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Supporting Information

trans-Hydroboration of Propargyl Alcohol Derivatives and Related Substrates

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SUPPORTING CRYSTALLOGRAPHIC INFORMATION

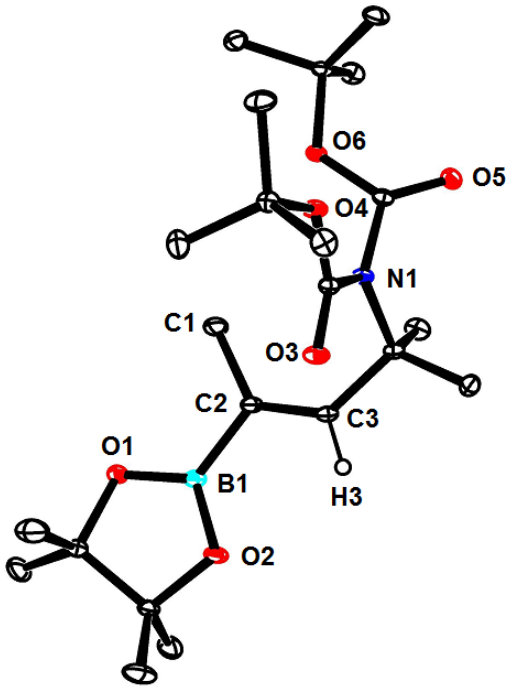


Figure S1. Structure of compound **41** in the solid state; hydrogen atoms – except for H3 residing *cis* to B1 – are omitted for clarity

X-ray Crystal Structure Analysis of Compound 41. C_{22} H_{40} B N O_6, *Mr* = 425.36 g · mol^{-1}, colorless prism, crystal size 0.155 x 0.131 x 0.056 mm^3, triclinic, space group $P\bar{1}$, *a* = 9.3956(16) Å, *b* = 10.6277(18) Å, *c* = 14.151(2) Å, α = 107.278(3)°, β = 107.244(3)°, γ = 97.655(3)°, *V* = 1250.1(4) $Å^3$, *T* = 100(2) K, *Z* = 2, D_{calc} = 1.130 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*α) = 0.080 mm^{-1}, Gaussian absorption correction (T_{min} = 0.99, T_{max} = 1.00), Bruker-AXS Kappa Mach3 APEX-II diffractometer, 1.612 < θ < 34.969°, 44934 measured reflections, 10936 independent reflections, 7434 reflections with $I > 2\sigma(I)$, R_{int} = 0.051.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.050 [$I > 2\sigma(I)$], wR_2 = 0.138, 420 parameters. The H atoms were refined using a riding model, *S* = 1.022, residual electron density 0.5 (0.80 Å from C2)/ -0.4 (0.22 Å from H1A) e · $Å^{-3}$. **CCDC-1910056**.

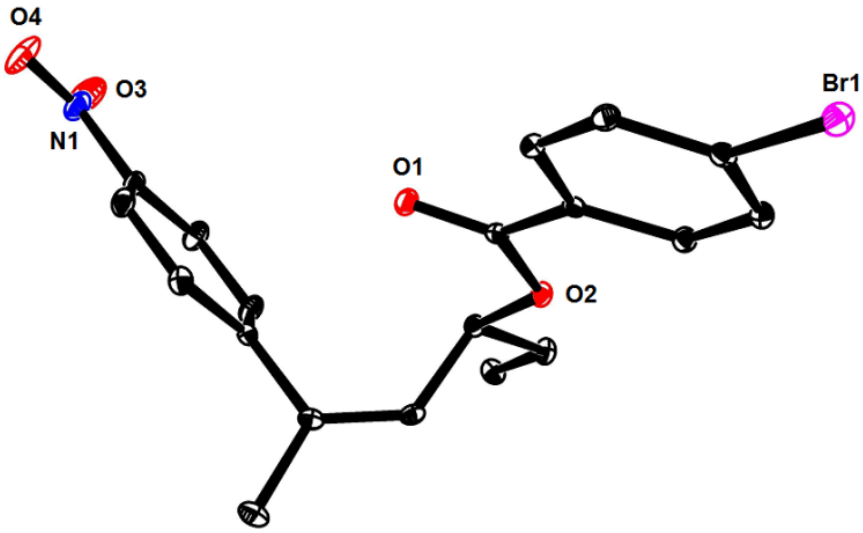


Figure S2. Structure of bromo benzoate **30** in the solid state, which proves that the parent alkenylboronate **8c** must have been formed by *trans* hydroboration; hydrogen atoms are omitted for clarity

X-ray Crystal Structure Analysis of Compound 30. C_{19} H_{18} Br N O_4, *Mr* = 404.25 g · mol^{-1}, colorless plate, crystal size 0.123 x 0.052 x 0.021 mm^3, monoclinic, space group $P2_1/c$, *a* = 19.464(3) Å, *b* = 12.6202(19) Å, *c* = 7.2159(11) Å, *β* = 93.174(3)°, *V* = 1769.8(5) $Å^3$, *T* = 100(2) K, *Z* = 4, D_{calc} = 1.517 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*α) = 2.346 mm^{-1}, Gaussian absorption correction (T_{min} = 0.81, T_{max} = 0.96), Bruker-AXS Kappa Mach3 APEX-II diffractometer, 3.145 < θ < 30.992°, 51422 measured reflections, 5625 independent reflections, 4926 reflections with $I > 2\sigma(I)$, R_{int} = 0.032.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.023 [$I > 2\sigma(I)$], wR_2 = 0.058, 232 parameters. The H atoms were refined using a riding model, *S* = 1.029, residual electron density 0.4 (0.69 Å from C8)/ -0.3 (0.52 Å from Br1) e · $Å^{-3}$. **CCDC-1910058**.

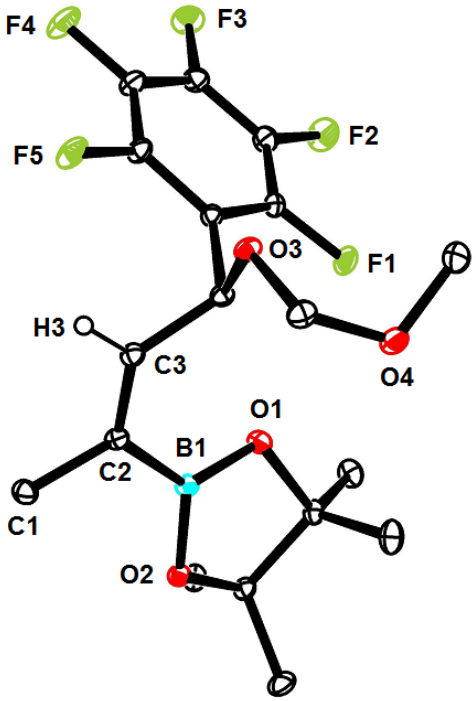


Figure S3. Structure of compound **21** in the solid state; hydrogen atoms – except for H3 residing *trans* to B1 – are omitted for clarity

X-ray Crystal Structure Analysis of Compound 21. C_{18} H_{22} B F_5 O_4, *Mr* = 408.16 g · mol^{-1}, colorless prism, crystal size 0.14 x 0.14 x 0.06 mm^3, monoclinic, space group $P2_1/c$, *a* = 10.9379(6) Å, *b* = 7.3102(6) Å, *c* = 24.362(2) Å, β = 100.590(6)°, *V* = 1914.8(3) $Å^3$, *T* = 100(2) K, *Z* = 4, D_{calc} = 1.416 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*α) = 0.128 mm^{-1}, Gaussian absorption correction (T_{min} = 0.98, T_{max} = 0.99), Bruker-AXS Kappa Mach3 APEX-II diffractometer, 2.913 < θ < 33.066°, 44172 measured reflections, 7239 independent reflections, 6063 reflections with $I > 2\sigma(I)$, R_{int} = 0.041.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.042 [$I > 2\sigma(I)$], wR_2 = 0.117, 275 parameters. The H atoms were refined using a riding model, *S* = 1.089, residual electron density 0.4 (0.73 Å from C2)/ -0.2 (0.54 Å from F1) e · $Å^{-3}$. **CCDC-1910057**.

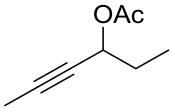
General: Unless otherwise noted, all reactions were carried out under an Ar atmosphere in flame-dried glassware using anhydrous solvents. Anhydrous solvents were prepared by distillation over the indicated drying agents prior to use and were manipulated under Ar: THF, Et_2O (Mg/anthracene), toluene (Na/K), CH_2Cl_2 (Mg), MeOH (activated 3 Å molecular sieves). Thin layer chromatography (TLC): Macherey-Nagel precoated plates (POLYGRAM®SIL/UV254). Flash chromatography: Merck silica gel 60 (40−63 µm) with technical grade solvents. Silica gel used to purify boronic esters was deactivated with triethylamine.[1] NMR: Spectra were recorded on Bruker DPX 300 or AV VIII 400 spectrometers in the solvents indicated; the solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_C = 77.16 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm); carbon centers directly bound to boron centers were typically not observed in the corresponding $^{13}C\{^1H\}$ NMR spectra due to line broadening. IR: Bruker ALPHA Platinum-ATR, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS: Finnigan MAT 8200 (EI, 70 eV), Bruker ESQ 3000 (ESI), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Finnigan Mat 95. Unless otherwise noted, all commercially available compounds (ABCR, Acros, Aldrich, Alfa Aesar, TCI) were used as received. $[Cp^*Rh(MeCN)_3][PF_6]$[2] and $[Cp^*RuCl]_4$ [3] were prepared following literature procedures and were stored under Ar. Compound **39** was prepared according to literature reports and spectra data was in agreement with previously.[4]

Isomeric ratios were determined from the ^1H NMR spectra of unpurified reaction products. The stereochemistry of the vinylboronic ester products was confirmed by nOe NMR spectroscopic studies, and the NMR spectra were compared against the products formed by *cis*-hydroboration via known Cu-catalyzed procedures.[5] Reported yields are for the isomeric mixtures (where more than one isomer was formed) and NMR spectroscopic data is tabulated for the major isomer. NMR spectra contain a mixture of isomers (where more than one isomer was formed).

Due to the limited stability of alkenylboronate products, attempts to obtain analytically pure samples by flash column chromatography often results in considerable loss of material. In particular, complete removal of other isomers can be challenging because of very similar retention times. Therefore, certain spectra do show trace impurities (usually < 5%, see S-27 ff.).

Substrates

Compound 7a. A flame-dried two-neck 100 mL round-bottom flask equipped with a magnetic stirring bar



was charged with 4-hexyn-3-ol (1.5 mL, 13.6 mmol), 40 mL of CH_2Cl_2, DMAP (478 mg, 4.1 mmol) and Et_3N (7.5 mL, 54.3 mmol). Lastly, acetic anhydride (2.5 mL, 27.1 mmol) was added, and the resulting mixture was stirred at room temperature under Ar overnight. Upon completion, the reaction was quenched with a sat. aqueous NH_4Cl solution (~40 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The organic layers were combined, washed with brine (~50 mL) and dried over Na_2SO_4, the drying agent was filtered off, and

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1 Kim, B.-S.; Hussain, M. M.; Hussain, N.; Walsh, P. J. *Chem. Eur. J.* **2014,** *20*, 11726-11739.

2 Mbaye, M. D.; Demerseman, B.; Renaud, J.-L.; Toupet, L.; Bruneau, C. *Adv. Synth. Catal.* **2004,** *346*, 835-841.

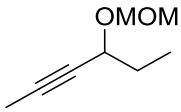
3 Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989,** *111*, 1698-1719.

4 Yukitoshi, F.; Kiitiro, U. *Bull. Chem. Soc. Jpn.* **1991,** *64*, 2013-2015.

5 Hesse, M. J.; Butts, C. P.; Willis, C. L.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2012,** *51*, 12444-12448.

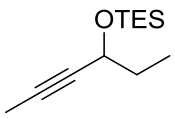
the filtrate was concentrated *in vacuo*. The crude product was purified by flash chromatography using 10% EtOAc in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a colorless oil (1.70 g, 89%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.28 (tq, $^{3}J_{HH}$ = 6.4 Hz, $^{5}J_{HH}$ = 2.2 Hz, 1H), 2.07 (s, 3H), 1.85 (d, $^{5}J_{HH}$ = 2.2 Hz, 3H), 1.78 – 1.71 (m, 2H), 0.99 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 170.3, 81.8, 76.7, 65.9, 28.4, 21.3, 9.5, 3.8. IR (ṽ, film, cm^{-1}): 2974, 2939, 2880, 2261, 1736, 1456, 1371, 1295, 1228, 1167, 1127, 1084, 1041, 1016, 956, 887, 830, 809, 756, 667, 605, 547, 530, 437. HRMS (ESI): *m*/*z* calcd for $C_8H_{12}O_2Na$ ([M+Na]$^{+}$): 163.0729; found: 163.0730.

Compound 7b. A flame-dried 50 mL Schlenk flask equipped with a magnetic stirring bar was charged



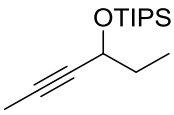
under Ar with 4-hexyn-3-ol (0.7 mL, 6.3 mmol) and 25 mL of CH_2Cl_2. Chloromethyl methyl ether (0.6 mL, 7.6 mmol) was injected into the flask and the resulting mixture was cooled to 0 °C. *N*,*N*-Diisopropylethylamine (1.4 mL, 8.2 mmol) was added dropwise to the cooled solution, and the resulting reaction mixture was allowed to slowly warm to room temperature overnight. The reaction was not complete, so an additional 400 µL of MOMCl and 1 mL of DIPEA were added. Once complete, the reaction was quenched with distilled H_2O (~25 mL), the organic layer was collected, and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The organic layers were combined, washed with brine (~40 mL), and then dried over Na_2SO_4. The drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash chromatography using 5% EtOAc in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a colorless oil (616 mg, 68%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.95 (d, $^{2}J_{HH}$ = 6.7 Hz, 1H), 4.58 (d, $^{2}J_{HH}$ = 6.7 Hz, 1H), 4.23 (tq, $^{3}J_{HH}$ = 6.4 Hz, $^{5}J_{HH}$ = 2.1 Hz, 1H), 3.37 (s, 3H), 1.85 (d, $^{5}J_{HH}$ = 2.1 Hz, 3H), 1.76 – 1.68 (m, 2H), 1.01 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 94.0, 81.7, 77.8, 67.3, 55.7, 29.2, 9.9, 3.7. IR (ṽ, film, cm^{-1}): 2974, 2939, 2880, 2261, 1736, 1456, 1371, 1295, 1228, 1167, 1127, 1084, 1041, 1016, 956, 887, 830, 809, 756, 667, 605, 547, 530, 437. HRMS (ESI): m/z calcd for $C_8H_{14}O_2Na$ ([M+Na]$^{+}$): 165.0886; found: 165.0888.

Compound 7c. A flame-dried 100 mL Schlenk flask equipped with a magnetic stirring bar was charged

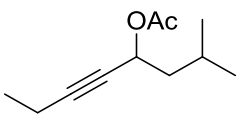


under Ar with 30 mL of CH_2Cl_2. The vessel was cooled to –78 °C, and 4-hexyn-3-ol (1 mL, 9.0 mmol) was added. Lutidine (1.6 mL, 13.6 mmol) was then injected, followed by triethylsilyl chloride (1.7 mL, 10 mmol). When the silane was added there was a notable effervescence. The reaction was allowed to slowly warm to room temperature overnight. The reaction mixture was washed with distilled H_2O (~30 mL). The organic layer was isolated and dried over Na_2SO_4, the drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash chromatography using 100% hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a colorless oil (2.1 g, quant.). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.25 (tq, $^{3}J_{HH}$ = 6.3 Hz, $^{5}J_{HH}$ = 2.1 Hz, 1H), 1.82 (d, $^{5}J_{HH}$ = 2.1 Hz, 3H), 1.68 – 1.61 (m, 2H), 1.00 – 0.94 (m, 12 H), 0.71 – 0.57 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 81.0, 79.9, 64.3, 32.2, 9.8, 6.9, 5.0, 3.7. IR (ṽ, film, cm^{-1}): 2954, 2938, 2919, 2876, 1459, 1414, 1379, 1347, 1238, 1157, 1117, 1098, 1075, 1058, 1003, 973, 900, 884, 833, 725, 670, 532, 428, 422. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{24}OSiNa$ ([M+Na]$^{+}$): 235.1489; found: 235.1489.

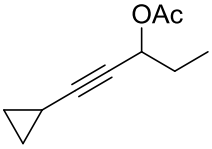
Compound 7d. A flame-dried two-neck 50 mL round-bottom flask equipped with a magnetic stirring bar was charged under Ar with 4-hexyn-3-ol (0.5 mL, 4.7 mmol) and 15 mL of CH_2Cl_2. The solution was cooled to –78 °C, lutidine (0.8 mL, 7.0 mmol) was introduced, followed by triisopropylsilyl triflate (1.5 mL, 5.6 mmol). The mixture was allowed to slowly warm to room temperature overnight. Once the reaction was complete, the mixture was washed with distilled H_2O (~25 mL) and brine (~25 mL). The organic phase was then dried over Na_2SO_4, the drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude material was purified by flash chromatography using 100% hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a colorless oil (981 mg, 83%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.37 (tq, $^3J_{HH}$ = 6.2 Hz, $^5J_{HH}$ = 2.1 Hz, 1H), 1.82 (d, $^5J_{HH}$ = 2.1 Hz, 3H), 1.67 (dq, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 6.2 Hz, 2H), 1.13 – 1.05 (m, 21 H), 0.98 (t, $^3J_{HH}$ = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 81.3, 79.9, 64.6, 32.3, 18.21, 18.17, 12.5, 9.6, 3.6. IR (ṽ, film, cm^{-1}): 2961, 2942, 2892, 2866, 1716, 1463, 1383, 1367, 1347, 1287, 1257, 1157, 1117, 1100, 1059, 1010, 919, 882, 829, 809, 716, 678, 656, 563, 529, 513, 484, 462, 449, 415. HRMS (ESI): m/z calcd for $C_{15}H_{30}OSiNa$ ([M+Na]$^+$): 277.1958; found: 277.1960.



Compound S1. A flame-dried 50 mL Schlenk flask equipped with a magnetic stirring bar was charged with 2-methyl-5-octyn-4-ol (1.2 mL, 7.1 mmol). The flask was flushed with Ar, and 20 mL of CH_2Cl_2 were added, followed by DMAP (280 mg, 2.1 mmol) and Et_3N (4 mL, 28.5 mmol). Lastly, acetic anhydride (1.4 mL, 14.3 mmolv.) was added and the resulting mixture was stirred at room temperature under Ar overnight. The reaction was quenched with a sat. aqueous NH_4Cl solution (~20 mL) and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL). The organic layers were combined, washed with brine (~20 mL) and dried over Na_2SO_4, the drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude material was purified by flash chromatography using 50% CH_2Cl_2 in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a colorless oil (942 mg, 73%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.40 (tt, $^3J_{HH}$ = 7.2 Hz, $^5J_{HH}$ = 2.0 Hz, 1H), 2.21 (qd, $^3J_{HH}$ = 7.5 Hz, $^5J_{HH}$ = 2.0 Hz, 2H), 2.06 (s, 3H), 1.84 – 1.72 (m, 1H), 1.69 – 1.56 (m, 2H), 1.12 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 0.93 (d, $^3J_{HH}$ = 6.5 Hz, 6 H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 170.3, 87.5, 77.3, 63.5, 44.1, 24.9, 22.7, 22.5, 21.3, 13.8, 12.6. IR (ṽ, film, cm^{-1}): 2958, 2872, 1740, 1469, 1370, 1319, 1227, 1164, 1120, 1045, 1015, 974, 961, 940, 921, 605, 560, 534. HRMS (ESI): *m*/*z* calcd for $C_{11}H_{18}O_2Na$ ([M+Na]$^+$): 205.1199; found: 205.1201.

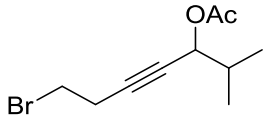


Compound S2. A flame-dried 100 mL Schlenk flask equipped with a magnetic stirring bar was charged with 19 mL of THF and ethynylcyclopropane (1 mL, 12 mmol). The solution was cooled to –78 °C before a 1.5 M solution of *n*-BuLi in hexane (6.7 mL, 10 mmol) was added dropwise to the vessel, and the resulting mixture was allowed to stir at –78 °C for 30 min. Propionaldehyde (0.9 mL, 12 mmol) was then added to the flask, and the resulting mixture was allowed to slowly warm to room temperature overnight. The reaction was quenched with acetic anhydride (1.1 mL, 12 mmol) at room temperature and the resulting cloudy, yellow mixture was stirred at room temperature. Once all of the alcohol was consumed, the sat. aqueous NH_4Cl solution (~20 mL) was added, the layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with brine (~20 mL) and dried over Na_2SO_4, the drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude



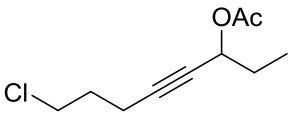
product was purified by flash chromatography using 5% EtOAc in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a colorless oil (1.43 g, 86%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.28 (td, $^{3}J_{HH}$ = 6.5 Hz, $^{5}J_{HH}$ = 1.9 Hz, 1H), 2.06 (s, 3H), 1.76 – 1.69 (m, 2H), 1.28 – 1.21 (m, 1H), 0.97 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H), 0.79 – 0.72 (m, 2H), 0.70 – 0.66 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 170.2, 89.4, 72.8, 65.8, 28.5, 21.3, 9.5, 8.5, -0.4. IR (ṽ, film, cm^{-1}): 3095, 3012, 2973, 2939, 2880, 2247, 1738, 1457, 1429, 1369, 1293, 1228, 1165, 1112, 1091, 1051, 1017, 954, 912, 888, 869, 813, 731, 605, 548, 476. HRMS (ESI): *m*/*z* calcd for $C_{10}H_{14}O_2Na$ ([M+Na]$^{+}$): 189.0886; found: 189.0887.

Compound S3. A flame-dried 50 mL Schlenk flask equipped with a magnetic stirring bar was charged



with 19 mL of THF and 4-bromo-1-butyne (0.9 mL, 10 mmol). The solution was cooled to −78 °C before a 1.45 M solution of *n*-BuLi in hexane (6.6 mL, 9.5 mmol) was added dropwise, and the resulting mixture was allowed to stir at −78 °C for 30 min. Isobutyraldehyde (1.1 mL, 12 mmol) was then added, and the resulting mixture was allowed to slowly warm to room temperature overnight. The reaction mixture was quenched with acetic anhydride (1.0 mL, 11 mmol) at room temperature. The cloudy mixture was stirred at room temperature; once all of the alcohol was consumed, sat. aqueous NH_4Cl solution (~20 mL) was added, the layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The organic layers were combined, washed with brine (~20 mL) and dried over Na_2SO_4. The drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude material was purified by flash chromatography using 5% EtOAc in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a colorless oil (1.52 g, 65%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.19 (dt, $^{3}J_{HH}$ = 5.6 Hz, $^{5}J_{HH}$ = 2.0 Hz, 1H), 3.43 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H), 2.79 (td, $^{3}J_{HH}$ = 7.2 Hz, $^{5}J_{HH}$ = 2.0 Hz, 2H), 2.08 (s, 3H), 2.02 – 1.92 (m, 1H), 1.02 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H), 0.99 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 170.3, 83.3, 78.6, 69.3, 32.6, 29.5, 23.4, 21.2, 18.4, 17.6. IR (ṽ, film, cm^{-1}): 2967, 2931, 2875, 1736, 1469, 1435, 1387, 1370, 1358, 1333, 1272, 1228, 1159, 1116, 1102, 1079, 1018, 981, 962, 944, 901, 873, 842, 818, 762, 668, 605, 566, 548, 510, 477, 457, 429, 413. HRMS (ESI): *m*/*z* calcd for $C_{10}H_{15}O_2BrNa$ ([M+Na]$^{+}$): 269.0148; found: 269.0149.

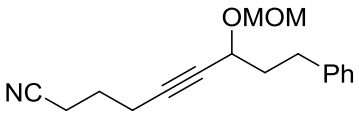
Compound S4. A flame-dried 50 mL Schlenk flask equipped with a magnetic stirring bar was charged



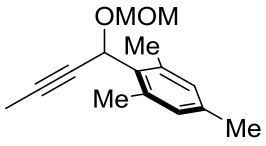
with 15 mL of THF and 5-chloro-1-pentyne (0.9 mL, 8.4 mmol). The solution was cooled to −78 °C, a 1.6 M solution of *n*-BuLi in hexane (5 mL, 8.0 mmol) was added dropwise, and the resulting mixture was stirred at −78 °C for 30 min. Propionaldehyde (0.7 mL, 10 mmol) was then added, and the resulting mixture was allowed to slowly warm to room temperature overnight. The reaction mixture was quenched with acetic anhydride (0.9 mL, 9 mmol) at room temperature. The cloudy mixture was stirred at room temperature, and once all of the alcohol was consumed, sat. aqueous NH_4Cl solution (~20 mL) was added, the layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The organic layers were combined, washed with brine (~20 mL) and dried over Na_2SO_4. The drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude material was purified by flash chromatography using 5% EtOAc in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a colorless oil (700 mg, 43%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.29 (tt, $^{3}J_{HH}$ = 6.5 Hz, $^{5}J_{HH}$ = 2.0 Hz, 1H), 3.63 (t, $^{3}J_{HH}$ = 6.4 Hz, 2H), 2.41 (td, $^{3}J_{HH}$ = 6.8 Hz, $^{5}J_{HH}$ = 2.0 Hz, 2H), 2.08 (s, 3H), 1.99 – 1.93 (m, 2H), 1.75 (p, $^{3}J_{HH}$ = 7.4 Hz, 2H), 0.99 (t, $^{3}J_{HH}$ = 7.4 Hz,

3H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 170.2, 84.2, 78.7, 65.7, 43.7, 31.3, 28.4, 21.2, 16.3, 9.5. IR (ṽ, film, cm^{-1}): 2971, 2939, 2879, 2252, 1736, 1434, 1371, 1292, 1228, 1165, 1125, 1084, 1042, 1016, 957, 888, 859, 827, 770, 725, 655, 606, 527. HRMS (ESI): *m*/*z* calcd for $C_{10}H_{15}ClO_2Na$ ($[M+Na]^+$): 225.0653; found: 225.0654.

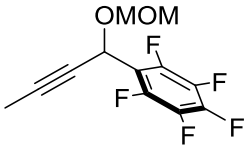
Compound S5. A flame-dried 25 mL Schlenk flask equipped with a magnetic stirring bar was charged with the requisite alcohol (299 mg, 1.3 mmol) and 5 mL of CH_2Cl_2. The solution was cooled to 0 °C before chloromethyl methyl ether (0.12 mL, 1.6 mmol) was injected. *N*,*N*-Diisopropylethylamine (0.3 mL, 1.7 mmol) was added dropwise to the cooled solution, and the resulting mixture was allowed to slowly warm to room temperature overnight. Once complete, the reaction was quenched with distilled H_2O (~5 mL), the organic layer was collected, and the aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL). The organic combined layers were washed with brine (~10 mL) and dried over Na_2SO_4. The drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash chromatography using 20% EtOAc in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a colorless oil (345 mg, 96%). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.31 – 7.28 (m, 2H), 7.22 – 7.18 (m, 3H), 4.92 (d, $^2J_{HH}$ = 6.8 Hz, 1H), 4.61 (d, $^2J_{HH}$ = 6.8 Hz, 1H), 4.33 (tt, $^3J_{HH}$ = 6.5 Hz, $^5J_{HH}$ = 1.9 Hz, 1H), 3.39 (s, 3H), 2.86 – 2.72 (m, 2H), 2.49 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 2.43 (td, $^3J_{HH}$ = 6.8 Hz, $^5J_{HH}$ = 1.9 Hz, 2H), 2.11 – 1.97 (m, 2H), 1.87 (p, $^3J_{HH}$ = 7.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 141.5, 128.58, 128.55, 126.1, 119.2, 94.3, 83.5, 80.8, 65.5, 55.9, 37.7, 31.7, 24.7, 18.0, 16.3. IR (ṽ, film, cm^{-1}): 3027, 2945, 2887, 2855, 2844, 2823, 2247, 1603, 1496, 1454, 1433, 1402, 1344, 1312, 1298, 1258, 1213, 1180, 1147, 1097, 1085, 1059, 1020, 968, 940, 918, 893, 885, 872, 845, 805, 787, 750, 700, 580, 492. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{21}NO_2Na$ ($[M+Na]^+$): 294.1464; found: 294.1464.



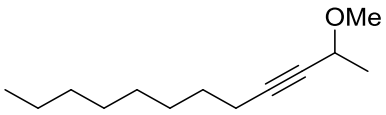
Compound S6. A flame-dried 50 mL Schlenk flask equipped with a magnetic stirring bar was charged with 2,4,6-trimethylbenzaldehyde (0.57 mL, 3.8 mmol) and 20 mL of THF. The resulting solution was cooled to 0 °C, a 0.5 M solution of 1-propynylmagnesium bromide in THF (10 mL, 5 mmol) was added dropwise, and the resulting mixture was allowed to warm to room temperature. After 1.5 h, the reaction was quenched with chloromethyl methyl ether (0.44 mL, 5.8 mmol) at room temperature. Stirring was continued overnight before a sat. aqueous NH_4Cl solution (~20 mL) was added. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The organic layers were combined and dried over Na_2SO_4. the drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude material was purified by flash chromatography using 5% EtOAc in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a pale yellow oil (979 mg, quant.). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 6.84 (br s, 2H), 4.85 (d, $^2J_{HH}$ = 6.8 Hz, 1H), 4.49 (d, $^2J_{HH}$ = 6.8 Hz, 1H), 3.37 (s, 3H), 2.46 (s, 6H), 2.25 (s, 3H), 1.85 (d, $^5J_{HH}$ = 2.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 137.8, 137.3, 131.9, 129.9, 93.3, 82.6, 76.8, 62.8, 55.6, 21.0, 20.3, 4.0. IR (ṽ, film, cm^{-1}): 2948, 2920, 2884, 2822, 1735, 1610, 1580, 1448, 1396, 1378, 1324, 1296, 1262, 1210, 1146, 1124, 1091, 1019, 963, 927, 913, 843, 800, 782, 734, 618, 581, 536, 495, 445, 409. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{20}O_2Na$ ($[M+Na]^+$): 255.1355; found: 255.1357.



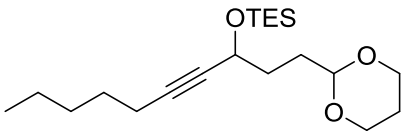
Compound S7. A flame-dried 50 mL Schlenk flask equipped with a magnetic stirring bar was charged with pentafluorobenzaldehyde (0.47 mL, 3.8 mmol) and 20 mL of THF. The resulting solution was cooled to 0 °C, a 0.5 M solution of 1-propynylmagnesium bromide in THF (10 mL, 5 mmol) was added dropwise, and the resulting mixture was allowed to warm to room temperature. After 1.5 h, the reaction was quenched with chloromethyl methyl ether (0.44 mL, 5.8 mmol) at room temperature. Stirring was continued overnight before a sat. aqueous NH_4Cl solution (~20 mL) was introduced. The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The organic layers were combined and dried over Na_2SO_4, the drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash chromatography using 5% EtOAc in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a pale yellow oil (1.06 g, 98%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.73 – 5.71 (m, 1H), 4.98 (d, $^2J_{HH}$ = 7.0 Hz, 1H), 4.60 (d, $^2J_{HH}$ = 7.0 Hz, 1H), 3.36 (s, 3H), 1.88 (d, $^5J_{HH}$ = 2.3 Hz, 3H). ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ –142.0 - –142.1 (m, 2F), –153.9 (tt, $^3J_{FF}$ = 21 Hz, $^4J_{FF}$ = 2 Hz, 1F), –161.7 - –161.9 (m, 2F). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 145.2 (dm, $^1J_{CF}$ ~ 257 Hz), 141.5 (dm, $^1J_{CF}$ ~ 256 Hz), 137.7 (dm, $^1J_{CF}$ ~ 254 Hz), 113.5, 94.1, 84.2, 73.9, 57.4, 55.9, 3.8. IR (ṽ, film, cm^{-1}): 2953, 2893, 2245, 1743, 1654, 1522, 1504, 1443, 1429, 1398, 1353, 1328, 1304, 1213, 1165, 1150, 1116, 1096, 1021, 994, 968, 928, 836, 762, 733, 693, 654, 597, 576, 492, 452. HRMS (ESI): *m*/*z* calcd for $C_{12}H_9O_2F_5Na$ ([M+Na]$^+$): 303.0415; found: 303.0416.



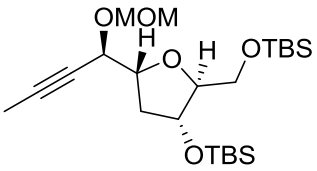
Compound S8. A flame-dried 50 mL Schlenk flask equipped with a magnetic stirring bar was charged with 1-decyne (2.0 mL, 11.1 mmol) and 10 mL of THF. The resulting solution was cooled to –78 °C before a 1.6 M solution of *n*-BuLi in hexane (5.8 mL, 9.3 mmol) was added dropwise, and the resulting mixture was stirred at –78 °C for 30 min. Then, 0.67 mL of *freshly distilled* acetaldehyde was added to the flask. The reaction was stirred at –78 °C for 10 min and was then warmed to room temperature. After 1 h an aliquot of the reaction mixture was quenched with distilled H_2O for GC/MS analysis, which showed the desired alcohol and unreacted alkyne. The reaction mixture was re-cooled to 0 °C and quenched with methyl iodide (750 µL, 12.0 mmol). The mixture was stirred overnight while slowly warming to room temperature. The reaction was quenched with a sat. aqueous $NaHCO_3$ solution (~10 mL), the layers were separated, and the aqueous phase was extracted with EtOAc (2 x 10 mL). The organic layers were combined, washed with brine (~20 mL) and dried over Na_2SO_4, the drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude material was purified by flash chromatography using 5% EtOAc in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a yellow oil (941 mg, 52%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.05 (qt, $^3J_{HH}$ = 6.6 Hz, $^5J_{HH}$ = 1.9 Hz, 1H), 3.38 (s, 3H), 2.21 (td, $^3J_{HH}$ = 7.1 Hz, $^5J_{HH}$ = 1.9 Hz, 2H), 1.54 – 1.47 (m, 2H), 1.40 – 1.27 (m, 13H), 0.90 – 0.86 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 85.9, 79.9, 67.2, 56.2, 32.0, 29.3, 29.2, 29.0, 28.9, 22.8, 22.5, 18.8, 14.3. IR (ṽ, film, cm^{-1}): 2985, 2925, 2855, 2819, 2244, 1464, 1371, 1331, 1205, 1148, 1114, 1083, 1059, 1001, 911, 852, 734, 649, 551, 469, 426, 409. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{24}ONa$ ([M+Na]$^+$): 219.1719; found: 219.1718.



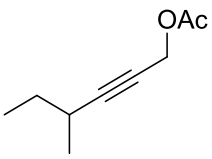
Compound S9. A flame-dried 50 mL Schlenk flask equipped with a magnetic stirring bar was charged with 2-octyn-1-al (0.57 mL, 4.0 mmol) and 10 mL of THF. The resulting solution was cooled to 0 °C before a 0.5 M solution of (1,3-dioxan-2-ylethyl)magnesium bromide in THF (9.7 mL, 4.8 mmol) was added dropwise. The resulting mixture was warmed to room temperature and stirred for 1.5 h, before the mixture was re-cooled to 0 °C and the reaction quenched with triethylsilyl chloride (0.88 mL, 5.2 mmol). Stirring was continued overnight while slowly warming to room temperature. Distilled water (10 mL) was added, the layers were separated, and the aqueous phase was extracted with EtOAc (2 x 10 mL). The organic layers were combined, washed with brine (~20 mL) and dried over Na_2SO_4. The drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude material was purified by flash chromatography using 5% EtOAc in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a yellow oil (1.33 g, 93%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.55 – 4-52 (m, 1H), 4.38 – 4.34 (m, 1H), 4.11 – 4.07 (m, 2H), 3.78 – 3.71 (m, 2H), 2.15 (td, $^3J_{HH}$ = 7.1 Hz, $^5J_{HH}$ = 1.9 Hz, 2H), 2.11 – 2.01 (m, 1H), 1.75 – 1.71 (m, 4H), 1.51 – 1.43 (m, 2H), 1.38 – 1.25 (m, 5H), 0.96 (t, $^3J_{HH}$ = 7.9 Hz, 9H), 0.89 (t, $^3J_{HH}$ = 7.1 Hz, 3H), 0.70 – 0.58 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 102.4, 84.8, 81.5, 67.0, 62.8, 33.6, 31.2, 28.5, 26.0, 22.4, 18.8, 14.1, 7.0, 5.0. IR (ṽ, film, cm^{-1}): 2954, 2933, 2875, 2851, 2731, 2660, 1459, 1431, 1405, 1378, 1339, 1282, 1240, 1216, 1145, 1096, 1044, 1004, 976, 941, 928, 893, 856, 797, 726, 672, 641, 551, 477. HRMS (ESI): *m*/*z* calcd for $C_{20}H_{38}O_3SiNa$ ([M+Na]$^+$): 377.2482; found: 377.2485.



Compound S10.[6] ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.94 (d, $^2J_{HH}$ = 6.5 Hz, 1H), 4.68 (d, $^3J_{HH}$ = 6.5 Hz, 1H), 4.52 (dq, $^3J_{HH}$ = 8.1 Hz, $^5J_{HH}$ = 2.1 Hz, 1H), 4.34 – 4.31 (m, 1H), 4.15 (td, $^3J_{HH}$ = 8.0 Hz, 4.4 Hz, 1H), 3.90 – 3.87 (m, 1H), 3.63 (dd, $^3J_{HH}$ = 10.8 Hz, 3.8 Hz, 1H), 3.50 (dd, $^3J_{HH}$ = 10.8 Hz, 5.8 Hz, 1H), 3.40 (s, 3H), 2.26 – 2.19 (m, 1H), 2.02 – 1.97 (m, 1H), 1.85 (d, $^5J_{HH}$ = 2.1 Hz, 3H), 0.894 (s, 9H), 0.885 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H), 0.04 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ 94.2, 87.3, 82.9, 81.1, 75.8, 73.2, 69.3, 63.5, 55.5, 37.4, 26.1, 25.8, 18.5, 18.0, 3.8, –4.6, –4.7, –5.2, –5.3. IR (ṽ, film, cm^{-1}): 2953, 2929, 2886, 2857, 1472, 1389, 1361, 1253, 1213, 1150, 1100, 1054, 1031, 938, 835, 776, 669. HRMS (ESI): *m*/*z* calcd for $C_{23}H_{46}O_5Si_2Na$ ([M+Na]$^+$): 481.2776; found: 481.2775.



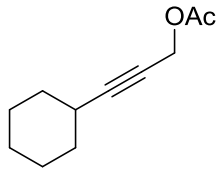
Compound S11. A flame-dried 50 mL Schlenk flask equipped with a magnetic stirring bar was charged with 18 mL of THF and 3-methyl-1-pentyne (1.1 mL, 9.7 mmol). The solution was cooled to –78 °C before a 1.45 M solution of *n*-BuLi in hexane (6.2 mL, 8.9 mmol) was added dropwise, and the resulting mixture was allowed to stir at –78 °C for 30 min. Paraformaldehyde (369 mg, 11.7 mmol) was then added and the resulting mixture was warmed to room temperature. The cloudy, yellow mixture was stirred at room temperature until all of the paraformaldehyde was consumed, the mixture was re-cooled to 0 °C and the reaction quenched with acetic anhydride (1.0 mL, 10.7 mmol). After stirring overnight, a sat. aqueous NH_4Cl solution (~20 mL) was added, the layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (2x10 mL). The organic layers were combined, washed with brine (~20 mL) and dried over Na_2SO_4. The drying agent was filtered off, the filtrate was concentrated *in vacuo* and the residue was



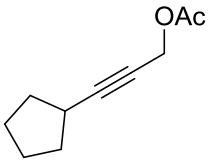
[6] Ilg, M. K., *Dissertation*, Technical University Dortmund, 2017

purified by flash chromatography using 5% EtOAc in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a colorless oil (1.387 g, 97%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.67 (d, $^{5}J_{HH}$ = 2.1 Hz, 2H), 2.45 – 2.35 (m, 1H), 2.09 (s, 3H), 1.50 – 1.42 (m, 2H), 1.15 (d, $^{3}J_{HH}$ = 7.0 Hz, 3H), 0.97 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 170.5, 92.0, 74.2, 53.0, 29.8, 27.7, 21.0, 20.5, 11.8. IR (ṽ, film, cm^{-1}): 2968, 2934, 2877, 2240, 1744, 1454, 1378, 1359, 1336, 1218, 1179, 1134, 1094, 1072, 1022, 966, 914, 828, 807, 787, 712, 628, 605, 524, 475, 440, 414. HRMS (ESI): *m*/*z* calcd for $C_9H_{14}O_2Na$ ($[M+Na]^+$): 177.0886; found: 177.0886.

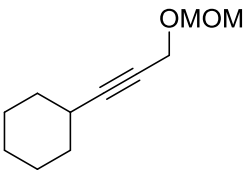
Compound S12. Prepared analogously using cyclohexylacetylene as the substrate; colorless oil (913 mg, 80%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.68 (d, $^{5}J_{HH}$ = 2.0 Hz, 2H), 2.43 – 2.36 (m, 1H), 2.09 (s, 3H), 1.83 – 1.77 (m, 2H), 1.72 – 1.65 (m, 2H), 1.54 – 1.49 (m, 1H), 1.47 – 1.38 (m, 2H), 1.35 – 1.23 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 170.6, 91.9, 73.9, 53.1, 32.6, 29.2, 25.9, 25.0, 21.0. IR (ṽ, film, cm^{-1}): 2929, 2854, 2236, 1744, 1449, 1377, 1359, 1317, 1217, 1156, 1131, 1085, 1022, 963, 918, 889, 861, 830, 632, 605, 552, 496, 473, 426, 405. HRMS (ESI): *m*/*z* calcd for $C_{11}H_{16}O_2Na$ ($[M+Na]^+$): 203.1042; found: 203.1043.



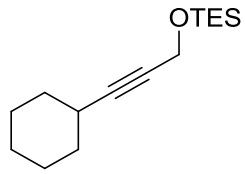
Compound S13. Prepared analogously using cyclopentylacetylene as the reagent; colorless oil (1.796 g, quant.). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.66 (d, $^{5}J_{HH}$ = 2.1 Hz, 2H), 2.63 (pt, $^{3}J_{HH}$ = 7.6 Hz, $^{5}J_{HH}$ = 2.1 Hz, 1H), 2.09 (s, 3H), 1.95 – 1.86 (m, 2H), 1.77 – 1.67 (m, 2H), 1.64 – 1.49 (m, 4H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 170.5, 92.0, 73.5, 53.1, 33.7, 30.2, 25.1, 21.0. IR (ṽ, film, cm^{-1}): 2958, 2871, 2239, 1741, 1452, 1377, 1359, 1218, 1105, 1021, 966, 922, 829, 631, 605, 546, 493, 447. HRMS (ESI): *m*/*z* calcd for $C_{10}H_{14}O_2Na$ ($[M+Na]^+$): 189.0886; found: 189.0887.



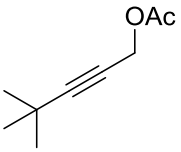
Compound S14. Prepared analogously using chloromethyl methyl ether instead of acetic anhydride to quench the reaction; colorless oil (938 mg, 81%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.71 (s, 2H), 4.21 (d, $^{5}J_{HH}$ = 2.0 Hz, 2H), 3.38 (s, 3H), 2.42 – 2.37 (m, 1H), 1.81 – 1.77 (m, 2H), 1.72 – 1.65 (m, 2H), 1.54 – 1.38 (m, 3H), 1.35 – 1.23 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 94.7, 91.3, 75.3, 55.7, 54.9, 32.7, 29.3, 26.0, 25.0. IR (ṽ, film, cm^{-1}): 2928, 2854, 2823, 2232, 1739, 1448, 1399, 1375, 1359, 1316, 1299, 1267, 1235, 1211, 1149, 1130, 1100, 1042, 988, 940, 921, 889, 859, 822, 767, 638, 589, 541, 498, 431. HRMS (ESI): *m*/*z* calcd for $C_{11}H_{18}O_2Na$ ($[M+Na]^+$): 205.1199; found: 205.1201.



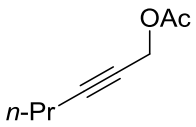
Compound S15. Prepared analogously using triethylchlorosilane instead of acetic anhydride to quench the reaction; colorless oil (649 mg, 40%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.31 (d, $^{5}J_{HH}$ = 2.0 Hz, 2H), 2.39 – 2.34 (m, 1H), 1.81 – 1.78 (m, 2H), 1.72 – 1.66 (m, 2H), 1.53 – 1.49 (m, 1H), 1.45 – 1.36 (m, 2H), 1.30 – 1.23 (m, 3H), 0.98 (t, $^{3}J_{HH}$ = 7.9 Hz, 9H), 0.65 (q, $^{3}J_{HH}$ = 7.9 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 89.6, 78.5, 51.8, 32.7, 29.3, 26.0, 25.1, 6.9, 4.7. IR (ṽ, film, cm^{-1}): 2930, 2875, 2855, 2228, 1449, 1414, 1367, 1262, 1236, 1150, 1129, 1080, 1003, 973, 889, 858, 766, 726, 671, 586, 466. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{29}OSi$ ($[M+H]^+$): 253.1982; found: 253.1982.



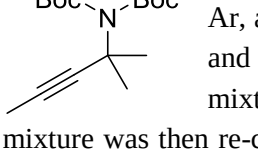
Compound S16. Prepared analogously using 3,3-dimethyl-1-butyne as the substrate; colorless oil (500 mg, 56% yield; the sample contained ~5% pentyl acetate as an impurity). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.66 (s, 2H), 2.09 (s, 3H), 1.22 (s, 9H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 170.5, 95.8, 72.5, 53.0, 30.9, 27.6, 21.0. IR (ṽ, film, cm^{-1}): 2970, 2869, 2248, 1746, 1476, 1457, 1439, 1378, 1361, 1266, 1219, 1073, 1021, 962, 914, 838, 734, 687, 648, 618, 603, 536, 503, 411. HRMS (ESI): *m*/*z* calcd for $C_9H_{14}O_2Na$ ($[M+Na]^+$): 177.0886; found: 177.0888.



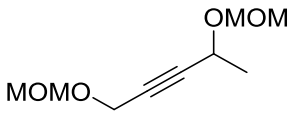
Compound S17. Prepared analogously using 2-hexyn-1-ol as the substrate; colorless oil (1.178 g, 92%). NMR spectral data are in agreement with literature reported values.[7] ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.67 (t, $^{5}J_{HH}$ = 2.2 Hz, 2H), 2.20 (tt, $^{3}J_{HH}$ = 7.1 Hz, $^{5}J_{HH}$ = 2.2 Hz, 2H), 2.09 (s, 3H), 1.58 – 1.49 (m, 2H), 0.98 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 170.5, 87.7, 74.2, 53.0, 22.0, 21.0, 20.9, 13.6. HRMS (ESI): *m*/*z* calcd for $C_8H_{12}O_2Na$ ($[M+Na]^+$): 163.0729; found: 163.0731.



Compound 40. A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with bis-Boc protected 2-methylbut-3-yn-2-amine (98 mg, 0.35 mmol).[8] The flask was flushed with Ar, and 2 mL of dry THF were added. The colorless solution was then cooled to –78 °C, and 0.5 mL of a 1.6 M solution of *n*-BuLi was added dropwise to the flask. The resulting mixture was stirred at –78 °C for 10 min and at 0 °C for another 20 min. The reaction mixture was then re-cooled to –78 °C, and 33 µL of MeI were added. The flask was then removed from the cooling bath and stirring was continued at ambient temperature. Once the reaction had reached completion, it was quenched with distilled water and the aqueous phase extracted with 2 x 5 mL of EtOAc. The combined organic extracts were washed with 25 mL of distilled water, and then 25 mL brine. The organic layer was collected, dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification of the crude product by flash chromatography using 5% EtOAc in hexane as the eluent afforded the desired product as a colorless oil (59 mg, 56%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 1.79 (s, 3H), 1.70 (s, 6H), 1.48 (s, 18H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 152.6, 82.2, 82.1, 78.6, 53.5, 28.7, 28.0, 3.8. IR (ṽ, film, cm^{-1}): 2980, 2935, 1750, 1715, 1478, 1456, 1392, 1367, 1327, 1293, 1256, 1237, 1162, 1138, 1106, 1081, 1052, 1035, 913, 850, 800, 774, 755, 488, 472. HRMS (ESI): *m/z* calcd for $C_{16}H_{27}NO_4Na$ ($[M+Na]^+$): 320.1832; found: 320.1835.



Compound 11.[9] A flame-dried 100 mL Schlenk flask equipped with a magnetic stirring bar was charged with 3-butyn-2-ol (0.57 mL, 7.3 mmol) and 20 mL of THF. The resulting solution was cooled to –78 °C before a 1.6 M solution of *n*-BuLi in hexane (10 mL, 16 mmol) was added dropwise, and the resulting mixture was stirred at –78 °C for 30 min. *Vigorous stirring during the addition of n-BuLi was necessary as the formation of a dianion results in a very thick reaction mixture*.



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7 Onishi, Y.; Nishimoto, Y.; Yasuda, M.; Baba, A. *Org. Lett.* **2014,** *16*, 1176-1179.

8 Kratochvíl, J.; Novák, Z.; Ghavre, M.; Nováková, L.; Růžička, A.; Kuneš, J.; Pour, M. *Org. Lett.* **2015,** *17*, 520-523.

9 Compare: Princival, J. L.; Ferreira, J. G. *Tetrahedron Letters* **2017,** *58*, 3525-3528.

In a second flame-dried 100 mL Schlenk flask equipped with a magnetic stirring bar, $CeCl_3$ (862 mg, 3.6 mmol) and paraformaldehyde (280 mg, 8.7 mmol) were added sequentially, followed by 15 mL of THF. The resulting faintly yellow solution was stirred at room temperature for ~30 min. Then, the cold solution of the dilithium salt (–78 °C) was transferred via a thick cannula to the $CeCl_3$ solution, which was stirred at room temperature. Stirring was continued overnight at room temperature, causing the formation of a thick orange suspension. The reaction was quenched with chloromethyl methyl ether (1.2 mL, 16 mmol). Once TLC indicated complete conversion, sat. aqueous NH_4Cl solution (~20 mL) was introduced, the layers were separated, and the aqueous phase was extracted with EtOAc (2 x 10 mL). The organic layers were combined, washed with brine (~20 mL) and dried over Na_2SO_4. The drying agent was filtered off, the filtrate was concentrated *in vacuo*, and the residue was purified by flash chromatography using 10% EtOAc in hexanes as the eluent. The fractions containing the product were collected and concentrated to afford the desired product as a colorless oil (501 mg, 36%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.90 (d, $^2J_{HH}$ = 6.8 Hz, 1H), 4.69 (s, 2H), 4.59 (d, $^2J_{HH}$ = 6.8 Hz, 1H), 4.49 (qt, $^3J_{HH}$ = 6.7 Hz, $^5J_{HH}$ = 1.6 Hz, 1H), 4.24 (d, $^5J_{HH}$ = 1.6 Hz, 2H), 3.372 (s, 3H), 3.368 (s, 3H), 1.45 (d, $^3J_{HH}$ = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 94.9, 94.2, 85.9, 80.5, 61.5, 55.71, 55.68, 54.5, 22.2. IR (ṽ, film, cm^{-1}): 2987, 2937, 2889, 2824, 2781, 1730, 1447, 1401, 1374, 1337, 1268, 1214, 1149, 1097, 1025, 992, 940, 918, 848, 750, 636, 600, 552, 437. HRMS (ESI): *m*/*z* calcd for $C_9H_{16}O_4Na$ ([M+Na]$^+$): 211.0941; found: 211.0942.

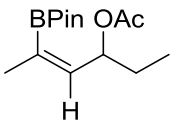
Ruthenium-Catalyzed Hydroboration Reactions

General Procedure for the Ruthenium-Catalyzed Hydroboration of Alkynes. The alkyne substrate (1.0 equiv.) was weighed into a flame-dried Schlenk tube, which was flushed with Ar. CH_2Cl_2 was added to give a 0.3 M colorless solution. [Cp*RuCl]$_4$ (0.0125 equiv.) was then added, causing a color change to dark purple, which is indicative π-complex formation.[10] The vessel was immersed in an ice bath, and (pin)BH (1.2 equiv.) was injected rapidly into the reaction mixture. The vessel was then sealed with a rubber stopper and removed from the ice bath. The resulting solution was stirred at room temperature under Ar, monitoring the reaction progression by GC/MS. Once the reaction was complete, the mixture was purified by rapid filtration through a plug of silica and quick elution of the product using CH_2Cl_2. The combined filtrates were evaporated *in vacuo* to afford the desired product.

Limiting the exposure time of the boronic ester derivatives to silica improved the yield of the isolated material.[1] In cases in which more than one isomer is formed, complete removal of other isomers by chromatographic means can therefore be challenging because of very similar retention times. As a consequence, certain spectra do show trace impurities (usually < 5%, cf. page S-27 ff).

The following compounds were prepared according to this procedure; only the data of the major isomer are compiled:

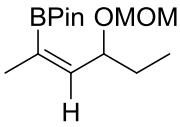
Compound 8a. Yellow oil (76 mg, 64%). ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ 5.89 – 5.87 (m, 1H), 5.77 (dt, $^3J_{HH}$ = 8.8 Hz, 6.6 Hz, 1H), 2.01 (s, 3H), 1.79 (d, $^4J_{HH}$ = 1.6 Hz, 3H), 1.71 – 1.63 (m, 1H), 1.57 – 1.48 (m, 1H), 1.28 (s, 6H), 1.27 (s, 6H), 0.87 (t, $^3J_{HH}$ = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ 170.5, 143.3, 83.5, 75.1, 28.2, 25.04, 25.03, 24.91, 24.89, 22.3, 21.6, 9.6. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.0. IR (ṽ, film,



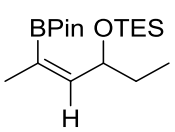
[10] Roşca, D.-A.; Radkowski, K.; Wolf, L. M.; Wagh, M.; Goddard, R.; Thiel, W.; Fürstner, A. *J. Am. Chem. Soc.* **2017,** *139*, 2443-2455.

cm^{-1}): 2976, 2936, 2879, 1733, 1642, 1453, 1421, 1391, 1370, 1305, 1268, 1237, 1166, 1142, 1114, 1087, 1017, 961, 891, 861, 834, 734, 711, 690, 672, 611, 579, 549, 518, 471, 408. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{25}BO_4Na$ ($[M+Na]^+$): 291.1738; found: 291.1737.

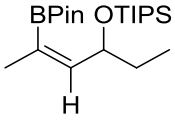
Compound 8b. Colorless oil (120 mg, 87%). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.84 (br d, $^3J_{HH}$ = 9.0 Hz, 1H), 4.67 (d, $^2J_{HH}$ = 6.4 Hz, 1H), 4.55 (dt, $^3J_{HH}$ = 9.0 Hz, 6.6 Hz, 1H), 4.54 (d, $^2J_{HH}$ = 6.4 Hz, 1H), 3.35 (s, 3H), 1.80 (d, $^4J_{HH}$ = 1.6 Hz, 3H), 1.69 – 1.58 (m, 1H), 1.51 – 1.41 (m, 1H), 1.26 (s, 12H), 0.90 (t, $^3J_{HH}$ = 7.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 145.9, 94.4, 83.3, 76.6, 55.4, 28.8, 25.0, 24.9, 22.3, 10.0. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.2. IR (ṽ, film, cm^{-1}): 2977, 2933, 2880, 1637, 1453, 1418, 1390, 1380, 1372, 1331, 1301, 1266, 1242, 1214, 1143, 1097, 1085, 1068, 964, 919, 891, 863, 835, 712, 691, 672, 579, 486, 459, 432, 413. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{27}BO_4Na$ ($[M+Na]^+$): 293.1895; found: 293.1895.



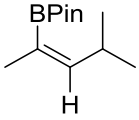
Compound 8c. Yellow oil (739 mg, 83%). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.96 – 5.93 (m, 1H), 4.73 (dt, $^3J_{HH}$ = 8.8 Hz, 6.6 Hz, 1H), 1.76 (d, $^4J_{HH}$ = 1.5 Hz, 3H), 1.58 – 1.47 (m, 1H), 1.43 – 1.32 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 0.93 (t, $^3J_{HH}$ = 7.9 Hz, 9H), 0.83 (t, $^3J_{HH}$ = 7.4 Hz, 3H), 0.58 (q, $^3J_{HH}$ = 7.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 150.6, 83.1, 72.5, 31.5, 25.1, 24.9, 22.3, 10.0, 7.0, 5.1. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.2. IR (ṽ, film, cm^{-1}): 2958, 2937, 2914, 2876, 1638, 1454, 1416, 1389, 1379, 1371, 1331, 1297, 1264, 1240, 1214, 1165, 1144, 1112, 1086, 1048, 1003, 963, 907, 864, 839, 815, 741, 691, 670, 579, 491, 419. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{37}BO_3SiNa$ ($[M+Na]^+$): 363.2497; found: 363.2499.



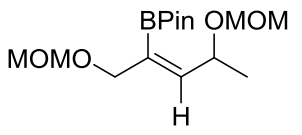
Compound 8d. Colorless oil (181 mg, 94%). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.98 – 5.95 (m, 1H), 4.90 – 4.84 (m, 1H), 1.77 (d, $^4J_{HH}$ = 1.6 Hz, 3H), 1.64 – 1.52 (m, 1H), 1.46 – 1.35 (m, 1H), 1.24 (s, 12H), 1.08 – 1.02 (m, 21H), 0.82 (t, $^3J_{HH}$ = 7.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 151.4, 83.0, 72.3, 31.7, 25.1, 24.9, 22.2, 18.3, 18.2, 12.5, 9.6. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 29.9. IR (ṽ, film, cm^{-1}): 2961, 2941, 2892, 2866, 1638, 1463, 1416, 1389, 1379, 1371, 1298, 1262, 1214, 1144, 1088, 1051, 1012, 964, 918, 882, 864, 832, 806, 757, 728, 712, 674, 656, 579, 509, 464, 421. HRMS (ESI): *m*/*z* calcd for $C_{21}H_{43}BO_3SiNa$ ($[M+Na]^+$): 405.2967; found: 405.2972.



Compound 10. Colorless oil (116 mg, 72%); this compound was not subjected to drying in high vacuum due to its volatility. ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.84 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 3.02 – 2.90 (m, 1H), 1.73 (d, $^4J_{HH}$ = 1.6 Hz, 3H), 1.26 (s, 12H), 0.93 (d, $^3J_{HH}$ = 6.6 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 154.7, 82.9, 29.8, 25.0, 23.6, 22.4. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.5. IR (ṽ, film, cm^{-1}): 2978, 2960, 2933, 2867, 1633, 1466, 1452, 1421, 1399, 1389, 1378, 1371, 1348, 1333, 1315, 1290, 1261, 1214, 1184, 1142, 1111, 1079, 1018, 966, 864, 848, 837, 714, 691, 671, 579. HRMS (ES): *m*/*z* calcd for $C_{12}H_{23}BO_2$ ($[M]^+$): 210.1786; found: 210.1786.

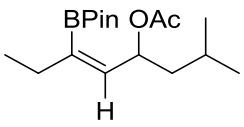


Compound 12. Orange oil (116 mg, 91%). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 6.14 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 4.83 – 4.76 (m, 1H), 4.65 – 4.63 (m, 3H), 4.56 (d, $^2J_{HH}$ = 6.6 Hz, 1H), 4.17 – 4.08 (m, 2H), 3.36 (s, 3H), 3.34 (s, 3H), 1.27 – 1.25 (m, 15 H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 147.5, 95.9, 94.4, 83.6, 71.2, 70.6, 55.32, 55.28, 25.0, 24.9, 21.8. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.0. IR (ṽ, film, cm^{-1}): 2977, 2930, 2885, 2822, 1643, 1445, 1403, 1371, 1302, 1256, 1214, 1143, 1098, 1025, 966,

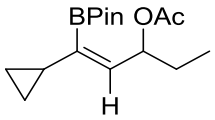


917, 884, 862, 835, 725, 685, 671, 632, 579, 494. HRMS (ESI): m/z calcd for $C_{15}H_{29}BO_6Na$ ([M+Na]$^+$): 339.1949; found: 339.1954.

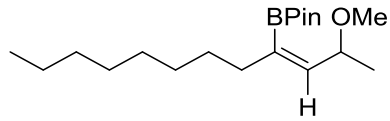
Compound 14. Colorless oil (139 mg, 90%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.94 (td, $^3J_{HH}$ = 8.6 Hz, 5.0 Hz, 1H), 5.80 (br d, $^3J_{HH}$ = 8.6 Hz, 1H), 2.26 – 2.07 (m, 2H), 2.00 (s, 3H), 1.63 – 1.56 (m, 2H), 1.29 (s, 6H), 1.28 (s, 6H), 1.27 – 1.26 (m, 1H), 0.98 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 0.93 (d, $^3J_{HH}$ = 6.2 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 170.4, 141.8, 83.5, 72.7, 44.4, 29.5, 25.2, 24.8, 24.6, 23.3, 22.3, 21.6, 14.3. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.3. IR (ṽ, film, cm^{-1}): 2959, 2932, 2871, 1734, 1639, 1467, 1425, 1404, 1370, 1327, 1301, 1261, 1237, 1166, 1141, 1110, 1015, 967, 949, 927, 860, 804, 727, 708, 684, 672, 612, 579, 520, 500. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{31}BO_4Na$ ([M+Na]$^+$): 333.2208; found: 333.2208.



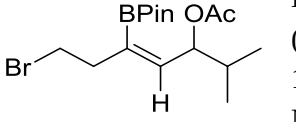
Compound 15. Prepared according to the general procedure but using 5 mol% catalyst (added in 1.25 mol% portions every 30 min); yellow oil (160 mg, 69%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.75 (br d, $^3J_{HH}$ = 9.1 Hz, 1H), 5.65 (dt, $^3J_{HH}$ = 9.1, 6.5 Hz, 1H), 2.01 (s, 3H), 1.71 – 1.61 (m, 1H), 1.58 – 1.51 (m, 1H), 1.50 – 1.43 (m, 1H), 1.284 (s, 6H), 1.279 (s, 6H), 0.86 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 0.67 – 0.63 (m, 2H), 0.57 – 0.48 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$): δ 170.4, 138.0, 83.7, 75.2, 28.3, 25.1, 24.8, 21.6, 16.5, 9.7, 7.1, 6.9. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 29.8. IR (ṽ, film, cm^{-1}): 2976, 2935, 2878, 1732, 1631, 1460, 1426, 1406, 1390, 1370, 1344, 1305, 1267, 1236, 1166, 1142, 1110, 1075, 1049, 1018, 960, 878, 852, 814, 720, 700, 671, 606, 579, 521, 470, 419. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{27}BO_4Na$ ([M+Na]$^+$): 317.1895; found: 317.1896.

