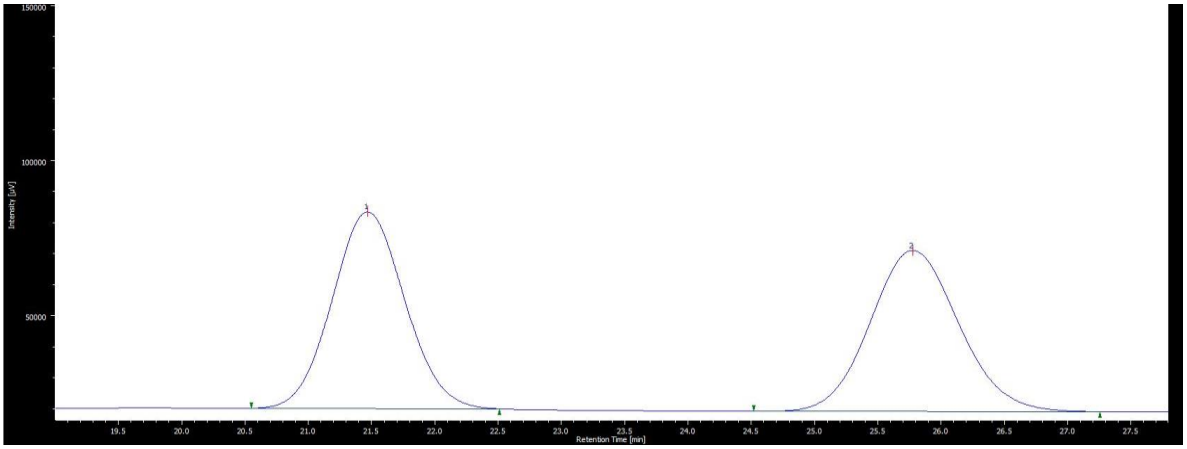
^{31}P NMR

HPLC analysis

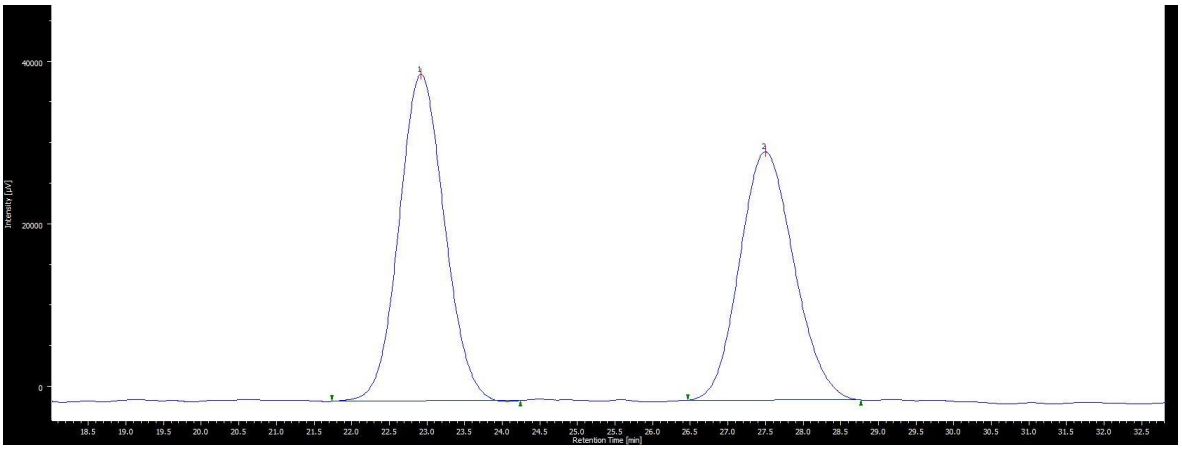
(*R*)-2-Methyl-4-(1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4a)



racemic-4a



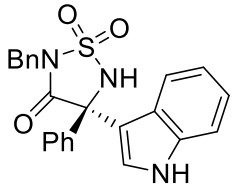
(*R*)-4a



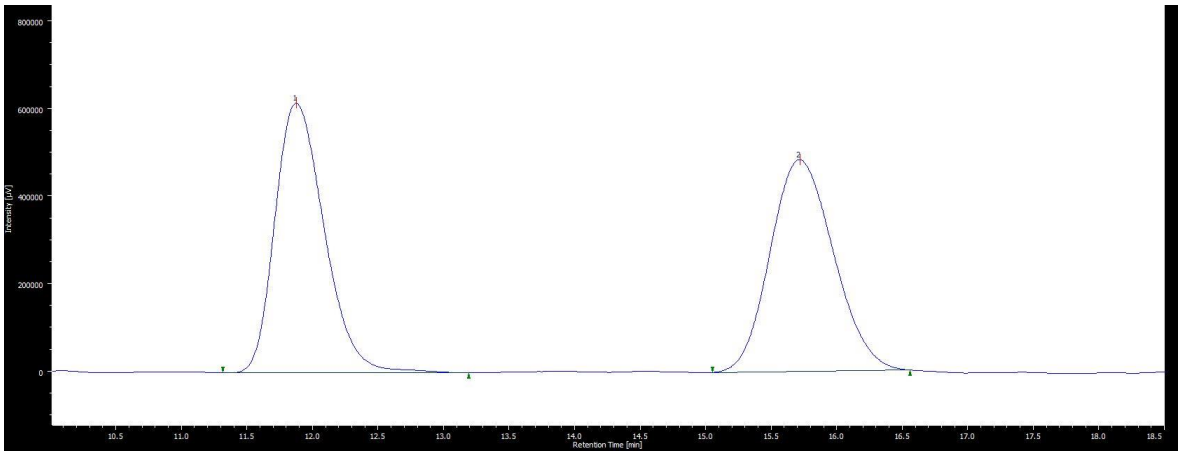
racemic-4a		
Peak	tR (min)	Area (%)
1	21.5	50.1
2	25.8	49.9

(*R*)-4a		
Peak	tR (min)	Area (%)
1	22.9	52.3
2	27.5	47.7

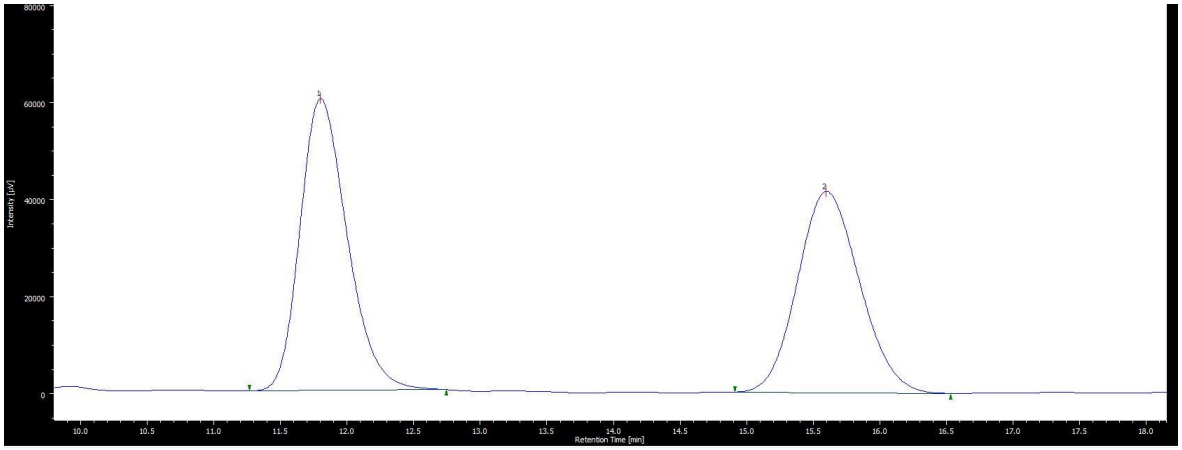
(*R*)-2-Benzyl-4-(1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4b)



racemic-4b



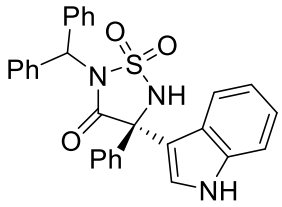
(*R*)-4b



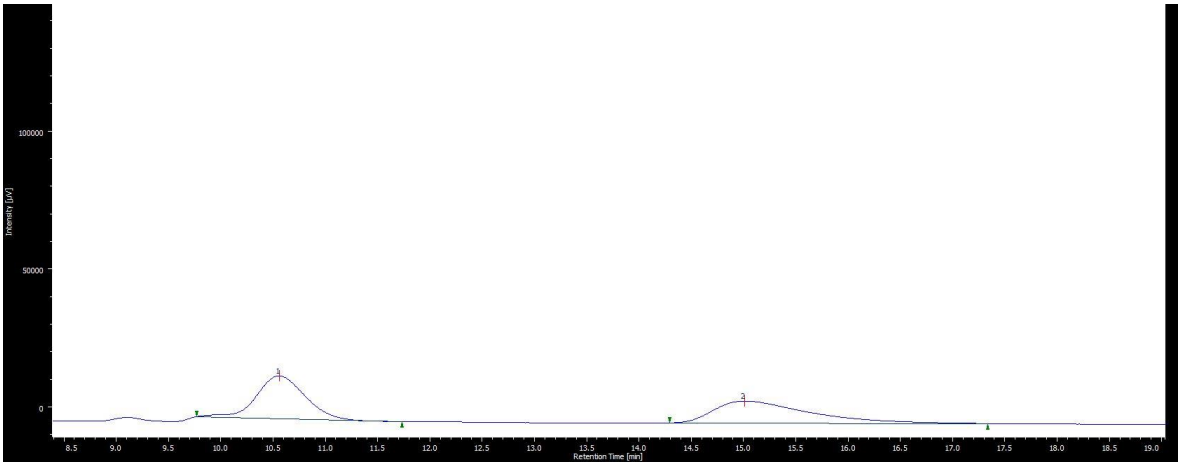
racemic-4b		
Peak	tR (min)	Area (%)
1	11.9	49.9
2	15.7	50.1

(*R*)-4b		
Peak	tR (min)	Area (%)
1	11.8	52.5
2	15.6	47.5

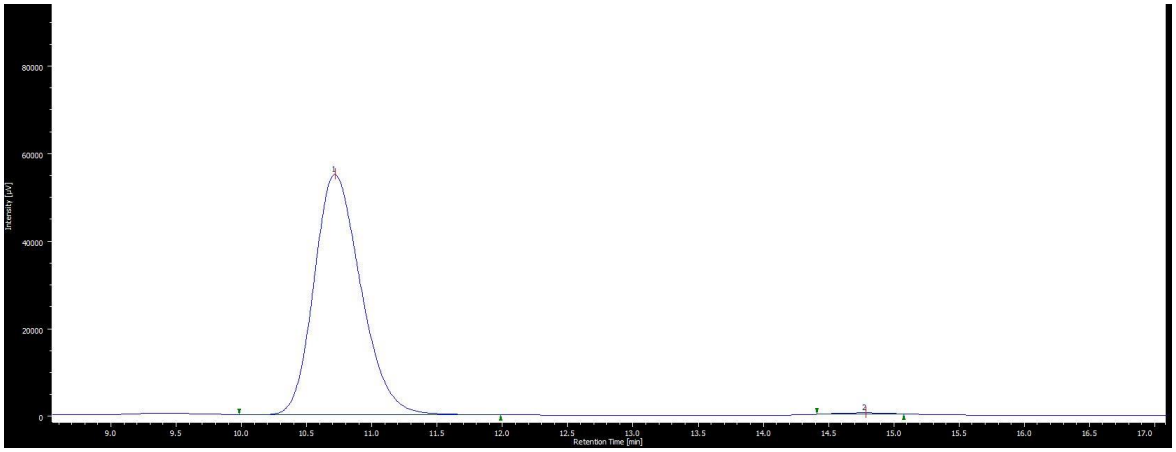
(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4c)



racemic-4c



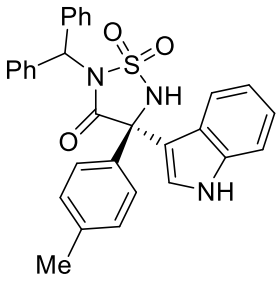
(*R*)-4c



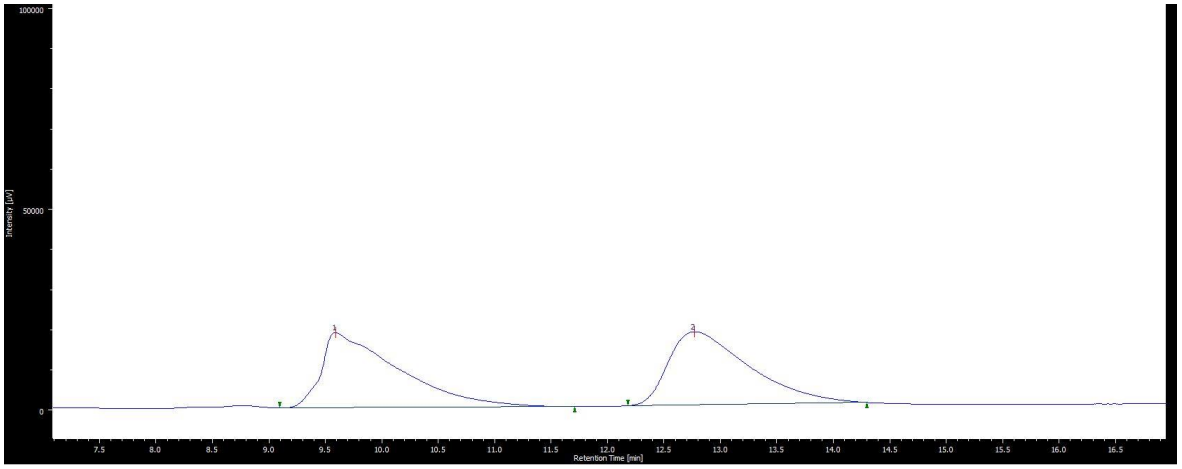
racemic-4c		
Peak	tR (min)	Area (%)
1	10.6	49.7
2	15.0	50.3

