Supporting Information for

Iridium-Catalyzed Asymmetric Allenylic Substitution of Racemic Tertiary Allenylic Alcohols with Indoles

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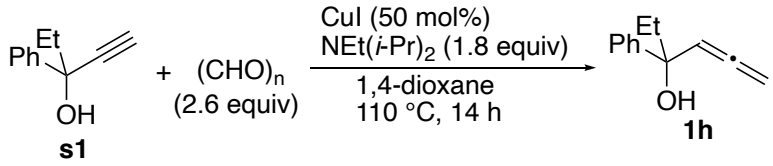
Contents of the Supporting Information

1. General Methods and Materials

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried argon. ^{1}H and ^{13}C NMR spectra were measured on JEOL ECX 500II spectrometers (500 MHz for ^{1}H, 126 MHz for ^{13}C) and JEOL JNM-ECZL 400 spectrometers (400 MHz for ^{1}H, 101 MHz for ^{13}C). Chemical shifts are reported in δ (ppm) referenced to tetramethylsilane (δ 0.00) for ^{1}H NMR and the residual peaks of $CDCl_3$ (δ 77.00) for ^{13}C NMR. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. High-resolution mass spectra were obtained with a JEOL JMS-700 Mstation. Chiral High Performance Liquid Chromatography (HPLC) was performed on a Shimadzu system under the conditions given for each measurement. Optical rotations were measured on a JASCO P-2200. Single-crystal X-ray diffraction was collected on Rigaku XtaLAB Synergy DW diffractometer with a multi-layer mirror monochromatized CuKα (λ = 1.54184 Å) radiation and Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite monochromatized Mo Kα (λ= 0.71069 Å) radiation. The products were purified by column chromatography on 63-210 mesh silica gel (Kanto Kagaku; Silica Gel 60N). All solvents were dried and distilled before use by the usual procedures. $[Ir(cod)Cl]_2$,[1] (*R*)-**L**,[2] allenylic alcohols **1a-1f**[3], **1g**[4], **1i**,[4] **1j**[5], **1k**,[5] **1l**,[6] **1m**,[7] 7-azaindole **4a**,[8] **4b**[8] were prepared as described in the literature. Indoles **2a-2i**, 7-azaindole **4c**, and $Yb(OTf)_3$ were purchased and used as received.

2. Procedure for the Preparation of Tertiary Allenylic Alcohol 1h

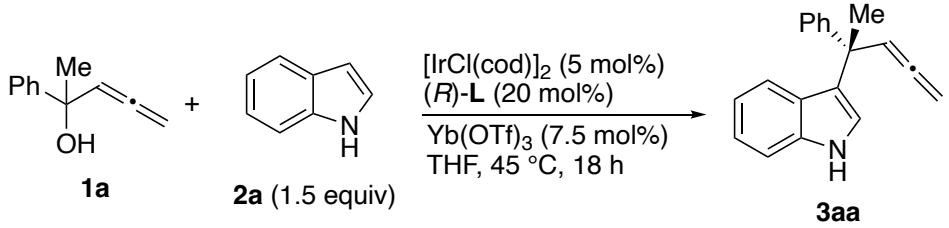


To a solution of **s1**[9] (582.2 mg, 3.634 mmol), formaldehyde (279.6 mg, 9.311 mmol), and CuI (348.7 mg, 1.831 mmol) in 1,4-dioxane (4 mL) was added diisopropylethylamine (652.3 mg, 6.446 mmol) at room temperature, and the mixture was stirred at 110 °C for 14 h. The mixture was quenched by short column chromatography (Et_2O), and concentrated on a rotary evaporator. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate = 8/2) to give compound **1h** (yellow liquid, 530.9 mg, 3.047 mmol, 84% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.43 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.27-7.22 (m, 1H), 5.57 (t, *J* = 6.6 Hz, 1H), 4.99 (dd, *J* = 10.9, 6.6 Hz, 1H), 4.94 (dd, *J* = 10.9, 6.9 Hz, 1H), 2.08-2.04 (m, 1H), 2.01-1.86 (m, 2H), 0.84 (t, *J* = 7.5 Hz, 3H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 205.7, 145.8, 128.0, 126.8, 125.3, 99.5, 79.4, 75.1, 35.5, 8.1. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{12}H_{14}O$ 174.1039; found 174.1039.

3. General Procedure for the Asymmetric Allenylic Substitution of Racemic Tertiary and Secondary Allenylic Alcohols 1 with Indoles 2 (Schemes 2 and 3)

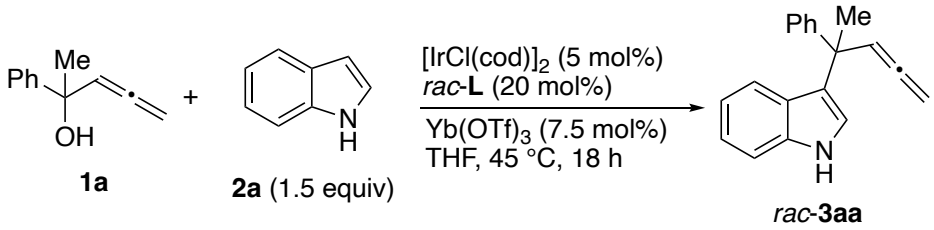
Representative Procedure for the Reaction of 1a with 2a



A mixture of $[Ir(cod)Cl]_2$ (13.4 mg, 0.0200 mmol), (*R*)-**L** (40.6 mg, 0.0800 mmol), **1a** (62.9 mg, 0.393 mmol) in THF (4.0 mL) was stirred at room temperature for 15 min. To the mixture was added **2a** (69.4 mg, 0.592 mmol) and $Yb(OTf)_3$ (18.6 mg, 0.0300 mmol), and the result was stirred at 45 °C for 18 h. After removal of the solvent on a rotary evaporator, the residue was subjected to column chromatography (silica gel, hexane/Et_2O = 90/10) to give compound **3aa** (94.8 mg, 0.366 mmol, 93% yield, 93% ee) as a brown solid.

4. General Procedure for the Synthesis of Racemic Allenylated Indoles

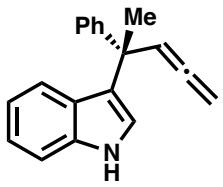
Representative Procedure for the Reaction of 1a with 2a



A mixture of $[Ir(cod)Cl]_2$ (13.4 mg, 0.0200 mmol), *rac*-**L** (40.7 mg, 0.0802 mmol), **1a** (63.2 mg, 0.394 mmol) in THF (4.0 mL) was stirred at room temperature for 15 min. To the mixture was added **2a** (70.9 mg, 0.605 mmol) and $Yb(OTf)_3$ (16.9 mg, 0.027 mmol), and the result was stirred at 45 °C for 18 h. After removal of the solvent on a rotary evaporator, the residue was subjected to column chromatography (silica gel, hexane/Et_2O = 90/10) to give compound *rac*-**3aa** (79.6 mg, 0.307 mmol, 78% yield) as a yellow oil.

5. Characterization of 3

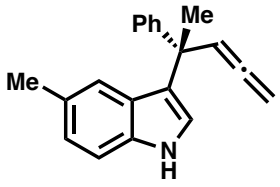
3-(2-Phenylpenta-3,4-dien-2-yl)-1*H*-indole (3aa)



3aa

3aa was prepared according to general procedure using **1a** (62.9 mg, 0.393 mmol) and **2a** (69.4 mg, 0.592 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3aa** (94.8 mg, 0.366 mmol, 93% yield, 93% ee) as a brown solid. The ee was measured by HPLC (Chiralpak AD-3 column, 0.5 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 26.2 min (*minor*), t_2 = 27.8 min (*major*)); $[\alpha]^{26}_D$ –58 (*c* 1.03, $CHCl_3$) for 93% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.39-7.33 (m, 3H), 7.30-7.24 (m, 2H), 7.21-7.16 (m, 1H), 7.15-7.10 (m, 2H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.93-6.88 (m, 1H), 5.91 (t, *J* = 6.6 Hz, 1H), 4.85 (dd, *J* = 10.4, 6.3 Hz, 1H), 4.81 (dd, *J* = 10.3, 6.9 Hz, 1H), 1.84 (s, 3H); ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 207.0, 147.9, 137.0, 128.0, 127.0, 126.0, 125.7, 123.6, 121.73, 121.66, 121.3, 119.0, 111.2, 99.7, 77.7, 42.9, 28.2. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{19}H_{17}N$ 259.1356; found 259.1359.

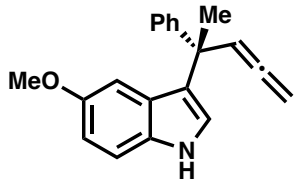
5-Methyl-3-(2-phenylpenta-3,4-dien-2-yl)-1*H*-indole (3ab)



3ab

3ab was prepared according to general procedure using **1a** (63.4 mg, 0.396 mmol) and **2b** (79.7 mg, 0.608 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3ab** (97.6 mg, 0.357 mmol, 90% yield, 90% ee) as a brown solid. The ee was measured by HPLC (Chiralpak AD-3, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t_1 = 28.7 min (*minor*), t_2 = 31.3 min (*major*)). $[\alpha]^{26}_D$ –68 (*c* 0.94, $CHCl_3$) for 90% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.39-7.34 (m, 2H), 7.30-7.15 (m, 4H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.95 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.87 (s, 1H), 5.91 (t, *J* = 6.6 Hz, 1H), 4.85 (dd, *J* = 10.3, 6.6 Hz, 2H), 4.81 (dd, *J* = 10.3, 6.6 Hz, 1H), 2.28 (s, 3H), 1.83 (s, 3H); ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 207.0, 147.9, 135.4, 128.2, 128.0, 127.0, 125.9, 123.4, 123.0, 121.8, 120.9, 110.8, 99.8, 77.6, 42.9, 28.2, 21.5. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{20}H_{19}N$ 273.1512; found 273.1518.

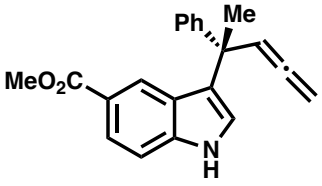
5-Methoxy-3-(2-phenylpenta-3,4-dien-2-yl)-1*H*-indole (3ac)



3ac

3ac was prepared according to general procedure using **1a** (64.0 mg, 0.399 mmol) and **2c** (88.4 mg, 0.601 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3ac** (108.3 mg, 0.374 mmol, 94% yield, 90% ee) as a brown solid. The ee was measured by HPLC (Chiralcel OJ-H, 1.0 mL/min, hexane/2-propanol = 90/10, 230 nm, t_1 = 42.4 min (*major*), t_2 =45.9 min (*minor*)). $[\alpha]^{27}_D$ –63 (*c* 0.99, $CHCl_3$) for 90% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.39-7.36 (m, 2H), 7.29-7.21 (m, 3H), 7.21-7.16 (m, 1H), 7.09 (d, *J* = 2.9 Hz, 1H), 6.78 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.47 (d, *J* = 2.3 Hz, 1H), 5.89 (t, *J* = 6.6 Hz, 1H), 4.85 (dd, *J* = 10.3, 6.9 Hz, 1H), 4.82 (dd, *J* = 10.3, 6.9 Hz, 1H), 3.60 (s, 3H), 1.83 (s, 3H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 207.0, 153.2, 147.7, 132.2, 128.0, 127.0, 126.2, 126.0, 123.3, 122.5, 111.74, 111.68, 103.4, 99.6, 77.6, 55.6, 42.8, 28.0. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{20}H_{19}NO$ 289.1461; found 289.1461.

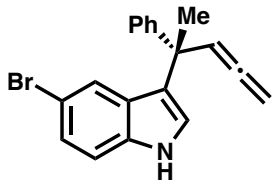
Methyl 3-(2-phenylpenta-3,4-dien-2-yl)-1*H*-indole-5-carboxylate (3ad)



3ad

3ad was prepared according to general procedure using **1a** (61.6 mg, 0.384 mmol) and **2d** (105.2 mg, 0.601 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (70/30) to afford **3ad** (78.7 mg, 0.248 mmol, 65% yield, 96% ee) as a white solid. The ee was measured by HPLC (Chiralcel OD-H, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 17.5 min (*major*), t_2 = 19.6 min (*minor*)). $[\alpha]^{27}_D$ –59 (*c* 1.01, $CHCl_3$) for 96% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.92 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.41-7.30 (m, 3H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 2.3 Hz, 1H), 5.90 (t, *J* = 6.6 Hz, 1H), 4.85 (dd, *J* = 10.3, 6.9 Hz, 1H), 4.81 (dd, *J* = 10.3, 6.9 Hz, 1H), 3.83 (s, 3H), 1.86 (s, 3H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 207.1, 168.1, 147.4, 139.7, 128.1, 126.9, 126.2, 125.5, 125.2, 124.3, 123.2, 123.0, 121.2, 110.9, 99.7, 77.9, 51.8, 43.0, 28.3. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{21}H_{19}NO_2$ 317.1410; found 317.1419.

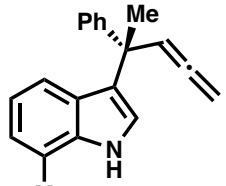
5-Bromo-3-(2-phenylpenta-3,4-dien-2-yl)-1*H*-indole (3ae)



3ae

3ae was prepared according to general procedure using **1a** (63.3 mg, 0.395 mmol) and **2e** (118.3 mg, 0.603 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (60/40) to afford **3ae** (107.4 mg, 0.3175 mmol, 80% yield, 96% ee) as a white solid. The ee was measured by HPLC (Chiralpak AD-3, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 10.8 min (*minor*), t_2 =11.5 min (*major*)). $[\alpha]^{27}_D$ –55 (*c* 0.97, $CHCl_3$) for 96% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.31-7.24 (m, 2H), 7.24-7.17 (m, 4H), 7.08 (d, *J* = 2.3 Hz, 1H), 5.84 (t, *J* = 6.6 Hz, 1H), 4.85 (dd, *J* = 10.3, 7.4 Hz, 1H), 4.81 (dd, *J* = 10.3, 6.9 Hz, 1H), 1.82 (s, 3H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 207.0, 147.3, 135.7, 128.1, 127.5, 126.9, 126.2, 124.7, 123.7, 123.6, 122.9, 112.6, 112.4, 99.5, 77.9, 42.9, 28.3. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{19}H_{16}BrN$ 337.0461; found 337.0465.

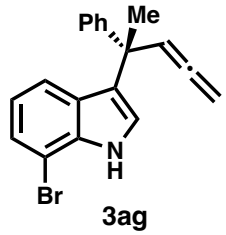
7-Methyl-3-(2-phenylpenta-3,4-dien-2-yl)-1*H*-indole (3af)



3af

3af was prepared according to general procedure using **1a** (62.7 mg, 0.391 mmol) and **2f** (79.7 mg, 0.608 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3af** (90.3 mg, 0.330 mmol, 84% yield, 91% ee) as a white solid. The ee was measured by HPLC (Chiralpak AD-3, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 8.1 min (*minor*), t_2 = 9.0 min (*major*)). $[\alpha]^{27}_D$ –40 (*c* 0.96, $CHCl_3$) for 91% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.39-7.33 (m, 2H), 7.29-7.22 (m, 2H), 7.21-7.15 (m, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.96-6.89 (m, 2H), 6.83 (dd, *J* = 8.0, 7.0 Hz, 1H), 5.91 (t, *J* = 6.6 Hz, 1H), 4.85 (dd, *J* = 10.3, 6.6 Hz, 1H), 4.81 (dd, *J* = 10.2, 6.6 Hz, 1H), 2.47 (s, 3H), 1.83 (s, 3H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 207.0, 148.0, 136.6, 128.0, 127.0, 126.0, 125.3, 124.2, 122.3, 121.3, 120.2, 119.3, 119.1, 99.8, 77.6, 42.9, 28.2, 16.6. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{20}H_{19}N$ 273.1512; found 273.1510.

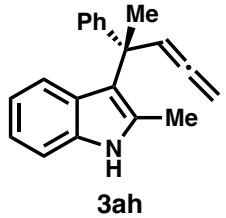
7-Bromo-3-(2-phenylpenta-3,4-dien-2-yl)-1*H*-indole (3ag)



3ag

3ag was prepared according to general procedure using **1a** (57.6 mg, 0.360 mmol) and **2g** (117.6 mg, 0.600 mmol). The crude reaction mixture was purified by column chromatography using hexane/toluene (85/15) to afford **3ag** (83.1 mg, 0.246 mmol, 68% yield, 95% ee) as a yellow solid. The ee was measured by HPLC (Chiralpak AD-3, 0.5 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 51.7 min (*minor*), t_2 = 57.1 min (*major*)). $[\alpha]^{27}_D$ –56 (*c* 1.02, $CHCl_3$) for 95% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.39–7.31 (m, 2H), 7.30-7.23 (m, 3H), 7.23-7.14 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.78 (t, *J* = 7.8 Hz, 1H), 5.86 (t, *J* = 6.6 Hz, 1H), 4.85 (dd, *J* = 10.4, 6.7 Hz, 1H), 4.81 (dd, *J* = 10.4, 6.6 Hz, 1H), 1.83 (s, 3H); ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 207.0, 147.6, 135.7, 128.1, 126.99, 126.97, 126.1, 125.1, 124.1, 122.2, 120.5, 120.3, 104.8, 99.5, 77.9, 43.1, 28.2. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{19}H_{16}BrN$ 337.0461; found 337.0470.

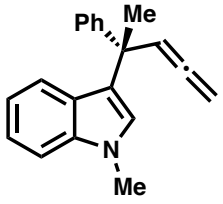
2-Methyl-3-(2-phenylpenta-3,4-dien-2-yl)-1*H*-indole (3ah)



3ah

3ah was prepared according to general procedure using **1a** (61.8 mg, 0.386 mmol) and **2h** (79.3 mg, 0.605 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3ah** (71.7 mg, 0.262 mmol, 68% yield, 20% ee) as a yellow solid. The ee was measured by HPLC (Chiralpak AD-3, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t_1 = 24.7 min (*minor*), t_2 = 26.0 min (*major*)). $[\alpha]^{27}_D$ +8 (*c* 0.98, $CHCl_3$) for 20% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.42-7.36 (m, 2H), 7.30-7.22 (m, 3H), 7.22-7.16 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.04 (td, *J* = 7.5, 1.3 Hz, 1H), 6.90-6.83 (m, 1H), 5.94 (td, *J* = 6.6, 1.9 Hz, 1H), 4.91-4.80 (m, 2H), 2.25 (s, 3H), 1.90 (d, *J* = 1.7 Hz, 3H); ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 206.7, 149.3, 134.9, 131.2, 128.1, 127.9, 126.8, 125.8, 120.9, 120.5, 118.8, 117.3, 110.0, 101.4, 77.8, 43.8, 27.7, 14.6. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{20}H_{19}N$ 273.1512; found 273.1510.

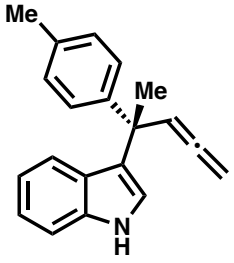
1-Methyl-3-(2-phenylpenta-3,4-dien-2-yl)-1*H*-indole (3ai)



3ai

3ai was prepared according to general procedure using **1a** (63.0 mg, 0.393 mmol) and **2i** (76.6 mg, 0.584 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3ai** (96.0 mg, 0.351 mmol, 89% yield, 93% ee) as a brown solid. The ee was measured by HPLC (Chiralcel OJ-H, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 11.6 min (*minor*), t_2 = 15.3 min (*major*)). $[\alpha]^{27}_D$ –55 (*c* 1.04, $CHCl_3$) for 93% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.30-7.23 (m, 3H), 7.21-7.13 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.94 (s, 1H), 6.92-6.87 (m, 1H), 5.90 (t, *J* = 6.6 Hz, 1H), 4.85 (dd, *J* = 10.3, 6.9 Hz, 1H), 4.82 (dd, *J* = 10.3, 6.9 Hz, 1H), 3.78 (s, 3H), 1.83 (s, 3H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 206.9, 148.1, 137.8, 128.0, 127.0, 126.5, 126.1, 126.0, 122.1, 121.4, 121.3, 118.5, 109.2, 99.9, 77.6, 42.9, 32.7, 28.3. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{20}H_{19}N$ 273.1512; found 273.1513.

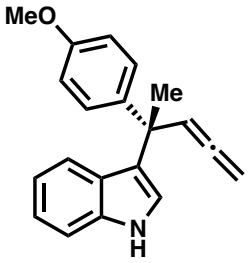
3-(2-(*p*-Tolyl)penta-3,4-dien-2-yl)-1*H*-indole (3ba)



3ba

3ba was prepared according to general procedure using **1b** (65.9 mg, 0.378 mmol) and **2a** (71.9 mg, 0.614 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3ba** (83.7 mg, 0.306 mmol, 81% yield, 87% ee) as a pale yellow oil. The ee was measured by HPLC (Chiralpak AD-3, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 9.8 min (*minor*), t_2 = 10.8 min (*major*)). $[\alpha]^{28}_D$ –26 (*c* 0.99, $CHCl_3$) for 87% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.27-7.22 (m, 2H), 7.15-7.04 (m, 5H), 6.91 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 5.89 (t, *J* = 6.6 Hz, 1H), 4.84 (dd, *J* = 10.2, 6.7 Hz, 1H), 4.80 (dd, *J* = 10.2, 6.6 Hz, 1H), 2.31 (s, 3H), 1.82 (s, 3H); ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 206.9, 144.9, 137.1, 135.4, 128.7, 126.9, 125.8, 123.8, 121.7, 121.6, 121.4, 119.0, 111.1, 99.9, 77.6, 42.5, 28.2, 20.9. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{20}H_{19}N$ 273.1512; found 273.1518.

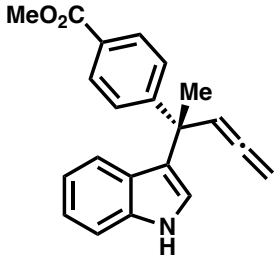
3-(2-(4-Methoxyphenyl)penta-3,4-dien-2-yl)-1*H*-indole (3ca)



3ca

3ca was prepared according to general procedure using **1c** (74.5 mg, 0.392 mmol) and **2a** (70.6 mg, 0.603 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (80/20) to afford **3ca** (79.6 mg, 0.275 mmol, 70% yield, 84% ee) as a brown oil. The ee was measured by HPLC (Chiralpak AD-3, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 16.0 min (*minor*), t_2 = 19.0 min (*major*)). $[\alpha]^{27}_D$ –16 (*c* 0.99, $CHCl_3$) for 84% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.30-7.23 (m, 2H), 7.15-7.08 (m, 2H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.91 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.82-6.76 (m, 2H), 5.88 (t, *J* = 6.6 Hz, 1H), 4.84 (dd, *J* = 10.2, 6.6 Hz, 1H), 4.80 (dd, *J* = 10.1, 6.5 Hz, 1H), 3.77 (s, 3H), 1.82 (s, 3H); ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 206.9, 157.7, 140.1, 137.1, 128.1, 125.7, 123.8, 121.7, 121.6, 121.3, 119.0, 113.3, 111.2, 100.0, 77.6, 55.1, 42.3, 28.3. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{20}H_{19}NO$ 289.1461; found 289.1464.

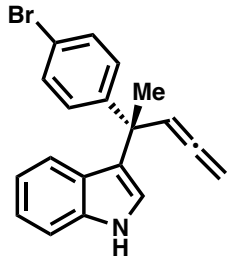
Methyl 4-(2-(1*H*-indol-3-yl)penta-3,4-dien-2-yl)benzoate (3da)



3da

3da was prepared according to general procedure using **1d** (84.9 mg, 0.389 mmol) and **2a** (70.3 mg, 0.600 mmol). The crude reaction mixture was purified by column chromatography using hexane/EtOAc (90/10) to afford **3da** (104.7 mg, 0.330 mmol, 85% yield, 92% ee) as a yellow oil. The ee was measured by HPLC (Chiralpak AD-3, 1.0 mL/min, hexane/2-propanol = 90/10, 230 nm, t_1 = 12.3 min (*minor*), t_2 = 14.6 min (*major*)). $[\alpha]^{27}_D$ +4 (*c* 0.16, $CHCl_3$) for 92% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.96-7.89 (m, 2H), 7.46-7.40 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.16-7.09 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.93-6.86 (m, 1H), 5.89 (t, *J* = 6.6 Hz, 1H), 4.87 (dd, *J* = 10.4, 6.6 Hz, 1H), 4.82 (dd, *J* = 10.5, 6.6 Hz, 1H), 3.88 (s, 3H), 1.84 (s, 3H); ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 207.0, 167.2, 153.4, 137.0, 129.4, 127.8, 127.1, 125.4, 122.7, 121.8, 121.7, 120.9, 119.1, 111.3, 99.2, 78.0, 52.0, 43.1, 28.0. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{21}H_{19}NO_2$ 317.1410; found 317.1417.

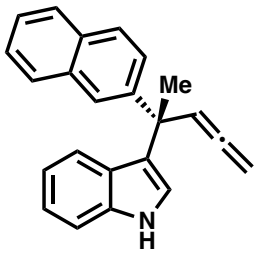
3-(2-(4-Bromophenyl)penta-3,4-dien-2-yl)-1*H*-indole (3ea)



3ea

3ea was prepared according to general procedure using **1e** (95.1 mg, 0.398 mmol) and **2a** (71.0 mg, 0.606 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3ea** (111.7 mg, 0.330 mmol, 83% yield, 92% ee) as a brown oil. The ee was measured by HPLC (Chiralpak AD-3, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 11.6 min (*minor*), t_2 = 12.6 min (*major*)). $[\alpha]^{27}_D$ –8 (*c* 1.02, $CHCl_3$) for 92% ee. ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.35 (t, *J* = 7.2 Hz, 3H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 2.9 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 5.85 (t, *J* = 6.6 Hz, 1H), 4.85 (dd, *J* = 10.3, 6.9 Hz, 1H), 4.81 (dd, *J* = 10.3, 6.3 Hz, 1H), 1.81 (s, 3H); $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ 206.9, 147.0, 137.1, 131.0, 129.0, 125.5, 123.0, 121.9, 121.6, 121.1, 119.9, 119.2, 111.2, 99.3, 78.0, 42.7, 28.2. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{19}H_{16}BrN$ 337.0461; found 337.0461.

3-(2-(Naphthalen-2-yl)penta-3,4-dien-2-yl)-1*H*-indole (3fa)

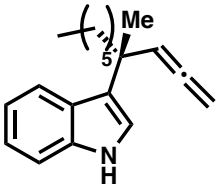


3fa

3fa was prepared according to general procedure using **1f** (84.2 mg, 0.400 mmol) and **2a** (70.3 mg, 0.600 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3fa** (100.5 mg, 0.3248 mmol, 81% yield, 89% ee) as a brown solid. The ee was measured by HPLC (Chiralpak AD-3, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 15.9 min (*minor*), t_2 = 18.6 min (*major*)). $[\alpha]^{26}_D$ –5 (*c* 0.98, $CHCl_3$) for 89% ee. ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.89 (s, 1H), 7.82–7.74 (m, 2H), 7.69 (d, *J* = 9.2 Hz, 1H), 7.47-7.39 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.00 (t, *J* = 6.6 Hz, 1H), 4.92-4.80 (m, 2H), 1.93 (s, 3H); $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) δ 207.1, 145.5, 137.1, 133.3,

132.0, 128.1, 127.6, 127.4, 126.3, 125.8, 125.7, 125.4, 124.8, 123.5, 121.8, 121.7, 121.2, 119.1, 111.2, 99.6, 77.8, 43.1, 28.0. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{23}H_{19}N$ 309.1512; found 309.1506.

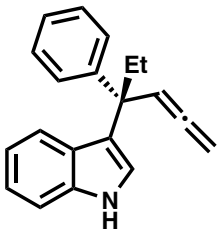
3-(4-Methyldeca-1,2-dien-4-yl)-1*H*-indole (3ga)



3ga

3ga was prepared according to general procedure using **1g** (63.1 mg, 0.375 mmol) and **2a** (69.7 mg, 0.595 mmol). The crude reaction mixture was purified by column chromatography using hexane/EtOAc (90/10) to afford **3ga** (43.4 mg, 0.162 mmol, 43% yield, 84% ee) as a yellow oil. The ee was measured by HPLC (Chiralcel OD-H, 0.5 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 13.1 min (*minor*), t_2 = 15.4 min (*major*)). $[\alpha]^{27}_D$ –6 (*c* 0.86, $CHCl_3$) for 84% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.19-7.14 (m, 1H), 7.11-7.05 (m, 1H), 6.97 (d, *J* = 2.3 Hz, 1H), 5.48 (t, *J* = 6.6 Hz, 1H), 4.84 (dd, *J* = 9.8, 6.9 Hz, 1H), 4.81 (dd, *J* = 9.8, 6.3 Hz, 1H), 2.02-1.93 (m, 1H), 1.88-1.79 (m, 1H), 1.49 (s, 3H), 1.30-1.10 (m, 8H), 0.83 (t, *J* = 6.9 Hz, 3H); ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 207.0, 137.0, 126.0, 123.7, 121.6, 121.2, 120.6, 118.9, 111.2, 100.1, 76.9, 40.9, 38.2, 31.8, 29.9, 25.8, 24.6, 22.7, 14.1. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{19}H_{25}N$ 267.1982; found 267.1975.

3-(3-Phenylhexa-4,5-dien-3-yl)-1*H*-indole (3ha)

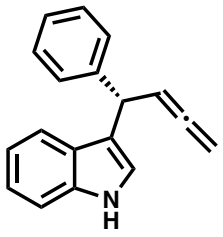


3ha

3ha was prepared according to general procedure using **1h** (68.0 mg, 0.390 mmol) and **2a** (70.7 mg, 0.603 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3ha** (54.9 mg, 0.201 mmol, 51% yield, 29% ee) as a yellow oil. The ee was measured by HPLC (Chiralpak AD-3, 1.5 mL/min, hexane/2-propanol = 99/1, 230 nm, t_1 = 20.3 min (*minor*), t_2 = 22.3 min (*major*)). $[\alpha]^{28}_D$ –23 (*c* 0.49, $CHCl_3$) for 29% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.33 (t, *J* = 7.7 Hz, 3H), 7.28-7.22 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.90-6.84 (m, 1H), 5.85 (t, *J* = 6.6 Hz, 1H), 4.77 (dd, *J* = 10.3, 6.6 Hz,

1H), 4.73 (dd, J = 10.3, 6.3 Hz, 1H), 2.39 (dq, J = 14.9, 7.1 Hz, 1H), 2.30 (dq, J = 14.9, 7.0 Hz, 1H), 0.75 (t, J = 7.2 Hz, 3H); $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ 207.3, 146.1, 136.9, 127.9, 127.8, 126.1, 125.9, 122.24, 122.23, 121.7, 121.5, 118.9, 111.0, 98.2, 77.4, 47.3, 31.9, 9.6. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{20}H_{19}N$ 273.1512; found 273.1512.

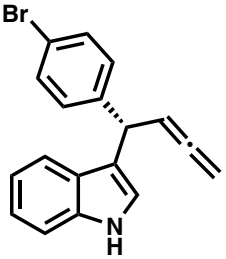
3-(1-Phenylbuta-2,3-dien-1-yl)-1*H*-indole (3ia)



3ia

3ia was prepared according to general procedure using **1i** (57.8 mg, 0.395 mmol) and **2a** (71.2 mg, 0.608 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3ia** (82.7 mg, 0.337 mmol, 85% yield, 98% ee) as a white solid. The ee was measured by HPLC (Chiralpak AD-3, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t_1 = 49.8 min (*minor*), t_2 = 53.3 min (*major*)). $[\alpha]^{27}_D$ +45 (*c* 1.03, $CHCl_3$) for 98% ee. ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.37-7.26 (m, 5H), 7.21 (t, J = 7.2 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.03 (t, J = 7.4 Hz, 1H), 6.95 (d, J = 2.3 Hz, 1H), 5.68 (q, J = 6.9 Hz, 1H), 4.98 (d, J = 8.1 Hz, 1H), 4.77-4.66 (m, 2H); $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) δ 208.5, 143.4, 136.6, 128.3, 128.1, 126.7, 126.4, 122.3, 122.1, 119.8, 119.4, 118.9, 111.1, 94.0, 76.3, 42.9. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{18}H_{15}N$ 245.1199; found 245.1198.

3-(1-(4-Bromophenyl)buta-2,3-dien-1-yl)-1*H*-indole (3ja)

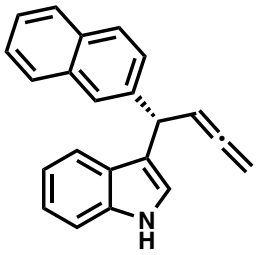


3ja

3ja was prepared according to general procedure using **1j** (90.0 mg, 0.400 mmol) and **2a** (70.7 mg, 0.603 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3ja** (111.2 mg, 0.3430 mmol, 86% yield, 97% ee) as a white solid. The ee was measured by HPLC (Chiralpak AD-3, 0.5 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 16.8 min (*minor*), t_2 = 18.1 min (*major*)). $[\alpha]^{27}_D$ +47 (*c* 0.93, $CHCl_3$) for 97% ee. ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.42-7.32 (m, 4H), 7.23-7.14 (m, 3H), 7.06-7.01 (m, 1H), 6.96 (d, J = 1.7 Hz, 1H), 5.64 (q, J = 7.1 Hz, 1H), 4.96-4.90 (m, 1H), 4.76-

4.67 (m, 2H); $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) δ 208.5, 142.4, 136.6, 131.3, 129.9, 126.5, 122.3, 122.2, 120.2, 119.6, 119.5, 118.3, 111.1, 93.6, 76.7, 42.3. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{18}H_{14}BrN$ 323.0304; found 323.0300.

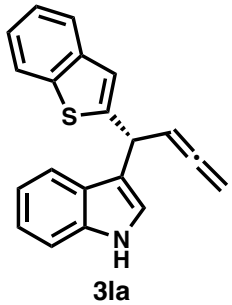
3-(1-(Naphthalen-2-yl)buta-2,3-dien-1-yl)-1*H*-indole (3ka)



3ka

3ka was prepared according to general procedure using **1k** (76.7 mg, 0.391 mmol) and **2a** (70.7 mg, 0.603 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (9/1) to afford **3ka** (94.5 mg, 0.320 mmol, 82% yield, 98% ee) as a pale brown solid. The ee was measured by HPLC (Chiralpak AD-3 column, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 24.1 min (*major*), t_2 = 25.8 min (*minor*)); $[\alpha]^{20}_D$ +68 (*c* 0.96, $CHCl_3$) for 98% ee. ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.83-7.73(m, 4H), 7.48-7.39 (m, 4H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.98-6.95 (m, 1H), 5.76 (q, *J* = 7.1 Hz, 1H), 5.15 (d, *J* = 7.5 Hz, 1H), 4.78-4.68 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 208.6, 140.9, 136.6, 133.5, 132.4, 127.8, 127.6, 127.0, 126.8, 126.2, 125.8, 125.4, 122.4, 122.1, 119.8, 119.4, 118.8, 111.1, 93.9, 76.4, 43.0; HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{22}H_{17}N$ 295.1356; found 295.1358.

3-(1-(Benzo[*b*]thiophen-2-yl)buta-2,3-dien-1-yl)-1*H*-indole (3la)

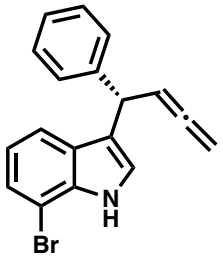


3la

3la was prepared according to general procedure using **1l** (80.1 mg, 0.396 mmol) and **2a** (70.5 mg, 0.602 mmol). The crude reaction mixture was purified by column chromatography using hexane/Et_2O (90/10) to afford **3la** (94.2 mg, 0.313 mmol, 79% yield, 98% ee) as a brown solid. The ee was measured by HPLC (Chiralcel OD-H, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 17.4 min (*major*), t_2 = 19.2 min (*minor*)). $[\alpha]^{27}_D$ +49 (*c* 1.04, $CHCl_3$) for 98% ee. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H),

7.54 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.31-7.15 (m, 3H), 7.15-7.02 (m, 3H), 5.76 (dt, J = 7.9, 6.6 Hz, 1H), 5.32-5.24 (m, 1H), 4.810 (d, J = 6.6 Hz, 1H), 4.805 (d, J = 6.6 Hz, 1H); ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 208.3, 148.8, 139.8, 139.6, 136.4, 126.3, 124.0, 123.6, 123.1, 122.3, 122.22, 122.17, 121.1, 119.57, 119.56, 117.7, 111.2, 93.5, 77.1, 39.1. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{20}H_{15}NS$ 301.0920; found 301.0913.

7-Bromo-3-(1-phenylbuta-2,3-dien-1-yl)-1*H*-indole (3ig)

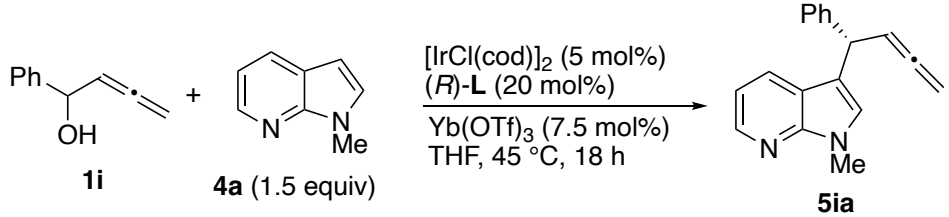


3ig

3ig was prepared according to general procedure using **1i** (59.1 mg, 0.404 mmol) and **2g** (114.7 mg, 0.585 mmol). The crude reaction mixture was purified by column chromatography using hexane/toluene (85/15) to afford **3ig** (108.2 mg, 0.3337 mmol, 83% yield, 99% ee) as a white solid. The ee was measured by HPLC (Chiralpak AD-3, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 9.8 min (*major*), t_2 = 10.9 min (*minor*)). $[\alpha]^{16}_D$ +49 (*c* 0.99, $CHCl_3$) for 99% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.33-7.27 (m, 5H), 7.24-7.19 (m, 1H), 7.01 (d, J = 1.7 Hz, 1H), 6.91 (t, J = 8.0 Hz, 1H), 5.66 (dt, J = 8.0, 6.6 Hz, 1H), 4.98–4.92 (m, 1H), 4.77-4.67 (m, 2H); ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 208.5, 143.0, 135.2, 128.3, 128.1, 127.9, 126.5, 124.4, 122.9, 120.5, 120.1, 119.0, 104.6, 93.7, 76.5, 43.0. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{18}H_{14}BrN$ 323.0304; found 323.0312.

6. General Procedure for the Asymmetric Allenylic Substitution of Racemic Secondary Alcohols 1 with 7-Azaindoles 4 (Schemes 4)

Representative Procedure for the Reaction of 1i with 4a

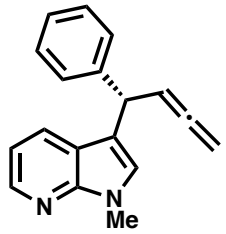


A mixture of $[Ir(cod)Cl]_2$ (13.6 mg, 0.0203 mmol), (*R*)-**L** (40.9 mg, 0.0806 mmol), **1i** (57.7 mg, 0.395 mmol) in THF (4.0 mL) was stirred at room temperature for 15 min. To the mixture was added **4a** (78.5 mg, 0.594 mmol) and $Yb(OTf)_3$ (18.8 mg, 0.0303 mmol), and the result was stirred at 45 °C for 18 h. After removal of the solvent on a rotary evaporator, the residue was subjected to column chromatography (silica gel, toluene/EtOAc = 95/5) to give

compound **5ia** (74.4 mg, 0.286 mmol, 72% yield, 99% ee).

7. Characterization of 5

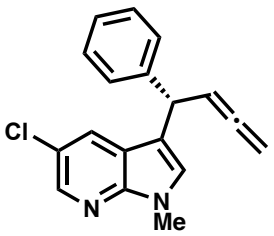
1-Methyl-3-(1-phenylbuta-2,3-dien-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (5ia)



5ia

5ia was prepared according to general procedure using **1i** (57.7 mg, 0.395 mmol) and **4a** (78.5 mg, 0.594 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc = 95/5 to afford **5ia** (74.4 mg, 0.286 mmol, 72% yield, 99% ee) as a brown oil. The ee was measured by HPLC (Chiralcel OD-H, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t_1 = 10.4 min (*major*), t_2 = 11.6 min (*minor*)). $[\alpha]^{28}_D$ +24 (*c* 0.98, $CHCl_3$) for 99% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.66 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.31 (d, J = 4.6 Hz, 4H), 7.28–7.21 (m, 1H), 6.95 (dd, *J* = 8.0, 4.9 Hz, 1H), 6.90 (s, 1H), 5.68-5.61 (m, 1H), 4.97-4.91 (m, 1H), 4.77–4.68 (m, 2H), 3.84 (s, 3H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 208.4, 148.2, 143.0, 142.8, 128.4, 128.1, 128.0, 127.0, 126.6, 119.6, 115.8, 115.0, 93.7, 76.5, 43.1, 31.1. HRMS (FAB) *m/z* $[M+H]^+$ calcd for $C_{18}H_{17}N_2$ 261.1386; found 261.1384.

5-Chloro-1-methyl-3-(1-phenylbuta-2,3-dien-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (5ib)

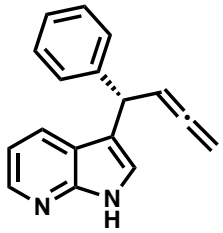


5ib

5ib was prepared according to general procedure using **1i** (56.3 mg, 0.385 mmol) and **4b** (99.9 mg, 0.600 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (100/1) to afford **5ib** (68.7 mg, 0.233 mmol, 61% yield, 99% ee) as a dark brown oil. The ee was measured by HPLC (Chiralcel OZ-H, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t_1 = 5.4 min (*minor*), t_2 = 6.2 min (*major*)). $[\alpha]^{29}_D$ +4.8 (*c* 0.99, $CHCl_3$) for 99% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.3 Hz, 1H), 7.63 (d, *J* = 2.6 Hz, 1H), 7.36–7.22 (m, 5H), 6.91 (s, 1H), 5.61 (q, *J* = 7.1 Hz, 1H), 4.91-4.85 (m, 1H), 4.79-4.68 (m, 2H), 3.81 (s, 3H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 208.4, 146.5, 142.5, 141.4,

128.6, 128.5, 128.0, 127.1, 126.8, 123.0, 120.1, 115.5, 93.5, 76.8, 42.8, 31.2. HRMS (FAB) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}ClN_2$ 295.0997; found 295.0998.

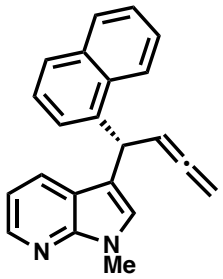
3-(1-Phenylbuta-2,3-dien-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (5ic)



5ic

3ic was prepared according to general procedure using **1i** (58.3 mg, 0.399 mmol) and **4c** (71.4 mg, 0.604 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (8/2) to afford **5ic** (59.1 mg, 0.240 mmol, 60% yield, >99.5% ee) as a brown oil. The ee was measured by HPLC (Chiralcel OD-H, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t_1 = 52.8 min (*major*), t_2 = 58.7 min (*minor*)). $[\alpha]^{29}_D$ +37 (*c* 1.01, $CHCl_3$) for >99.5% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.9 (s, 1H), 8.27 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.70 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.35-7.27 (m, 4H), 7.27-7.20 (m, 1H), 7.11 (s, 1H), 6.98 (dd, *J* = 7.5, 4.9 Hz, 1H), 5.67 (q, *J* = 6.9 Hz, 1H), 4.99-4.93 (m, 1H), 4.77-4.66 (m, 2H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 208.5, 149.3, 143.0, 142.4, 128.4, 128.3, 128.1, 126.6, 123.1, 119.6, 117.1, 115.3, 93.7, 76.5, 43.1. HRMS (FAB) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}N_2$ 247.1230; found 247.1228.

1-Methyl-3-(1-(naphthalen-1-yl)buta-2,3-dien-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (5ma)

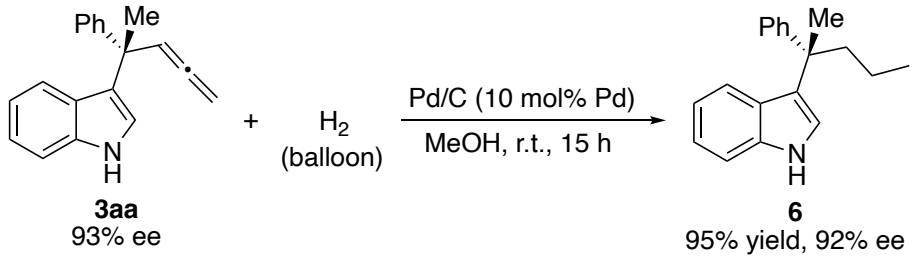


5ma

5ma was prepared according to general procedure using **1m** (78.5 mg, 0.400 mmol) and **4a** (79.7 mg, 0.603 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (99/1) to afford **5ma** (87.9 mg, 0.283 mmol, 71% yield, 98% ee) as a dark brown oil. The ee was measured by HPLC (Chiralcel OD-H, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t_1 = 12.5 min (*minor*), t_2 = 14.4 min (*major*)). $[\alpha]^{29}_D$ –16 (*c* 1.00, $CHCl_3$) for 98% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 5.2, 1.4 Hz, 1H), 8.15-8.10 (m, 1H), 7.90-7.85 (m, 1H), 7.76 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.68 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.49-7.37 (m, 4H), 6.94 (dd, *J* = 7.5, 4.9 Hz, 1H), 6.81 (s, 1H), 5.77-5.69 (m, 2H), 4.71-4.61

(m, 2H), 3.79 (s, 3H); $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) δ 208.8, 148.3, 142.9, 138.6, 134.0, 131.5, 128.8, 127.9, 127.6, 127.4, 125.9, 125.5, 125.44, 125.37, 123.9, 119.7, 115.5, 115.0, 93.6, 76.7, 38.8, 31.1. HRMS (FAB) *m/z* $[M+H]^+$ calcd for $C_{22}H_{19}N_2$ 311.1543; found 311.1540.

