Supporting Information

I_2-mediated nucleophilic substitution of alcohols with sulfoximines

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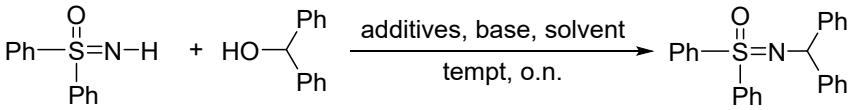
1. General Information

All commercially available reagents and solvent were obtained from commercial providers and used without further purification. Flasks and tubes were dried in an oven prior to use. Unless otherwise stated, all the anhydrous solvents and reagents were obtained from commercial available sources without further purification. Thin-layer chromatography (TLC) was conducted using glass plates pre-coated silica gel and detected with a fluorescent indicator (254 nm). Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H, $^{19}F\{^{1}H\}$, and ^{13}C NMR spectra were recorded on Bruker Avance-400 (400 MHz) spectrometer 400 MHz for ^{1}H, 376 MHz for $^{19}F\{^{1}H\}$, and 100 MHz for ^{13}C. Chemical shifts (δ) were expressed in ppm downfield to TMS at δ = 0 ppm and coupling constants (*J*) were expressed in Hz. $^{19}F\{^{1}H\}$ spectra were referenced externally to $CFCl_3$ (0.00 ppm). Sulfoximines[1] were prepared using literature procedures.

2. Experimental Procedure

2.1 Typical Procedure I: Reaction of diphenyl sulfoximine (1a) with benzhydryl alcohol (2a)

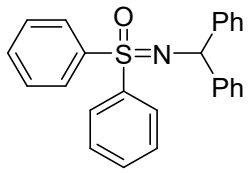


1a **2a** **3a**

In an oven dried 25 mL Schlenk tube charged with **1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 equiv), I_2 (2 equiv), Et_3SiH (2.0 equiv), base (2.0 equiv.), and DCE (0.5 mL). The reaction mixture was stirred at 80 ºC overnight under air. After removing the volatiles, the crude residue was eluted using petroleum ether/ethyl acetate (PE/EA) by column chromatography over silica gel (300-400 mesh), affording the analytically pure product **3a** in 84% yield.

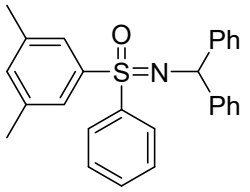
3. Characterization Data for the Products

(Benzhydrylimino)diphenyl-l6-sulfanone (3a)



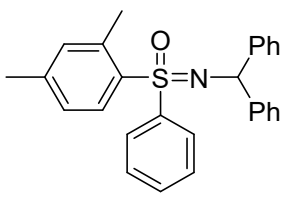
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a yellow solid in 84% yield (0.168 mmol, 64.4 mg, mp 100.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.91 (m, 4H), 7.46–7.38 (m, 10H), 7.26–7.15 (m, 6H) 5.41(s, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.89, 141.06, 132.38, 129.03, 128.77, 128.18, 127.50, 126.50, 61.77. This compound is known.[2]

(Benzhydrylimino)(3,5-dimethylphenyl)(phenyl)-l6-sulfanone (3b)



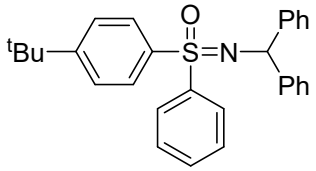
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to a yellow solid in 84% yield (0.168 mmol, 69.1 mg, mp 128.2 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 7.51−7.40 (m, 9H), 7.31−7.27 (m, 4H), 7.22-7.19 (m, 2H), 7.11(s, 1H), 5.44 (s, 1H), 2.29 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.99, 145.88, 141.33, 140.51, 138.93, 134.14, 132.21, 128.92, 128.65, 128.09, 127.59, 127.51, 126.42, 126.38, 61.65, 21.22. HRMS m/z: Calcd for $C_{27}H_{25}NOSNa$ $[M+Na]^+$: 434.1555, Found: 434.1557.

(Benzhydrylimino)(2,4-dimethylphenyl)(phenyl)-l6-sulfanone (3c)



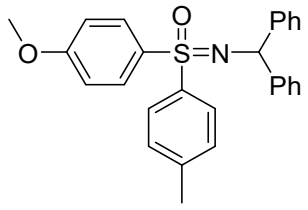
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a yellow solid in 75% yield (0.150 mmol, 61.7 mg, mp 125.3 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H),7.39−7.38 (m, 1H), 7.34−7.25 (m, 6H), 7.18−7.12 (m, 4H), 7.08−7.04 (m, 3H), 6.82(s, 1H), 5.28 (s, 1H), 2.26 (s, 3H), 2.05 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 146.08, 145.76, 143.32, 141.08, 138.31, 135.31, 133.42, 132.02, 131.12, 128.66, 128.63, 128.03, 127.49, 127.43, 126.90, 126.33, 61.63, 21.24, 20.06. HRMS m/z: Calcd for $C_{27}H_{25}NOSNa$ $[M+Na]^+$: 434.1555, Found: 434.1558.

(Benzhydrylimino)(4-(tert-butyl)phenyl)(phenyl)-l6-sulfanone (3d)



The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 68% yield (0.136 mmol, 59.8 mg, mp 106.7 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.51−7.42 (m, 9H), 7.31−7.27 (m, 4H), 7.22−7.19 (m, 2H), 5.46 (s, 1H), 1.33 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 156.04, 145.97, 141.34, 137.95, 132.17, 128.92, 128.73, 128.54, 128.50, 128.10, 128.07, 127.53, 127.51, 126.39, 126.37, 126.01, 61.65, 35.04, 31.10. HRMS m/z: Calcd for $C_{29}H_{29}NOSNa$ $[M+Na]^+$: 426.1868, Found:426.1869

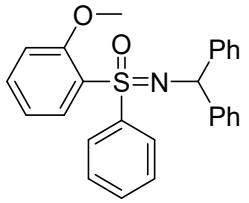
(Benzhydrylimino)(4-methoxyphenyl)(p-tolyl)-l6-sulfanone (3e)



The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a yellow solid in 65% yield (0.130 mmol, 55.6 mg, mp 84.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H),7.32−7.30 (m, 4H), 7.18−7.15 (m, 4H), 7.11−7.06 (m, 4H), 6.77 (d, *J* = 8.0 Hz, 2H),

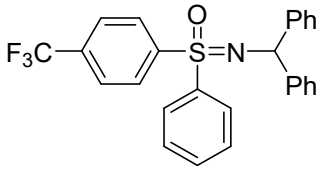
5.30 (s, 1H), 3.69 (s, 3H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.75, 146.13, 146.11, 142.86, 138.57, 132.68, 130.79, 129.65, 128.57, 128.14, 128.13, 127.53, 127.51, 126.40, 126.38, 114.23, 61.80, 55.58, 21.47. HRMS m/z: Calcd for $C_{27}H_{25}NO2SNa$ $[M+Na]^+$: 450.1504, Found:450.1502

(Benzhydrylimino)(2-methoxyphenyl)(phenyl)-l6-sulfanone (3f)



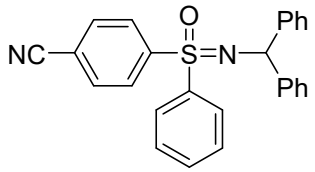
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 52% yield (0.168 mmol, 44.5 mg, mp 92.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.15 (m, 1H), 8.01−7.98 (m, 2H),7.42−7.38 (m, 1H), 7.36−7.24 (m, 6H), 7.22−7.20 (m, 2H), 7.17−7.10 (m, 4H), 7.07−7.02 (m, 2H), 6.56 (d, J = 8.0 Hz, 1H), 5.27 (s, 1H), 3.21 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.80, 146.13, 145.83, 141.05, 134.59, 132.12, 131.96, 129.56, 128.51, 128.12, 128.00, 127.82, 127.61, 127.56, 127.52, 126.58, 126.26, 126.15, 120.29, 111.83, 61.69, 54.79. HRMS m/z: Calcd for $C_{26}H_{23}NO2SNa$ $[M+Na]^+$: 436.1347, Found:436.1347

(Benzhydrylimino)(phenyl)(4-(trifluoromethyl)phenyl)-l6-sulfanone (3g)



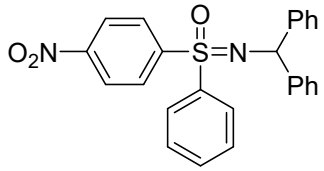
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 99% yield (0.198 mmol, 89.4 mg, mp 123.8 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.85 (m, 4H), 7.52 (d, J = 8.0 Hz, 2H),7.42−7.39 (m, 1H), 7.35−7.31 (m, 4H), 7.27−7.25 (m, 2H), δ 7.19−7.11 (m, 4H), δ 7.08−7.04 (m, 2H), 5.36 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 145.48, 145.34, 145.10 (br), 140.23, 134.40, 134.08, 133.75, 133.42, 132.91, 129.27, 129.20, 128.82, 128.26, 127.47, 127.38, 126.69, 126.66, 126.07, 126.04, 61.64. HRMS m/z: Calcd for $C_{26}H_{20}F_3NOSNa$ $[M+Na]^+$: 474.1115, Found: 474.1113

4-(N-benzhydrylphenylsulfonimidoyl)benzonitrile (3h)



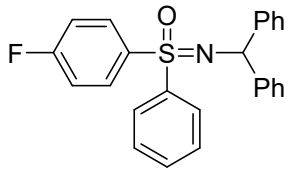
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 94% yield (0.188 mmol, 76.8 mg, mp 99.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 4H), 7.67−7.65(m, 2H), 7.59-7.55 (m, 1H), 7.51−7.44 (m, 4H), 7.39−7.37 (m, 2H), δ 7.33−7.18 (m, 6H), 5.50 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 146.01, 145.27, 145.13, 139.90, 133.10, 132.66, 129.35, 129.23, 128.81, 128.28, 128.26, 127.45, 127.32, 126.76, 126.71, 117.54, 115.84, 61.56. HRMS m/z: Calcd for $C_{26}H_{20}N_2OSNa$ $[M+Na]^+$: 431.1194, Found: 431.1197

(Benzhydrylimino)(4-nitrophenyl)(phenyl)-l6-sulfanone (3i)



The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a yellow solid in 88% yield (0.176 mmol, 75.4 mg, mp 134.2 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22−8.19 (m, 2H), δ 8.05−7.99 (m, 4H),7.60−7.56 (m, 1H), 7.52−7.48 (m, 2H), 7.45−7.43 (m, 2H), δ 7.38−7.36 (m, 2H), δ 7.33-7.17 (m, 6H), 5.51 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 149.79, 147.61, 145.17, 145.03, 139.77, 133.19, 129.85, 129.39, 128.83, 128.29, 128.27, 127.44, 127.29, 126.80, 126.73, 124.04, 61.56. HRMS m/z: Calcd for $C_{25}H_{20}N_2O_3SNa$ $[M+Na]^+$: 451.1092, Found: 451.1090

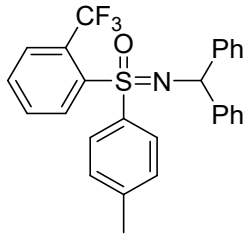
(Benzhydrylimino)(4-fluorophenyl)(phenyl)-l6-sulfanone (3j)



The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 78% yield (0.156 mmol, 62.6 mg, mp 120.1 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.94 (s, 4H), 7.53−7.07 (m, 15H), 5.45 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 166.34, 163.81, 145.66, 140.90, 137.02, 132.51,

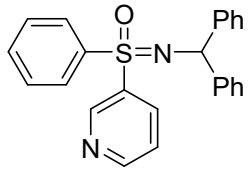
131.51, 131.41, 129.11, 128.62, 128.22, 128.20, 127.45, 127.41, 126.58, 126.54, 116.30, 116.07, 61.68. ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.20. HRMS m/z: Calcd for $C_{25}H_{20}FNOSNa$ $[M+Na]^+$: 424.1147, Found: 424.1147

(Benzhydrylimino)(p-tolyl)(2-(trifluoromethyl)phenyl)-l6-sulfanone (3k)



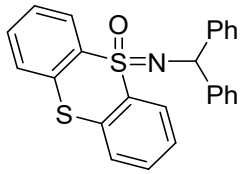
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a yellow solid in 85% yield (0.170 mmol, 79.1 mg, mp 115.8 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.74−.67(m, 3H), 7.46−7.42 (m, 1H), 7.38−7.34 (m, 1H), 7.31−7.29 (m, 2H), δ 7.26−7.24 (m, 2H), δ 7.18−7.03 (m, 8H), 5.38 (s, 1H), 2.30 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.63, 145.20, 143.40, 141.07, 138.09, 133.31, 132.09, 131.91, 129.49, 128.57, 128.37, 128.30, 128.15, 128.10, 127.58, 127.45, 126.52, 126.45, 77.38, 77.06, 76.75, 61.85, 21.54. ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.89. HRMS m/z: Calcd for $C_{27}H_{22}F_3NOSNa$ $[M+Na]^+$: 488.1272, Found: 488.1270

(Benzhydrylimino)(phenyl)(pyridin-3-yl)-l6-sulfanone (3l)



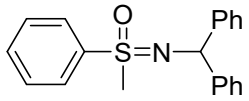
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a yellow solid in 67% yield (0.134 mmol, 51.5 mg, mp 123.8 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.155 (d, *J* = 4.0 Hz, 1H), 8.69 (d, *J* = 8.0 Hz, 1H),8.15−8.12 (m, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.56−7.53 (m, 1H), 7.49−7.44 (m, 4H), 7.41−7.39 (m, 2H), 7.32−7.26 (m, 5H), δ 7.24−7.17 (m, 2H), 5.51 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 152.69, 149.78, 145.35, 145.25, 140.32, 137.92, 136.23, 132.90, 129.29, 128.72, 128.28, 128.24, 127.45, 127.35, 126.72, 126.65, 123.54, 61.60. HRMS m/z: Calcd for $C_{24}H_{20}N_2OSNa$ $[M+Na]^+$: 407.1194, Found: 407.1197

5-(Benzhydrylimino)-5H-5l4-thianthrene 5-oxide (3m)



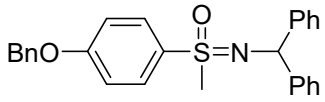
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a yellow solid in 56% yield (0.112 mmol, 46.3 mg, mp 141.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.04 (m, 2H), 7.40-7.30 (m, 6H), 7.07−6.99 (m, 10H), 5.19 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 144.38, 135.00, 134.48, 131.29, 128.57, 127.92, 127.61, 127.38, 126.99, 126.44, 61.78. HRMS m/z: Calcd for $C_{25}H_{19}NOS_2Na$ $[M+Na]^+$: 436.0806, Found: 436.0805

(Benzhydrylimino)(methyl)(phenyl)-l6-sulfanone (3n)



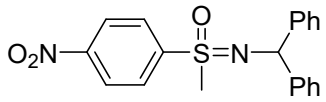
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 70% yield (0.140 mmol, 45.0 mg, mp 117.8 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.69 (m, 2H), 7.47−7.43(m, 1H), 7.36−7.31 (m, 4H), 7.21−7.02 (m, 8H), 5.27 (s, 1H). 3.02 (s, 3H).^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 145.79, 145.25, 140.04, 132.70, 129.09, 128.56, 128.17, 128.11, 127.58, 127.45, 126.52, 126.46, 61.44, 45.55. HRMS m/z: Calcd for $C_{20}H_{19}NOSNa$ $[M+Na]^+$: 344.1085, Found: 344.1085

(Benzhydrylimino)(4-(benzyloxy)phenyl)(methyl)-l6-sulfanone(3o)



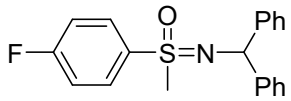
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 56% yield (0.112 mmol, 47.9 mg, mp 125.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 2H), 7.45−7.42(m, 7H), 7.31−7.27 (m, 4H), 7.25−7.14 (m, 4H), 7.00−6.98 (m, 2H), 5.37 (s, 1H), 5.14 (s, 2H), 3.11 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 162.17, 145.93, 145.48, 135.98, 131.64, 130.73, 128.74, 128.35, 128.12, 128.09, 127.61, 127.48, 127.46, 126.43, 126.38, 115.12, 70.32, 61.40, 45.87. HRMS m/z: Calcd for $C_{27}H_{25}NO_2SNa$ $[M+Na]^+$: 450.1504, Found: 450.1503

(Benzhydrylimino)(methyl)(4-nitrophenyl)-l6-sulfanone (3p)



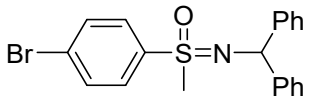
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a pale-yellow solid in 60% yield (0.120 mmol, 44.0 mg, mp 113.2 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.43−7.41 (m, 2H), 7.33−7.28 (m, 2H), 7.24−7.12 (m, 6H), 5.42 (s, 1H), 3.18 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 150.06, 146.73, 144.93, 144.34, 129.68, 128.23, 127.67, 127.24, 126.83, 126.74, 124.03, 61.23, 45.44. This compound is known.[2]

(Benzhydrylimino)(4-fluorophenyl)(methyl)-l6-sulfanone (3q)



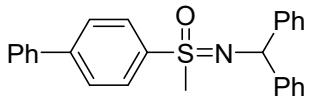
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 65% yield (0.130 mmol, 51.9 mg, mp 87.7 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.77 (m, 2H), 7.43−7.41 (m, 2H), 7.32−7.16 (m, 8H), 7.12−7.08 (m, 2H), 5.37 (s, 1H), 3.13 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 166.51, 163.98, 145.57, 145.06, 136.13 (d, *J* = 3 Hz), 131.30, 131.20, 128.16, 127.59, 127.36, 126.55, 116.31, 116.08, 61.31, 45.78. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.81. HRMS m/z: Calcd for $C_{20}H_{18}F_3NOSNa$ $[M+Na]^+$: 362.0991, Found: 362.0990

(Benzhydrylimino)(4-bromophenyl)(methyl)-l6-sulfanone (3r)



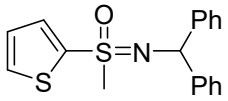
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a yellow solid in 78% yield (0.156 mmol, 62.5 mg, mp 127.6 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65−7.63 (m, 2H), 7.57−7.55 (m, 2H), 7.44−7.41 (m, 2H), 7.32−7.28 (m, 2H), 7.26−7.17 (m, 6H), 5.37 (s, 1H), 3.12 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 145.51, 144.97, 139.30, 132.30, 130.16, 128.19, 127.84, 127.59, 127.36, 126.59, 61.37, 45.63. This compound is known.[2]

[1,1'-biphenyl]-4-yl(benzhydrylimino)(methyl)-l6-sulfanone (3s)



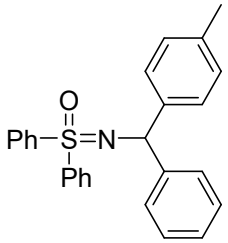
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 80% yield (0.160 mmol, 63.6mg, mp 123.8 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.85 (m, 2H), 7.66−7.46 (m, 9H), 7.31−7.22 (m, 8H), 5.43 (s, 1H), 3.19 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 145.81, 145.64, 145.30, 139.47, 138.63, 129.11, 129.07, 128.47, 128.17, 128.13, 127.73, 127.66, 127.47, 127.37, 126.52, 126.45, 61.46, 45.68. HRMS m/z: Calcd for $C_{26}H_{23}NOSNa$ $[M+Na]^+$: 420.1398, Found: 420.1396

(Benzhydrylimino)(methyl)(thiophen-2-yl)-l6-sulfanone (3t)



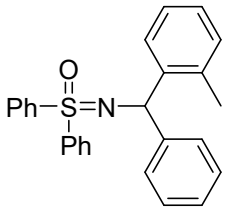
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 72% yield (0.144 mmol, 47.2 mg, mp 135.6 °C). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.63−7.61 (m, 1H), 7.42−7.18 (m, 12H), 7.03−7.2 (m, 1H), 5.53 (s, 1H), 3.34 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) *δ* 145.33, 144.81, 141.57, 133.76, 133.70, 128.20, 128.18, 127.91, 127.62, 127.50, 126.62, 77.36, 77.04, 76.72, 61.49, 47.64. HRMS m/z: Calcd for $C_{18}H_{17}NOS_2Na$ $[M+Na]^+$: 350.0649, Found: 350.0649

Diphenyl((phenyl(p-tolyl)methyl)imino)-l6-sulfanone (3w)



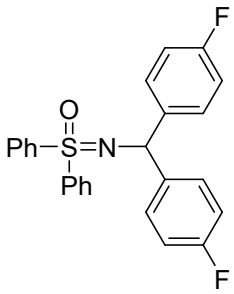
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a yellow solid in 72% yield (0.144 mmol, 57.2 mg, mp 87.7 °C). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.97−7.96 (m, 4H), 7.52−7.49 (m, 2H), 7.46−7.42 (m, 6H), 7.32−7.27 (m, 4H), 7.21−7.20 (m, 1H), 7.11−7.09 (m, 2H), 5.41 (s, 1H), 2.33 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 146.03, 142.99, 141.05, 135.93, 132.32, 128.99, 128.87, 128.79, 128.14, 127.39, 127.35, 126.39, 61.57, 21.12. HRMS m/z: Calcd for $C_{26}H_{23}NOSNa$ $[M+Na]^+$: 420.1398, Found: 420.1398

Diphenyl((phenyl(o-tolyl)methyl)imino)-l6-sulfanone (3x)



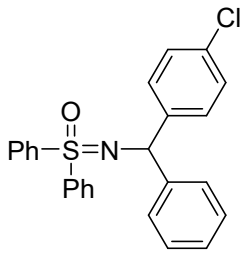
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a yellow solid in 80% yield (0.160 mmol, 63.6 mg, mp 92.2 °C). ^{1}H R (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 1H), 7.50−7.44 (m, 4H), 7.41−7.37 (m, 4H), 7.30−7.24 (m, 3H), 7.19−7.15 (m, 2H), 7.07−7.05 (m, 1H), 5.65 (s, 1H), 2.04 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 144.92, 143.53, 141.26, 141.24, 134.95, 132.32, 132.23, 130.21, 128.98, 128.92, 128.78, 128.60, 128.43, 128.03, 127.63, 126.55, 126.24, 126.00, 58.39, 19.56. HRMS m/z: Calcd for $C_{26}H_{23}NOSNa$ $[M+Na]^+$: 420.1398, Found: 420.1398

((Dis(4-fluorophenyl)methyl)imino)diphenyl-l6-sulfanone (3za)



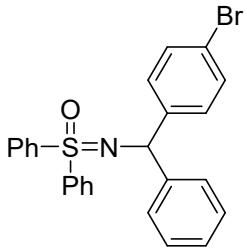
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 80% yield (0.160 mmol, 67.1 mg, mp 113.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.81 (m, 4H), 7.42−7.38 (m, 2H), 7.35−7.31 (m, 4H), 7.26−7.21 (m, 4H), 6.88−6.82 (m, 4H), 5.30 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 162.84, 160.41, 141.50, 141.47, 140.79, 132.54, 129.10, 128.93, 128.85, 128.64, 115.07, 114.86, 60.30. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.61. HRMS m/z: Calcd for $C_{25}H_{19}F_2NOSNa$ $[M+Na]^+$: 442.1053, Found: 442.1050

(((4-chlorophenyl)(phenyl)methyl)imino)diphenyl-l6-sulfanone (3zb)



