Supporting Information

for

Development of the "diverted Heck" reaction for the synthesis of five-membered rings

Kevin Breitwieser, and Peter Chen*

Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule (ETH) Zürich, CH-8093 Zürich, Switzerland

ABSTRACT: The "diverted Heck" reaction has been shown to be a potent method to synthesize cyclopropanes from electron-rich olefins and iodomethyl trifluoroborate. Nevertheless, it is not mechanistically limited to the three-membered rings. The synthesis of five-membered rings using bifunctional substrates with a halide moiety and an organometallic group is described. Furthermore, the reactions of the respective boron and tin-based substrates are further investigated and optimized.

Correspondence to: peter.chen@org.chem.ethz.ch

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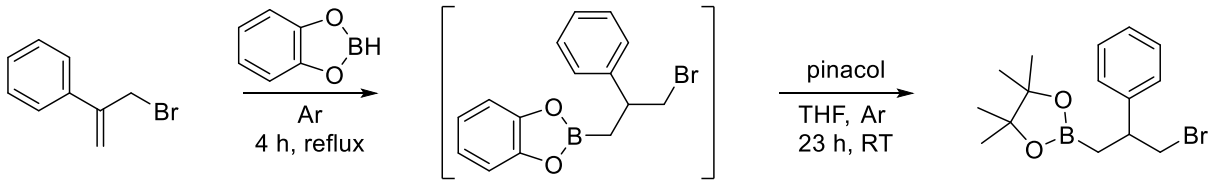
I-General remarks

Unless otherwise stated, all reactions were carried out under an argon or nitrogen atmosphere using standard Schlenk or glovebox techniques with anhydrous solvents. Pressure reactions were carried out with the assistance of the high pressure lab of ETH Zürich. Deuterated chloroform was acquired from Cambridge Isotope Laboratories. Acetone (99.8% extra dry), *N*,*N*-dimethylformamide (99.8% extra dry over molsieve), acetonitrile (99.9% extra dry over molsieve), ethyl acetate (99.9% extra dry over molsieve), ethylene glycol (99.8%) and isopropanol (99.5% over molsieve) were acquired from Acros Organics and used as received. *N*,*N*-dimethylacetamide (DMA) (99.5%) was acquired from Acros Organics and stored over additional molsieve 3A. Fluorobenzene (99%) and DMSO (≥99.5% over molsieve) were acquired from Sigma-Aldrich and used as received. THF (>99.5%) and diethyl ether (99.8%) were obtained from Sigma-Aldrich and distilled from Na/benzophenone under nitrogen before use. Hexane (>95%) was bought from Sigma-Aldrich and distilled from Na/benzophenone/TEGDME under nitrogen before use. tert-Butanol (anhydrous, 99.9%) was acquired from AlfaAesar and used as received. Toluene (>99.5%) was bought from VWR and was distilled from Na under nitrogen before use. Methanol (≥99.8%) was obtained from VWR and was distilled from Mg under nitrogen before use. Deionized water was sparged with argon for several hours before use. 4-Bromo-3-methylbenzotrifluoride (96%), catecholborane (97%) and cesium fluoride (99.9%) were acquired from abcr and used as received. Trimethyltin chloride (99%), palladium(II) acetate (99.9%) and tetrakis(triphenylphosphine)palladium(0) (99%) were bought from Acros Organics and used as received. Zinc dust (≥98%), tributyltin chloride (96%), bis(triphenylphosphine)palladium(II) dichloride (≥99.99% trace metals basis), magnesium (99.98% trace metals basis) *n*-butyl lithium (2.5 M in hexane), tosyl chloride (≥98%), potassium carbonate (99.99% trace metals basis), bis(tri(*o*-tolyl)phosphine)palladium(II) dichloride, iodine (99.8-100.5%), dicyclopentadiene, tBuXPhos Pd G3 and phosphorus trichloride (99%) were obtained from Sigma-Aldrich and used as received. Lithium chloride (≥98.0%) was bought from Sigma-Aldrich and was dried at 130 °C and 10^{-2} mbar for 4 h before use. Norbornene (99%) was acquired from Sigma-Aldrich and was distilled under argon before use. *o*-Bromobenzyl bromide and *o*-bromobenzyl alcohol was obtained from Apollo Scientific and used as received. Sodium iodide (>99%) was bought from Chemie Brunschwig and used as received. Iodomethylboronic acid pinacol ester (95%) was acquired from Combiblocks and used as received. 1,2-Dibromoethane (≥98.0%), tetrakis(triphenylphosphine)nickel(0) (≥98.0%) and Pd/C (10%) were obtained from Fluka and used as received. Copper(I) iodide (>98%) was bought from Fluka and was dried at 200 °C and 10^{-2} mbar for 8 h before use. *o*-Bromoiodobenzene, 1,1'-bis(diphenylphosphino)ferrocenepalladium(II) dichloride, pinacol (98%) and *o*-Iodobenzyl bromide were obtained from Fluorochem and used as received. Indene (>93%) and *N*-nitrosodiphenylamine was bought from TCI and used as received. *o*-(Bromomethyl)phenyl triflate,[1] tris(4-methoxy-2-methylphenyl)phosphine,[2] α-(bromomethyl)styrene[3] and tris(o-tolyl)arsine[4] were prepared according to literature procedures with spectra matching the ones reported in the references. (1,3-Dimethyl-1,3-dihydro-2*H*-benzimidazol-2-ylidene)diiodo(pyridine)palladium(II)[5] and (SP-4-2)-dichlorobis[2-(isocyano-κC)-2-methylpropane]palladium[6] were prepared according to procedures reported earlier. Complexes of palladium(II) chloride and triaryl phosphines or triaryl arsines were prepared following a literature procedure.[7] NMR spectra were measured with a Bruker Avance III 400 MHz, Bruker Neo 400 MHz or Bruker Neo 500 MHz spectrometer using $CDCl_3$ as solvent. 500 MHz spectra were measured by the NMR service of ETH Zürich. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal for chloroform (7.26 ppm and 77.16 ppm) as an internal reference. ^{13}C, ^{19}F and ^{31}P spectra were measured with ^{1}H-decoupling. High resolution mass spectra were acquired by the Molecular and Biomolecular Analysis Service (MoBiAS) of ETH Zürich, using a Bruker maXis ESI-Qq-TOF-MS or Thermo scientific Q Exactive GC Orbitrap with direct probe (EI) for mass spectra. GC-MS measurements were carried out using a ThermoFinnigan Trace GC + Trace MS and a Supelco Equity™-5 30 m x 0.25 mm column with 0.25 µm film. GC-FID measurements were conducted using a Finnigan Focus GC or a Shimadzu GC-2025 with a ThermoScientific TR-5MS 30 m x 0.25 mm column with 0.25 µm film. GC-FID quantifications were carried out using calibration curves and undecane as an internal standard.

II-Synthetic procedures

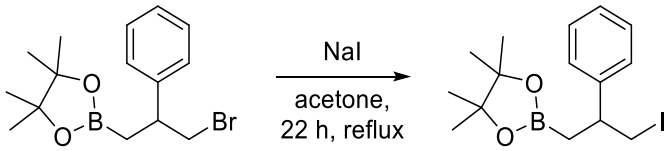
A: Bifunctional reagent synthesis:

3-Bromo-2-phenylboronic acid pinacol ester:



2.0550 g (10.428 mmol, 1 eq.) α-(bromomethyl)styrene and 2.2 mL (20,640 mmol, 2 eq.) catecholborane were heated to 120 °C for 2.5 h. 20 mL pentane and 0.5 mL water were added (gas evolution!), and the mixture was dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was dissolved in 16 mL dry THF under argon and 1.5036 g (12.724 mmol, 1.2 eq.) pinacol was added. The mixture was stirred at RT for 23 h and concentrated. The residue was vigorously stirred in 50 mL pentane for 15 min, and the mixture was cooled to -15 °C. The precipitate was removed by filtration, the filtrate was concentrated and the residue was purified by column chromatography (ethyl acetate:petrol ether 40/60 0:1 → 1:100). 1.8964 g (5.834 mmol, 55.9 %) of a colorless liquid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 6.96 (m, 5H), 3.52 (qd, J = 9.8, 7.0 Hz, 2H), 3.29 – 3.06 (m, 1H), 1.38 (dd, J = 15.6, 6.2 Hz, 1H), 1.15 (dd, J = 15.6, 9.6 Hz, 1H), 1.03 (s, 6H), 1.00 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.64. ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.78, 128.46, 127.67, 127.00, 83.35, 43.83, 41.15, 24.83, 24.68, 17.51. HRMS (ESI-QTOF) calcd for $C_{15}H_{23}BBrO_2$ $[M+H]^+$ 325.0972, found 325.0973.

3-Iodo-2-phenylboronic acid pinacol ester:

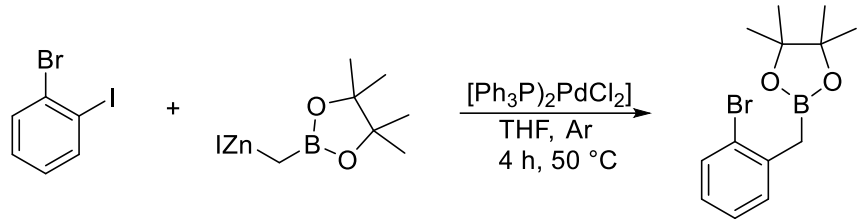


466.7 mg (1.436 mmol, 1 eq.) 3-bromo-2-phenylpropylboronic acid pinacol ester was dissolved in 2 mL acetone and 434.4 mg (2.898 mmol, 2 eq.) sodium iodide was added. The mixture was heated to reflux for 22 h. The yellow suspension was cooled to RT and the suspended solid was dissolved by addition of water. The mixture was extracted with pentane (2x 5 mL) and the combined organic phases were washed with aqueous sodium thiosulfate solution (0.5 M, 10 mL), dried (MgSO4) and filtered through a pad of silica, washing with additional ethyl acetate. The filtrate was concentrated *in vacuo* to obtain 430.8 mg (1.158 mmol, 80.6 %) of a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.10 (m, 5H), 3.46 (dd, J = 7.0, 2.3 Hz, 2H), 3.19 (dq, J = 9.8, 6.7 Hz, 1H), 1.49 (dd, J = 15.5, 5.9 Hz, 1H), 1.34 – 1.20 (m, 1H), 1.12 (s, 6H), 1.09 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.68. ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.29, 128.37, 127.36, 126.89, 83.25, 43.92, 24.78, 24.63, 19.21 (weak), 16.79. HRMS (ESI-QTOF) calcd for $C_{15}H_{23}BIO_2$ $[M+H]^+$ 373.0833, found 373.0828.

According to GC-MS, the product contains traces of two isomers $C_{15}H_{23}BO_2$ (PhC_3H_6BPin).

_o_-Bromobenzylboronic acid pinacol ester (1):

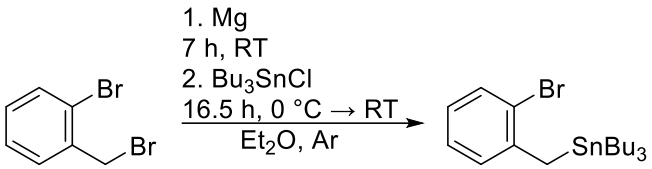
This reagent was prepared from a modified reported procedure.[8]



3.1367 g (47.969 mmol, 4.7 eq.) zinc powder was suspended in 4 mL dry THF. 0.2 mL (2.321 mmol, 0.2 eq.) 1,2-dibromoethane was added, followed by a solution of 4.0932 g (15.279 mmol, 1.5 eq.) iodomethylboronic acid pinacol ester in 8 mL dry THF, and the suspension was stirred at RT for 2 h. The solution was transferred to a solution of 284.4 mg (0.405 mmol, 0.04 eq.) bis(triphenylphosphine)palladium(II) dichloride and 2.8316 g (10.009 mmol, 1 eq.) *o*-bromoiodobenzene in 40 mL dry THF. The reaction solution was heated to 50 °C for 4 h. The mixture was concentrated and the residue was taken up in 10 mL petrol ether 40/60. The solution was washed with water (2x 10 mL) and brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude red liquid was purified by column chromatography (petrol ether 40/60:ethyl acetate 50:1) to obtain 1.8743 g (6.310 mmol, 63.0%) of a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.9, 1.3 Hz, 1H), 7.24 (dd, J = 7.6, 1.9 Hz, 1H), 7.19 (td, J = 7.4, 1.3 Hz, 1H), 7.00 (td, J = 7.6, 1.9 Hz, 1H), 2.44 (s, 2H), 1.26 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.45. ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.48, 132.35, 130.75, 127.36, 126.74, 124.70, 83.59, 24.83, 21.66 (weak). HRMS (ESI-QTOF) calcd for $C_{13}H_{19}BBrO_2$ $[M+H]^+$ 297.0658, found 297.0656.

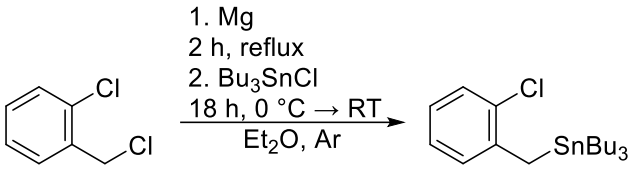
_o_-Bromobenzyl(tributyl)stannane (2a):

This reagent was prepared from a modified reported procedure.[9]



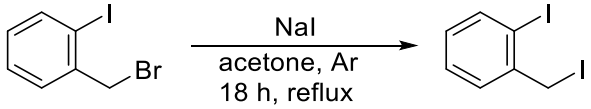
589.7 mg (24.258 mmol, 1 eq.) magnesium turnings was suspended in 30 mL dry diethyl ether and a crystal of iodine was added. A solution of 5.9987 g (24.002 mmol, 1 eq.) *o*-bromobenzyl bromide was added and the mixture was stirred at RT for 7 h. The reaction mixture was cooled to 0 °C and 6.5 mL (23.962 mmol, 1 eq.) tributyltin chloride was added. It was stirred at RT for 16.5 h. 50 mL aqueous sodium hydroxide solution (1 M) was added, and the mixture stirred for 1 h at RT. The aqueous phase was extracted with diethyl ether (2x 40 mL) and the combined ether phases were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was filtered through a pad of silica, washing with additional pentane, and the filtrate was concentrated to obtain 7.7353 g (16.813 mmol, 70.2%) of a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 7.9, 1.3 Hz, 1H), 7.18 – 7.10 (m, 1H), 7.10 (dd, J = 7.7, 2.0 Hz, 1H), 6.86 (ddd, J = 8.0, 6.9, 2.0 Hz, 1H), 2.49 (s, 2H), 1.52 – 1.42 (m, 6H), 1.34 – 1.23 (m, 6H), 0.93 – 0.85 (m, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.11, 132.50, 128.51, 127.36, 124.57, 122.70, 29.13, 27.48, 20.35, 13.83, 10.31. HRMS (EI) calcd for $C_{19}H_{32}BrSn$ $[M-H]^+$ 459.0704, found 459.0692; calcd for $C_{15}H_{24}BrSn$ $[M-Bu]^+$ 403.0078, found 403.0066; calcd for $C_{12}H_{27}Sn$ $[SnBu_3]^+$ 291.1129, found 291.1128.

***o*-Chlorobenzyl(tributyl)stannane (2b):**



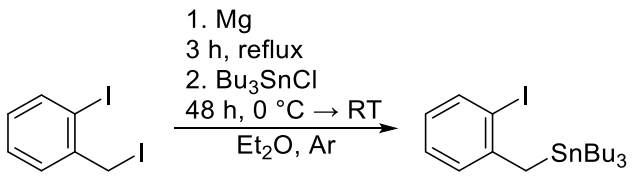
305.0 mg (12.546 mmol, 1 eq.) magnesium turnings was suspended in 16 mL dry diethyl ether. A crystal of iodine was added, followed by slow addition of 1.6 mL (12.659 mmol, 1 eq.) *o*-chlorobenzyl chloride in 47 mL dry diethyl ether. The mixture was heated to reflux for 2 h and cooled to 0 °C. 3.4 mL (12.534 mmol, 1 eq.) tributyltin chloride was added, and the mixture stirred at RT for 18 h. 25 mL aqueous sodium hydroxide solution (1 M) was added, and the suspension stirred at RT for 1 h. The aqueous phase was extracted with equal volume of diethyl ether, and the combined organic phases were washed with water (30 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residual yellow liquid was purified by column chromatography (pentane) to obtain 3.2547 g (7.831 mmol, 62.5%) of a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, J = 8.6, 1.0 Hz, 1H), 7.13 – 7.05 (m, 2H), 6.95 (ddd, J = 8.0, 4.9, 3.9 Hz, 1H), 2.45 (s, 2H), 1.59 – 1.38 (m, 6H), 1.37 – 1.22 (m, 6H), 1.00 – 0.74 (m, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.33, 131.72, 129.21, 128.71, 126.71, 124.36, 29.11, 27.47, 17.30, 13.81, 10.19. HRMS (EI) calcd for $C_{19}H_{32}ClSn$ $[M\text{-}H]^+$ 415.1209, found 415.1203; calcd for $C_{15}H_{24}ClSn$ $[M\text{-}Bu]^+$ 359.0583, found 359.0577; calcd for $C_{12}H_{27}Sn$ $[SnBu_3]^+$ 291.1129, found 291.1128.

***o*-Iodobenzyl iodide:**



2.0365 g (6.859 mmol, 1 eq.) *o*-iodobenzyl bromide was dissolved in 9 mL acetone. 2.0228 g (13.495 mmol, 2 eq.) sodium iodide was added and the mixture was heated to reflux for 18 h. The suspension was cooled to RT and diluted with 20 mL hexane. The mixture was filtered and the yellow filtrate was concentrated *in vacuo*. The residue was taken up in 20 mL hexane, filtered and washed with 20 mL aq. sat. Na_2SO_3. It was dried (Na_2SO_4), filtered, and concentrated. 1.6797 g (4.884 mmol, 71.2%) of a yellowish solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 7.9, 1.3 Hz, 1H), 7.47 (dd, J = 7.7, 1.7 Hz, 1H), 7.29 (ddd, J = 7.5, 1.3 Hz, 1H), 6.93 (ddd, J = 7.9, 7.4, 1.7 Hz, 1H), 4.55 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.53, 140.34, 129.88, 129.65, 129.10, 99.92, 12.42. HRMS (EI) calcd for $C_7H_6I_2$ $[M]^+$ 343.8553, found 343.8551. NMR spectra match literature.[10]

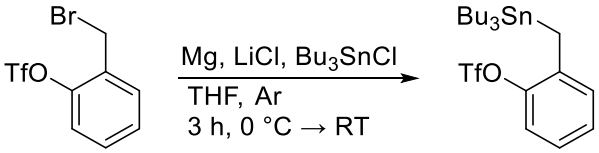
***o*-Iodobenzyl(tributyl)stannane (2c):**



54.0 mg (1.851 mmol, 1.1 eq.) magnesium turnings were suspended in 2 mL dry Et_2O and a crystal of iodine was added. A solution of 605.2 mg (1.760 mmol, 1 eq.) *o*-iodobenzyl iodide in 11 mL dry Et_2O was slowly added and the turbid mixture was stirred at RT for 3 h. The suspension was cannula filtered into another flask and cooled to 0 °C. 0.47 mL (1.733 mmol, 1 eq.) tributyltin chloride was added and the mixture was warmed to RT while stirring for 48 h. The reaction was quenched by addition of 5 mL aq. sat. NH_4Cl. The organic phase was washed with 1 M aq. NaOH (2x 12 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by column chromatography (hexane) to obtain

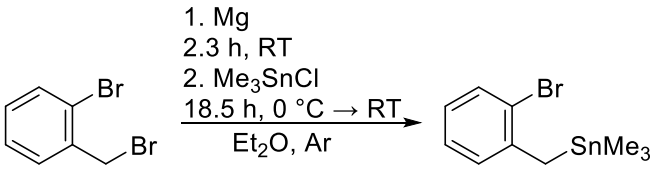
the product as 74.2 mg (0.146 mmol, 8.4%) of a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 7.9, 1.3 Hz, 1H), 7.18 – 7.10 (m, 1H), 7.10 (dd, J = 7.7, 2.0 Hz, 1H), 6.86 (ddd, J = 8.0, 6.9, 2.0 Hz, 1H), 2.49 (s, 2H), 1.52 – 1.42 (m, 6H), 1.34 – 1.23 (m, 6H), 0.89 (td, J = 8.1, 7.6, 4.5 Hz, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.11, 132.50, 128.51, 127.36, 124.57, 122.70, 29.13, 27.48, 20.35, 13.83, 10.31. HRMS (EI) calcd for $C_{19}H_{32}ISn$ $[M-H]^+$ 507.0565, found 507.0565; calcd for $C_{15}H_{24}ISn$ $[M-Bu]^+$ 450.9939, found 450.9938; calcd for $C_{12}H_{27}Sn$ $[SnBu_3]^+$ 291.1129, found 291.1128.

***o*-((Tributylstannyl)methyl)phenyl triflate (2d):**



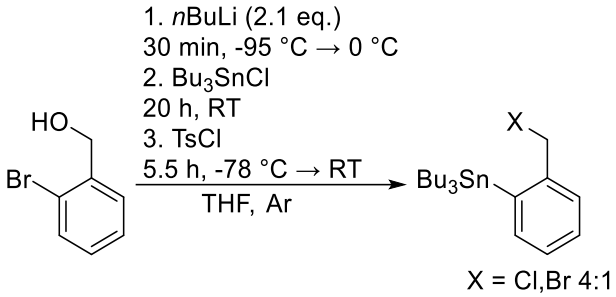
163.5 mg (6.727 mmol, 1.1 eq.) magnesium turnings, 314.2 mg (7.412 mmol, 1.2 eq.) lithium chloride and 2.0 mL (7.373 mmol, 1.2 eq.) tributyltin chloride were suspended in 15 mL dry THF and stirred at RT for 30 min. The mixture was cooled to 0 °C and 1.9195 g *o*-(bromomethyl)phenyl triflate was added. Stirring was continued for 20 min at 0 °C and 2.7 h at RT. 15 mL hexane was added and the mixture filtered through celite. The suspension was concentrated and the residue extracted with hexane. The extracts were filtered and concentrated *in vacuo* to obtain a yellow liquid. The crude product was purified by column chromatography (hexane) to obtain 1.6273 g (3.075 mmol, 51.1%) of a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 2H), 7.12 (dd, J = 7.7, 2.0 Hz, 1H), 7.03 (ddd, J = 8.7, 6.9, 1.9 Hz, 1H), 2.34 (s, 2H), 1.48 – 1.35 (m, 6H), 1.33 – 1.19 (m, 6H), 0.93 – 0.73 (m, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.80, 137.62, 130.10, 128.24, 124.62, 121.30, 118.77 (q, J = 320.5 Hz), 28.98, 27.43, 13.74, 13.13, 9.99. ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.08. HRMS (ESI-QTOF) calcd for $C_{20}H_{33}F_3NaO_3SSn$ $[M+Na]^+$ 553.1019, found 553.1019.

***o*-Bromobenzyl(trimethyl)stannane (2e):**



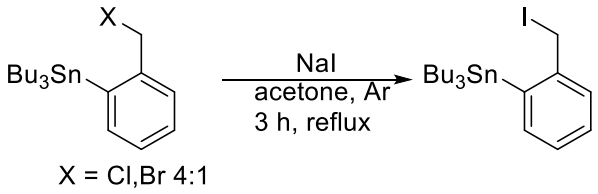
Under argon, 494.2 mg (20.329 mmol, 1 eq.) magnesium turnings and a crystal of iodine were suspended in 25 mL dry diethyl ether. A solution of 5.0079 g (20.037 mmol, 1 eq.) *o*-bromobenzyl bromide in 55 mL dry diethyl ether was slowly added and the mixture stirred at RT for 2.3 h. The reaction mixture was cooled to 0 °C and 4.0125 g (20.139 mmol, 1 eq.) trimethyltin chloride was added. The mixture was stirred at RT for 18.5 h. 30 mL aqueous sodium hydroxide solution (1 M) was added and the mixture stirred at RT for 1 h. The aqueous phase was extracted with diethyl ether (3x 20 mL), and the combines organic phases were dried (MgSO4), filtered and concentrated *in vacuo*. The residue was filtered through a pad of silica (pentane) and the filtrate concentrated. The residue was distilled under reduced pressure (9 mbar, 160 °C) to obtain 3.7786 g (11.319 mmol, 56.6%) of a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 8.0, 1.4 Hz, 1H), 7.14 (td, J = 7.4, 1.4 Hz, 1H), 7.07 (dd, J = 7.7, 1.9 Hz, 1H), 6.86 (ddd, J = 7.9, 7.2, 1.8 Hz, 1H), 2.49 (s, 2H), 0.11 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.59, 132.56, 128.38, 127.43, 124.78, 122.72, 22.41, -8.87. HRMS (EI) calcd for $C_9H_{12}BrSn$ $[M-Me]^+$ 318.9139, found 318.9130.

Tributyl(2-(bromo/chloromethyl)phenyl)stannane:



3.0007 g (16.044 mmol, 1 eq.) *o*-bromobenzylic alcohol was dissolved in 60 mL dry THF and cooled to -95 °C. 13.5 mL (33.690 mmol, 2.1 eq.) *n*-butyl lithium (2.5 M in hexane) was slowly added and the mixture stirred at 0 °C for 30 min. 4.4 mL (16.221 mmol, 1 eq.) tributyltin chloride was added and the mixture stirred at RT for 20 h. The yellowish suspension was cooled to 0 °C and 3.3838 g (17.746 mmol, 1.1 eq.) tosyl chloride was added. The mixture was stirred at 0 °C for 5.5 h. To the resulting colorless gel was added 5 mL water and the organic phase was washed with water (5 mL) and brine (7 mL), dried (Na2SO4), filtered and concentrated *in vacuo*. The residue was purified by column chromatography (petrol ether 40/60:ethyl acetate 1:0 → 20:1) to obtain 3.4452 g of a colorless liquid. GC-MS finds two compounds with $[M\text{-}Bu]^+$ 359.38 and 403.35 (highest peaks) fitting for tributyl(2 (chloromethyl)phenyl)stannane and tributyl(2-(bromomethyl)phenyl)stannane respectively and showing the corresponding isotope patterns. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 1H), 7.51 – 7.44 (m, 1H), 7.36 (td, J = 7.4, 1.6 Hz, 1H), 7.33 – 7.27 (m, 1H), 4.60 (s, 1.6H, X=Cl), 4.54 (s, 0.4H, X=Br), 1.69 – 1.48 (m, 6H), 1.47 – 1.30 (m, 6H), 1.25 – 1.13 (m, 6H), 0.95 (td, J = 7.3, 1.3 Hz, 9H), indicating a chloride/bromide ratio of 4:1. ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.71 (X=Br), 144.36 (X=Cl), 143.30 (X=Br), 143.11 (X=Cl), 137.32 (X=Br), 137.24 (X=Cl), 130.13 (X=Br), 129.66 (X=Cl), 128.85 (X=Br), 128.79 (X=Cl), 127.78 (X=Cl), 127.71 (X=Br), 49.45 (X=Cl), 37.45 (X=Br), 29.26 (X=Br), 29.23 (X=Cl), 27.52, 13.79, 10.79 (X=Br), 10.74 (X=Cl). HRMS (EI, compound 1) calcd for $C_{11}H_{16}ClSn$ $[M\text{-}(Bu+butene)]^+$ 302.9957, found 302.9951; HRMS (EI, compound 2) calcd for $C_{11}H_{16}BrSn$ $[M\text{-}(Bu+butene)]^+$ 346.9443, found 346.9436.

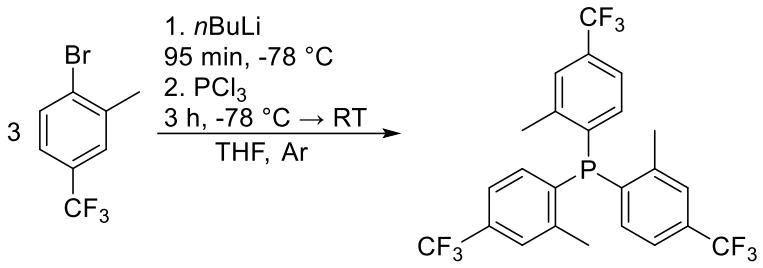
Tributyl(2-(iodomethyl)phenyl)stannane (2f):



Under argon, 1.0490 g (~2.471 mmol, 1 eq.) of tributyl(2-(bromo/chloromethyl)phenylstannane mixture was dissolved in 3.2 mL acetone. 708.0 mg (4.723 mmol, 2 eq.) sodium iodide was added and the mixture was heated to reflux for 3 h. 10 mL hexane was added and the mixture filtered and concentrated *in vacuo*. The residual yellow liquid was filtered through a pad of silica (hexane) to obtain 945.3 mg (1.864 mmol, 75.4%) of a yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.7, 1.3 Hz, 1H), 7.43 (dd, J = 7.3, 1.6 Hz, 1H), 7.31 (td, J = 7.3, 1.3 Hz, 1H), 7.23 (td, J = 7.3, 1.3 Hz, 1H), 4.53 (s, 2H), 1.72 – 1.52 (m, 6H), 1.41 (h, J = 7.3 Hz, 6H), 1.35 – 1.12 (m, 6H), 0.96 (td, J = 7.3, 1.6 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.22, 142.29, 137.19, 129.97, 128.95, 127.18, 29.31, 27.53, 13.81, 10.81, 10.76. HRMS (EI) calcd for $C_{19}H_{32}ISn$ $[M\text{-}H]^+$ 507.0565, found 507.0565; calcd for $C_{11}H_{16}ISn$ $[M\text{-}Bu]^+$ 394.9313, found 394.9309; calcd for $C_{15}H_{25}ISn$ $[M\text{-}(I+butene)]^+$ 325.0973, found 325.0969.

B: Ligand synthesis:

Tris(2-methyl-4-(trifluoromethyl)phenyl)phosphine:

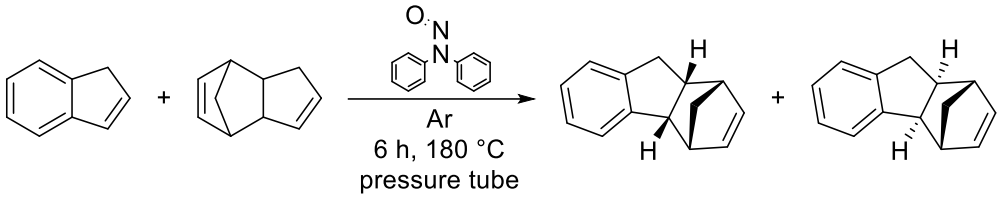


993.4 mg (4.156 mmol, 3 eq.) 4-bromo-3-methylbenzotrifluoride was dissolved in 24 mL dry THF and cooled to -78 °C. 1.8 mL (4.5 mmol, 3 eq.) *n*-butyl lithium (2.5 M in hexane) was added and the mixture stirred at -78 °C for 95 min. 204.8 mg (1.491 mmol, 1.1 eq.) phosphorus trichloride was added. The mixture turned dark red first, then quickly to light yellow. Stirring was continued while warming to RT for 3 h. 1.5 mL methanol are added and them mixture concentrated *in vacuo*. The residue is washed with methanol to obtain 368.5 mg (0.721 mmol, 48.4%) of a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 4.7, 1.8 Hz, 3H), 7.37 (dd, J = 8.0, 1.9 Hz, 3H), 6.79 (dd, J = 8.0, 3.8 Hz, 3H), 2.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.81 (d, J = 27.3 Hz), 137.89 (d, J = 12.7 Hz), 133.39, 131.64 (q, J = 32.4 Hz), 127.11 (qd, J = 3.6, 0.8 Hz), 124.12 (q, J = 272.4 Hz), 123.30 (q, J = 3.7 Hz), 21.37 (d, J = 21.5 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.90 (d, J = 1.3 Hz). ^{31}P NMR (162 MHz, CDCl3) δ -29.04 – 29.14 (m). HRMS (ESI-QTOF) calcd for $C_{24}H_{19}F_9P$ $[M+H]^+$ 509.1075, found 509.1075.

C: GC reference synthesis

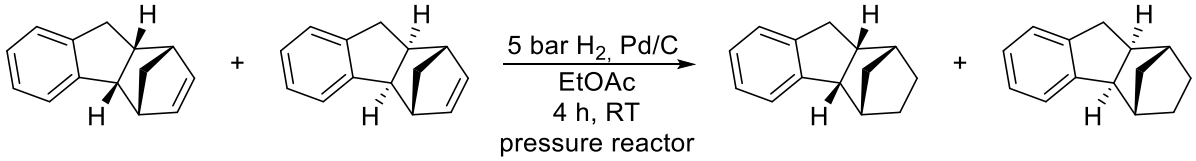
***exo*/*endo*- 4,4a,9,9a-tetrahydro-1H-1,4-methanofluorene:**

This compound was prepared from a modified reported procedure.[11]



10.5532 g (90.851 mmol, 4 eq.) indene, 3.0418 g (23.007 mmol, 1 eq.) dicyclopentadiene and 6.4 mg (0.032 mmol, 0.001 eq.) N-nitrosodiphenylamine was heated to 180 °C (ramp: 1 K/min) in a pressure tube and kept at 180 °C for additional 3 h. The mixture was cooled to RT and the residual orange liquid was distilled under reduced pressure (0.5 mbar, 140 °C) to obtain 813.3 mg of a colorless liquid that is used without further purification. GC-MS shows two isomers of the target molecule (m/z = 182, ratio 4:1) and a small peak with m/z = 198 (tricyclopentadiene).

***exo*/*endo*-2,3,4,4a,9,9a-Hexahydro-1H-1,4-methanofluorene:**



800 mg *exo*/*endo*-2,3,4,4a,9,9a-Hexahydro-1H-1,4-methanofluorene was dissolved in 18 mL ethyl acetate. 90.5 mg palladium/charcoal was added and the mixture hydrogenated in a hydrogenation apparatus under 5 bar of hydrogen for 4 h. The reaction mixture was filtered through celite and the

filtrate concentrated in vacuo. The residue is filtered through a silica pad (pentane) and concentrated to obtain 680.1 mg of a colorless liquid. GC-MS shows two isomers of the target molecule (m/z = 184, ratio 8:1) and a small peak with m/z = 202 (hydrogenated tricyclopentadiene). Main peaks in NMR: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.08 (m, 4H), 3.74 – 3.57 (m, 1H), 3.03 – 2.93 (m, 1H), 2.88 (ddd, J = 17.6, 3.2, 1.3 Hz, 1H), 2.84 – 2.77 (m, 1H), 2.60 – 2.52 (m, 1H), 2.35 – 2.28 (m, 1H), 1.69 (dp, J = 9.3, 1.7 Hz, 1H), 1.57 (dt, J = 9.3, 1.7 Hz, 1H), 1.36 – 1.14 (m, 3H), 0.90 – 0.75 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.97, 144.92, 126.48, 126.05, 125.60, 124.81, 52.65, 43.18, 41.63, 41.43, 41.17, 32.40, 25.00, 21.94. Comparing with literature[12] identifies the main product as the *endo*-product.

