Supporting Information

Vinyl Sulfone Synthesis via Copper-Catalyzed Three-Component Decarboxylative Addition

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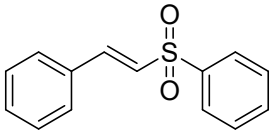
Content

I. Synthesis of Vinyl Sulfones

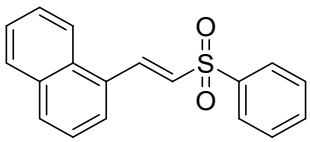
Aryl propiolic acid (1.0 mmol), aryl boronic acid (1.5 mmol), potassium disulfite (445 mg, 2.0 mmol), copper bromide(II) (45 mg, 0.2 mmol), 1,10-phenanthroline monohydrate (40 mg, 0.2 mmol), acetic acid (60 mg, 1.0 mmol) and monoglyme (2 mL) were added to the reaction vial. The mixture was stirred at 100 °C for 17 h. The mixture was filtered once the reaction was complete, the filtrate was washed with water/brine, and the aqueous solution was extracted with ethyl acetate. The organic layer was dried over magnesium sulfate. Evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography on silica gel with hexane and ethyl acetate (20:1)



(*E*)-(2-(Phenylsulfonyl)vinyl)benzene (3aa)[1]

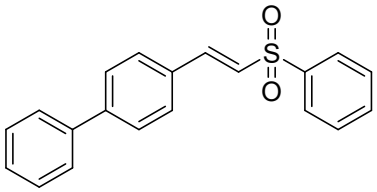
Phenylpropiolic acid (146 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3aa** (191 mg, 0.78 mmol, 78%). Pale yellow solid; m.p. 62–63 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.70 (d, *J* = 15.4 Hz, 1H), 7.65–7.61 (m, 1H), 7.58–7.54 (m, 2H), 7.51–7.48 (m, 2H), 7.44–7.38 (m, 3H), 6.88 (d, *J* = 15.4 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 140.8, 133.6, 132.5, 131.4, 129.5, 129.3, 128.8, 127.8, 127.4;
MS (EI) m/z = 244.1 (M^+)



(*E*)-1-(2-(phenylsulfonyl)vinyl)naphthalene (3ba)[2]

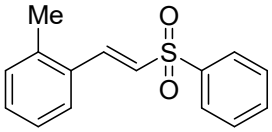
3-(Naphthalen-1-yl)propiolic acid (196 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ba** (218 mg, 0.74 mmol, 74%). White solid; m.p. 99–101 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 15.2 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 8.09–7.97 (m, 2H), 7.96–7.86 (m, 2H), 7.70–7.64 (m, 2H), 7.63–7.55 (m, 4H), 7.49–7.45 (m, 1H), 6.98 (d, *J* = 15.2 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 139.5, 133.7, 133.4, 131.5, 131.3, 129.6, 129.5, 129.4, 128.9, 127.7, 127.3, 126.5, 125.7, 125.3, 123.0;
MS (EI) m/z = 294.1 (M^+)



(*E*)-4-(2-(phenylsulfonyl)vinyl)-1,1'-biphenyl (3ca)[1]

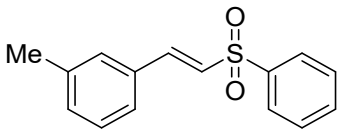
3-([1,1'-Biphenyl]-4-yl)propiolic acid (222 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ca** (202 mg, 0.63 mmol, 63%). White solid; m.p. 110–112 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03–7.94 (m, 2H), 7.74 (d, *J* = 15.4 Hz, 1H), 7.67–7.61 (m, 4H), 7.60–7.54 (m, 5H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.41–7.37 (m, 1H), 6.91 (d, *J* = 15.4 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 142.0, 140.7, 139.7, 133.3, 131.2, 129.3, 129.1, 128.9, 128.1, 127.6, 127.6 (overlap), 127.0, 126.9;
MS (EI) m/z = 320.1 (M^+)



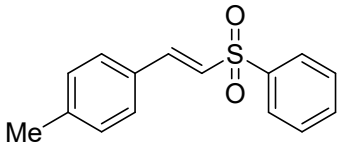
(*E*)-1-Methyl-2-(2-(phenylsulfonyl)vinyl)benzene (3da)[2]

3-(*o*-Tolyl)propiolic acid (160 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3da** (168 mg, 0.65 mmol, 65%). White solid; m.p. 112–115 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05–7.90 (m, 3H), 7.66–7.61 (m, 1H), 7.60–7.53 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.34–7.28 (m, 1H), 7.25–7.17 (m, 2H), 6.80 (d, *J* = 15.3 Hz, 1H), 2.47 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 140.1, 138.2, 133.3, 131.3, 131.1, 130.9, 129.3, 128.2, 127.7, 126.9, 126.5, 19.8;
MS (EI) m/z = 258.1 (M^+)



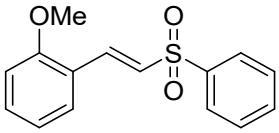
(*E*)-1-Methyl-3-(2-(phenylsulfonyl)vinyl)benzene (3ea)[2]

3-(*m*-Tolyl)propiolic acid (160 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ea** (181 mg, 0.70 mmol, 70%). Pale yellow solid; m.p. 105–106 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99–7.94 (m, 2H), 7.67 (d, *J* = 15.4 Hz, 1H), 7.65–7.60 (m, 1H), 7.58–7.53 (m, 2H), 7.32–7.28 (m, 3H), 7.25–7.22 (m, 1H), 6.86 (d, *J* = 15.4 Hz, 1H), 2.36 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 140.8, 138.8, 133.3, 132.3, 132.1, 129.3, 129.1, 129.0, 127.6, 127.0, 125.8, 21.3;
MS (EI) m/z = 258.1 (M^+)



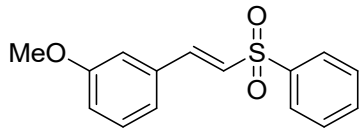
(*E*)-1-Methyl-4-(2-(phenylsulfonyl)vinyl)benzene (3fa)[3]

3-(*p*-Tolyl)propiolic acid (160 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3fa** (176 mg, 0.68 mmol, 68%). White solid; m.p. 138 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.4 Hz, 2H), 7.58 (d, *J* = 15.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.73 (d, *J* = 15.4 Hz, 1H), 2.29 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 141.8, 140.9, 133.2, 129.8, 129.6, 129.2, 128.5, 127.5, 126.0, 21.5;
MS (EI) m/z = 258.1 (M^+)



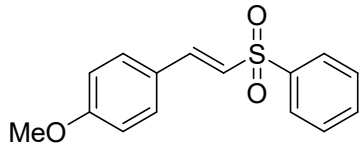
(*E*)/(*Z*)-2-Methoxyl-4-(2-(phenylsulfonyl)vinyl)benzene (3ga)[2]

3-(2-Methoxyphenyl)propiolic acid (176 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ga** (187 mg, 0.68 mmol, 68%). Pale yellow solid; m.p. 97–98 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01–7.93 (m, 2H), 7.90 (d, *J* = 15.5 Hz, 1H), 7.62–7.58 (m, 1H), 7.56–7.51 (m, 2H), 7.43–7.36 (m, 2H), 7.08 (d, *J* = 15.5 Hz, 0.9H), 6.98–6.91 (m, 2H), 6.55 (d, *J* = 11.8 Hz, 0.1H), 3.88 (s, 2.7H), 3.71 (s, 0.3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8 (M), 141.2 (M), 141.0 (m), 138.6 (M), 138.1 (m), 133.1 (M), 133.0 (m), 132.5 (M), 132.0 (m), 131.3 (m), 131.2 (m), 130.8 (M), 129.2 (M), 128.6 (m), 127.8 (M), 127.6 (M), 121.2 (M), 120.8 (M), 120.0 (m), 111.2 (M), 109.9 (m), 55.5 (M), 55.3 (m); (*E*)/(*Z*) = 10/1, M : major ((*E*) isomer), m : minor ((*Z*) isomer);
MS (EI) m/z = 274.1 (M^+)



(*E*)-3-Methoxyl-4-(2-(phenylsulfonyl)vinyl)benzene (3ha)[3]

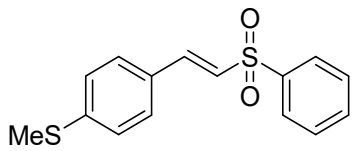
3-(3-Methoxyphenyl)propiolic acid (176 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ha** (198 mg, 0.72 mmol, 72%). White solid; m.p. 120 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99–7.93 (m, 2H), 7.66 (d, *J* = 15.3 Hz, 1H), 7.64–7.59 (m, 1H), 7.58–7.53 (m, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.09–7.07 (m, 1H), 7.00–6.95 (m, 2H), 6.86 (d, *J* = 15.4 Hz, 1H), 3.82 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 142.4, 140.7, 133.6, 133.4, 130.1, 129.3, 127.7, 127.5, 121.2, 117.1, 113.4, 55.4;
MS (EI) m/z = 274.1 (M^+)



(*E*)-1-Methoxyl-4-(2-(phenylsulfonyl)vinyl)benzene (3ia)[3]

3-(4-Methoxyphenyl)propiolic acid (176 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ia** (203 mg, 0.74 mmol, 74%). White solid; m.p. 120 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.67–7.59 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 15.3 Hz, 1H), 3.84 (s, 3H);

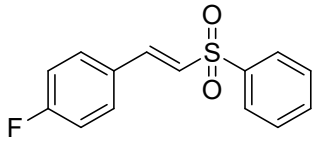
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1, 142.3, 141.1, 133.2, 130.4, 129.3, 127.5, 124.9, 124.4, 114.5, 55.5;
MS (EI) m/z = 274.1 (M^+)



(*E*)-Methyl (4-(2-(phenylsulfonyl)vinyl)phenyl)sulfane (3ja)

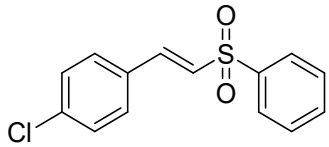
3-(4-Methylthiophenyl)propiolic acid (192 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ja** (231 mg, 0.79 mmol, 79%). Yellow solid; m.p. 112–115 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00–7.89 (m, 2H), 7.66–7.59 (m, 2H), 7.57–7.52 (m, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 15.4 Hz, 1H), 2.49 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 141.9, 140.8, 133.2, 129.2, 128.8, 128.6, 127.5, 125.9, 125.8, 14.9;
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{15}H_{14}O_2S_2$ 290.0430; Found: 290.0429.



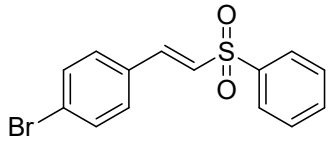
(*E*)-1-Fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (**3ka**)[1]

3-(4-Fluorophenyl)propiolic acid (164 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445mg, 2.0 mmol) afforded **3ka** (178 mg, 0.68 mmol, 68%). White solid; m.p. 92–93 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00–7.90 (m, 2H), 7.69–7.61 (m, 2H), 7.59–7.53 (m, 2H), 7.52–7.46 (m, 2H), 7.13–7.05 (m, 2H), 6.81 (d, *J* = 15.9 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3 (d, *J* = 254.5 Hz), 141.2, 140.6, 133.5, 130.6 (d, *J* = 8.8 Hz), 129.4, 128.6 (d, *J* = 3.4 Hz), 127.7, 127.0 (d, *J* = 2.3 Hz), 116.3 (d, *J* = 22.7 Hz);
MS (EI) m/z = 262.0 (M^+)



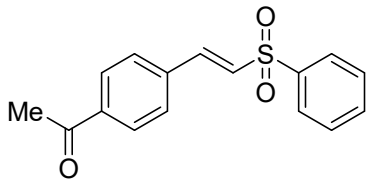
(*E*)-1-Chloro-4-(2-(phenylsulfonyl)vinyl)benzene (**3la**)[1]

3-(4-Chlorophenyl)propiolic acid (181 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3la** (181 mg, 0.65 mmol, 65%). White solid; m.p. 128–130 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.3 Hz, 2H), 7.59–7.53 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 15.4 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 140.5, 137.3, 133.5, 130.8, 129.7, 129.4, 129.4 (overlap), 127.9, 127.7;
MS (EI) m/z = 278.0 (M^+)



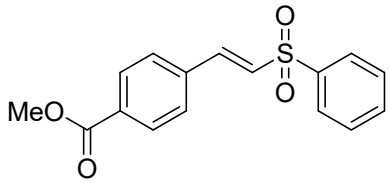
(*E*)-1-Bromo-4-(2-(phenylsulfonyl)vinyl)benzene (**3ma**)[1]

3-(4-Bromophenyl)propiolic acid (225 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ma** (200 mg, 0.62 mmol, 62%). White solid; m.p. 138–139 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98–7.91 (m, 2H), 7.66–7.60 (m, 2H), 7.59–7.50 (m, 4H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 15.4 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 140.4, 133.6, 132.4, 131.2, 129.9, 129.4, 127.9, 127.7, 125.7;
MS (EI) m/z = 322.0 (M^+)



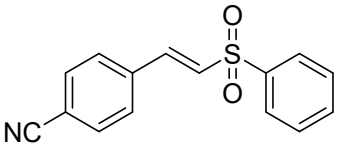
(*E*)-1-(4-(2-(Phenylsulfonyl)vinyl)phenyl)ethanone (3na)[4]

3-(4-Acetylphenyl)propiolic acid (188 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3na** (189 mg, 0.66 mmol, 66%). White solid; m.p. 148–150 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02–7.92 (m, 4H), 7.71 (d, *J* = 15.4 Hz, 1H), 7.67–7.62 (m, 1H), 7.61–7.52 (m, 4H), 6.97 (d, *J* = 15.4 Hz, 1H), 2.61 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 140.7, 140.2, 138.7, 136.6, 133.7, 129.8, 129.5, 128.9, 128.7, 127.8, 26.7;
MS (EI) m/z = 286.1 (M^+)



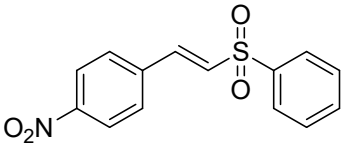
(*E*)-Methyl 4-(2-(phenylsulfonyl)vinyl)benzoate (3oa)[5]

3-(4-(Methoxycarbonyl)phenyl)propiolic acid (204 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3oa** (218 mg, 0.72 mmol, 72%). White solid; m.p. 152–155 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 8.00–7.92 (m, 2H), 7.71 (d, *J* = 15.5 Hz, 1H), 7.67–7.62 (m, 1H), 7.60–7.52 (m, 4H), 6.97 (d, *J* = 15.4 Hz, 1H), 3.93 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 140.9, 140.2, 136.5, 133.6, 132.2, 130.2, 129.7, 129.4, 128.4, 127.8, 52.4;
MS (EI) m/z = 302.1 (M^+)



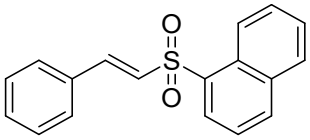
(*E*)-4-(2-(phenylsulfonyl)vinyl)benzonitrile (3pa)[4]

3-(4-Cyanophenyl)propiolic acid (171 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3pa** (143 mg, 0.53 mmol, 53%). White solid; m.p. 113–115 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–7.84 (m, 2H), 7.70–7.62 (m, 4H), 7.61–7.52 (m, 4H), 6.97 (d, *J* = 15.4 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7, 136.6, 133.8, 132.7, 132.1, 131.0, 129.5, 128.9, 127.8, 118.0, 114.3;
MS (EI) m/z = 269.0 (M^+)



(*E*)-1-Nitro-4-(2-(phenylsulfonyl)vinyl)benzene (3qa)[3]

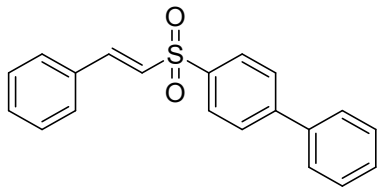
3-(4-Nitrophenyl)propiolic acid (191 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3qa** (130 mg, 0.45 mmol, 45%). Yellow solid; m.p. 169–170 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 8.02–7.91 (m, 2H), 7.73 (d, *J* = 15.5 Hz, 1H), 7.70–7.63 (m, 3H), 7.62–7.57 (m, 2H), 7.03 (d, *J* = 15.5 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 139.8, 139.2, 138.4, 133.9, 131.7, 129.6, 129.3, 127.9, 124.3;
MS (EI) m/z = 289.0 (M^+)



(*E*)-1-(Styrylsulfonyl)naphthalene (3ab)[6]

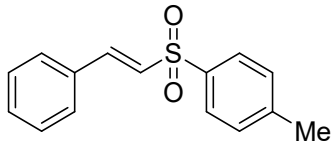
Phenylpropiolic acid (146 mg, 1.0 mmol) and 1-naphthylboronic acid (258 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ab** (183 mg, 0.62 mmol, 62%). White solid; m.p. 138–139 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.6 Hz, 1H), 8.43 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 15.4 Hz, 1H), 7.71–7.65 (m, 1H), 7.64–7.57 (m, 2H), 7.47 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.41–7.31 (m, 3H), 7.01 (d, *J* = 15.4 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 135.4, 135.1, 134.2, 132.3, 131.1, 129.8, 129.1, 129.0, 128.6, 128.5, 128.5 (overlap), 127.5, 126.9, 124.6, 124.2;
MS (EI) m/z = 294.1 (M^+)



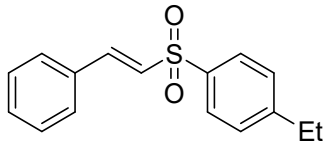
(*E*)-4-(Styrylsulfonyl)-1,1'-biphenyl(3ac)[7]

Phenylpropiolic acid (146 mg, 1.0 mmol) and 4-biphenylboronic acid (297 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ac** (215 mg, 0.67 mmol, 67%). White solid; m.p. 154–156 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 15.3 Hz, 1H), 7.63–7.59 (m, 2H), 7.53–7.48 (m, 4H), 7.46–7.39 (m, 4H), 6.93 (d, *J* = 15.4 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 142.4, 139.2 (overlap 2C), 132.4, 131.3, 129.1, 129.1 (overlap), 128.6, 128.2, 128.0, 127.4, 127.3;
MS (EI) m/z = 320.1 (M^+)



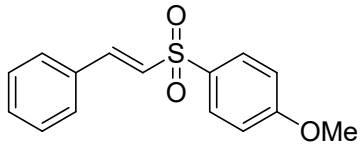
(*E*)-1-Methyl-4-(styrylsulfonyl)benzene (3ad)[8]

Phenylpropiolic acid (146 mg, 1.0 mmol) and (*p*-methylphenyl)boronic acid (204 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ad** (209 mg, 0.81 mmol, 81%). Pale yellow solid; m.p. 102–103 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87–7.79 (m, 2H), 7.67 (d, *J* = 15.4 Hz, 1H), 7.51–7.46 (m, 2H), 7.43–7.37 (m, 3H), 7.37–7.34 (m, 2H), 6.86 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 141.9, 137.7, 132.5, 131.1, 130.0, 129.1, 128.5, 127.7, 127.6, 21.6;
MS (EI) m/z = 258.1 (M^+)



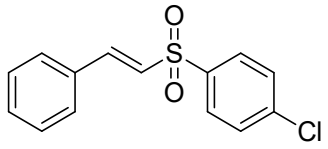
(*E*)-1-Ethyl-4-(styrylsulfonyl)benzene (3ae)[6]

Phenylpropiolic acid (146 mg, 1.0 mmol) and (4-ethylphenyl)boronic acid (225 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ae** (218 mg, 0.80 mmol, 80%). White solid; m.p. 101–102 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 15.4 Hz, 1H), 7.51–7.46 (m, 2H), 7.42–7.40 (m, 2H), 7.40–7.35 (m, 3H), 6.87 (d, *J* = 15.4 Hz, 1H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 141.9, 137.9, 132.5, 131.1, 129.1, 128.8, 128.5, 127.8, 127.6, 28.9, 15.2;
MS (EI) m/z = 272.1 (M^+)



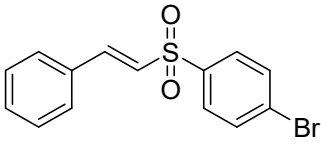
(*E*)-1-Methoxy-4-(styrylsulfonyl)benzene (3af)[8]

Phenylpropiolic acid (146 mg, 1.0 mmol) and (4-methoxyphenyl)boronic acid (228 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3af** (211 mg, 0.77 mmol, 77%). Pale yellow solid; m.p. 110–112 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91–7.85 (m, 2H), 7.64 (d, *J* = 15.4 Hz, 1H), 7.50–7.46 (m, 2H), 7.42–7.37 (m, 3H), 7.04–6.99 (m, 2H), 6.86 (d, *J* = 15.4 Hz, 1H), 3.88 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 141.4, 132.5, 132.2, 131.0, 129.9, 129.0, 128.5, 127.9, 114.6, 55.7;
MS (EI) m/z = 274.1 (M^+)



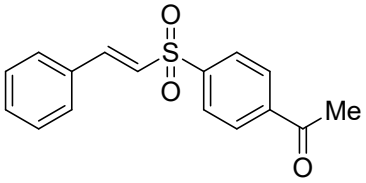
(*E*)-1-Chloro-4-(styrylsulfonyl)benzene (3ag)[8]

Phenylpropiolic acid (146 mg, 1.0 mmol) and (4-chlorophenyl)boronic acid (235 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ag** (170 mg, 0.61 mmol, 61%). Pale yellow solid; m.p. 107–108 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 15.4 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 6.5 Hz, 2H), 7.36–7.30 (m, 3H), 6.76 (d, *J* = 15.4 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 140.1, 139.2, 132.1, 131.4, 129.7, 129.2, 129.2 (overlap), 128.7, 126.8;
MS (EI) m/z = 278.0 (M^+)



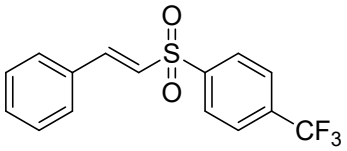
(*E*)-1-Bromo-4-(styrylsulfonyl)benzene (**3ah**)[8]

Phenylpropiolic acid (146 mg, 1.0 mmol) and (4-bromophenyl)boronic acid (301 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ah** (200 mg, 0.62 mmol, 62%). Pale yellow solid; m.p. 107–108 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85–7.79 (m, 2H), 7.73–7.67 (m, 3H), 7.51–7.47 (m, 2H), 7.45–7.38 (m, 3H), 6.85 (d, *J* = 15.4 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 139.7, 132.7, 132.1, 131.5, 129.2, 129.1, 128.7, 126.7;
MS (EI) m/z = 322.0 (M^+)



(*E*)-1-(4-(Styrylsulfonyl)phenyl)ethanone (**3ai**)

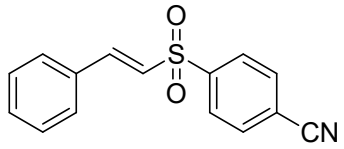
Phenylpropiolic acid (146 mg, 1.0 mmol) and 4-acetylphenylboronic acid (246 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ai** (146 mg, 0.51 mmol, 51%). White solid; m.p. 129–133 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12–8.09 (m, 2H), 8.07–8.04 (m, 2H), 7.74 (d, *J* = 15.4 Hz, 1H), 7.52–7.48 (m, 2H), 7.46–7.38 (m, 3H), 6.87 (d, *J* = 15.4 Hz, 1H), 2.65 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 144.6, 143.8, 140.5, 132.1, 131.5, 129.2, 129.1, 128.7, 128.0, 126.4, 26.9;
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{14}O_3S$ 286.0658; Found: 286.0654



(*E*)-1-(2-(Styrylsulfonyl)-4-(trifluoromethyl)benzene (**3aj**)[7]

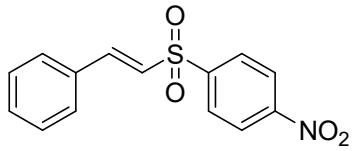
Phenylpropiolic acid (146 mg, 1.0 mmol) and 4-(trifluoromethyl)phenylboronic acid (285 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3aj** (159 mg, 0.51 mmol, 51%). White solid; m.p. 78–80 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 15.4 Hz, 1H), 7.53–7.49 (m, 2H), 7.47–7.39 (m, 3H), 6.87 (d, *J* = 15.4 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 144.1, 135.0 (q, *J* = 33.1 Hz), 132.0, 131.6, 129.2, 128.7, 128.2, 126.5 (q, *J* = 3.7 Hz), 126.3, 123.0 (q, *J* = 273.4 Hz);

MS (EI) m/z = 312.0 (M^+)



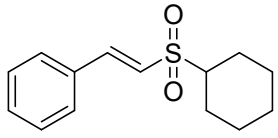
(*E*)-4-(Styrylsulfonyl)benzonitrile (3ak)[7]

Phenylpropiolic acid (146 mg, 1.0 mmol) and 4-cyanophenylboronic acid (220 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ak** (121 mg, 0.45 mmol, 45%). White solid; m.p. 175–176 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11–8.06 (m, 2H), 7.88–7.84 (m, 2H), 7.76 (d, *J* = 15.4 Hz, 1H), 7.53–7.49 (m, 2H), 7.49–7.41 (m, 3H), 6.85 (d, *J* = 15.4 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 144.7, 133.1, 131.8, 131.8, 129.2, 128.8, 128.3, 125.7, 117.1, 117.1;
MS (EI) m/z = 269.0 (M^+)