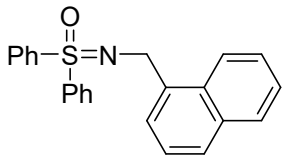
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a pink solid in 86% yield (0.172 mmol, 71.9 mg, mp 104.4 °C). ^{1}H R (400 MHz, $CDCl_3$) δ 7.98−7.92 (m, 4H), 7.54−7.49 (m, 2H), 7.47−7.35 (m, 8H), 7.32−7.28 (m, 2H), 7.26−7.20 (m, 3H), 5.41 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 145.37, 144.50, 141.00, 140.82, 132.44, 132.14, 129.04, 128.86, 128.73, 128.62, 128.25, 127.35, 126.68, 61.11. HRMS m/z: Calcd for $C_{25}H_{20}ClNOSNa$ $[M+Na]^+$: 440.0852, Found: 440.0854

(((4-bromophenyl)(phenyl)methyl)imino)diphenyl-l6-sulfanone (3zc)



The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 76% yield (0.152 mmol, 70.3 mg, mp 101.8 °C). ^{1}H R (400 MHz, $CDCl_3$) δ 7.97−7.91 (m, 4H), 7.54−7.49 (m, 2H), 7.47−7.38 (m, 8H), 7.31−7.27 (m, 4H), 7.23−7.19 (m, 1H), 5.39 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 145.28, 145.01, 140.97, 140.81, 132.44, 131.19, 129.25, 129.04, 128.72, 128.61, 128.25, 127.34, 126.68, 120.32, 61.16. HRMS m/z: Calcd for $C_{25}H_{20}BrNOSNa$ $[M+Na]^+$: 485.0347, Found: 485.0349

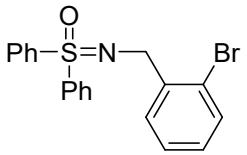
((Naphthalen-1-ylmethyl)imino)diphenyl-l6-sulfanone (3zd)



The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 85% yield (0.170 mmol, 60.8 mg, mp 135.0 °C). ^{1}H R (400 MHz, $CDCl_3$) δ 8.13−8.11 (m, 1H), 8.01−7.99 (m, 4H), 7.85−7.83

(m, 1H), 7.74−7.72 (m, 2H), 7.51−7.41 (m, 9H), 4.75 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 140.87, 136.92, 133.61, 132.43, 131.48, 129.15, 128.55, 128.53, 127.21, 125.75, 125.58, 125.44, 124.88, 123.77, 44.95. HRMS m/z: Calcd for $C_{23}H_{19}NOSNa$ $[M+Na]^+$: 380.1085, Found: 380.1082

((2-bromobenzyl)imino)diphenyl-l6-sulfanone (3ze)



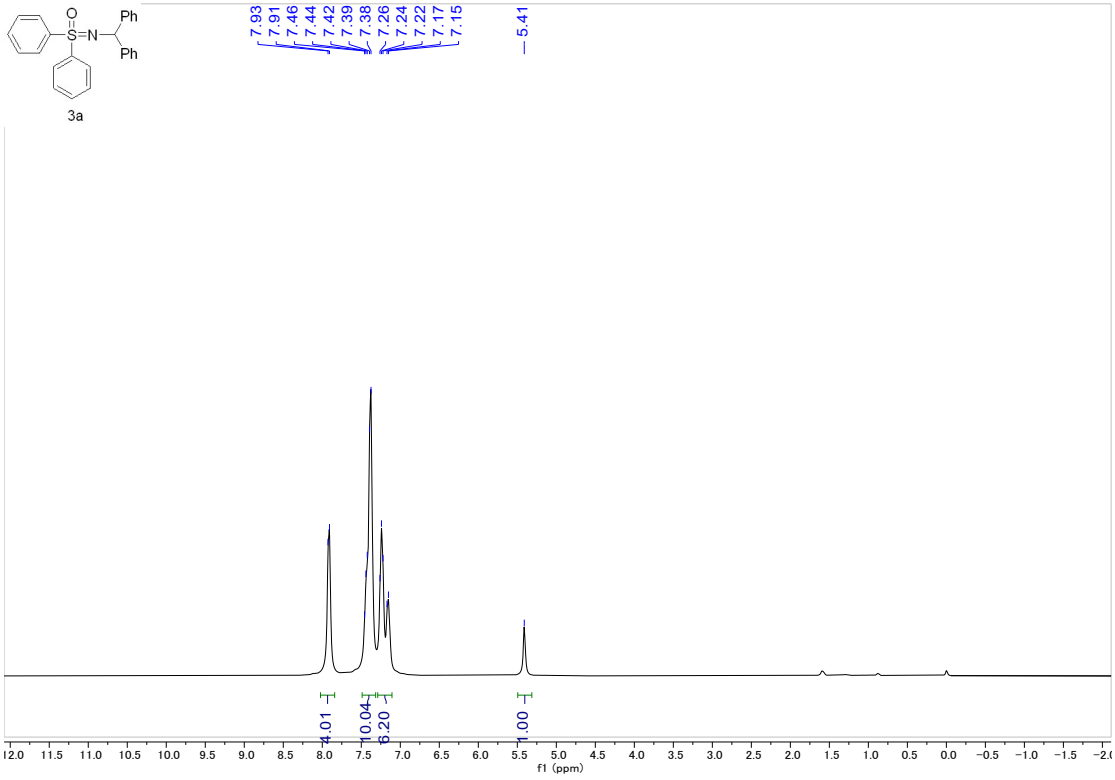
The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA to afford a white solid in 80% yield (0.160 mmol, 61.8 mg, mp 131.9 °C). ^{1}H R (400 MHz, $CDCl_3$) δ 8.02 (d, J = 4.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.53−7.45 (m, 7H), 7.36−7.32 (m, 1H), 7.11−7.07 (m, 1H), 4.33 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 140.70, 140.50, 132.57, 132.13, 129.31, 129.26, 128.55, 127.95, 127.39, 122.94, 47.30. HRMS m/z: Calcd for $C_{19}H_{16}BrNOSNa$ $[M+Na]^+$: 408.0034, Found: 408.0035

4. References

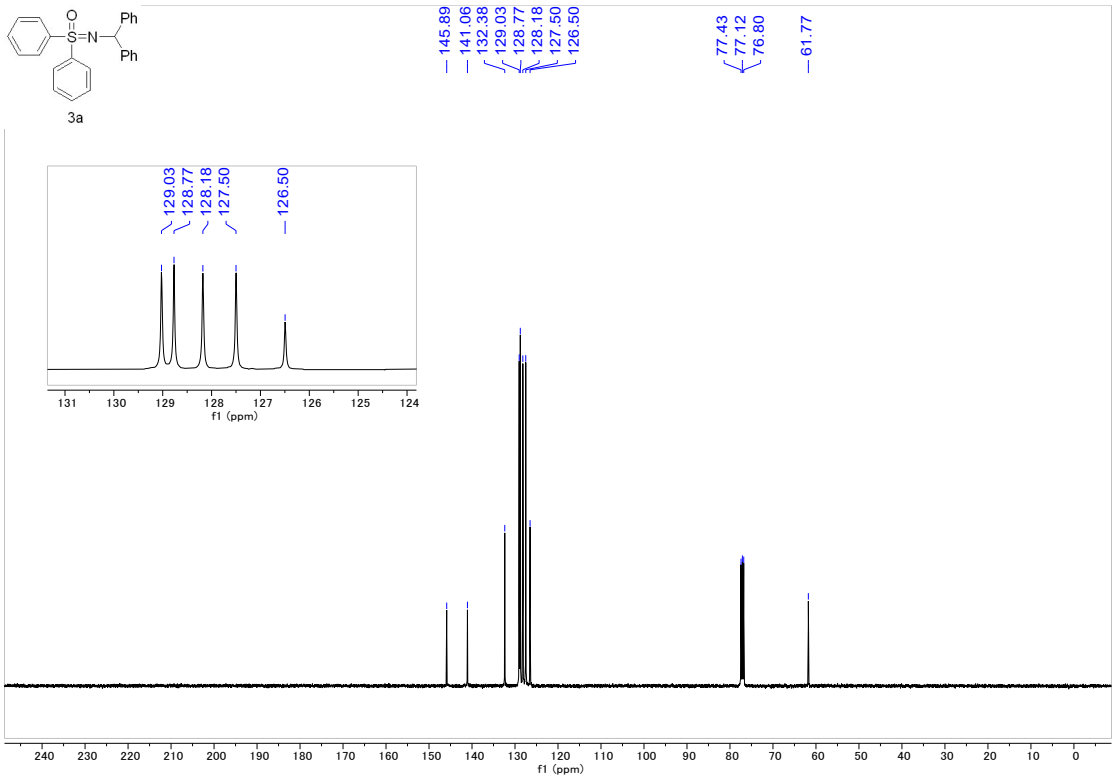
(1) A. Tota, M. Zenzola, S. J. Chawner, S. S. John-Campbell, C. Carlucci, G. Romanazzi, L. Degennaro, J. A. Bull and R. Luisi, *Chem.Commun.*, 2017, **53**, 348-351.

(2) Y. Cheng, W. Dong, L. Wang, K. Parthasarathy and C. Bolm, *Org. Lett.*, 2014, **16**, 2000-2002.

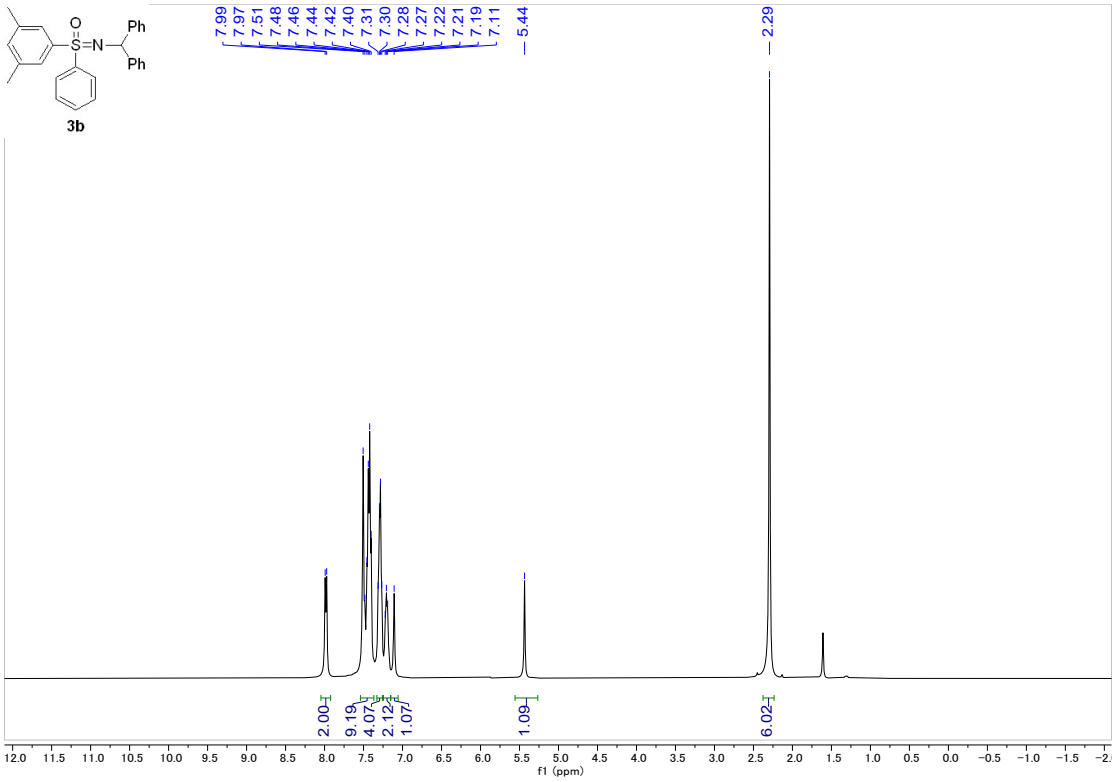
5. Copies of ^{1}H, ^{13}C NMR, ^{19}F NMR Spectra of the Products



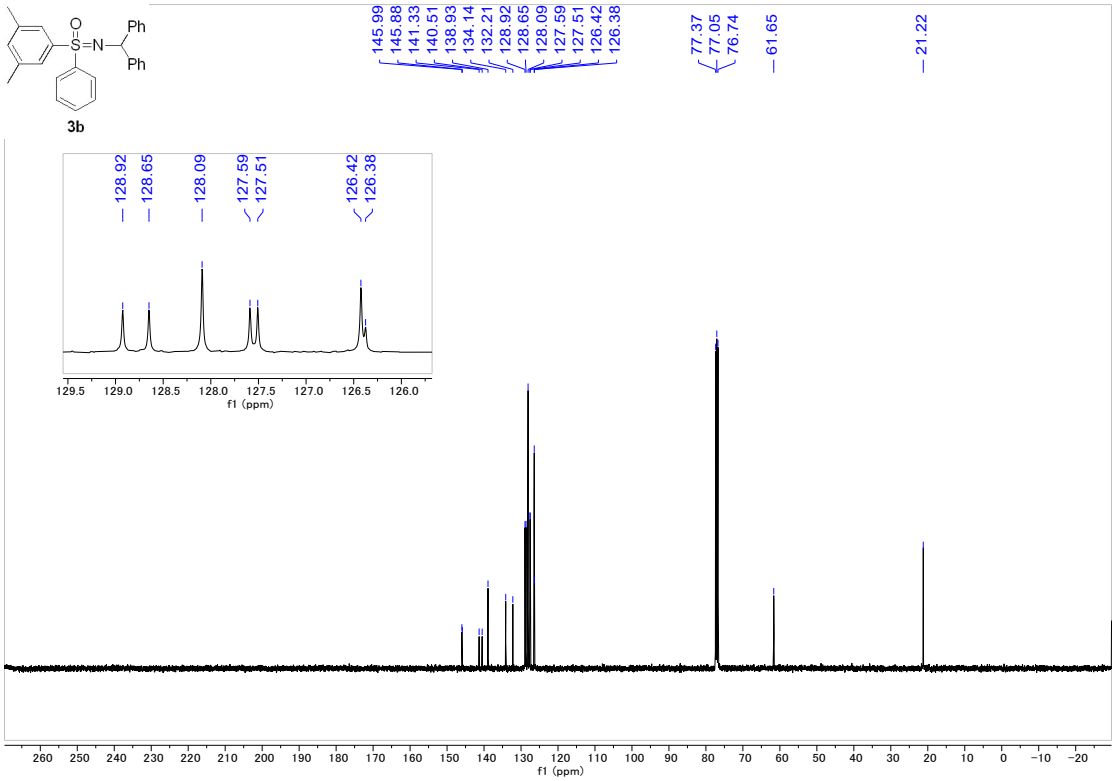
^{1}H NMR ($CDCl_3$, 400 MHz) of **3a**



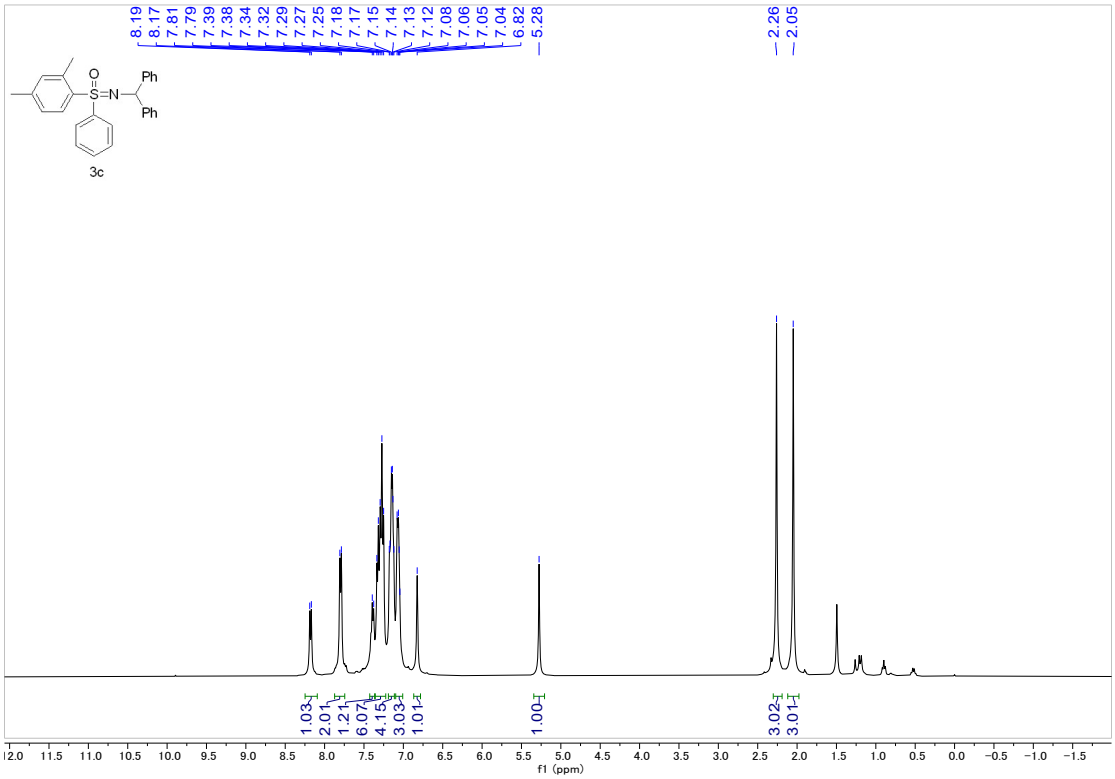
^{13}C NMR ($CDCl_3$, 100 MHz) of **3a**



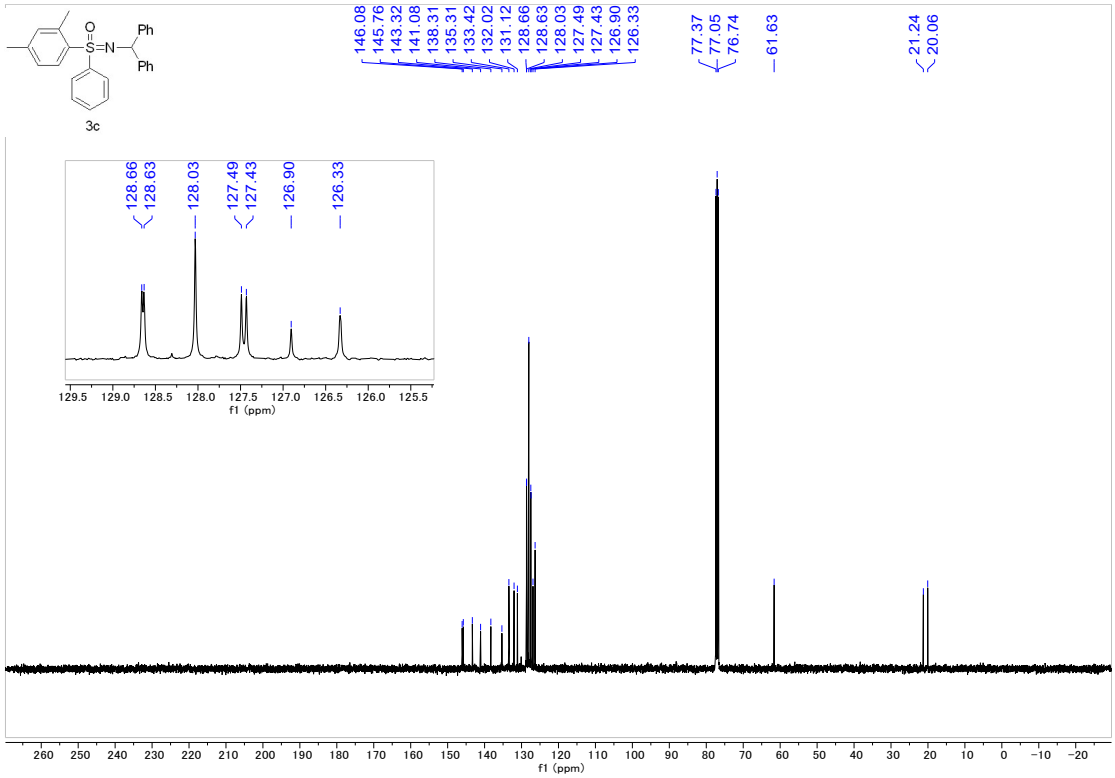
^{1}H NMR ($CDCl_3$, 400 MHz) of **3b**



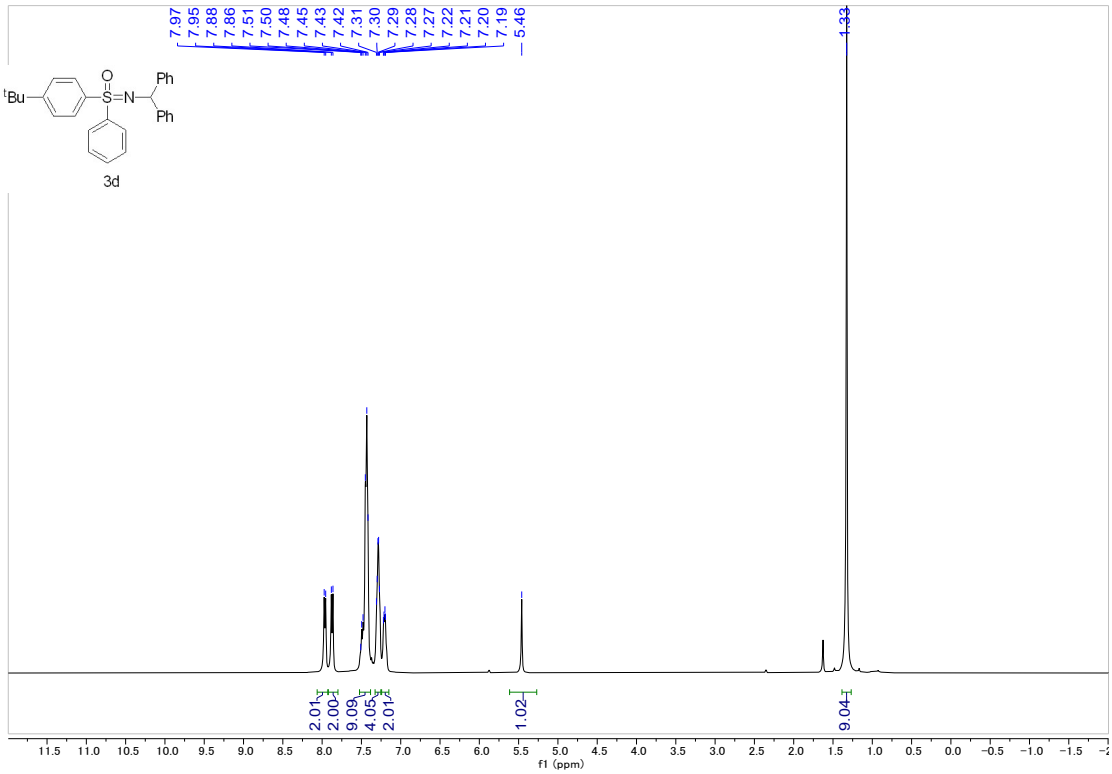
^{13}C NMR ($CDCl_3$, 100 MHz) of **3b**



