Supporting Information

Enantioselective synthesis of tetrahydrocyclopenta[*b*]indole bearing a chiral quaternary carbon center *via* Pd(II)-SPRIX-catalyzed C–H activation

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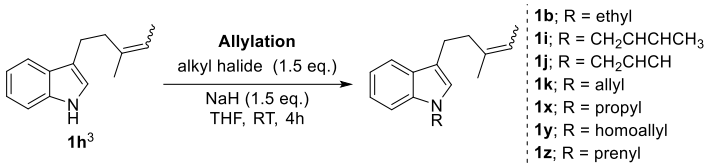
1. General

All reactions were performed with standard Schlenk technique under N_2 atmosphere. Anhydrous dichloromethane, diethylether, THF, toluene and DMF were purchased from Kanto Chemicals and further purified by passage through activated alumina using a Glass Contour solvent purification system.[1] Other solvents were purified prior to use by standard techniques.[2] All other chemicals were purchased from commercial suppliers and used as received. Reactions were monitored by thin layer chromatography, on glass plates coated with silica gel with fluorescent indicator (Merck). Column chromatography was conducted on Kishida Silica Gel (spherical, 63–200 μm). Melting points were measured using Yanaco melting point apparatus MP-S9 and were uncorrected. All NMR spectra were recorded at 25 °C on JEOL ECS400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) or Bruker AVANCE II (175 MHz for ^{13}C-NMR). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR are given relative to $CDCl_3$ (δ 77.16). Data for ^{1}H-NMR are reported as follows: chemical shifts (δ ppm), multiplicity, (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets), integration and coupling constants (Hz). In the cases of *E/Z*-olefins, ^{1}H NMR data of the minor olefinic isomer showed only the signals of different chemical shifts to that of the major one because the other signals are completely overlapped. ESI mass spectra were recorded on a Thermo Fisher LTQ ORBITRAP XL. HPLC analyses were performed on JASCO HPLC system (JASCO PU 2080 pump and MD-2010 UV/Vis detector) using a mixture of hexane and *i*-PrOH eluents. Two types of HPLC columns have been used: Daicel columns: CHIRALPAK (AD-H, AD-3, AS-3, IF), CHIRALCEL (OD-H, OJ); YMC columns: CHIRAL ART Cellulose-C, CHIRAL ART Cellulose-SB. Optical rotations were measured with JASCO P-1030 polarimeter. FT-IR spectra were recorded on a JASCO FT-IR system (FT/IR4100). 1-Methyl-3-(3-methylpent-3-en-1-yl)-1*H*-indole (**1a**),[3] 1-benzyl-3-(3-methylpent-3-en-1-yl)-1*H*-indole (**1c**)[3] were synthesized according to the reported procedures. The self-tuning single mode Biotage Initiator Microwave Synthesizer was used to perform in the case of microwave conditions.

2. Preparation of substrates 1

General procedures

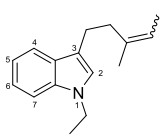
Synthesis of alkenylindoles 1b, 1i-k, and 1x-z



Allylation

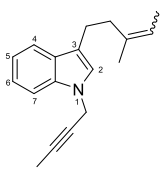
Sodium hydride (60%) (2 eq.) was added to a solution of unprotected alkenylindole **1h** (1.0 mmol) in THF (4.0 mL) at 0 °C. The resulting mixture was stirred for 10 min at 0 °C. After stirring for 1h at room temperature, alkyl halide (1.5 eq.) was added dropwisely at 0 °C, and then the reaction mixture was stirred for 4 h at room temperature. After the complete consumption of the starting material, the reaction mixture was quenched by sat. aq. NH_4Cl (5 mL) at 0 °C, and extracted with ether (3 x 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting oil was purified by column chromatography (hexane/Et_2O = 95/5) to provide the corresponding protected alkenylindoles **1b**, **1i-k**, and **1x-z**.

1-Ethyl-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1b)



1b: Colorless oil (82%, 63/37 mixture of *Z*/*E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.62-7.58 (m, 1H, H-4), 7.31-7.28 (m, 1H, H-7), 7.22-7.16 (m, 1H, ArH), 7.11-7.06 (m, 1H, ArH), 5.31-5.25 (m, 1H, C=C<u>H</u>-CH_3), 4.14-4.08 (m, 2H, N(Indole)-<u>CH_2</u>-CH_3), 2.86-2.78 (m, 2H, Indole-<u>CH_2</u>-CH_2), 2.44-2.35 (m, 2H, Indole-CH_2-<u>CH_2</u>), 1.78-1.77 (m, 3H, CH_2-C(<u>CH_3</u>)), 1.57-1.53 (m, 3H, C=CH-<u>CH_3</u>), 1.45-1.40 (m, 3H, N(Indole)-CH_2-<u>CH_3</u>); *E*-isomer: δ 1.70-1.69 (m, 3H, CH_2-C(<u>CH_3</u>)), 1.61-1.58 (m, 3H, C=CH-<u>CH_3</u>); ^{13}C-NMR ($CDCl_3$) δ 136.3, 136.2, 136.1, 128.2, 124.2, 121.4, 121.36, 119.4, 119.2, 119.17, 118.6, 118.5, 115.5, 109.3, 40.8, 40.6, 32.7, 24.2, 23.64, 23.6, 16.0, 15.7, 13.5, 13.4; HRMS (ESI) calcd for $C_{16}H_{22}N$ m/z = 228.1747 [$(M+H)^+$], found m/z = 228.1747; IR (KBr): ν 3047, 2972, 2924, 1607, 1558, 1461, 1363, 1224, 1146, 1078, 800, 737 cm^{-1}.

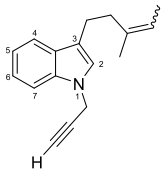
1-(But-2-yn-1-yl)-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1i)



1i: Colorless oil (31%, 57/43 mixture of *Z*/*E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*- isomer: δ 7.62-7.58 (m, 1H, ArH), 7.36-7.33 (m, 1H, ArH), 7.24-7.19 (m, 1H, ArH), 7.13-7.08 (m, 1H, ArH), 7.00 (s, 1H, H-2), 5.32-5.23 (m, 1H, C(CH_3)=C<u>H</u>-CH_3), 4.76-4.74 (m, 4H, N-<u>CH_2</u>-C), 2.85-2.78 (m, 2H, Indole-<u>CH_2</u>-CH_2), 2.45-2.36 (m, 2H, Indole-CH_2-<u>CH_2</u>), 1.81-1.80 (m, 3H, C≡C-CH_3), 1.78-1.76 (m, 3H, CH_2-C(<u>CH_3</u>)), 1.57-1.55 (m, 3H, C=CH-<u>CH_3</u>); *E*-isomer: δ 6.97 (s, 1H, H-2), 1.70 (s, 3H, CH_2-C(<u>CH_3</u>)), 1.61-1.59 (m, 3H, C=CH-<u>CH_3</u>); ^{13}C-NMR ($CDCl_3$) δ 136.25, 136.23, 136.19, 136.1, 128.5, 124.4, 121.74, 121.72, 119.5, 119.3, 119.2, 119.1, 119.0, 118.7, 116.1,

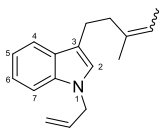
109.49, 109.46, 81.09, 81.07, 73.7, 40.5, 36.1, 32.5, 24.2, 23.6, 15.9, 13.5, 13.4, 3.7; HRMS (ESI) calcd for $C_{18}H_{22}N$ m/z = 252.1747 [$(M+H)^+$], found m/z = 252.1747; IR (KBr): ν 3048, 2920, 2856, 2232, 1608, 1552, 1461, 1341, 1254, 1187, 1145, 1020, 797, 739 cm^{-1}.

3-(3-Methylpent-3-en-1-yl)-1-(prop-2-yn-1-yl)-1*H*-indole (1j)



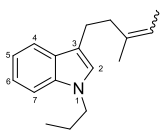
1j: Colorless oil (49%, 57:43 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.62-7.58 (m, 1H, H-4), 7.32-7.30 (m, 1H, H-7), 7.24-7.19 (m, 1H, ArH), 7.14-7.09 (m, 1H, ArH), 6.95 (s, 1H, H-2), 5.30-5.23 (m, 1H, C=CH-CH_3), 4.74 (d, 2H, CH_2-C≡CH, *J* = 2.40 Hz), 2.84-2.77 (m, 2H, Indole-CH_2-CH_2), 2.43-2.31 (m, 3H, Indole-CH_2-CH_2, CH_2-C≡CH), 1.77-1.75 (m, 3H, CH_2-C(CH_3)), 1.55-1.53 (m, 3H, C=CH-CH_3); *E*-isomer: δ 6.92 (s, 1H, H-2), 4.73 (d, 2H, CH_2-C≡CH, *J* = 2.80 Hz), 1.69 (s, 3H, CH_2-C(CH_3)), 1.60-1.58 (m, 3H, C=CH-CH_3); ^{13}C-NMR ($CDCl_3$) δ 136.2, 136.0, 135.9, 128.6, 124.3, 121.94, 121.92, 119.5, 119.4, 119.3, 119.26, 118.7, 116.6, 109.4, 109.3, 78.2, 78.18, 73.3, 73.28, 40.3, 35.6, 32.4, 24.1, 23.6, 23.5, 15.9, 13.5, 13.4; HRMS (ESI) calcd for $C_{17}H_{20}N$, m/z = 238.1590 [$(M+H)^+$], found m/z = 238.1591; IR (KBr): ν 3292, 3055, 3029, 2959, 2922, 2856, 2124, 1614, 1480, 1466, 1372, 1335, 1185, 1148, 1014, 804, 739, 655 cm^{-1}.

1-Allyl-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1k)



1k: Pale yellow oil (63%, 56:44 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.63-7.59 (m, 1H, H-4), 7.29-7.26 (m, 1H, H-7), 7.21-7.17 (m, 1H, ArH), 7.12-7.07 (m, 1H, ArH), 6.89 (s, 1H, H-2), 6.03-5.93 (m, 1H, CH_2-CH=CH_2), 5.31-5.30 (m, 1H, C(CH_3)=CH-CH_3), 5.20-5.15 (m. 1H, CH_2-CH=CH_{2a}), 5.11-5.04 (m. 1H, CH_2-CH=CH_{2b}), 4.69-4.66 (m, 2H, CH_2-CH=CH_2), 2.86-2.79 (m, 2H, Indole-CH_2-CH_2), 2.44-2.35 (m, 2H, Indole-CH_2-CH_2), 1.77-1.76 (m, 3H, CH_2-C(CH_3)), 1.56-1.53 (m, 3H, C=CH-CH_3); *E*-isomer: δ 6.87 (s, 1H, H-2), 1.70 (s, 3H, CH_2-C(CH_3)), 1.60-1.58 (m, 3H, C=CH-CH_3); ^{13}C-NMR ($CDCl_3$) δ 136.5, 136.2, 136.0, 133.9, 133.88, 128.3, 125.0, 121.6, 121.5, 119.4, 119.2, 119.15, 118.8, 118.75, 118.7, 117.1, 117.08, 115.9, 109.6, 109.57, 48.75, 48.7, 40.5, 32.6, 24.1, 23.6, 23.57, 15.9, 13.5, 13.4; HRMS (ESI) calcd for $C_{17}H_{22}N$ m/z = 240.1747 [$(M+Na)^+$], found m/z = 240.1747; IR (KBr): ν 3049, 2920, 2857, 1461, 1368, 1330, 1190, 923, 792, 739 cm^{-1}.

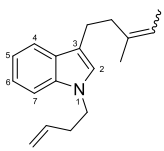
3-(3-Methylpent-3-en-1-yl)-1-propyl-1*H*-indole (1x)



1x: Colorless oil (43%, 57:43 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.62-7.58 (m, 1H, H-4), 7.31-7.28 (m, 1H, H-7), 7.20-7.17 (m, 1H, ArH), 7.10-7.06 (m, 1H, ArH), 6.90 (s, 1H, H-2), 5.30-5.23 (m, 1H, C(CH_3)=CH-CH_3), 4.05-4.01 (m, 2H, N(Indole)-CH_2), 2.86-2.79 (m, 2H, Indole-CH_2-CH_2), 2.44-2.35 (m, 2H, Indole-CH_2-CH_2), 1.89-1.79 (m, 2H, CH_2-CH_2-CH_3), 1.77-1.76 (m, 3H, CH_2-C(CH_3)), 1.54 (d, 3H, C=CH-CH_3, *J* = 7.20 Hz), 0.94-0.88 (m, 3H, CH_2-CH_2-CH_3); *E*-isomer: δ 6.87 (s, 1H, H-2), 1.69 (s, 3H, CH_2-C(CH_3)), 1.60 (d, 3H, C=CH-CH_3, *J* = 6.40 Hz); ^{13}C-NMR ($CDCl_3$) δ 136.4, 136.39, 136.3, 136.1, 128.1, 125.09, 125.06,

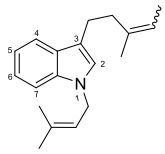
121.3, 121.29, 119.4, 119.2, 119.1, 118.6, 118.5, 118.45, 115.2, 115.19, 109.43, 109.4, 47.9, 40.5, 32.6, 24.1, 23.8, 23.7, 23.6, 23.56, 15.9, 15.5, 13.4, 11.7; HRMS (ESI) calcd for $C_{17}H_{24}N$ m/z = 242.1903 [$(M+H)^+$], found m/z = 242.1904; IR (KBr): ν 3047, 2959, 2925, 2867, 1611, 1559, 1461, 1365, 1321, 1206, 1146, 798, 738 cm^{-1}.

1-(But-3-en-1-yl)-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1y)



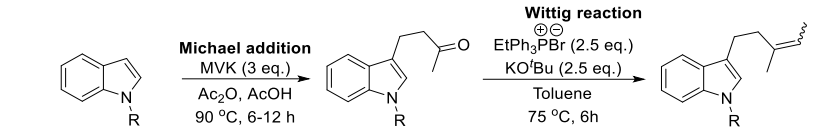
1y: Yellowish oil (21%, 63:37 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.62-7.58 (m, 1H, ArH), 7.31-7.28 (m, 1H, ArH), 7.22-7.17 (m, 1H, ArH), 7.12-7.07 (m, 1H, ArH), 6.89 (s, 1H, H-2), 5.83-5.72 (m, 1H, CH_2-CH_2-$\underline{CH}$=CH_2), 5.31-5.23 (m, 1H, C=$\underline{CH}$-CH_3), 5.11-5.03 (m, 2H, CH_2-CH_2-CH=$\underline{CH_2}$), 4.14-4.10 (m, 2H, $\underline{CH_2}$-CH_2-CH=CH_2), 2.85-2.78 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.58-2.52 (m, 2H, CH_2-$\underline{CH_2}$-CH=CH_2), 2.43-2.35 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.77-1.76 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.55-1.53 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 6.86 (s, 1H, H-2), 1.70-1.69 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.60-1.58 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 136.29, 136.27, 136.2, 136.1, 135.0, 134.98, 128.2, 124.9, 121.44, 121.41, 119.4, 119.2, 119.2, 118.7, 118.6, 117.34, 117.31, 115.50, 115.47, 109.4, 109.3, 45.9, 40.5, 34.81, 34.79, 32.5, 24.1, 23.6, 23.5, 15.9, 13.5, 13.4; HRMS (ESI) calcd for $C_{18}H_{24}N$ m/z = 254.1903 [$(M+H)^+$], found m/z = 254.1904; IR (KBr): ν 3053, 2923, 2856, 1461, 1364, 1185, 1004, 916, 737 cm^{-1}.

1-(3-Methylbut-2-en-1-yl)-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1z)



1z: Colorless oil (64%, 57:43 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.62-7.58 (m, 1H, H-4), 7.30-7.27 (m, 1H, H-7, *J* = 8.40 Hz), 7.21-7.16 (m, 1H, ArH), 7.11-7.06 (m, 1H, ArH), 6.90 (s, 1H, H-2), 5.38-5.34 (m, 1H, CH_2-$\underline{CH}$=C(CH_3)$_2$), 5.32-5.23 (m, 1H, C=$\underline{CH}$-CH_3), 4.65-4.63 (m, 2H, $\underline{CH_2}$-CH=C(CH_3)$_2$), 2.85-2.78 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.44-2.35 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.82 (s, 3H, CH_2-CH=C($\underline{CH_3}$)$_{2a}$), 1.78-1.77 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.76 (s, 3H, CH_2-CH=C($\underline{CH_3}$)$_{2b}$), 1.57-1.55 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 6.87 (s, 1H, H-2), 1.70 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.61-1.59 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 136.4, 136.3, 136.2, 135.9, 128.2, 124.5, 121.4, 121.3, 120.4, 119.4, 119.2, 119.1, 118.63, 118.58, 115.5, 109.53, 109.50, 44.0, 40.6, 32.6, 25.8, 24.2, 23.6, 18.1, 15.9, 13.5, 13.4; HRMS (ESI) calcd for $C_{19}H_{26}N$ m/z = 268.2060 [$(M+H)^+$], found m/z = 268.2061; IR (KBr): ν 3052, 2964, 2921, 2857, 1458, 1368, 1321, 1177, 800, 729 cm^{-1}.

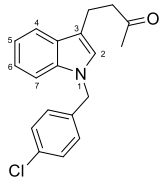
Synthesis of alkenylindoles 1c and 1d



Michael addition

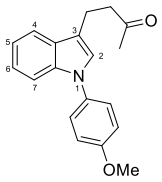
Butenone (0.2 mL) was added to a solution of indole **S1d**, **e** (0.65 mmol) in a mixture of glacial acetic acid (0.4 mL) and acetic anhydride (0.13 mL). The resulting mixture was heated at 90 °C for 6-12 h. After the consumption of indole, the reaction mixture was cooled to 0 °C and then quenched with water (2 mL), neutralized with solid $NaHCO_3$, and extracted with ether (3 x 5 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resulting residues were charged to column chromatography and eluted with a solvent mixture (hexane/EtOAc = 7/3) to provide pure products **S'1d**, **e**.

4-(1-(4-chlorobenzyl)-1*H*-indol-3-yl)butan-2-one (S'1d)



S'1d:Yellow oil (63%); ^{1}H-NMR ($CDCl_3$) δ 7.58 (d, 1H, H-4, *J* = 7.60 Hz), 7.21-7.07 (m, 5H, ArH), 6.96 (m, 2H, ArH), 6.86 (s, 1H, H-2), 5.14 (s, 2H, N(Indole)-$\underline{CH_2}$-C_6H_4), 3.02 (t, 2H, Indole-$\underline{CH_2}$-CH_2-CO), 2.80 (t, 2H, Indole-CH_2-$\underline{CH_2}$-CO), 2.10 (s, 3H, CO-CH_3); ^{13}C-NMR ($CDCl_3$) δ 208.6, 136.5, 136.2, 133.3, 128.9 (2C), 128.1 (2C), 128.0, 125.5, 122.0, 119.2, 119.0, 114.7, 109.6, 49.2, 44.1, 30.1, 19.3; HRMS (ESI) calcd for $C_{19}H_{18}ClNNaO$ m/z = 334.0969 [$(M+Na)^+$], found m/z = 334.0970; IR (KBr): ν 2955, 2925, 2853, 1713, 1661, 1491, 1467, 1357, 1173, 1014, 788, 742 cm^{-1}.

4-(1-(4-Methoxyphenyl)-1*H*-indol-3-yl)butan-2-one (S'1e)



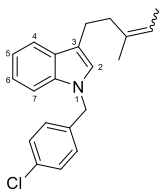
S'1e: Yellow oil (57%); ^{1}H-NMR ($CDCl_3$) δ 7.60 (dd, 1H, H-4, *J* = 7.20, 2.00 Hz), 7.41 (dd, 1H, H-7, *J* = 7.20, 1.20 Hz), 7.29-7.27 (m, 2H, ArH), 7.18-7.09 (m, 2H, H-5, H-6), 7.02 (s, 1H, H-2), 6.94-6.91 (m, 2H, ArH), 3.76 (s, 3H, OCH_3), 3.04 (t, 2H, Indole-$\underline{CH_2}$-CH_2-CO, *J* = 7.60 Hz), 2.80 (t, 2H, Indole-CH_2-$\underline{CH_2}$-CO, *J* = 7.60 Hz), 2.08 (s, 3H, CO-CH_3); ^{13}C-NMR ($CDCl_3$) δ 208.2, 157.0, 136.3, 132.6, 128.2, 125.50, 125.47, 122.3, 122.2, 119.6, 118.9, 115.5, 114.6 (2C), 110.3, 55.4, 43.8, 29.8, 19.0; HRMS (ESI) calcd for $C_{19}H_{19}NNaO_2$ m/z = 316.1308 [$(M+Na)^+$], found m/z = 316.1308; IR (KBr): ν 3049, 3001, 2932, 2838, 1715, 1514, 1460, 1249, 1173, 1135, 1033, 836, 742 cm^{-1}.

Wittig reaction

A mixture of alkyltriphenylphosphonium bromide (2.5 eq.) and potassium *tert*-butoxide (2.5 eq.) in toluene were stirred at room temperature for 1 h. The resulting red solution was cooled to 0 °C, indolyl ketone **S'1d**, **e** (0.39 mmol) was added followed by heating the reaction mixture to 75 °C. After heating the reaction

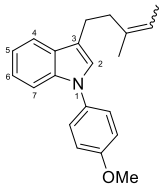
mixture for 6 h at 75 °C, the mixture was cooled to 0 °C, quenched with sat. aq. NH_4Cl (10 mL), and extracted with EtOAc (2 x 10 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting oil was purified by column chromatography (hexane/EtOAc = 4/1) to provide pure alkenylindoles **1d**, **e**.

1-(4-Chlorobenzyl)-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1d)



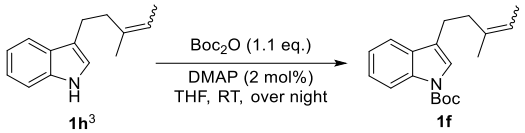
1d: Colorless oil (83%, 57:43 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.65-7.61 (m, 1H, ArH), 7.25-7.22 (m, 2H, ArH), 7.20-7.15 (m, 2H, ArH), 7.14-7.08 (m, 1H, ArH), 7.02-6.98 (m, 2H, ArH), 6.89 (s, 1H, H-2), 5.28-5.21 (m, 3H, C=$\underline{CH}$-CH_3, N(Indole)-$\underline{CH_2}$-C_6H_4), 2.87-2.80 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.44-2.35 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.76-1.75 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.53-1.51 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 6.86 (s, 1H, H-2), 1.68 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.59-1.57 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 136.7, 139.64, 136.55, 136.51, 136.1, 135.9, 133.44, 133.41, 129.0, 128.4, 128.20, 128.17, 125.2, 121.92, 121.88, 119.6, 119.4, 119.3, 119.12, 119.06, 118.8, 116.44, 116.42, 109.59, 109.56, 49.35, 49.32, 40.4, 32.5, 24.1, 23.6, 23.5, 15.9, 13.5, 13.4; HRMS (ESI): calcd for $C_{21}H_{23}ClN$ m/z = 324.1514 ($[M+H]^+$); found, m/z = 324.1512; IR (KBr): ν 3050, 2921, 2855, 1606, 1461, 1336, 1176, 1092, 1015, 806, 737 cm^{-1}.

1-(4-Methoxyphenyl)-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1e)



1e: Colorless oil (77%, 55:45 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.68-7.64 (m, 1H, H-4), 7.45-7.43 (m, 1H, H-7), 7.39-7.30 (m, 2H, ArH), 7.21-7.18 (m, 2H, ArH), 7.09 (s, 1H, H-2), 7.01-6.97 (m, 2H, ArH), 5.35-5.25 (m, 1H, C=$\underline{CH}$-CH_3, 3.84 (s, 3H, OCH_3), 2.91-2.84 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.49-2.40 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.80-1.78 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.58-1.55 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 7.06 (s, 1H, H-2), 1.72 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.62-1.60 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 158.0, 157.99, 136.5, 136.1, 136.0, 134.0, 133.8, 133.2, 133.1, 128.8, 128.74, 128.66, 128.59, 125.8, 125.4, 122.25, 122.22, 119.6, 119.5, 119.3, 119.2, 118.8, 117.3, 114.8, 110.44, 110.41, 55.7, 40.3, 32.4, 24.1, 23.6, 23.5, 16.0, 13.6, 13.5, 1.2; HRMS (ESI): calcd for $C_{21}H_{24}NO$ m/z = 306.1852 ($[M+H]^+$); found, m/z = 306.1851; IR (KBr): ν 3049, 3025, 2999, 2958, 2929, 2918, 2855, 2838, 1612, 1514, 1460, 1442, 1300, 1286, 1249, 1230, 1181, 1134, 1035, 835, 800, 740586, 542 cm^{-1}.

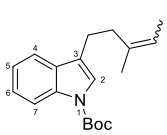
Synthesis of *tert*-butyl 3-(3-methylpent-3-en-1-yl)-1*H*-indole-1-carboxylate (1f)



1h[3] **1f**

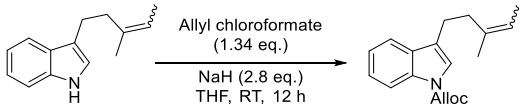
To a solution of alkenylindole **1h** (1.0 mmol, 200 mg) and 4-dimethylaminopyridine (DMAP) (2 mol%, 0.02 mmol, 2 mg) in THF (15.0 mL), di-*tert*-butyl dicarbonate (1.1 eq., 1.1 mmol, 420 mg) was added at room temperature. After stirring overnight under nitrogen, the solvent was removed *in vacuo* and the

remaining residues was purified by column chromatography (hexane/EtOAc = 4/1) to give the product **1f** (274 mg, 91%).



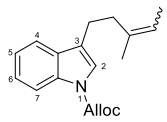
1f: Colorless oil (57:43 mixture of *Z/E*-olefin isomers). ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 8.12 (brs, 1H, ArH), 7.55-7.51 (m, 1H, ArH), 7.37-7.21 (m, 3H, ArH), 5.34-5.25 (m, 1H, C=CH-CH_3), 2.79-2.72 (m, 2H, Indole-CH_2-CH_2), 2.43 (t, 2H, Indole-CH_2-CH_2, *J* = 8.80 Hz), 1.77-1.76 (m, 3H, CH_2-C(CH_3)), 1.663 (s, 9H, C(CH_3)$_3$), 1.61-1.59 (m 3H, C=CH-CH_3); *E*-isomer: δ 2.35 (t, 2H, Indole-CH_2-CH_2, *J* = 8.80 Hz), 1.70 (s, 3H, CH_2-C(CH_3)), 1.659 (s, 9H, C(CH_3)$_3$), 1.58-1.56 (m 3H, C=CH-CH_3); ^{13}C-NMR ($CDCl_3$) δ 150.0, 135.6, 135.5, 135.4, 130.94, 130.88, 124.32, 124.28, 122.4, 122.34, 122.29, 121.3, 121.26, 119.9, 119.09, 119.07, 119.02, 115.4, 115.3, 83.4, 39.3, 31.3, 28.4, 23.8, 23.5, 23.3; HRMS (ESI) calcd for $C_{19}H_{25}NNaO_2$ m/z = 322.1778 [$(M+Na)^+$], found m/z = 322.1778; IR (KBr): ν 3052, 3030, 2978, 2930, 2860, 1732, 1476, 1454, 1376, 1308, 1254, 1225, 1158, 1091, 1018, 859, 767, 744 cm^{-1}.

Synthesis of allyl 3-(3-methylpent-3-en-1-yl)-1*H*-indole-1-carboxylate (1g)



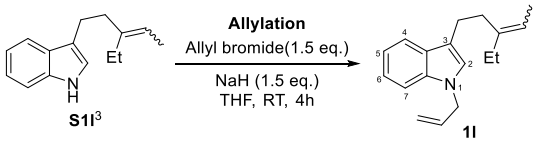
1h[4] **1g**

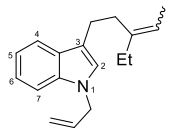
To a solution of alkenylindole **1h** (1.0 mmol, 200 mg) in THF, sodium hydride (60%) (2.8 eq., 2.8 mmol, 112.4 mg) was added at 0 °C. The resulting mixture was stirred for 10 min at room temperature followed dropwise addition of allyl chloroformate (1.34 eq, 1.34 mmol, 0.14 mL). The reaction mixture was stirred for 12 h at room temperature before dilution with diethyl ether and quenching with sat. aq. NH_4Cl. After that, the reaction mixture was extracted with ether (3 x 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting oil was purified by column chromatography (hexane/Et_2O = 95/5) to give the product **1g** (14.2 mg, brsm 35%).



1g: Colorless oil (59:41 mixture of *Z/E*-olefin isomers). ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 8.16 (brs, 1H, H-2), 7.56-7.52 (m, 1H, ArH), 7.41-7.39 (m, 1H, ArH), 7.35-7.31 (m, 1H, ArH), 7.28-7.23 (m, 1H, ArH), 6.13-6.03 (m, 1H, CO_2-CH_2-CH=CH_2), 5.49-5.43 (m, 1H, CO_2-CH_2-CH=CH_{2a}), 5.37-5.33 (m, 1H, CO_2-CH_2-CH=CH_{2b}), 5.30-5.25 (m, 1H, C=CH-CH_3), 4.92-4.90 (m, 2H, CO_2-CH_2-CH=CH_2), 2.80-2.73 (m, 2H, Indole-CH_2-CH_2), 2.43 (t, 2H, Indole-CH_2-CH_2, *J* = 8.80 Hz), 1.77-1.76 (m, 3H, CH_2-C(CH_3)), 1.55-1.53 (m, 3H, C=CH-CH_3); *E*-isomer: δ 2.38 (t, 2H, Indole-CH_2-CH_2, *J* = 8.00 Hz), 1.69 (s, 3H, CH_2-C(CH_3)), 1.61-1.58 (m, 3H, C=CH-CH_3); ^{13}C-NMR ($CDCl_3$) δ 135.4, 135.3, 131.8, 124.7, 124.6, 122.84, 122.79, 122.3, 122.2, 121.92, 121.87, 120.0, 119.30, 119.26, 119.22, 119.19, 119.13, 115.41, 115.38, 67.5, 67.4, 39.2, 31.3, 23.9, 23.5, 23.3, 15.9, 13.5, 13.4; HRMS (ESI) calcd for $C_{18}H_{22}NO_2$ m/z = 284.1645 [$(M+H)^+$], found m/z = 284.1646; IR (KBr): ν 2954, 2924, 2854, 1738, 1456, 1392, 1349, 1307, 1245, 1216, 1161, 1089, 1081, 1033, 763, 745 cm^{-1}.

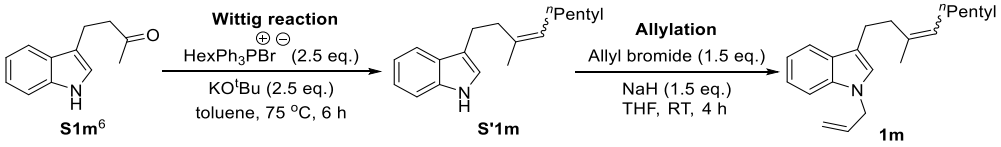
Synthesis of 1-allyl-3-(3-ethylpent-3-en-1-yl)-1*H*-indole (1l): Similar to the synthesis of alkenylindoles **1b**, **1i-k**, and **1x-z**.



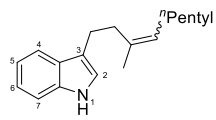


1l: Pale yellow oil (59%, 52:48 mixture of olefin isomers); ^{1}H-NMR ($CDCl_3$) Major isomer: δ 7.63-7.59 (m, 1H, H-4), 7.29-7.27 (m, 1H, H-7), 7.21-7.17 (m, 1H, ArH), 7.12-7.07 (m, 1H, ArH), 6.87 (s, 1H, H-2), 6.03-5.93 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.29-5.23 (m, 1H, C=$\underline{CH}$-CH_3), 5.20-5.16 (m, 1H, CH_2-CH=$\underline{CH_{2a}}$), 5.12-5.05 (m, 1H, CH_2-CH=$\underline{CH_{2b}}$), 4.69-4.66 (m, 2H, $\underline{CH_2}$-CH=CH_2), 2.85-2.77 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.45-2.36 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 2.16-2.06 (m, 2H, $\underline{CH_2}$-CH_3), 1.62-1.59 (m, 2H, C=CH$\underline{CH_3}$), 1.05-0.99 (m, 3H, CH_2-$\underline{CH_3}$); Minor isomer: δ 6.89 (s, 1H, H-2); ^{13}C-NMR ($CDCl_3$) δ 142.0, 141.9, 136.5, 133.9, 133.87, 128.2, 124.9, 121.6, 121.5, 119.2, 119.16, 118.8, 118.75, 118.1, 117.7, 117.2, 117.1, 116.0, 115.95, 109.6 109.57, 48.7, 37.4, 31.1, 29.9, 24.3, 24.0, 23.1, 13.4, 13.2, 13.1, 13.0; HRMS (ESI) calcd for $C_{18}H_{24}N$ m/z = 254.1903 [$(M+H)^+$], found m/z = 254.1904; IR (KBr): ν 3050, 2962, 2924, 2863, 1610, 1561, 1461, 1366, 1329, 1189, 992, 924, 825, 738 cm^{-1}.

Synthesis of alkenylindole 1m

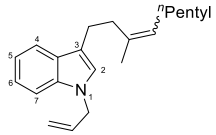


Wittig reaction: Similar to the synthesis of alkenylindoles **1d**, **e**.



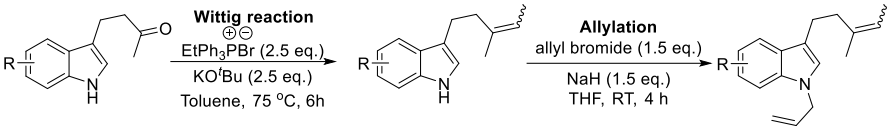
S'1m: Yellow oil; (62%, 53:47 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.88 (brs, 1H, NH), 7.64-7.61 (m, 1H, H-4), 7.34-7.32 (m, 1H, H-7), 7.21-7.16 (m, 1H, ArH), 7.14-7.09 (m, 1H, ArH), 6.98-6.96 (m, 1H, ArH), 5.23-5.16 (m, 1H, C=$\underline{CH}$-CH_3), 2.87-2.80 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.44-2.36 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 2.02-1.92 (m, 2H, C=CH-$\underline{CH_2}$), 1.78-177 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.36-1.22 (m, 6H, $\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.90-0.85 (m, 3H, CH_2-CH_2-CH_2-$\underline{CH_3}$); *E*-isomer: δ 1.69 (s, 3H, CH_2-C($\underline{CH_3}$)); ^{13}C-NMR ($CDCl_3$) δ 136.4, 136.36, 135.0, 134.97, 127.7, 127.6, 126.1, 125.2, 122.0, 121.9, 121.1, 119.2, 119.16, 119.1, 119.0, 116.9, 111.2, 111.1, 66.0, 40.3, 32.7, 31.7, 31.69, 29.9, 29.7, 28.1, 28.0, 24.2, 24.0, 23.6, 22.8, 16.2, 15.4, 14.3, 14.2; HRMS (ESI) calcd for $C_{18}H_{26}N$ m/z = 256.2060 [$(M+H)^+$], found m/z = 256.2061; IR (KBr): ν 3418, 3057, 2956, 2925, 2853, 1619, 1456, 1419, 1377, 1338, 1223, 1091, 1010, 740, 580 cm^{-1}.

Allylation: Similar to the synthesis of alkenylindoles **1b**, **1i-k**, and **1x-z**.



1m: Colorless oil (62%, 53/47 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.62-7.60 (m, 1H, H-4), 7.29-7.27 (m, 1H, H-7), 7.21-7.17 (m, 1H, H-5), 7.12-7.08 (m, 1H, H-6), 6.89 (s, 1H, H-2), 6.03-5.93 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.22-5.05 (m, 3H, CH_2-CH=$\underline{CH_2}$, C=$\underline{CH}$-CH_3), 4.69-4.66 (m, 2H, $\underline{CH_2}$-CH=CH_2), 2.86-2.79 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.43-2.32 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 2.01-1.92 (m, 2H, C=CH-$\underline{CH_2}$), 1.78 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.35-1.19 (m, 6H, $\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.90-0.85 (m, 3H, CH_2-CH_2-CH_2-$\underline{CH_3}$); *E*-isomer: δ 6.87 (s, 1H, H-2), 1.69 (s, 3H, CH_2-C($\underline{CH_3}$)); ^{13}C-NMR ($CDCl_3$) δ 136.53, 136.48, 135.07, 135.00, 133.9, 128.3, 128.8, 126.1, 125.2, 125.0, 124.9, 121.7, 121.5, 119.2, 119.15, 118.8, 118.7, 117.2, 117.1, 115.9, 115.8, 109.6, 109.5, 48.8, 48.7, 40.5, 32.9, 31.8, 31.7, 30.0, 29.7, 28.1, 28.0, 24.1, 23.9, 23.7, 22.8, 16.2, 14.3; HRMS (ESI) calcd for $C_{21}H_{30}N$ m/z = 296.2373 [$(M+H)^+$], found m/z = 296.2373; IR (KBr): ν 3048, 2923, 2857, 1461, 1369, 922, 736, 428 cm^{-1}.

Synthesis of alkenylindoles 1n-u

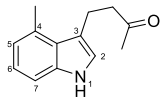


S1n; R = 6-Cl[3]
S1o; R = 5-Br[6]
S1p; R = 5-NO_2[7]
S1q; R = 5-MeO[6]
S1r; R = 5-Me[8]
S1s; R = 4-MeO[7]
S1t; R = 4-Me
S1u; R = 7-Me[9]

S'1n; R = 6-Cl
S'1o; R = 5-Br
S'1p; R = 5-NO_2
S'1q; R = 5-MeO
S'1r; R = 5-Me
S'1s; R = 4-MeO
S'1t; R = 4-Me
S'1u; R = 7-Me

1n; R = 6-Cl
1o; R = 5-Br
1p; R = 5-NO_2
1q; R = 5-MeO
1r; R = 5-Me
1s; R = 4-MeO
1t; R = 4-Me
1u; R = 7-Me

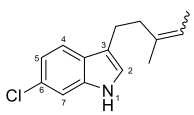
Synthesis of 4-(4-Methyl-1*H*-indol-3-yl)butan-2-one (S1t): Based upon triflic acid catalyzed Michael reactions of indole with methyl vinyl ketone.[6]



Beige solid (73%); M.p. 152-153 °C; ^{1}H-NMR ($CDCl_3$) δ 7.93 (brs, 1H, NH), 7.19 (d, 1H, H-5, *J* = 7.60 Hz), 7.08-7.04 (m, 1H, H-6), 6.94 (d, 1H, H-2, *J* = 2.40 Hz), 6.84 (d, 1H, H-7, *J* = 6.80 Hz), 3.24 (t, 2H, Indole-$\underline{CH_2}$-CH_2-CO, *J* = 8.00 Hz), 2.84 (t, 2H, Indole-CH_2-$\underline{CH_2}$-CO, *J* = 8.00 Hz), 2.71 (s, 3H, CO-CH_3), 2.17 (s, 3H, Ar-CH_3); ^{13}C-NMR ($CDCl_3$) δ 208.7, 136.9, 130.8, 125.8, 122.3, 121.7, 121.2, 116.2, 109.2, 45.5, 30.2, 21.4, 20.4; HRMS (ESI) calcd for $C_{13}H_{16}NO$ m/z = 202.1226 [$(M+H)^+$], found m/z = 202.1226; IR (KBr): ν 3080, 3303, 3049, 2953, 2929, 2905, 2889, 2860, 1698, 1577, 1434, 1410, 1354, 1338, 1264, 1229, 1166, 1148, 797, 778, 756, 736, 695, 592, 573, 556 cm^{-1}.

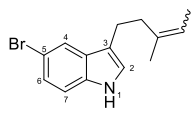
Wittig reaction: Similar to the synthesis of alkenylindoles **1d**, **e**.

6-Chloro-3-(3-methylpent-3-en-1-yl)-1*H*-indole (S'1n)



S'1n: Colorless oil (51%, 51:49 mixture of *Z*/*E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.86 (brs, 1H, NH), 7.53-7.48 (m, 1H, H-4), 7.32-7.31 (m, 1H, H-7), 7.09-7.08 (m, 1H, H-5), 6.97-6.96 (m, 1H, H-2), 5.30-5.22 (m, 1H, C=$\underline{CH}$-CH_3), 2.83-2.77 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.42-2.34 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.75-1.74 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.60-1.57 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 7.07-7.06 (m, 1H, H-5), 6.95-6.94 (m, 1H, H-2), 1.68 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.51-1.49 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 136.7, 135.83, 135.75, 127.91, 127.89, 126.3, 121.74, 121.72, 120.0, 119.93, 119.87, 119.7, 118.9, 117.2, 117.1, 111.08, 111.06, 66.0, 40.2, 32.2, 24.0, 23.6, 23.4, 15.9, 15.4, 13.5, 13.4; HRMS (APCI) calcd for $C_{14}H_{17}ClN$ m/z = 234.1044 [$(M+H)^+$], found m/z = 234.1041; IR (KBr): ν 3427, 2965, 2917, 2856, 1618, 1549, 1474, 1454, 1400, 1376, 1334, 1231, 1131, 1092, 1062, 905, 845, 802, 587 cm^{-1}.

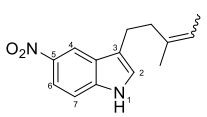
5-Bromo-3-(3-methylpent-3-en-1-yl)-1*H*-indole (S'1o)



S'1o: Colorless oil (42%, 57:43 mixture of *Z*/*E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.91 (brs, 1H, NH), 7.74-7.70 (m, 1H, H-4), 7.27-7.24 (m, 1H, ArH), 7.21-7.18 (m, 1H, ArH), 6.98 (d, 1H, H-2, *J* = 2.00 Hz), 5.30-5.23 (m, 1H, C=$\underline{CH}$-CH_3),

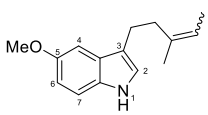
2.81-2.75 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.40 (t, 2H, Indole-CH_2-$\underline{CH_2}$, *J* = 8.00 Hz), 1.75-1.74 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.52-1.50 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 6.96 (d, 1H, H-2, *J* = 2.40 Hz), 2.35 (t, 2H, Indole-CH_2-$\underline{CH_2}$, *J* = 7.60 Hz), 1.68 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.60-1.58 (m, 3H, C=CH-$\underline{CH_3}$),; ^{13}C-NMR ($CDCl_3$) δ 135.8, 135.7, 135.0, 129.54, 129.52, 124.81, 124.78, 122.4, 121.73, 121.66, 119.8, 119.0, 116.8, 116.7, 112.59, 112.57, 112.52, 40.2, 32.1, 23.9, 23.5, 23.3, 15.9, 13.5, 13.4; HRMS (ESI) calcd for $C_{14}H_{17}BrN$ m/z = 278.0539 [$(M+H)^+$], found m/z = 278.0539; IR (KBr): ν 3431, 2920, 2856, 1569, 1452, 1323, 1221, 1091, 873, 791, 582 cm^{-1}.

3-(3-Methylpent-3-en-1-yl)-5-nitro-1*H*-indole (S'1p)



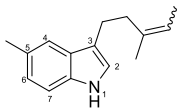
S'1p: Yellow solid (54%, 52:48 mixture of *Z/E*-olefin isomers); M.p. 77-78 °C; ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 8.60 (d, 1H, H-4, *J* = 1.60 Hz), 8.34 (brs, 1H, NH), 8.09 (t, 1H, H-6, *J* = 1.60 Hz), 7.39 (d, 1H, H-7, *J* = 2.40 Hz), 7.15-7.13 (m, 1H, H-2), 5.30-5.24 (m, 1H, C=$\underline{CH}$-CH_3), 2.91-2.85 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.44 (t, 2H, Indole-CH_2-$\underline{CH_2}$, *J* = 8.40 Hz), 1.77-1.75 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.60-1.58 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 8.58 (d, 1H, H-4, *J* = 2.00 Hz), 8.11 (t, 1H, H-6, *J* = 2.00 Hz), 7.36 (d, 1H, H-7, *J* = 2.80 Hz), 2.39 (t, 2H, Indole-CH_2-$\underline{CH_2}$, *J* = 7.60 Hz), 1.70 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.45-1.47 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 141.52, 141.49, 139.4, 135.3, 135.2, 127.2, 124.3, 120.1, 119.6, 119.3, 119.4, 117.74, 117.71, 116.6, 116.5, 111.1, 40.1, 32.0, 23.7, 23.5, 23.1, 15.9, 13.5, 13.4; HRMS (ESI) calcd for $C_{14}H_{16}N_2NaO_2$ m/z = 267.1104 [$(M+Na)^+$], found m/z = 267.1106; IR (KBr): ν 3348, 2976, 2919, 2856, 1623, 1576, 1509, 1464, 1379, 1322, 1232, 1098, 1049, 807, 742, 652, 593, 548 cm^{-1}.

5-Methoxy-3-(3-methylpent-3-en-1-yl)-1*H*-indole (S'1q)



S'1q: Yellow oil (65%, 64:36 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) Z-isomer: δ 7.79 (brs, 1H, NH), 7.25-7.22 (m, 1H, ArH), 7.07 (d, 1H, ArH, *J* = 2.80 Hz), 6.98 (d, 1H, ArH, *J* = 2.00 Hz), 6.87-6.83 (m, 1H, ArH), 5.31-5.25 (m, 1H, C=$\underline{CH}$-CH_3), 3.87 (s, 3H, OCH_3), 2.83-2.77 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.45-2.36 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.78-1.76 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.56-1.54 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 7.04 (d, 1H, ArH, *J* = 2.00 Hz), 6.96 (d, 1H, ArH, *J* = 2.40 Hz), 1.70 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.61-1.59 (m, 3H, CH_2-C($\underline{CH_3}$)); ^{13}C-NMR ($CDCl_3$) δ 153.9, 136.2, 136.0, 131.6, 128.0, 122.0, 119.5, 118.7, 116.6, 122.1, 111.88, 111.86, 100.93, 100.87, 56.1, 56.0, 40.1, 32.1, 24.1, 23.6, 16.0, 13.5, 13.4; HRMS (ESI) calcd for $C_{15}H_{20}NO$ m/z = 230.1539 [$(M+H)^+$], found m/z = 230.1539; IR (KBr): ν 3416, 2924, 2856, 1623, 1584, 1480, 1448, 1290, 1214, 1173, 1035, 924, 795 cm^{-1}.

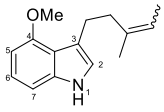
5-Methyl-3-(3-methylpent-3-en-1-yl)-1*H*-indole (S'1r)



S'1r: Colorless oil (72%, 57:43 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.79 (brs, 1H, NH), 7.40-7.38 (m, 1H, ArH), 7.25-7.22 (m, 1H, ArH), 7.02-6.93 (m, 2H, ArH), 5.33-5.23 (m, 1H, C=$\underline{CH}$-CH_3), 2.84-2.77 (m, 2H, Indole-$\underline{CH_2}$-CH_2),

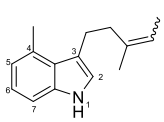
2.47-2.26 (m, 5H, Ar-CH_3, Indole-CH_2-$\underline{CH_2}$), 1.78-1.76 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.56-1.54 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 1.70 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.61-1.59 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 136.2, 136.1, 134.8, 128.43, 128.38, 127.9, 123.59, 123.57, 121.2, 119.4, 118.7, 118.65, 118.62, 116.5, 110.8, 66.0, 40.3, 32.3, 24.2, 23.6, 21.68, 21.66, 16.0, 15.4, 13.5, 13.4; HRMS (ESI) calcd for $C_{15}H_{20}N$ m/z = 214.1590 [$(M+H)^+$], found m/z = 214.1591; IR (KBr): ν 3415, 2922, 2858, 1696, 1450, 1371, 1226, 1089, 792, 592 cm^{-1}.

4-Methoxy-3-(3-methylpent-3-en-1-yl)-1*H*-indole (S'1s)



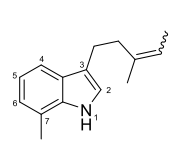
S'1s: Colorless oil (75%, 66:34 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.84 (brs, 1H, NH), 7.10-7.05 (m, 1H, ArH), 6.95-6.93 (m, 1H, ArH), 6.85-6.83 (m, 1H, ArH), 6.50-6.47 (m, 1H, H-2), 5.30-5.21 (m, 1H, C=$\underline{CH}$-CH_3), 3.93 (s, 3H, OCH_3), 2.98-2.90 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.43-2.34 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.78-1.77 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.61-1.57 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 3.92 (s, 3H, OCH_3), 1.71-1.70 (m, 3H, CH_2-C($\underline{CH_3}$)); ^{13}C-NMR ($CDCl_3$) δ 155.12, 155.07, 138.3, 138.2, 136.2, 136.68, 122.79, 122.76, 119.9, 119.8, 119.0, 118.3, 117.75, 117.73, 117.59, 117.54, 104.5, 99.4, 55.2, 55.1, 41.9, 34.1, 26.2, 25.5, 23.7, 15.9, 13.5, 13.3; HRMS (ESI) calcd for $C_{15}H_{20}NO$ m/z = 230.1539 [$(M+H)^+$], found m/z = 230.1540; IR (KBr): ν 3411, 2922, 2853, 1581, 1502, 1456, 1358, 1255, 1083, 778, 733 cm^{-1}.

4-Methyl-3-(3-methylpent-3-en-1-yl)-1*H*-indole (S'1t)



S'1t: Colorless oil (78%, 58:42 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.87 (brs, 1H, NH), 7.18-7.16 (m, 1H, ArH), 7.06-7.02 (m, 1H, ArH), 6.95-6.92 (m, 1H, ArH), 6.84-6.82 (m, 1H, ArH), 5.34-5.24 (m, 1H, C(CH_3)=$\underline{CH}$-CH_3), 3.03-2.96 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.74 (s, 3H, Ar-CH_3), 2.44-2.34 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.78-1.76 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.57-1.54 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 2.72 (s, 3H, Ar-CH_3), 1.70 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.61-1.60 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 136.9, 136.05, 136.00, 131.10, 131.06, 126.11, 126.08, 122.04, 122.01, 121.34, 121.29, 121.01, 121.00, 119.5, 118.7, 118.0, 109.1, 66.0, 41.8, 33.6, 26.3, 25.6, 23.6, 20.5, 16.0, 15.4, 13.5, 13.4; HRMS (ESI) calcd for $C_{15}H_{20}N$ m/z = 214.1590 [$(M+H)^+$], found m/z = 214.1591; IR (KBr): ν 3410, 3047, 2924, 2861, 1498 cm^{-1}.

7-Methyl-3-(3-methylpent-3-en-1-yl)-1*H*-indole (S'1u)

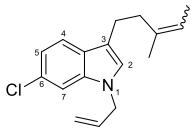


S'1u: Colorless oil (74%, 63:37 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.80 (brs, 1H, NH), 7.50-7.46 (m, 1H, H-4), 7.07-7.02 (m, 1H, ArH), 7.00-6.96 (m, 2H, ArH), 5.32-5.23 (m, 1H, C(CH_3)=$\underline{CH}$-CH_3), 2.86-2.79 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.47-2.36 (m, 5H, Ar-CH_3, Indole-CH_2-$\underline{CH_2}$), 1.78-1.76 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.56-1.55 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 1.70 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.61-1.59 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 136.2, 136.1, 136.0, 135.9, 127.2, 122.54, 122.51, 120.8, 120.3, 119.5, 119.4, 118.6, 117.5, 116.8, 116.7,

40.4, 32.4, 24.3, 23.7, 23.6, 16.7, 13.9, 13.5, 13.4; HRMS (ESI) calcd for $C_{15}H_{20}N$ m/z 214.1590 [$(M+H)^+$], found m/z = 214.1591; IR (KBr): ν 3421, 3048, 2956, 2921, 2858, 1441, 1346, 786, 745, 580 cm^{-1}.

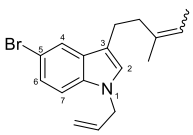
Allylation: Similar to the synthesis of alkenylindoles **1b**, **1i-k**, and **1x-z**.

1-Allyl-6-chloro-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1n)



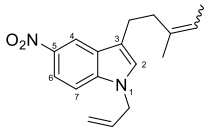
1n: Colorless oil (80%, 58:42 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.51-7.46 (m, 1H, ArH), 7.25-7.24 (m, 1H, ArH), 7.07-7.03 (m, 1H, ArH), 6.86 (s, 1H, H-2), 5.99-5.90 (m, 1H, CH_2-CH=CH_2), 5.28-5.17 (m, 2H, C=CH-CH_3, CH_2-CH=CH_{2a}), 5.09-5.02 (m, 1H, CH_2-CH=CH_{2b}), 4.63-4.60 (m, 2H, CH_2-CH=CH_2), 2.82-2.75 (m, 2H, Indole-CH_2-CH_2), 2.39 (t, 2H, Indole-CH_2-CH_2, *J* = 8.40 Hz), 1.75-1.73 (m, 3H, CH_2-C(CH_3)), 1.52-1.50 (m, 3H, C=CH-CH_3); *E*-isomer: δ 6.83 (s, 1H, H-2), 2.34 (t, 2H, Indole-CH_2-CH_2, *J* = 7.60 Hz), 1.68 (s, 3H, CH_2-C(CH_3)), 1.59-1.57 (m, 3H, C=CH-CH_3); ^{13}C-NMR ($CDCl_3$) δ 136.92, 135.86, 135.75, 133.40, 133.38, 127.7, 127.6, 126.9, 125.7, 120.1, 120.0, 119.7, 119.52, 119.47, 118.9, 117.5, 117.4, 116.1, 109.7, 109.6, 48.83, 48.80, 40.4, 32.4, 24.0, 23.6, 23.4, 15.9, 13.5, 13.4; HRMS (ESI) calcd for $C_{17}H_{21}ClN$ m/z = 274.1357 [$(M+H)^+$], found m/z = 274.1358; IR (KBr): ν 3074, 2921, 2858, 1608, 1550, 1463, 1372, 1327, 1189, 1064, 925, 843, 800 cm^{-1}.

