Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Ligand-Controlled, Pd/CuH-Catalyzed Reductive Cross-Coupling of Terminal Alkenes and *N*-Heteroaryl Bromides

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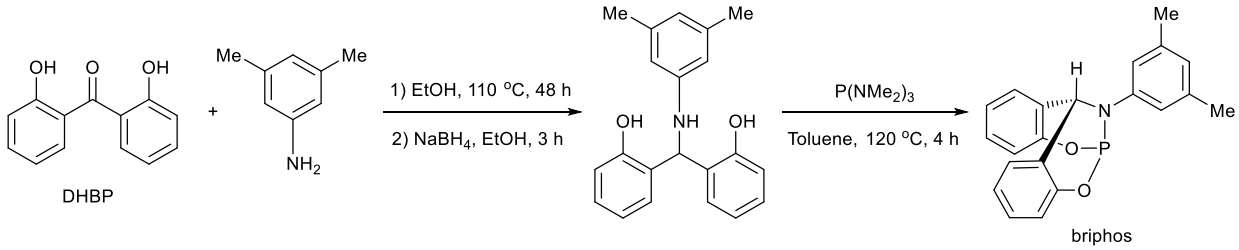
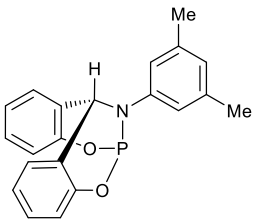
1. General information

Commercially available compounds were used without further purification or drying. Anhydrous solvents were used as received from a SureSeal bottle without further purification or drying ("anhydrous"). Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminum plates (Merck). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm or 366 nm). Flash column chromatography was performed on Merck silica gel (40-63 mesh). ^{1}H NMR (400 or 500 MHz), ^{13}C{^{1}H} NMR (100 or 126 MHz), ^{19}F{^{1}H} NMR (376 MHz), ^{29}Si{^{1}H} NMR (99 MHz), and ^{31}P{^{1}H} NMR (162 MHz) spectra were recorded on a Bruker Ascend 400 or 500, or a Bruker Avance III HD spectrometer and were reported in ppm, relative to residual protonated solvent peak ($CDCl_3$). All coupling constants (*J* values) were reported in Hertz (Hz). Mass spectra were obtained using a Bruker Daltonik micro TOF-Q II high-resolution mass spectrometer (ESI) at the KAIST Analyst Center for Research Advancement.

2. Preparation of briphos ligand



To a stirred solution of 2,2´-dihydroxybenzophenone (**DHBP**, 2.14 g, 10.0 mmol) in 15 mL of EtOH was added 3,5-dimethylaniline (30 mmol). The resulting solution was stirred at 110 °C for 48 h. The conversion for the imine formation was 95% determined by ^{1}H NMR spectra of aliquots in $CDCl_3$. After cooling to ambient temperature, 1.13 g of $NaBH_4$ (30.0 mmol) was added to the reaction flask. After stirring for 3 h, saturated $NaHCO_3$ solution (20 mL) was poured into the flask and the mixture was extracted with CH_2Cl_2 (3× 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product dissolved in 20 mL of toluene was mixed with hexamethylphosphorous triamide (HMPT, 2.18 mL, 12.0 mmol) at ambient temperature. Then the resulting solution was heated to 120 °C for 4 h under N_2 atmosphere. After cooling to ambient temperature, the solution was concentrated under reduced pressure. Purification of the crude mixture by a flash column chromatography on silica gel with ethyl acetate/hexane yielded a white solid (2.47 g, 71%).



briphos

White solid (2.47 g, 71% yield).

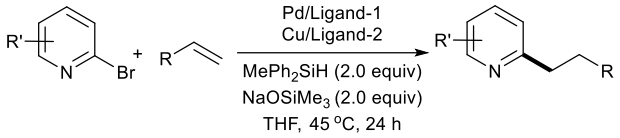
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 2H), 7.11 – 7.01 (m, 4H), 6.78 (s, 2H), 6.73 (s, 1H), 5.62 (d, *J* = 4.0 Hz, 1H), 2.29 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.4, 149.3, 144.3, 144.1, 139.4, 128.9, 127.5, 127.4, 127.1, 125.3, 125.3, 122.9, 119.1, 119.1, 118.9, 118.8, 55.0, 21.5.

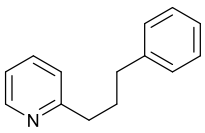
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 90.5

HRMS (ESI) calculated for $C_{21}H_{18}NO_2P$ [M+Na]$^{+}$: 370.0973, Found: 370.0956.

3. General procedure for reductive cross-coupling



In a glove box filled with argon, a 5 mL vial equipped with a magnetic bar was charged with CuOAc (1.0 mg, 0.008 mmol) and the corresponding ligand (0.0088 mmol) in anhydrous tetrahydrofuran (0.1 mL). After stirring for 30 min, methyldiphenylsilane (0.4 mmol) and sodium trimethylsilanolate (0.4 mmol) were added and stirred for additional 30 min. Another 5 mL vial equipped with a magnetic bar was charged with [Pd(cinnamyl)Cl]$_2$ (1.0 mg, 0.002 mmol) and the corresponding ligand (0.0088 mmol) in anhydrous tetrahydrofuran (0.1 mL) and stirred for 30 min. The solution was transferred into the other reaction mixture, then the alkene (0.2 mmol) was added to the reaction vial, along with the aryl bromide (0.3 mmol). The reaction mixture was taken out of the glove box then stirred at 45 °C for 24 h. After the reaction, the mixture was cooled to ambient temperature and passed through a pad of silica gel with ethyl acetate and the solvent was removed under vacuum. The product was purified by a flash column chromatography on silica gel with ethyl acetate/hexane.



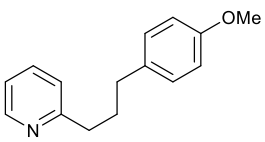
3a

Yellow liquid (36.6 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.59 (s, 1H), 7.37 – 7.23 (m, 2H), 7.23 – 6.98 (m, 5H), 2.84 (t, *J* = 7.9 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.08 (t, *J* = 7.8 Hz, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.1, 149.3, 142.2, 136.5, 128.6, 128.4, 125.9, 122.9, 121.2, 38.0, 35.7, 31.6.

HRMS (ESI) calculated for $C_{14}H_{15}N$ [M+H]$^{+}$: 198.1277, Found: 198.1275



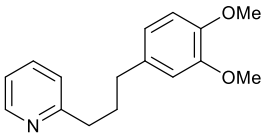
3b

Yellow liquid (40.9 mg, 90% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.14 (m, 8.4 Hz, 4H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.85 (t, *J* = 7.8 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 2.06 (t, *J* = 7.8 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.8, 157.8, 148.8, 136.7, 134.1, 129.4, 123.0, 121.1, 113.8, 55.3, 37.6, 34.6, 31.7.

HRMS (ESI) calculated for $C_{15}H_{17}NO$ [M+H]$^{+}$: 228.1383, Found: 228.1385



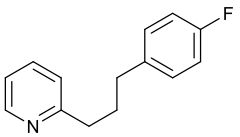
3c

Yellow liquid (47.3 mg, 92% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.19 – 7.00 (m, 2H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.71 (d, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 2.83 (t, *J* = 7.8 Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.05 (t, *J* = 7.7 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.9, 148.9, 148.9, 147.2, 136.8, 134.8, 123.1, 121.2, 120.3, 111.9, 111.3, 56.0, 55.9, 37.7, 35.2, 31.7.

HRMS (ESI) calculated for $C_{16}H_{19}NO_2$ [M+H]$^+$: 258.1489, Found: 258.1491



3d

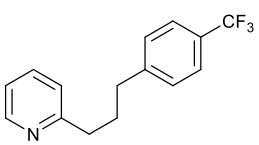
Yellow liquid (38.3 mg, 89% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.14 (m, 4H), 6.95 (t, *J* = 8.7 Hz, 2H), 2.82 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.05 (t, *J* = 7.8 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.3, 161.8, 160.4, 149.2, 137.8, 137.8, 136.6, 129.9, 129.9, 123.0, 121.2, 115.2, 115.1, 37.8, 34.8, 31.6.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -117.9.

HRMS (ESI) calculated for $C_{14}H_{14}FN$ [M+H]$^+$: 216.1183, Found: 216.1193



3e

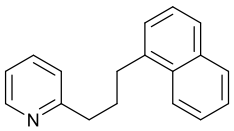
Yellow liquid (33.9 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.5 Hz, 1H), 7.60 (td, *J* = 7.7, 1.9 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.17 – 7.08 (m, 2H), 2.86 – 2.80 (m, 2H), 2.74 (t, *J* = 7.7 Hz, 2H), 2.15 – 2.03 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.2, 148.9, 145.9, 136.3, 128.5, 128.3, 128.0, 127.8, 127.5, 127.4, 125.2, 125.0, 124.9, 123.0, 122.6, 120.9, 120.9, 37.3, 35.1, 30.8.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.30.

HRMS (ESI) calculated for $C_{15}H_{14}F_3N$ [M+H]$^+$: 266.1151 , Found: 266.1151



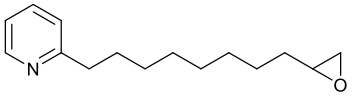
3f

Yellow liquid (45.4 mg, 92% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.48 (p, *J* = 6.9 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 7.27 – 7.04 (m, 1H), 3.17 (t, *J* = 7.7 Hz, 2H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.24 (t, *J* = 7.8 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.7, 148.9, 138.2, 136.7, 134.0, 131.9, 128.8, 126.7, 126.1, 125.8, 125.6, 125.5, 123.9, 123.1, 121.2, 38.1, 32.7, 30.7.

HRMS (ESI) calculated for $C_{18}H_{17}N$ [M+H]$^+$: 248.1434, Found: 248.1441



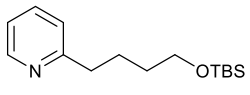
3g

Orange liquid (31.7 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 5.0 Hz, 1H), 7.57 (td, *J* = 7.6, 1.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 7.5, 4.9 Hz, 1H), 2.87 (dq, *J* = 5.7, 2.8 Hz, 1H), 2.83 – 2.74 (m, 2H), 2.74 – 2.66 (m, 1H), 2.44 (dd, *J* = 5.0, 2.7 Hz, 1H), 1.70 (q, *J* = 7.5 Hz, 2H), 1.57 – 1.46 (m, 2H), 1.47 – 1.37 (m, 2H), 1.36 – 1.24 (m, 8H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.5, 149.1, 136.5, 122.9, 121.0, 52.5, 47.2, 38.4, 32.6, 30.0, 29.5, 29.5, 29.5, 29.4, 26.0.

HRMS (ESI) calculated for $C_{15}H_{23}NO$ [M+H]$^+$: 234.1852, Found: 234.1857



3h

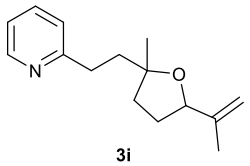
White liquid (40.3 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 – 8.29 (m, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 6.0 Hz, 1H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.80 (t, *J* = 7.7 Hz, 2H), 1.77 (p, *J* = 7.6 Hz, 2H), 1.68 – 1.49 (m, 2H), 0.87 (s, 9H), 0.02 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.2, 149.1, 136.4, 122.8, 121.0, 63.0, 38.0, 32.5, 31.3, 26.1, 26.0, 18.4, -5.3.

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$) δ 18.6.

HRMS (ESI) calculated for $C_{15}H_{27}NOSi$ [M+H]$^{+}$: 266.1935, Found: 266.1940



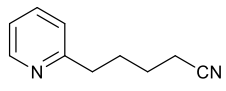
3i

White liquid (36.7 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.68 – 7.40 (m, 1H), 7.18 (s, 1H), 7.10 (s, 1H), 5.07 – 4.92 (m, 1H), 4.82 – 4.74 (m, 1H), 4.37 (dt, *J* = 13.6, 7.4 Hz, 1H), 2.89 (d, *J* = 9.0 Hz, 2H), 2.13 – 1.84 (m, 4H), 1.76 (m, 2H), 1.72 (s, 3H), 1.30 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.5, 149.0, 146.2, 145.9, 136.7, 123.0, 121.1, 110.5, 110.3, 83.1, 82.9, 82.5, 81.7, 41.9, 41.2, 37.3, 37.3, 33.7, 33.5, 31.6, 31.4, 29.8, 26.8, 26.2, 18.2, 17.9.

HRMS (ESI) calculated for $C_{15}H_{21}NO$ [M+Na]$^{+}$: 254.1515, Found: 254.1518



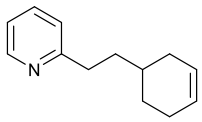
3j

White liquid (17.9 mg, 56% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.1 Hz, 1H), 7.75 (td, *J* = 7.8, 2.0 Hz, 1H), 7.27 (d, *J* = 6.7 Hz, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.40 (t, *J* = 7.1 Hz, 2H), 1.94 (dd, *J* = 9.4, 6.1 Hz, 2H), 1.75 (q, *J* = 7.5 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.64, 148.58, 137.58, 123.35, 121.77, 119.71, 36.85, 28.75, 25.06, 17.18.

HRMS (ESI) calculated for $C_{10}H_{12}N_2$ [M+H]$^{+}$: 161.1073, Found: 161.1078



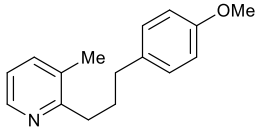
3k

Pale yellow liquid (34.4 mg, 92% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.9 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.09 (dd, *J* = 7.5, 4.9 Hz, 1H), 5.65 (d, *J* = 2.6 Hz, 2H), 2.83 (t, *J* = 8.1 Hz, 2H), 2.32 – 2.09 (m, 1H), 2.11 – 1.99 (m, 1H), 1.80 (dd, *J* = 12.7, 3.7 Hz, 1H), 1.71 (dq, *J* = 13.9, 7.5, 6.1 Hz, 3H), 1.64 – 1.54 (m, 1H), 1.27 (dtd, *J* = 12.3, 10.0, 6.6 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.6, 149.2, 136.5, 127.2, 126.6, 122.8, 121.0, 36.9, 35.9, 33.5, 31.9, 28.9, 25.3.

HRMS (ESI) calculated for $C_{13}H_{17}N$ [M+H]$^{+}$: 188.1434, Found: 188.1442



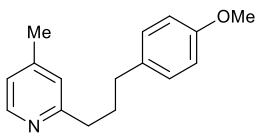
3l

Yellow liquid (31.8 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 3.8 Hz, 1H), 7.44 – 7.32 (m, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 7.02 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.84 – 2.76 (m, 2H), 2.67 (t, *J* = 7.7 Hz, 2H), 2.25 (s, 3H), 2.01 (tt, *J* = 9.8, 6.7 Hz, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.3, 157.8, 146.6, 137.7, 134.4, 131.1, 129.4, 121.2, 113.8, 55.4, 35.0, 30.6, 18.8.

HRMS (ESI) calculated for $C_{16}H_{19}NO$ [M+H]$^{+}$: 242.1539, Found: 242.1549



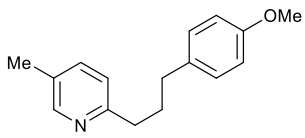
3m

Yellow liquid (37.1 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 – 8.33 (m, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.98 – 6.94 (m, 1H), 6.92 (dd, *J* = 5.1, 1.6 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 2.81 – 2.74 (m, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.31 (s, 3H), 2.07 – 1.96 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.8, 157.9, 149.0, 147.5, 134.4, 129.5, 123.8, 122.2, 113.9, 55.4, 37.8, 34.8, 31.9, 21.1.

HRMS (ESI) calculated for $C_{16}H_{19}NO$ [M+H]$^+$: 242.1539, Found: 242.1538



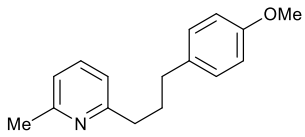
3n

Yellow liquid (45.8 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 2.3 Hz, 1H), 7.38 (dd, *J* = 7.9, 2.3 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 2.81 – 2.74 (m, 2H), 2.64 – 2.58 (m, 2H), 2.28 (s, 3H), 2.05 – 1.97 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.1, 157.8, 149.6, 137.0, 134.4, 130.2, 129.4, 122.3, 113.8, 55.3, 37.4, 34.7, 31.9, 18.1.

HRMS (ESI) calculated for $C_{16}H_{19}NO$ [M+H]$^+$: 242.1539, Found: 242.1543



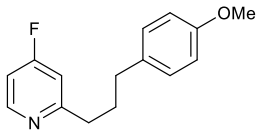
3o

Yellow liquid (47.2 mg, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.94 (t, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 2.82 – 2.75 (m, 2H), 2.66 – 2.59 (m, 2H), 2.53 (s, 3H), 2.06 – 1.96 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.5, 157.8, 157.8, 136.6, 134.4, 129.4, 120.6, 119.6, 113.8, 55.3, 38.1, 34.8, 32.1, 24.6.

HRMS (ESI) calculated for $C_{16}H_{19}NO$ [M+H]$^+$: 242.1539, Found: 242.1548



3p

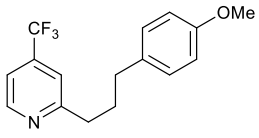
Yellow liquid (39.0 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.83 (t, *J* = 7.7 Hz, 4H), 3.78 (s, 3H), 2.81 (t, *J* = 7.8 Hz, 2H), 2.66 – 2.59 (m, 2H), 2.09 – 1.98 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 170.1, 168.0, 165.6, 157.9, 151.6, 134.0, 129.4, 113.9, 110.5, 110.4, 109.3, 109.1, 55.3, 37.8, 34.6, 31.4.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -103.2.

HRMS (ESI) calculated for $C_{15}H_{16}FNO$ [M+Na]$^+$: 268.1108, Found: 268.1127



3q

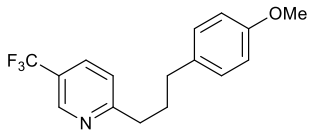
Yellow liquid (40.6 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.0 Hz, 1H), 7.32 (d, *J* = 5.5 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.94 – 2.85 (m, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.07 (tt, *J* = 9.3, 6.8 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 163.8, 158.0, 150.2, 139.1, 138.9, 138.6, 138.3, 133.9, 129.5, 126.3, 124.1, 121.9, 119.8, 118.6, 118.5, 116.8, 116.8, 113.9, 55.4, 37.8, 34.6, 31.5.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -64.8.

HRMS (ESI) calculated for $C_{16}H_{16}F_3NO$ [M+Na]$^+$: 318.1076, Found: 318.1076



3r

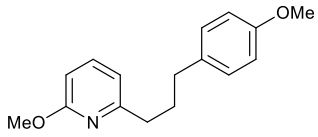
Yellow liquid (36.1 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (dt, *J* = 2.0, 1.0 Hz, 1H), 7.81 (ddd, *J* = 8.2, 2.4, 0.7 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.15 – 7.06 (m, 2H), 6.90 – 6.77 (m, 2H), 3.79 (s, 3H), 2.91 – 2.85 (m, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.06 (tt, *J* = 9.2, 6.8 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.2, 158.0, 146.3, 146.3, 146.2, 146.2, 133.9, 133.6, 133.5, 133.5, 133.5, 129.5, 127.1, 125.0, 124.7, 124.4, 124.1, 123.9, 122.8, 122.7, 120.6, 113.9, 55.4, 37.8, 34.6, 31.4.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.2.

HRMS (ESI) calculated for $C_{16}H_{16}F_3NO$ [M+H]$^+$: 296.1257, Found: 296.1260



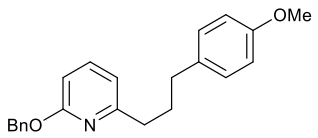
3s

Yellow liquid (41.6 mg, 81% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 8.2 Hz, 1H), 3.95 (s, 3H), 3.80 (s, 3H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 2.06 (p, *J* = 7.7 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 163.8, 160.0, 157.8, 138.8, 134.6, 129.4, 115.3, 113.8, 107.4, 55.3, 53.3, 37.3, 34.6, 31.2.

HRMS (ESI) calculated for $C_{16}H_{19}NO_2$ [M+Na]$^+$: 280.1308, Found: 280.1324



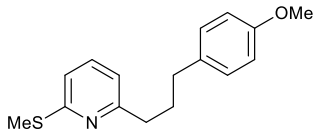
3t

colorless liquid (48.6 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 3H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 5.40 (s, 2H), 3.80 (s, 3H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.64 – 2.58 (m, 2H), 2.10 – 1.99 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.2, 159.8, 157.9, 139.0, 137.8, 134.6, 129.5, 128.5, 128.2, 127.8, 115.6, 113.8, 108.1, 67.5, 55.4, 37.2, 34.6, 31.2.

HRMS (ESI) calculated for $C_{22}H_{23}NO_2$ [M+Na]$^+$: 356.1621, Found: 356.1627



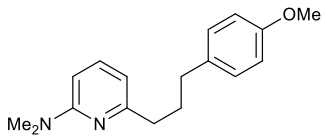
3u

Pale yellow liquid (53.1 mg, 97% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.7 Hz, 1H), 7.15 – 7.09 (m, 2H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.81 (dd, *J* = 7.5, 0.9 Hz, 1H), 3.79 (s, 3H), 2.81 – 2.75 (m, 2H), 2.66 – 2.60 (m, 2H), 2.57 (s, 3H), 2.12 – 1.99 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 159.1, 157.8, 136.2, 134.4, 129.5, 118.4, 118.2, 113.8, 55.3, 37.6, 34.6, 31.2, 13.4.

HRMS (ESI) calculated for $C_{16}H_{19}NOS$ [M+H]$^+$: 274.1260, Found: 274.1260



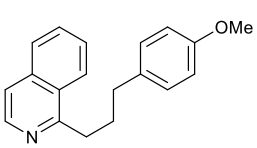
3v

Pale yellow liquid (42.5 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.42 (d, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 3.10 (s, 6H), 2.67 (dt, *J* = 17.3, 7.7 Hz, 4H), 2.12 – 2.02 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.2, 159.2, 157.7, 137.4, 134.9, 129.5, 113.8, 110.4, 102.8, 55.3, 38.0, 37.8, 34.7, 31.2.

HRMS (ESI) calculated for $C_{17}H_{22}N_2O$ [M+H]$^+$: 271.1805, Found: 271.1816



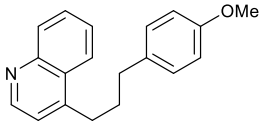
3w

Brown solid (46.8 mg, 84% yield). Mp : 76-79 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 5.7 Hz, 1H), 8.04 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.67 – 7.61 (m, 1H), 7.55 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.49 (d, *J* = 5.7 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.88 – 6.80 (m, 2H), 3.78 (s, 3H), 3.37 – 3.26 (m, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.18 (p, *J* = 7.8 Hz, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.0, 157.9, 141.9, 136.3, 134.2, 129.9, 129.5, 127.5, 127.1, 127.0, 125.3, 119.3, 113.9, 55.3, 35.1, 34.9, 31.5.

HRMS (ESI) calculated for $C_{19}H_{19}NO$ [M+H]$^+$: 278.1539, Found: 278.1540



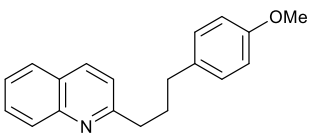
3x

Yellow liquid (42.7 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.52 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.28 – 7.18 (m, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.13 – 3.00 (m, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.07 (tt, *J* = 9.2, 6.8 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.0, 150.2, 148.3, 133.7, 130.4, 129.4, 129.1, 127.8, 126.4, 123.6, 120.9, 113.9, 55.3, 34.9, 31.8, 31.5.

HRMS (ESI) calculated for $C_{19}H_{19}NO$ [M+H]$^+$: 278.1539, Found: 278.1542



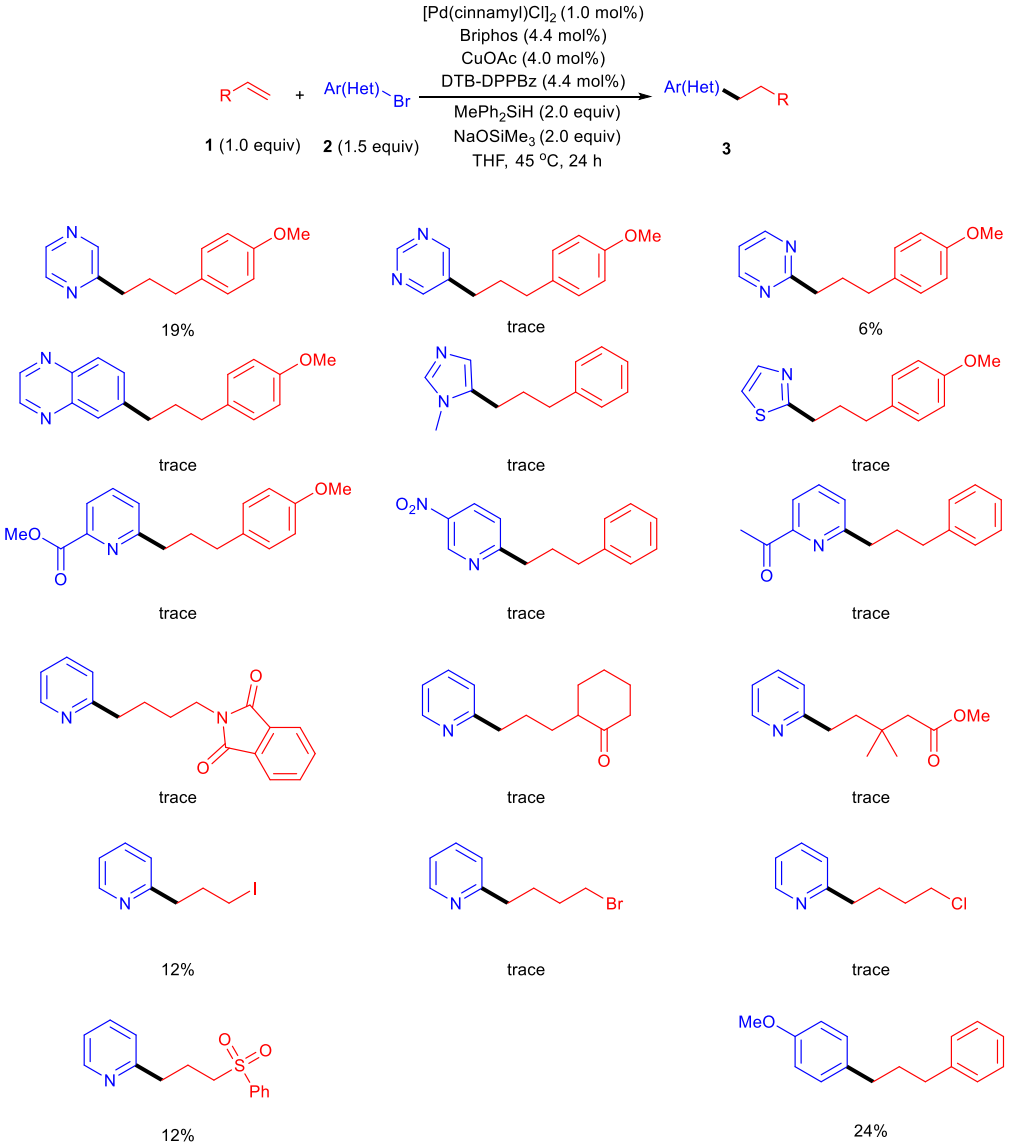
3y

Yellow liquid (24.9 mg, 45% yield).

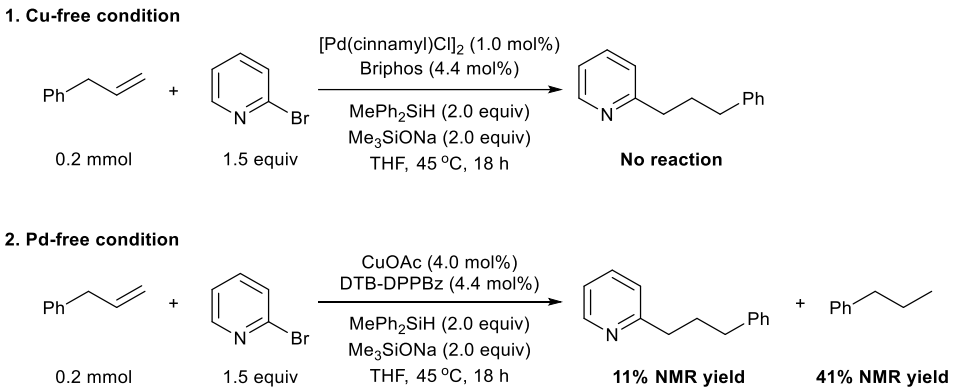
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.78 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.49 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 3.06 – 2.98 (m, 2H), 2.73 – 2.65 (m, 2H), 2.20 – 2.08 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.7, 157.9, 148.0, 136.4, 134.3, 134.1, 129.5, 128.9, 127.6, 126.9, 125.8, 121.5, 113.9, 55.4, 38.9, 34.9, 31.9.

