Supporting Information

for

Synthesis of 2-Isoxazoline *N*-Oxides by Copper-Mediated Radical Annulation of Alkenes with α-Nitrobenzyl Bromides

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1. General

Instrumentation

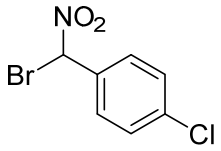
Glassware was dried in an oven (130 °C) and heated under reduced pressure before use. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. Silica gel column chromatography was carried out using Silica gel 60 N (spherical, neutral, 40–100 μm) from Kanto Chemicals Co., Ltd. NMR spectra (^1H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$) were recorded on Varian INOVA-600 (600 MHz), Mercury-400 (400 MHz), or 300-NMR ASW (300 MHz) spectrometers. Chemical shifts (δ) are in parts per million relative to $CDCl_3$ at 7.26 ppm for ^1H and at 77.16 ppm for $^{13}C\{^1H\}$, respectively. The $^{19}F\{^1H\}$ NMR spectra were measured by using CCl_3F (δ = 0.00 ppm) as an external standard. The NMR yields were determined by ^1H NMR spectra with dibromomethane as an internal standard. Infrared spectra were recorded on a SHIMADZU IRPrestige-21 spectrophotometer. HRMS analyses were obtained by using an ESI-TOF mass spectrometer (Burker micrOTOF). Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer. The experiments that require heating were carried out in a heat block. The reaction under microwave irradiation was carried out in a 5-mL glass pressure vial, which is a commercially available vial using a focused microwave unit (Biotage Initiator). It took 7 min to reach 250 °C. After reaching the indicated temperature, controlled microwave irradiation started and continued for 1 h, keeping the reaction temperature constant.

Chemicals

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Copper(II) hydroxide was purchased from FUJIFILM Wako Pure Chemical Corporation. Dimethyl sulfoxide was obtained from Kanto Chemical Co., Inc. Alkenes **1** were purchased from commercial suppliers. Bromides **2** were prepared according to the literature[1] and showed the identical spectra reported.

2. Experimental Procedures and Spectroscopic Data for the New Compounds

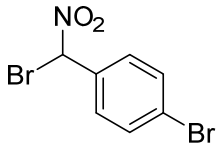
4-Chloro[bromo(nitro)methyl]benzene (2d)



2d

The compound **2d** was prepared as a colorless oil according to the literature (1.03 g, 96%).[1] R_f = 0.27 (hexane/ ethyl acetate = 15:1). IR (neat): 3019 (w), 2899 (w), 1566 (s), 1346 (s), 1207 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.62-7.58 (m, 2H), 7.45-7.41 (m, 2H), 6.86 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 137.9, 131.4, 129.8, 129.6, 79.5. Calcd for $C_7H_5BrClNO_2$: C, 33.57; H, 2.01; N, 5.59. Found: C, 33.51; H, 1.76; N, 5.50.

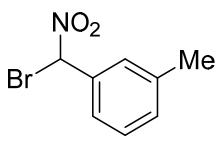
4-Bromo[bromo(nitro)methyl]benzene (2e)



2e

The compound **2e** was prepared as a colorless oil according to the literature (432 mg, 38%).[1] R_f = 0.24 (hexane/ dichloromethane = 5:1). IR (neat): 3019 (w), 2897 (w), 1566 (s), 1344 (s), 1206 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 7.61-7.58 (m, 2H), 7.55-7.51 (m, 2H), 6.85 (s, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 132.6, 131.9, 130.0, 126.2, 79.6. Calcd for $C_7H_5Br_2NO_2$: C, 28.51; H, 1.71; N, 4.75. Found: C, 28.32; H, 1.51; N, 4.59.

3-Methyl[bromo(nitro)methyl]benzene (2f)

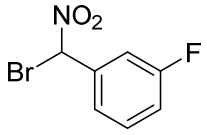


2f

The compound **2f** was prepared as a colorless oil according to the literature (1.16 g, 69%).[1] R_f = 0.31 (hexane/chloroform = 3:1). IR (neat):3021 (m), 2922 (m), 1566 (s), 1348 (s), 1190 (m) cm^{-1}. ^1H NMR

(400 MHz, $CDCl_3$, rt): δ 7.44 (d, J = 9.2 Hz, 2H), 7.35-7.27 (m, 2H), 6.87 (s, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 139.4, 132.9, 132.3, 129.2, 128.8, 125.4, 80.7, 21.4. Calcd for $C_8H_8BrNO_2$: C, 41.77; H, 3.51; N, 6.09. Found: C, 41.71; H, 3.43; N, 6.04.

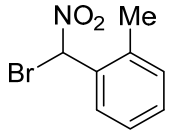
3-Fluoro[bromo(nitro)methyl]benzene (2g)



2g

The compound **2g** was prepared as a colorless oil according to the literature (671 mg, 61%).[1] R_f = 0.33 (hexane/ethyl acetate = 10:1). IR (neat): 3073 (w), 3022 (w), 2903 (w), 1568 (s), 1348 (s), 1267 (s) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, rt): δ 7.44-7.40 (m, 3H), 7.20-7.17 (m, 1H), 6.88 (s, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 162.8 (d, $^1J_{C–F}$ = 250 Hz), 134.9 (d, $^3J_{C–F}$ = 8.1 Hz), 131.0 (d, $^3J_{C–F}$ = 8.0 Hz), 124.1 (d, $^4J_{C–F}$ = 3.2 Hz), 118.8 (d, $^2J_{C–F}$ = 22 Hz), 115.8 (d, $^2J_{C–F}$ = 24 Hz), 79.4 (d, $^4J_{C–F}$ = 1.5 Hz); $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, rt): δ –110.3. Calcd for $C_7H_5BrFNO_2$: C, 35.93; H, 2.15; N, 5.99. Found: C, 35.90; H, 2.07; N, 5.91.

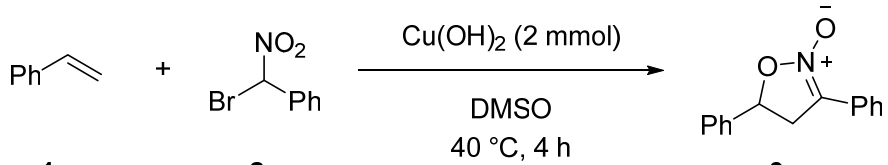
2-Methyl[bromo(nitro)methyl]benzene (2h)



2h

The compound **2h** was prepared as a colorless oil according to the literature (1.23 g, 77%).[1] R_f = 0.27 (hexane/chloroform = 3:1). IR (neat): 3030 (w), 2905 (w), 1566 (s), 1348 (m), 1206 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.70 (dd, J = 7.6, 1.6 Hz, 1H), 7.38-7.29 (m, 2H), 7.23-7.21 (m, 2H), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 136.1, 131.8, 131.3, 131.1, 128.4, 127.5, 78.1, 19.2. Calcd for $C_8H_8BrNO_2$: C, 41.77; H, 3.51; N, 6.09. Found: C, 41.57; H, 3.40; N, 6.05.

A Typical Procedure for Copper-Mediated Annulation of Alkenes with *α*-Nitrobenzyl Bromides: Synthesis of 3,5-Diphenyl-2-isoxazoline *N*-Oxide (3aa)

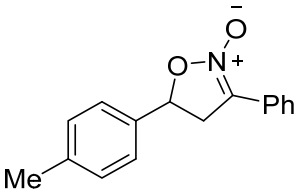


1a (2.4 mmol) **2a** (2 mmol) **3aa**

Under an argon atmosphere, copper(II) hydroxide (195 mg, 2 mmol) was placed in a 20-mL Schlenk tube. Dimethyl sulfoxide (DMSO, 2.5 mL) was then added, followed by the addition of styrene (**1a**, 250 mg, 2.4 mmol) and [bromo(nitro)methyl]benzene (**2a**, 432 mg, 2 mmol) at room temperature. The mixture was stirred at 40 °C for 4 h in a heat block. After the mixture was cooled to room temperature, water (50 mL) was added to the mixture. The mixture was extracted with ethyl acetate (10 mL) three times. The combined organic layers were washed with brine (50 mL) and dried over anhydrous sodium sulfate. After the volatiles were evaporated, the resulting residue was purified by silica gel column chromatography (toluene) to provide **3aa** as white solid (358 mg, 1.50 mmol, 75%).

R_f = 0.23 (toluene). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.96-7.93 (m, 2H), 7.49-7.37 (m, 8H), 5.75 (dd, J = 9.6, 7.6 Hz, 1H), 3.94 (dd, J = 16.4, 9.6 Hz, 1H), 3.55 (dd, J = 16.4, 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 138.8, 129.7, 129.1, 129.0, 128.9, 126.8, 126.3, 125.9, 114.1, 75.9, 40.5. Compound **3aa** was consistent with the literature data.[2]

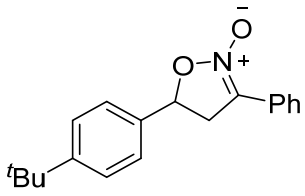
5-(4-Methylphenyl)-3-phenyl-2-isoxazoline *N*-Oxide (3ba)



3ba

The product **3ba** was obtained as a white solid (79.2 mg, 0.313 mmol, 78%). R_f = 0.22 (hexane/ ethyl acetate = 6:1). Mp: 131-132 °C. IR (KBr): 3055 (w), 2916 (w), 1609 (s), 1225 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.96-7.93 (m, 2H), 7.47-7.35 (m, 5H), 7.22 (d, J = 8.0 Hz, 2H), 5.69 (dd, J = 9.2, 8.4 Hz, 1H), 3.88 (dd, J = 16.4, 9.2 Hz, 1H), 3.53 (dd, J = 16.4, 8.4 Hz, 1H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rt): δ 138.9, 135.6, 129.7, 129.6, 128.9, 126.9, 126.3, 126.0, 114.3, 76.0, 40.4, 21.3. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.70; H, 5.65; N, 5.44.

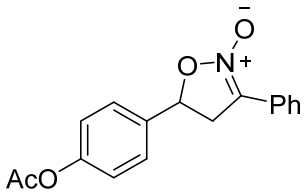
5-[4-(*tert*-Butyl)phenyl]-3-phenyl-2-isoxazoline *N*-Oxide (3ca)



3ca

The product **3ca** was obtained as a white solid (107.1 mg, 0.363 mmol, 91%). R_f = 0.24 (hexane/ ethyl acetate = 6:1). Mp: 139-140 °C. IR (KBr): 2961 (m), 2905 (w), 1612 (s), 1234 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.96-7.94 (m, 2H), 7.48-7.38 (m, 7H), 5.72 (dd, J = 9.2, 7.6 Hz, 1H), 3.90 (dd, J = 16.4, 9.2 Hz, 1H), 3.56 (dd, J = 16.4, 7.6 Hz, 1H), 1.33 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 152.2, 135.6, 129.6, 128.9, 126.9, 126.3, 126.0, 125.8, 114.3, 75.9, 40.3, 34.8, 31.4. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.03; H, 7.37; N, 4.56.

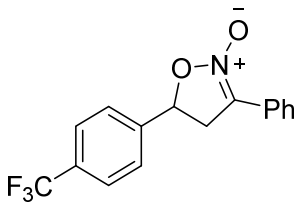
5-(4-Acetoxyphenyl)-3-phenyl-2-isoxazoline *N*-Oxide (3da)



3da

The product **3da** was obtained as a white solid (93.1 mg, 0.313 mmol, 78%). R_f = 0.29 (hexane/ ethyl acetate = 4:1). Mp: 134-135 °C. IR (KBr): 3053 (w), 2941 (w), 1751 (s), 1609 (s), 1225 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.93-7.90 (m, 2H), 7.48-7.37 (m, 5H), 7.15-7.11 (m, 2H), 5.70 (dd, J = 9.6, 7.6 Hz, 1H), 3.90 (dd, J = 16.4, 9.6 Hz, 1H), 3.51 (dd, J = 16.4, 7.6 Hz, 1H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 169.4, 151.0, 136.4, 129.7, 128.9, 127.1, 126.7, 126.3, 122.3, 113.9, 75.2, 40.4, 21.2. Calcd for $C_{17}H_{15}NO_4$: C, 68.68; H, 5.09; N, 4.71. Found: C, 68.43; H, 4.84; N, 4.66.

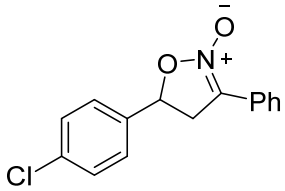
3-Phenyl-5-[4-(trifluoromethyl)phenyl]-2-isoxazoline *N*-Oxide (3ea)



3ea

The product **3ea** was obtained as a white solid (82.4 mg, 0.268 mmol, 67%). R_f = 0.23 (hexane/ ethyl acetate = 4:1). Mp: 175-176 °C. IR (KBr): 2938 (w), 1612 (s), 1331 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 7.93-7.89 (m, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.49-7.38 (m, 3H), 5.79 (dd, J = 9.6, 7.2 Hz, 1H), 4.01 (dd, J = 16.2, 9.6 Hz, 1H), 3.51 (dd, J = 16.2, 7.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 143.1, 131.2 (q, $^2J_{C–F}$ = 33 Hz), 129.9, 129.0, 126.5, 126.3, 126.2 (q, $^3J_{C–F}$ = 3.5 Hz), 126.0, 124.0 (q, $^1J_{C–F}$ = 270 Hz), 113.5, 74.8, 40.6; $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, rt): δ –62.7. Calcd for $C_{16}H_{12}F_3NO_2$: C, 62.54; H, 3.94; N, 4.56. Found: C, 62.67; H, 3.62; N, 4.52.

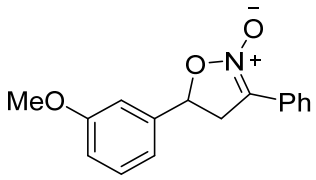
5-(4-Chlorophenyl)-3-phenyl-2-isoxazoline *N*-Oxide (3fa)



3fa

The product **3fa** was obtained as a white solid (84.1 mg, 0.307 mmol, 77%). R_f = 0.29 (hexane/ ethyl acetate = 6:1). Mp: 162-163 °C. IR (KBr): 3055 (w), 2924 (w), 1609 (s), 1223 (s), cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.93-7.90 (m, 2H), 7.48-7.35 (m, 7H), 5.71 (dd, J = 9.6, 7.6 Hz, 1H), 3.94 (dd, J = 16.4, 9.6 Hz, 1H), 3.50 (dd, J = 16.4, 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 137.4, 134.9, 129.8, 129.4, 129.0, 127.3, 126.7, 126.3, 113.8, 75.1, 40.5. Calcd for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; N, 5.12. Found: C, 66.01; H, 4.51; N, 4.91.

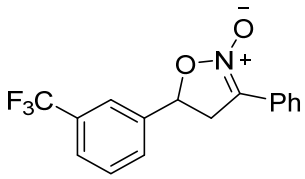
5-(3-Methoxyphenyl)-3-phenyl-2-isoxazoline *N*-Oxide (3ga)



3ga

The product **3ga** was obtained as a white solid (101.5 mg, 0.377 mmol, 94%). R_f = 0.23 (hexane/ ethyl acetate = 4:1). Mp: 73-74 °C. IR (KBr): 3053 (m), 2959 (m), 2337 (m), 1603 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.95-7.92 (m, 2H), 7.47-7.37 (m, 3H), 7.35-7.31 (m, 1H), 7.04-7.01 (m, 2H), 6.90 (ddd, J = 8.4, 2.4, 1.2 Hz, 1H), 5.70 (dd, J = 9.6, 7.6 Hz, 1H), 3.91 (dd, J = 16.4, 9.6 Hz, 1H), 3.82 (s, 3H), 3.53 (dd, J = 16.4, 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 160.2, 140.4, 130.2, 129.7, 128.9, 126.8, 126.3, 118.0, 114.5, 114.1, 111.2, 75.7, 55.5, 40.5. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.12; H, 5.42; N, 5.13.

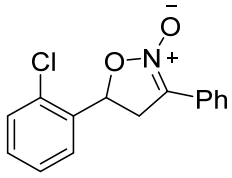
3-Phenyl-5-[3-(trifluoromethyl)phenyl]-2-isoxazoline *N*-Oxide (3ha)



3ha

The product **3ah** was obtained as a white solid (75.6 mg, 0.246 mmol, 62%). R_f = 0.25 (hexane/ ethyl acetate = 4:1). Mp: 115-116 °C. IR (KBr): 3059 (w), 2943 (w), 2920 (w), 1611 (s), 1337 (s), 1223 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 7.94-7.90 (m, 2H), 7.72-7.38 (m, 7H), 5.79 (dd, J = 9.6, 7.5 Hz, 1H), 4.00 (dd, J = 16.2, 9.6 Hz, 1H), 3.53 (dd, J = 16.2, 7.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 140.1, 131.6 (q, $^2J_{C–F}$ = 33 Hz), 129.9, 129.8, 129.1, 129.0, 126.5, 126.3, 125.8 (q, $^3J_{C–F}$ = 3.5 Hz), 123.9 (q, $^1J_{C–F}$ = 270 Hz), 122.7 (q, $^3J_{C–F}$ = 3.8 Hz), 113.6, 74.9, 40.6; $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, rt): δ –62.7. Calcd for $C_{16}H_{12}F_3NO_2$: C, 62.54; H, 3.94; N, 4.56. Found: C, 62.78; H, 3.56; N, 4.36.

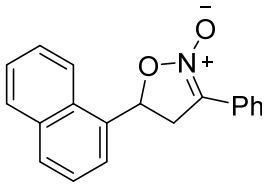
5-(2-Chlorophenyl)-3-phenyl-2-isoxazoline *N*-Oxide (3ia)



3ia

The product **3ia** was obtained as a white solid (85.7 mg, 0.313 mmol, 78%). R_f = 0.27 (hexane/ ethyl acetate = 8:1). Mp: 87-88 °C. IR (KBr): 3071 (w), 2930 (w), 1620 (s), 1236 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.94-7.91 (m, 2H) 7.72 (dd, J = 7.6, 1.6 Hz, 1H), 7.47-7.28 (m, 6H), 6.02 (dd, J = 10.0, 5.6 Hz, 1H), 4.15 (dd, J = 16.4, 10.0 Hz, 1H), 3.41 (dd, J = 16.4, 5.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 137.4, 131.1, 130.0, 129.8, 129.7, 128.9, 127.6, 126.7, 126.4, 126.3, 113.5, 72.5, 39.9. Calcd for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; N, 5.12. Found: C, 65.78; H, 4.34; N, 5.05.

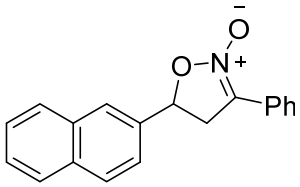
5-(1-Naphthyl)-3-phenyl-2-isoxazoline *N*-Oxide (3ja)



3ja

The product **3ja** was obtained as a white solid (86.3 mg, 0.298 mmol, 75%). R_f = 0.16 (hexane/ ethyl acetate = 8:1). Mp: 96-97 °C. IR (KBr): 3055 (m), 2918 (w), 1616 (s), 1236 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 7.95-7.84 (m, 6H), 7.63-7.35 (m, 6H), 6.43 (dd, J = 9.9, 6.6 Hz, 1H), 4.18 (dd, J = 16.2, 9.9 Hz, 1H), 3.60 (dd, J = 16.2, 6.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 134.4, 134.2, 129.7, 129.51, 129.50, 129.2, 128.9, 126.9, 126.8, 126.3, 126.1, 125.7, 122.6, 122.4, 114.0, 73.3, 40.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{15}NNaO_2$: 312.1000. Found: 312.1001.

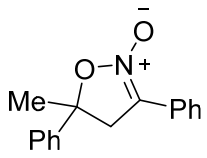
5-(2-Naphthyl)-3-phenyl-2-isoxazoline *N*-Oxide (3ka)



3ka

The product **3ka** was obtained as a white solid (80.9 mg, 0.280 mmol, 70%). R_f = 0.25 (hexane/ ethyl acetate = 6:1). Mp: 165-166 °C. IR (KBr): 3053 (w), 1609 (s), 1225 (s) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, rt): δ 7.95 (t, J = 7.2 Hz, 3H), 7.91 (d, J = 8.4 Hz, 1H), 7.87-7.85 (m, 2H), 7.55-7.51 (m, 3H), 7.46 (t, J = 7.8 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 5.89 (t, J = 9.0 Hz, 1H), 3.98 (dd, J = 16.2, 10.2 Hz, 1H), 3.62 (dd, J = 16.2, 7.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 136.0, 133.5, 133.2, 129.7, 129.3, 128.9, 128.2, 127.9, 126.81 (2C), 126.75, 126.3, 125.3, 123.1, 114.1, 76.0, 40.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{15}NNaO_2$: 312.1000. Found: 312.0975.