(*E*)-1-Nitro-4-(styrylsulfonyl)benzene (3al)[1]

Phenylpropiolic acid (146 mg, 1.0 mmol) and 4-nitrophenylboronic acid (250 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3al** (110 mg, 0.38 mmol, 38%). Yellow solid; m.p. 148–150 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44–8.36 (m, 2H), 8.20–8.10 (m, 2H), 7.78 (d, *J* = 15.4 Hz, 1H), 7.54–7.50 (m, 2H), 7.49–7.41 (m, 3H), 6.87 (d, *J* = 15.4 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 146.5, 145.0, 131.9, 131.8, 129.2, 129.0, 128.8, 125.7, 124.6;
MS (EI) m/z = 289.0 (M^+)



(*E*)-(2-(Cyclohexylsulfonyl)vinyl)benzene (3ao)[9]

Phenylpropiolic acid (146 mg, 1.0 mmol) and cyclohexylboronic acid (191 mg, 1.5 mmol) and potassium disulfite (445 mg, 2.0 mmol) afforded **3ao** (37 mg, 0.15 mmol, 15%). Colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63–7.49 (m, 3H), 7.49–7.38 (m, 3H), 6.78 (d, *J* = 15.5 Hz, 1H), 2.88 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.28–2.19 (m, 2H), 1.97–1.88 (m, 2H), 1.76–1.70 (m, 1H), 1.51 (qd, *J* = 12.5, 3.4 Hz, 2H), 1.31–1.22 (m, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 132.4, 131.3, 129.1, 128.5, 122.8, 62.7, 29.7, 25.5, 25.1;
MS (EI) m/z = 250.1 (M^+)

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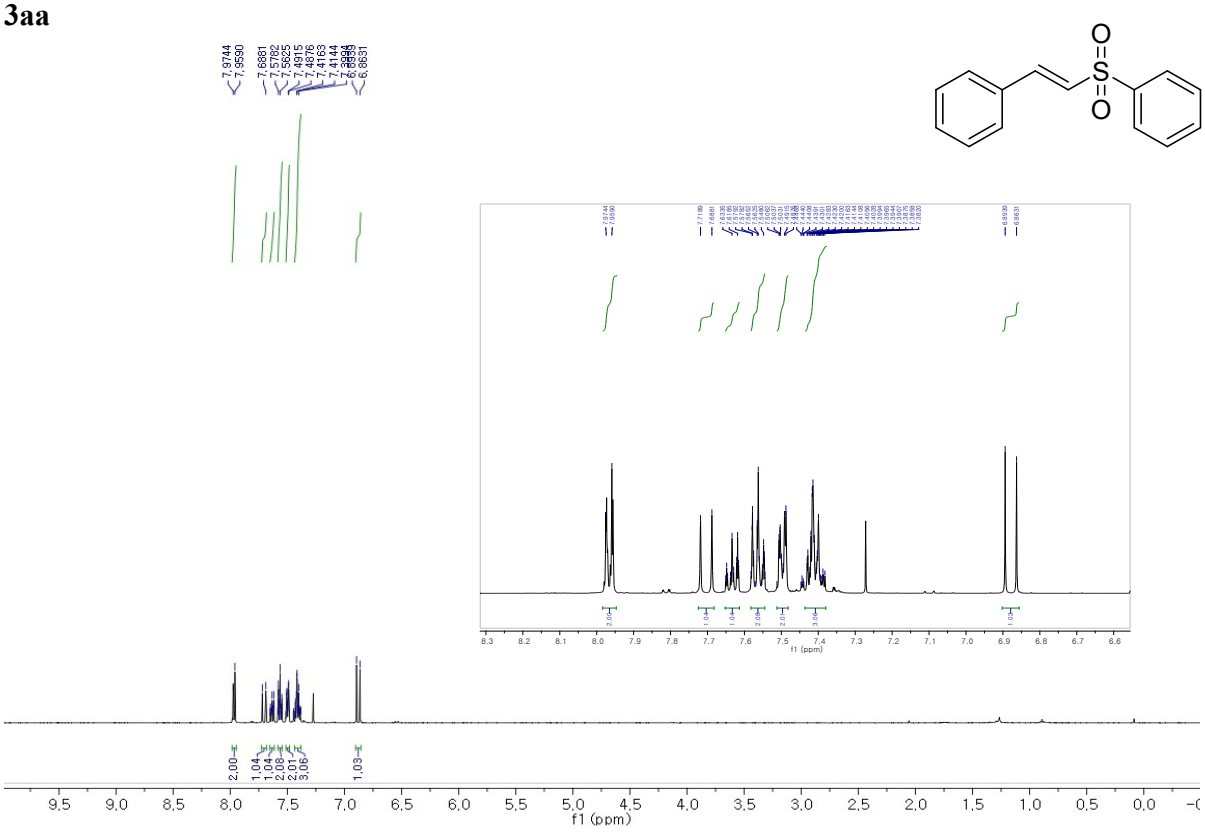
9. T. Zhu, J. Shen, Y. Sun and J. Wu, *Chem. Commun.,* 2021, **57**, 915.

