

Electronic Supplementary Information

Highly Enantioselective Synthesis of Cyclic Sulfamidates and Sulfamides via Rhodium- Catalyzed Transfer Hydrogenation

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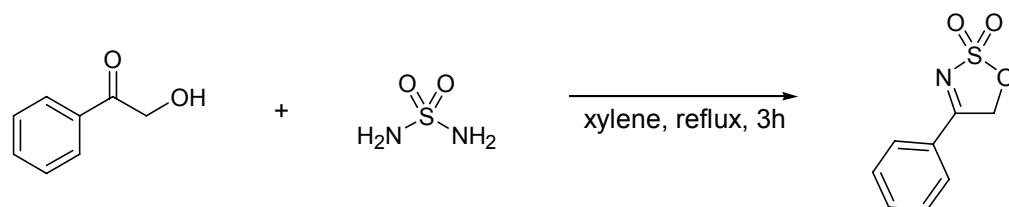
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General for one-pot preparation of cyclic *N*-sulfonylimines. The starting α -hydroxy ketones are the known compounds and were prepared according to the reported procedures,¹⁻⁴ via direct α -hydroxylation of aryl methylketones under acidic conditions using [bis(trifluoroacetoxy)]iodobenzene¹ or hypervalent iodine oxidation of silyl enol ethers.² It was found that aromatic and heteroaromatic substrates were uniformly converted to the corresponding oxathiazole derivatives **5**. For the synthesis of **5a-5g**, sulfamide **2** was employed in refluxing xylene, whereas, for **5h-5l**, trichloroethyl sulfamate **4** was better and then used in refluxing toluene. Remarkably, in the presence of gaseous hydrogen chloride,⁵ the reaction of the same α -hydroxy ketones with sulfamide **2** furnished the thiadiazoles **6a-6k** in moderate yields.

A representative procedure for the synthesis of 4-phenyl-5*H*-[1,2,3]-oxathiazole-2,2-dioxide (5a**).**^{6,7}

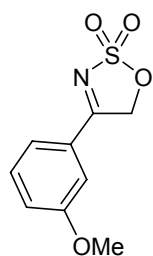


2-Hydroxyacetophenone (100 mg, 0.73 mmol) and sulfamide (105.5 mg, 1.1 mmol) were charged in 10 mL of xylene and the combined contents were refluxed for 3 hr at 180°C. The reaction mixture was concentrated to dryness. The crude was diluted with EtOAc and washed with water and then brine. The organic layer was dried over Na₂SO₄ and the solvent was removed. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 2/1) to give 89 mg (62%) of **5a**: ¹H NMR (300 MHz, CDCl₃) δ 7.92 (d, 2H, J = 8.5 Hz), 7.75 (t, 1H, J = 7.4 Hz), 7.59 (t, 2H, J = 7.9 Hz), 5.58 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 175.4,

135.9, 129.7, 128.9, 127.2, 74.4; EIMS (70eV) m/z (rel intensity) 197 (M^+ , 48), 103 (100);

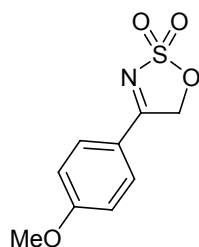
HRMS (EI) calcd for $C_8H_7NO_3S$: 197.0147, found: 197.0147.

4-(3-Methoxyphenyl)-5H-[1,2,3]-oxathiazole-2,2-dioxide (5b).^{6,7}



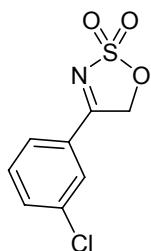
Yield: 57%; 1H NMR (300 MHz, $CDCl_3$) δ 7.50 (t, 1H, $J = 2.5$ Hz), 7.46 (d, 1H, $J = 8.0$ Hz), 7.39-7.35 (m, 1H), 7.28-7.24 (m, 1H), 5.57 (s, 2H), 3.89 (s, 3H); EIMS (70eV) m/z (rel intensity) 227 (M^+ , 23), 133 (100), 103 (26), 90 (11).

4-(4-Methoxyphenyl)-5H-[1,2,3]-oxathiazole-2,2-dioxide (5c).⁷



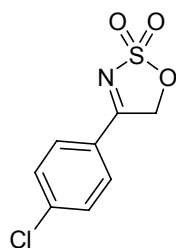
Yield: 59%; 1H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, 2H, $J = 9.1$ Hz), 7.45 (d, 2H, $J = 9.0$ Hz), 5.54 (s, 2H), 3.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 165.9, 131.4, 119.4, 115.2, 74.1, 55.9; EIMS (70eV) m/z (rel intensity) 227 (M^+ , 19), 133 (100), 103 (21), 90 (18); HRMS (EI) calcd for $C_9H_9NO_4S$: 227.0252, found: 227.0250.

4-(3-Chlorophenyl)-5H-[1,2,3]-oxathiazole-2,2-dioxide (5d).⁷



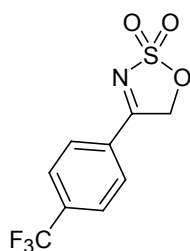
Yield: 50%; ^1H NMR (300 MHz, CDCl_3) δ 7.92 (t, 1H, $J = 1.9$ Hz), 7.81-7.77 (m, 1H), 7.73-7.69 (m, 1H), 7.49 (t, 1H, $J = 7.9$ Hz), 5.57 (s, 2H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 177.8, 135.2, 124.1, 131.4, 129.2, 128.9, 127.9, 77.0; EIMS (70eV) m/z (rel intensity) 231 (M^+ , 19), 137 (100), 102 (13).

4-(4-Chlorophenyl)-5H-[1,2,3]-oxathiazole-2,2-dioxide (5e).⁷



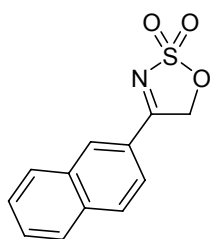
Yield: 46%; ^1H NMR (300 MHz, CDCl_3) δ 7.85 (d, 2H, $J = 8.8$ Hz), 7.57 (d, 2H, $J = 8.8$ Hz), 5.56 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 177.7, 140.6, 131.1, 129.6, 126.0, 76.9; EIMS (70eV) m/z (rel intensity) 231 (M^+ , 12), 136 (100), 102 (20), 75 (14); HRMS (EI) calcd for $\text{C}_8\text{H}_6\text{ClNO}_3\text{S}$: 230.9757, found: 230.9755.

4-(4-Trifluoromethylphenyl)-5H-[1,2,3]-oxathiazole-2,2-dioxide (5f).



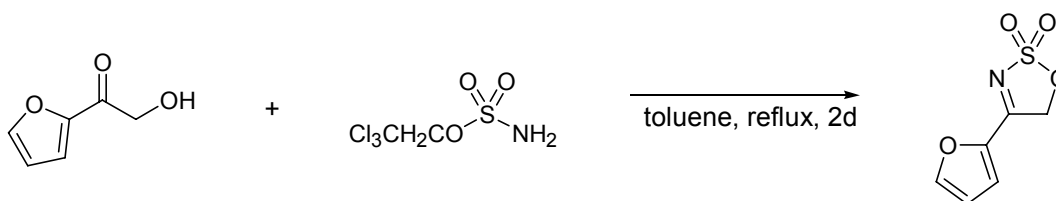
Yield: 65%; ^1H NMR (300 MHz, CDCl_3) δ 8.05 (d, 2H, $J = 8.2$ Hz), 7.83 (d, 2H, $J = 8.2$ Hz), 5.62 (s, 2H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 177.9, 134.3 (q, $J_{\text{F-C}} = 32.4$ Hz), 130.9, 120.2, 126.2 (q, $J_{\text{F-C}} = 3.6$ Hz), 123.4 (q, $J_{\text{F-C}} = 272.3$ Hz), 77.2; EIMS (70eV) m/z (rel intensity) 265 (M^+ , 6), 171 (100), 152 (24), 144 (12), 121 (38); HRMS (EI) calcd for $\text{C}_9\text{H}_6\text{F}_3\text{NO}_3\text{S}$: 265.0020, found: 265.0021.

4-(2-Naphthyl)-5H-[1,2,3]-oxathiazole-2,2-dioxide (5g).



Yield: 47%; ^1H NMR (300 MHz, CDCl_3) δ 8.33 (s, 1H), 8.01 (d, 2H, $J = 1.3$ Hz), 7.95 (t, 2H, $J = 9.4$ Hz), 7.74-7.61 (m, 2H), 5.73 (s, 2H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 178.3, 135.9, 132.4, 131.9, 129.9, 129.6, 129.2, 128.0, 127.7, 124.5, 123.7, 76.9; EIMS (70eV) m/z (rel intensity) 247 (M^+ , 18), 153 (100), 126 (17); HRMS (EI) calcd for $\text{C}_{12}\text{H}_9\text{NO}_3\text{S}$: 247.0303, found: 247.0305.

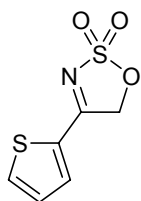
A representative procedure for the synthesis of 4-(2-furyl)-5H-[1,2,3]-oxathiazole-2,2-dioxide (5h).



1-(2-Furyl)-2-hydroxyethanone (200 mg, 1.59 mmol) and 2,2,2-trichloroethyl sulfamate (724.8 mg, 3.17 mmol) were charged in 15 mL of toluene and the combined contents were

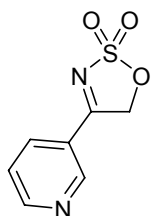
refluxed for 2 days at 130°C. The reaction mixture was concentrated to dryness. The crude was diluted with EtOAc and washed with water and then brine. The organic layer was dried over Na₂SO₄ and the solvent was removed. The residue was purified by column chromatography on silica gel (hexane/EtOAc/methylene chloride = 2/1/1) to give 177 mg (60%) of **5h**: ¹H NMR (300 MHz, CDCl₃) δ 7.83-7.82 (m, 1H), 7.57 (dd, 1H, *J* = 3.7 and 0.6 Hz), 6.77 (dd, 1H, *J* = 3.7 and 1.7 Hz), 5.49 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 164.5, 150.1, 144.0, 122.0, 114.3, 73.5; EIMS (70eV) *m/z* (rel intensity) 187 (M⁺, 34), 93 (100), 64 (11).

4-(2-Thienyl)-5H-[1,2,3]oxathiazole-2,2-dioxide (5i).



Yield = 36%; ¹H NMR (300 MHz, CDCl₃) δ 7.94 (d, 1H, *J* = 5.0 Hz), 7.75 (d, 1H, *J* = 3.9 Hz), 7.29 (t, 1H, *J* = 4.4 Hz), 5.53 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 168.9, 137.8, 135.1, 131.0, 129.5, 74.0; EIMS (70eV) *m/z* (rel intensity) 203 (M⁺, 74), 109 (100), 82 (4).

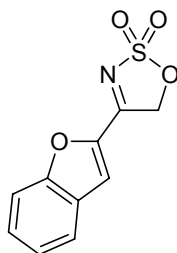
4-(3-Pyridinyl)-5H-[1,2,3]oxathiazole-2,2-dioxide (5j).



Yield = 24%; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.14 (d, 1H, *J* = 1.5 Hz), 8.93 (dd, 1H, *J* = 5.0 and 1.5 Hz), 8.41 (dt, 1H, *J* = 7.7 and 1.8 Hz), 7.70 (ddd, 1H, *J* = 8.1 and 4.9 and 0.7 Hz),

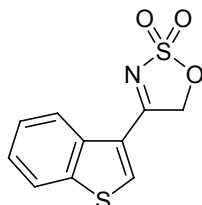
6.17 (s, 2H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 177.7, 155.5, 150.0, 136.7, 124.4, 123.7, 77.0;
EIMS (70eV) m/z (rel intensity) 198 (M^+ , 22), 104 (100), 77 (27).

4-(2-Benzofuryl)-5H-[1,2,3]oxathiazole-2,2-dioxide (5k).



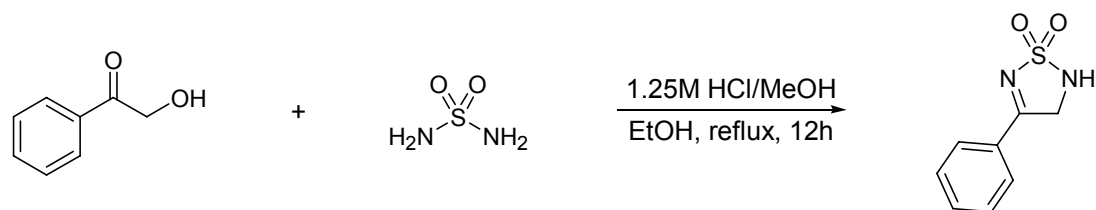
Yield = 52%; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 8.25 (s, 1H), 7.94 (d, 1H, $J = 7.9$ Hz), 7.84 (d, 1H, $J = 7.9$ Hz), 7.66 (t, 1H, $J = 7.6$ Hz), 7.46 (t, 1H, $J = 7.7$ Hz), 6.07 (s, 2H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 168.0, 156.2, 144.1, 130.0, 126.7, 124.8, 123.9, 120.0, 112.4, 75.9; EIMS (70eV) m/z (rel intensity) 237 (M^+ , 43), 143 (100), 115 (23).

4-(3-Benzothieryl)-5H-[1,2,3]oxathiazole-2,2-dioxide (5l).



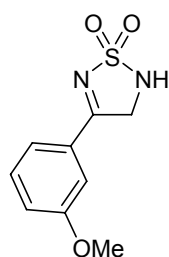
Yield = 41%; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 9.09 (s, 1H), 8.62 (d, 1H, $J = 8.1$ Hz), 8.23 (d, 1H, $J = 8.1$ Hz), 7.68-7.56 (m, 2H), 6.16 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 171.7, 144.2, 139.4, 135.0, 126.6, 126.2, 124.1, 123.7, 123.6, 76.8; EIMS (70eV) m/z (rel intensity) 253 (M^+ , 72), 159 (100), 132 (3).

A representative procedure for the synthesis of 4-phenyl-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (6a).⁵



2-Hydroxyacetophenone (500 mg, 3.67 mmol) and sulfamide (529 mg, 5.51 mmol) were charged in 20 mL of EtOH. To this mixture, 6 mL of 1.25M solution of alcoholic HCl was added and then the combined mixtures were refluxed overnight at 110 °C. The volatile materials were removed in vacuo. The crude was diluted in EtOAc and then washed with 5% NaHCO₃ solution and water. The organic layer was dried over Na₂SO₄ and the solvent was removed. The residue was purified by flash chromatography (hexane/EtOAc = 2/1) to give 605 mg (84%) of **6a**: ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.01 (d, 2H, *J* = 4.8 Hz), 7.93 (t, 1H, *J* = 2.7 Hz), 7.73 (t, 1H, *J* = 4.5 Hz), 7.60 (t, 2H, *J* = 4.8 Hz), 4.87 (d, 2H, *J* = 3.0 Hz); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 177.4, 134.5, 129.3, 129.0, 128.9, 52.6; EIMS (70eV) *m/z* (rel intensity) 196 (M⁺, 35), 132 (39), 105 (82), 77 (100); HRMS (EI) calcd for C₈H₈N₂O₂S: 196.0306, found: 196.0310.

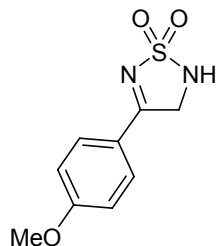
4-(3-Methoxyphenyl)-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (6b).



Yield: 41%; ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.94 (s, 1H), 7.60-7.57 (m, 1H), 7.53-7.47 (m, 2H), 7.31-7.27 (m, 1H), 4.84 (d, 2H, *J* = 2.9 Hz), 3.83 (s, 1H); ¹³C NMR (75 MHz, DMSO-

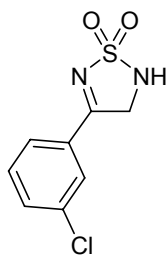
d_6) δ 177.6, 159.9, 130.8, 130.6, 121.7, 121.0, 113.6, 55.8, 53.1; EIMS (70eV) m/z (rel intensity) 226 (M^+ , 17), 133 (100), 103 (30), 90 (13); HRMS (EI) calcd for $C_9H_{10}N_2O_3S$: 226.0412, found: 226.0407.

4-(4-Methoxyphenyl)-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (6c).



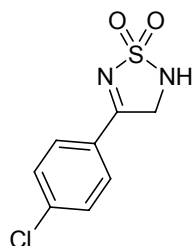
Yield: 30%; 1H NMR (300 MHz, $DMSO-d_6$) δ 7.98 (d, $J = 9.0$ Hz, 2H), 7.79 (t, $J = 5.2$ Hz, 1H), 7.14 (d, $J = 9.0$ Hz, 2H), 4.81 (d, $J = 5.0$ Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $DMSO-d_6$) δ 176.2, 164.3, 131.3, 121.3, 114.7, 55.7, 52.3; EIMS (70eV) m/z (rel intensity) 226 (M^+ , 7), 133 (100), 103 (22), 90 (22), 63 (11).

4-(3-Chlorophenyl)-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (6d).



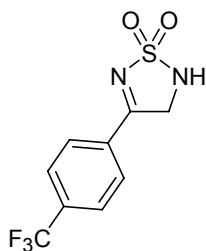
Yield: 43%; 1H NMR (300 MHz, $CDCl_3$) δ 7.92 (t, 1H, $J = 1.9$ Hz), 7.82-7.79 (m, 1H), 7.67-7.63 (m, 1H), 7.49 (t, 1H, $J = 8.1$ Hz), 4.84-4.76 (m, 1H), 4.74 (d, 2H, $J = 5.4$ Hz); ^{13}C NMR (75 MHz, $DMSO-d_6$) δ 176.5, 134.1, 133.9, 131.1, 131.0, 128.5, 127.5, 52.7; EIMS (70eV) m/z (rel intensity) 230 (M^+ , 4), 128 (100), 101 (31), 75 (14); HRMS (EI) calcd for $C_8H_7ClN_2O_2S$: 229.9917, found: 229.9909.

4-(4-Chlorophenyl)-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (6e).



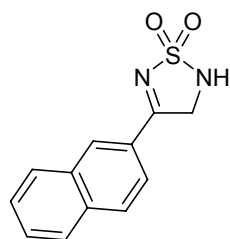
Yield: 53%; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 8.01 (d, 2H, $J = 8.5$ Hz), 7.99-7.92 (m, 1H), 7.66 (d, 2H, $J = 8.5$ Hz), 4.84 (d, 2H, $J = 4.9$ Hz); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 176.8, 139.8, 131.1, 129.7, 128.3, 53.0; EIMS (70eV) m/z (rel intensity) 230 (M^+ , 7), 137 (100), 102 (24), 75 (16); HRMS (EI) calcd for $\text{C}_8\text{H}_7\text{ClN}_2\text{O}_2\text{S}$: 229.9917, found: 229.9909.

4-(4-Trifluoromethylphenyl)-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (6f).



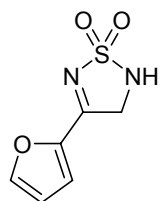
Yield: 42%; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 8.23 (d, 2H, $J = 9.0$ Hz), 8.12 (t, 1H, $J = 4.5$ Hz), 7.99 (d, 2H, $J = 9.0$ Hz), 4.94 (d, 2H, $J = 4.7$ Hz); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 176.5, 133.5 (q, $J_{\text{F-C}} = 32.3$ Hz), 132.8, 129.7, 126.0 (q, $J_{\text{F-C}} = 3.7$ Hz), 123.6 (q, $J_{\text{F-C}} = 272.8$ Hz), 52.8; EIMS (70eV) m/z (rel intensity) 265 (M^+ , 1), 172 (100), 152 (24), 144 (15), 121 (34); HRMS (EI) calcd for $\text{C}_9\text{H}_7\text{F}_3\text{N}_2\text{O}_2\text{S}$: 264.0180, found: 264.0175.

4-(2-Naphthyl)-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (6g).



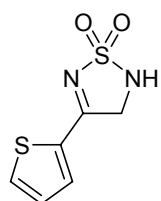
Yield: 66%; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 8.71 (s, 1H), 8.15-8.05 (m, 4H), 7.77-7.65 (m, 2H), 7.31 (brs, 1H), 5.02 (s, 2H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 177.2, 135.5, 132.1, 131.3, 129.5, 129.3, 128.9, 127.9, 127.4, 126.4, 123.9, 52.6; EIMS (70eV) m/z (rel intensity) 246 (M^+ , 11), 153 (100), 125 (20); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$: 246.0463, found: 246.0463.

4-(2-Furyl)-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (6h).



Yield: 9%; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 8.22 (dd, 1H, $J = 1.7$ and 0.7 Hz), 7.76 (t, 1H, $J = 5.2$ Hz), 7.69 (dd, 1H, $J = 3.7$ and 0.7 Hz), 6.88 (dd, 1H, $J = 3.7$ and 1.7 Hz), 4.68 (d, 2H, $J = 5.4$ Hz); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 165.8, 150.1, 144.8, 122.0, 113.7, 51.6; EIMS (70eV) m/z (rel intensity) 186 (M^+ , 31), 93 (100), 64 (7).

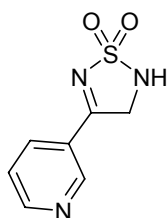
4-(2-Thienyl)-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (6i).



Yield: 27%; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 8.20 (dd, 1H, $J = 5.1$ and 1.2 Hz), 8.05 (dd,

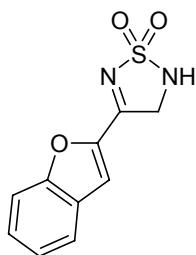
1H, $J = 3.9$ and 1.1 Hz), 7.85 (t, 1H, $J = 5.4$ Hz), 7.36 (dd, 1H, $J = 5.0$ and 3.9 Hz), 4.82 (d, 2H, $J = 5.4$ Hz); ^{13}C NMR (75 MHz, DMSO- d_6) δ 171.2, 136.9, 136.3, 132.4, 129.4, 52.5; EIMS (70eV) m/z (rel intensity) 202 (M^+ , 12), 109 (100), 58 (12).

4-(3-Pyridinyl)-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (6j).



Yield: 20%; ^1H NMR (300 MHz, DMSO- d_6) δ 9.13 (d, 1H, $J = 2.1$ Hz), 8.85 (dd, 1H, $J = 4.8$ and 1.6 Hz), 8.37 (dt, 1H, $J = 8.1$ and 1.9 Hz), 8.04 (t, 1H, $J = 4.7$ Hz), 7.6 (dd, 1H, $J = 8.0$ and 4.8 Hz), 4.9 (d, 2H, $J = 4.8$ Hz); ^{13}C NMR (75 MHz, DMSO- d_6) δ 176.2, 154.6, 149.7, 136.4, 125.3, 124.2, 52.7; EIMS (70eV) m/z (rel intensity) 198 ($\text{M}^+ + 1$, 6), 133 (5), 105 (100), 77 (20);

4-(2-Benzofuryl)-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (6k).

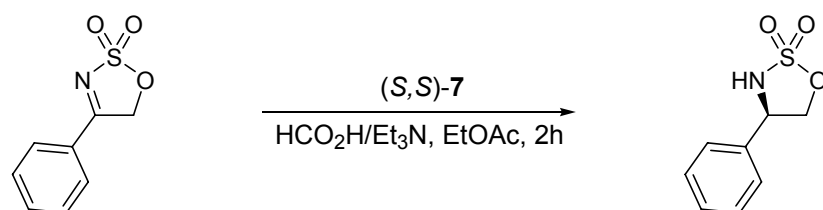


Yield: 18%; ^1H NMR (300 MHz, DMSO- d_6) δ 8.13 (s, 1H), 7.96 (t, 1H, $J = 4.8$ Hz), 7.89 (d, 1H, $J = 7.9$ Hz), 7.80 (d, 1H, $J = 8.3$ Hz), 7.61 (td, 1H, $J = 7.1$ and 1.2 Hz), 7.43 (t, 1H, $J = 7.9$ Hz), 4.83 (d, 2H, $J = 4.9$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 167.8, 156.4, 146.5, 129.7, 127.3, 124.9, 124.0, 118.1, 112.7, 52.5; EIMS (70eV) m/z (rel intensity) 236 (M^+ , 56), 143

(100), 115 (15).

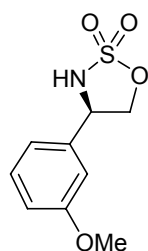
General for Rh-catalyzed asymmetric transfer hydrogenation. According to the literature procedure, the (*S,S*)-Rh **7** was prepared from the reaction of (*1S,2S*)-*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine with dichloro(pentamethylcyclopentadienyl)rhodium (III) dimer in the presence of triethylamine.^{8,9} It should be noted that the catalyst were used without any purification, so the catalyst includes an equal molar of hydrochloride/triethylamine salt. The catalyst is very stable and insensitive to atmospheric manipulations, and does not show any deterioration in the catalytic activity compared to that prepared from recrystallization. The formic acid/triethylamine (molar ratio = 5/2) azeotrope was prepared by the double distillation of the mixtures.¹⁰ The *ee* values were measured by chiral HPLC analysis using a Daicel Chiralcel OD-H, OJ-H, or Chiralpak AD-H column at 215 nm. The racemic amines (\pm)-**8** and (\pm)-**10** were prepared respectively by sodium borohydride reduction of the corresponding amines in some cases, and used as standards for *ee* determination. The absolute configuration was determined by comparing the sign of the specific rotation with the literature data and/or chemical modifications to the known compounds.^{6,7,11,12} Unless otherwise indicated, the absolute configuration was assigned by analogy.

A representative procedure for the synthesis of (*R*)-4-phenyl-[1,2,3]-oxathiazolidine-2,2-dioxide (8a**).**^{6,7}



Into a two-neck flask, were added (*S,S*)-Rh **7** (3.9 mg, equivalent to 0.005 mmol) and **5a** (197 mg, 1 mmol) under a slight stream of argon. To this mixture, ethyl acetate (5 mL) and then an azeotropic mixture of HCO₂H/Et₃N (molar ratio = 5/2, 0.2 mL) were added via a syringe. The combined contents were stirred for 2h. The reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (3x5 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated and then the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 2/1) to give 195 mg (98%) of **8a**. ¹H NMR (300 MHz, CDCl₃) δ 7.42 (m, 5H), 5.08 (dt, 1H, *J* = 8.4 and 6.9 Hz), 4.84 (dd, 1H, *J* = 8.7 and 6.8 Hz), 4.79 (br, 1H), 4.46 (t, 1H, *J* = 8.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 135.3, 129.6, 129.4, 126.7, 75.0, 59.6; EIMS (70eV) *m/z* (rel intensity) 199 (M⁺, 7), 169 (33), 104 (100); HRMS (EI) calcd for C₈H₉NO₃S: 199.0303, found: 199.0302; [α]_D²³ = -37.1 (*c* 0.70, CHCl₃); HPLC (Chiralcel AD-H column, ⁱPrOH/hexane = 15/85, 0.8 mL/min): *t*₁ = 11.7 min (*R*), *t*₂ = 13.2 min (*S*); *ee* = 98%.

(*R*)-4-(3-Methoxyphenyl)-[1,2,3]-oxathiazolidine-2,2-dioxide (8b).^{6,7}

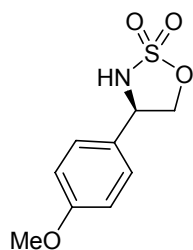


Yield = 89%; ¹H NMR (300 MHz, CDCl₃) δ 7.32 (t, 1H, *J* = 7.8 Hz), 6.98-6.89 (m, 3H), 5.07-5.01 (m, 2H), 4.82 (t, 1H, *J* = 8.5 Hz), 4.42 (t, 1H, *J* = 8.5 Hz), 3.81 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) 160.2, 136.9, 130.5, 118.7, 114.9, 112.2, 75.1, 59.4, 55.4; EIMS (70eV) *m/z* (rel intensity) 229 (M⁺, 39), 134 (100), 105 (47), 77 (15), 65 (14); [α]_D²³ = -32.1 (*c* 0.29,

CHCl₃); HPLC (Chiralcel AD-H column, *i*PrOH/hexane = 20/80, 0.8 mL/min): *t*₁ = 10.5 min

(*R*), *t*₂ = 11.7 min (*S*); *ee* = 97%.

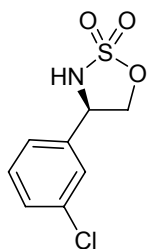
(*R*)-4-(4-Methoxyphenyl)-[1,2,3]-oxathiazolidine-2,2-dioxide (8c).⁷



Yield = 86%; ¹H NMR (300 MHz, CDCl₃) δ 7.35 (d, 2H, *J* = 8.7 Hz), 6.94 (d, 2H, *J* = 8.7 Hz), 5.03 (q, 1H, *J* = 6.8 Hz), 4.79 (dd, 1H, *J* = 8.7 and 6.7 Hz), 4.64 (d, 1H, *J* = 6.2 Hz), 4.44 (t, 1H, *J* = 8.7 Hz), 3.82 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) 160.5, 128.2, 126.9, 114.7, 75.3, 59.3, 55.4; EIMS (70eV) *m/z* (rel intensity) 229 (M⁺, 4), 135 (100), 91 (12), 77 (18), 65 (60); [α]_D²³ = -34.4 (*c* 0.50, CHCl₃); HPLC (Chiralcel AD-H column, *i*PrOH/hexane = 20/80,

0.8 mL/min): *t*₁ = 11.0 min (*R*), *t*₂ = 12.7 min (*S*); *ee* = 97%.

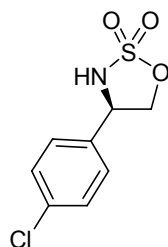
(*R*)-4-(3-Chlorophenyl)-[1,2,3]-oxathiazolidine-2,2-dioxide (8d).⁷



Yield = 96%; ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.58 (d, 1H, *J* = 5.5 Hz), 7.53-7.52 (m, 1H), 7.49-7.40 (m, 3H), 5.17-5.11 (m, 1H), 4.96 (dd, 1H, *J* = 8.7 and 7.0 Hz), 4.38 (dd, 1H, *J* = 8.7

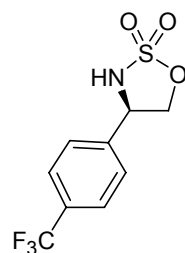
and 6.9 Hz); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): 140.2, 133.3, 130.6, 128.3, 126.6, 125.4, 74.6, 57.6; EIMS (70eV) m/z (rel intensity) 233 (M^+ , 6), 202 (12), 138 (100), 111 (16), 75 (19); HRMS (EI) calcd for $\text{C}_8\text{H}_8\text{ClNO}_3\text{S}$: 232.9913, found: 232.9913; $[\alpha]_D^{23} = -33.6$ (c 0.42, CHCl_3); HPLC (Chiralcel AD-H column, $^i\text{PrOH/hexane} = 20/80$, 0.8 mL/min): $t_1 = 8.5$ min (R), $t_2 = 9.4$ min (S); $ee = 99\%$.

(*R*)-4-(4-Chlorophenyl)-[1,2,3]-oxathiazolidine-2,2-dioxide (8e).⁷



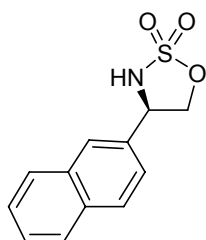
Yield = 82%; ^1H NMR (300 MHz, CDCl_3) δ 7.43-7.35 (m, 4H), 5.06 (q, 1H, $J = 6.9$ Hz), 4.90 (d, 1H, $J = 5.0$ Hz), 4.84 (dd, 1H, $J = 8.7$ and 6.9 Hz), 4.39 (t, 1H, $J = 8.4$ Hz); ^{13}C NMR (75 MHz, CDCl_3) 135.5, 134.2, 129.6, 128.1, 74.6, 58.9; EIMS (70eV) m/z (rel intensity) 233 (M^+ , 10), 203 (14), 139 (100), 110 (13), 75 (14); $[\alpha]_D^{23} = -31.9$ (c 0.36, CHCl_3); HPLC (Chiralcel AD-H column, $^i\text{PrOH/hexane} = 20/80$, 0.8 mL/min) $t_1 = 8.9$ min (R), $t_2 = 11.3$ min (S); $ee = 97\%$.

(*R*)-4-(4-Trifluoromethylphenyl)-[1,2,3]-oxathiazolidine-2,2-dioxide (8f).



Yield = 77%; ^1H NMR (300 MHz, CDCl_3) δ 7.71 (d, 2H, $J = 8.2$ Hz), 7.58 (d, 2H, $J = 8.1$ Hz), 5.16 (q, 1H, $J = 7.4$ Hz), 4.95 (brs, 1H), 4.90 (dd, 1H, $J = 8.8$ and 7.2 Hz), 4.41 (dd, 1H, $J = 8.8$ and 7.8 Hz); ^{13}C NMR (75 MHz, CDCl_3) 139.9, 131.7 (q, $J_{\text{F-C}} = 32.6$ Hz), 127.1, 126.4 (q, $J_{\text{F-C}} = 3.6$ Hz), 123.5 (q, $J_{\text{F-C}} = 272.7$ Hz), 74.5, 58.9; EIMS (70eV) m/z (rel intensity) 267 (M^+ , 1), 139 (7), 111 (20), 97 (28), 71 (47), 57 (100); $[\alpha]_{\text{D}}^{23} = -26.1$ (c 0.33, CHCl_3); HPLC (Chiralcel AD-H column, $^i\text{PrOH}$ /hexane = 20/80, 0.8 mL/min): $t_1 = 7.4$ min (R), $t_2 = 9.7$ min (S); $ee = 97\%$.

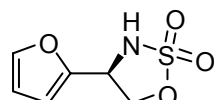
(R)-4-(2-Naphthyl)-[1,2,3]-oxathiazolidine-2,2-dioxide (8g).