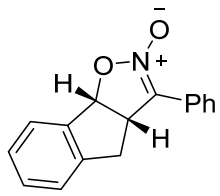
5-Methyl-3,5-diphenyl-2-isoxazoline *N*-Oxide (3la)



3la

The product **3la** was obtained as a white solid (73.4 mg, 0.290 mmol, 72%). R_f = 0.25 (hexane/ ethyl acetate = 6:1). Mp: 74-75 °C. IR (KBr): 3057 (w), 3022 (w), 2994 (w), 1611 (s), 1236 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 7.93-7.90 (m, 2H), 7.55-7.45 (m, 2H), 7.44-7.29 (m, 6H), 3.72 (d, J = 16.2 Hz, 1H), 3.66 (d, J = 16.2 Hz, 1H), 1.86 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 143.8, 129.5, 128.9, 128.8, 128.0, 127.0, 126.2, 124.3, 115.2, 81.1, 46.1, 28.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{15}NNaO_2$: 276.1000. Found: 276.0982.

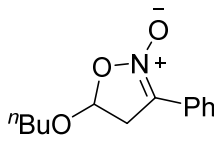
***cis*-3-Phenyl-3a,8b-dihydro-4*H*-indeno[2,1-*d*]-2-isoxazoline *N*-Oxide (3ma)**



3ma

The product **3ma** was obtained as a white solid (66.7 mg, 0.265 mmol, 66%). R_f = 0.21 (hexane/ ethyl acetate = 6:1). Mp: 158-159 °C. IR (KBr): 3059 (m), 2949 (m), 1607 (s), 1227 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 7.99-7.95 (m, 2H), 7.57-7.24 (m, 7H), 6.11 (d, J = 9.0 Hz, 1H), 4.70 (td, J = 9.0, 3.3 Hz, 1H), 3.57 (dd, J = 16.5, 9.0 Hz, 1H), 3.32 (dd, J = 16.5, 3.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 141.5, 139.1, 130.4, 129.5, 129.0, 128.0, 126.7, 126.6, 126.5, 125.2, 117.6, 81.8, 47.6, 37.8. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.42; H, 5.26; N, 5.50.

5-Butoxy-3-phenyl-2-isoxazoline *N*-Oxide (3na)

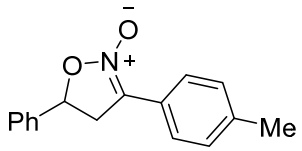


3na

The product **3na** was obtained as a colorless oil (39.1 mg, 0.166 mmol, 42%). R_f = 0.23 (hexane/ ethyl

acetate = 6:1). IR (neat): 2959 (m), 2872 (m), 1618 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 7.94-7.89 (m, 2H), 7.48-7.36 (m, 3H), 5.55 (dd, *J* = 6.6, 0.9 Hz, 1H), 3.93 (dt, *J* = 9.3, 6.6 Hz, 1H), 3.72 (dd, *J* = 17.1, 6.6 Hz, 1H), 3.55 (dt, *J* = 9.3, 6.6 Hz, 1H), 3.35 (dd, *J* = 17.1, 0.9 Hz, 1H), 1.65-1.55 (m, 2H), 1.44-1.32 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 129.6, 128.8, 126.7, 126.3, 113.5, 96.8, 68.8, 39.4, 31.5, 19.2, 13.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{17}NNaO_3$: 258.1106. Found: 258.1106.

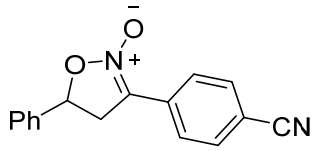
3-(4-Methylphenyl)-5-phenyl-2-isoxazoline *N*-Oxide (3ab)



3ab

The product **3ab** was obtained as a white solid (68.2 mg, 0.279 mmol, 67%). R_f = 0.34 (hexane/ ethyl acetate = 4:1). Mp: 73-74 °C. IR (KBr): 3030 (w), 1615 (s), 1227 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.48-7.33 (m, 5H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.72 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.91 (dd, *J* = 16.4, 9.6 Hz, 1H), 3.53 (dd, *J* = 16.4, 7.6 Hz, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 140.0, 138.8, 129.6, 129.0, 128.9, 126.3, 125.9, 123.9, 114.2, 75.8, 40.5, 21.6. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.63; H, 6.26; N, 5.49.

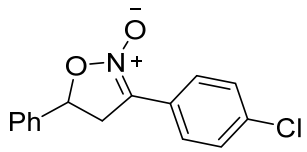
3-(4-Cyanophenyl)-5-phenyl-2-isoxazoline *N*-Oxide (3ac)



3ac

The product **3ac** was obtained as a white solid (91.4 mg, 0.346 mmol, 86%). R_f = 0.35 (hexane/ ethyl acetate = 2:1). Mp: 97-98 °C. IR (KBr): 2924 (w), 2853 (w), 2224 (m), 1618 (s), 1589 (s), 1240 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 8.05-8.01 (m, 2H), 7.75-7.71 (m, 2H), 7.48-7.40 (m, 5H), 5.80 (dd, *J* = 9.3, 7.8 Hz, 1H), 3.94 (dd, *J* = 16.2, 9.3 Hz, 1H), 3.57 (dd, *J* = 16.2, 7.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 138.1, 132.6, 131.2, 129.3_4, 129.2_8, 126.4, 125.9, 118.5, 113.3, 112.5, 76.3, 39.9. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60. Found: C, 72.97; H, 4.64; N, 10.35.

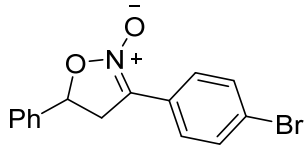
3-(4-Chlorophenyl)-5-phenyl-2-isoxazoline *N*-Oxide (3ad)



3ad

The product **3ad** was obtained as a white solid (84.6 mg, 0.309 mmol, 77%). R_f = 0.23 (hexane/ ethyl acetate = 6:1). Mp: 134-135 °C. IR (KBr): 3088 (w), 3036 (w), 2938 (w), 1607 (s), 1229 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.90-7.87 (m, 2H), 7.48-7.36 (m, 7H), 5.75 (dd, J = 9.6, 7.6 Hz, 1H), 3.91 (dd, J = 16.0, 9.6 Hz, 1H), 3.53 (dd, J = 16.0, 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 138.5, 135.3, 129.1_5 (2C), 129.1_0, 127.5, 125.9, 125.4, 113.5, 75.9, 40.2. Calcd for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; N, 5.12. Found: C, 65.99; H, 4.05; N, 5.12.

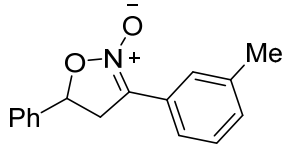
3-(4-Bromophenyl)-5-phenyl-2-isoxazoline *N*-Oxide (3ae)



3ae

The product **3ae** was obtained as a white solid (101.7 mg, 0.320 mmol, 80%). R_f = 0.28 (hexane/ ethyl acetate = 8:1). Mp: 150-151 °C. IR (KBr): 3036 (w), 2936 (w), 1607 (s), 1229 (s) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, rt): δ 7.82-7.80 (m, 2H), 7.59-7.56 (m, 2H), 7.47-7.37 (m, 5H), 5.74 (dd, J = 9.6, 7.8 Hz, 1H), 3.90 (dd, J = 16.2, 9.6 Hz, 1H), 3.53 (dd, J = 16.2, 7.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 138.5, 132.2, 129.2, 129.1, 127.7, 125.9, 125.8, 123.7, 113.6, 76.0, 40.2. Calcd for $C_{15}H_{12}BrNO_2$: C, 56.63; H, 3.80; N, 4.40. Found: C, 56.77; H, 3.72; N, 4.23.

3-(3-Methylphenyl)-5-phenyl-2-isoxazoline *N*-Oxide (3af)

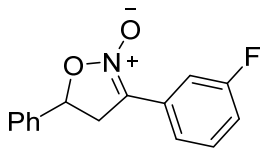


3af

The product **3af** was obtained as a white solid (84.9 mg, 0.335 mmol, 84%). R_f = 0.31 (hexane/ ethyl acetate = 6:1). Mp: 95-96 °C. IR (KBr): 3034 (w), 2920 (w), 1603 (s), 1234 (s) cm^{-1}. ^1H NMR (400

MHz, $CDCl_3$, rt): δ 7.79 (s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.48-7.32 (m, 6H), 7.21 (d, J = 7.6 Hz, 1H), 5.72 (dd, J = 9.6, 7.6 Hz, 1H), 3.92 (dd, J = 16.4, 9.6 Hz, 1H), 3.53 (dd, J = 16.4, 7.6 Hz, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 138.9, 138.6, 130.5, 129.1, 129.0, 128.8, 126.8, 126.7, 125.9, 123.6, 114.2, 75.8, 40.6, 21.7. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.71; H, 6.00; N, 5.51.

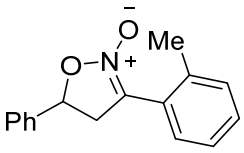
3-(3-Fluorophenyl)-5-phenyl-2-isoxazoline *N*-Oxide (3ag)



3ag

The product **3ag** was obtained as a white solid (83.4 mg, 0.324 mmol, 81%). R_f = 0.23 (hexane/ ethyl acetate = 6:1). Mp: 106-107 °C. IR (KBr): 3076 (w), 2934 (w), 1595 (s), 1227 (s) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, rt): δ 7.82 (dt, J = 10.8, 1.8 Hz, 1H), 7.58 (ddd, J = 7.8, 1.8, 0.6 Hz, 1H), 7.48-7.36 (m, 6H), 7.09 (tdd, J = 8.4, 2.4, 0.6 Hz, 1H), 5.75 (dd, J = 9.6, 7.8 Hz, 1H), 3.91 (dd, J = 16.2, 9.6 Hz, 1H), 3.53 (dd, J = 16.2, 7.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 162.9 (d, $^1J_{C–F}$ = 240 Hz), 138.5, 130.4 (d, $^3J_{C–F}$ = 8.9 Hz), 129.2, 129.1, 128.9 (d, $^3J_{C–F}$ = 9.3 Hz), 125.9, 122.1 (d, $^4J_{C–F}$ = 2.7 Hz), 116.6 (d, $^2J_{C–F}$ = 21 Hz), 113.5 (d, $^4J_{C–F}$ = 2.6 Hz), 113.1 (d, $^2J_{C–F}$ = 25 Hz), 76.0, 40.3; $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, rt): δ –111.4. Calcd for $C_{15}H_{12}FNO_2$: C, 70.03; H, 4.70; N, 5.44. Found: C, 70.16; H, 4.75; N, 5.28.

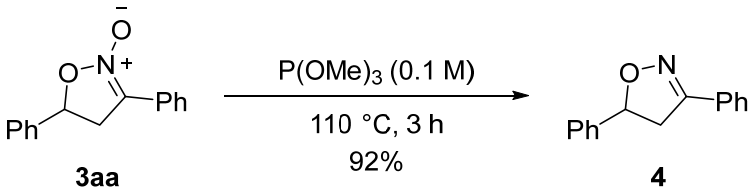
3-(2-Methylphenyl)-5-phenyl-2-isoxazoline *N*-Oxide (3ah)



3ah

The product **3ah** was obtained as a colorless oil (38.3 mg, 0.151 mmol, 38%). R_f = 0.21 (hexane/ ethyl acetate = 3:1). IR (neat): 3061 (w), 2922 (w), 1626 (s), 1231 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.50-7.22 (m, 9H), 5.78 (dd, J = 9.2, 7.2 Hz, 1H), 3.87 (dd, J = 16.8, 9.2 Hz, 1H), 3.46 (dd, J = 16.8, 7.6 Hz, 1H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 138.9, 137.9, 131.2, 129.9, 129.1, 128.9, 128.2, 126.6, 126.0, 125.6, 114.4, 76.4, 42.8, 20.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{15}NNaO_2$: 276.1000. Found: 276.0983.

Reduction of 2-Isoxazoline *N*-Oxide 3aa: Synthesis of 3,5-Diphenyl-2-isoxazoline (4)

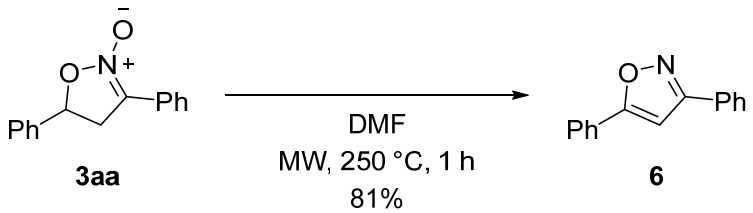


3aa **4**

Under an argon atmosphere, 2-isoxazoline *N*-oxide (**3aa**, 95.7 mg, 0.4 mmol) was placed in a 20-mL Schlenk tube. Trimethylphosphite (4.0 mL, 34 mmol) was then added at room temperature. The mixture was stirred at 110 °C for 3 h. After the mixture was cooled to room temperature, hydrochloric acid (1 N, 30 mL) was added to the mixture. The mixture was extracted with ethyl acetate (10 mL) three times. The combined organic layers were washed with brine (50 mL) and dried over anhydrous sodium sulfate. After the volatiles were evaporated, the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 8/1) to provide **4** as a white solid (82.6 mg, 0.367 mmol, 92%).

R_f = 0.40 (hexane/ethyl acetate = 8/1). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 7.72-7.70 (m, 2H), 7.43-7.37 (m, 7H), 7.33 (tt, J = 7.2, 1.8 Hz, 1H), 5.75 (dd, J = 11.4, 8.4 Hz, 1H), 3.79 (dd, J = 16.8, 11.4 Hz, 1H), 3.35 (dd, J = 16.8, 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 156.2, 141.1, 130.3, 129.6, 128.89, 128.87, 128.4, 126.9, 126.0, 82.7, 43.3. Compound **4** was consistent with the literature data.[3]

Dehydroration of 2-Isoxazoline *N*-Oxide 3aa: Synthesis of 3,5-Diphenylisoxazole (6)



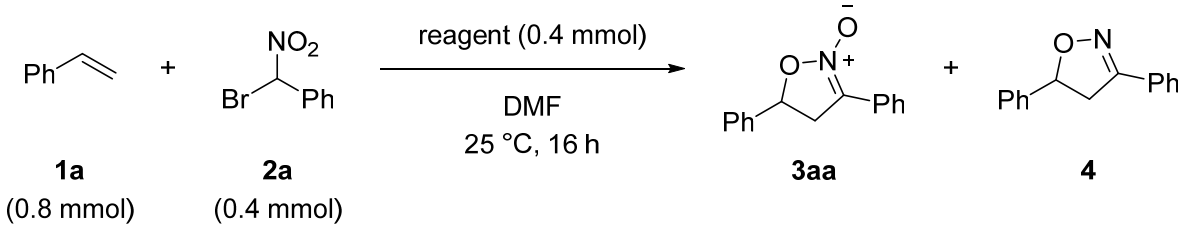
3aa **6**

2-Isoxazoline *N*-oxide (**3aa**, 95.7 mg 0.4 mmol) was placed in a 5-mL glass pressure vial. *N*,*N*-Dimethylformamide (DMF, 2.4 mL) was then added at room temperature. The vial was flushed with argon and sealed with a PTFE-silicone septum. The mixture was stirred at 250 °C for 1 h in the microwave reactor. After the mixture was cooled to room temperature, water (50 mL) was added to the mixture. The mixture was extracted with ethyl acetate (10 mL) three times. The combined organic layers were washed with brine (50 mL) and dried over anhydrous sodium sulfate. After the volatiles were evaporated, the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 8/1) to provide **6** as a white solid (72.0 mg, 0.325 mmol, 81%).

R_f = 0.37 (hexane/ethyl acetate = 8/1). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 7.89-7.84 (m, 4H), 7.51-7.45 (m, 6H), 6.84 (s, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 170.5, 163.1, 130.4, 130.2, 129.3, 129.1$_5$, 129.0$_7$, 127.6, 127.0, 126.0, 97.6. Compound **6** was consistent with the literature data.[3]

3. Optimization of Reaction Conditions

Table S1. Reagent Screening[a]

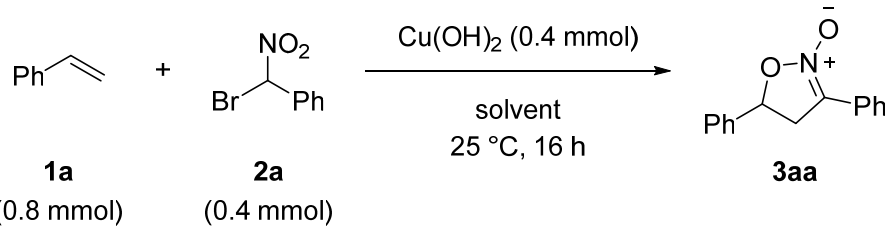


1a (0.8 mmol) **2a** (0.4 mmol) **3aa** **4**

entry	reagent	NMR yield (%)[b]	
		3aa	**4**
1	none	0	0
2	Cu	7	28
3	CuCN	4	0
4	CuI	15	0
5	$Cu(OH)_2$	75	0
6	$Cu(OAc)_2$	48	0
7	CuF_2	46	0
8	$CuBr_2$	0	0
9	$Cu(acac)_2$	0	0
10	LiOH	36	13
11	NaOH	56	10
12	$KHCO_3$	29	29
13	KOH	25	22
14	KOAc	16	10
15	KO^{t}Bu	17	18
16	NEt_3	9	7

[a]**1a** (0.8 mmol), **2a** (0.4 mmol), and reagent (0.4 mmol) in DMF (0.5 mL) at 25 °C for 16 h. [b]Determined by ^{1}H NMR analysis of the crude mixture, using dibromomethane as an internal standard.

Table S2. Solvent Screening[a]



1a (0.8 mmol) **2a** (0.4 mmol) **3aa**

entry	solvent	NMR yield (%)[b]
1	DMSO	96
2	DMF	75
3	DMPU	44
4	DMA	35
5	DMI	11

[a]**1a** (0.8 mmol), **2a** (0.4 mmol), and $Cu(OH)_2$ (0.4 mmol) in solvent (0.5 mL) at 25 °C for 16 h. [b]Determined by ^{1}H NMR analysis of the crude mixture, using dibromomethane as an internal standard.

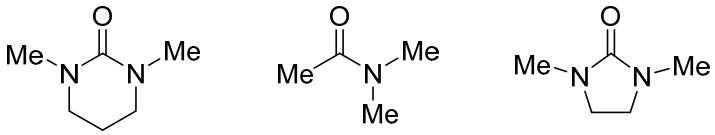
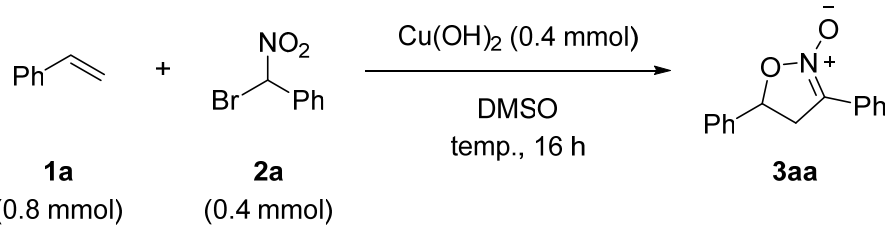


Table S3. Reaction Temperature[a]

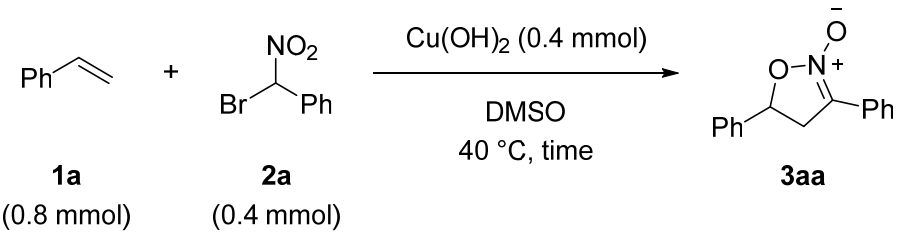


1a (0.8 mmol) **2a** (0.4 mmol) **3aa**

entry	temp. (°C)	NMR yield (%)[b]
1	25	96
2	40	82
3	50	0

[a]**1a** (0.8 mmol), **2a** (0.4 mmol), and $Cu(OH)_2$ (0.4 mmol) in DMSO (0.5 mL) for 16 h. [b]Determined by ^{1}H NMR analysis of the crude mixture, using dibromomethane as an internal standard.

Table S4. Time Course[a]

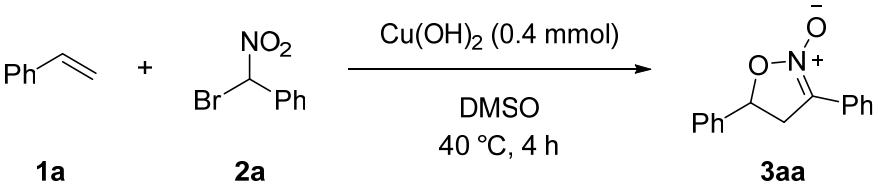


1a (0.8 mmol) **2a** (0.4 mmol) **3aa**

entry	time (h)	NMR yield (%)[b]
1	2	68
2	4	94
3	8	93
4	16	82

[a]**1a** (0.8 mmol), **2a** (0.4 mmol), and $Cu(OH)_2$ (0.4 mmol) in DMSO (0.5 mL) at 40 °C. [b]Determined by ^{1}H NMR analysis of the crude mixture, using dibromomethane as an internal standard.