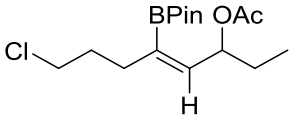


Compound 16. Yellow oil (198 mg, 78%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.78 (dt, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H), 4.33 (dq, $^3J_{HH}$ = 8.8 Hz, 6.3 Hz, 1H), 3.25 (s, 3H), 2.13 – 2.10 (m, 2H), 1.38 – 1.35 (m, 2H), 1.27 (s, 12H), 1.26 – 1.23 (m, 10H), 1.19 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 0.89 – 0.86 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 146.2, 83.3, 75.4, 56.0, 36.7, 32.0, 30.0, 29.6, 29.41, 29.37, 25.0, 24.9, 22.8, 21.8, 14.3. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.8. IR (ṽ, film, cm^{-1}): 2976, 2924, 2854, 2818, 1633, 1465, 1390, 1371, 1344, 1295, 1255, 1202, 1144, 1107, 1090, 965, 910, 863, 842, 734, 707, 672, 579, 520. HRMS (ESI): *m*/*z* calcd for $C_{19}H_{37}BO_3Na$ ([M+Na]$^+$): 347.2728; found: 347.2730.



Compound 17. Yellow oil (451 mg, 80%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.94 (br d, $^3J_{HH}$ = 9.1 Hz, 1H), 5.73 (dd, $^3J_{HH}$ = 9.1 Hz, 6.2 Hz, 1H), 3.48 – 3.44 (m, 2H), 2.83 – 2.76 (m, 1H), 2.59 – 2.52 (m, 1H), 2.02 (s, 3H), 1.91 – 1.83 (m, 1H), 1.28 (s, 6H), 1.27 (s, 6H), 0.93 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 0.92 (d, $^3J_{HH}$ = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ 170.5, 145.4, 83.7, 77.7, 40.2, 33.6, 32.7, 25.1, 24.8, 21.5, 18.2, 18.1. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 29.8. IR (ṽ, film, cm^{-1}): 2974, 2933, 1733, 1638, 1469, 1428, 1406, 1371, 1302, 1236, 1213, 1166, 1141, 1110, 1073, 1018, 966, 905, 861, 833, 758, 722, 701, 670, 607, 579, 550, 522, 499, 444, 420. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{28}BBrO_4Na$ ([M+Na]$^+$): 397.1156; found: 397.1156.

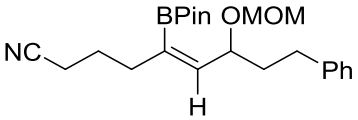




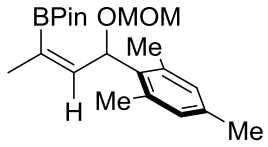
Compound 18. Orange oil (120 mg, 93%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.89 (br d, $^3J_{HH}$ = 8.8 Hz, 1H), 5.75 (dt, $^3J_{HH}$ = 8.8 Hz, 6.5 Hz, 1H), 3.52 – 3.48 (m, 2H), 2.34 – 2.26 (m, 1H), 2.25 – 2.18 (m, 1H), 2.01 (s, 3H),

1.91 – 1.82 (m, 2H), 1.72 – 1.61 (m, 1H), 1.57 – 1.49 (m, 1H), 1.28 (s, 6H), 1.27 (s, 6H), 0.88 (t, $^{3}J_{HH}$ = 7.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 170.5, 144.1, 83.6, 75.0, 44.6, 33.7, 32.5, 28.2, 25.1, 24.8, 21.6, 9.6. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.2. IR (ṽ, film, cm^{-1}): 2975, 2935, 2877, 1733, 1638, 1426, 1405, 1370, 1307, 1237, 1166, 1142, 1111, 1083, 1018, 964, 894, 861, 779, 710, 672, 654, 609, 579, 519, 474. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{28}BClO_4Na$ ($[M+Na]^+$): 353.1661; found: 353.1662.

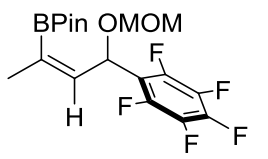
Compound 19. Yellow oil (201 mg, 98%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.29 – 7.27 (m, 1H), 7.22 – 7.15 (m, 4H), 5.96 (br d, $^{3}J_{HH}$ = 8.8 Hz, 1H), 4.71 – 4.65 (m, 2H), 4.58 (d, $^{2}J_{HH}$ = 6.6 Hz, 1H), 3.37 (s, 3H), 2.80 – 2.73 (m, 1H), 2.68 – 2.60 (m,1H), 2.34 – 2.24 (m, 4H), 1.99 – 1.89 (m, 1H), 1.81 – 1.73 (m, 3H), 1.23 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 147.9, 142.4, 128.6, 128.4, 125.8, 120.0, 94.8, 83.6, 75.1, 55.6, 37.7, 35.5, 31.9, 25.6, 25.0, 24.8, 16.5. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.1. IR (ṽ, film, cm^{-1}): 3061, 3026, 2977, 2931, 2820, 2245, 1633, 1603, 1496, 1454, 1424, 1401, 1391, 1380, 1372, 1304, 1261, 1214, 1166, 1142, 1124, 1095, 1030, 965, 918, 861, 831, 749, 699, 672, 622, 579, 541, 518, 497. HRMS (ESI): *m*/*z* calcd for $C_{23}H_{34}BNO_4Na$ ($[M+Na]^+$): 422.2473; found: 422.2475.



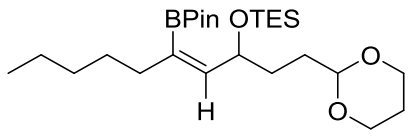
Compound 20. Yellow oil (245 mg, 86%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ 6.82 (s, 2H), 6.42 (dq, $^{3}J_{HH}$ = 9.3 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H), 6.13 (d, $^{3}J_{HH}$ = 9.3 Hz, 1H), 4.64 (d, $^{3}J_{HH}$ = 6.5 Hz, 1H), 4.53 (d, $^{3}J_{HH}$ = 6.5 Hz, 1H), 3.36 (s, 3H), 2.44 (s, 6H), 2.25 (s, 3H), 1.82 (d, $^{4}J_{HH}$ = 1.5 Hz, 3H), 1.30 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 142.3, 137.5, 136.9, 133.6, 130.1, 93.6, 83.4, 72.9, 55.6, 25.1, 25.0, 23.0, 21.0, 20.9. ^{11}B NMR (96 MHz, 298 K, $CDCl_3$): δ 29.9. IR (ṽ, film, cm^{-1}): 2977, 2925, 2883, 1632, 1611, 1450, 1419, 1390, 1373, 1337, 1322, 1295, 1259, 1242, 1213, 1142, 1132, 1093, 1025, 965, 947, 930, 915, 862, 851, 836, 790, 741, 710, 689, 672, 594, 580, 551, 524, 478, 454, 412. HRMS (ESI): *m*/*z* calcd for $C_{21}H_{33}BO_4Na$ ($[M+Na]^+$): 383.2364; found: 383.2362.



Compound 21. Prepared according to the general procedure and isolated as a yellow oil (296 mg, 93%); crystals suitable for X-ray diffraction were grown at –20 °C, which proved to be highly temperature-sensitive. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ 6.46 (br d, $^{3}J_{HH}$ = 9.1 Hz, 1H), 6.20 (d, $^{3}J_{HH}$ = 9.1 Hz, 1H), 4.73 (d, $^{2}J_{HH}$ = 6.7 Hz, 1H), 4.58 (d, $^{2}J_{HH}$ = 6.7 Hz, 1H), 3.30 (s, 3H), 1.83 (d, $^{4}J_{HH}$ = 1.6 Hz, 3H), 1.28 (s, 6H), 1.27 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 145.3 (dm, $^{1}J_{CF}$ ~ 251 Hz), 141.3 (t, $^{4}J_{CF}$ = 3 Hz), 140.8 (dm, $^{1}J_{CF}$ ~ 254 Hz), 137.6 (dm, $^{1}J_{CF}$ ~ 253 Hz), 115.6, 94.6, 83.8, 68.1, 55.5, 25.0, 24.8, 22.3. ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ –140.8 - –141.0 (m, 2F), –155.6 (t, $^{3}J_{FF}$ = 21 Hz, 1F), –162.4 - –162.6 (m, 2F). ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 29.8. IR (ṽ, film, cm^{-1}): 2981, 2942, 2889, 1651, 1520, 1502, 1452, 1421, 1392, 1381, 1373, 1302, 1263, 1251, 1214, 1139, 1120, 1096, 1027, 990, 965, 931, 862, 834, 778, 743, 713, 674, 653, 628, 578, 520, 487, 427. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{22}BF_5O_4Na$ ($[M+Na]^+$): 431.1424; found: 431.1425.

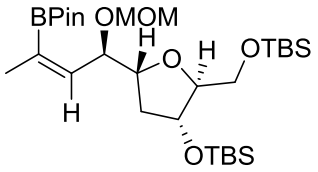


Compound 22. Yellow oil (60 mg, 82%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.88 (d, $^{3}J_{HH}$ = 8.8 Hz, 1H), 4.78 (dt, $^{3}J_{HH}$ = 8.8 Hz, 6.2 Hz, 1H), 4.51 (t, $^{3}J_{HH}$ = 5.0 Hz, 1H), 4.11 – 4.06 (m, 2H), 3.77 – 3.70 (m, 2H), 2.13 – 2.01 (m, 3H), 1.69 – 1.30 (m, 11H), 1.25 (s, 12H), 0.92 (t, $^{3}J_{HH}$ = 7.9 Hz, 9H), 0.87 (t, $^{3}J_{HH}$

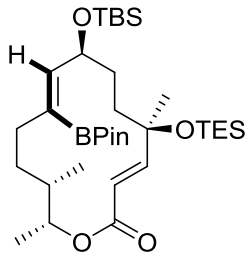


= 7.0 Hz, 3H), 0.57 (q, $^3J_{HH}$ = 7.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 149.4, 102.8, 83.0, 70.9, 67.05, 67.02, 36.6, 33.3, 31.7, 31.4, 29.8, 26.0, 25.1, 24.9, 22.7, 14.2, 7.0, 5.1. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.5. IR (ṽ, film, cm^{-1}): 2955, 2928, 2874, 2851, 1633, 1460, 1399, 1378, 1296, 1243, 1214, 1144, 1075, 1003, 965, 863, 831, 803, 725, 672, 580, 476. HRMS (ESI): *m*/*z* calcd for $C_{26}H_{51}BO_5SiNa$ ($[M+Na]^+$): 505.3491; found: 505.3492.

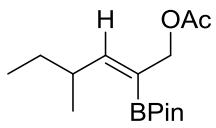
Compound 23. Colorless oil (12 mg, 91%). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.87 (dq, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 4.72 – 4.60 (m, 3H), 4.27 – 4.21 (m, 1H), 3.97 (dt, $^3J_{HH}$ = 9.2 Hz, 6.6 Hz, 1H), 3.75 – 3.69 (m, 2H), 3.66 – 3.60 (m, 1H), 3.36 (s, 3H), 2.05 (dt, $^2J_{HH}$ = 12.2, $^3J_{HH}$ = 6.9 Hz, 1H), 1.84 – 1.76 (m, 4H), 1.26 (s, 12H), 0.88 (s, 9H), 0.87 (s, 9H), 0.05 (s, 6H), 0.04 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 141.3, 94.6, 85.0, 83.4, 80.2, 77.3, 72.2, 63.1, 55.4, 37.5, 26.1, 25.9, 25.0, 24.7, 22.4, 18.5, 18.1, –4.5, –4.7, –5.1, –5.3. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.5. IR (ṽ, film, cm^{-1}): 2954, 2929, 2887, 2857, 1638, 1472, 1390, 1298, 1252, 1215, 1145, 1111, 1036, 990, 940, 863, 836, 777, 672, 456, 432. HRMS (ESI): *m*/*z* calcd for $C_{29}H_{59}BO_7Si_2Na$ ($[M+Na]^+$): 609.3785; found: 609.3785.



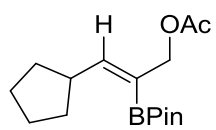
Compound 24. Prepared from the cycloalkyne precursor described in ref. [11]; colorless oil (21 mg, 84%). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 6.68 (d, $^3J_{HH}$ = 15.3 Hz, 1H), 5.90 (d, $^3J_{HH}$ = 15.3 Hz, 1H), 5.75 (br d, $^3J_{HH}$ = 8.9 Hz, 1H), 4.68 – 4.63 (m, 1H), 4.57 – 4.50 (m, 1H), 2.30 – 2.21 (m, 1H), 1.84 – 1.41 (m, 8H), 1.30 – 1.28 (m, 6H), 1.260 (s, 6H), 1.256 (s, 6H), 0.96 (t, $^3J_{HH}$ = 7.9 Hz, 9H), 0.94 (s, 3H), 0.84 (s, 9H), 0.61 (q, $^3J_{HH}$ = 7.9 Hz, 6H), –0.00 (s, 3H), –0.04 (s, 3H). $^3C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 166.7, 155.4, 150.5, 119.1, 83.2, 75.6, 74.5, 70.9, 38.5, 36.4, 33.8, 32.1, 31.5, 27.8, 26.0, 25.1, 24.9, 19.5, 18.3, 16.1, 7.3, 6.9, –4.1, –4.6. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.1. IR (ṽ, film, cm^{-1}): 2955, 2934, 2877, 2857, 1715, 1646, 1460, 1402, 1372, 1302, 1252, 1159, 1146, 1107, 1086, 1064, 1006, 966, 892, 835, 775, 743, 726, 671, 577, 524. HRMS (ESI): *m*/*z* calcd for $C_{34}H_{65}BO_6Si_2Na$ ($[M+Na]^+$): 659.4305; found: 659.4311.



Compound 25. Yellow oil (133 mg, 91%). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 6.00 (d, $^3J_{HH}$ = 10.0 Hz, 1H), 4.64 (dd, $^2J_{HH}$ = 12.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 4.57 (dd, $^2J_{HH}$ = 12.0 Hz, $^4J_{HH}$ = 1.1 Hz, 1H), 2.82 – 2.71 (m, 1H), 2.04 (s, 3H), 1.37 – 1.30 (m, 1H), 1.26 (s, 12H), 1.24 – 1.17 (m, 1H), 0.96 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 0.83 (t, $^3J_{HH}$ = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 171.0, 156.1, 83.3, 68.9, 36.7, 30.2, 25.0, 24.8, 21.3, 20.9, 12.0. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.3. IR (ṽ, film, cm^{-1}): 2963, 2932, 2874, 1738, 1638, 1459, 1430, 1410, 1372, 1305, 1290, 1227, 1165, 1142, 1102, 1022, 966, 931, 889, 862, 827, 790, 710, 689, 672, 606, 579, 552, 520, 434. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{27}BO_4Na$ ($[M+Na]^+$): 305.1895; found: 305.1895.



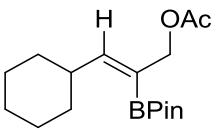
Compound 27. Yellow oil (94 mg, 64%). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 6.17 (d, $^3J_{HH}$ = 9.6 Hz, 1H), 4.60 (d, $^4J_{HH}$ = 1.3 Hz, 2H), 3.17 – 3.06 (m, 1H), 2.04 (s, 3H), 1.85 – 1.78 (m, 2H), 1.68 – 1.56 (m, 4H), 1.26 (s, 12H), 1.25 – 1.20 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 171.1, 155.7, 83.3, 69.0, 41.5, 34.0, 25.9, 24.9, 21.3. ^{11}B



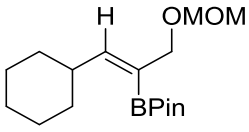
[11] Rummelt, S. M.; Preindl, J.; Sommer, H.; Fürstner, A. *Angew. Chem. Int. Engl*. **2015**, *54*, 6241-6245

NMR (128 MHz, 298 K, $CDCl_3$): δ 30.2. IR (ṽ, film, cm^{-1}): 2976, 2950, 2867, 1737, 1638, 1434, 1412, 1372, 1311, 1292, 1227, 1166, 1142, 1111, 1022, 965, 863, 832, 730, 711, 672, 606, 579, 444. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{27}BO_4Na$ ($[M+Na]^+$): 317.1895; found: 317.1895.

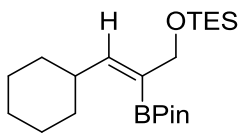
Compound 28a. Yellow oil (144 mg, 87%). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 6.10 (d, $^3J_{HH}$ = 9.4 Hz, 1H), 4.59 (d, $^4J_{HH}$ = 1.4 Hz, 2H), 2.70 – 2.61 (m, 1H), 2.03 (s, 3H), 1.73 – 1.62 (m, 7H), 1.27 (s, 12H), 1.21 – 1.13 (m, 1H), 1.11 – 1.01 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 171.0, 155.7, 83.3, 68.9, 39.6, 33.5, 26.1, 25.9, 24.9, 21.3. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.4. IR (ṽ, film, cm^{-1}): 2978, 2924, 2850, 1737, 1637, 1447, 1411, 1371, 1296, 1224, 1142, 1108, 1023, 966, 902, 863, 756, 711, 672, 606. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{29}BO_4Na$ ($[M+Na]^+$): 331.2051; found: 331.2052.



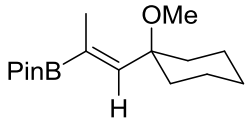
Compound 28b. Yellow oil (91 mg, 72%). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 6.09 (d, $^3J_{HH}$ = 9.4 Hz, 1H), 4.63 (s, 2H), 4.07 (d, $^4J_{HH}$ = 1.3 Hz, 2H), 3.36 (s, 3H), 2.69 – 2.59 (m, 1H), 1.72 – 1.61 (m, 7H), 1.26 (s, 12H), 1.19 – 1.13 (m, 1H), 1.10 – 1.01 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 154.7, 95.6, 83.2, 71.7, 55.2, 39.7, 33.6, 26.1, 26.0, 24.9. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.6. IR (ṽ, film, cm^{-1}): 2978, 2923, 2850, 1635, 1410, 1370, 1293, 1270, 1213, 1143, 1104, 1041, 999, 966, 917, 864, 732. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{31}BO_4Na$ ($[M+Na]^+$): 333.2208; found: 333.2207.



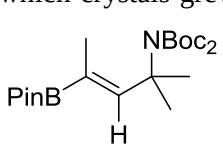
Compound 28c. Yellow oil (138 mg, 93%). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 6.09 (d, $^3J_{HH}$ = 9.4 Hz, 1H), 4.19 (d, $^4J_{HH}$ = 1.7 Hz, 2H), 2.71 – 2.61 (m, 1H), 1.71 – 1.62 (m, 7H), 1.25 (s, 12H), 1.20 – 1.13 (m, 1H), 1.09 – 1.03 (m, 2H), 0.97 – 0.93 (m, 9H), 0.62 – 0.58 (m, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 150.8, 82.9, 66.3, 39.3, 33.7, 26.2, 26.1, 24.9, 7.0, 4.7. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.6. IR (ṽ, film, cm^{-1}): 2977, 2952, 2923, 2876, 2850, 1634, 1460, 1448, 1409, 1389, 1370, 1340, 1292, 1268, 1255, 1227, 1144, 1108, 1055, 1034, 1005, 967, 926, 904, 865, 817, 724, 685, 671, 579. HRMS (EI): *m*/*z* calcd for $C_{21}H_{41}BO_3Si$ ($[M]^+$): 380.2913; found: 380.2914.



Compound 39. Yellow oil (37 mg, 86%). ^1H NMR (400 MHz, 298 K, C_6D_6): δ 6.50 (q, $^4J_{HH}$ = 1.8 Hz, 1H) 3.06 (s, 3H), 2.29 (d, $^4J_{HH}$ = 1.7 Hz, 3H), 2.17 – 1.99 (m, 2H), 1.71 – 1.59 (m, 3H), 1.58 – 1.45 (m, 3H), 1.37 (s, 9H), 1.35 – 1.28 (m, 2H), 1.09 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, C_6D_6): δ 148.6, 83.4, 80.1, 77.6, 49.3, 35.3, 27.9, 26.0, 25.0, 22.1, 15.0. ^{11}B NMR (96 MHz, 298 K, $CDCl_3$): δ 30.7 (br s). IR (ṽ, film, cm^{-1}): 2978, 2931, 2857, 2120, 1738, 1626, 1448, 1369, 1333, 1292, 1255, 1215, 1142, 1111, 1076, 967, 912, 863, 848, 796, 760, 720, 690, 669, 579, 521, 459. HRMS (EI): *m/z* calcd for $C_{16}H_{29}BO_{23}$ ($[M]^+$): 280.2204; found: 280.2204.

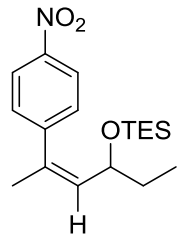


Compound 41. Prepared according to the general procedure and isolated as a thick colorless oil, from which crystals grew when kept at 8 °C (66 mg, quant.). ^1H NMR (400 MHz, 298 K, $CDCl_3$): δ 6.30 (q, $^4J_{HH}$ = 1.8 Hz, 1H), 1.84 (d, $^4J_{HH}$ = 1.8 Hz, 3H), 1.52 (s, 6H), 1.46 (s, 18H), 1.24 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 153.0, 150.2, 83.4, 82.0, 58.6, 28.0, 27.3, 25.0, 14.3. ^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ 30.9 (s). IR (ṽ, film, cm^{-1}): 2979, 2934, 2255, 1746, 1713, 1628, 1457, 1391, 1368, 1331, 1274, 1142, 1106, 1081, 1035, 967, 911, 852, 803, 775, 730, 692, 670, 648, 578, 468. HRMS (ESI): *m/z* calcd for $C_{22}H_{40}BNO_6Na$ ($[M+Na]^+$): 448.2841; found: 448.2842.



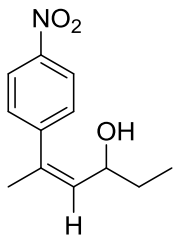
Functionalization Reactions

Compound 29. $Pd(OAc)_2$ (1.8 mg, 0.008 mmol), SPhos (5.7 mg, 0.014 mmol), and 4-bromonitrobenzene



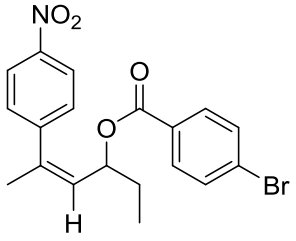
(29 mg, 0.14 mmol) were added sequentially to a flame-dried two-neck round-bottom flask equipped with a magnetic stir bar. The flask was flushed with Ar, and then a solution of compound **8c** (62 mg, 0.18 mmol) in 0.3 mL of dry, degassed THF was injected. The vessel which had contained the vinylboronic ester was rinsed twice with 0.5 mL THF, and the rinses were also transferred to the reaction flask. 0.45 mL of a degassed, aqueous 3 M NaOH solution was added to the yellow solution. The flask was equipped with a reflux condenser and the biphasic mixture was stirred at 70 °C under Ar for 15 h. The mixture was diluted with EtOAc (5 mL) and the organic layer washed with distilled H_2O (5 mL) and brine (5 mL). The organic phase was dried over Na_2SO_4, the drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude material was purified by flash chromatography to afford the desired product as a yellow oil (42 mg, 88%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.23 – 8.20 (m, 2H), 7.33 – 7.30 (m, 2H), 5.59 (dq, $^3J_{HH}$ = 9.3 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 3.95 – 3.89 (m, 1H), 2.06 (d, $^4J_{HH}$ = 1.5 Hz, 3H), 1.63 – 1.56 (m, 1H), 1.53 – 1.44 (m, 1H), 0.89 – 0.83 (m, 12H), 0.41 (q, $^3J_{HH}$ = 7.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 148.8, 146.9, 134.4, 133.8, 128.8, 123.6, 70.9, 31.6, 25.3, 10.0, 6.9, 5.1. IR (ṽ, film, cm^{-1}): 2957, 2936, 2913, 2876, 1597, 1520, 1459, 1345, 1238, 1088, 1049, 1004, 974, 855, 830, 742, 702. HRMS (EI): *m*/*z* calcd for $C_{18}H_{29}NO_3Si$ ($[M]^+$): 335.1911; found: 335.1911.

Compound S18. 300 µL of a 1 M TBAF solution in THF were added dropwise to a solution of compound



29 (70 mg, 0.2 mmol) in 3 mL of THF at 0 °C, causing a color change from yellow to pinky-red. Once TLC showed that all of the starting material was consumed, distilled H_2O (3 mL) and EtOAc (3 mL) were added. The layers were separated and the aqueous phase extracted with EtOAc (2x3 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by preparative TLC using 40% EtOAc in hexanes as the eluent to give the title compound as a colorless oil (35 mg, 76%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.23 – 8.20 (m, 2H), 7.41 – 7.37 (m, 2H), 5.58 (dq, $^3J_{HH}$ = 9.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 3.93 – 3.86 (m, 1H), 2.09 (d, $^4J_{HH}$ = 1.5 Hz, 3H), 1.62 – 1.55 (m, 1H), 1.54 – 1.45 (m, 1H), 1.37 (br d, $^3J_{HH}$ = 4.2 Hz, 1H), 0.85 (t, $^3J_{HH}$ = 7.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 148.4, 147.1, 138.1, 132.0, 128.9, 123.7, 70.6, 30.8, 25.4, 9.9. IR (ṽ, film, cm^{-1}): 2975, 2922, 2850, 2802, 1719, 1638, 1449, 1406, 1389, 1370, 1343, 1328, 1292, 1268, 1224, 1204, 1143, 1116, 1070, 1034, 1006, 965, 925, 909, 862, 800, 746, 720, 695, 672, 634, 580, 541, 442, 415. HRMS (EI): *m*/*z* calcd for $C_{12}H_{15}NO_3$ ($[M]^+$): 221.1046; found: 221.1047.

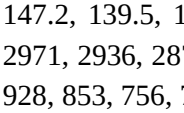
Compound 30. A flame-dried tube Schlenk equipped with a magnetic stirring bar was charged under Ar



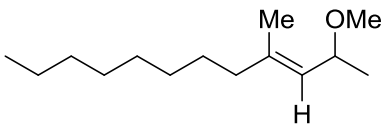
with compound **S18** (43 mg, 0.19 mmol) and 1.5 mL of CH_2Cl_2. 4-Bromobenzoyl chloride (57 mg, 0.26 mmol), Et_3N (50 µL, 0.39 mmol), and DMAP (2 mg, 0.02 mmol) were successively added and the resulting yellow solution was stirred at room temperature overnight. The reaction was quenched with sat. aqueous NH_4Cl and the resulting phases were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 2 mL). The combined organic layers were washed with Na_2SO_4, the drying agent was removed by filtration, and the filtrate was concentrated *in vacuo*. The crude material was purified by flash chromatography using 5% EtOAc in hexanes as the eluent to give the title compound as a yellow oil (49 mg, 63%). Crystals suitable

for X-ray diffraction were grown at 8 °C over one week. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.25 – 8.21 (m, 2H), 7.87 – 7.84 (m, 2H), 7.59 – 7.56 (m, 2H), 7.46 – 7.42 (m, 2H), 5.61 (dq, $^{3}J_{HH}$ = 9.4 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H), 5.24 (dt, $^{3}J_{HH}$ = 9.4 Hz, 6.6 Hz, 1H), 2.09 (d, $^{4}J_{HH}$ = 1.5 Hz, 3H), 1.83 – 1.72 (m, 1H), 1.70 – 1.60 (m, 1H), 0.87 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 165.1, 148.2, 147.2, 139.5, 131.8, 131.2, 129.5, 128.8, 128.2, 127.4, 123.9, 74.3, 28.2, 25.8, 9.7. IR (ṽ, film, cm^{-1}): 2971, 2936, 2877, 1714, 1591, 1518, 1484, 1461, 1397, 1344, 1299, 1265, 1173, 1102, 1067, 1037, 1011, 928, 853, 756, 735, 701, 683, 627, 610, 574, 453. HRMS (ESI): *m*/*z* calcd for $C_{19}H_{18}BrNO_4Na$ ($[M+Na]^+$): 426.0312; found: 426.0313.

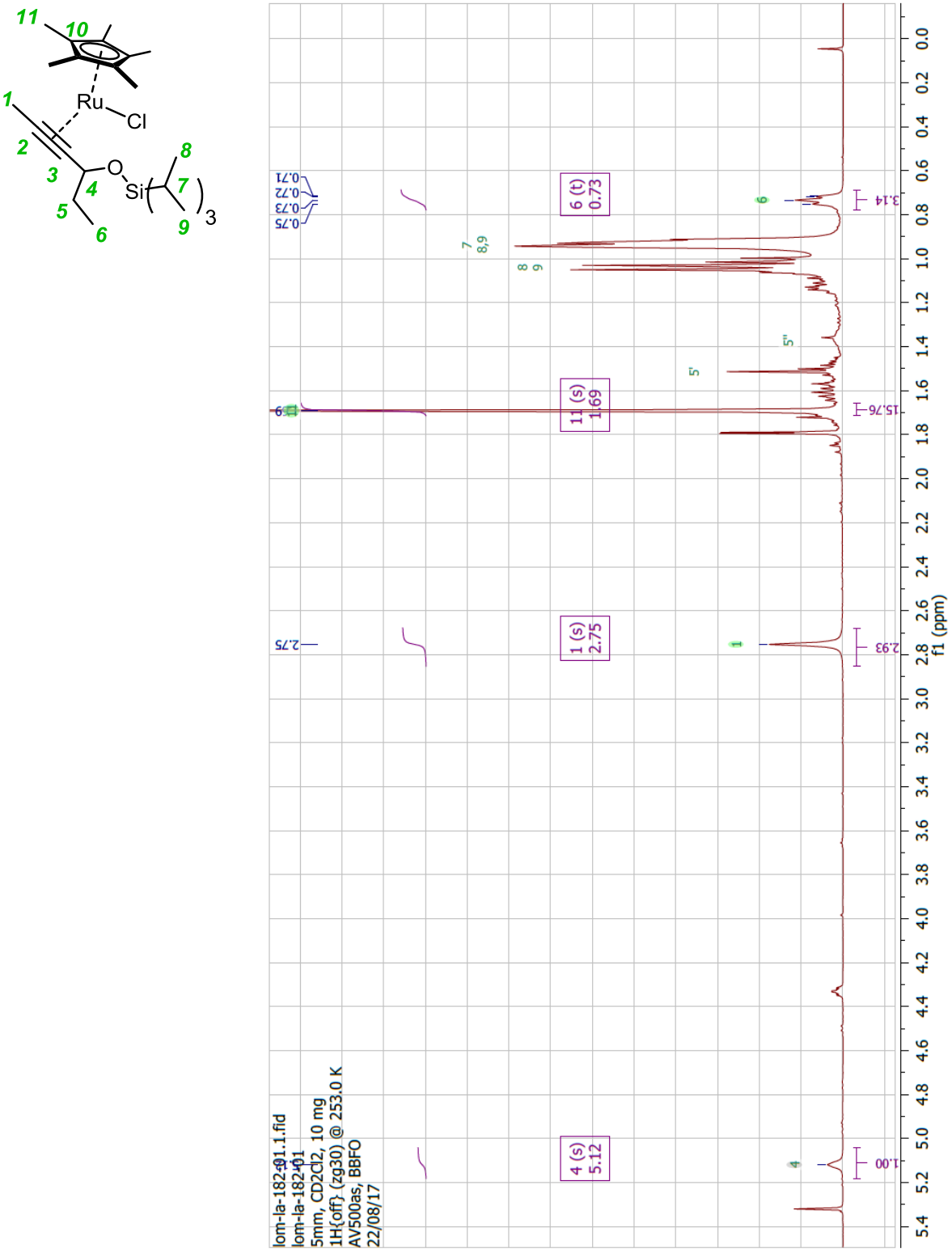
Compound 31. Compound **8c** (34 mg, 0.1 mmol) was transferred to a 10 mL round-bottom flask equipped with a magnetic stirring bar. 0.5 mL of THF and 0.5 mL of distilled H_2O were added, followed by $NaBO_3 \cdot 4H_2O$ (77 mg, 0.5 mmol). The mixture was vigorously stirred open to air until TLC indicated that the starting material was completely consumed. The mixture was filtered through a plug of silica and Na_2SO_4, eluting with EtOAc. The combined filtrates were concentrated *in vacuo* and the crude material was purified by flash chromatography using 5% EtOAc in hexanes as the eluent. The fractions containing the desired product were combined and concentrated to afford the title compound as a colorless oil (17 mg, 73%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 4.13 – 4.07 (m, 1H), 2.60 (dd, $^{2}J_{HH}$ = 15.2 Hz, $^{3}J_{HH}$ = 7.1 Hz, 1H), 2.47 (dd, $^{2}J_{HH}$ = 15.2 Hz, $^{3}J_{HH}$ = 5.0 Hz, 1H), 2.16 (s, 3H), 1.52 – 1.45 (m, 2H), 0.94 (t, $^{3}J_{HH}$ = 7.9 Hz, 9H), 0.87 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H), 0.62 – 0.55 (m, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 208.3, 70.3, 50.7, 31.8, 30.7, 9.6, 7.0, 5.1. IR (ṽ, film, cm^{-1}): 2956, 2913, 2877, 1717, 1460, 1415, 1356, 1238, 1169, 1085, 1045, 1006, 871, 815, 725, 672, 516. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{27}O_2Si$ ($[M+H]^+$): 231.1775; found: 231.1776.

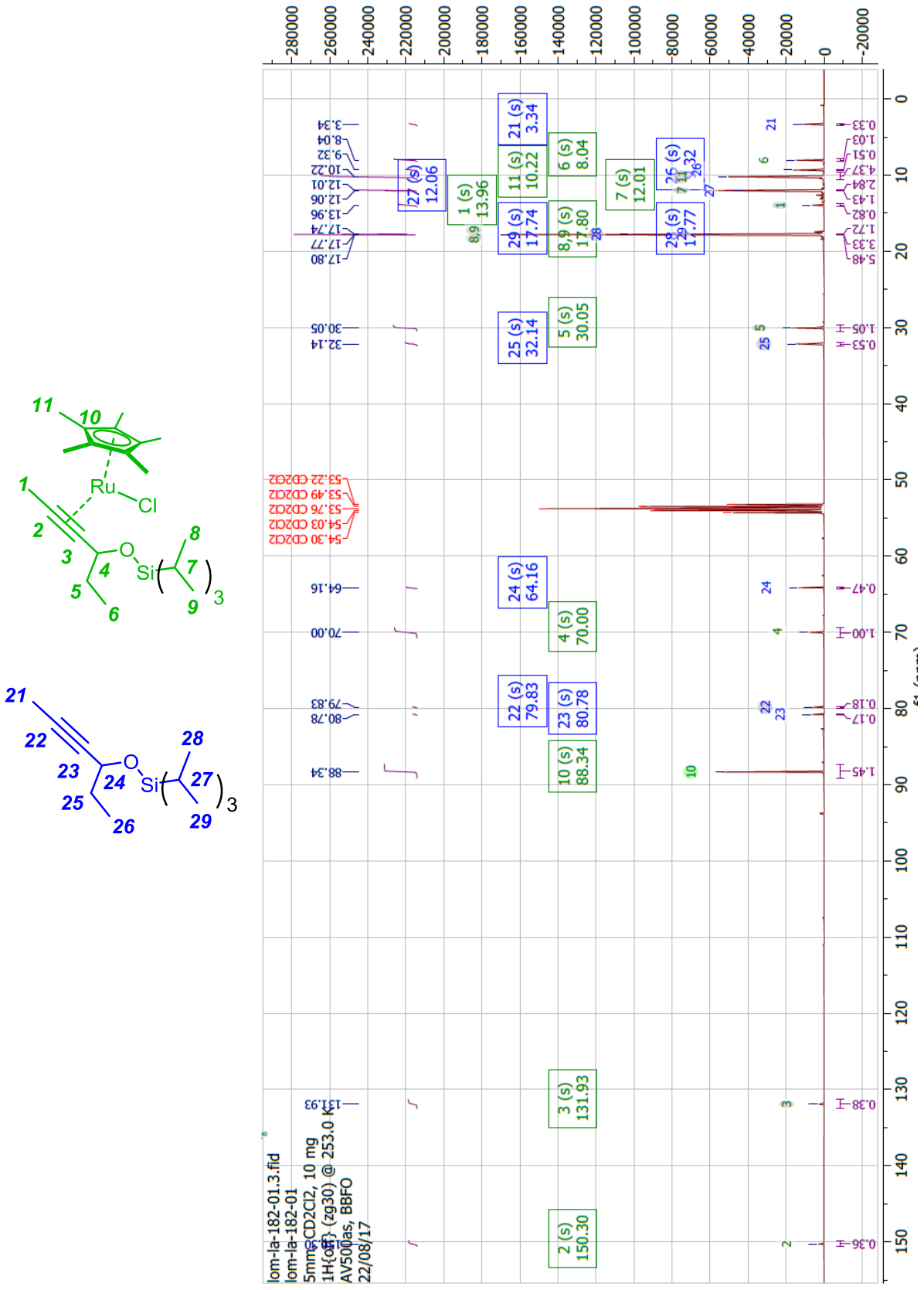


"One Pot" *trans*-Hydroboration/Functionalization 'Sequence. Preparation of Compound 32. A 5 mL round-bottom flask equipped with a magnetic stirring bar was charged with alkyne **S12** (89.8 mg, 0.457 mmol) and THF (0.5 mL). $[Cp^*RuCl]_4$ (5.96 mg, 0.0055 mmol) was added to the colorless solution, causing a color change to faintly purple-brown. The mixture was cooled to 0°C before (pin)BH (80 µL, 0.549 mmol) was introduced. Stirring was continued at ambient temperature for 100 min before a 3 M solution of degassed, aqueous NaOH (1.4 mL, 4.1 mmol) was added. Effervescence was observed, indicative of unreacted (pin)BH being quenched. Then, $Pd(OAc)_2$ (5.8 mg, 0.02 mmol), SPhos (19.4 mg, 0.05 mmol), and 2.5 mL of degassed THF were added, followed by MeI (85 µL, 1.4 mmol). The flask was equipped with a reflux condenser, and the biphasic mixture was stirred at 65 °C under Ar for 4 h. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 4 mL). The combined organic layers were dried over Na_2SO_4. the drying agent was filtered off, and the filtrate was concentrated *in vacuo*. The crude material was purified by flash chromatography using 1% EtOAc in hexanes as the eluent to give the title compound as a yellow oil (79 mg, 82%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 5.06 – 5.02 (m, 1H), 4.04 (dq, $^{3}J_{HH}$ = 8.8, 6.2 Hz, 1H), 3.24 (s, 3H), 2.00 (td, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2H), 1.65 (d, $^{4}J_{HH}$ = 1.4 Hz, 3H), 1.44 – 1.37 (m, 2H), 1.30 – 1.22 (m, 10H), 1.18 (d, $^{3}J_{HH}$ = 6.2 Hz, 3H), 0.89 – 0.86 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ 139.0, 127.0, 73.4, 55.6, 39.8, 32.0, 29.6, 29.5, 29.4, 27.9, 22.8, 21.5, 16.5, 14.3. IR (ṽ, film, cm^{-1}): 2957, 2924, 2855, 2815, 1669, 1463, 1370, 1324, 1193, 1108, 1078, 844, 722, 535, 486. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{28}ONa$ ($[M+Na]^+$): 235.2032; found: 235.2033.



Characterization of Complex **13** (arbitrary numbering scheme as shown in the Inserts)

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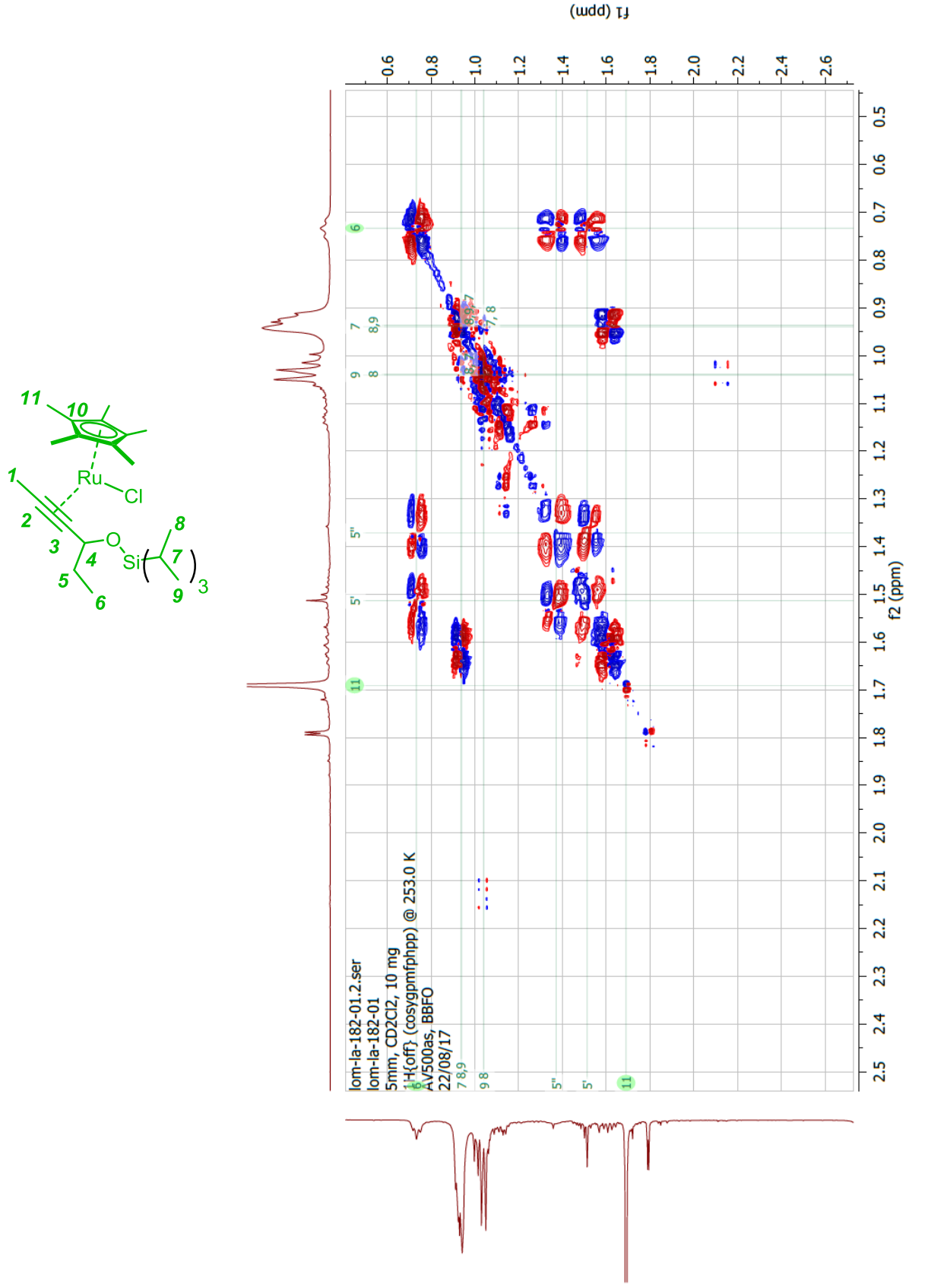
AV500as, BBFO
22/08/17
Ru
Cl
O
Si
3
O
Si
3


11
10
Ru
Cl
1
2
3
4
5
6
O
Si
8
7
9
3
f1 (ppm)
f2 (ppm)
lom-la-182-01.2.ser
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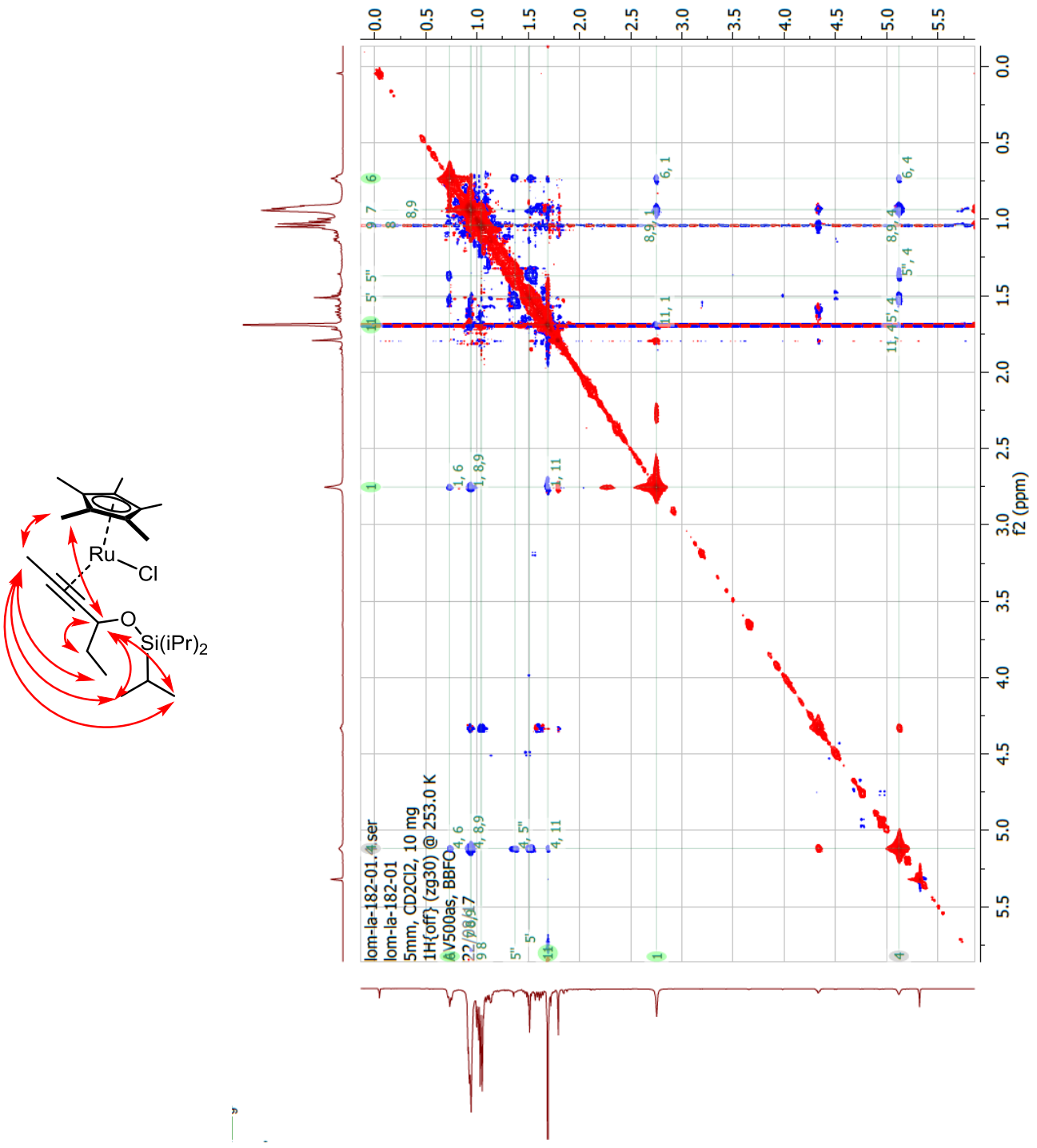
5mm, CD2Cl2, 10 mg
1H{off} (cosygpmfphpp) @ 253.0 K
AV500as, BBFO
22/08/17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Cl
O
Si(iPr)2
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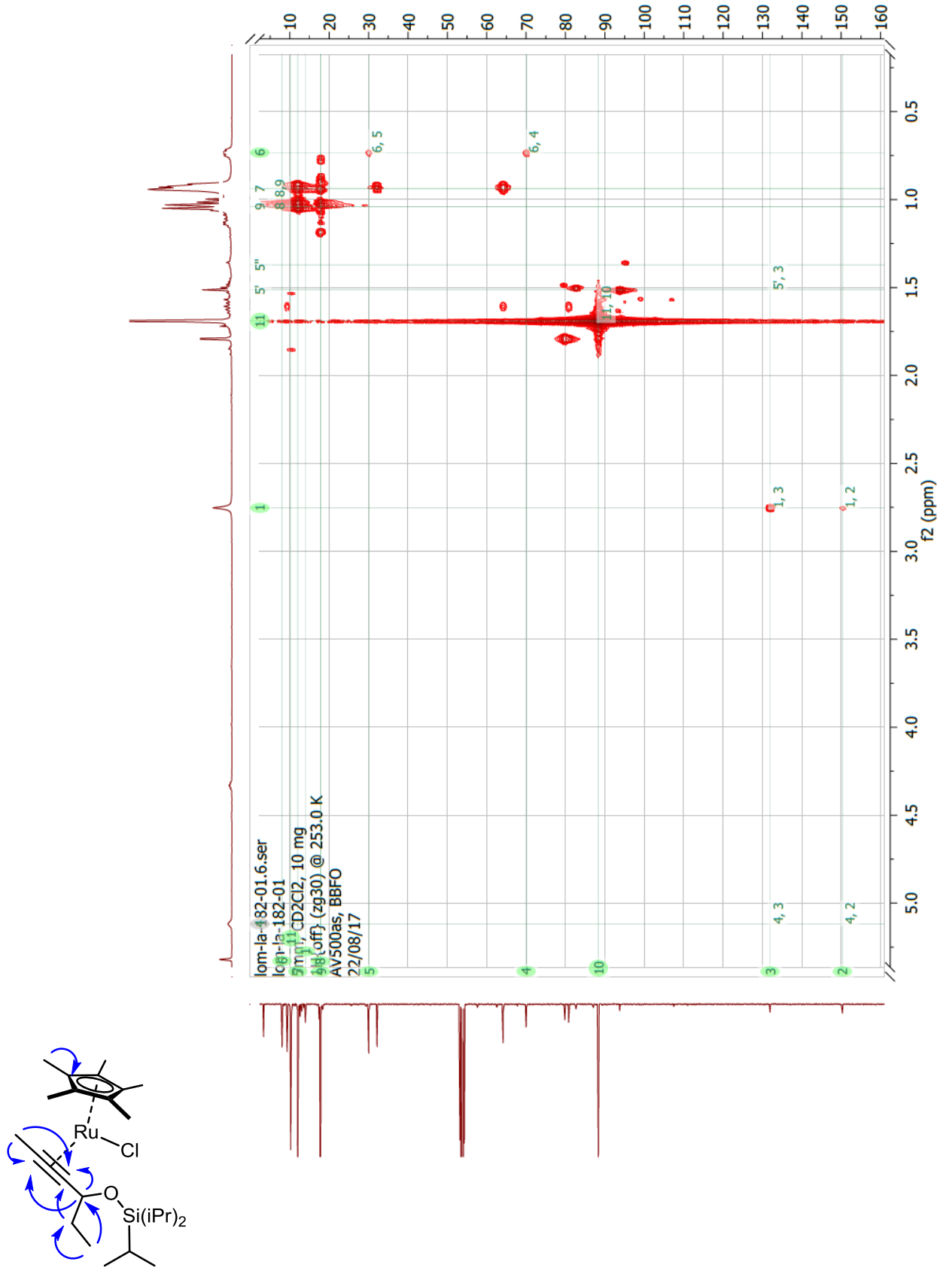
AV500as, BBFO
f2 (ppm)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f2 (ppm)
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Cl
O
Si(iPr)2

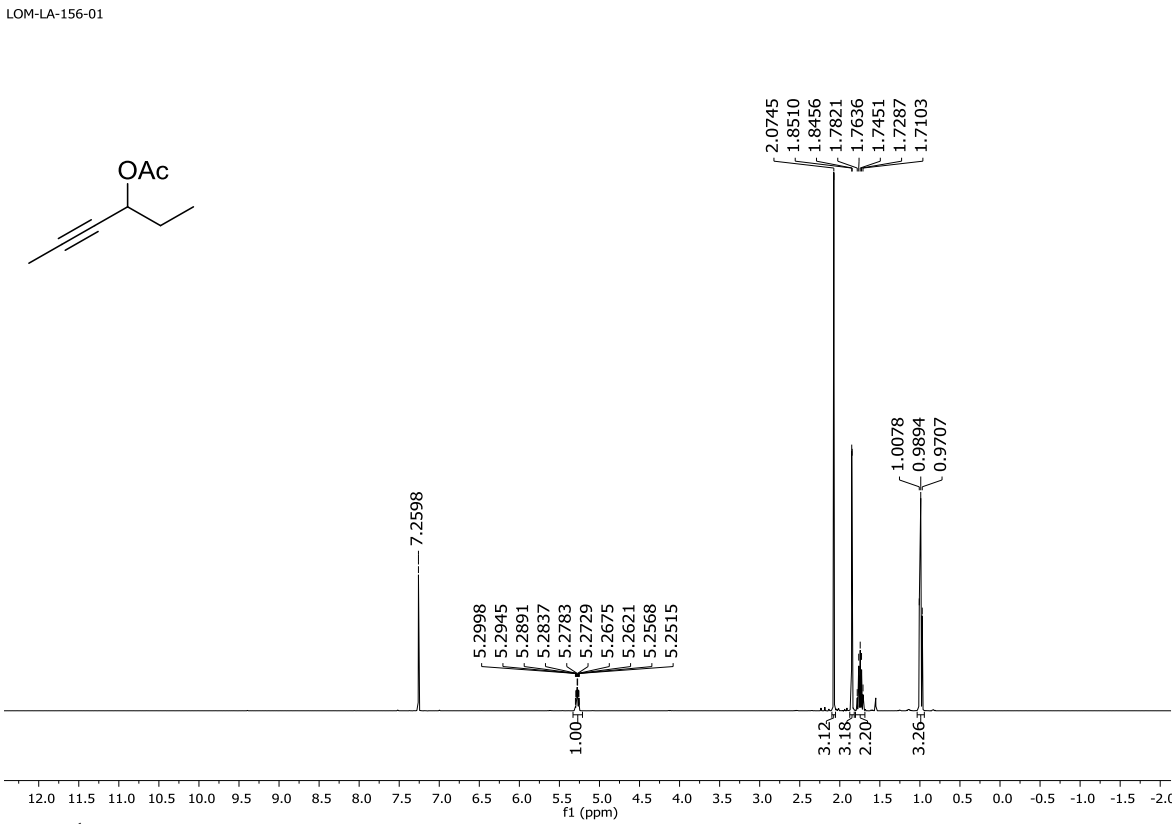

Figure 1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7a**.

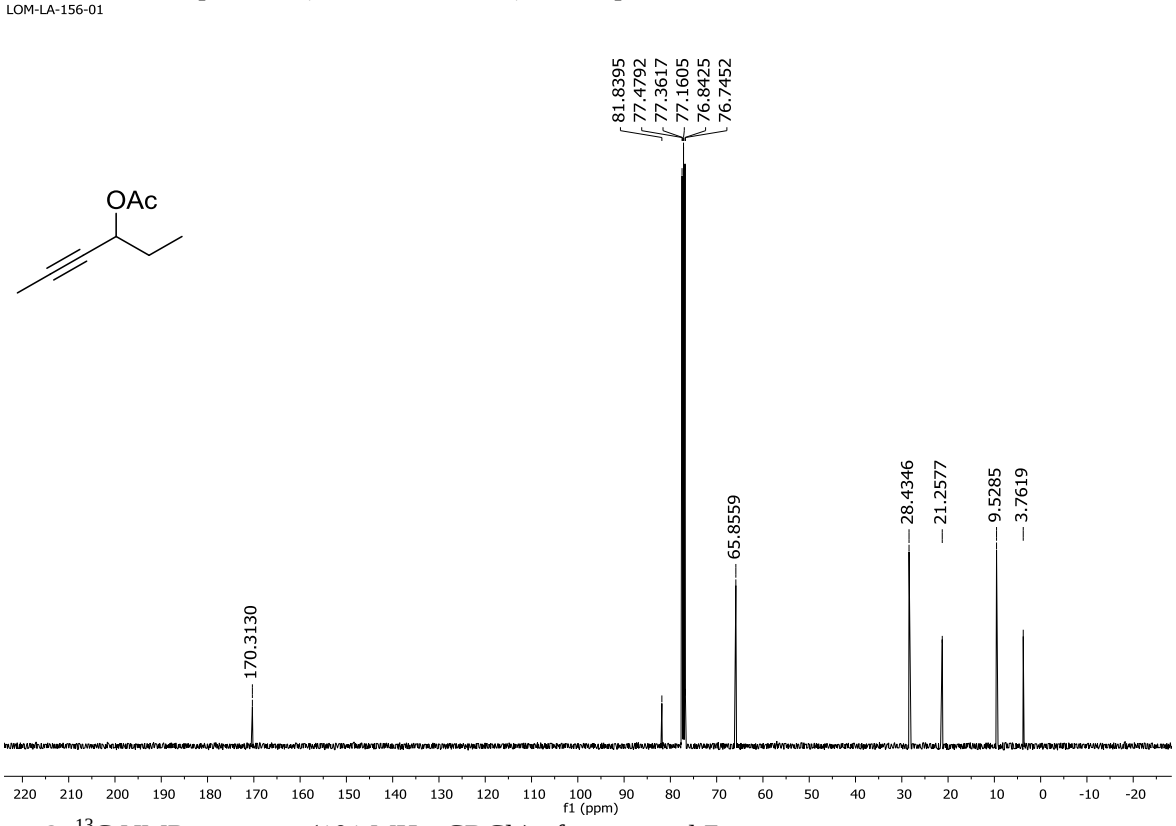

Figure 2: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **7a**.

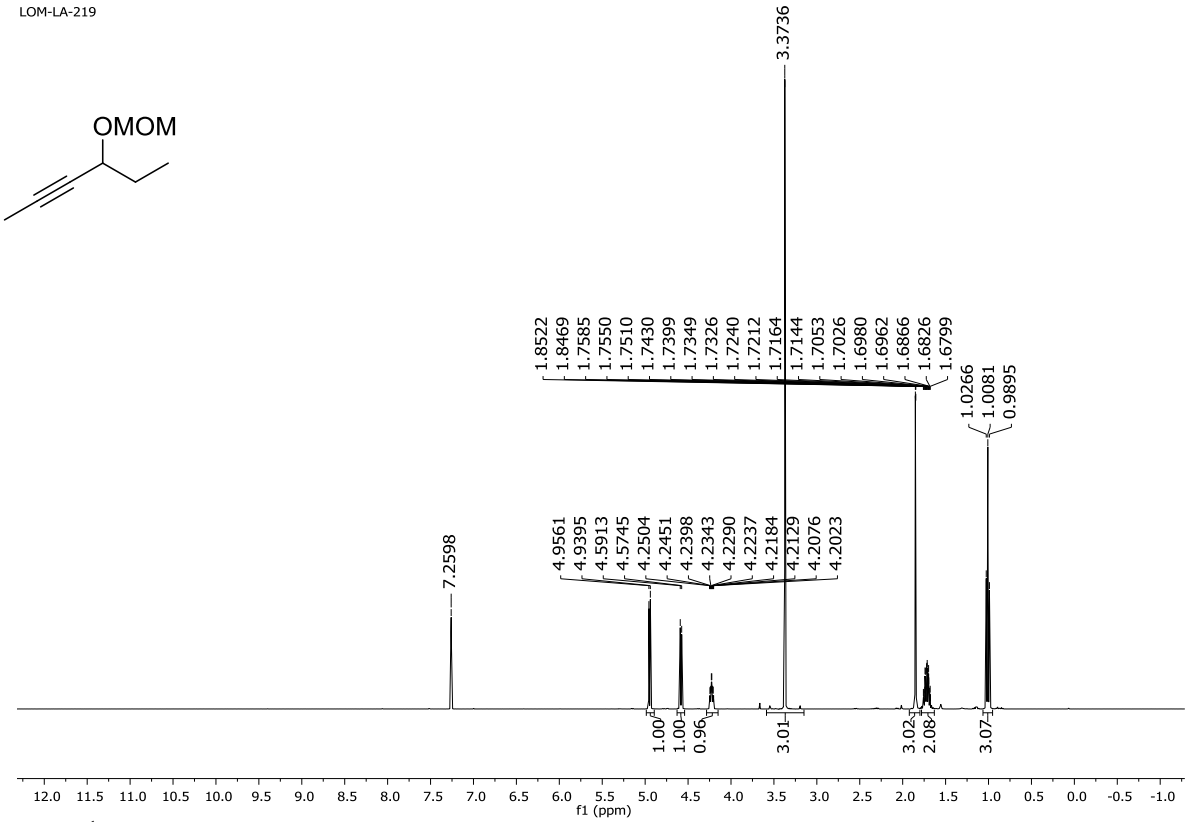

Figure 3: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7b**.

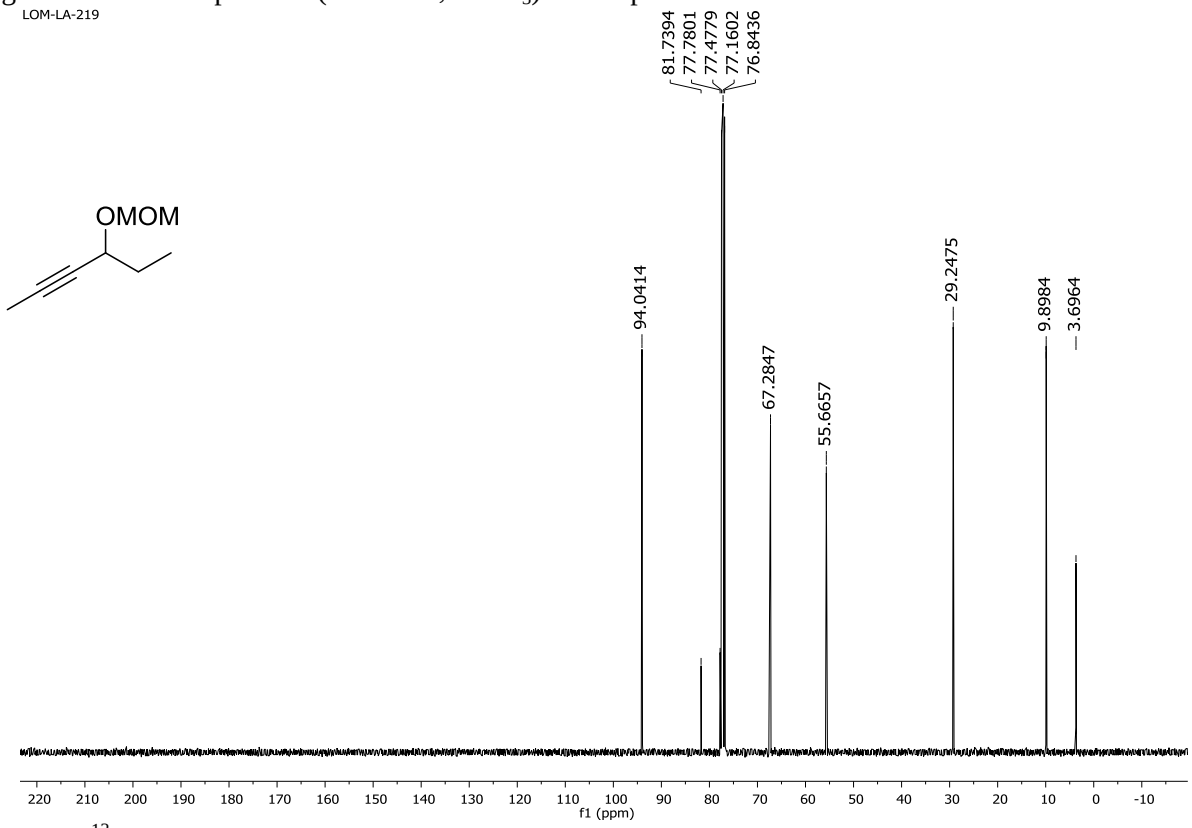

Figure 4: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **7b**.

