Supporting Information
for
Mechanism-based Design and Optimization of a Catalytic Electrophilic Cyclopropanation without Diazomethane

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ABSTRACT: Iodomethylboron compounds, either the trifluoroborate or a boronic ester, cyclopropanate electron-rich olefins and unprotected allylic alcohols with Pd catalysts according to a novel, designed catalytic cycle. Proposed intermediates in a "diverted Heck" mechanism are observed by means of spectroscopic studies, and by isolation and X-ray crystallographic characterization, which together with reaction kinetics, point to a separation of rate-determining and product-determining steps, and a mechanism-based optimization of the yield, selectivity, and scope of the catalytic electrophilic cyclopropanation. The reaction with crystalline, air-stable, non-hygroscopic and non-toxic reagents provides an alternative to Simmons-Smith-type reactions, as well as cyclopropanation procedures that require the use of diazomethane.

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I-GENERAL REMARKS

Unless otherwise stated, all reactions were carried out under an Argon or N_2 atmosphere using standard Schlenk or glovebox techniques with anhydrous solvents. Solvents and reagents were acquired from Aldrich, Fluka, Acros Organics, ABCR Chemicals and TCI. Deuterated solvents were obtained from Amar Chemicals. Extra molecular sieves were added to the purchased solvents and the solvents stored in the glovebox. N,N-dimethylformamide (>=99.5%, over molecular sieves [H_2O <=0.005%]), N,N-dimethylacetamide (>=99.5%, over molecular sieves [H_2O <=0.01%]) and 1,2-dimethoxyethane (DME, >=99.5%, over molecular sieves [H_2O <=0.005%]) were acquired from Sigma-Aldrich and stored in the glovebox before use. THF was freshly distilled from Na over benzophenone before use, or was alternatively stored after distillation in the glovebox before use. Methanol (>=99.5%, over molecular sieves [H_2O <=0.01%]), ethylene glycol anhydrous (98.5%) and glycerol anhydrous puriss. (99.5%) were acquired from Sigma-Aldrich (>=99.5%, over molecular sieves [H_2O <=0.01%]) or Acros Organics (99.8%, extra dry over molecular sieves). The internal standard undecane (>=99.8%), cyclooctene (**1a**, >=99.5%), n-hexanal (97%), anhydrous pinacol, cyclododecene (**1k**, >=96.0% GC), cyclododecanone (>99%) (+/-)-*cis*-bicyclo[3.2.0]hept-2-en-6-one (**1m**, >=98.0% GC) and 1-octene (**1o**, >=97%) were acquired from Fluka. ICH_2BF_3K (>98.0%) was acquired from TCI and further purified by washing several times with Et_2O and drying under high vacuum, then stored in the glovebox. $BrCH_2BF_3K$ (>98.0%) was acquired from TCI and used without further purification after storage in the glovebox. 2-(Iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [iodomethylboronic acid, pinacol ester] (98%) was acquired from Combi-Blocks Inc. and used without further purification after storage in the freezer. K_2CO_3 (99.99% trace metal basis) was acquired from Sigma-Aldrich and used without further purification. 1-Methyl-1-cyclopentene (**1b**, >98.0%), *cis*-5-decene (**1t**, >98.0% GC), 1,4-epoxy-1,4-dihydronaphthalene (**1n**, >98.0% GC), β-caryophyllene (**1j**, >90.0% GC) and 2-nonene (**30b**, >94.0% GC) were acquired from TCI. α-Pinene (**1e**, 98%), (-)-myrtenol (**1d**, 95%), camphene (**1l**, 95%), 1-nonene (**1p**, 96%), 2-methyl-1-nonene (**3p**, 97%) and *trans*-5-decene (**1s**, >=99%) were purchased from Sigma-Aldrich and used without further purification. 1,2-Propanediol (>=99.5%), *cis*-1,2-cyclohexanediol (99%) and 1,3-propanediol (98%) were purchased from Sigma Aldrich and used as received. 2,3 Butanediol (>=99.0%), *trans*-1,2-cyclohexanediol (98%), 2,4-pentanediol (99%) were purchased from Fluka and used as received. *Cis*-2-Hexen-1-ol (**1i**, 95%) and 2,3-dibromo-1-propene (85%) were acquired from ABCR chemicals and used without further purification. Cycloheptene (**1c,** 90%) and *trans*-2-hexen-1-ol (**1h**, 96%) were purchased from Acros Organics and used without further purification. Cyclohexene (**1d,** ≥99%) was purchased from Sigma-Aldrich, distilled from Na and stored in the glove box. n-BuLi (1.6 M in hexanes), pentylmagnesium chloride (2.0 M in THF), (trimethylsilyl)methyllithium (1.0 M in pentane) and TMEDA (>=99.5%) were acquired from Sigma-Aldrich and used without purification. 1-Bromomethyl cyclopropane (95%) was acquired from Maybridge and used without purification. 2-Methyl-2-pentenal (97%) and bromo-2-methylpropene (97%) were acquired from Sigma-Aldrich and used as received. $NaBH_4$ was acquired from Merck Millipore and

used without purification. *Trans*-di-μ-acetatobis[2-(di-o-tolylphosphino)benzyl]dipalladium(II) (**Cat2**, 98%) was acquired from ABCR chemicals and stored in the glovebox before use. Tri(o-tolyl)phosphine (**L1**, 97%), dichlorobis(tri-o-tolylphosphine)palladium(II) (**Cat1**, 97%), tBuXPhos Pd G3 (97%), bis(dibenzylideneacetone)palladium (0), dichloro(1,5-cyclooctadiene)palladium(II) ([COD]$PdCl_2$, 99%), and [1,1′-bis(di-tert-butylphosphino)ferrocene]dichloropalladium(II) (**Cat4**, 98%) were acquired from Sigma-Aldrich and used as such. $Pd(tBu_3P)_2$ (**Cat3**, 98%) was acquired from Acros Organics and used without purification. Bicyclo[6.1.0]nonane (**2a**), bicyclo[4.1.0]heptane (or norcarane, **2d**) and n-hexylcyclopropane (**2o**) were prepared according to a reported procedure.[1] Methylenecyclooctane (**3a**) was prepared according to a reported procedure.[2] The obtained data are consistent with those reported in the reference. 2,7,7-Trimethyltricyclo[4.1.1.$0^{2,4}$]octane(**2e**) was prepared following a reported procedure.[3] 2-Methylenehexan-1-ol (**3h**) was prepared from n-hexanal following a procedure in reference (3), and the obtained data matched those reported in that reference. 2-Methylpent-2-en-1-ol (**1g**) was prepared from 2-methyl-2-pentenal according to the procedure reported in reference (5). Physical and spectroscopic data are consistent with those reported in that reference. 1,2-Bis(di-o-tolylphosphino)ethane (**L2**) was prepared as described earlier.[6] 1,1'-Bis(di-o-tolylphosphino)ferrocene (**5**) was prepared by a procedure analogous to the one used for the synthesis of 1,2-bis(di-o-tolylphosphino)ethane. $(PR_3)_2PdCl_2$ complexes were prepared following a procedure reported earlier.[7] NMR data were recorded at 300, 400 or 600 MHz (Bruker AV300, AV400, AV600 spectrometers) with $CDCl_3$, CD_3OD, THF-d_8 or DMF-d_7 as solvents. Chemical shifts (δ) are reported in ppm with the residual solvent signal as internal standard (chloroform at 7.26 ppm and 77.00 ppm for ^1H and ^{13}C spectroscopy, respectively; methanol at 3.31 ppm and 49.00 ppm for ^1H and ^{13}C spectroscopy, respectively; tetrahydrofuran at 3.58 and 67.57 for ^1H and ^{13}C spectroscopy, respectively; dimethylformamide at 2.75, 2.92, 8.03 ppm for ^1H spectroscopy). ^{13}C-NMR spectra were recorded with complete ^1H-decoupling. Service measurements were performed by the NMR service team of the Laboratorium für Organische Chemie, ETH Zürich by Mr. Rainer Frankenstein, Mr. René Arnold and Mr. Stephan Burkhardt under supervision of Dr. Marc-Oliver Ebert. X-ray structural analysis was performed by the X-ray crystallography group of the Laboratorium für Organische Chemie, ETH-Zürich. High resolution mass spectra were recorded from the mass spectrometry service of the ETH Zürich Laboratorium für Organische Chemie with a Micromass (Waters) AutoSpec Ultima (EI) or a Bruker solariX (MALDI-FTICR). GC-FID analysis was performed on a Finnigan Focus GC with a Zebron ZB-5MS, 30mx0.25 mm column or a Restek Rtx-Wax, 30mx0.25 mm column using a flame ionization detector. Qualitative gas phase studies were performed on a Thermo Finnigan TSQ Quantum ESI-MS/MS instrument. Charged species were generated by electrospray ionization (ESI) from diluted (~ 10^{-5} mol/l) solutions freshly prepared in the glovebox, taken into a Hamilton gas-tight syringe and used immediately. All samples were electrosprayed with a flow rate of 5 ml/min.

II- SYNTHETIC AND EXPERIMENTAL PROCEDURES

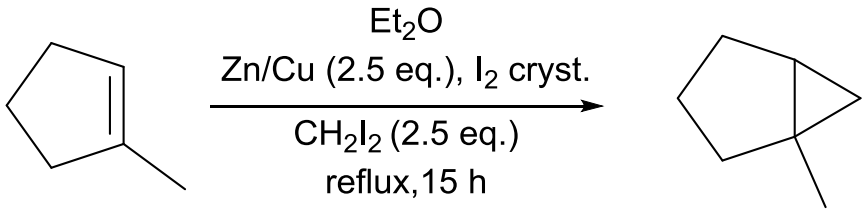
Bicyclo[6.1.0]nonane (2a)

The title compound was prepared according to the following representative procedure for the scale-up of the methylenation reaction of olefins to mmol (gram) amounts:

Representative procedure for the scale-up of the methylenation reaction of olefins to mmol (gram) amounts. A 250 ml oven-dried round-bottom flask equipped with an oven-dried magnetic stir bar was charged in a N_2-filled glovebox with powdered K_2CO_3 (4.04 g, 5.0 equiv.), anhydrous EG (5 ml), and anhydrous DMA (20 ml). The resulting mixture was stirred vigorously. $[(o\text{-tolyl})_3P]_2PdCl_2$ (230 mg, 5 mol%), $(o\text{-tolyl})_3P$ (89 mg, 5 mol%), ICH_2BF_3K (2.18 g, 1.5 equiv.), and the olefin (5.85 mmol) were added to the mixture under stirring. 60 ml of DMA were used to rinse the vials utilized to weigh all the reagents and were subsequently added to the reaction mixture. The round bottom flask was then closed, removed from the glovebox, and stirred at 75 °C for the indicated time. At the end of the reaction, which was monitored by GC/MS, the flask was cooled to 0 °C and its contents were poured over Celite. The filter cake was washed with Et_2O (3x50 ml). The filtrate was transferred to a separatory funnel and H_2O (200 ml) was added. The organic layer was separated and the aqueous layer was extracted with Et_2O (2x100 ml). The fractions were combined, dried over Na_2SO_4 or $MgSO_4$, filtered, and the ether solution removed by a rotary evaporator. The resulting oil residue was purified by flash column chromatography over silica gel.

Flash chromatography using pentane as eluent and slow evaporation of the solvent yielded 654 mg (90%) of a mixture of bicyclo[6.1.0]nonane (**2a**) and methylenecyclooctane (**3a**) (50:1 ratio of products in favor of the cyclopropane) as a colorless oil. MS (EI): 124 (32, $[M]^+$), 96 (94), 81 (77), 67 (100), 54 (73), 41 (27). HRMS (EI, ($[M]^+$)): m/z calcd for C_9H_{16} 124.1247; Found 124.1247.

1-Methylbicyclo[3.1.0]hexane (2b)



The procedure is analogous to the one depicted in reference (8) for the cyclopropanation of cyclopentene. A mixture of 27.5 g (0.213 mol, 2.5 eq.) of Zn/Cu couple and a crystal of iodine was stirred under 50 mL of dry ether under argon until the brown color disappeared. A mixture of 7 g (0.085 mol) of 1-methylcyclopentene, and 17.2 ml (0.213 mol, 2.5 eq.) of methylene iodide was added in portion. The mixture was then refluxed for 15 h. The mixture was filtered through celite and poured into 40 mL of a cooled saturated NH_4Cl solution. The organic layer was separated and washed with 3x40 ml NH_4Cl, 3x40 ml $NaHCO_3$ and 1 x 40 ml H_2O. After drying over $MgSO_4$,

the solvent was completely removed by distillation to yield 4.9 g (60%) of 1-methylbicyclo[3.1.0]hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 – 1.59 (m, 3H), 1.59 – 1.45 (m, 2H), 1.25 – 1.07 (m, 4H), 0.89 (dt, $^3J_{HH}$ = 8.0 Hz and $^3J_{HH}$ = 4.0 Hz, 1H), 0.30 (dd, $^3J_{HH}$ = 4.0 Hz, $^2J_{HH}$ = 4.6 Hz, 1H), 0.16 (dd, $^3J_{HH}$ = 8.0 Hz and $^2J_{HH}$ = 4.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 33.78, 27.93, 24.13, 23.93, 21.68, 21.54, 12.92. ^{13}C NMR values are in accordance with the literature data.[9] MS (EI): 96 (32, $[M]^+$), 81 (100), 68 (30), 55 (28), 41 (8). HRMS (EI, ($[M]^+$)): m/z calcd for C_7H_{12} 96.0934; Found 96.0931. HRMS (EI, ($[M-CH_3]^+$)): m/z calcd for C_7H_{12} 81.0699; Found 81.0699.

Bicyclo[5.1.0]octane (2c)

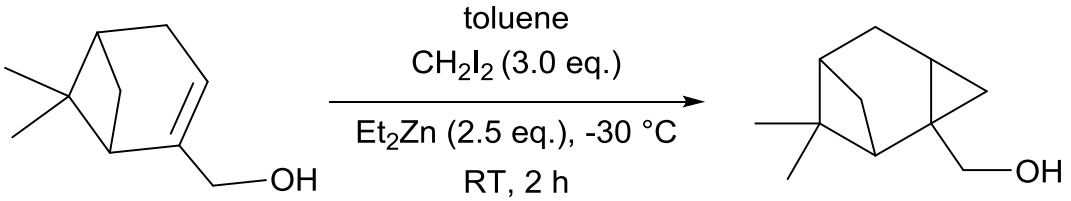
The title compound was prepared by a similar procedure used for the synthesis of 1-methylbicyclo[3.1.0]hexane. 4.5 g (79%) of **2c** were obtained as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22-2.05 (m, 2H), 1.89-1.77 (m, 1H), 1.76-1.64 (m, 2H), 1.42-1.28 (m, 2H), 1.27 – 1.05 (m, 1H), 1.00 – 0.73 (m, 4H), 0.68 (m, 1H), 0.07 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 32.69, 31.07, 29.83, 16.43, 14.84. MS (EI): 110 (8, $[M]^+$), 95 (14), 81(25), 67 (35), 54 (18), 41 (15). HRMS EI, ($[M]^+$)): m/z calcd for C_8H_{14} 110.1090; Found 110.1092.

2,7,7-Trimethyltricyclo[4.1.1.0^{2,4}]octane (2e)

The title compound was prepared in 70 % as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 – 2.01 (m, 2H), 1.89 (dd, $^3J_{HH}$ = 6.3 Hz and $^3J_{HH}$ = 5.1 Hz, 1H), 1.76 – 1.61 (m, 2H), 1.29 (s, 3H), 1.12 (s, 3H), 1.08 (s, 3H), 0.98 (d, $^2J_{HH}$ = 10.6 Hz, 1H), 0.82 – 0.71 (m, 2H), 0.31 – 0.20 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 45.38, 41.50, 40.93, 27.34, 26.99, 26.89, 26.83, 25.42, 21.00, 20.26, 18.90, 15.87. MS (EI): 150 (3), 135 (32, $[M-CH_3]^+$), 109 (74), 94 (100), 82 (56), 69 (47), 55 (17), 41 (25). HRMS (EI, ($[M-CH_3]^+$)): m/z calcd for $C_{10}H_{15}$ 135.1169; Found 135.1167.

(7,7-Dimethyltricyclo[4.1.1.0^{2,4}]octan-2-yl)methanol (2f)

The title compound was prepared from a modified reported procedure.[10]



To a solution of (-)-myrtenol (2.5 g, 1.0 eq.) and diiodomethane (3.0 eq.) in dry toluene (20 ml), was added drop wise a 1M solution of diethyl zinc (49.25 ml, 3.0 eq.) at -30 °C. Full conversion was observed within 2 h stirring at ambient temperature. The reaction was quenched at 0 °C by the addition of an aqueous HCl solution (1 M) and extracted with diethyl ether. The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified using a quick filtration over silica gel by eluting with a pentane/Et_2O mixture (5/1). Concentration of the eluent under reduced pressure resulted in the compound as an orange oil (R_f (pentane/ Et_2O (5/1)) = 0.17, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (dd, $^2J_{HH}$ = 11.0 Hz and $^3J_{HH}$ = 1.4 Hz, 1H), 3.02 (d, $^2J_{HH}$ = 11.0 Hz, 1H), 2.23 (dd, $^3J_{HH}$ = 6.4 Hz and $^3J_{HH}$ = 5.2 Hz, 1H), 2.15-2.07 (m, 1H), 2.07-1.98 (m, 1H), 1.75 – 1.64 (m, 2H), 1.36 (t, $^3J_{HH}$ = 5.2 Hz, 1H), 1.27 (s, 3H), 0.98 (s, 3H), 0.95 (d, $^2J_{HH}$ = 10.7 Hz, 1H), 0.93 – 0.83 (m, 2H), 0.45 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 70.16, 41.49, 40.90, 40.67, 27.77, 26.91, 26.64,

26.38, 20.82, 15.89, 13.36. MS (EI): 166(1, $[M]^+$), 148(12), 135 (27), 123 (17), 110 (76), 93 (43), 82 (100), 67 (71), 55 (31), 41 (44). HRMS (EI, ($[M]^+$)): m/z calcd for $C_{11}H_{18}O$ 166.1353; Found 166.1358. HRMS (EI, ($[M\text{-}CH_3O]^+$)): m/z calcd for $C_{10}H_{15}$ 135.1169; Found 135.1169.

The title compound was isolated in 86% following the representative procedure for the scale-up of the methylenation reaction of olefins to mmol (gram) amounts. Spectroscopic data (NMR and MS) are the same as the one reported for **2f** prepared above. HRMS (EI, ($[M]^+$)): m/z calcd for $C_{11}H_{18}O$, 166.1353; Found 166.1353. ~5.4% of the corresponding aldehyde (**3f**) was isolated alongside the cyclopropane. ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.72, 40.85, 40.54, 38.49, 37.34, 26.51, 26.17, 25.66, 20.84, 20.34, 17.23.

(2-Ethyl-1-methylcyclopropyl)methanol (2g)
The title compound was prepared analogously to a reported procedure[11] using 2-methylpent-2-en-1-ol as substrate. 2.1 g (31%) of a colourless oil were obtained, R_f (Hexane/AcOEt(10/1)) = 0.25. ^1H NMR (400 MHz, $CDCl_3$) δ 3.36 – 3.27 (m, 2H), 1.43 – 1.37 (m, 1H), 1.33 (p, $^3J_{HH}$ = 7.3 Hz, 2H), 1.13 (s, 3H), 0.96 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.57 (dtd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.9 Hz and $^3J_{HH}$ = 5.2 Hz, 1H), 0.50 (dd, $^3J_{HH}$ = 8.8 Hz and $^2J_{HH}$ = 4.2 Hz, 1H), -0.02 – -0.06 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 72.64, 23.77, 22.33, 22.31, 16.53, 15.11, 14.41. HRMS (EI, ($[M\text{-}C_2H_5]^+$)): m/z calcd for C_5H_9O 85.0648; Found 85.0650. HRMS (EI, ($[M\text{-}CH_3O]^+$)): m/z calcd for C_6H_{11} 83.0856; Found 83.0857.

***Trans*-2-propylcyclopropylmethanol (2h)**
The title compound was prepared analogously to a reported procedure[11] using (E)-hex-2-en-1-ol as substrate. Colourless oil, 20%, R_f (Hexane/AcOEt (4/1)) = 0.22. ^1H NMR (400 MHz, $CDCl_3$) δ 3.50 – 3.22 (m, 2H), 1.57 (s, 1H), 1.44 – 1.32 (m, 2H), 1.26 – 1.16 (m, 2H), 0.90 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.86 – 0.76 (m, 1H), 0.63 – 0.53 (m, 1H), 0.35 (dt, $^2J_{HH}$ = 8.5 Hz and $^3J_{HH}$ =4.7 Hz, 1H), 0.29 (dt, $^2J_{HH}$ = 8.5 Hz and $^3J_{HH}$ = 4.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 67.31, 35.85, 22.81, 21.25, 17.05, 14.03, 9.99. MS (EI): 96(11, $[M\text{-}H_2O]^+$), 81 (39), 73 (65), 67 (22), 55 (100), 41 (56), 29 (12). HRMS (EI, ($[M\text{-}H_2O]^+$)): m/z calcd for C_7H_{12} 96.0934; Found 96.0931.

***Cis*-2-propylcyclopropylmethanol (2i)**
The title compound was prepared analogously to a reported procedure[11] using (Z)-hex-2-en-1-ol as substrate. Colourless oil, 64%, R_f (Hexane/AcOEt (4/1)) = 0.3. ^1H NMR (400 MHz, $CDCl_3$) δ 3.67 – 3.52 (m, 2H), 1.59 – 1.51 (m, 1H), 1.49 – 1.33 (m, 3H), 1.27 – 1.14 (m, 1H), 1.13 – 1.01 (m, 1H), 0.97 – 0.79 (m, 4H), 0.73 – 0.63 (m, 1H), -0.02 – -0.08 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 62.98, 30.66, 23.17, 17.90, 15.81, 13.94, 9.42. MS (EI): 96(10, $[M\text{-}H_2O]^+$), 81 (35), 73 (80), 67 (22), 55 (100), 41 (61), 29 (13). HRMS (EI, ($[M\text{-}H_2O]^+$)): m/z calcd for C_7H_{12} 96.0934; Found 96.0929.

4,12,12-Trimethyl-9-methylenetricyclo[8.2.0.0^{4,6}]dodecane (2j)
The title compound was prepared according to the representative procedure for the scale-up of the methylenation reaction of olefins to mmol (gram) amounts, and obtained as a colorless oil, 68%, R_f (Hexane) = 0.78. Analytical data (NMR) are consistent with the ones described in the literature.[12] MS (EI): 218 (6, $[M]^+$), 203 (47, $[M\text{-}CH_3]^+$), 175 (55), 161 (44), 147 (44), 133 (60), 119 (34), 107 (85), 93 (100), 81 (58), 69 (90), 55 (27), 41 (18). HRMS (EI, ($[M]^+$)): m/z calcd for $C_{16}H_{26}$ 218.2029; Found 218.2026.

HRMS (EI, ([M-CH_3]$^+$)): m/z calcd for $C_{15}H_{23}$ 203.1795; Found 203.1799. Elemental analysis: Anal. Calcd for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found: C, 87.86.51; H, 12.25.

Bicyclo[10.1.0]tridecane (2k)
The title compound was prepared as a colorless oil, bp. 110 °C/13 mbar from cyclododecene (96% purity, contains some cyclododecane) by a similar procedure used for the synthesis of 1-methylbicyclo[3.1.0]hexane. Analytical data (NMR, MS) are consistent with the ones described in the literature.[13]

Tricyclo[4.2.0.$o^{2,4}$]octan-7-one (2m)
The title compound was prepared from (+/-)-*cis*-Bicyclo[3.2.0]hept-2-en-6-one in 77% as a light orange oil. R_f (Hexane/EtOAc (10/1)) = 0.33 according to the representative procedure for the scale-up of the methylenation reaction of olefins to mmol (gram) amounts. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38-3.24 (m, 1H), 3.16 – 3.01 (m, 1H), 2.89 – 2.77 (m, 2H), 2.30 – 2.17 (m, 1H), 1.93 (dd, $^3J_{HH}$ = 13.7 Hz and $^3J_{HH}$ = 10.3 Hz, 1H), 1.54 – 1.47 (m, 1H), 1.47 – 1.41 (m, 1H), 0.75 – 0.66 (m, 1H), -0.07 – -0.13 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.44, 63.92, 50.79, 34.72, 31.82, 25.42, 20.13, 13.16. Minor isomer: ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.25, 67.89, 48.50, 31.84, 30.24, 25.22, 23.40, 8.79. MS (EI): 122 (2, [M]$^+$), 80 (100), 68 (10), 55 (10). HRMS (EI, ([M]$^+$)): HRMS (EI, ([M]$^+$)): m/z calcd for $C_8H_{10}O$ 122.0727; Found 122.0730.

***Exo*-Cyclopropanated Oxabenzonorbornadiene (2n)**
The title compound was prepared according to the representative procedure for the scale-up of the methylenation reaction of olefins to mmol (gram) amounts. An additional washing of the organic layers with 10% NaOH was included in the work-up. The product was obtained by column chromatography in 26% yield as a colorless oil. R_f (Hexane/EtOAc (20/1)) = 0.36. Analytical data (NMR) are consistent with the ones described in the literature.[14] MS (EI): 158 (31, [M]$^+$), 129 (100), 115 (13). HRMS (EI, ([M]$^+$)): m/z calcd for $C_{11}H_{10}O$, 158.0727; Found 158.0725. Elemental analysis: Anal. Calcd for $C_{11}H_{10}O$: C, 83.52; H, 6.37. Found: C, 83.51; H, 6.43.

N-heptylcyclopropane (2p)
The title compound was prepared by a similar procedure used for the synthesis of 1-methylbicyclo[3.1.0]hexane in 78% as a colorless oil, bp. 57-59 °C/13 mbar. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 – 1.33 (m, 2H), 1.33 – 1.22 (m, 8H), 1.18 (q, $^3J_{HH}$ = 7.0 Hz, 2H), 0.93 – 0.85 (m, 3H), 0.71 – 0.58 (m, 1H), 0.42 – 0.35 (m, 2H), 0.02 – -0.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 34.97, 32.10, 29.84, 29.70, 29.57, 22.87, 14.28, 11.08, 4.51. MS (EI): 140 (7), 112 (20), 97 (28), 83 (47), 70 (100), 56 (91), 43 (38).

N-octylcyclopropane (2q)
The title compound was prepared by a similar procedure used for the synthesis of 1-methylbicyclo[3.1.0]hexane in 66% as a colorless oil, bp. 72-75 °C/13 mbar. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 – 1.34 (m, 2H), 1.34 – 1.24 (m, 10H), 1.18 (q, $^3J_{HH}$ = 7.0 Hz, 2H), 0.92 – 0.85 (m, 3H), 0.71 – 0.59 (m, 1H), 0.42 – 0.35 (m, 2H), 0.02 – -0.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 34.98, 32.12, 29.88, 29.85, 29.76, 29.70, 29.55, 22.88, 14.28,

11.09, 4.52. MS (EI): 154 (5, $[M]^+$), 126 (14), 111 (14), 97 (51), 83 (70), 70 (93), 56 (100), 43 (68). HRMS (EI, ($[M]^+$)): m/z calcd for $C_{11}H_{22}$ 154.1716; Found 154.1716.

***Trans*-1,2-dibutylcyclopropane (2s)**

The title compound was prepared by a similar procedure used for the synthesis of 1-methylbicyclo[3.1.0]hexane in 72% as a colorless oil, bp. 63-64 °C/17 mbar. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 – 1.08 (m, 12H), 0.89 (t, $^3J_{HH}$ = 7.2 Hz, 6H), 0.36 (ddd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 5.8 Hz, $^3J_{HH}$ = 4.2 Hz, 2H), 0.18 – 0.08 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 34.23, 32.09, 22.74, 18.92, 14.31, 14.27, 11.92. MS (EI): 154 (37, $[M]^+$), 111 (8), 97 (16), 83 (32), 69 (93), 55 (100), 43 (33). HRMS (EI, ($[M]^+$)): m/z calcd for $C_{11}H_{22}$ 154.1716; Found 154.1718.

***Cis*-1,2-dibutylcyclopropane (2t)**

The title compound was prepared by a similar procedure used for the synthesis of 1-methylbicyclo[3.1.0]hexane. **2s** was prepared in 72% as a colorless oil, bp. 68 °C/17 mbar. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 – 1.27 (m, 10H), 1.21 – 1.10 (m, 2H), 0.96 – 0.85 (m, 6H), 0.70 – 0.61 (m, 2H), 0.60 – 0.52 (m, 1H), -0.33 (td, $^3J_{HH}$ = 5.5 Hz and $^2J_{HH}$ = 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 32.63, 28.56, 22.86, 15.90, 14.33, 11.06. MS (EI): 154 (29, $[M]^+$), 111 (11), 97 (28), 83 (27), 69 (81), 55 (100), 43 (34). HRMS (EI, ($[M]^+$)): m/z calcd for $C_{11}H_{22}$ 154.1716; Found 154.1716.

Methylenecyclododecane (3k)

The title compound was prepared from cyclododecanone according to a modified procedure.[15] At -78 °C under argon, a solution of ((trimethylsilyl)methyl)lithium 1 M in pentane (18 ml, 18 mmol) is added dropwise to a solution of cyclododecanone (3.28 g, 18 mmol) in THF (25 ml). The reaction mixture is stirred for 2 h at that temperature, after which time the reaction vessel was warmed to ambient temperature and stirred for another 15 min before the addition of 2% aqueous HCl (200 ml) solution and followed by extraction with Et_2O (3x100 ml). The organic layers are dried ($MgSO_4$) and the solvent evaporated to give a colorless oil that was stirred in a two-phase mixture composed of 60 mL of pentane and 60 mL of 50% aqueous acetic acid for ca. 18 h. The layers were separated and the organic phase was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. Short column chromatography of the residue with pentane yielded 1.07 g (33%) of **3k** as a colorless oil, whose analytical data (NMR) are consistent with the ones described in the literature.[16] MS (EI): 180 (57, $[M]^+$), 123 (17), 109 (40), 96 (100), 82 (98), 68 (62), 56 (80), 41 (18). HRMS (EI, ($[M]^+$)): m/z calcd for $C_{11}H_{10}O$, 180.1873; Found 180.1876.

2-Methyloct-1-ene (30a)

The title compound was prepared according to the following procedure: a 2 M solution of n-pentylMgCl in THF (11 ml, 22 mmol) is added dropwise to a stirred solution of 3-bromo-2-methylprop-1-ene (2 ml, 20 mmol) in THF (160 ml) at 0 °C under argon atmosphere. The resulting mixture was allowed to warm to room temperature and was stirred overnight. The excess of Grignard reagent is quenched with diluted aqueous HCl. Following an extraction with pentane (3x150 ml), washing the extract with H_2O

(2x200 ml), drying with Na_2SO_4, filtration, evaporation of the solvent, and distillation yielded 1.95 g (77%, traces of decane are present) of the title compound as a colorless oil. Analytical data (NMR) are consistent with the ones described in the literature.[17] MS (EI): 126 (23, $[M]^+$), 98 (4), 69 (23), 56 (92), 43 (33), 18 (100). HRMS (EI, ($[M]^+$)): m/z calcd for C_9H_{18} 126.1403; Found 126.1400.

5-Methylenedecane (3s)

The title compound was prepared analogously to a reported procedure.[18] In brief, the preparation was carried out in a 250 ml flask previously dried and filled with Argon. A solution of n-BuMgCl 2 M in Et_2O (11 ml, 22 mmol) is added at ambient temperature to a stirred solution of 2,3-dibromopropene (4g, 20 mmol) in THF (160ml). After 18 h, (dppp)$NiCl_2$ (345 mg, 0.64 mmol) is added to the mixture, then a solution of n-BuMgCl 2 M in Et_2O (11 ml, 22 mmol) is slowly added dropwise, and stirring is continued for 4h. Excess of Grignard reagent is quenched with diluted aqueous HCl. Extraction with Et_2O (3x150 ml), washing the extract with H_2O (2x200 ml), drying with Na_2SO_4, filtration, evaporation of the solvent and purification by vacuum distillation yielded 2.18 g (71%) as a colorless oil, bp. 65-68 °C/17 mbar. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 – 4.68 (m, 2H), 2.00 (td, $^3J_{HH}$ = 7.8 Hz and $^2J_{HH}$ = 3.0 Hz, 4H), 1.50 – 1.20 (m, 10H), 0.90 (td, $^3J_{HH}$ = 7.2 Hz and $^2J_{HH}$ = 5.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.56, 108.47, 36.22, 35.95, 31.85, 30.21, 27.68, 22.76, 22.71, 22.68, 14.22, 14.16. MS (EI): 154 (14, $[M]^+$), 97 (13), 84 (12), 70 (37), 56 (100), 43 (15). HRMS (EI, ($[M]^+$)): m/z calcd for $C_{11}H_{22}$ 154.1716; Found 154.1721.

Potassium bis(ethyleneglycolato)borate (4)

The title compound was prepared following procedure depicted in reference (19). A white poorly soluble solid, was formed. ^{1}H NMR (500 MHz, DMF-d_7) δ 3.55 (s, 2H), 3.13 (s, 1H). ^{11}B NMR (160 MHz, DMF-d_7) δ 11.24. ^{11}B NMR (160 MHz, DMF-d_7: EG-d_6 (16:1)) δ 10.55, 7.00. Elemental analysis indicates that some K_2CO_3 precipitate with the product. Elemental analysis: Anal. Calcd for $C_{4.93}H_8BK_{2.86}O_{6.79}$ ($C_4H_8O_4BK$+0.93 K_2CO_3): C, 19.83; H, 2.70. Found: C, 19.82; H, 2.70.

1,1'-Bis(di-o-tolylphosphino)ferrocene (5)

The title compound is obtained with a yield of 64% (white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.08 (m, 2H), 7.23 – 7.08 (m, 2H), 6.99 – 6.93 (m, 1H), 4.25 (t, $^3J_{HH}$ = 1.8 Hz, 1H), 4.07 (q, $^3J_{HH}$ = 1.8 Hz, 1H), 2.47 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ -37.32. ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.80, 141.54, 137.60, 137.49, 133.32, 129.85, 129.80, 128.42, 125.54, 125.52, 76.62, 74.26, 74.11, 72.19, 72.18, 72.15, 72.14, 21.43, 21.21.

1,2-Bis(di-o-tolylphosphino)ethane (6)

The title compound is obtained in 76% as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.5 Hz, 4H), 7.18 – 7.12 (m, 4H), 7.09 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.5 Hz, 4H), 7.06 – 7.00 (m, 4H), 2.40 (s, 12H), 2.06 (t, $^3J_{HH}$ = 4.3 Hz, 4H). ^{31}P NMR (162 MHz, $CDCl_3$) δ -33.64. ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.52, 142.40, 142.27, 136.43, 136.36, 136.29, 131.08, 130.09, 130.06, 130.04, 128.46, 126.03, 22.71, 22.68, 21.37, 21.27, 21.16.

Tris(2-methyl-4-fluorophenyl)phosphine (7)
The title compound was prepared quantitatively according to a reported procedure, see reference (20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.92 (m, 3H), 6.80 (td, $^{3}J_{HH}$ = 8.5 Hz and $^{4}J_{HH}$ = 2.7 Hz, 3H), 6.69-6.60 (m, 3H), 2.37 (s, 9H). ^{31}P NMR (162 MHz, $CDCl_3$) δ -33.64 (q, $^{5}J_{PF}$ = 3.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.42 (d, $^{5}J_{FP}$ = 4.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.66, 162.19, 145.37, 145.29, 145.08, 145.01, 134.71, 134.63, 129.57, 129.54, 129.47, 129.43, 117.42, 117.36, 117.21, 117.16, 113.40, 113.39, 113.20, 113.19, 21.26, 21.25, 21.05, 21.03.

Preparation of the Pd complex 8
A 25 ml oven-dried round bottom flask was brought into a N_2-filled glovebox and charged with K_2CO_3 (136 mg, 4.0 equiv.), ICH_2BF_3K (183.4 mg, 3.0 equiv.), and DMF (1 ml). The Buchwald palladium precatalyst tBuXPhos Pd G3 (196 mg, 0.246 mmol, 1.0 equiv.) in DMF (1 ml) was added into this mixture under stirring at ambient temperature and the vial containing the precatalyst was rinsed with another 1 ml DMF and transferred to the reaction mixture. Stirring was continued for 10 min before the removal of the solvent by rotary evaporation. A mixture of DCM/pentane (5 ml/10 ml) was added to the resulting residue and filtered over Celite. The Celite filter cake was washed with pentane (5 ml). The solvents were slowly evaporated on a rotary evaporator under moderate vacuum (no water bath) until lots of clear green micro crystals appeared in the flask. Evaporation was stopped and the crystals were isolated by filtration, washed with a small volume of cold pentane, and dried under high vacuum. These crystals were suitable for X-ray analysis. 126 mg of product are obtained (NMR reveals the presence of 9*H*-carbazole). ^{1}H NMR (400 MHz, CH_2Cl_2-d_2) δ 7.99 (tq, $^{3}J_{HH}$ = 6.5 Hz and $^{4}J_{HP}$ = 2.2 Hz, 1H, aryl C*H*), 7.57-7.51 (m, 2H, aryl C*H*), 7.28 – 7.27 (m, 2H, aryl C*H*), 7.19 – 7.11 (m, 1H, aryl C*H*), 3.02 (hept, $^{3}J_{HH}$ = 6.9 Hz, 1H, iPr C*H*), 2.45 (hept, $^{3}J_{HH}$ = 6.7 Hz, 2H, iPr C*H*), 1.56 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, iPr CH_3), 1.48 (d, $^{3}J_{HP}$ = 15.1 Hz, 18H, tBu), 1.36 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, iPr CH_3), 1.19 (qd, $^{3}J_{HF}$ = 8.0 Hz and $^{3}J_{HP}$ = 1.6 Hz, 2H, PdCH_2BF_3), 0.95 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, iPr CH_3). ^{31}P NMR (162 MHz, CH_2Cl_2-d_2) δ 75.42 (q, $^{4}J_{PF}$ = 32.6 Hz). ^{19}F NMR (376 MHz, CH_2Cl_2-d_2) δ -140.53 (s, PdCH$_2$BF_3). ^{11}B NMR (160 MHz, CH_2Cl_2-d_2) δ 5.38 (s, PdCH$_2$BF_3). HRMS (MALDI-FTICR/DCTB, ([M-BF_3]$^+$)): m/z calcd for $C_{30}H_{47}$PPd 544.2456; Found: 544.2456.

[1,1′-Bis(di-o-tolylphosphino)ferrocene]dichloropalladium(II) (Cat5). ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.34. Elemental analysis: Anal. Calcd for $C_{83}H_{80}P_4Cl_4Fe_2Pd_2$ ($C_{38}H_{36}P_2Cl_2FePd$ + 0.5 toluene): C, 59.77; H, 4.83; P, 7.43; Cl, 8.50. Found: C, 59.53; H, 4.78; P, 7.53; Cl, 8.53.

[1,2-Bis(di-o-tolylphosphino)ethane]dichloropalladium(II) (Cat6). **Cat6** is poorly soluble in non-coordinating solvents. HRMS (MALDI-FTICR/DCTB, ([M-Cl]$^+$)): m/z calcd for $C_{30}H_{32}P_2$ClPd 595.0705; Found: 595.0685.

Dichlorobis(2,4-dimethylphenyl)phosphine)palladium(II) (Cat7). ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.42. Elemental analysis: Anal. Calcd for $C_{48}H_{54}P_2Cl_2Pd$: C, 66.25; H, 6.25; P, 7.12; Cl, 8.15. Found: C, 65.92; H, 6.26; P, 6.93; Cl, 8.29.

Dichlorobis((2-methyl-4-fluorophenyl)phosphine)palladium(II) (Cat9). ^{31}P NMR (122 MHz, $CDCl_3$) δ 19.68. Elemental analysis: Anal. Calcd for $C_{42}H_{36}F_6P_2Cl_2Pd$: C, 56.43; H, 4.06; F, 12.75; P, 6.93; Cl, 7.93. Found: C, 56.52; H, 3.94; F, 12.58; P, 6.72; Cl, 7.83.

III- CYCLOPROPANATION EXPERIMENTS

Representative methylenation procedure in DMA/EG or THF/EG. An oven-dried Schlenk (2.5 or 5 ml) equipped with a Teflon Young valve and an oven-dried magnetic stir bar was charged in a N_2-filled glovebox with powdered K_2CO_3 (80.9 mg, 5.0 equiv.) and anhydrous ethylene glycol (EG, 0.1 ml). The mixture was vigorously stirred for 10 min before, and during, the addition of a solution of anhydrous dimethylacetamide (DMA, 0.6 ml) containing Pd-catalyst $[(o\text{-tolyl})_3P]_2PdCl_2$ (4.6 mg, 5 mol%), ICH_2BF_3K (34.8 mg, 1.2 equiv.) and cyclooctene (COE, 15.2 µl, 0.117 mmol). The rest of the anhydrous DMA (2x0.5 ml) was utilized to rinse the vial containing the previous solution and then added to the reaction mixture. The tube was sealed, removed from the glovebox, and heated to 75 °C for 22 h. The reaction mixture was then rapidly cooled to 0 °C in an ice bath for 15 min and a work-up was conducted.

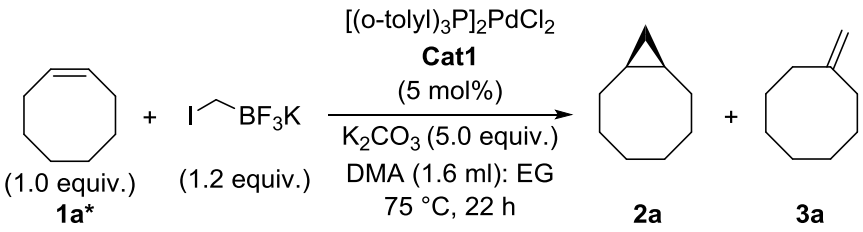
Representative methylenation procedure in DMA/MeOH. A 5 ml oven-dried Schlenk (2.5 or 5 ml) equipped with a Teflon Young valve and an oven-dried magnetic stir bar was charged in a N_2-filled glovebox with powdered K_2CO_3 (80.9 mg, 5.0 equiv.) and anhydrous MeOH (0.5 ml). The mixture was vigorously stirred for 10 min before, and during, the addition of a solution of anhydrous DMA (0.6 ml) containing Pd-catalyst $[(o\text{-tolyl})_3P]_2PdCl_2$ (4.6 mg, 5 mol%), ICH_2BF_3K (34.8 mg, 1.2 equiv.) and COE (15.2 µl, 0.117 mmol). The rest of the anhydrous DMA (2x0.5 ml) and anhydrous MeOH (0.3 ml) was utilized to rinse the vial containing the previous solution and then added to the reaction mixture. The tube was sealed, removed from the glovebox and heated to 75 °C for 22 h. The reaction mixture was then rapidly cooled to 0 °C in an ice bath for 15 min and a work-up was conducted.

Procedure for small-scale work-up. The internal standard, undecane (10 µl, around 0.40 equiv. for 0.117 mmol scale of olefin), was added to the tube with the reaction mixture, followed by Et_2O (2x35 ml/mmol substrate). The solution was transferred to a 15 ml glass vial. The Schlenk tube was rinsed with H_2O (45 ml/mmol substrate) or saturated NH_4Cl for the allylic alcohols. The aqueous layer was transferred to the 15 ml glass vial and the layers were separated. The organic phase was transferred to another 15 ml glass vial, washed with H_2O (45 ml/mmol substrate) and brine (45 ml/mmol substrate), dried over $MgSO_4$, and then filtered through celite. The resulting solution was analyzed by GC-FID.

A. Screenings and cyclopropanation of various olefins

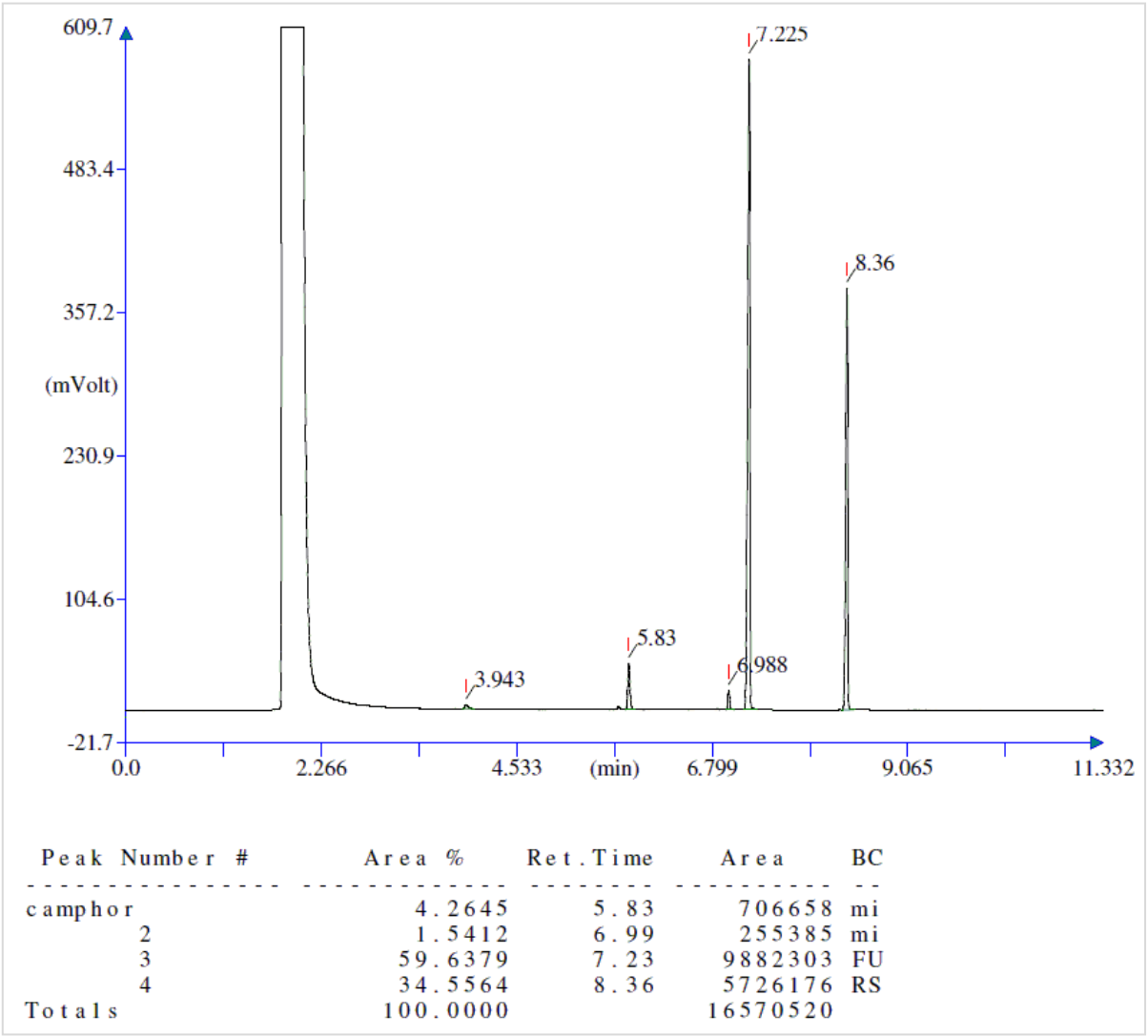
A-1. Ethylene Glycol (EG) as co-solvent

Table SI-1. Optimization of DMA/Ethylene glycol ratio.



no.	DMA:EG (ratio)	**2a** [%][a]	**3a** [%][a]	Rem. **1a** [%][a]	Total [%][a]	Ratio **2a**/**3a**
1	8:1	83.8	3.0	14.4	101.3	27.6
2	10:1	89.4	2.1	9.1	100.6	43.0
3	16:1	93.6	2.3	7.1	103.0	40.5
4	20:1	93.6	2.4	7.5	103.5	38.3
5	32:1	86.5	2.2	12.1	100.8	39.2

[a]Yields were evaluated by GC-FID. **1a***: 0.117 mmol.

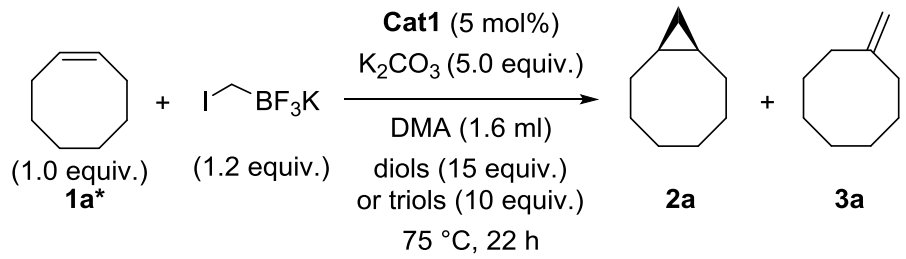


Peak Number #	Area %	Ret.Time	Area	BC
camphor	4.2645	5.83	706658	mi
2	1.5412	6.99	255385	mi
3	59.6379	7.23	9882303	FU
4	34.5564	8.36	5726176	RS
Totals	100.0000		16570520	

Figure SI-1. Representative GC chromatogram of the methylenation of cyclooctene. Retention times: toluene (tR= 3.94 min), cyclooctene (tR= 5.83 min), methylenecyclooctane (tR= 6.99 min), bicyclo[6.1.0]nonane (tR= 7.23 min), undecane (tR= 8.36 min; internal standard).

A-2. Various diols & triol as co-solvent

Table SI-2. Screening of some diols and triol.