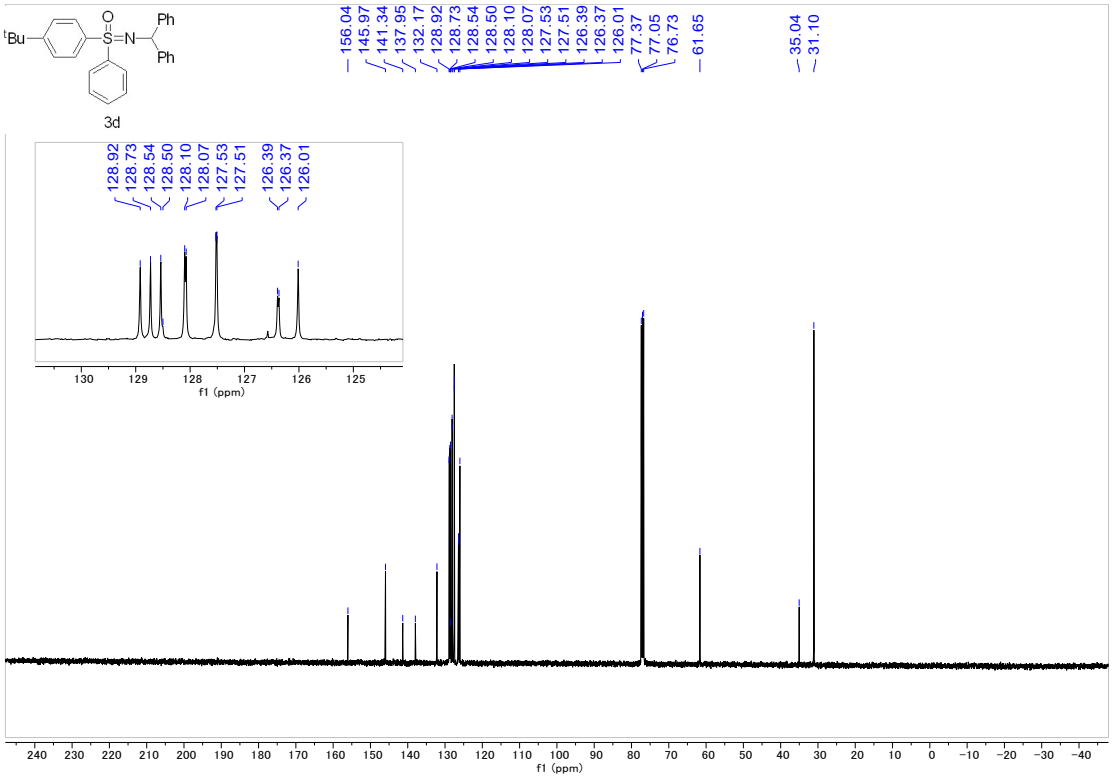
^{1}H NMR ($CDCl_3$, 400 MHz) of **3c**



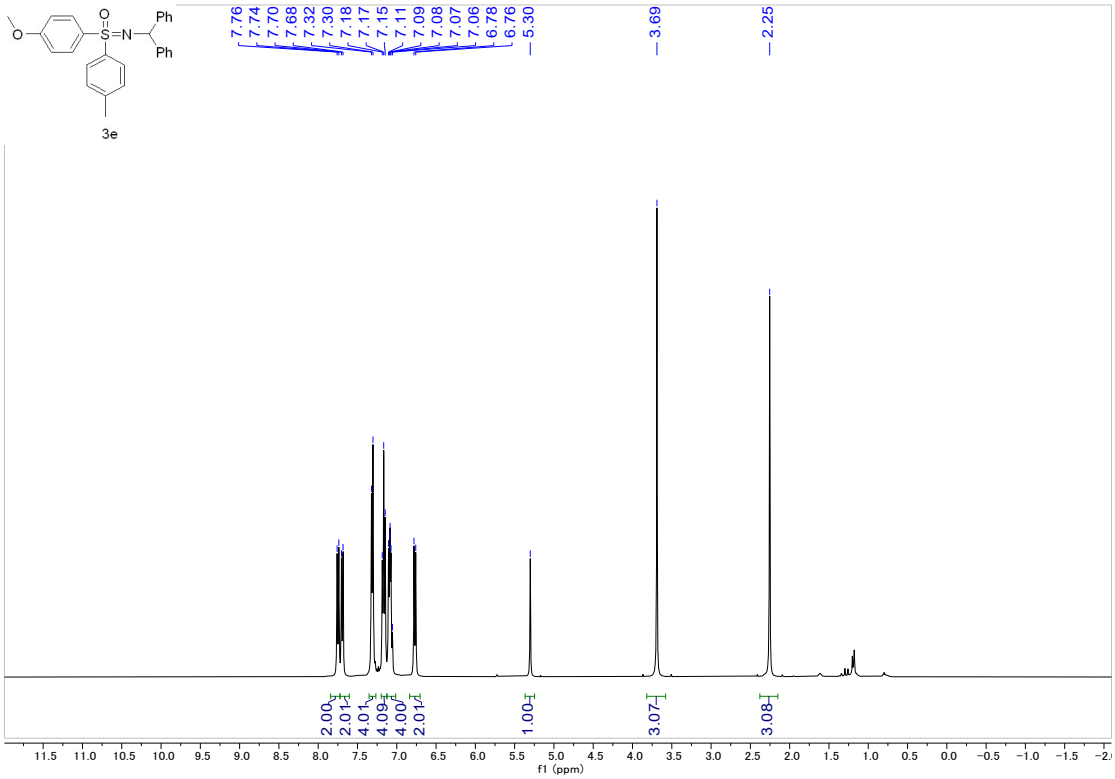
^{13}C NMR ($CDCl_3$, 100 MHz) of **3c**



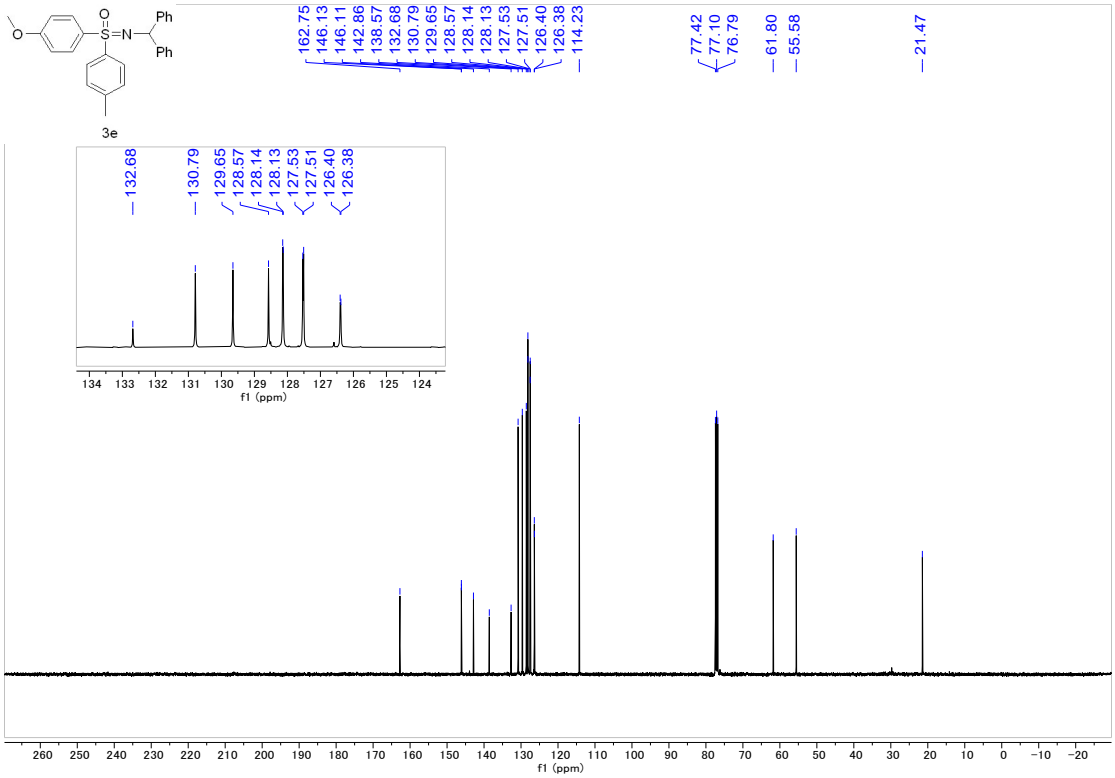
^{1}H NMR ($CDCl_3$, 400 MHz) of **3d**



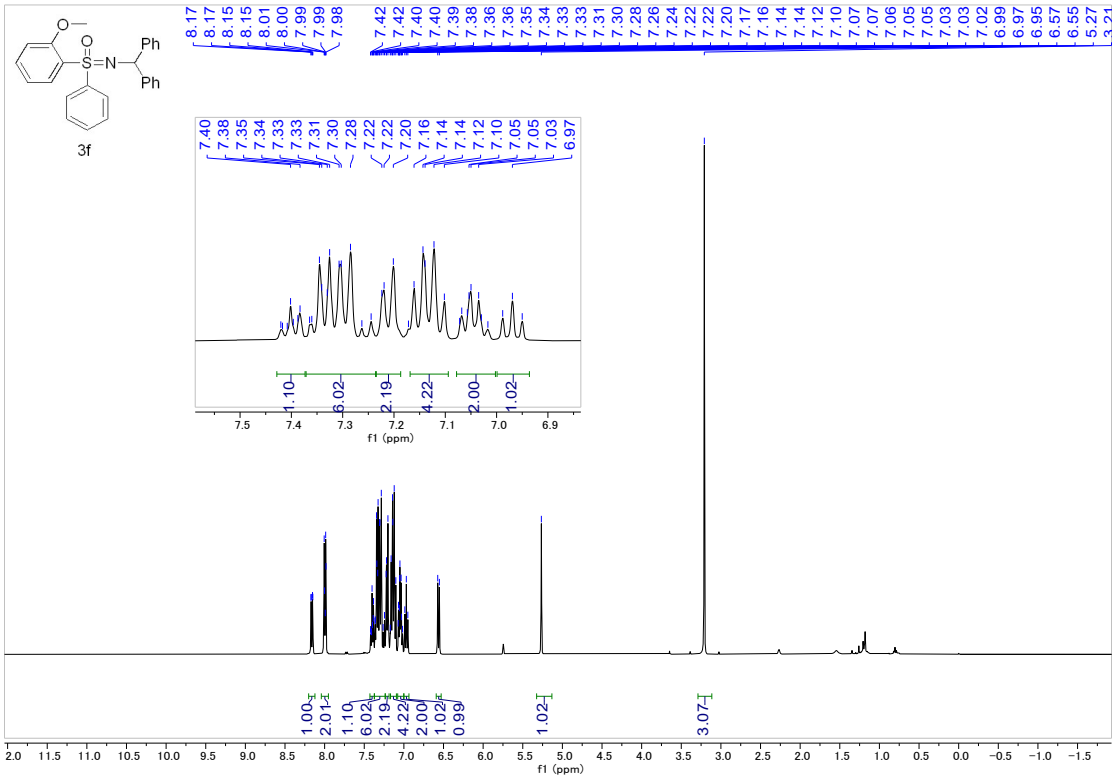
^{13}C NMR ($CDCl_3$, 100 MHz) of **3d**



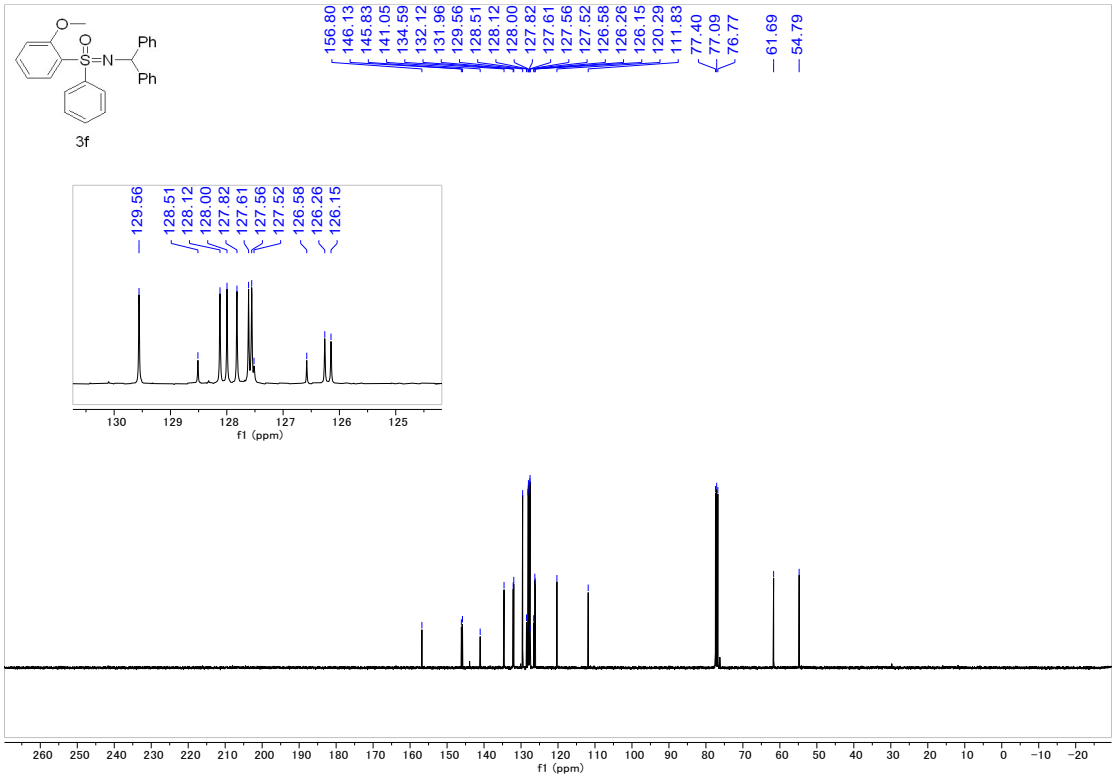
^{1}H NMR ($CDCl_3$, 400 MHz) of **3e**



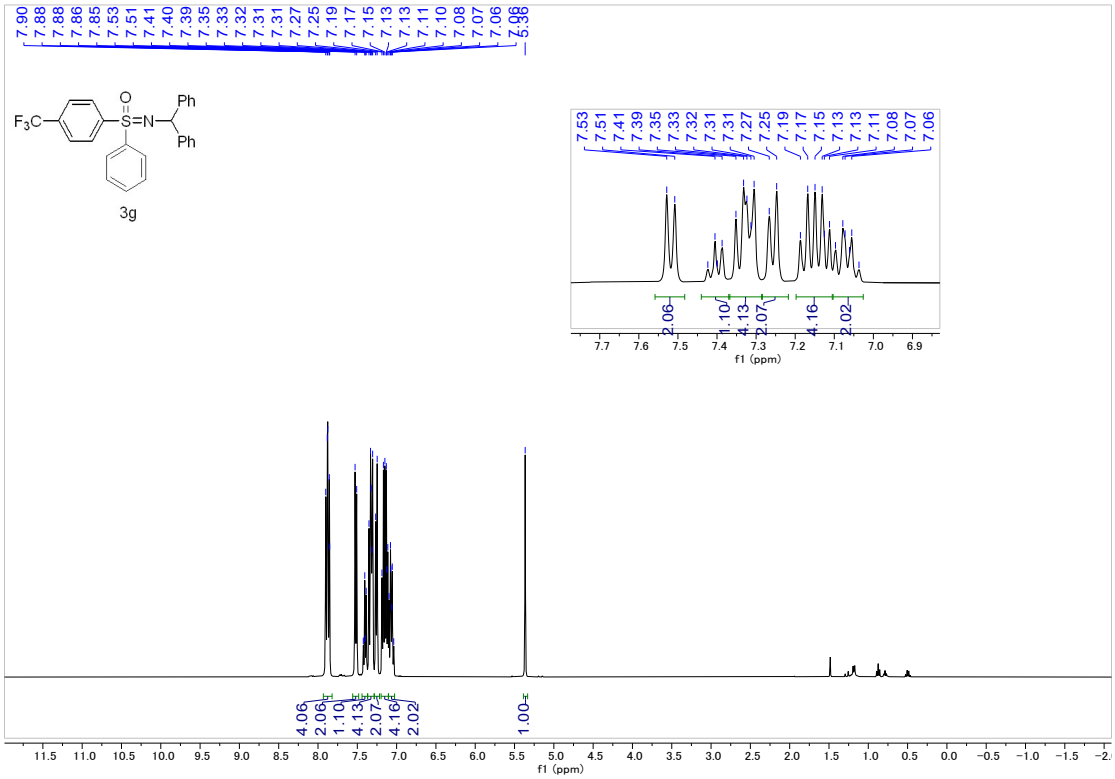
^{13}C NMR ($CDCl_3$, 100 MHz) of **3e**



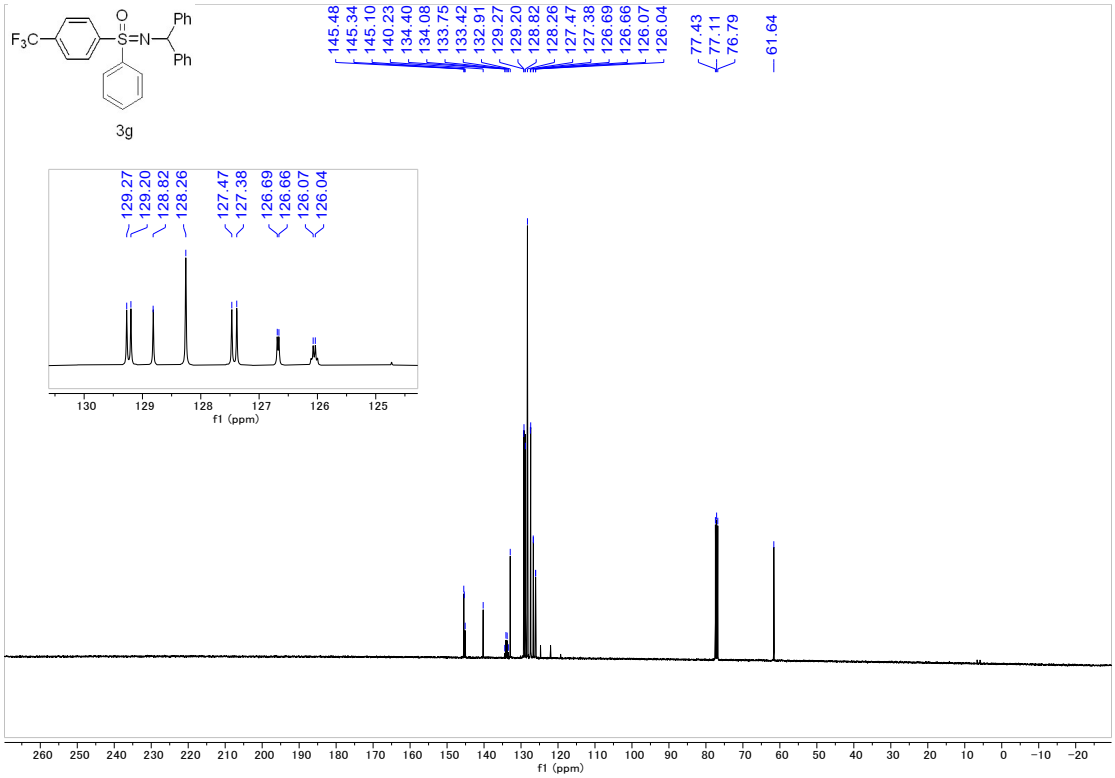
^{1}H NMR ($CDCl_3$, 400 MHz) of **3f**



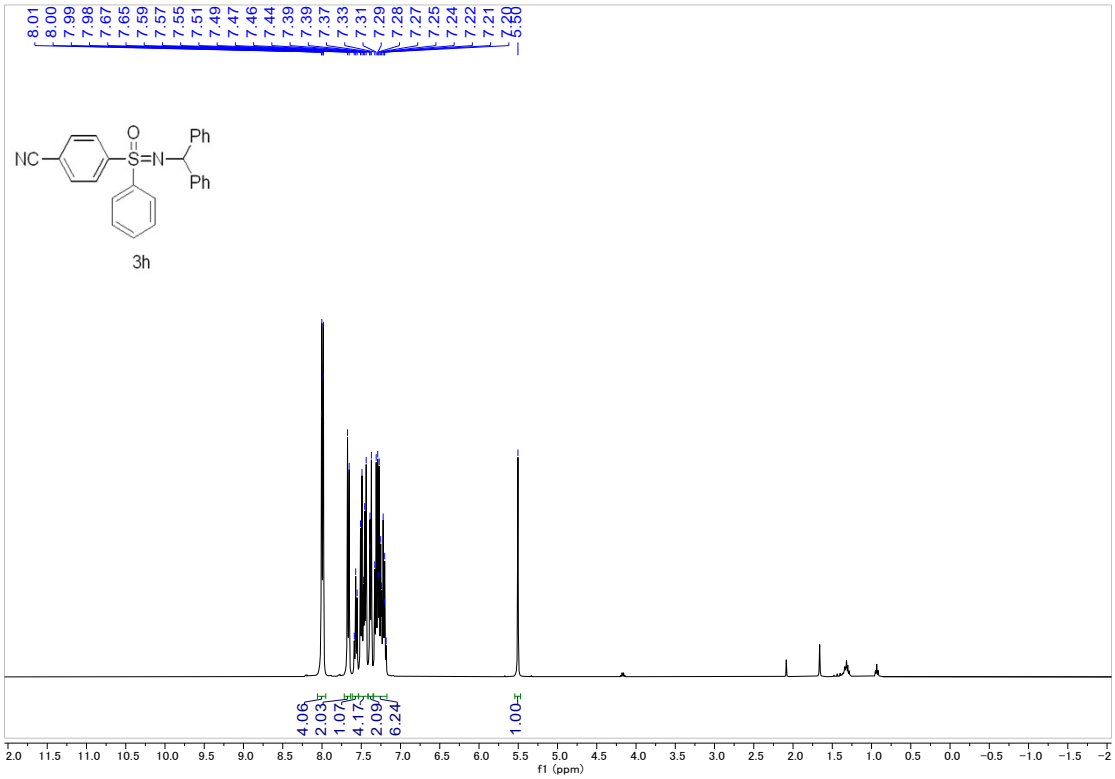
^{13}C NMR ($CDCl_3$, 100 MHz) of **3f**