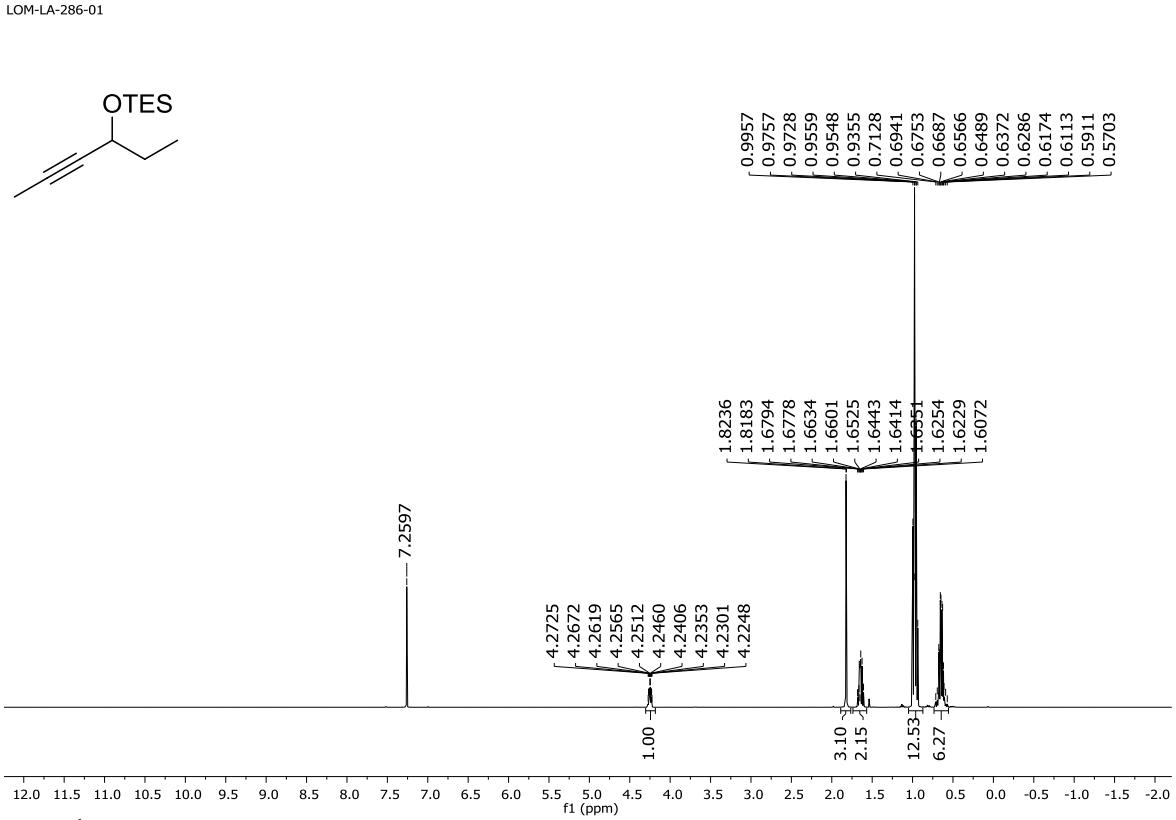

Figure 5: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7c**.

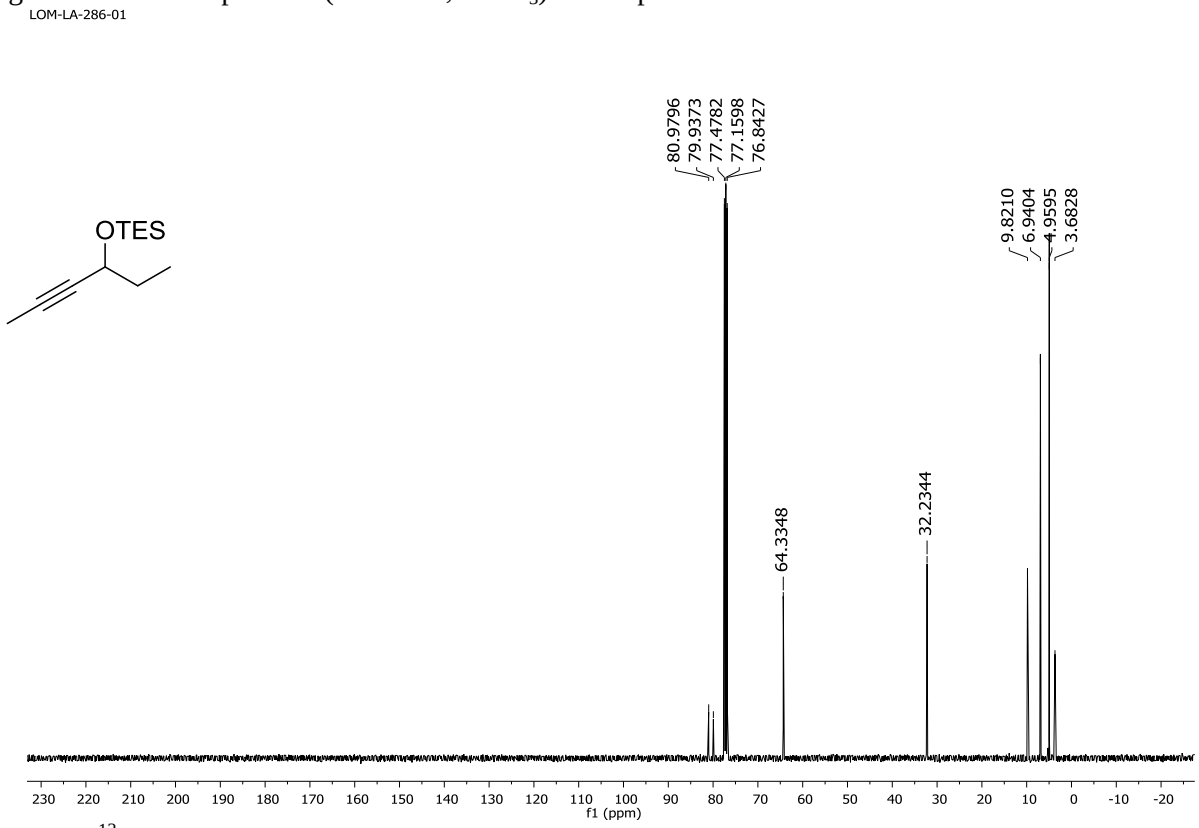

Figure 6: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **7c**.

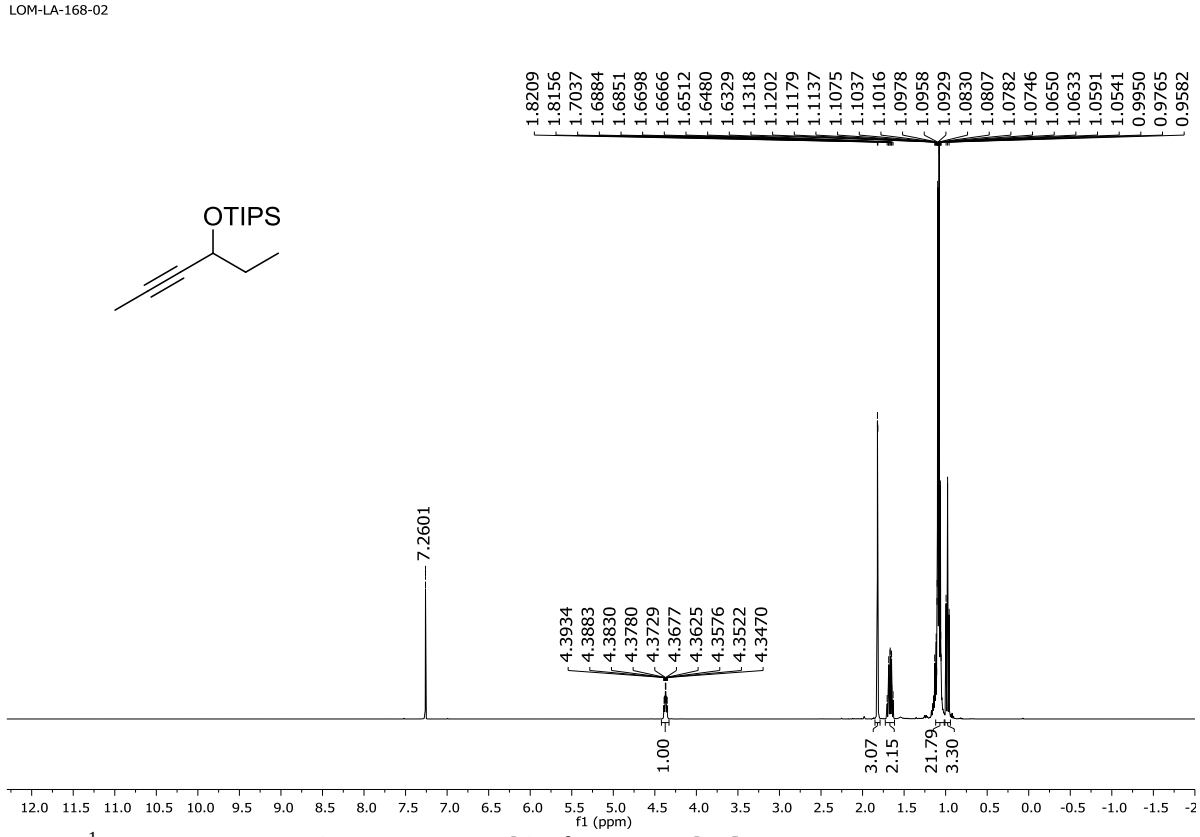

Figure 7: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7d**.

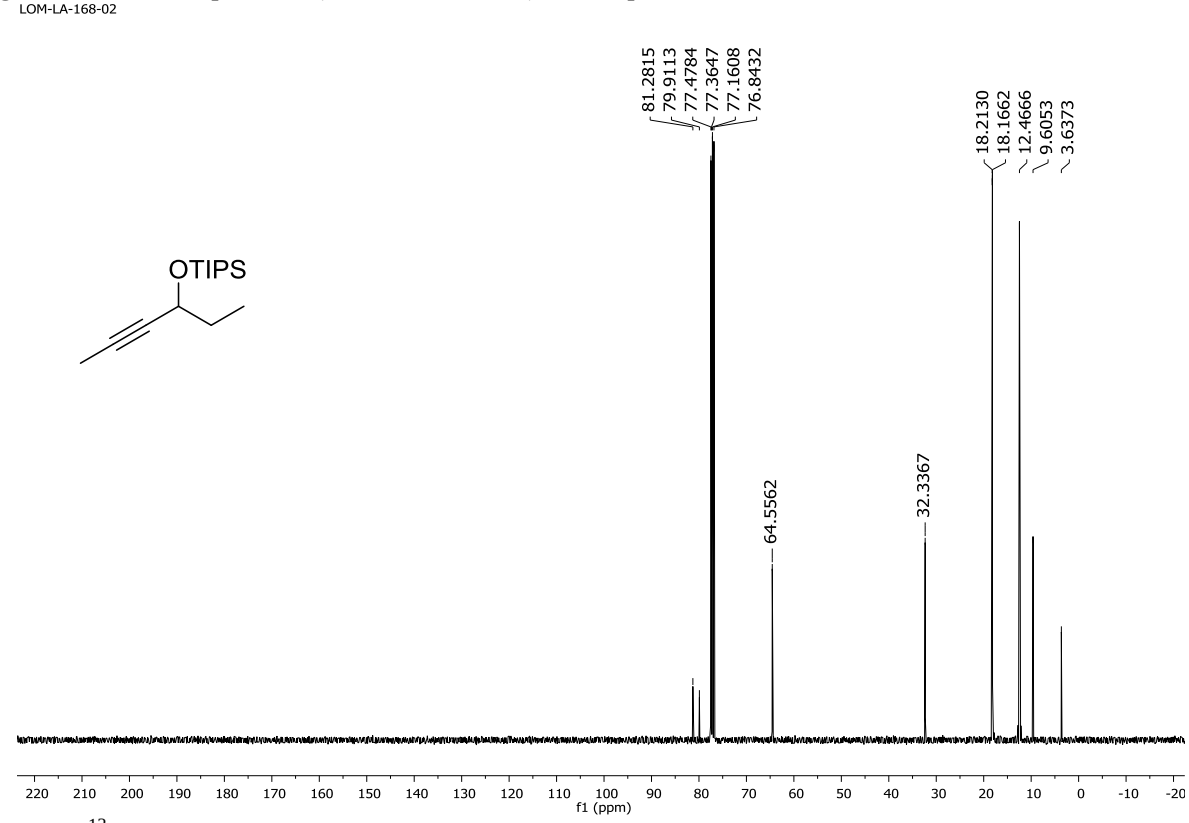

Figure 8: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **7d**.

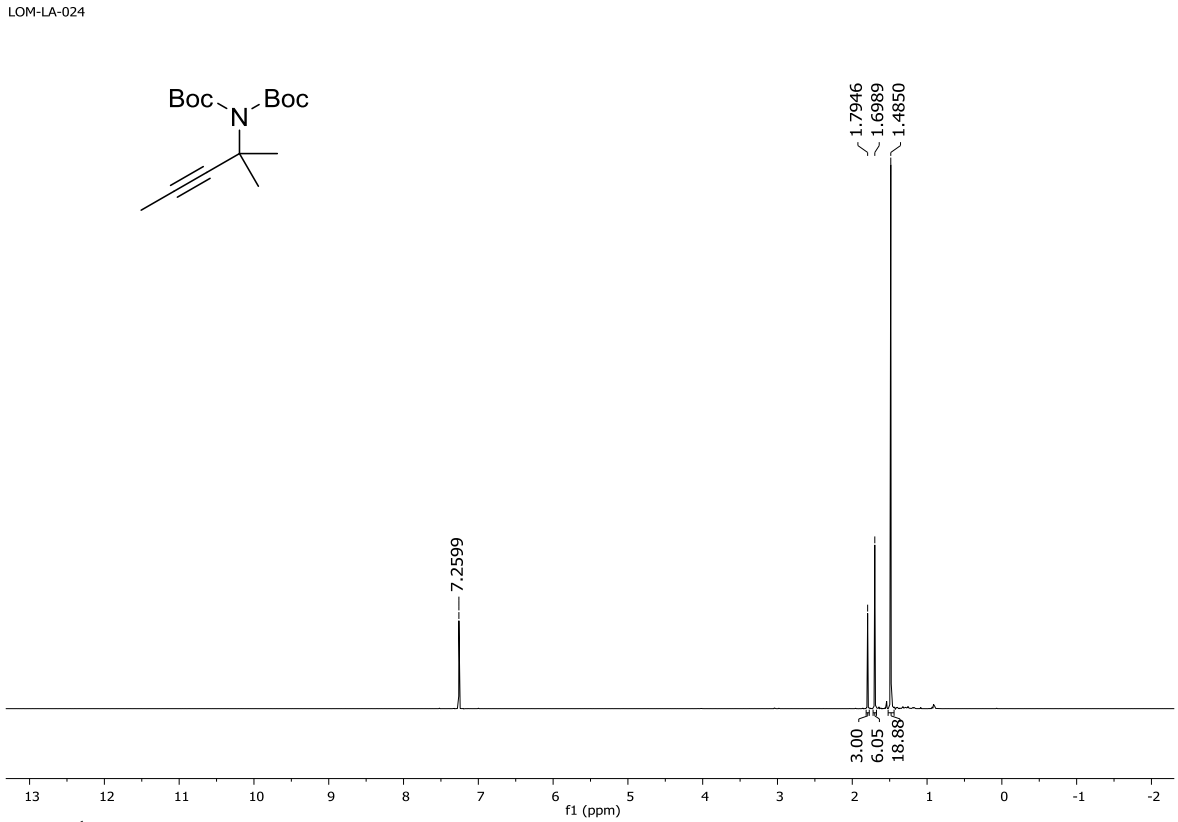

Figure 9: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **40**.

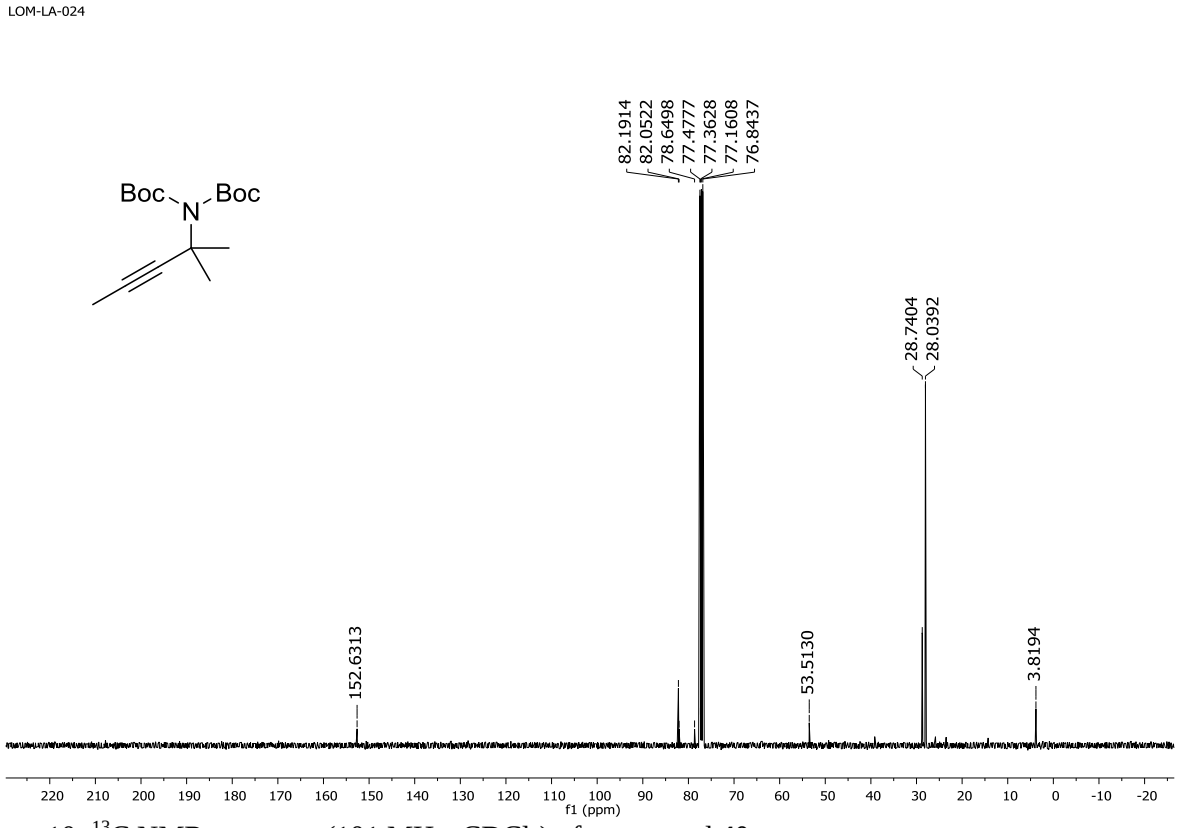

Figure 10: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **40**.

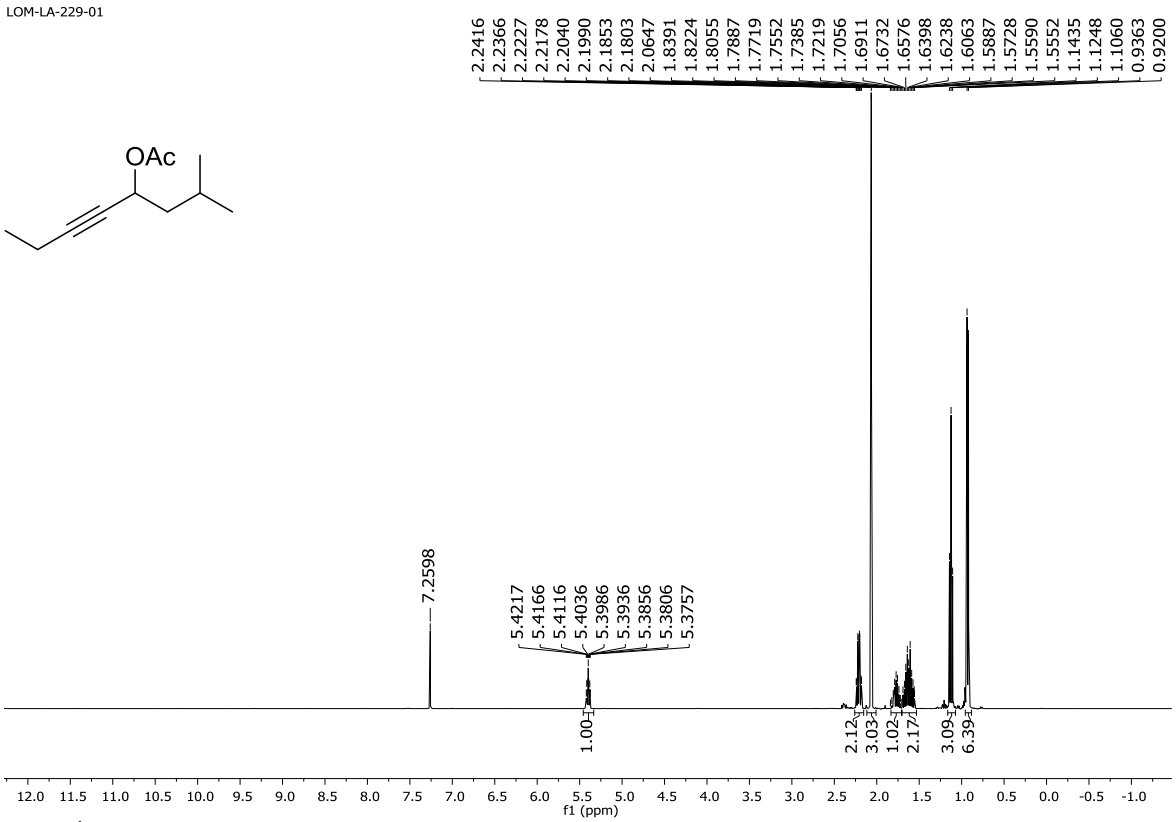

Figure 1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S1**.

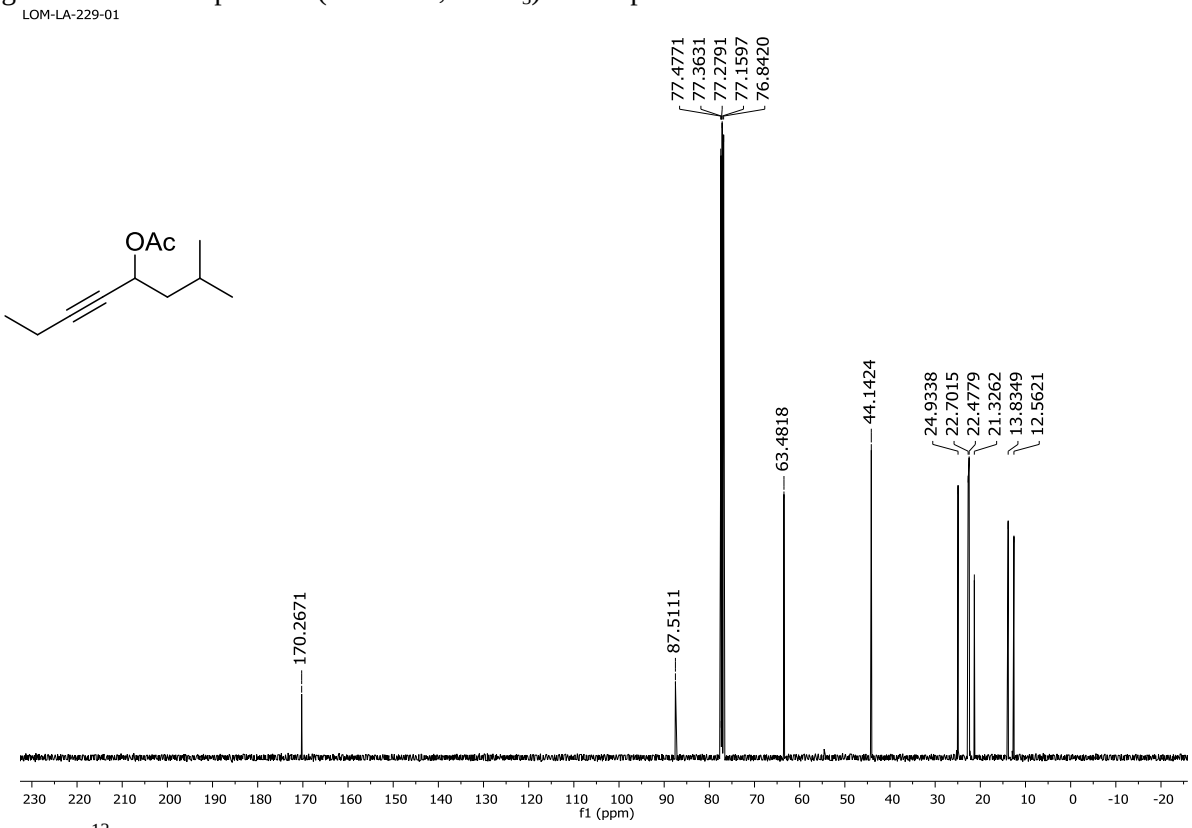

Figure 2: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S1**.

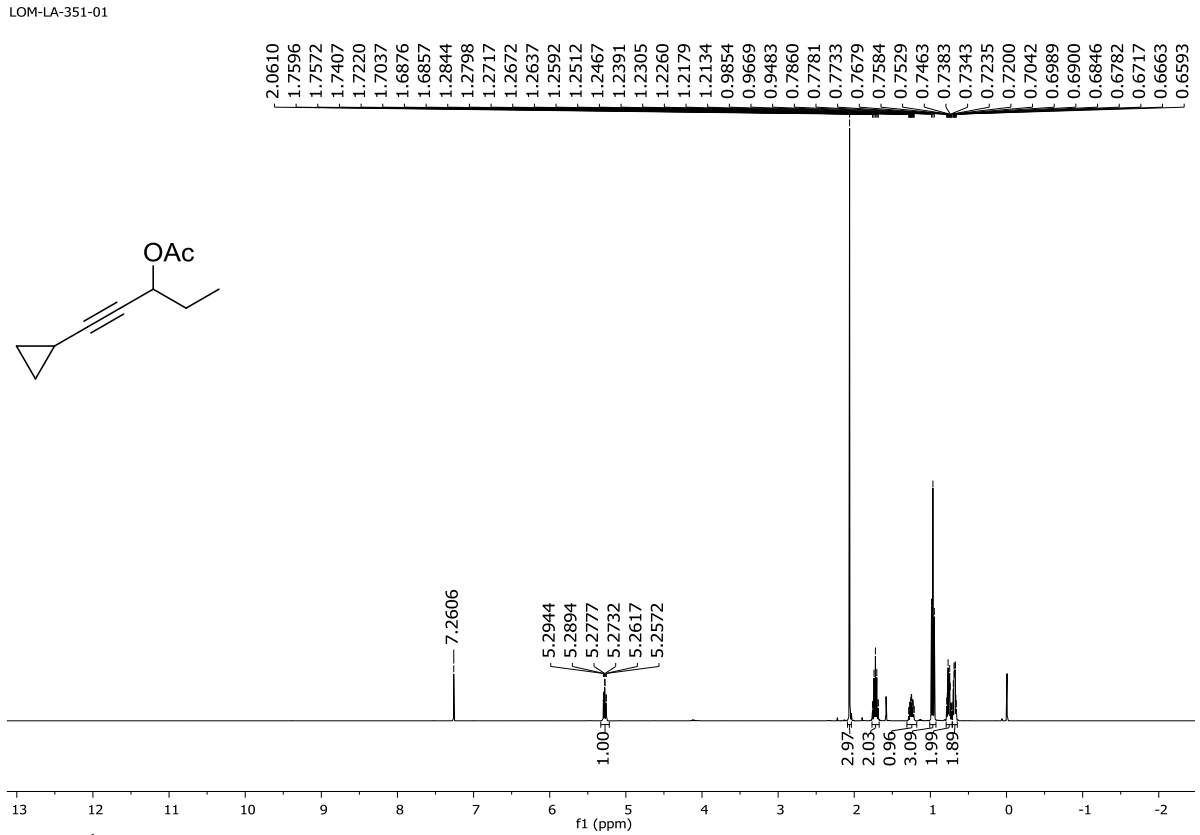

Figure 3: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S2**.

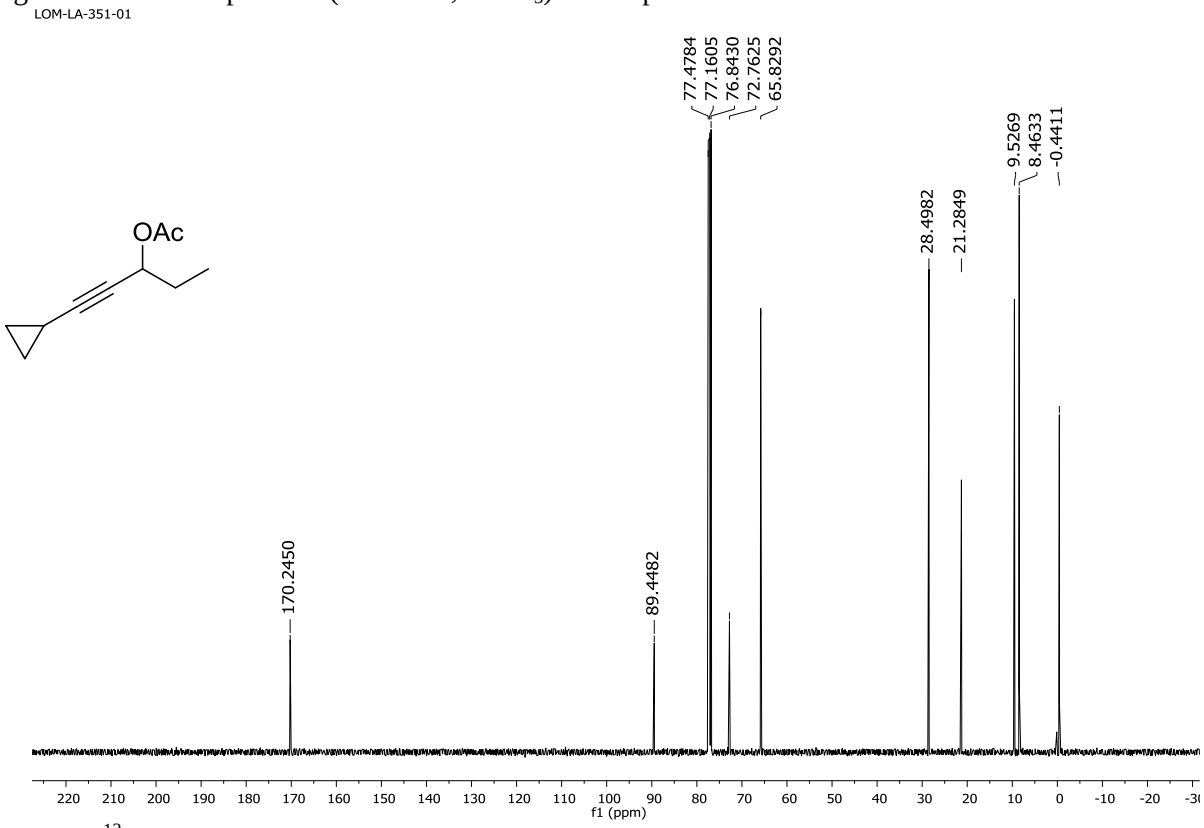

Figure 4: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S2**.

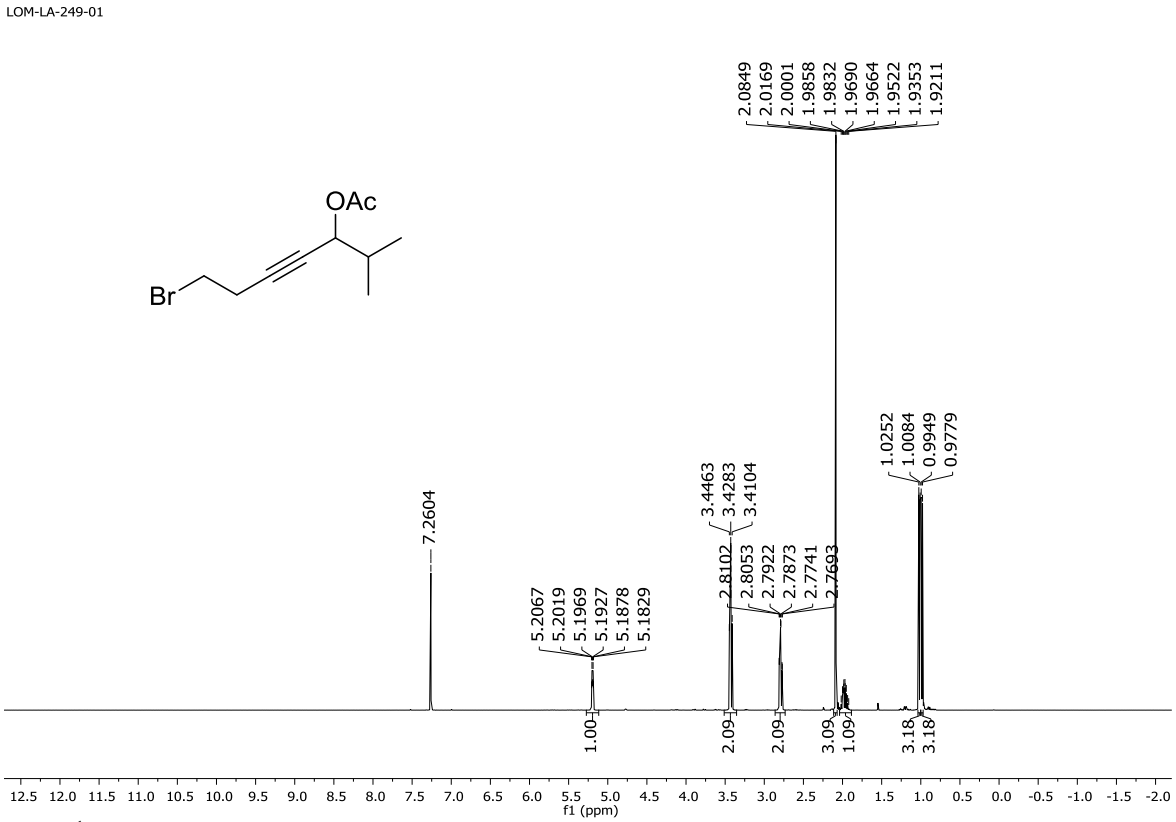

Figure 5: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S3**.

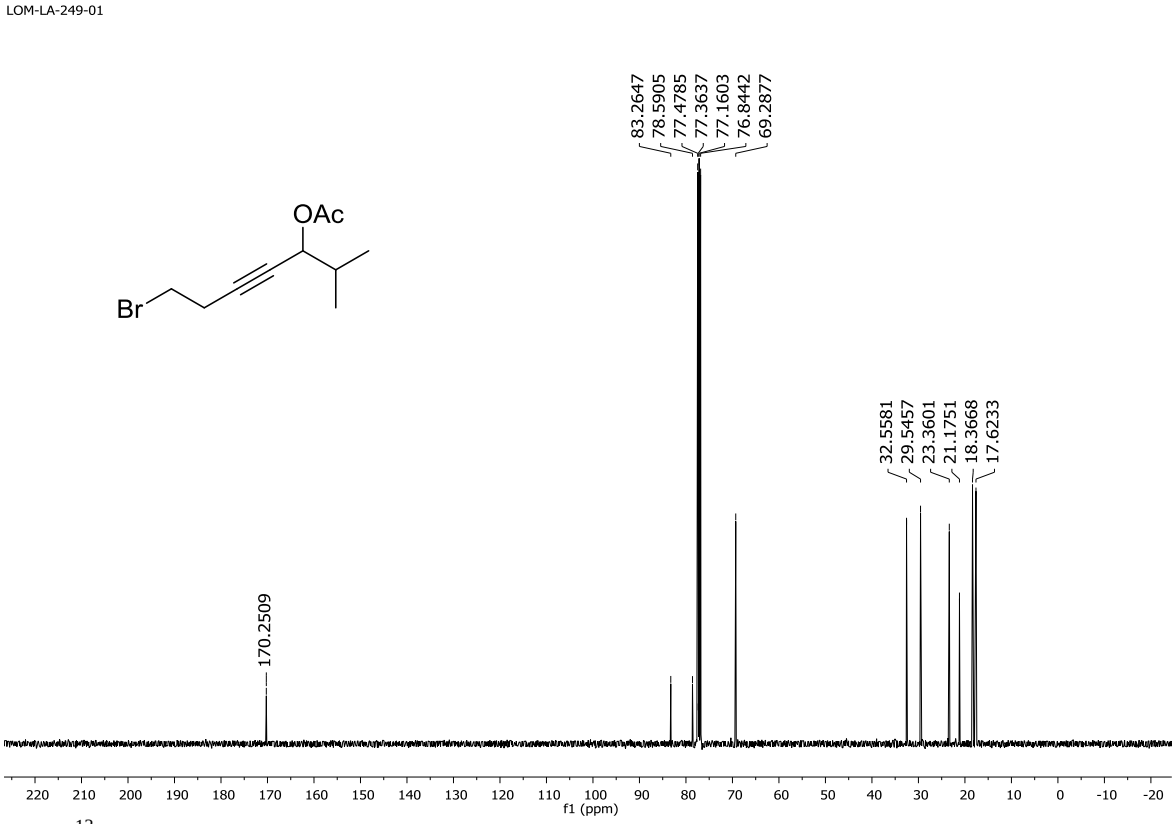

Figure 6: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S3**.

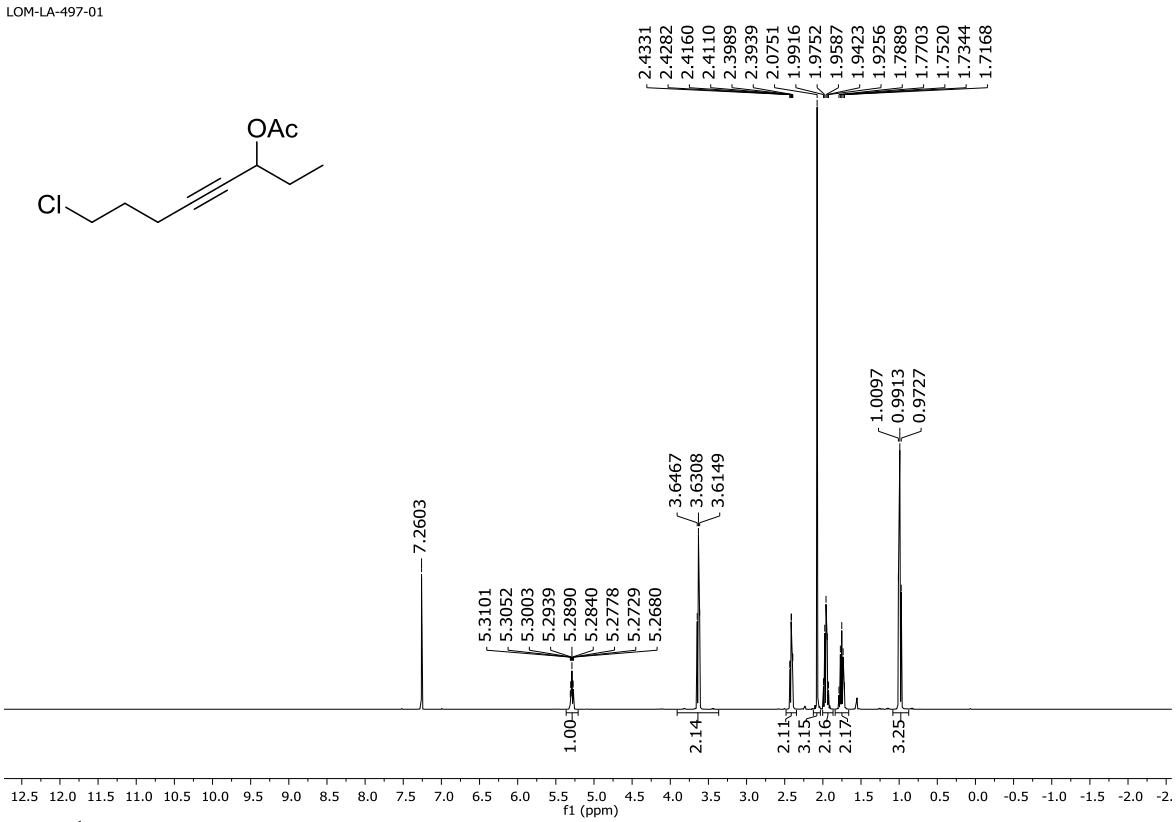

Figure 7: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S4**.

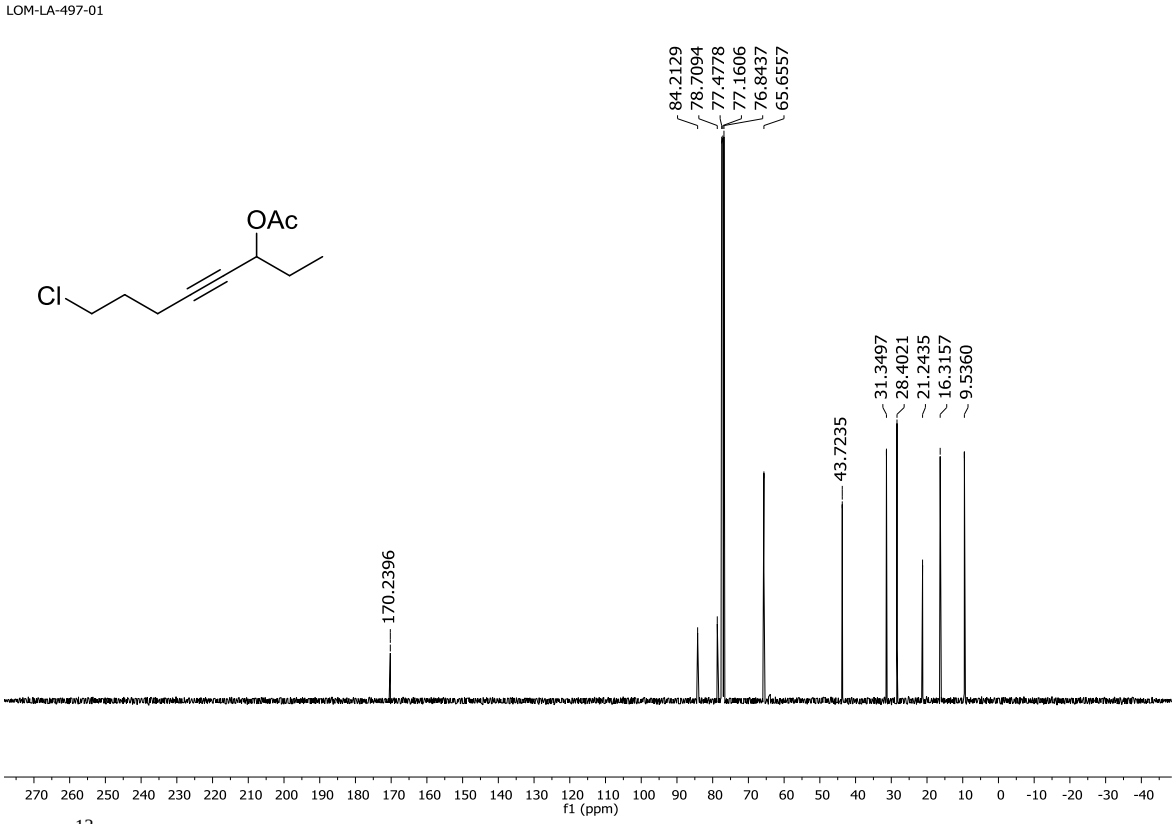

Figure 8: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S4**.

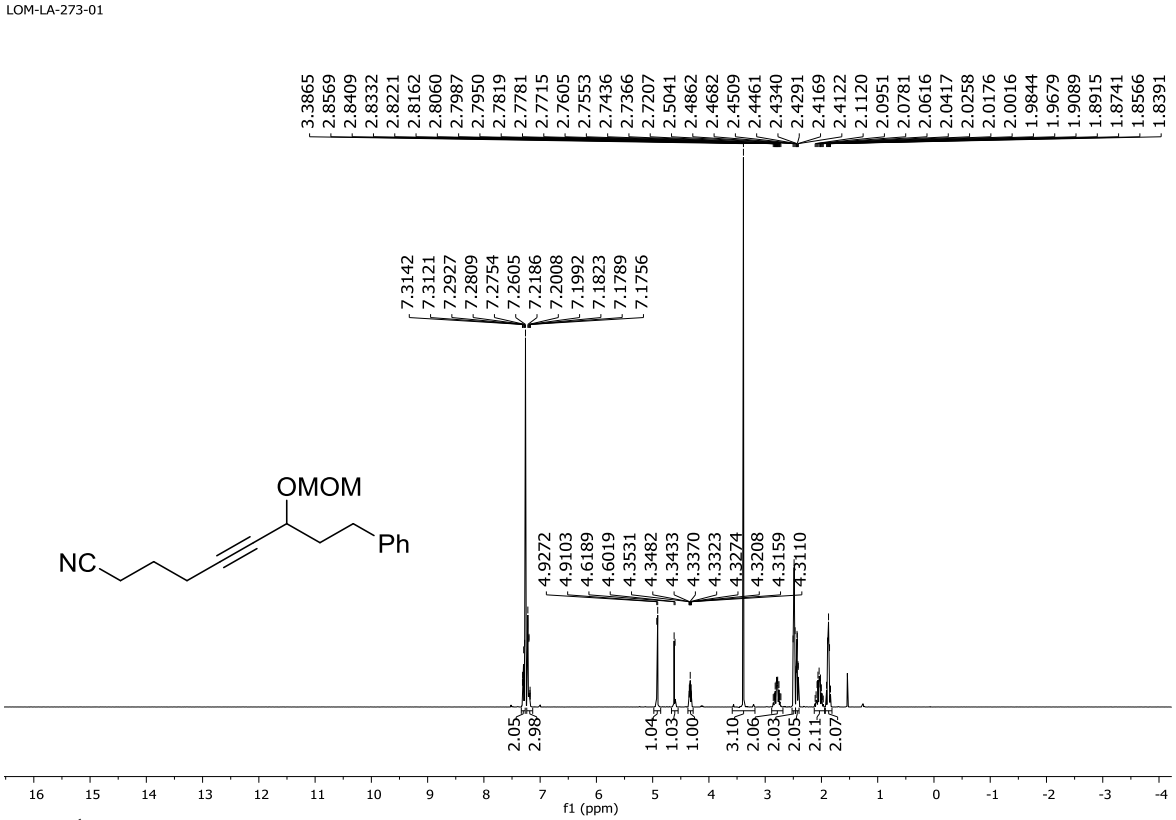

Figure 9: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S5**.

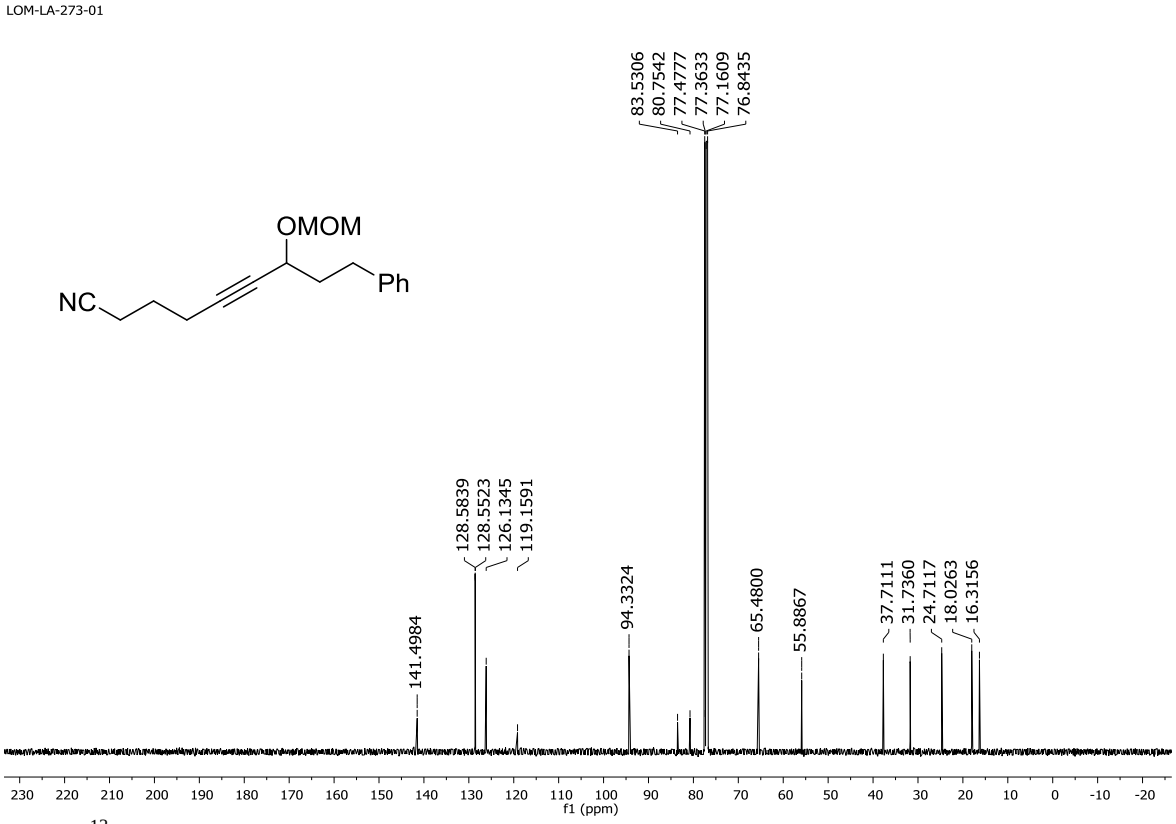

Figure 10: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S5**.

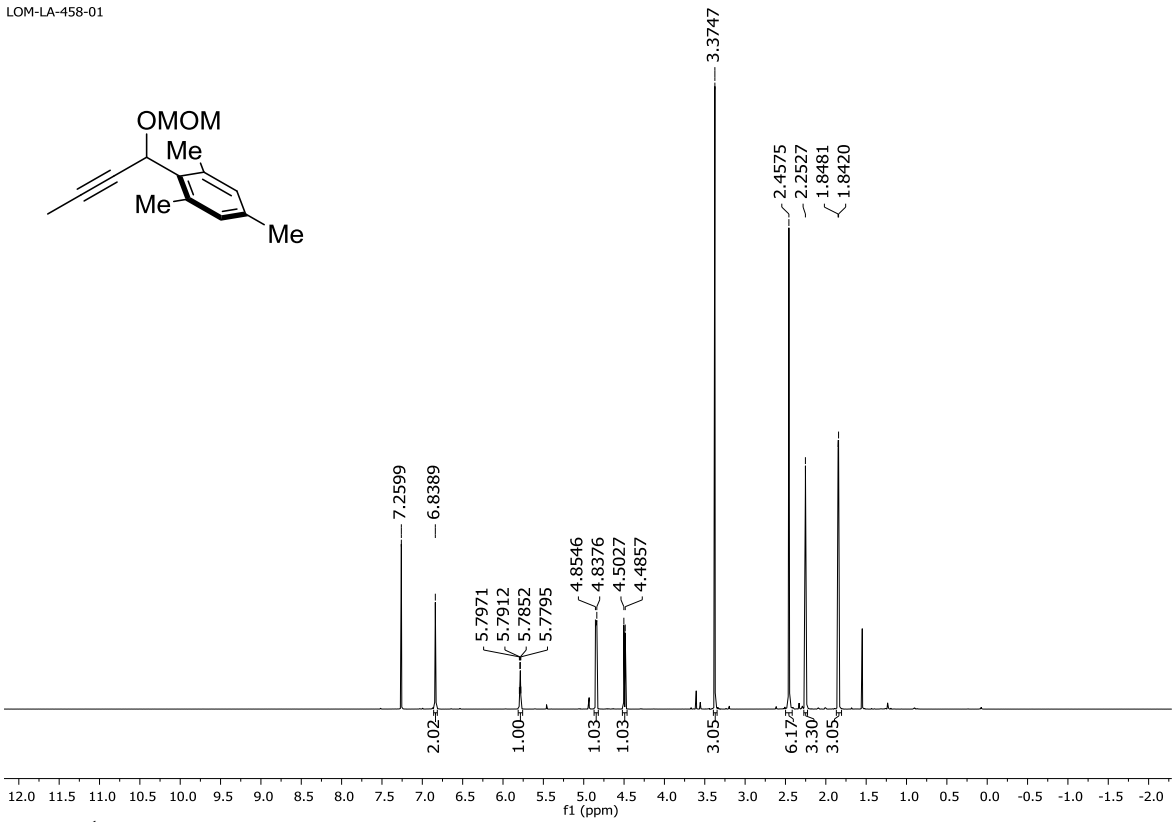

Figure 11: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S6**.

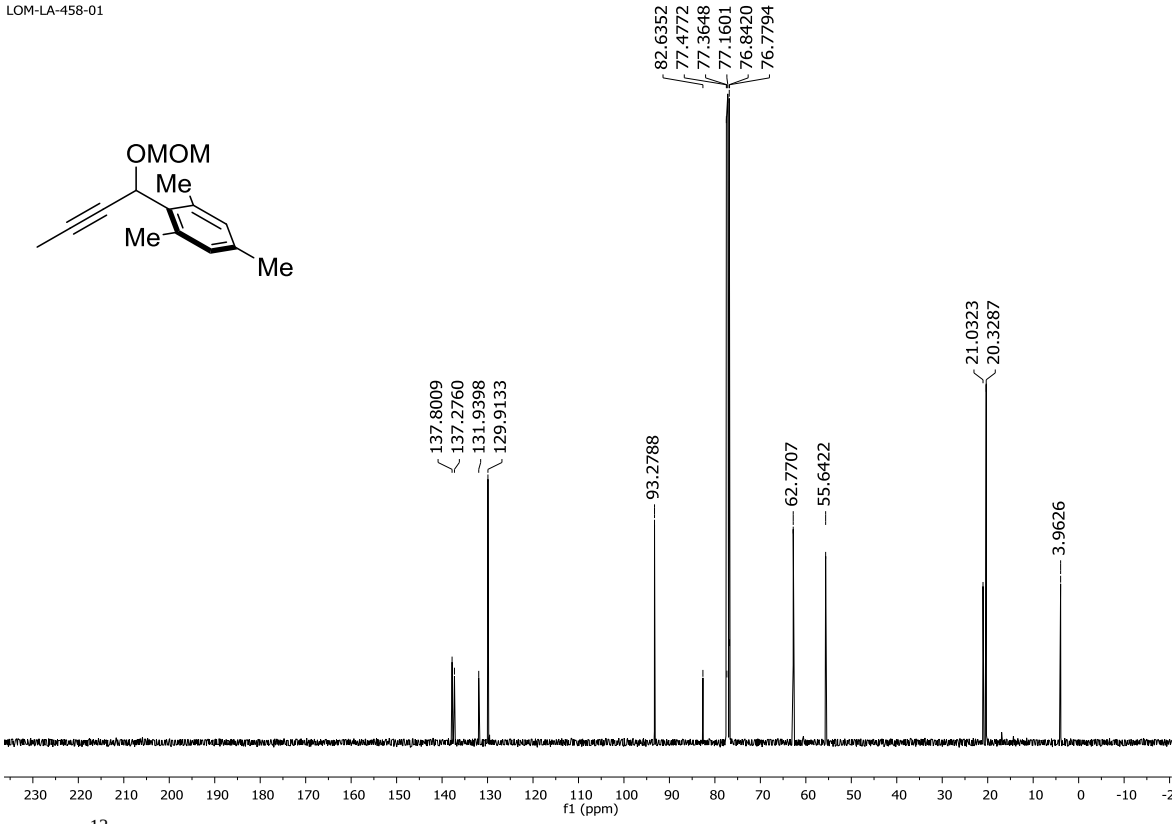

Figure 12: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S6**.

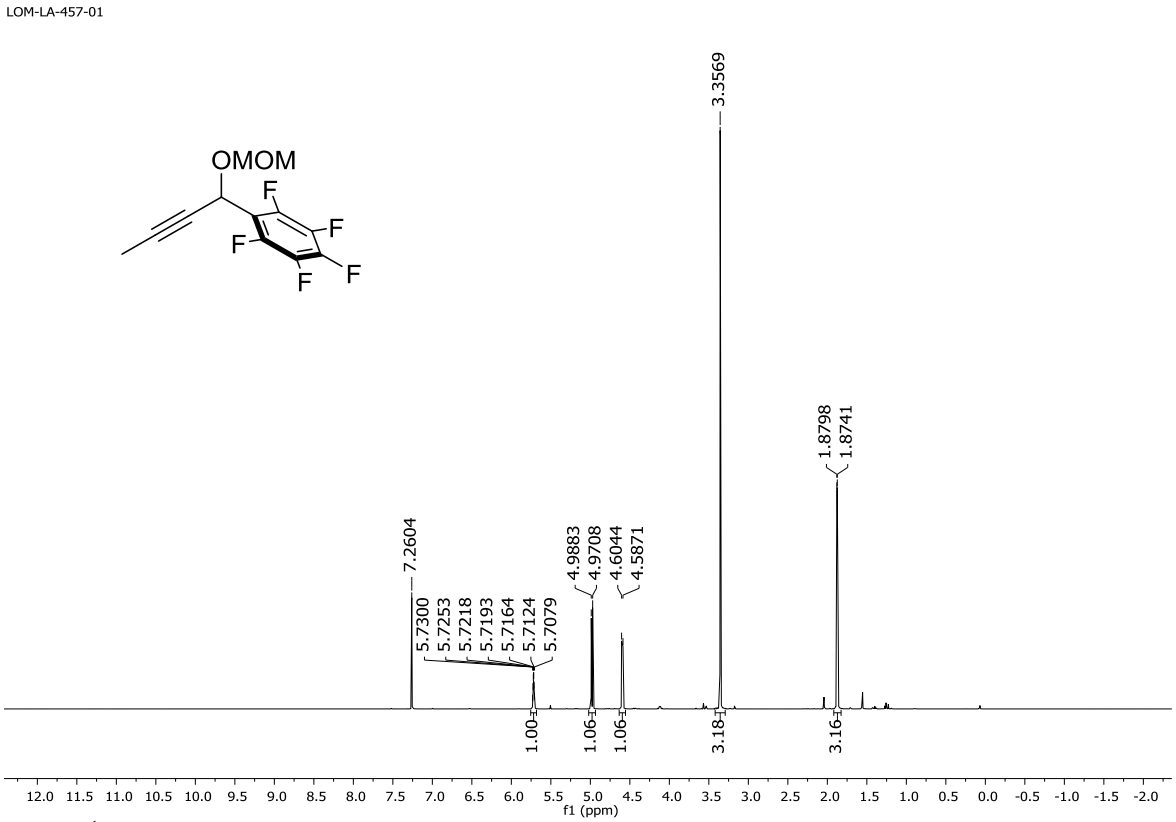

Figure 13: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S7**.

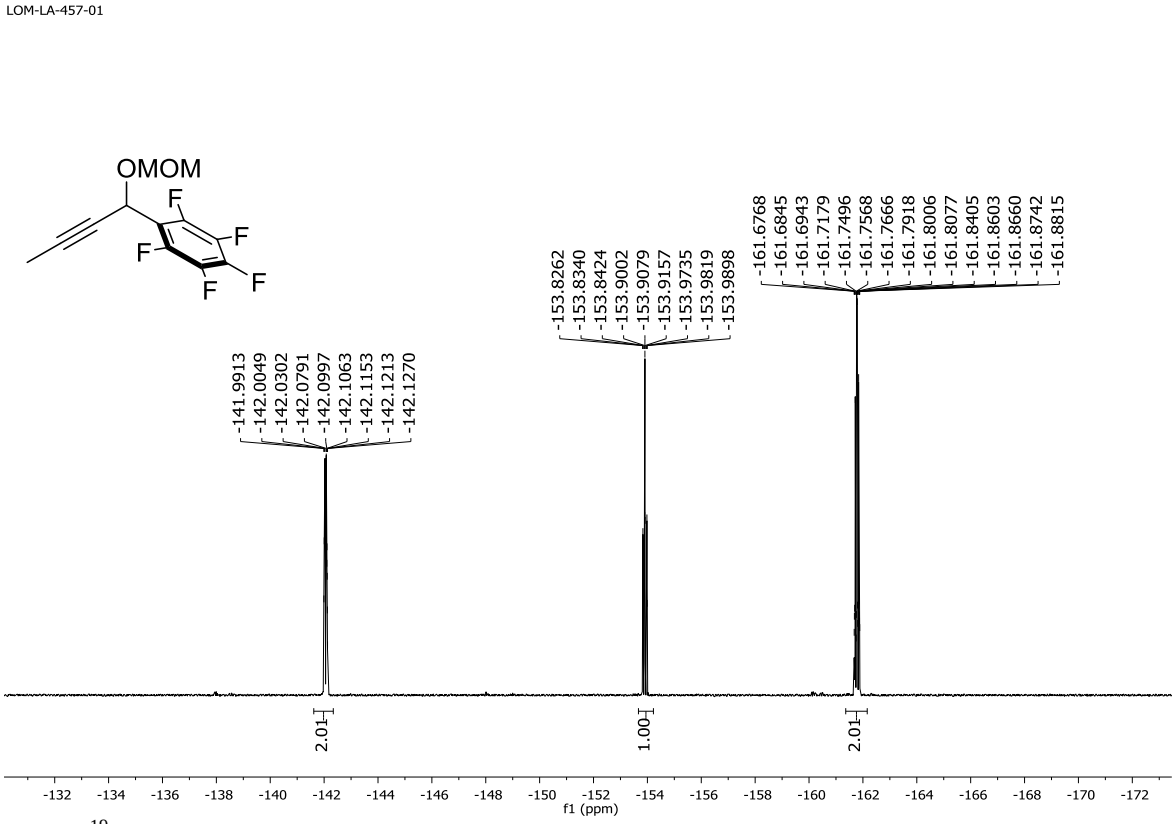

Figure 14: ^{19}F NMR spectrum (282 MHz, $CDCl_3$) of compound **S7**.

