Supporting Information

Palladium Catalyzed Cross-Couplings of *trans*-Vinylboranes with Alkyl Bromides: A Reversed-Polarity Alternative to B-Alkyl Suzuki Reactions

*Petros Danielsen Siapkaras,[a] Kristian Sørnes,[b] Jens Mortansson Jelstrup Nolsøe,[c] Filip Ekholm,[d] Eirik Johansson Solum[e] and Marius Aursnes[a]**

[a] Faculty of Chemistry, Biotechnology and Food Science, Norwegian University of Life Sciences, Ås NO-1433, Norway.

[b] Department of Chemistry, University of Oslo, Norway, Oslo NO-0371, Norway.

[c] Faculty of Biosciences and Aquaculture, Nord University, Bodø NO-8049, Norway.

[d] Department of Chemistry, University of Helsinki, Helsinki FI-00014, Finland.

[e] Faculty of Nursing and Health Sciences, Nord University, Bodø NO-8049, Norway.

Innhold

Experimental procedures

Methyl (*R*)-4-((*tert*-butyldimethylsilyl)oxy)hex-5-ynoate (9b) Known methyl (*R*)-4-((*tert*-butyldimethylsilyl)oxy)-6-(trimethylsilyl)hex-5-ynoate[1] (**9a**) (1.00 g, 3.04 mmol, 1.00 equiv.) was dissolved in methanol (30 mL) and the flask was cooled to 0 °C in an ice-water-bath. K_2CO_3 (421 mg, 3.04 mmol, 1.00 equiv.) was added in one portion and the reaction mixture was allowed to warm to room temperature. When the deprotection process was deemed complete (TLC analysis), the flask was cooled back to 0 °C and quenched by the addition of phosphate buffer (20 mL, pH = 7). NaCl (~2 g) was added and the aqueous phase was extracted with heptane (5 x ~30 mL). The combined organic phase was dried (Na_2SO_4), filtrated and concentrated *in vacuo*. The crude material thus obtained was purified by flash column chromatography (SiO_2, 5% EtOAc in heptane) to give the titled product as an oil (711 mg, 2.77 mmol, 91%). R_f (5% EtOAc in heptane) =0.29; $[\alpha]_D^{25}$= +91 (c = 1.1, CH_2Cl_2)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.46 (td, *J* = 6.1, 2.1 Hz, 1H), 3.68 (s, 3H), 2.53 – 2.45 (m, 2H), 2.39 (d, *J* = 2.1 Hz, 1H), 2.06 – 1.94 (m, 2H), 0.90 (s, 9H), 0.12 (d, *J* = 12.6 Hz, 6H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.8, 84.8, 72.7, 61.7, 51.7, 33.5, 29.6, 25.9, 18.3, -4.5, -5.0;

(*E*)-7-phenylhept-5-enenitrile (3). *Method III was employed for hydroboration*. A flame-dried flask A under nitrogen was charged with 3-phenyl-1-propyne (100 mg, 0.861 mmol, 1.00 equiv.). 9-BBN-H (0.5 M in THF, 3.44 mL, 1.72 mmol, 2.00 equiv.) was then added, and the solution was allowed to stir overnight. Next, benzaldehyde (Sure/Seal™ flask, 87.5 µL, 0.861 mmol, 1.00 equiv.) was added dropwise and the solution was stirred for 6 h. (Theoretically, this corresponds to 1.20 equiv. of vinylborane relative to the alkyl bromide.)

Cross-coupling. An undried flask B was charged with Cs_2CO_3 (841 mg, 2.58 mmol, 3.00 equiv.), and the flask was evacuated and backfilled with dry nitrogen gas. PCy_3-Pd-G4 (22.9 mg, 0.0344 mmol, 4.00 mol%) and $HPCy_3BF_4$ (12.7 mg, 0.0344 mmol, 4.00 mol%) were quickly added, and then the flask was again evacuated and backfilled with dry nitrogen gas (3x). 4-Bromobutyronitrile

(106 mg, 0.717 mmol, 1.00 equiv.) was added to flask A and this resulting solution was then added to the flask B containing the catalyst system and base to initiate the reaction. The suspension was stirred rapidly overnight and then filtered through a plug of silica gel. The plug was washed thoroughly with Et_2O, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 0 → 20% Et_2O in heptane) to give product **3** as an oil (109 mg, 0.588 mmol, 82%). R_f (20% Et_2O in heptane) = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.25 – 7.12 (m, 3H), 5.69 (dtt, *J* = 14.9, 6.7, 1.4 Hz, 1H), 5.44 (dtt, *J* = 15.2, 6.8, 1.5 Hz, 1H), 3.36 (d, *J* = 6.7 Hz, 2H), 2.33 (t, *J* = 7.2 Hz, 2H), 2.23 – 2.16 (m, 2H), 1.75 (p, *J* = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.5, 131.6, 129.0, 128.6, 126.2, 119.8, 39.1, 31.3, 25.2, 16.5; HRESIMS *m/z* 208.1096 $[M + Na]^+$ (calcd for $C_{13}H_{15}NNa$, 208.1097).

(*E*)-(5-(benzyloxy)pent-1-en-1-yl)trimethylsilane (4). *Method III was employed for hydroboration*. A flame-dried flask A under nitrogen was charged with trimethylsilylacetylene (100 mg, 1.02 mmol, 1.00 equiv.). 9-BBN-H (0.5 M in THF, 4.07 mL, 2.04 mmol, 2.00 equiv.) was then added, and the solution was allowed to stir overnight. Next, benzaldehyde (Sure/Seal™ flask, 104 µL, 1.02 mmol, 1.00 equiv.) was added dropwise and the solution was stirred for 6 h. (Theoretically, this corresponds to 1.20 equiv. of vinylborane relative to the alkyl bromide.)

Cross-coupling. An undried flask B was charged with Cs_2CO_3 (995 mg, 3.05 mmol, 3.00 equiv.), and the flask was evacuated and backfilled with dry nitrogen gas. PCy_3-Pd-G4 (27.0 mg, 0.0407 mmol, 4.00 mol%) and $HPCy_3BF_4$ (15.0 mg, 0.0407 mmol, 4.00 mol%) were quickly added, and then the flask was again evacuated and backfilled with dry nitrogen gas (3x). Benzyl 3-bromopropyl ether (194 mg, 0.848 mmol, 1.00 equiv.) was added to flask A and this resulting solution was then added to the flask B containing the catalyst system and base to initiate the reaction. The suspension was stirred rapidly overnight and then filtered through a plug of silica gel. The plug was washed thoroughly with Et_2O, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 0 → 5% Et_2O in heptane) to

give product **4** as an oil (162 mg, 0.652 mmol, 77%). R_f (4% Et_2O in heptane) = 0.30; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 5H), 6.02 (dt, *J* = 18.5, 6.2 Hz, 1H), 5.64 (dt, *J* = 18.5, 1.5 Hz, 1H), 4.50 (s, 2H), 3.48 (t, *J* = 6.5 Hz, 2H), 2.20 (tdd, *J* = 7.8, 6.2, 1.6 Hz, 2H), 1.73 (p, *J* = 6.6 Hz, 2H), 0.04 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.5, 138.8, 130.4, 128.5, 127.8, 127.6, 73.0, 69.9, 33.3, 28.9, -1.0; HRESIMS m/z 271.1487 [M + Na]+ (calcd for $C_{15}H_{24}OSiNa$, 271.1489).

Ethyl (*E*)-6-(pyridin-3-yl)hex-5-enoate (5). *Method I was employed for hydroboration*. A flame-dried flask A under nitrogen was charged with 3-ethynylpyridine (100 mg, 0.970 mmol, 1.00 equiv.) and azeotropically dried with 2-MeTHF (anhydrous over molecular sieves, 2 x ~0.5 mL). The flask was evacuated and backfilled with dry nitrogen gas (3x). Next, the flask was cooled to 0 °C in an ice-water-bath and then 9-BBN-H (0.5 M in THF, 1.94 mL, 0.970 mmol, 1.00 equiv.) was added in a dropwise manner. The reaction mixture was stirred overnight while warming up to room temperature. The reaction mixture was diluted with anhydrous THF (1.94 mL). (Theoretically, this corresponds to 1.20 equiv. of vinylborane relative to the alkyl bromide.)

Cross-coupling. An undried flask B was charged with Cs_2CO_3 (948 mg, 2.91 mmol, 3.00 equiv.) and the flask was evacuated and backfilled with dry nitrogen gas. PCy_3-Pd-G4 (25.8 mg, 0.0388 mmol, 4.00 mol%) and $HPCy_3BF_4$ (14.3 mg, 0.0388 mmol, 4.00 mol%) were quickly added, and then the flask was again evacuated and backfilled with dry nitrogen gas (3x). Ethyl 4-bromobutyrate (158 mg, 0.810 mmol, 1.00 equiv.) was added to the hydroboration solution in flask A and this resulting solution was then added to the flask B containing the catalyst system and base to initiate the reaction. The suspension was stirred rapidly overnight and then filtered through a plug of silica gel. The plug was washed thoroughly with EtOAc, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 0 →80% EtOAc in heptane) to give product **5** as an oil (53 mg, 0.24 mmol, 30%). R_f (50% EtOAc in heptane) = 0.16; ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.2 Hz, 1H), 8.42 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.64 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.24 – 7.18 (m, 1H), 6.41 – 6.34 (m, 1H), 6.25 (dt, *J* = 15.9, 6.8 Hz, 1H),

4.12 (q, *J* = 7.1 Hz, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 2.27 (ddd, *J* = 7.8, 6.8, 1.3 Hz, 2H), 1.83 (p, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.6, 148.2, 148.1, 133.2, 132.6, 132.3, 127.4, 123.5, 60.5, 33.8, 32.6, 24.5, 14.4; HRESIMS *m/z* 220.1328 $[M + H]^+$ (calcd for $C_{13}H_{18}NO_2$, 220.1332).

(*E*)-2-(dec-2-en-1-yl)isoindoline-1,3-dione (6). *Method III was employed for hydroboration*. A flame-dried flask A under nitrogen was charged with *N*-propargylphthalimide (100 mg, 0.540 mmol, 1.00 equiv.) and azeotropically dried with 2-MeTHF (anhydrous over molecular sieves, 2 x ~0.5 mL). The flask was evacuated and backfilled with dry nitrogen gas (3x). 9-BBN-H (0.5 M in THF, 2.16 mL, 1.08 mmol, 2.00 equiv.) was then added, and the solution was allowed to stir overnight. Next, benzaldehyde (Sure/Seal™ flask, 54.9 µL, 0.540 mmol, 1.00 equiv.) was added dropwise and the solution was stirred for 6 h. (Theoretically, this corresponds to 1.20 equiv. of vinylborane relative to the alkyl bromide.)

Cross-coupling. An undried flask B was charged with Cs_2CO_3 (528 mg, 1.62 mmol, 3.00 equiv.), and the flask was evacuated and backfilled with dry nitrogen gas. PCy_3-Pd-G4 (14.3 mg, 0.0216 mmol, 4.00 mol%) and $HPCy_3BF_4$ (7.95 mg, 0.0216 mmol, 4.00 mol%) were quickly added, and then the flask was again evacuated and backfilled with dry nitrogen gas (3x). 1-Bromoheptane (80.6 mg, 0.450 mmol, 1.00 equiv.) was added to flask A and this resulting solution was then added to the flask B containing the catalyst system and base to initiate the reaction. The suspension was stirred rapidly overnight and then filtered through a plug of silica gel. The plug was washed thoroughly with EtOAc, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 0 → 15% EtOAc in heptane) to give product **6**[2] as an oil (100 mg, 0.350 mmol, 78%). R_f (10% EtOAc in heptane) = 0.16; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.64 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.68 (dtt, *J* = 14.8, 6.7, 1.3 Hz, 1H), 5.48 – 5.38 (m, 1H), 4.16 (dq, *J* = 6.2, 1.1 Hz, 2H), 1.99 – 1.88 (m, 2H), 1.30 – 1.13 (m, 11H), 0.81 – 0.76 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.0, 135.4, 133.9, 132.2, 123.2,

123.0, 39.6, 32.1, 31.8, 29.1, 28.9, 22.6, 14.1; HRESIMS *m/z* 308.1620 $[M + Na]^+$ (calcd for $C_{18}H_{23}NO_2Na$, 308.1621).

(*S*,*E*)-(5,9-dimethyldeca-1,8-dien-1-yl)trimethylsilane (7). *Method III was employed for hydroboration*. A flame-dried flask A under nitrogen was charged with trimethylsilylacetylene (1000 mg, 10.2 mmol, 1.00 equiv.). 9-BBN-H (0.5 M in THF, 40.7 mL, 20.4 mmol, 2.00 equiv.) was then added, and the solution was allowed to stir overnight. Next, benzaldehyde (Sure/Seal™ flask, 1.03 mL, 10.2 mmol, 1.00 equiv.) was added dropwise and the solution was stirred for 8 h. (Theoretically, this corresponds to 1.20 equiv. of vinylborane relative to the alkyl bromide.)

Cross-coupling. An undried flask B was charged with Cs_2CO_3 (9.95 g, 30.5 mmol, 3.00 equiv.), and the flask was evacuated and backfilled with dry nitrogen gas. PCy_3-Pd-G4 (270 mg, 0.407 mmol, 4.00 mol%) and $HPCy_3BF_4$ (150 mg, 0.407 mmol, 4.00 mol%) were quickly added, and then the flask was again evacuated and backfilled with dry nitrogen gas (3x). (*S*)-(+)-citronellyl bromide (1859 mg, 8.48 mmol, 1.00 equiv.) was added to flask A and this resulting solution was then added to the flask B containing the catalyst system and base to initiate the reaction. The flask and syringe were washed with a small amount of THF (~5 mL) and this was added to the flask with the catalyst system. The suspension was stirred rapidly overnight and then filtered through a plug of silica gel. The plug was washed thoroughly with Et_2O, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 0 → 1% Et_2O in heptane) to give product **4** as an oil (1640 mg, 6.88 mmol, 81%). R_f (1% Et_2O in heptane) = 0.65; $[\alpha]_D^{25}$ = +57.0 (c = 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (dt, *J* = 18.5, 6.2 Hz, 1H), 5.62 (dt, *J* = 18.6, 1.6 Hz, 1H), 5.10 (m, 1H), 2.20 – 2.02 (m, 2H), 2.02 – 1.88 (m, 2H), 1.68 (q, *J* = 1.3 Hz, 3H), 1.63 – 1.57 (m, 3H), 1.47 – 1.25 (m, 4H), 1.18 – 1.09 (m, 1H), 0.87 (d, *J* = 6.4 Hz, 3H), 0.04 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.8, 131.2, 129.5, 125.1, 37.2, 36.0, 34.4, 32.2, 25.9, 25.7, 19.7, 17.8, -1.0; HRESIMS *m/z* 255.2136 $[M + H]^+$ (calcd for $C_{15}H_{31}O_2Si$, 255.2139).

(*R,E*)-((13-(1,3-dioxolan-2-yl)tridec-10-en-2-yl)oxy)(*tert*-butyl)dimethylsilane (8). *Method III was employed for hydroboration*. A flame-dried flask A under nitrogen was charged with (*R*)-*tert*-butyldimethyl(undec-10-yn-2-yloxy)silane[3] (150 mg, 0.531 mmol, 1.00 equiv.) and azeotropically dried with 2-MeTHF (anhydrous over molecular sieves, 2 x ~0.5 mL). The flask was evacuated and backfilled with dry nitrogen gas (3x). 9-BBN-H (0.5 M in THF, 2.12 mL, 1.06 mmol, 2.00 equiv.) was then added, and the solution was allowed to stir overnight. Next, benzaldehyde (Sure/Seal™ flask, 54.0 µL, 0.531 mmol, 1.00 equiv.) was added dropwise and the solution was stirred for 6 h. (Theoretically, this corresponds to 1.20 equiv. of vinylborane relative to the alkyl bromide.)

Cross-coupling. An undried flask B was charged with Cs_2CO_3 (519 mg, 1.59 mmol, 3.00 equiv.), and the flask was evacuated and backfilled with dry nitrogen gas. PCy_3-Pd-G4 (14.1 mg, 0.0212 mmol, 4.00 mol%) and $HPCy_3BF_4$ (7.82 mg, 0.0212 mmol, 4.00 mol%) were quickly added, and then the flask was again evacuated and backfilled with dry nitrogen gas (3x). 2-(2-Bromoethyl)-1,3-dioxolane (80.1 mg, 0.442 mmol, 1.00 equiv.) was added to flask A and this resulting solution was then added to the flask B containing the catalyst system and base to initiate the reaction. The suspension was stirred rapidly overnight and then filtered through a plug of silica gel. The plug was washed thoroughly with Et_2O, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 0 → 15% Et_2O in heptane) to give product **8** as an oil (146 mg, 0.380 mmol, 86%). R_f (10% EtOAc in heptane) = 0.37; $[\alpha]_D^{25}$= -29.3 (c = 1.00, CH_2Cl_2)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 – 5.33 (m, 2H), 4.86 (t, *J* = 4.8 Hz, 1H), 4.06 – 3.81 (m, 4H), 3.80 – 3.72 (m, 1H), 2.17 – 2.06 (m, 2H), 2.01 – 1.91 (m, 2H), 1.76 – 1.67 (m, 2H), 1.47 – 1.21 (m, 12H), 1.11 (d, *J* = 6.1 Hz, 3H), 0.88 (s, 9H), 0.04 (d, *J* = 0.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 131.2, 129.1, 104.3, 68.8, 65.0, 39.9, 34.0, 32.7, 29.8, 29.7, 29.7, 29.3, 27.3, 26.1, 26.0, 24.0, 18.3, -4.3, -4.5; HRESIMS *m/z* 407.2951 $[M + Na]^+$ (calcd for $C_{22}H_{44}O_3SiNa$, 407.2952).

Methyl (4*R*,9*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-9,13-dimethyltetradeca-5,12-dienoate (10). *Method I was employed for hydroboration*. A flame-dried flask A under nitrogen was charged

with *methyl (R)-4-((tert-butyldimethylsilyl)oxy)hex-5-ynoate* (100 mg, 0.390 mmol, 1.00 equiv.) and azeotropically dried with 2-MeTHF (anhydrous over molecular sieves, 2 x ~0.5 mL). The flask was evacuated and backfilled with dry nitrogen gas (3x). Next, the flask was cooled to 0 °C in an ice-water-bath and then 9-BBN-H (0.5 M in THF, 0.780 mL, 0.390 mmol, 1.00 equiv.) was added in a dropwise manner. The reaction mixture was stirred overnight while warming up to room temperature. The reaction mixture was diluted with anhydrous THF (0.78 mL). (Theoretically, this corresponds to 1.20 equiv. of vinylborane relative to the alkyl bromide.)

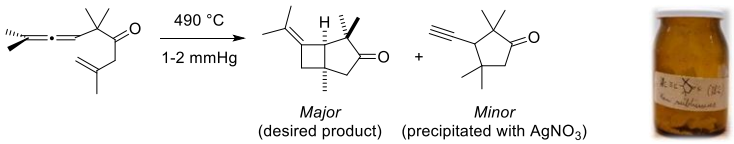
Cross-coupling. An undried flask B was charged with Cs_2CO_3 (381 mg, 1.17 mmol, 3.00 equiv.) and the flask was evacuated and backfilled with dry nitrogen gas. PCy_3-Pd-G4 (10.4 mg, 0.0156 mmol, 4.00 mol%) and $HPCy_3BF_4$ (5.74 mg, 0.0156 mmol, 4.00 mol%) were quickly added, and then the flask was again evacuated and backfilled with dry nitrogen gas (3x). (*S*)-(+)-citronellyl bromide (71.2 mg, 0.325 mmol, 1.00 equiv.) was added to the hydroboration solution in flask A and this resulting solution was then added to the flask B containing the catalyst system and base to initiate the reaction. The suspension was stirred rapidly overnight and then filtered through a plug of silica gel. The plug was washed thoroughly with Et_2O, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 0 →10% Et_2O in heptane) to give product **10** as an oil (103 mg, 0.26 mmol, 80%). R_f (5% EtOAc in heptane) = 0.29; $[\alpha]_D^{25}$= +8.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (dtd, *J* = 15.5, 6.7, 1.0 Hz, 1H), 5.35 (ddt, *J* = 15.4, 6.8, 1.4 Hz, 1H), 5.14 – 5.05 (m, 1H), 4.09 (q, *J* = 6.3 Hz, 1H), 3.66 (s, 3H), 2.35 (dd, *J* = 8.2, 7.1 Hz, 2H), 2.09 – 1.86 (m, 4H), 1.82 – 1.73 (m, 2H), 1.68 (q, *J* = 1.4 Hz, 3H), 1.60 (d, *J* = 1.3 Hz, 3H), 1.42 – 1.10 (m, 5H), 0.87 (d, *J* = 2.0 Hz, 9H), 0.86 (d, *J* = 5.5 Hz, 3H), 0.02 (d, *J* = 6.9 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.3, 132.5, 131.4, 131.1, 124.9, 72.6, 51.5, 37.0, 36.5, 33.2, 31.9, 29.8, 29.6, 25.9, 25.7, 25.5, 19.4, 18.2, 17.6, -4.2, -4.9; HRESIMS *m/z* 419.2950 $[M + Na]^+$ (calcd for $C_{23}H_{44}NO_3SiNa$, 419.2952).

***Cis*-3-ethynyl-2,2,4,4-tetramethylcyclopentan-1-ol (11b)** To a stirred solution of 3-ethynyl-2,2,4,4-tetramethylcyclopentan-1-one* (1.00 g, 6.09 mmol, 1.00 equiv) in MeOH (30 mL), $NaBH_4$ (461 mg, 12.2 mmol, 2.00 equiv) was added portionwise at 0 °C. The reaction mixture was stirred at this temperature for 45 min and then quenched with sat. aq. NH_4Cl (10 mL). EtOAc (30 mL) was added, and the biphasic mixture was separated. The aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic phases were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo* to give the **11b** (898 mg, 5.40 mmol, 89%, d.r. 20:1 based on ^{1}H NMR) as a colorless oil, which was used in the next step without further purification. R_f (20% EtOAc in heptane) = 0.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (dd, *J* = 10.6, 7.4 Hz, 1H), 2.27 – 2.16 (m, 2H), 1.90 (dd, *J* = 12.8, 7.4 Hz, 1H), 1.56 (dd, *J* = 12.9, 10.6 Hz, 1H), 1.43 (s, 1H), 1.14 (s, 3H), 1.06 (s, 6H), 0.95 (s, 3H). ^{13}C NMR (101 MHz, CDCl*3*) δ 82.3, 79.1, 73.4, 51.8, 47.1, 46.2, 35.9, 33.2, 28.8, 27.1, 16.5. HRESIMS *m/z* 189.1251 $[M + Na]^+$ (calcd for $C_{11}H_{18}NaO$, 189.1250).

***Tert*-butyl(((*cis*)-3-ethynyl-2,2,4,4-tetramethylcyclopentyl)oxy)dimethylsilane (11c)** To a stirred solution of *cis*-3-ethynyl-2,2,4,4-tetramethylcyclopentan-1-ol (**11b**) (890 mg, 5.35 mmol, 1.00 equiv) in CH_2Cl_2 (18 mL) at 0 °C were added 2,6-lutidine (1.25 mL, 10.7 mmol, 2.00 equiv) and TBSOTf (1.47 mL, 6.40, 1.20 equiv). The reaction mixture was stirred at this temperature for 1h. The reaction was then quenched with sat. aq. NH_4Cl (15 mL) and the biphasic mixture was

* This alkyne was obtained as a byproduct in a thermal intramolecular [2+2] cycloaddition of a precursor allene in the synthesis of (±)-lineatin.[1] In December 1981, during purification of the desired bicyclic compound, the alkyne was precipitated with $AgNO_3$, regenerated with NaCN and purified by sublimation. Thereafter, it was guarded from being thrown away for over 40 years.

(1) Skattebøl, L.; Stenstrøm, Y. *Tetrahedron Lett*., **1983**, 3021-3024. Skattebøl, L.; Stenstrøm, Y. *Acta Chem. Scand*., **1985**, 291-304.



separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. The crude product was purified with flash column chromatography (SiO_2, 0 → 2% EtOAc in heptane) to give compound **11c** as a colorless oil (1.35 g, 4.81 mmol, 90%). R_f (2% EtOAc in heptane) = 0.67. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (dd, *J* = 10.2, 7.3 Hz, 1H), 2.18 (s, 2H), 1.72 (dd, *J* = 12.7, 7.3 Hz, 1H), 1.61 – 1.51 (m, 1H), 1.13 (s, 3H), 1.04 (s, 3H), 0.99 (s, 3H), 0.91 (s, 3H), 0.90 – 0.84 (m, 9H), 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl^3$) δ 82.8, 78.9, 73.0, 51.3, 47.6, 46.7, 36.0, 33.4, 28.8, 27.5, 25.9, 25.9, 18.2, 17.0, -4.3, -4.8. HRESIMS *m/z* 303.2106 $[M + Na]^+$ (calcd for $C_{17}H_{32}NaOSi$, 303.2115).

Benzyl (*E*)-(8-(*cis*-3-((tert-butyldimethylsilyl)oxy)-2,2,5,5-tetramethylcyclopentyl)oct-7-en-1-yl)carbamate (11) Method I was employed for hydroboration. A flame-dried flask A under nitrogen was charged with *tert*-butyl(((*cis*)-3-ethynyl-2,2,4,4-tetramethylcyclopentyl)oxy)dimethylsilane (100 mg, 0.356 mmol, 1.00 equiv.) and azeotropically dried with 2-MeTHF (anhydrous over molecular sieves, 2 x ~0.5 mL). The flask was evacuated and backfilled with dry nitrogen gas (3x). 9-BBN-H (0.5 M in THF, 713 µL, 0.356 mmol, 1.00 equiv.) was then added, and the solution was allowed to stir overnight. The reaction mixture was diluted with anhydrous THF (0.71 mL). (Theoretically, this corresponds to 1.20 equiv. of vinylborane relative to the alkyl bromide.)

Cross-coupling. An undried flask B was charged with Cs_2CO_3 (348 mg, 1.07 mmol, 3.00 equiv.), and the flask was evacuated and backfilled with dry nitrogen gas. PCy_3-Pd-G4 (9.47 mg, 0.0143 mmol, 4.00 mol%), $HPCy_3BF_4$ (5.25 mg, 0.0143 mmol, 4.00 mol%) and benzyl (6-bromohexyl)carbamate (93.3 mg, 0.297 mmol, 1.00 equiv.) were quickly added, and then the flask was again evacuated and backfilled with dry nitrogen gas (3x). The resulting solution from flask A was then added to the flask B containing the catalyst system and base to initiate the reaction. The suspension was stirred rapidly overnight and then filtered through a plug of silica

gel. The plug was washed thoroughly with Et_2O, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 0 → 20% EtOAc in heptane) to give product **11** (116 mg, 0.225 mmol, 76%). R_f (20% EtOAc in heptane) = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.26 (m, 5H), 5.39 – 5.24 (m, 2H), 5.10 (s, 2H), 4.71 (s, 1H), 3.62 (dd, *J* = 10.2, 7.3 Hz, 1H), 3.19 (q, *J* = 6.7 Hz, 2H), 2.03 (q, *J* = 6.1 Hz, 2H), 1.68 (dd, *J* = 12.7, 7.3 Hz, 1H), 1.58 (dd, *J* = 18.8, 8.7 Hz, 2H), 1.52 – 1.42 (m, 2H), 1.42 – 1.23 (m, 6H), 0.93 (s, 3H), 0.90 (s, 3H), 0.89 (s, 9H), 0.79 (s, 3H), 0.76 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 136.8, 133.1, 128.7, 128.3, 128.2, 127.6, 79.5, 66.7, 61.6, 47.9, 46.4, 41.3, 36.8, 33.2, 32.7, 30.1, 29.7, 28.8, 27.9, 27.3, 26.7, 26.0, 18.3, 16.1, -4.3, -4.8. HRESIMS *m/z* 538.3673 $[M + Na]^+$ (calcd for $C_{31}H_{53}NNaO_3Si$, 538.3687).

Methyl (*E*)-4-(8-(((benzyloxy)carbonyl)amino)oct-1-en-1-yl)benzoate (12) Method III was employed for hydroboration. A flame-dried flask A under nitrogen was charged with methyl 4-ethynylbenzoate (100 mg, 0.624 mmol, 1.00 equiv.) and azeotropically dried with 2-MeTHF (anhydrous over molecular sieves, 2 x ~0.5 mL). The flask was evacuated and backfilled with dry nitrogen gas (3x). 9-BBN-H (0.5 M in THF, 2.50 mL, 1.25 mmol, 2.00 equiv.) was then added, and the solution was allowed to stir overnight. Next, benzaldehyde (Sure/Seal™ flask, 63.5 µL, 0.624 mmol, 1.00 equiv.) was added dropwise and the solution was stirred for 6 h. (Theoretically, this corresponds to 1.20 equiv. of vinylborane relative to the alkyl bromide.)