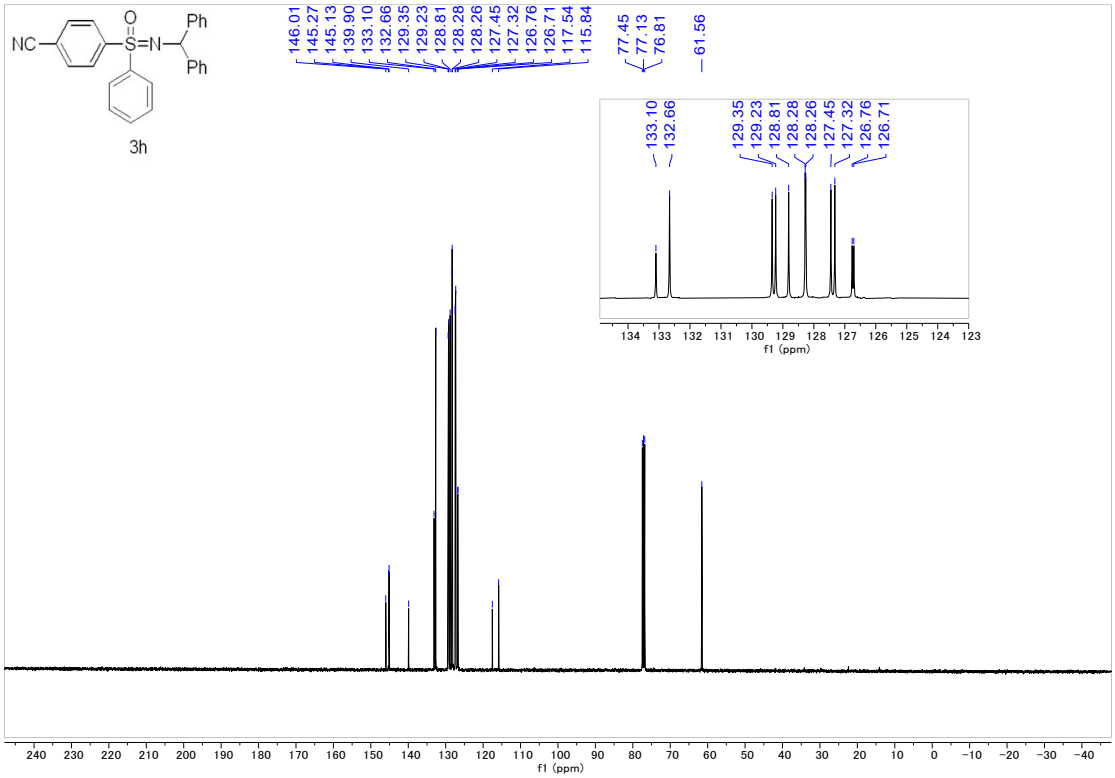
^{1}H NMR ($CDCl_3$, 400 MHz) of **3g**



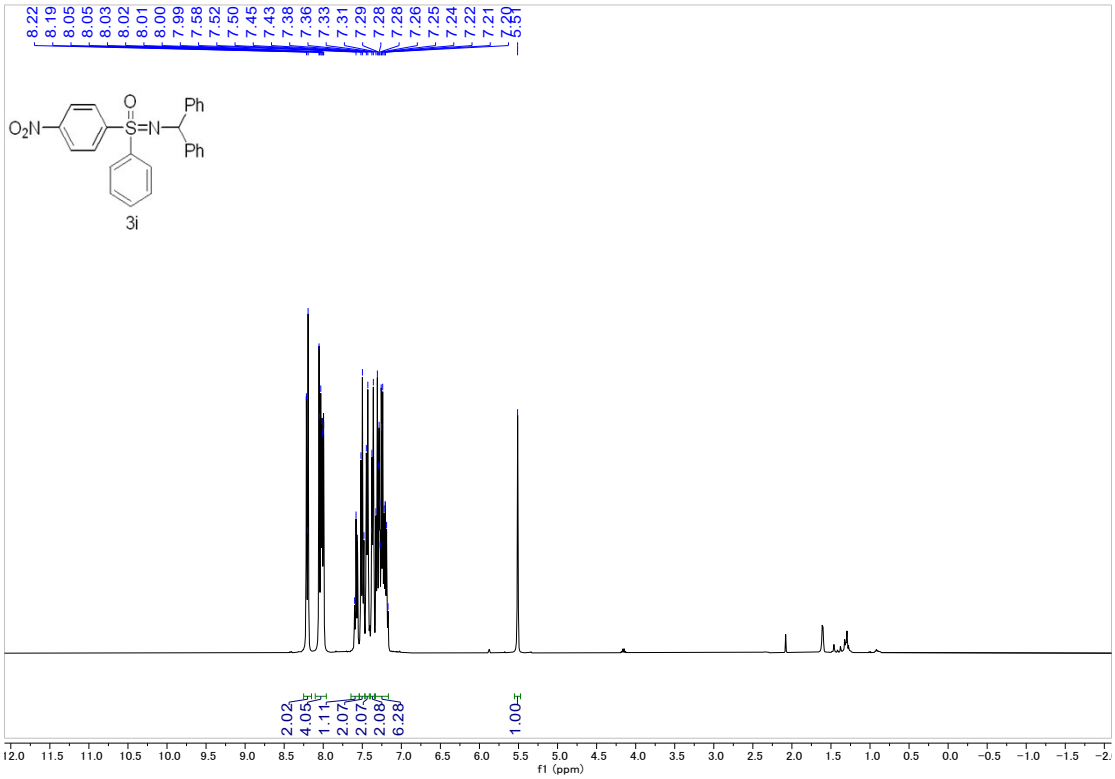
^{13}C NMR ($CDCl_3$, 100 MHz) of **3g**



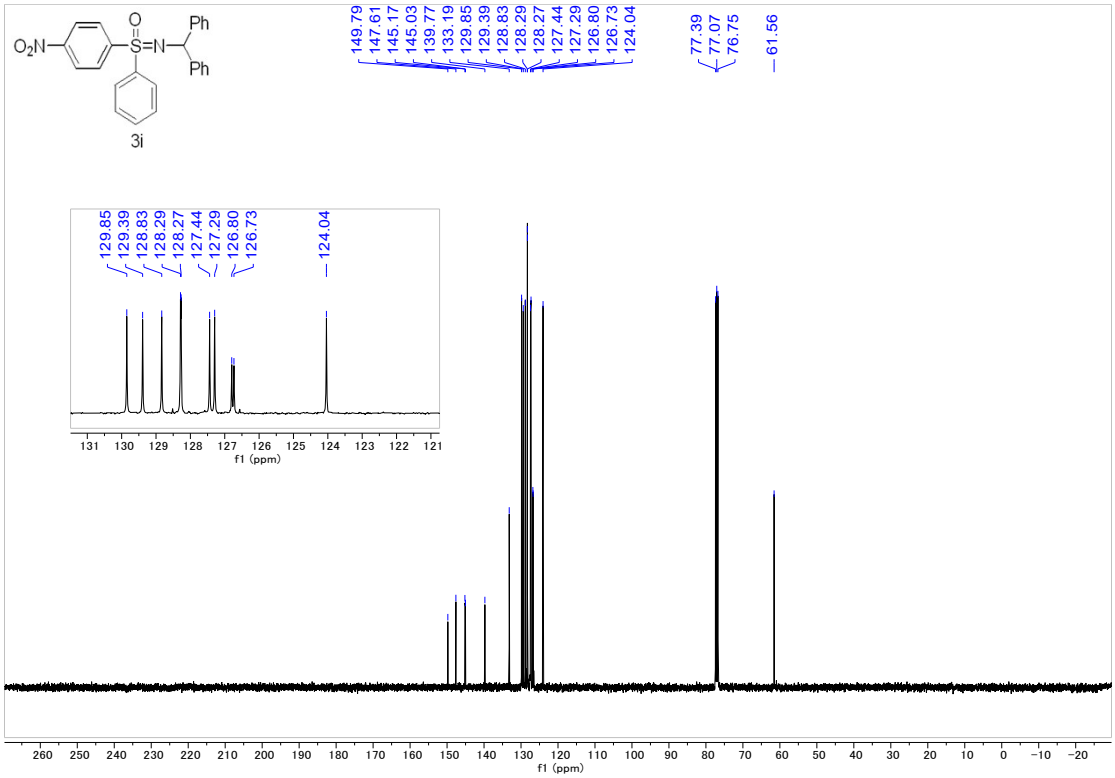
^{1}H NMR ($CDCl_3$, 400 MHz) of **3h**



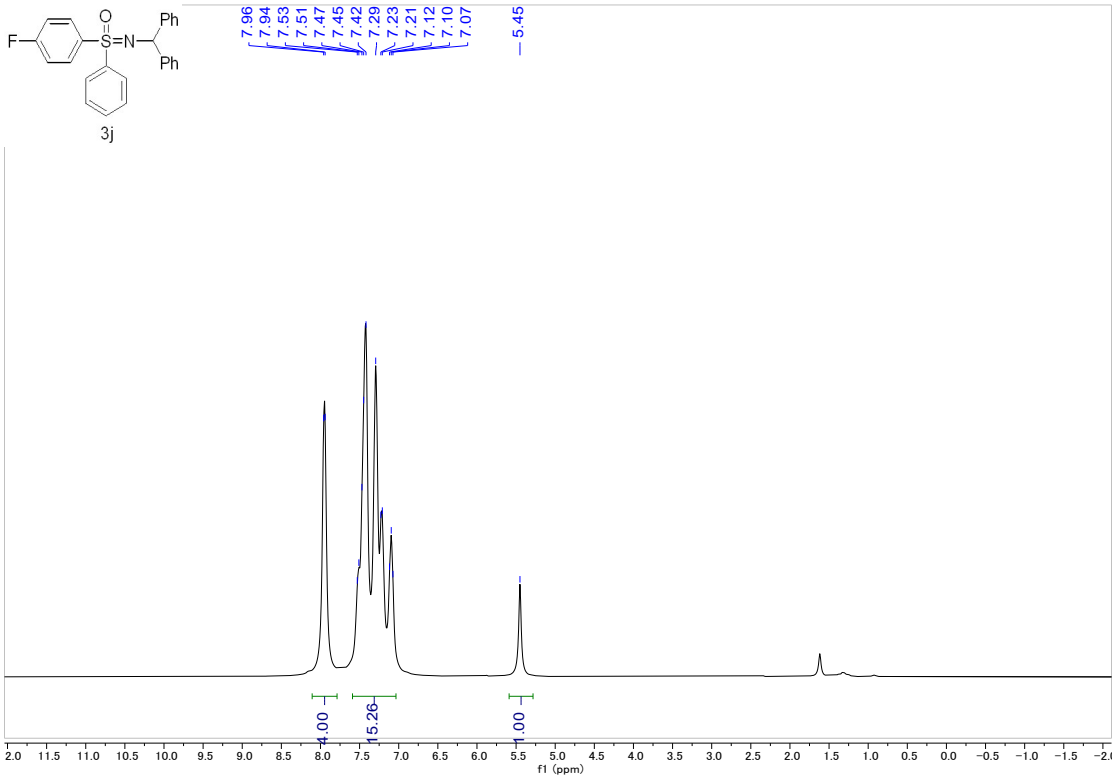
^{13}C NMR ($CDCl_3$, 100 MHz) of **3h**



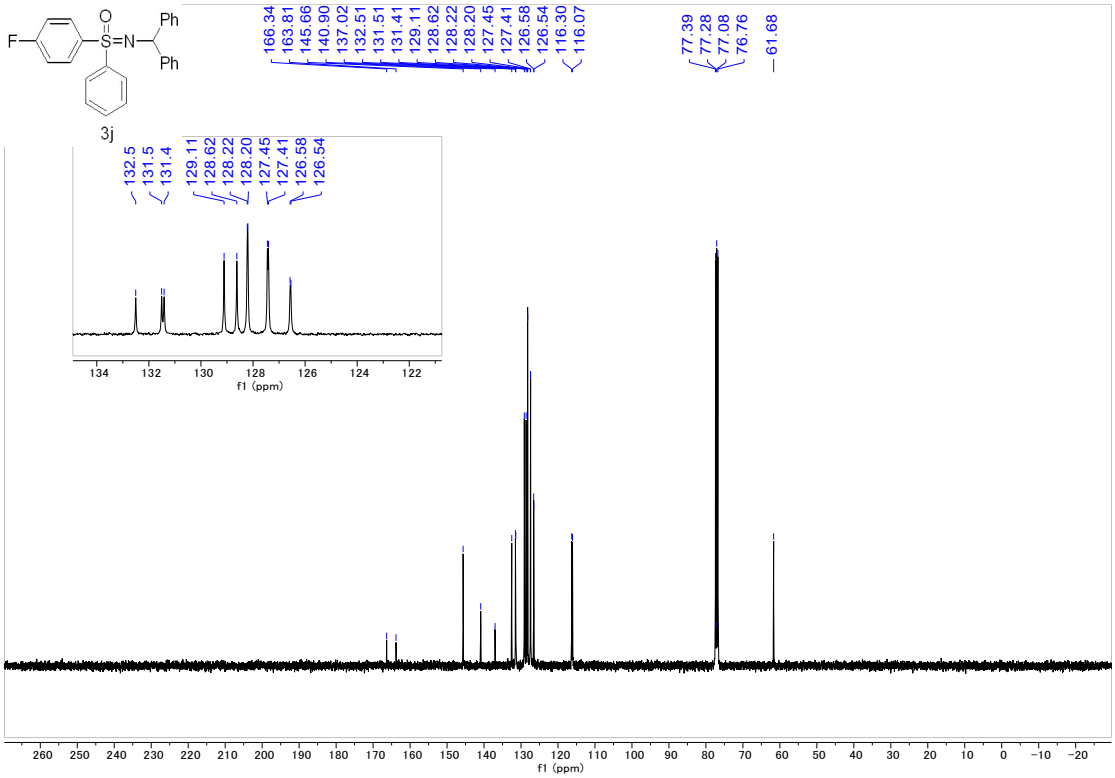
^{1}H NMR ($CDCl_3$, 400 MHz) of **3i**



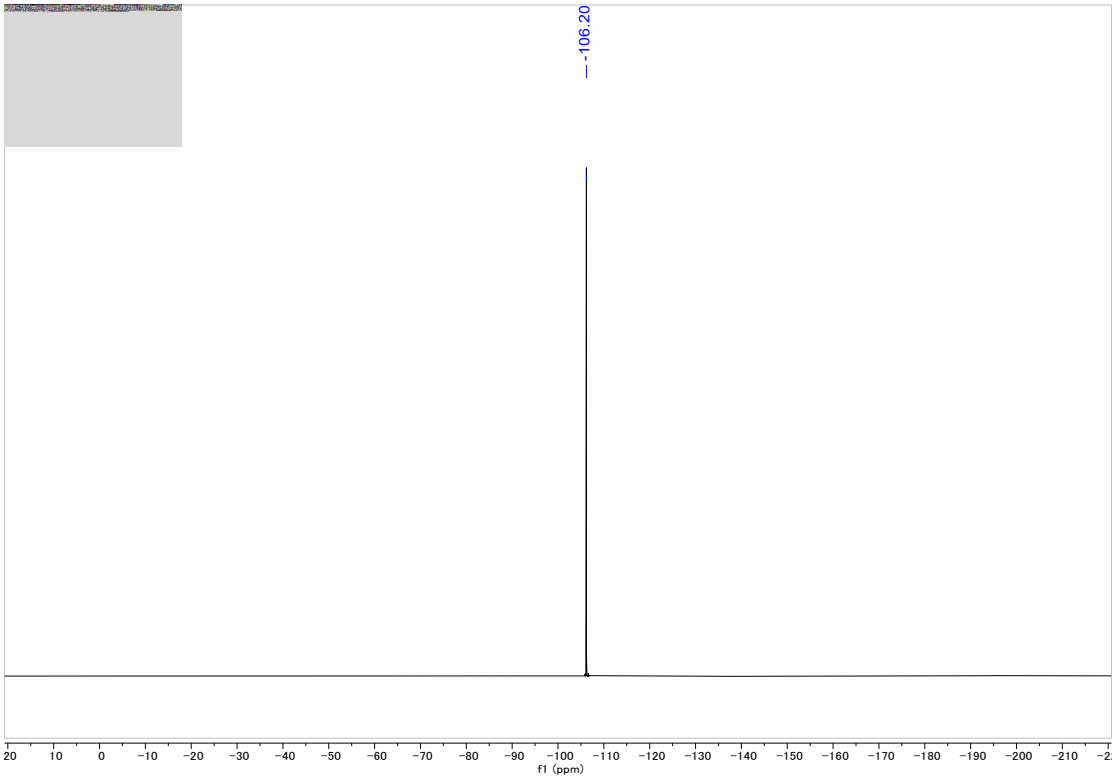
^{13}C NMR ($CDCl_3$, 100 MHz) of **3i**



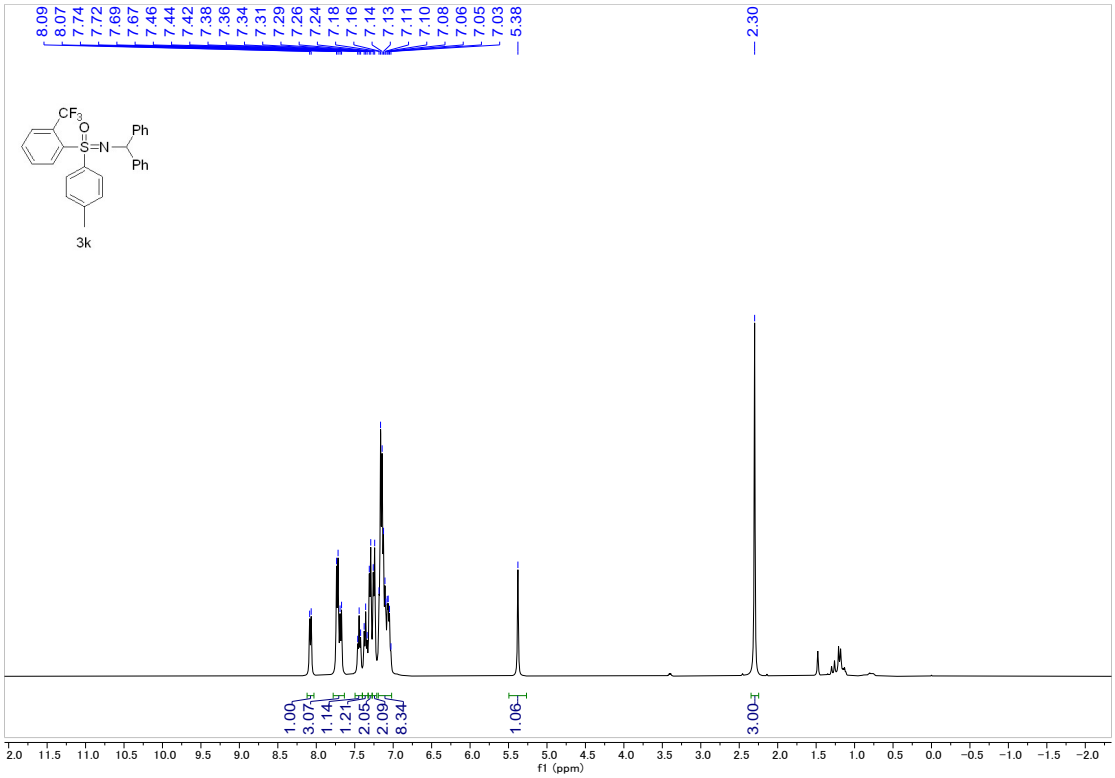
^{1}H NMR ($CDCl_3$, 400 MHz) of **3j**



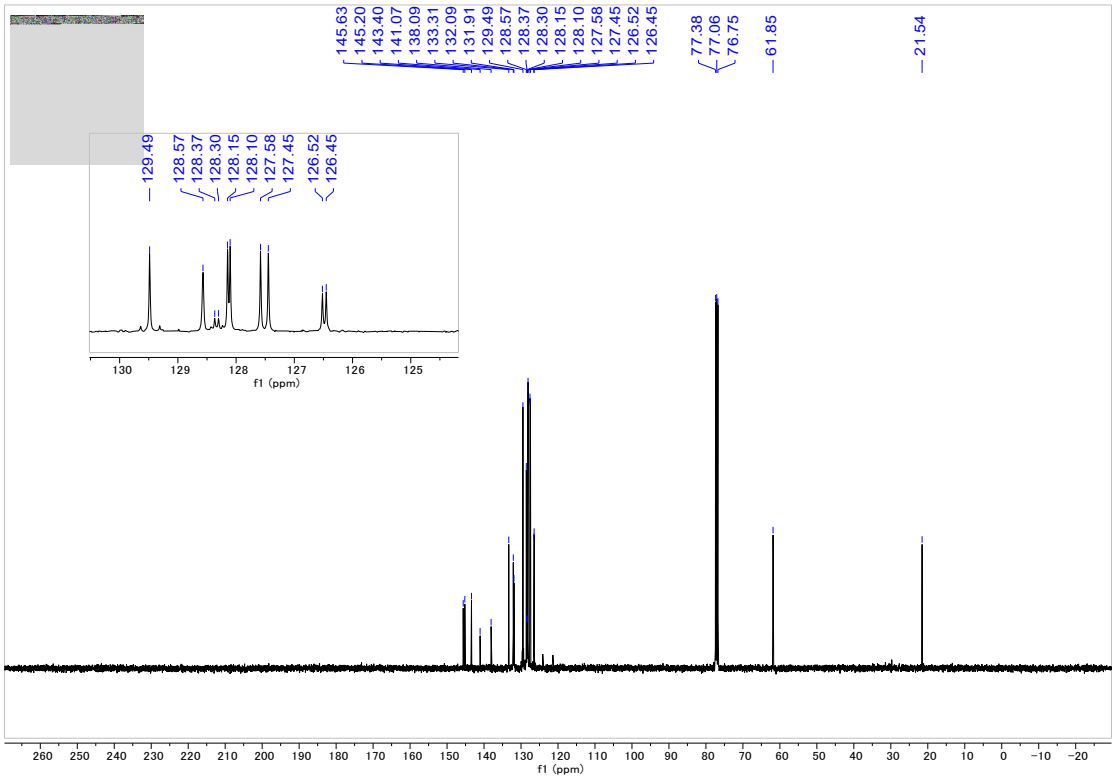
^{13}C NMR ($CDCl_3$, 100 MHz) of **3j**