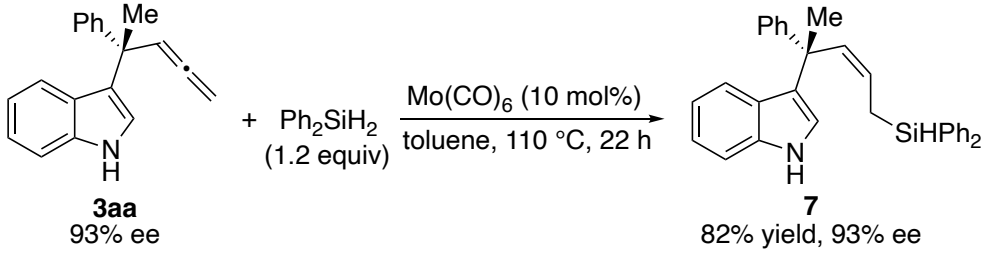
8. Procedure for the Hydrogenation of Allenylated Indole 3aa (Scheme 5)



To Pd/C (63.6 mg, 5%, 0.0298 mmol Pd) was added the solution of **3aa** (77.7 g, 0.300 mmol, 93% ee) in MeOH (3.0 mL) at room temperature. After the mixture was stirred under a hydrogen atmosphere at room temperature for 15 h, Pd/C was filtered off by celite. The filtrate was concentrated on a rotary evaporator. The residue was subjected to short column chromatography (silica gel, Et_2O) to give **6** (74.8 mg, 0.284 mmol, 95% yield, 92% ee) as a red-purple oil.

Compound **6:** The ee was measured by HPLC (OJ-H column, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t_1 = 31.4 min (*minor*), t_2 = 35.4 min (*major*)); $[\alpha]^{26}_D$ +10 (*c* 0.49, $CHCl_3$) for 92% ee. ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.34-7.27 (m, 3H), 7.25-7.19 (m, 2H), 7.17-7.11 (m, 1H), 7.11-7.05 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.87-6.81 (m, 1H), 2.25-2.17 (m, 1H), 2.12-2.03 (m, 1H), 1.70 (s, 3H), 1.23-1.04 (m, 2H), 0.85 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 149.1, 137.0, 127.8, 126.9, 126.1, 125.4, 125.1, 121.5, 121.3, 121.2, 118.8, 110.9, 44.0, 42.4, 27.5, 17.9, 14.8; HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{19}H_{21}N$ 263.1669; found 263.1674.

9. Procedure for the Mo-Catalyzed Hydrosilylation of Allenylated Indole 3aa with Diphenylsilane (Scheme 5)[10]



To a solution of **3aa** (78.0 mg, 0.301 mmol, 93% ee) and $Mo(CO)_6$ (8.2 mg, 0.031 mmol) in toluene (0.3 mL) was added diphenylsilane (67.3 mg, 0.365 mmol) at room

temperature. After the mixture was stirred at 110 °C for 22 h, it was filtered with Celite (Et_2O), and the filtrate was concentrated on a rotary evaporator. The residue was subjected to column chromatography (silica gel, hexane/EtOAc = 9/1) to give compound **7** (108.6 mg, 0.2448 mmol, 82% yield, 93% ee) as a pale pink oil.

Compound **7:** The ee was measured by HPLC (Chiralpak AD-3 column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t_1 = 55.6 min (*minor*), t_2 = 60.0 min (*major*)); $[\alpha]^{26}_D$ –17 (*c* 0.98, $CHCl_3$) for 93% ee. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.40-7.26 (m, 14H), 7.26-7.19 (m, 2H), 7.18-7.11 (m, 2H), 6.99-6.94 (m, 1H), 6.75 (d, *J* = 2.9 Hz, 1H), 6.09-6.03 (m, 1H), 5.53 (dt, *J* = 11.5, 8.7 Hz, 1H), 4.51 (t, *J* = 3.7 Hz, 1H), 1.90 (s, 3H), 1.70 (ddd, *J* = 8.6, 3.7, 1.6 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.6, 137.3, 137.2, 135.1, 133.89, 133.87, 129.5, 127.9, 127.8, 127.6, 126.2, 125.7, 125.6, 124.5, 122.2, 121.8, 121.7, 118.9, 111.1, 44.8, 30.0, 14.7; HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{31}H_{29}NSi$ 443.2064; found 443.2070.

10. The data for X-ray crystal structure of compounds (*S*)-3ag and (*S*)-3ig

Data for the X-ray crystal structure of compound (*S*)-3ag

A colorless block crystal (size = 0.26×0.21×0.15 mm) of **3ag** was coated with paraffin oil and mounted in a loop. The ORTEP drawing of **3ag** is shown in Figure S1. All of the C, N and Br atoms were refined anisotropically. All of the hydrogen atoms were refined isotropically. Further details of the crystal structure of **3ag** have been deposited at the Cambridge Crystallographic Centre (deposition number: CCDC 2382169). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif/.

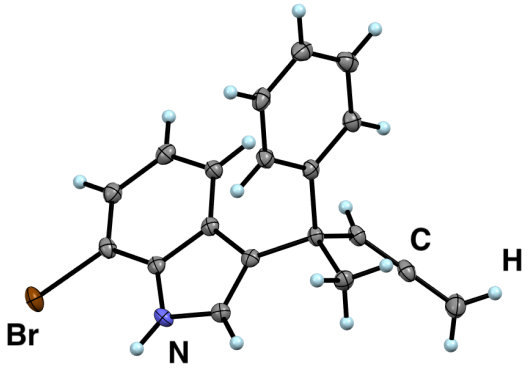


Figure S1. ORTEP illustration of **3ag** with thermal ellipsoids drawn at the 50% probability level.

Table S1. Crystal data of **3ag**.

Empirical Formula	$C_{19}H_{16}BrN$
Formula Weight	338.24
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.26 × 0.21 × 0.15 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 8.52880(10) Å
	b = 6.05890(10) Å
	c = 14.83580(10) Å
	β = 90.3240(10) °
	V = 766.63 $Å^3$
Space Group	$P2_1$ (#4)
Z value	2
D_{calc}	1.465 g/cm^3
F_{000}	344
μ(CuKα)	35.742 cm^{-1}

Table S2. Intensity Measurements.

Diffractometer	XtaLAB Synergy
Radiation	CuKα (λ = 1.54184 Å) multi-layer mirror monochromated
Temperature	100.0 K
No. of Reflections Measured	Total: 15912 Unique: 3272 (R_{int} = 0.0233) Parsons quotients (Flack x parameter): 1444
Corrections	Lorentz-polarization Absorption (trans. factors: 0.340 – 1.000)

Table S3. Structure Solution and Refinement.

Structure Solution	Direct Methods (SHELXT Version 2018/2)
Refinement	Full-matrix least-squares on F^2 (SHELXL Version 2018/3)
Function Minimized	Σ w $(F_0^2 - F_c^2)^2$
Least Squares Weights	$w = 1/[\sigma^2(F_0^2) + (0.0246 \cdot P)^2 + 0.2482 \cdot P]$ where $P = (Max(F_0^2,0)+2Fc^2)/3$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	3272
Residuals: R1 (I>2.00σ(I))	0.0176
Residuals: R (All reflections)	0.0176
Residuals: wR2 (All reflections)	0.0467
Goodness of Fit Indicator	1.082
Flack parameter (Persons' quotients = 1444)	-0.019(7)
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.172 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.216 $e^-/Å^3$

Data for the X-ray crystal structure of compound (*S*)-3ig

A colorless block crystal (size = 0.6 × 0.5 × 0.3 mm) of **3ig** was coated with paraffin oil and mounted in a loop. The ORTEP drawing of **3ig** is shown in Figure S2. All of the C, N and Br atoms were refined anisotropically. All of the hydrogen atoms were refined isotropically. Further details of the crystal structure of **3ig** have been deposited at the Cambridge Crystallographic Centre (deposition number: CCDC 2382171). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif/.

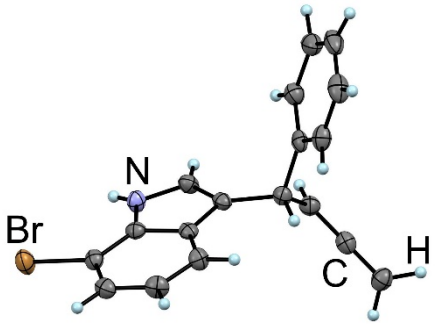


Figure S2. ORTEP illustration of **3ig** with thermal ellipsoids drawn at the 50% probability level.

Table S4. Crystal data of **3ig**.

Empirical Formula	$C_{18}H_{14}BrN$
Formula Weight	324.22
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.6 × 0.5 × 0.3 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 5.754(3) Å
	b = 8.657(5) Å
	c = 14.376(7) Å
	β = 94.56(2) °
	V = 713.8(7) $Å^3$
Space Group	$P2_1$ (#4)
Z value	2
D_{calc}	1.508 g/cm^3
F_{000}	328.00
μ(MoKα)	28.763 cm^{-1}

Table S5. Intensity Measurements.

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å)
	graphite monochromated
Temperature	173.0 K
No. of Reflections Measured	Total: 7048
	Unique: 3257 (R_{int} = 0.0538)
	Parsons quotients (Flack x parameter): 1257
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.330 – 0.422)

Table S6. Structure Solution and Refinement.

Structure Solution	Direct Methods (SHELXT Version 2018/2)
Refinement	Full-matrix least-squares on F^2 (SHELXL Version 2018/3)
Function Minimized	$\Sigma\ w\ (F_0^2 - F_c^2)^2$
Least Squares Weights	$w = 1/[\sigma^2(F_0^2) + (0.0239 \cdot P)^2 + 0.0000 \cdot P]$
	where $P = (Max(F_0^2,0)+2Fc^2)/3$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	3257
Residuals: R1 (I>2.00σ(I))	0.0309
Residuals: R (All reflections)	0.0331
Residuals: wR2 (All reflections)	0.0703
Goodness of Fit Indicator	0.996
Flack parameter (Persons' quotients = 1257)	–0.024(9)
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.43 $e^-/Å^3$
Minimum peak in Final Diff. Map	–0.46 $e^-/Å^3$

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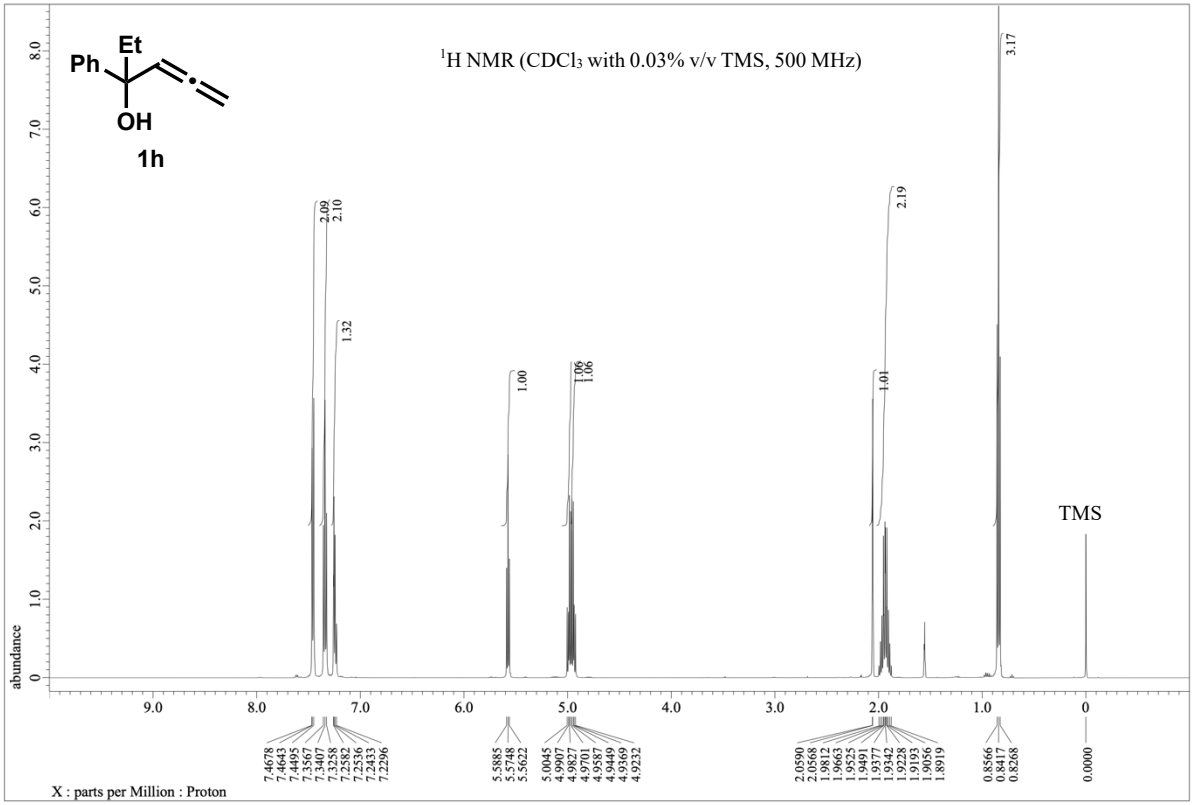
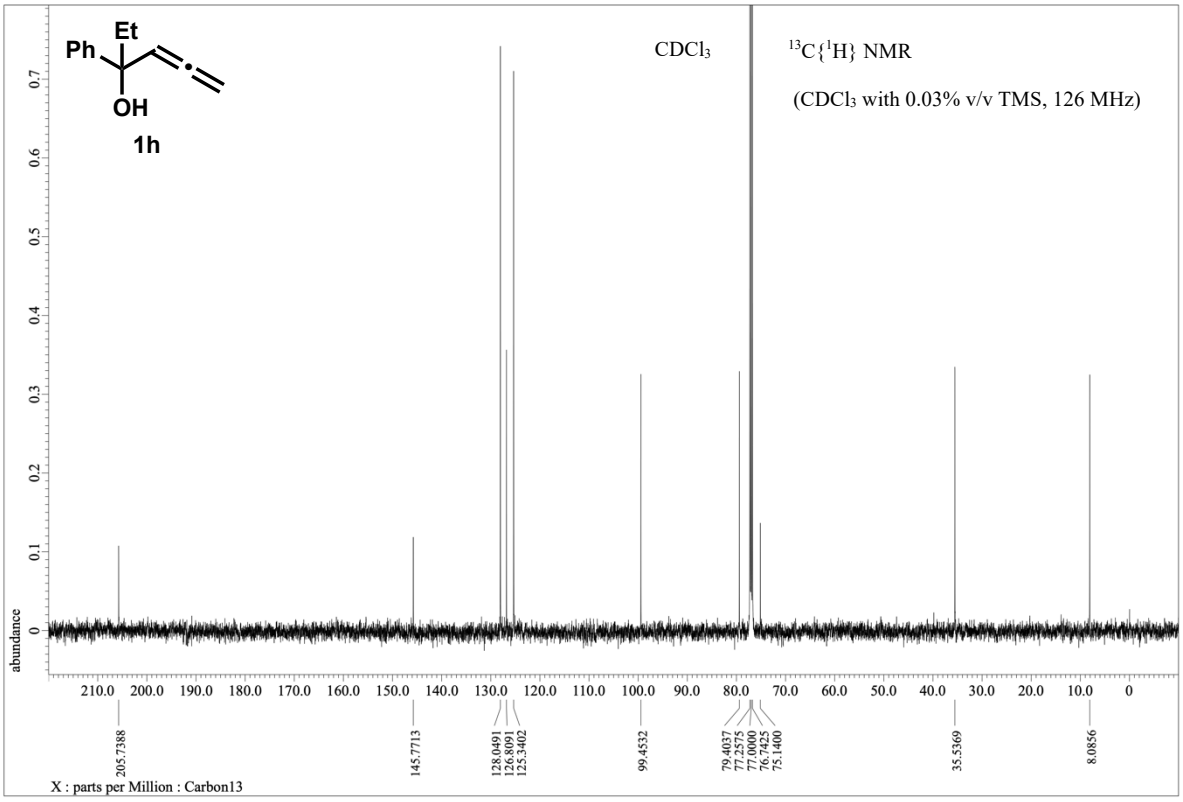
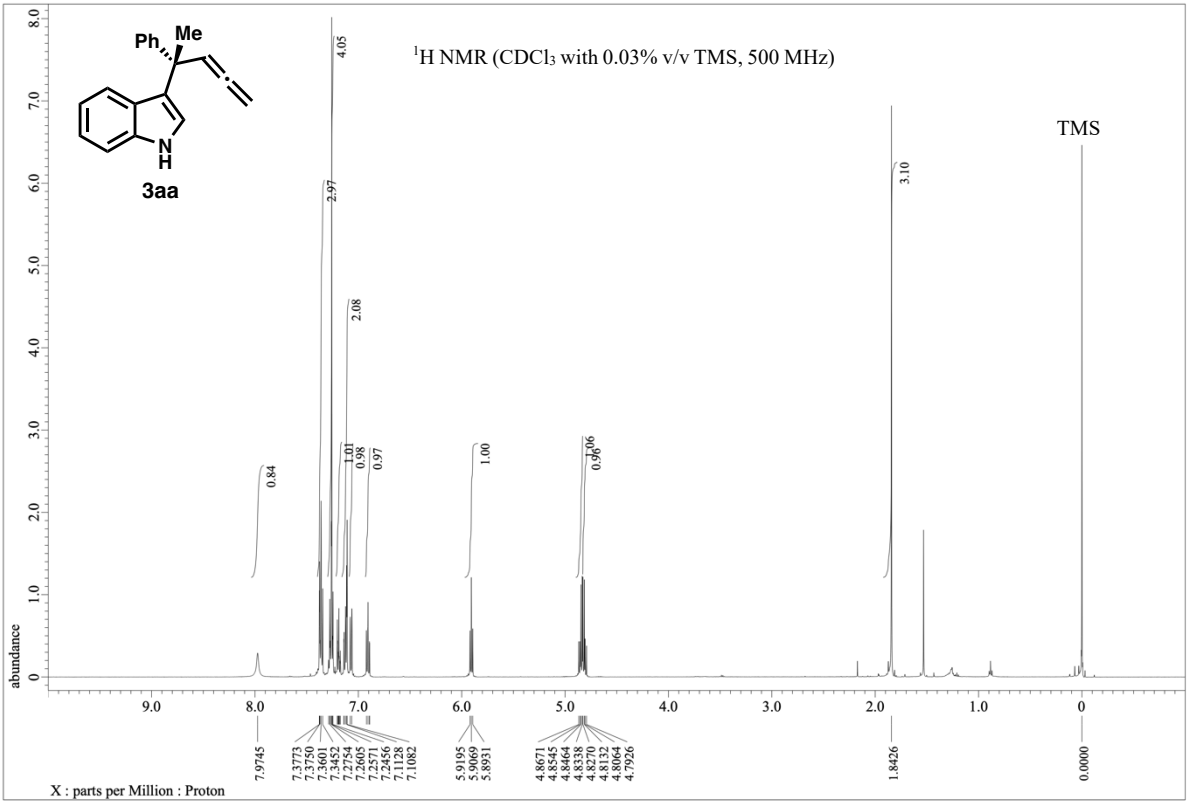
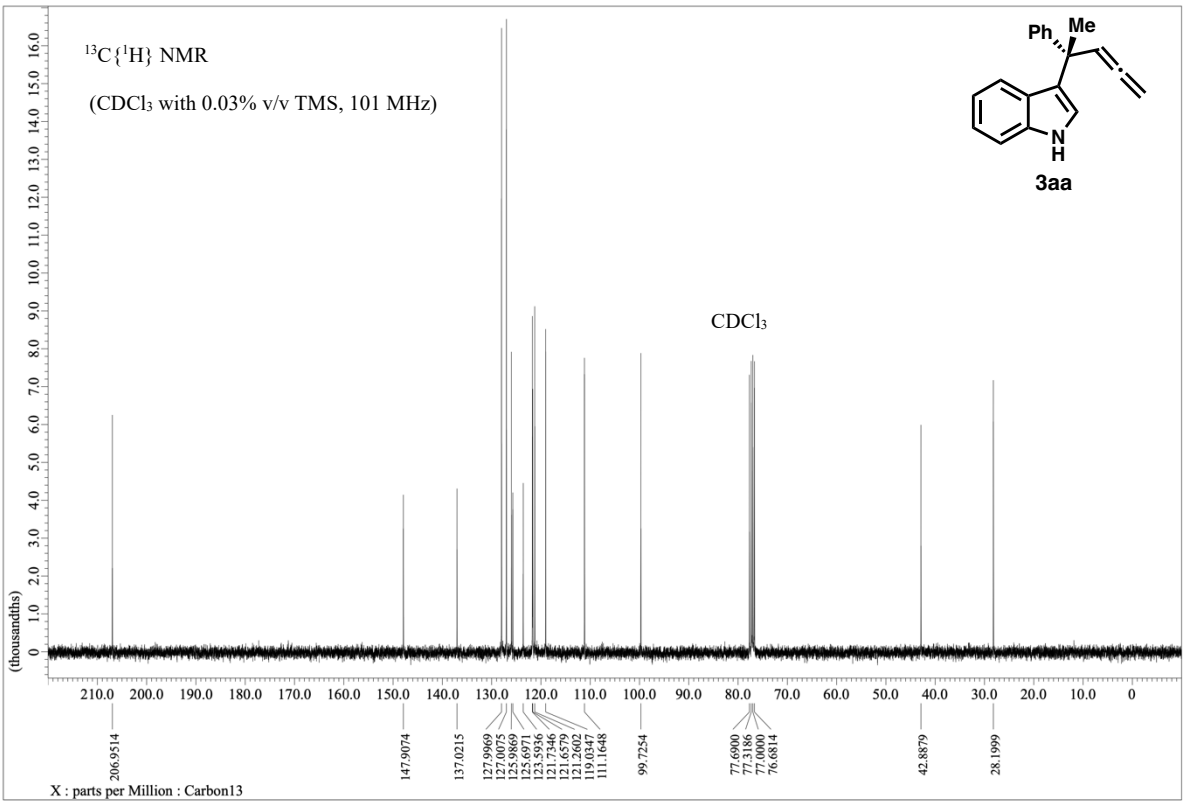
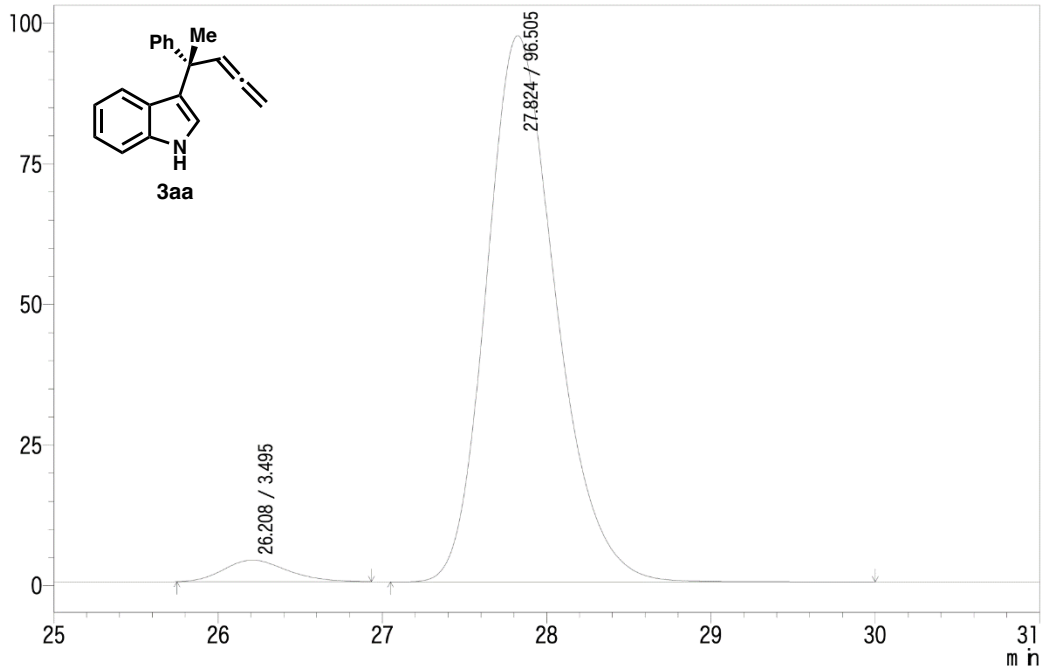
12. ^{1}H and ^{13}C NMR Charts and HPLC Charts



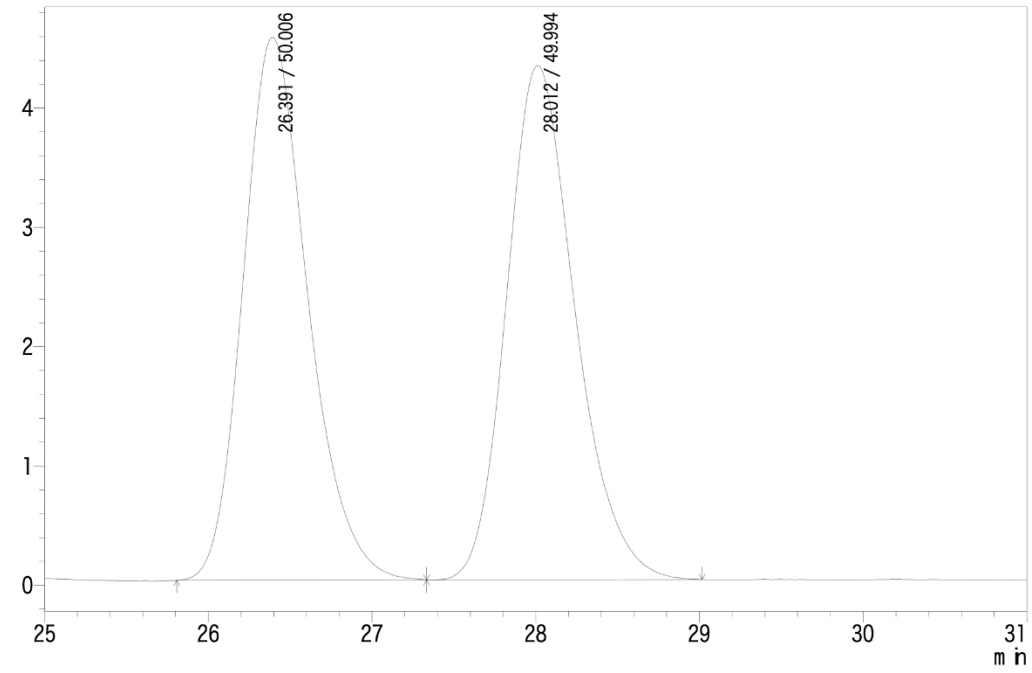



Ph
Me
N
H
3aa
^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 500 MHz)
TMS
CDCl$_3$
abundance
X : parts per Million : Proton

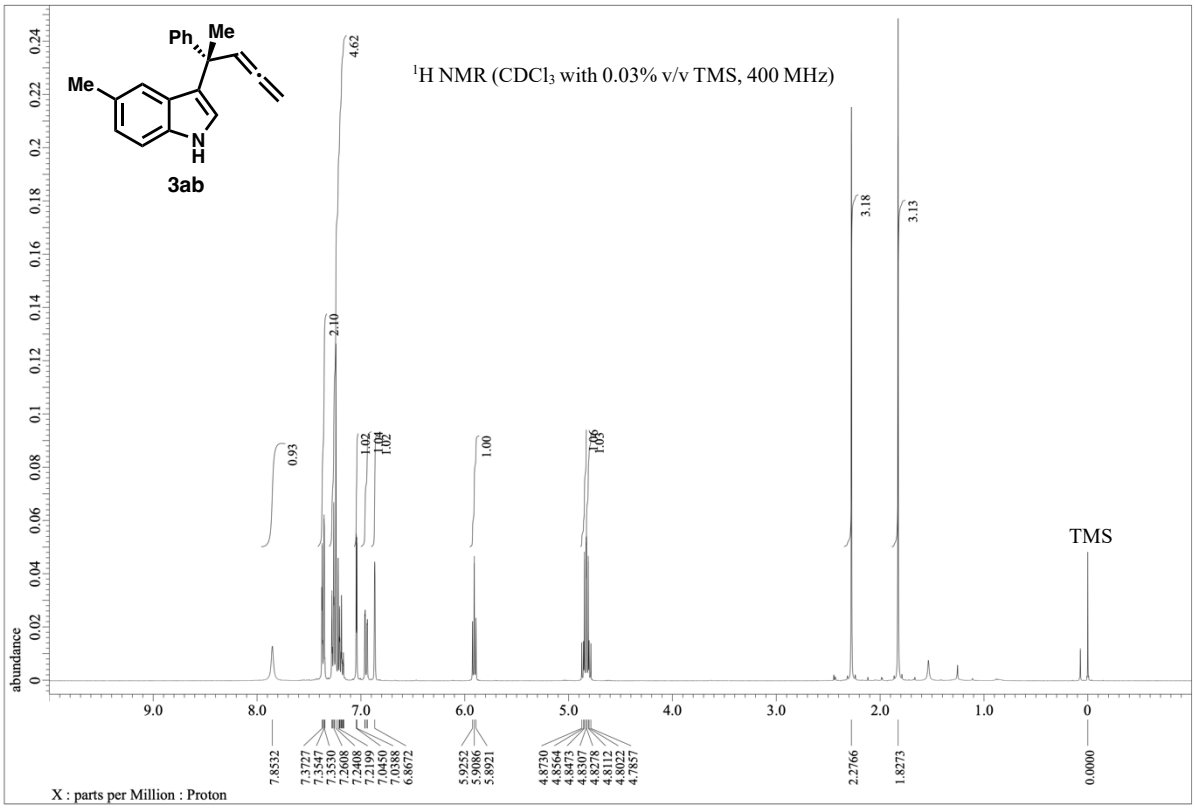

^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 101 MHz)
Ph
Me
N
H
3aa
CDCl$_3$
(thousandths)
X : parts per Million : Carbon13

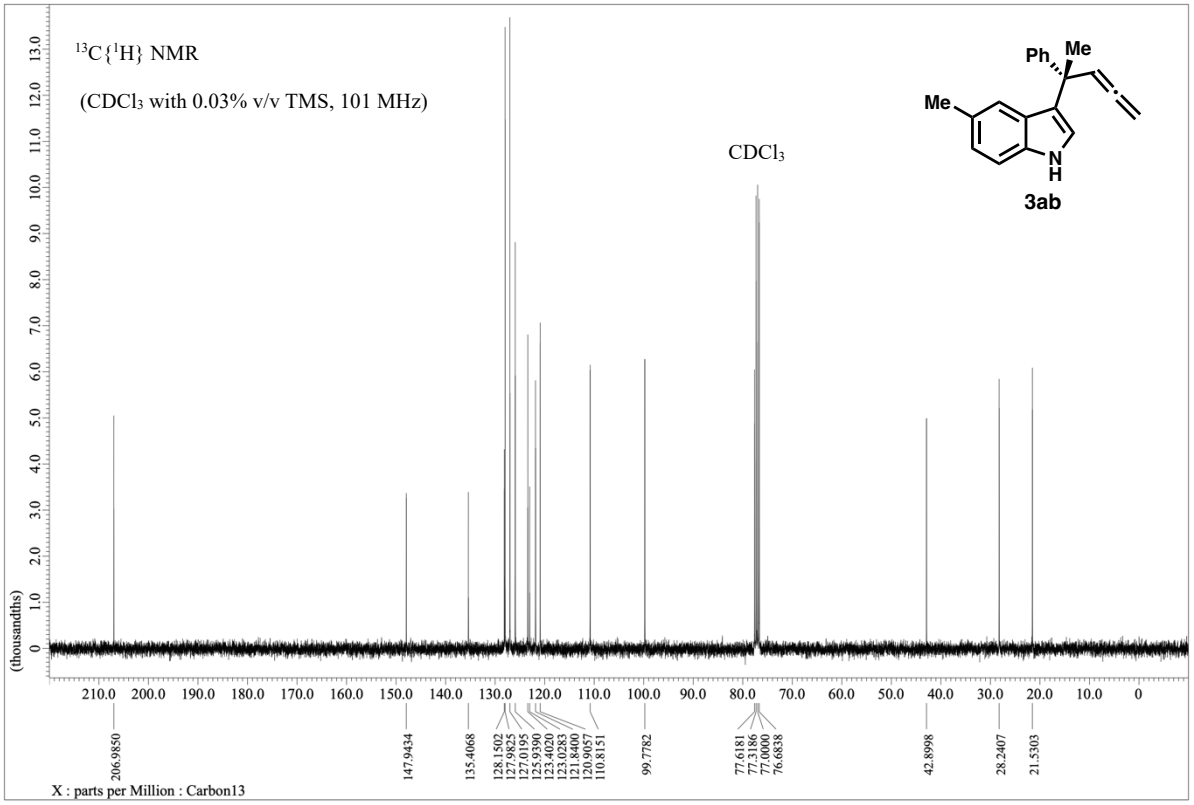


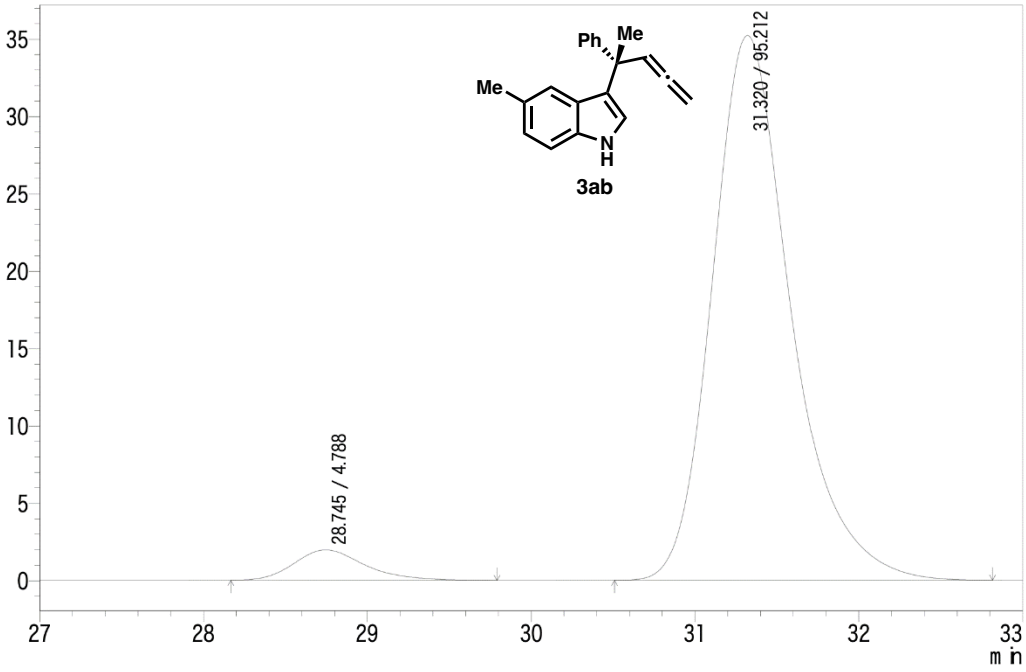
peak#	retention time	area%
1	26.208	3.495
2	27.824	96.505
Total		100.000



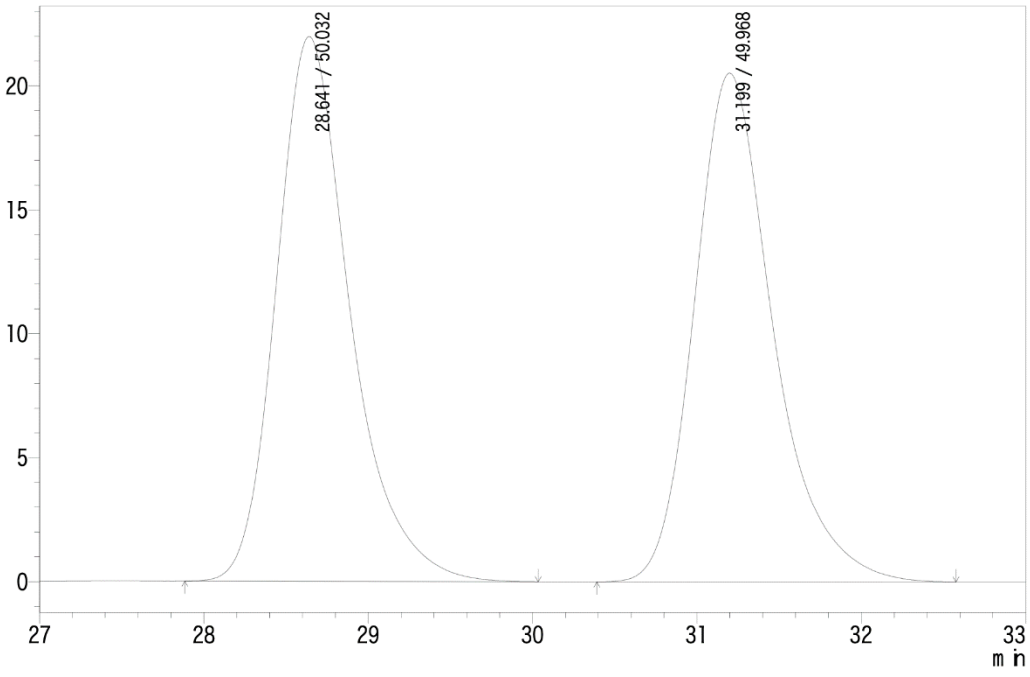
peak#	retention time	area%
1	26.391	50.006
2	28.012	49.994
Total		100.000


Ph
Me
Me
N
H
3ab
^{1}H NMR ($CDCl_3$ with 0.03% v/v TMS, 400 MHz)
4.62
2.10
3.18
3.13
0.93
1.00
TMS
abundance
X : parts per Million : Proton

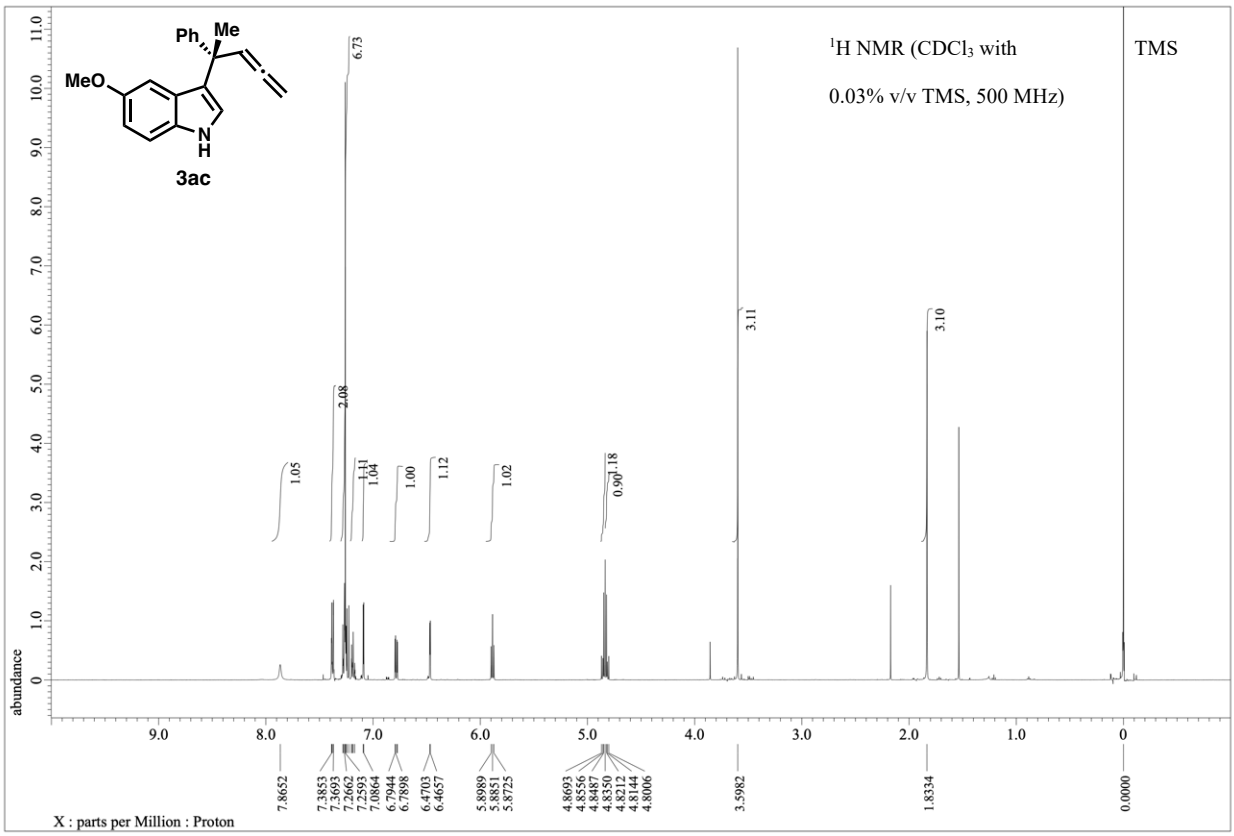

^{13}C{^{1}H} NMR
($CDCl_3$ with 0.03% v/v TMS, 101 MHz)
$CDCl_3$
Ph
Me
Me
N
H
3ab
(thousandths)
X : parts per Million : Carbon13

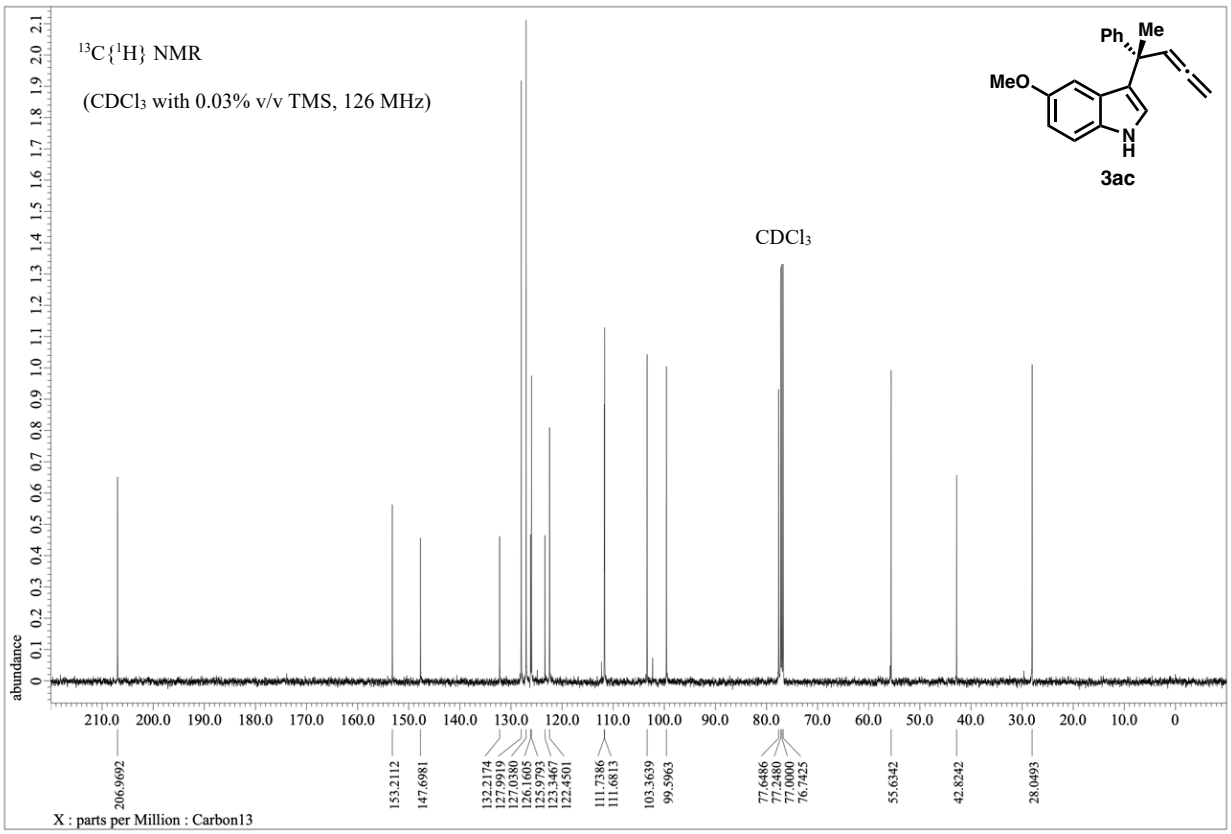


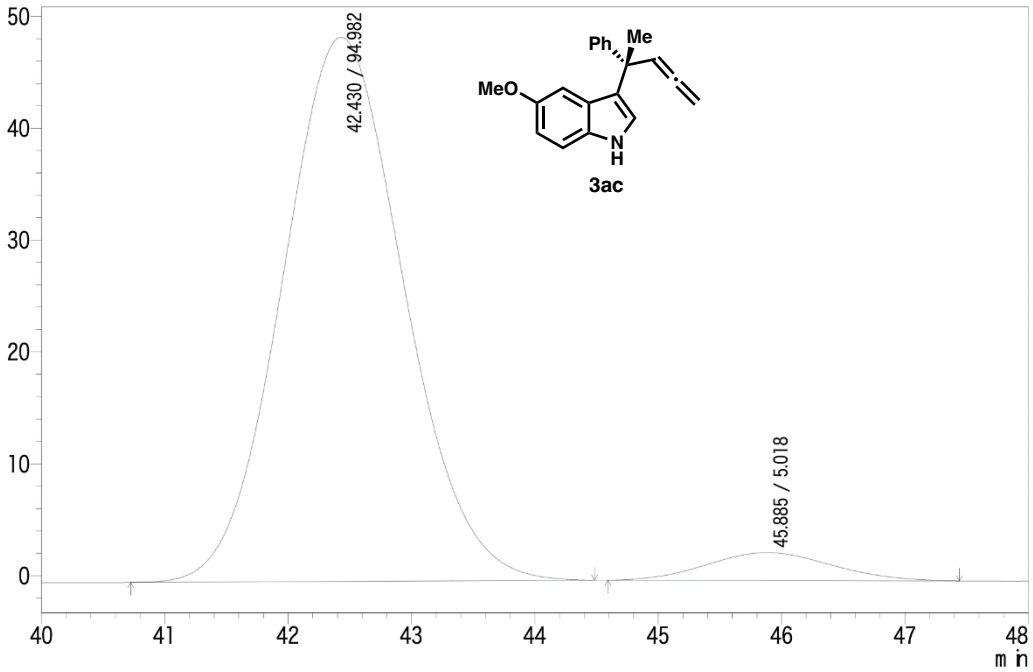
peak#	retention time	area%
1	28.745	4.788
2	31.320	95.212
Total		100.000