(*R*)-4c		
Peak	tR (min)	Area (%)
1	10.7	99.5
2	14.8	0.5

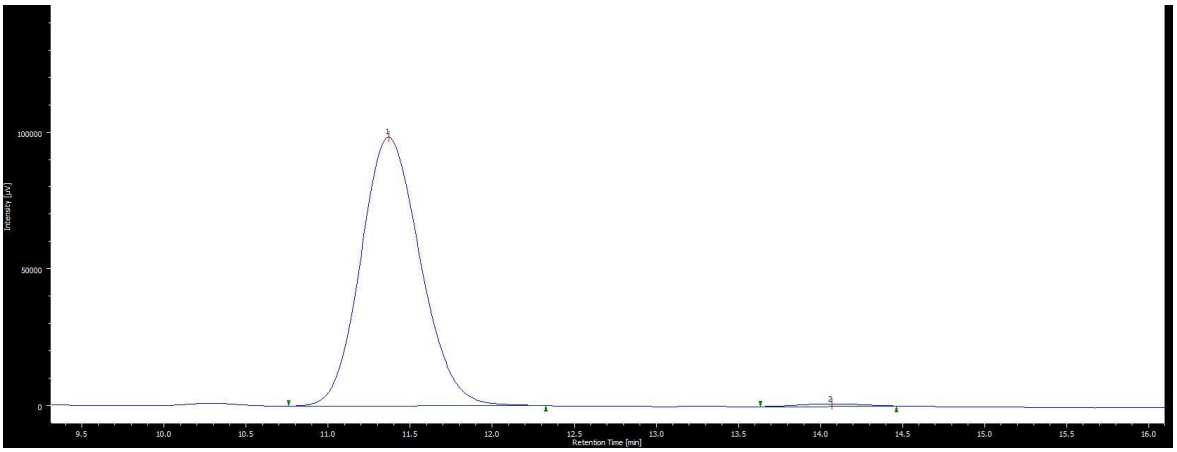
(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-4-(*p*-tolyl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4d)



racemic-4d



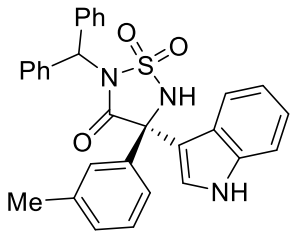
(*R*)-4d



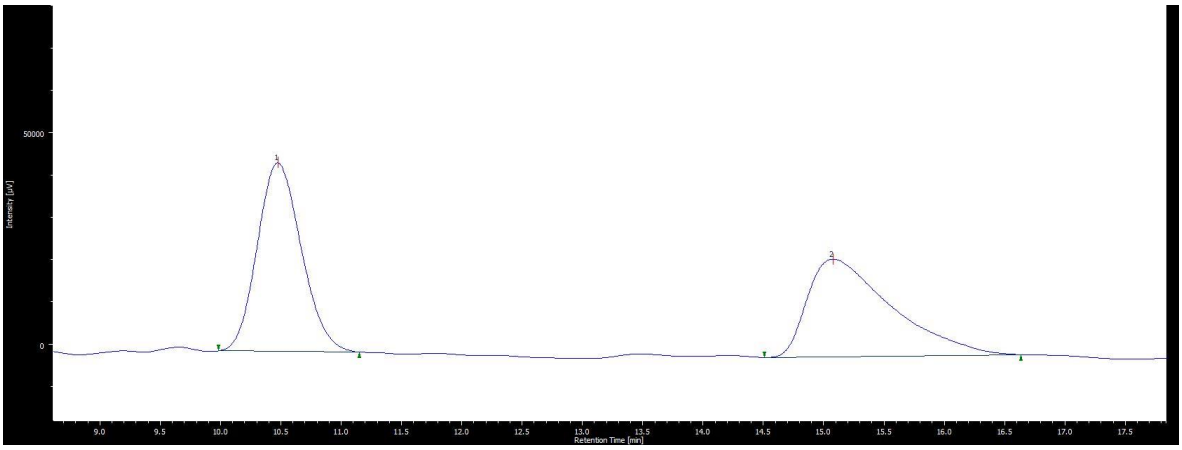
racemic-4d		
Peak	tR (min)	Area (%)
1	9.6	49.5
2	12.8	50.5

(*R*)-4d		
Peak	tR (min)	Area (%)
1	11.4	99.1
2	14.1	0.9

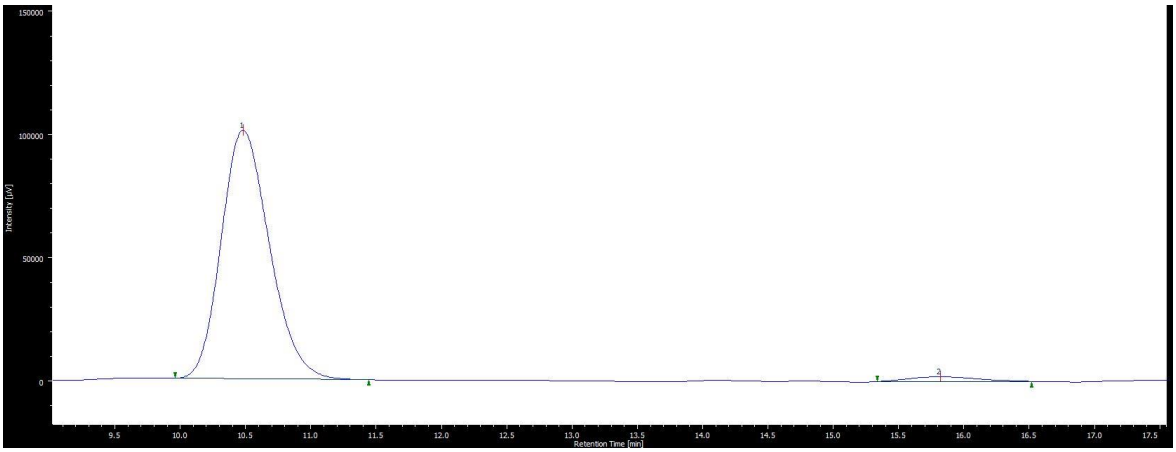
(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-3-(4-methylphenyl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4e)



racemic-4e



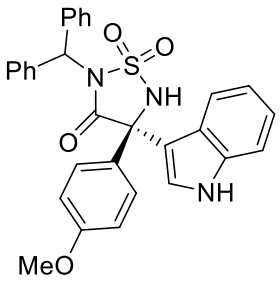
(*R*)-4e



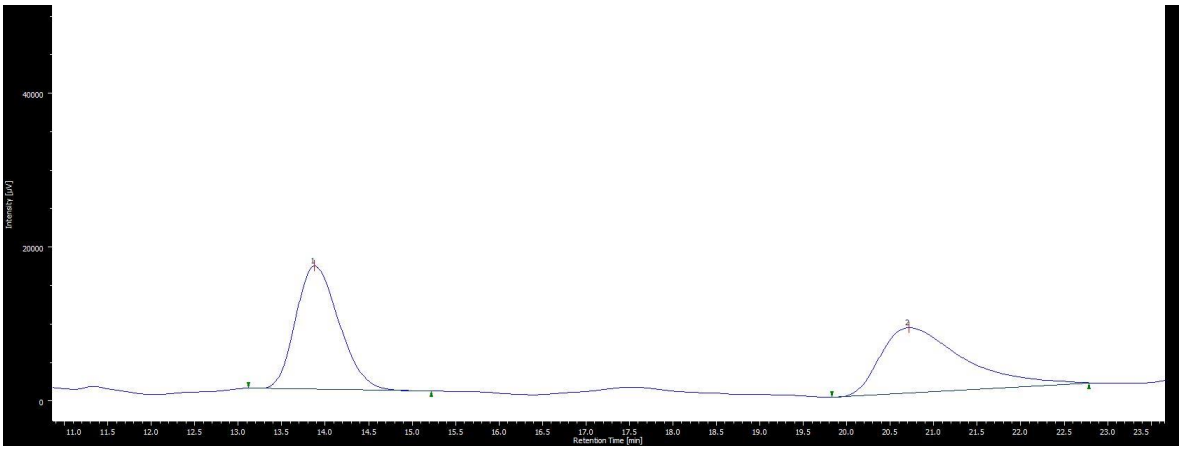
racemic-4e		
Peak	tR (min)	Area (%)
1	10.5	50.4
2	15.1	49.6

(*R*)-4e		
Peak	tR (min)	Area (%)
1	10.5	97.4
2	15.8	2.6

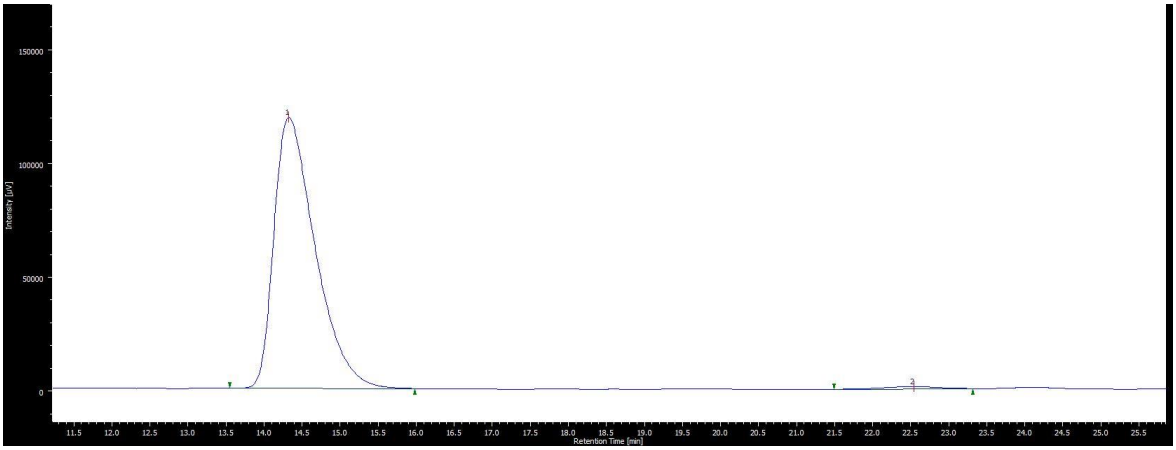
(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4f)



racemic-4f



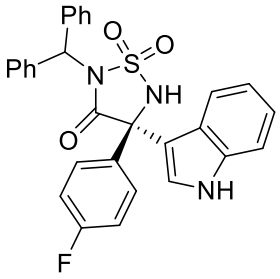
(*R*)-4f



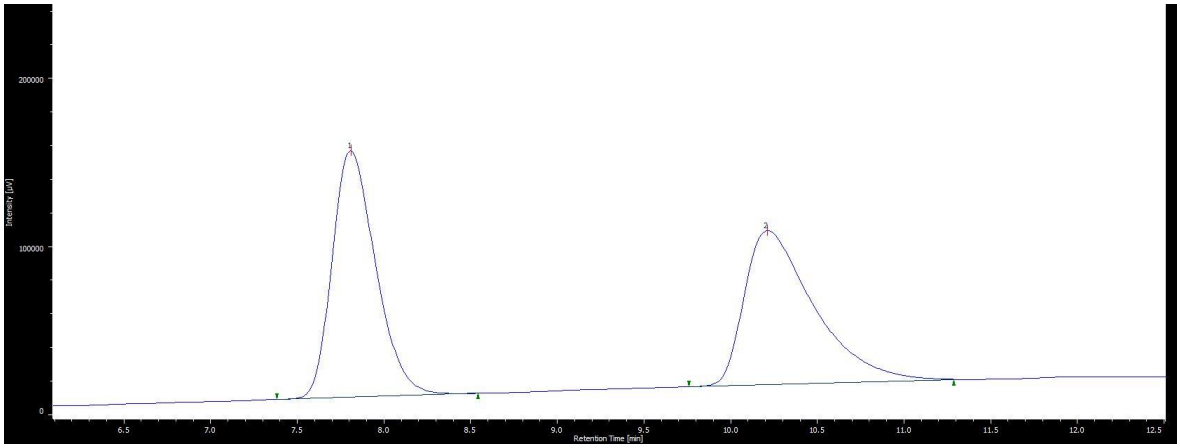
racemic-4f		
Peak	tR (min)	Area (%)
1	13.9	49.8
2	20.7	50.2