III-Cyclopentenation experiments

A: Cyclopentanation experiments with o-bromobenzylboronic acid pinacol ester (1)

1) Reaction in DMA/EG with K_2CO_3

Inside a nitrogen-filled glovebox, a 9 mL screw-cap vial with an oven-dried magnetic stir bar was charged with K_2CO_3 (80.9 mg, 5.0 equiv) and 0.1 mL anhydrous ethylene glycol (EG). The mixture was stirred for 10 min. A solution of $[(o\text{-tolyl})_3P]_2PdCl_2$ (4.6 mg, 5 mol%), *o*-bromobenzylboronic acid pinacol ester (41.6 mg, 1.2 equiv), and norbornene (11.0 mg, 1 equiv) in 0.6 mL DMA was added. Additional DMA (2 × 0.5 mL) was used to rinse the vials used for transfer and weighing substrates and catalyst and added to the reaction mixture. The vial was sealed, removed from the glovebox, and heated to 75 °C for 22 h. The mixture was cooled to 0 °C for 10 min and 5 µL undecane was added (internal reference). The contents of the vial were extracted with Et_2O (2 × 4 mL) and water (5 mL) and the organic phase was washed with water (5 mL) and brine (5 mL), dried ($MgSO_4$), filtered through celite and analyzed by GC-MS and GC-FID.

3-Iodo-2-phenylpropylboronic acid pinacol ester:

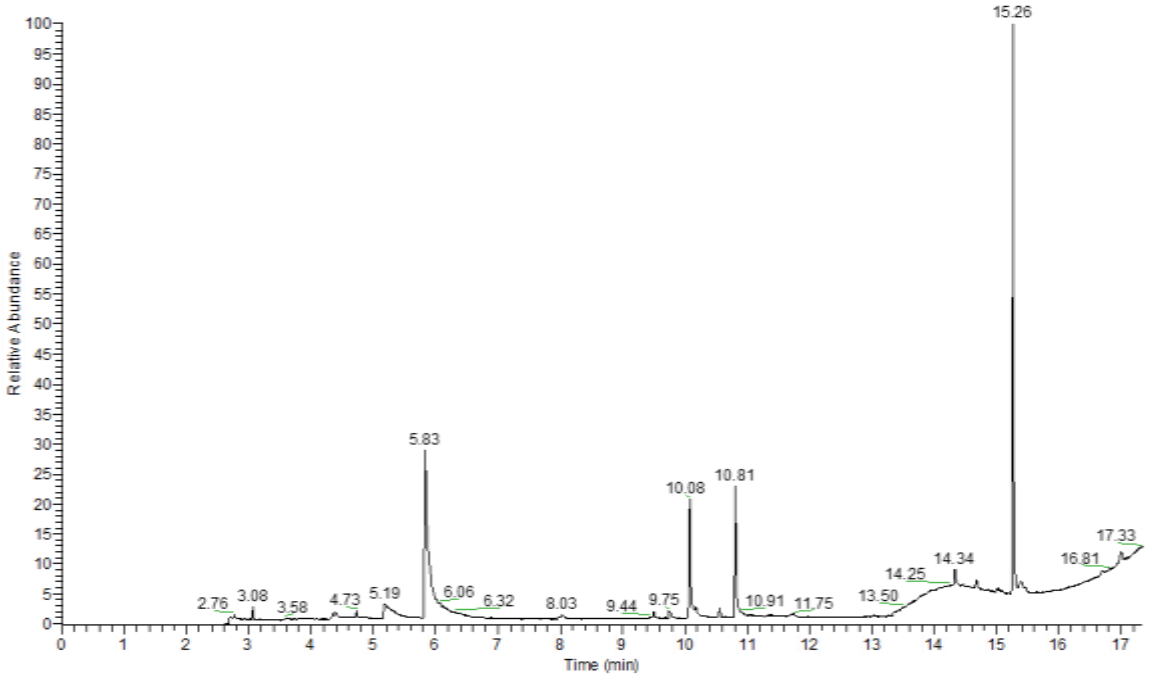


Figure SI-1. GC-MS chromatogram for the attempted cyclopentenation of norbornene using 3-iodo-2-phenylpropylboronic acid pinacol ester (**1**). Retention times phenylcyclopropane (t_R= 5.19 min), undecane (t_R= 5.83 min; internal standard), $C_{15}H_{23}BO_2$ (PhC_3H_6BPin) (t_R= 10.08 min; 10.81 min), tris(*o*-tolyl)phosphine (t_R= 15.26 min).

***o*-Bromobenzylboronic acid pinacol ester:**

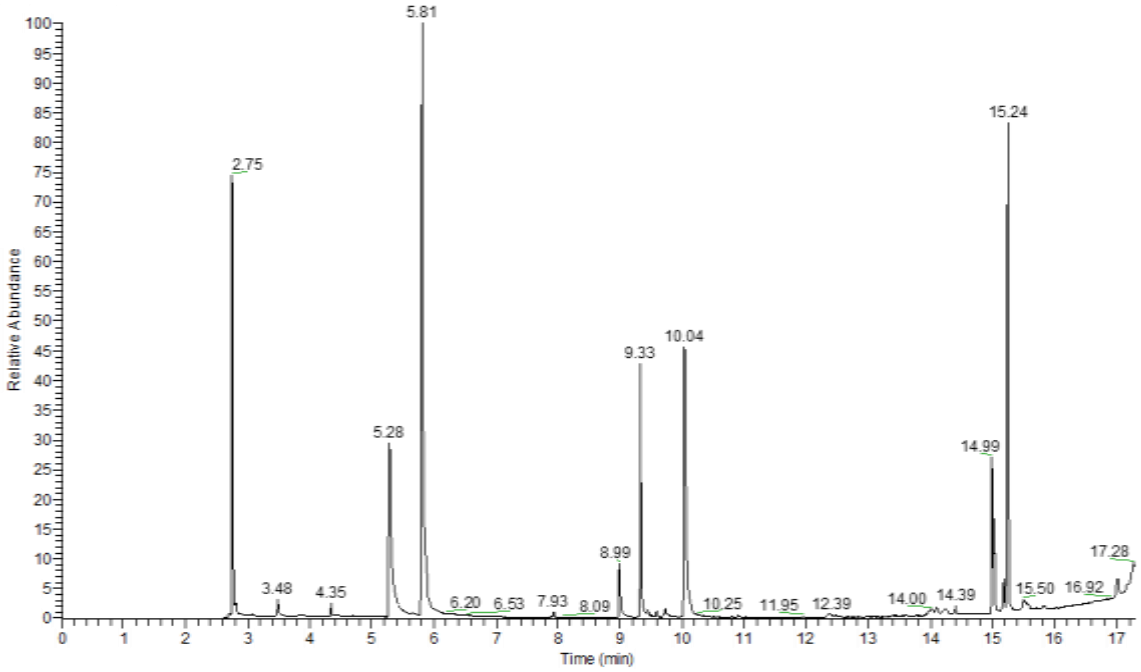


Figure SI- 2. GC-MS chromatogram for the attempted cyclopentenation of norbornene using *o*-bromobenzylboronic acid pinacol ester (**1**). Retention times toluene (t_R= 2.75 min), *o*-bromotoluene (t_R= 5.28 min), undecane (t_R= 5.81 min; internal standard), $C_{14}H_{16}$ (t_R= 9.33 min), $C_{14}H_{18}$ (t_R= 10.04 min), tris(*o*-tolyl)phosphine (t_R= 15.24 min).

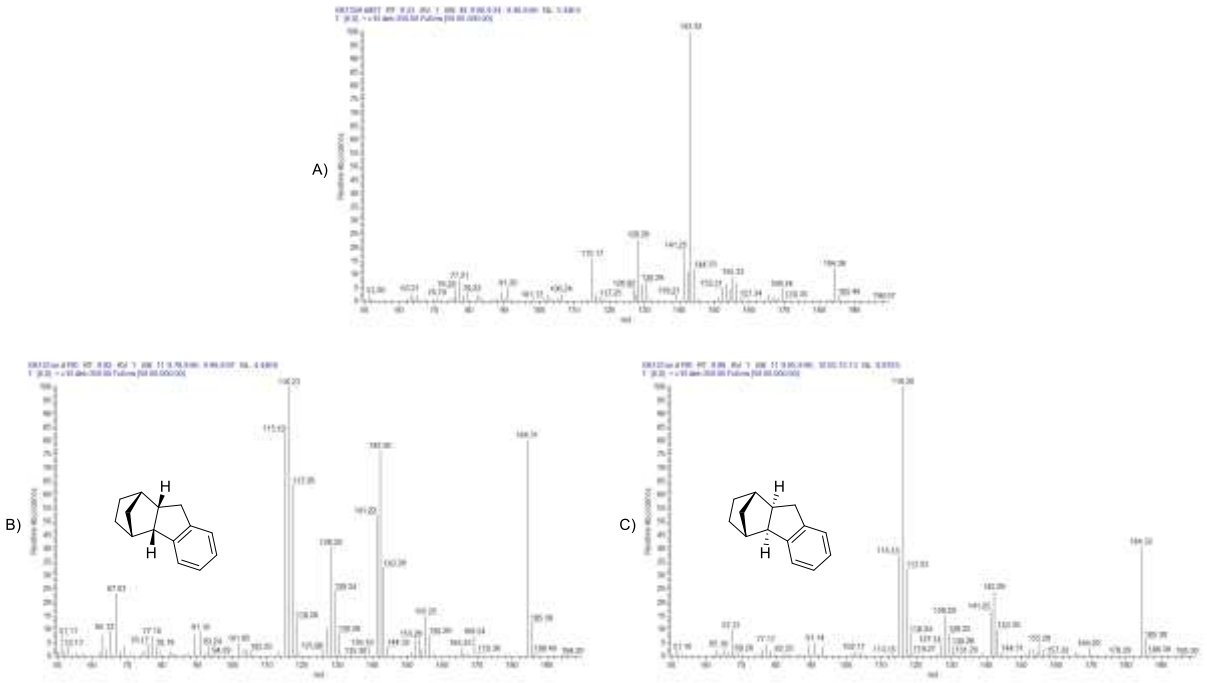
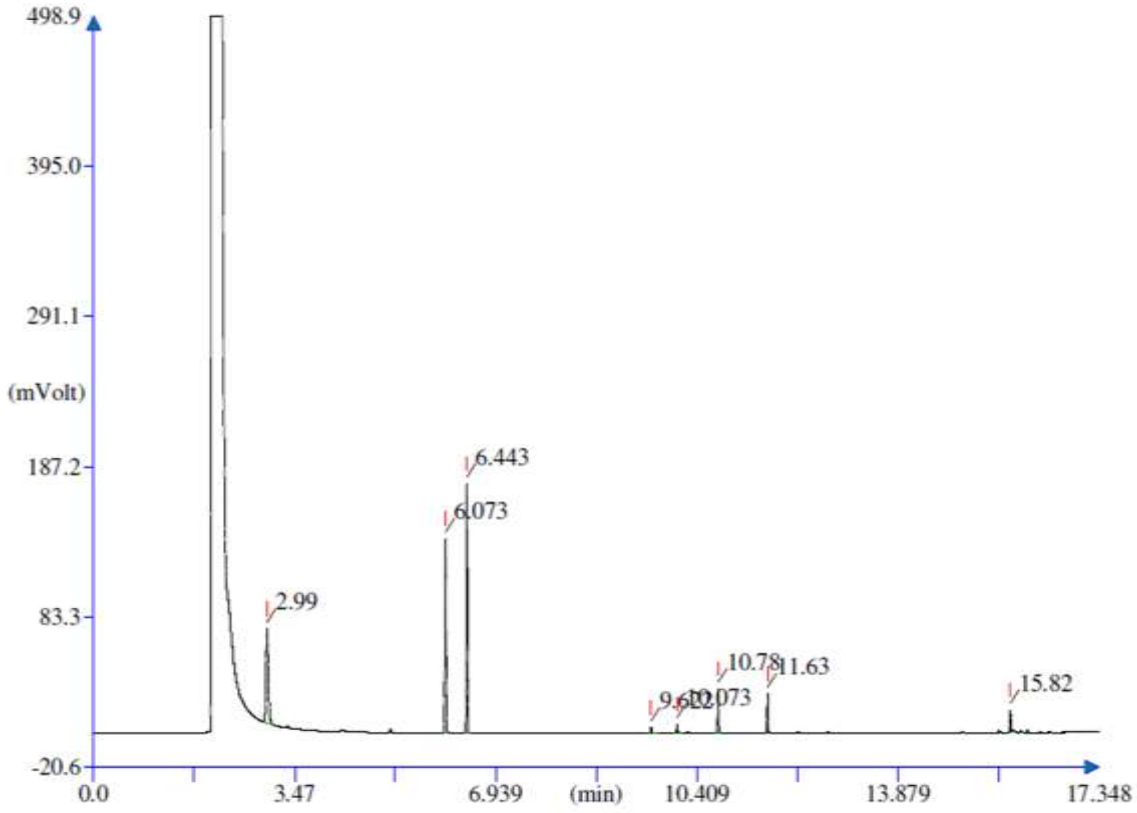


Figure SI-3. EI-MS spectrum of the product from the palladium-catalyzed reaction of o-bromobenzylboronic acid pinacol ester and norbornene in DMA/EG with potassium carbonate (A) compared to the EI-MS spectra of the expected *endo* (B) and *exo* (C) products.

2) Reaction in DMA with CsF

Inside a nitrogen-filled glovebox, a 9 mL screw-cap vial with an oven-dried magnetic stir bar was charged with CsF (21.4 mg, 1.2 equiv). A solution of $[(o\text{-tolyl})_3P]_2PdCl_2$ (4.6 mg, 5 mol%), *o*-bromobenzylboronic acid pinacol ester (41.6 mg, 1.2 equiv), and norbornene (11.0 mg, 1 equiv) in 0.6 mL DMA was added. Additional DMA (2 × 0.5 mL) was used to rinse the vials used for transfer and weighing substrates and catalyst and added to the reaction mixture. The vial was sealed, removed from the glovebox, and heated to 75 °C for 22 h. The mixture was cooled to 0 °C for 10 min and 5 µL undecane was added (internal reference). The contents of the vial were extracted with Et_2O (2 × 4 mL) and water (5 mL) and the organic phase was washed with water (5 mL) and brine (5 mL), dried ($MgSO_4$), filtered through celite and analyzed by GC-MS and GC-FID.



Peak Number #	Area %	Ret.Time	Area	BC
1	28.7995	2.99	1871102	mi
2	25.6326	6.07	1665350	mi
3	29.8971	6.44	1942414	RS
4	0.7419	9.62	48203	mi
5	1.1872	10.07	77135	mi
6	5.6244	10.78	365419	mi
7	4.7071	11.63	305822	RS
8	3.4102	15.82	221560	FU
Totals	100.0000		6497004	

Figure SI-4. GC-FID (Finnigan Focus GC) chromatogram for the attempted cyclopentenation of norbornene using *o*-bromobenzylboronic acid pinacol ester (**1**). Retention times norbornene (t_R= 2.99 min),

o-bromotoluene (t_R= 6.07 min), undecane (t_R= 6.44 min; internal standard), *exo* -2,3,4,4a,9,9a-Hexahydro-1*H*-1,4-methanofluorene (t_R= 10.78 min).

2) Kinetics of boronate decomposition for *o*-bromobenzylboronic acid pinacol ester (1)

Kinetics in the DMA/EG/K_2CO_3 system. Inside a nitrogen-filled glovebox, an oven-dried 20 mL Schlenk tube with an oven-dried magnetic stir bar was charged with K_2CO_3 (406.2, 5 equiv) and 0.5 mL ethylene glycol, and the mixture was stirred at RT for 10 min. A solution of [(*o*-tolyl)$_3$P]$_2$PdCl$_2$ (22.8 mg, 5 mol%), *o*-bromobenzylboronic acid pinacol ester (208.3 mg, 1.2 equiv), and norbornene (55.3 mg, 1 equiv) in 3 mL DMA was added. DMA (2 × 2.5 mL) was used to rinse the vials used for transfer and weighing substrates and catalyst and added to the reaction mixture. 30 µL undecane was added. The tube was sealed with a rubber septum, removed from the glove box, and attached to an argon-filled Schlenk line. A sample (0.3 mL, t = 0) was taken and the mixture was heated to 75 °C. Samples were taken in regular intervals. The samples were cooled to 0 °C for 10 min and were diluted with 1.4 mL Et_2O. They were washed with water (2 × 0.9 mL) and brine (0.9 mL) and were passed through a pipette filled anhydrous $MgSO_4$. The samples were diluted with Et_2O and analyzed via GC-FID.

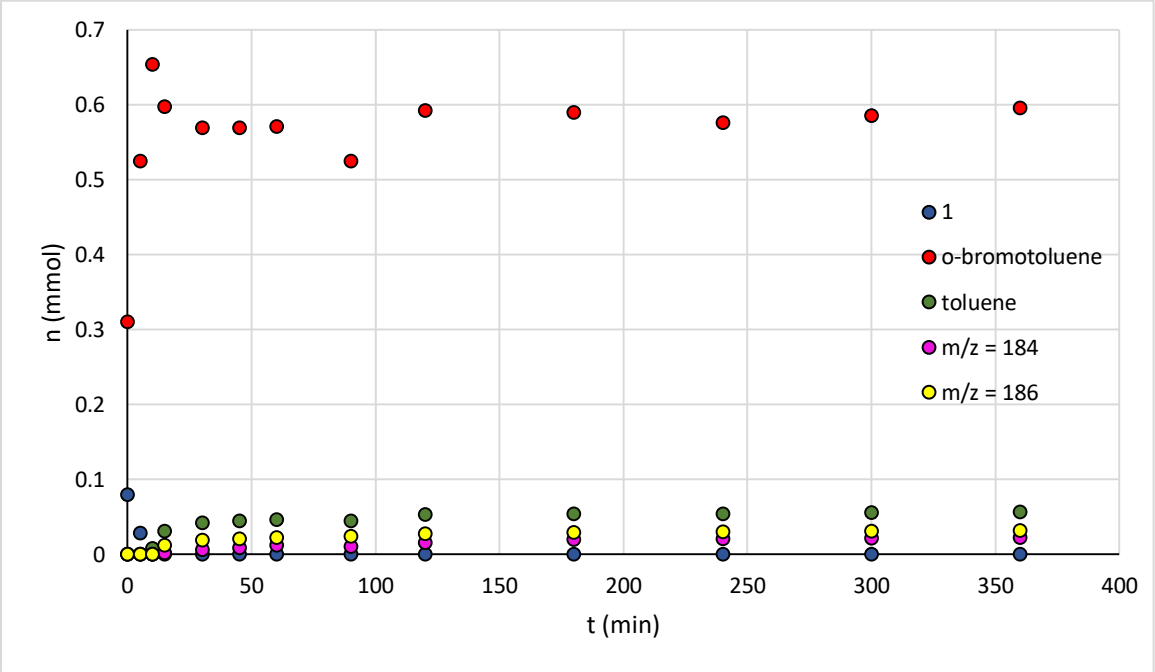


Figure SI-5. Kinetic profile for the first 6 h in the DMA/EG/K_2CO_3 system. All data obtained from GC-FID measurements. Amount of substances calculated from calibration curves (*o*-bromobenzylboronic acid pinacol ester (1), *o*-bromotoluene, toluene) or were estimated by assuming equal-per-carbon response[13] (m/z = 184, m/z = 186).

Kinetics in the iPrOH/CsF system. Inside a nitrogen-filled glovebox, an oven-dried 20 mL Schlenk tube with an oven-dried magnetic stir bar was charged with CsF (106.5 mg, 1.2 equiv). A solution of [(*o*-tolyl)$_3$P]$_2$PdCl$_2$ (22.8 mg, 5 mol%), *o*-bromobenzylboronic acid pinacol ester (208.3 mg, 1.2 equiv), and norbornene (55.3 mg, 1 equiv) in 3 mL ^{i}PrOH was added. ^{i}PrOH (2 × 2.5 mL) was used to rinse the vials used for transfer and weighing substrates and catalyst and added to the reaction mixture. 30 µL undecane was added. The tube was sealed with a rubber septum, removed from the glove box, and attached to an argon-filled Schlenk line. A sample (0.3 mL, t = 0) was taken and the mixture was heated to 75 °C. Samples were taken in regular intervals. The samples were cooled to 0 °C for 10 min and were diluted with 1.4 mL Et_2O. They were washed with water (2 × 0.9 mL) and brine (0.9 mL) and were passed through a pipette filled anhydrous $MgSO_4$. The samples were diluted with Et_2O and analyzed via GC-FID.

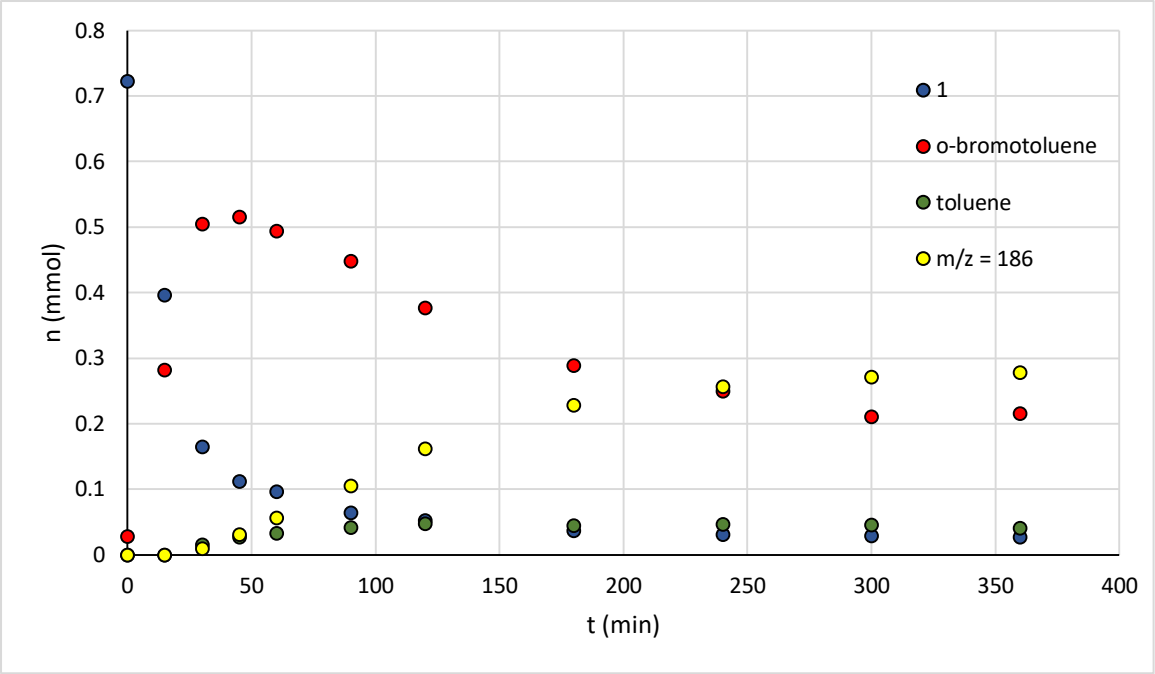


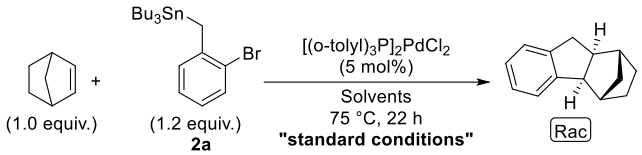
Figure SI-6. Kinetic profile for the first 6 h in the ^{i}PrOH/CsF system. All data obtained from GC-FID measurements. Amount of substances calculated from calibration curves (*o*-bromobenzylboronic acid pinacol ester (1), *o*-bromotoluene, toluene) or were estimated by assuming equal-per-carbon response[13] (m/z m/z = 186).

B: Cyclopentanation experiments with stannanes (2a-f)

1) Solvent screening

Representative procedure for solvent screening: Inside a nitrogen-filled glovebox, to a 9 mL screw-cap vial with an oven-dried magnetic stir bar was added a solution of $[(o\text{-tolyl})_3P]_2PdCl_2$ (4.6 mg, 5 mol%), *o*-bromobenzyltributylstannane (64.4 mg, 1.2 equiv), and norbornene (11.0 mg, 1 equiv) in 0.6 mL DMA. Additional DMA (2 × 0.5 mL) was used to rinse the vials used for transfer and weighing substrates and catalyst and added to the reaction mixture. The vial was sealed, removed from the glovebox, and heated to 75 °C for 22 h. The mixture was cooled to 0 °C for 10 min and 5 µL undecane was added (internal reference). The contents of the vial were extracted with Et_2O (2 × 4 mL) and water (5 mL) and the organic phase was washed with water (5 mL) and brine (5 mL), dried ($MgSO_4$), filtered through celite and analyzed by GC-MS and GC-FID.

Table SI-1. Solvent screening for the "diverted Heck" cyclopentenation of norbornene with *o*-bromobenzyltributylstannane (2a).[a]

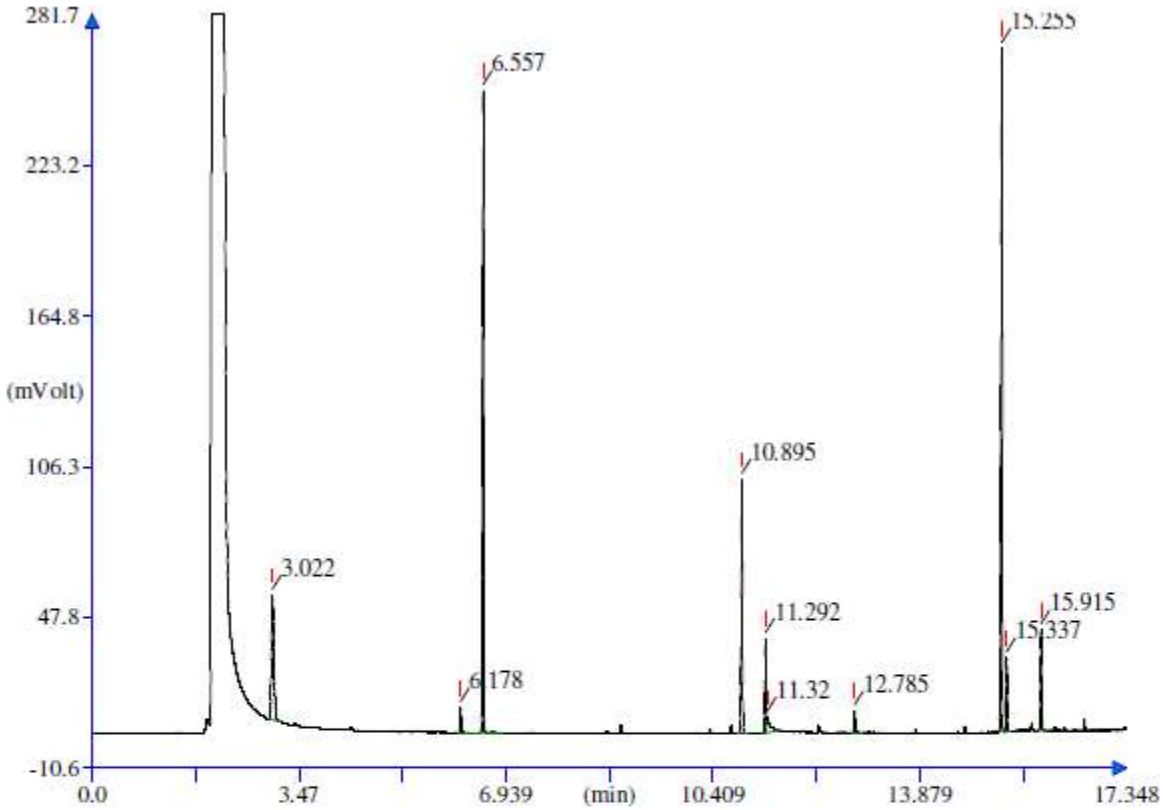


no.	solvent	yield (%)[b]	Conv. **2a** (%)[b]
1	hexane	2.1	8.8
2	toluene	4.2	16.8
3	fluorobenzene	5.1	28.9
4	THF	0.7	9.6
5	ethyl acetate	4.2	16.4
6	acetone	1.5	7.3
7	DMA	9.1	52.6
8	DMF	13.2	62.4
9	^{t}BuOH	19.2	47.3
10	DMSO	10.2	89.2
11	acetonitrile	3.2	16.7
12	^{i}PrOH	13.7	30.9
13	MeOH	18.2	58.0
14	ethylene glycol	10.3	62.2
15	water[c]	10.7	23.3

[a]Standard conditions: norbornene (11.0 mg, 1.0 equiv), stannane **2** (64.4 mg, 1.2 equiv), [(*o*-tolyl)$_3$P]$_2$PdCl$_2$ (4.6 mg, 5 mol%), 1.6 mL solvent, 75 °C, 22 h.

[b]Yields and conversions were evaluated by GC-FID.

[c]All components except for solvent were put into a 9 mL screw-cap vial with a septum cap. The degassed water was added outside of the glovebox through the septum.



Peak Number #	Area %	Ret.Time	Area	BC
1	11.8958	3.02	1316797	mi
2	1.2840	6.18	142132	mi
3	27.2800	6.56	3019752	mi
4	11.2468	10.90	1244954	mi
5	3.5781	11.29	396077	mi
6	2.0251	11.32	224173	mi
7	1.0500	12.79	116232	mi
8	34.5638	15.26	3826025	mi
9	2.8171	15.34	311842	mi
10	4.2592	15.92	471473	mi
Totals	100.0000		11069460	

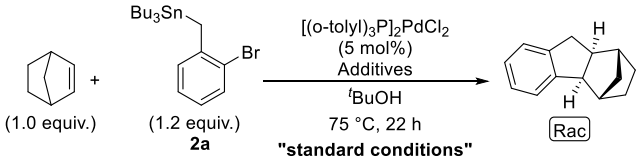
Figure SI-7. Representative GC-FID (Finnigan Focus GC) chromatogram for solvent screening for the cyclopentenation of norbornene using *o*-bromobenzyl(tributyl) stannane (**1**). Retention times norbornene (t_R= 3.02 min), *o*-bromotoluene (t_R= 6.18 min), undecane (t_R= 6.56 min; internal standard), *exo*-2,3,4,4a,9,9a-Hexahydro-1*H*-1,4-methanofluorene (t_R= 10.90 min), *o*-bromobenzyl(tributyl) stannane (t_R= 15.26 min). In this case, the solvent was *tert*-butanol.

2) Additive screening

Representative procedure for additive screening: Inside a nitrogen-filled glovebox, a 9 mL screw-cap vial with an oven-dried magnetic stir bar was charged with CsF (21.3 mg, 1.2 equiv). A solution of $[(o\text{-tolyl})_3P]_2PdCl_2$ (4.6 mg, 5 mol%), *o*-bromobenzyltributylstannane (64.4 mg, 1.2 equiv), and norbornene (11.0 mg, 1 equiv) in 0.6 mL ^{t}BuOH was added. ^{t}BuOH (2 × 0.5 mL) was used to rinse the vials used for transfer and weighing substrates and catalyst and added to the reaction mixture. The vial was sealed, removed from the glovebox, and heated to 75 °C for 22 h. The mixture was cooled to 0 °C for 10 min and 5 µL undecane was added (internal reference). The contents of the vial were

extracted with Et_2O (2 × 4 mL) and water (5 mL) and the organic phase was washed with water (5 mL) and brine (5 mL), dried ($MgSO_4$), filtered through celite and analyzed by GC-MS and GC-FID.

Table SI-2. Additive screening for the "diverted Heck" cyclopentenation of norbornene with *o*-bromobenzyltributylstannane (2a).[a]

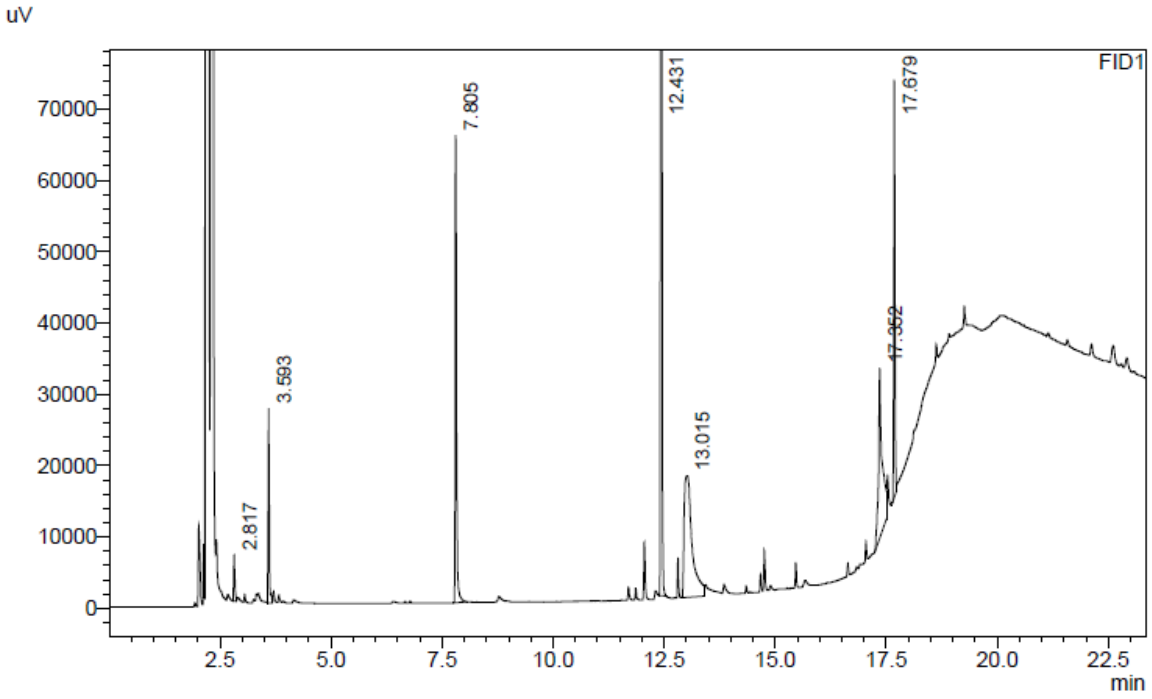


no.	additive	yield (%)[b]	Conv. **2a** (%)[b]
1	none	19.2	47.3
2	LiCl (1.2 equiv.)	10.8	99.1
3	CuI (0.1 equiv.)	6.8	95.9
4	CuI (0.2 equiv.)	2.7	3.9
5	CuI (1.2 equiv.)	1.4	35.4
6	CsF (1.2 equiv.)	42.2	100
7	CsF (2.4 equiv.)	32.3	100
8	CsF (1.2 equiv.) CuI (0.1 equiv)	7.0	21.6
9	CsF (1.2 equiv.) CuI (0.2 equiv)	3.6	39.6
10	CsF (2.4 equiv.) CuI (0.1 equiv)	3.6	44.8
11	CsF (2.4 equiv.) CuI (0.2 equiv)	6.7	53.5
12[c]	CsF (1.2 equiv.)	83.1	87.8

[a]Standard conditions: norbornene (11.0 mg, 1.0 equiv), stannane **2** (64.4 mg, 1.2 equiv), $[(o\text{-tolyl})_3P]_2PdCl_2$ (4.6 mg, 5 mol%), 1.6 mL ^{t}BuOH, 75 °C, 22 h.