Yield = 86%, ^1H NMR (300 MHz, CDCl_3) δ 7.93 (d, 1H, $J = 8.6$ Hz), 7.88-7.83 (m, 3H), 7.58-7.50 (m, 3H), 5.25 (q, 1H, $J = 7.1$ Hz), 4.91 (dd, 1H, $J = 8.8$ and 6.9 Hz), 4.79 (d, 1H, $J = 6.2$ Hz), 4.55 (t, 1H, $J = 8.6$ Hz); ^{13}C NMR (75 MHz, CDCl_3) 133.6, 133.1, 132.5, 129.7, 128.0, 127.9, 127.1, 127.0, 126.5, 123.3, 74.7, 59.8; EIMS (70eV) m/z (rel intensity) 249 (M^+ ,

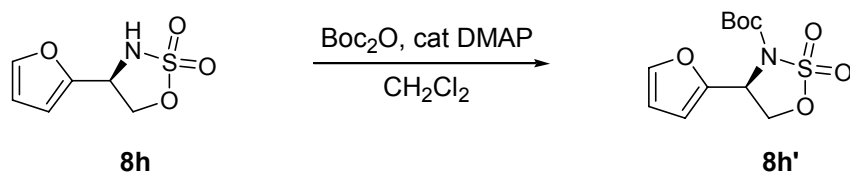
15), 155 (100), 127 (29), 77 (11); $[\alpha]_D^{23} = -31.5$ (c 0.36, CHCl_3); HPLC (Chiralcel AD-H column, $^i\text{PrOH}$ /hexane = 20/80, 0.8 mL/min): $t_1 = 11.3$ min (R), $t_2 = 14.0$ min (S); $ee = 97\%$.

(S)-4-(2-Furyl)-[1,2,3]-oxathiazolidine-2,2-dioxide (8h).



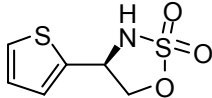
Yield = 97%; ^1H NMR (300 MHz, CDCl_3) δ 7.48 (dd, 1H, $J = 1.8$ and 0.7 Hz), 6.51 (d, 1H, $J = 3.3$ Hz), 6.42 (dd, 1H, $J = 3.3$ and 1.8 Hz), 5.12 (q, 1H, $J = 7.2$ Hz), 4.79-4.63 (m, 3H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 149.6, 143.7, 110.7, 109.0, 72.1, 52.1; EIMS (70eV) m/z (rel intensity) 189 (M^+ , 15), 159 (11), 95 (100); $[\alpha]_D^{23} = -8.6$ (c 0.25, CHCl_3); HPLC separation failed.

Preparation of (S)-N-boc-4-(2-furyl)-[1,2,3]-oxathiazolidine-2,2-dioxide (8h')

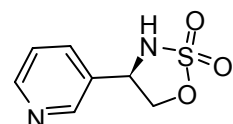


N -Boc-**8h** was obtained in 72% yield, by the treatment of Boc_2O (1.2 equiv) with **8h** in the presence of the catalytic amount of DMAP in dichloromethane. ^1H NMR (300 MHz, CDCl_3) δ 7.44 (dd, 1H, $J = 1.8$ and 0.8 Hz), 6.48 (d, 1H, $J = 3.3$ Hz), 6.39 (dd, 1H, $J = 3.3$ and 1.8 Hz), 5.40 (dd, 1H, $J = 6.3$ and 3.3 Hz), 4.81 (dd, 1H, $J = 9.2$ and 6.4 Hz), 4.65 (dd, 1H, $J = 9.2$ and 3.3 Hz), 1.51 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.5, 148.1, 110.9, 109.6, 85.9, 69.2, 54.3; HPLC (Chiralcel AD-H column, $^i\text{PrOH}$ /hexane = 15/85, 0.8 mL/min): $t_1 = 9.8$ min (R), $t_2 = 10.4$ min (S); $ee = 98\%$.

(S)-4-(2-Thienyl)-[1,2,3]-oxathiazolidine-2,2-dioxide (8i).

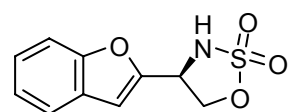
 Yield = 98%; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.40 (dd, 1H, $J = 5.1$ and 1.2 Hz), 7.21-7.13 (m, 1H), 7.05 (dd, 1H, $J = 5.1$ and 3.6 Hz), 5.34 (q, 1H, $J = 6.6$ Hz), 4.85 (dd, 1H, $J = 8.7$ and 6.6 Hz), 4.83 (br, 1H), 4.56 (t, 1H, $J = 8.6$ Hz); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 137.3, 127.6, 127.2, 127.1, 75.3, 55.4; EIMS (70eV) m/z (rel intensity) 205 (M^+ , 19), 175 (24), 111(100); $[\alpha]_{\text{D}}^{23} = -7.4$ (c 0.67, CHCl_3); HPLC (Chiralcel AD-H column, $^i\text{PrOH}$ /hexane = 15/85, 0.8 mL/min): $t_1 = 13.7$ min (R), $t_2 = 14.9$ min (S); $ee = 99\%$.

(R)-4-(3-Pyridinyl)-[1,2,3]-oxathiazolidine-2,2-dioxide (8j).



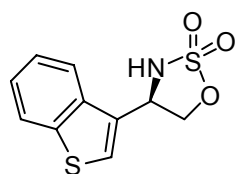
Yield = 91%; $^1\text{H NMR}$ (300 MHz, CD_3OD) δ 8.64 (d, 1H, $J = 2.3$ Hz), 8.54 (dd, 1H, $J = 4.9$ and 1.6 Hz), 8.02-7.98 (m, 1H), 7.49 (ddd, 1H, $J = 8.0$, 4.9 and 0.6 Hz), 5.16 (t, 1H, $J = 7.0$ Hz), 4.96 (dd, 1H, $J = 8.8$ and 7.1 Hz), 4.41 (dd, 1H, $J = 8.8$ and 6.8 Hz); $^{13}\text{C NMR}$ (75 MHz, CD_3OD) δ 150.3, 148.9, 136.7, 140.0, 125.5, 75.6, 58.0; EIMS (70eV) m/z (rel intensity) 200 (M^+ , 9), 170 (26), 106 (100); Determination of optical rotation was failed due to the solubility problem; HPLC (Chiralcel AD-H column, $^i\text{PrOH}$ /hexane = 15/85, 0.8 mL/min): $t_1 = 14.2$ min (R), $t_2 = 16.6$ min (S); $ee = 99\%$.

(S)-4-(2-Benzofuryl)-[1,2,3]-oxathiazolidine-2,2-dioxide (8k).



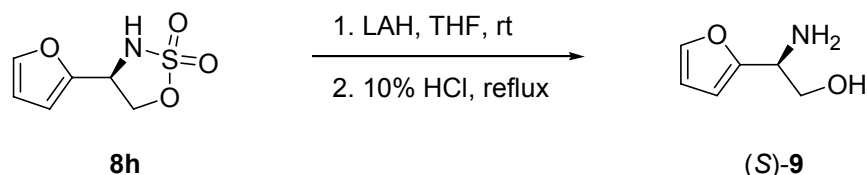
Yield = 84%; ^1H NMR (300 MHz, CDCl_3) δ 7.59 (d, 1H, $J = 7.6$ Hz), 7.49 (d, 1H, $J = 8.5$ Hz), 7.36 (dt, 1H, $J = 7.3$ and 1.4 Hz), 7.27 (dt, 1H, $J = 7.5$ and 1.0 Hz), 6.89 (s, 1H), 5.23 (q, 1H, $J = 7.4$ Hz), 4.94 (d, 1H, $J = 7.3$ Hz), 4.85 (dd, 1H, $J = 8.6$ and 8.8 Hz), 4.76 (dd, 1H, $J = 8.4$ and 7.7); ^{13}C NMR (75 MHz, CDCl_3) δ 155.2, 149.4, 127.3, 125.6, 123.6, 121.7, 111.5, 107.0, 72.7, 53.7; EIMS (70eV) m/z (rel intensity) 239 (M^+ , 29), 145 (100); $[\alpha]_{\text{D}}^{23} = -23.0$ (c 0.50, CHCl_3); HPLC (Chiralcel AD-H column, $^i\text{PrOH}$ /hexane = 15/85, 0.8 mL/min): $t_1 = 12.0$ min (R), $t_2 = 14.0$ min (S); $ee = 98\%$.

(*R*)-4-(3-Benzofuryl)-[1,2,3]-oxathiazolidine-2,2-dioxide (8l).



Yield = 30%; ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 8.56 (d, 1H, $J = 6.8$ Hz), 8.09-7.93 (m, 2H), 7.87 (d, 1H, $J = 0.7$ Hz), 7.50-7.39 (m, 2H), 5.48 (dq, 1H, $J = 6.9$ and 0.9 Hz), 5.08 (dd, 1H, $J = 8.6$ and 6.8 Hz), 4.65 (dd, 1H, $J = 8.6$ and 7.2 Hz); HPLC (Chiralcel AD-H column, $^i\text{PrOH}$ /hexane = 15/85, 0.8 mL/min): $t_1 = 15.3$ min (R), $t_2 = 16.5$ min (S); $ee = 98\%$.

Synthesis of (*S*)-2-(2-furyl)-2-aminoethanol (*S*)-9.¹¹

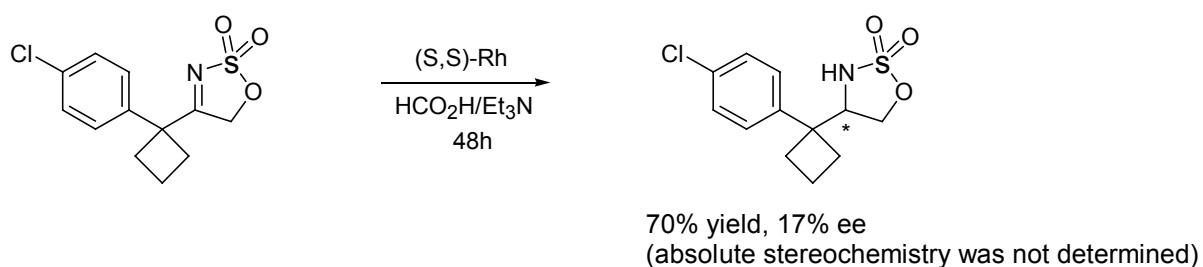
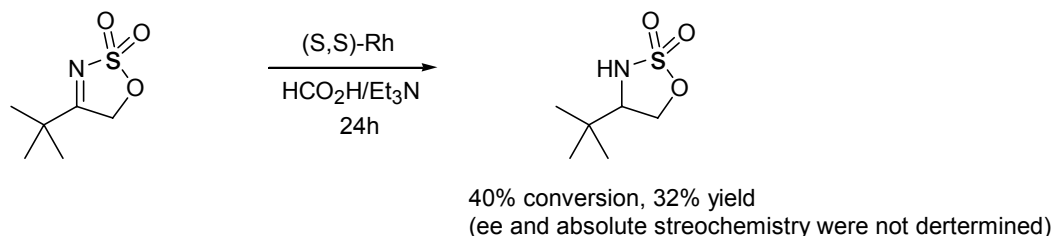
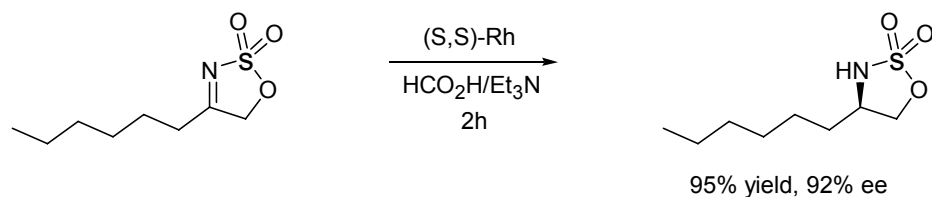


To a suspension of LAH (78 mg, 2.06 mmol) in THF (5 mL), **8h** (130mg, 0.68 mmol) in THF (2 mL) was added dropwise at 0°. The mixture was allowed to stir at room temperature for

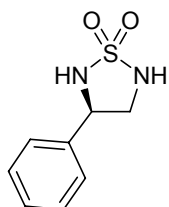
1h, and then 10% HCl solution was added slowly to this mixture. The resulting mixtures were refluxed for 1h, and then cooled to room temperature. To this mixture, 3*N* NaOH solution was introduced. The aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layers were dried and concentrated. The crude was purified by column chromatography on silica gel (CH₂Cl₂/MeOH = 3/1) to give 54 mg (62%) of (*S*)-**9**. ¹H NMR (300 MHz, CDCl₃) δ 7.36 (dd, 1H, *J* = 1.7 and 0.8 Hz), 6.33 (dd, 1H, *J* = 3.2 and 1.9 Hz), 6.19 (d, 1H, *J* = 3.2 Hz), 4.04 (dd, 1H, *J* = 7.7 and 4.5 Hz), 3.82 (dd, 1H, *J* = 10.7 and 4.5 Hz), 3.66 (dd, 1H, *J* = 10.7 and 7.8 Hz), 1.99 (brs, 3H); [α]_D²⁰ = -12.4 (*c* 0.33, MeOH).

Transfer hydrogenation on the substrates with alkyl-substituents.

Several substrates with alkyl substituent had been examined within the transfer hydrogenation conditions; however, enantioselectivity of alkyl substrates was poor comparing to that of the aromatic substrates described in this manuscript. The reaction was sluggish and, furthermore, higher degrees of substitution ultimately led to a dramatic drop in enantioselectivity. The results are not surprising, since an attractive interaction between arene ligand of the catalyst and aryl substrate is of great importance in the favoured transition state.¹³

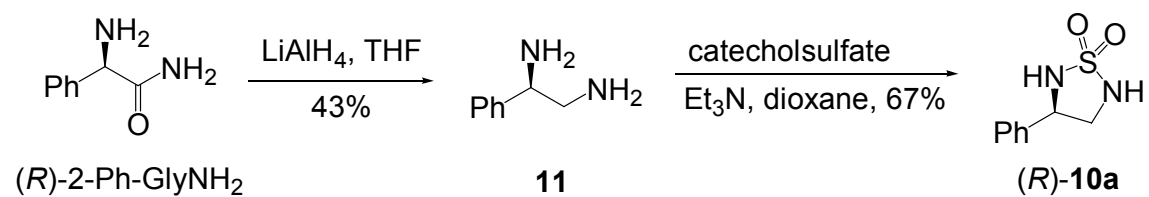


(R)-3-Phenyl-1,2,5-thiadiazolidine-1,1-dioxide (10a).



Yield = 93%; ¹H NMR (300 MHz, CDCl₃) δ 7.38 (m, 5H), 4.94 (q, 1H, *J* = 6.3 Hz), 4.65 (d, 1H, *J* = 5.8 Hz), 4.59 (t, 1H, *J* = 6.4 Hz), 3.89 (dt, 1H, *J* = 11.8 and 6.6 Hz), 3.50 (dt, 1H, *J* = 11.7 and 7.8 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 137.7, 129.2, 128.9, 126.4, 61.3, 51.8; HRMS (EI) calcd for C₈H₁₀N₂O₂S: 198.0463, found: 198.0462; [α]_D²³ = -49.2 (*c* 0.59, MeOH); HPLC (Chiralcel AD-H column, *i*PrOH/hexane = 20/80, 0.8 mL/min): *t*₁ = 13.2 min (*R*), *t*₂ = 15.1 min (*S*); *ee* = 98%.

Determination of the absolute configuration of (*R*)-**10a**.¹²

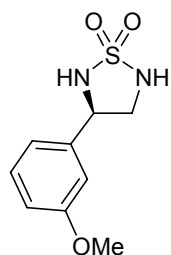


Synthesis of (*R*)-**10a** was carried out according to the known procedures. The synthesis included LAH reduction of (*R*)-2-phenylglycinamide¹⁴ and transformation of the resulting diamine **11** into the desired thiadiazolidine (*R*)-**10a**, employing catecholsulfate with triethylamine in dioxane. The synthetic product was fully matched in the spectral and optical data of the catalytic one.¹²

Deprotection of **10a** to **11**.

The deprotection of the sulfamide **10a** was easily achieved according to the previously reported procedure.¹⁵

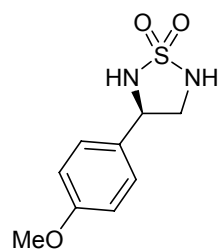
(*R*)-3-(3-Methoxyphenyl)-1,2,5-thiadiazolidine-1,1-dioxide (**10b**).



Yield = 86%; ¹H NMR (300 MHz, CDCl₃) δ 7.29 (t, 1H, *J* = 8.1 Hz), 6.97-6.96 (m, 2H), 6.87-6.84 (m, 1H), 4.96 (brs, 1H), 4.91-4.87 (m, 2H), 3.88-3.82 (m, 1H), 3.79 (s, 1H), 3.46-3.40 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) 159.9, 139.6, 130.1, 118.4, 113.9, 111.87, 61.07, 55.25, 51.52; EIMS (70eV) *m/z* (rel intensity) 228 (M⁺, 7), 134 (100), 105 (43); HRMS calcd for C₉H₁₂N₂O₃S: 228.0569, found: 228.0571; [α]_D²⁸ = -34.1 (*c* 0.40, CHCl₃); HPLC

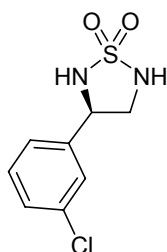
(Chiralcel AD-H column, ⁱPrOH/hexane = 20/80, 0.8 mL/min): $t_1 = 14.8$ min (*R*), $t_2 = 16.7$ min (*S*); $ee = 83\%$.

(*R*)-3-(4-Methoxyphenyl)-1,2,5-thiadiazolidine-1,1-dioxide (10c).



Yield = 86%; ¹H NMR (300 MHz, CDCl₃) δ 7.34 (d, 2H, $J = 8.8$ Hz), 6.93 (d, 2H, $J = 8.6$ Hz), 4.88 (dd, 1H, $J = 14.0$ and 6.5 Hz), 4.53 (d, 2H, $J = 5.7$ Hz), 3.89-3.77 (m, 3H), 3.82 (s, 3H), 3.49 (dt, 1H, $J = 11.7$ and 8.1 Hz); ¹³C NMR (75 MHz, CD₃OD) δ 161.1, 132.8, 128.9, 115.1, 62.1, 55.7, 52.6; HRMS (EI) calcd for C₉H₁₂N₂O₃S: 228.0569, found: 228.0569; $[\alpha]_D^{21} = -43.7$ (c 0.27, MeOH); HPLC (Chiralcel AD-H column, ⁱPrOH/hexane = 30/70, 0.8 mL/min): $t_1 = 10.4$ min (*S*), $t_2 = 12.1$ min (*R*); $ee = 98\%$.

(*R*)-3-(3-chlorophenyl)-1,2,5-thiadiazolidine-1,1-dioxide (10d).

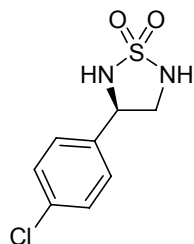


Yield = 84%; ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.63 (brs, 1H), 7.49 (t, 1H, $J = 1.8$ Hz), 7.43-7.34 (m, 3H), 7.18 (brs, 1H), 4.80 (t, 1H, $J = 6.8$ Hz), 3.80-3.74 (m, 1H), 3.09-3.03 (m, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆) 143.5, 133.1, 130.3, 127.5, 126.2, 125.1, 59.0, 50.4; EIMS (70eV) m/z (rel intensity) 233 (M^+ , 1), 138 (100), 111 (19), 77 (24); $[\alpha]_D^{27} = -48.9$ (c 0.50,

CHCl₃); HPLC (Chiralcel AD-H column, ⁱPrOH/hexane = 20/80, 0.8 mL/min): t₁ = 10.6 min

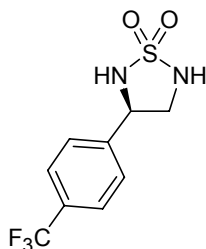
(*R*), t₂ = 12.6 min (*S*); *ee* = 97%.

(*R*)-3-(4-chlorophenyl)-1,2,5-thiadiazolidine-1,1-dioxide (10e).



Yield = 87%; ¹H NMR (300 MHz, CDCl₃): δ 7.41-7.35 (m, 4H), 4.92 (q, 1H, *J* = 6.4 Hz), 4.64 (brs, 1H), 4.50 (brs, 1H), 3.94-3.85 (m, 1H), 3.49-3.40 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) 136.4, 134.6, 129.3, 127.6, 60.4, 51.5; EIMS (70eV) *m/z* (rel intensity) 232 (M⁺, 0.1), 138 (100), 112 (16), 75 (14); Positive-ion FAB-MS *m/z* 233 ([M + H]⁺, 37); [α]_D²⁸ = -33.6 (*c* 0.55, CHCl₃); HPLC (Chiralcel AD-H column, ⁱPrOH/hexane = 20/80, 0.8 mL/min): t₁ = 11.9 min (*R*), t₂ = 15.8 min (*S*); *ee* = 98%.

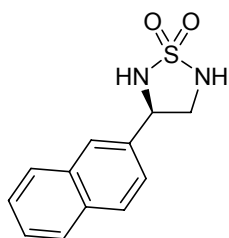
(*R*)-3-(4-trifluoromethylphenyl)-1,2,5-thiadiazolidine-1,1-dioxide (10f).



Yield = 86%; ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.62 (dd, 4H, *J* = 32.3 and 8.3 Hz), 7.68 (d, 1H, *J* = 6.7 Hz), 7.18 (t, 1H, *J* = 7.5 Hz), 4.90 (q, 1H, *J* = 6.5 Hz), 3.85-3.77 (m, 1H), 3.13-3.04 (m, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆) 145.6, 128.2 (q, *J*_{F-C} = 32.2 Hz), 127.2, 125.3

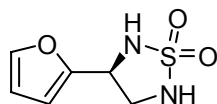
(q, $J_{F-C} = 3.6$ Hz), 124.1 (q, $J_{F-C} = 272.0$ Hz), 59.2, 50.4; EIMS (70eV) m/z (rel intensity) 266 (M^+ , 1), 172 (67), 144 (16), 63 (25), 56 (45); $[\alpha]_D^{27} = -42.7$ (c 0.41, MeOH); HRMS (EI) calcd for $C_9H_9F_3N_2O_2S$: 266.0337, found: 266.0340; HPLC (Chiralcel AD-H column, i PrOH/hexane = 20/80, 0.8 mL/min): $t_1 = 8.8$ min (R), $t_2 = 13.1$ min (S); $ee = 97\%$.

(R)-3-(2-Naphthyl)-1,2,5-thiadiazolidine-1,1-dioxide (10g).



Yield = 91%; 1H NMR (300 MHz, $CDCl_3$) δ 7.92-7.83 (m, 4H), 7.55-7.48 (m, 3H), 5.10 (q, 1H, $J = 6.6$ Hz), 4.65 (d, 1H, $J = 5.9$ Hz), 4.49 (t, 1H, $J = 6.9$ Hz), 4.00-3.91 (m, 1H), 3.64-3.55 (m, 1H); ^{13}C NMR (75 MHz, $DMSO-d_6$) 138.0, 132.6, 132.4, 128.2, 127.7, 127.5, 126.3, 126.0, 125.0, 124.5, 59.9, 50.4; EIMS (70eV) m/z (rel intensity) 248 (M^+ , 3), 155 (100), 127 (25), 77 (7); HRMS (EI) calcd for $C_{12}H_{12}N_2O_2S$: 248.0619, found: 248.0638; $[\alpha]_D^{27} = -30.6$ (c 0.38, MeOH); HPLC (Chiralcel AD-H column, i PrOH/hexane = 20/80, 0.8 mL/min): $t_1 = 15.1$ min (R), $t_2 = 20.3$ min (S); $ee = 90\%$.

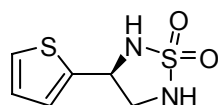
(S)-3-(2-Furyl)-1,2,5-thiadiazolidine-1,1-dioxide (10h).



Yield = 87%; 1H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, 1H, $J = 1.8$ and 0.8 Hz), 6.47-6.34 (m,

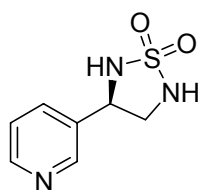
2H), 4.94 (t, 1H, $J = 6.0$ Hz), 4.65 (s, 2H), 3.89-3.61 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.8, 143.5, 110.8, 109.0, 55.4, 49.2; EIMS (70eV) m/z (rel intensity) 189 ($\text{M}^+ + 1$, 47), 121 (23), 95 (100); $[\alpha]_{\text{D}}^{22} = -1.2$ (c 0.45, CHCl_3); HPLC separation failed.

(S)-3-(2-thienyl)-1,2,5-thiadiazolidine-1,1-dioxide (10i).



Yield = 93%; ^1H NMR (300 MHz, CDCl_3) δ 7.34 (dd, 1H, $J = 5.1$ and 1.2 Hz), 7.16-7.10 (m, 1H), 7.02 (dd, 1H, $J = 5.1$ and 3.6 Hz), 5.17 (q, 1H, $J = 6.4$ Hz), 4.66 (s, 2H), 3.91 (dt, 1H, $J = 12.0$ and 6.6 Hz), 3.61 (dt, 1H, $J = 11.8$ and 7.5 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 140.5, 127.5, 126.3, 126.0, 57.4, 52.2; EIMS (70eV) m/z (rel intensity) 205 ($\text{M}^+ + 1$, 2), 140 (5), 123 (9), 110 (100); $[\alpha]_{\text{D}}^{23} = -8.8$ (c 0.45, CHCl_3); HPLC (Chiralcel AD-H column, i PrOH/hexane = 15/85, 0.8 mL/min): $t_1 = 22.7$ min (R), $t_2 = 24.2$ min (S); $ee = 98\%$.

(R)-3-(3-Pyridinyl)-1,2,5-thiadiazolidine-1,1-dioxide (10j).

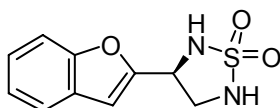


Yield = 45%; ^1H NMR (300 MHz, CD_3OD) δ 8.59 (d, 2H, $J = 42.1$ Hz), 8.00 (d, 1H, $J = 8.0$ Hz), 7.48 (dd, 1H, $J = 7.6$ and 4.9 Hz), 4.97 (t, 1H, $J = 6.6$ Hz), 3.91 (dd, 1H, $J = 11.8$ and 7.0 Hz), 3.35-3.29 (m, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 149.6, 148.6, 136.5, 125.4, 68.4, 59.7; 52.0; EIMS (70eV) m/z (rel intensity) 200 ($\text{M}^+ + 1$, 4), 106 (100), 79 (35); $[\alpha]_{\text{D}}^{27} = -$

46.1 (*c* 0.17, MeOH); HPLC (Chiralcel AD-H column, ⁱPrOH/hexane = 20/80, 0.8 mL/min):

*t*₁ = 15.1 min (*R*), *t*₂ = 16.0 min (*S*); *ee* = 73%.

(*S*)-3-(Benzofuran-2-yl)-1,2,5-thiadiazolidine-1,1-dioxide (10k).

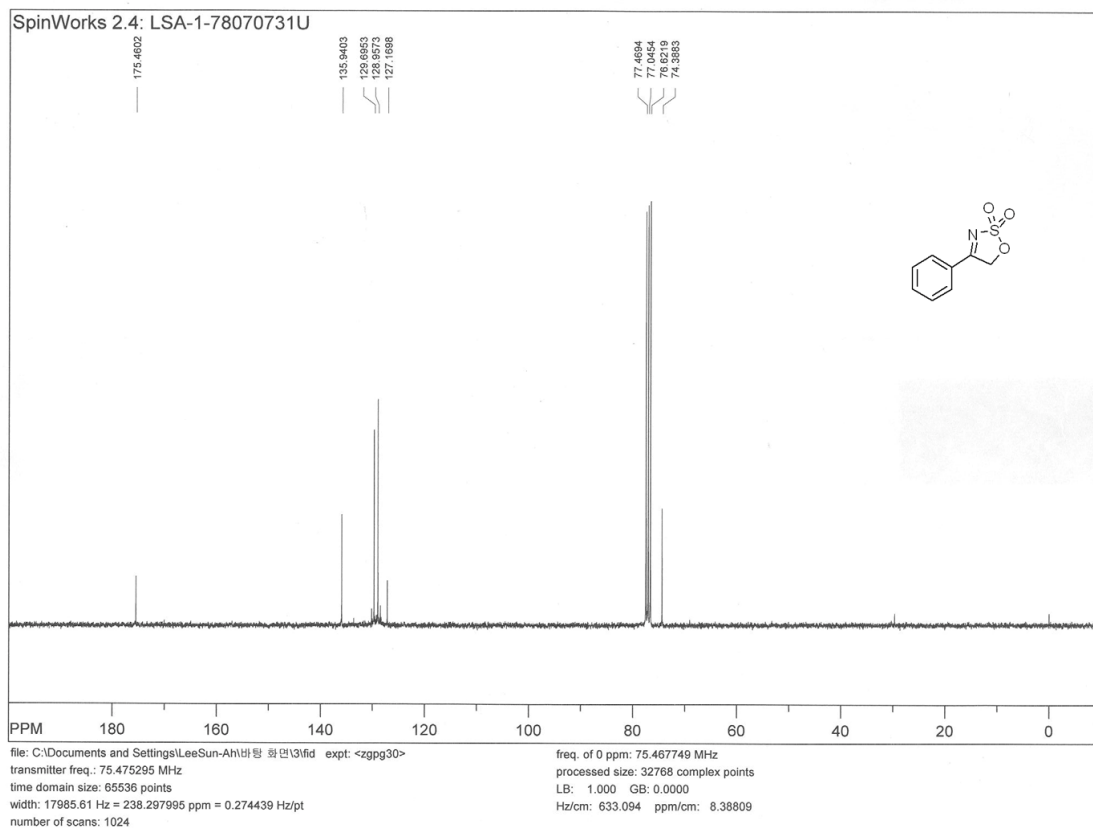
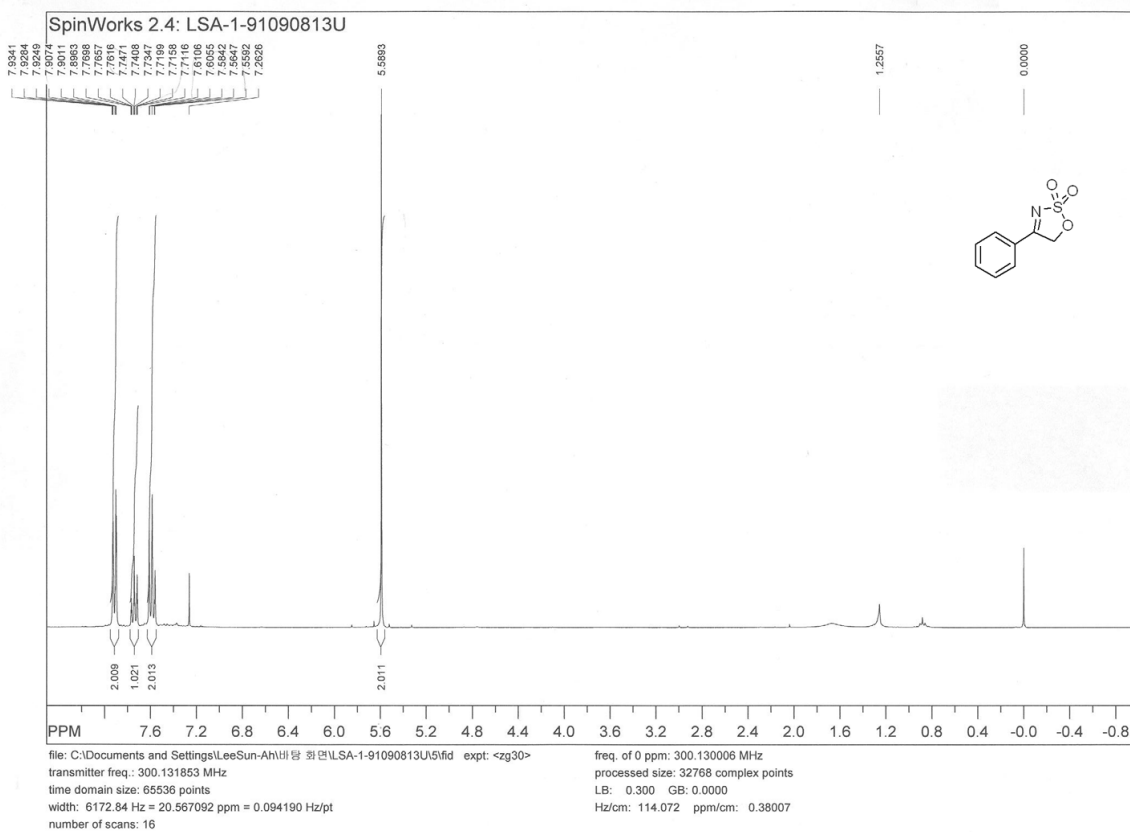


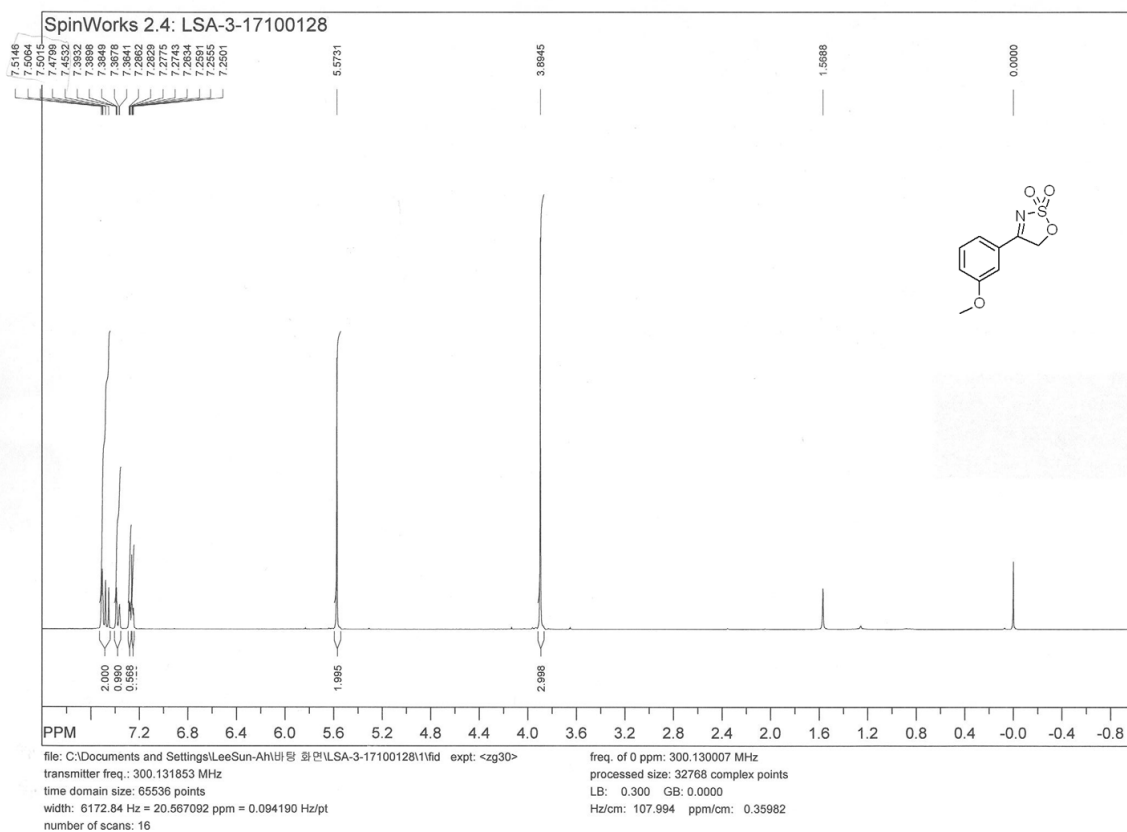
Yield = 87%; ¹H NMR (300 MHz, CDCl₃) δ 7.57 (d, 1H, *J* = 7.8 Hz), 7.47(d, 1H, *J* = 7.6 Hz), 7.37-7.21 (m, 2H), 6.85 (s, 1H), 5.07 (q, 1H, *J* = 6.0 Hz), 4.73 (d, 1H, *J* = 6.3 Hz), 6.85 (s, 1H, *J* = 7.7 Hz), 3.96-3.76 (m, 2H); ¹³C NMR (75 MHz, CD₃OD) δ 156.7, 156.6, 129.5, 125.6, 124.1, 122.2, 112.1, 105.7, 56.7, 49.3; EIMS (70eV) *m/z* (rel intensity) 238 (M⁺, 3), 174 (3), 145 (100), 118 (16); [α]_D²³ = -32.0 (*c* 0.30, MeOH); HPLC (Chiralcel AD-H column, ⁱPrOH/hexane = 20/80, 0.8 mL/min): *t*₁ = 12.2 min (*R*), *t*₂ = 14.1 min (*S*); *ee* = 91%.