(*R*)-4f		
Peak	tR (min)	Area (%)
1	14.3	98.9
2	22.5	1.1

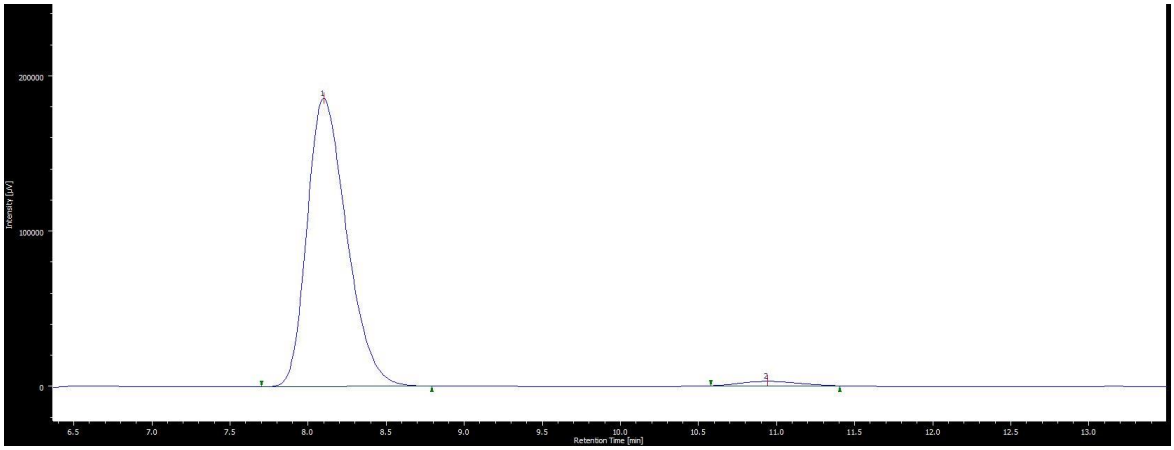
(*R*)-2-Benzhydryl-4-(4-fluorophenyl)-4-(1*H*-indol-3-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4g)



racemic-4g



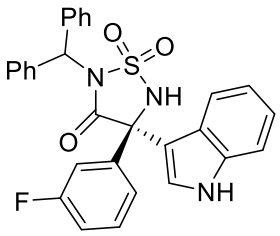
(*R*)-4g



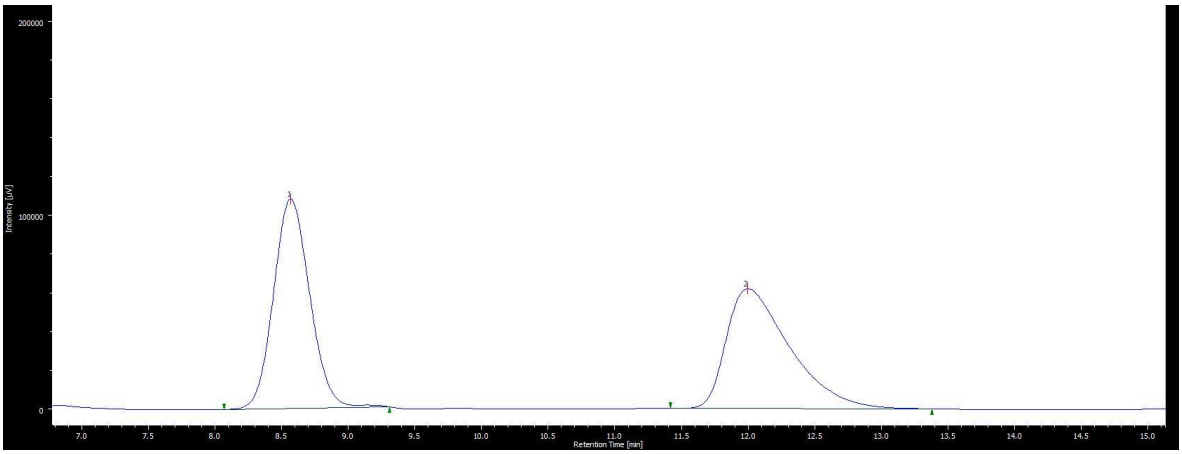
racemic-4g		
Peak	tR (min)	Area (%)
1	7.8	50.0
2	10.2	50.0

(*R*)-4g		
Peak	tR (min)	Area (%)
1	8.1	97.8
2	10.9	2.2

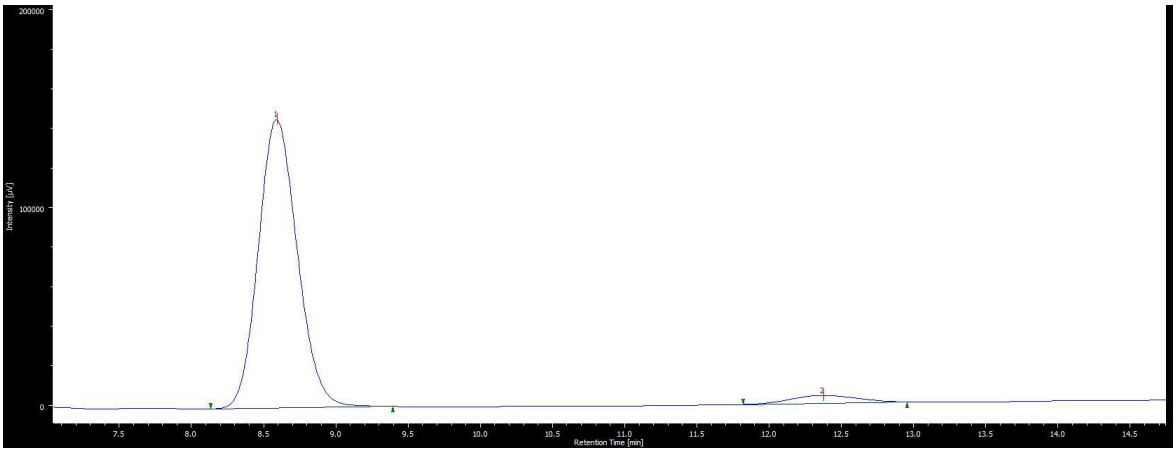
(*R*)-2-Benzhydryl-4-(4-fluorophenyl)-4-(1*H*-indol-3-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4h)



racemic-4h



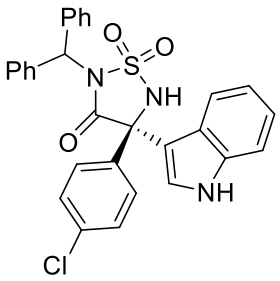
(*R*)-4h



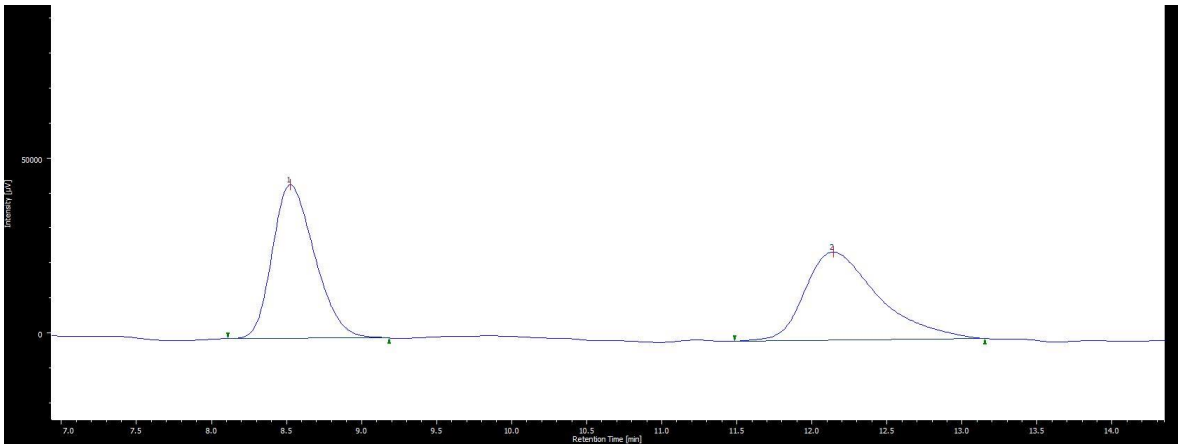
racemic-4h		
Peak	tR (min)	Area (%)
1	8.6	50.1
2	12.0	49.9

(*R*)-4h		
Peak	tR (min)	Area (%)
1	8.6	95.6
2	12.4	4.4

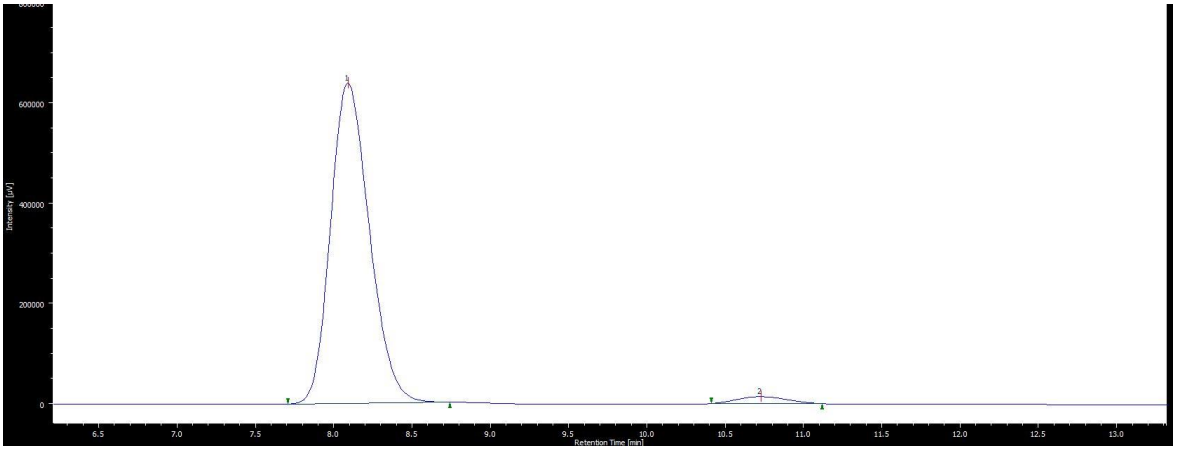
(*R*)-2-Benzhydryl-4-(4-chlorophenyl)-4-(1*H*-indol-3-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4i)



racemic-4i



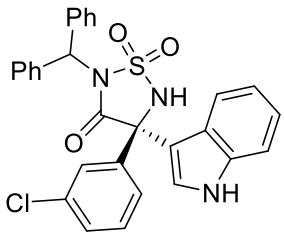
(*R*)-4i



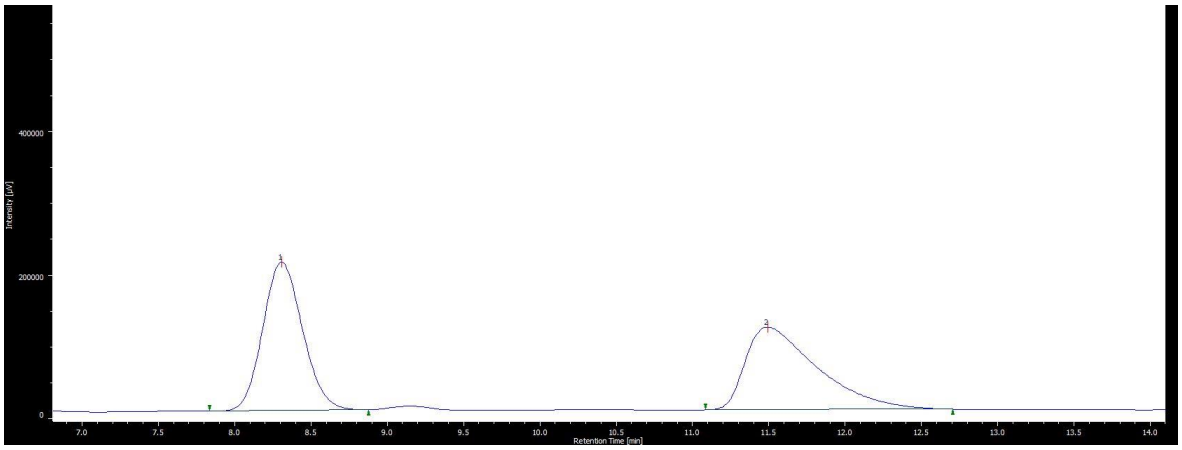
racemic-4i		
Peak	tR (min)	Area (%)
1	8.5	50.2
2	12.1	49.8