[b]Yields and conversions were evaluated by GC-FID.

[c]Reaction run in ^{i}PrOH instead of ^{t}BuOH.



<Peak Table>

FID1

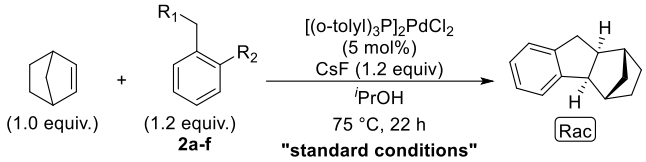
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	2.817	12788	6419	1.267			
2	3.593	49128	26785	4.867		V	
3	7.805	132610	64984	13.137			
4	12.431	365334	198196	36.192		M	
5	13.015	213813	17020	21.182			
6	17.352	131726	23528	13.050			
7	17.679	104032	57833	10.306			
Total		1009432	394765				

Figure SI-8. Representative GC-FID (Shimadzu GC-2025) chromatogram for additive screening for the cyclopentenation of norbornene using *o*-bromobenzyl(tributyl) stannane (**1**). Retention times norbornene (t_R= 3.59 min), undecane (t_R= 7.81 min; internal standard), *exo* -2,3,4,4a,9,9a-Hexahydro-1*H*-1,4-methanofluorene (t_R= 12.43 min). In this case, 1.2 eq. CsF was added.

3) Reagent screening

Representative Cyclopentenation Procedure for Reagent Screening. Inside a nitrogen-filled glovebox, a 9 mL screw-cap vial with an oven-dried magnetic stir bar was charged with CsF (21.3 mg, 1.2 equiv). A solution of $[(o\text{-tolyl})_3P]_2PdCl_2$ (4.6 mg, 5 mol%), *o*-bromobenzyltributylstannane (64.4 mg, 1.2 equiv), and norbornene (11.0 mg, 1 equiv) in 0.6 mL ^{i}PrOH was added. ^{i}PrOH (2 × 0.5 mL) was used to rinse the vials used for transfer and weighing substrates and catalyst and added to the reaction mixture. The vial was sealed, removed from the glovebox, and heated to 75 °C for 22 h. The mixture was cooled to 0 °C for 10 min and 5 µL undecane was added (internal reference). The contents of the vial were extracted with Et_2O (2 × 4 mL) and water (5 mL) and the organic phase was washed with water (5 mL) and brine (5 mL), dried ($MgSO_4$), filtered through celite and analyzed by GC-MS and GC-FID.

Table SI-3. Reagent screening for the "diverted Heck" cyclopentenation of norbornene.[a]



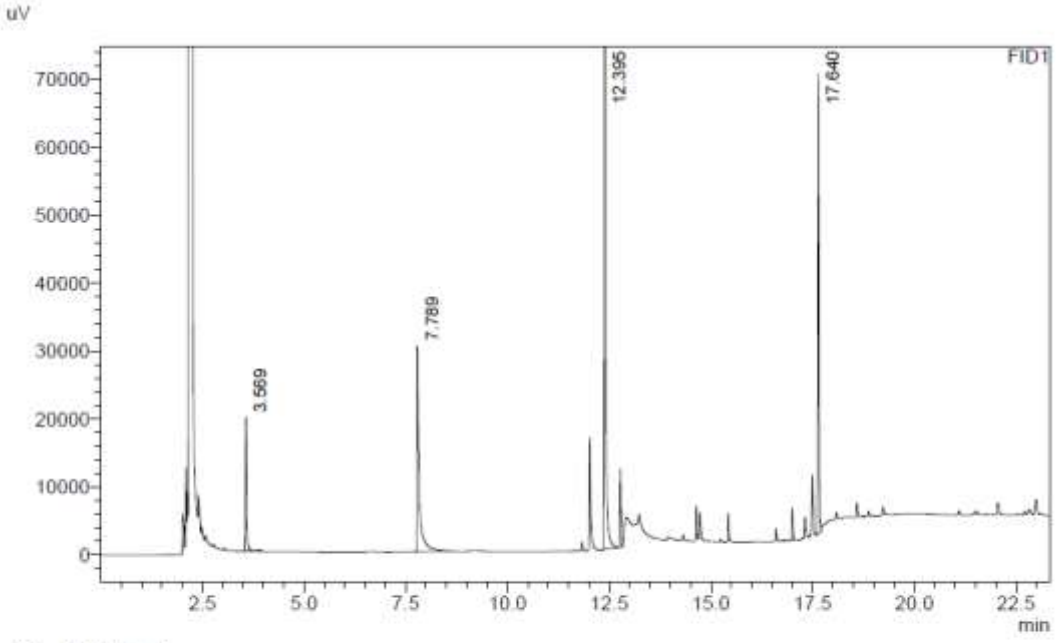
2a: $R_1 = SnBu_3$ $R_2 = Br$
2b: $R_1 = SnBu_3$ $R_2 = Cl$
2c: $R_1 = SnBu_3$ $R_2 = I$
2d: $R_1 = SnBu_3$ $R_2 = OTf$
2e: $R_1 = SnMe_3$ $R_2 = Br$
2f: $R_1 = I$ $R_2 = SnBu_3$

no.	reagent	yield (%)[b]	Conv. **2a-f** (%)[b]
1	**2a**	83.1	87.8
2	**2b**	0.6	28.4
3[c]	**2c**	36.0	38.2
4	**2d**	0.0	7.5
5	**2e**	76.6	94.2
6	**2f**	24.4	>99

[a]Standard conditions: norbornene (11.0 mg, 1.0 equiv), stannane **2a-f** (1.2 equiv), CsF (21.3 mg, 1.2 equiv.), [(*o*-tolyl)$_3$P]$_2$PdCl$_2$ (4.6 mg, 5 mol%), 1.6 mL ^{i}PrOH, 75 °C, 22 h.

[b]Yields were evaluated by GC-FID.

[c]Reaction was conducted with all volumes and masses of solvents and reagents cut in half.



<Peak Table>

FID1

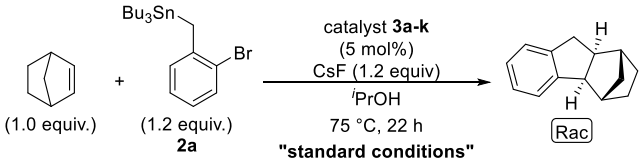
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.569	40670	19499	0.000	ppm		Norbornene
2	7.789	112306	30068	0.000	ppm		Undecane
3	12.395	404953	201564	0.000	ppm	M	DHP
4	17.640	121394	66846	0.000	ppm		o-Bromobenzyltributylstannane
Total		679323	317978				

Figure SI-9. Representative GC-FID (Shimadzu GC-2025) chromatogram for reagent screening for the cyclopentenation of norbornene using *o*-bromobenzyl(tributyl) stannane (**1**). Retention times norbornene (t_R= 2.99 min), undecane (t_R= 6.45 min; internal standard), *exo* -2,3,4,4a,9,9a-Hexahydro-1*H*-1,4-methanofluorene (t_R= 10.79 min). In this case, **2a** was used.

4) Catalyst screening

For catalyst screening, the representative cyclopentanation procedure for reagent screening was used.

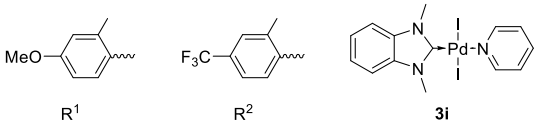
Table SI-4. Catalyst screening for the "diverted Heck" cyclopentenation of norbornene.[a]



no.	catalyst	yield (%)[b]	Conv. **2a** (%)[b]
1	[(*o*-tol$_3$P)$_2$PdCl$_2$] (**3a**)	64.0	>99
2	[(R$^1_3$P)$_2$PdCl$_2$] (**3b**)	68.4	98.3
3	[(R$^2_3$P)$_2$PdCl$_2$] (**3c**)	75.6	91.3
4	[(*o*-tol$_3$P)$_2$PdCl$_2$] (**3d**)	22.4	63.7
5	[(Ph$_3$P)$_4$Pd] (**3e**)	35.7	72.5
6	[(Ph$_3$P)$_4$Ni] (**3f**)	30.2	49.6
7	[(dppf)PdCl$_2$] (**3g**)	50.8	83.7
8	tBuXPhos Pd G3 (**3h**)	2.0	89.5
9	**3i**	0.0	<1
10	[(^{t}BuNC)$_2$PdCl$_2$] (**3j**)	0.0	<1
11	Pd(OAc)$_2$ (**3k**)	0,0	<1

[a]Standard conditions: norbornene (11.0 mg, 1.0 equiv), stannane **2a** (64.4 mg, 1.2 equiv.), CsF (21.3 mg, 1.2 equiv.), catalyst **3a-k** (5 mol%), 1.6 mL ^{i}PrOH, 75 °C, 22 h.

[b]Yields were evaluated by GC-FID.



5) Isolation of the cyclopentenation product

Inside a nitrogen-filled glovebox, an oven-dried 250 mL two-neck flask with an oven-dried magnetic stir bar was charged with CsF (495.2 mg, 1.2 equiv). A solution of [(o tolyl)$_3$P]$_2$PdCl$_2$ (109.7 mg, 5 mol%), *o*-bromobenzyltributylstannane (1499.9 mg, 1.2 equiv), and norbornene (256.5 mg, 1 equiv) in 37.5 mL ^{t}BuOH was added. The flask was fitted with a glass stopper and glass tap, removed from the glovebox and attached to an argon-filled Schlenk line. The mixture was heated to 75 °C for 22 h. The mixture was cooled to 0 °C and diluted with 75 mL Et$_2$O. It was washed with water (2 × 40 mL) and brine (40 mL), dried (MgSO$_4$) and filtered through a pad of silica, washing with additional pentane. The solution was concentrated and the residue was purified by column chromatography (hexane) twice. The product exo-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene was obtained as 58.8 mg (12%) of a color-less oil. 1H NMR (400 MHz, CDCl3) δ 7.23 – 7.09 (m, 4H), 3.27 (dd, J = 17.1, 10.2 Hz, 1H), 3.15 (d, J = 7.9 Hz, 1H), 2.62 (dd, J = 17.1, 3.4 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.29 (s, 1H), 2.11 (s, 1H), 1.69 – 1.50 (m, 2H), 1.48 – 1.37 (m, 1H), 1.34 – 1.22 (m, 1H), 1.19 – 1.08 (m, 1H), 1.06 – 0.95 (m, 1H). 13C NMR (101 MHz, CDCl3) δ 146.51, 144.95, 126.36, 126.32, 124.62, 124.15, 55.60, 45.02, 43.87, 43.56, 39.47, 32.55, 29.13, 28.96. HRMS (EI) calcd for $C_{14}H_{16}$ $[M]^+$ 184.1247, found 184.1244.

The NOESY spectrum of the product shows couplings of the protons 17 and 20, and 19 and 18. Those couplings are only possible for the *exo* isomer as shown in Figure SI-7 below.

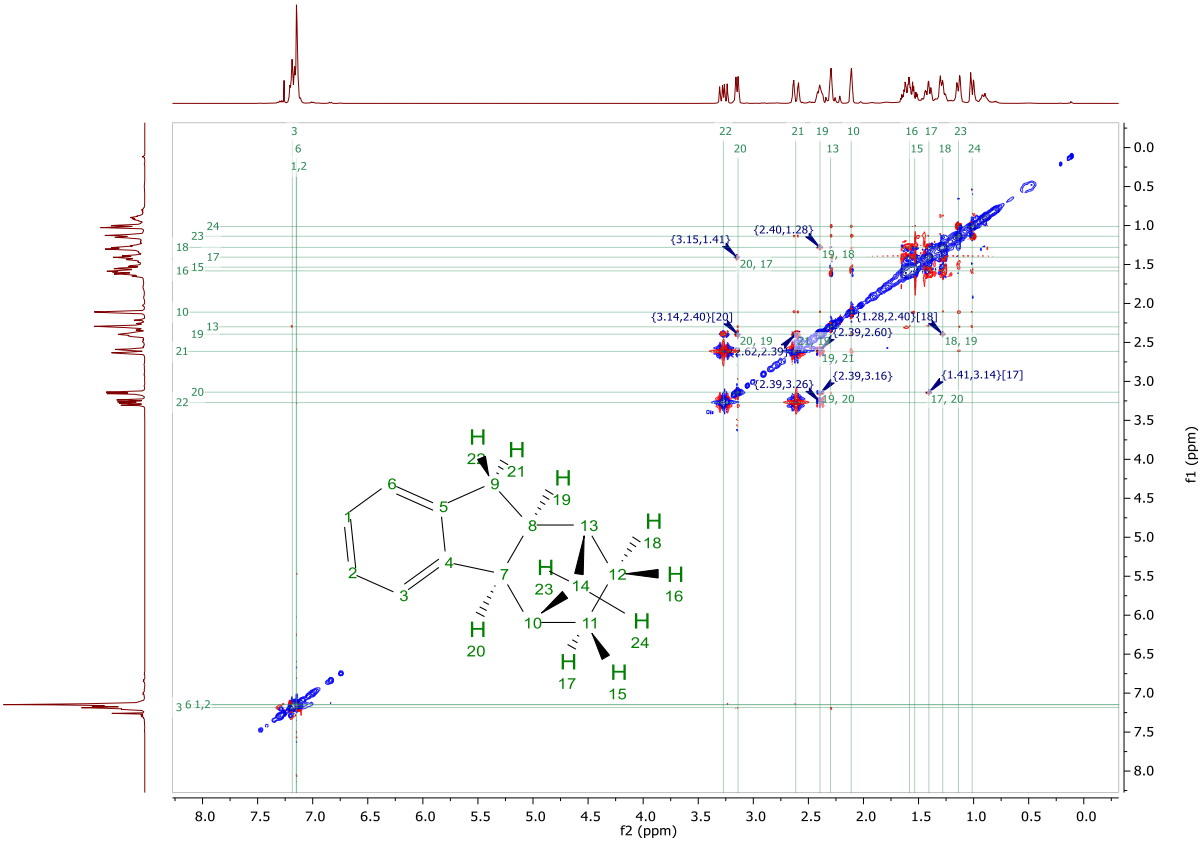
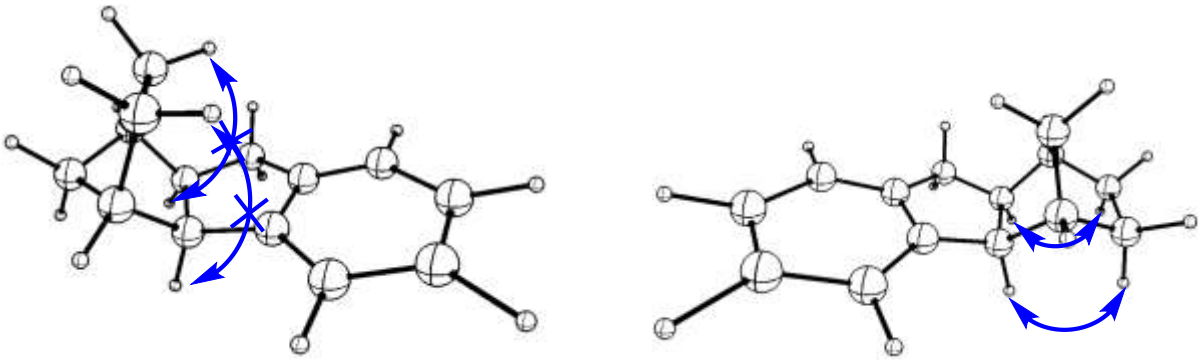


Figure SI-10. NOESY (^{1}H (500 MHz), ^{1}H (500 MHz), $CDCl_3$) spectrum of *exo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene from the „diverted Heck“ reaction of **2a** and norbornene.



endo *exo*

Figure SI-11. Explanation of the couplings observed in the NOESY spectrum, confirming the *exo* isomer.

IV-References

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V-Spectra

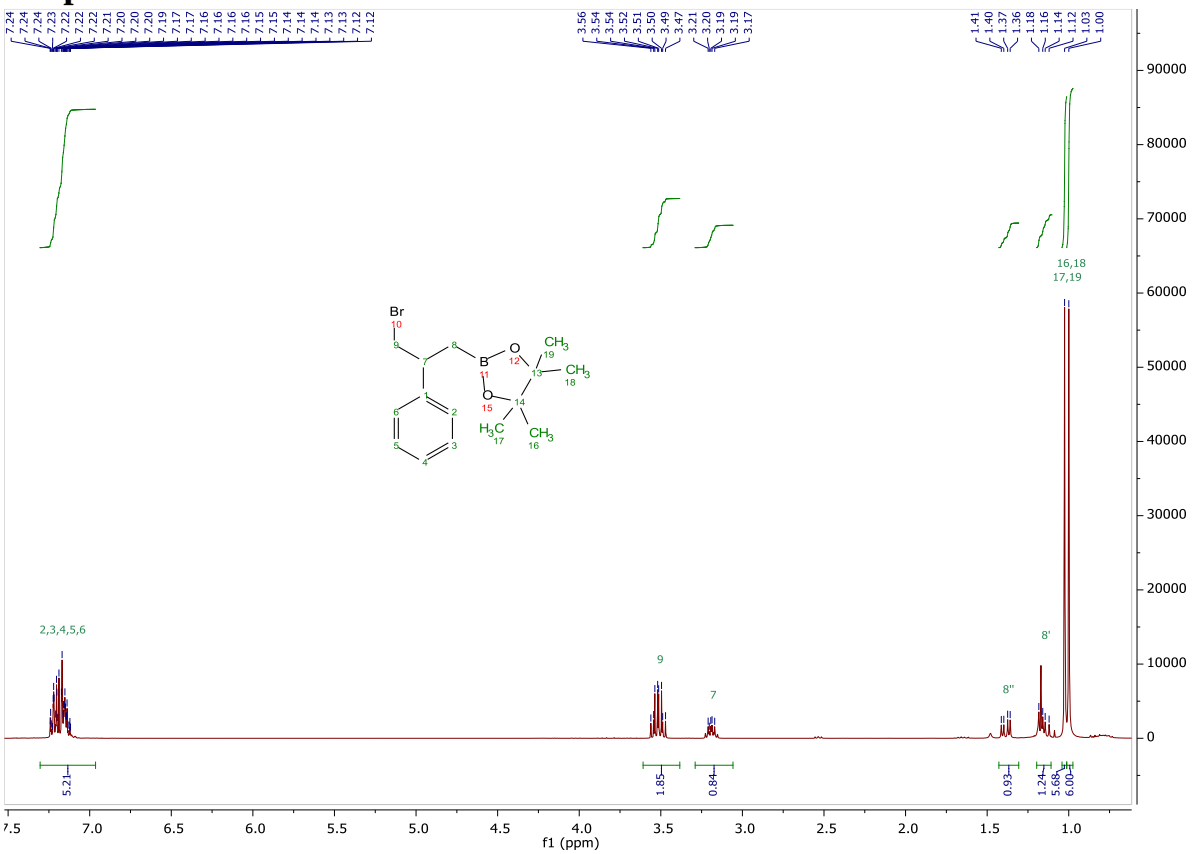

Figure SI-12. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-bromo-2-phenylpropylboronic acid pinacol ester.

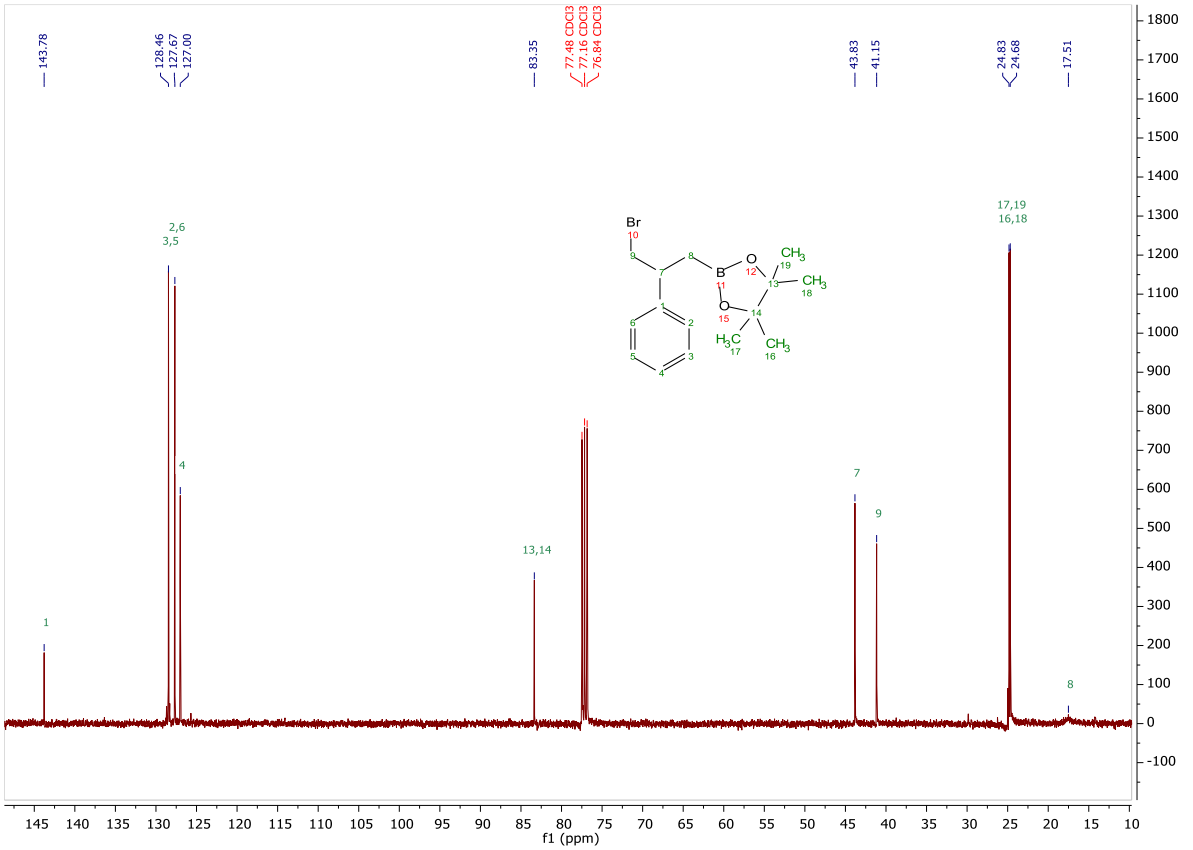

Figure SI-13. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3-bromo-2-phenylpropylboronic acid pinacol ester.

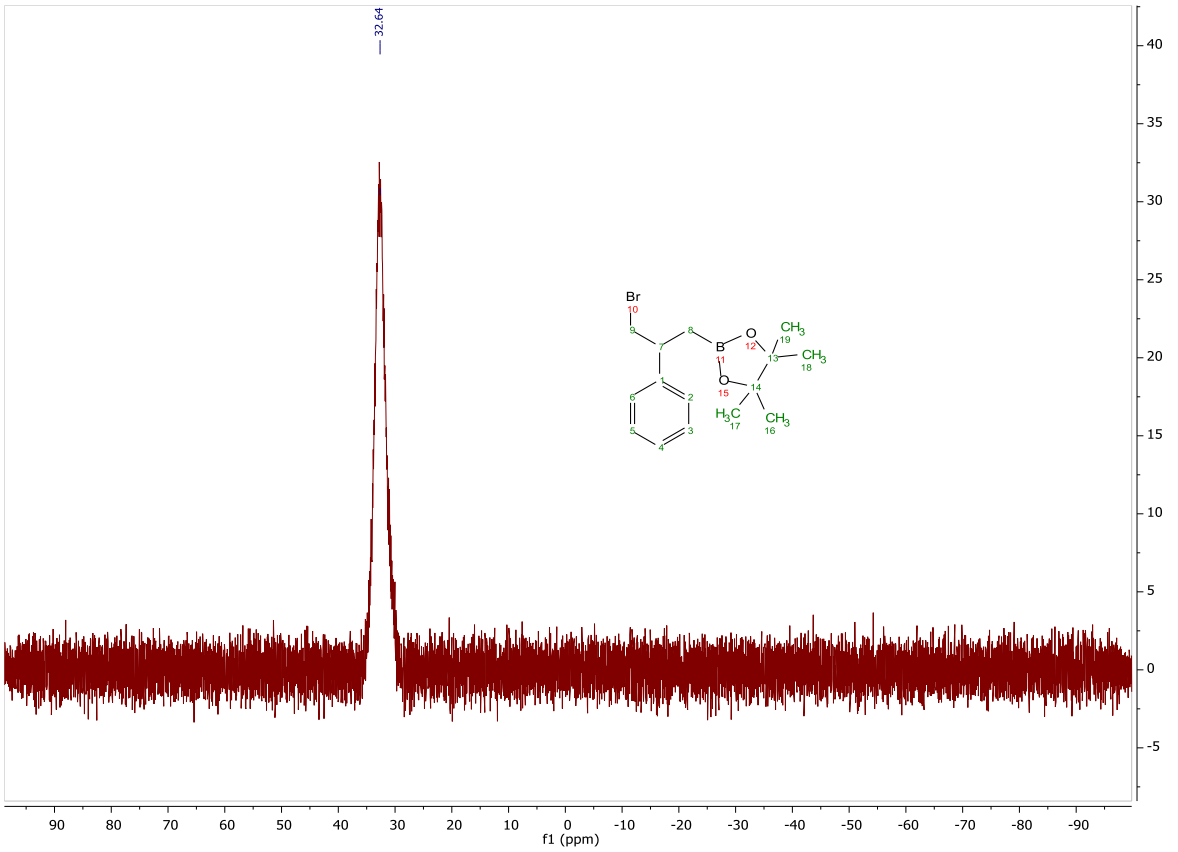

Figure SI-14. ^{11}B NMR (128 MHz, $CDCl_3$) spectrum of 3-bromo-2-phenylpropylboronic acid pinacol ester.

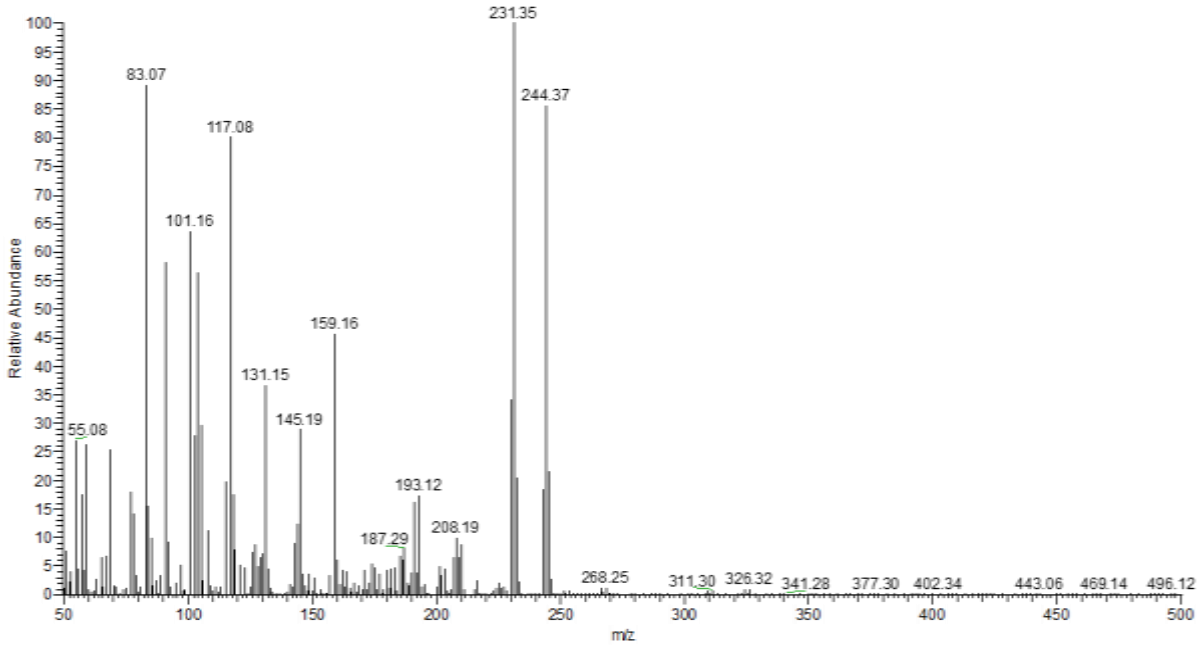

Figure SI-15. EI-MS spectrum of 3-bromo-2-phenylpropylboronic acid pinacol ester.

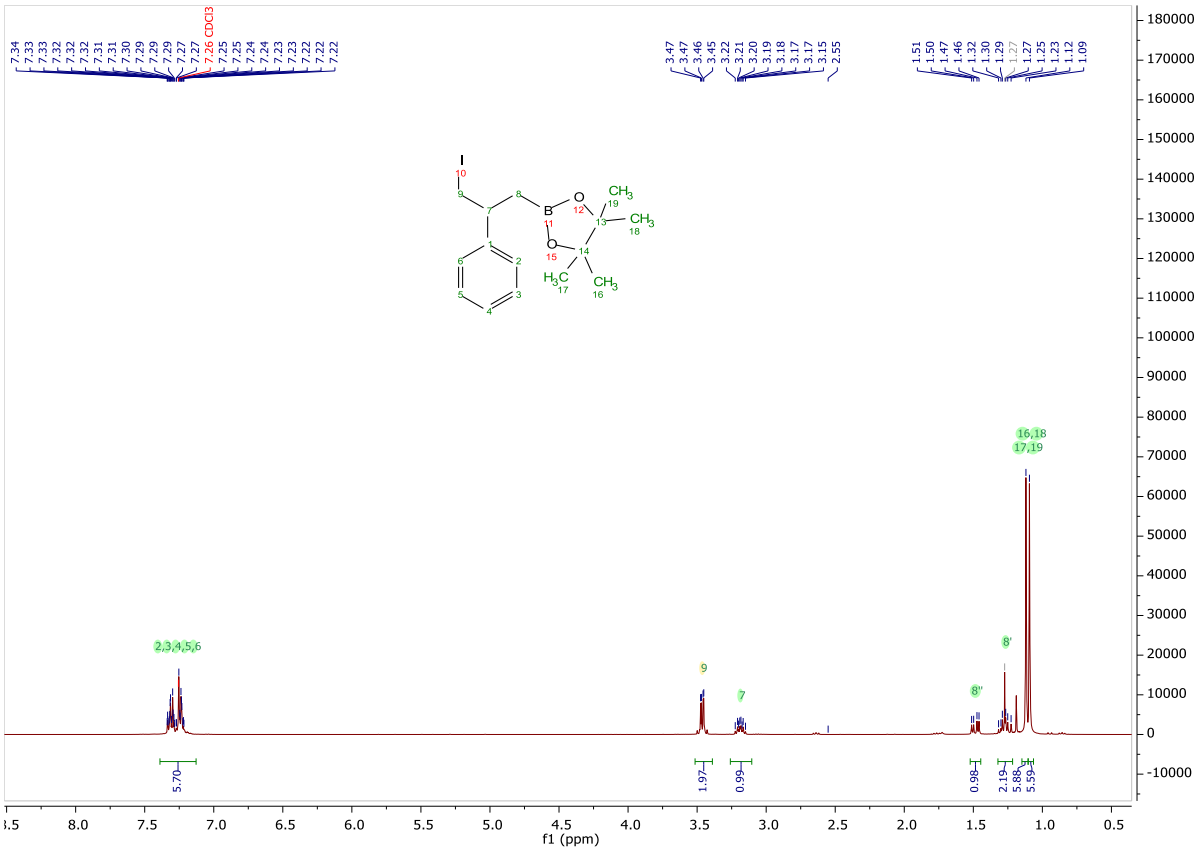

Figure SI-16. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-iodo-2-phenylpropylboronic acid pinacol ester. The integral for proton 8’ is higher due to overlap with minor impurities.

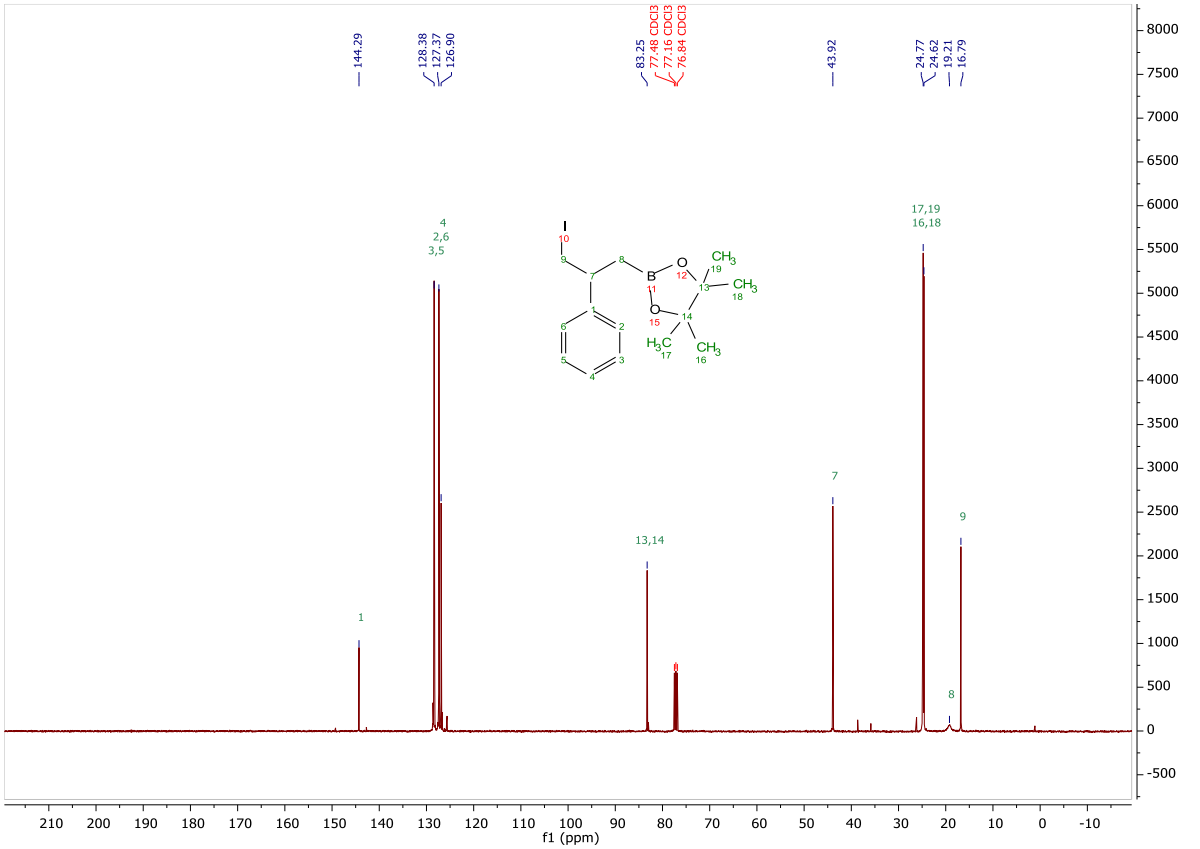

Figure SI-17. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3-iodo-2-phenylpropylboronic acid pinacol ester.