HRMS (ESI) calculated for $C_{19}H_{19}NO$ [M+H]$^+$: 278.1539, Found: 278.1548

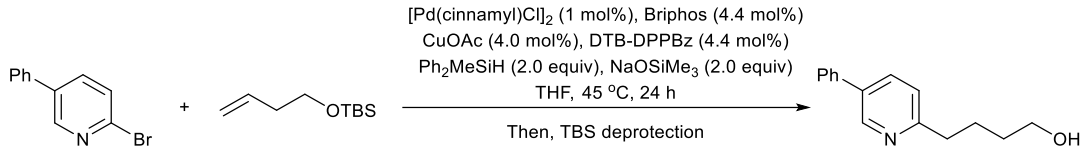


Scheme S1. Substrate scope to demonstrate the functional group tolerance. (Yields were determined by ^{1}H NMR. Mesitylene was used as an internal standard.)



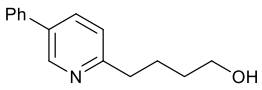
Scheme S2. Reductive cross-coupling only by Pd or CuH catalysis. (Yields were determined by ^{1}H NMR. Mesitylene was used as an internal standard.)

4. Procedure for synthesis of clathryimine B



2z **1h** **3z**

In a glove box filled with argon, a 5 mL vial equipped with a magnetic bar was charged with CuOAc (24.5 mg, 0.2 mmol) and DTB-DPPBz (197 mg, 0.22 mmol) in anhydrous tetrahydrofuran (2.5 mL). After stirring for 30 min, methyldiphenylsilane (10.0 mmol) and sodium trimethylsilanolate (10.0 mmol) were added and stirred for additional 30 min. Another 5 mL vial equipped with a magnetic bar was charged with $[Pd(cinnamyl)Cl]_2$ (25.9 mg, 0.05 mmol) and briphos ligand (76.4 mg, 0.22 mmol) in anhydrous tetrahydrofuran (2.5 mL) and stirred for 30 min. Both solution were transferred into 25 mL RBF, then 4-*tert*-butyldimethylsilyloxy-1-butene (5.5 mmol) was added to the reaction mixture, along with 2-bromo-5-phenylpyridine (1.17 g, 5.0 mmol). The reaction mixture was taken out of the glove box then stirred at 45 °C for 24 h. After the reaction, the mixture was cooled to ambient temperature and passed through a pad of silica gel with ethyl acetate and the solvent was removed under vacuum. A 250 mL RBF equipped with a magnetic bar was charged with the crude mixture in dry tetrahydrofuran (1 M). 1 M TBAF solution in THF (25.0 mmol) was slowly added and the reaction was stirred for 4 hours at room temperature. After the reaction, the mixture was diluted with distilled water and extracted with diethyl ether. The organic layer was washed with brine and dried over $MgSO_4$, and the solvent was removed under vacuum. The product **3z** was purified by a flash column chromatography on silica gel with ethyl acetate/hexane to yield a yellow liquid (0.76 g, 67%).



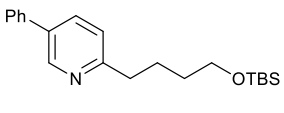
3z

Yellow liquid (0.76 g, 67% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 1H), 3.70 (t, *J* = 6.3 Hz, 2H), 2.88 (t, *J* = 7.7 Hz, 2H), 1.86 (p, *J* = 7.5 Hz, 2H), 1.67 (p, *J* = 6.7 Hz, 2H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 160.7, 147.1, 137.6, 135.3, 134.3, 129.1, 128.0, 127.0, 123.0, 62.1, 37.1, 32.2, 26.1.

HRMS (ESI) calculated for $C_{15}H_{17}NO$ $[M+H]^+$: 228.1383, Found: 228.1383



3hz

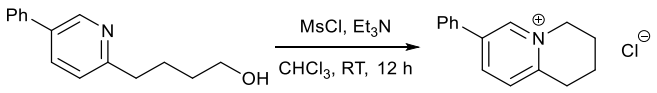
Colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 – 8.58 (m, 1H), 7.72 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.51 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.40 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 2.83 (t, *J* = 7.8 Hz, 2H), 1.81 (dt, *J* = 15.4, 7.9 Hz, 2H), 1.60 (dt, *J* = 14.1, 6.5 Hz, 2H), 0.89 (s, 9H), 0.04 (s, 6H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 161.0, 147.5, 137.8, 134.6, 134.1, 133.8, 128.9, 127.7, 127.7, 126.9, 122.5, 62.9, 37.6, 32.5, 26.1, 25.9, 18.3, -5.3.

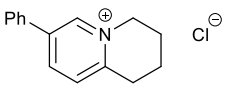
$^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$) δ 18.5.

HRMS (ESI) calculated for $C_{21}H_{31}NOSi$ $[M+Na]^+$: 364.2067, Found: 364.2064



3z **Clathryimine B**

A 100 mL RBF equipped with a magnetic bar was charged with 5-Phenyl-2-pyridinebutanol **3z** (0.76 g, 3.35 mmol) in anhydrous chloroform (50 mL), and treated with triethylamine (3.0 equiv) and mesyl chloride (2.0 equiv). The reaction mixture was stirred at room temperature for 12 hours. After the reaction, distilled water was added to the mixture, followed by sodium hydroxide solution to reach *pH* 12. The product was extracted with dichloromethane and dried over $MgSO_4$, and the solvent was removed under vacuum. The product (clathryimine B) was purified by a flash column chromatography on silica gel with dichloromethane/ethanol to yield brown viscous oil (0.38 g, 46%).



Clathryimine B

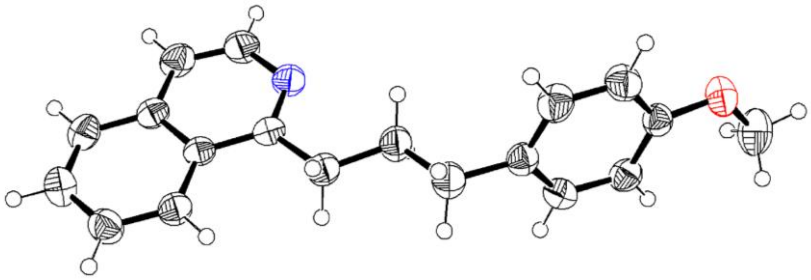
Brown viscous oil (0.38 g, 46% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.86 (d, *J* = 2.1 Hz, 1H), 8.43 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.87 (dd, *J* = 12.4, 7.9 Hz, 3H), 7.42 (dt, *J* = 23.5, 7.3 Hz, 3H), 5.09 (t, *J* = 6.1 Hz, 2H), 3.26 (t, *J* = 6.7 Hz, 2H), 2.14 (p, *J* = 6.5 Hz, 2H), 1.99 (p, *J* = 6.7 Hz, 2H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 153.7, 143.7, 141.7, 138.3, 132.8, 130.2, 129.7, 128.7, 127.6, 56.2, 28.4, 21.3, 17.8.

HRMS (ESI) calculated for $C_{15}H_{16}N$ $[M]^+$: 210.1277, Found: 210.1264

5. Crystal structure



ORTEP representation (50% probability) of the crystal structure of **3w**

Empirical formula	C19 H19 N O	
Formula weight	277.35	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.660(4) Å	α= 90°.
	b = 14.860(8) Å	β= 102.555(17)°.
	c = 10.952(5) Å	γ = 90°.
Volume	1534.5(13) $Å^3$	
Z	4	
Density (calculated)	1.201 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	592	
Crystal size	0.265 x 0.125 x 0.051 mm^3	
Theta range for data collection	2.347 to 28.347°.	
Index ranges	-12<=h<=12, -19<=k<=19, -14<=l<=11	
Reflections collected	14412	
Independent reflections	3793 [R(int) = 0.0953]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.5411	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3793 / 0 / 191	
Goodness-of-fit on F^2	0.988	
Final R indices [I>2sigma(I)]	R1 = 0.0682, wR2 = 0.1700	
R indices (all data)	R1 = 0.1434, wR2 = 0.2149	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.352 and -0.388 $e.Å^{-3}$	

6. NMR spectra of metal complexes

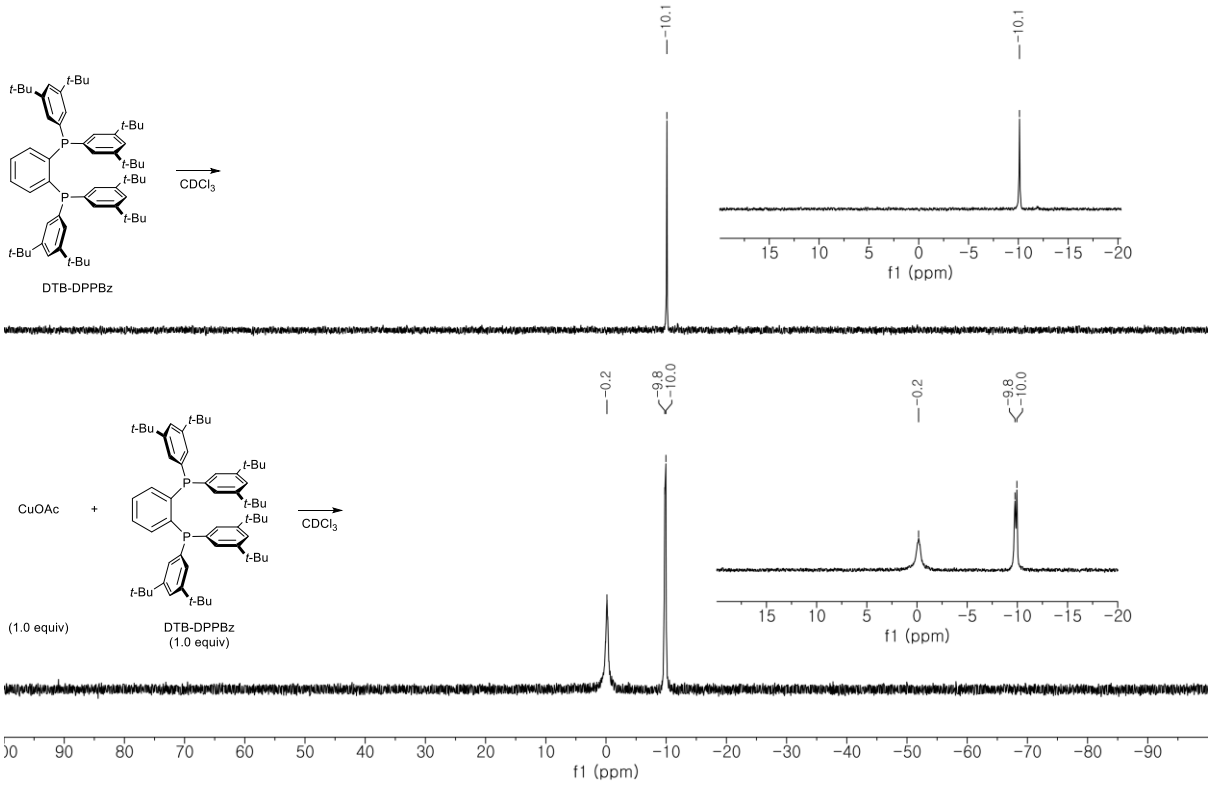


Figure S1. Stacked $^{31}P\{^{1}H\}$ NMR spectra showing ligation of DTB-DPPBz with CuOAc.

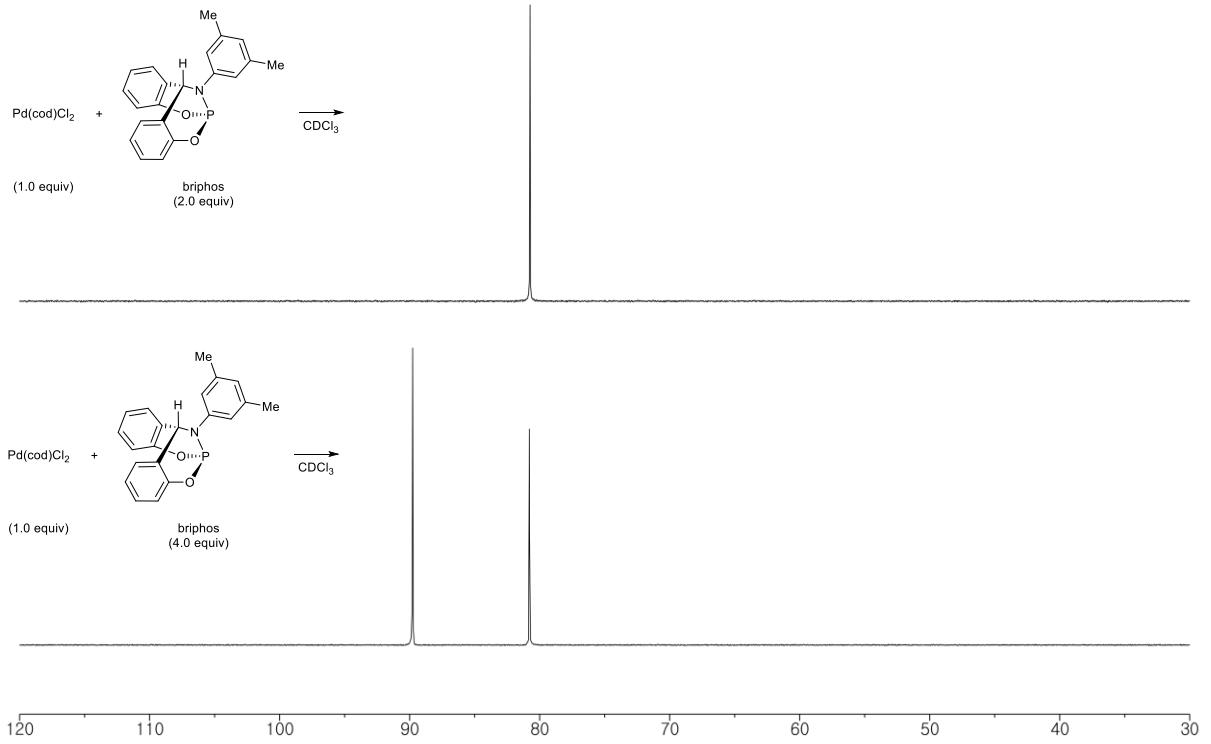


Figure S2. Stacked $^{31}P\{^{1}H\}$ NMR spectra showing 2:1 ligation of Briphos with $Pd(cod)Cl_2$.

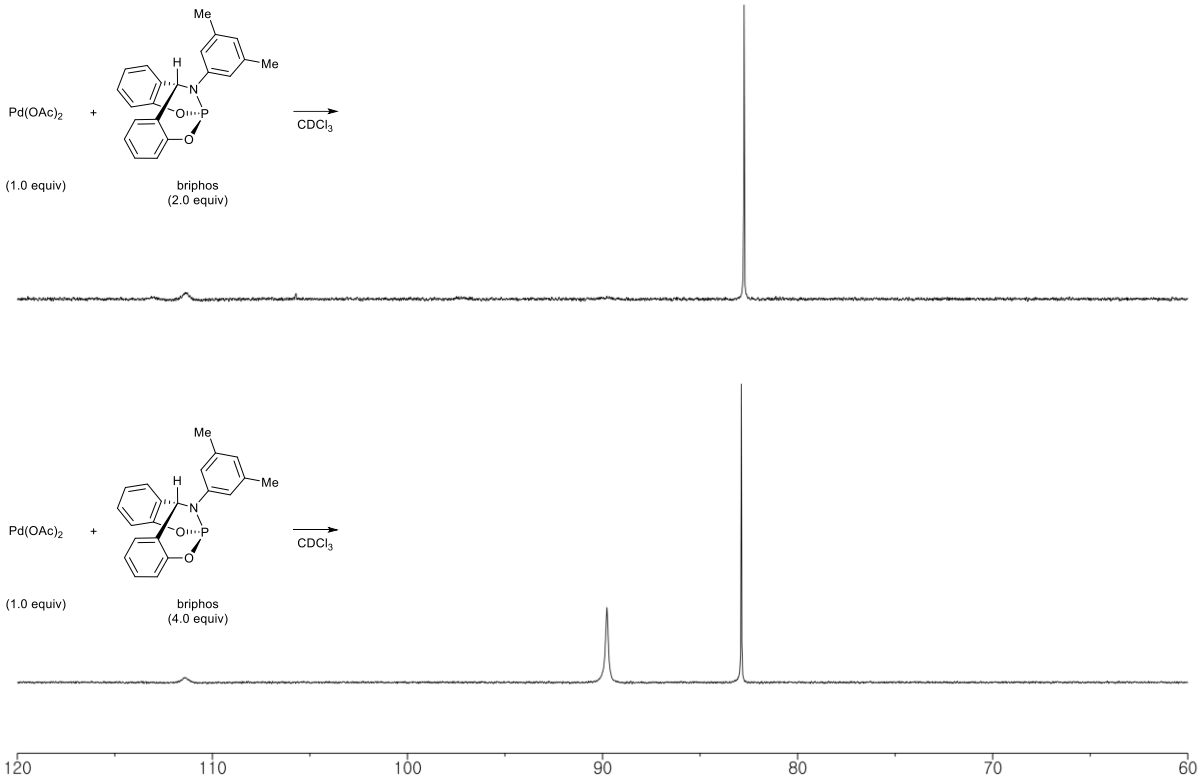
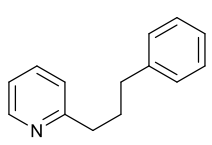


Figure S3. Stacked $^{31}P\{^{1}H\}$ NMR spectra showing 2:1 ligation of Briphos with $Pd(OAc)_2$.

7. References

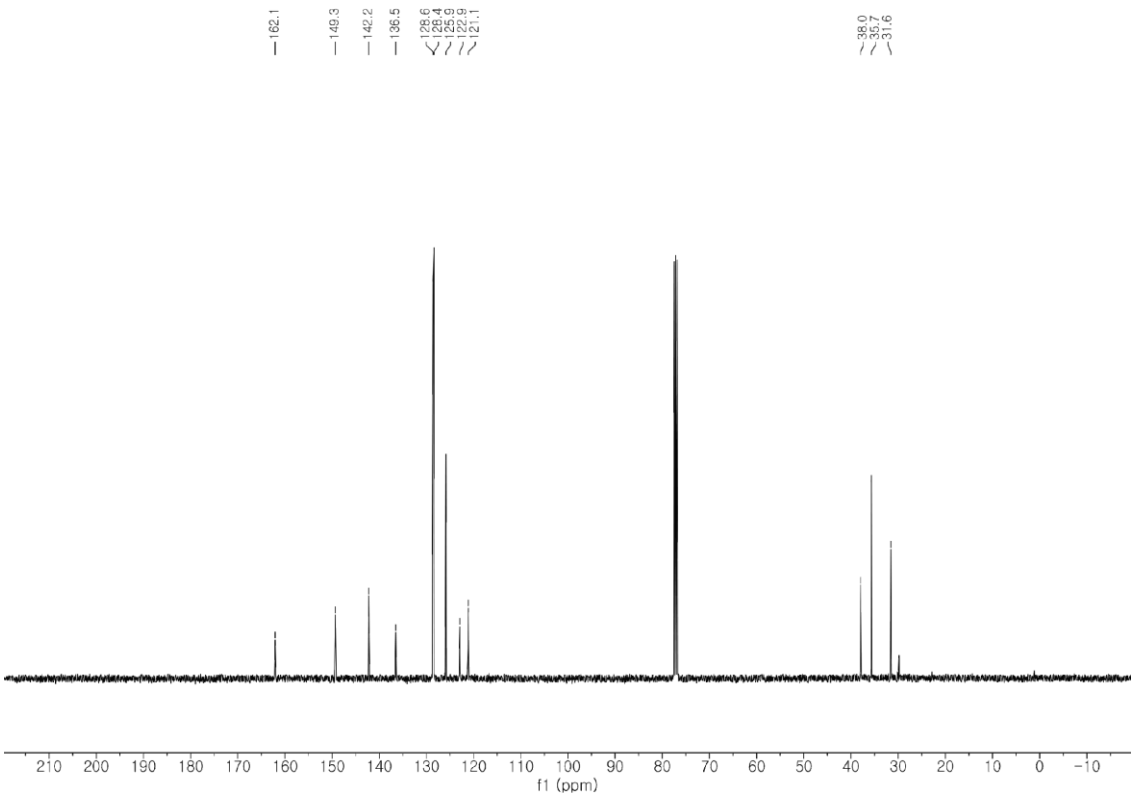
1. A. Lee, S. Ahn, K. Kang, M. S. Seo, Y. Kim, W. Y. Kim, H. Kim, *Org. Lett.*, 2014, **16**, 5490.
2. C. Q. O'Broin, P. J. Guiry, *Org. Lett.*, 2020, **22**, 879.
3. A. K. Ghosh, J. Li, *Org. Lett.*, 2009, **11**, 4164.
4. S. Sperry, P. Crews, *Tetrahedron Lett.*, 1996, **37**, 2389.

8. NMR spectra

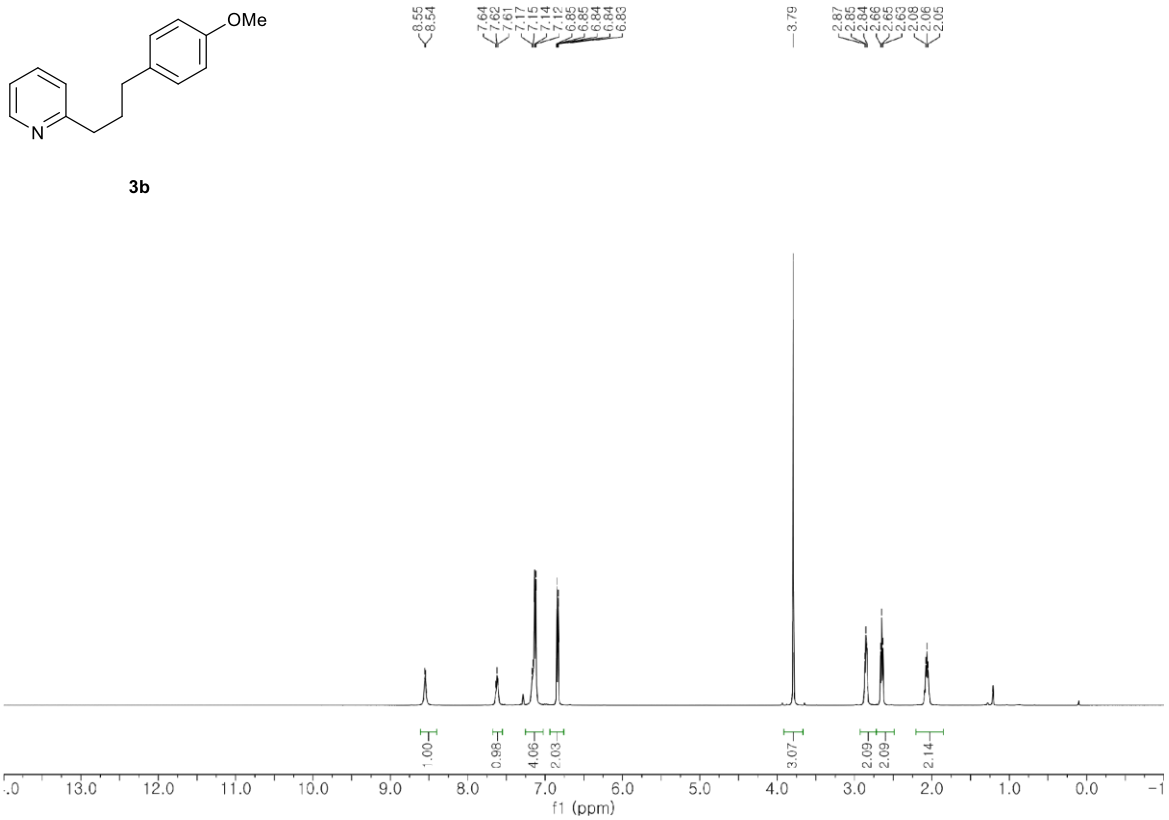


3a

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

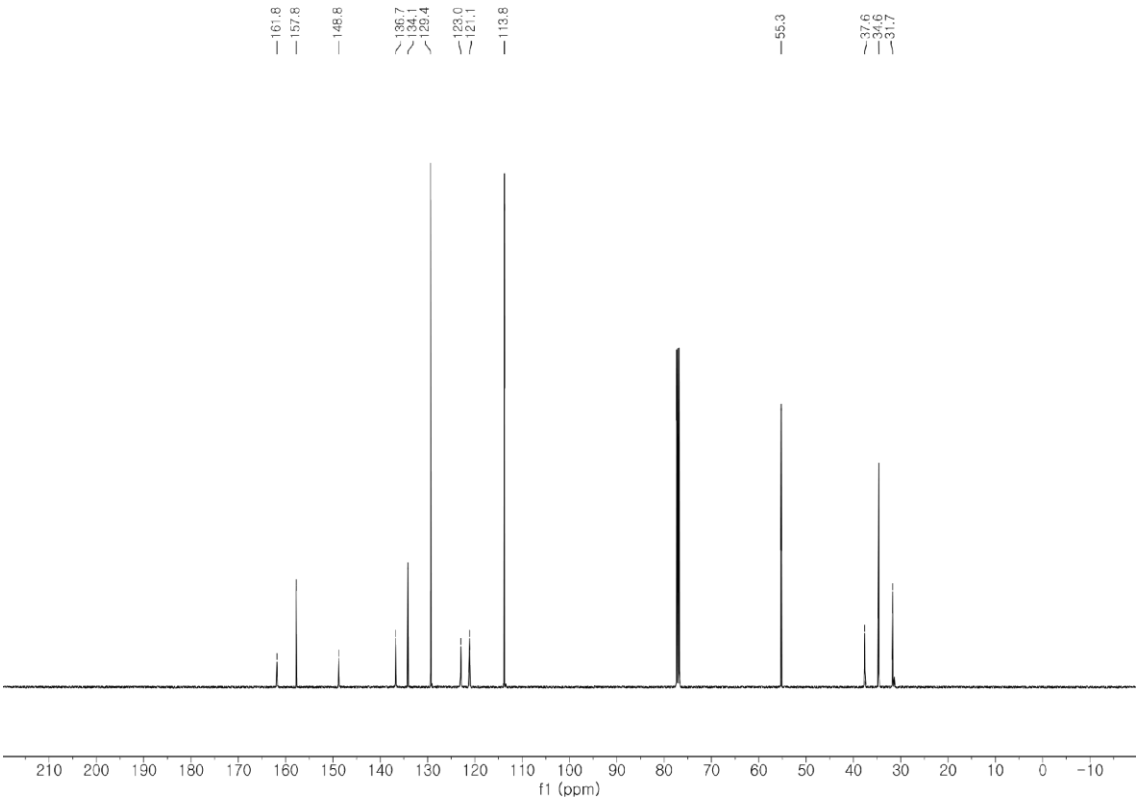


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3a**

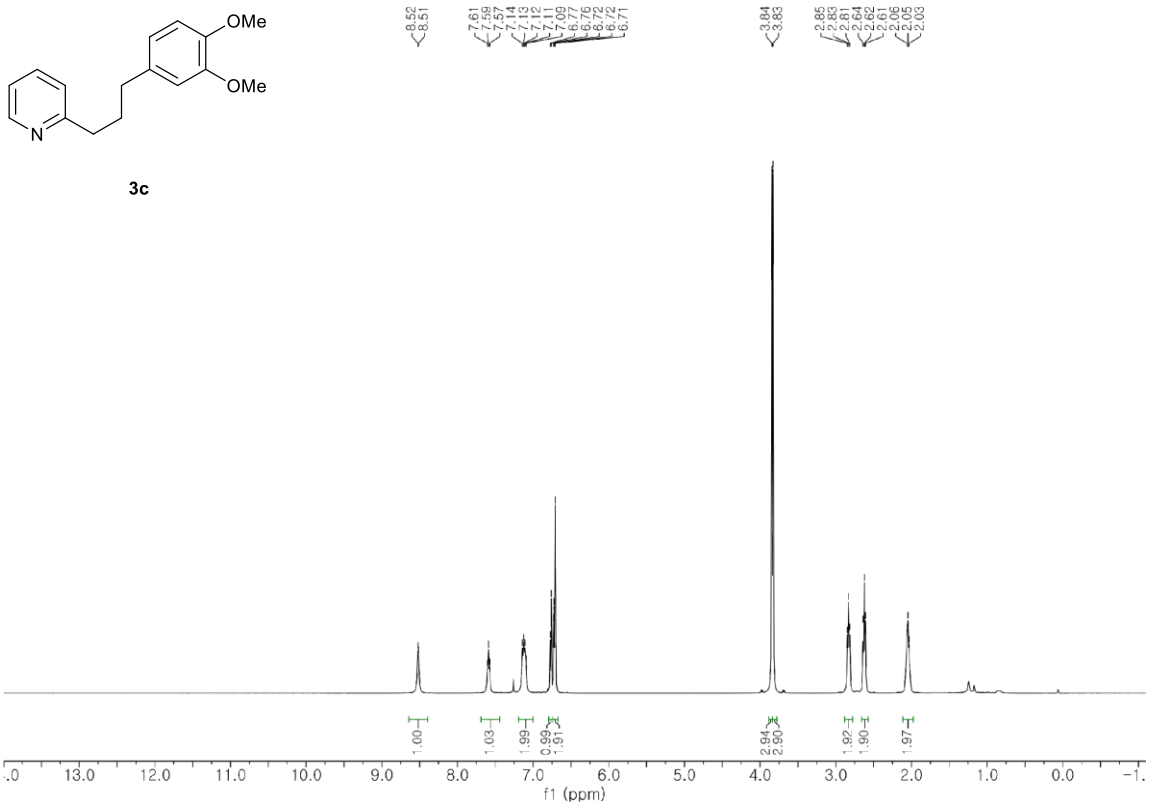


3b

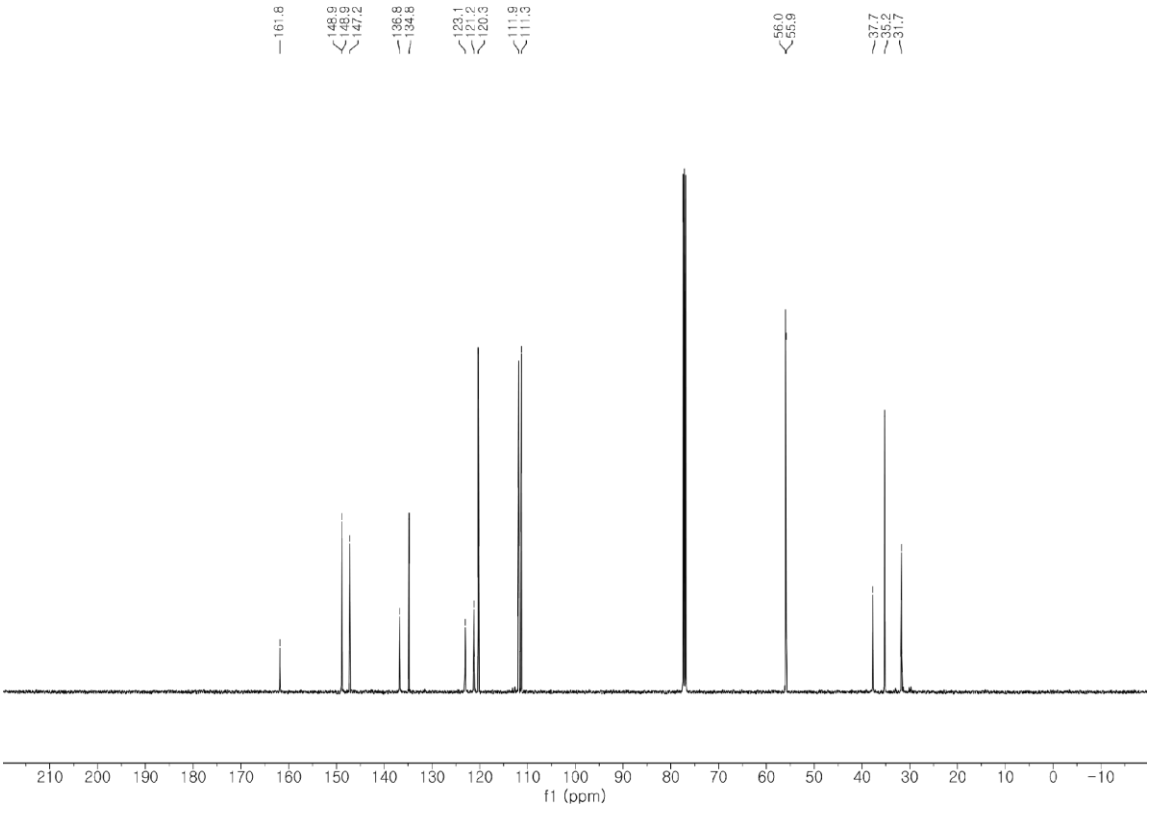
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3b**