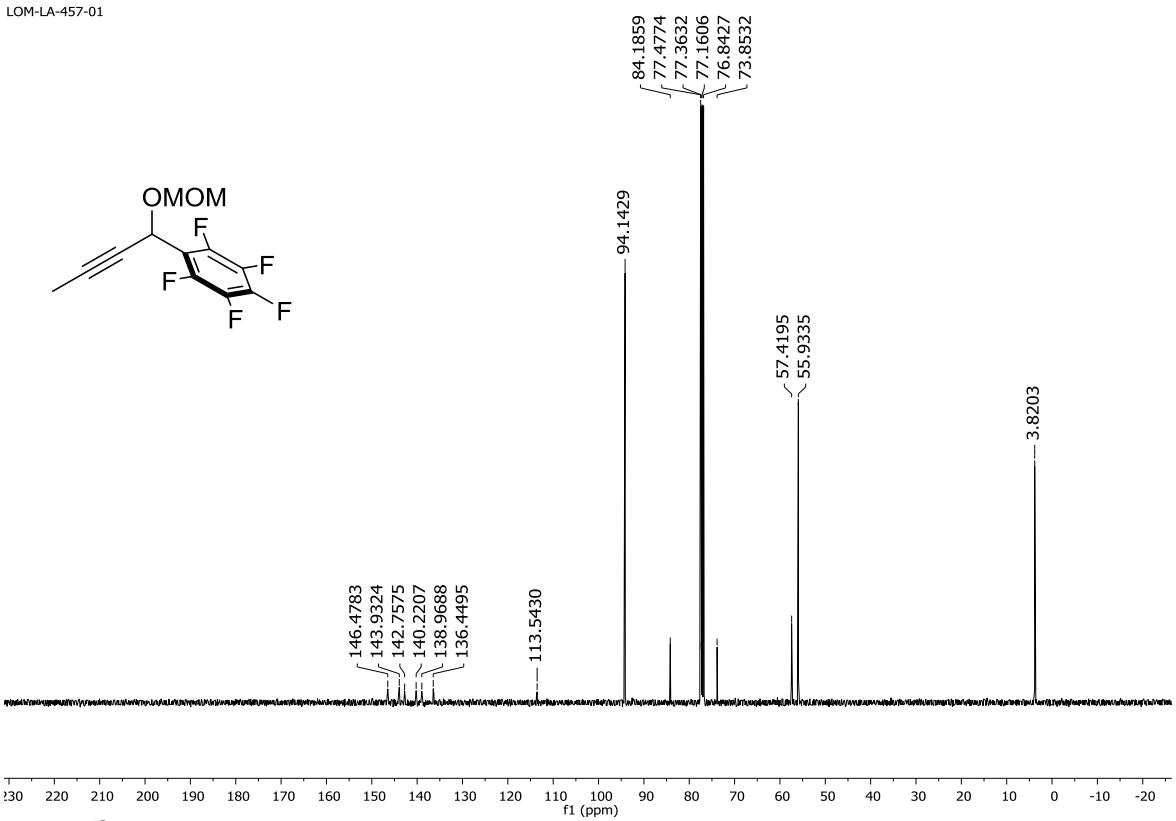

Figure 15: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S7**.

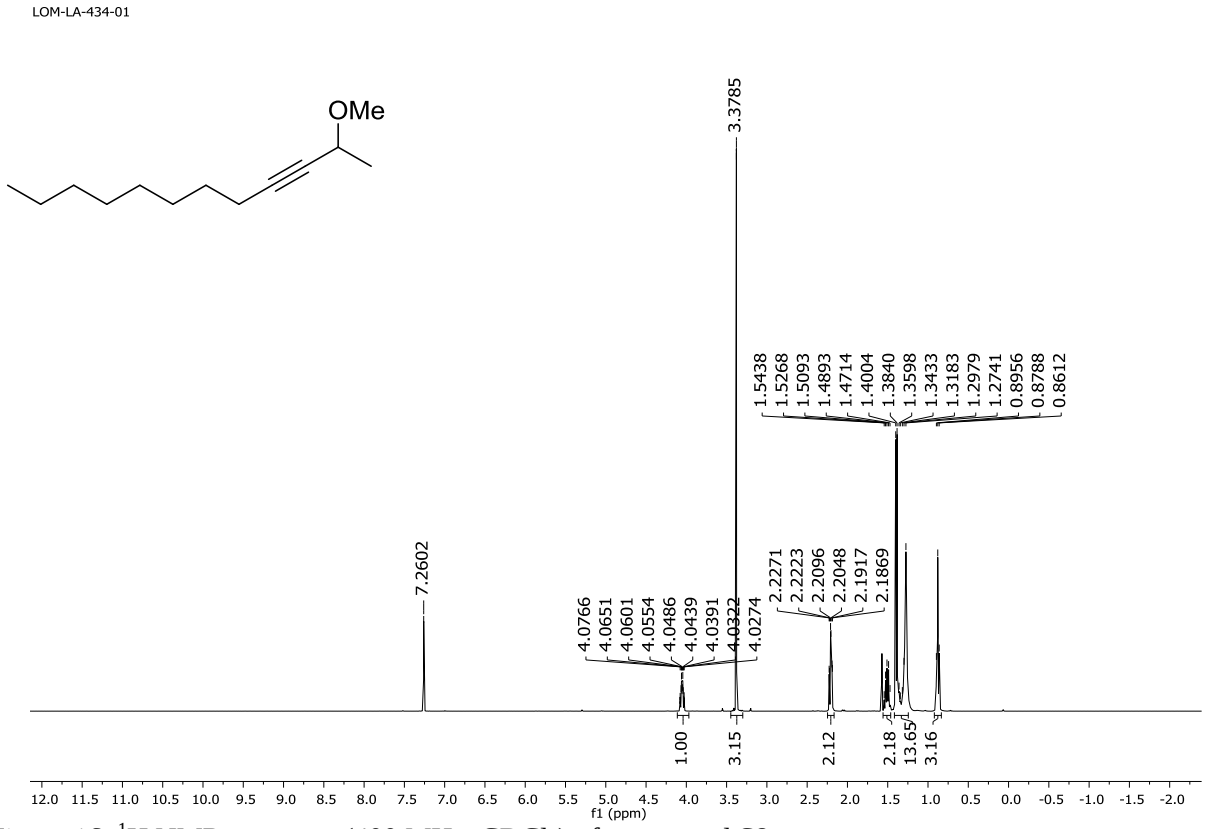

Figure 16: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S8**.

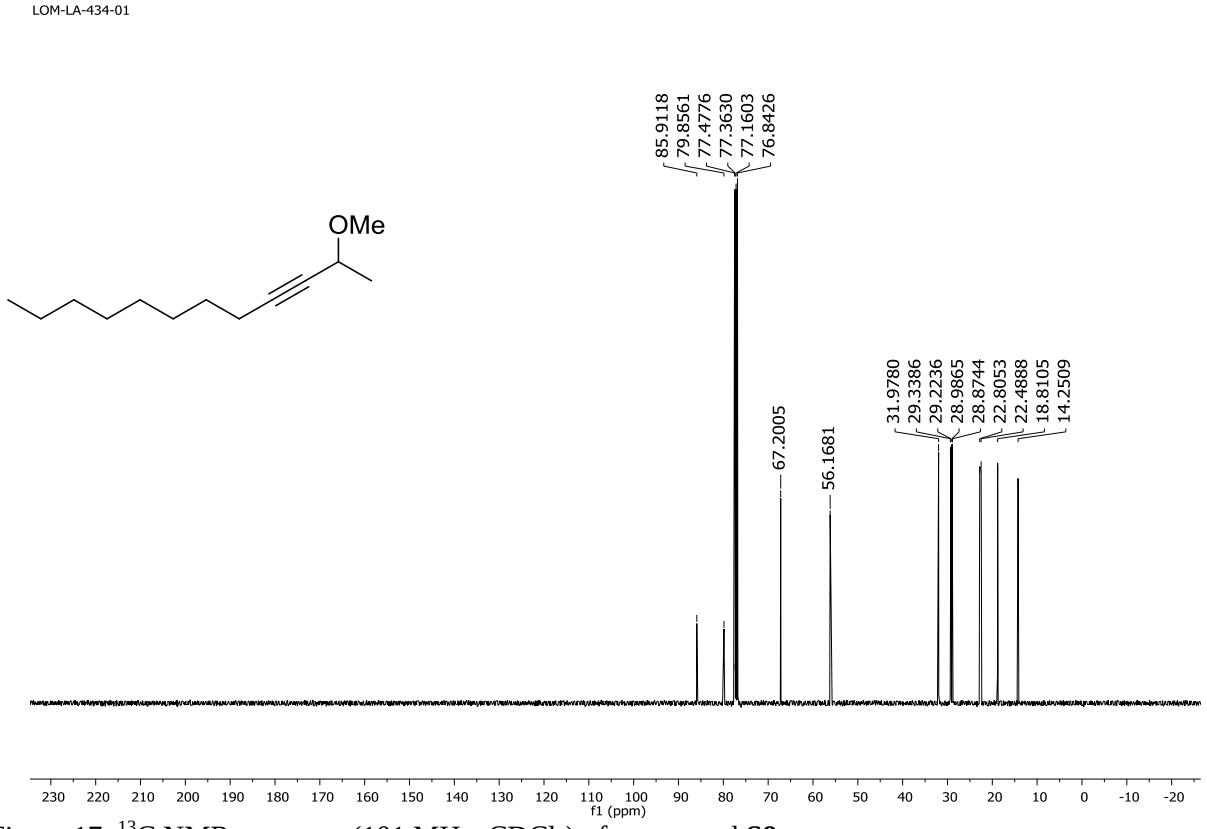

Figure 17: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S8**.

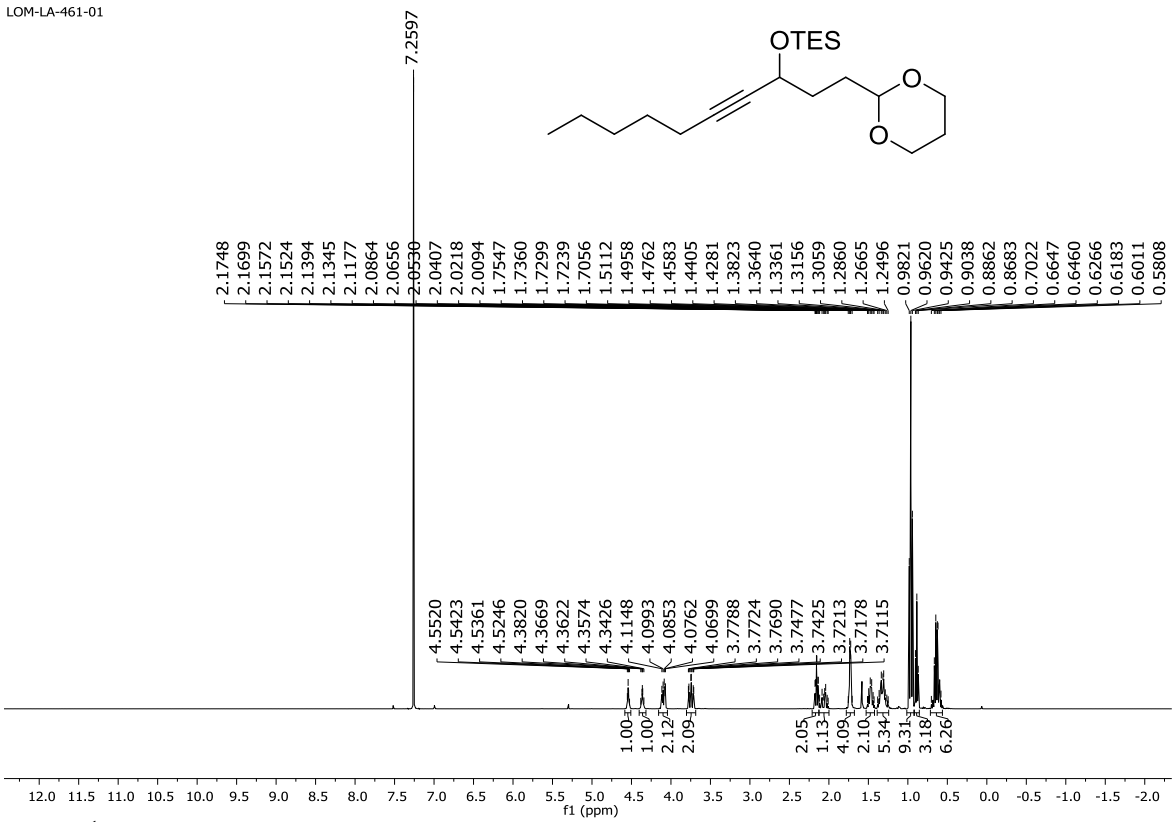

Figure 18: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S9**.

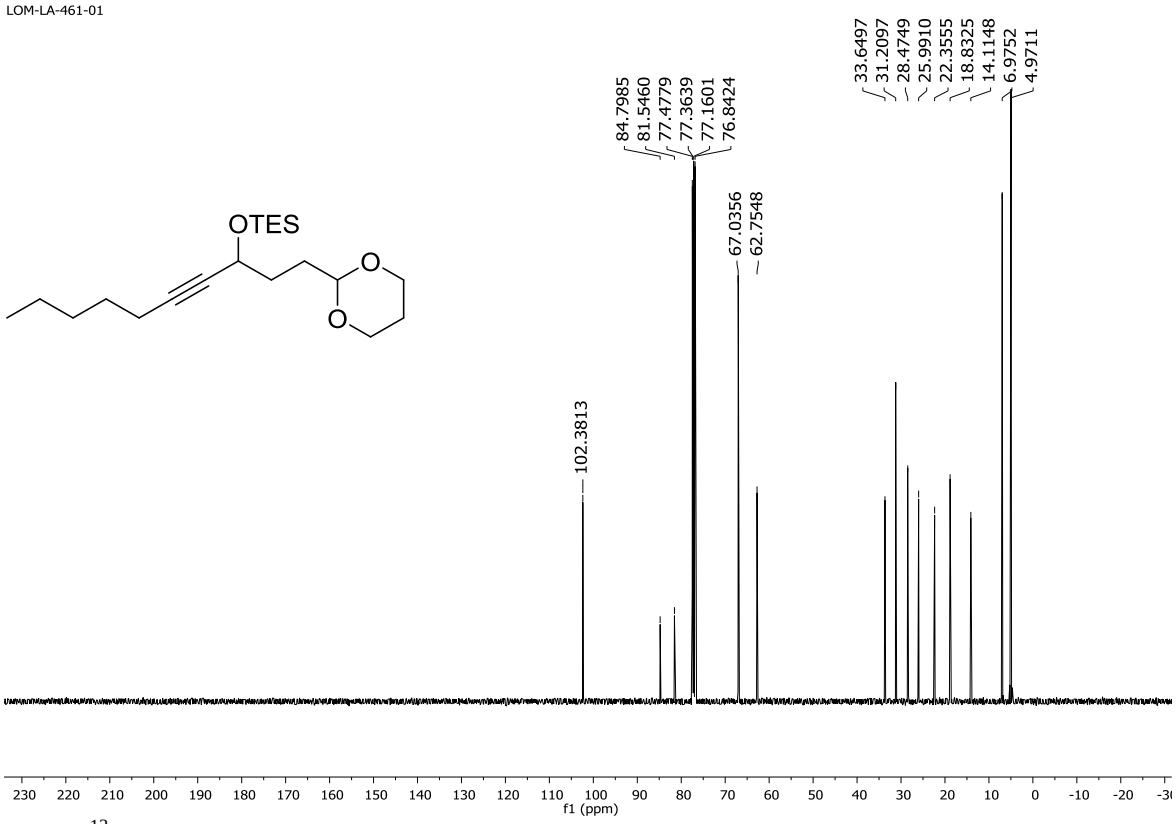

Figure 19: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S9**.

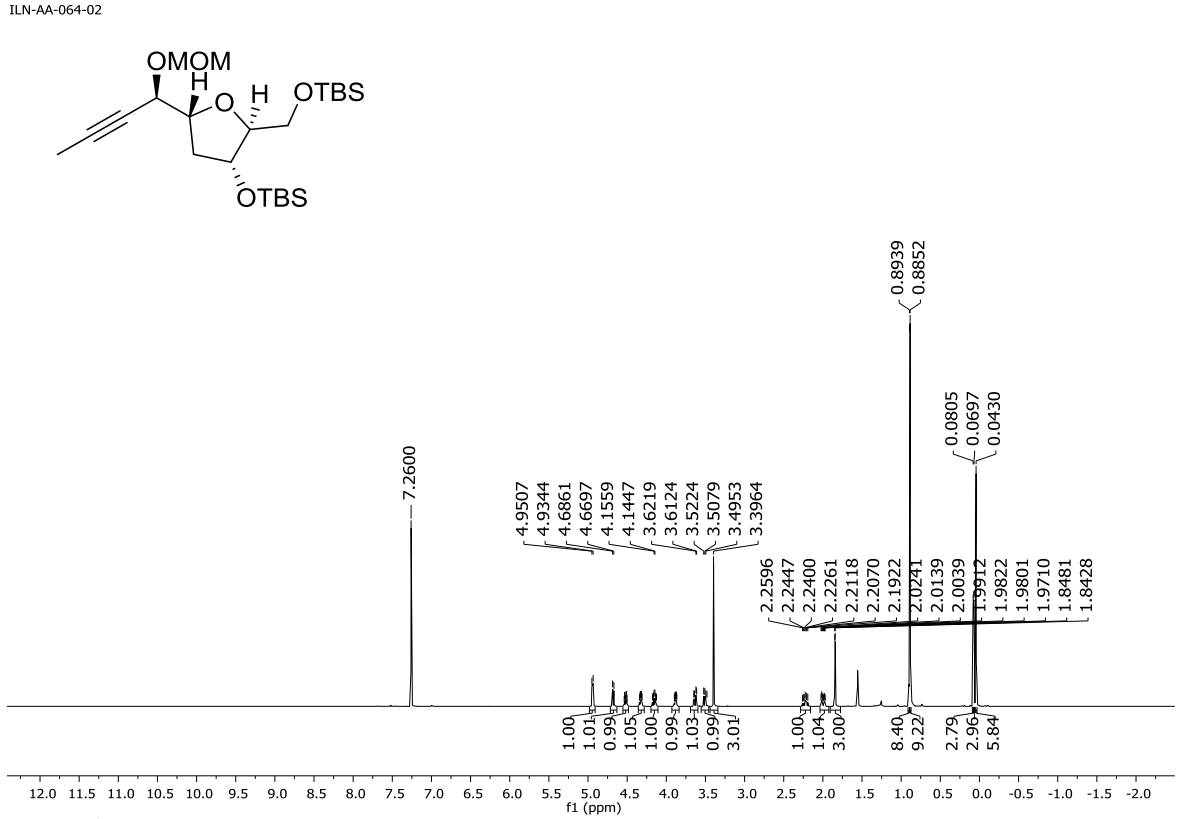

Figure 20: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S10**.

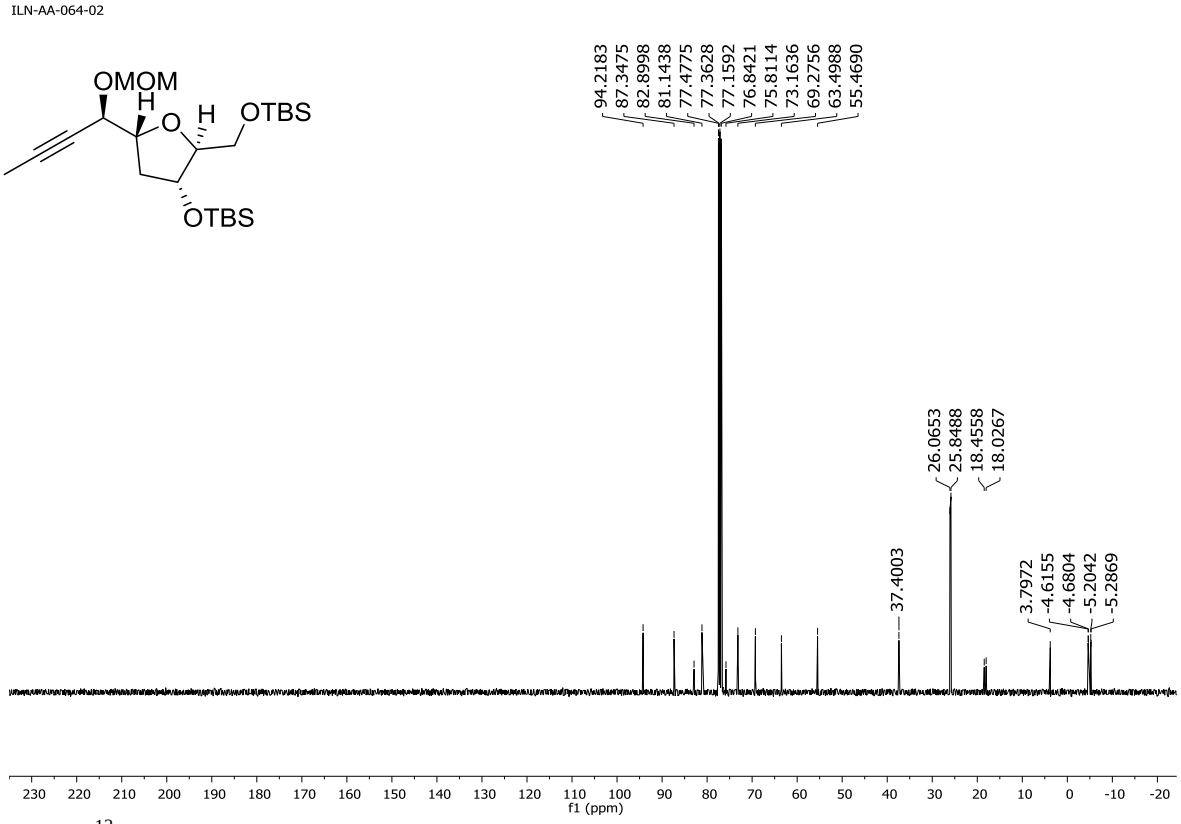

Figure 21: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S10**.

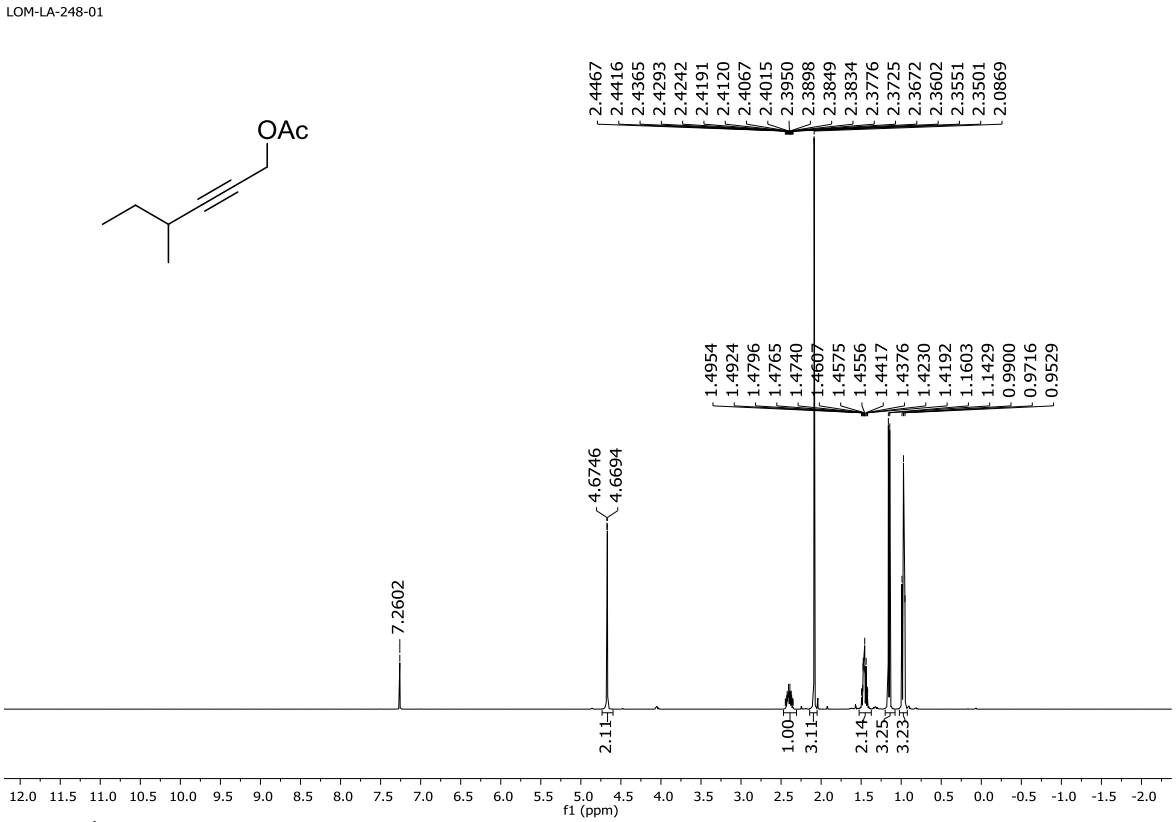

Figure 22: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S11**.

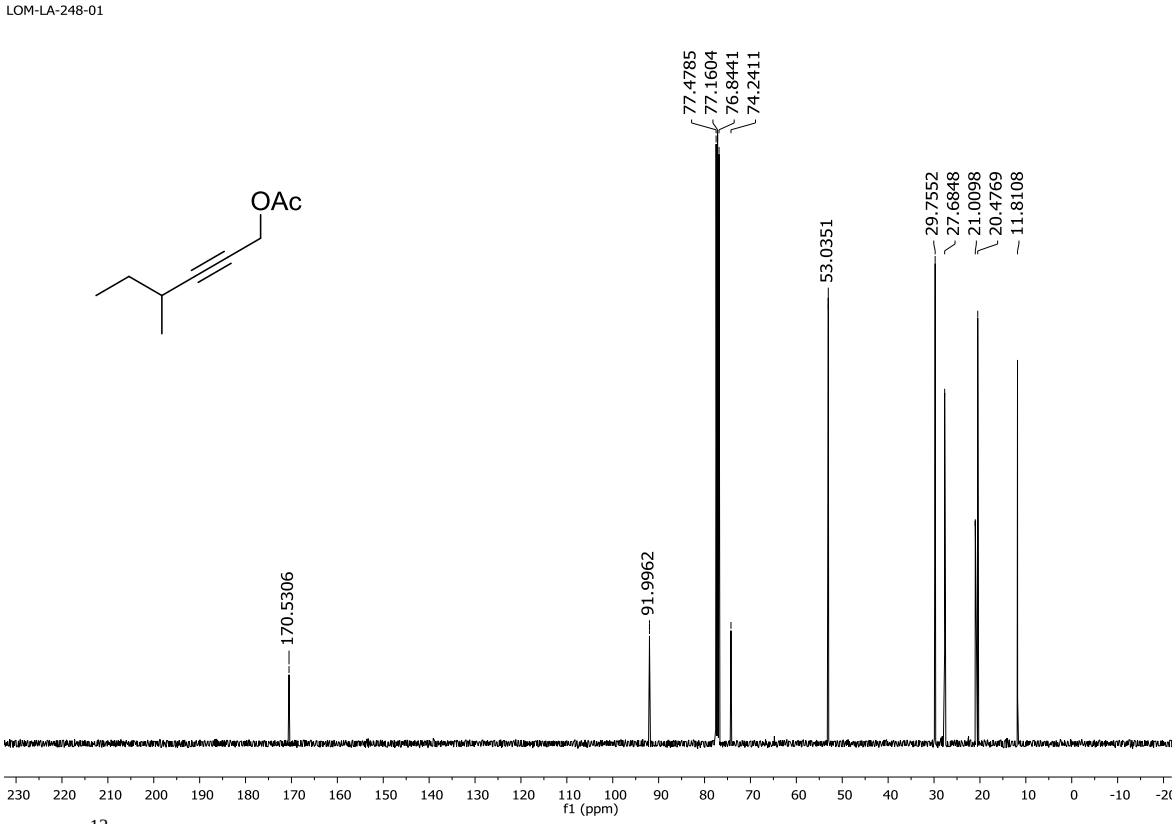

Figure 23: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S11**.

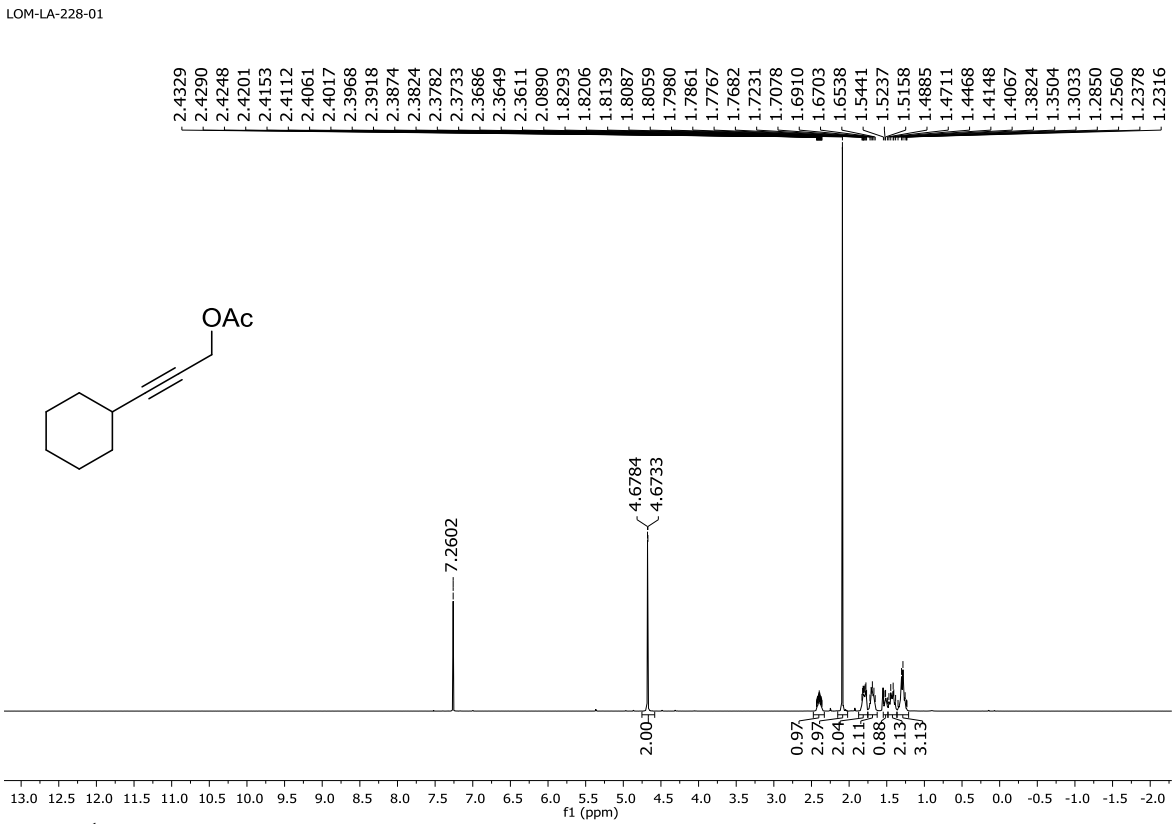

Figure 24: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S12**.

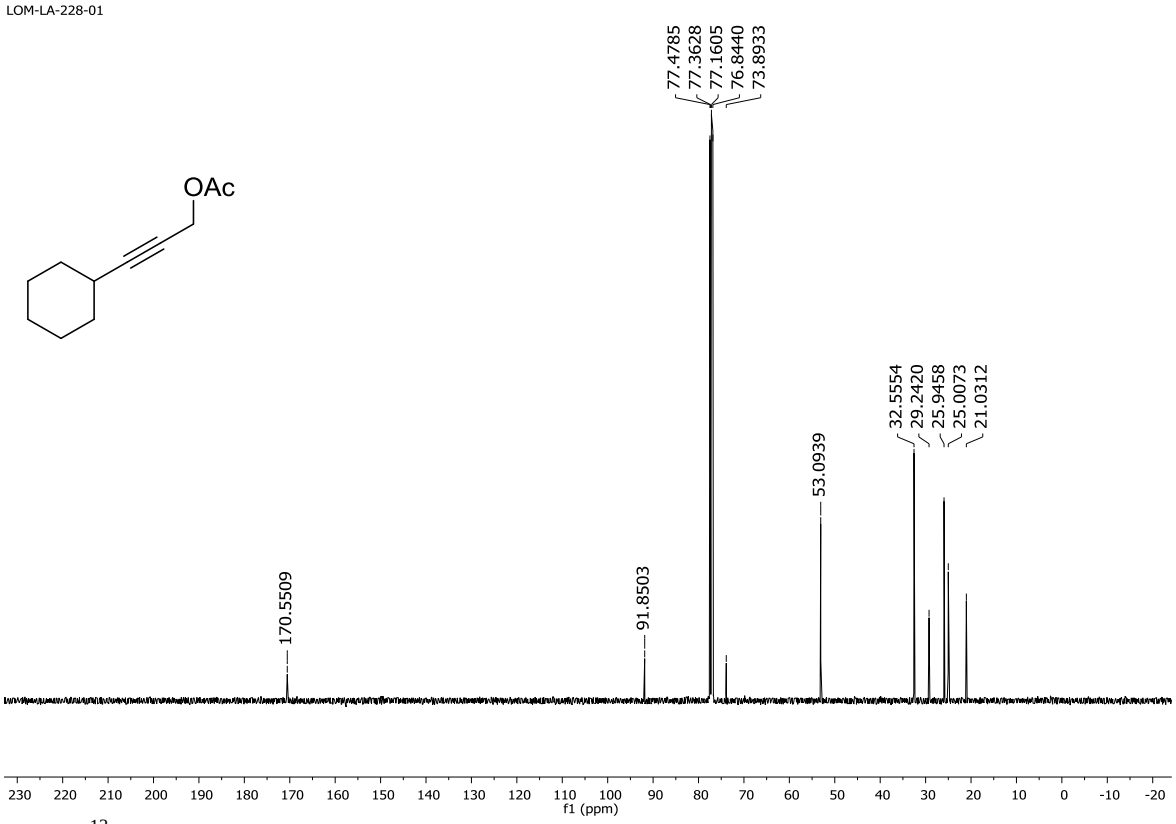

Figure 25: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S12**.

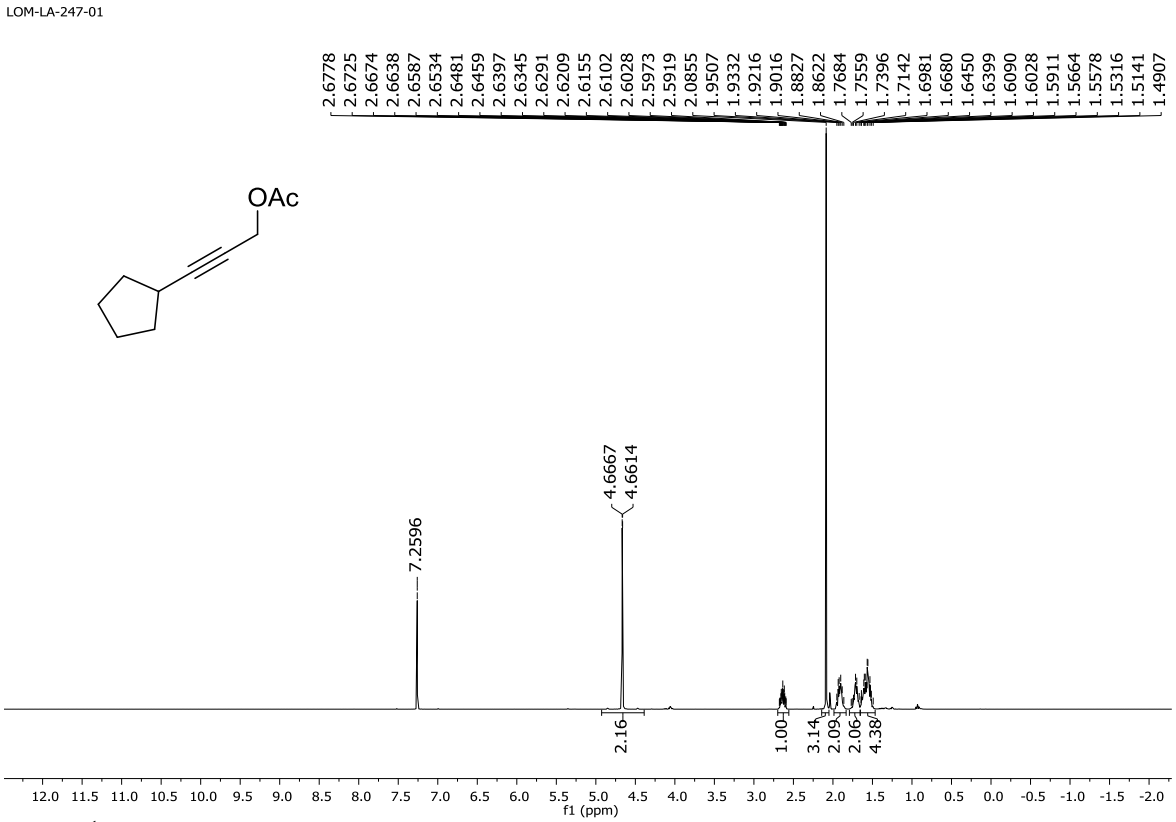

Figure 26: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S13**.

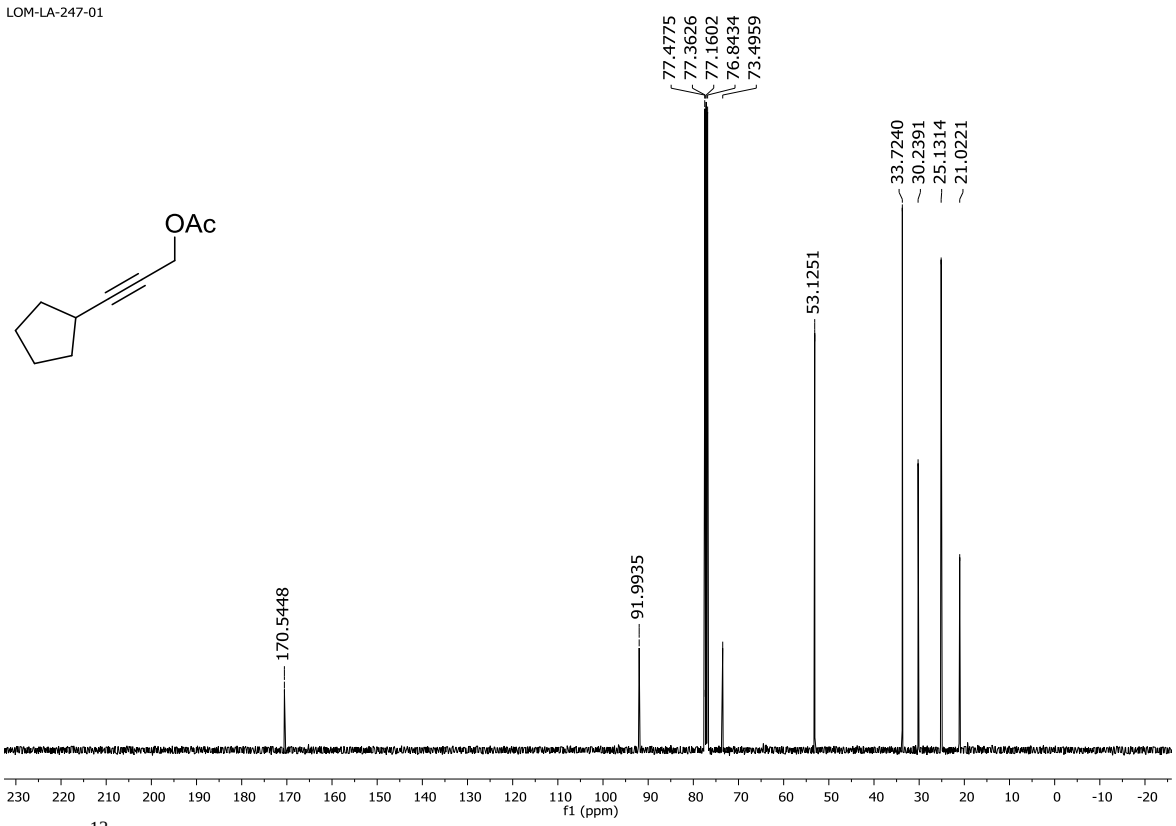

Figure 27: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S13**.

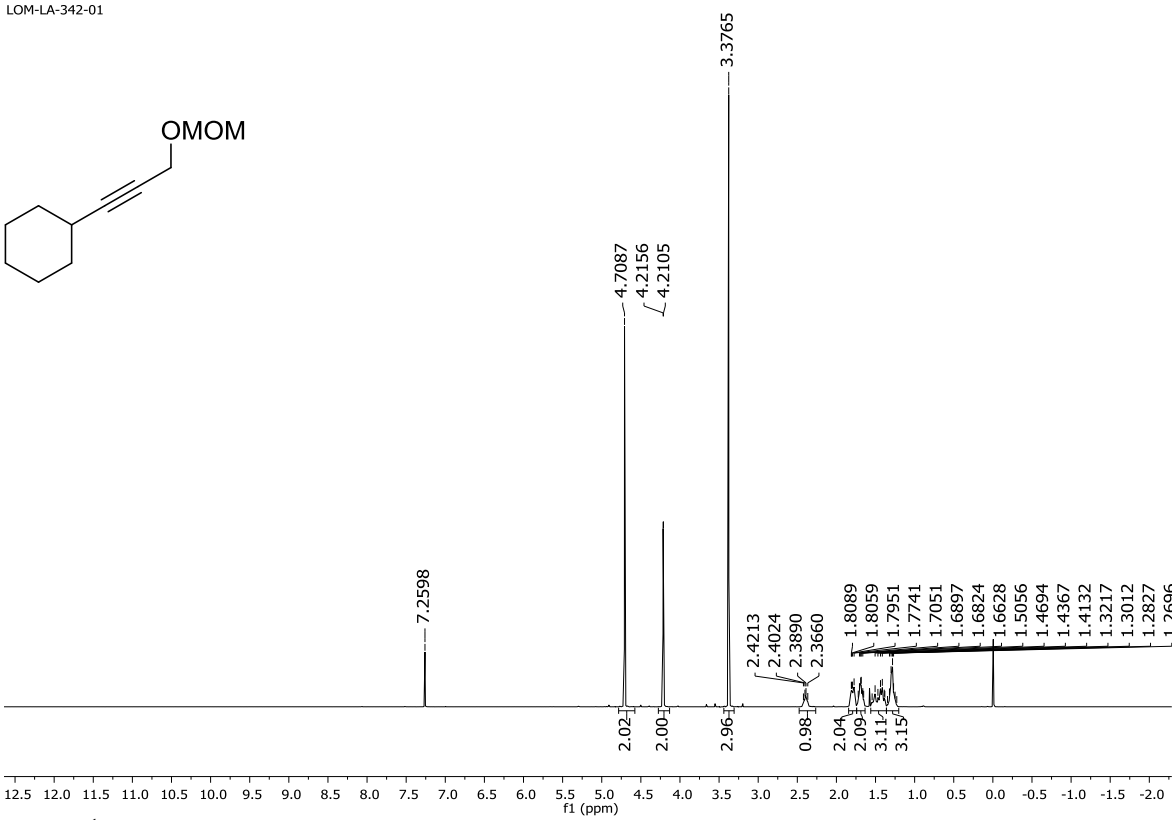

Figure 28: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S14**.

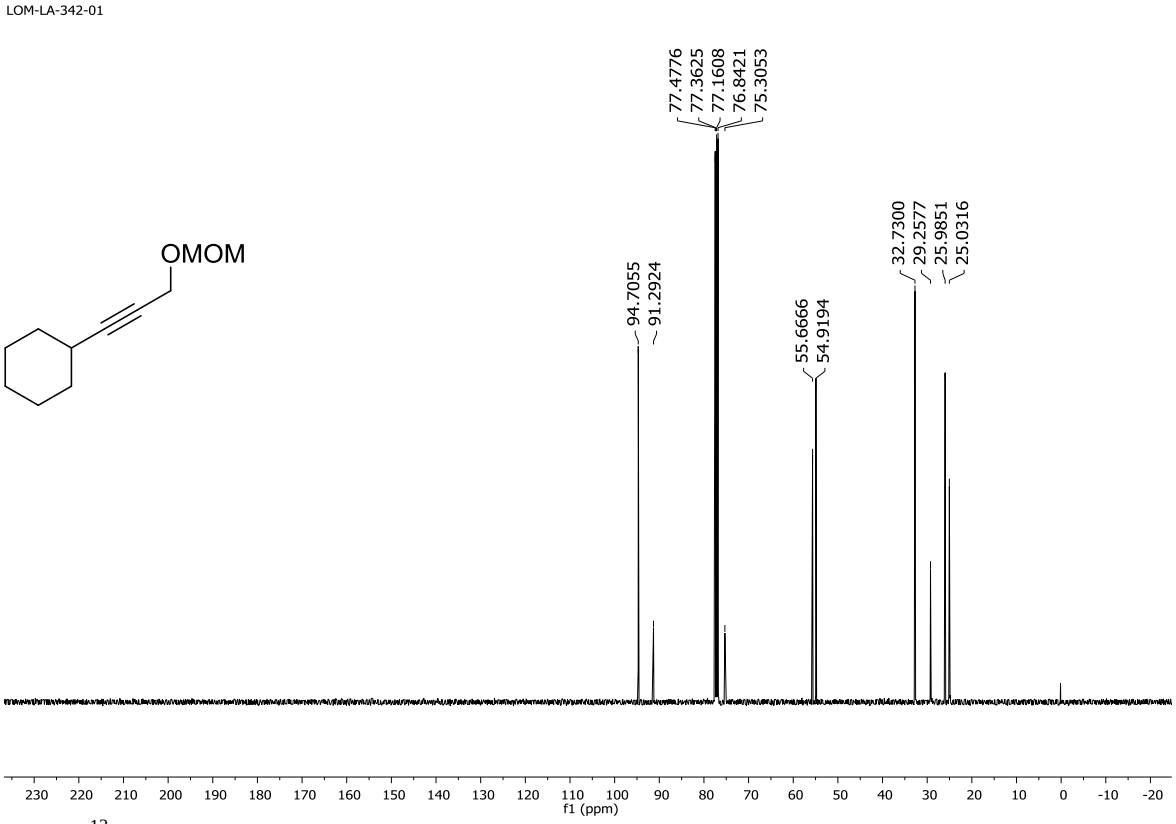

Figure 29: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S14**.

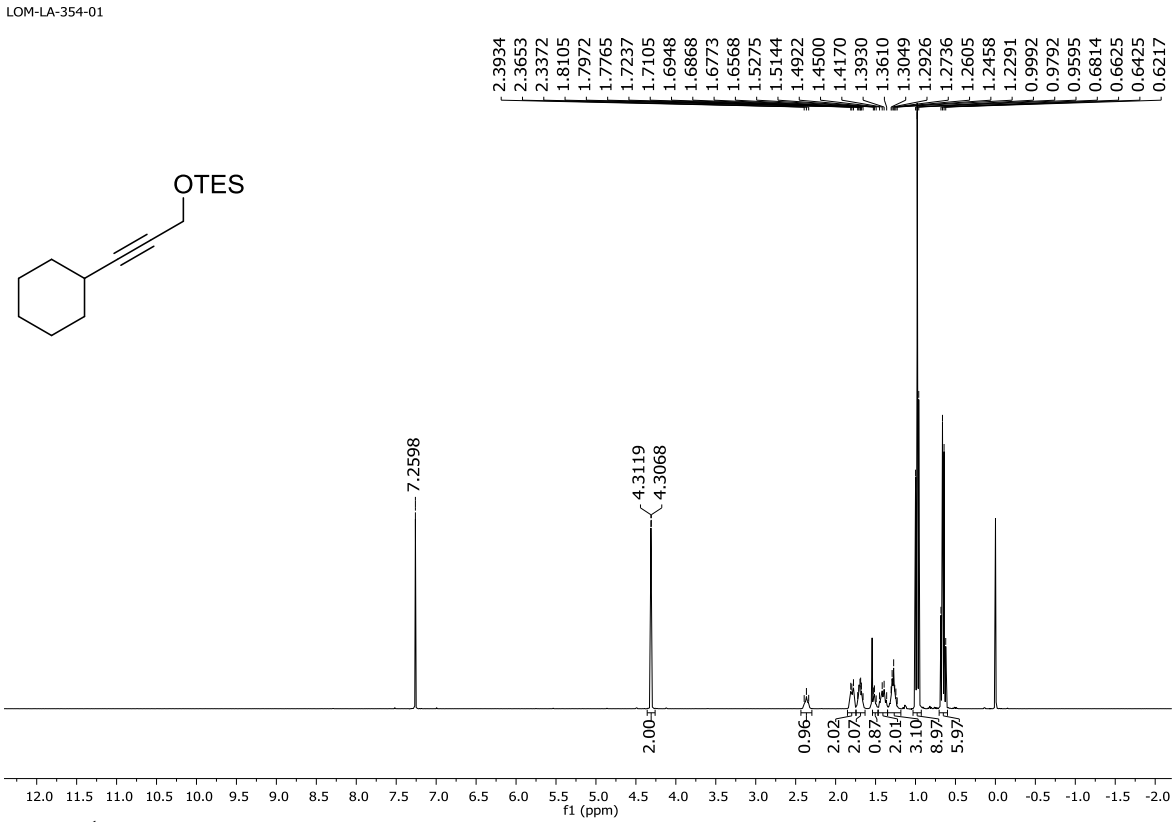

Figure 30: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S15**.

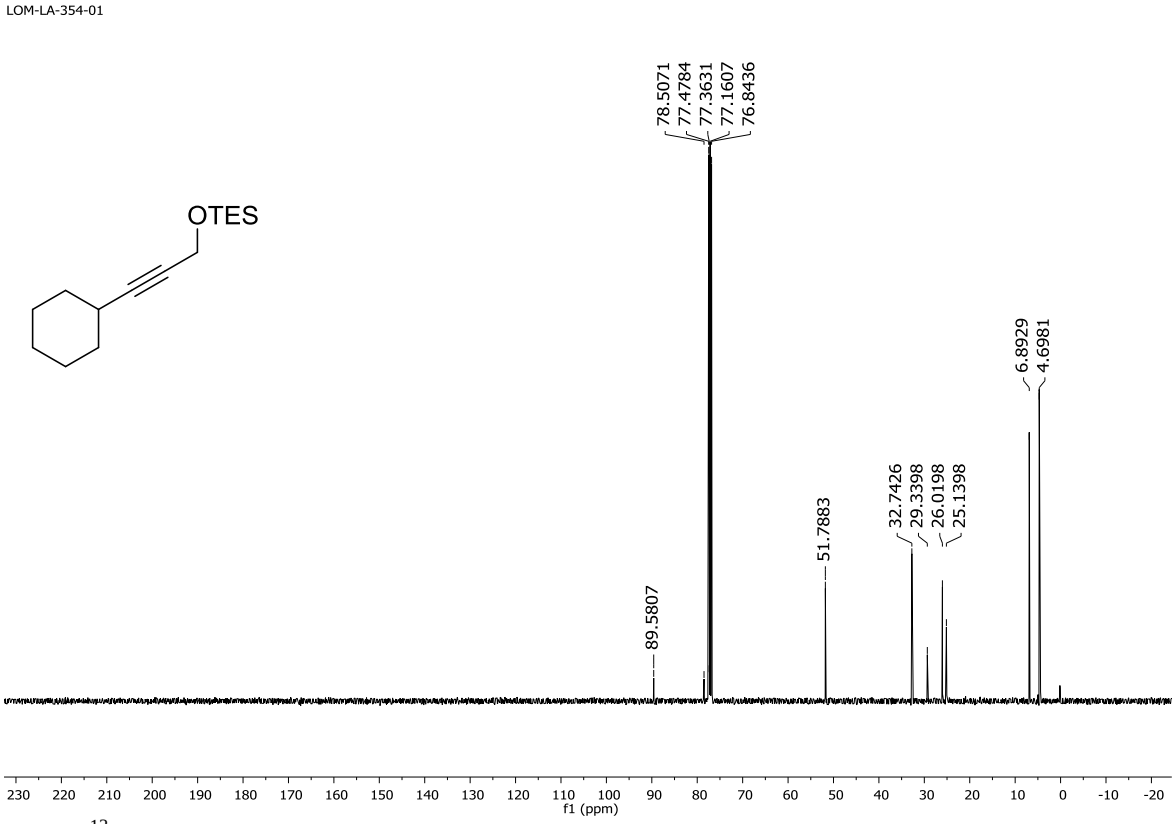

Figure 31: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S15**.

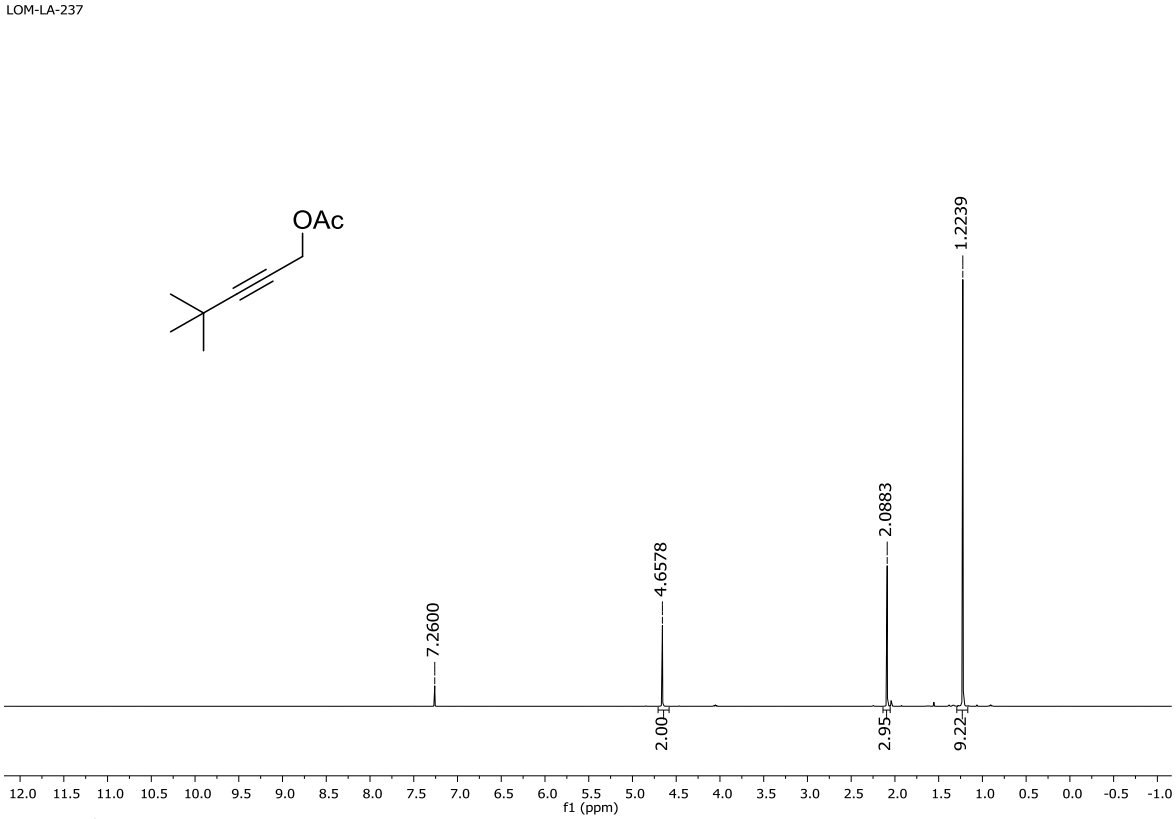

Figure 32: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S16**.

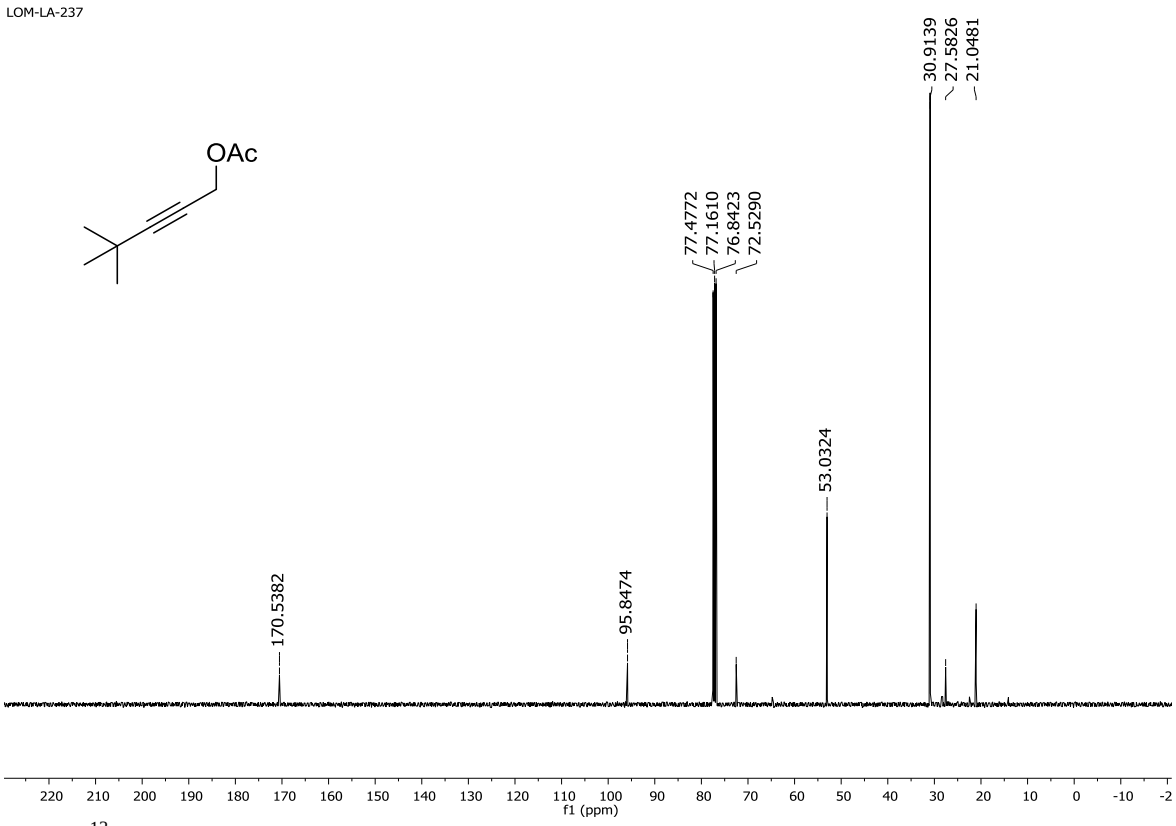

Figure 33: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S16**.

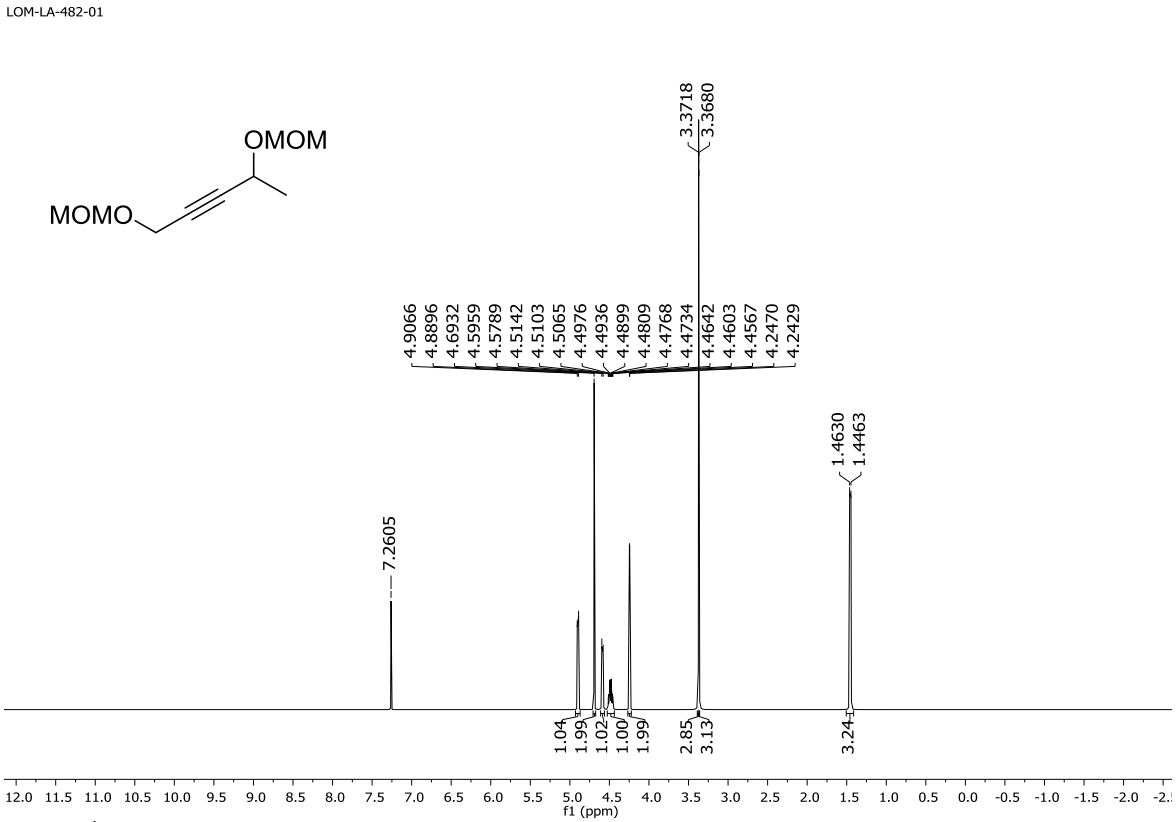

Figure 34: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **11**.

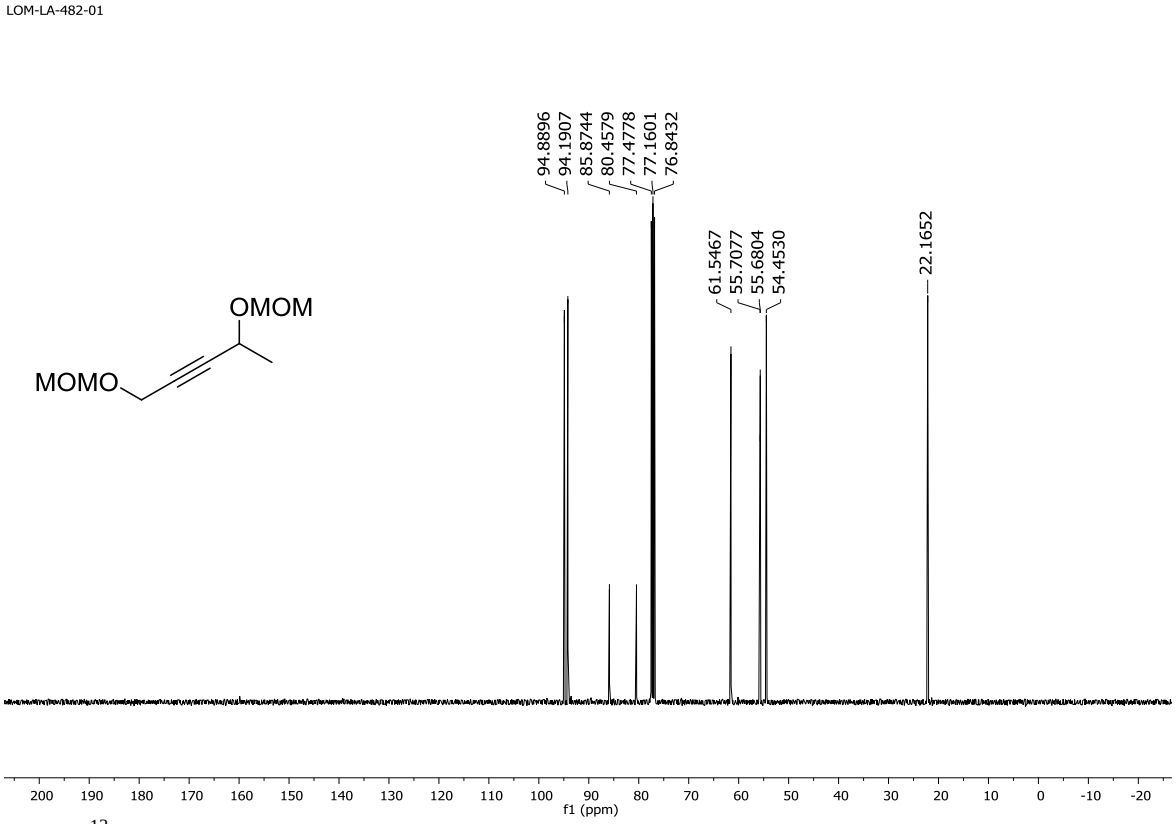

Figure 35: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **11**.