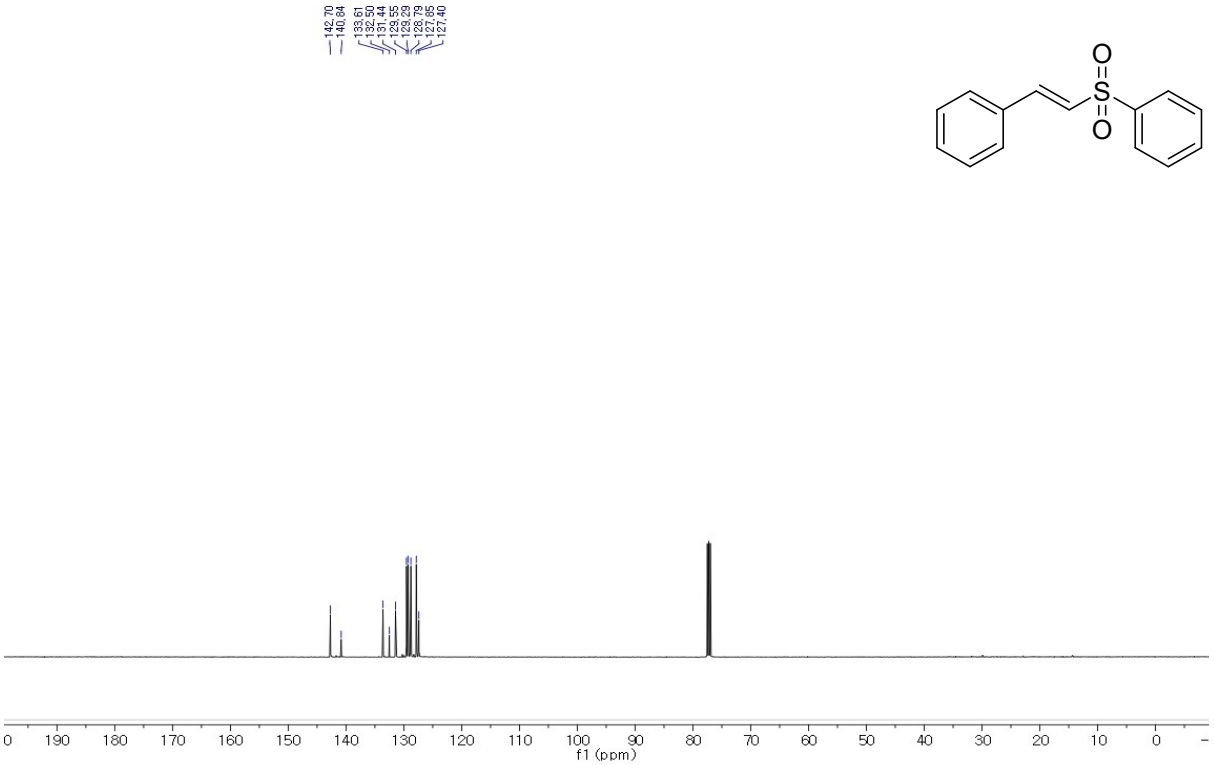
III. NMR Spectra

^{1}H NMR

3aa



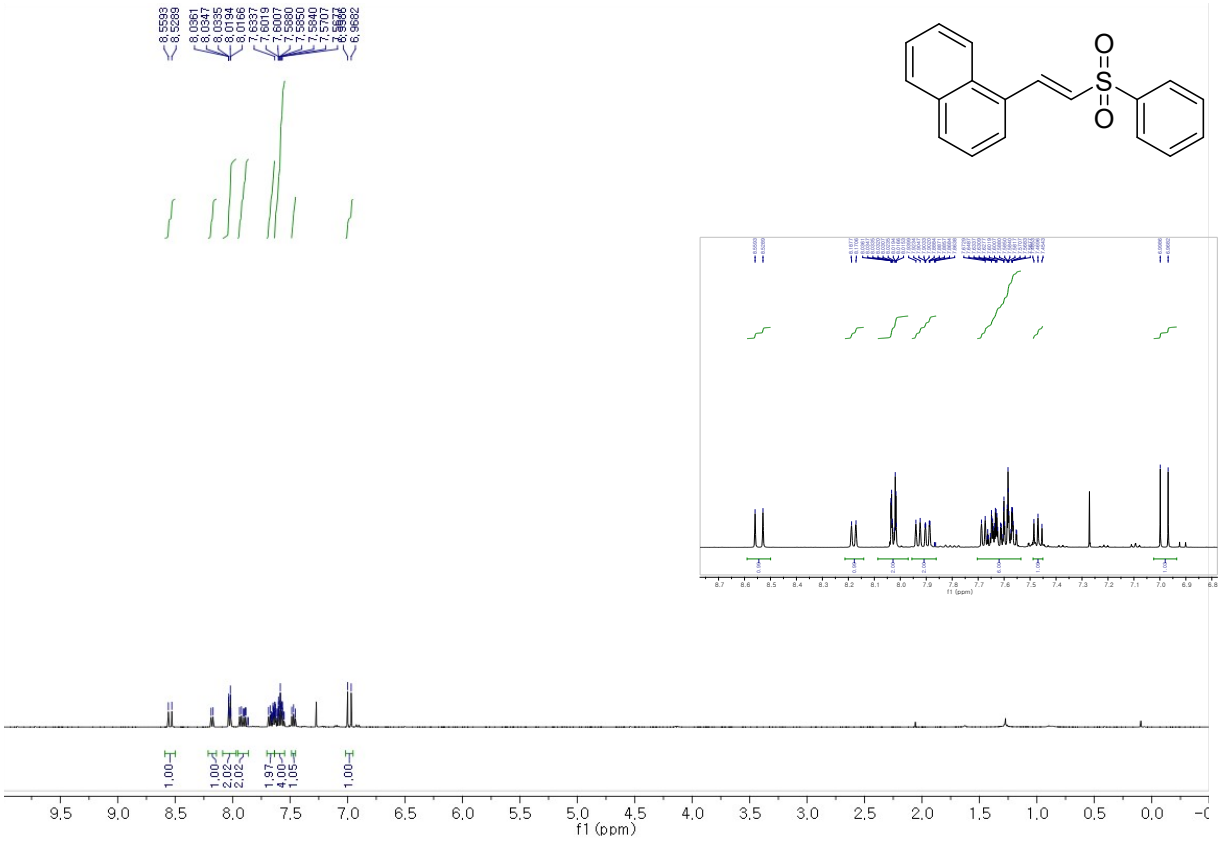
^{13}C NMR



3aa

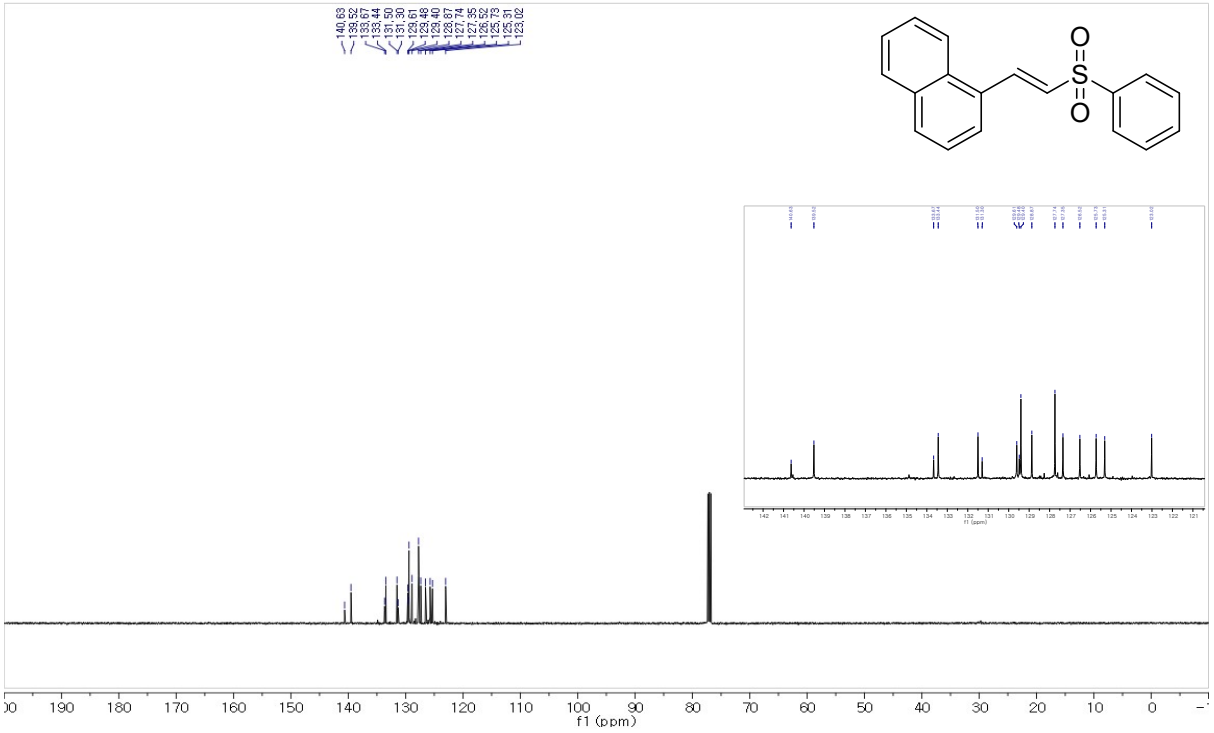
^{1}H NMR

3ba



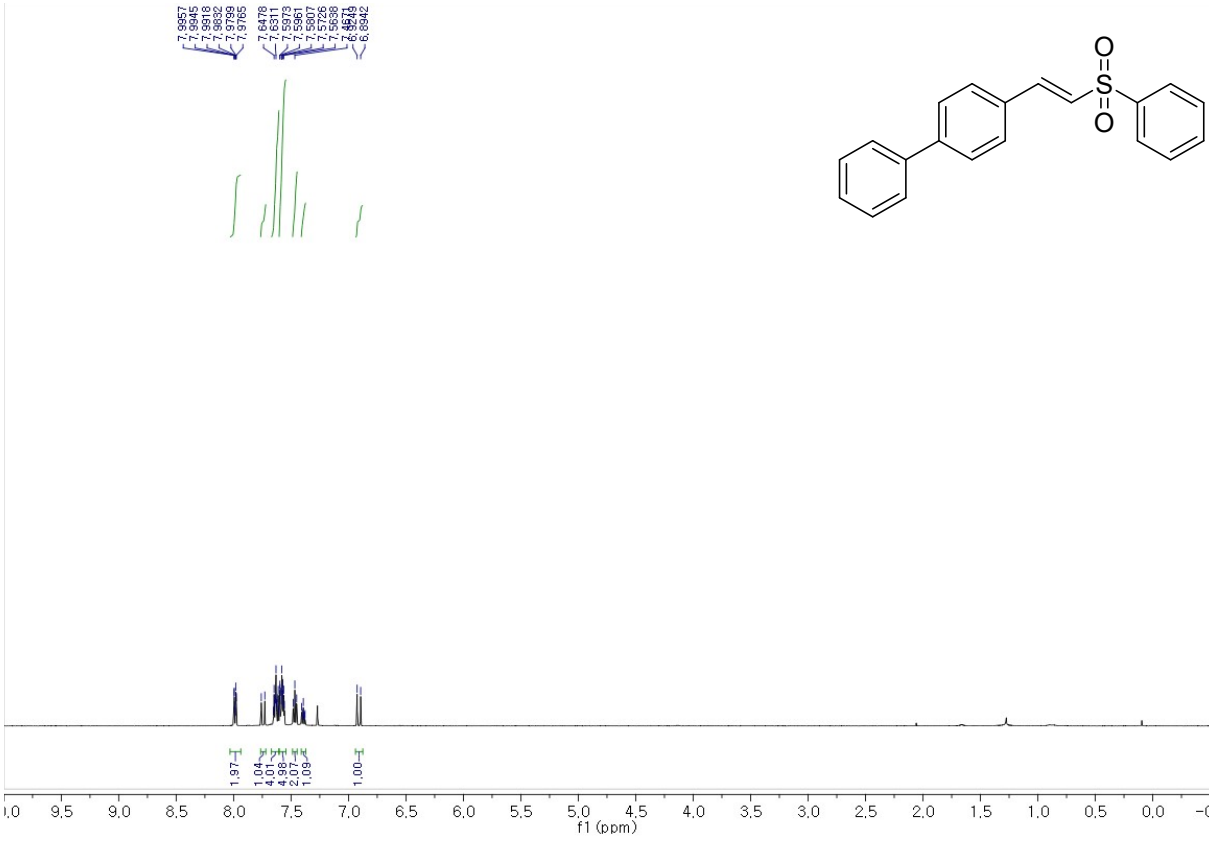
^{13}C NMR

3ba



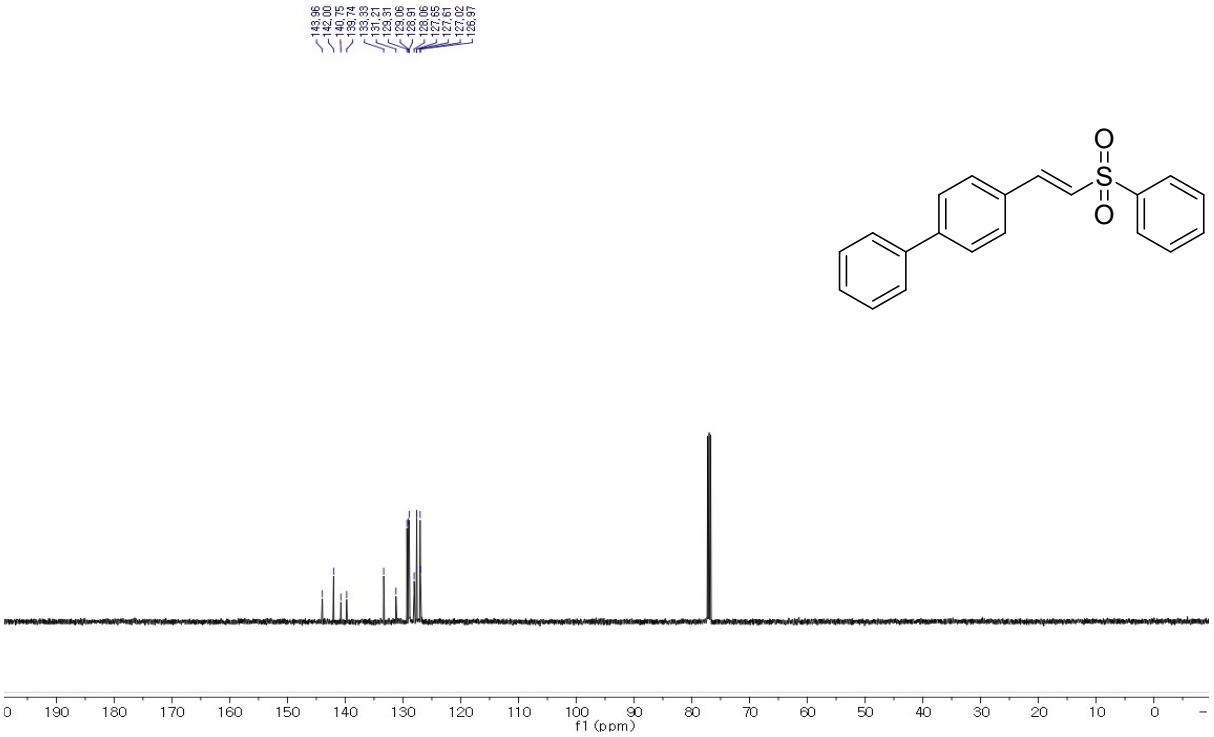
^{1}H NMR

3ca



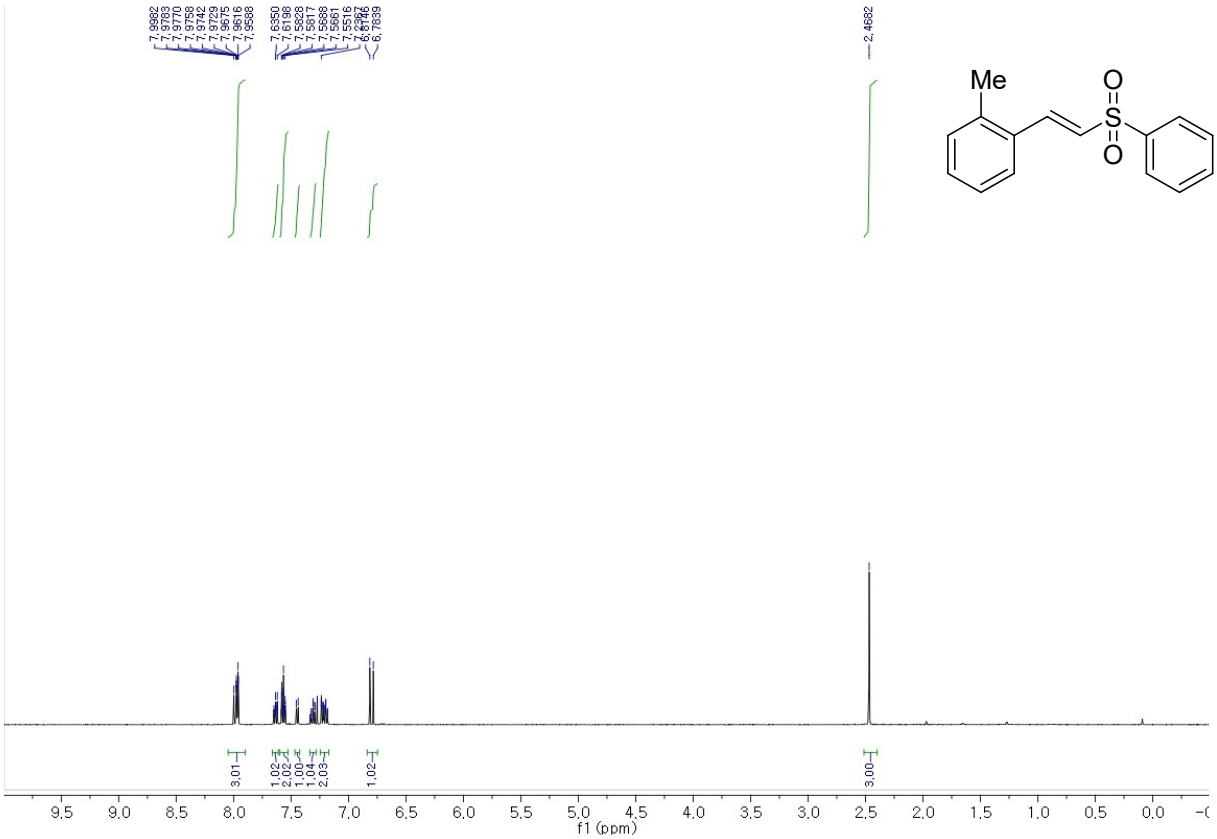
^{13}C NMR

3ca



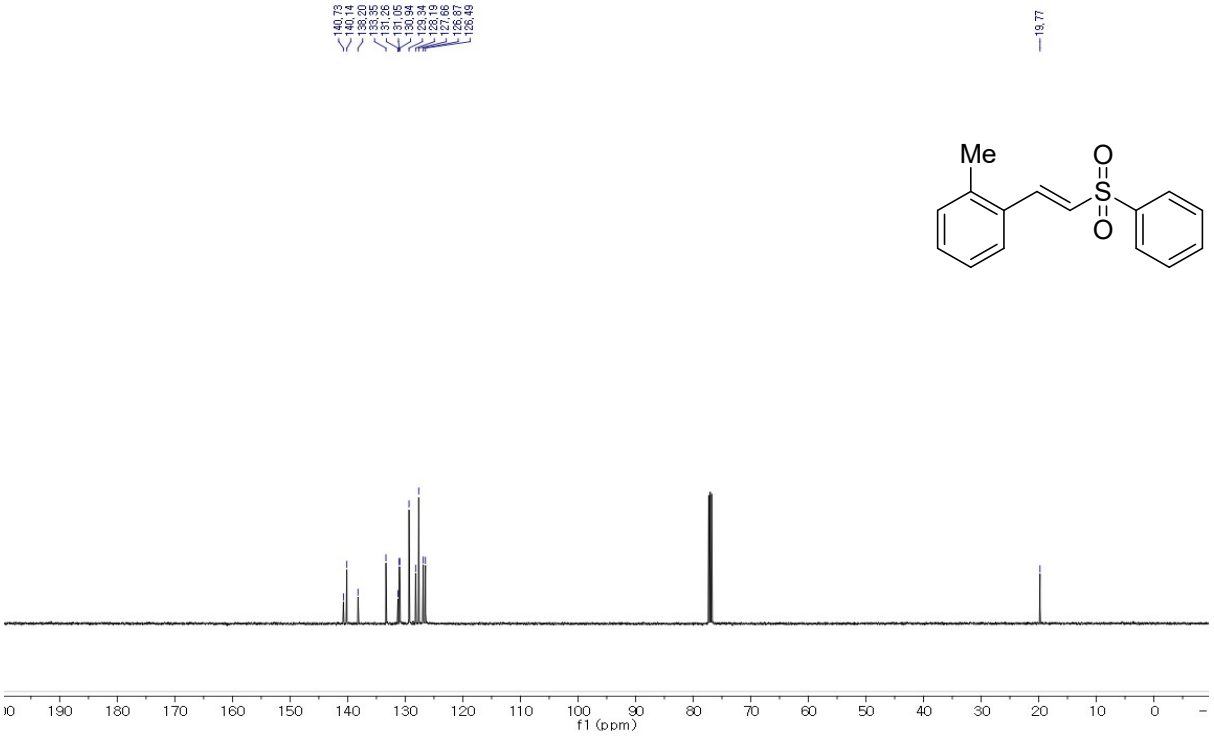
^{1}H NMR

3da



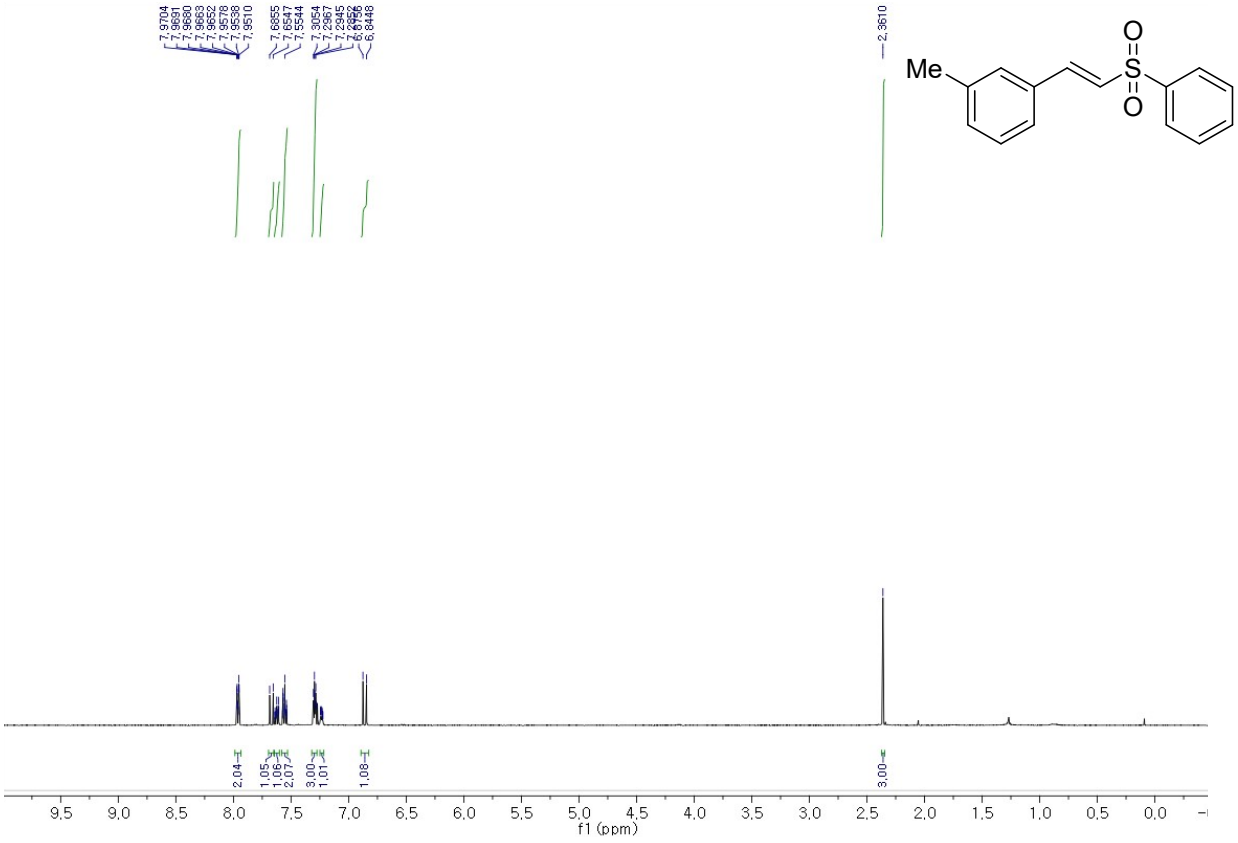
^{13}C NMR

3da


140.73
140.14
138.20
133.35
131.35
131.05
130.94
129.34
128.19
127.66
126.87
126.49
19.77
Me
O
S
O
f1 (ppm)

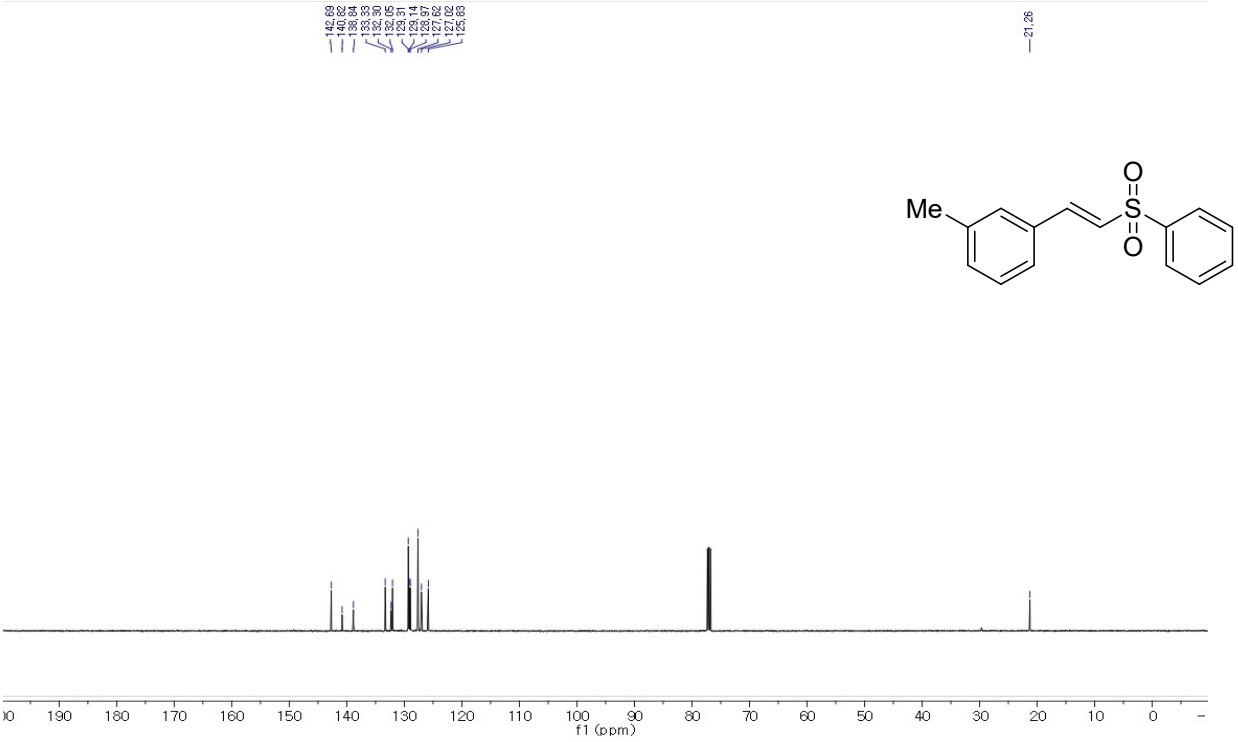
^{1}H NMR

3ea



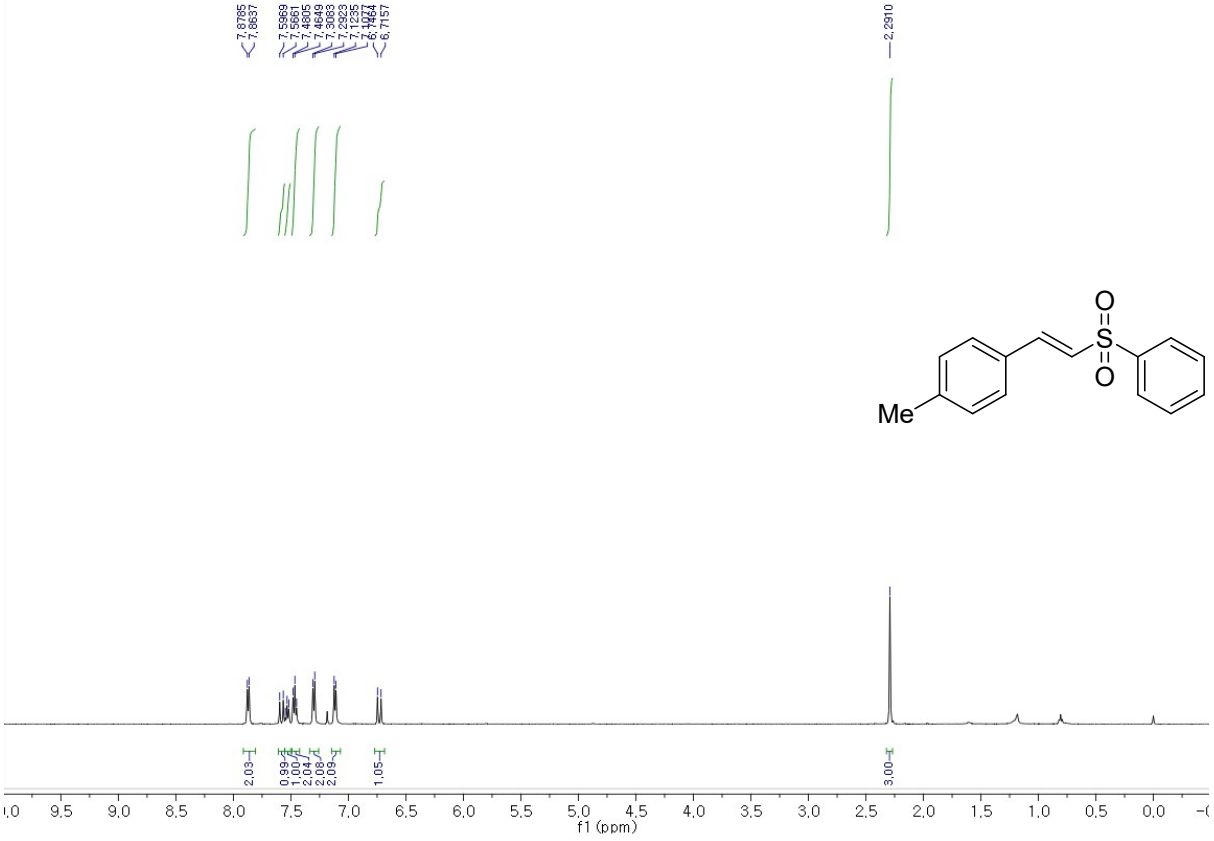
^{13}C NMR

3ea



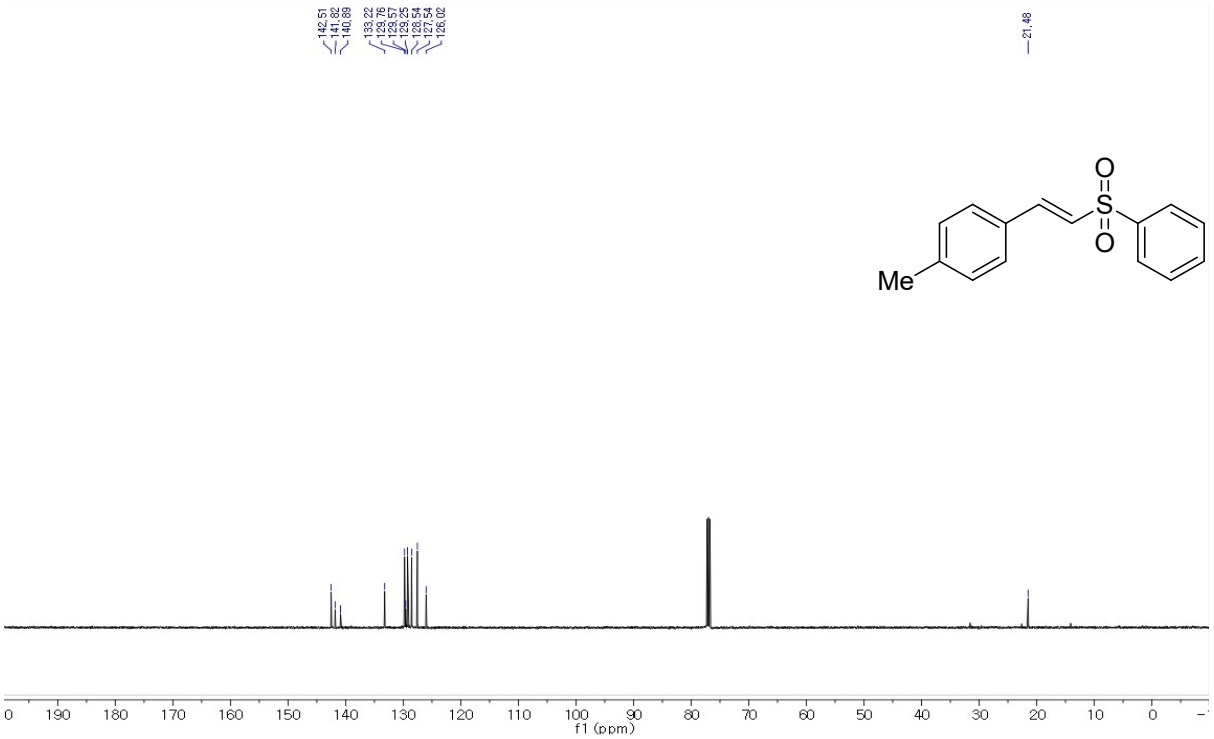
^{1}H NMR

3fa



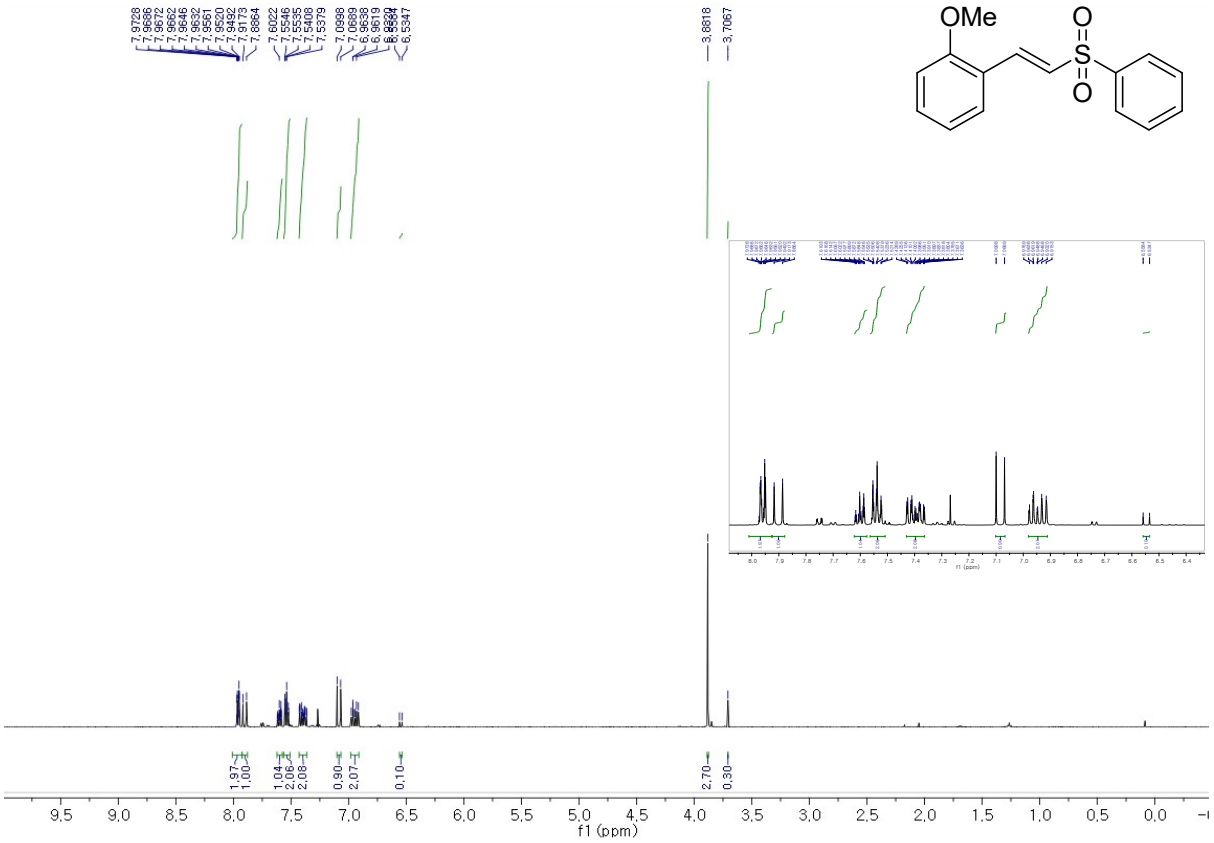
^{13}C NMR

3fa



^{1}H NMR

3ga



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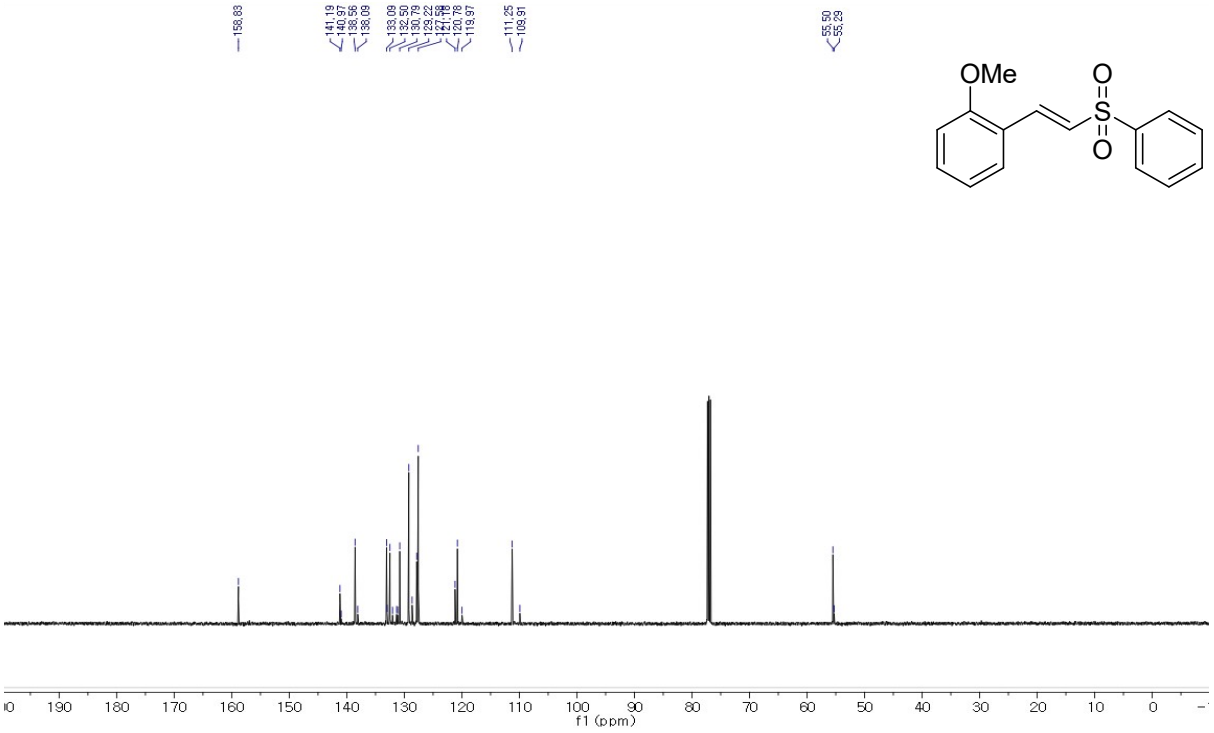
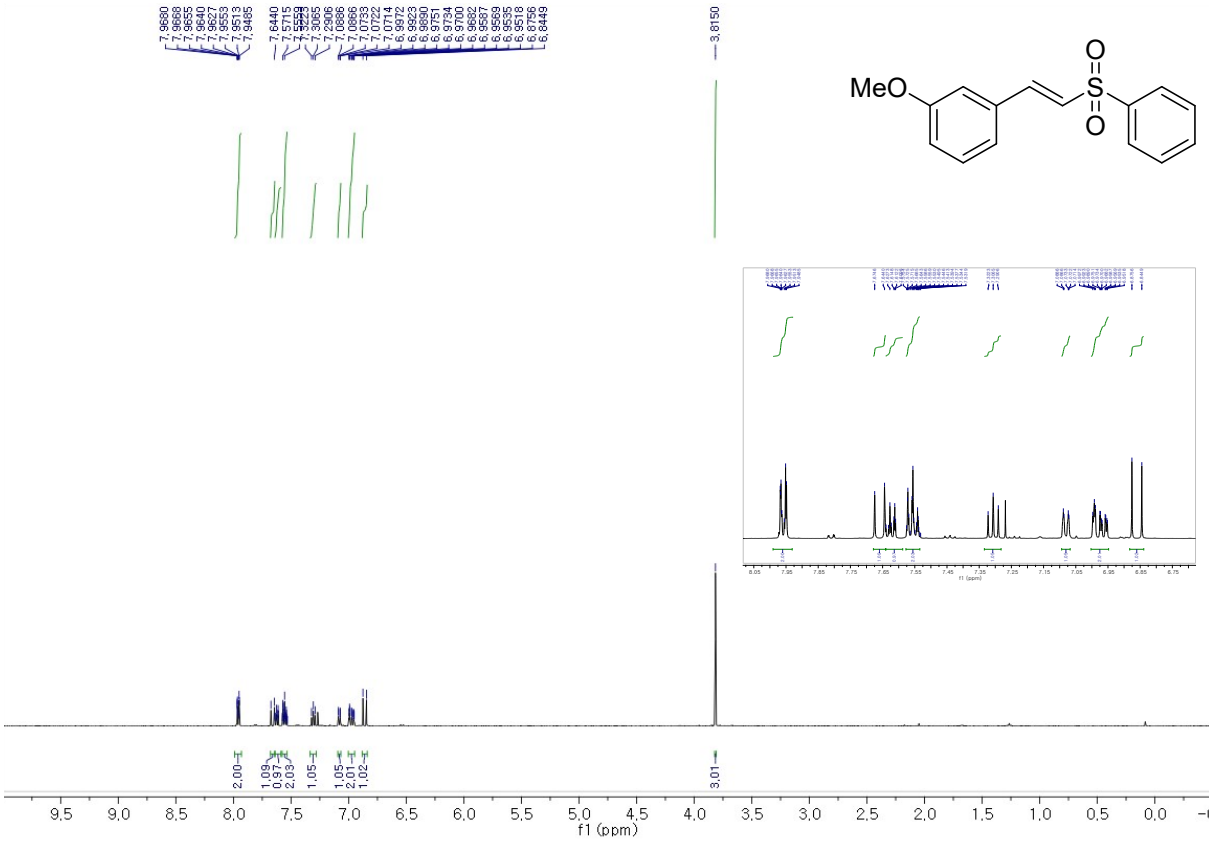