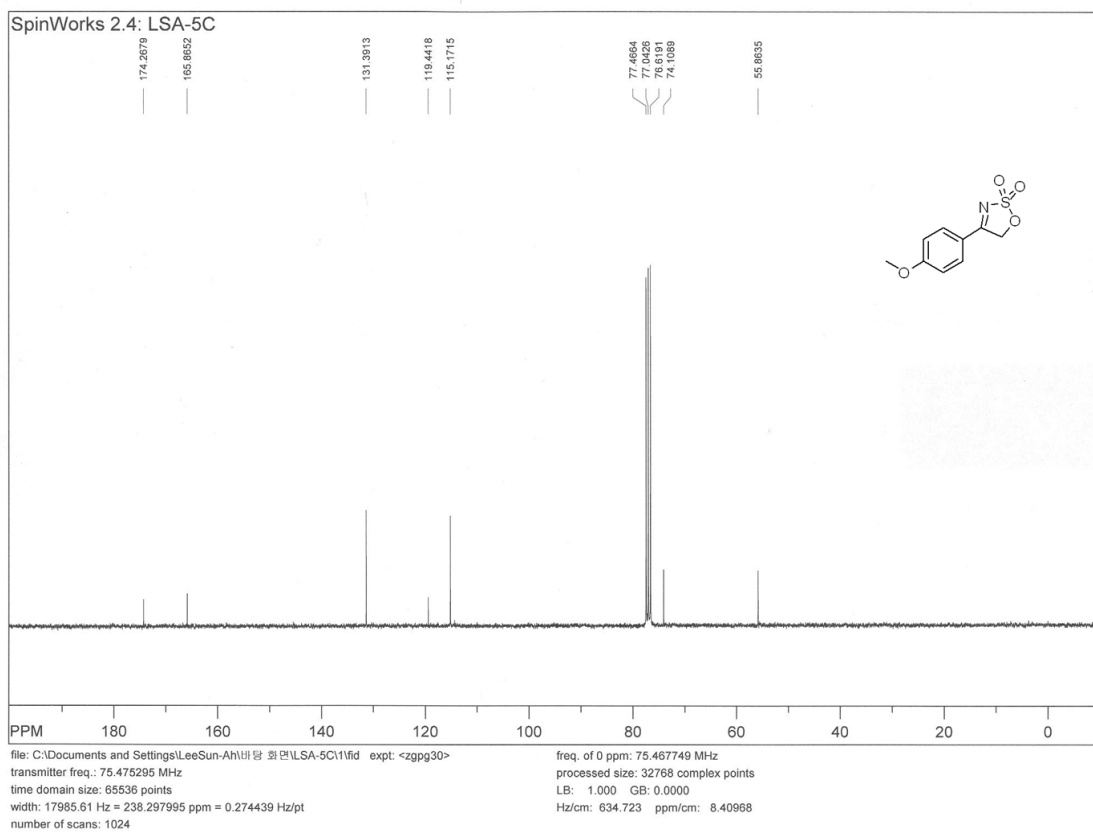
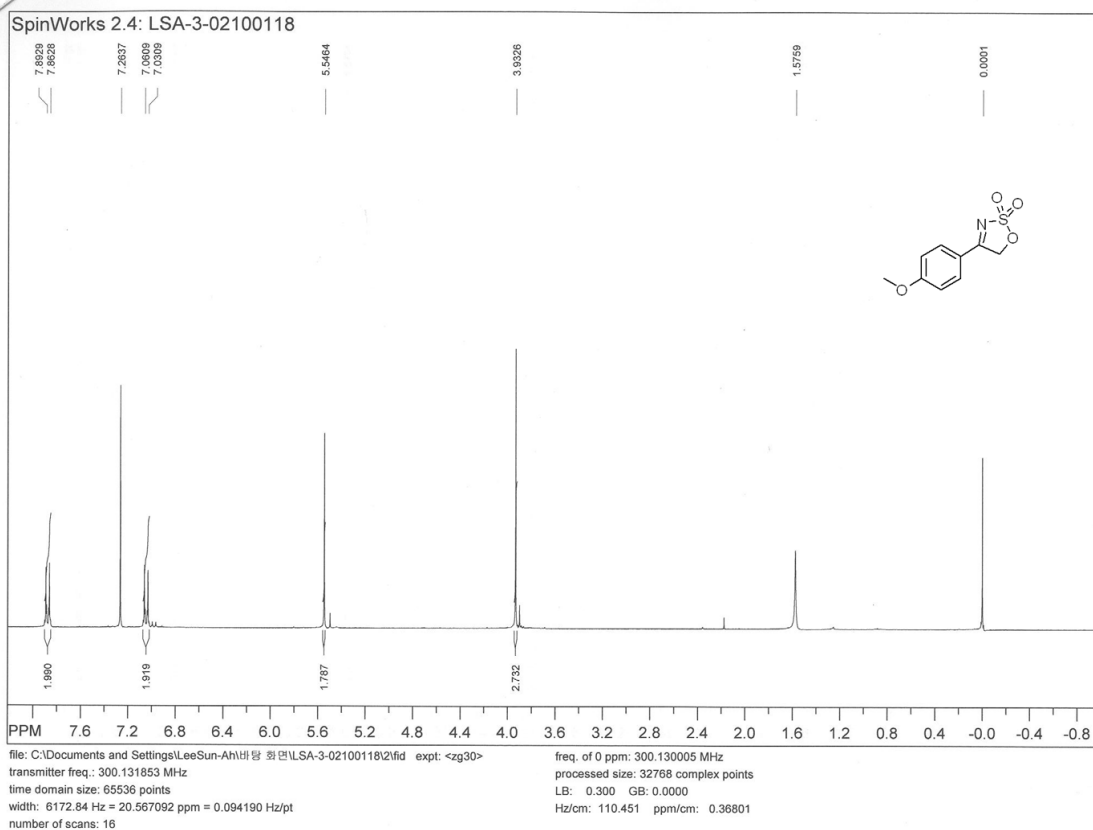
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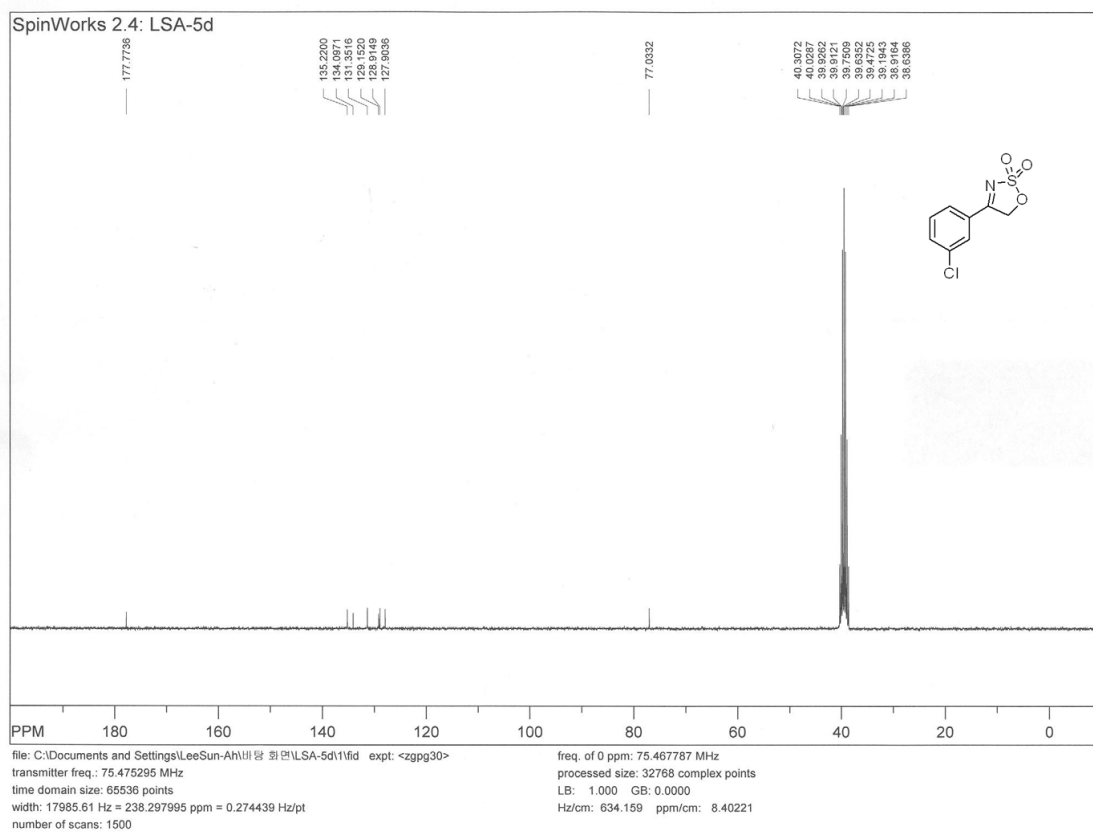
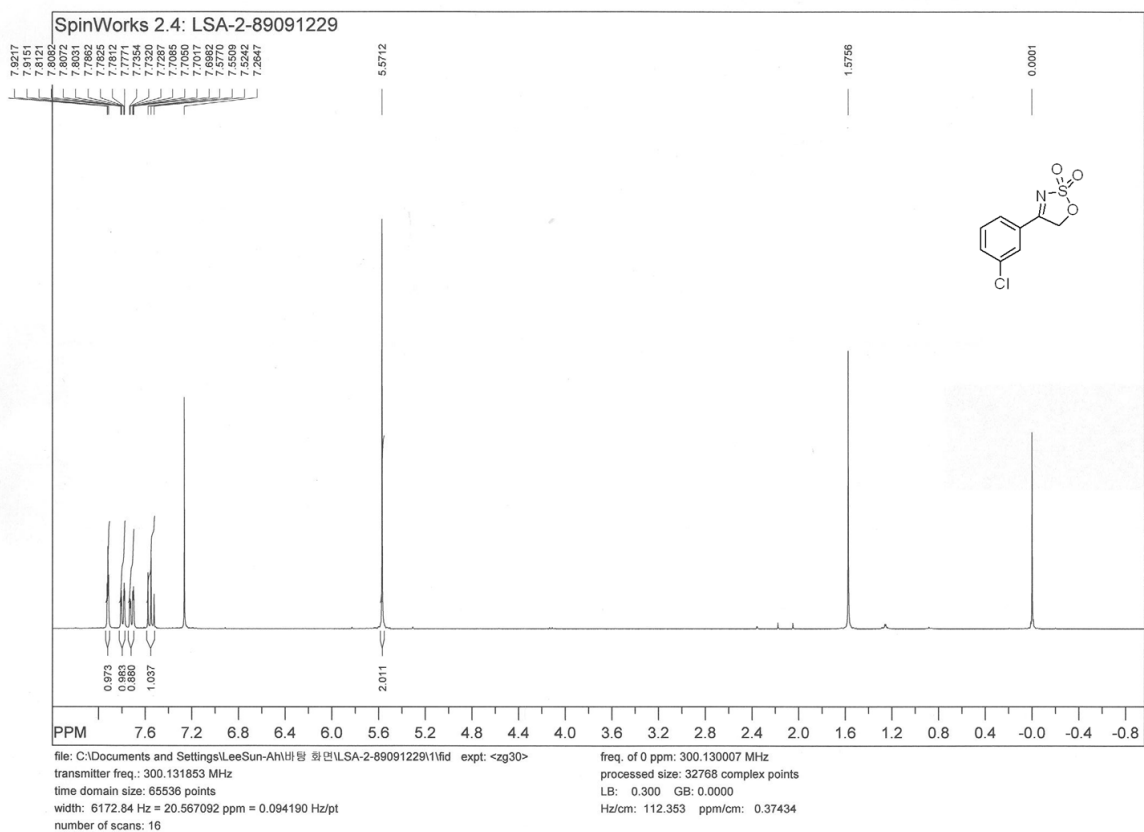
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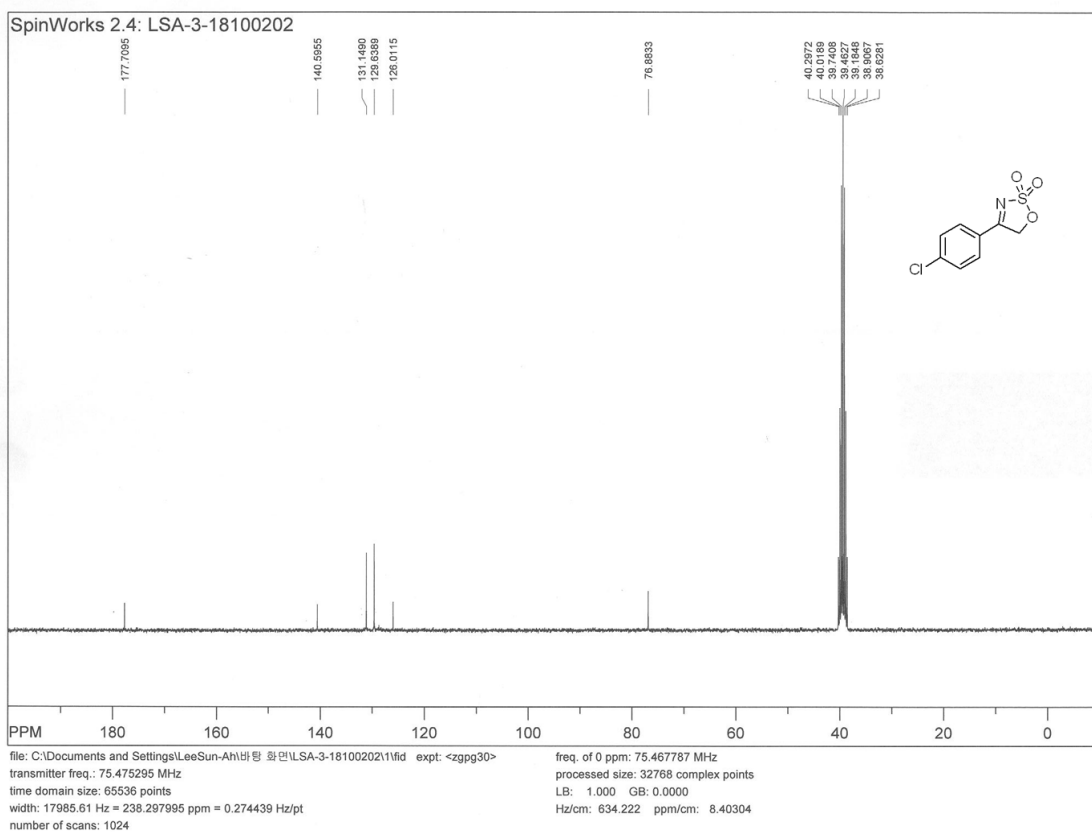
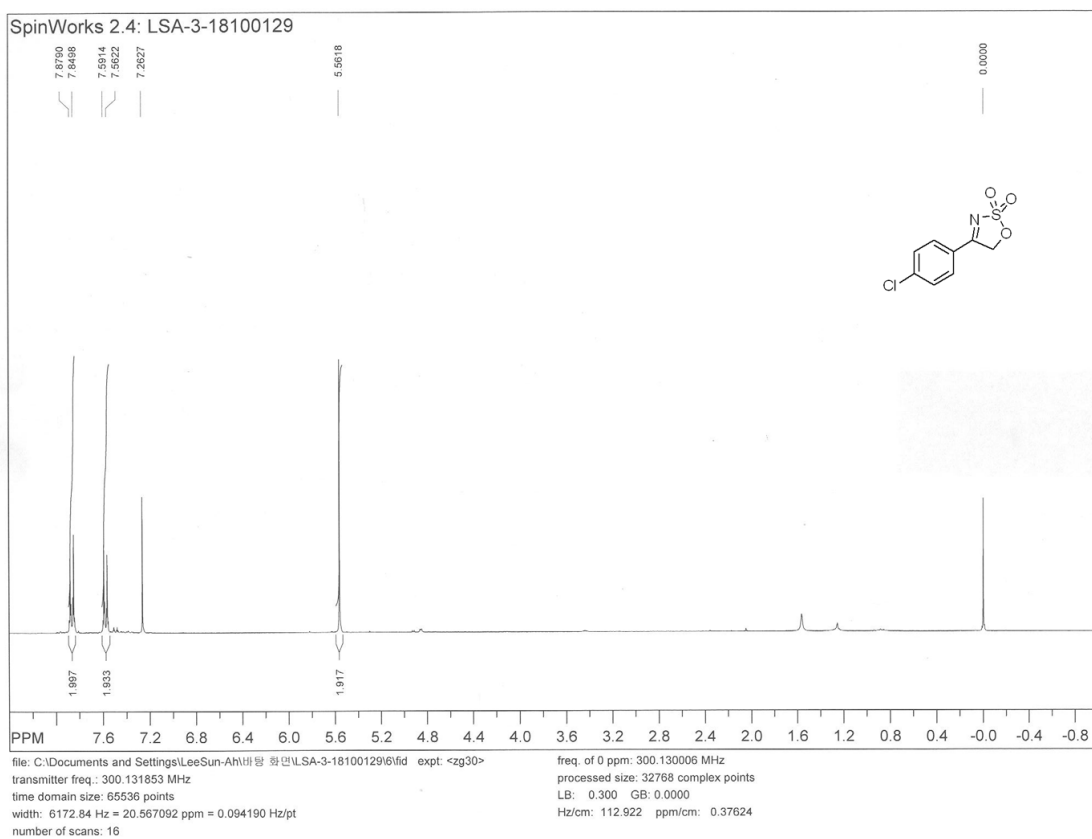
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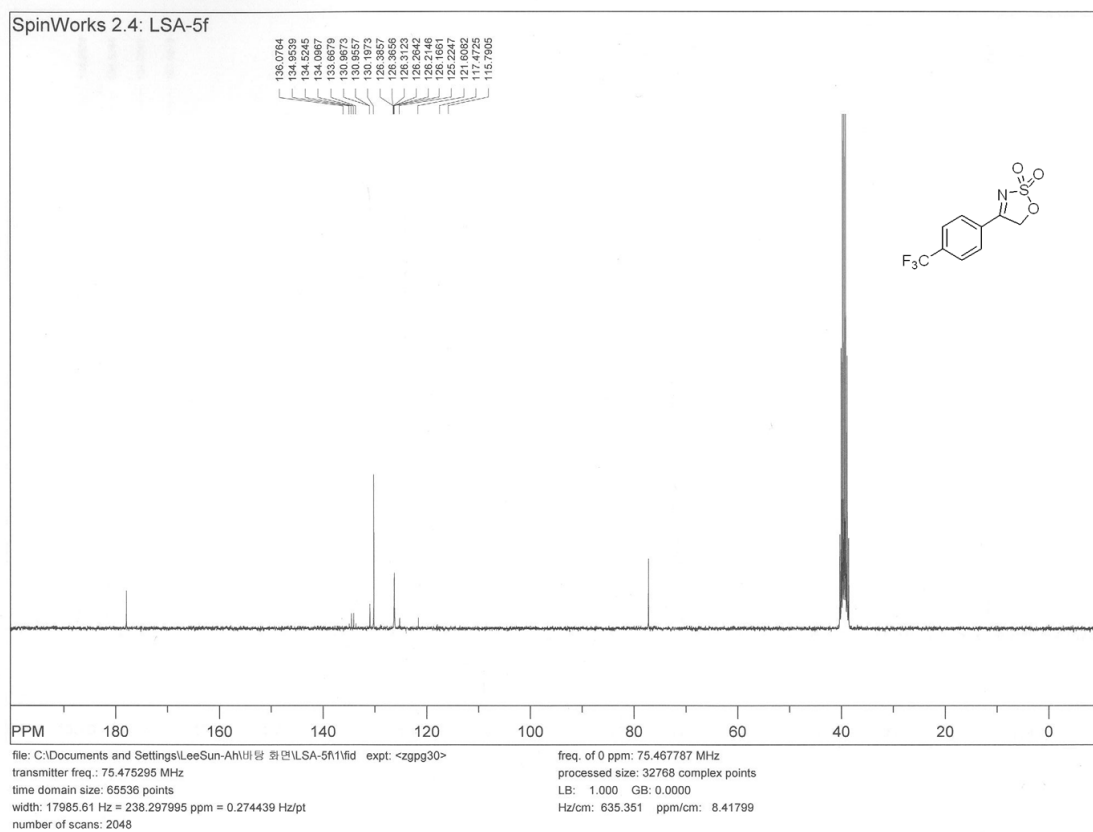
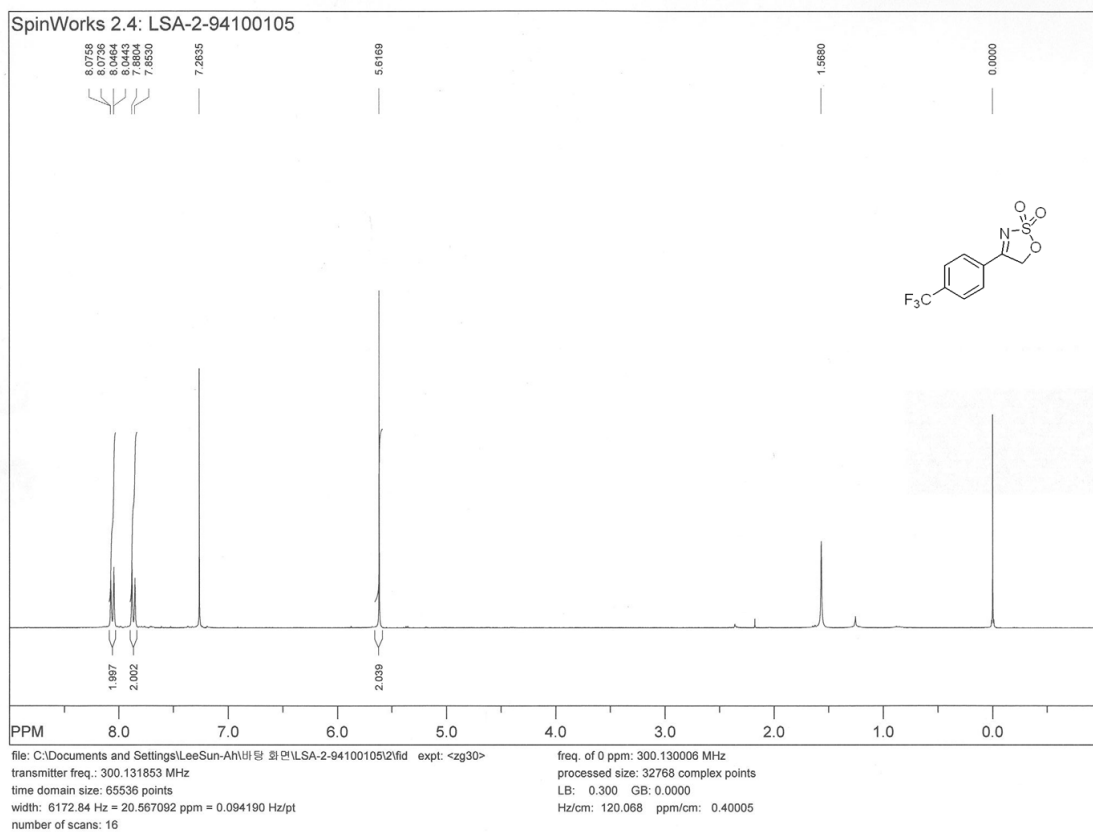


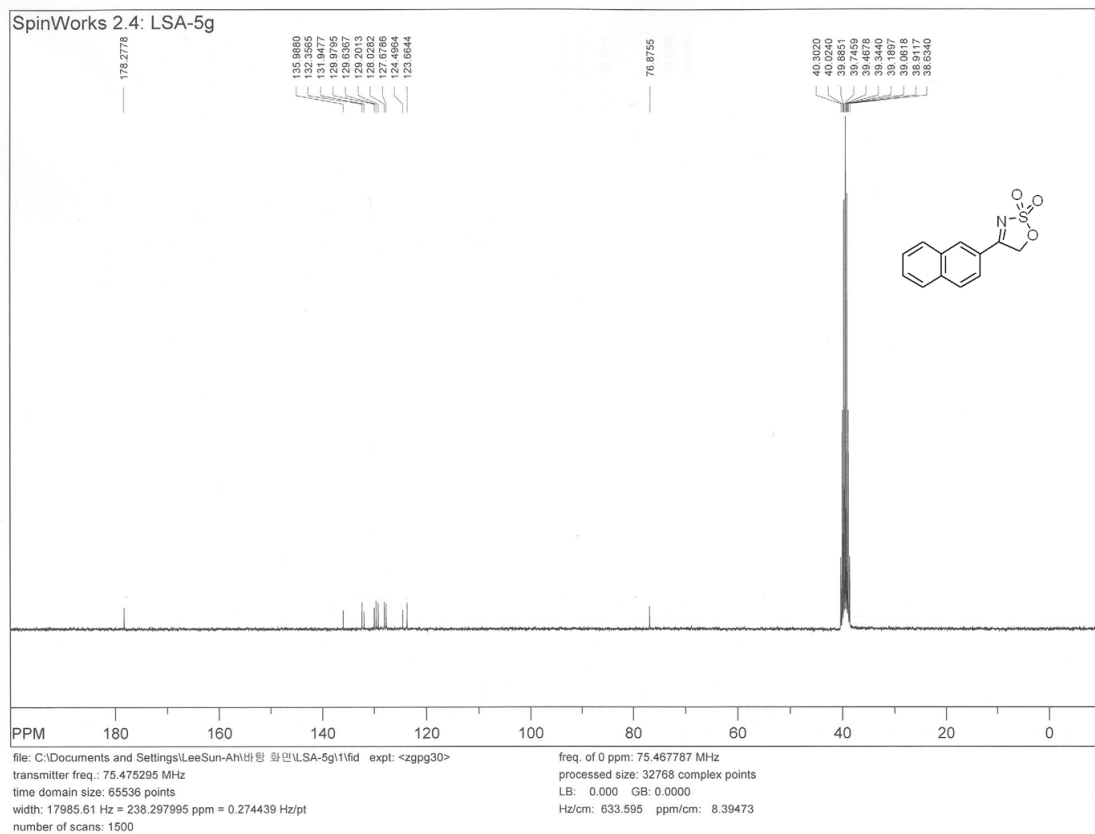
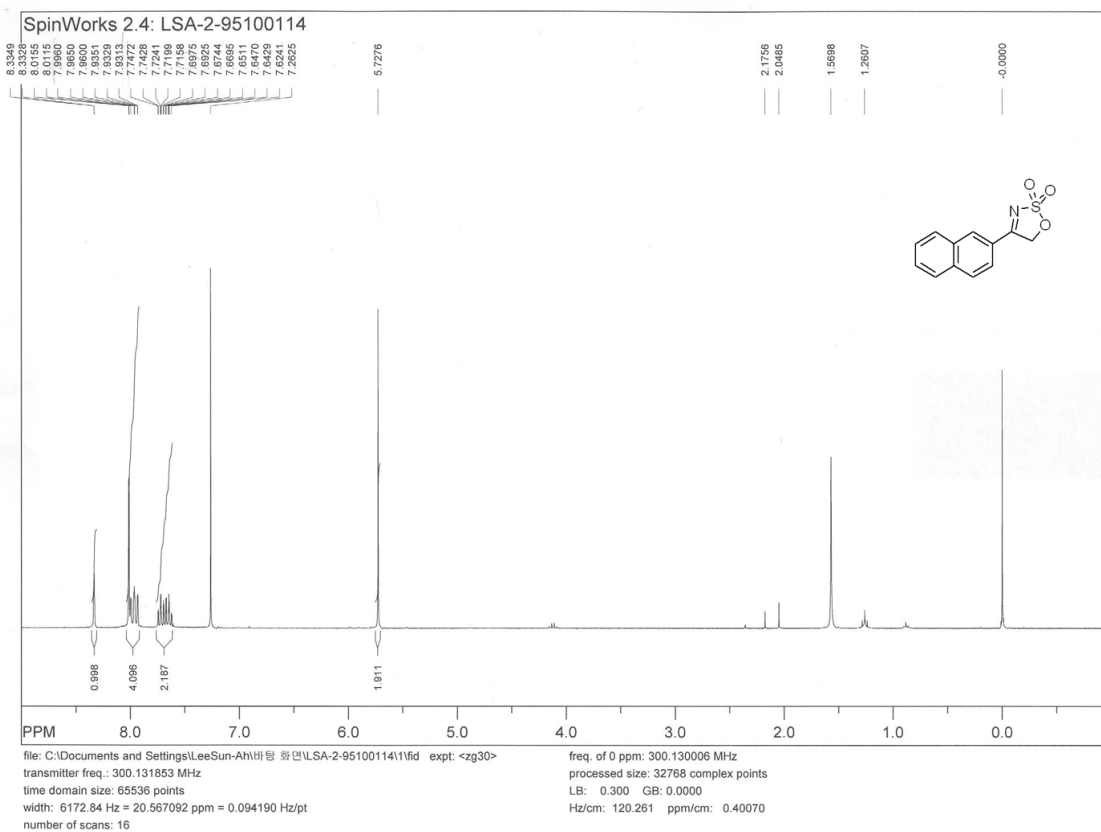