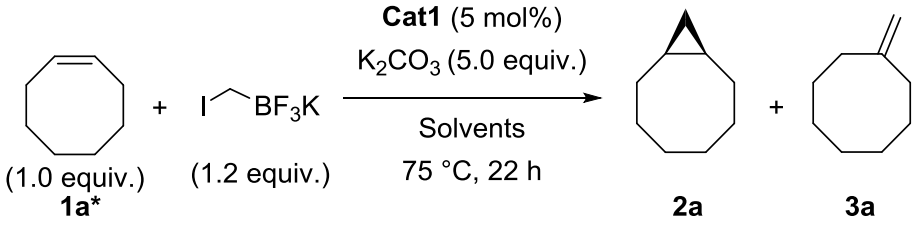


no.	Diols or Triol	**2a** [%][a]	**3a** [%][a]	Rem. **1a** [%][a]	Total [%][a]	Ratio **2a**/**3a**
1	Ethylene glycol	93.6	2.3	7.1	103.0	40.5
2	1,2-propanediol	68.9	1.8	32.1	102.8	39.3
3	Glycerol	71.9	5.6	24.1	101.2	13.7
4	2,3 butanediol	5.6	1.6	91.9	99.0	3.6
5	*cis*-1,2-Cyclohexanediol	54.4	3.9	39.1	97.5	13.8
6	*trans*-1,2-Cyclohexanediol	59.0	10.2	28.5	98.0	5.8
7	Pinacol	0.3	0.9	95.7	97.0	0.4
8	Pinacol[b]	0.4	1.1	98.3	99.8	0.4
9	Catechol	0.3	2.0	92.3	94.6	0.2
10	1,3-propanediol	4.2	0.5	96.7	101.4	8.8
11	2,4-pentanediol	0.2	0.4	94.6	95.3	0.4

[a]Yields were evaluated by GC-FID. **1a***: 0.117 mmol.

A-3. Additions cyclopropanation reactions of cyclooctene

Table SI-3. Additional results of the cyclopropanation of cyclooctene.

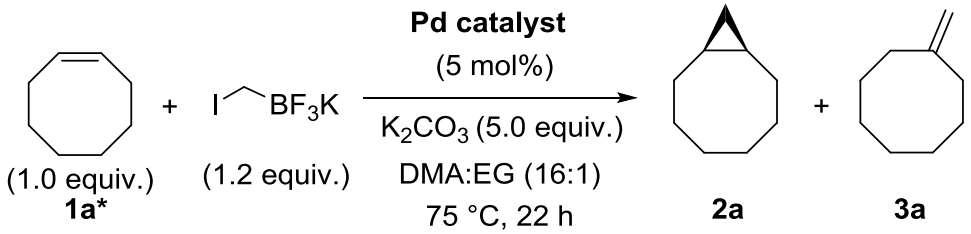


no.	Solvents (ratio)	**2a** [%][a]	**3a** [%][a]	Rem. **1a** [%][a]	Total [%][a]	Ratio **2a**/**3a**
1[b]	DMA/MeOH (2/1)	76.0	1.0	26.7	103.7	73.0
2[b,c]	DMA/MeOH (2/1)	64.7	1.5	39.3	105.5	42.0
3	DMA/MeOH (2/1)	76.5	0.5	24.5	101.5	147.9
4	MeOH (1.6 ml)	25.4	0	75.5	100.9	-
5	DMA (1.6 ml)	0	0.8	100.1	101.0	0
6	DMA/EG (16/1)	93.6	2.3	7.1	103.0	40.5
7[d]	DMA/EG (16/1)	97.9	2.1	0	100.1	45.9
8	DME/EG (16/1)	25.7	1.2	75.6	102.5	21.1

9	THF/EG (16/1)	12.9	0.4	89.7	103.1	29.5
10[e]	DMA/EG (16/1)	44.0	1.9	51.7	103.1	22.7

[a]Yields were evaluated by GC-FID. [b]3 equiv. of base used. [c]reaction done at 85 °C. [d]In the presence of extra **L1** (5 mol%), ICH_2BF_3K (1.5 equiv.), 24 h. [e]Cs_2CO_3 used instead of K_2CO_3. **1a***: 0.117 mmol.

Table SI-4. Various catalysts tested in the cyclopropanation of cyclooctene in DMA:EG (16:1).

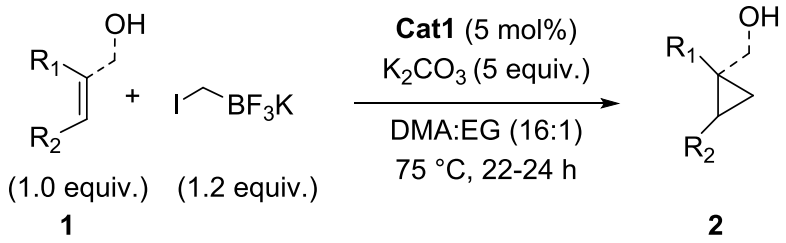


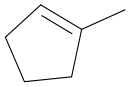
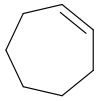
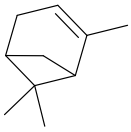
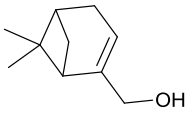
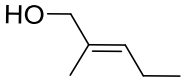
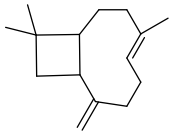
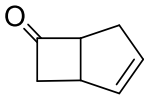
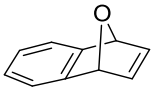
no.	Catalysts	**2a** [%][a]	**3a** [%][a]	Rem. **1a** [%][a]	Total [%][a]	Ratio **2a**/**3a**
1	**Cat1**	93.6	2.3	7.1	103.0	40.5
2	[COD]$PdCl_2$/**L1** (1:1)	71.6	1.7	25.63	98.9	42.9
3	[COD]$PdCl_2$/**L1** (2:1)	85.5	2.1	11.3	98.8	40.9
4	**Cat3**	53.7	1.2	45.8	100.8	43.7
5	**Cat4**	70.1	2.0	24.5	96.6	34.9
6	**Cat5**	34.7	0.8	63.0	98.5	43.7
7	**Cat6**	2.3	0	98.3	100.6	-
8	**Cat7**	96.7	2.3	4.8	103.8	42.3
9	**Cat9**	90.8	2.3	7.8	100.9	39.4

[a]Yields were evaluated by GC-FID. **1a***: 0.117 mmol.

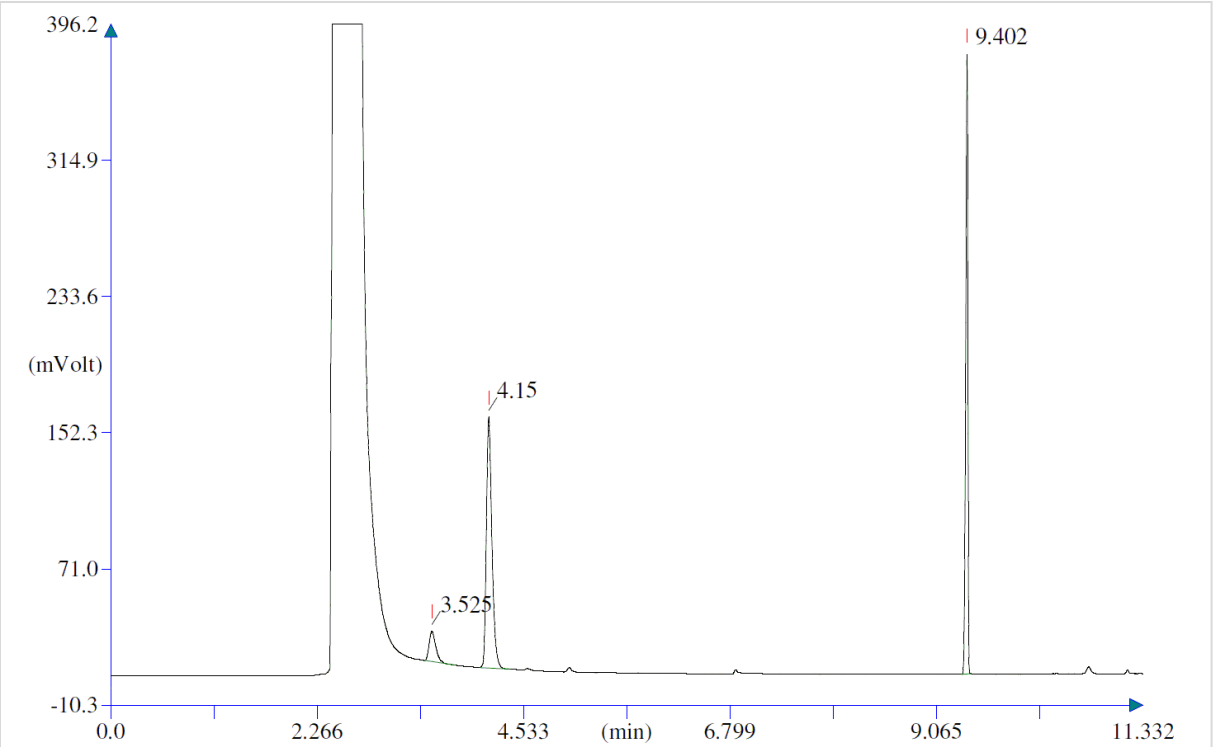
A-4. Cyclopropanation reaction of other olefins

Table SI-5. Cyclopropanation reaction of other olefins.



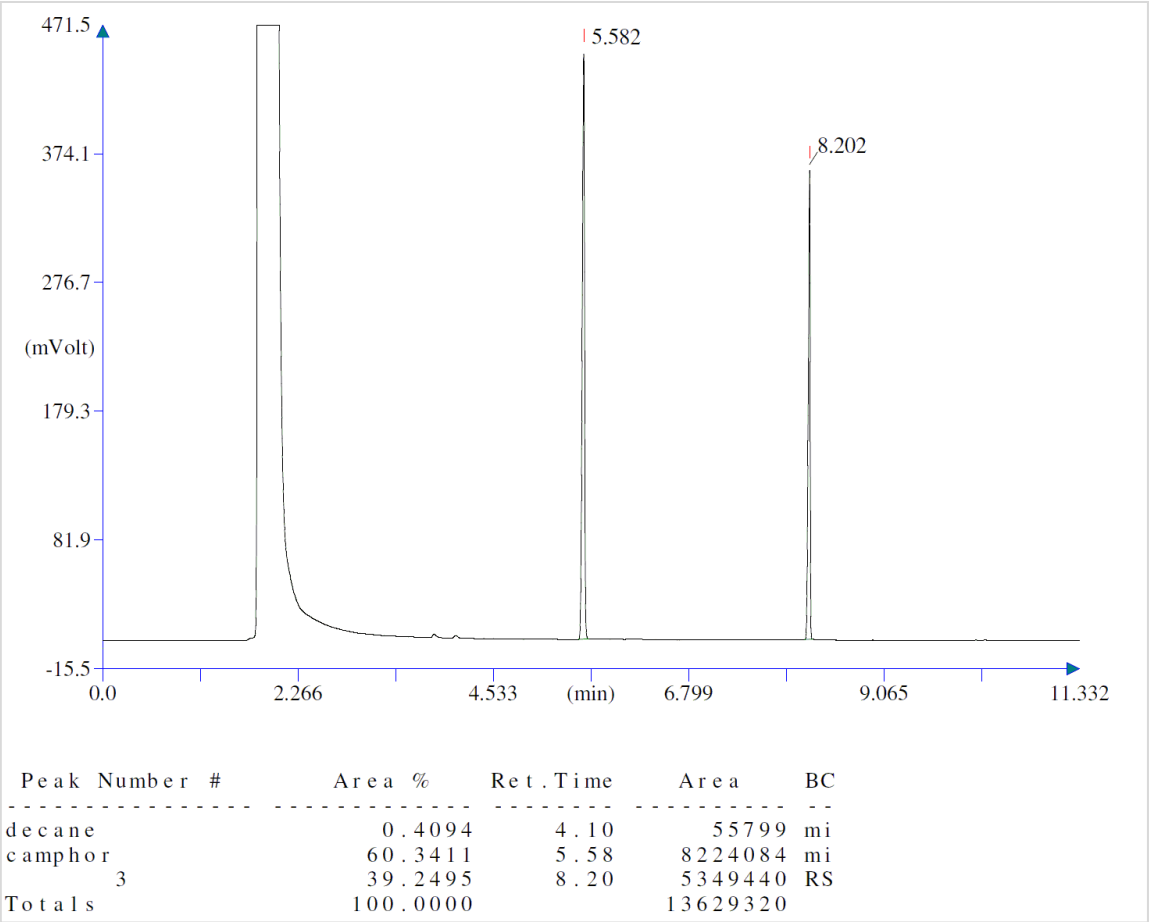
no.	Olefins	Cyclopropane [%][a]	Rem. **1** [%][a]	Total [%][a]
1[b]		88.1	12.7	100.7
2		98.0	0.8	98.7
3		59.1[c] 74.2[d]	39.4[c] 27.6[d]	98.3[c] 101.8[d]
4[b]		38.5	53.5	92.0
5		74.8	17.5	92.3
6		35.3	42.0	77.2
7[e]		72.1	14.4	86.5
8[e,f]		81.2	0	81.2
9[e,f]		28.5	0	28.5

[a]Yields were evaluated by GC-FID. [b]Work up solutions maintained at 0 °C. [c]After 48 h. [d]1.0 equiv. of ICH_2BF_3K added 18 h later and reaction stopped 24 h later. [e]1.5 equiv. of ICH_2BF_3K used. [f]In the presence of **L1** (5 mol%).



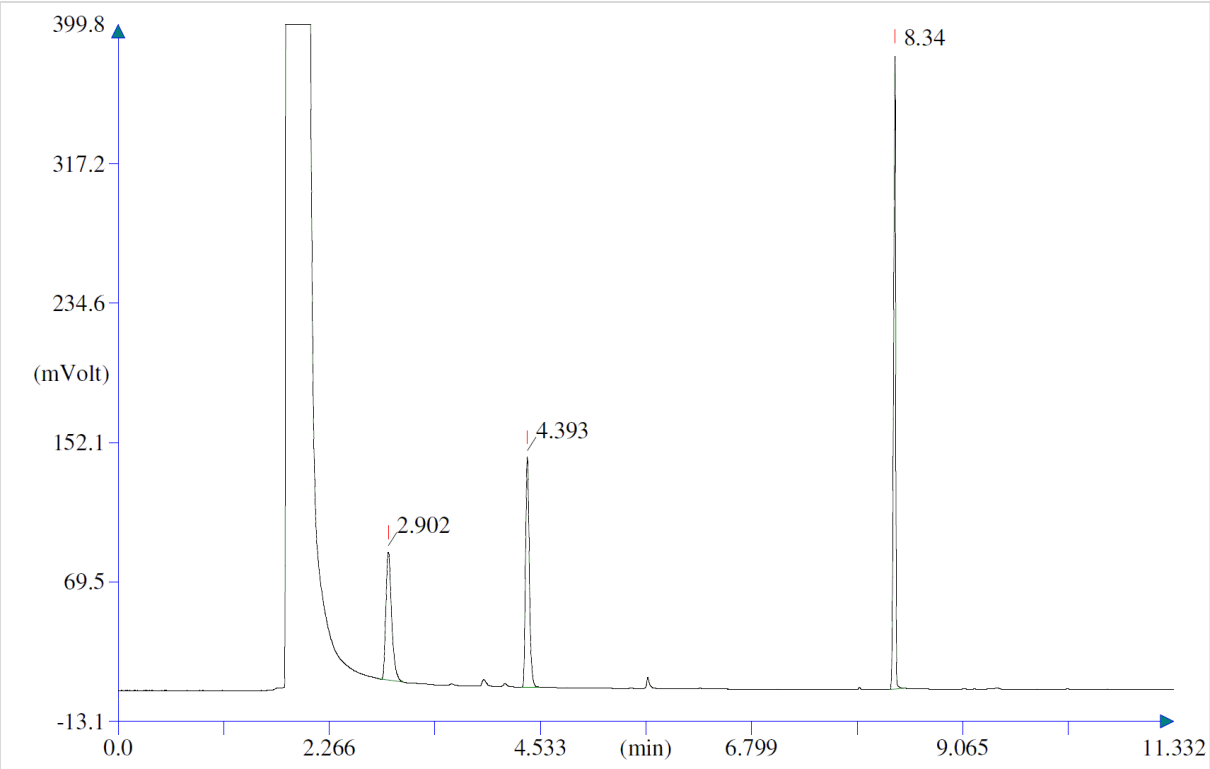
Peak Number #	Area %	Ret.Time	Area	BC
1	6.8337	3.53	900963	RS
decane	47.9433	4.15	6320937	RS
3	45.2231	9.40	5962302	RS
Totals	100.0000		13184200	

Figure SI-2. Representative GC chromatogram of the methylenation of 1-methylcyclopentene. Retention times: 1-methylcyclopentene (tR= 3.53 min), 1-methylbicyclo[3.1.0]hexane (tR= 4.15 min), undecane (tR= 9.4 min; internal standard).



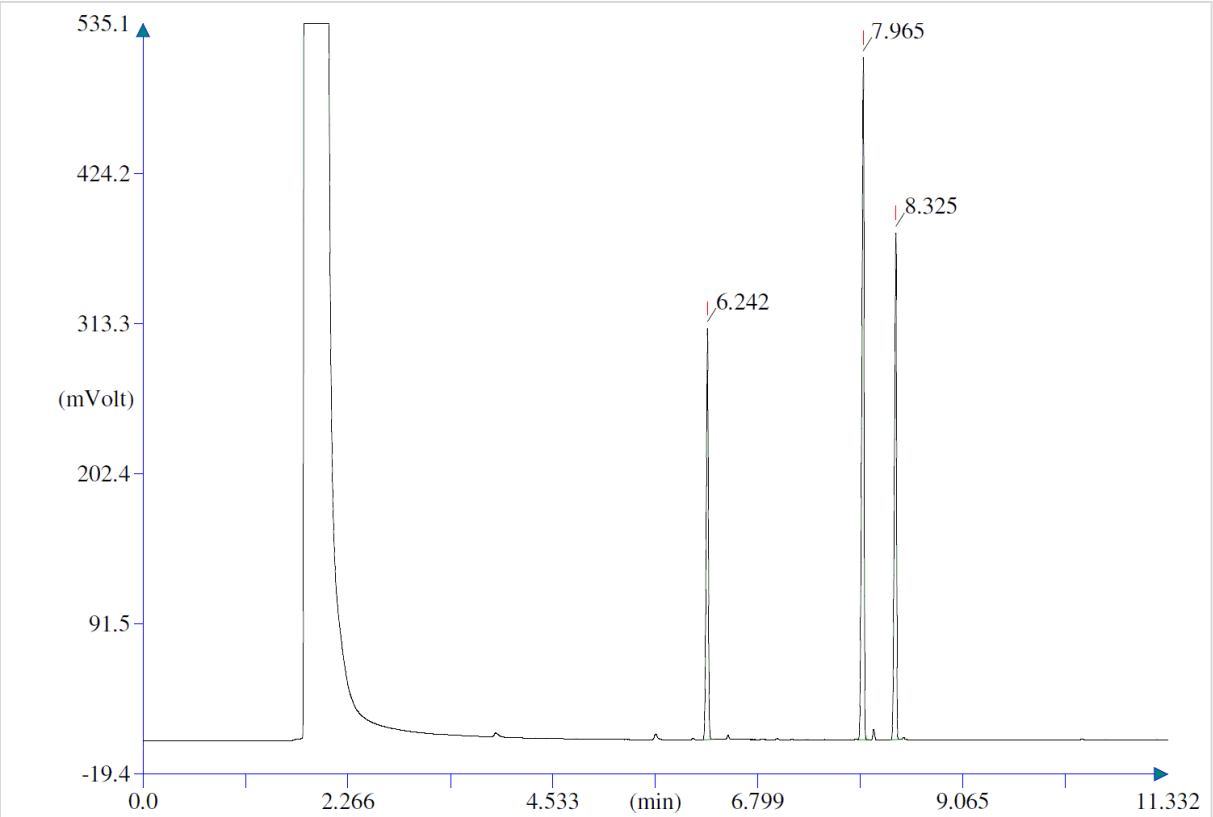
Peak Number #	Area %	Ret.Time	Area	BC
decane	0.4094	4.10	55799	mi
camphor	60.3411	5.58	8224084	mi
3	39.2495	8.20	5349440	RS
Totals	100.0000		13629320	

Figure SI-3. Representative GC chromatogram of the methylenation of cycloheptene. Retention times cycloheptene (tR= 4.10 min), bicyclo[5.1.0]octane (tR= 5.58 min), undecane (tR= 8.20 min; internal standard).



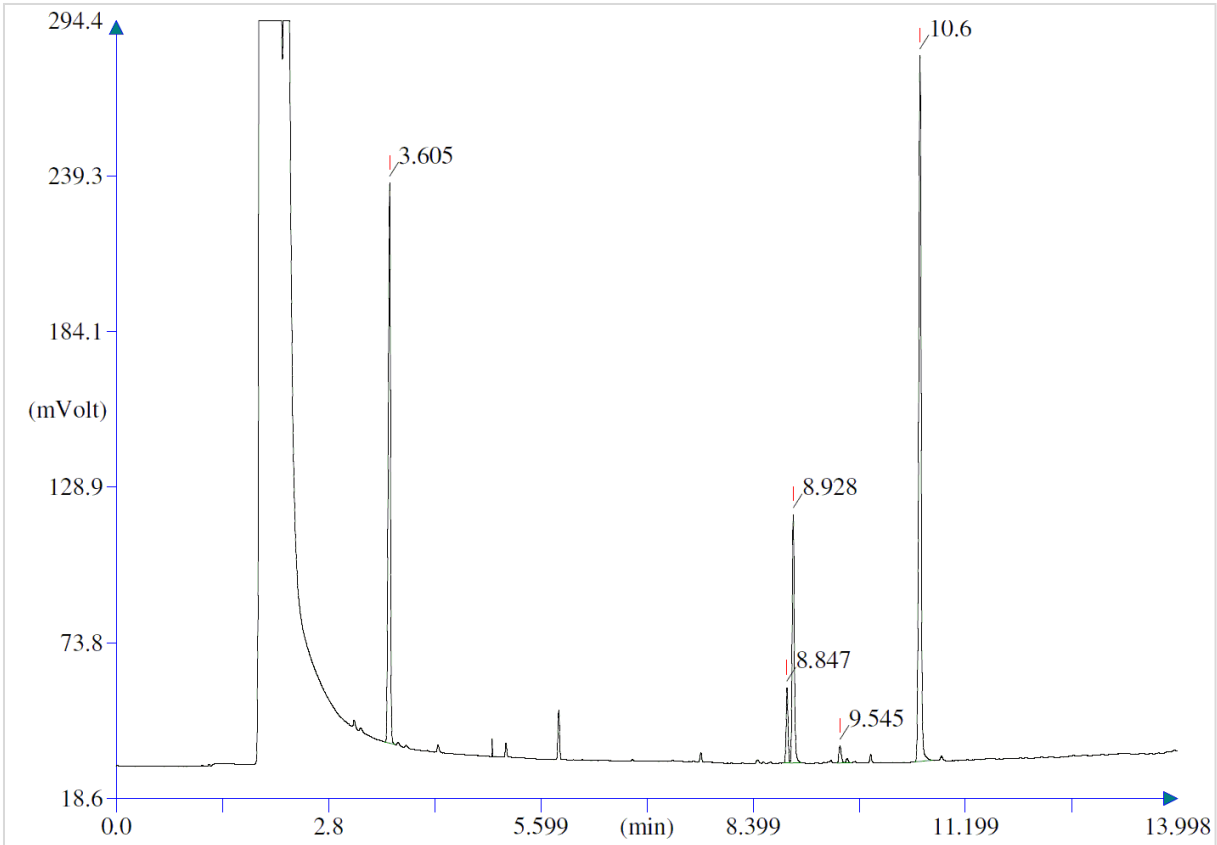
Peak Number #	Area %	Ret.Time	Area	BC
1	25.3655	2.90	3265816	mi
2	29.3331	4.39	3776643	mi
3	45.3014	8.34	5832575	mi
Totals	100.0000		12875030	

Figure SI-4. Representative GC chromatogram of the methylenation of cyclohexene. Retention times cyclohexene (tR= 2.90 min), norcarane (tR= 4.39 min), undecane (tR= 8.34 min; internal standard).



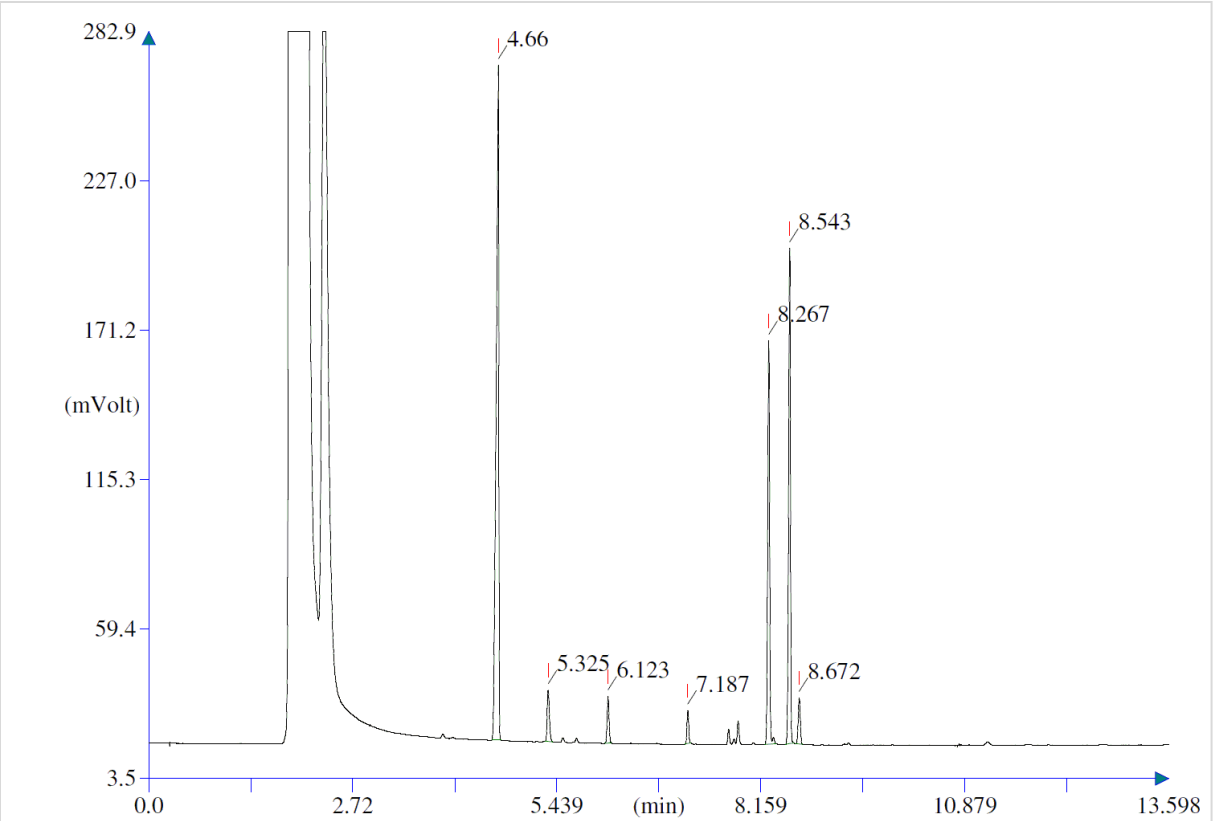
Peak Number #	Area %	Ret.Time	Area	BC
1	25.6336	6.24	4941757	RS
2	43.6472	7.97	8414494	FU
3	30.7191	8.33	5922158	RS
Totals	100.0000		19278410	

Figure SI-5. Representative GC chromatogram of the methylenation of α-pinene. Retention times α-pinene (tR= 6.24 min), 2,7,7-trimethyltricyclo[4.1.1.$0^{2,4}$]octane (tR= 7.97 min), undecane (tR= 8.33 min; internal standard).



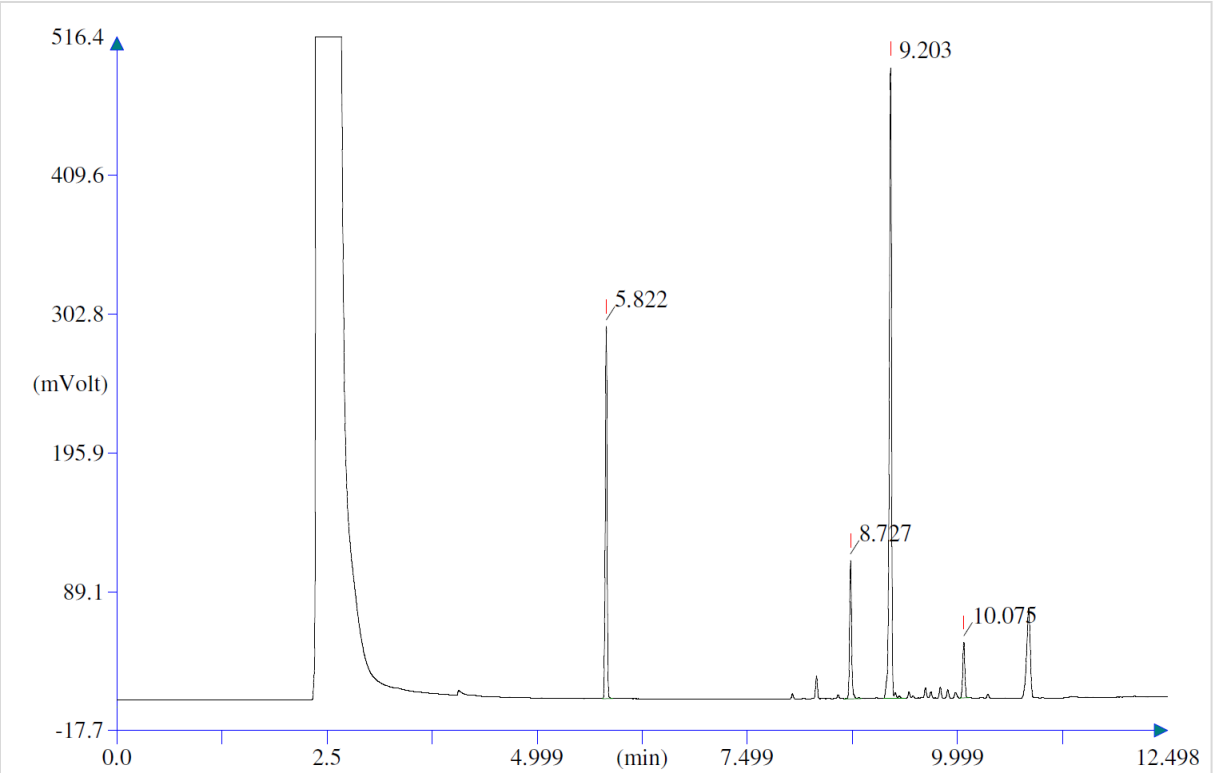
Peak Number #	Area %	Ret.Time	Area	BC
1	33.1728	3.61	3967521	FU
camphor	2.0760	5.84	248287	RS
3	3.8421	8.85	459518	FU
4	14.0244	8.93	1677344	FU
5	1.3141	9.55	157174	FU
6	45.5706	10.60	5450308	RS
Totals	100.0000		11960150	

Figure SI-6. Representative GC chromatogram of the methylenation of (-)-myrtenol. Retention times undecane (tR= 3.61 min; internal standard), (-)-myrtenol (tR= 8.93 min), (7,7-dimethyltricyclo[4.1.1.$o^{2,4}$]octan-2-yl)methanol (tR= 10.60 min).



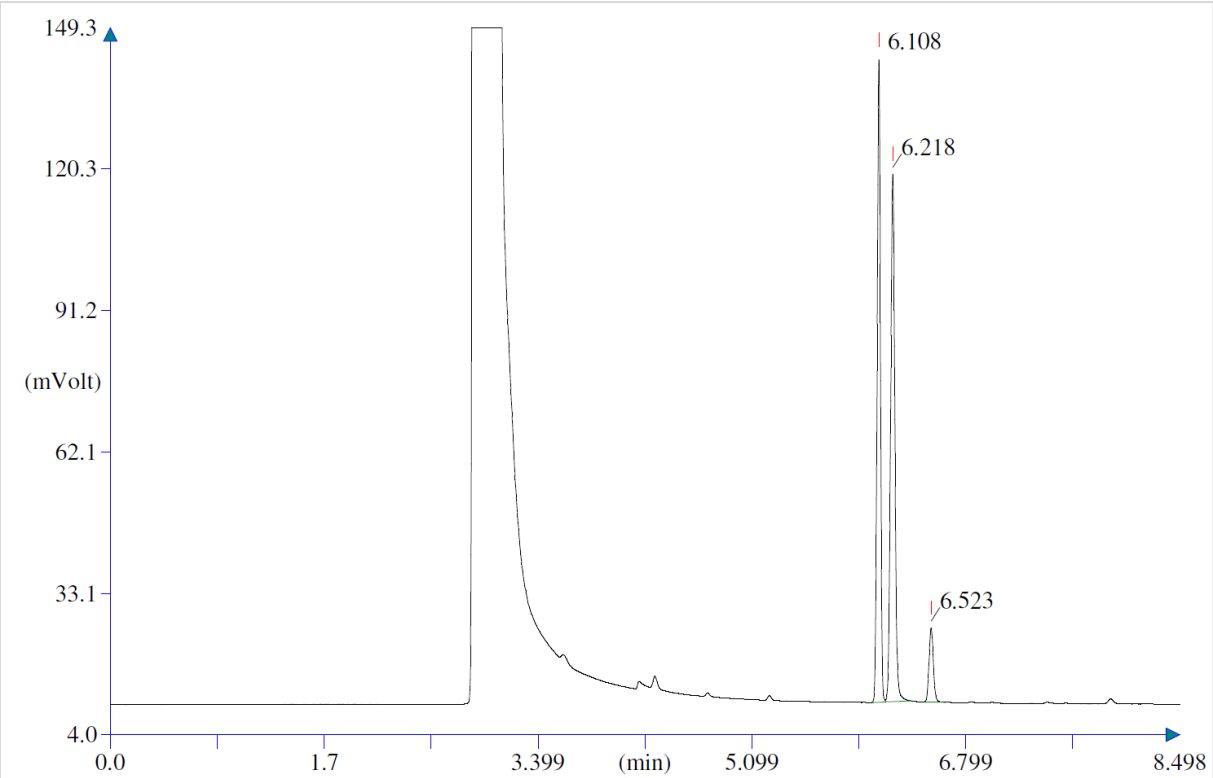
Peak Number #	Area %	Ret.Time	Area	BC
1	46.2118	4.66	6235818	RS
2	2.9216	5.33	394236	RS
3	2.3245	6.12	313663	RS
4	1.4721	7.19	198645	RS
5	0.9310	7.73	125623	mi
6	1.0747	7.86	145014	mi
7	19.0676	8.27	2572983	mi
8	0.3050	8.33	41152	mi
9	23.3441	8.55	3150055	RS
10	2.3477	8.67	316799	RS
Totals	100.0000		13493990	

Figure SI-7. Representative GC chromatogram of the methylenation of 2-methylpent-2-en-1-ol. Retention times undecane (tR= 4.66 min; internal standard), (2-ethyl-1-methylcyclopropyl)methanol (tR= 8.27 min), 2-methylpent-2-en-1-ol (tR= 8.55 min).



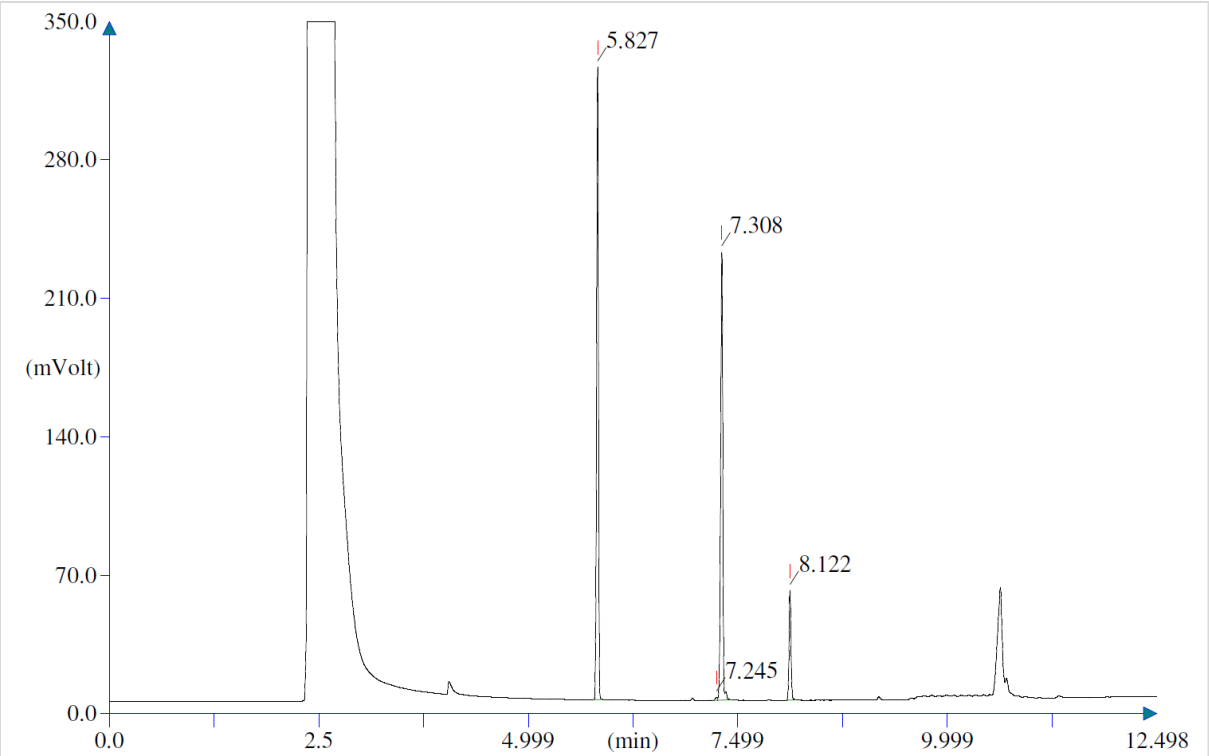
Peak Number #	Area %	Ret.Time	Area	BC
camphor	27.0869	5.82	4271274	mi
2	11.2448	8.73	1773164	mi
3	57.0782	9.20	9000537	mi
4	4.5901	10.08	723811	mi
Totals	100.0000		15768790	

Figure SI-8. Representative GC chromatogram of the methylenation of β-caryophyllene in DMA/EG (16/1). Retention times undecane (tR= 5.82 min, internal standard), β-caryophyllene (tR= 8.73 min), 4,12,12-trimethyl-9-methylenetricyclo[8.2.0.$o^{4,6}$]dodecane (tR= 9.20 min).



Peak Number #	Area %	Ret.Time	Area	BC
1	45.3429	6.11	2435541	mi
2	47.9409	6.22	2575086	mi
3	6.7162	6.52	360753	mi
Totals	100.0000		5371379	

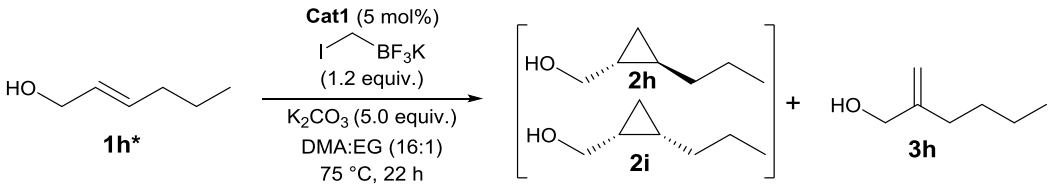
Figure SI-9. Representative GC chromatogram of the methylenation of bicyclo[3.2.0]hept-2-en-6-one in DMA/EG (16/1). Retention times undecane (tR= 6.11 min, internal standard), tricyclo[4.2.0.02,4]octan-7-one (anti) (tR= 6.22 min), tricyclo[4.2.0.02,4]octan-7-one (syn) (tR= 6.52 min).



Peak Number #	Area %	Ret.Time	Area	BC
camphor	49.2192	5.83	4790641	mi
2	0.2799	7.25	27243	mi
3	41.0762	7.31	3998067	mi
4	9.4247	8.12	917333	mi
Totals	100.0000		9733283	

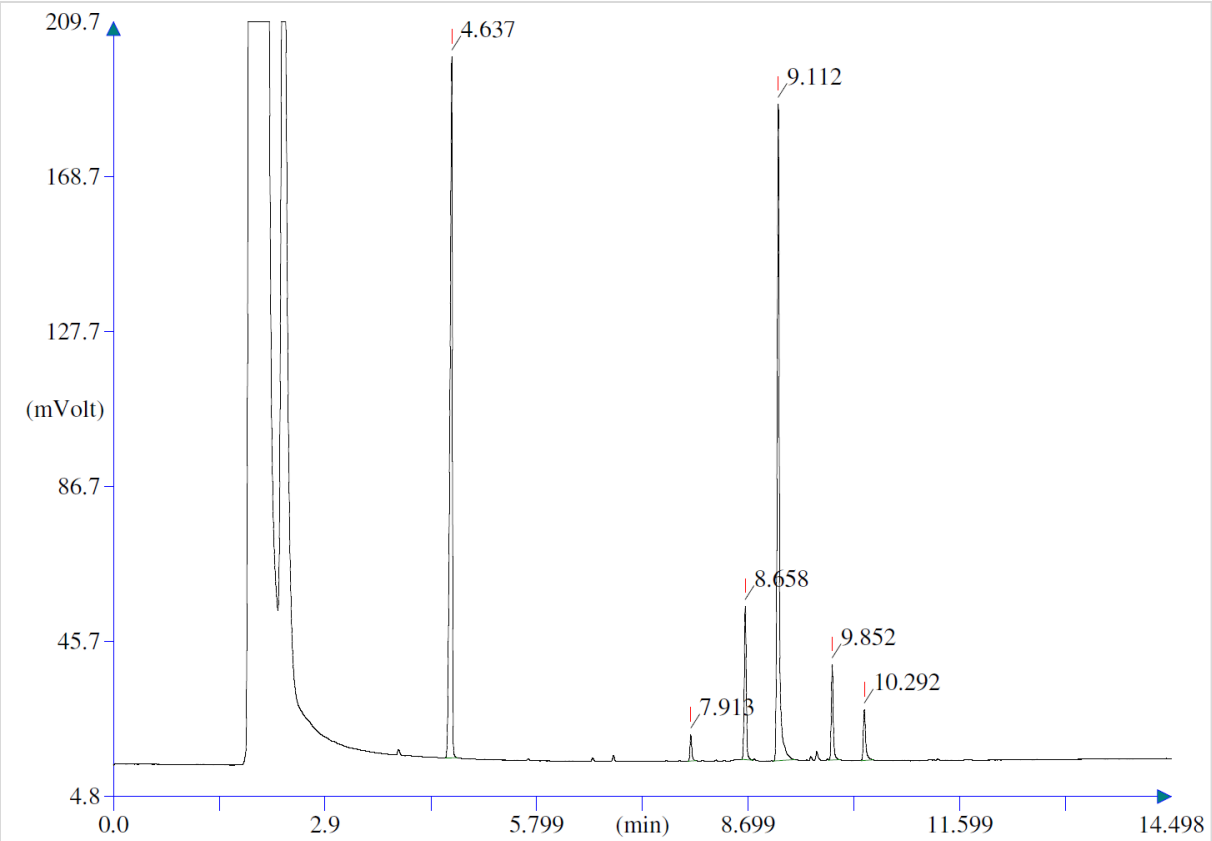
Figure SI-10. Representative GC chromatogram of the methylenation of oxabenzonorbornadiene in DMA/EG (16/1). Retention times undecane (tR= 5.83 min, internal standard), oxabenzonorbornadiene (tR= 7.31 min), cyclopropanated oxabenzonorbornadiene (tR= 8.12 min).

Table SI-6. Cyclopropanation reaction of (E)-hex-2-en-1-ol.



2h [%][a]	**2i** [%][a]	**3h** [%][a]	Rem. **1h** [%][a]	Total [%][a]	Ratio **2**/**3h**
65.7	0.9	10.1	15.1	91.7	6.6

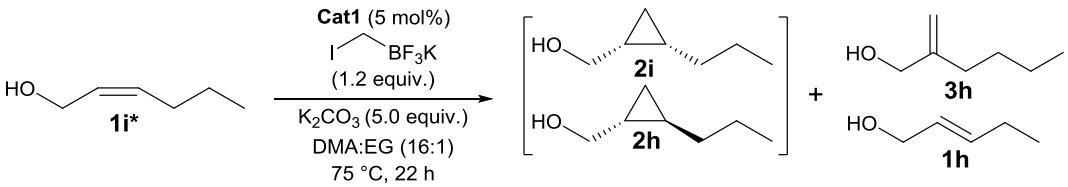
[a]Yields were evaluated by GC-FID. **1h***: 0.117 mmol.



Peak Number #	Area %	Ret.Time	Area	BC
1	44.8949	4.64	4363658	RS
2	1.2812	7.91	124531	RS
3	8.0247	8.66	779977	RS
4	37.9911	9.11	3692625	RS
5	4.7968	9.85	466232	FU
6	3.0114	10.29	292702	RS
Totals	100.0000		9719724	

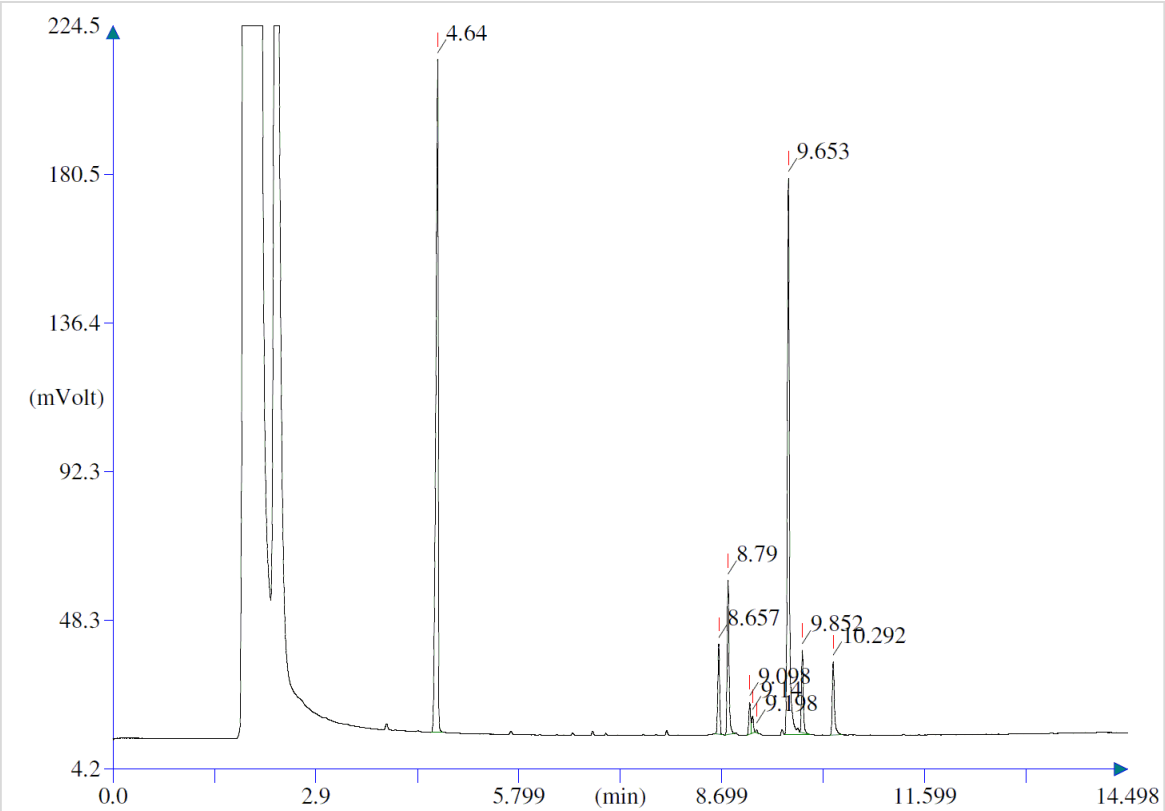
Figure SI-11. Representative GC chromatogram of the methylenation of *trans*-hexen-1-ol. Retention times undecane (tR= 4.64 min; internal standard), *trans*-hexen-1-ol (tR= 8.66 min), *trans*-2-propylcyclopropylmethanol (tR= 9.11 min), *cis*-2-propylcyclopropylmethanol (tR= 9.65 min), 2-methylenehexan-1-ol (tR= 9.85 min).

Table SI-7. Cyclopropanation reaction of (Z)-hex-2-en-1-ol.



2i [%][a]	**2h** [%][a]	**3h** [%][a]	Rem. **1i** [%][a]	**1h** [%][a]	Total [%][a]	Ratio **2**/**3h**
61.8	2.8	6.8	14.8	8.4	94.6	9.6

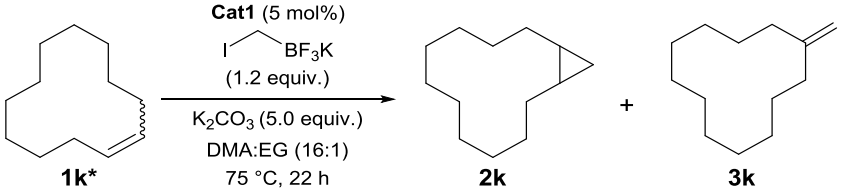
[a]Yields were evaluated by GC-FID. **1i***: 0.117 mmol.