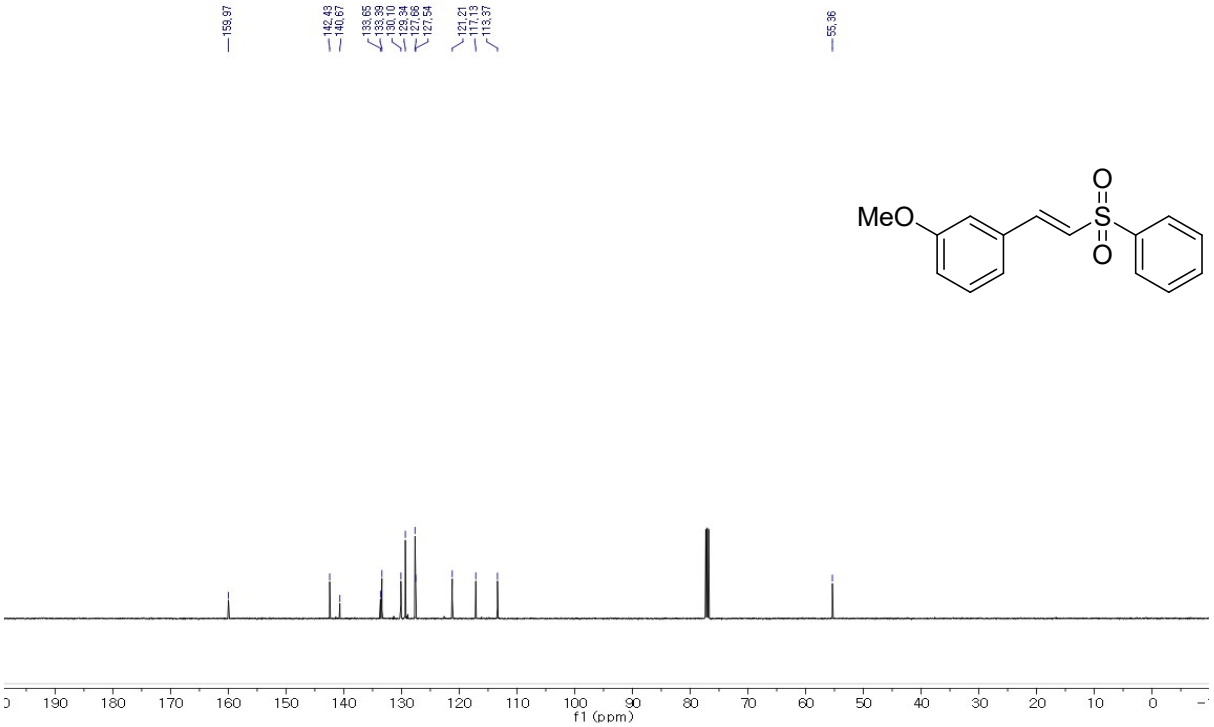
^{1}H NMR

3ha



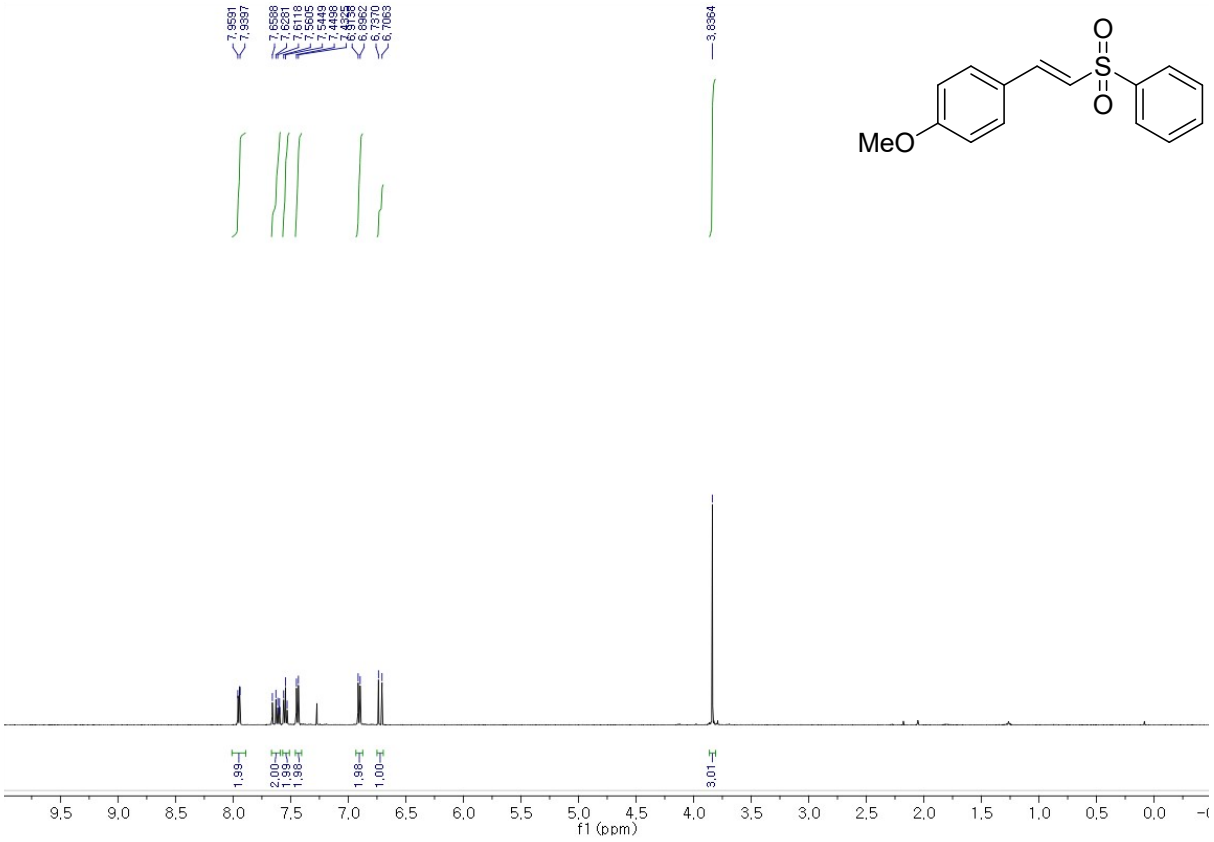
^{13}C NMR

3ha



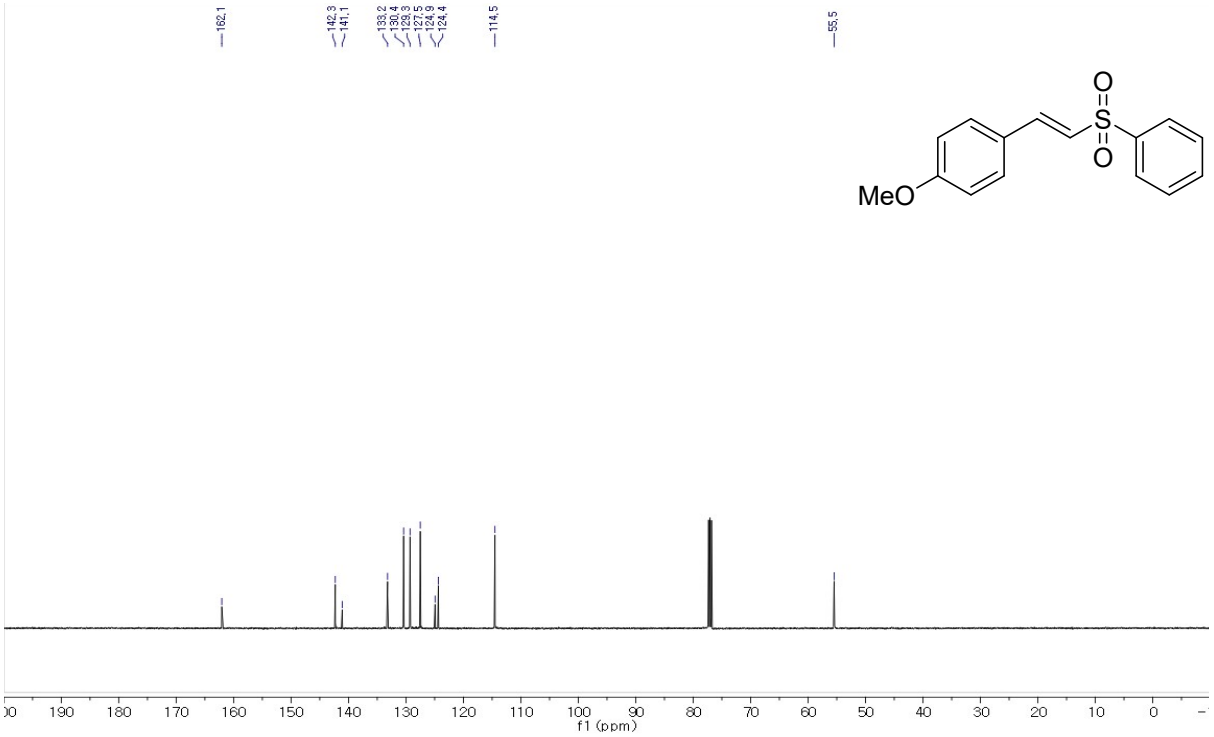
^{1}H NMR

3ia



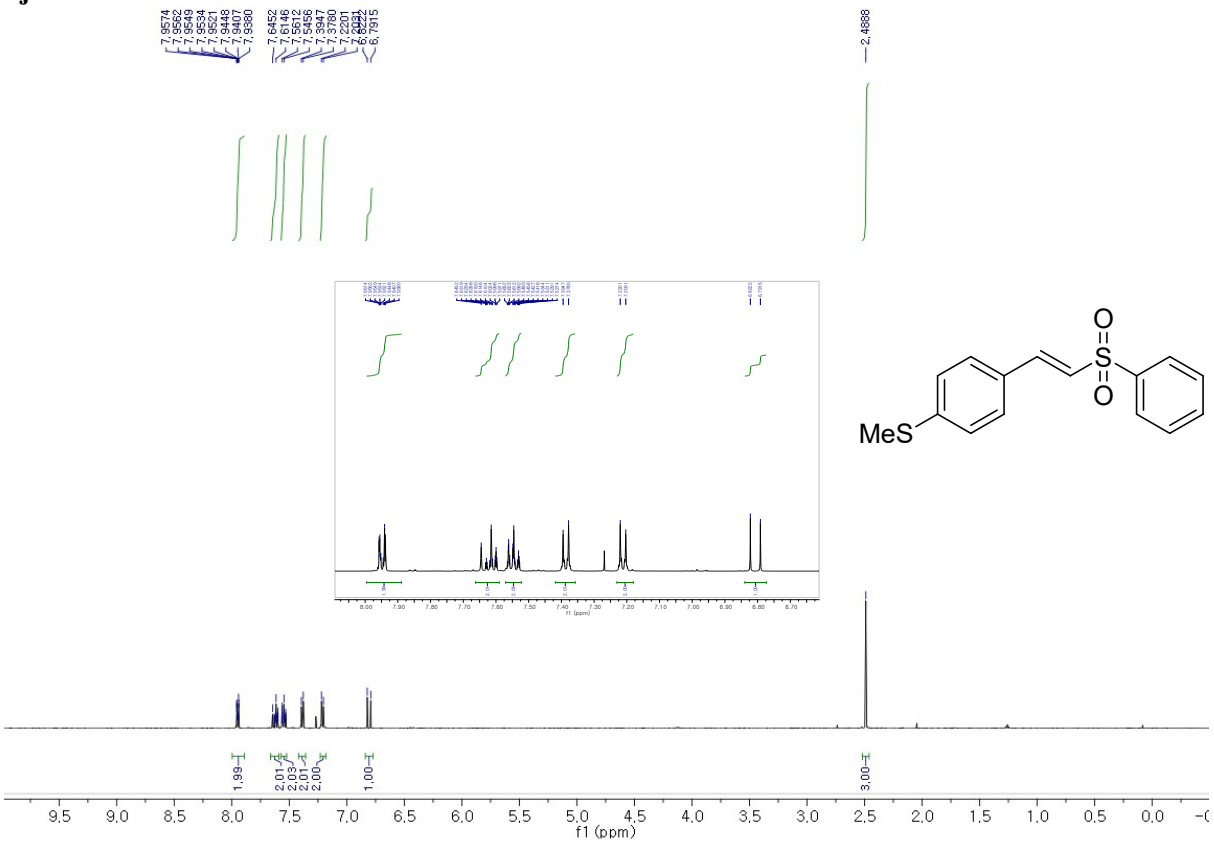
^{13}C NMR

3ia



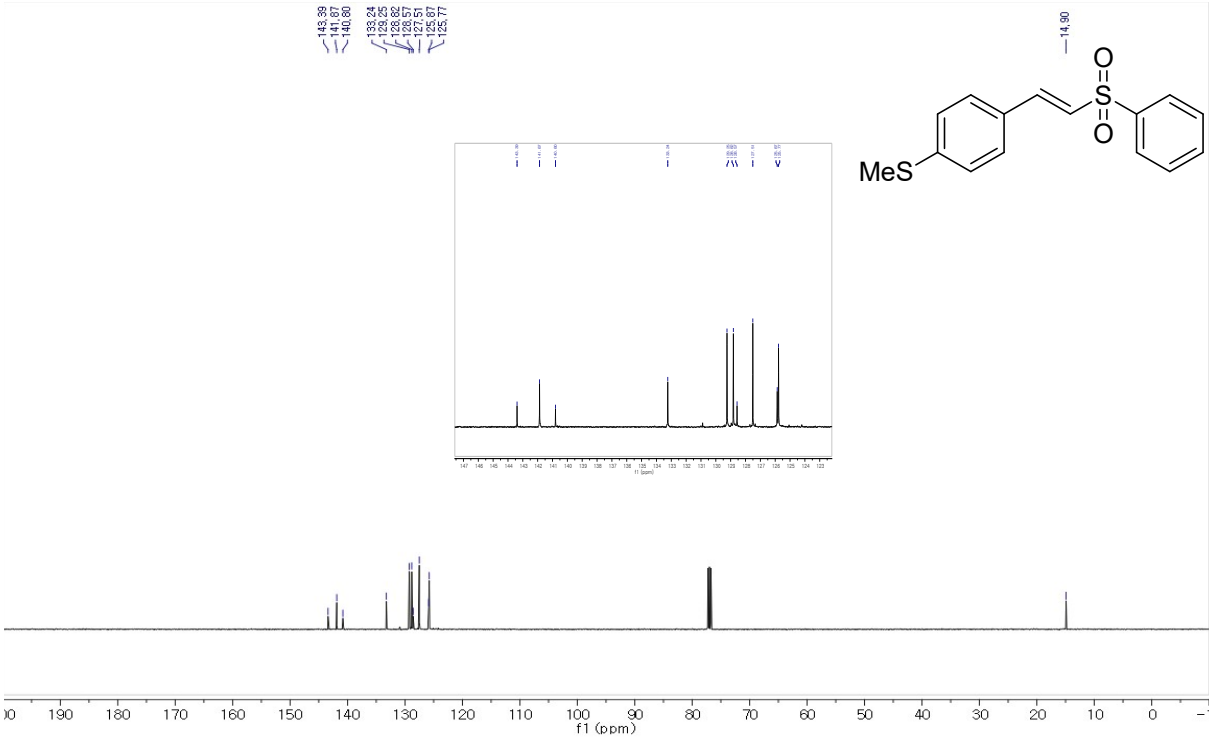
^{1}H NMR

3ja



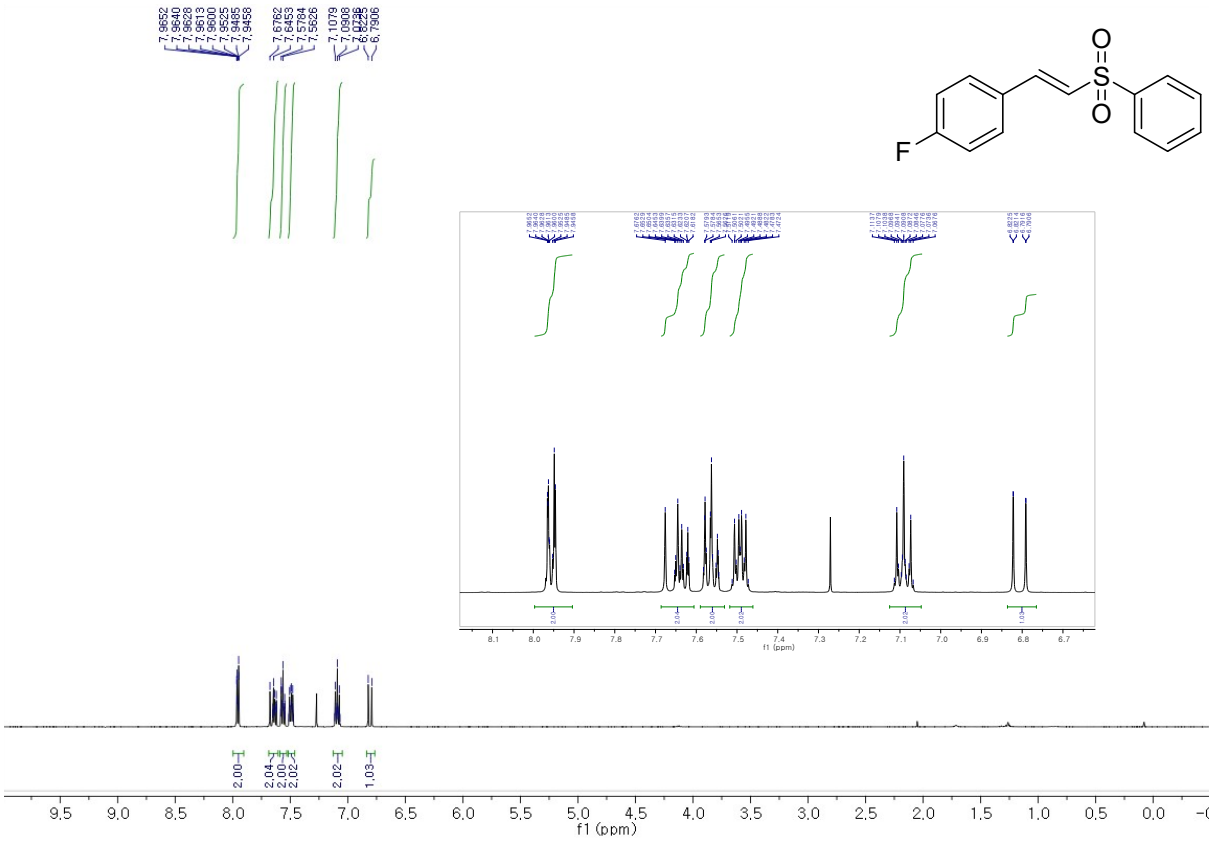
^{13}C NMR

3ja



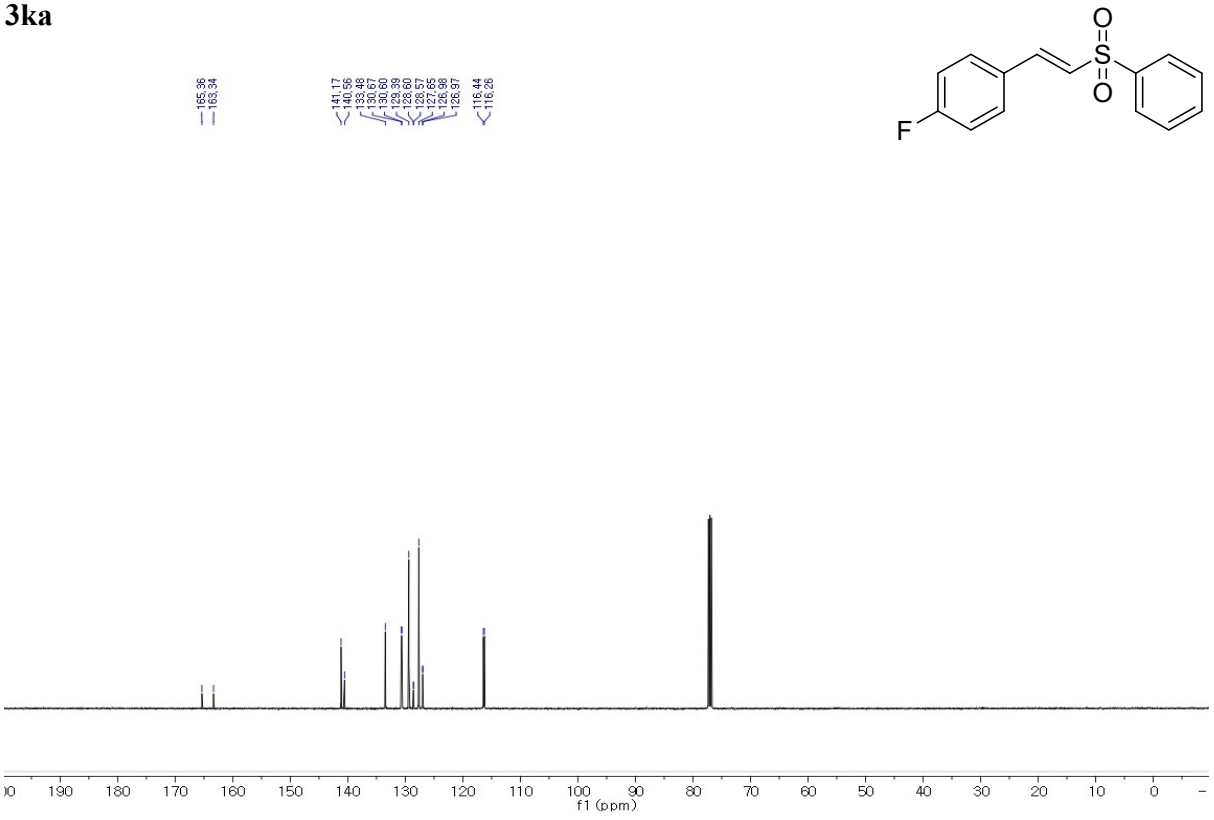
^{1}H NMR

3ka



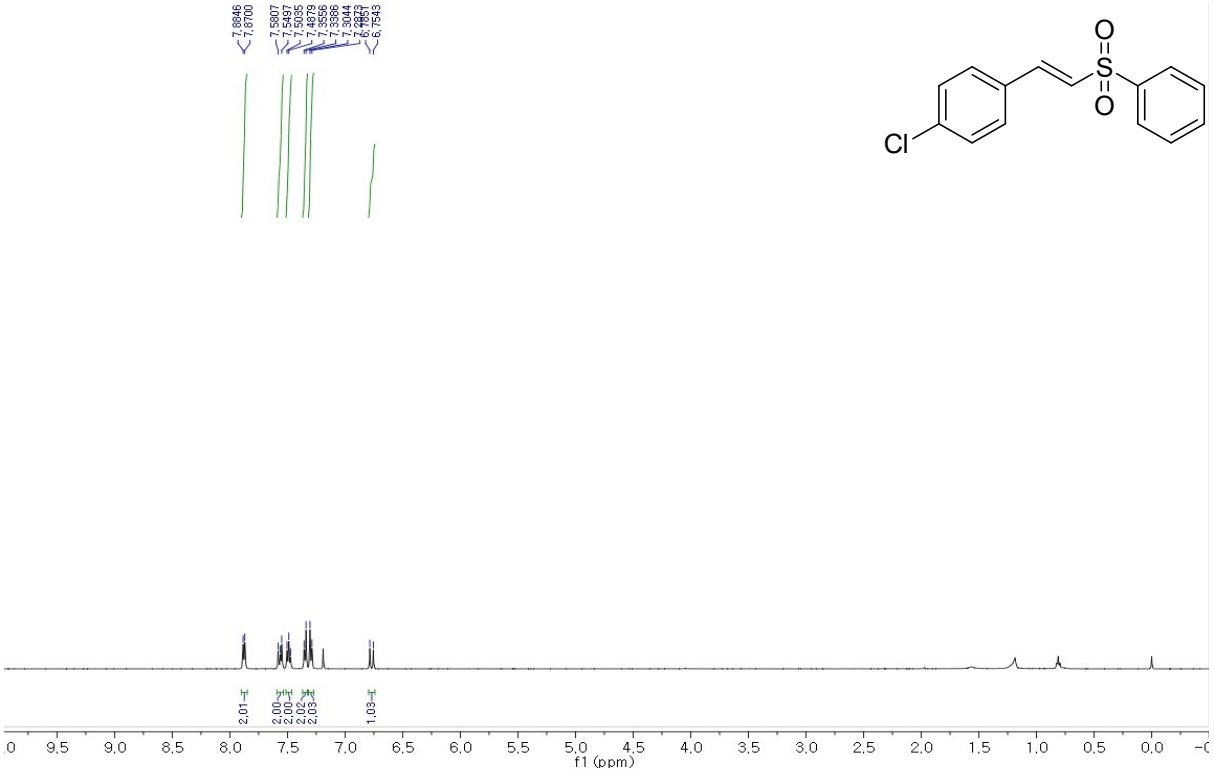
^{13}C NMR