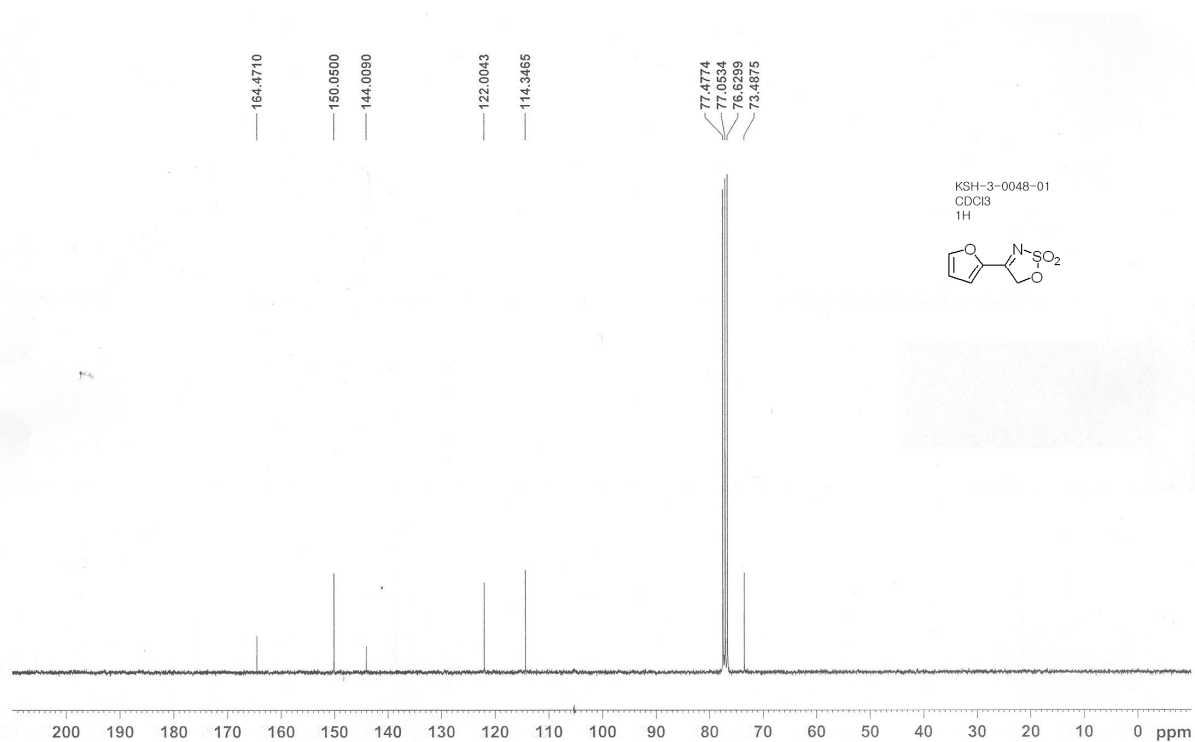
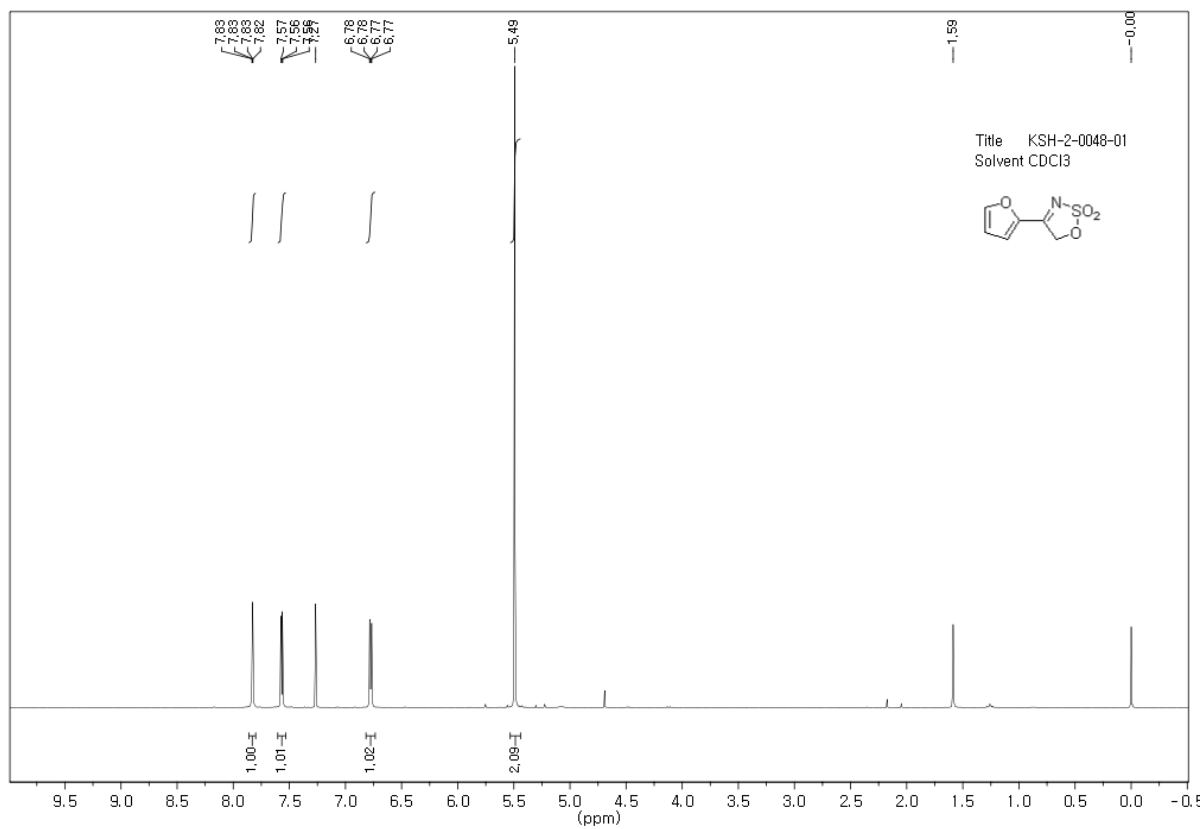


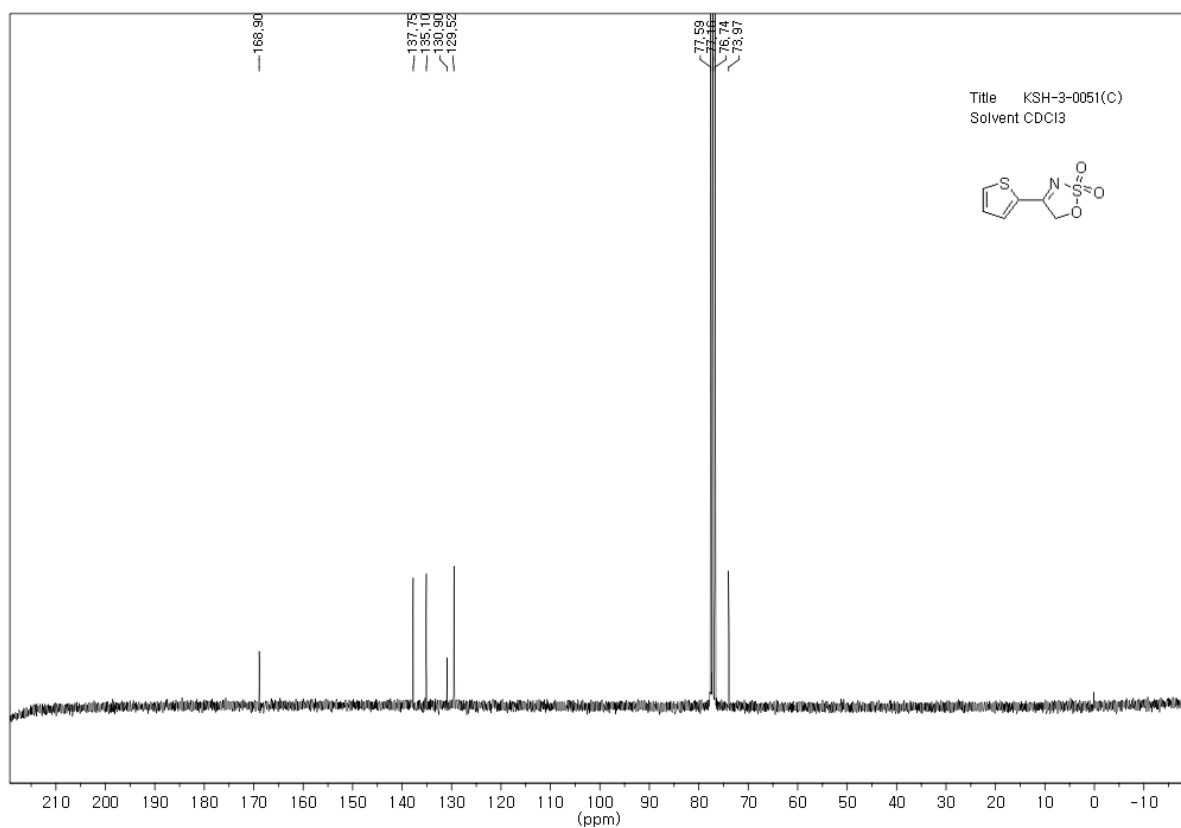
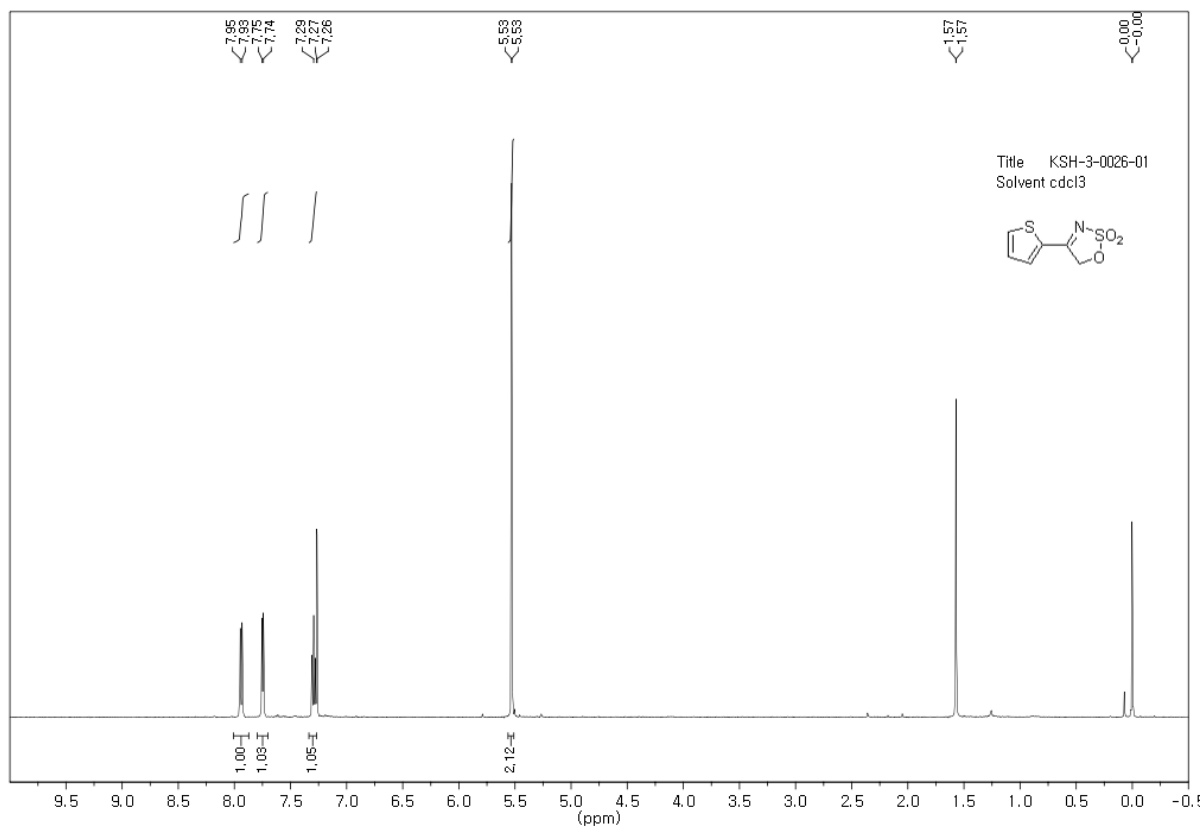


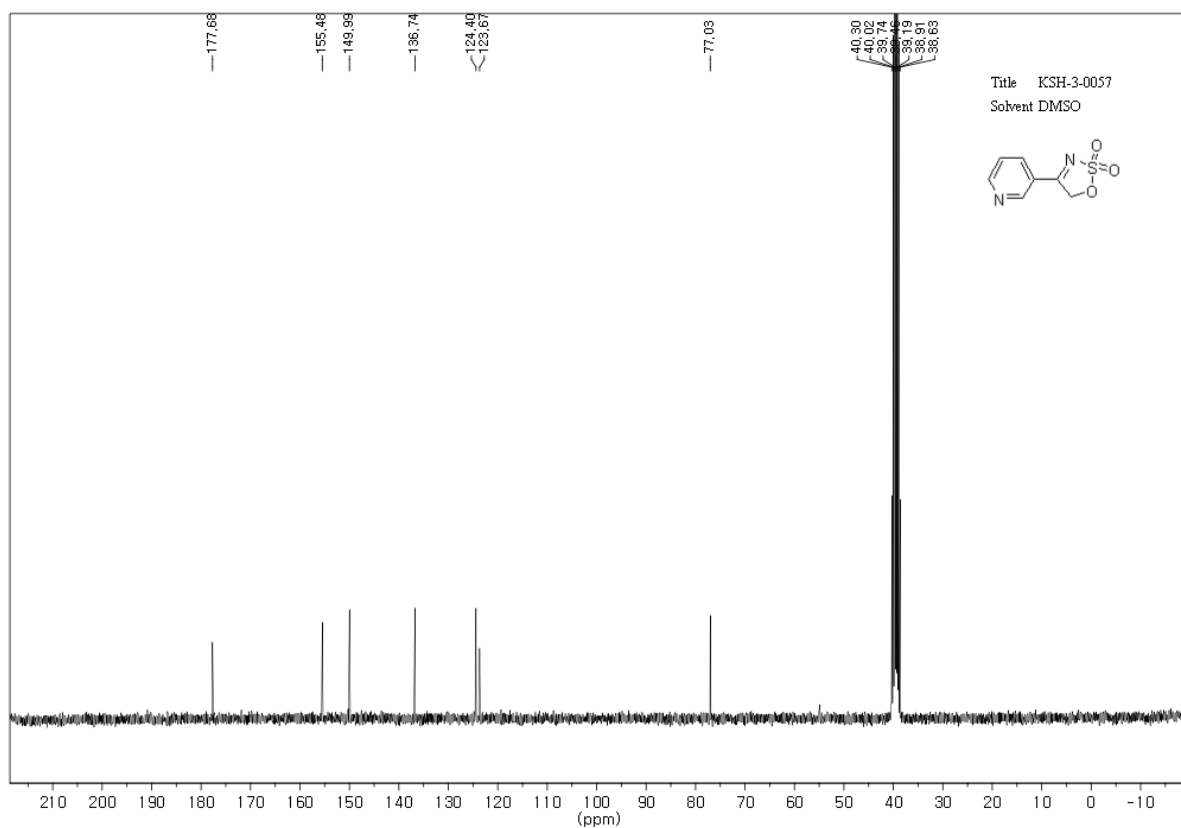
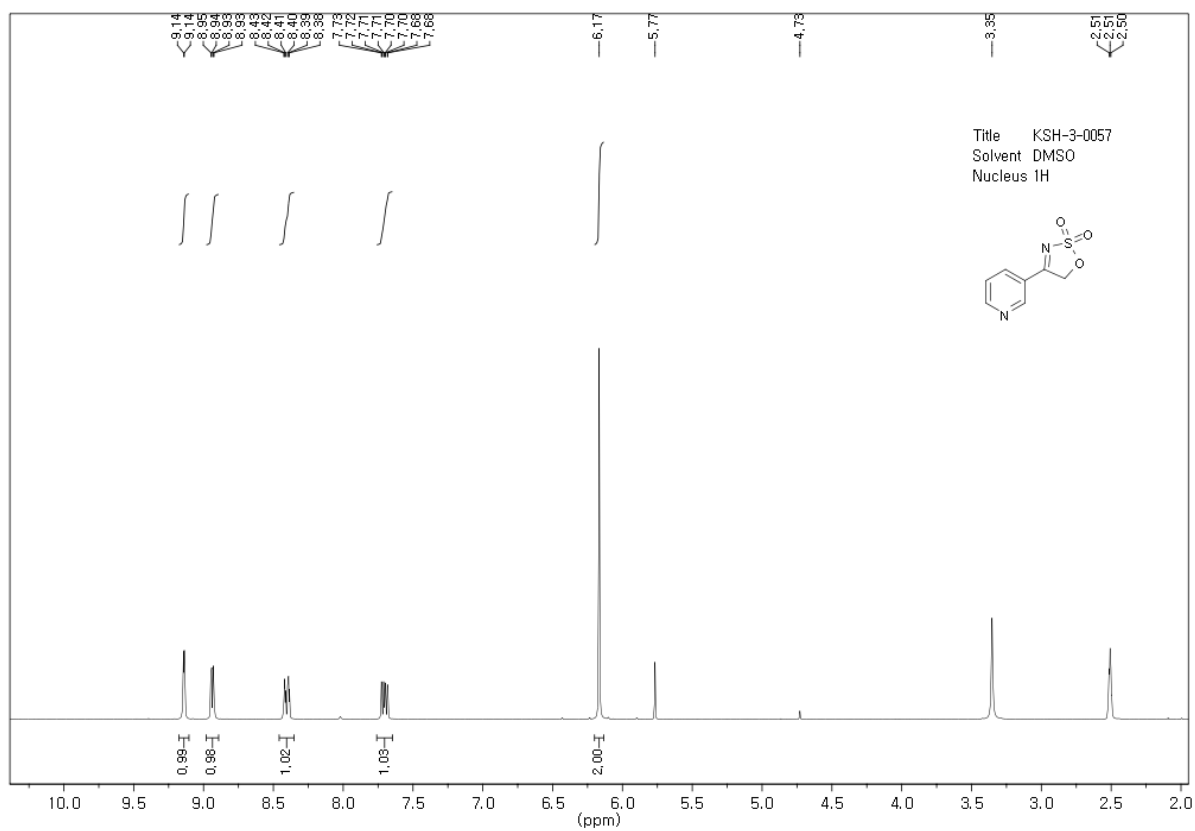


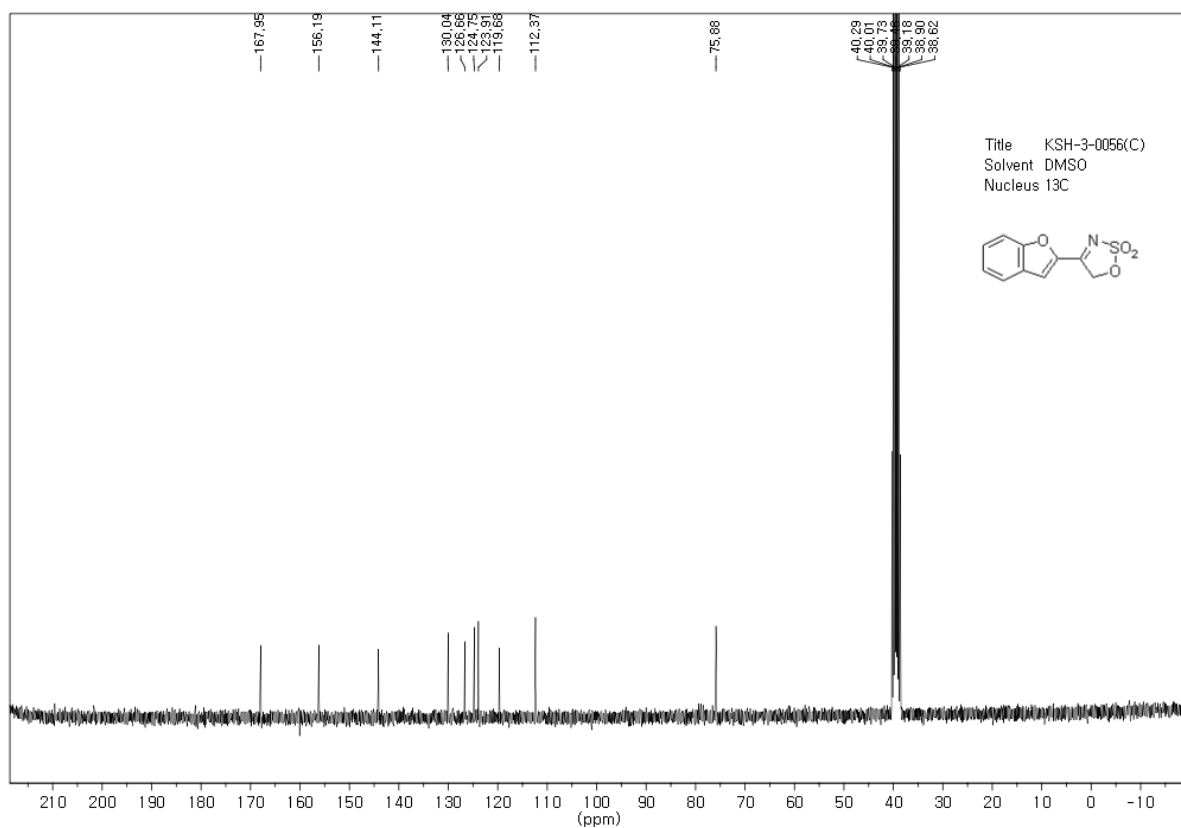
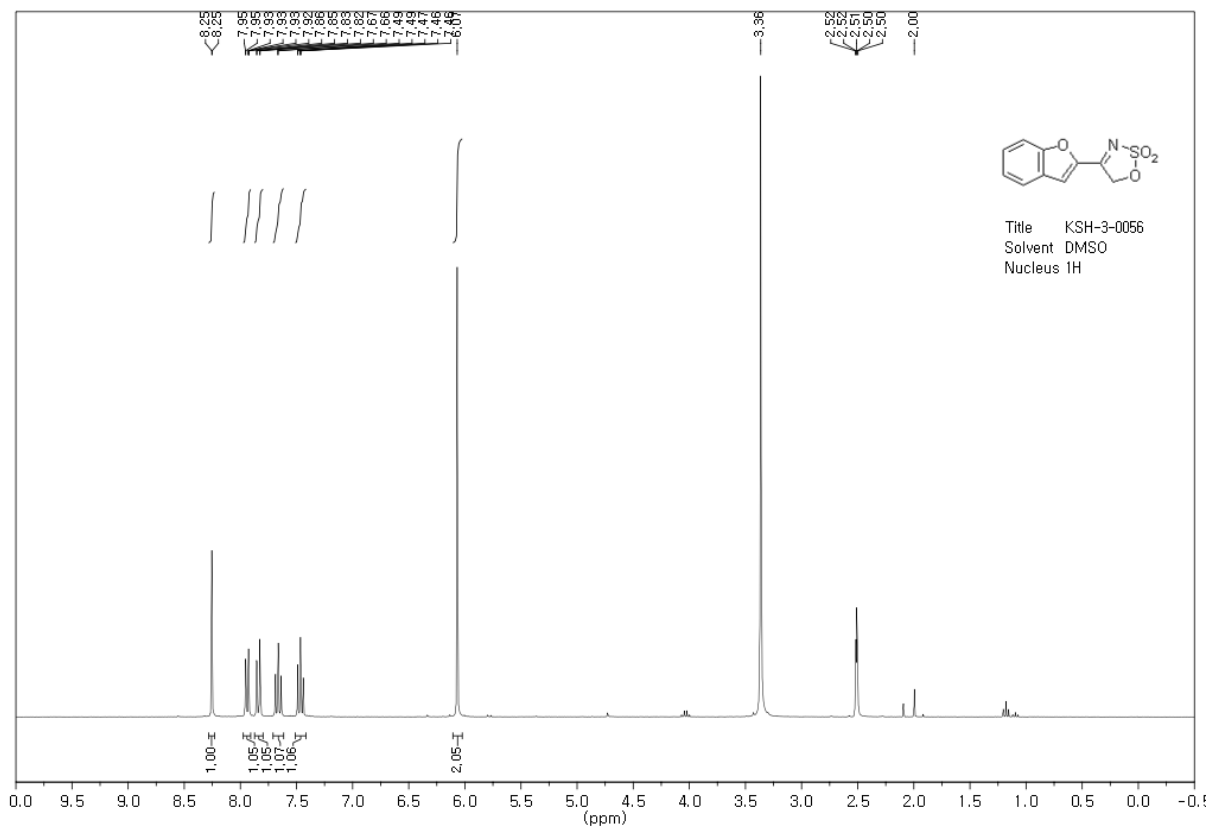


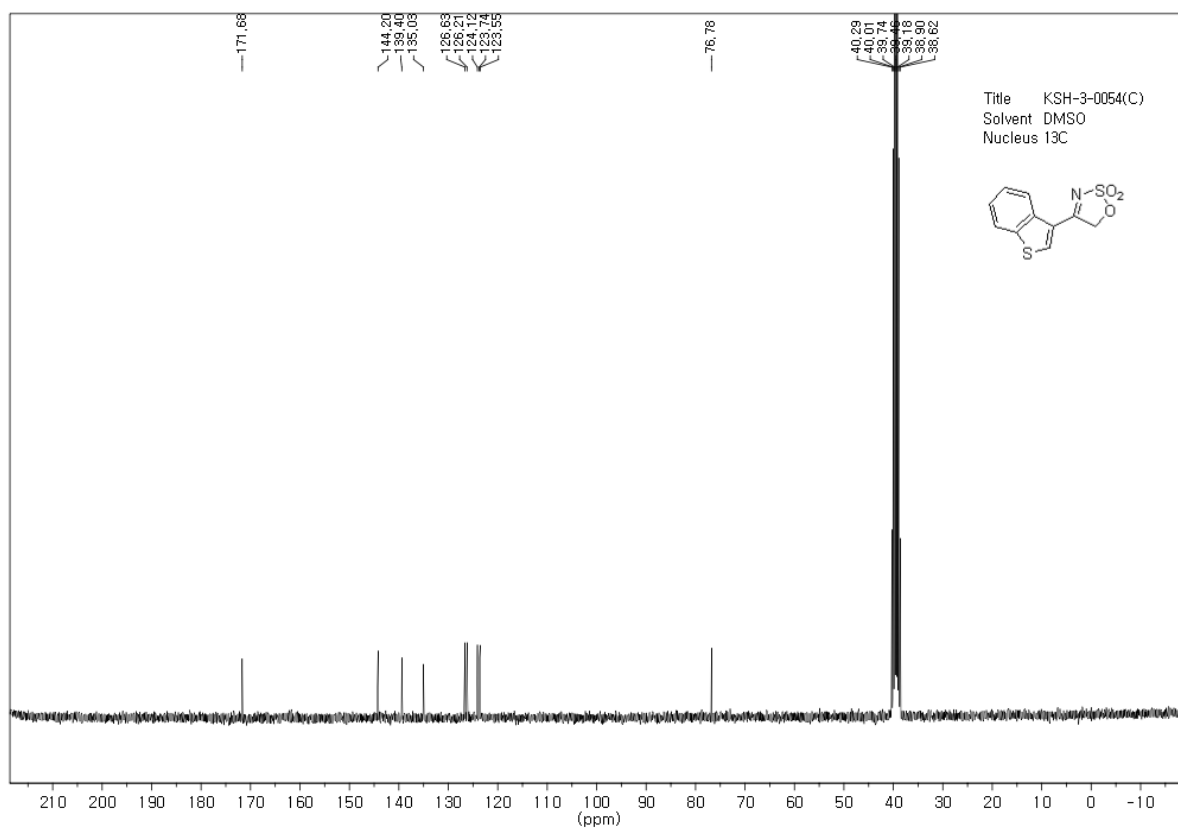
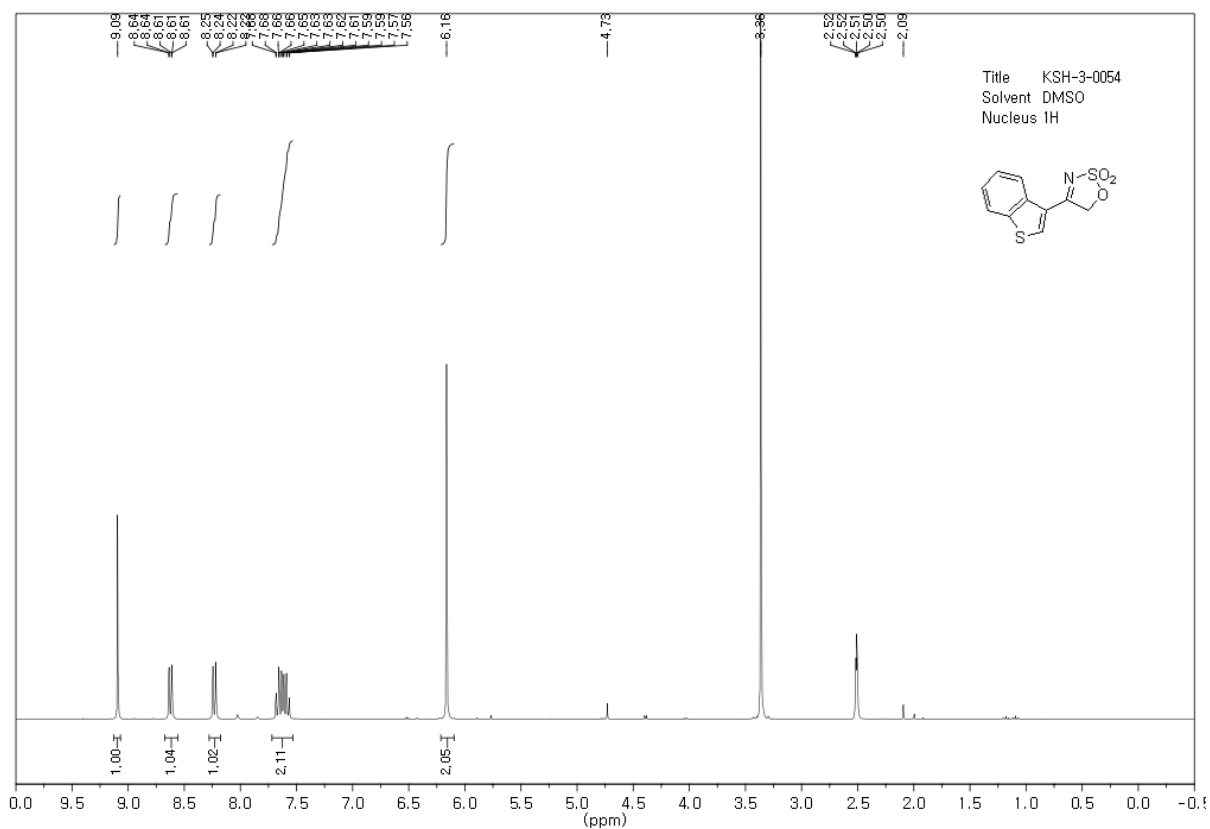


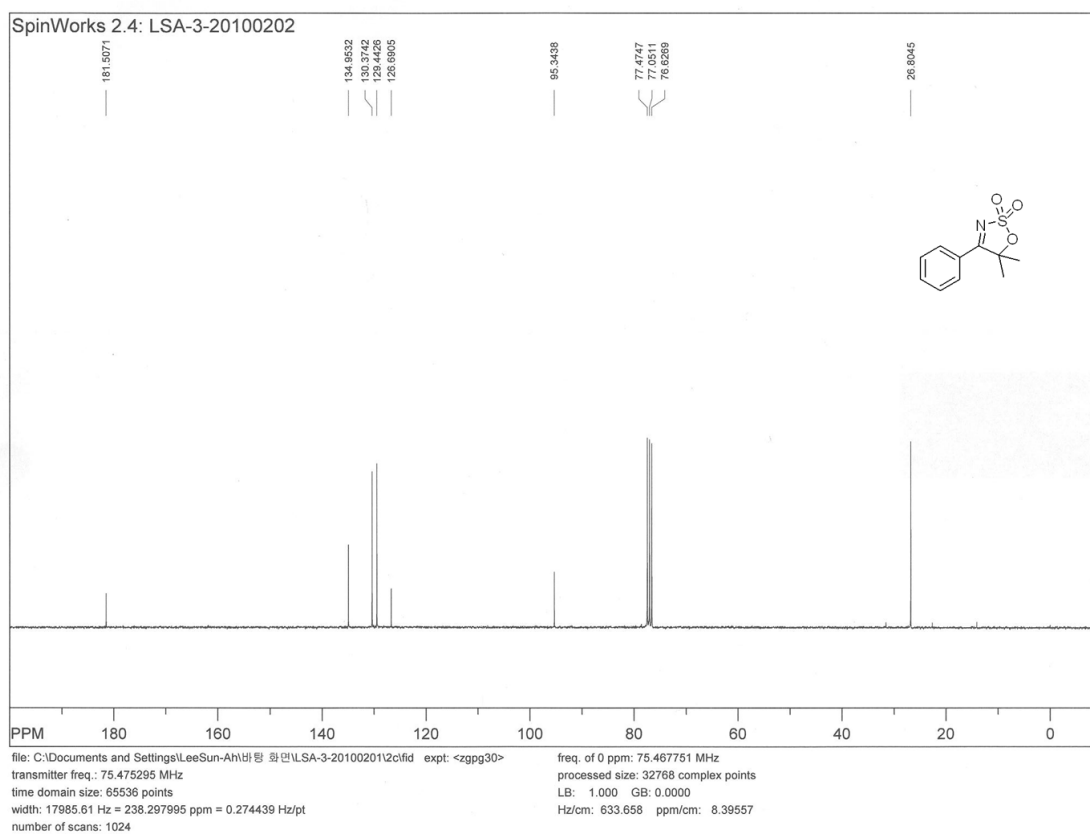
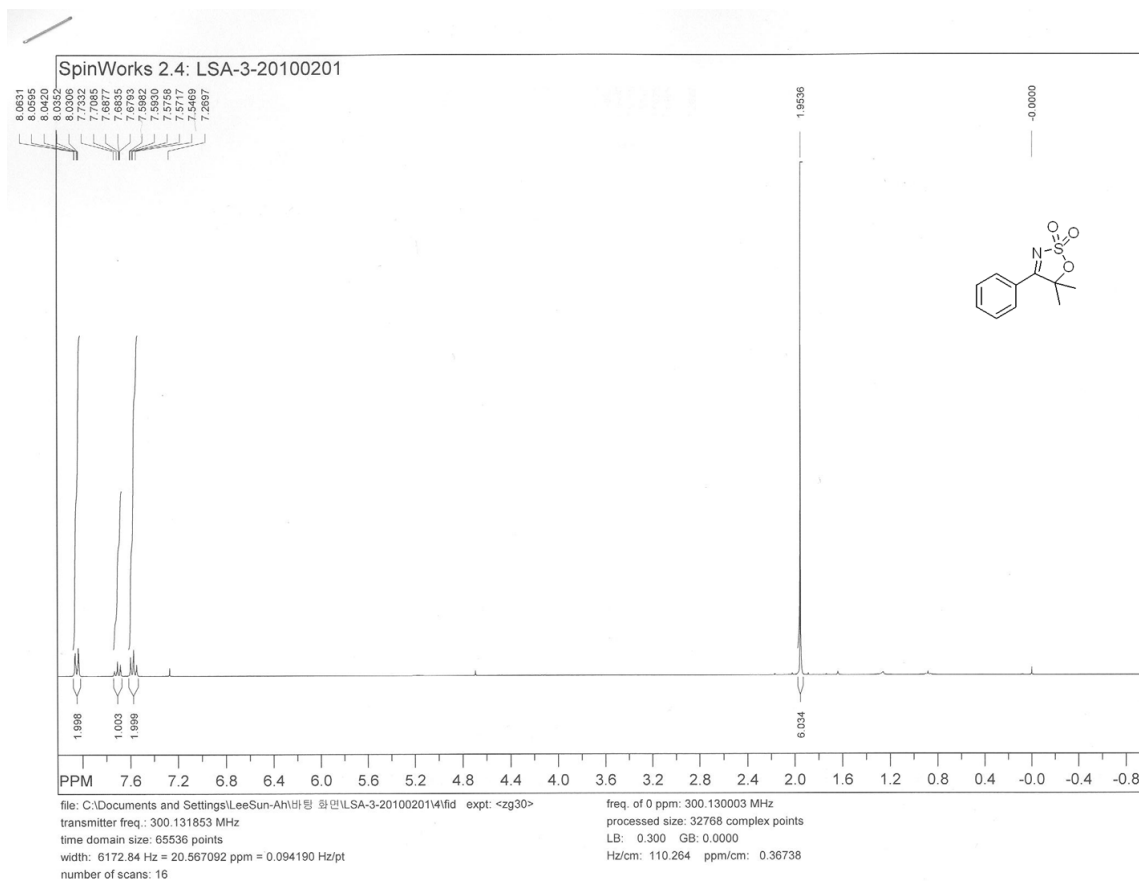