Table S5. Ratios of Substrates[a]

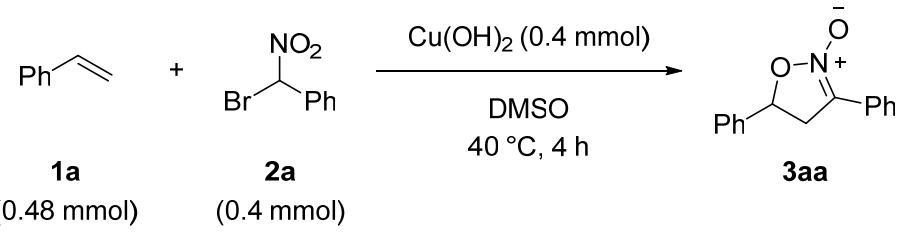


1a **2a** **3aa**

entry	**1a** (mmol)	**2a** (mmol)	NMR yield (%)[b]
1	0.4	0.8	96
2	0.4	0.48	93
3	0.4	0.4	76
4	0.48	0.4	quant.
5	0.8	0.4	94

[a]**1a**, **2a**, and $Cu(OH)_2$ (0.4 mmol) in DMSO (0.5 mL) at 40 °C for 4 h. [b]Determined by ^{1}H NMR analysis of the crude mixture, using dibromomethane as an internal standard.

Table S6. Concentrations of Substrates[a]



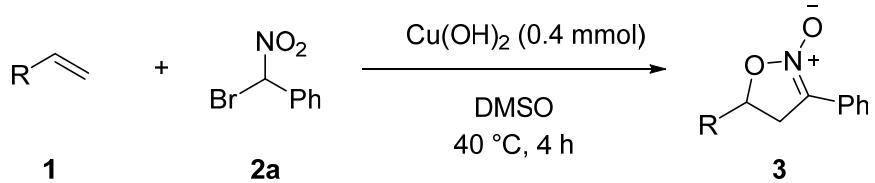
1a (0.48 mmol) **2a** (0.4 mmol) **3aa**

entry	DMSO (mL)	NMR yield (%)[b]
1	0.3	quant.
2	0.5	quant. (81[c])
3	1	69

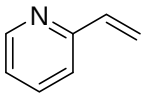
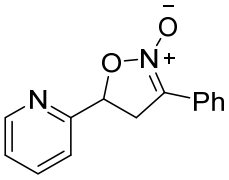
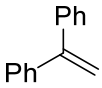
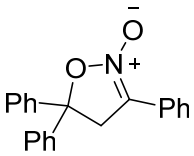
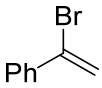
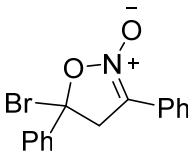
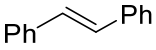
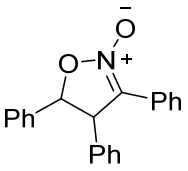
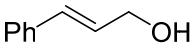
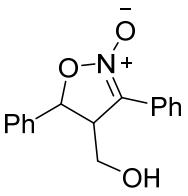
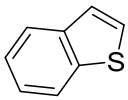
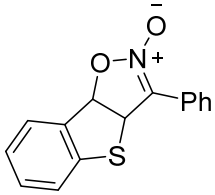
[a]**1a** (0.48 mmol), **2a** (0.4 mmol), and $Cu(OH)_2$ (0.4 mmol) in DMSO at 40 °C for 4 h. [b]Determined by ^{1}H NMR analysis of the crude mixture, using dibromomethane as an internal standard. [c]An isolated yield.

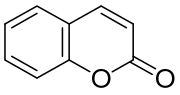
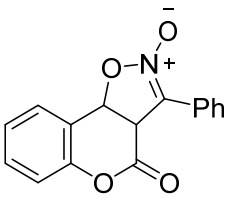
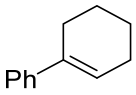
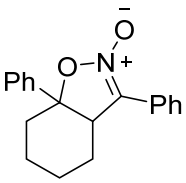
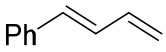
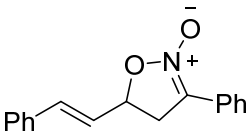
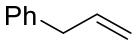
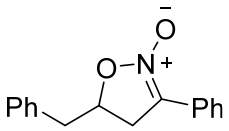
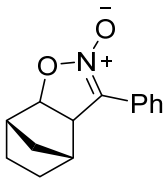
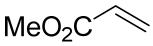
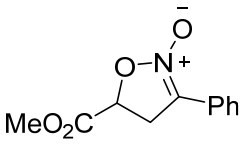
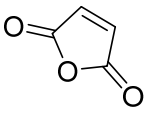
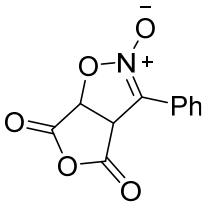
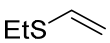
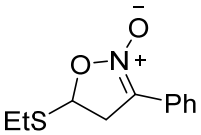
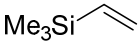
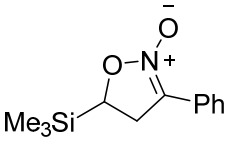
4. Substrate Limitation[a]

Table S7. Limitation of Alkenes



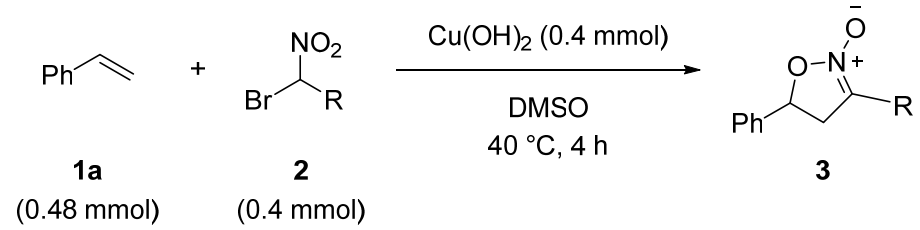
1 (0.48 mmol) **2a** (0.4 mmol) **3**

entry	**1**	**3**	NMR yield (%)[b]
1			0
2			0
3			0
4			0
5			0
6			0

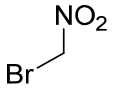
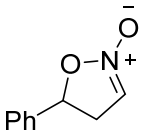
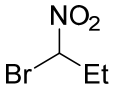
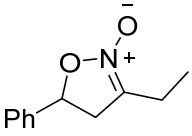
7			0
8			0
9			0
10			0
11			0
12			0
13			0
14			0
15			0

[a]**1** (0.48 mmol), **2a** (0.4 mmol), and $Cu(OH)_2$ (0.4 mmol) in DMSO (0.5 mL) at 40 °C for 4 h. [b]Determined by ^1H NMR analysis of the crude mixture, using dibromomethane as an internal standard.

Table S8. Limitation of Bromides

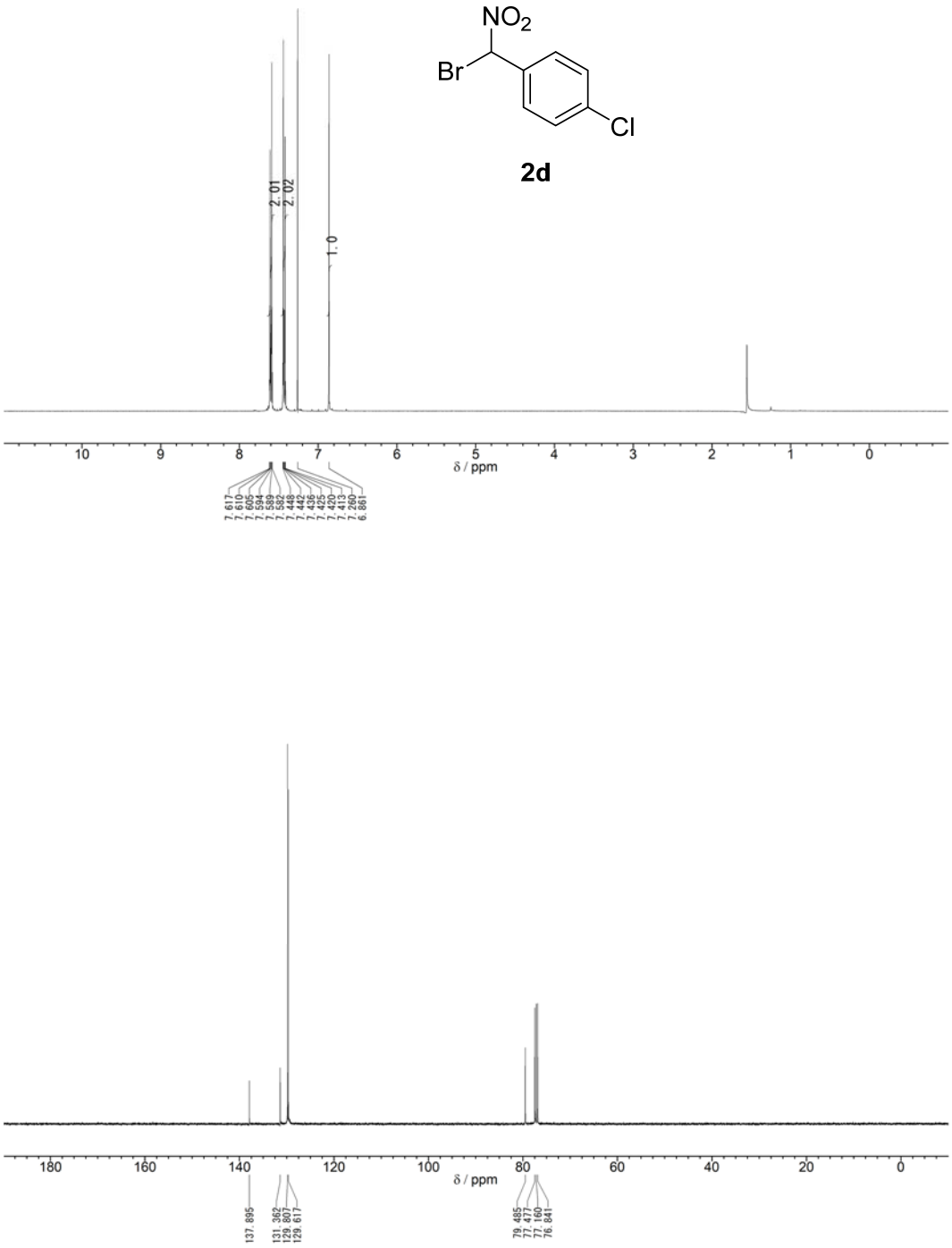


1a (0.48 mmol) **2** (0.4 mmol) **3**

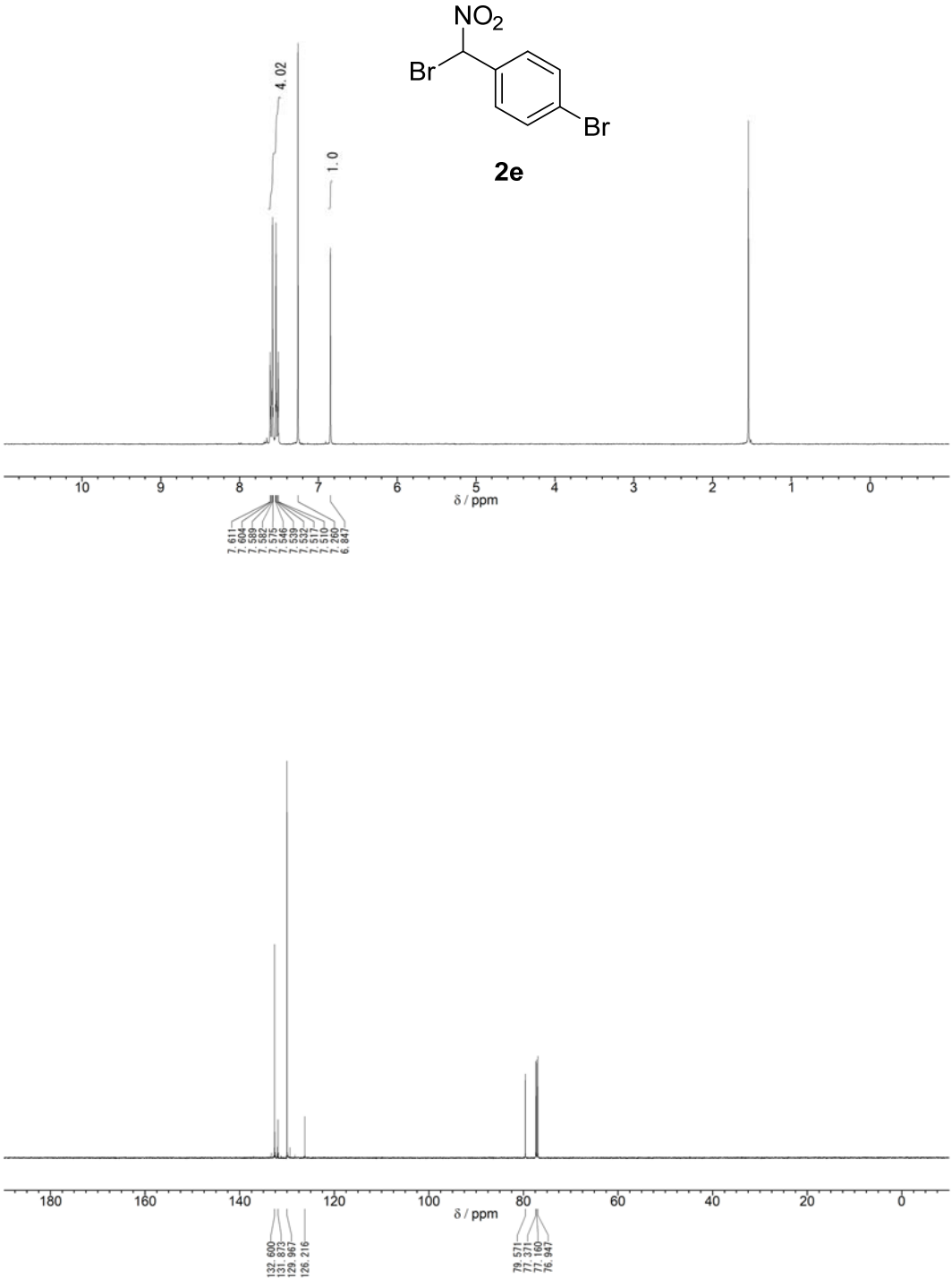
entry	**2**	**3**	NMR yield (%)[b]
1			0
2			0

[a]**1a** (0.48 mmol), **2** (0.4 mmol), and $Cu(OH)_2$ (0.4 mmol) in DMSO (0.5 mL) at 40 °C for 4 h. [b]Determined by ^1H NMR analysis of the crude mixture, using dibromomethane as an internal standard.

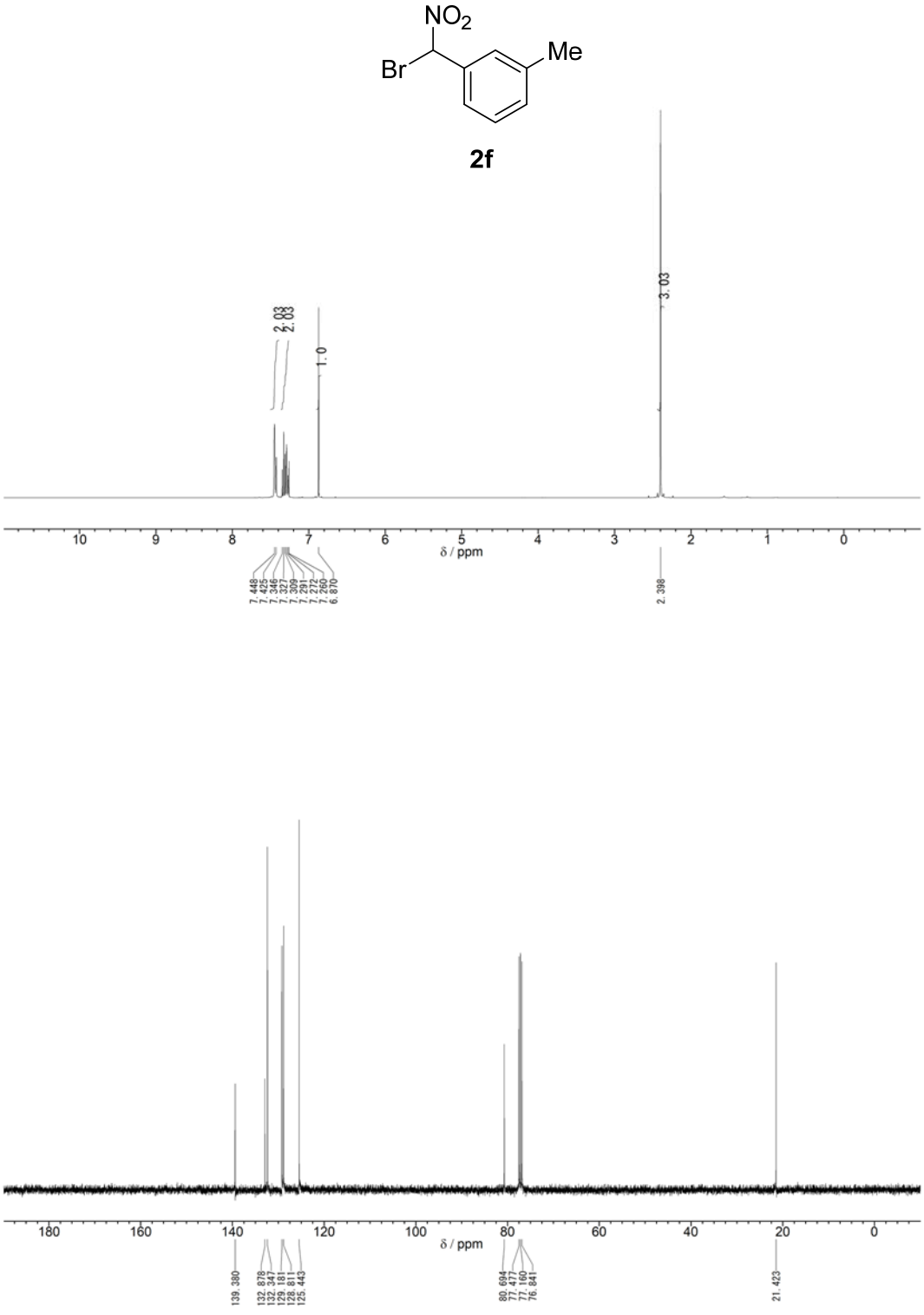
5. Copies of ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR Charts for the New Compounds



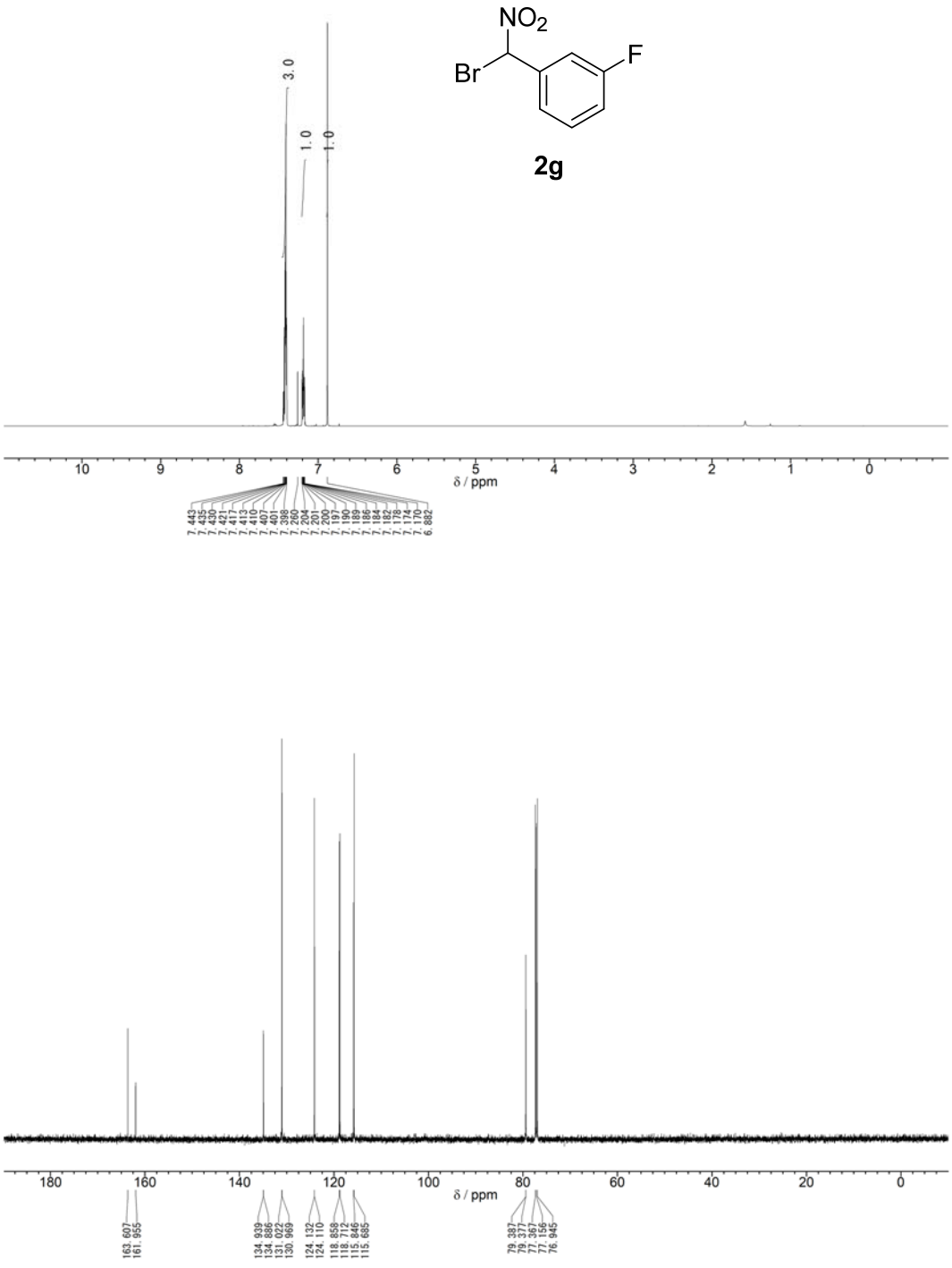
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (100 MHz) spectra of **2d** ($CDCl_3$, rt).