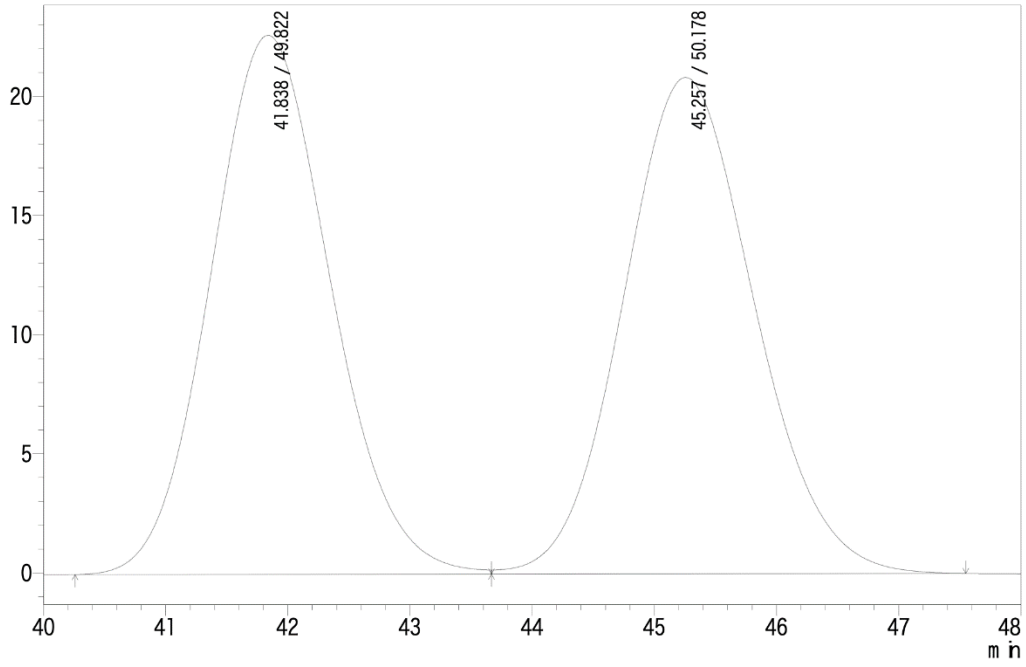
peak#	retention time	area%
1	28.641	50.032
2	31.199	49.968
Total		100.000


Ph
Me
MeO
N
H
3ac
^{1}H NMR ($CDCl_3$ with
0.03% v/v TMS, 500 MHz)
TMS
6.73
3.11
3.10
2.08
1.05
1.11
1.04
1.00
1.12
1.02
0.90
1.18
abundance
X : parts per Million : Proton
7.8652
7.3853
7.3693
7.2662
7.2593
7.0864
6.7944
6.7898
6.4703
6.4657
5.8989
5.8851
5.8725
4.8693
4.8556
4.8487
4.8350
4.8212
4.8144
4.8006
3.5982
1.8334
0.0000

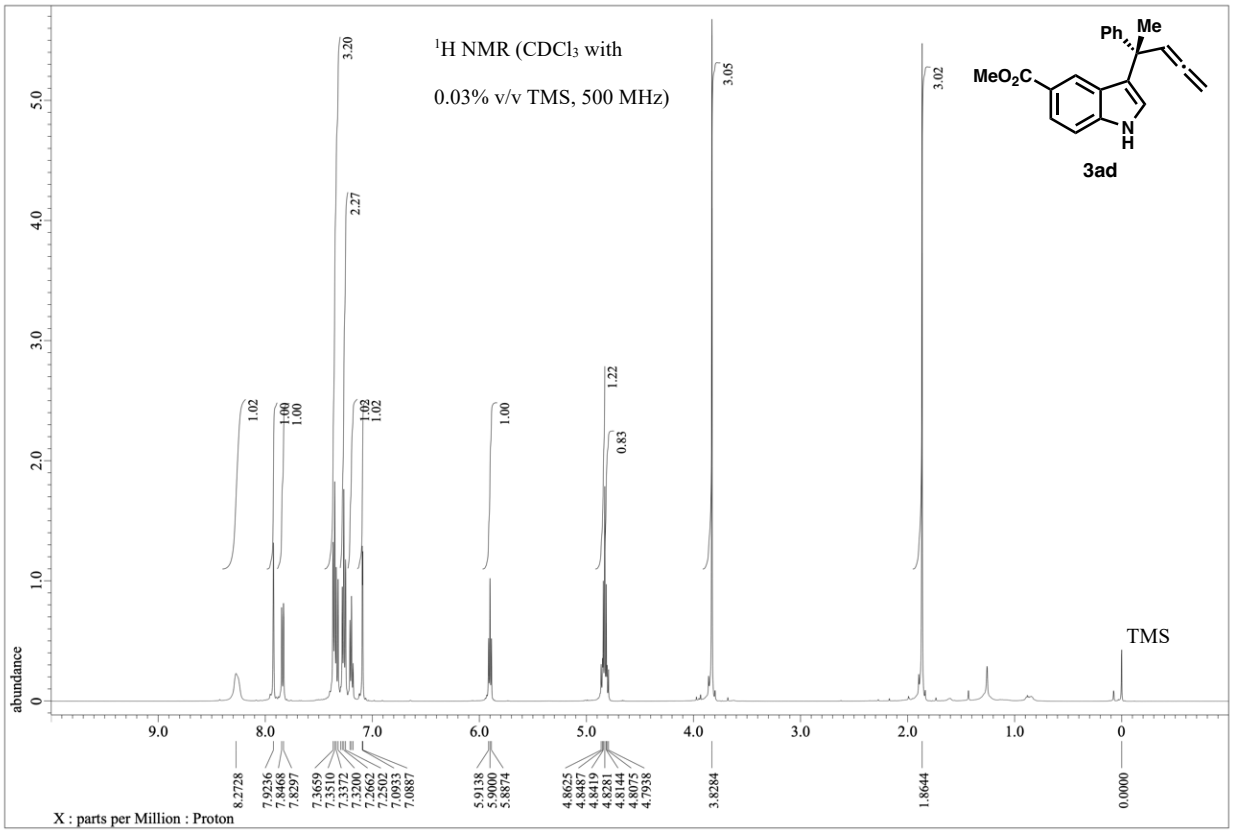

$^{13}C\{^1H\}$ NMR
($CDCl_3$ with 0.03% v/v TMS, 126 MHz)
Ph
Me
MeO
N
H
3ac
$CDCl_3$
abundance
X : parts per Million : Carbon13
206.9692
153.2112
147.6981
132.2174
129.0919
127.0380
126.1605
125.9793
123.3467
122.4501
111.7386
111.6813
103.3639
99.5963
77.6486
77.2480
77.0000
76.7425
55.6342
42.8242
28.0493

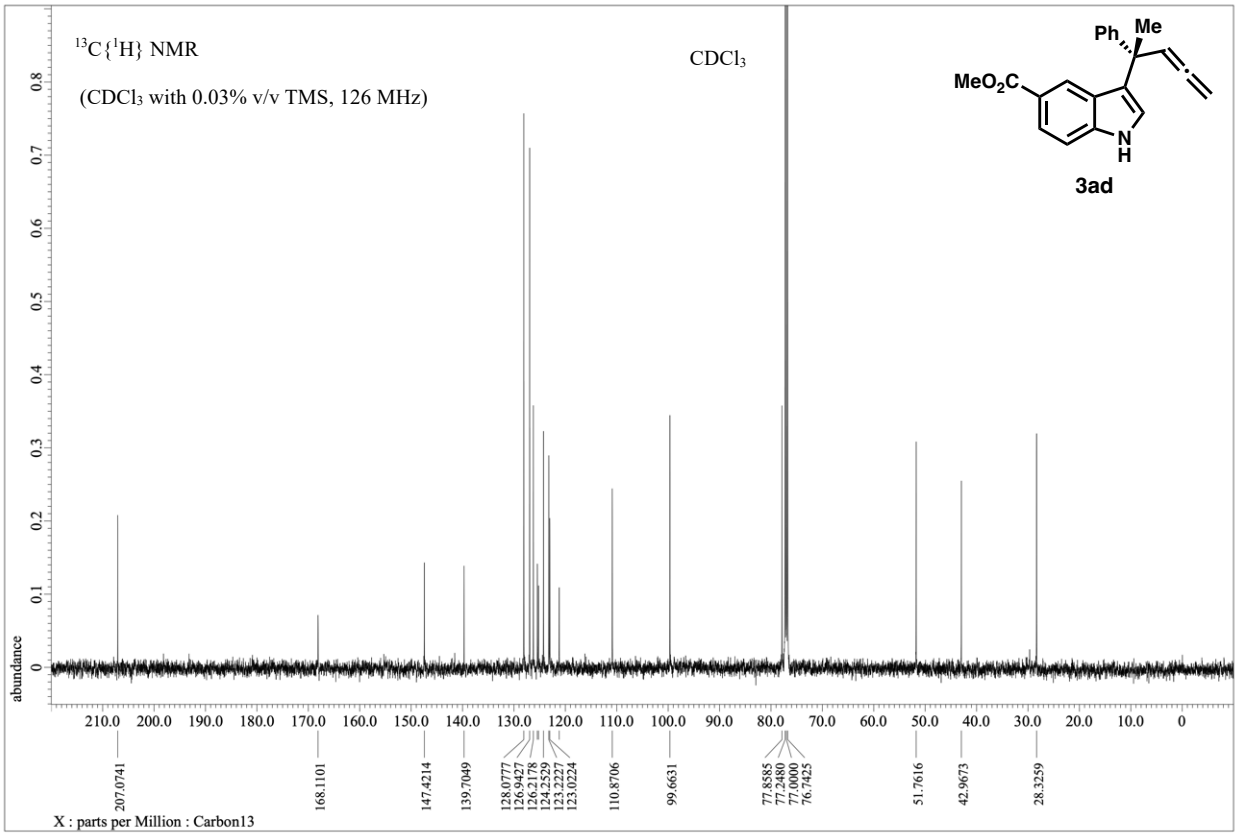


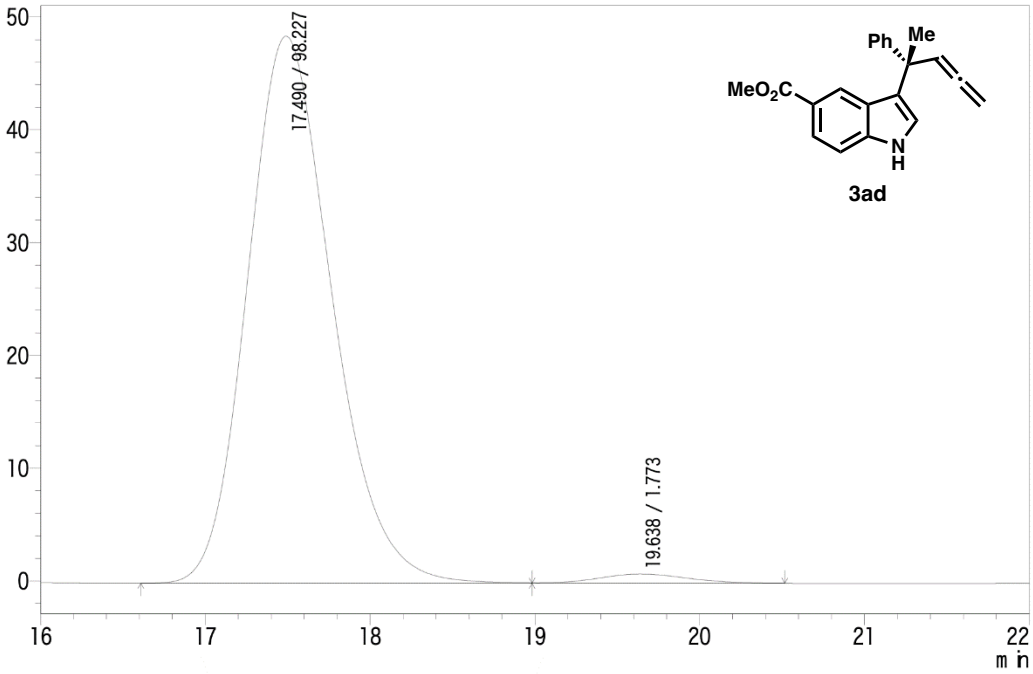
peak#	retention time	area%
1	42.430	94.982
2	45.885	5.018
Total		100.000



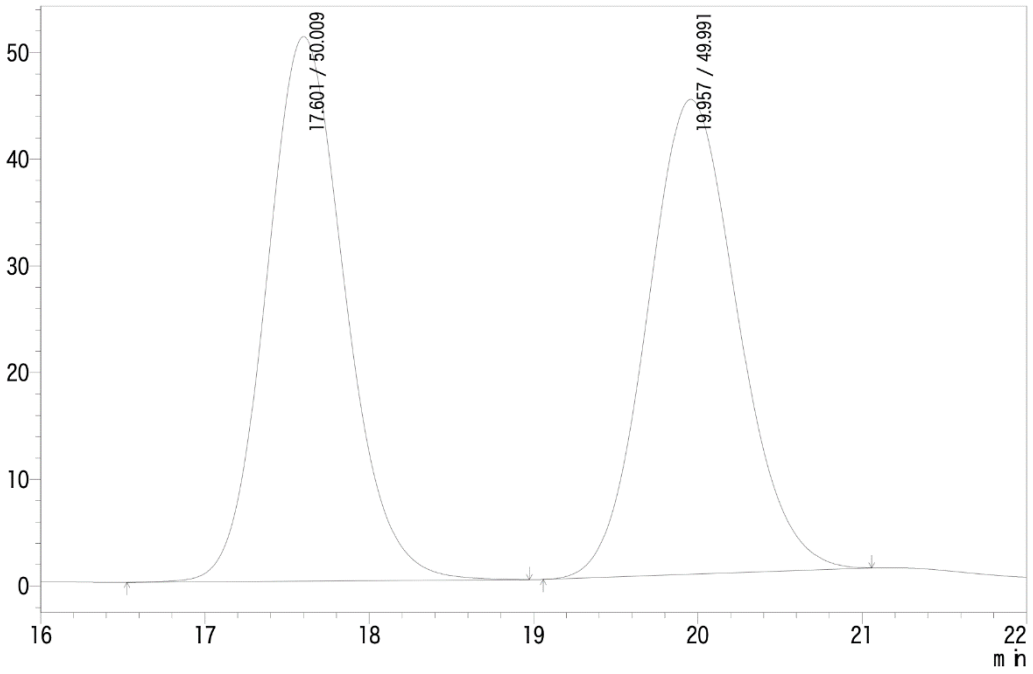
peak#	retention time	area%
1	41.838	49.822
2	45.257	50.178
Total		100.000


^{1}H NMR (CDCl$_3$ with
0.03% v/v TMS, 500 MHz)
Ph
Me
MeO$_2$C
N
H
3ad
TMS
abundance
X : parts per Million : Proton

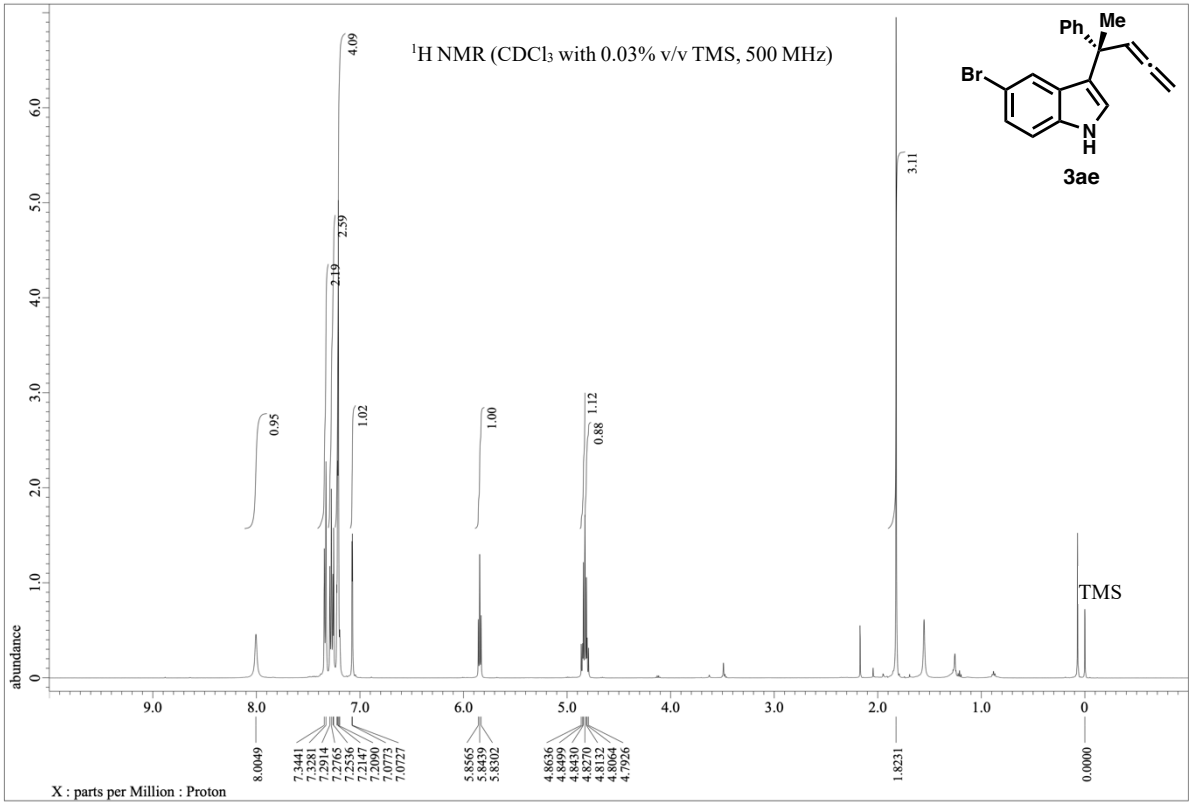

^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 126 MHz)
CDCl$_3$
Ph
Me
MeO$_2$C
N
H
3ad
abundance
X : parts per Million : Carbon13

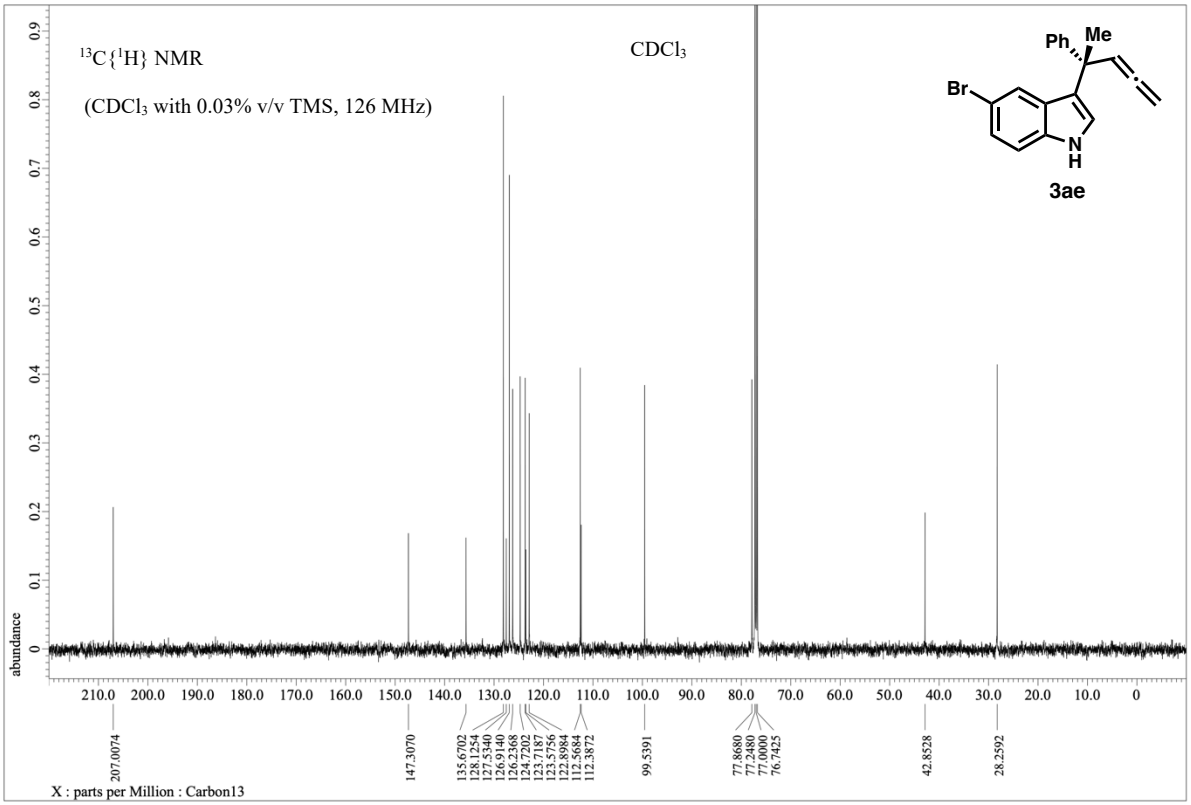


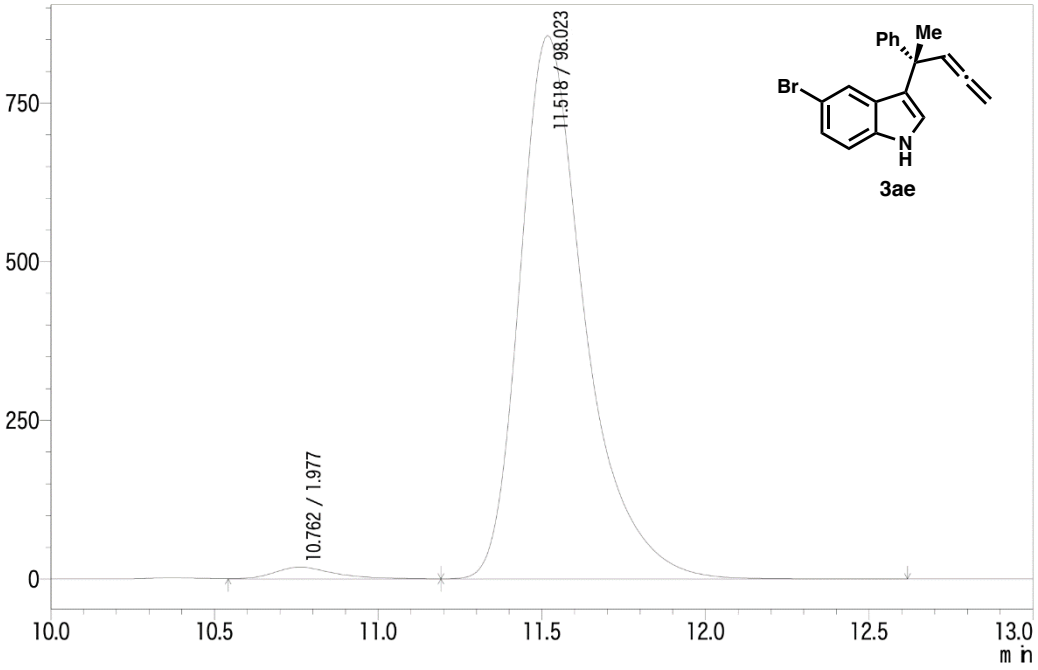
peak#	retention time	area%
1	17.490	98.227
2	19.638	1.773
Total		100.000



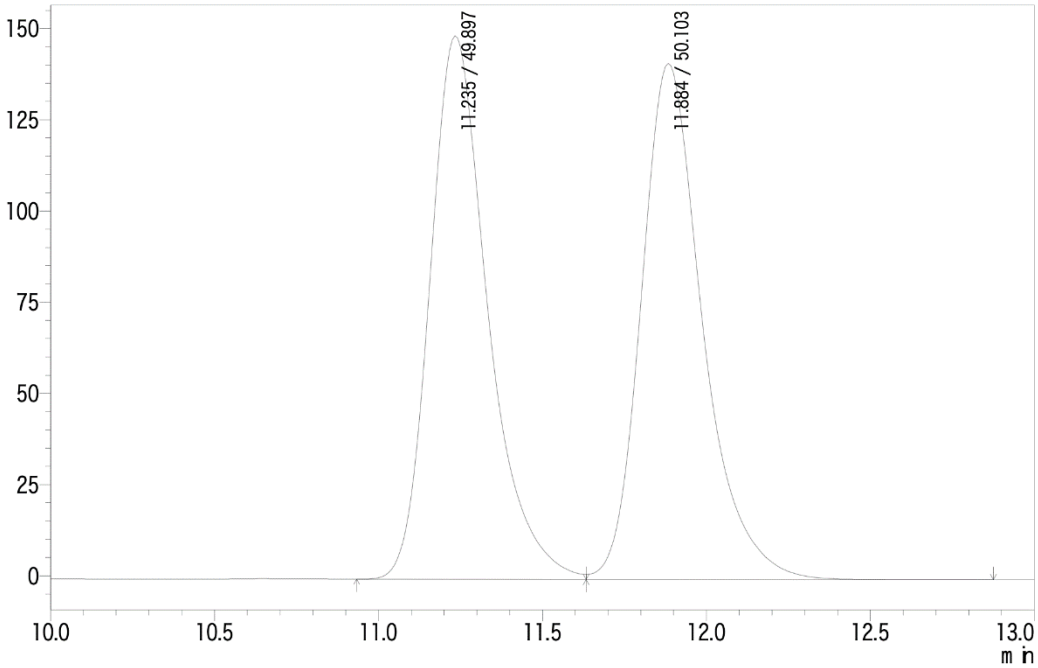
peak#	retention time	area%
1	17.601	50.009
2	19.957	49.991
Total		100.000


^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 500 MHz)
Ph
Me
Br
N
H
3ae
TMS
abundance
X : parts per Million : Proton

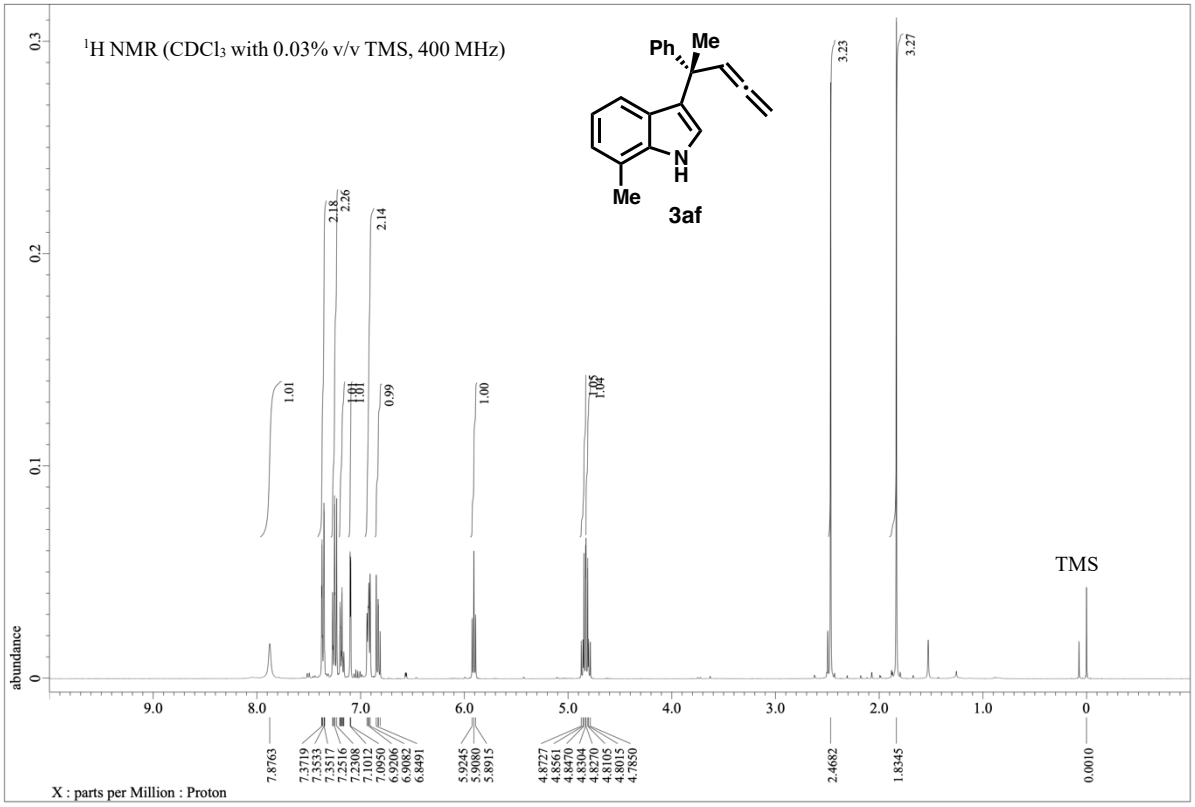

^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 126 MHz)
CDCl$_3$
Ph
Me
Br
N
H
3ae
abundance
X : parts per Million : Carbon13

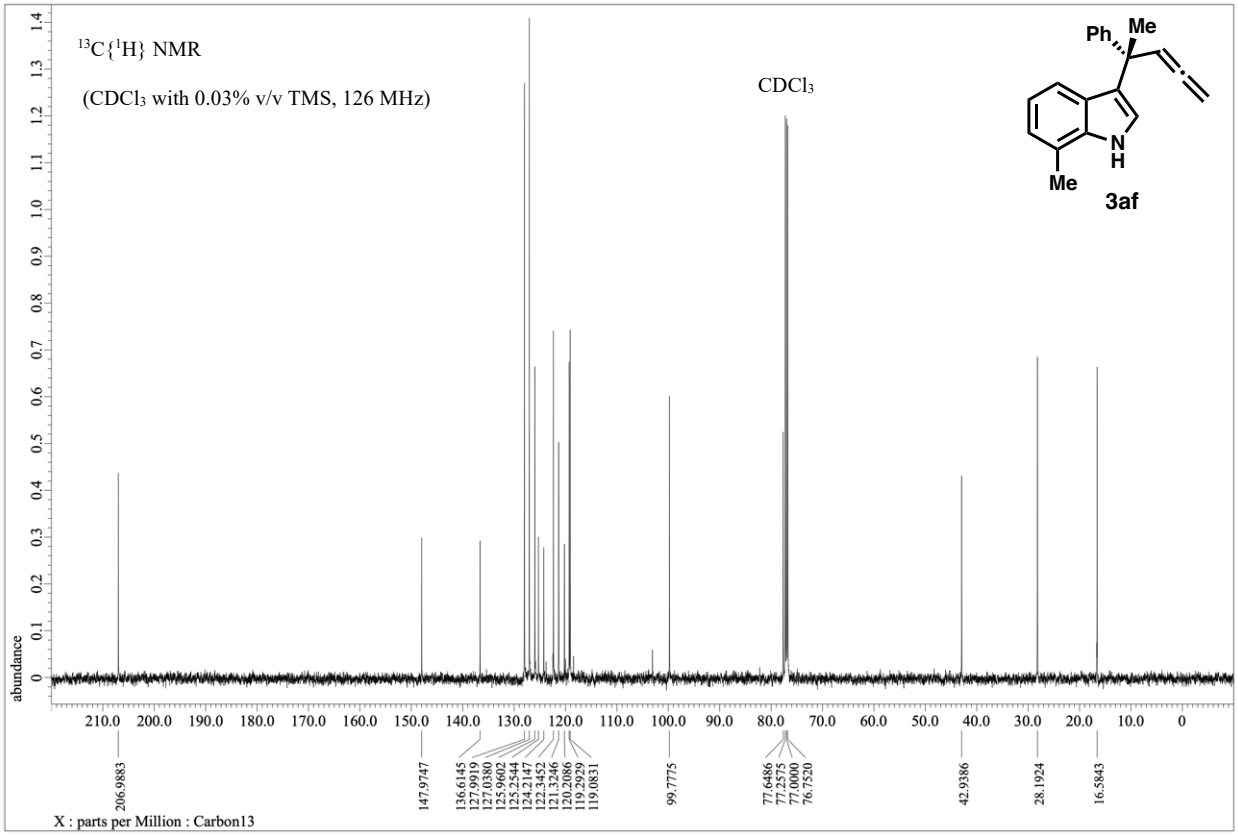


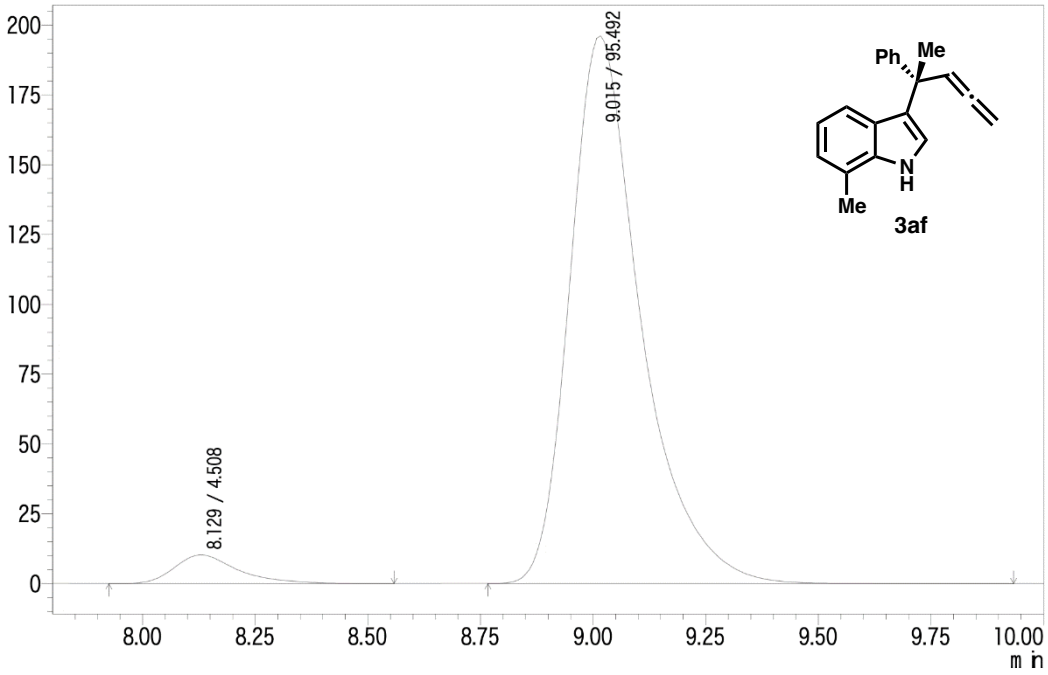
peak#	retention time	area%
1	10.762	1.977
2	11.518	98.023
Total		100.000



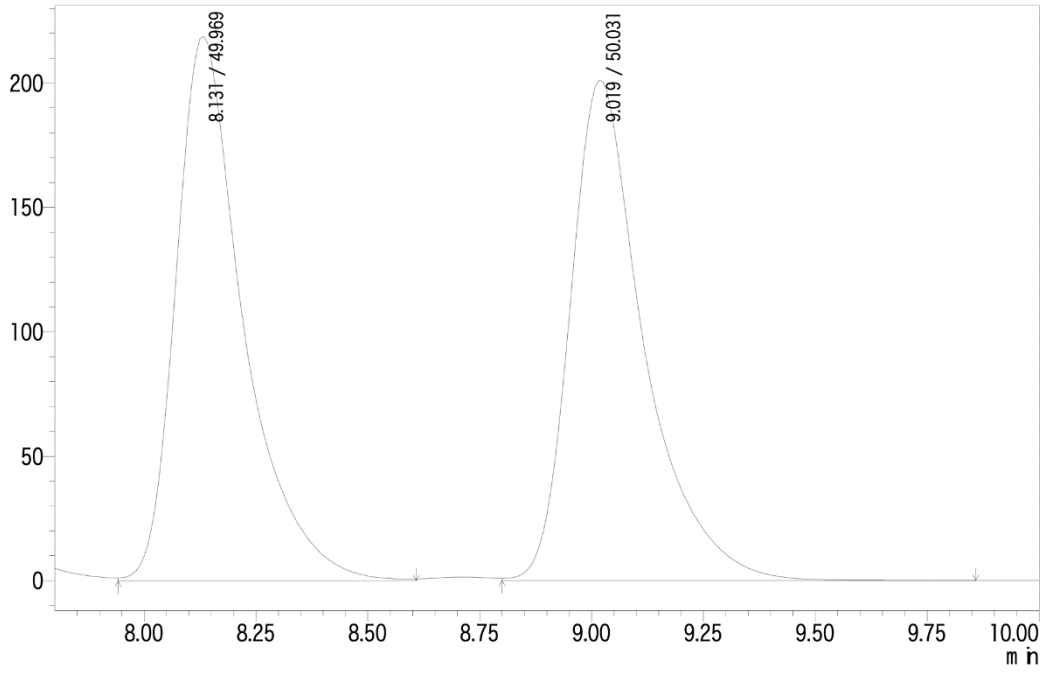
peak#	retention time	area%
1	11.235	49.897
2	11.884	50.103
Total		100.000


^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 400 MHz)
Ph
Me
N
H
Me
3af
TMS
abundance
X : parts per Million : Proton

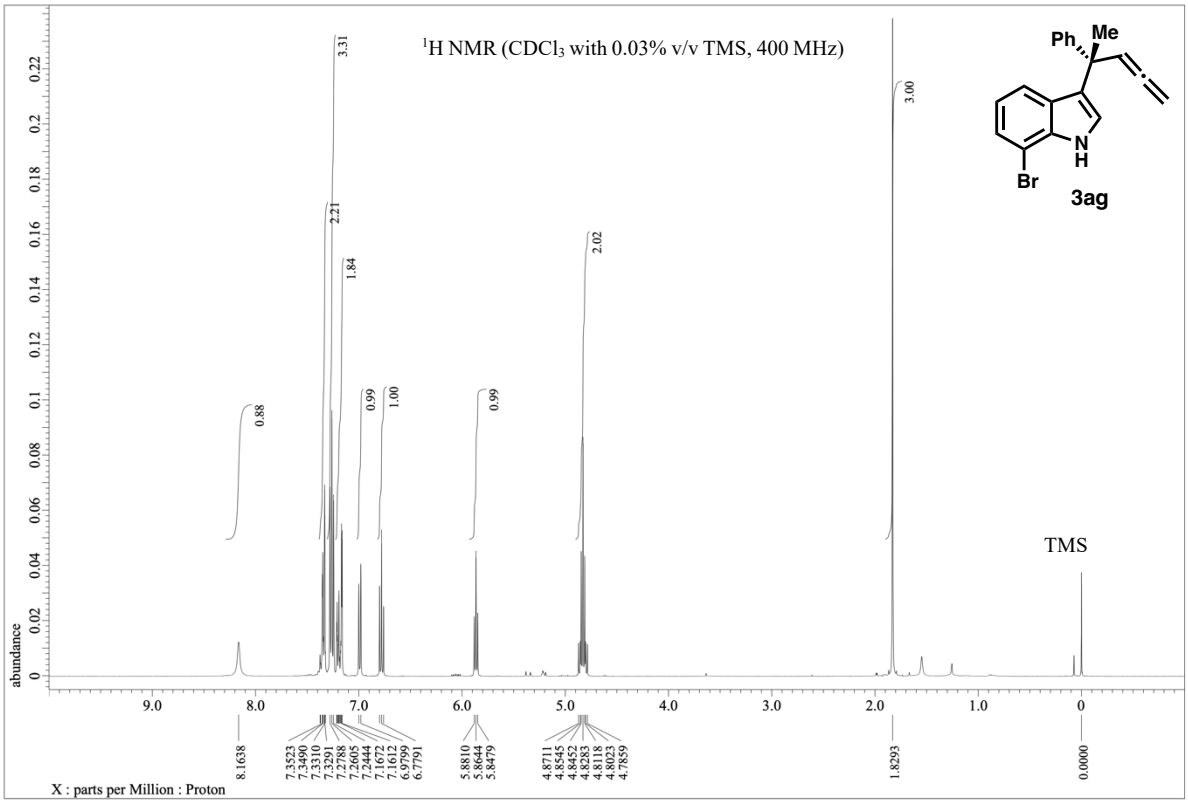

^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 126 MHz)
CDCl$_3$
Ph
Me
N
H
Me
3af
abundance
X : parts per Million : Carbon13

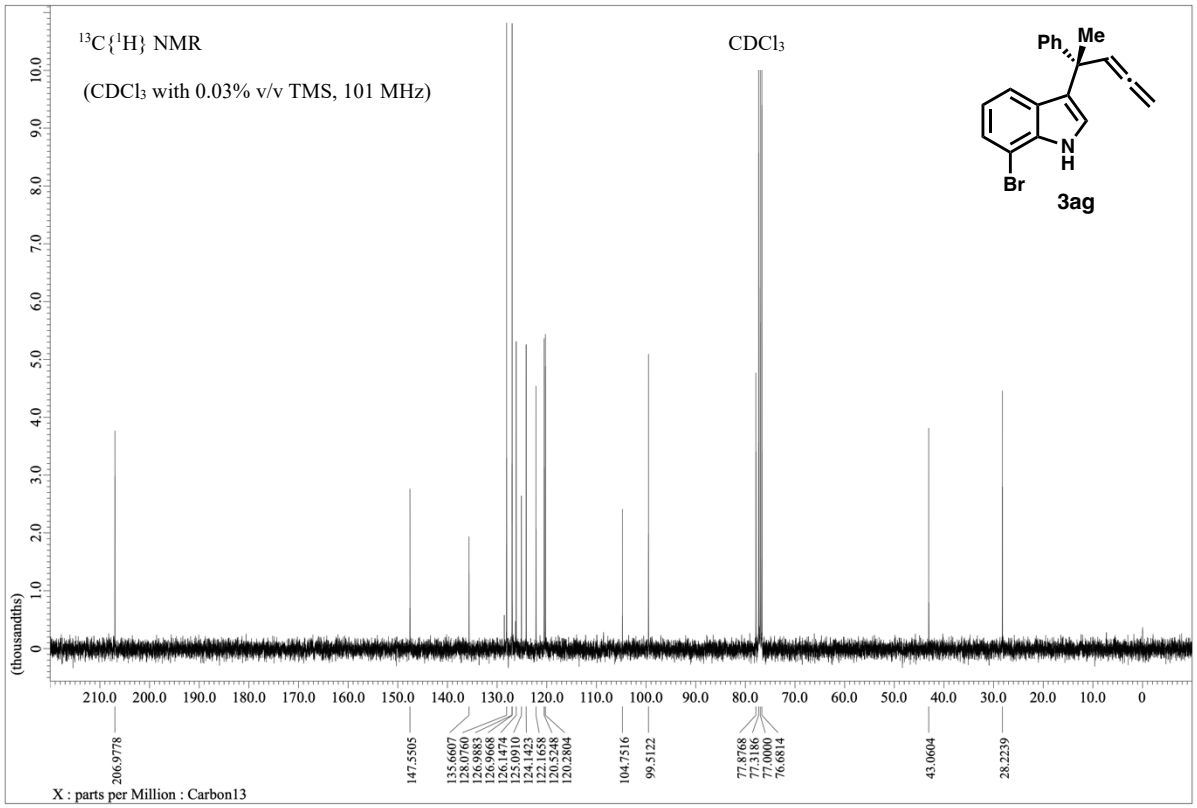


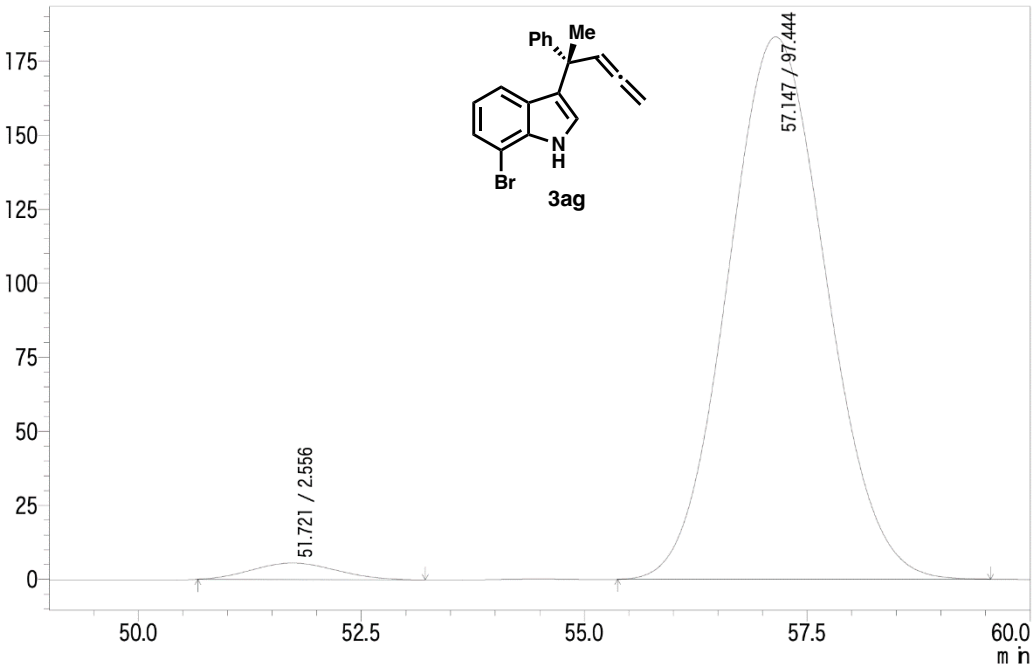
peak#	retention time	area%
1	8.129	4.508
2	9.015	95.492
Total		100.000