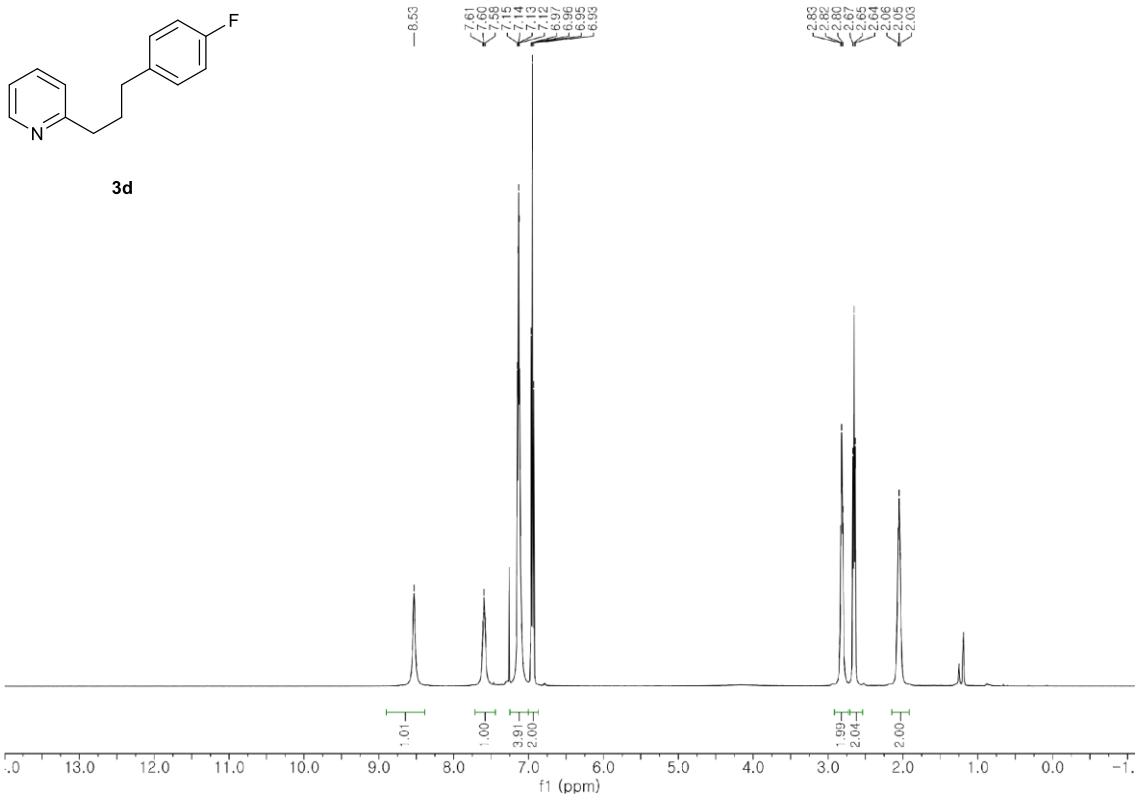
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3b**



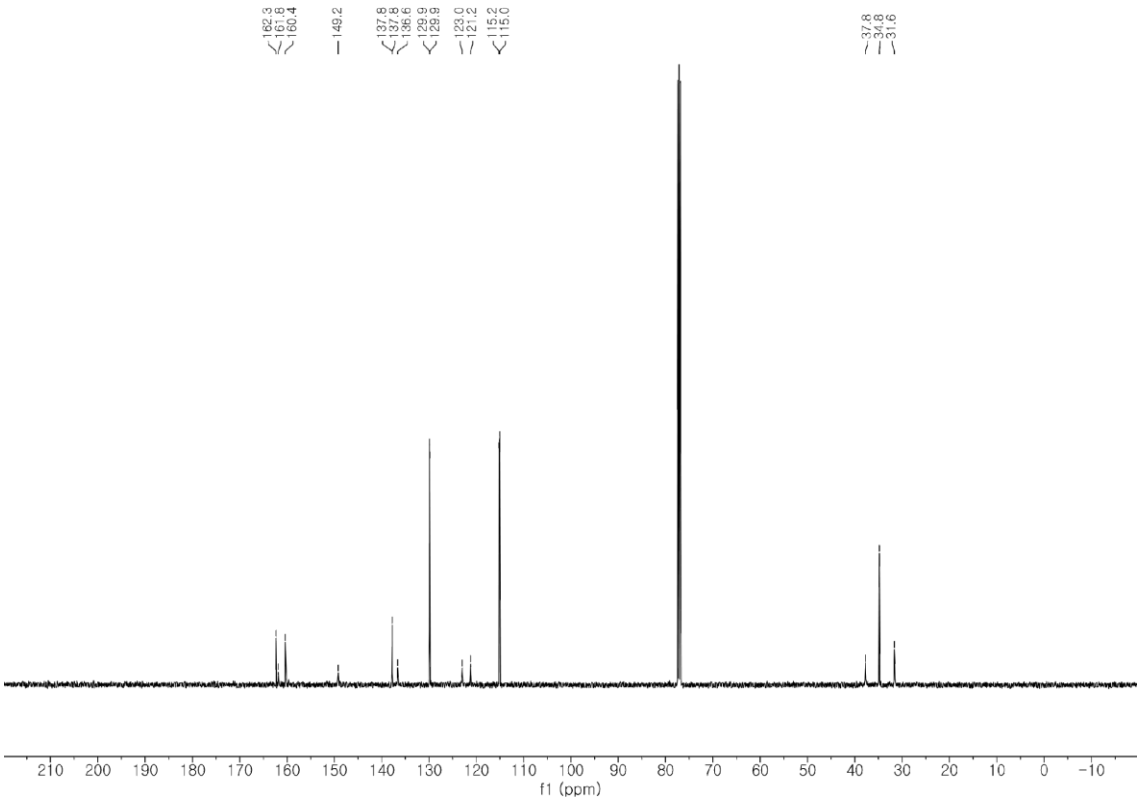
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3c**



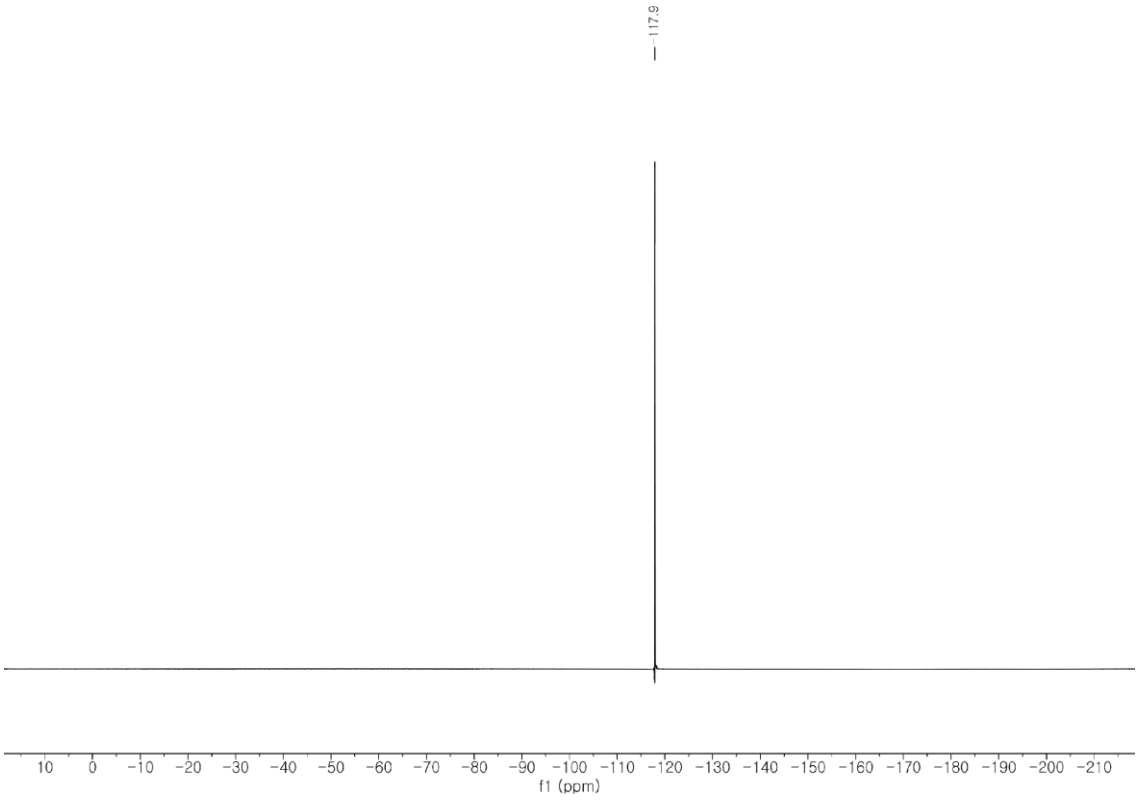
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3c**



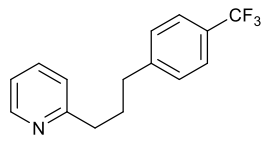
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3d**



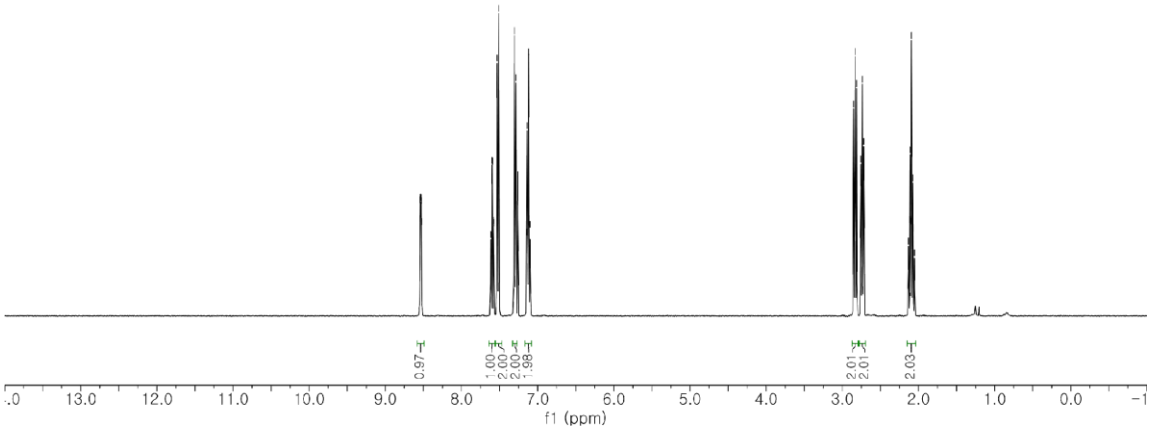
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3d**



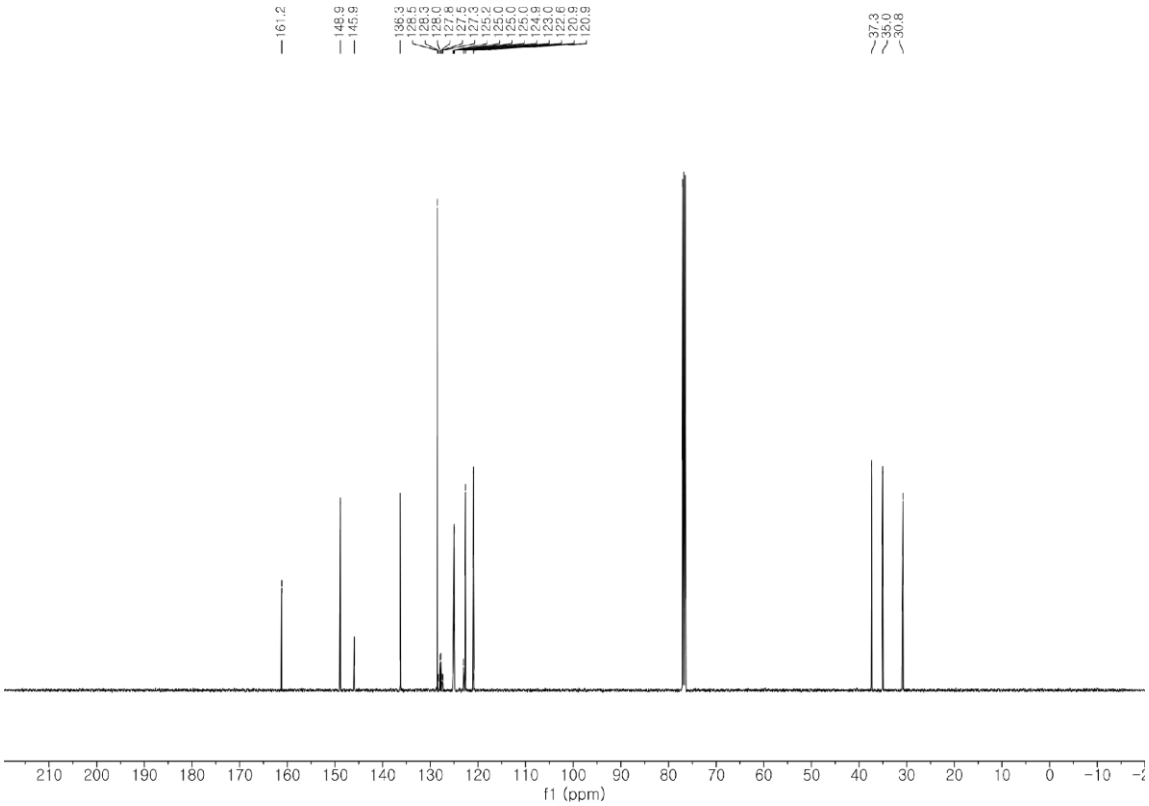
$^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, $CDCl_3$) of **3d**



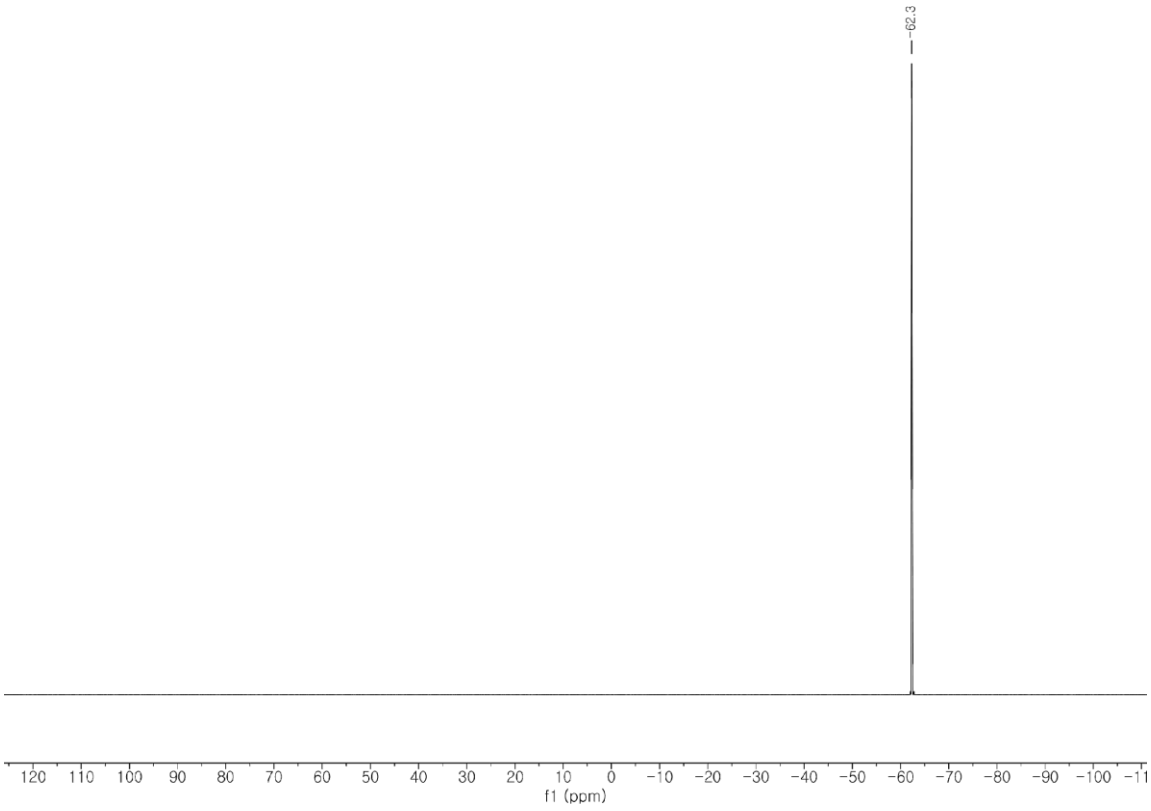
3e



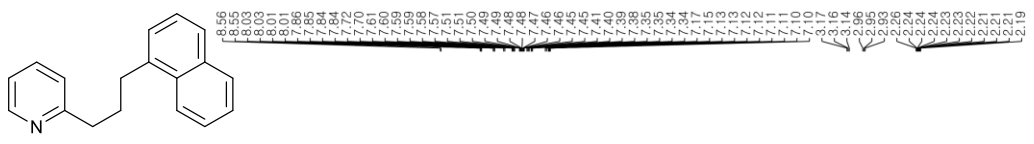
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3e**



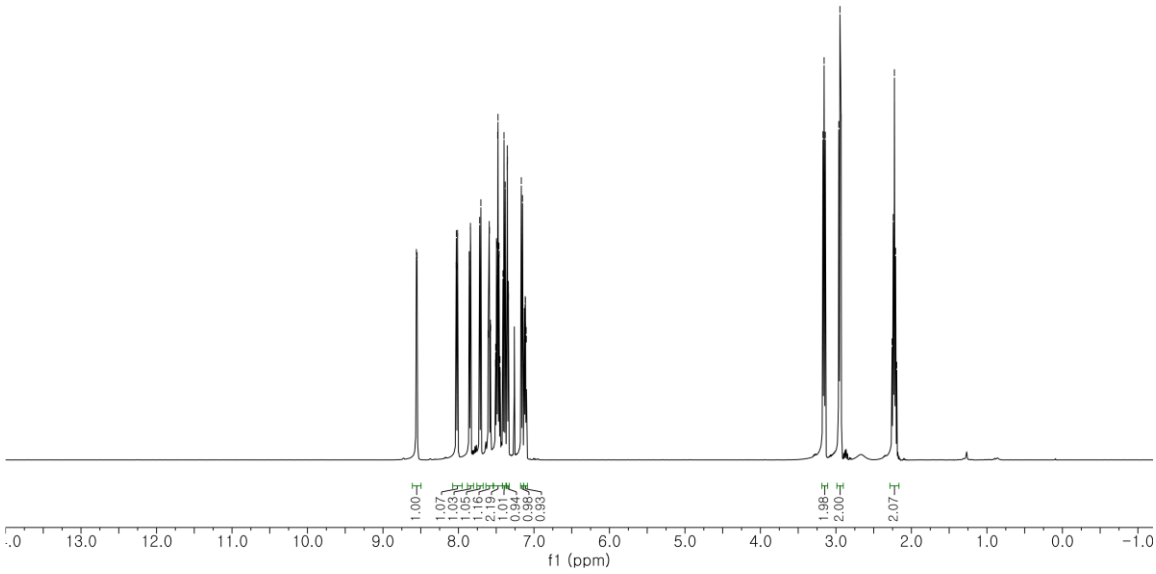
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **3e**



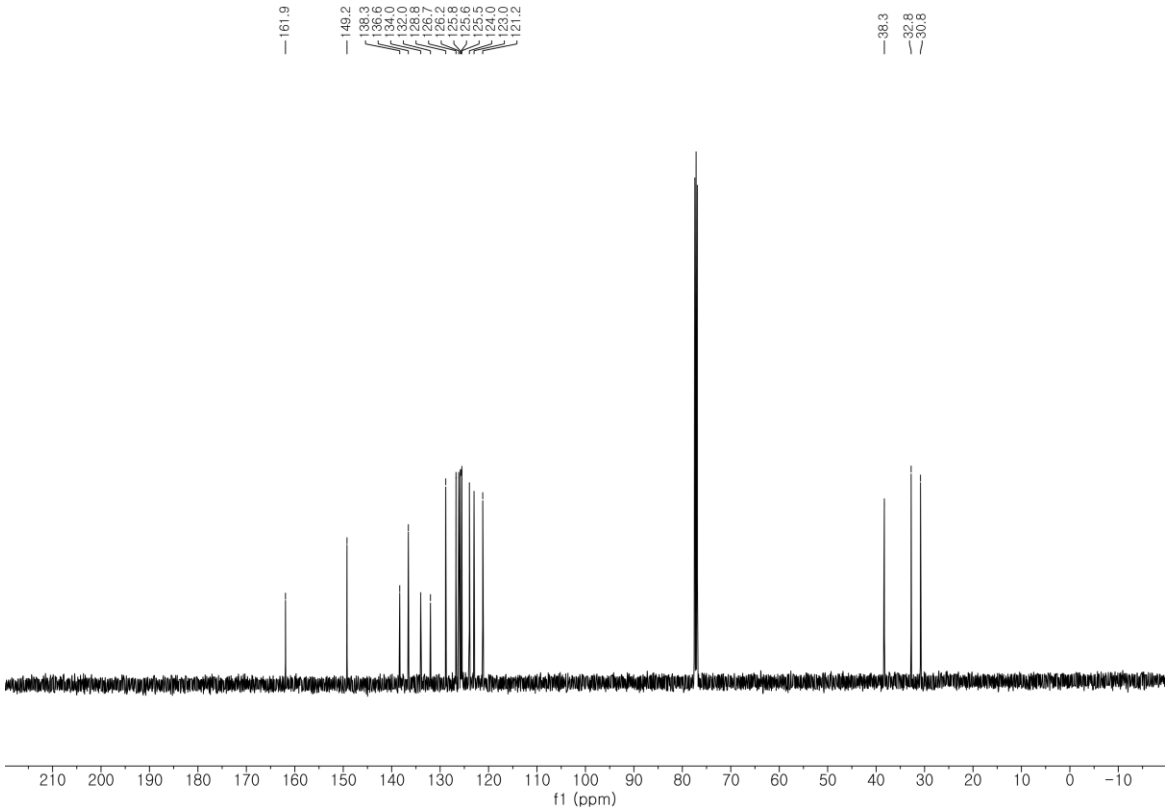
$^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, $CDCl_3$) of **3e**