(*R*)-4i		
Peak	tR (min)	Area (%)
1	8.1	97.3
2	10.7	2.7

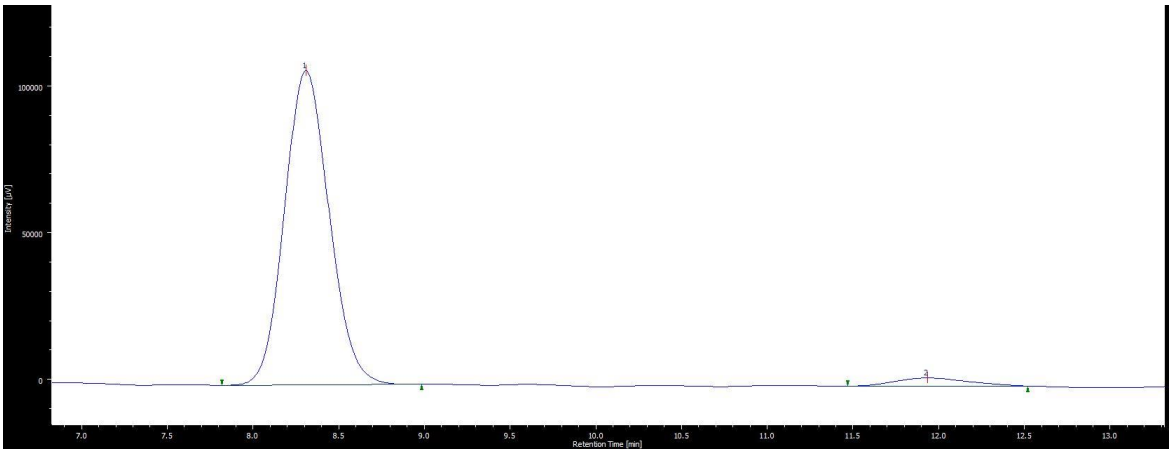
(*R*)-2-Benzhydryl-4-(3-chlorophenyl)-4-(1*H*-indol-3-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4j)



racemic-4j



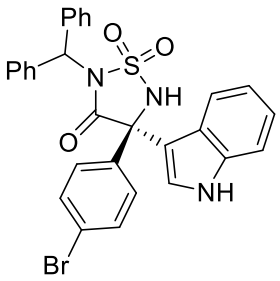
(*R*)-4j



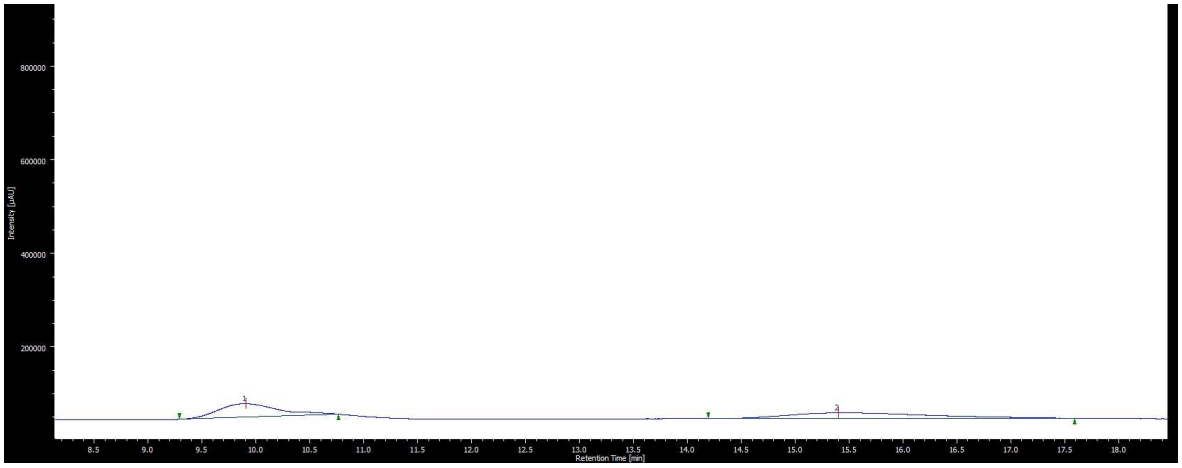
racemic-4j		
Peak	tR (min)	Area (%)
1	8.3	50.0
2	11.5	50.0

(*R*)-4j		
Peak	tR (min)	Area (%)
1	8.3	97.5
2	11.9	2.5

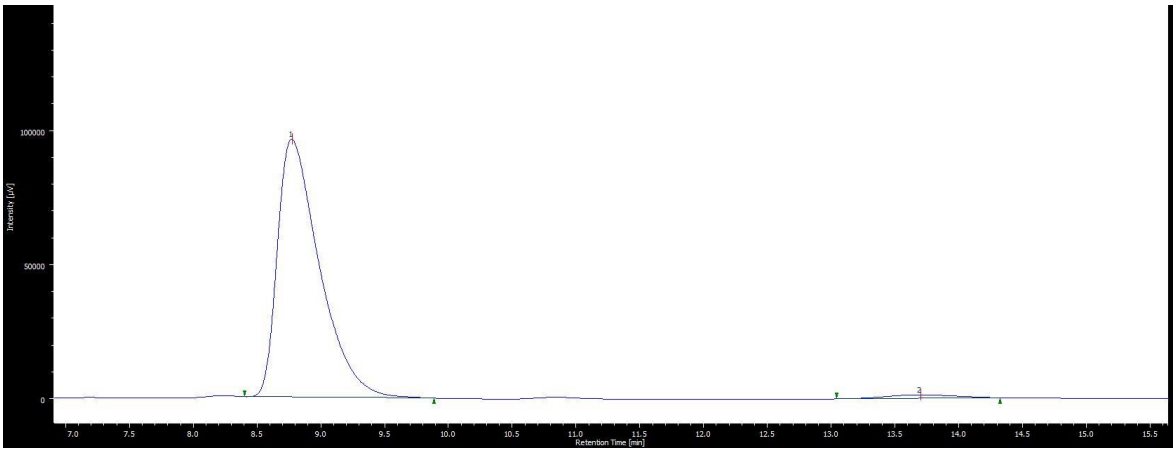
(*R*)-2-Benzhydryl-4-(4-bromophenyl)-4-(1*H*-indol-3-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4k)



racemic-4k



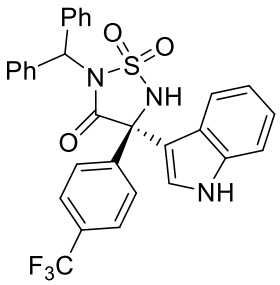
(*R*)-4k



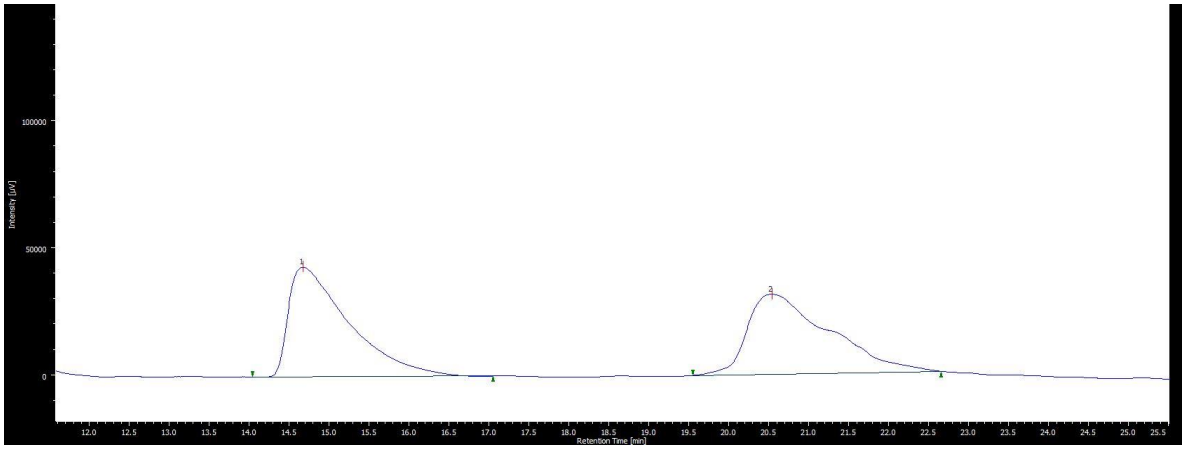
racemic-4k		
Peak	tR (min)	Area (%)
1	9.9	50.1
2	15.4	49.9

(*R*)-4k		
Peak	tR (min)	Area (%)
1	8.8	97.8
2	13.7	2.2

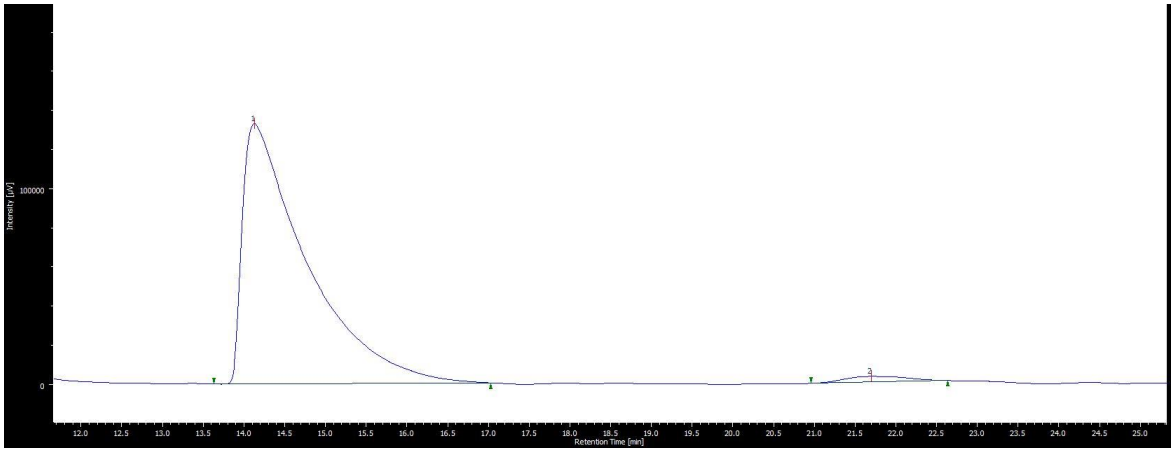
(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-4-[4-(trifluoromethyl)phenyl]-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4l)



racemic-4l



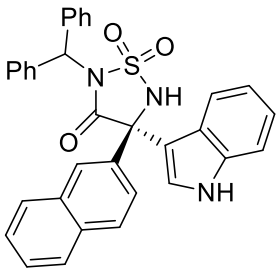
(*R*)-4l



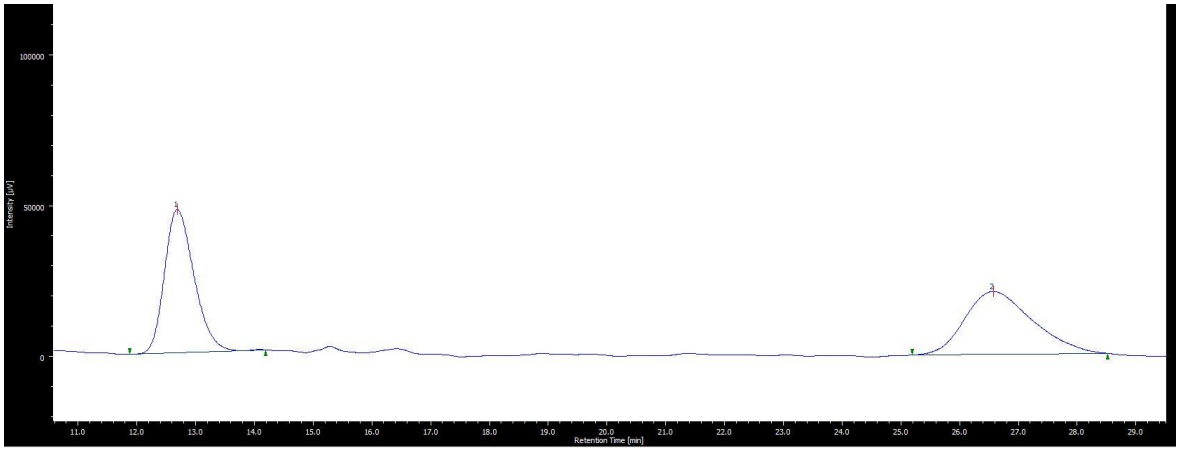
racemic-4l		
Peak	tR (min)	Area (%)
1	14.7	50.2
2	20.5	49.8