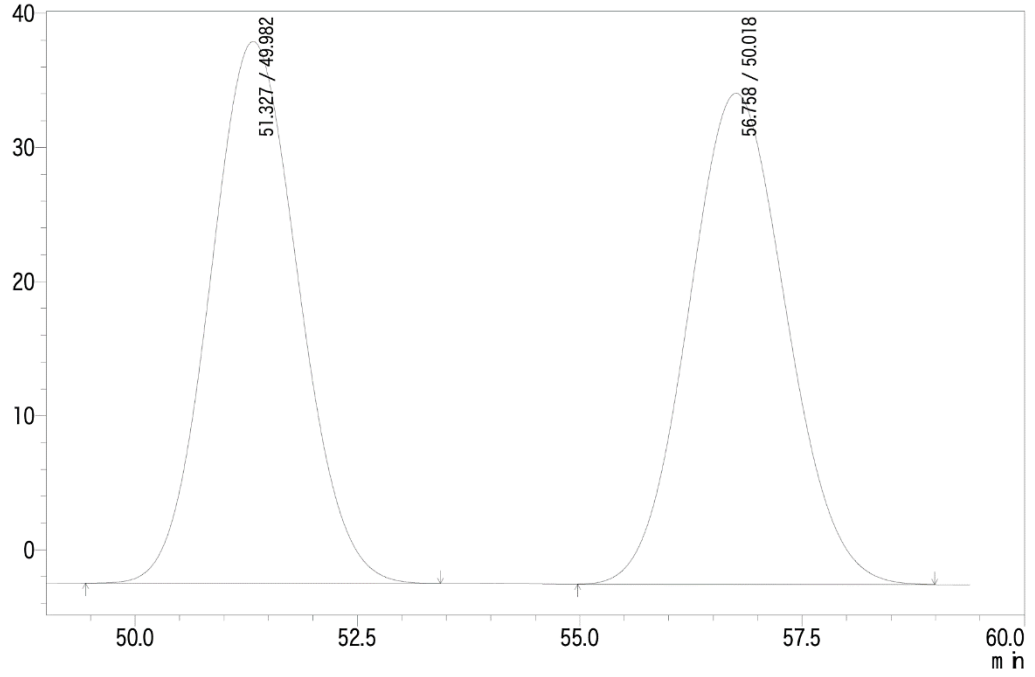
peak#	retention time	area%
1	8.131	49.969
2	9.019	50.031
Total		100.000


^{1}H NMR ($CDCl_3$ with 0.03% v/v TMS, 400 MHz)
Ph
Me
N
H
Br
3ag
TMS
abundance
X : parts per Million : Proton

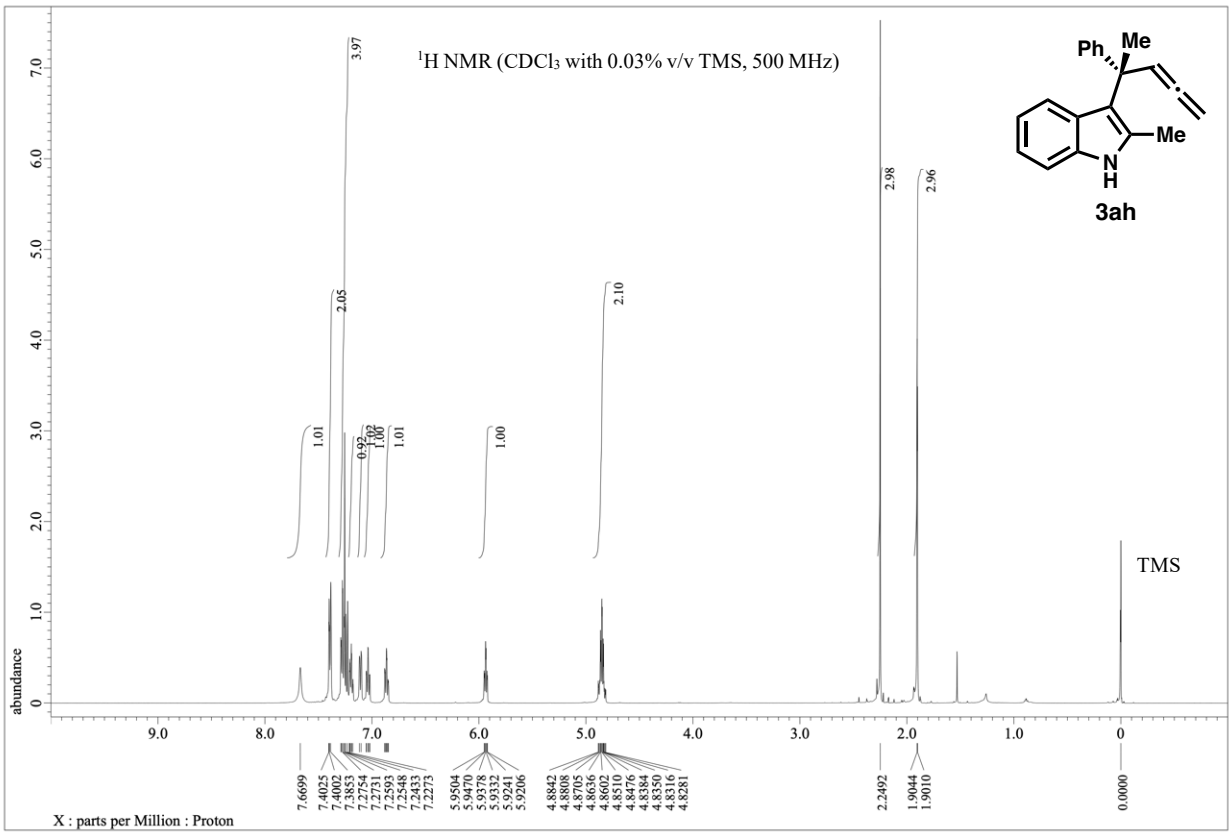

^{13}C{^{1}H} NMR
($CDCl_3$ with 0.03% v/v TMS, 101 MHz)
$CDCl_3$
Ph
Me
N
H
Br
3ag
(thousandths)
X : parts per Million : Carbon13

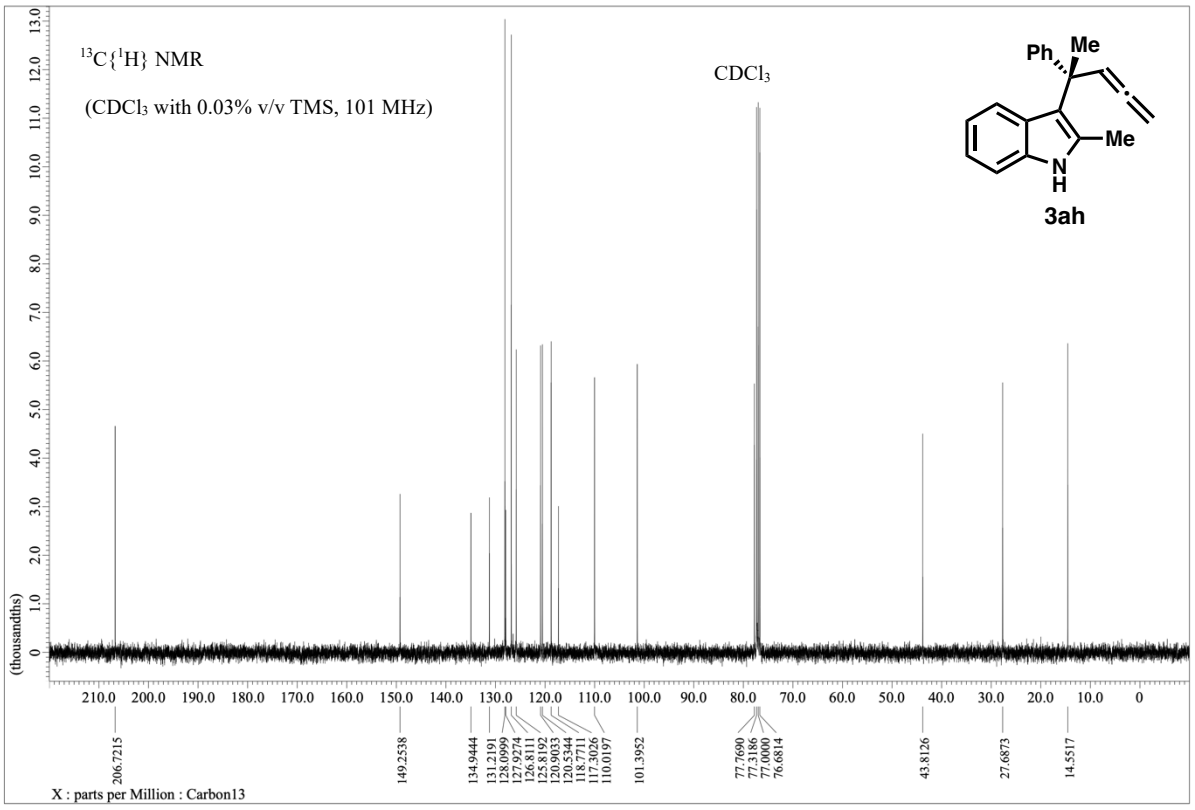


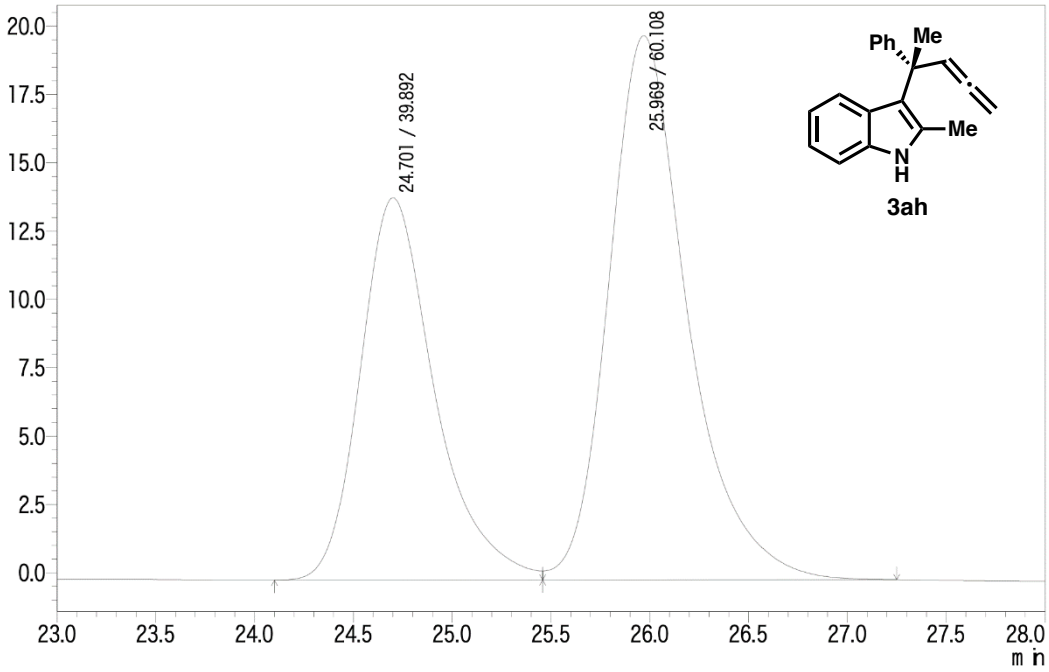
peak#	retention time	area%
1	51.721	2.556
2	57.147	97.444
Total		100.000



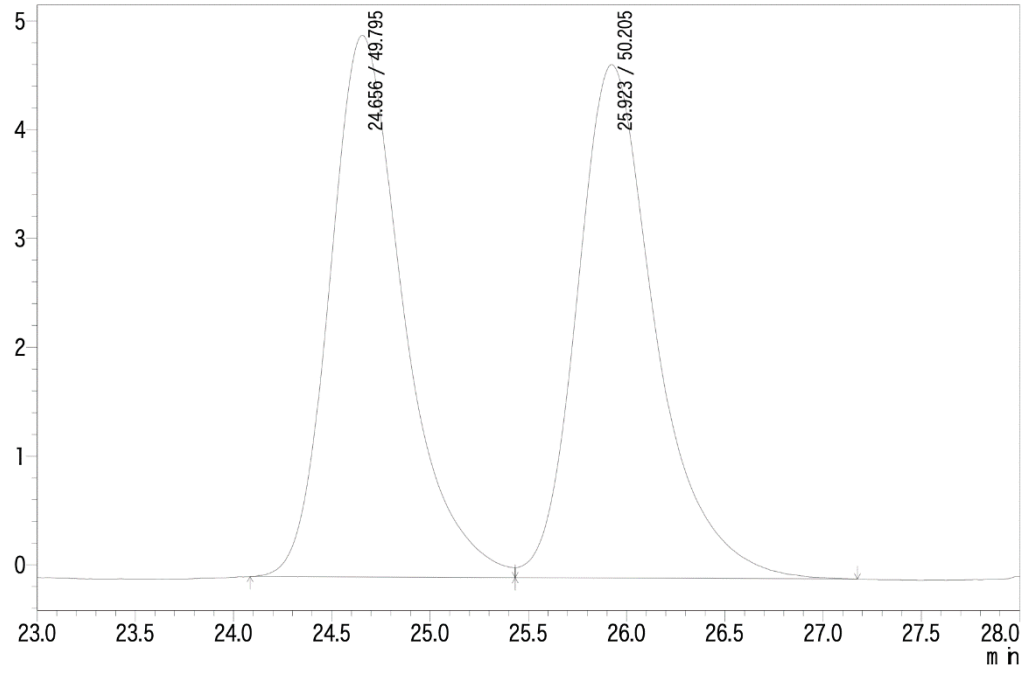
peak#	retention time	area%
1	51.327	49.982
2	56.758	50.018
Total		100.000


^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 500 MHz)
Ph
Me
Me
N
H
3ah
TMS
abundance
X : parts per Million : Proton

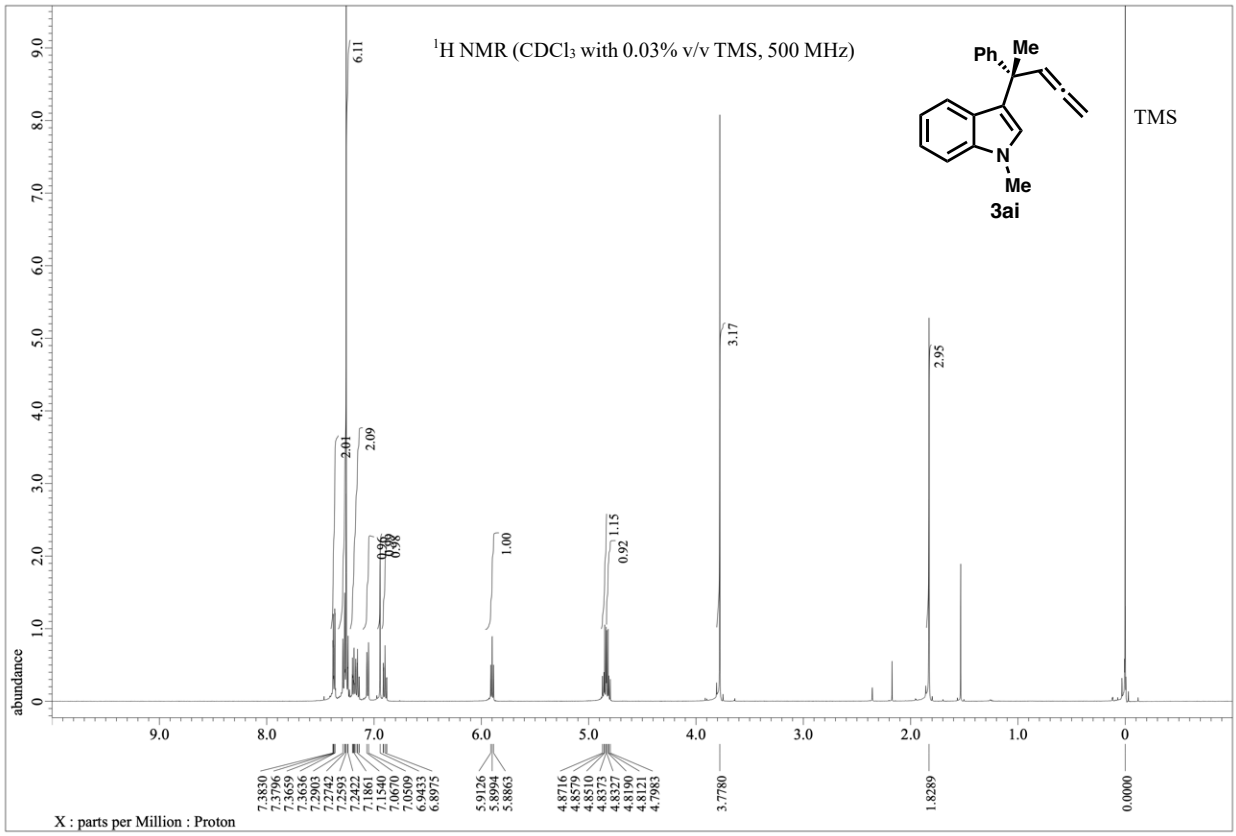

^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 101 MHz)
CDCl$_3$
Ph
Me
Me
N
H
3ah
(thousandths)
X : parts per Million : Carbon13

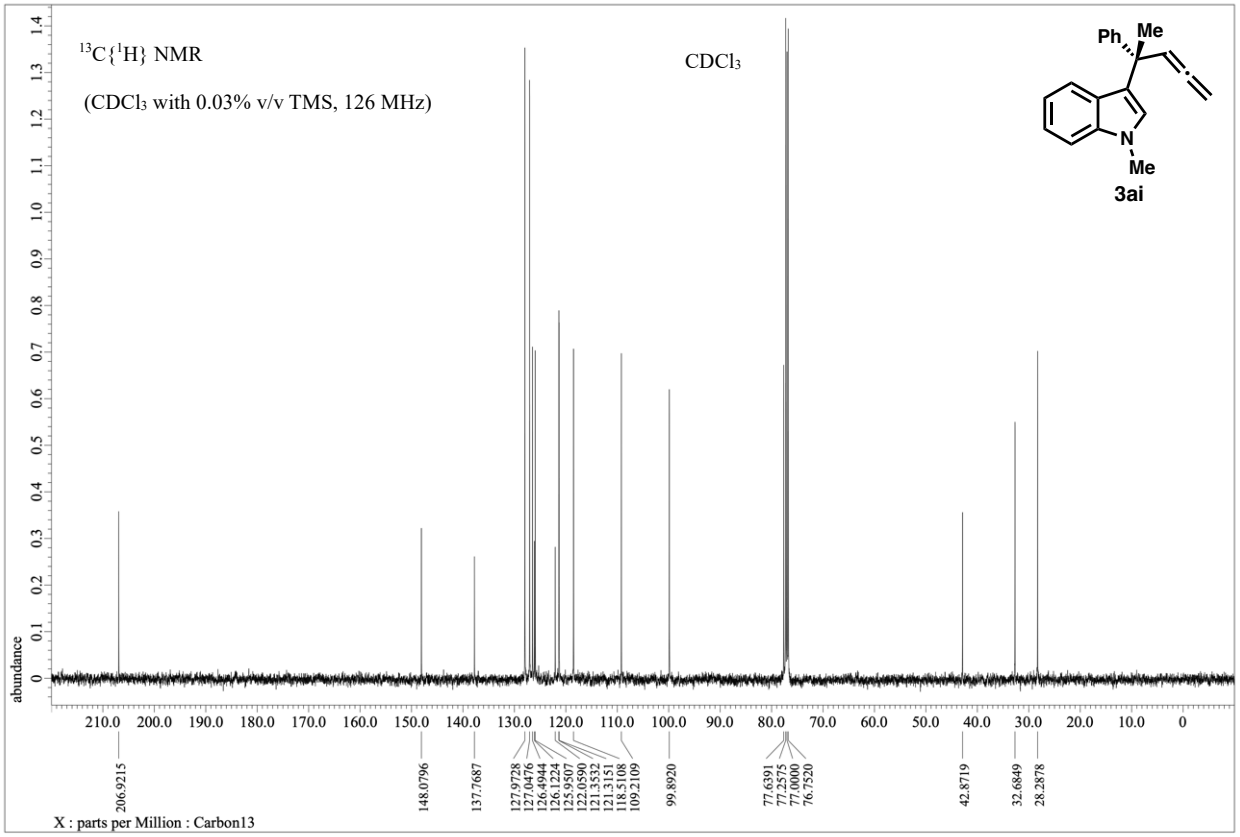


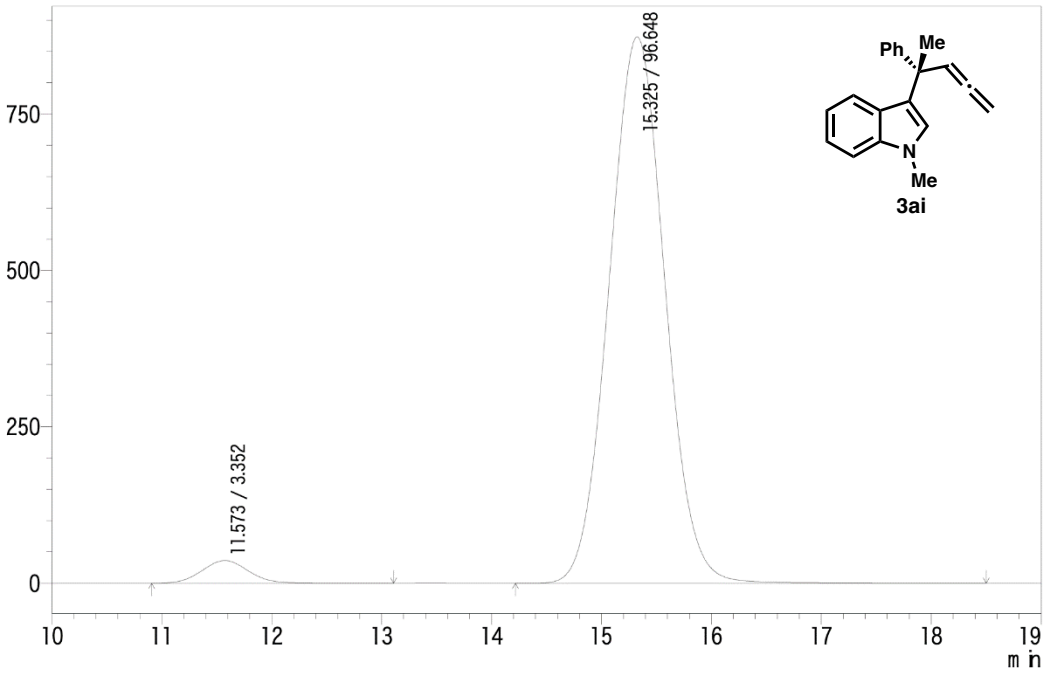
peak#	retention time	area%
1	24.701	39.892
2	25.969	60.108
Total		100.000



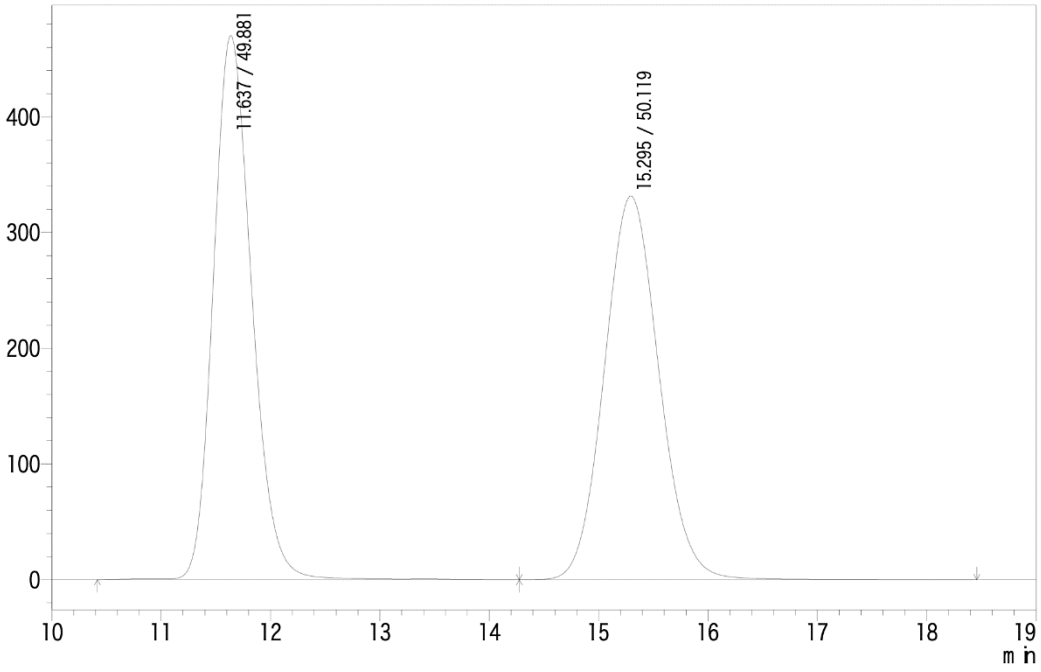
peak#	retention time	area%
1	24.656	49.795
2	25.923	50.205
Total		100.000


^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 500 MHz)
TMS
Ph
Me
N
Me
3ai
abundance
X : parts per Million : Proton

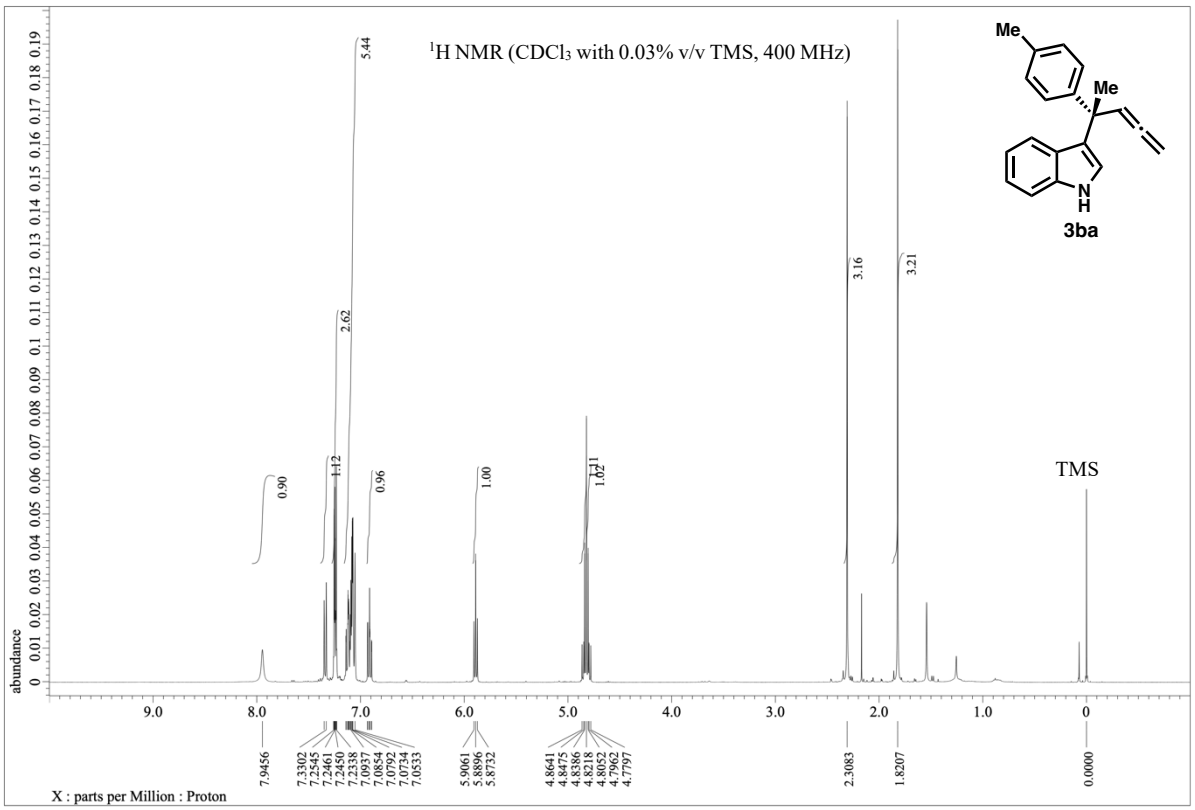

^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 126 MHz)
CDCl$_3$
Ph
Me
N
Me
3ai
abundance
X : parts per Million : Carbon13

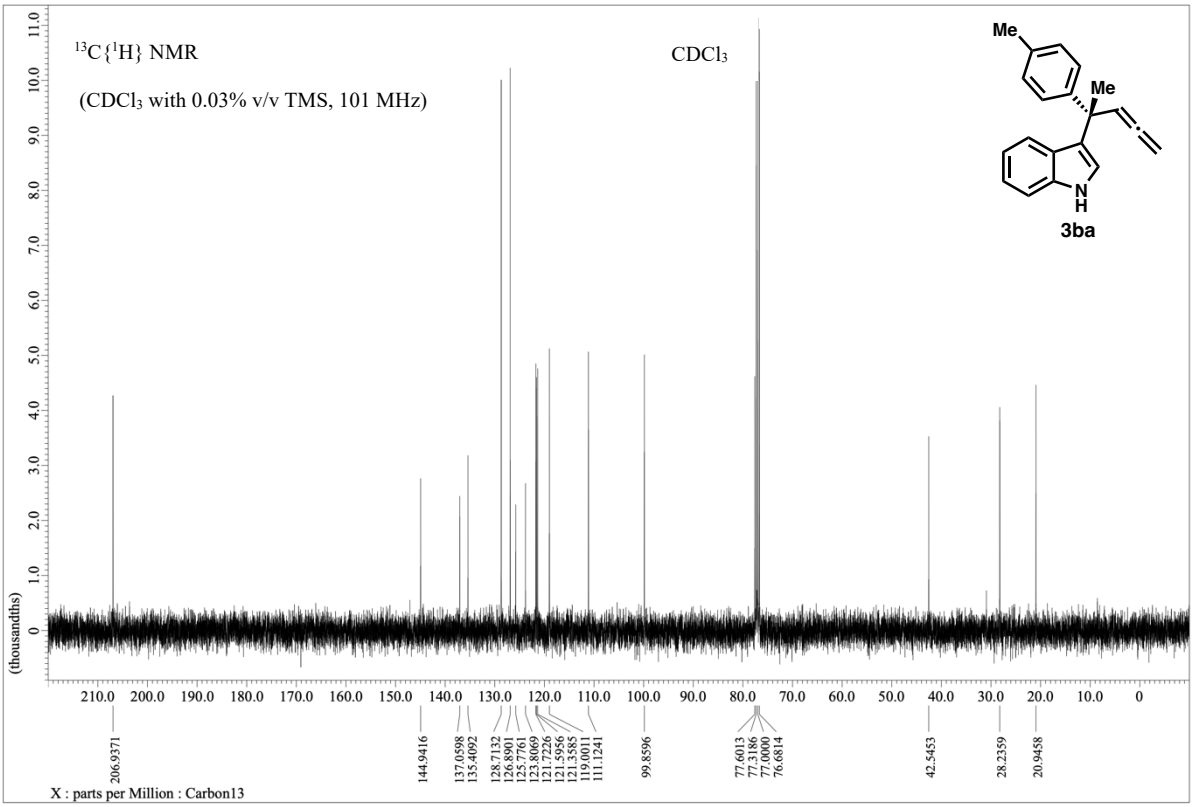


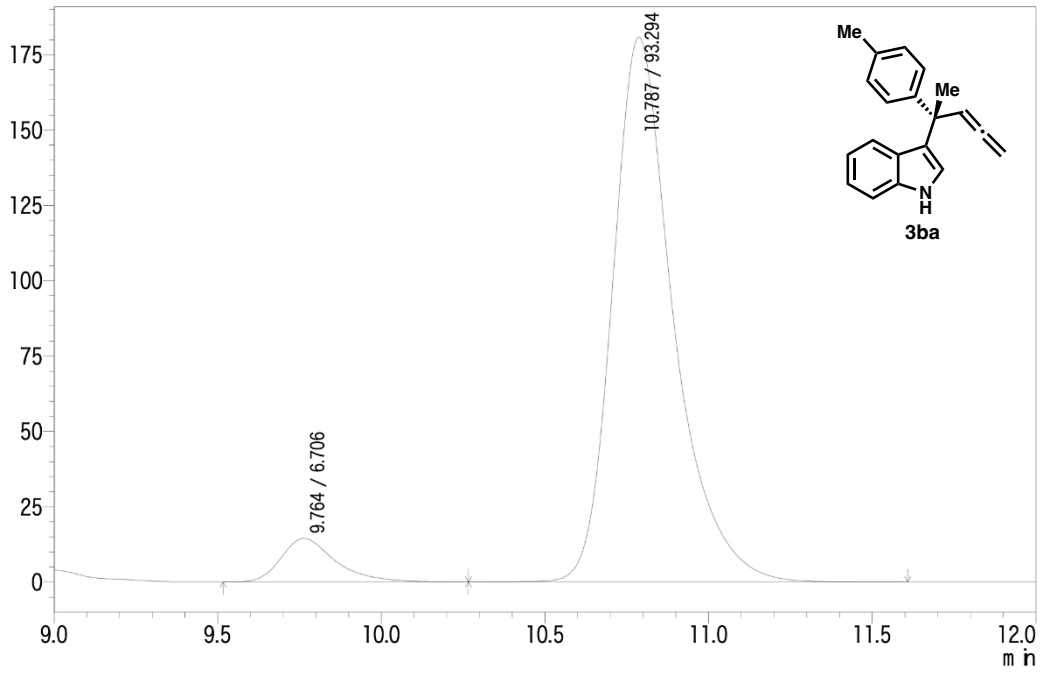
peak#	retention time	area%
1	11.573	3.352
2	15.325	96.648
Total		100.000



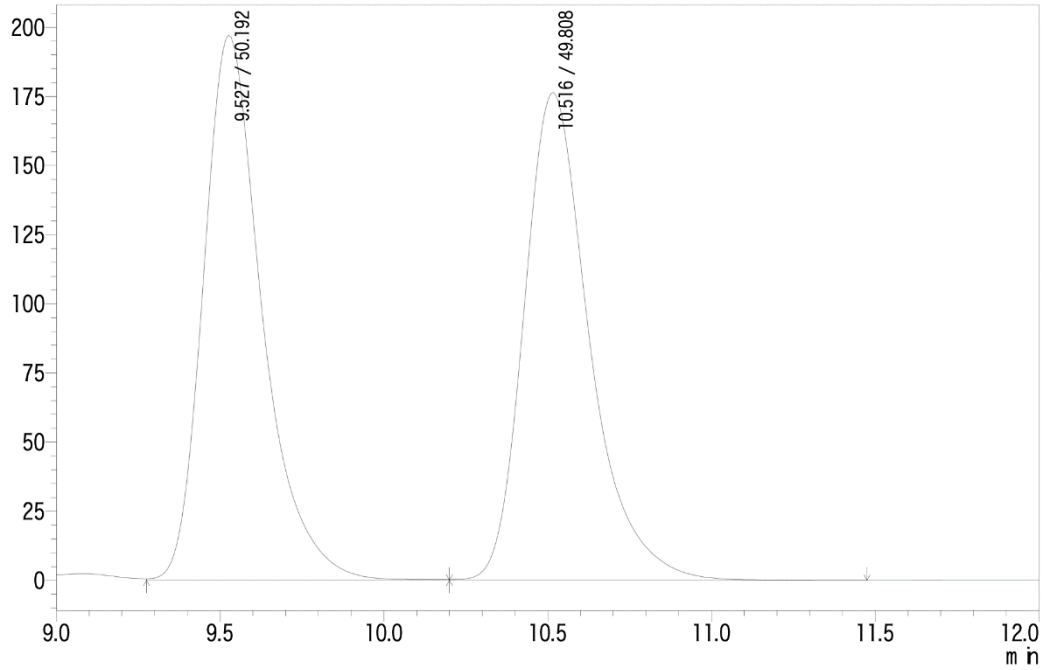
peak#	retention time	area%
1	11.637	49.881
2	15.295	50.119
Total		100.000


^{1}H NMR ($CDCl_3$ with 0.03% v/v TMS, 400 MHz)
Me
Me
N
H
3ba
TMS
abundance
X : parts per Million : Proton

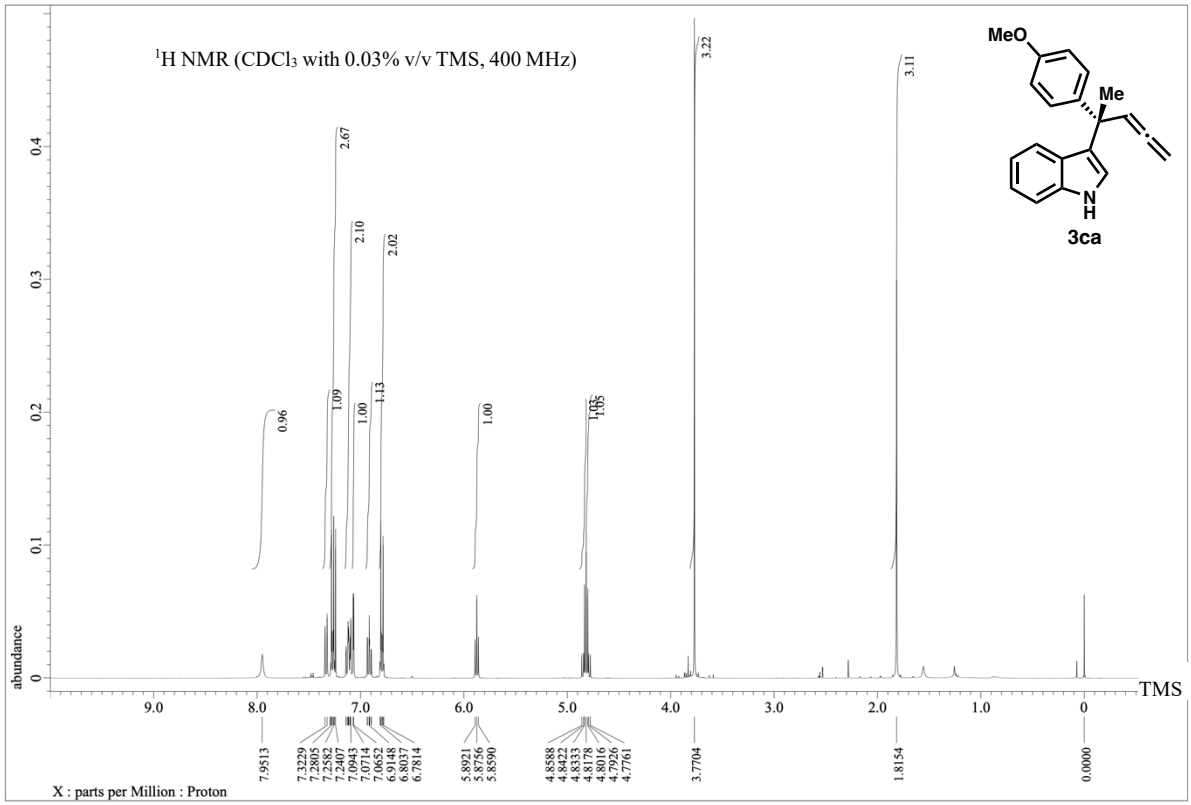

^{13}C{^{1}H} NMR
($CDCl_3$ with 0.03% v/v TMS, 101 MHz)
$CDCl_3$
Me
Me
N
H
3ba
(thousandths)
X : parts per Million : Carbon13

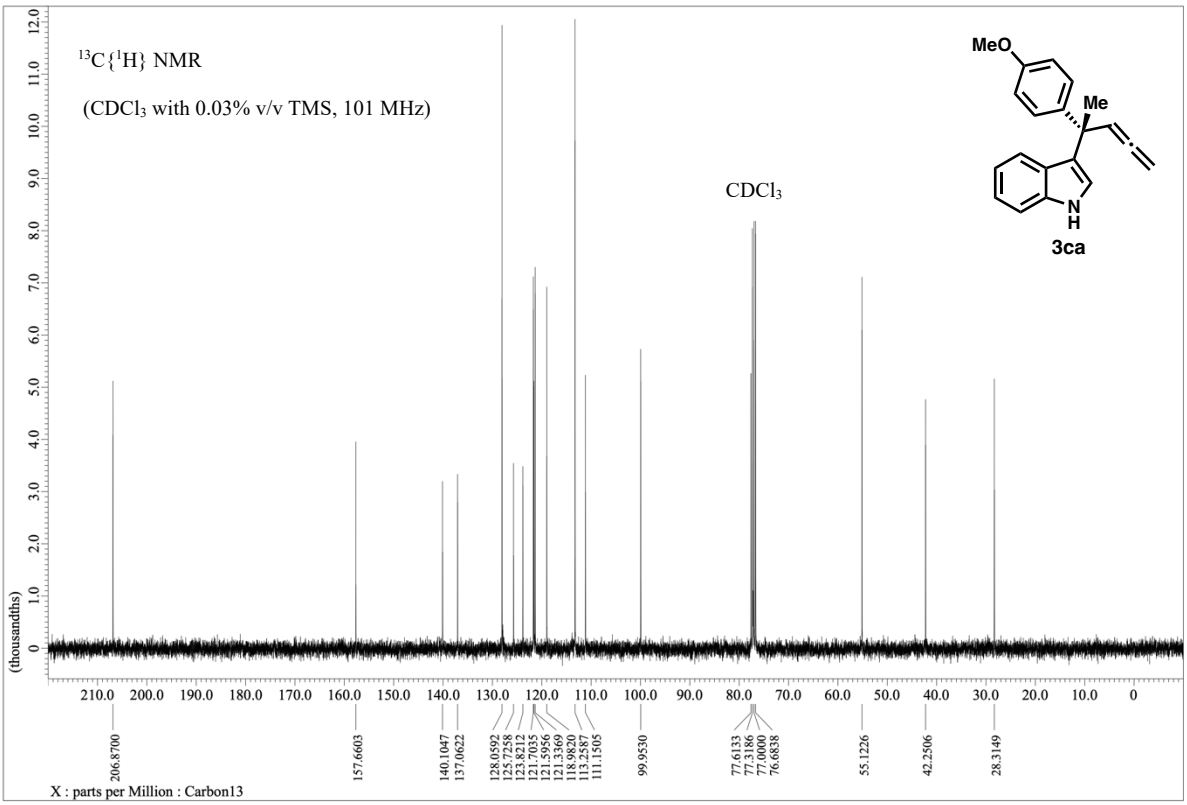


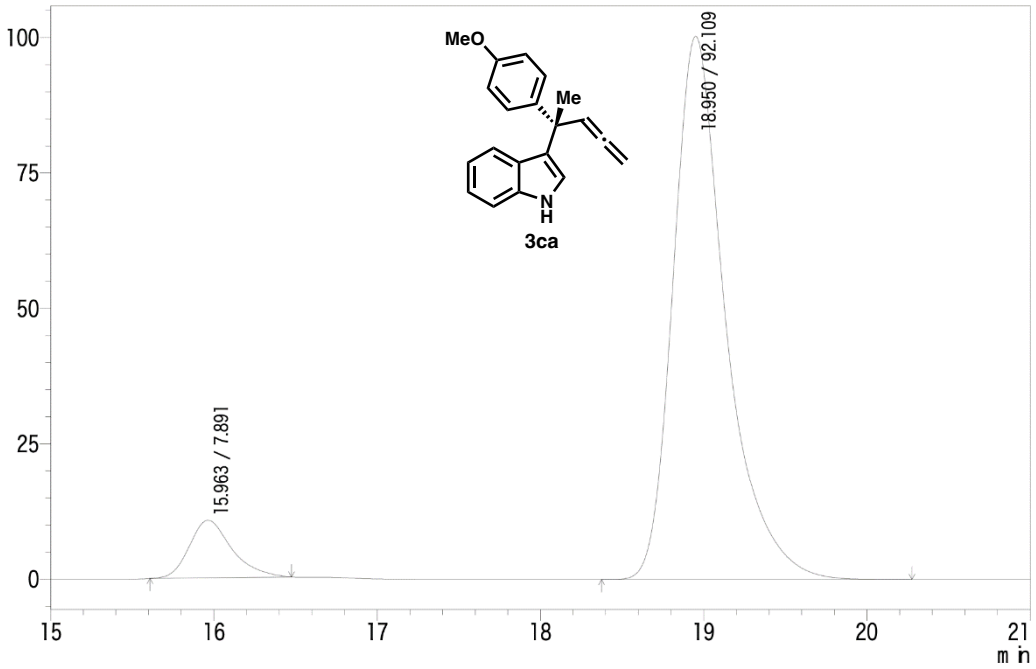
peak#	retention time	area%
1	9.764	6.706
2	10.787	93.294
Total		100.000