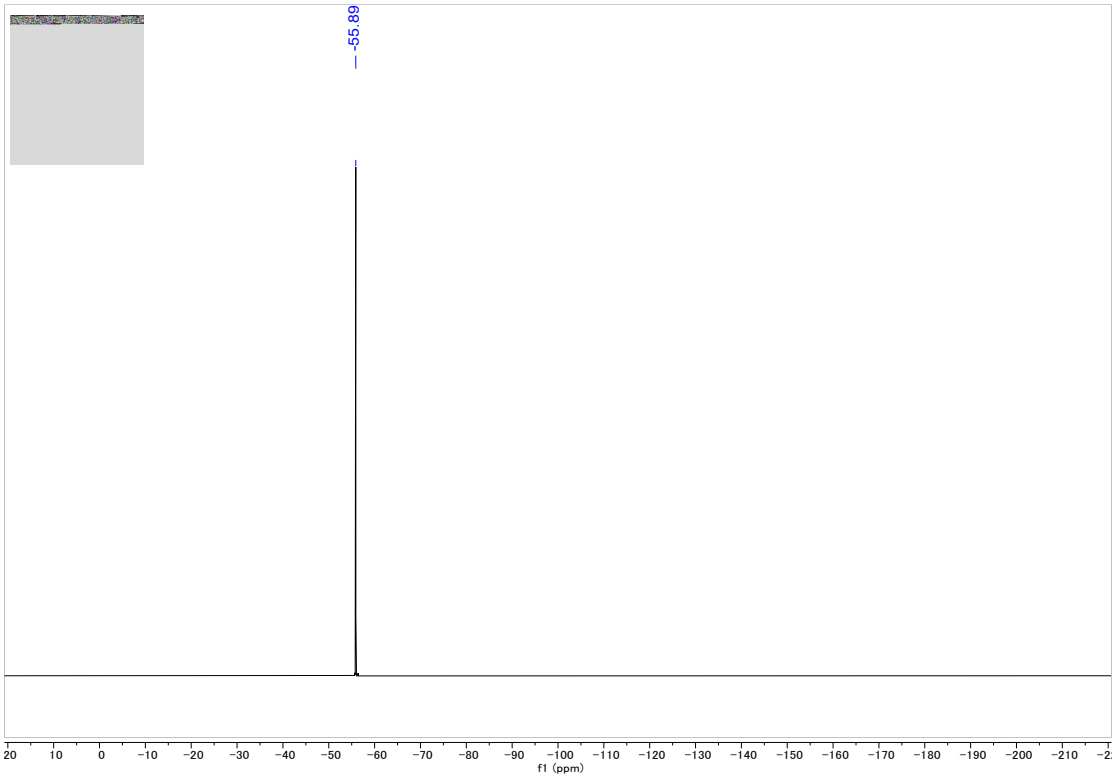
^{19}F NMR (376 MHz, CDCl3) of **3j**



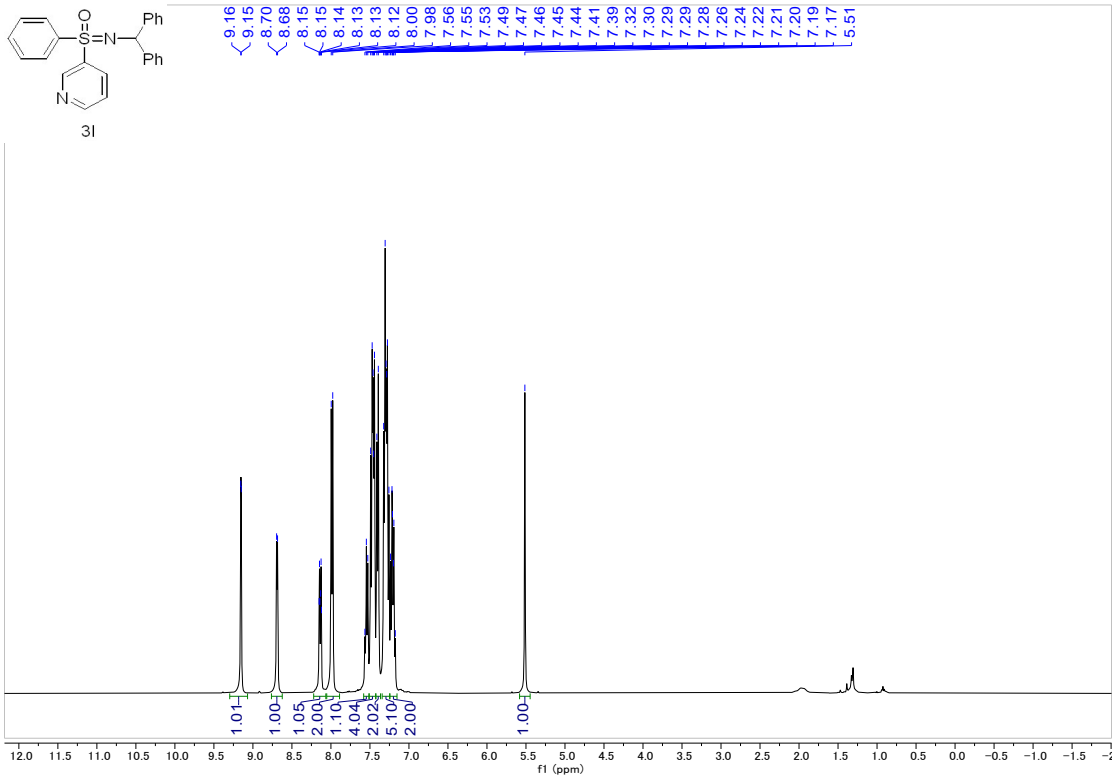
^{1}H NMR ($CDCl_3$, 400 MHz) of **3k**



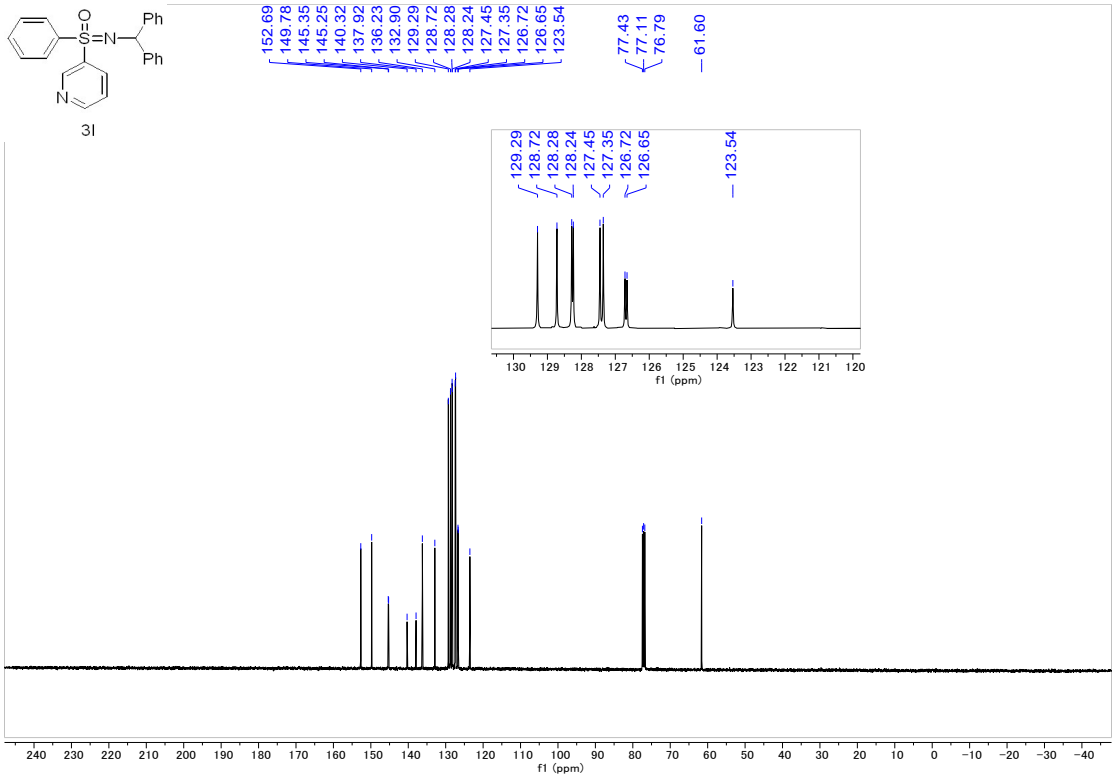
^{13}C NMR ($CDCl_3$, 100 MHz) of **3k**



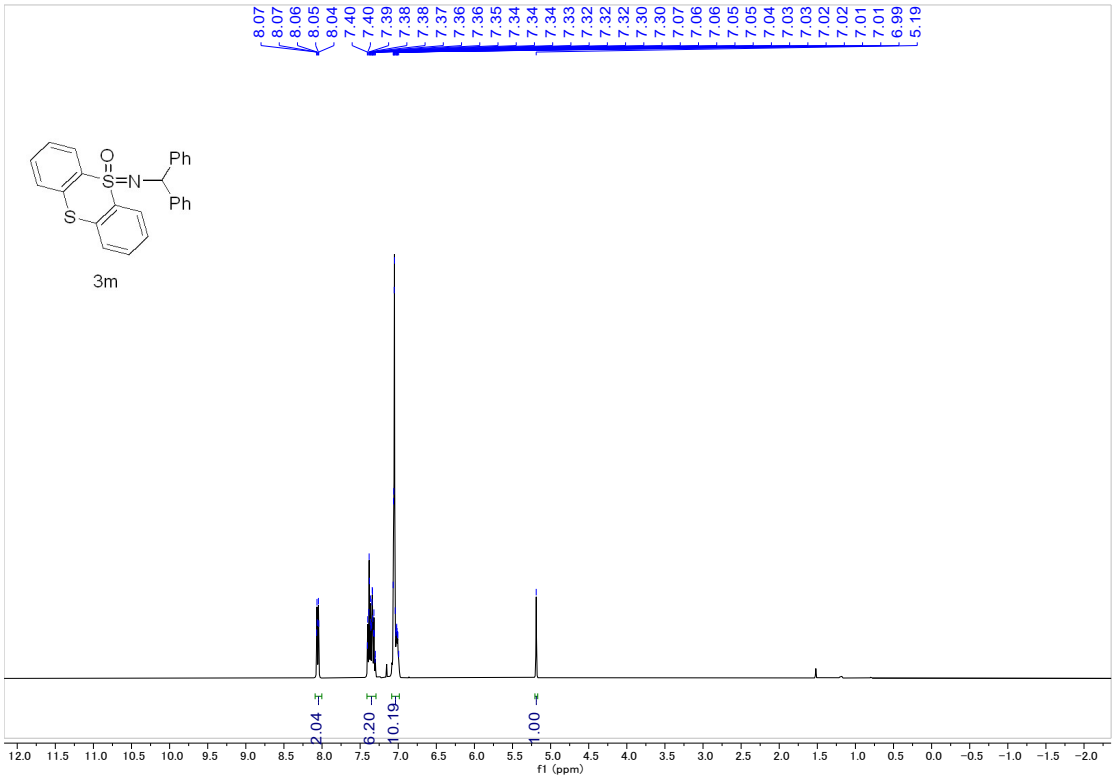
^{19}F NMR (376 MHz, CDCl3) of **3k**



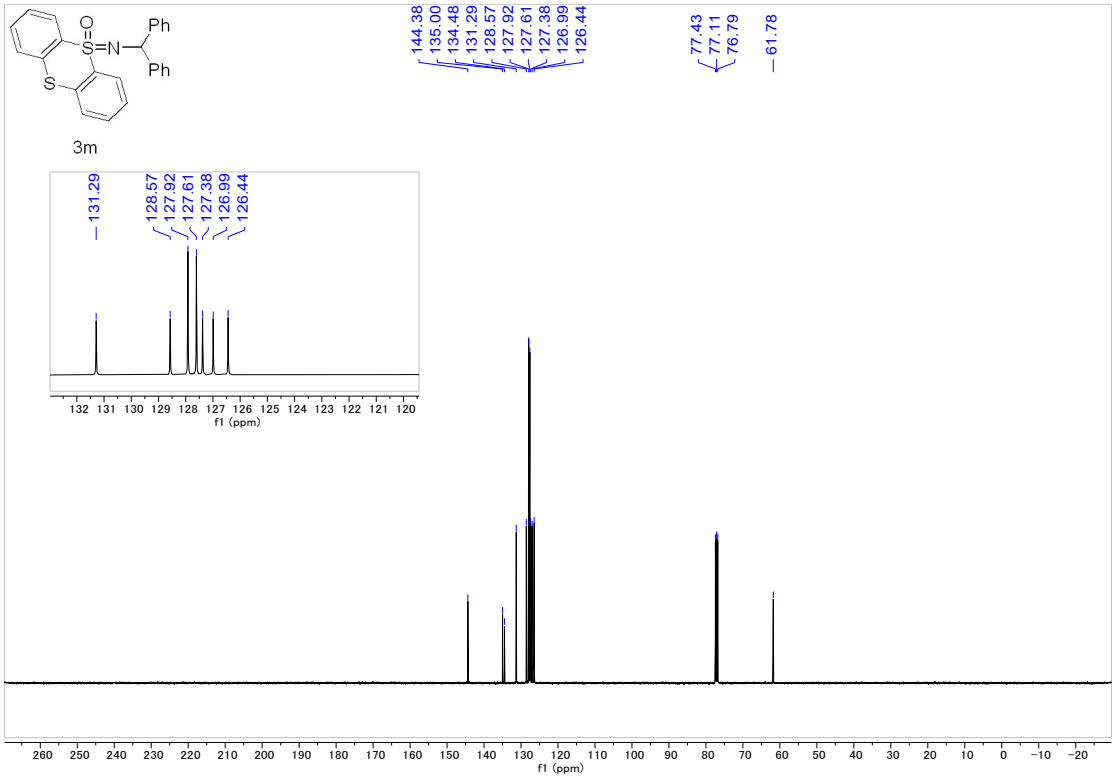
^{1}H NMR ($CDCl_3$, 400 MHz) of **3l**



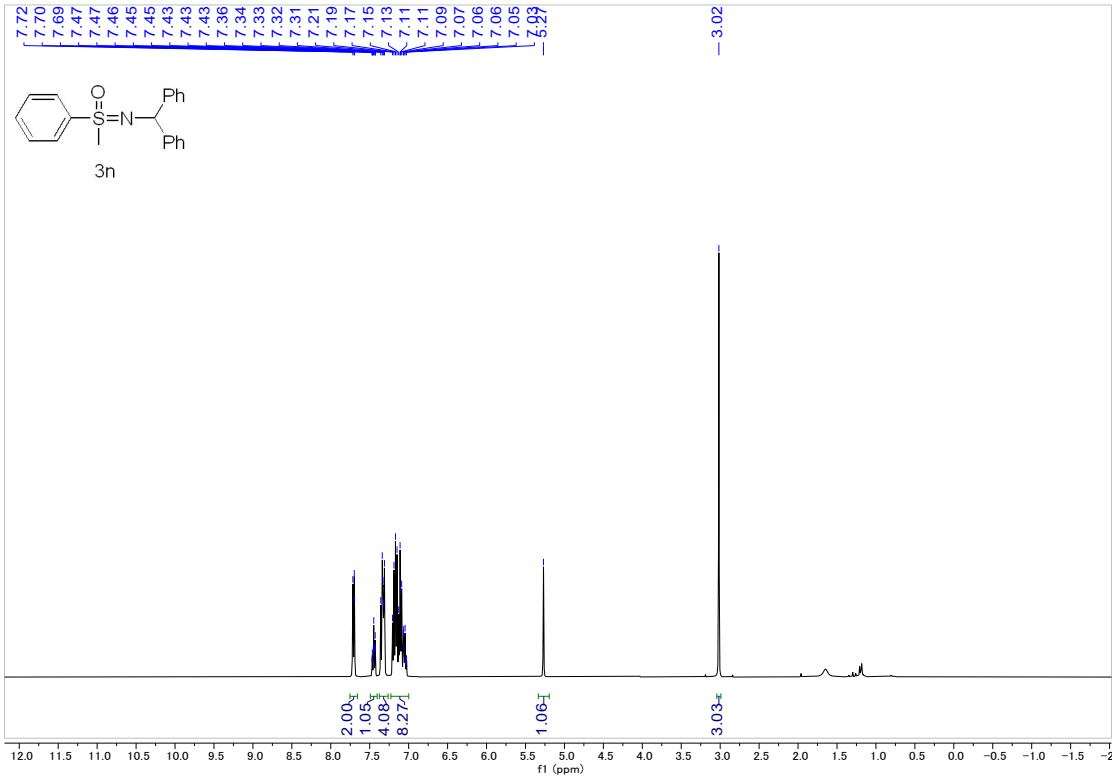
^{13}C NMR ($CDCl_3$, 100 MHz) of **3l**



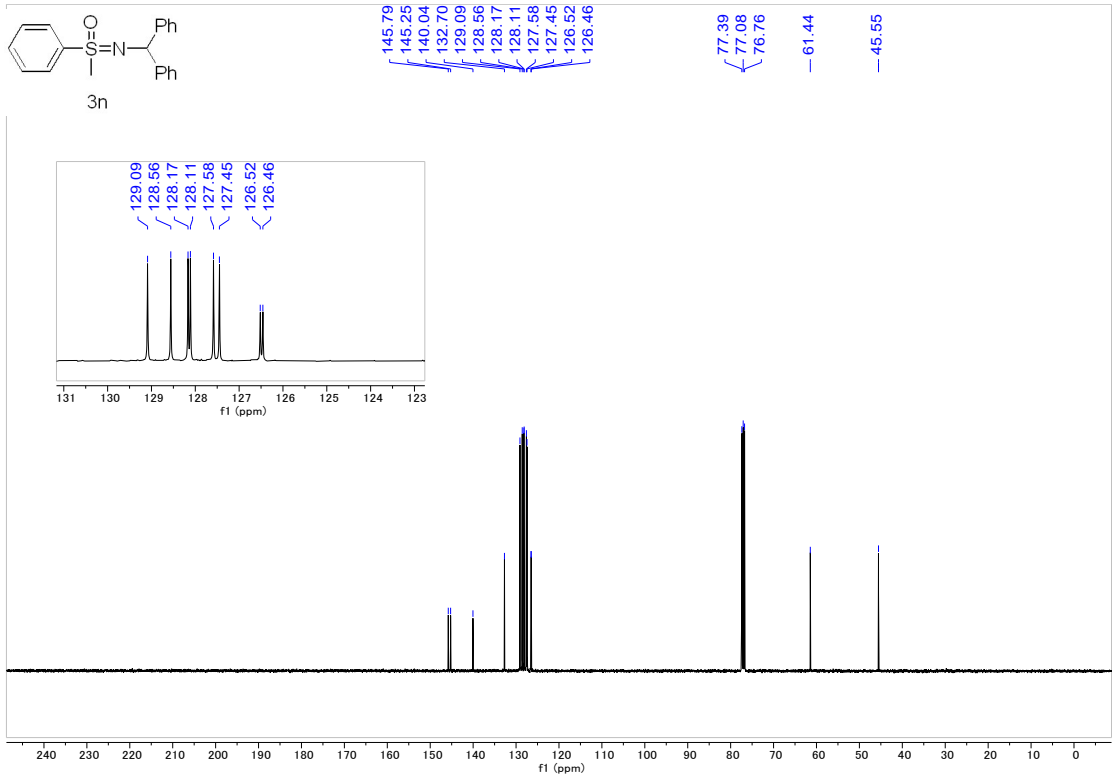
^{1}H NMR ($CDCl_3$, 400 MHz) of **3m**



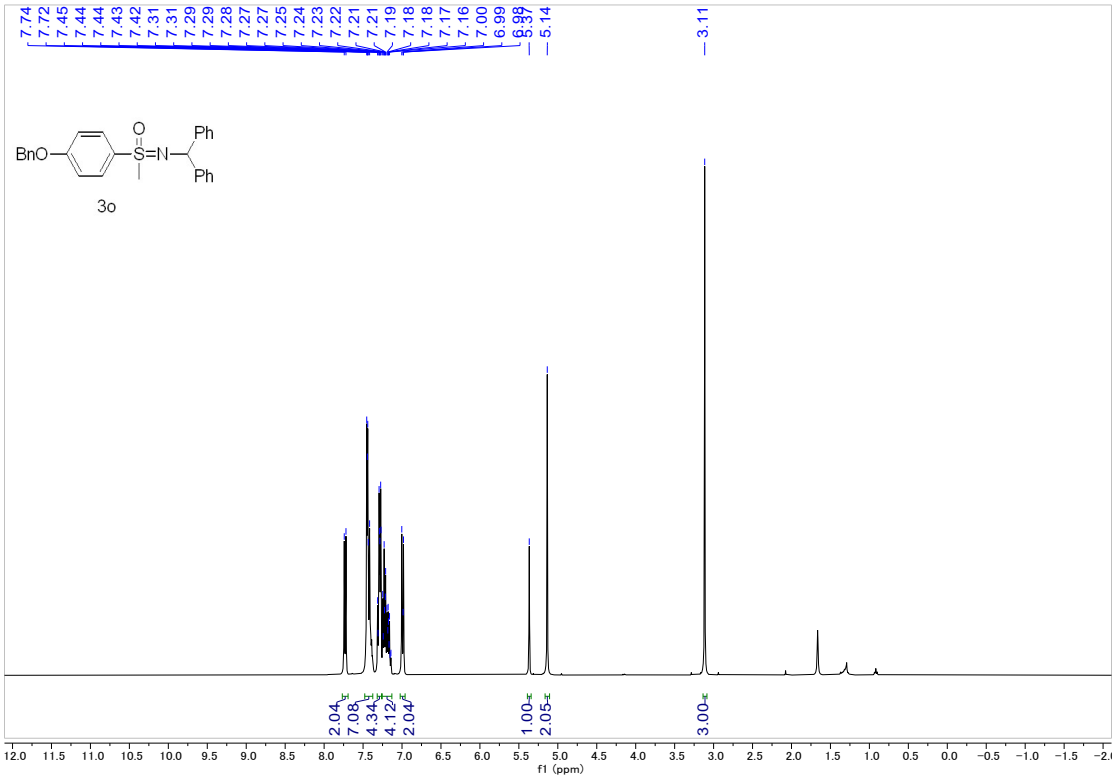
^{13}C NMR ($CDCl_3$, 100 MHz) of **3m**



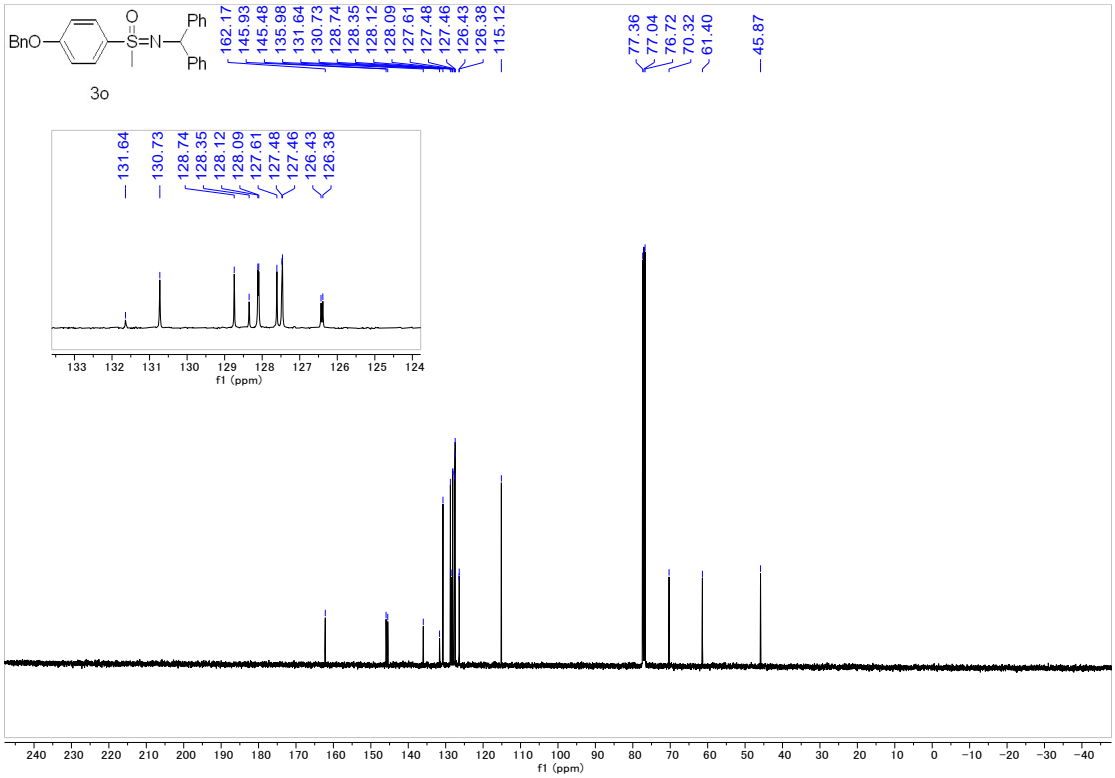
^{1}H NMR ($CDCl_3$, 400 MHz) of **3n**



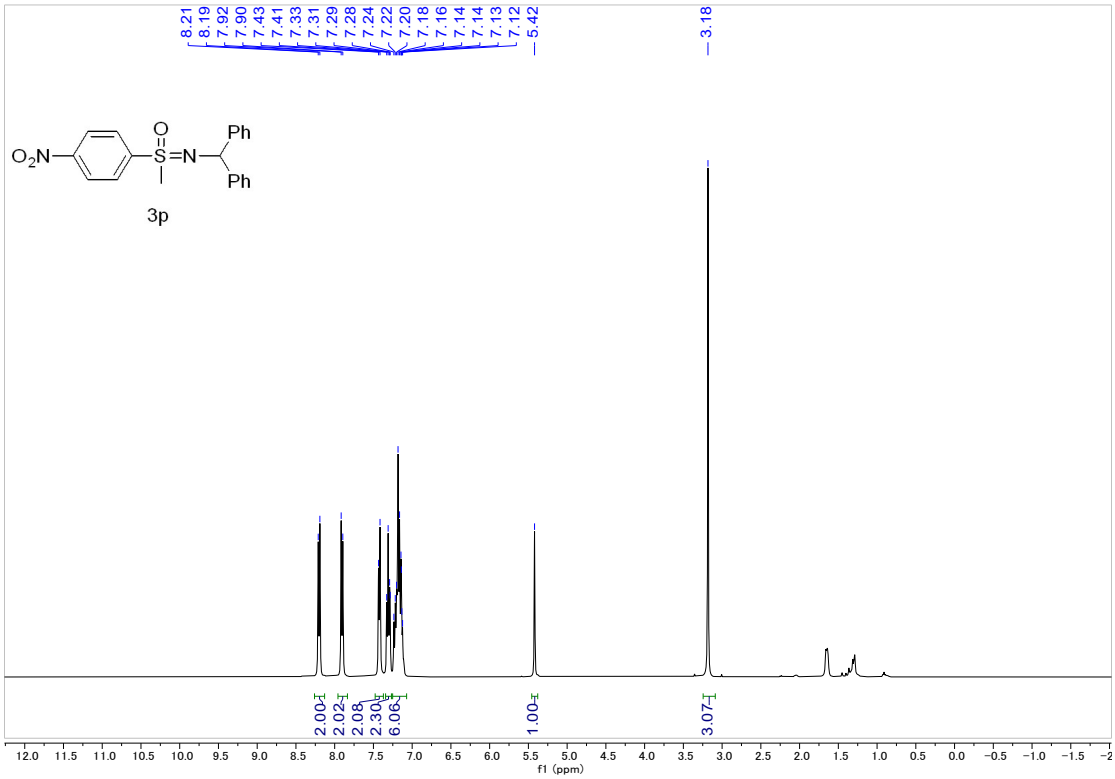
^{13}C NMR ($CDCl_3$, 100 MHz) of **3n**