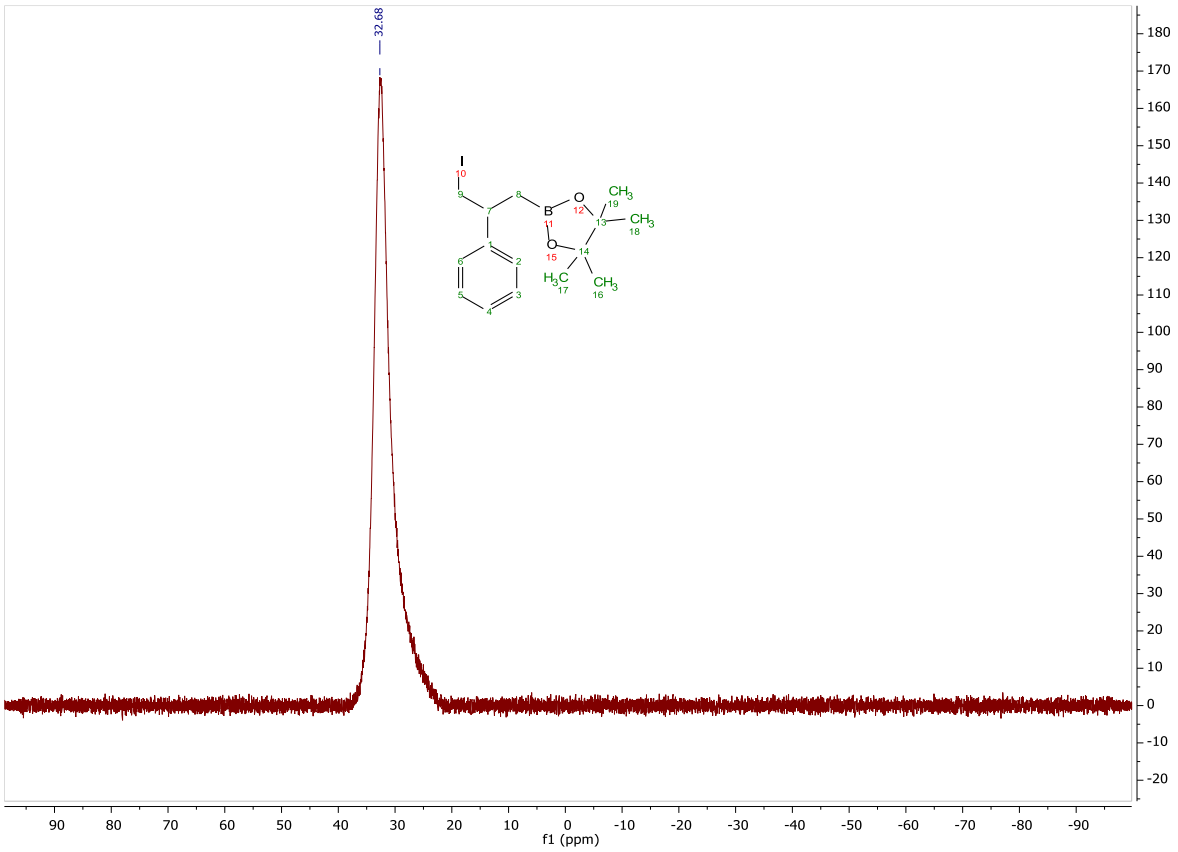

Figure SI-18. ^{11}B NMR (128 MHz, $CDCl_3$) spectrum of 3-iodo-2-phenylpropylboronic acid pinacol ester.

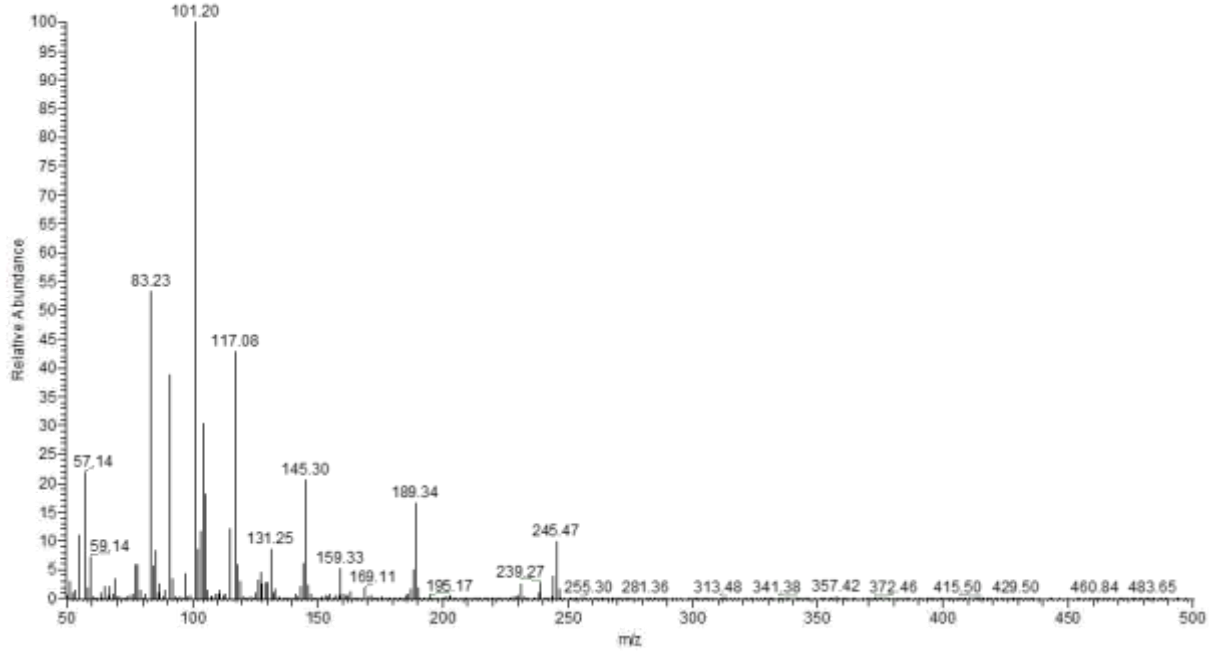

Figure SI-19. EI-MS spectrum of 3-iodo-2-phenylpropylboronic acid pinacol ester.

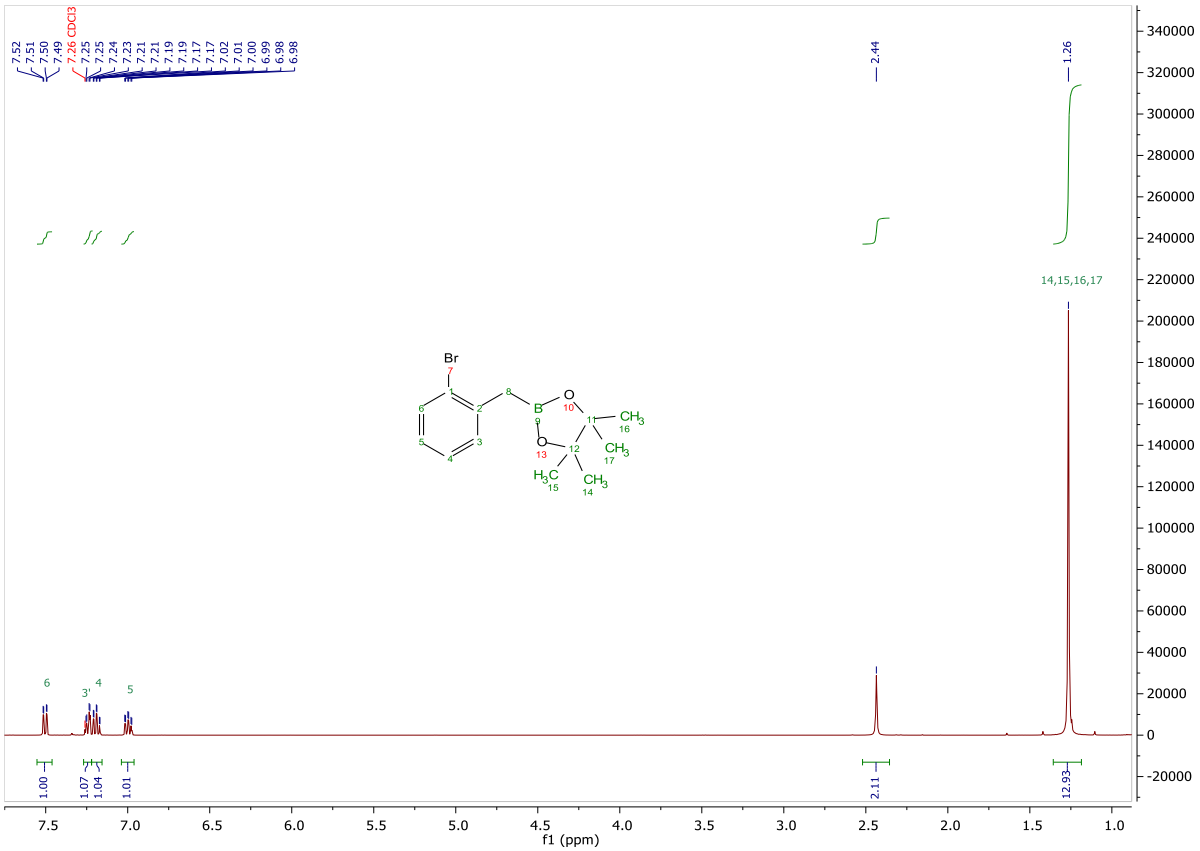

Figure SI-20. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-bromophenylmethylboronic acid pinacol ester (**1**).

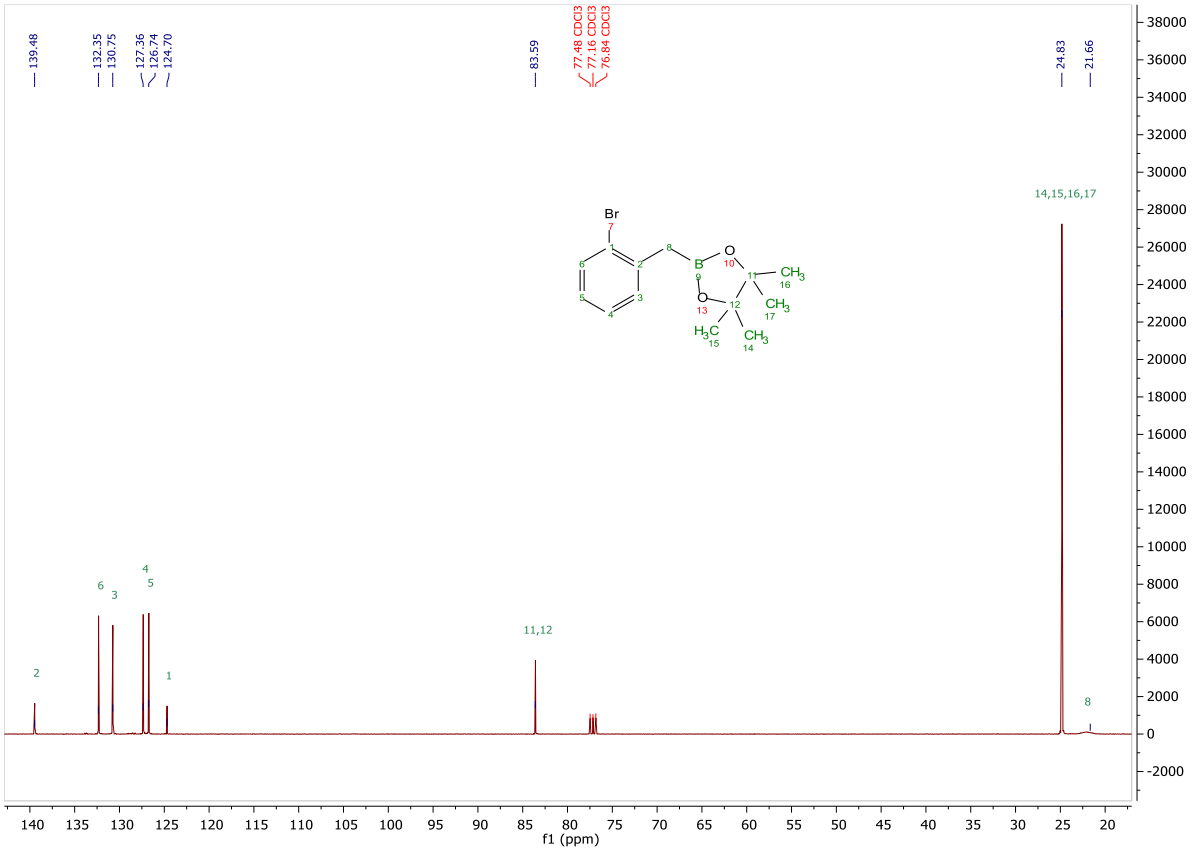

Figure SI-21. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-bromophenylmethylboronic acid pinacol ester (**1**).

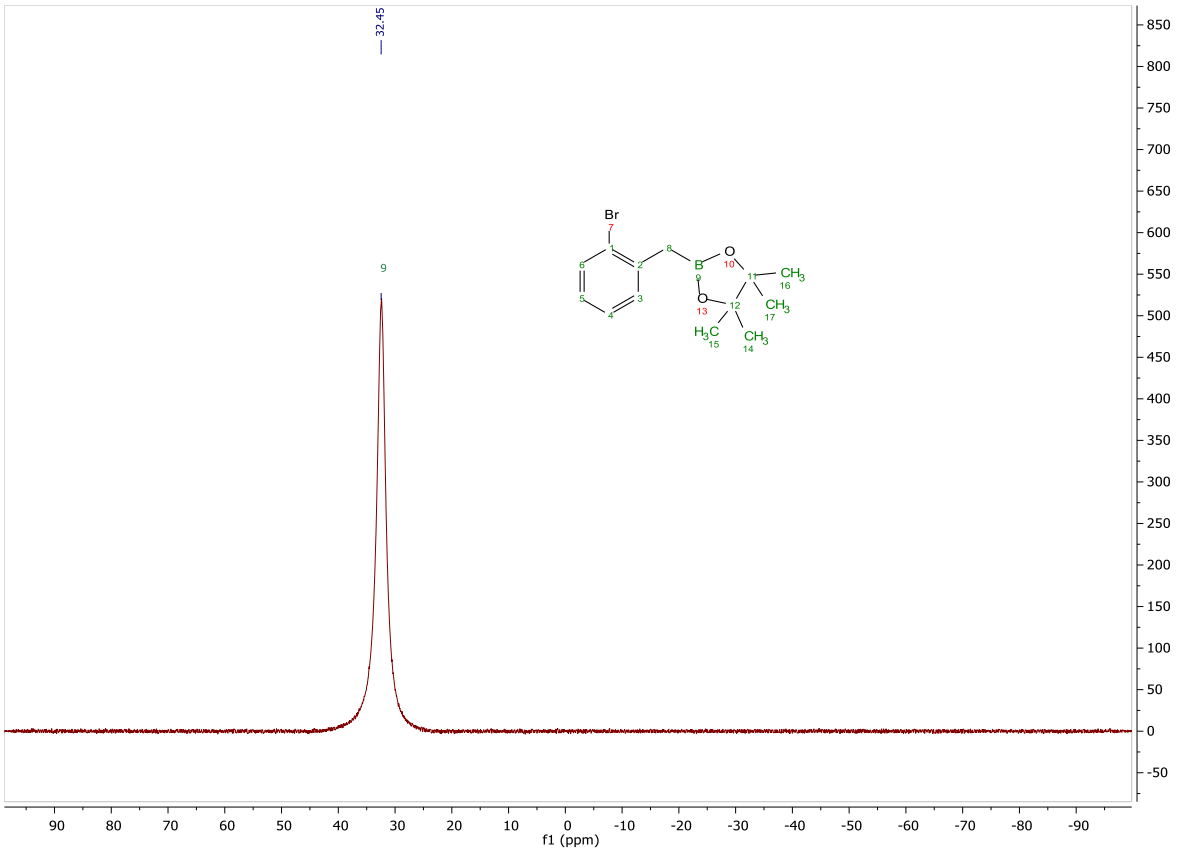

Figure SI-22. ^{11}B NMR (128 MHz, $CDCl_3$) spectrum of 2-bromophenylmethylboronic acid pinacol ester (**1**).

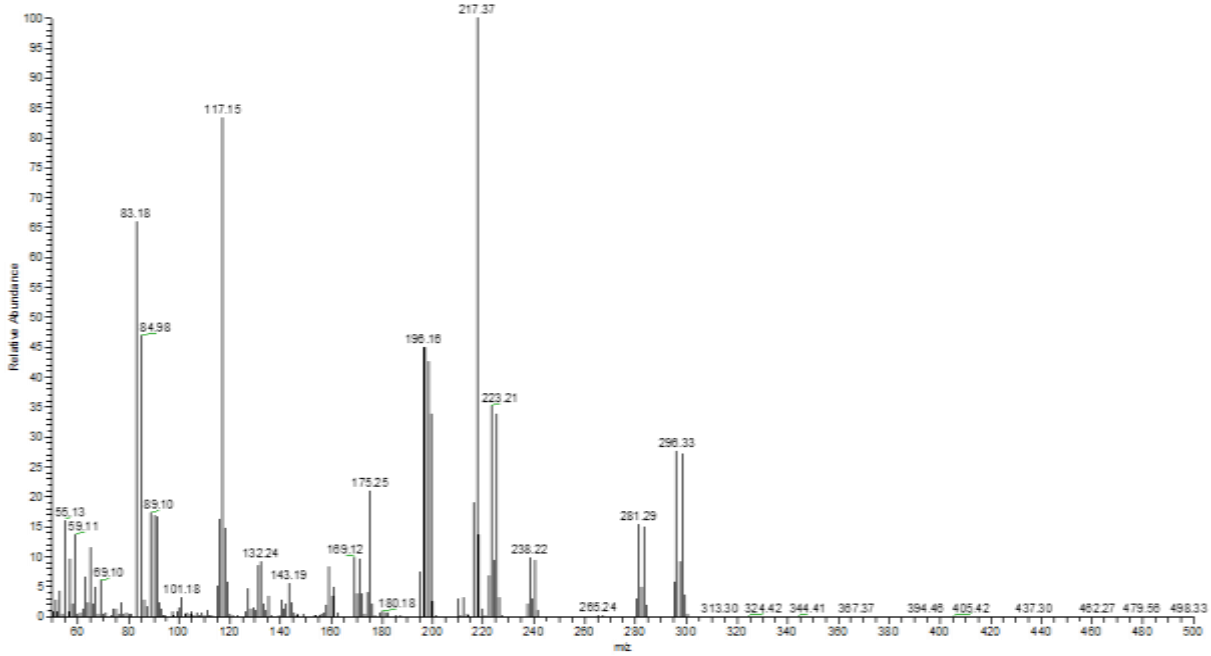

Figure SI-23. EI-MS spectrum of 2-bromophenylmethylboronic acid pinacol ester (**1**).

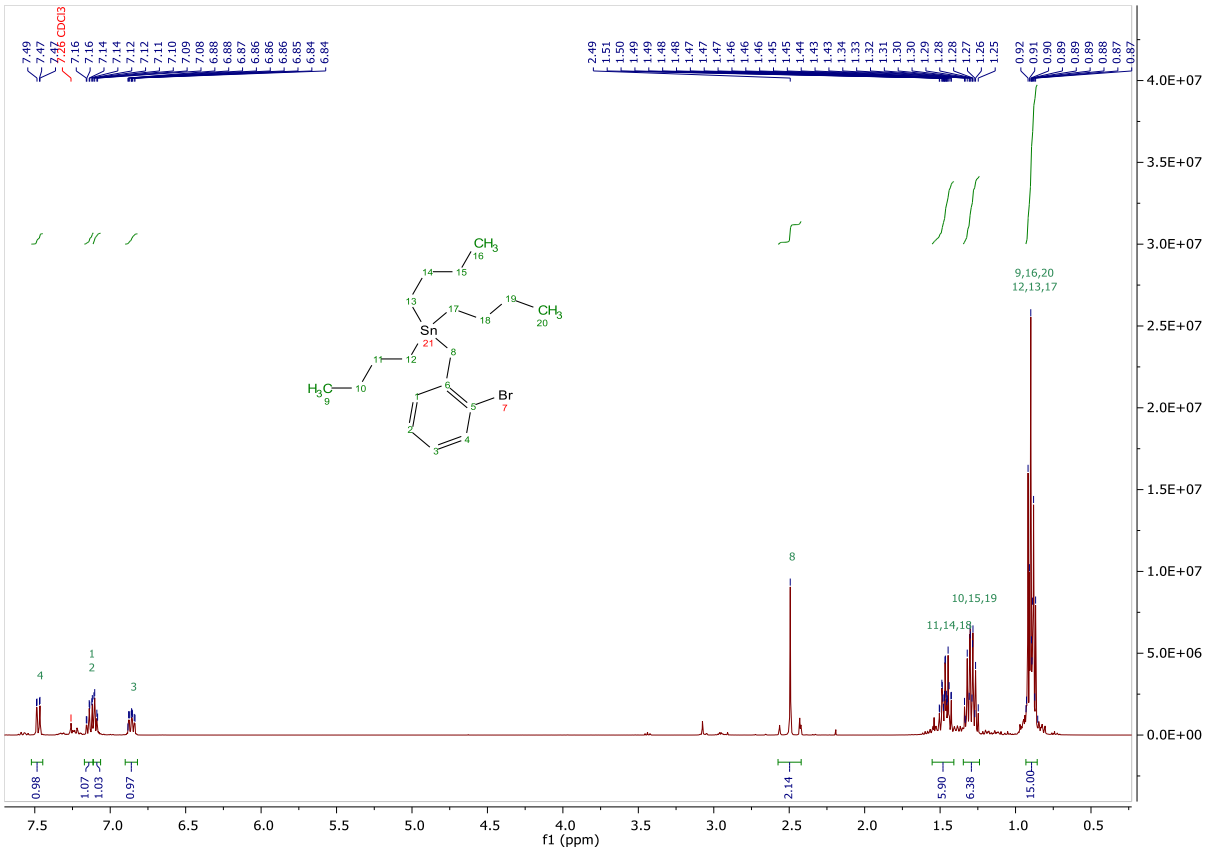

Figure SI-24. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-bromophenylmethyl(tributyl)stannane (**2a**).

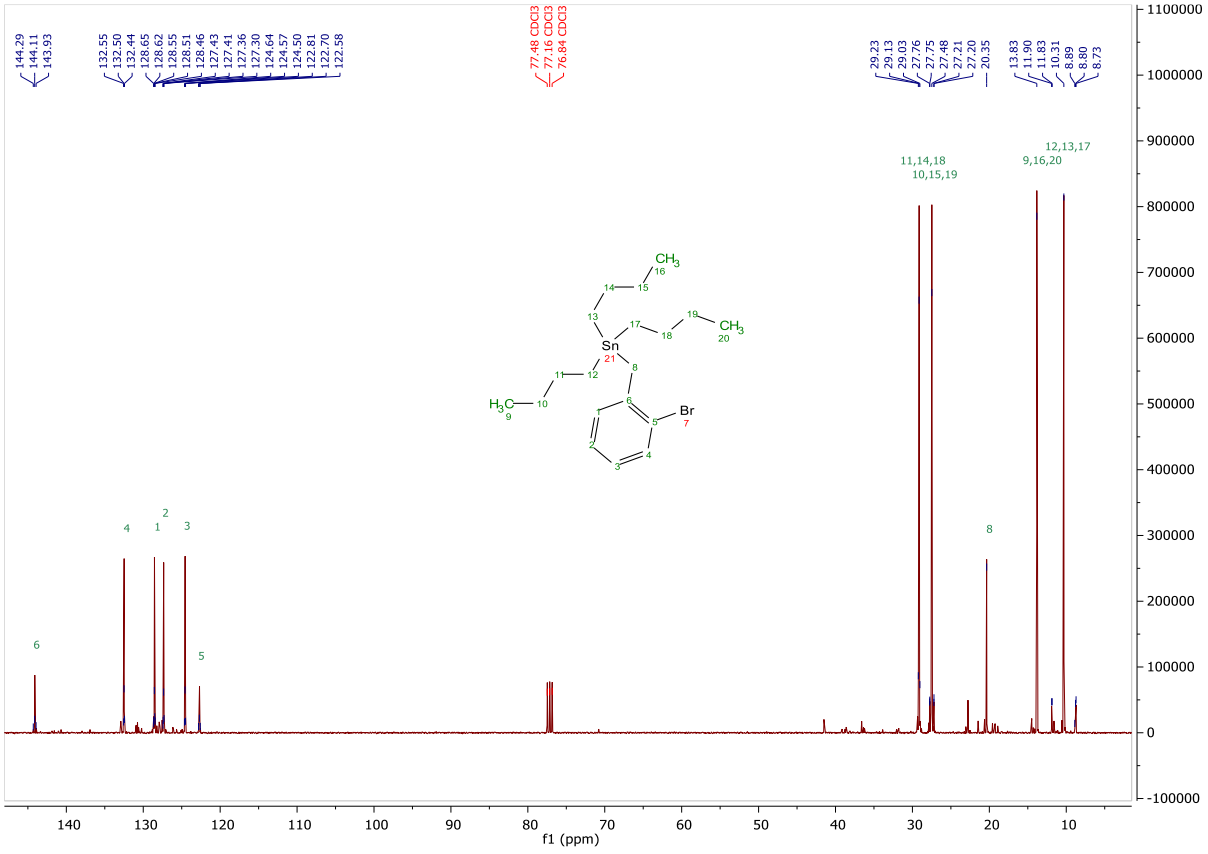

Figure SI-25. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-bromophenylmethyl(tributyl)stannane (**2a**).

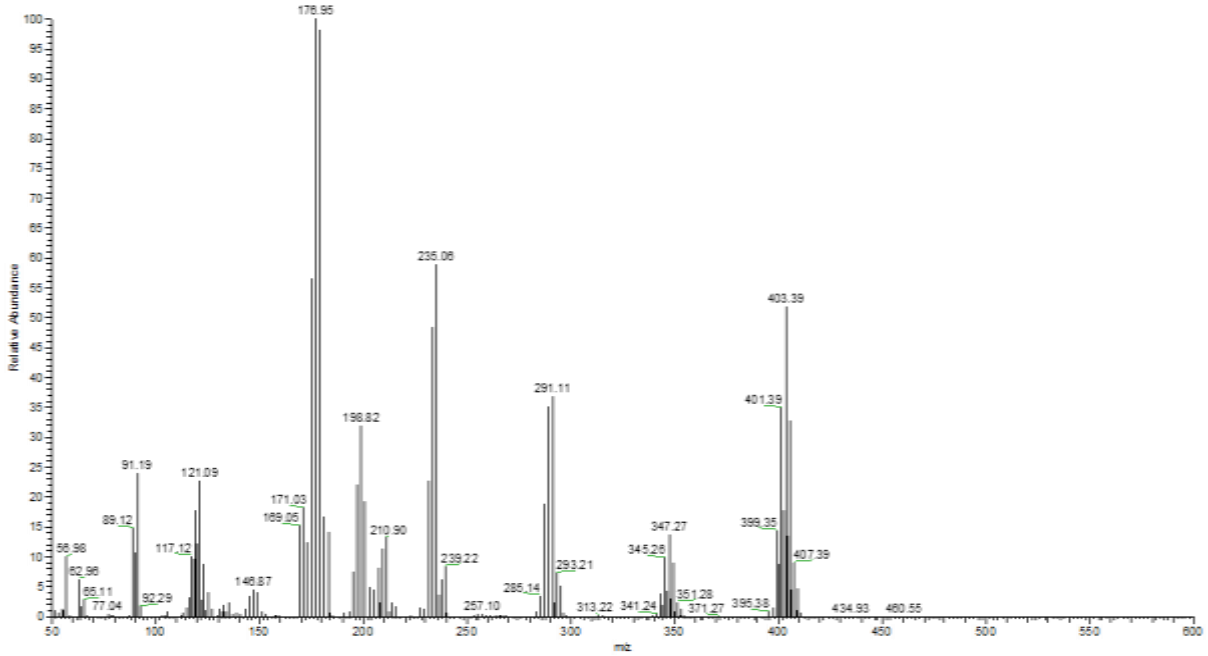

Figure SI-26. EI-MS spectrum of 2-bromophenylmethyl(tributyl)stannane (**2a**).

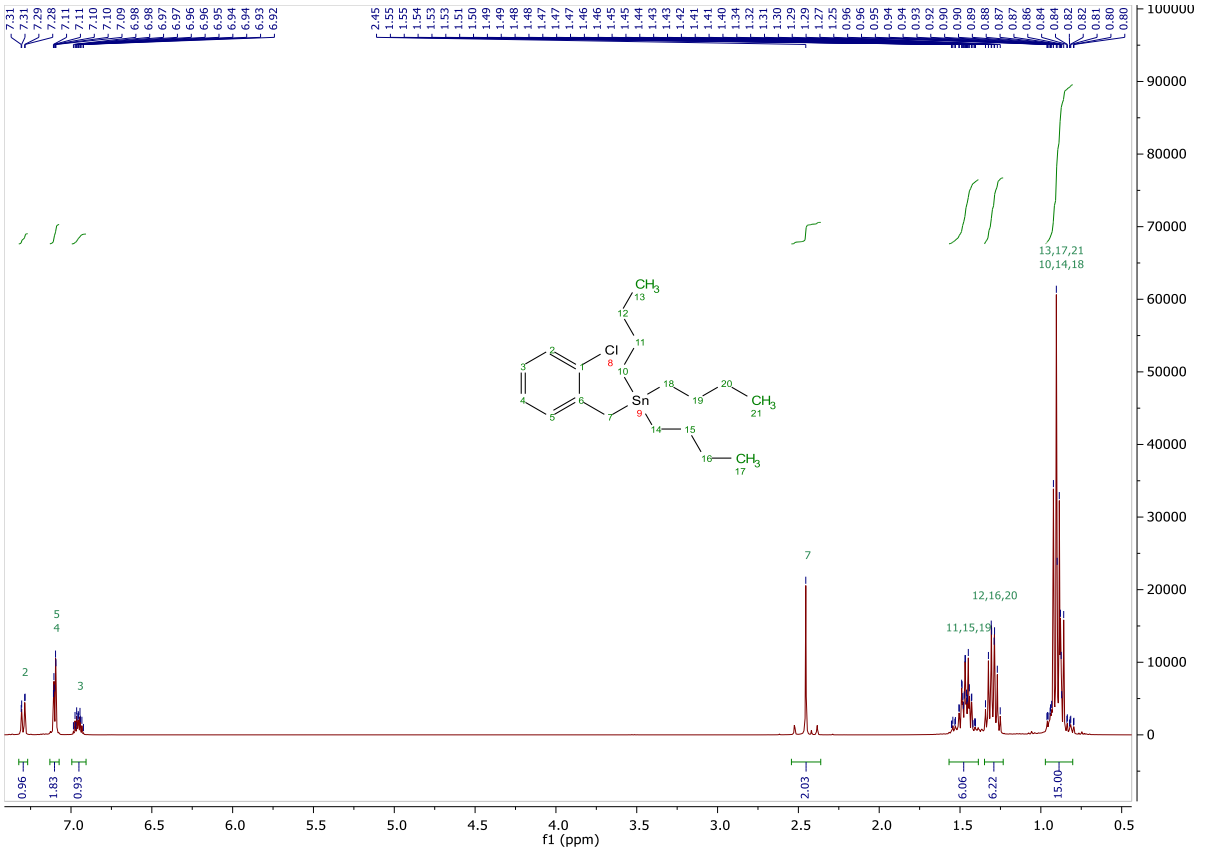

Figure SI-27. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-chlorophenylmethyl(tributyl)stannane (**2a**).

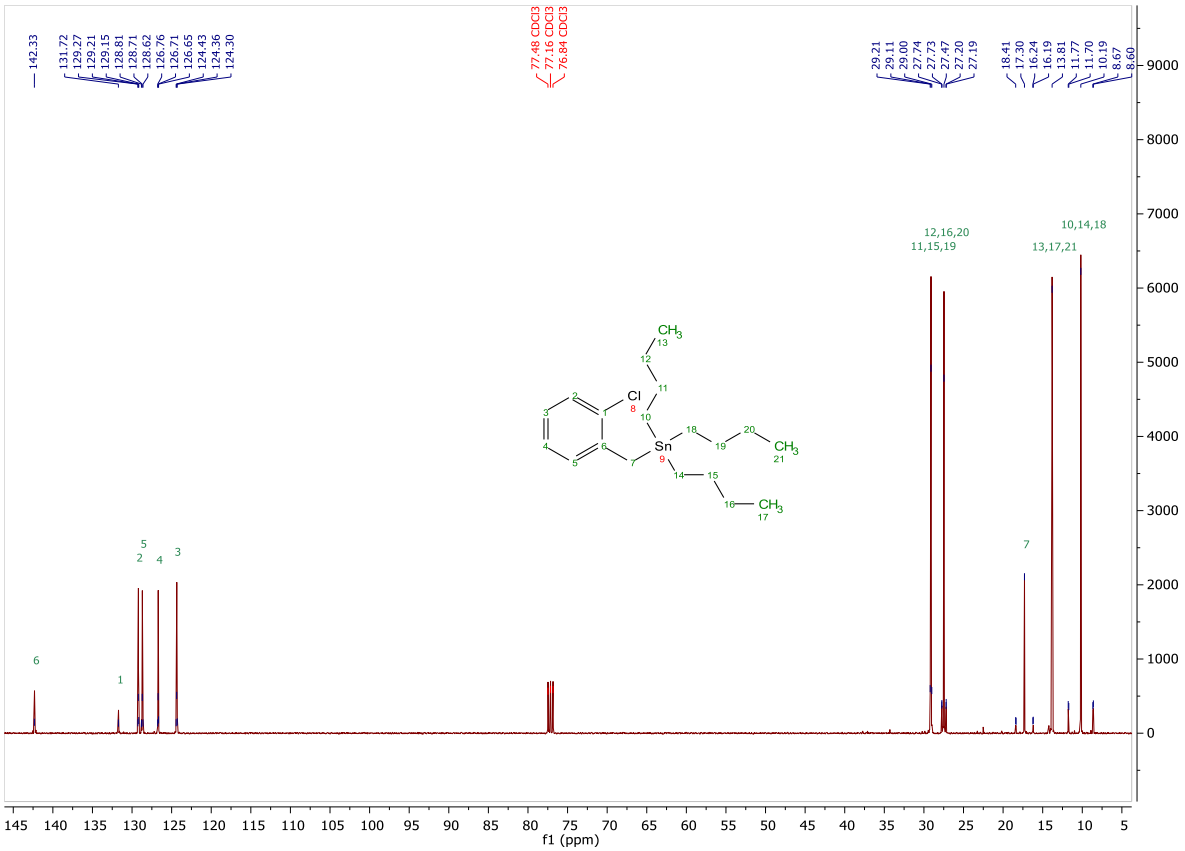

Figure SI-28. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-chlorophenylmethyl(tributyl)stannane (**2a**).