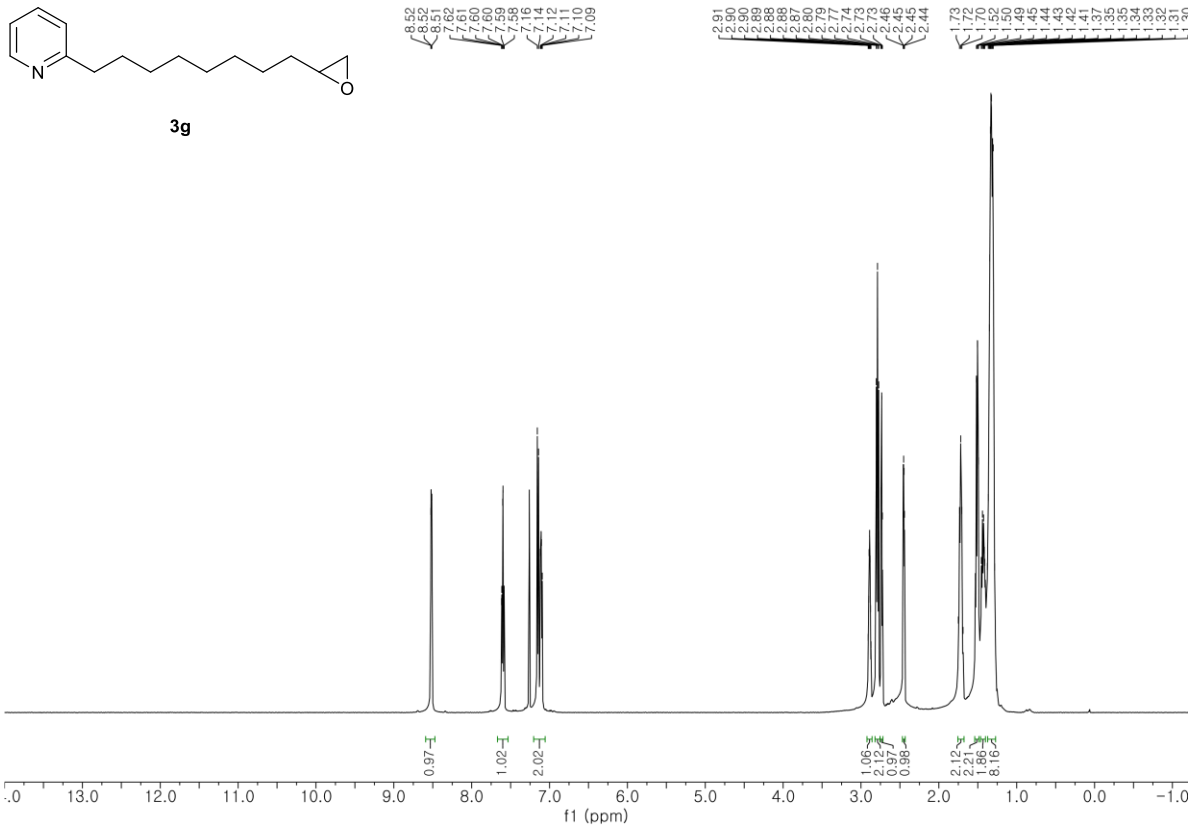
3f



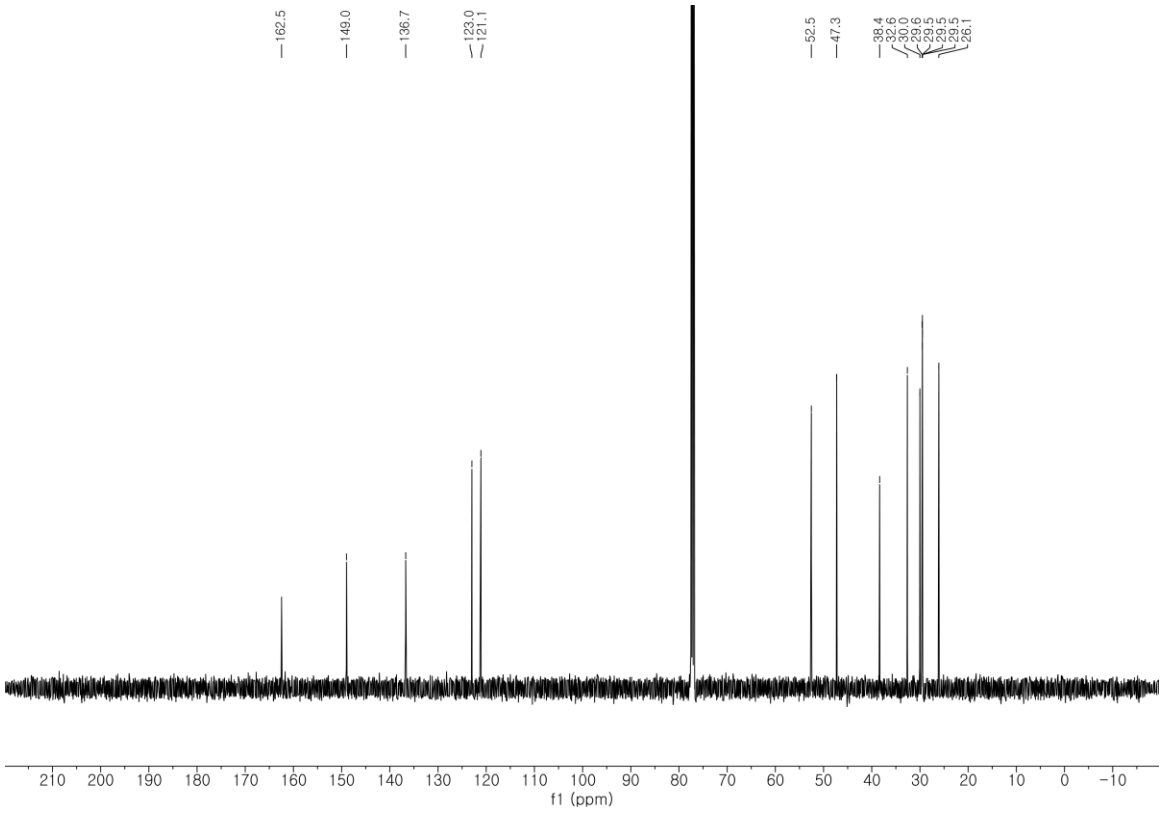
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3f**



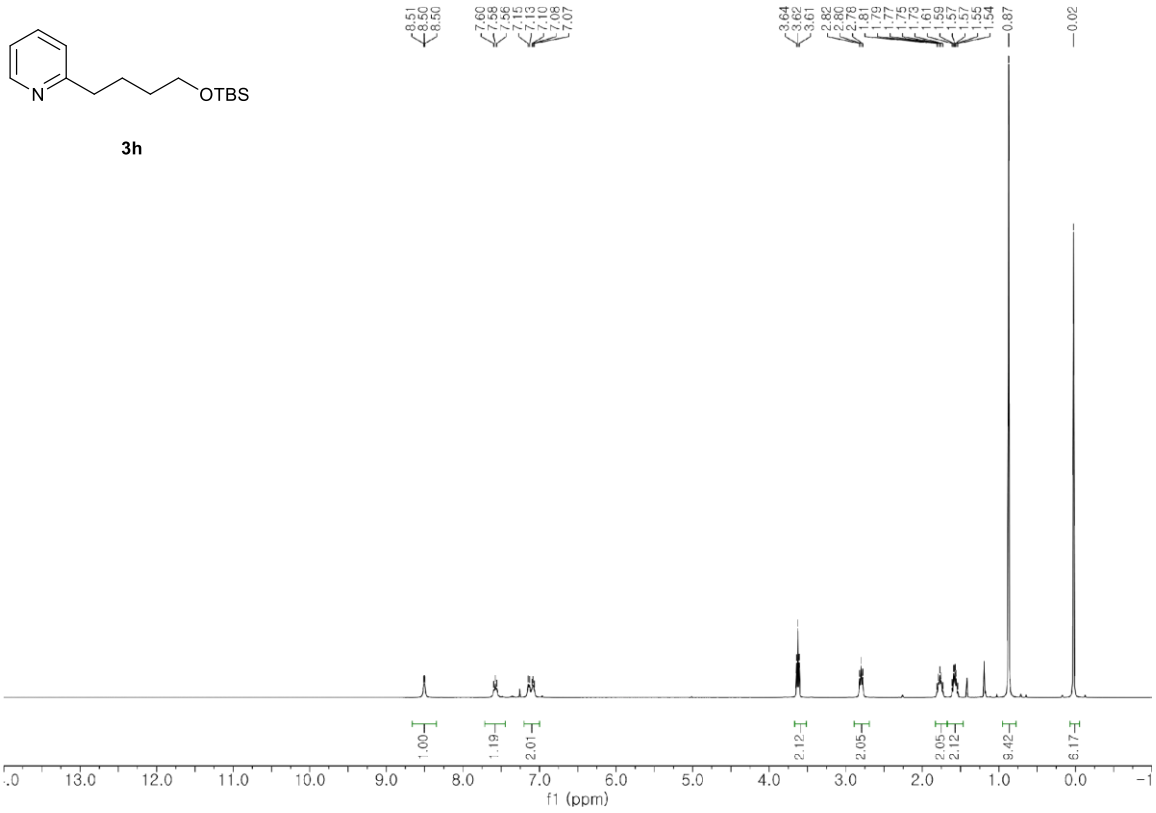
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3f**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3g**

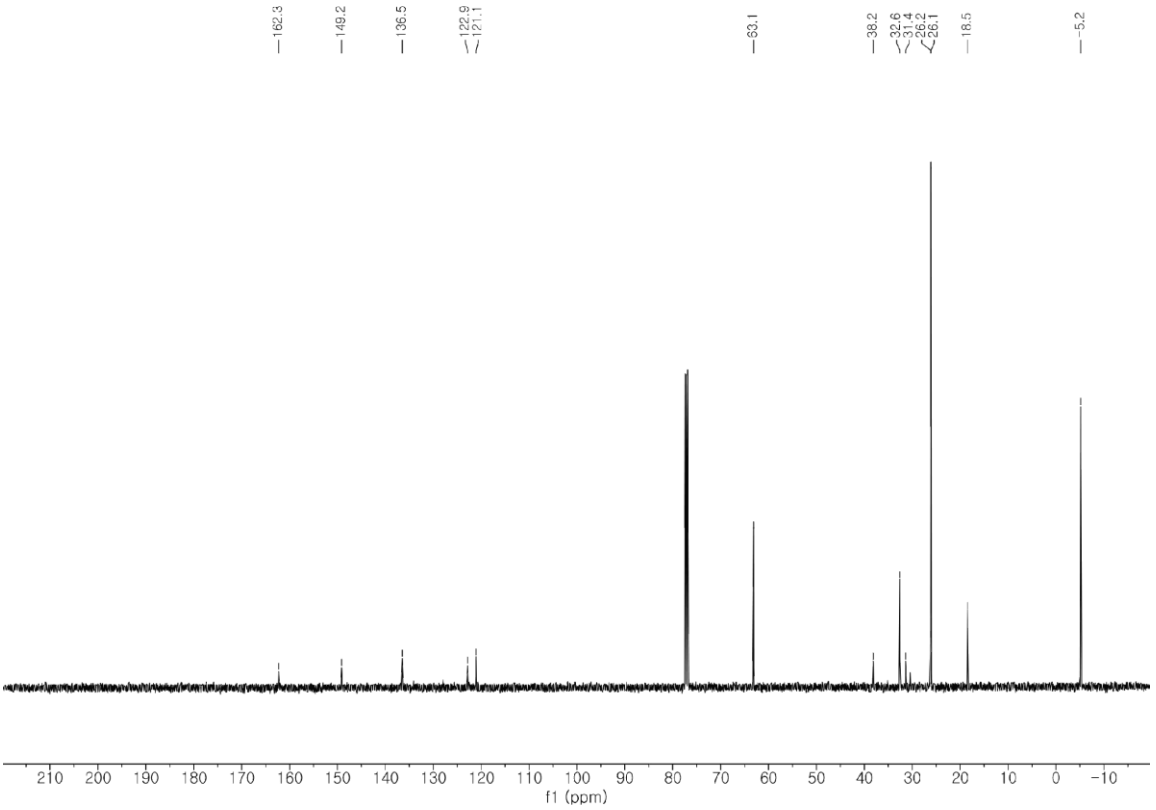


^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3g**

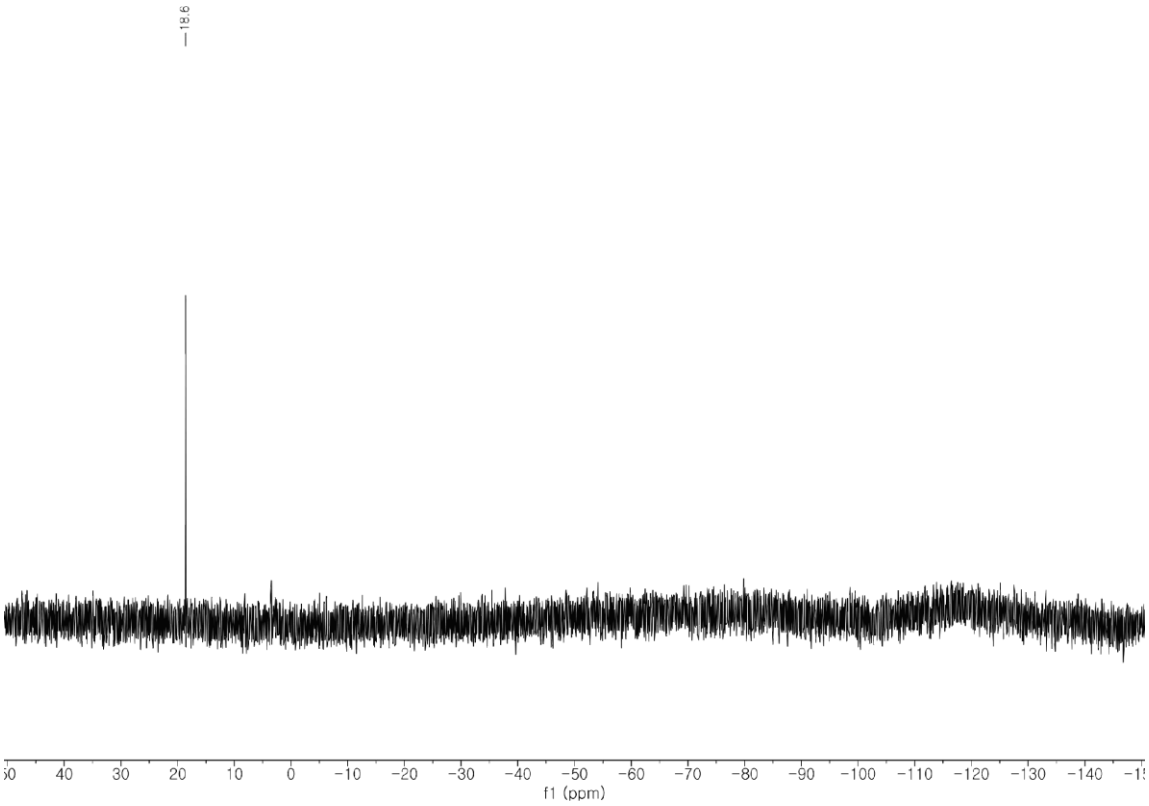


3h

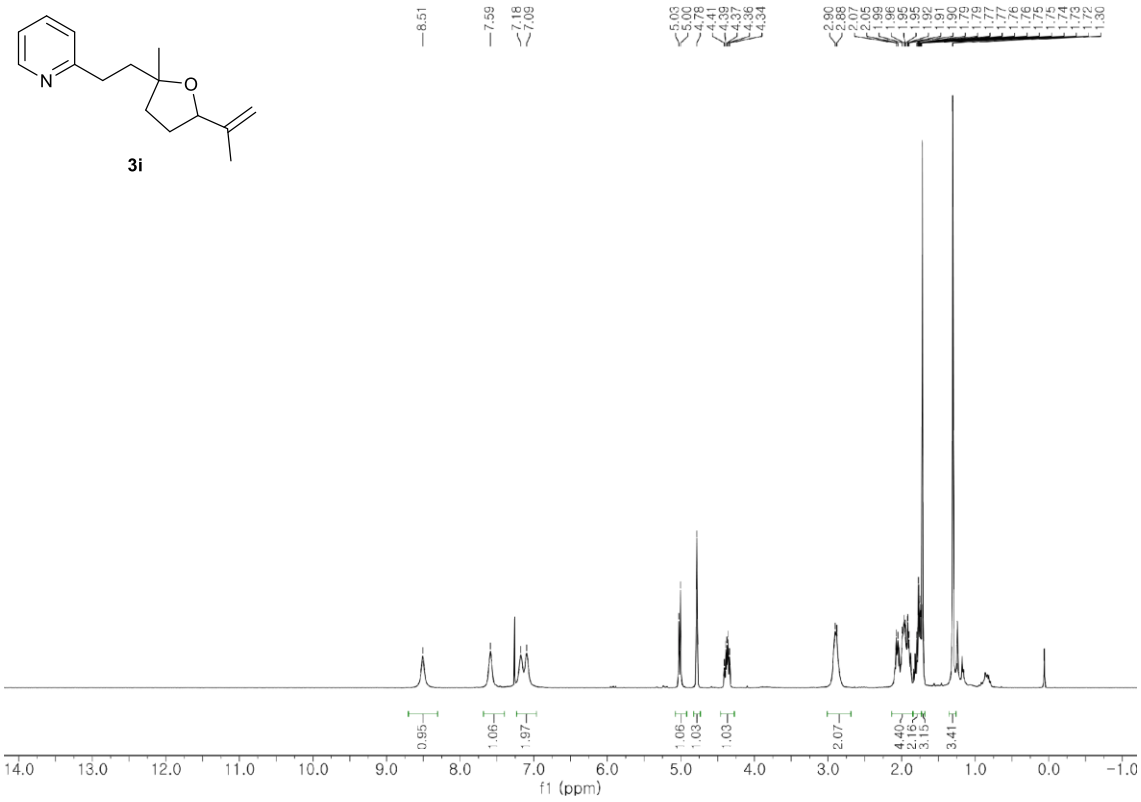
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3h**



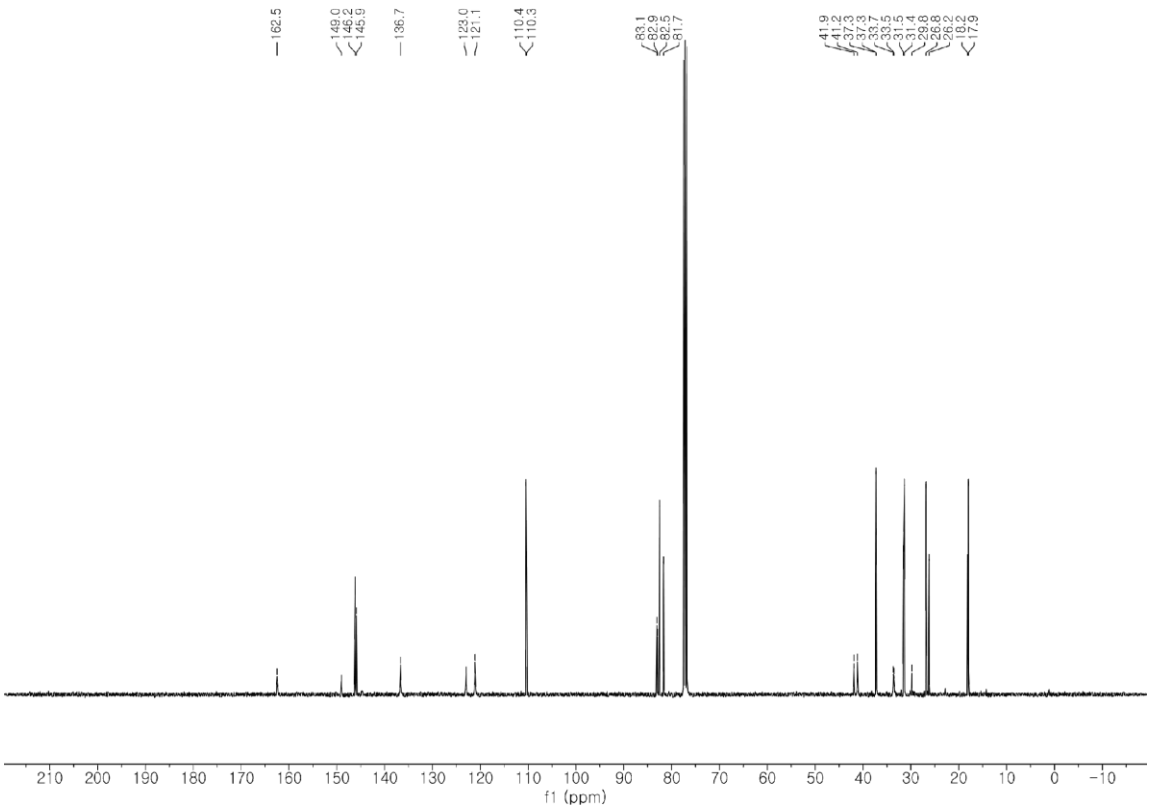
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3h**



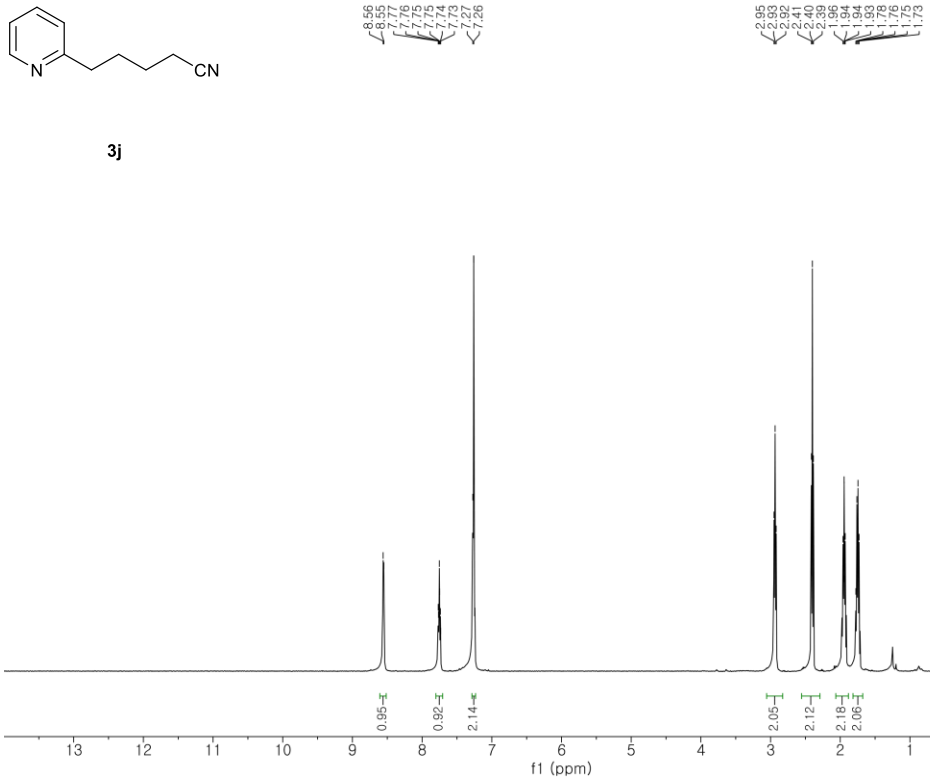
$^{29}Si\{^{1}H\}$ NMR spectrum (99 MHz, $CDCl_3$) of **3h**