1-Allyl-5-bromo-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1o)



1o: Colorless oil (52%, 52:48 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.72 (d, 1H, H-4, *J* = 1.6 Hz), 7.26 (t, 1H, H-6, *J* = 2.0 Hz), 7.14 (d, 1H, H-7, *J* = 8.80 Hz), 6.88 (s, 1H, H-2), 6.00-5.90 (m, 1H, CH_2-CH=CH_2), 5.28-5.23 (m, 1H, C=CH-CH_3), 5.20-5.16 (m, 1H, CH_2-CH=CH_{2a}), 5.07-4.99 (m, 1H, CH_2-CH=CH_{2b}), 4.66-4.63 (m, 2H, CH_2-CH=CH_2), 2.80-2.73 (m, 2H, Indole-CH_2-CH_2), 2.41-2.32 (m, 2H, Indole-CH_2-CH_2), 1.76-1.74 (m, 3H, CH_2-C(CH_3)), 1.52-1.50 (m, 3H, C=CH-CH_3); *E*-isomer: δ 7.70 (d, 1H, H-4, *J* = 1.6 Hz), 7.24 (t, 1H, H-6, *J* = 1.6 Hz), 7.12 (d, 1H, H-7, *J* = 8.80 Hz), 6.86 (s, 1H, H-2), 1.68 (s, 3H, CH_2-C(CH_3)), 1.59-1.57 (m, 3H, C=CH-CH_3); ^{13}C-NMR ($CDCl_3$) δ 135.8, 135.7, 135.1, 133.44, 133.4, 130.0, 126.3, 126.25, 124.35, 124.3, 121.8, 121.75, 119.7, 119.0, 117.4, 117.3, 115.5, 112.2, 112.17, 111.1, 111.08, 48.9, 48.86, 40.4, 32.3, 23.9, 23.6, 23.3, 15.9, 13.5, 13.4; HRMS (ESI) calcd for $C_{17}H_{21}BrN$ m/z = 318.0852 [$(M+H)^+$], found m/z = 318.0852; IR (KBr): ν 2924, 2856, 1465, 1376, 1193, 991, 927, 784 cm^{-1}.

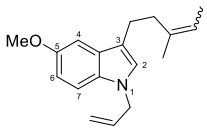
1-Allyl-3-(3-methylpent-3-en-1-yl)-5-nitro-1*H*-indole (1p)



1p: Yellow oil (83%, 53:47 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 8.58 (d, 1H, ArH, *J* = 2.40 Hz), 8.11 (t, 1H, ArH, *J* = 2.40 Hz), 7.29 (d, 1H, ArH, *J* = 2.80 Hz), 7.02 (s, 1H, H-2), 6.01-5.94 (m, 1H, CH_2-CH=CH_2), 5.29-5.23 (m, 1H, C=CH-CH_3, CH_2-CH=CH_{2a}), 5.10-5.03 (m, 1H, CH_2-CH=CH_{2b}), 4.74-4.71 (m, 2H, CH_2-CH=CH_2), 2.89-2.83 (m, 2H, Indole-CH_2-CH_2), 2.43 (t, 2H, Indole-CH_2-CH_2, *J* = 8.00 Hz),

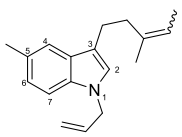
1.76-1.75 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.49-1.47 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 8.56 (d, 1H, ArH, *J* = 2.40 Hz), 8.09 (t, 1H, ArH, *J* = 2.40 Hz), 7.27 (d, 1H, ArH, *J* = 2.00 Hz), 7.00 (s, 1H, H-2), 2.37 (t, 2H, Indole-CH_2-$\underline{CH_2}$, *J* = 8.00 Hz), 1.69 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.59-1.57 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 141.15, 141.11, 139.3, 135.3, 135.2, 132.68, 132.65, 128.2, 127.6, 120.1, 119.4, 118.8, 118.7, 118.0, 117.9, 117.33, 117.31, 116.7, 116.6, 109.42, 109.39, 49.11, 49.07, 40.2, 32.1, 23.6, 23.5, 23.1, 15.9, 13.5, 13.4; HRMS (ESI) calcd for $C_{17}H_{20}N_2NaO_2$ m/z = 307.1417 [$(M+Na)^+$], found m/z = 307.1417; IR (KBr): ν 3083, 2922, 2859, 1617, 1571, 1515, 1476, 1389, 1330, 798, 742 cm^{-1}.

1-allyl-5-methoxy-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1q)



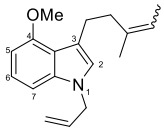
1q: Colorless oil (46%, 53:47 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.16 (dd, 1H, H-4, *J* = 2.8, 9.20 Hz), 7.04 (dd, 1H, H-7, *J* = 2.4, 10.80 Hz), 6.87-6.84 (m, 2H, H-2, H-6), 6.87-6.84 (m, 2H, H-2, H-6), 6.01-5.91 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.30-5.25 (m, 1H, C=$\underline{CH}$-CH_3), 5.18-5.14 (m, 1H, CH_2-CH=$\underline{CH_{2a}}$), 5.10-5.02 (m, 1H, CH_2-CH=$\underline{CH_{2b}}$), 4.64-4.61 (m, 2H, $\underline{CH_2}$-CH=CH_2), 3.86 (s, 3H, OCH_3), 2.82-2.75 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.43-2.34 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.78-1.76 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.56-1.54 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 1.70 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.60-1.59 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 153.7, 136.2, 136.1, 134.0, 133.99, 131.9, 131.86, 128.5, 125.7, 125.6, 119.4, 118.7, 117.1, 117.0, 115.3, 111.6, 110.4, 110.35, 101.1, 101.06, 56.1, 56.05, 48.95, 48.9, 40.3, 32.3, 24.1, 23.6, 23.58, 16.0, 13.5, 13.4; HRMS (ESI) calcd for $C_{18}H_{24}NO$ m/z = 270.1852 [$(M+H)^+$], found m/z = 270.1852; IR (KBr): ν 3074, 2921, 2857, 1618, 1580, 1485, 1448, 1223, 1041, 920, 792 cm^{-1}.

1-Allyl-5-methyl-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1r)



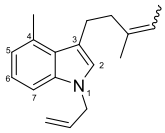
1r: Colorless oil (53%, 57:43 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.39-7.37 (m, 1H, H-4), 7.17-7.15 (m, 1H, H-6), 7.03-7.00 (m, 1H, H-7), 6.85 (s, 1H, H-2), 6.01-5.91 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.31-5.23 (m, 1H, C=$\underline{CH}$-CH_3), 5.18-5.13 (m, 1H, CH_2-CH=$\underline{CH_{2a}}$), 5.09-5.02 (m, 1H, CH_2-CH=$\underline{CH_{2b}}$), 4.66-4.63 (m, 2H, $\underline{CH_2}$-CH=CH_2), 2.83-2.76 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.46 (s, 3H, Ar-CH_3), 2.41 (t, 2H, Indole-CH_2-$\underline{CH_2}$, *J* = 8.80 Hz), 1.77-1.76 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.56-1.54 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 6.82 (s, 1H, H-2), 2.36 (t, 2H, Indole-CH_2-$\underline{CH_2}$, *J* = 8.00 Hz), 1.69 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.61-1.58 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ ^{13}C-NMR ($CDCl_3$) δ 136.3, 136.1, 135.0, 134.0, 128.5, 128.0, 127.9, 125.10, 125.06, 123.2, 123.1, 119.4, 118.9, 118.8, 118.6, 117.0, 116.9, 115.3, 109.31, 109.28, 48.8, 48.7, 40.5, 32.5, 24.1, 23.62, 23.57, 21.6, 16.0, 13.5, 13.4; HRMS (ESI) calcd for $C_{18}H_{24}N$ m/z = 254.1903 [$(M+H)^+$], found m/z = 254.1905; IR (KBr): ν 3016, 2919, 2858, 1483, 1446, 1377, 1300, 1186, 989, 921, 785 cm^{-1}.

1-Allyl-4-methoxy-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1s)



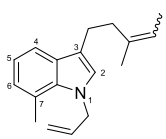
1s: Colorless oil (56%, 65:35 mixture of *Z*/*E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.10-7.05 (m, 1H, ArH), 6.88-6.85 (m, 1H, ArH), 6.74 (s, 1H, H-2), 6.48-6.45 (m, 1H, ArH), 5.99-5.91 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.30-5.21 (m, 1H, C=$\underline{CH}$-CH_3), 5.18-5.13 (m, 1H, CH_2-CH=$\underline{CH_{2a}}$), 5.09-5.01 (m, 1H, CH_2-CH=$\underline{CH_{2b}}$), 4.62-4.59 (m, 2H, $\underline{CH_2}$-CH=CH_2), 3.912 (s, 3H, OCH_3), 2.96-2.88 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.41-2.32 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.78-1.76 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.60-1.57 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 6.71 (s, 1H, H-2), 3.908 (s, 3H, OCH3), 1.70 (s, 3H, CH_2-C($\underline{CH_3}$)); ^{13}C-NMR ($CDCl_3$) δ 155.2, 155.1, 138.4, 138.3, 136.8, 136.7, 133.9, 123.9, 123.8, 122.34, 122.30, 118.9, 118.3, 118.0, 117.9, 117.1, 117.0, 116.6, 103.0, 102.9, 99.1, 55.2, 55.1, 48.9, 48.8, 42.1, 34.3, 26.2, 25.4, 23.7, 15.9, 13.5, 13.3; HRMS (ESI) calcd for $C_{18}H_{24}NO$ m/z = 270.1852 [$(M+H)^+$], found m/z = 270.1852; IR (KBr): ν 3074, 2920, 2858, 1577, 1496, 1456, 1332, 1256, 1191, 1091, 1067, 923, 727 cm^{-1}.

1-Allyl-4-methyl-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1t)



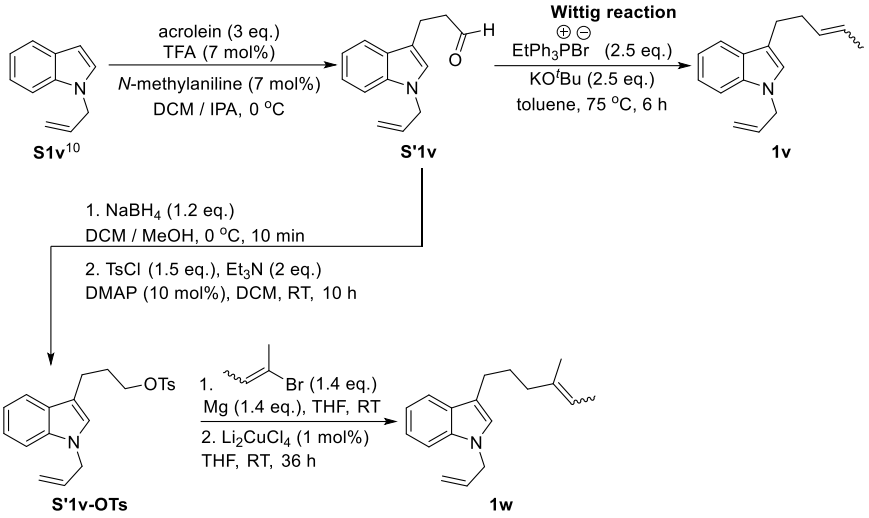
1t: Colorless oil (50%, 58:42 mixture of olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.12-7.03 (m, 2H, ArH), 6.86-6.81 (m, 2H, ArH), 6.02-5.91 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.32-5.24 (m, 1H, C=$\underline{CH}$-CH_3), 5.19-5.15 (m, 1H, CH_2-CH=$\underline{CH_{2a}}$), 5.11-5.04 (m, 1H, CH_2-CH=$\underline{CH_{2b}}$), 4.66-4.63 (m, 2H, $\underline{CH_2}$-CH=CH_2), 3.02-2.95 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.73 (s, 3H, Ar-CH_3), 2.40 (t, 2H, Indole-CH_2-$\underline{CH_2}$, *J* = 8.40 Hz), 1.78-1.76 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.57-1.54 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 2.72 (s, 3H, Ar-CH_3), 2.35 (t, 2H, Indole-CH_2-$\underline{CH_2}$, *J* = 8.80 Hz), 1.70-1.69 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.62-1.59 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 136.9, 136.1, 136.0, 133.9, 133.8, 131.29, 131.25, 126.7, 125.3, 125.2, 121.59, 121.56, 120.7, 120.6, 119.4, 118.7, 117.15, 117.09, 116.83, 116.81, 107.52, 107.49, 48.8, 48.7, 42.0, 33.8, 26.3, 25.6, 23.7, 20.50, 20.48, 16.0, 13.5, 13.4; HRMS (ESI) calcd for $C_{18}H_{24}N$ m/z = 254.1903 [$(M+H)^+$], found m/z = 254.1904; IR (KBr): ν 3041, 2921, 2861, 1554, 1448, 1375, 1327, 1241, 1195, 1151, 1064, 992, 923, 744 cm^{-1}.

1-Allyl-7-methyl-3-(3-methylpent-3-en-1-yl)-1*H*-indole (1u)



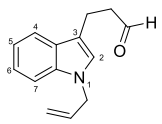
1u: Pale yellow oil (52%, 69:31 mixture of *Z*/*E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) Z-isomer: δ 7.47-7.42 (m, 1H, H-4), 7.01-6.96 (m, 1H, H-5), 6.91-6.89 (m, 1H, H-6), 6.80 (s, 1H, H-2), 6.07-5.97 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.29-5.22 (m, 1H, C=$\underline{CH}$-CH_3), 5.13-5.09 (m, 1H, CH_2-CH=$\underline{CH_{2a}}$), 4.90-4.87 (m, 2H, $\underline{CH_2}$-CH=CH_2), 4.81-4.73 (m, 1H, CH_2-CH=$\underline{CH_{2b}}$), 2.83-2.76 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.66 (s, 3H, Ar-CH_3), 2.43-2.34 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.77-1.75 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.56-1.54 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 6.77 (s, 1H, H-2), 2.65 (s, 3H, Ar-CH_3), 1.69 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.59-1.57 (m, 3H, C=CH-$\underline{CH_3}$); ^{13}C-NMR ($CDCl_3$) δ 136.2, 136.0, 135.8, 135.3, 129.2, 126.81, 126.76, 124.52, 124.48, 121.0, 119.4, 119.1, 119.0, 118.7, 117.2, 117.1, 115.90, 115.85, 50.75, 50.72, 40.4, 32.4, 24.0, 23.6, 23.5, 19.6, 13.5, 13.4; HRMS (ESI) calcd for $C_{18}H_{24}N$ m/z = 254.1903 [$(M+H)^+$], found m/z = 254.1903; IR (KBr): ν 3041, 2964, 2921, 2860, 1596, 1452, 1414, 1364, 1325, 1184, 1076, 993, 921, 785, 743 cm^{-1}.

Synthesis of alkenylindole 1v and 1w



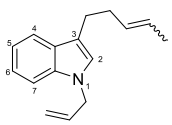
3-(1-allyl-1*H*-indol-3-yl)propanal (S'1v)

At room temperature, *N*-methylaniline (0.83 mmol, 91 μL) and trifluoroacetic acid (0.83 mmol, 64 μL) were added to a solution of acrolein (37.0 mmol, 2.4 mL) in CH_2Cl_2/*i*-PrOH (85/15) (24.2 mL). Then, the mixture was cooled to 0 °C, followed by adding 1-allyl-1*H*-indole **S1v**. The reaction was stirred at 0 °C for 6 h, and then filtered through a short pad of silica gel using ether as solvent. Finally, the filtrate was concentrated *in vacuo* and purified by column chromatography (hexane/DCM = 7/3) to give the product **S'1v** (1.3 g, 61% yield) as a yellow oil.



S'1v: ^{1}H-NMR ($CDCl_3$) δ 9.84 (t, 1H, CHO, *J* = 1.60 Hz), 7.58 (d, 1H, H-4, *J* = 8.40 Hz), 7.29 (d, 1H, H-7, *J* = 8.40 Hz), 7.23-7.19 (m, 1H, H-5), 7.14-7.10 (m, 1H, H-6), 6.89 (s, 1H, H-2), 6.00-5.93 (m, 1H, $\underline{CH}$=CH_2), 5.20-5.17 (m, 1H, CH=$\underline{CH_{2a}}$), 5.11-5.5.05 (m, 1H, CH=$\underline{CH_{2b}}$), 4.68-4.66 (m, 2H, $\underline{CH_2}$-CH=CH_2), 3.11 (t, 2H, Indole-$\underline{CH_2}$-CH_2, *J* = 7.20 Hz), 2.84 (td, 2H, Indole-CH_2-$\underline{CH_2}$, *J* = 1.60, 7.20 Hz); ^{13}C-NMR ($CDCl_3$): δ 202.6, 136.6, 133.6, 127.8, 125.4, 121.9, 119.1, 118.9, 117.3, 113.6, 109.7, 48.7, 44.2, 17.9; HRMS (ESI) calcd for $C_{14}H_{15}NNaO$ m/z = 236.1046 [$(M+Na)^+$], found m/z = 236.1047; IR (KBr): ν 2973, 2928, 2907, 2868, 2825, 2723, 1724, 1468, 1370, 1333, 991, 924, 741, 536 cm^{-1}.

1-Allyl-3-(pent-3-en-1-yl)-1*H*-indole (1v): Similar to the synthesis of alkenylindoles **1d**, **e**.

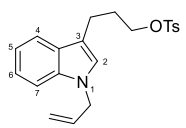


1v: Colorless oil (75%, 88:12 mixture of *Z/E*-olefin isomers); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.62-7.58 (m, 1H, ArH), 7.29-7.27 (m, 1H, ArH), 7.21-7.17 (m, 1H, ArH), 7.12-7.08 (m, 1H, ArH), 6.89 (s, 1H, H-2), 6.03-5.93 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.59-5.44 (m, 2H, $\underline{CH}$=$\underline{CH}$-CH_3), 5.19-5.16 (m, 1H, CH_2-CH=$\underline{CH_{2a}}$), 5.10-5.06 (m, 1H, CH_2-CH=$\underline{CH_{2b}}$), 4.69-4.66 (m, 2H, $\underline{CH_2}$-CH=CH_2), 2.82-2.78 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.48-2.43 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.62-1.60 (m, 3H, CH=CH-$\underline{CH_3}$); *E*-isomer: δ 6.87 (s, 1H, H-2), 2.41-2.36 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.67-1.65 (m, 3H, CH=CH-$\underline{CH_3}$), ^{13}C-NMR ($CDCl_3$): δ 136.5, 133.9, 131.4, 130.6, 128.3, 125.2, 125.1, 124.3, 121.6,

119.3, 119.2, 118.8, 117.14, 117.10, 115.6, 109.6, 48.7, 33.4, 27.8, 25.5, 25.2, 18.1, 13.0; HRMS (ESI) calcd for $C_{16}H_{20}N$ m/z = 226.1590 [$(M+H)^+$], found m/z = 226.1591; IR (KBr): ν 3054, 3016, 2917, 2852, 1469, 1439, 1368, 1326, 1198, 991, 928, 739, 695, 540, 435 cm^{-1}.

3-(1-Allyl-1*H*-indol-3-yl)propyl 4-methylbenzenesulfonate (S'1v-OTs)[3]

To a solution of aldehyde **S'1v** (9.8 mmol, 2.1 g) in dichloromethane (5 mL) and methanol (5 mL) at 0 °C, sodium borohydride (1.2 eq. 11.8 mmol, 0.5 g) was added portionwise over 10 min. After quenching the reaction with HCl_{aq} (1M) at 0 °C, the reaction mixture was extracted with dichloromethane and dried over sodium sulfate. The combined organic solvent was removed *in vacuo* to give the corresponding alcohol as pure colorless oil (2.1 g, 99% yield, the product is sensitive to silica gel). Subsequently, the produced alcohol was dissolved in dichloromethane (77 mL), followed by cooling to 0 °C. Tosyl chloride (5 eq., 23.1 mmol, 4.4 g) was added at 0 °C, followed by adding Et_3N (6.5 eq., 30.1 mmol, 3.1 g, 4.3 mL) and DMAP (35 mol%, 1.6 mmol, 189 mg). The resulting mixture was stirred at room temperature for 10 h until the consumption of the starting materials. The reaction was quenched with. aq. NH_4Cl at 0 °C. The mixture was extracted with dichloromethane and then dried over sodium sulfate. After removing the solvent under educed pressure, the residues were loaded to silica gel column chromatography (hexane/DCM = 1/1) to give the corresponding tosyl ester **S'1v-OTs** (2.7 g, 74% yield) as a colorless oil.

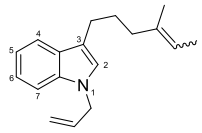


S'1v-OTs: ^{1}H-NMR ($CDCl_3$) δ 7.79-7.76 (m, 2H, ArH), 7.48 (d, 1H, ArH, *J* = 8.00 Hz), 7.31-7.23 (m, 3H, ArH), 7.20-7.16 (m, 1H, ArH), 7.09-7.05 (m, 1H, ArH), 6.76 (s, 1H, H-2), 5.99-5.89 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.18-5.15 (m, 1H, CH_2-CH=$\underline{CH_{2a}}$), 5.06-5.01 (m, 1H, CH_2-CH=$\underline{CH_{2b}}$), 4.64-4.62 (m, 2H, $\underline{CH_2}$-CH=CH_2), 4.07 (t, 2H, Indole-CH_2-CH_2-$\underline{CH_2}$-OTs, *J* = 6.00 Hz), 2.79 (t, 2H, Indole-$\underline{CH_2}$-CH_2-CH_2-OTs, *J* = 6.80 Hz), 2.43 (s, 3H, Ar-CH_3), 2.02 (p, 2H, Indole-CH_2-$\underline{CH_2}$-CH_2-OTs, *J* = 6.40 Hz); ^{13}C-NMR ($CDCl_3$): δ 144.8, 136.6, 133.7, 133.2, 129.9 (2C), 128.0 (2C), 127.8, 125.6, 121.7, 119.0, 118.9, 117.2, 113.4, 109.7, 70.1, 48.7, 29.3, 21.8, 20.9; HRMS (ESI) calcd for $C_{21}H_{24}NO_3S$ m/z = 370.1471 [$(M+H)^+$], found m/z = 370.1474; IR (KBr): ν 3054, 2923, 2858, 1604, 1462, 1357, 1179, 1095, 923, 816, 740, 660, 559 cm^{-1}.

1-Allyl-3-(4-methylhex-4-en-1-yl)-1*H*-indole (1w)[3]

To a suspension of magnesium turnings (1.4 eq., 3.8 mmol, 92 mg) in THF (7.6 mL), few drops of 1,2-dibromoethane were added under nitrogen followed by stirring 1 h at room temperature. The Grignard reagent was prepared by adding 2-bromobut-2-ene (1.4 eq., 3.85 mmol, 0.52 g, 0.39 mL). With the activated magnesium. After stirring 2 h at room temperature, the resulting solution was cannulated at -78 °C to other flask containing a solution of tosylate **S'1v-OTs** (2.7 mmol, 1 g) in THF (2.7 mL), followed by adding lithium tetrachlorocuprate [0.1 M in THF] (1 mol%, 0.027 mmol, 271 µL). The reaction mixture was stirred at room temperature for 48 h under TLC monitering. The reaction mixture was quenched with HCl (2 M), diluted by water, extracted by Et_2O and washed with water then brine. The organic layer was dried with Na_2SO_4, and the solvent was removed under reduced pressure. The remaining residues were loaded to silica

gel column chromatography (*n*-hexane) to give product **1w** (224.8 mg, 33%, 78:22 mixture of *Z/E*-olefin isomers) as colorless oil.

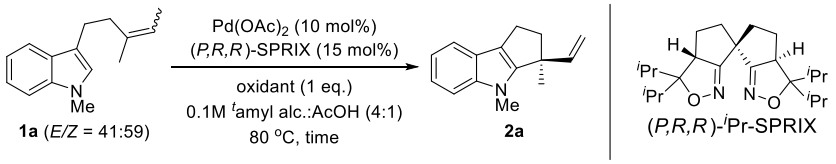


1w: ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.61-7.57 (m, 1H, H-4), 7.28-7.26 (m, 1H, H-7), 7.20-7.16 (m, 1H, ArH), 7.11-7.07 (m, 1H, ArH), 6.87 (s, 1H, H-2), 6.03-5.93 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.26-5.21 (m, 1H, C=$\underline{CH}$-CH_3), 5.19-5.15 (m, 1H, CH_2-CH=$\underline{CH_{2a}}$), 5.10-5.05 (m, 1H, CH_2-CH=$\underline{CH_{2b}}$), 4.69-4.66 (m, 1H, $\underline{CH_2}$-CH=CH_2), 2.76-2.69 (m, 2H, Indole-$\underline{CH_2}$-CH_2-CH_2), 2.14 (t, 2H, Indole-CH_2-CH_2-$\underline{CH_2}$, *J* = 7.60 Hz), 1.84-1.76 (m, 2H, Indole-CH_2-$\underline{CH_2}$-CH_2), 1.70-1.69 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.59-1.54 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 6.86 (s, 1H, H-2), 2.08 (t, 2H, Indole-CH_2-CH_2-$\underline{CH_2}$, *J* = 8.00 Hz), 1.61 (s, 3H, CH_2-C($\underline{CH_3}$)); ^{13}C-NMR ($CDCl_3$) δ 136.6, 136.2, 135.9, 133.9, 128.3, 125.4, 125.00, 121.6, 121.5, 119.30, 119.27, 119.21, 118.8, 118.7, 118.5, 117.1, 116.04, 116.00, 109.5, 48.7, 39.7, 28.7, 28.5, 25.1, 24.9, 23.5, 15.8, 13.5, 13.4; HRMS (ESI) calcd for $C_{18}H_{24}N$ m/z = 254.1903 [$(M+H)^+$], found m/z = 254.1904; IR (KBr): ν 3052, 2926, 2849, 1462, 1370, 1332, 1189, 921, 737, 472 cm^{-1}

3. Optimization of reaction conditions

3.1. Screening of oxidants

Table S1[a]

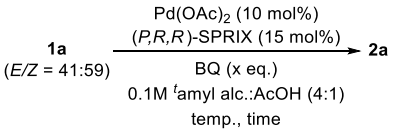


Entry	Oxidant	Time (h)	Conversion (%)	Yield of **2a** (%)	ee of **2a** (%)[b]
1	O_2 (1 atm.)	72	91	8[c]	13
2	Benzoquinone (BQ)	4	100	75	37
3	Ag_2CO_3	12	100	50	55
4	$Cu(OAc)_2$	12	52	18	37
5	$K_2S_2O_8$	12	100	Complex mixture	---
6	TBHP	12	100	25[c]	25
7	$PhI(OAc)_2$	12	100	Complex mixture	---

[a]All reactions were carried out in 0.0469 mmol scale at 0.1M ^{t}amyl alc.:AcOH (4:1) under N_2. [b]Determined by HPLC (YMC CHIRAL ART Cellulose-SB). [c]Determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard.

3.2. Screening of temperatures and oxidant molar ratio

Table S2[a]

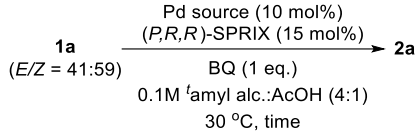


Entry	Temp. (°C)	BQ (x eq.)	Time (h)	Yield of **2a** (%)	ee of **2a** (%)[b]
1	80	1	4	75	37
2	30	1	60	77	61
3	25	1	72	16	84
4	30	0.95	60	71	64
5	30	2	60	39	70

[a]All reactions were carried out in 0.0469 mmol scale at 0.1M ^{t}amyl alc.:AcOH (4:1) under N_2. [b]Determined by HPLC (YMC CHIRAL ART Cellulose-SB).

3.3. Screening of palladium sources

Table S3[a]

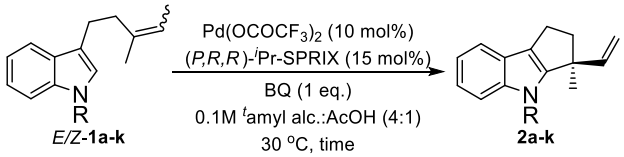


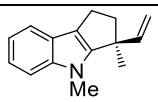
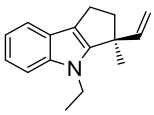
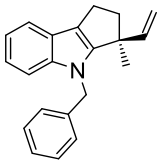
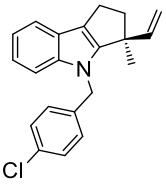
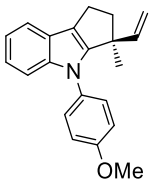
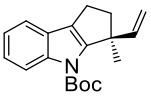
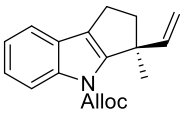
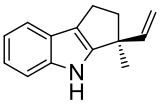
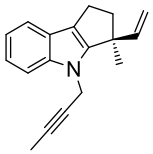
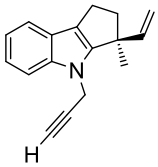
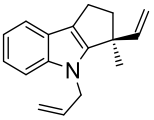
Entry	Pd source	Time (h)	Yield of **2a** (%)	ee of **2a** (%)[b]
1	$Pd(OAc)_2$	60	77	61
2	$Pd(OCOCF_3)_2$	40	66	80
3	$Pd(acac)_2$	64	31	74
4	$Pd(F_6\text{-}acac)_2$	43	16	-3[c]
5	$[(allyl]PdCl]_2$[d]	64	16	33
6	$PdCl_2$	48	No reaction	---
7	$PdBr_2$	48	No reaction	---

[a]All reactions were carried out in 0.0469 mmol scale at 0.1M tamyl alc.:AcOH (4:1) under N_2. [b]Determined by HPLC (YMC CHIRAL Cellulose-SB). [c]Opposite enantiomer was obtained. [d]5 mol%.

3.4. Screening of protecting groups

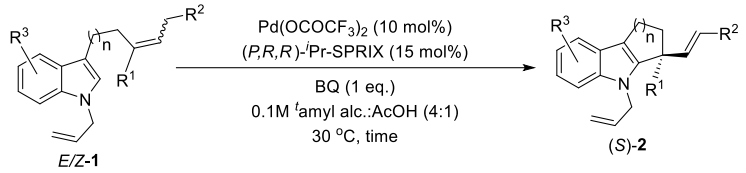
Table S4[a]



			
2a 66%, 80% ee 40 h	**2b** 60%, 84% ee 45 h	**2c** 82%, 48% ee 72 h	**2d** 60%, 72% ee 60 h
			
2e No reaction	**2f** No reaction	**2g** No reaction	**2h** No reaction
			
2i Not detected (Complex mixture)	**2j** Not detected (Complex mixture)	**2k** Quant, 90% ee 24 h	

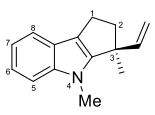
[a] All reactions were carried out in 0.0469 mmol scale at 0.1M ^{t}amyl alc.:AcOH (4:1) under N_2.

4. Pd(II)-SPRIX-catalyzed enantioselective annulation of 1



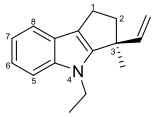
A mixture of $Pd(TFA)_2$ (10 mol %, 0.00469 mmol, 1.6 mg) and (*P*,*R*,*R*)-^{i}Pr-SPRIX (15 mol%, 0.007 mmol, 2.6 mg) was dissolved in dry dichloromethane (1 mL) After stirring under nitrogen atmosphere at 30 °C for 2 h, the solvent was distilled off and the resulting yellow Pd complex was kept under vacuum for 10 min. To the dried Pd complex, *p*-benzoquinone (1 eq., 0.0469 mmol, 5.1 mg) and alkenylindole **1** (0.0469 mmol) were added under nitrogen. Dry ^{t}amyl alcohol (0.4 mL) was added, followed by stirring at 30 °C for 10 mins until dissolving of the solid materials to give a turbid deep red solution. Then, acetic acid (0.1 mL) was added, and subsequently, a clear red solution was obtained which was stirred under nitrogen atmosphere at 30 °C until the consumption of starting material **1**. The solvent was removed under vacuum, and the remaining syrup was purified by PTLC (hexane/Et_2O = 9.5/0.5) to give the pure products **2**. In the synthesis of product **2p**, the reaction was performed at 60 °C.

(*S*)-3,4-Dimethyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2a)[3]



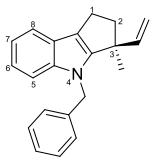
2a: Colorless oil (66%, 40 h); ^{1}H-NMR ($CDCl_3$) δ 7.45 (d, 1H, H-8, *J* = 8.00 Hz), 7.22 (d, 1H, H-5, *J* = 8.40 Hz), 7.15-7.11 (m, 1H, ArH), 7.08-7.04 (m, 1H, ArH), 6.08 (dd, 1H, $\underline{CH}$=CH_2, *J* = 10.40, 17.20 Hz), 5.04 (dd, 1H, CH=$\underline{CH}_{2a}$, *J* = 1.20, 10.40 Hz), 4.96 (dd, 1H, CH=$\underline{CH}_{2b}$, *J* = 1.20, 17.20 Hz), 3.62 (s, 3H, N-CH_3), 2.81 (t, 2H, C1H_2, *J* = 6.80 Hz), 2.55-2.48 (m, 1H, C2H_{2a}), 2.38-2.32 (m, 1H, C2H_{2b}), 1.49 (s, 3H, C3-CH_3); Enantiomeric excess: 80%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 14.2 min, major peak: t_R = 11.5 min; $[\alpha]_D^{25}$ = +26.5 (*c* 0.13, $CHCl_3$).

(*S*)-4-Ethyl-3-methyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2b)



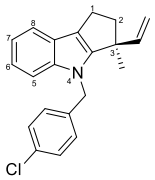
2b: Colorless oil (60%, 45 h); ^{1}H-NMR ($CDCl_3$) δ 7.47-7.45 (m, 1H, ArH), 7.28-7.24 (m, 1H, ArH), 7.14-7.04 (m, 2H, ArH), 6.08 (dd, 1H, $\underline{CH}$=CH_2, *J* = 10.40, 17.60 Hz), 5.05 (dd, 1H, CH=$\underline{CH}_{2a}$, *J* = 2.00, 10.40 Hz), 4.99 (dd, 1H, CH=$\underline{CH}_{2b}$, *J* = 2.00, 17.60 Hz), 4.14-4.01 (m, 2H, $\underline{CH}_2$-CH_3), 2.86-2.75 (m, 2H, C1H_2), 2.53-2.47 (m, 1H, C2H_{2a}), 2.37-2.30 (m, 1H, C2H_{2b}), 1.50 (s, 3H, C3-CH_3), 1.34 (t, 3H, CH_2-$\underline{CH}_3$, *J* = 7.20 Hz); ^{13}C-NMR ($CDCl_3$) δ 148.3, 145.2, 140.5, 124.2, 120.3, 119.1, 119.0, 117.4, 111.9, 109.7, 46.5, 46.3, 38.6, 23.7, 22.7, 15.6; HRMS (ESI) calcd for $C_{16}H_{20}N$ m/z = 226.1590 [$(M+H)^+$], found m/z = 226.1592; Enantiomeric excess: 84%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 14.6 min, major peak: t_R = 10.6 min; $[\alpha]_D^{25}$ = +27.0 (*c* 0.13, $CHCl_3$); IR (KBr): ν 3051, 2967, 2934, 2856, 1458, 1371, 1345, 1166, 914, 738, 699 cm^{-1}.

(*S*)-4-Benzyl-3-methyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2c)[3]



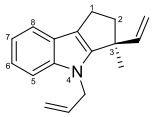
2c: Colorless oil (82%, 72 h); ^{1}H-NMR ($CDCl_3$) δ 7.51-7.48 (m, 1H, ArH), 7.27-7.18 (m, 3H,ArH), 7.10-7.02 (m, 3H,ArH), 6.98-6.97 (m, 2H,ArH), 6.03 (dd, 1H, CH=CH_2, *J* = 10.80, 17.60 Hz), 5.27 (s, 2H, N-CH_2), 5.01-4.94 (m, 2H, CH=CH_2), 2.88-2.84 (m, 2H, C1H_2), 2.56-2.49 (m, 1H, C2H_{2a}), 2.37-2.31 (m, 1H, C2H_{2b}), 1.32 (s, 3H, C3-CH_3); Enantiomeric excess: 48%, determined by HPLC (YMC CHIRAL ART Cellulose-C, eluent: *n*-hexane/2-propanol = 5/1, flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 47.4 min, major peak: t_R = 24.3 min; $[\alpha]_D^{25}$ = +34.5 (*c* 0.22, $CHCl_3$).

(*S*)-4-(4-Chlorobenzyl)-3-methyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2d)



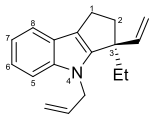
2d: White solid (60%, 60 h); M.p. 51-52 ºC; ^{1}H-NMR ($CDCl_3$) δ 7.49 (dd, 1H, ArH, *J* = 2.00, 6.40 Hz), 7.23-7.20 (m, 2H,ArH), 7.11-7.01 (m, 3H,ArH), 6.91 (m, 2H, ArH), 6.01 (dd, 1H, CH=CH_2, *J* = 10.40, 17.60 Hz), 5.23 (s, 2H, N-CH_2), 5.01-4.93 (m, 2H, CH=CH_2), 2.91-2.80 (m, 2H, C1H_2), 2.56-2.49 (m, 1H, C2H_{2a}), 2.37-2.31 (m, 1H, C2H_{2b}), 1.31 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$) δ 148.7, 144.9, 141.2, 136.9, 132.9, 128.8 (2C), 127.4 (2C), 124.4, 120.9, 119.6, 119.1, 118.3, 112.3, 110.2, 46.7, 46.4, 46.2, 23.7, 22.7; HRMS (ESI) calcd for $C_{21}H_{21}ClN$ m/z = 322.1357 [$(M+H)^+$], found m/z = 322.1359; Enantiomeric excess: 72%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25°C, 254 nm) minor peak: t_R = 19.1 min, major peak: t_R = 17.0 min; $[\alpha]_D^{24}$ = +50.3 (*c* 0.18, $CHCl_3$); IR (KBr): ν 3081, 3052, 3028, 2997, 2953, 2925, 2854, 1634, 1491, 1458, 1441, 1409, 1375, 1346, 1296, 1167, 1095, 1014, 917, 821, 790, 740 cm^{-1}.

(*S*)-4-Allyl-3-methyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2k)



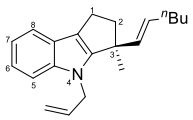
2k: Colorless oil (quant., 24 h); ^{1}H-NMR ($CDCl_3$) δ 7.46 (dd, 1H, H-8, *J* = 1.20, 6.80 Hz), 7.20 (dd, 1H, H-5, *J* = 1.20, 7.20 Hz), 7.13-7.05 (m, 2H, H-6, H-7), 6.07 (dd, 1H, CH=CH_2, *J* = 10.40, 17.60 Hz), 5.95-5.85 (m, 1H, CH_2-CH=CH_2), 5.14-4.93 (m, 4H, CH=CH_2, CH_2-CH=CH_2), 4.70-4.59 (m, 2H, CH_2-CH=CH_2), 2.84-2.77 (m, 2H, C1H_2), 2.54-2.48 (m, 1H, C2H_{2a}), 2.37-2.27 (m, 1H, C2H_{2b}), 1.45 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$) δ 148.5, 145.2, 141.1, 133.9, 124.3, 120.5, 119.3, 119.0, 117.7, 116.5, 112.0, 110.3, 46.4, 46.3, 46.2, 23.8, 22.7; HRMS (ESI) calcd for $C_{17}H_{20}N$ m/z = 238.1590 [$(M+H)^+$], found m/z = 238.1591; Enantiomeric excess: 90%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 11.3 min, major peak: t_R = 9.9 min; $[\alpha]_D^{25}$ = +50.4 (*c* 0.21, $CHCl_3$); By using *Z*-enriched **1k** (*E*/*Z* = 19/81): Enantiomeric excess: 92%, minor peak: t_R = 11.0 min, major peak: t_R = 9.3 min; By using *E*-enriched **1k** (*E*/*Z* = 79/21): Enantiomeric excess: 80%, minor peak: t_R = 11.1 min, major peak: t_R = 9.6 min; IR (KBr): ν 3081, 3053, 2959, 2930, 2854, 1634, 1458, 1413, 1373, 1346, 1327, 1169, 1016, 992, 915, 738, 715, 700, 545 cm^{-1}.

(*S*)-4-Allyl-3-ethyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2l)



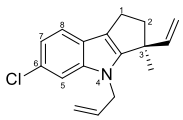
2l: Colorless oil (57%, 24 h); ^{1}H-NMR ($CDCl_3$) δ 7.47-7.46 (m, 1H, ArH), 7.23-7.20 (m, 1H, ArH), 7.13-7.05 (m, 2H, ArH), 6.09 (dd, 1H, $\underline{CH}$=CH_2, *J* = 10.40, 17.20 Hz), 5.94-5.84 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.15-4.92 (m, 4H, CH=$\underline{CH_2}$, CH_2-CH=$\underline{CH_2}$), 4.71-4.57 (m, 2H, $\underline{CH_2}$-CH=CH_2), 2.82-2.78 (m, 2H, C1H_2), 2.48-2.43 (m, 2H, C2H_2), 1.90-1.84 (m, 2H, $\underline{CH_2}$-CH_3), 0.82 (t, 3H, CH_2-$\underline{CH_3}$, *J* = 7.20 Hz); ^{13}C-NMR ($CDCl_3$) δ 146.7, 144.9, 141.4, 133.9, 124.3, 120.4, 119.2, 119.1, 118.9, 116.5, 112.2, 110.4, 50.7, 46.7, 42.6, 30.3, 23.2, 9.2, HRMS (ESI) calcd for $C_{18}H_{22}N$ m/z = 252.1747 [$(M+H)^+$], found m/z = 252.1748; Enantiomeric excess: 86%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 0.5 mL/min, 25 °C, 254 nm) minor peak: t_R = 23.8 min, major peak: t_R = 24.7 min; $[\alpha]_D^{25}$ = +14.9 (*c* 0.13, $CHCl_3$); IR (KBr): ν 3076, 3055, 2958, 2927, 2858, 1456, 1372, 1336, 994, 918, 784, 745 cm^{-1}.

(*S*,*E*)-4-Allyl-3-(hex-1-en-1-yl)-3-methyl-1,2,3,4-tetrahydrocyclopenta[b]indole (*E*-2m)



***E*-2m**: Colorless oil (84%, 36 h); ^{1}H-NMR ($CDCl_3$) δ 7.46-7.44 (m, 1H, H-8), 7.21-7.19 (m, 1H, H-5), 7.12-7.05 (m, 2H, H-6, H-7), 5.94-5.84 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.65 (d, 1H, $\underline{CH}$=CH-CH_2, *J* = 15.60 Hz), 5.37 (dt, 1H, CH=$\underline{CH}$-CH_2, *J* = 6.80, 15.60 Hz), 5.12 (dd, 1H, CH_2-CH=$\underline{CH_{2a}}$, *J* = 1.60, 10.40 Hz), 4.96 (dd, 1H, CH_2-CH=$\underline{CH_{2b}}$, *J* = 1.60, 17.20 Hz), 4.70-4.58 (m, 2H, $\underline{CH_2}$-CH=CH_2), 2.85-2.74 (m, 2H, C1H_2), 2.50-2.44 (m, 1H, C2H_{2a}), 2.35-2.27 (m, 1H, C2H_{2b}), 2.04-1.99 (m, 2H, CH=CH-$\underline{CH_2}$), 1.42 (s, 3H, C3-CH_3), 1.37-1.29 (m, 4H, $\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.88 (t, 3H, CH_2-CH_2-$\underline{CH_3}$, *J* = 7.20 Hz); ^{13}C-NMR ($CDCl_3$) δ 149.3, 141.1, 137.0, 134.0, 128.1, 124.4, 120.3, 119.2, 118.9, 117.4, 116.4, 110.2, 47.0, 46.3, 45.4, 32.3, 31.9, 24.7, 22.6, 22.4, 14.1; HRMS (ESI) calcd for $C_{21}H_{28}N$, m/z = 294.2216 [$(M+H)^+$], found m/z = 294.2217; Enantiomeric excess: 66%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 10.1 min, major peak: t_R = 8.0 min; $[\alpha]_D^{24}$ = +8.6 (*c* 0.23, $CHCl_3$); IR (KBr): ν 3052, 3017, 2959, 2926, 2858, 1456, 1371, 1339, 978, 921, 783, 745 cm^{-1}.

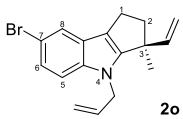
(*S*)-4-Allyl-6-chloro-3-methyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2n)



2n: Colorless oil (69%, 60 h); ^{1}H-NMR ($CDCl_3$) δ 7.34 (d, 1H, H-8, *J* = 8.80 Hz), 7.18 (d, 1H, H-5, *J* = 2.00 Hz), 7.03 (dd, 1H, H-7, *J* = 2.00, 8.80 Hz), 6.04 (dd, 1H, $\underline{CH}$=CH_2, *J* = 10.80, 17.60 Hz), 5.91-5.82 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.16-4.91 (m, 4H, CH=$\underline{CH_2}$, CH_2-CH=$\underline{CH_2}$), 4.65-4.52 (m, 2H, $\underline{CH_2}$-CH=CH_2), 2.84-2.73 (m, 2H, C1H_2), 2.53-2.46 (m, 1H, C2H_{2a}), 2.36-2.27 (m, 1H, C2H_{2b}), 1.44 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$) δ 149.4, 144.9, 141.5, 133.4, 126.5, 122.9, 119.9, 119.7, 117.9, 116.8, 112.3, 110.3, 46.4 (2C), 46.3, 23.8, 22.6; HRMS (ESI) calcd for $C_{17}H_{19}ClN$ m/z = 272.1201 [$(M+H)^+$], found m/z = 272.1201; Enantiomeric excess: 86%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 7.7 min, major peak: t_R = 7.0 min; $[\alpha]_D^{21}$ = +66.5 (*c* 1.68, $CHCl_3$); IR (KBr): ν 3083, 2958, 2927,

2855, 1635, 1609, 1552, 1469, 1455, 1428, 1416, 1374, 1313, 1245, 1062, 1024, 994, 919, 853, 839, 802, 596 cm^{-1}.

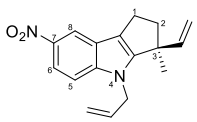
(*S*)-4-Allyl-7-bromo-3-methyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2o)



2o

2o: Colorless oil (40%, 72 h); ^{1}H-NMR ($CDCl_3$) δ 7.58 (d, 1H, H-8, *J* = 1.60 Hz), 7.18 (dd, 1H, H-6, *J* = 1.60, 8.80 Hz), 7.06 (d, 1H, H-5, *J* = 8.80 Hz), 6.04 (dd, 1H, CH=CH_2, *J* = 10.80, 17.60 Hz), 5.91-5.82 (m, 1H, CH_2-CH=CH_2), 5.15-5.11 (m, 1H, CH_2-CH=CH_{2a}), 5.06 (dd, 1H, CH=CH_{2a} *J* = 1.20, 10.80 Hz), 4.98 (dd, 1H, CH=CH_{2b} *J* = 1.20, 17.60 Hz), 4.93-4.88 (m, 1H, CH_2-CH=CH_{2b}), 4.68-4.55 (m, 2H, CH_2-CH=CH_2), 2.83-2.72 (m, 2H, C1H_2), 2.53-2.47 (m, 1H, C2H_{2a}), 2.36-2.30 (m, 1H, C2H_{2b}), 1.44 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$) δ 149.9, 144.8, 139.7, 133.4, 125.8, 123.1, 121.6, 117.3, 116.6, 112.6, 112.3, 111.7, 46.4, 46.3, 46.2, 23.7, 22.5; HRMS (ESI) calcd for $C_{17}H_{19}BrN$ m/z = 316.0695 [$(M+H)^+$], found m/z = 316.0697; Enantiomeric excess: 82%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 9.9 min, major peak: t_R = 7.8 min; $[\alpha]_D^{25}$ = +58.3 (*c* 0.12, $CHCl_3$); IR (KBr): ν 3080, 2925, 2857, 1454, 1362, 1326, 1169, 993, 920, 867, 788 cm^{-1}.

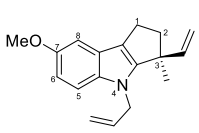
(*S*)-4-Allyl-3-methyl-7-nitro-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2p)



2p

2p: Yellow oil (19%, 12 h at 60 °C); ^{1}H-NMR ($CDCl_3$) δ 8.42 (d, 1H, H-8, *J* = 2.00 Hz), 8.02 (dd, 1H, H-6, *J* = 2.00, 9.20 Hz), 7.20 (d, 1H, H-5, *J* = 9.20 Hz), 6.05 (dd, 1H, CH=CH_2, *J* = 10.40, 17.20 Hz), 5.94-5.85 (m, 1H, CH_2-CH=CH_2), 5.20-4.89 (m, 4H, CH=CH_2, CH_2-CH=CH_2), 4.75-4.62 (m, 2H, CH_2-CH=CH_2), 2.91-2.80 (m, 2H, C1H_2), 2.58-2.52 (m, 1H, C2H_{2a}), 2.42-2.35 (m, 1H, C2H_{2b}), 1.48 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$) δ 152.1, 144.2, 144.0, 141.4, 132.7, 123.4, 120.3, 117.2, 116.3, 116.2, 112.8, 110.0, 46.6, 46.4, 46.2, 23.7, 22.5; HRMS (ESI) calcd for $C_{17}H_{18}N_2NaO_2$ m/z = 305.1260 [$(M+Na)^+$], found m/z = 305.1259; Enantiomeric excess: 78%, determined by HPLC (Daicel Chiralpak AS-3, hexane/2-propanol = 50/1 , flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 17.1 min, major peak: t_R = 15.5 min; $[\alpha]_D^{18}$ = +15.2 (*c* 0.50, $CHCl_3$); IR (KBr): ν 3084, 2929, 2859, 1514, 1464, 1332, 1087, 922, 786 cm^{-1}.

(*S*)-4-Allyl-7-methoxy-3-methyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2q)

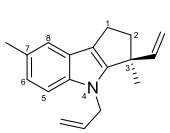


2q

2q: Colorless oil (83%, 24 h); ^{1}H-NMR ($CDCl_3$) δ 7.09 (d, 1H, H-5, *J* = 9.00 Hz), 6.94 (d, 1H, H-8, *J* = 2.00 Hz), 6.77 (dd, 1H, H-6, *J* = 2.00, 9.00 Hz), 6.06 (dd, 1H, CH=CH_2, *J* = 10.80, 17.60 Hz), 5.93-5.83 (m, 1H, CH_2-CH=CH_2), 5.13-4.92 (m, 4H, CH=CH_2, CH_2-CH=CH_2) 4.66-4.54 (m, 2H, CH_2-CH=CH_2), 3.84 (s, 3H, OCH_3), 2.85-2.74 (m, 2H, C1H_2), 2.53-2.46 (m, 1H, C2H_{2a}), 2.35-2.27 (m, 1H, C2H_{2b}), 1.44 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$) δ 154.1, 149.3, 145.2, 136.3, 134.1, 124.4, 117.3, 116.4, 112.0, 110.9, 110.3, 101.3, 56.1, 46.4 (2C), 46.2, 23.8, 22.6; HRMS (ESI) calcd for$C_{18}H_{22}NO$ m/z = 268.1696 [$(M+H)^+$], found m/z = 268.1697; Enantiomeric excess: 90%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C,

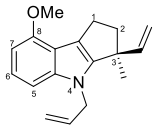
254 nm) minor peak: t_R = 62.4 min, major peak: t_R = 36.1 min; $[\alpha]_D^{25}$ = +48.1 (*c* 0.21, $CHCl_3$); IR (KBr): ν 3081, 2933, 2855, 1624, 1574, 1461, 1330, 1218, 1162, 1039, 994, 917, 791 cm^{-1}.

(*S*)-4-allyl-3,7-dimethyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2r)



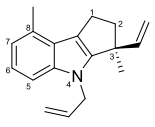
2r: Colorless oil (83%, 12 h); ^{1}H-NMR ($CDCl_3$) δ 7.25-7.24 (m, 1H, ArH), 7.09 (d, 1H, ArH, *J* = 8.00 Hz), 6.93 (dd, 1H, H-6, *J* = 1.60, 8.00 Hz), 6.05 (dd, 1H, CH=CH_2, *J* = 10.40, 17.20 Hz), 5.93-5.83 (m, 1H, CH_2-CH=CH_2), 5.12-4.91 (m, 4H, CH=CH_2, CH_2-CH=CH_2), 4.66-4.54 (m, 2H, CH_2-CH=CH_2), 2.84-2.73 (m, 2H, $C1H_2$), 2.52-2.43 (m, 4H, Ar-CH_3, $C2H_{2a}$), 2.35-2.27 (m, 1H, $C2H_{2b}$), 1.44 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$) δ 148.6, 145.3, 139.5, 134.0, 128.5, 124.5, 121.9, 118.8, 117.2, 116.3, 112.0, 109.9, 46.4, 46.3, 46.2, 23.9, 22.6, 21.6; HRMS (ESI) calcd for $C_{18}H_{22}N$ m/z = 252.1747 [$(M+H)^+$], found m/z = 252.1747; Enantiomeric excess: 88%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 9.3 min, major peak: t_R = 7.9 min; $[\alpha]_D^{21}$ = +50.5 (*c* 1.64, $CHCl_3$); IR (KBr): ν 3080, 3013, 2927, 2857, 1636, 1569, 1460, 1365, 1331, 1167, 994, 917, 790 cm^{-1}.

(*S*)-4-Allyl-8-methoxy-3-methyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2s)



2s: Colorless oil (75%, 8h); ^{1}H-NMR ($CDCl_3$) δ 7.01 (t, 1H, H-6, *J* = 7.60 Hz), 6.82 (d, 1H, ArH, *J* = 8.40 Hz), 6.49 (d, 1H, ArH, *J* = 8.00 Hz), 6.05 (dd, 1H, CH=CH_2, *J* = 10.40, 17.20 Hz), 5.93-5.83 (m, 1H, CH_2-CH=CH_2), 5.13-4.90 (m, 4H, CH=CH_2, CH_2-CH=CH_2), 4.62-4.58 (m, 2H, CH_2-CH=CH_2), 3.91 (s, 3H, OCH_3), 2.97-2.93 (m, 2H, $C2H_2$), 2.52-2.45 (m, 1H, $C2H_{2a}$), 2.34-2.28 (m, 1H, $C2H_{2b}$), 1.43 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$) δ 153.5, 146.8, 145.4, 142.5, 133.9, 121.4, 116.7, 116.4, 114.8, 111.9, 103.9, 99.8, 55.5, 46.7, 46.5, 46.1, 24.1, 23.8; HRMS (ESI) calcd for $C_{18}H_{22}NO$ m/z = 268.1696 [$(M+H)^+$], found m/z = 268.1698; Enantiomeric excess: 94%, determined by HPLC (DAICEL Chiralpak AD-H, eluent: *n*-hexane, flow rate: 0.5 mL/min, 25 °C, 254 nm) minor peak: t_R = 31.6 min, major peak: t_R = 20.4 min; $[\alpha]_D^{20}$ = +47.9 (*c* 1.88, $CHCl_3$); IR (KBr): ν 3079, 2936, 2859, 1569, 1496, 1454, 1361, 1256, 1103, 918, 783cm^{-1}.