Peak Number #	Area %	Ret.Time	Area	BC
1	44.2945	4.64	4745159	RS
2	4.4438	8.66	476051	RS
3	7.8153	8.79	837239	mi
4	1.6093	9.10	172400	mi
5	0.7036	9.14	75377	mi
6	0.1097	9.20	11755	RS
7	32.3047	9.65	3460720	mi
8	4.3594	9.85	467017	mi
9	4.3597	10.29	467044	mi
Totals	100.0000		10712760	

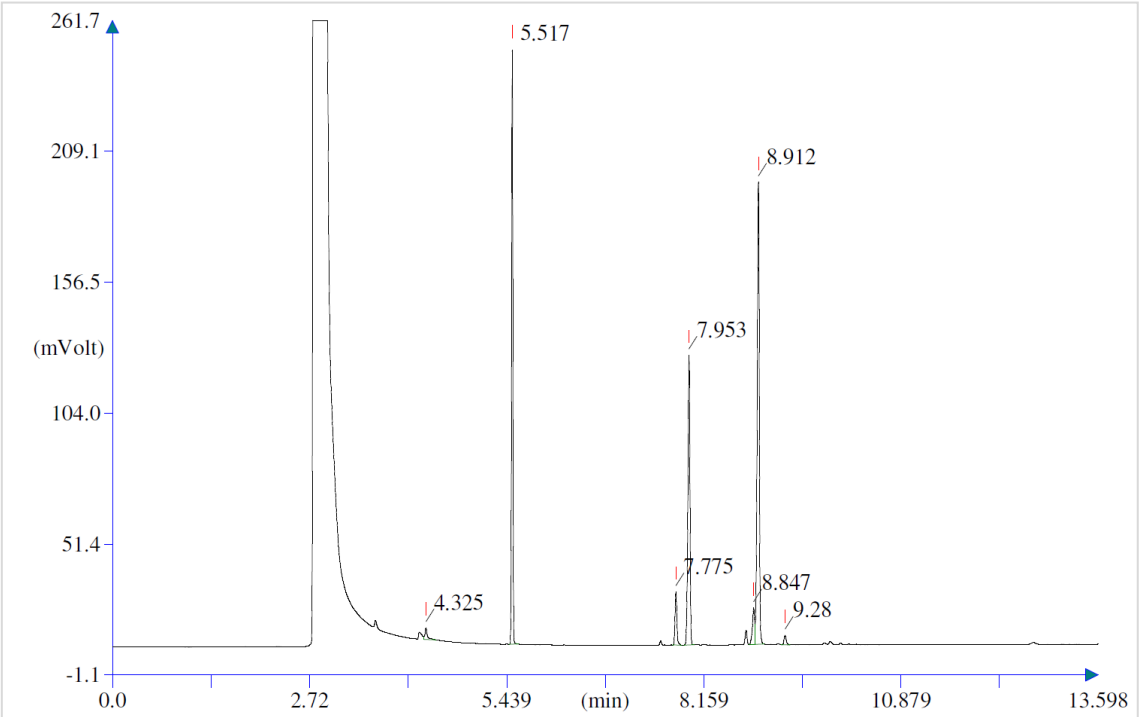
Figure SI-12. Representative GC chromatogram of the methylenation of *cis*-hexen-1-ol. Retention times undecane (tR= 4.64 min; internal standard), *trans*-hexen-1-ol (tR= 8.66 min), *cis*-hexen-1-ol (tR= 8.79 min), *trans*-2-propylcyclopropylmethanol (tR= 9.10 min), *cis*-2-propylcyclopropylmethanol (tR= 9.65 min), 2-methylenehexan-1-ol (tR= 9.85 min).

Table SI-8. Cyclopropanation reaction of cyclododecene (*cis* + *trans*).



2k [%][a]	**3k** [%][a]	Rem. **1k** [%][a]	Total [%][a]	Ratio **2k**/**3k**
57.0	4.5	79.6	98.0	12.7

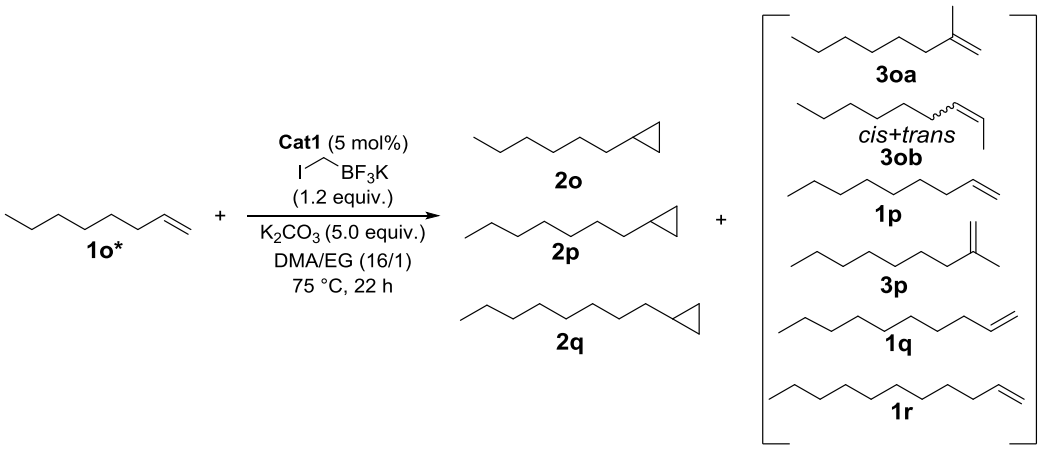
[a]Yields were evaluated by GC-FID. **1k***: 0.117 mmol.



Peak Number #	Area %	Ret.Time	Area	BC
1	1.1083	4.33	108067	FU
camphor	28.9565	5.52	2823369	RS
3	3.8752	7.78	377843	RS
4	23.2834	7.95	2270221	mi
5	3.3793	8.85	329493	mi
6	38.5612	8.91	3759872	mi
7	0.8362	9.28	81530	mi
Totals	100.0000		9750394	

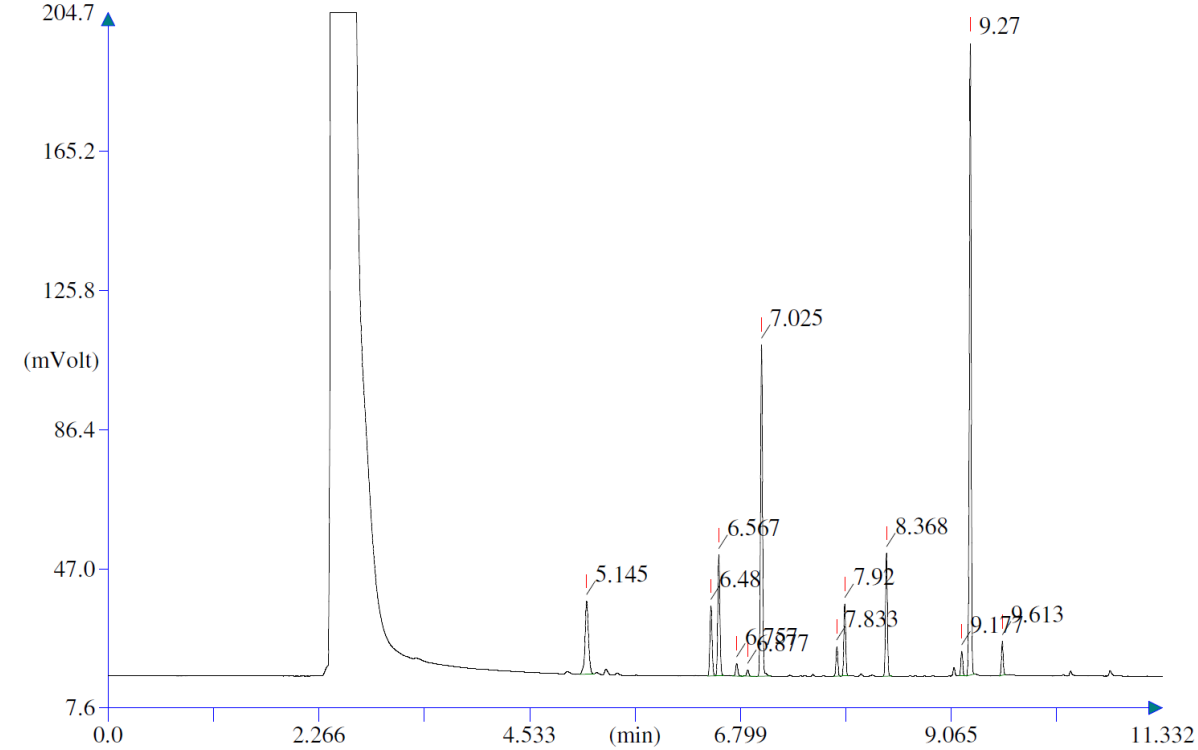
Figure SI-13. Representative GC chromatogram of the methylenation of cyclododecene (*cis* + *trans*) in DMA/EG (16/1). Retention times undecane (tR= 5.52 min, internal standard), cyclododecene (tR= 7.78 min (*trans*) & 7.95 (*cis*)), methylenecyclododecane (tR= 8.85 min), bicyclo[10.1.0]tridecane (tR= 8.91 min (*trans*) & 9.28 min (*cis*)).

Table SI-9. Cyclopropanation reaction of 1-octene.



20[a]	2p[a]	2q[a]	10[a]	30a[a]	30b[a]	1p[a]	3p[a]	1q[a]	1r[a]	Total[a]	Ratio[2/(30a+30b+3p+1p+1q+1r)]
29	9	2	12	7	2	10	2	5	2	80	1.4

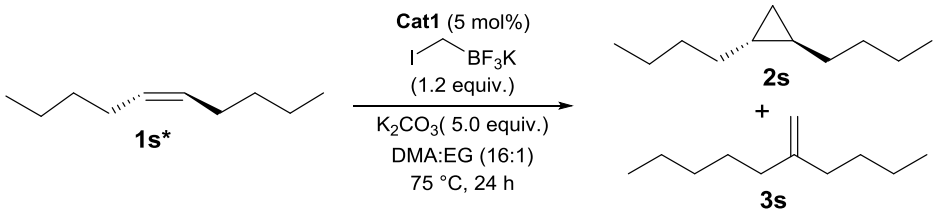
[a]Yields in percentage were evaluated by GC-FID. **10***: 0.117 mmol.



Peak Number #	Area %	Ret.Time	Area	BC
1	8.0422	5.15	521364	RS
2	4.9252	6.48	319294	RS
3	8.1526	6.57	528519	RS
2h3p	0.8845	6.76	57340	mi
5	0.4314	6.88	27968	mi
6	21.5951	7.03	1399973	mi
7	1.8023	7.83	116840	RS
8	4.3076	7.92	279256	mi
9	7.3848	8.37	478744	mi
10	1.4934	9.18	96816	RS
11	38.9513	9.27	2525150	RS
12	2.0296	9.61	131574	RS
Totals	100.0000		6482838	

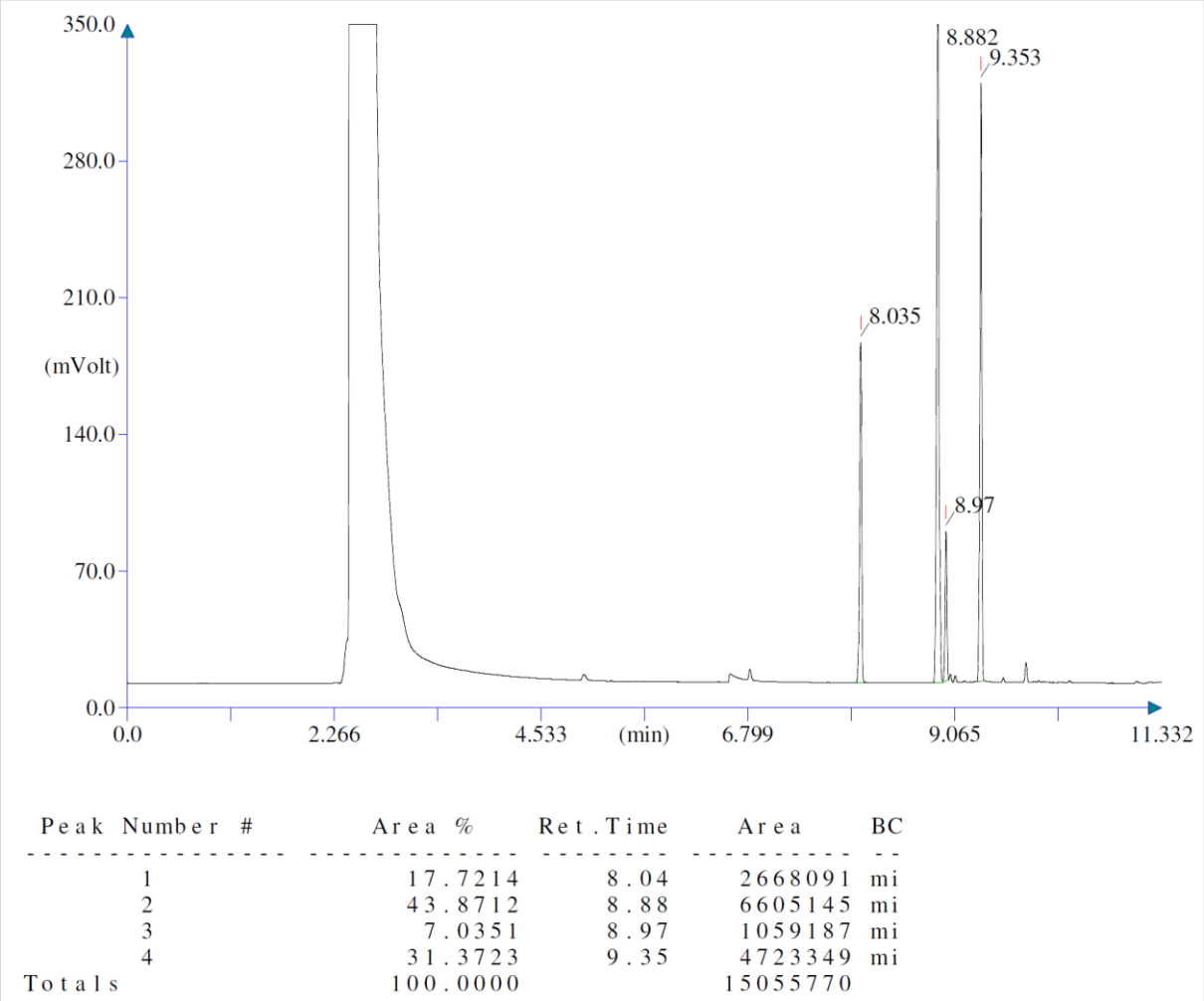
Figure SI-14. Representative GC chromatogram of the methylenation of 1-octene in DMA/EG (16/1). Retention times 1-octene (tR= 5.14 min, internal standard), 2-methylnon-1-ene (tR= 6.48 min), 1-nonene (tR= 6.57 min), 2-nonene (tR= 6.76 & 6.88 min), n-hexylcyclopropane (tR= 7.03 min), 2-methylnon-1-ene (tR= 7.83 min), 1-decene (tR= 7.92 min), n-heptylcyclopropane (tR= 8.37 min), 1-undecene (tR= 9.18 min), undecane (tR= 9.27 min, internal standard), n-octylcyclopropane (tR= 9.61 min).

Table SI-10. Cyclopropanation reaction of (E)-dec-5-ene.



2s [%][a]	**3s** [%][a]	Rem. **1s** [%][a]	Total [%][a]	Ratio **2s**/**3s**
55.9	10.2	31.1	97.2	5.5
61.5[b]	11.2[b]	25.4[b]	98.1[b]	5.5[b]
56.5[c]	10.7[c]	30.8[c]	98.0[c]	5.3[c]

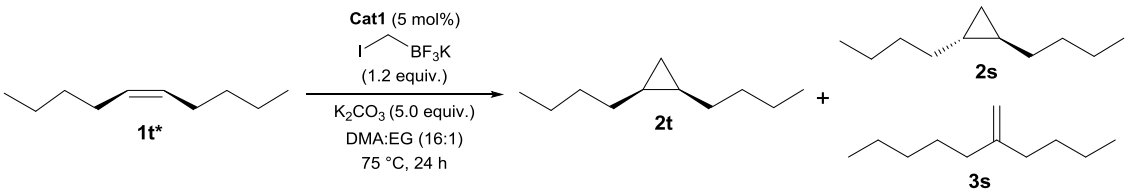
[a]Yields were evaluated by GC-FID. [b]In the presence of **L1** (5 mol%). [c]48 h in the presence of **L1** (10 mol%). **1s***: 0.117 mmol.



Peak Number #	Area %	Ret.Time	Area	BC
1	17.7214	8.04	2668091	mi
2	43.8712	8.88	6605145	mi
3	7.0351	8.97	1059187	mi
4	31.3723	9.35	4723349	mi
Totals	100.0000		15055770	

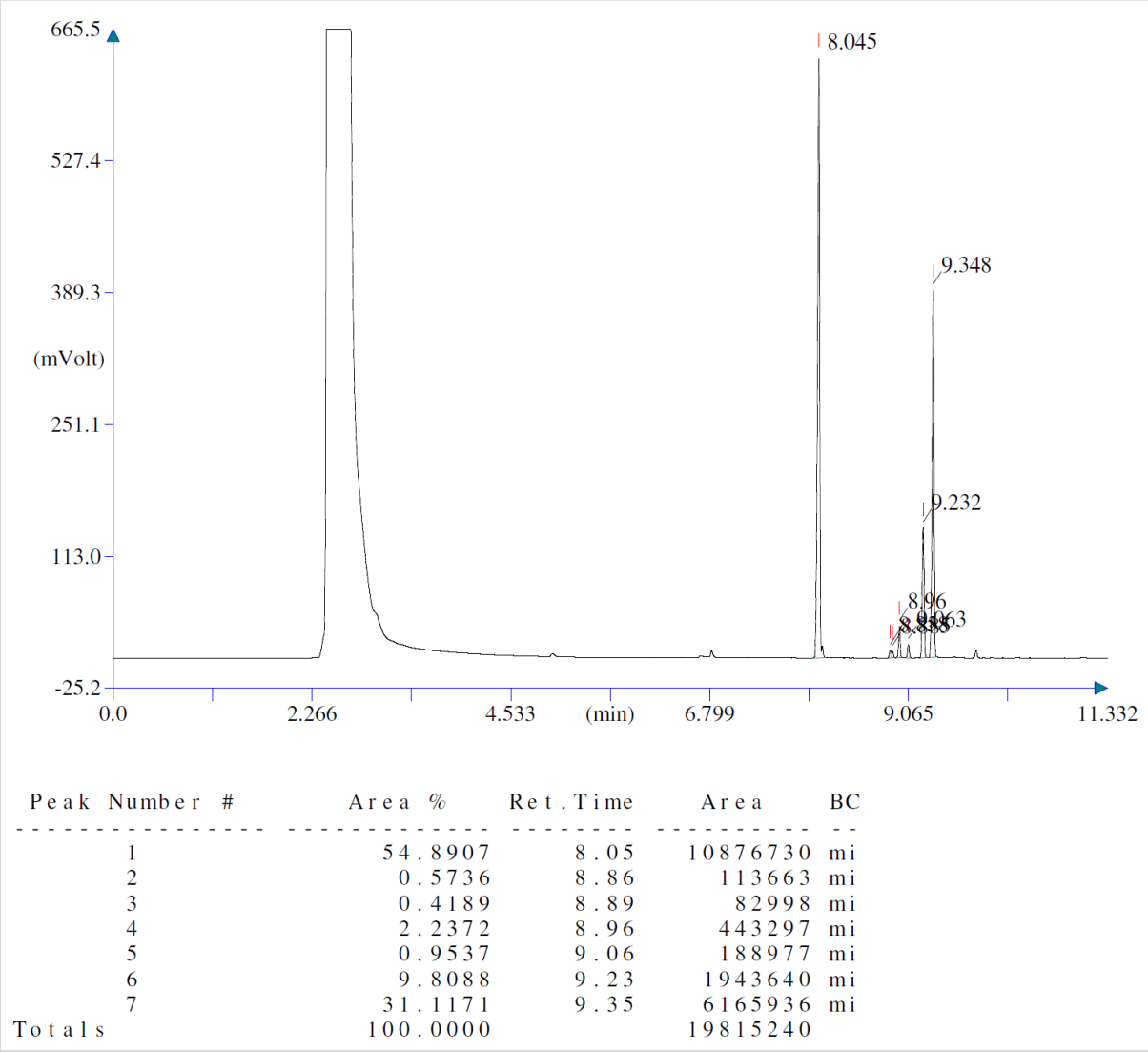
Figure SI-15. Representative GC chromatogram of the methylenation of *trans*-5-decene in DMA/EG (16/1). Retention times *trans*-5-decene (tR= 8.04 min), *trans*-1,2-dibutylcyclopropane (tR= 8.88 min), 5-methylenedecane (tR= 8.97 min), undecane (tR= 9.35 min; internal standard).

Table SI-11. Cyclopropanation reaction of (Z)-dec-5-ene.



2t [%][a]	**2s** [%][a]	**3s** [%][a]	Rem. **1s** [%][a]	Total [%][a]	Ratio **2**/**3s**
14.4	0.8	3.6	77.3	95.9	4.2
8.6[b]	0.7	2.4[b]	86.9[b]	98.4[b]	3.9[b]

[a]Yields were evaluated by GC-FID. [b]In the presence of **L1** (5 mol%). **1t***: 0.117 mmol.

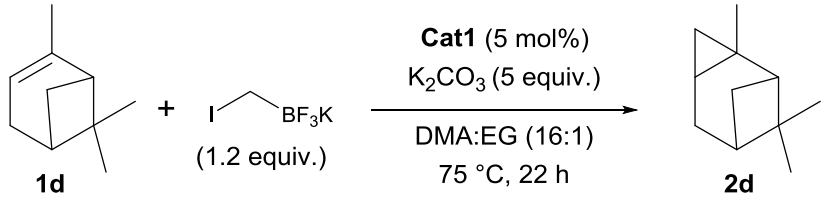


Peak Number #	Area %	Ret.Time	Area	BC
1	54.8907	8.05	10876730	mi
2	0.5736	8.86	113663	mi
3	0.4189	8.89	82998	mi
4	2.2372	8.96	443297	mi
5	0.9537	9.06	188977	mi
6	9.8088	9.23	1943640	mi
7	31.1171	9.35	6165936	mi
Totals	100.0000		19815240	

Figure SI-16. Representative GC chromatogram of the methylenation of *cis*-5-decene in DMA/EG (16/1). Retention times *cis*-5-decene (tR= 8.05 min), *trans*-1,2-dibutylcyclopropane (tR= 8.86 min), *cis*-1,2-dibutylcyclopropane (tR= 9.23 min), 5-methylenedecane (tR= 8.96 min), undecane (tR= 9.35 min; internal standard).

A-5. Identification of the diastereomer formed in the case of α-pinene

Comparison with the authentic synthesized sample



The methylenation procedure was followed using 0.117 mmol of α-pinene (**1d**). At the end of the reaction, the work up procedure described earlier was followed excepting the addition of the internal standard undecane. The organic phase was dried over $MgSO_4$ after extraction and solvent removed on rotatory evaporator. ^{1}H NMR spectrum was taken and compared with the authentic prepared sample **2d.**

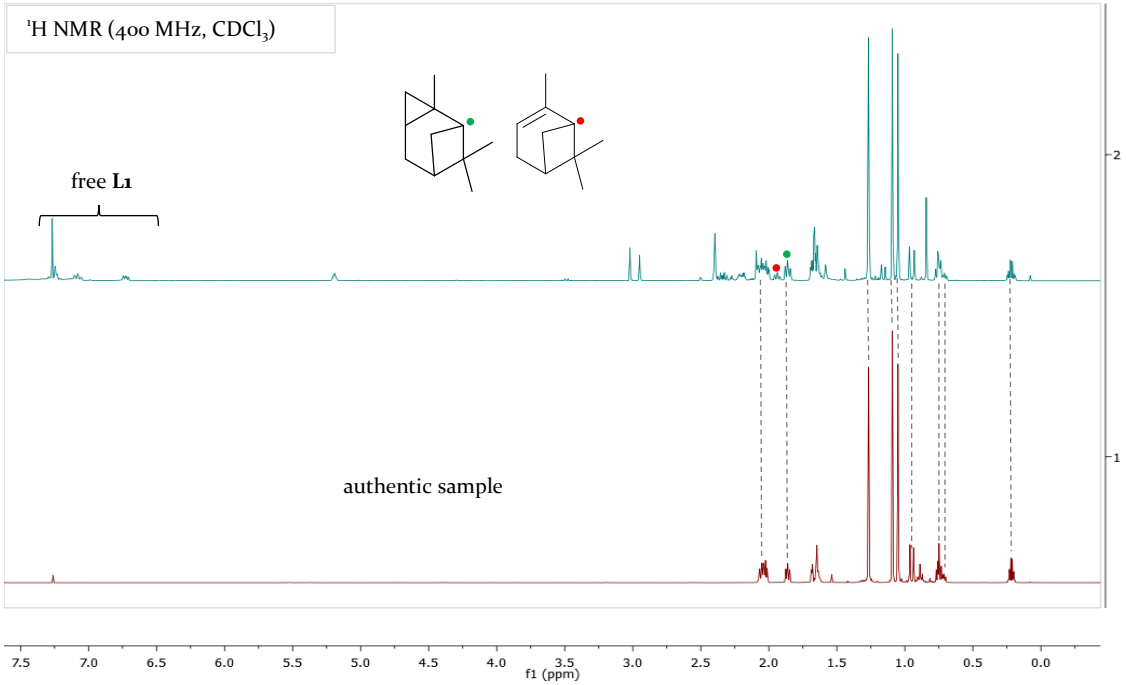


Figure SI-17. ^{1}H-NMR spectra of the authentic cyclopropane of α-pinene (**2d**) and the one prepared using the iodomethyltrifluoroborate as methylenating reagent also containing the remaining starting material and free phosphine.

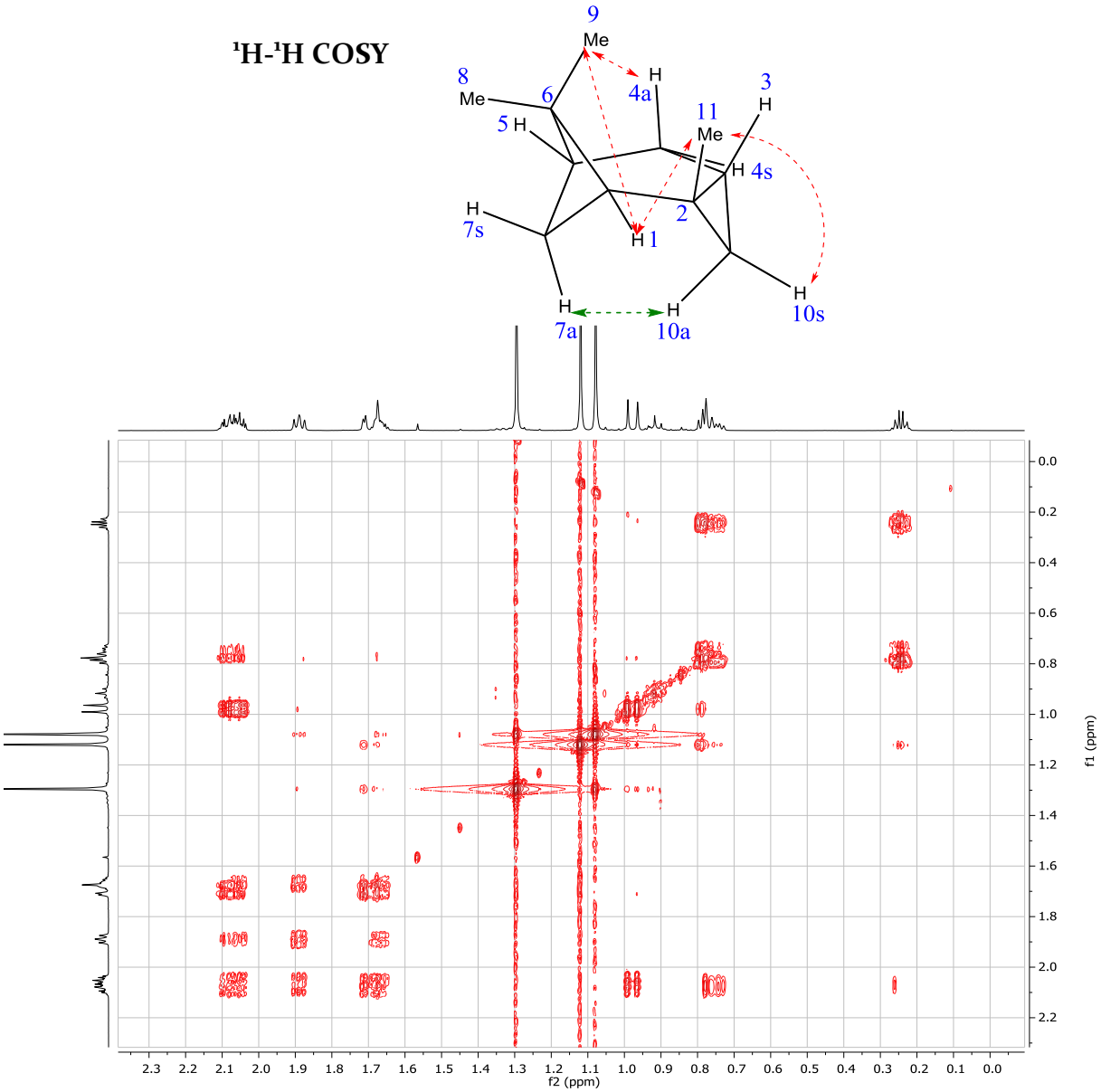


Figure SI-18. ^{1}H-^{1}H COSY of the authentic cyclopropane of α-pinene (**2d**).

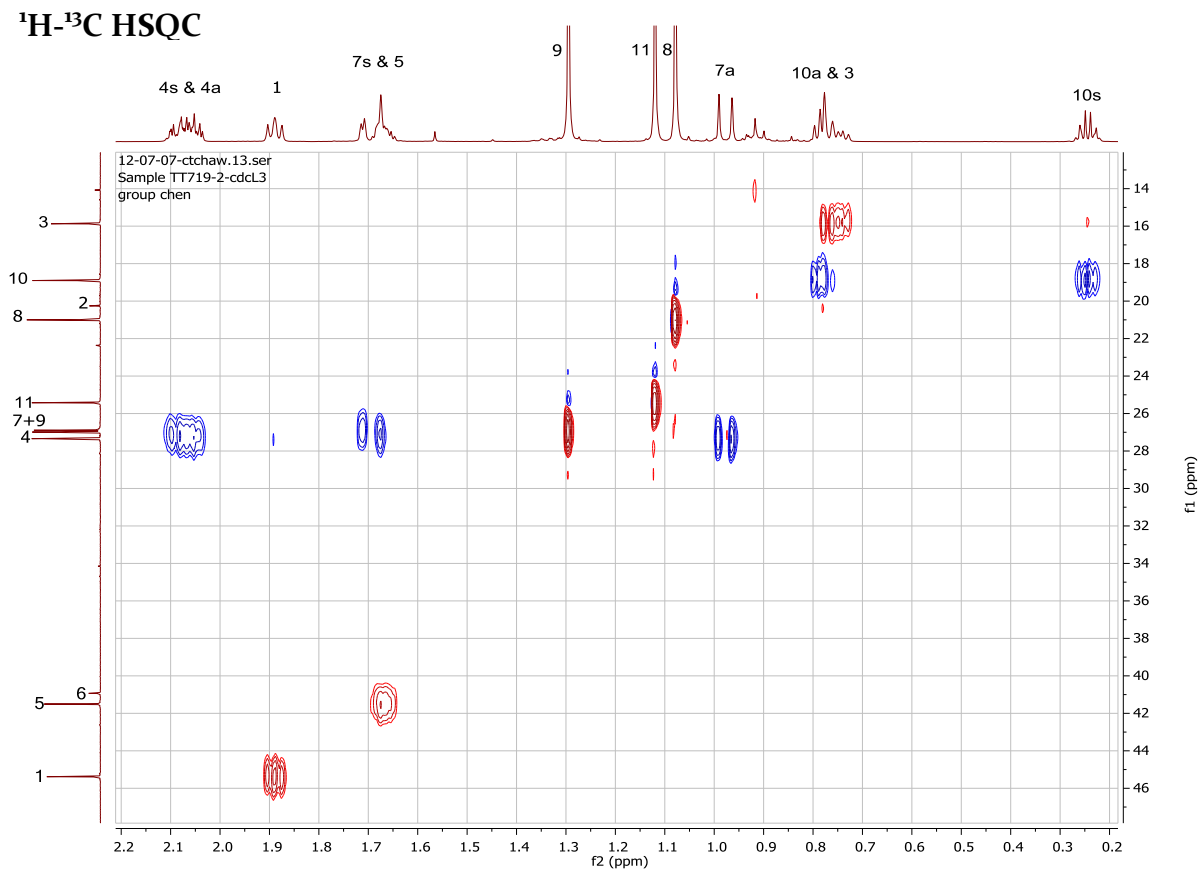


Figure SI-19. ^{1}H-^{13}C HSQC of the authentic cyclopropane of α-pinene (**2d**).

NOESY Experiment: Complete [1]H NMR assignments of α-pinene can be found in reference (21).

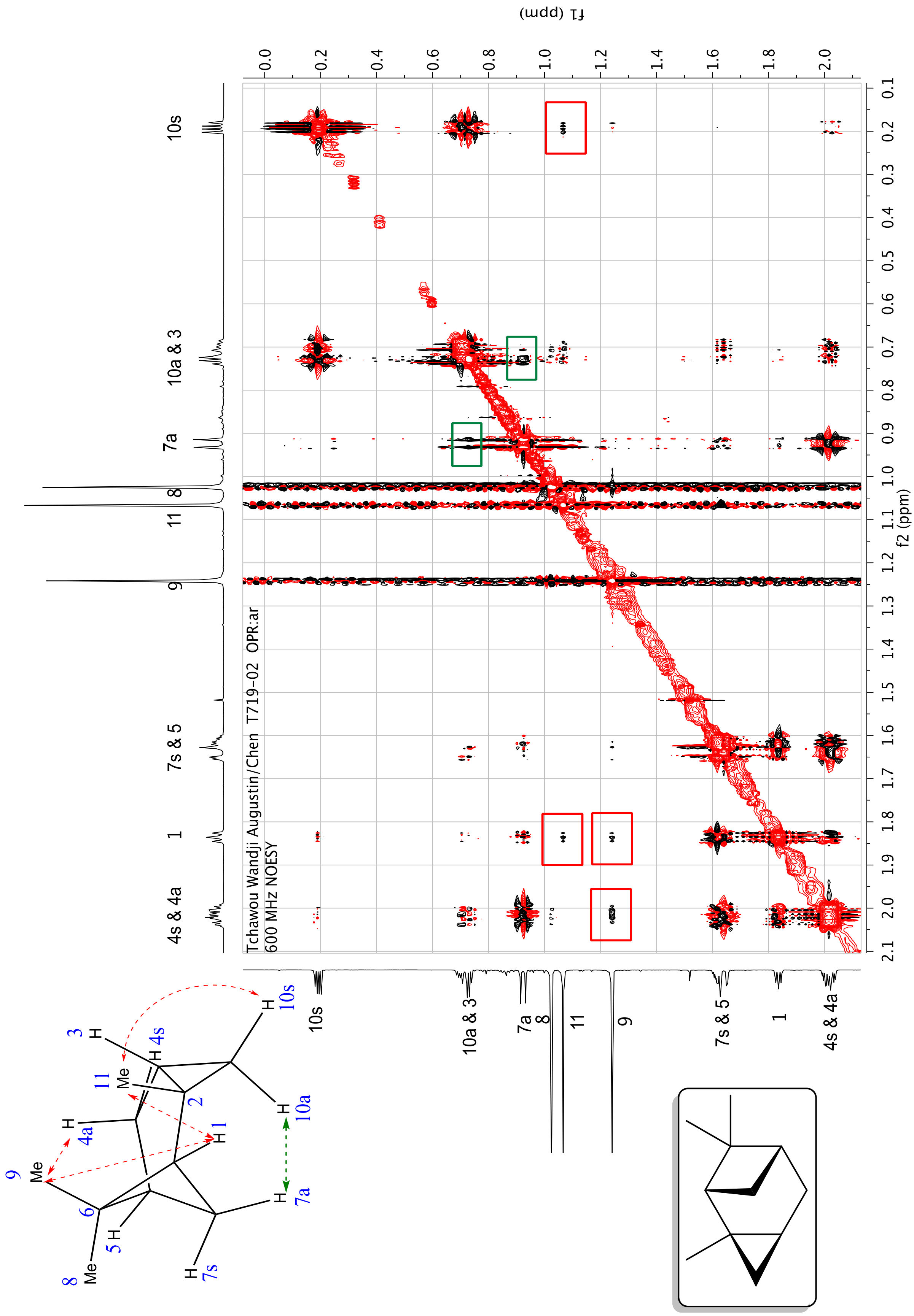
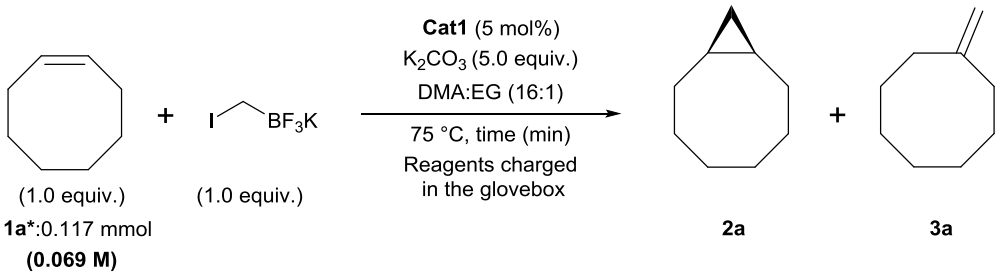


Figure SI-20. NOESY of the authentic cyclopropane of α-pinene (**2d**).

B. Kinetics Studies



Each time point in a kinetic run was acquired with the following procedure. An oven-dried Schlenk (2.5 or 5 ml) equipped with a Teflon Young valve and an oven-dried magnetic stir bar was charged in a N_2-filled glovebox with powdered K_2CO_3 (80.9 mg, 5.0 equiv.) and anhydrous EG (0.1 ml). The mixture was vigorously stirred for 10 min before, and during, the addition of a solution of anhydrous DMA (0.6 ml) containing either the Pd-catalyst $[(o\text{-tolyl})_3P]_2PdCl_2$ (4.6 mg, 5 mol%) or the mixture of $(o\text{-tolyl})_3P$ (1.78 mg, 5 mol%) and the Pd-catalyst $[COD]PdCl_2$ (1.67 mg, 5 mol%), ICH_2BF_3K (34.8 mg, 1.2 equiv.) and COE (15.2 µL, 0.117 mmol). The rest of the anhydrous DMA (2x0.5 ml) was utilized to rinse the vial containing the previous solution and then added to the reaction mixture. The tube was sealed, removed from the glovebox and heated to 75 °C for the indicated reaction time. Then the reaction mixture was rapidly cooled to 0 °C in an ice bath for 15 min and a work-up was conducted. The resulting solution was analyzed by GC-FID.

B-1. Influence of ICH_2BF_3K

Table SI-12. Initial concentrations of ICH_2BF_3K and excess to determine its influence on the reaction rate.

Run	ICH_2BF_3K [mM]	ICH_2BF_3K [mM]	Excess [mM]
1 (black)	0.117	0.069	0
2 (blue)	0.140	0.082	0.013

Table SI-13. Results from the kinetic runs based on Table SI-12.

	Run 1		Run 2	
Time [min]	COE rem. [mg]	COE conc. [10^{-2} mM]	COE rem. [mg]	COE conc. [10^{-2} mM]
0	12.89	6.88	12.89	6.88
30	11.80	6.30	12.20	6.51
60	10.09	5.39	10.33	5.51
90	8.52	4.55	8.69	4.64
120	7.65	4.09	7.38	3.94
150	6.03	3.22	6.01	3.21
180	5.34	2.85	4.84	2.58
210	4.11	2.19	4.03	2.15
240	3.47	1.85	3.21	1.72
270	3.11	1.66	2.22	1.18
300	3.03	1.62	1.88	1.00
360	2.93	1.56	1.44	0.77

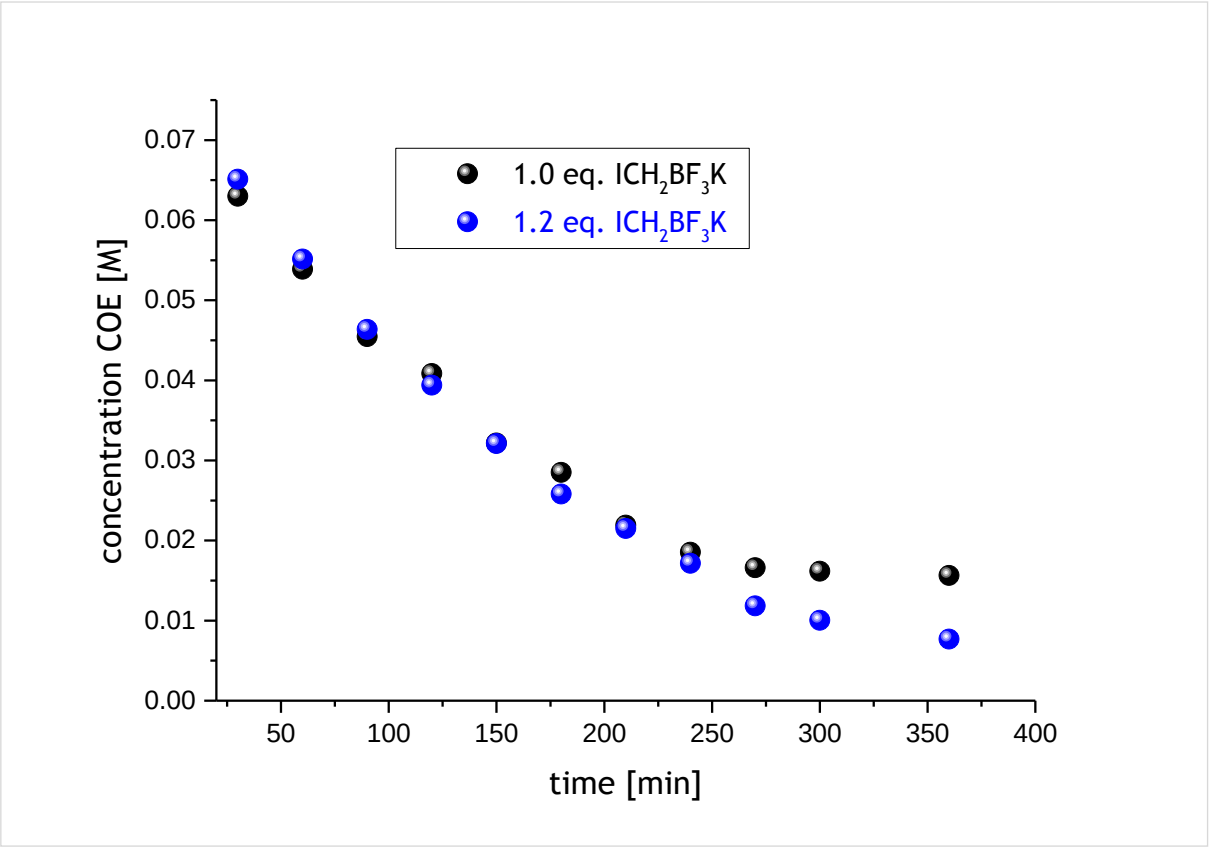


Figure SI-21. Influence of the methylenating agent on the rate of the reaction. The kinetic profiles overlay until the deactivation of the catalyst starts.

B-2. Influence of the olefin COE

Table SI-14. Initial concentrations of COE and excess to determine its influence on the reaction rate.

Run	COE [mM]	COE [mM]	Excess [mM]
1 (black)	0.117	0.069	0
2 (red)	0.140	0.082	0.013

Table SI-15. Results from the kinetic runs based on Table SI-14.

	Run 1		Run 2	
Time [min]	COE rem. [mg]	COE conc. [10^{-2} mM]	COE rem. [mg]	COE conc. [10^{-2} mM]
0	12.89	6.88	15.52	6.90
30	11.80	6.30	13.91	6.19
60	10.09	5.39	11.96	5.32
90	8.52	4.55	10.13	4.51
120	7.65	4.09	8.42	3.75
150	6.03	3.22	6.93	3.08
180	5.34	2.85	6.29	2.80
210	4.11	2.19	5.79	2.58
240	3.47	1.85	5.48	2.44
270	3.11	1.66	5.12	2.28
300	3.03	1.62	4.91	2.18
360	2.93	1.56	4.81	2.14

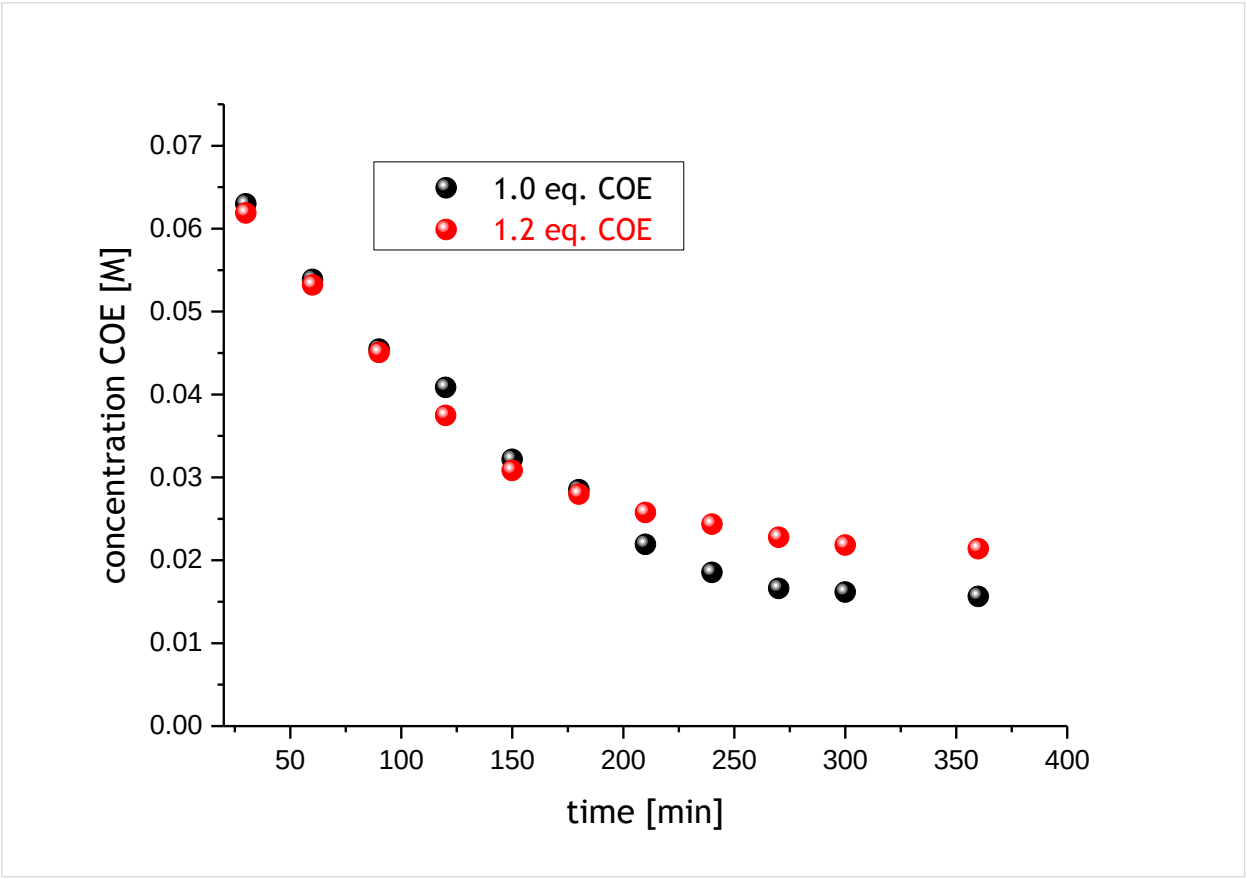


Figure SI-22. Influence of the olefin on the rate of the reaction. The kinetic profiles overlay until the deactivation of the catalyst starts.

B-3. Influence of catalyst loading

Table SI-16. Initial catalyst loadings to determine its influence on the reaction rate.

Run	Catalyst loading [mol%]
1 (black)	5
2 (red)	10

Table SI-17. Results from the kinetic runs based on Table SI-16.

	Run 1		Run 2	
Time [min]	COE rem. [mg]	COE conc. [10^{-2} mM]	COE rem. [mg]	COE conc. [10^{-2} mM]
0	12.89	6.88	12.89	6.88
30	11.80	6.30	11.59	6.18
60	10.09	5.39	9.24	4.93
90	8.52	4.55	7.18	3.84
120	7.65	4.09	5.35	2.86
150	6.03	3.21	4.64	2.47
180	5.34	2.85	4.12	2.20
210	4.11	2.19	3.61	1.93
240	3.47	1.85	3.10	1.65
270	3.11	1.66	2.80	1.50
300	3.03	1.62	2.52	1.35
360	2.93	1.56	2.34	1.25

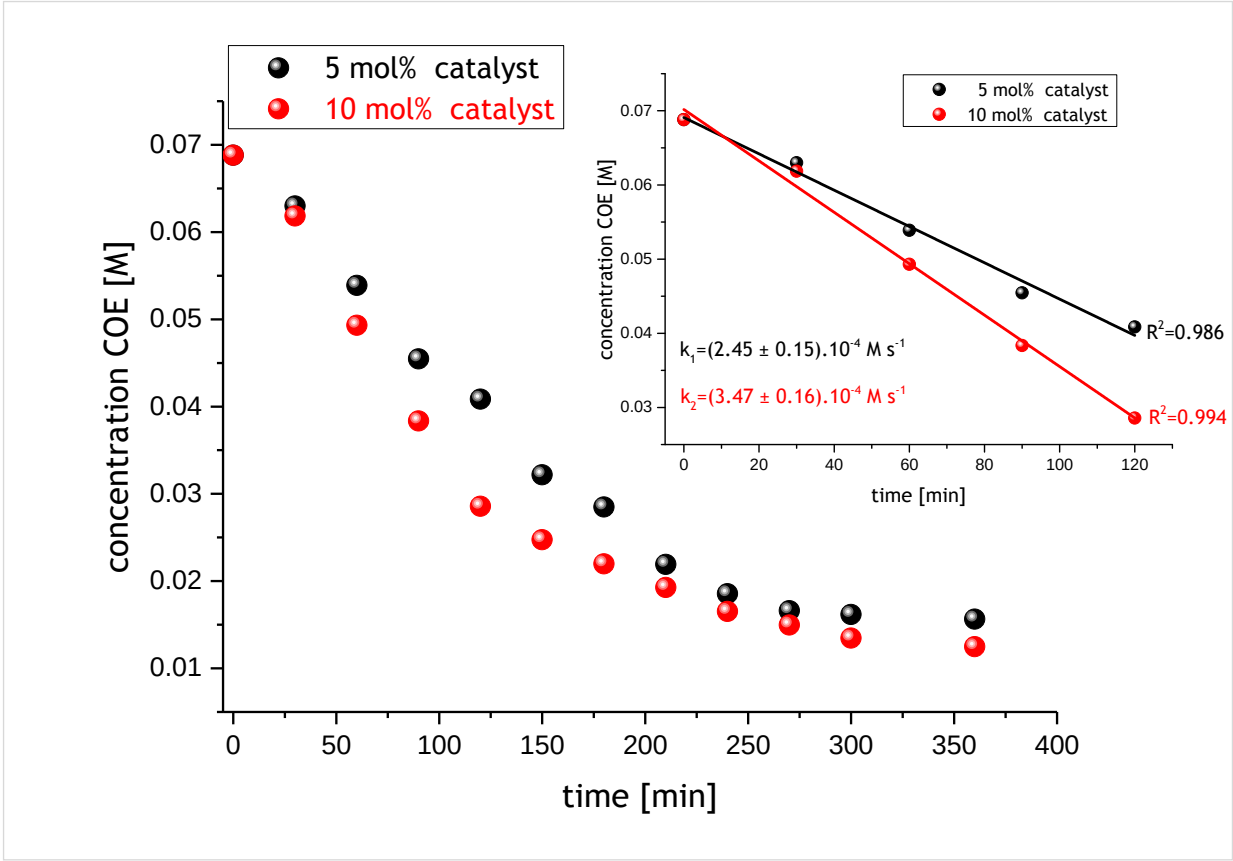


Figure SI-23. Influence of the catalyst loading on the rate of the reaction. Doubling the catalyst loading increases the initial rate of the reaction by 1.416 corresponding to a reaction order of **0.50** with respect to the Pd catalyst.