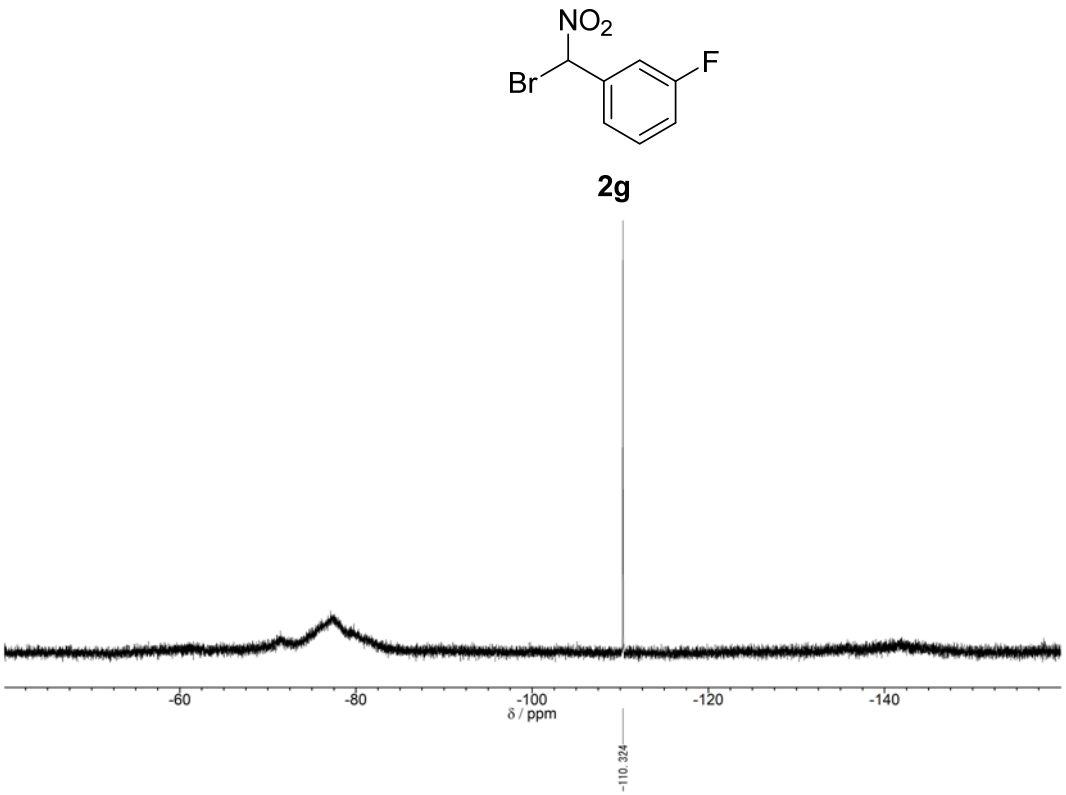
^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **2e** ($CDCl_3$, rt).



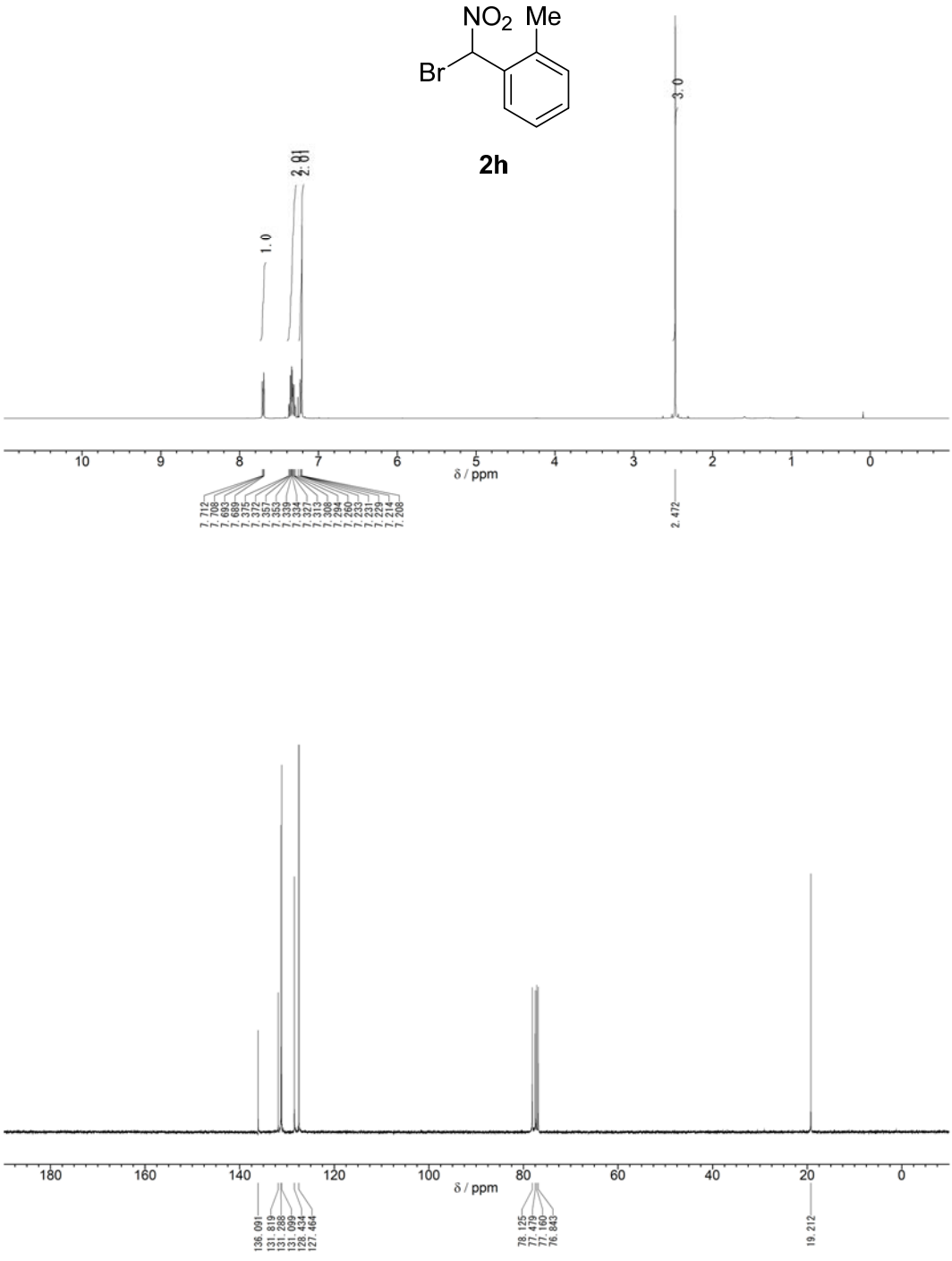
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **2f** ($CDCl_3$, rt).



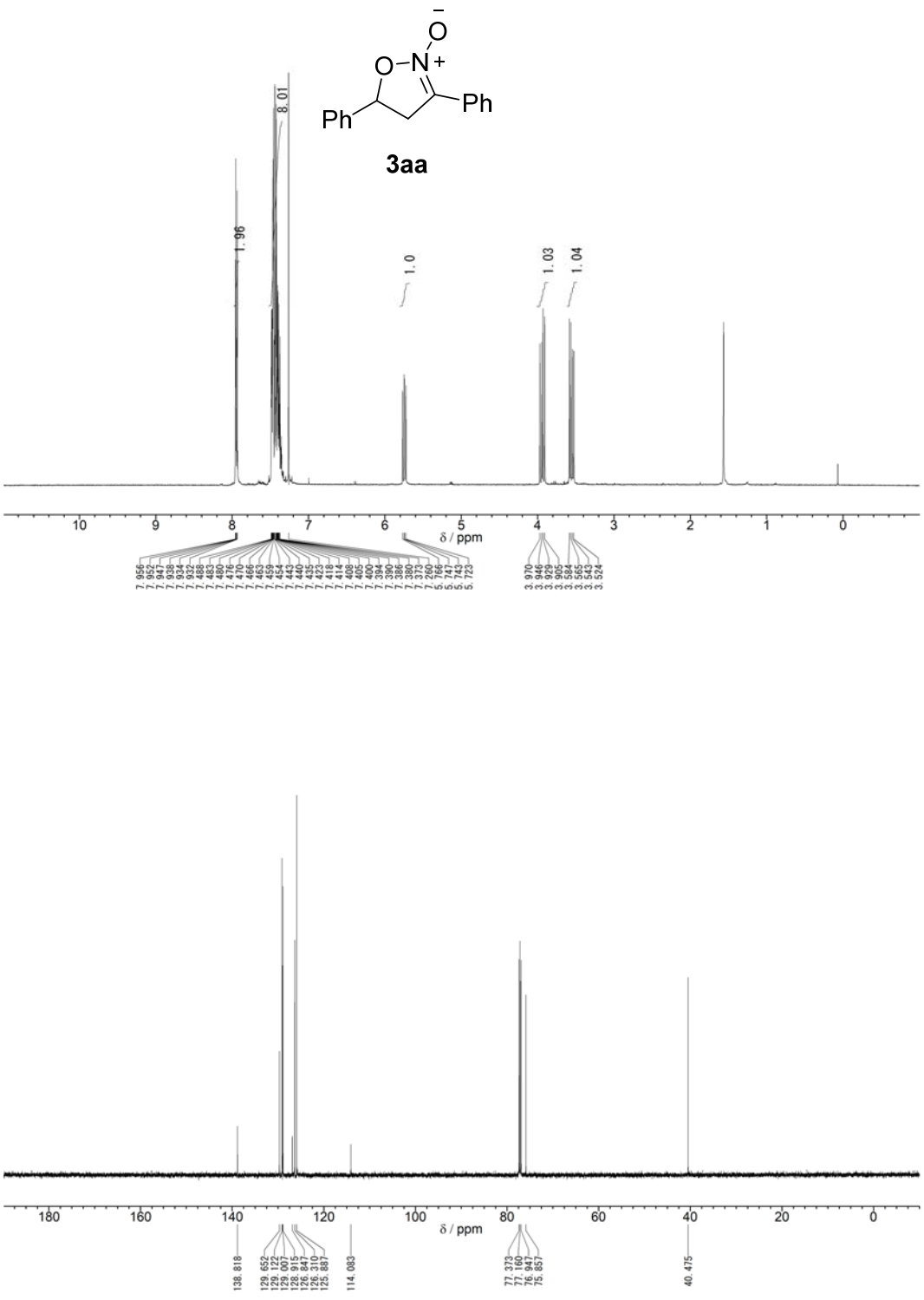
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **2g** ($CDCl_3$, rt).



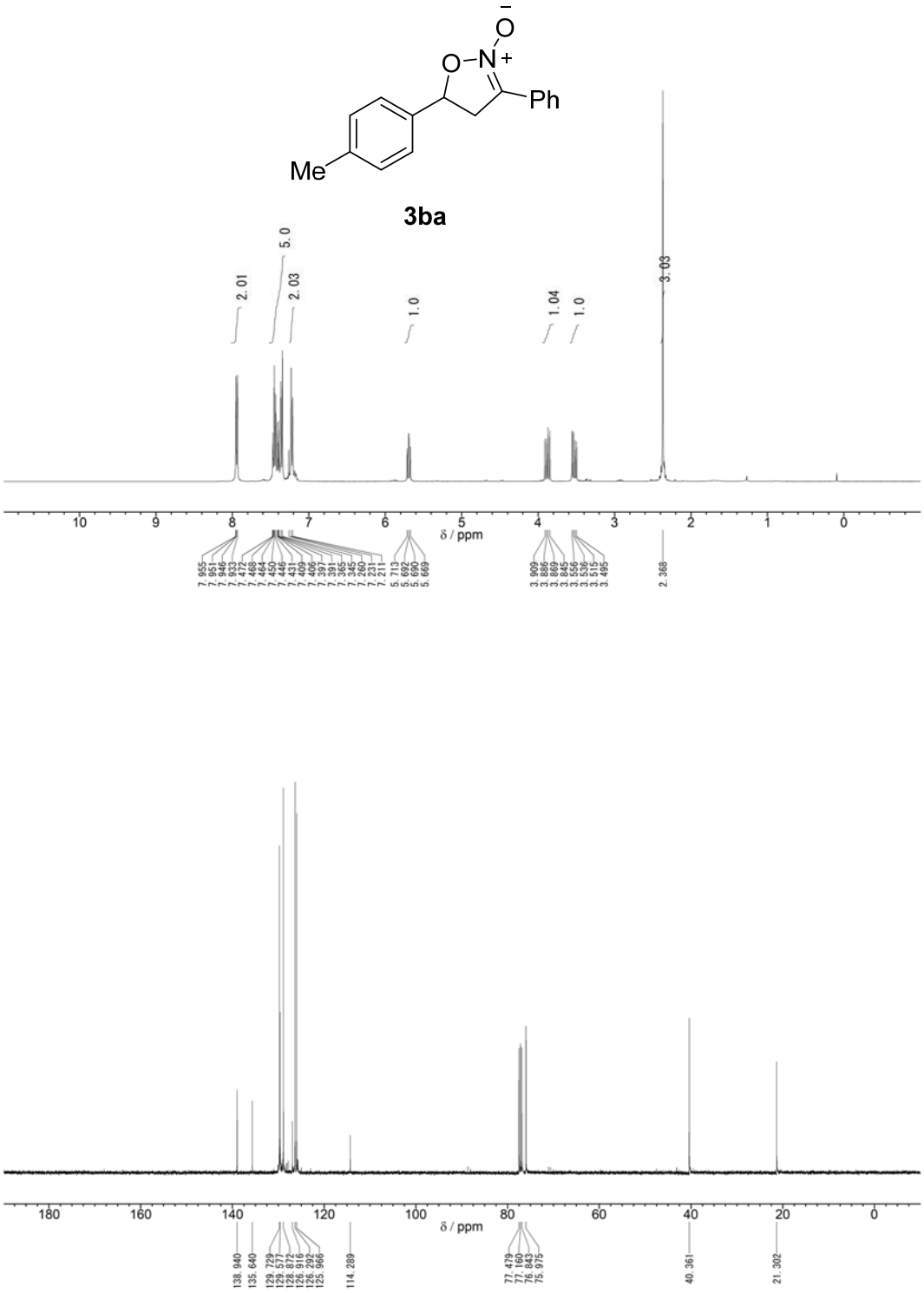
$^{19}F\{^{1}H\}$ NMR (282 MHz) spectrum of **2g** ($CDCl_3$, rt).



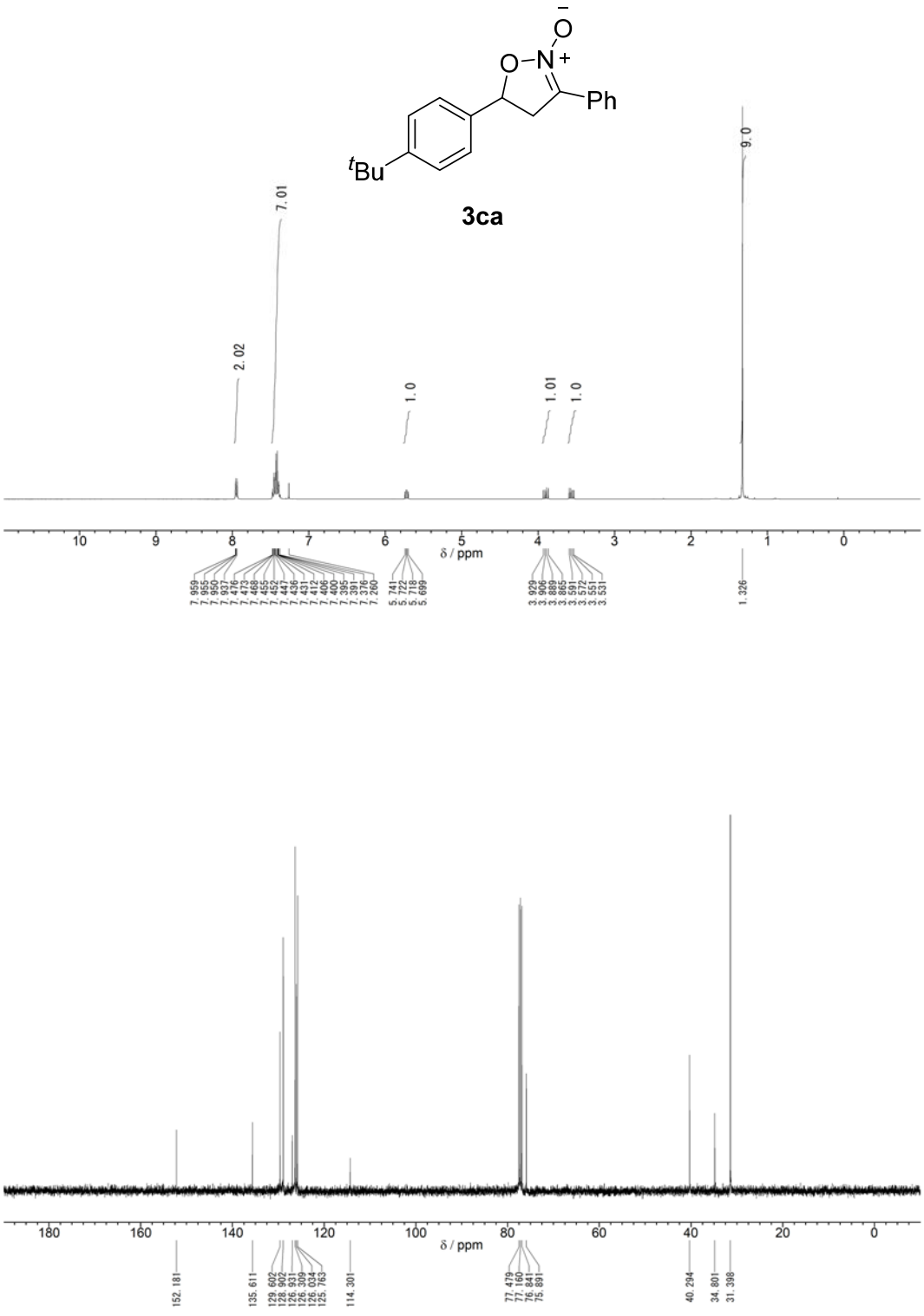
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **2h** ($CDCl_3$, rt).