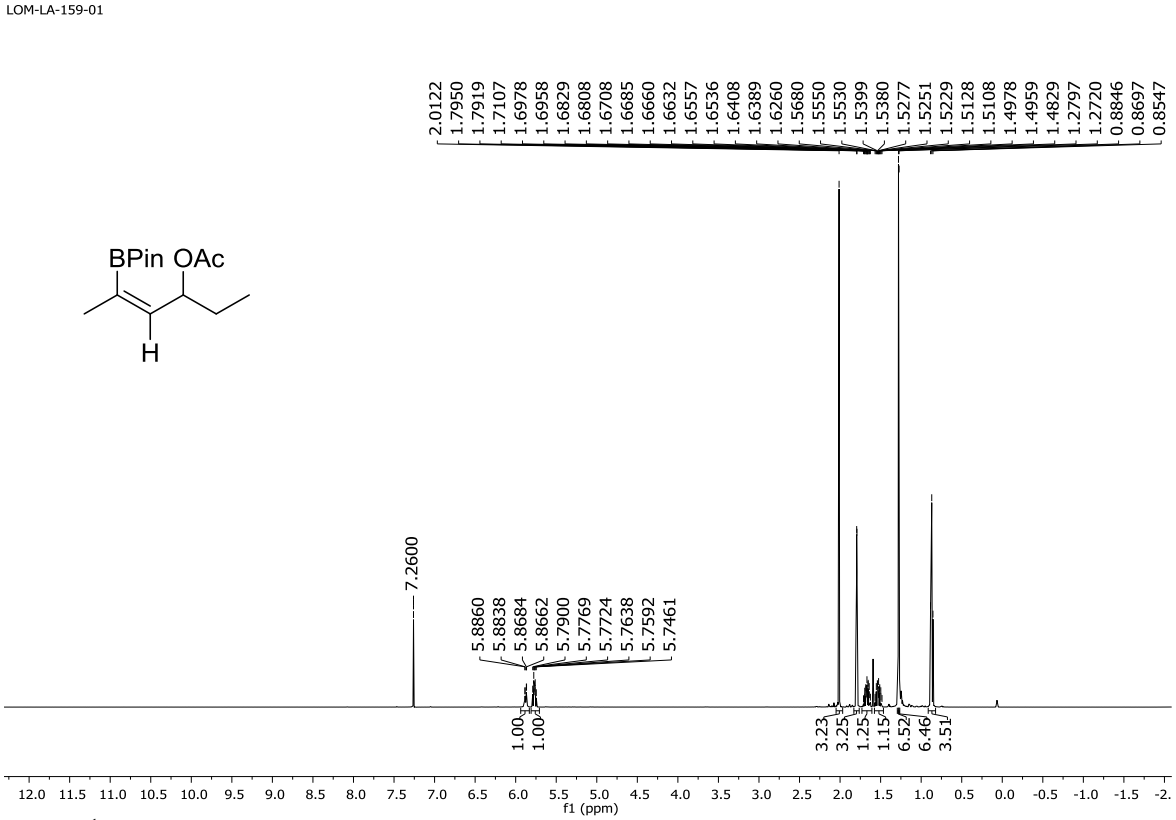

Figure 46: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8a**.

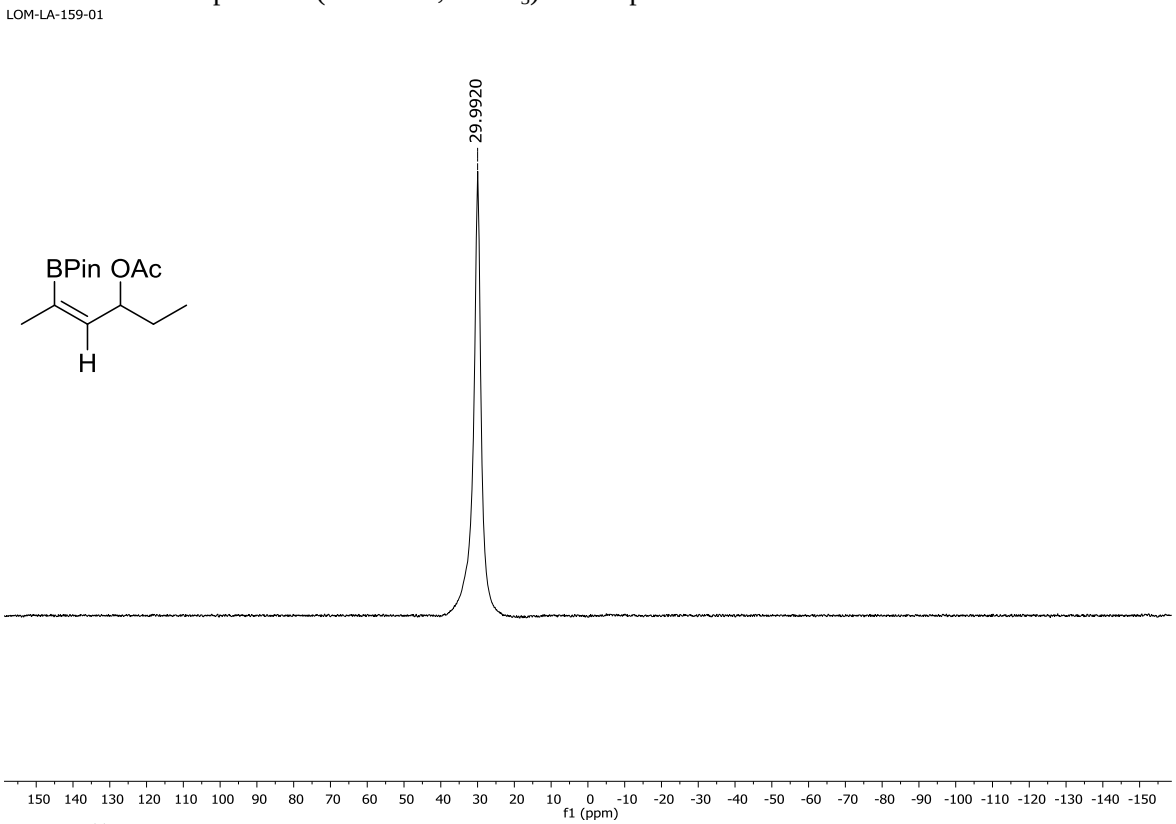

Figure 47: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **8a**.

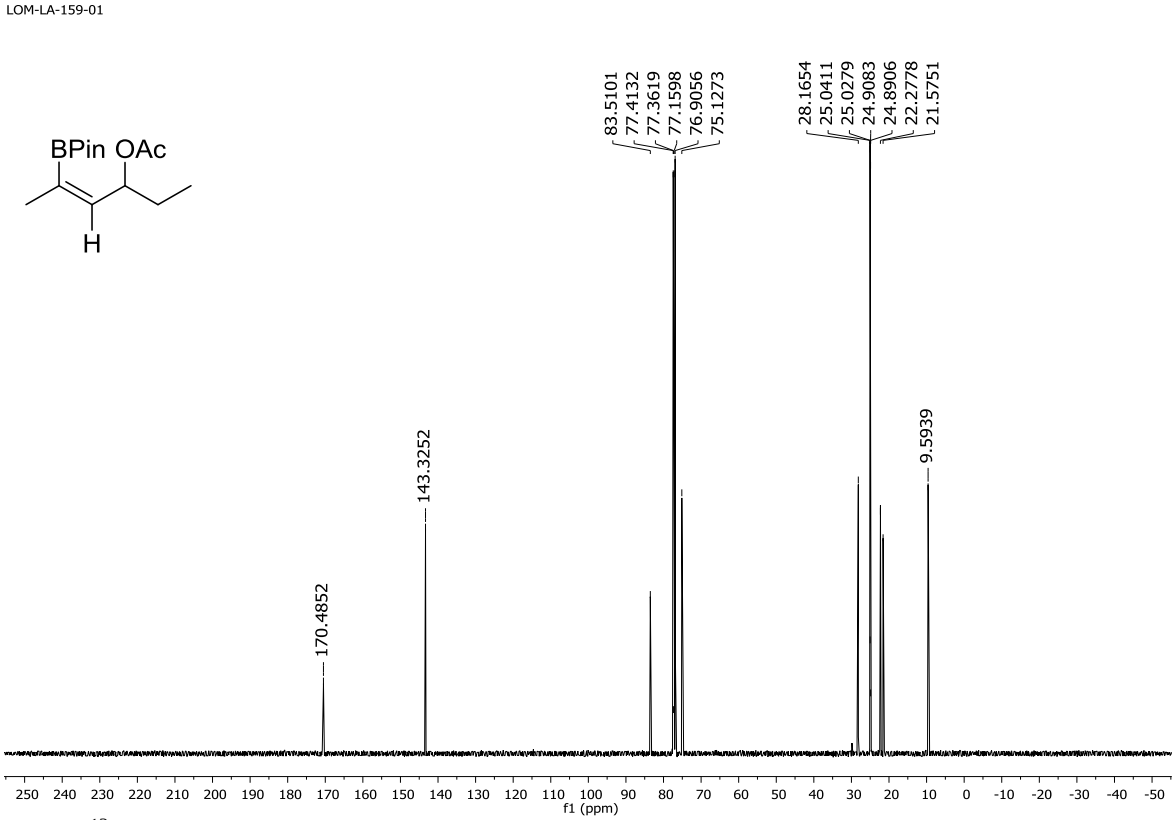

Figure 48: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **8a**.

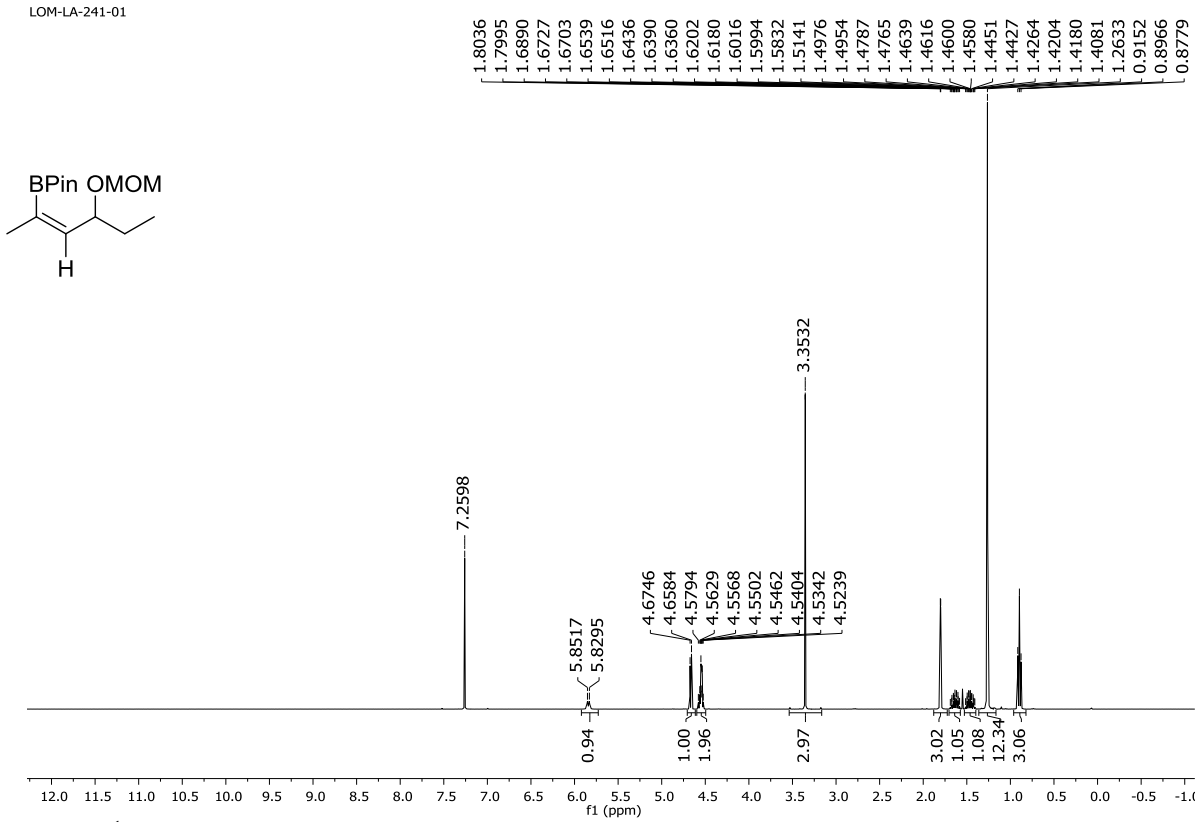

Figure 49: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8b**.

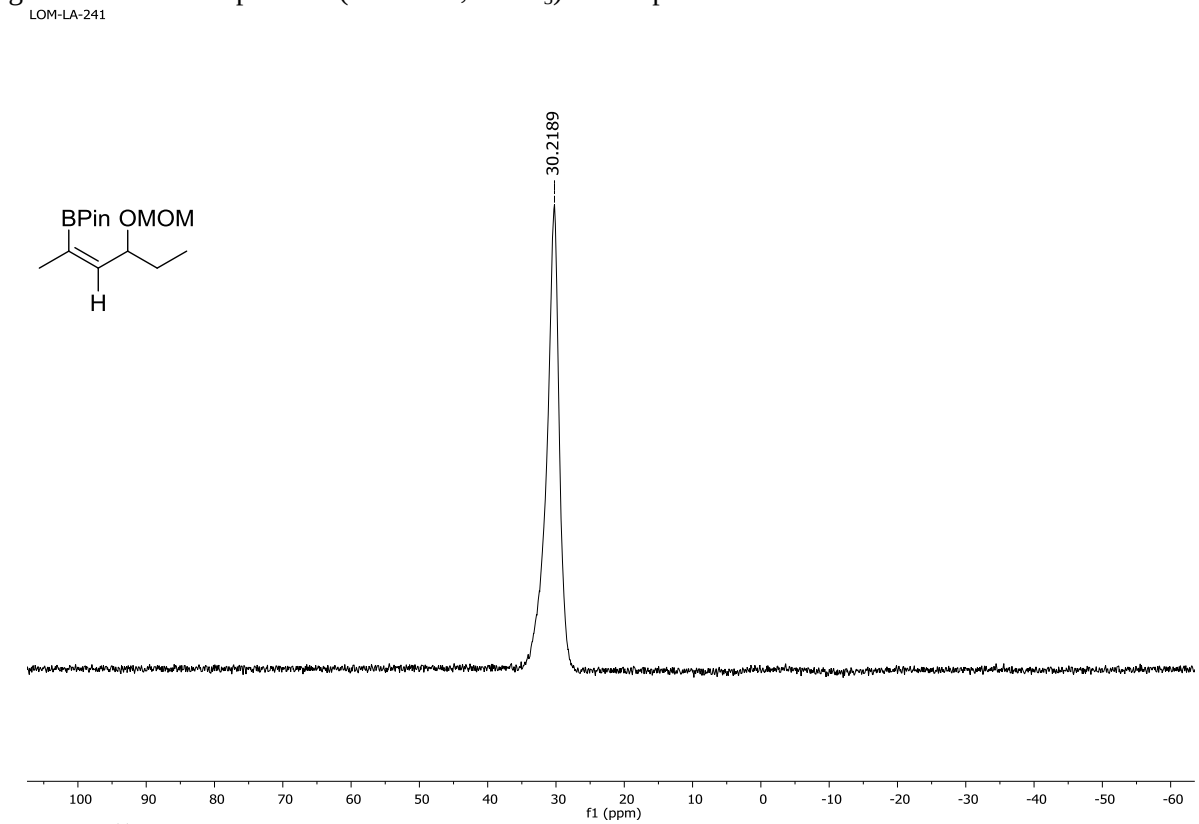

Figure 50: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **8b**.

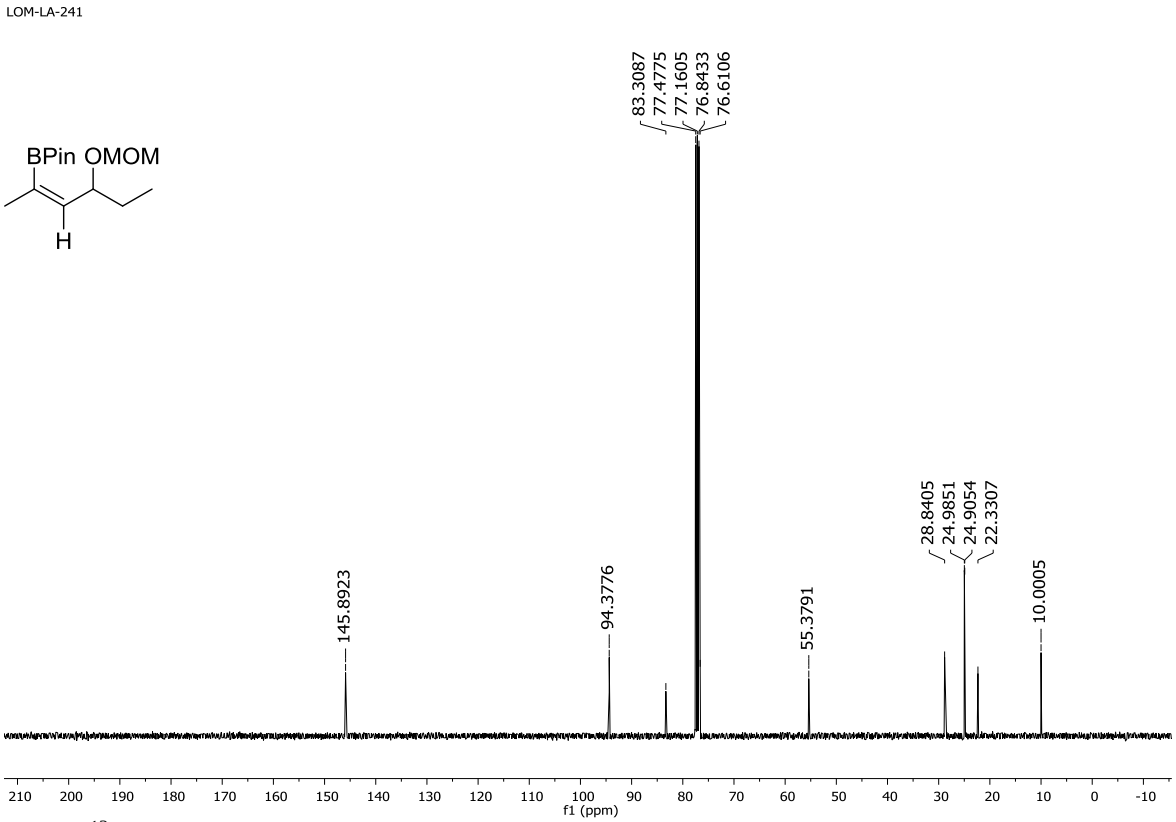

Figure 51: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **8b**.

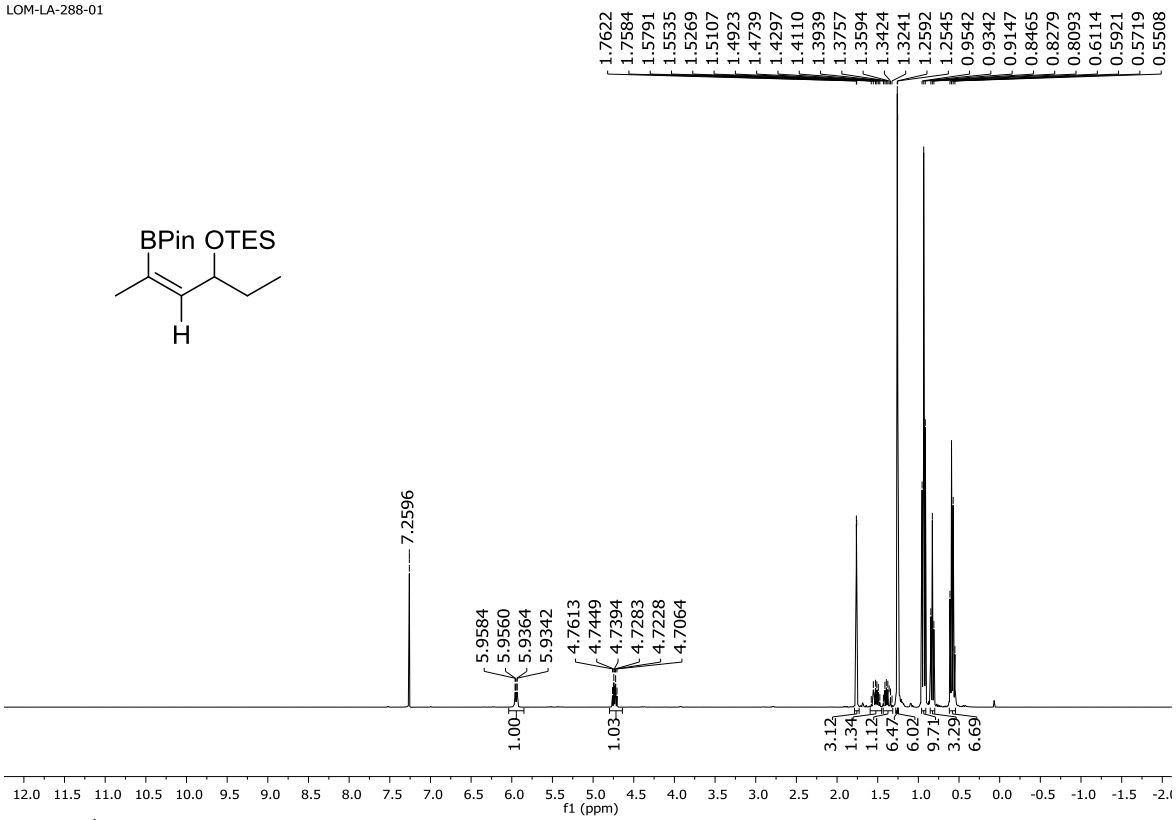

Figure 52: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8c**.

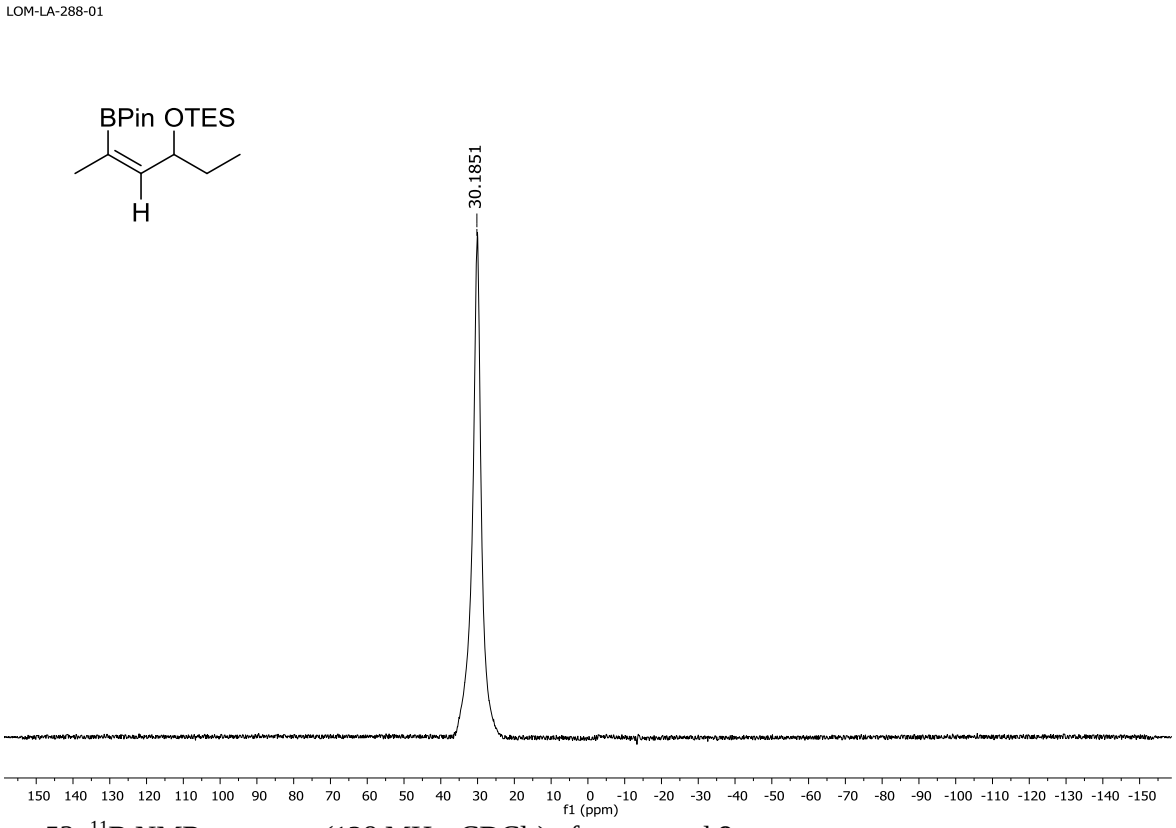

Figure 53: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **8c**.

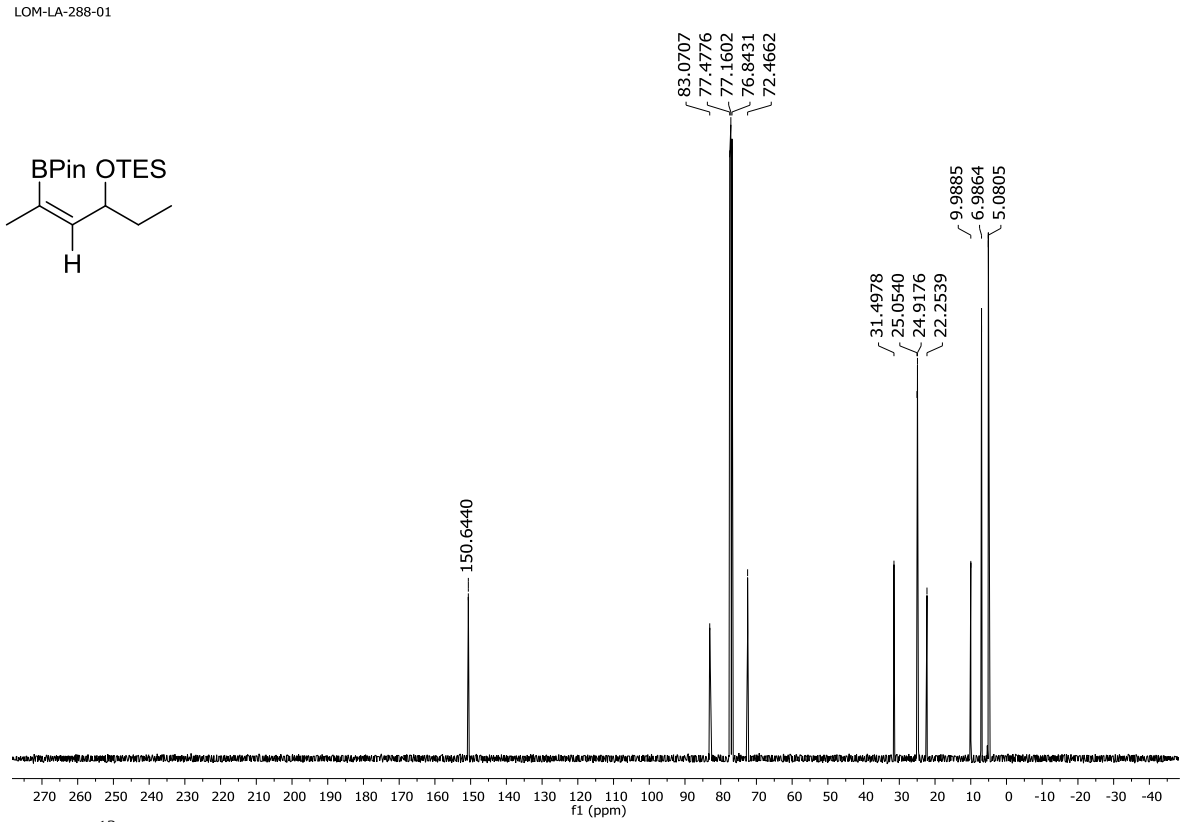

Figure 54: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **8c**.

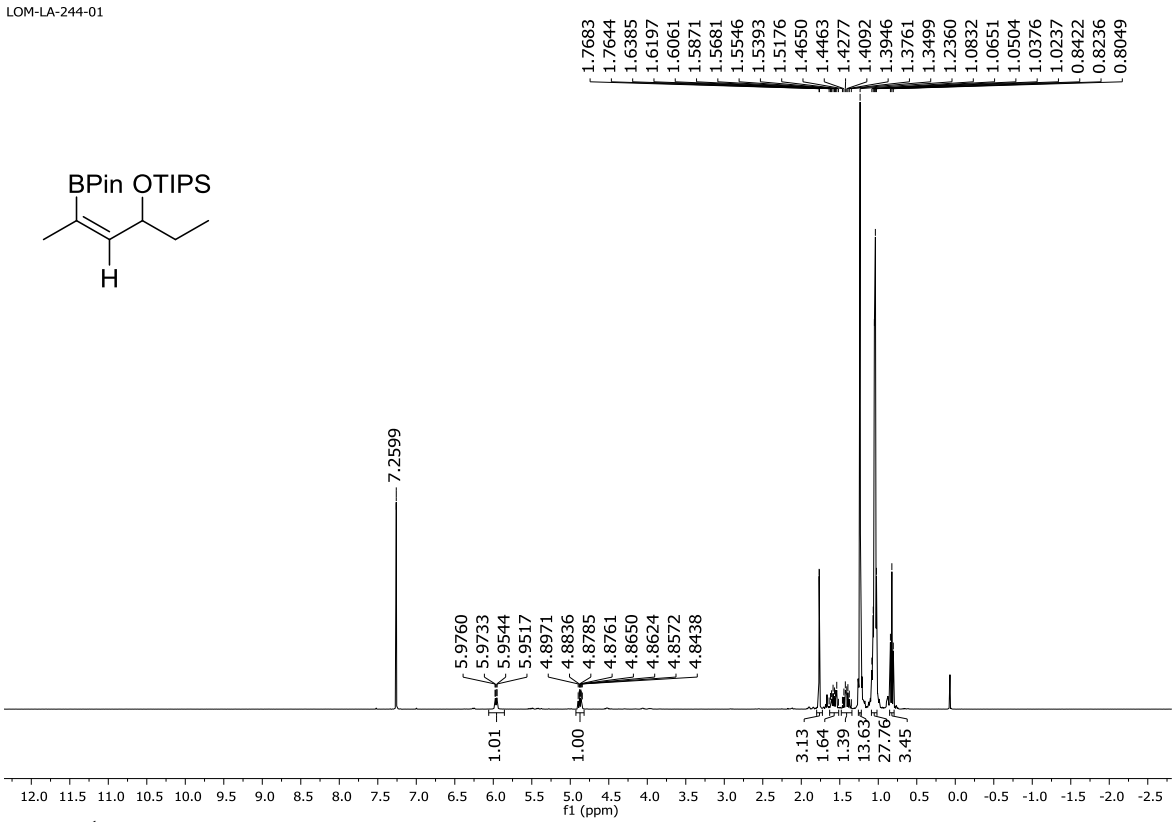

Figure 55: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8d**.

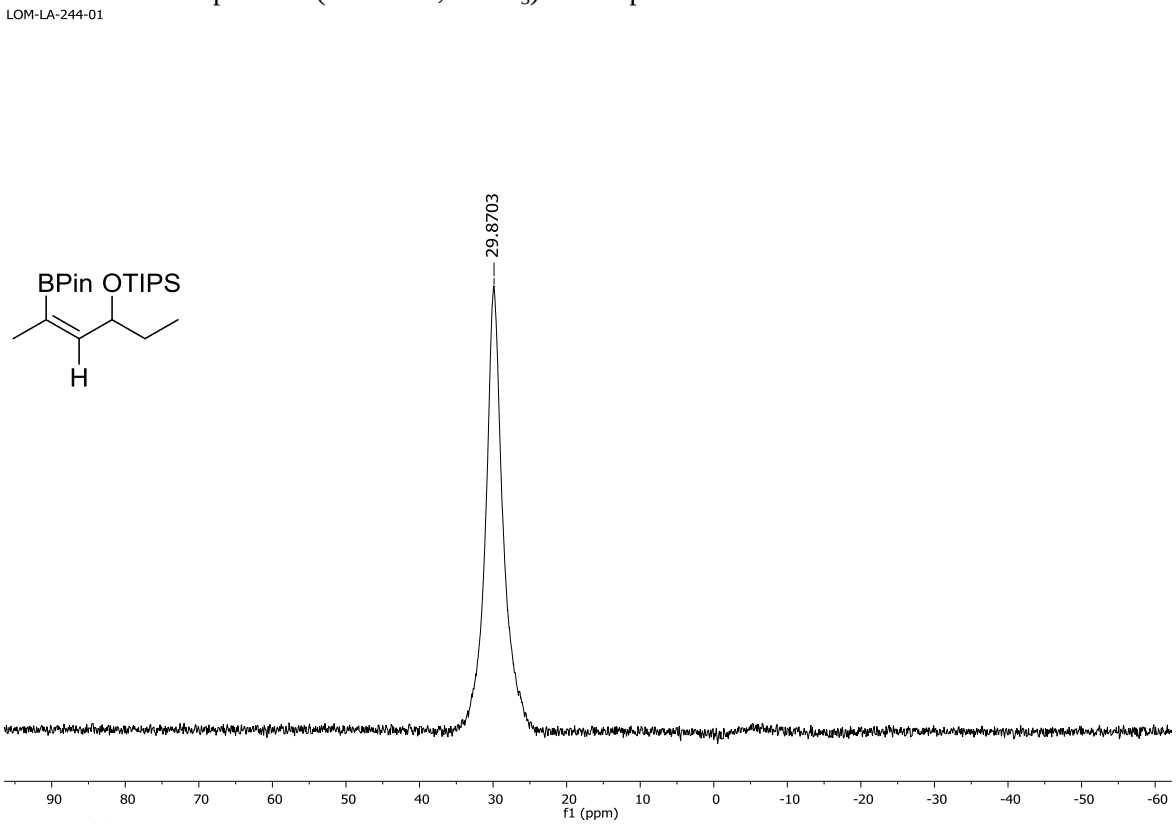

Figure 56: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **8d**.

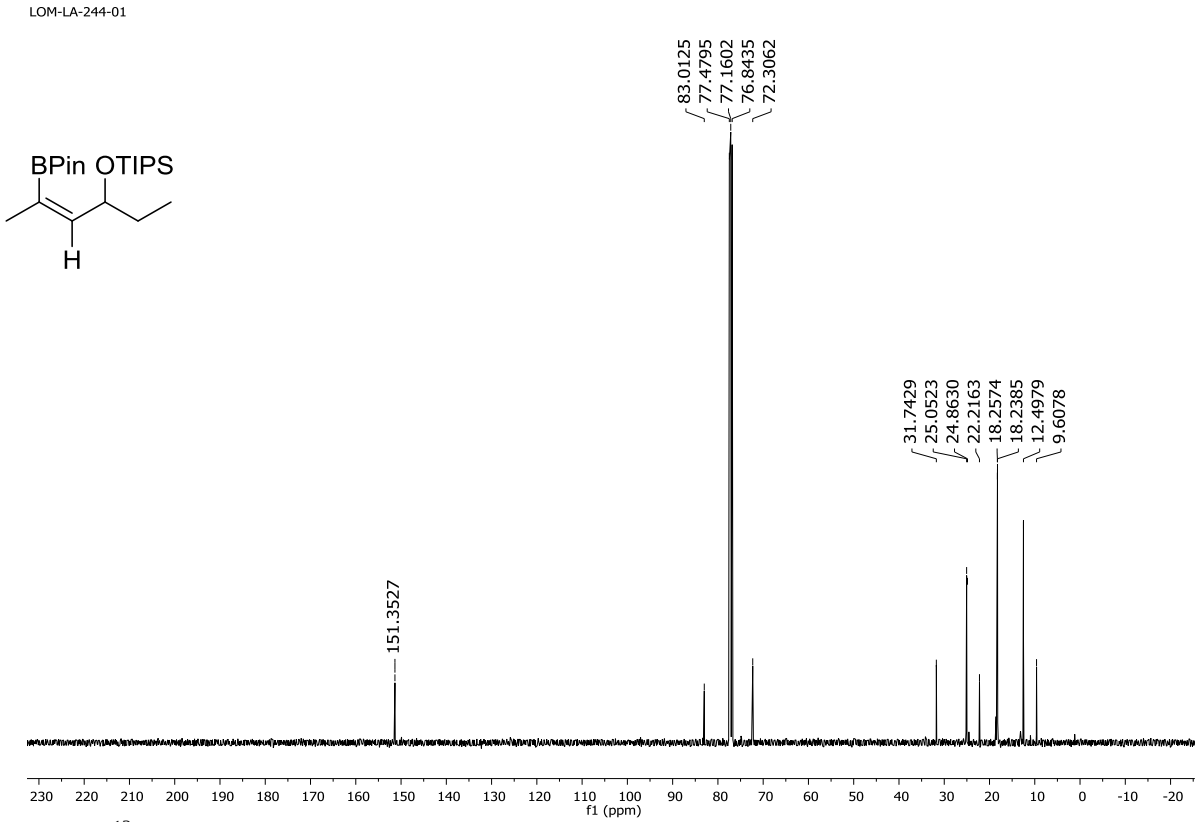

Figure 57: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **8d**.

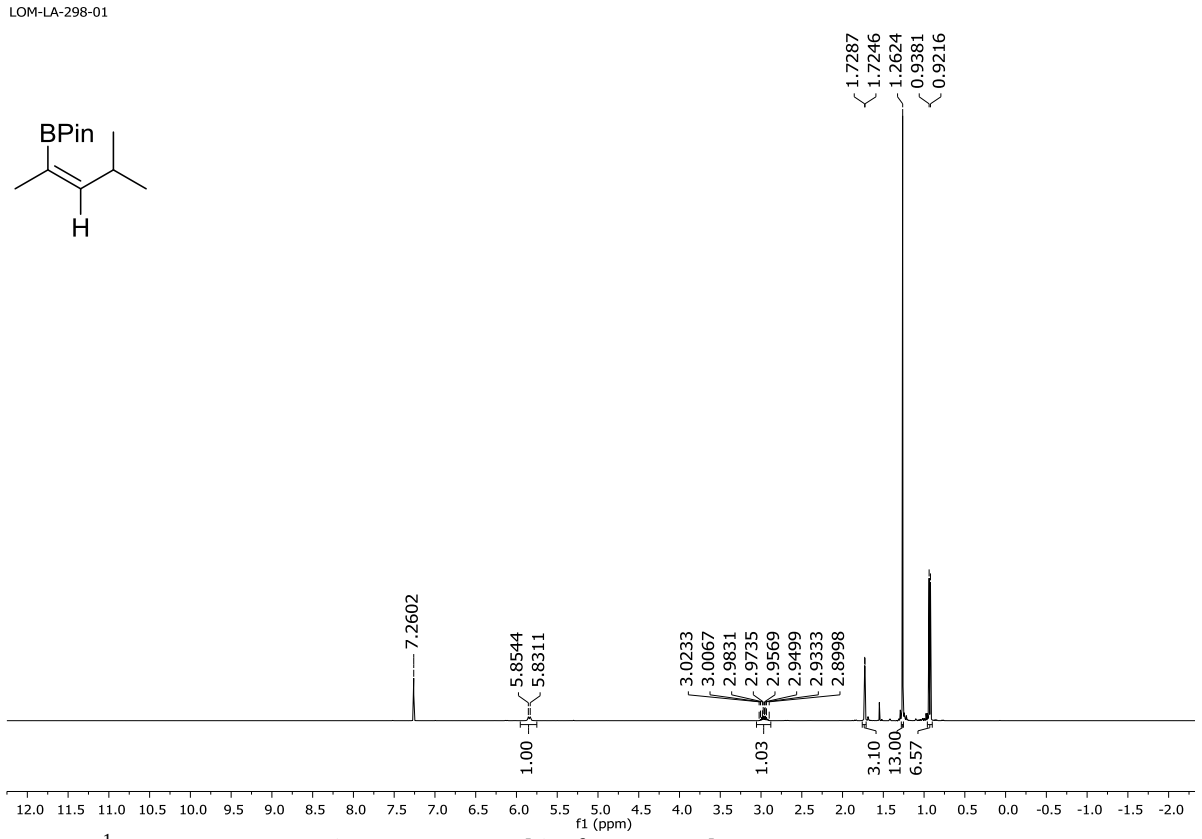

Figure 58: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **10**.

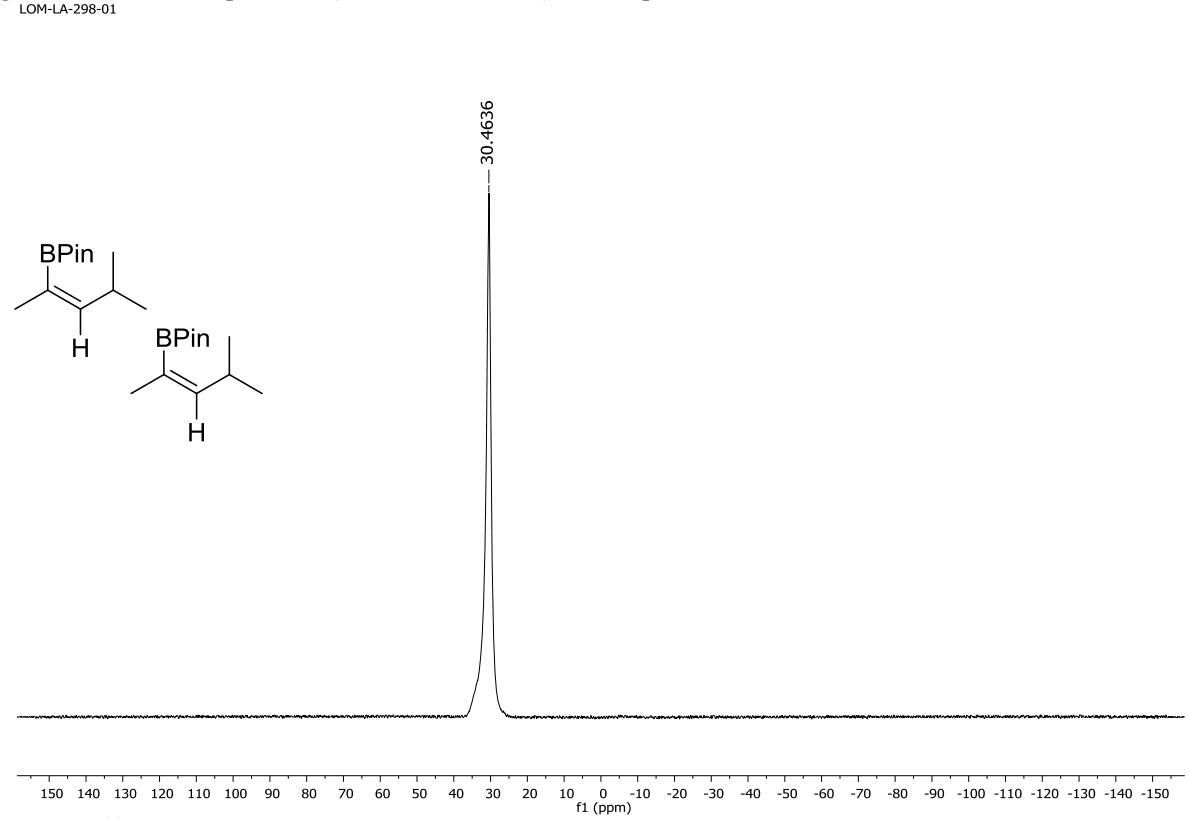

Figure 59: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **10**.

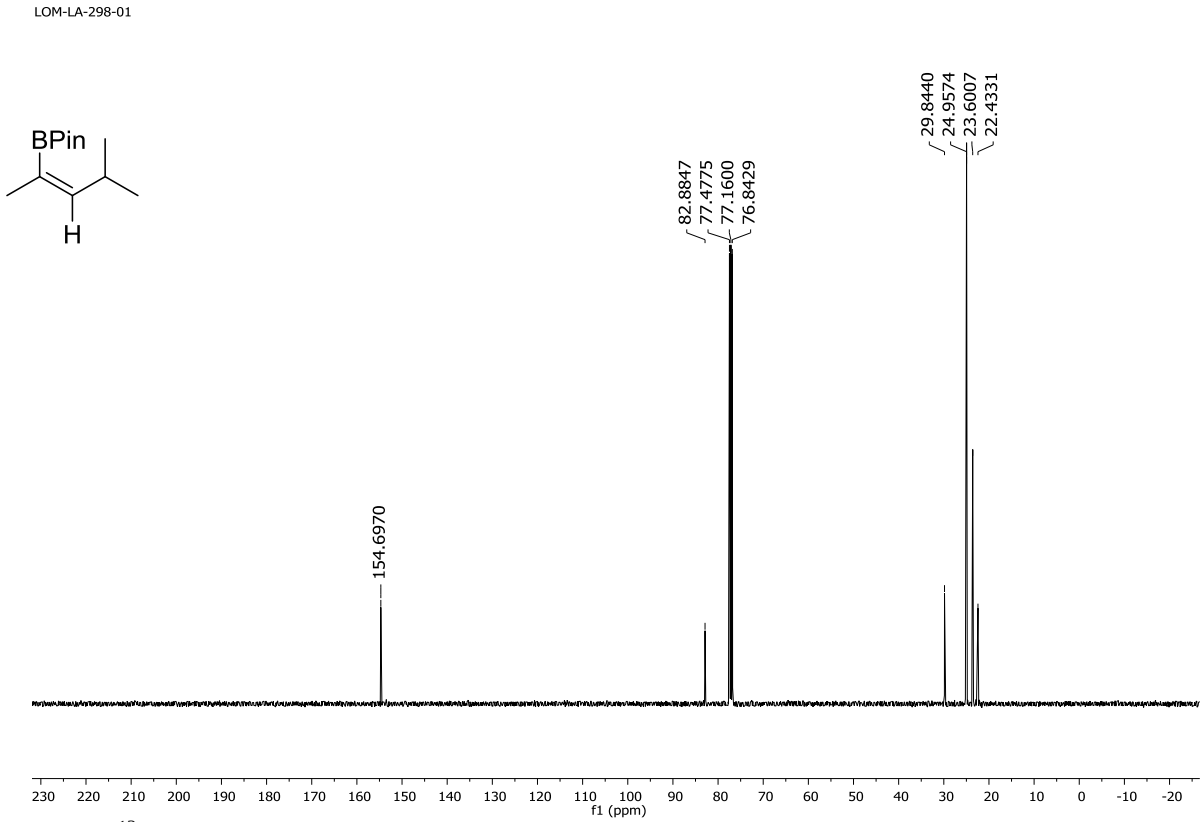

Figure 60: ^{13}C NMR spectrum (128 MHz, $CDCl_3$) of compound **10**.

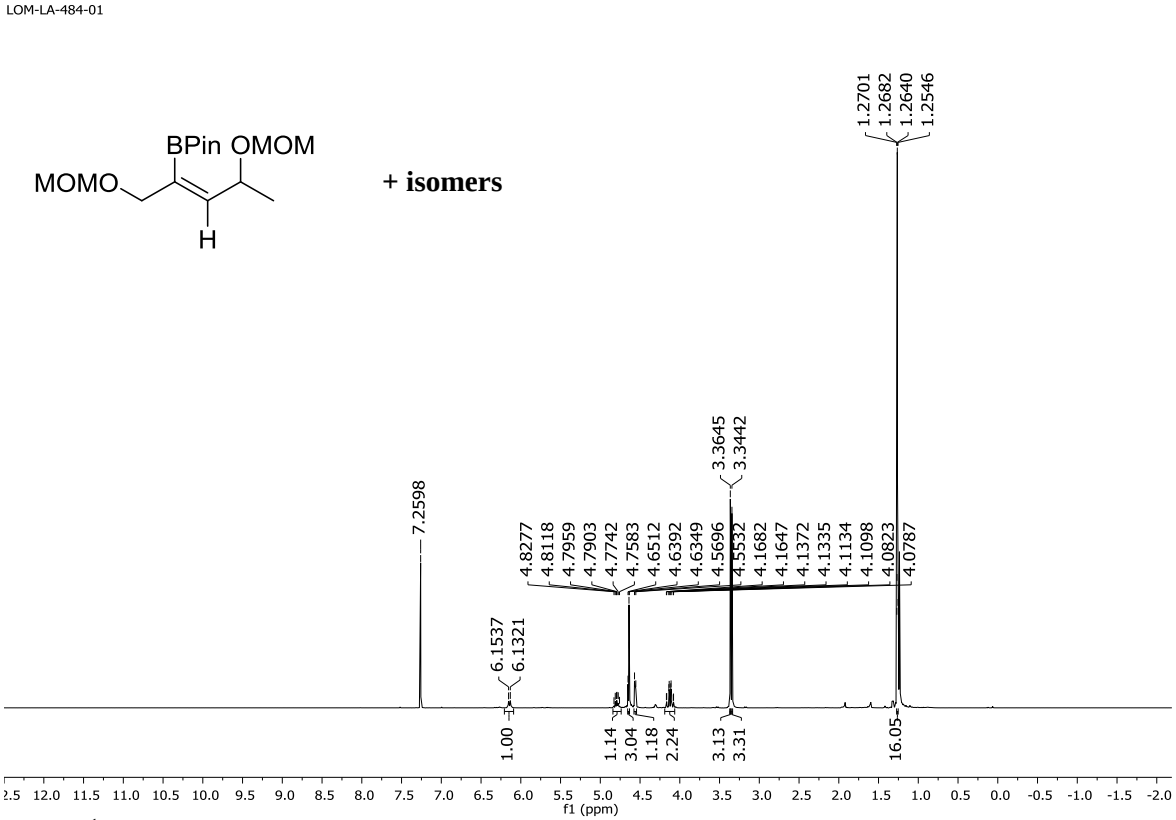

Figure 61: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **12**.

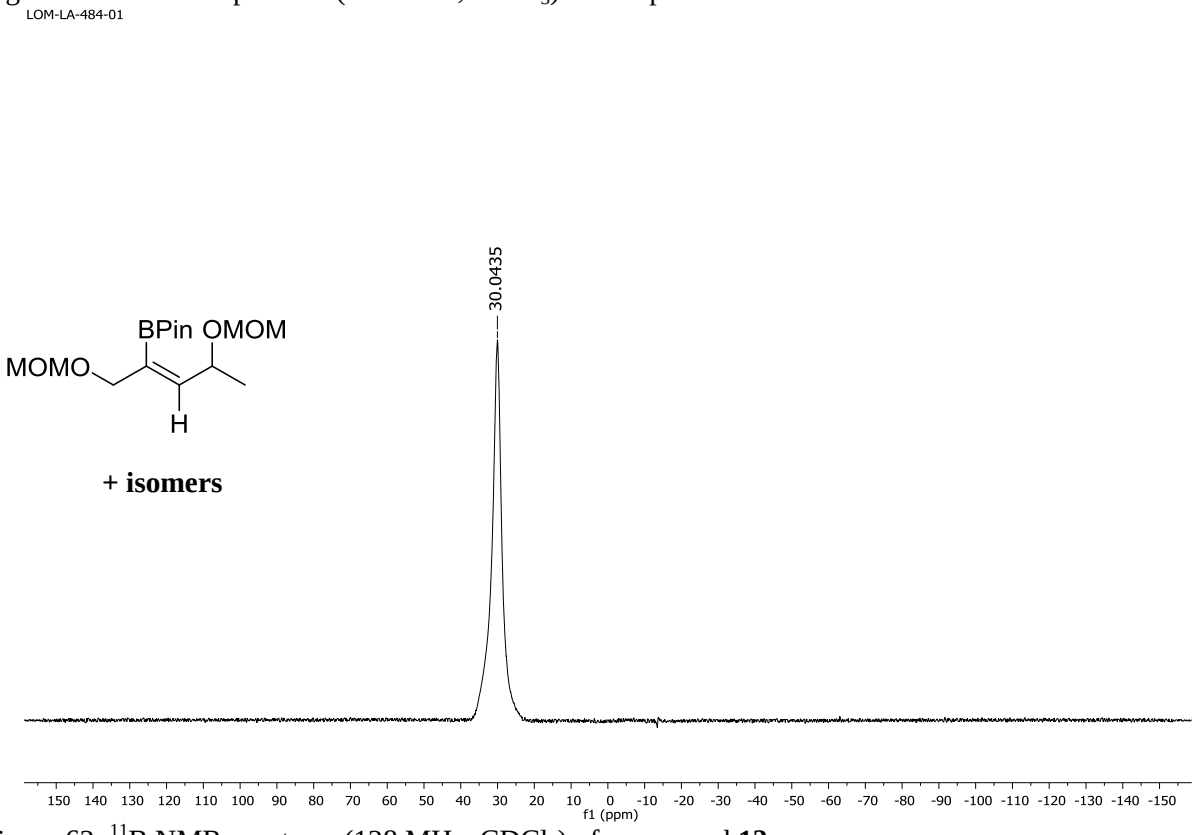

Figure 62: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **12**.

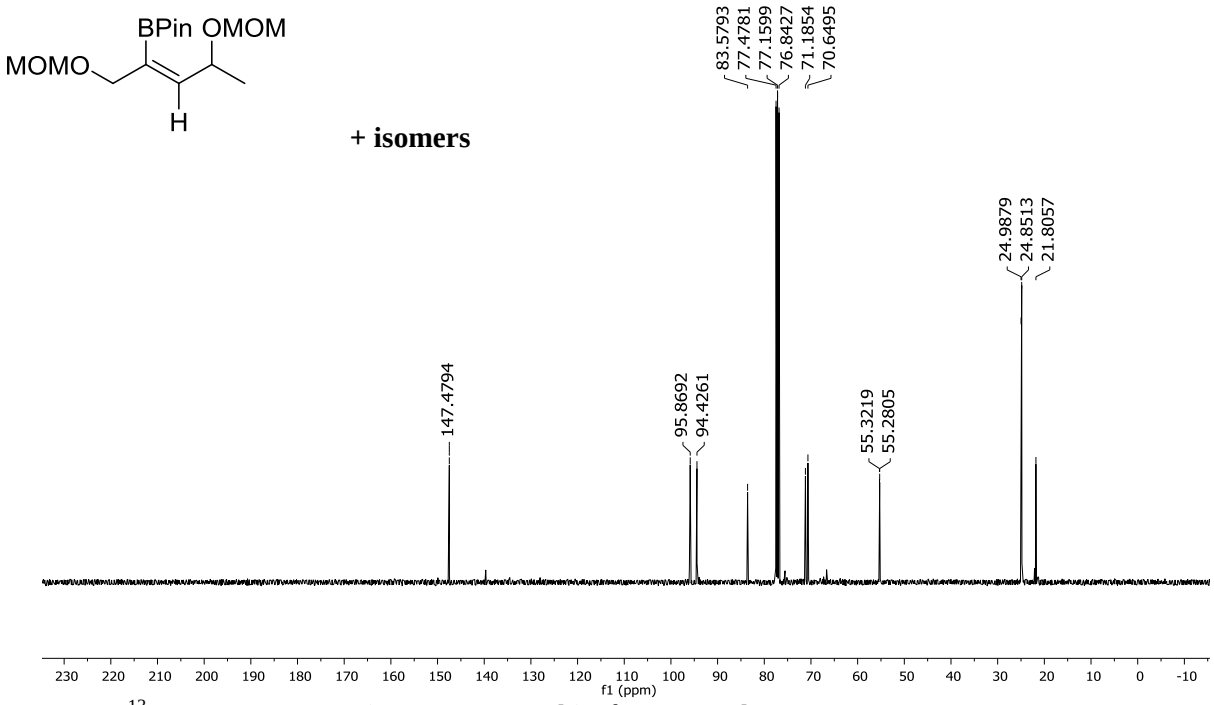

Figure 63: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **12**.

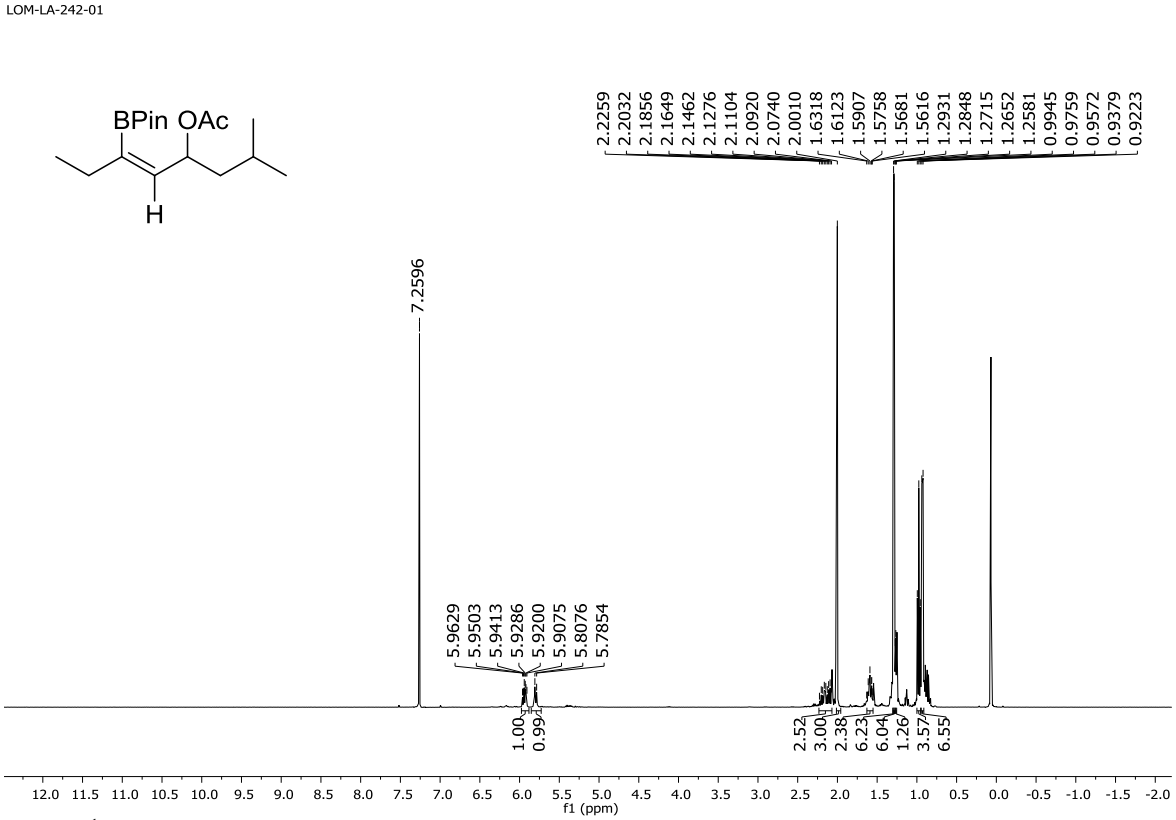

Figure 64: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **14**.

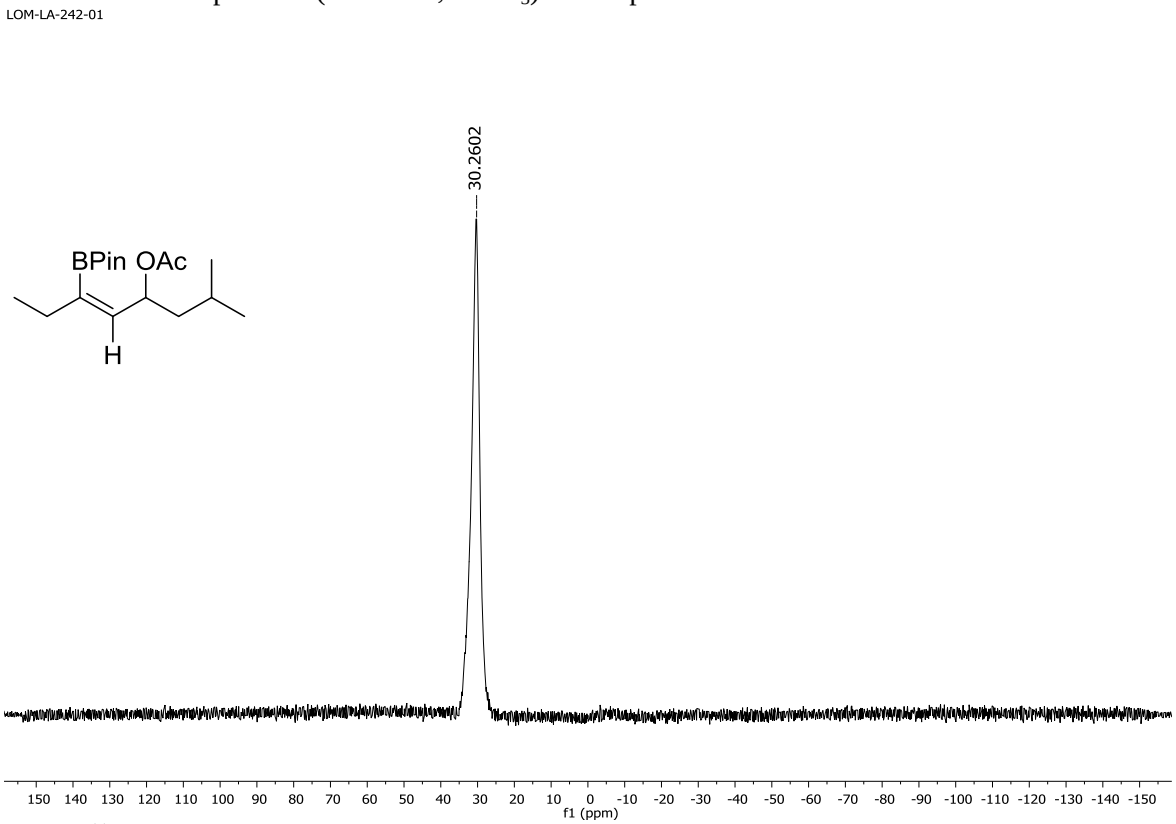

Figure 65: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **14**.

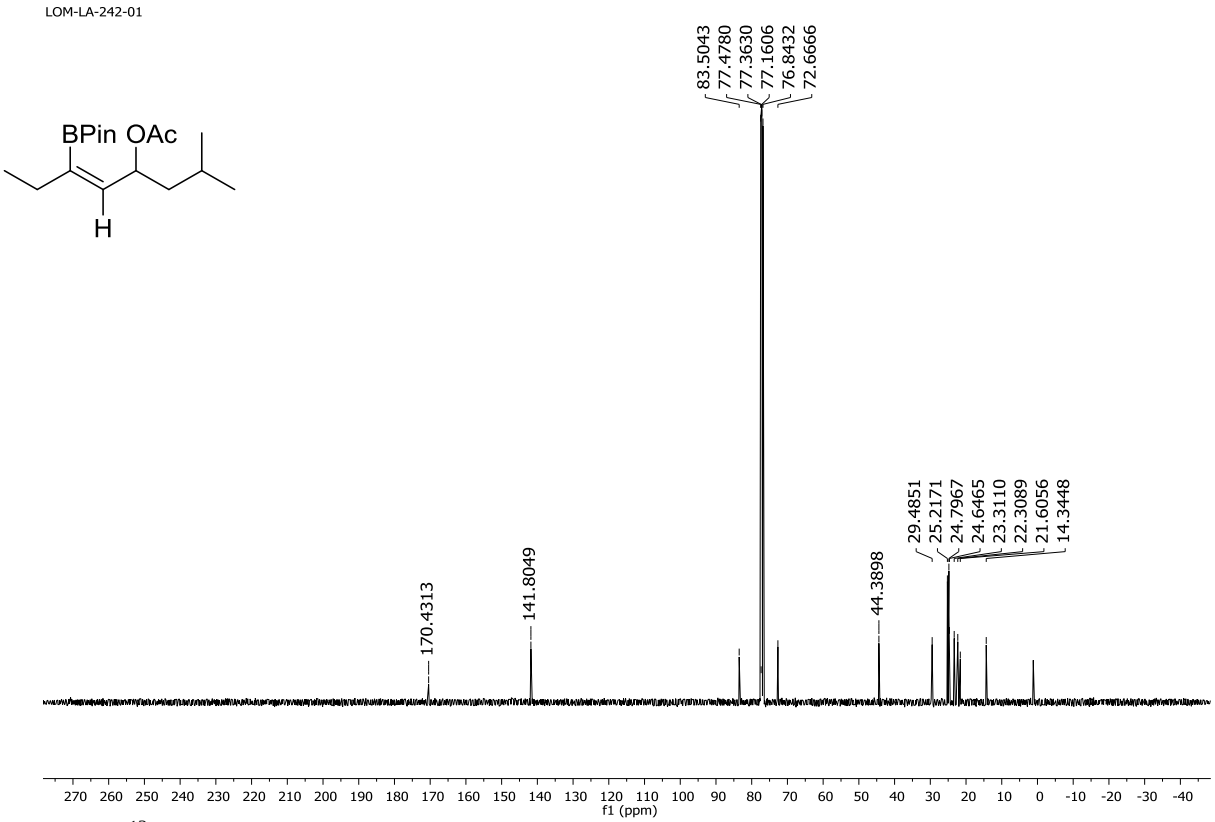

Figure 66: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **14**.