B-4. Influence of the co-solvent concentration

Table SI-18. Initial solvents ratios (and volumes) to determine the influence EG on the reaction rate.

Run	DMA:EG ratio (volumes [ml])
1 (black)	16:1 (1.6:0.1)
2 (red)	32:1 (1.6:0.05)

Table SI-19. Results from the kinetic runs based on Table SI-18.

	Run 1		Run 2	
Time [min]	COE rem. [mg]	COE conc. [10^{-2} mM]	COE rem. [mg]	COE conc. [10^{-2} mM]
0	12.89	6.88	15.52	7.09
30	11.80	6.30	11.42	6.28
60	10.09	5.39	9.11	5.01
90	8.52	4.55	7.21	3.96
120	7.65	4.09	6.21	3.42
150	6.03	3.21	4.93	2.71
180	5.34	2.85	4.05	2.22
210	4.11	2.19	10.03	2.01
240	3.47	1.85	10.75	1.92
270	3.11	1.66	11.02	1.82
300	3.03	1.62	11.30	1.56
360	2.93	1.56	11.08	1.47

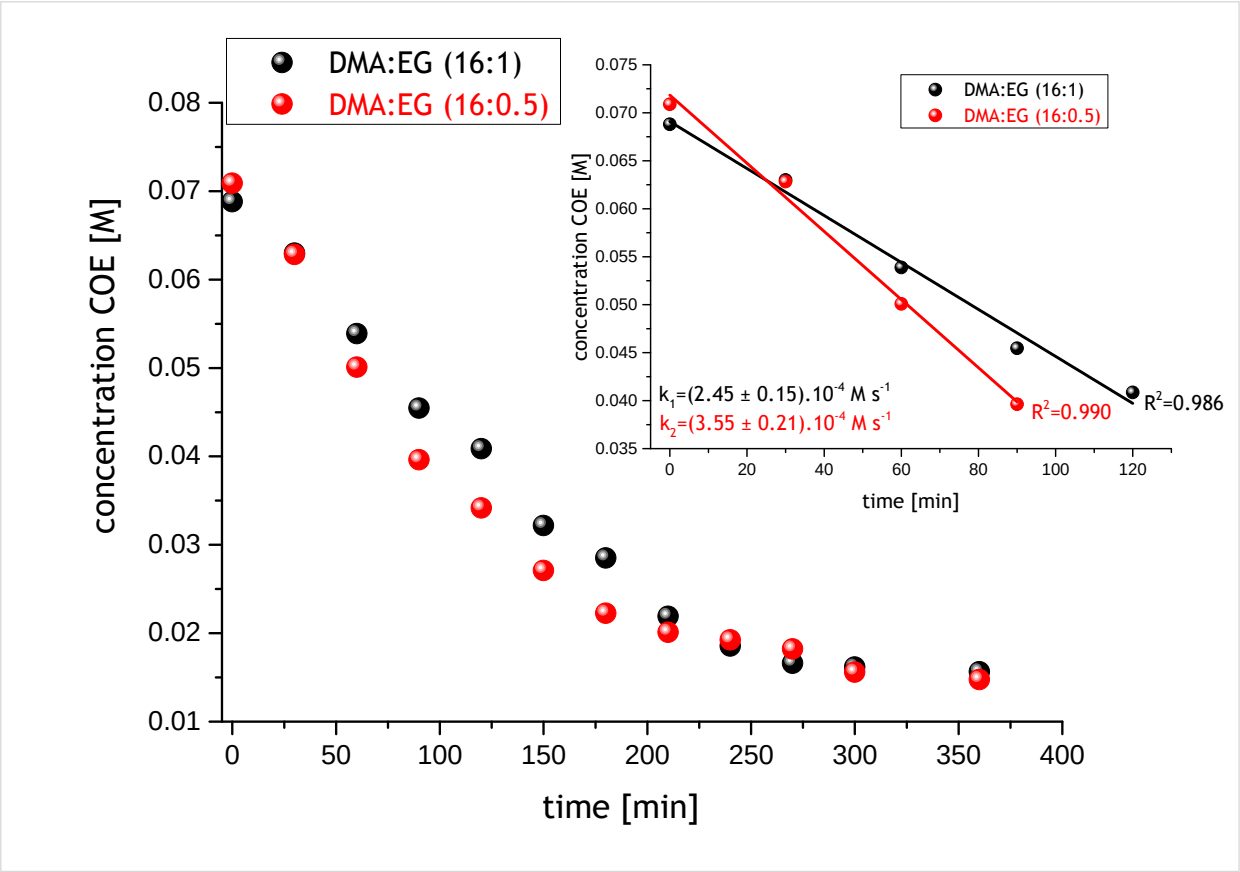


Figure SI-24. Influence of the co-solvent on the rate of the reaction. Two-fold reduction in the volume of the EG increases the initial rate of the reaction by 1.44 corresponding to a reaction order of **-0.53** with respect to the EG.

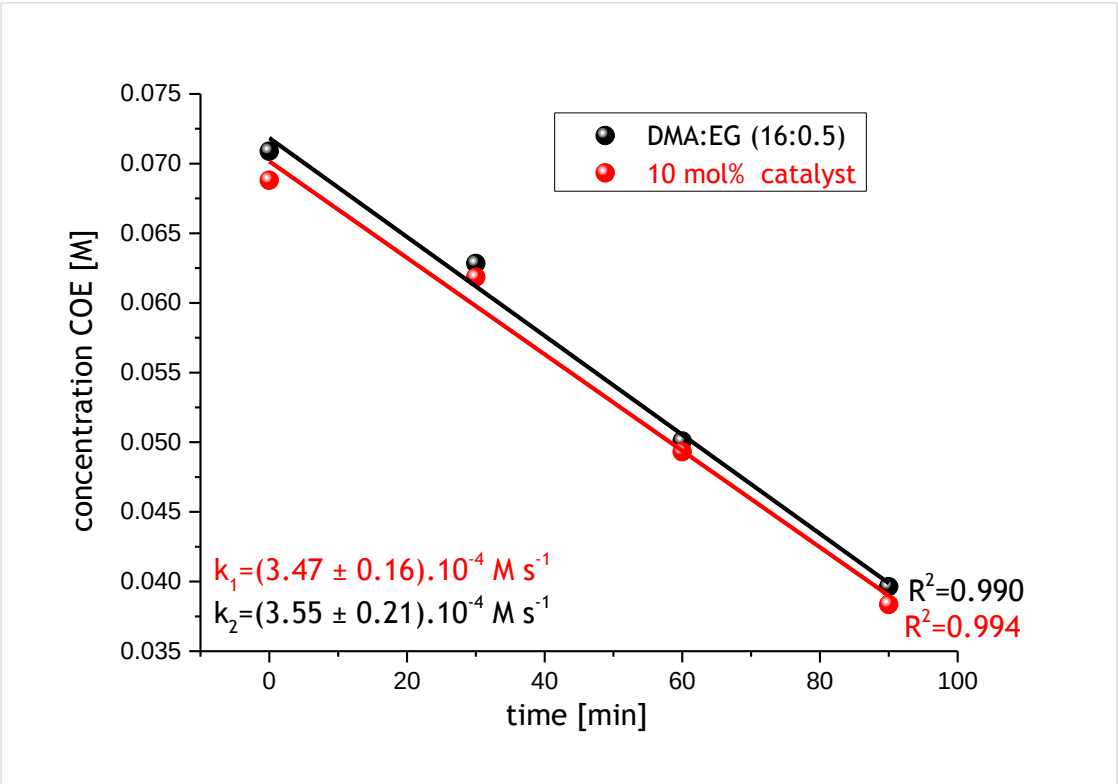


Figure SI-25. Influence of the olefin concentration on the initial reaction rate: Negligible difference.

B-5. Influence of the phosphine ligand

Table SI-20. Initial equivalences of phosphine ligand to determine its influence on the initial reaction rate.

Run	$(o\text{-tolyl})_3P$ [equiv.]	$[COD]PdCl_2$ [mol %]
1(black)	1	5
2(red)	2	5

Table SI-21. Results from the kinetic runs based on Table SI-20.

	Run 1		Run 2	
Time [min]	COE rem. [mg]	COE conc. [10^{-2} mM]	COE rem. [mg]	COE conc. [10^{-2} mM]
0	12.89	6.88	12.89	6.88
60	9.56	5.10	8.97	4.79
90	7.87	4.20	7.92	4.23
120	6.71	3.58	6.24	3.33

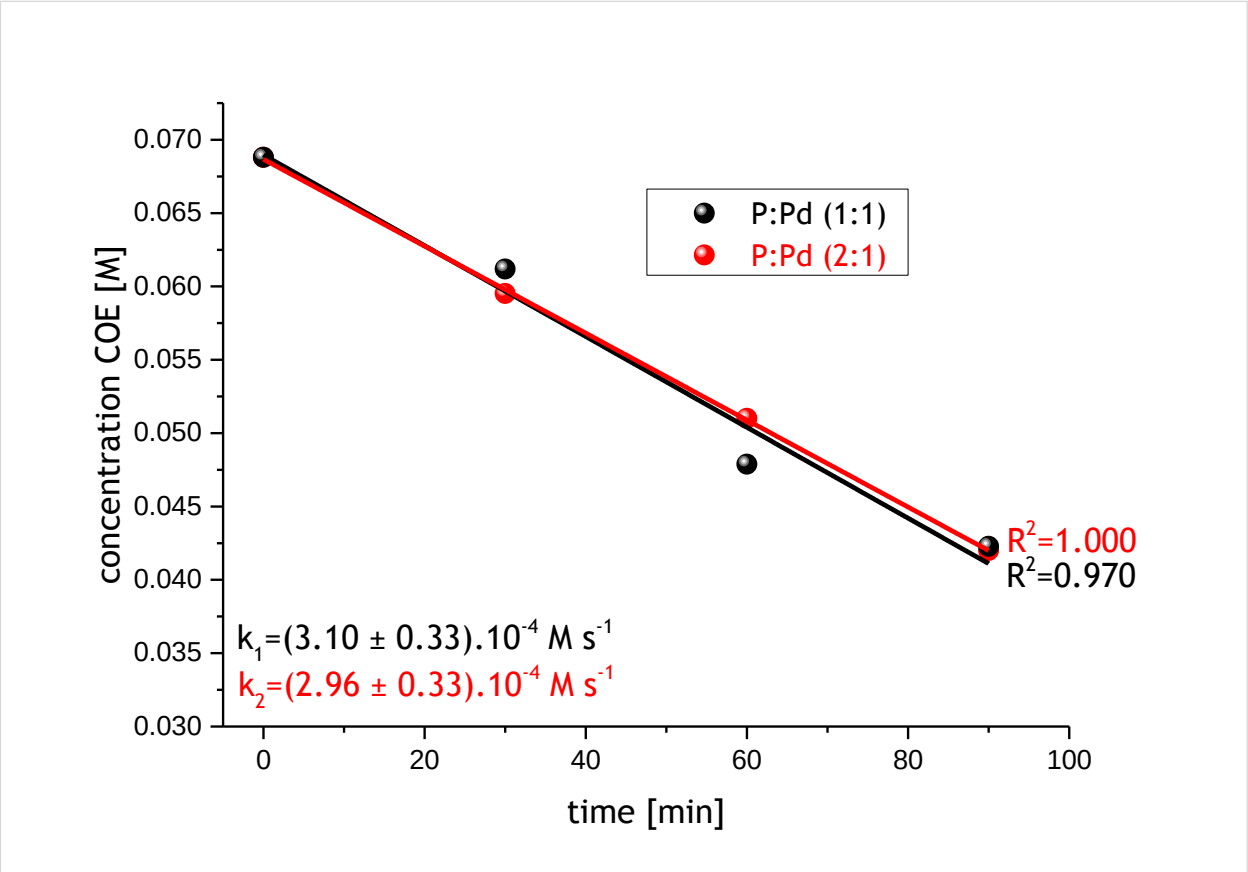
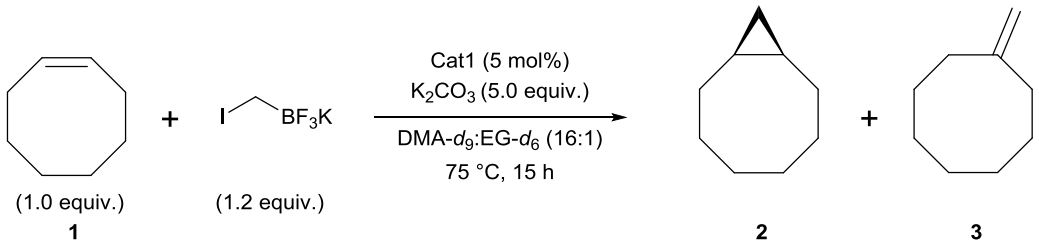


Figure SI-26. Influence of the phosphine concentration on the initial reaction rate: Negligible difference.

C. Spectroscopic Studies

C-1. NMR monitoring methylenation reaction of COE



An oven-dried NMR tube equipped with a Teflon screw cap was transferred into a N_2-filled glovebox and charged with powdered K_2CO_3 (0.195 mmol, 5.0 equiv.). A 1.5 ml oven-dried vial was charged with $[(o\text{-tolyl})_3P]_2PdCl_2$ (1.53 mg, 5 mol%), ICH_2BF_3K (9.67 mg, 1.2 equiv.) and COE (5.1 µL, 0.039 mmol), anhydrous EG-d_6 (0.33 ml) and anhydrous DMA-d_9 (2.33 ml). The solution was then transferred to the NMR tube and the vial rinsed with anhydrous DMA-d_9 (2x1.5 ml). The rinse solution was added to the NMR tube. The NMR tube was sealed, shaken, and maintained at 75 °C for 16 h. 60.3%, GC yield, cyclopropane formed.

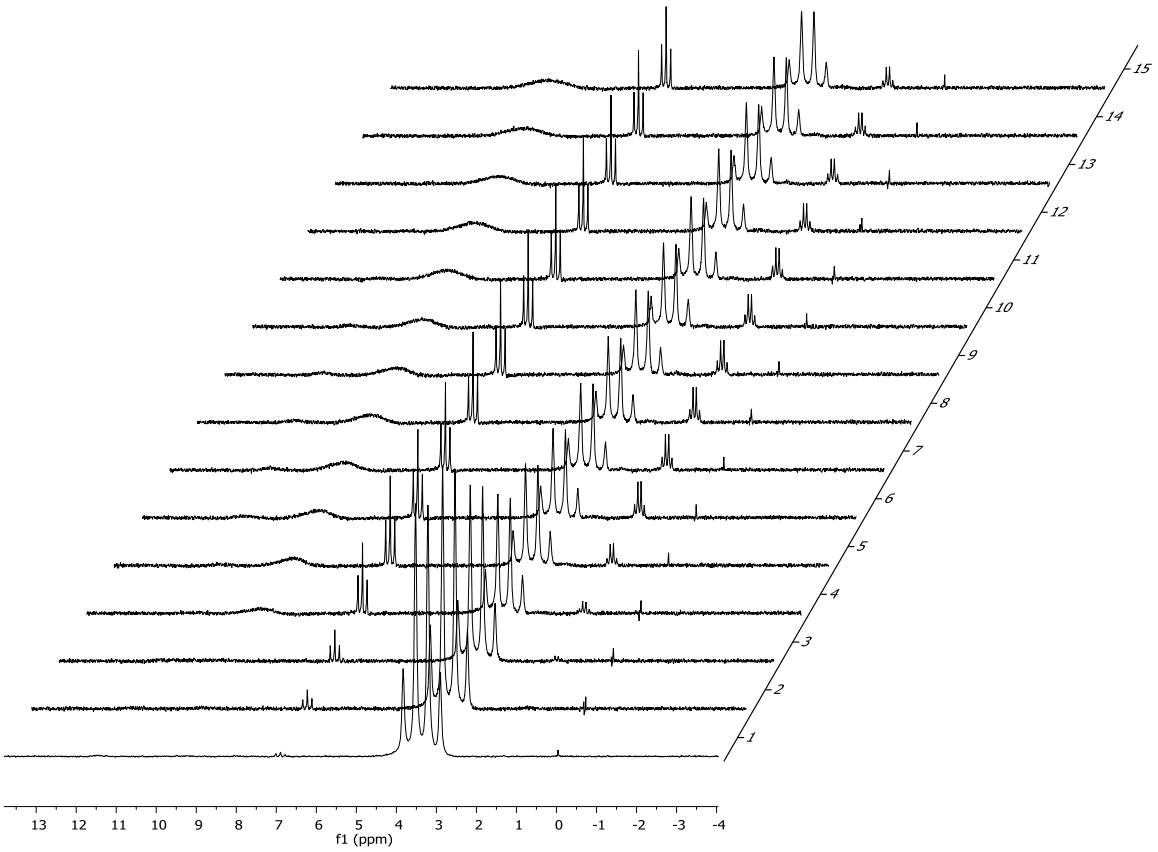


Figure SI-27. Methylenation reaction of COE monitored by ^{11}B NMR recorded at 75 °C.

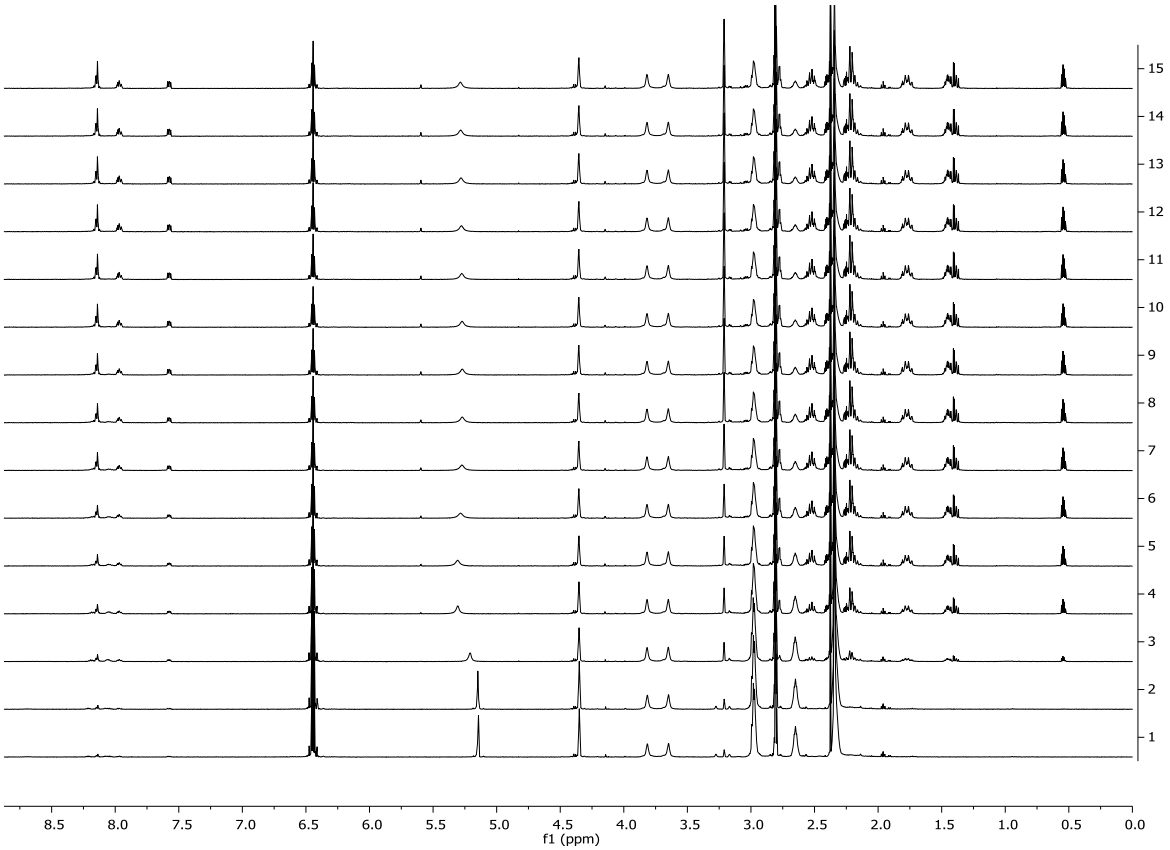
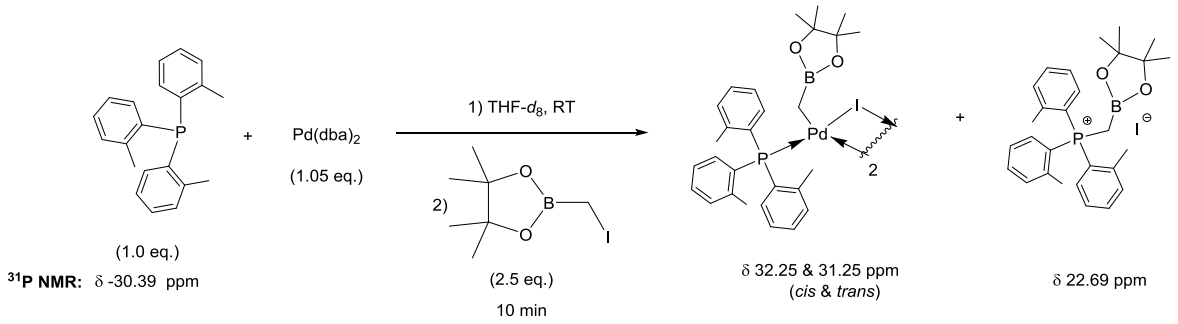


Figure SI-28. Methylenation reaction of COE monitored by ^{1}H NMR recorded at 75 °C.

C-2. Oxidative addition of ICH_2Bpin in THF



An oven-dried NMR tube was brought into a N_2-filled glovebox and charged with $Pd(dba)_2$ (30 mg, 0.052 mmol, 1.05 equiv.), $(o\text{-tolyl})_3P$ (15 mg, 0.049 mmol, 1.0 equiv.), and anhydrous THF-d_8 (0.4 ml). The tube was then closed and agitated for ~5 min. A 1.5 ml oven-dried vial was charged with ICH_2Bpin (33 mg, 0.123 mmol, 2.5 equiv.) and anhydrous THF-d_8 (0.2 ml). The solution was then transferred to the NMR tube. The tube was closed with a cap and agitated for 15 min, and NMR was taken at room temperature. The dark red solution turned yellow with deposit of a greenish solid. ^{31}P NMR (202 MHz, THF-d_8) δ 32.25, 31.25, 27.13, 22.69, -30.39. ^{11}B NMR (160 MHz, THF-d_8) δ 31.71, 22.46.

Gas phase studies. In the glovebox, 0.1 ml of the reaction mixture was diluted to ~10^{-5} M in dry MeCN or dry THF and use immediately for gas phase studies. Conditions: spray voltage: 5 kV, collision offset: 35 V, tube lens offset: 100 V and capillary temperature: 50 °C or 170 °C. Collision-induced dissociation (CID) experiments were done with an argon pressure of 0.5 mTorr in the collision cell.

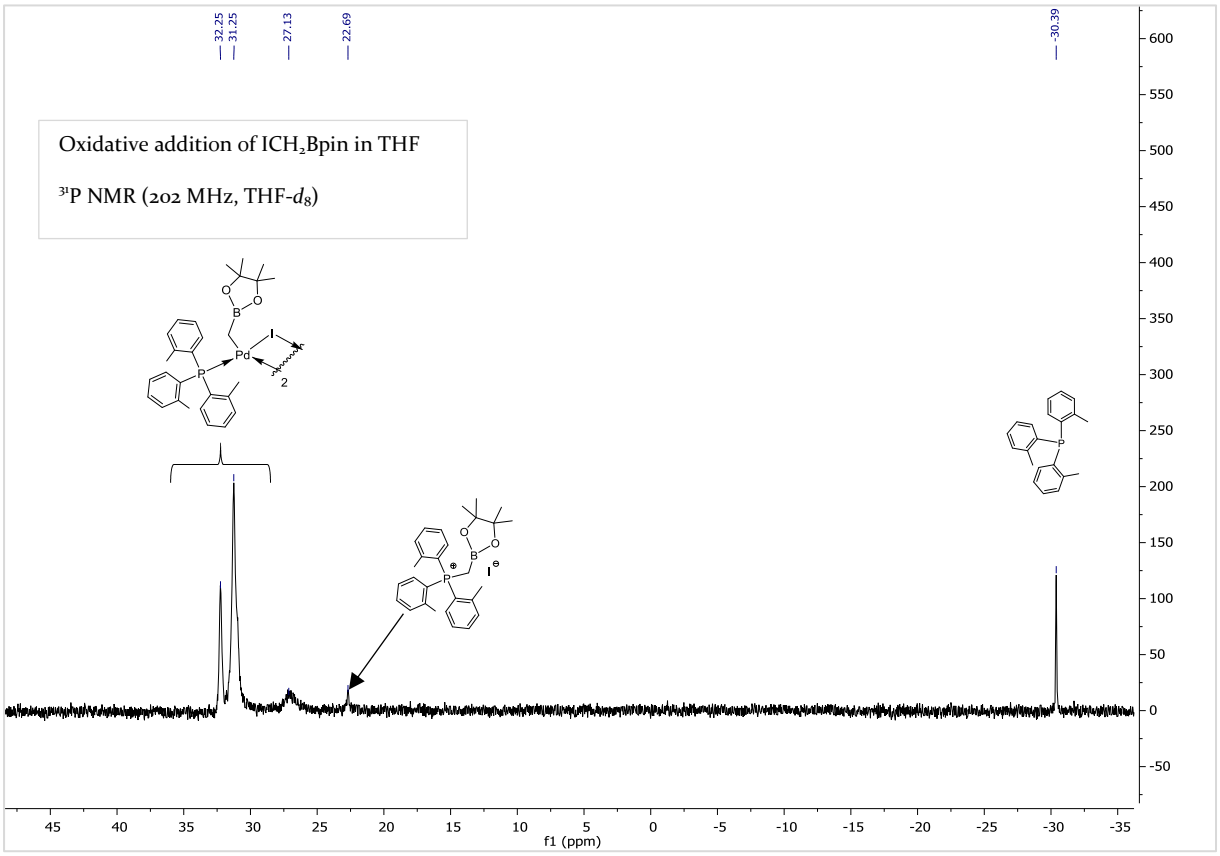


Figure SI-29. ^{31}P NMR spectrum showing the products of the oxidative addition of ICH_2Bpin to a Pd(0) complex.

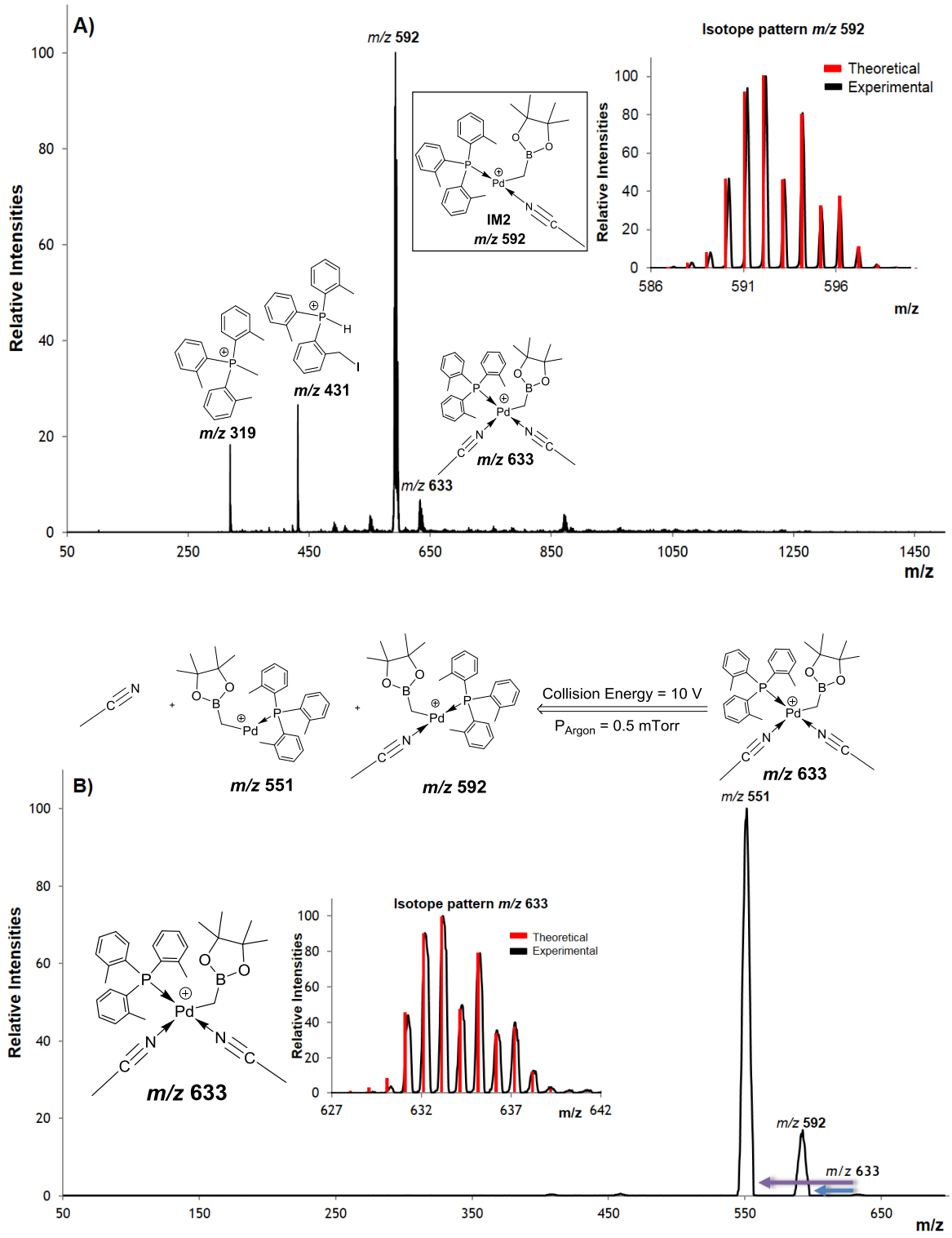
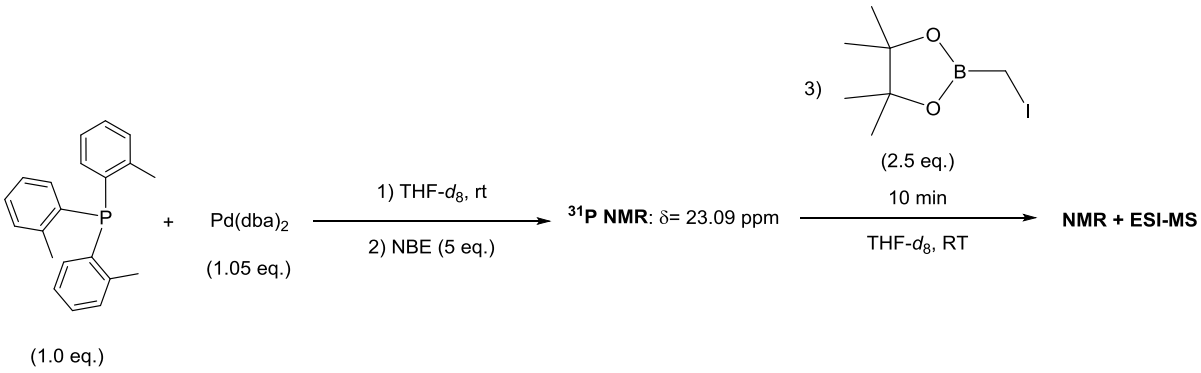


Figure SI-30. A) Full scan in the positive mode showing products of oxidative addition and substitution by MeCN. **B)** CID on cation *m/z* 633. Collision gas pressure: 0.5 mTorr, Collision Energy: 10 V (center-of-mass reference frame).

C-3. Oxidative addition of ICH_2Bpin in the presence of NBE in THF



An oven dried NMR tube was transferred into a N_2-filled glovebox and charged with $Pd(dba)_2$ (30 mg, 0.052 mmol, 1.05 equiv.), $(o\text{-tolyl})_3P$ (15 mg, 0.049 mmol, 1.0 equiv.) and anhydrous THF-d_8 (0.4 ml). The tube was closed and agitated for ~5 min. NBE (23.07 mg, 0.245 mmol, 5 equiv.) in anhydrous THF (0.2ml) was added and an NMR of the resulting orange solution was taken 30 mis later. The tube was then transferred back to the glovebox and charged with ICH_2Bpin (33 mg, 0.123 mmol, 2.5 equiv.). Another NMR was taken and the mixture was heated to 60 °C for 10 min and cooled to room temperature, diluted and use immediately for gas phase studies.

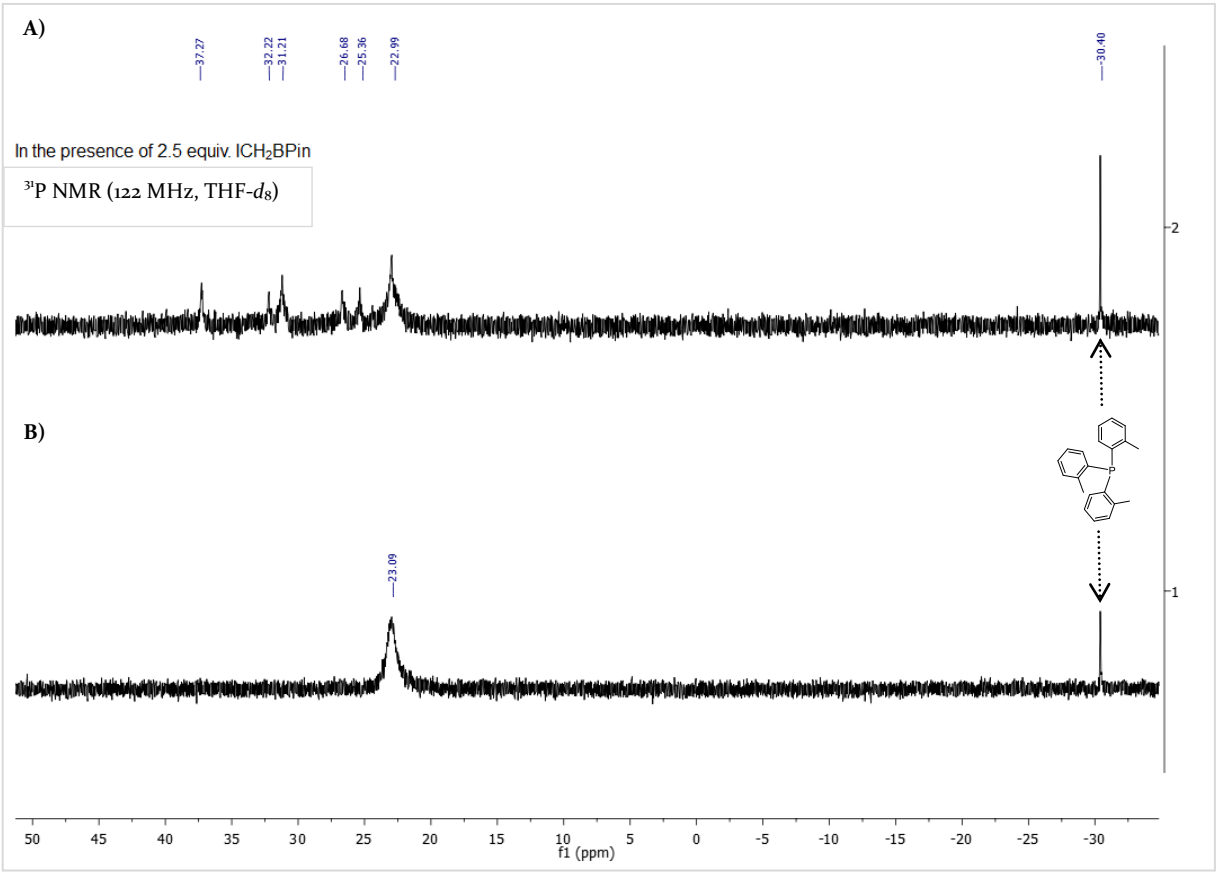
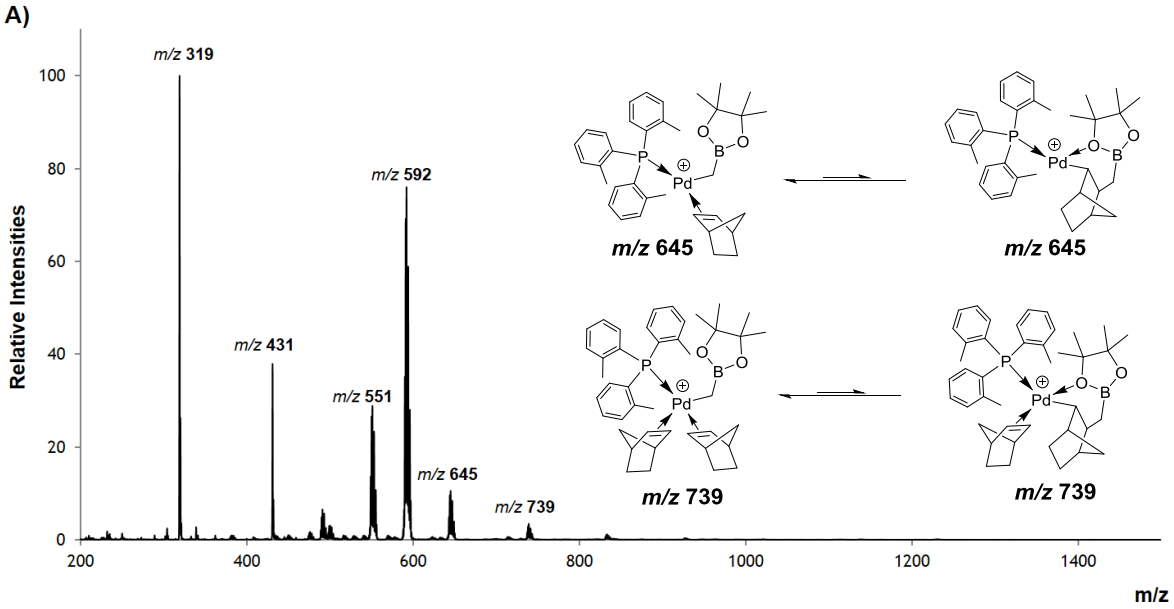
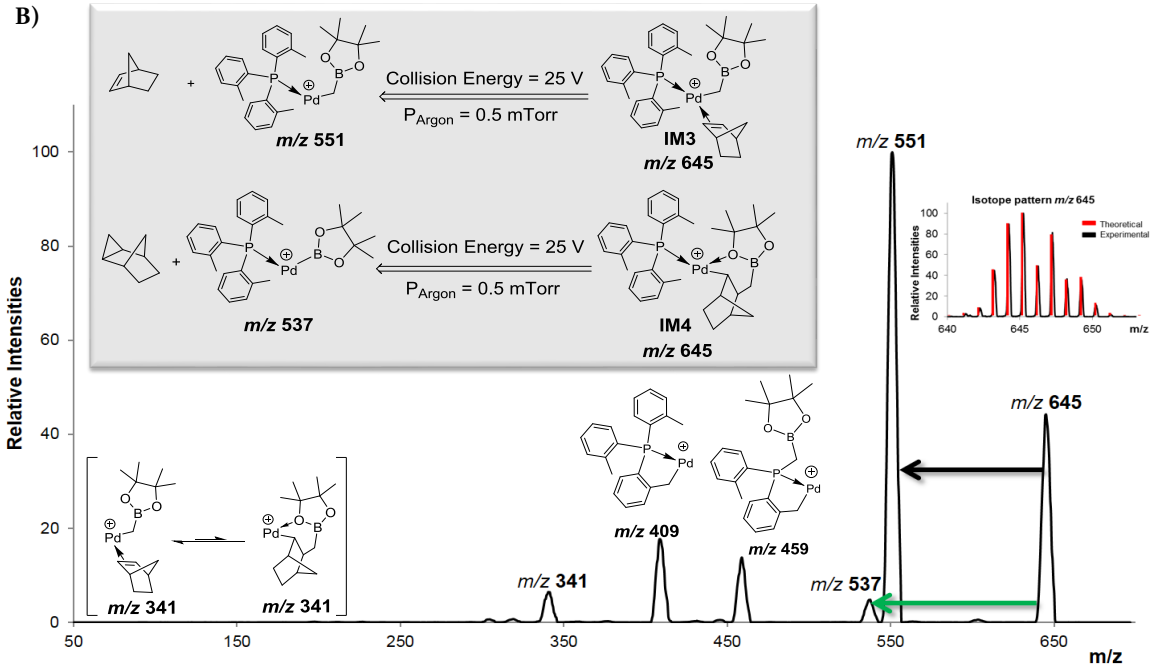


Figure SI-31. ^{31}P NMR spectrum showing in **B)** the products of the complexation of NBE on a Pd metal, and in A) products of oxidative addition of ICH_2Bpin on the resulting Pd(0) complex in THF-d_8.


A)
Relative Intensities
m/z
m/z 319
m/z 592
m/z 431
m/z 551
m/z 645
m/z 739
m/z 645
m/z 645
m/z 739
m/z 739


B)
Collision Energy = 25 V
P Argon = 0.5 mTorr
m/z 551
IM3
m/z 645
Collision Energy = 25 V
P Argon = 0.5 mTorr
m/z 537
IM4
m/z 645
m/z 551
Isotope pattern m/z 645
Theoretical
Experimental
Relative Intensities
m/z
m/z 645
m/z 409
m/z 459
m/z 341
m/z 537
m/z 341
m/z 341
Relative Intensities
m/z

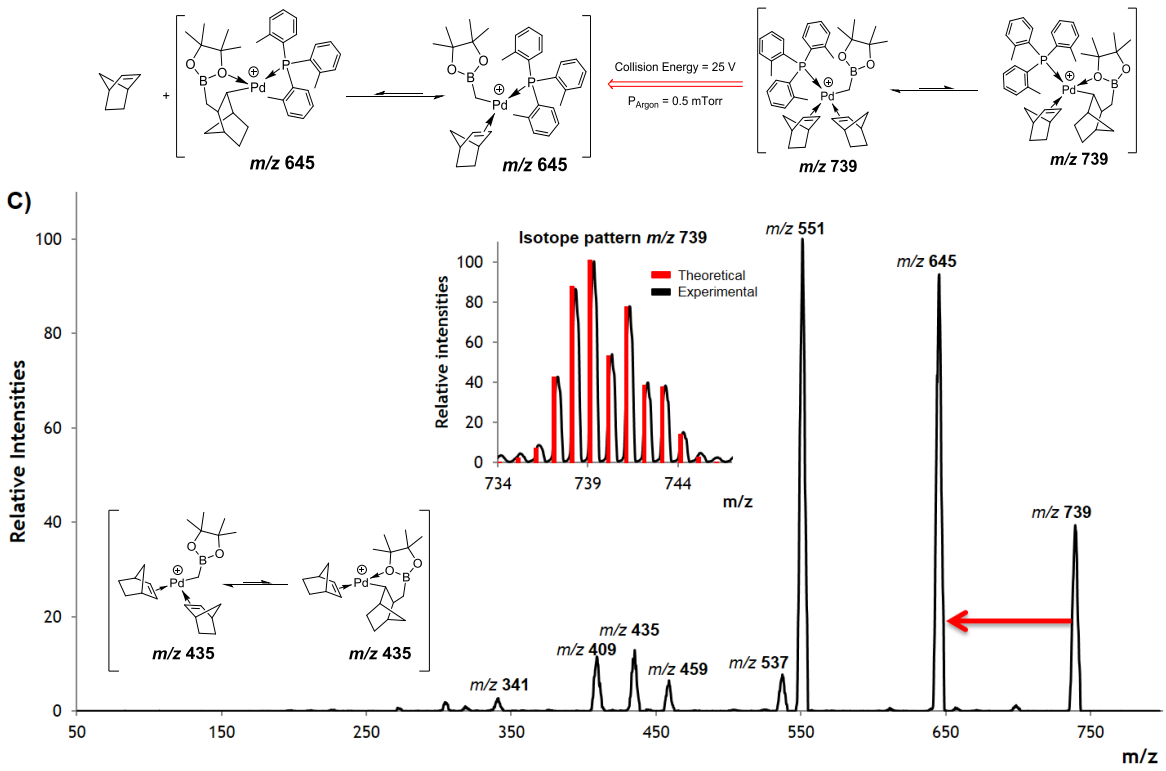
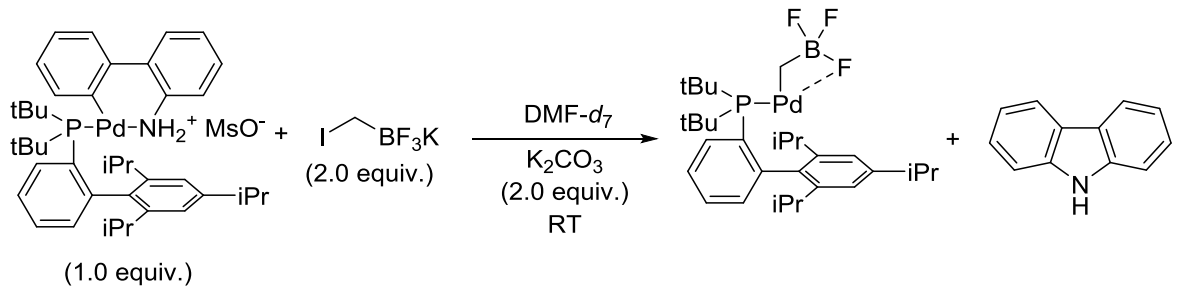


Figure SI-32. A) Full scan in the positive mode showing products of oxidative addition and substitution by MeCN and NBE. **B)** CID on the cation *m/z* 645. **C)** CID on the cation *m/z* 645. For both, Collision gas pressure: 0.5 mTorr, Collision Energy: 25 V (center-of-mass reference frame).

C-4. Oxidative addition of ICH_2BF_3K in DMF



An oven-dried NMR tube was brought into a N_2-filled glovebox and charged with the Pd complex t-BuXPhos Pd G3 (4.8 mg, 6.0 µmol, 1.0 equiv.), ICH_2BF_3K (3.0 mg, 1.2 µmol, 2.0 equiv.) and powdered K_2CO_3 (1.7 mg, 1.2 µmol, 2.0 equiv.), successively dissolved in anhydrous DMF-d_7 (0.6 ml). The tube was then closed and agitated for ~5 min and NMR was taken at room temperature. ^{1}H NMR (400 MHz, DMF-d_7) δ 11.26 (s, 1H, carbazole N*H*), 8.22 – 8.18 (m, 1H, Pd complex aryl C*H*), 8.17 (d, $^3J_{HH}$ = 7.8 Hz, 2H, carbazole C*H*), 7.71 – 7.63 (m, 2H, Pd complex aryl C*H*), 7.55 (d, $^3J_{HH}$ = 8.2 Hz, 2H, carbazole C*H*), 7.44 – 7.37 (m, 2H, carbazole C*H*), 7.36 (s, 2H, Pd complex aryl C*H*), 7.28 – 7.23 (m, 1H, Pd complex aryl C*H*), 7.21 – 7.15 (m, 2H, carbazole C*H*), 3.48 (s, H_2O), 2.98 (hept, $^3J_{HH}$ = 6.9 Hz, 1H, Pd complex iPr C*H*), 2.46 (hept, $^3J_{HH}$ = 6.7 Hz, 2H, Pd complex iPr C*H*), 2.42 (s, $CH_3SO_3^-$), 1.83 (s, $ICH_2BF_3^-$), 1.55 (d, $^3J_{HH}$ = 6.7 Hz, 6H, Pd complex iPr CH_3), 1.48 (d, $^3J_{HP}$ = 15.1 Hz, 18H, Pd complex tBu), 1.32 (d, $^3J_{HH}$ = 6.9 Hz,

6H, Pd complex iPr CH_3), 1.16 – 1.08 (m, 2H, PdCH_2BF_3), 0.95 (d, $^3J_{HH}$ = 6.5 Hz, 6H, Pd complex iPr CH_3). ^{31}P NMR (122 MHz, DMF-d_7) δ 75.49 (q, $^4J_{PF}$ = 32.1 Hz). ^{19}F NMR (282 MHz, DMF-d_7) δ -139.21 (s, PdCH$_2$BF_3), -143.55 (m, $^2J_{FB}$ = 48.6 Hz, ICH$_2$BF_3), -151.24. The mixture was diluted in THF and immediately use for gas phase studies.