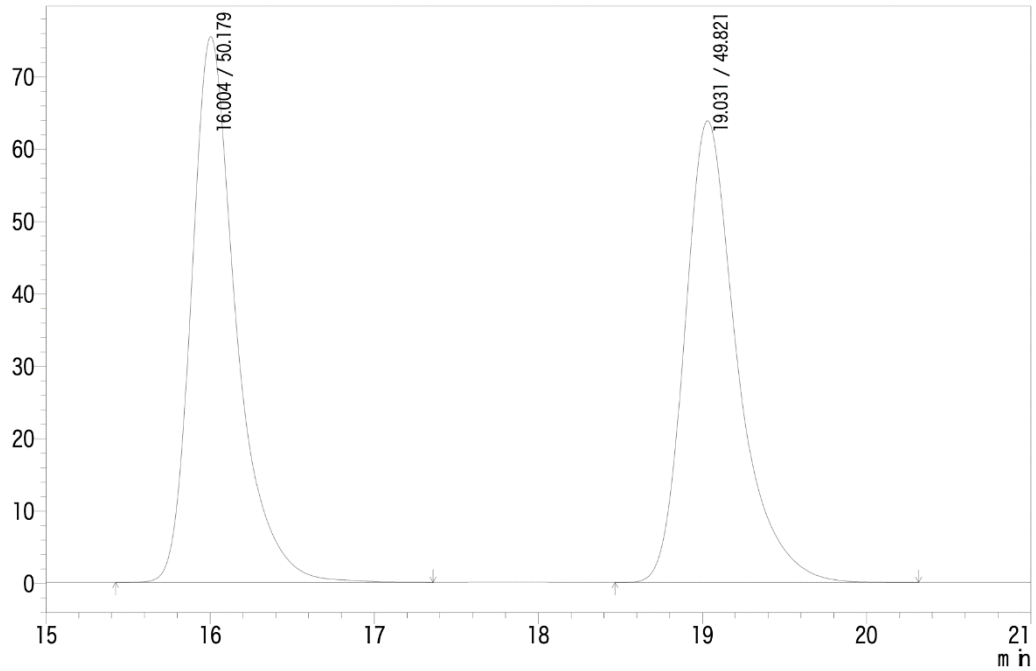
peak#	retention time	area%
1	9.527	50.192
2	10.516	49.808
Total		100.000


^{1}H NMR ($CDCl_3$ with 0.03% v/v TMS, 400 MHz)
MeO
Me
N
H
3ca
abundance
TMS
X : parts per Million : Proton

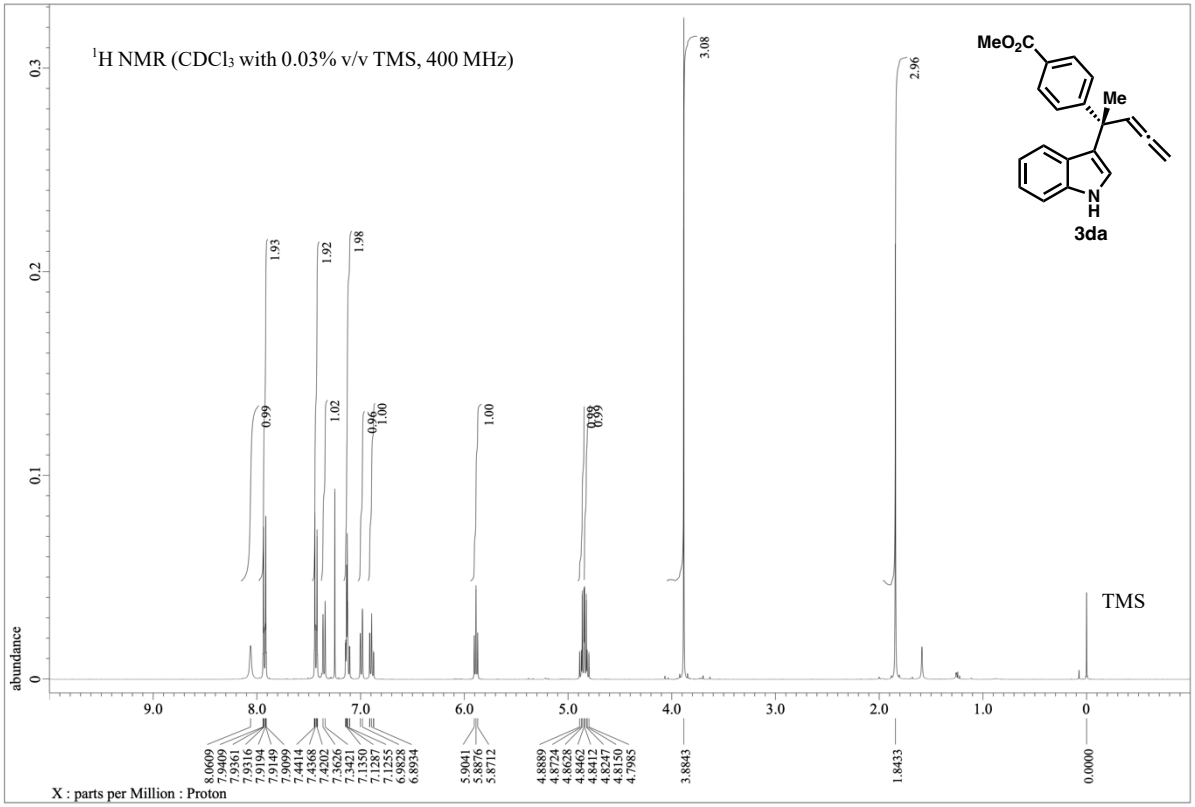

^{13}C{^{1}H} NMR
($CDCl_3$ with 0.03% v/v TMS, 101 MHz)
$CDCl_3$
MeO
Me
N
H
3ca
(thousandths)
X : parts per Million : Carbon13

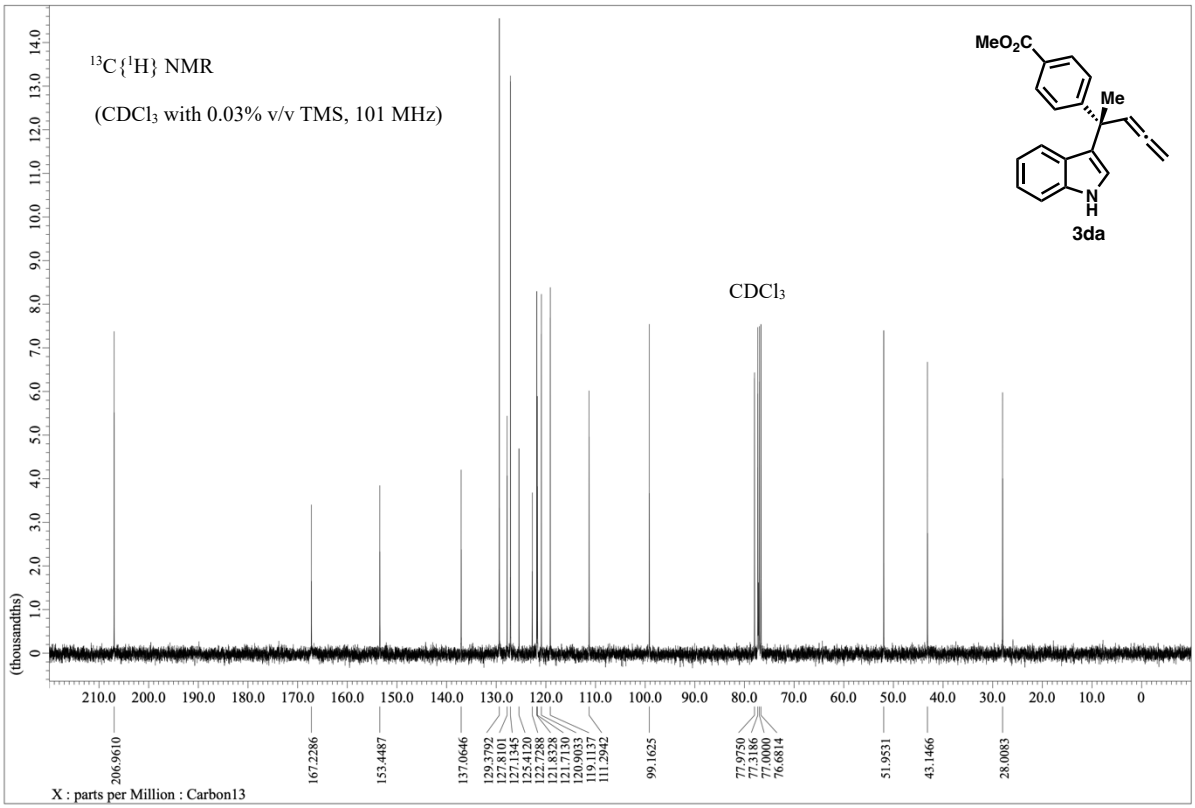


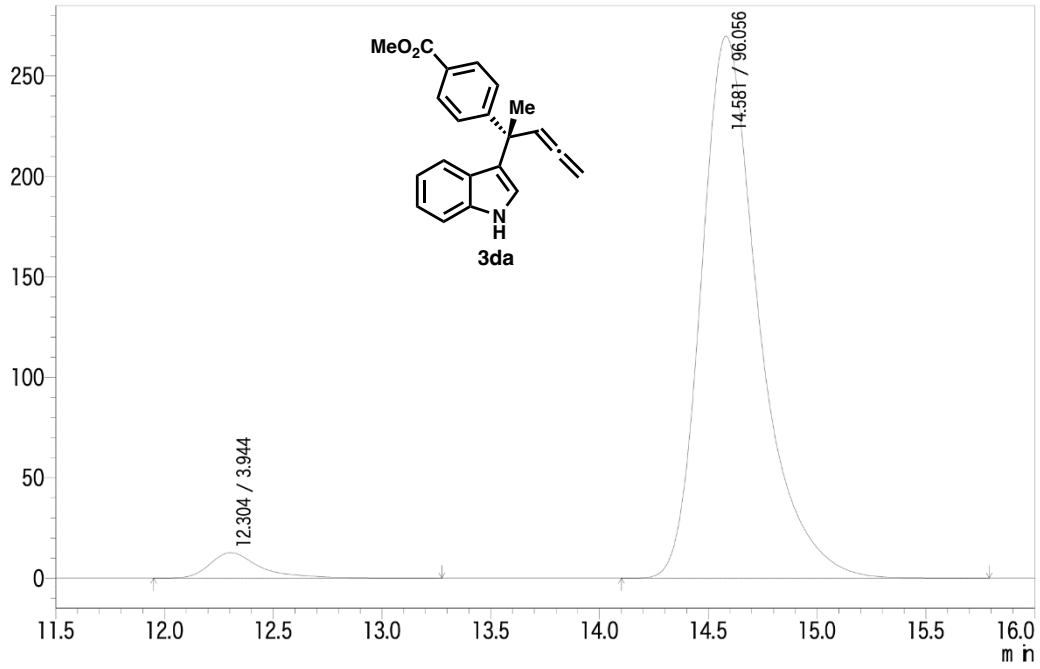
peak#	retention time	area%
1	15.963	7.891
2	18.950	92.109
Total		100.000



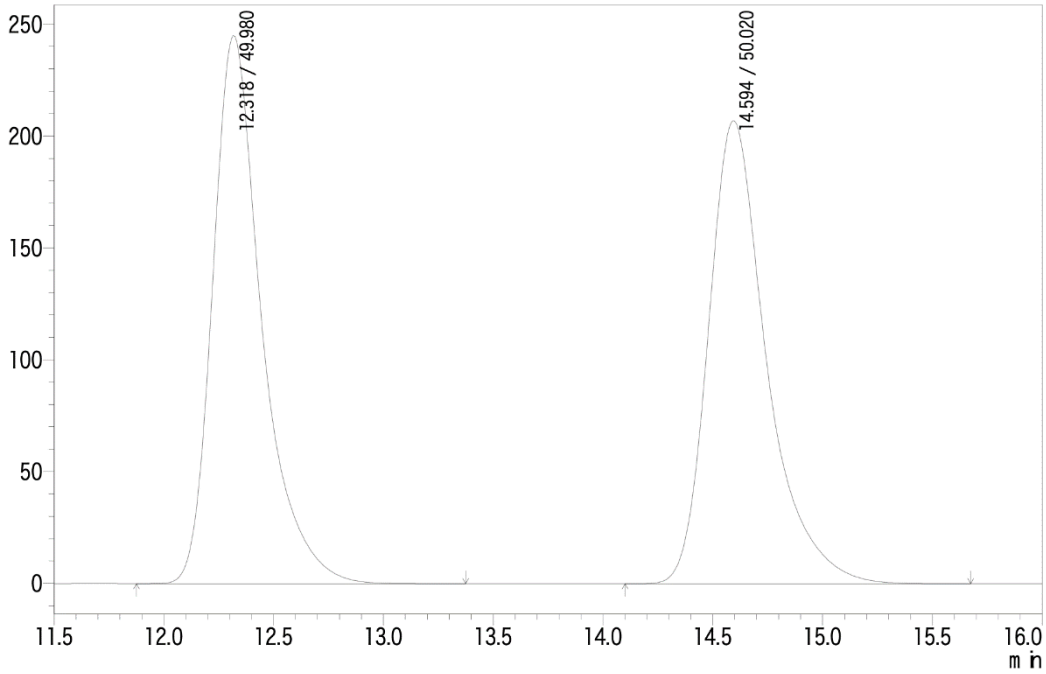
peak#	retention time	area%
1	16.004	50.179
2	19.031	49.821
Total		100.000


^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 400 MHz)
MeO$_2$C
Me
N
H
3da
TMS
abundance
X : parts per Million : Proton

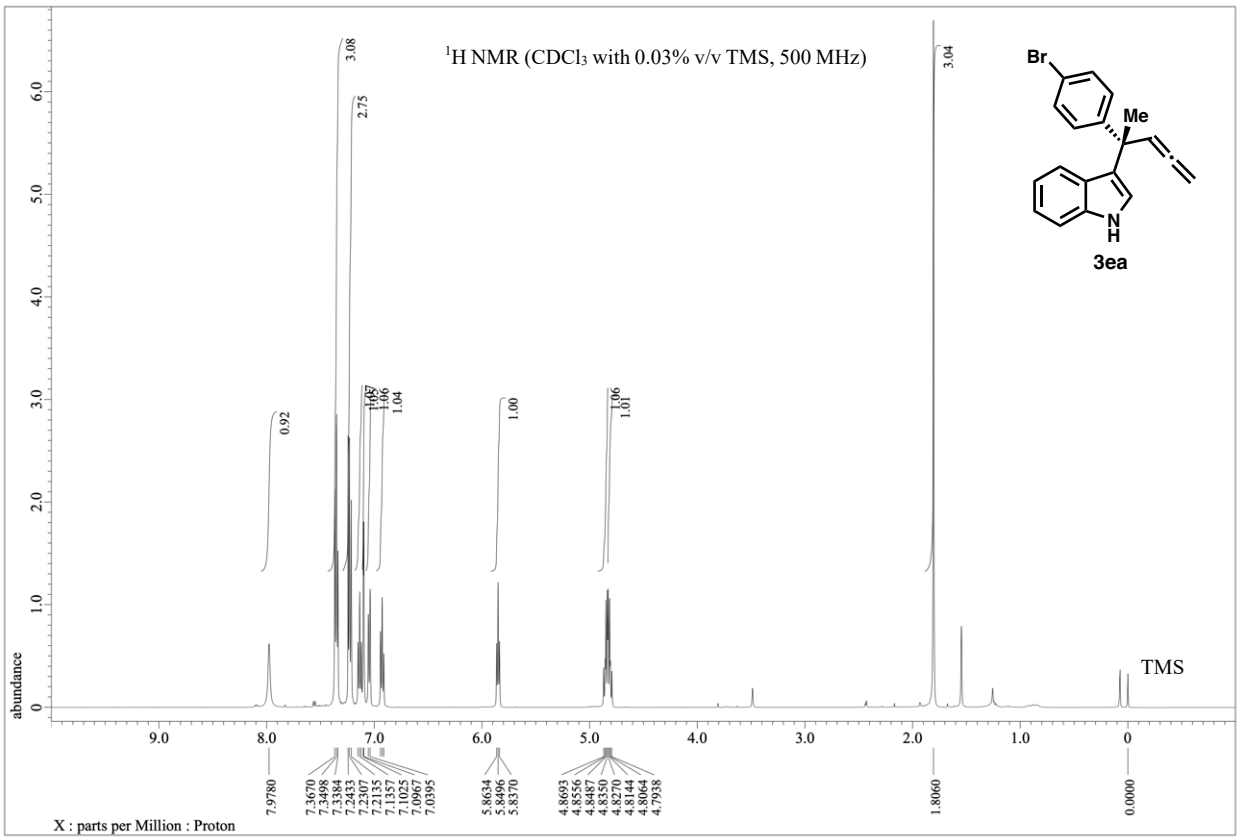

^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 101 MHz)
MeO$_2$C
Me
N
H
3da
CDCl$_3$
(thousandths)
X : parts per Million : Carbon13

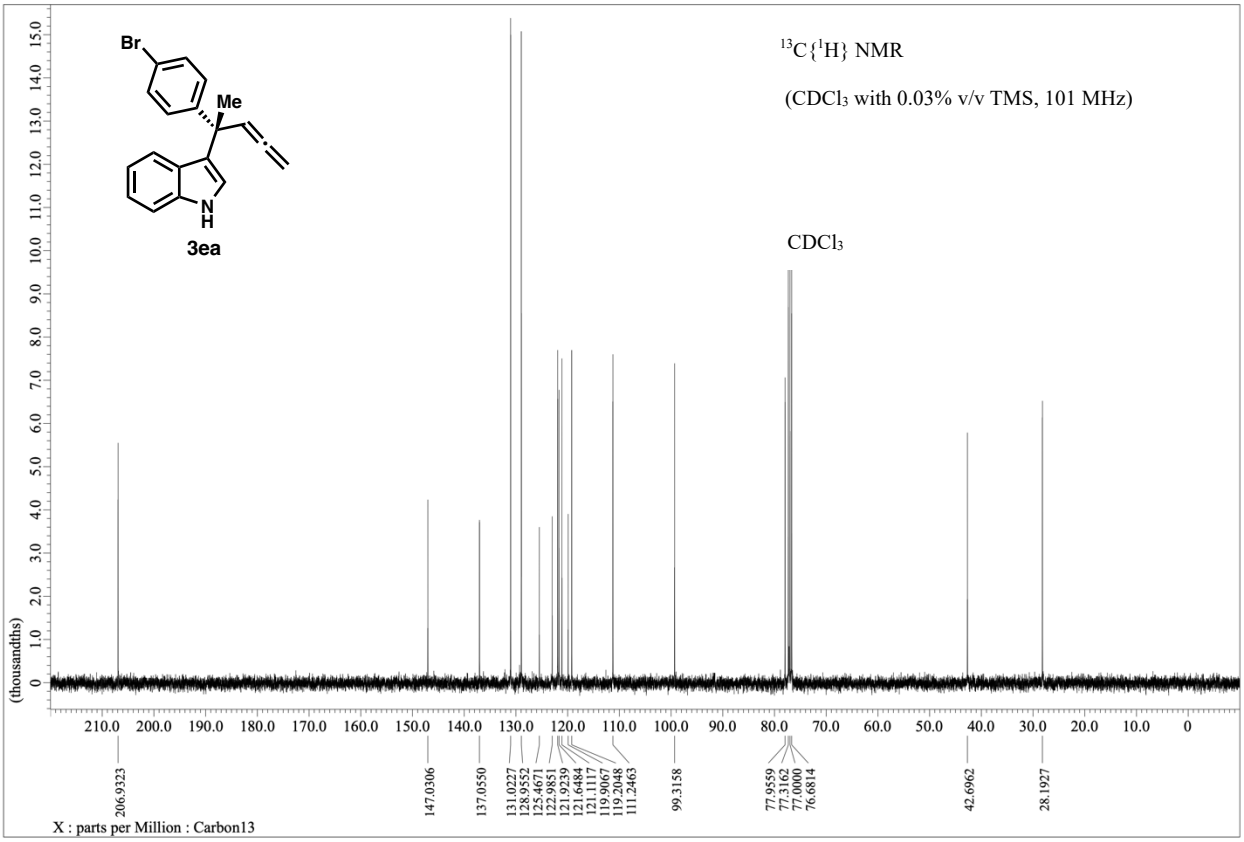


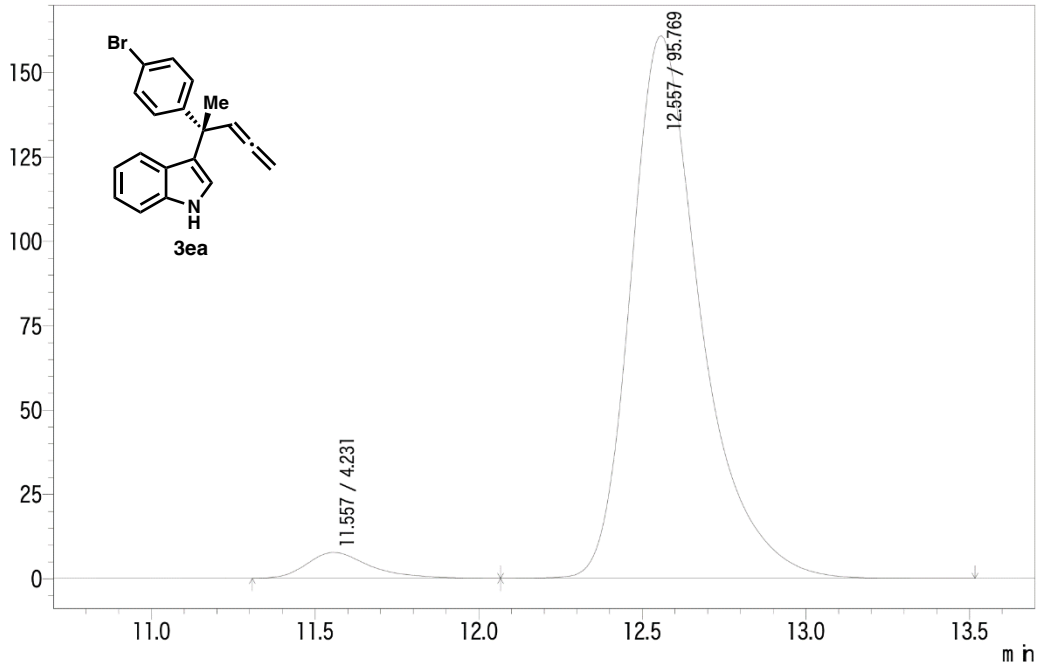
peak#	retention time	area%
1	12.304	3.944
2	14.581	96.056
Total		100.000



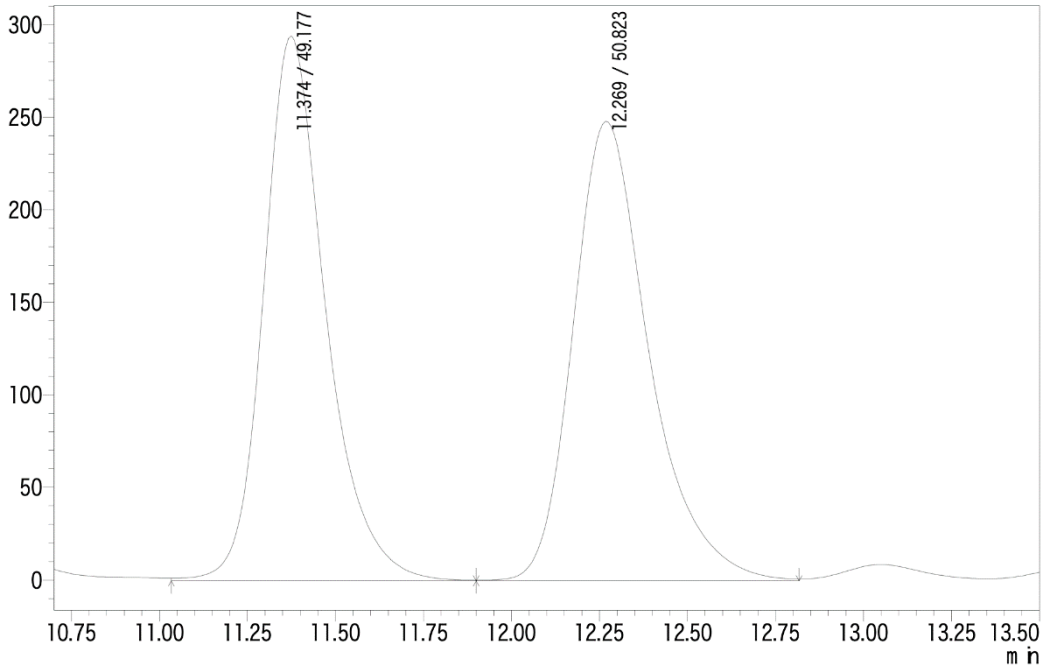
peak#	retention time	area%
1	12.318	49.980
2	14.594	50.020
Total		100.000


^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 500 MHz)
Br
Me
N
H
3ea
TMS
abundance
X : parts per Million : Proton

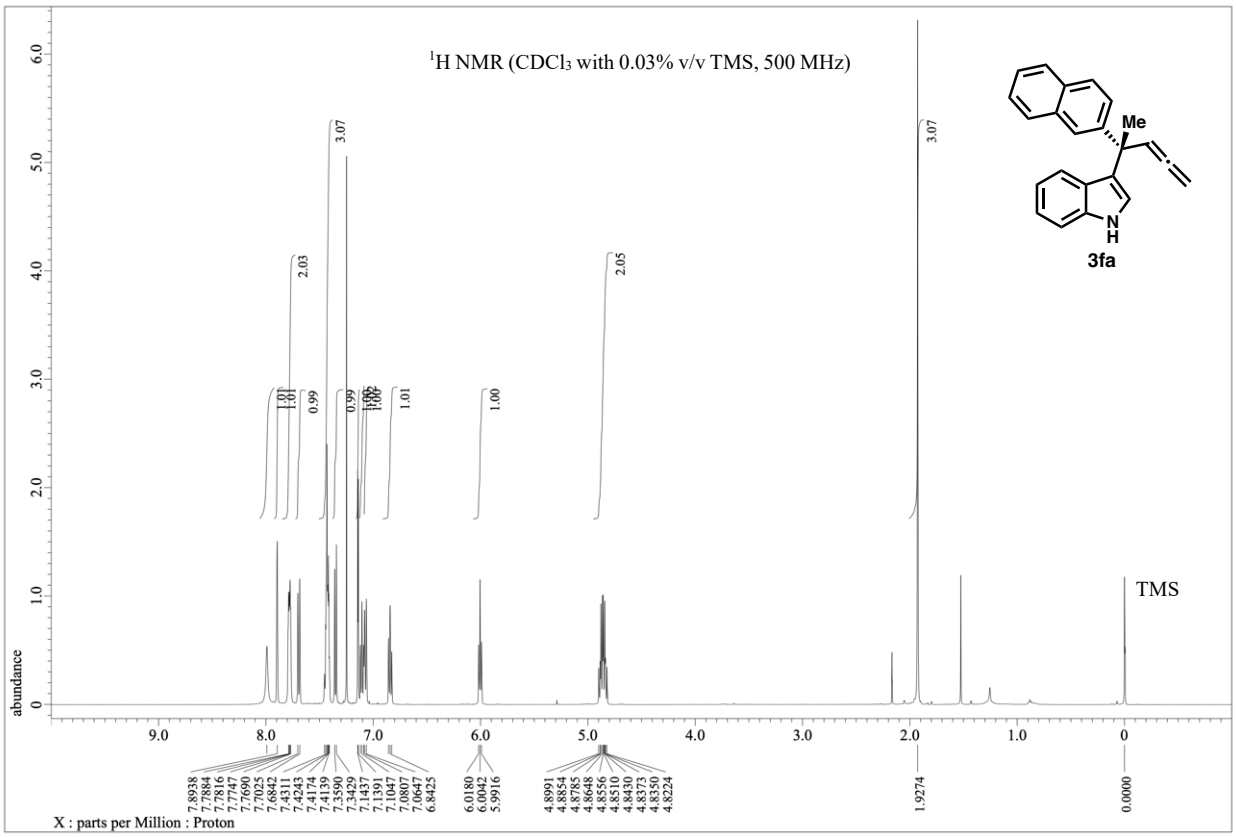

^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 101 MHz)
Br
Me
N
H
3ea
CDCl$_3$
(thousandths)
X : parts per Million : Carbon13

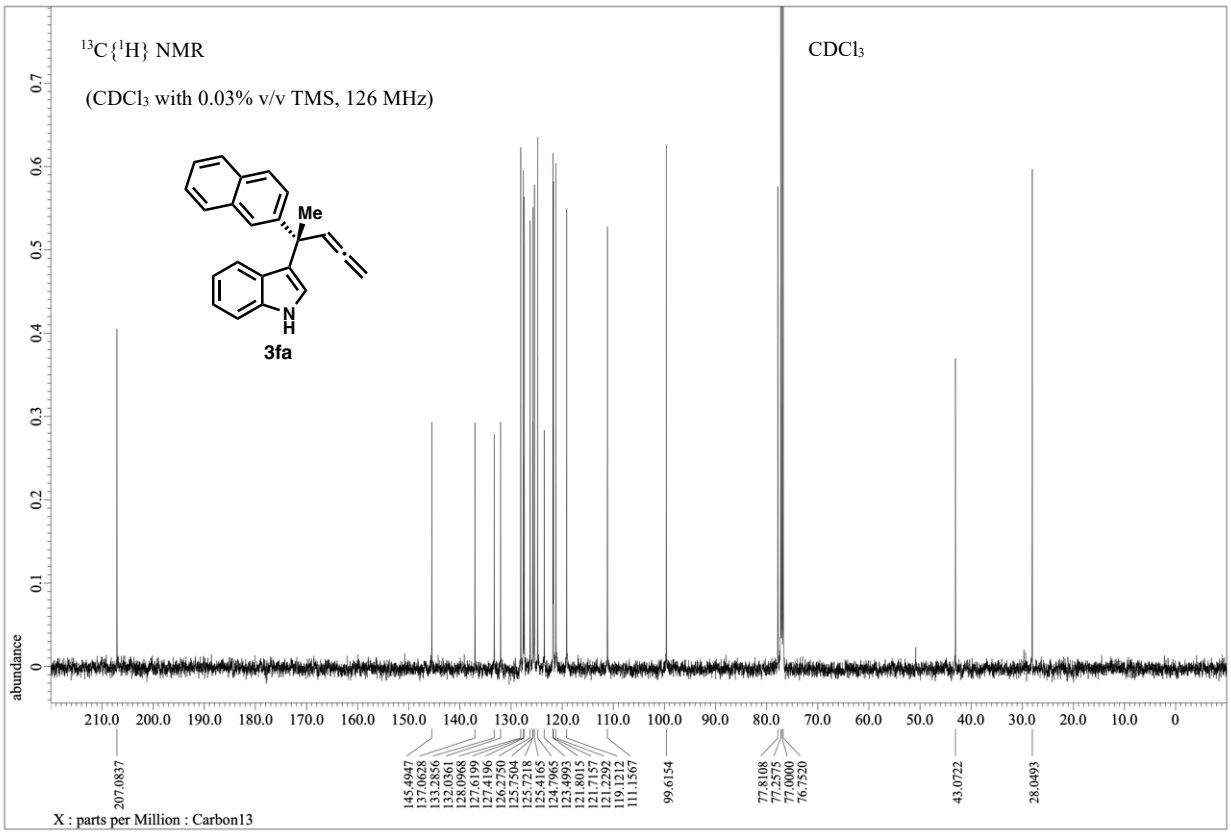


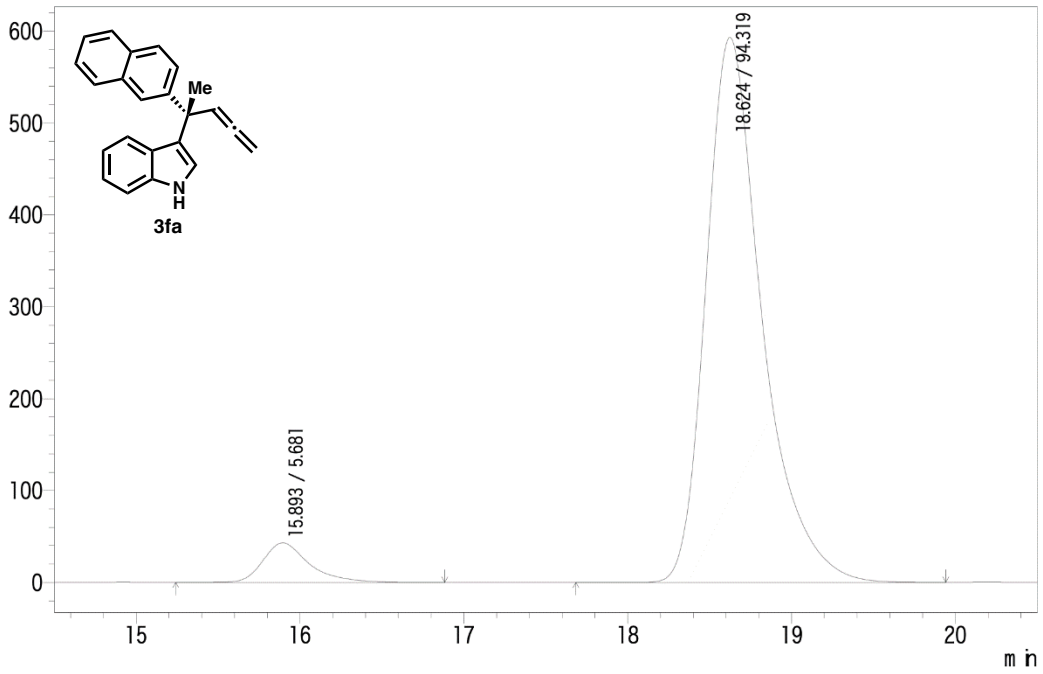
peak#	retention time	area%
1	11.557	4.231
2	12.557	95.769
Total		100.000



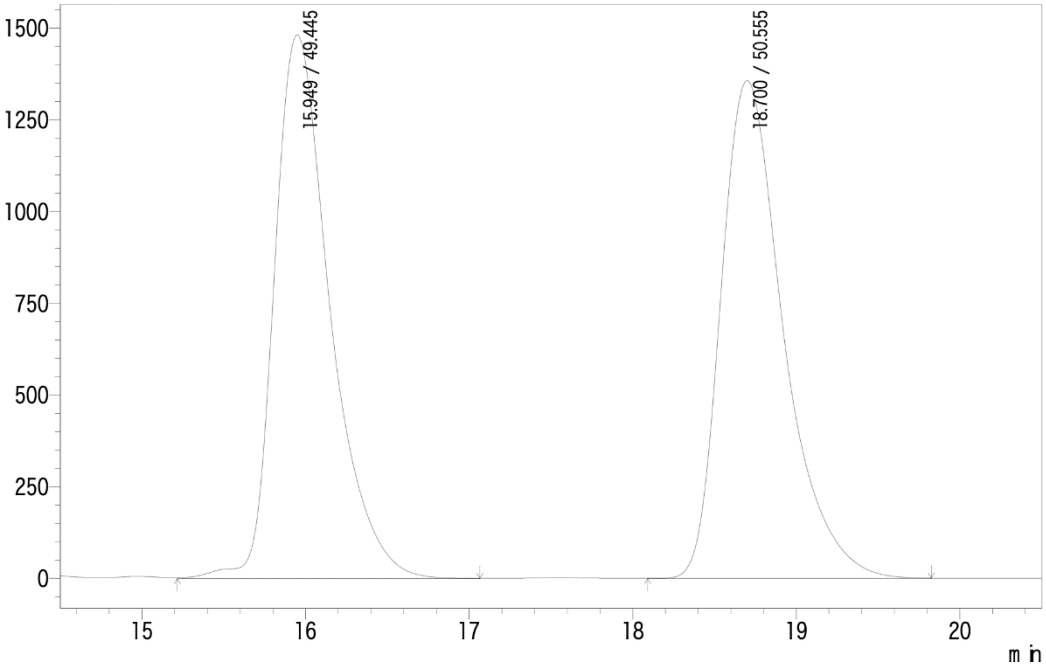
peak#	retention time	area%
1	11.374	49.177
2	12.269	50.823
Total		100.000


^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 500 MHz)
Me
N
H
3fa
TMS
abundance
X : parts per Million : Proton

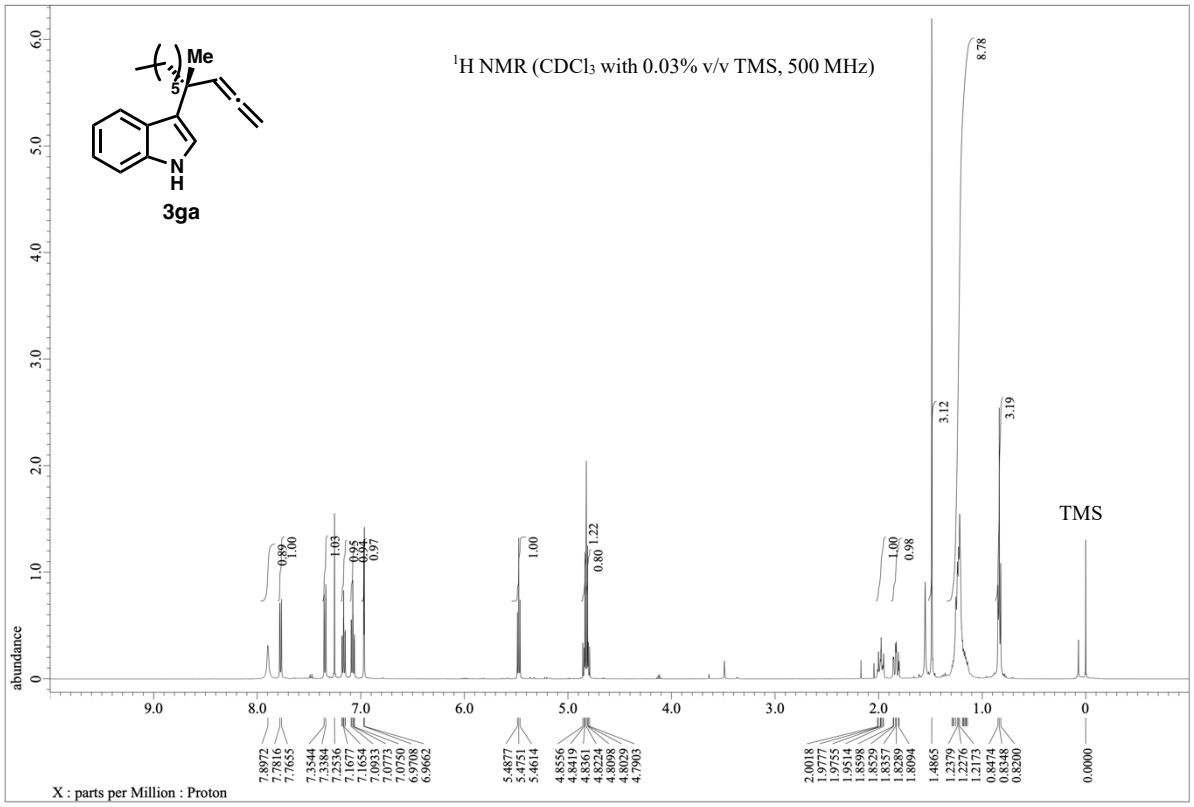

^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 126 MHz)
CDCl$_3$
Me
N
H
3fa
abundance
X : parts per Million : Carbon13

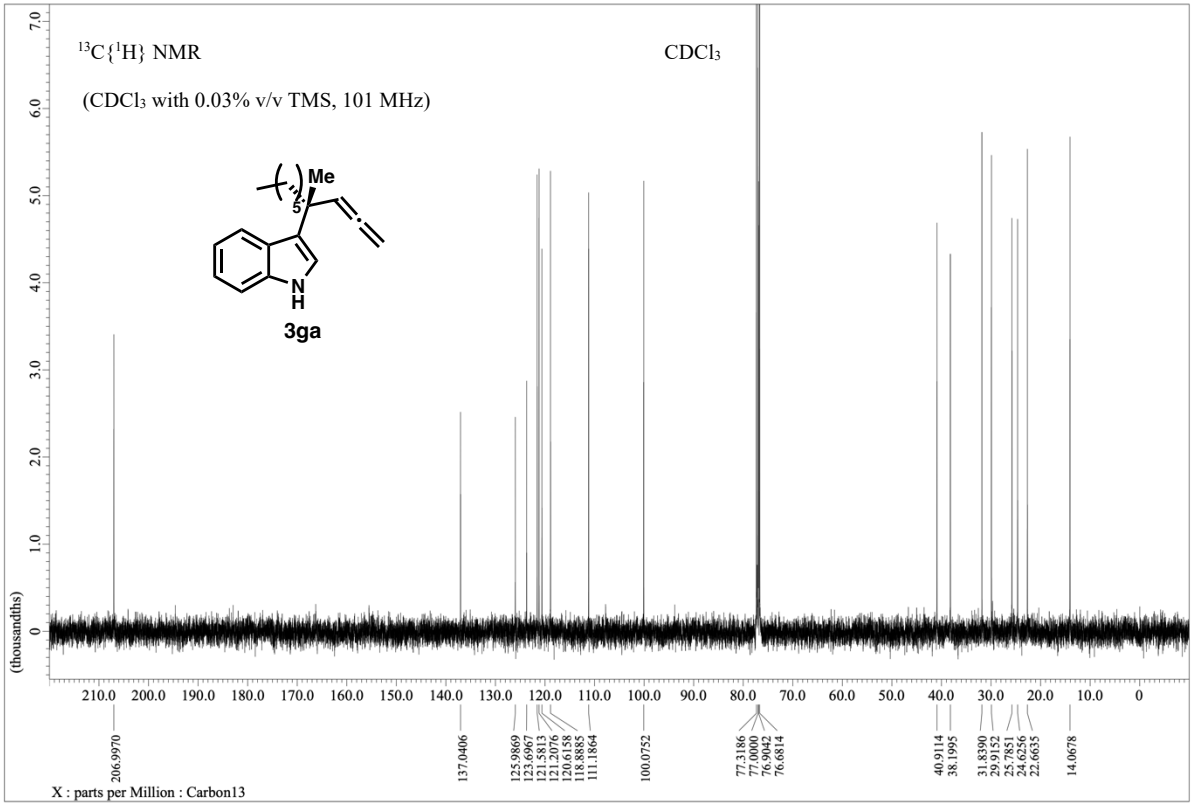


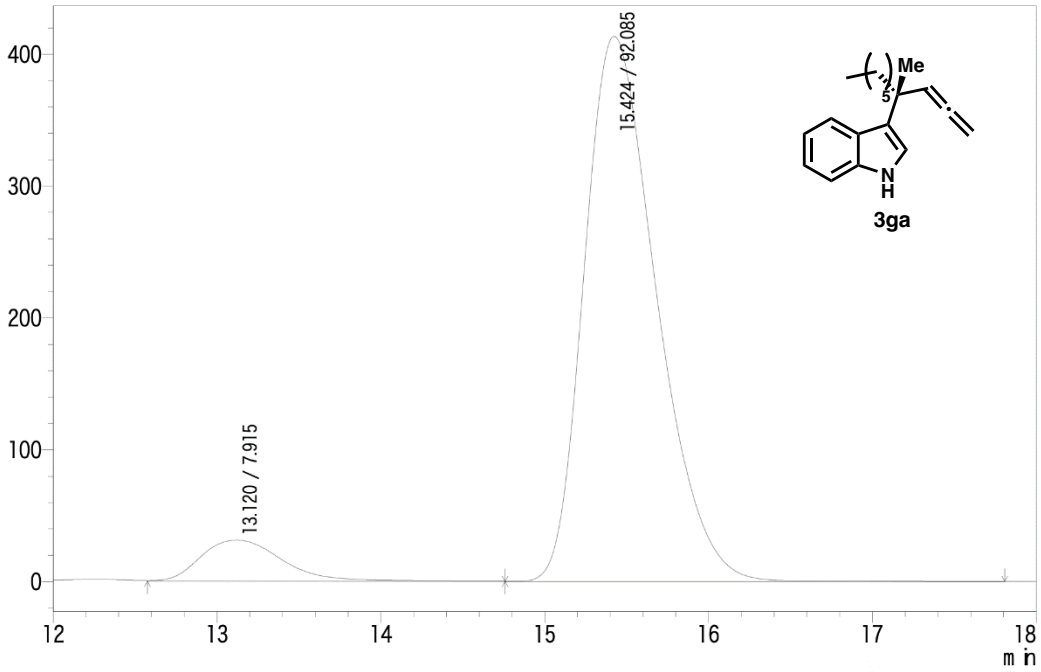
peak#	retention time	area%
1	15.893	5.681
2	18.624	94.319
Total		100.000