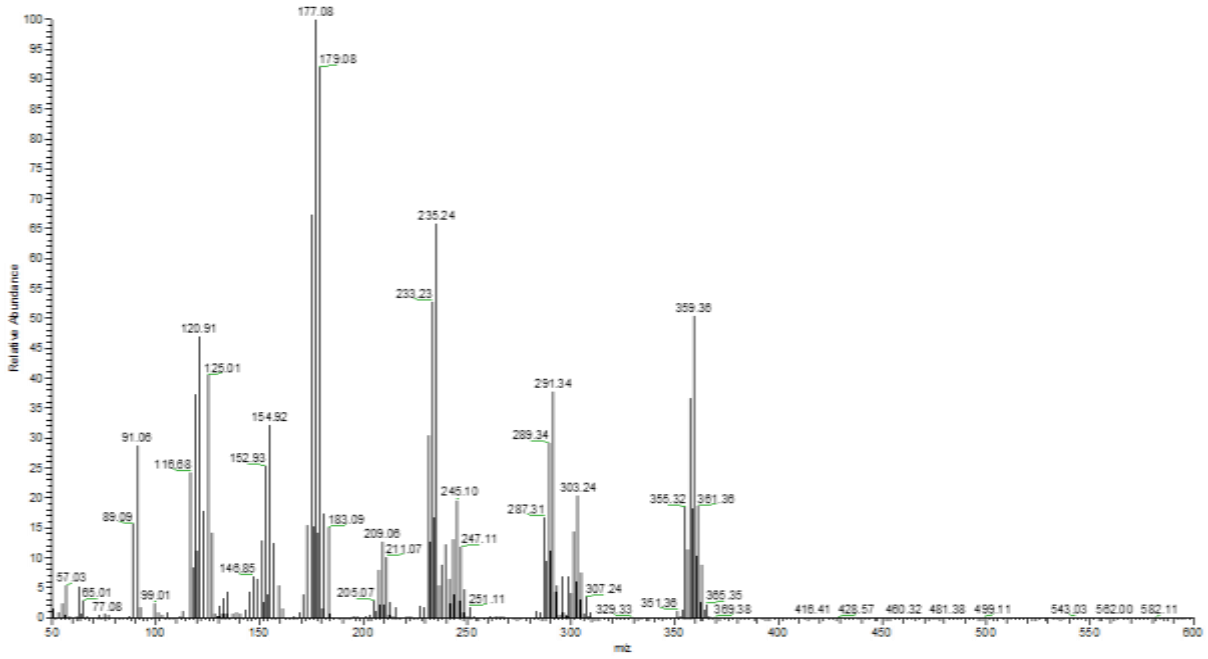

Figure SI-29. EI-MS spectrum of 2-chlorophenylmethyl(tributyl)stannane (**2a**).

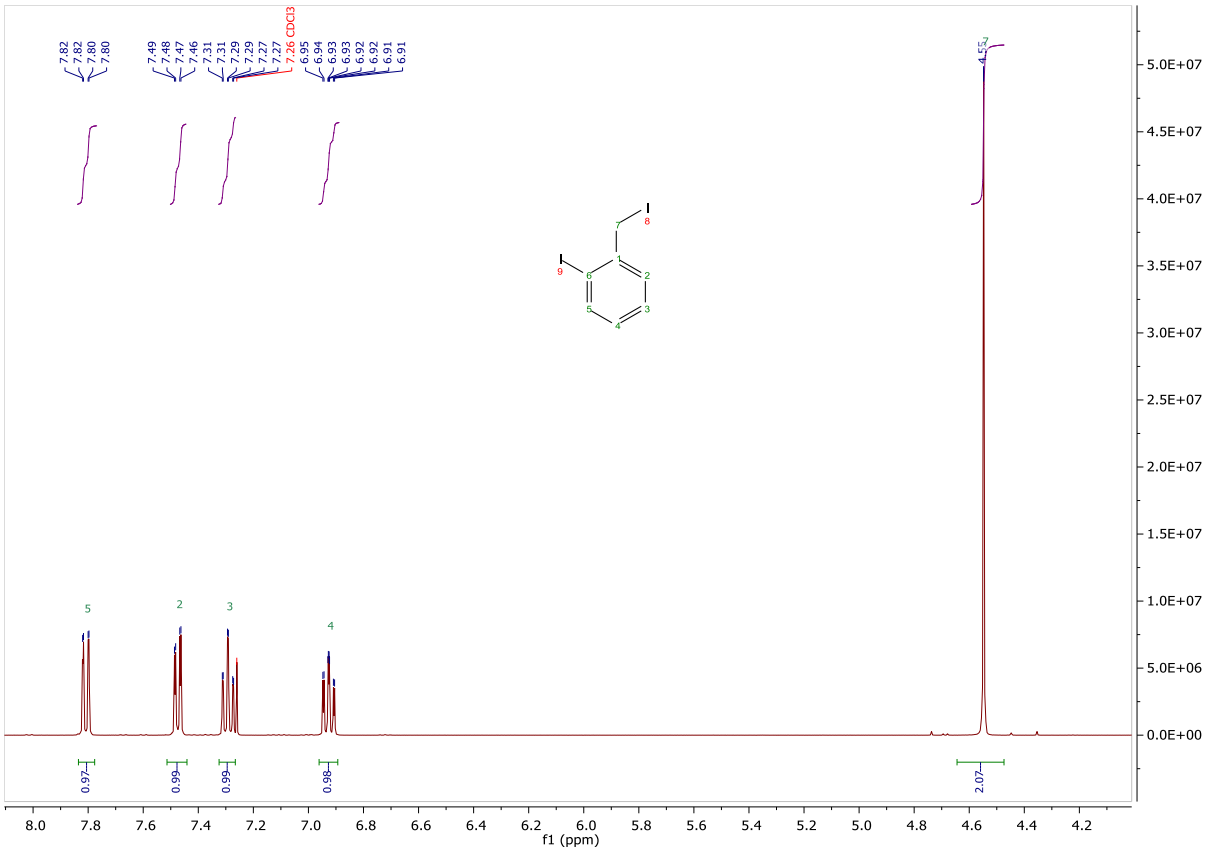

Figure SI-30. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-iodobenzyl iodide.

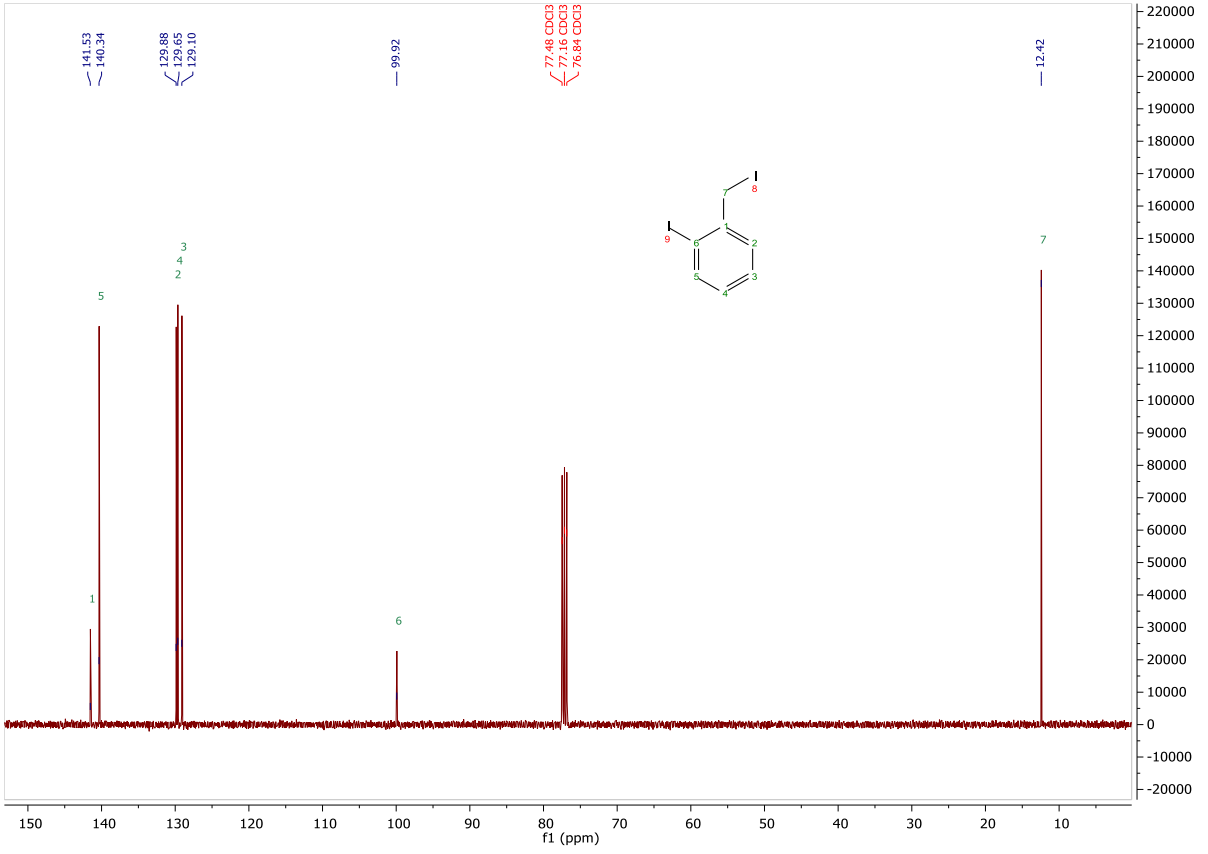

Figure SI-31. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-iodobenzyl iodide.

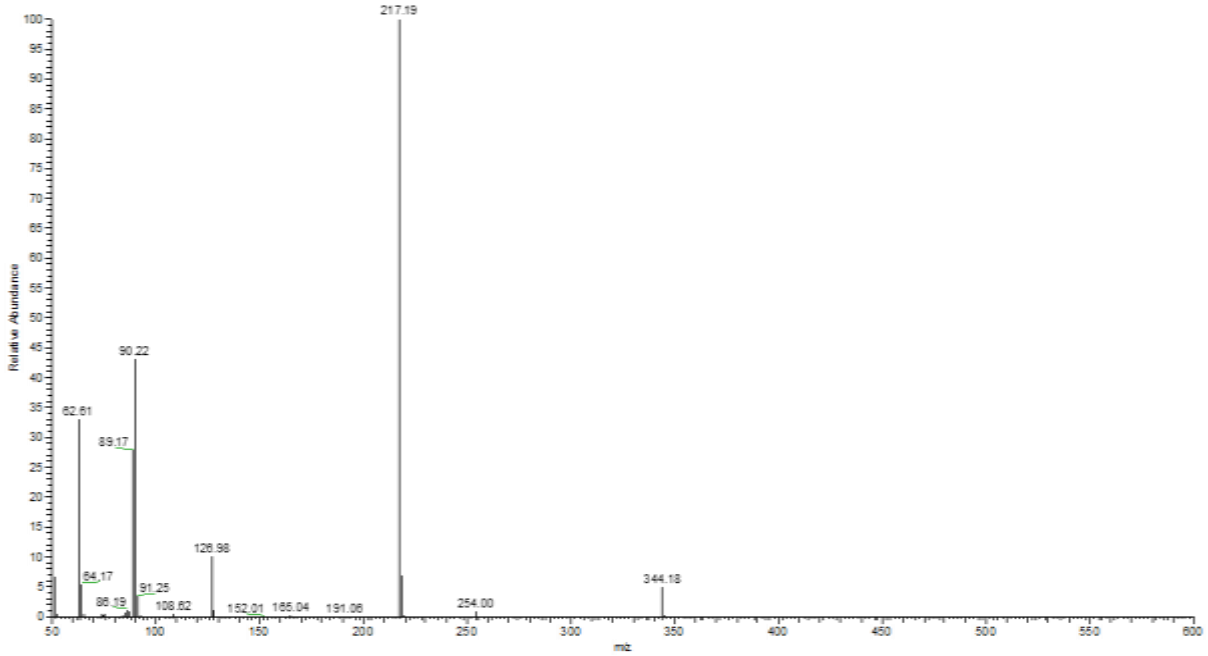

Figure SI-32. EI-MS spectrum of 2-iodobenzyl iodide.

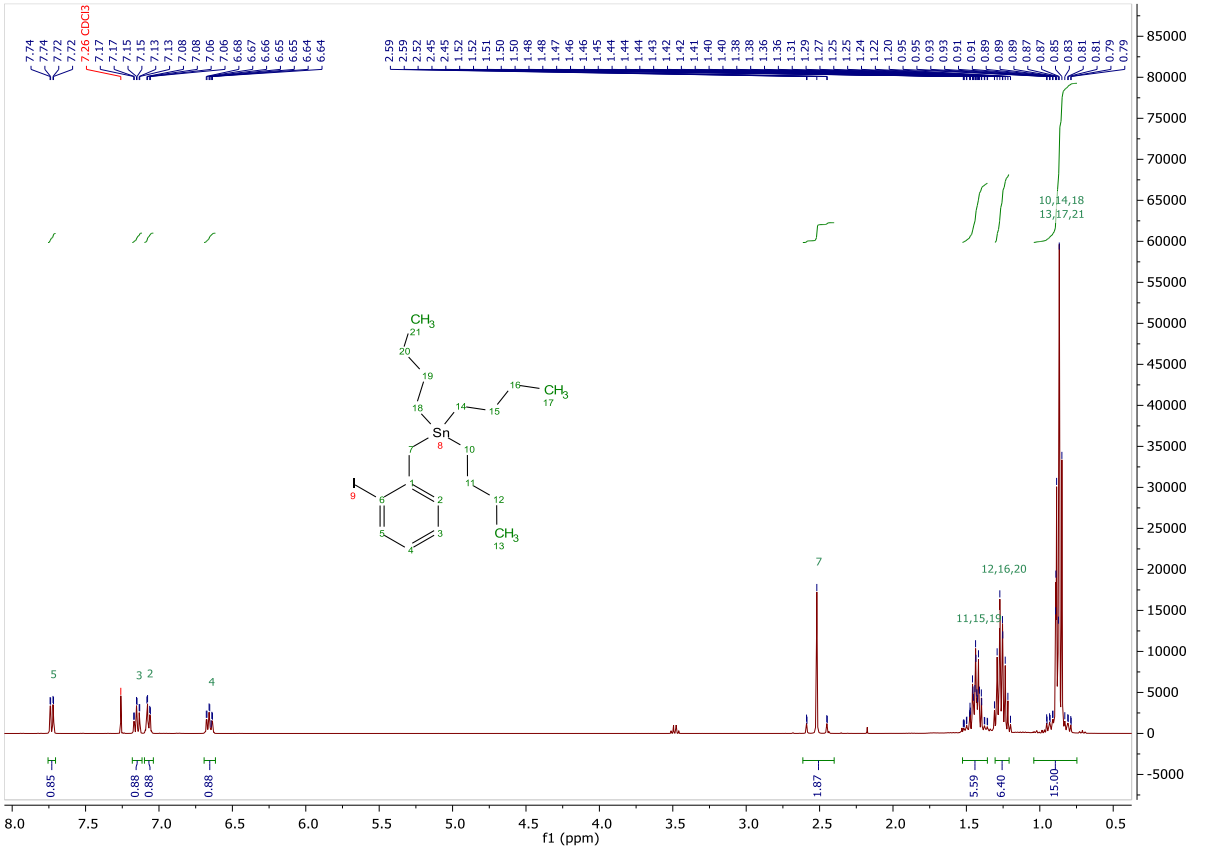

Figure SI-33. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-iodophenylmethyl(tributyl)stannane (**2c**).

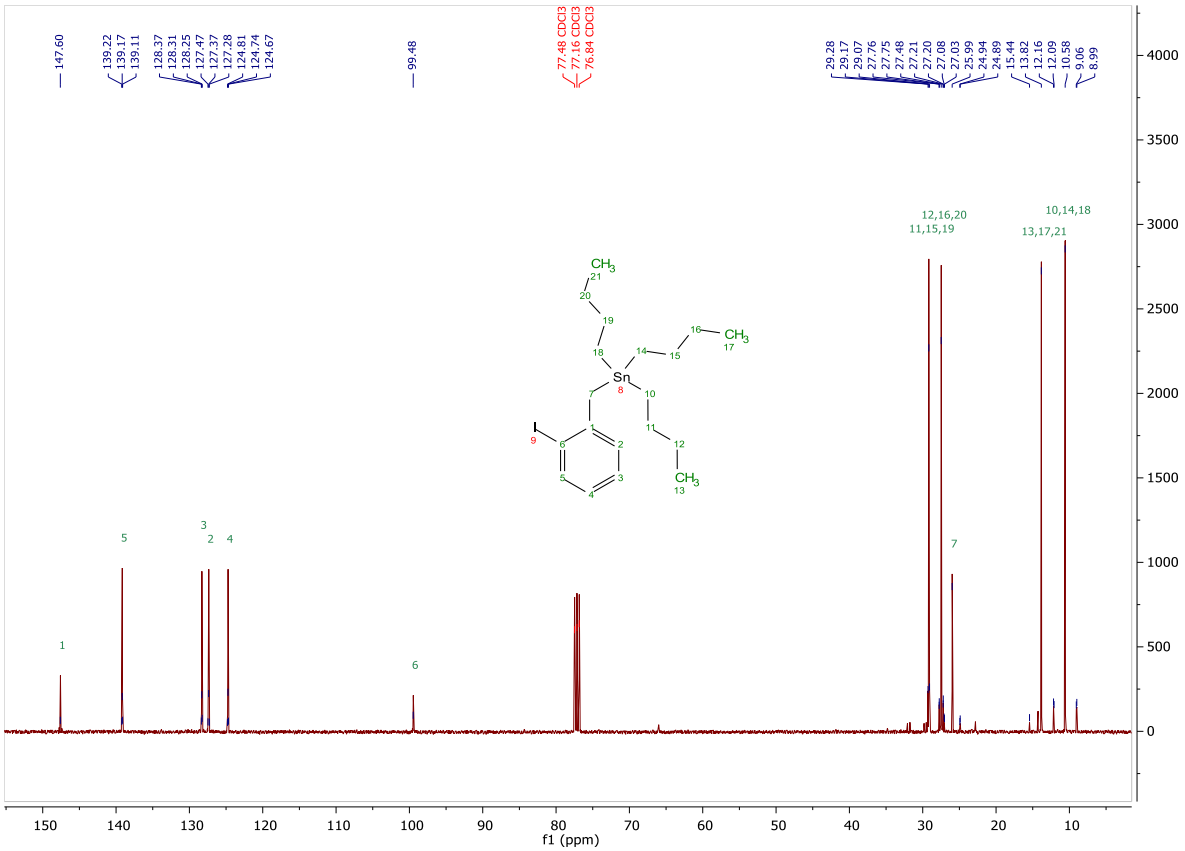

Figure SI-34. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-iodophenylmethyl(tributyl)stannane (**2c**).

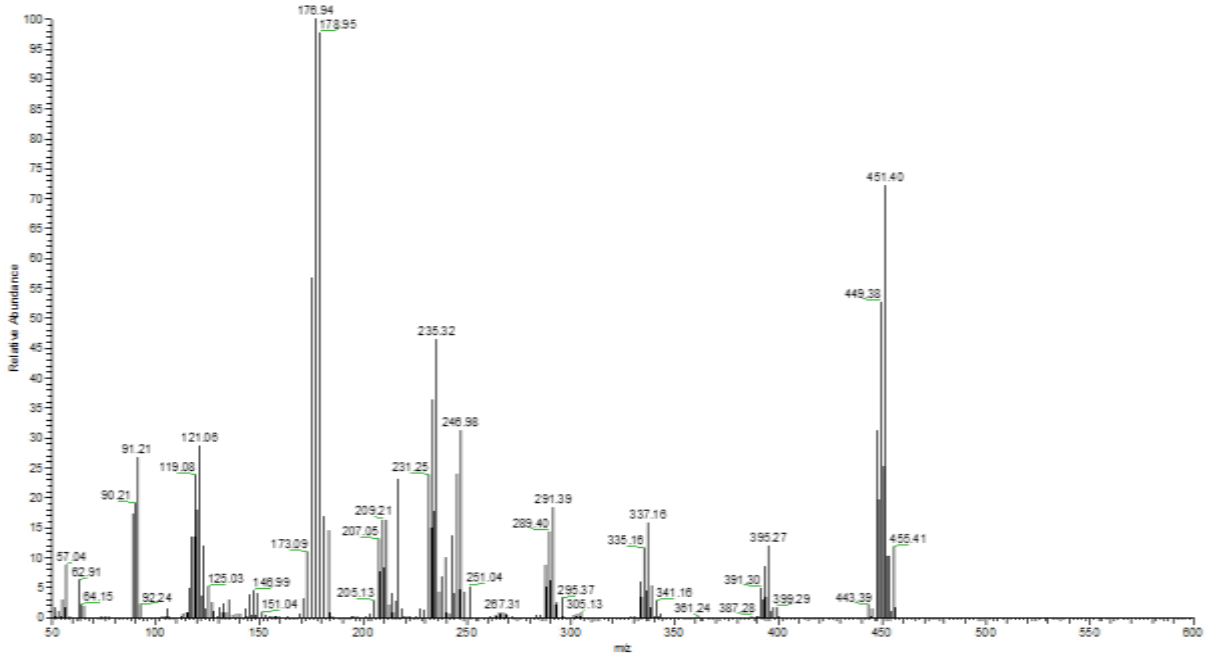

Figure SI-35. EI-MS spectrum of 2-iodophenylmethyl(tributyl)stannane (**2c**).

2-((Tributylstannyl)methyl)phenyl triflate (2d):

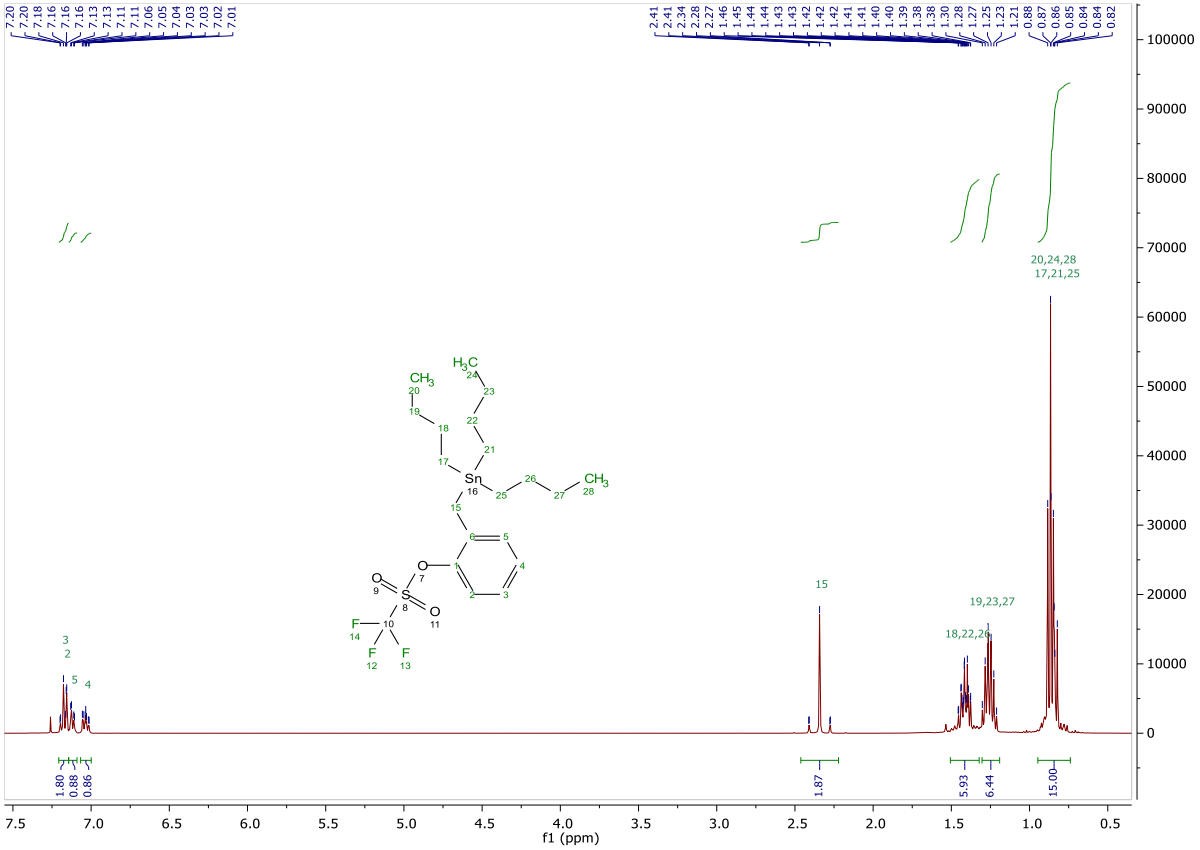

Figure SI-36. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-((tributylstannyl)methyl)phenyl triflate (**2d**).

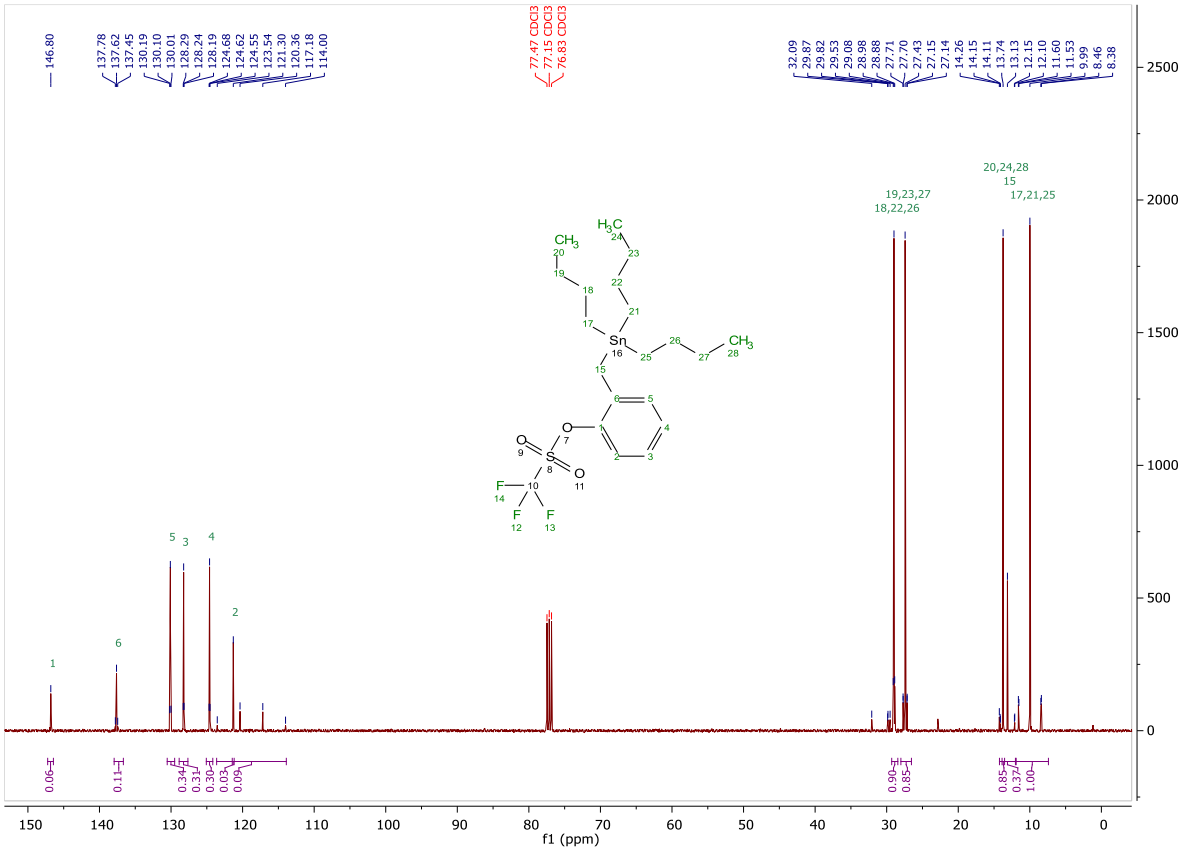

Figure SI-37. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-((tributylstannyl)methyl)phenyl triflate (**2d**).

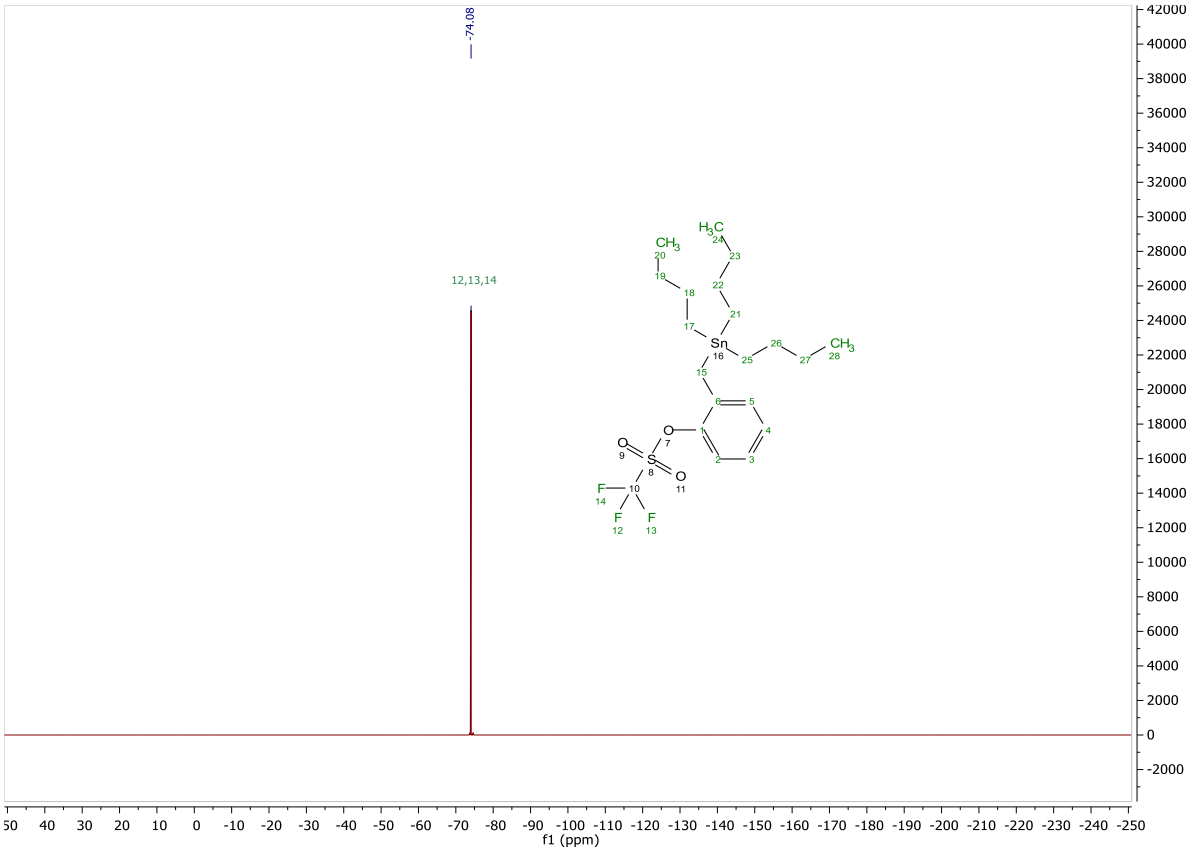

Figure SI-38. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of 2-((tributylstannyl)methyl)phenyl triflate (**2d**).

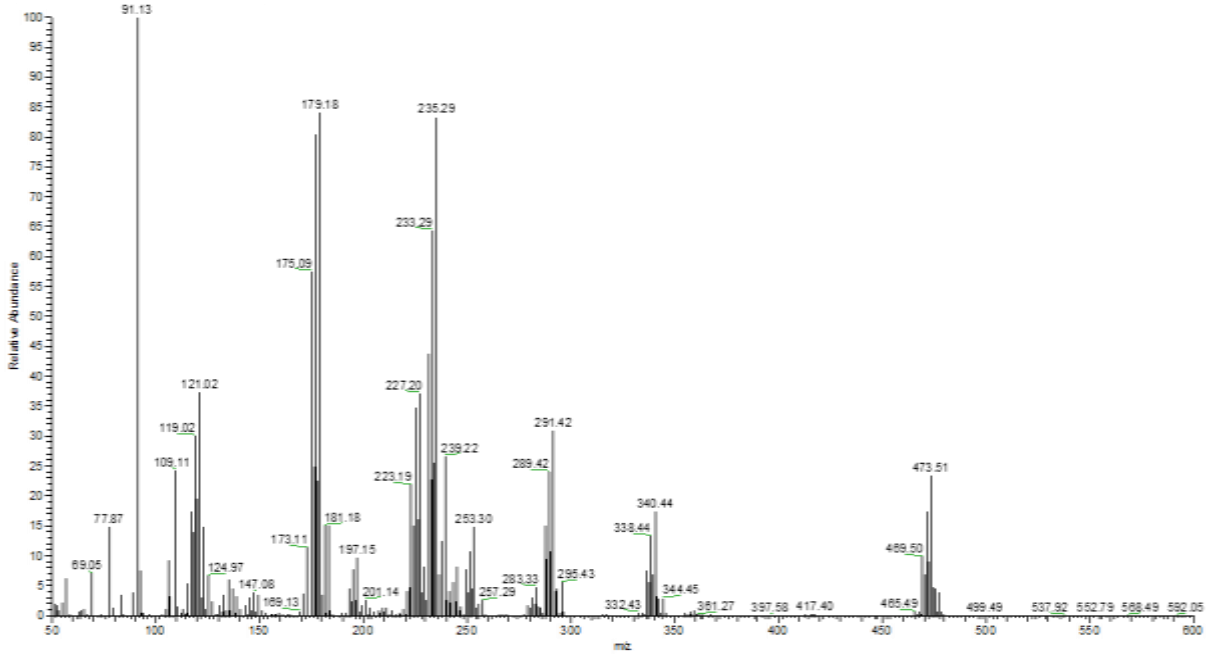

Figure SI-39. EI-MS spectrum of 2-((tributylstannyl)methyl)phenyl triflate (**2d**).