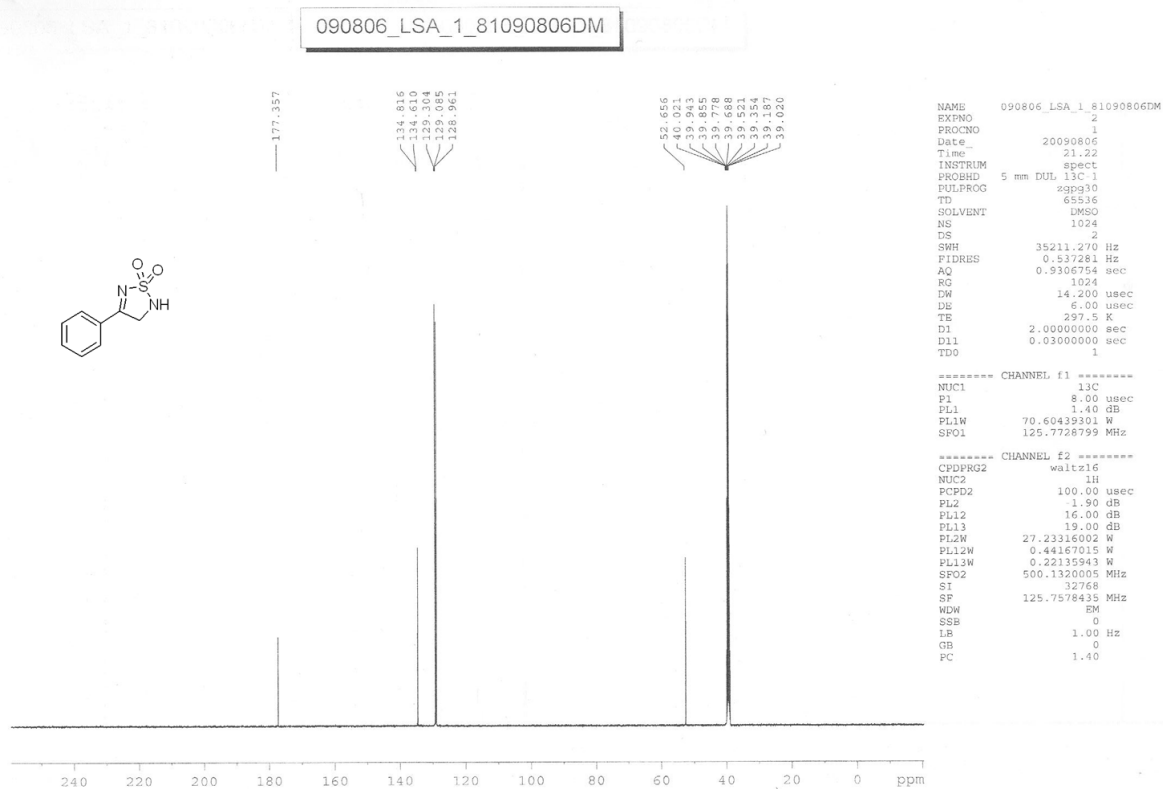
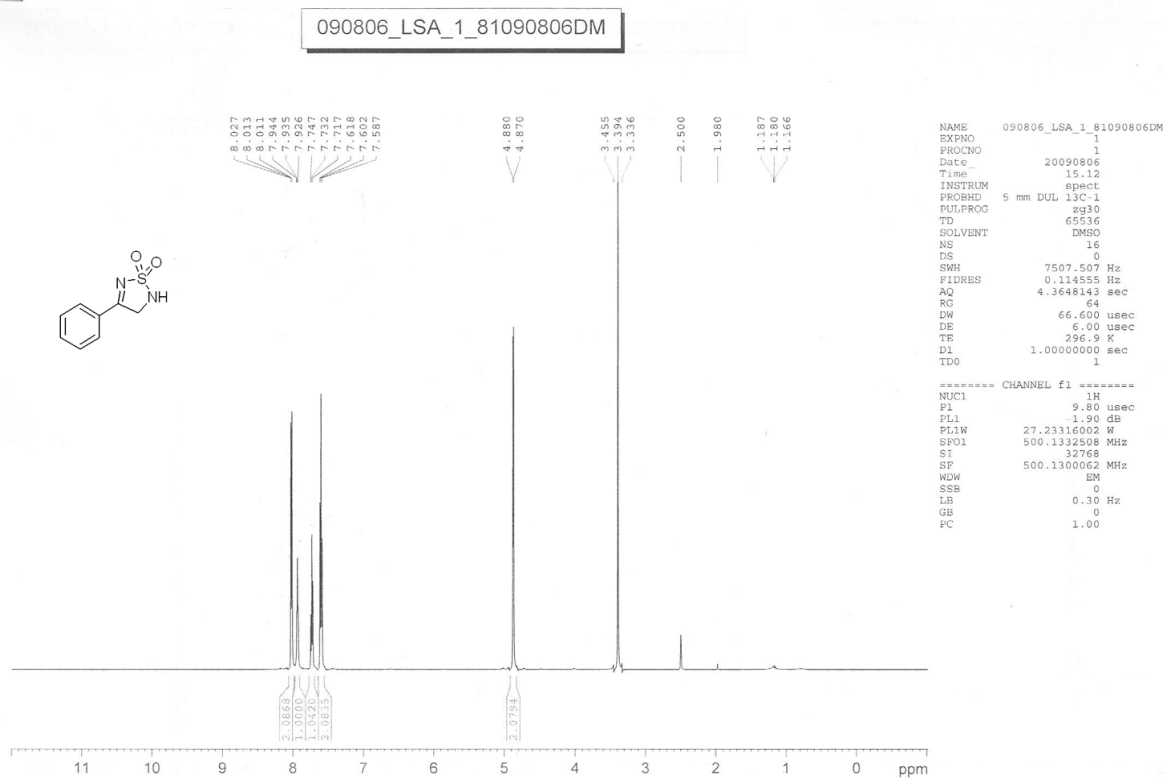


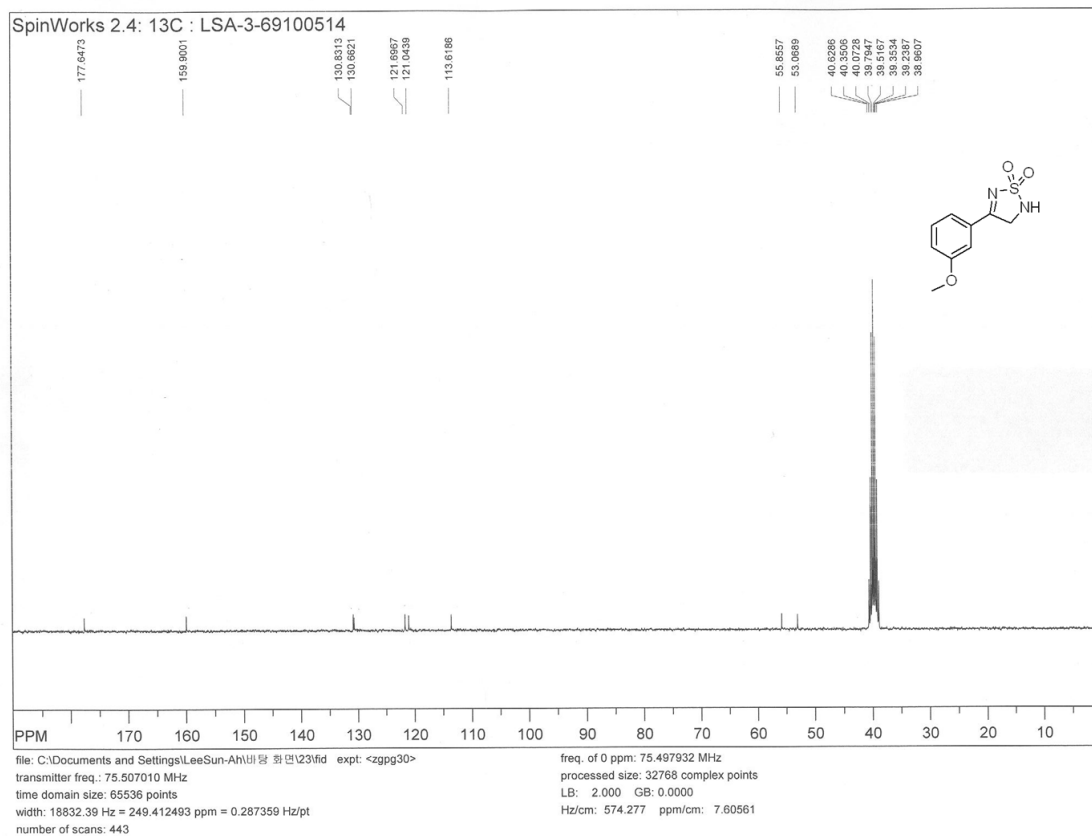
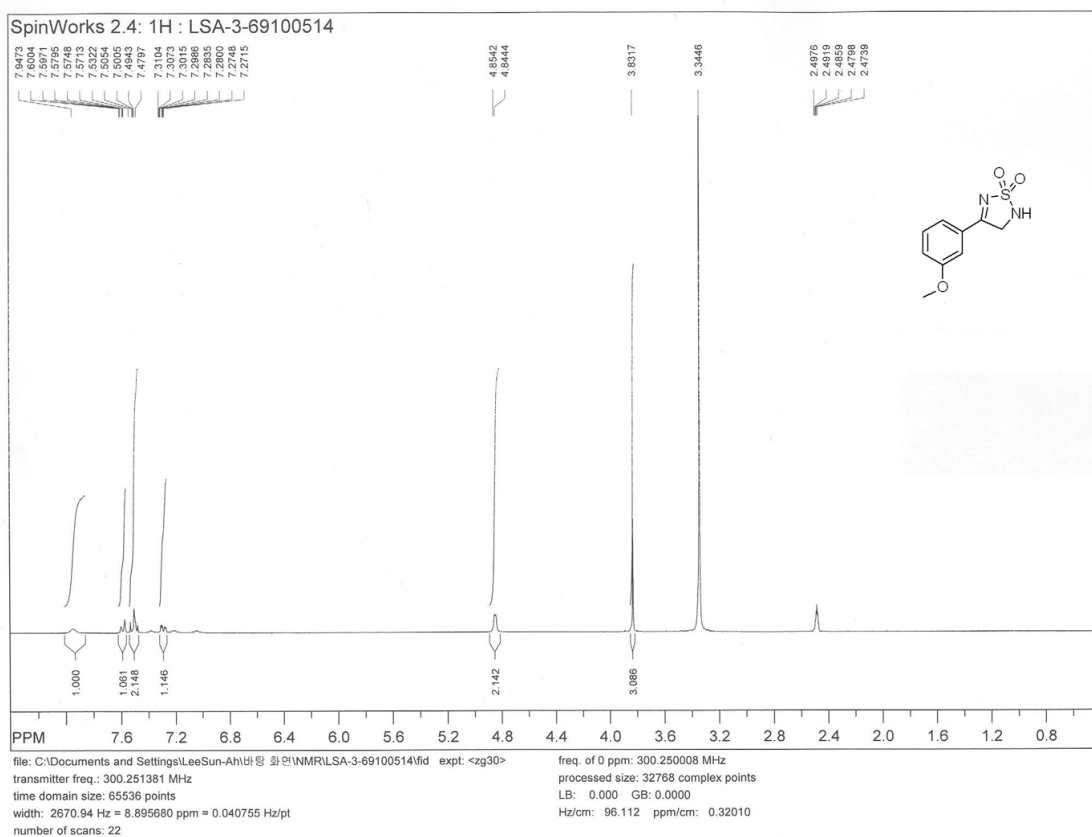


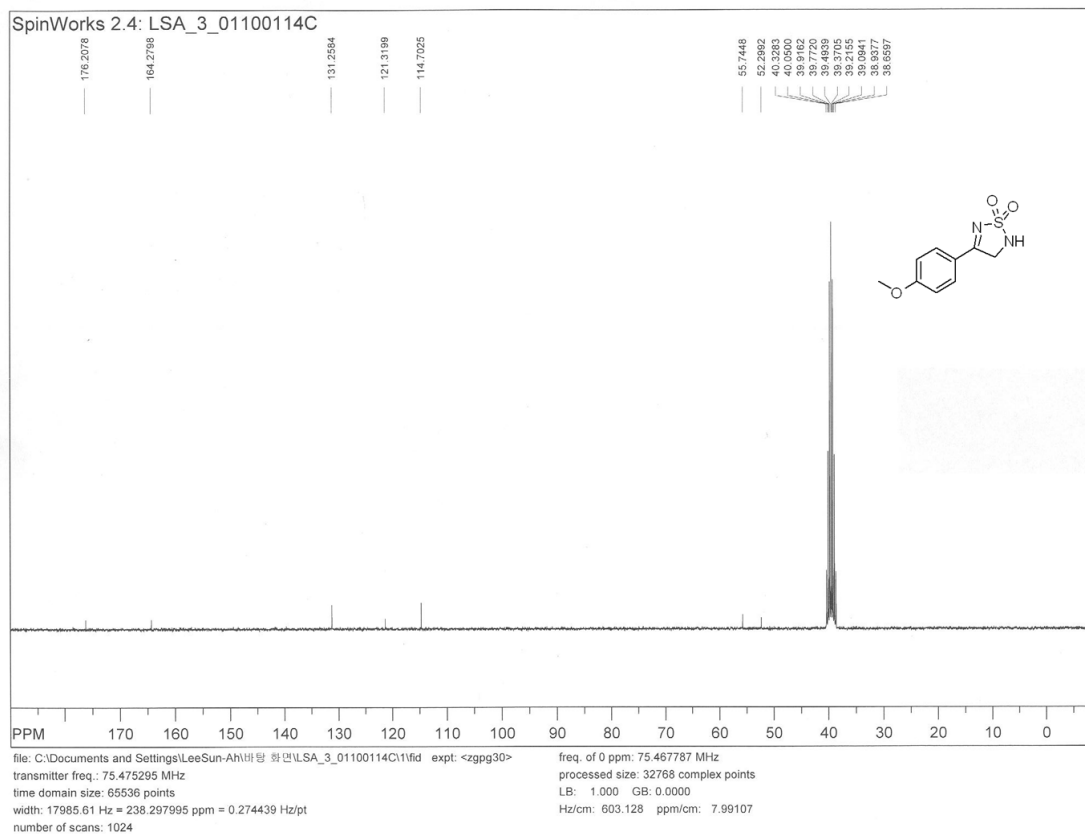
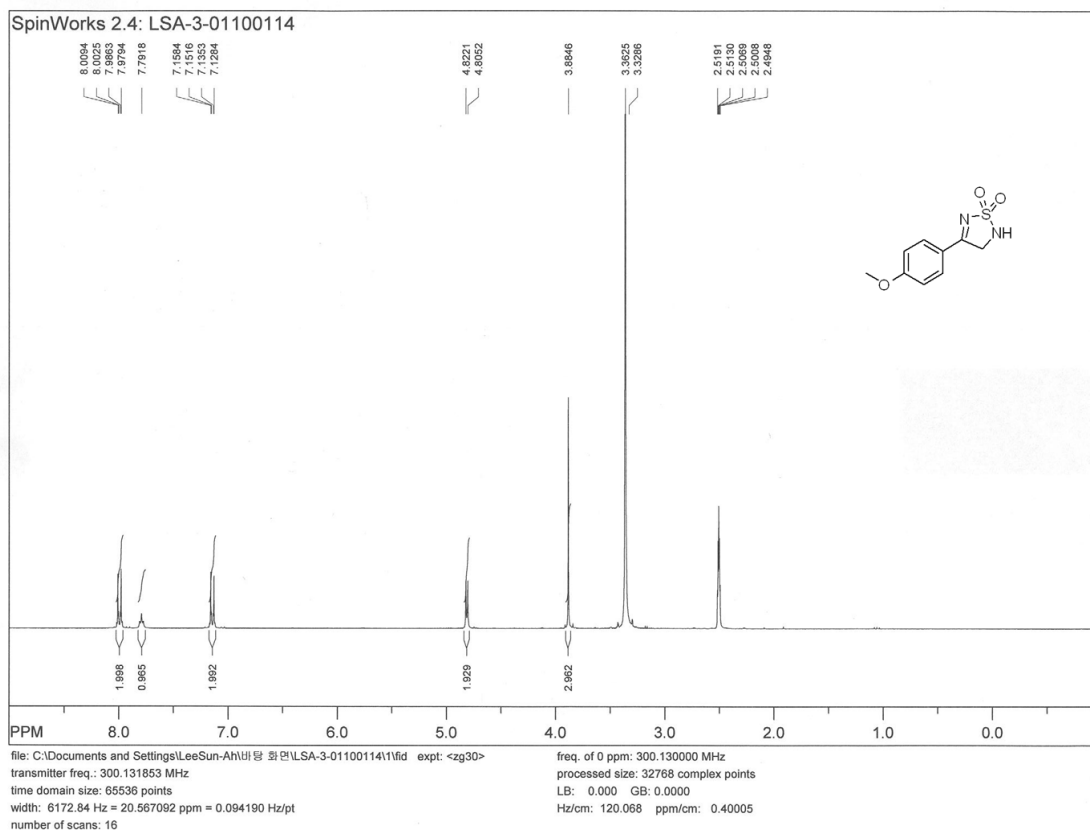


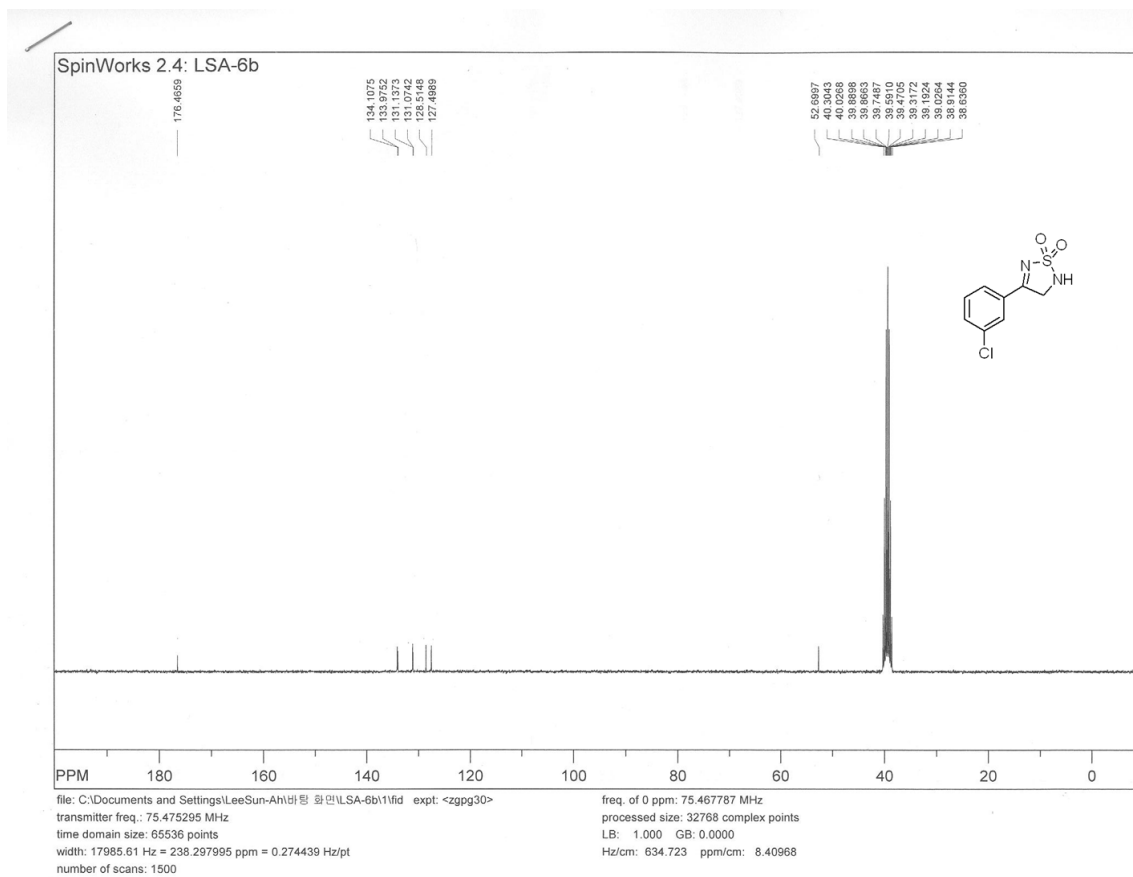
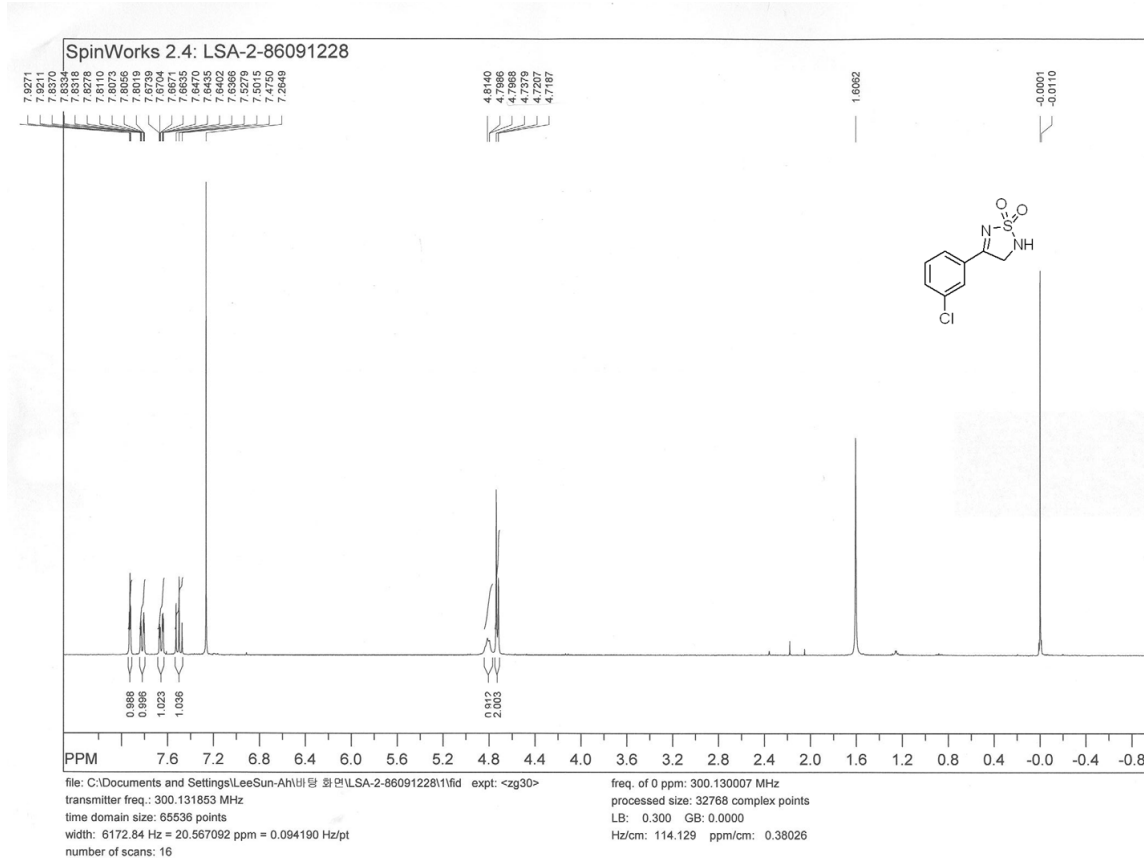


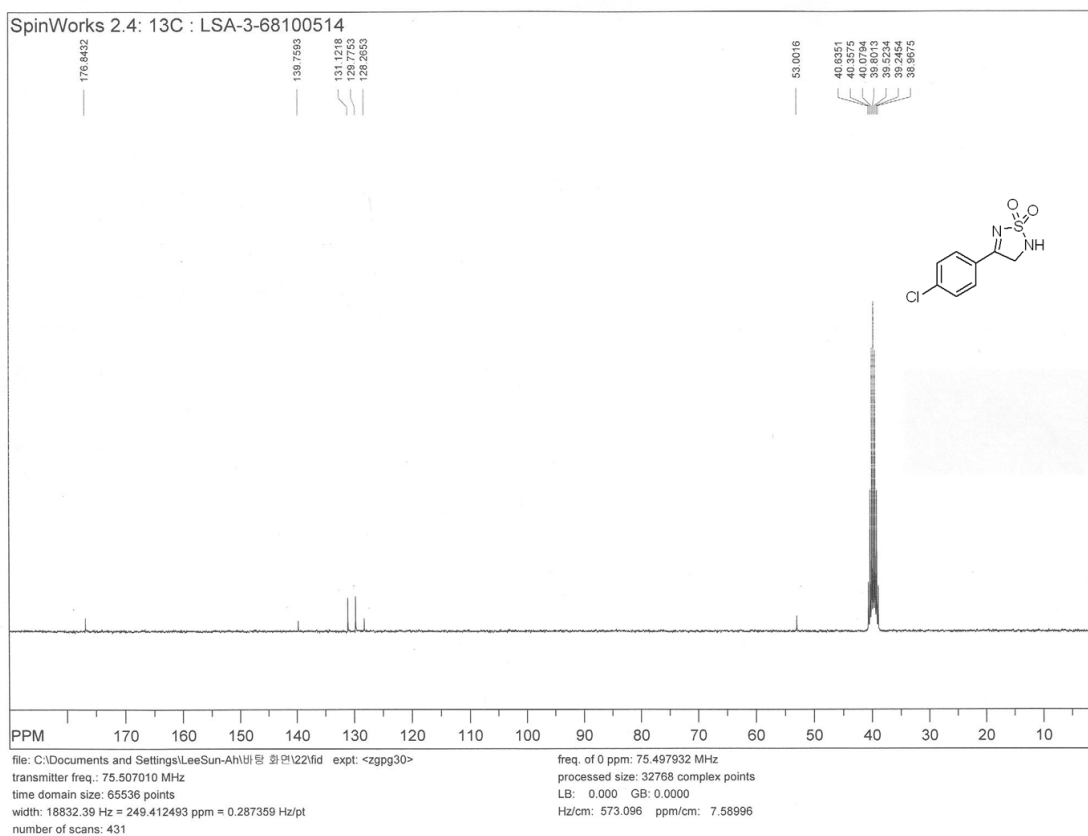
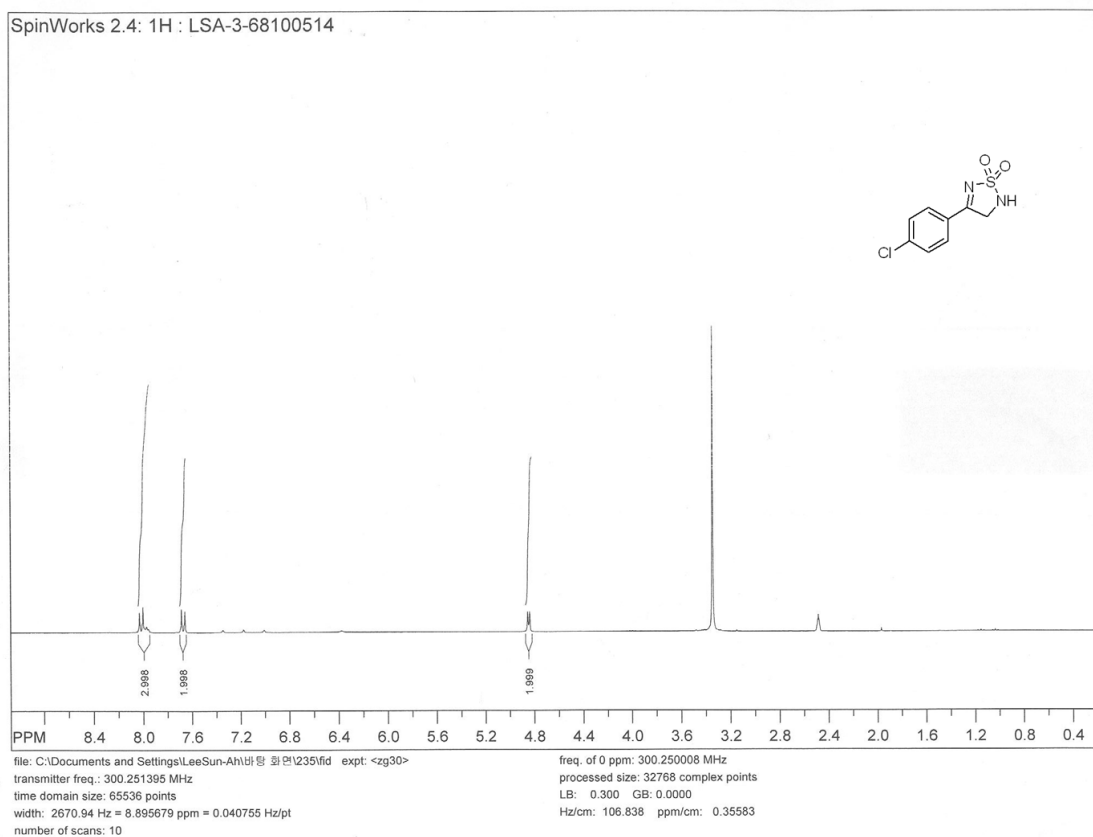


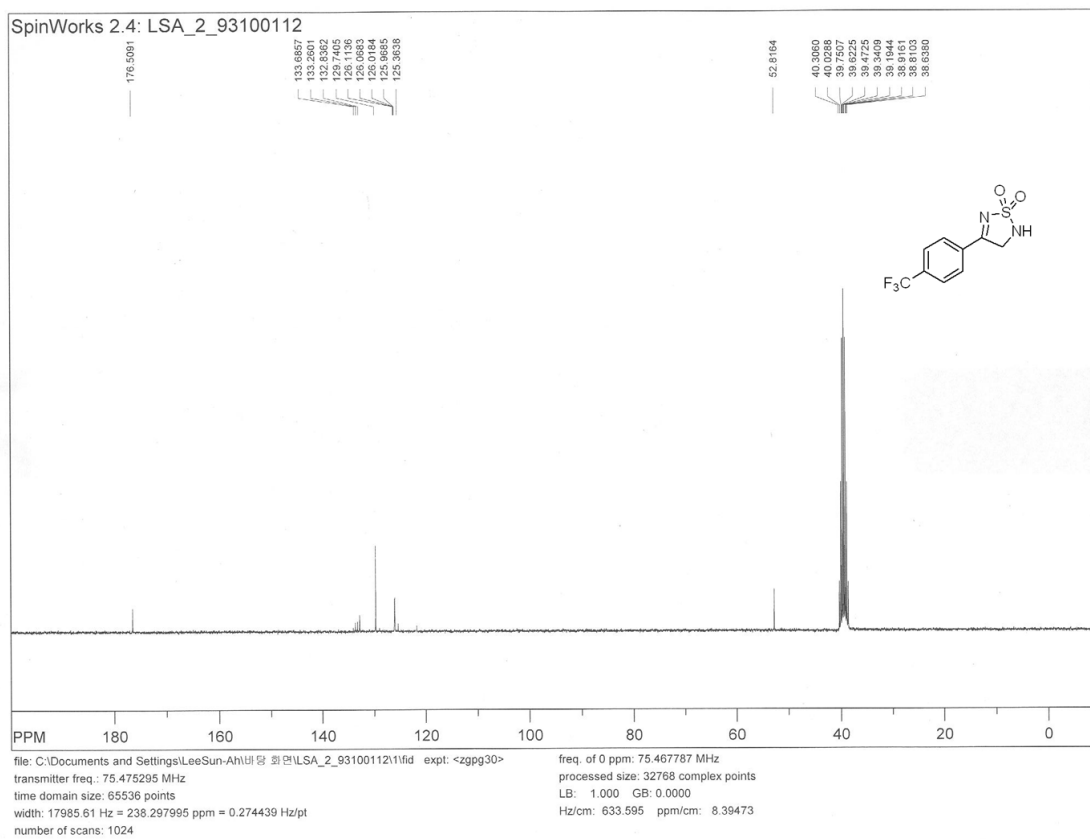
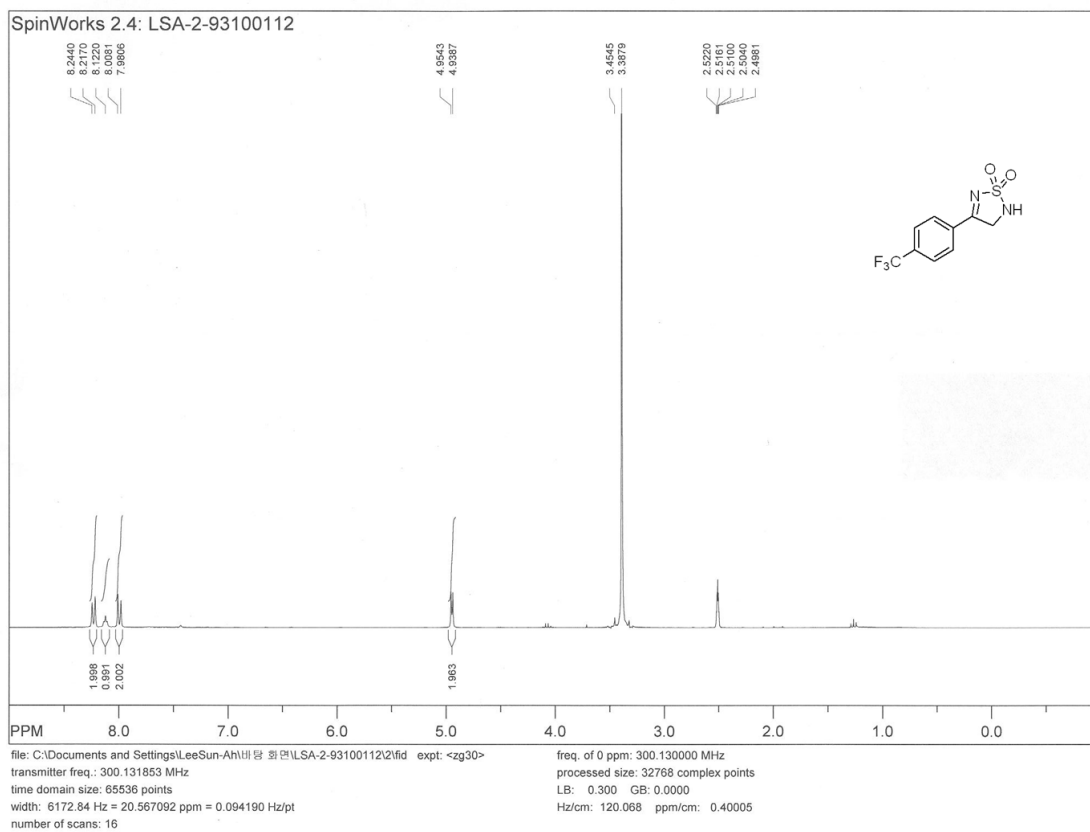