3ka



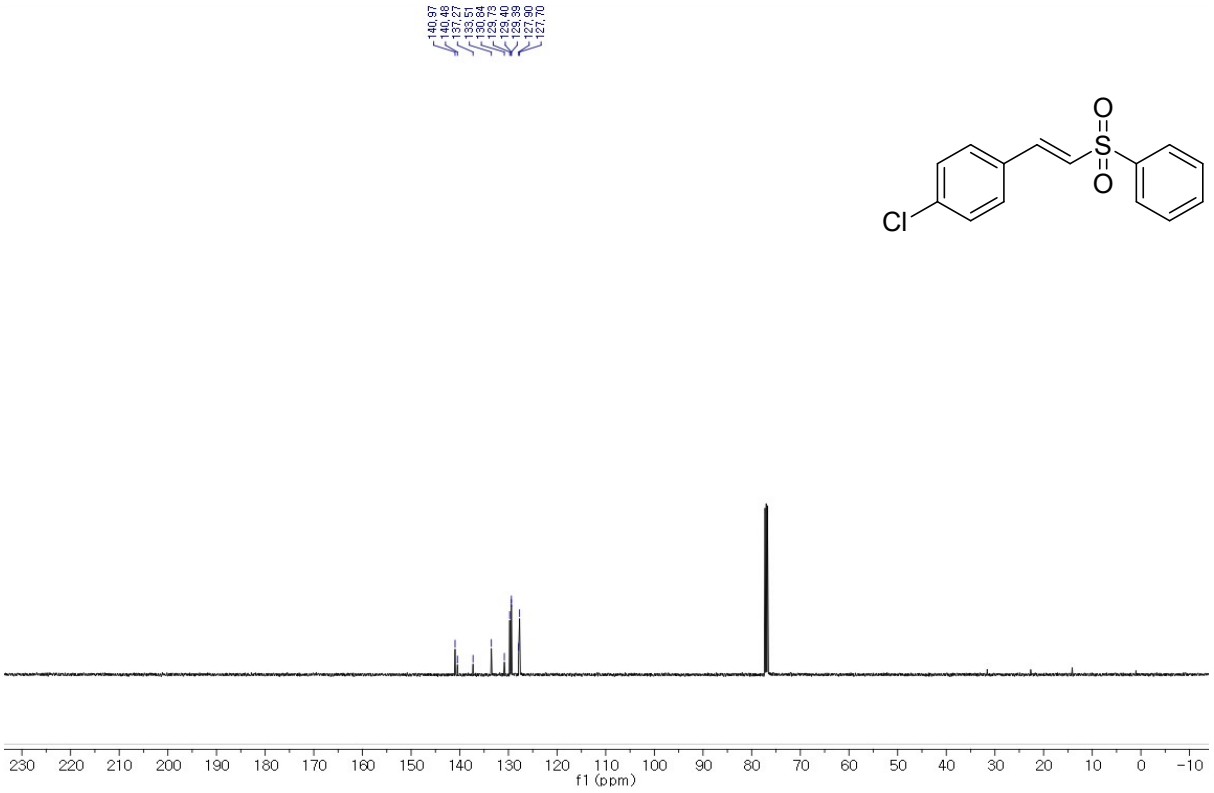
^{1}H NMR

3la



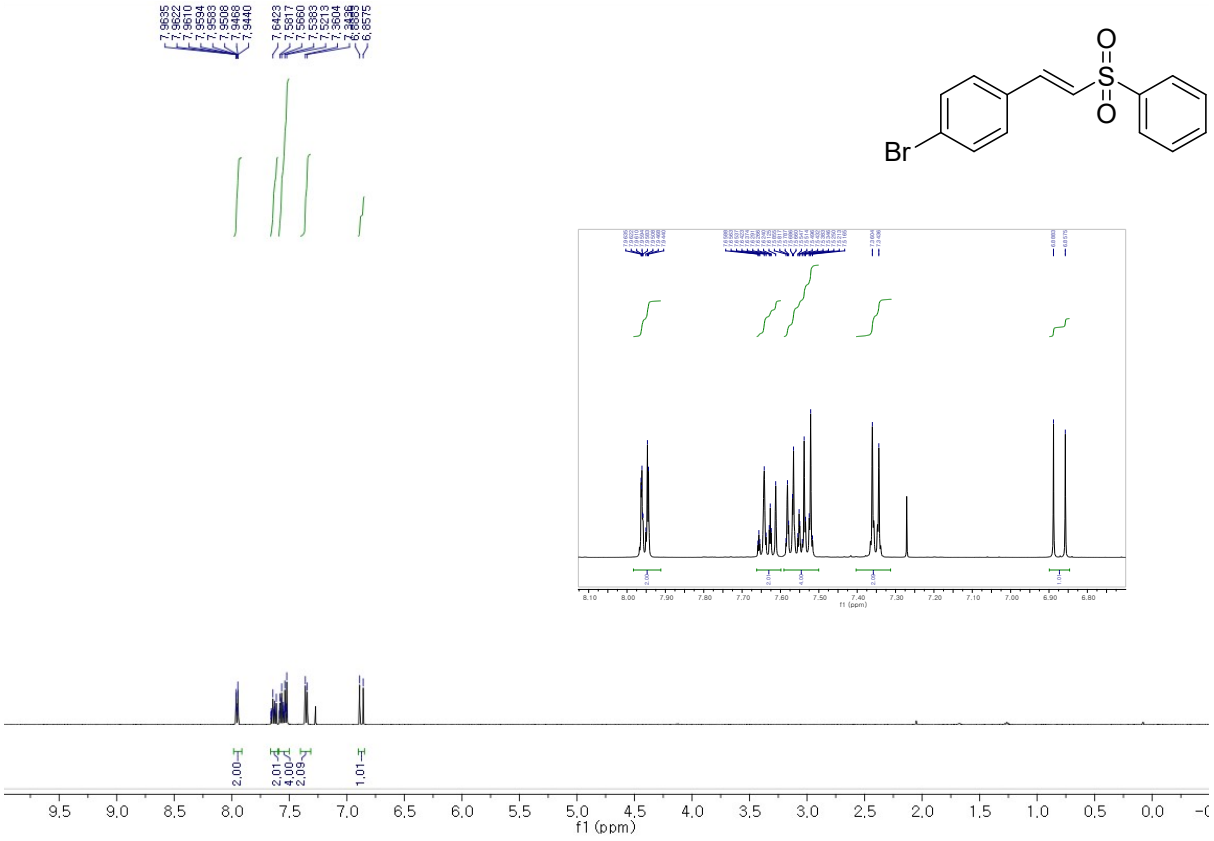
^{13}C NMR

3la



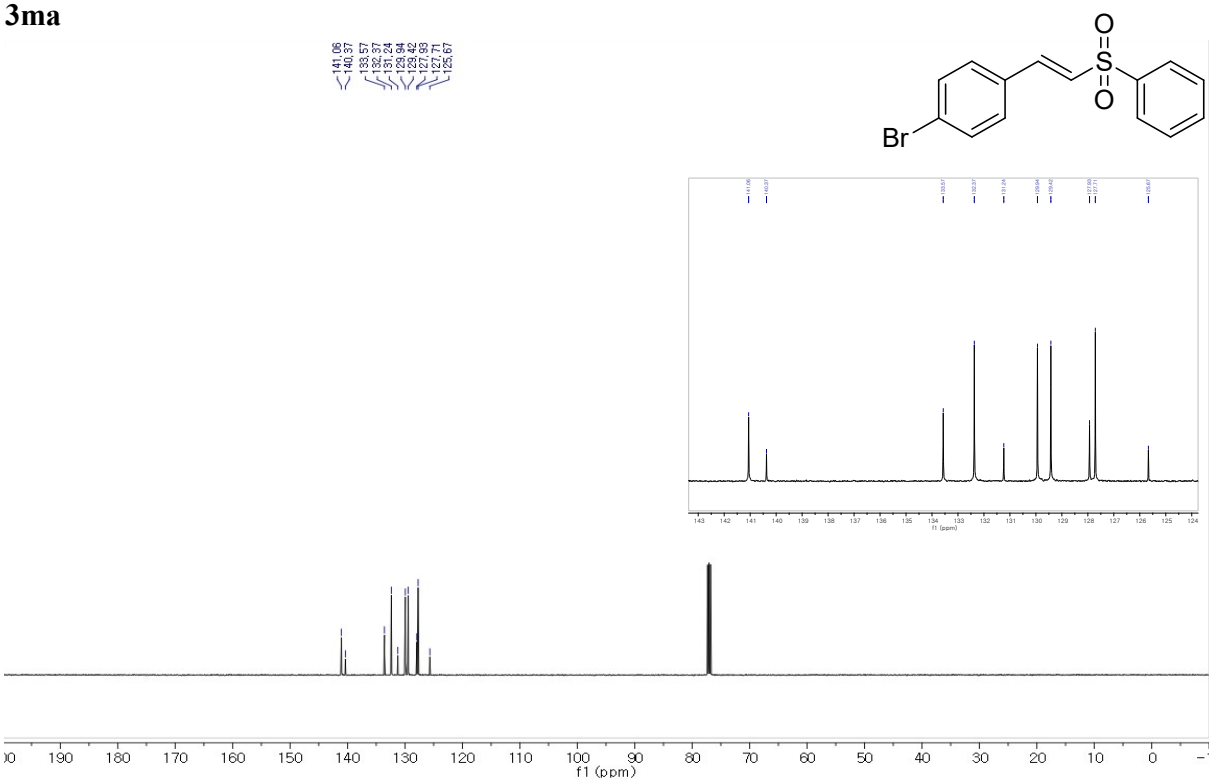
^{1}H NMR

3ma

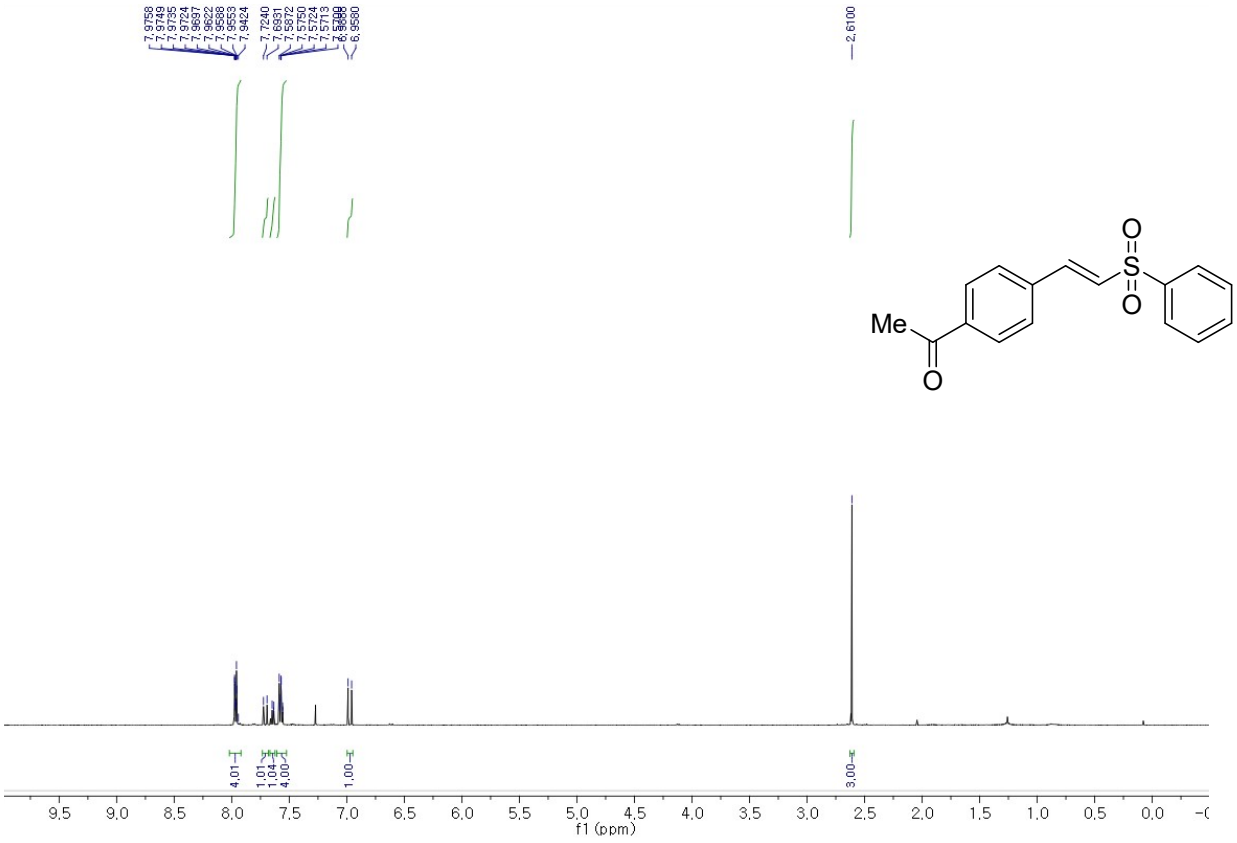


^{13}C NMR

3ma

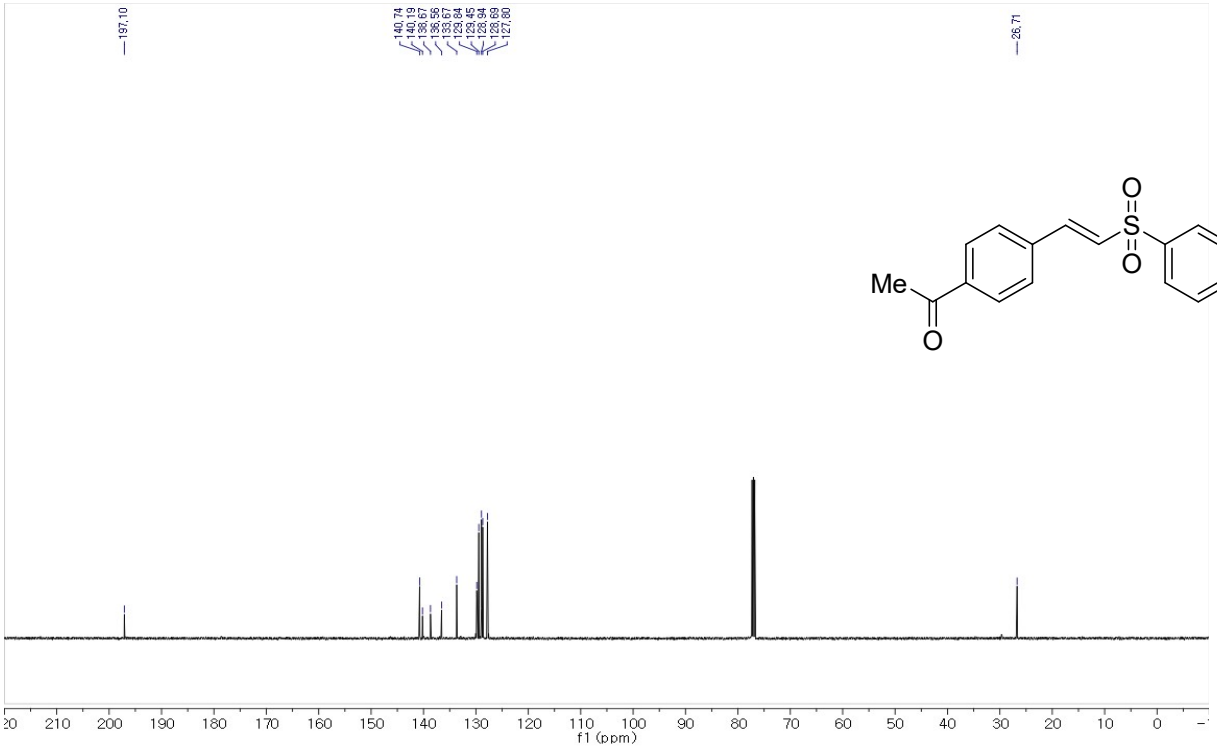


^{1}H NMR



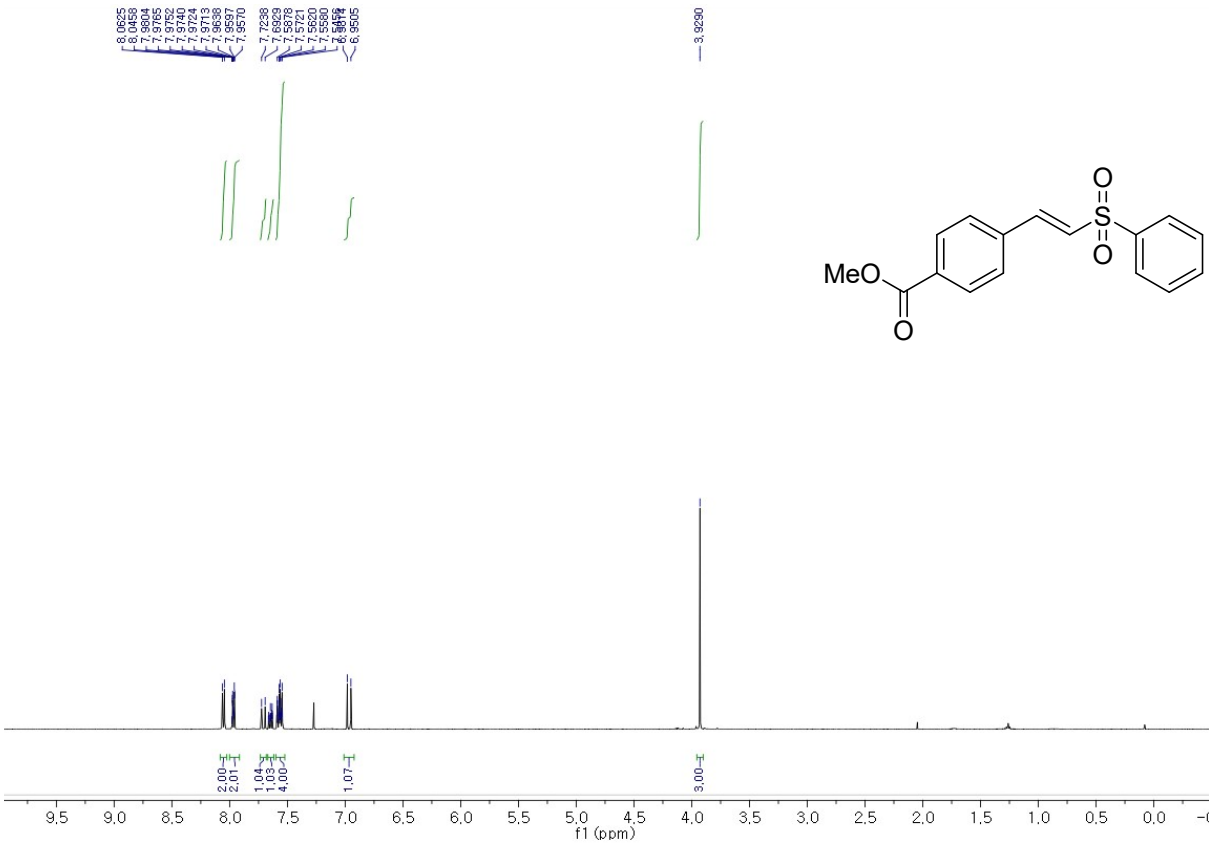
3na

^{13}C NMR


197.10
140.74
140.19
138.67
136.56
133.67
129.84
129.45
129.34
128.69
127.80
26.71
Me
O
O=S=O
f1 (ppm)