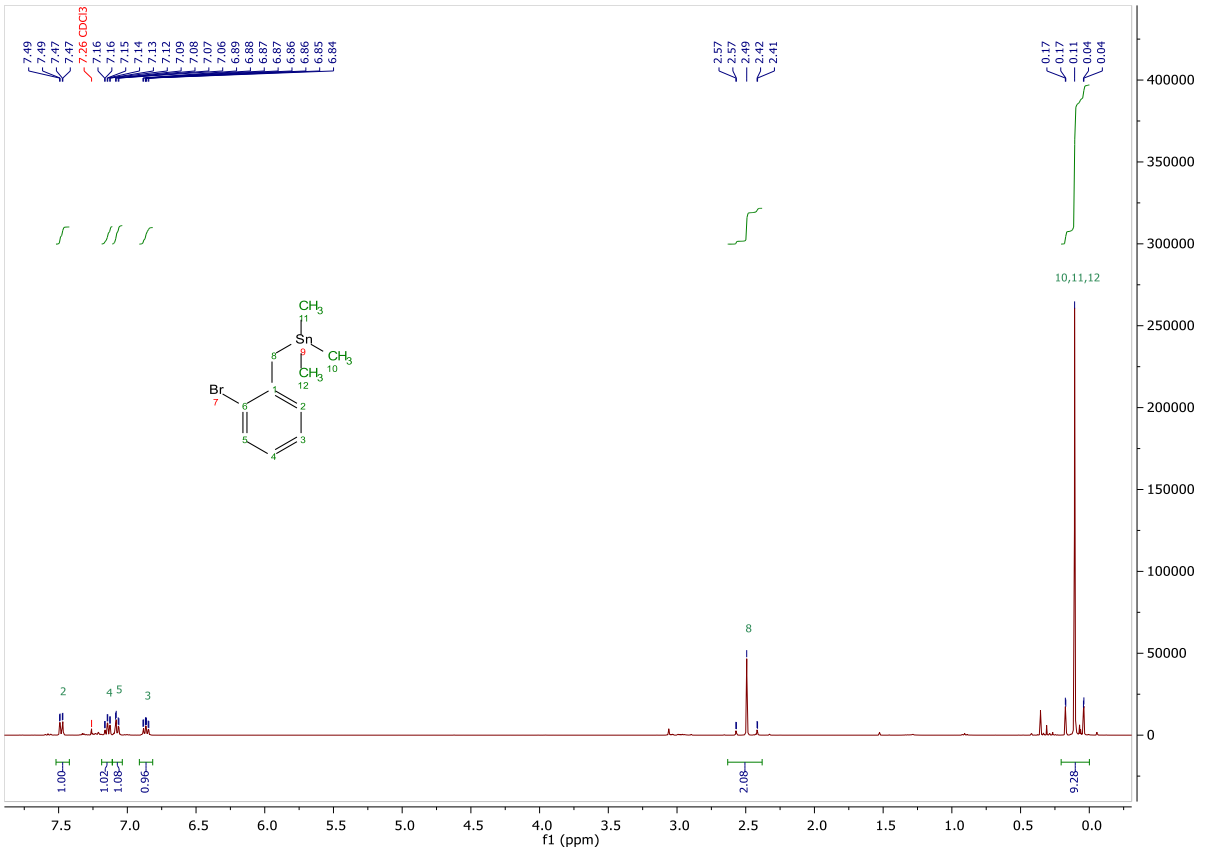

Figure SI-40. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-bromophenylmethyl(trimethyl)stannane (**2e**).

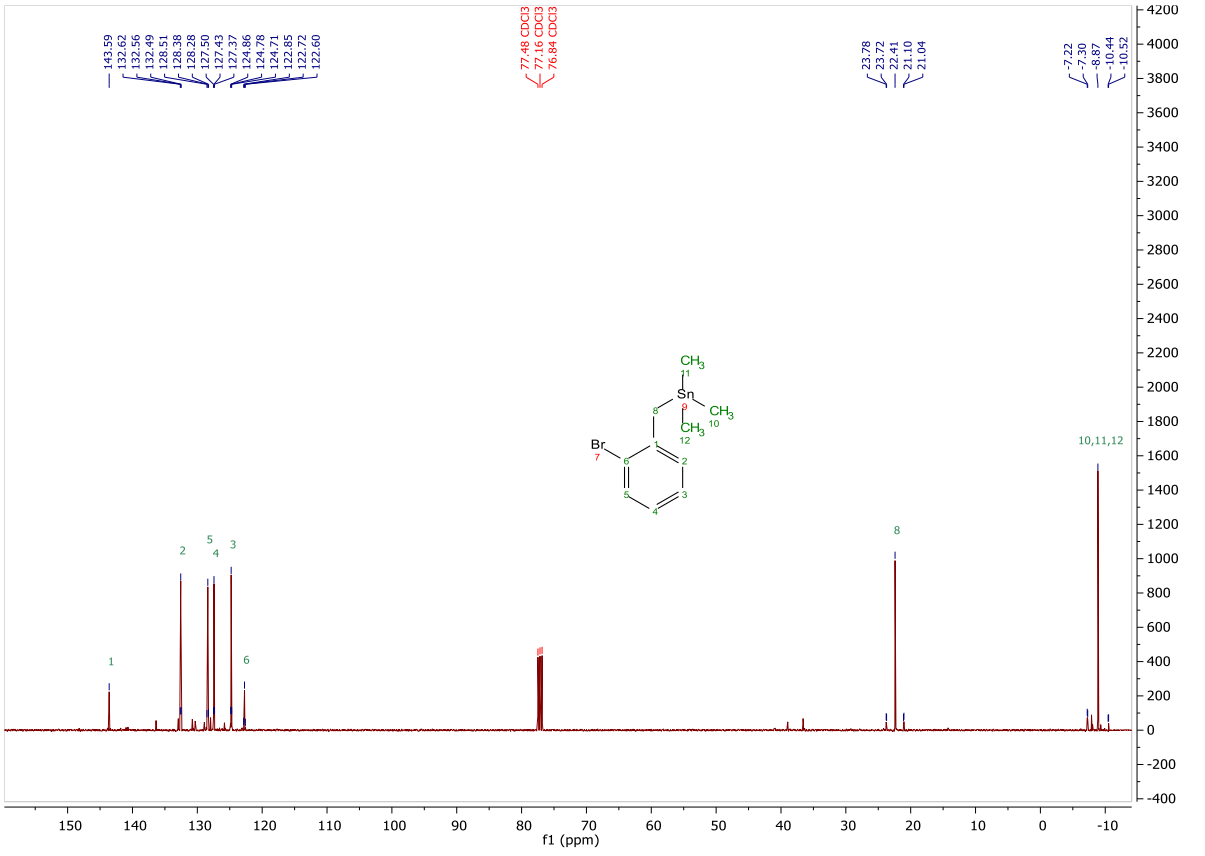

Figure SI-41. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-bromophenylmethyl(trimethyl)stannane (**2e**).

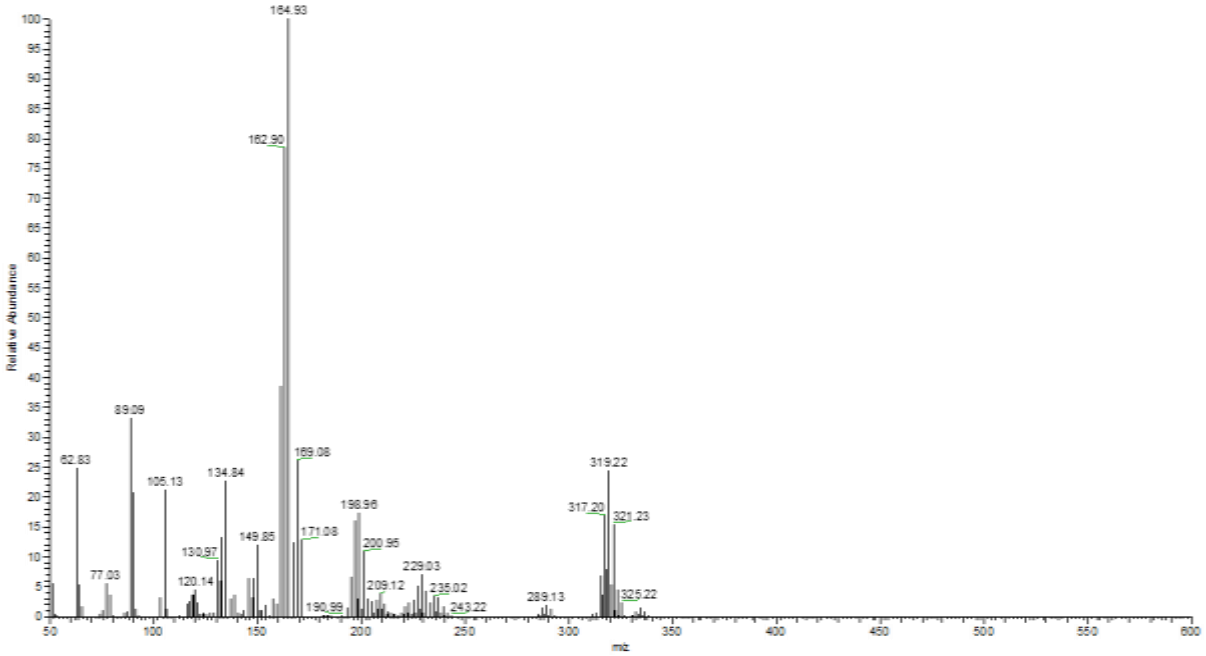

Figure SI-42. EI-MS spectrum of 2-bromophenylmethyl(trimethyl)stannane (**2e**).

Tributyl(2-(bromo/chloromethyl)phenyl)stannane:

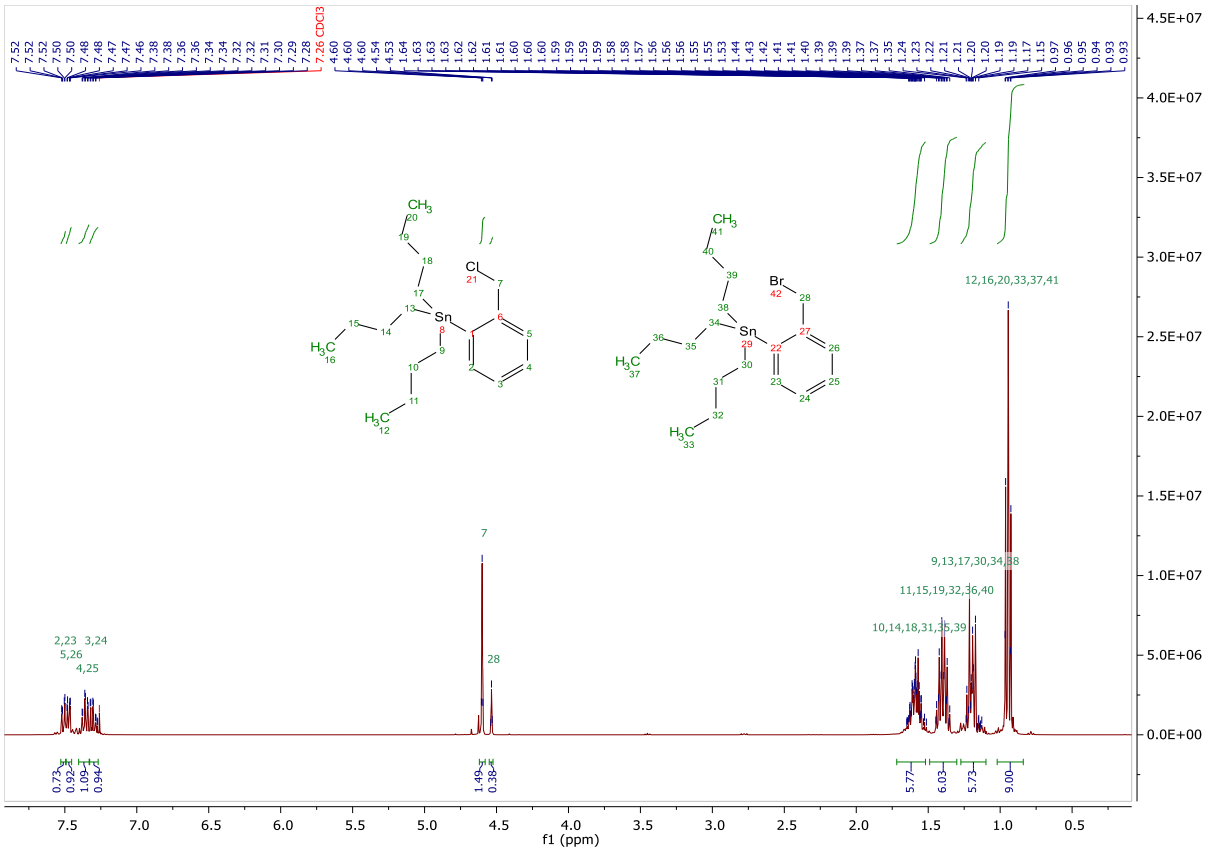

Figure SI-43. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of a 4:1 mixture of tributyl(2-(chloromethyl)phenyl)stannane and tributyl(2-(bromomethyl)phenyl)stannane.

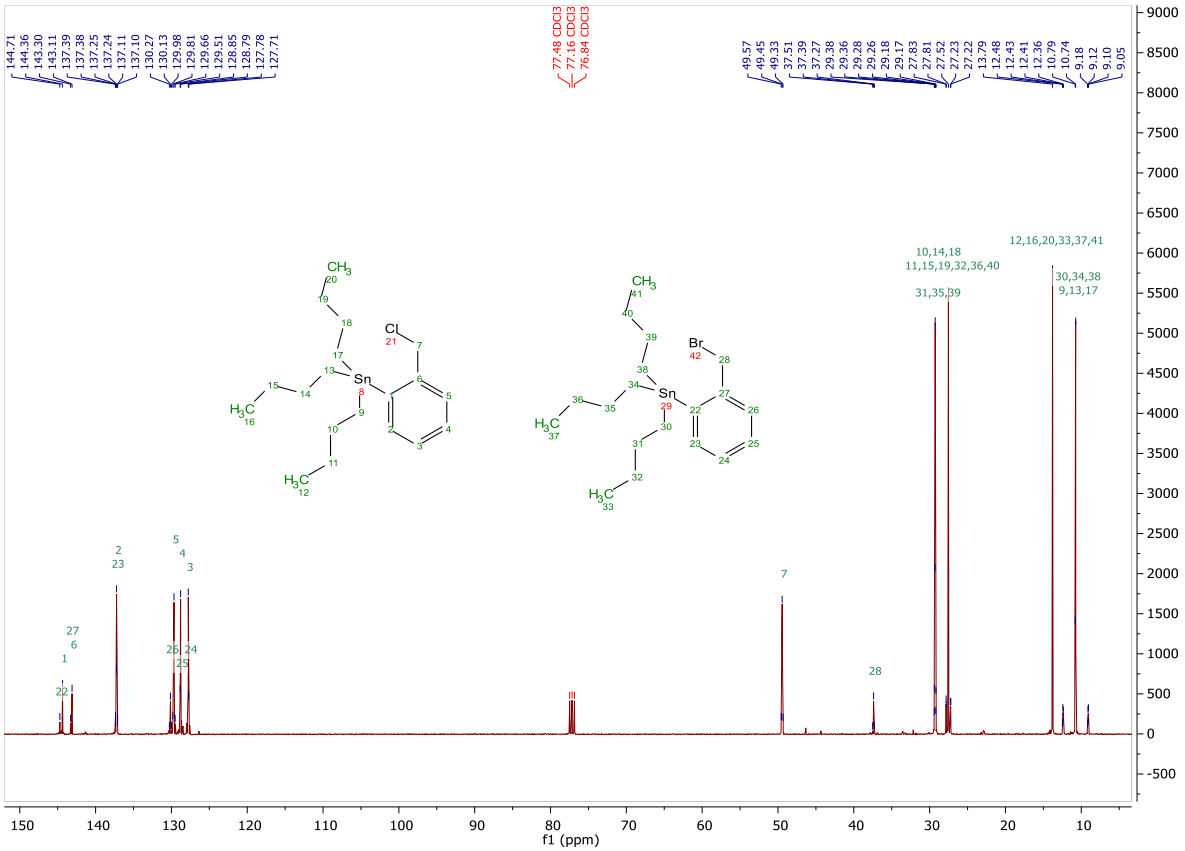

Figure SI-44. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of a 4:1 mixture of tributyl(2-(chloromethyl)phenyl)stannane and tributyl(2-(bromomethyl)phenyl)stannane.

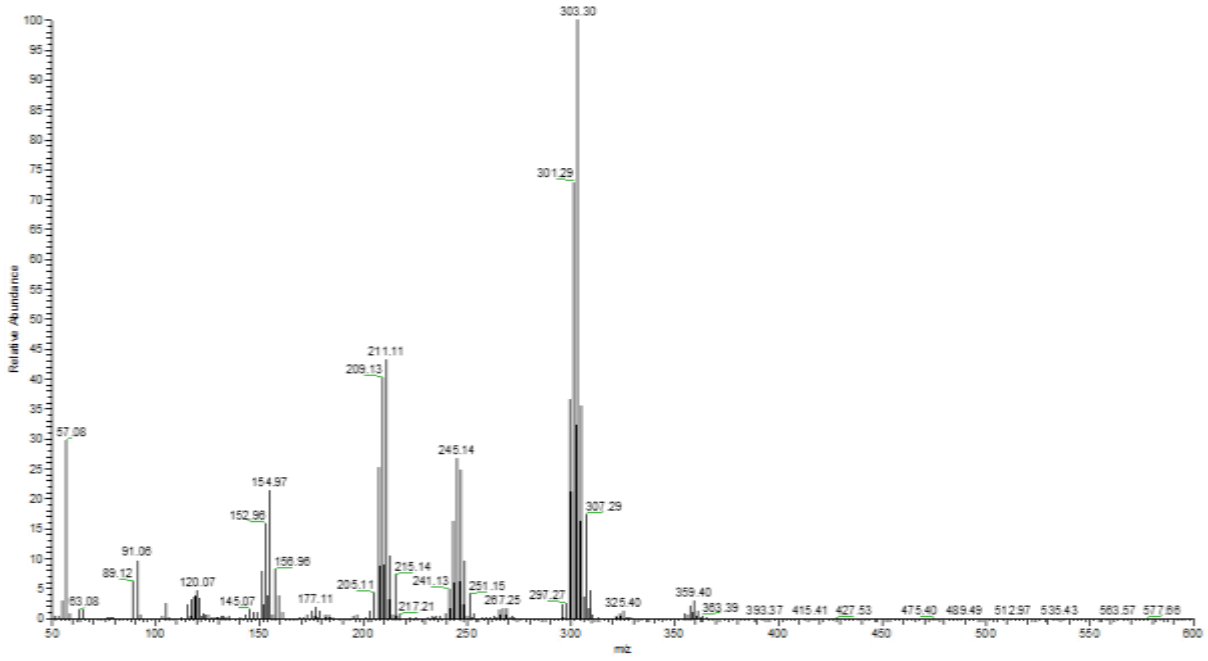

Figure SI-45. EI-MS spectrum of tributyl(2-(chloromethyl)phenyl)stannane.

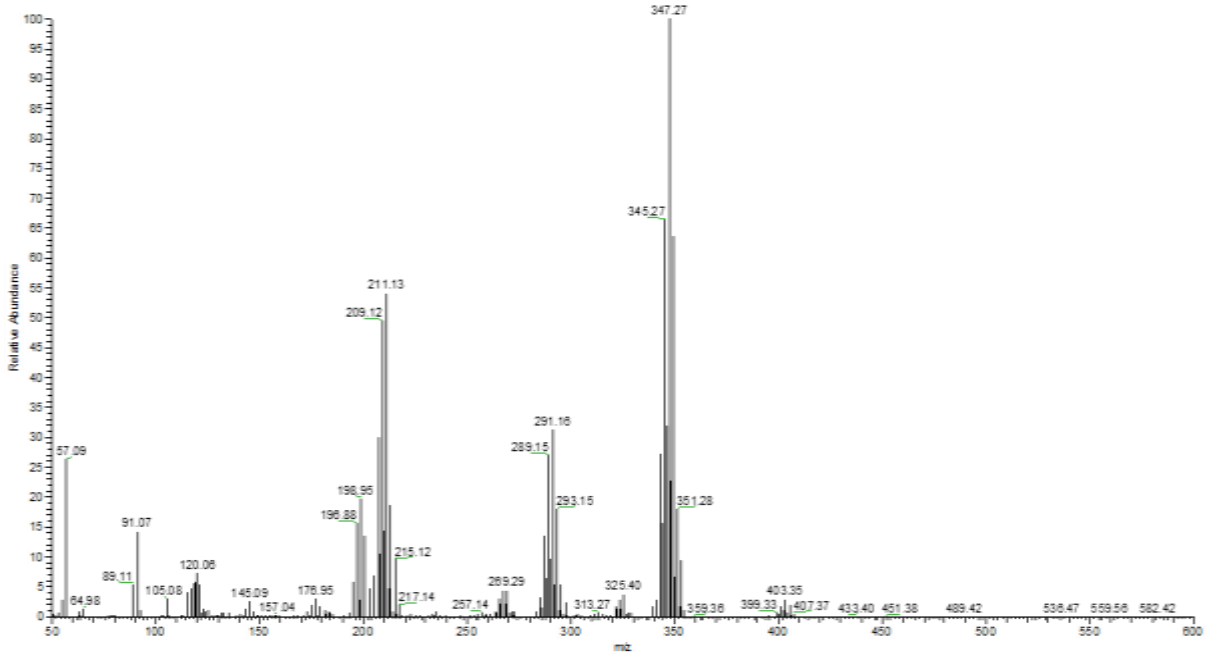

Figure SI-46. EI-MS spectrum of tributyl(2-(bromomethyl)phenyl)stannane.

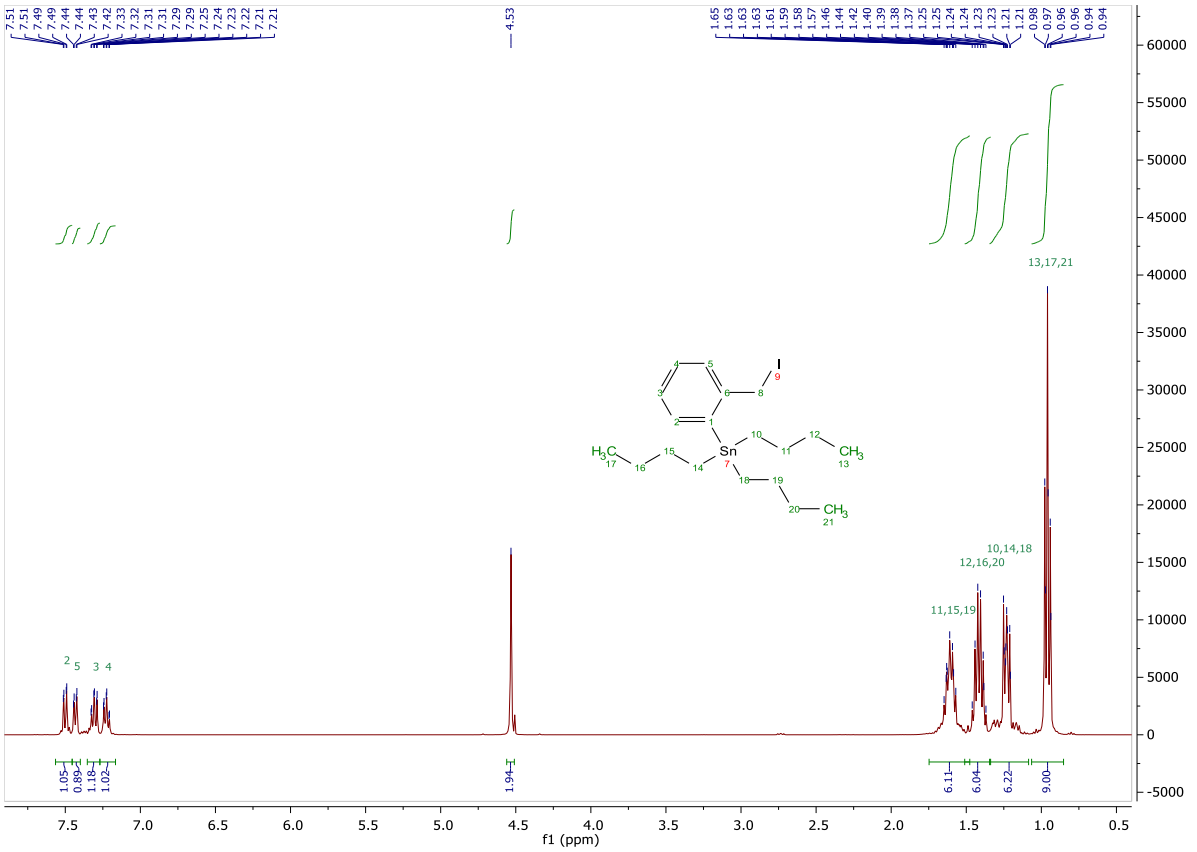

Figure SI-47. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of tributyl(2-(iodomethyl)phenyl)stannane.

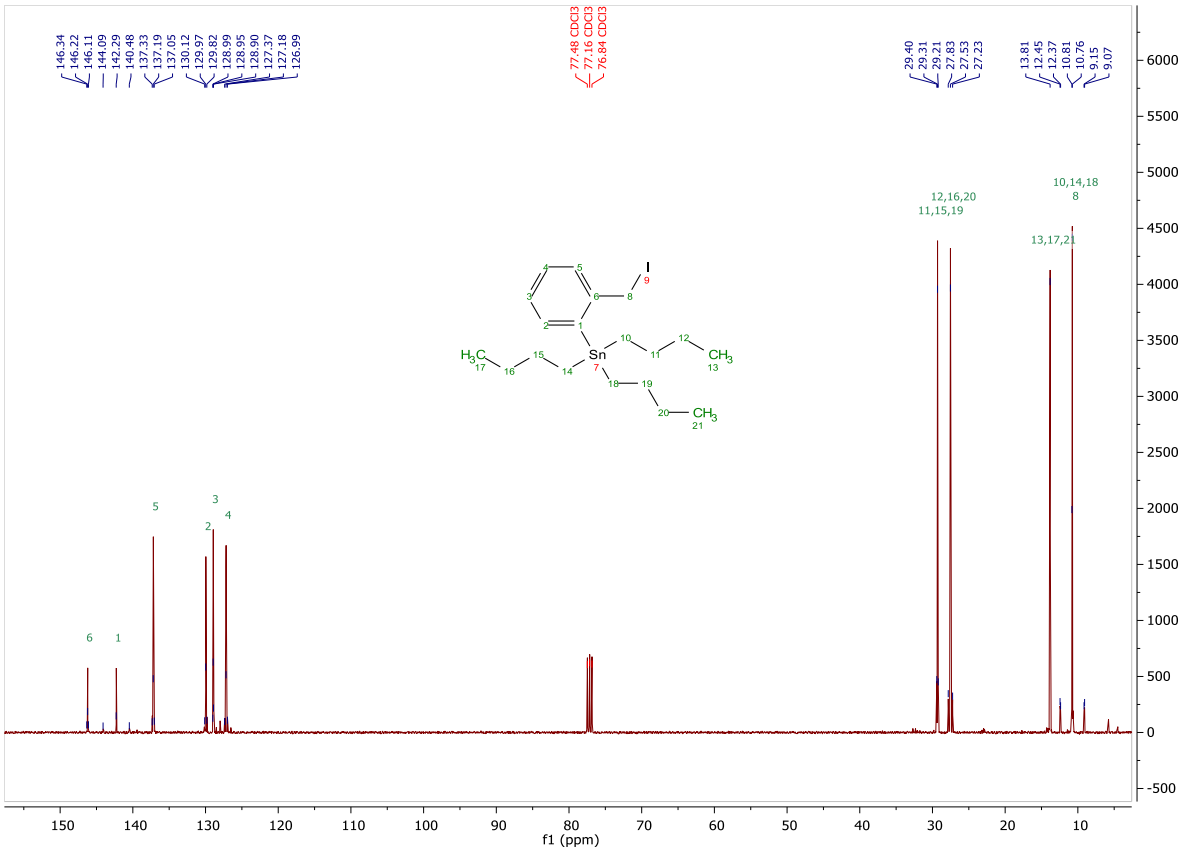

Figure SI-48. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of tributyl(2-(iodomethyl)phenyl)stannane.

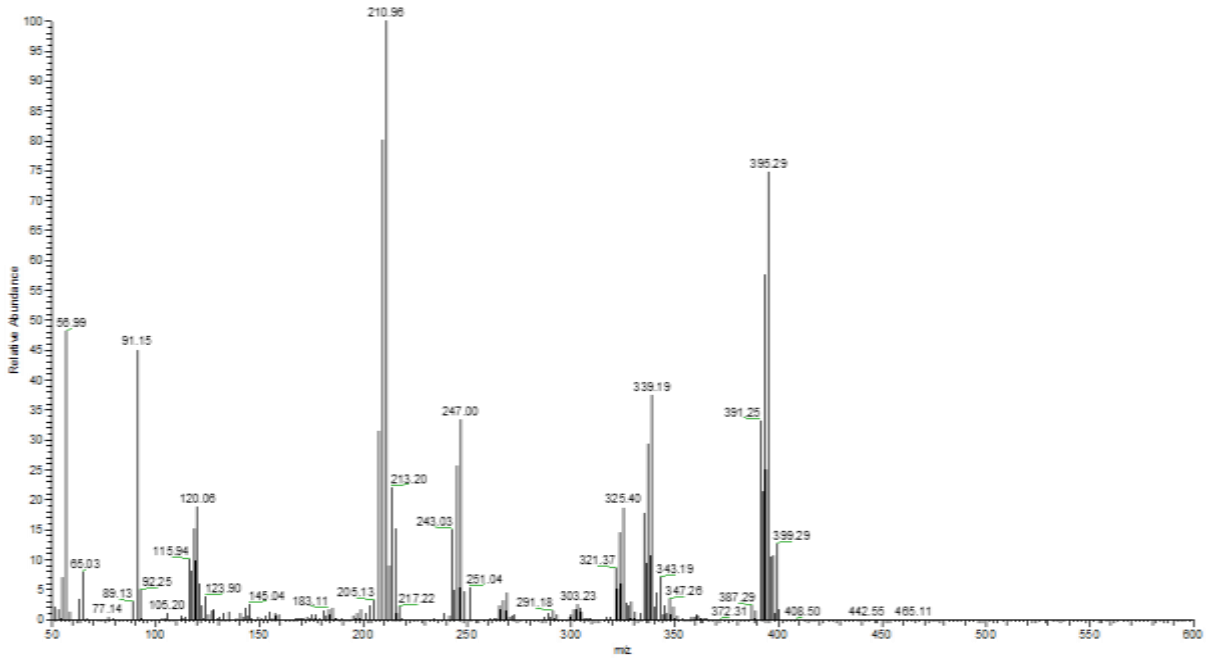

Figure SI-49. EI-MS spectrum of tributyl(2-(iodomethyl)phenyl)stannane.

Tris(2-methyl-4-(trifluoromethyl)phenyl)phosphine:

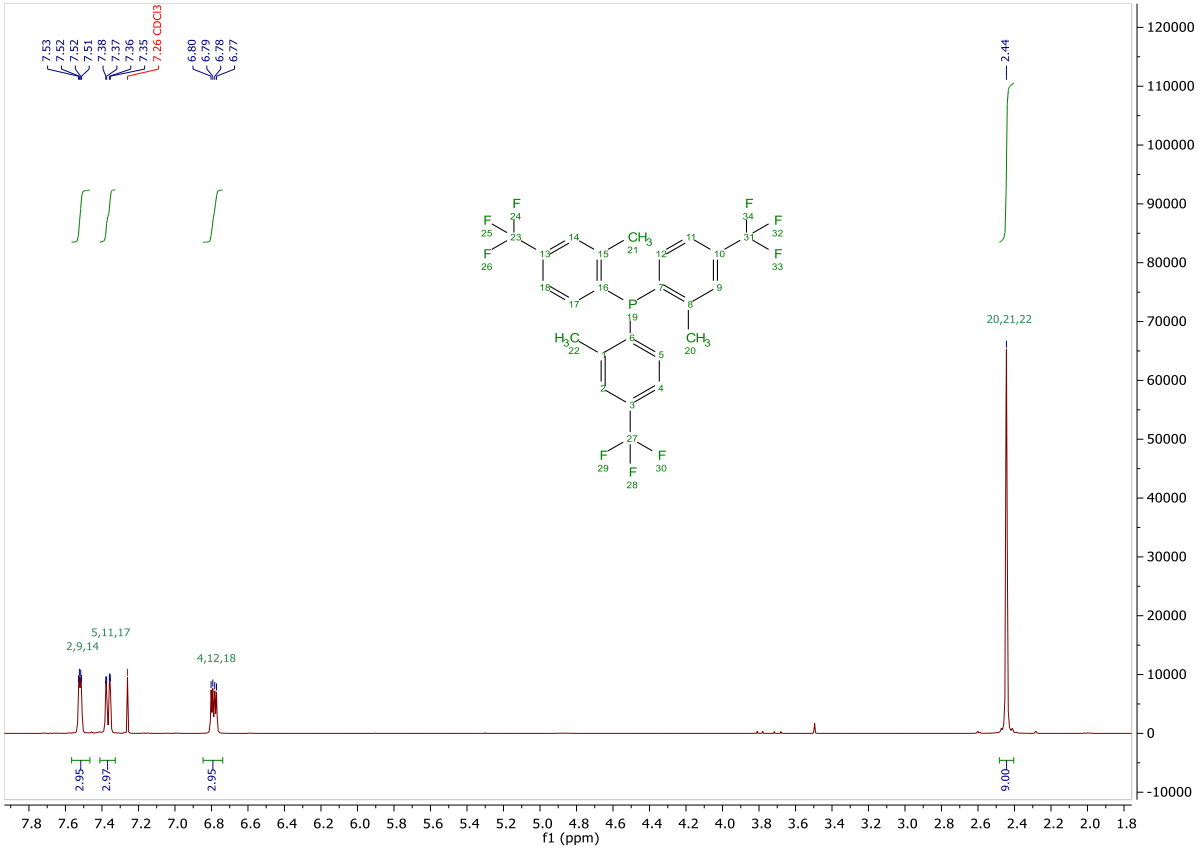

Figure SI-50. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of tris(2-methyl-4-(trifluoromethyl)phenyl)phosphine.