Cross-coupling. An undried flask B was charged with Cs_2CO_3 (610 mg, 1.87 mmol, 3.00 equiv.), and the flask was evacuated and backfilled with dry nitrogen gas. PCy_3-Pd-G4 (16.6 mg, 0.0250 mmol, 4.00 mol%), $HPCy_3BF_4$ (9.20 mg, 0.0250 mmol, 4.00 mol%) and benzyl (6-bromohexyl)carbamate (163 mg, 0.520 mmol, 1.00 equiv.) were quickly added, and then the flask was again evacuated and backfilled with dry nitrogen gas (3x). The resulting solution from flask A was then added to the flask B containing the catalyst system and base to initiate the reaction. The suspension was stirred rapidly overnight and then filtered through a plug of silica gel. The plug

was washed thoroughly with Et_2O, and the filtrate was concentrated *in vacuo*. The crude product was triturated with heptane (~3 mL) and then purified by flash column chromatography (SiO_2, 0 → 30% EtOAc in heptane) to give product **12** (173 mg, 0.437 mmol, 84%). R_f(30% EtOAc in heptane) = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.28 (m, 7H), 6.45 – 6.29 (m, 2H), 5.09 (s, 2H), 4.72 (s, 1H), 3.90 (s, 3H), 3.20 (q, *J* = 6.7 Hz, 2H), 2.28 – 2.14 (m, 2H), 1.56 – 1.43 (m, 4H), 1.41 – 1.28 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 156.5, 142.5, 136.8, 134.1, 130.0, 129.3, 128.7, 128.4, 128.2, 125.9, 66.7, 52.1, 41.2, 33.2, 30.1, 29.2, 29.0, 26.7. HRESIMS *m/z* 418.1975 $[M + Na]^+$ (calcd for $C_{24}H_{29}NNaO_4$, 418.1989).

Benzyl (*E*)-(8-(4-methoxyphenyl)oct-7-en-1-yl)carbamate (13) Method III was employed for hydroboration. A flame-dried flask A under nitrogen was charged with 4-ethynylanisole (100 mg, 0.757 mmol, 1.00 equiv.) and azeotropically dried with 2-MeTHF (anhydrous over molecular sieves, 2 x ~0.5 mL). The flask was evacuated and backfilled with dry nitrogen gas (3x). 9-BBN-H (0.5 M in THF, 3.03 mL, 1.51 mmol, 2.00 equiv.) was then added, and the solution was allowed to stir overnight. Next, benzaldehyde (Sure/Seal™ flask, 77.0 µL, 0.757 mmol, 1.00 equiv.) was added dropwise and the solution was stirred for 6 h. (Theoretically, this corresponds to 1.20 equiv. of vinylborane relative to the alkyl bromide.)

Cross-coupling. An undried flask B was charged with Cs_2CO_3 (740 mg, 2.27 mmol, 3.00 equiv.), and the flask was evacuated and backfilled with dry nitrogen gas. PCy_3-Pd-G4 (20.1 mg, 0.0303 mmol, 4.00 mol%), $HPCy_3BF_4$ (11.1 mg, 0.0303 mmol, 4.00 mol%) and benzyl (6-bromohexyl)carbamate (198 mg, 0.631 mmol, 1.00 equiv.) were quickly added, and then the flask was again evacuated and backfilled with dry nitrogen gas (3x). The resulting solution from flask A was then added to the flask B containing the catalyst system and base to initiate the reaction. The suspension was stirred rapidly overnight and then filtered through a plug of silica gel. The plug was washed thoroughly with Et_2O, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 0 → 30% EtOAc in heptane) to give product

13 (183 mg, 0.498 mmol, 79%). R_f(30% EtOAc in heptane) = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 7H), 6.87 – 6.79 (m, 2H), 6.36 – 6.26 (m, 1H), 6.06 (dt, J = 15.8, 6.9 Hz, 1H), 5.10 (s, 2H), 4.71 (s, 1H), 3.80 (s, 3H), 3.19 (q, J = 6.7 Hz, 2H), 2.22 – 2.11 (m, 2H), 1.48 (dt, J = 22.4, 7.0 Hz, 4H), 1.40 – 1.27 (m, 4H); ^{13}C NMR (101 MHz, CDCl3) δ 158.8, 156.5, 136.8, 130.9, 129.3, 128.9, 128.7, 128.3, 128.2, 127.1, 114.1, 66.7, 55.4, 41.2, 33.0, 30.1, 29.5, 29.0, 26.8. HRESIMS *m/z* 390.2043 $[M + Na]^+$ (calcd for $C_{23}H_{29}NNaO_3$, 390.2040).

^{1}H and ^{13}C NMR-spectra

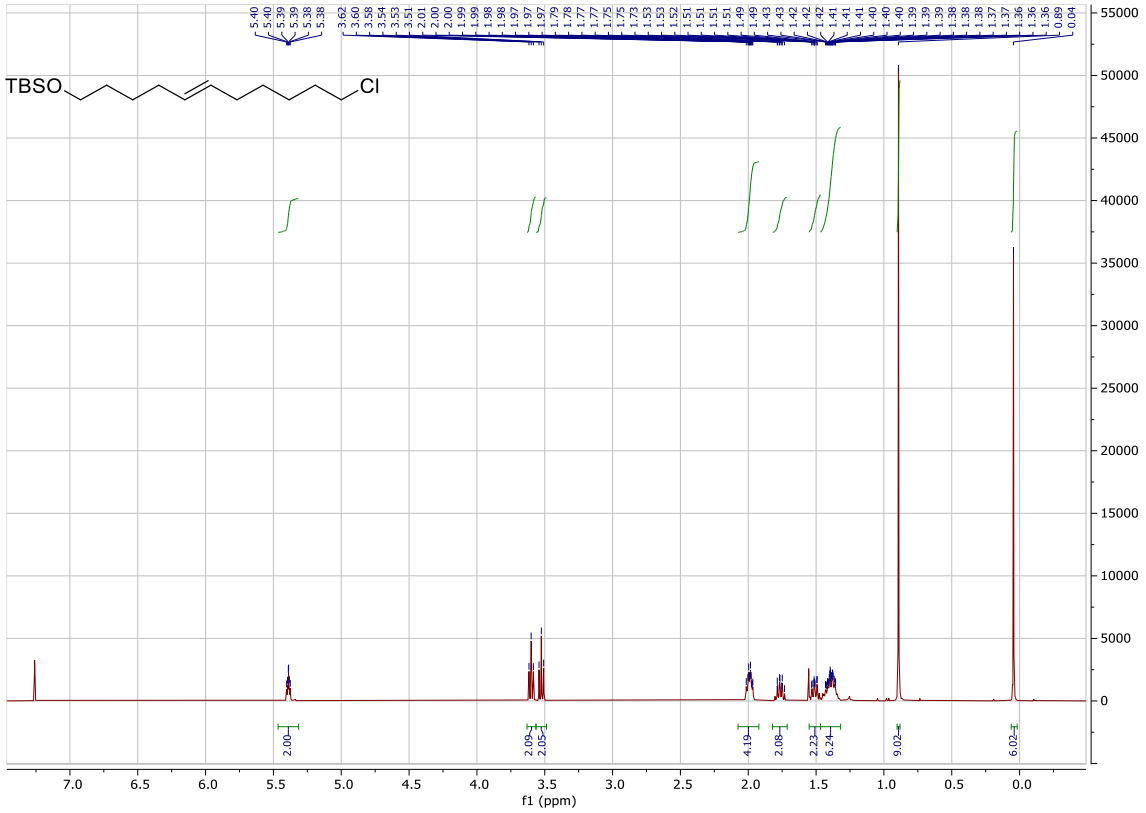


Figure S-1 ^{1}H-NMR spectrum of compound **1**.

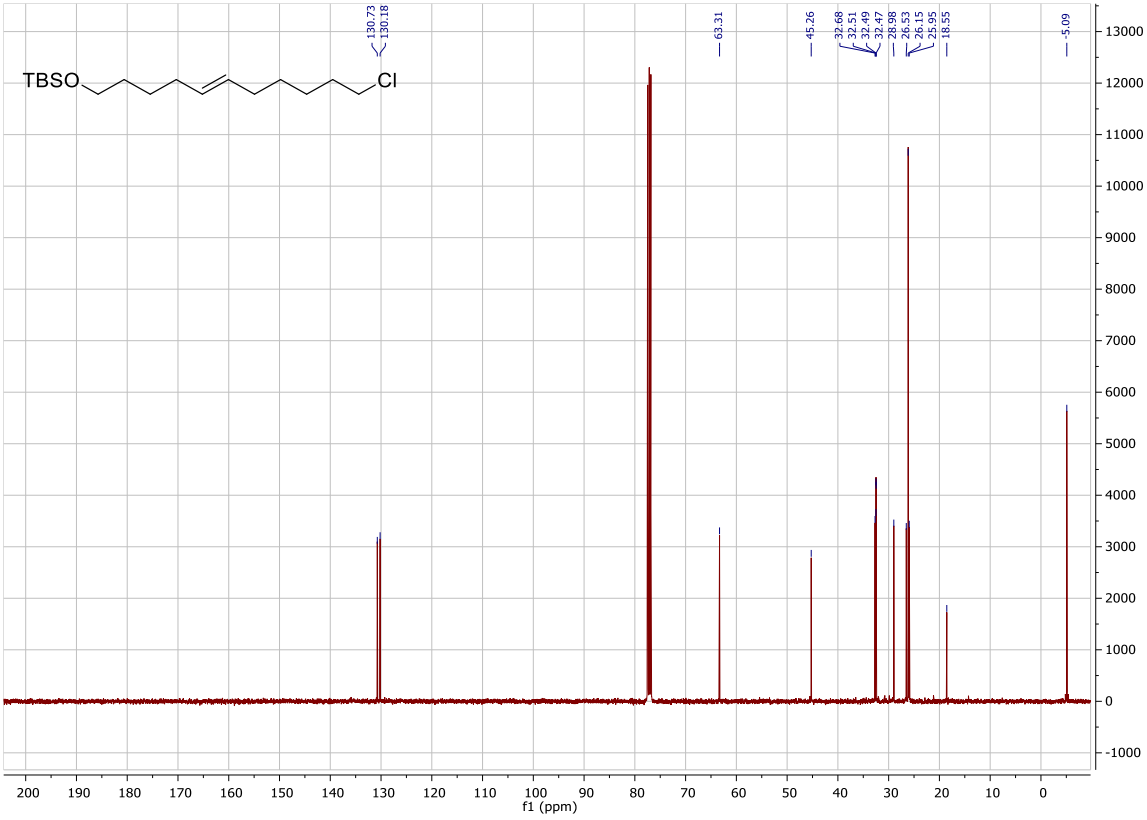


Figure S-2 ^{13}C NMR spectrum of compound **1**.

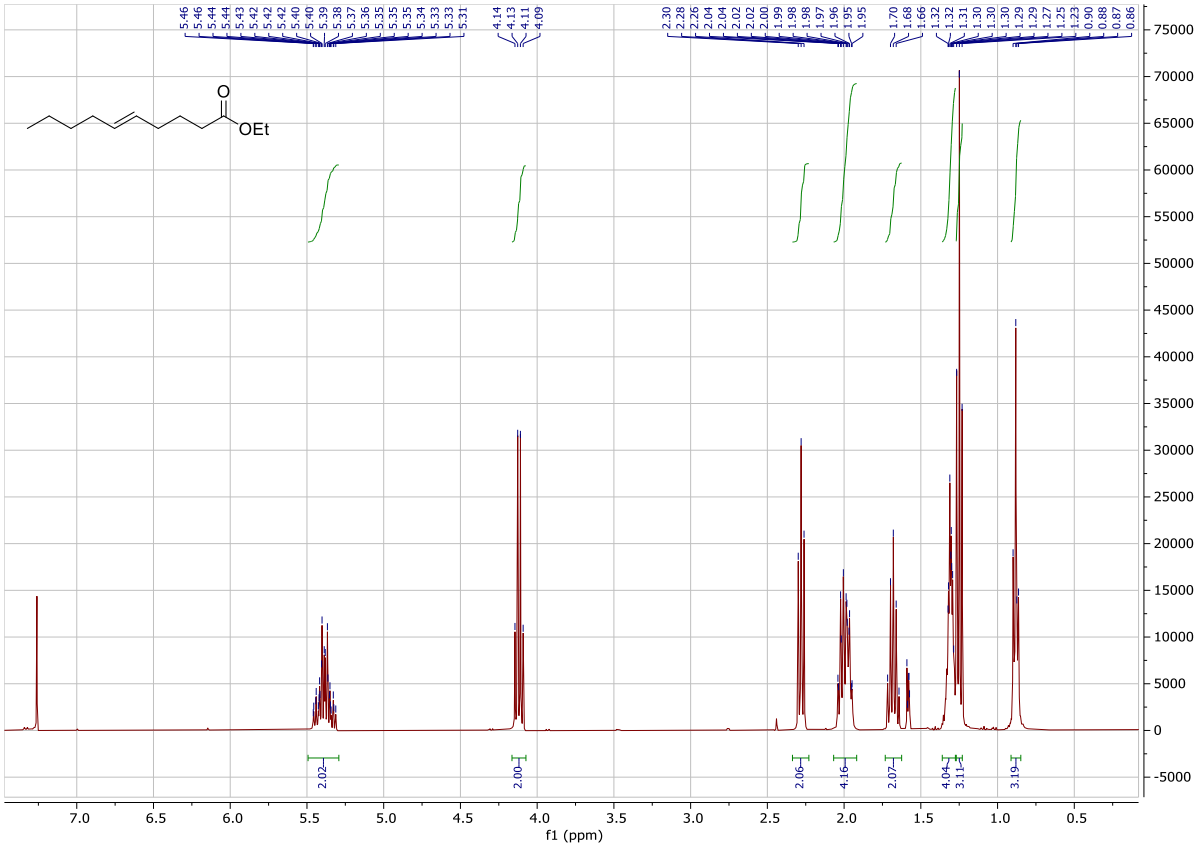


Figure S-3 ^{1}H-NMR spectrum of compound **2**.

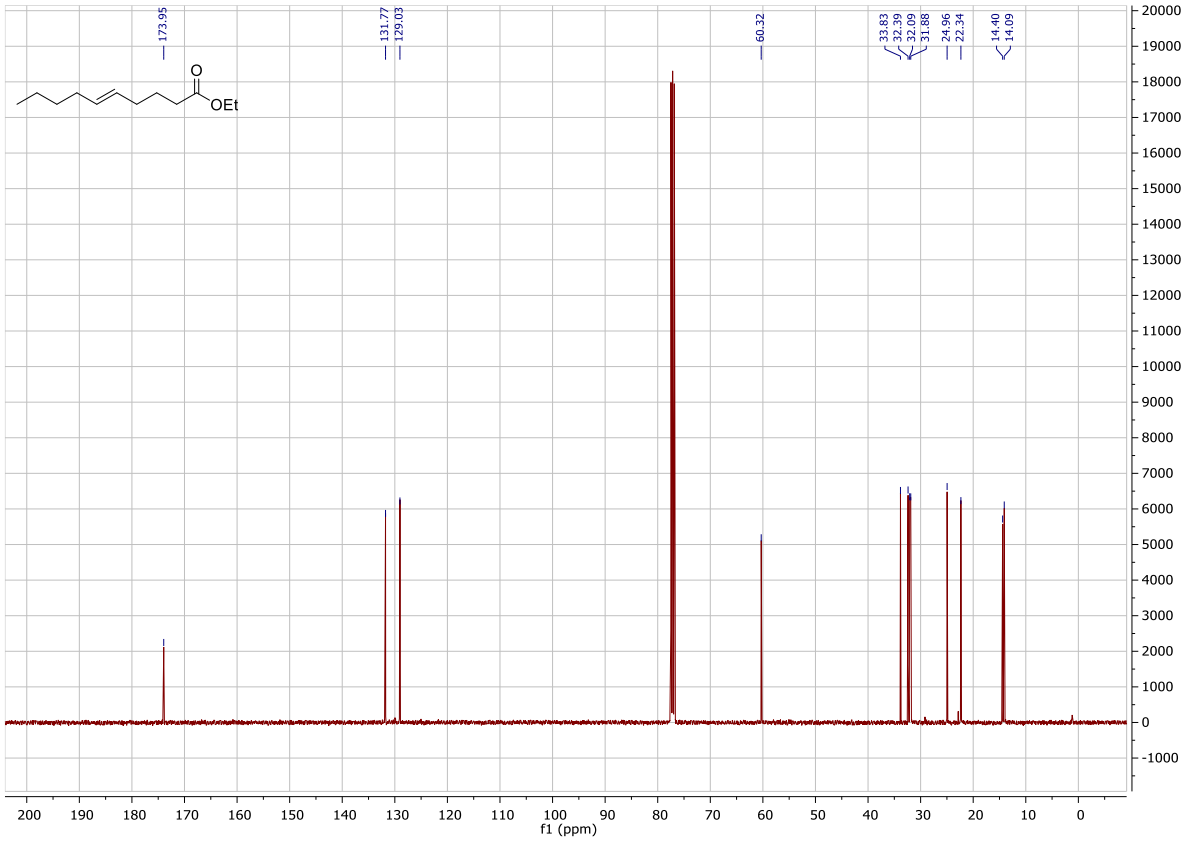


Figure S-4 ^{13}C NMR spectrum of compound **2**.

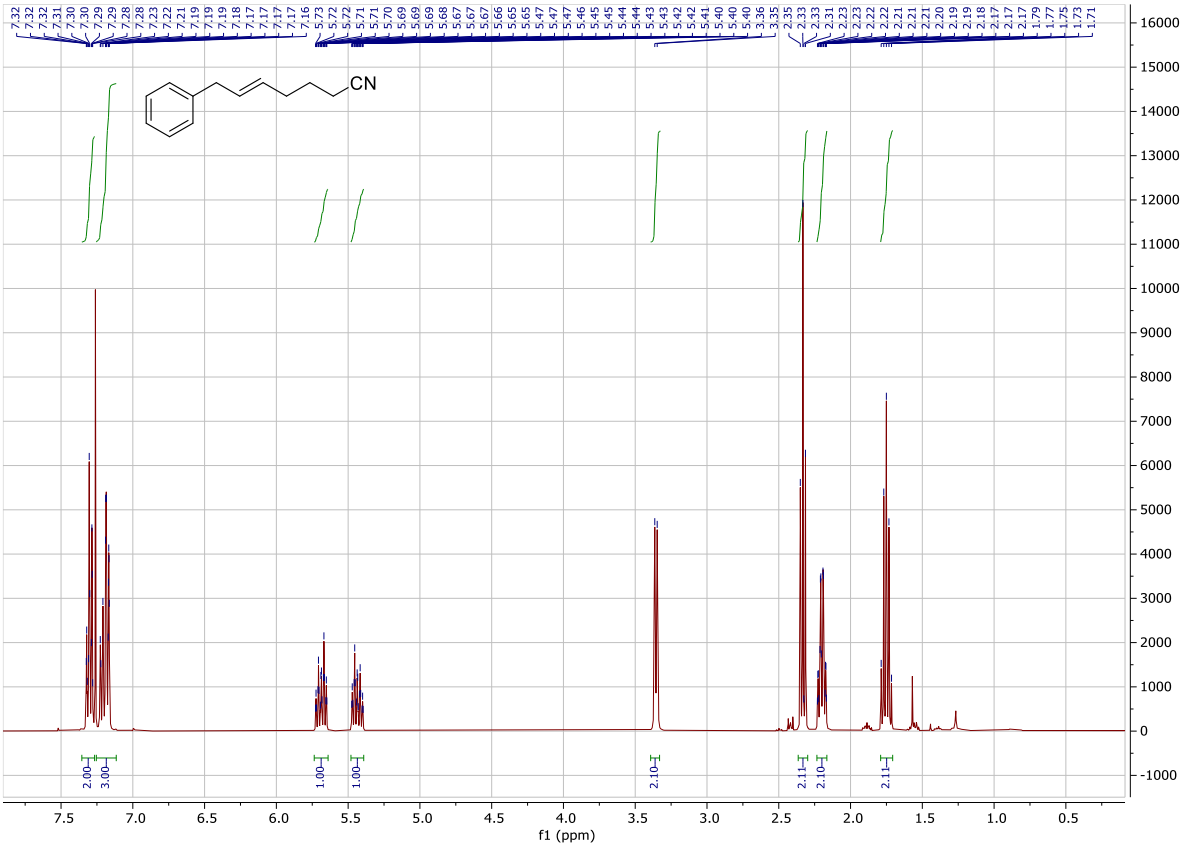


Figure S-5 ^{1}H-NMR spectrum of compound **3**.

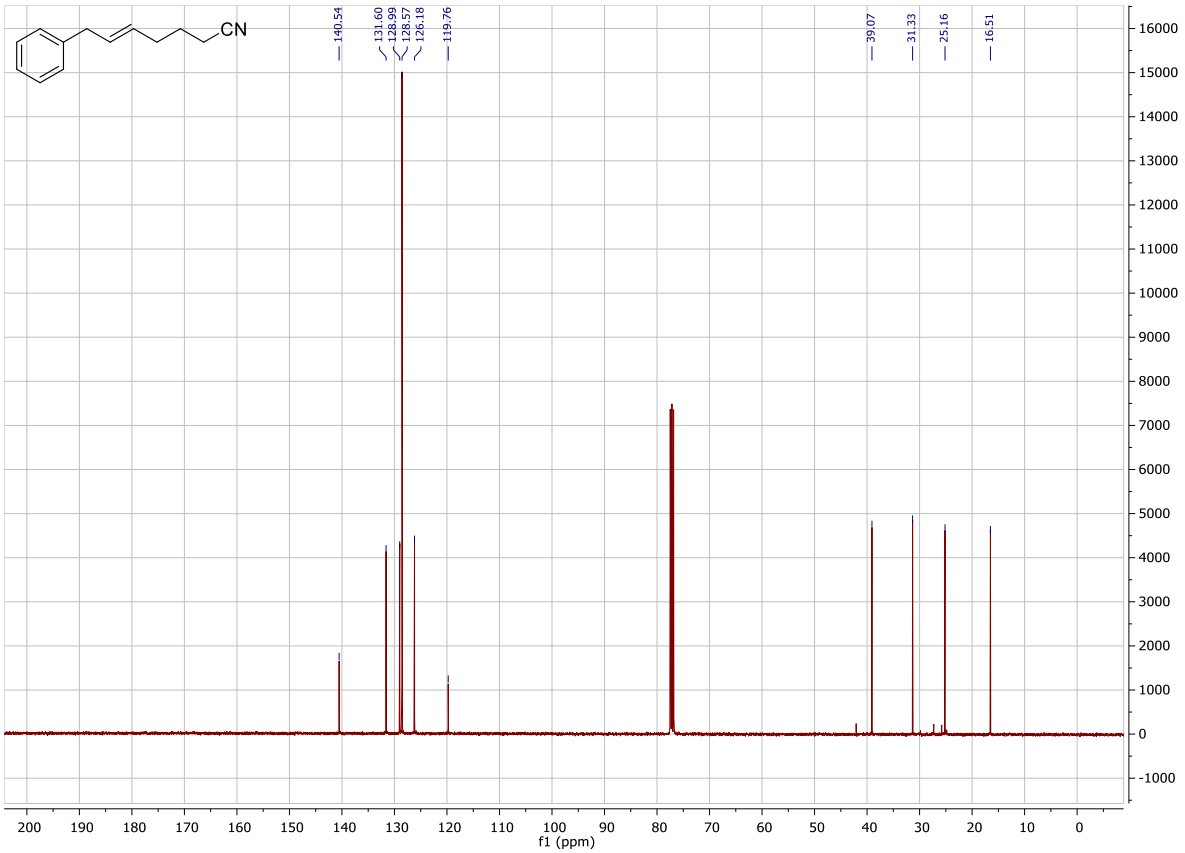


Figure S-6 ^{13}C NMR spectrum of compound **3**.

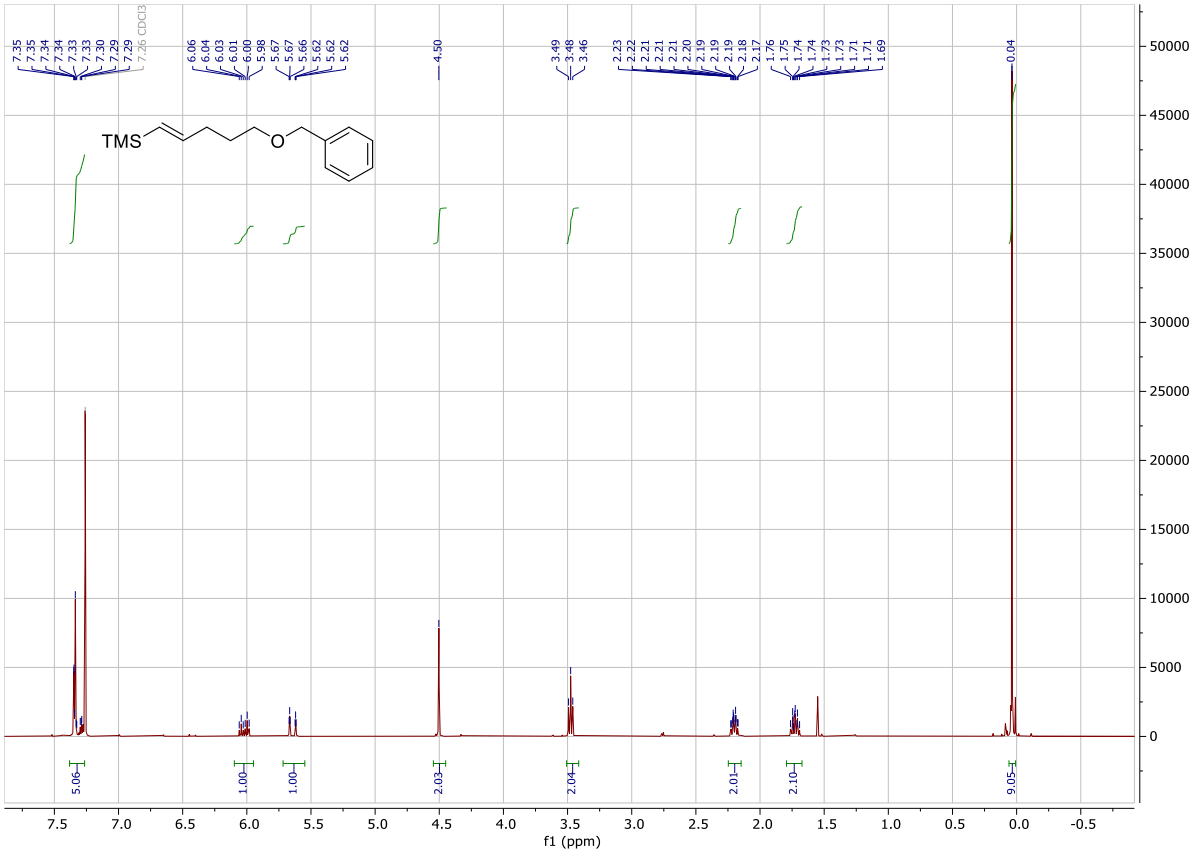


Figure S-7 ^{1}H-NMR spectrum of compound **4**.

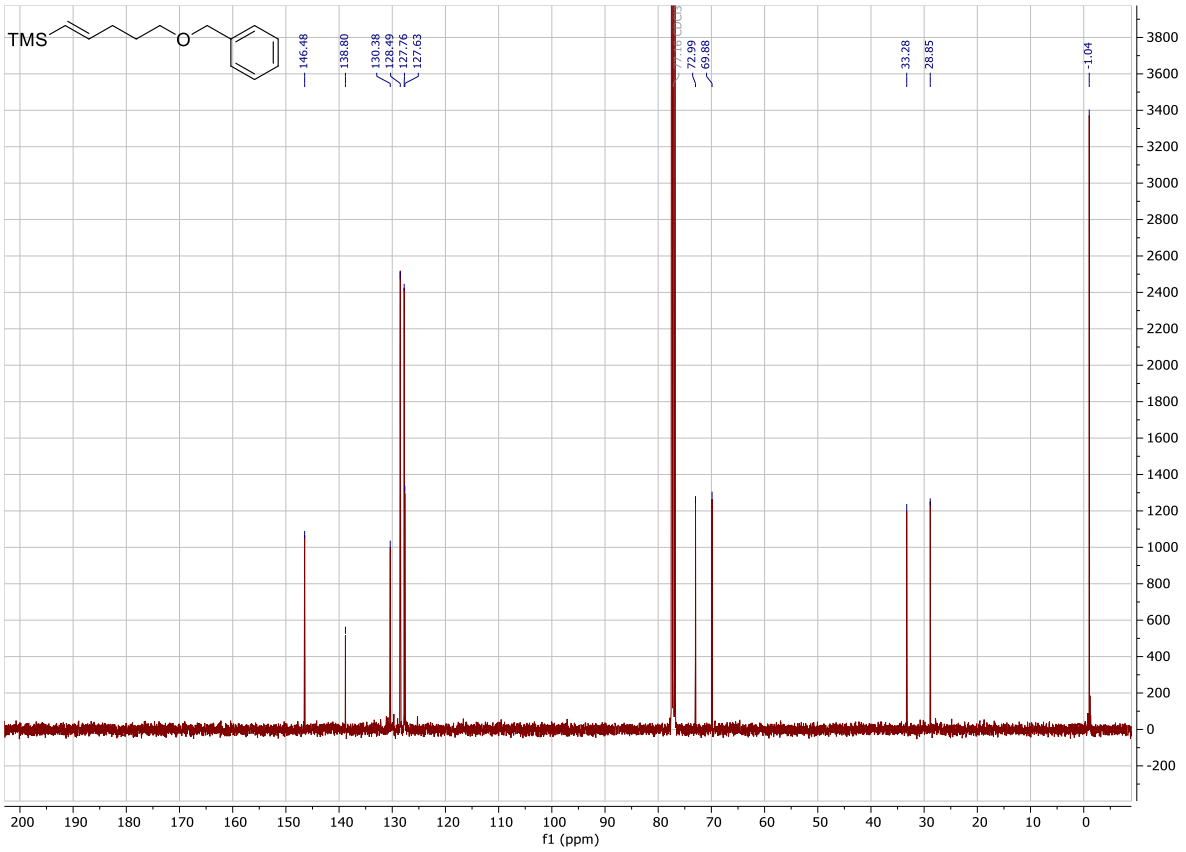


Figure S-8 ^{13}C NMR spectrum of compound **4**.