(*R*)-4l		
Peak	tR (min)	Area (%)
1	14.1	97.9
2	21.7	2.1

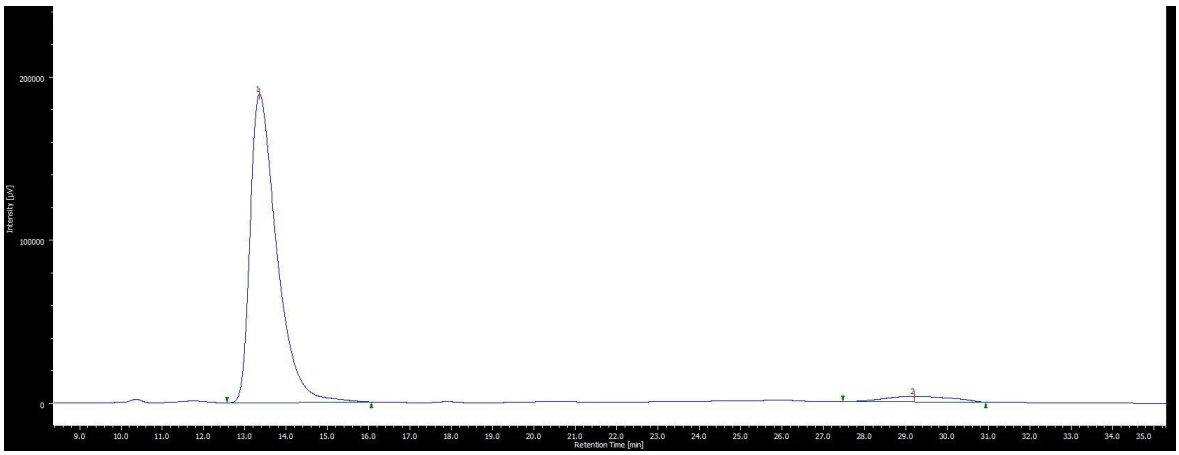
(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-4-(naphthalen-2-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4m)



racemic-4m



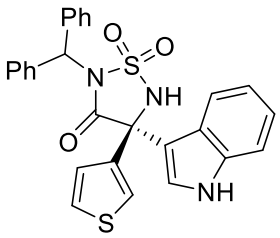
(*R*)-4m



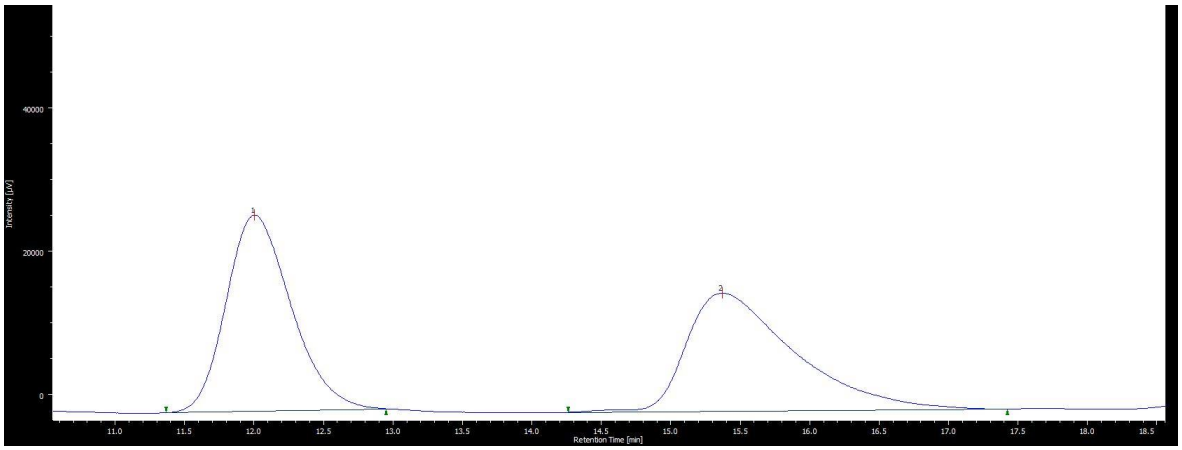
racemic-4m		
Peak	tR (min)	Area (%)
1	12.7	49.9
2	26.6	50.1

(*R*)-4m		
Peak	tR (min)	Area (%)
1	13.4	95.7
2	29.2	4.3

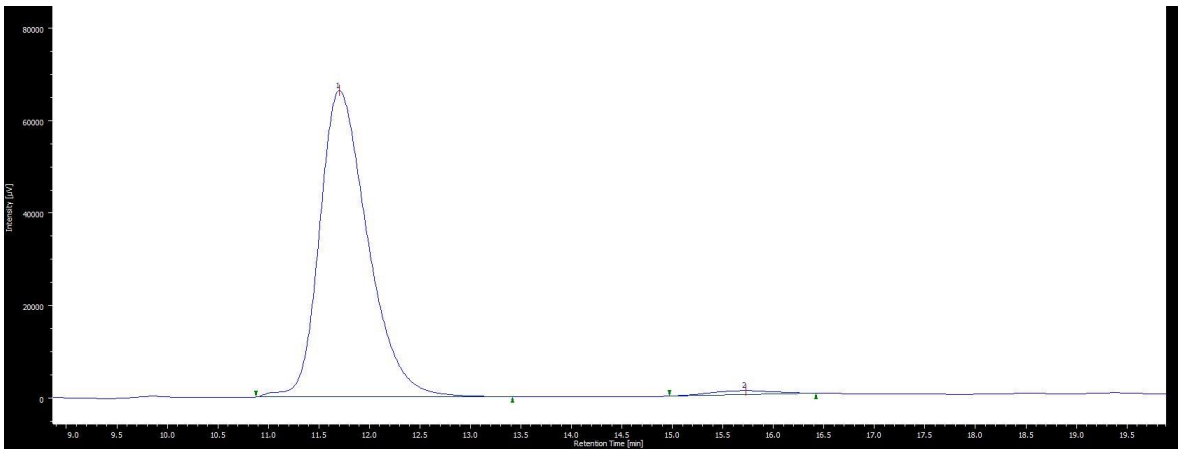
(*R*)-2-Benzhydryl-4-(1*H*-indol-3-yl)-4-(thiophen-3-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (4n)



racemic-4n



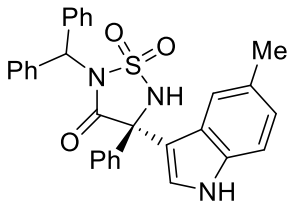
(*R*)-4n



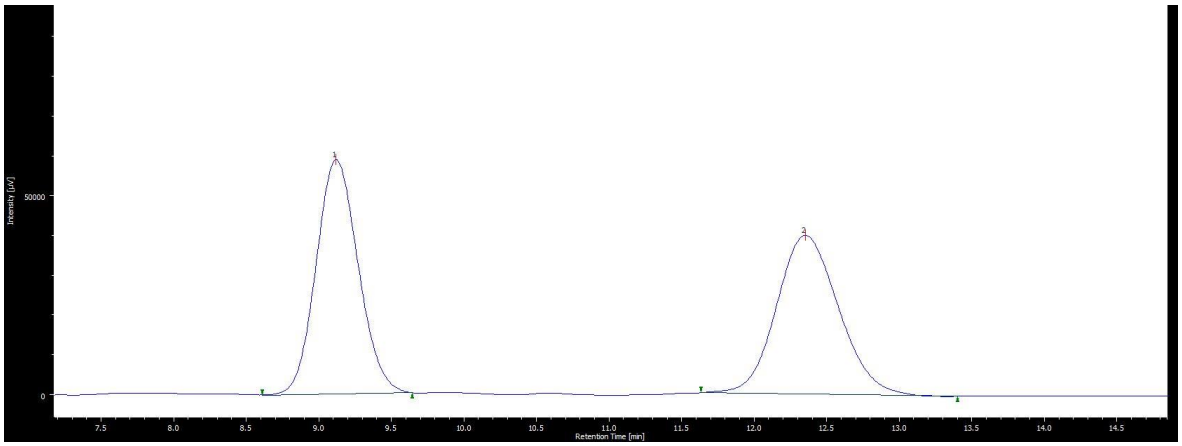
racemic-4n		
Peak	tR (min)	Area (%)
1	12.0	50.0
2	15.4	50.0

(*R*)-4n		
Peak	tR (min)	Area (%)
1	11.7	98.3
2	15.7	1.7

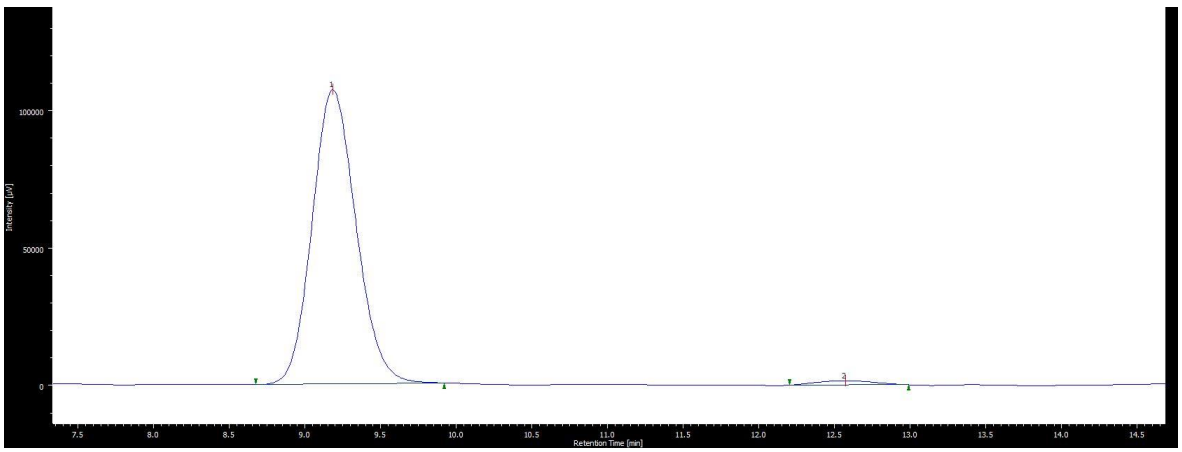
(*R*)-2-Benzhydryl-4-(5-methyl-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (5)



racemic-5



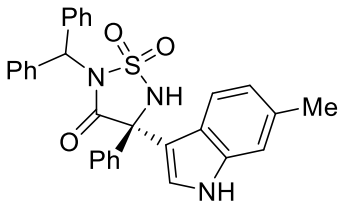
(*R*)-5



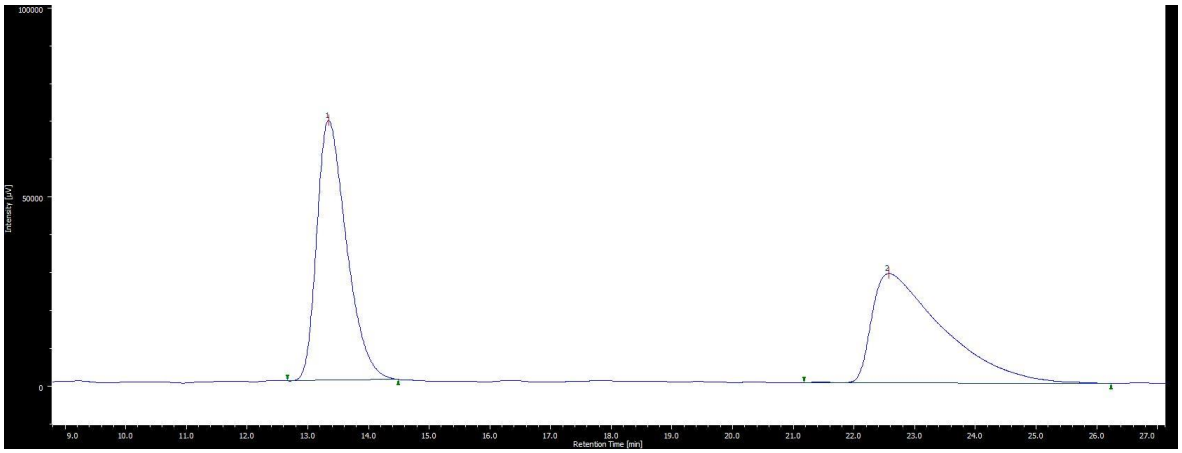
racemic-5		
Peak	tR (min)	Area (%)
1	9.1	50.0
2	12.4	50.0