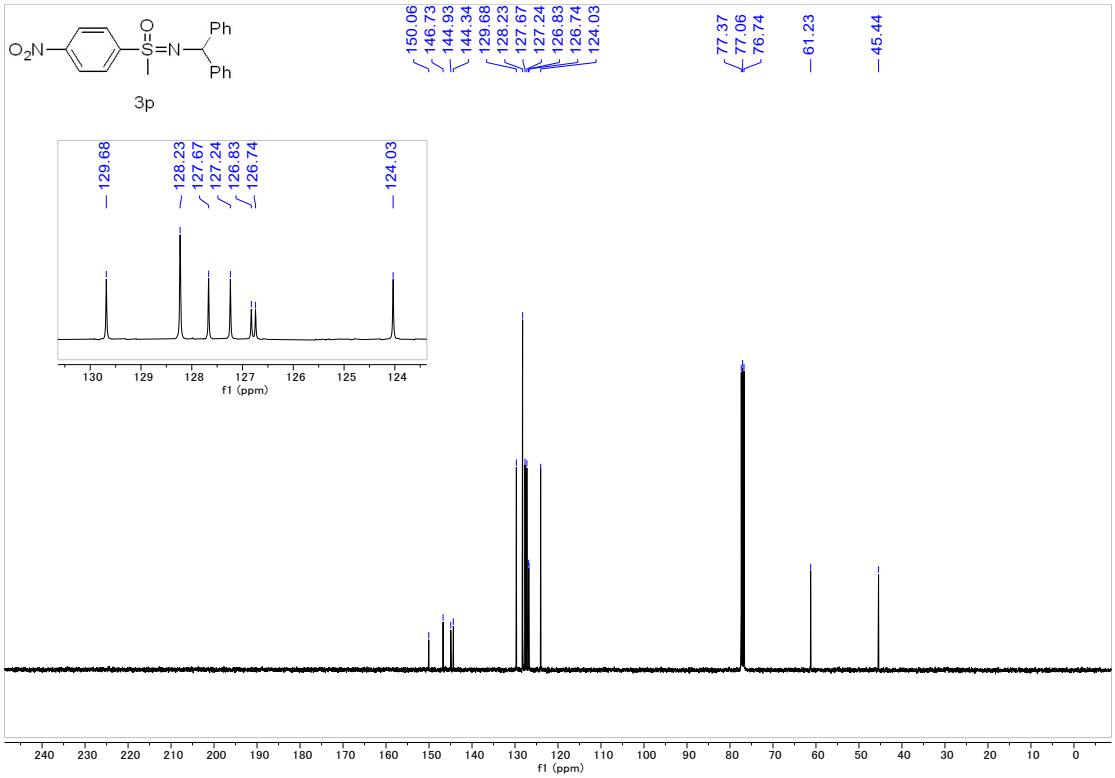
^{1}H NMR ($CDCl_3$, 400 MHz) of **3o**



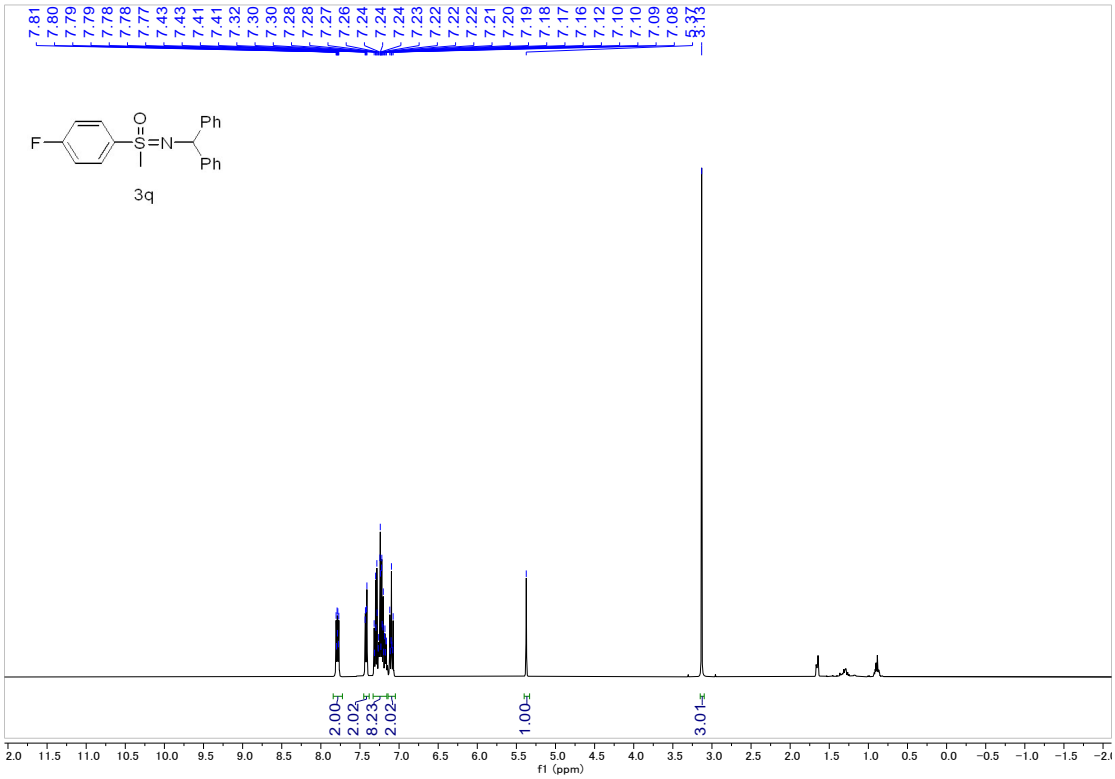
^{13}C NMR ($CDCl_3$, 100 MHz) of **3o**



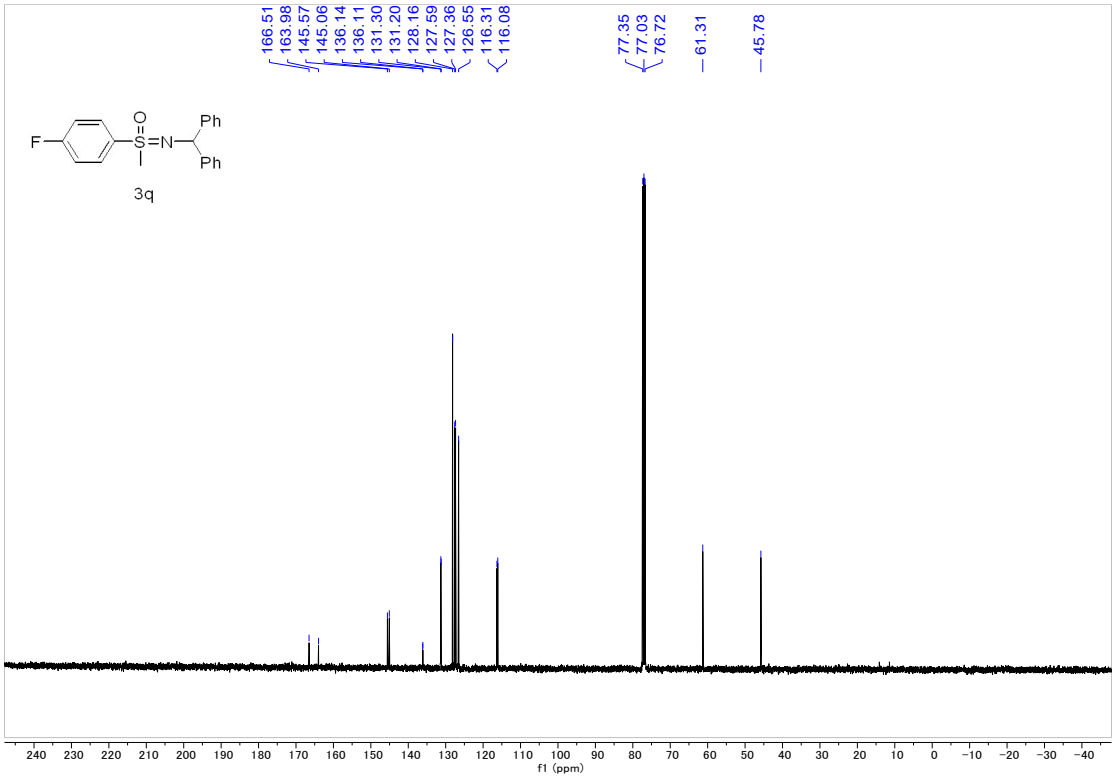
^{1}H NMR ($CDCl_3$, 400 MHz) of **3p**



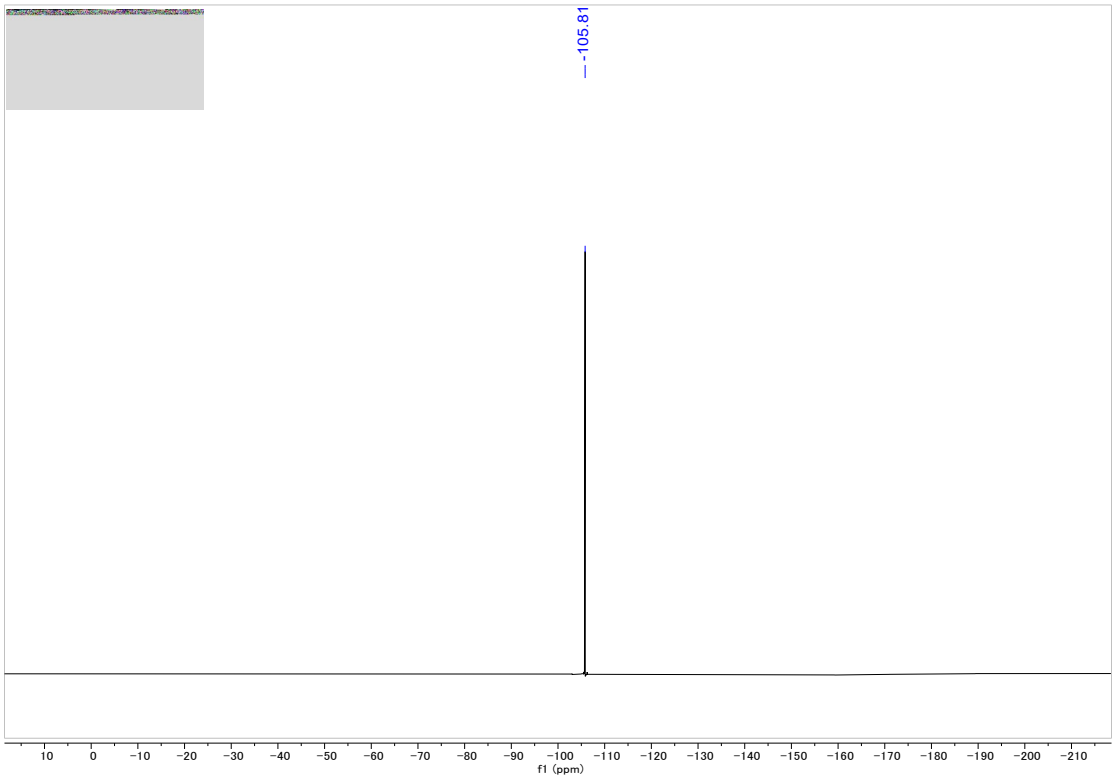
^{13}C NMR ($CDCl_3$, 100 MHz) of **3p**



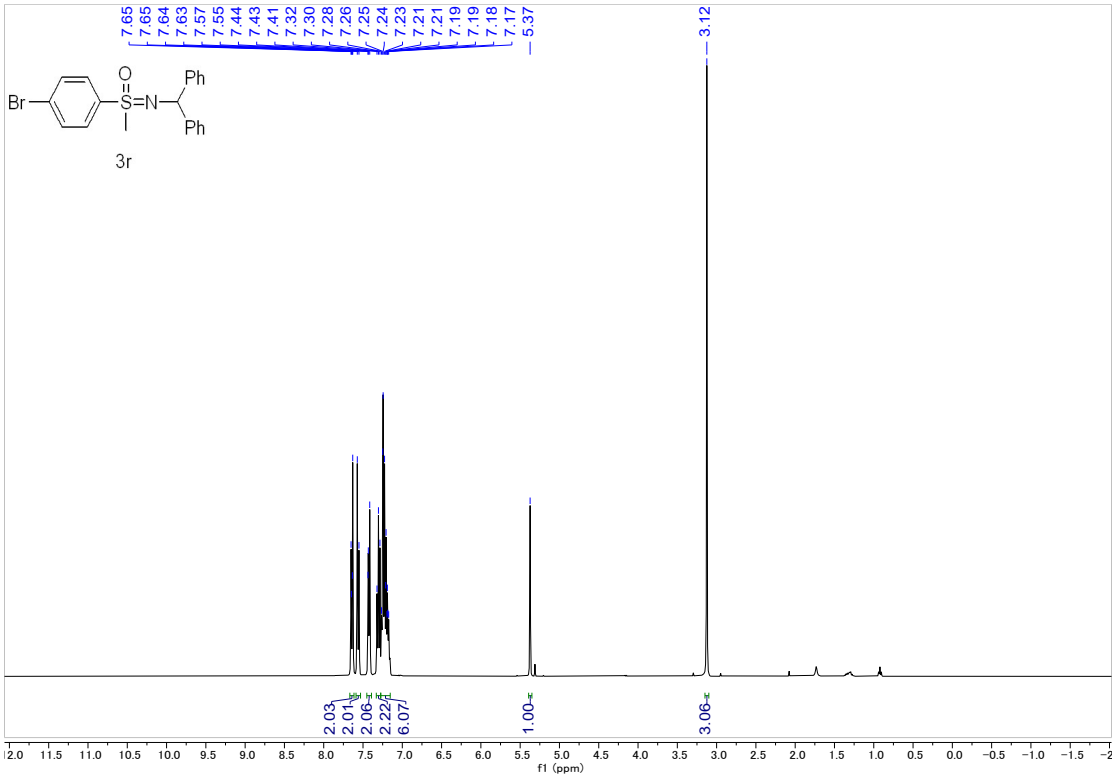
^{1}H NMR ($CDCl_3$, 400 MHz) of **3q**



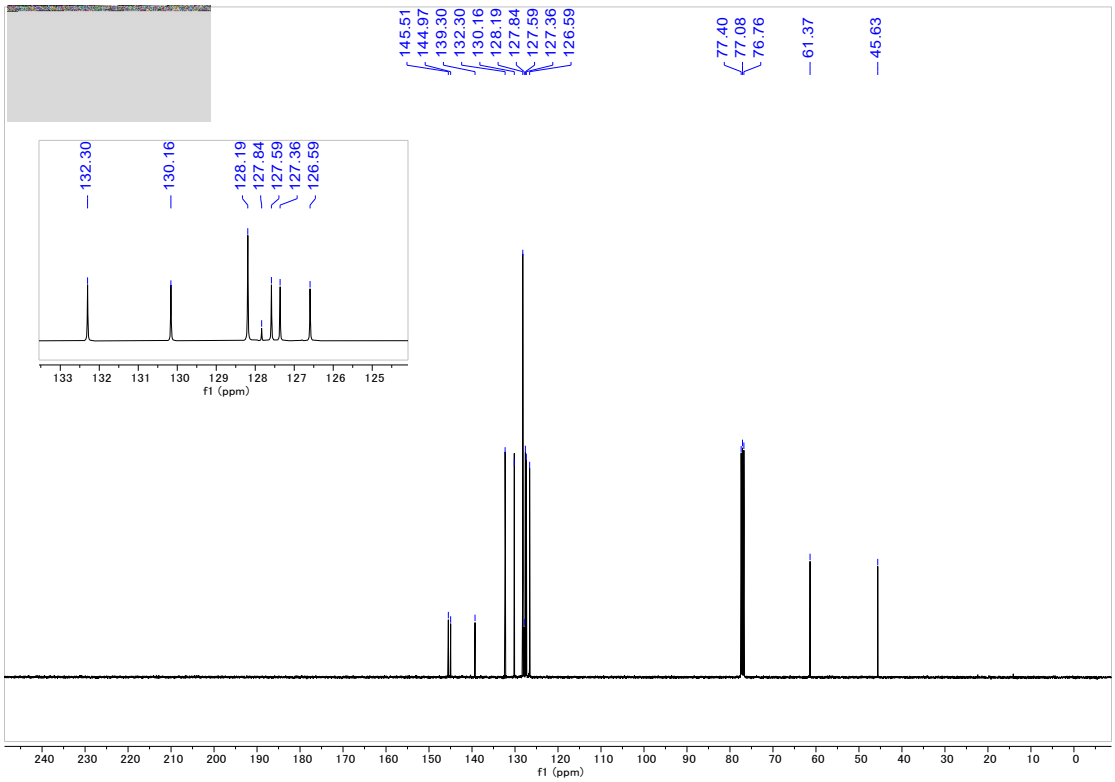
^{13}C NMR ($CDCl_3$, 100 MHz) of **3q**



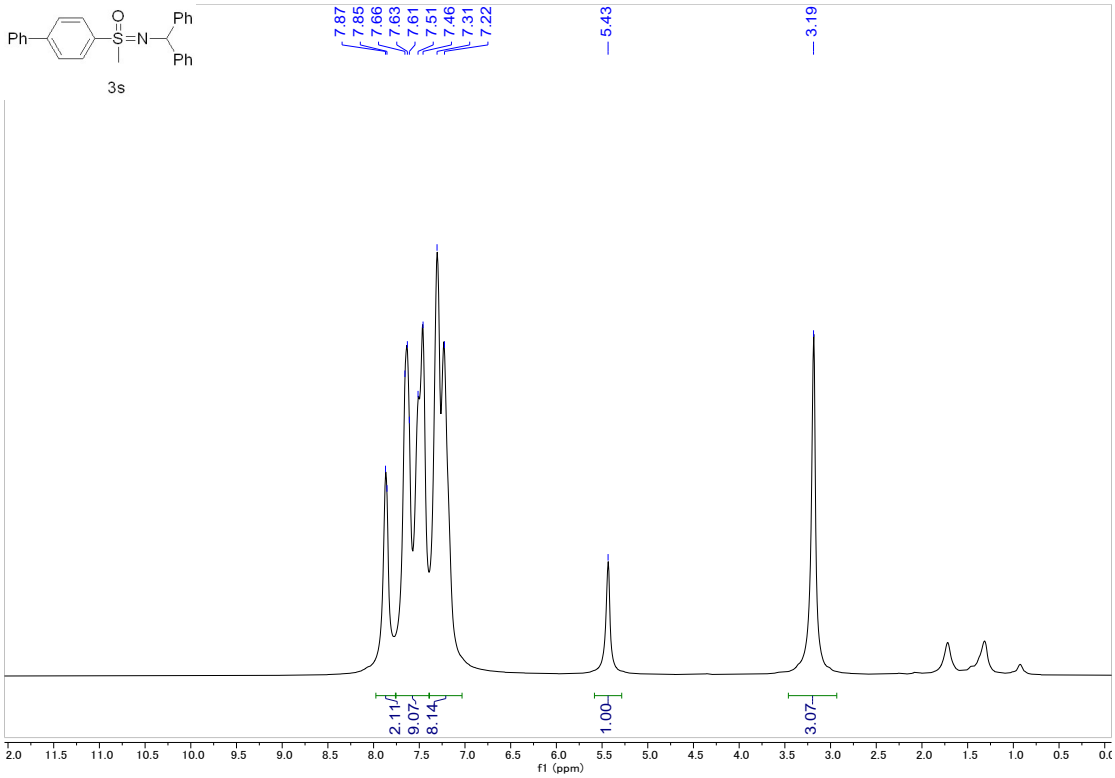
^{19}F NMR (376 MHz, CDCl3) of **3q**



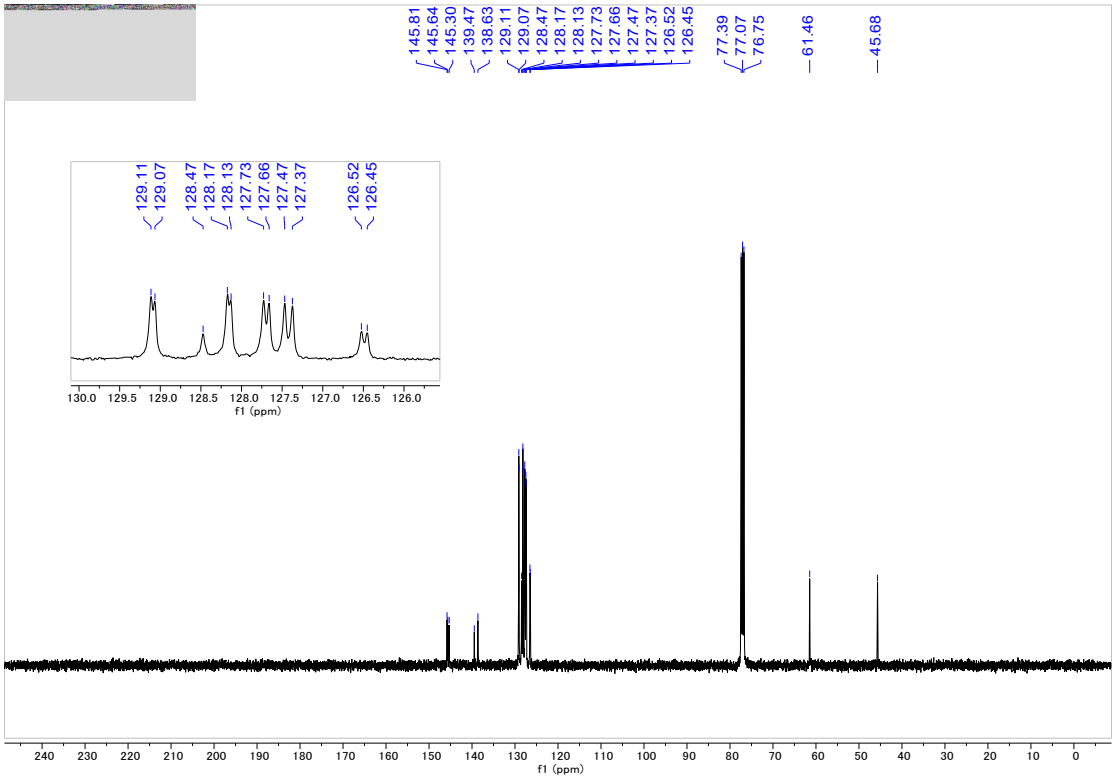
^{1}H NMR ($CDCl_3$, 400 MHz) of **3r**



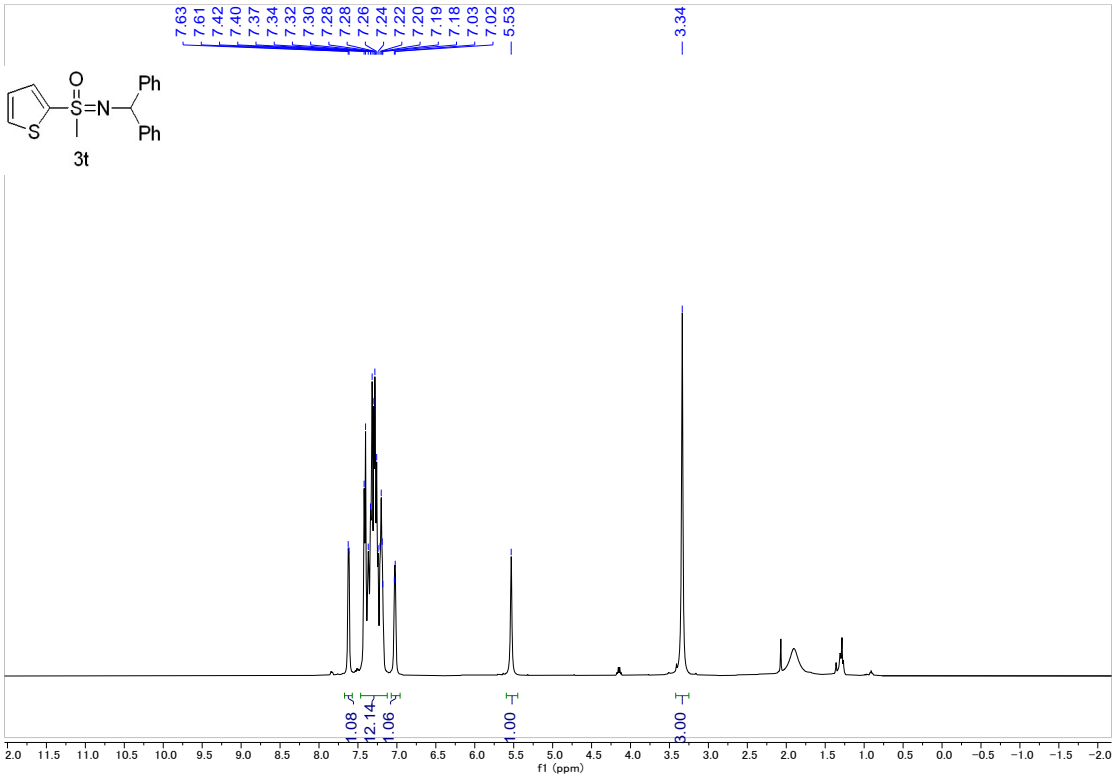
^{13}C NMR ($CDCl_3$, 100 MHz) of **3r**