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

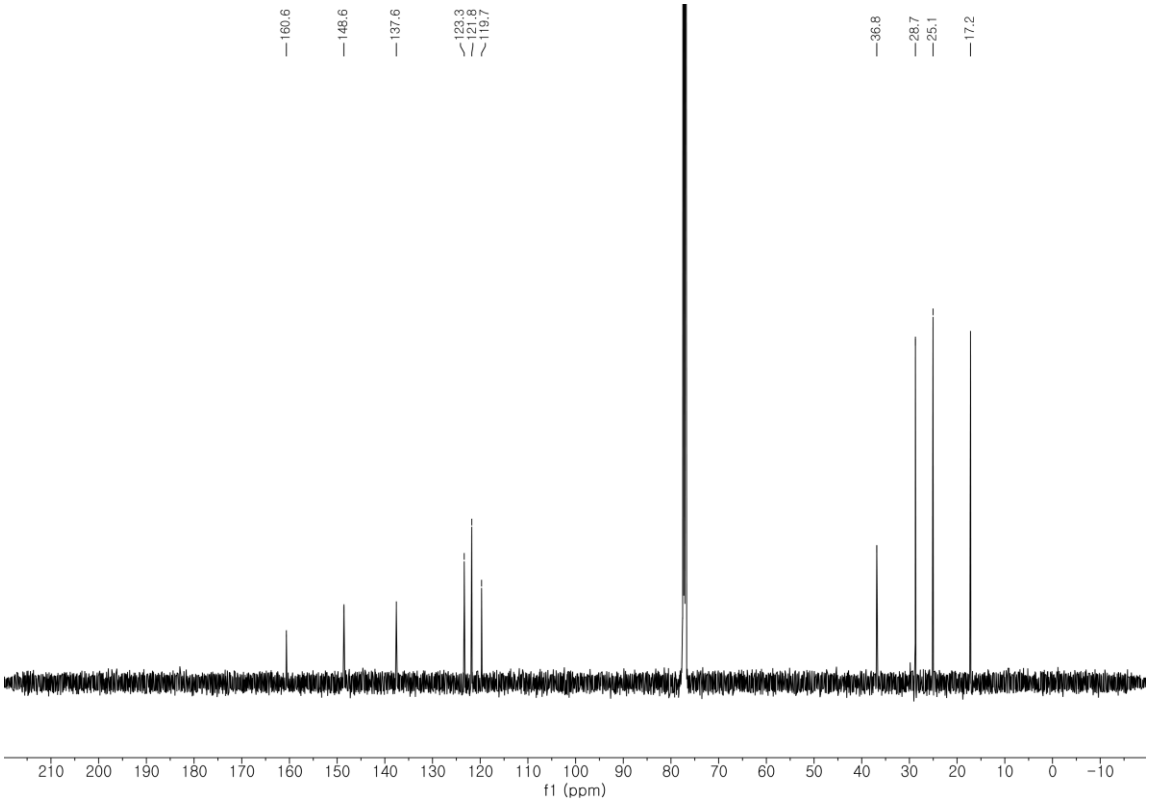


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3i**

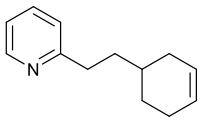


3j

^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3j**

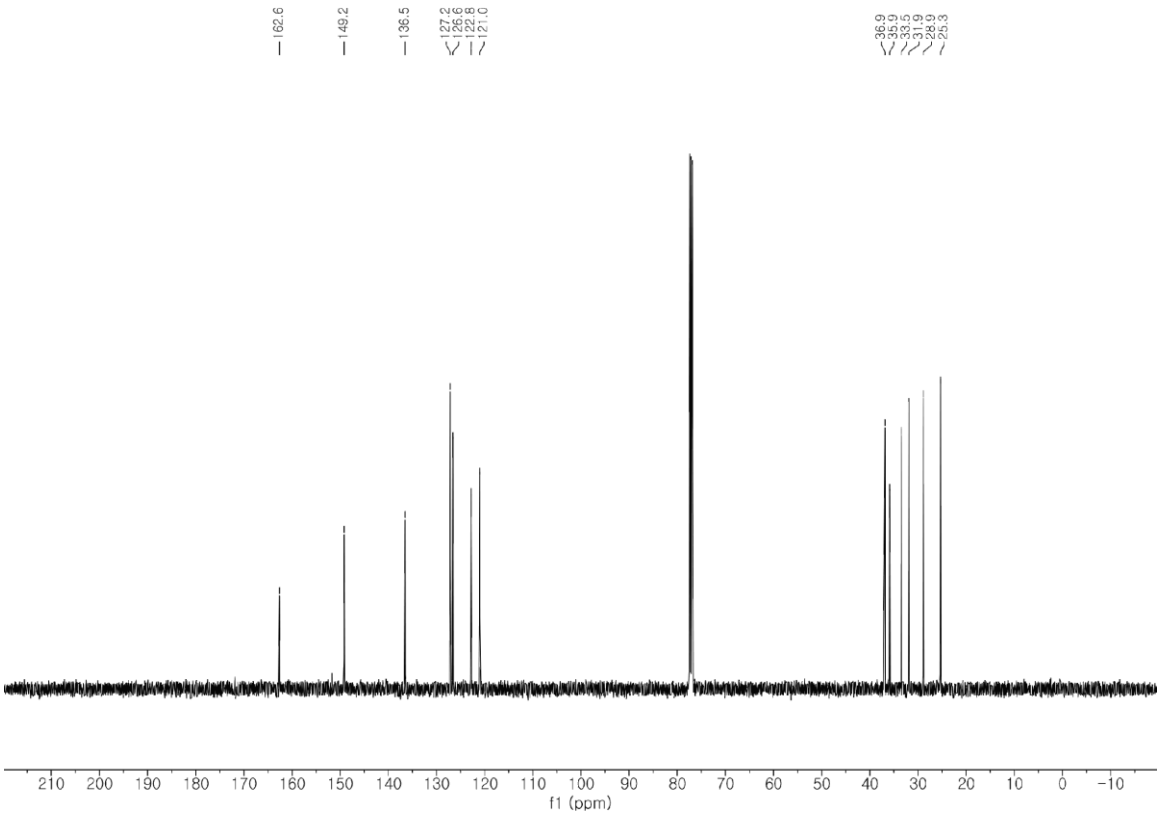


^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3j**

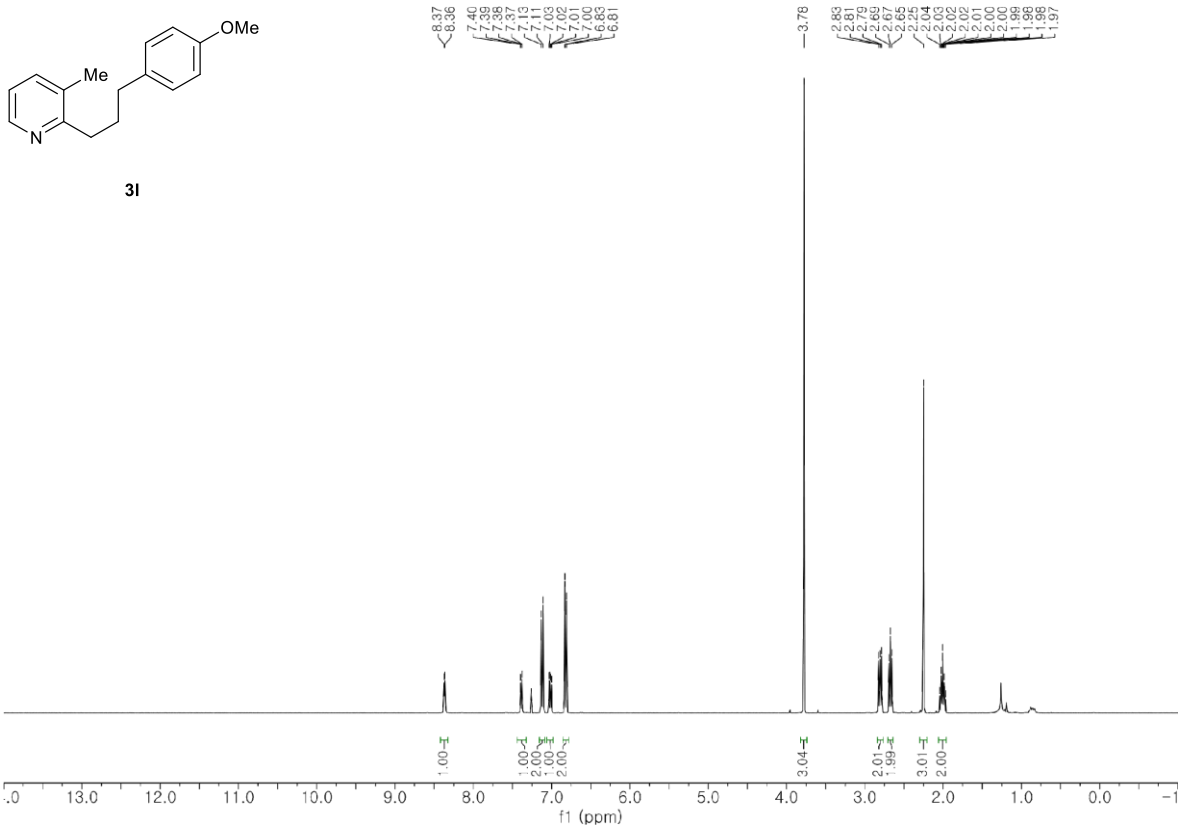


3k

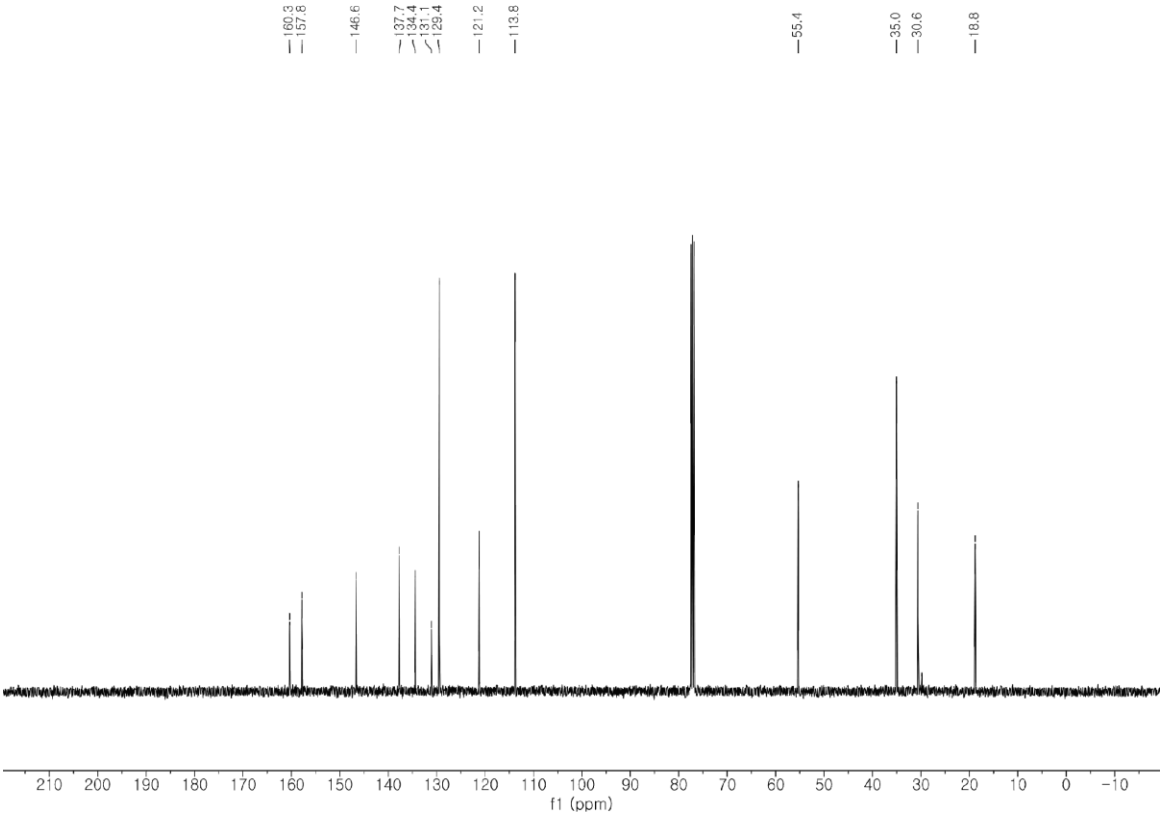
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3k**



^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3k**



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



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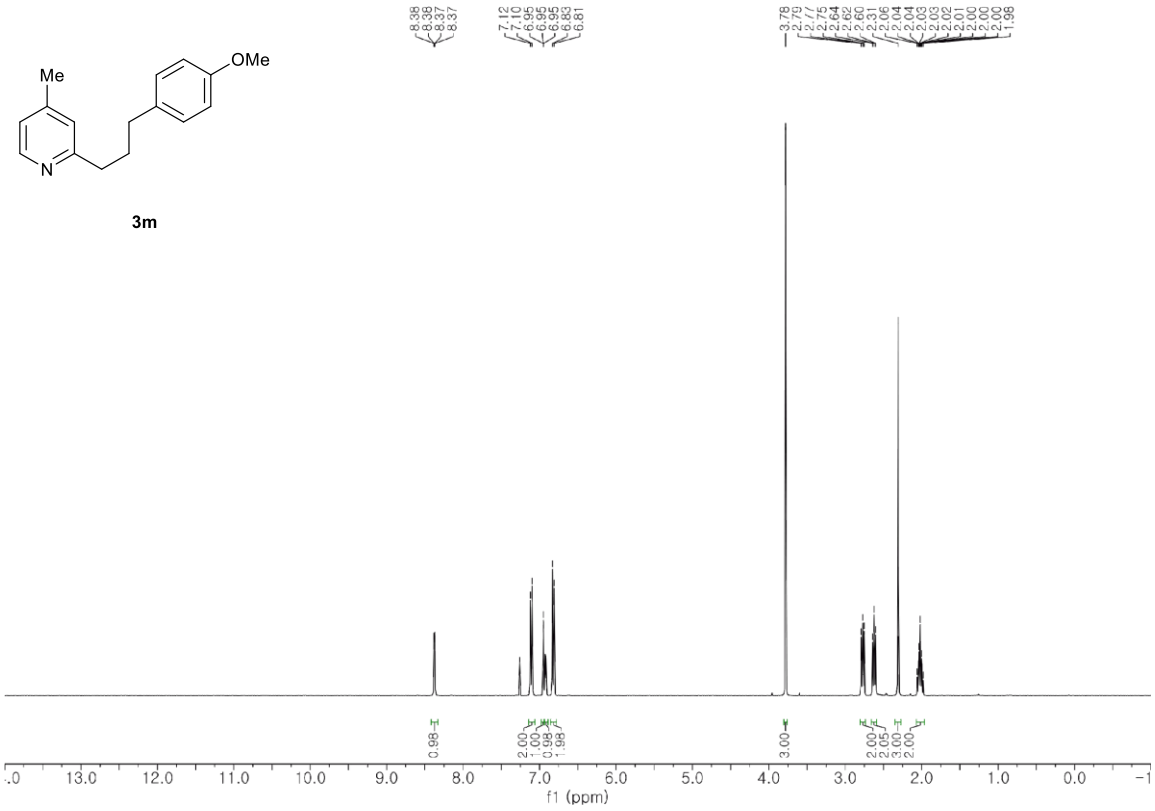
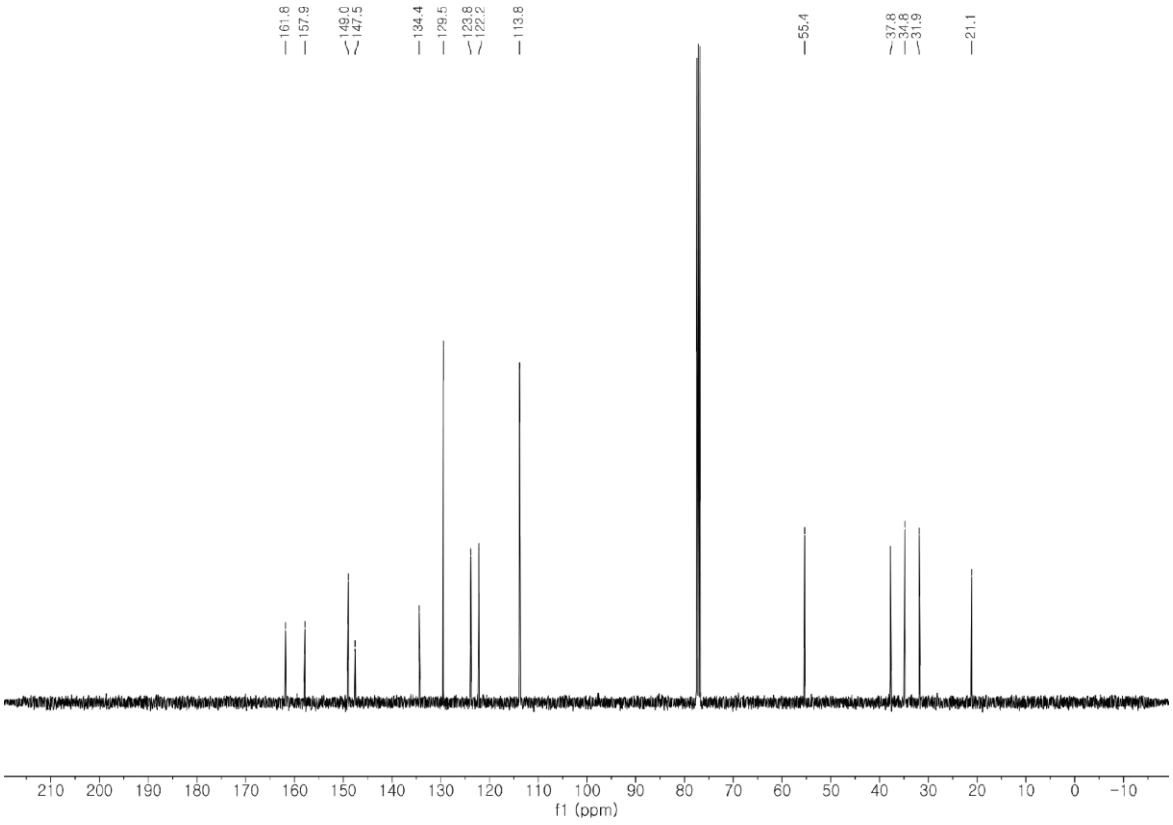


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3m**



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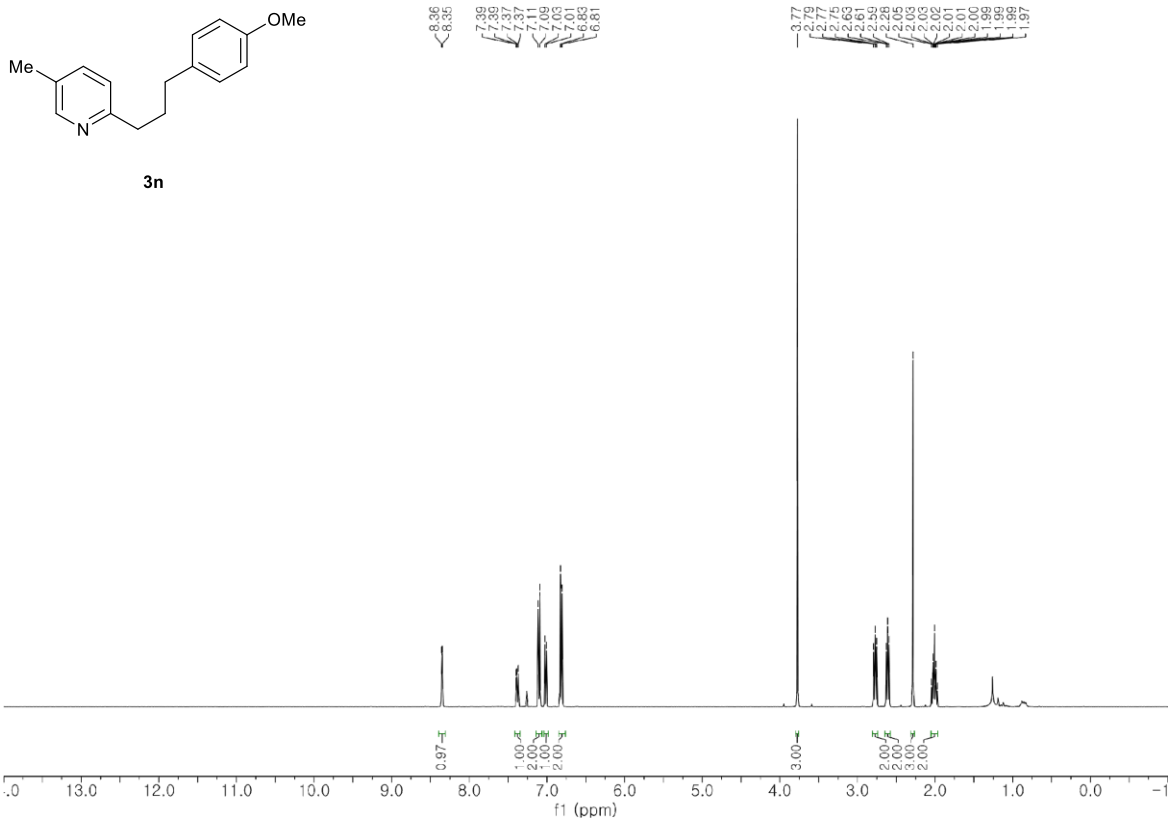
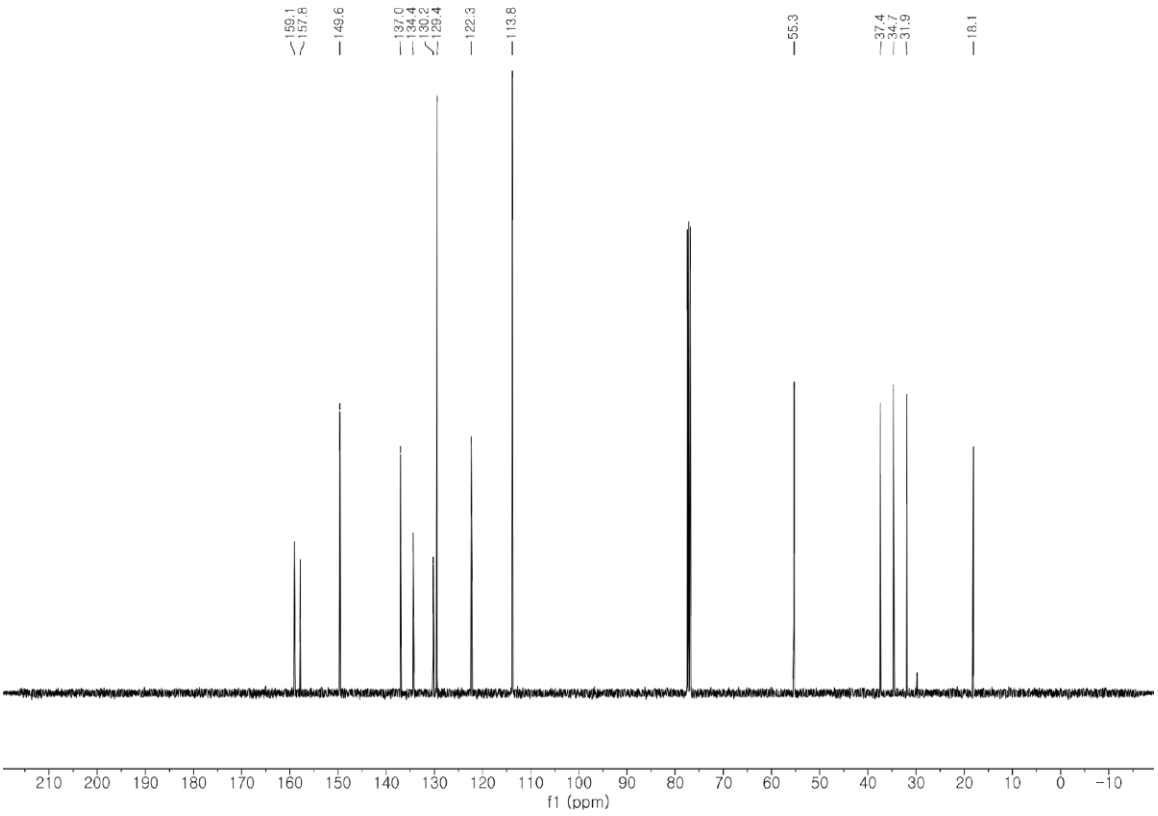
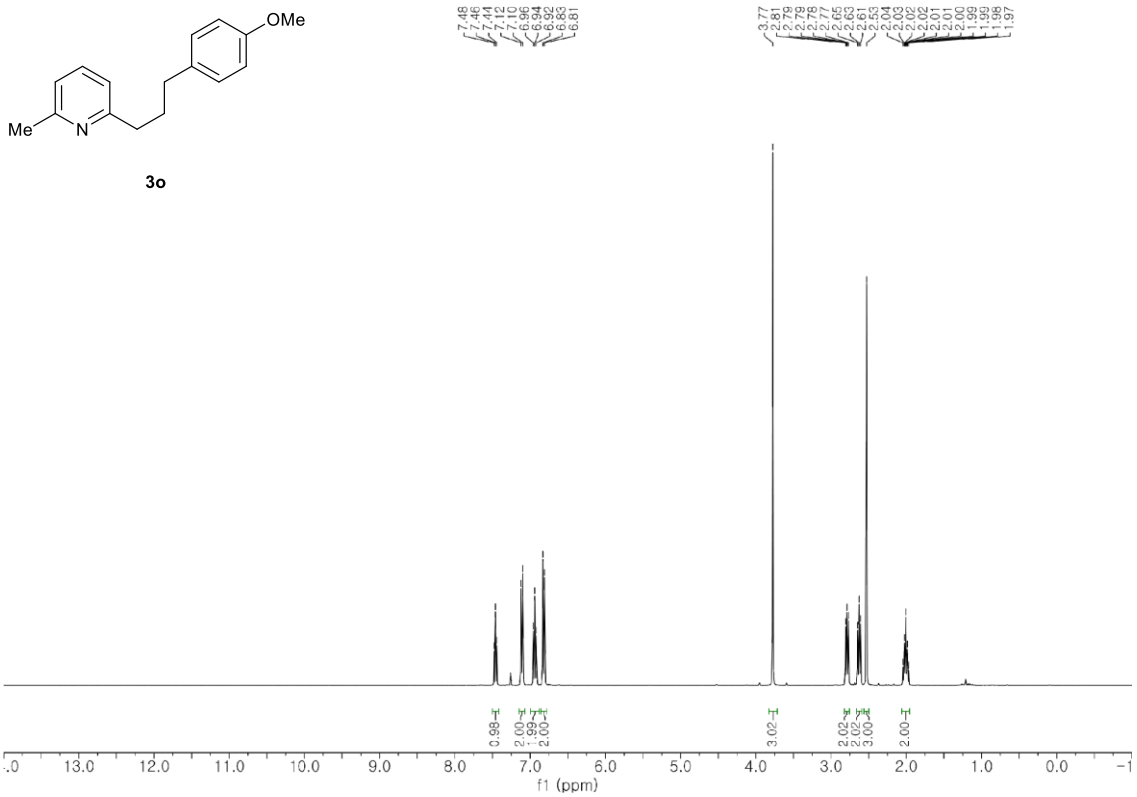


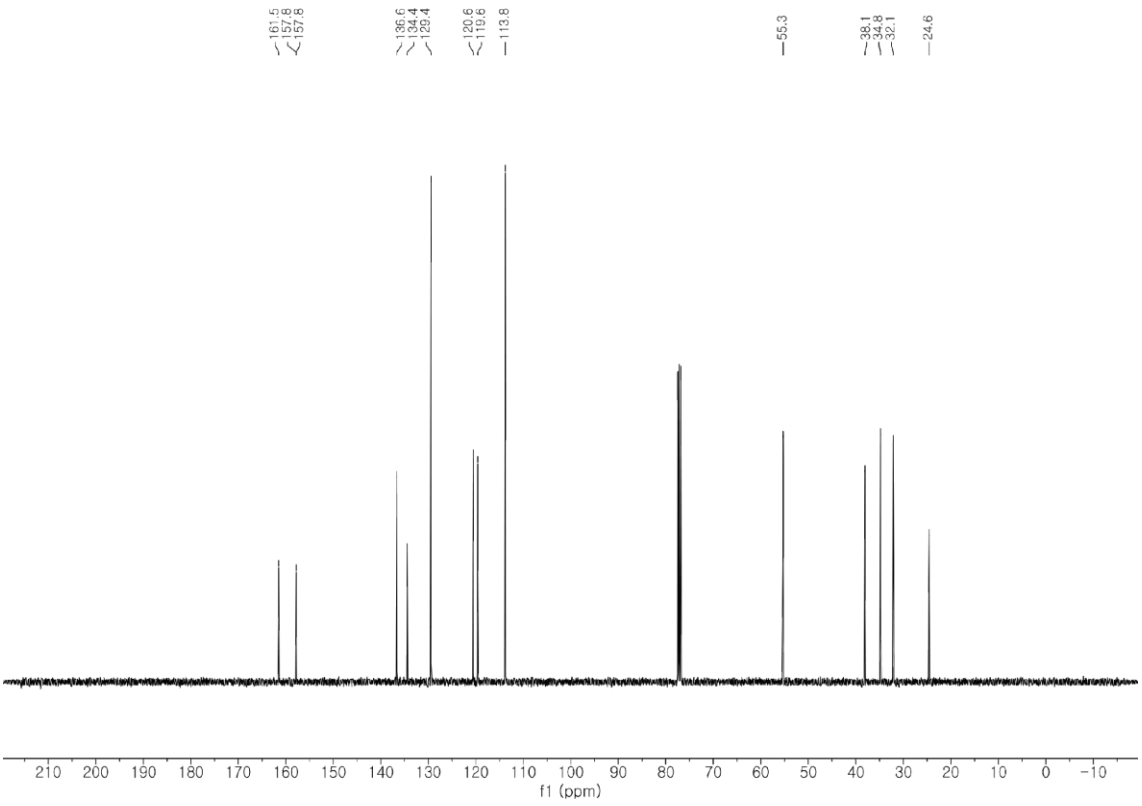
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3n**



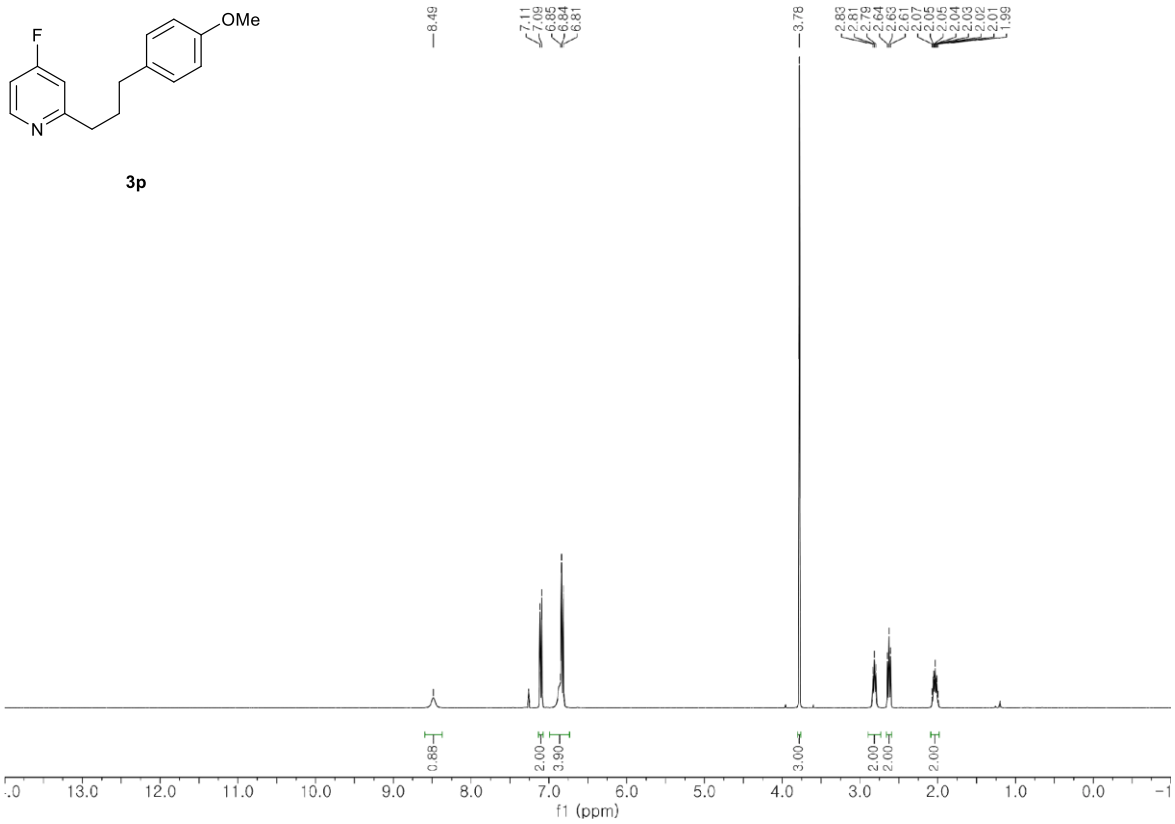
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3n**



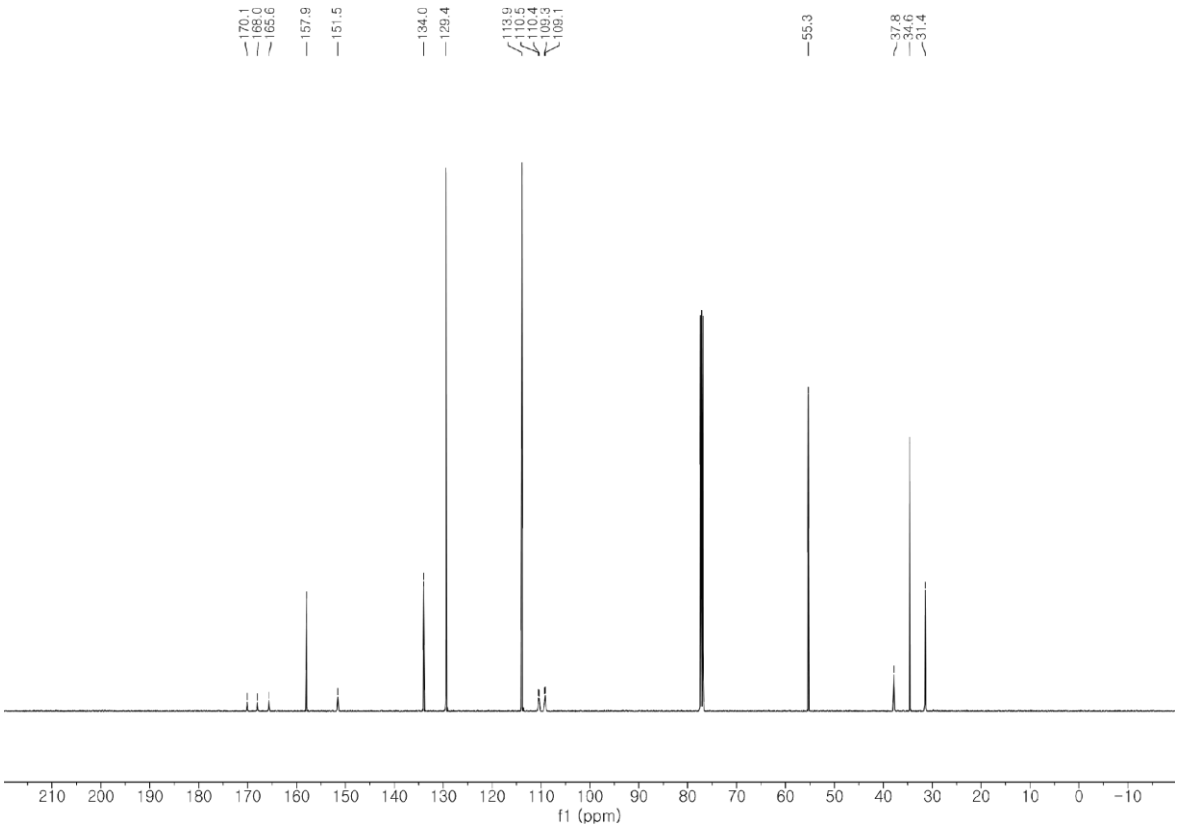
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3o**