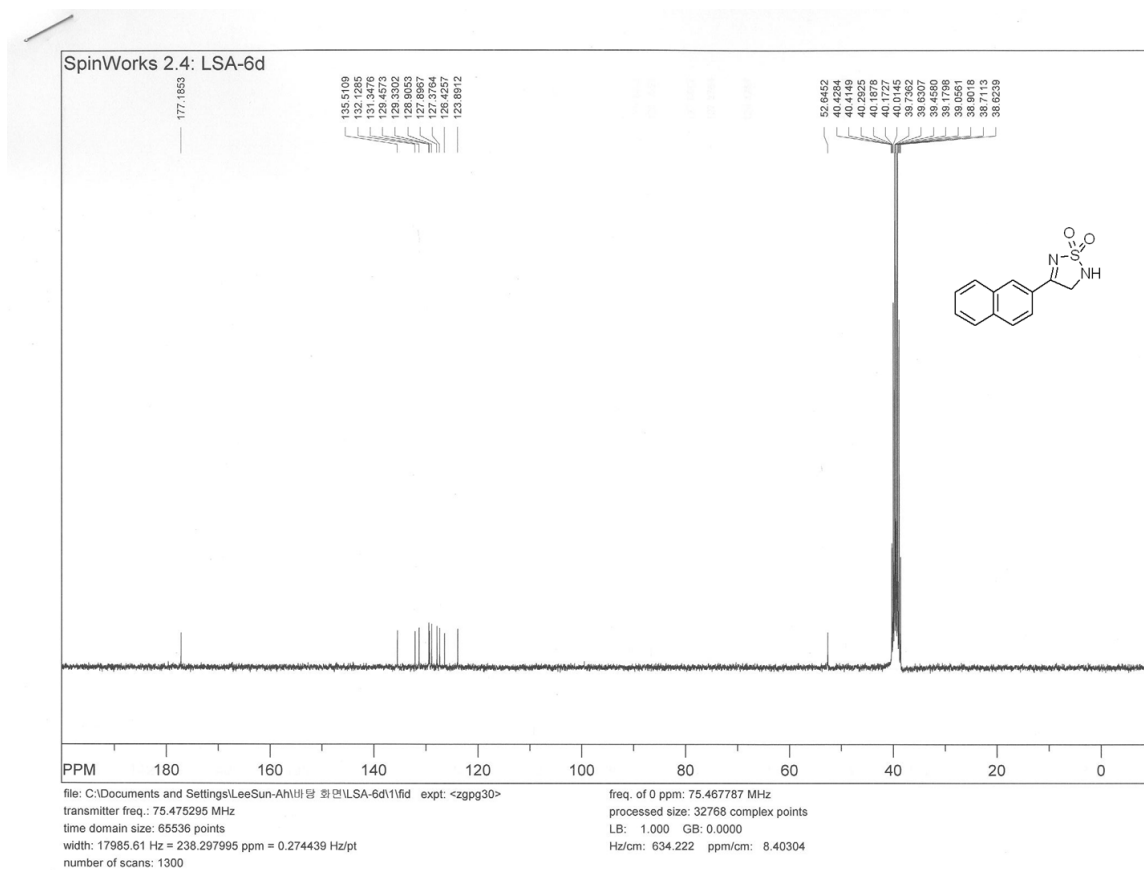
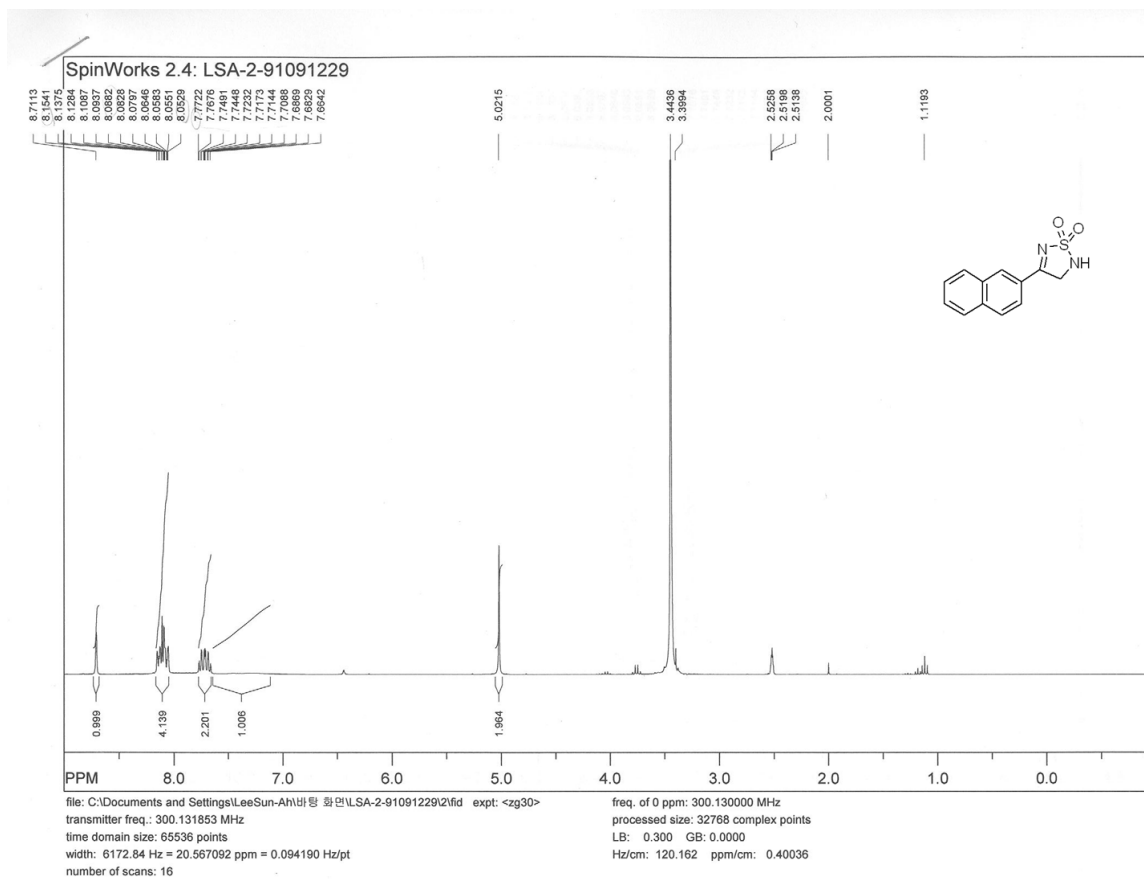


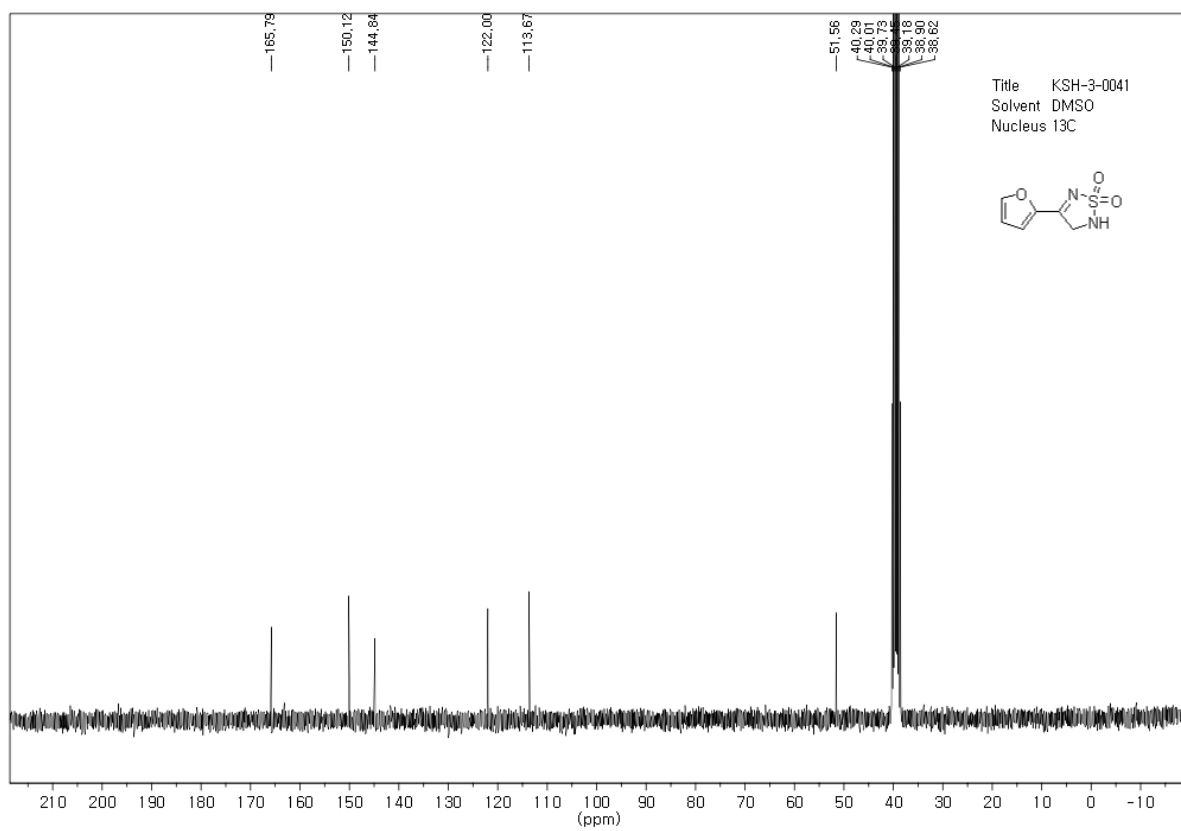
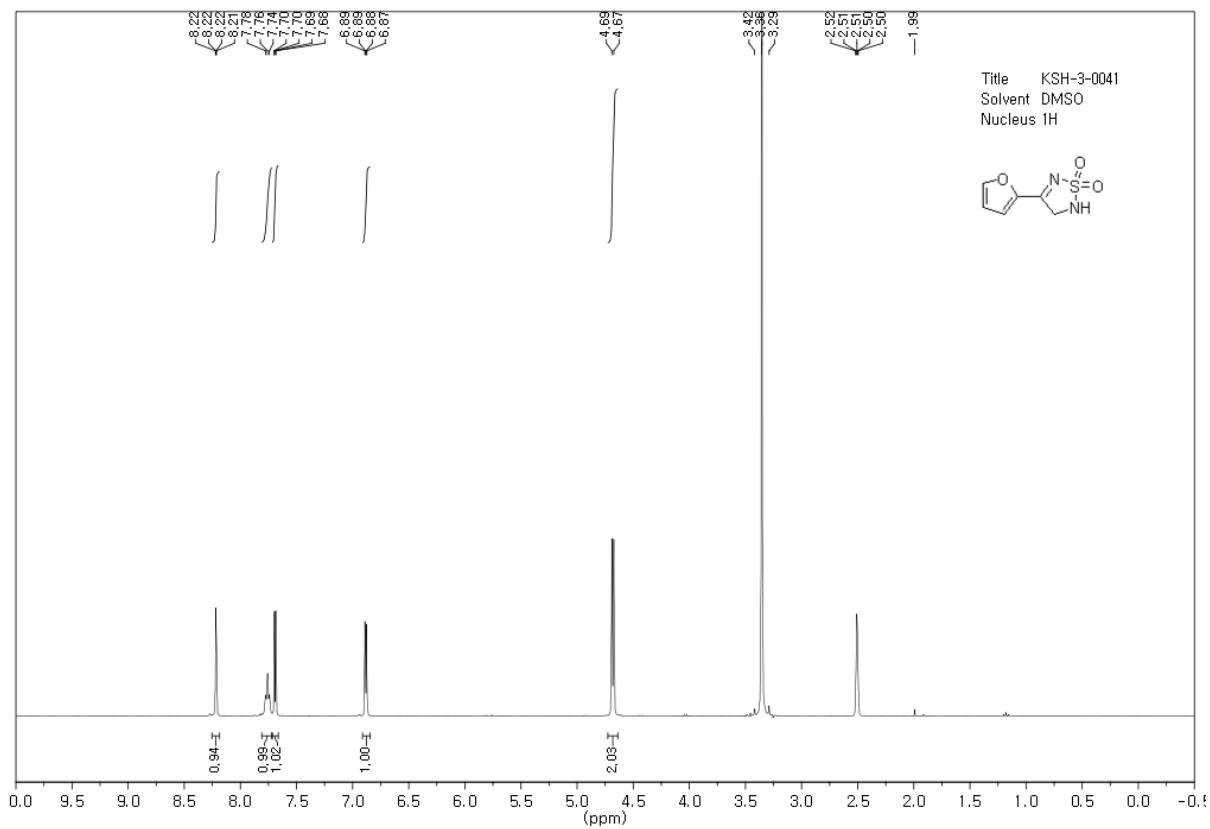


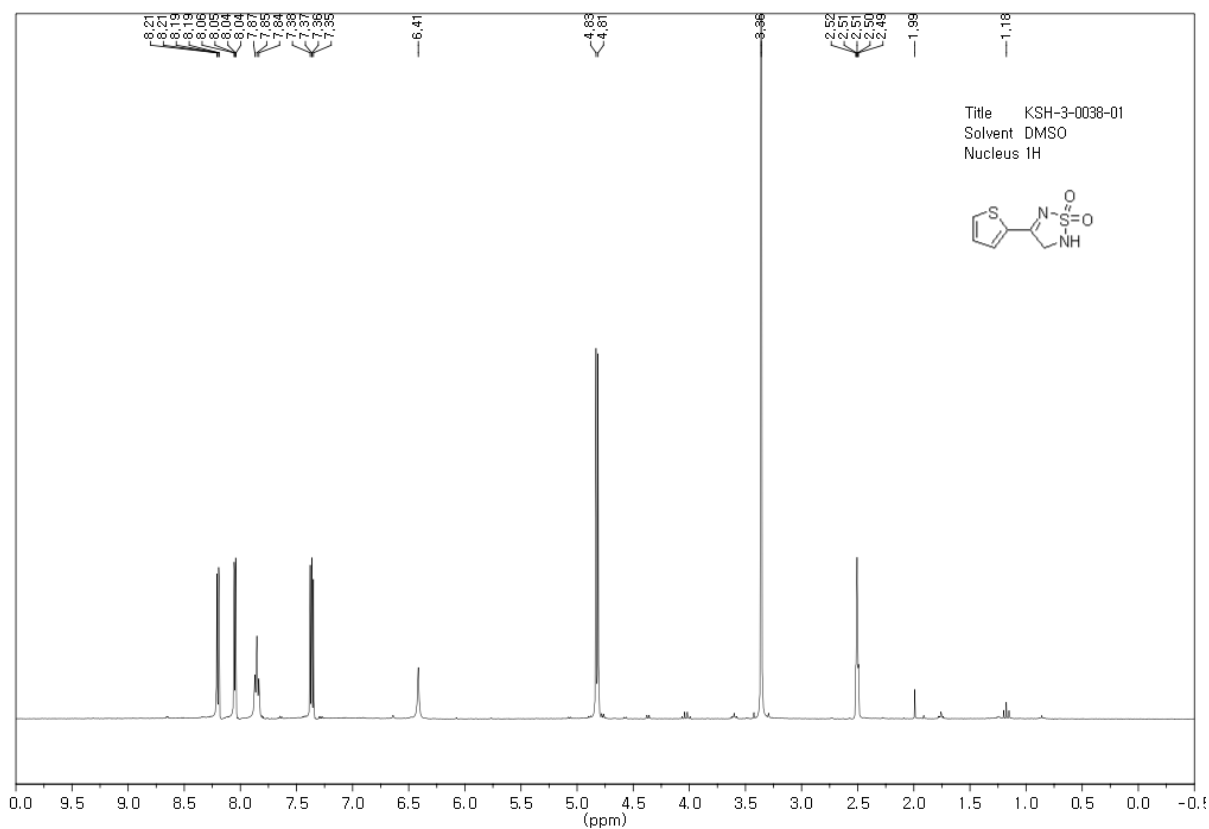




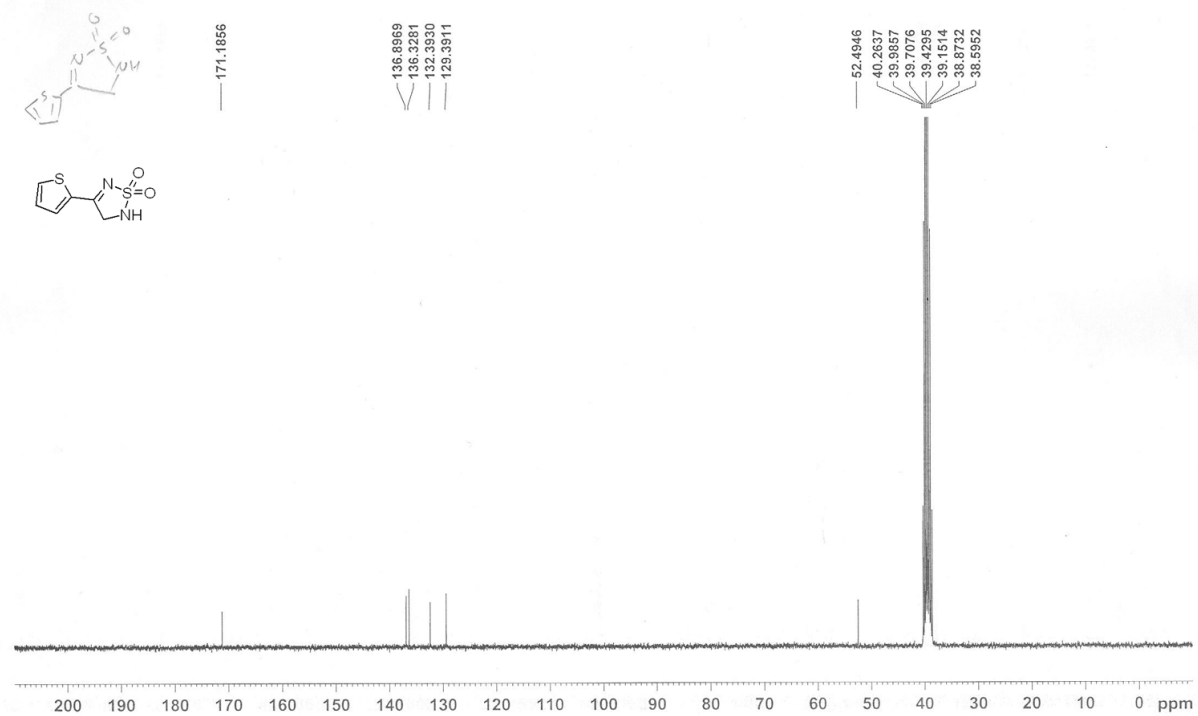


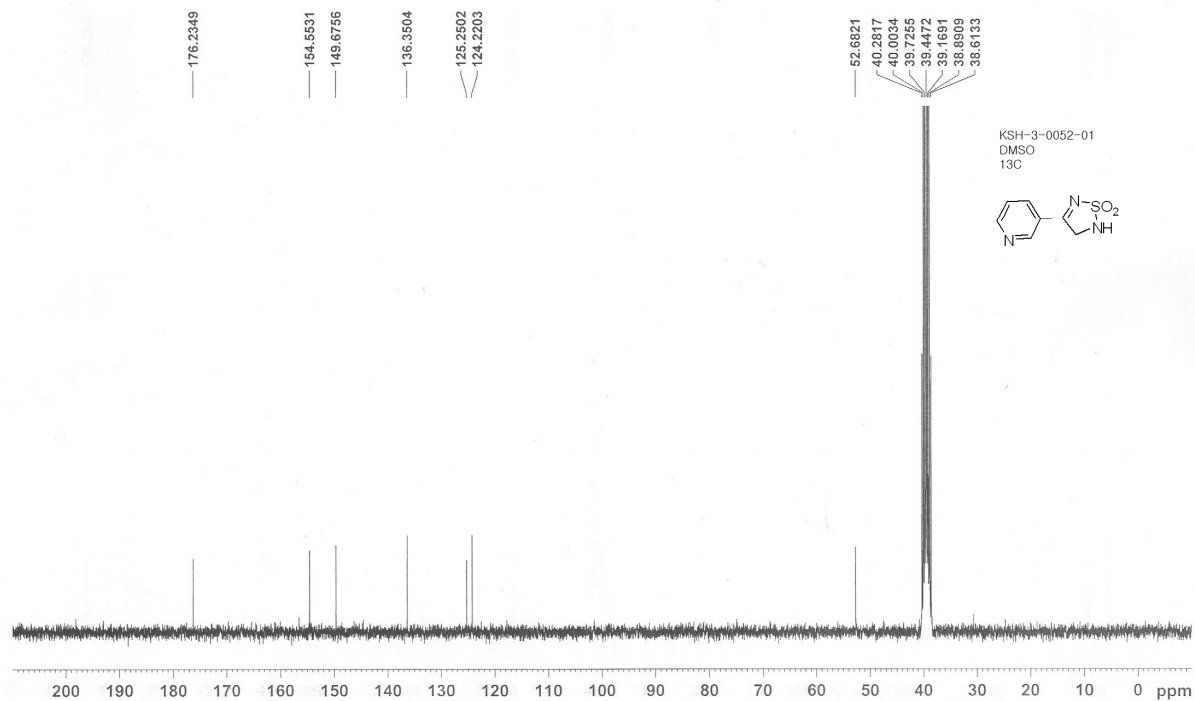
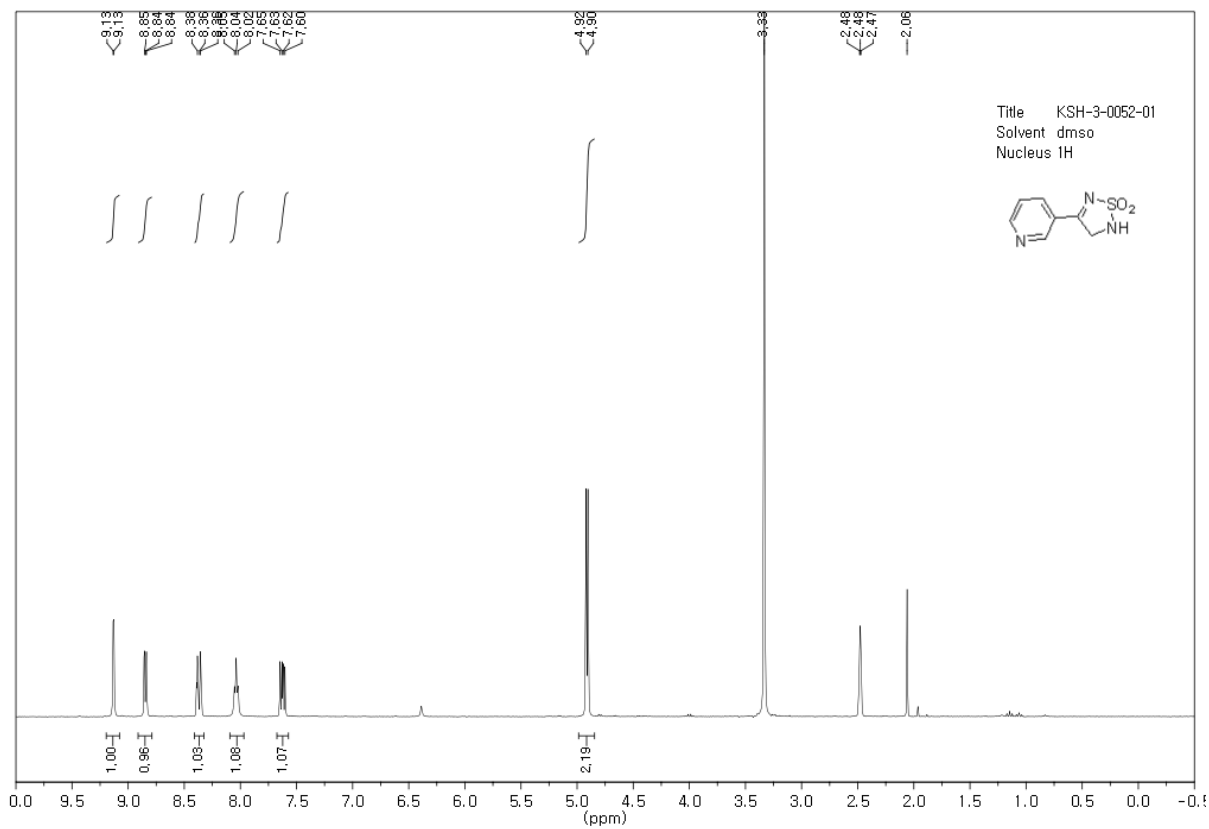


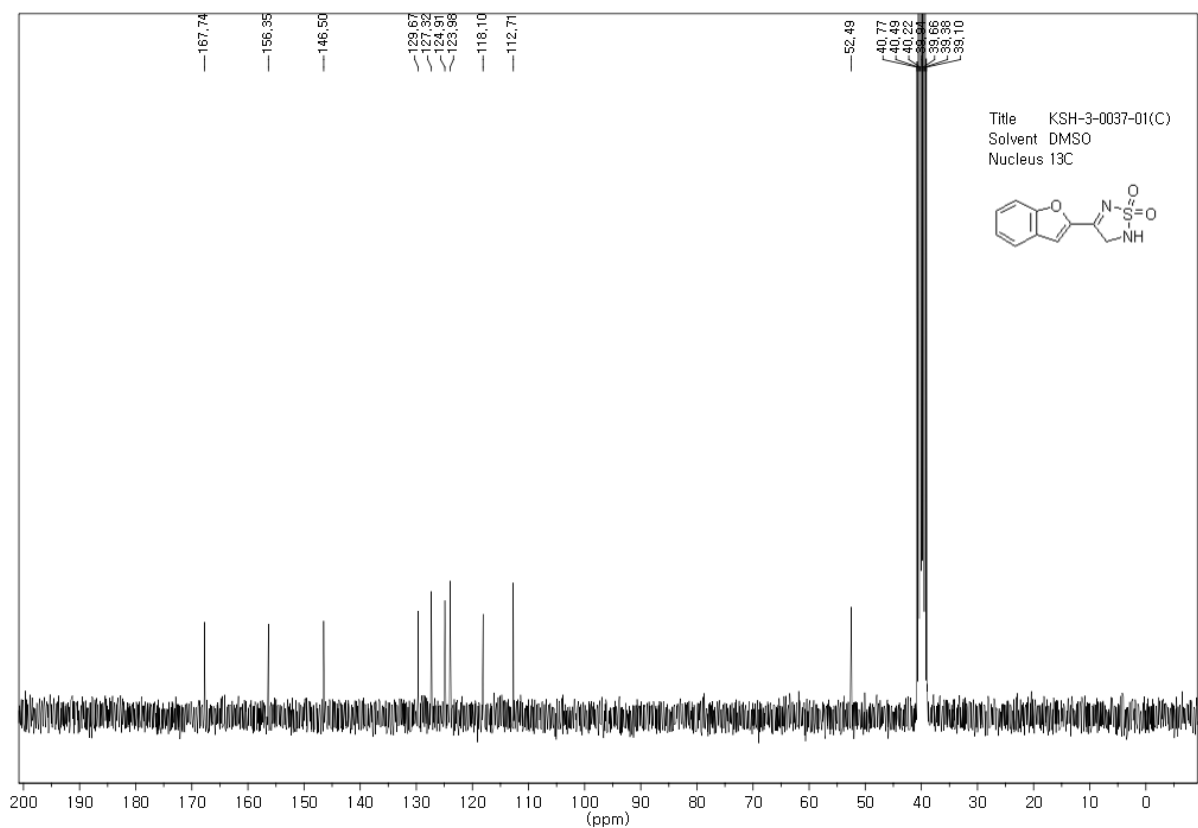
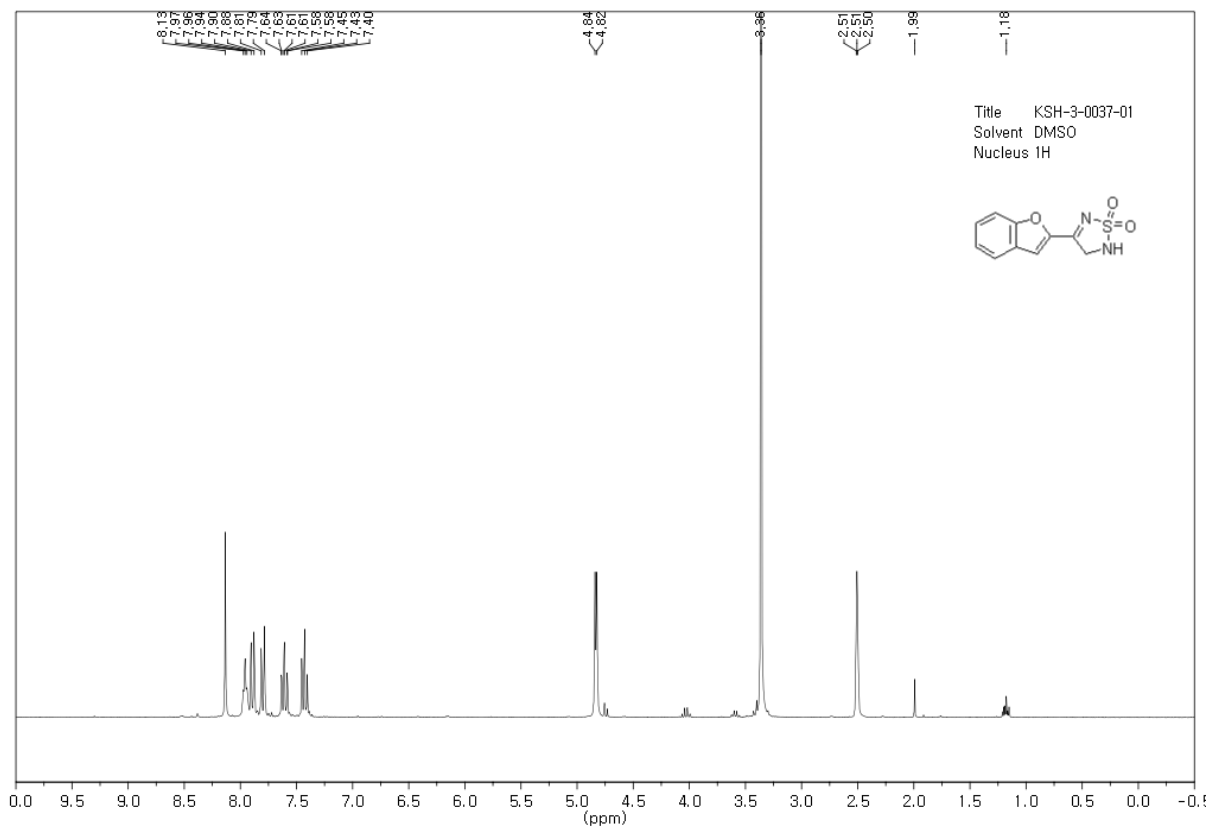