(*R*)-5		
Peak	tR (min)	Area (%)
1	9.2	98.1
2	12.6	1.9

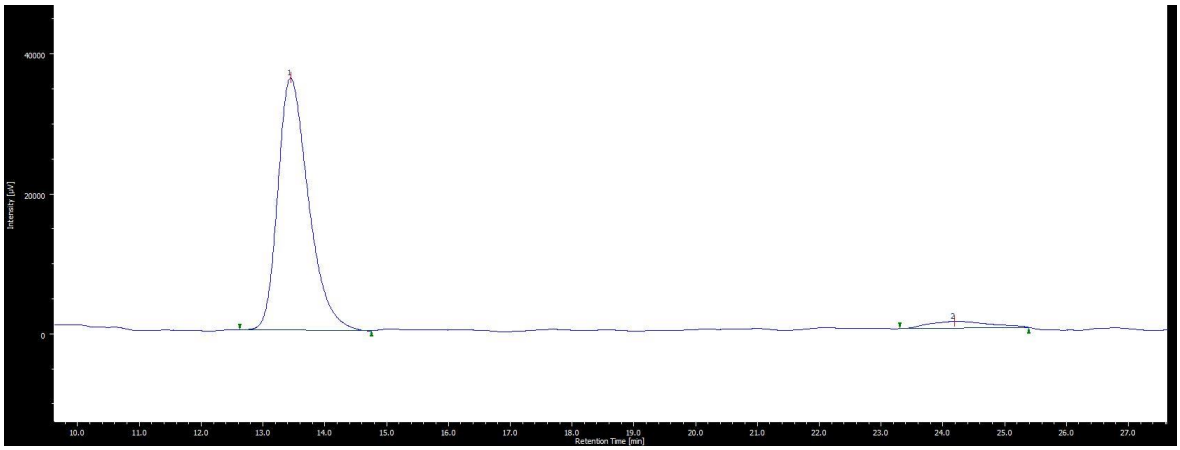
(*R*)-2-Benzhydryl-4-(6-methyl-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (6)



racemic-6



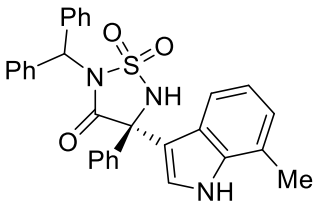
(*R*)-6



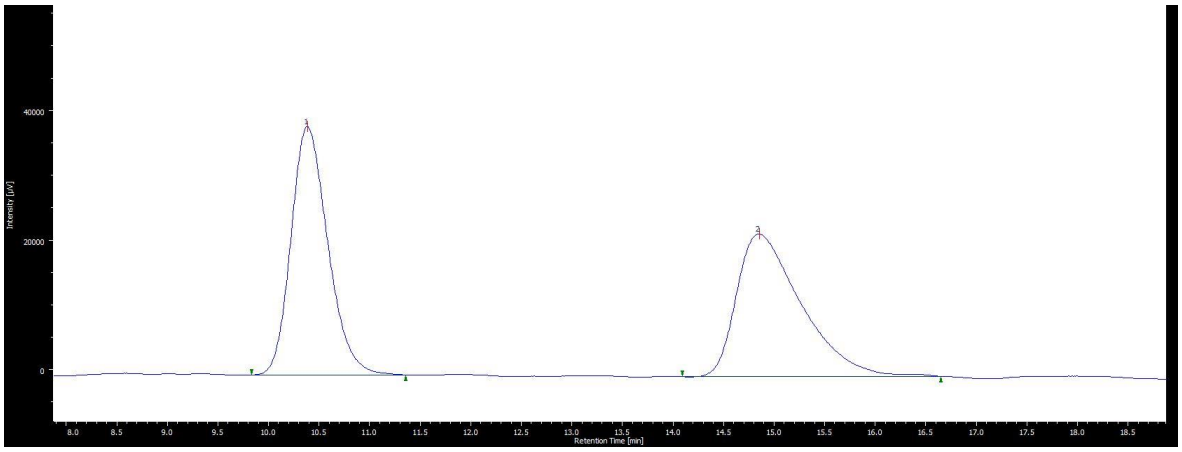
racemic-6		
Peak	tR (min)	Area (%)
1	13.3	50.1
2	22.6	49.9

(*R*)-6		
Peak	tR (min)	Area (%)
1	13.5	95.0
2	24.2	5.0

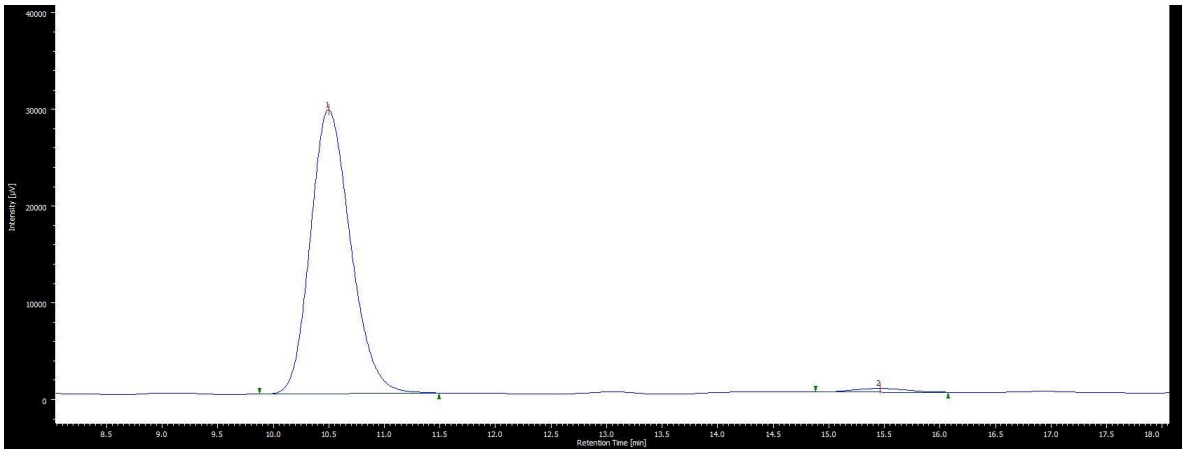
(*R*)-2-Benzhydryl-4-(7-methyl-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (7)



racemic-7



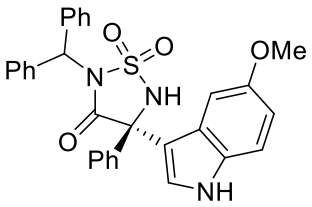
(*R*)-7



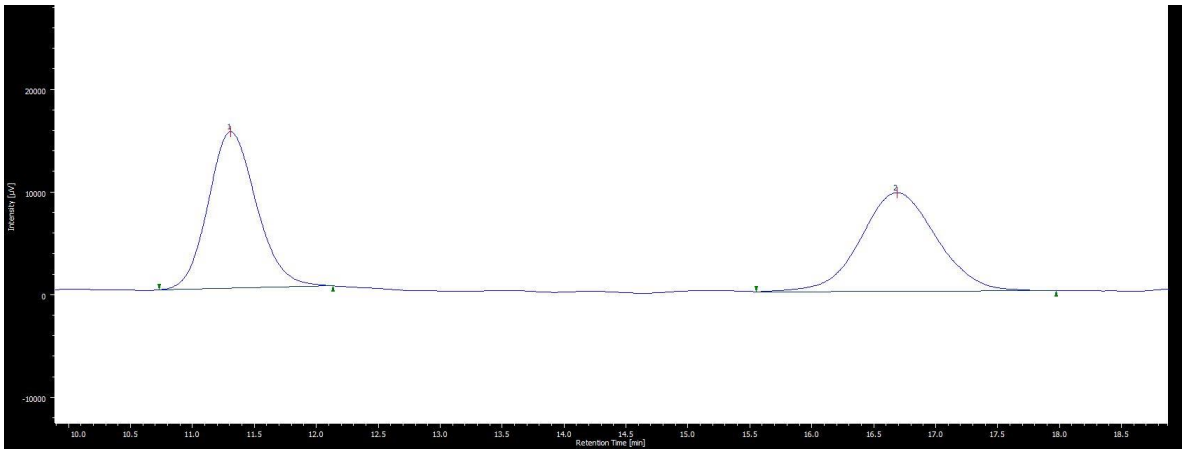
racemic-7		
Peak	tR (min)	Area (%)
1	10.4	49.9
2	14.9	50.1

(*R*)-7		
Peak	tR (min)	Area (%)
1	10.5	98.4
2	15.5	1.6

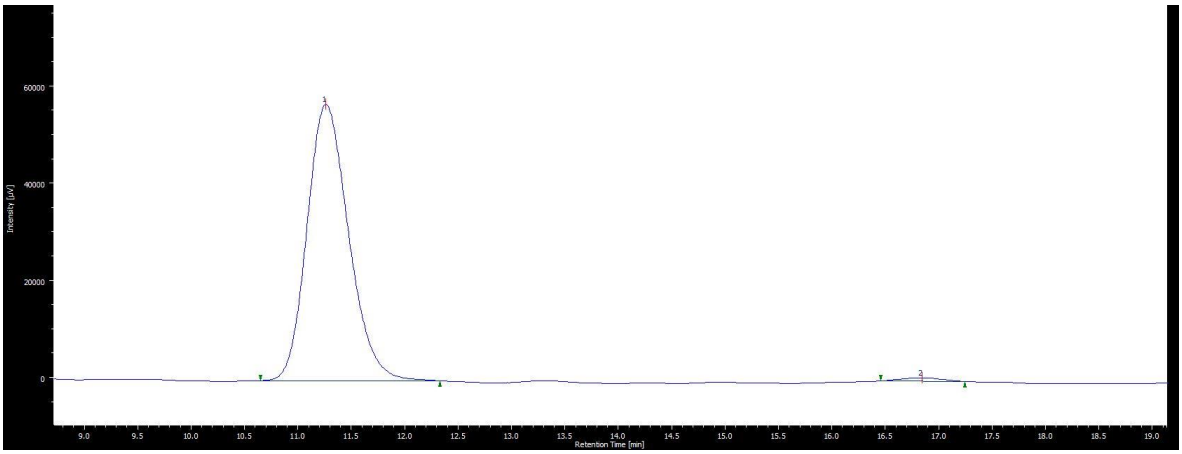
(*R*)-2-Benzhydryl-4-(5-methoxy-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (8)



racemic-8



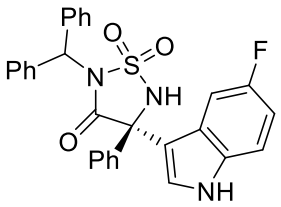
(*R*)-8



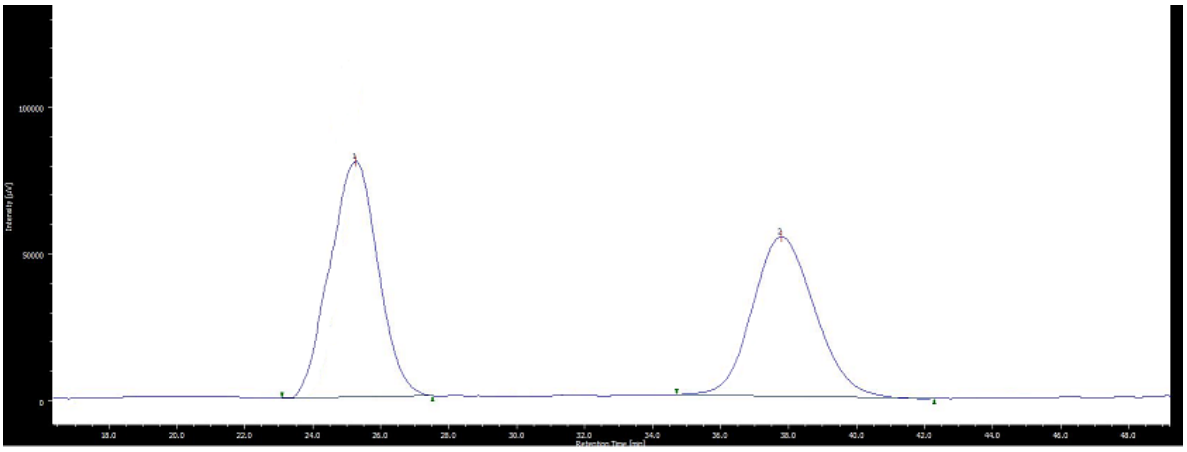
racemic-8		
Peak	tR (min)	Area (%)
1	11.3	50.2
2	16.7	49.8