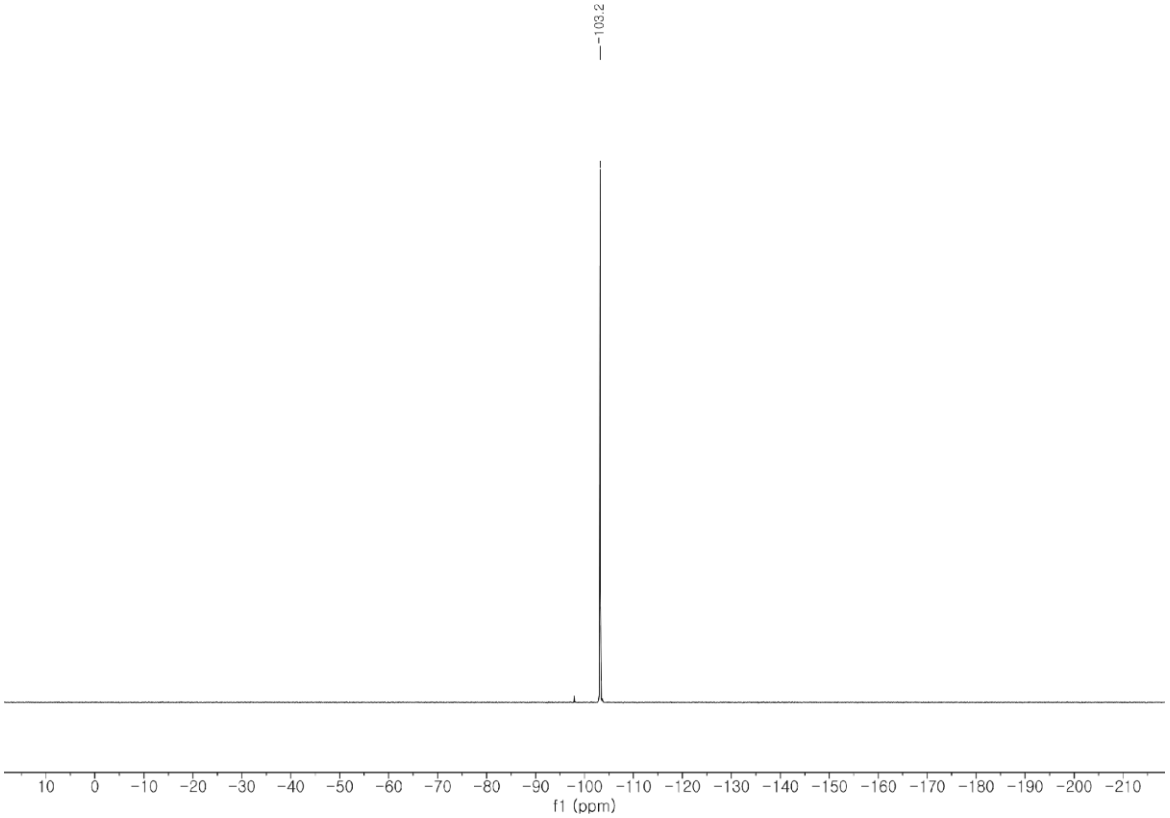
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3o**



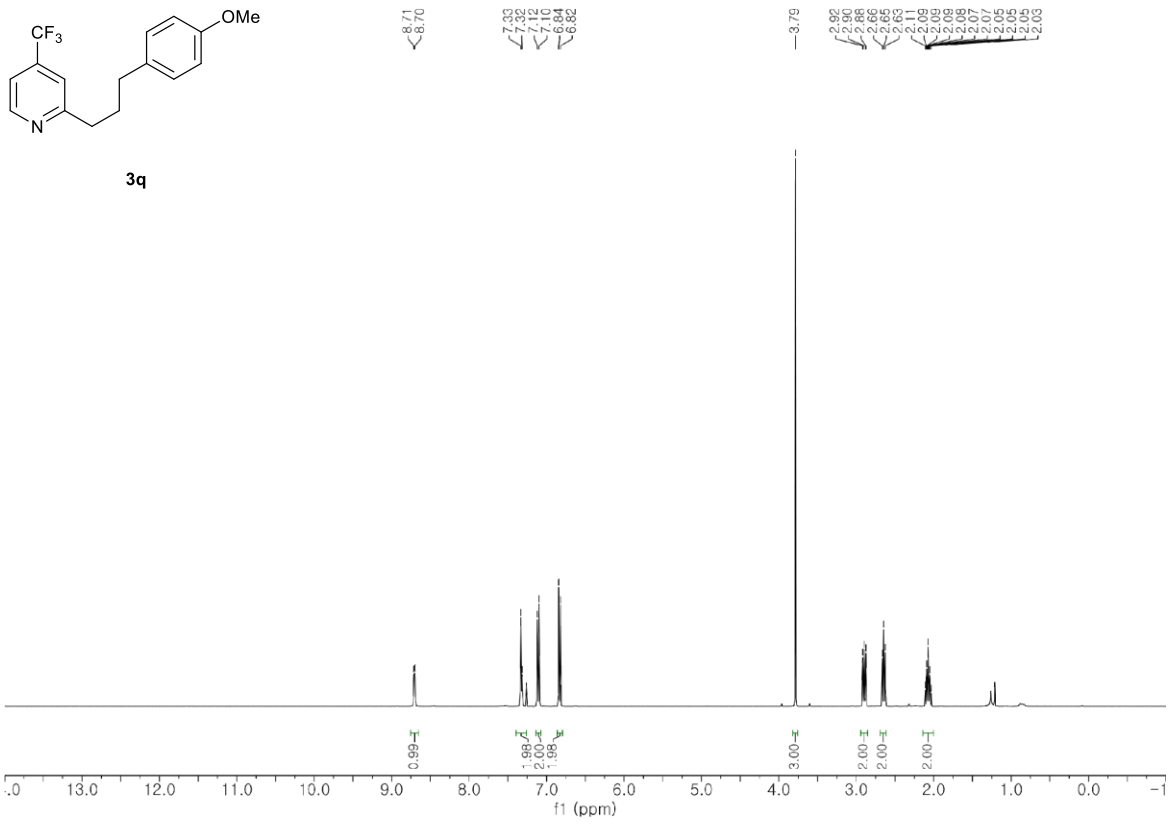
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3p**



^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3p**

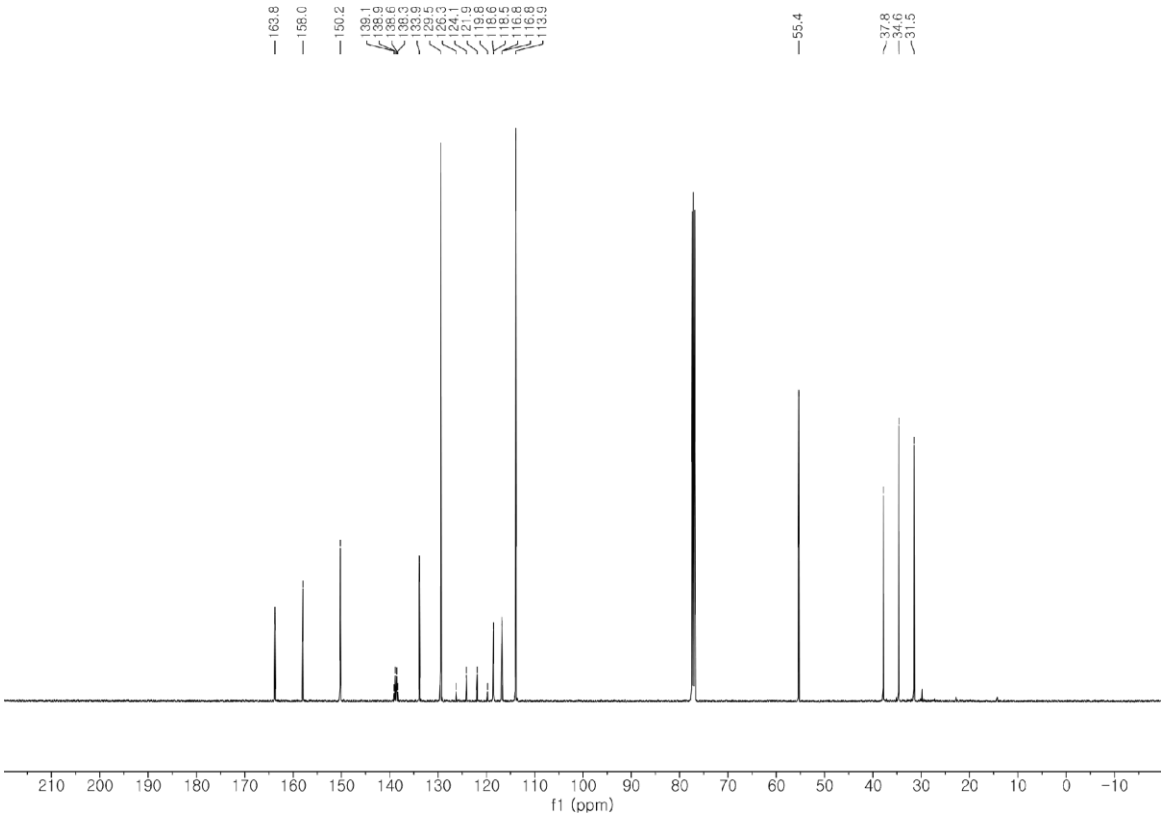


$^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, $CDCl_3$) of **3p**

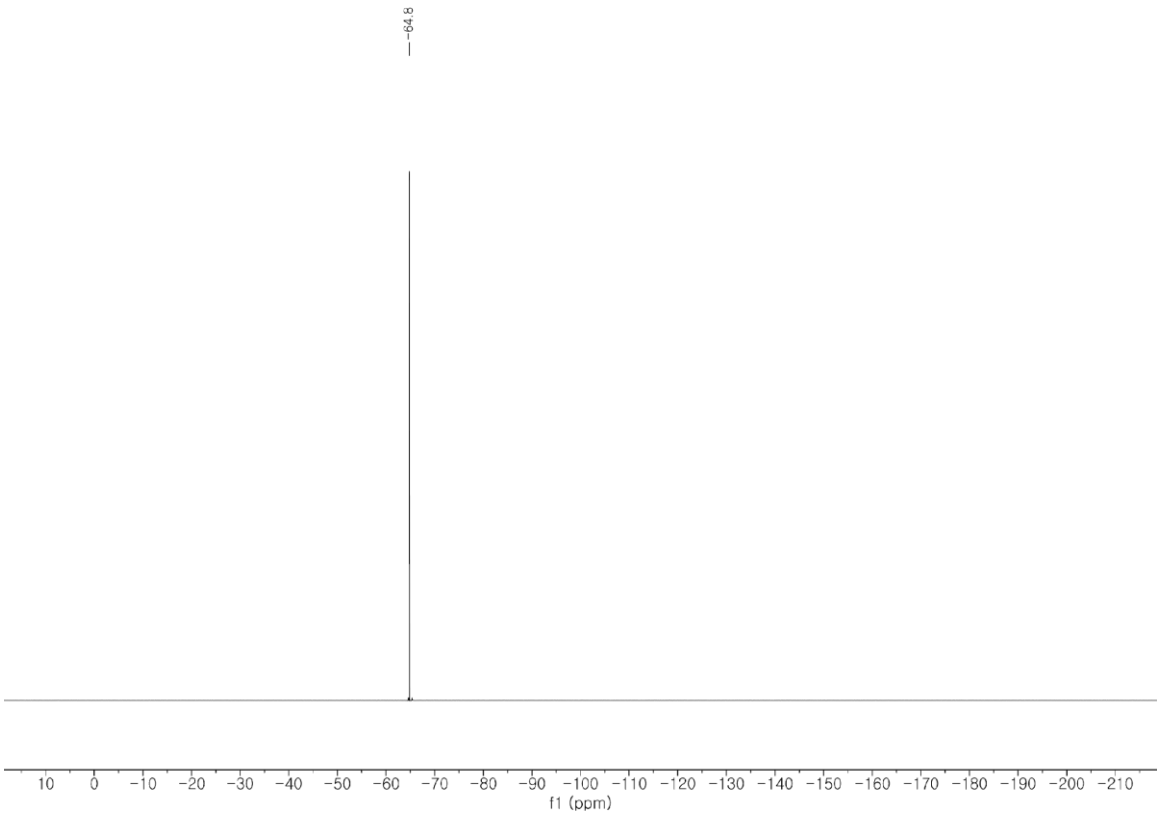


3q

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



$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **3q**



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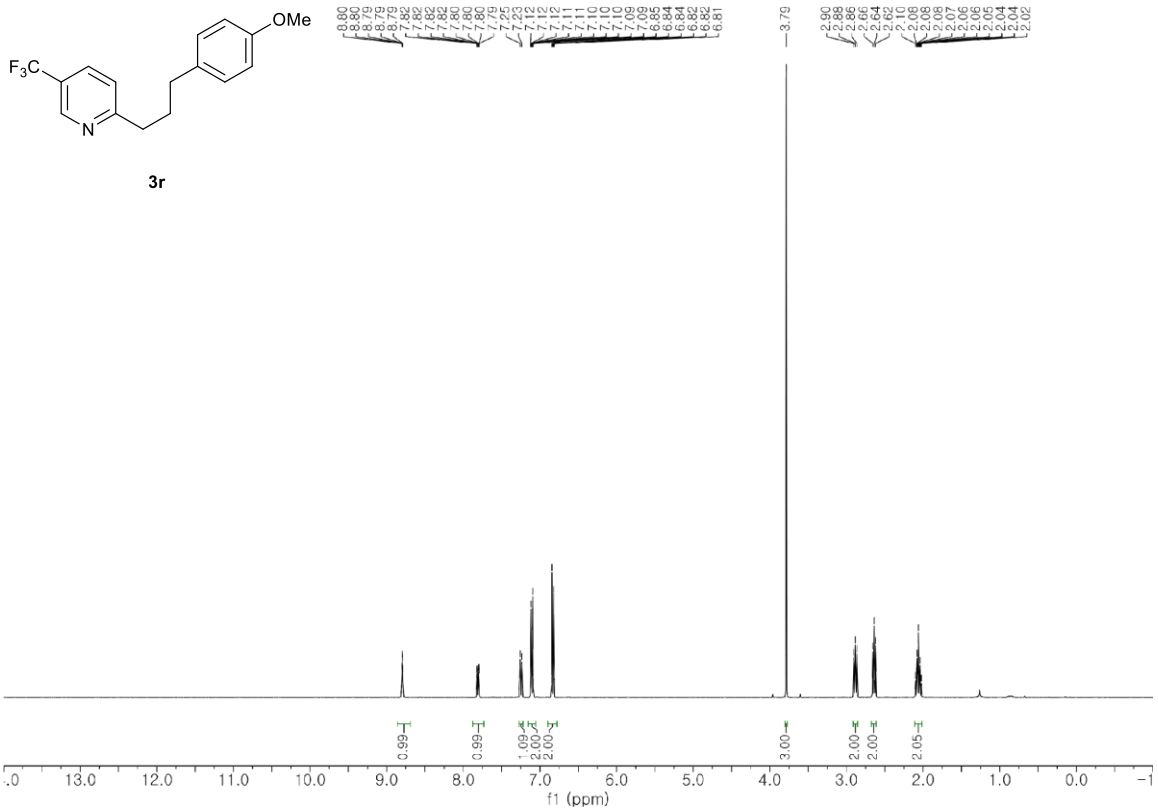
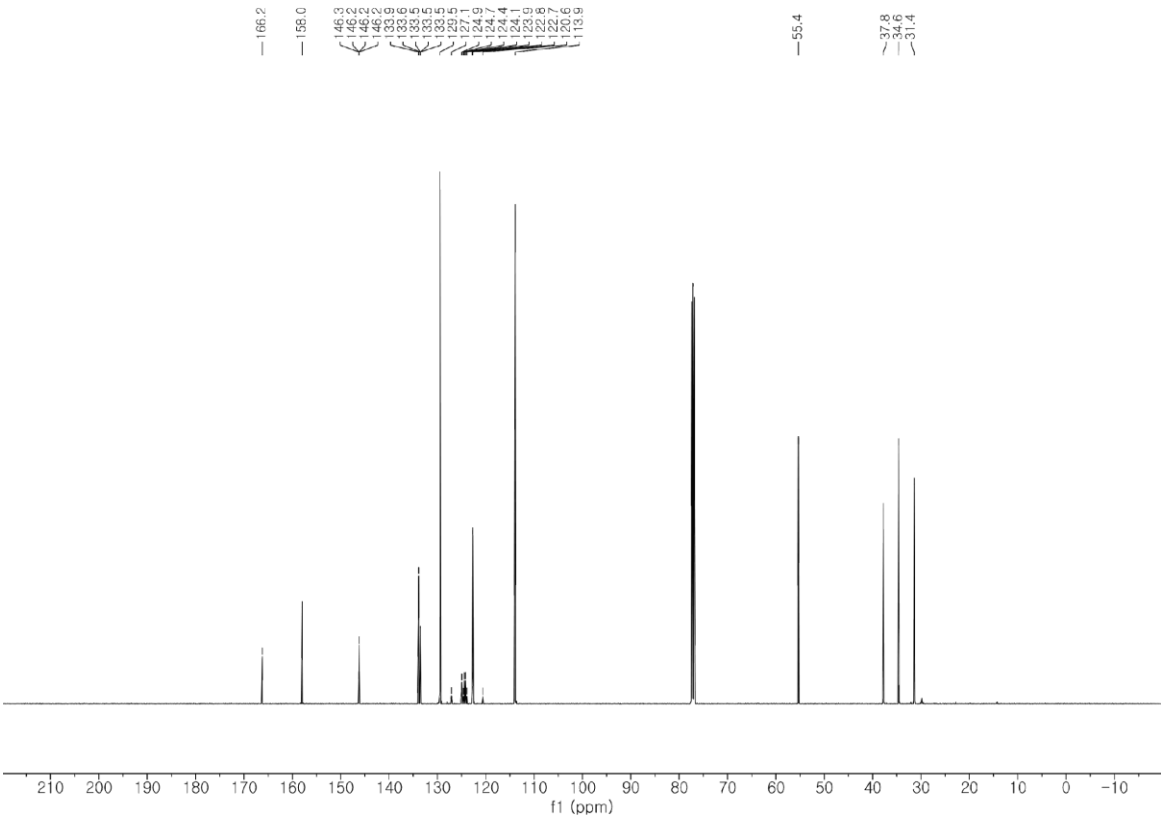


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3r**



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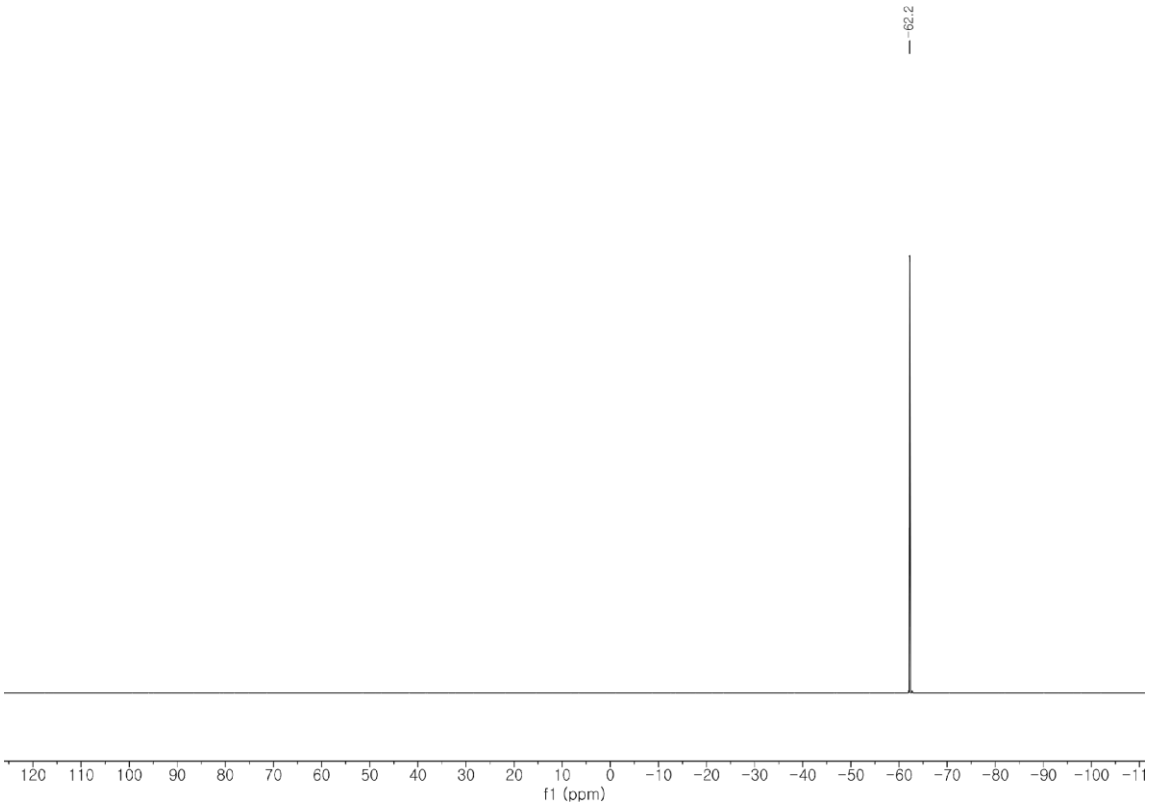

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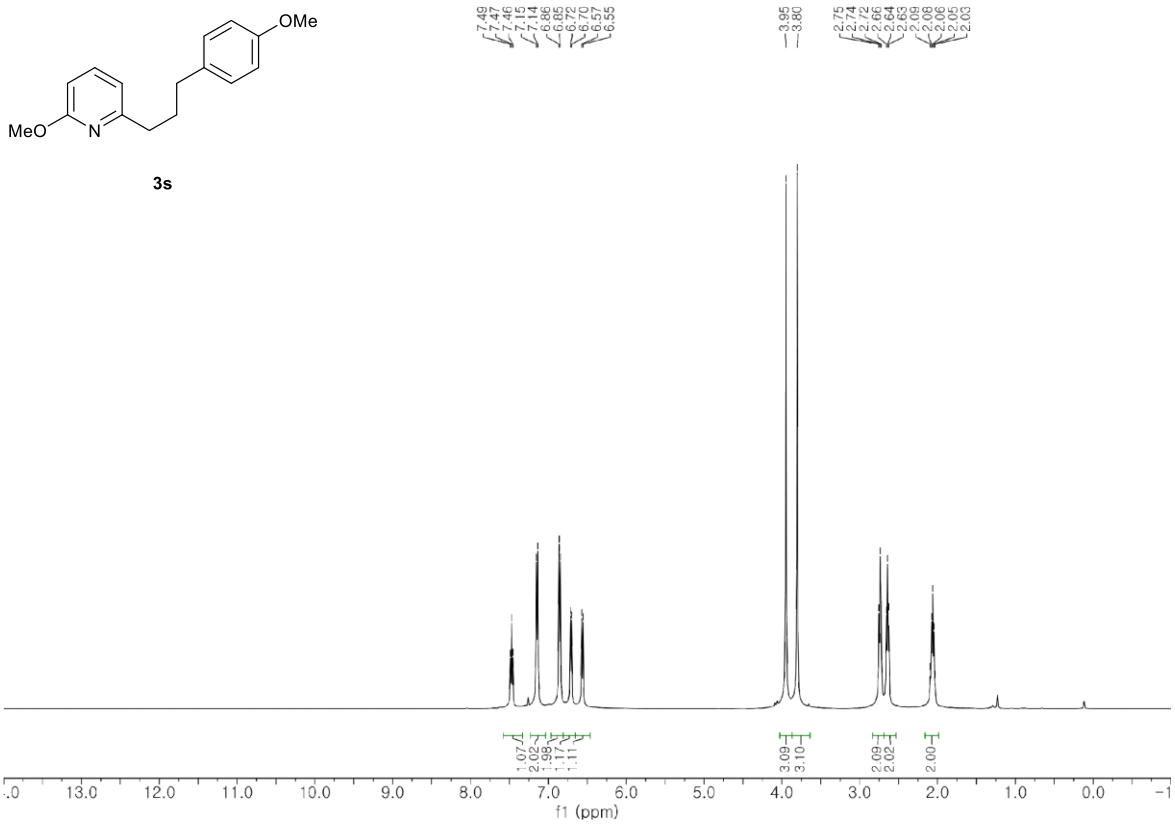
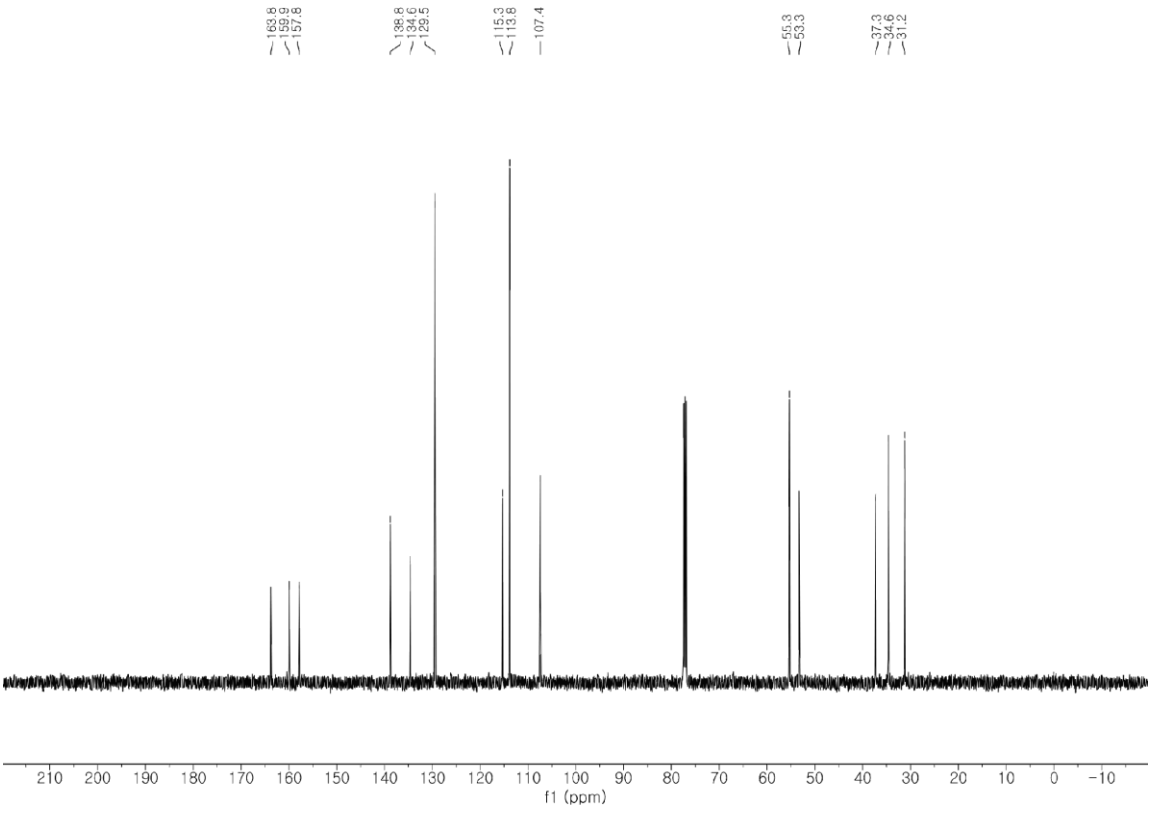
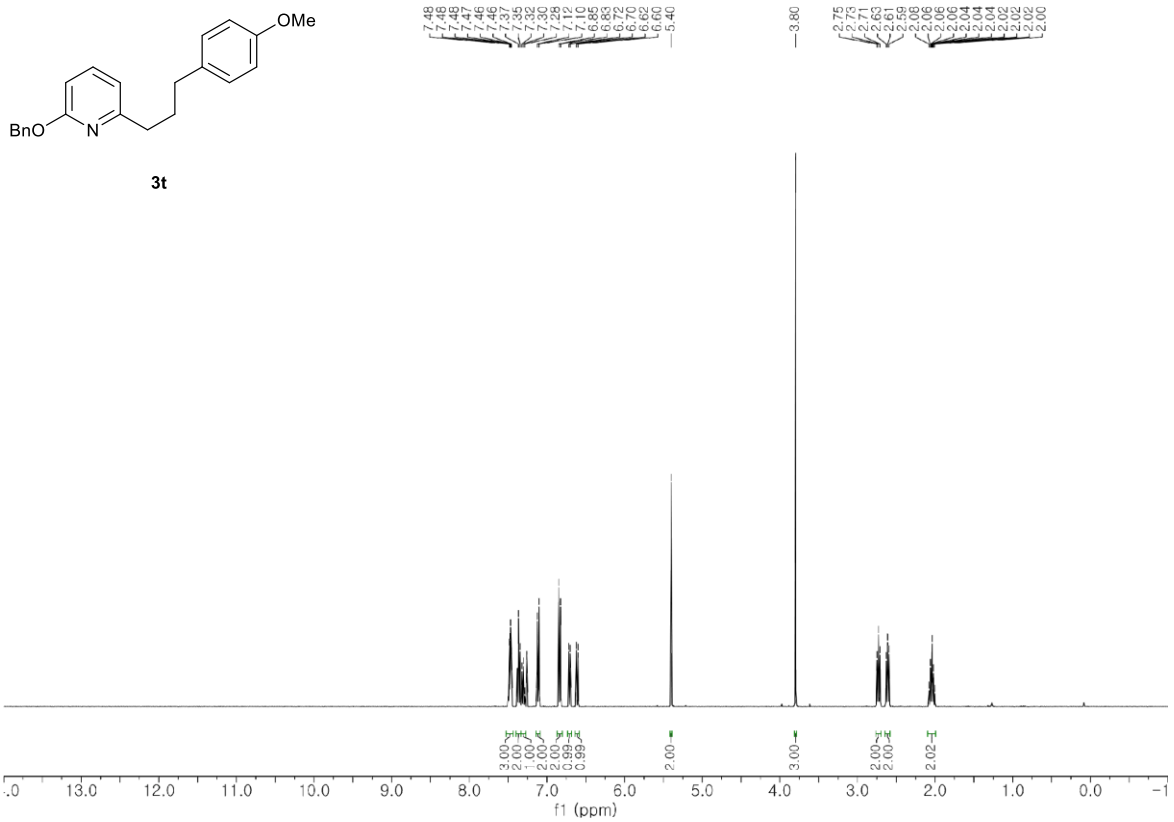