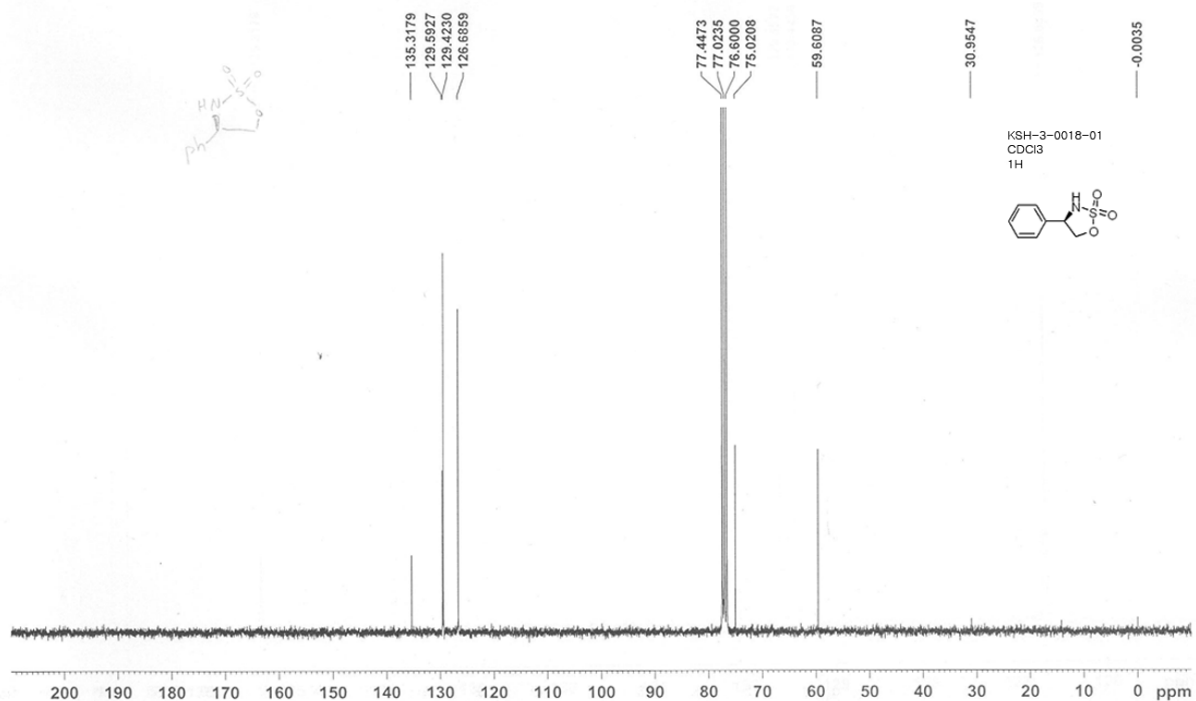
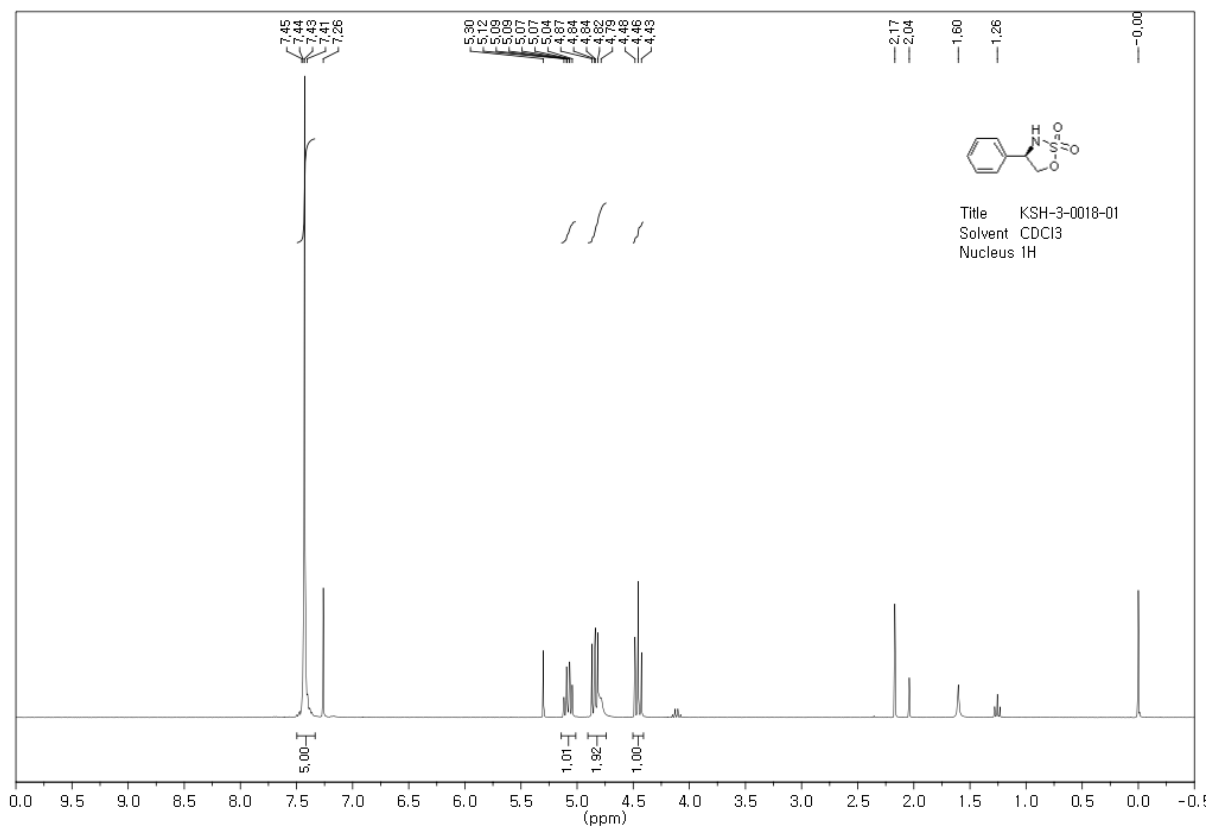


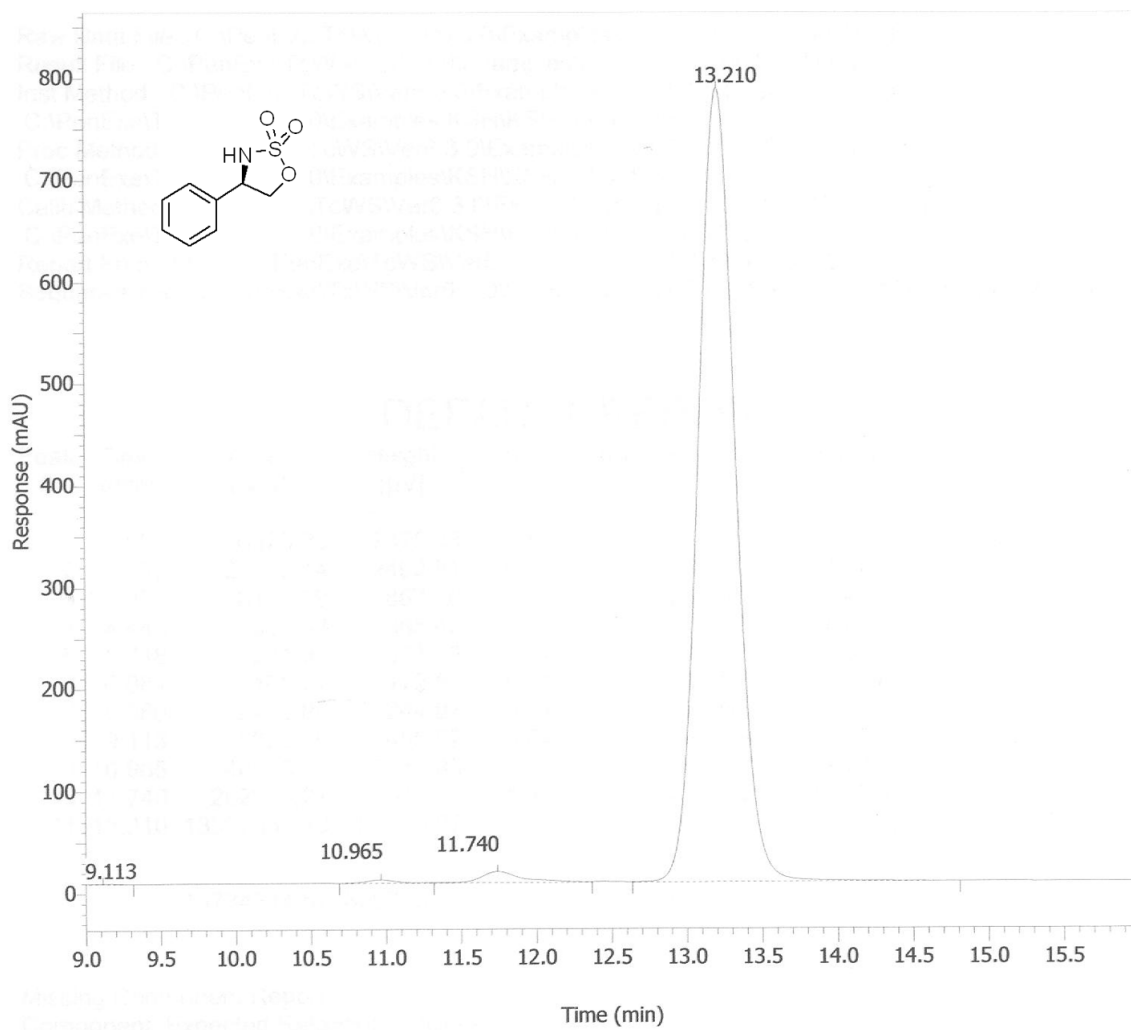
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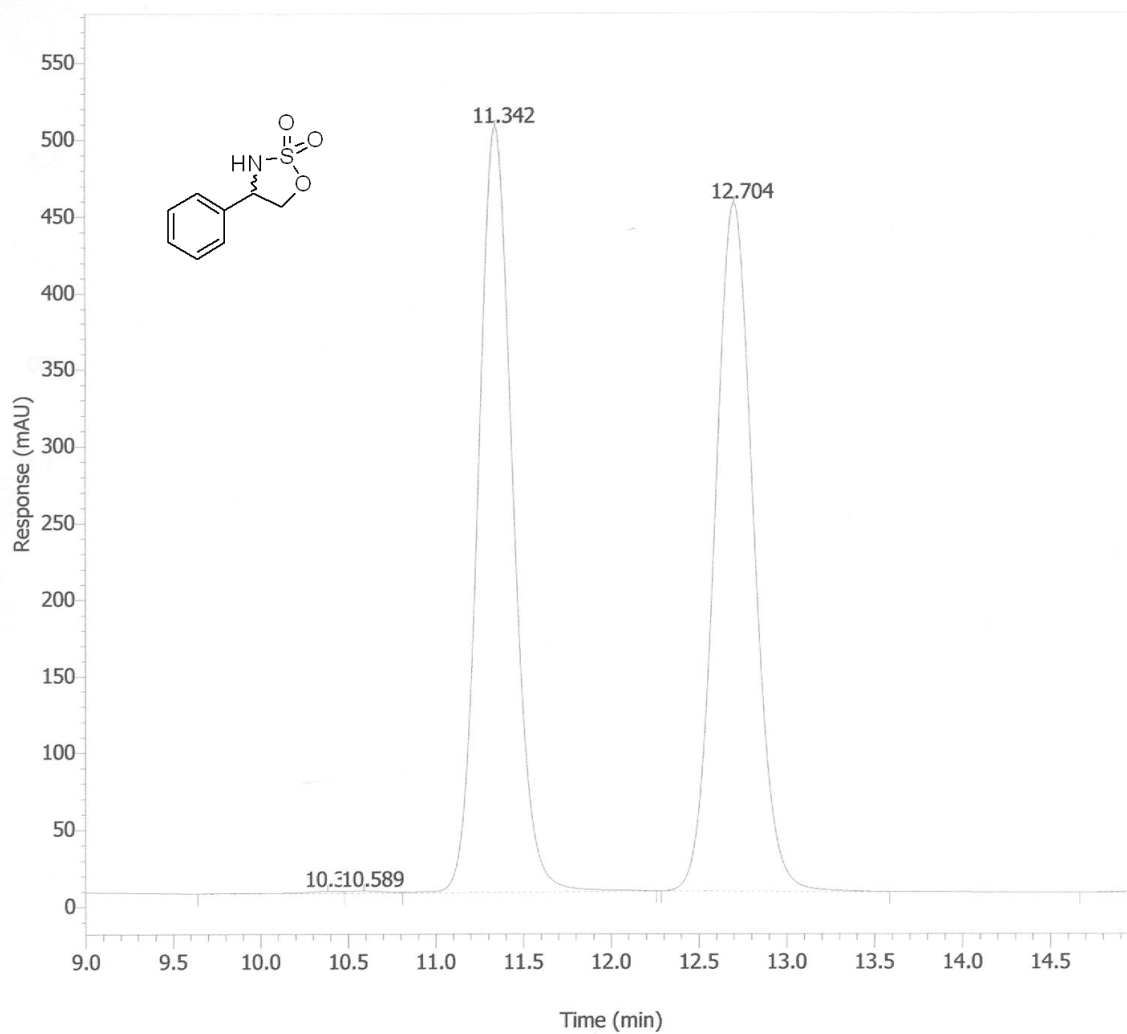


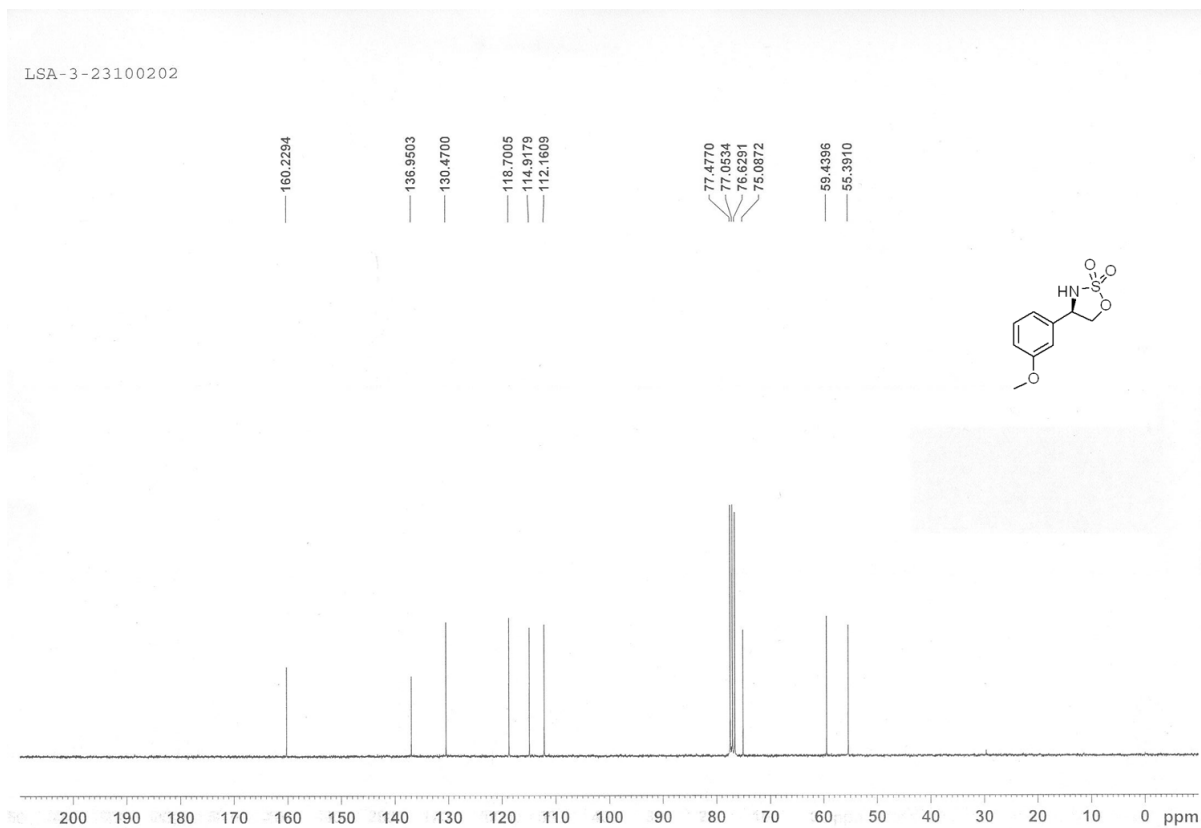
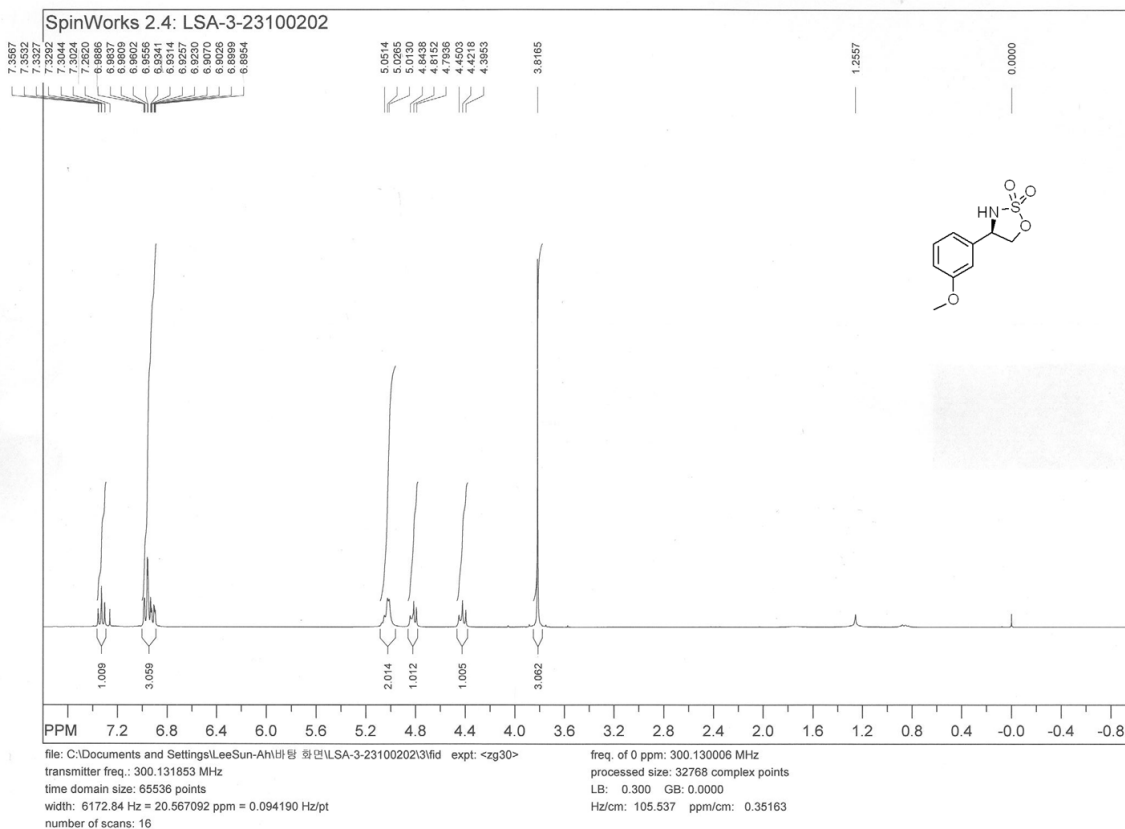