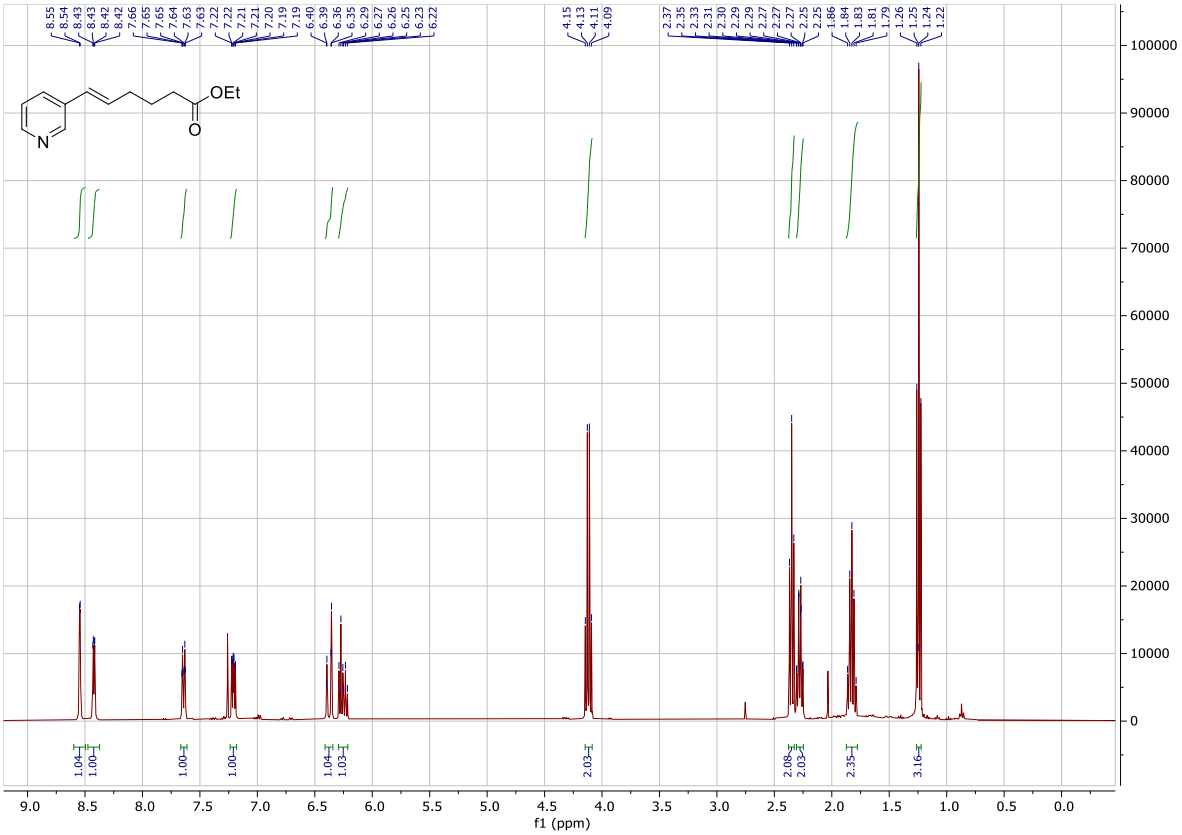


Figure S-9 ^{1}H-NMR spectrum of compound **5**.

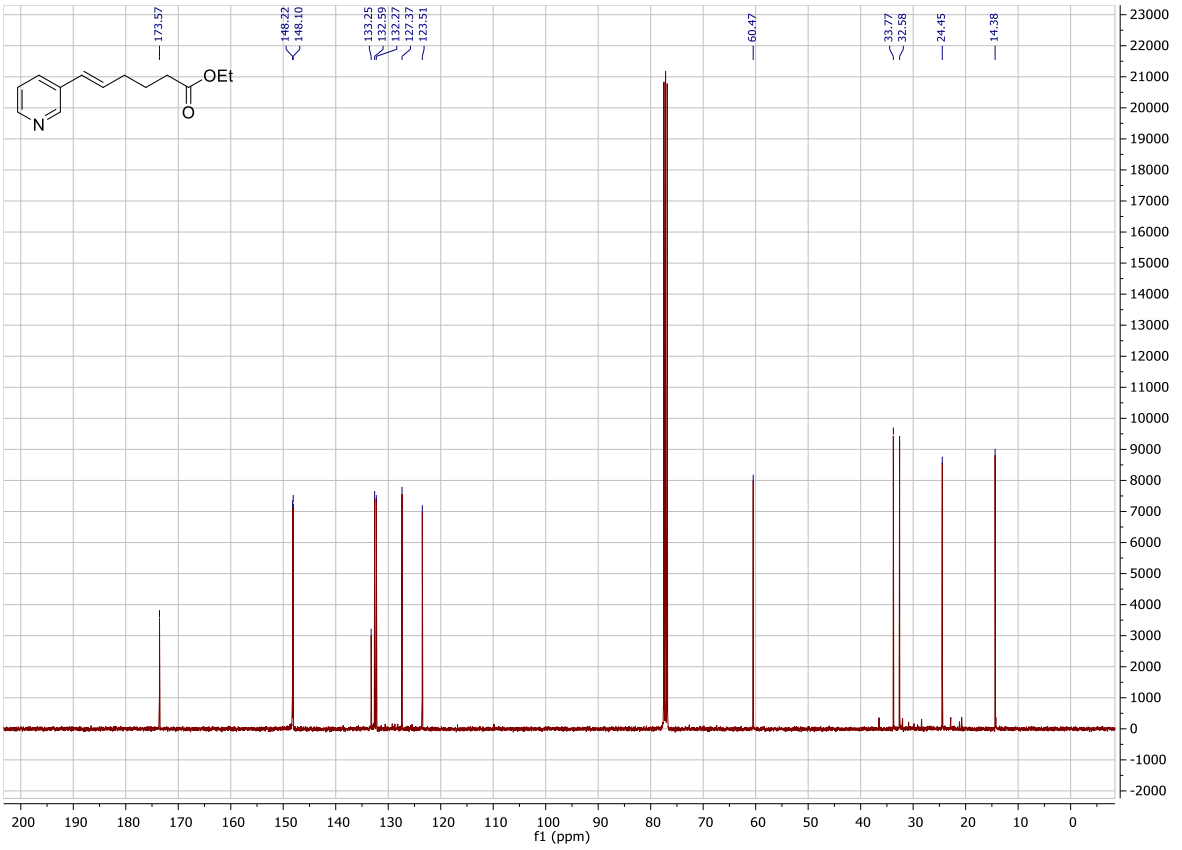


Figure S-10 ^{13}C NMR spectrum of compound **5**.

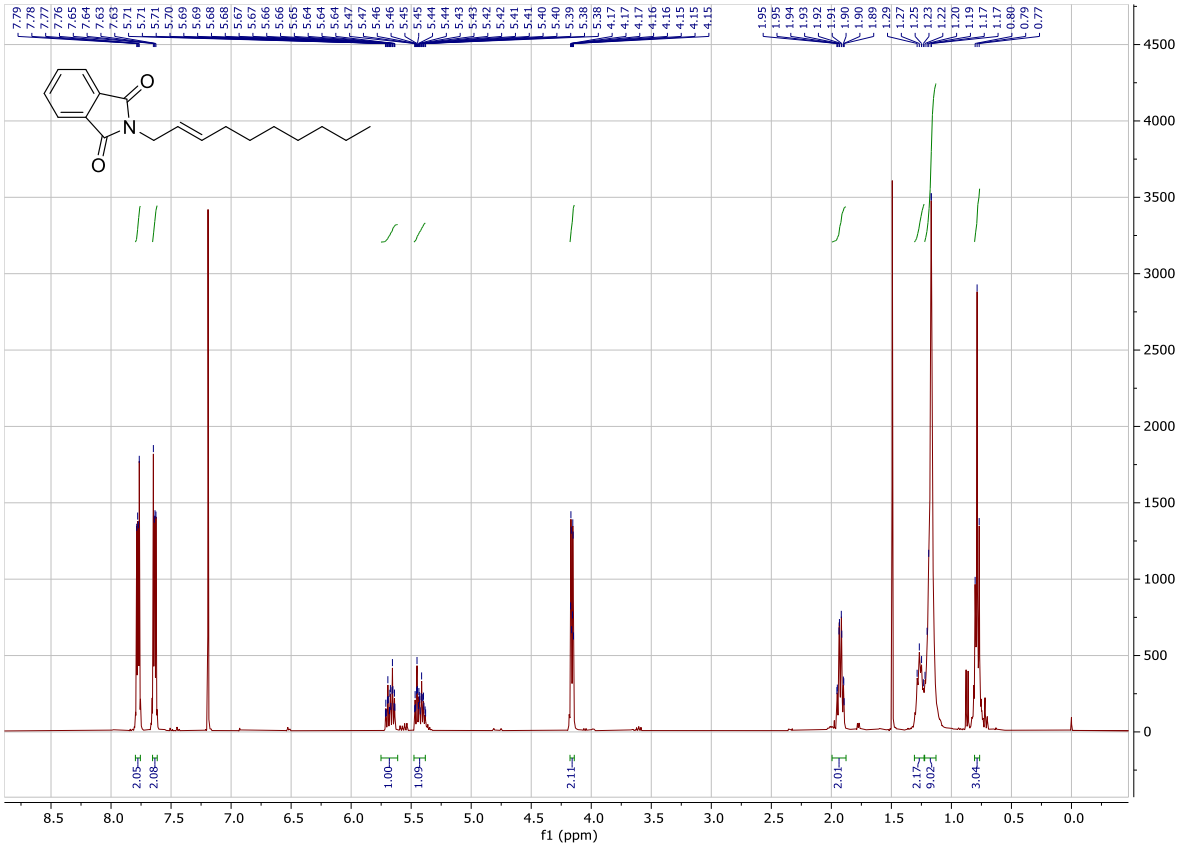


Figure S-11 ^{1}H-NMR spectrum of compound **6**.

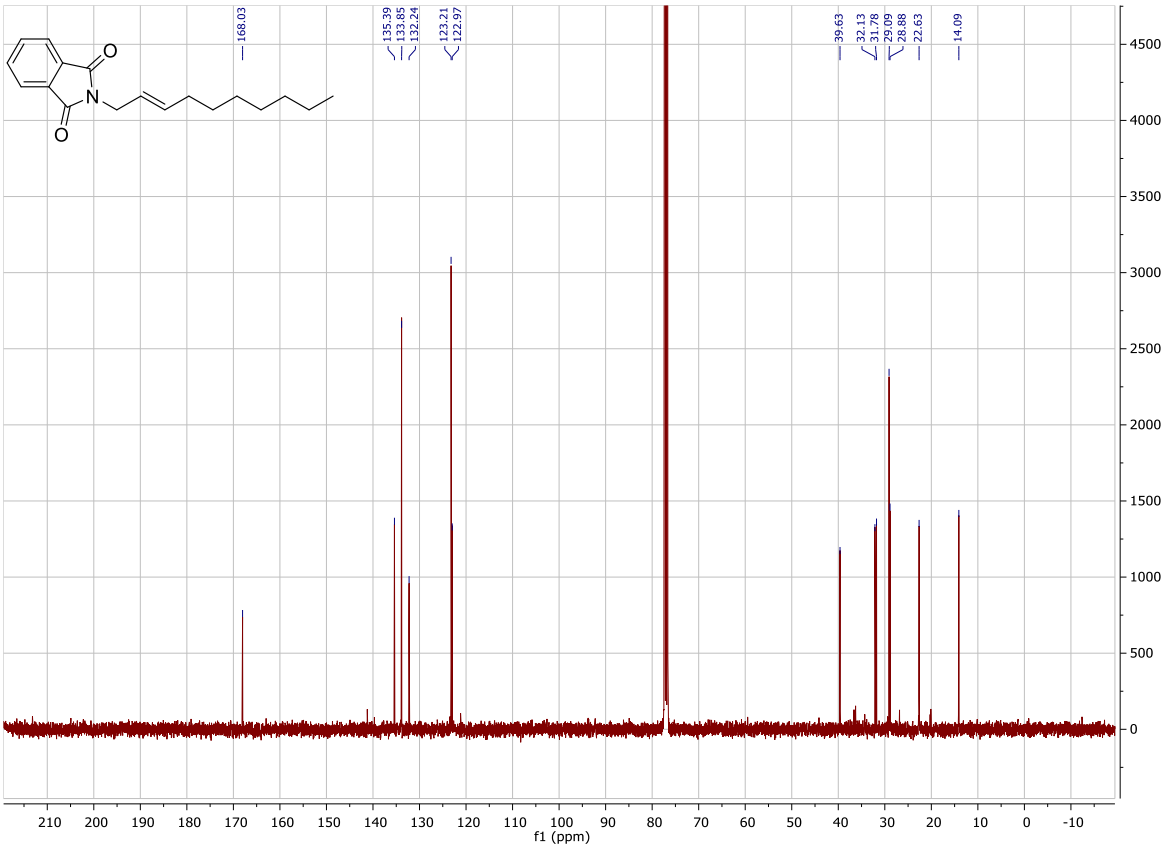


Figure S-12 ^{13}C NMR spectrum of compound **6**.

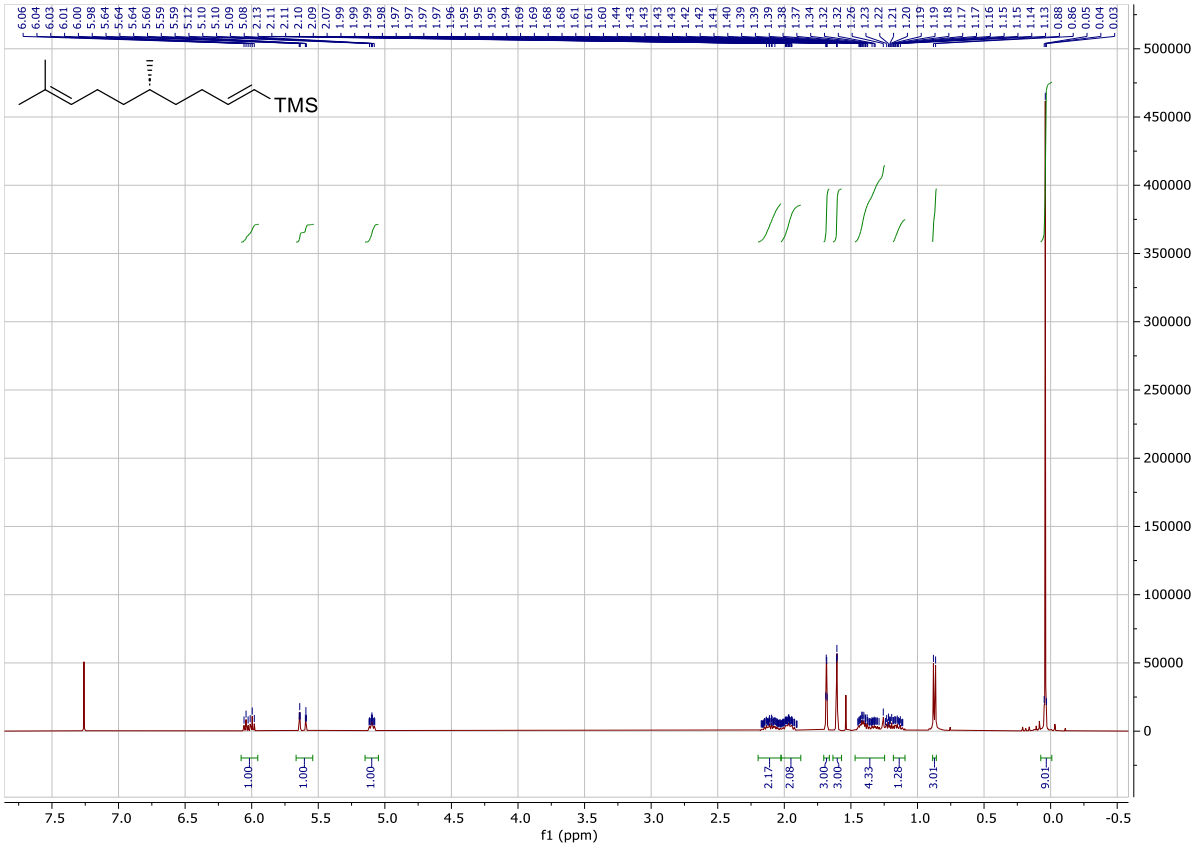


Figure S-13 ^{1}H-NMR spectrum of compound **7**.

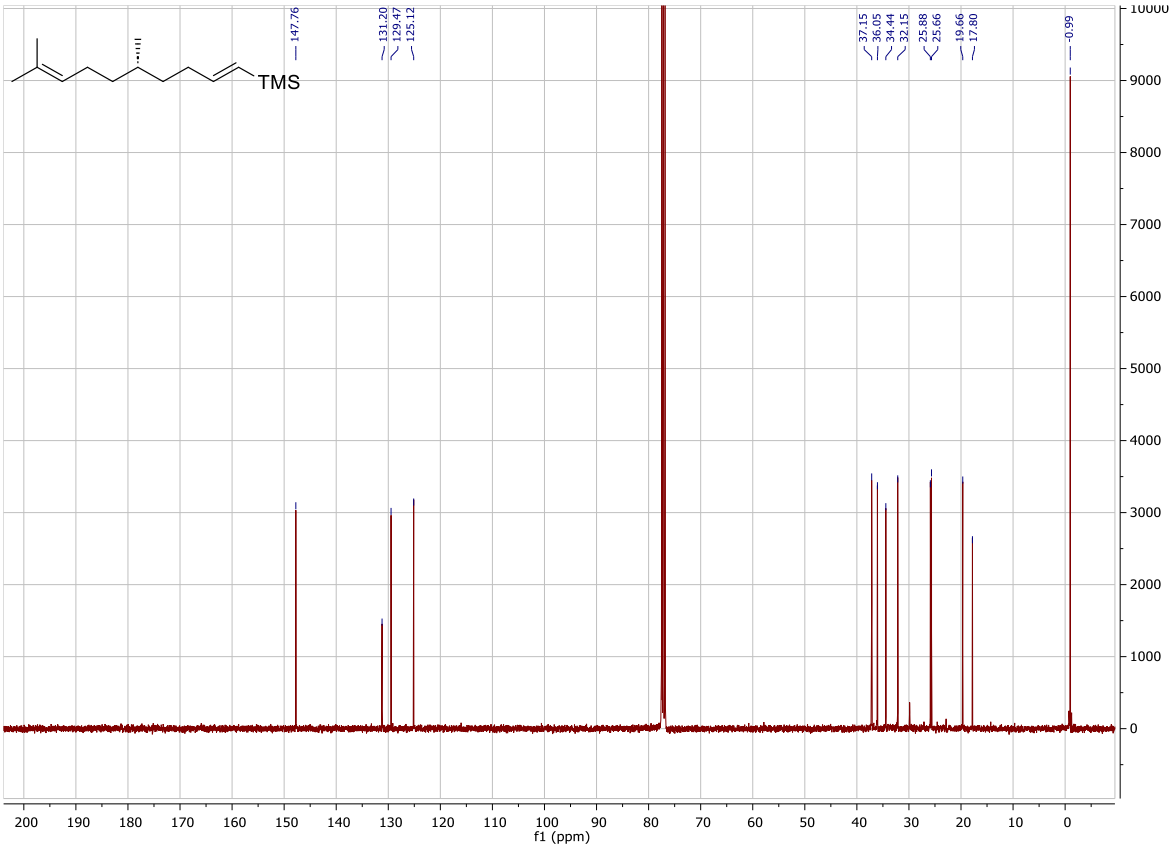


Figure S-14 ^{13}C NMR spectrum of compound **7**.

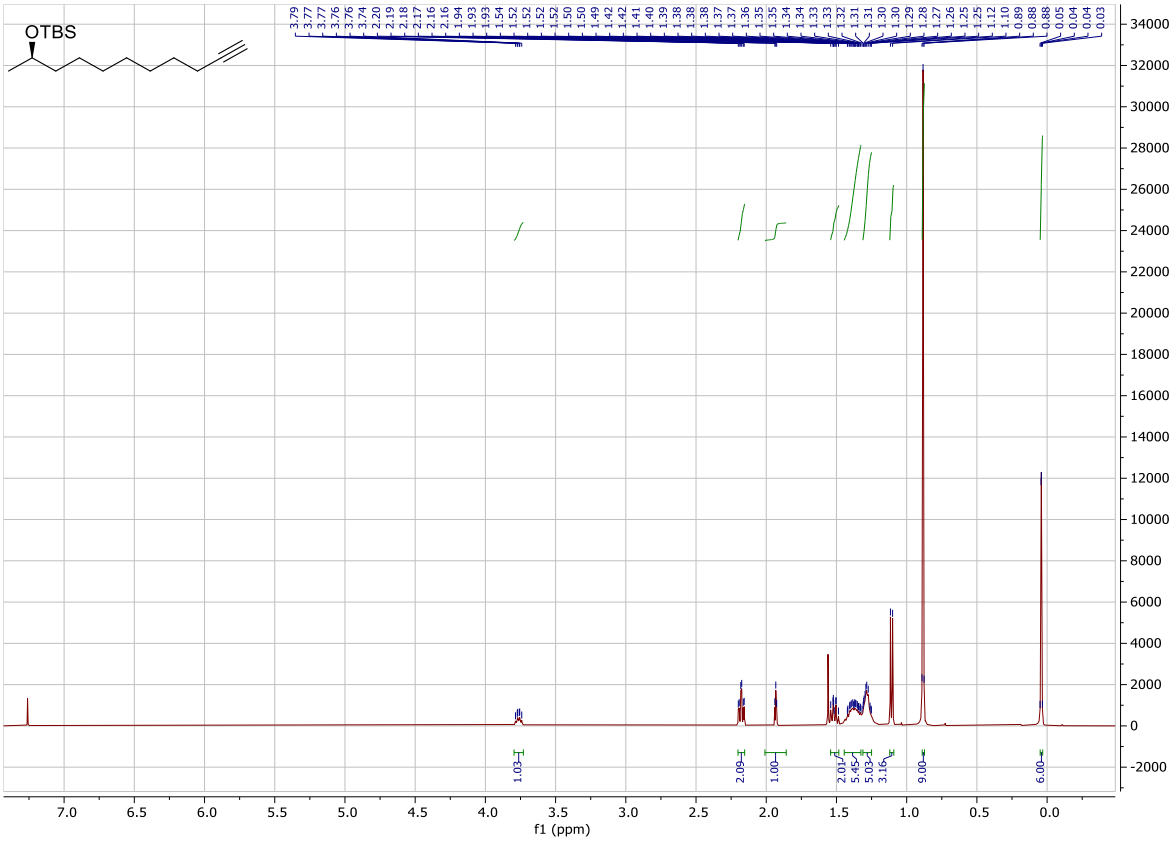


Figure S-15 ^{1}H-NMR spectrum of compound **8a**.

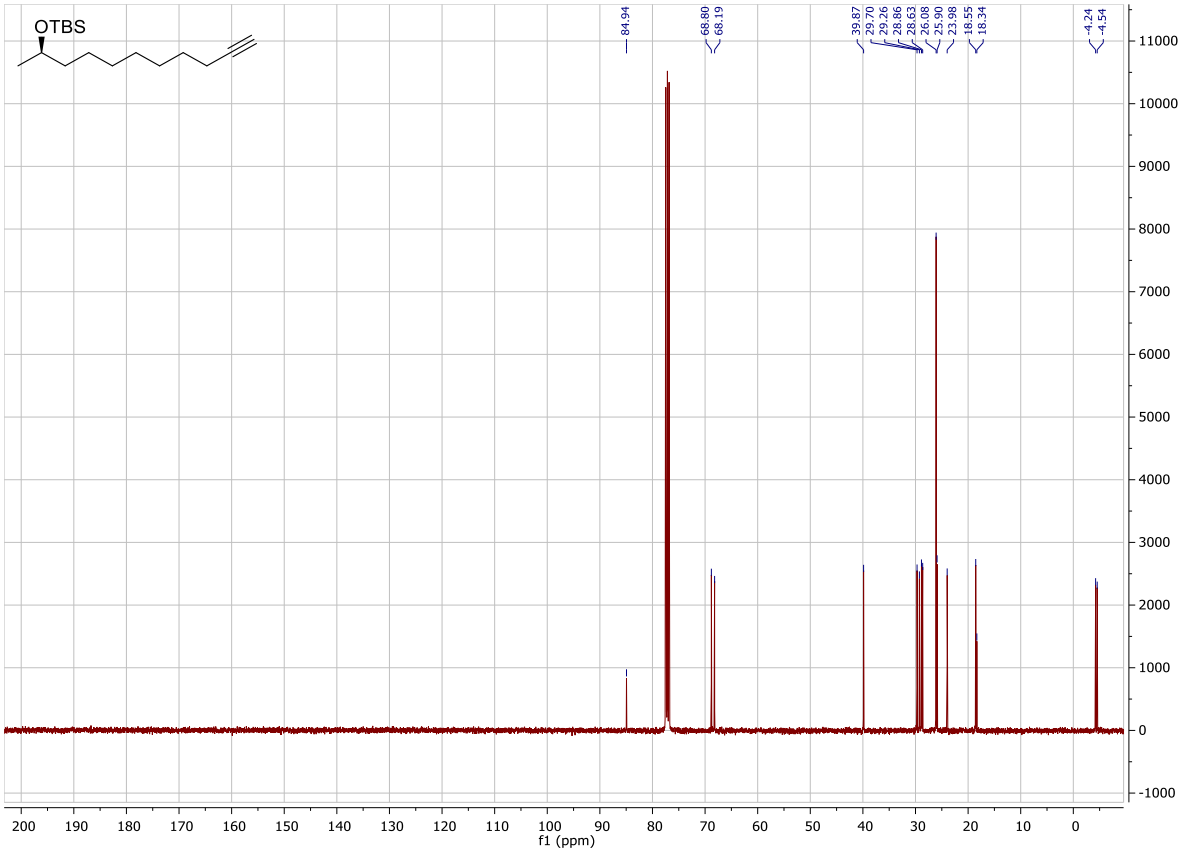


Figure S-16 ^{13}C NMR spectrum of compound **8a**.

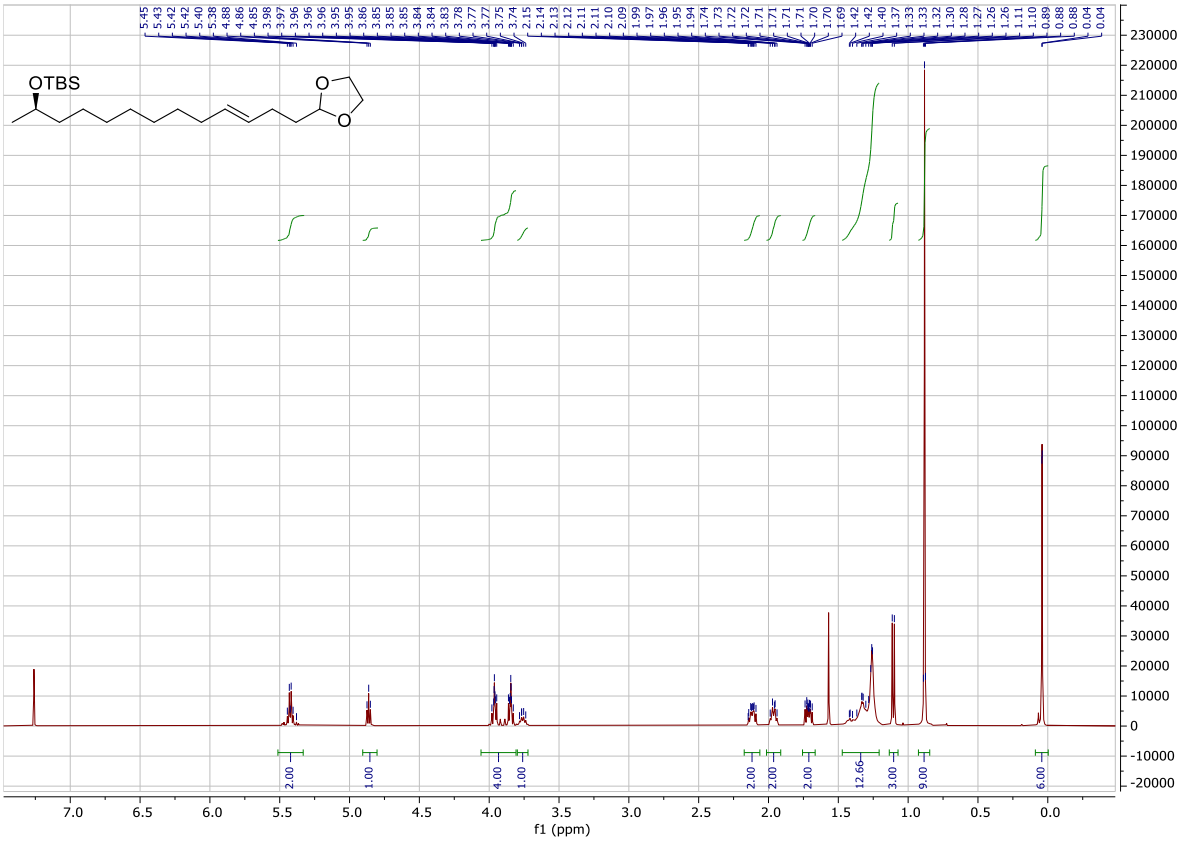


Figure S-17 ^{1}H-NMR spectrum of compound **8**.