(*R*)-8		
Peak	tR (min)	Area (%)
1	11.3	98.8
2	16.8	1.2

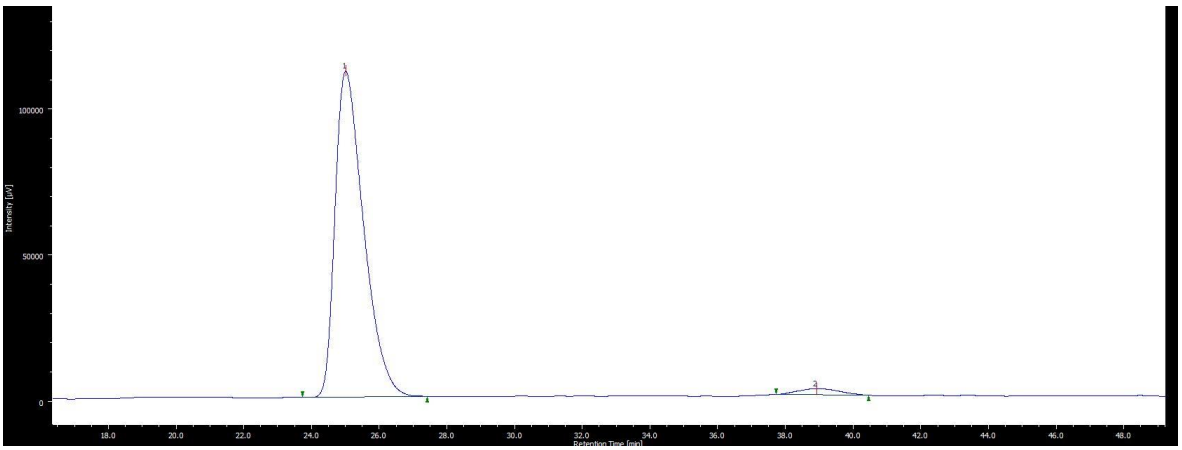
(*R*)-2-Benzhydryl-4-(5-fluoro-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (9)



racemic-9



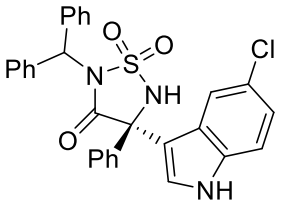
(*R*)-9



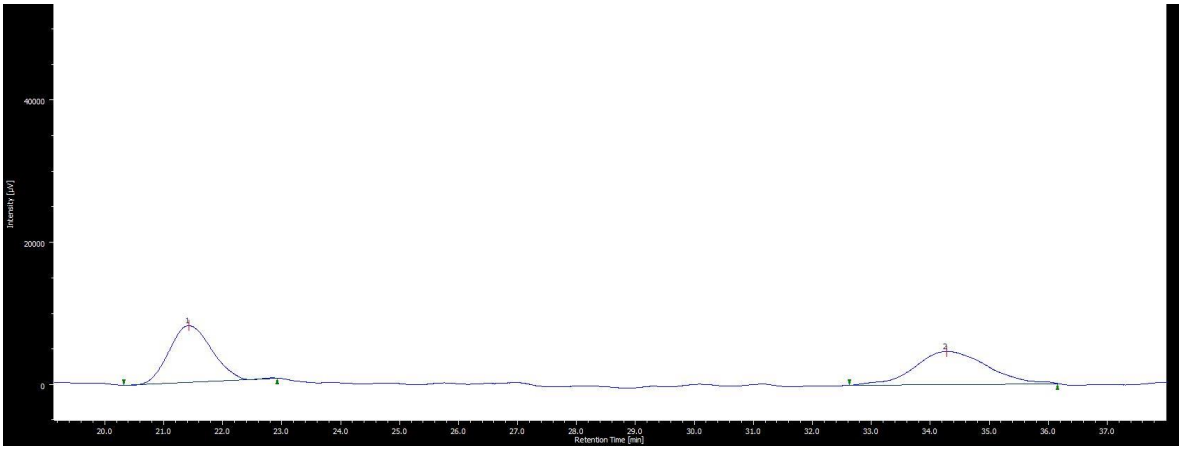
racemic-9		
Peak	tR (min)	Area (%)
1	24.6	50.4
2	38.0	49.6

(*R*)-9		
Peak	tR (min)	Area (%)
1	25.0	97.3
2	38.9	2.7

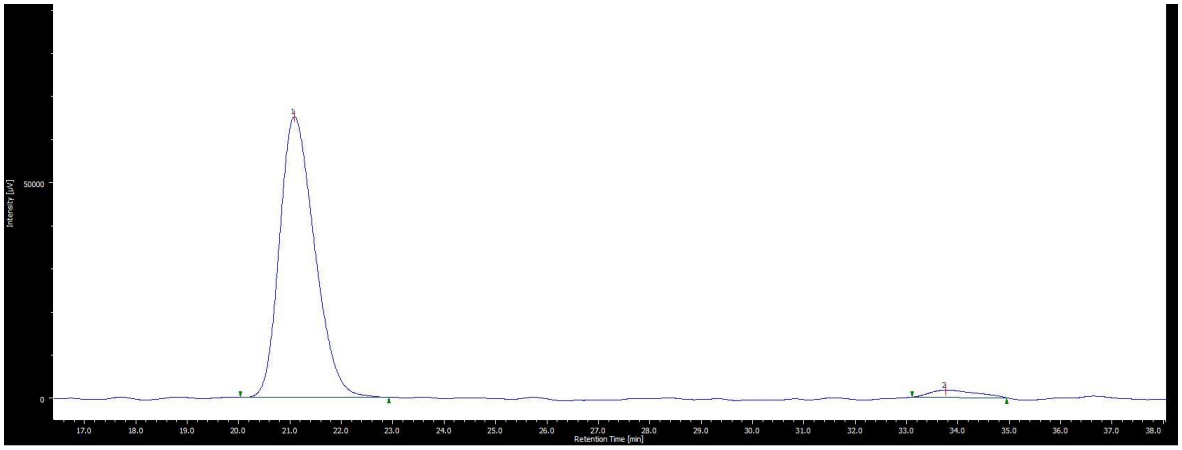
(*R*)-2-Benzhydryl-4-(5-chloro-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (10)



racemic-10



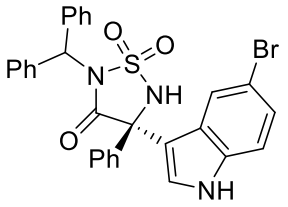
(*R*)-10



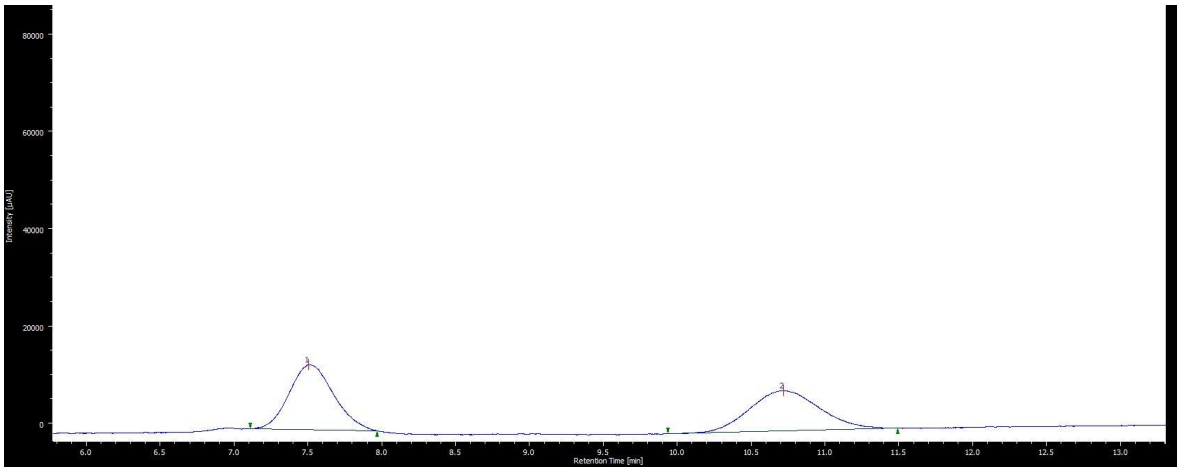
racemic-10		
Peak	tR (min)	Area (%)
1	21.4	49.9
2	34.3	50.1

(*R*)-10		
Peak	tR (min)	Area (%)
1	21.1	96.6
2	33.8	3.4

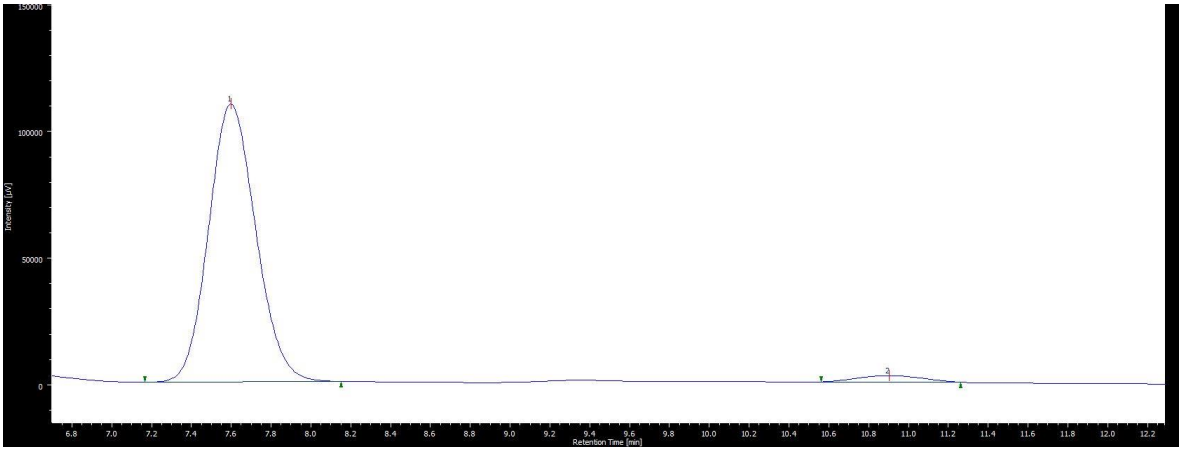
(*R*)-2-Benzhydryl-4-(5-bromo-1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (11)



racemic-11



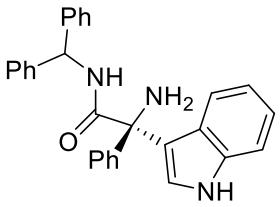
(*R*)-11



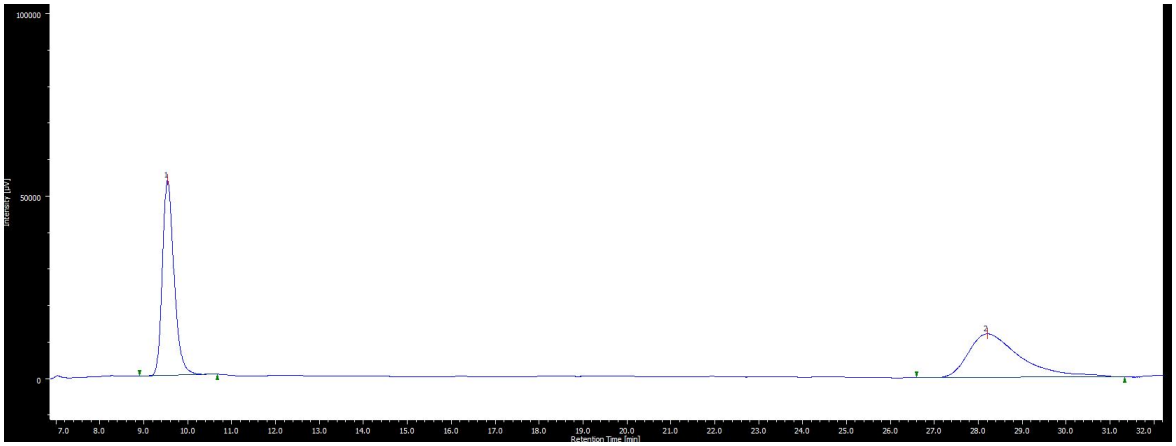
racemic-11		
Peak	tR (min)	Area (%)
1	7.5	50.5
2	10.7	49.5