3na

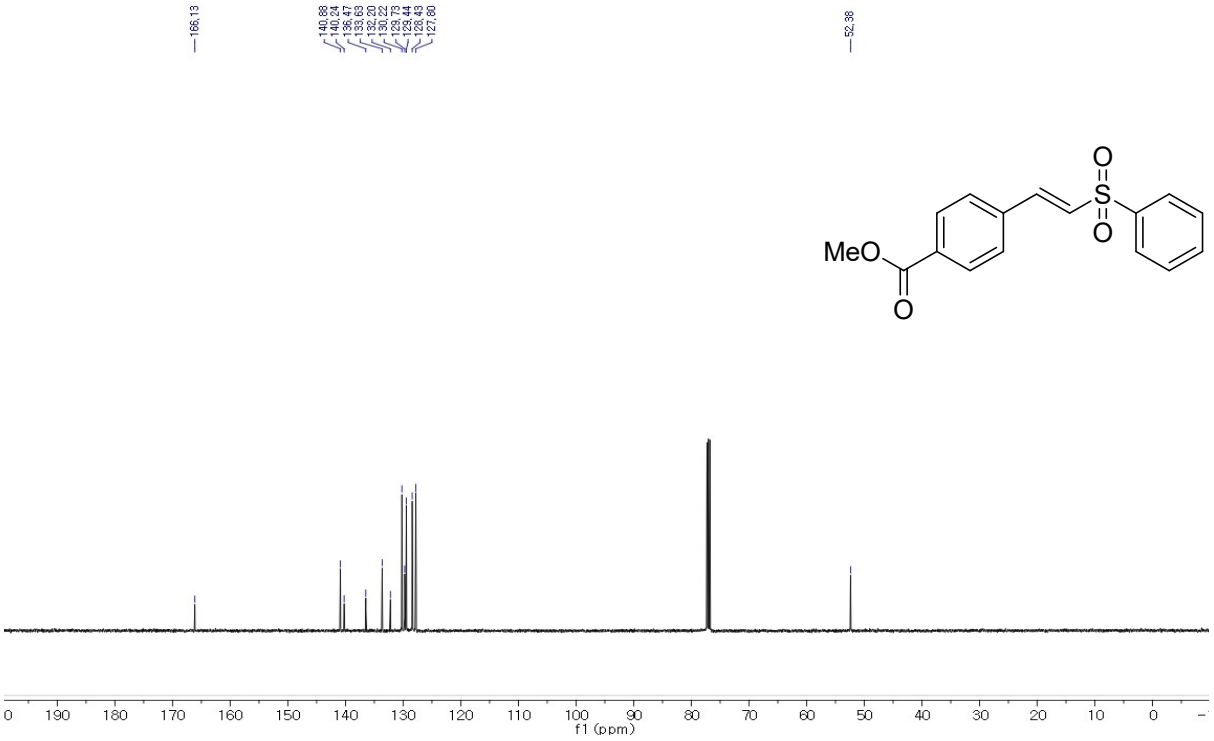
^{1}H NMR



3oa

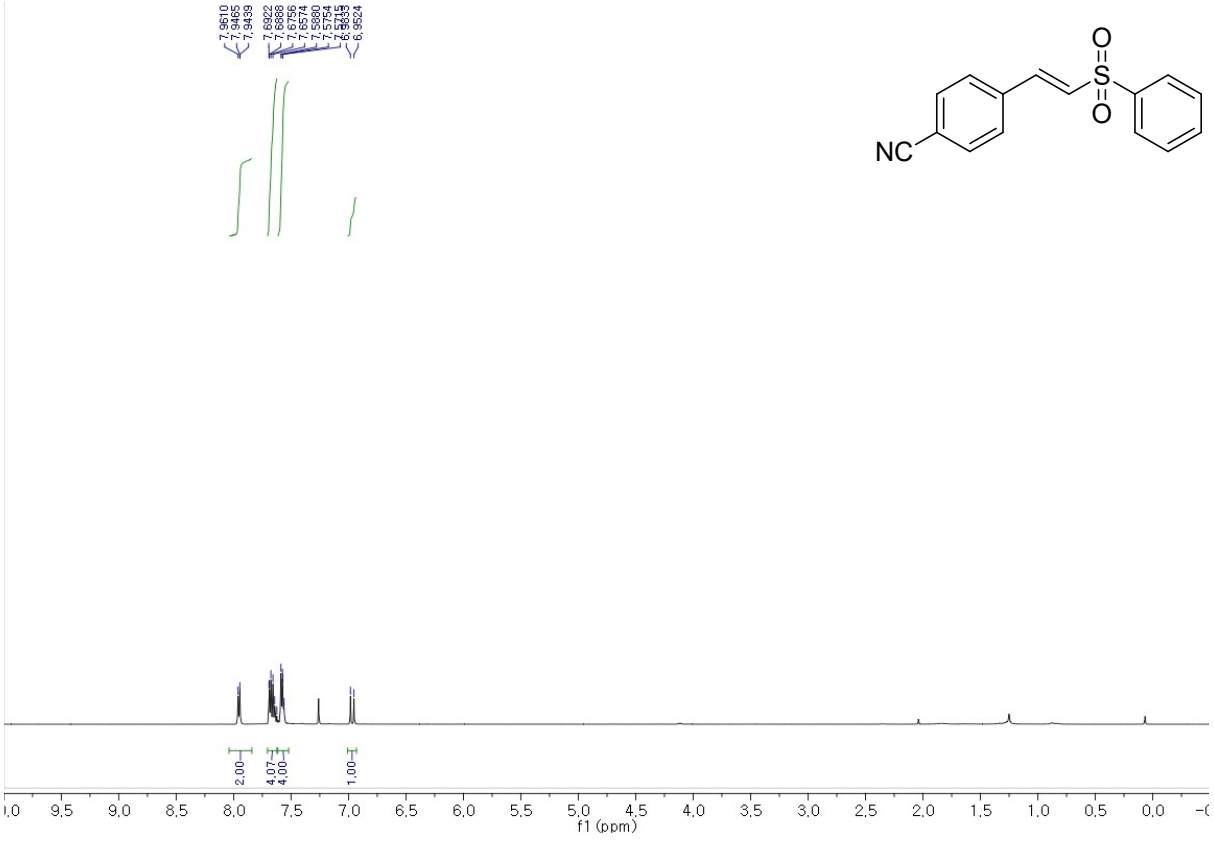
^{13}C NMR

3oa



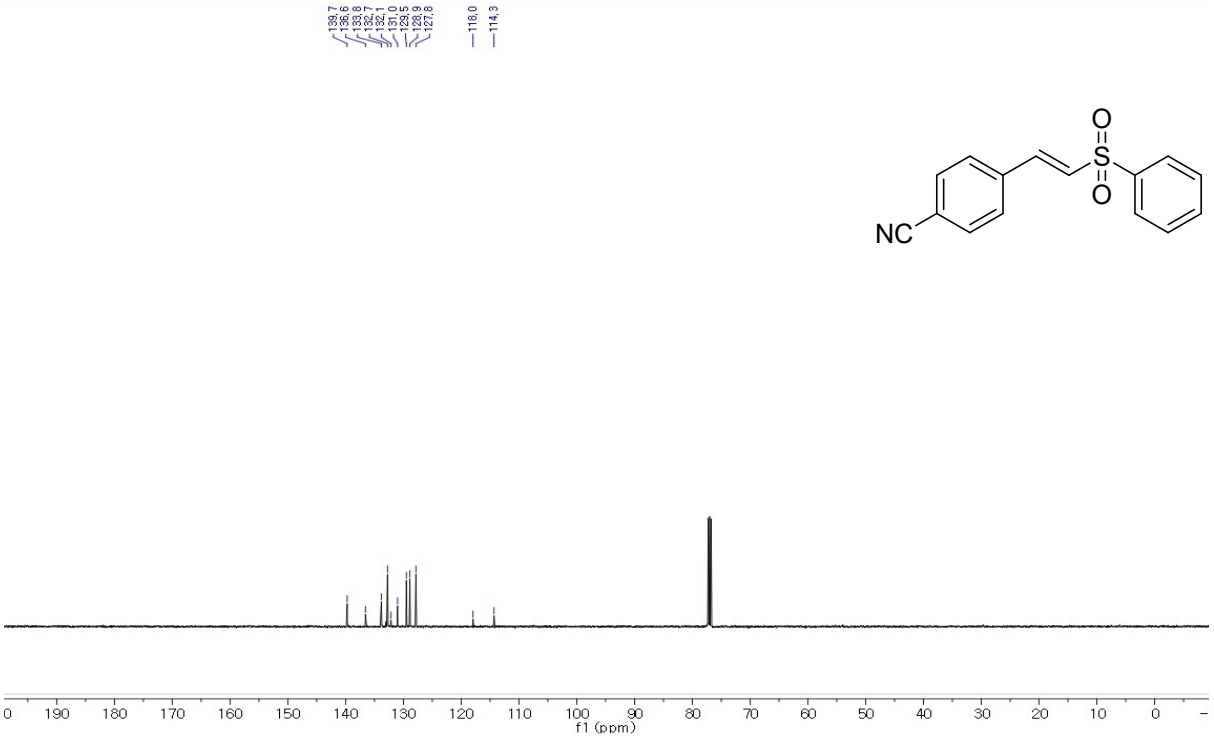
^{1}H NMR

3pa



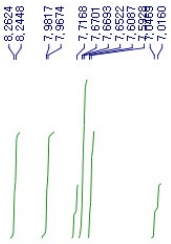
^{13}C NMR

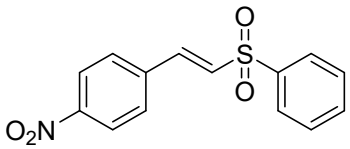
3pa

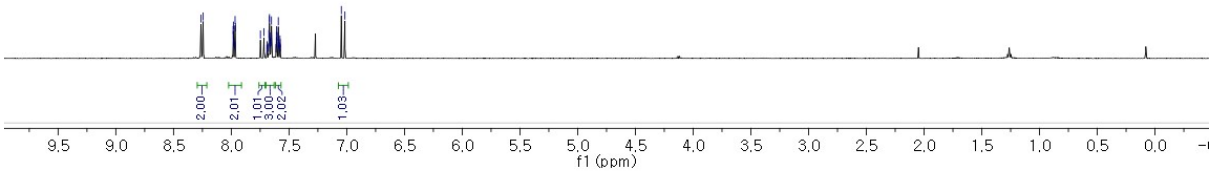


^{1}H NMR

3qa

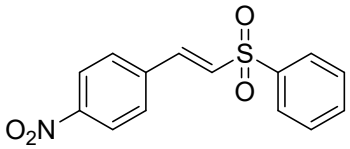


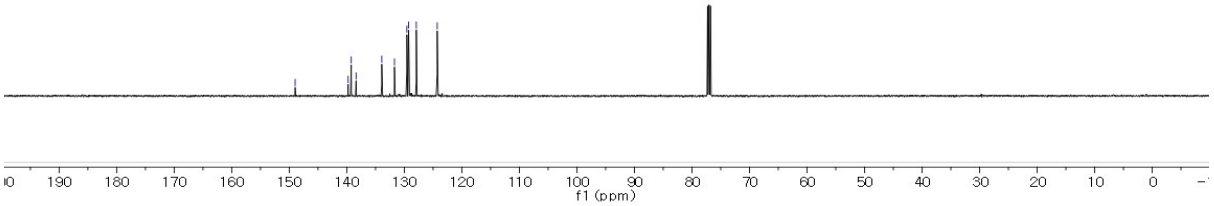




^{13}C NMR

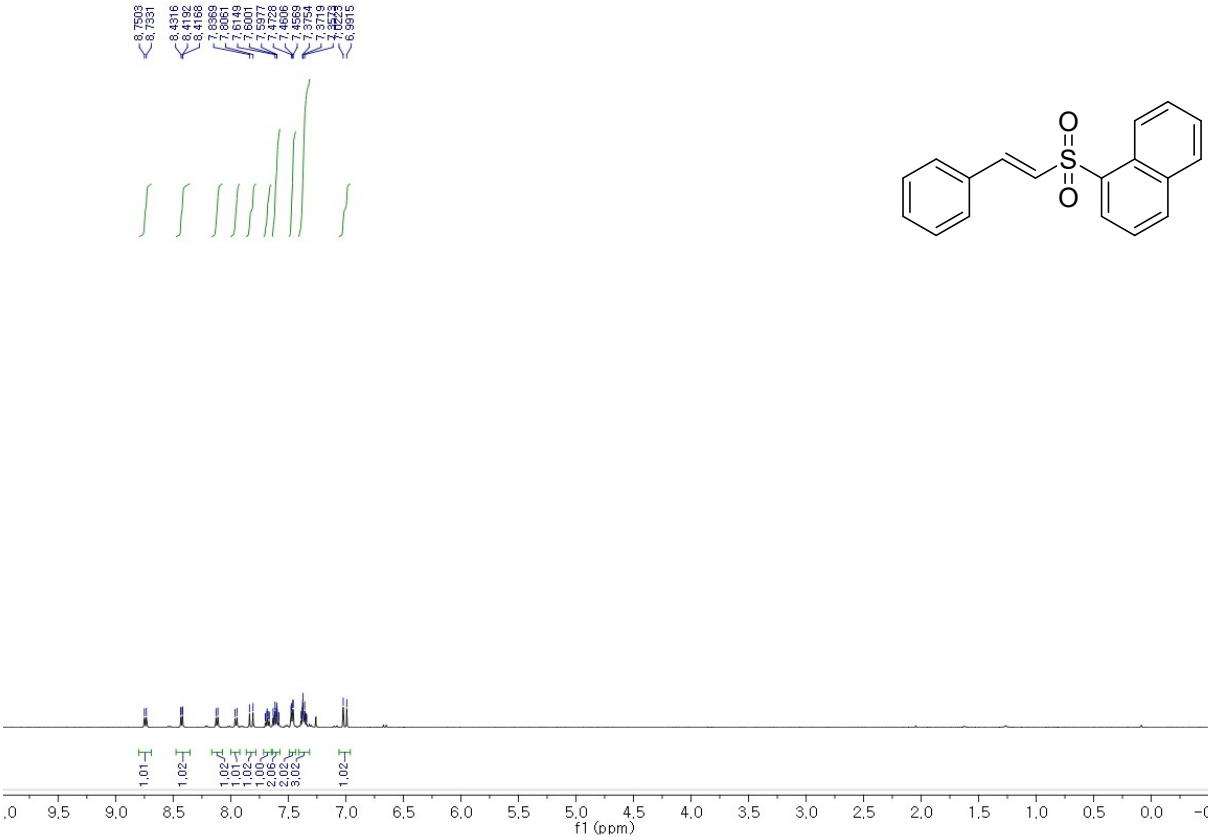
3qa





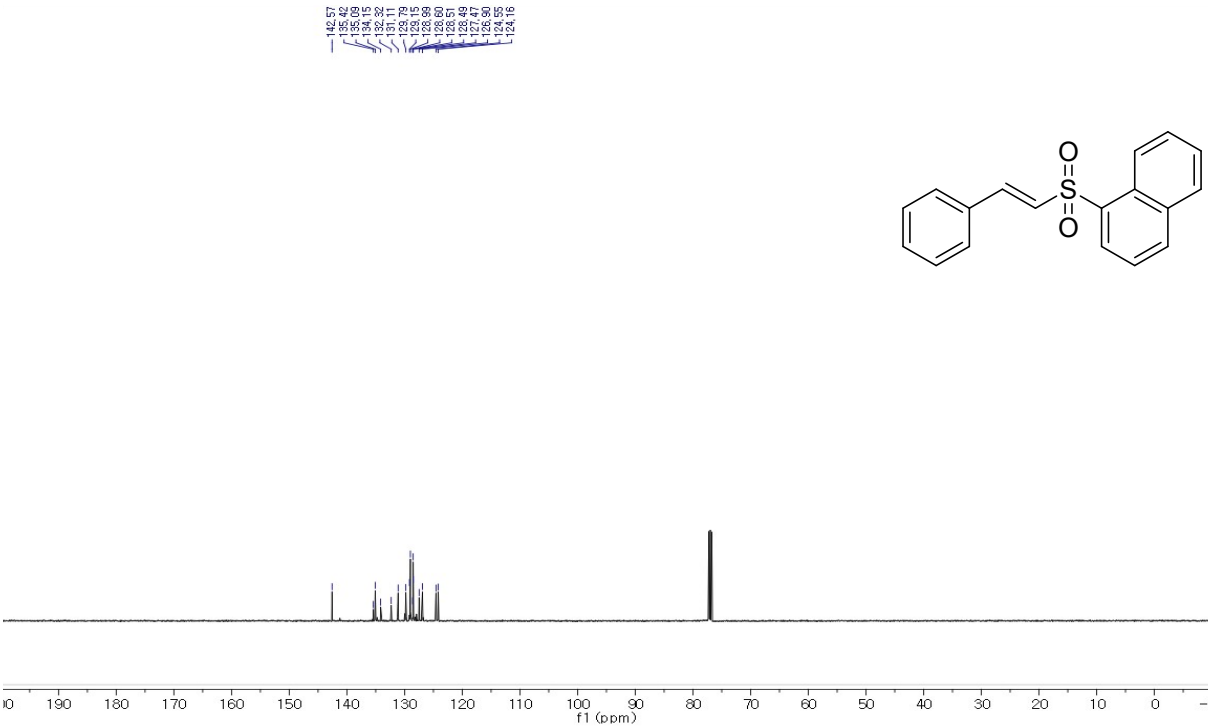
^{1}H NMR

3ab



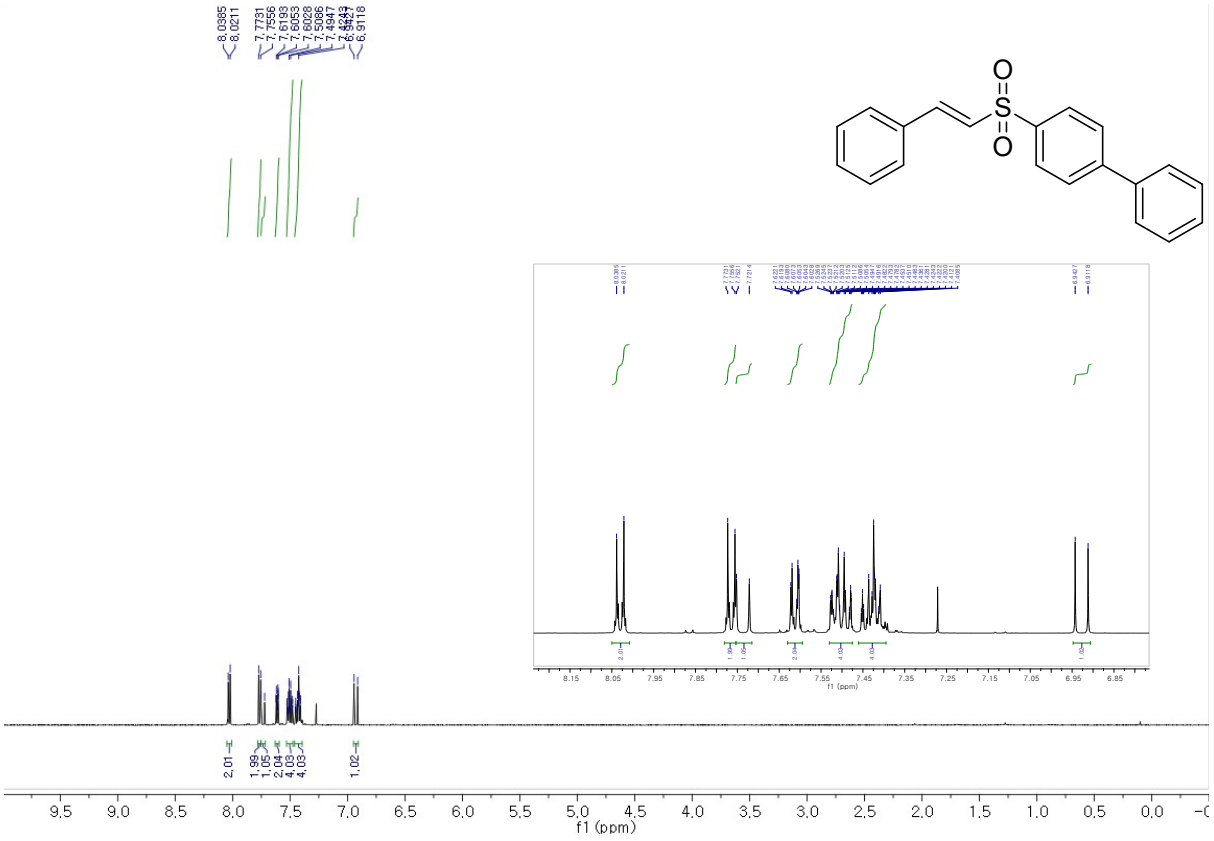
^{13}C NMR

3ab