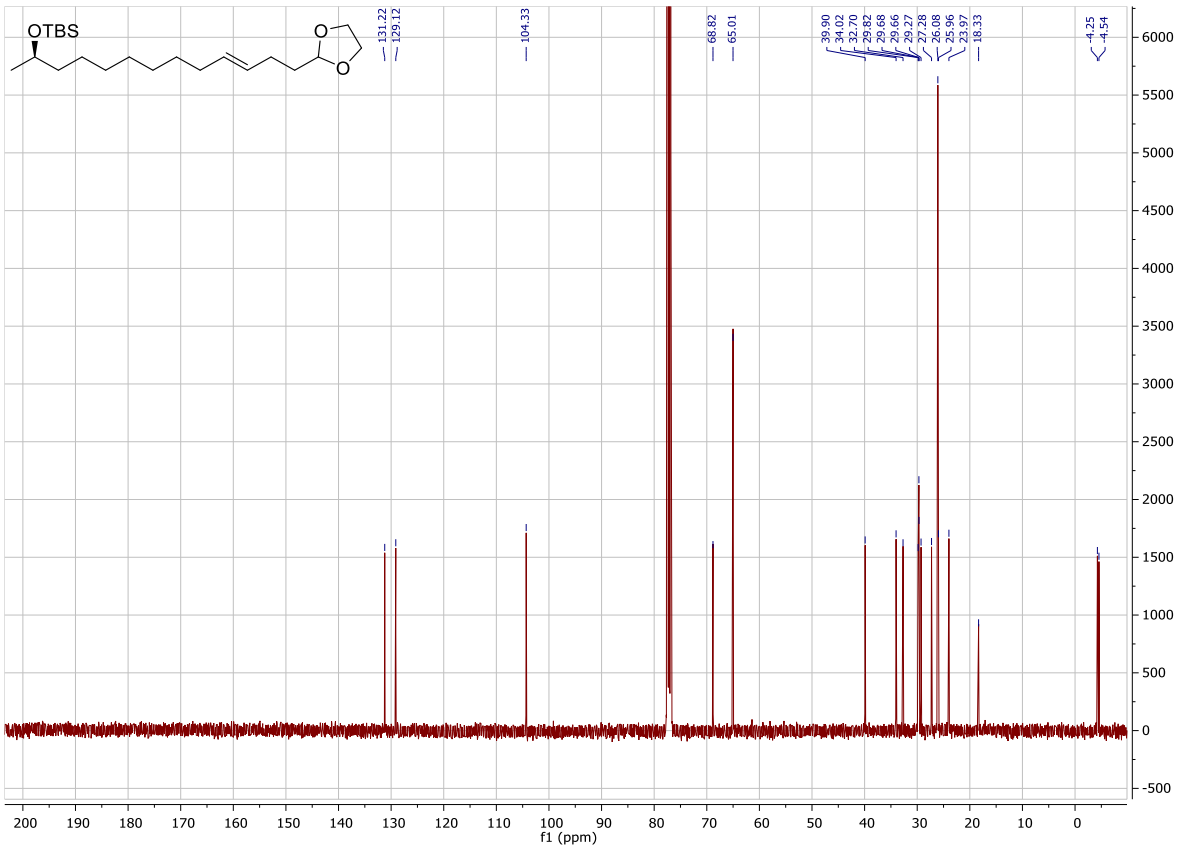


Figure S-18 ^{13}C NMR spectrum of compound **8**.

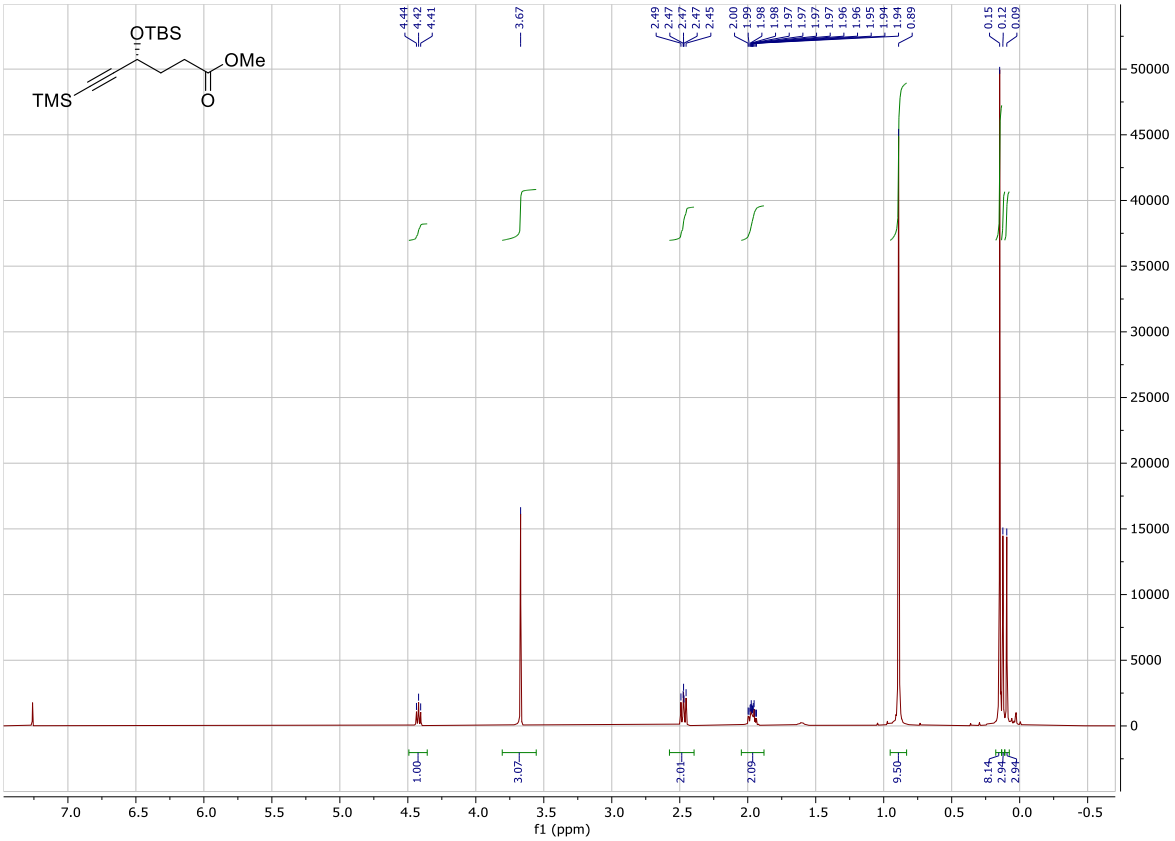


Figure S-19 ^{1}H-NMR spectrum of compound **9a.**

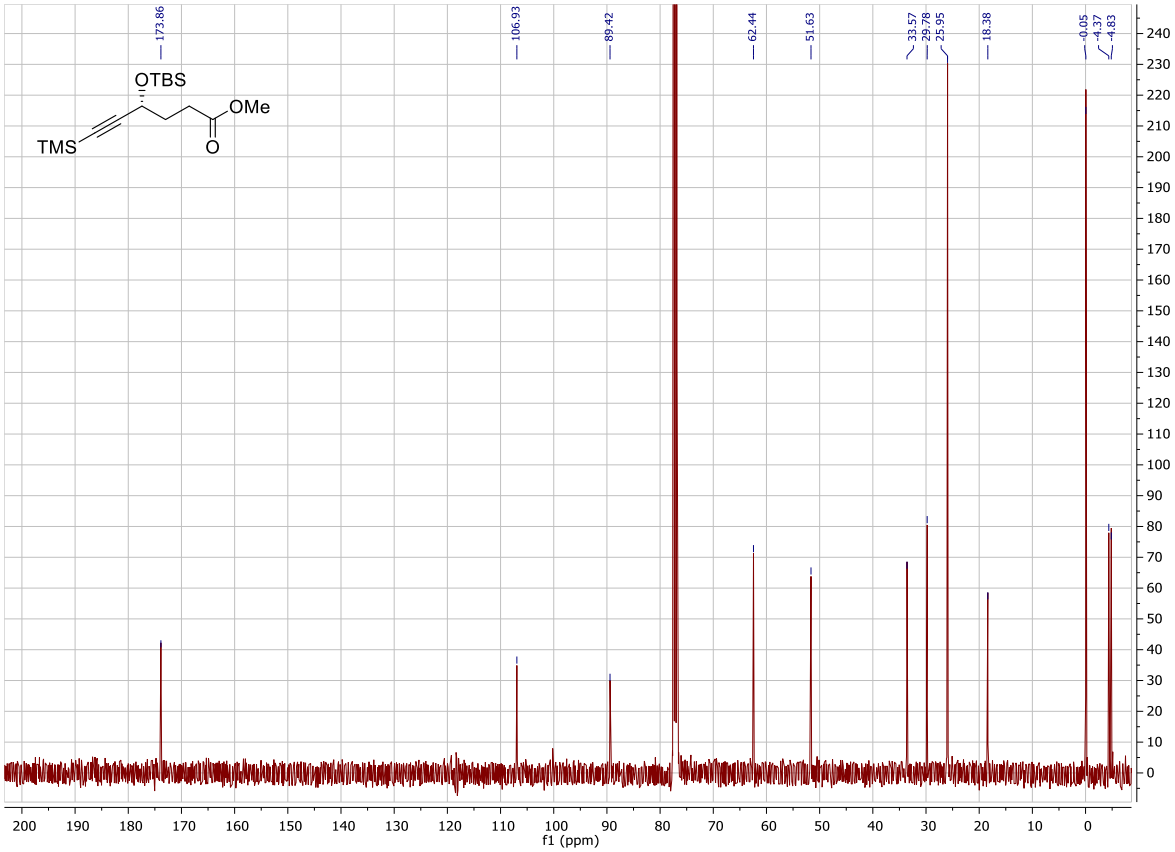


Figure S-20 ^{13}C NMR spectrum of compound **9a.**

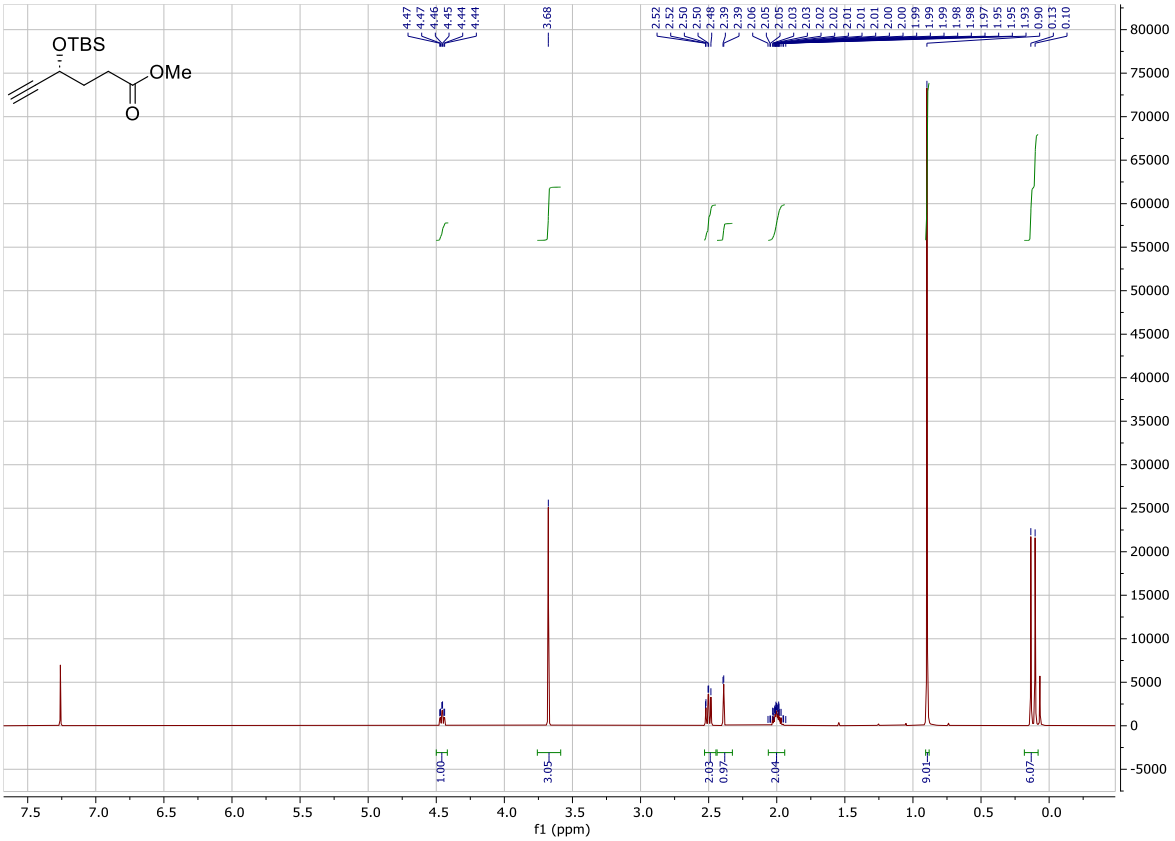


Figure S-21 ^{1}H-NMR spectrum of compound **9b.**

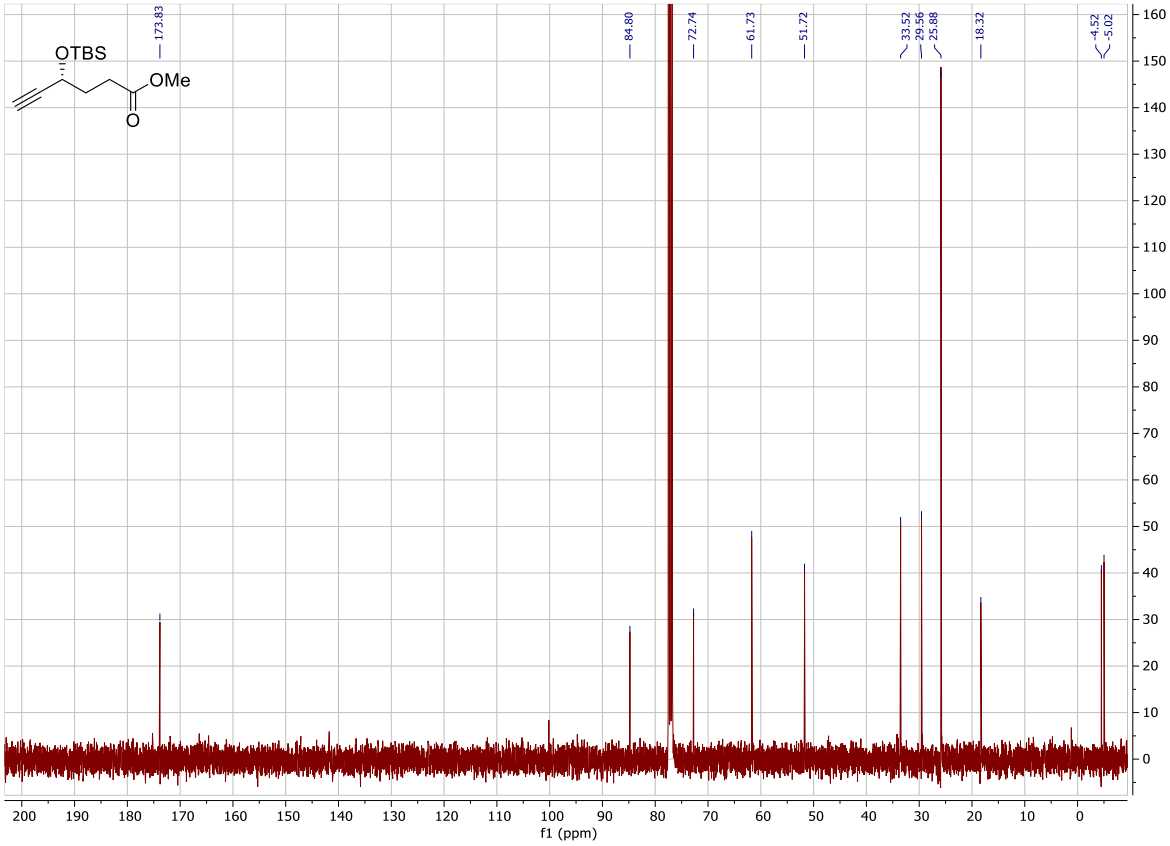


Figure S-22 ^{13}C NMR spectrum of compound **9b.**

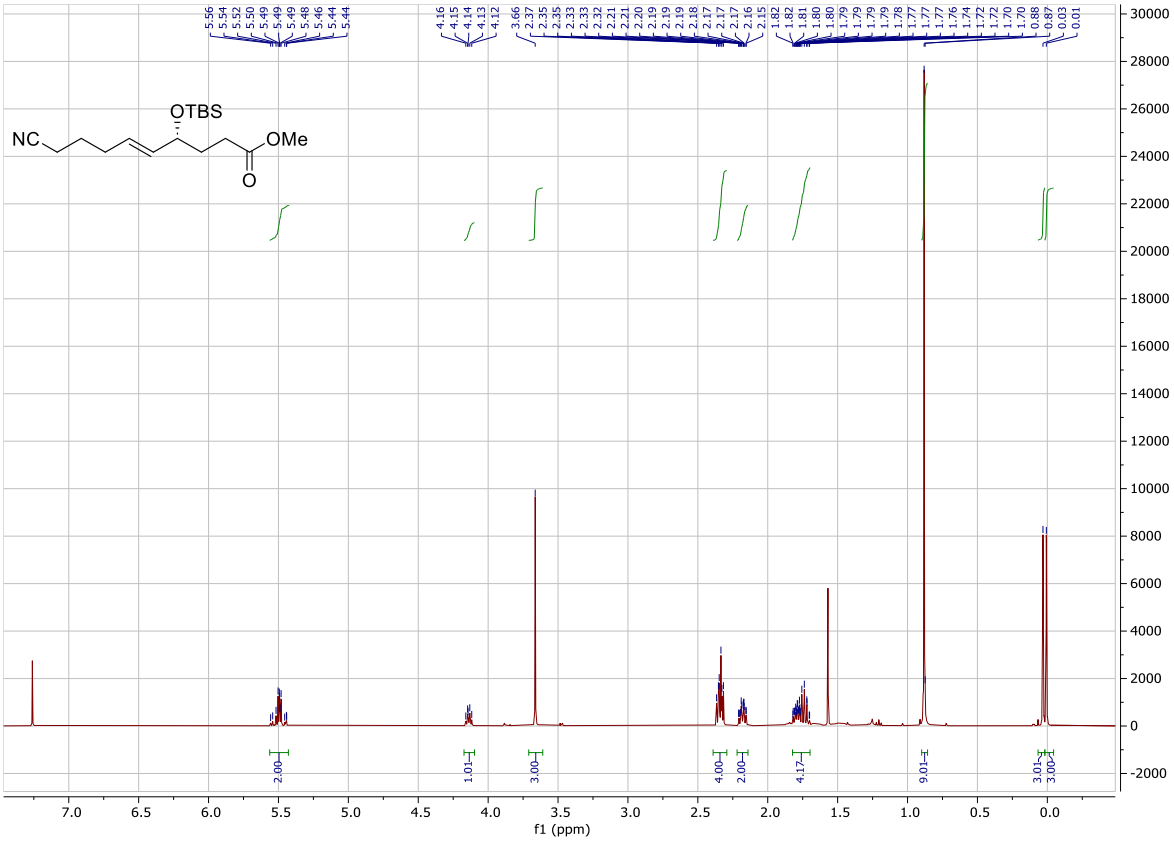


Figure S-23 ^{1}H-NMR spectrum of compound **9**.

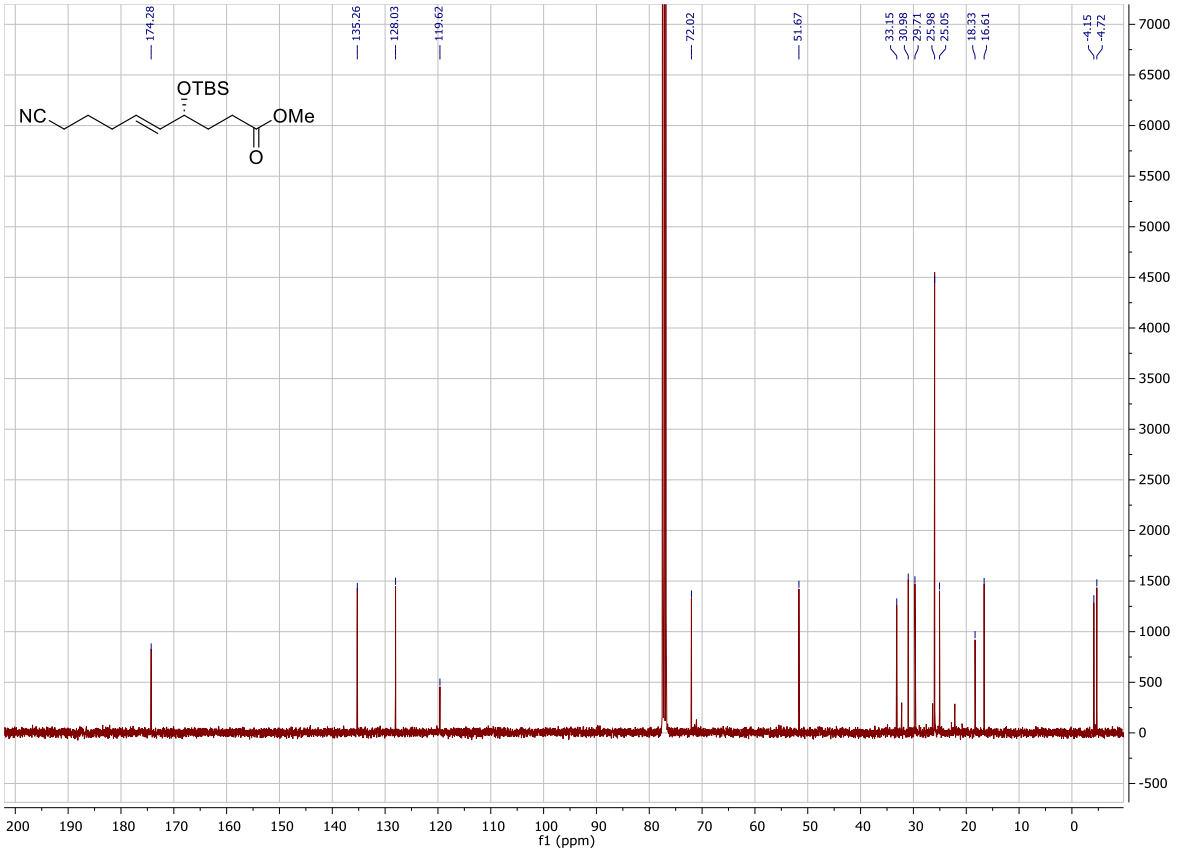


Figure S-24 ^{13}C NMR spectrum of compound **9**.

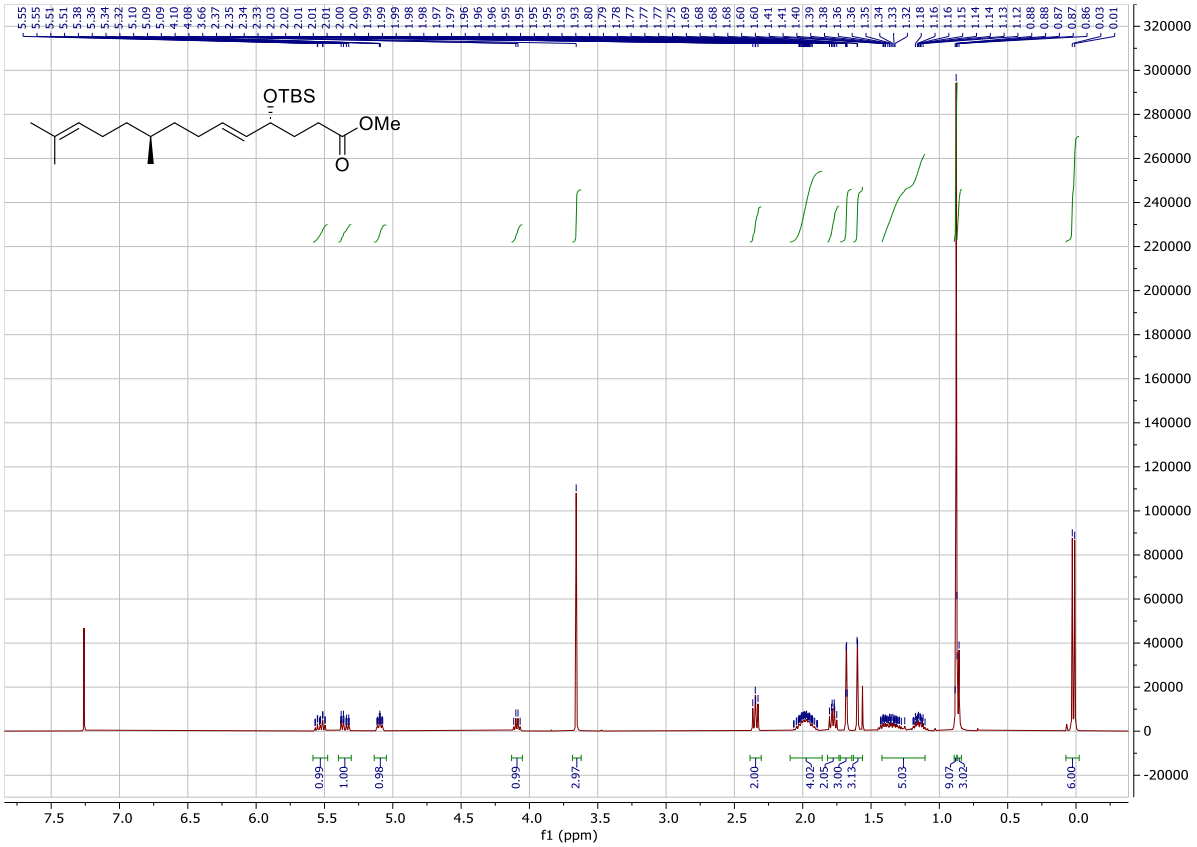


Figure S-25 ^{1}H-NMR spectrum of compound **10**.

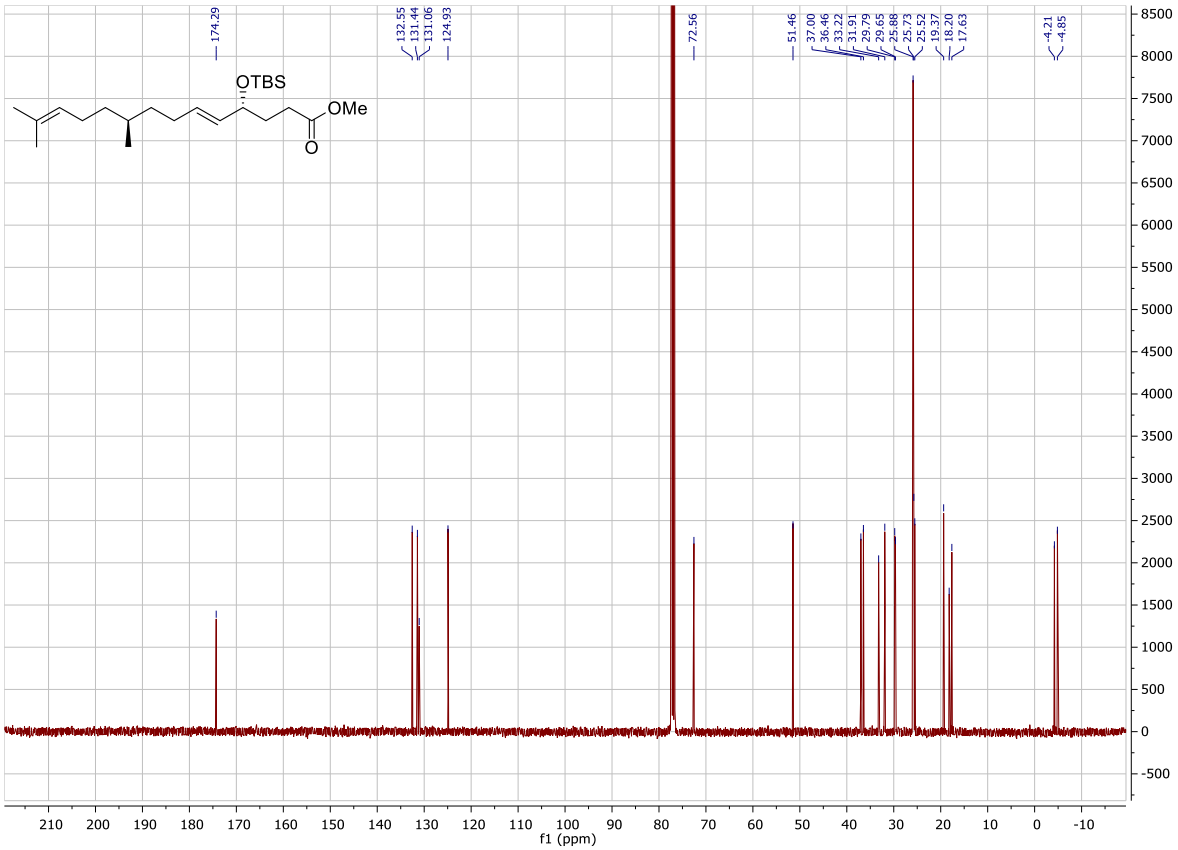


Figure S-26 ^{13}C NMR spectrum of compound **10**.