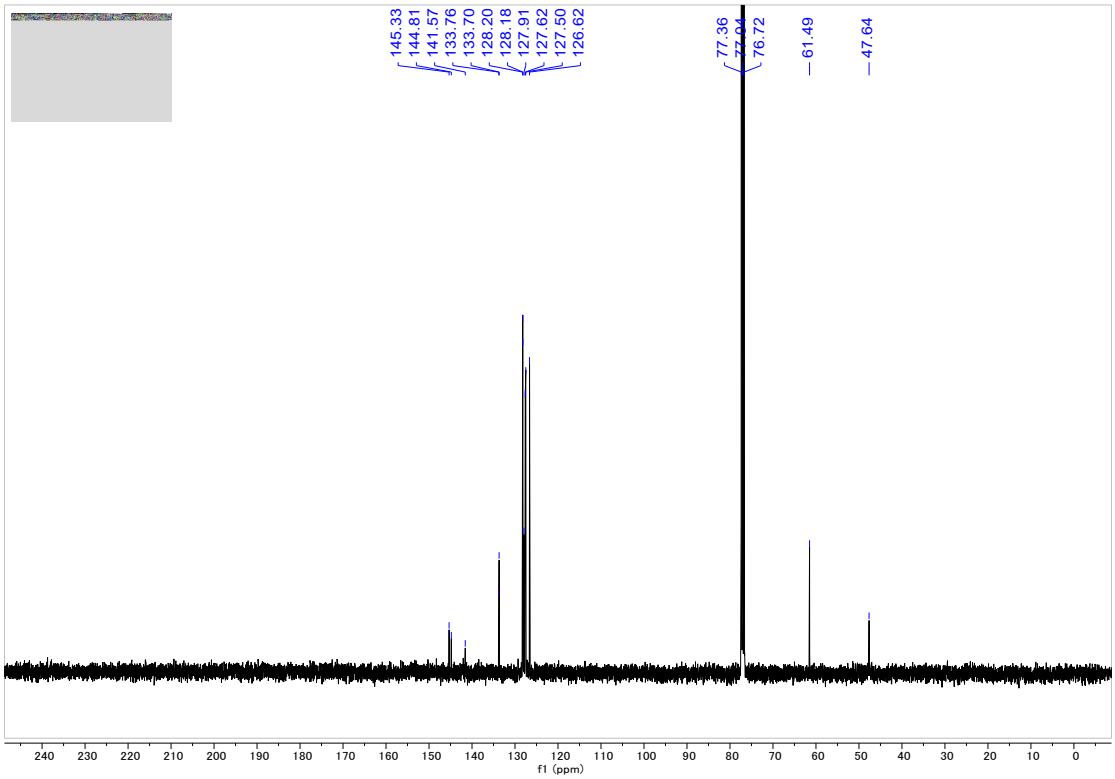
^{1}H NMR ($CDCl_3$, 400 MHz) of **3s**



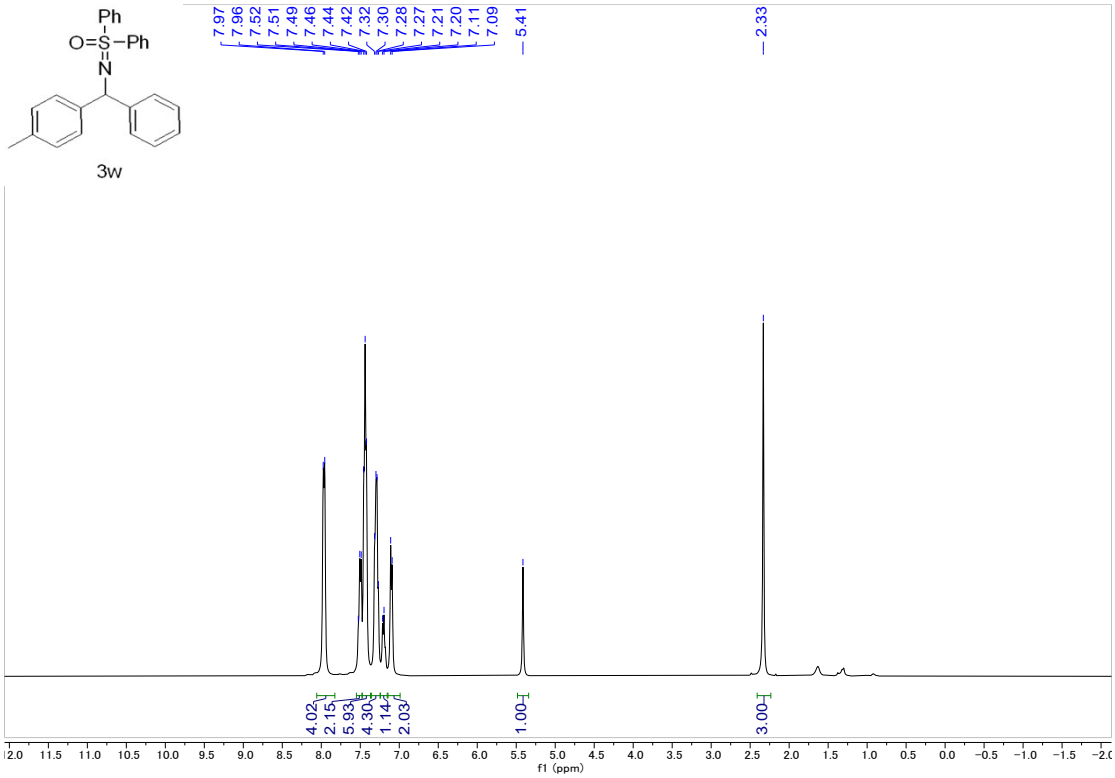
^{13}C NMR ($CDCl_3$, 100 MHz) of **3s**



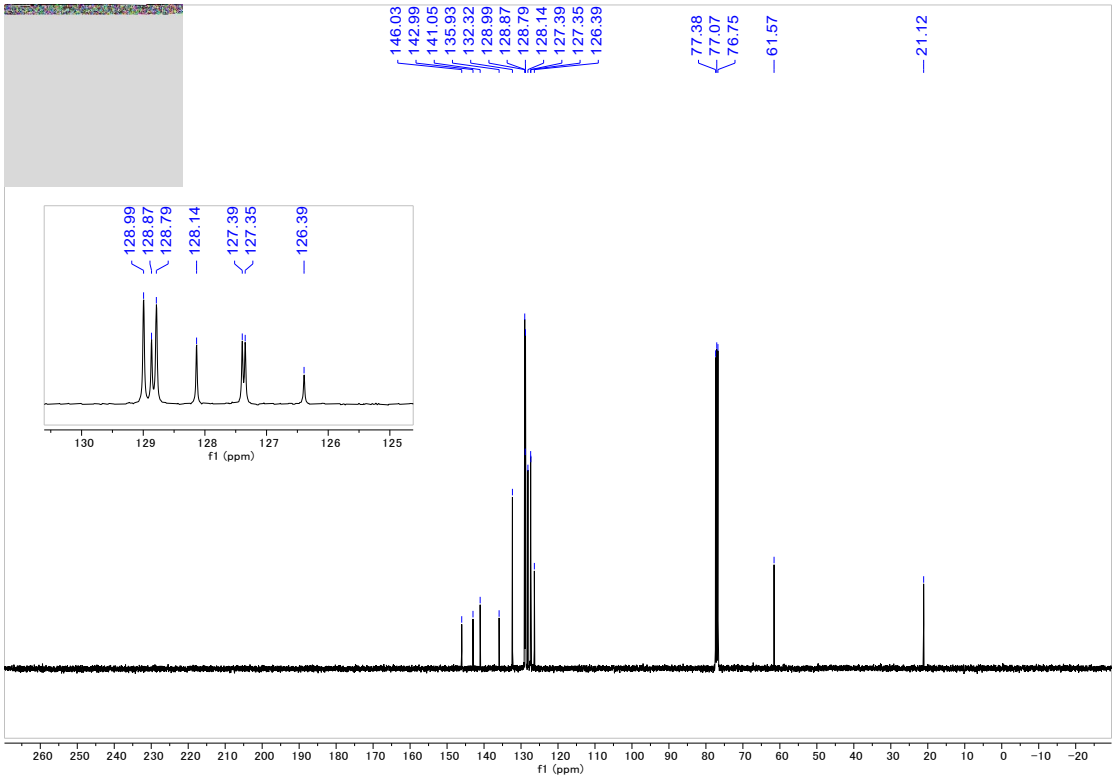
^{1}H NMR ($CDCl_3$, 400 MHz) of **3t**



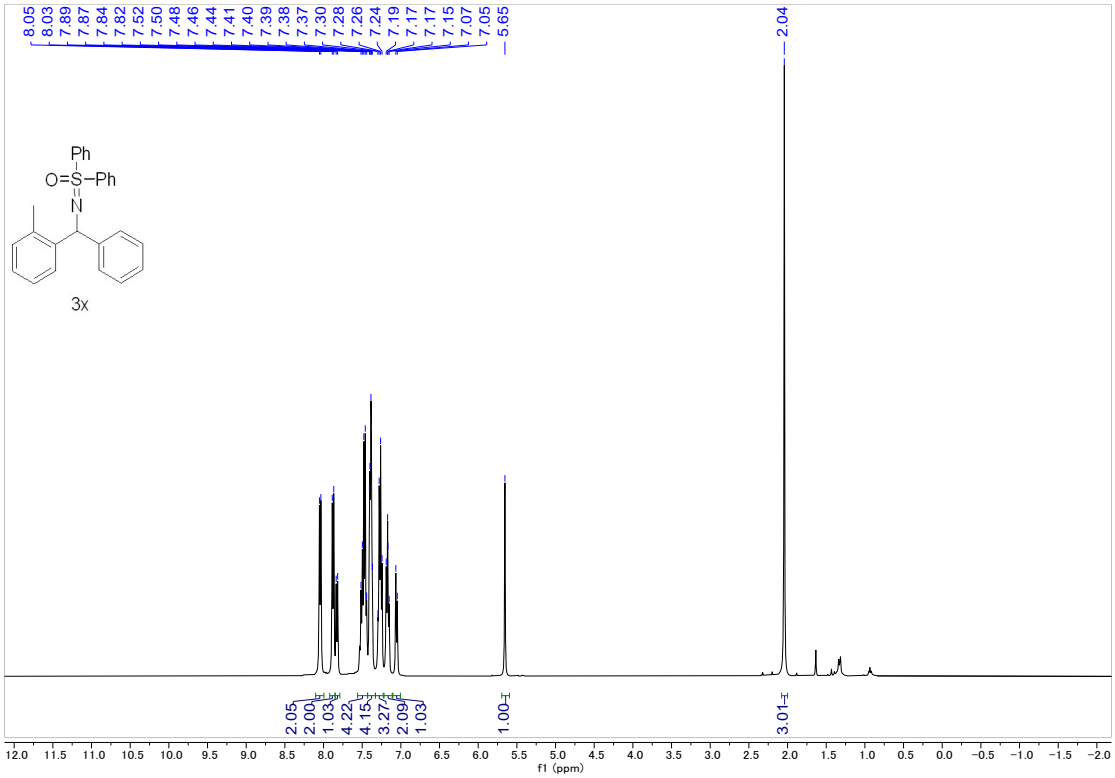
^{13}C NMR ($CDCl_3$, 100 MHz) of **3t**



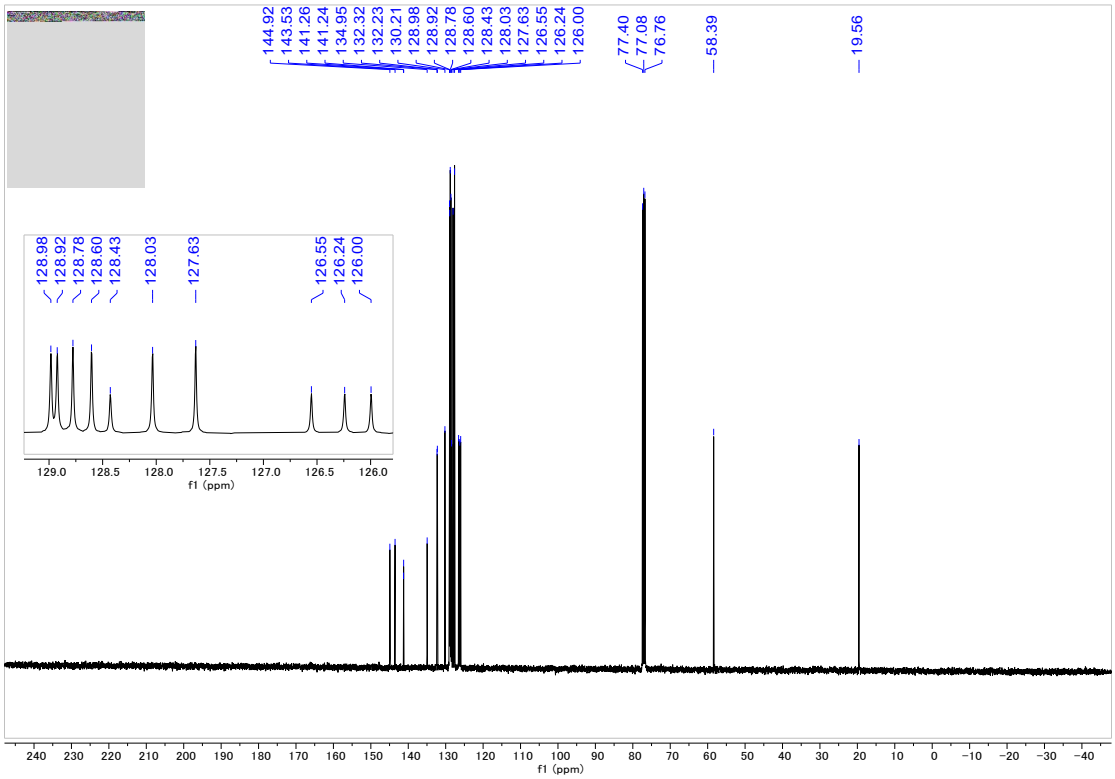
^{1}H NMR ($CDCl_3$, 400 MHz) of **3w**



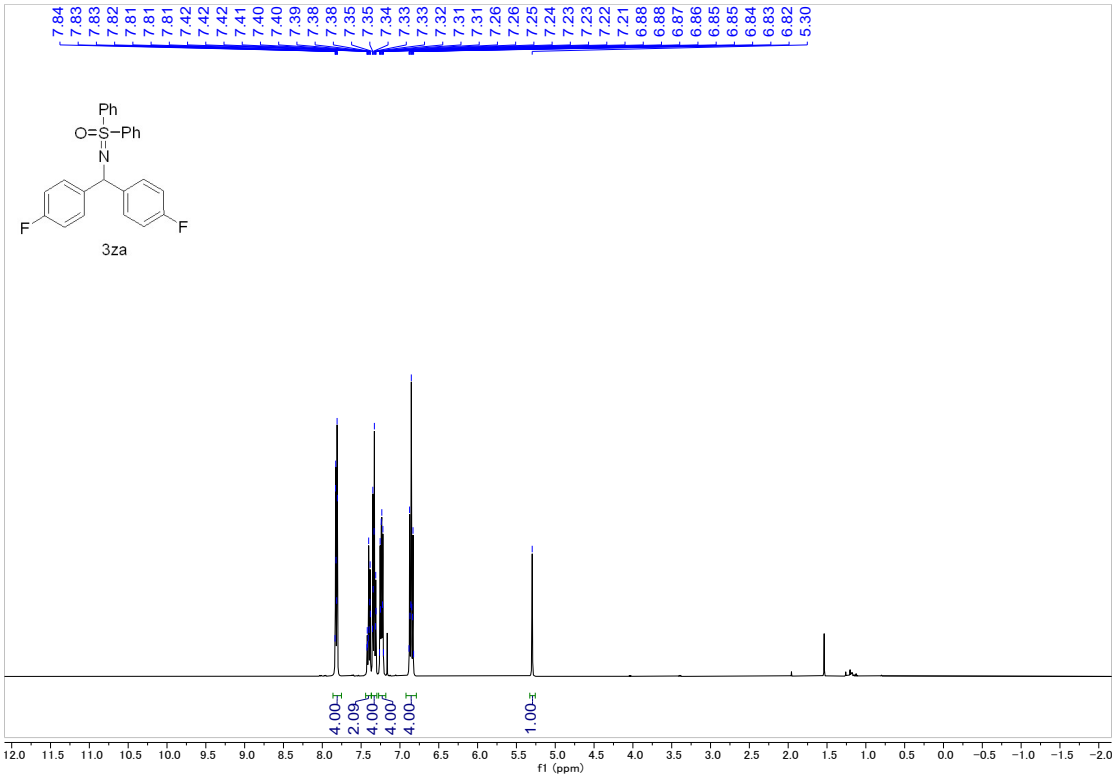
^{13}C NMR ($CDCl_3$, 100 MHz) of **3w**



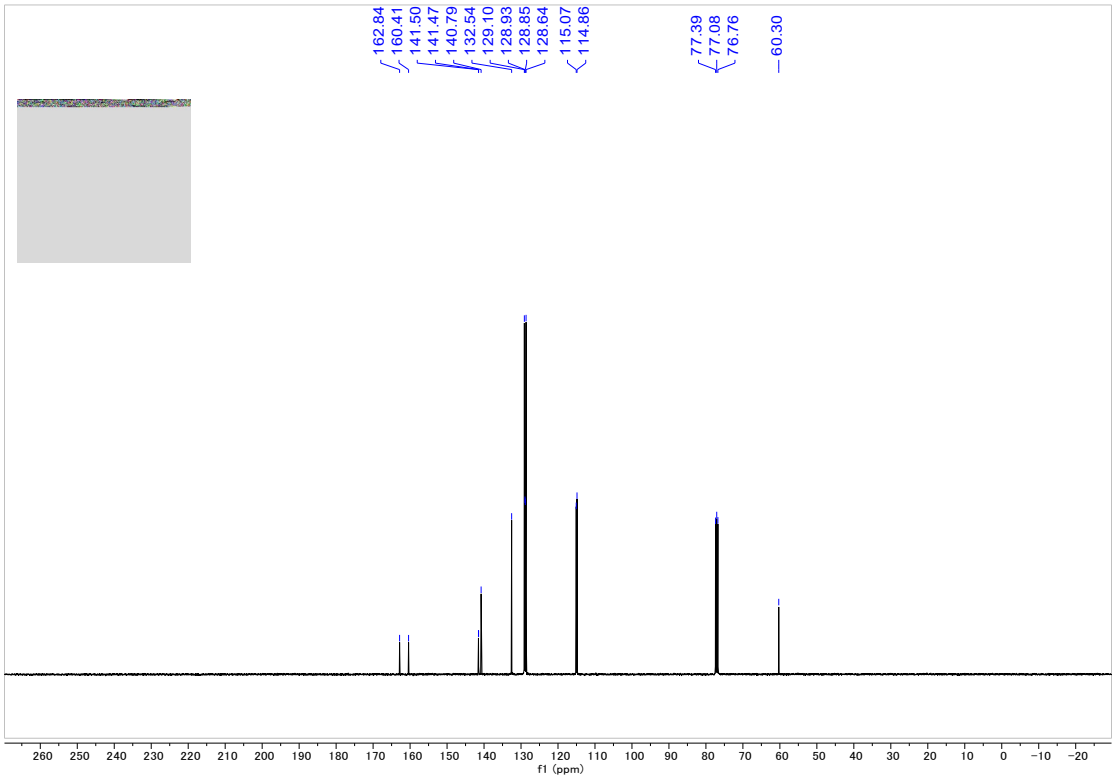
^{1}H NMR ($CDCl_3$, 400 MHz) of **3x**



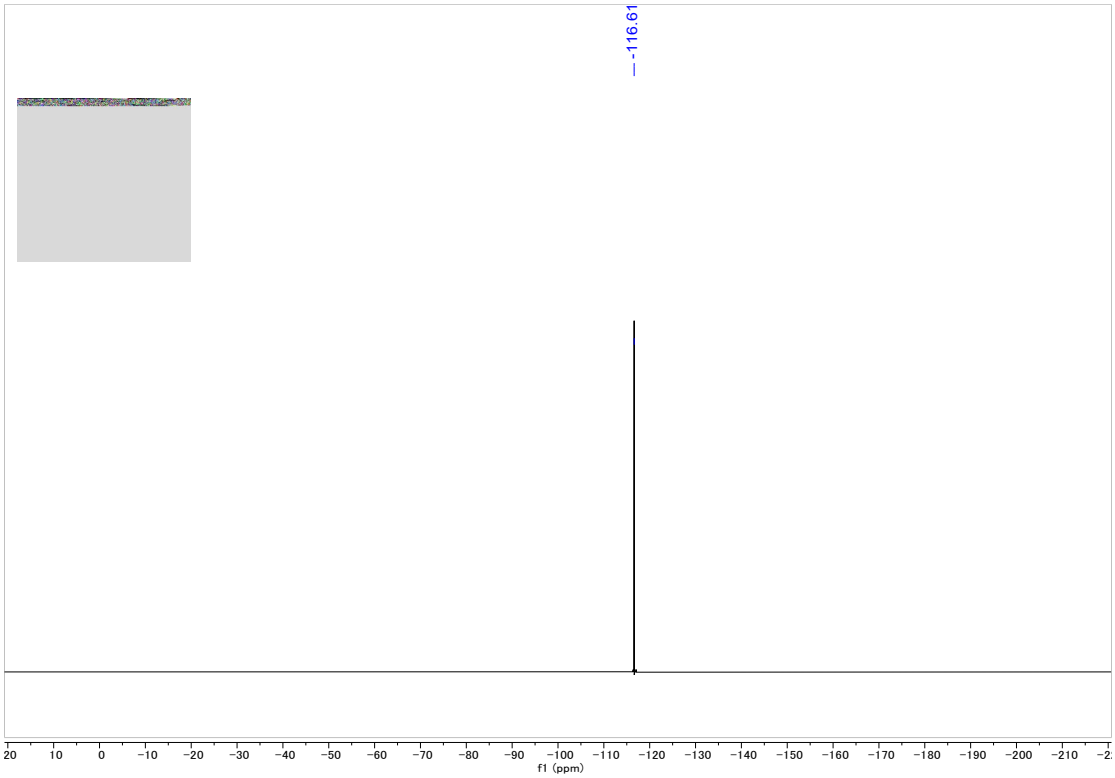
^{13}C NMR ($CDCl_3$, 100 MHz) of **3x**