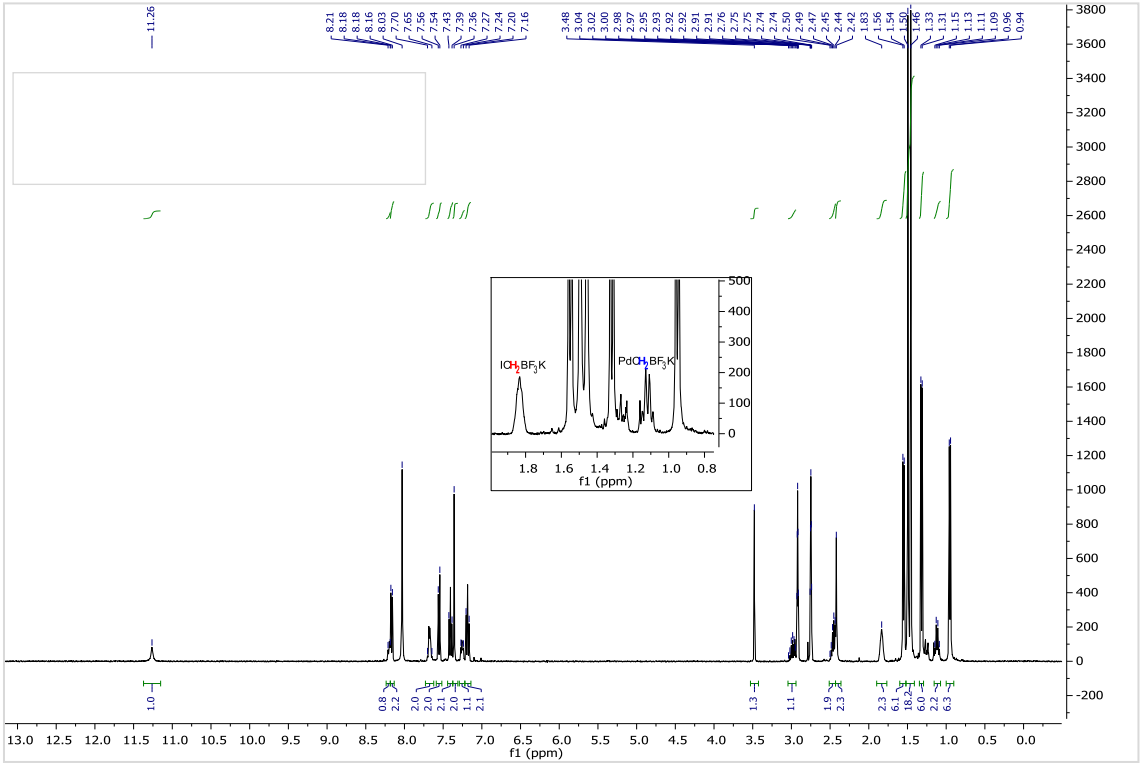


Figure SI-33. ^{1}H NMR spectra showing the products of the oxidative addition of ICH$_2$BF_3K on an *in situ* generated Pd(0) in DMF-d_7.

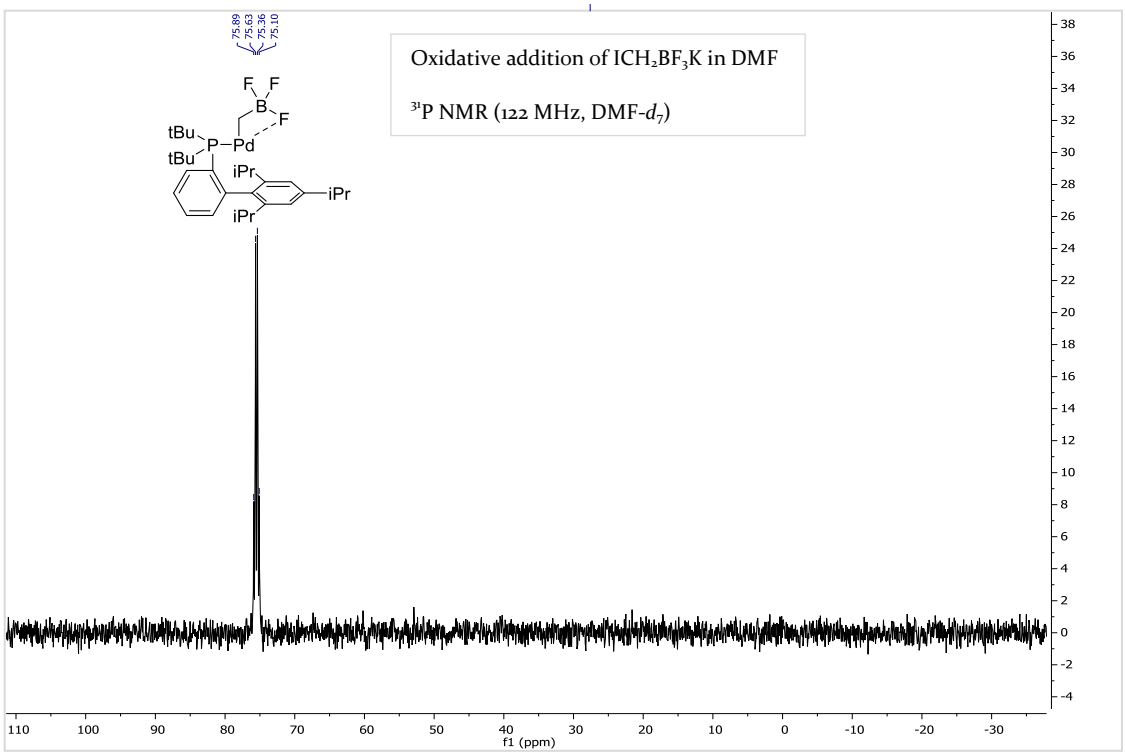


Figure SI-34. ^{31}P NMR spectra showing the products of the oxidative addition of ICH$_2$BF_3K on an *in situ* generated Pd(0) in DMF-d_7.

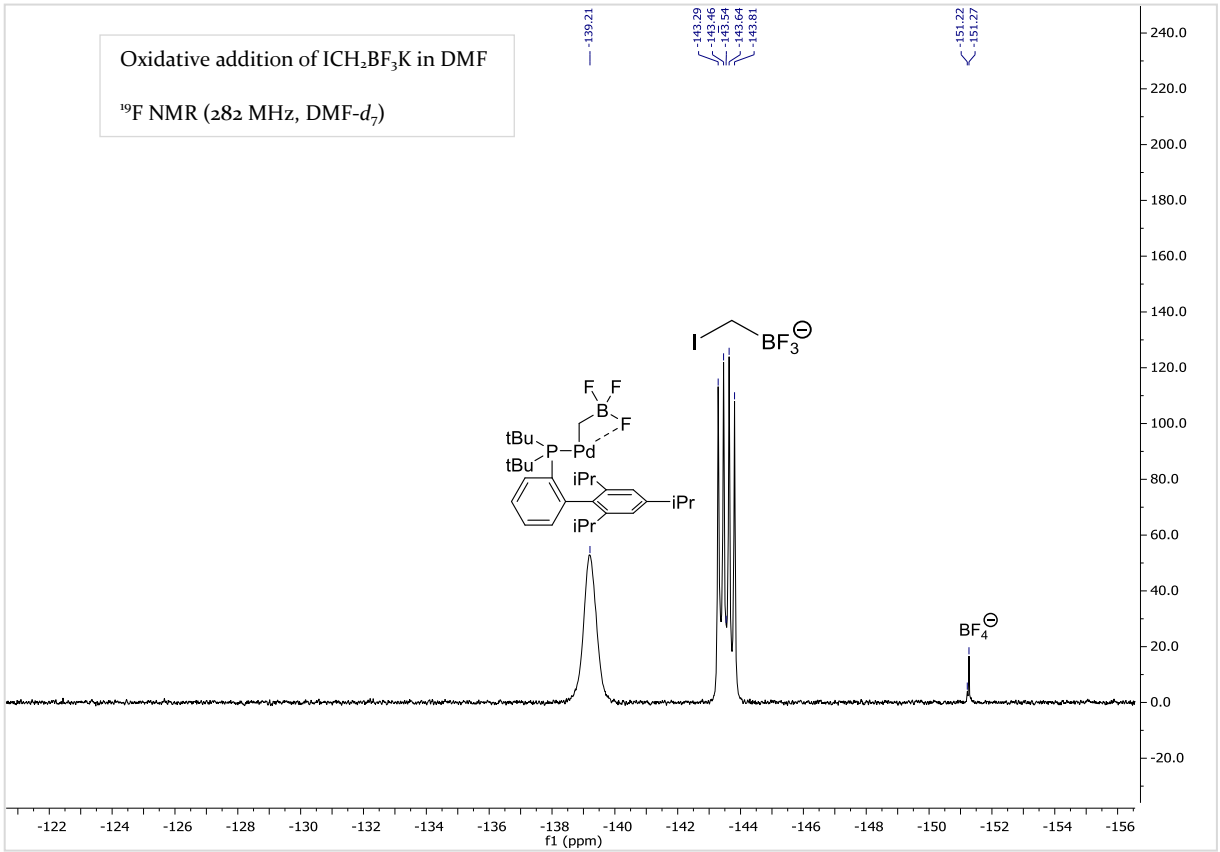


Figure SI-35. ^{19}F NMR spectra showing the products of the oxidative addition of ICH_2BF_3K on an *in situ* generated Pd(0) in DMF-d_7.

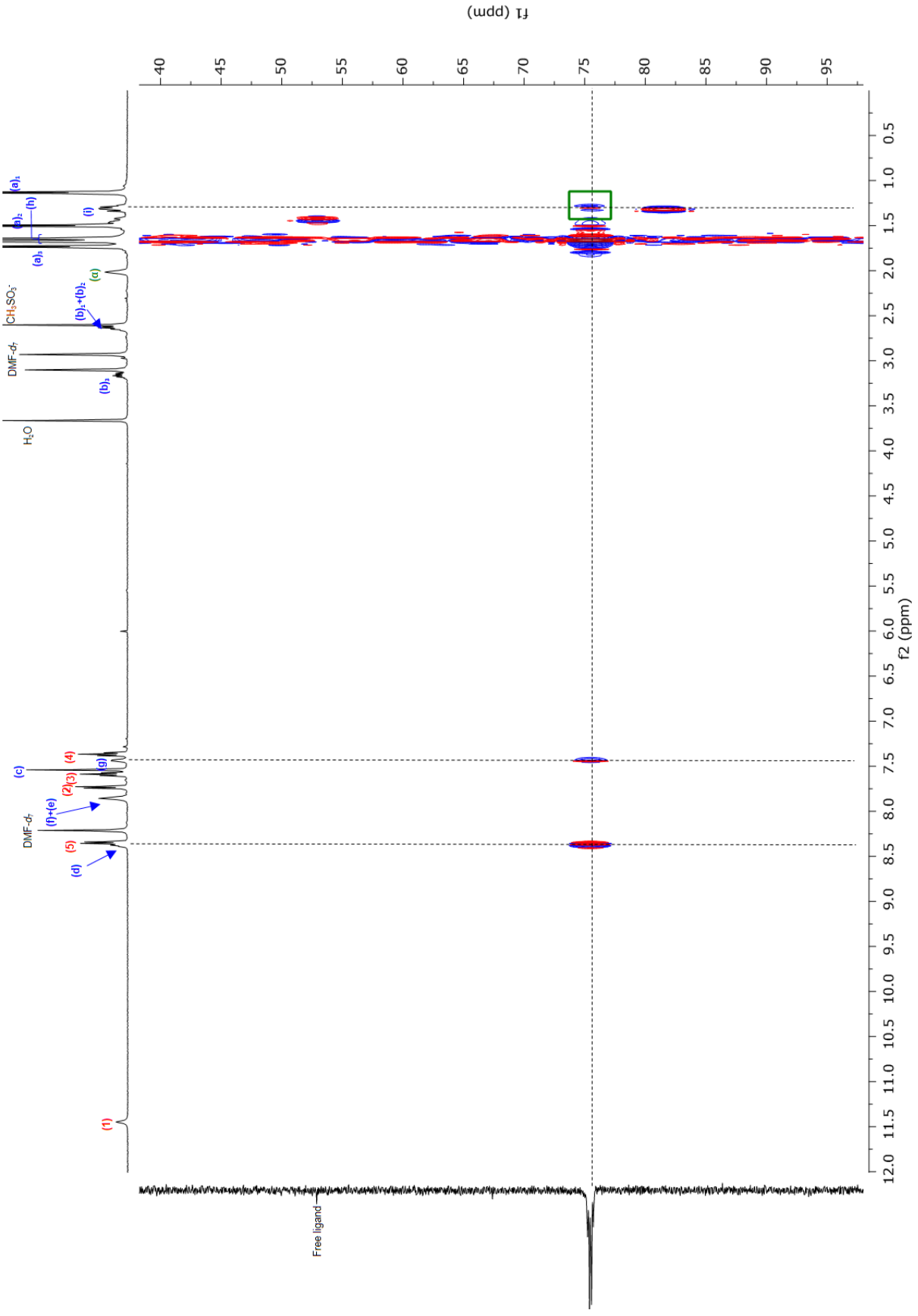


Figure SI-36. ^{1}H-^{31}P HMBC spectrum showing the couplings between the methylene protons and the phosphine through Pd.

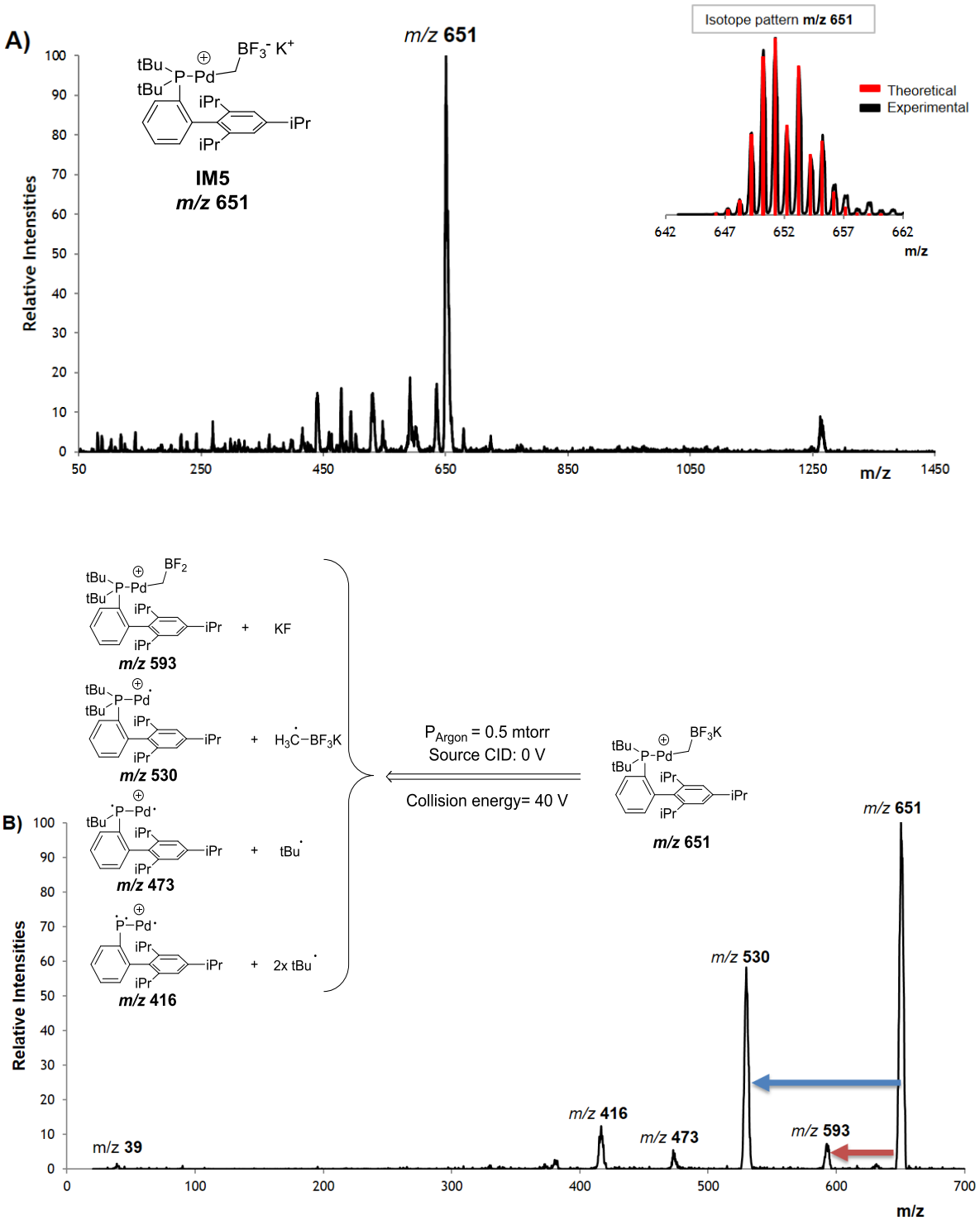
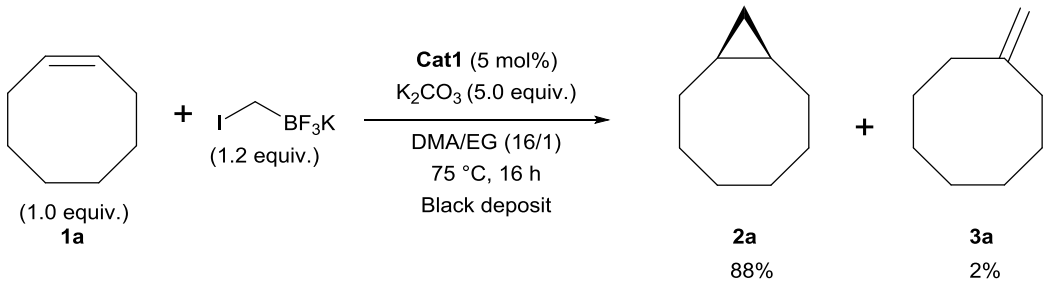


Figure SI-37. A) Full scan in the positive mode showing products of oxidative addition of ICH_2BF_3K. Source CID of 50 V needed for cleaner spectrum. **B)** CID on the cation *m/z* 651. Source CID=0 V, Collision gas pressure: 0.5 mTorr, Collision Energy: 40 V (center-of-mass reference frame).

D. Control experiments

The methylenation procedures were followed and only the reagents needed for each experiment were charged in the oven-dried Schlenk tube. The tube was sealed, removed from the glovebox and heated to 75 °C for 16 h. At the end of the indicated time, the Schlenk tube was cooled to 0 °C for 15 min, dried and transferred to the glovebox. 0.6 ml of the solution were filtered and transferred into an oven-dried NMR tube placed in an external NMR tube containing the reference solvent DMF-d_7. The tubes were closed and NMR was taken at room temperature.

D-1. Cyclopropanation of cyclooctene



Two reactions were performed separately. The work up procedure is done for one in order to get the GC yield and the other reaction is submitted spectroscopic observations. The reaction mixture was dark grey, due to the decomposition of the Pd catalyst. The cyclopropane was formed in 88%. Only free ligand observed in the ^{31}P NMR spectrum. ^{11}B NMR (160 MHz, DMF-d_7) δ 10.55, 7.03, 2.46 (q, $^2J_{BF}$ = 49.5 Hz), -0.96. ^{19}F NMR (470 MHz, DMF-d_7) δ -143.39 (m, $^2J_{FB}$ = 48.3 Hz), -150.76 – -151.54 (m). ^{31}P NMR (202 MHz, DMF-d_7) δ -30.40.

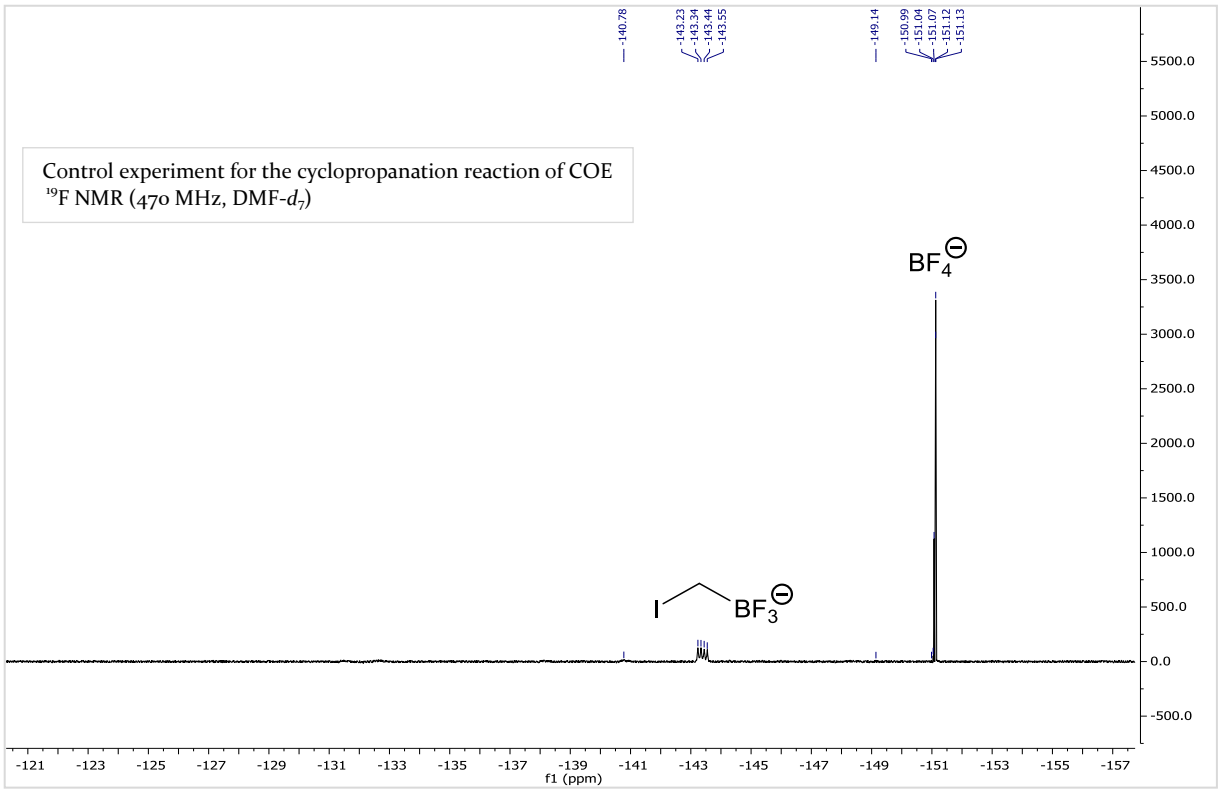


Figure SI-38. ^{19}F NMR spectra showing the products of the Pd catalyzed methylenation of COE.

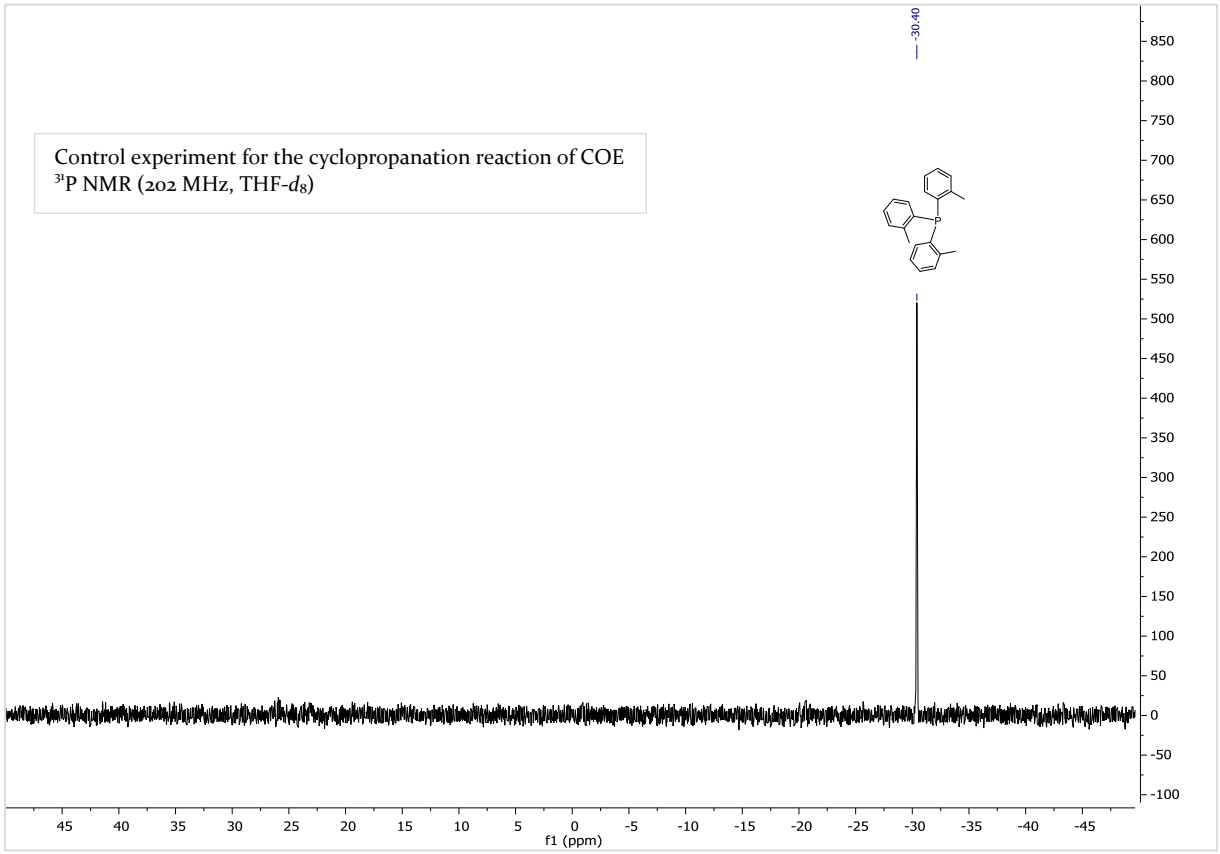


Figure SI-39. ^{31}P NMR spectra showing the products of the Pd catalyzed methylenation of COE.

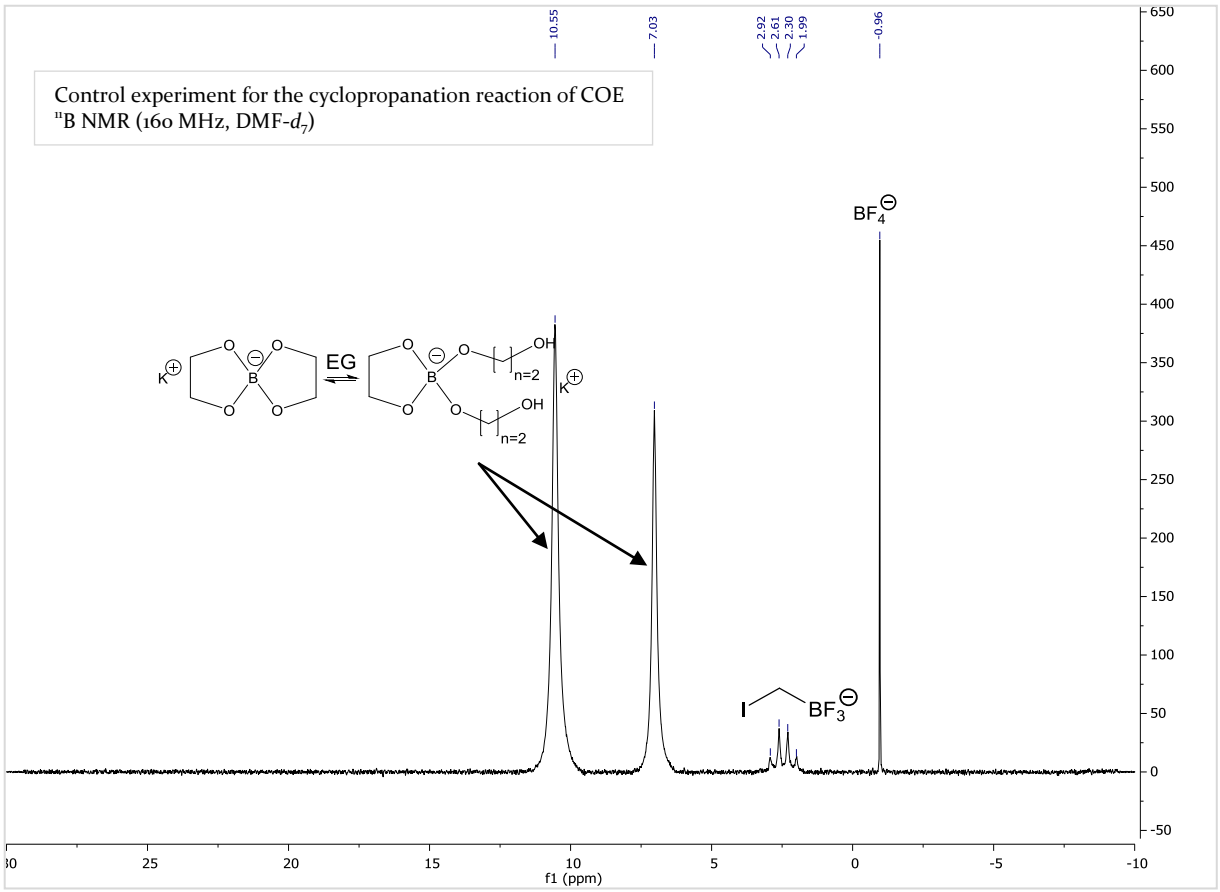


Figure SI-40. ^{11}B NMR spectra showing the products of the Pd catalyzed methylenation of COE.

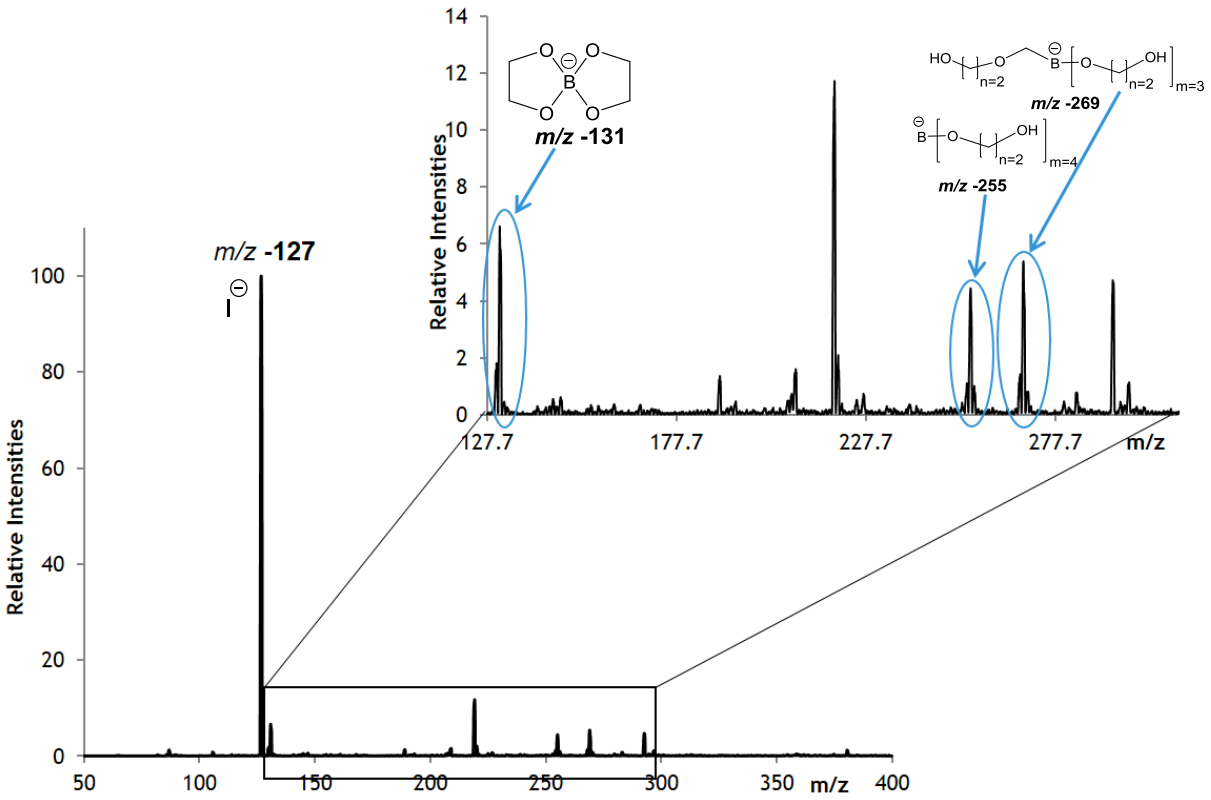
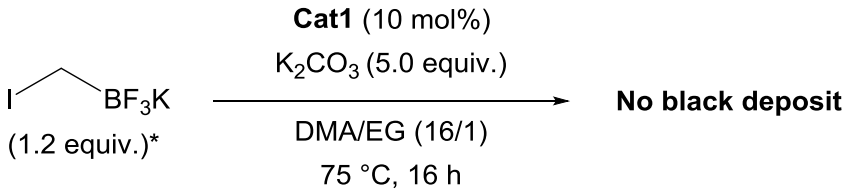


Figure SI-41. ESI-MS Scanning in the negative mode allows the detection of anions *m/z* -131, *m/z* -255, *m/z* -269.

D-2. In the absence of olefin



* relative to COE when present (standard conditions)

The final mixture was orange at the end of the indicated time and no black precipitate was present. ^{31}P NMR (202 MHz, DMF-d_7) δ 40.44, 35.64, -30.40. ^{11}B NMR (160 MHz, DMF-d_7) δ 10.51, 8.75, 7.00, 2.44 (q, $^{2}J_{BF}$ = 48.9 Hz), -0.97. ^{19}F NMR (470 MHz, DMF-d_7) δ -132.45, -138.32, -140.40, -143.54 (m, $^{2}J_{FB}$ = 47.0 Hz), -151.25.

The catalyst is still active in the absence of the olefin, but the amount of the methylene transfer agent is reduced.

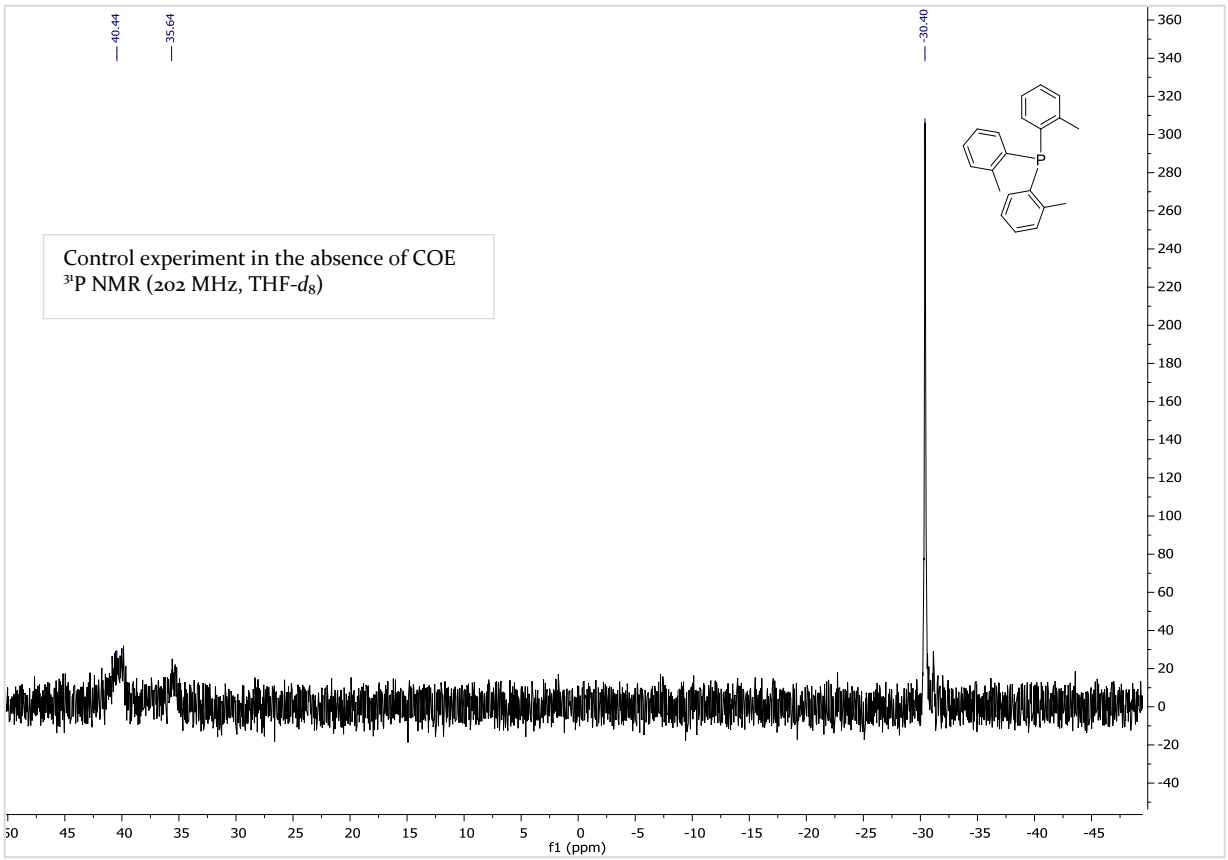


Figure SI-42. ^{31}P NMR spectra showing the products of the control experiment in the absence of COE.

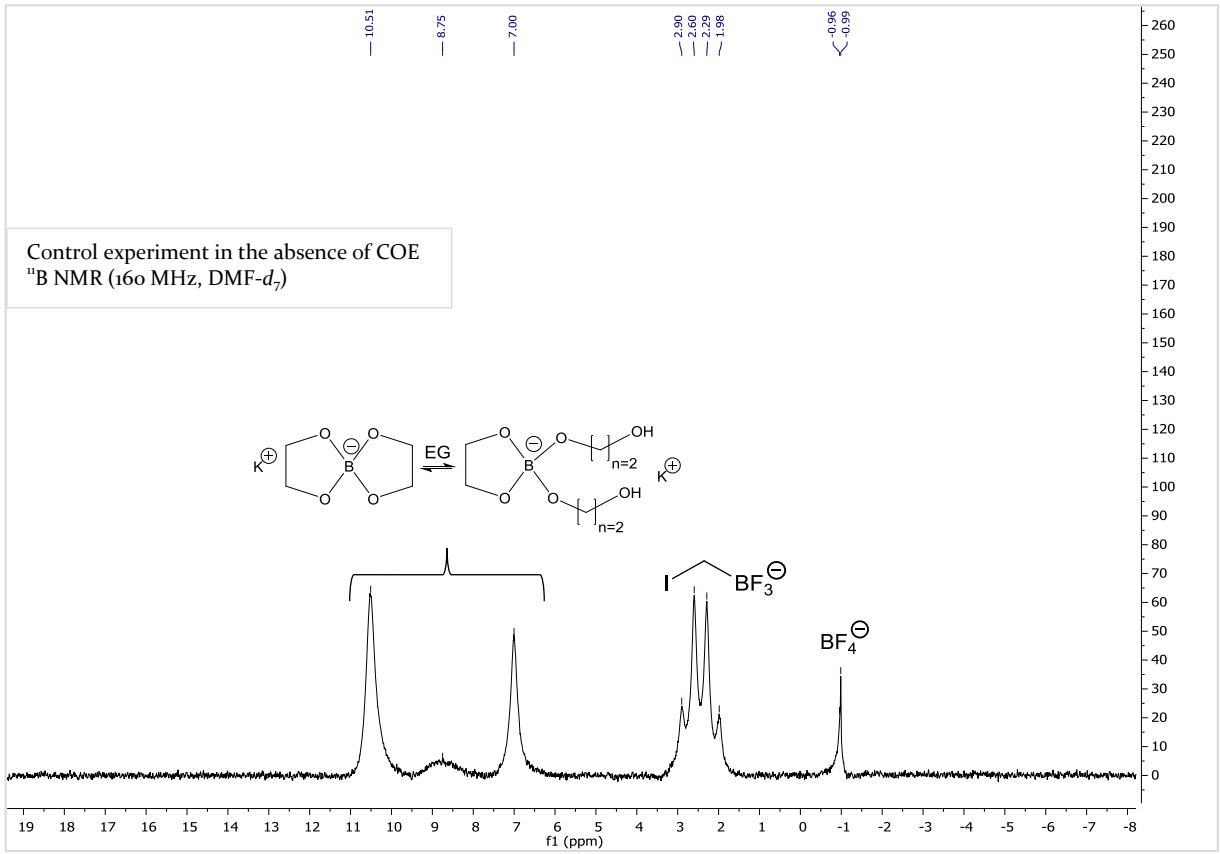


Figure SI-43. ^{11}B NMR spectra showing the products of the control experiment in the absence of COE.

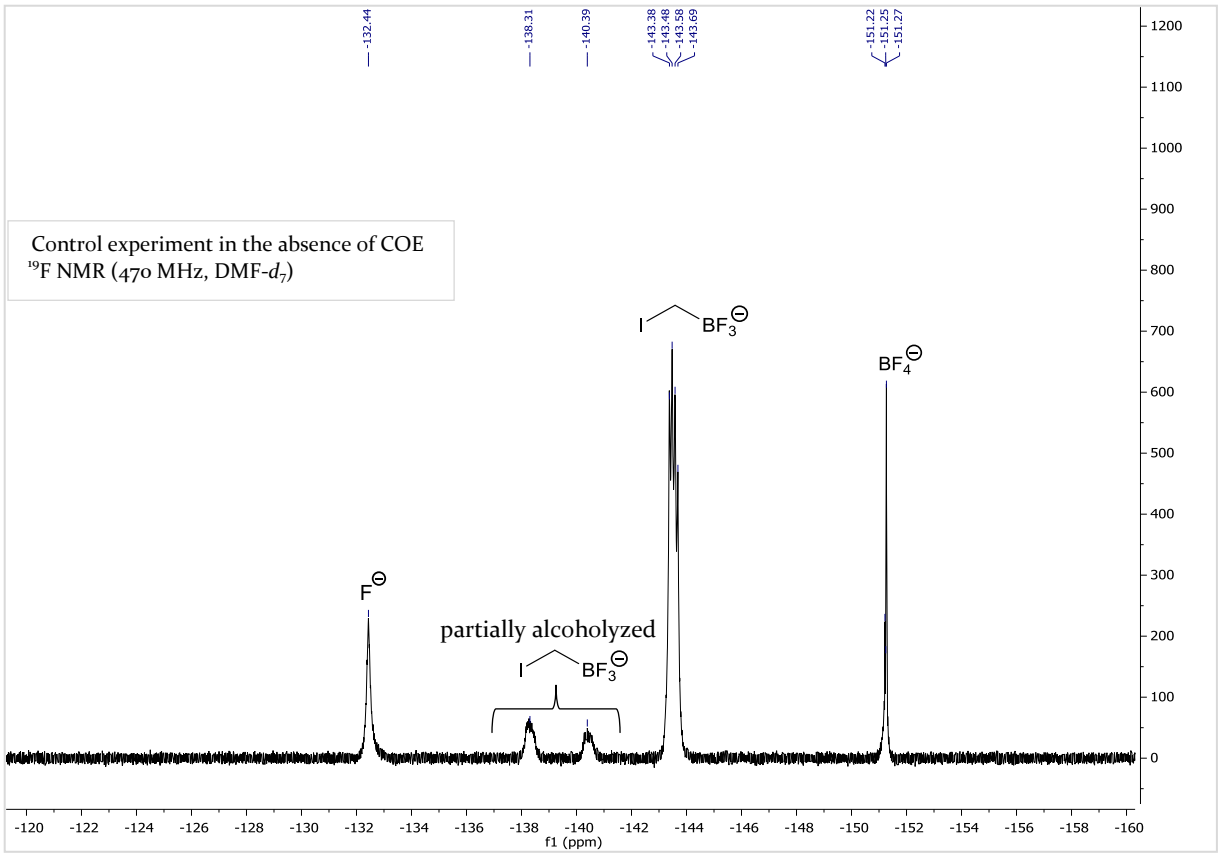
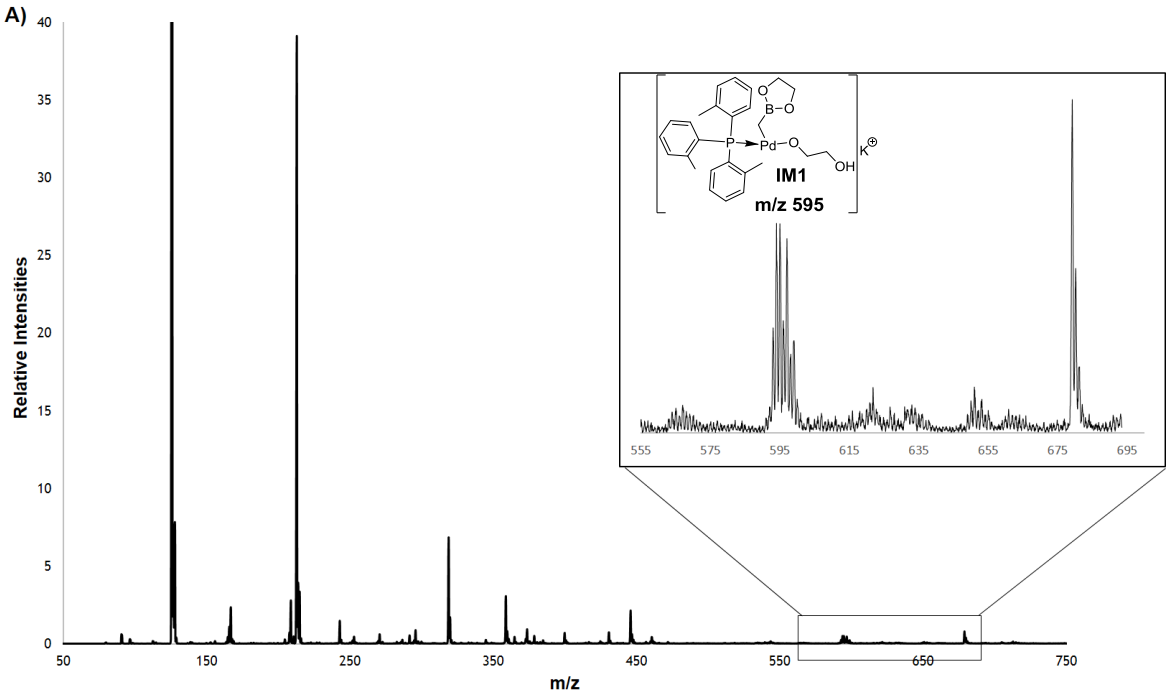


Figure SI-44. ^{19}F NMR spectra showing the products of the control experiment in the absence of COE.



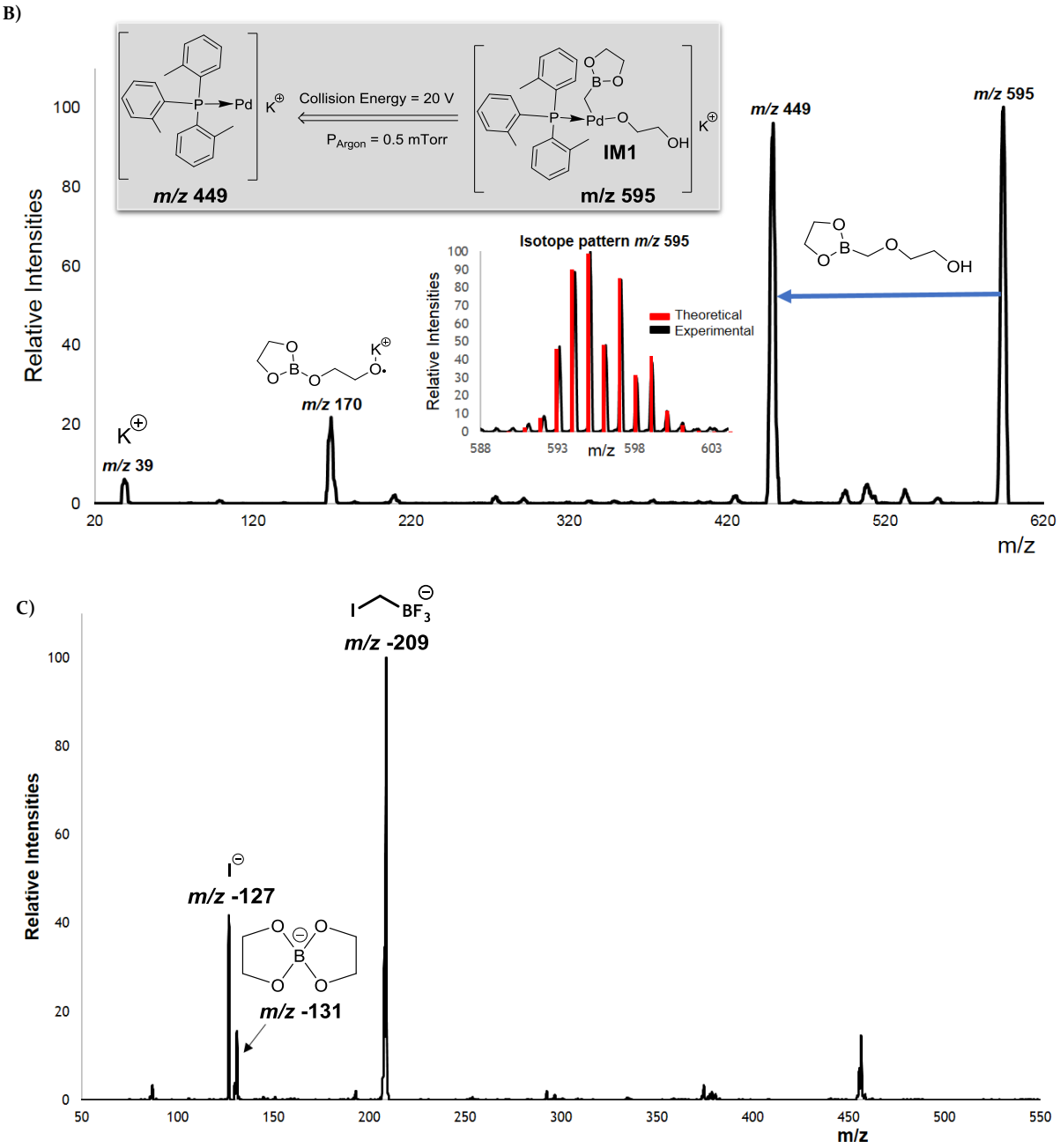
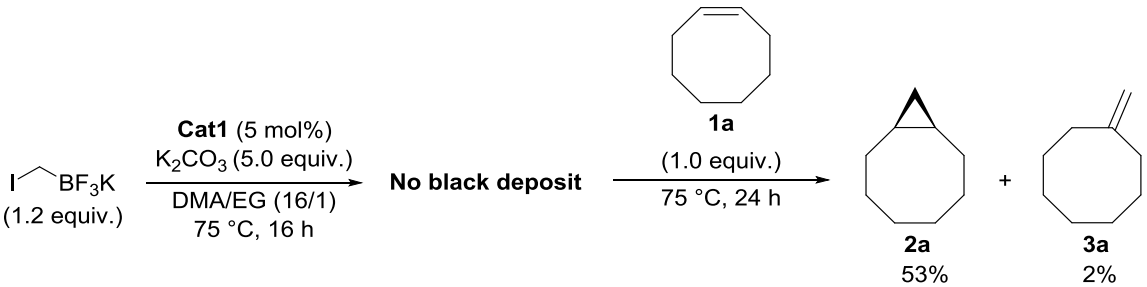
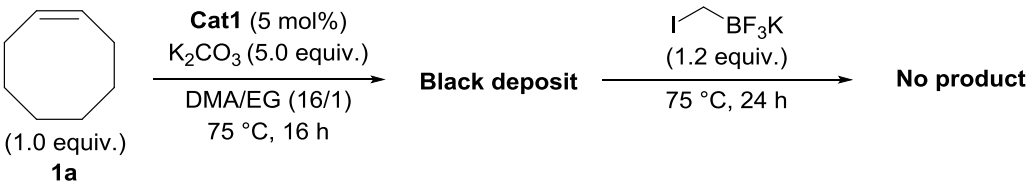


Figure SI-45. A) Full scan in the positive mode. **B)** CID on the cation *m/z* 645. Collision gas pressure: 0.5 mTorr, Collision Energy: 25 V (center-of-mass reference frame). **C)** Scanning in the negative mode allows the detection of the anion *m/z* -131.