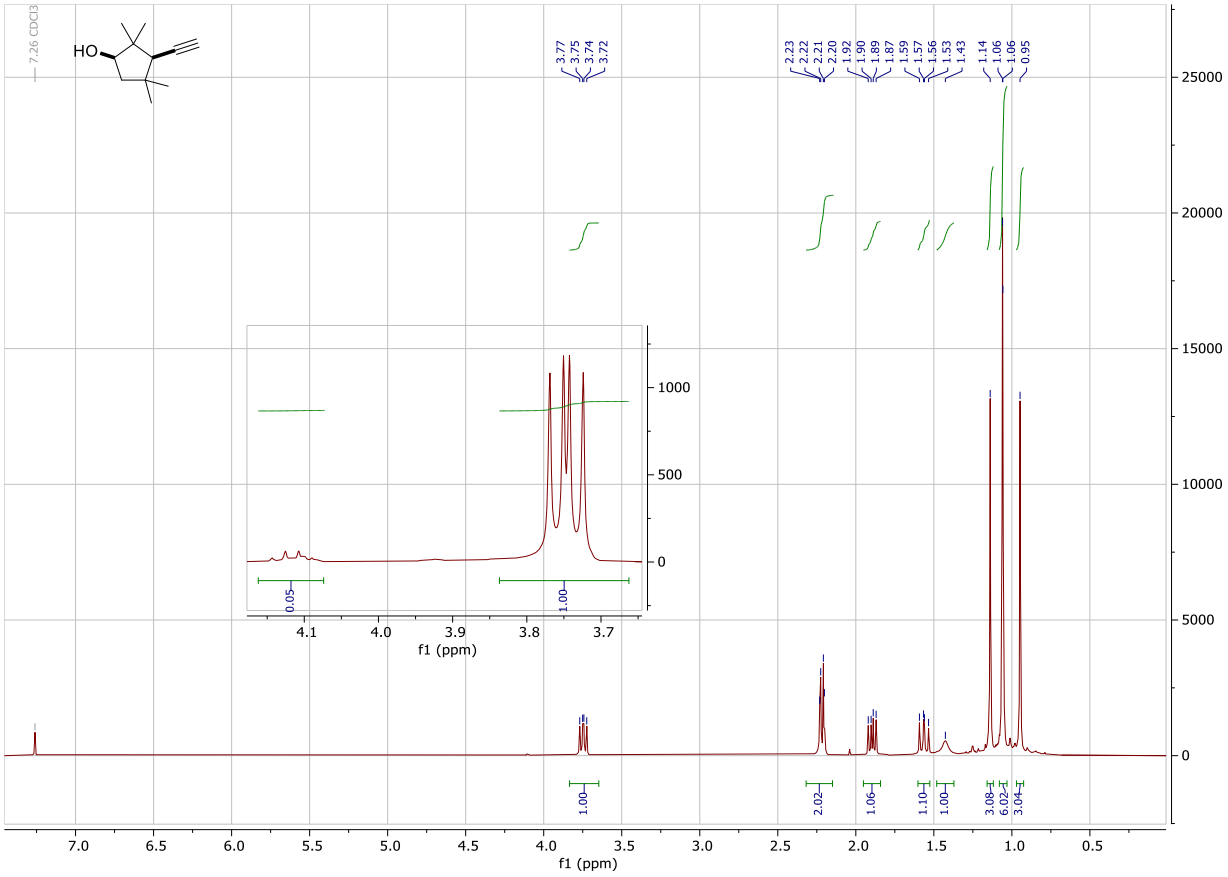


Figure S-27 ^{1}H-NMR spectrum of compound **11b**.

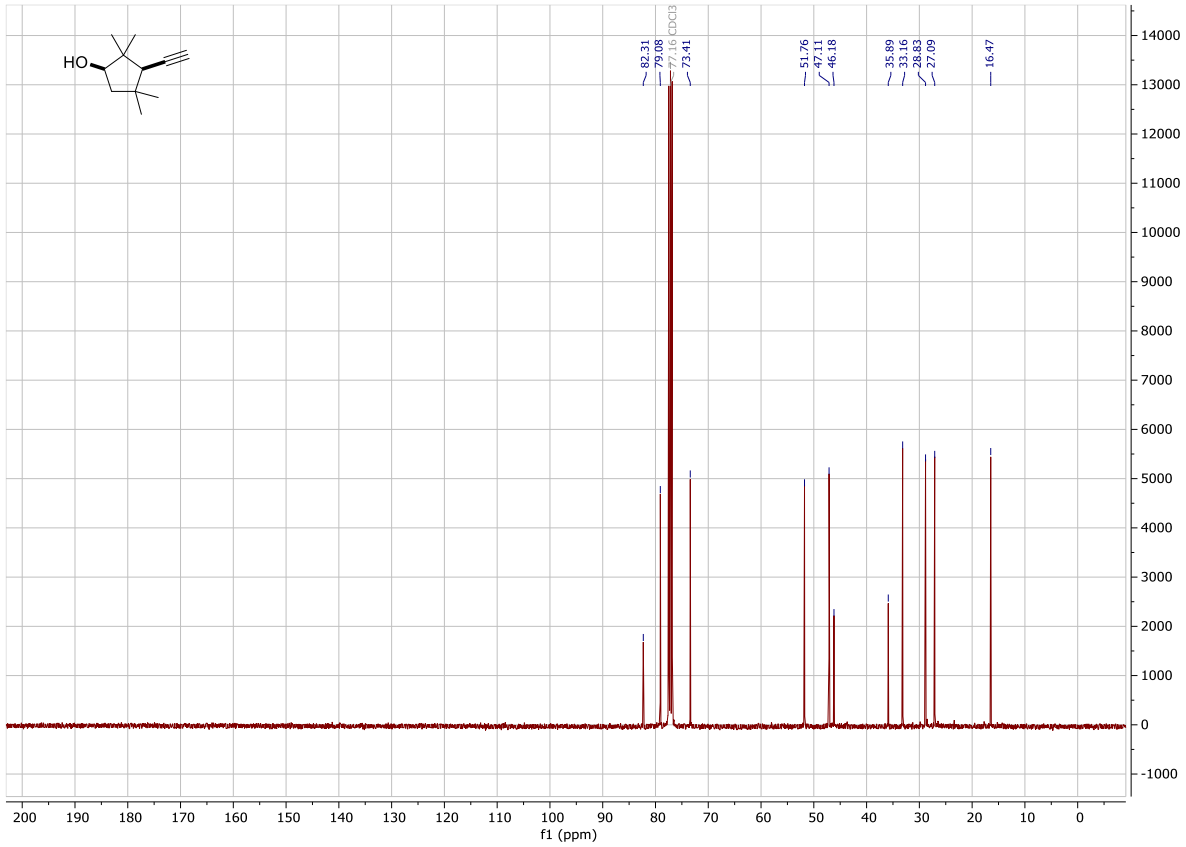


Figure 28 ^{13}C NMR spectrum of compound **11b**.

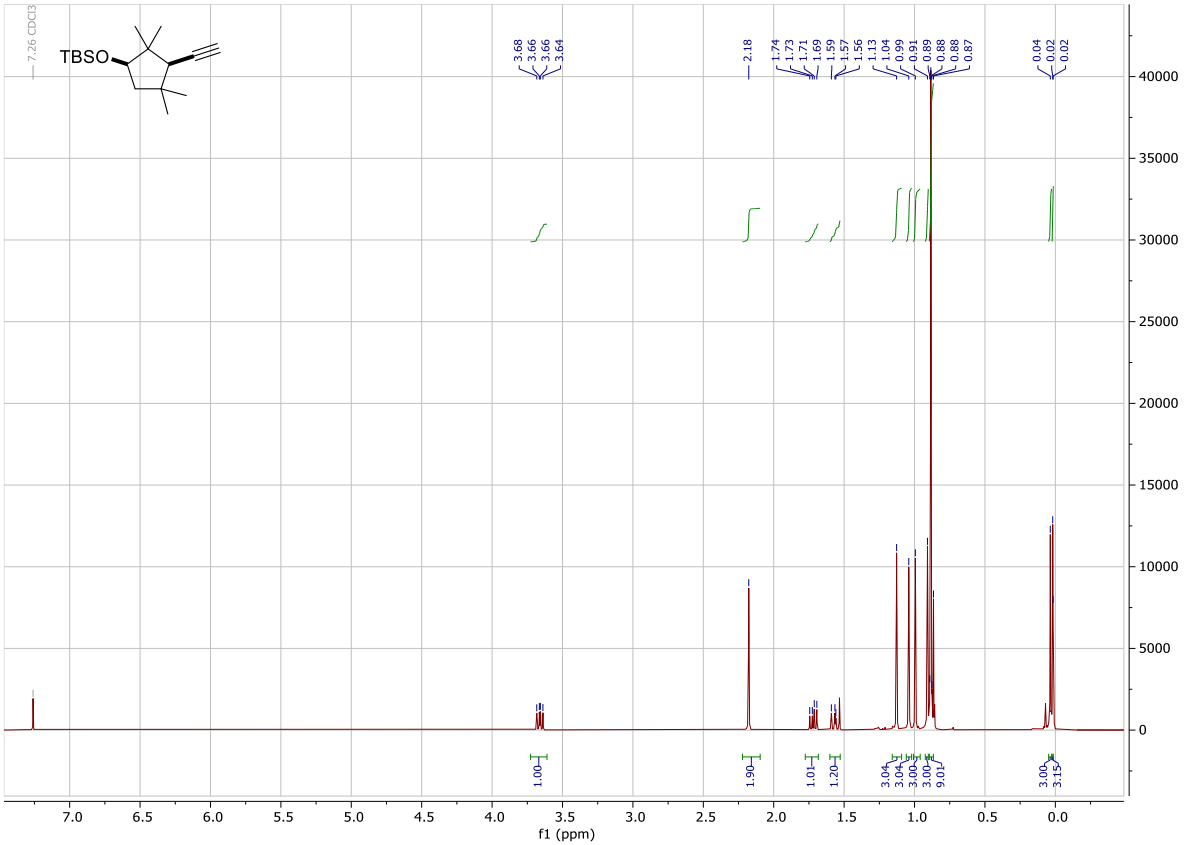


Figure S-29 ^{1}H-NMR spectrum of compound **11c**.

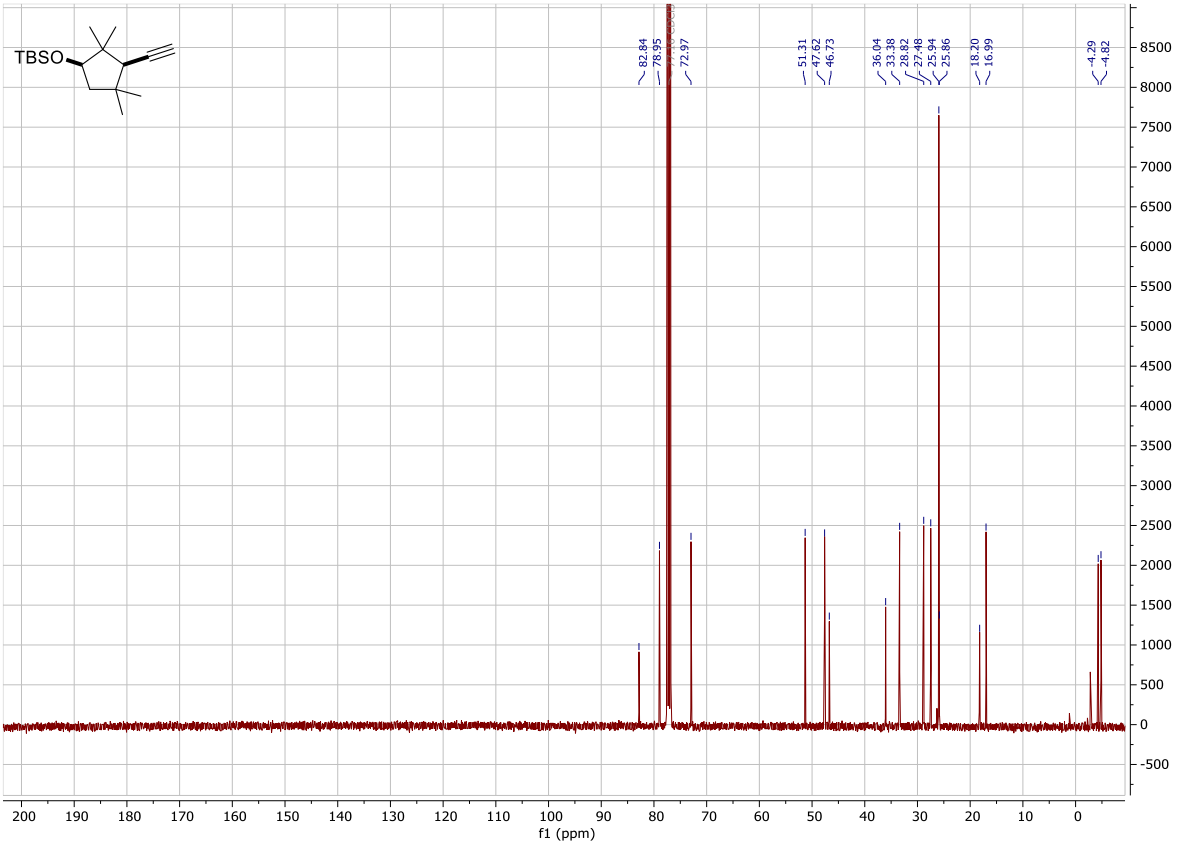


Figure 30 ^{13}C NMR spectrum of compound **11c**.

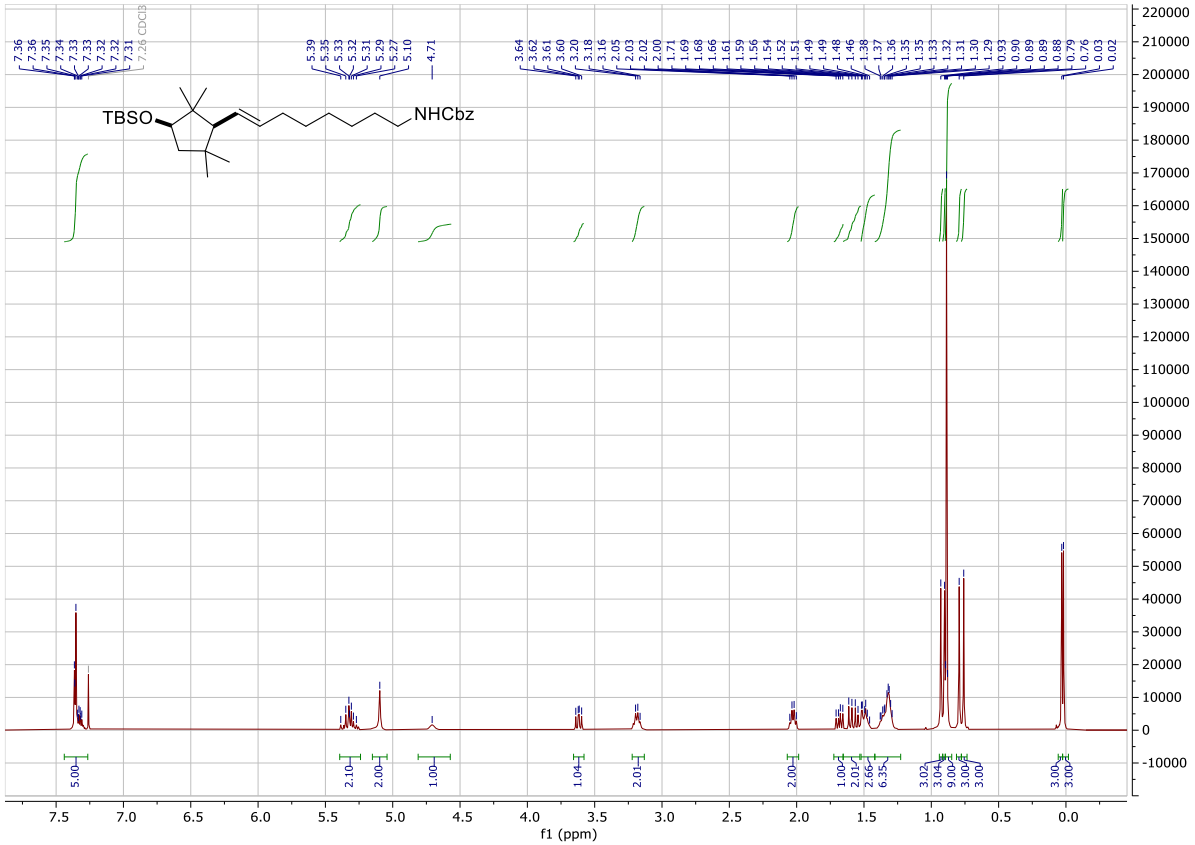


Figure S-31 ^{1}H-NMR spectrum of compound **11**.

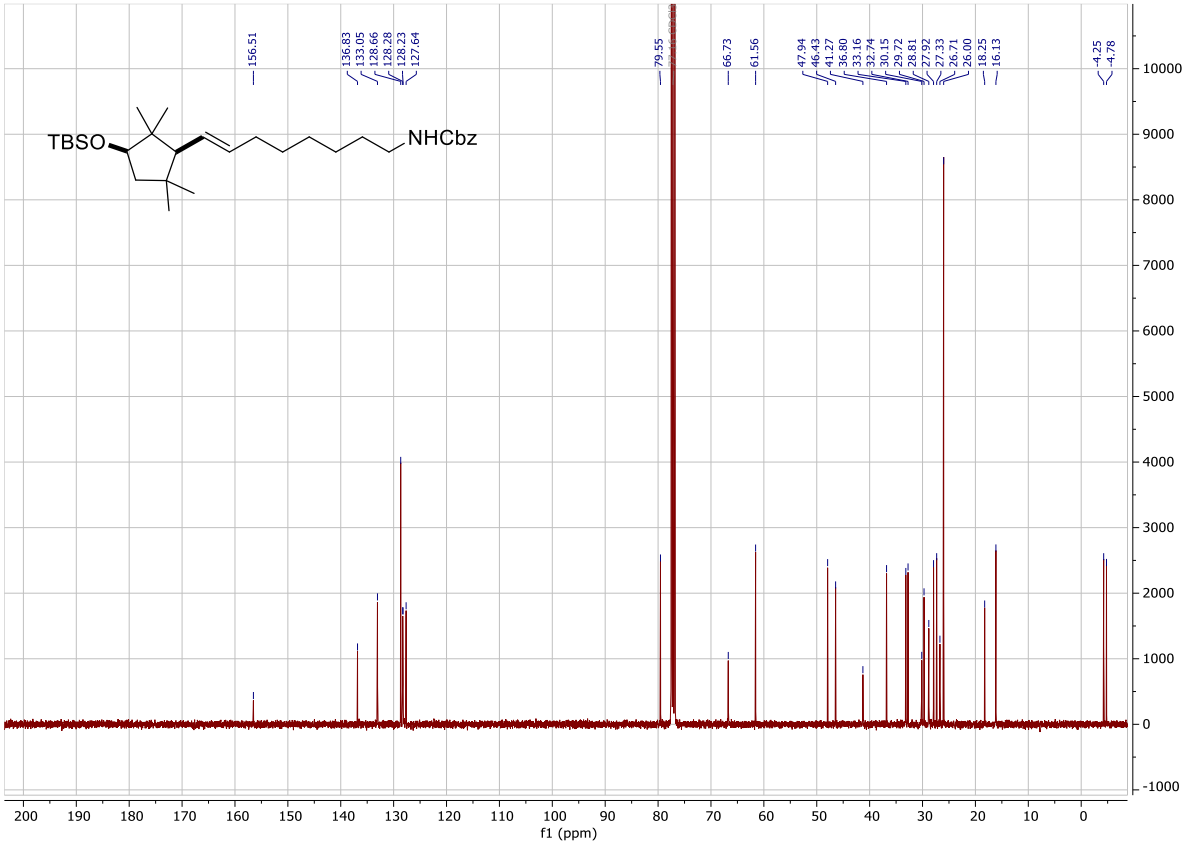


Figure 32 ^{13}C NMR spectrum of compound **11**.

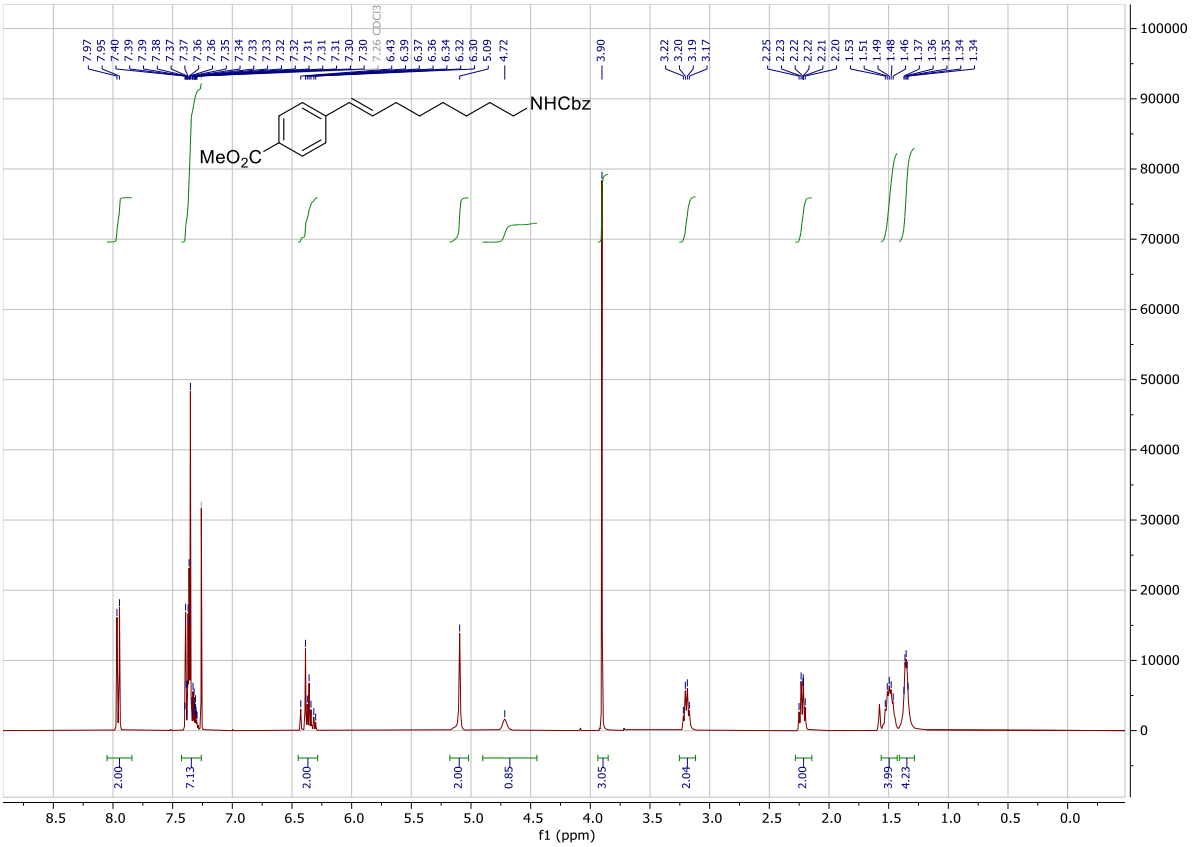


Figure S-33 ^{1}H-NMR spectrum of compound **12**.

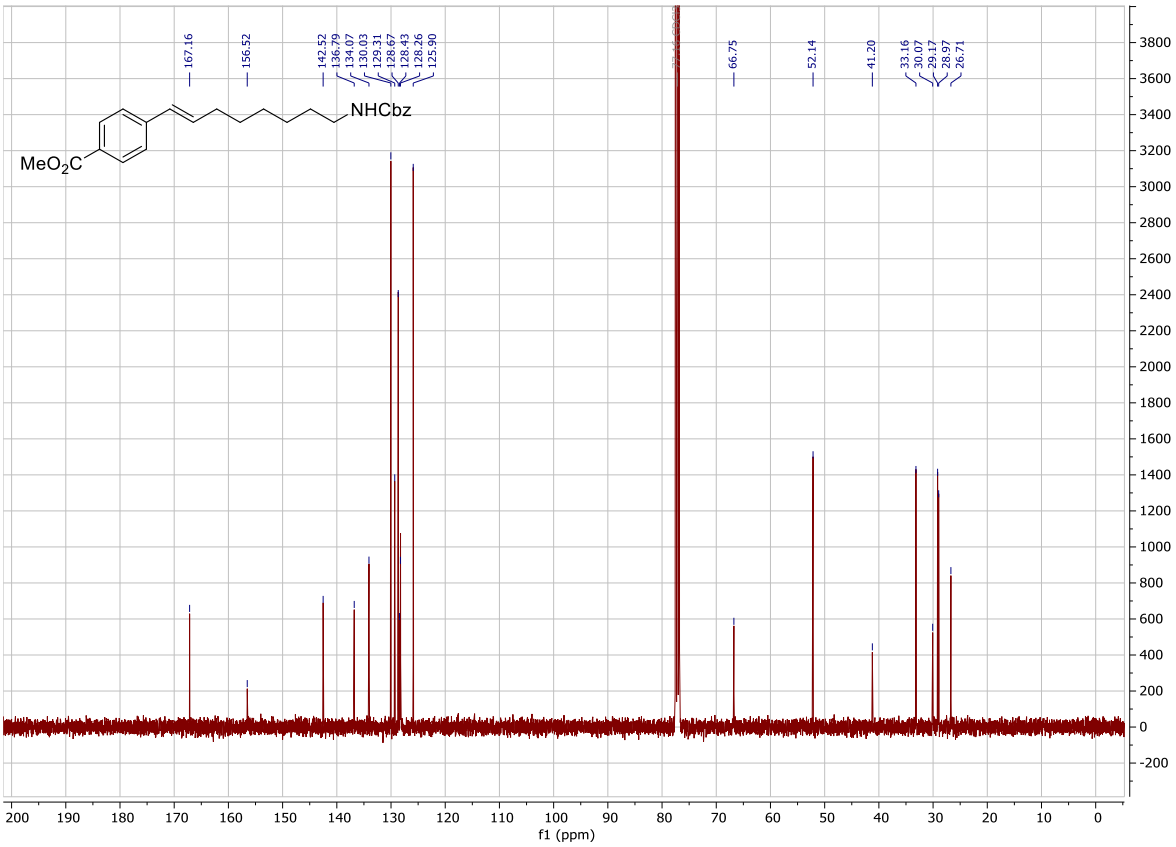


Figure 34 ^{13}C NMR spectrum of compound **12**.

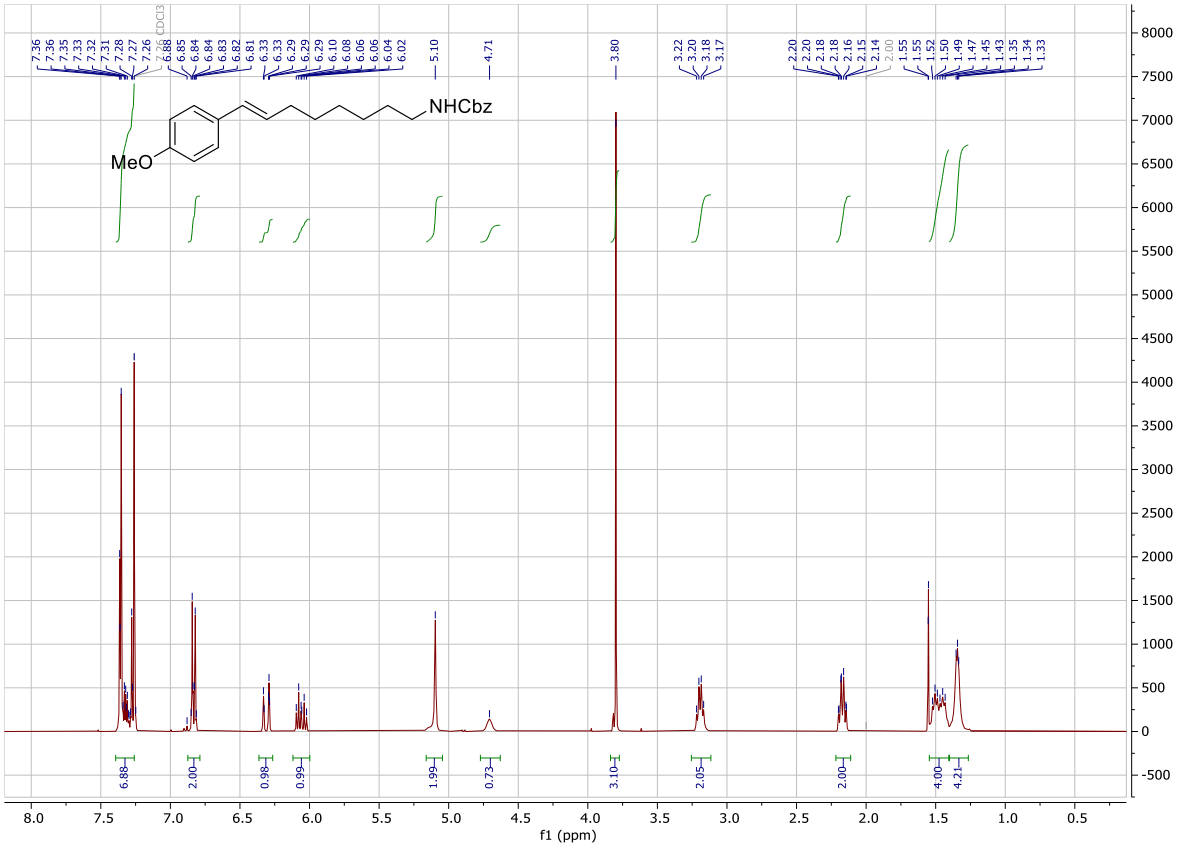


Figure S-35 ^{1}H-NMR spectrum of compound **13**.