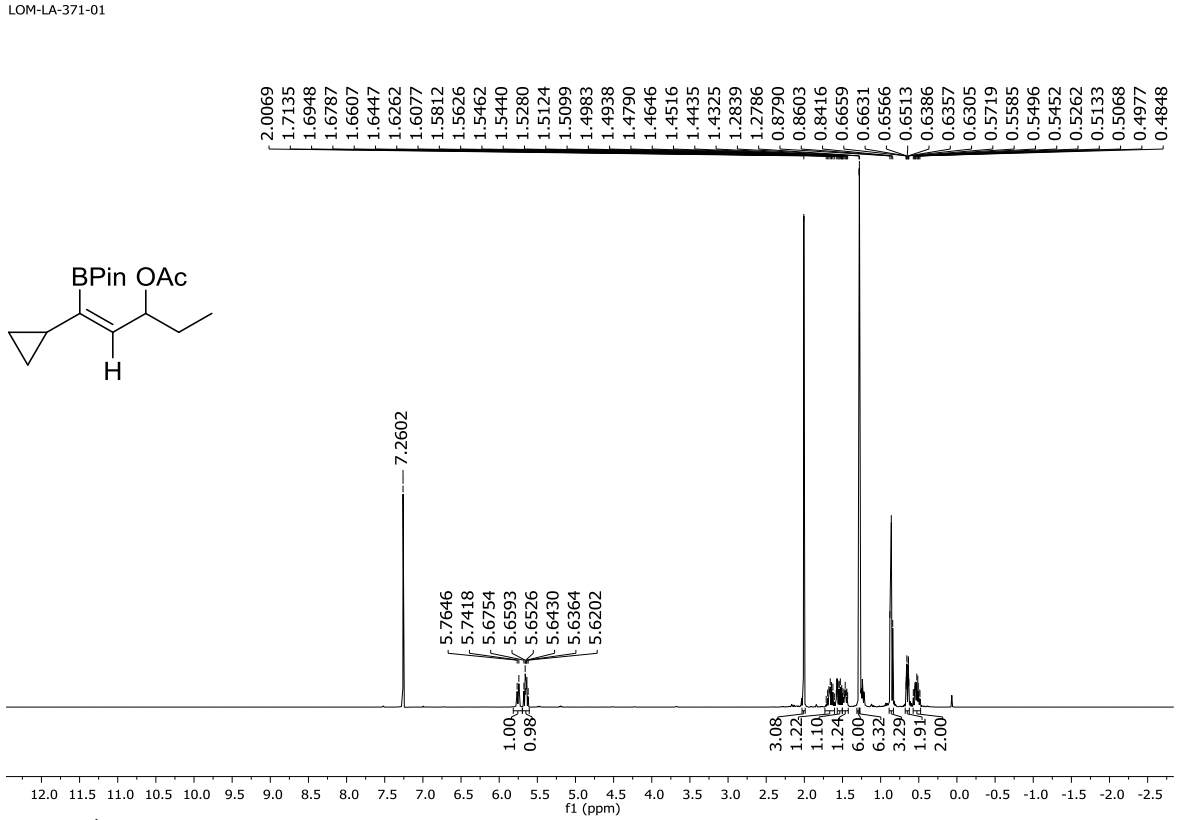

Figure 67: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **15**.

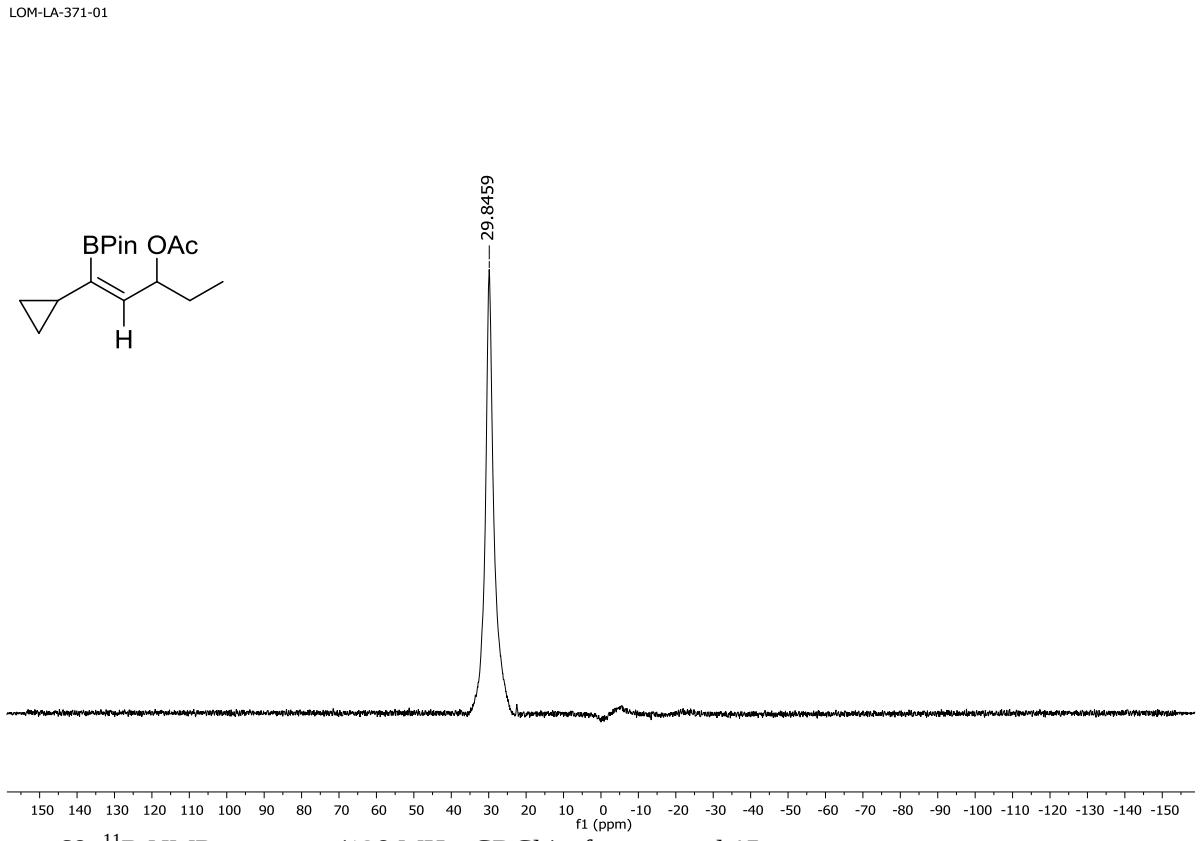

Figure 68: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **15**.

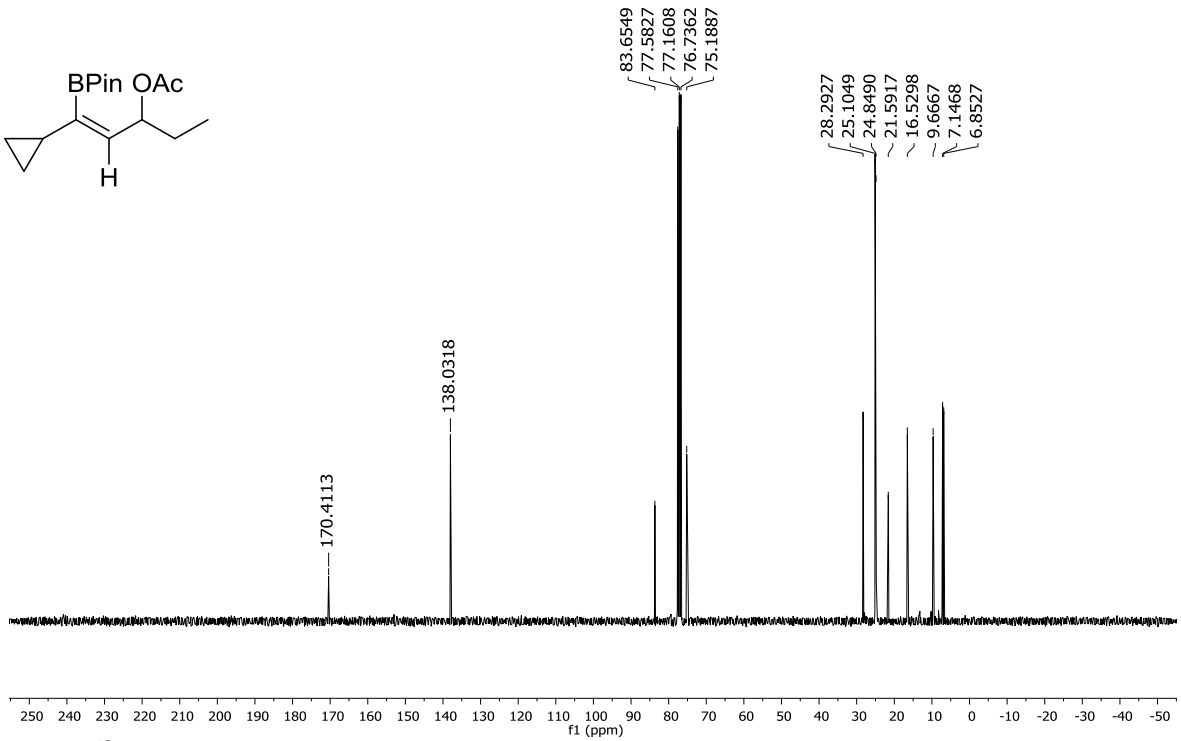

Figure 69: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **15**.

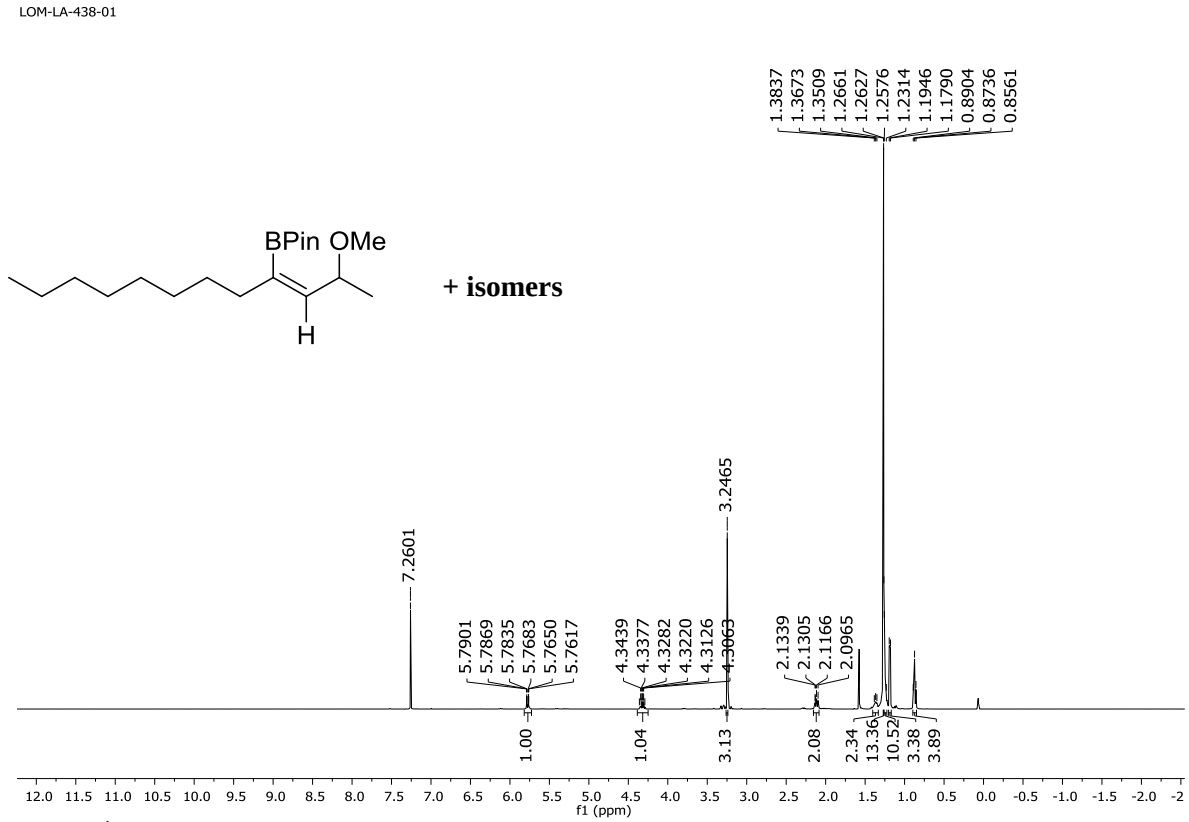

Figure 70: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **16**.

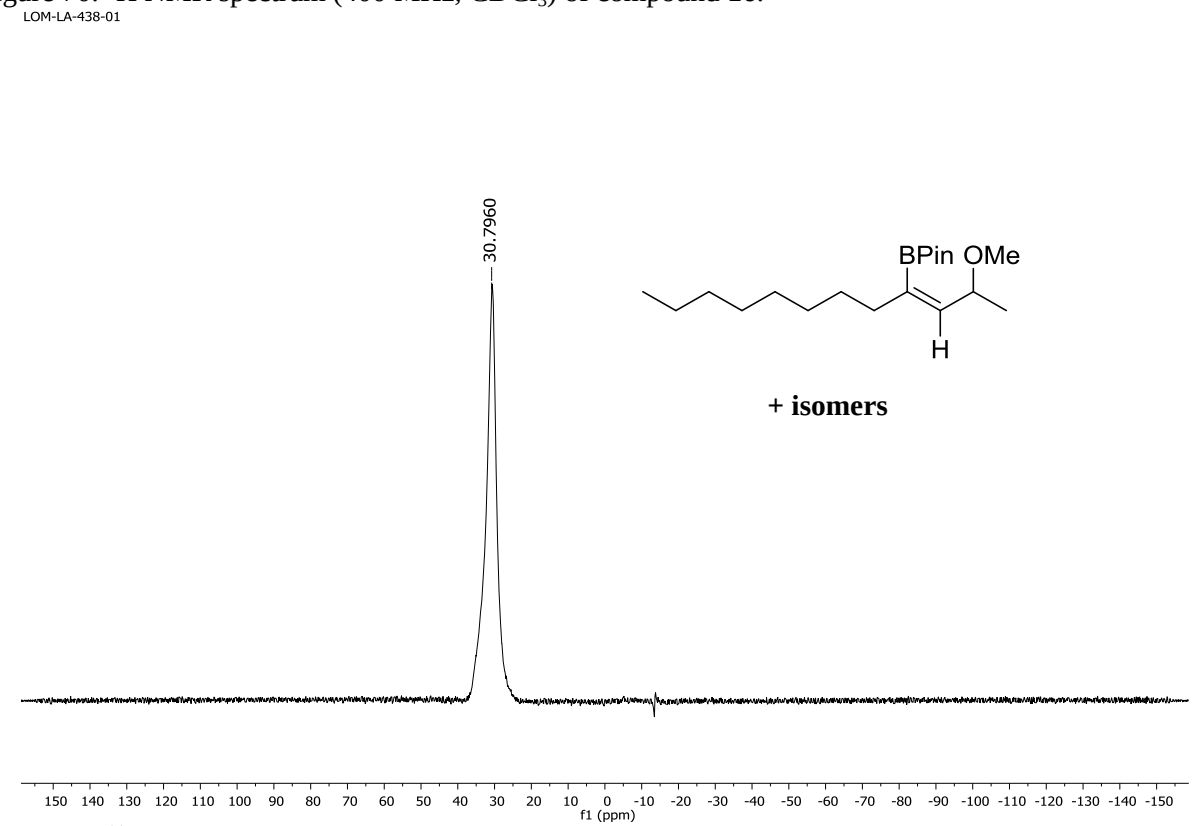

Figure 71: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **16**.

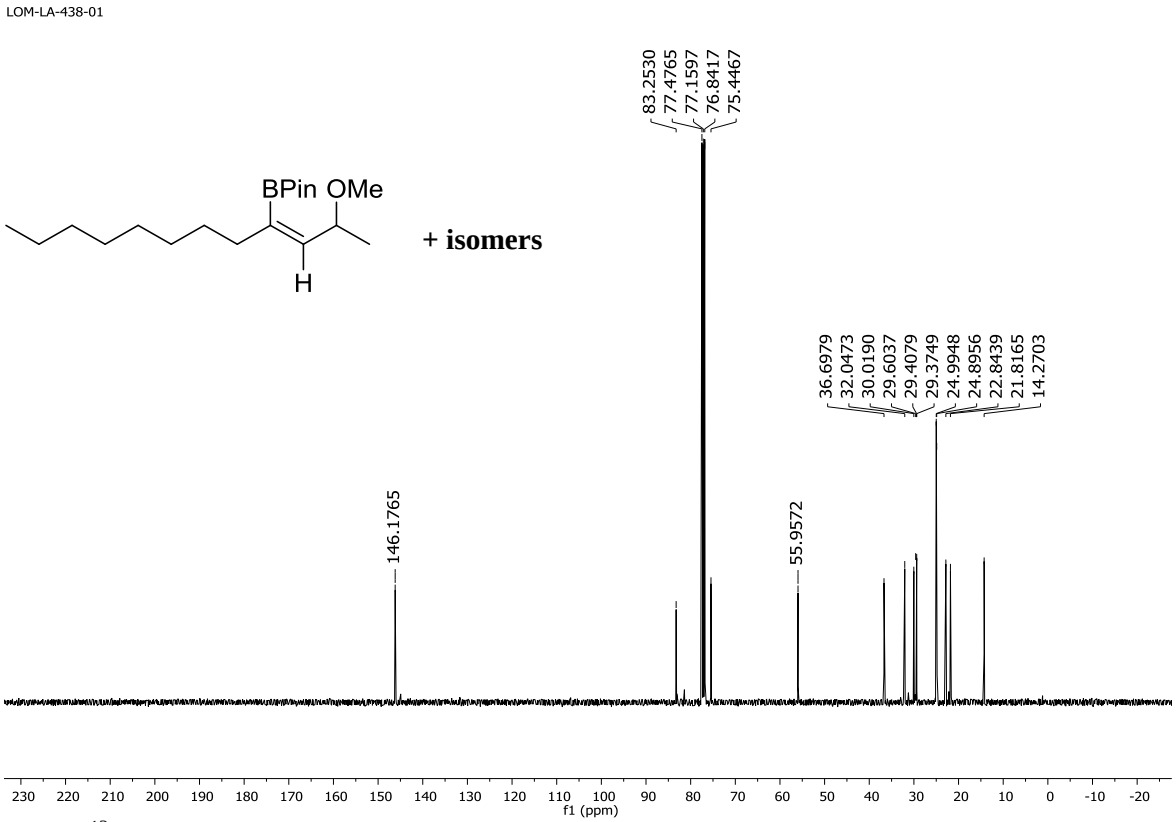

Figure 72: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **16**.

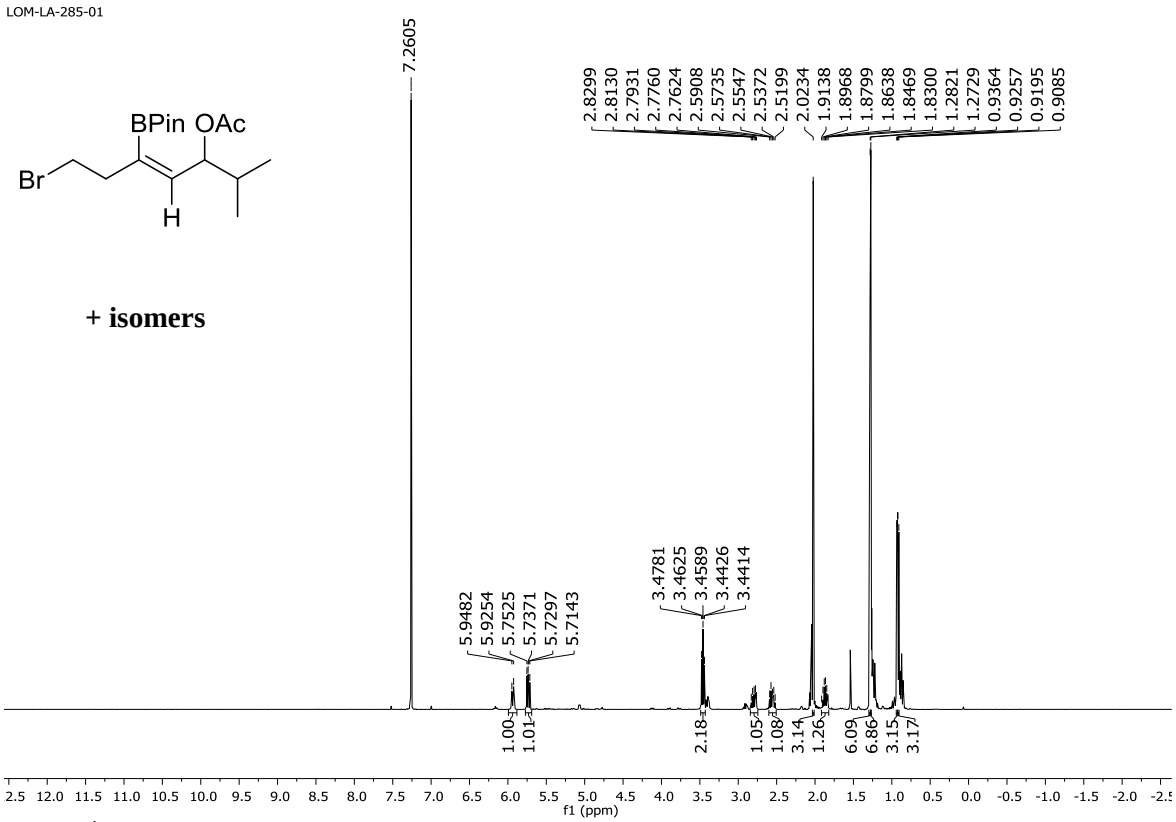

Figure 36: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **17**.

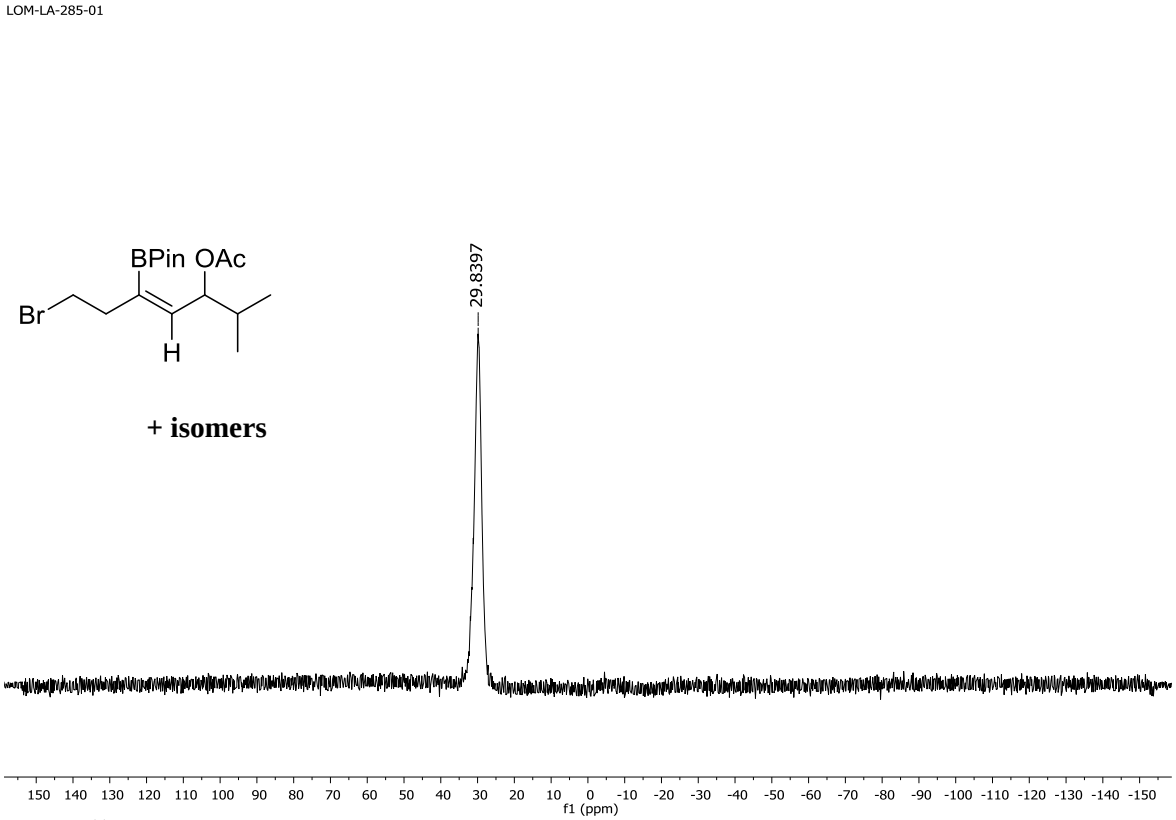

Figure 37: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **17**.

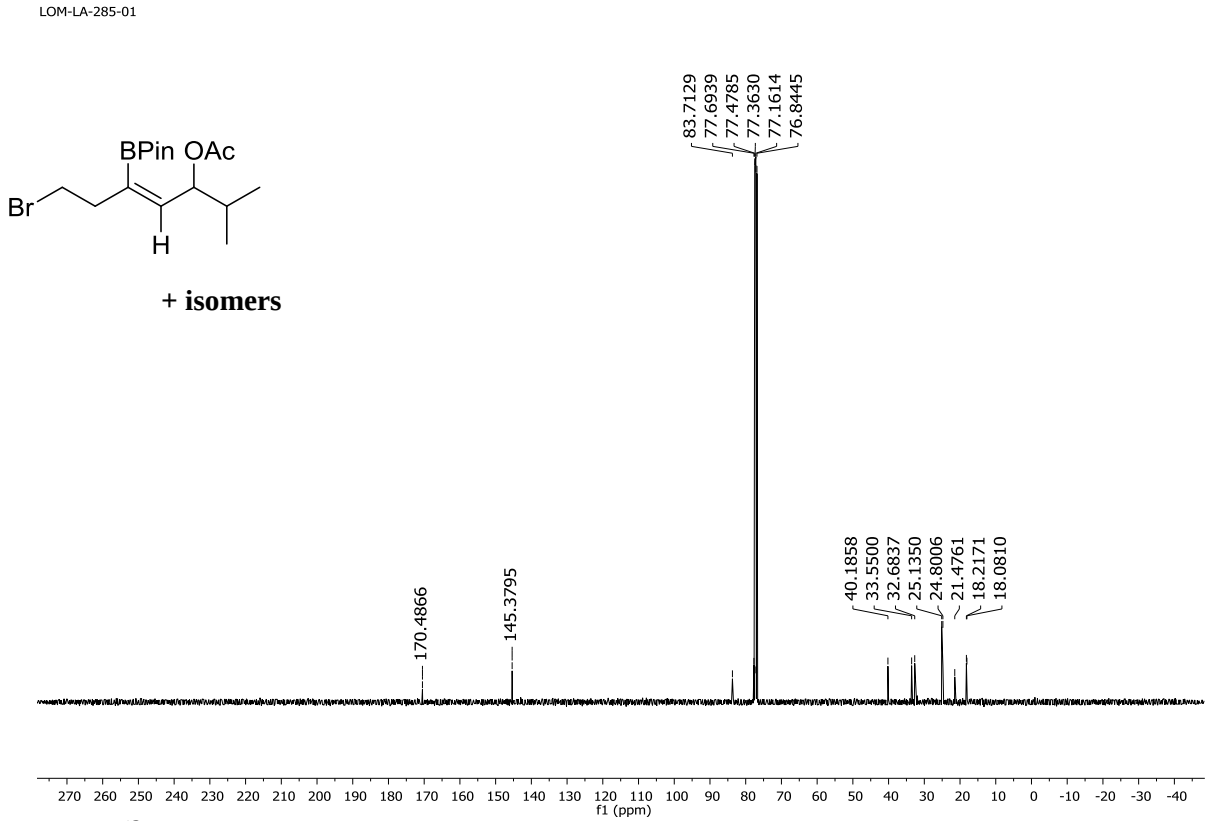

Figure 38: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **17**.

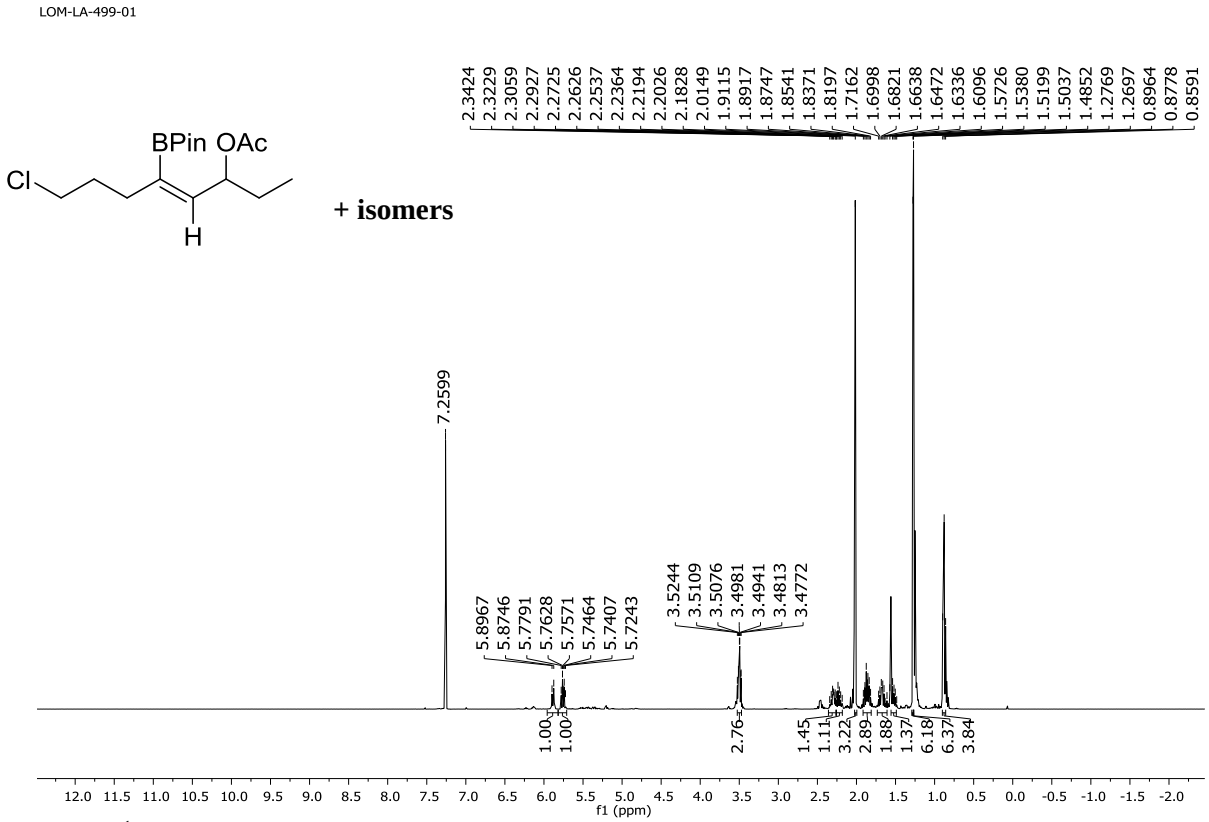

Figure 39: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **18**.

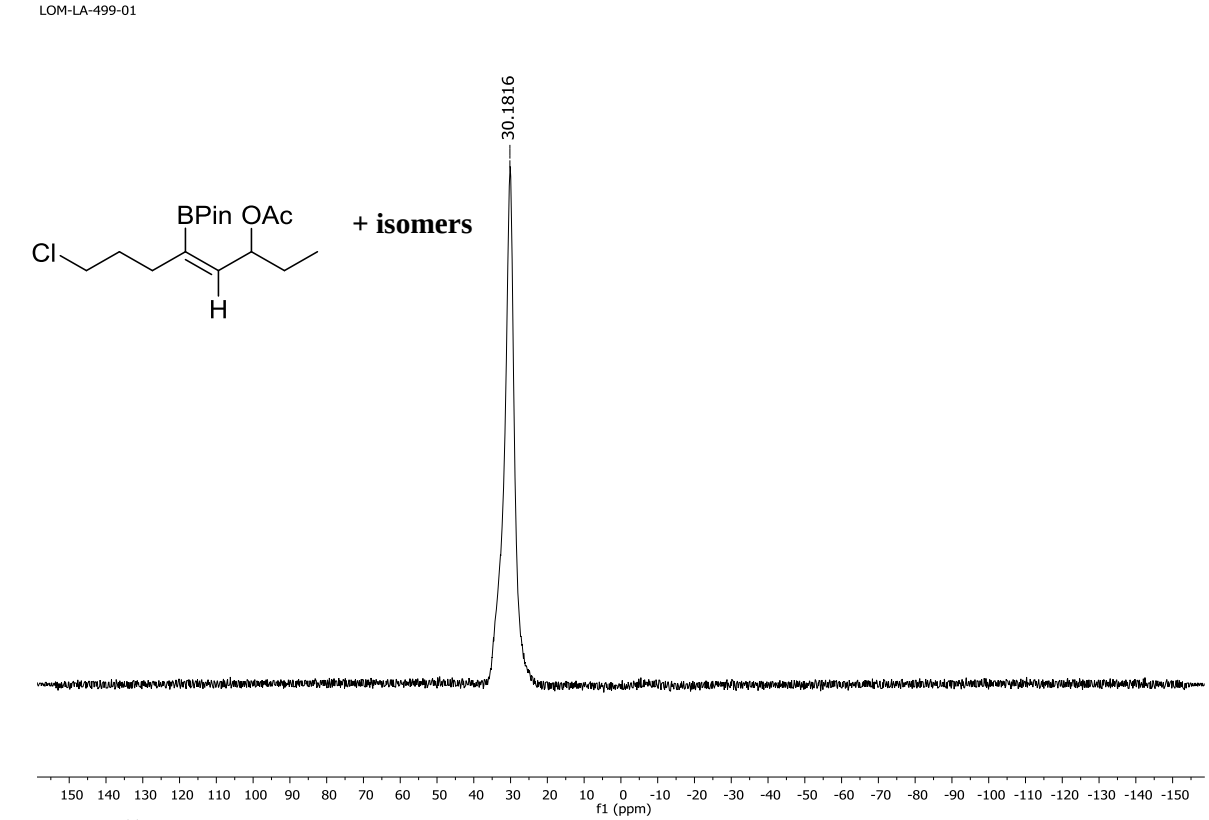

Figure 40: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **18**.

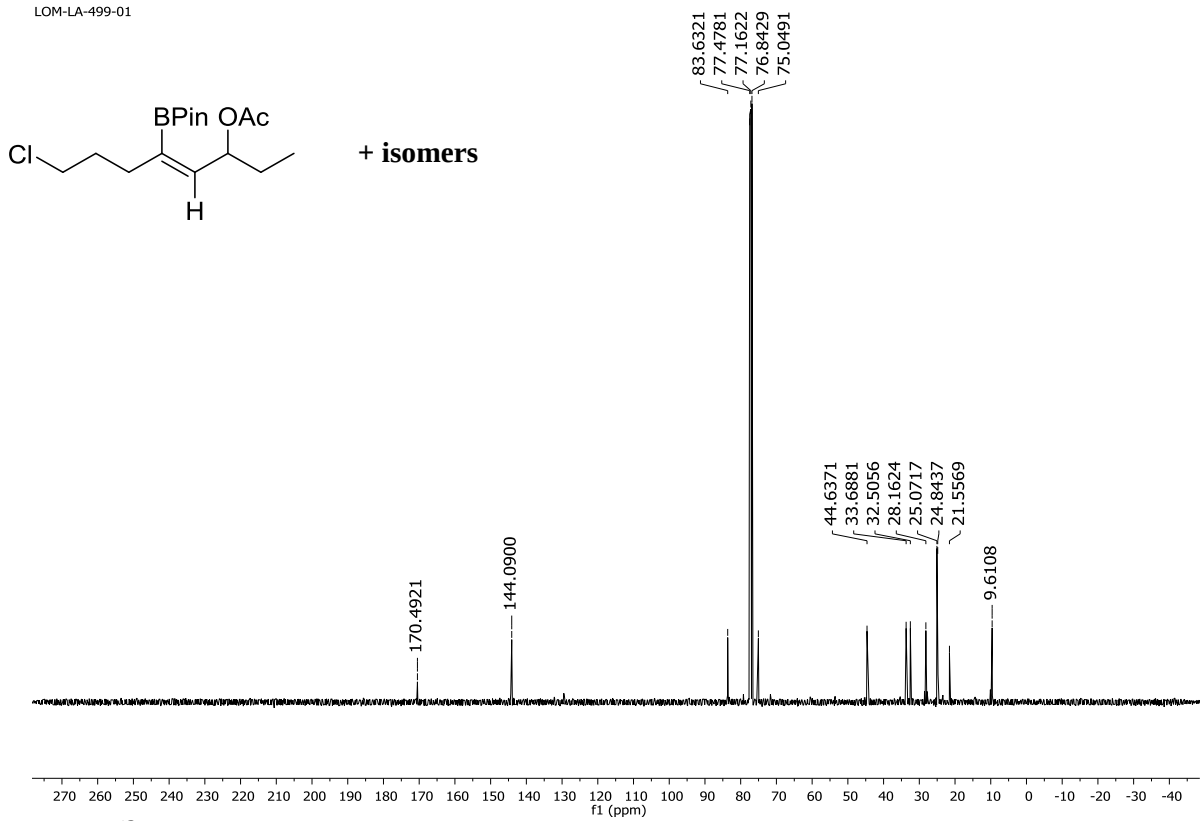

Figure 41: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **18**.

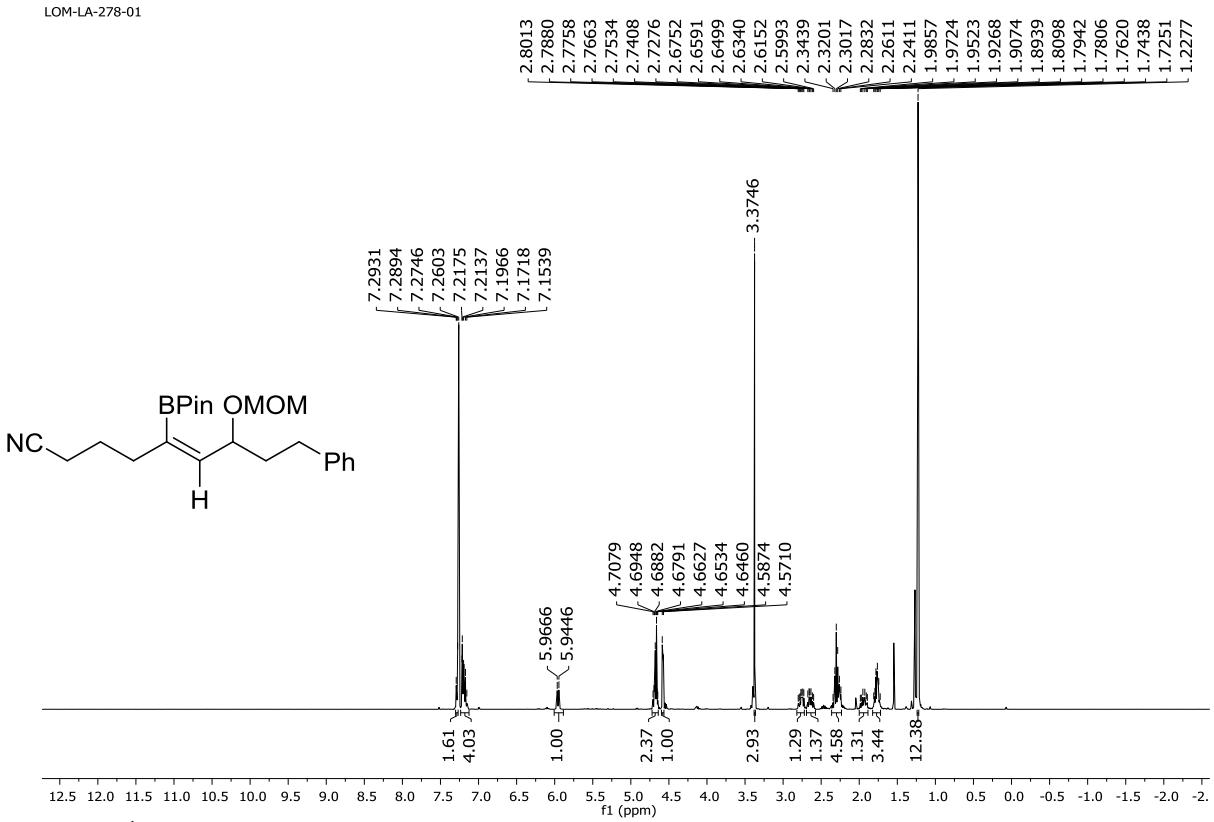

Figure 42: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **19**.

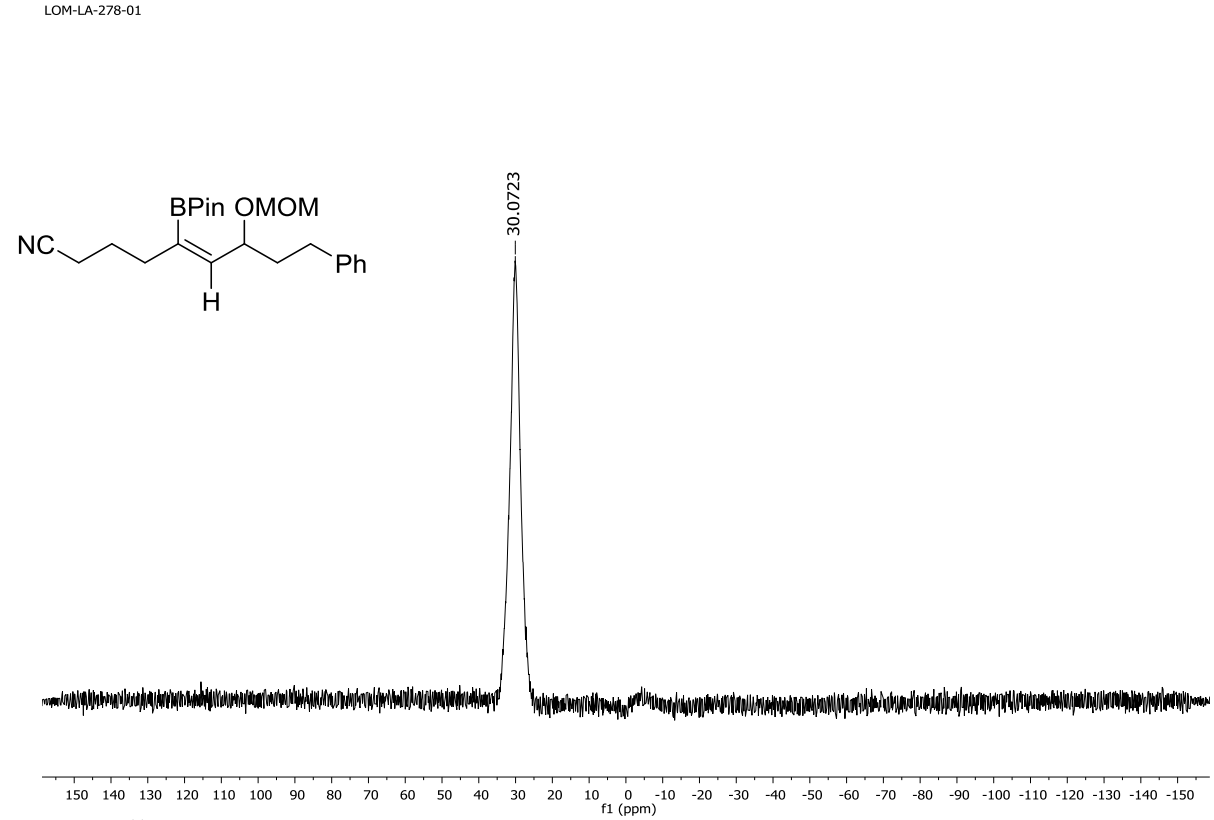

Figure 43: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **19**.

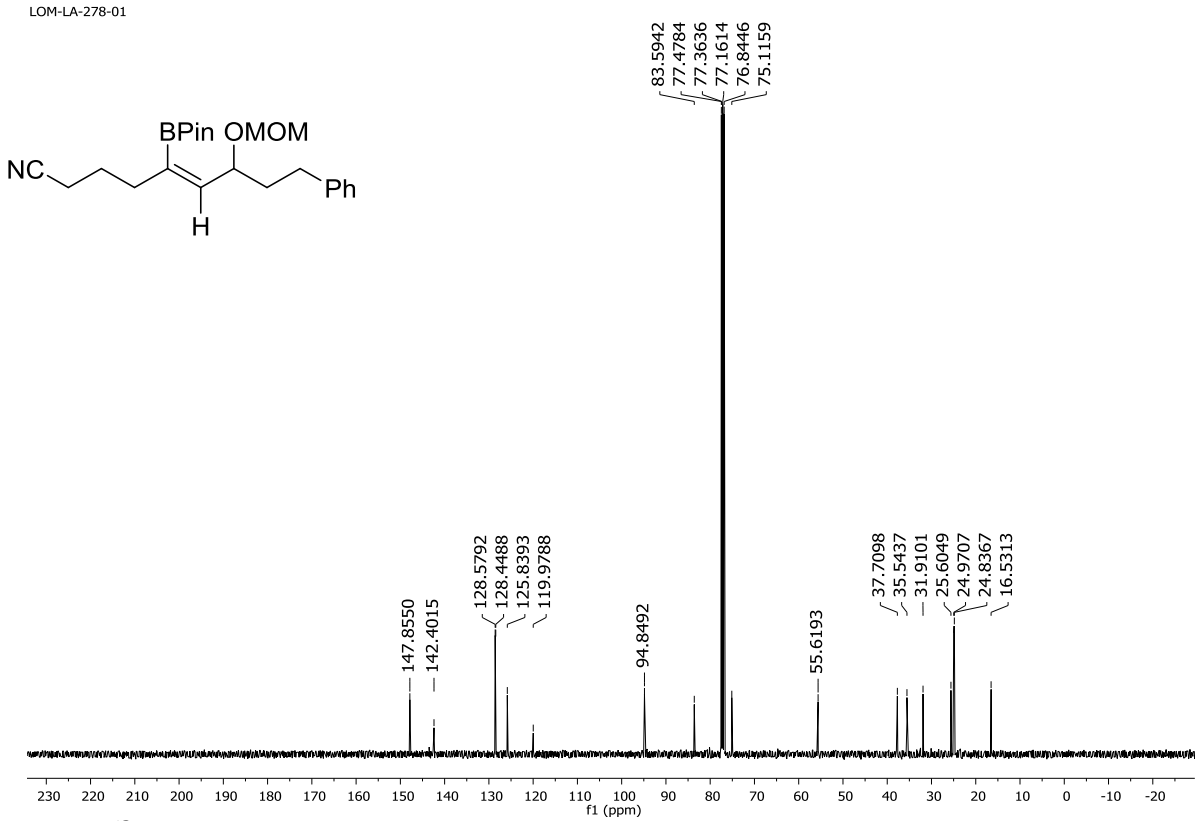

Figure 44: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **19**.

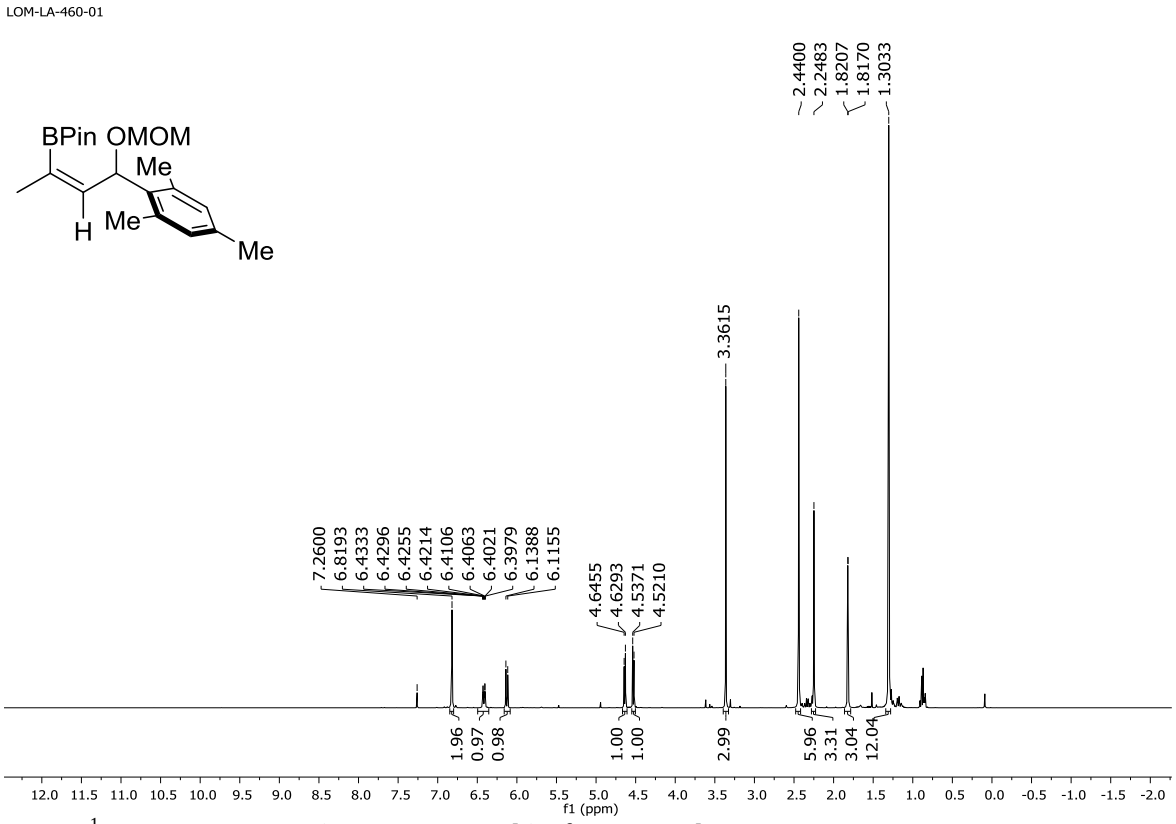

Figure 45: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **20**.

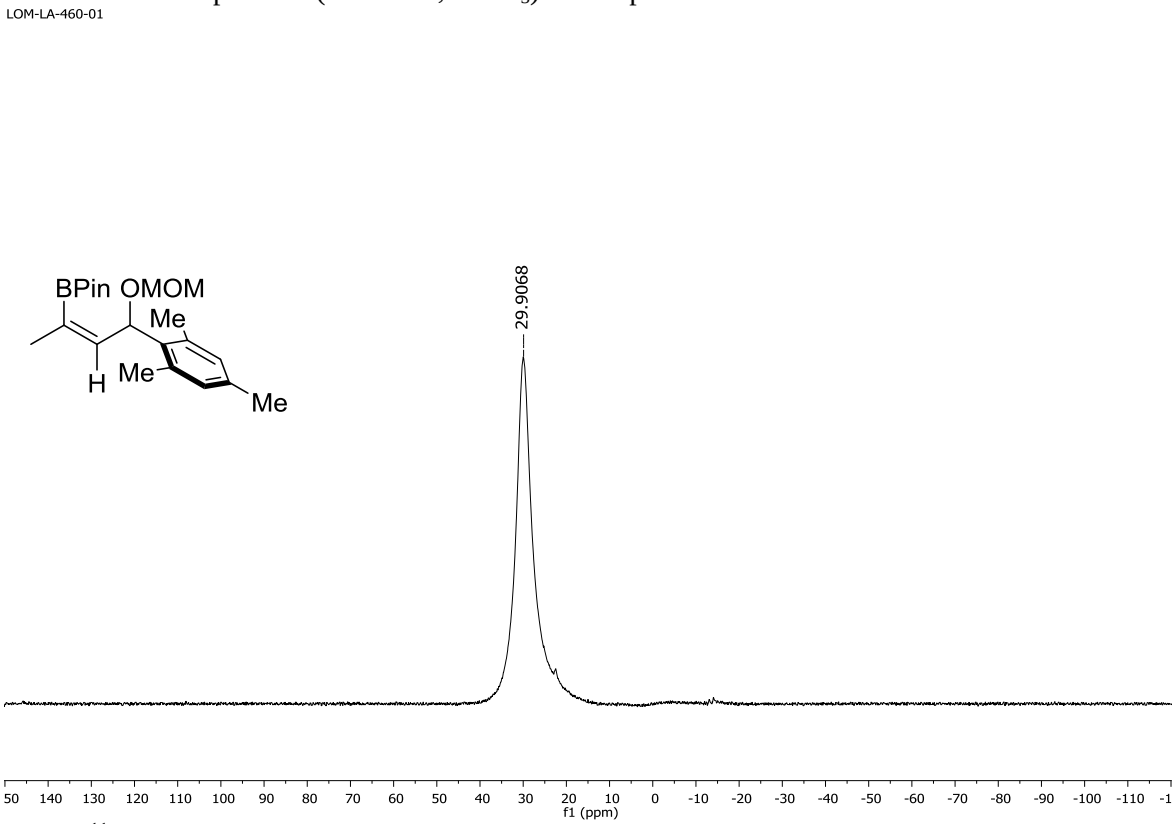

Figure 46: ^{11}B NMR spectrum (96 MHz, $CDCl_3$) of compound **20** (contains trace PinBOH).

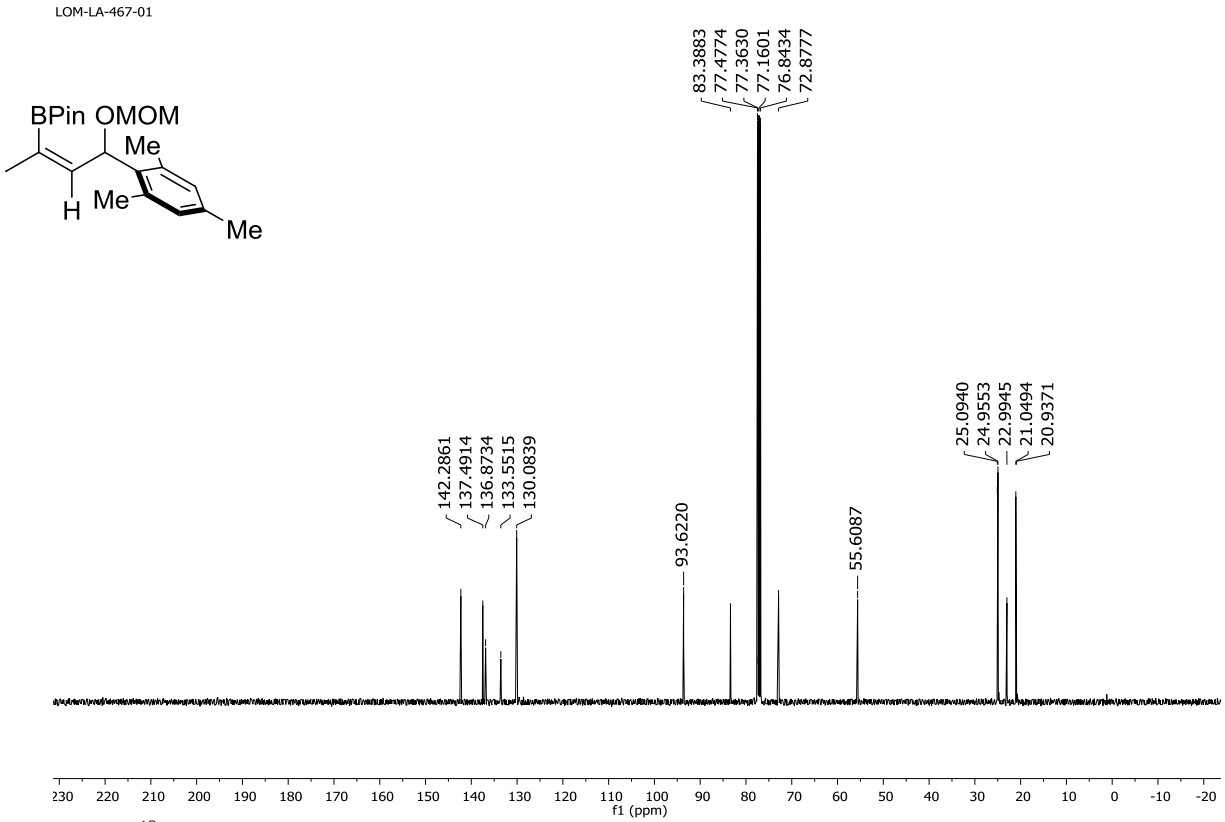

Figure 47: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **20**.

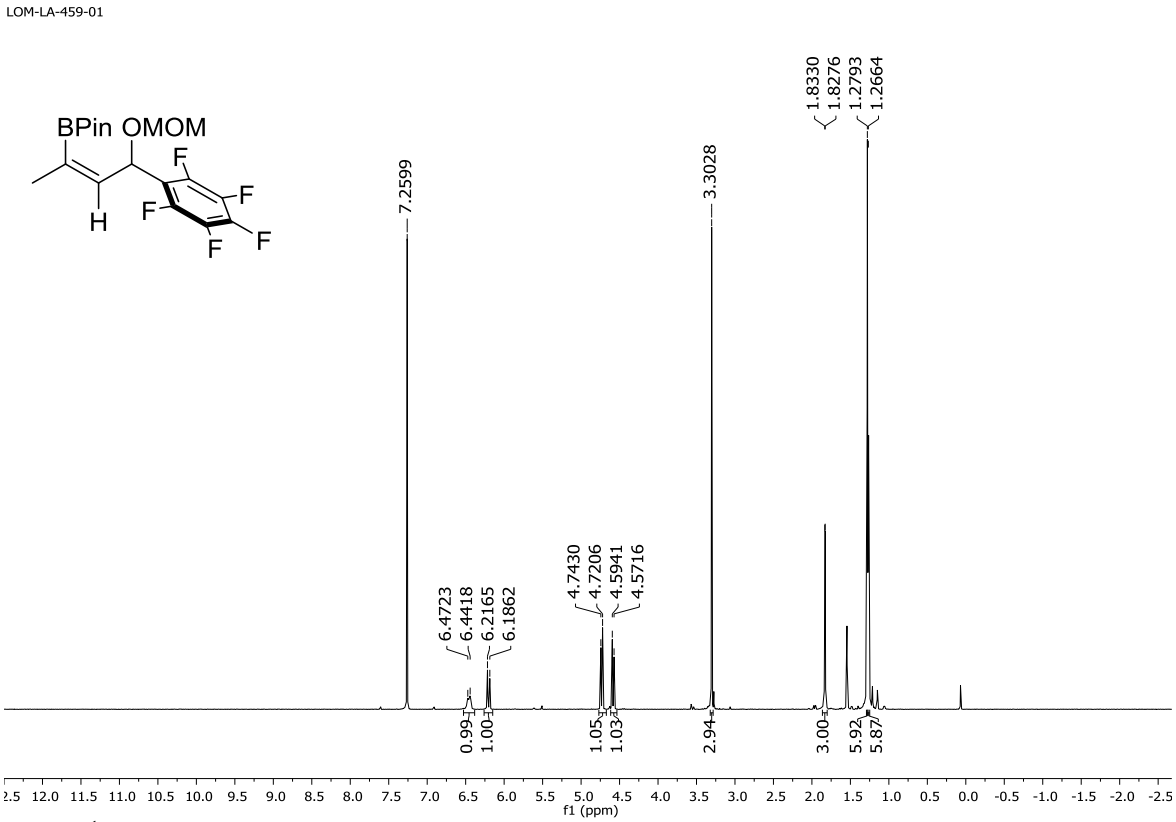

Figure 48: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **21**.

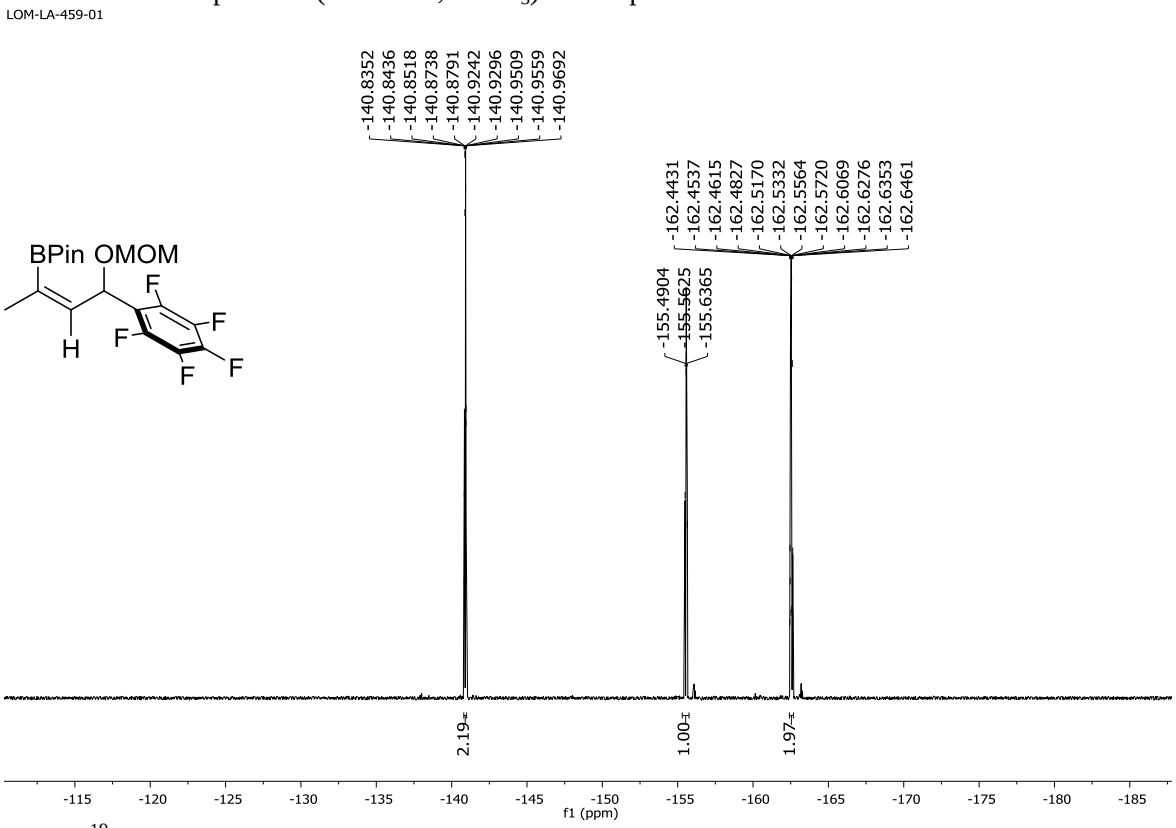

Figure 49: ^{19}F NMR spectrum (282 MHz, $CDCl_3$) of compound **21**.