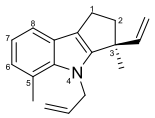
(*S*)-4-Allyl-3,8-dimethyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2t)



2t: Colorless oil (81%, 48 h); ^{1}H-NMR ($CDCl_3$) δ 7.04-6.94 (m, 2H, ArH), 6.84-6.82 (m, 1H, ArH), 6.06 (dd, 1H, CH=CH_2, *J* = 10.80, 17.60 Hz), 5.93-5.84 (m, 1H, CH_2-CH=CH_2), 5.13-4.93 (m, 4H, CH=CH_2, CH_2-CH=CH_2), 4.67-4.55 (m, 2H, CH_2-CH=CH_2), 3.05-2.94 (m, 2H, $C1H_2$), 2.58 (s, 3H, Ar-CH_3), 2.54-2.47 (m, 1H, $C2H_{2a}$), 2.36-2.27 (m, 1H, $C2H_{2b}$), 1.44 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$) δ 147.7, 145.3, 140.9, 133.9, 129.8, 124.1, 120.9, 119.8, 117.6, 116.4, 112.0, 107.9, 46.6, 46.4, 45.9, 24.3, 23.9, 19.1; HRMS (ESI) calcd for $C_{18}H_{22}N$ m/z = 252.1747 [$(M+H)^+$], found m/z = 252.1747; Enantiomeric excess: 96%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 11.2 min, major peak: t_R = 8.5 min;

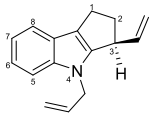
$[\alpha]_D^{21}$ = +45.7 (*c* 1.44, $CHCl_3$); IR (KBr): ν 3082, 3047, 2957, 2925, 2854, 1635, 1561, 1457, 1427, 1359, 992, 916, 769, 740 cm^{-1}.

(*S*)-4-Allyl-3,5-dimethyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2u)



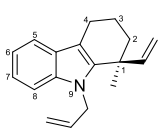
2u: Colorless oil (quant., 24 h); ^{1}H-NMR ($CDCl_3$) δ 7.29 (d, 1H, H-8, *J* = 8.00 Hz), 6.97-6.94 (m, 1H, H-7), 6.82 (d, 1H, H-6, *J* = 6.40 Hz), 6.05 (dd, 1H, CH=CH_2, *J* = 10.40, 17.20 Hz), 6.00-5.91 (m, 1H, CH_2-CH=CH_2), 5.10-5.06 (m, 1H, CH_2-CH=CH_{2a}), 5.04 (dd, 1H, CH=CH_{2a}, *J* = 1.60, 8.00 Hz), 5.01 (dd, 1H, CH=CH_{2b}, *J* = 1.60, 14.80 Hz), 4.90-4.73 (m, 2H, CH_2-CH=CH_2), 4.67-4.61 (m, 1H, CH_2-CH=CH_{2b}), 2.85-2.74 (m, 2H, C1H_2), 2.63 (s, 3H, Ar-CH_3), 2.52-2.45 (m, 1H, C2H_{2a}), 2.33-2.27 (m, 1H, C2H_{2b}), 1.42 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$) δ 149.0, 145.4, 139.8, 136.4, 125.1, 123.8, 121.6, 119.5, 118.2, 117.0, 115.3, 111.9, 47.8, 46.6, 46.5, 23.7, 22.6, 19.3; HRMS (ESI) calcd for $C_{18}H_{22}N$ m/z = 252.1747 [$(M+H)^+$], found m/z = 252.1747; Enantiomeric excess: 93%, determined by HPLC (DAICEL Chiralpak IF, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 18.4 min, major peak: t_R = 17.3 min; $[\alpha]_D^{25}$ = +72.7 (*c* 0.20, $CHCl_3$); IR (KBr): ν 3078, 3047, 2939, 2857, 1450, 1406, 1373, 1327, 1153, 994, 917, 772, 742 cm^{-1}.

(*S*)-4-Allyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2v)



2v: Yellow oil (49%, 48 h); ^{1}H-NMR ($CDCl_3$) δ 7.46 (dd, 1H, H-8, *J* = 1.60, 6.80 Hz), 7.23 (d, 1H, H-5, *J* = 1.60, 8.00 Hz), 7.14-7.10 (m, 1H, ArH), 7.09-7.05 (m, 1H, ArH), 5.95-5.84 (m, 2H, CH=CH_2, CH_2-CH=CH_2), 5.16-4.94 (m, 4H, CH=CH_2, CH_2-CH=CH_2), 4.71-4.59 (m, 2H, CH_2-CH=CH_2), 3.88-3.82 (m, 1H, C3H), 2.93-2.88 (m, 1H, C2H_{2a}), 2.84-2.75 (m, 2H, C1H_2), 2.32-2.23 (m, 1H, C2H_{2b}); ^{13}C-NMR ($CDCl_3$) δ 145.9, 141.2, 140.8, 134.0, 124.3, 120.5, 119.3, 119.0, 118.7, 116.5, 114.8, 110.1, 46.5, 43.6, 37.3, 23.7; HRMS (ESI) calcd for $C_{16}H_{18}N$ m/z = 224.1434 [$(M+H)^+$], found m/z = 224.1434; Enantiomeric excess: 99%, determined by HPLC (DAICEL Chiralcel OJ, eluent: *n*-hexane, flow rate: 0.5 mL/min, 25 °C, 254 nm) minor peak: t_R = 23.9 min, major peak: t_R = 18.1 min; $[\alpha]_D^{25}$ = +32.8 (*c* 0.09, $CHCl_3$); IR (KBr): ν 3070, 3056, 2927, 2856, 1457, 1370, 1340, 1296, 1168, 991, 919, 783, 742 cm^{-1}.

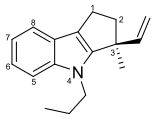
(*S*)-9-Allyl-1-methyl-1-vinyl-2,3,4,9-tetrahydro-1*H*-carbazole (2w)



2w: Colorless oil (30%, 24 h); ^{1}H-NMR ($CDCl_3$) δ 7.49 (dd, 1H, H-5, *J* = 0.80, 8.00 Hz), 7.19 (d, 1H, H-8, *J* = 8.00 Hz), 7.15-7.11 (m, 1H, ArH), 7.09-7.05 (m, 1H, ArH), 5.99 (dd, 1H, CH=CH_2, *J* = 10.80, 17.60 Hz), 5.94-5.85 (m, 1H, CH_2-CH=CH_2), 5.15-5.10 (m, 2H, CH_2-CH=CH_{2a}, CH=CH_{2a}), 4.96-4.80 (m, 3H, CH_2-CH=CH_{2b}, CH=CH_{2b}, CH_{2a}-CH=CH_2), 4.67-4.60 (m, 1H, CH_{2b}-CH=CH_2), 2.75-2.72 (m, 2H, C4H_2), 1.86-1.68 (m, 4H, C2H_2, C3H_2), 1.46 (s, 3H, C1-CH_3); ^{13}C-NMR ($CDCl_3$) δ 146.3, 139.0, 137.1, 134.2, 127.1, 121.2, 118.9, 118.2, 116.3, 113.5, 110.6, 109.8, 47.1, 41.2, 39.2, 25.7, 22.0, 19.8; HRMS (ESI) calcd for $C_{18}H_{22}N$ m/z = 252.1747 [$(M+H)^+$], found m/z = 252.1748; Enantiomeric excess: 8%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-

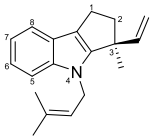
hexane, flow rate: 1 mL/min, 25 °C, 310 nm) minor peak: t_R = 8.8 min, major peak: t_R = 8.4 min; $[\alpha]_D^{21}$ = -1.7 (*c* 0.60, $CHCl_3$); IR (KBr): ν 2929, 2851, 1463, 1359, 995, 920, 784 cm^{-1}.

(*S*)-3-Methyl-4-propyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2x)



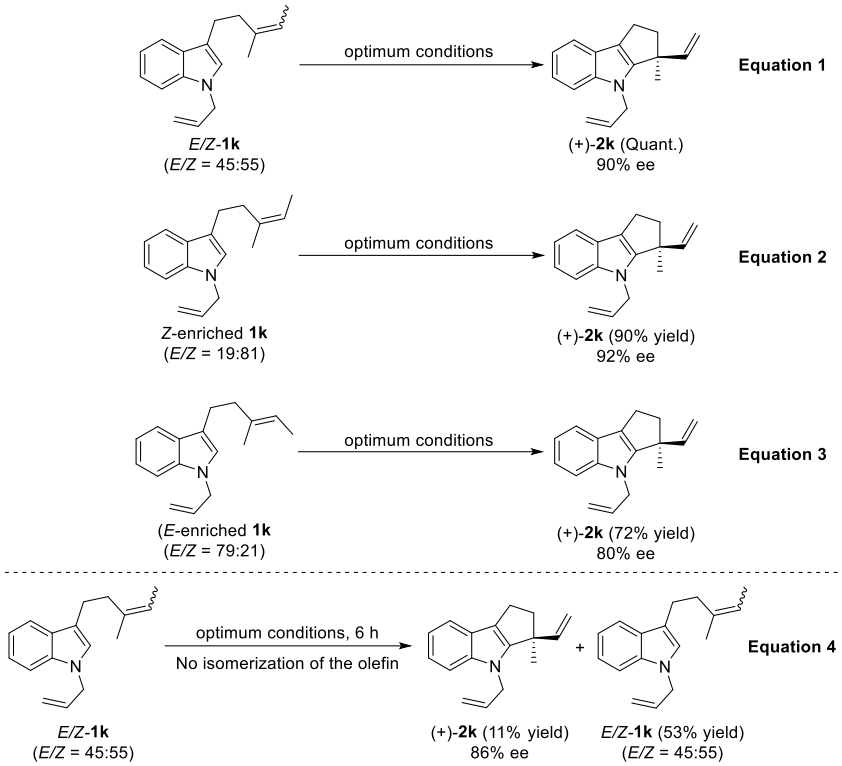
2x: Pale yellow oil (37%, 60 h); ^{1}H-NMR ($CDCl_3$) δ 7.46-7.44 (m, 1H, H-8), 7.26-7.24 (m, 1H, H-5), 7.13-7.04 (m, 2H, H-6, H-7), 6.07 (dd, 1H, CH=CH_2, *J* = 10.80, 17.60 Hz), 5.04 (dd, 1H, CH=CH_{2a}, *J* = 1.20, 10.40 Hz), 4.98 (dd, 1H, CH=CH_{2b}, *J* = 1.20, 17.20 Hz), 3.99-3.88 (m, 2H, CH_2-CH_2-CH_3), 2.86-2.75 (m, 2H, $C1H_2$), 2.53-2.46 (m, 1H, $C2H_{2a}$), 2.36-2.27 (m, 1H, $C2H_{2b}$), 1.84-1.72 (m, 2H, CH_2-CH_2-CH_3), 1.49 (s, 3H, C3-CH_3), 0.95 (t, 3H, CH_2-CH2-CH_3, *J* = 7.60 Hz); ^{13}C-NMR ($CDCl_3$) δ 148.5, 145.3, 141.0, 124.1, 120.3, 119.03, 118.97, 117.5, 111.8, 110.0, 46.5, 46.3, 45.8, 23.8, 23.7, 22.6, 11.6; HRMS (ESI) calcd for $C_{17}H_{22}N$ m/z = 240.1747 [$(M+H)^+$], found m/z = 240.1747; Enantiomeric excess: 76%, determined by HPLC (YMC CHIRAL ART Cellulose-C, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 13.4 min, major peak: t_R = 12.3 min; $[\alpha]_D^{24}$ = +12.2 (*c* 0.08, $CHCl_3$); IR (KBr): ν 3051, 2960, 2862, 1628, 1564, 1458, 1369, 1298, 1166, 1007, 913, 737, 705 cm^{-1}.

3-Methyl-4-(3-methylbut-2-en-1-yl)-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (2z)



2z: Pale yellow oil (71%, 48 h); ^{1}H-NMR ($CDCl_3$) δ 7.45 (d, 1H, H-8, *J* = 7.20 Hz), 7.19 (d, 1H, H-5, *J* = 8.00 Hz), 7.12-7.04 (m, 2H, H-6, H-7), 6.08 (dd, 1H, CH=CH_2, *J* = 10.80, 17.60 Hz), 5.19-5.16 (m, 1H, CH=$C(CH_3)_2$) 5.06-4.99 (m, 2H, CH=CH_2), 4.68-4.57 (m, 2H, CH_2-CH=$C(CH_3)_2$), 2.87-2.76 (m, 2H, $C1H_2$), 2.54-2.47 (m, 1H, $C2H_{2a}$), 2.36-2.27 (m, 1H, $C2H_{2b}$), 1.80 (s, 3H, CH=$C(CH_3)_{2a}$), 1.68 (s, 3H, CH=$C(CH_3)_{2b}$), 1.46 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$) δ 148.6, 145.3, 140.9, 133.7, 124.3, 121.6, 120.3, 119.1, 118.9, 117.5, 112.0, 110.2, 46.5, 46.2, 42.3, 25.7, 23.8, 22.7, 18.3; HRMS (ESI) calcd for $C_{19}H_{24}N$ m/z = 266.1903 [$(M+H)^+$], found m/z = 266.1903; Enantiomeric excess: 8%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm) minor peak: t_R = 9.5 min, major peak: t_R = 10.1 min; $[\alpha]_D^{25}$ = +9.9 (*c* 0.18, $CHCl_3$); IR (KBr): ν 3051, 2928, 2857, 1455, 1371, 915, 784, 744 cm^{-1}

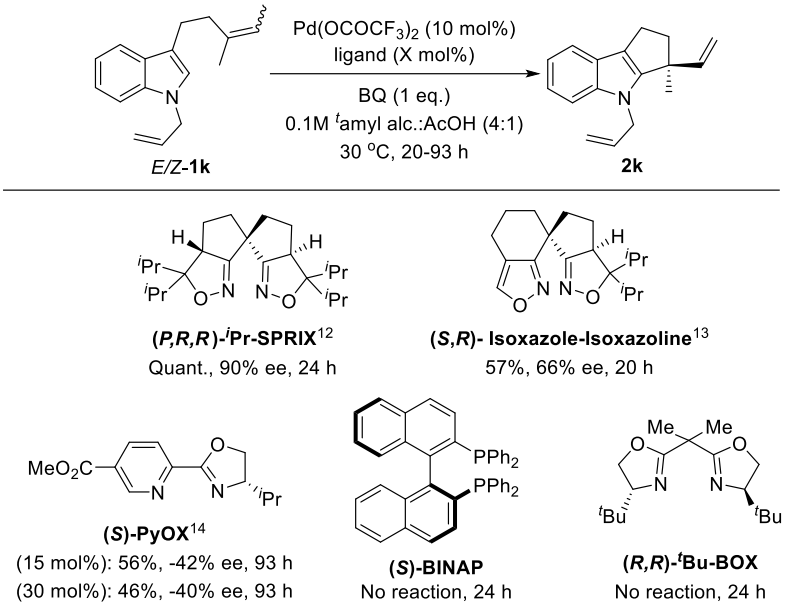
5. Effect of olefin's stereochemical nature on the reaction outcomes



E- or *Z*-enriched substrates **1k** were obtained from substrate *E/Z*-**1k** (*E/Z* = 45:55) by conventional flash column chromatography on silver(I)-impregnated silica gel.[11]

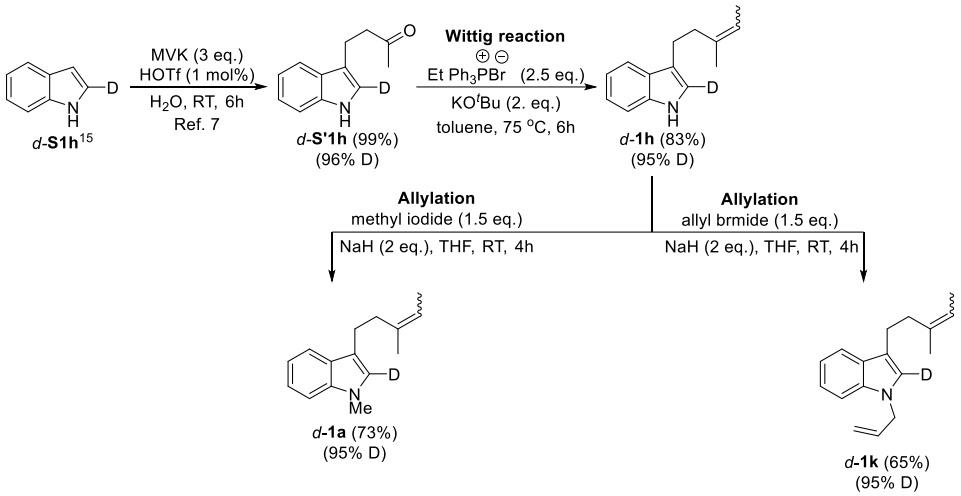
6. Comparison of SPRIX with other ligands

To showcase the role of the SPRIX ligand in the anulation, a study was performed to compare SPRIX with other reported ligands under our optimized reaction conditions. SPRIX was detected to be the best ligand for this process, as no other ligand promoted this cyclization efficiently. The use of (*S*)-PyOx, (*R*,*R*)-^{t}Bu-BOX, or (*S*)-BINAP resulted in a sluggish reaction or no product.

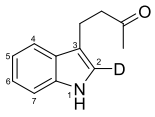


7. Isotope labelling study

Synthesis of the deuterated substrates *d*-1a and *d*-1k

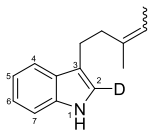


2-*D*-4-(1*H*-indol-3-yl)butan-2-one (*d*-S'1h): Based upon triflic acid catalyzed Michael reactions of indole with methyl vinyl ketone.[6]



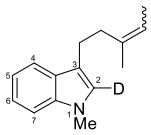
d-**S'1h**: Beige solid (99%, 96% D); m.p. 80-81 °C; ^{1}H-NMR ($CDCl_3$) δ 7.95 (brs, NH, 1H), 7.59 (dd, 1H, H-4, *J* = 8.00, 1.20 Hz), 7.36 (d, 1H, H-7, *J* = 8.40 Hz), 7.22-7.18 (m, 1H, ArH), 7.14-7.10 (m, 1H, ArH), 3.05 (t, 2H, Indole-$\underline{CH_2}$-CH_2-CO, *J* = 7.60 Hz), 2.85 (t, 2H, Indole-CH_2-$\underline{CH_2}$-CO, *J* = 7.60 Hz), 2.14 (s, 3H, CO-CH_3); HRMS (ESI) calcd for $C_{12}H_{12}DNNaO$ m/z = 211.0952 [$(M+Na)^+$], found m/z = 211.0952.

2-*D*-3-(3-methylpent-3-en-1-yl)-1*H*-indole-2-d (*d*-1h): Similar to the synthesis of alkenylindoles **1d**, **e**.



d-**1h** : Pale yellow oil (83%, 62:38 mixture of *Z/E*-olefin isomers, 95% D); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.89 (brs, 1H, NH), 7.65-7.60 (m, 1H, H-4), 7.36-7.34 (m, 1H, H-7), 7.21-7.16 (m, 1H, ArH), 7.14-7.09 (m, 1H, ArH), 5.32-5.23 (m, 1H, C=$\underline{CH}$-CH_3), 2.87-2.80 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.46-2.37 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.78-1.76 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.55-1.53 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 1.70 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.61-1.59 (m, 3H, C=CH-$\underline{CH_3}$); HRMS (ESI) calcd for $C_{14}H_{17}DN$, m/z = 201.1497 [$(M+H)^+$], found m/z = 201.1496.

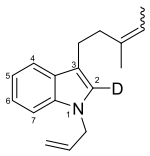
2-*D*-1-methyl-3-(3-methylpent-3-en-1-yl)-1*H*-indole (*d*-1a): Similar to the synthesis of alkenylindoles **1b**, **1i-k**, and **1x-z**



d-**1a**: Pale yellow oil (73%, 62:38 mixture of *Z/E*-olefin isomers, 95% D); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.63-7.59 (m, 1H, H-4), 7.30-7.27 (m, 1H, H-7), 7.24-7.19 (m, 1H, ArH), 7.12-7.08 (m, 1H, ArH), 5.33-5.23 (m, 1H, C=$\underline{CH}$-CH_3), 3.74 (s, 3H, NCH_3), 2.86-2.78 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.44-2.35 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.78-1.77 (m, 3H, CH_2-C($\underline{CH_3}$)), 1.57-1.55 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 3.73 (s, 3H, NCH_3), 1.70 (s, 3H, CH_2-C($\underline{CH_3}$)),

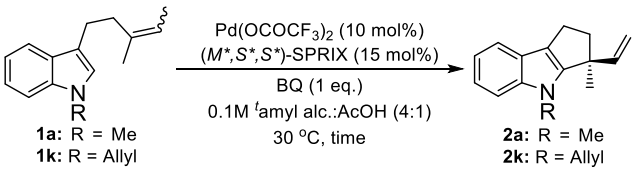
1.61-1.59 (m, 3H, C=CH-$\underline{CH_3}$); HRMS (ESI) calcd for $C_{15}H_{19}DN$ m/z = 215.1653 [$(M+H)^+$], found m/z = 215.1653.

2-*D*-1-allyl-3-(3-methylpent-3-en-1-yl)-1*H*-indole (*d*-1k): Similar to the synthesis of alkenylindoles **1b**, **1i-k**, and **1x-z**.



d-**1k** : Pale yellow oil (65%, 62:38 mixture of *Z*/*E*-olefin isomers, 95% D); ^{1}H-NMR ($CDCl_3$) *Z*-isomer: δ 7.63-7.59 (m, 1H, H-4), 7.29-7.26 (m, 1H, H-7), 7.21-7.16 (m, 1H, ArH), 7.12-7.07 (m, 1H, ArH), 6.03-5.93 (m, 1H, CH_2-$\underline{CH}$=$CH_{2)}$, 5.31-5.23 (m, 1H, C=$\underline{CH}$-CH_3), 5.20-5.15 (m, 1H, CH_2-CH=$\underline{CH_{2a}}$), 5.11-5.04 (m, 1H, CH_2-CH=$\underline{CH_{2b}}$), 4.69-4.66 (m, 2H, $\underline{CH_2}$-CH=CH_2), 2.86-2.79 (m, 2H, Indole-$\underline{CH_2}$-CH_2), 2.44-2.35 (m, 2H, Indole-CH_2-$\underline{CH_2}$), 1.77-1.76 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.56-1.54 (m, 3H, C=CH-$\underline{CH_3}$); *E*-isomer: δ 1.69 (s, 3H, CH_2-C($\underline{CH_3}$)), 1.60-1.58 (m, 3H, C=CH-$\underline{CH_3}$); HRMS (ESI) calcd for $C_{17}H_{21}DN$ m/z = 241.1810 [$(M+H)^+$], found m/z = 241.1810.

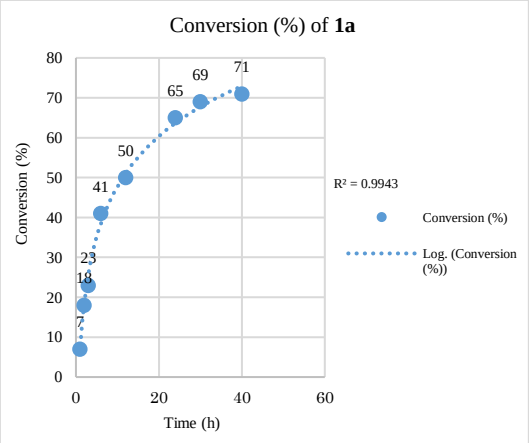
Follow up of the reaction time course

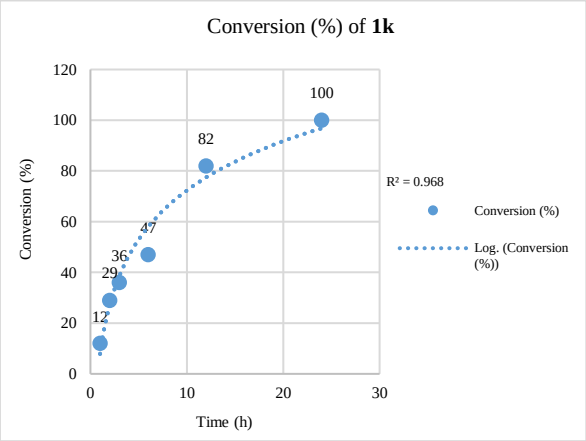


A mixture of $Pd(TFA)_2$ (10 mol %, 0.002345 mmol, 0.8 mg) and (*M**,*S**,*S**)-^{i}Pr-SPRIX (15 mol %, 0.0035 mmol, 1.3 mg) was dissolved in 0.5 mL dry dichloromethane and stirred under nitrogen atmosphere at 30 °C for 2 h. After that, the solvent was distilled off and the resulting yellow Pd complex was kept under vacuum for 10 min. To the dried Pd complex, *p*-benzoquinone (1 eq., 0.02345 mmol, 2.6 mg) and alkenylindole **1a**, **k** (0.02345 mmol) were added under nitrogen. Dry ^{t}amyl alcohol (0.2 mL) was added followed by stirring at 30 °C for 10 mins until dissolving of the solid materials to give a turbid deep red solution. Then, acetic acid (50 µL) was added, and subsequently, a clear red solution was obtained which was stirred under nitrogen atmosphere at 30 °C. The reaction was stopped different times (1, 2, 3, 6, 12, and 24 h) by passing through short silica pad using Et_2O as an eluent. The solvent was removed under vacuum, and the remaining residues was connected to Schleck line for 30 min. The conversion was determined by ^{1}H-NMR.

Table S5. Follow up of the reaction time course of substrates 1a and 1k

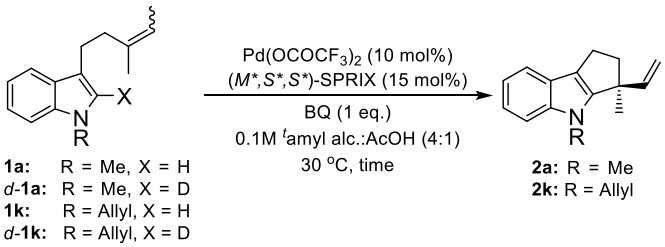
Entry	Time (h)	Conversion (%) of 1a	Conversion (%) of 1k
1	1	7	12
2	2	18	29
3	3	23	36
4	6	41	47
5	12	50	82
6	24	65	100
7	30	69	--
8	40	71	--





Result: The determination of kinetic isotopic effect (KIE) will be determined in the time range (1 to 5 h)

Calculation of the kinetic isotopic effect (KIE)

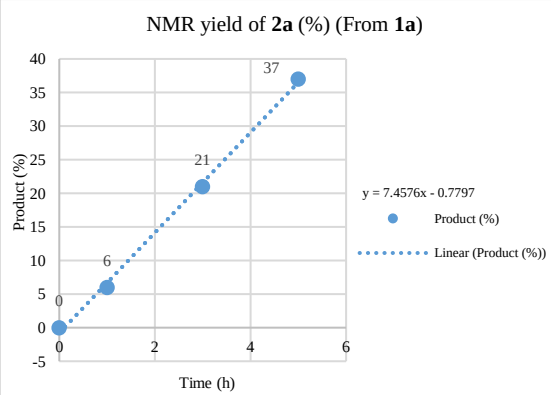


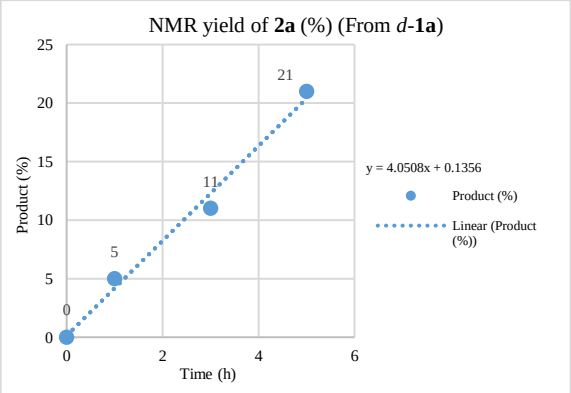
A mixture of $Pd(TFA)_2$ (10 mol %, 0.002345 mmol, 0.8 mg) and (*M**,*S**,*S**)-^{i}Pr-SPRIX (15 mol %, 0.0035 mmol, 1.3 mg) was dissolved in dry dichloromethane (0.5 mL). After stirring under nitrogen atmosphere at 30 °C for 2 h, the solvent was distilled off and the resulting yellow Pd complex was kept under vacuum for 10 min. To the dried Pd complex, *p*-benzoquinone (1 eq., 0.02345 mmol, 2.6 mg) and deuterated alkenylindole *d*-**1** (or alkenylindole **1**) (0.02345 mmol) were added under nitrogen. Dry ^{t}amyl alcohol (0.2

mL) was added followed by stirring at 30 °C for 10 mins until dissolving of the solid materials to give a turbid deep red solution. Then, acetic acid (50 µL) was added, and subsequently, a clear red solution was obtained which was stirred under nitrogen atmosphere at 30 °C. The reaction was stopped different times (1, 3, and 5 h) by passing through short silica pad using Et_2O as eluent. The solvent was removed under vacuum, and the remaining residues was connected to Schleck line for 30 min. The yields of the products *d*-**2** (or **2**) were determined by using ^{1}H-NMR in the presence of dimethyl terephthalate (0.00469mmol, 0.9 mg) as internal standard.

Table S6. Determination of the kinetic isotopic effect of the reaction using substrate (*d*-)1a

Entry	Time (h)	NMR yield of 2a (%) (From 1a)	NMR yield of 2a (%) (From *d*-1a)
1	0	0	0
2	1	6	5
3	3	21	11
4	5	37	21

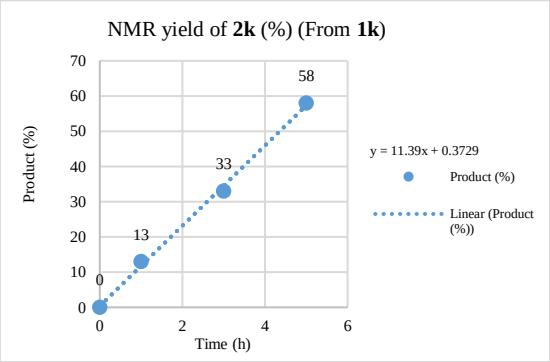


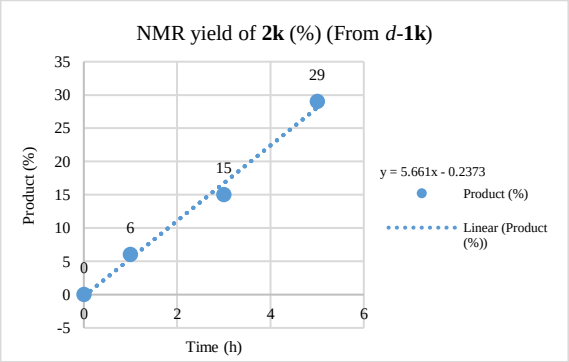


Result: KIE = k_H/k_D = 7.457/4.0508 = 1.84

Table S7. Determination of the kinetic isotopic effect of the reaction using substrate (*d*-)1k

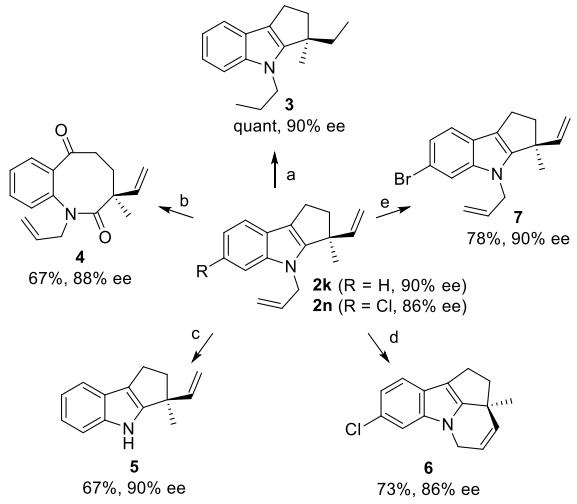
Entry	Time (h)	NMR yield of 2k (%) (From 1k)	NMR yield of 2k (%) (From *d*-1k)
1	0	0	0
2	1	13	6
3	3	33	15
4	5	58	29





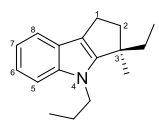
Result: KIE = k_H/k_D = 11.39/5.66 = 2.01

8. Synthetic applications of product 2



(*R*)-3-ethyl-3-methyl-4-propyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (3)

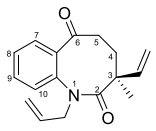
A mixture of indole **2k** (0.02 mmol, 4.4 mg) and Pd/C (10 wt. %, 0.45 mg) in dichloromethane (0.5 mL) was stirred under H_2 (1 atm.) for 3 h at 25 °C. The reaction mixture was filtered through celite using dichloromethane. The solvent was removed under reduced pressure to give the pure product **3** (quant, 2.8 g) as a colorless oil.



3: ^{1}H-NMR ($CDCl_3$) δ 7.42 (dd, 1H, H-8, *J* = 1.60, 8.40 Hz), 7.24 (dd, 1H, H-5, *J* = 1.20, 8.00 Hz), 7.12-7.03 (m, 2H, H-6, H-7), 4.06-3.93 (m, 2H, N-$\underline{CH_2}$-CH_2-CH_2), 2.81-2.69 (m, 2H, H-1), 2.47-2.41 (m, 1H, H-2a), 2.27-2.20 (m, 1H, H-2b), 1.88-1.66 (m, 4H, $\underline{CH_2}$-CH_3, N-CH_2-$\underline{CH_2}$-CH_3), 1.39 (s, 3H, C3-CH_3), 1.00 (t, 3H, CH_3, *J* = 8.00 Hz), 0.82 (t, 3H, CH_3, *J* = 7.20 Hz) ; ^{13}C-NMR ($CDCl_3$): δ 149.7, 141.1, 124.3, 120.0, 118.9, 118.8, 117.4, 109.8, 46.3, 44.6, 43.3, 33.8, 27.0, 23.8, 22.9, 11.8, 9.7; HRMS (ESI) calcd for $C_{17}H_{24}N$ m/z = 242.1903 [$(M+Na)^+$], found m/z = 242.1904; Enantiomeric excess: 90%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate 0.3 mL/min, 25 °C, 254 nm) minor peak: t_R = 27.5 min, major peak: t_R = 29.3 min; $[\alpha]_D^{21}$ = -21.8 (*c* 0.38, $CHCl_3$); IR (KBr): ν 3050, 2959, 2863, 1460, 1371, 1297, 1174, 738 cm^{-1}.

(*S*)-1-allyl-3-methyl-3-vinyl-4,5-dihydrobenzo[*b*]azocine-2,6(1*H*,3*H*)- dione (4)

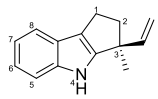
To a suspension of indole **2k** (0.036 mmol, 16 mg) in methanol (0.5 mL) at room temperature, a solution of sodium periodate (4.3 eq., 0.16 mmol, 30 mg) in water (0.24 mL) was added. The reaction mixture was stirred at room temperature for 3 h. After the complete consumption of the starting materials **2k**, the reaction was quenched with water, followed by extraction with dichloromethane. The collected organic layers were dried by using anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified by gel permeation chromatography (eluent: $CHCl_3$, pressure: 1.0 MPa, flow rate: 3.8 ml/min) to give the product **4** (6.5 mg, 67% yield) as yellowish oil.



4: ^{1}H-NMR ($CDCl_3$) δ 7.50-7.46 (m, 2H, ArH), 7.41-7.38 (m, 1H, ArH), 7.18 (d, 1H, ArH, *J* = 7.60 Hz), 5.85-5.75 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.57 (dd, 1H, $\underline{CH}$=CH_2, *J* = 10.80, 17.60 Hz), 5.11-4.71 (m, 4H, CH=$\underline{CH_2}$, CH_2-CH=$\underline{CH_2}$), 4.42 (dd, 1H, $\underline{CH_{2a}}$-CH=CH_2, *J* = 6.80, 14.40 Hz), 4.06 (dd, 1H, $\underline{CH_{2b}}$-CH=CH_2, *J* = 6.80, 14.40 Hz), 2.82-2.69 (m, 2H, H-5), 1.96-1.89 (m, 1H, H-4a), 1.82-1.77 (m, 1H, H-4b), 1.35 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$): δ 205.2, 172.8, 142.0, 140.1, 138.6, 132.3, 132.2, 129.9, 128.8, 128.1, 119.3, 112.8, 55.5, 49.8, 40.4, 34.2, 28.8; HRMS (ESI) calcd for $C_{17}H_{19}NNaO_2$, m/z = 292.1308 [$(M+Na)^+$], found m/z = 292.1308; Enantiomeric excess: 88%, determined by HPLC (DAICEL Chiralpak AD-3, eluent: *n*-hexane/2-propanol = 20/1, flow rate: 0.5 mL/min, 25 °C, 254 nm) minor peak: t_R = 14.2 min, major peak: t_R = 12.4 min; $[\alpha]_D^{21}$ = -55.2 (*c* 0.94, $CHCl_3$); IR (KBr): ν 3077, 2976, 2935, 1697, 1649, 1599, 1451, 1380, 1281, 1248, 922, 768 cm^{-1}.

(*S*)-3-methyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (5)

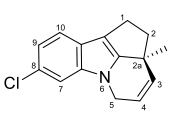
A mixture of indole **2k** (0.03 mmol, 7.7 mg) and $RhCl_3.nH_2O$ (20 mol%, 0.006 mmol, 1.3 mg) in 2-propanol (0.8 mL) was microwaved at 100 °C for 5h. After cooling to room temperature, the reaction mixture was purified by PTLC (*n*-hexane/Et_2O = 9.5/0.5) to give the pure product **5** (3.6 mg, 67% yield) as colorless oil.



5: ^{1}H-NMR ($CDCl_3$) δ 7.74 (brs, 1H, NH), 7.48-7.45 (m, 1H, ArH), 7.32-7.29 (m, 1H, ArH), 7.13-7.06 (m, 2H, ArH), 6.05 (dd, 1H, $\underline{CH}$=CH_2, *J* = 10.00, 17.80 Hz), 5.00 (dd, 1H, CH=$\underline{CH_{2a}}$, *J* = 1.20, 10.00 Hz), 4.96 (dd, 1H, CH=$\underline{CH_{2b}}$, *J* = 1.20, 17.80 Hz), 2.85-2.81 (m, 2H, $C1H_2$), 2.54-2.46 (m, 1H, $C2H_{2a}$), 2.40-2.33 (m, 1H, $C2H_{2b}$), 1.42 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$): δ 148.1, 145.3, 141.0, 125.0, 120.9, 119.7, 118.9, 118.6, 111.9, 111.7, 46.0, 45.6, 24.5, 23.0; HRMS (ESI) calcd for $C_{14}H_{16}N$ m/z = 198.1277 [$(M+H)^+$], found m/z = 198.1277; Enantiomeric excess: 90%, determined by HPLC (YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane/2-propanol = 20/1, flow rate: 0.3 mL/min, 25 °C, 280 nm) minor peak: t_R = 26.7 min, major peak: t_R = 23.7 min; $[\alpha]_D^{25}$ = +6.2 (*c* 0.45, $CHCl_3$); IR (KBr): ν 3407, 2925, 2857, 1660, 1458, 1371, 1304, 784 cm^{-1}.

(*S*)-8-Chloro-2a-methyl-1,2,2a,5-tetrahydrobenzo[*b*]cyclopenta[*hi*]indolizine (6)

Grubbs Catalyst, 2nd Generation (18 mol%, 0.0066 mmol, 5.6 mg) was added to a solution of indole **2n** (0.037 mmol, 9.9 mg) in dichloromethane (36 mL). The reaction was stirred at room temperature for 3 h under nitrogen. After the filtration of the reaction mixture, the solvent was evaporated under vacuum, and the residue was purified by gel permeation chromatography (eluent: $CHCl_3$, pressure: 1.0 MPa, flow rate: 3.8 ml/min) to give the product **6** (6.6 mg, 73% yield) as colorless oil.

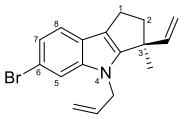


6: ^{1}H-NMR ($CDCl_3$) δ 7.58 (d, 1H, H-8, *J* = 1.60 Hz), 7.18 (dd, 1H, H-6, *J* = 1.60, 8.80 Hz), 7.06 (d, 1H, H-5, *J* = 8.80 Hz), 6.04 (dd, 1H, $\underline{CH}$=CH_2, *J* = 10.80, 17.60 Hz), 5.91-5.82 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.15-5.11 (m, 1H, CH_2-CH=$\underline{CH_{2a}}$), 5.06 (dd, 1H, CH=$\underline{CH_{2a}}$ *J* = 1.20, 10.80 Hz), 4.98 (dd, 1H, CH=$\underline{CH_{2b}}$ *J* = 1.20, 17.60 Hz), 4.93-4.88 (m, 1H, CH_2-CH=$\underline{CH_{2b}}$), 4.68-4.55 (m, 2H, $\underline{CH_2}$-CH=CH_2), 2.83-2.72 (m, 2H, $C1H_2$), 2.53-2.47 (m, 1H, $C2H_{2a}$), 2.36-2.30 (m, 1H, $C2H_{2b}$), 1.44 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$): δ 154.4, 143.0, 135.4, 126.3, 125.5, 122.2,

120.4, 119.6, 113.2, 110.8, 46.0, 44.6, 39.4, 26.2, 24.4; HRMS (ESI) calcd for $C_{15}H_{15}ClN$ m/z = 244.0888 [$(M+H)^+$], found m/z = 244.0888; Enantiomeric excess: 86%, determined by HPLC (DAICEL Chiralcel OD-H, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 300 nm) minor peak: t_R = 8.0 min, major peak: t_R = 5.6 min; $[\alpha]_D^{21}$ = -54.4 (*c* 0.84, $CHCl_3$); IR (KBr): ν 2950, 2855, 1680, 1613, 1488, 1454, 1441, 1335, 1065, 786 cm^{-1}.

(*S*)-4-allyl-6-bromo-3-methyl-3-vinyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (7)

To a solution of indole **2k** (0.0379 mmol, 9 mg) in in dichloromethane (1.3 mL), *N*-bromosuccinimide (0.0379 mmol, 6.8 mL) was added. The reaction was stirred at room temperature for 3 h. After that, the solvent was removed under reduced pressure and the remaining residues was purified by PTLC (hexane/Et_2O = 9.5/0.5) to give the pure products **7** (9.4 mg, 78% yield) as colorless oil.

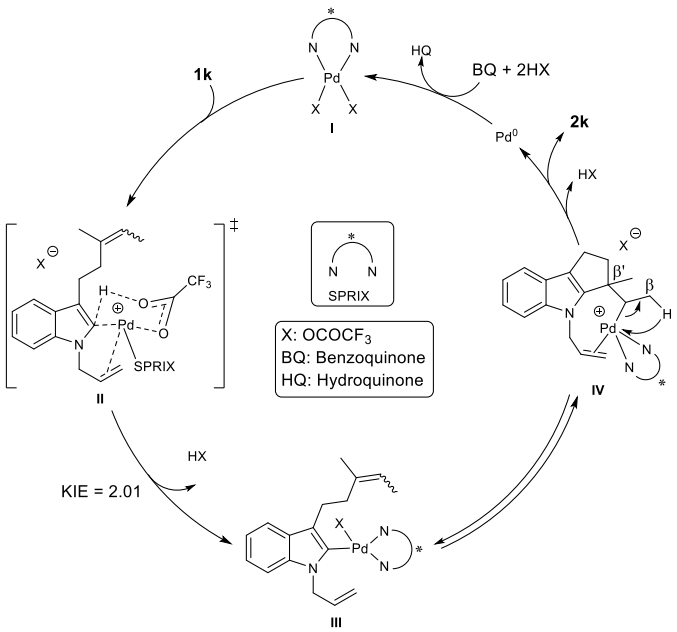


2k: ^{1}H-NMR ($CDCl_3$) δ 7.33 (d, 1H, H-5, *J* = 2.00 Hz), 7.30 (d, 1H, H-8, *J* = 8.00 Hz), 7.16 (dd, 1H, H-7, *J* = 2.00, 8.00 Hz), 6.04 (dd, 1H, $\underline{CH}$=CH_2, *J* = 10.80, 17.60 Hz), 5.92-5.83 (m, 1H, CH_2-$\underline{CH}$=CH_2), 5.16-5.13 (m, 1H, CH_2-CH=$\underline{CH_{2a}}$), 5.06 (dd, 1H, CH=$\underline{CH_{2a}}$ *J* = 0.80, 10.00 Hz), 5.00-4.90 (m, 2H, CH=$\underline{CH_{2b}}$, CH_2-CH=$\underline{CH_{2b}}$), 4.66-4.53 (m, 2H, $\underline{CH_2}$-CH=CH_2), 2.84-2.73 (m, 2H, C1H_2), 2.53-2.47 (m, 1H, C2H_{2a}), 2.36-2.27 (m, 1H, C2H_{2b}), 1.44 (s, 3H, C3-CH_3); ^{13}C-NMR ($CDCl_3$): δ 149.3, 144.8, 141.9, 133.3, 123.1, 122.4, 120.1, 117.9, 116.8, 114.0, 113.3, 112.3, 46.4 (2C), 46.3, 23.8, 22.6; HRMS (ESI) calcd for $C_{17}H_{19}BrN$ m/z = 316.0695 [$(M+H)^+$], found m/z = 316.0696; Enantiomeric excess: 90%, determined by HPLC (YMC CHIRAL ART Cellulose-C, eluent: *n*-hexane, flow rate: 0.3 mL/min, 25 °C, 254 nm) minor peak: t_R = 29.9 min, major peak: t_R = 27.1 min; $[\alpha]_D^{21}$ = +43.8 (*c* 1.44, $CHCl_3$); IR (KBr): ν 3079, 2932, 2857, 1460, 1370, 995, 919, 840, 798 cm^{-1}.

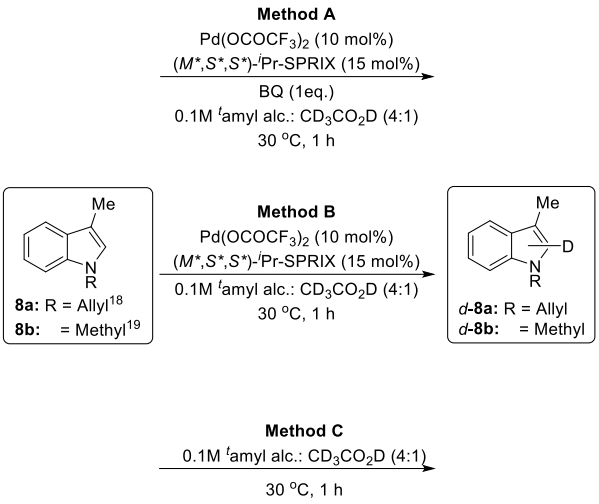
9. Mechanism

Although the reaction mechanism is still controversial, we proposed the catalytic cycle as follow:

The weakly coordinating allyl group played an assistant role[16] by stabilizing the infant six-membered transition state *via* coordination to the palladium center, as shown in **II**.[17] Cleavage of the C–H bond proceeded *via* a concerted transfer of the hydrogen atom to the trifluoroacetate anion, which acts as an intramolecular base. The results of the screening of palladium salts (Table S3) could be attributed to the dual role of (trifluoro)acetate as ligand and intramolecular base.[17] Subsequently, the generation of palladium intermediate **III** was accomplished *via* the extrusion of trifluoracetic acid. Further, palladium intermediate **III** underwent olefin insertion to give the sterically hindered intermediate **IV**, which can undergo *β*-carbon elimination as a side-reaction pathway. The weak coordination of the allyl group to the palladium center of intermediate **IV** could help suppress the *β*-carbon elimination pathway. Consequently, the intermediate **IV** underwent *β*-hydride elimination to give product **2k** with the formation of Pd^0 to be re-oxidized with benzoquinone, regenerating the active species **I**. Detailed mechanistic study involving DFT calculations is currently underway.



10. Deuteration test



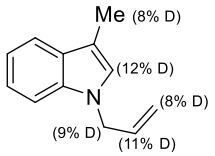
Method A: A mixture of $Pd(TFA)_2$ (10 mol %, 0.00469 mmol, 1.6 mg) and (*P*,*R*,*R*)-^{i}Pr-SPRIX (15 mol %, 0.007 mmol, 2.6 mg) was dissolved in 1 mL dry dichloromethane and stirred under nitrogen atmosphere at 30 °C for 2 h. After that, the solvent was distilled off and the resulting yellow Pd complex was kept under vacuum for 10 min. To the dried Pd complex, *p*-benzoquinone (1 eq., 0.0469 mmol, 5.1 mg) and indole **8a,b** (0.0469 mmol) were added under nitrogen. Dry ^{t}amyl alcohol (0.4 mL) was added followed by stirring at 30 °C for 10 mins until dissolving of the solid materials to give a turbid deep red solution. Then, CD_3CO_2D (0.1 mL) was added, and subsequently, a clear red solution was obtained which was stirred under nitrogen atmosphere at 30 °C for 1 h. The reaction mixture was passed through short silica pad using Et_2O as eluent. The solvent was removed under vacuum, and the remaining residues was connected to Schleck line for 30 min. The deuteration ratio was determined using H-NMR.

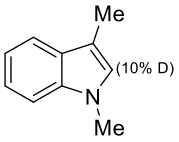
Method B: It is same as **method A**, but by excluding the addition of BQ.