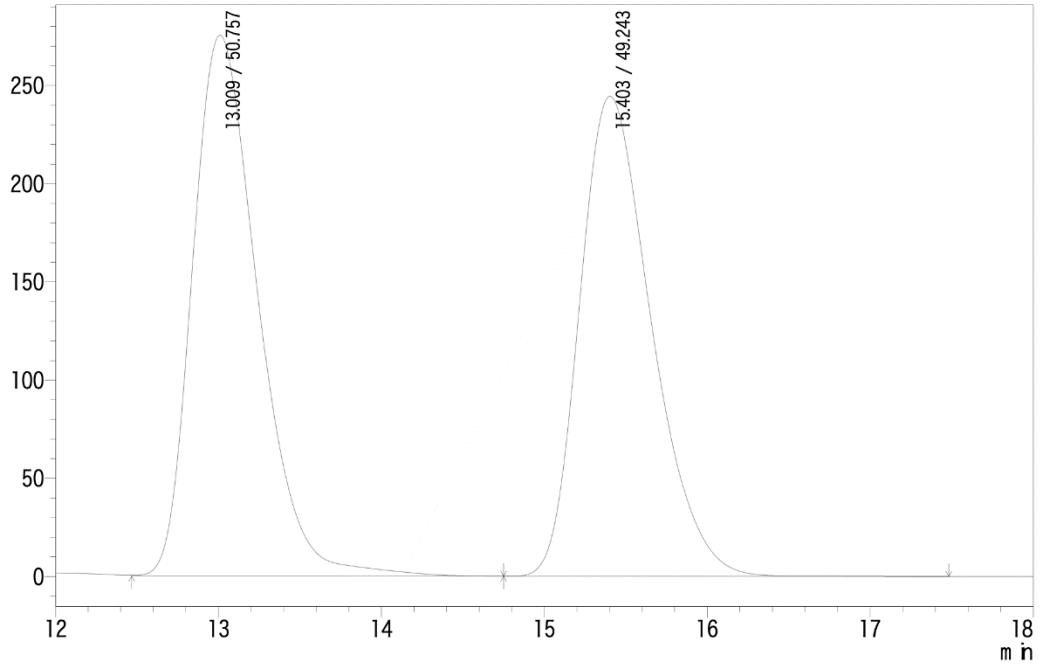
peak#	retention time	area%
1	15.949	49.445
2	18.700	50.555
Total		100.000


Me
5
N
H
3ga
^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 500 MHz)
8.78
3.12
3.19
TMS
abundance
X : parts per Million : Proton

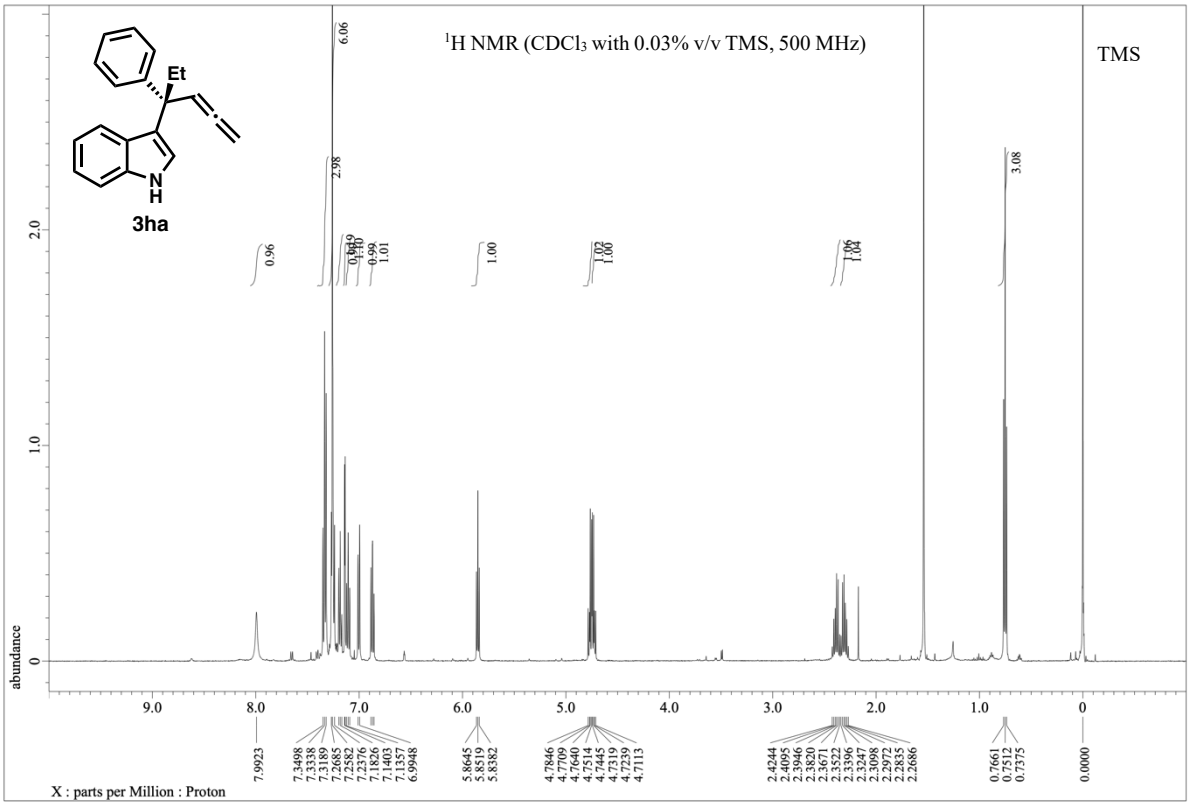

^{13}C{^{1}H} NMR
CDCl$_3$
(CDCl$_3$ with 0.03% v/v TMS, 101 MHz)
Me
5
N
H
3ga
(thousandths)
X : parts per Million : Carbon13

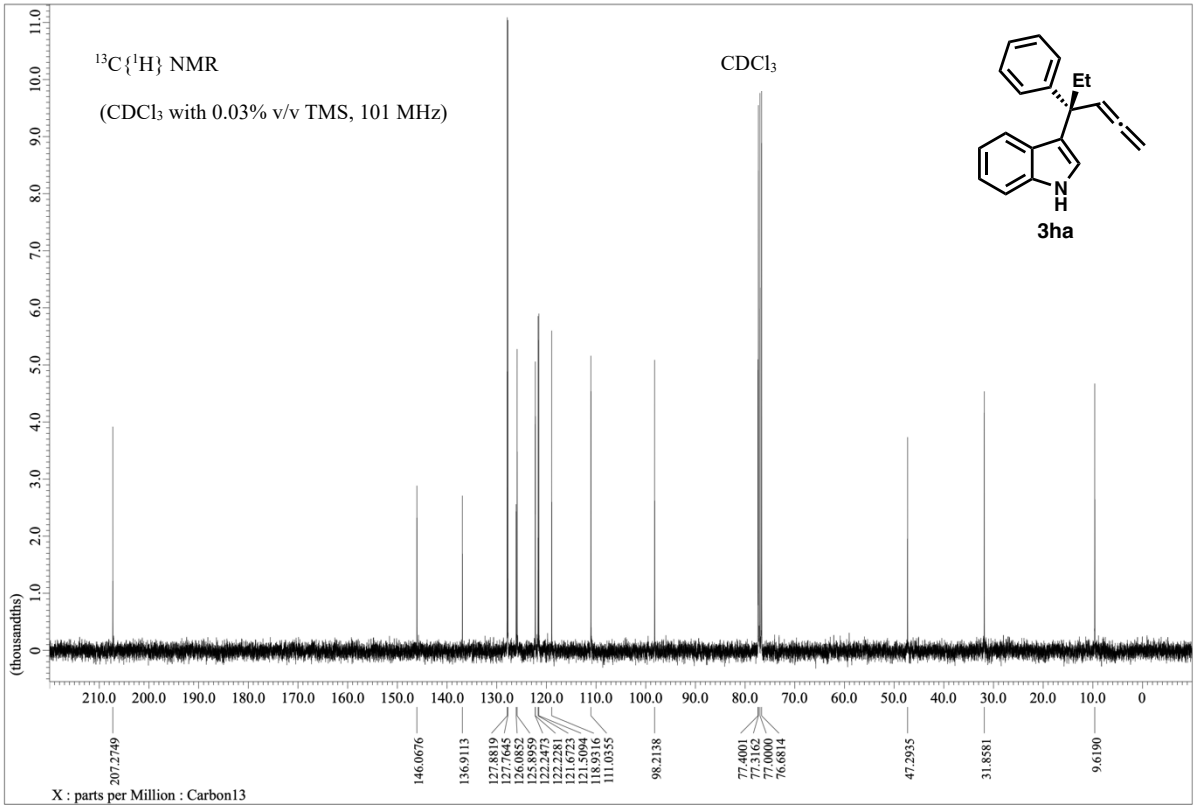


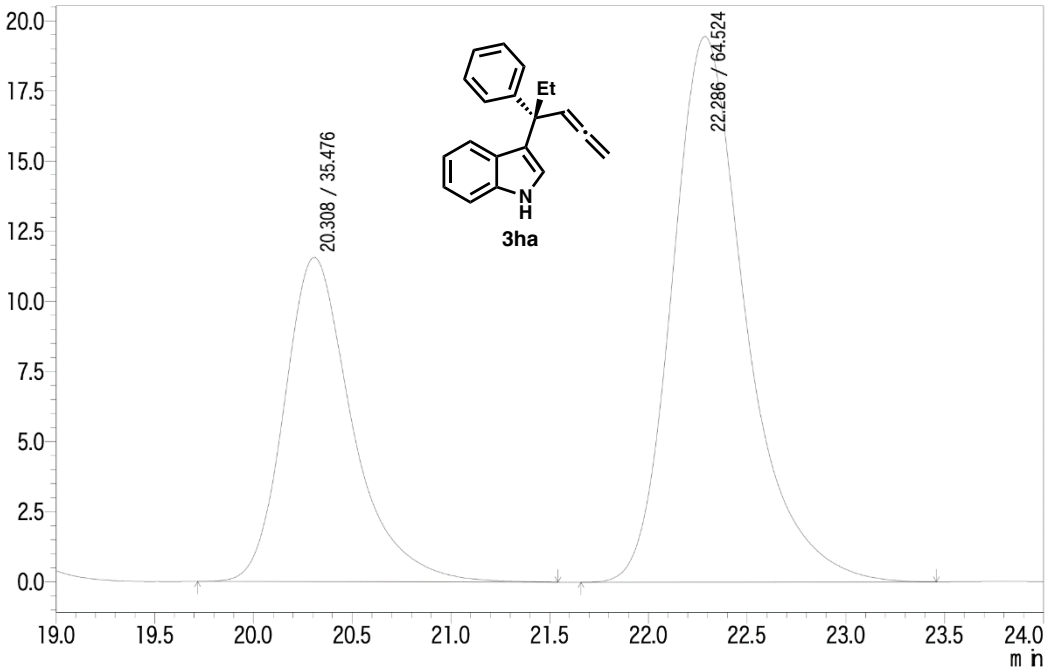
peak#	retention time	area%
1	13.120	7.915
2	15.424	92.085
Total		100.000



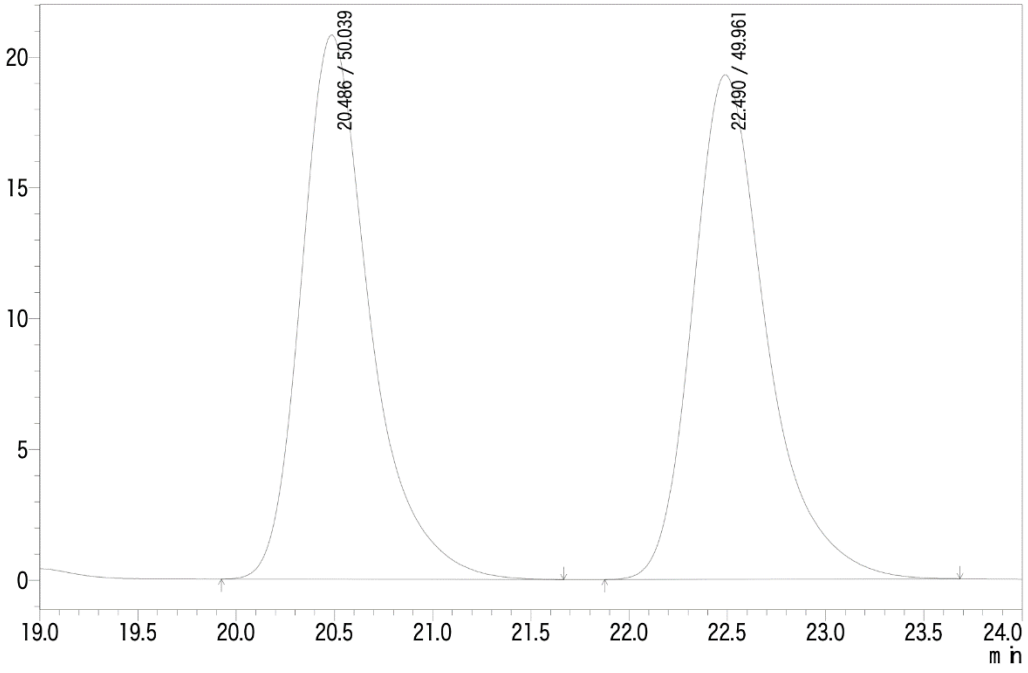
peak#	retention time	area%
1	13.009	50.757
2	15.403	49.243
Total		100.000


^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 500 MHz)
TMS
Et
N
H
3ha
abundance
X : parts per Million : Proton

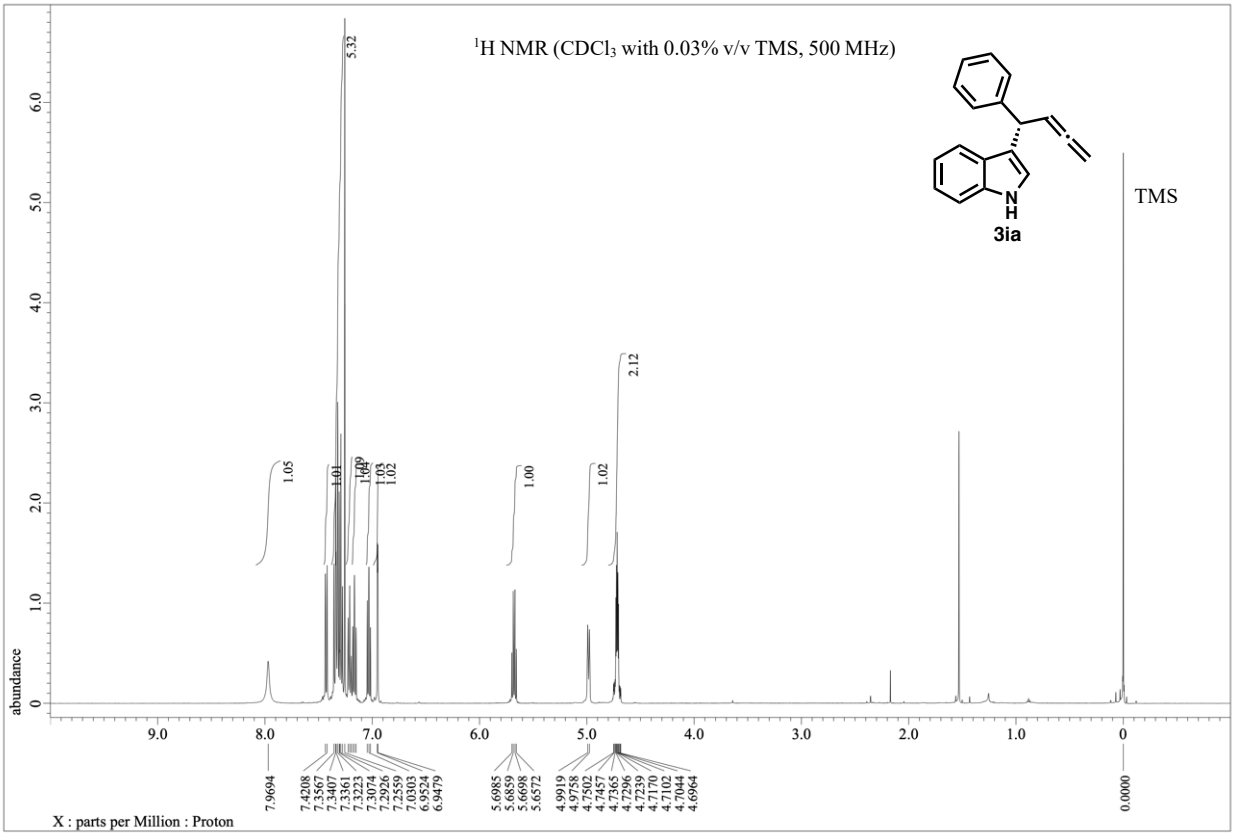

^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 101 MHz)
CDCl$_3$
Et
N
H
3ha
(thousandths)
X : parts per Million : Carbon13

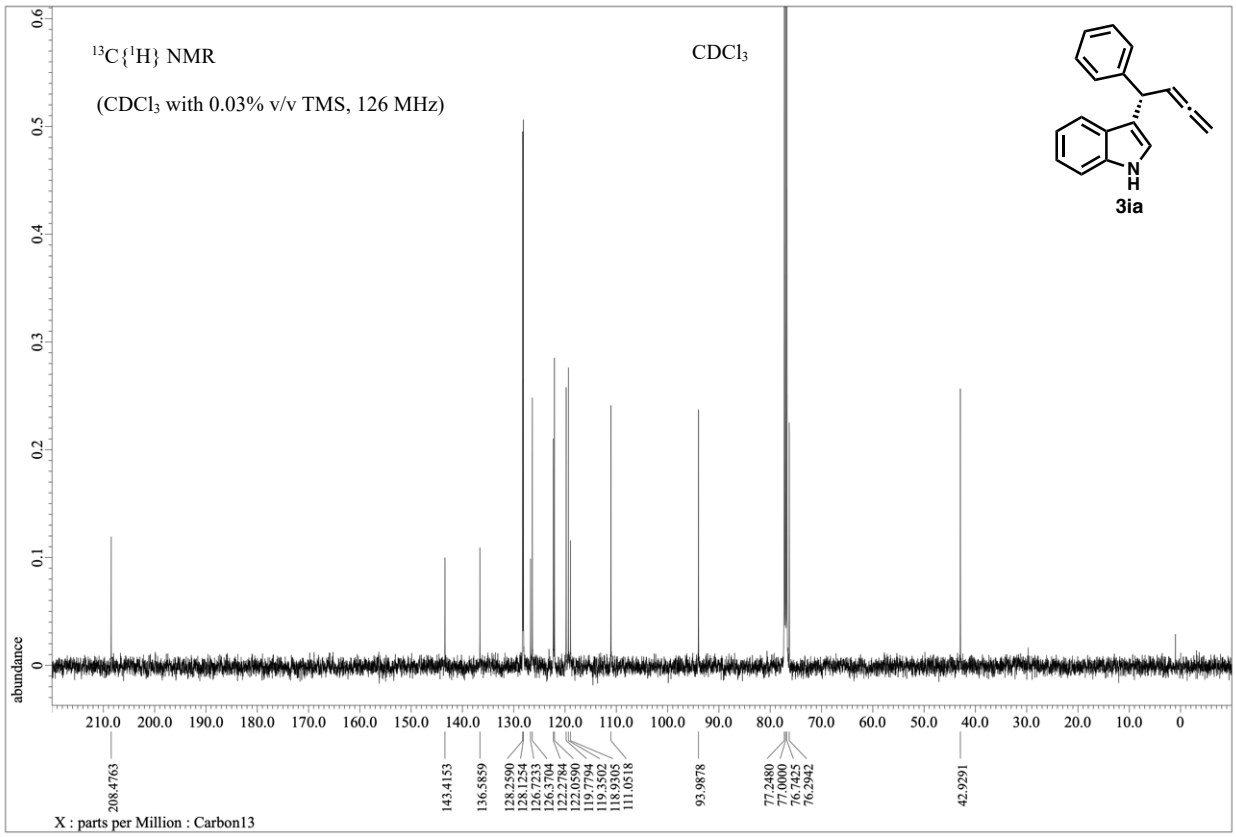


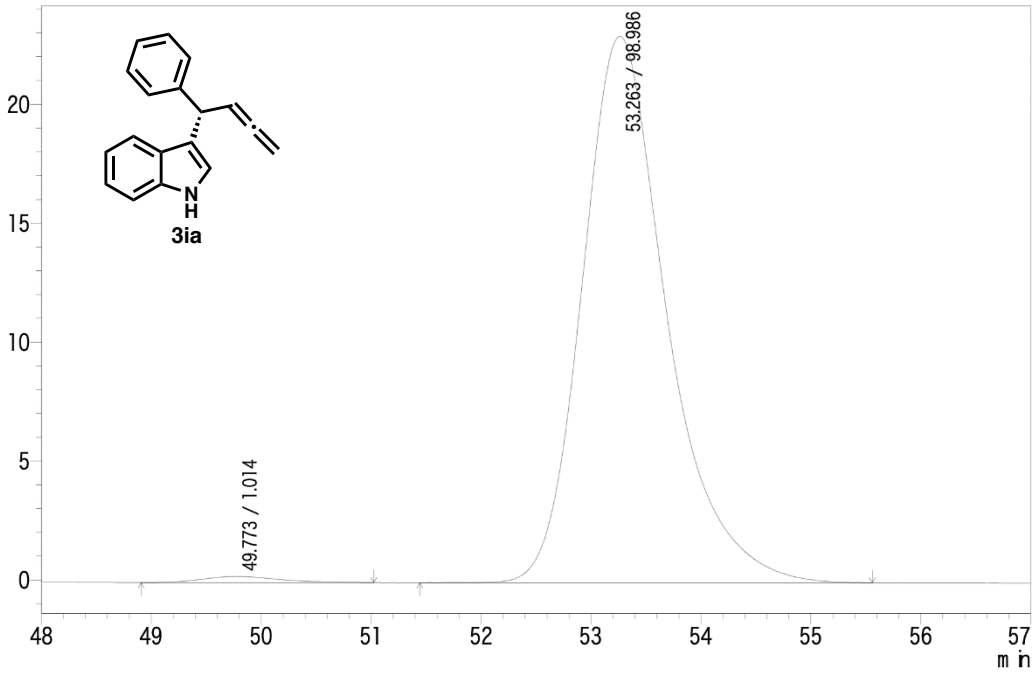
peak#	retention time	area%
1	20.308	35.476
2	22.286	64.524
Total		100.000



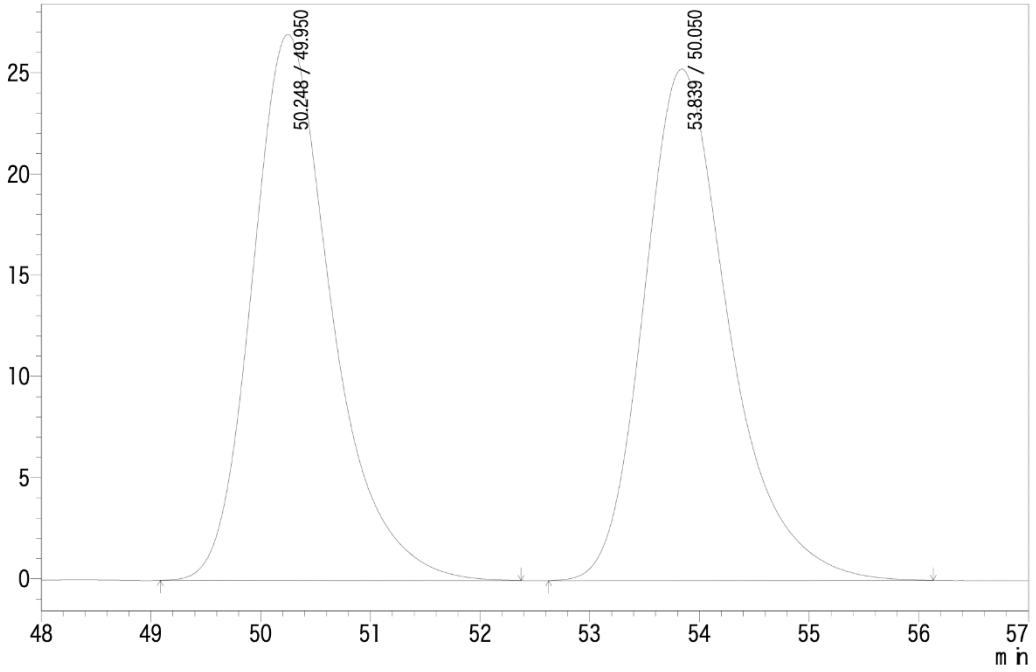
peak#	retention time	area%
1	20.486	50.039
2	22.490	49.961
Total		100.000


^{1}H NMR ($CDCl_3$ with 0.03% v/v TMS, 500 MHz)
3ia
TMS
abundance
X : parts per Million : Proton

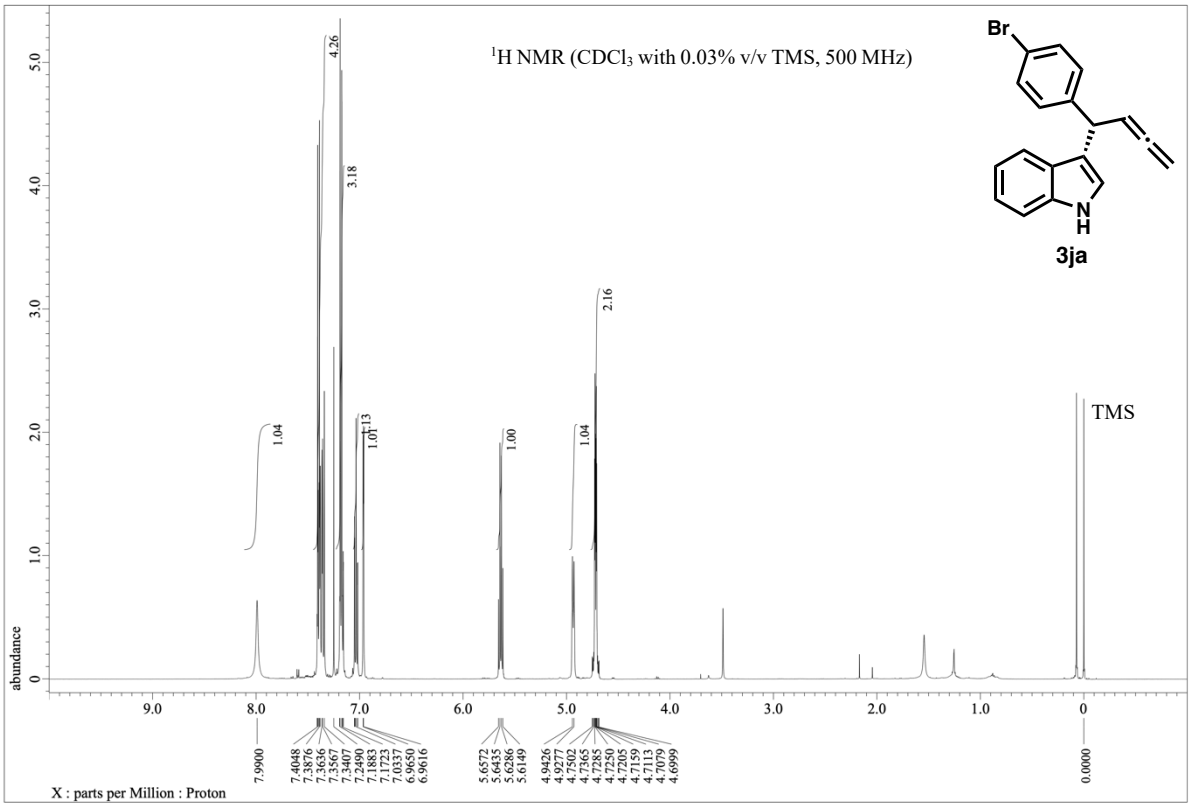

$^{13}C\{^1H\}$ NMR
($CDCl_3$ with 0.03% v/v TMS, 126 MHz)
$CDCl_3$
3ia
abundance
X : parts per Million : Carbon13

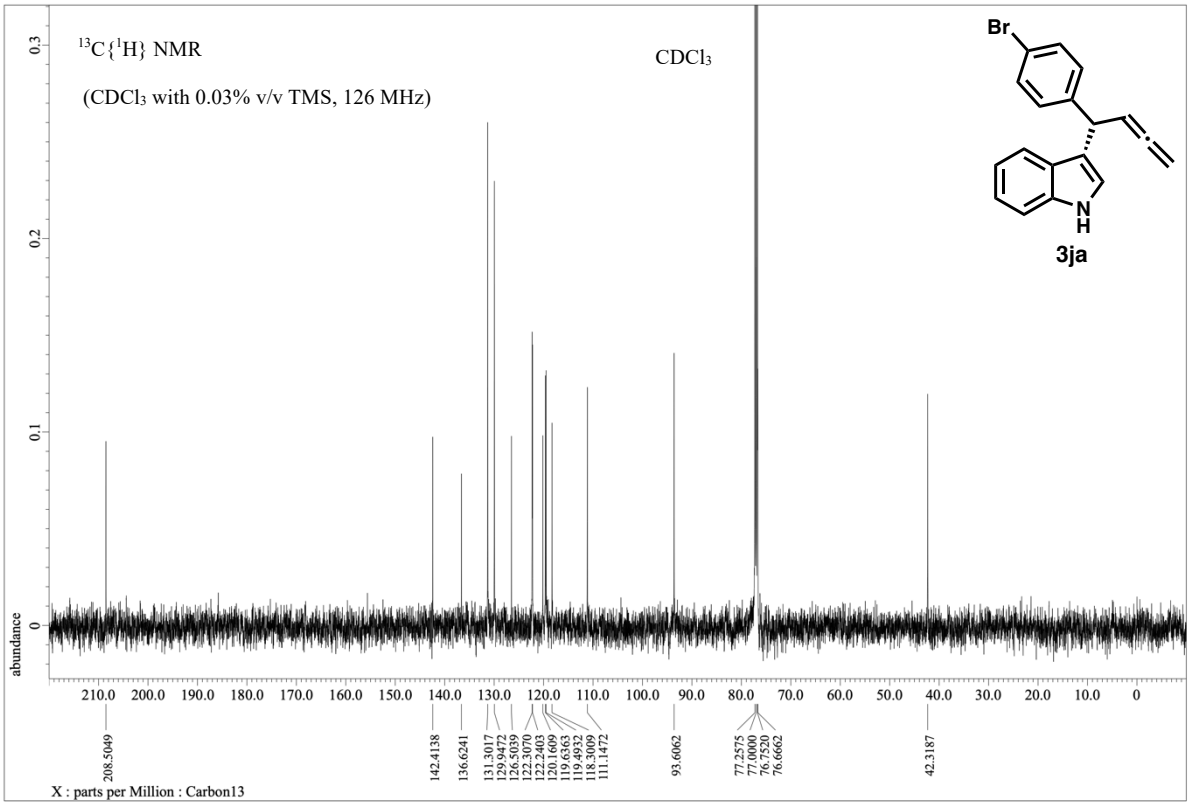


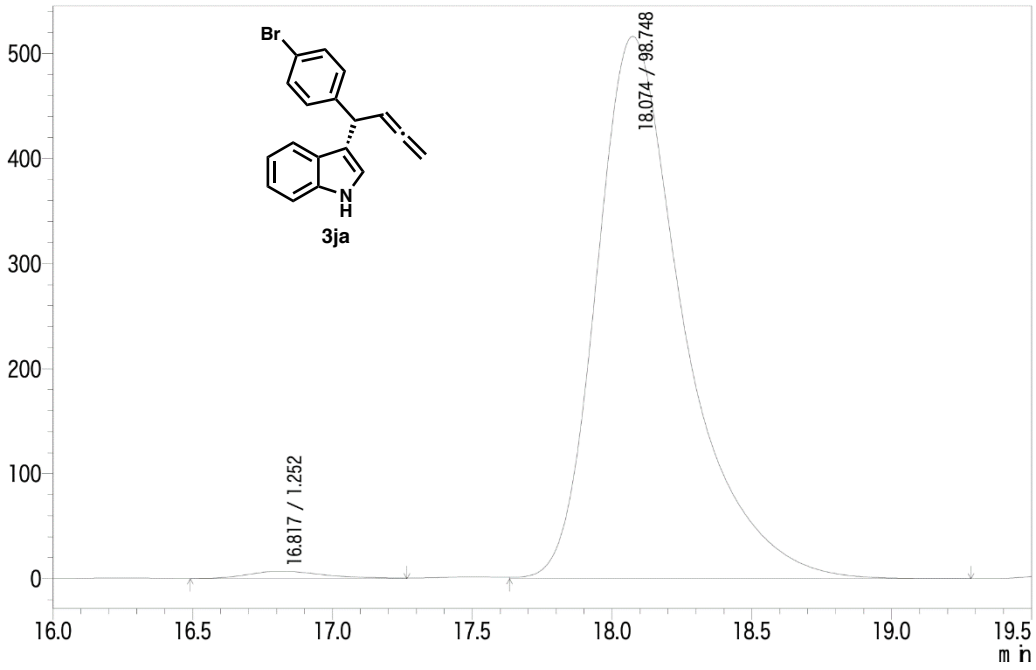
peak#	retention time	area%
1	49.773	1.014
2	53.263	98.986
Total		100.000



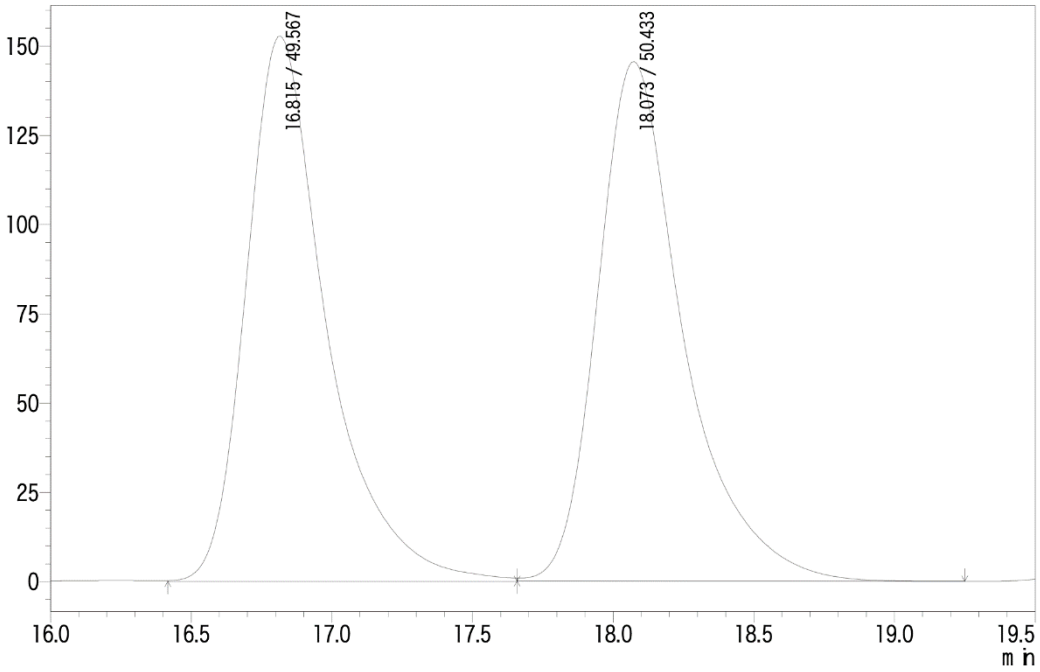
peak#	retention time	area%
1	50.248	49.950
2	53.839	50.050
Total		100.000


^{1}H NMR ($CDCl_3$ with 0.03% v/v TMS, 500 MHz)
Br
N
H
3ja
TMS
abundance
X : parts per Million : Proton

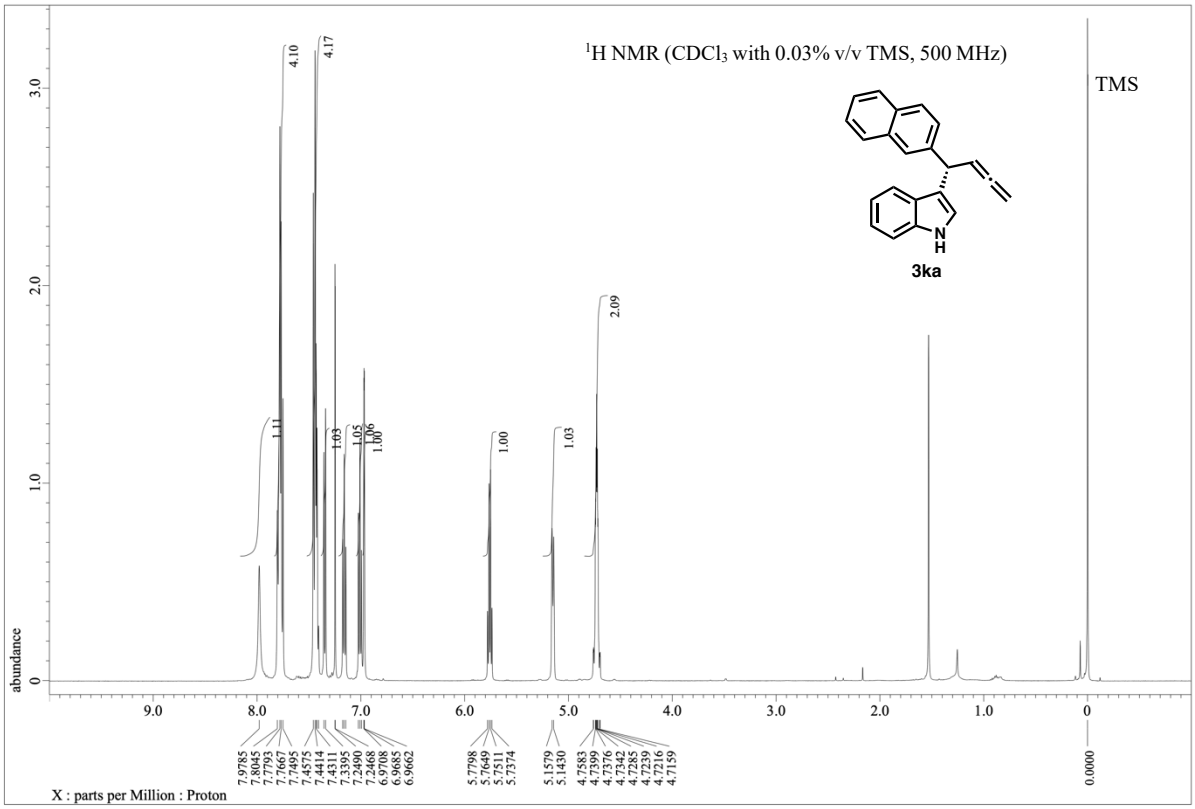

$^{13}C\{^1H\}$ NMR
($CDCl_3$ with 0.03% v/v TMS, 126 MHz)
$CDCl_3$
Br
N
H
3ja
abundance
X : parts per Million : Carbon13

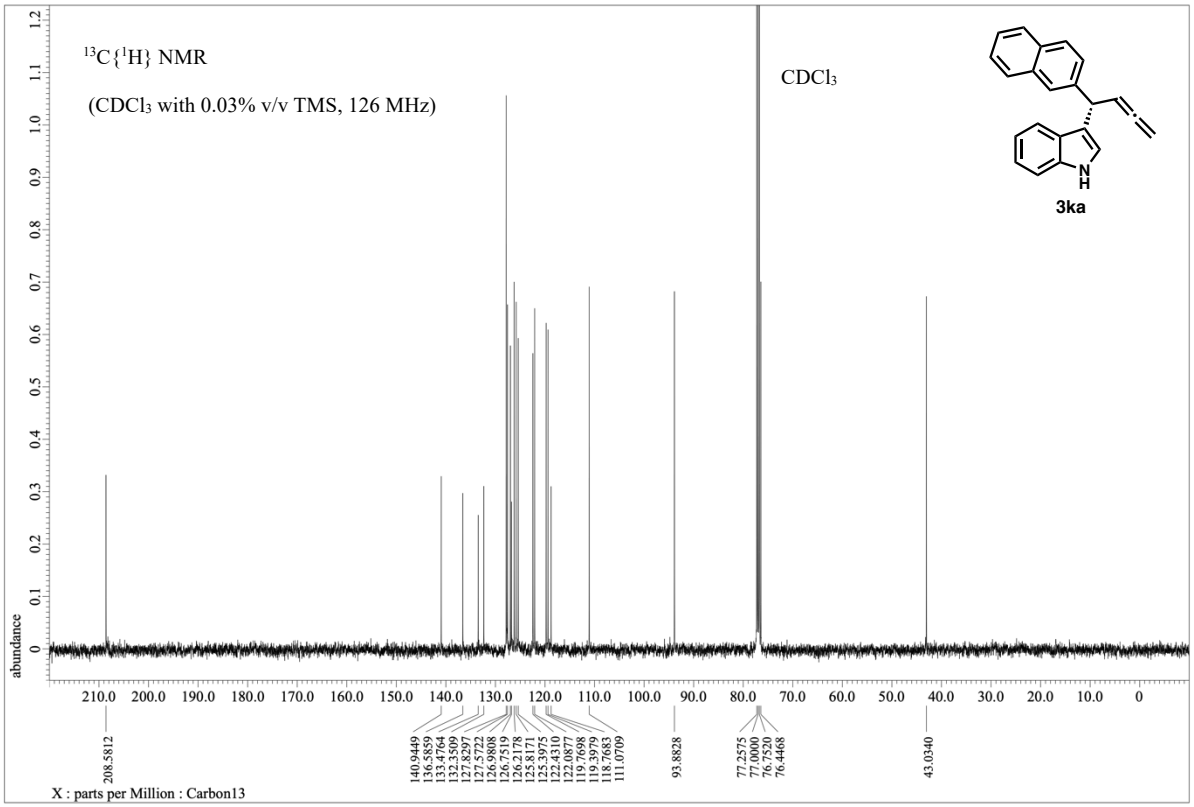


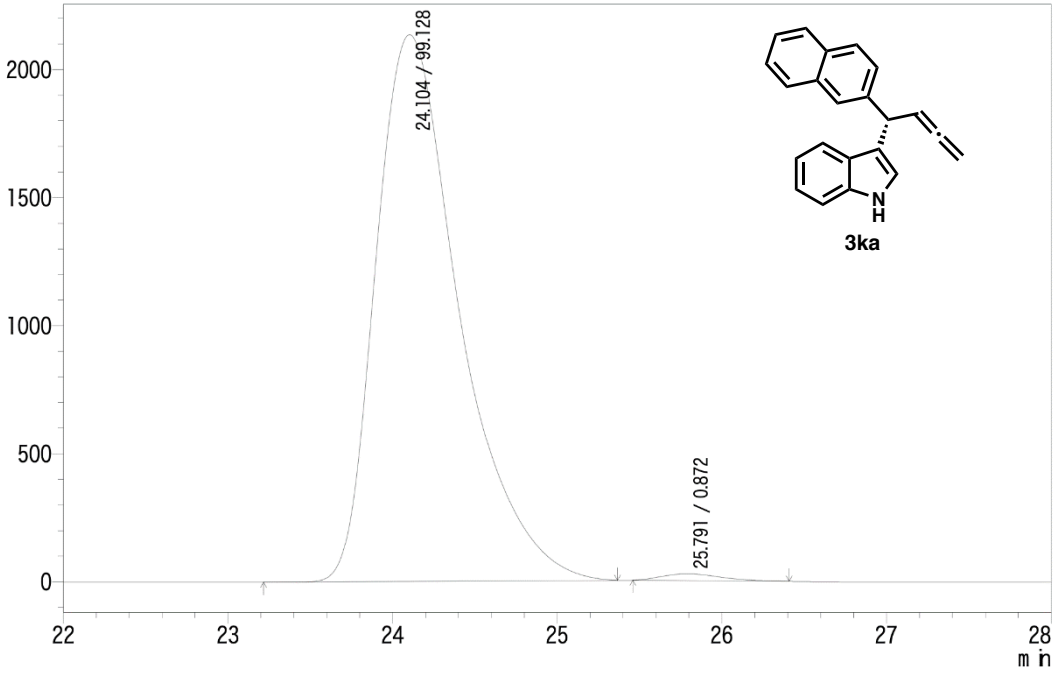
peak#	retention time	area%
1	16.817	1.252
2	18.074	98.748
Total		100.000