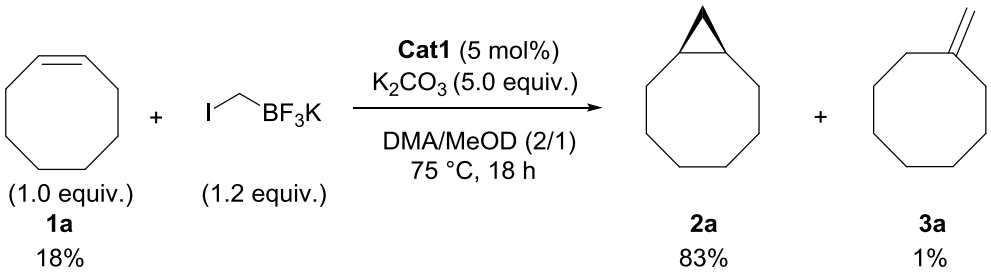
D-3. Cyclooctene added 16 h later to the reaction mixture



D-4. ICH_2BF_3K added 16 h later to the reaction mixture



D-5. Cyclopropanation of COE in deuterated methanol



Detection of traces of methylphosphonium cation, originating from the P-C reductive elimination from the metal center and hydrolysis by ESI/MS in the positive mode, allows to get an idea of the degree of C-H activation of the phosphine ligand.

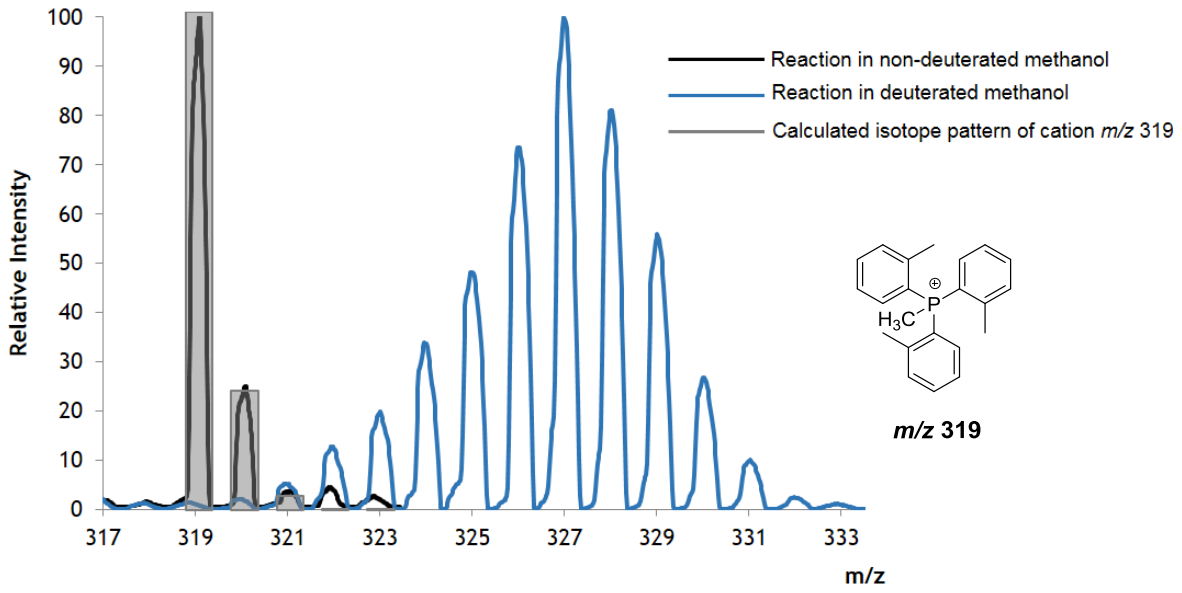


Figure SI-46. Observed mass distribution of the different isotopologues of methylphosphonium cation formed present in traces at the end of the reaction in MeOH (black line) and MeOH-d_4 (blue line).

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V-NMR SPECTRA AND CALIBRATION CURVES

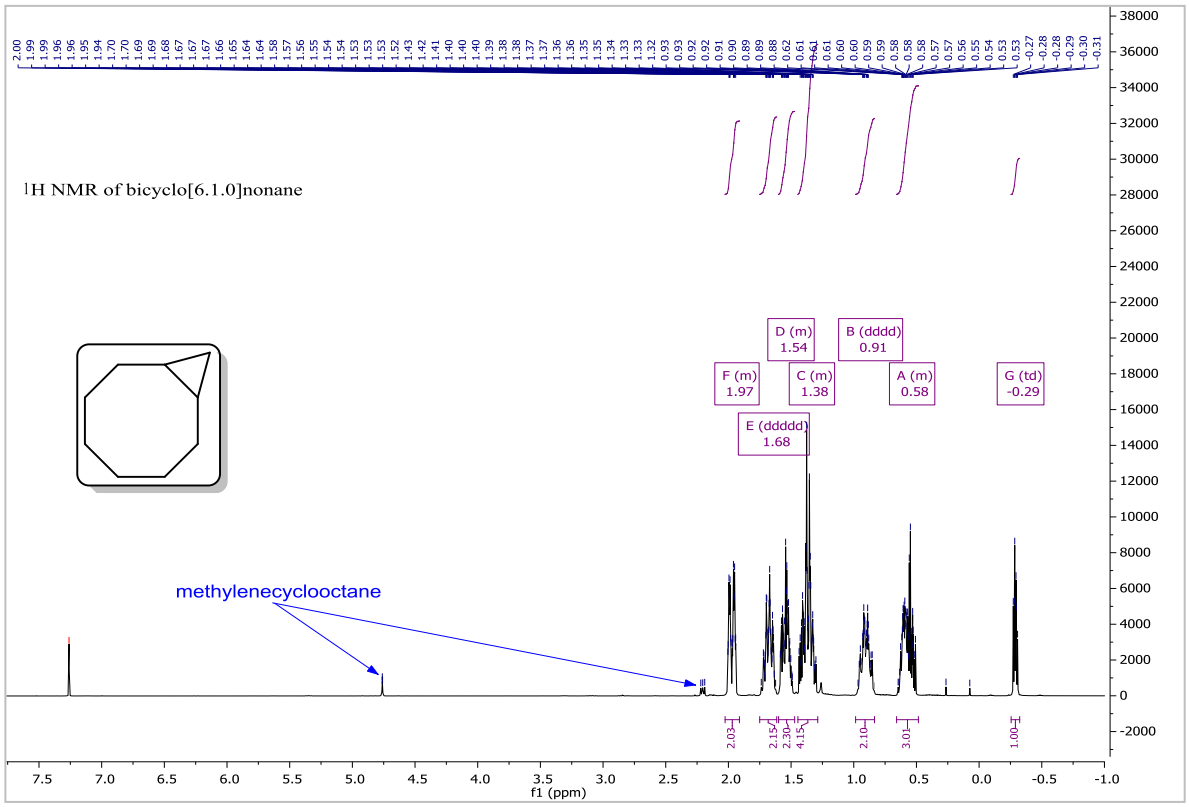


Figure SI-47. ^{1}H NMR spectra of bicyclo[6.1.0]nonane (**2a**) with traces of methylenecyclooctane (**3a**).

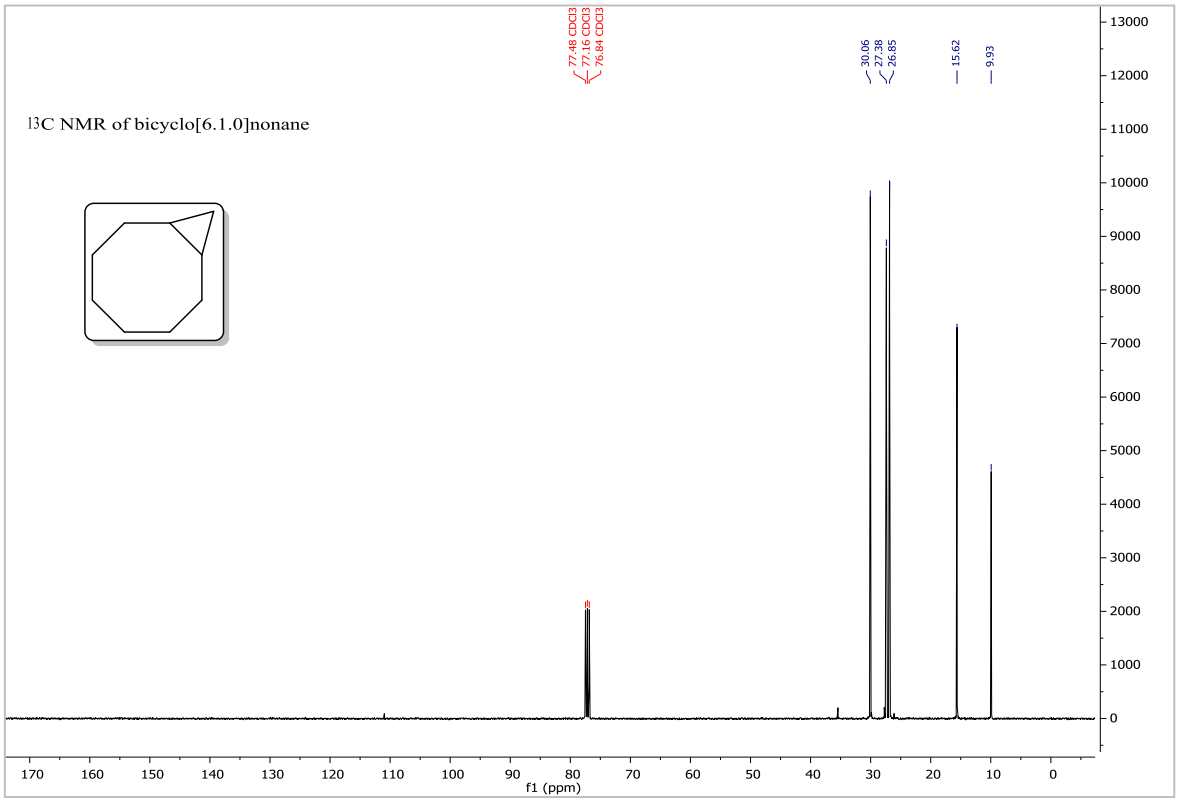


Figure SI-48. ^{13}C NMR spectra of bicyclo[6.1.0]nonane (**2a**) with traces of methylenecyclooctane (**3a**).

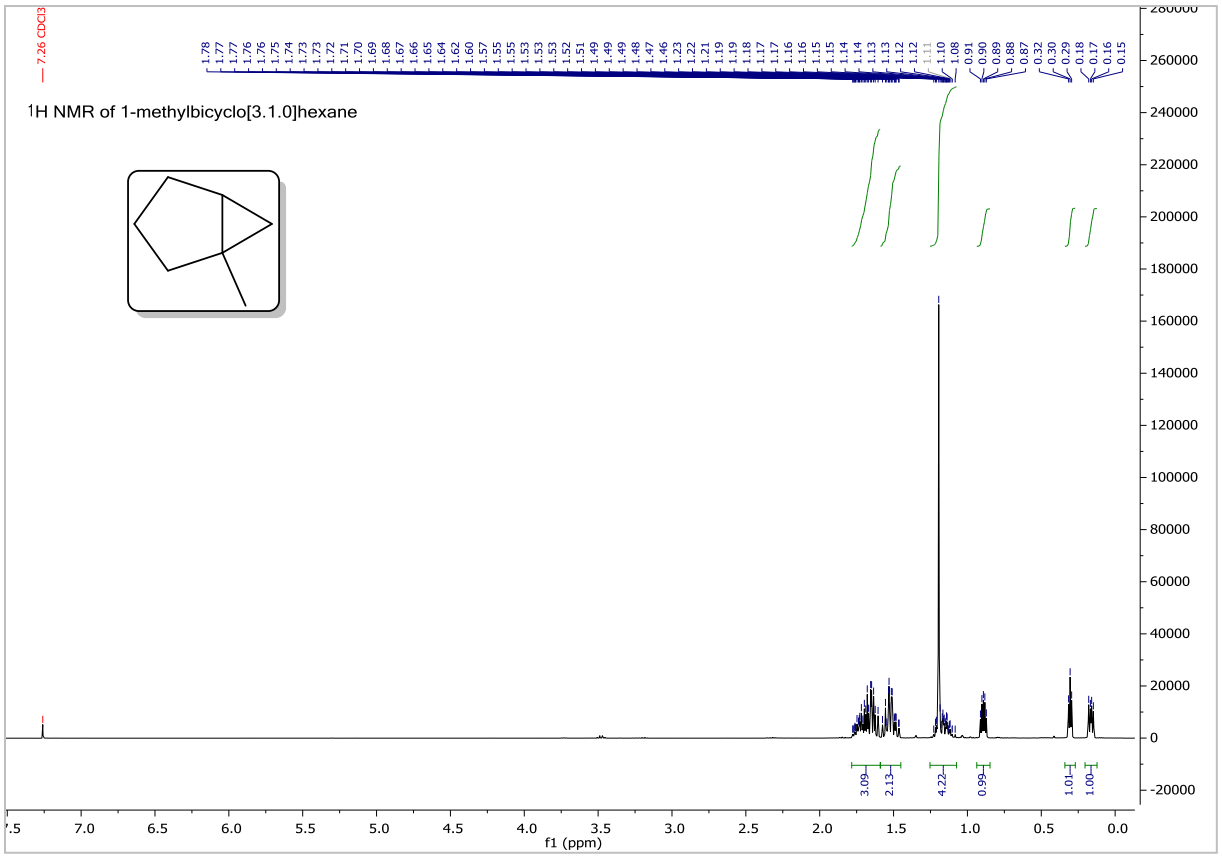


Figure SI-49. ^{1}H NMR spectra of 1-methylbicyclo[3.1.0]hexane (**2b**).

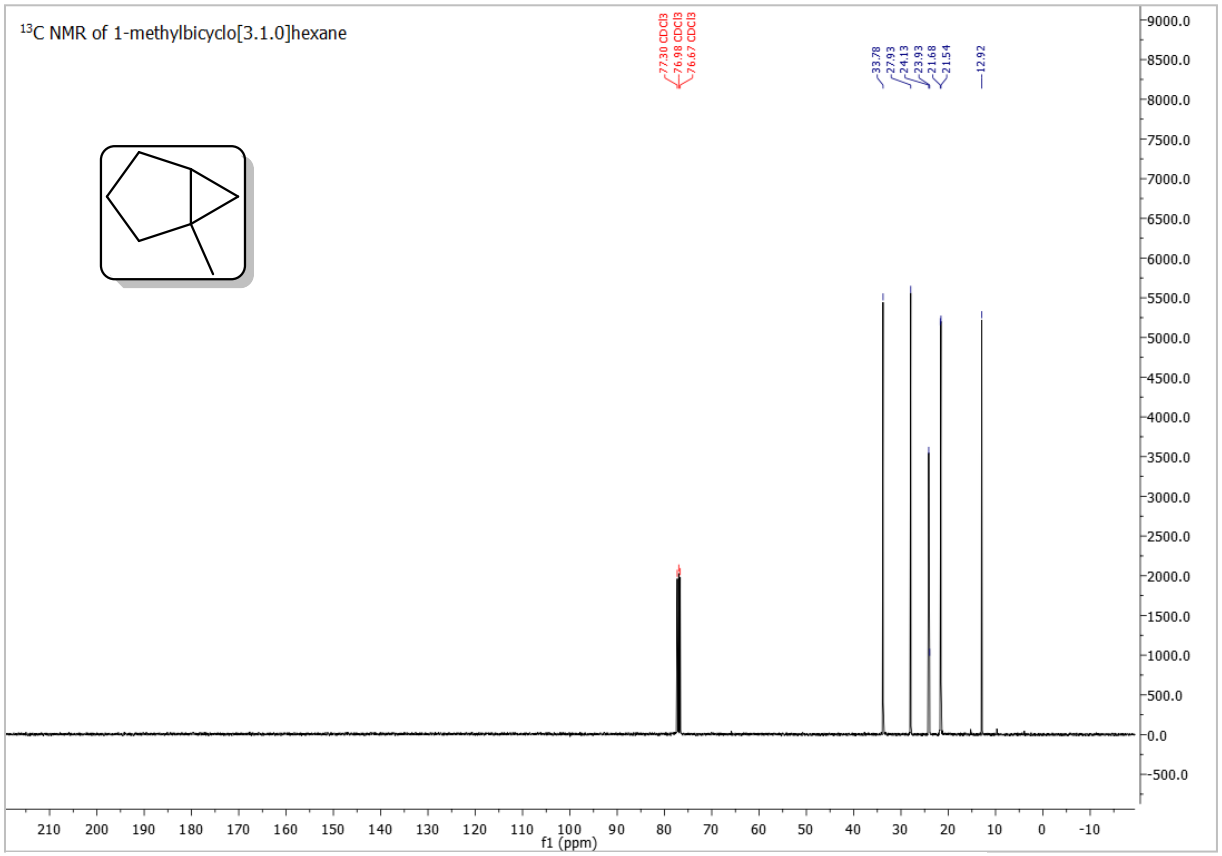


Figure SI-50. ^{13}C NMR spectra of 1-methylbicyclo[3.1.0]hexane (**2b**)

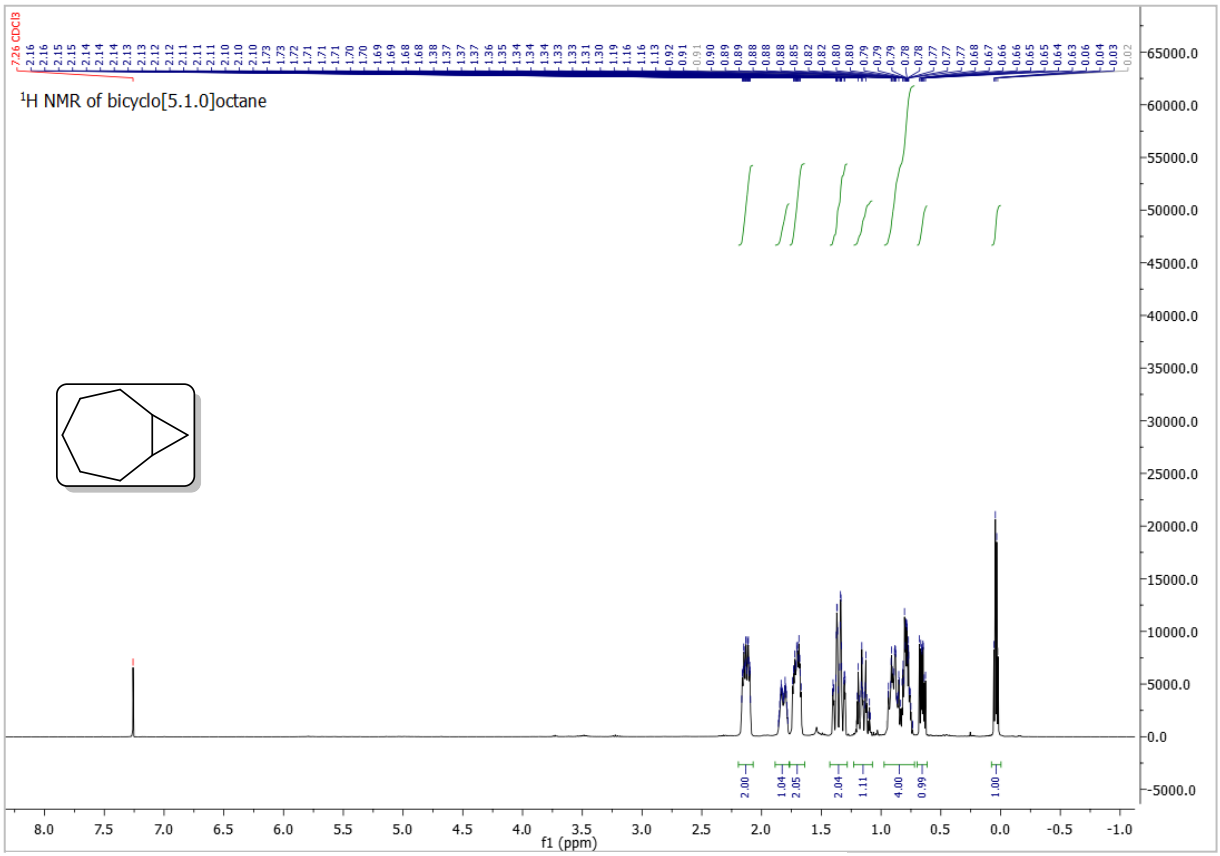


Figure SI-51. ^{1}H NMR spectra of bicyclo[5.1.0]octane (**2c**).

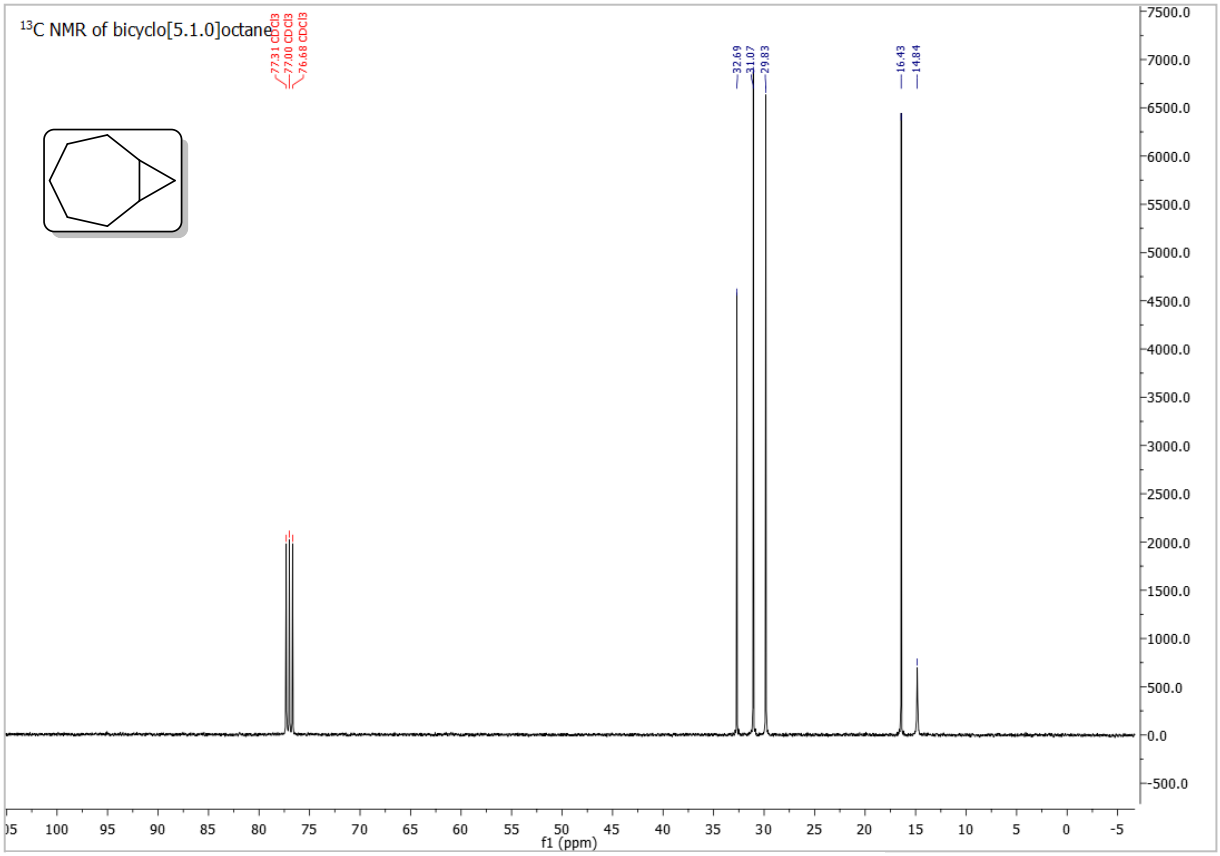


Figure SI-52. ^{13}C NMR spectra of bicyclo[5.1.0]octane (**2c**).

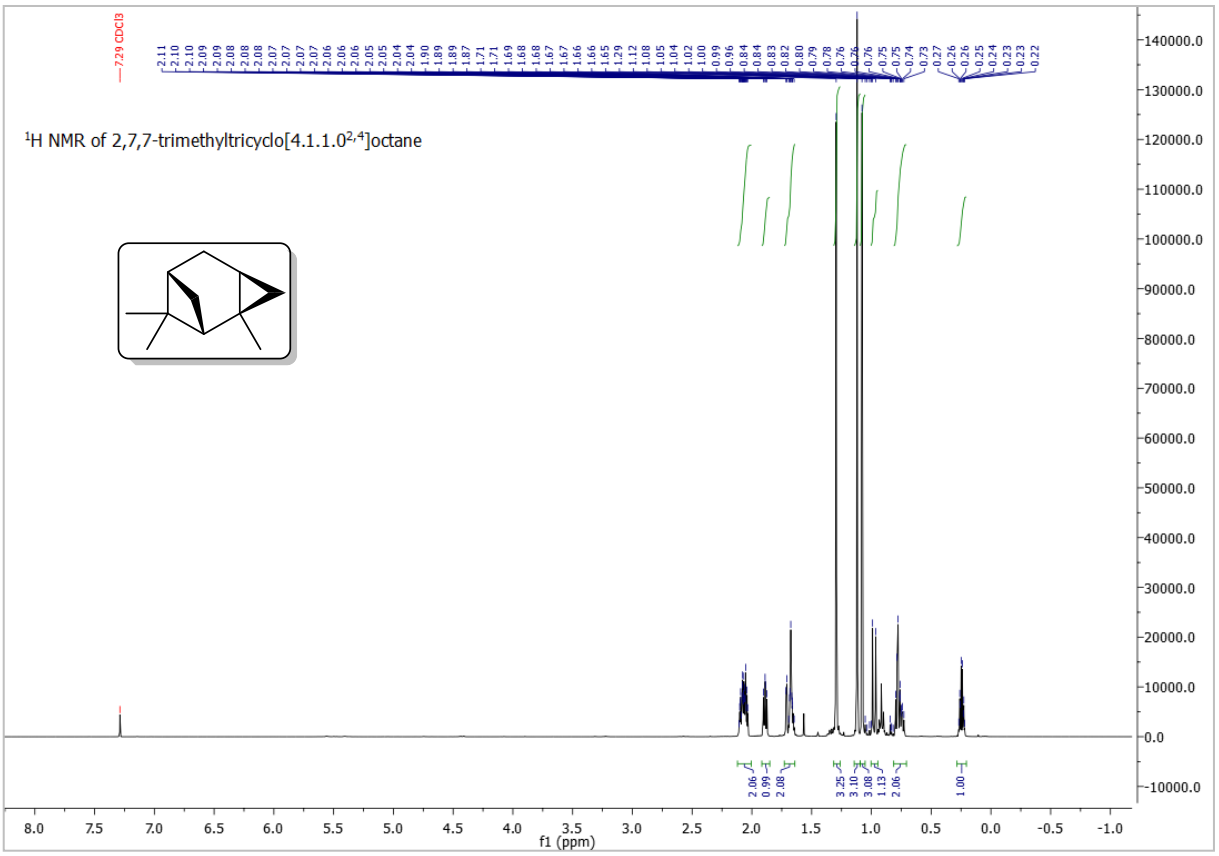


Figure SI-53. ^{1}H NMR spectra of 2,7,7-trimethyltricyclo[4.1.1.0^{2,4}]octane (**2e**).

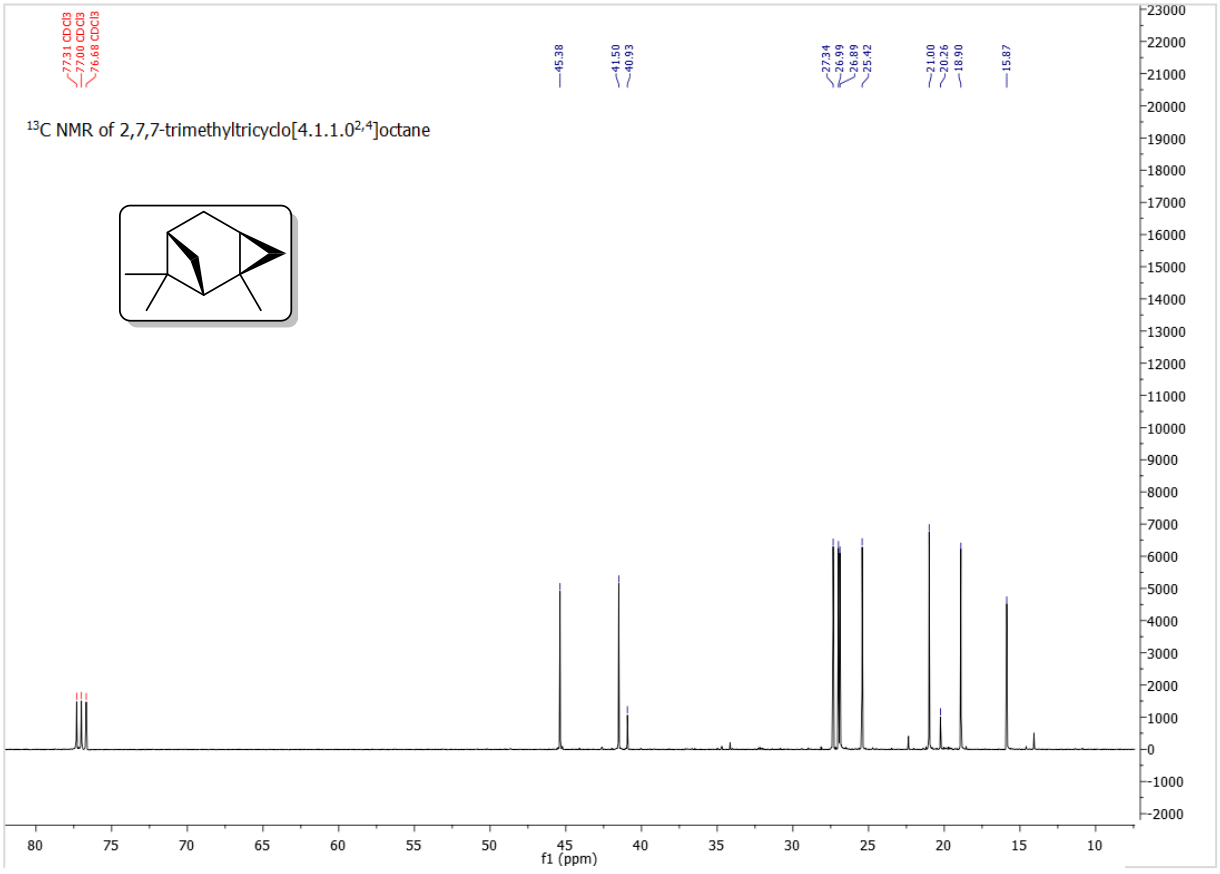


Figure SI-54. ^{13}C NMR spectra of 2,7,7-trimethyltricyclo[4.1.1.0^{2,4}]octane (**2e**).

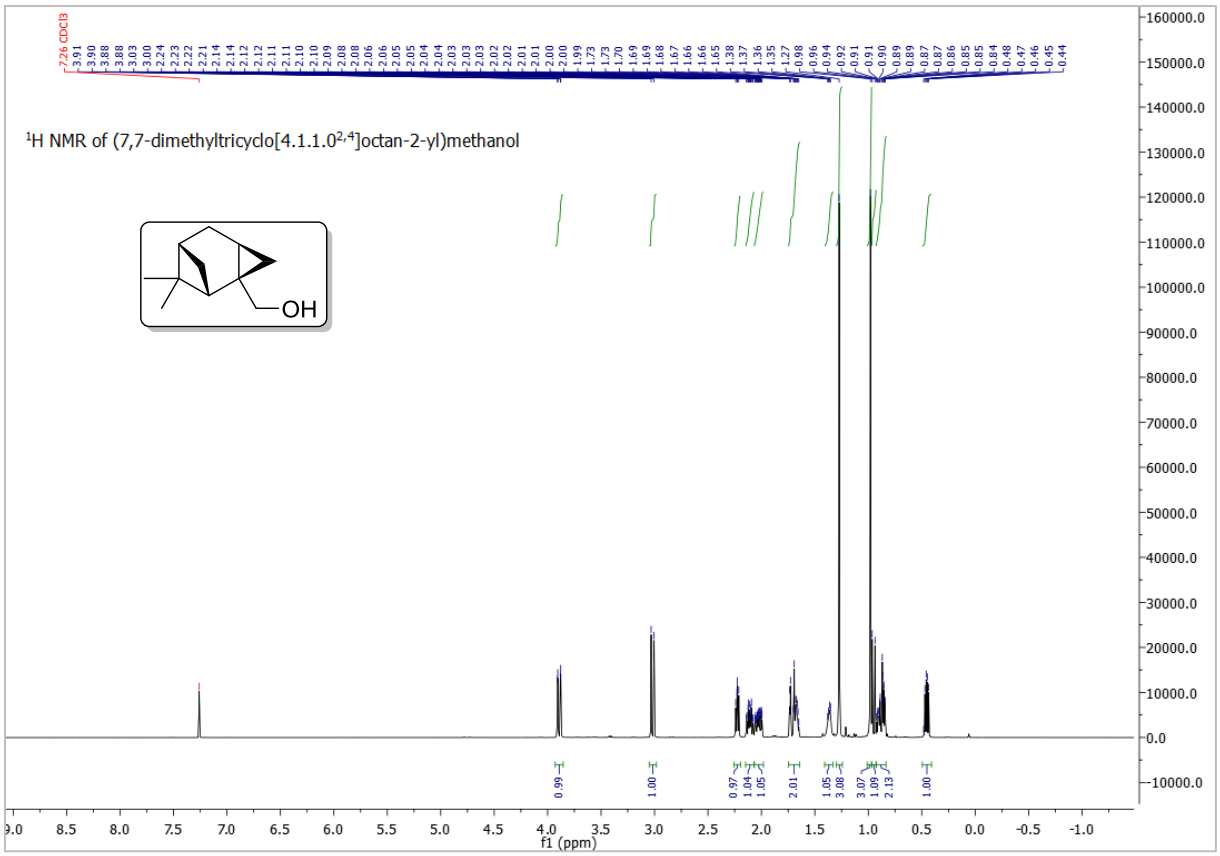


Figure SI-55. ^{1}H NMR spectra of (7,7-dimethyltricyclo[4.1.1.o^{2,4}]octan-2-yl)methanol (**2f**).

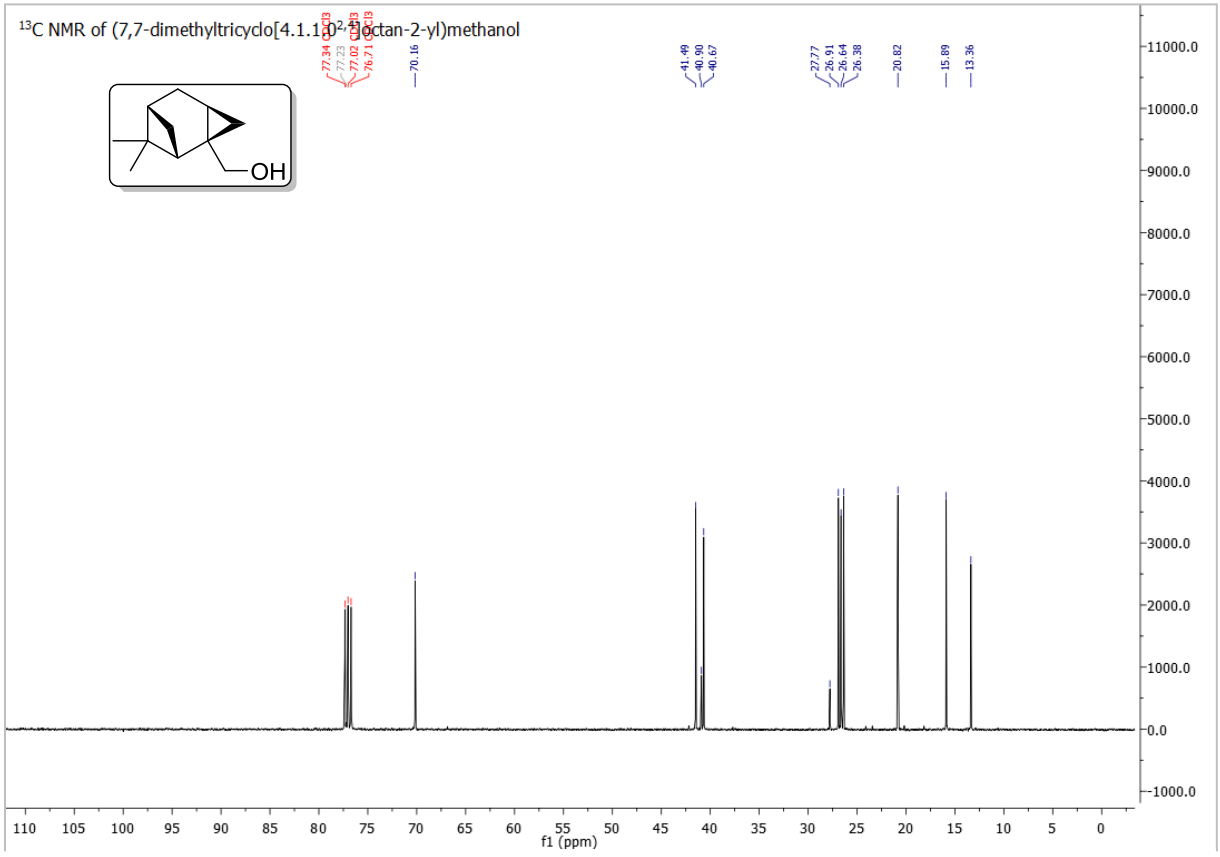


Figure SI-56. ^{13}C NMR spectra of (7,7-dimethyltricyclo[4.1.1.o^{2,4}]octan-2-yl)methanol (**2f**).

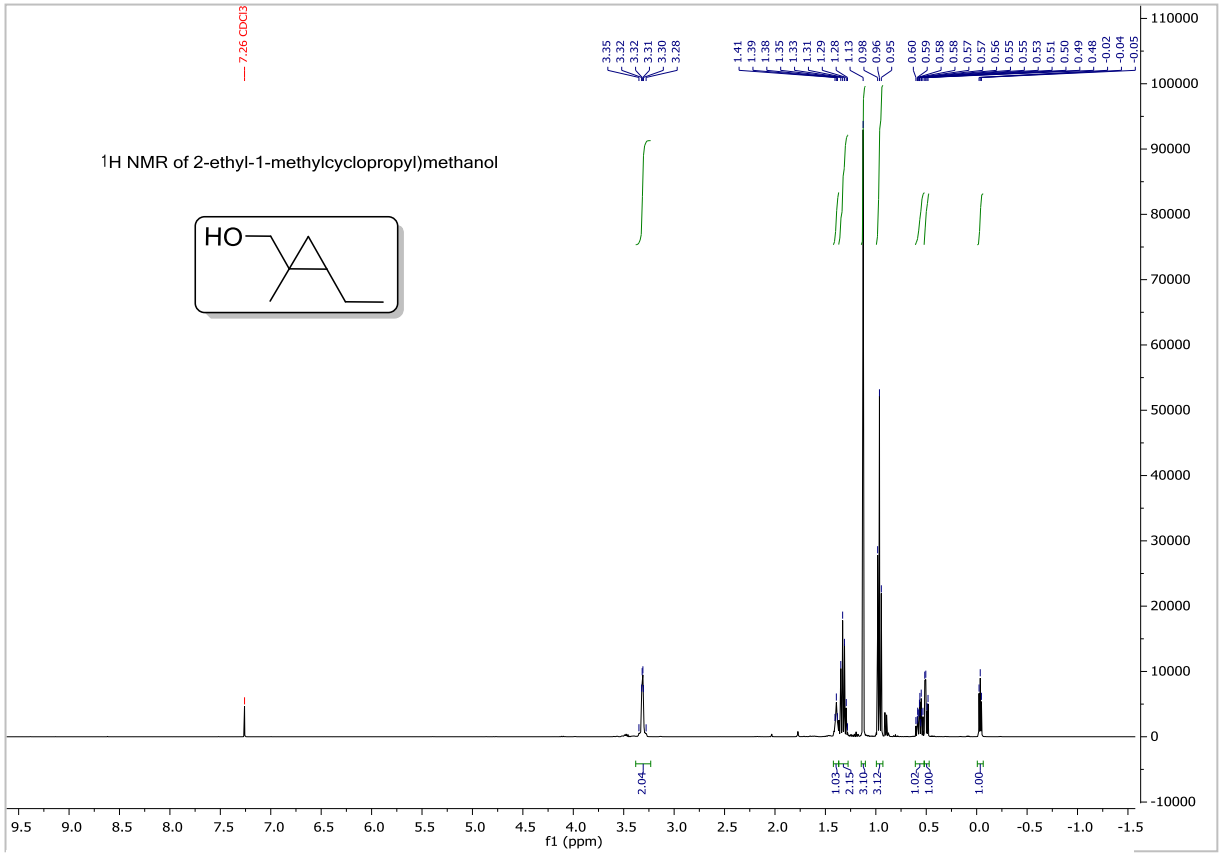
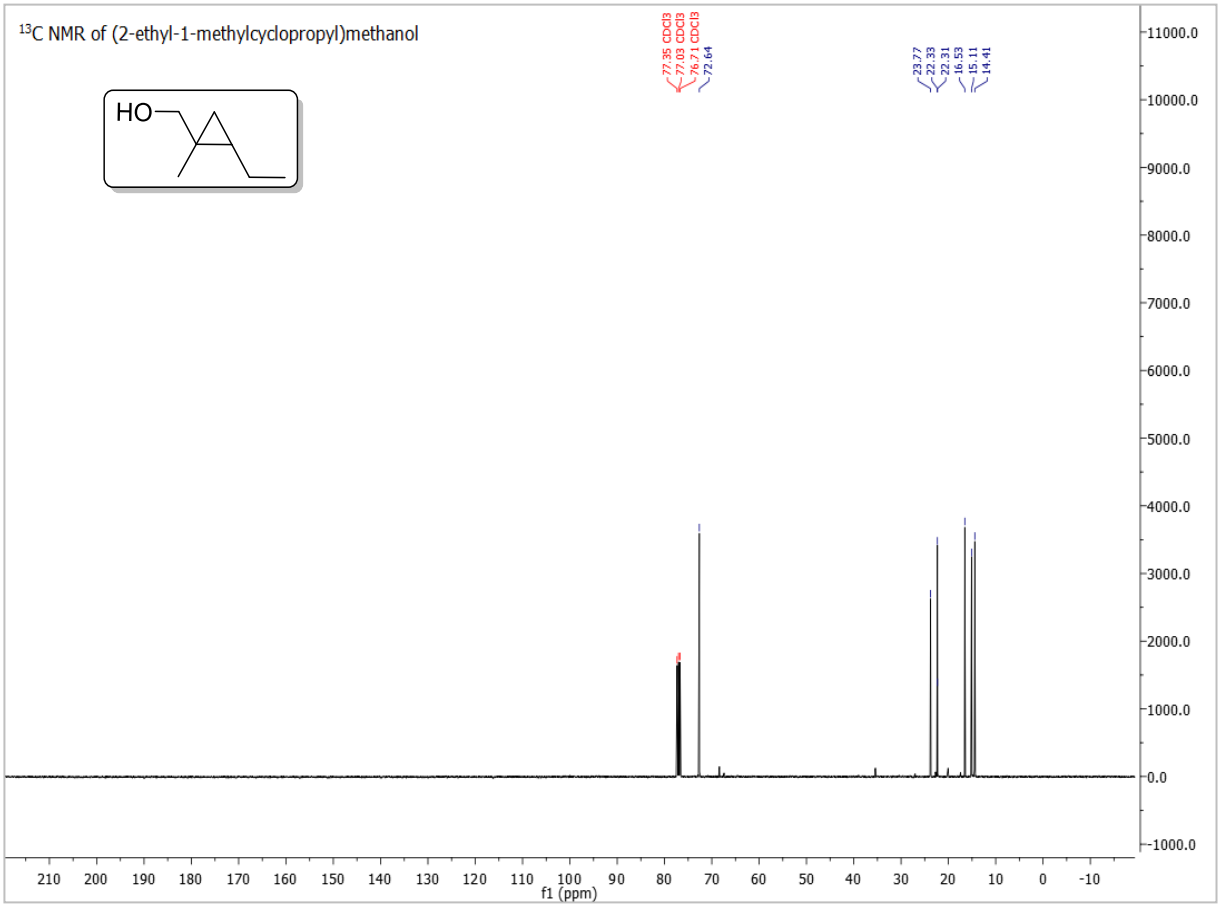


Figure SI-57. ^{1}H NMR spectra of (2-ethyl-1-methylcyclopropyl)methanol (**2g**).



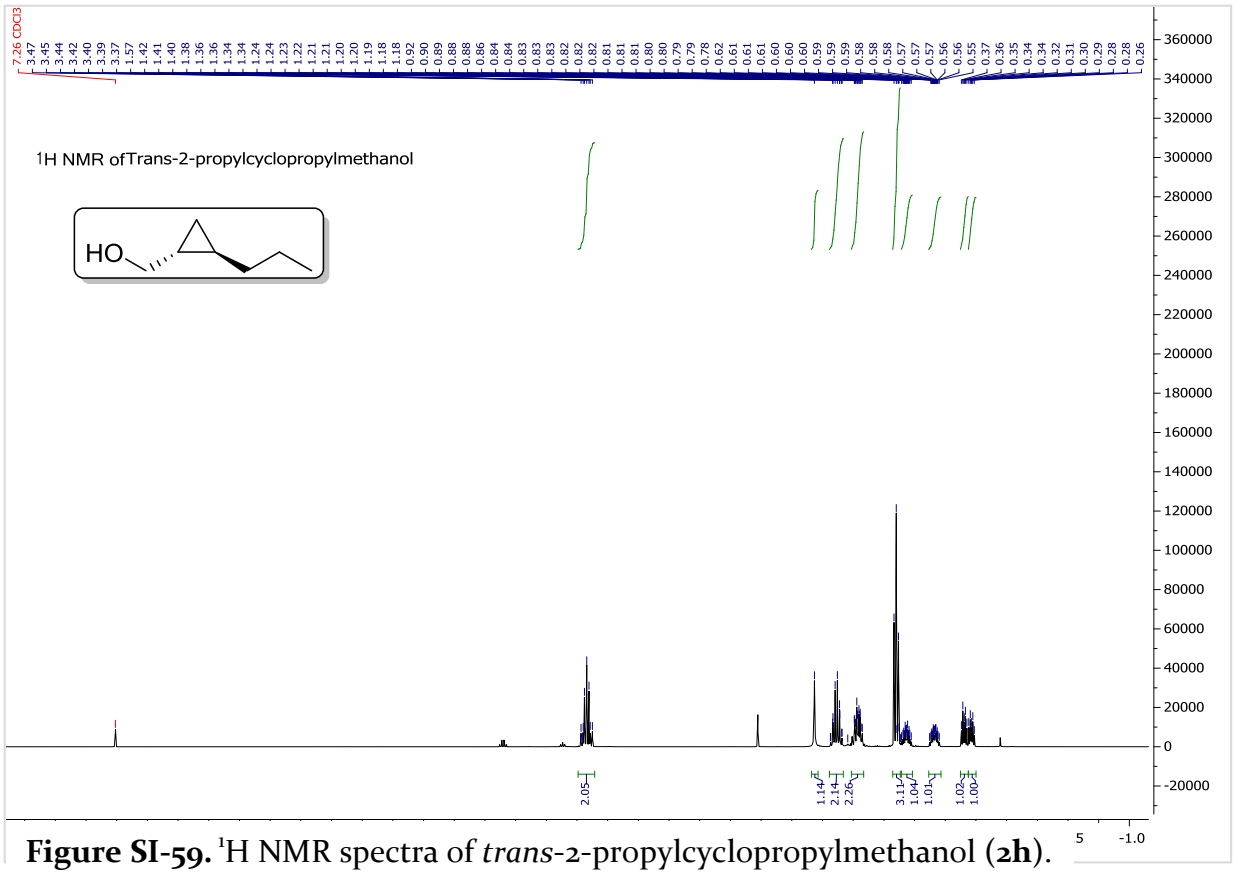


Figure SI-59. ^{1}H NMR spectra of *trans*-2-propylcyclopropylmethanol (**2h**).