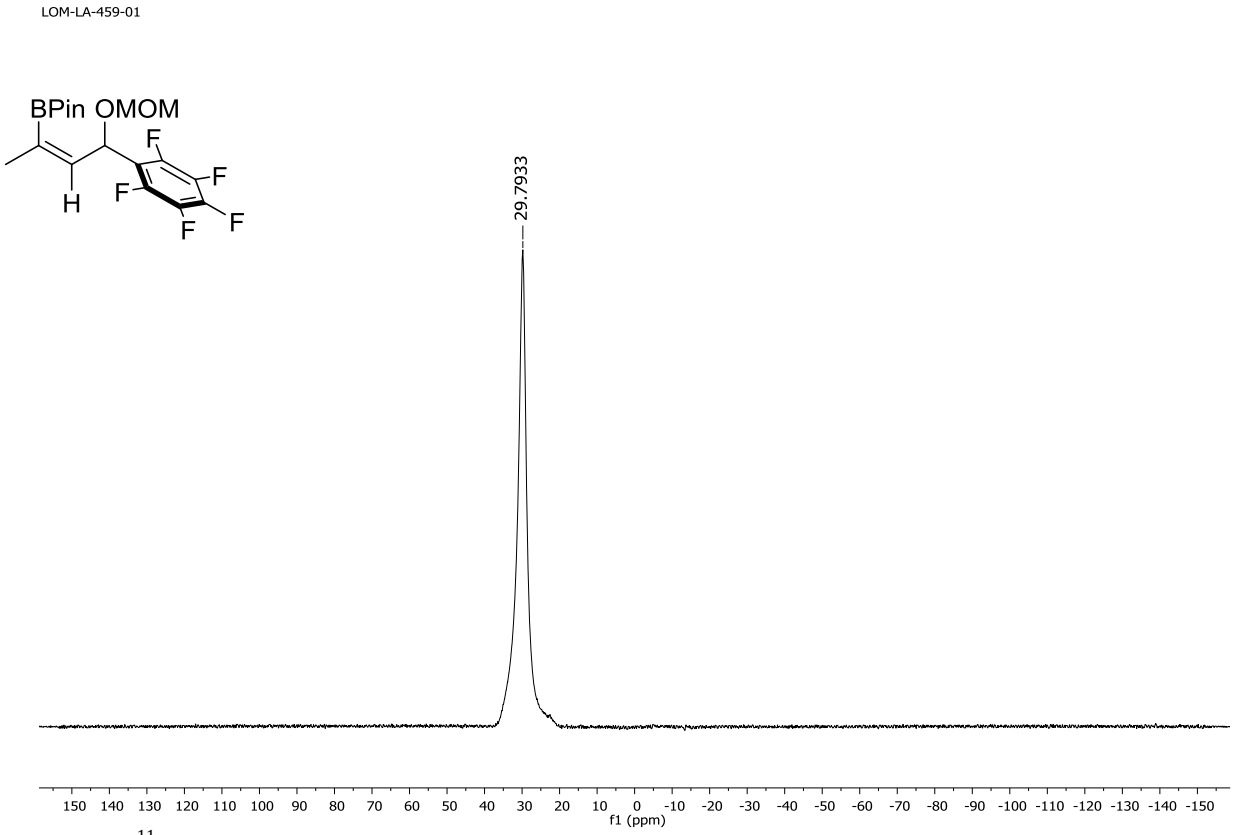

Figure 50: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **21**.

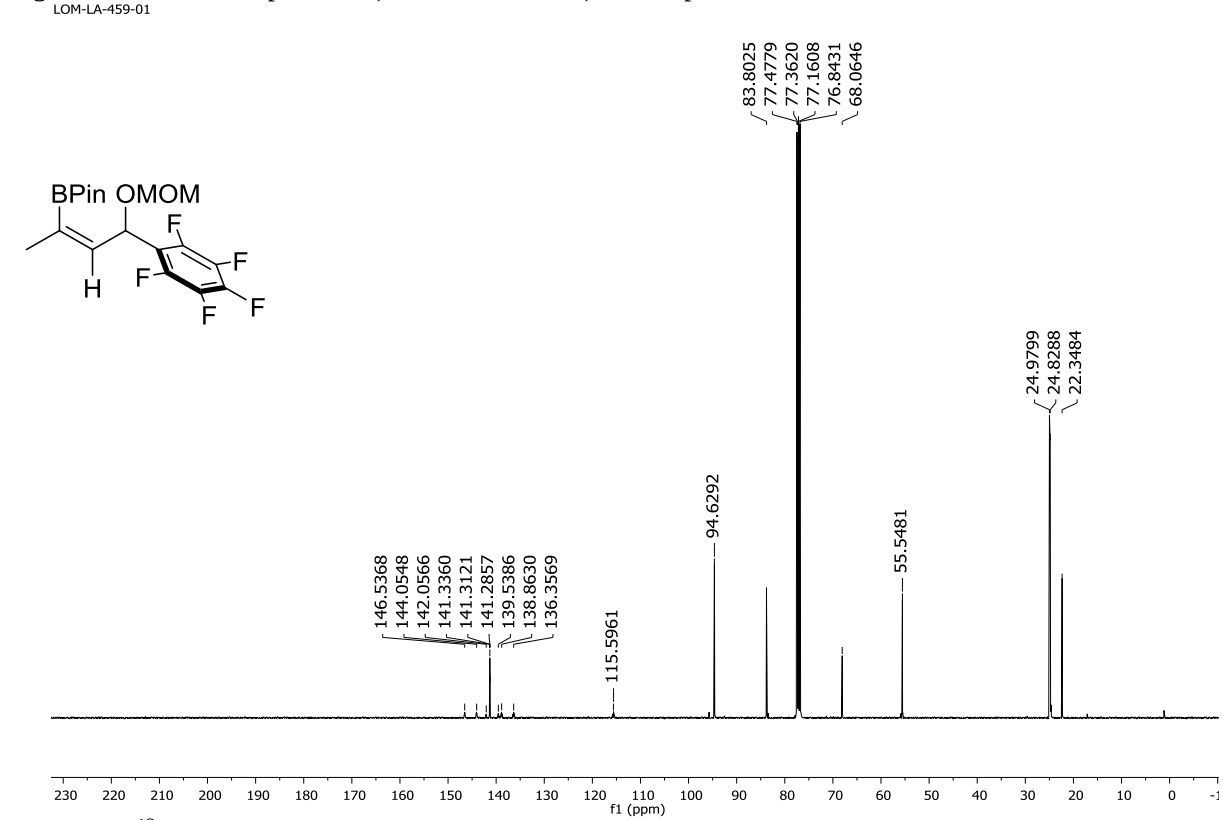

Figure 51: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **21**.

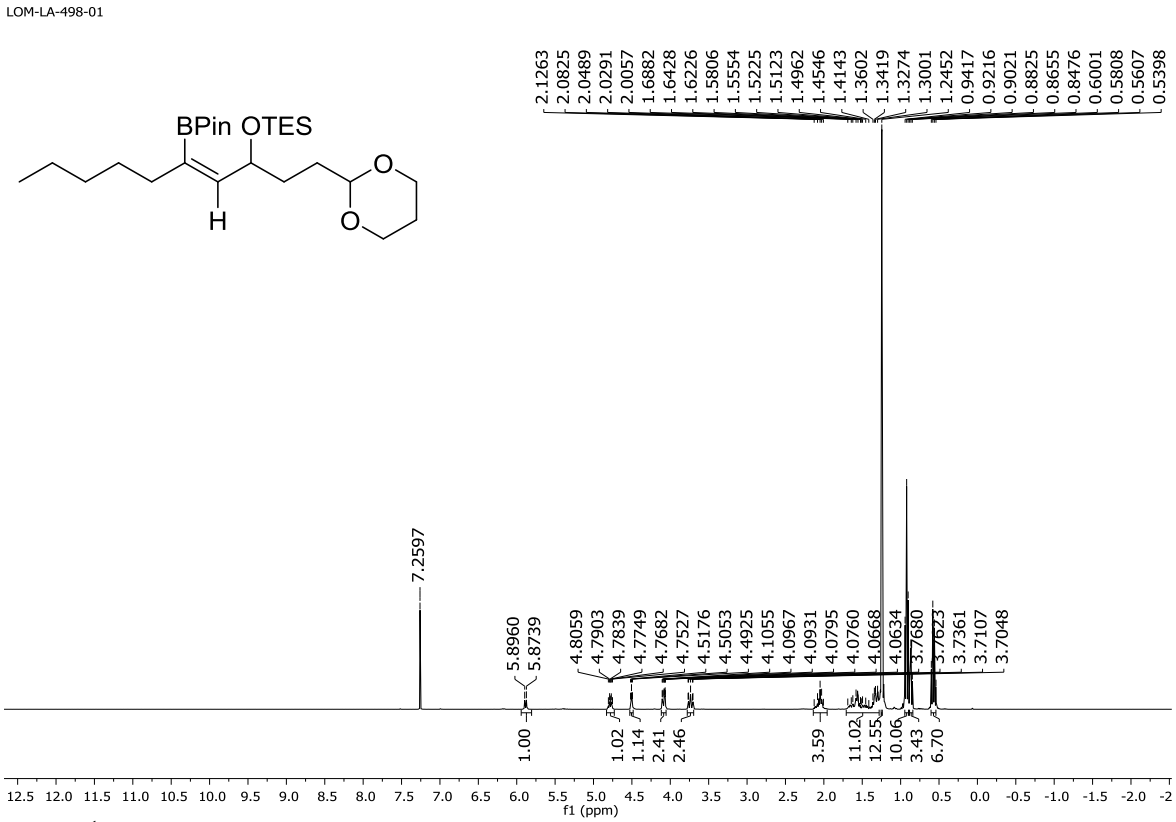

Figure 89: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **22**.

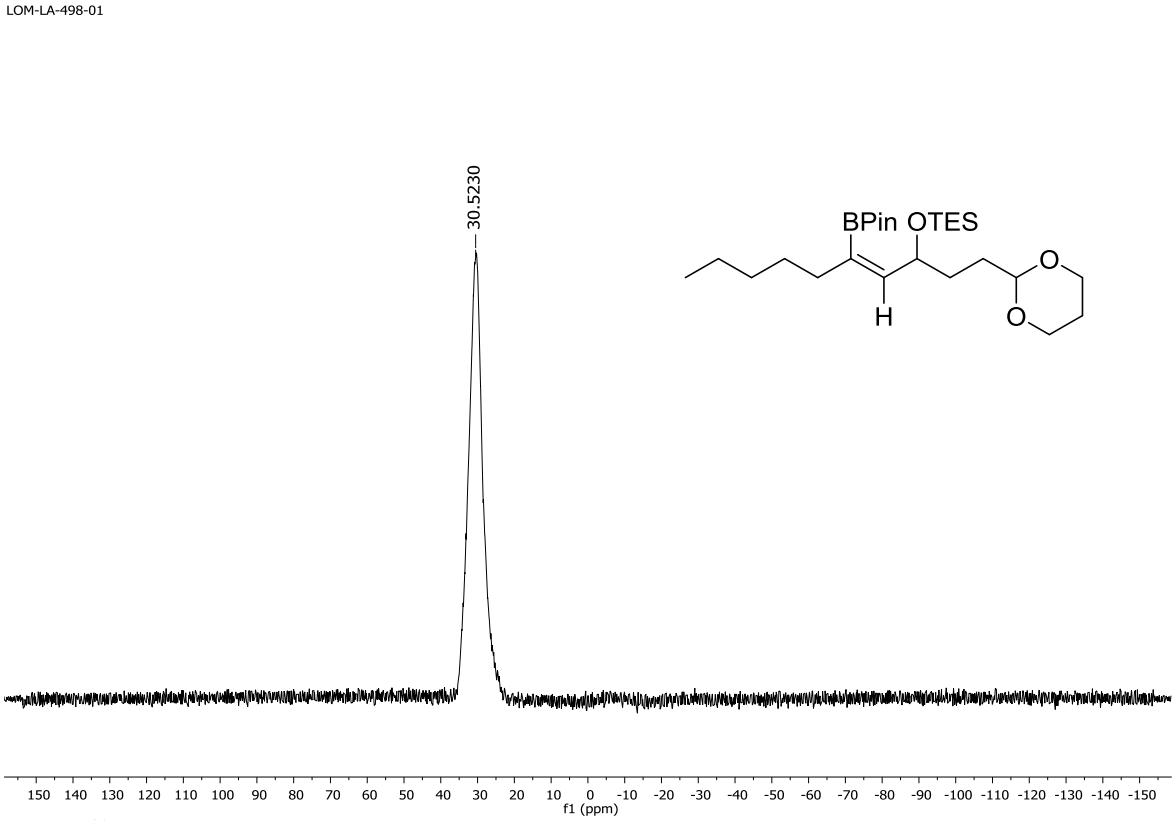

Figure 90: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **22**.

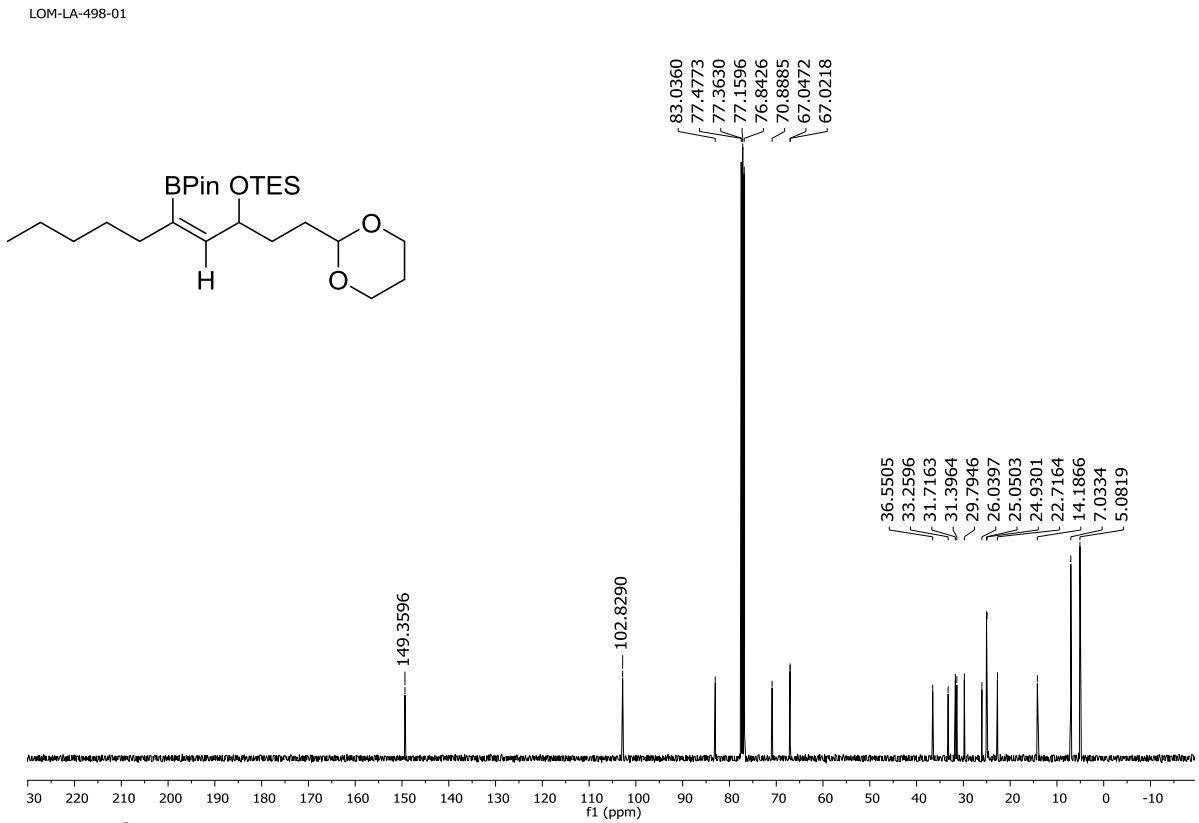

Figure 91: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **22**.

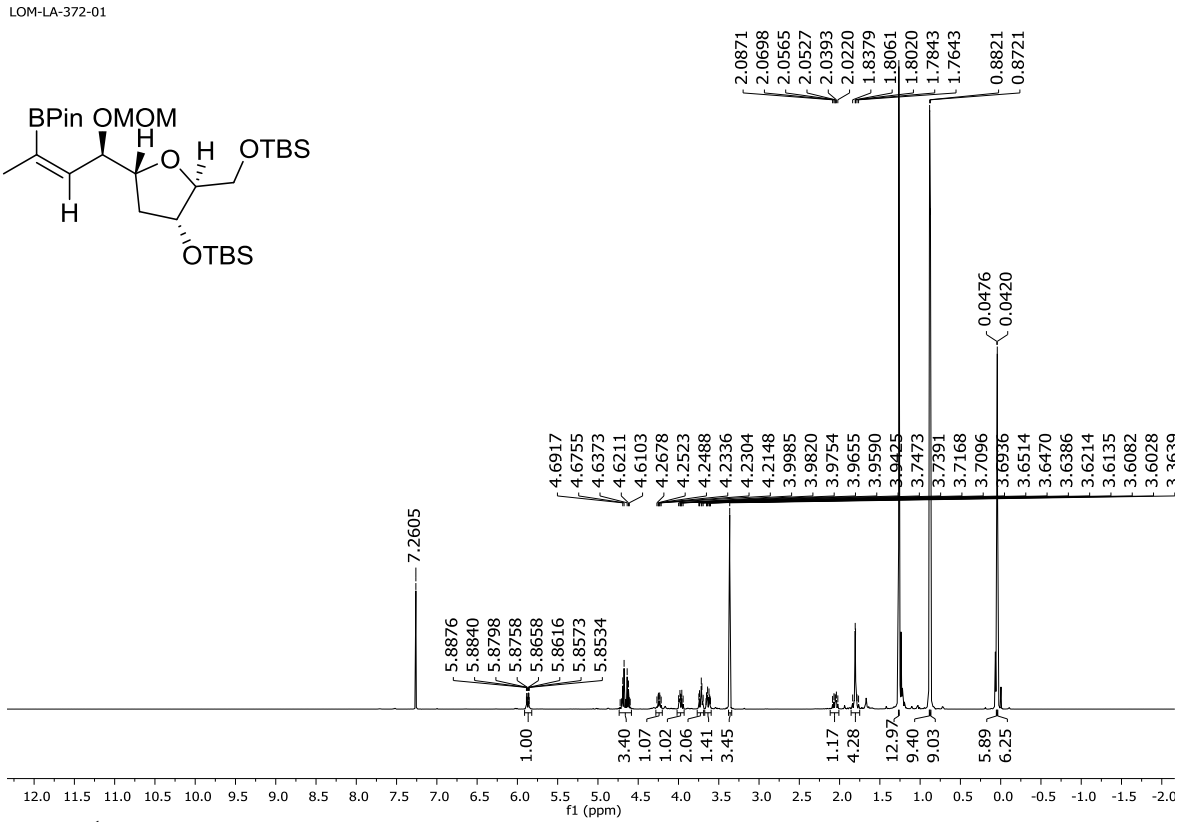

Figure 92: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **23**.

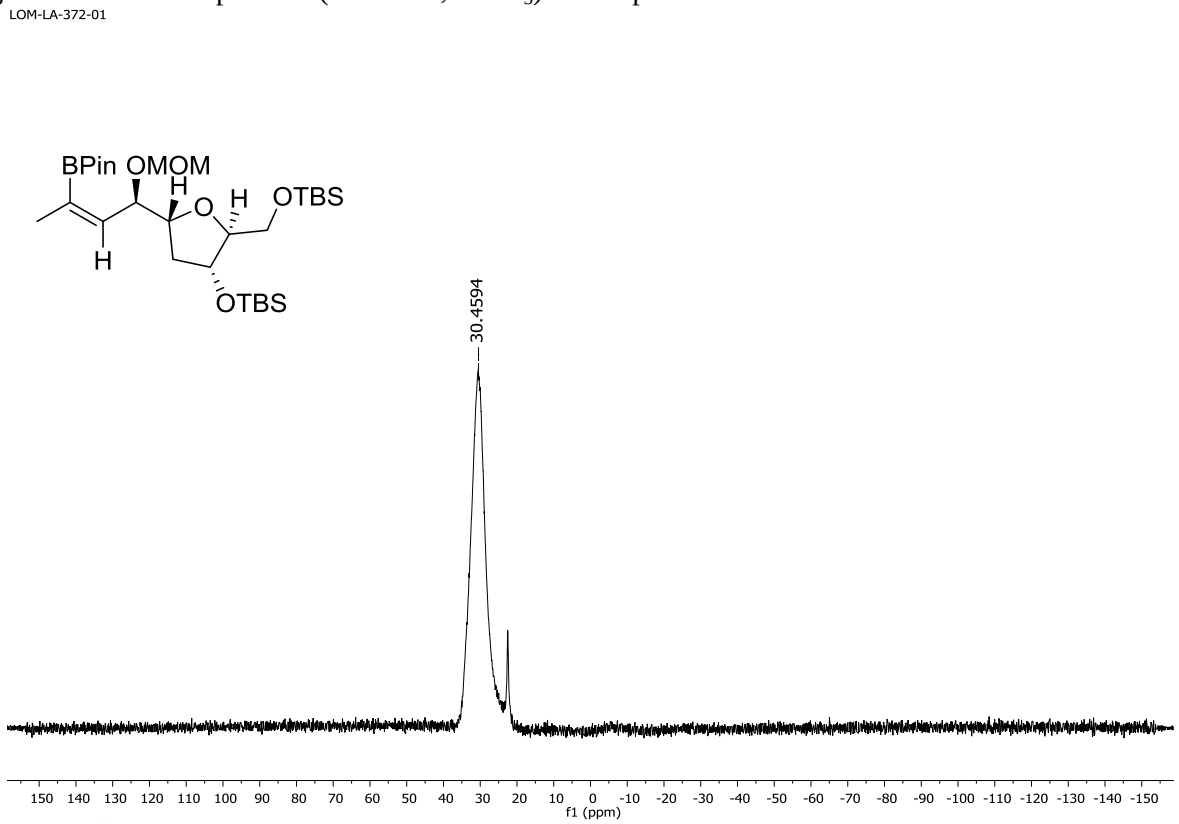

Figure 93: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **23** (contains trace PinBOH)

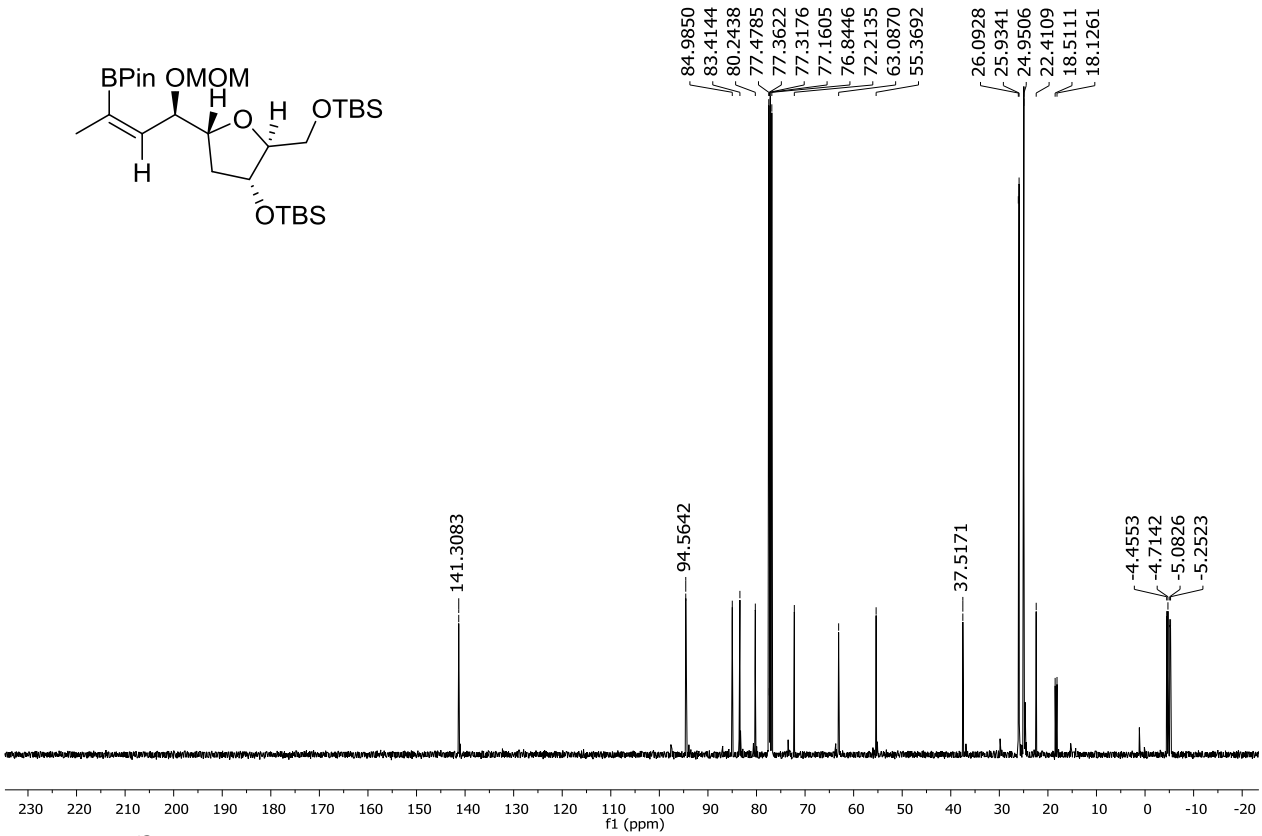

Figure 94: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **23**.

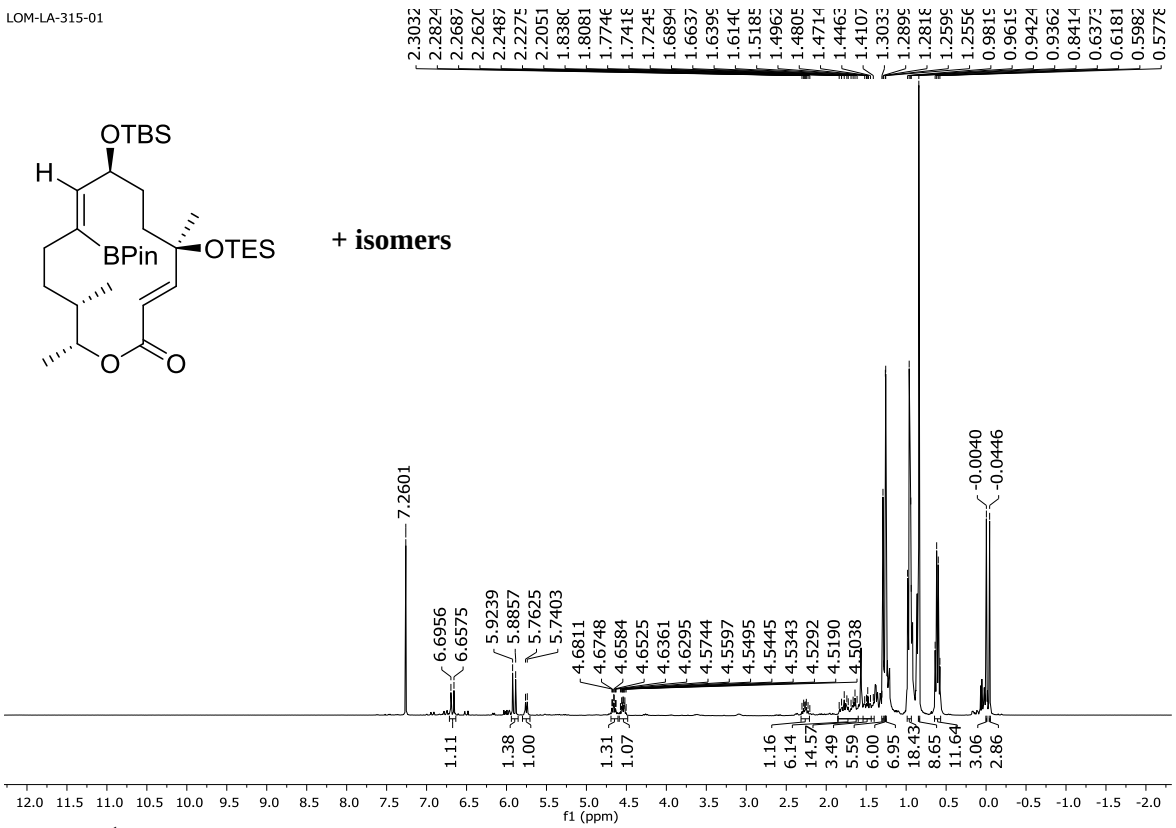

Figure 95: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **24** (contains minor amounts of unidentified impurities).

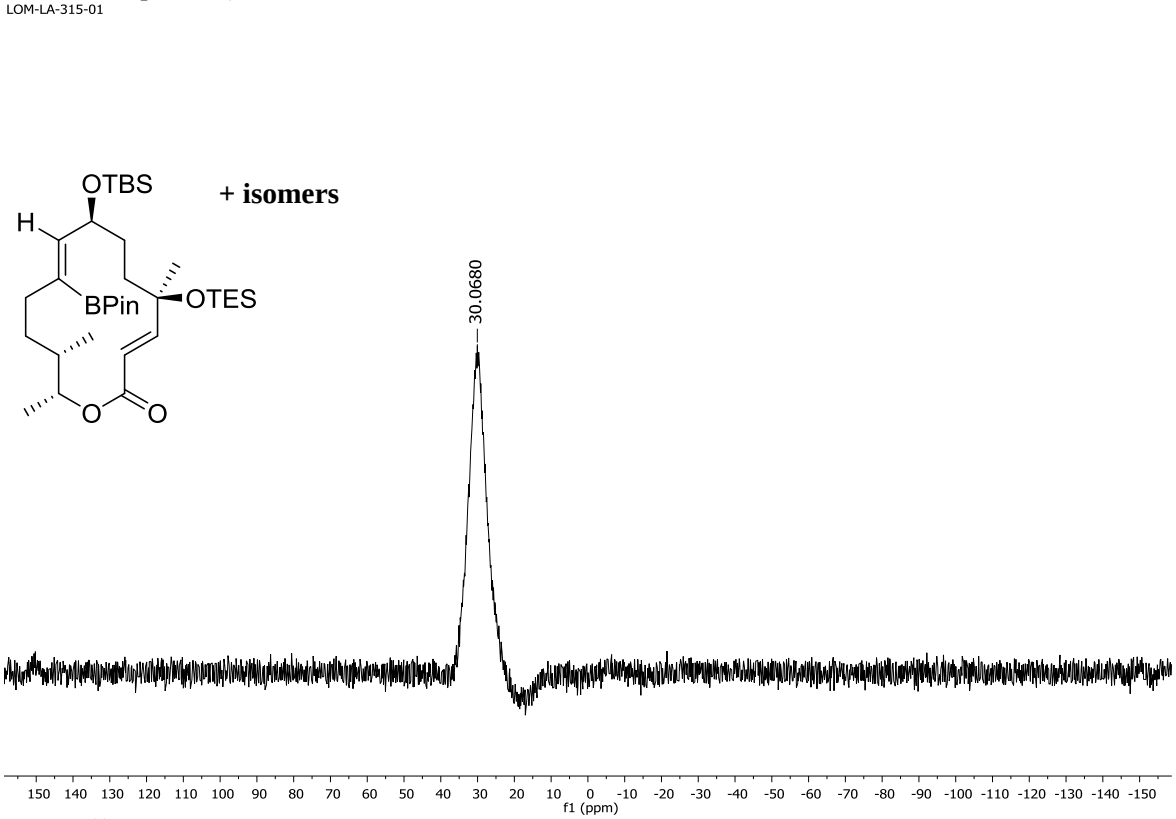

Figure 96: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **24**.

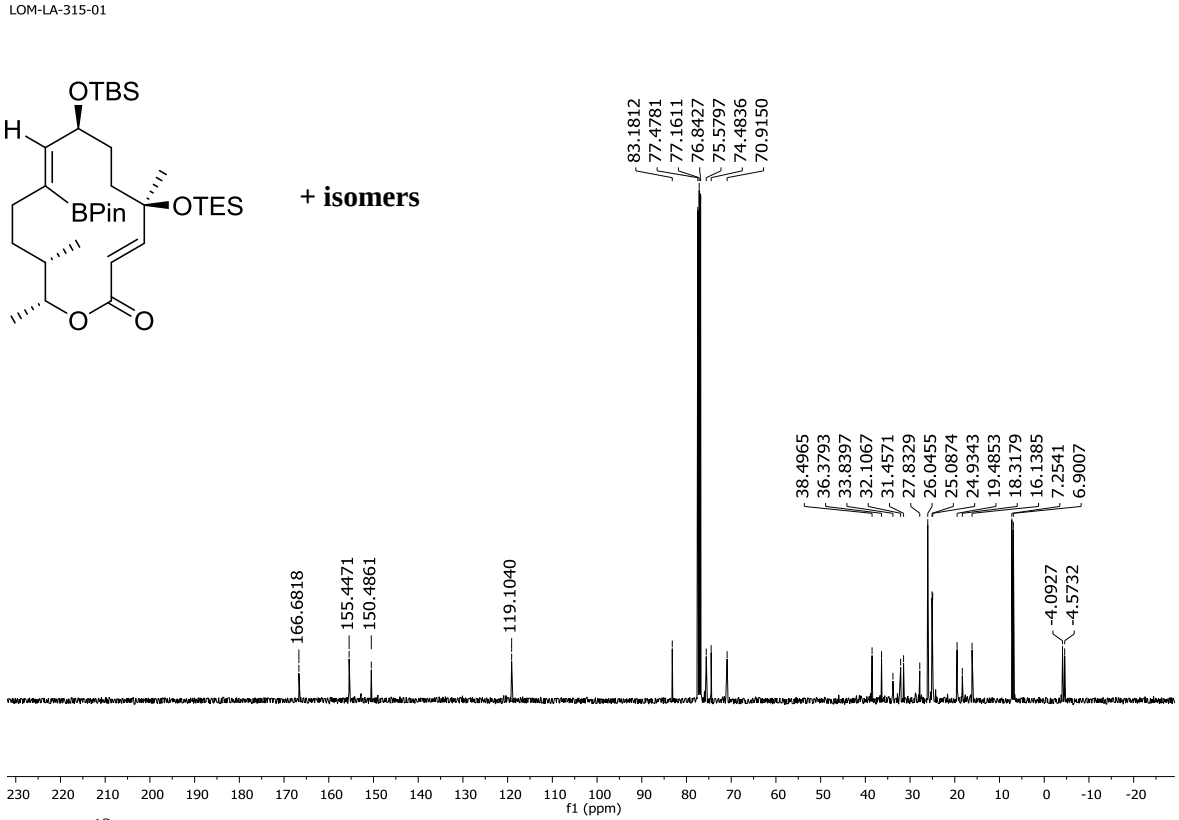

Figure 97: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **24**.

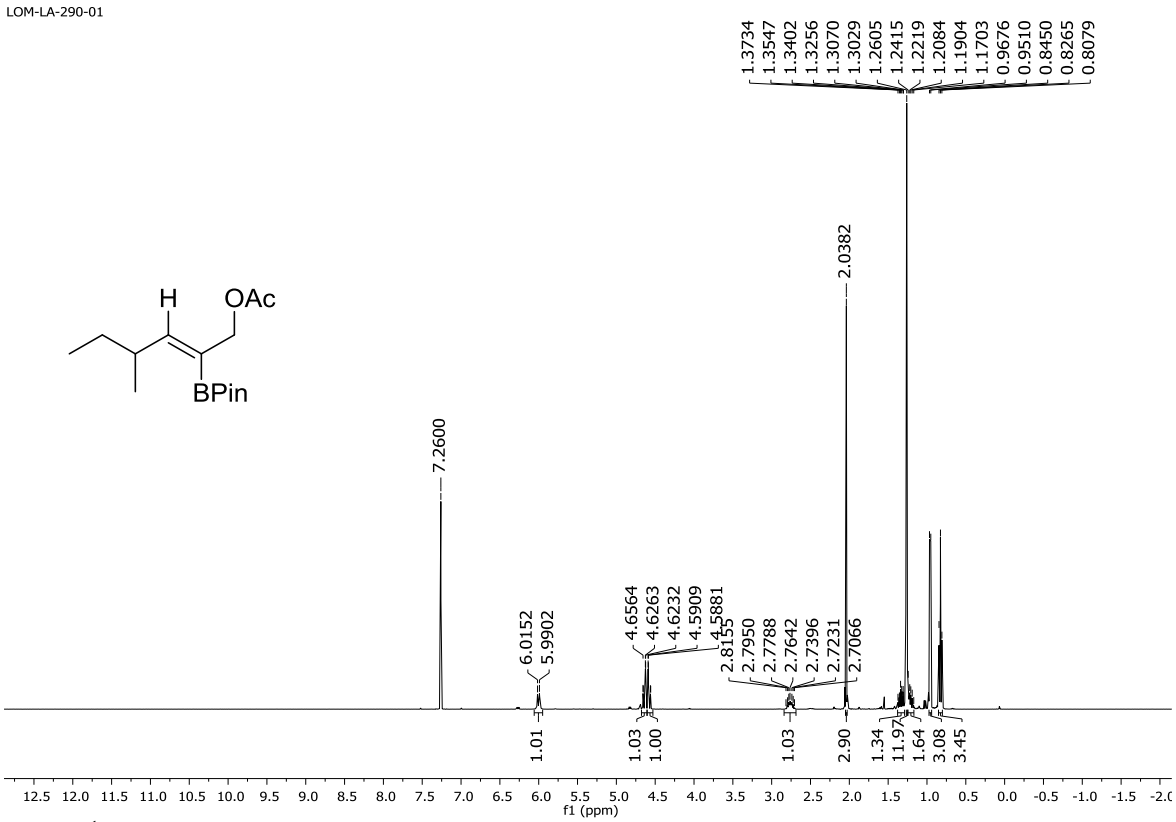

Figure 98: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25**.

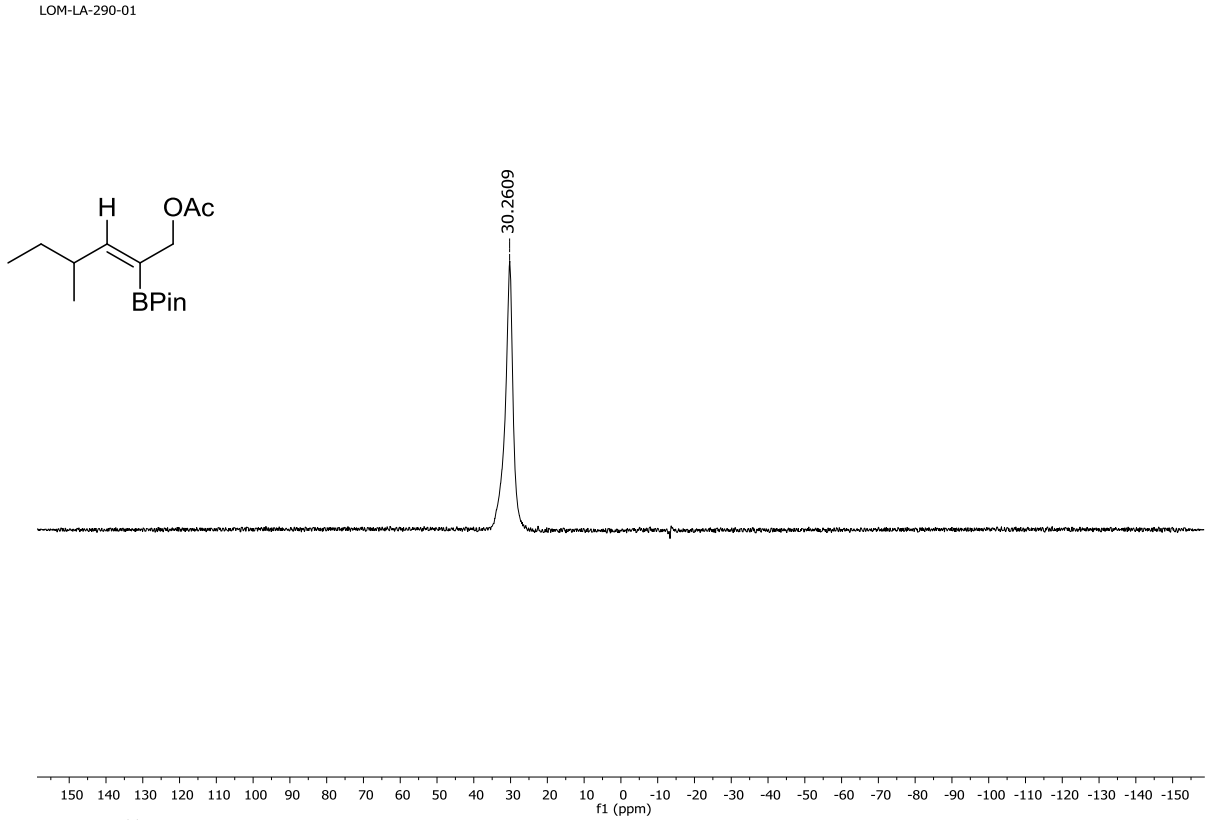

Figure 99: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **25**.

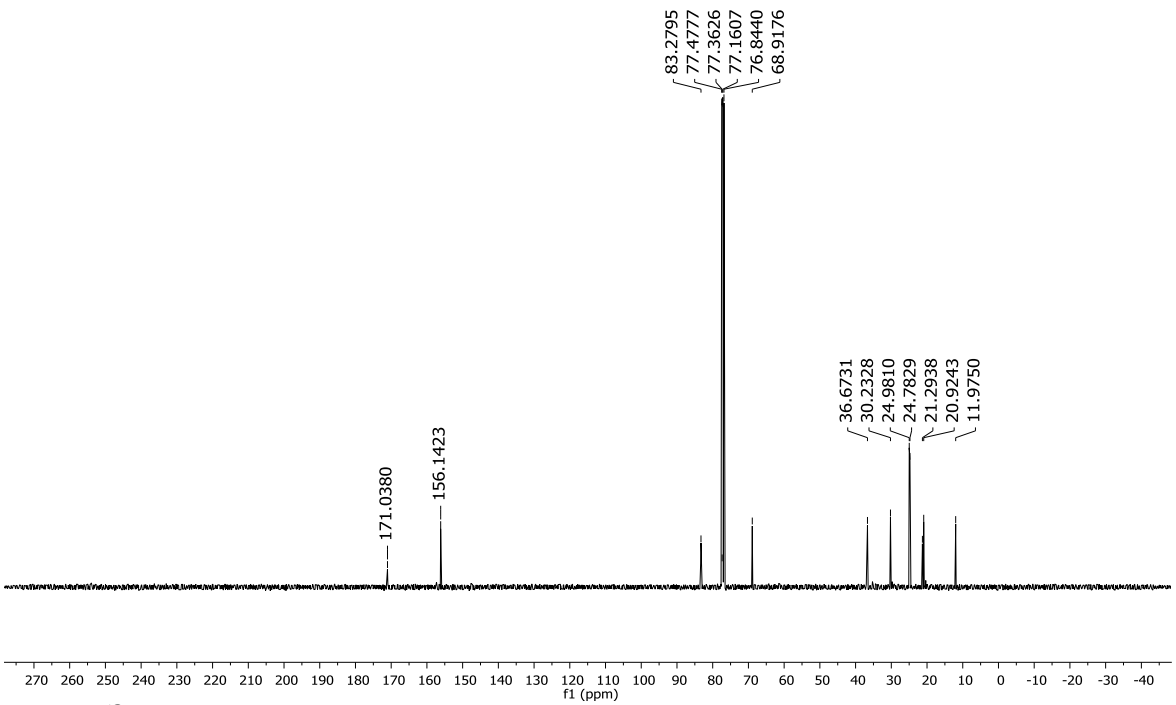

Figure 100: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **25**.

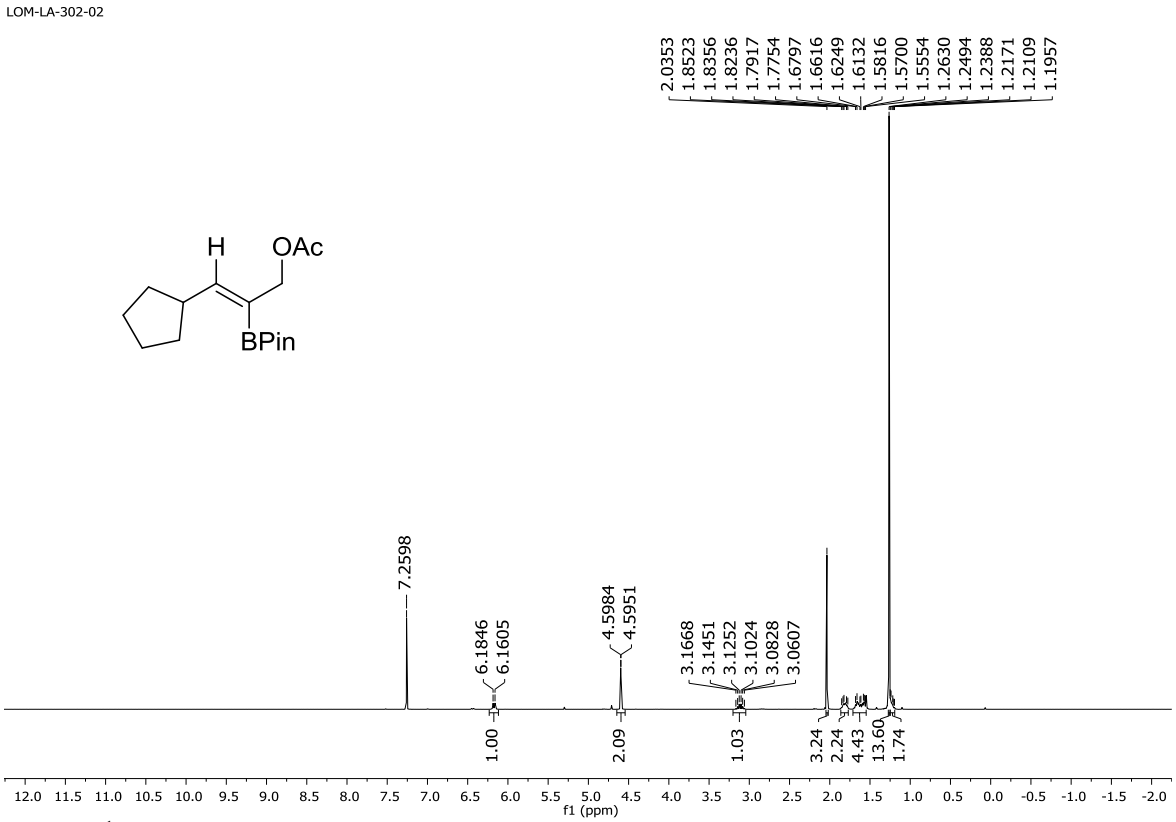

Figure 101: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **27**.

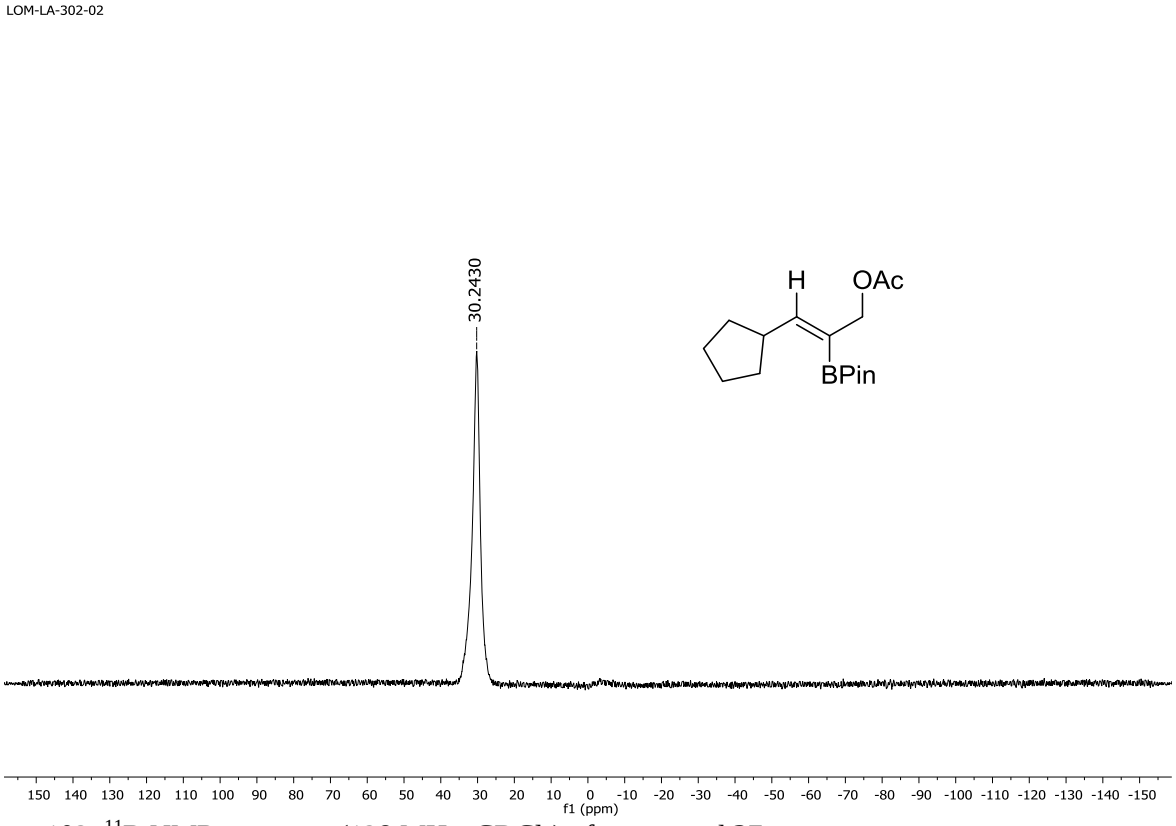

Figure 102: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **27**.

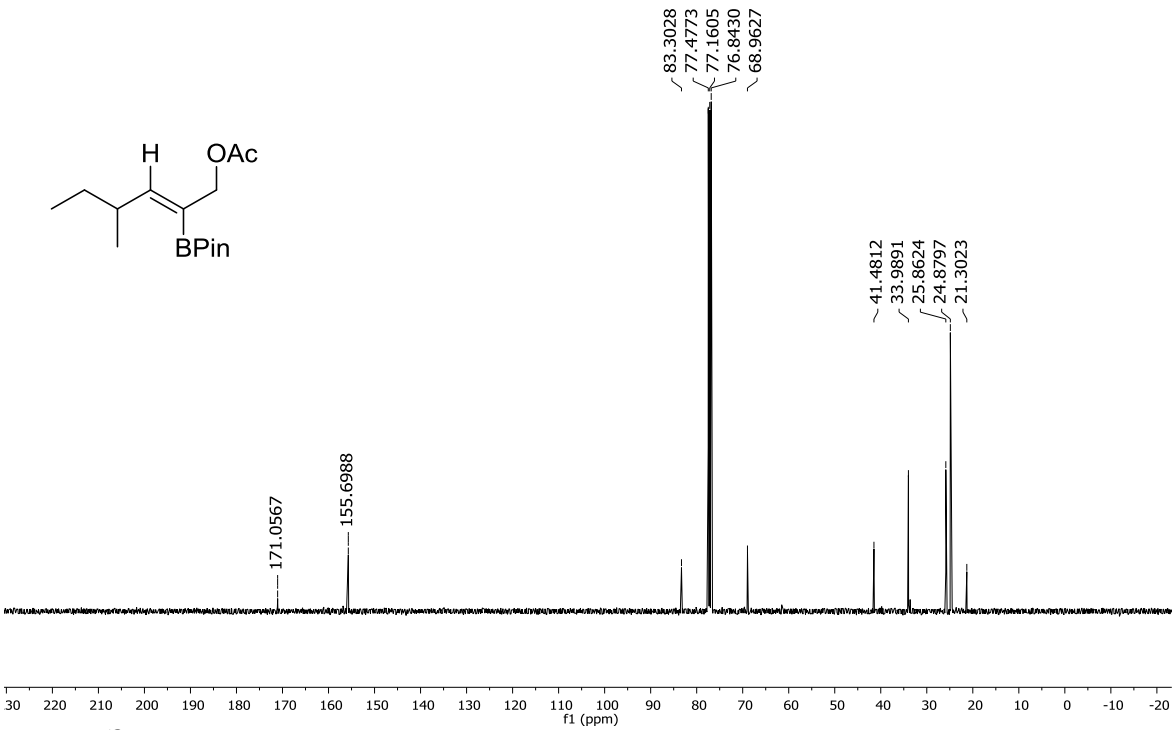

Figure 103: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **27**.

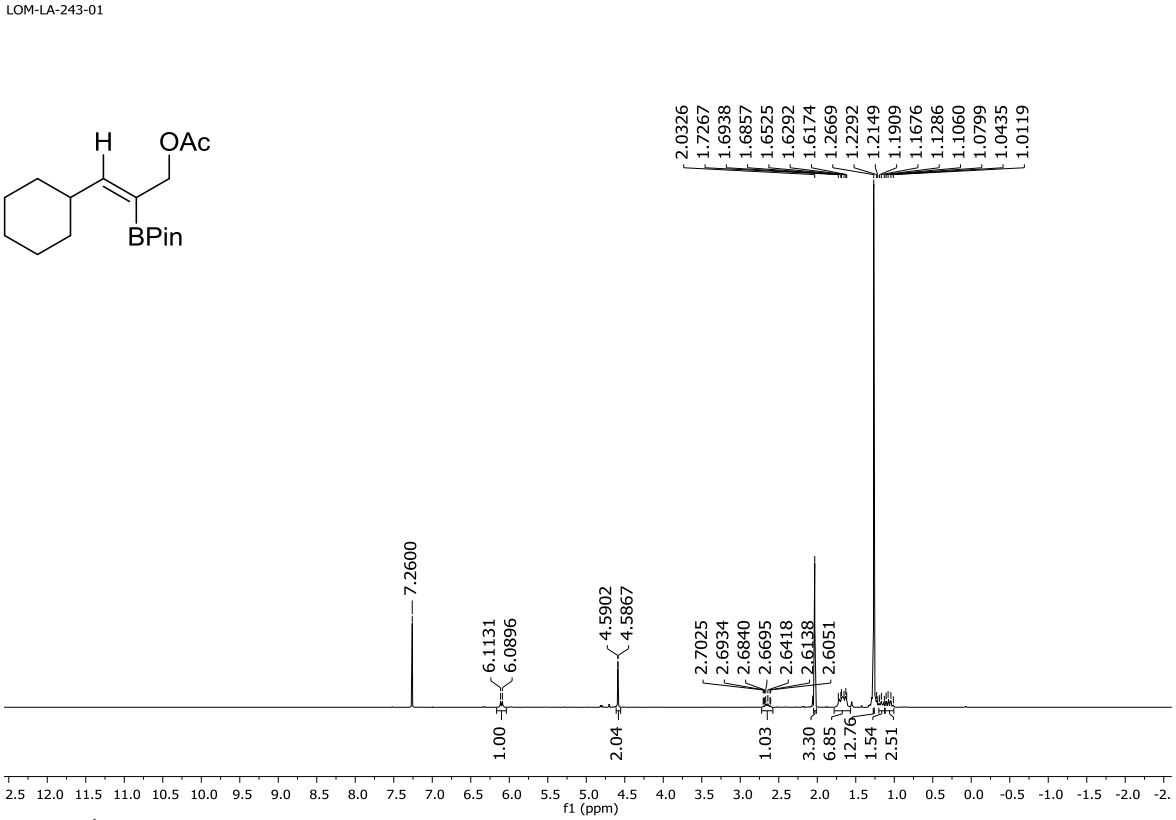

Figure 52: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **28a**.

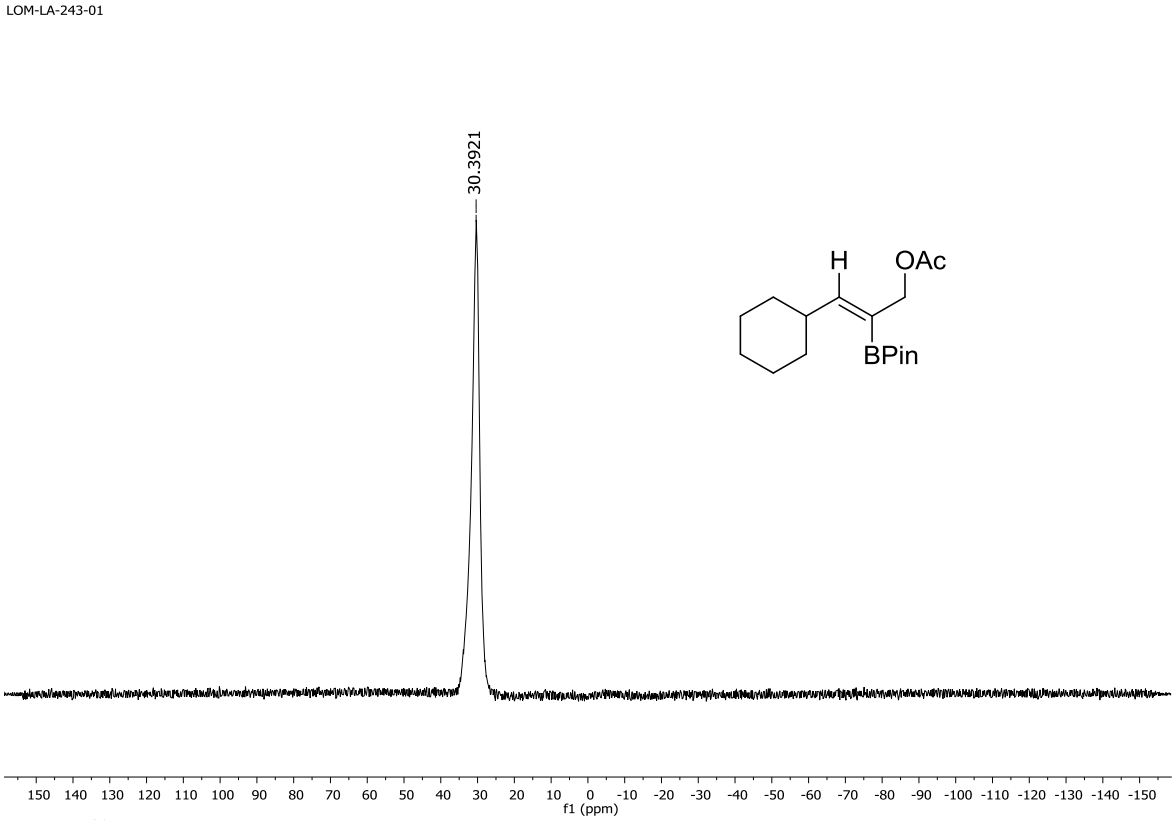

Figure 53: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **28a**.

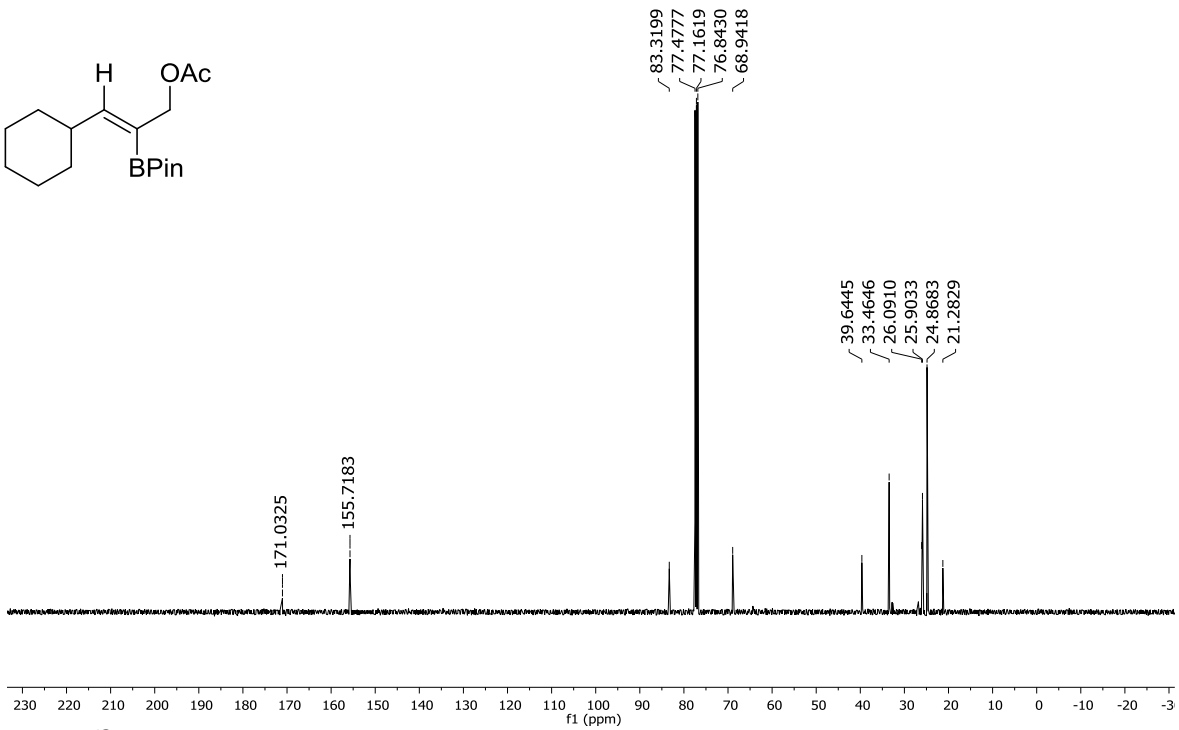

Figure 54: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **28a**.