Method C: It is same as **method A,** but by excluding the addition of Pd-SPRIX complex and BQ. It is a mixing of starting materials **8a,b** with the solvent systems ^{t}amyl alcohol (0.4 mL) and CD_3CO_2D (0.1 mL) at 30 °C for 1h

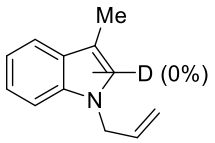
Method A

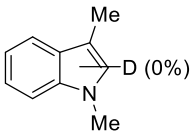

Method B





Method C





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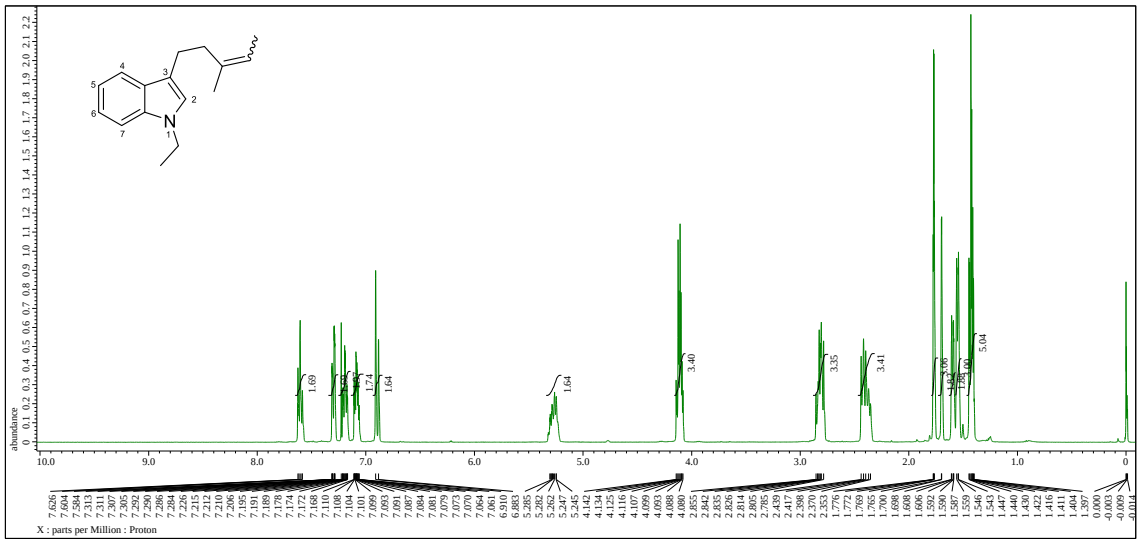
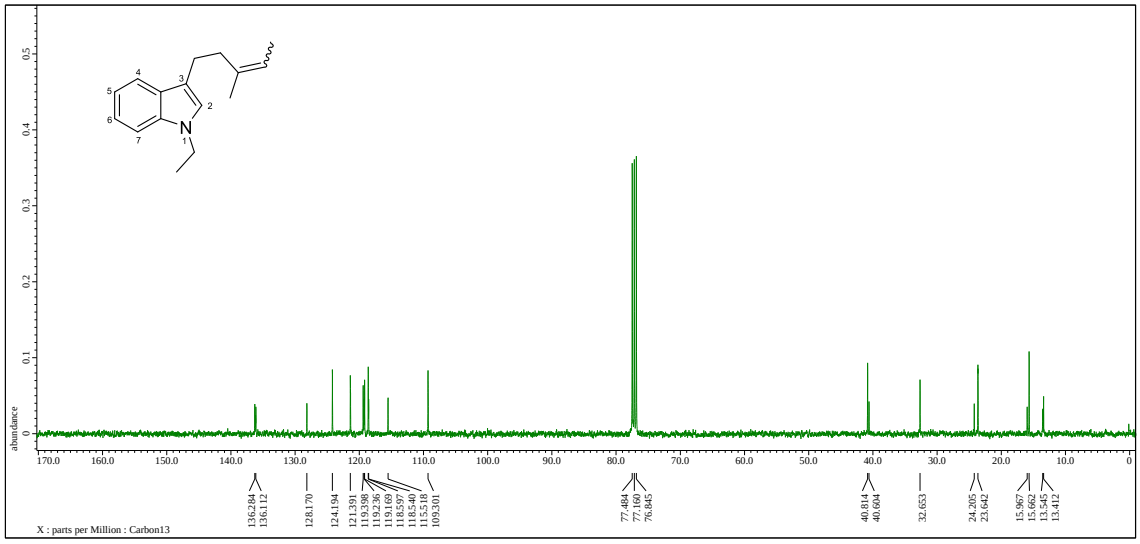
12. NMR Spectra

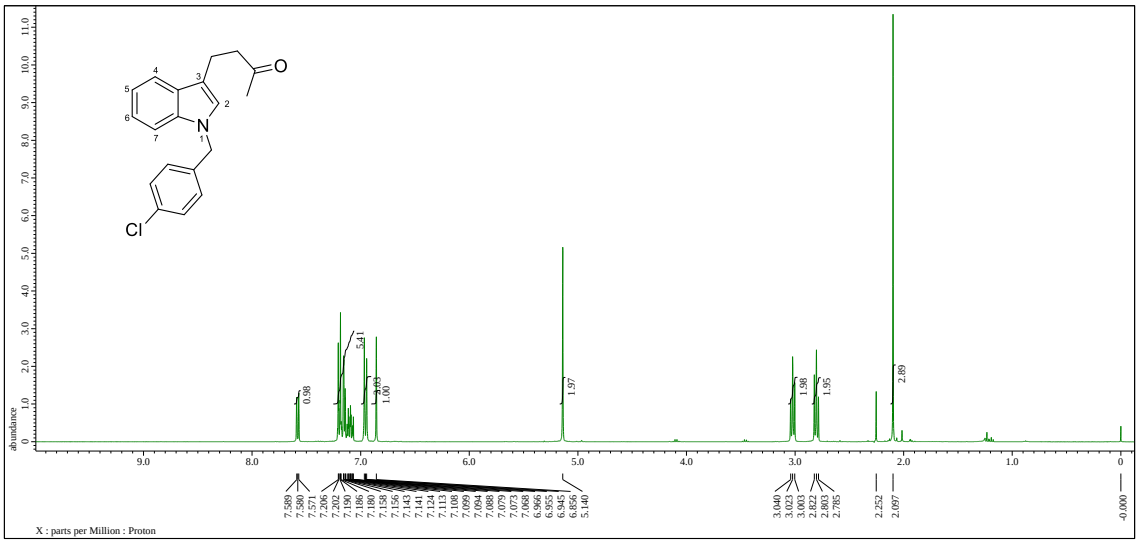
12.1. Substrates



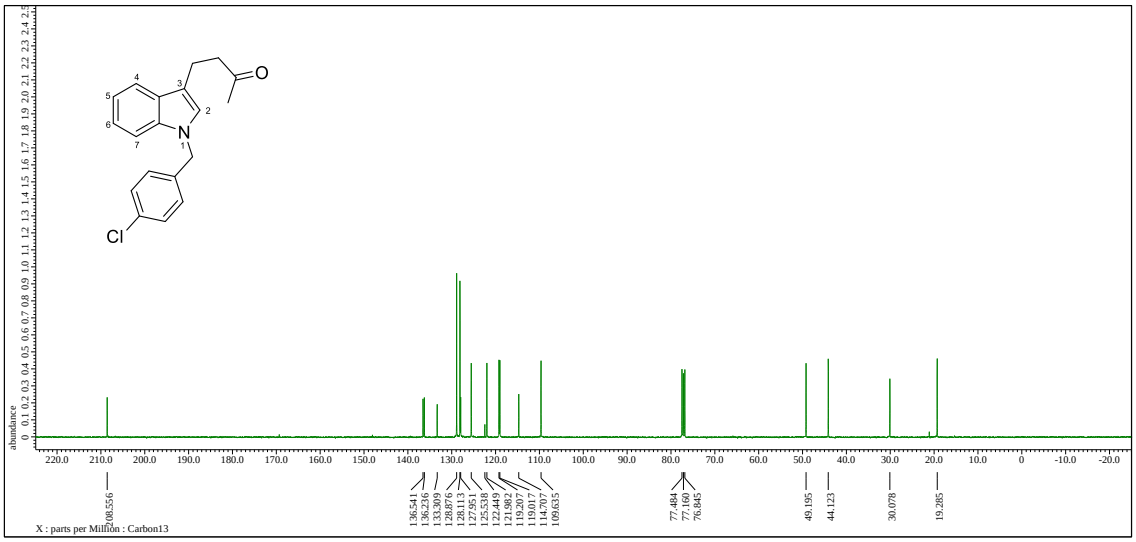
^{1}H NMR spectrum of compound **1b** (63:37 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



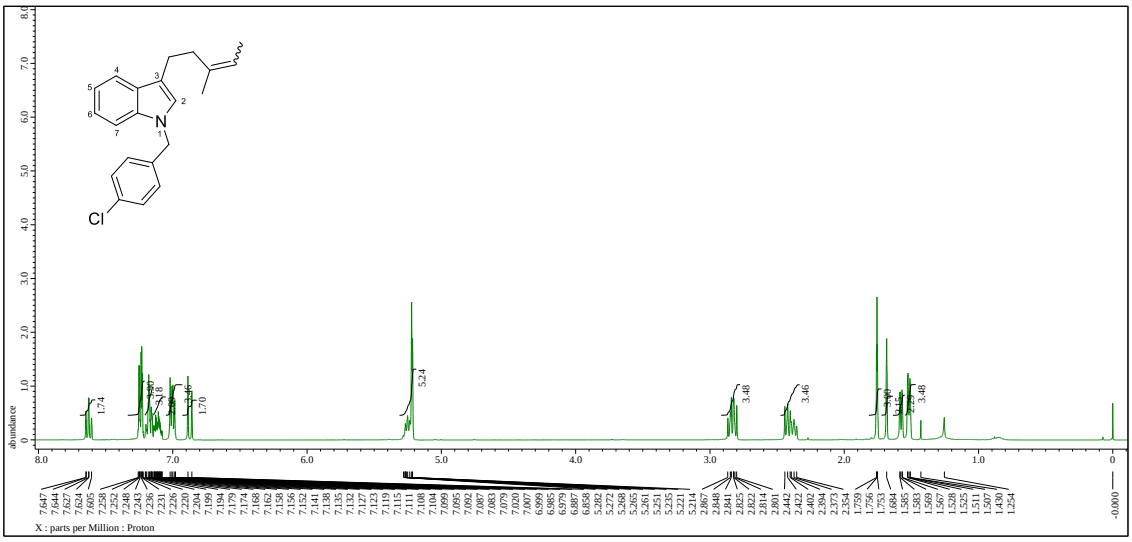
^{13}C NMR spectrum of compound **1b** (63:37 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



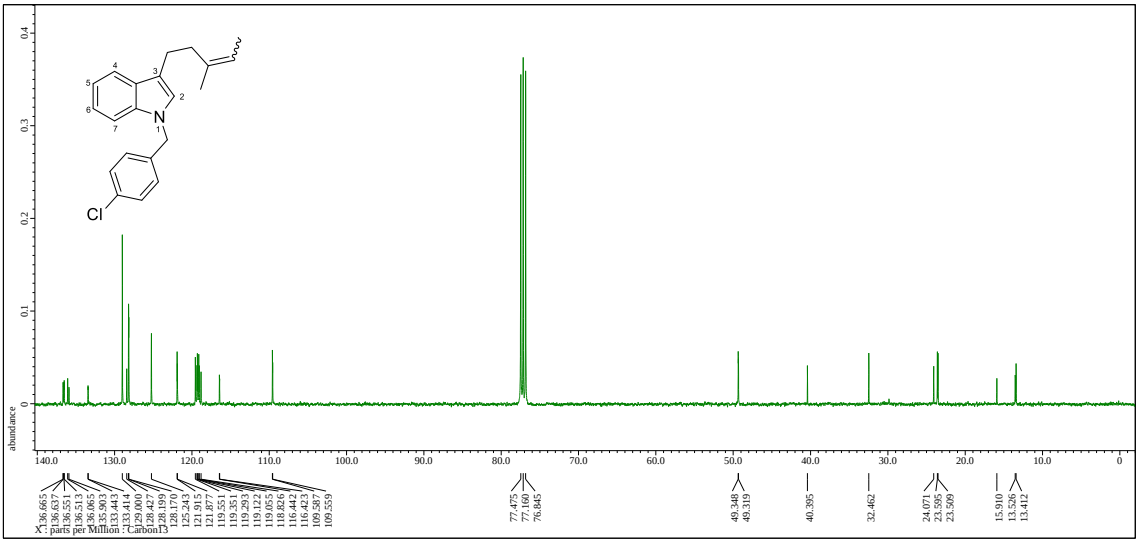
^{1}H NMR spectrum of compound **S'1d** (400 MHz, $CDCl_3$)



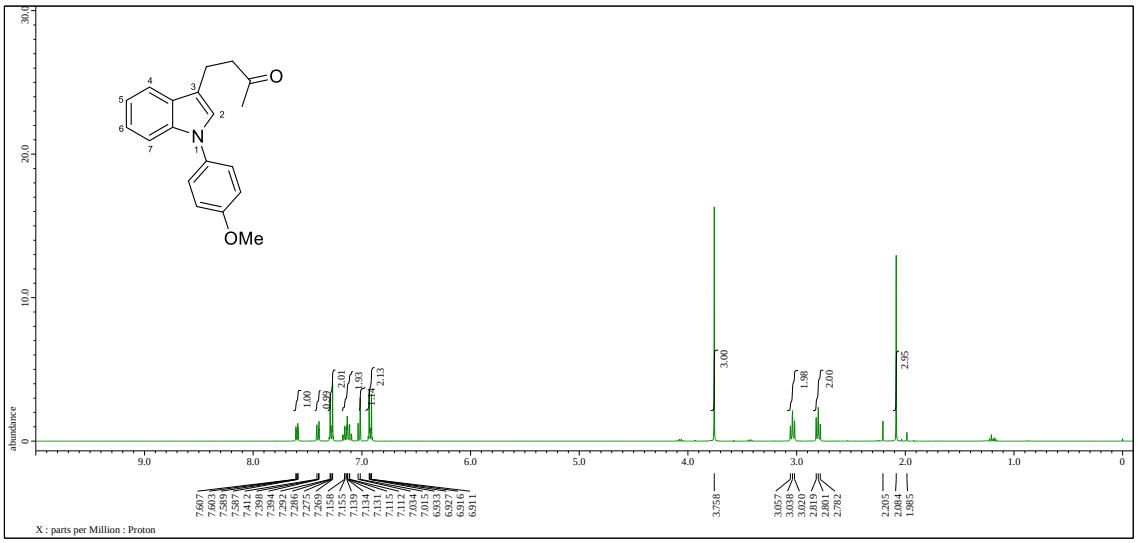
^{13}C NMR spectrum of compound **S'1d** (100 MHz, $CDCl_3$)



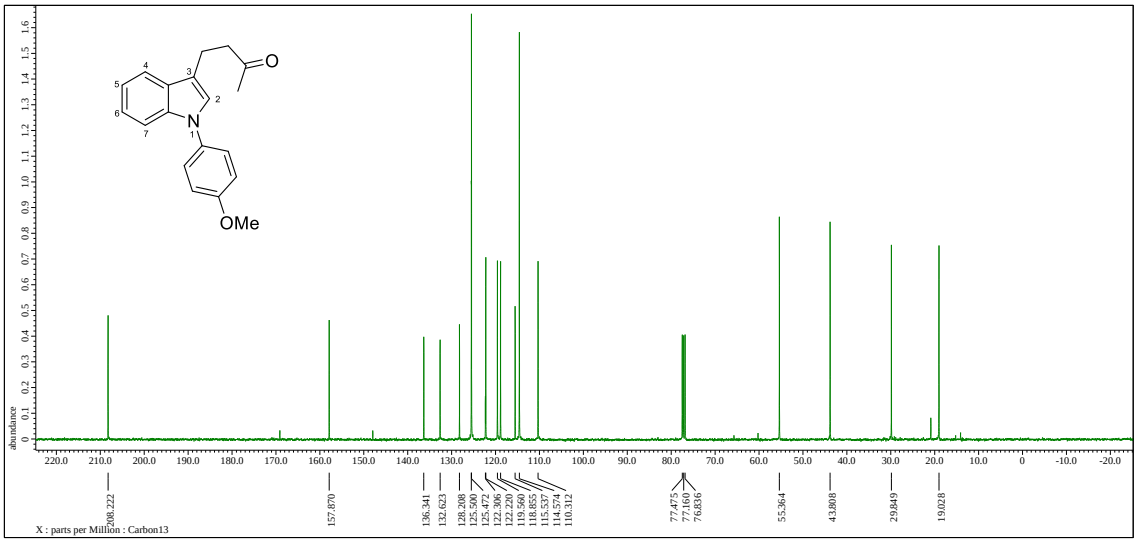
^{1}H NMR spectrum of compound **1d** (57:43 mixture of *E/Z*-olefin isomers) (400 MHz, $CDCl_3$)



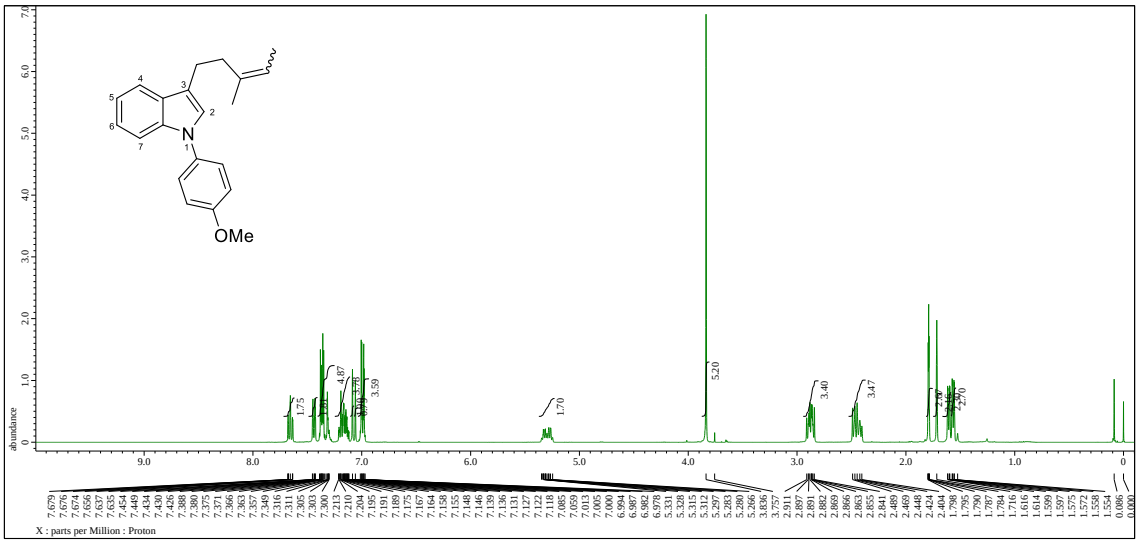
^{13}C NMR spectrum of compound **1d** (57:43 mixture of *E/Z*-olefin isomers) (100 MHz, $CDCl_3$)



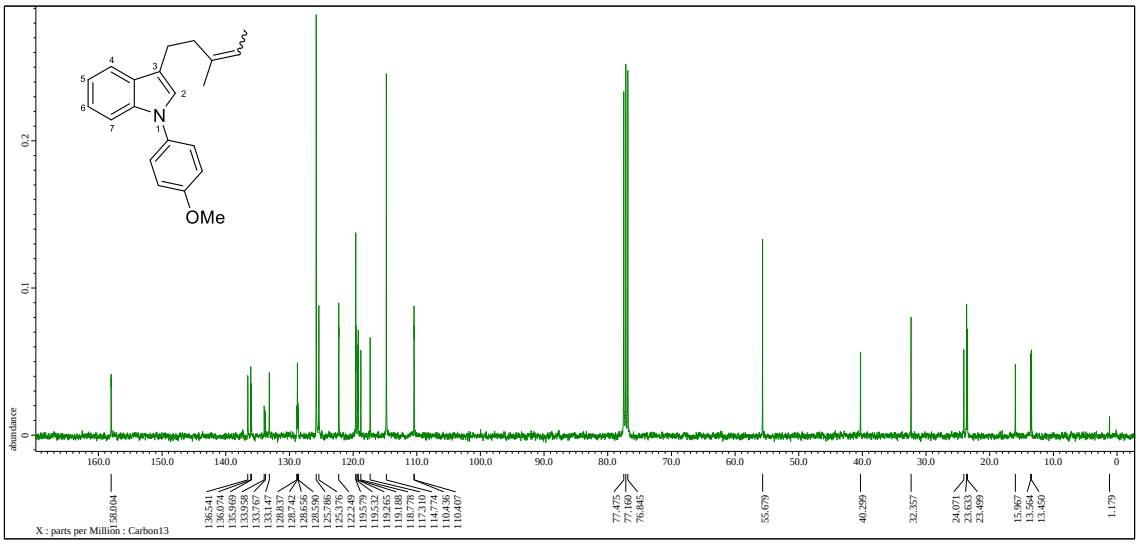
^{1}H NMR spectrum of compound **S'1e** (400 MHz, $CDCl_3$)



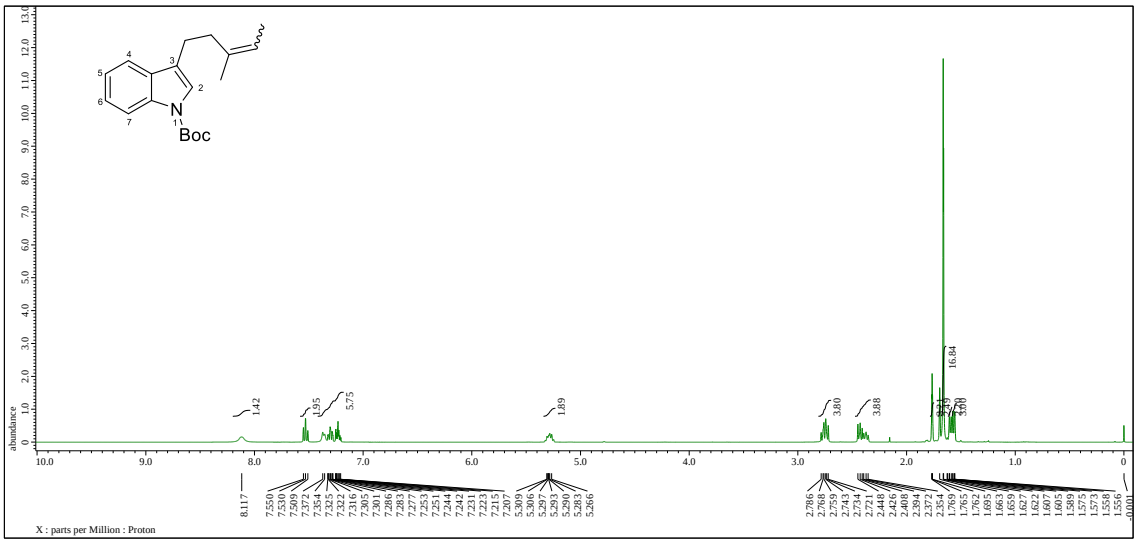
^{13}C NMR spectrum of compound **S'1e** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **1e** (55:45 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **1e** (55:45 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



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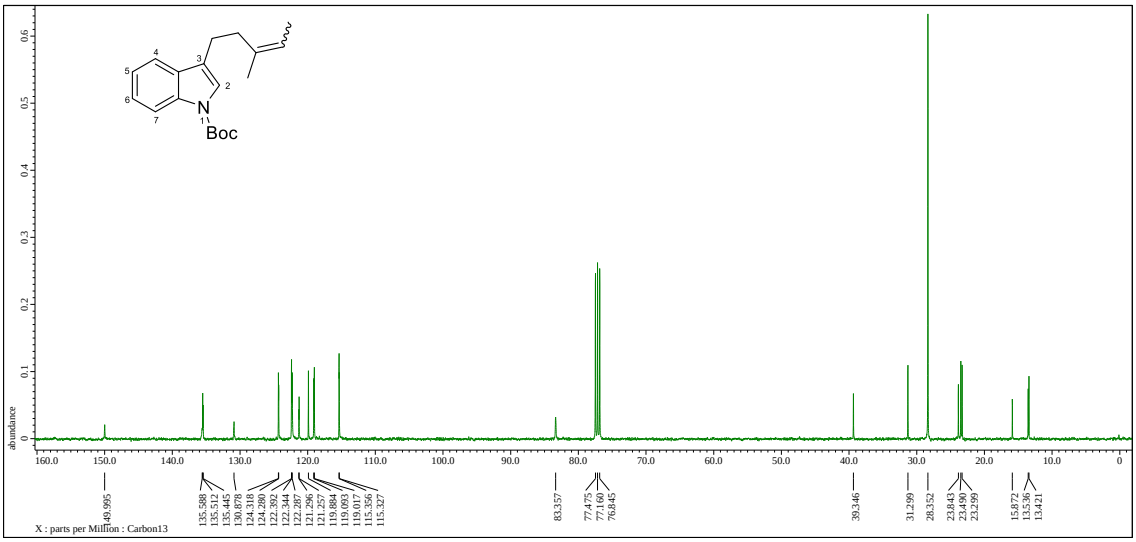
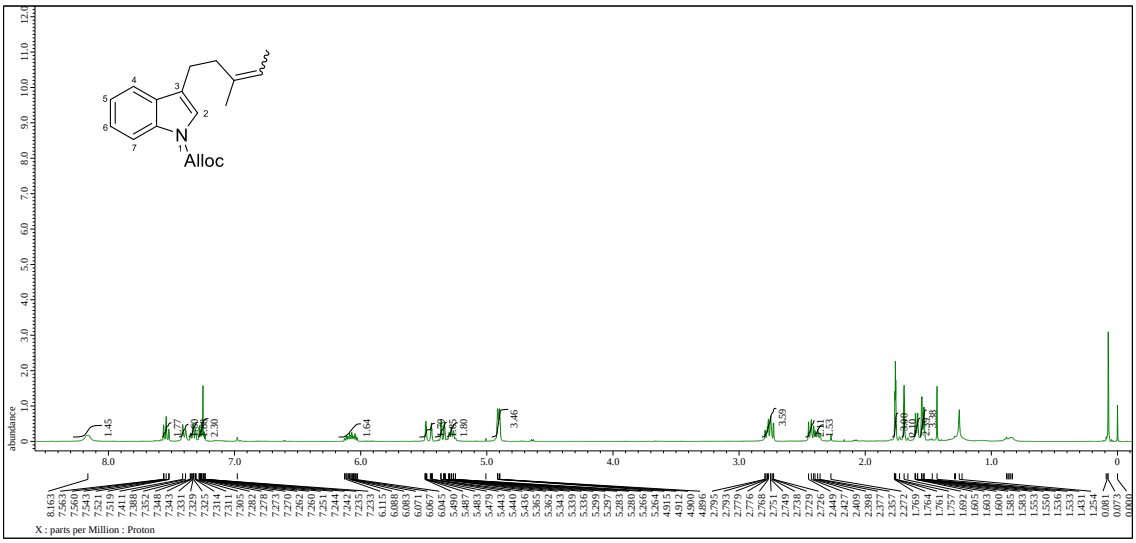


^{13}C NMR spectrum of compound **1f** (57:43 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



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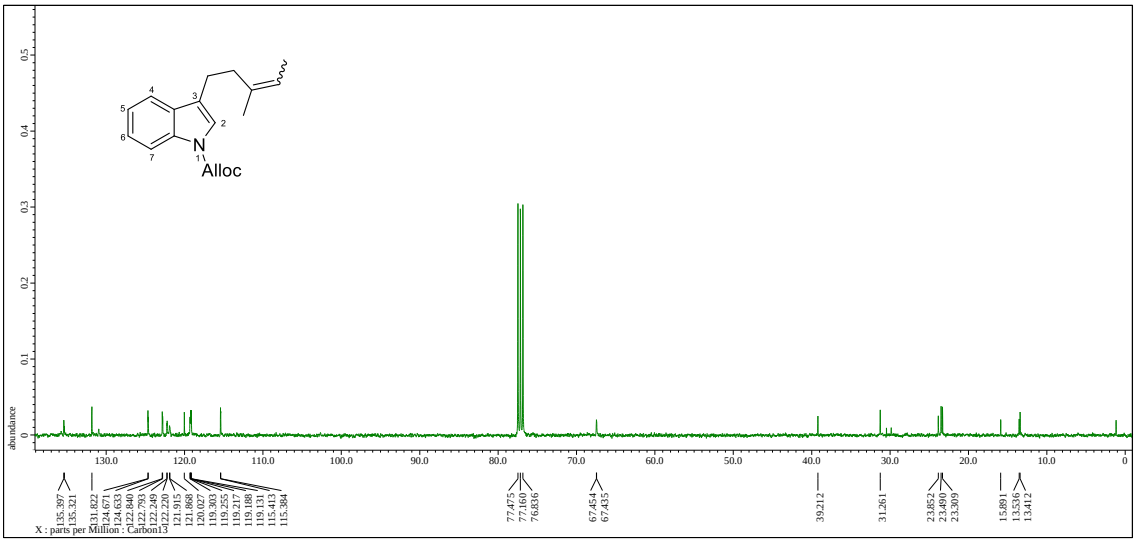
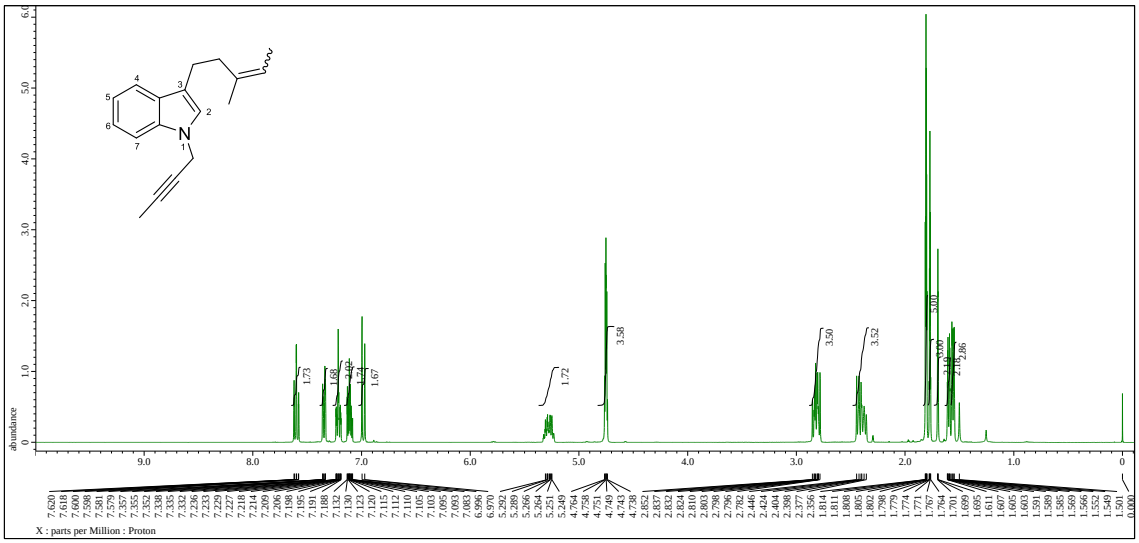
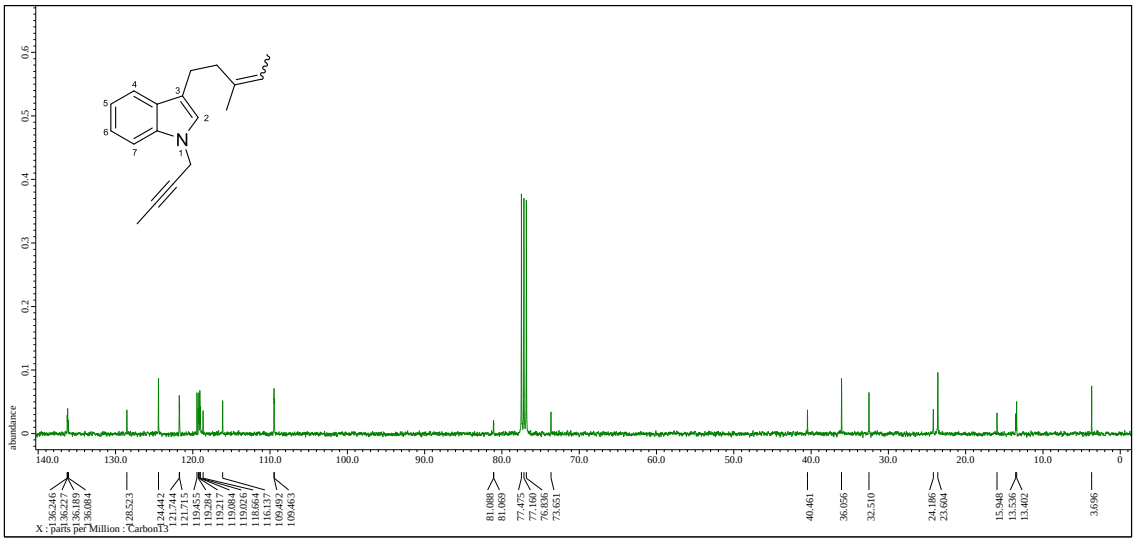


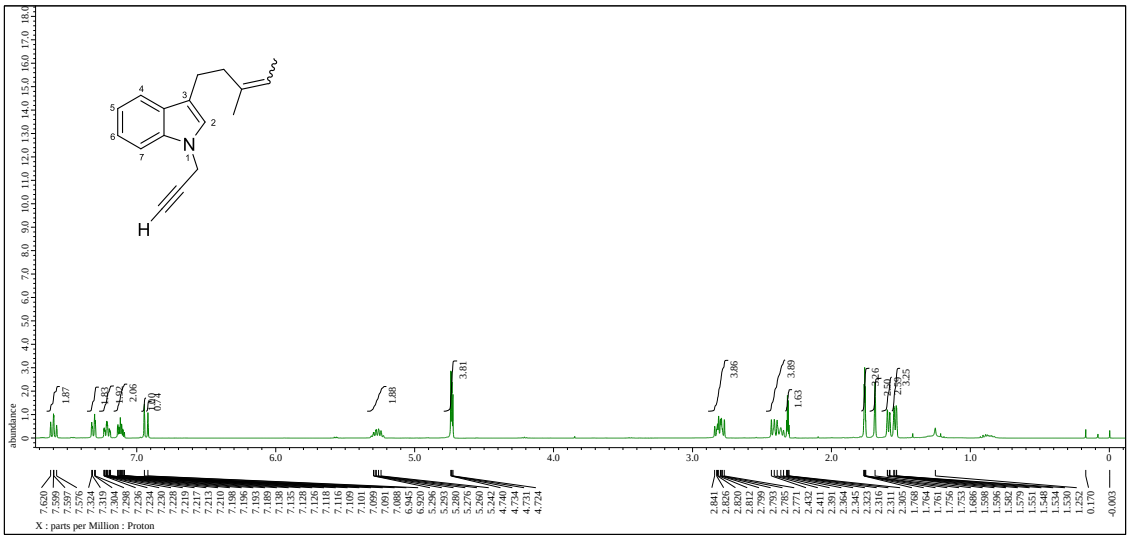
^{13}C NMR spectrum of compound **1g** (59:41 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **1i** (57:43 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **1i** (57:43 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



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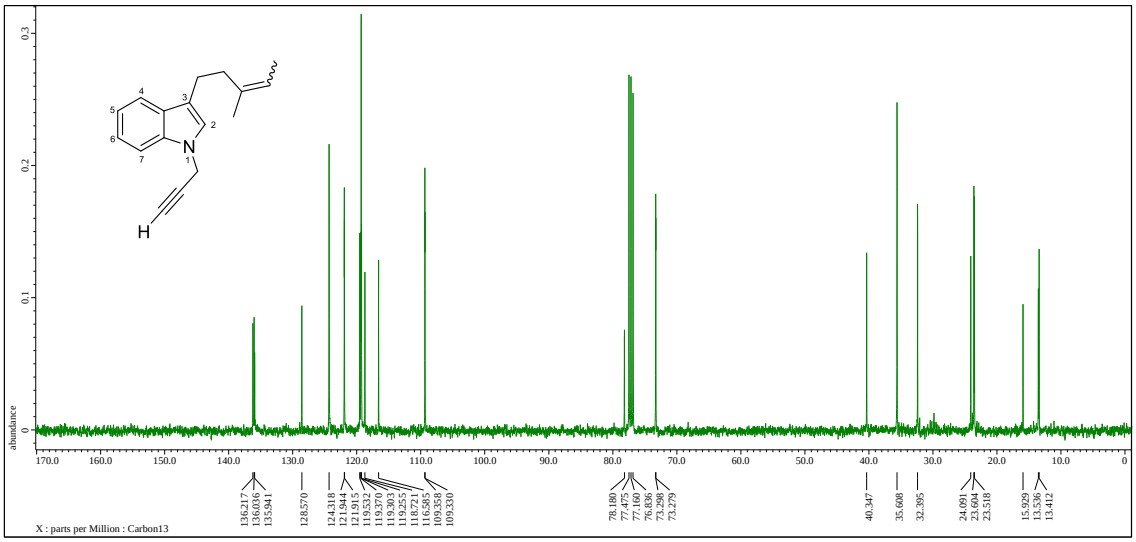
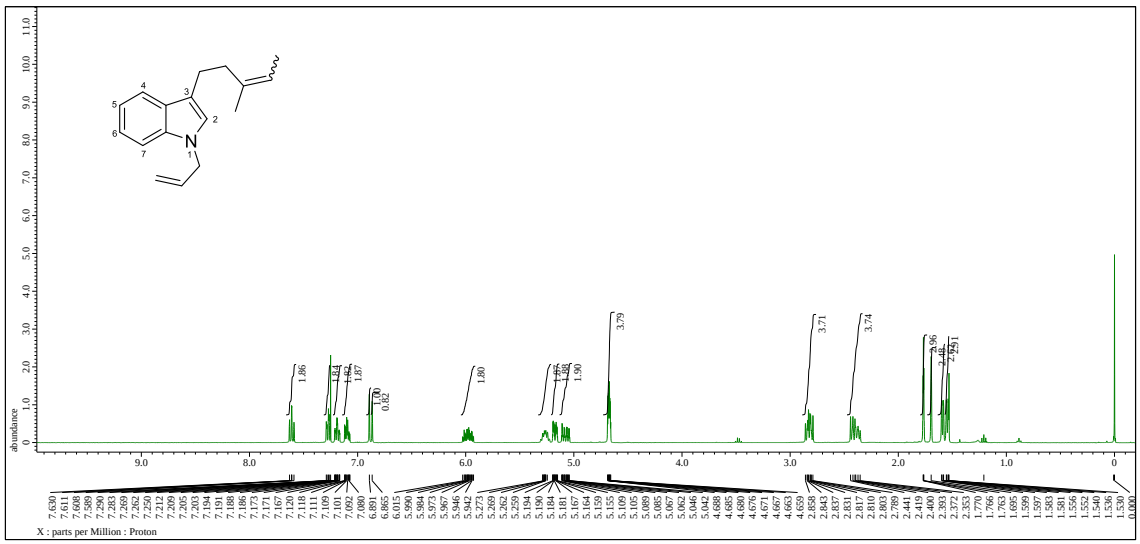
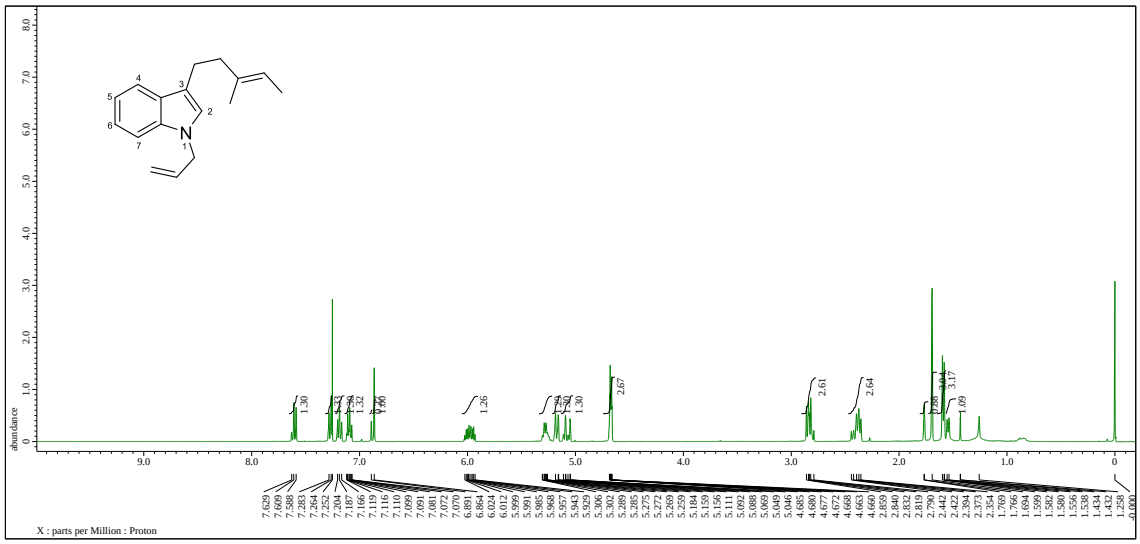


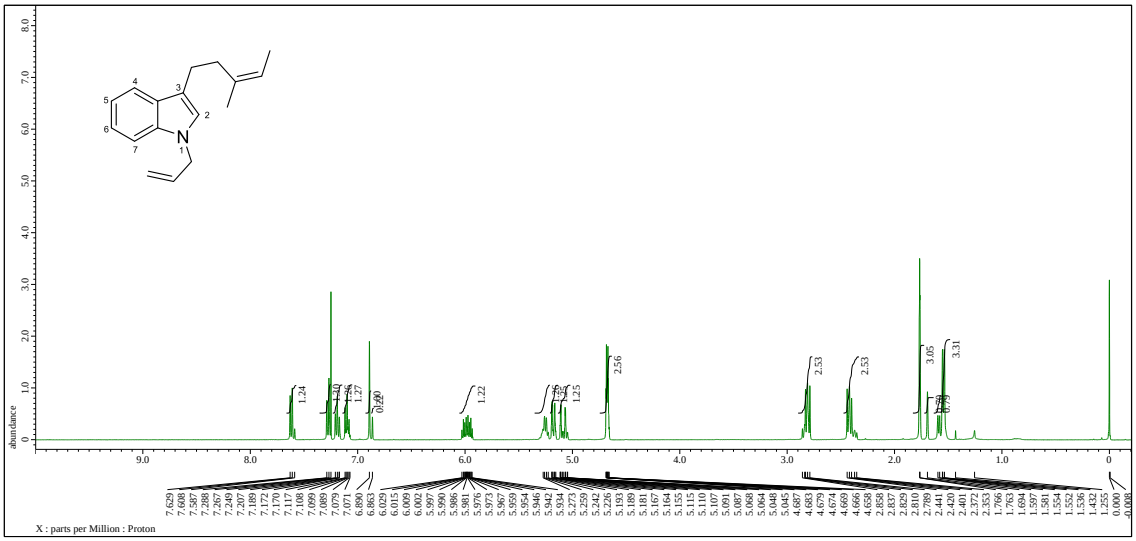
^{13}C NMR spectrum of compound **1j** (57:43 *Z/E*-mixture of olefin isomers) (100 MHz, $CDCl_3$)



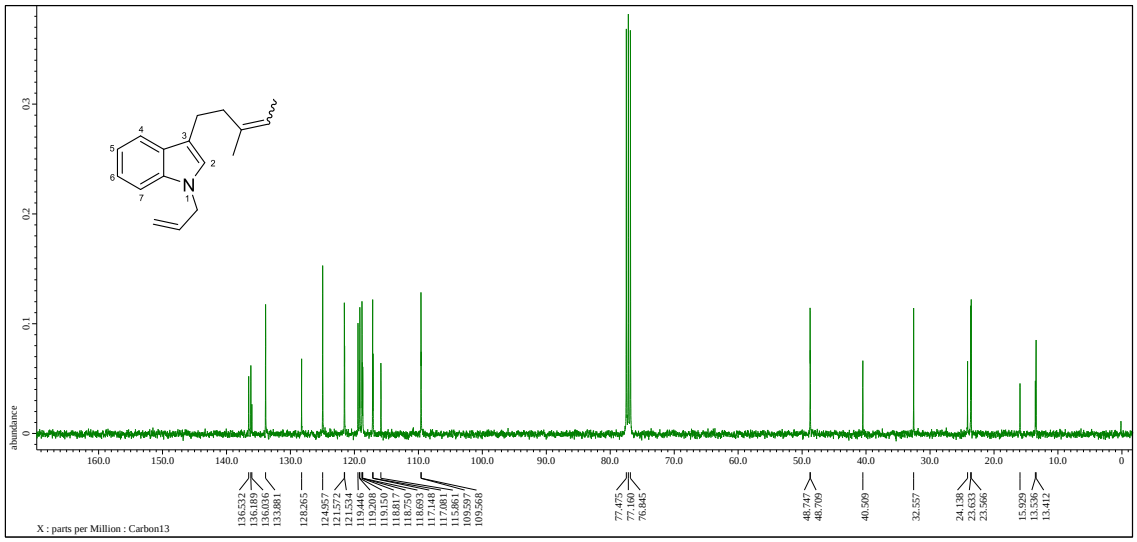
^{1}H NMR spectrum of compound **1k** (55:45 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound *E*-enriched **1k** (*E/Z* = 79/21) (400 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound *Z*-enriched **1k** (*E*/*Z* = 19/81) (400 MHz, $CDCl_3$)



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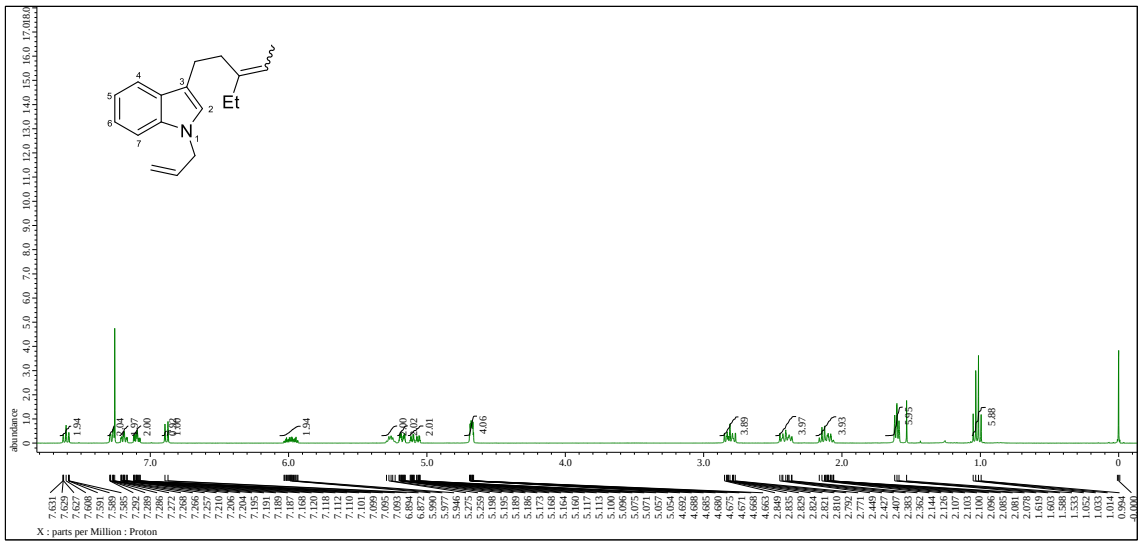

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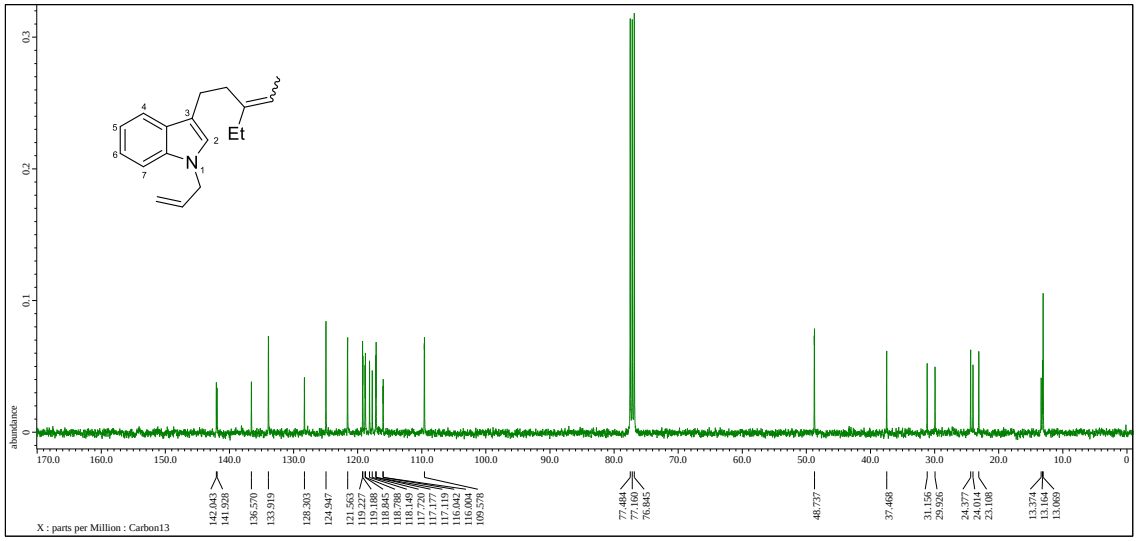

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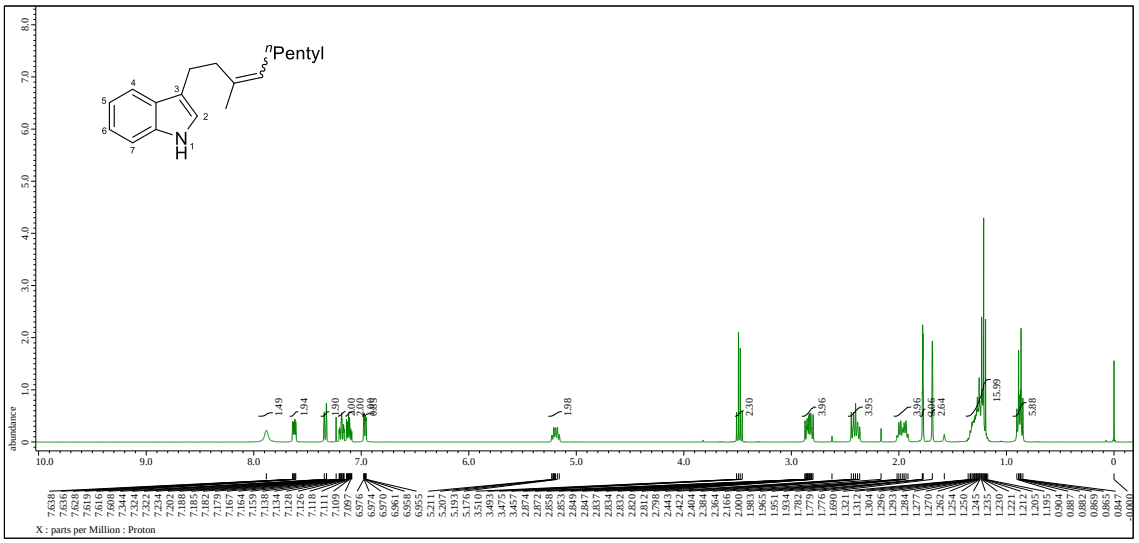

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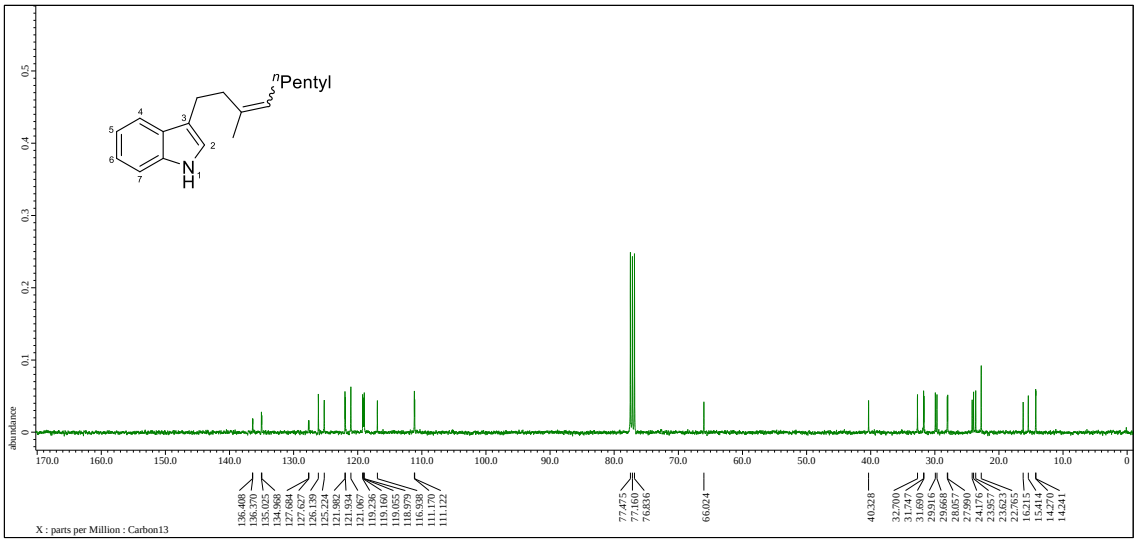

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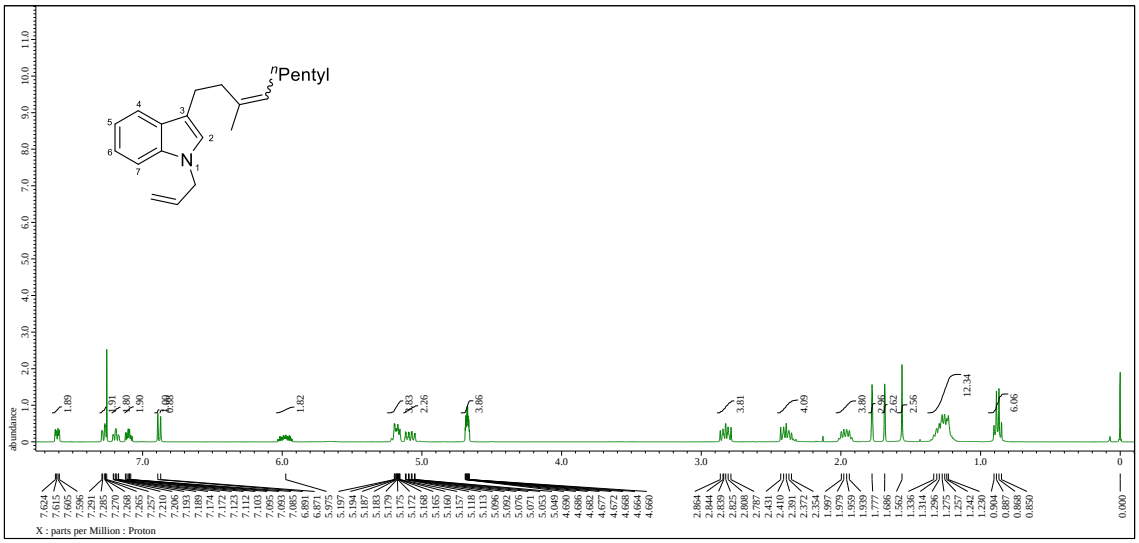

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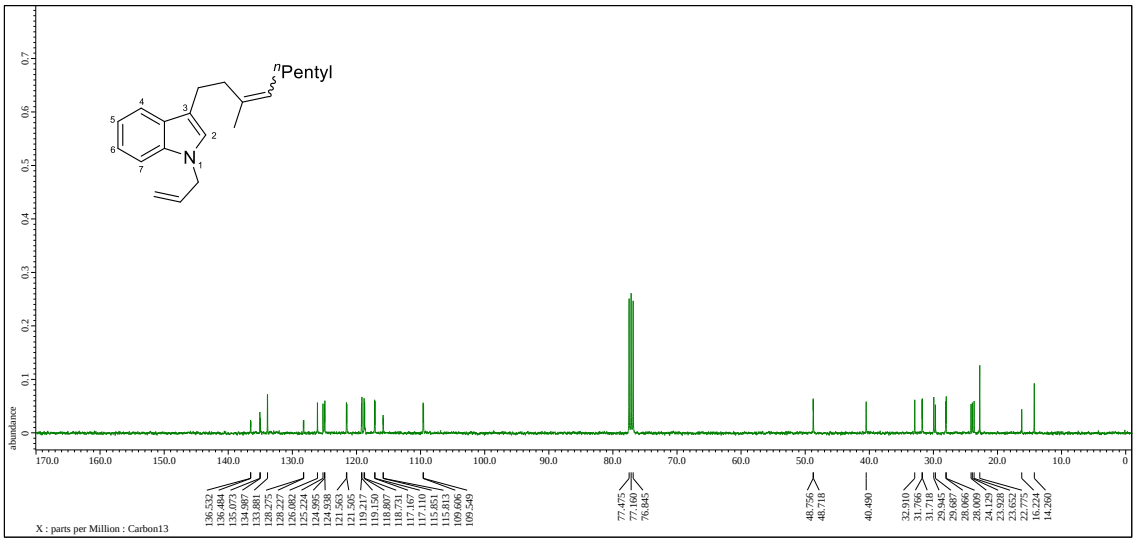

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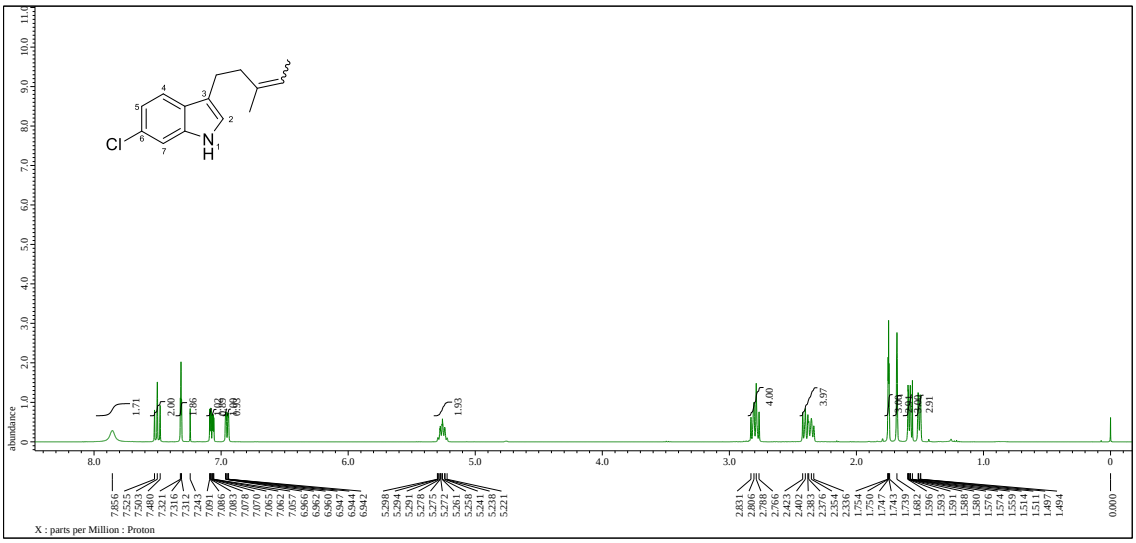
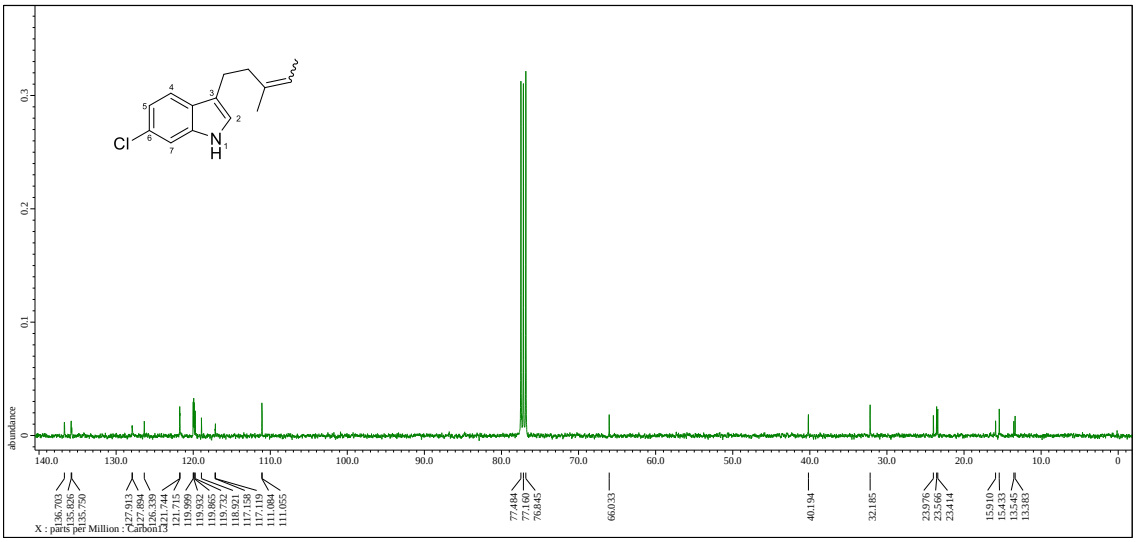
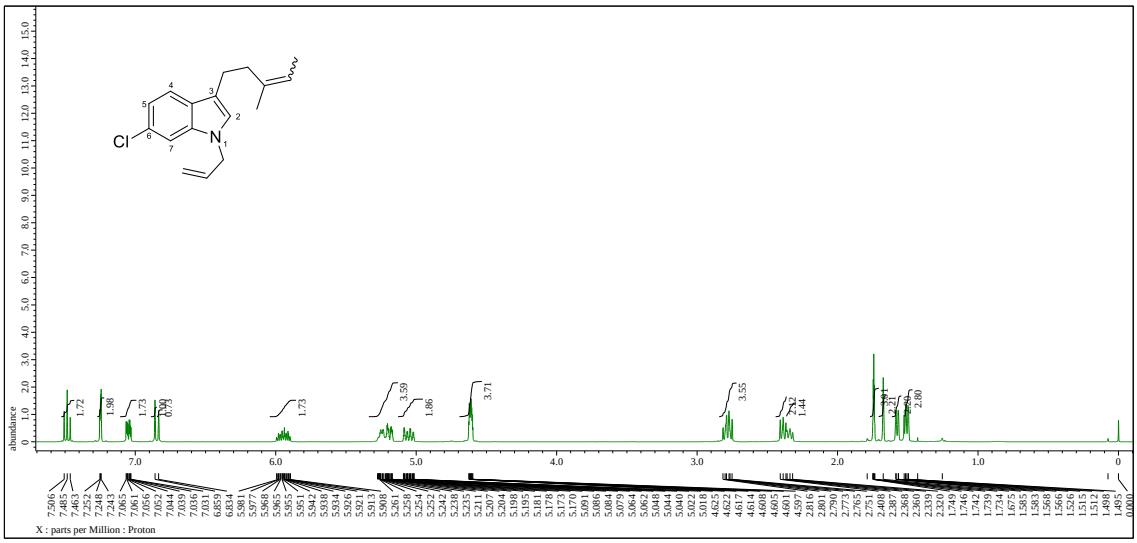