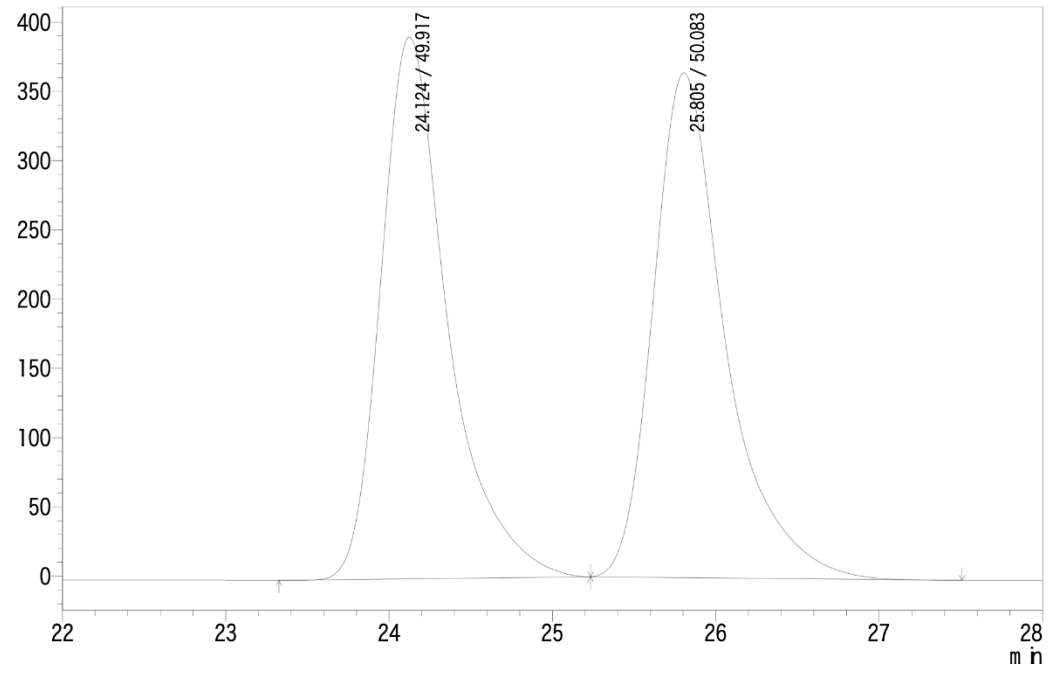
peak#	retention time	area%
1	16.815	49.567
2	18.073	50.433
Total		100.000


^{1}H NMR ($CDCl_3$ with 0.03% v/v TMS, 500 MHz)
TMS
3ka
abundance
X : parts per Million : Proton

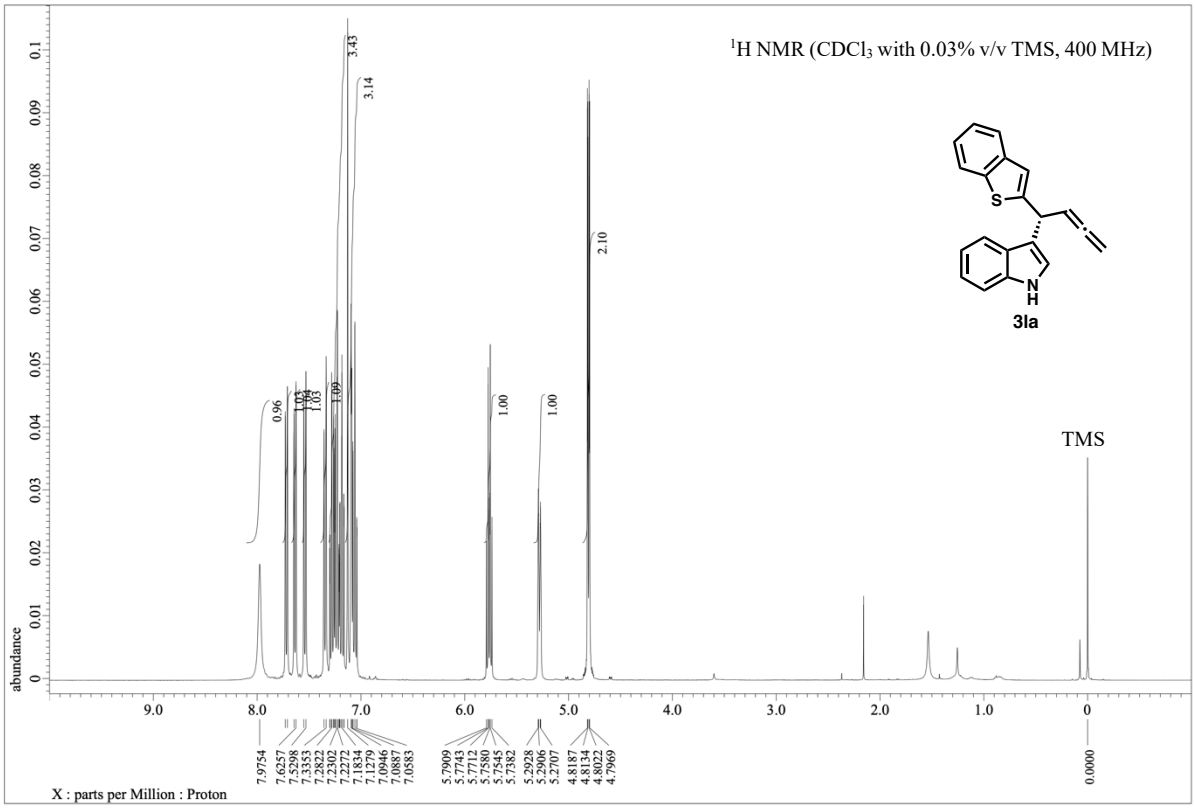

^{13}C{^{1}H} NMR
($CDCl_3$ with 0.03% v/v TMS, 126 MHz)
$CDCl_3$
3ka
abundance
X : parts per Million : Carbon13

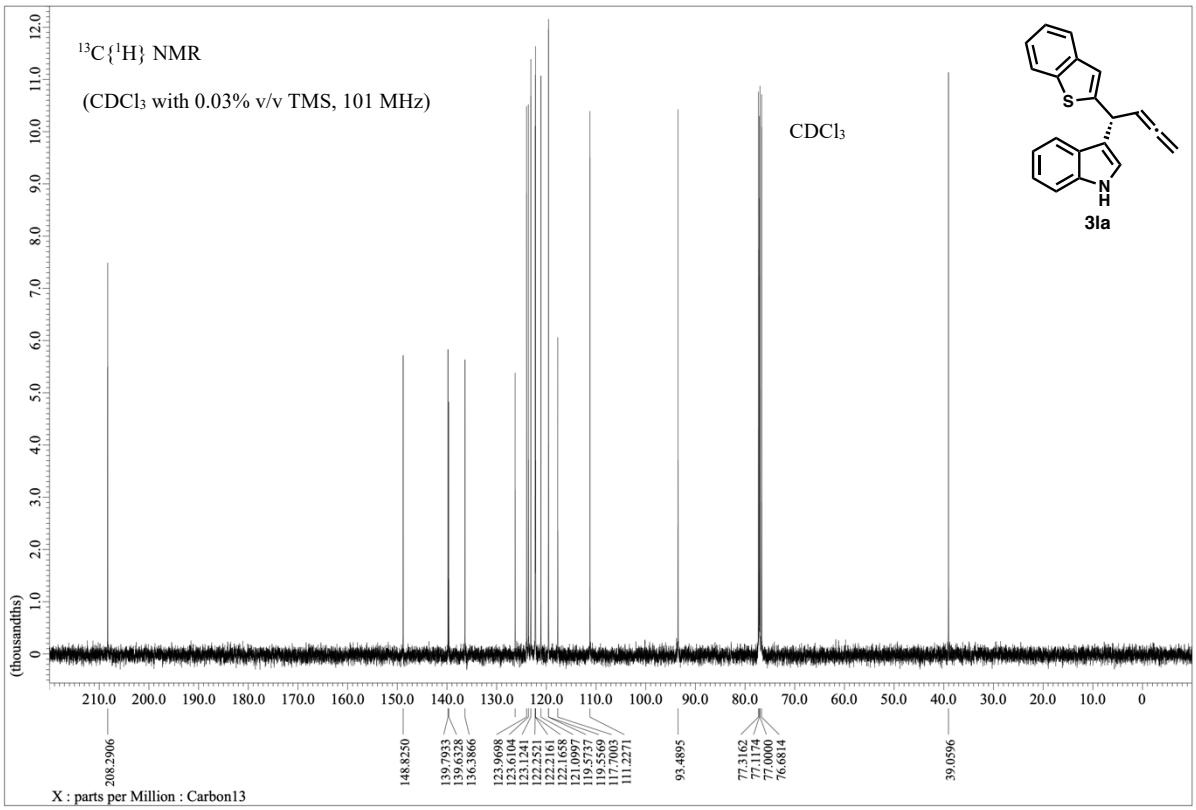


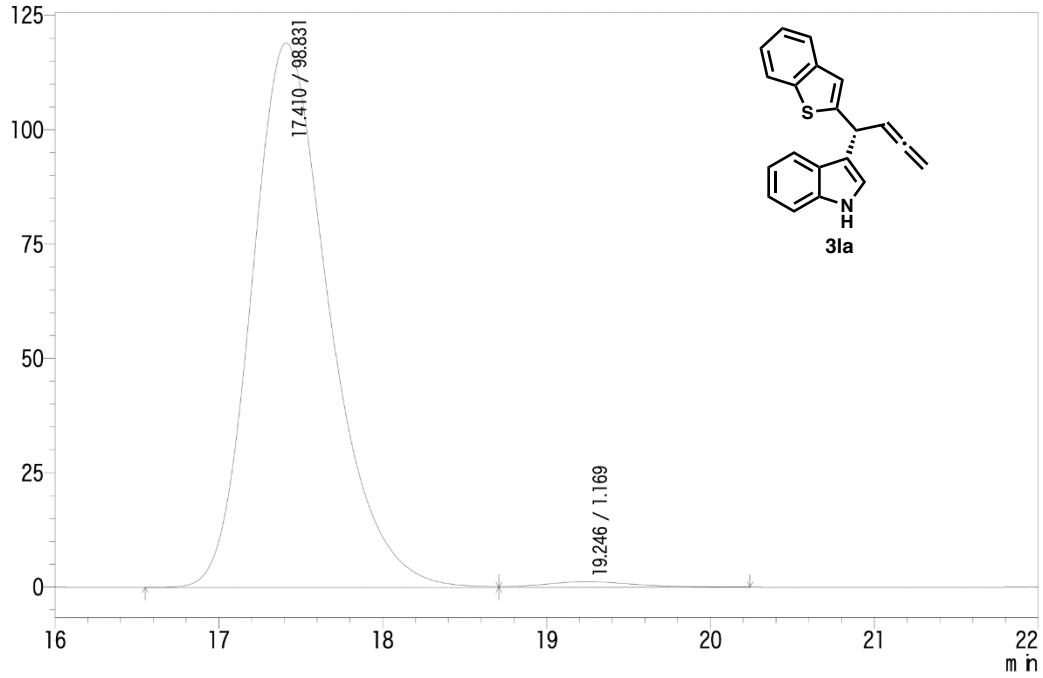
peak#	retention time	area%
1	24.104	99.128
2	25.791	0.872
Total		100.000



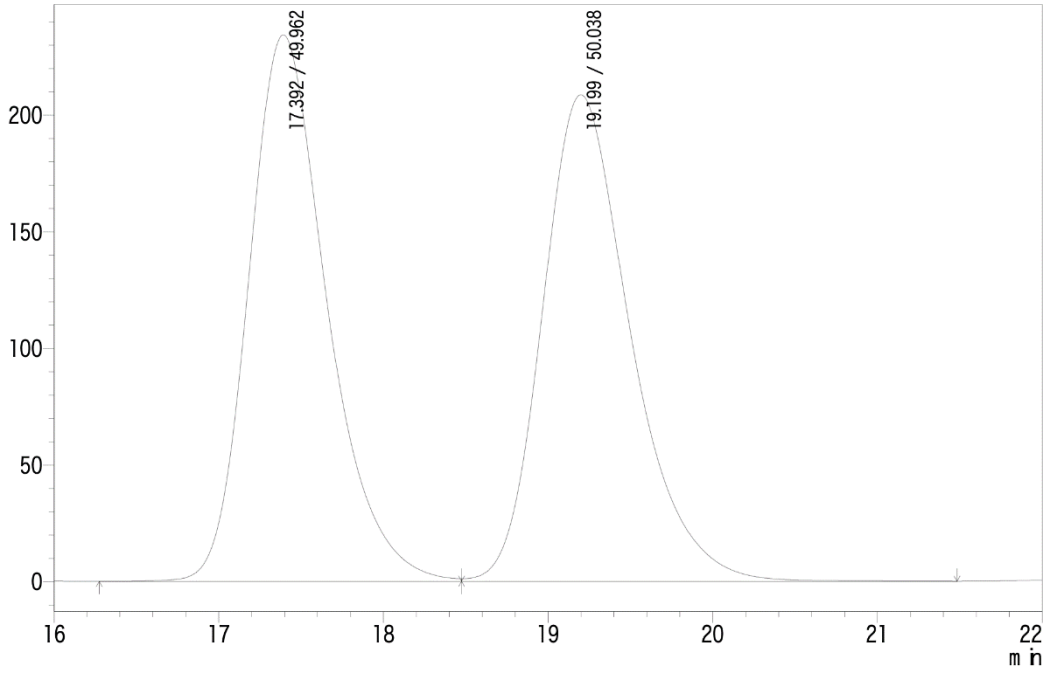
peak#	retention time	area%
1	24.124	49.917
2	25.805	50.083
Total		100.000


^{1}H NMR ($CDCl_3$ with 0.03% v/v TMS, 400 MHz)
3la
TMS
abundance
X : parts per Million : Proton

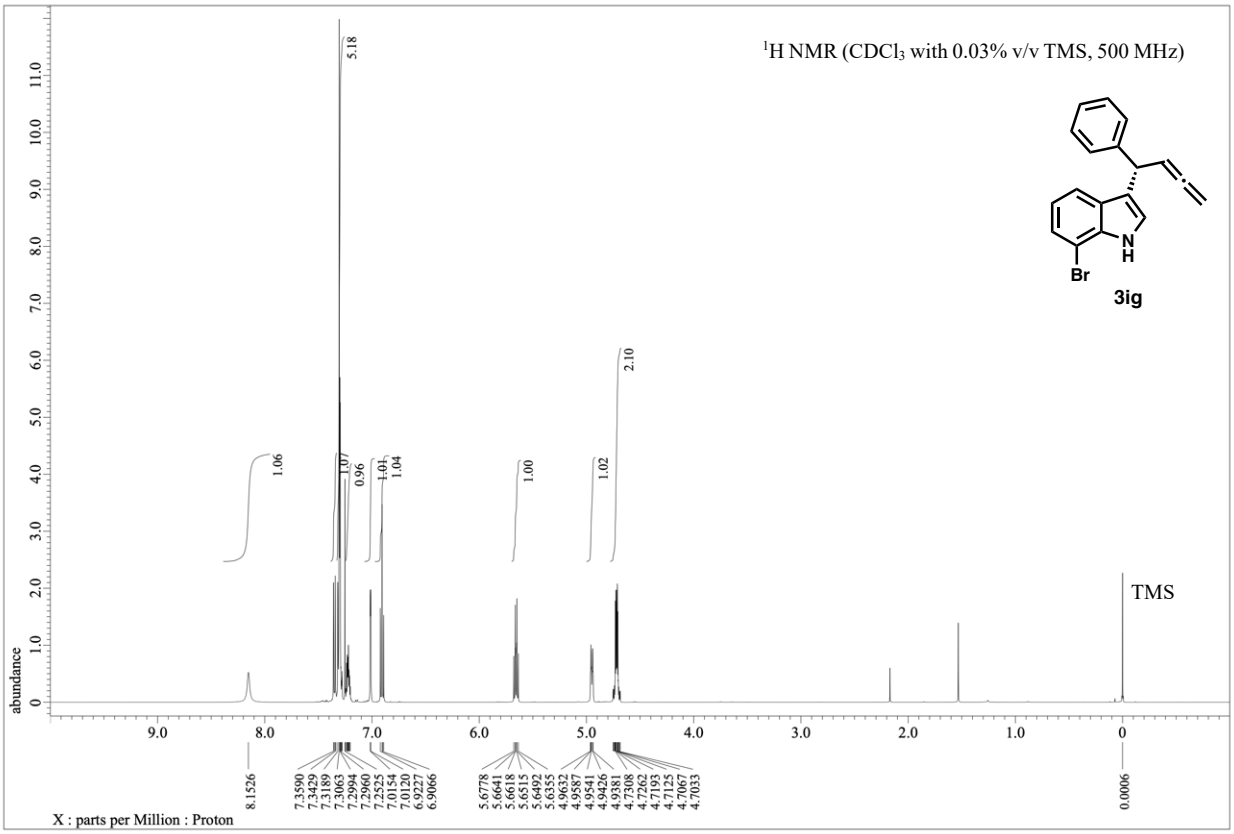

$^{13}C\{^{1}H\}$ NMR
($CDCl_3$ with 0.03% v/v TMS, 101 MHz)
$CDCl_3$
3la
(thousandths)
X : parts per Million : Carbon13

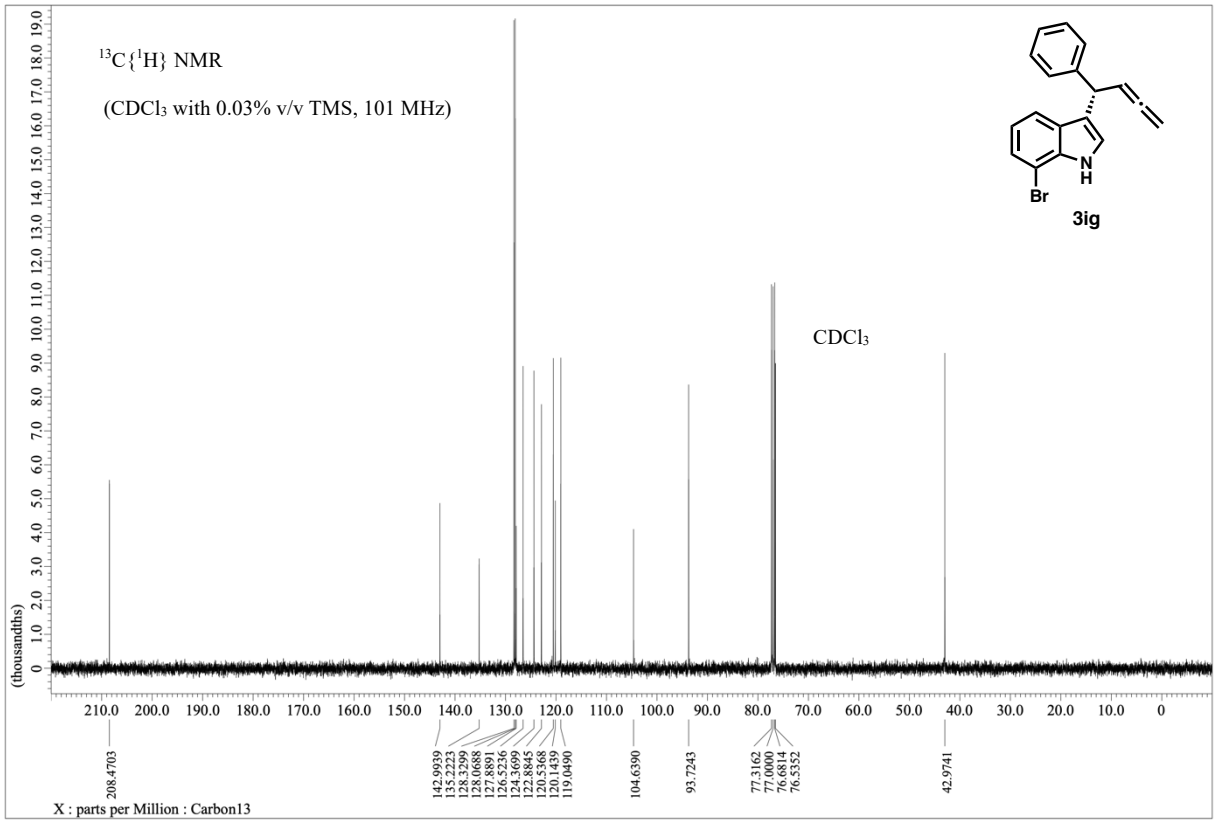


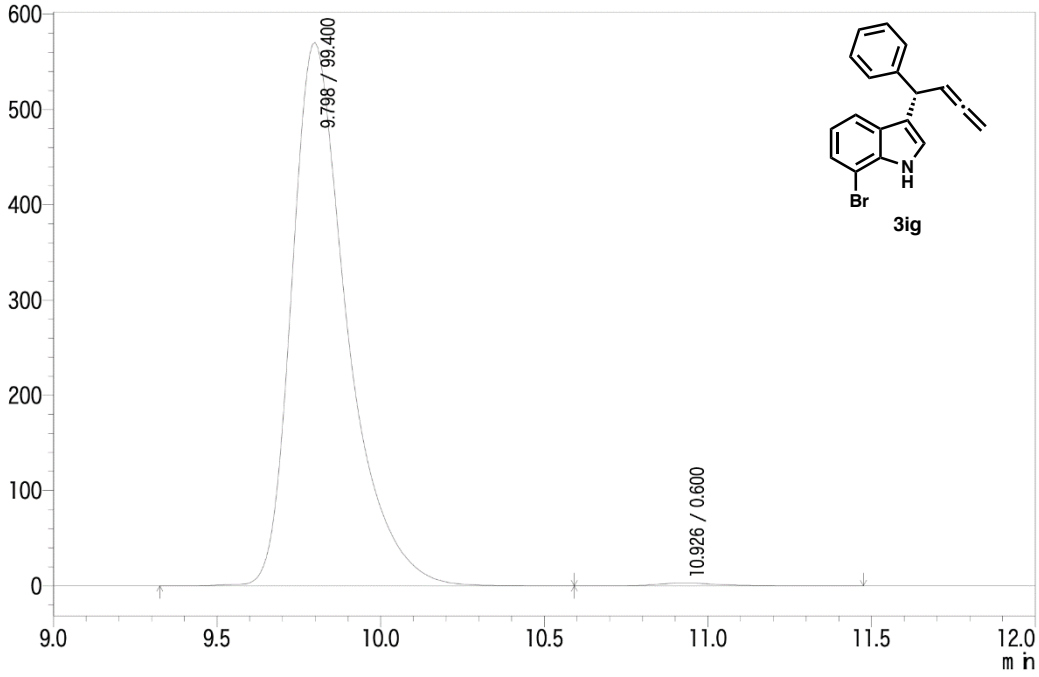
peak#	retention time	area%
1	17.410	98.831
2	19.246	1.169
Total		100.000



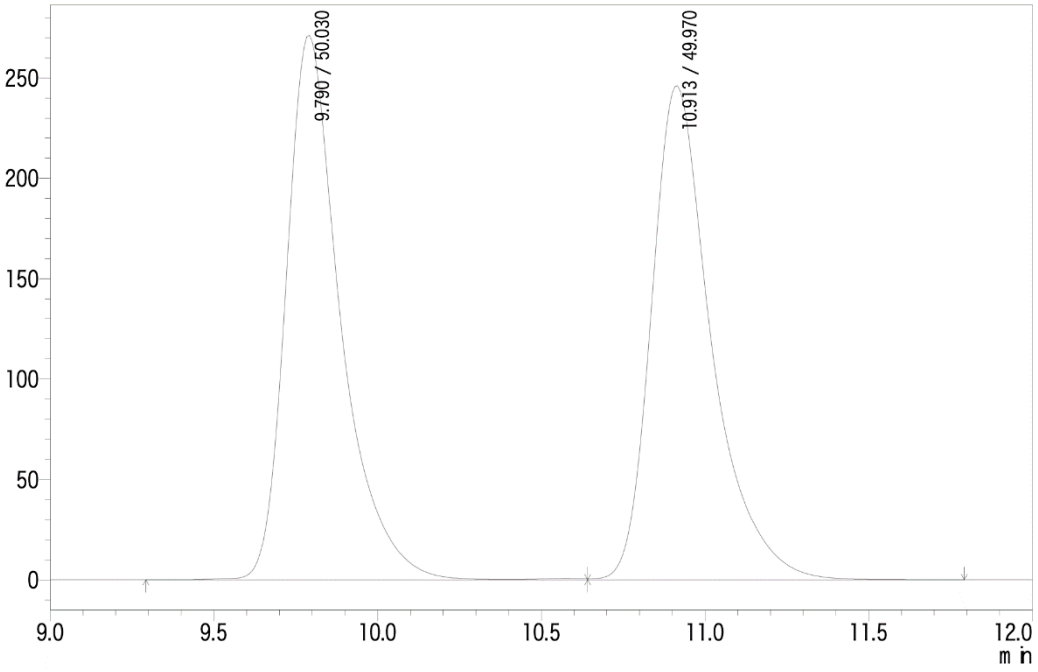
peak#	retention time	area%
1	17.392	49.962
2	19.199	50.038
Total		100.000


^{1}H NMR ($CDCl_3$ with 0.03% v/v TMS, 500 MHz)
3ig
TMS
abundance
X : parts per Million : Proton

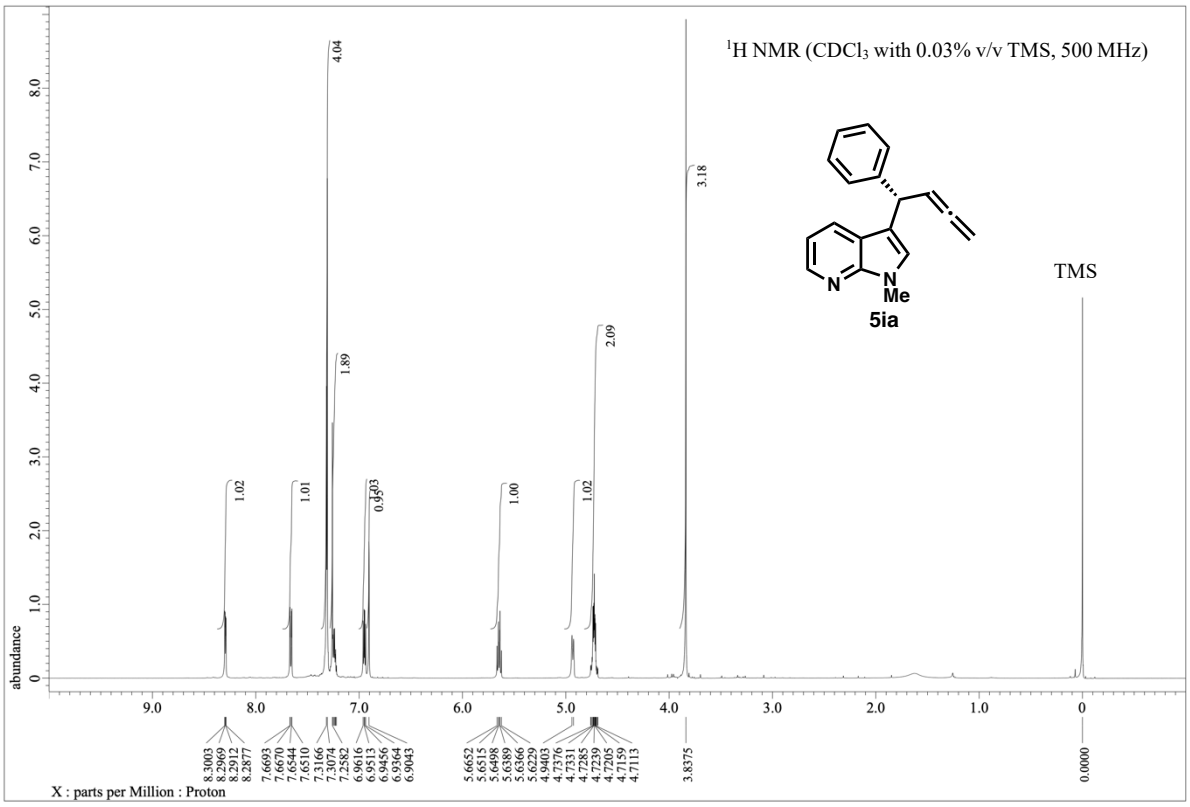

$^{13}C\{^1H\}$ NMR
($CDCl_3$ with 0.03% v/v TMS, 101 MHz)
3ig
$CDCl_3$
(thousandths)
X : parts per Million : Carbon13

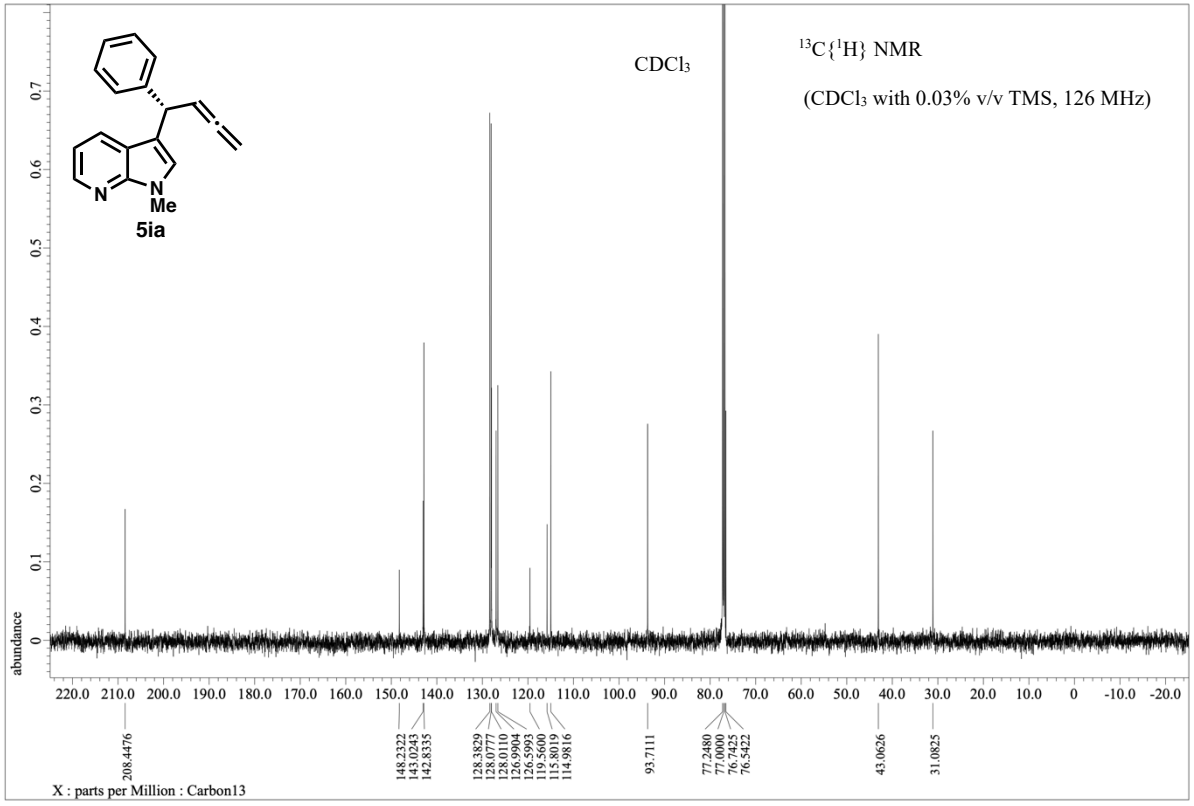


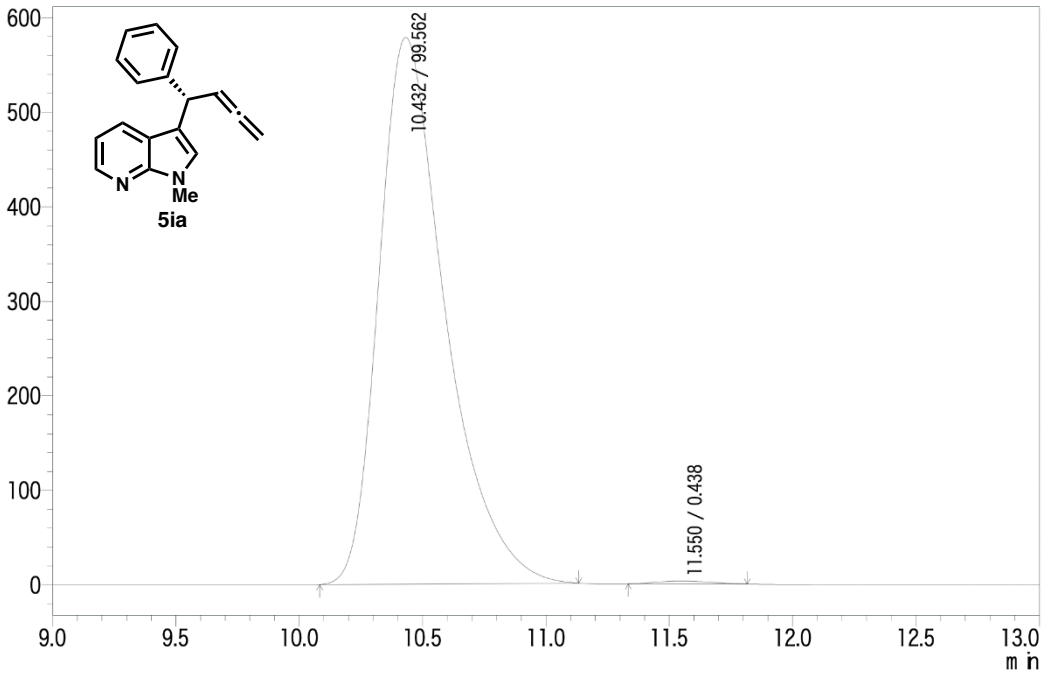
peak#	retention time	area%
1	9.798	99.400
2	10.926	0.600
Total		100.000



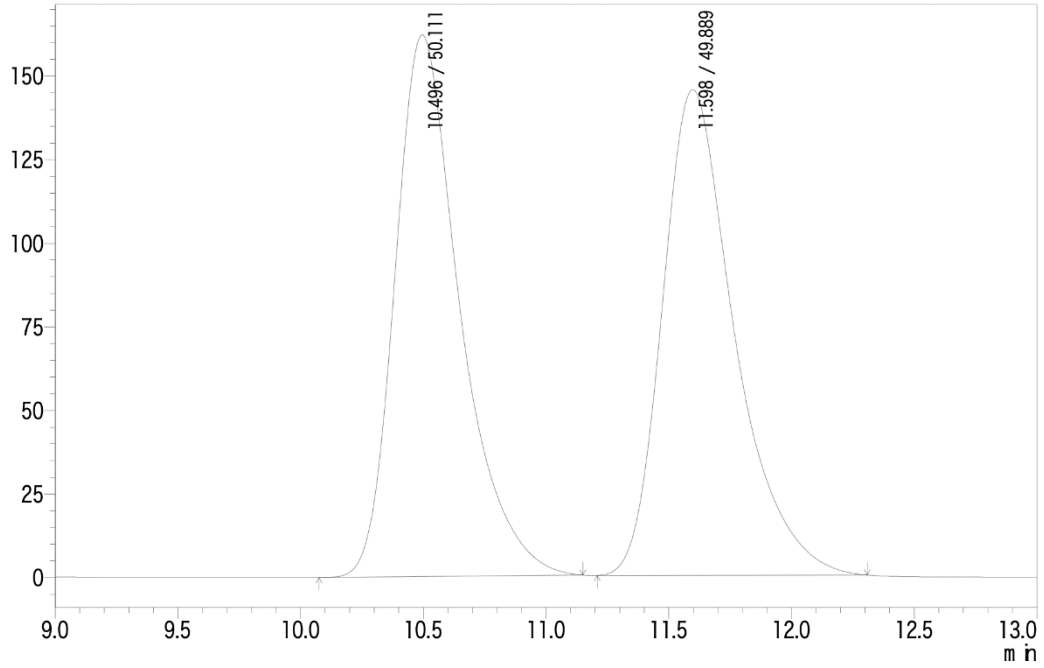
peak#	retention time	area%
1	9.790	50.030
2	10.913	49.970
Total		100.000


^{1}H NMR ($CDCl_3$ with 0.03% v/v TMS, 500 MHz)
5ia
TMS
abundance
X : parts per Million : Proton

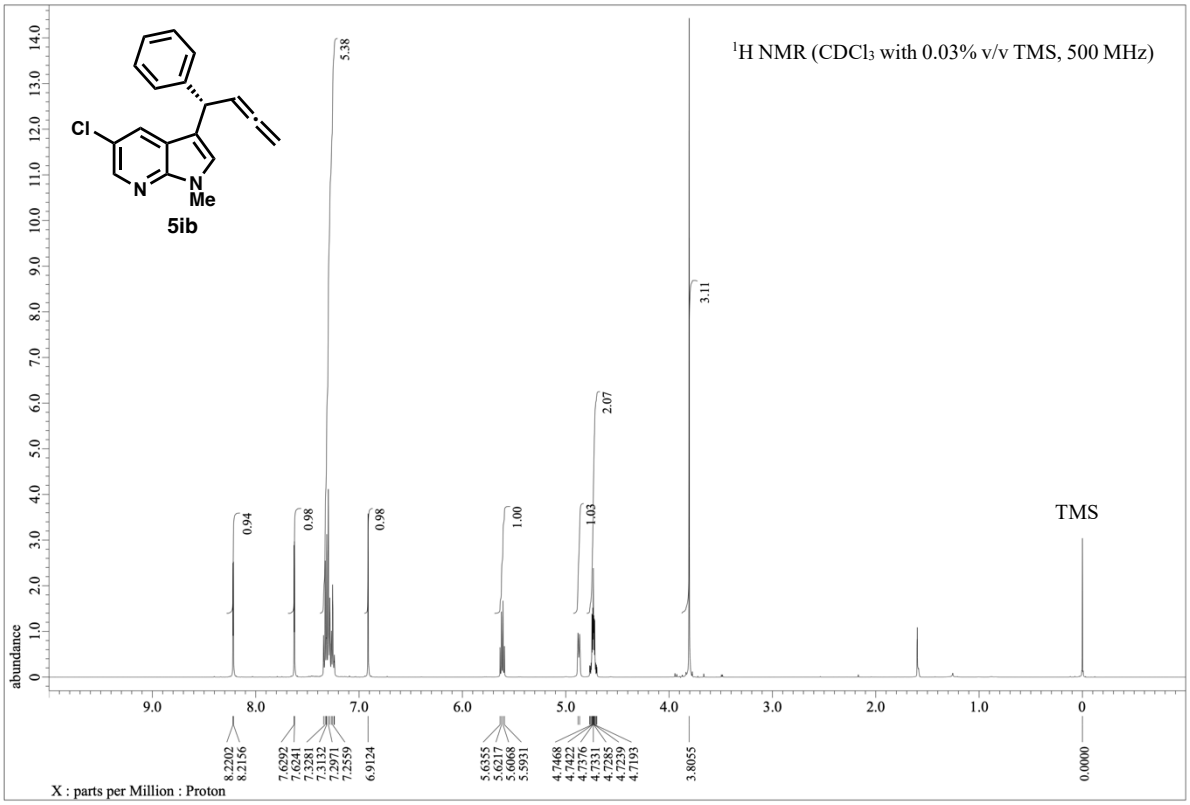

$CDCl_3$
$^{13}C\{^1H\}$ NMR
($CDCl_3$ with 0.03% v/v TMS, 126 MHz)
5ia
abundance
X : parts per Million : Carbon13

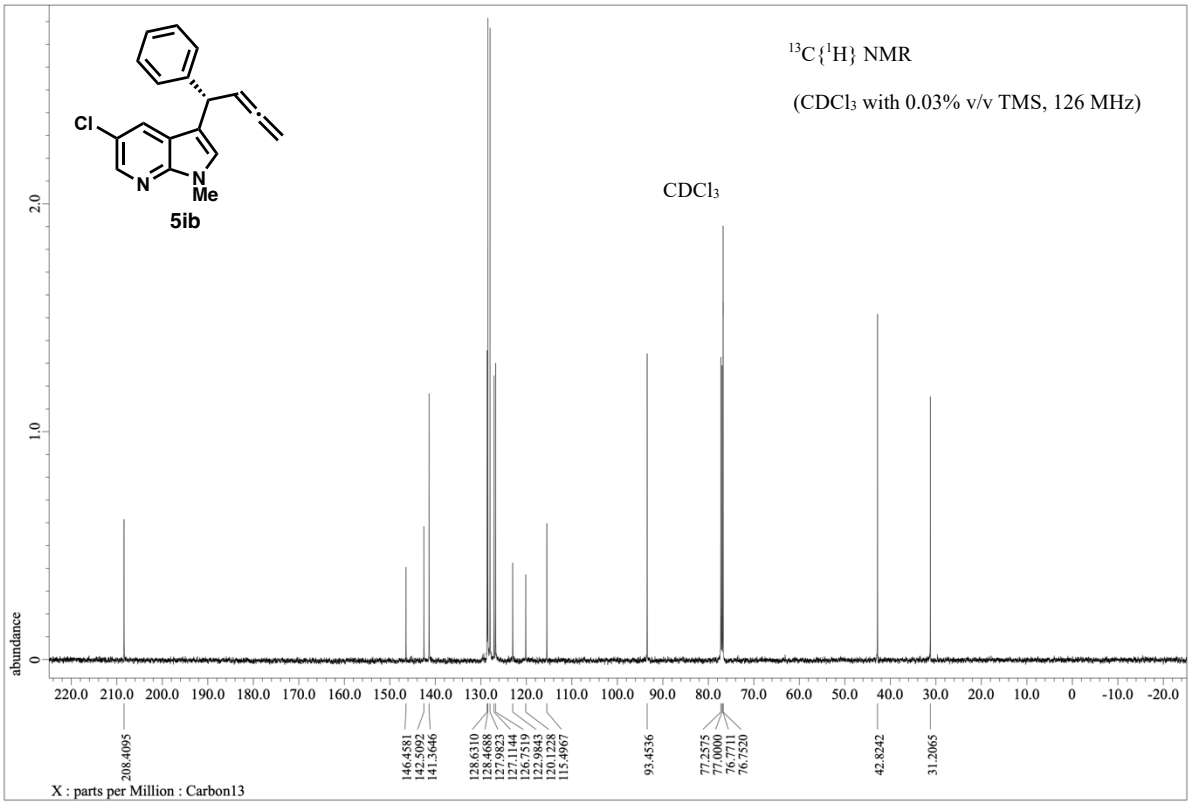


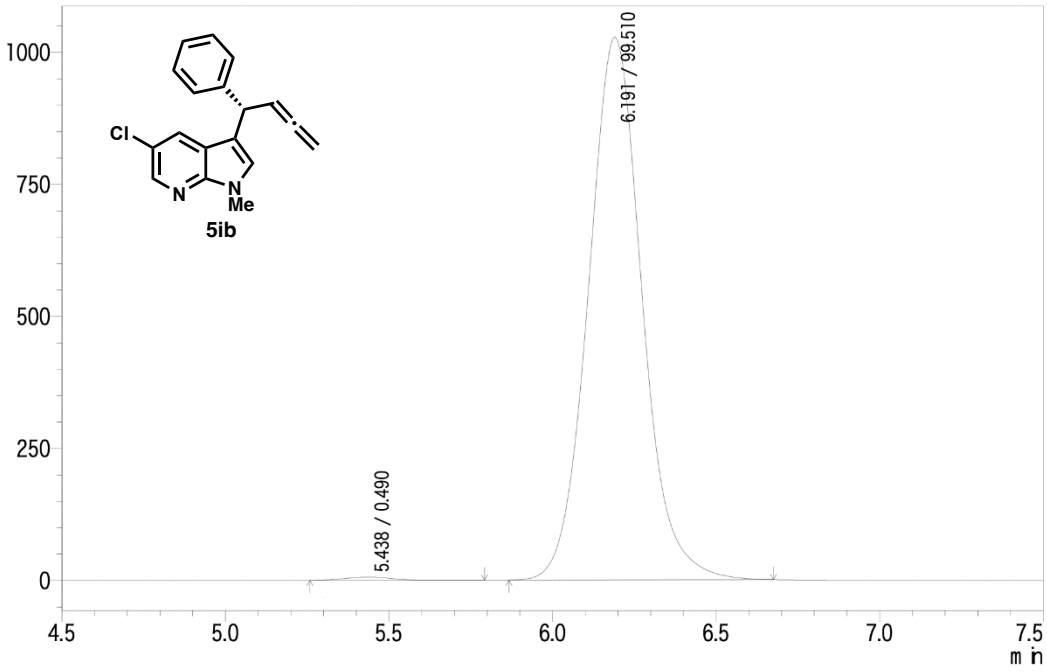
peak#	retention time	area%
1	10.432	99.562
2	11.550	0.438
Total		100.000



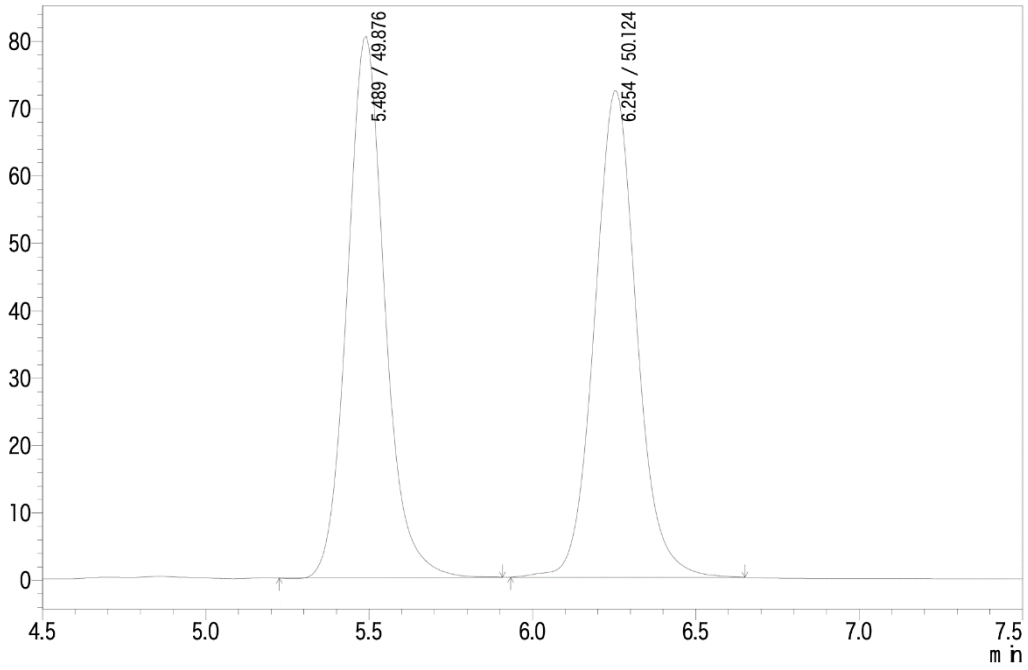
peak#	retention time	area%
1	10.496	50.111
2	11.598	49.889
Total		100.000