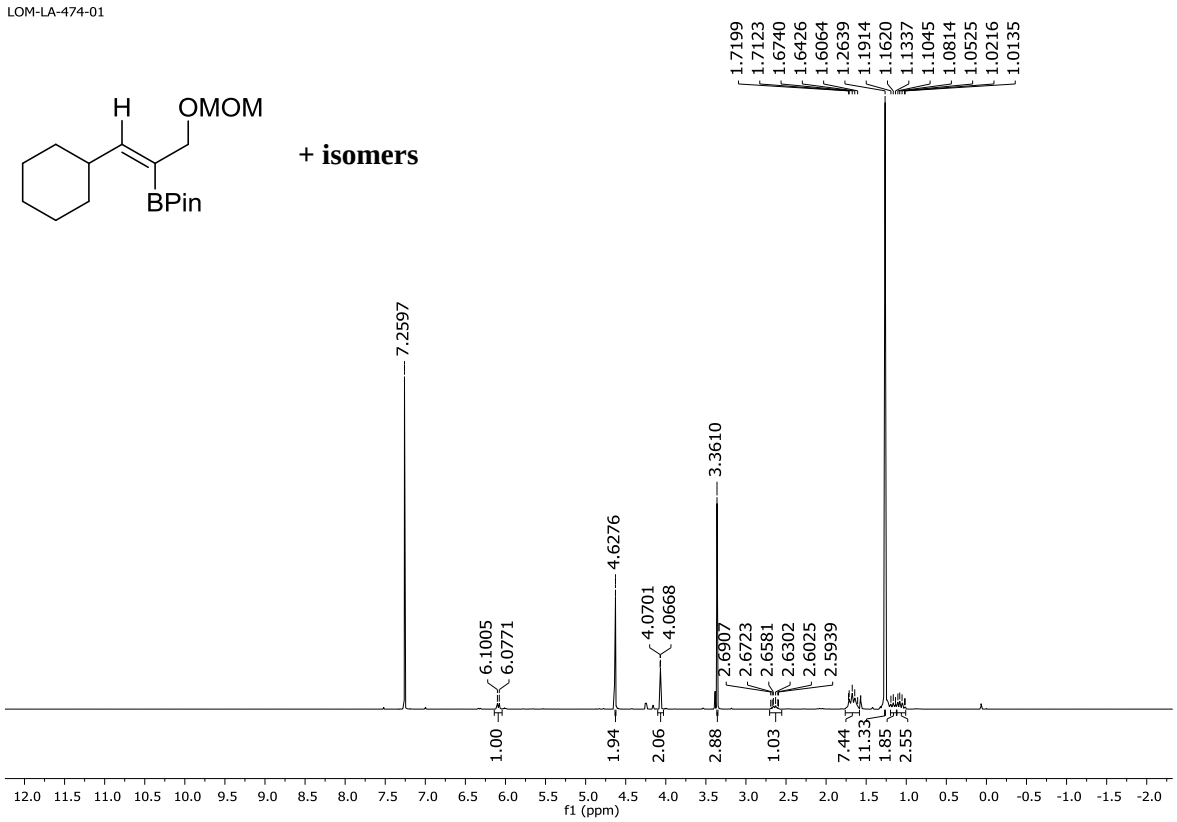

Figure 107: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **28b**.

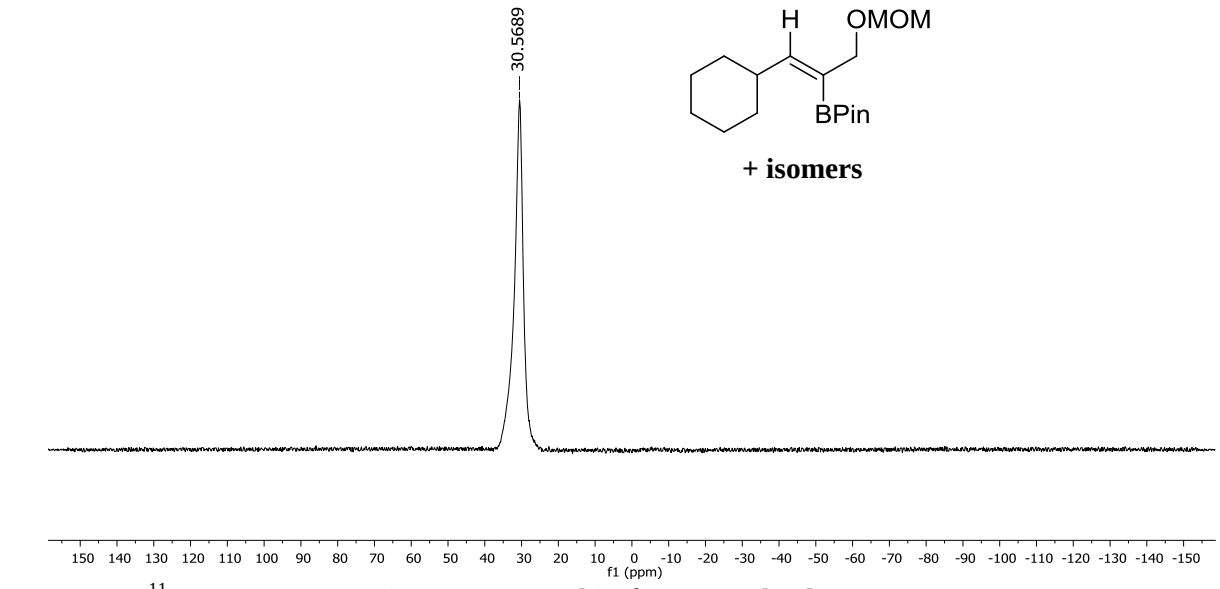

Figure 108: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **28b**.

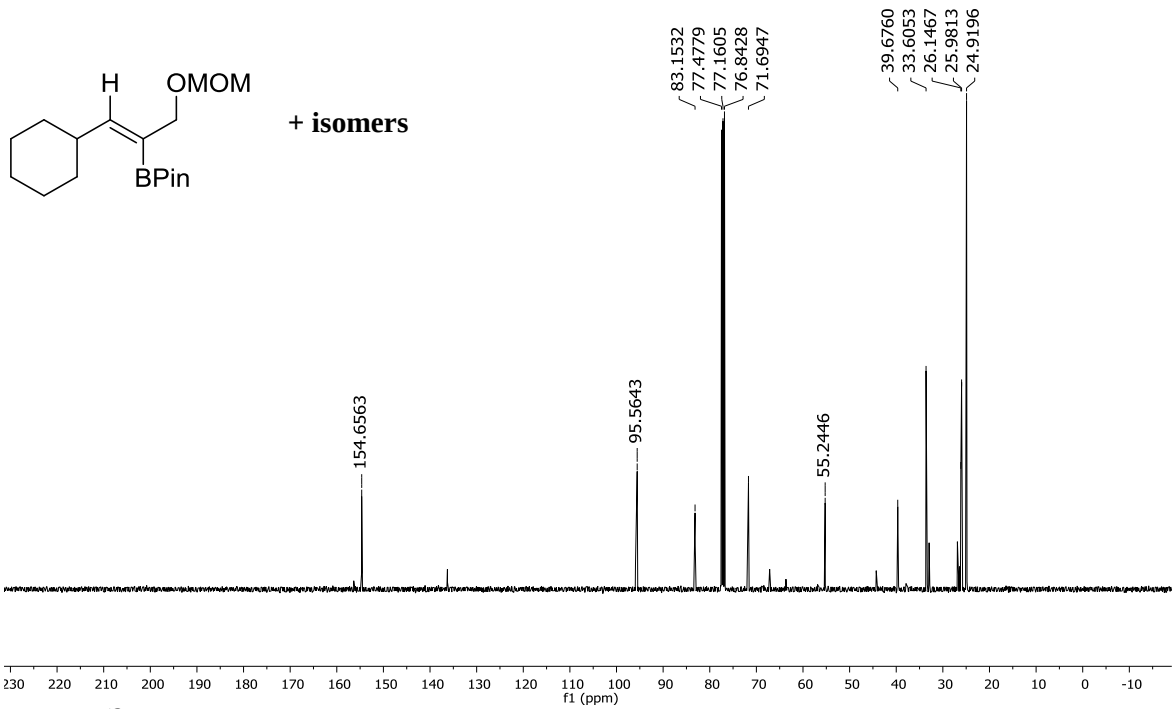

Figure 109: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **28b**.

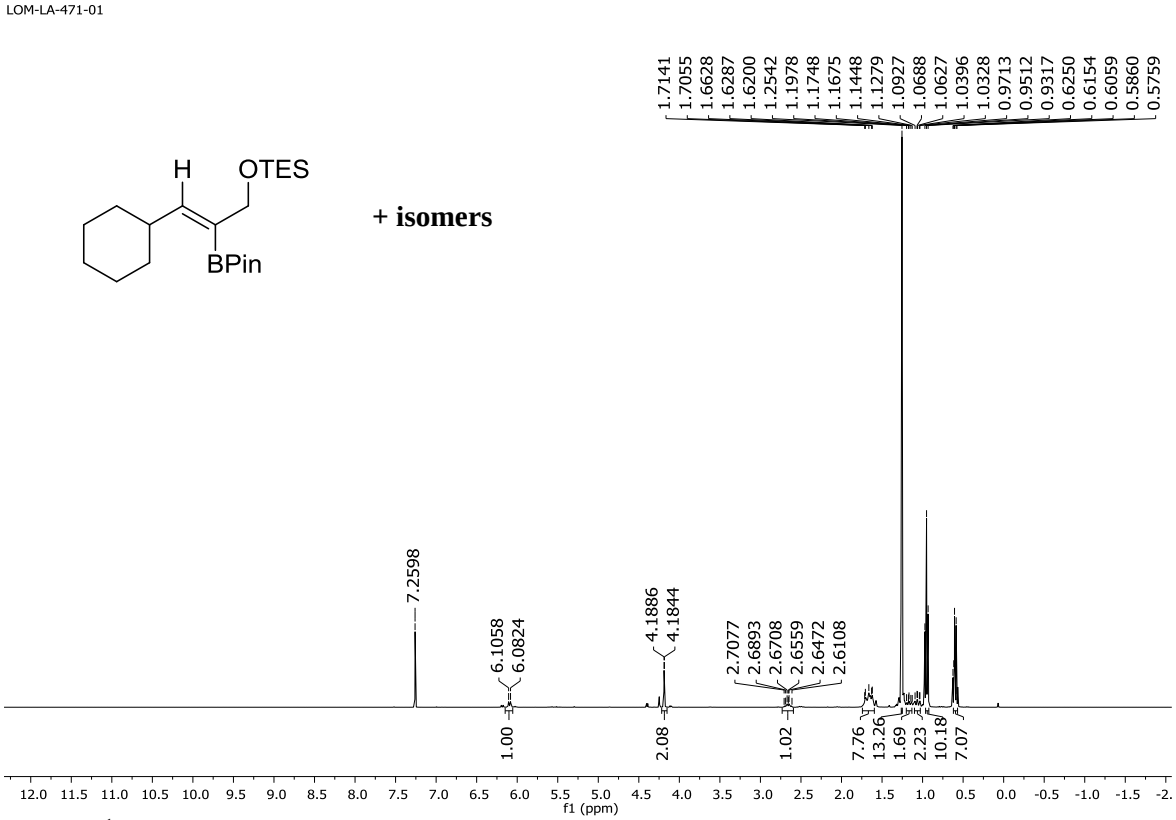

Figure 110: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **28c**.

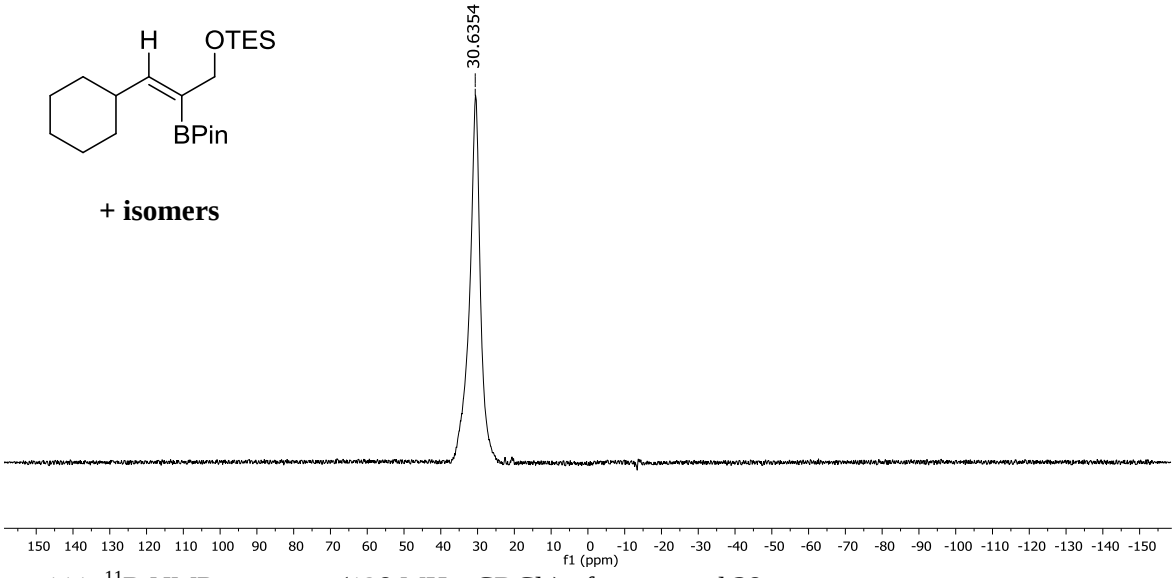

Figure 111: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **28c**.

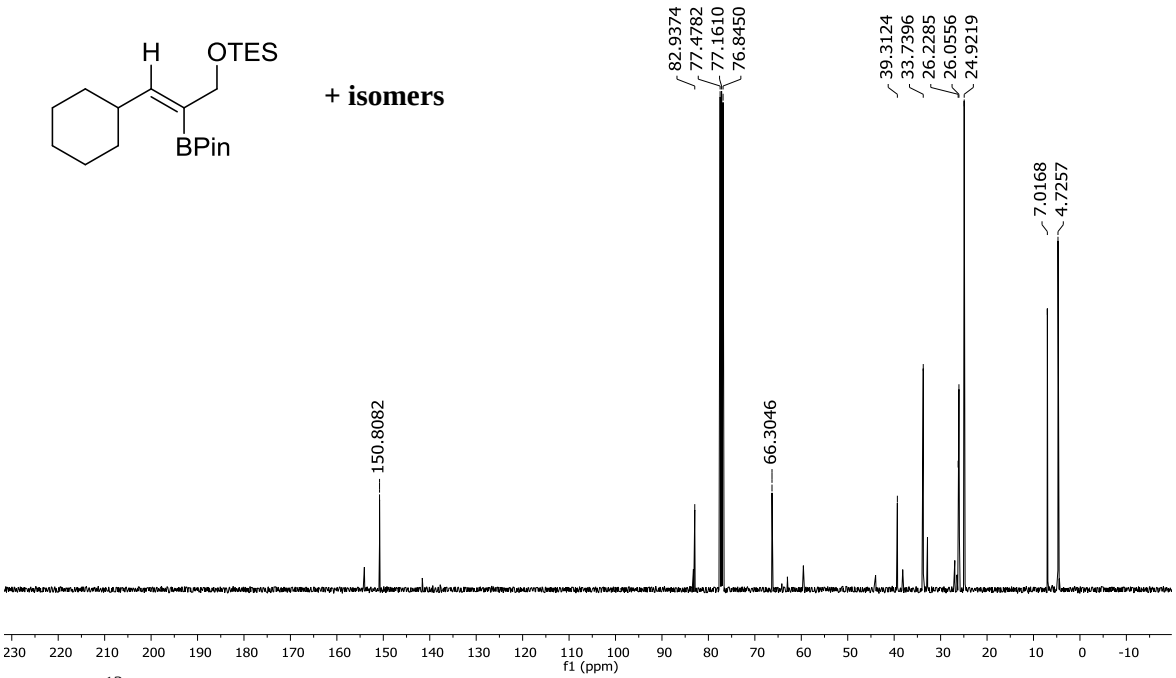

Figure 112: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **28c**.

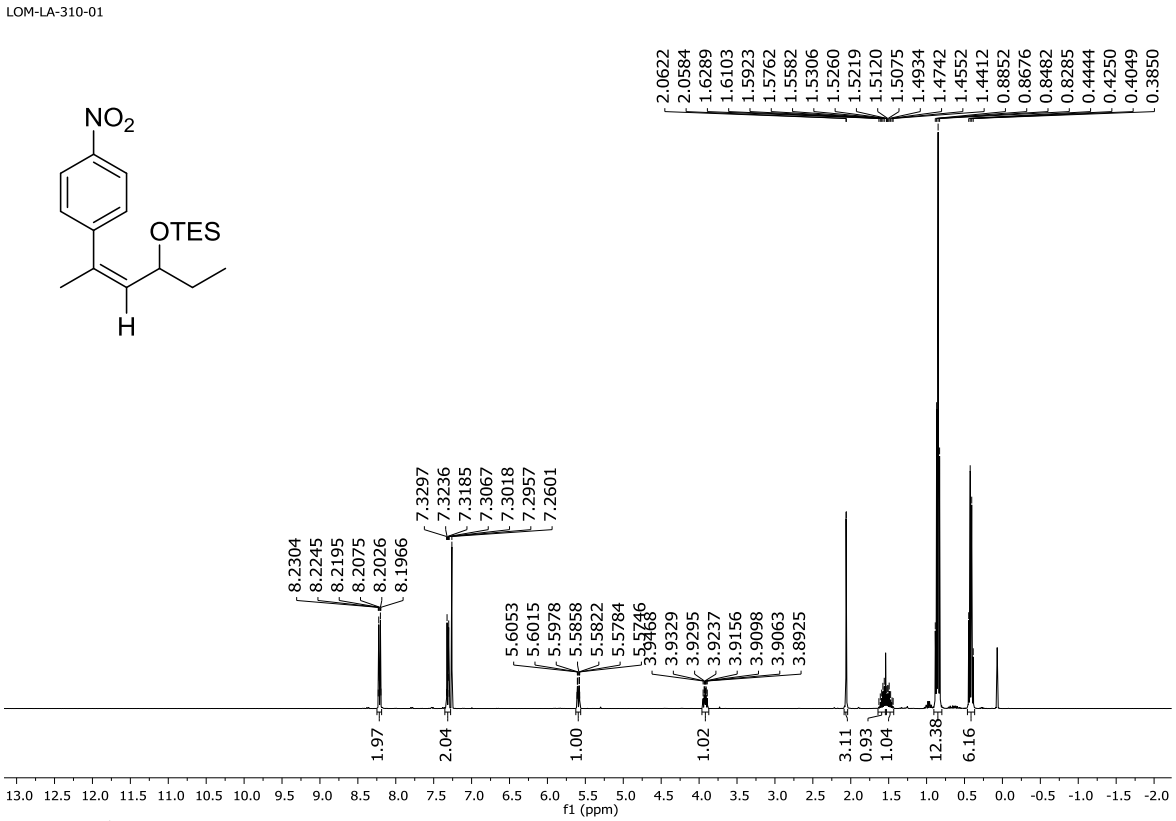

Figure 113: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **29**.

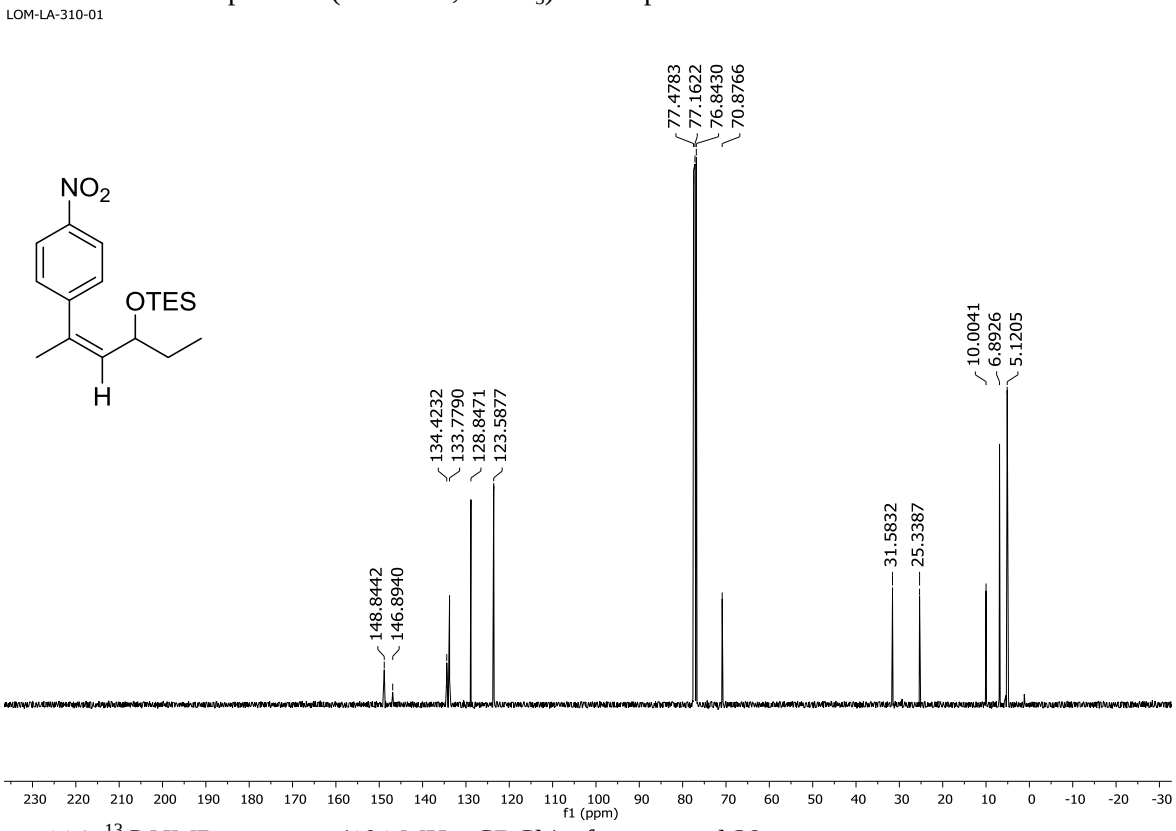

Figure 114: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **29**.

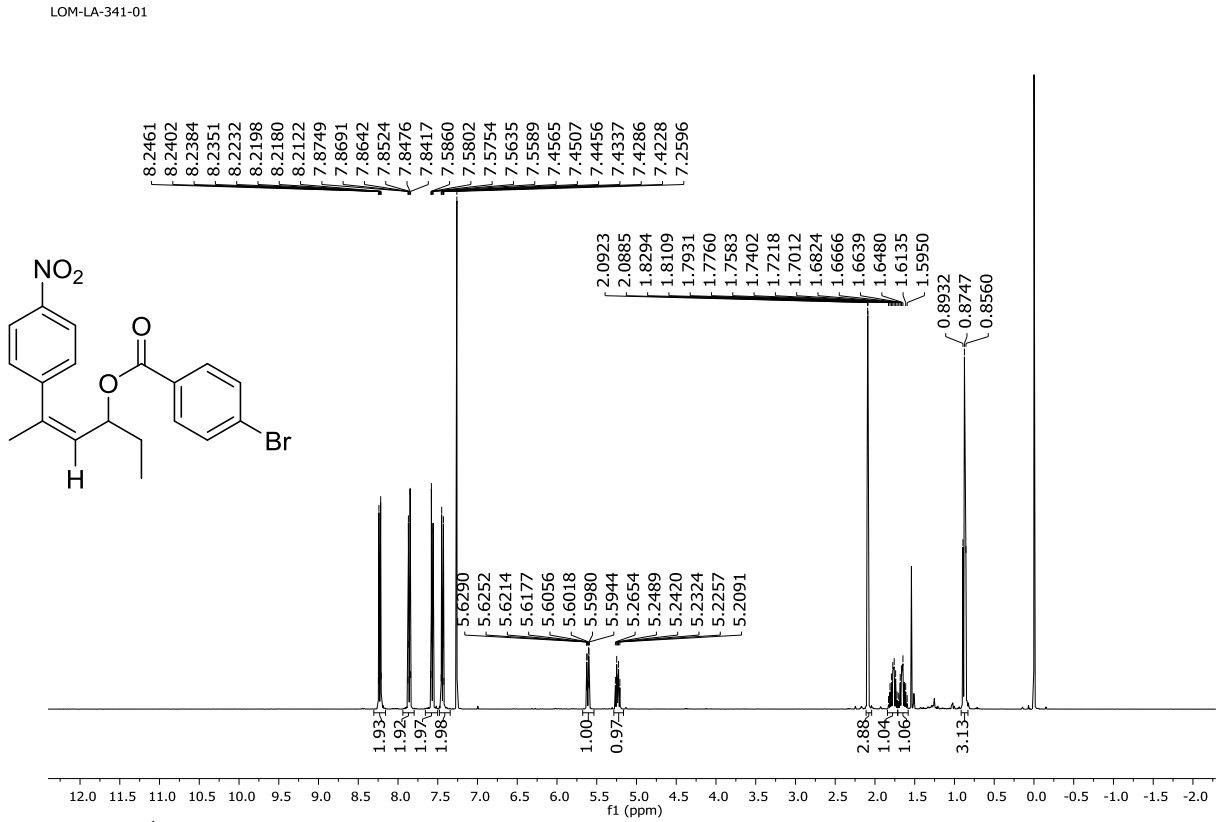

Figure 115: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **30**.

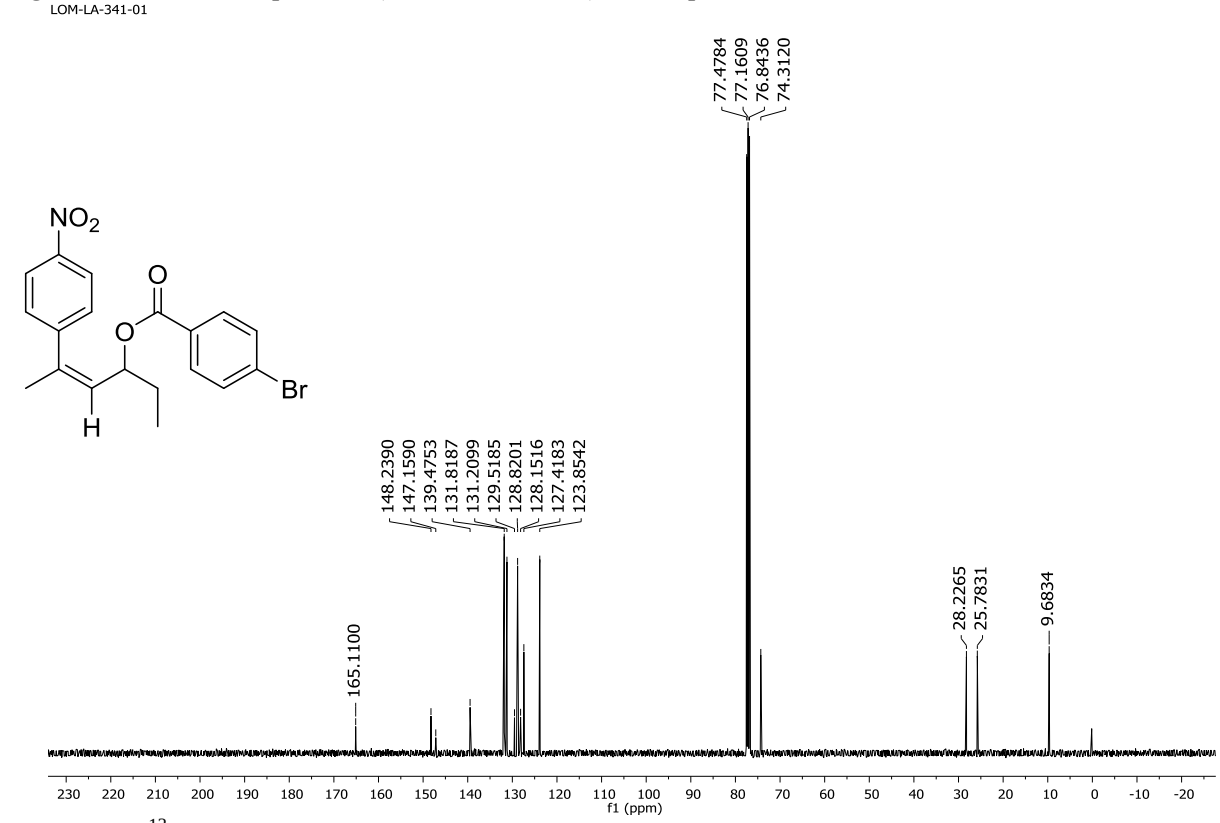

Figure 116: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **30**.

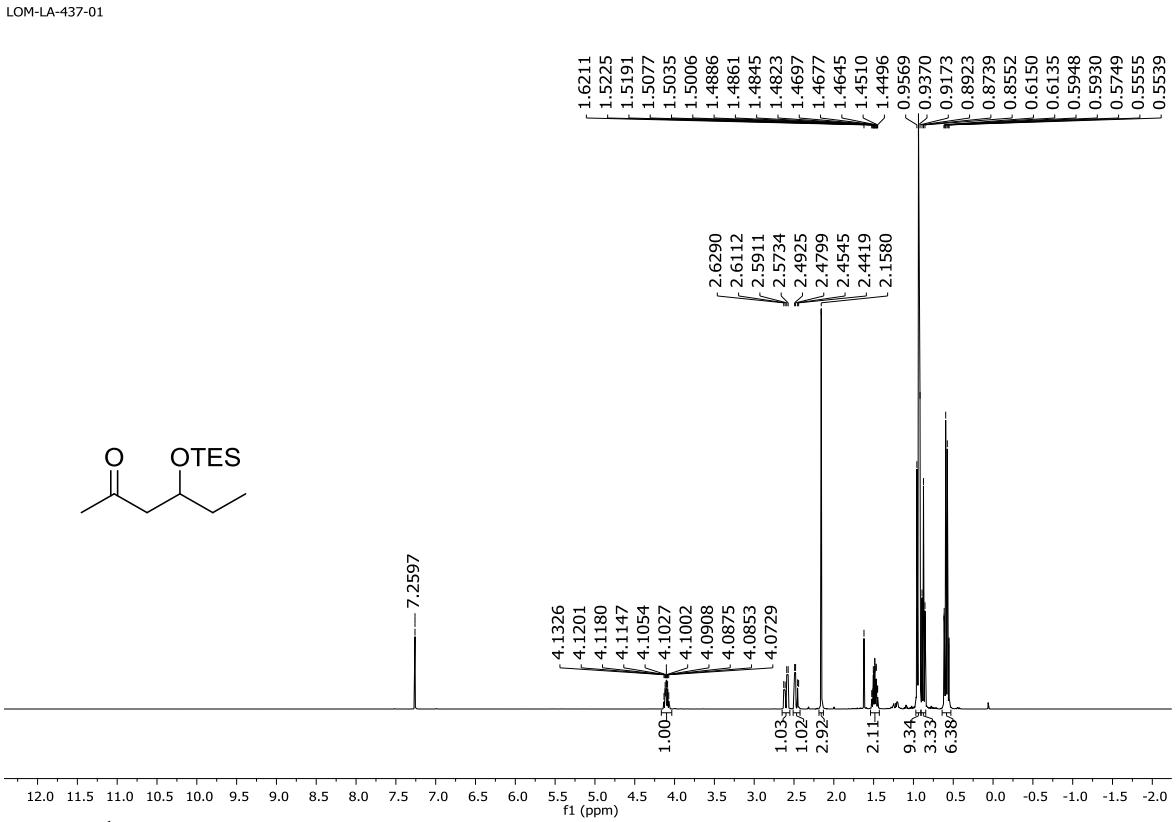

Figure 117: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **31**.

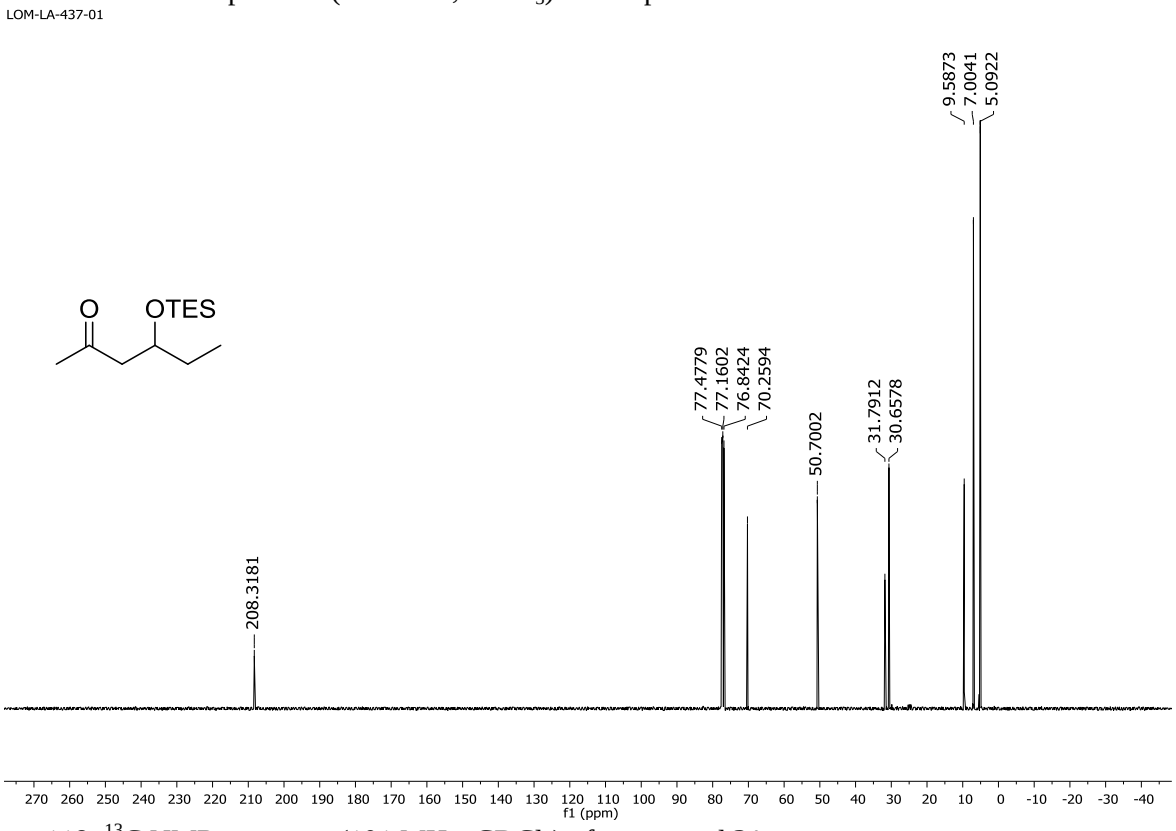

Figure 118: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **31**.

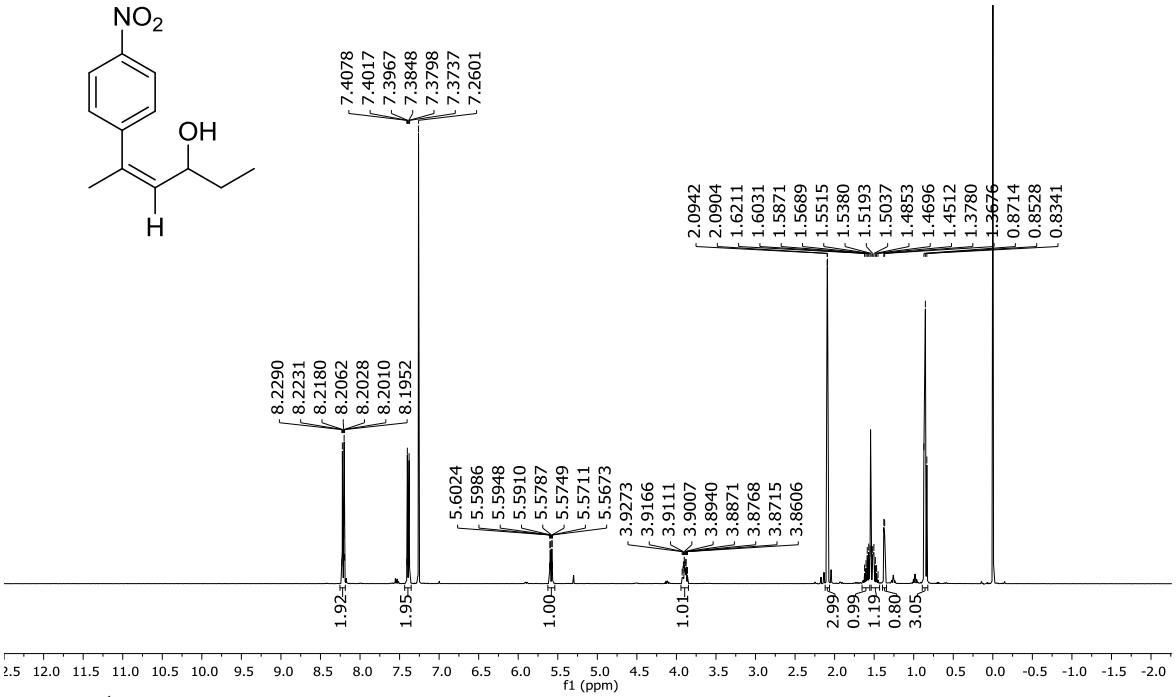

Figure 119: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S18**.

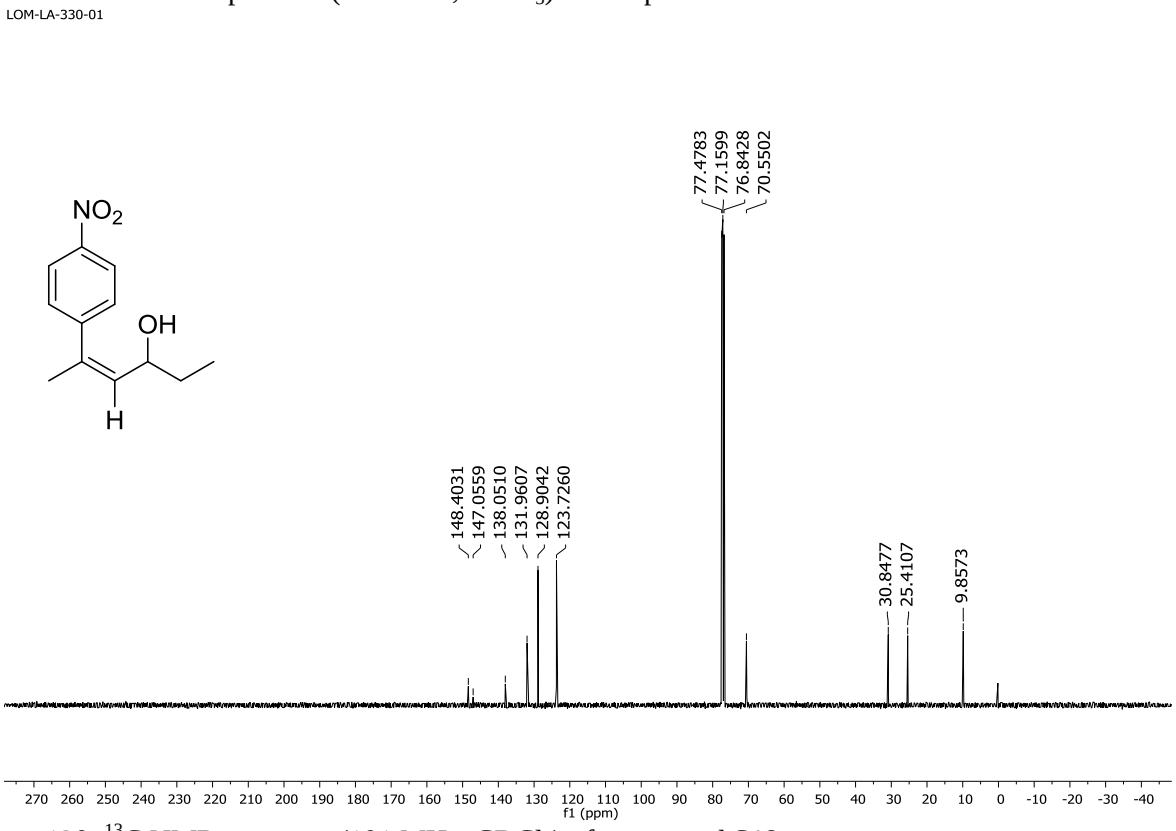

Figure 120: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S18**.

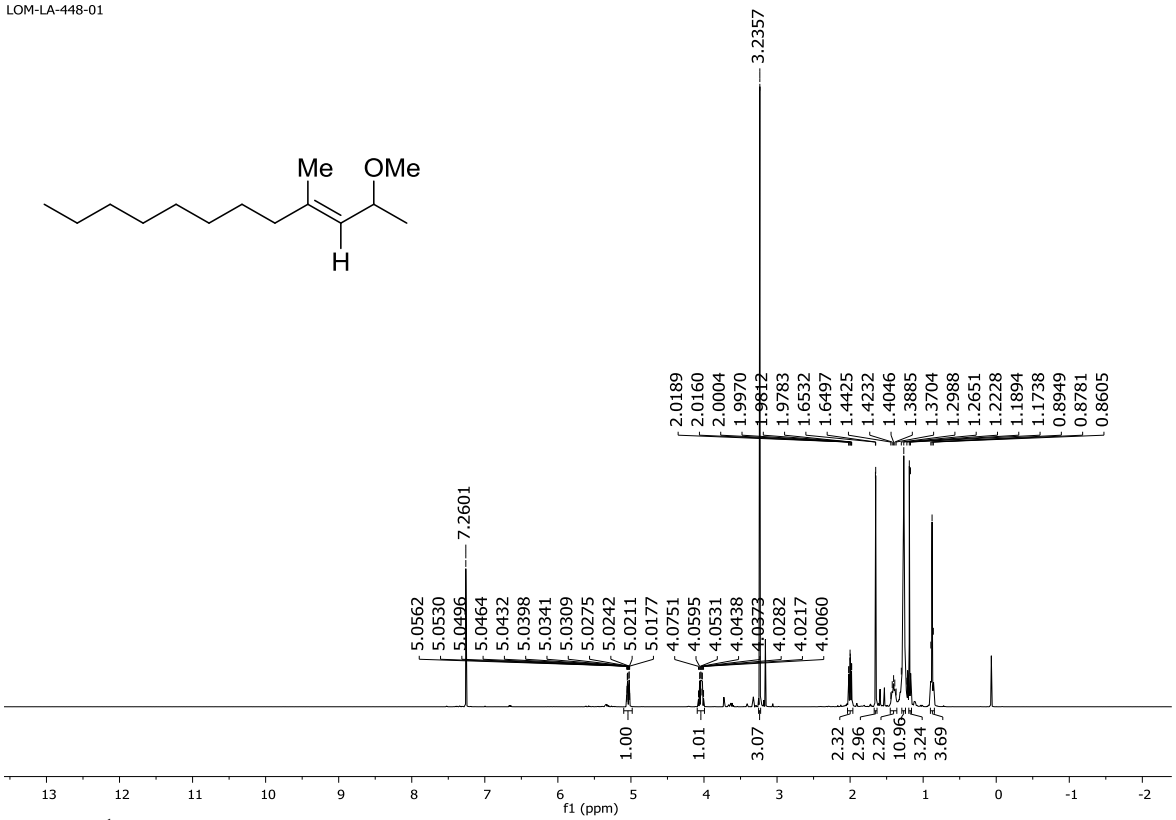

Figure 121: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **32** (contains trace amounts of unknown impurities)

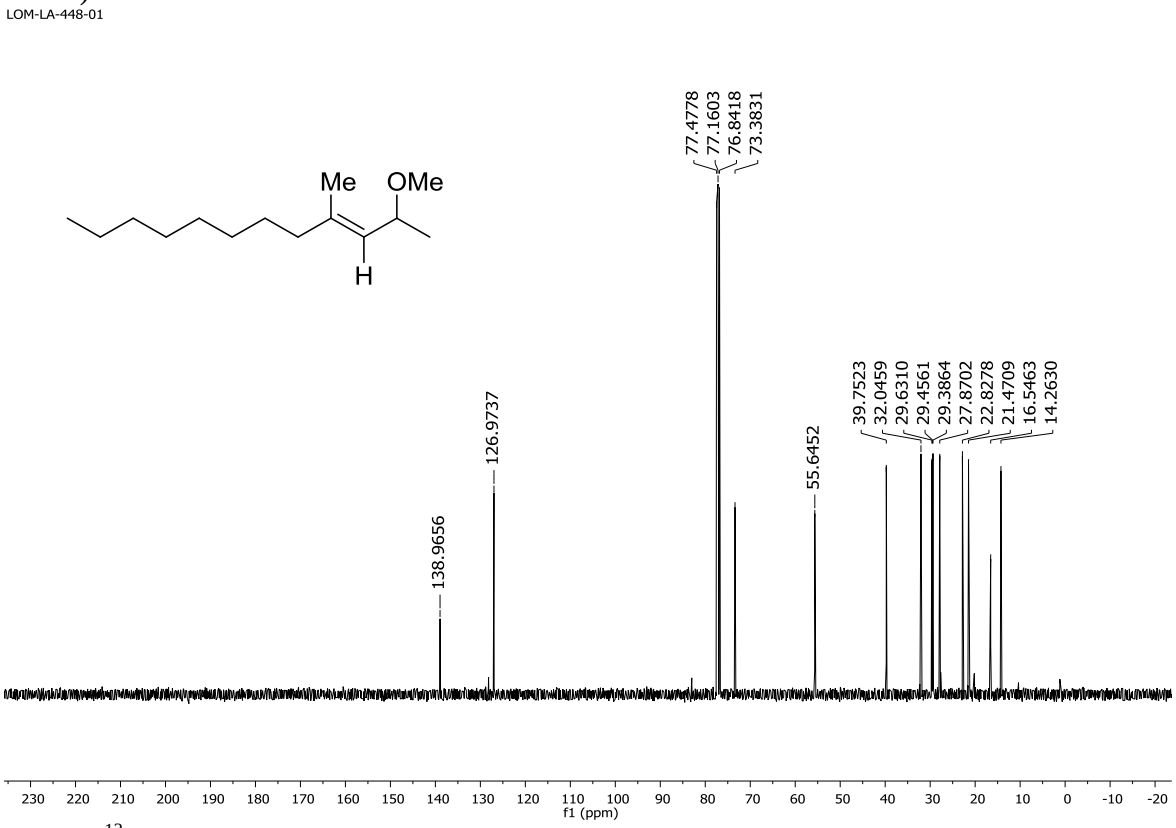

Figure 122: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **32**.

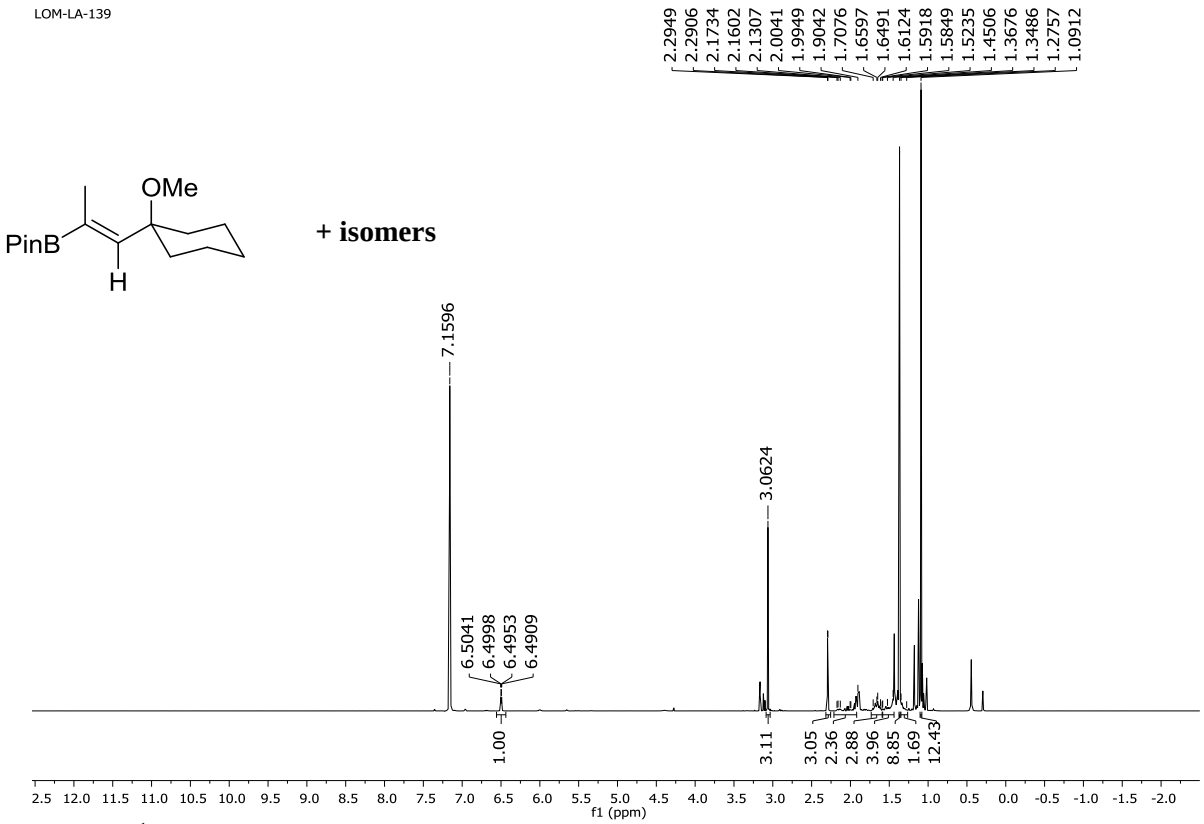

Figure 123: ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **39** (contains trace amounts of unknown impurities).

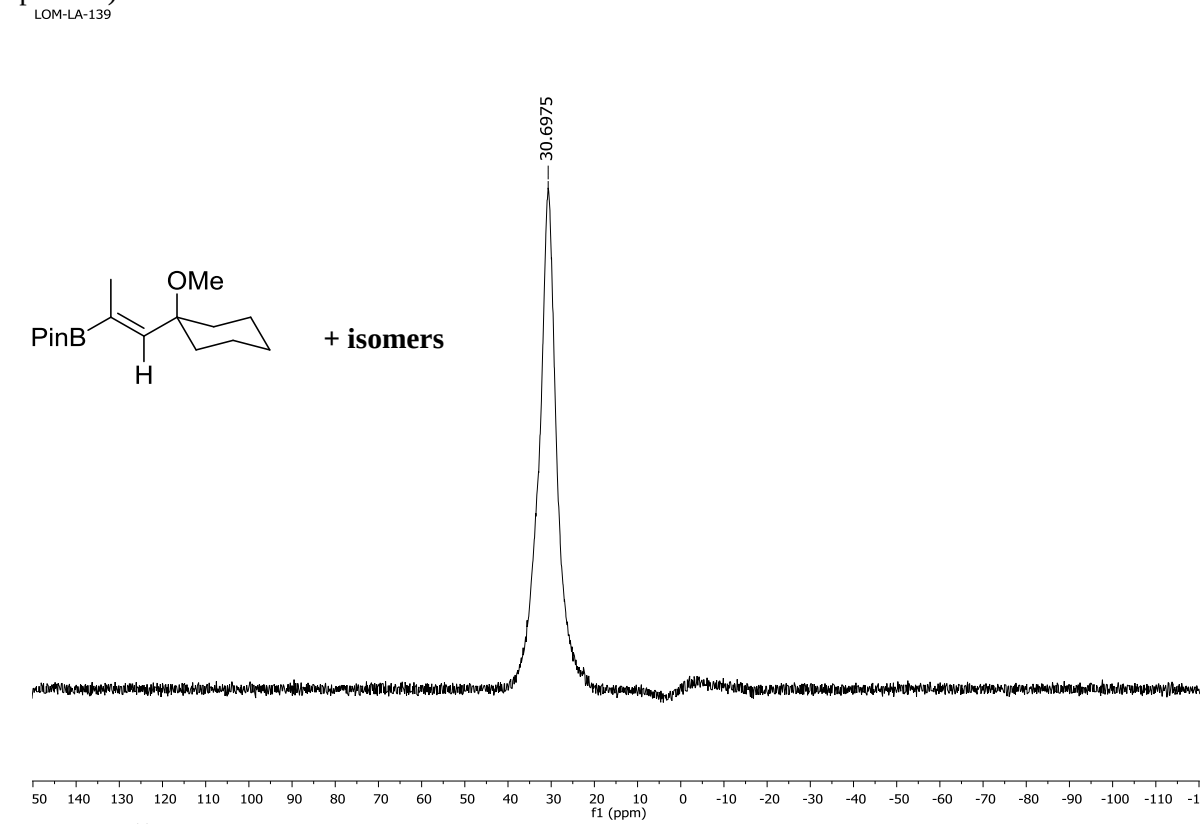

Figure 124: ^{11}B NMR spectrum (96 MHz, $CDCl_3$) of compound **39**.

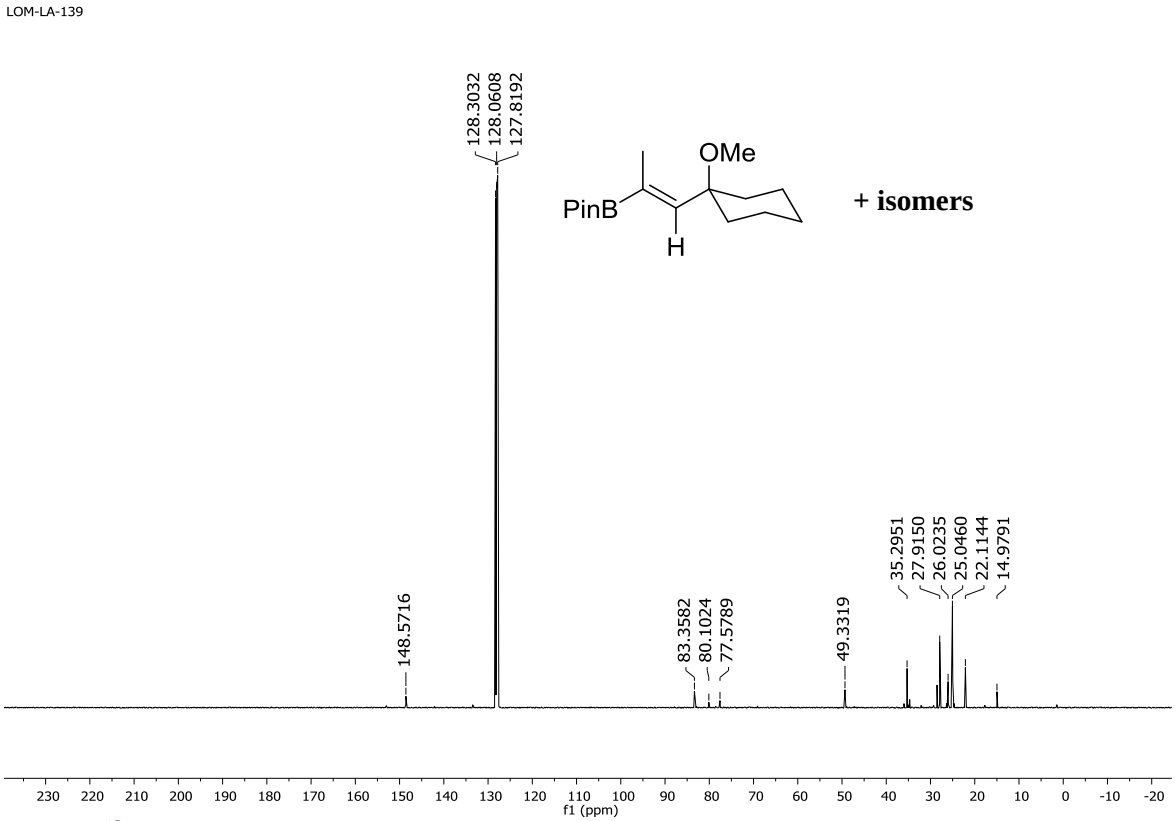

Figure 125: ^{13}C NMR spectrum (101 MHz, C_6D_6) of compound **39** (contains trace amounts of unknown impurities).

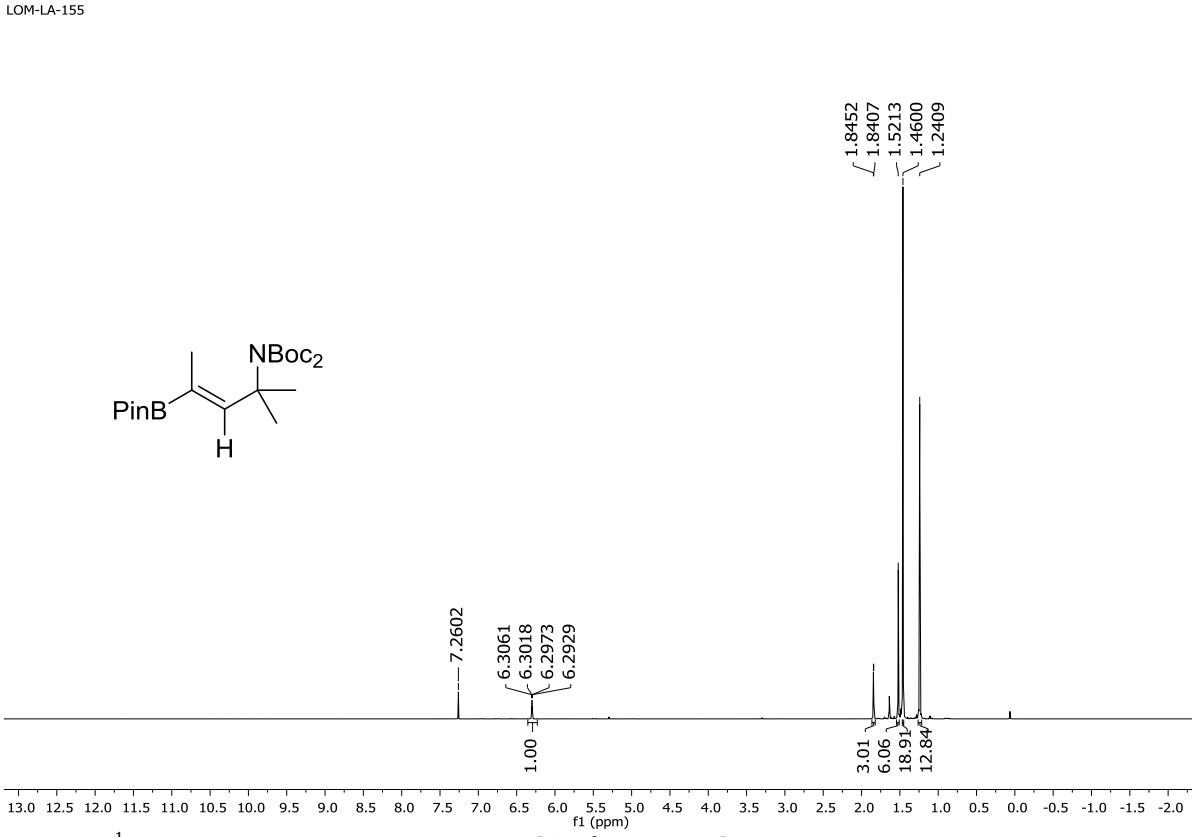

Figure 126: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **41**.

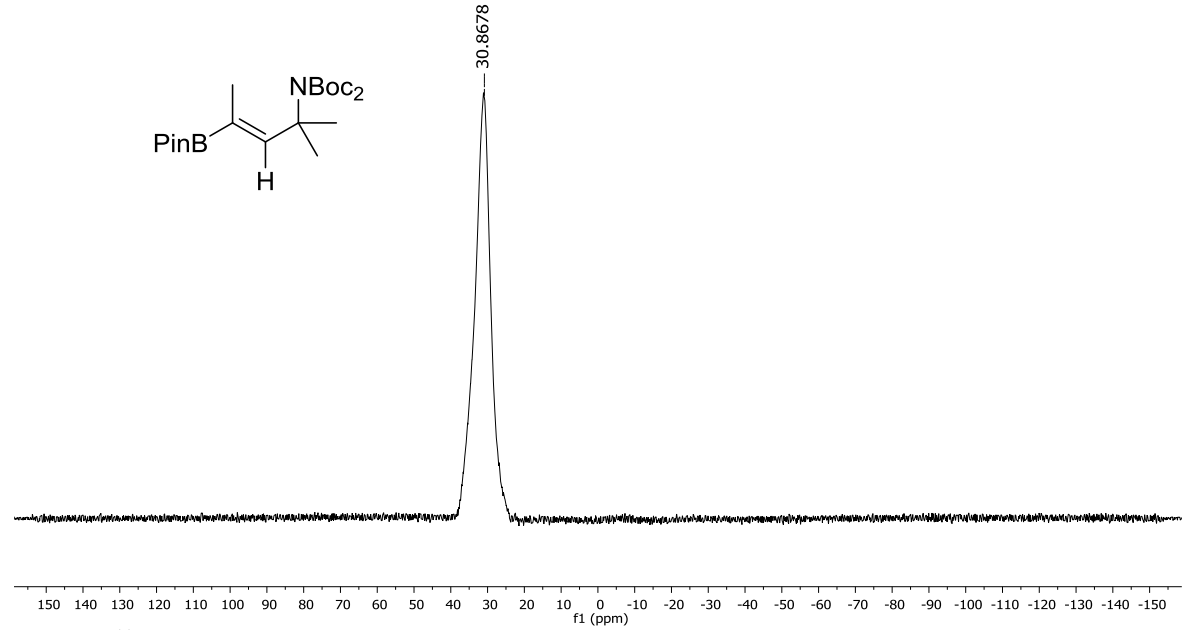

Figure 127: ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **41**.

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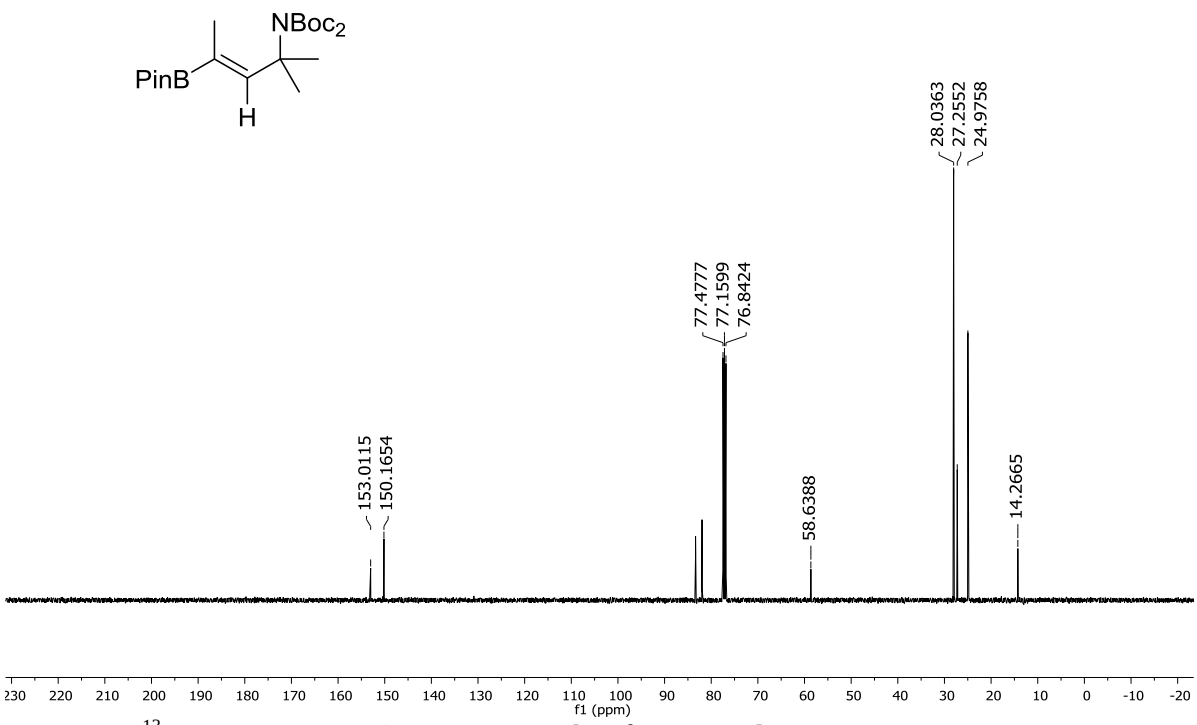

Figure 128: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **41**.