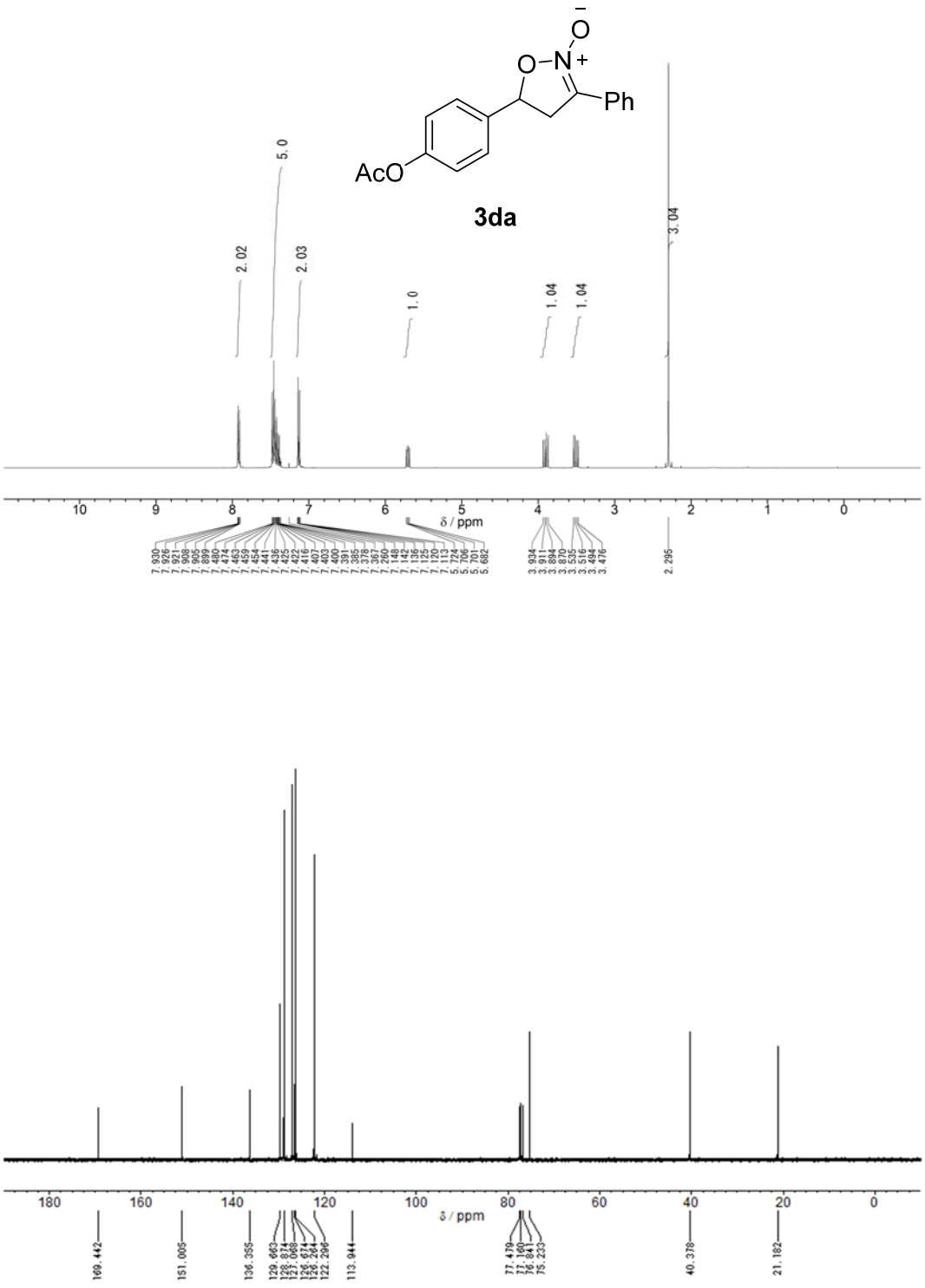
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3aa** ($CDCl_3$, rt).



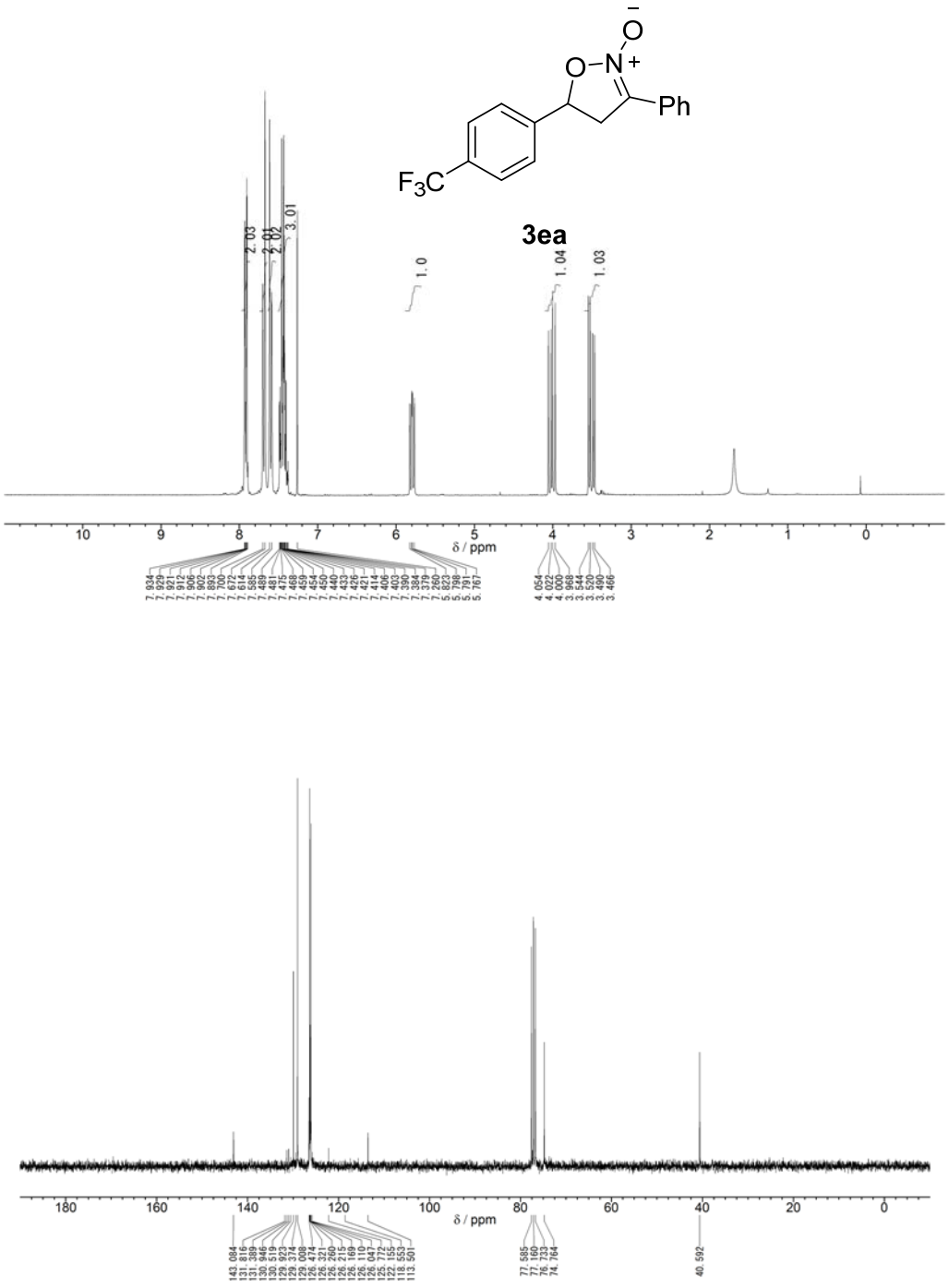
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3ba** ($CDCl_3$, rt).



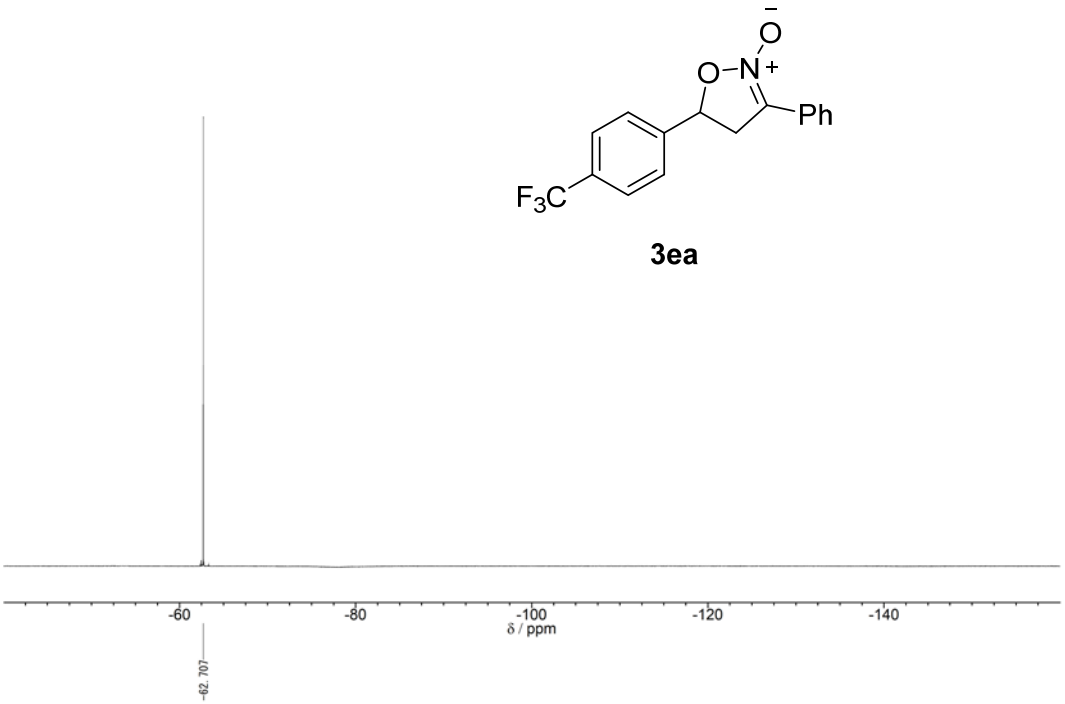
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of major-**3ca** ($CDCl_3$, rt).



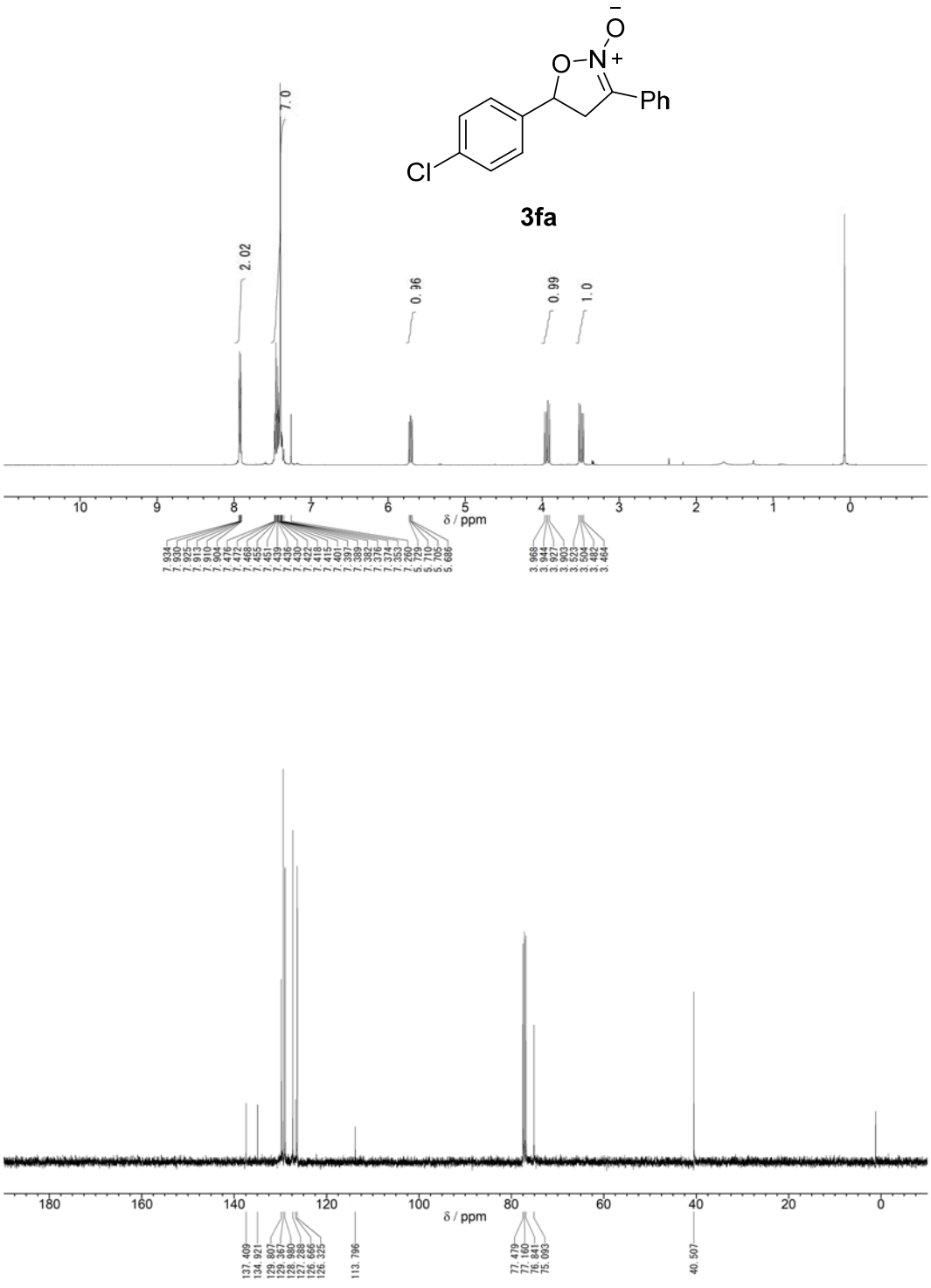
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of minor-**3da** ($CDCl_3$, rt).



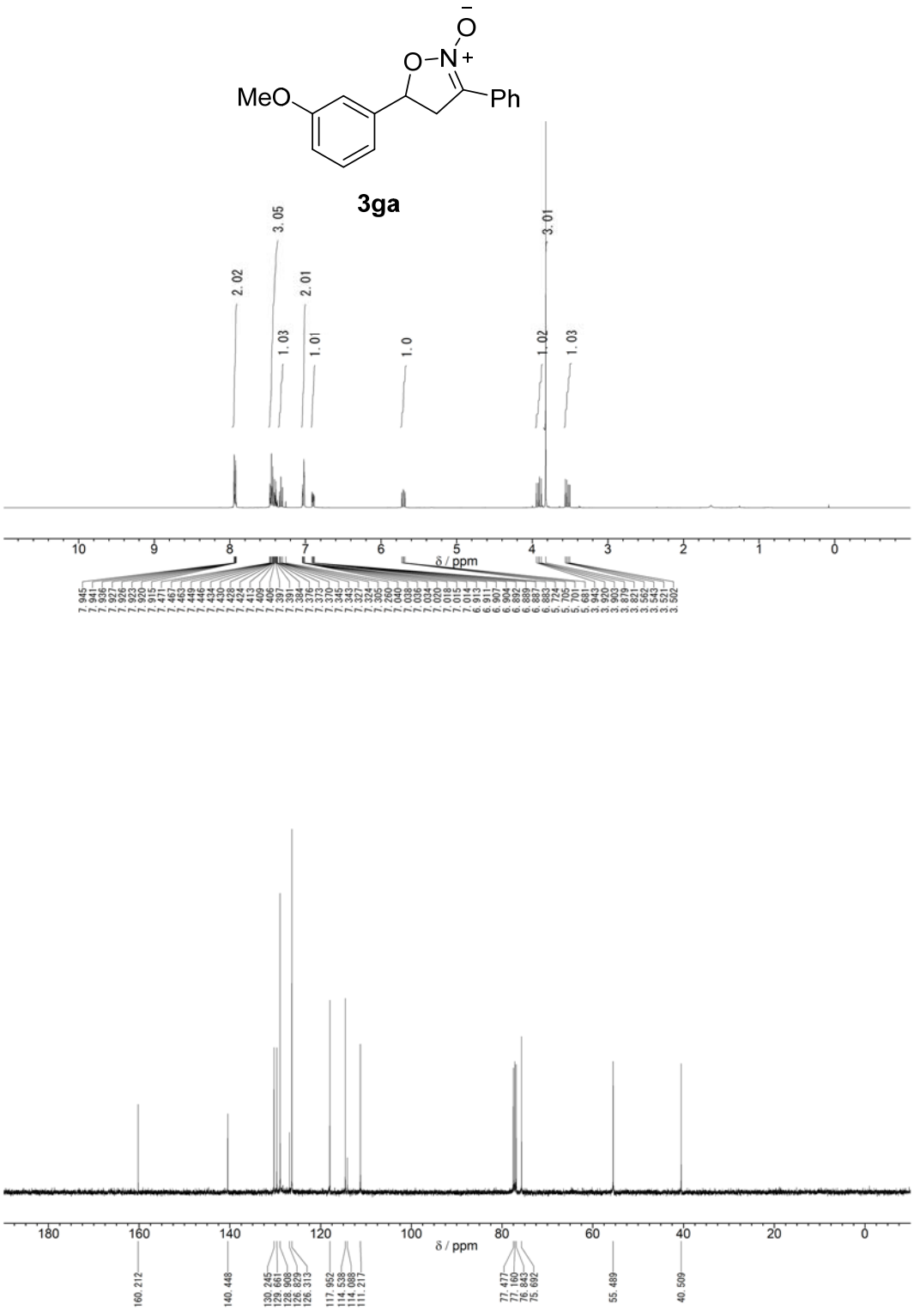
^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **3ea** ($CDCl_3$, rt).



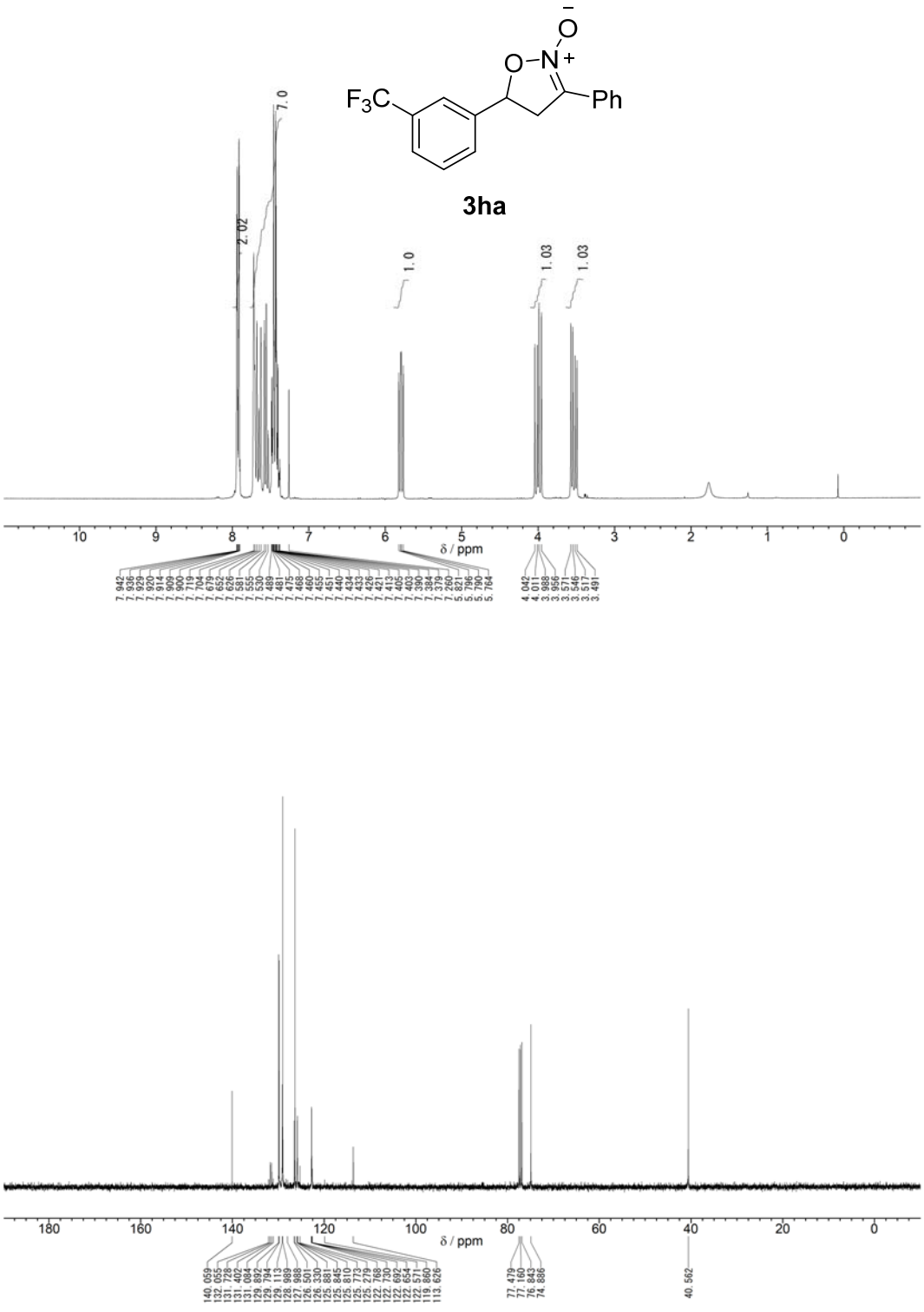
$^{19}F\{^{1}H\}$ NMR (282 MHz) spectrum of **3ea** ($CDCl_3$, rt).