(*R*)-11		
Peak	tR (min)	Area (%)
1	7.6	96.1
2	10.9	3.1

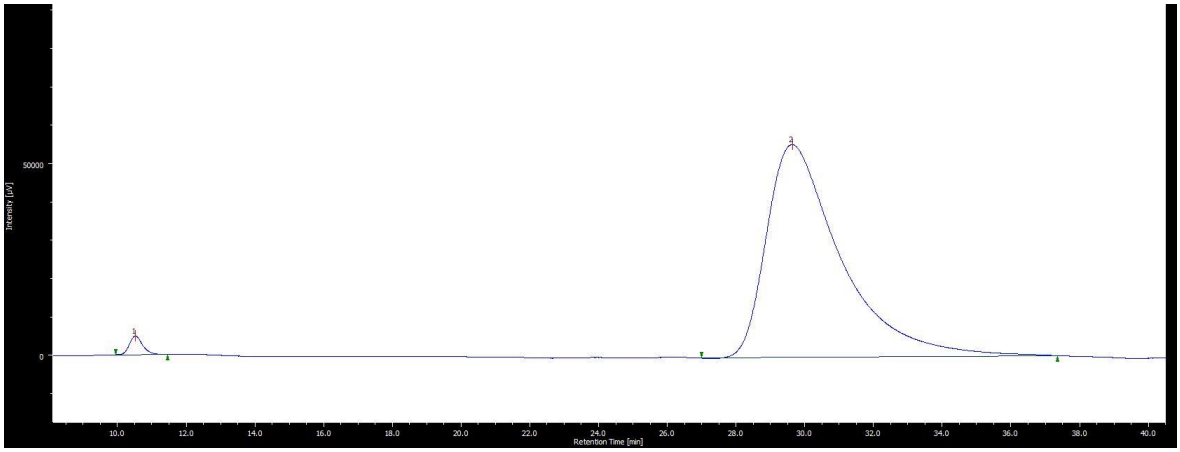
(*R*)-2-Amino-*N*-benzhydryl-2-(1*H*-indol-3-yl)-2-phenylacetamide (13)



racemic-13



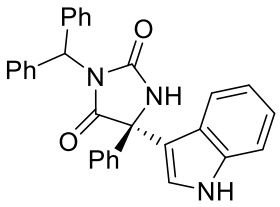
(*R*)-13



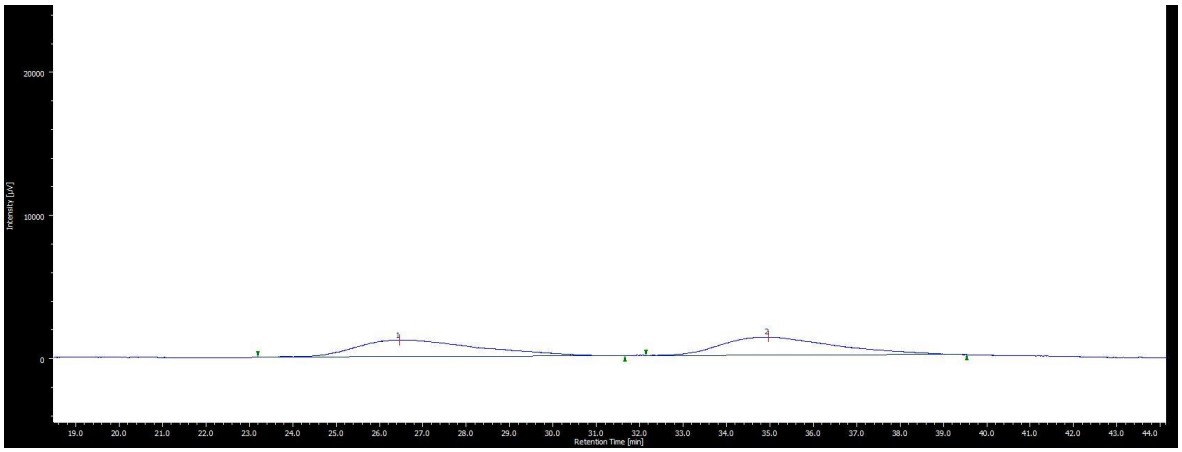
racemic-13		
Peak	tR (min)	Area (%)
1	9.2	50.2
2	28.2	49.8

(*R*)-13		
Peak	tR (min)	Area (%)
1	10.6	1.5
2	29.7	98.5

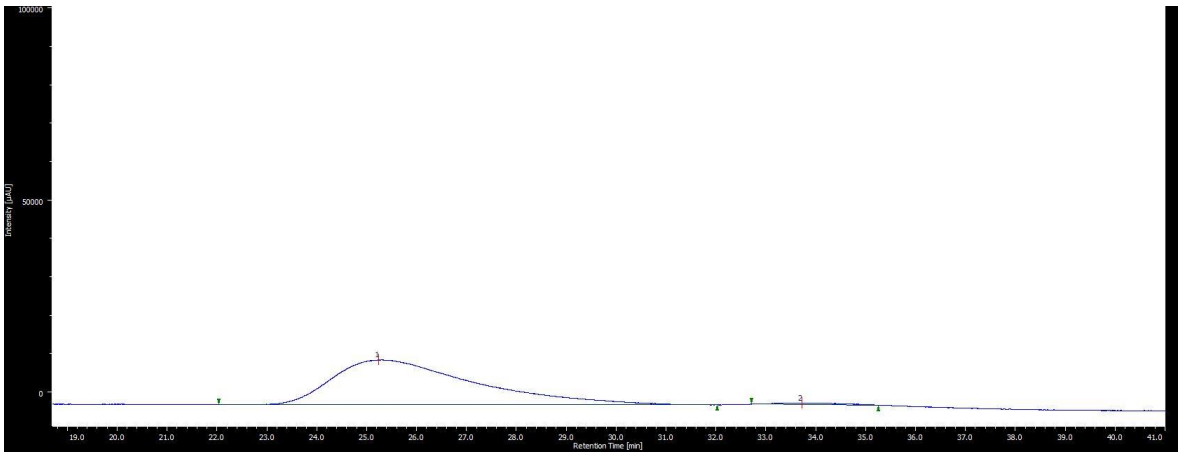
(*R*)-3-Benzhydryl-5-(1*H*-indol-3-yl)-5-phenylimidazolidine-2,4-dione (14)



racemic-14



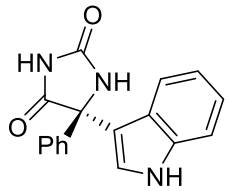
(*R*)-14



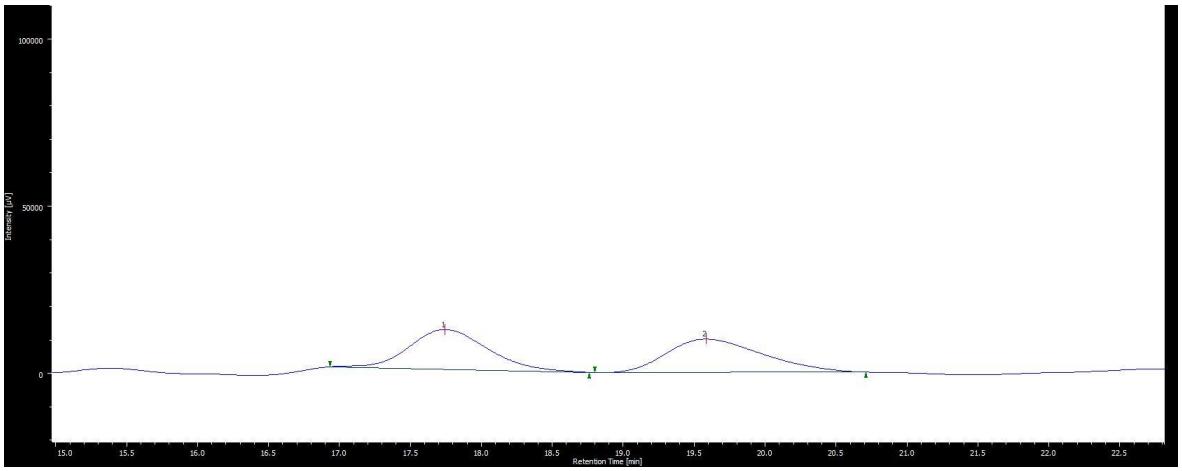
racemic-14		
Peak	tR (min)	Area (%)
1	26.5	49.5
2	35.0	50.5

(*R*)-14		
Peak	tR (min)	Area (%)
1	25.2	98.5
2	35.0	1.5

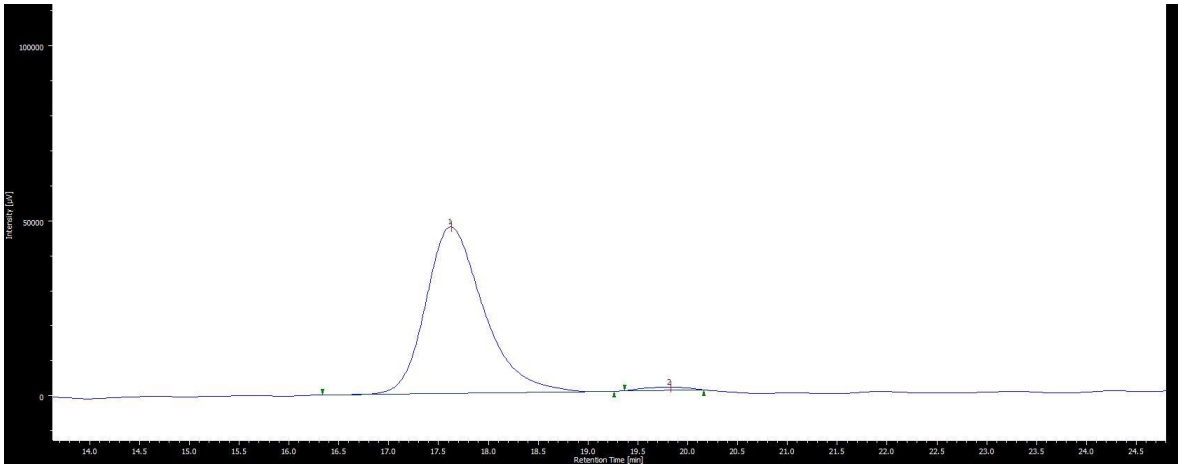
(*R*)-5-(1*H*-indol-3-yl)-5-phenylimidazolidine-2,4-dione (15)



racemic-15



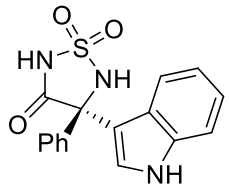
(*R*)-15



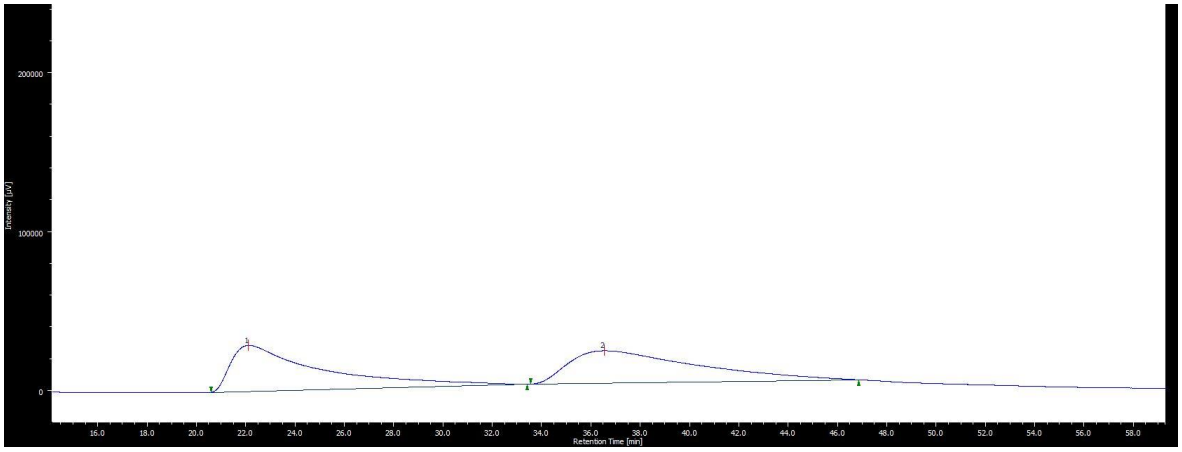
racemic-15		
Peak	tR (min)	Area (%)
1	17.7	49.5
2	19.6	50.5

(*R*)-15		
Peak	tR (min)	Area (%)
1	17.6	98.6
2	19.8	1.3

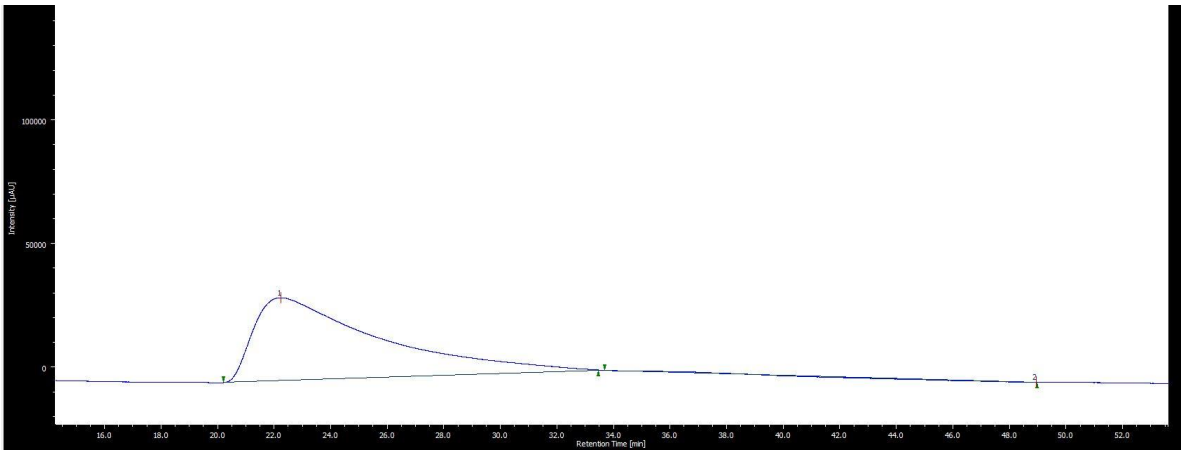
(*R*)-4-(1*H*-indol-3-yl)-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (16)



racemic-16



(*R*)-16



racemic-16		
Peak	tR (min)	Area (%)
1	22.1	49.4
2	36.5	50.6

(*R*)-16		
Peak	tR (min)	Area (%)
1	22.3	98.6
2	34.5	1.4