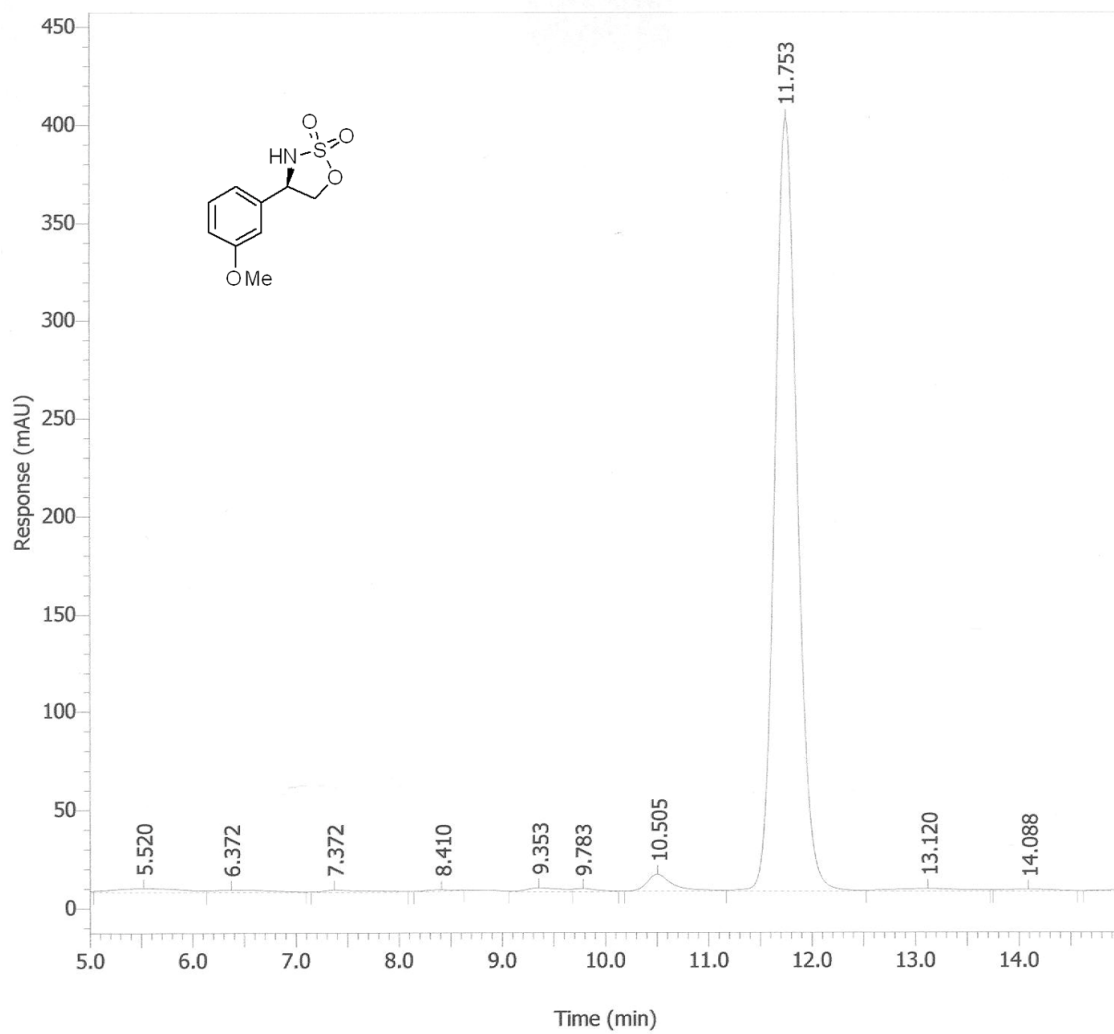


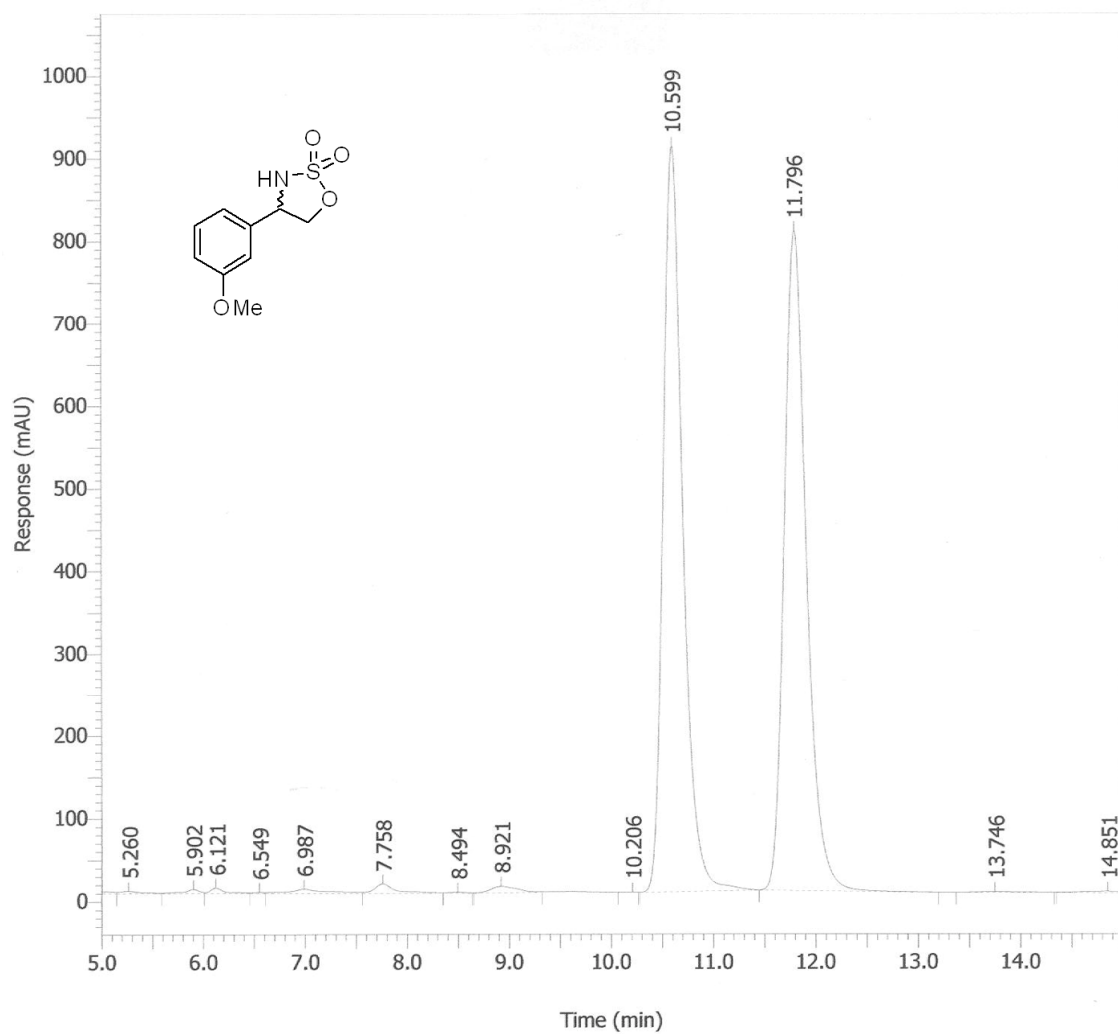


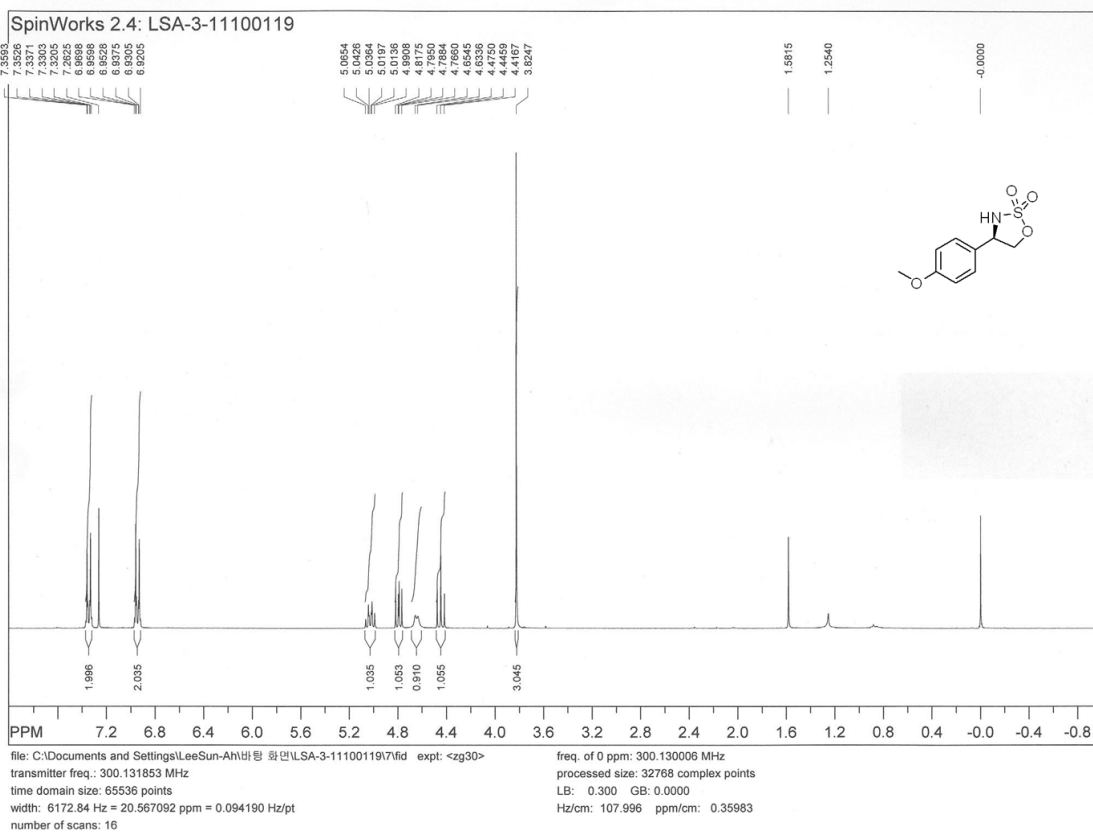




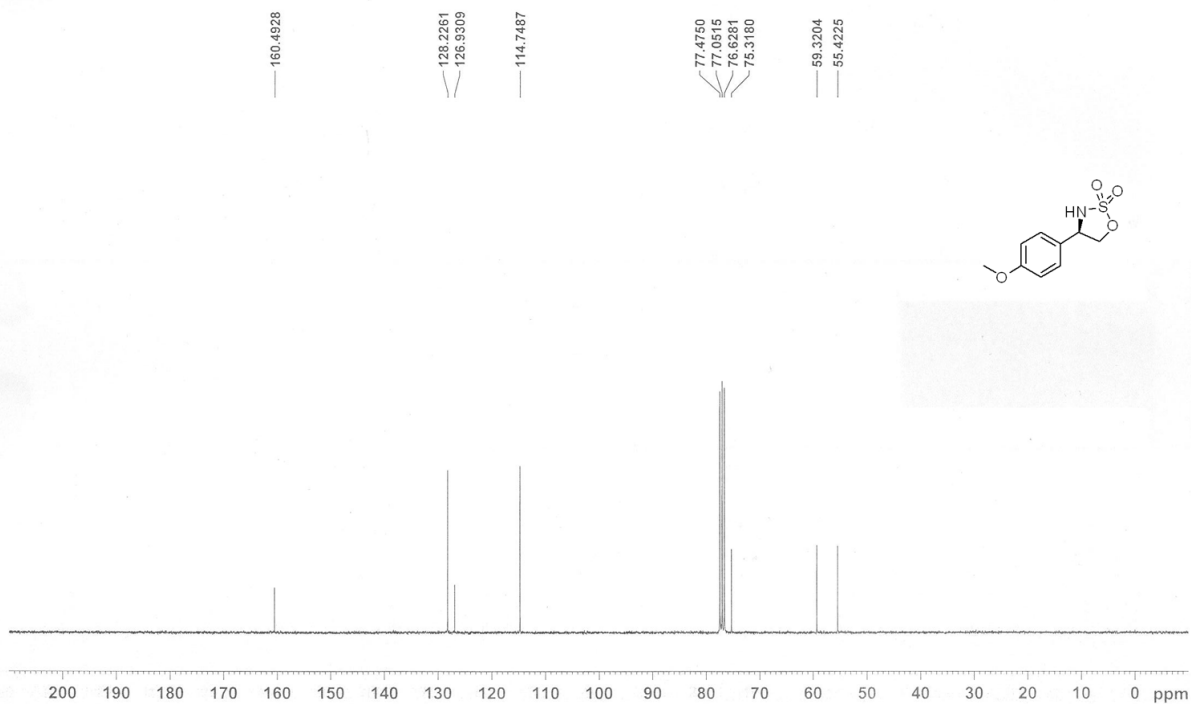


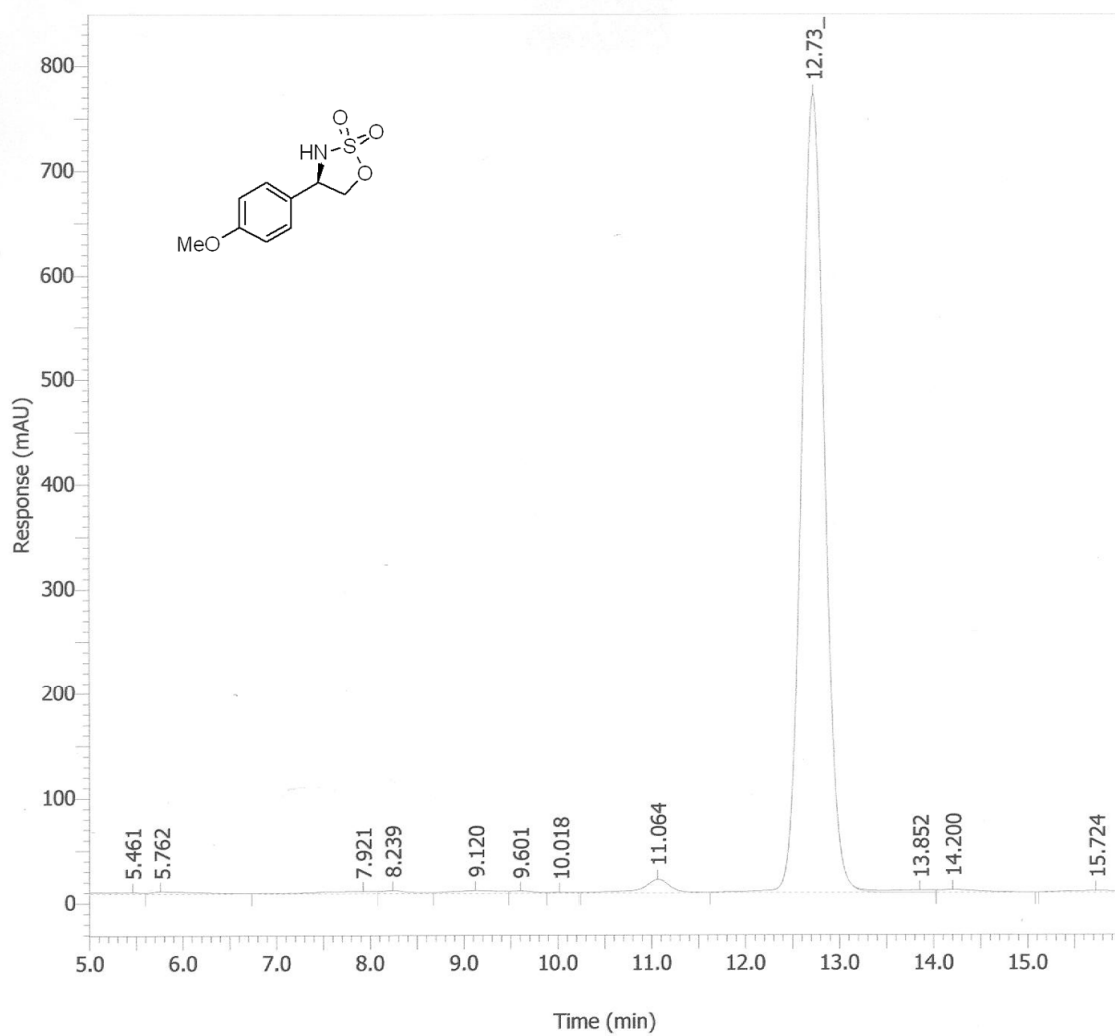


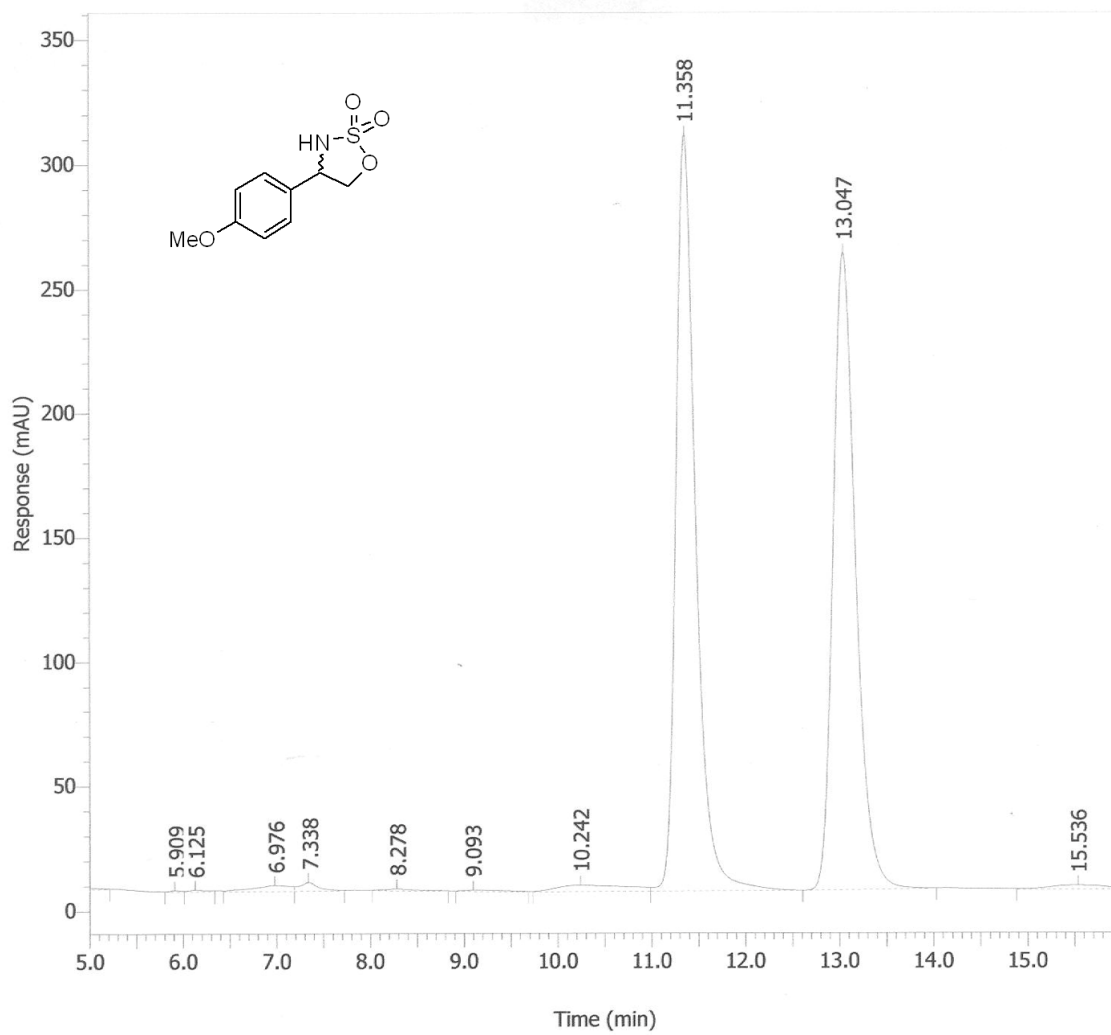


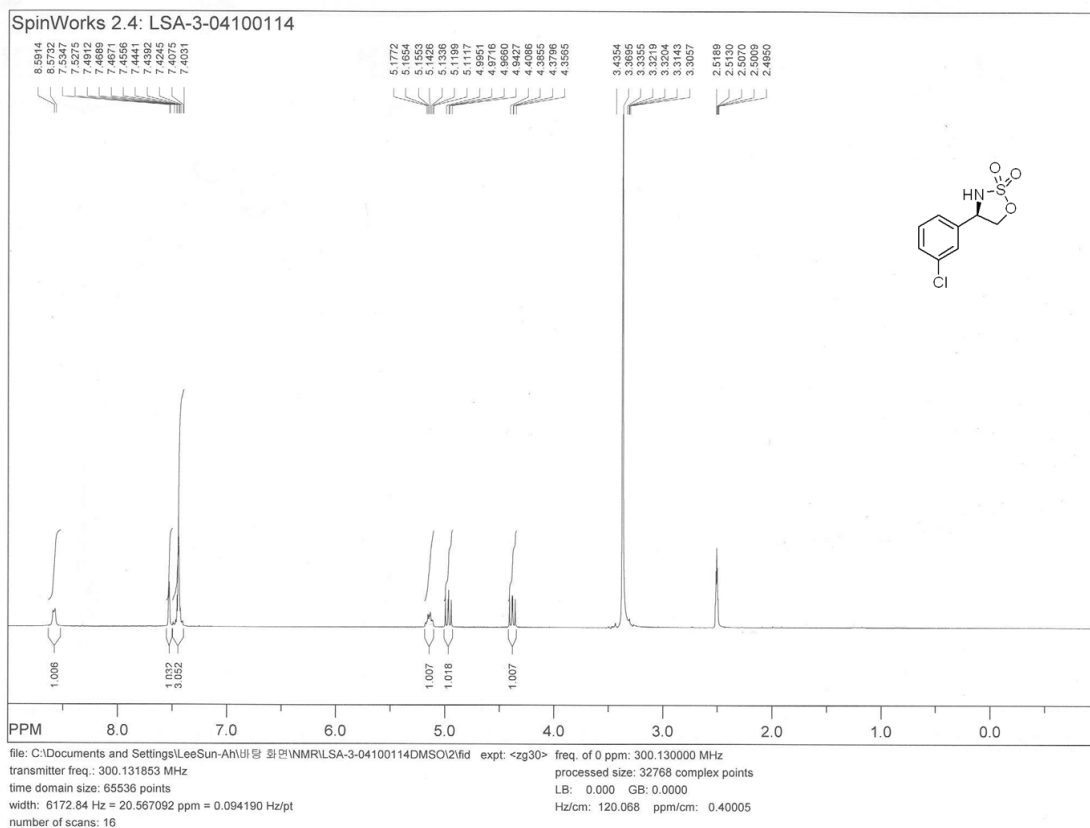


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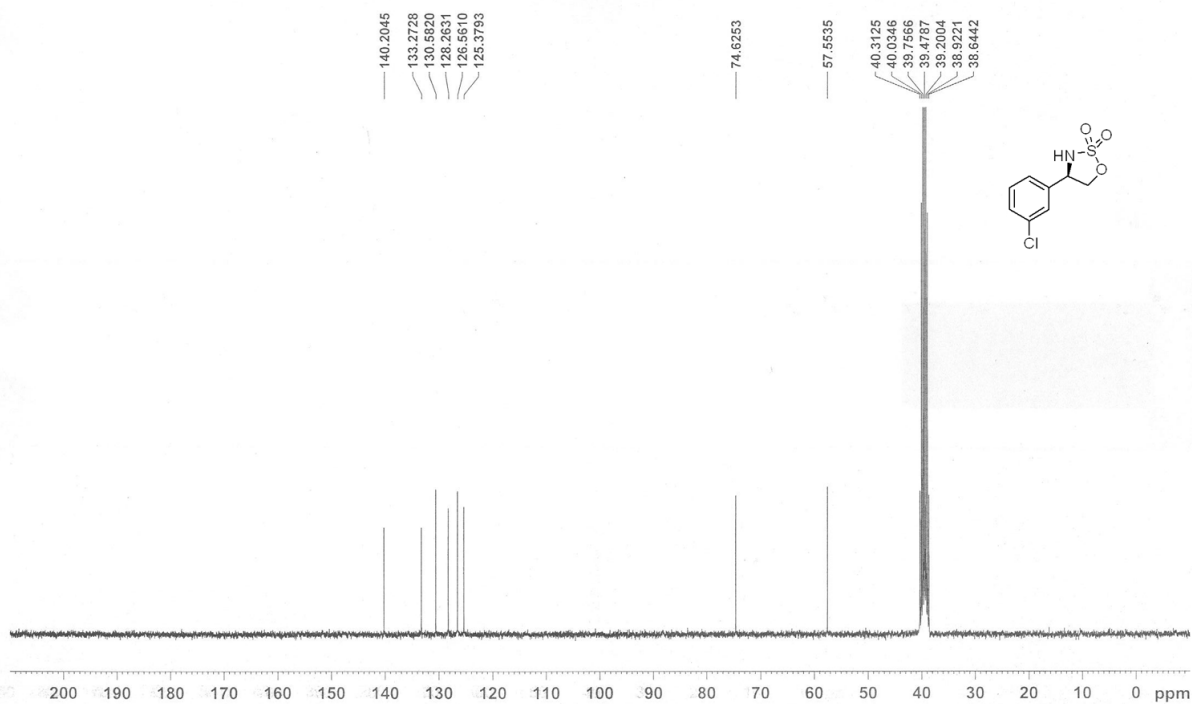


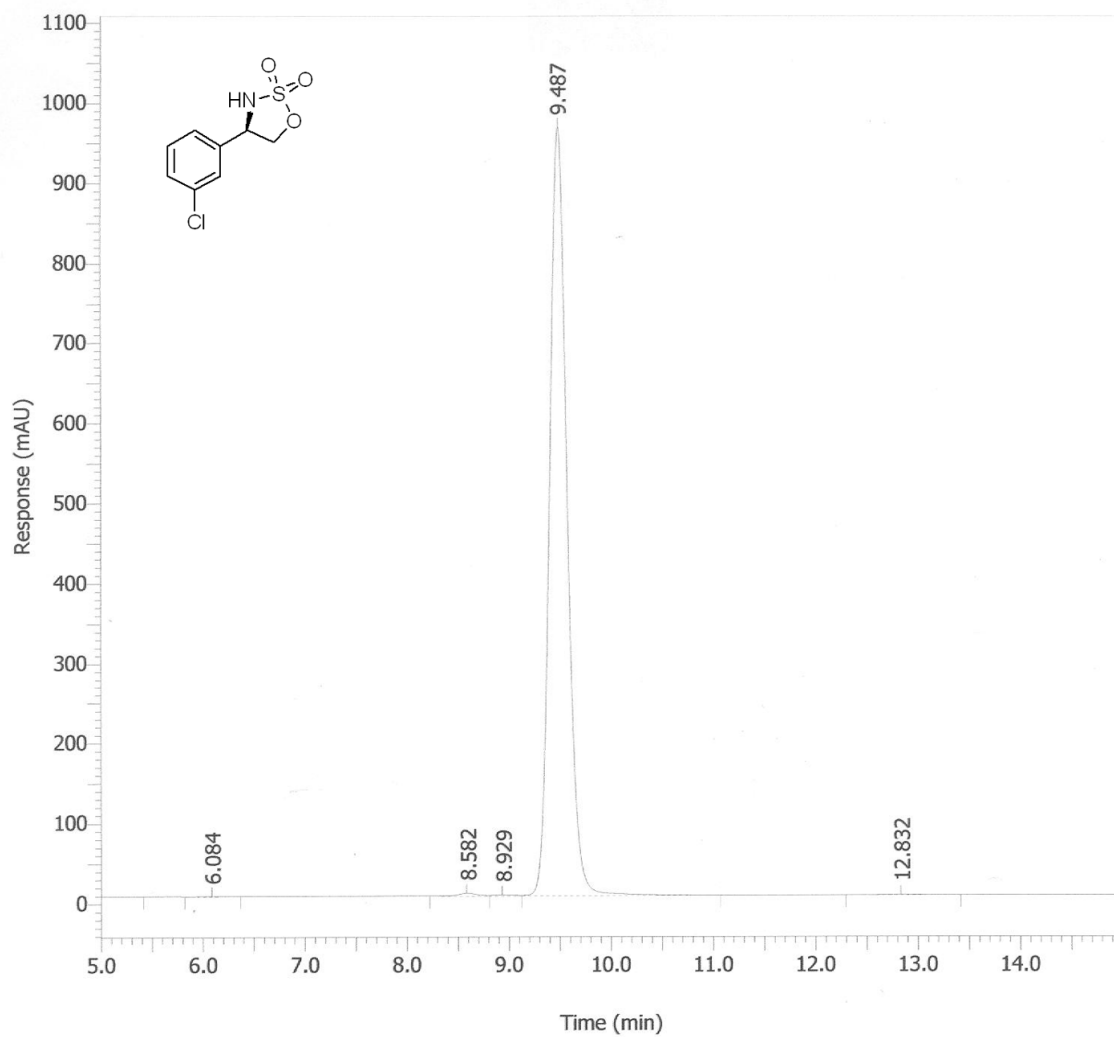


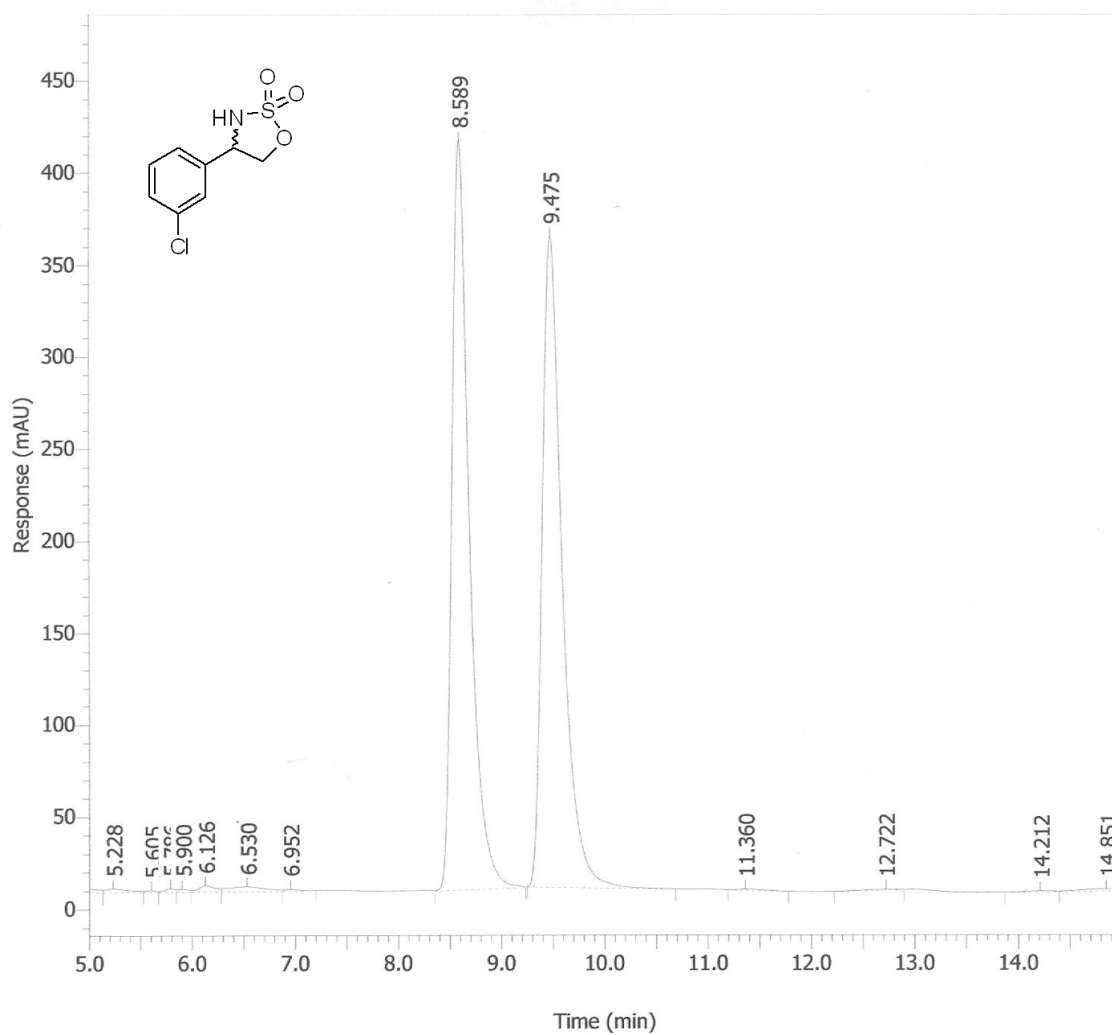


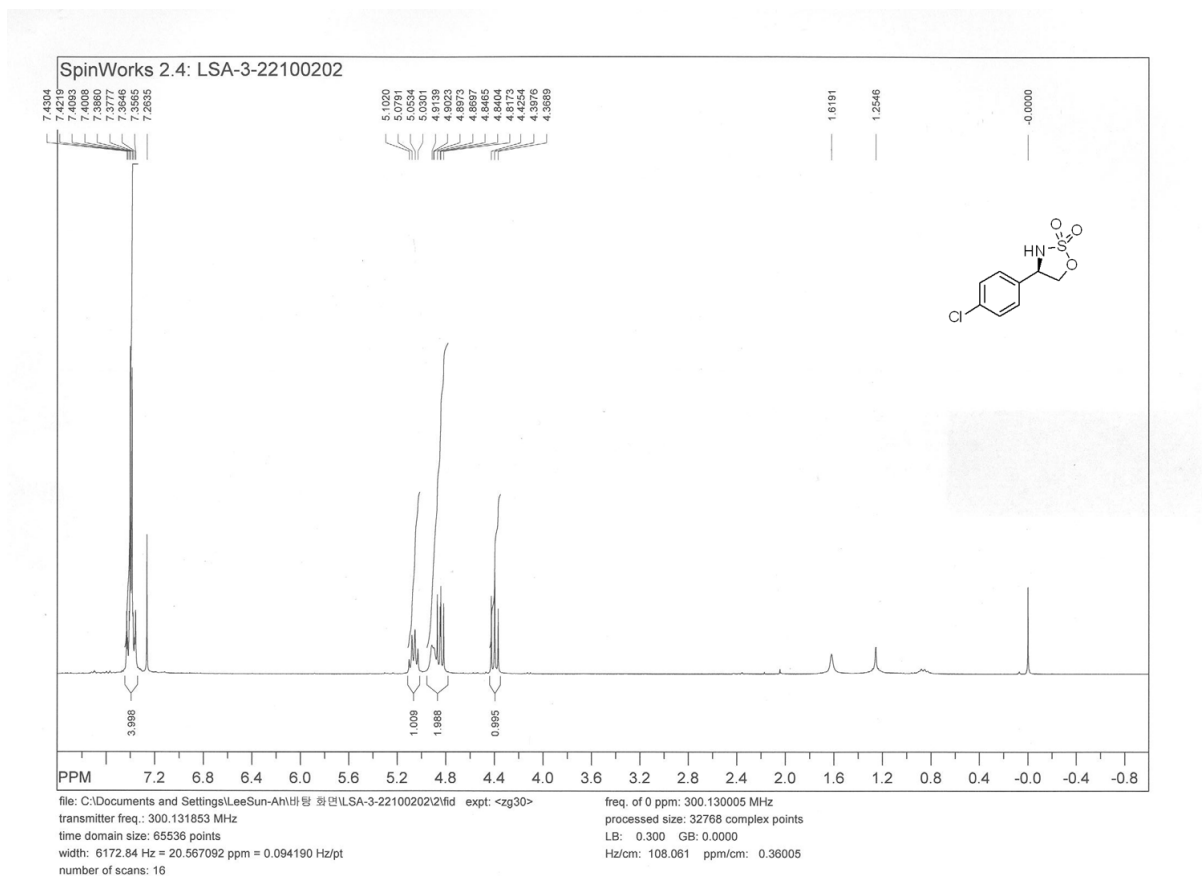


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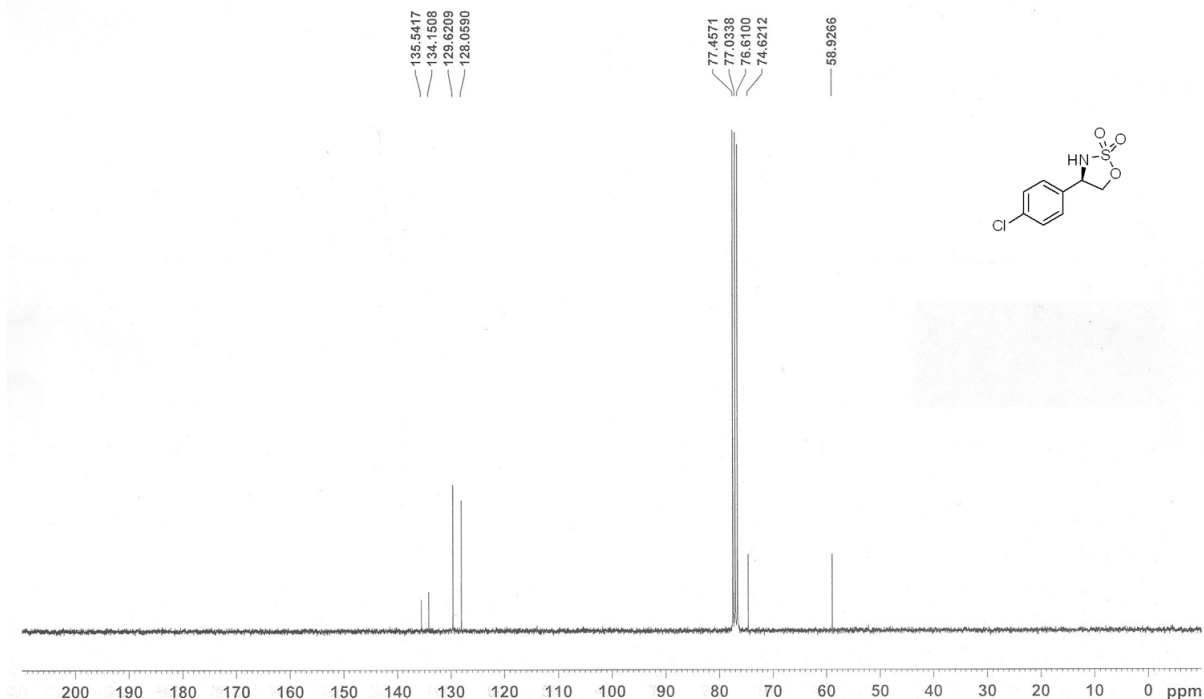


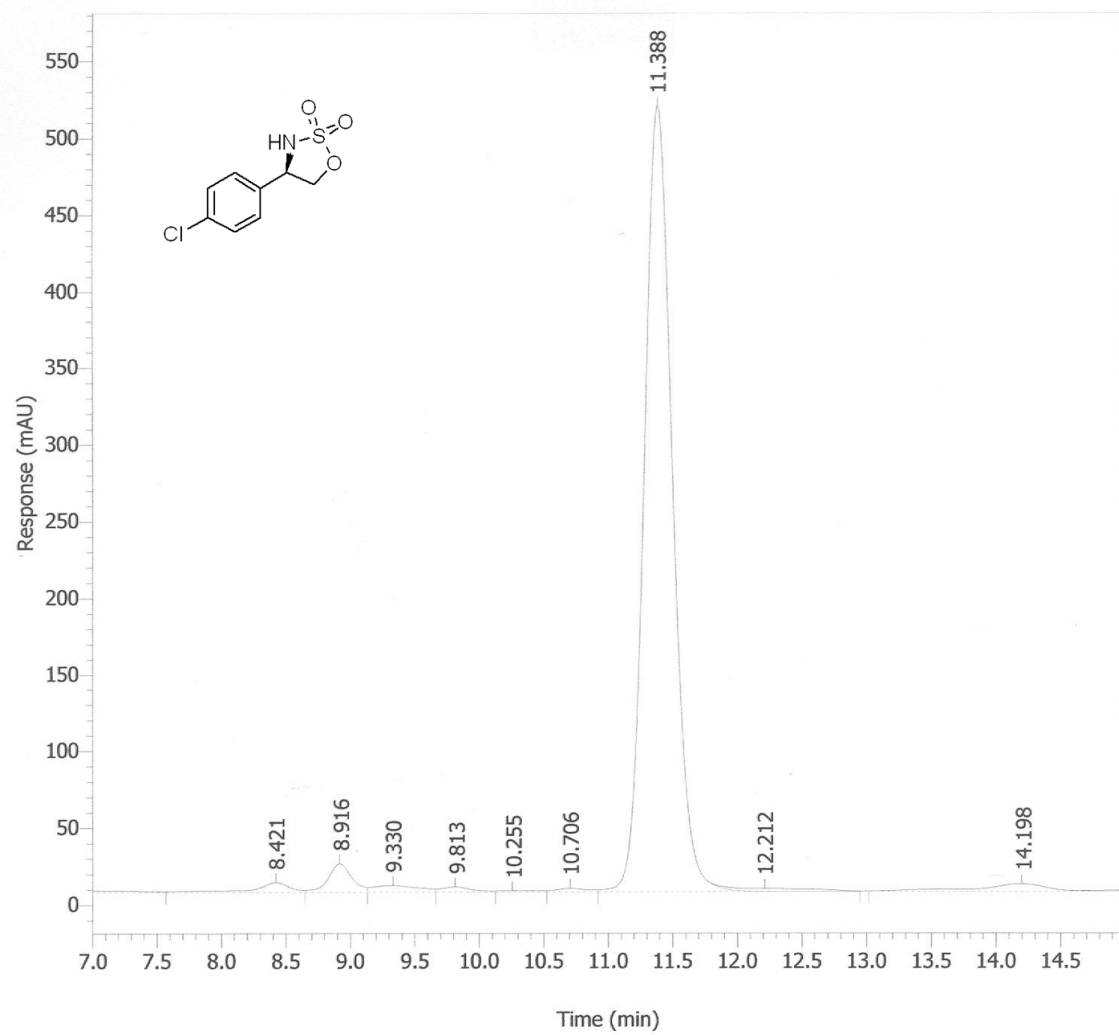


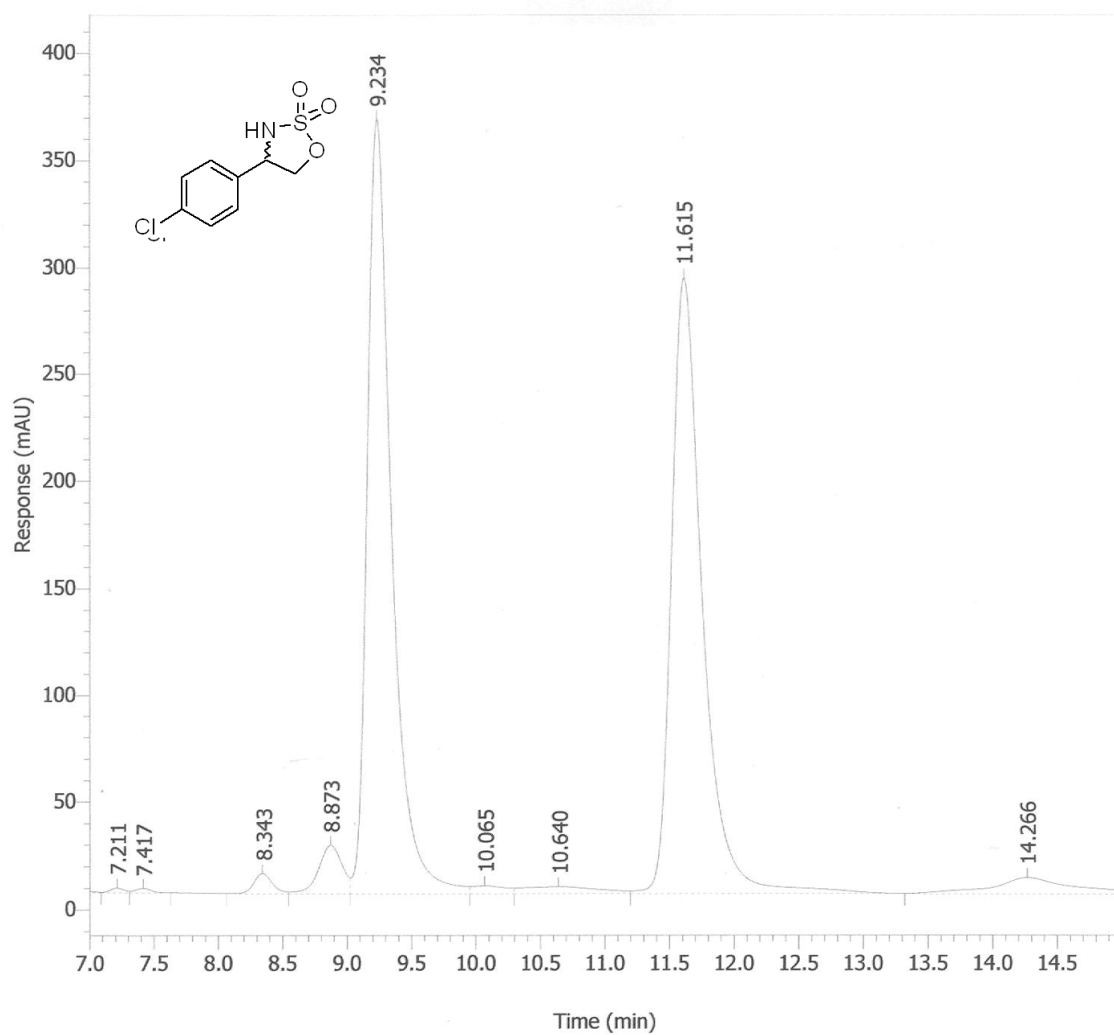


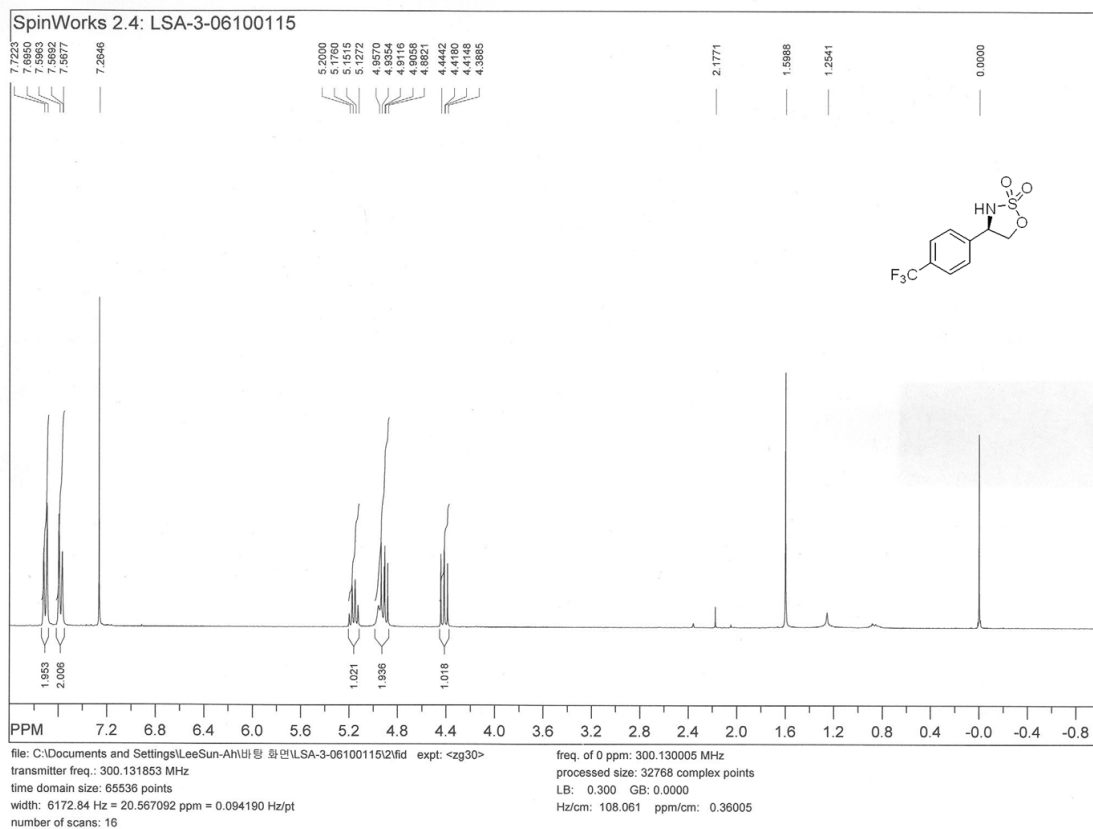


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LSA-3-06100115