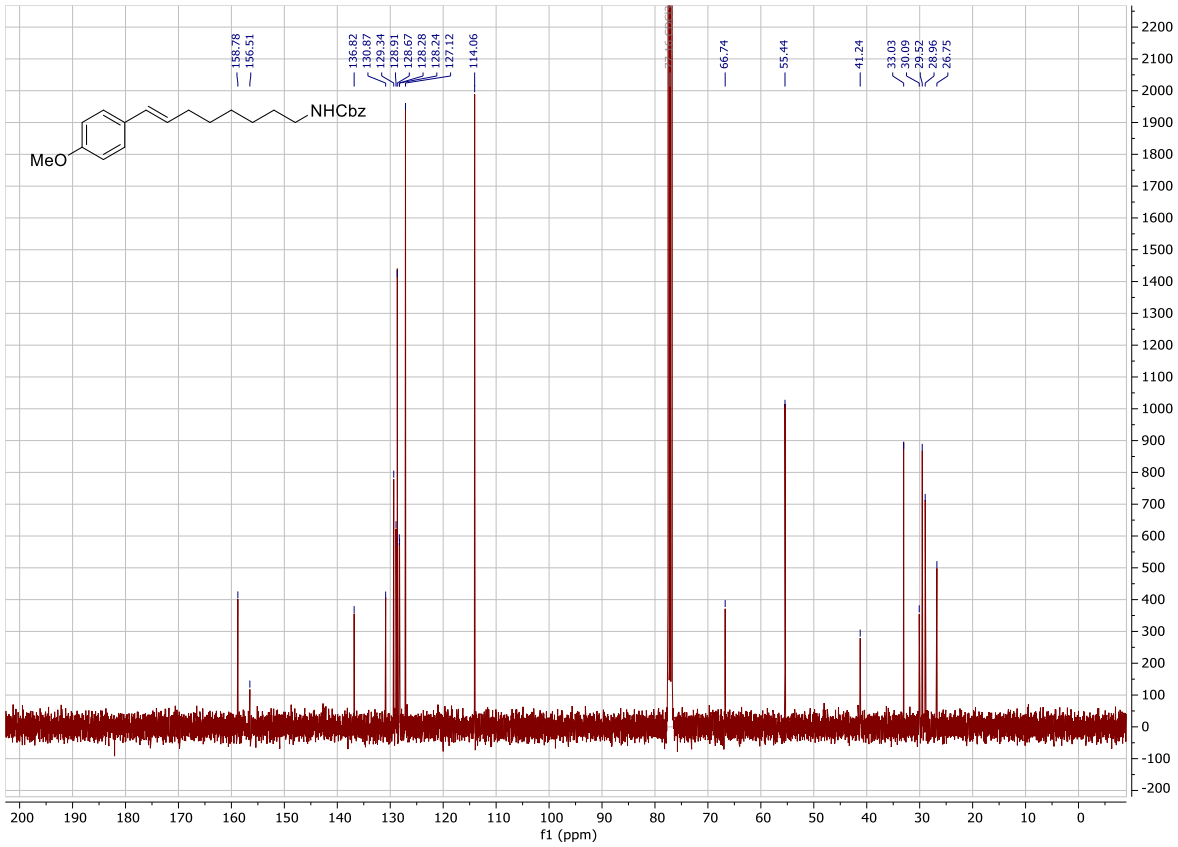


Figure 36 ^{13}C NMR spectrum of compound **13**.

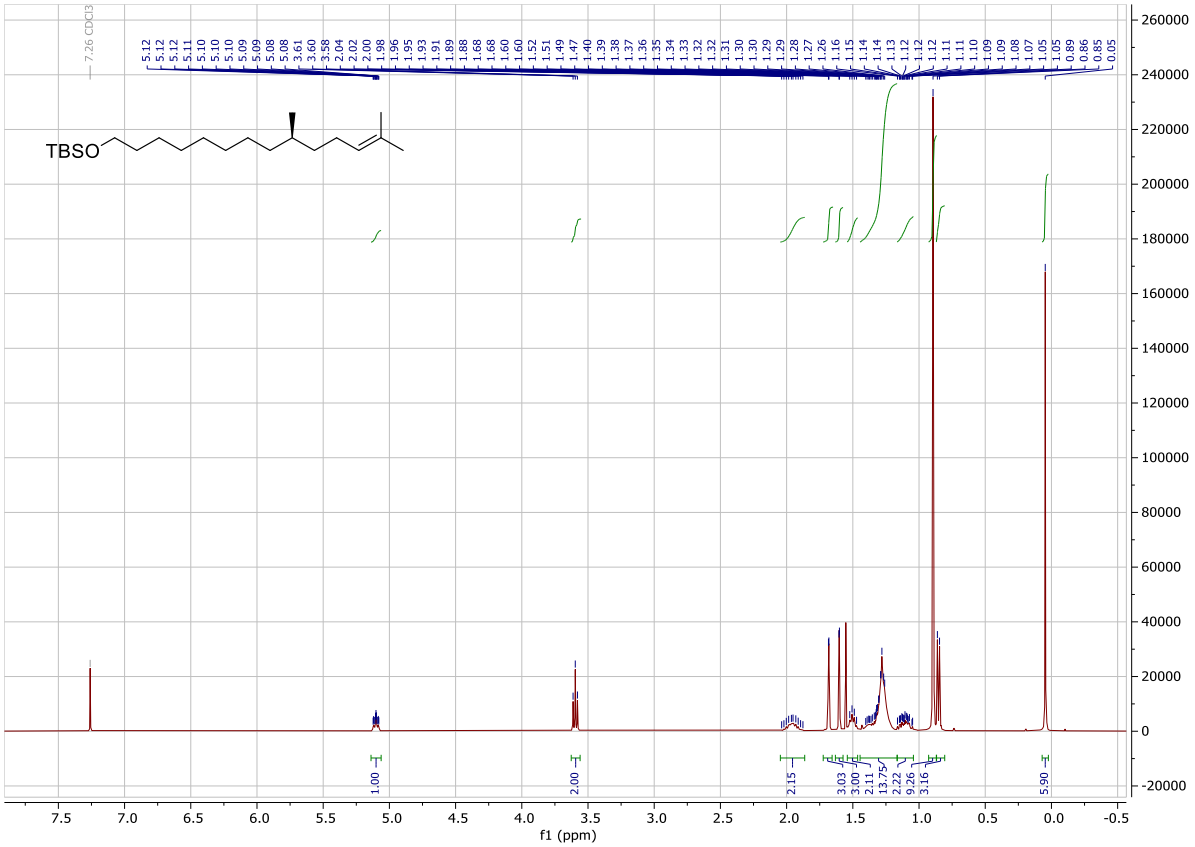


Figure S-37 ^{1}H-NMR spectrum of compound **14**.

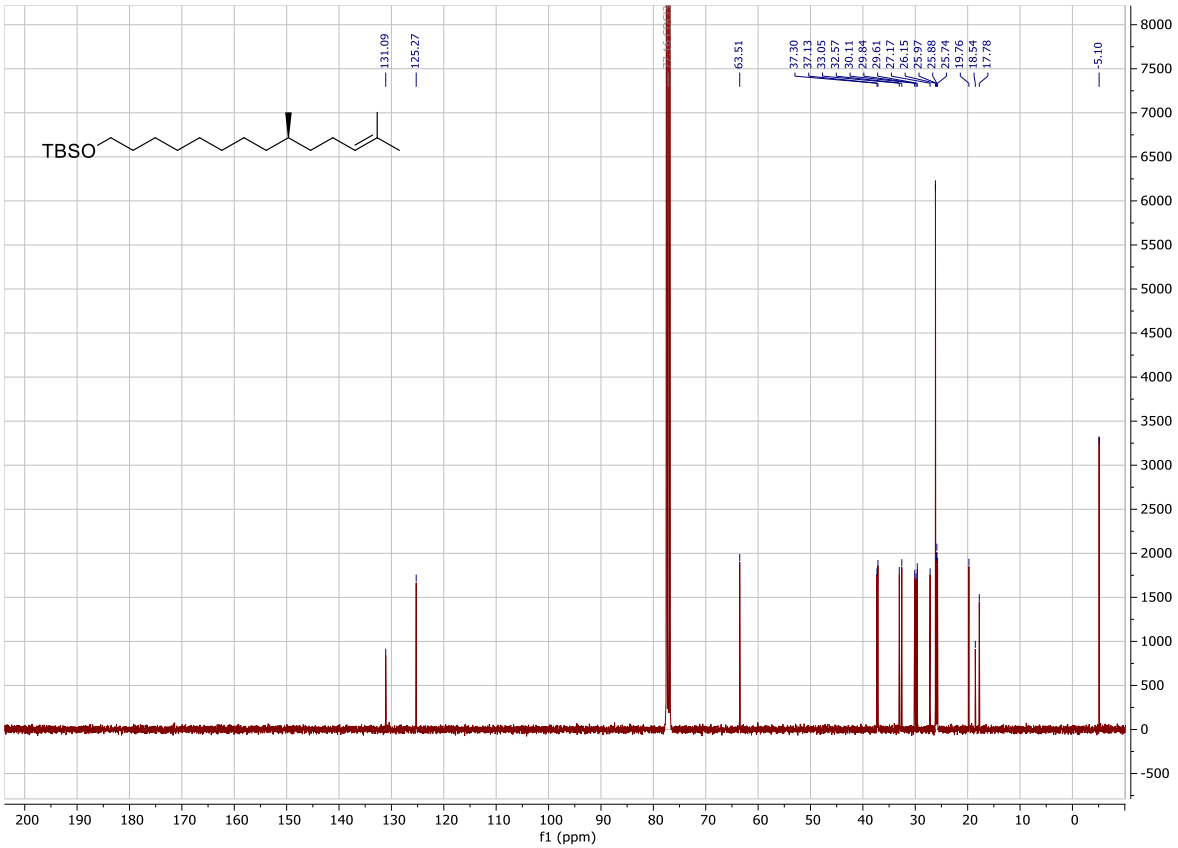


Figure S-38 ^{13}C NMR spectrum of compound **14**.

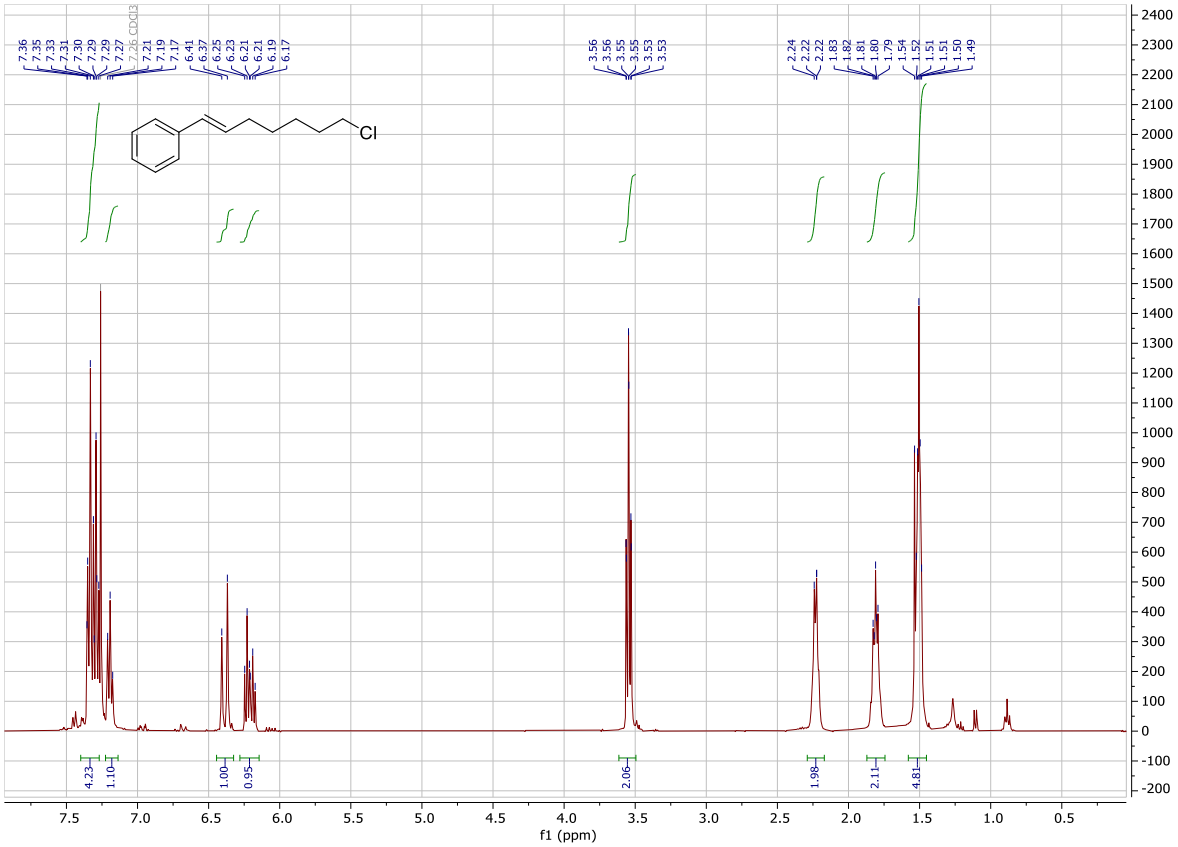


Figure S-39 ^{1}H-NMR spectrum of compound **15**.

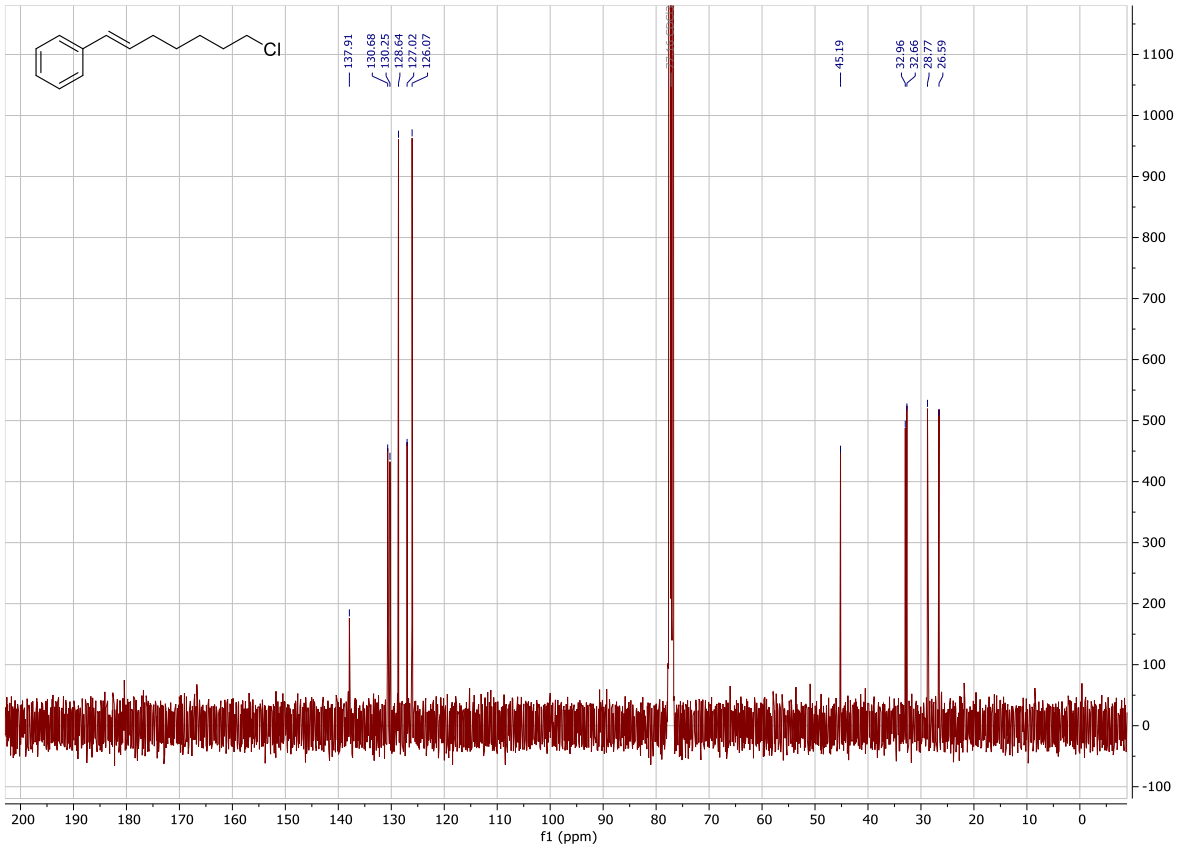


Figure 40 ^{13}C NMR spectrum of compound **15**.

Quantum Mechanical Spectral Analysis (QMSA) employing Chemadder

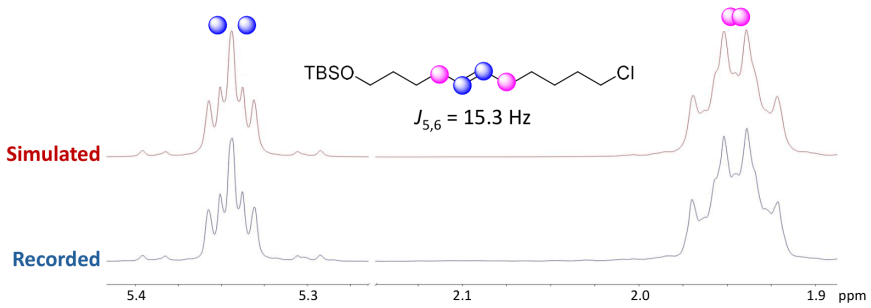


Figure S-41 Selected ^{1}H NMR resonances of the product from Entry 1: Comparison of simulated and experimental signals.

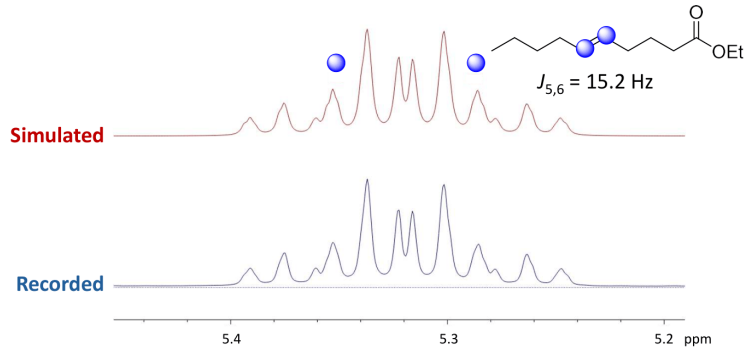


Figure S-42 Selected ^{1}H NMR resonances of the product from Entry 2: Comparison of simulated and experimental signals.

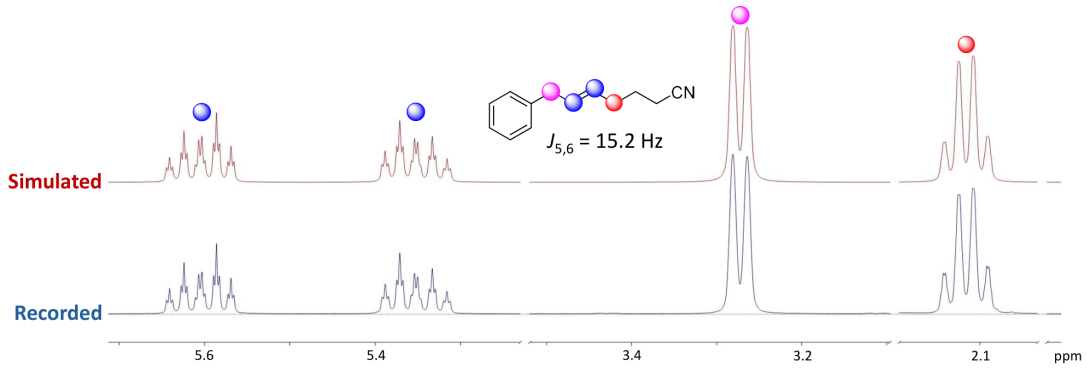


Figure S-43 Selected ^{1}H NMR resonances of the product from Entry 3: Comparison of simulated and experimental signals.

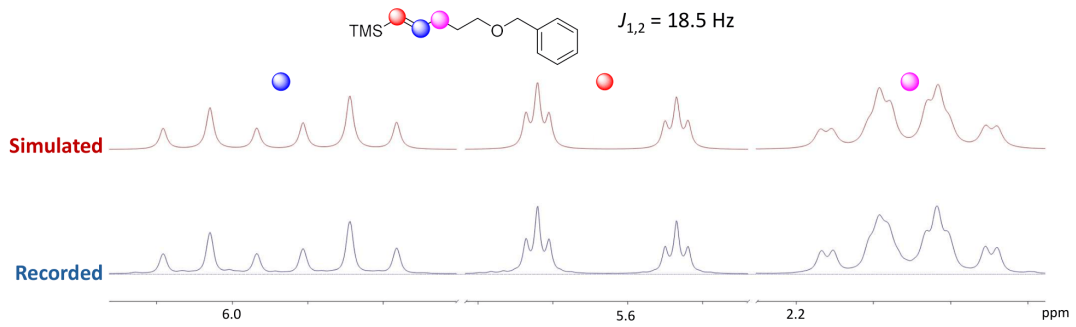


Figure S-44 Selected ^{1}H NMR resonances of the product from Entry 4: Comparison of simulated and experimental signals.

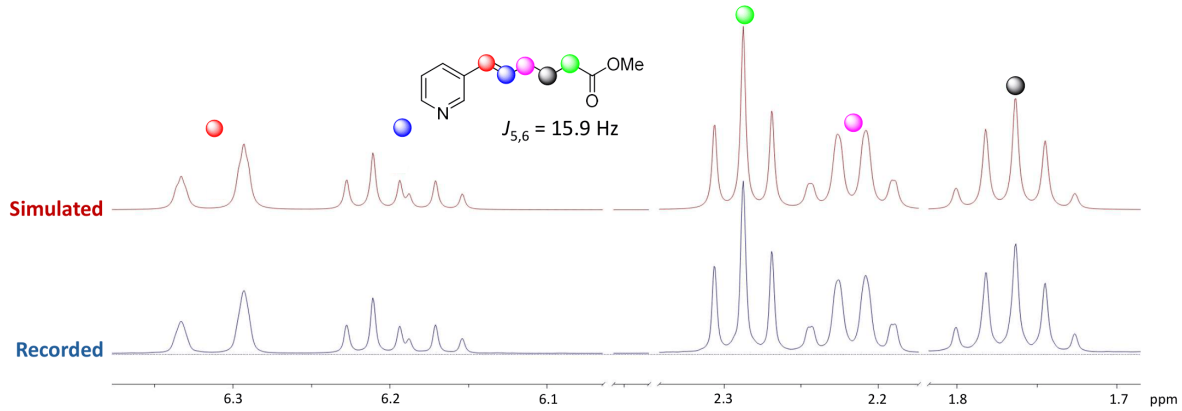


Figure S-45 Selected ^{1}H NMR resonances of the product from Entry 5: Comparison of simulated and experimental signals.

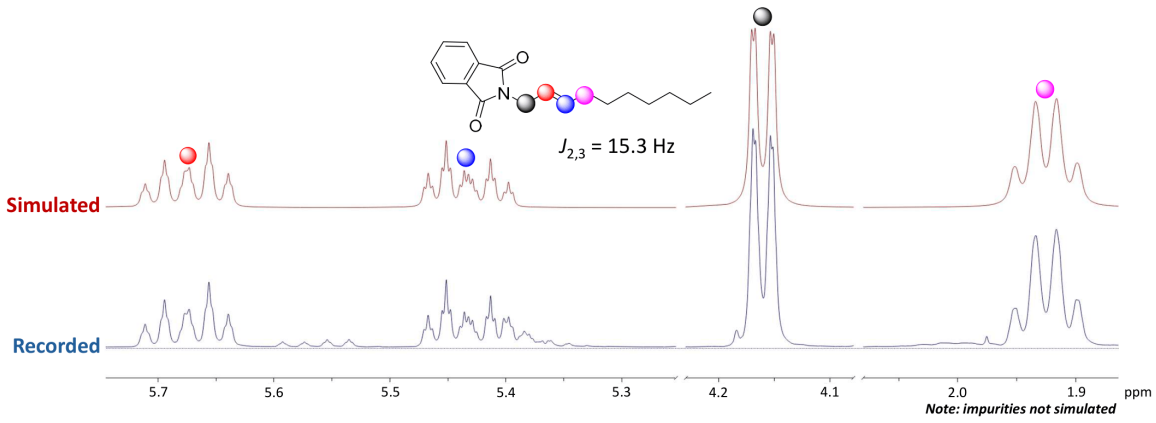


Figure S-46 Selected ^{1}H NMR resonances of the product from Entry 6: Comparison of simulated and experimental signals.

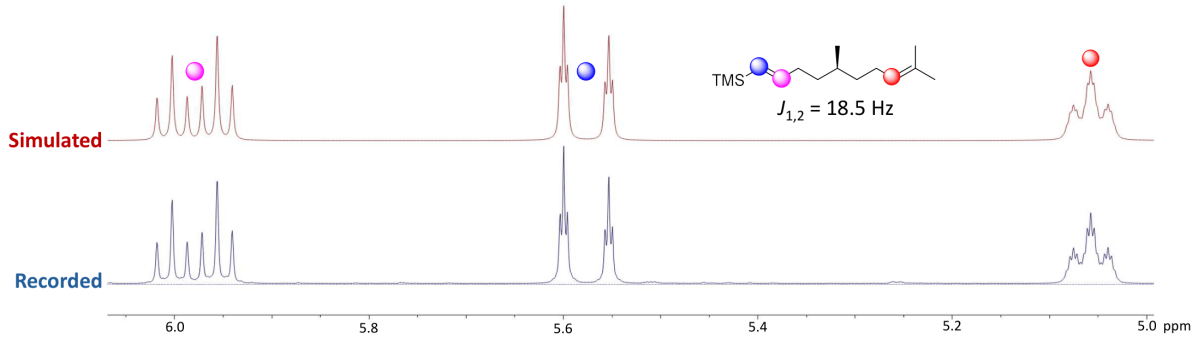


Figure S-47 Selected ^{1}H NMR resonances of the product from Entry 7: Comparison of simulated and experimental signals.

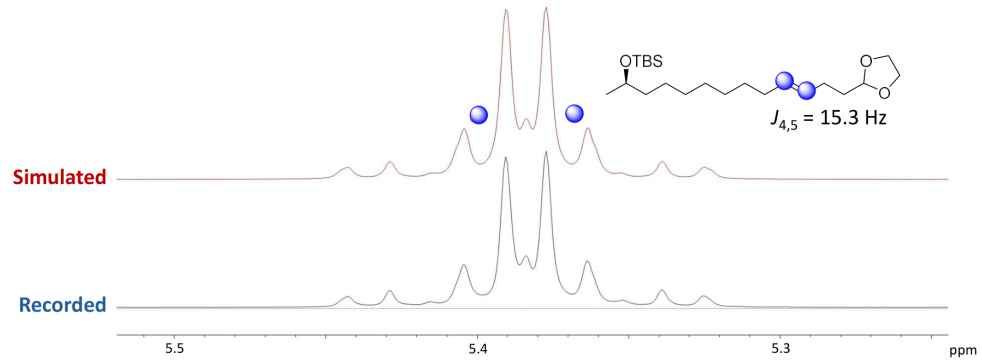


Figure S-48 Selected ^{1}H NMR resonances of the product from Entry 8: Comparison of simulated and experimental signals.

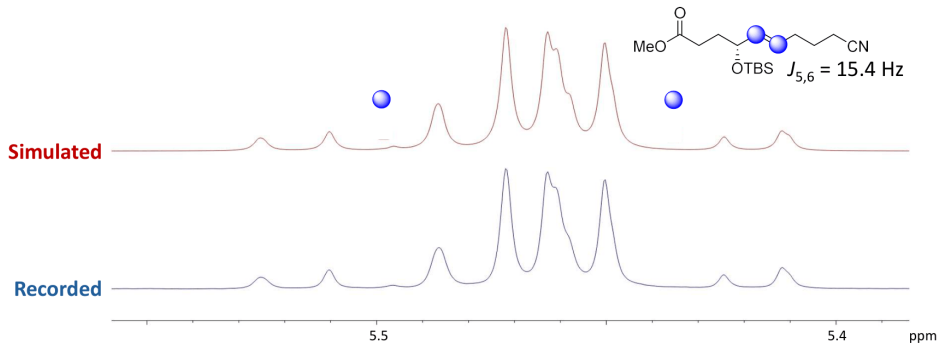


Figure S-49 Selected ^{1}H NMR resonances of the product from Entry 9: Comparison of simulated and experimental signals.

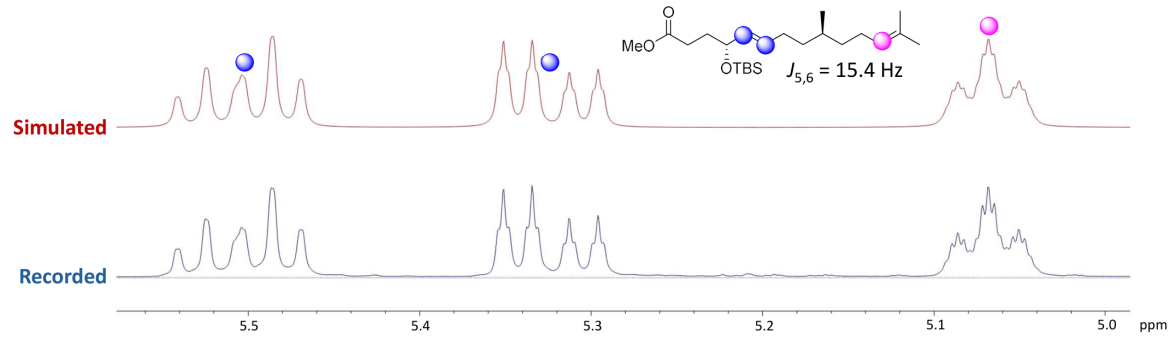


Figure S-50 Selected [1]H NMR resonances of the product from Entry 10: Comparison of simulated and experimental signals.