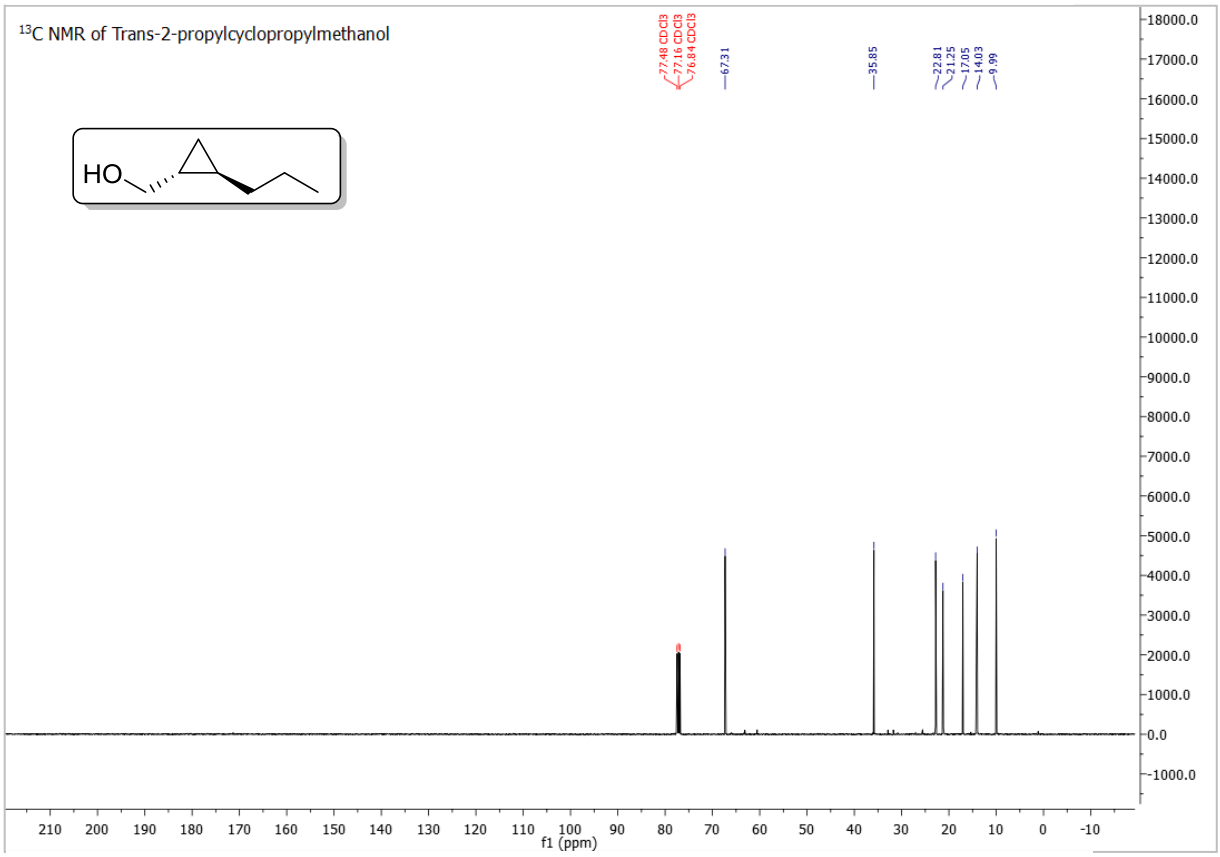


Figure SI-60. ^{13}C NMR spectra of *trans*-2-propylcyclopropylmethanol (**2h**).

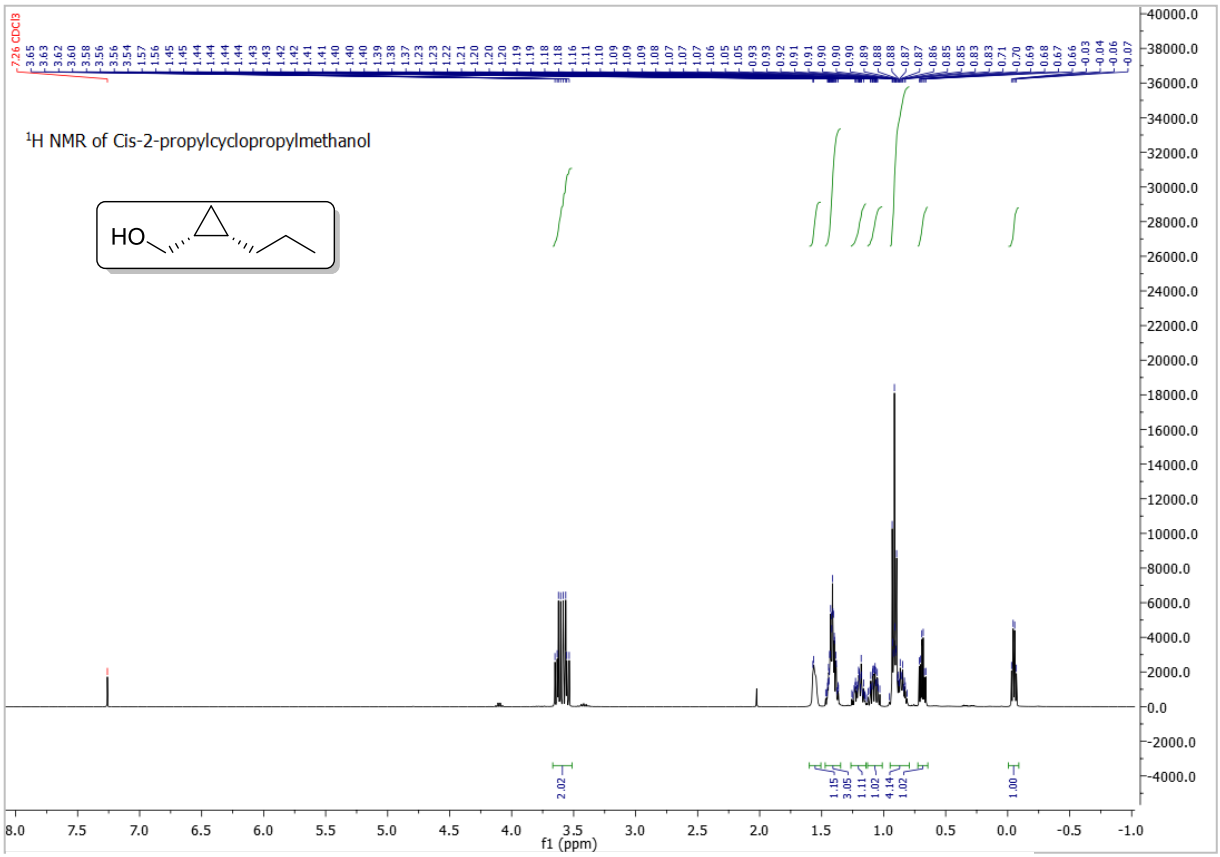


Figure SI-61. ^{1}H NMR spectra of *cis*-2-propylcyclopropylmethanol (**2i**).

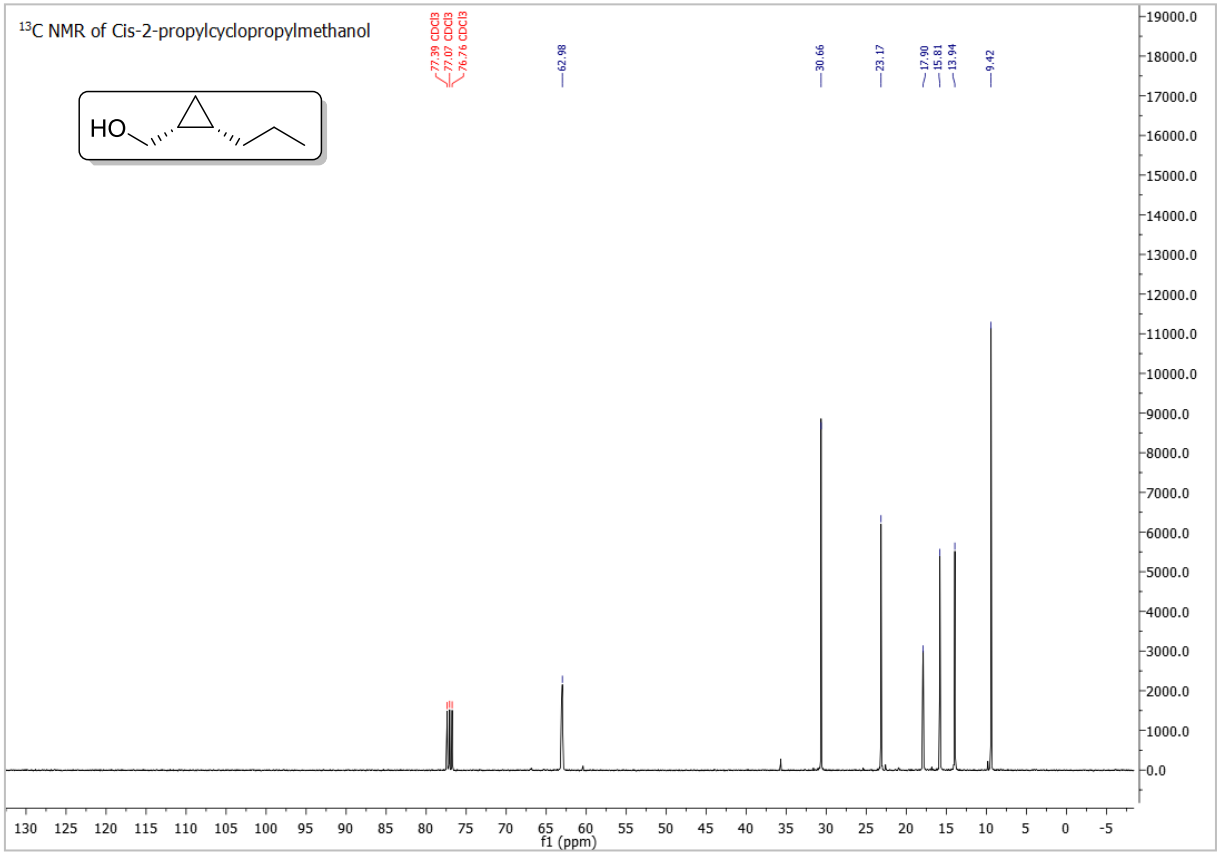


Figure SI-62. ^{13}C NMR spectra of *cis*-2-propylcyclopropylmethanol (**2i**).

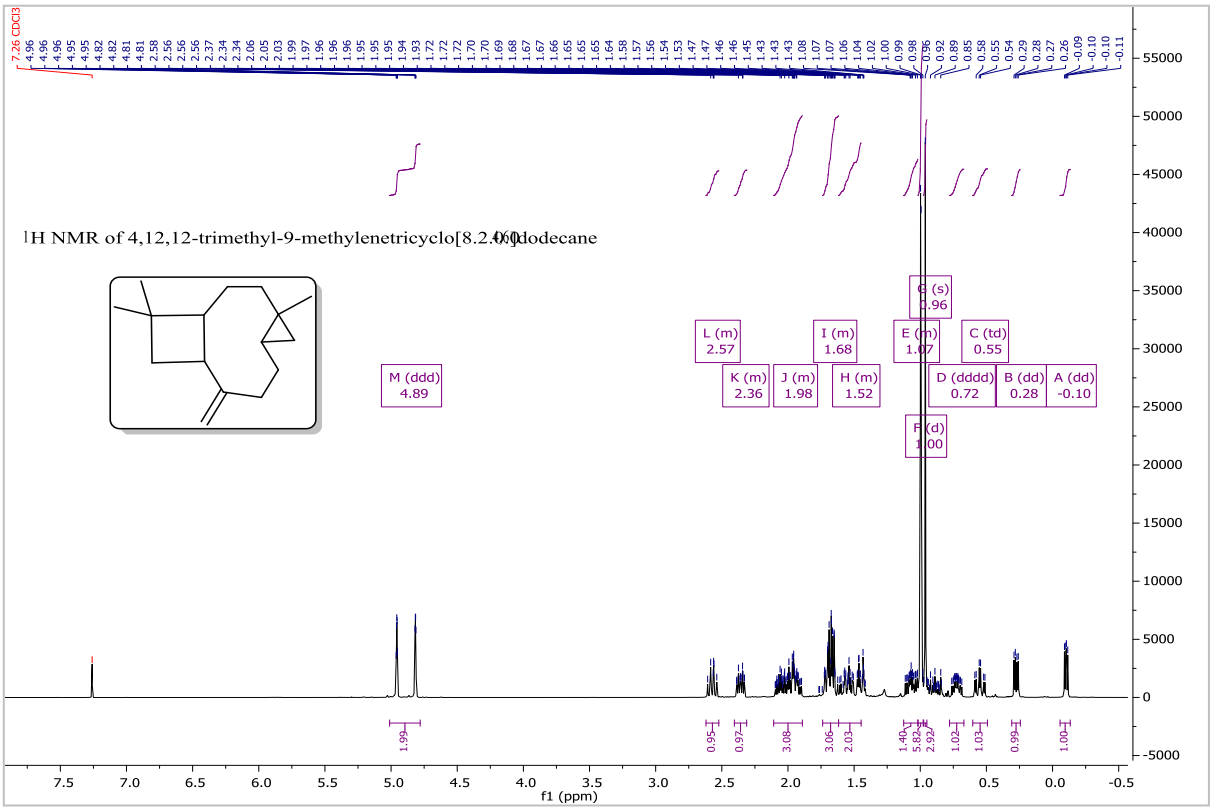


Figure SI-63. ^{1}H NMR spectra of 4,12,12-trimethyl-9-methylenetricyclo[8.2.0.0^{4,6}]dodecane (**2j**).

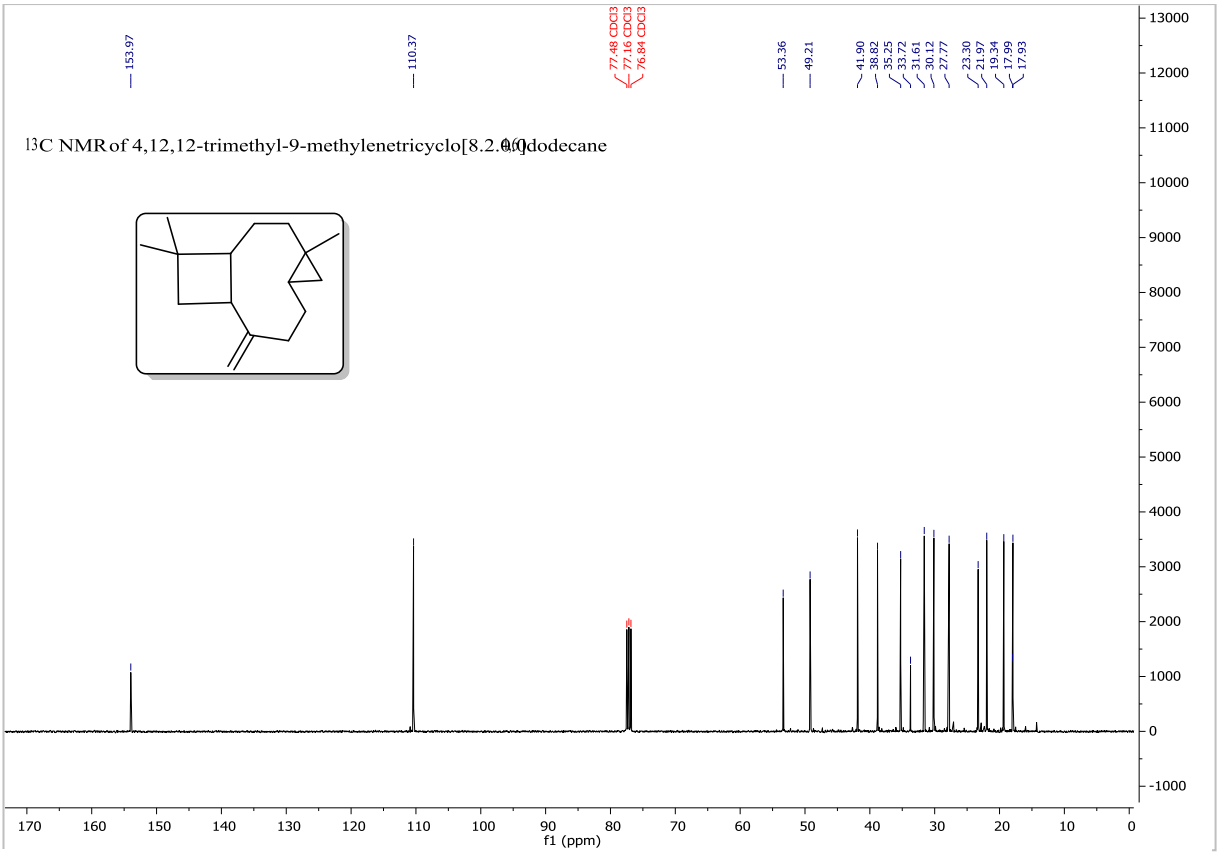


Figure SI-64. ^{13}C NMR spectra of 4,12,12-trimethyl-9-methylenetricyclo[8.2.0.0^{4,6}]dodecane (**2j**).

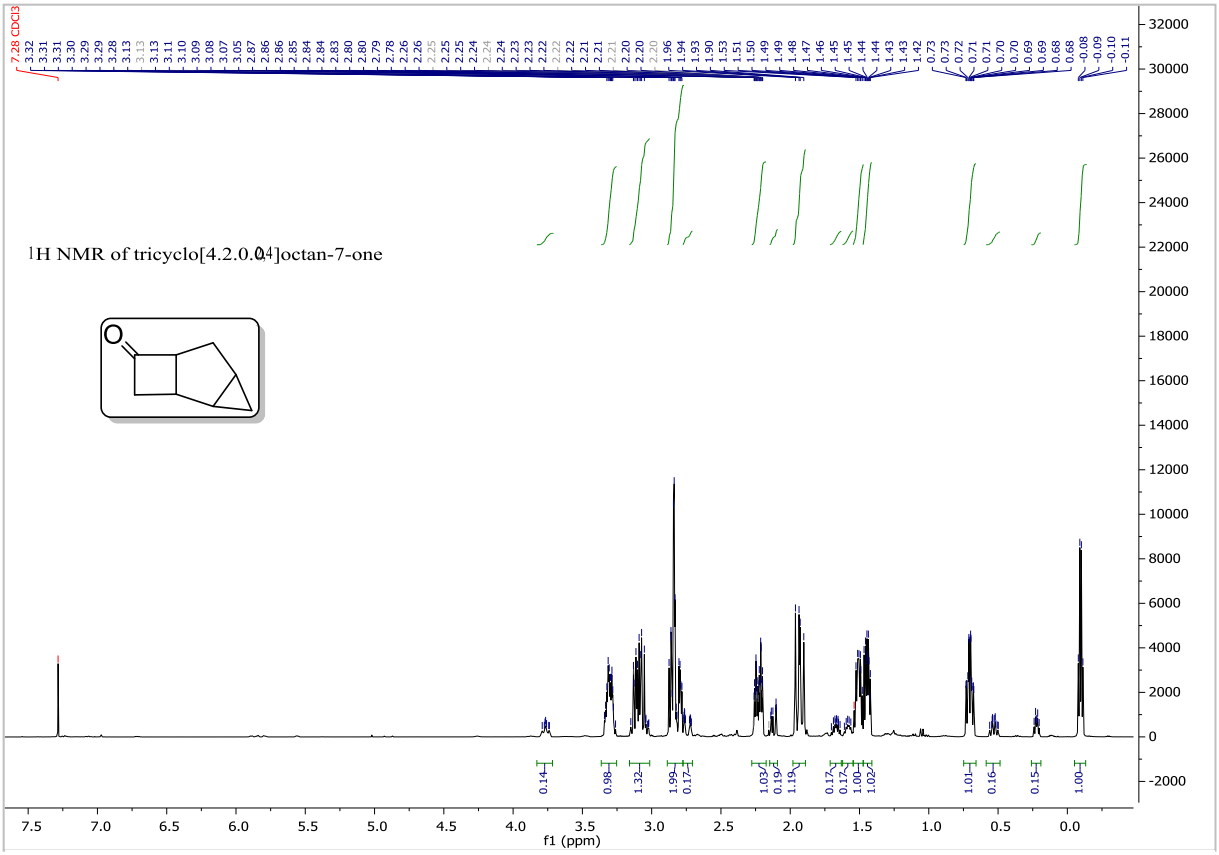
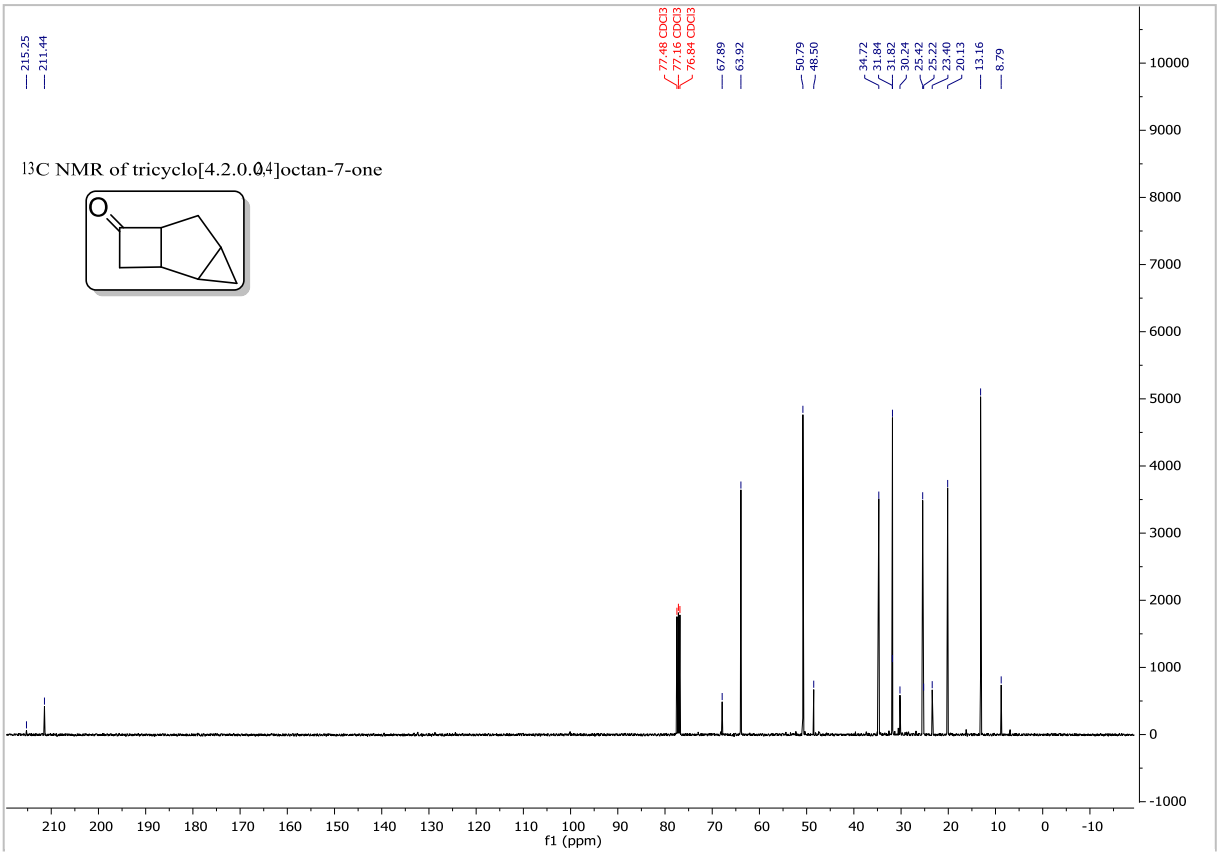


Figure SI-65. ^{1}H NMR spectra of **t**ricyclo[4.2.0.0^{2,4}]octan-7-one (**2m**).



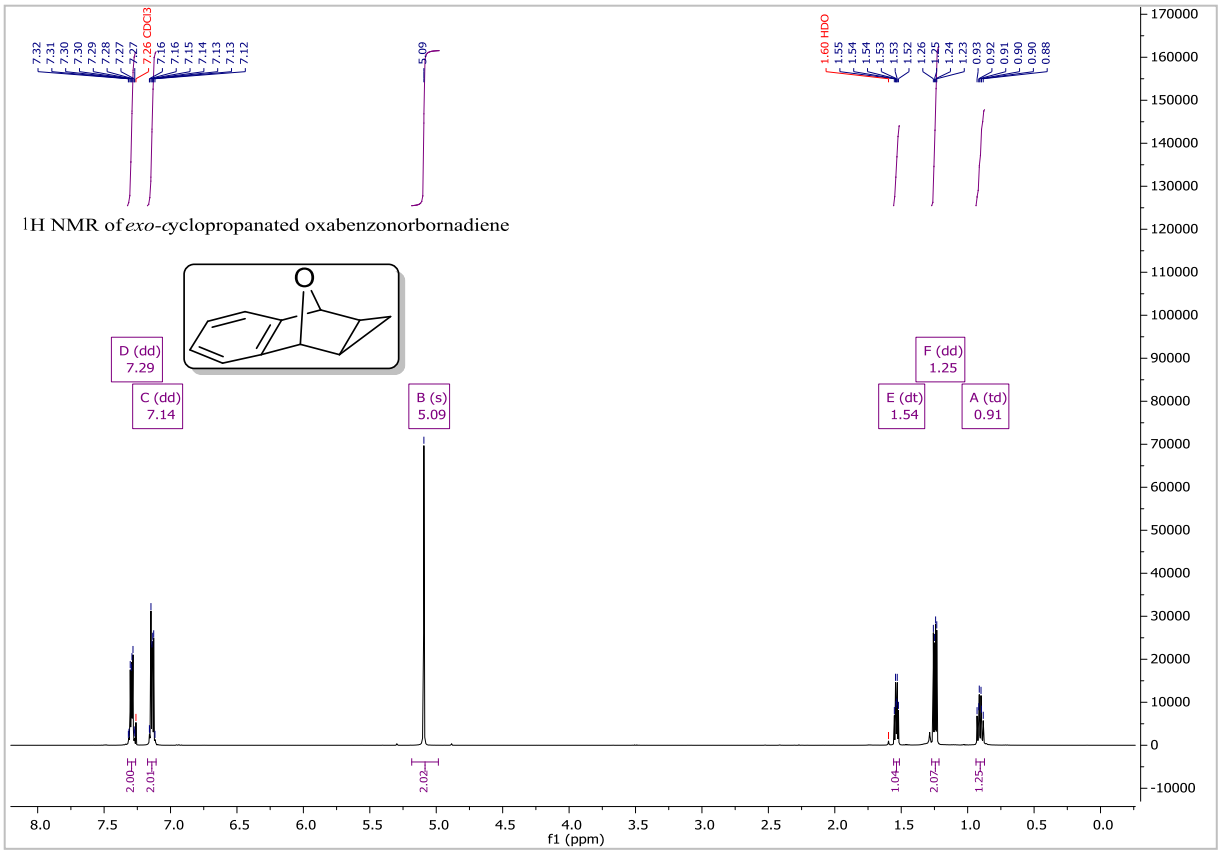


Figure SI-67. ^{1}H NMR spectra of *exo*-cyclopropanated oxabenzonorbornadiene (**2n**).

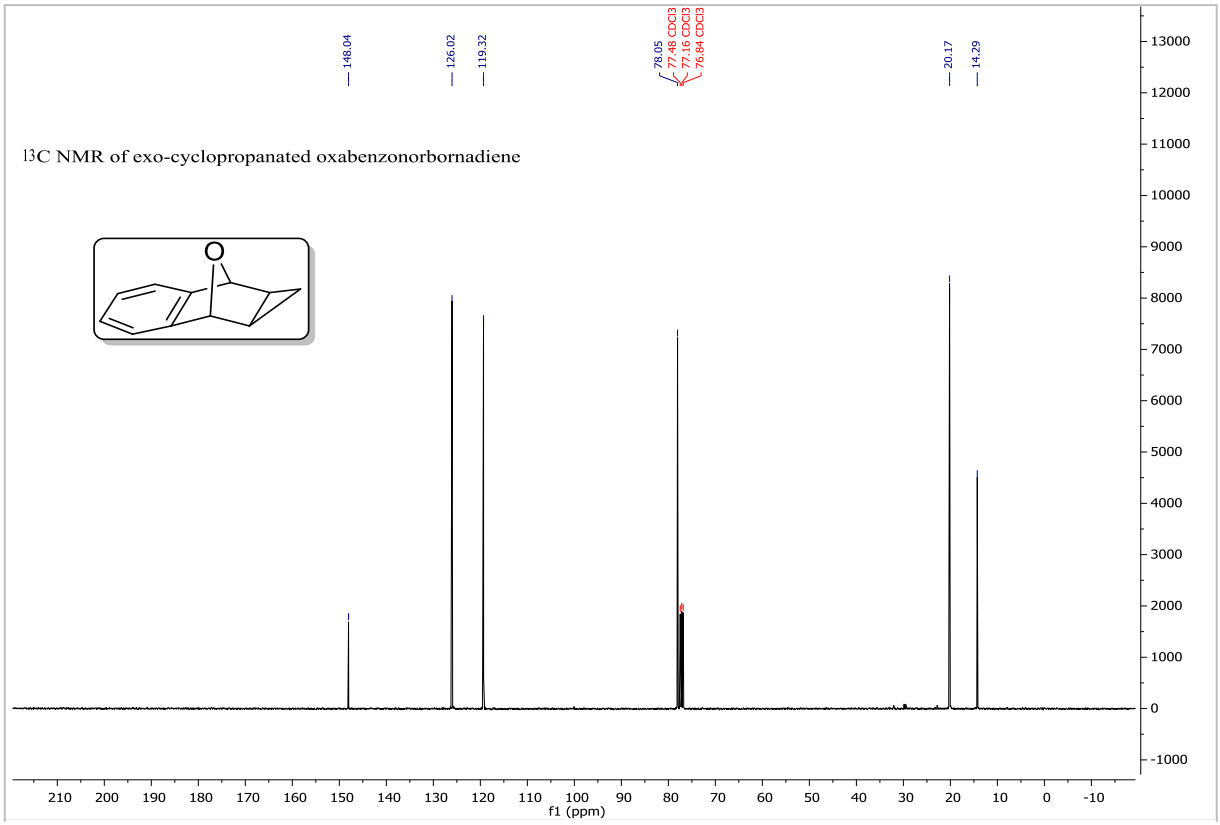


Figure SI-68. ^{13}C NMR spectra of *exo*-cyclopropanated oxabenzonorbornadiene (**2n**).

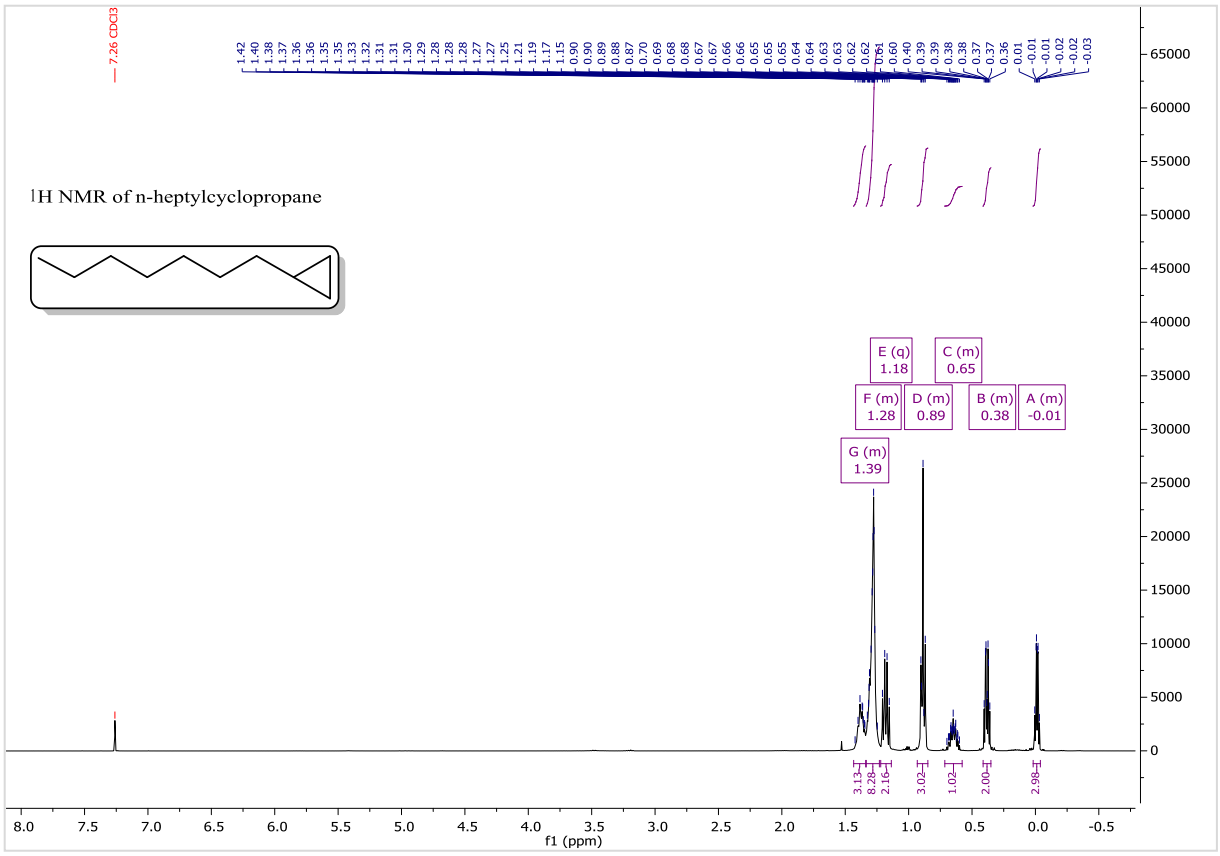


Figure SI-69. ^{1}H NMR spectra of n-heptylcyclopropane (**2p**).

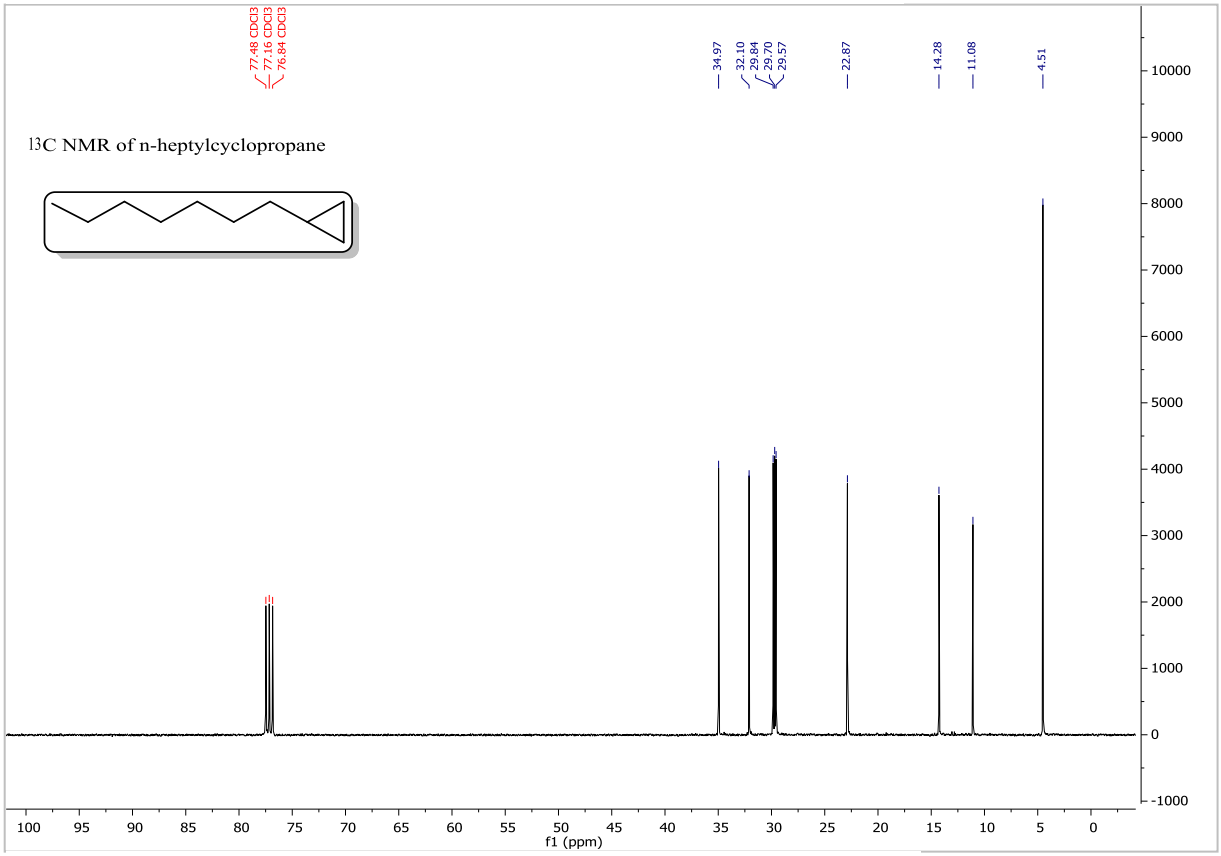


Figure SI-70. ^{13}C NMR spectra of n-heptylcyclopropane (**2p**).

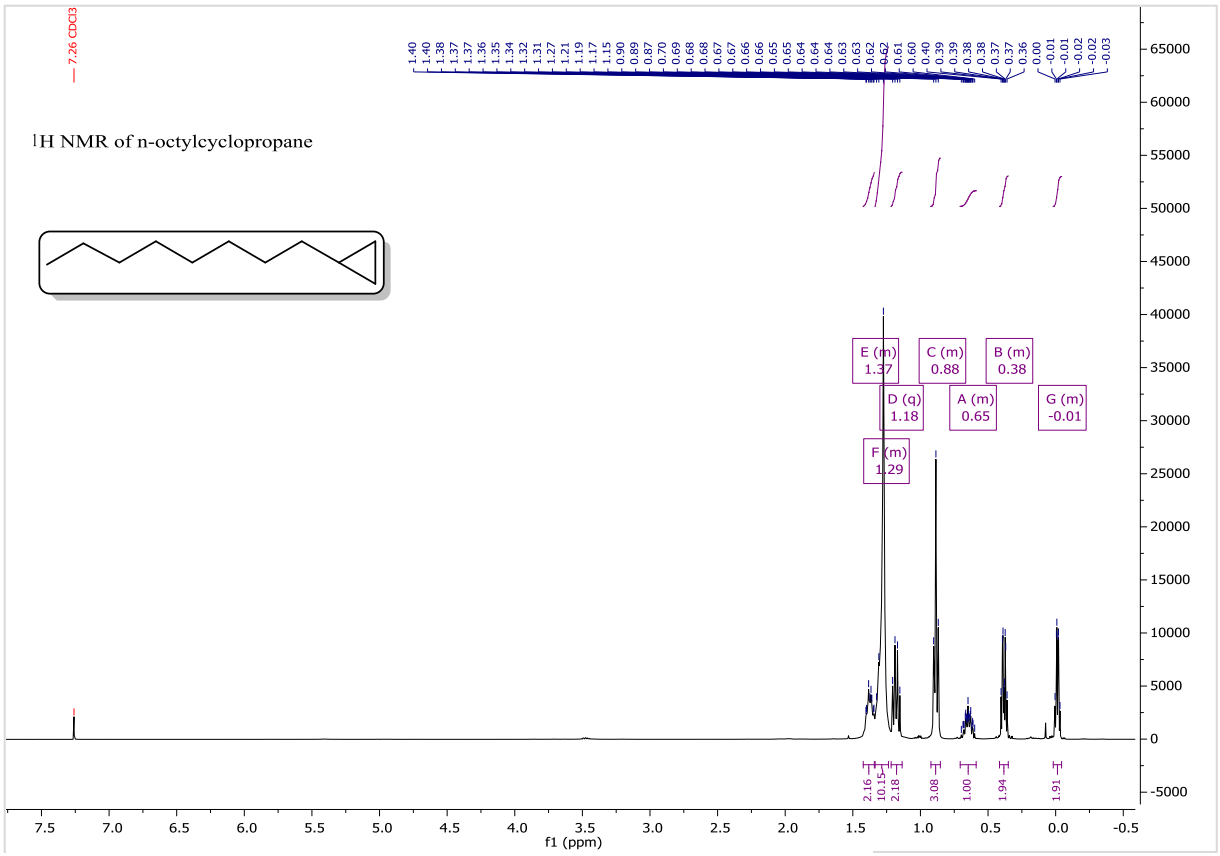


Figure SI-71. ^{1}H NMR spectra of n-octylcyclopropane (**2q**).

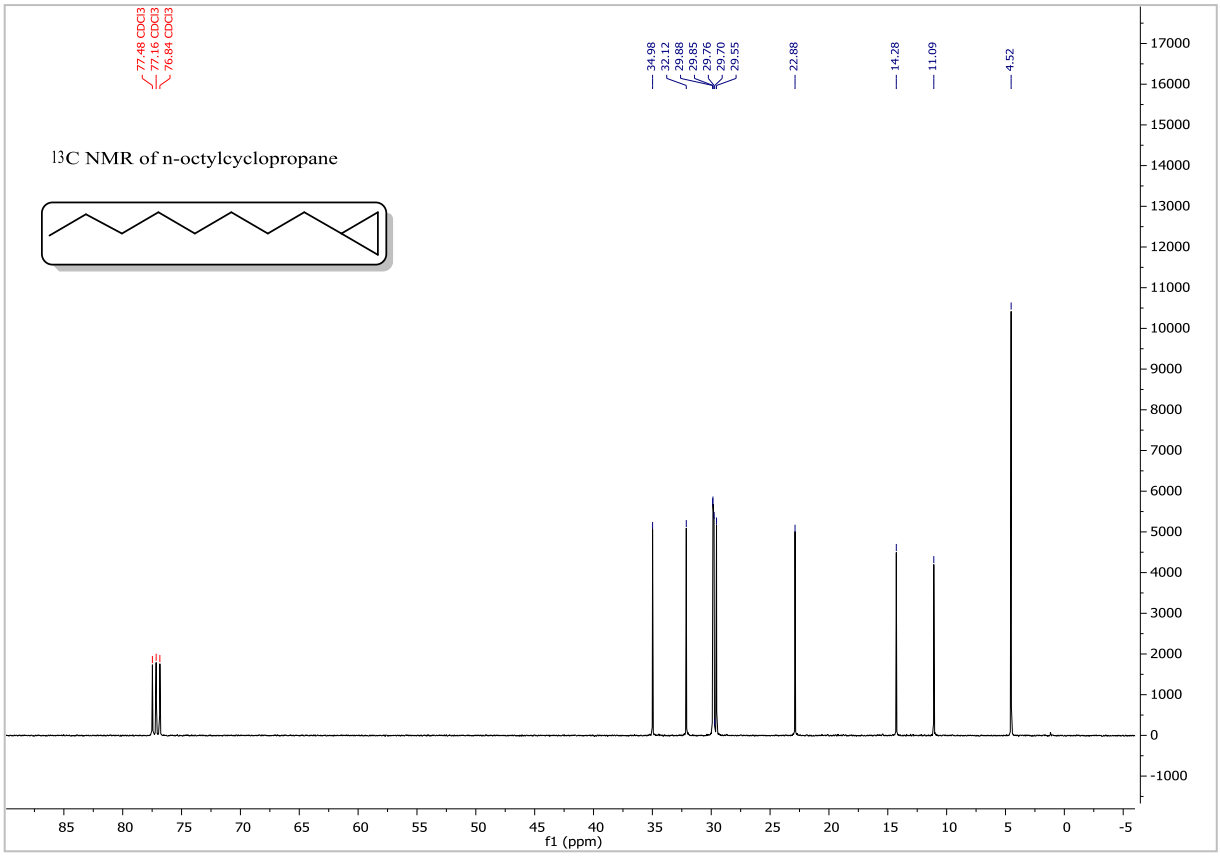


Figure SI-72. ^{13}C NMR spectra of n-octylcyclopropane (**2q**).

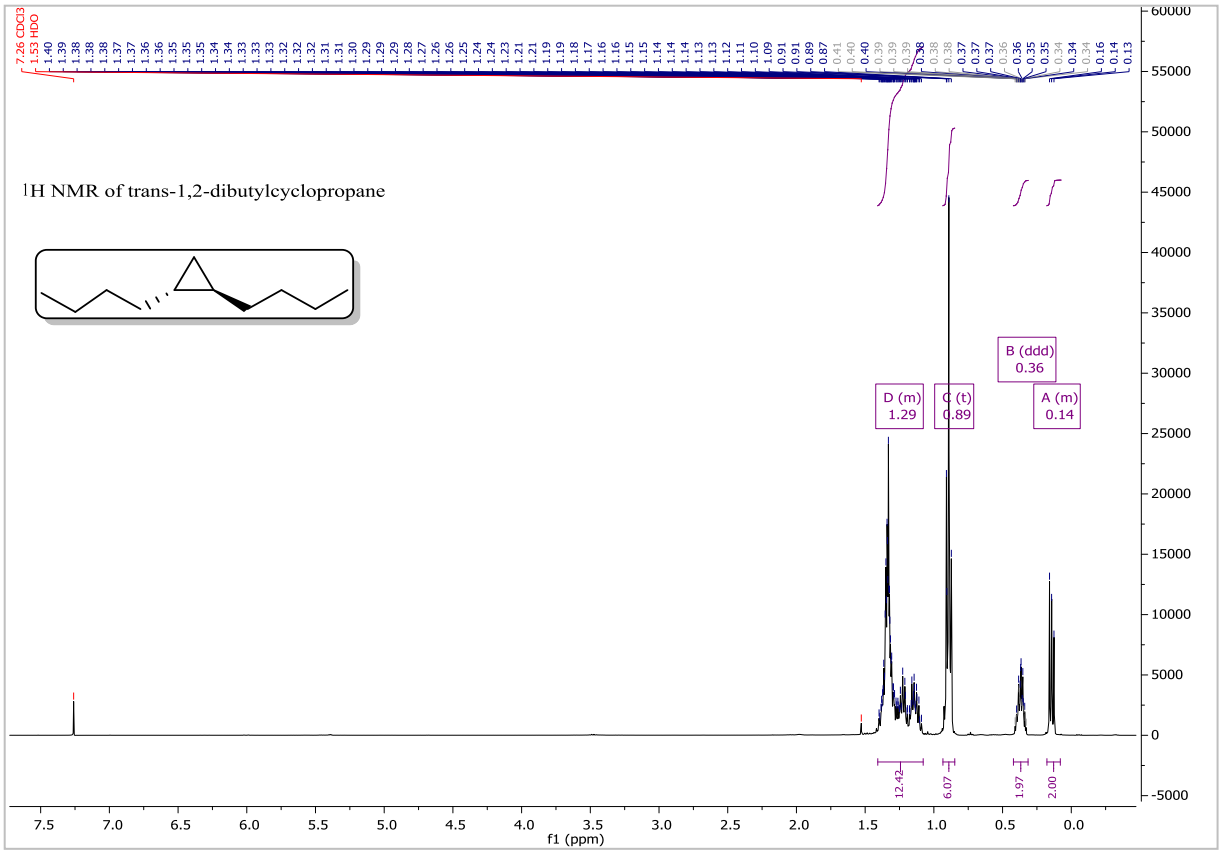


Figure SI-73. ^{1}H NMR spectra of *trans*-1,2-dibutylcyclopropane (**2s**).

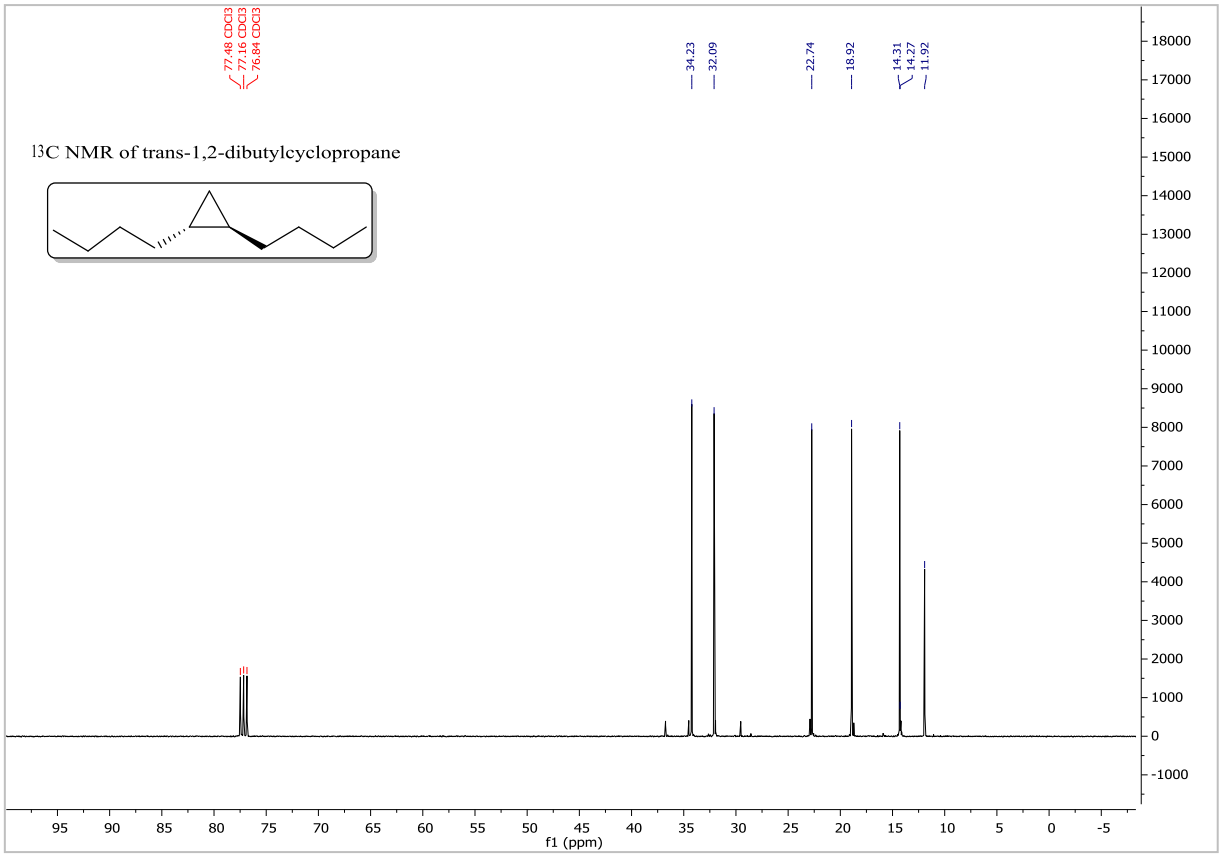


Figure SI-74. ^{13}C NMR spectra of *trans*-1,2-dibutylcyclopropane (**2s**).