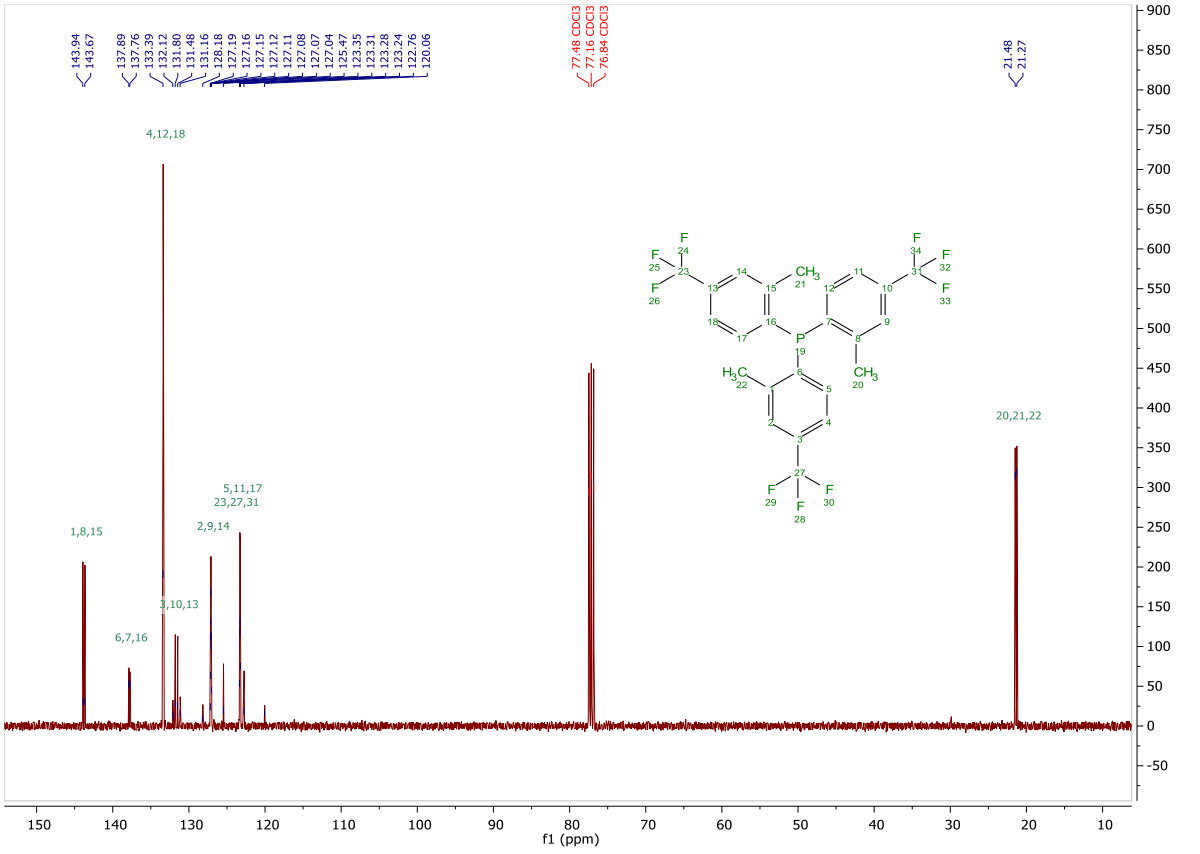

Figure SI-51. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of tris(2-methyl-4-(trifluoromethyl)phenyl)phosphine.

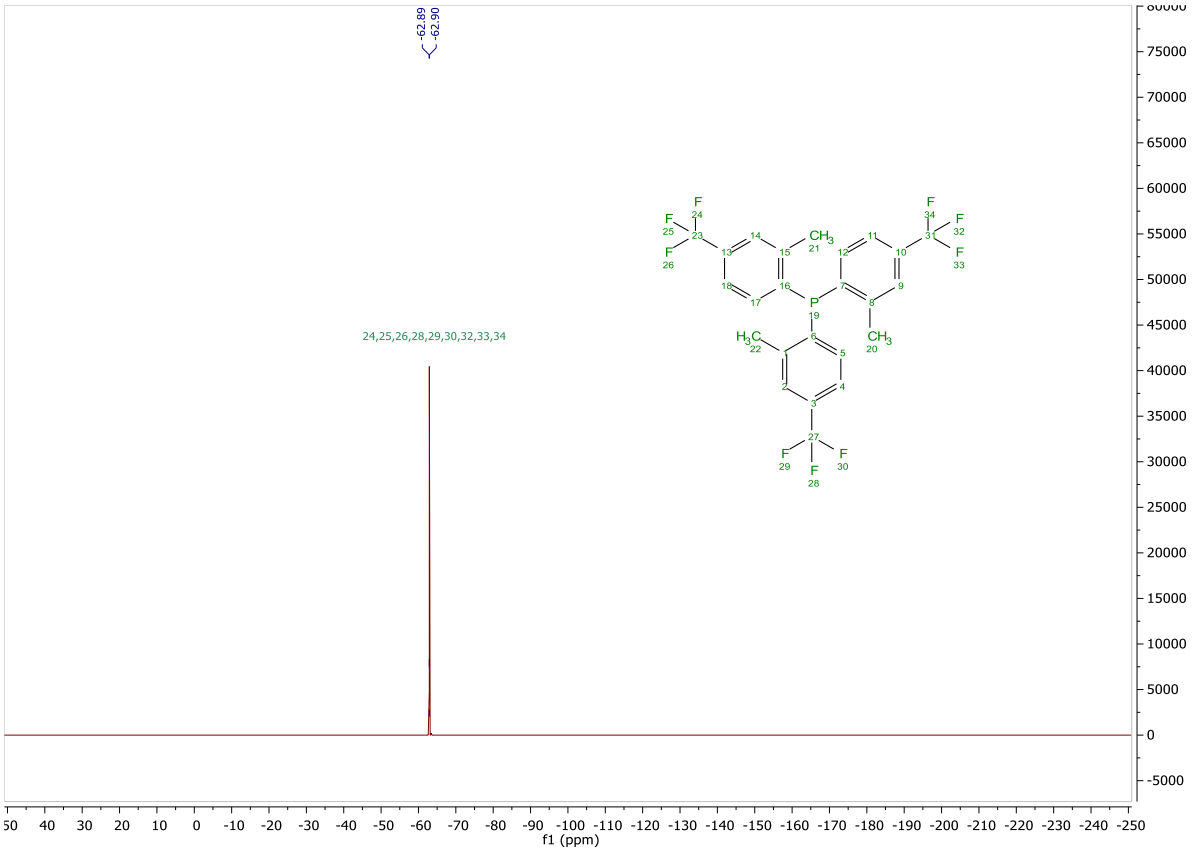

Figure SI-52. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of tris(2-methyl-4-(trifluoromethyl)phenyl)phosphine.

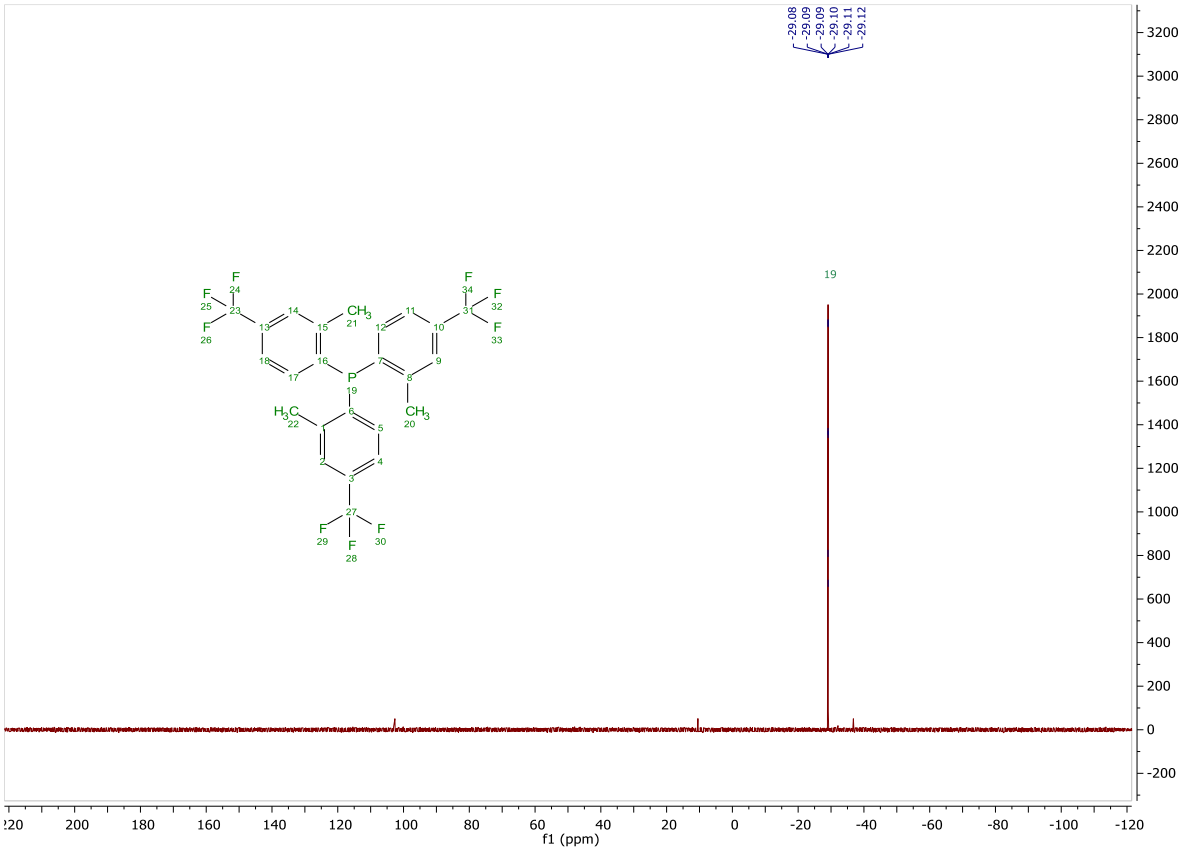

Figure SI-53. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of tris(2-methyl-4-(trifluoromethyl)phenyl)phosphine.

***exo*/*endo*-2,3,4,4a,9,9a-Hexahydro-1H-1,4-methanofluorene:**

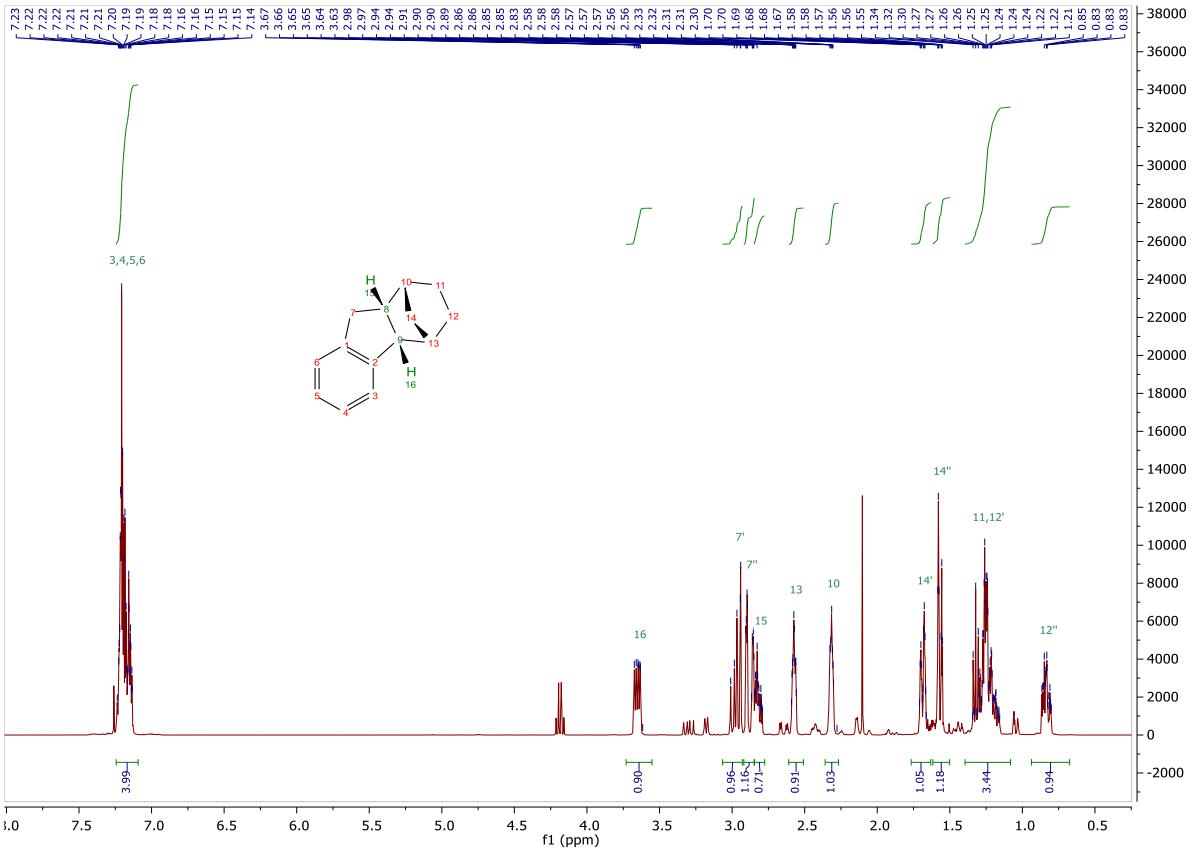

Figure SI-54. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of a mixture of (mainly) *endo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene and *exo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene.

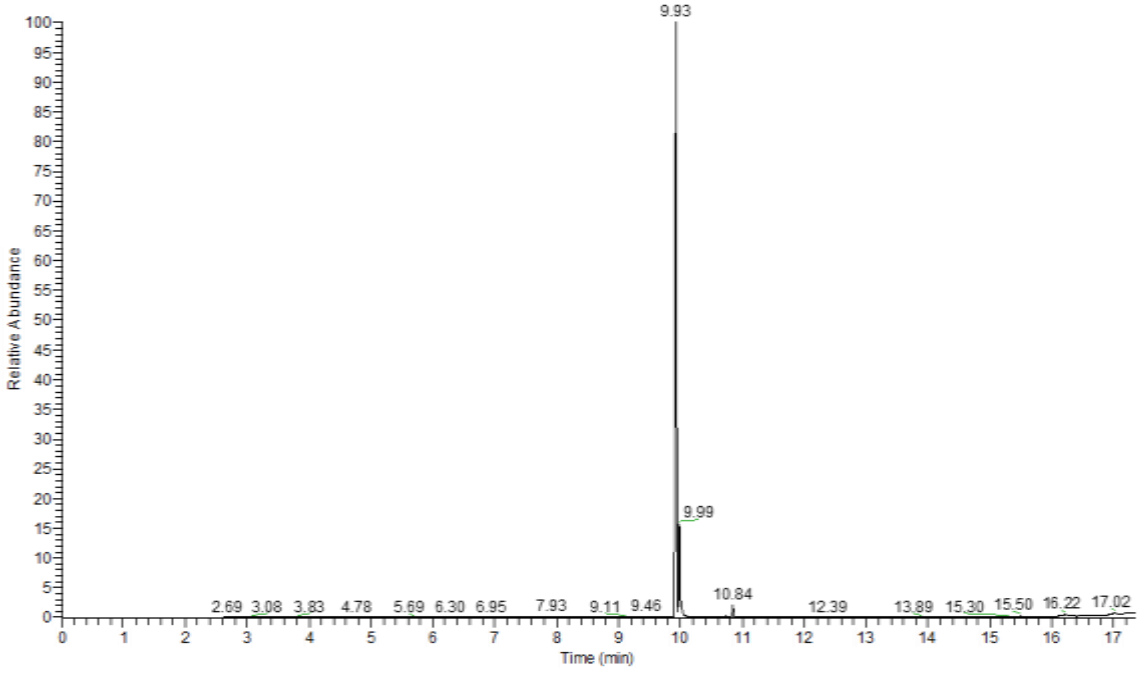

Figure SI-55. GC-MS chromatogram of a mixture of *endo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene (t_R= 9.93 min) and *exo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene (t_R= 9.99 min).

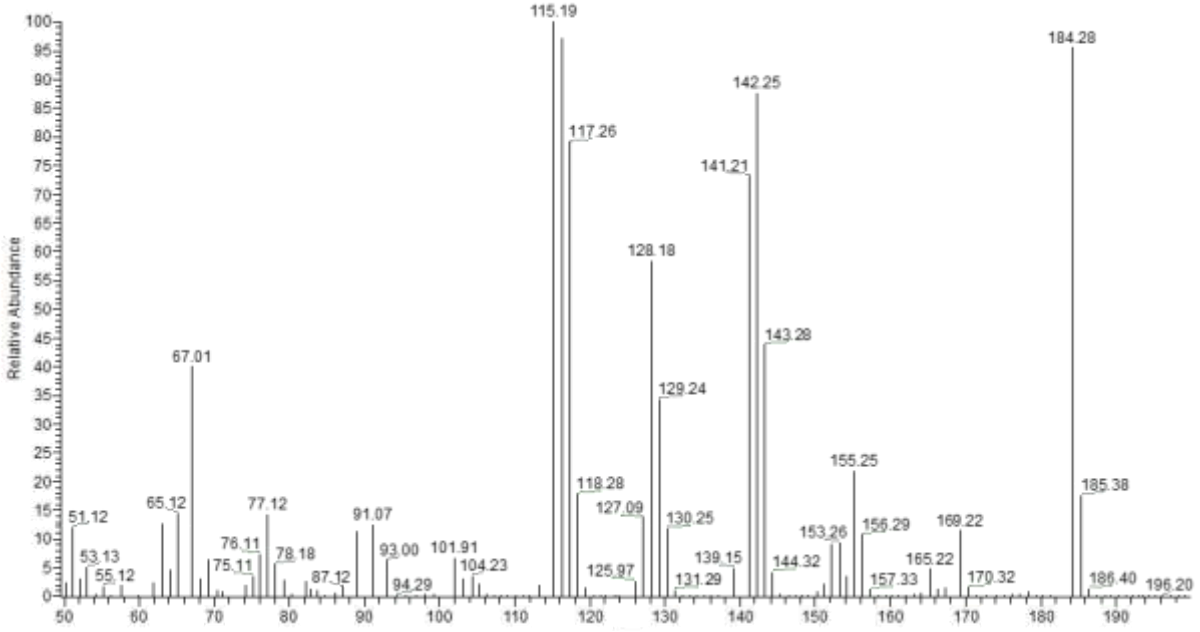

Figure SI-56. EI-MS spectrum of *endo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene.

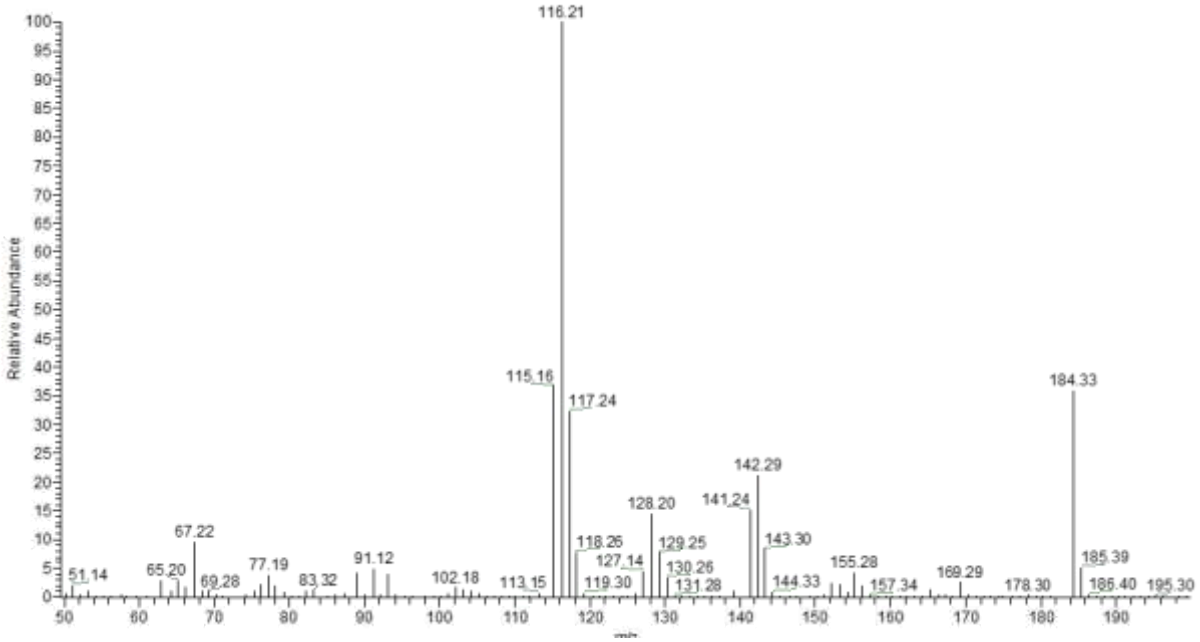

Figure SI-57. EI-MS spectrum of *exo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene.

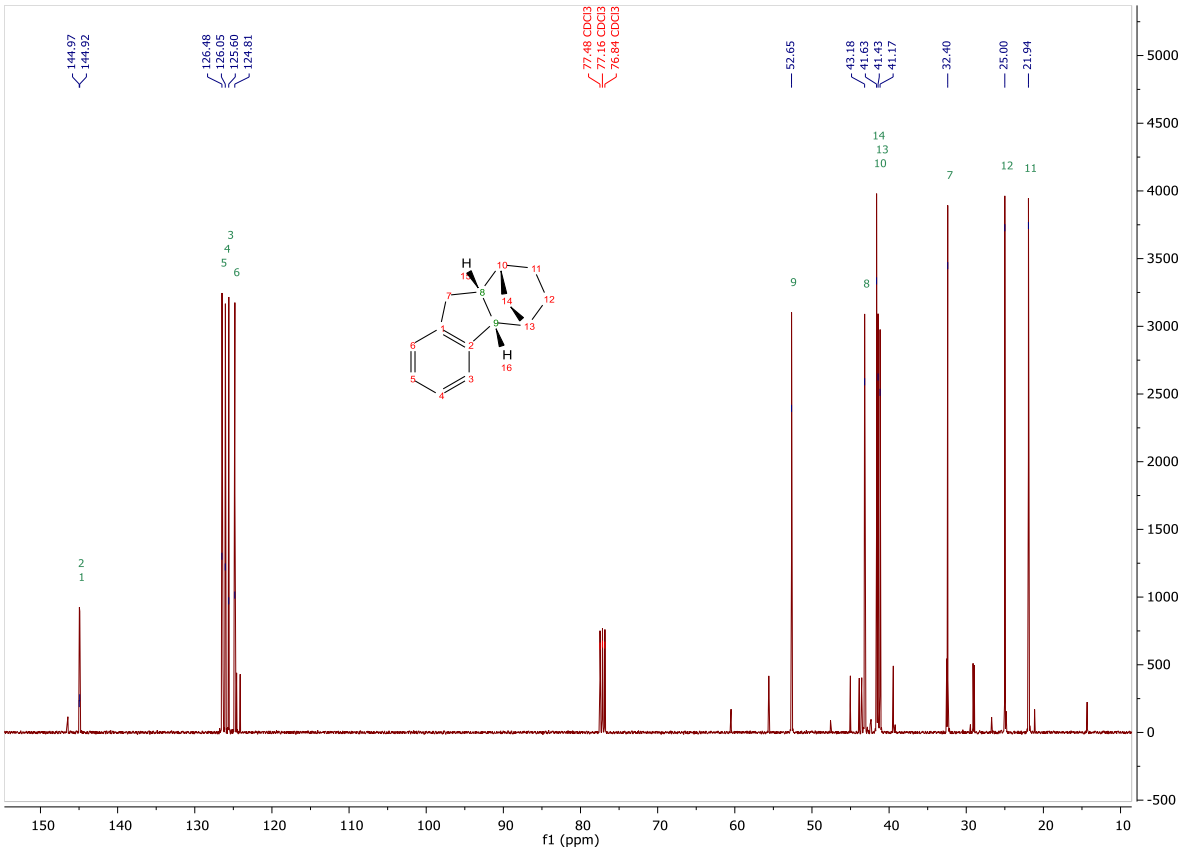

Figure SI-58. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of a mixture of *exo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene and (mainly) *endo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene.

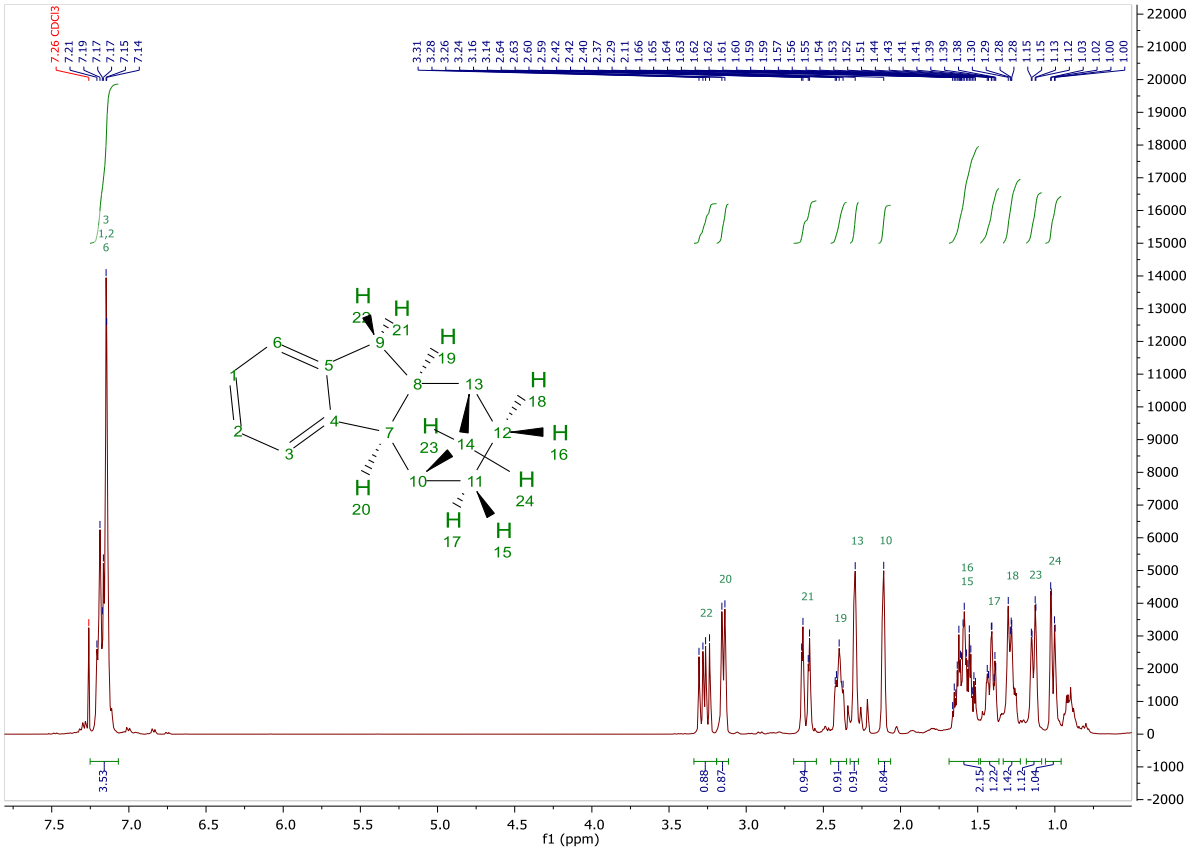

Figure SI-59. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *exo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene from the „diverted Heck“ reaction of **2a** and norbornene.

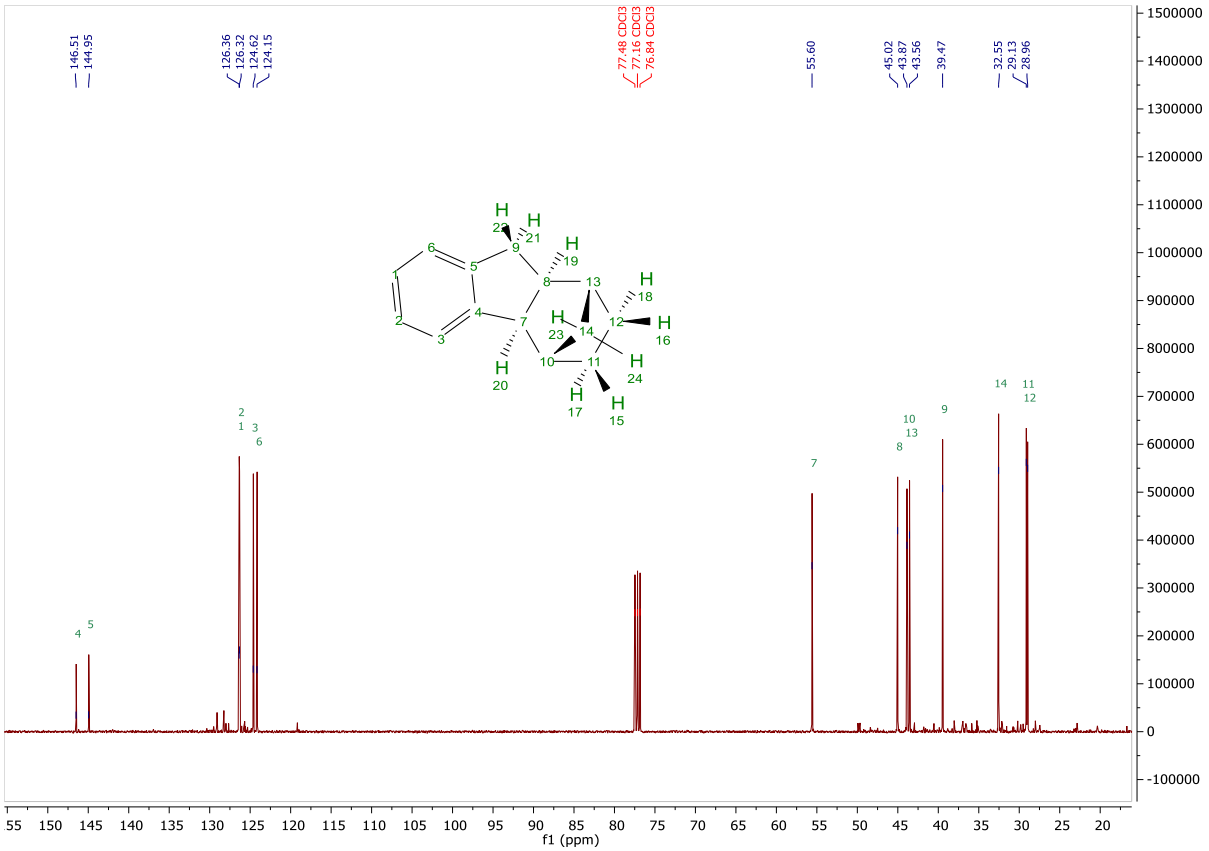

Figure SI-60. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of *exo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene from the „diverted Heck“ reaction of **2a** and norbornene.

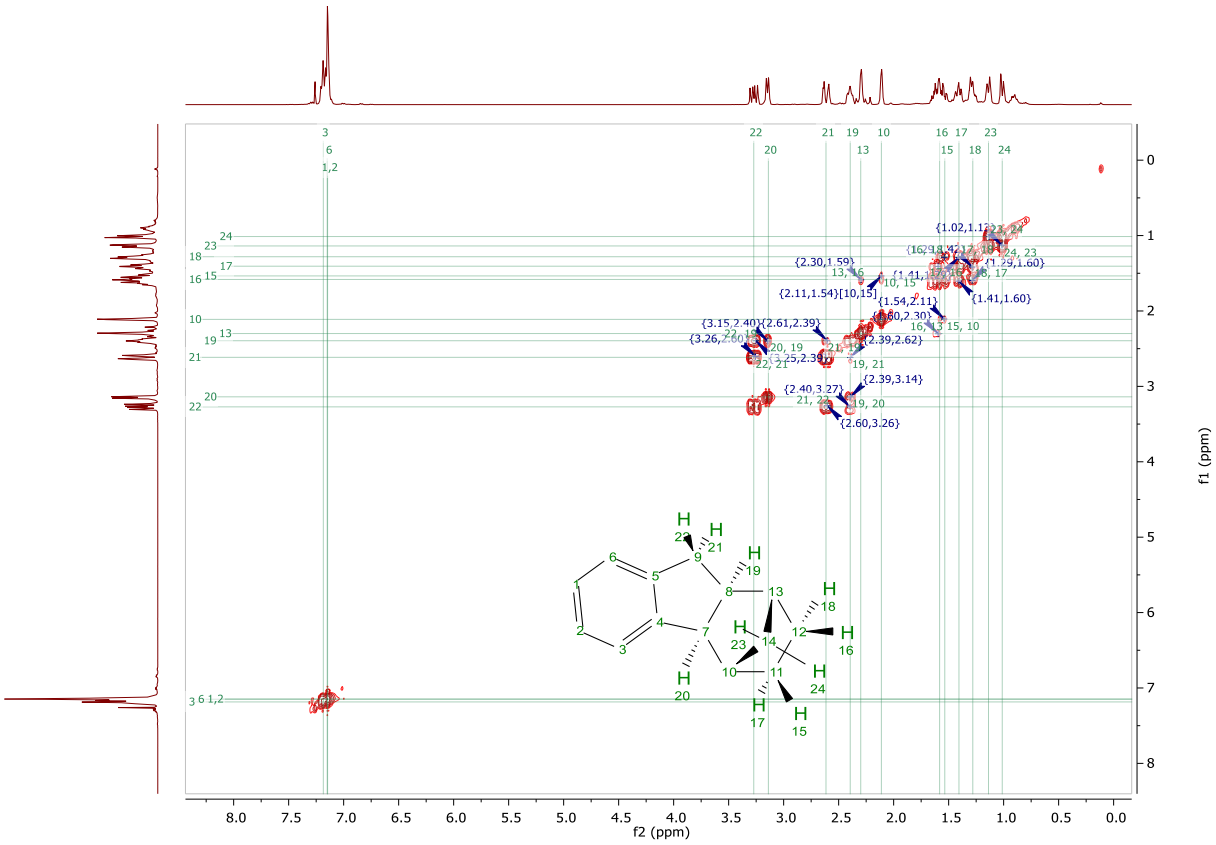

Figure SI-61. COSY (^{1}H (400 MHz), ^{1}H (400 MHz), $CDCl_3$) spectrum of *exo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene from the „diverted Heck“ reaction of **2a** and norbornene.