^{1}H NMR spectrum of compound **S'1n** (51:49 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **S'1n** (51:49 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



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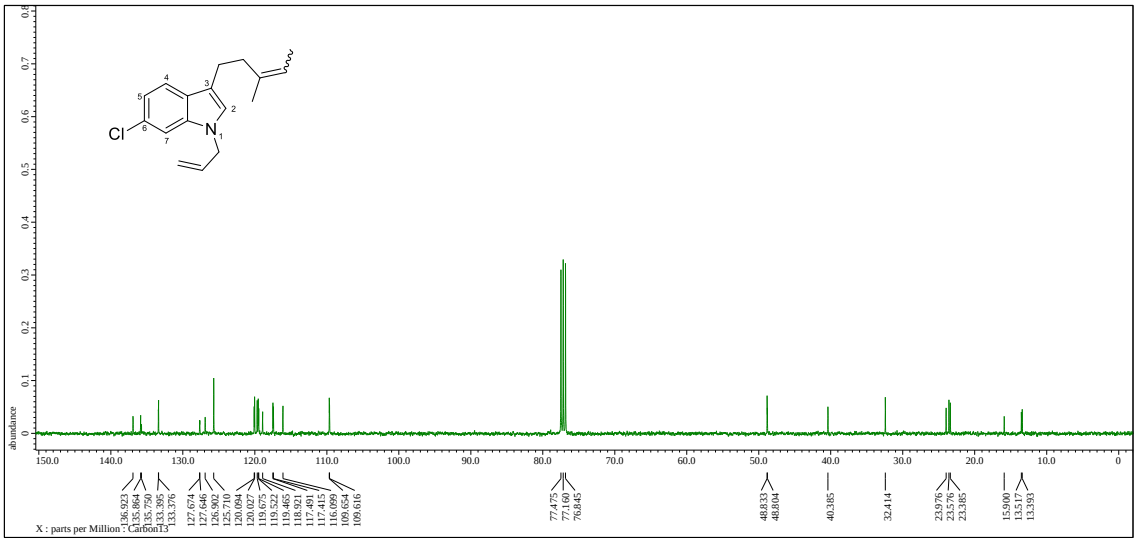

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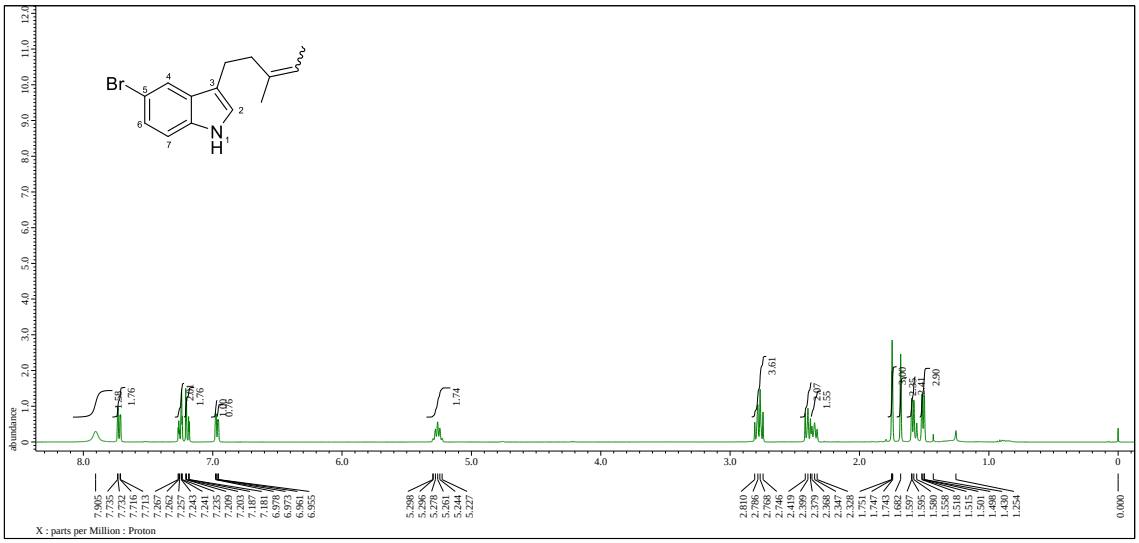
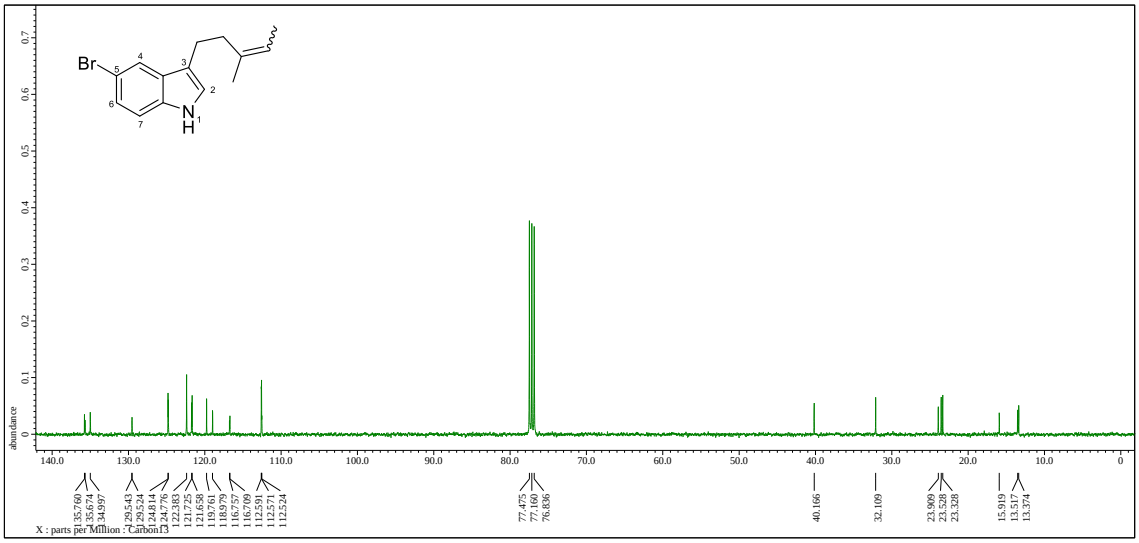
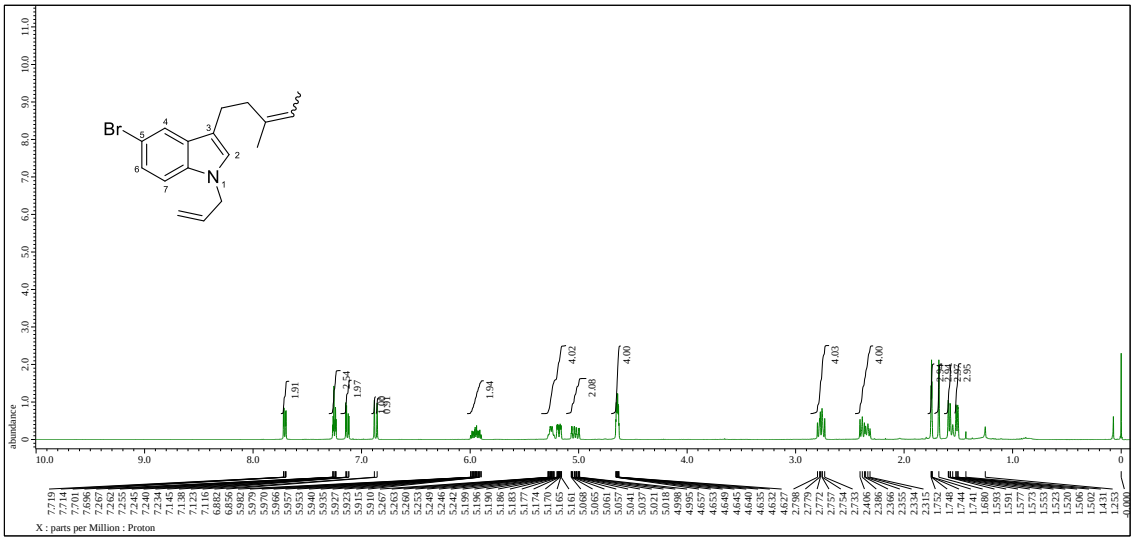


^{1}H NMR spectrum of compound **S'1o** (57:43 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **S'1o** (57:43 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



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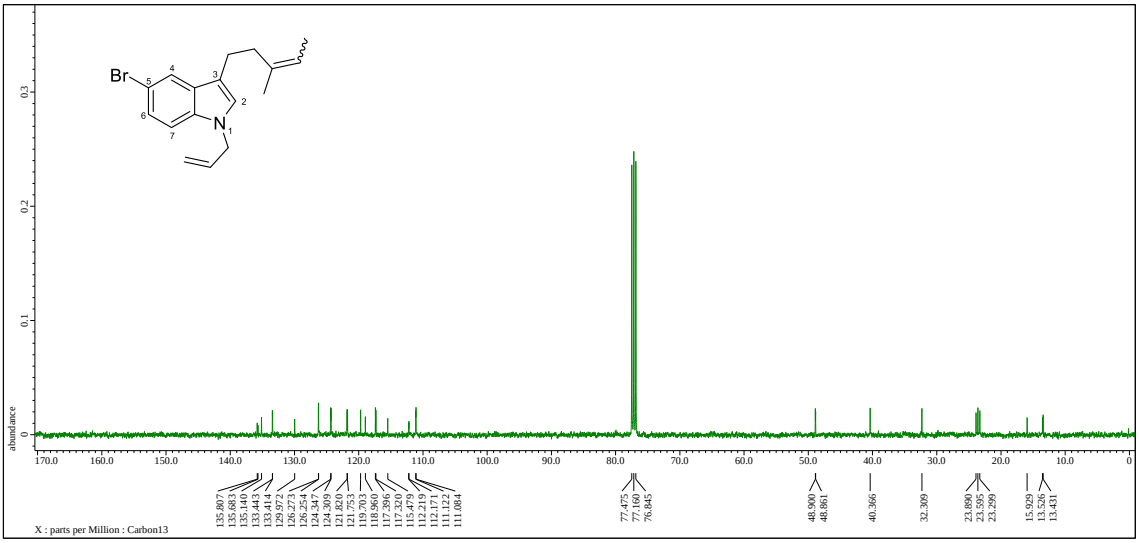

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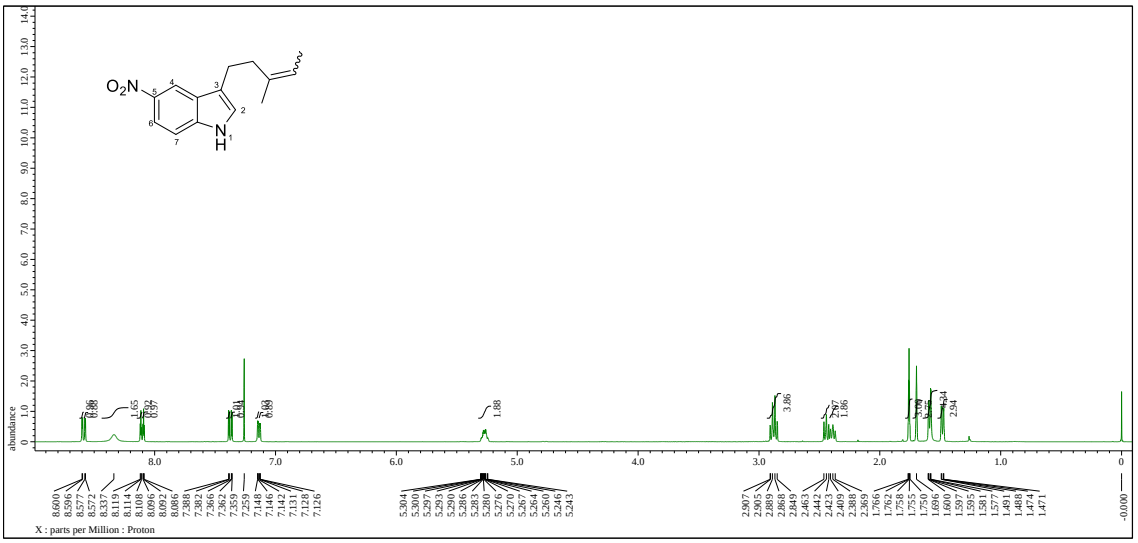
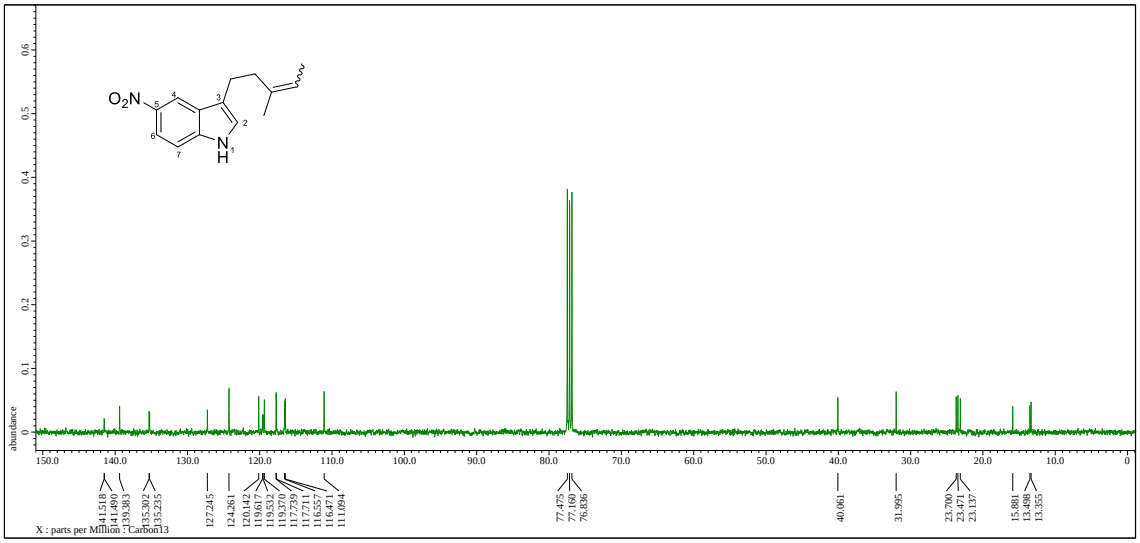


^{1}H NMR spectrum of compound **S'1p** (52:48 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



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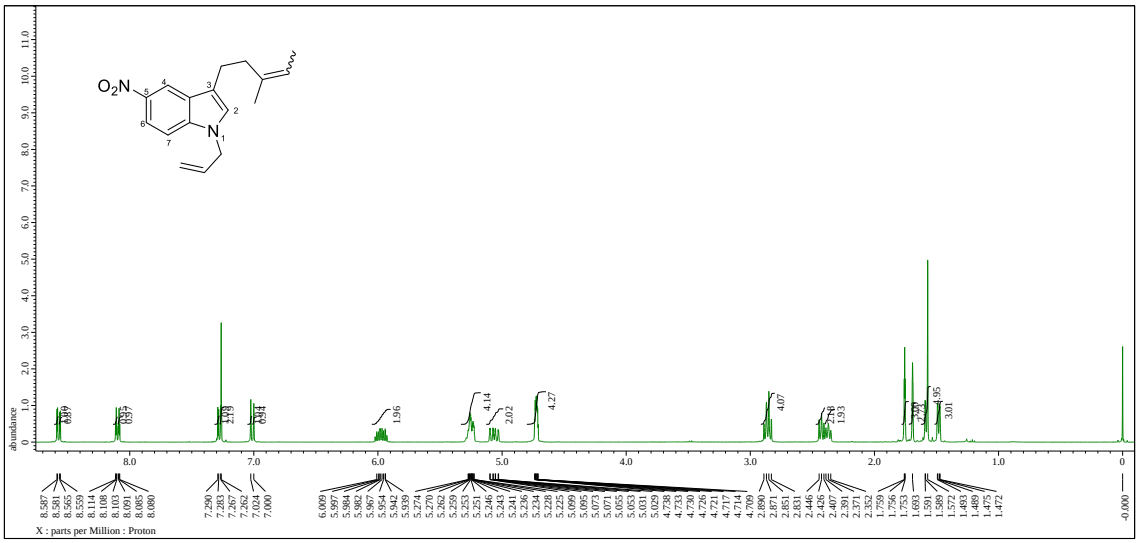
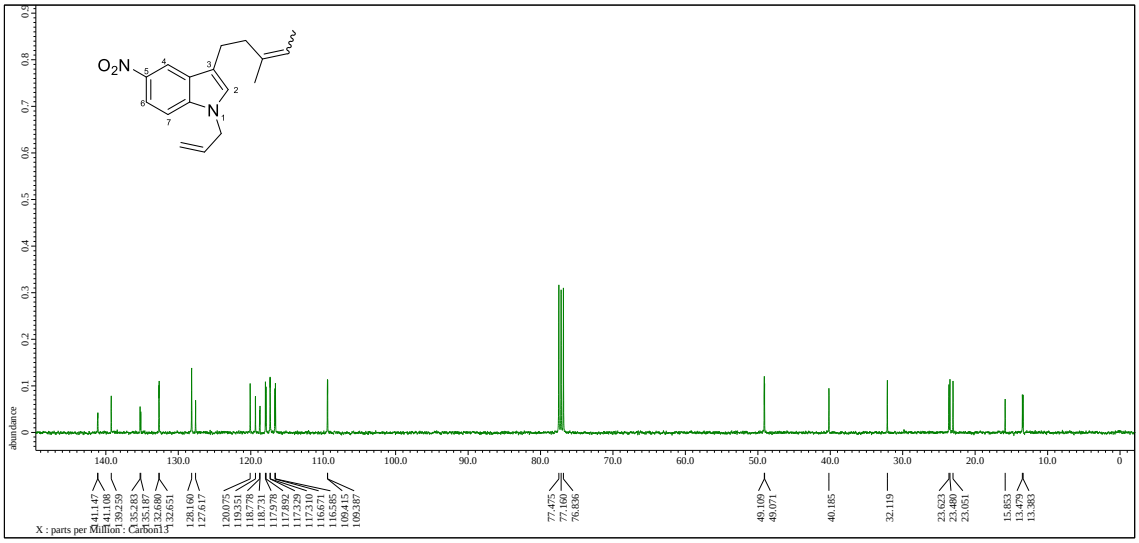
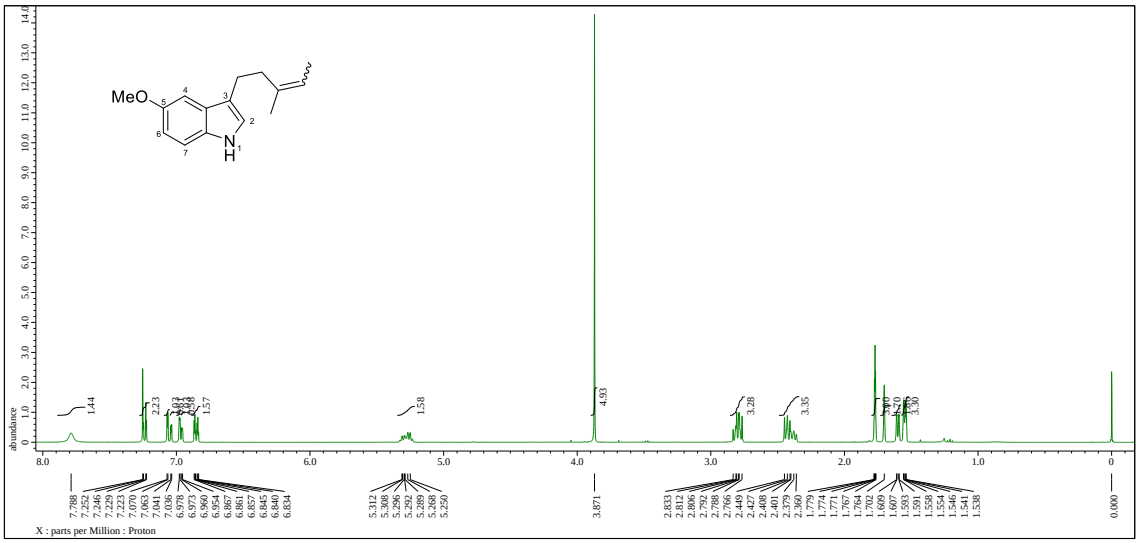


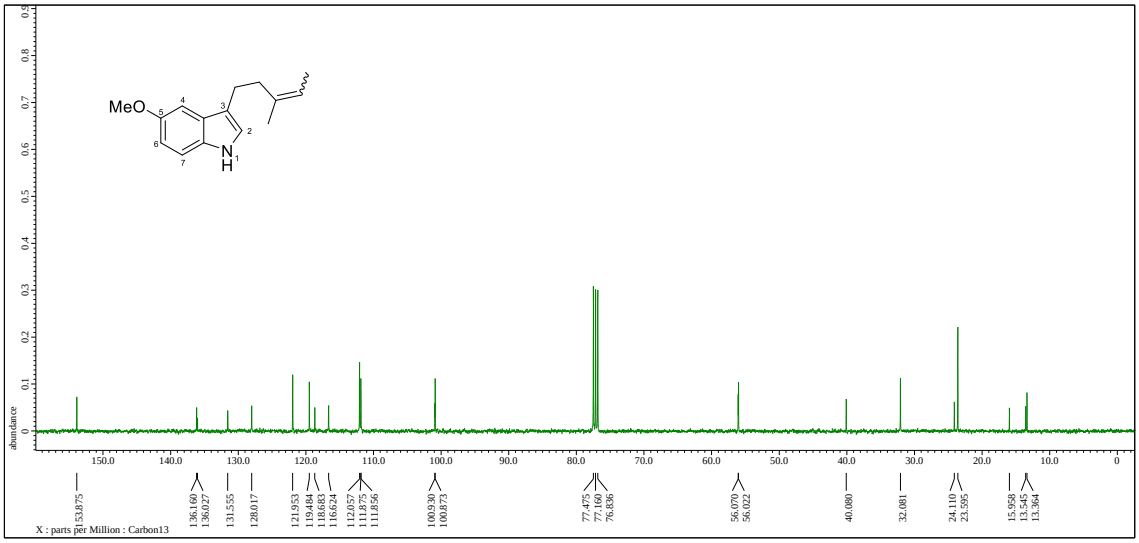
^{1}H NMR spectrum of compound **1p** (53:47 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **1p** (53:47 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **S'1q** (64:36 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



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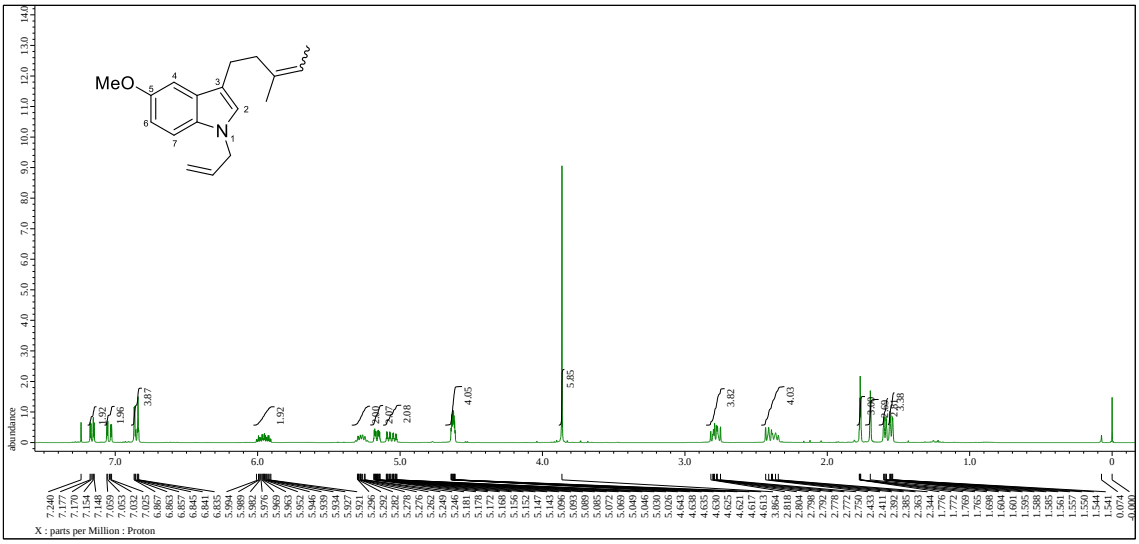
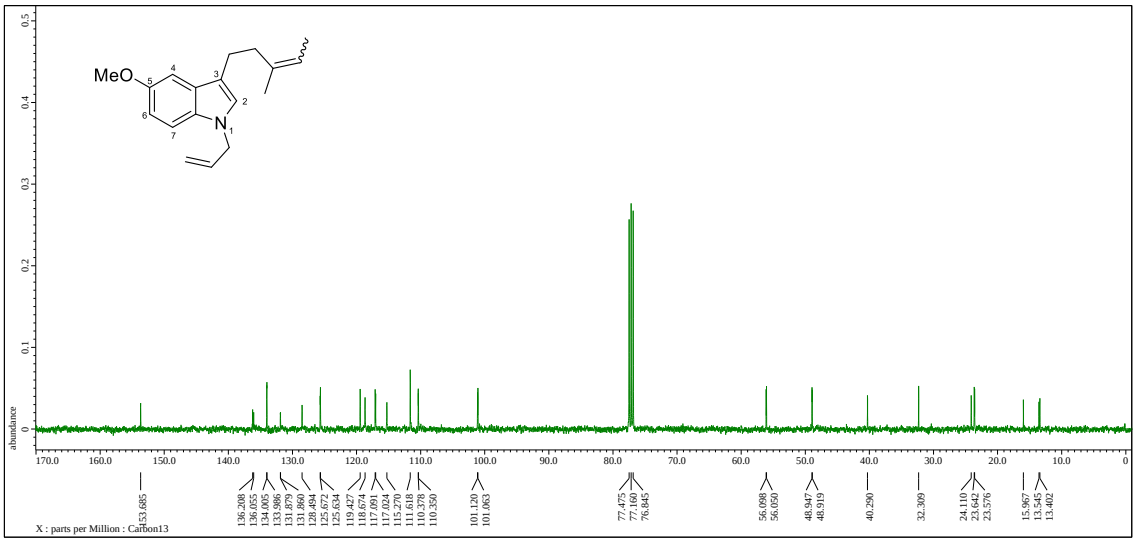
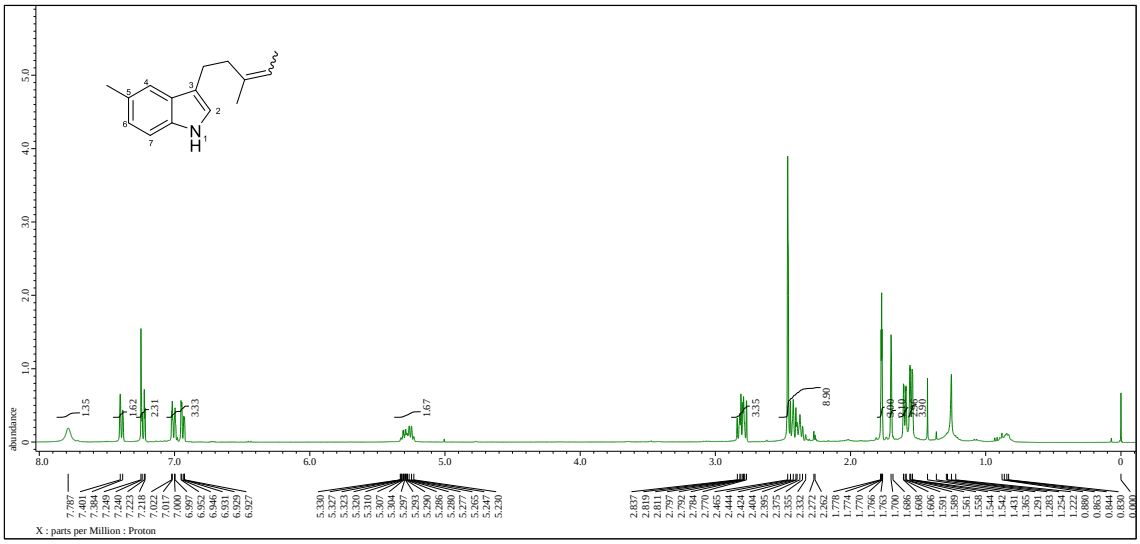


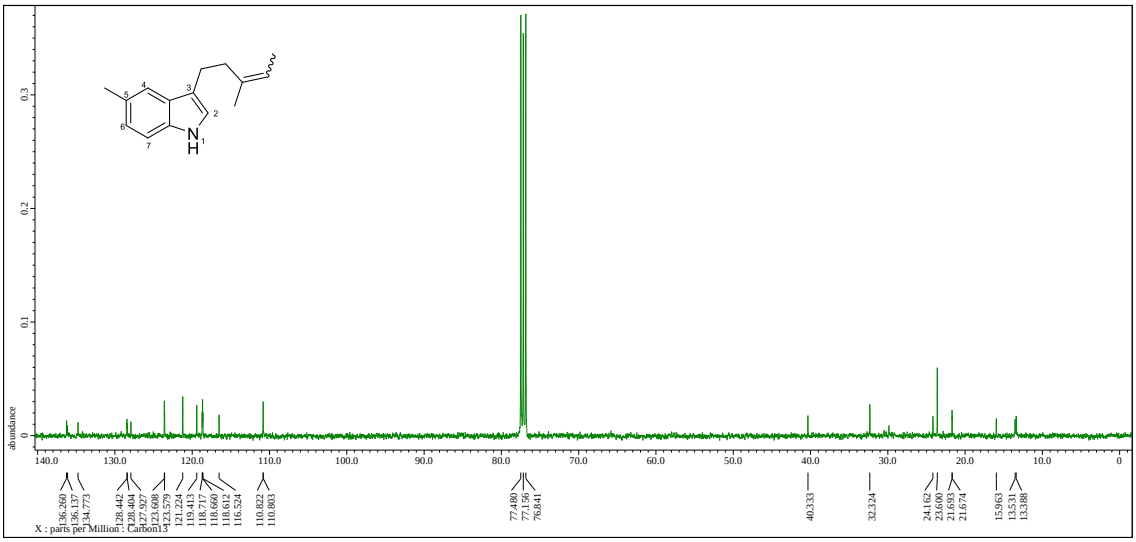
^{1}H NMR spectrum of compound **1q** (53:47 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



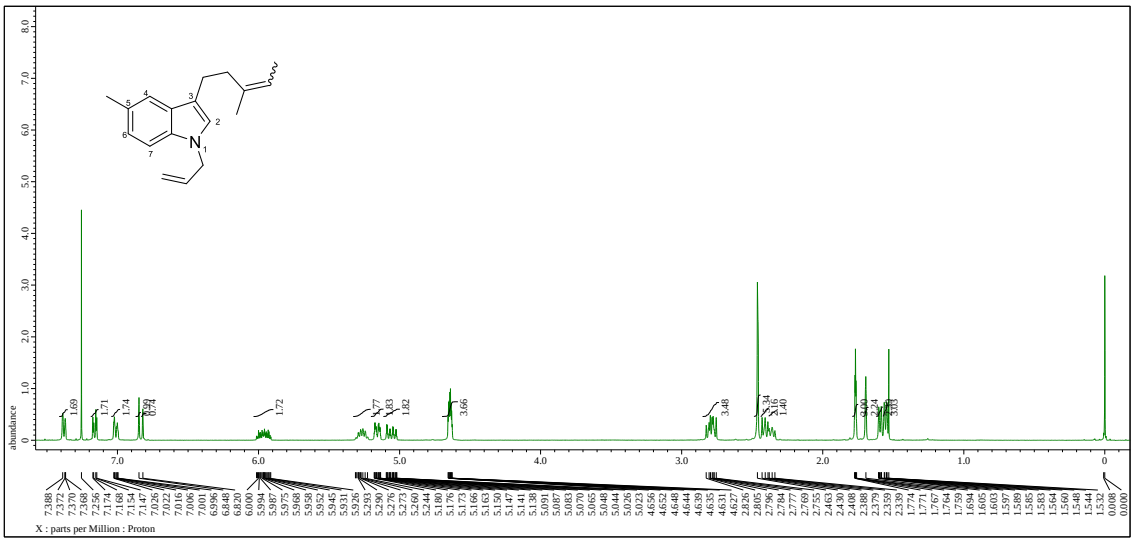
^{13}C NMR spectrum of compound **1q** (53:47 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



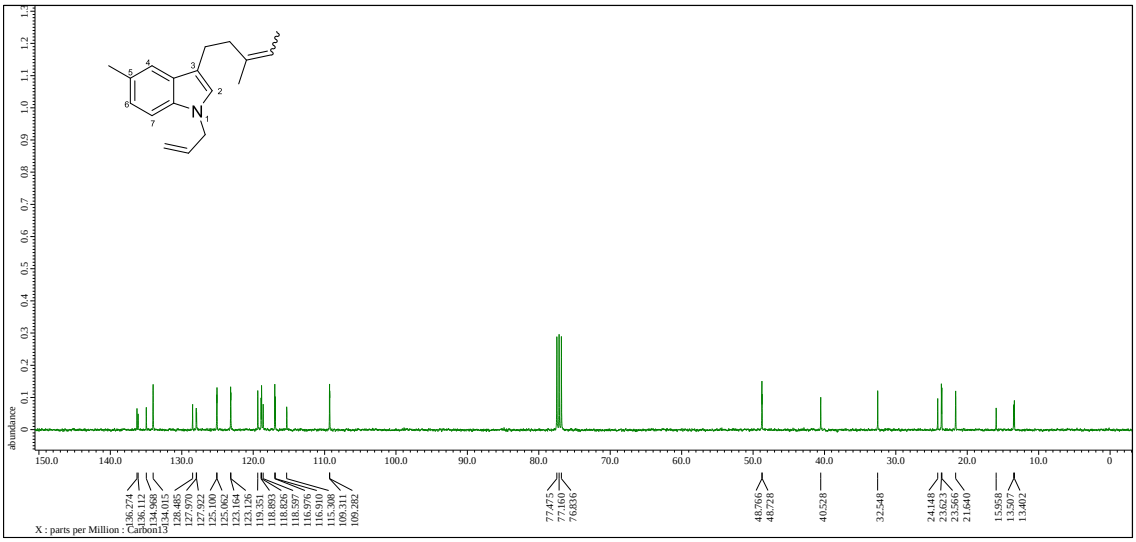
^{1}H NMR spectrum of compound **S'1r** (53:47 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



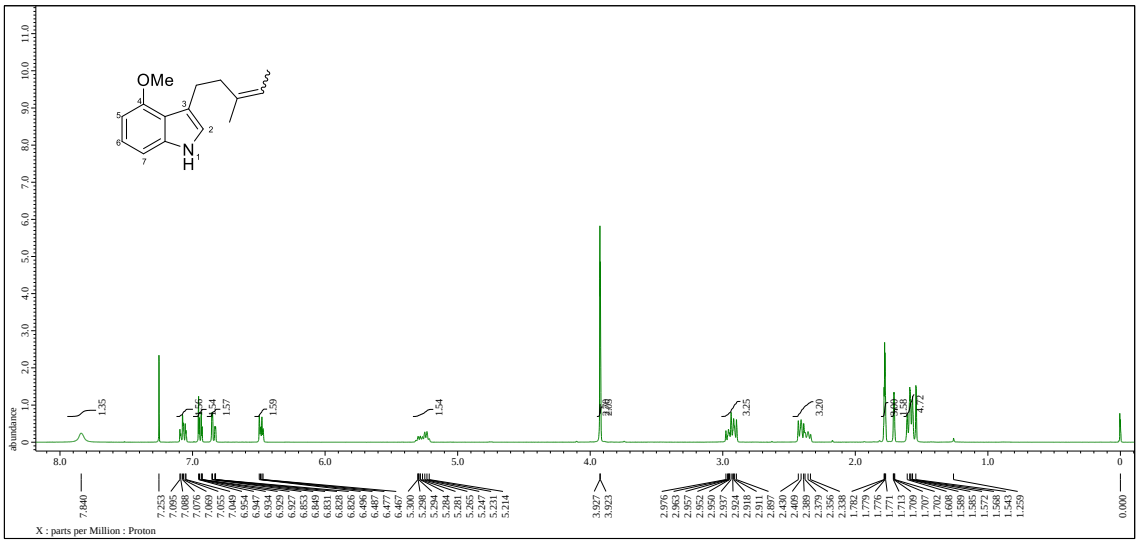
^{13}C NMR spectrum of compound **S'1r** (53:47 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



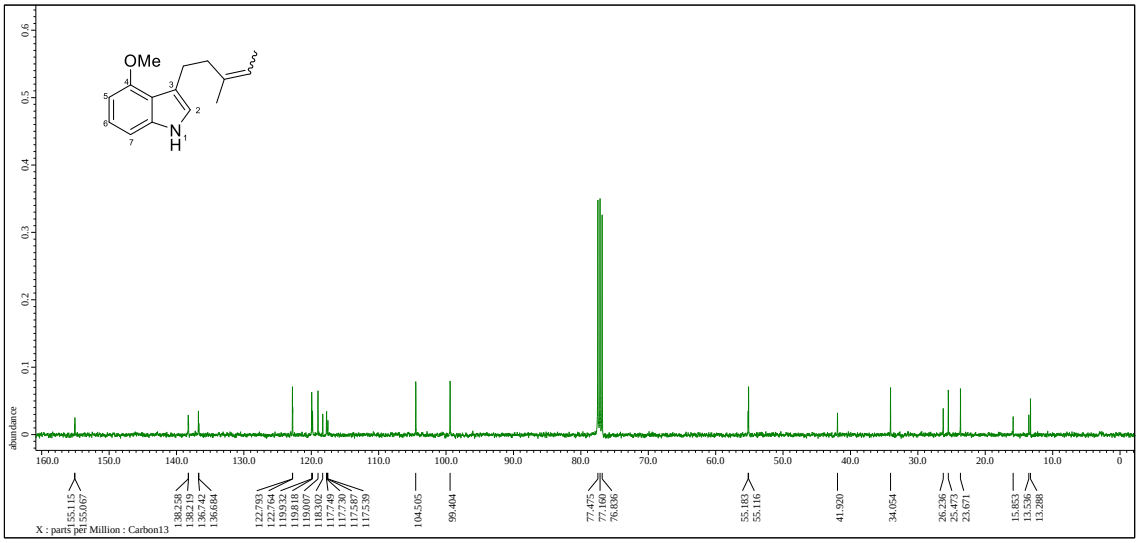
^{1}H NMR spectrum of compound **1r** (53:47 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



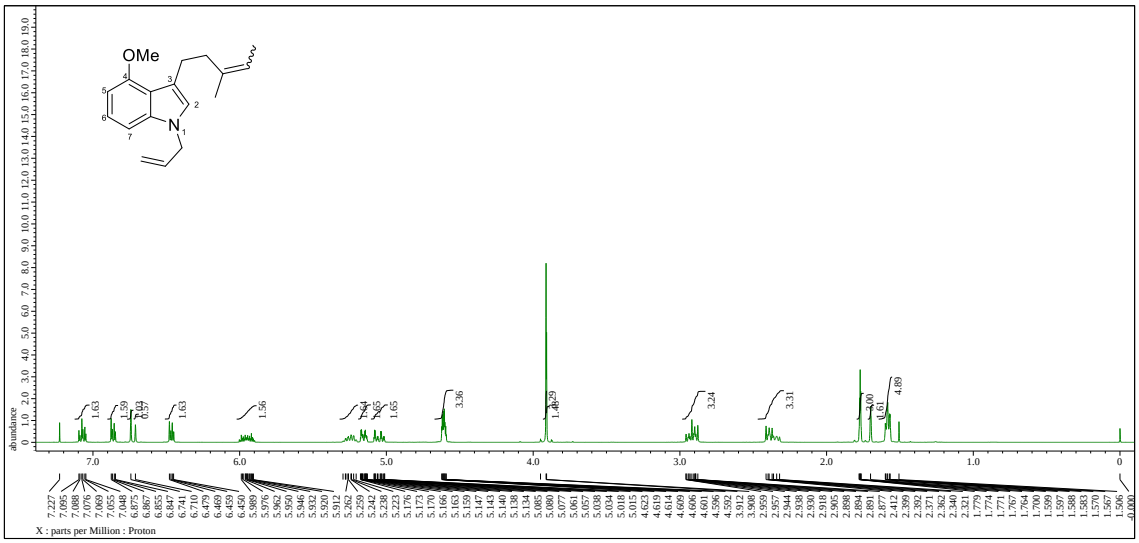
^{13}C NMR spectrum of compound **1r** (53:47 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



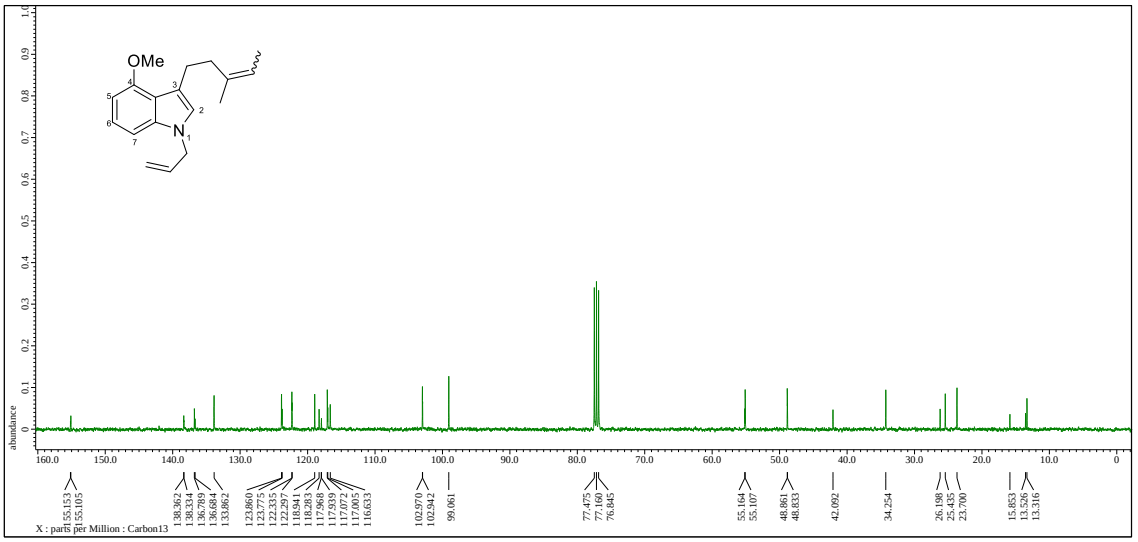
^{1}H NMR spectrum of compound **S'1s** (66:34 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



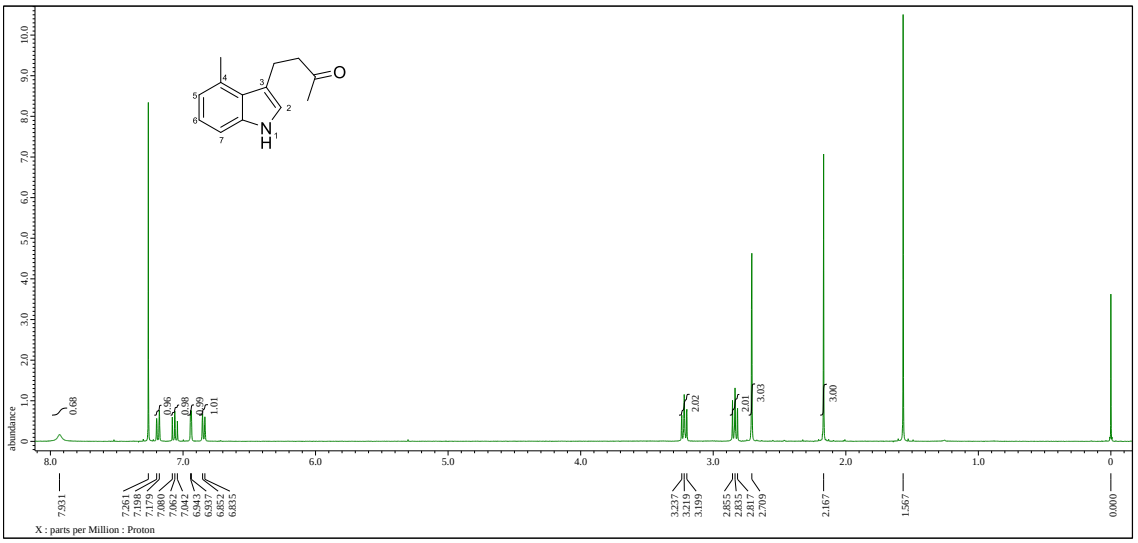
^{13}C NMR spectrum of compound **S'1s** (66:34 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



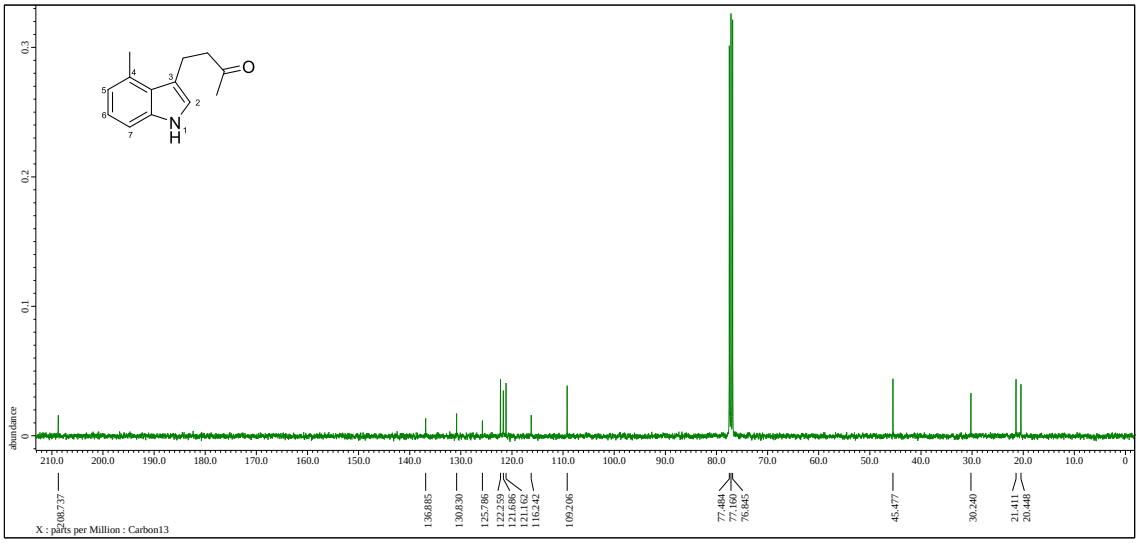
^{1}H NMR spectrum of compound **1s** (65:35 mixture of *Z*/*E*-olefin isomers) (400 MHz, $CDCl_3$)



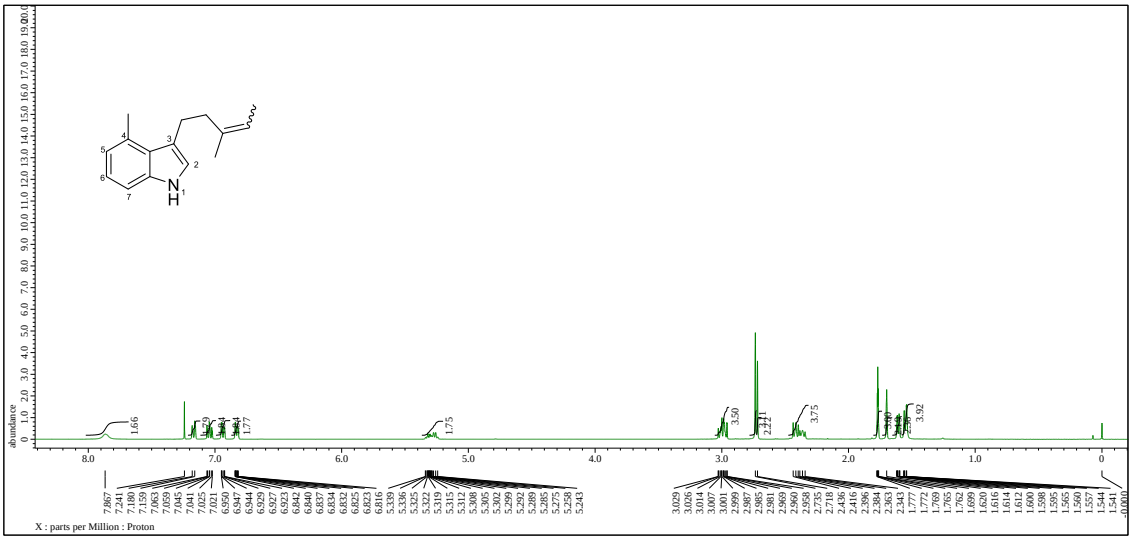
^{13}C NMR spectrum of compound **1s** (65:35 mixture of *Z*/*E*-olefin isomers) (100 MHz, $CDCl_3$)



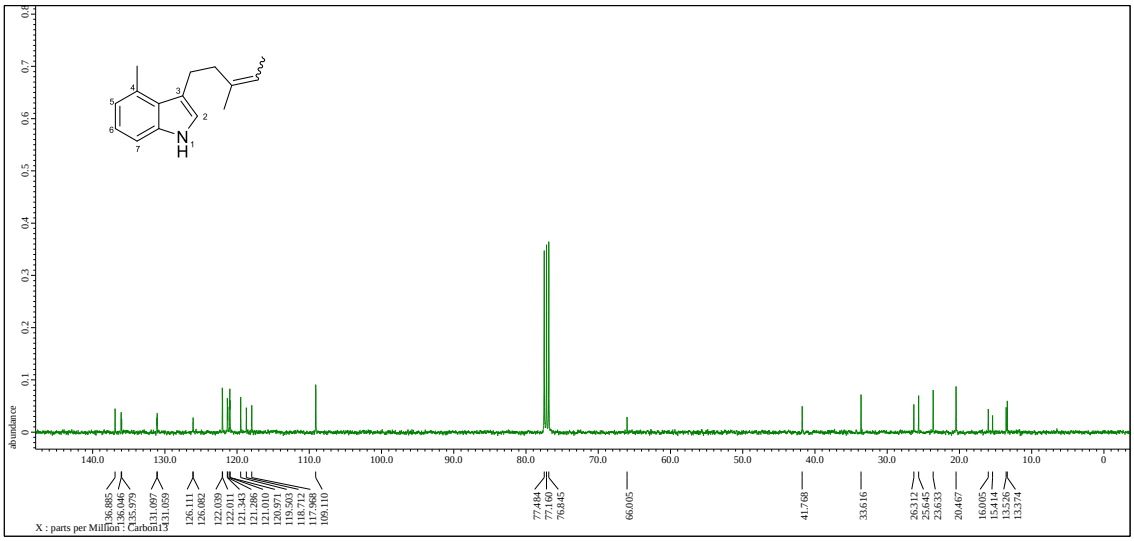
^{1}H NMR spectrum of compound **S1t** (400 MHz, $CDCl_3$)



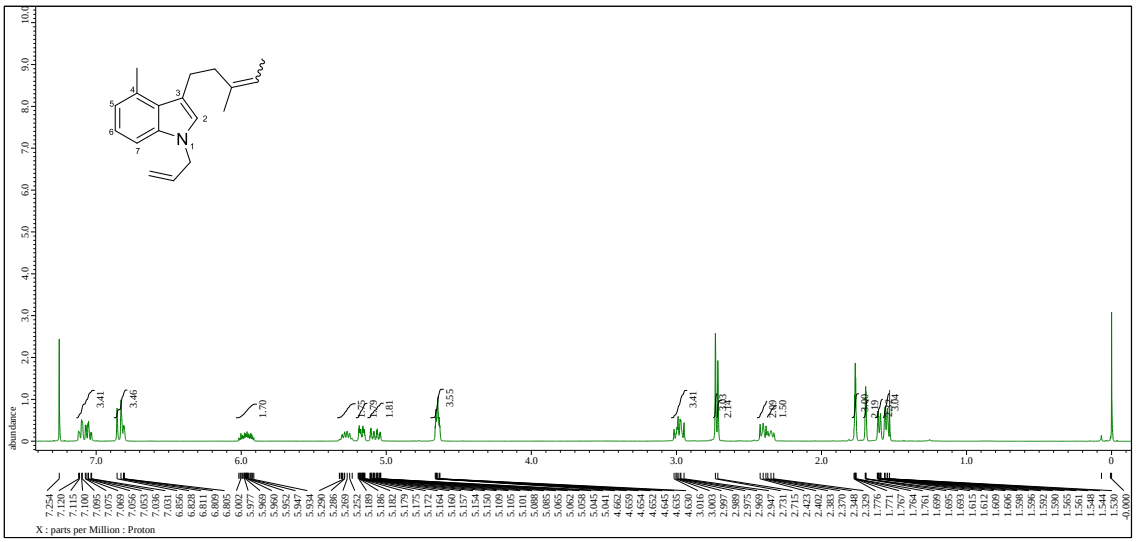
^{13}C NMR spectrum of compound **S1t** (100 MHz, $CDCl_3$)