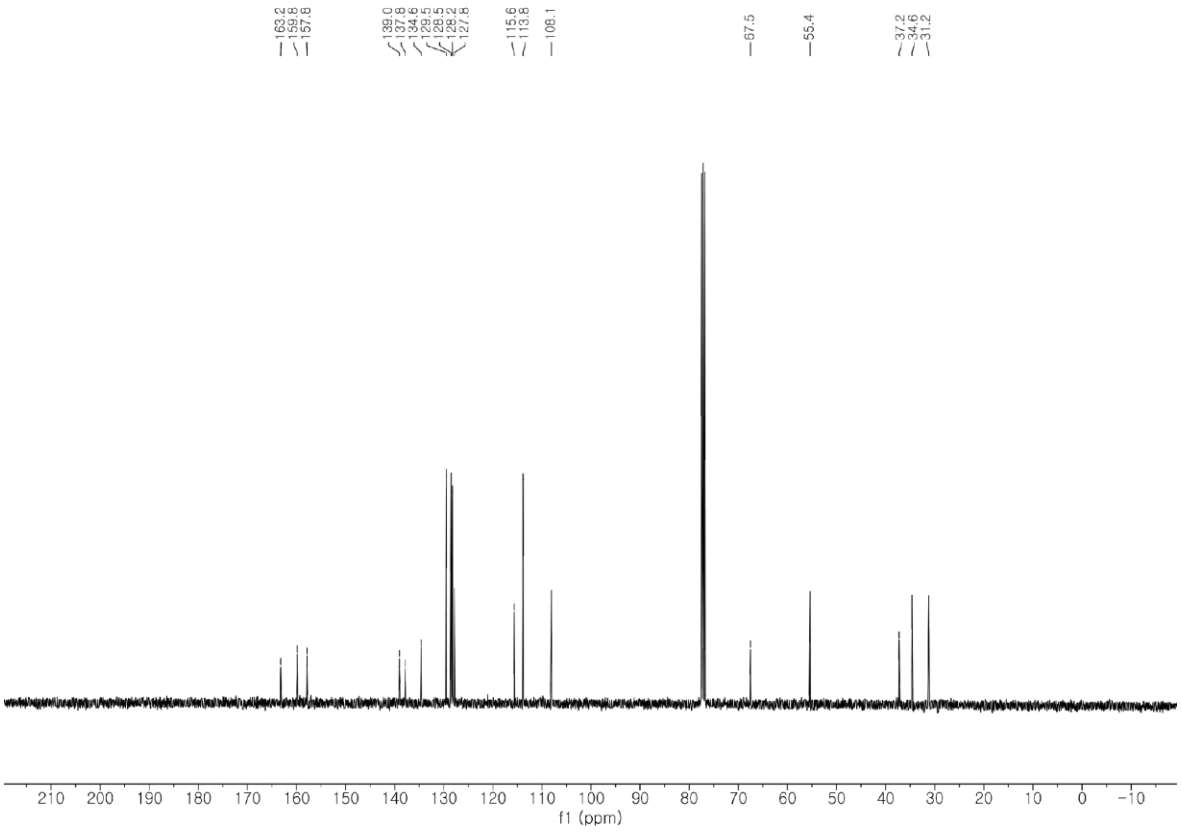
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3s**



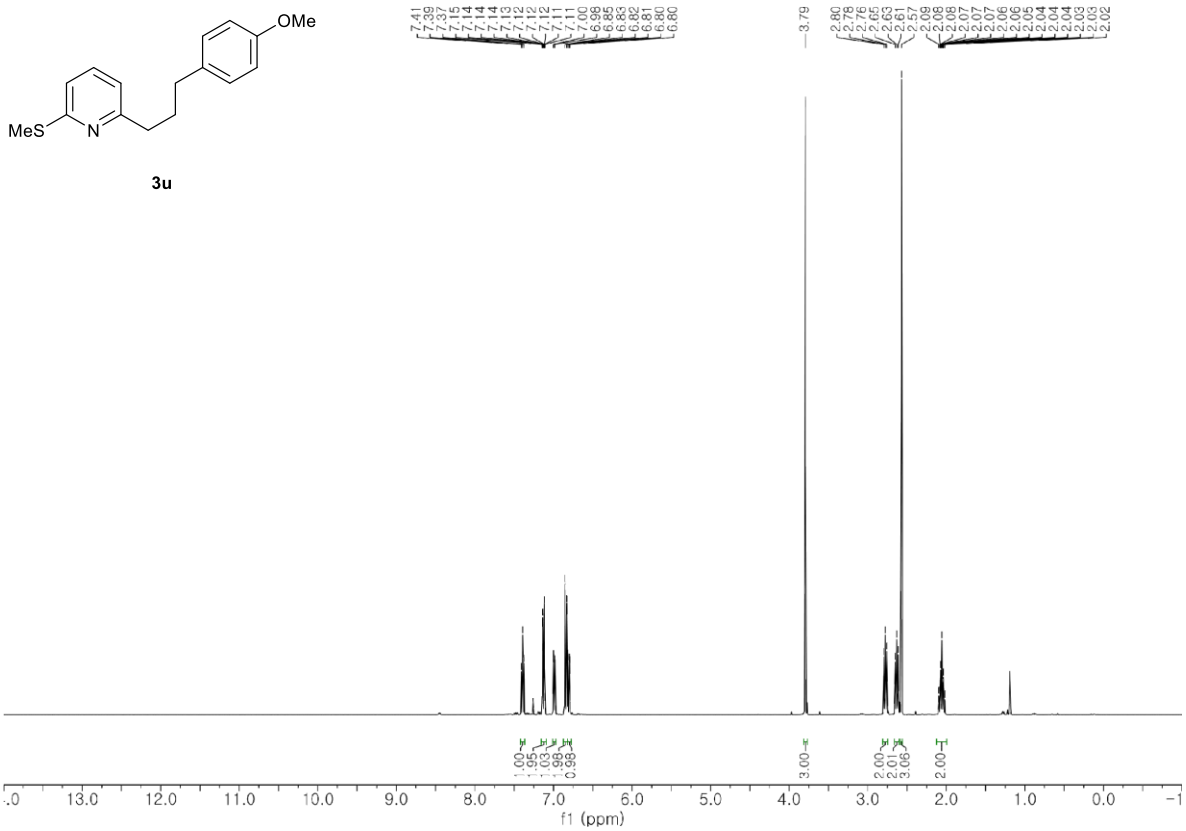
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3s**



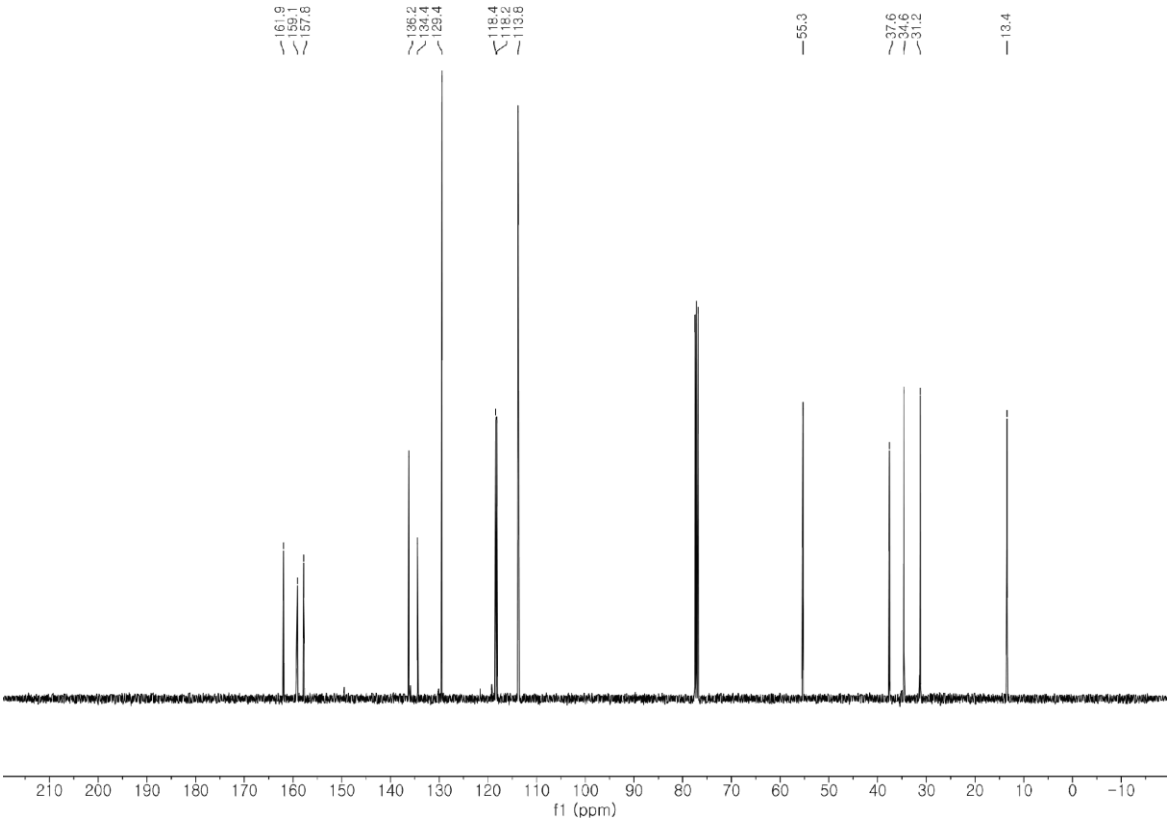
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3t**



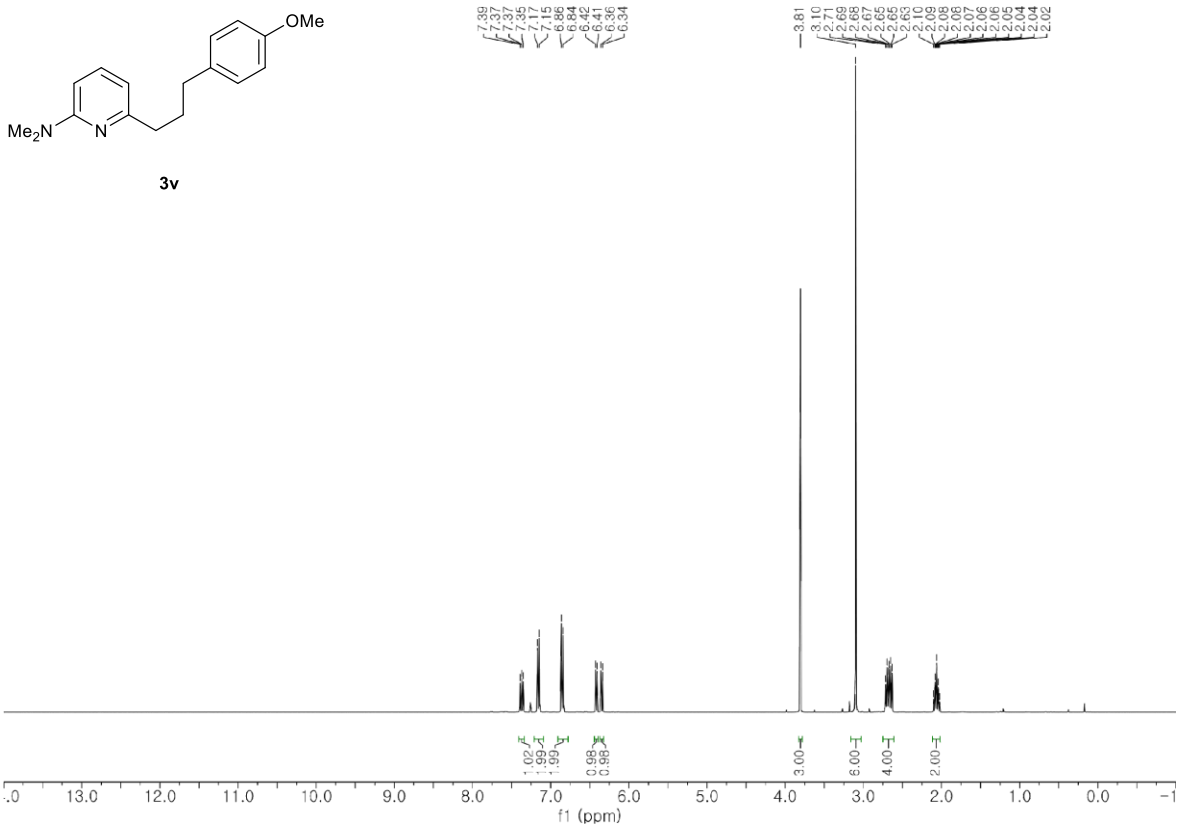
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **3t**



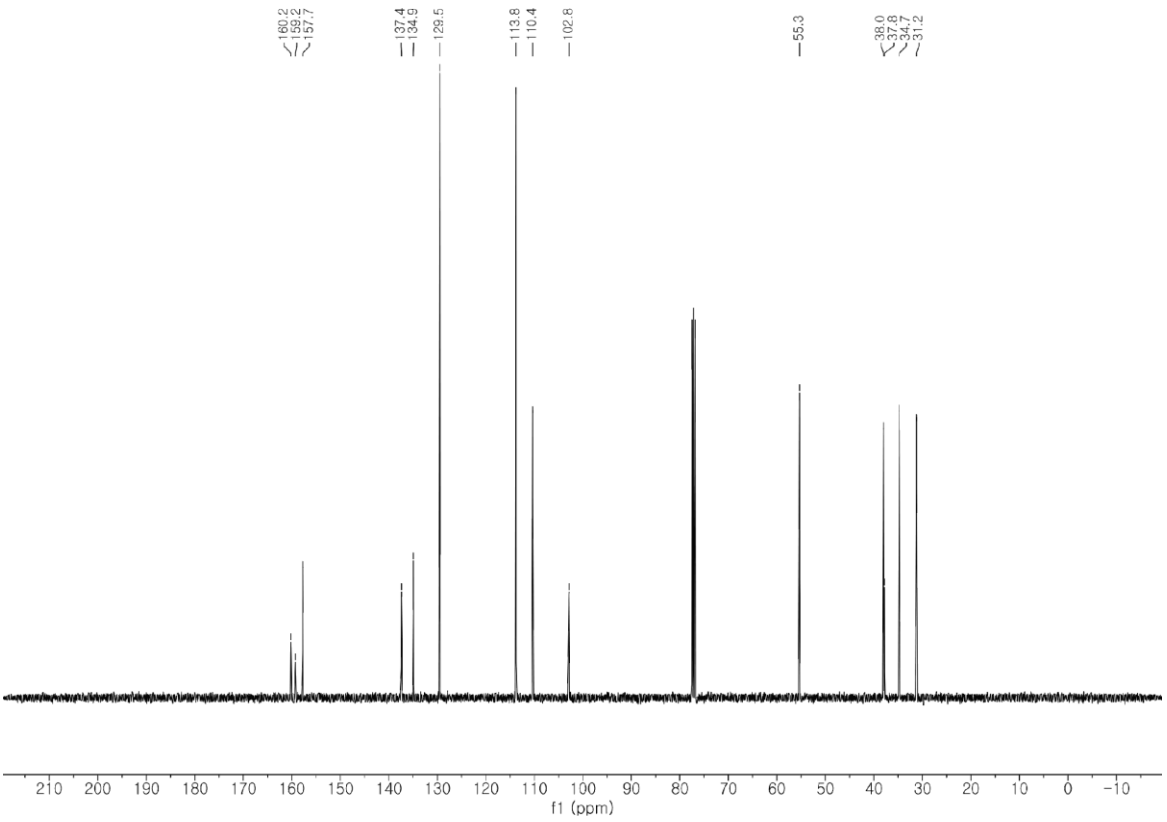
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3u**



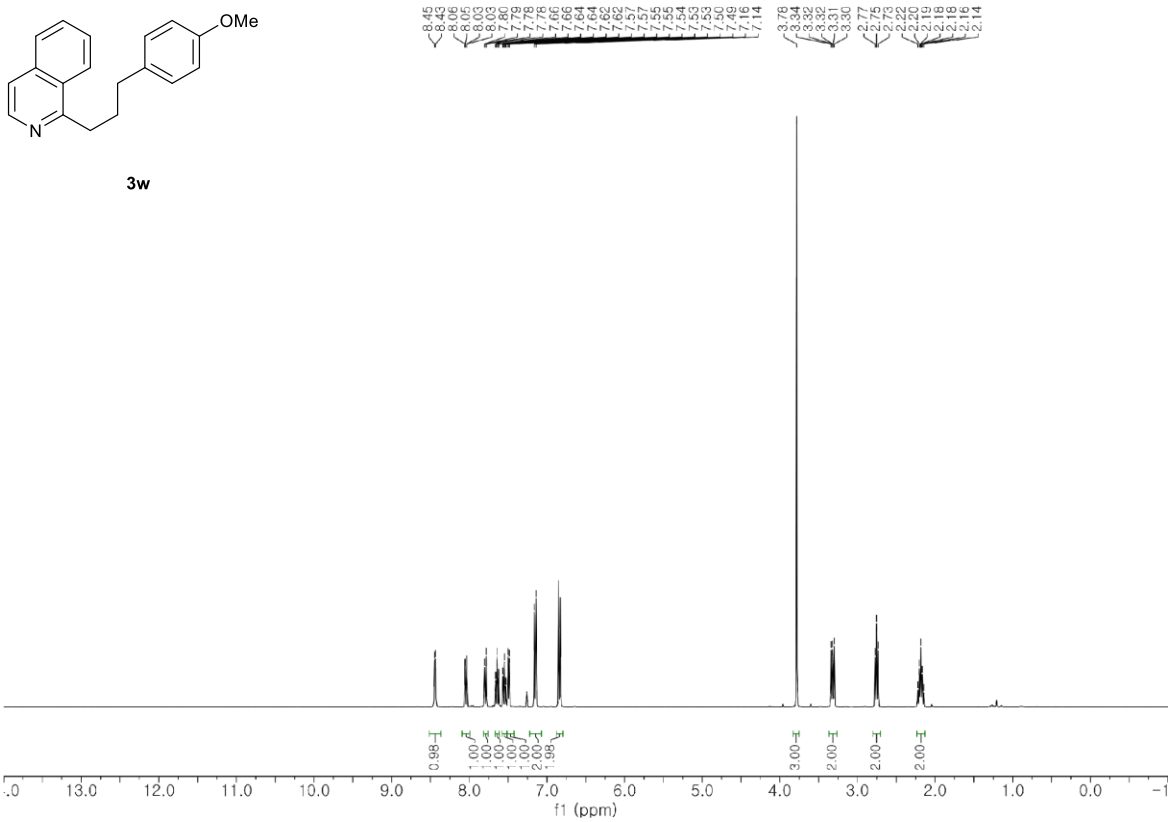
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3u**



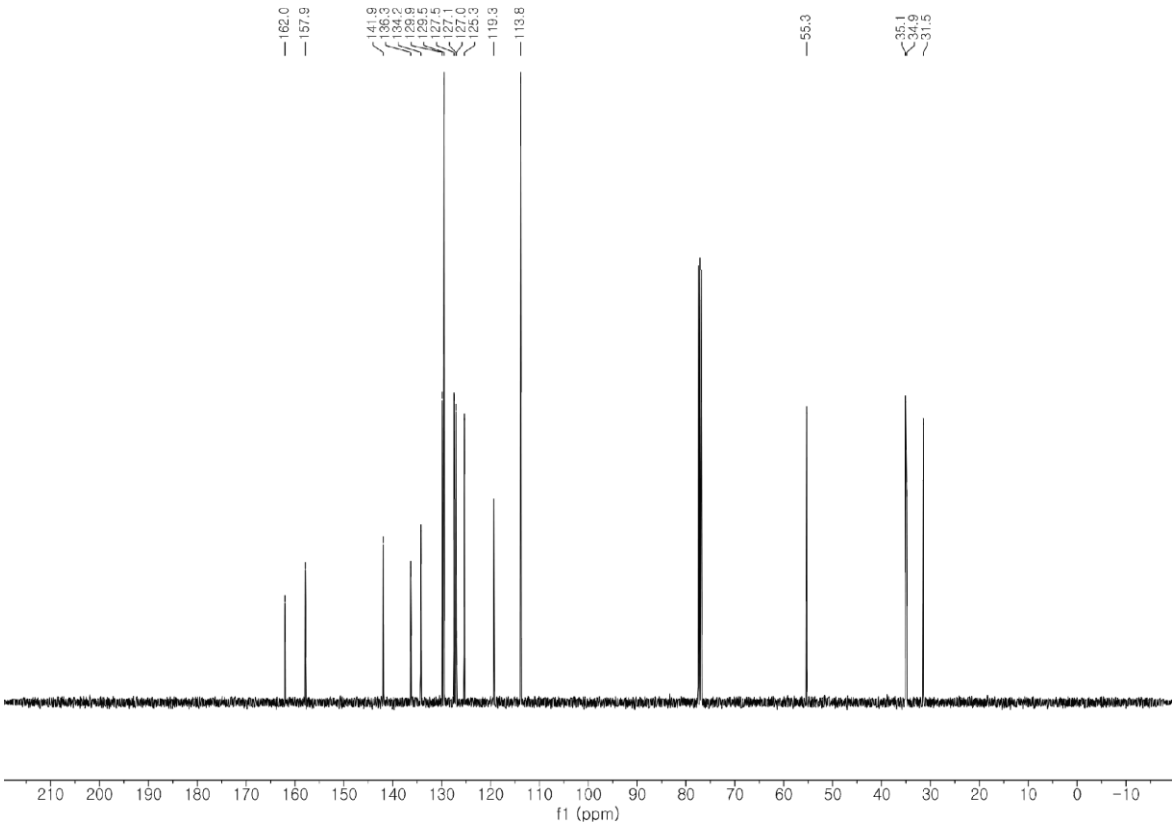
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3v**



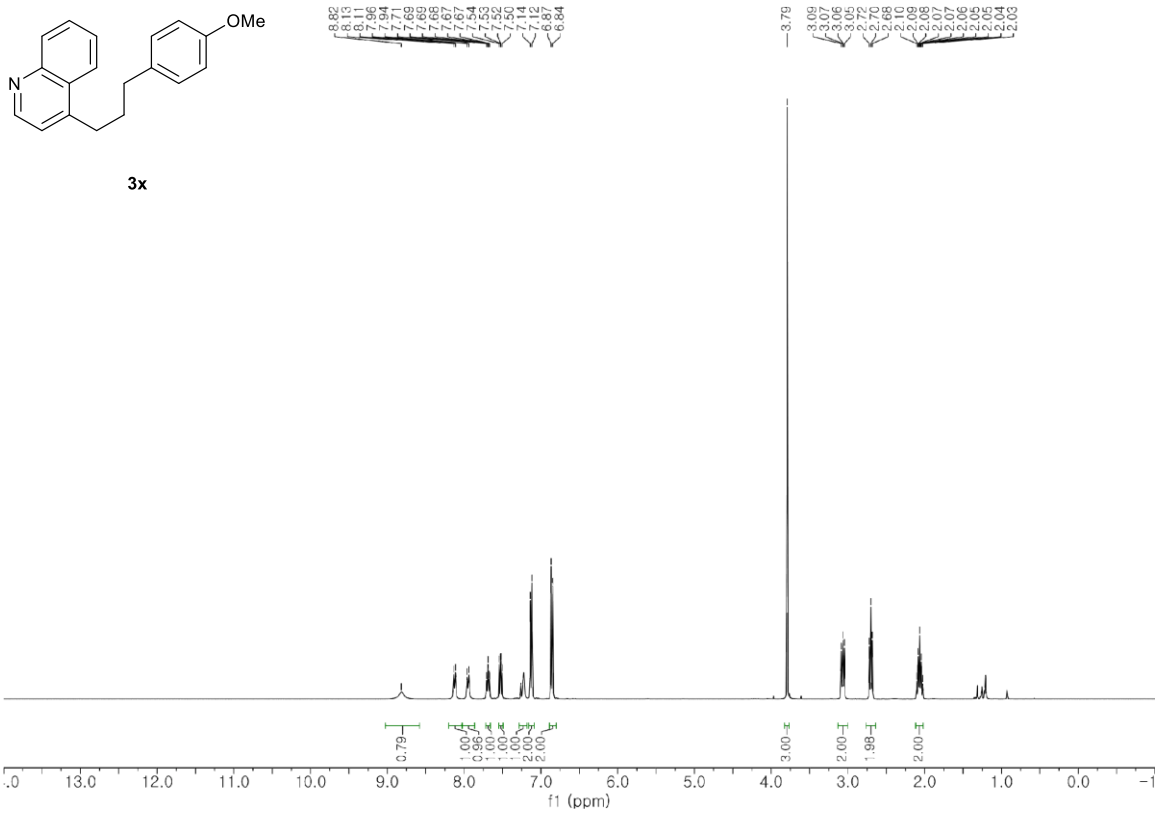
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3v**



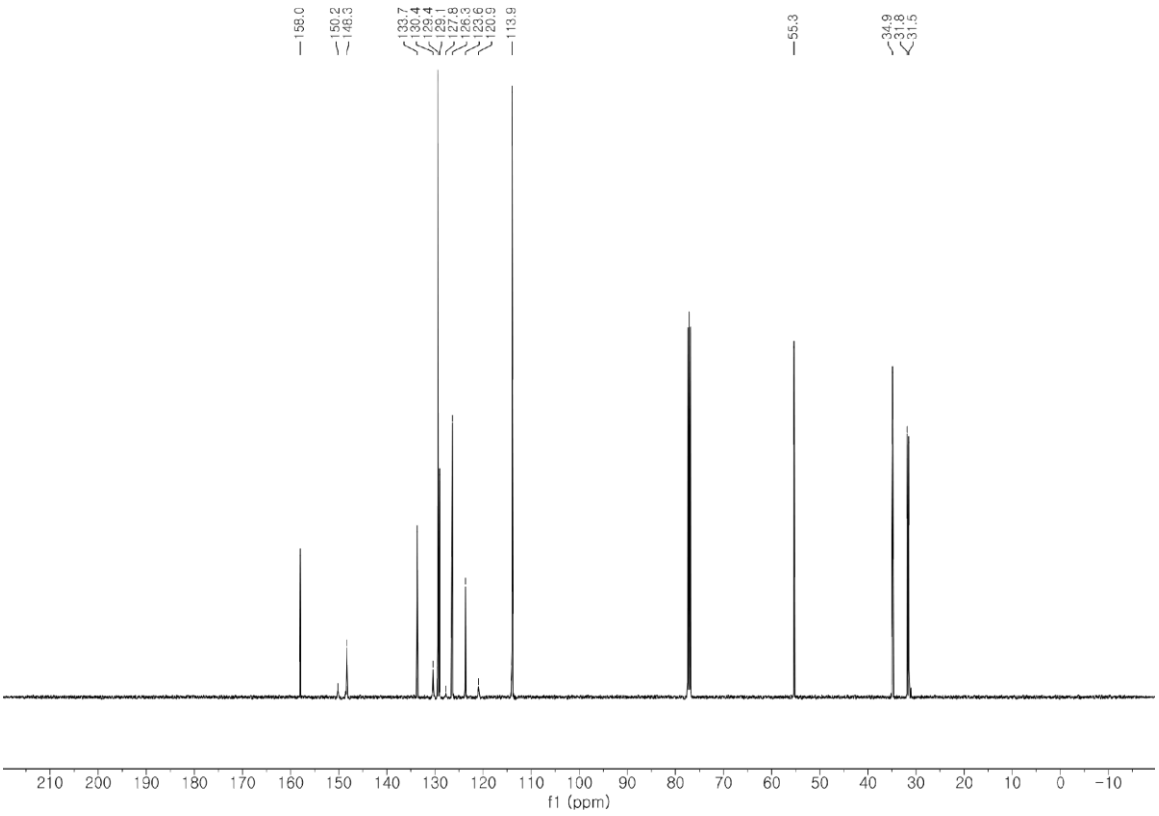
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3w**