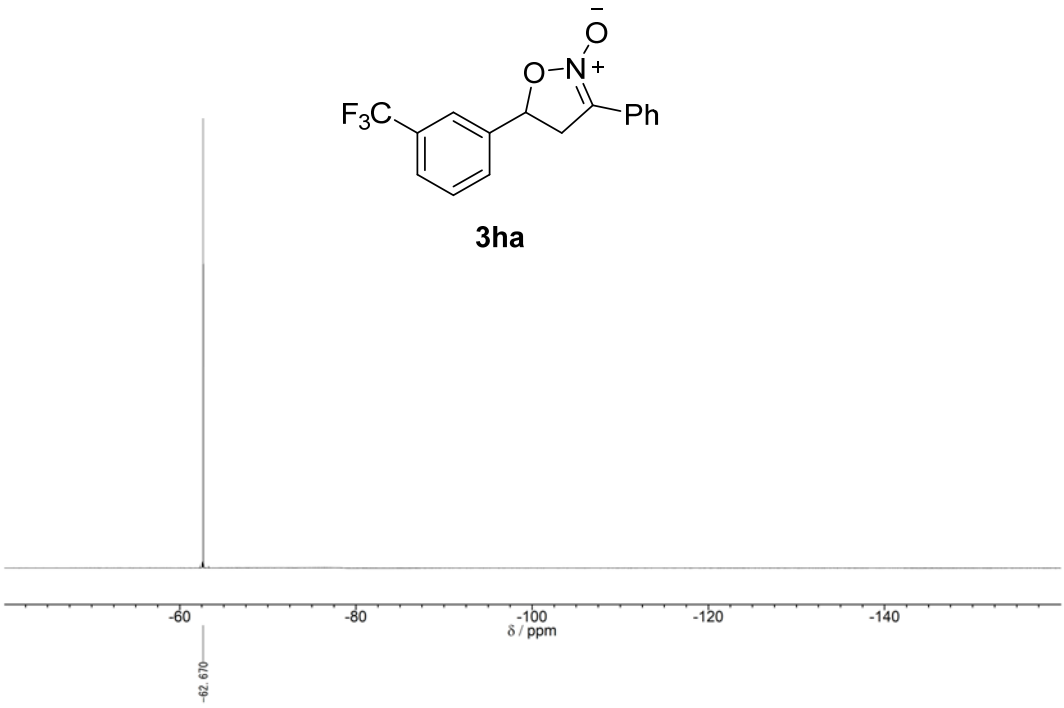
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3fa** ($CDCl_3$, rt).



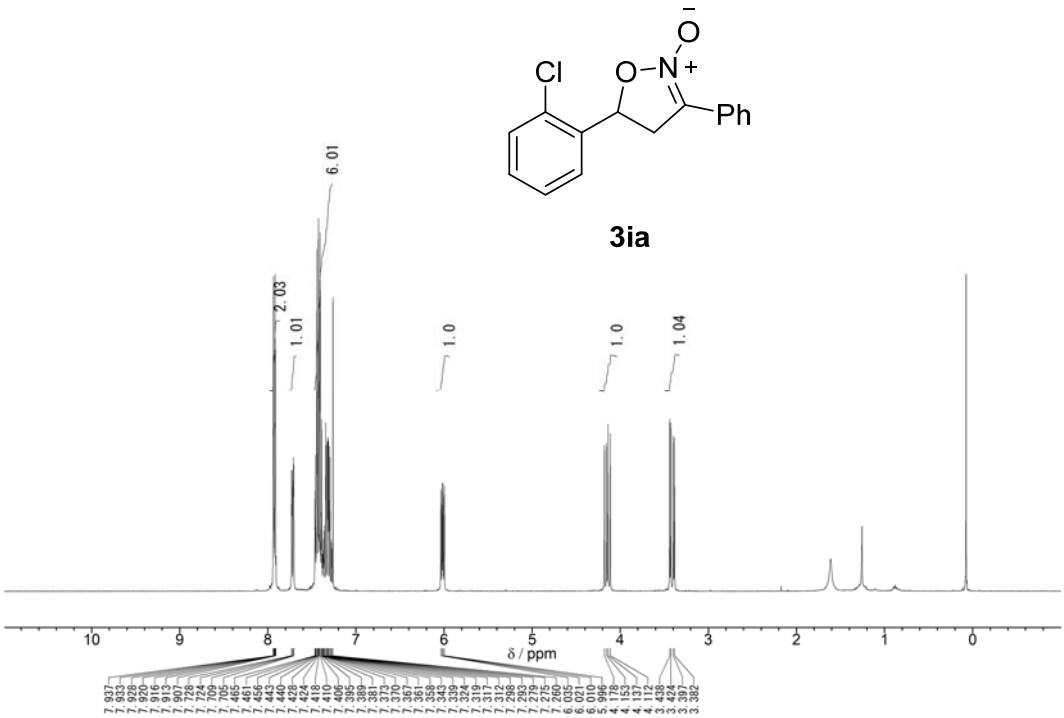
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3ga** ($CDCl_3$, rt).

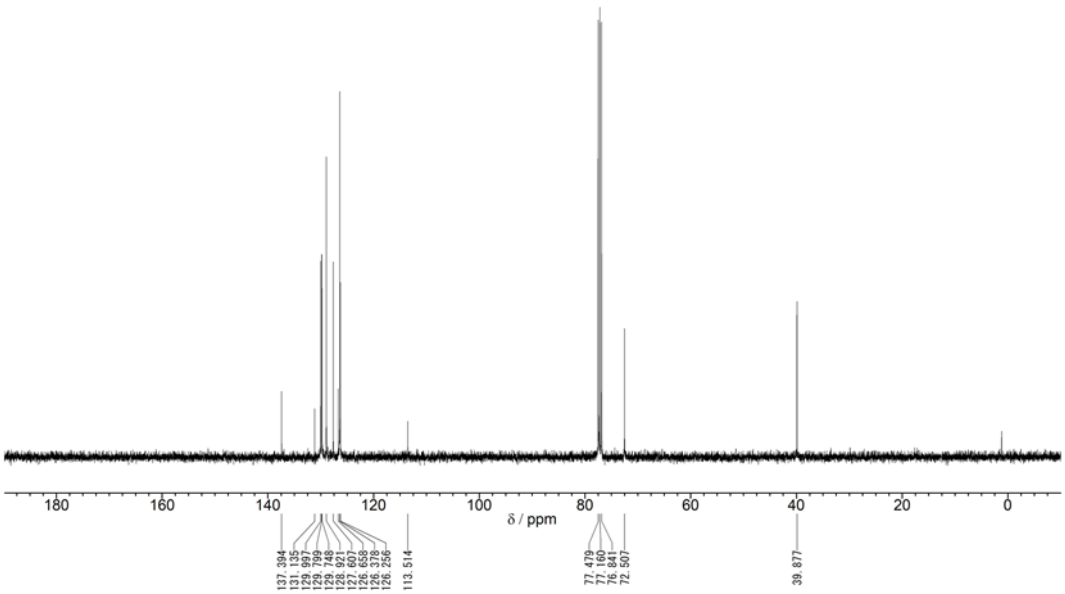


^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3ha** ($CDCl_3$, rt).

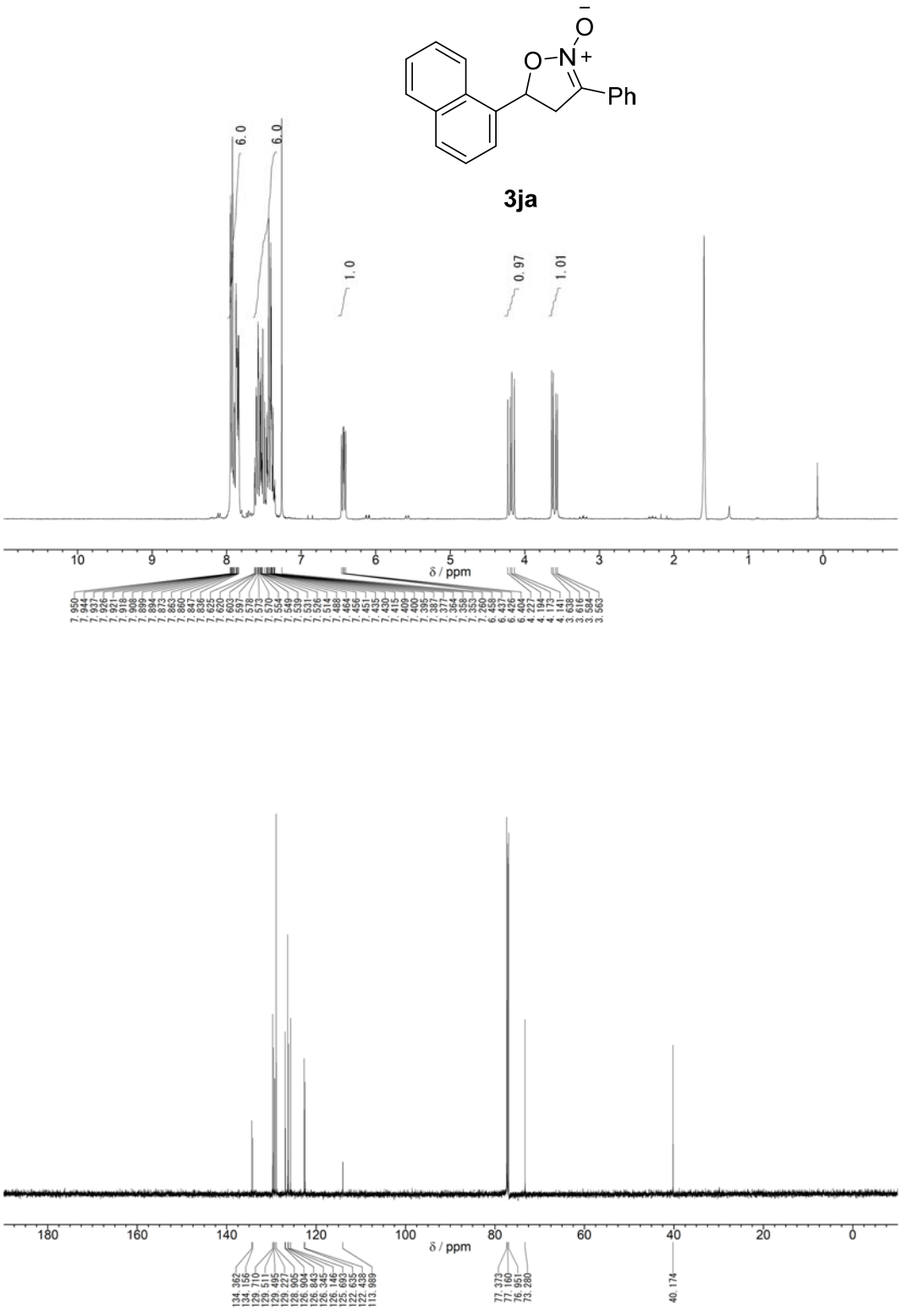


$^{19}F\{^{1}H\}$ NMR (282 MHz) spectrum of **3ha** ($CDCl_3$, rt).

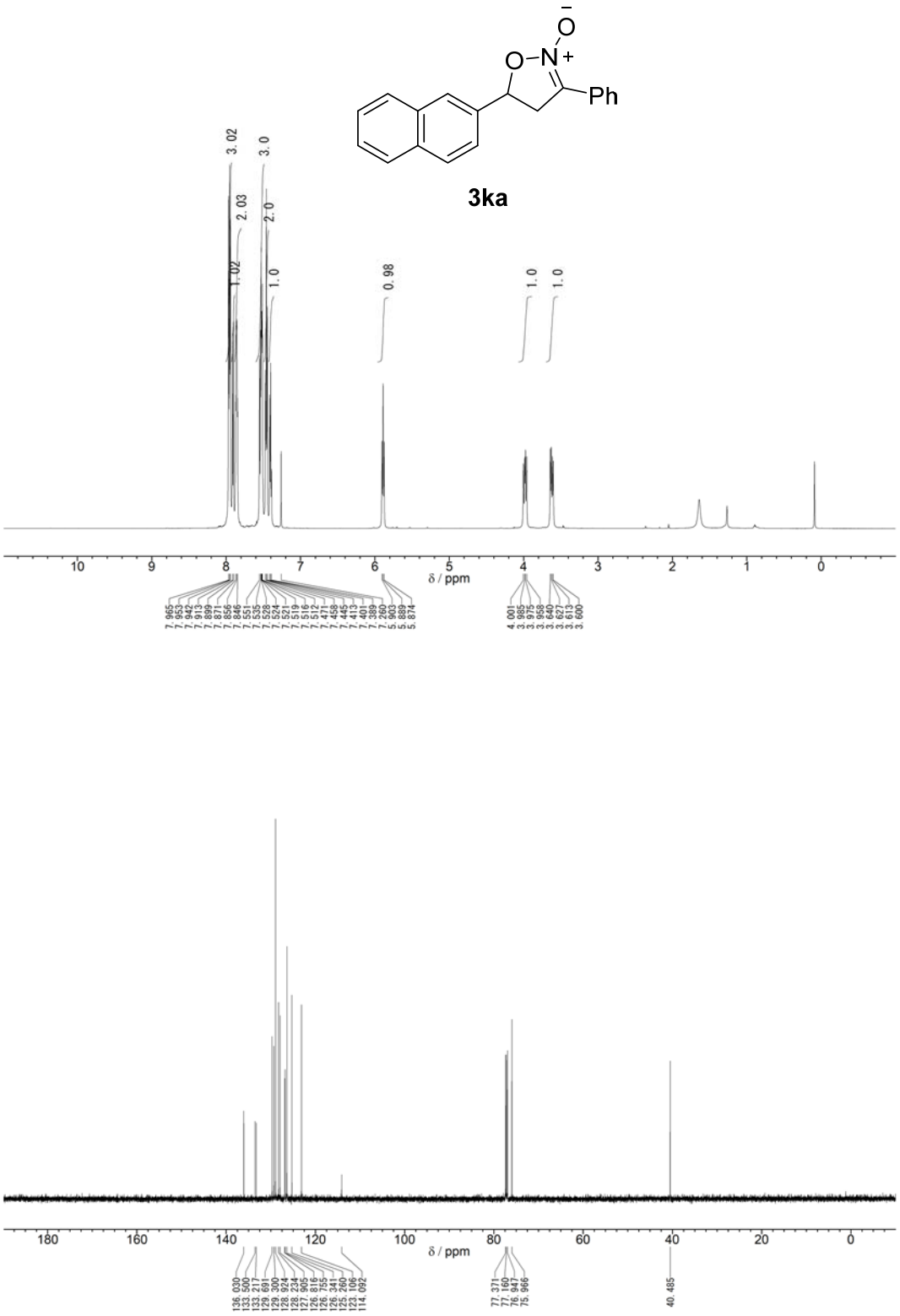




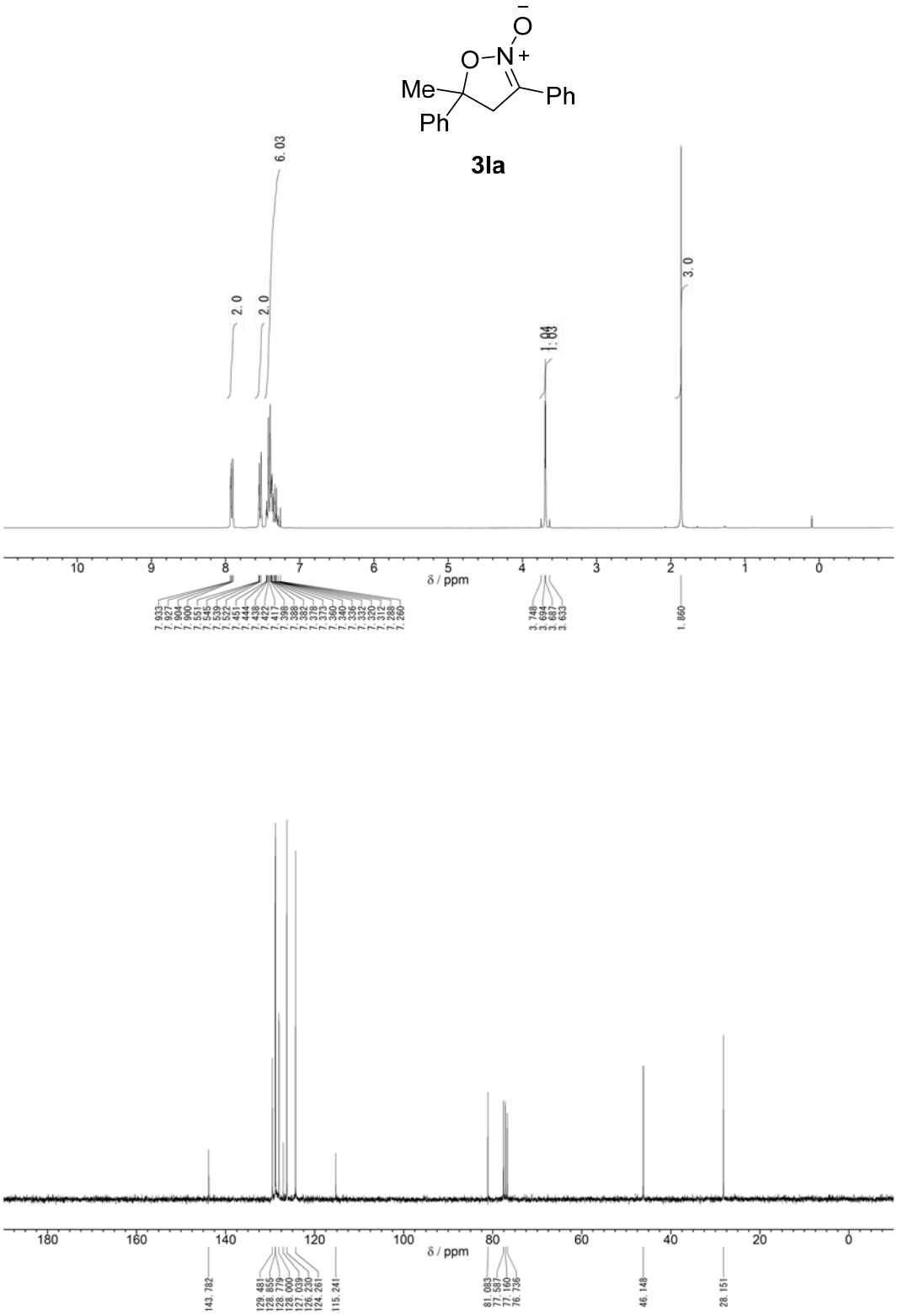
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3ia** ($CDCl_3$, rt).



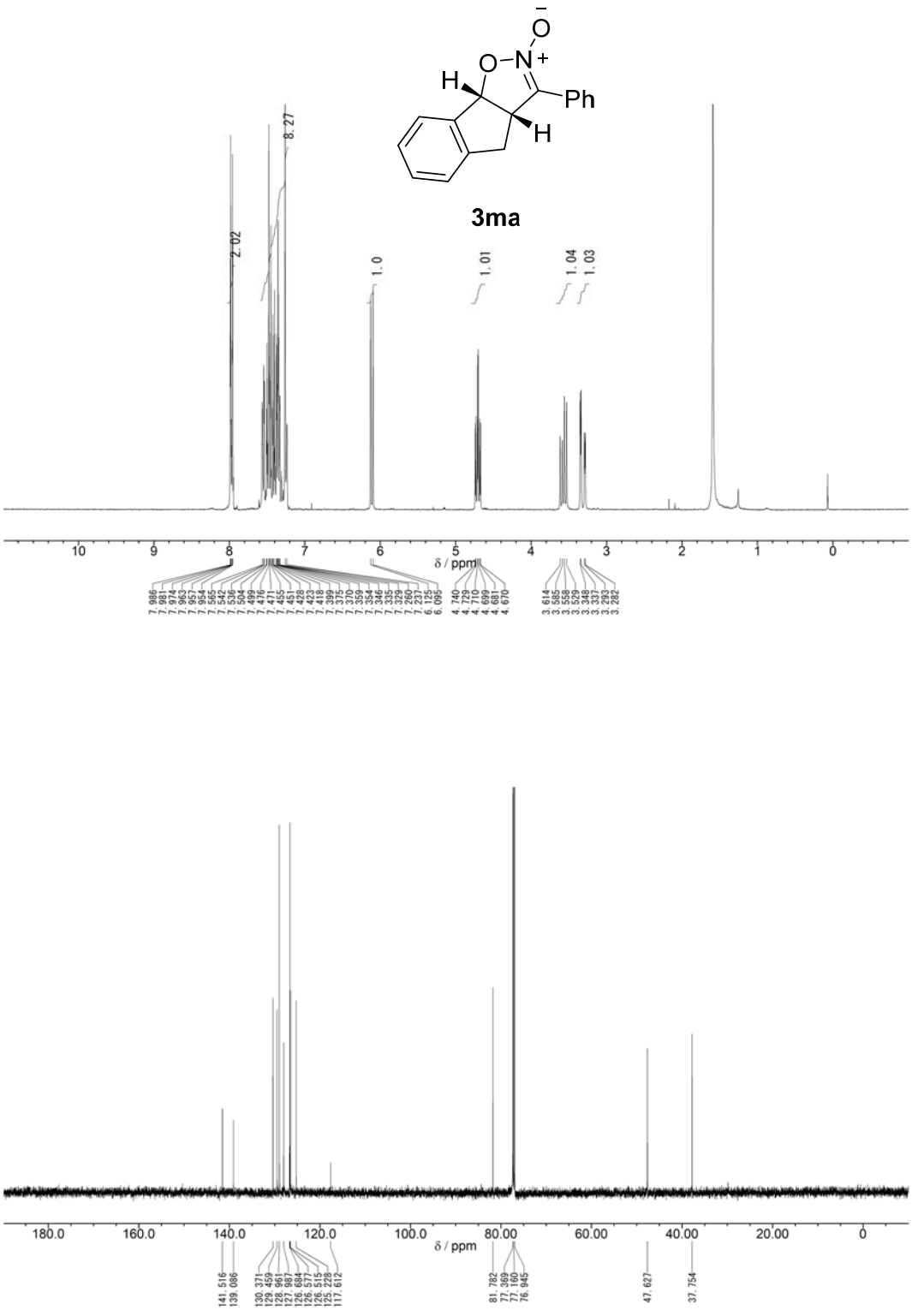
^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ja** ($CDCl_3$, rt).