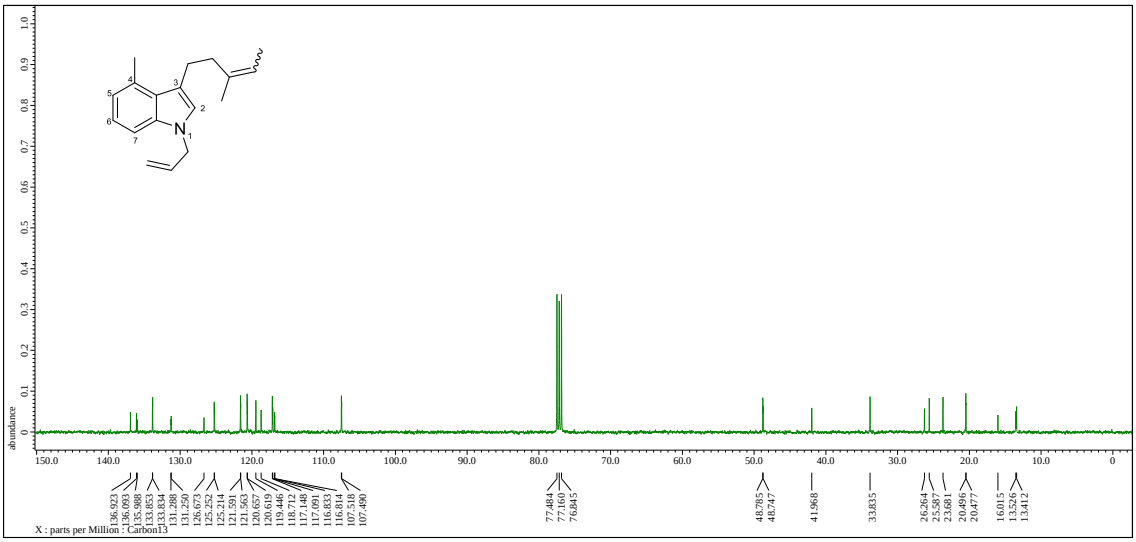
^{1}H NMR spectrum of compound **S'1t** (58:42 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



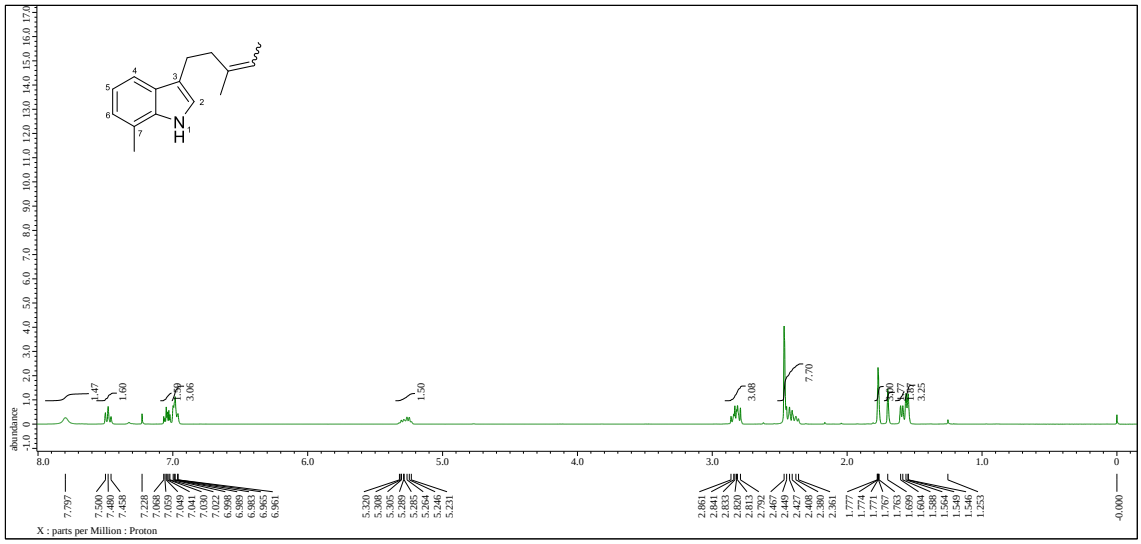
^{13}C NMR spectrum of compound **S'1t** (58:42 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



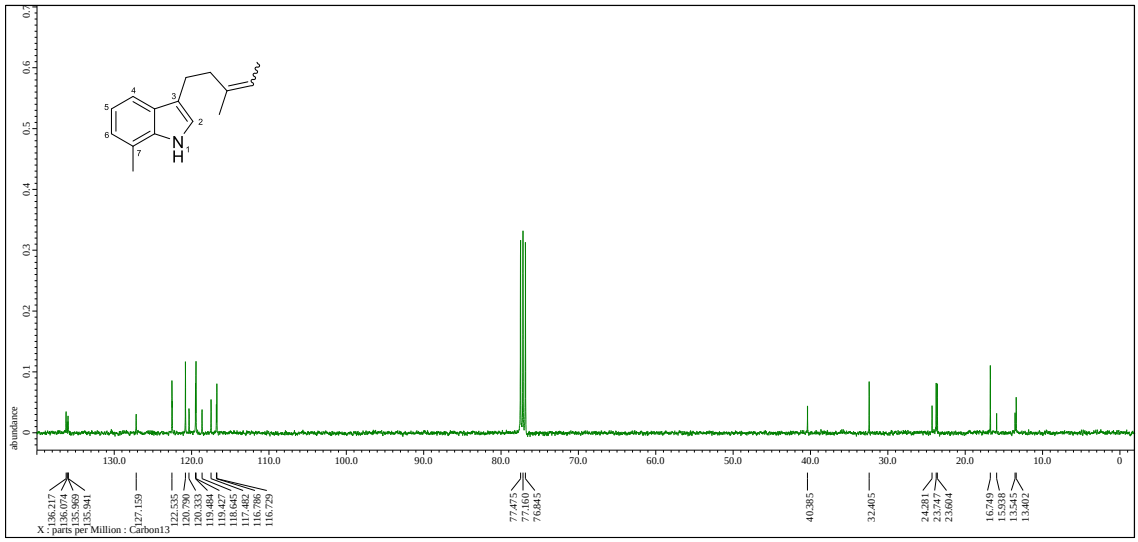
^{1}H NMR spectrum of compound **1t** (59:42 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



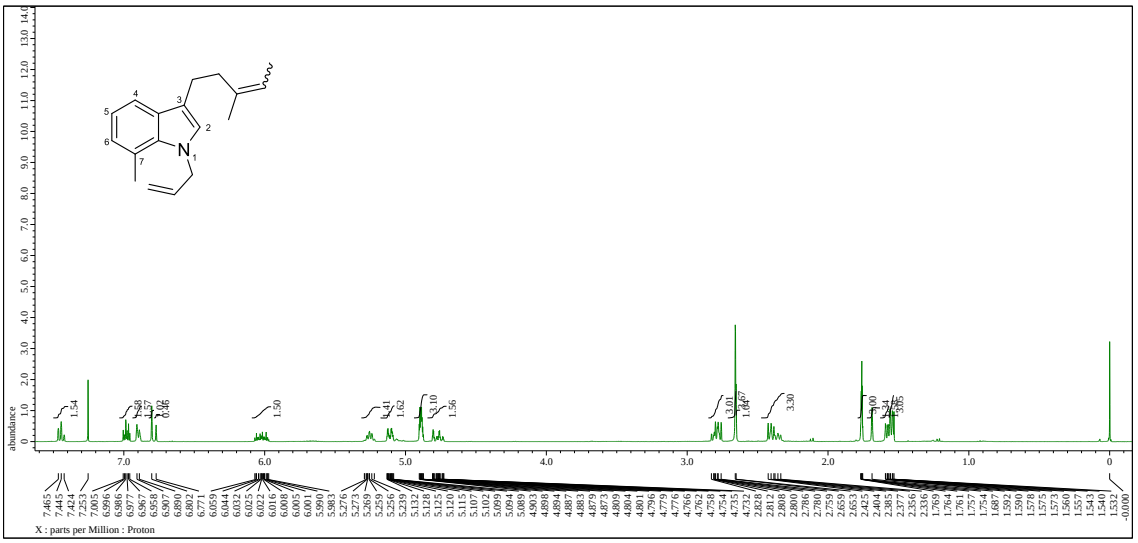
^{13}C NMR spectrum of compound **1t** (59:42 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



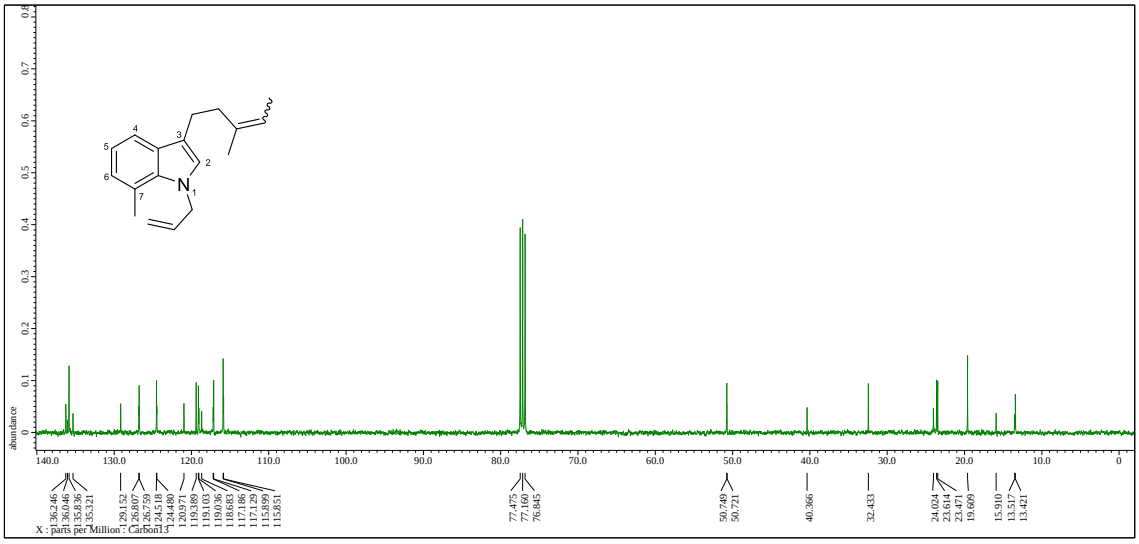
^{1}H NMR spectrum of compound **S'1u** (63:37 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



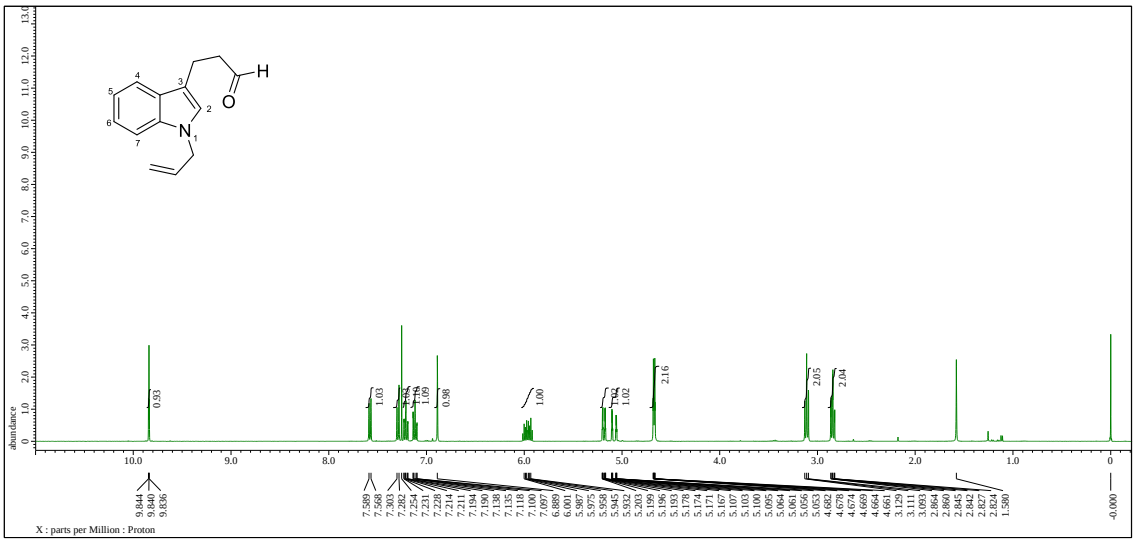
^{13}C NMR spectrum of compound **S'1u** (63:37 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



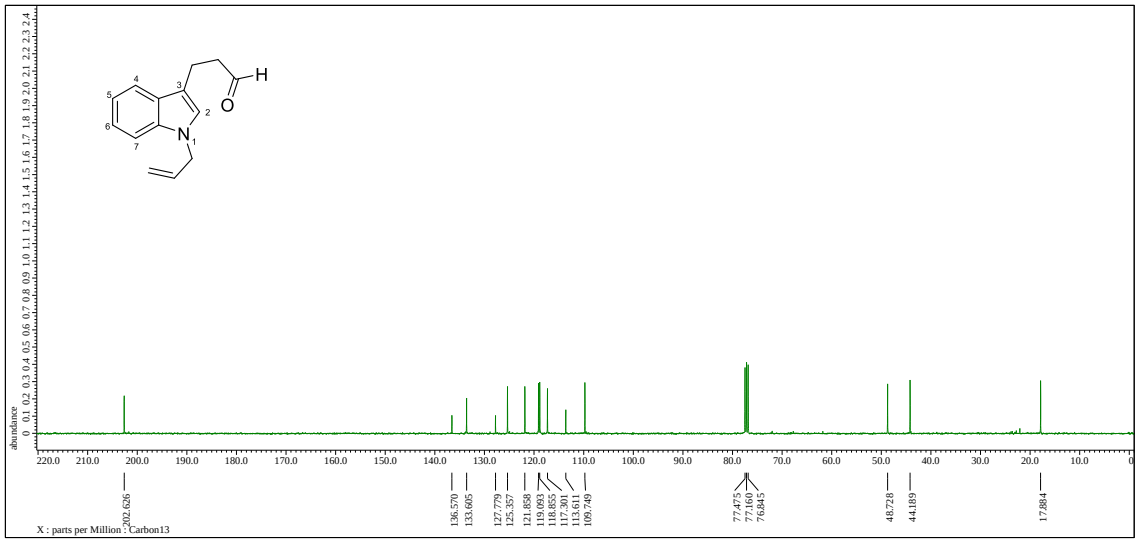
^{1}H NMR spectrum of compound **1u** (69:31 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



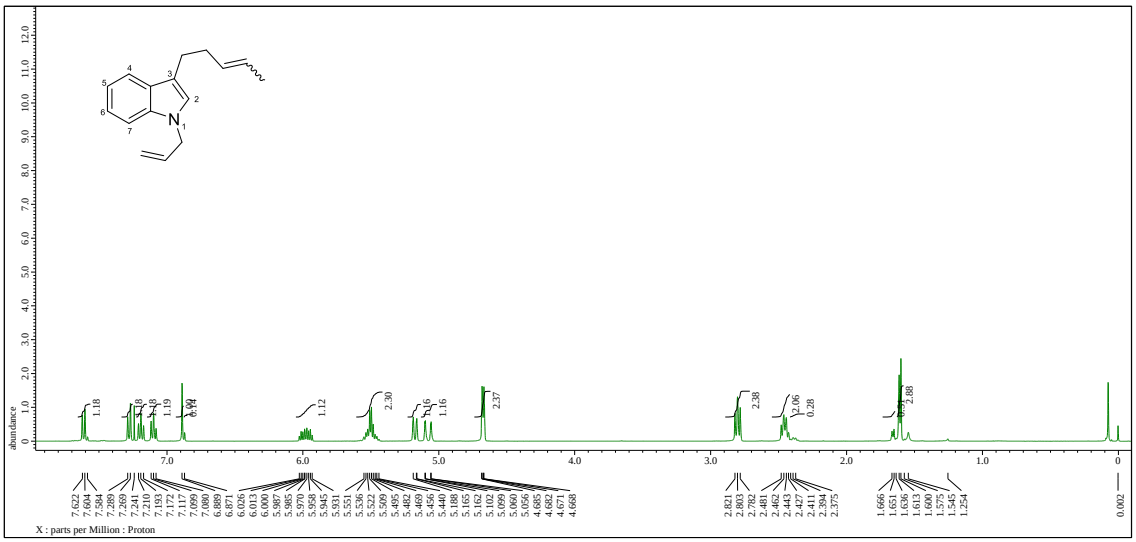
^{13}C NMR spectrum of compound **1u** (69:31 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



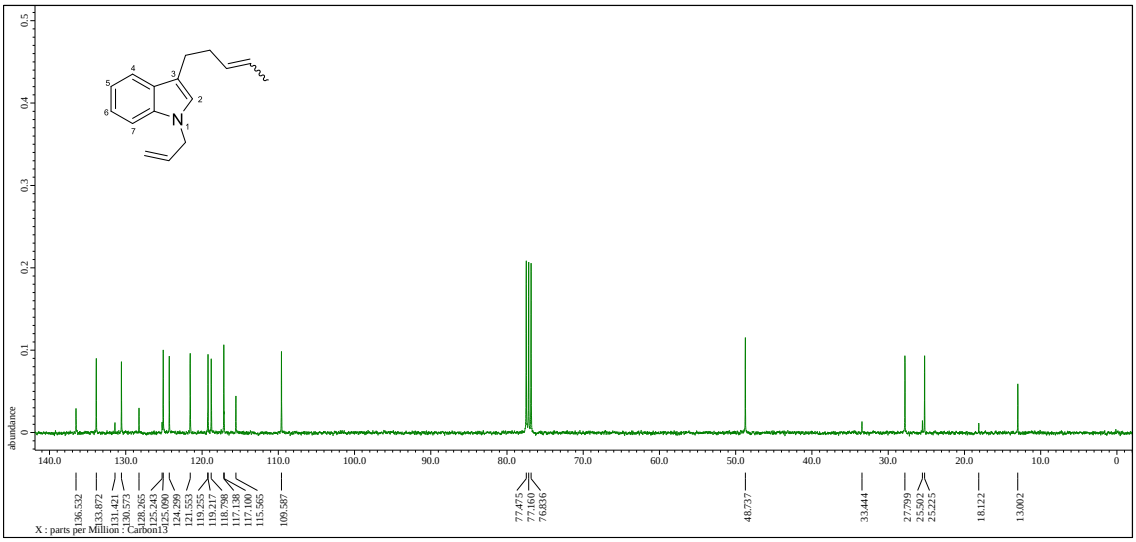
^{1}H NMR spectrum of compound **S'1v** (400 MHz, $CDCl_3$)



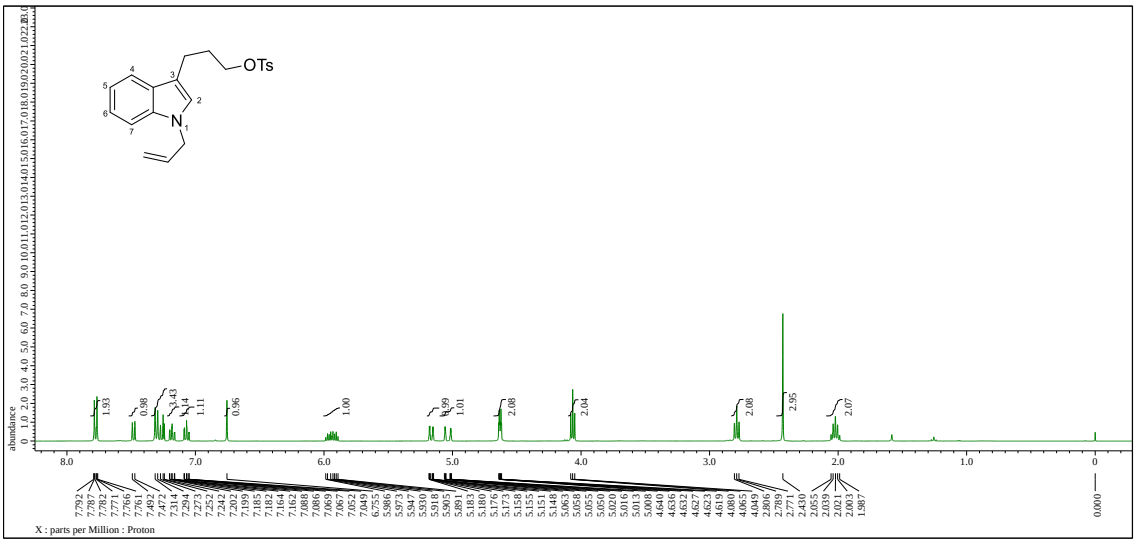
^{13}C NMR spectrum of compound **S'1v** (100 MHz, $CDCl_3$)



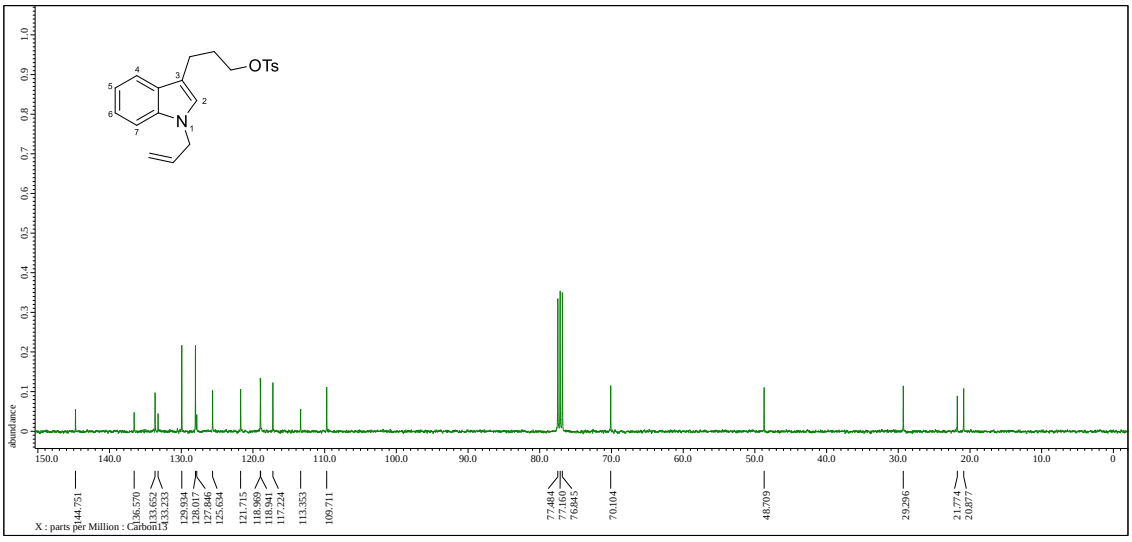
^{1}H NMR spectrum of compound **1v** (88:12 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



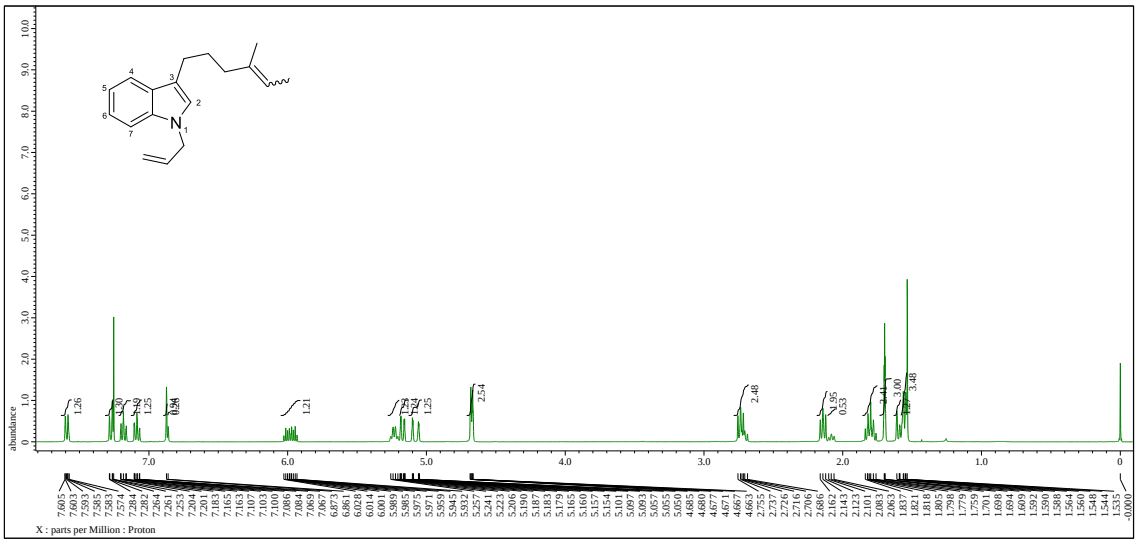
^{13}C NMR spectrum of compound **1v** (88:12 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



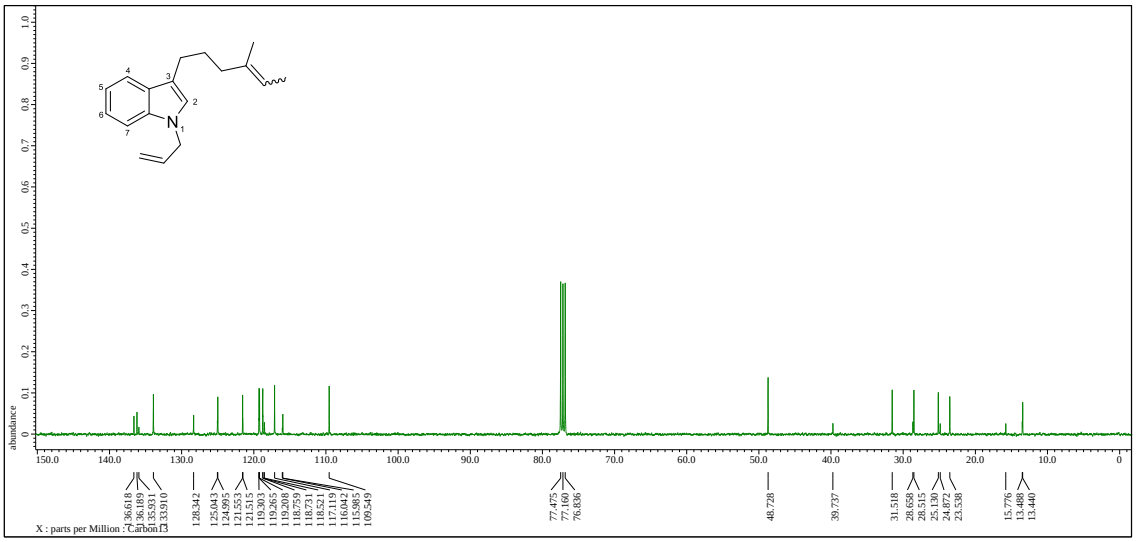
^{1}H NMR spectrum of compound **S'1v-OTs** (400 MHz, $CDCl_3$)



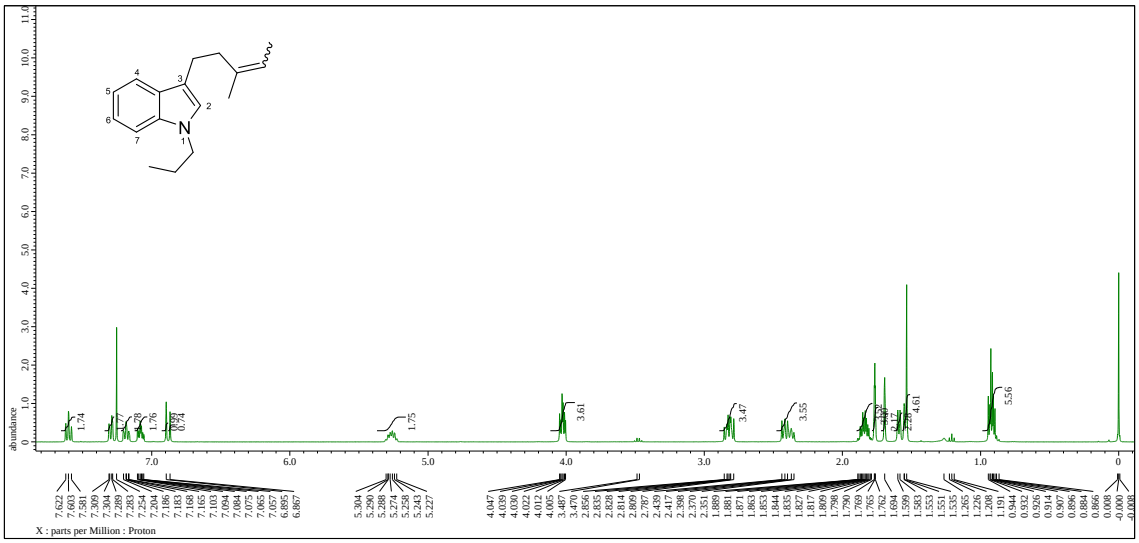
^{13}C NMR spectrum of compound **S'1v-OTs** (100 MHz, $CDCl_3$)



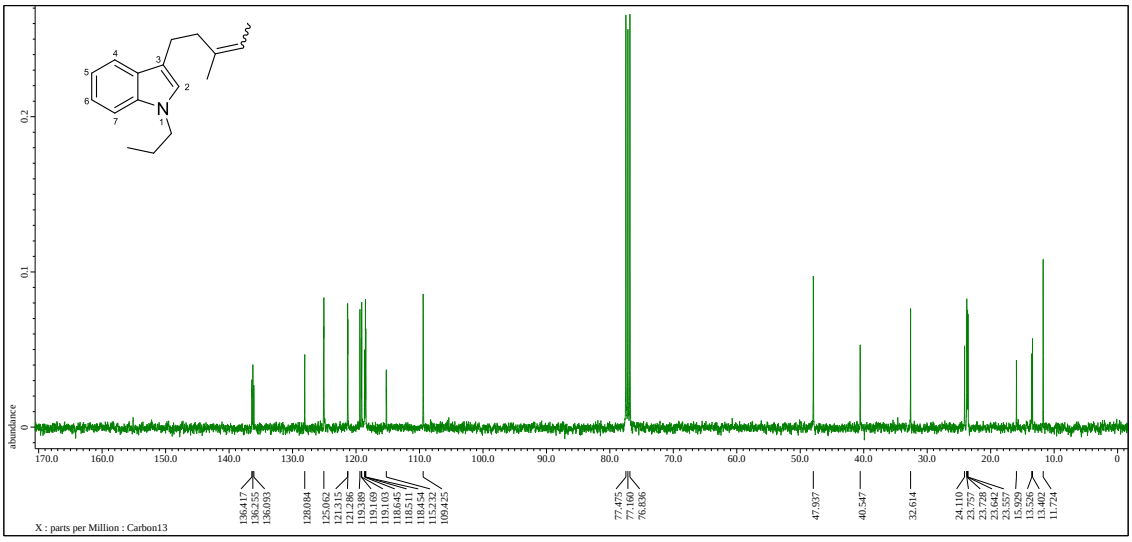
^{1}H NMR spectrum of compound **1w** (78:22 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



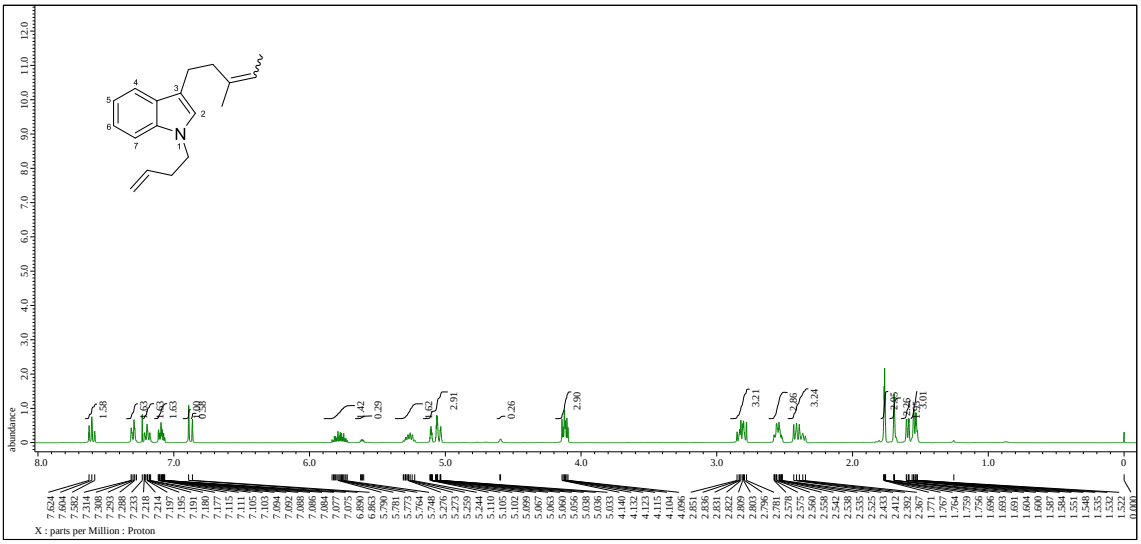
^{13}C NMR spectrum of compound **1w** (79:21 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



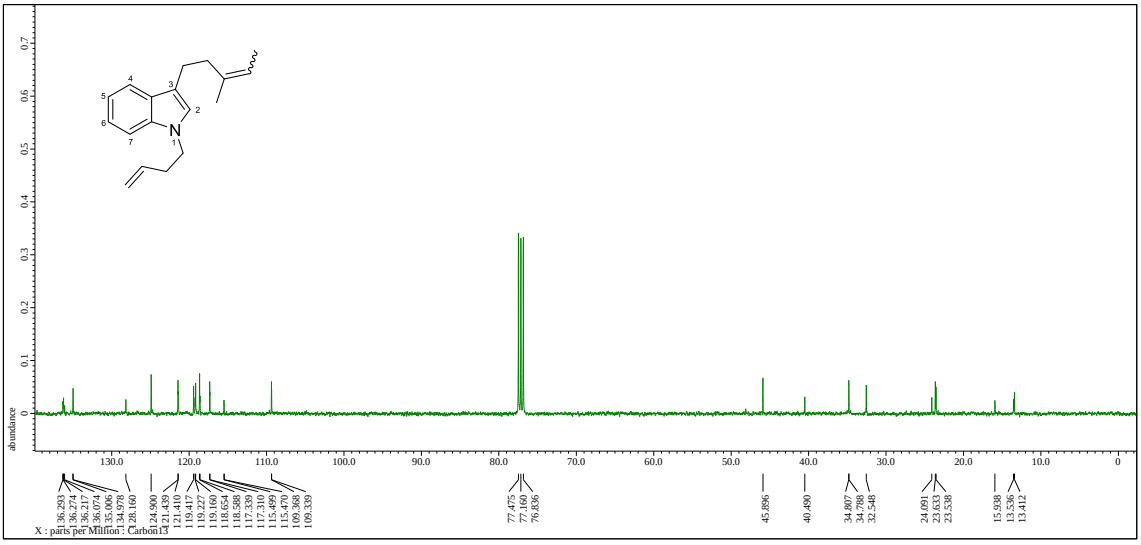
^{1}H NMR spectrum of compound **1x** (57:43 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



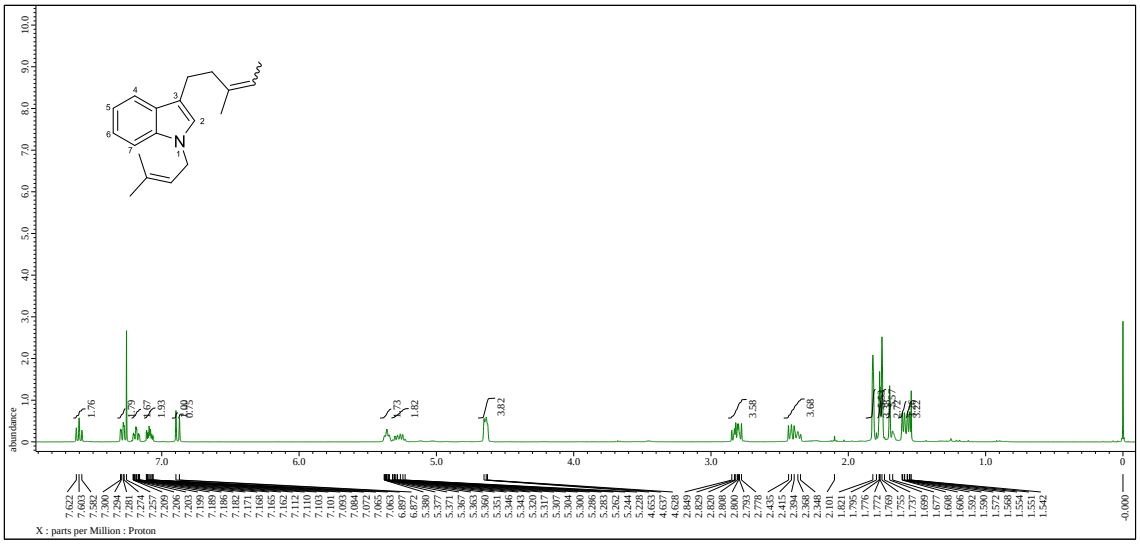
^{13}C NMR spectrum of compound **1x** (57:43 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)



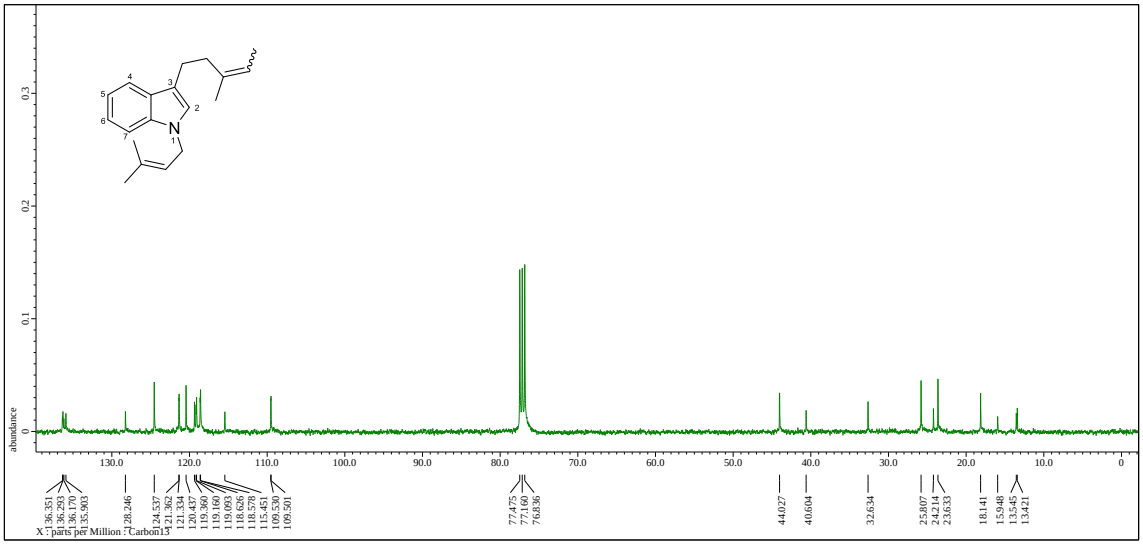
^{1}H NMR spectrum of compound **1y** (63:37 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **1y** (63:37 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)

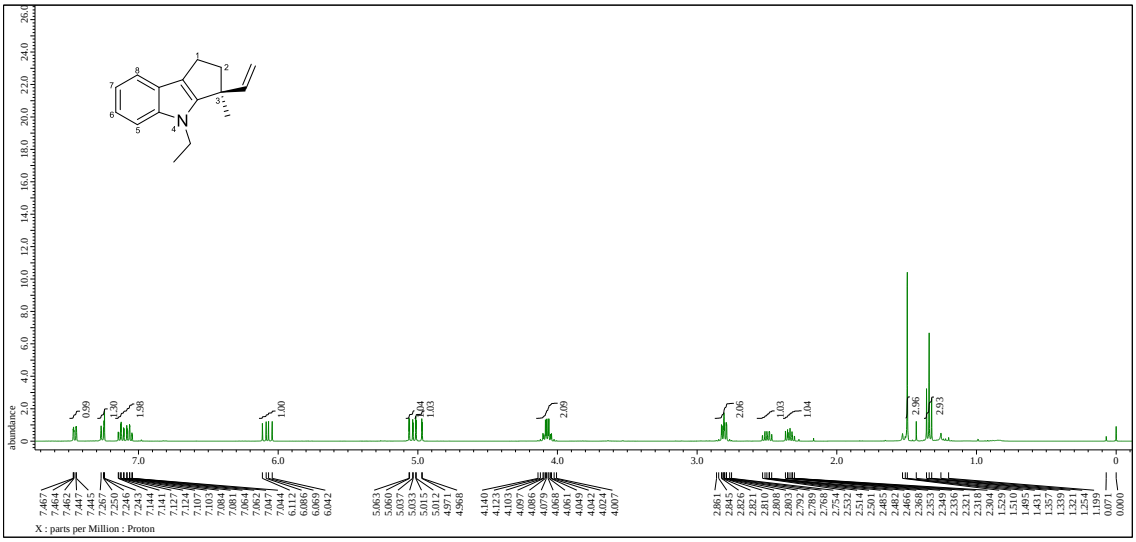


^{1}H NMR spectrum of compound **1z** (57:43 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)

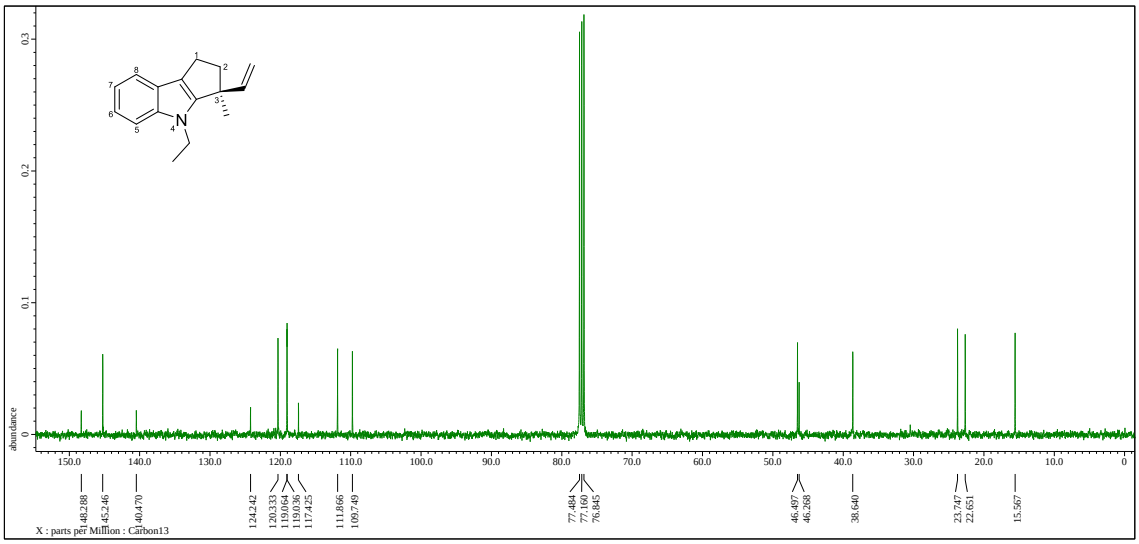


^{13}C NMR spectrum of compound **1z** (57:43 mixture of *Z/E*-olefin isomers) (100 MHz, $CDCl_3$)

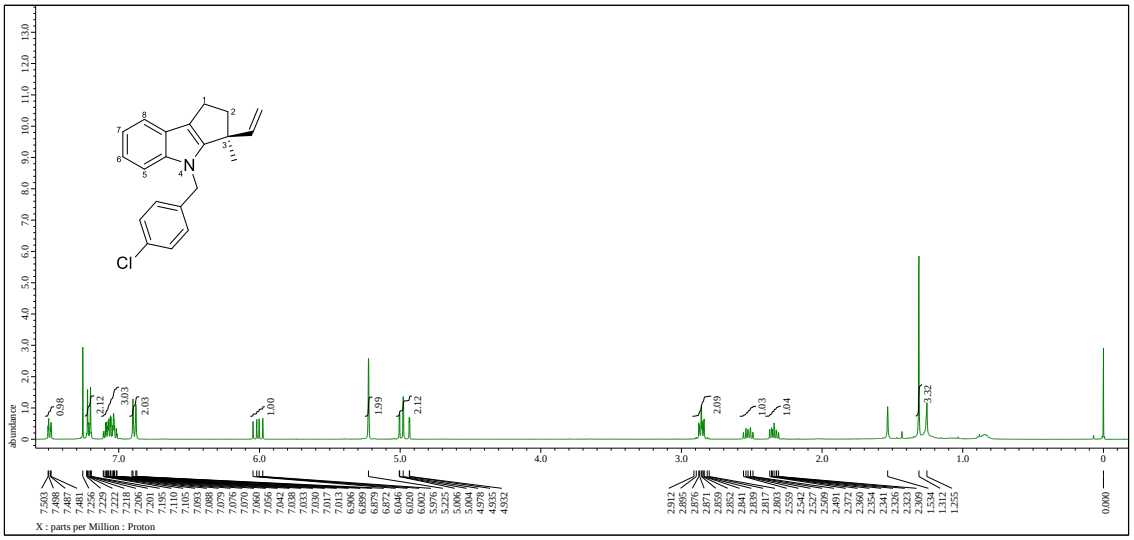
12.2. Products



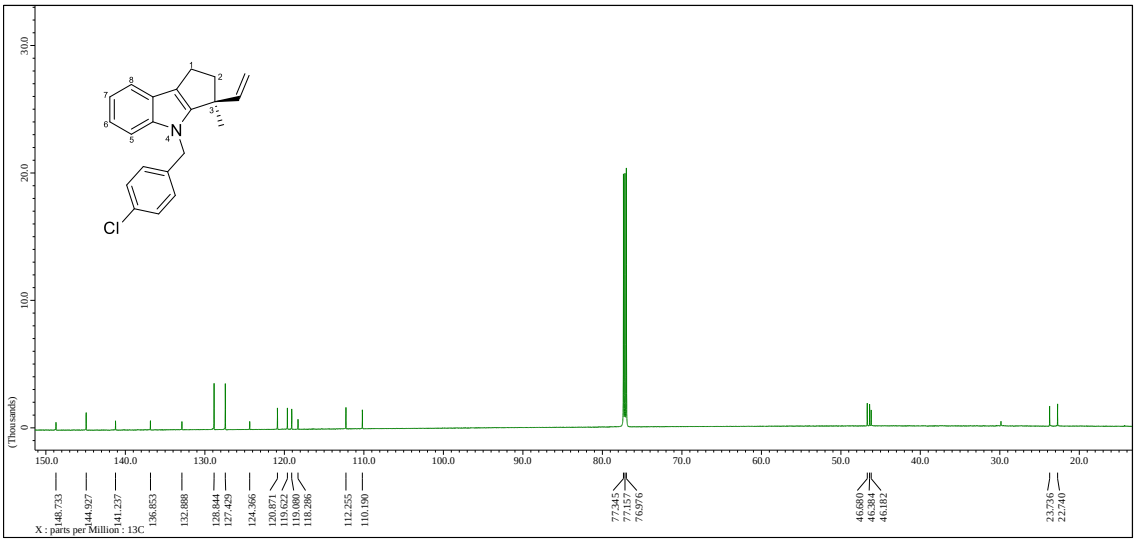
^{1}H NMR spectrum of compound **2b** (400 MHz, $CDCl_3$)



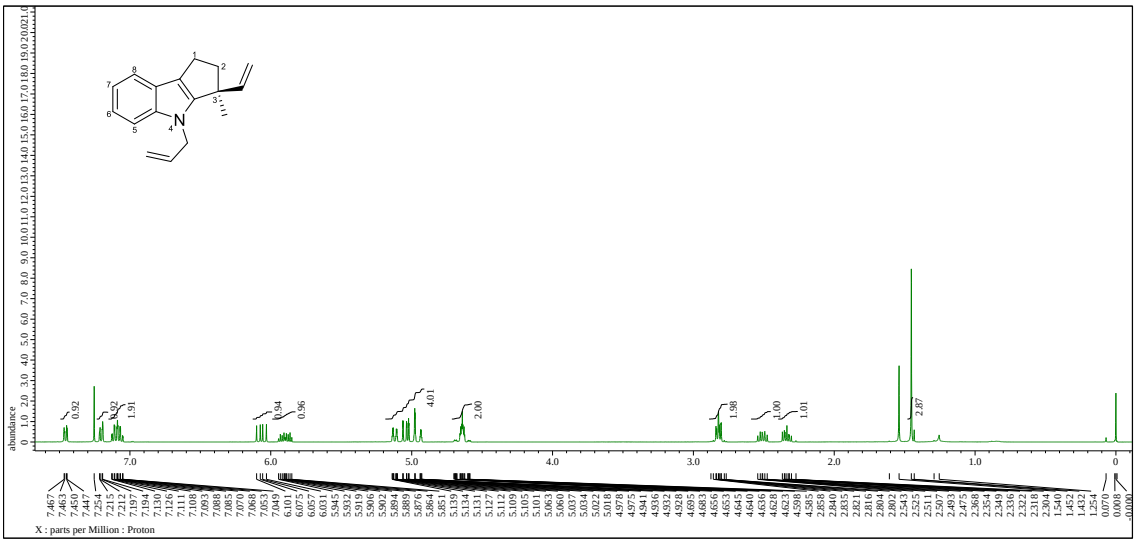
^{13}C NMR spectrum of compound **2b** (100 MHz, $CDCl_3$)



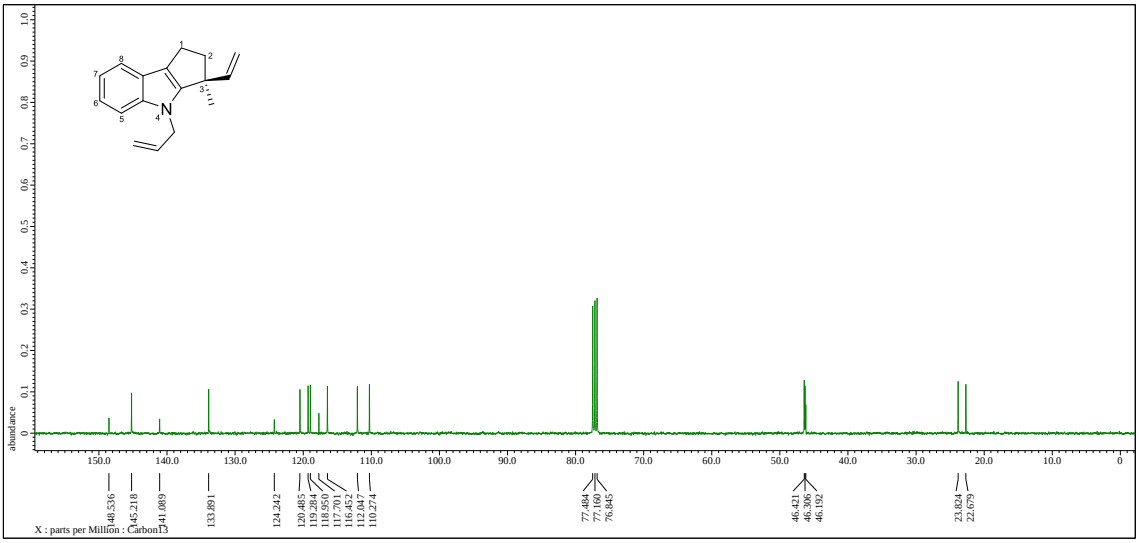
^{1}H NMR spectrum of compound **2d** (400 MHz, $CDCl_3$)



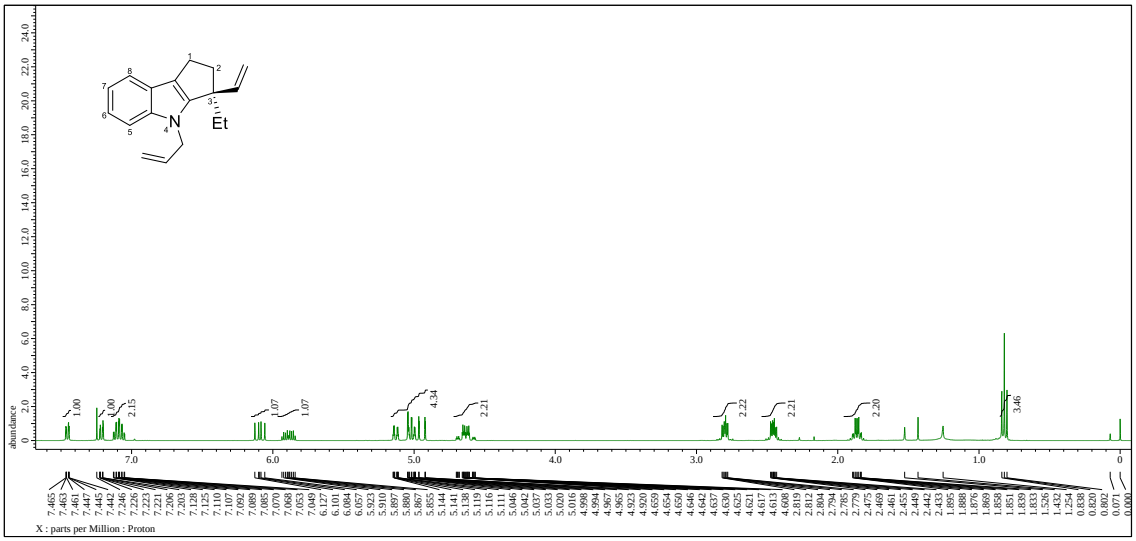
^{13}C NMR spectrum of compound **2d** (170 MHz, $CDCl_3$)



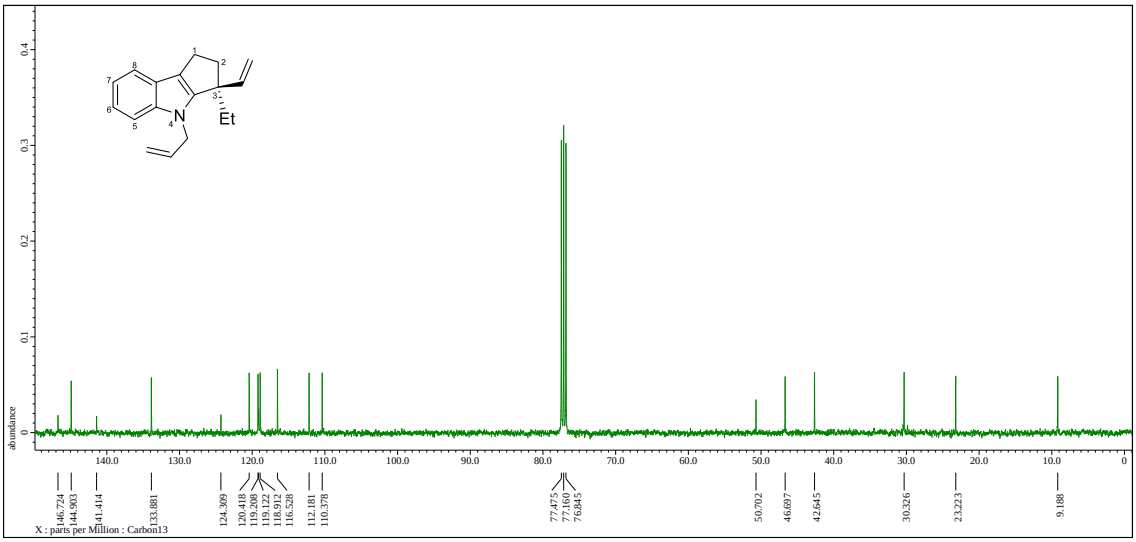
^{1}H NMR spectrum of compound **2k** (400 MHz, $CDCl_3$)