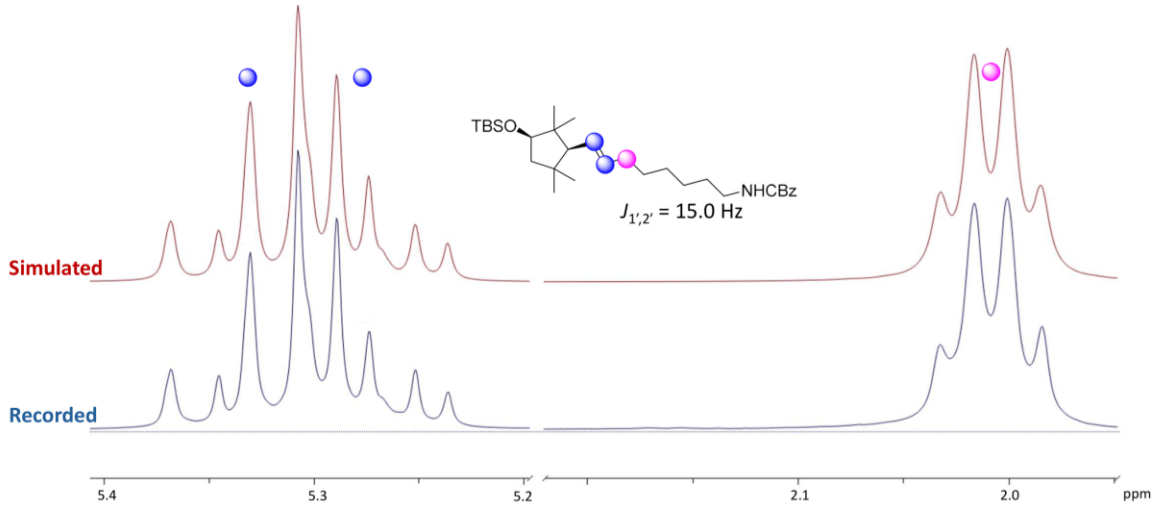


Figure S-51 Selected [1]H NMR resonances of the product from Entry 11: Comparison of simulated and experimental signals.

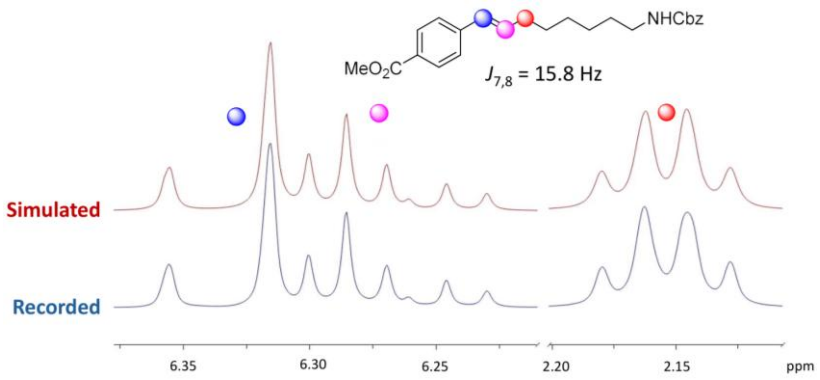


Figure S-52 Selected [1]H NMR resonances of the product from Entry 12: Comparison of simulated and experimental signals.

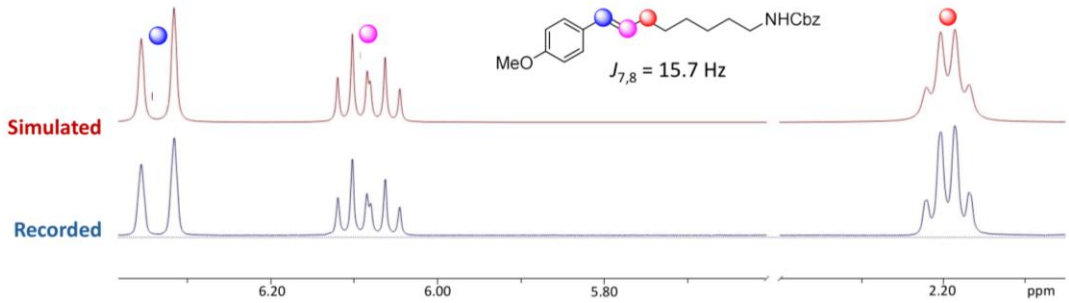


Figure S-53 Selected [1]H NMR resonances of the product from Entry 13: Comparison of simulated and experimental signals.

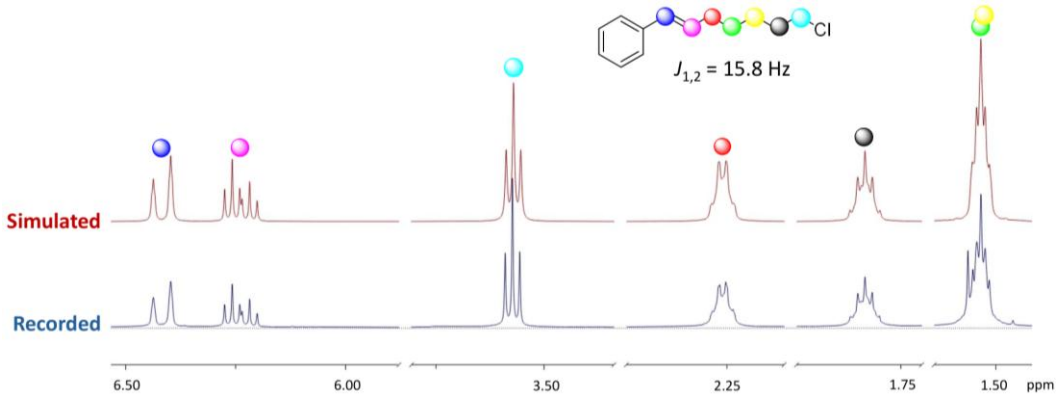
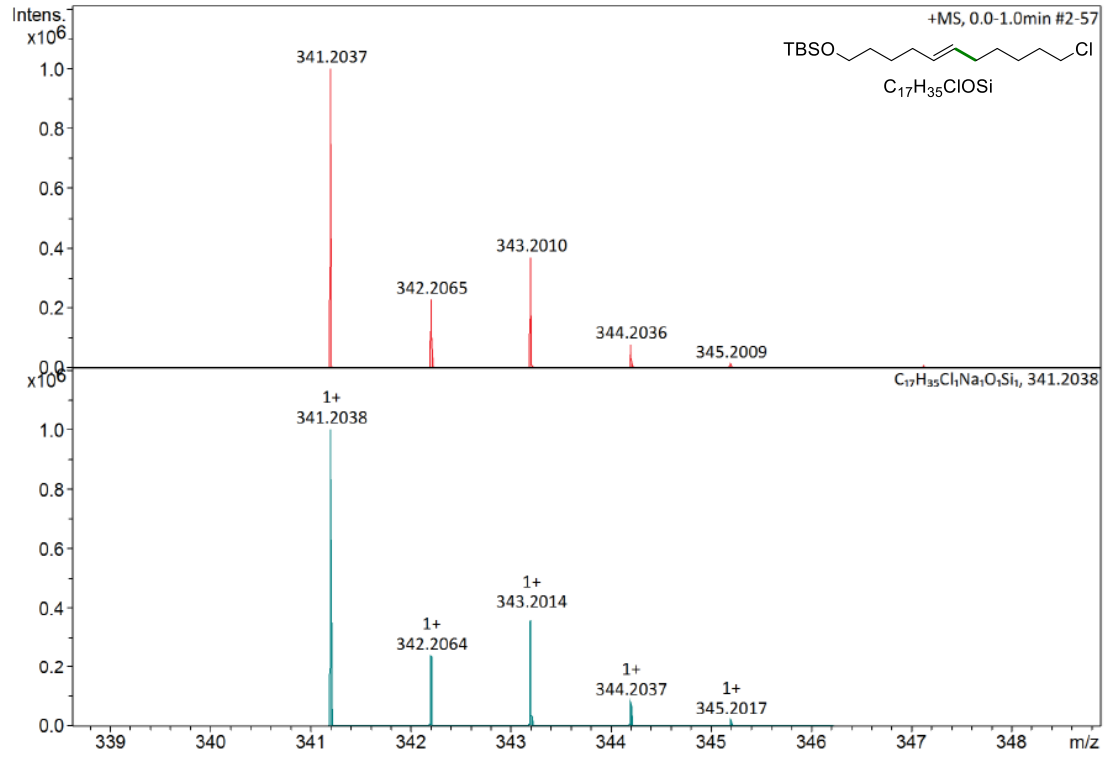


Figure S-54 Selected [1]H NMR resonances of the product from product **15**: Comparison of simulated and experimental signals.

HRMS-spectra

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.5 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Corona	0 nA	Set Divert Valve	Source
				Set APCI Heater	0 °C

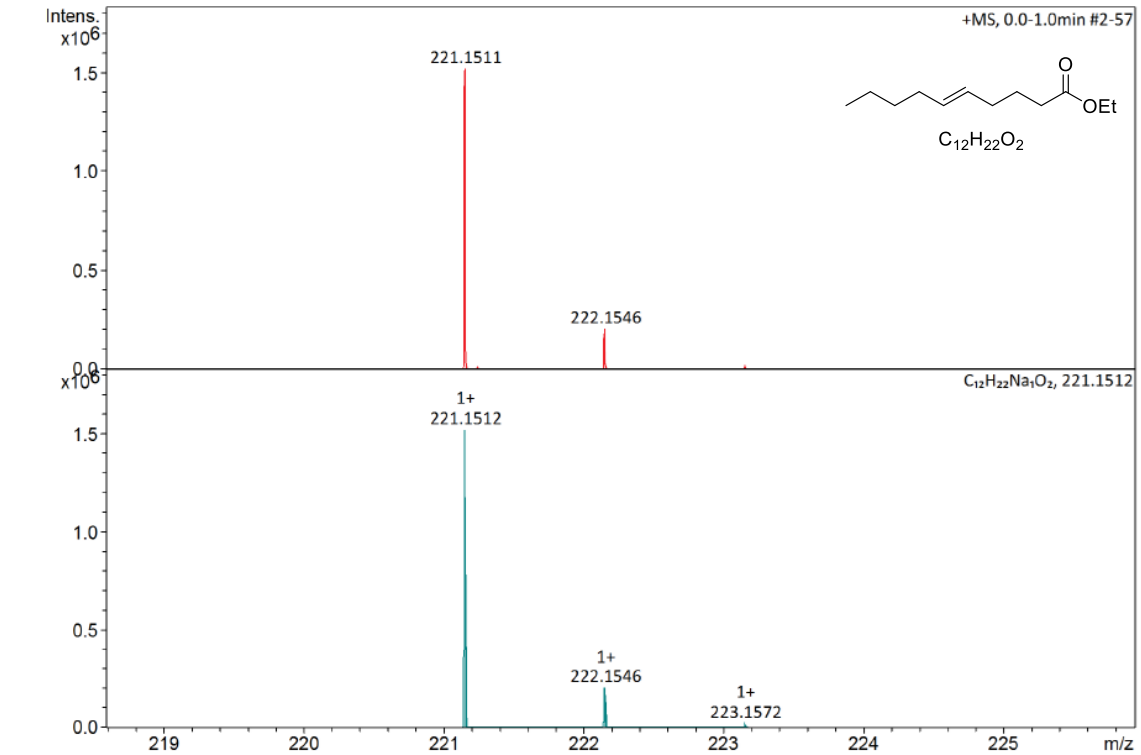


Meas. m/z	Ion Formula	m/z	err [ppm]
341.2037	C17H35ClNaOSi	341.2038	0.2

Figure S-55 HRMS of **1**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.5 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Corona	0 nA	Set Divert Valve	Source
				Set APCI Heater	0 °C

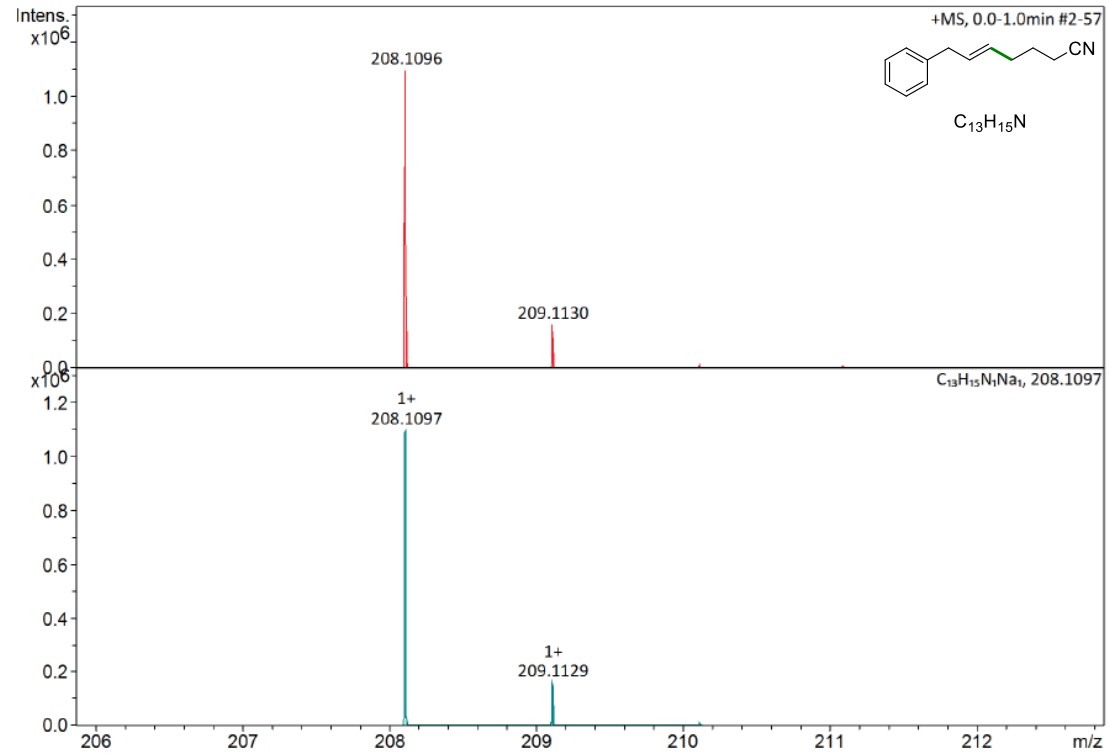


Meas. m/z	Ion Formula	m/z	err [ppm]
221.1511	C12H22NaO2	221.1512	0.4

Figure S-56 HRMS of **2**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.5 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Corona	0 nA	Set Divert Valve	Source
				Set APCI Heater	0 °C

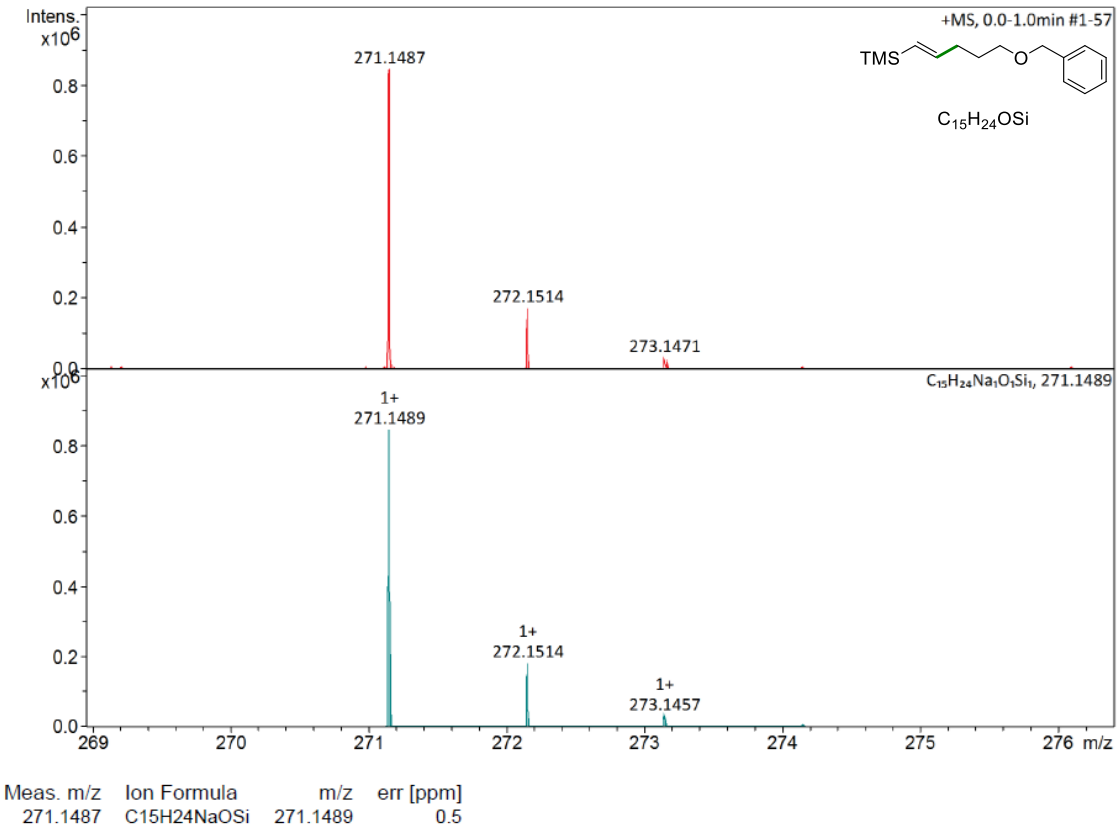


Meas. m/z	Ion Formula	m/z	err [ppm]
208.1096	C13H15NNa	208.1097	0.2

Figure S-57 HRMS of **3**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.5 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Corona	0 nA	Set Divert Valve	Source
				Set APCI Heater	0 °C

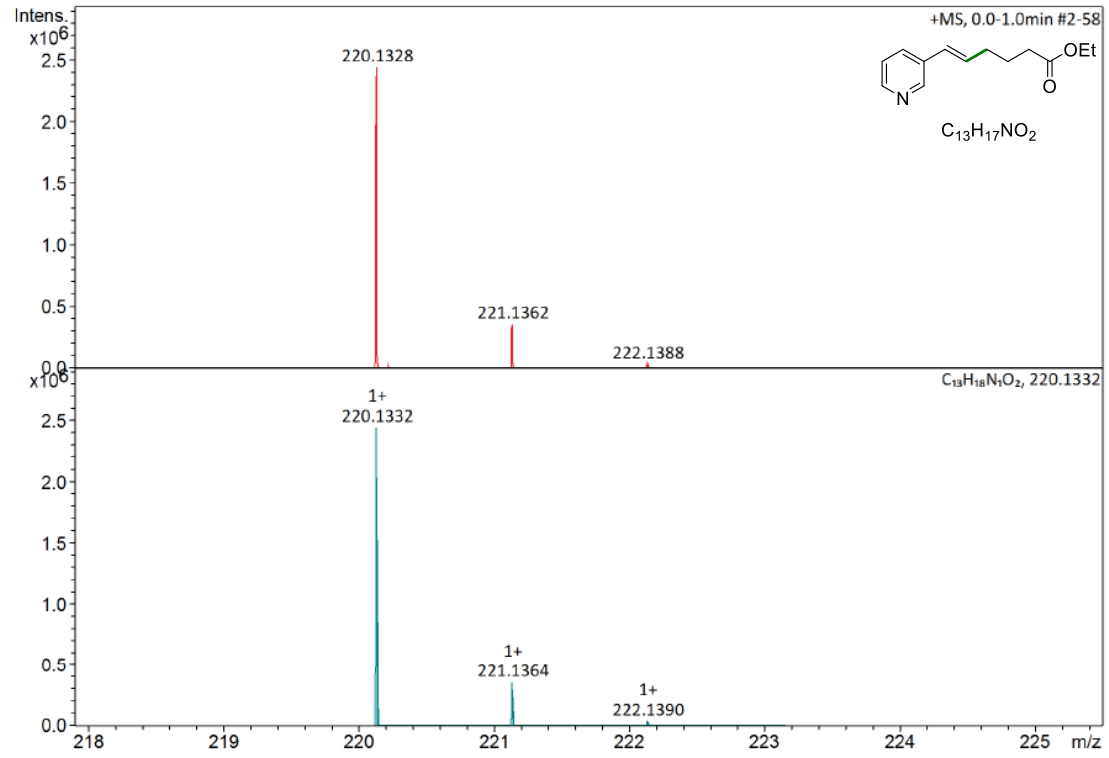


Meas. m/z	Ion Formula	m/z	err [ppm]
271.1487	C15H24NaOSi	271.1489	0.5

Figure S-58 HRMS of **4**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.5 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Corona	0 nA	Set Divert Valve	Source
				Set APCI Heater	0 °C

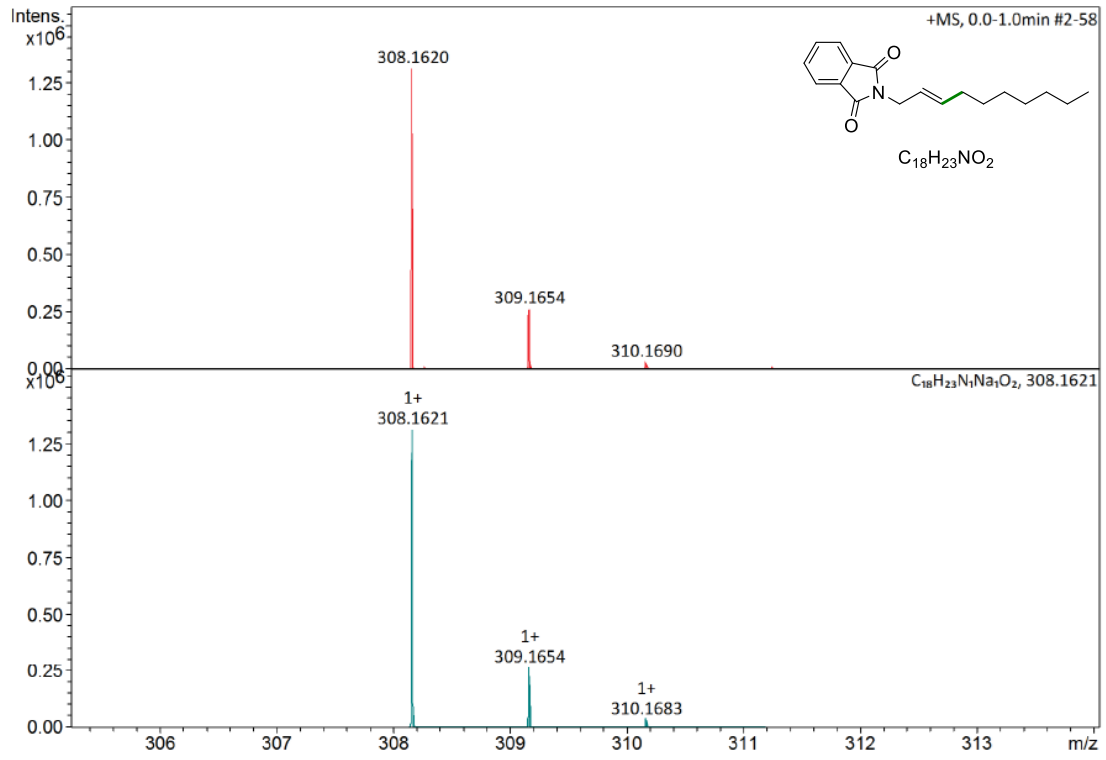


Meas. m/z	Ion Formula	m/z	err [ppm]
220.1328	C13H18NO2	220.1332	1.7
242.1148	C13H17NNaO2	242.1151	1.2

Figure S-59 HRMS of **5**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.5 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Corona	0 nA	Set Divert Valve	Source
				Set APCI Heater	0 °C

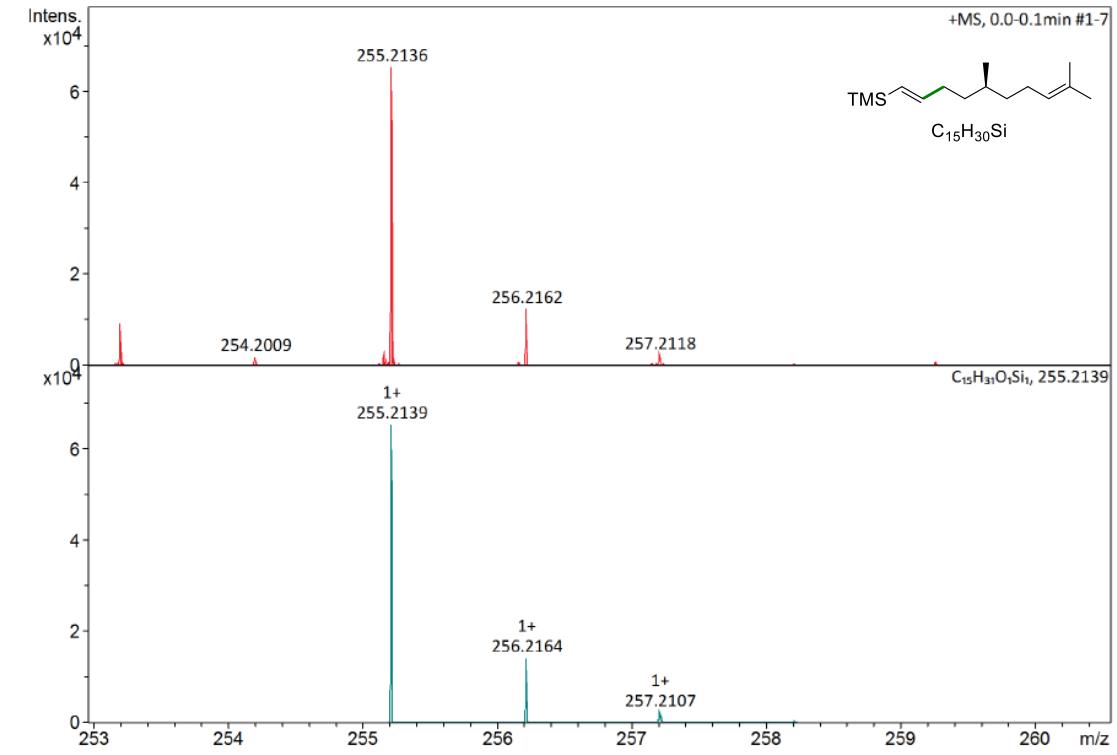


Meas. m/z	Ion Formula	m/z	err [ppm]
308.1620	C18H23NNaO2	308.1621	0.4
340.1882	C19H27NNaO3	340.1883	0.2

Figure S-60 HRMS of **6**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	APCI	Set Capillary	3000 V	Set Nebulizer	1.6 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	3.0 l/min
Scan End	1550 m/z	Set Corona	5000 nA	Set Divert Valve	Waste
				Set APCI Heater	100 °C

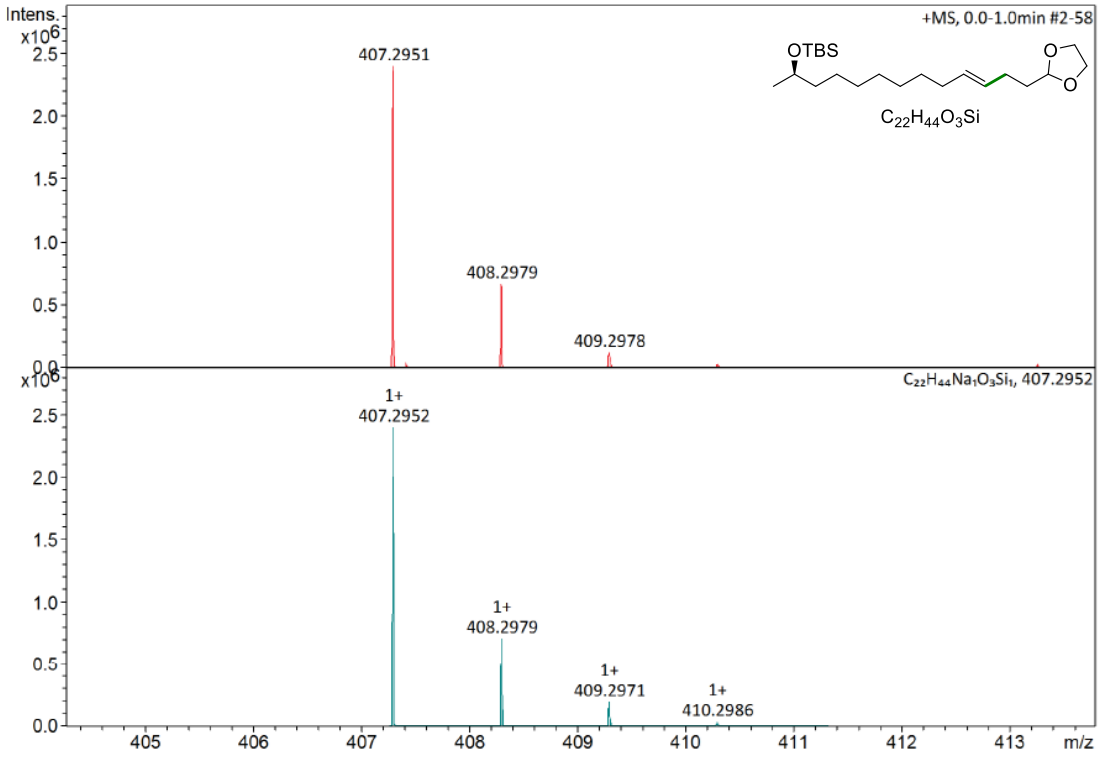


Meas. m/z	Ion Formula	m/z	err [ppm]
255.2136	C15H31OSi	255.2139	1.2

Figure S-61 HRMS of **7**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.5 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Corona	0 nA	Set Divert Valve	Source
				Set APCI Heater	0 °C