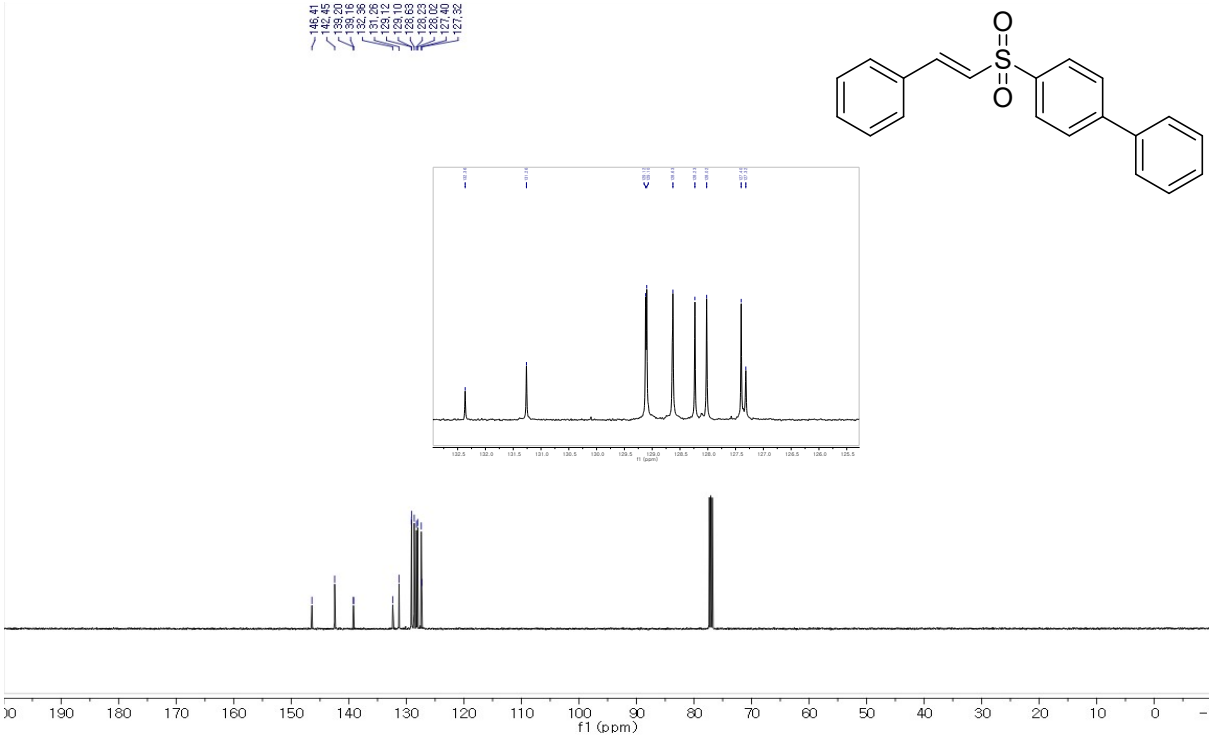
^{1}H NMR

3ac

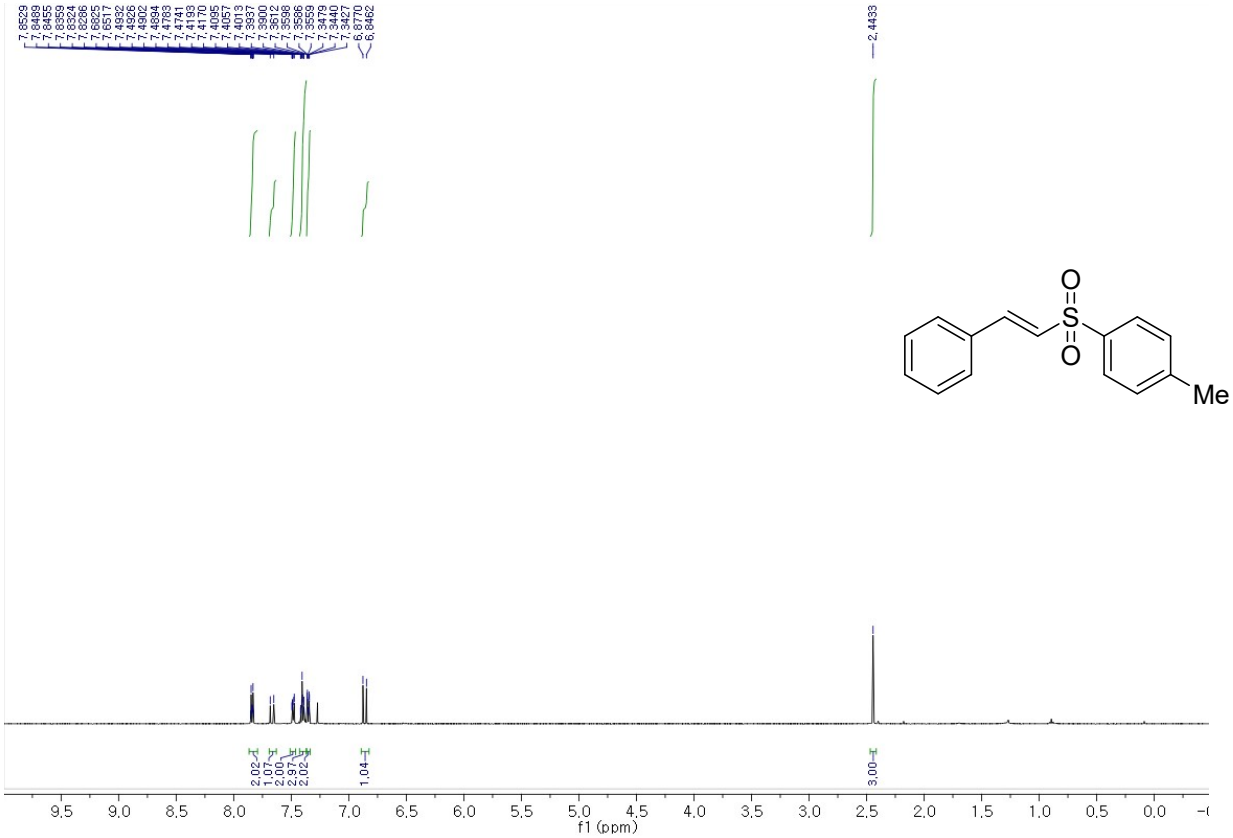


^{13}C NMR

3ac



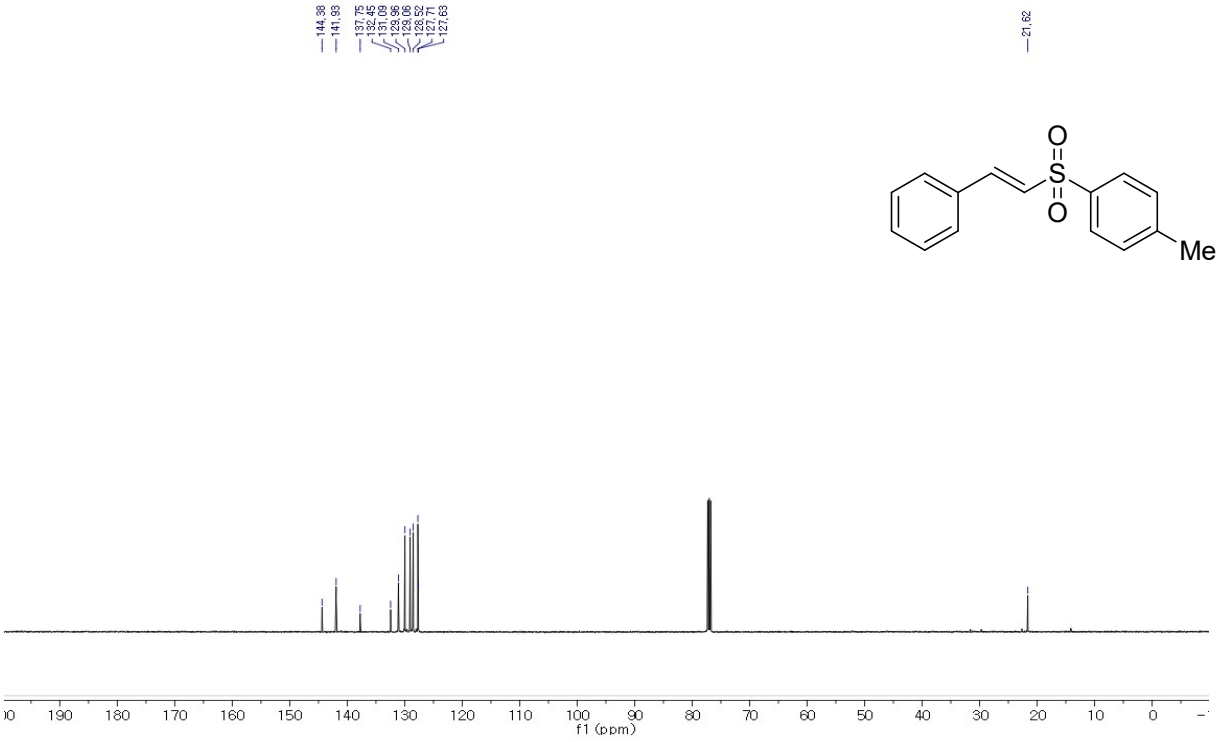
^{1}H NMR



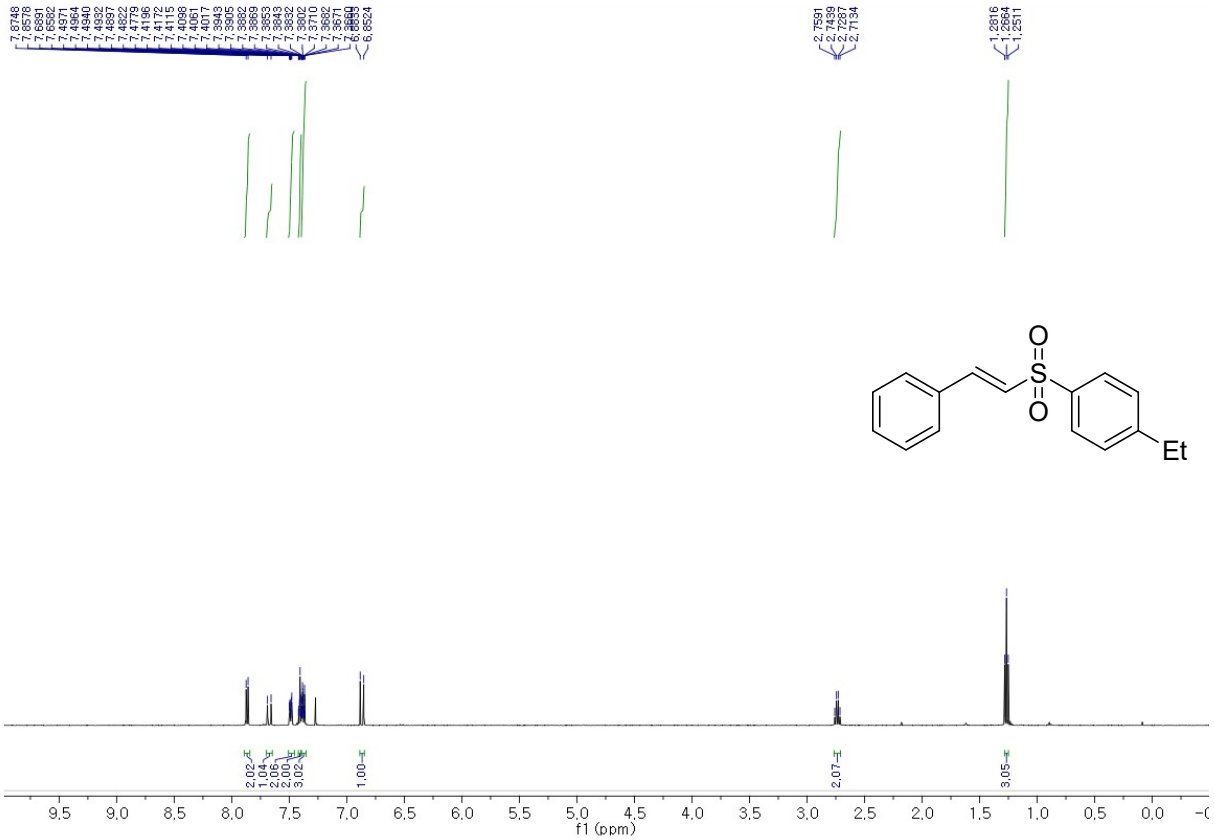
3ad

^{13}C NMR

3ad



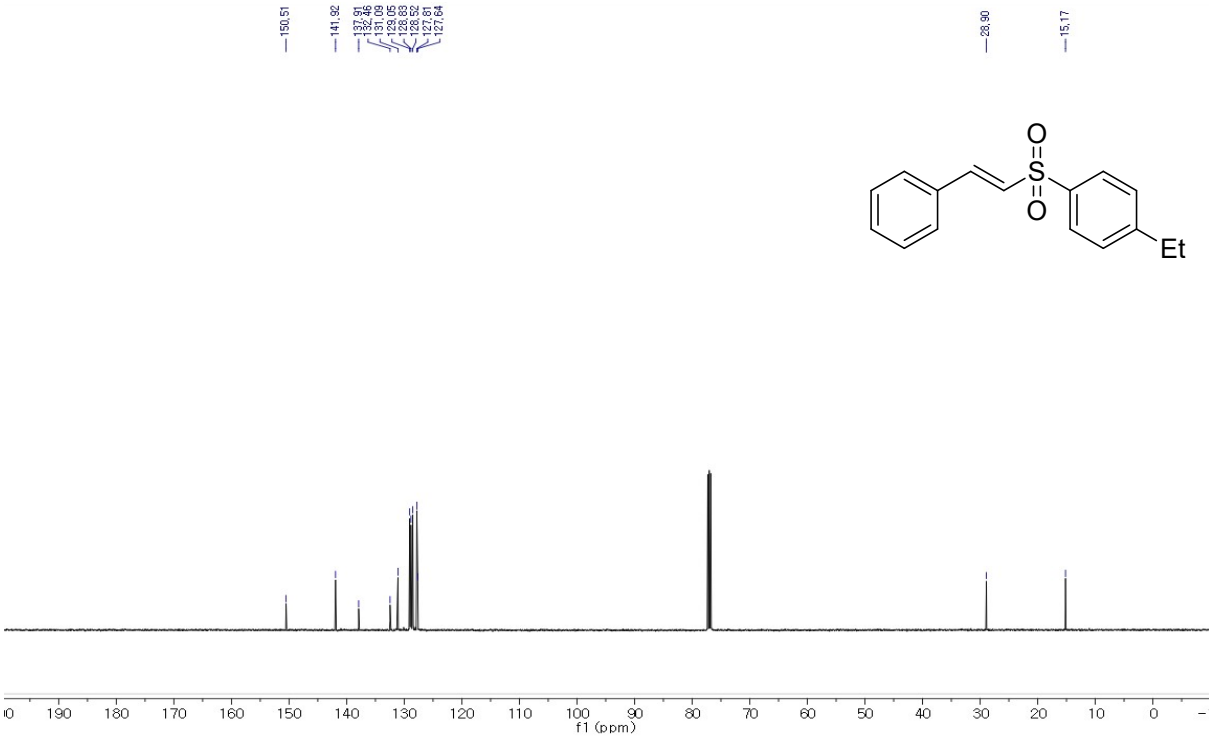
^{1}H NMR



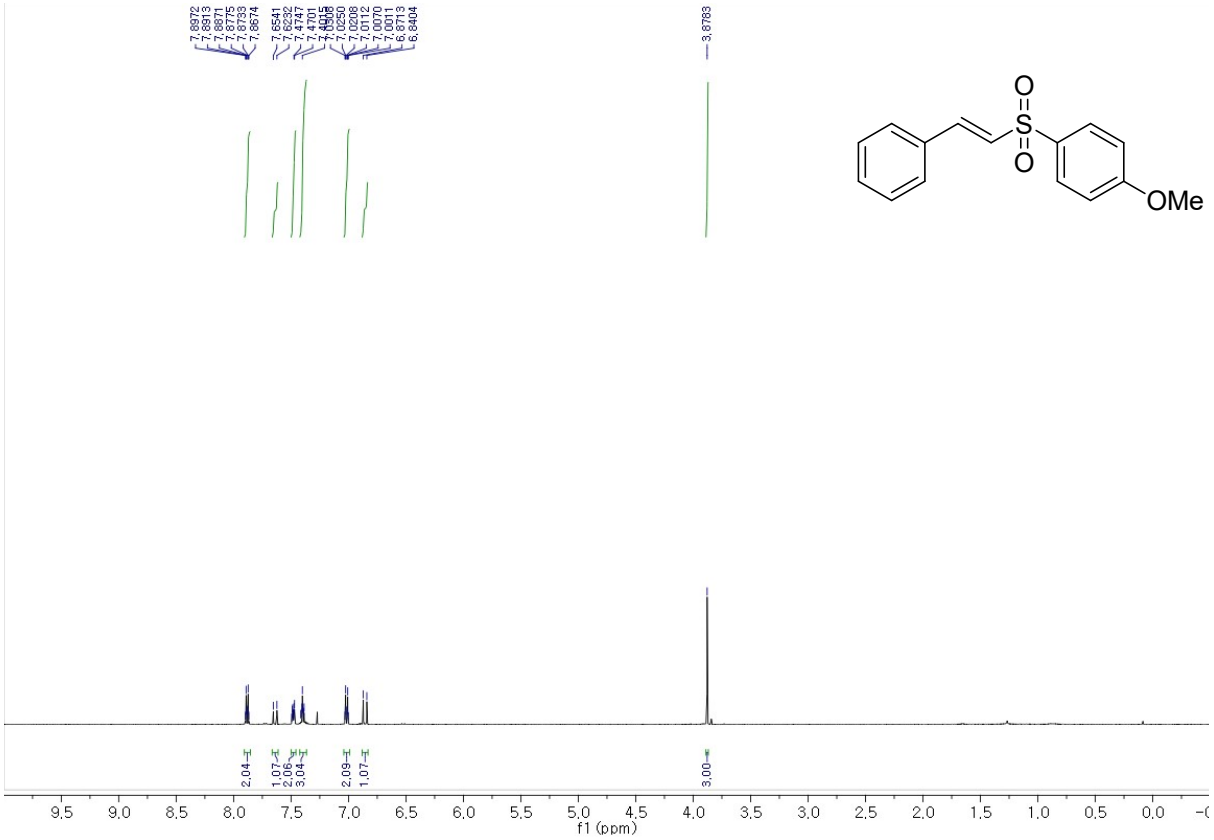
3ae

^{13}C NMR

3ae



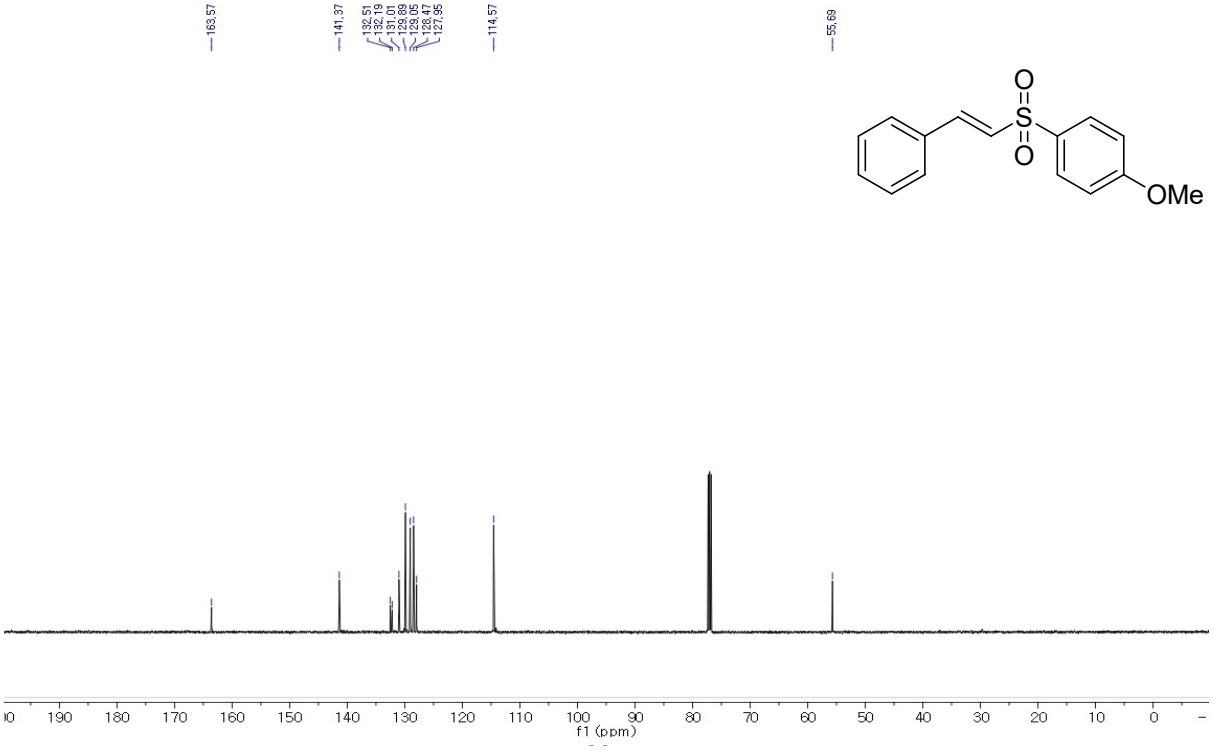
^{1}H NMR



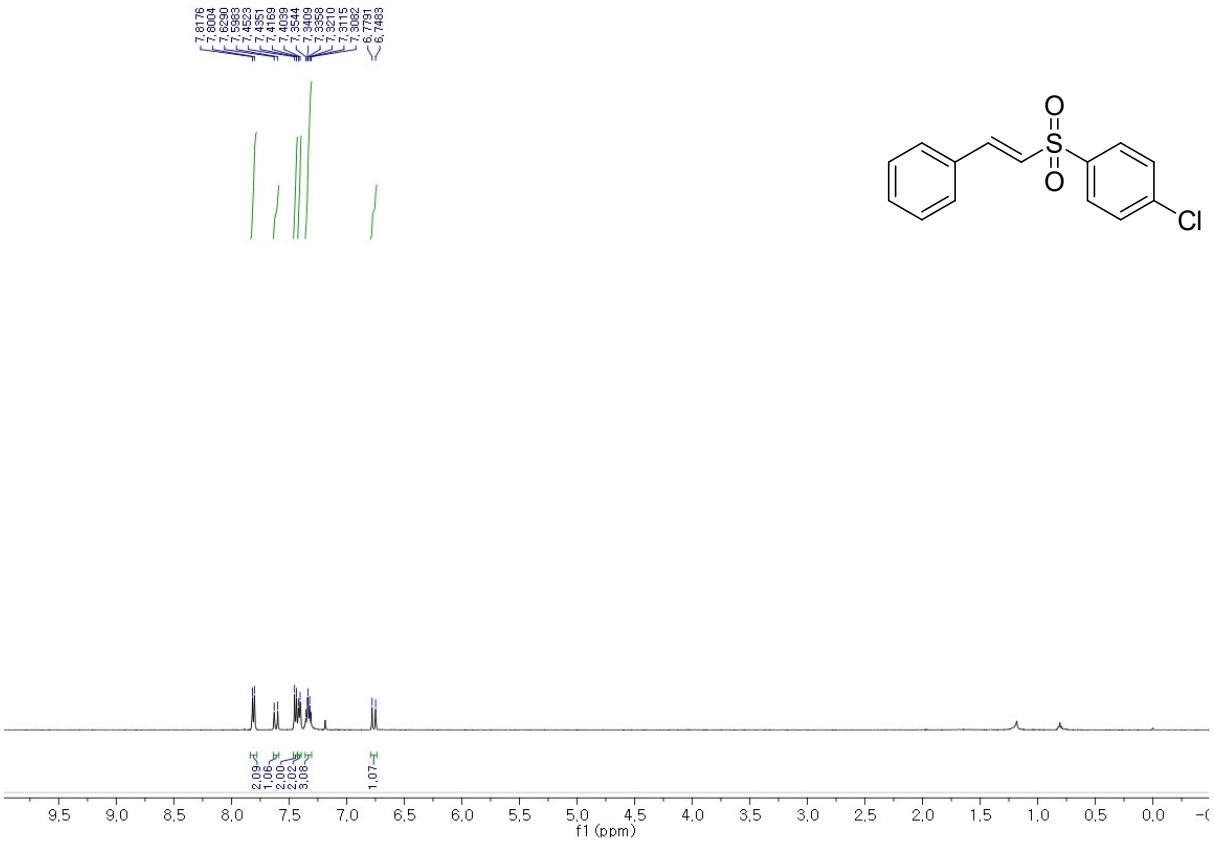
3af

^{13}C NMR

3af



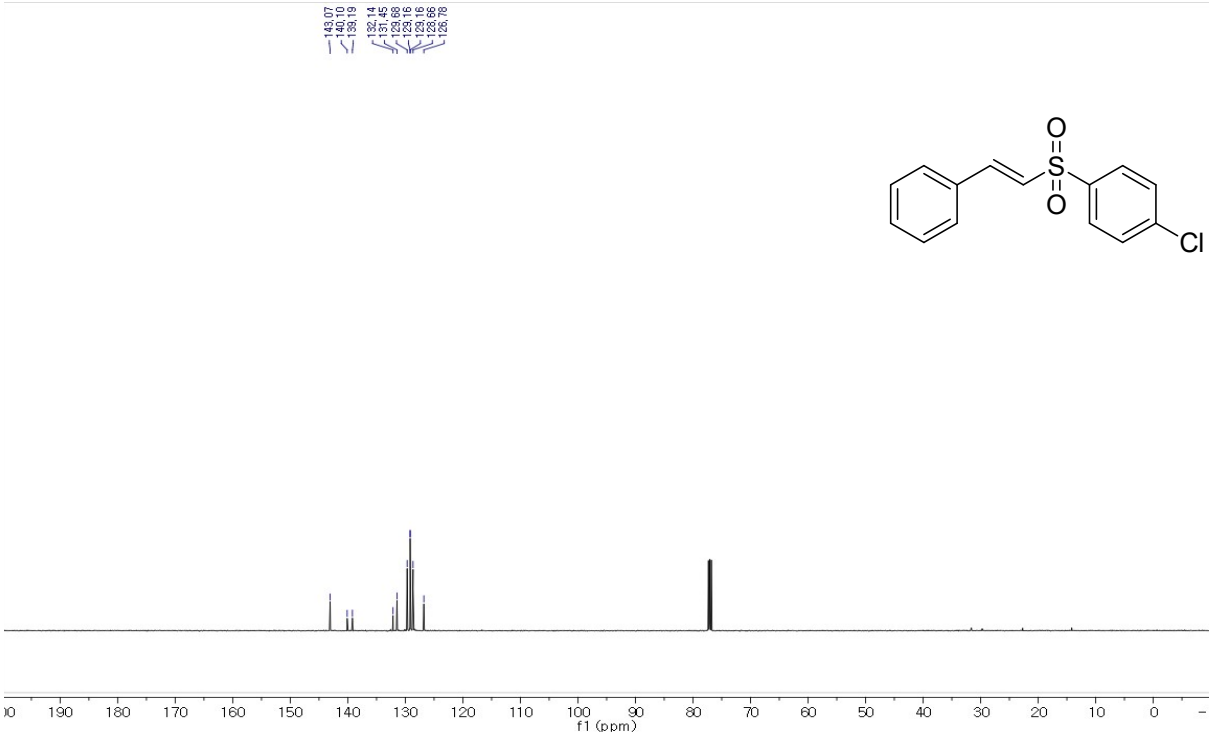
^{1}H NMR



3ag

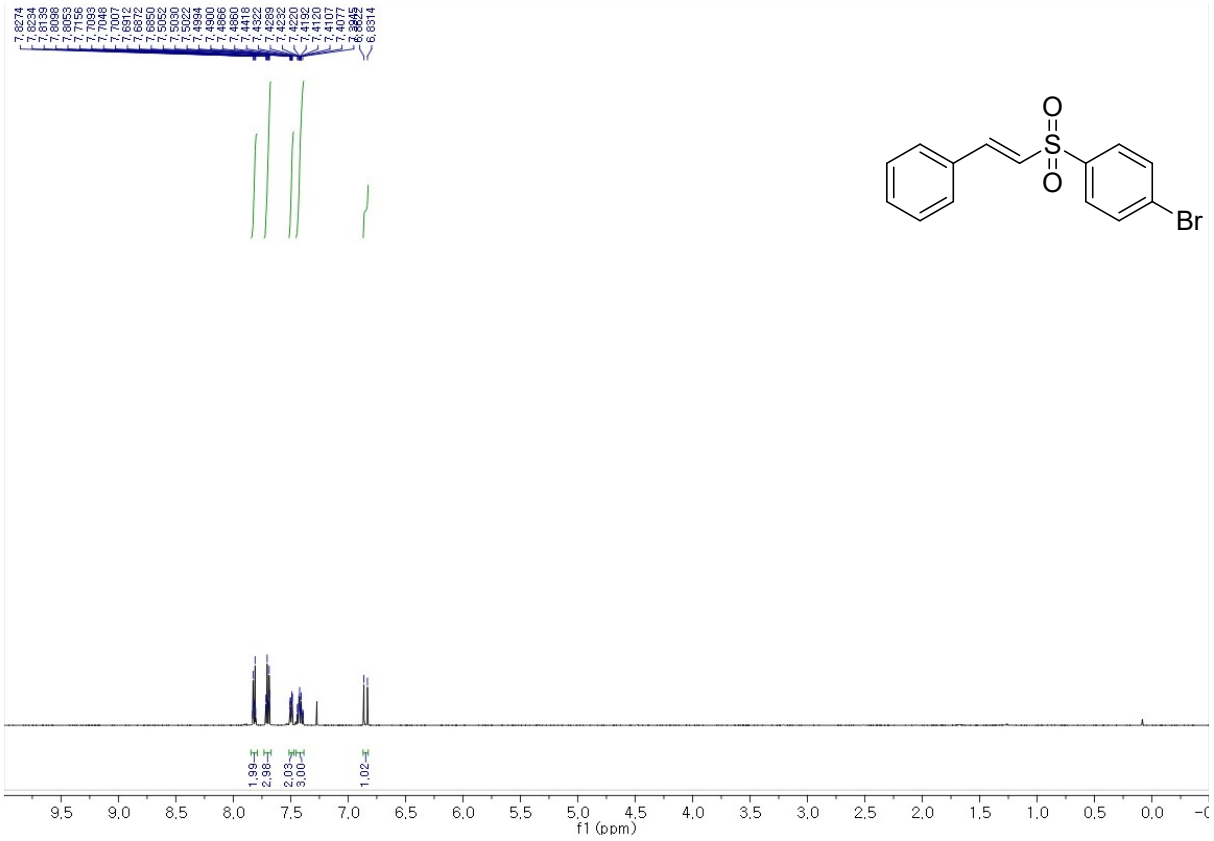
^{13}C NMR

3ag