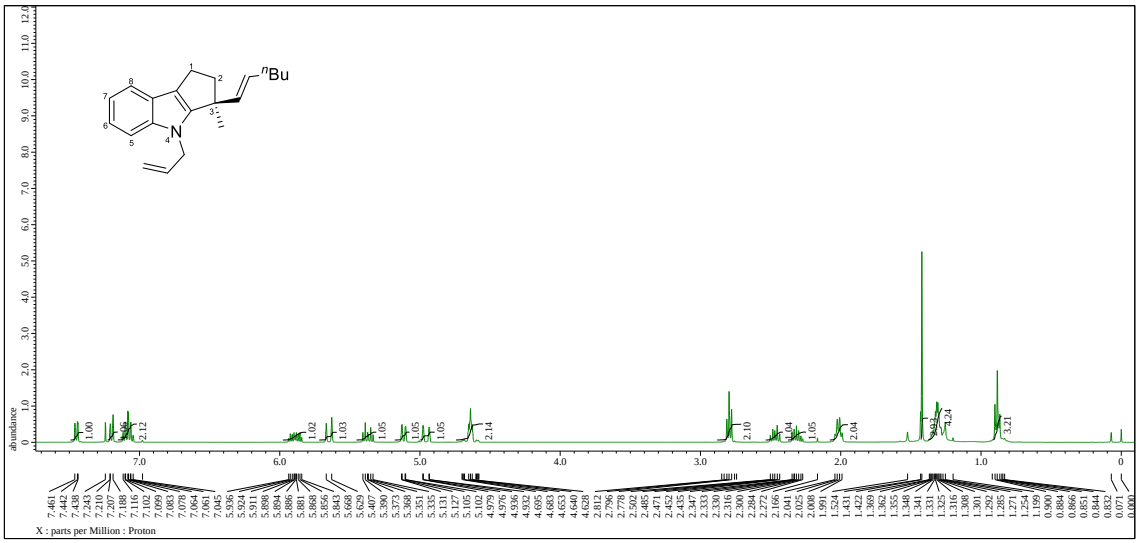
^{13}C NMR spectrum of compound **2k** (100 MHz, $CDCl_3$)



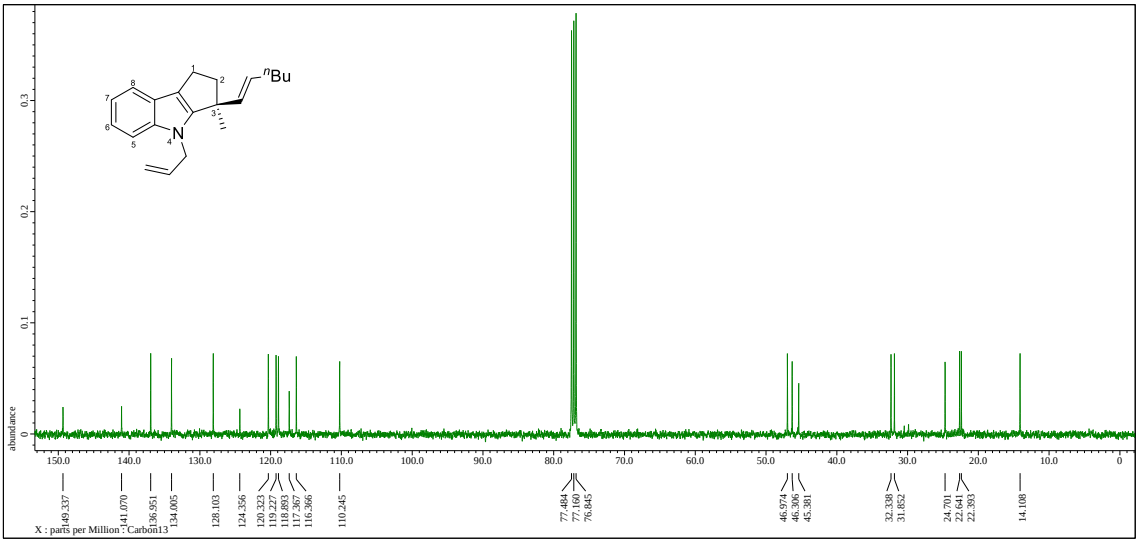
^{1}H NMR spectrum of compound **2l** (400 MHz, $CDCl_3$)



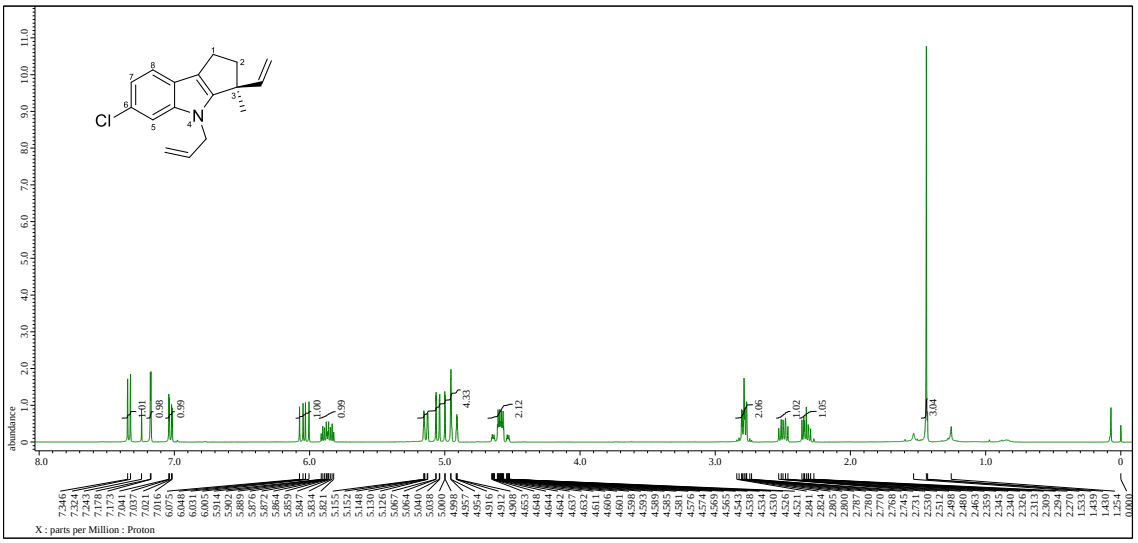
^{13}C NMR spectrum of compound **2l** (100 MHz, $CDCl_3$)



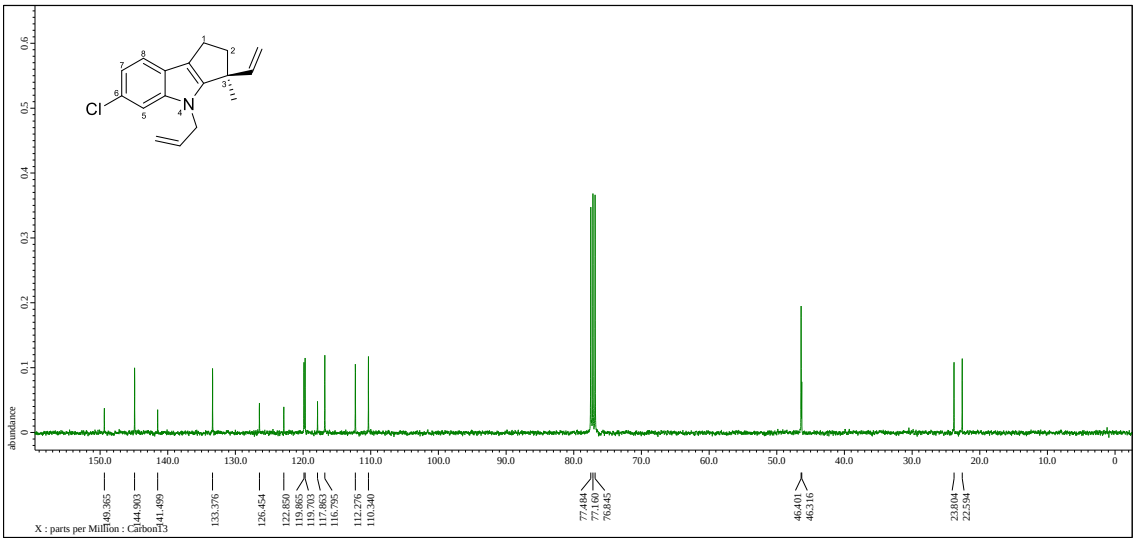
^{1}H NMR spectrum of compound *E*-**2m** (400 MHz, $CDCl_3$)



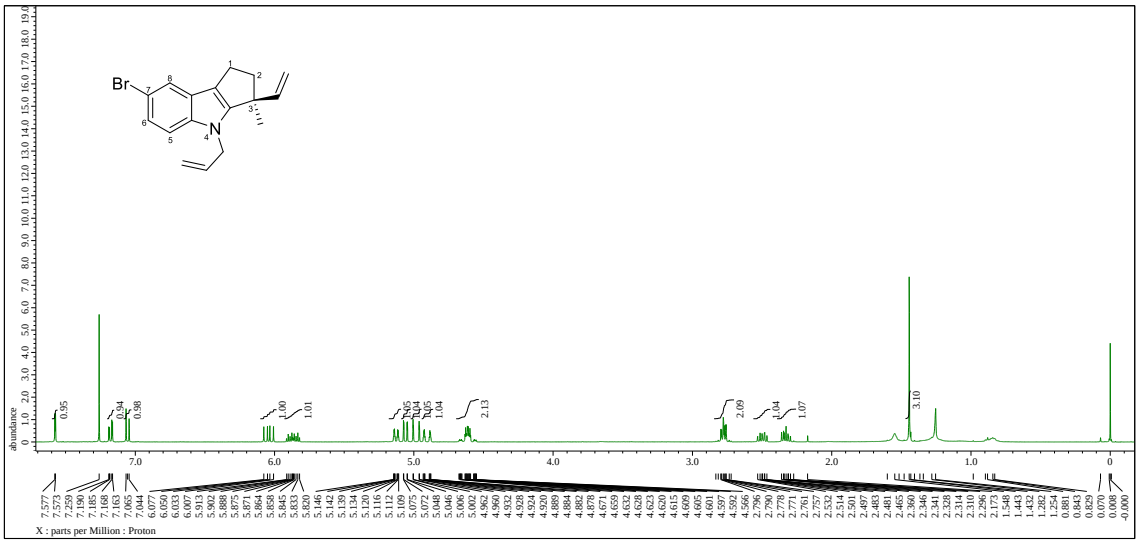
^{13}C NMR spectrum of compound *E*-**2m** (100 MHz, $CDCl_3$)



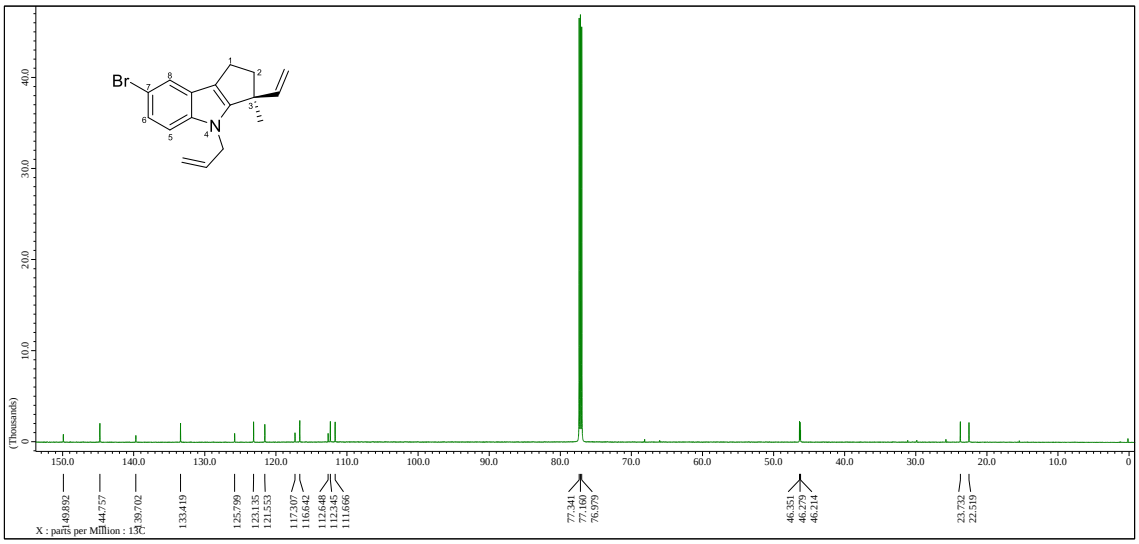
^{1}H NMR spectrum of compound **2n** (400 MHz, $CDCl_3$)



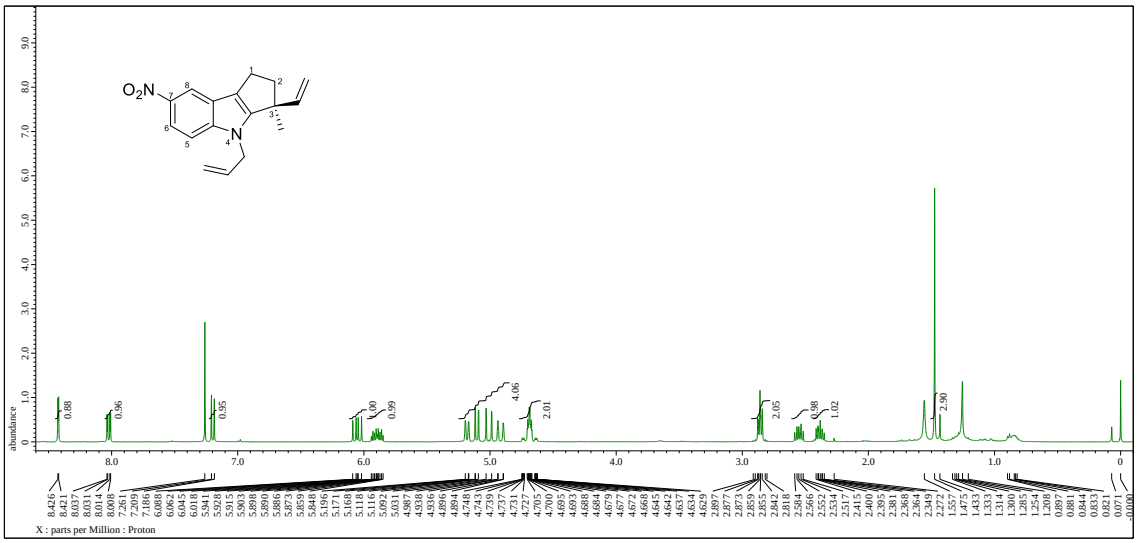
^{13}C NMR spectrum of compound **2n** (100 MHz, $CDCl_3$)



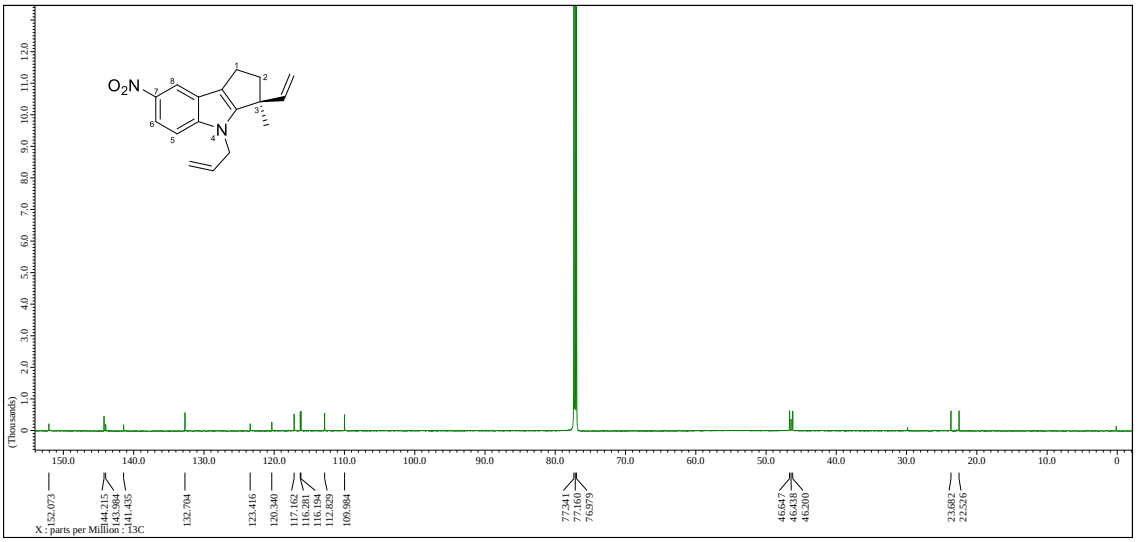
^{1}H NMR spectrum of compound **2o** (900 MHz, $CDCl_3$)



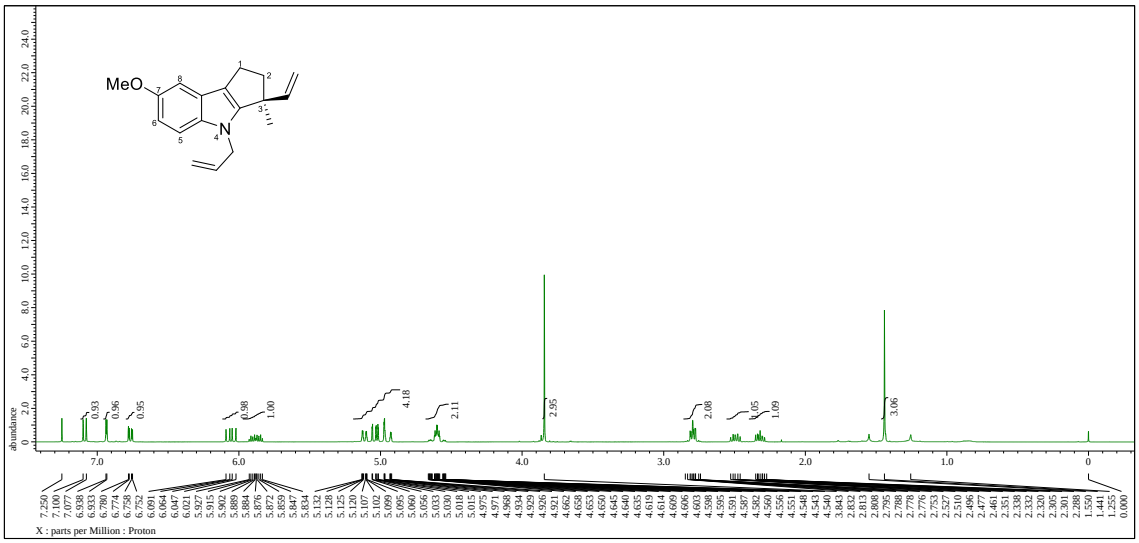
^{13}C NMR spectrum of compound **2o** (900 MHz, $CDCl_3$)



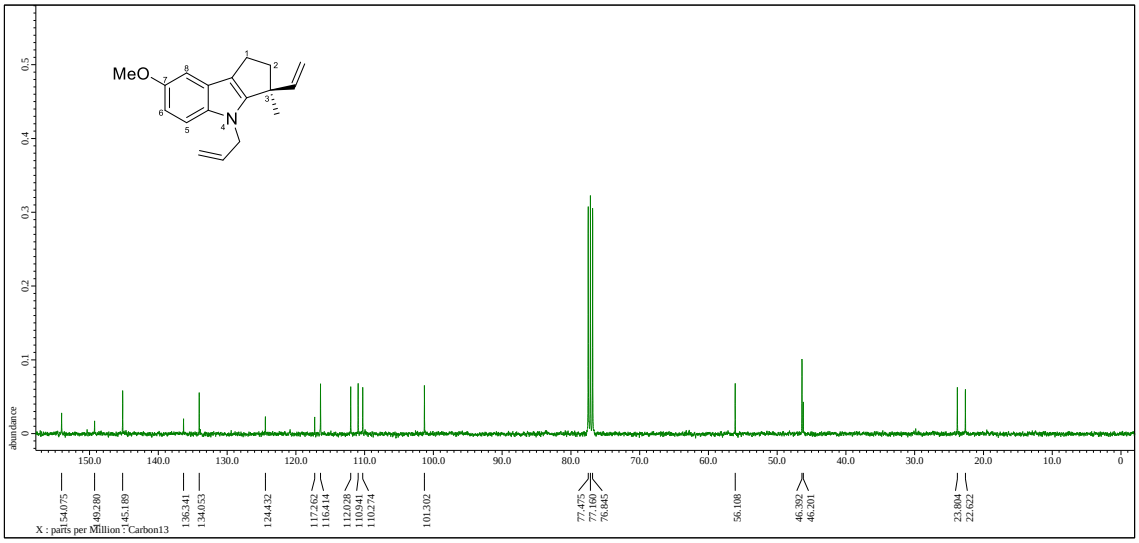
^{1}H NMR spectrum of compound **2p** (400 MHz, $CDCl_3$)



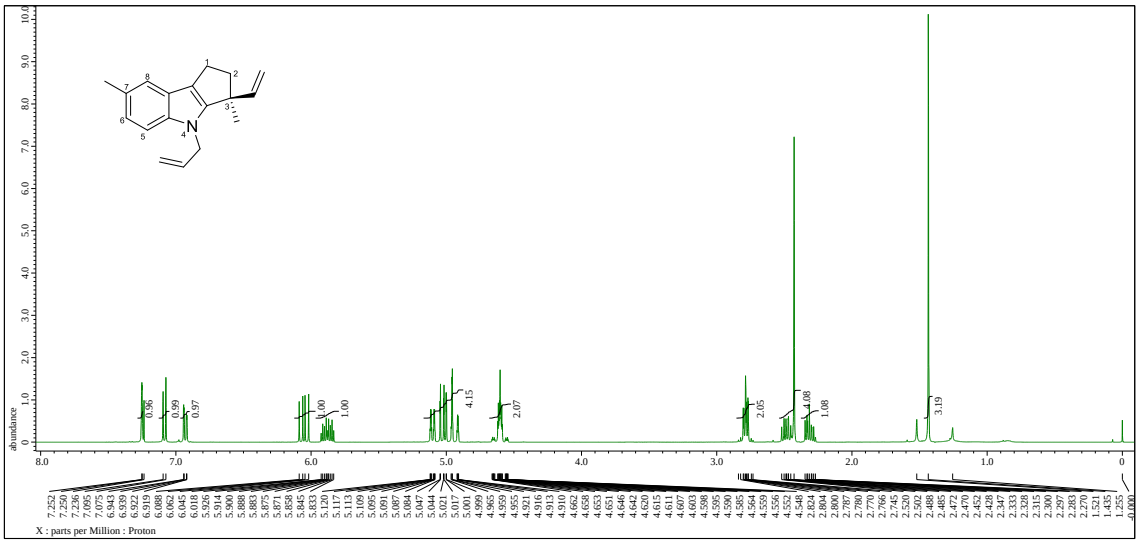
^{13}C NMR spectrum of compound **2p** (170 MHz, $CDCl_3$)



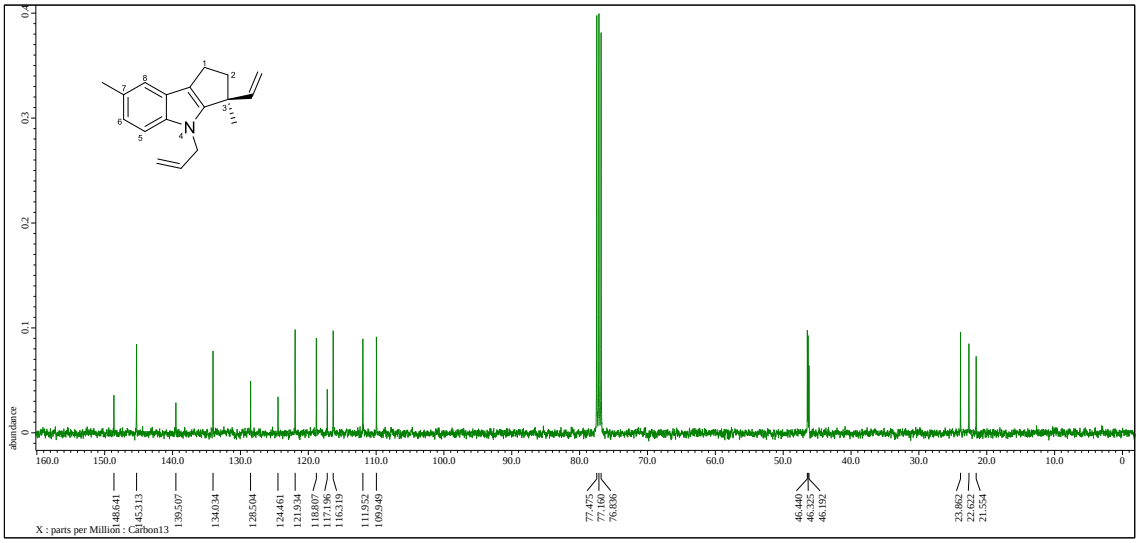
^{1}H NMR spectrum of compound **2q** (400 MHz, $CDCl_3$)



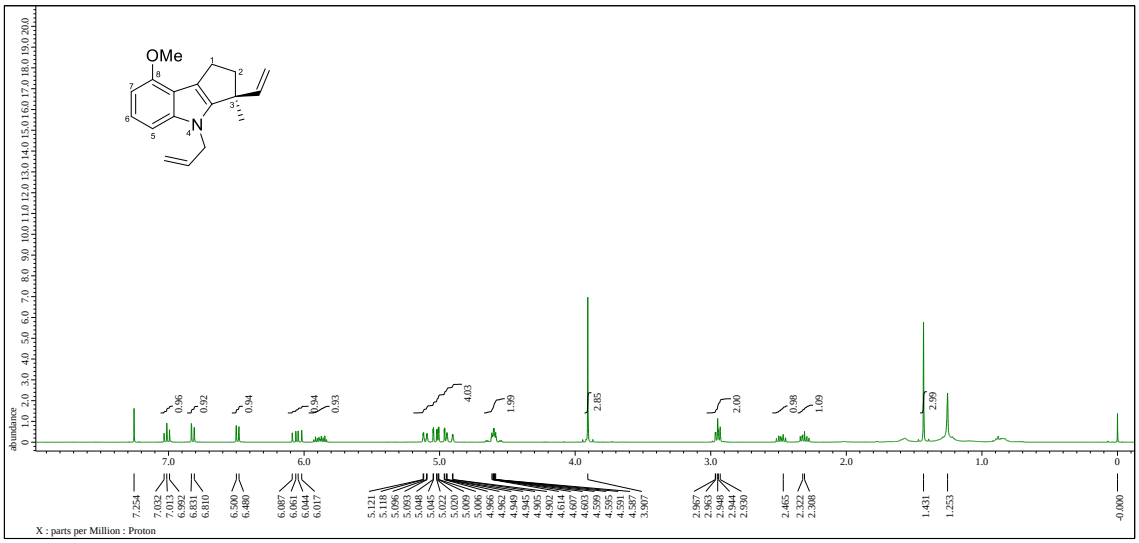
^{13}C NMR spectrum of compound **2q** (100 MHz, $CDCl_3$)



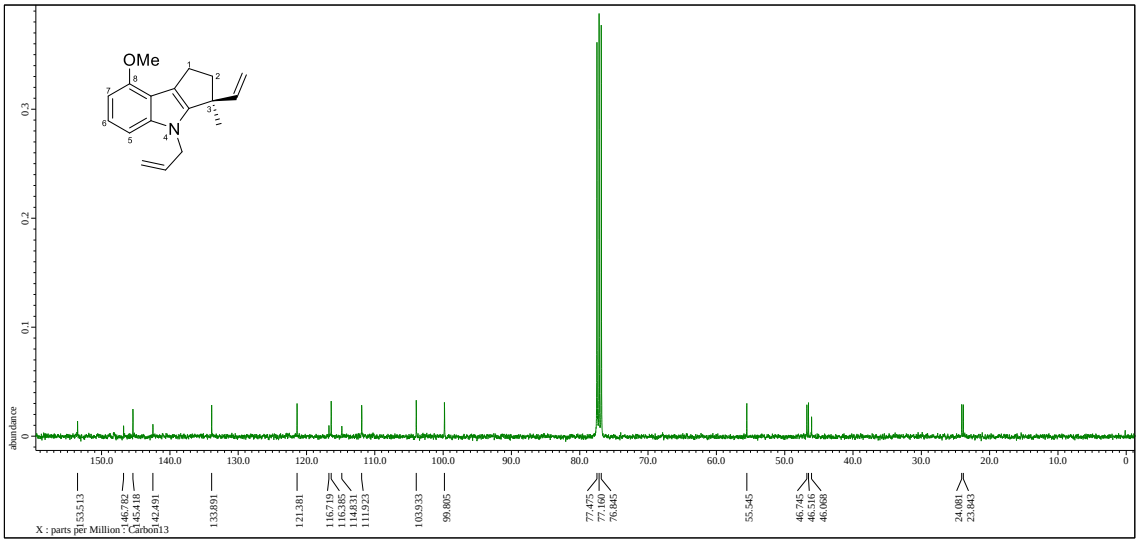
^{1}H NMR spectrum of compound **2r** (400 MHz, $CDCl_3$)



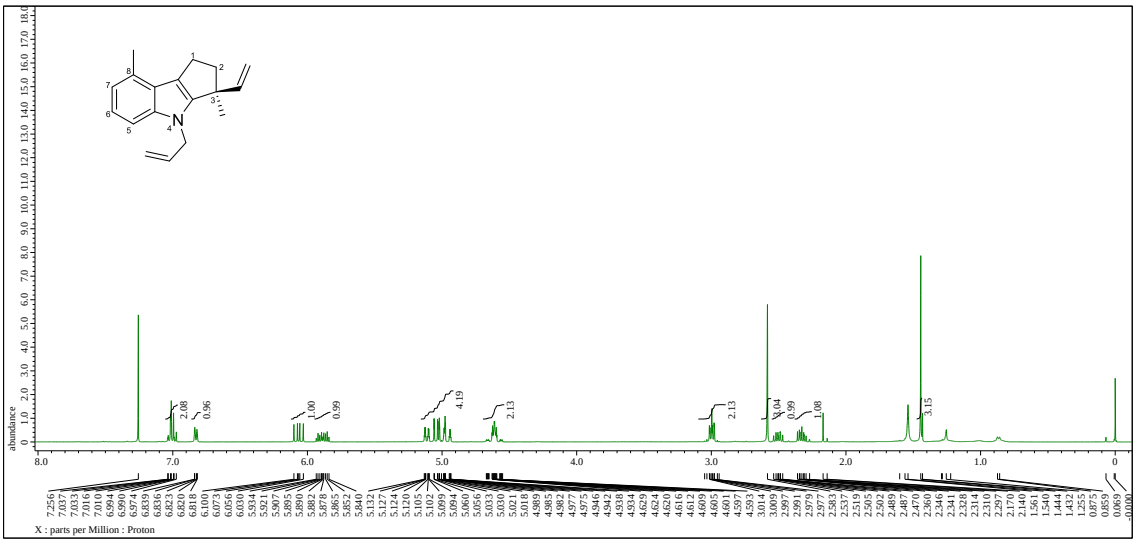
^{13}C NMR spectrum of compound **2r** (100 MHz, $CDCl_3$)



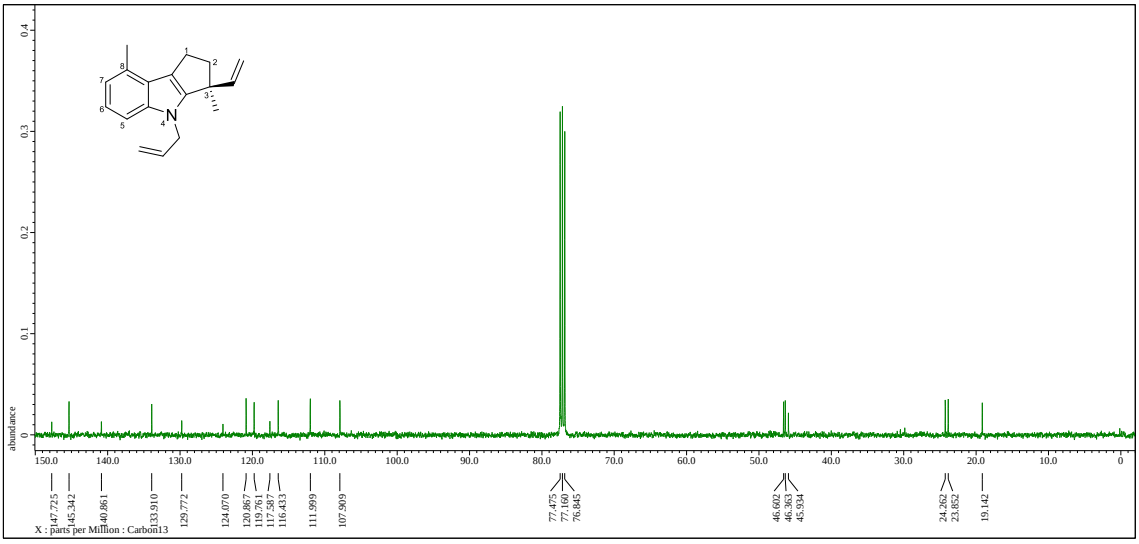
^{1}H NMR spectrum of compound **2s** (400 MHz, $CDCl_3$)



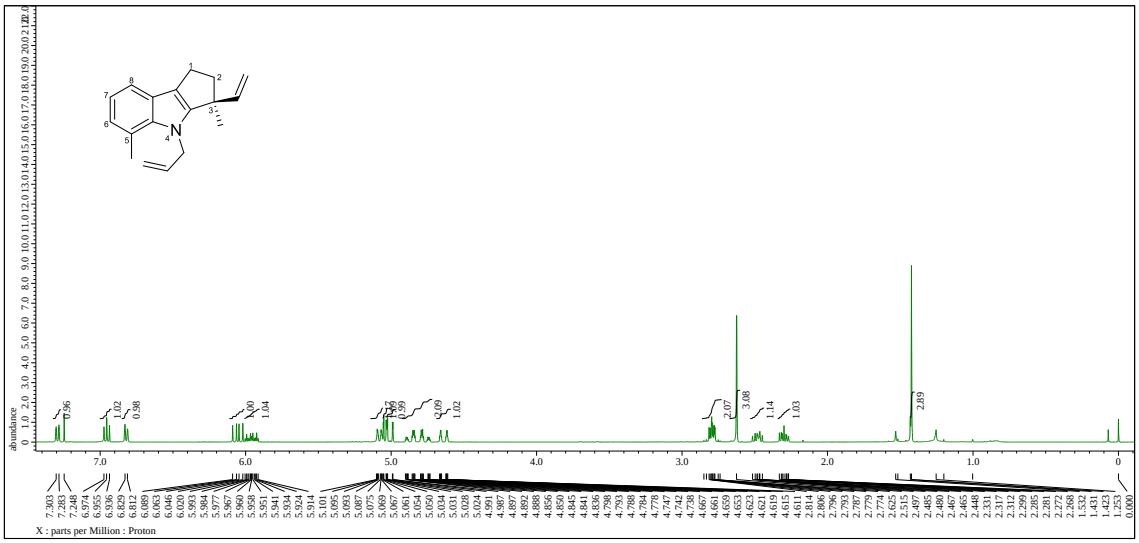
^{13}C NMR spectrum of compound **2s** (100 MHz, $CDCl_3$)



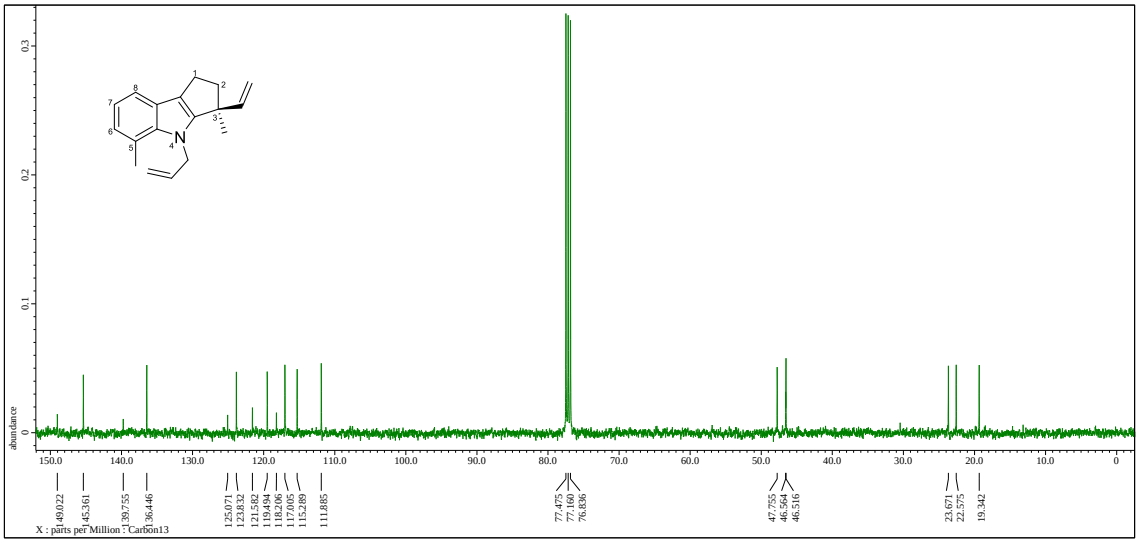
^{1}H NMR spectrum of compound **2t** (400 MHz, $CDCl_3$)



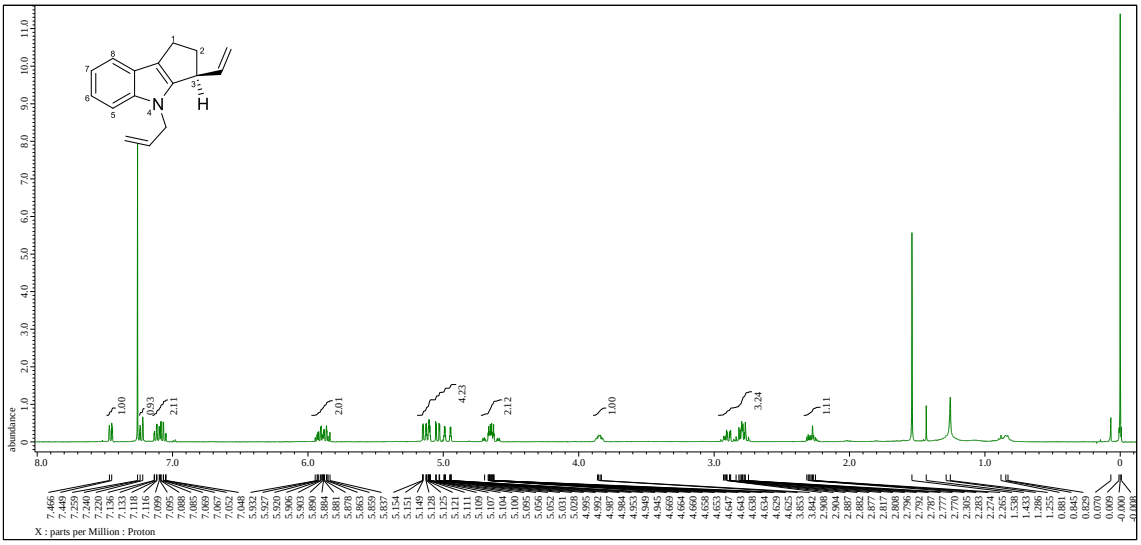
^{13}C NMR spectrum of compound **2t** (100 MHz, $CDCl_3$)



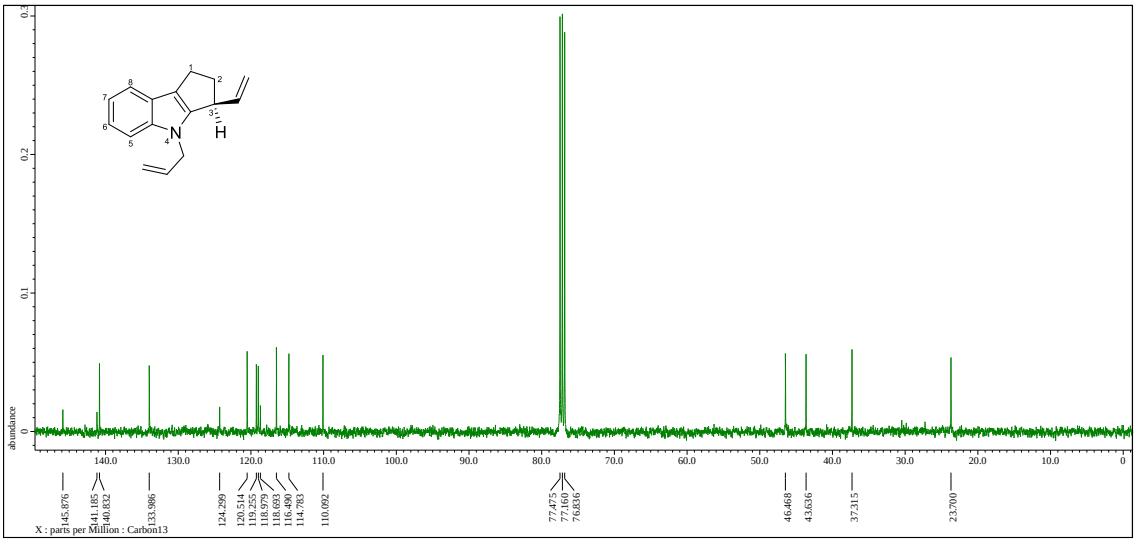
^{1}H NMR spectrum of compound **2u** (400 MHz, $CDCl_3$)



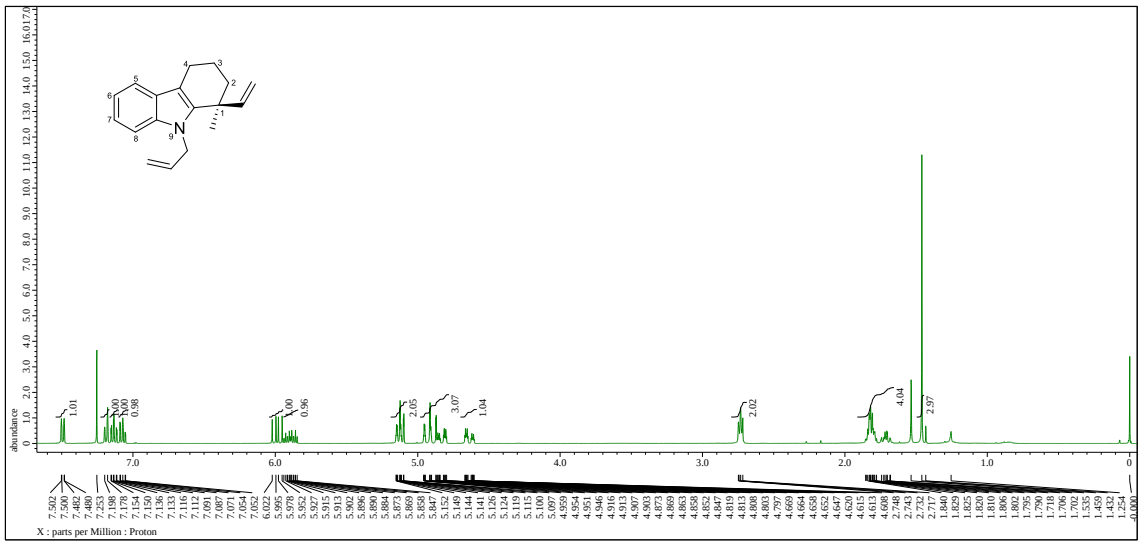
^{13}C NMR spectrum of compound **2u** (100 MHz, $CDCl_3$)



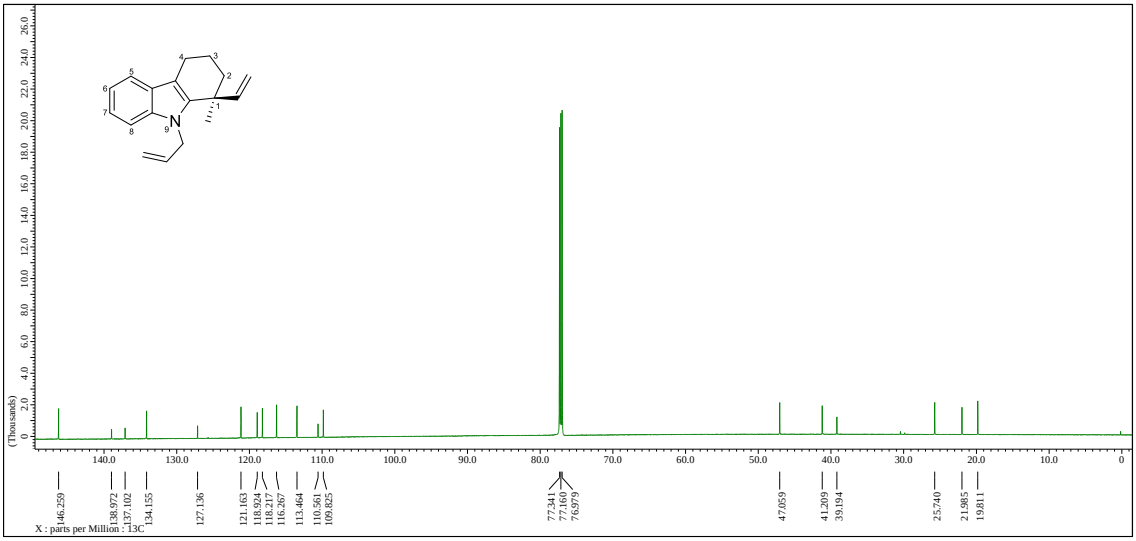
^{1}H NMR spectrum of compound **2v** (400 MHz, $CDCl_3$)



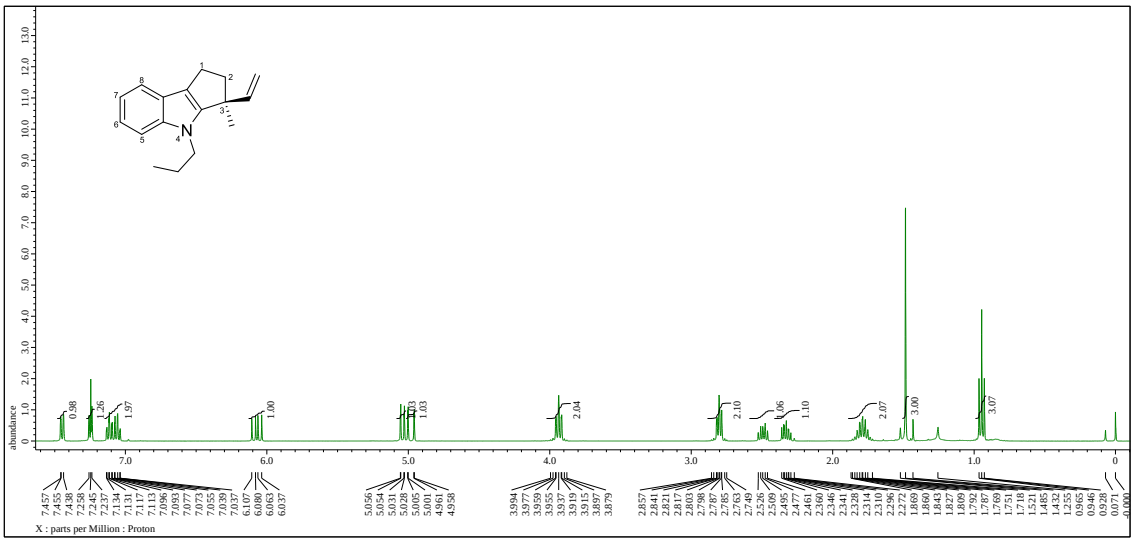
^{13}C NMR spectrum of compound **2v** (100 MHz, $CDCl_3$)



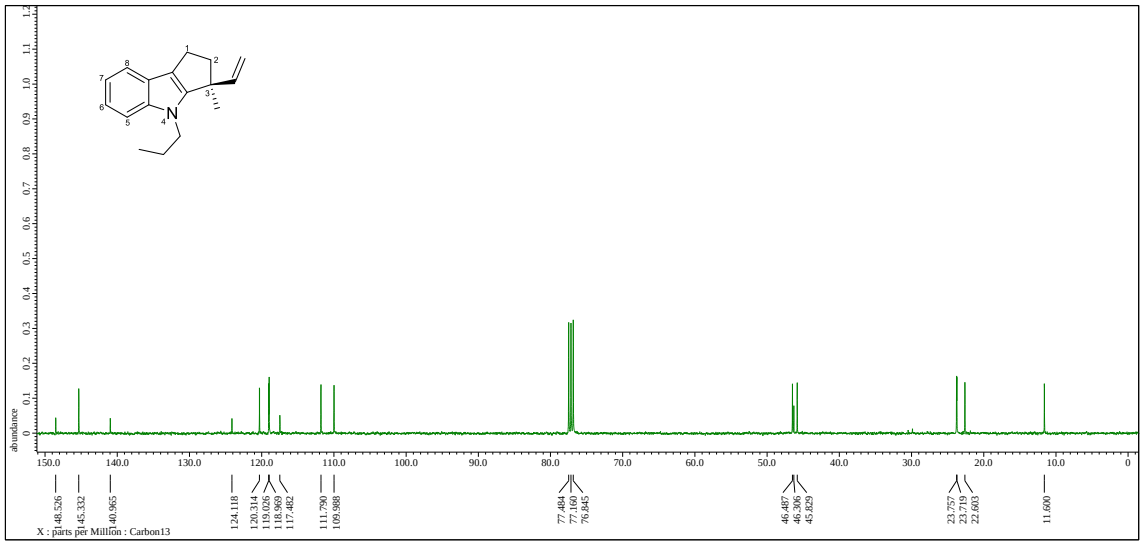
^{1}H NMR spectrum of compound **2w** (400 MHz, $CDCl_3$)



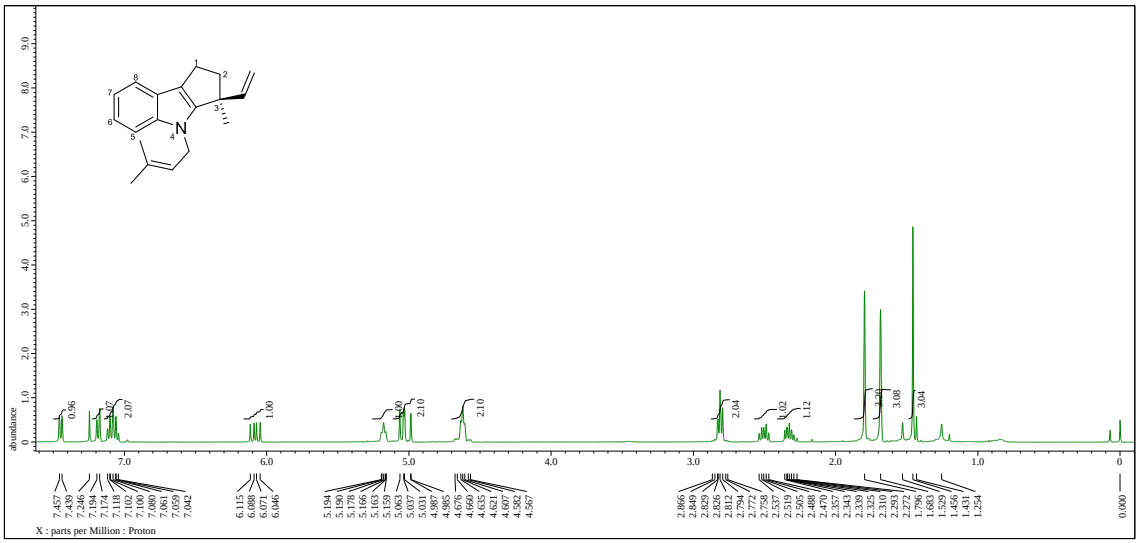
^{13}C NMR spectrum of compound **2w** (170 MHz, $CDCl_3$)



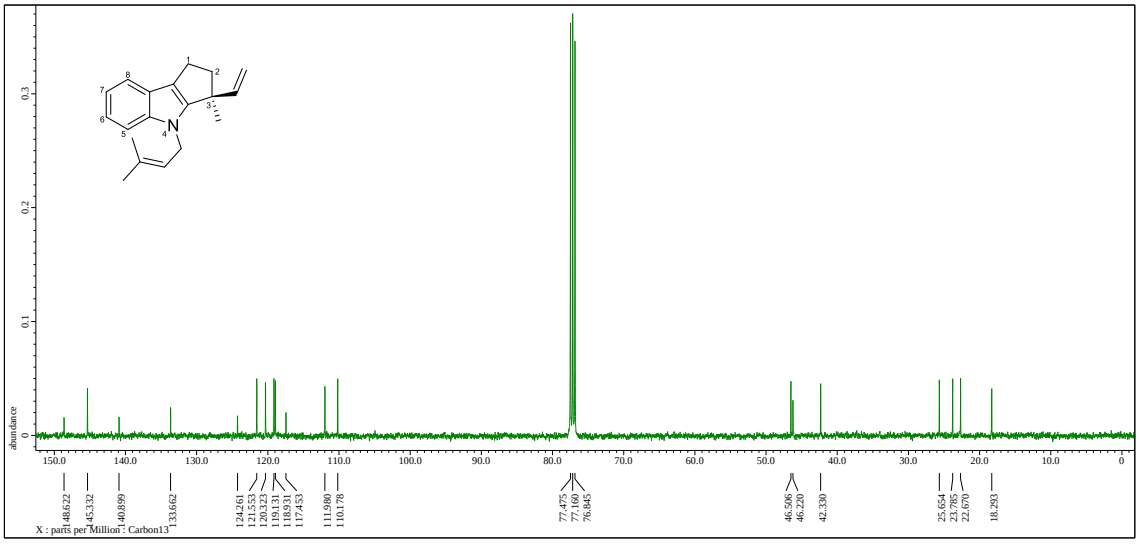
^{1}H NMR spectrum of compound **2x** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **2x** (100 MHz, $CDCl_3$)