^{1}H NMR ($CDCl_3$ with 0.03% v/v TMS, 500 MHz)
Cl
N
N
Me
5ib
5.38
3.11
2.07
1.03
1.00
0.98
0.98
0.94
TMS
abundance
X : parts per Million : Proton

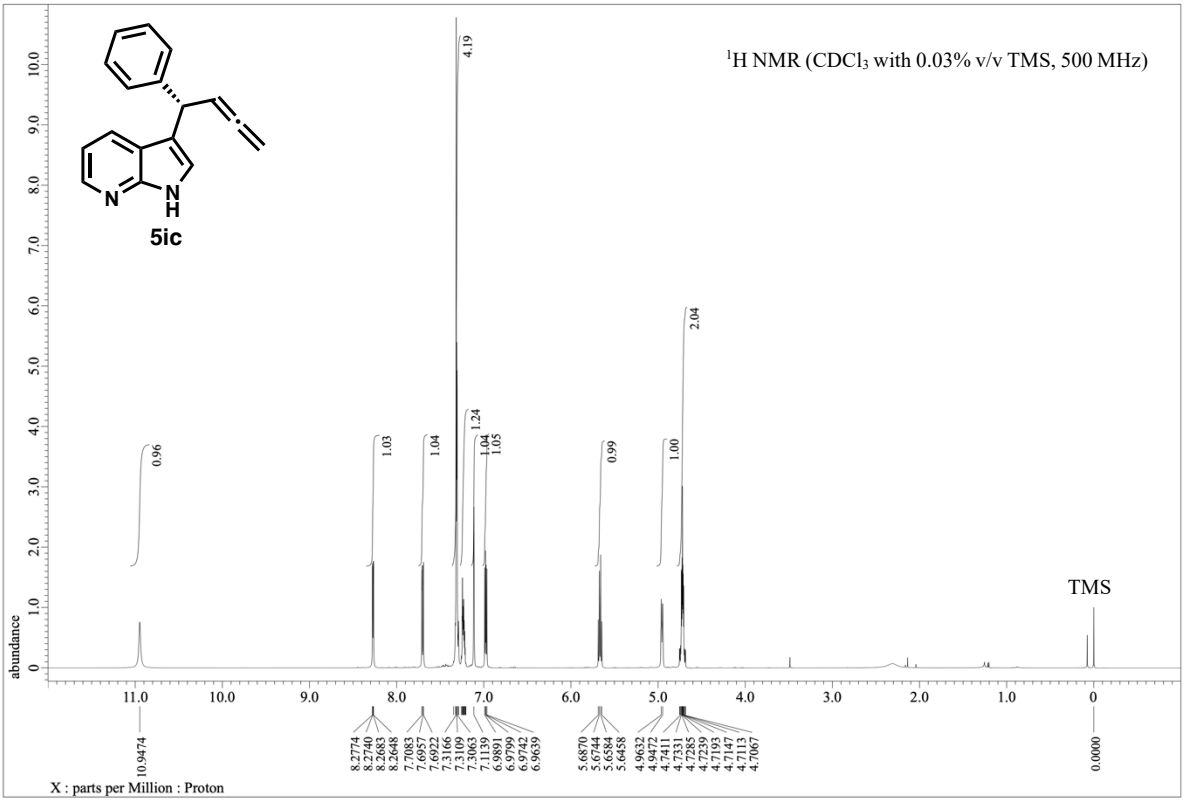

$^{13}C\{^1H\}$ NMR
($CDCl_3$ with 0.03% v/v TMS, 126 MHz)
Cl
N
N
Me
5ib
$CDCl_3$
abundance
X : parts per Million : Carbon13

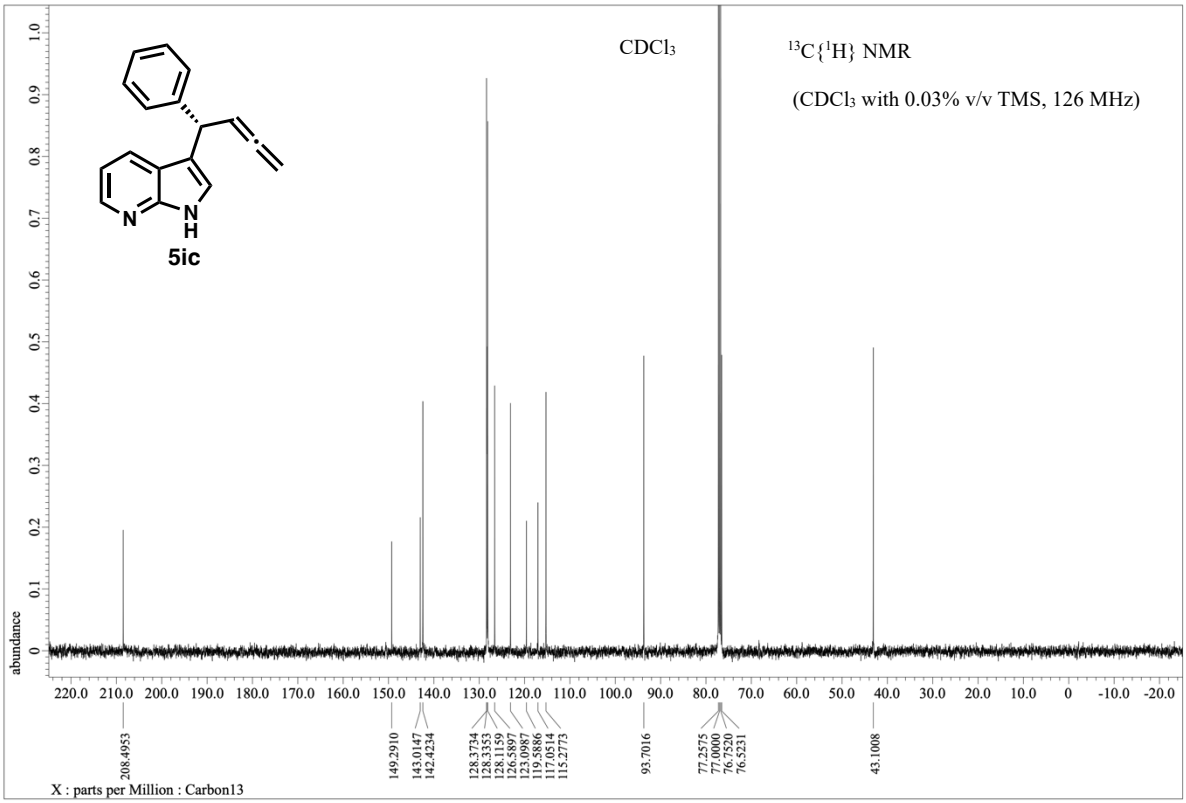


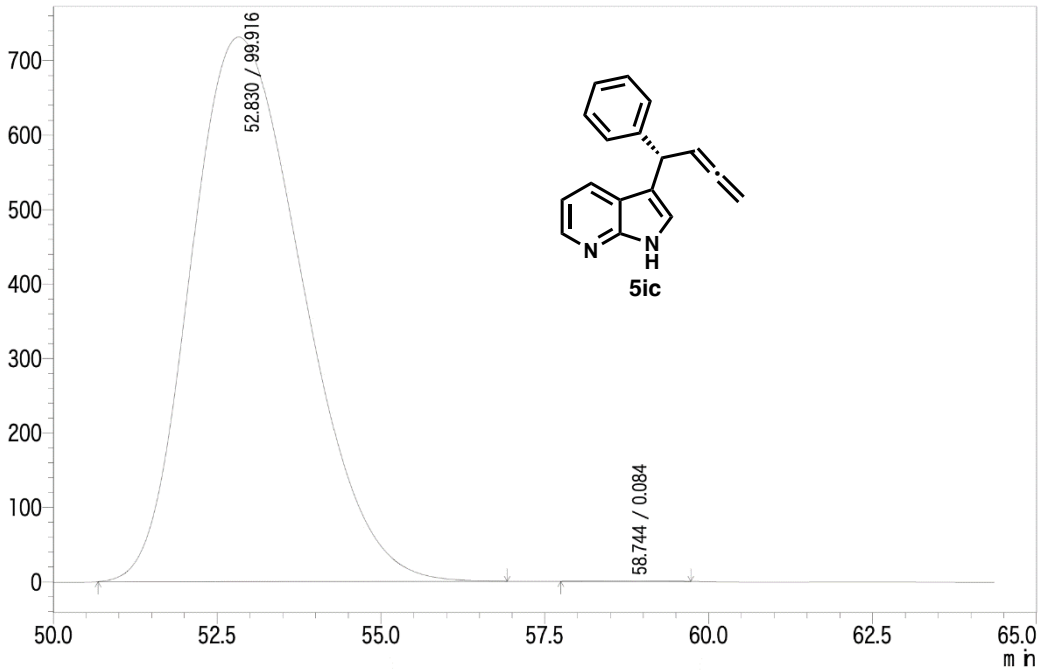
peak#	retention time	area%
1	5.438	0.490
2	6.191	99.510
Total		100.000



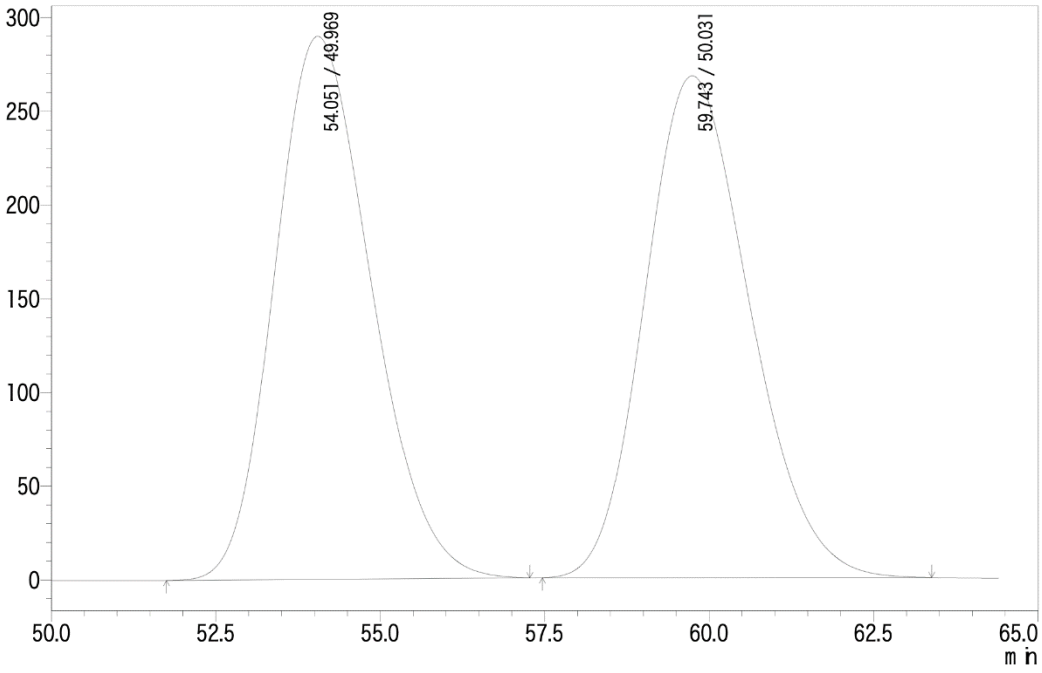
peak#	retention time	area%
1	5.489	49.876
2	6.254	50.124
Total		100.000


5ic
^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 500 MHz)
TMS
abundance
X : parts per Million : Proton

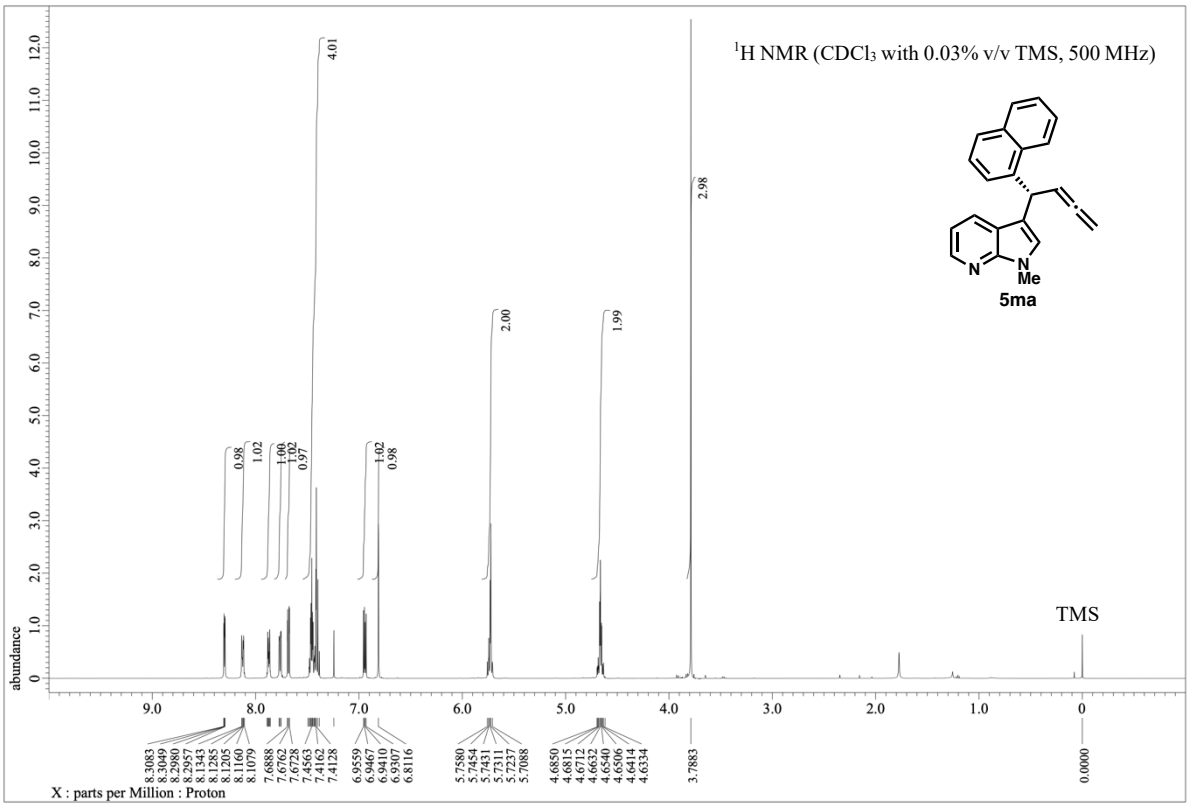

5ic
CDCl$_3$
^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 126 MHz)
abundance
X : parts per Million : Carbon13

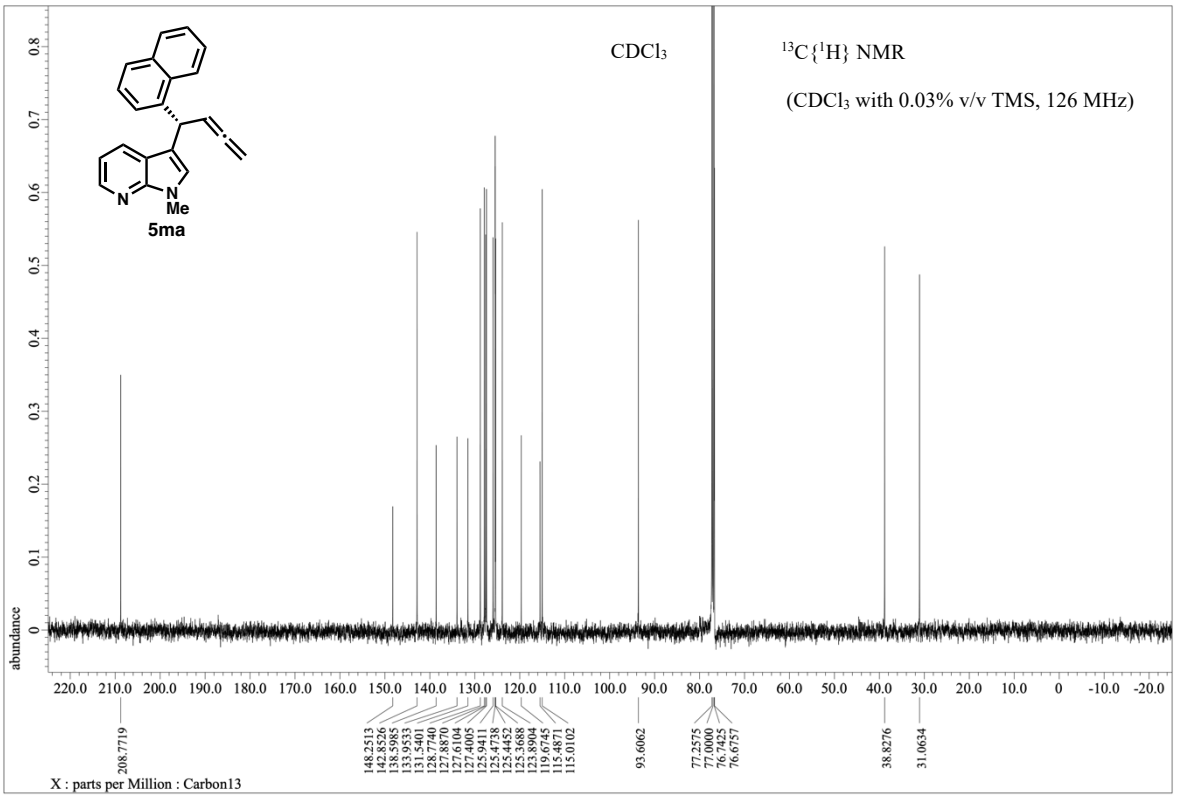


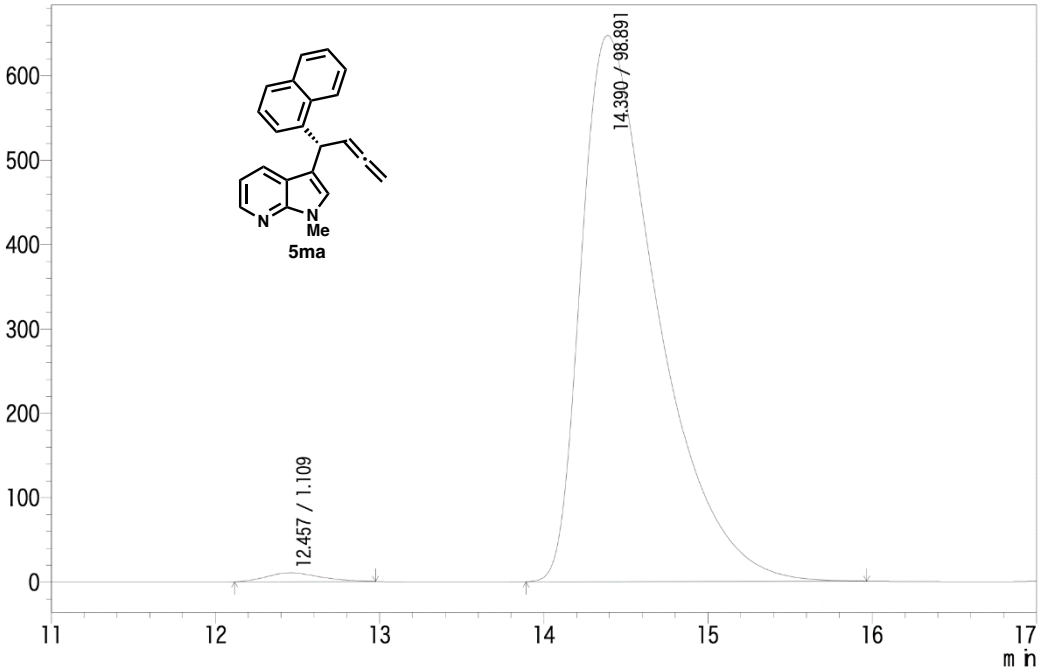
peak#	retention time	area%
1	52.830	99.916
2	58.744	0.084
Total		100.000



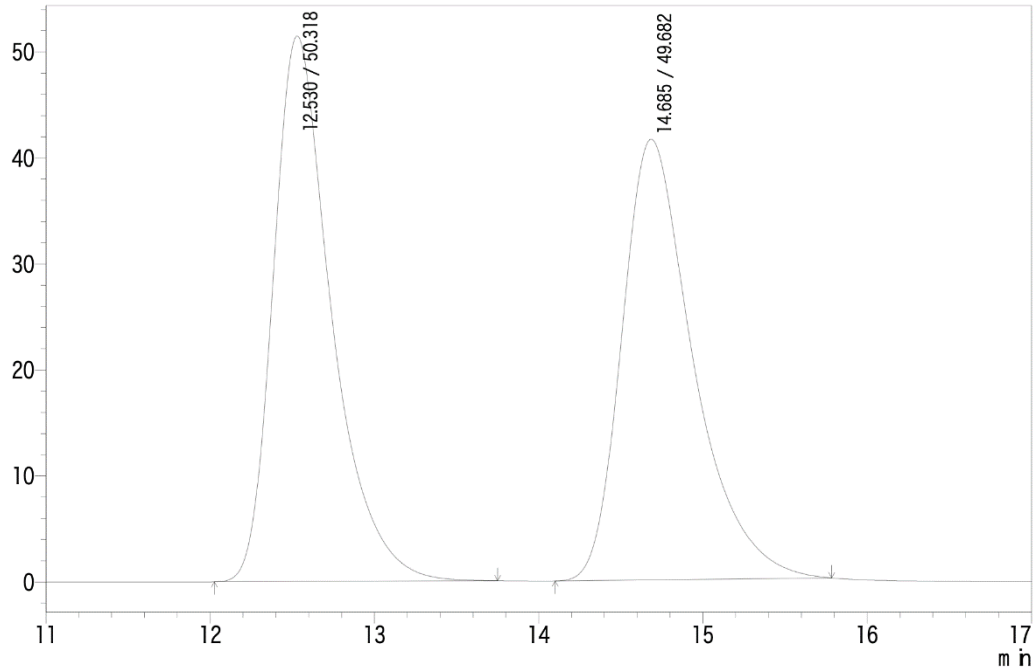
peak#	retention time	area%
1	54.051	49.969
2	59.743	50.031
Total		100.000


^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 500 MHz)
5ma
TMS
abundance
X : parts per Million : Proton

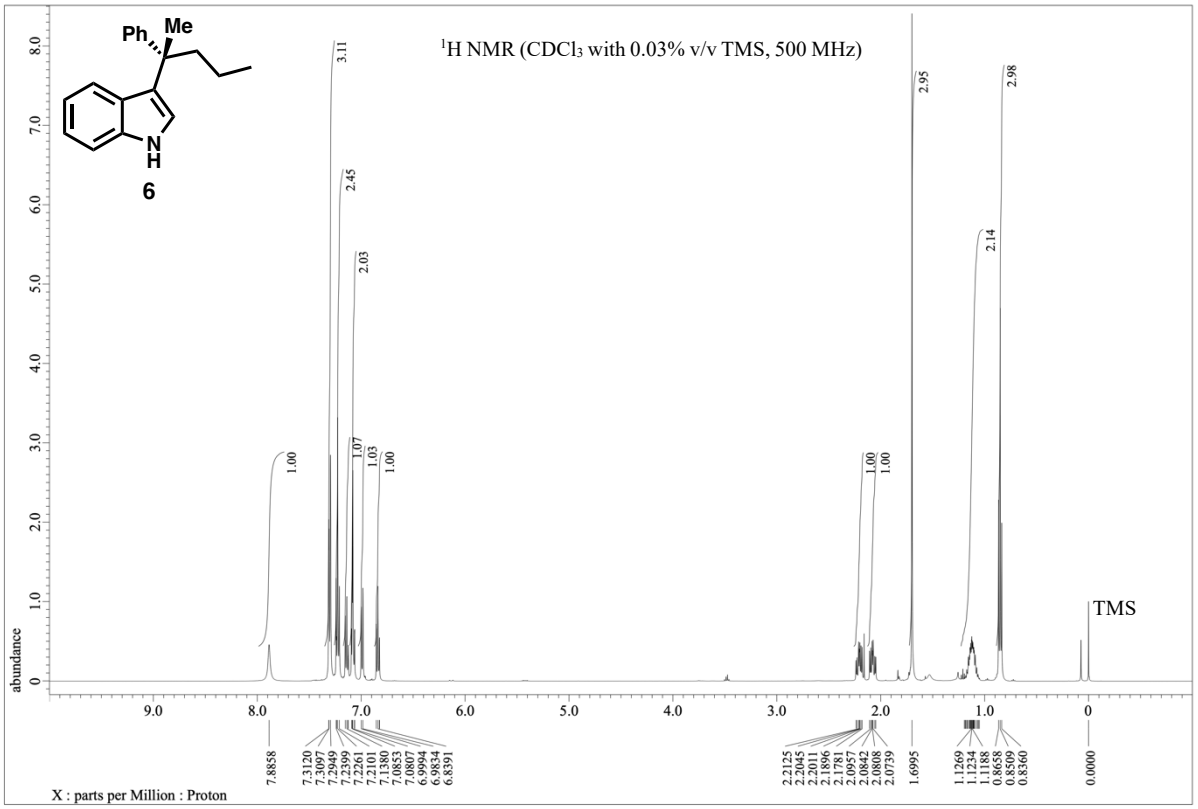

CDCl$_3$
^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 126 MHz)
5ma
abundance
X : parts per Million : Carbon13

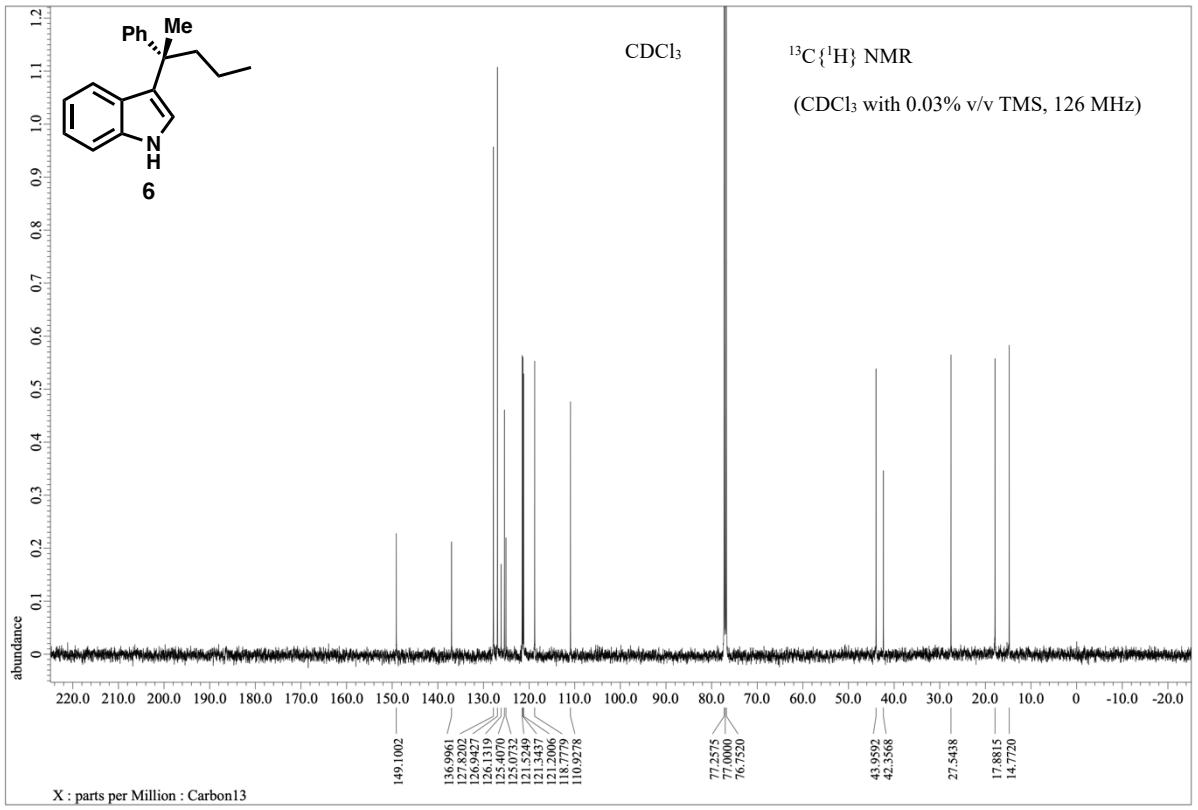


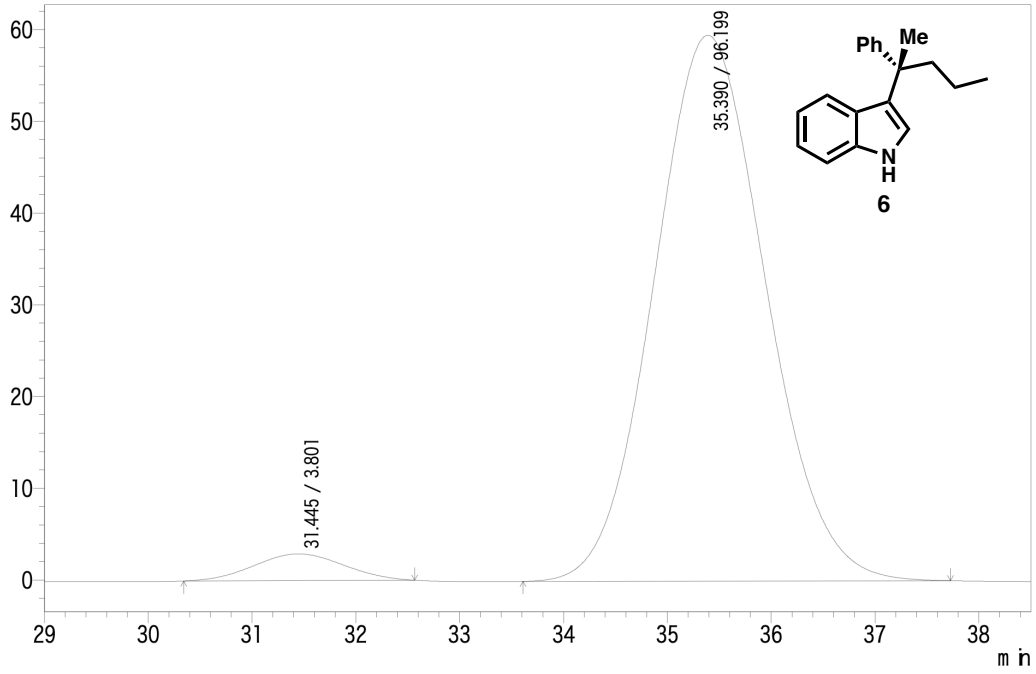
peak#	retention time	area%
1	12.457	1.109
2	14.390	98.891
Total		100.000



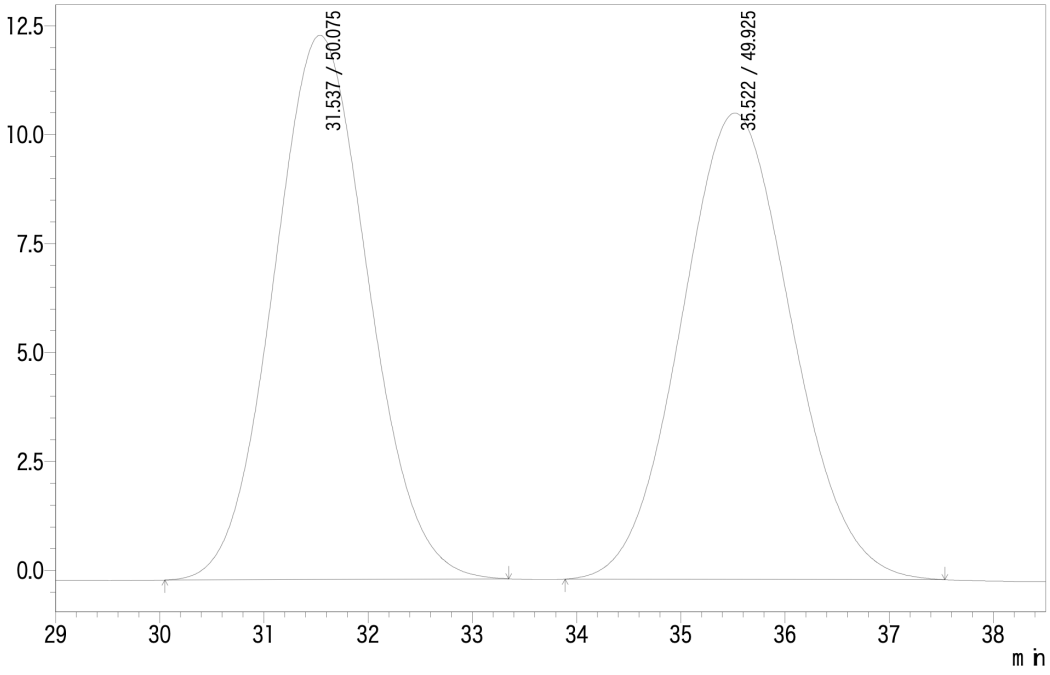
peak#	retention time	area%
1	12.530	50.318
2	14.685	49.682
Total		100.000


Ph
Me
N
H
6
^{1}H NMR (CDCl$_3$ with 0.03% v/v TMS, 500 MHz)
TMS
abundance
X : parts per Million : Proton

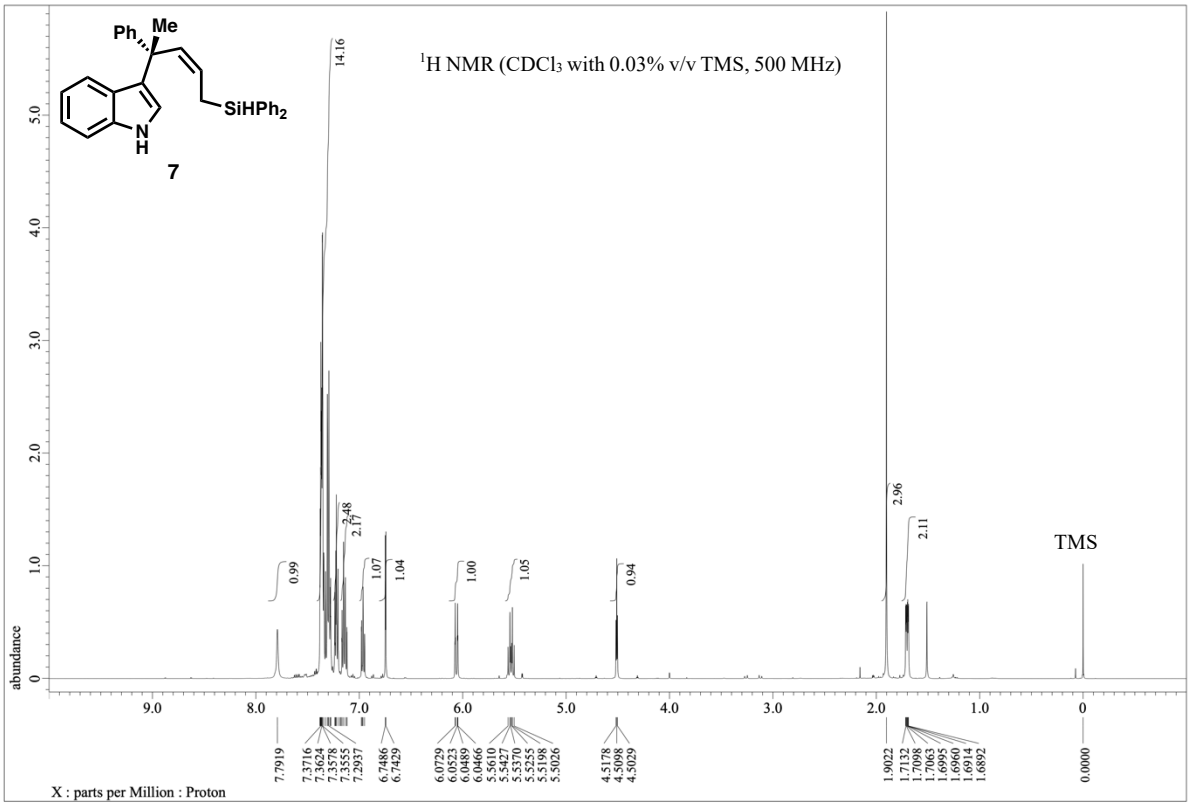

Ph
Me
N
H
6
CDCl$_3$
^{13}C{^{1}H} NMR
(CDCl$_3$ with 0.03% v/v TMS, 126 MHz)
abundance
X : parts per Million : Carbon13

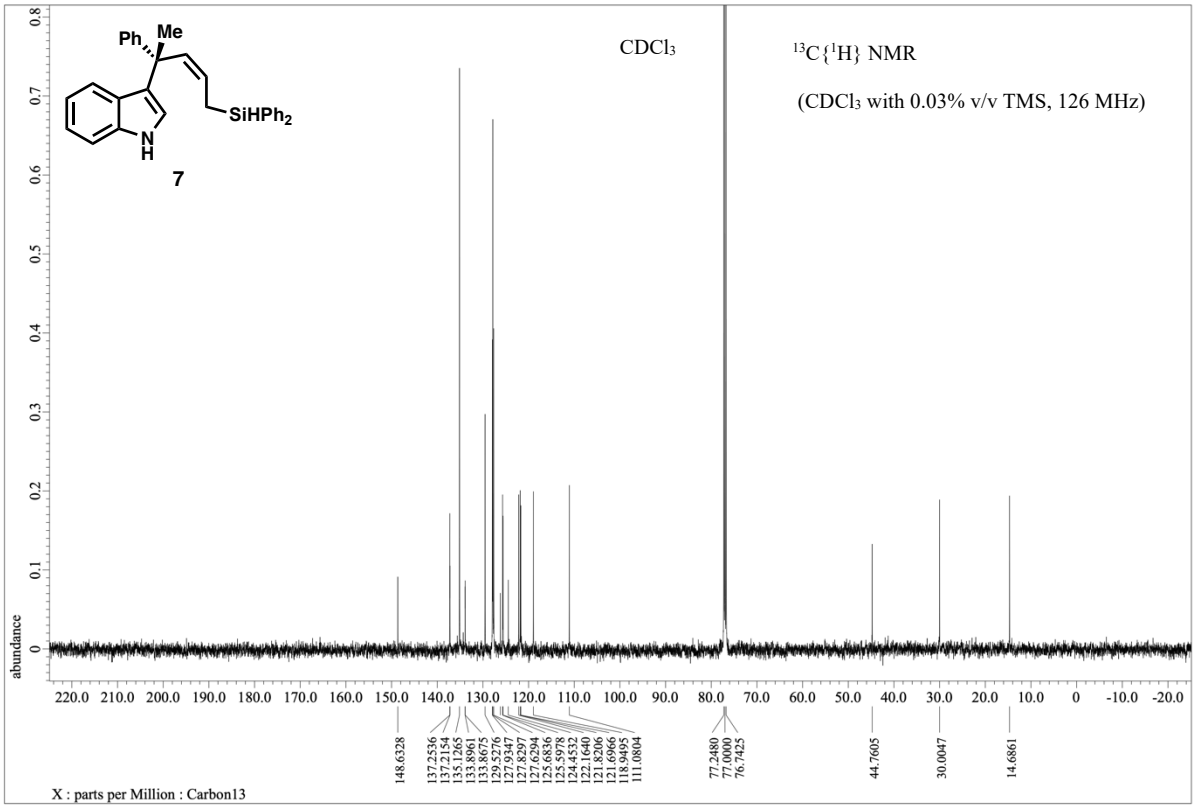


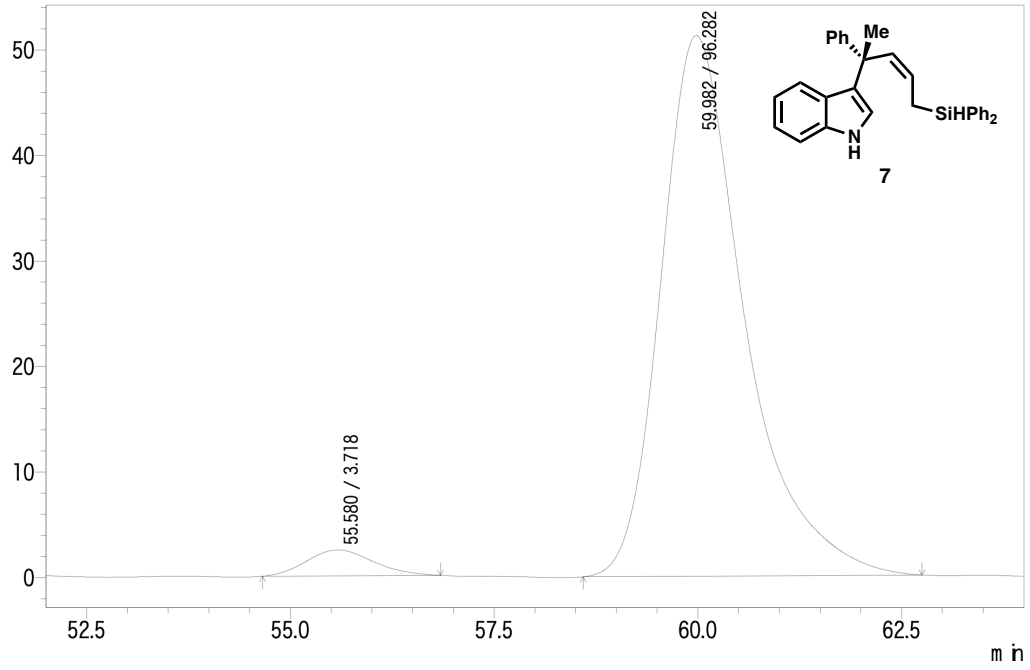
peak#	retention time	area%
1	31.445	3.801
2	35.390	96.199
Total		100.000



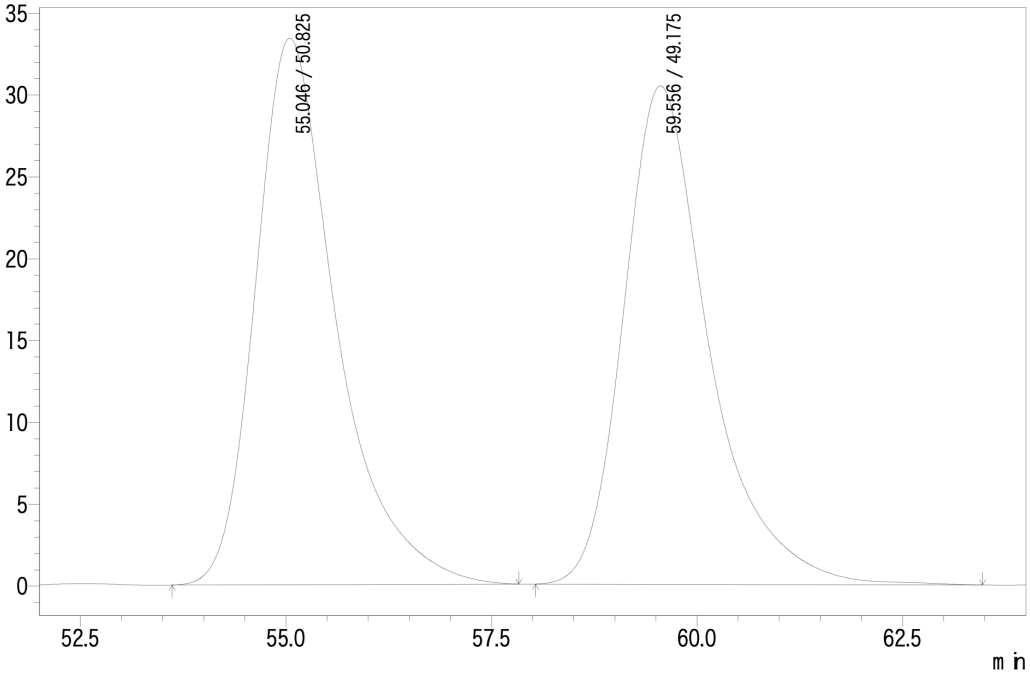
peak#	retention time	area%
1	31.537	50.075
2	35.522	49.925
Total		100.000


Ph
Me
SiHPh2
N
H
7
1H NMR (CDCl3 with 0.03% v/v TMS, 500 MHz)
TMS
abundance
X : parts per Million : Proton


Ph
Me
SiHPh2
N
H
7
CDCl3
13C{1H} NMR
(CDCl3 with 0.03% v/v TMS, 126 MHz)
abundance
X : parts per Million : Carbon13



peak#	retention time	area%
1	55.580	3.718
2	59.982	96.282
Total		100.000



peak#	retention time	area%
1	55.046	50.825
2	59.556	49.175
Total		100.000