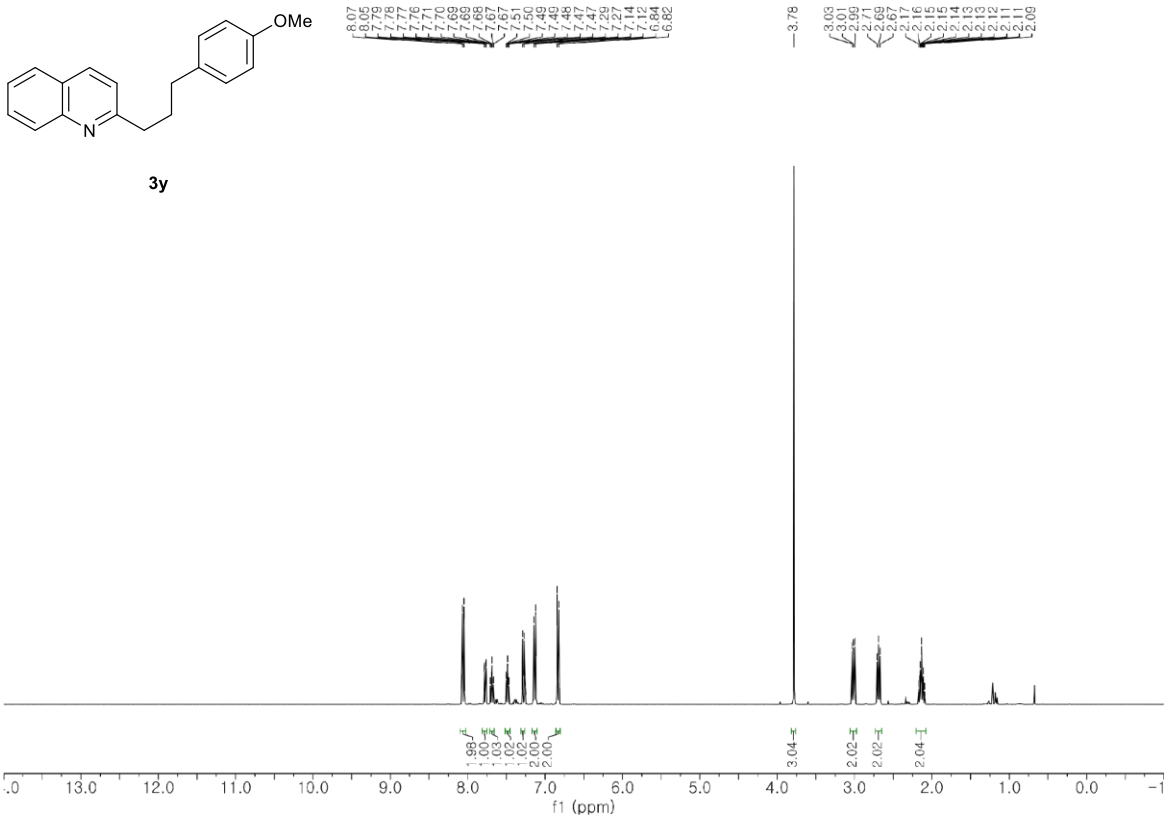
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3w**



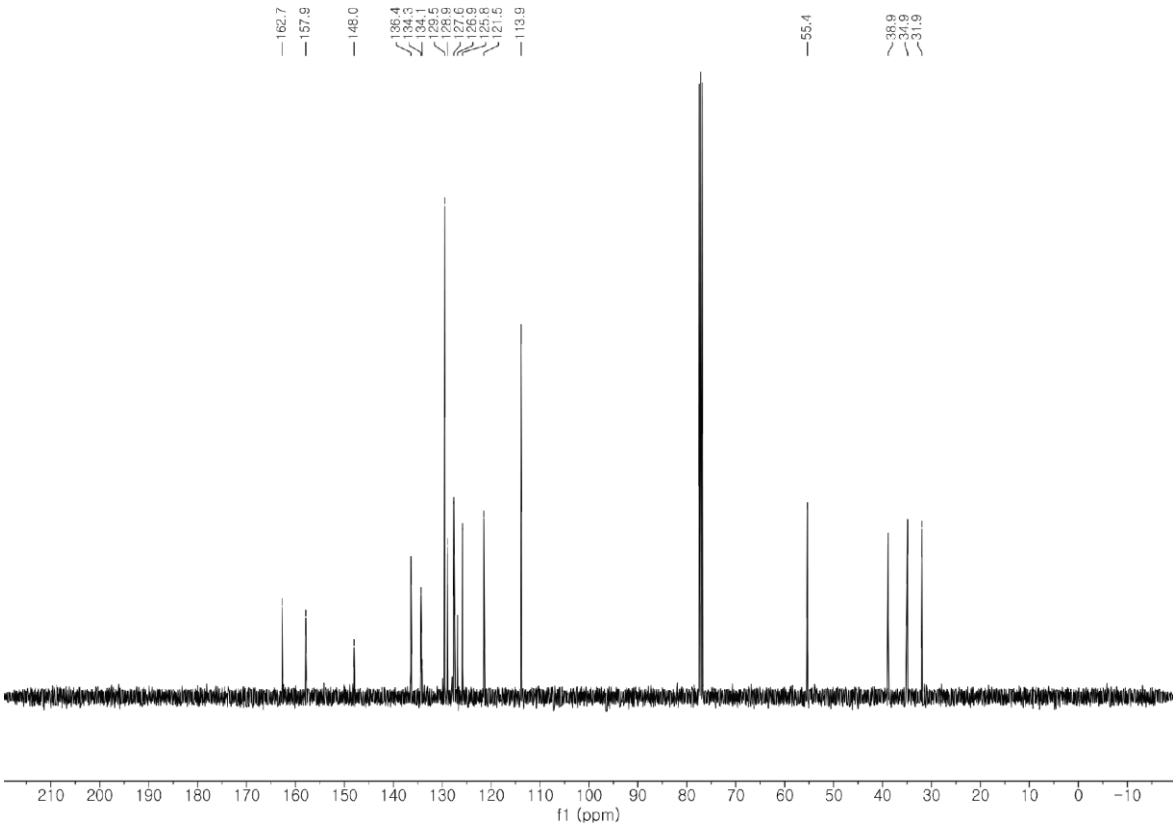
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3x**



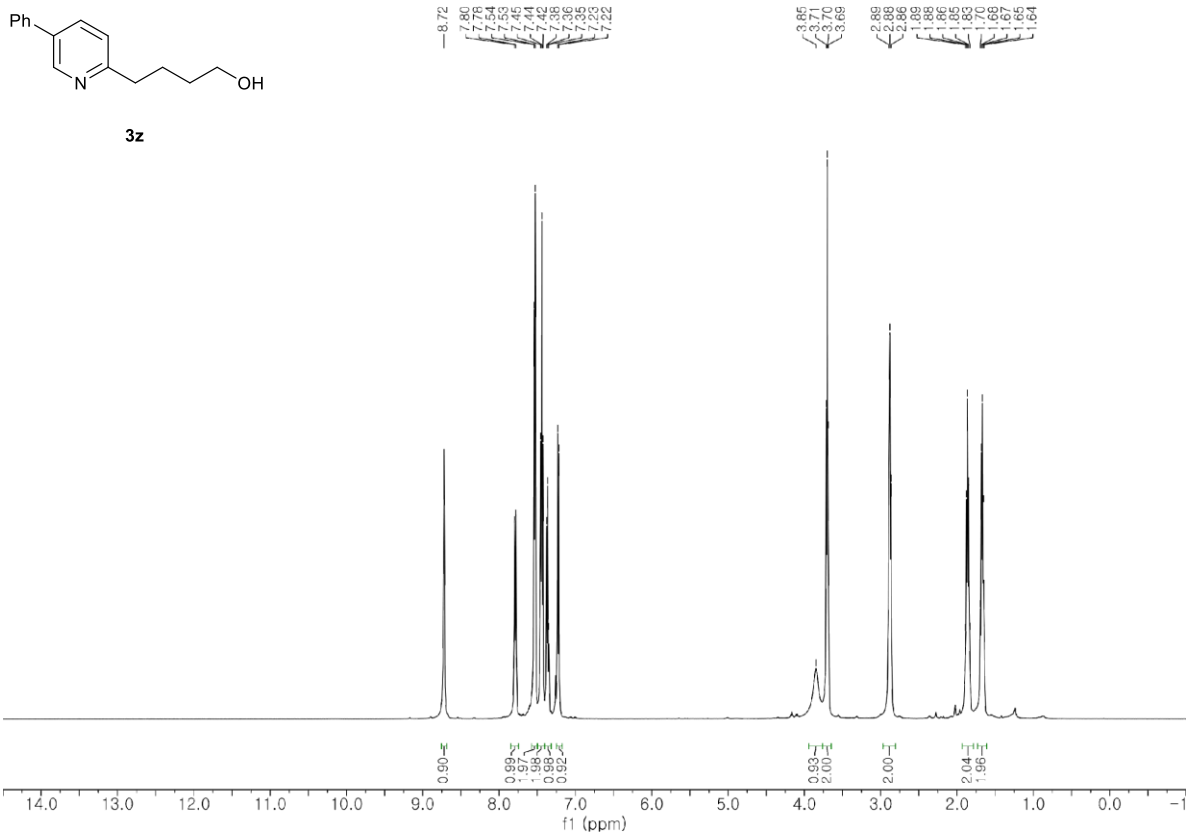
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3x**



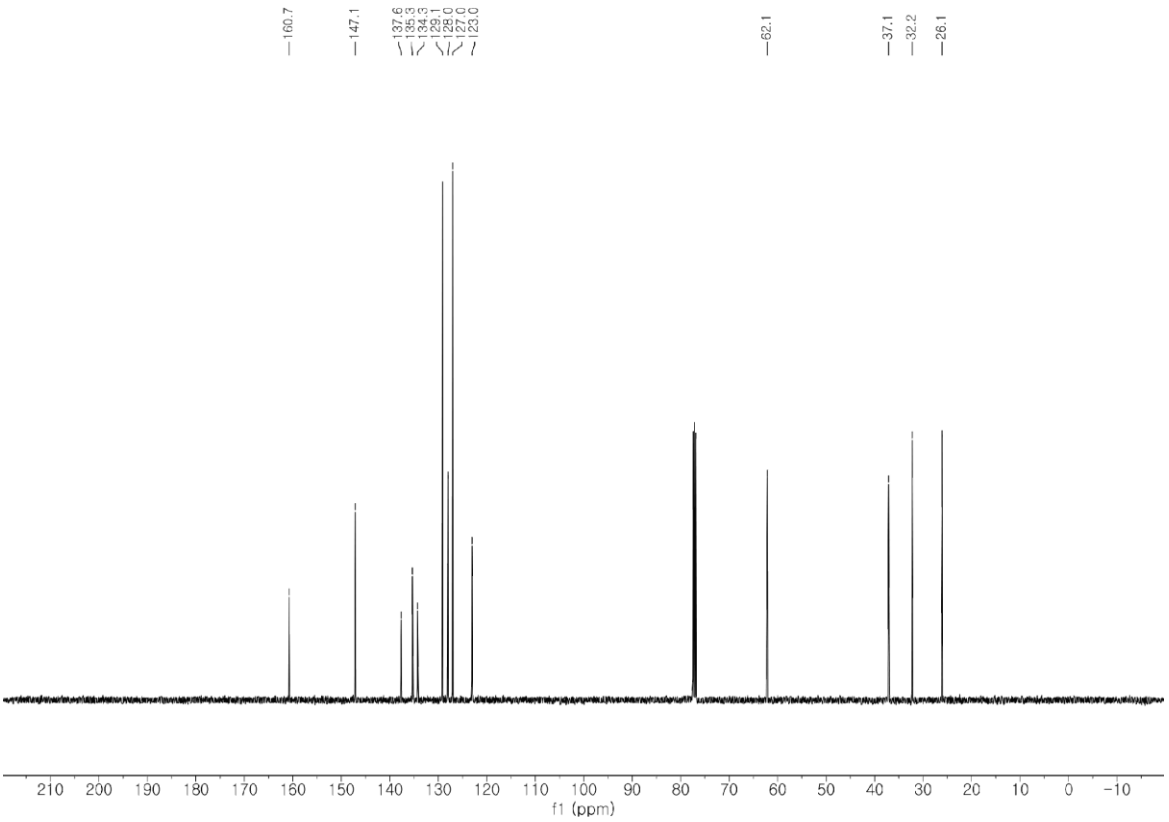
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3y**



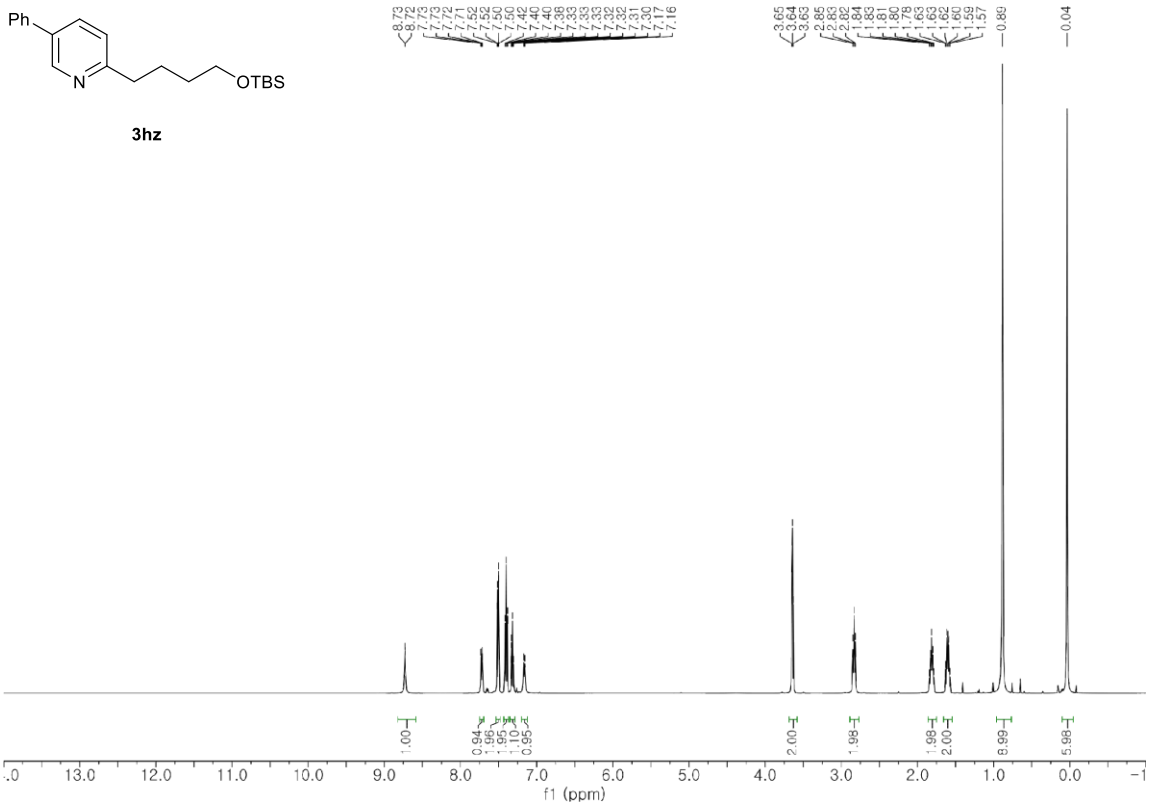
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **3y**



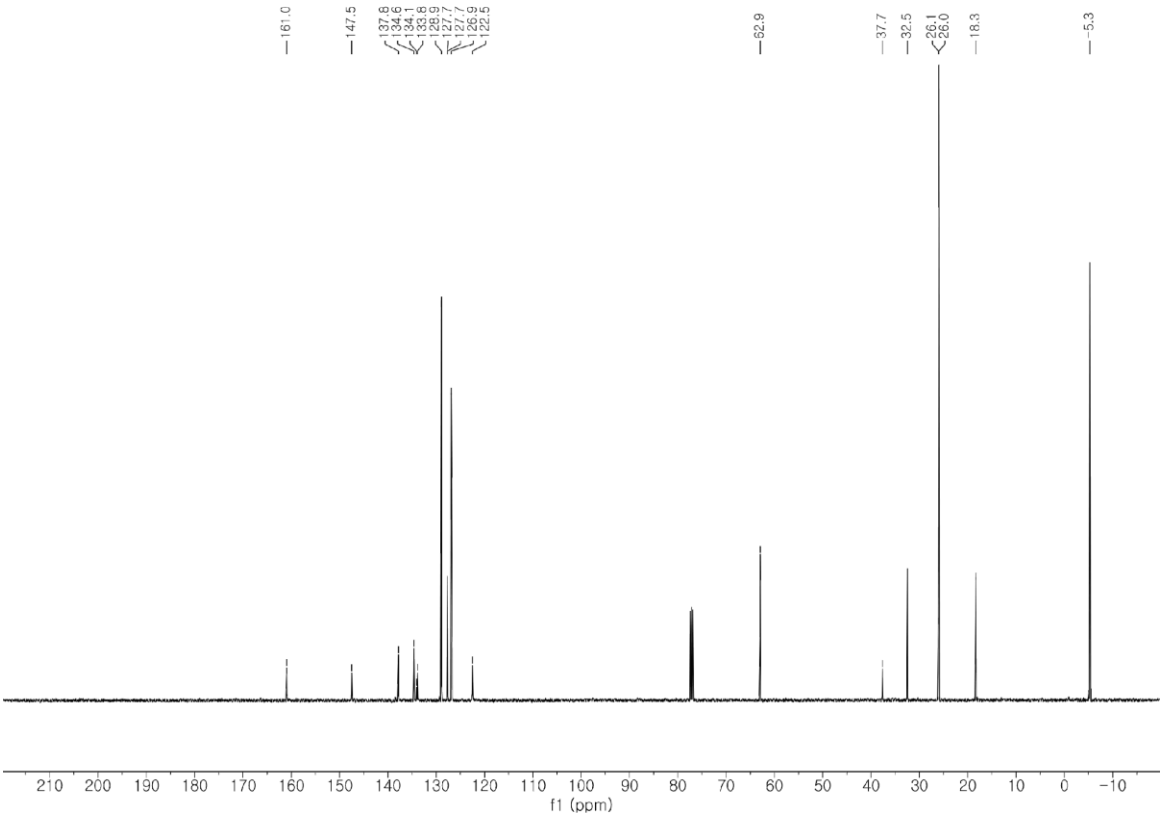
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3z**



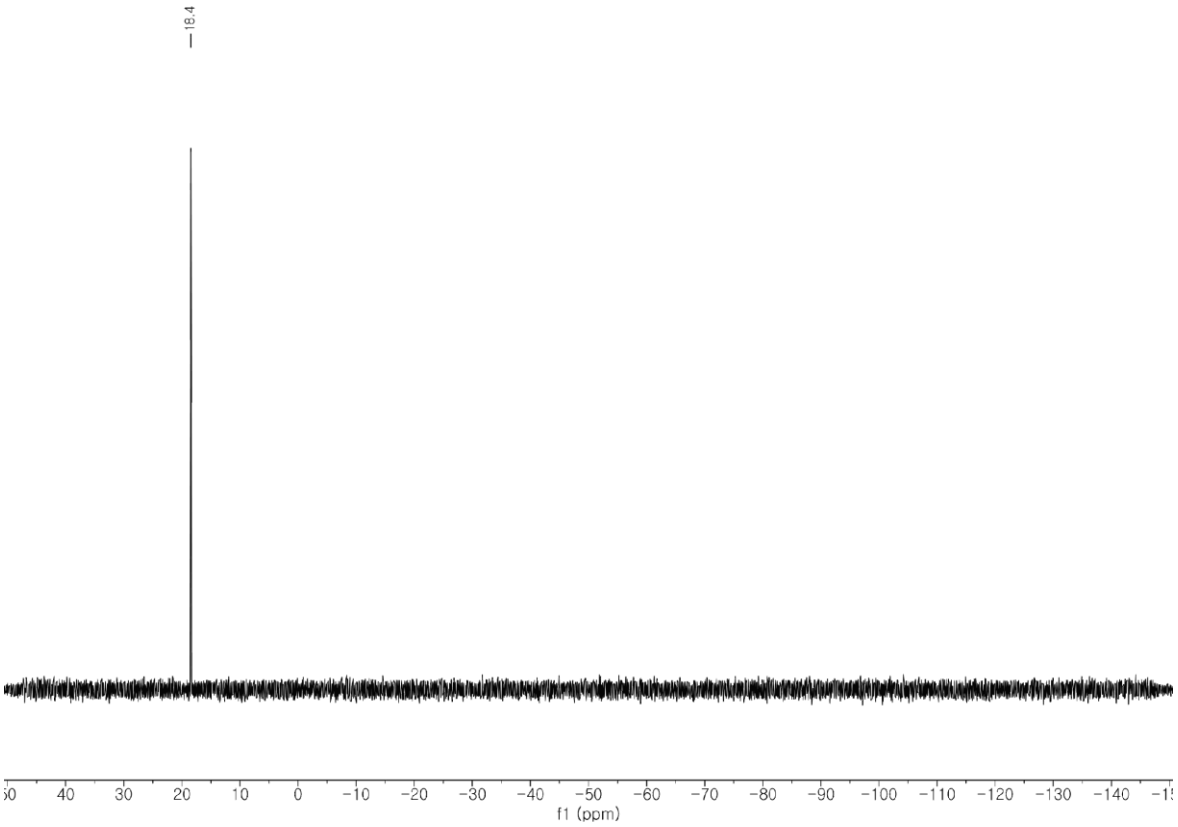
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3z**



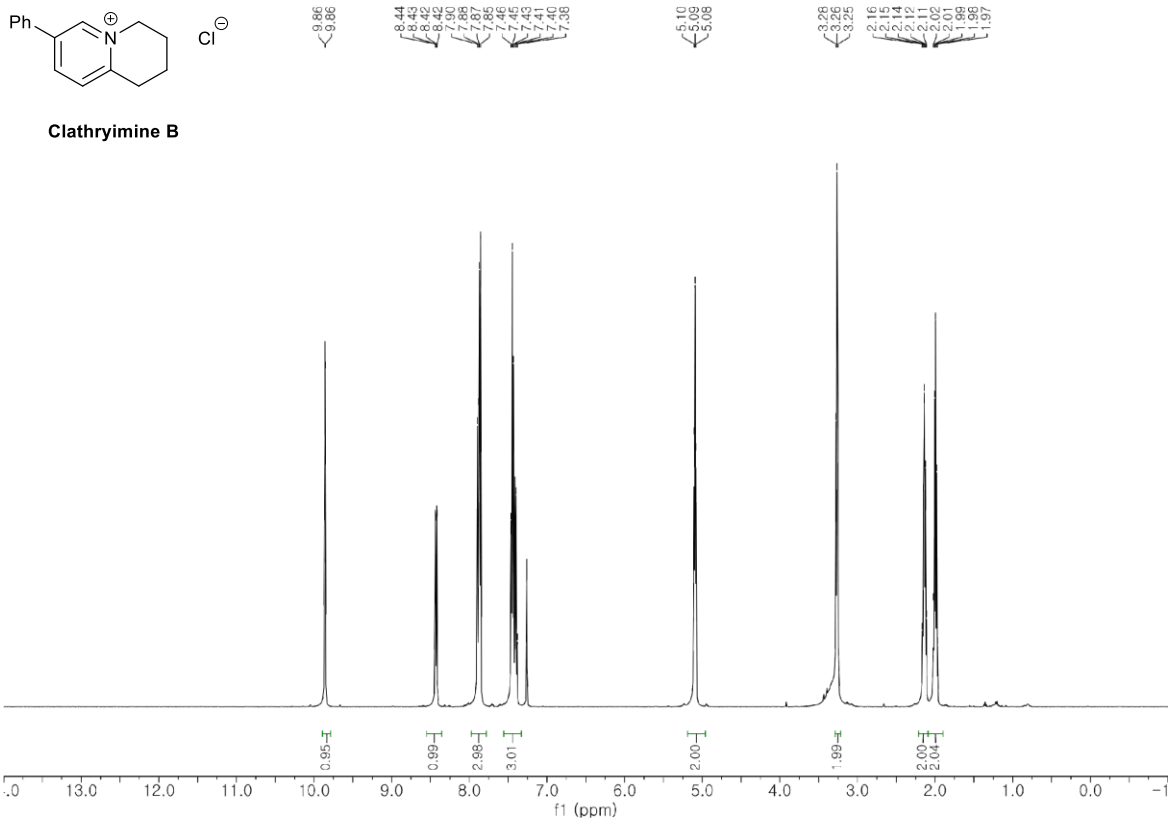
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3hz**



^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **3hz**

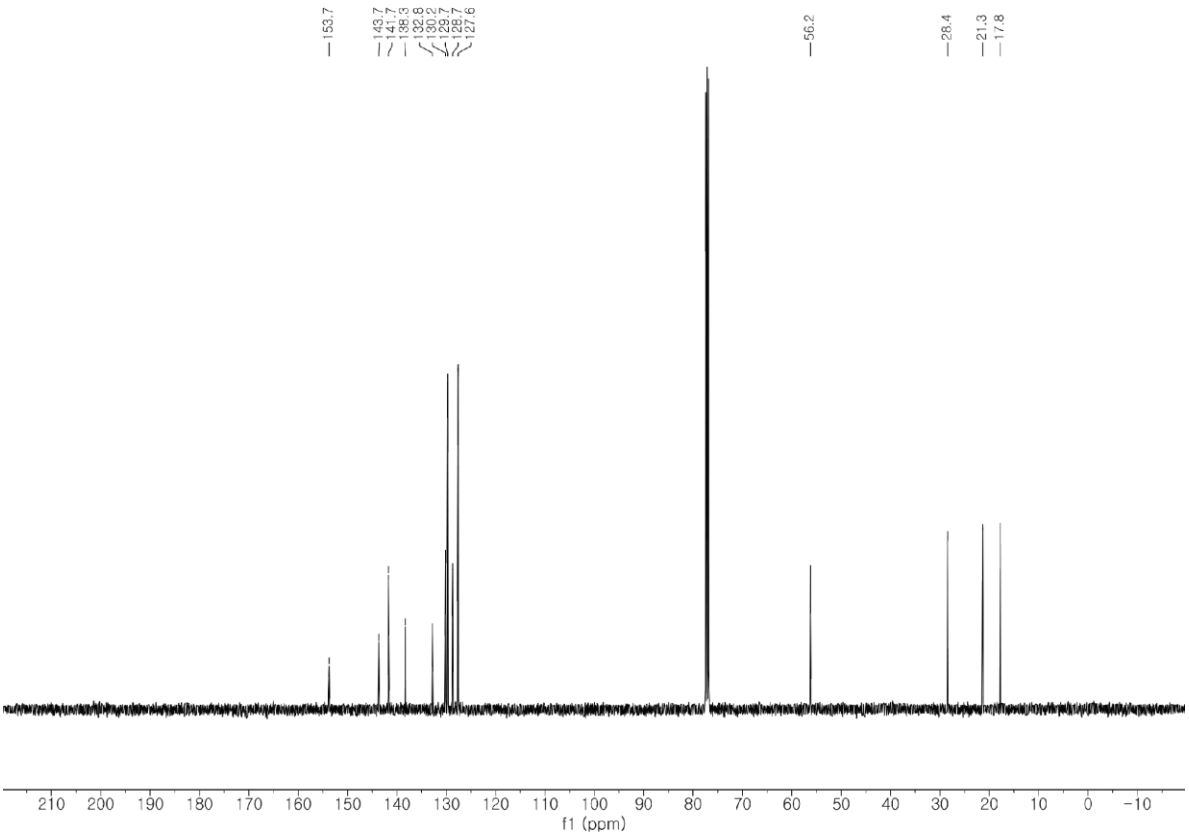


$^{29}Si\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **3hz**



Clathryimine B

^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **Clathryimine B**



^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **Clathryimine B**