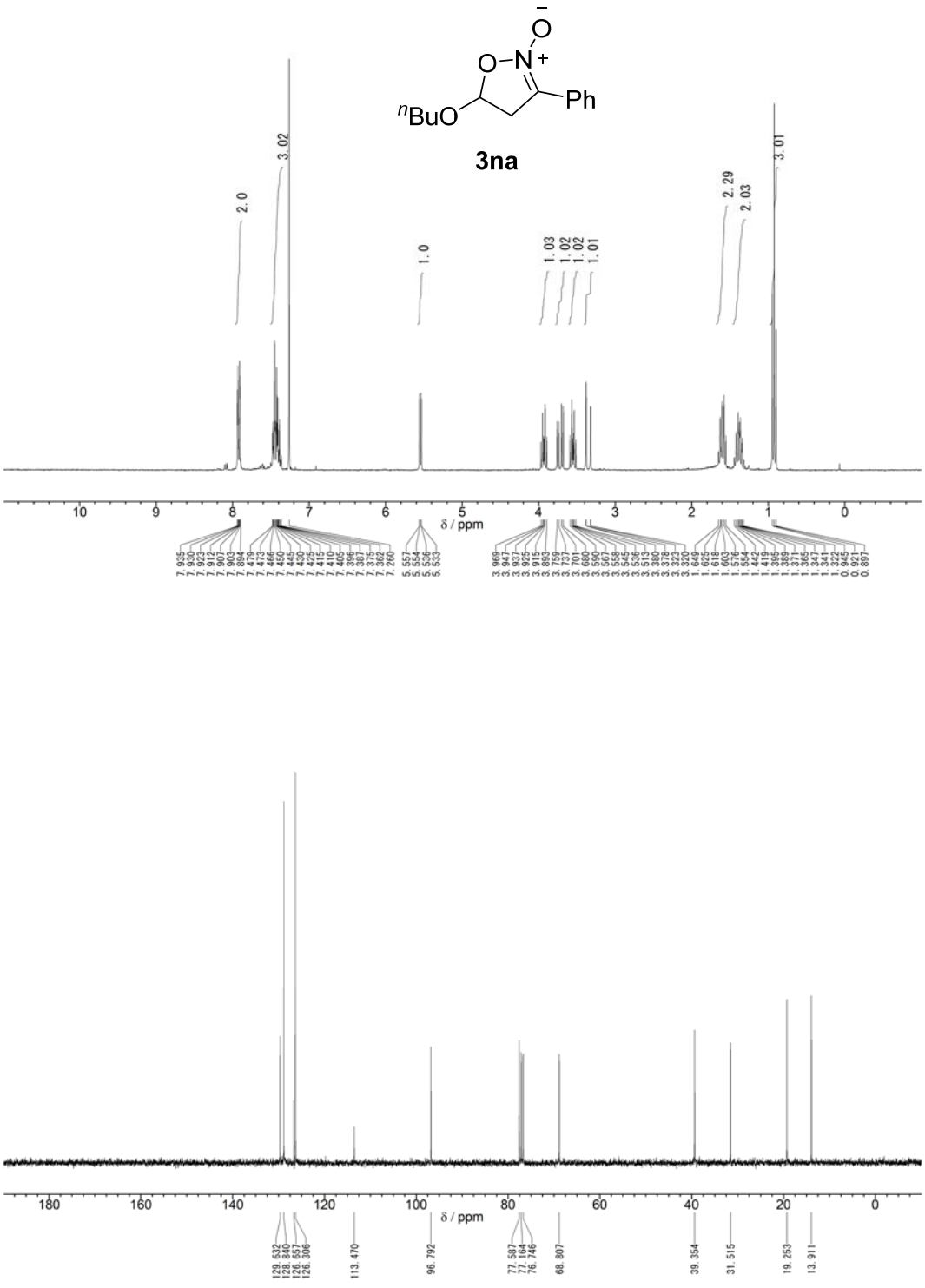
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ka** ($CDCl_3$, rt).



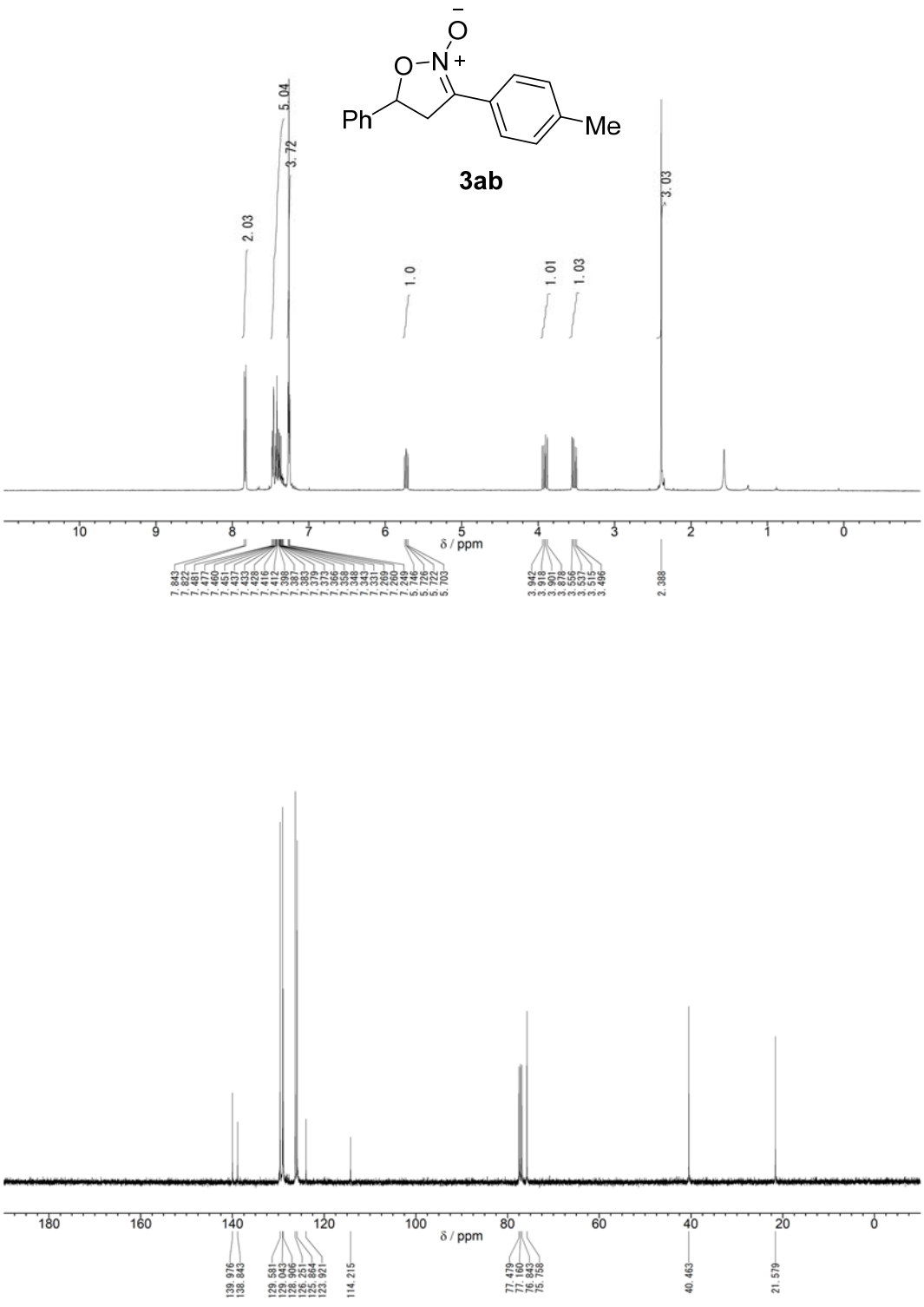
^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **3la** ($CDCl_3$, rt).



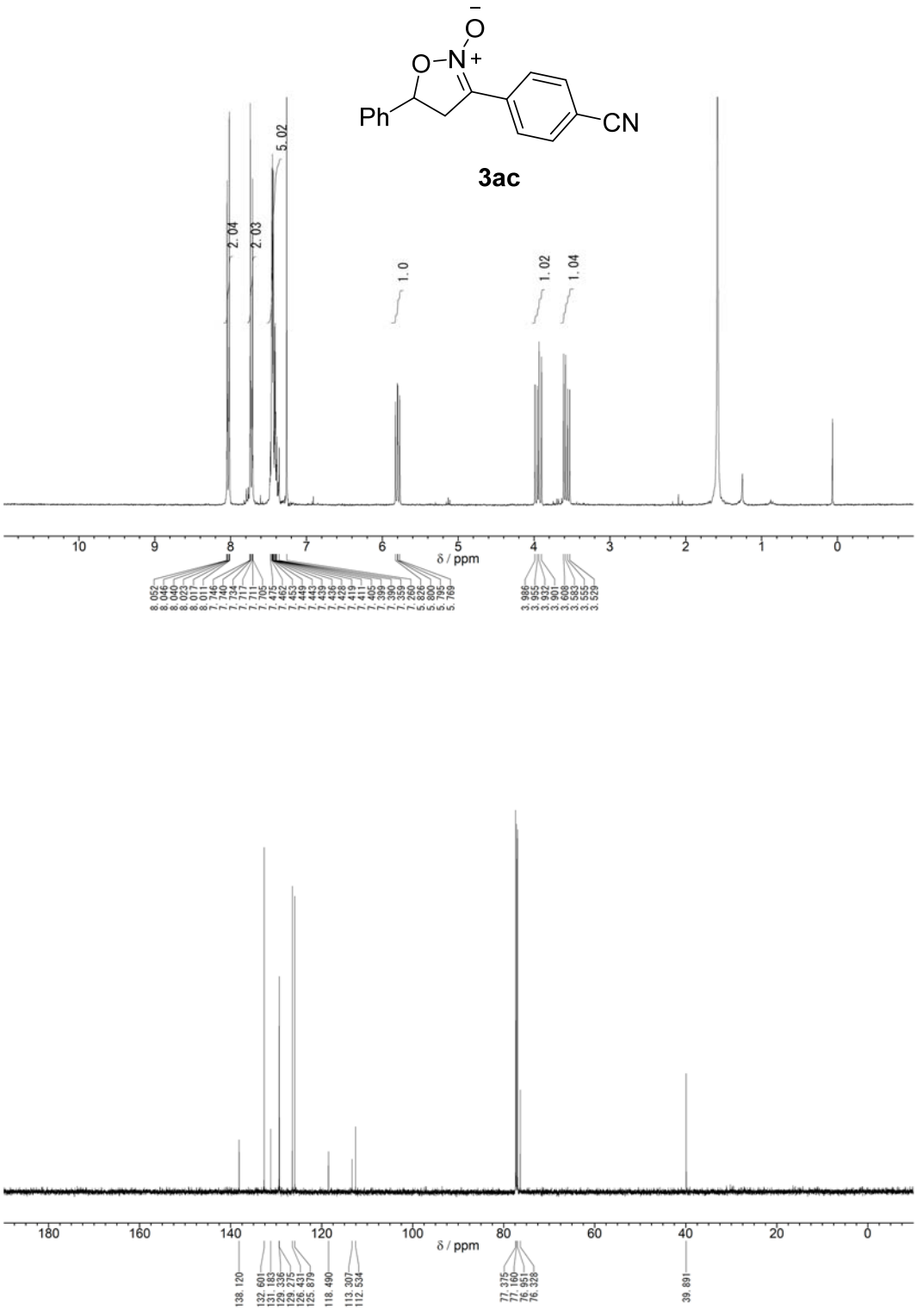
^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ma** ($CDCl_3$, rt).



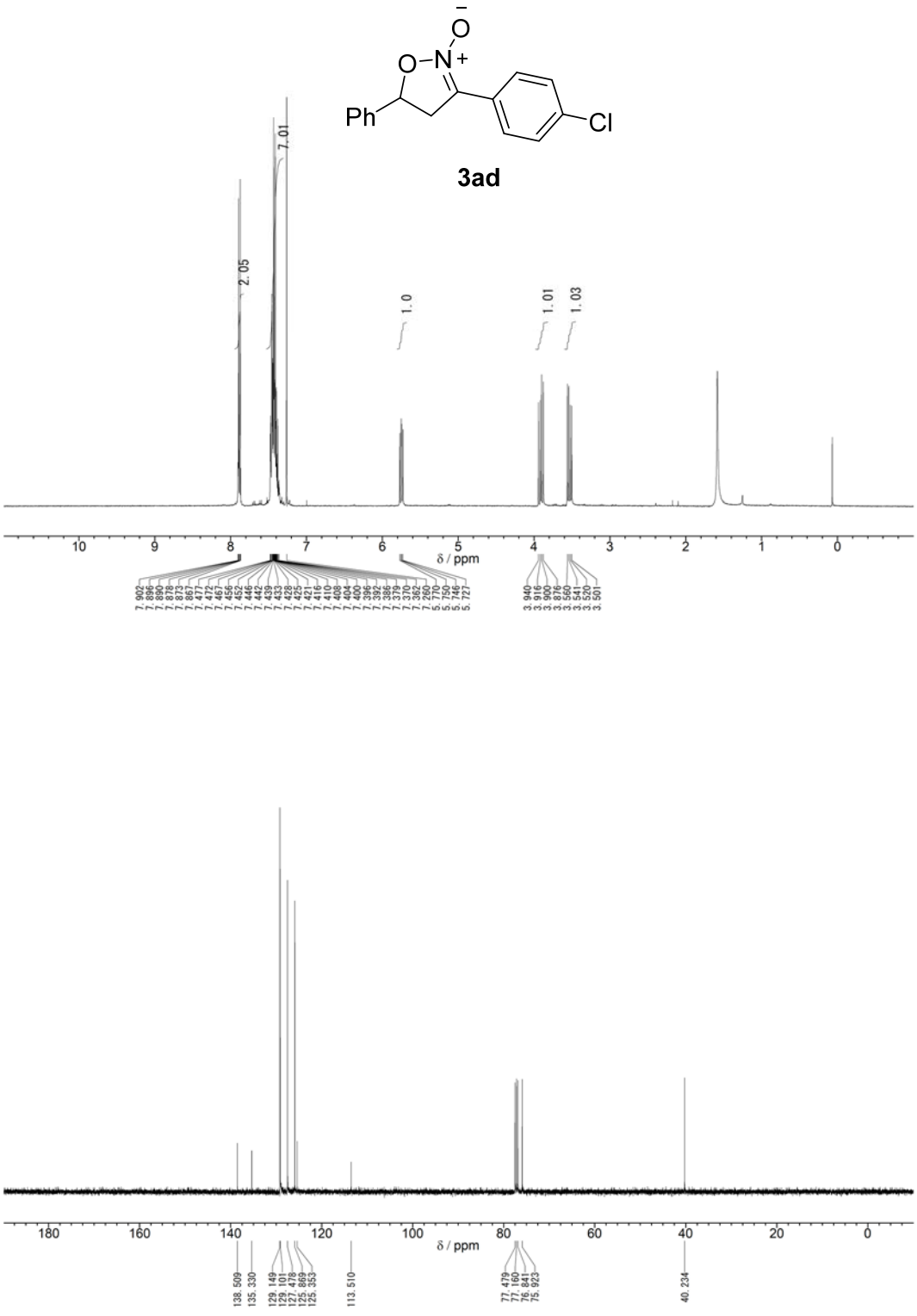
^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **3na** ($CDCl_3$, rt).



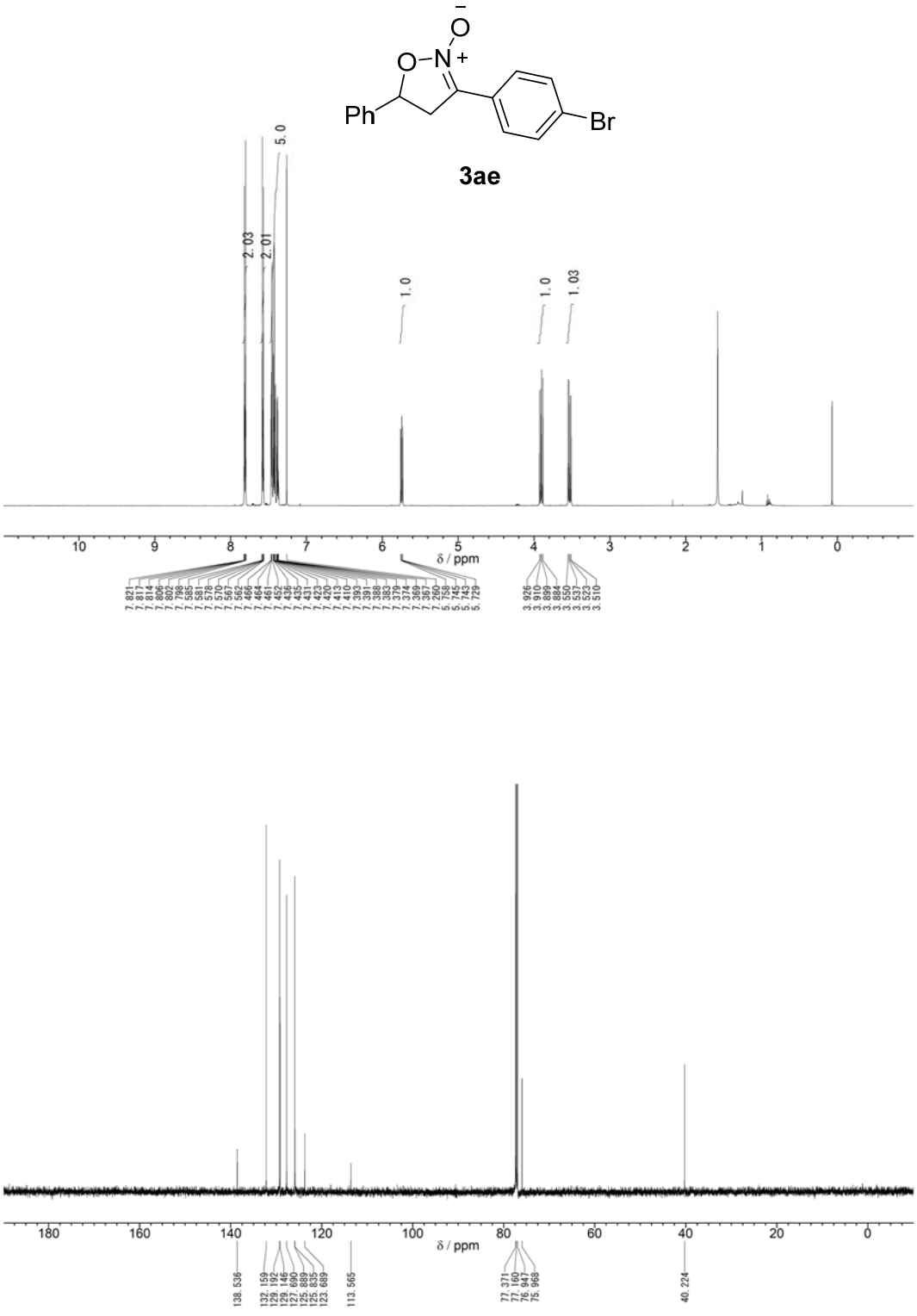
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3ab** ($CDCl_3$, rt).