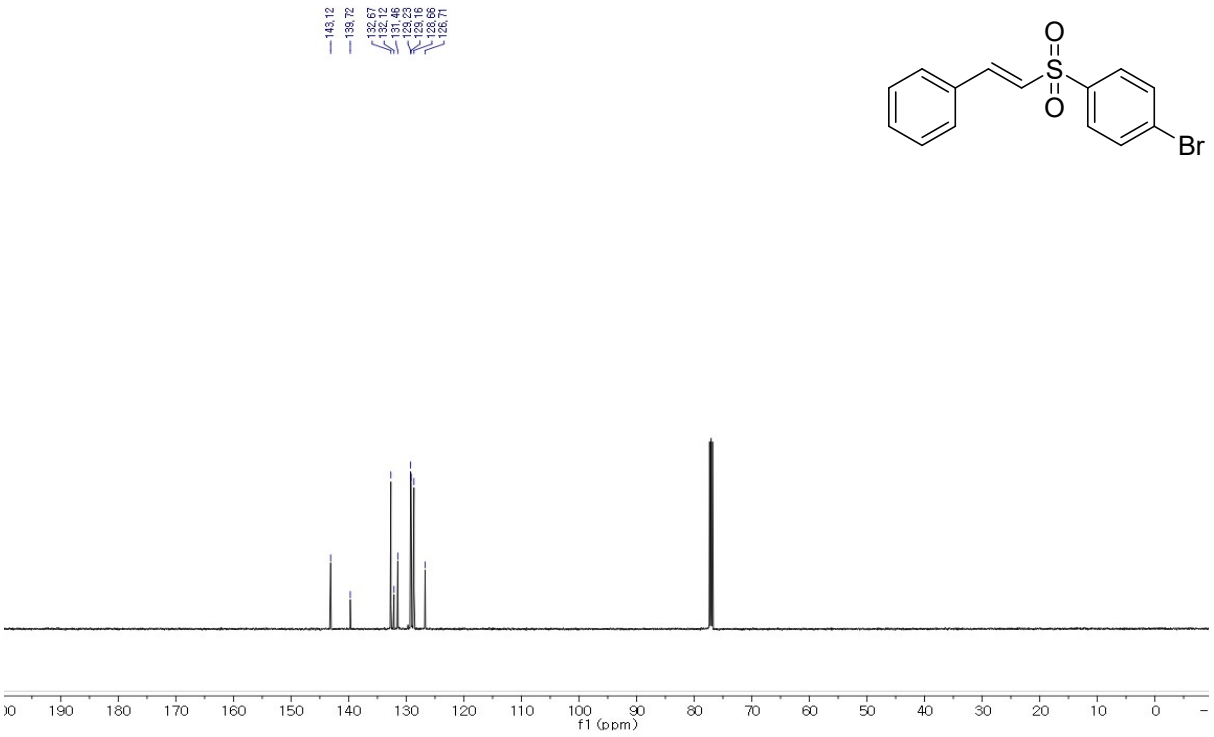
^{1}H NMR

3ah



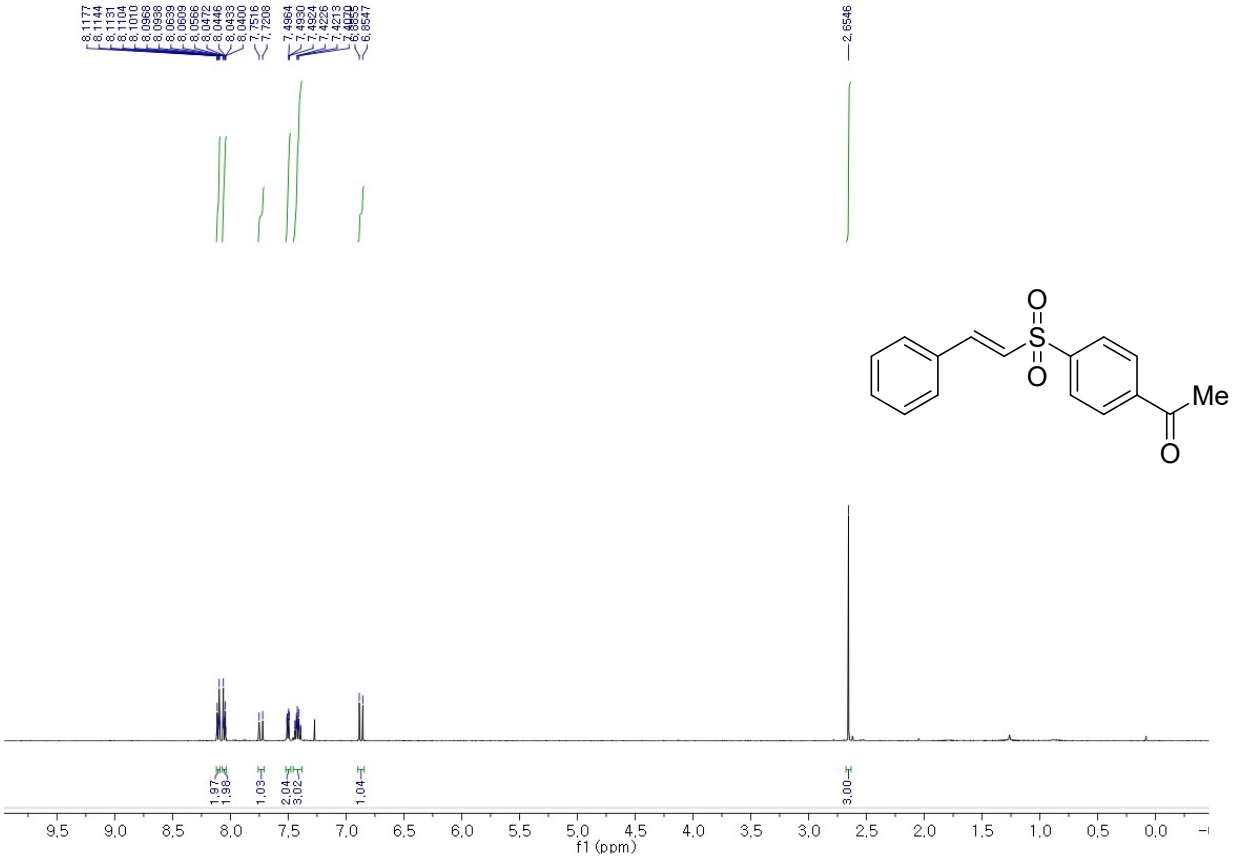
^{13}C NMR

3ah



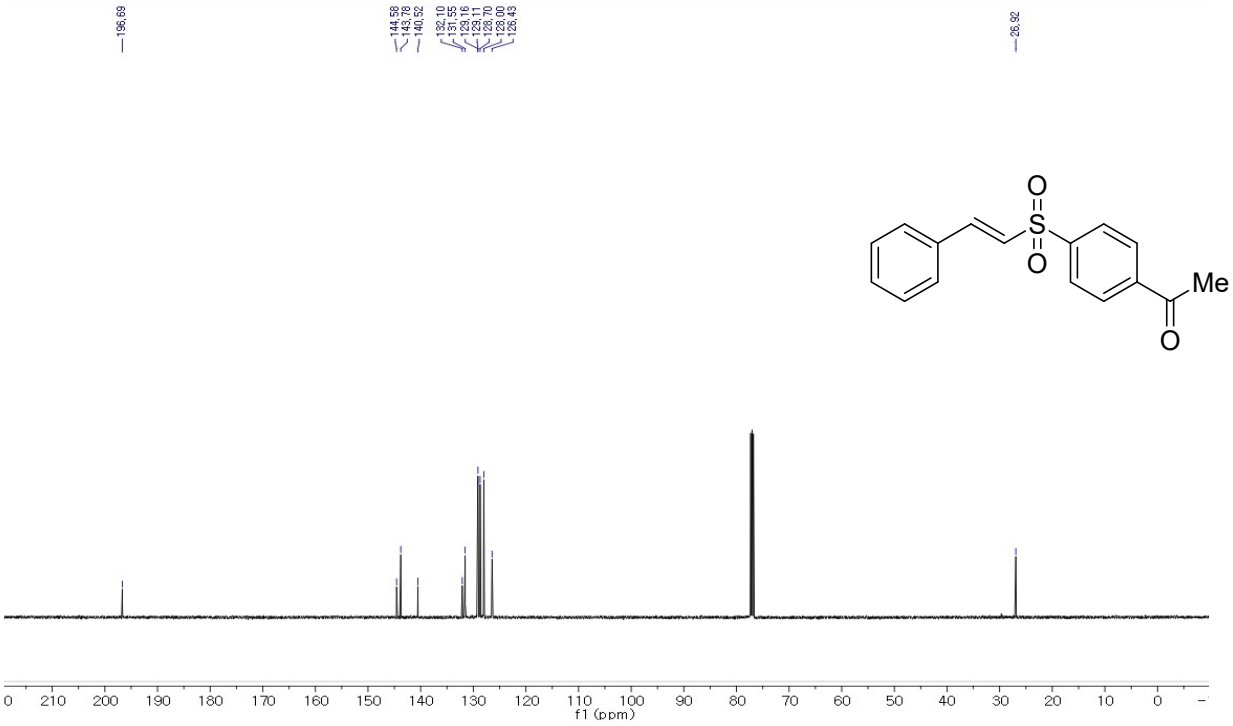
^{1}H NMR

3ai

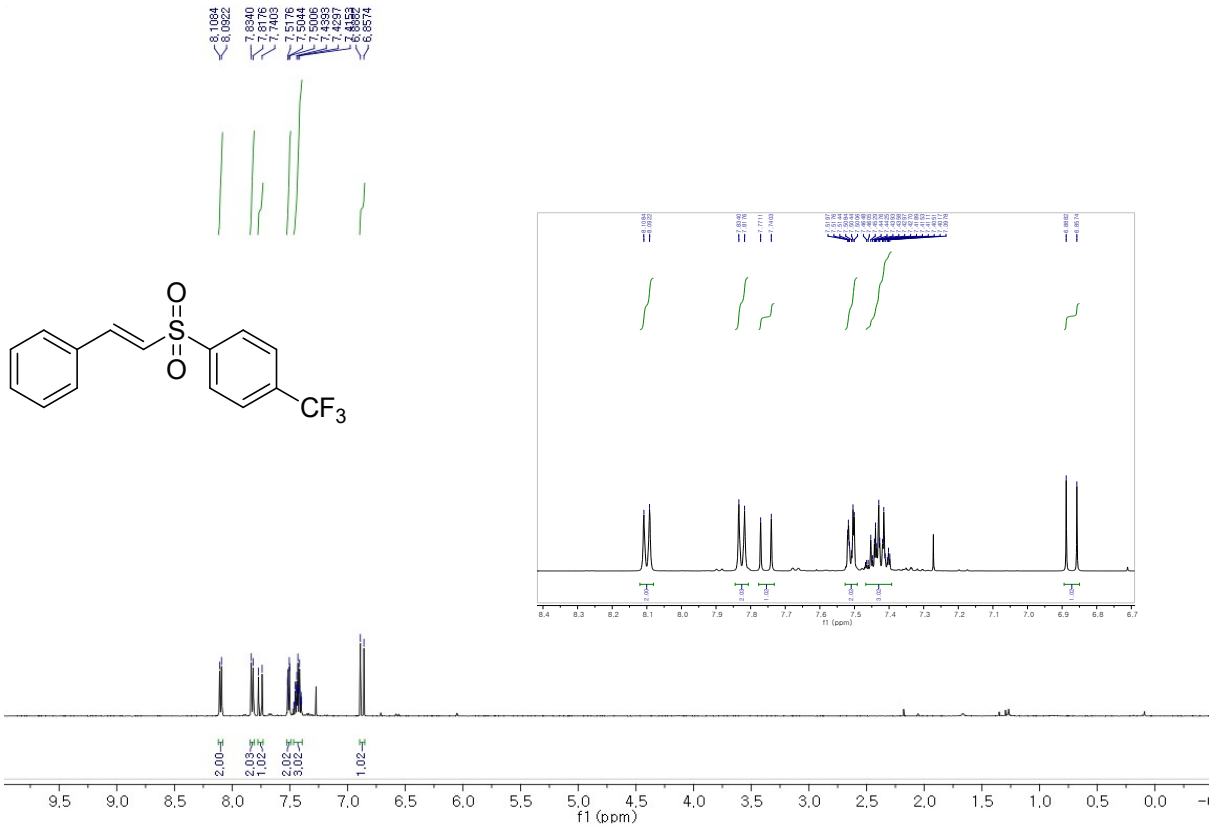


^{13}C NMR

3ai



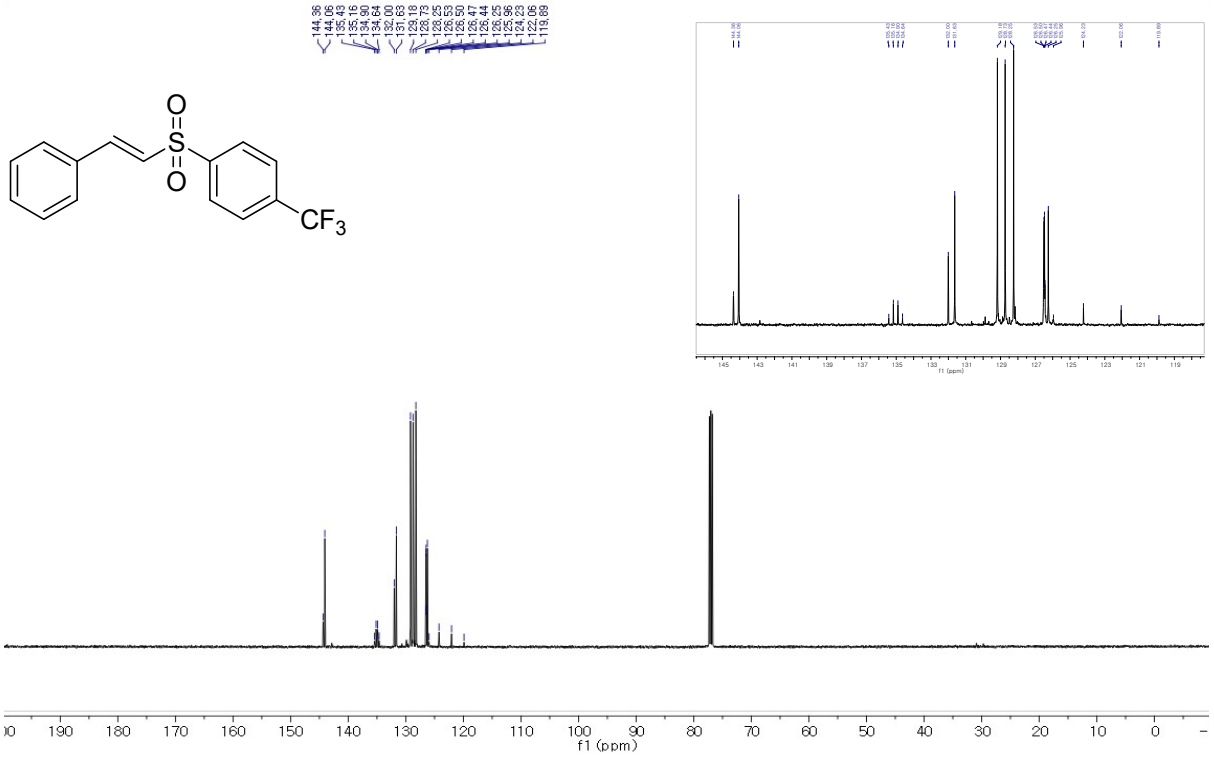
^{1}H NMR



3aj

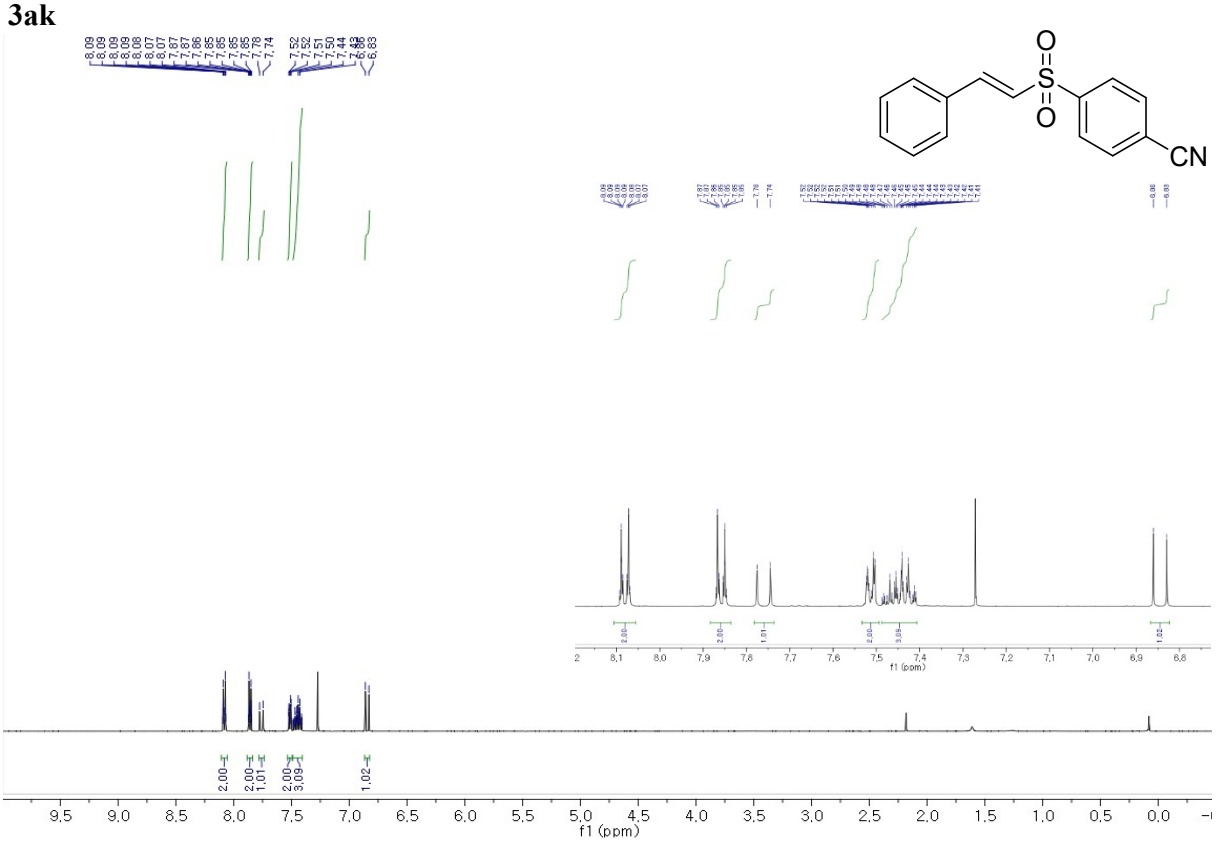
^{13}C NMR

3aj



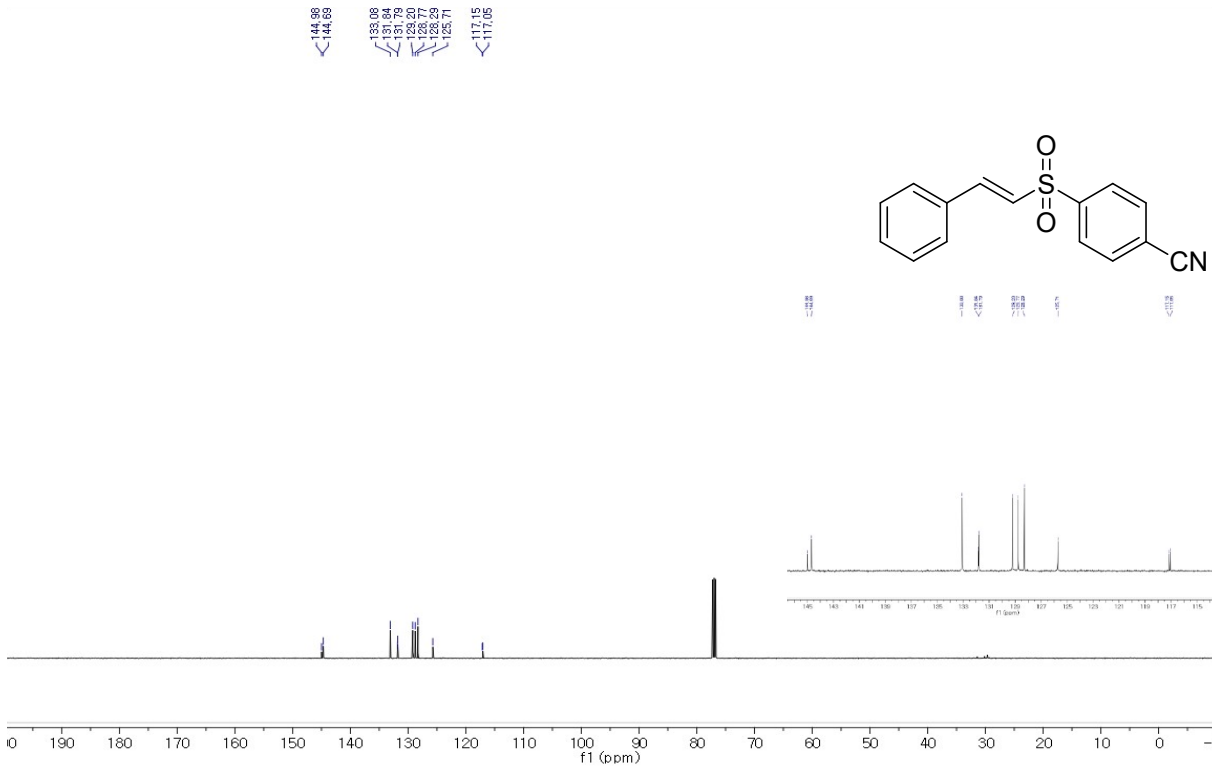
^{1}H NMR

3ak



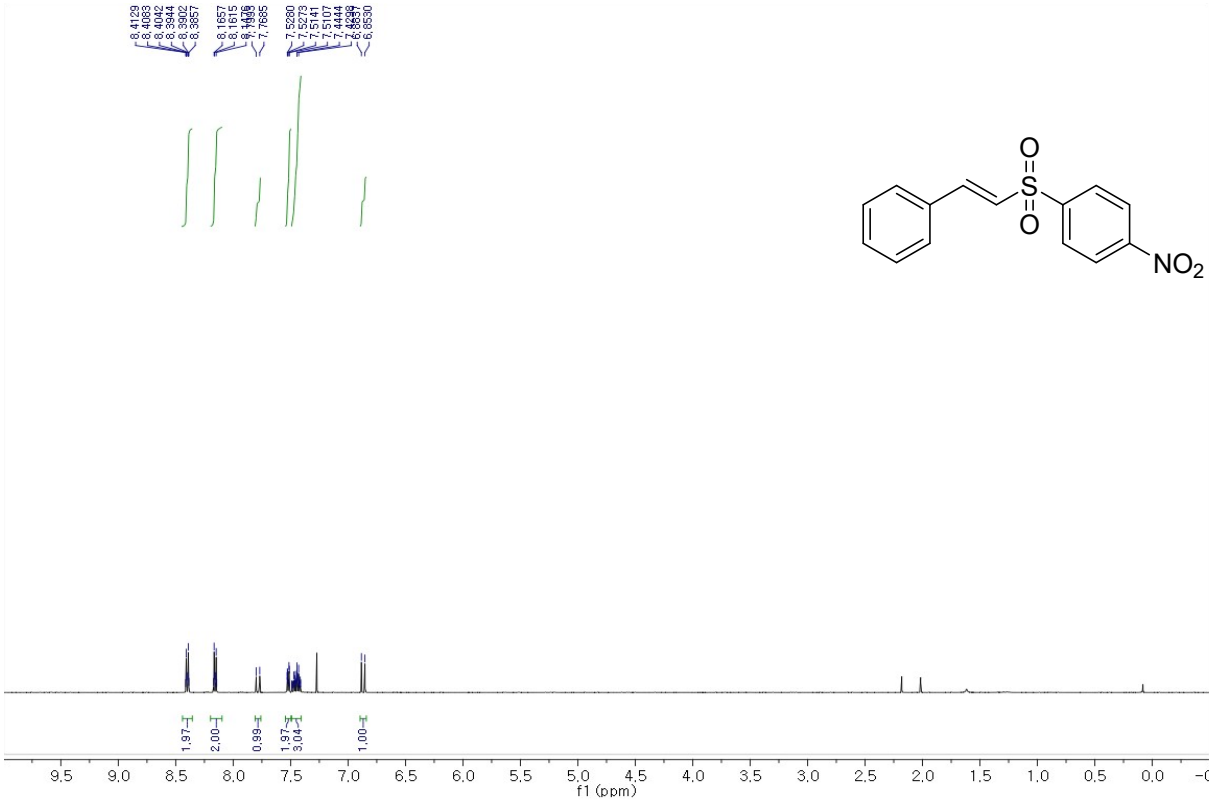
^{13}C NMR

3ak



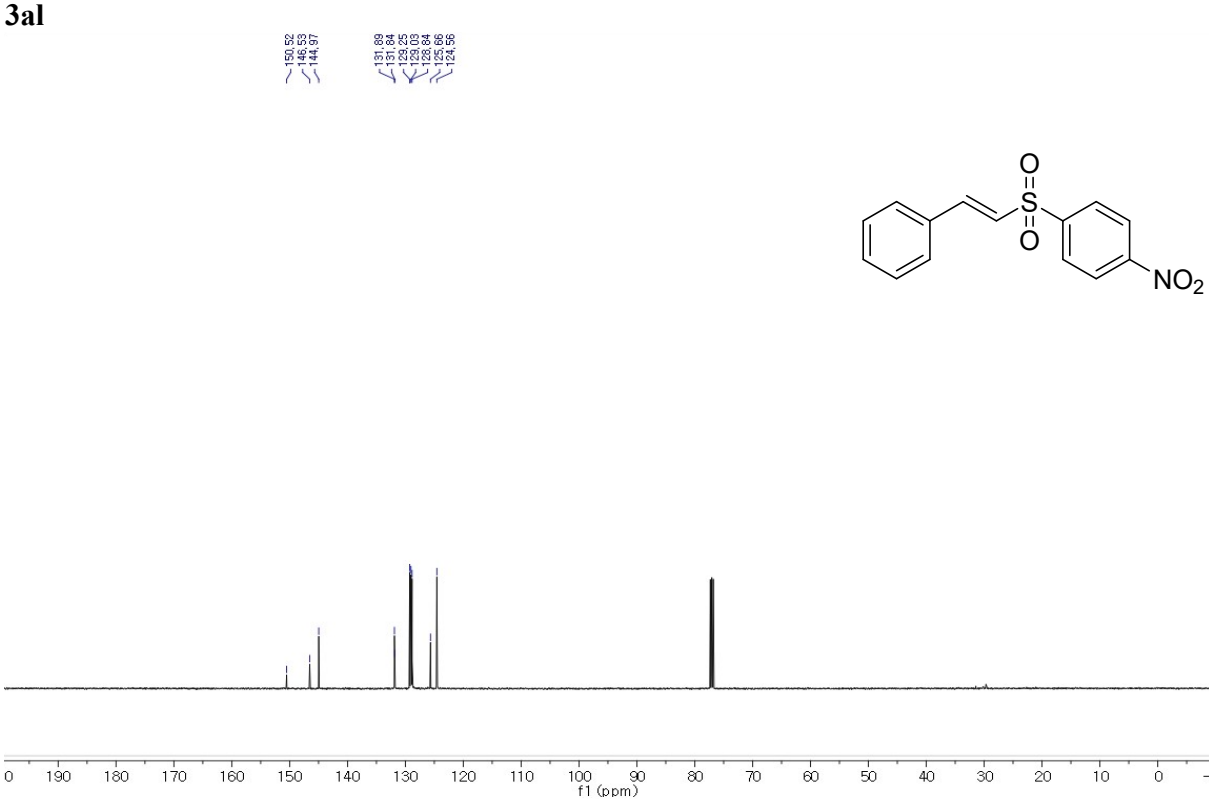
^{1}H NMR

3al



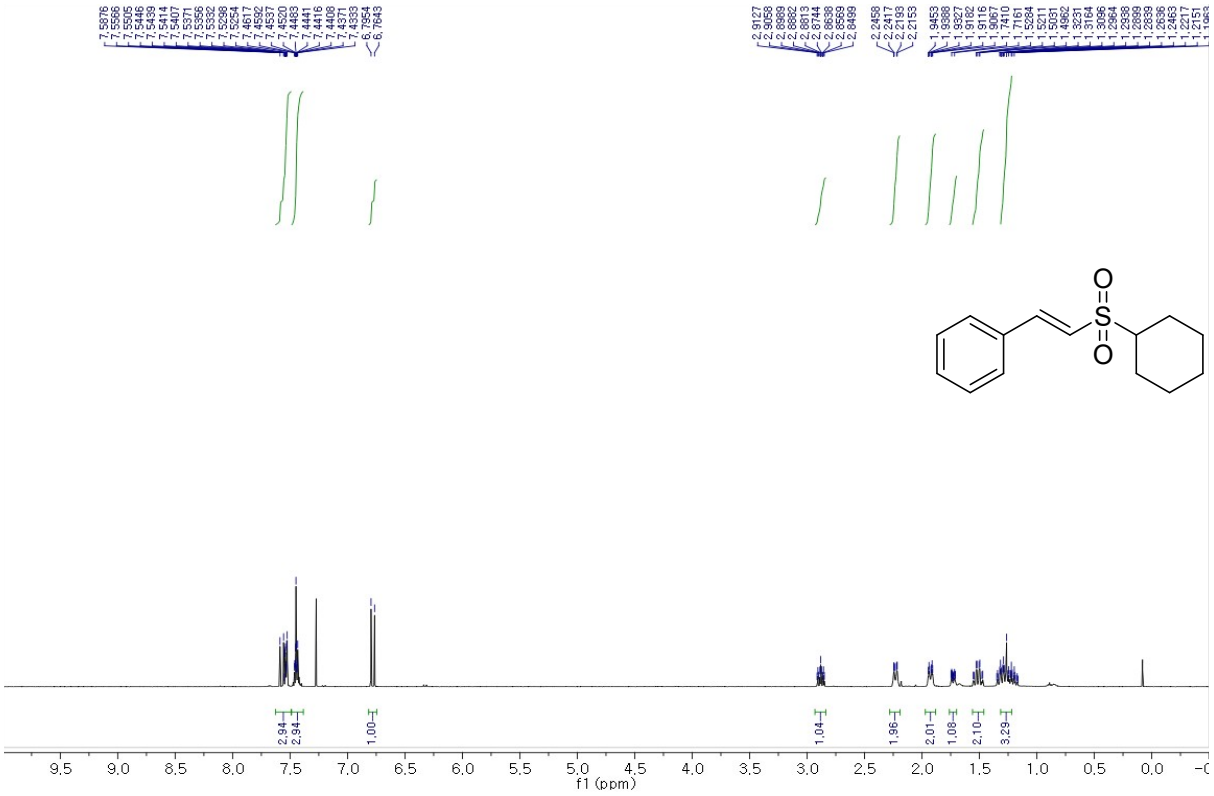
^{13}C NMR

3al



^{1}H NMR

3ao



^{13}C NMR

3ao