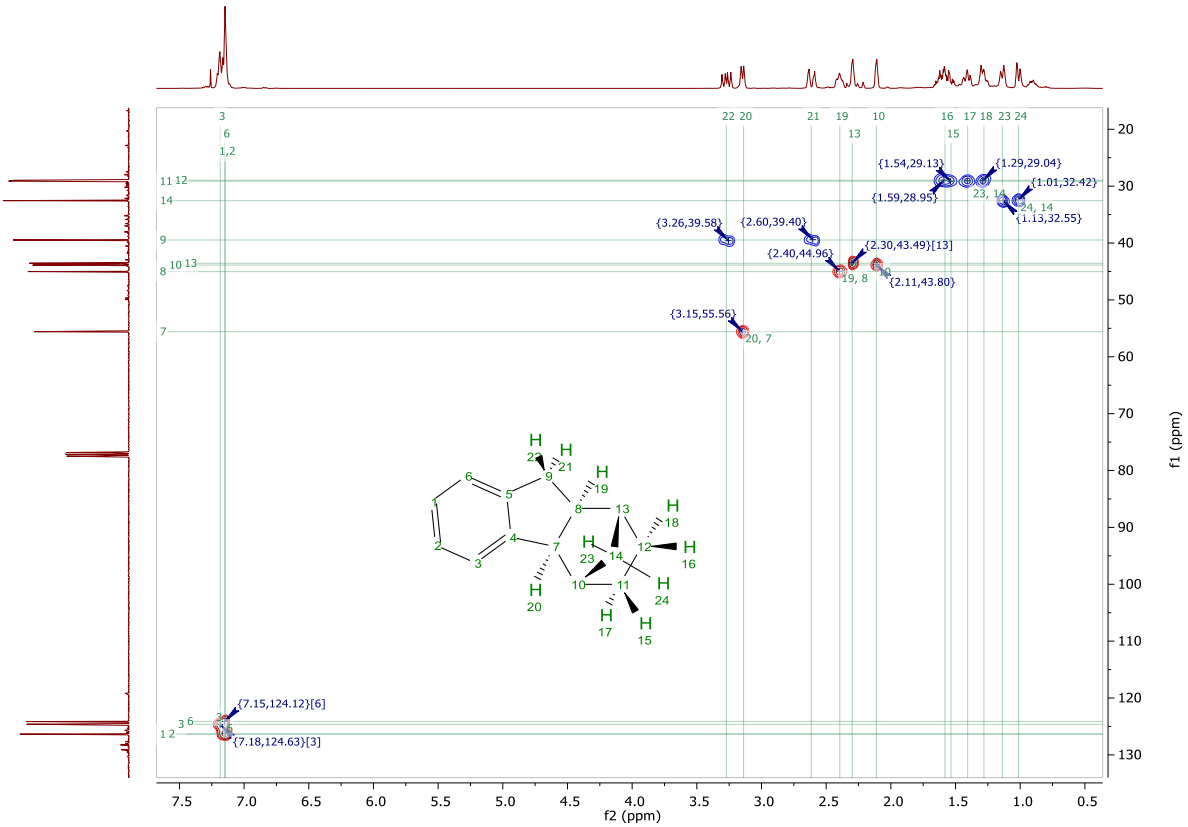

Figure SI-62. HSQC (^{13}C (101 MHz), ^{1}H (400 MHz), $CDCl_3$) spectrum of *exo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene from the „diverted Heck“ reaction of **2a** and norbornene.

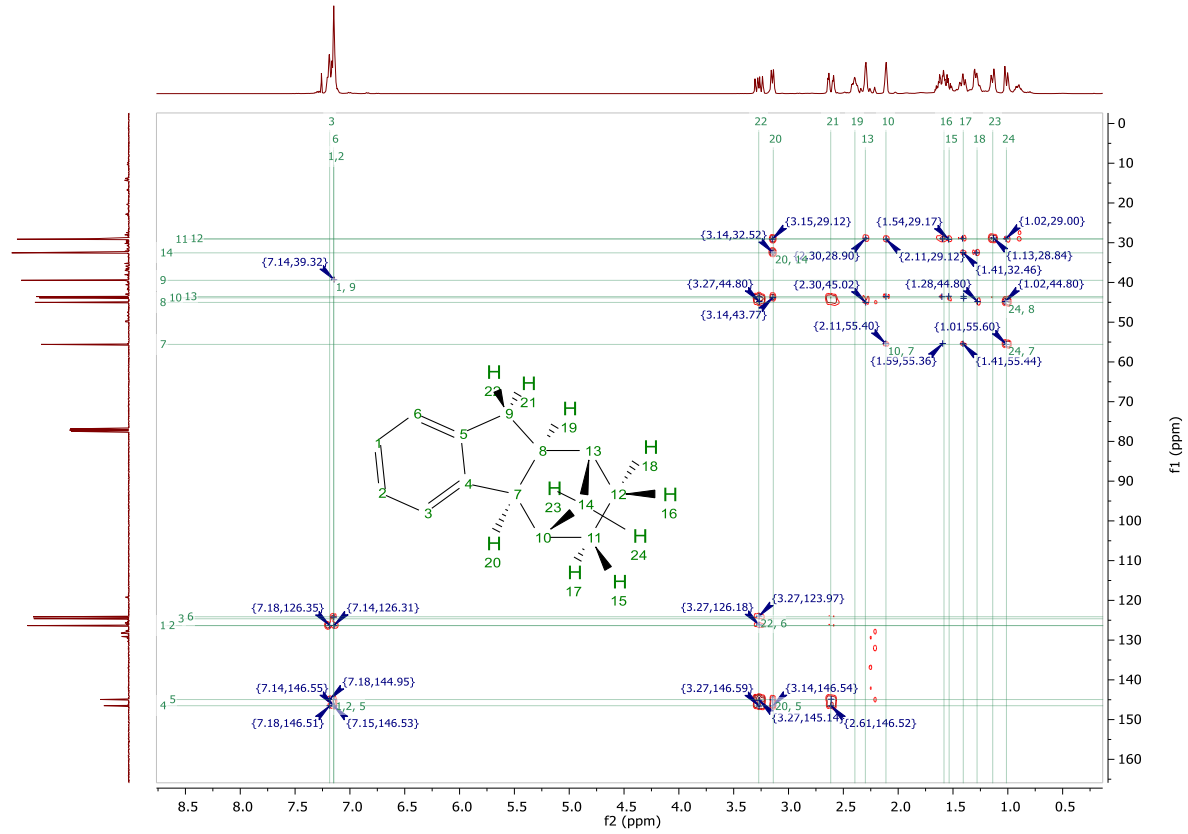

Figure SI-63. HMBC (^{13}C (101 MHz), ^{1}H (400 MHz), $CDCl_3$) spectrum of *exo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene from the „diverted Heck“ reaction of **2a** and norbornene.

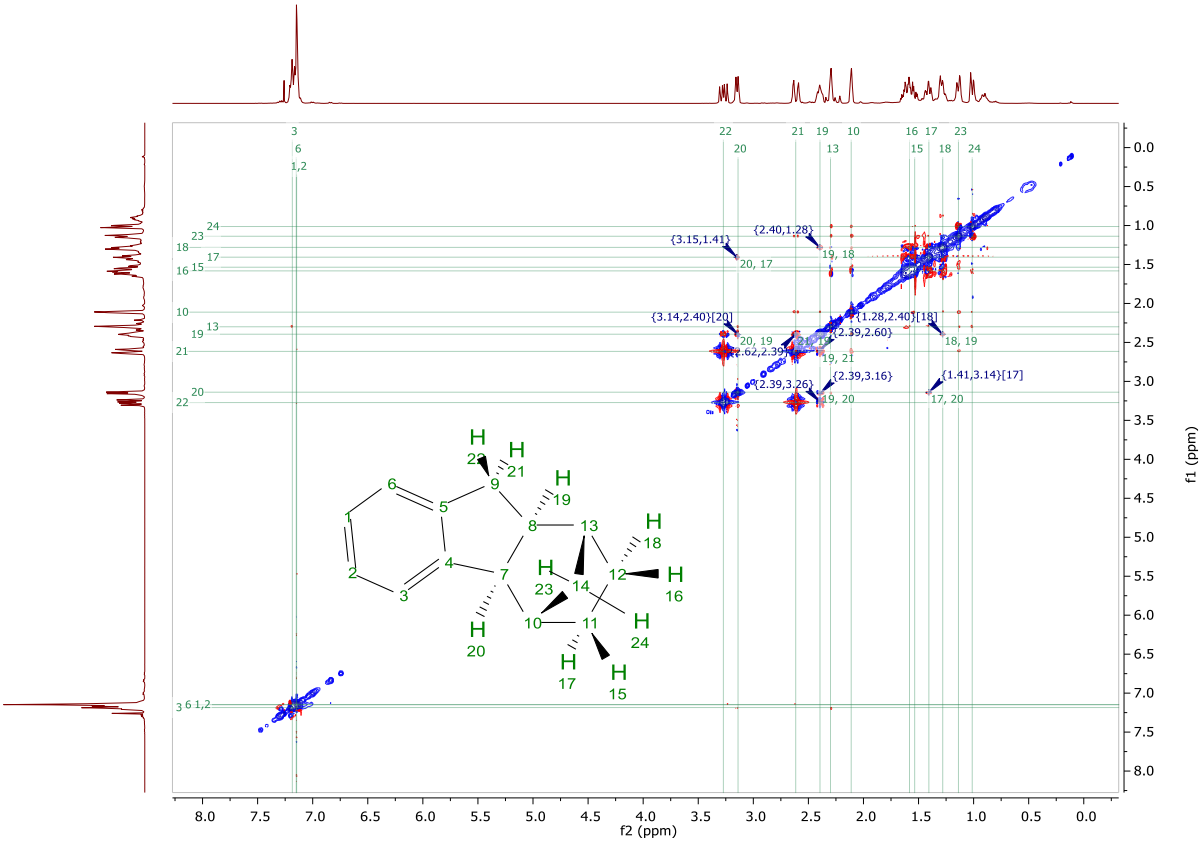

Figure SI-64. NOESY (^{1}H (500 MHz), ^{1}H (500 MHz), $CDCl_3$) spectrum of *exo*-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene from the „diverted Heck“ reaction of **2a** and norbornene.

VI-Calibration curves

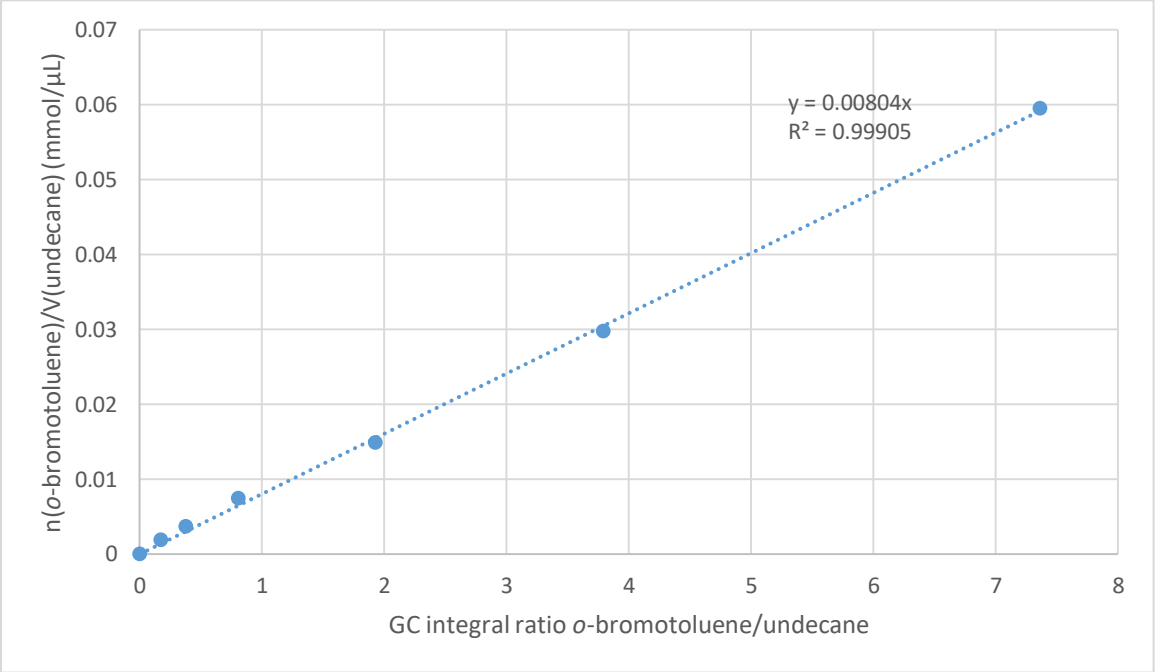

Figure SI-65. GC-FID calibration (Shimadzu GC-2025) for *o*-bromotoluene with undecane as internal standard.

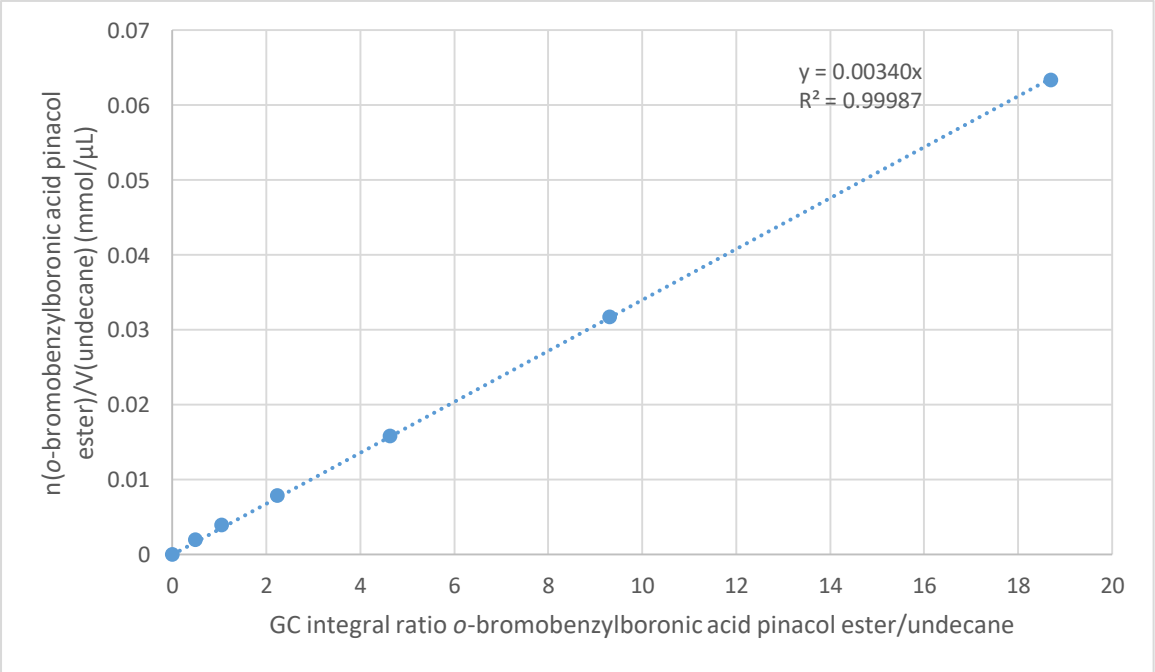

Figure SI-66. GC-FID calibration (Shimadzu GC-2025) for *o*-bromobenzylboronic acid pinacol ester with undecane as internal standard.

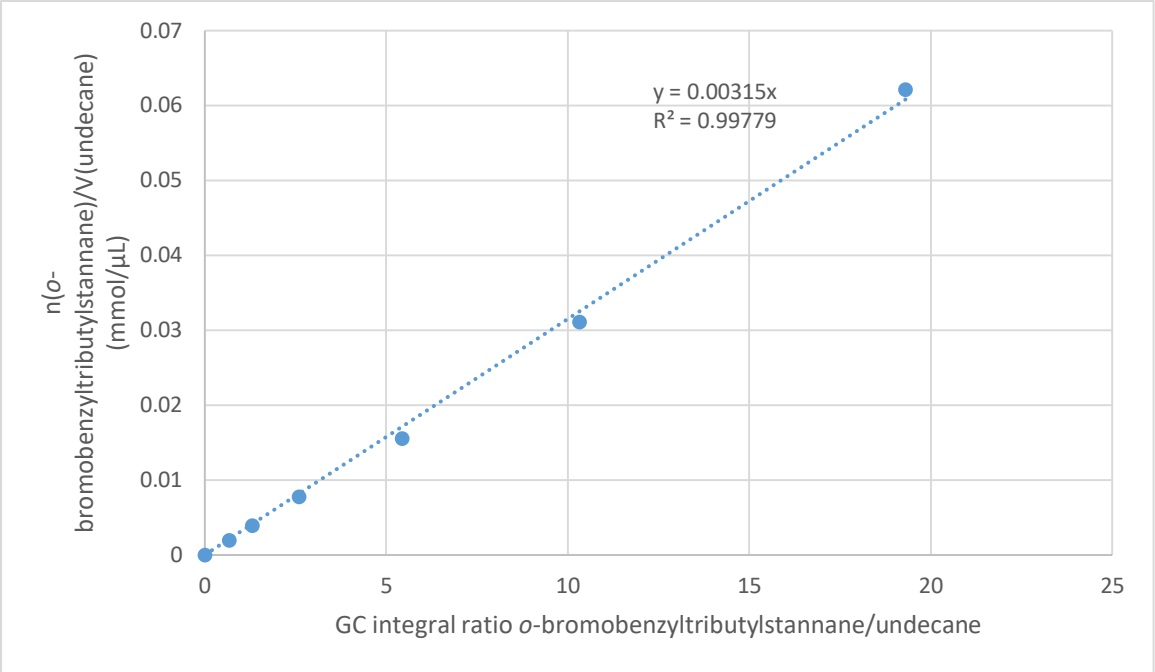

Figure SI-67. GC-FID calibration (Shimadzu GC-2025) for *o*-bromobenzyltributylstannane with undecane as internal standard.

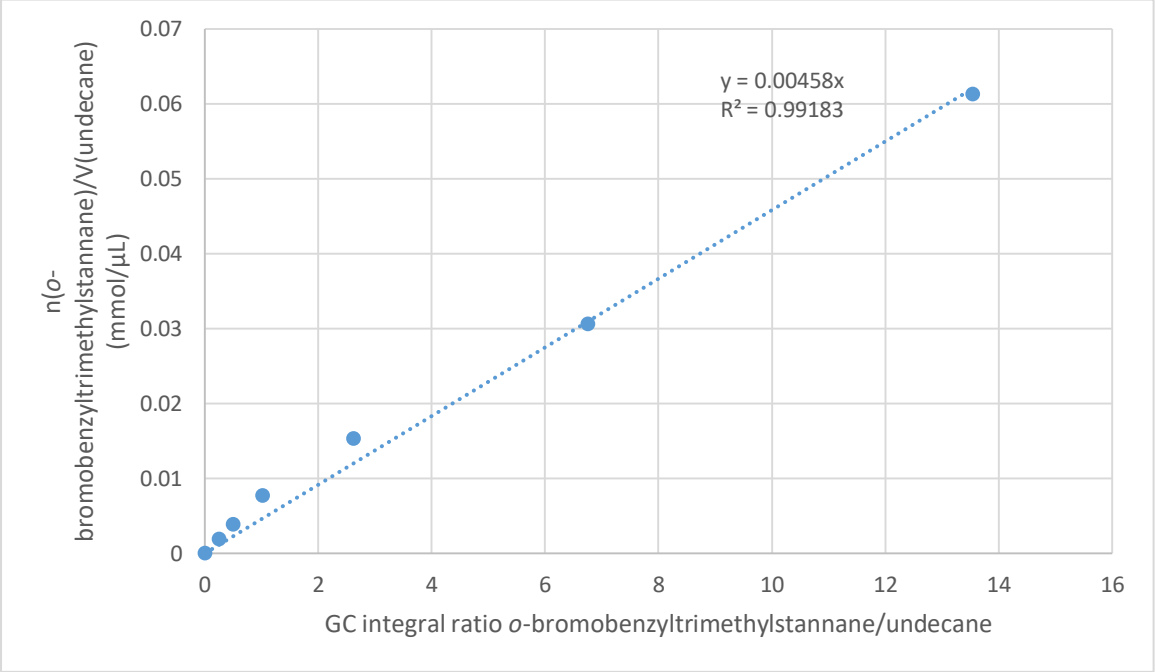

Figure SI-68. GC-FID calibration (Shimadzu GC-2025) for *o*-bromobenzyltrimethylstannane with undecane as internal standard.

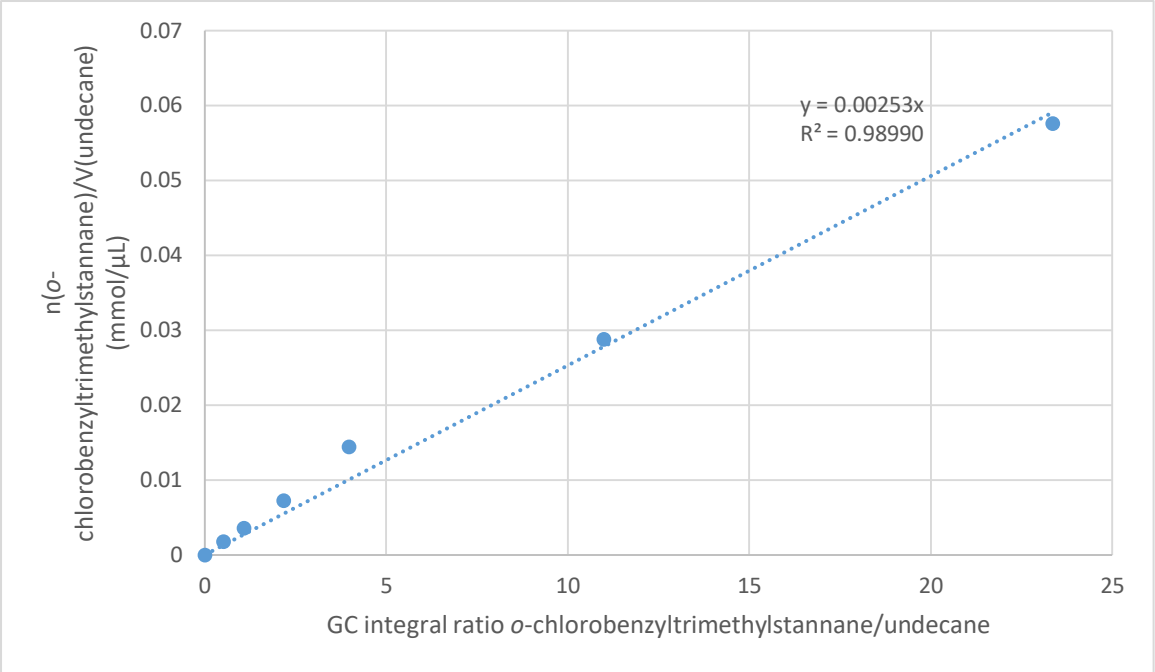

Figure SI-69. GC-FID calibration (Shimadzu GC-2025) for *o*-chlorobenzyltrimethylstannane with undecane as internal standard.

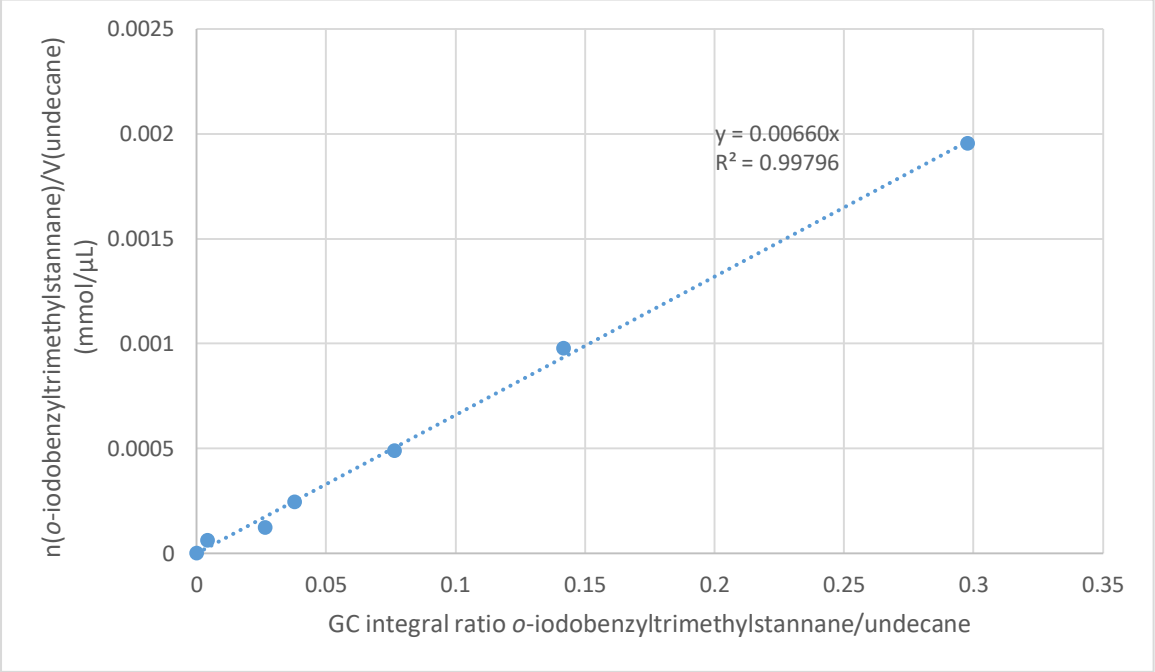

Figure SI-70. GC-FID calibration (Shimadzu GC-2025) for *o*-iodobenzyltrimethylstannane with undecane as internal standard.

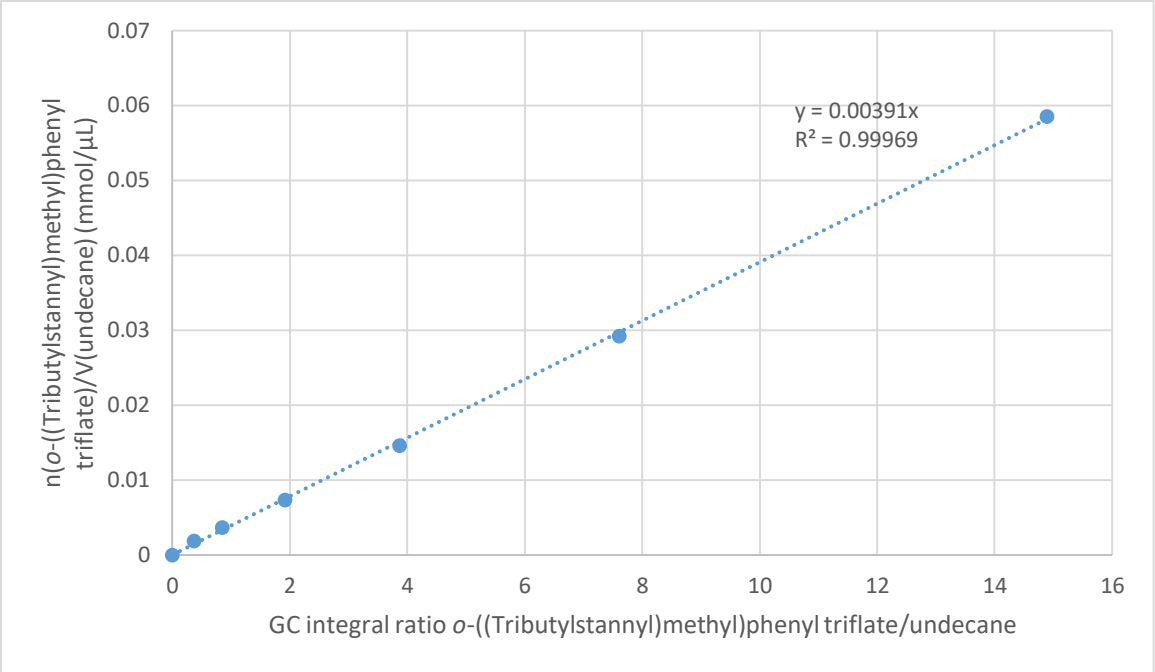

Figure SI-71. GC-FID calibration (Shimadzu GC-2025) for *o*-((Tributylstannyl)methyl)phenyl triflate with undecane as internal standard.

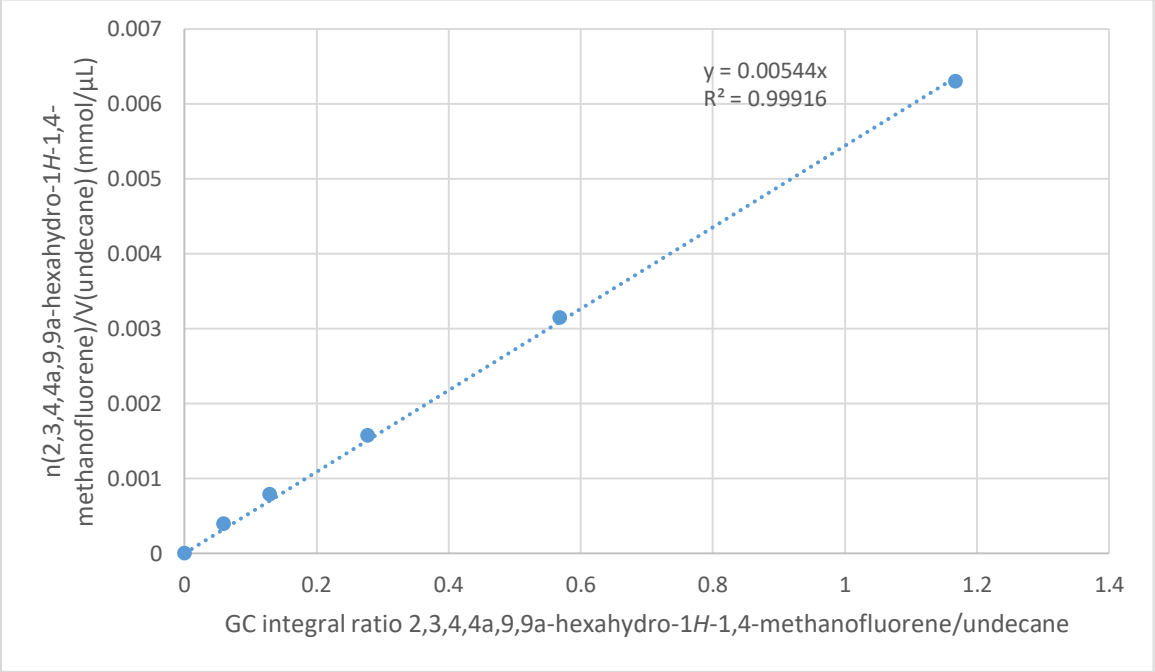

Figure SI-72. GC-FID calibration (Shimadzu GC-2025) for 2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene with undecane as internal standard.

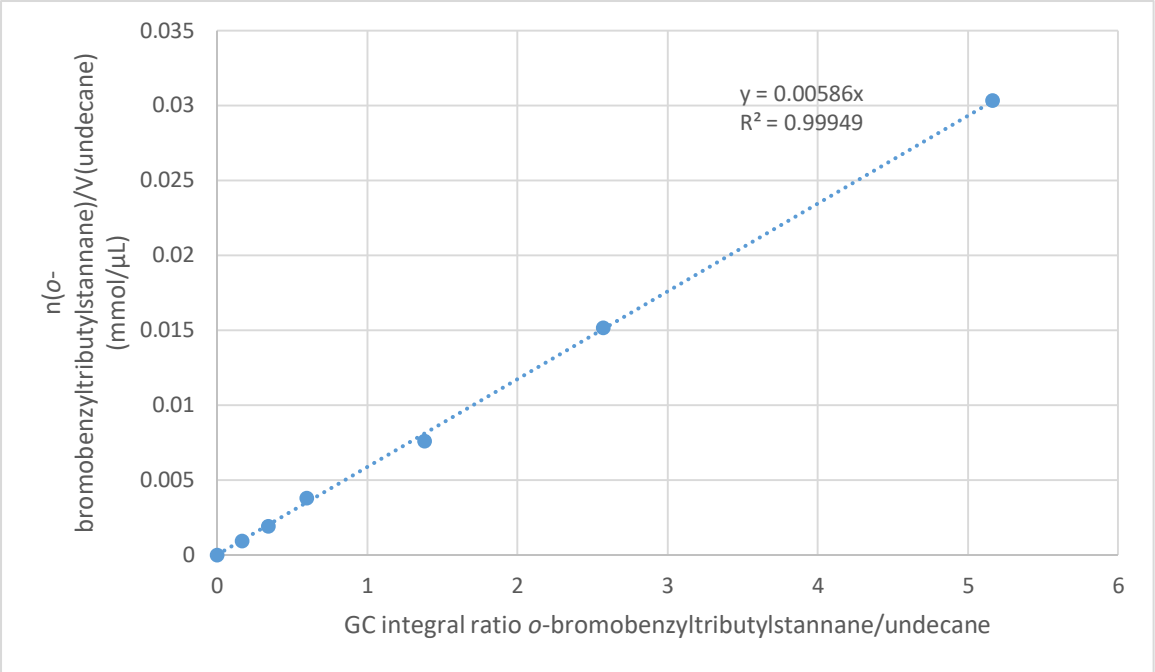

Figure SI-73. GC-FID calibration (Finnigan Focus GC) for *o*-bromobenzyltributylstannane with undecane as internal standard.

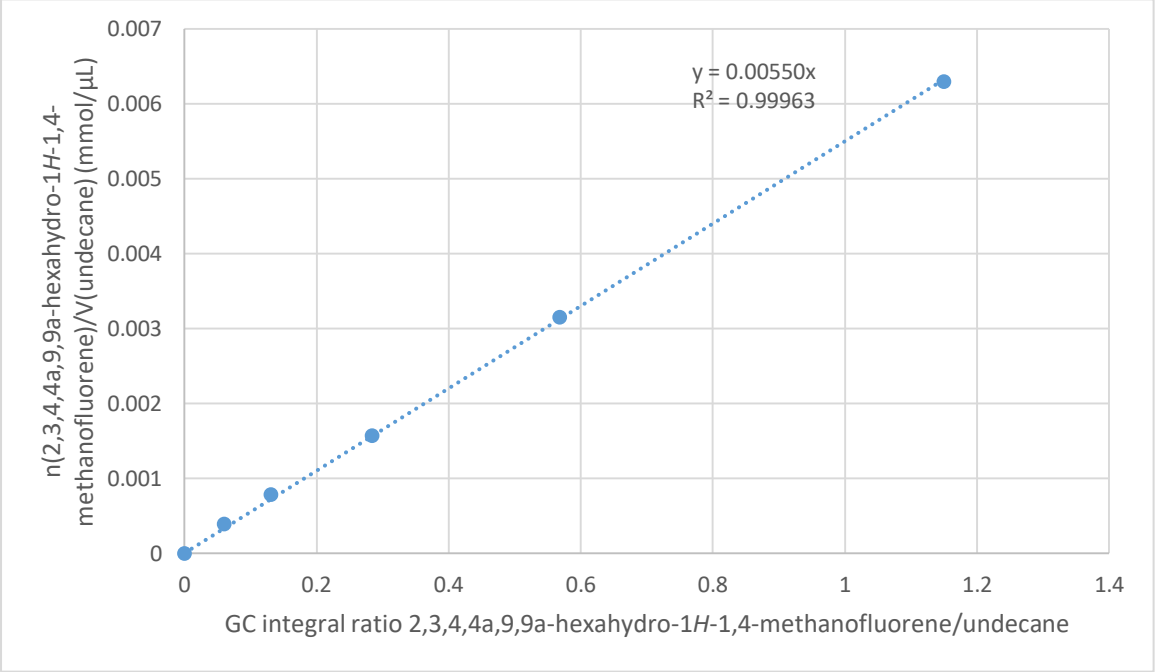

Figure SI-74. GC-FID calibration (Finnigan Focus GC) for 2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene with undecane as internal standard.