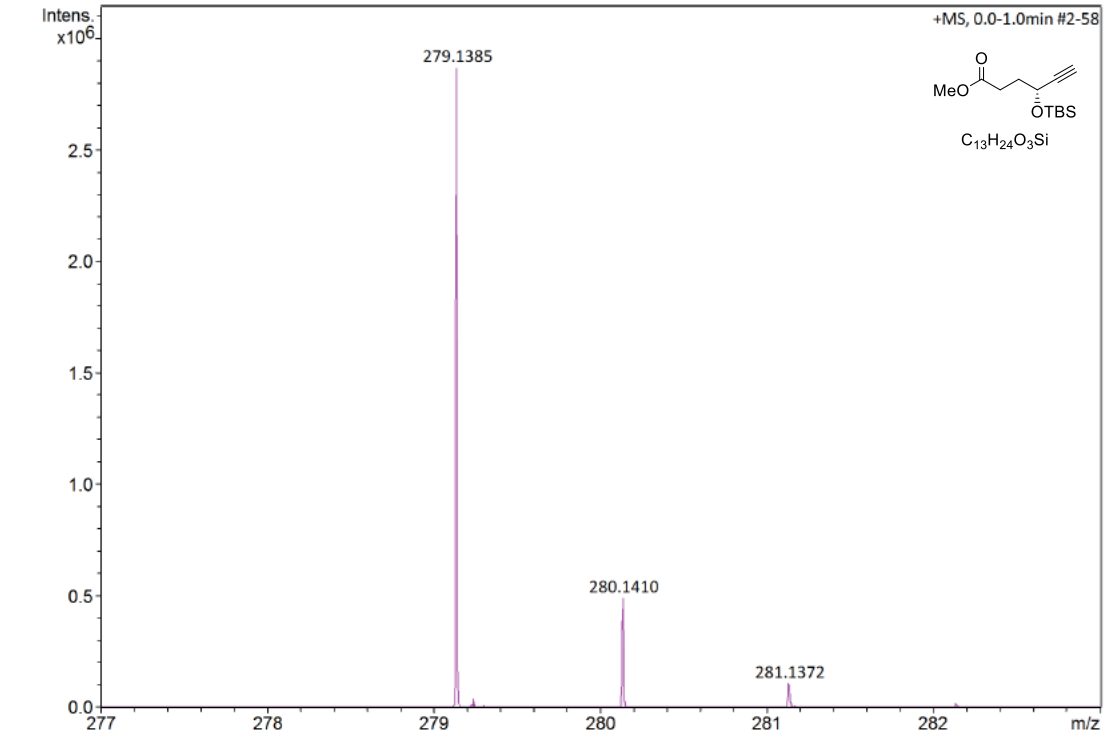


Meas. m/z	Ion Formula	m/z	err [ppm]
407.2951	C22H44NaO3Si	407.2952	0.3

Figure S-62 HRMS of **8**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.5 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Corona	0 nA	Set Divert Valve	Waste
				Set APCI Heater	0 °C

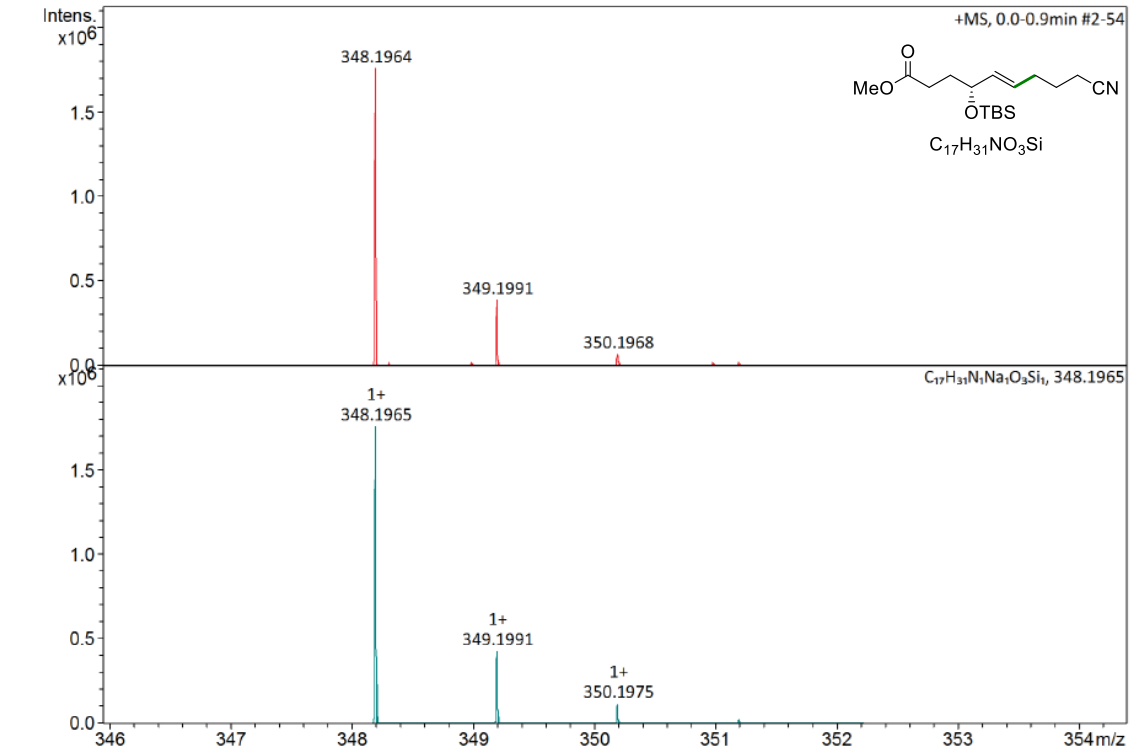


Meas. m/z	Ion Formula	m/z	err [ppm]
279.1385	C13H24NaO3Si	279.1387	0.8

Figure S-63 HRMS of **9b**.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.5 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Corona	0 nA	Set Divert Valve	Source
				Set APCI Heater	0 °C

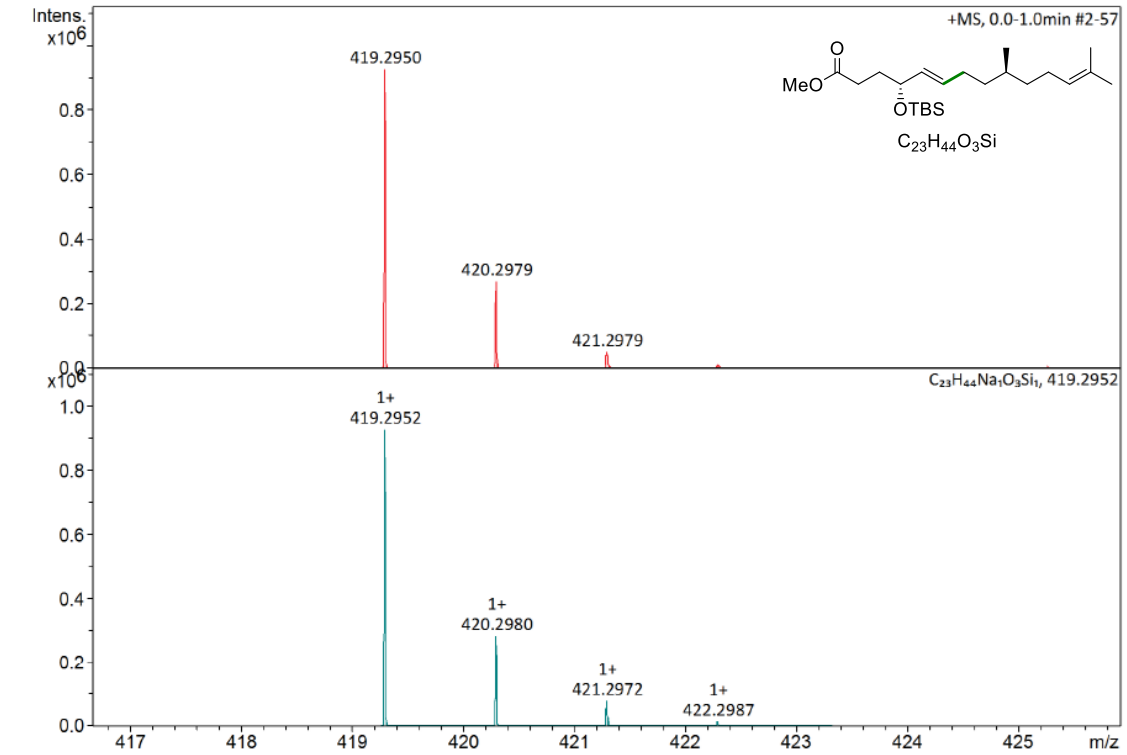


Meas. m/z	Ion Formula	m/z	err [ppm]
348.1964	C17H31NNaO3Si	348.1965	0.4

Figure S-64 HRMS of **9**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.5 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Corona	0 nA	Set Divert Valve	Source
				Set APCI Heater	0 °C

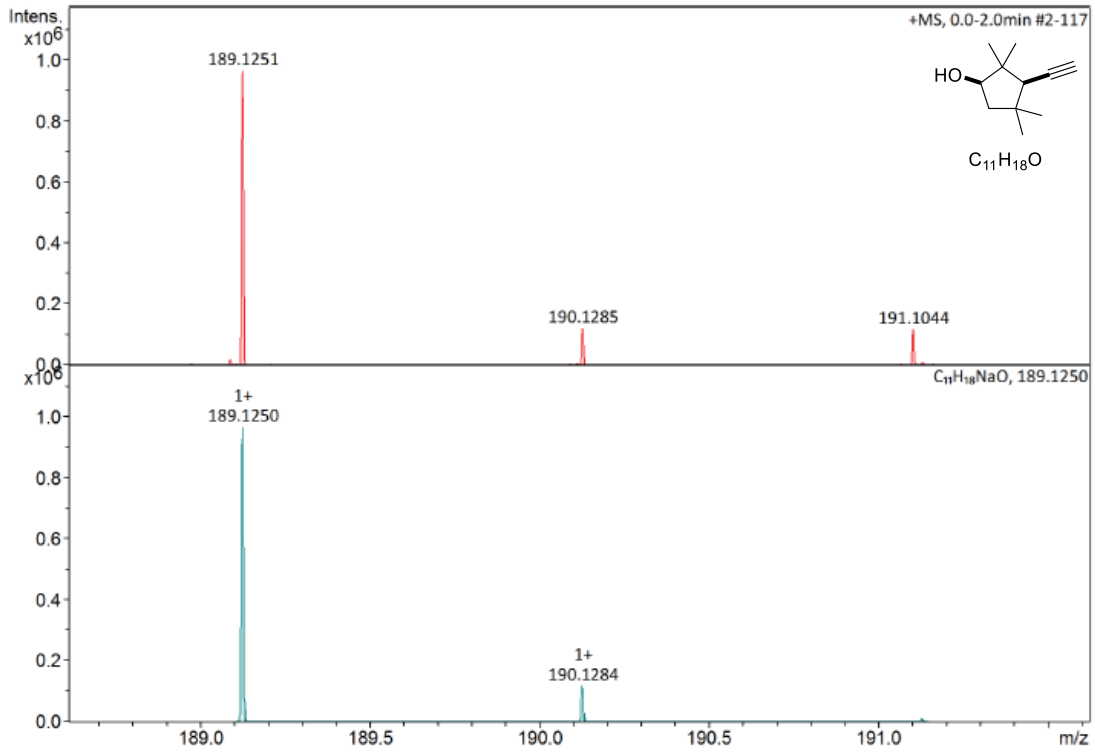


Meas. m/z	Ion Formula	m/z	err [ppm]
419.2950	C23H44NaO3Si	419.2952	0.3

Figure S-65 HRMS of **10**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.4 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Corona	0 nA	Set Divert Valve	Waste
				Set APCI Heater	0 °C

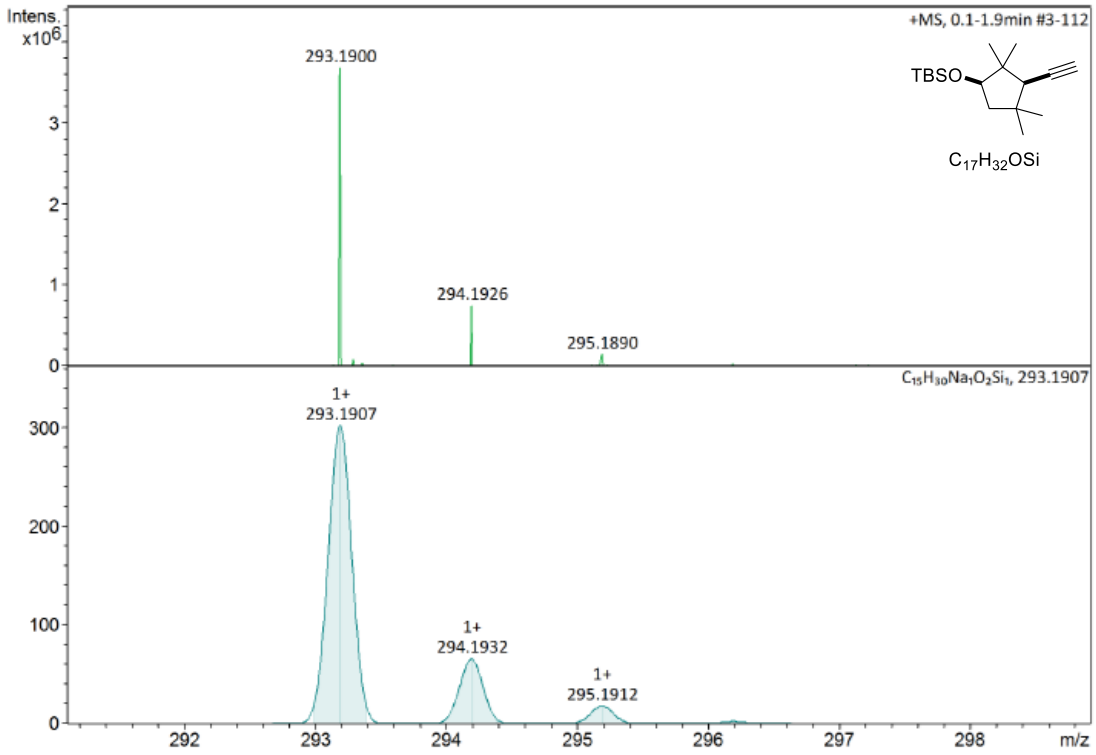


Meas. m/z	Ion Formula	m/z	err [ppm]
179.1044	C7H11N6	179.1040	-2.7
	C9H16NaO2	179.1043	-1.1
189.1251	C8H17N2O3	189.1234	-9.3
	C11H18NaO	189.1250	-0.8
195.0993	C7H11N6O	195.0989	-2.1
	C9H16NaO3	195.0992	-0.7
209.1148	C8H13N6O	209.1145	-1.5
	C10H18NaO3	209.1148	-0.1
237.1460	C10H17N6O	237.1458	-0.7
	C12H22NaO3	237.1461	0.5
357.2396	C19H29N6O	357.2397	0.4
	C21H34NaO3	357.2400	1.1
519.3644	C26H51N2O8	519.3640	-0.7
	C26H44N10Na	519.3643	-0.2

Figure 66 HRMS of **11b**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.4 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Corona	0 nA	Set Divert Valve	Waste
				Set APCI Heater	0 °C

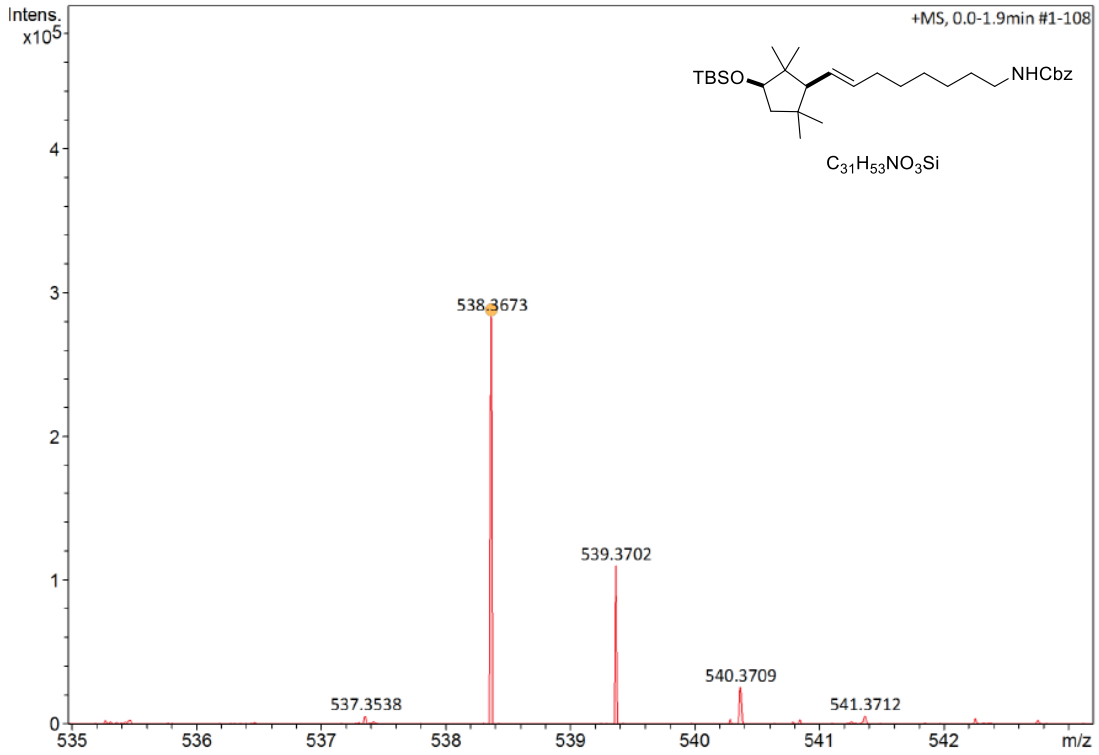


Meas. m/z	Ion Formula	m/z	err [ppm]
287.1459	C17H23O2Si	287.1462	0.9
	C9H16N10Na	287.1452	-2.7
293.1900	C15H30NaO2Si	293.1907	2.6
303.2106	C14H31N2O3Si	303.2098	-2.6
	C17H32NaOSi	303.2115	2.7
311.2006	C13H27N6OSi	311.2010	1.3
	C15H32NaO3Si	311.2013	2.2
351.2316	C15H35N2O5Si	351.2310	-1.9
	C18H36NaO3Si	351.2326	2.7
451.3020	C29H43O2Si	451.3027	1.6
	C27H44NaO2Si	451.3003	-3.8
563.3902	C32H51N6OSi	563.3888	-2.4
	C34H56NaO3Si	563.3891	-1.9

Figure 67 HRMS of **11c**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.5 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Corona	0 nA	Set Divert Valve	Waste
				Set APCI Heater	0 °C

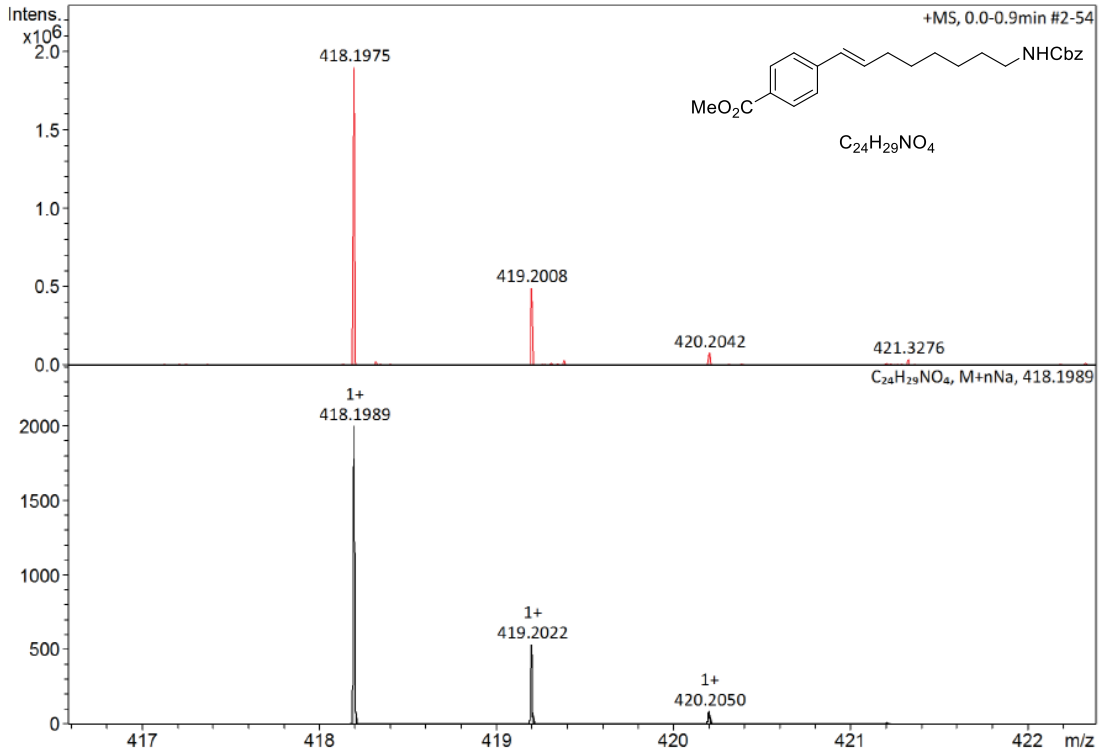


Meas. m/z	Ion Formula	m/z	err [ppm]
295.1936	C13H31O5Si	295.1935	-0.3
323.2249	C15H35O5Si	323.2248	-0.1
538.3673	C27H49N7NaOSi	538.3660	-2.3
	C29H54NNa2O3Si	538.3663	-1.8
	C31H53NNaO3Si	538.3687	2.7

Figure S-68 HRMS of **11**: *Top*: experimental HRMS spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.4 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Corona	0 nA	Set Divert Valve	Waste
				Set APCI Heater	0 °C

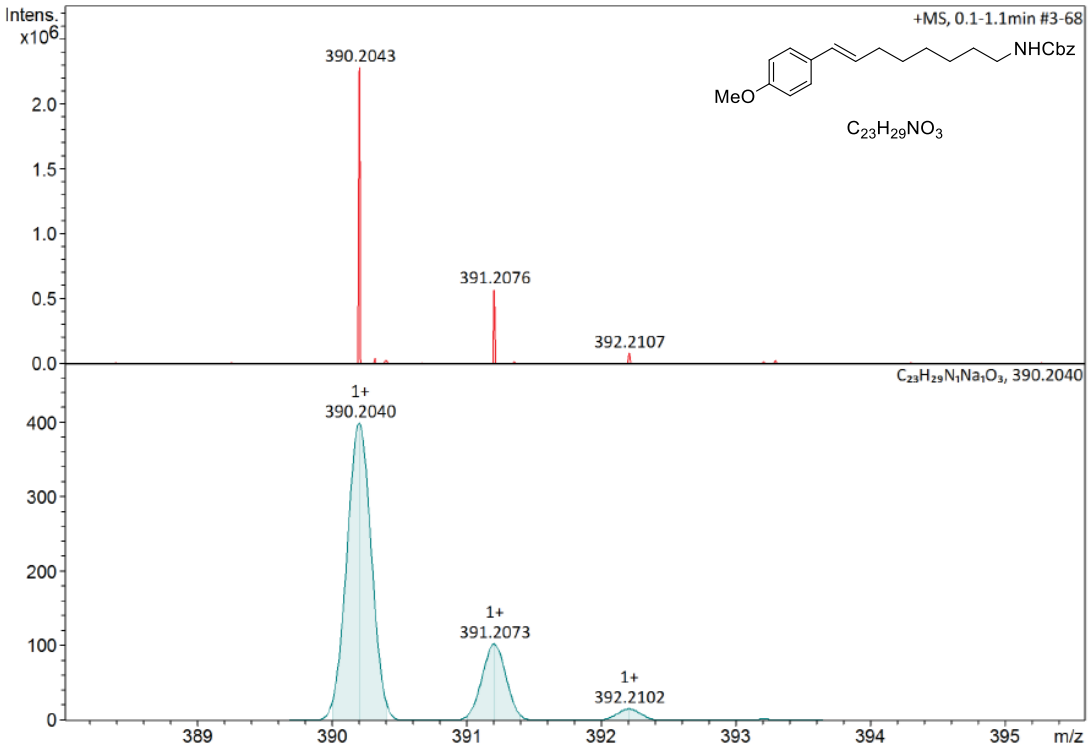


Meas. m/z	Ion Formula	m/z	err [ppm]
418.1975	C21H28N3O6	418.1973	-0.5
	C24H29NNaO4	418.1989	3.4
	C20H25N7NaO2	418.1962	-3.1
434.1713	C24H24N3O5	434.1710	-0.7
	C23H21N7NaO	434.1700	-3.1
	C27H25NNaO3	434.1727	3.0

Figure S-69 HRMS of **12**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	3500 V	Set Nebulizer	0.4 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Corona	0 nA	Set Divert Valve	Waste
				Set APCI Heater	0 °C

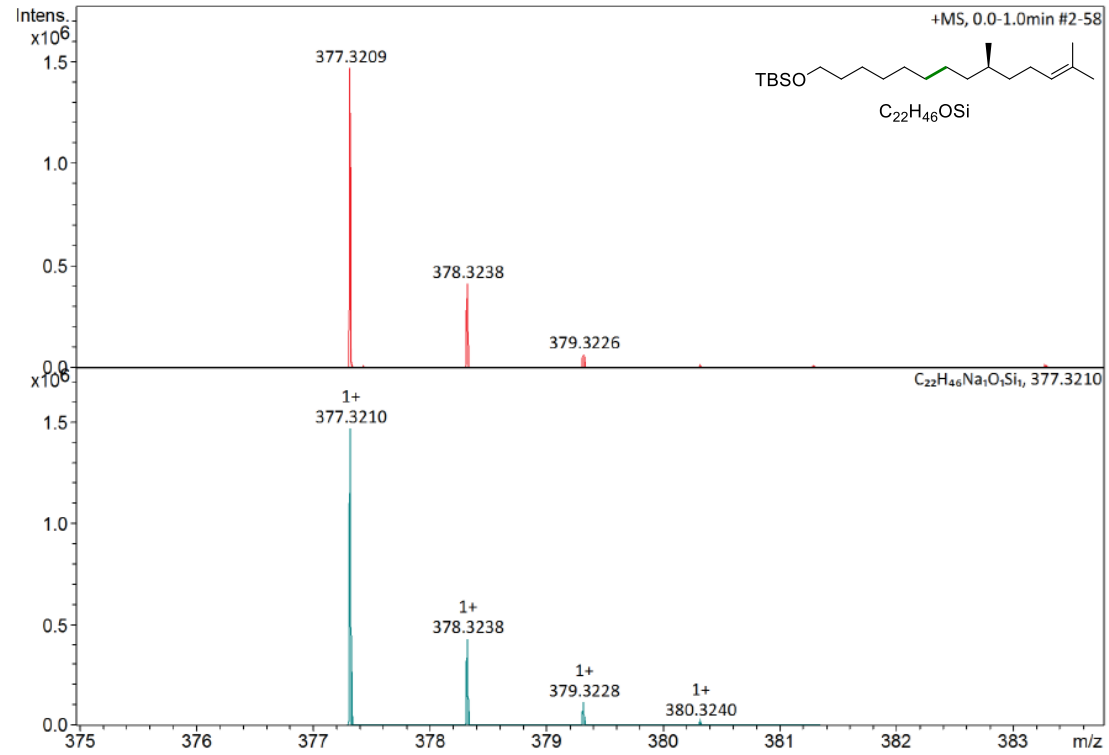


Meas. m/z	Ion Formula	m/z	err [ppm]
390.2043	C21H24N7O	390.2037	-1.5
	C23H29NNaO3	390.2040	-0.8
406.1782	C24H20N7	406.1775	-1.8
	C26H25NNaO2	406.1777	-1.1

Figure 70 HRMS of **13**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

Acquisition Parameter

Source Type	ESI	Set Capillary	4000 V	Set Nebulizer	0.5 Bar
Focus	Not active	Set End Plate Offset	-500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Charging Voltage	2000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Corona	0 nA	Set Divert Valve	Source
				Set APCI Heater	0 °C



Meas. m/z	Ion Formula	m/z	err [ppm]
377.3209	C22H46NaOSi	377.3210	0.3

Figure S-71 HRMS of **14**: *Top*: experimental HRMS spectrum. *Bottom*: simulated spectrum.

References

(1) Takahashi, K.; Arai, Y.; Ikegami-Kawai, M.; Honda, T. The formal synthesis of (+)-15-deoxy-Δ12,14-prostaglandin J2 by utilizing SmI2-promoted intramolecular coupling of bromoalkynes and α,β-unsaturated esters. *Tetrahedron* **2020**, *76* (19), 131148.
(2) DeLuca, R. J.; Edwards, J. L.; Steffens, L. D.; Michel, B. W.; Qiao, X. Z., C.; Cook, S. P.; Sigman, M. S. Wacker-Type Oxidation of Internal Alkenes using Pd(Quinox) and TBHP. *J. Org. Chem.* **2013**, *78* (4), 1682–1686.
(3) Xing, Y.; O'Doherty, G. A. De Novo Asymmetric Synthesis of Cladospolide B−D: Structural Reassignment of Cladospolide D via the Synthesis of its Enantiomer. *Org. Lett.* **2009**, *11* (5), 1107–1110.