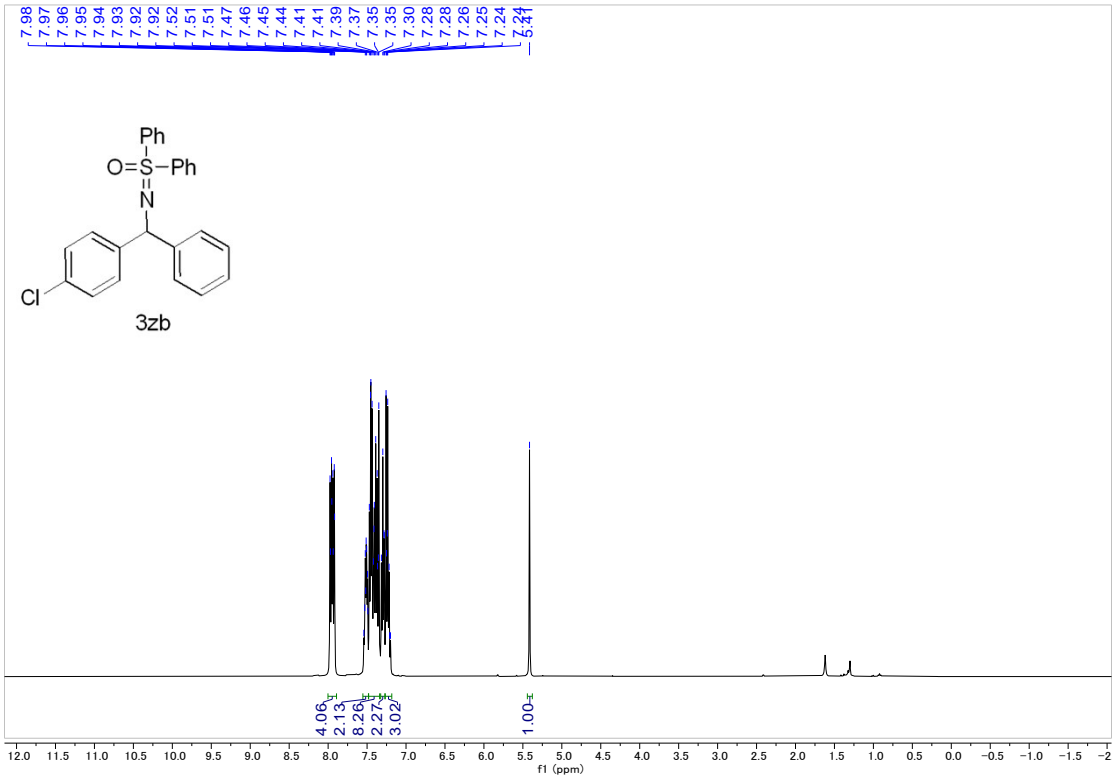
^{1}H NMR ($CDCl_3$, 400 MHz) of **3za**



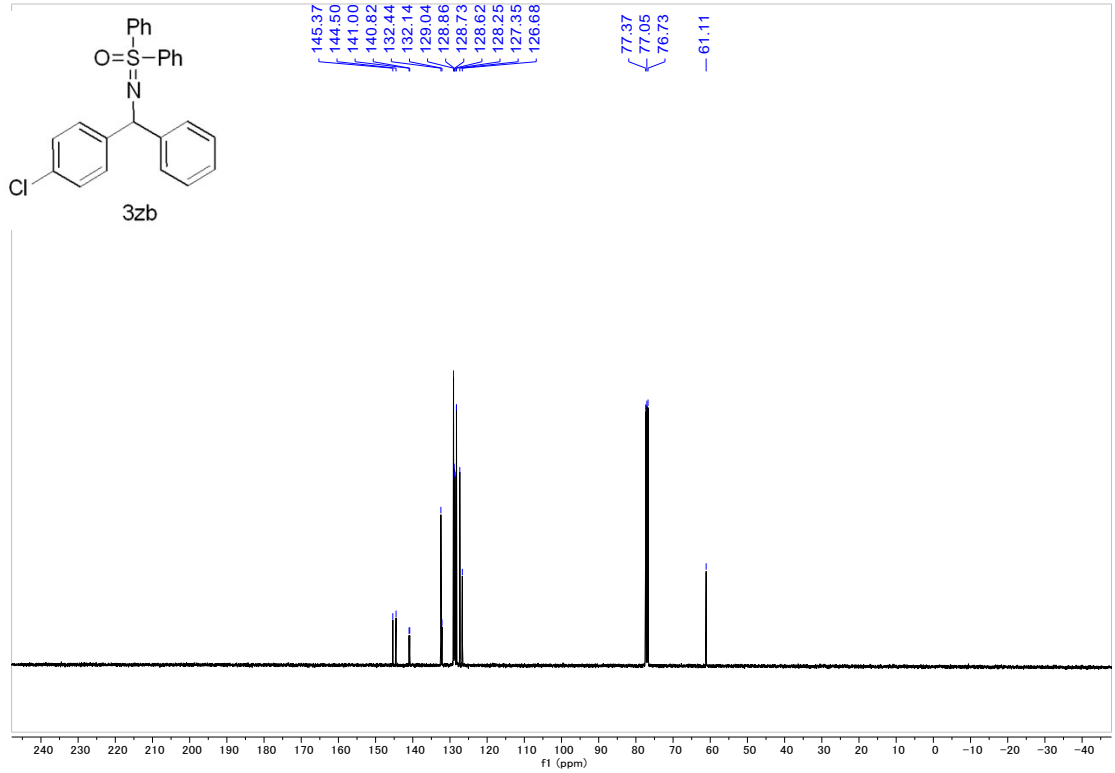
^{13}C NMR ($CDCl_3$, 100 MHz) of **3za**



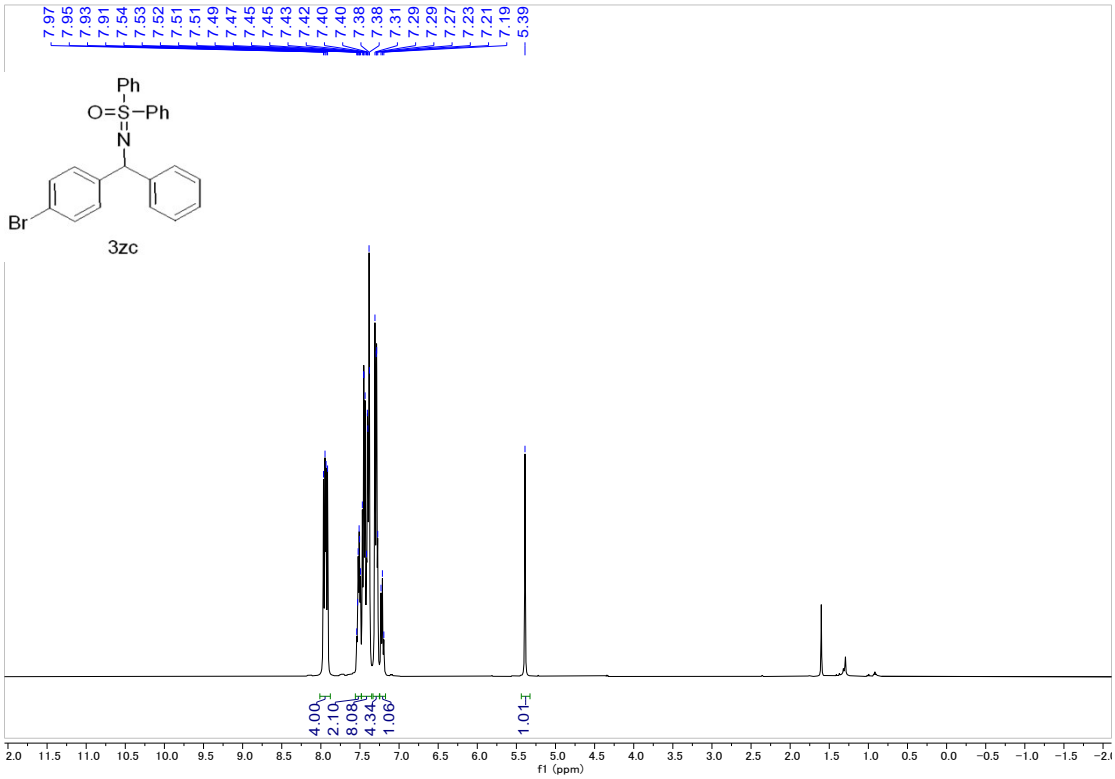
^{19}F NMR (376 MHz, CDCl3) of **3za**



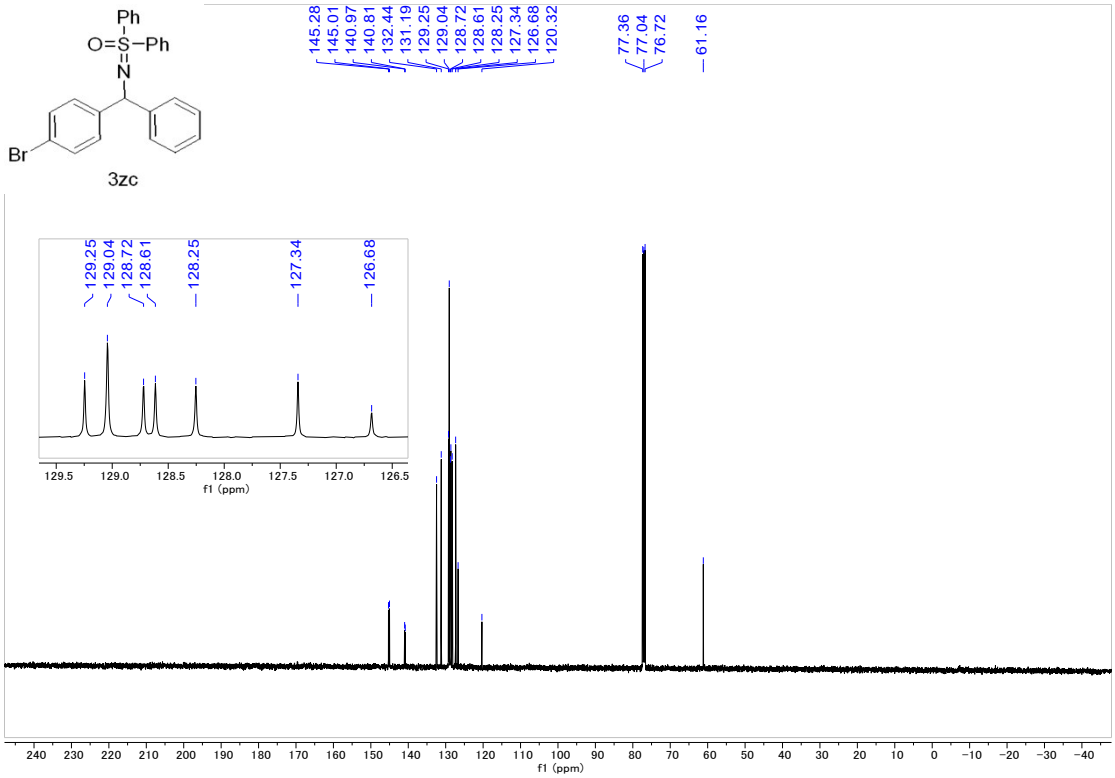
^{1}H NMR ($CDCl_3$, 400 MHz) of **3zb**



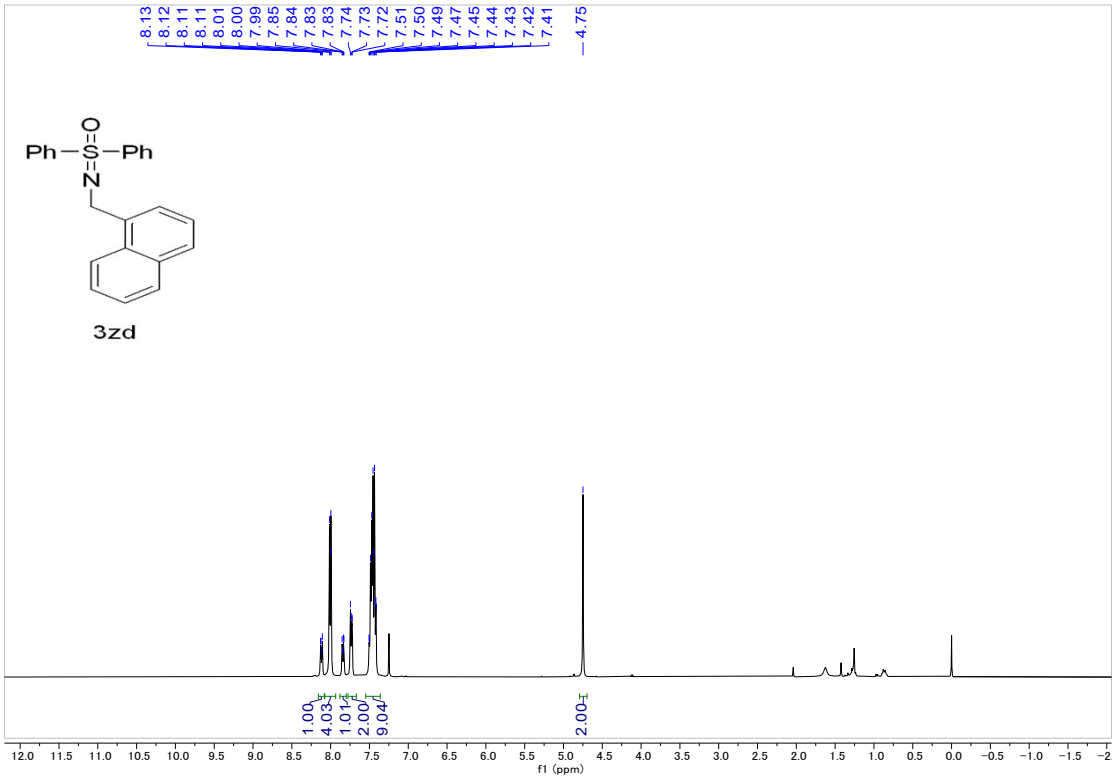
^{13}C NMR ($CDCl_3$, 100 MHz) of **3zb**



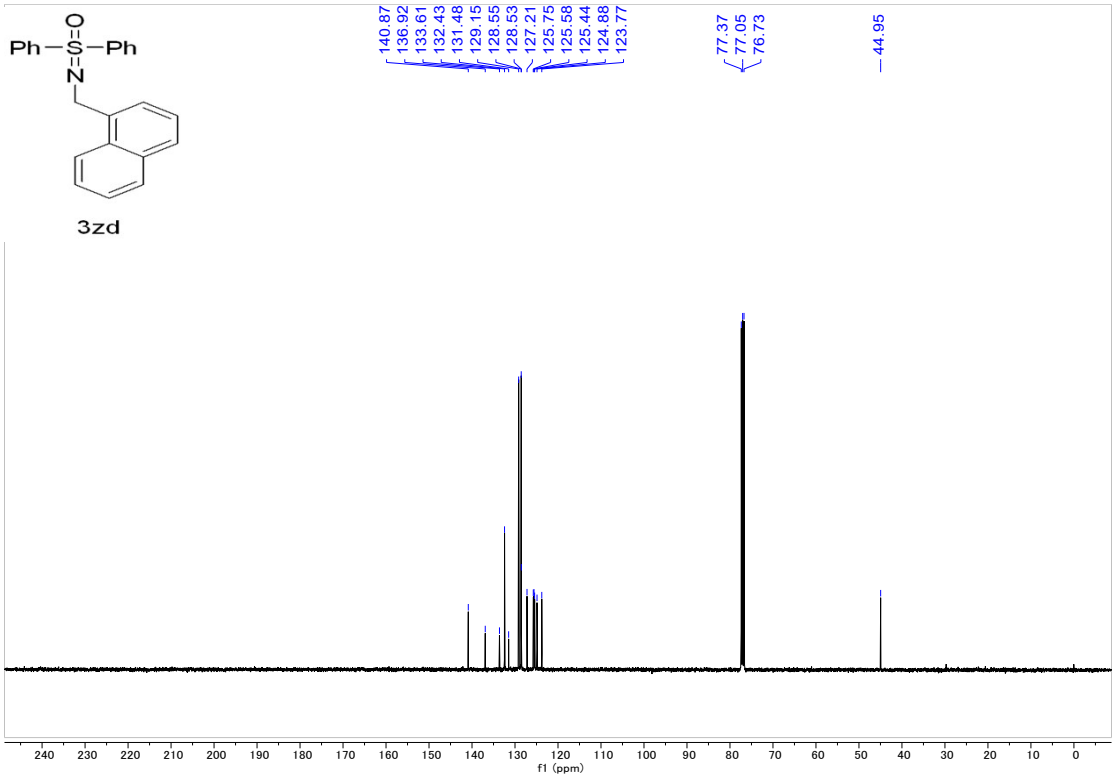
^{1}H NMR ($CDCl_3$, 400 MHz) of **3zc**



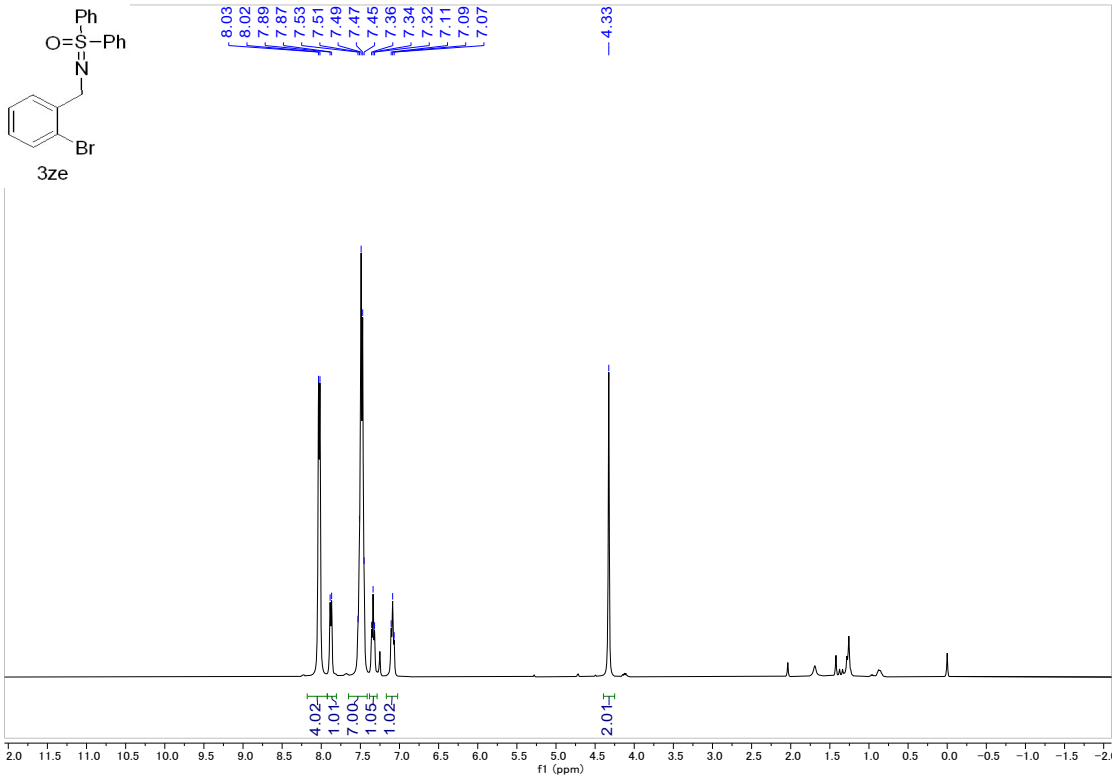
^{13}C NMR ($CDCl_3$, 100 MHz) of **3zc**



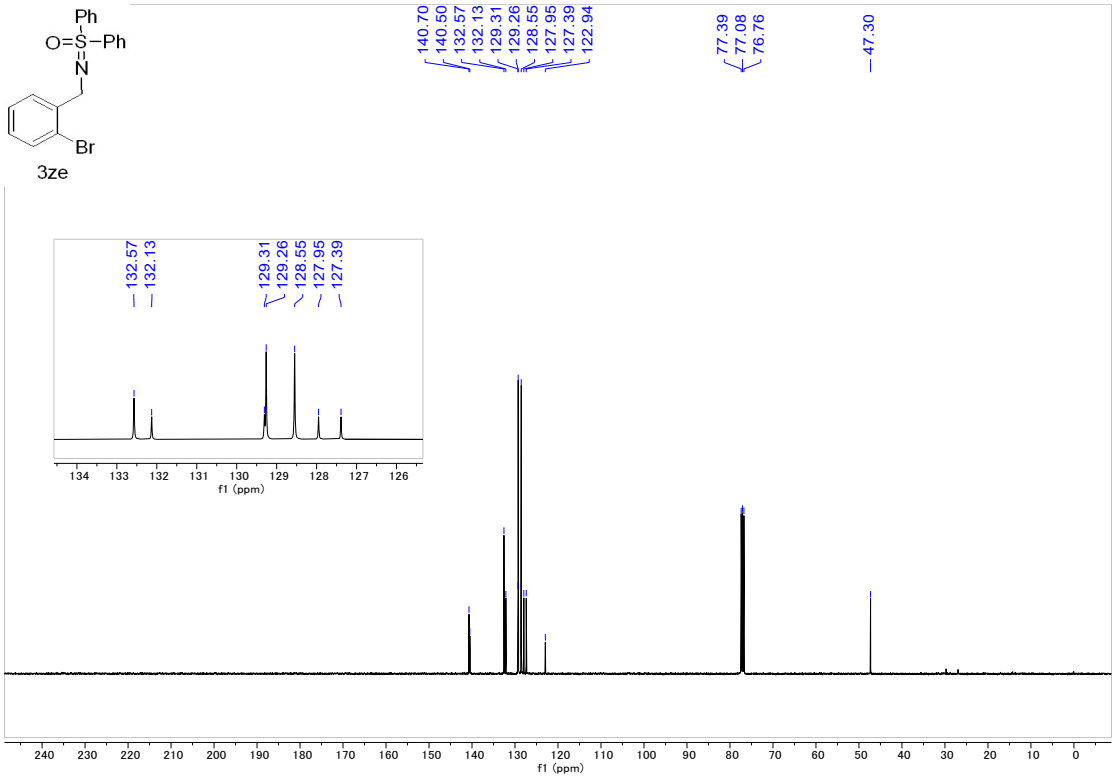
^{1}H NMR ($CDCl_3$, 400 MHz) of **3zd**



^{13}C NMR ($CDCl_3$, 100 MHz) of **3zd**



^{1}H NMR ($CDCl_3$, 400 MHz) of **3ze**



^{13}C NMR ($CDCl_3$, 100 MHz) of **3ze**