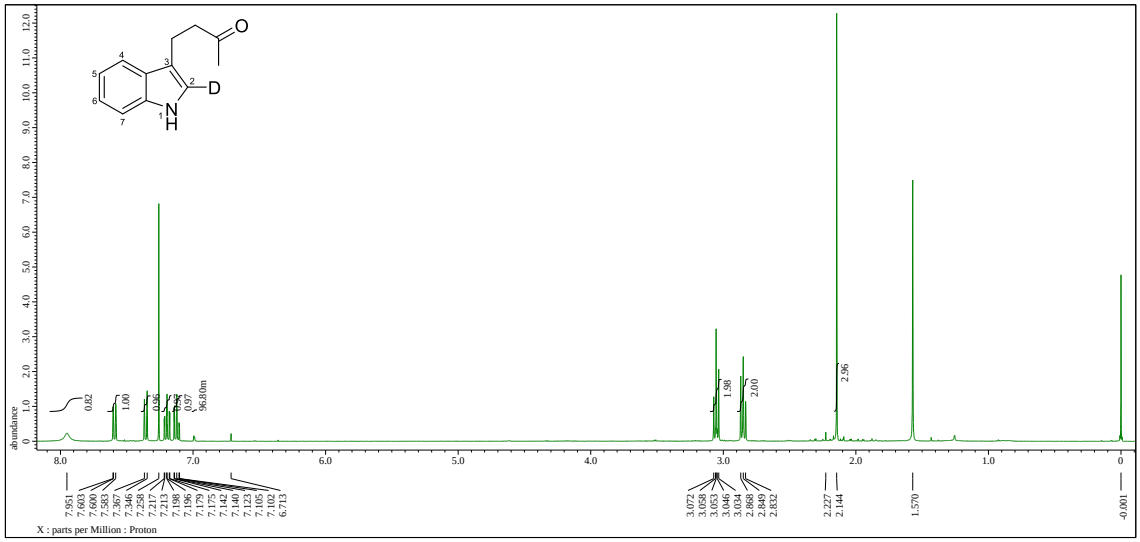


^{1}H NMR spectrum of compound **2z** (400 MHz, $CDCl_3$)

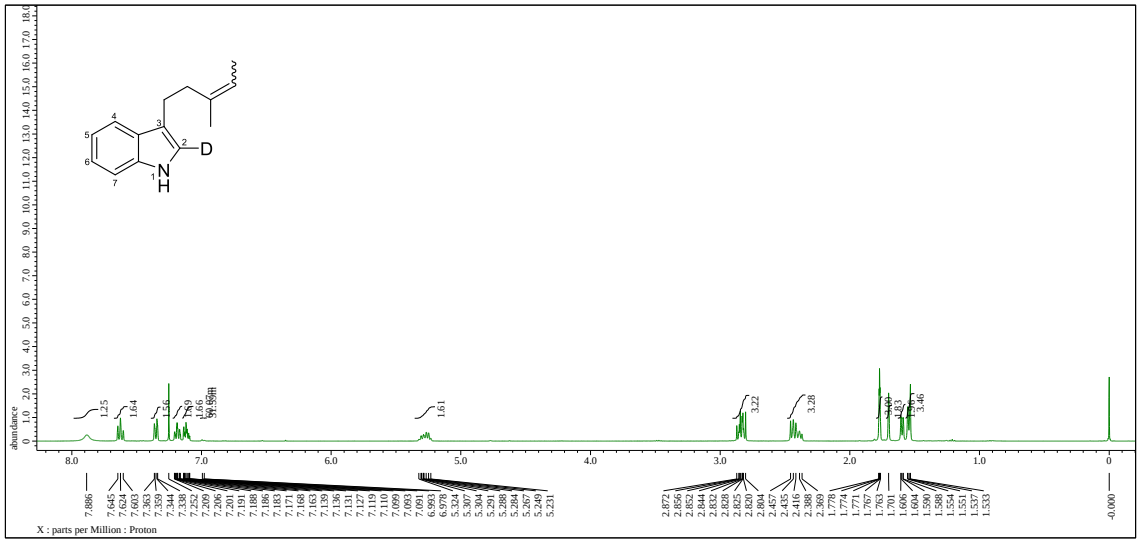


^{13}C NMR spectrum of compound **2z** (100 MHz, $CDCl_3$)

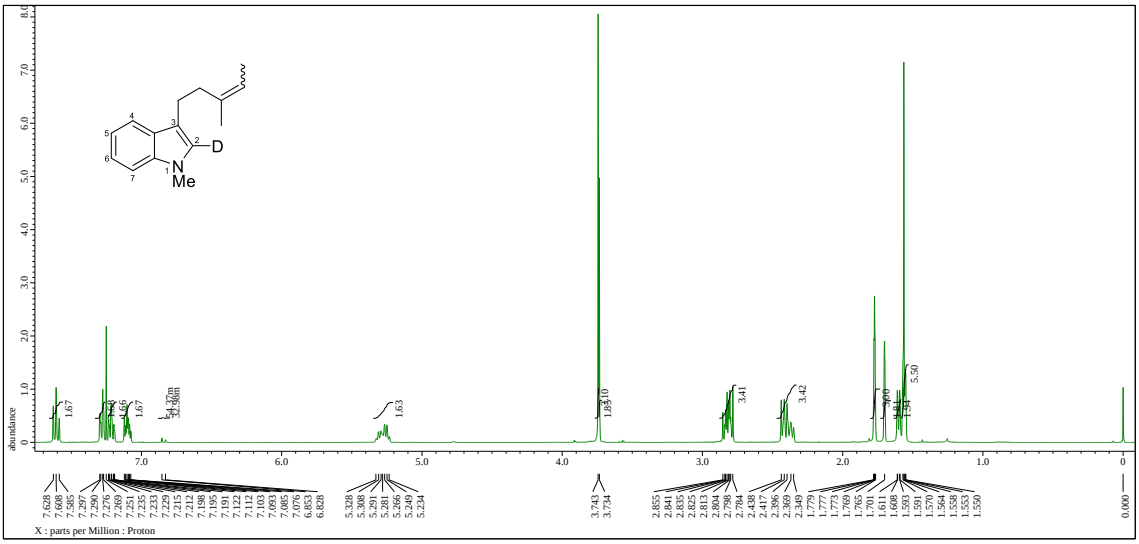
12.3. Deuterated substrates



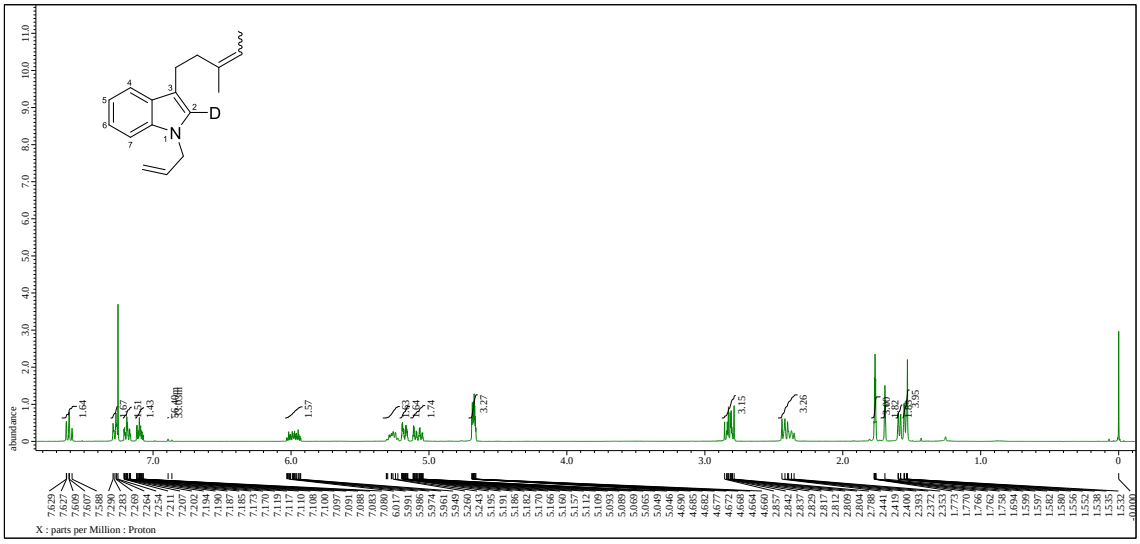
^{1}H NMR spectrum of compound *d*-**S'1h** (400 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound *d*-**1h** (62:38 mixture of *Z/E*-olefin isomers) (400 MHz, $CDCl_3$)

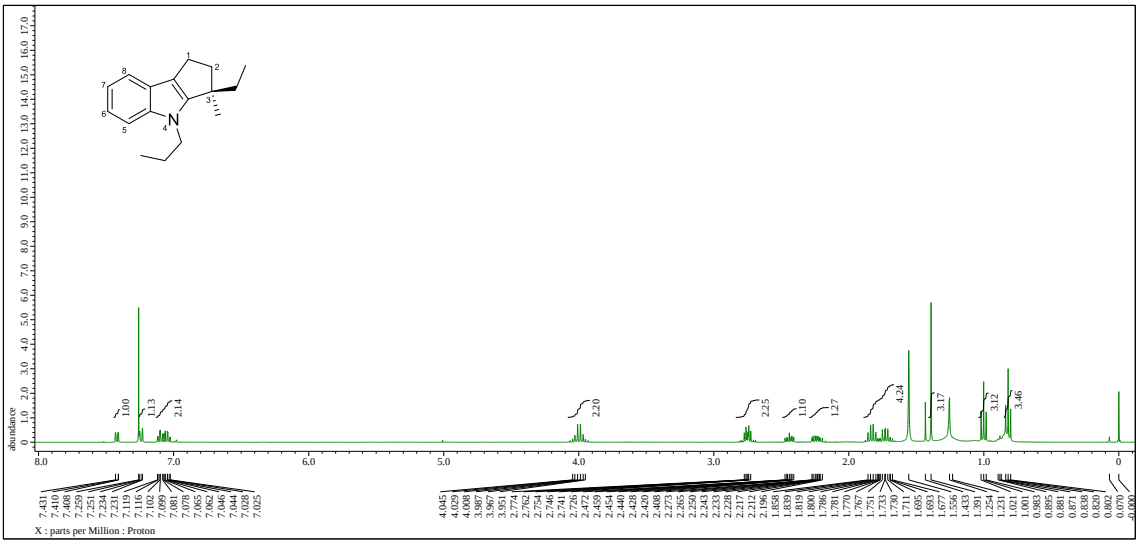


^{1}H NMR spectrum of compound *d*-**1a** (62:38 mixture of *Z*/*E*-olefin isomers) (400 MHz, $CDCl_3$)

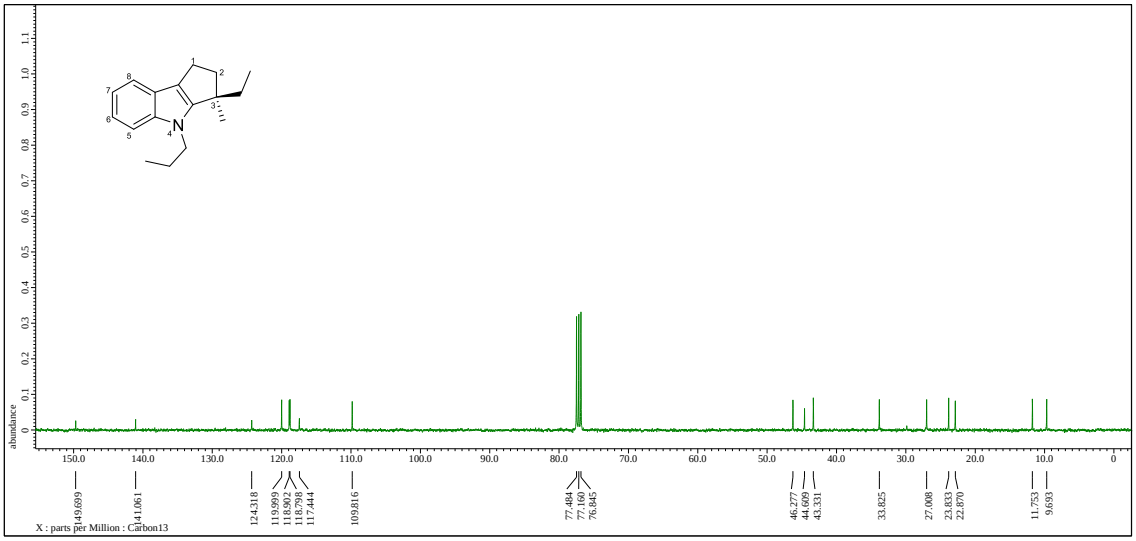


^{1}H NMR spectrum of compound *d*-**1k** (62:38 mixture of *Z*/*E*-olefin isomers) (400 MHz, $CDCl_3$)

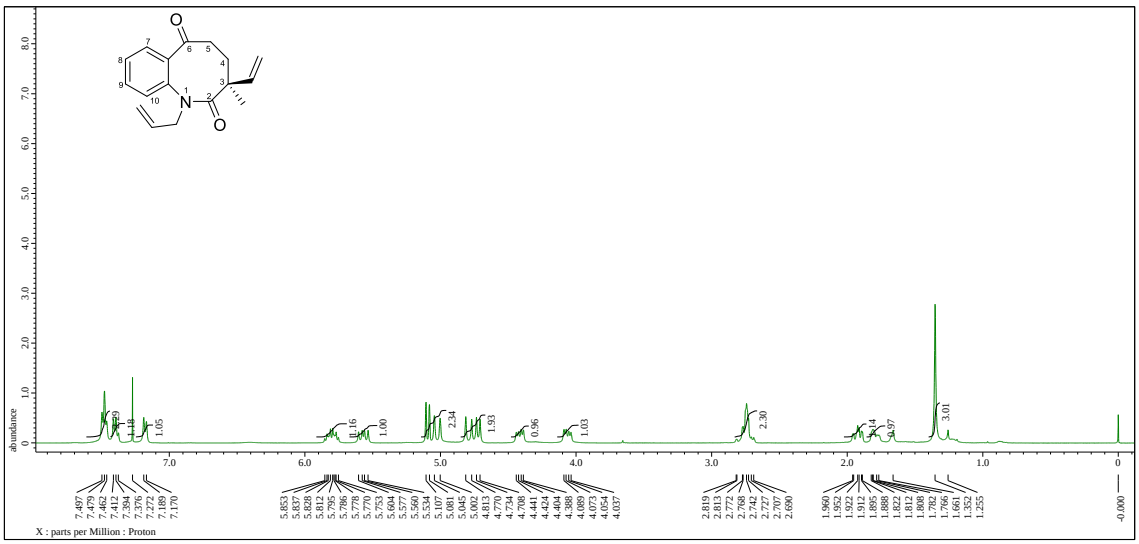
12.4. Synthetic applications of the products



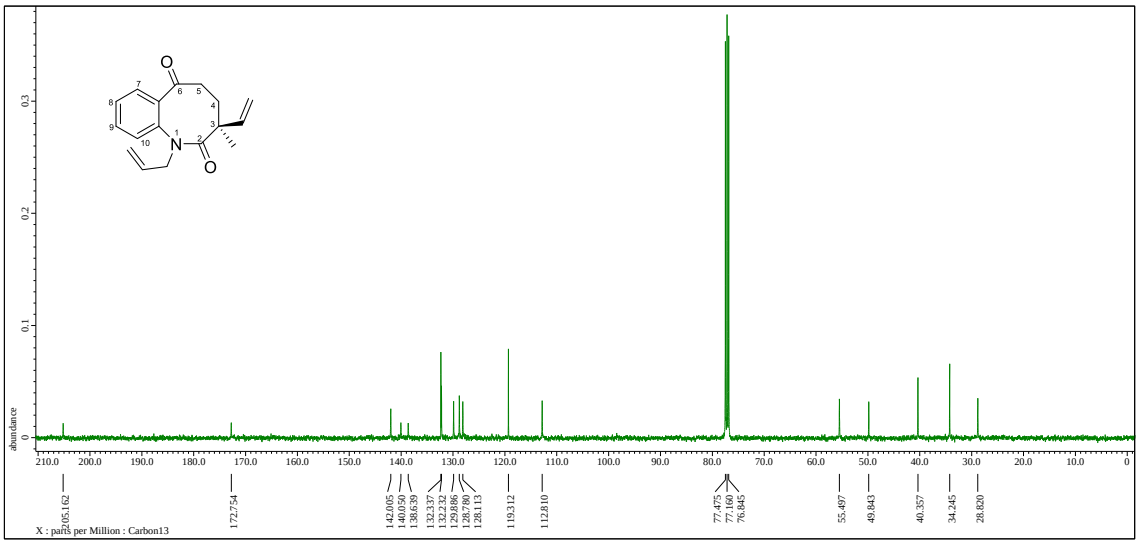
^{1}H NMR spectrum of compound **3** (400 MHz, $CDCl_3$)



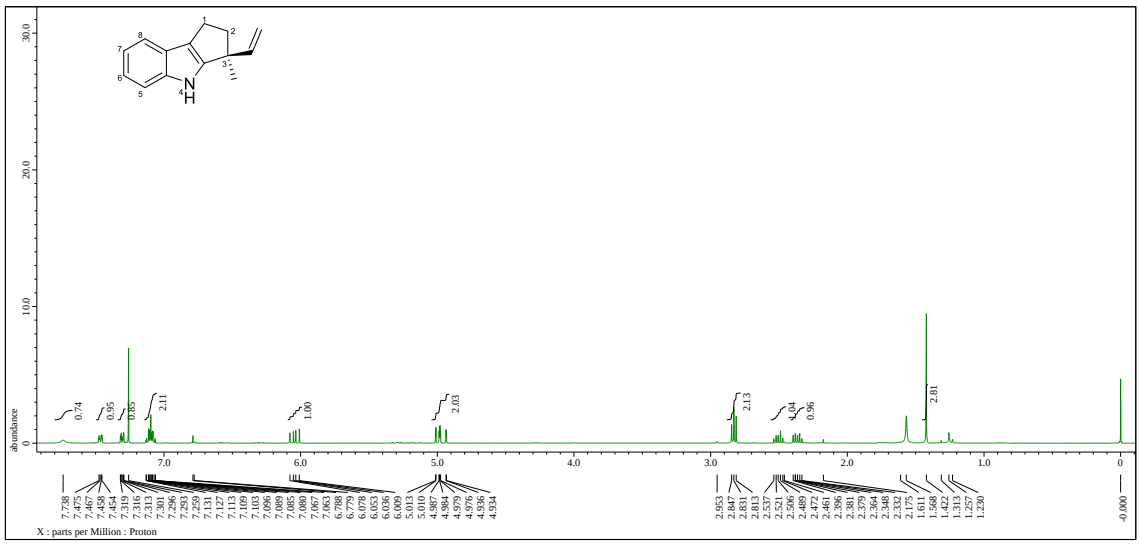
^{13}C NMR spectrum of compound **3** (100 MHz, $CDCl_3$)



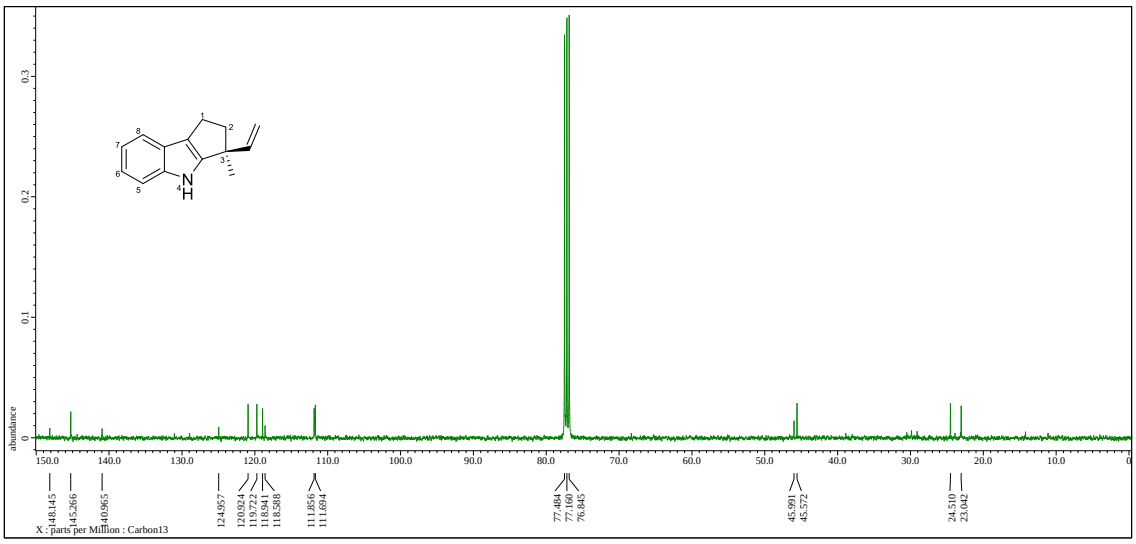
^{1}H NMR spectrum of compound **4** (400 MHz, $CDCl_3$)



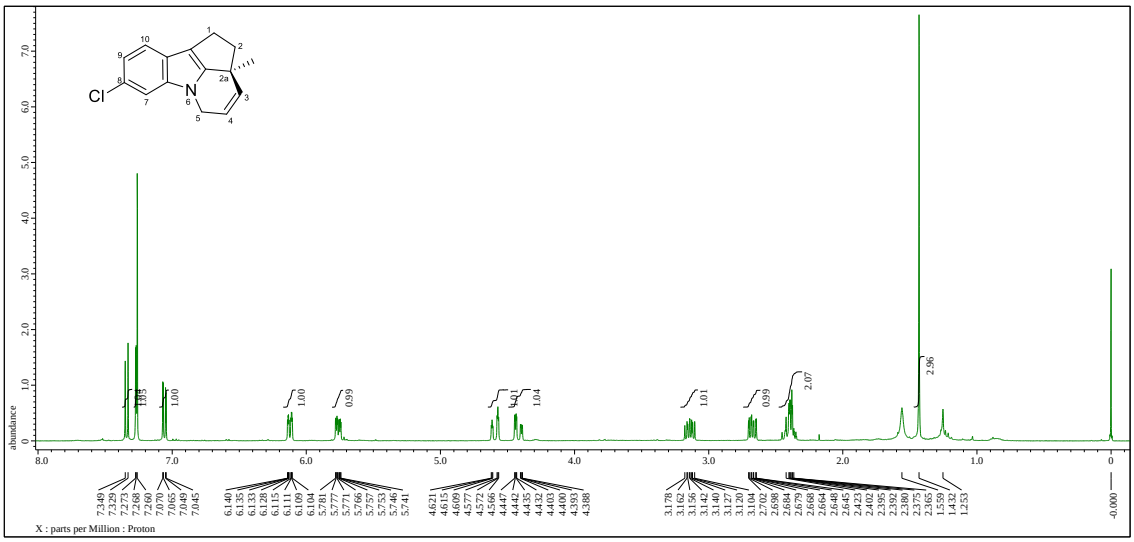
^{13}C NMR spectrum of compound **4** (100 MHz, $CDCl_3$)



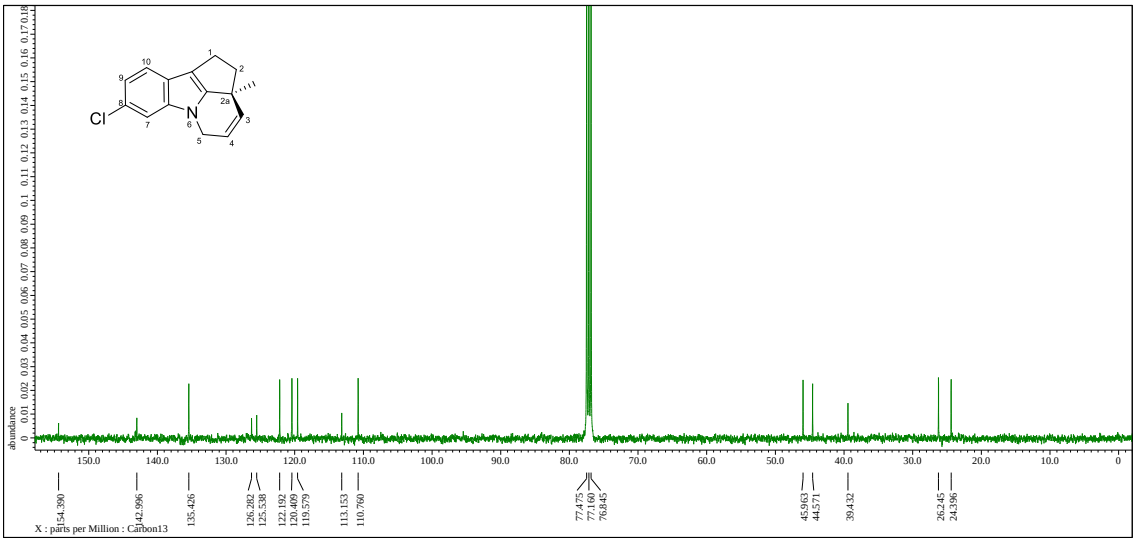
^{1}H NMR spectrum of compound **5** (400 MHz, $CDCl_3$)



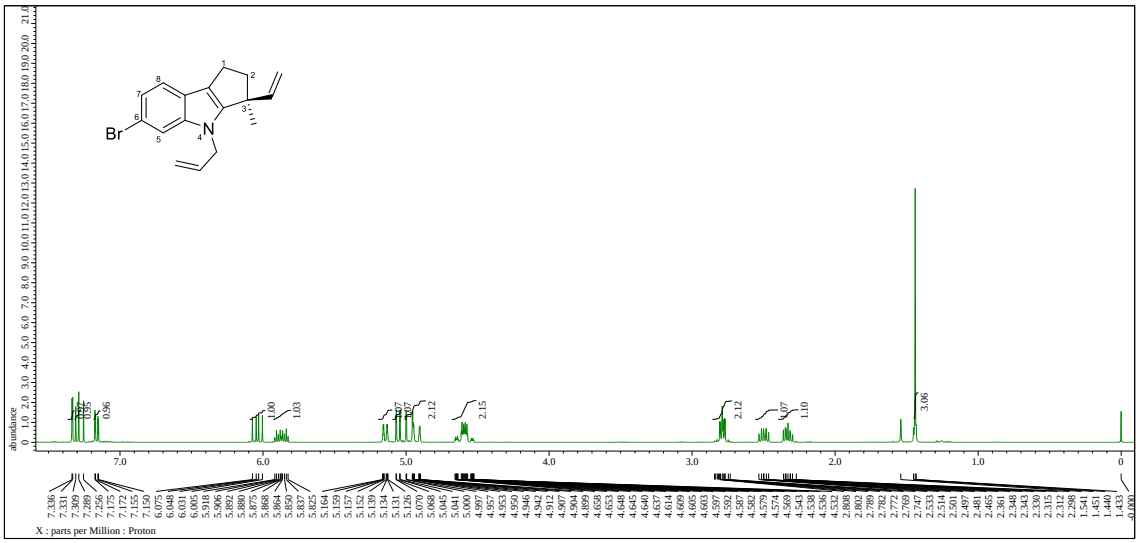
^{13}C NMR spectrum of compound **5** (100 MHz, $CDCl_3$)



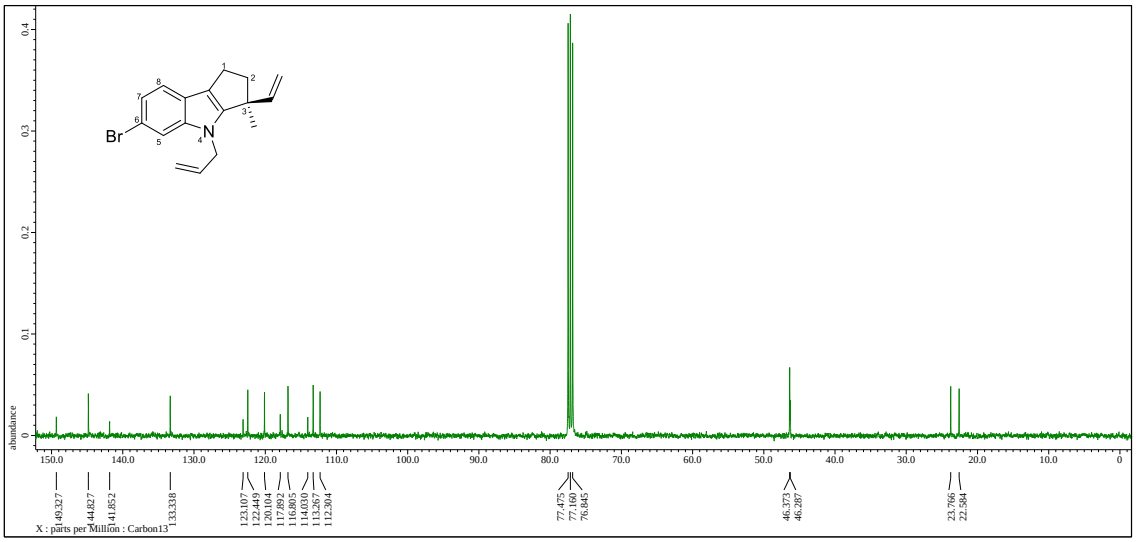
^{1}H NMR spectrum of compound **6** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **6** (100 MHz, $CDCl_3$)

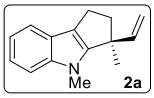


^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$)



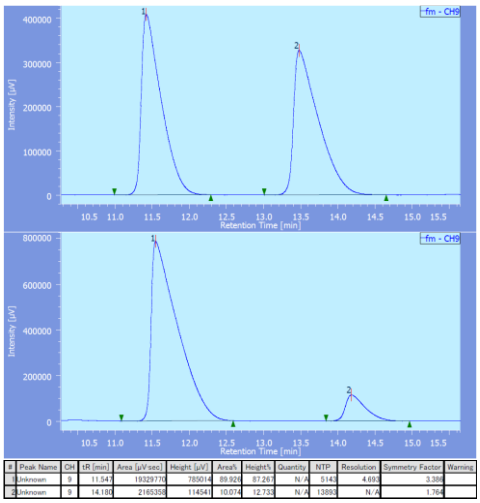
^{13}C NMR spectrum of compound **7** (100 MHz, $CDCl_3$)

13. HPLC Charts

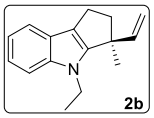


Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm

ee = 80%

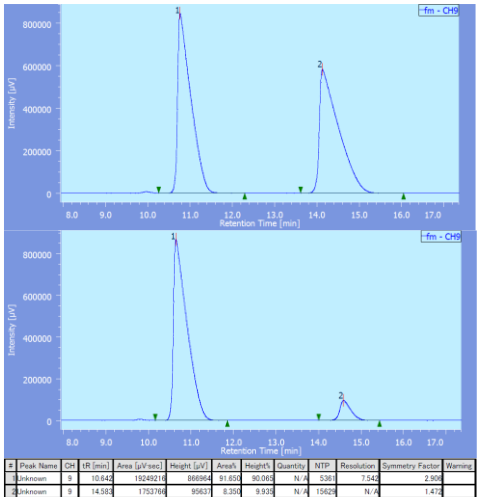


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	11.547	19329770	785014	89.926	87.267	N/A	5143	4.693	3.386	
2	Unknown	9	14.180	2165358	114541	10.074	12.733	N/A	13893	N/A	1.766	

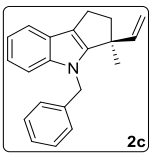


Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm

ee = 84%

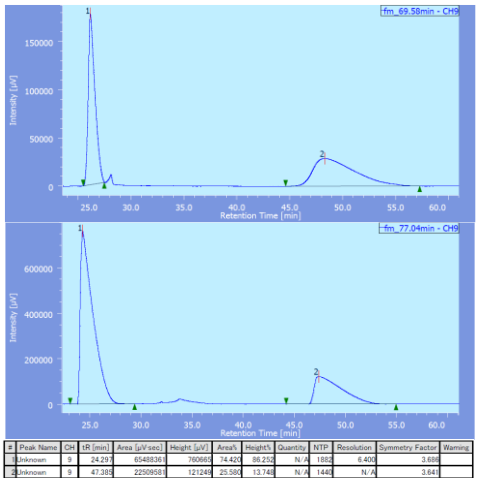


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	10.843	1924921	86696	91.651	90.063	N/A	536	7.542	2.906	
2	Unknown	9	14.583	1753766	9563	8.349	9.937	N/A	15629	N/A	1.473	

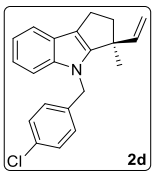


Conditions: YMC CHIRAL ART Cellulose-C, eluent: *n*-hexane/2-propanol = 5/1, flow rate: 1 mL/min, 25 °C, 254 nm

ee = 48%

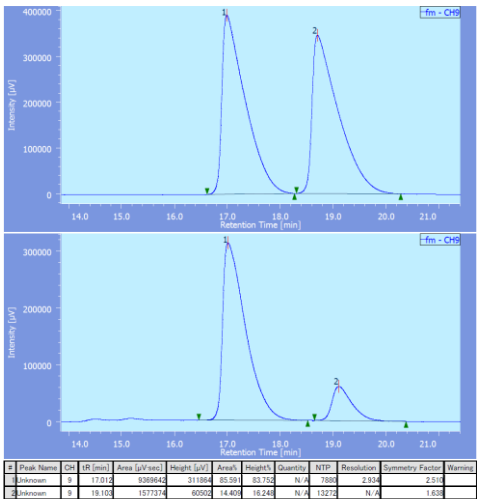


#	Peak Name	CH	tR [min]	Area [μV*sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	24.297	65488361	760665	74.420	86.252	N/A	1882	6.400	3.686	
2	Unknown	9	47.385	22509581	121249	25.580	13.748	N/A	1440	N/A	3.641	

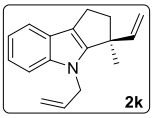


Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25°C, 254 nm

ee = 72%

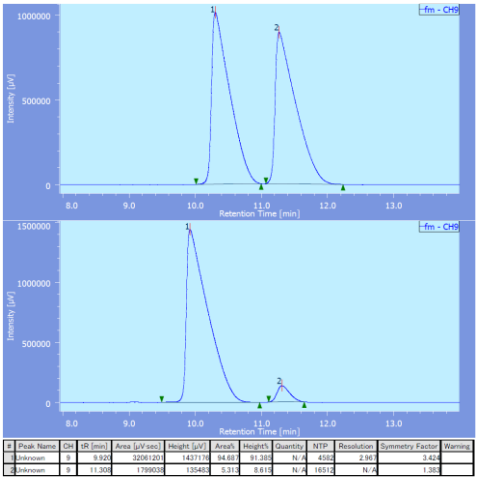


#	Peak Name	CH	tR [min]	Area [μV*sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	17.012	9369642	311864	85.591	83.752	N/A	7885	2.934	2.510	
2	Unknown	9	19.103	1577374	60502	14.409	16.248	N/A	13272	N/A	1.638	



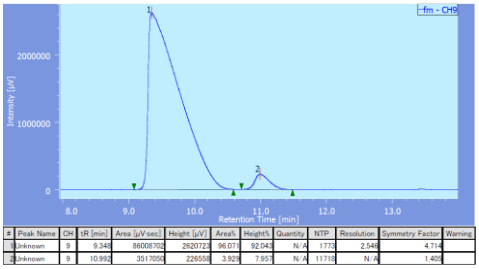
Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm

ee = 90%



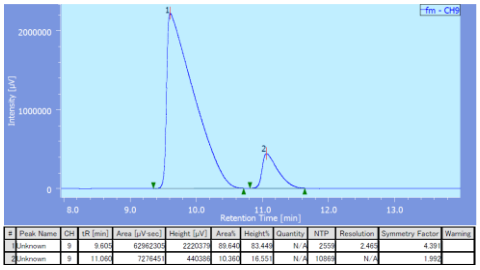
Using *Z*-enriched substrate **1k** (*E*:*Z* = 19:81)

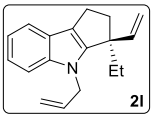
ee = 92%



Using *E*-enriched substrate **1k** (*E*:*Z* = 79:21)

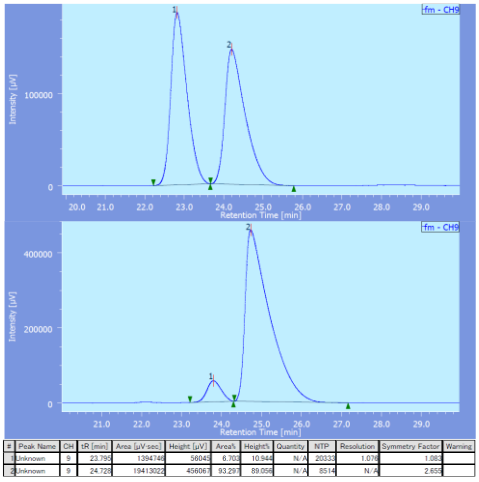
ee = 80%

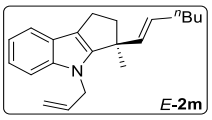




Conditions: YMC CHIRAL ART Cellulose-C, eluent: *n*-hexane, flow rate: 0.5 mL/min, 25 °C, 254 nm

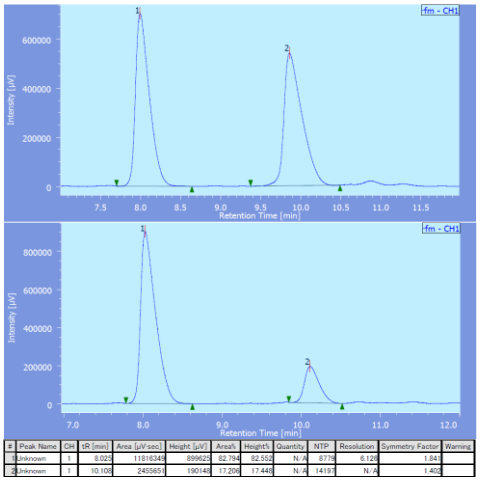
ee = 86%

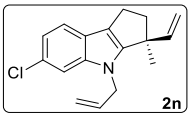




Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm

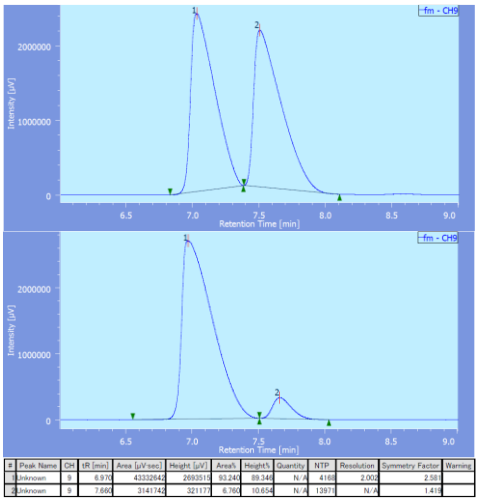
ee = 66%

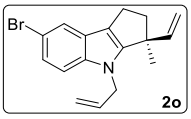




Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm

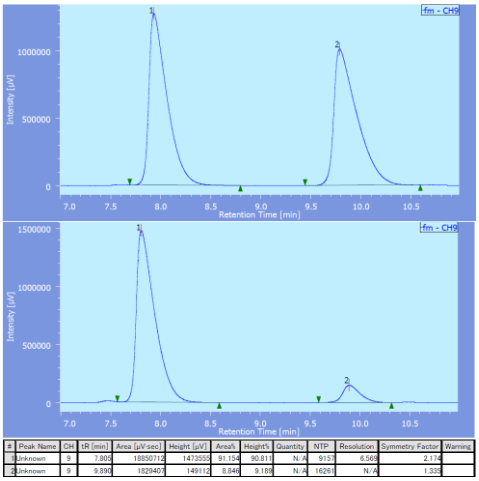
ee = 86%

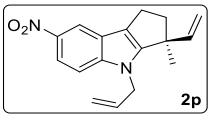




Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm

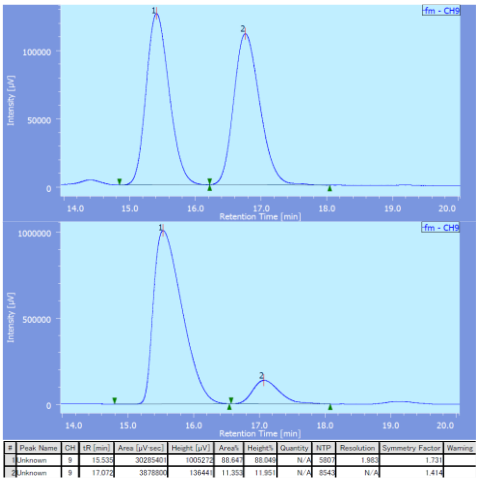
ee = 82%

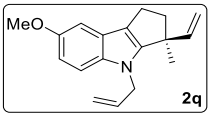




Conditions: DAICEL CHIRALPAK AS-3, eluent: *n*-hexane/2-propanol = 50/1 , flow rate: 1 mL/min, 25 °C, 254 nm

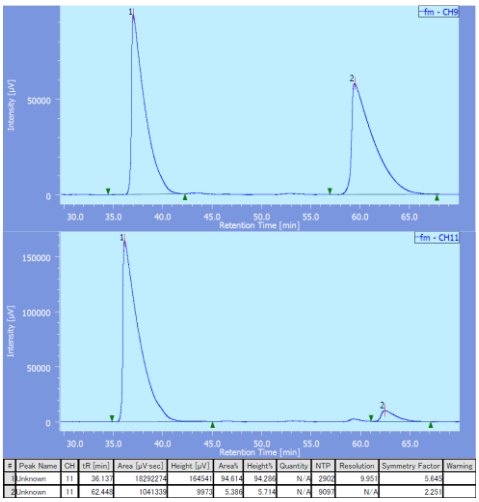
ee = 78%

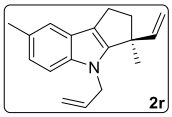




Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm

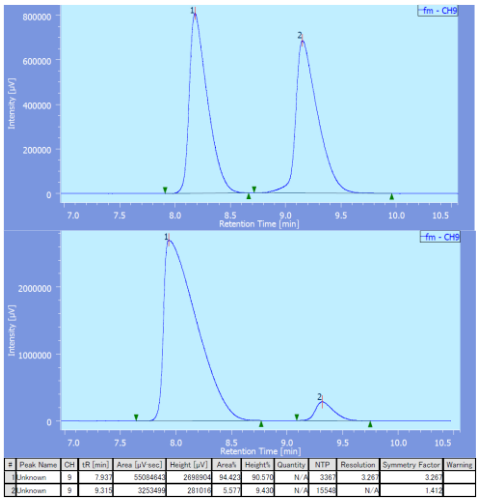
ee = 90%

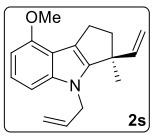




Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm

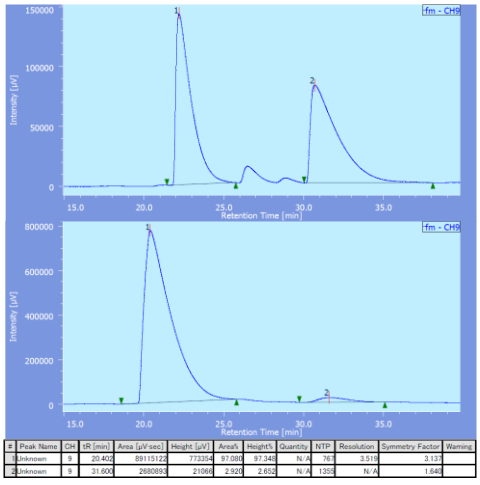
ee = 88%

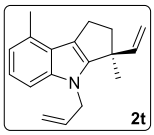




Conditions: DAICEL CHIRALPAK AD-H, eluent: *n*-hexane, flow rate: 0.5 mL/min, 25 °C, 254 nm

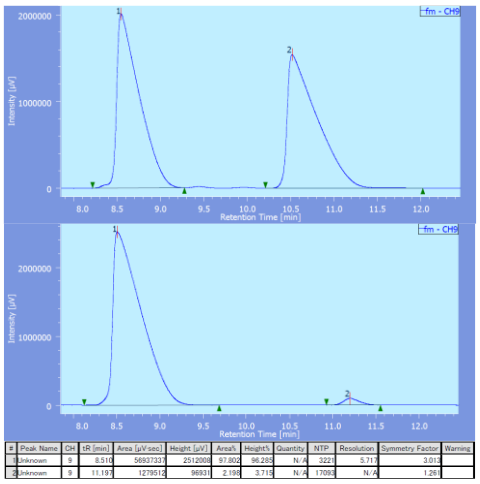
ee = 94%

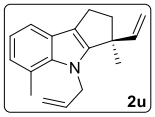




Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm

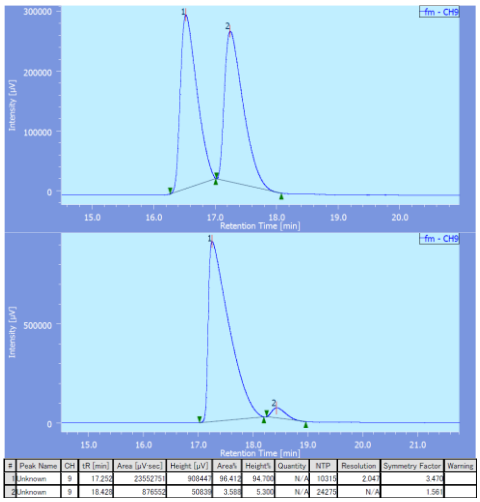
ee = 96%

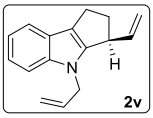




Conditions: DAICEL CHIRALPAK IF, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm

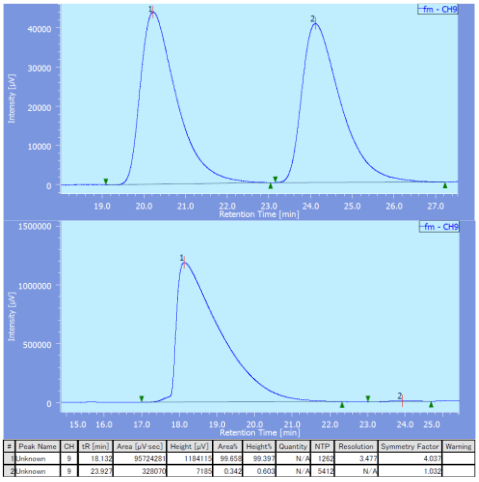
ee = 93%



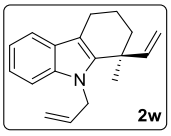


Conditions: DAICEL CHIRALCEL OJ, eluent: *n*-hexane, flow rate: 0.5 mL/min, 25 °C, 254 nm

ee = 99%

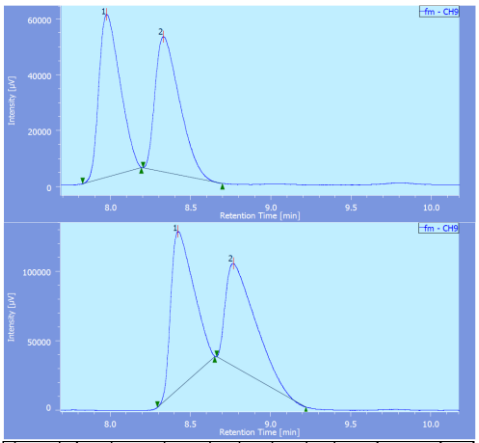


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	18.132	95724281	1184116	99.698	99.397	N/A	1282		3.477	
2	Unknown	9	23.927	328070	7185	0.342	0.603	N/A	5412	N/A	1.032	

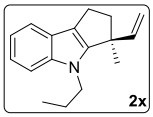


Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 310 nm

ee = 8%

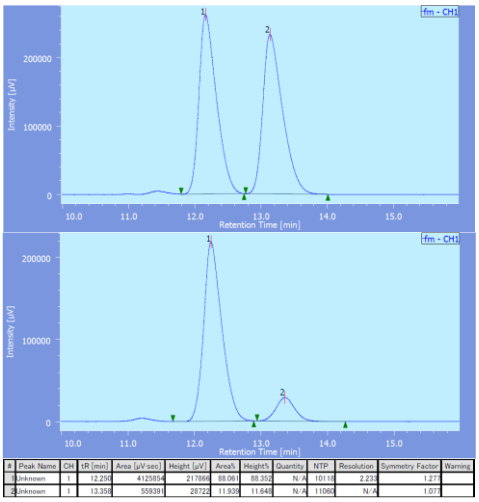


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.422	1105205	113359	53.600	60.654	N/A	15476	1.106	1.686	
2	Unknown	9	8.767	956733	73537	46.400	39.346	N/A	9765	N/A	2.306	

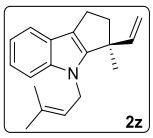


Conditions: YMC CHIRAL ART Cellulose-C, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm

ee = 76%

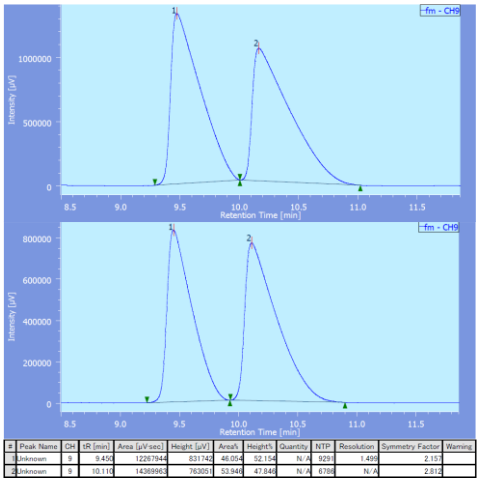


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	12.290	4125854	217866	88.061	88.352	N/A	10110	2.233	1.273	
2	Unknown	1	13.358	559391	28722	11.939	11.648	N/A	11066	N/A	1.073	

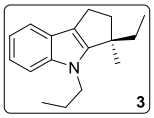


Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 1 mL/min, 25 °C, 254 nm

ee = 8%

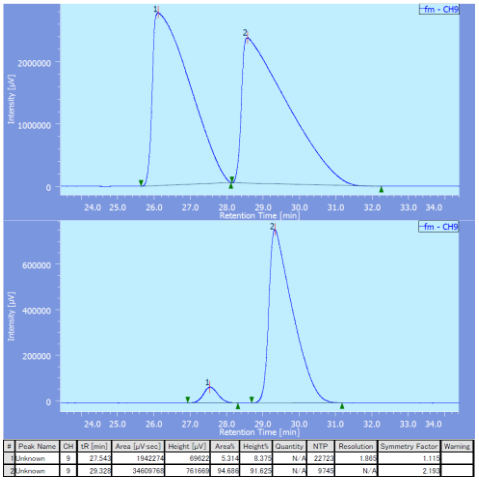


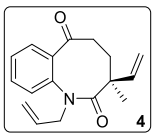
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	9.450	1226784	831740	46.054	52.154	N/A	9291	1.499	2.153	
2	Unknown	9	10.110	1436996	763051	53.946	47.846	N/A	6786	N/A	2.812	



Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane, flow rate: 0.3 mL/min, 25 °C, 254 nm

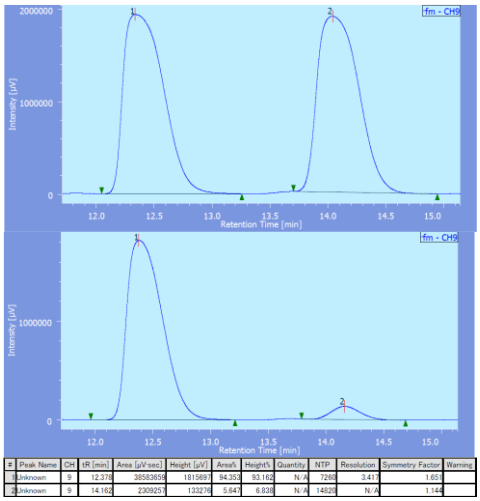
ee = 90%

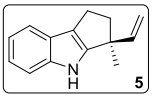




Conditions: DAICEL CHIRALPAK AD-3, eluent: *n*-hexane/2-propanol = 20/1, flow rate: 0.5 mL/min, 25 °C, 254 nm

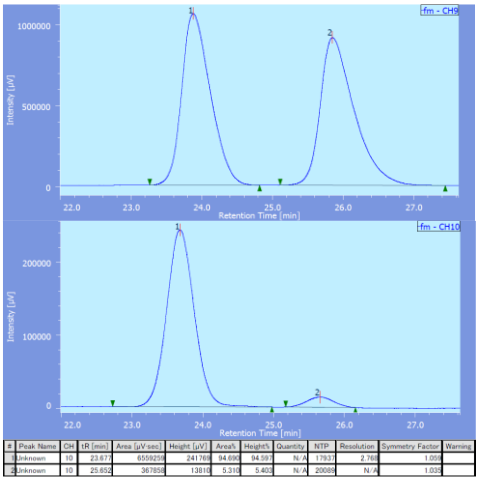
ee = 88%

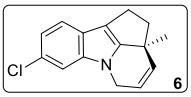




Conditions: YMC CHIRAL ART Cellulose-SB, eluent: *n*-hexane/2-propanol = 20/1, flow rate: 0.3 mL/min, 25 °C, 280 nm

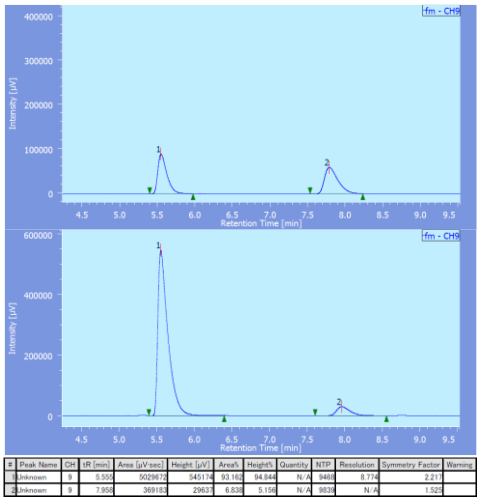
ee = 90%

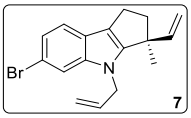




Conditions: DAICEL CHIRALCEL OD-H, eluent: *n*-hexane, flow rate 1 mL/min, 25 °C, 300 nm

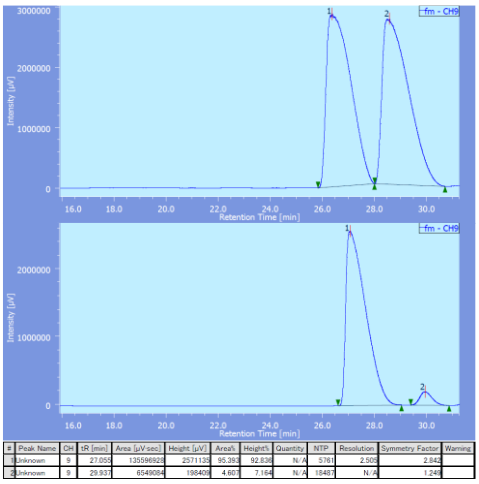
ee = 86%





Conditions: YMC CHIRAL ART Cellulose-C, eluent: *n*-hexane, flow rate: 0.3 mL/min, 25 °C, 254 nm

ee = 90%



#	Peak Name	CH	tR [min]	Area [μV sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	27.059	135596928	2571135	95.393	92.636	N/A	5761	2.505	2.842	
2	Unknown	9	29.937	6549084	198409	4.607	7.164	N/A	18483	N/A	1.249	