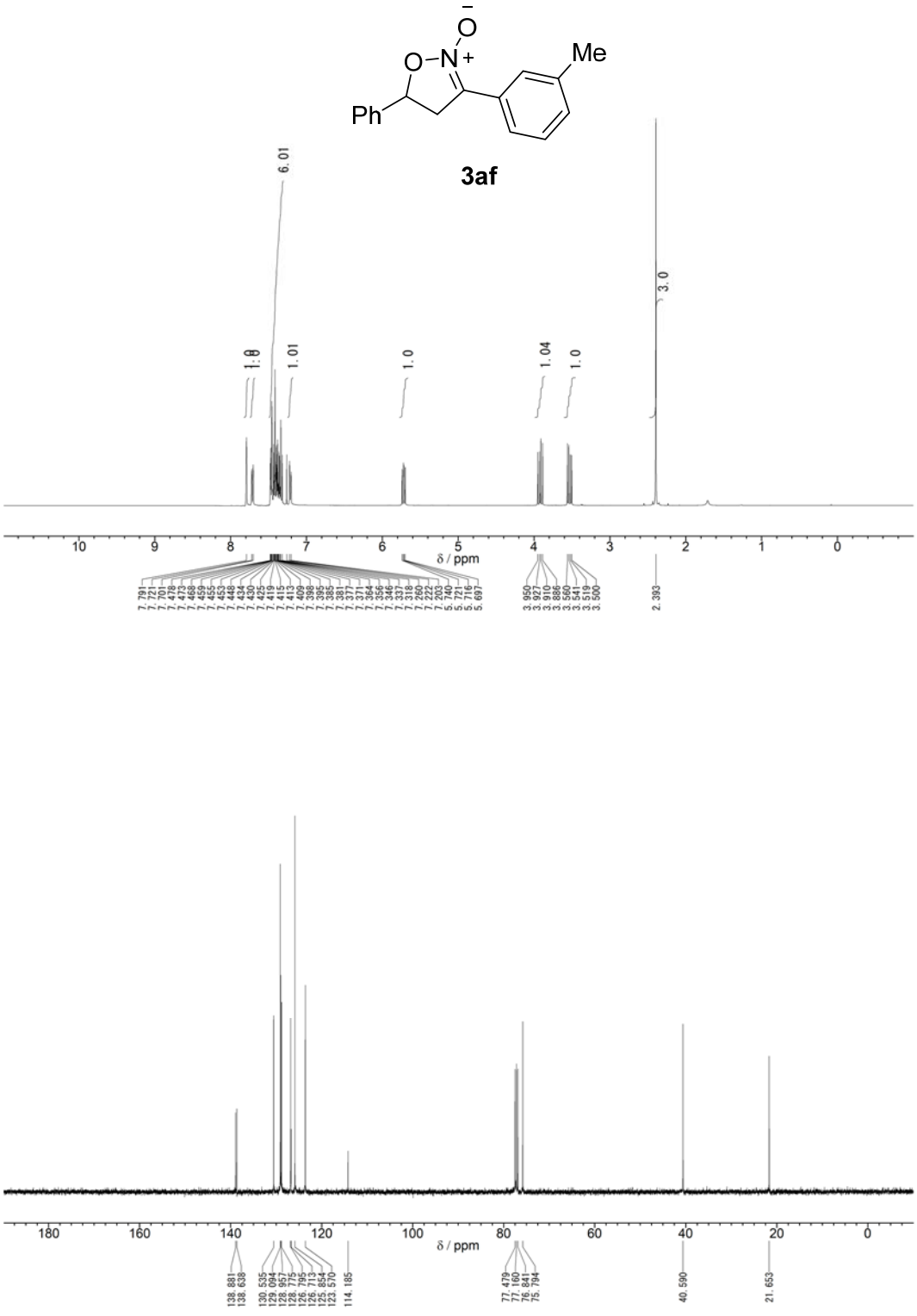
^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ac** ($CDCl_3$, rt).



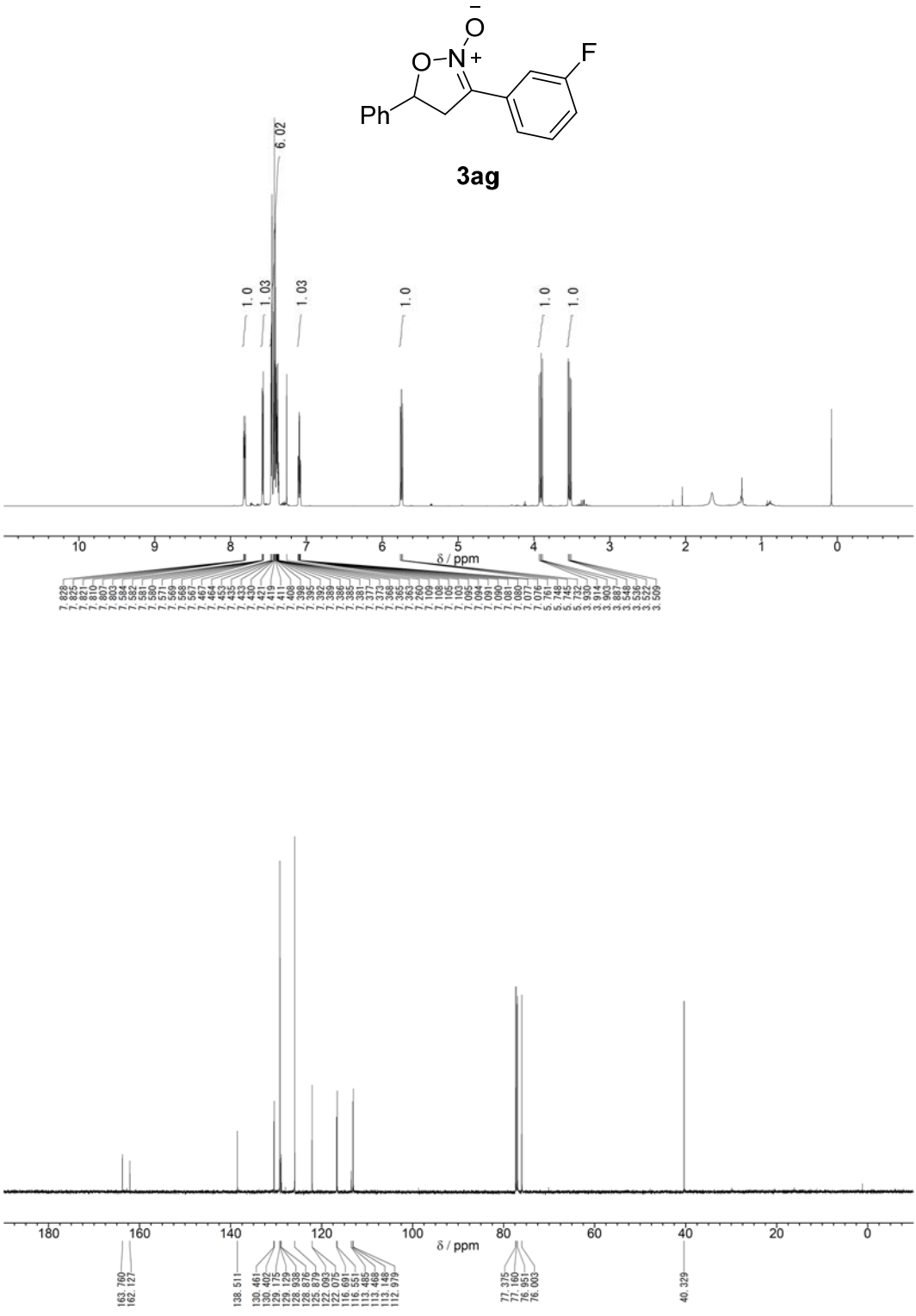
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3ad** ($CDCl_3$, rt).



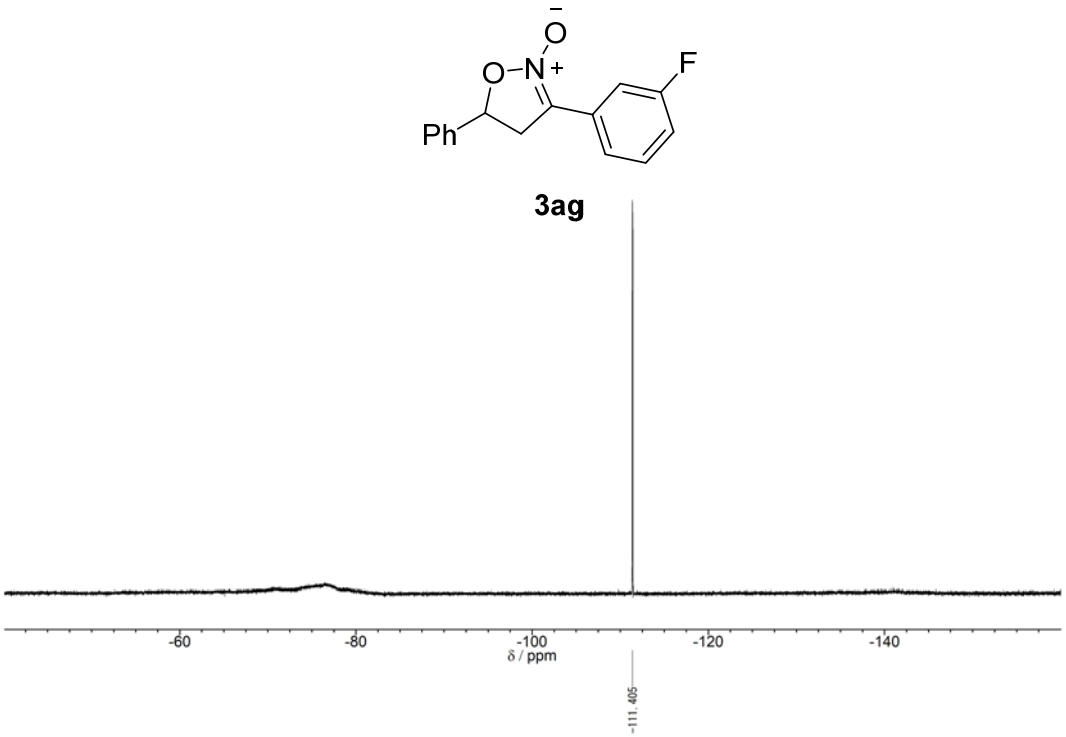
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ae** ($CDCl_3$, rt).



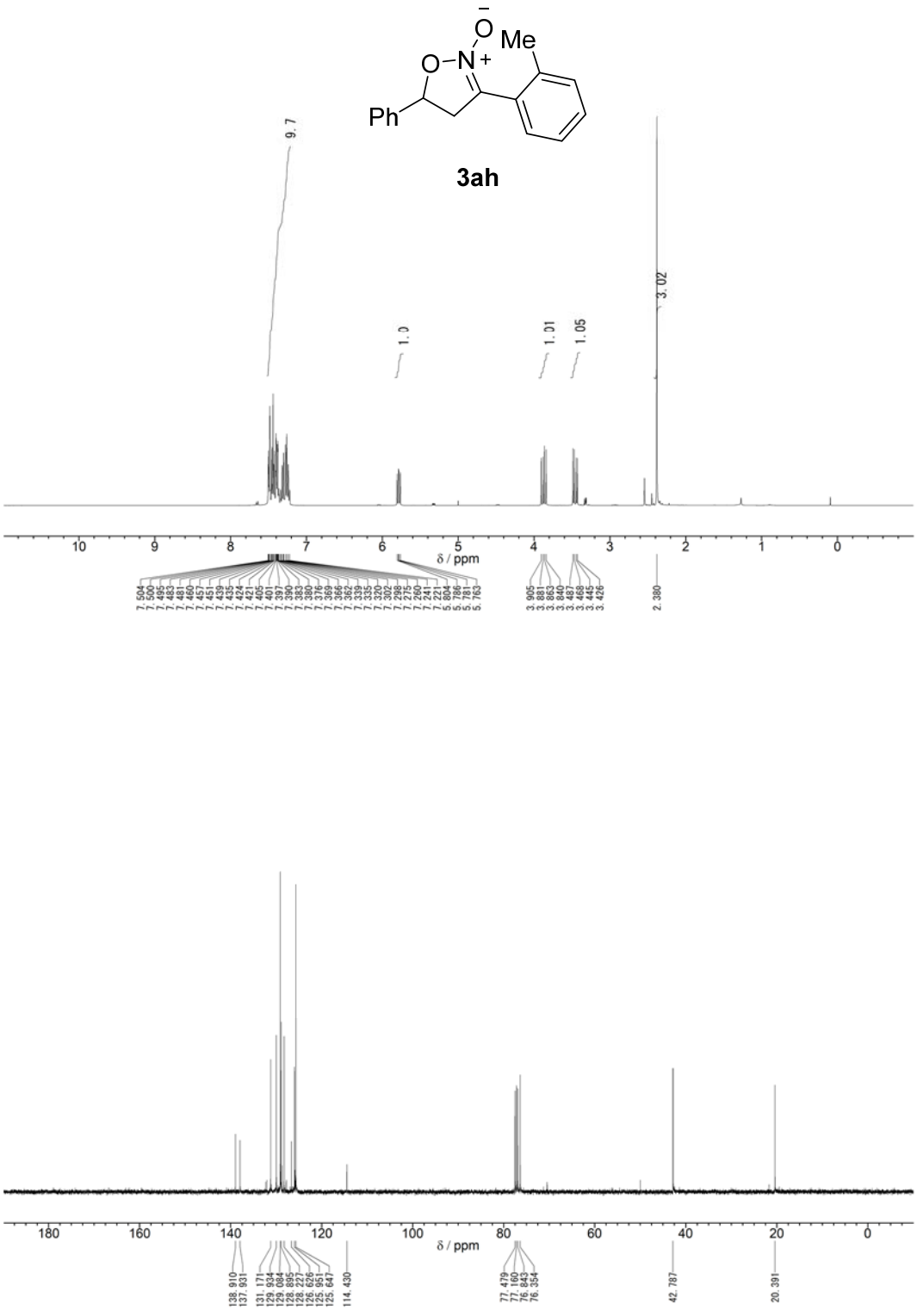
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3af** ($CDCl_3$, rt).



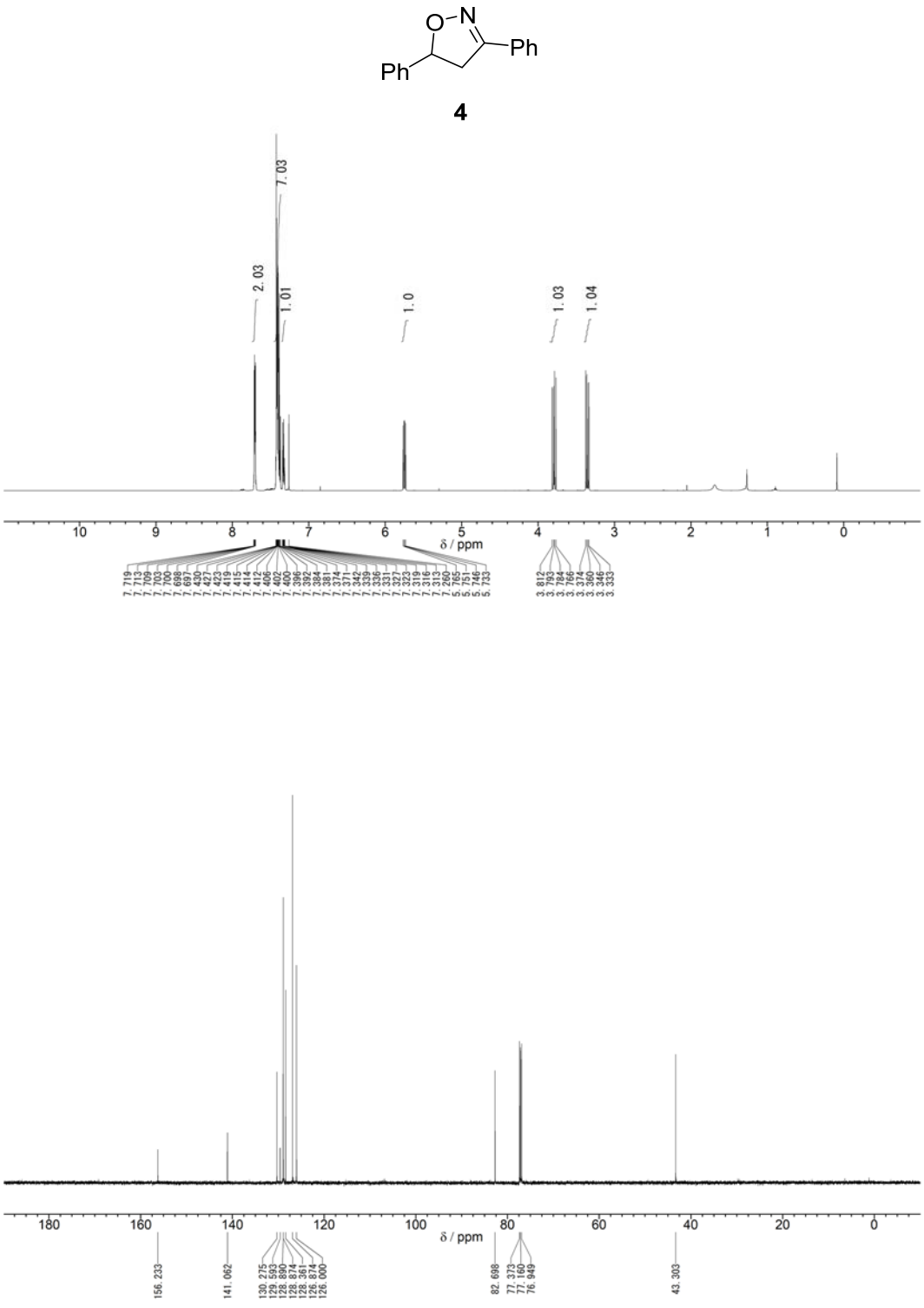
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ag** ($CDCl_3$, rt).



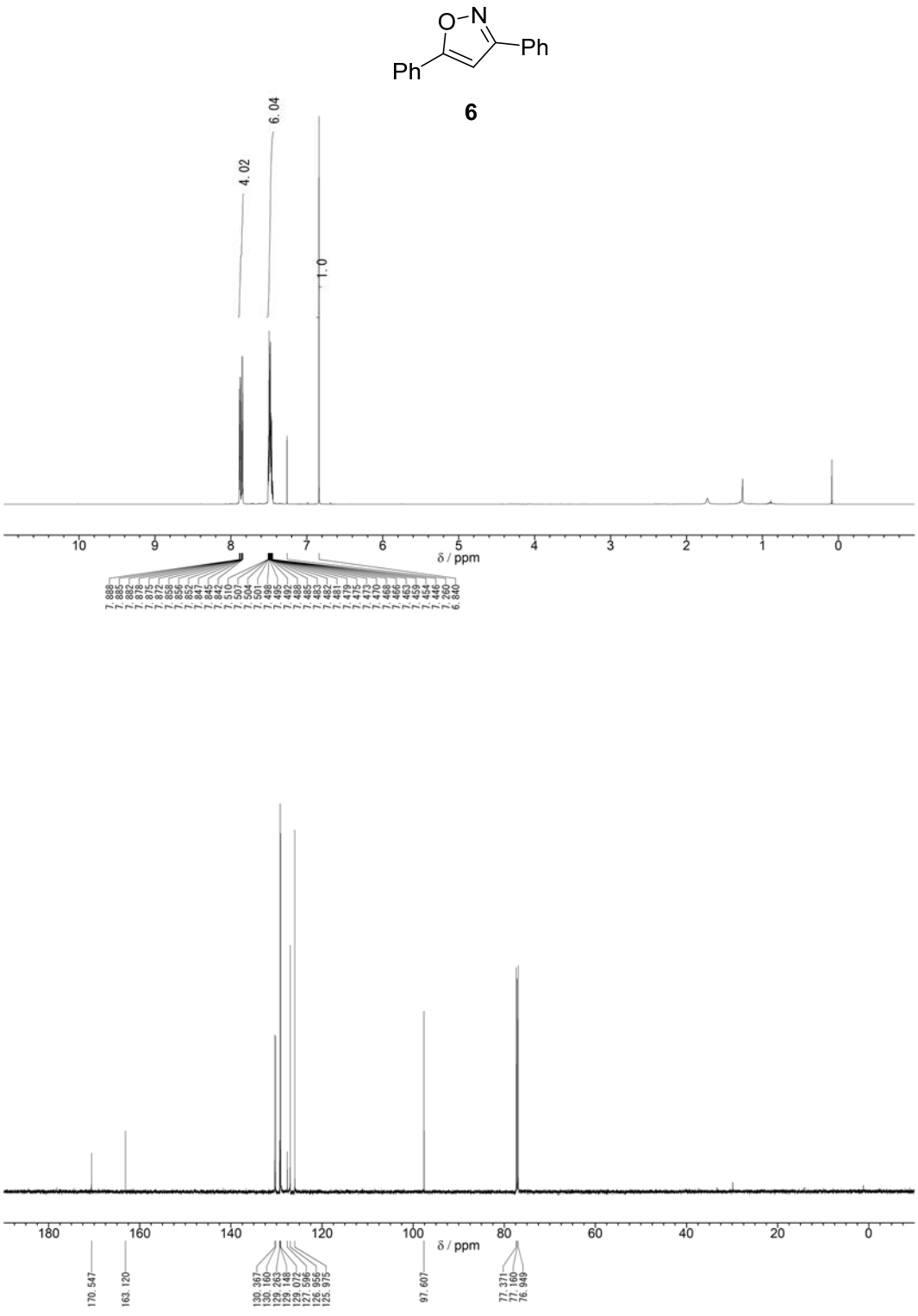
$^{19}F\{^{1}H\}$ NMR (282 MHz) spectrum of **3ag** ($CDCl_3$, rt).



^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3ah** ($CDCl_3$, rt)



^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **4** ($CDCl_3$, rt)



^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **6** ($CDCl_3$, rt)

6. References

1. Erickson, A. S.; Kornblum, N. *J. Org. Chem.* **1977**, *42*, 3764–3765.
2. Raihan, M. J.; Kavala, V.; Habib, P. M.; Guan, Q.-Z.; Kuo, C.-W.; Yao, C.-F. *J. Org. Chem.* **2011**, *76*, 424–434.
3. Shi, D; Qin, H.-T.; Zhu, C.; Liu, F. *Eur*. *J*. *Org*. *Chem*. **2015**, *2015*, 5084–5088.