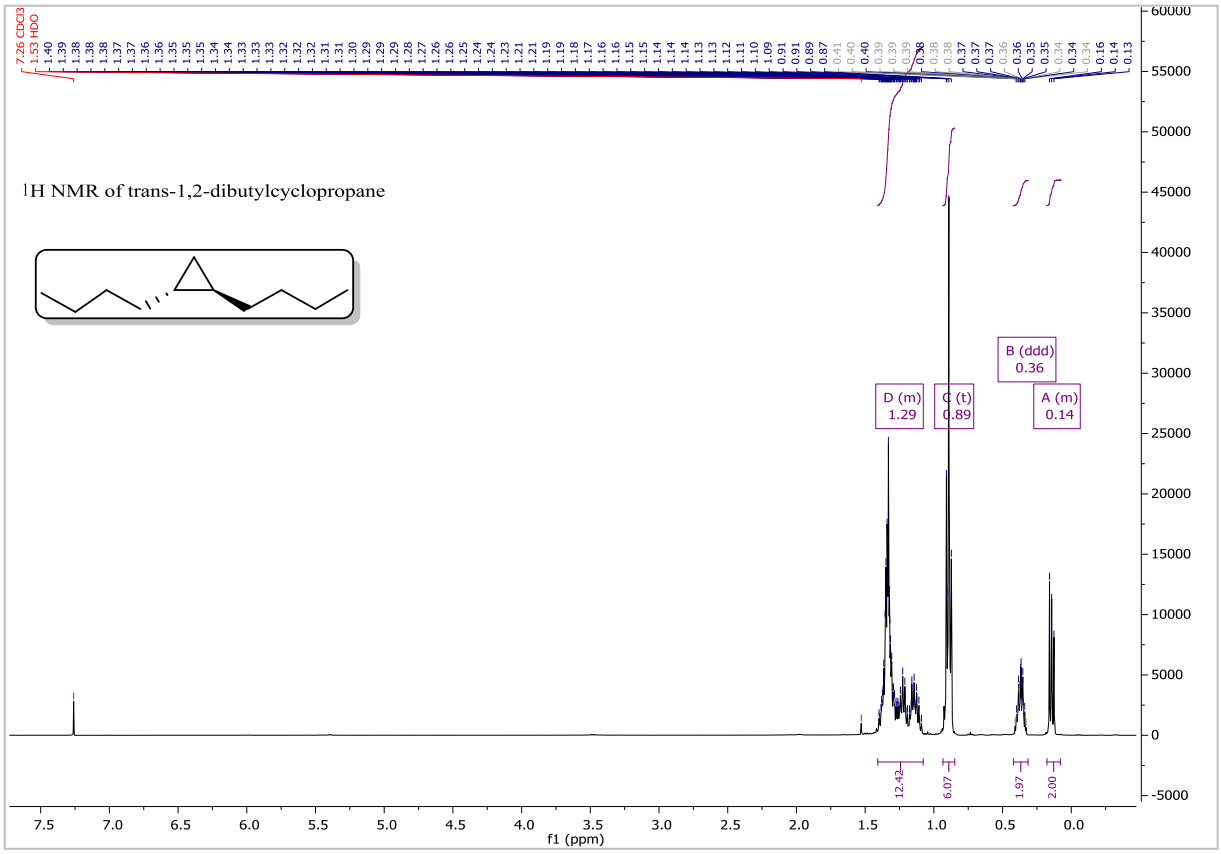


Figure SI-75. ^{1}H NMR spectra of *cis*-1,2-dibutylcyclopropane (**2t**).

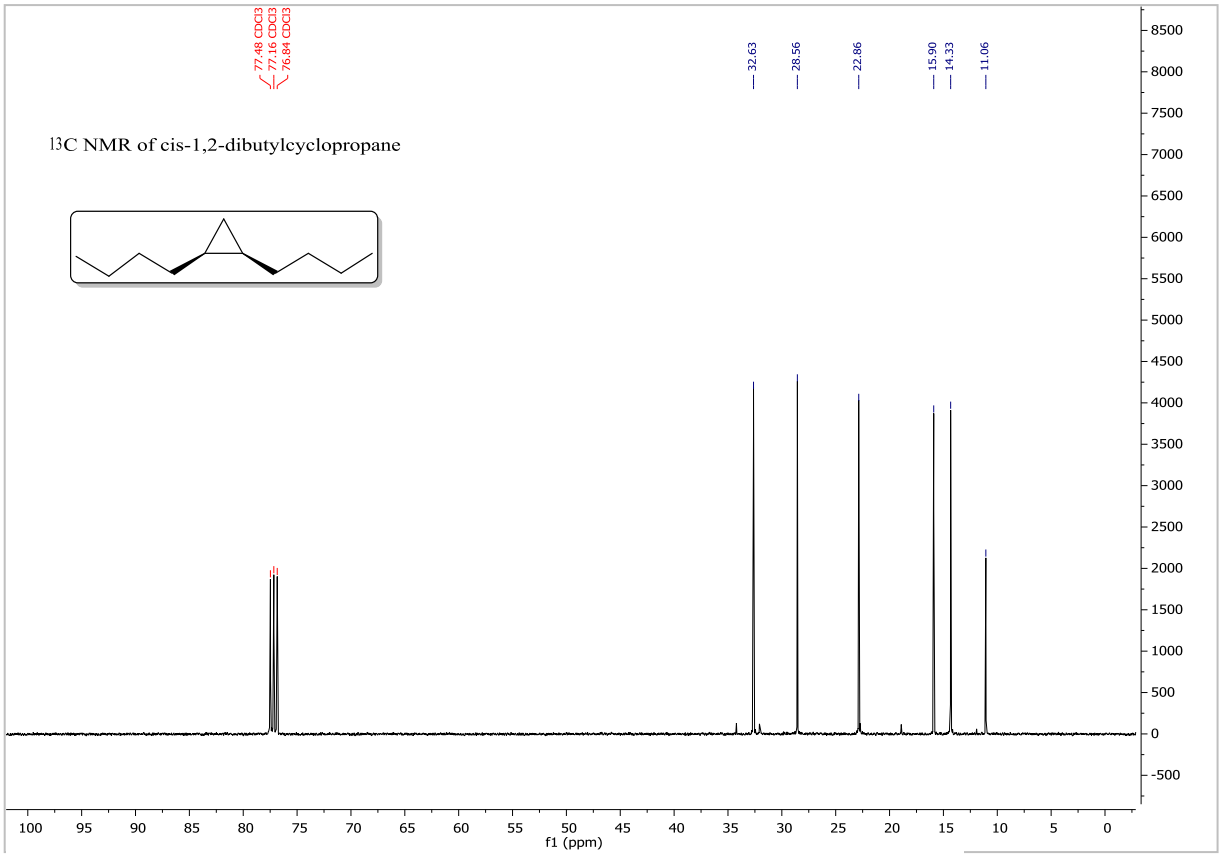


Figure SI-76. ^{13}C NMR spectra of *cis*-1,2-dibutylcyclopropane (**2t**).

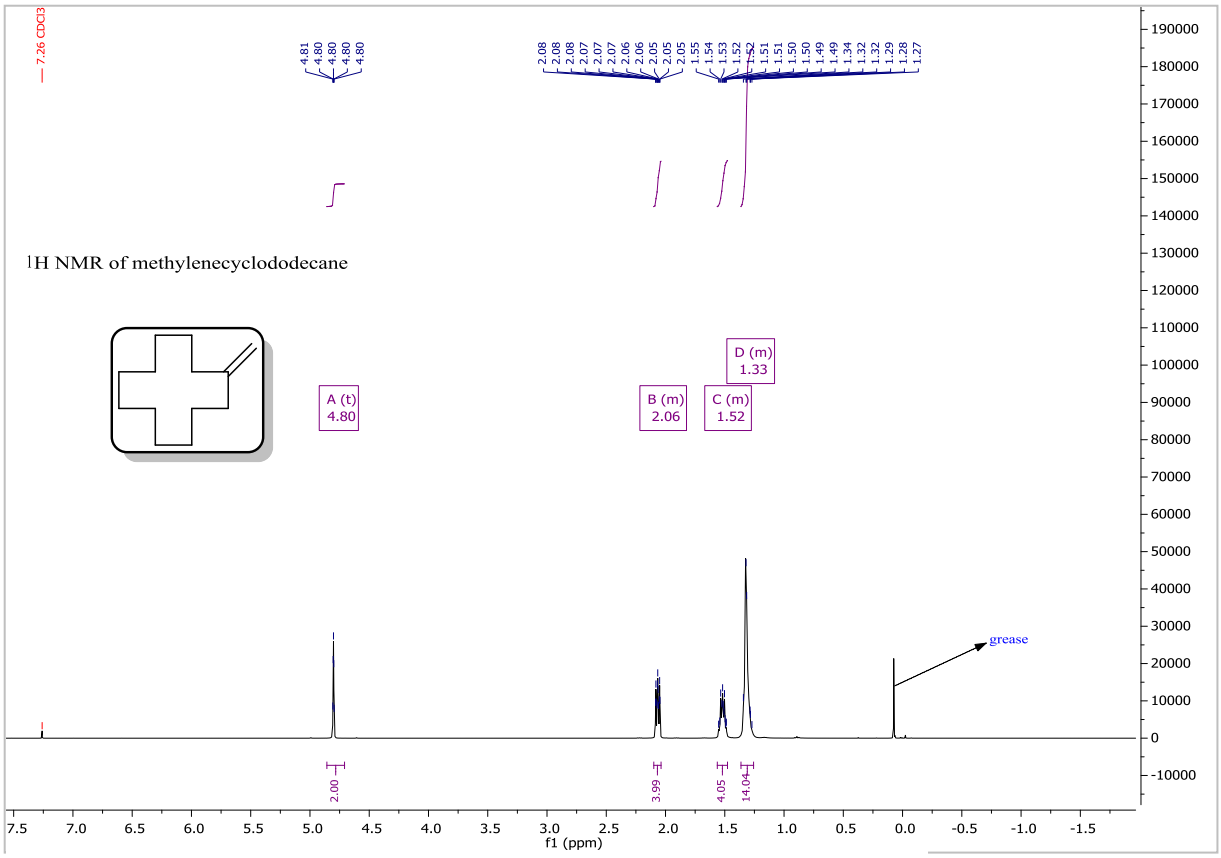


Figure SI-77. ^{1}H NMR spectra of methylenecyclododecane (**3k**).

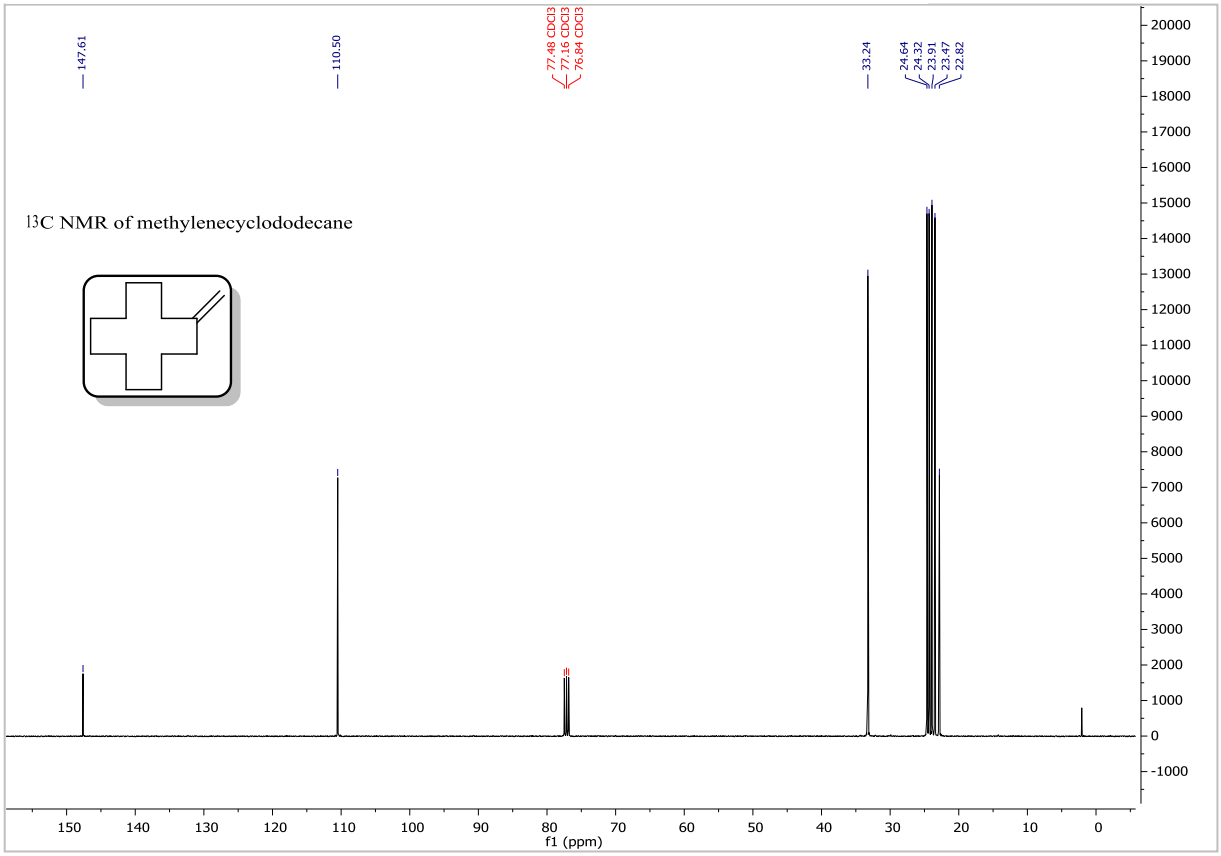


Figure SI-78. ^{13}C NMR spectra of methylenecyclododecane

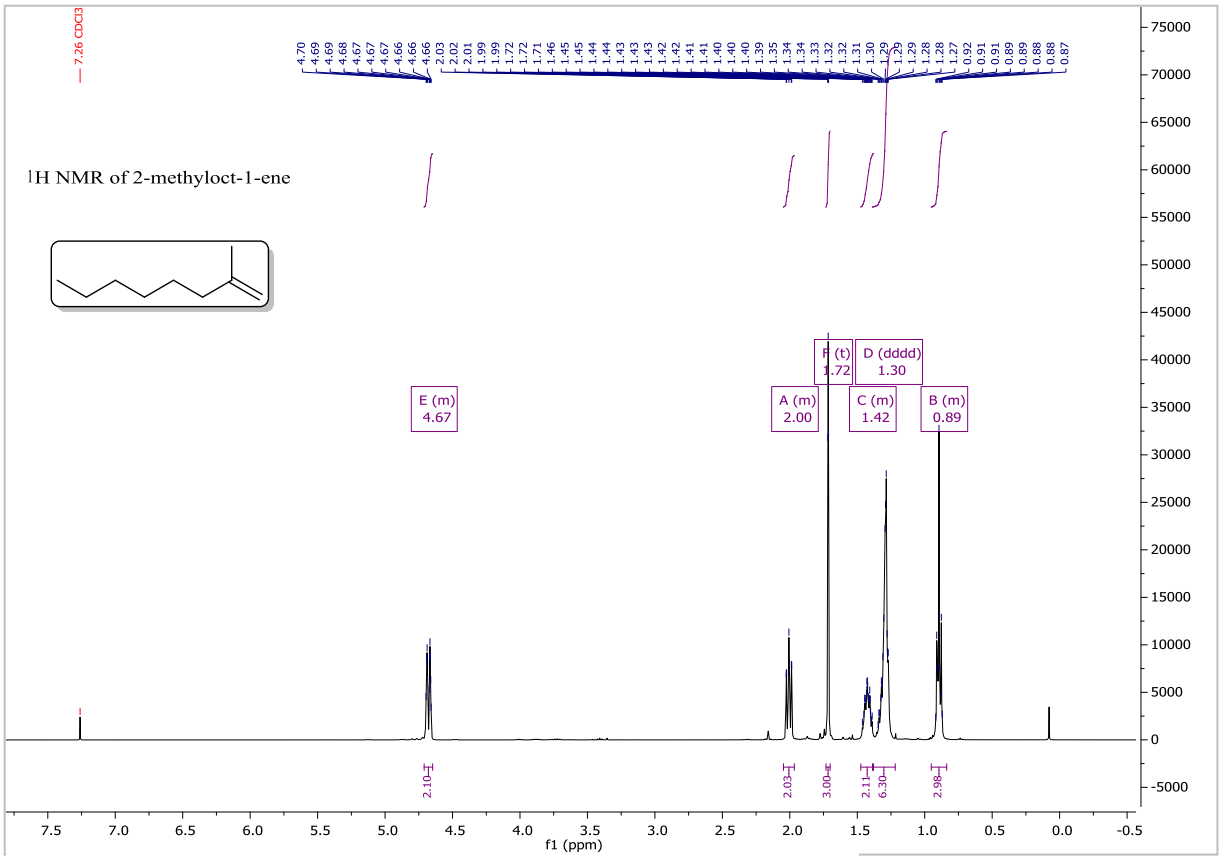


Figure SI-79. ^{1}H NMR spectra of 2-methyloct-1-ene (**30a**).

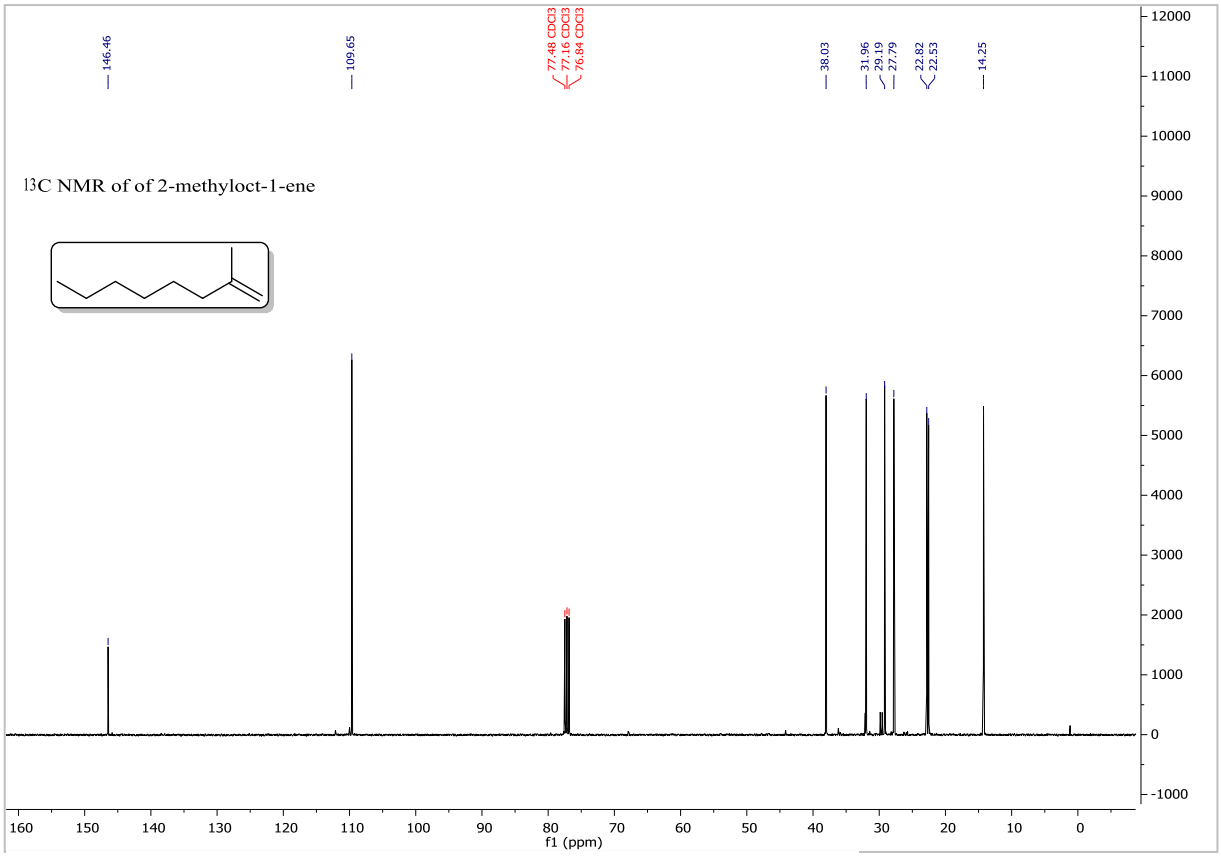


Figure SI-80. ^{13}C NMR spectra of 2-methyloct-1-ene (**30a**).

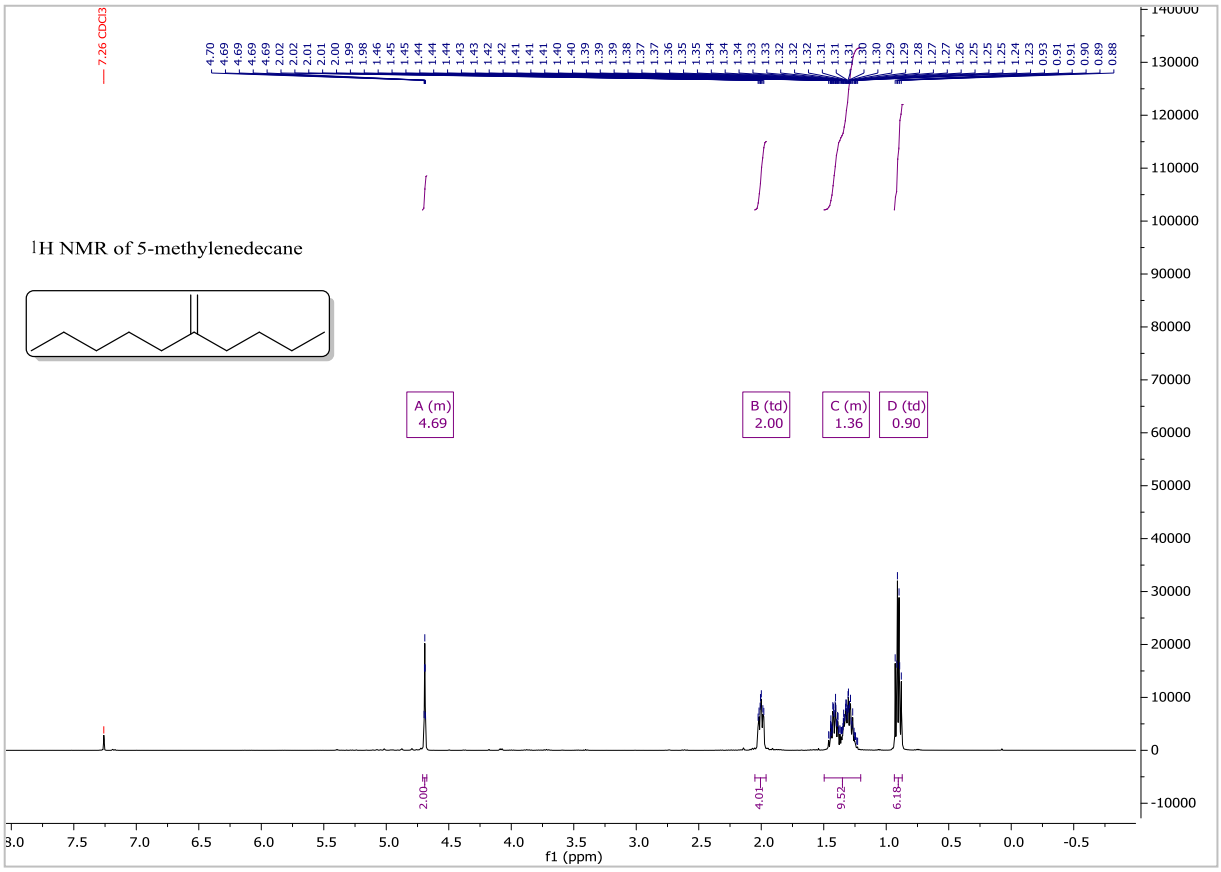


Figure SI-81. ^{1}H NMR spectra of 5-methylenedecane (**3s**).

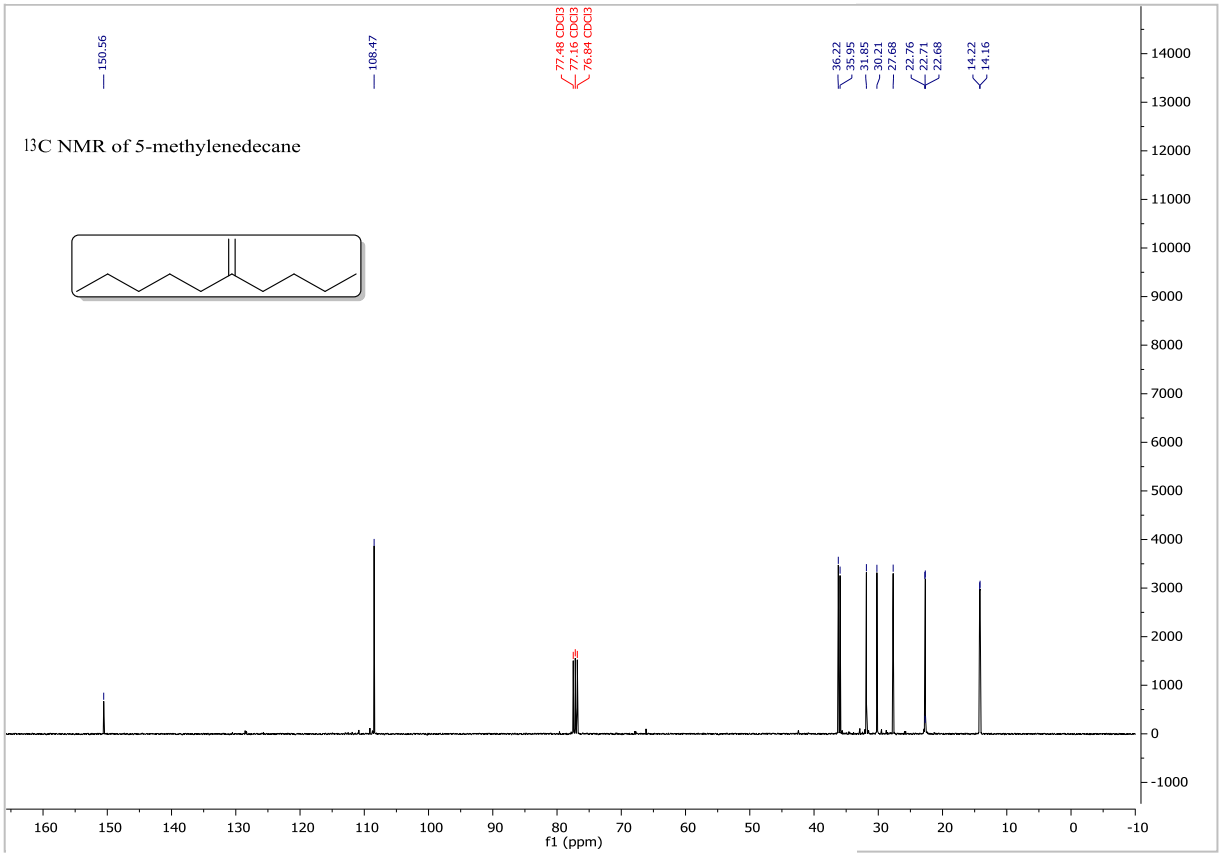


Figure SI-82. ^{13}C NMR spectra of 5-methylenedecane (**3s**).

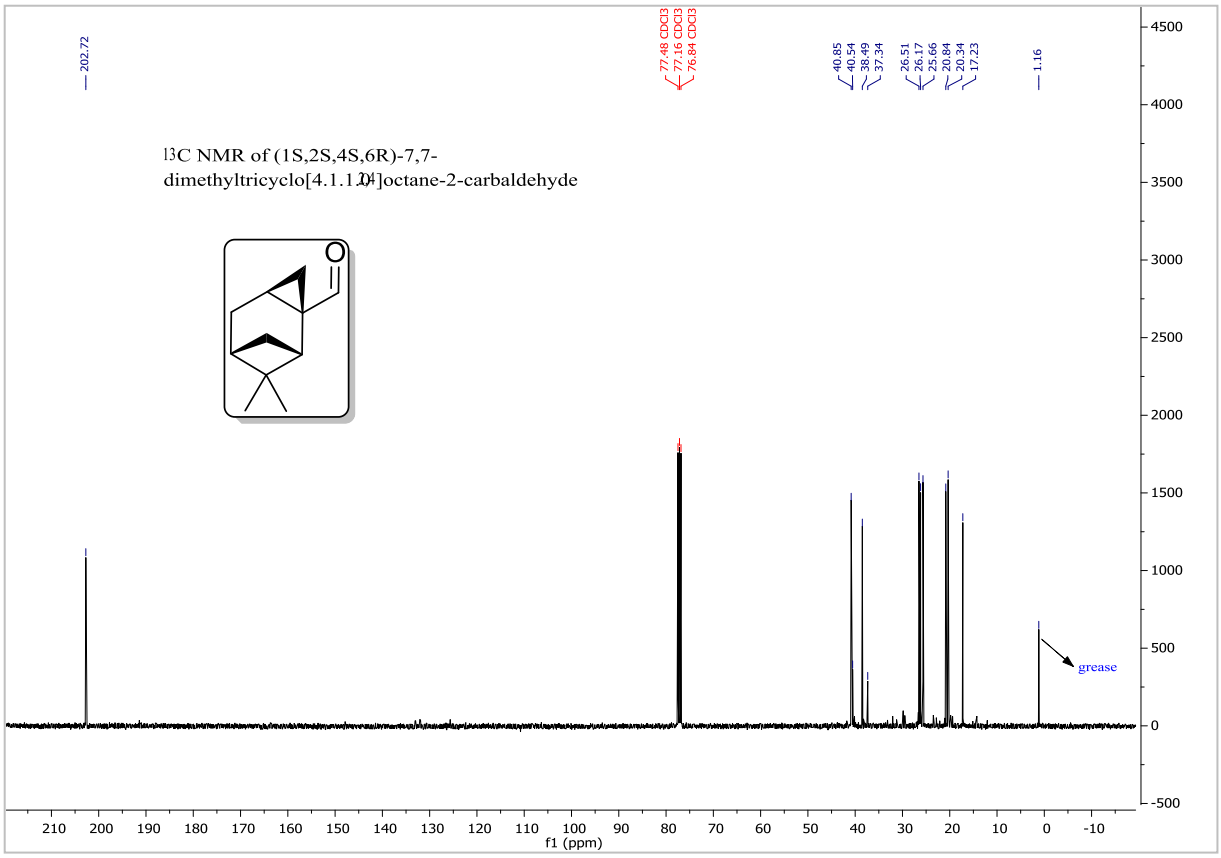


Figure SI-83. ^{13}C NMR spectra of 7,7-dimethyltricyclo[4.1.1.$o^{2,4}$]octane-2-carbaldehyde (**3f**).

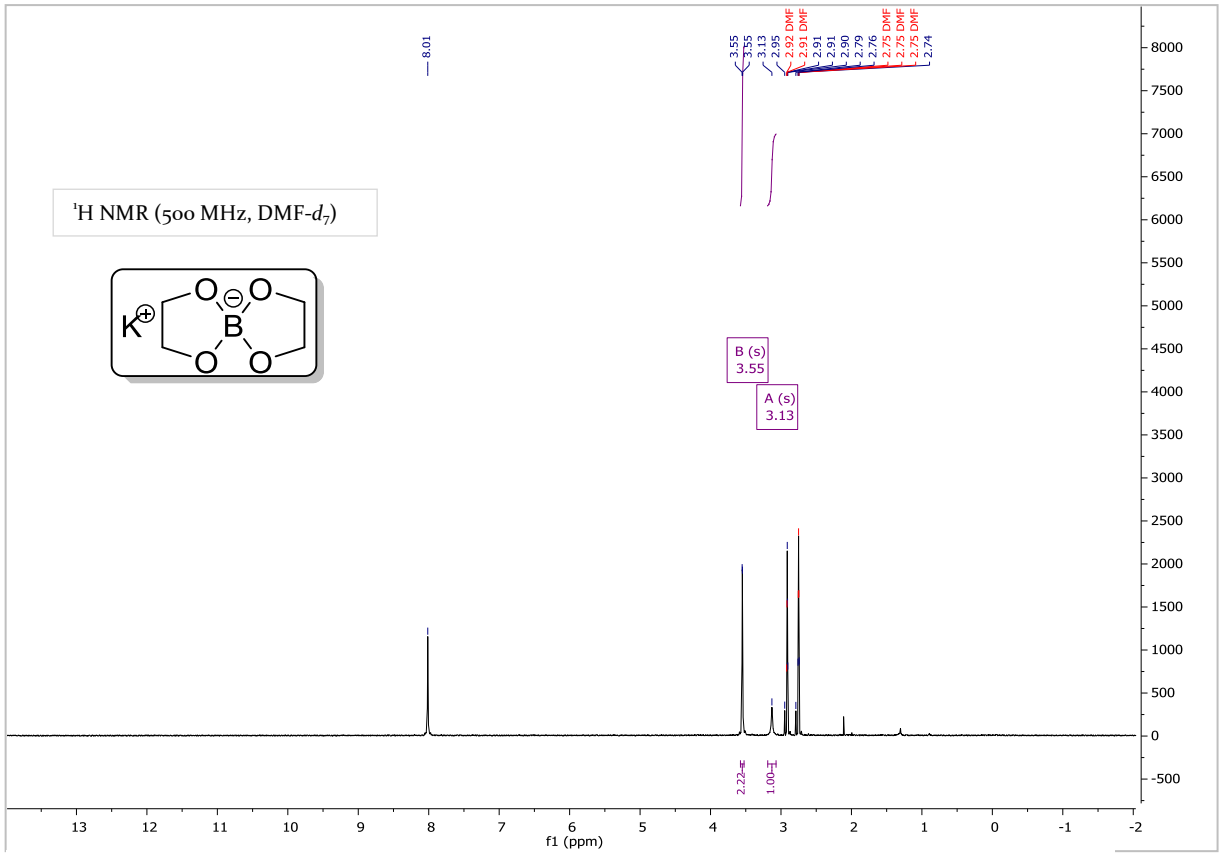


Figure SI-84. ^{1}H NMR spectra of potassium bis(ethyleneglycolato)borate (**4**).

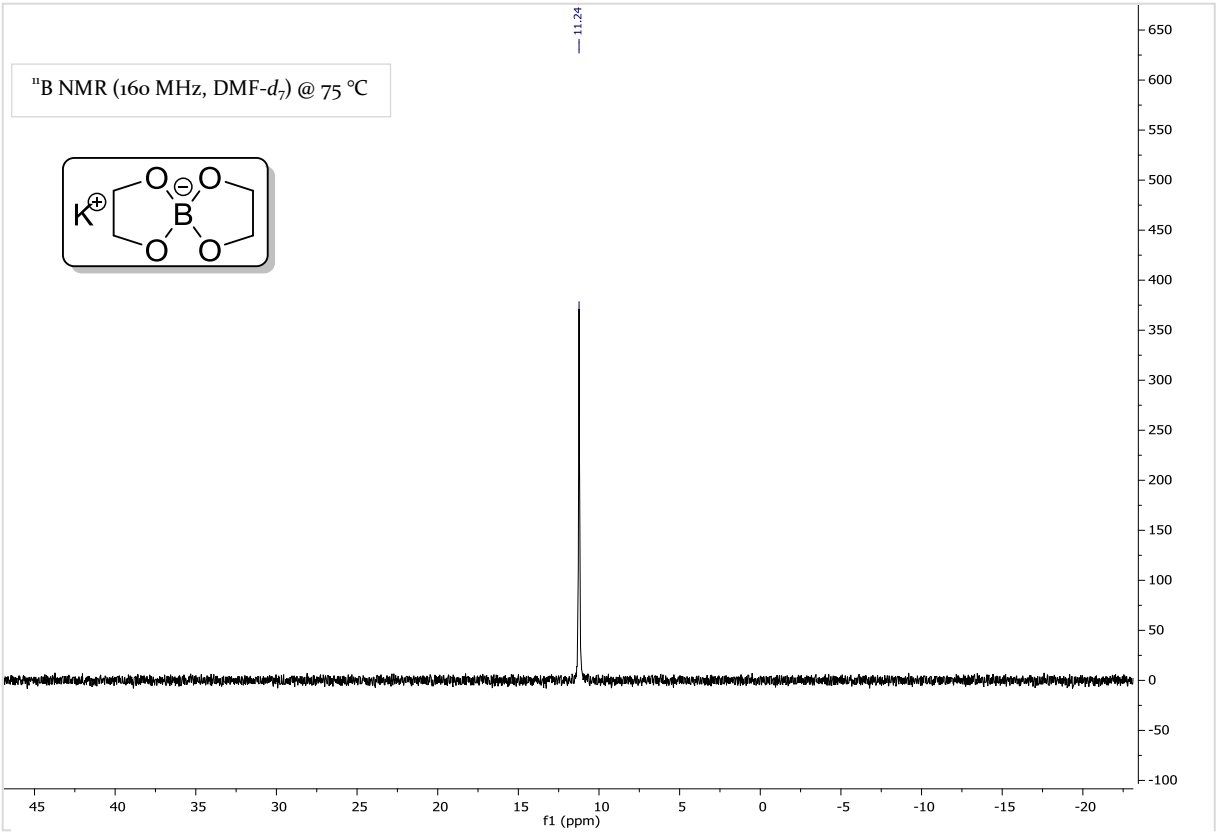


Figure SI-85. ^{11}B NMR spectra of potassium bis(ethyleneglycolato)borate (**4**) at 75

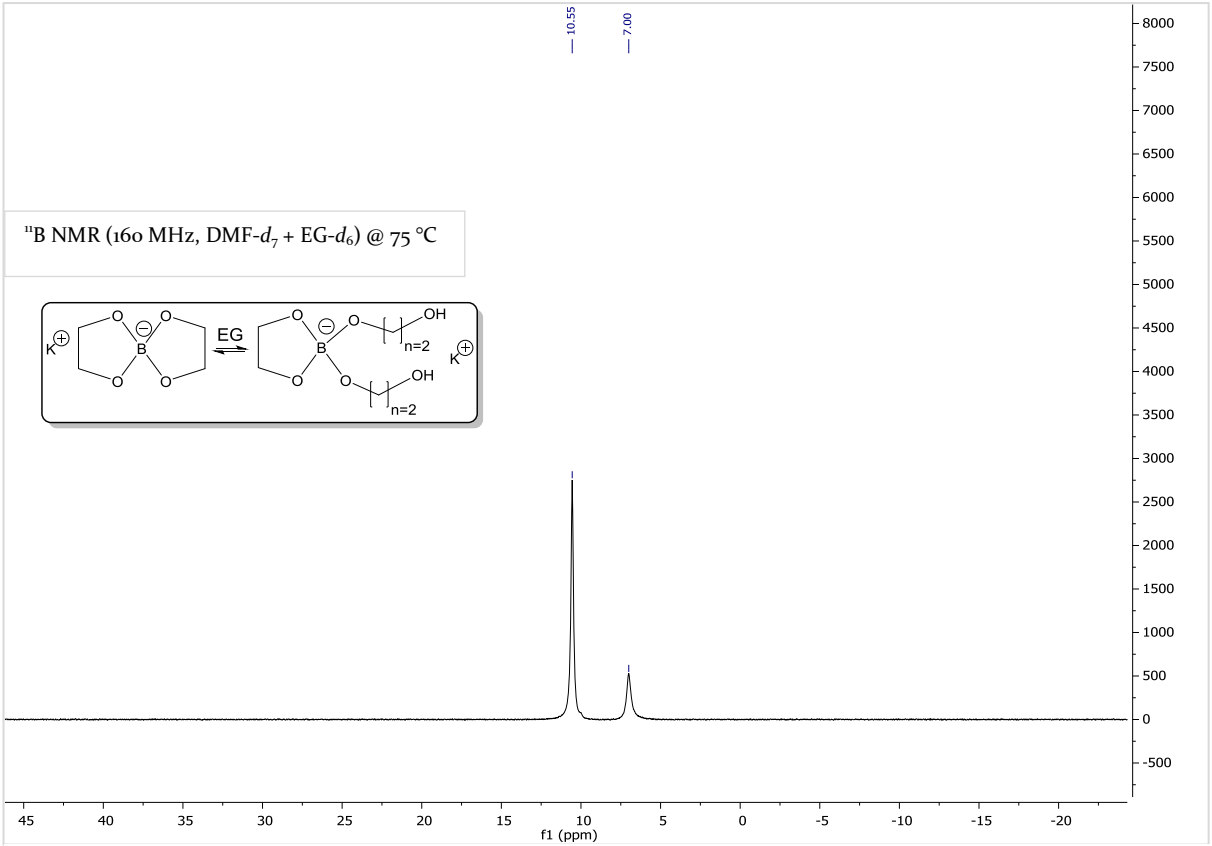


Figure SI-86. ^{11}B NMR spectra of potassium bis(ethyleneglycolato)borate (**4**) at 75 °C in the presence of EG-d_6; DMF-d_7:EG-d_6 (16:1).

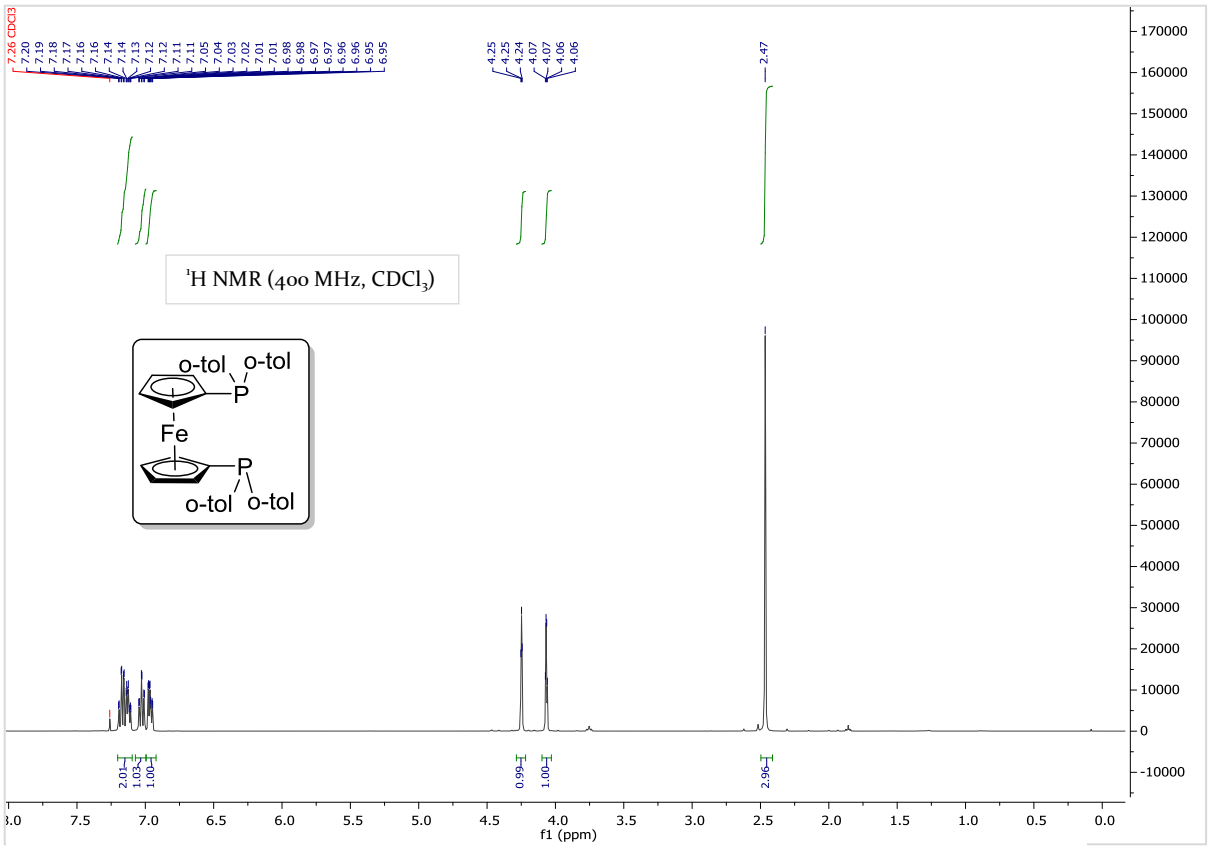


Figure SI-87. ^{1}H NMR spectra of 1,1'-bis(di-o-tolylphosphino)ferrocene (**5**).

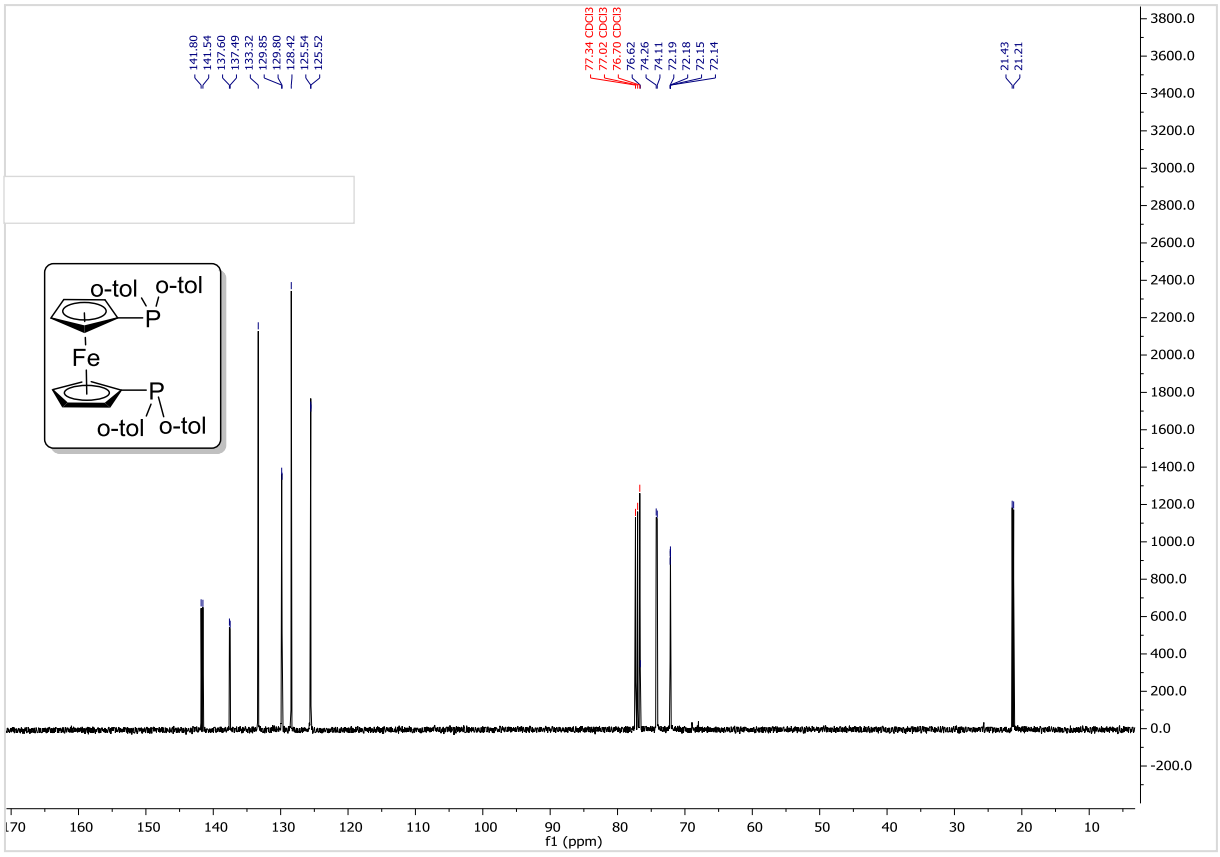


Figure SI-88. ^{13}C NMR spectra of 1,1'-bis(di-o-tolylphosphino)ferrocene (**5**).

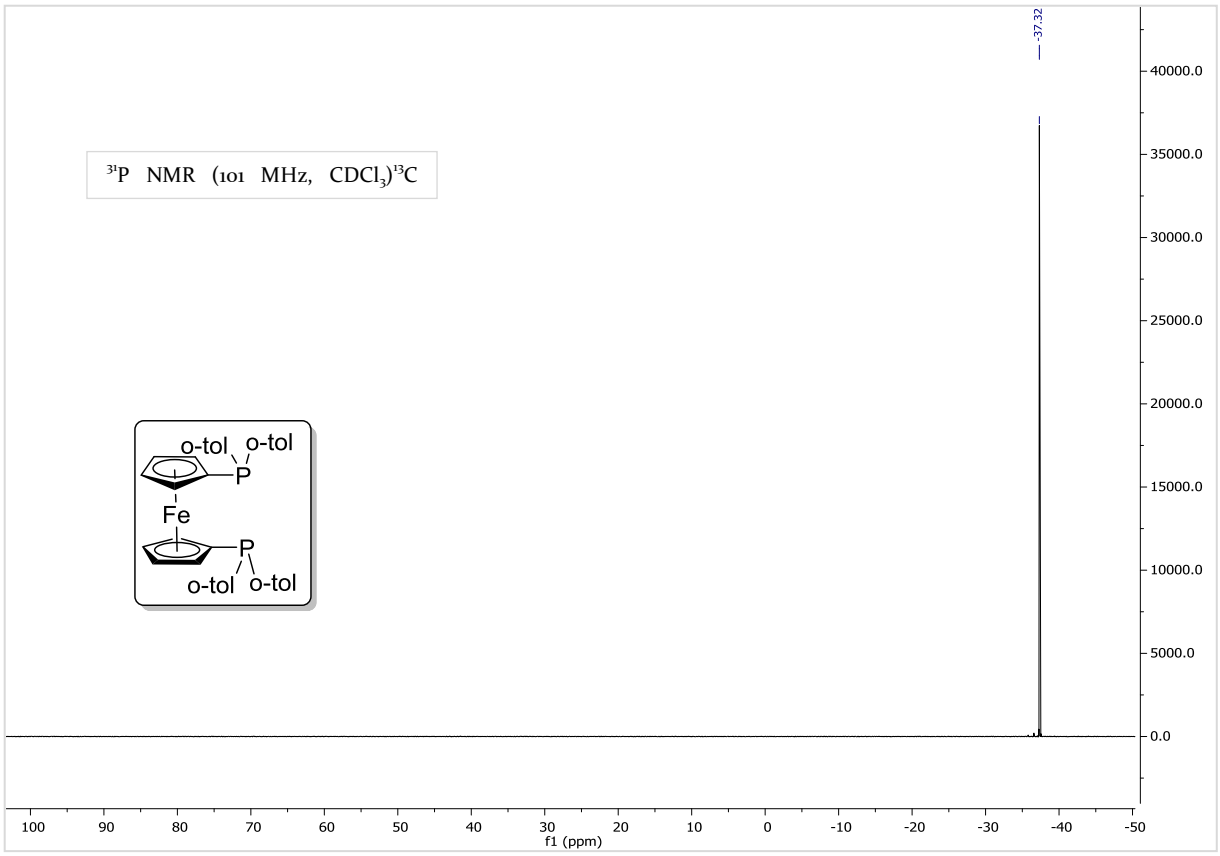


Figure SI-89. ^{31}P NMR spectra of 1,1'-bis(di-o-tolylphosphino)ferrocene (**5**).

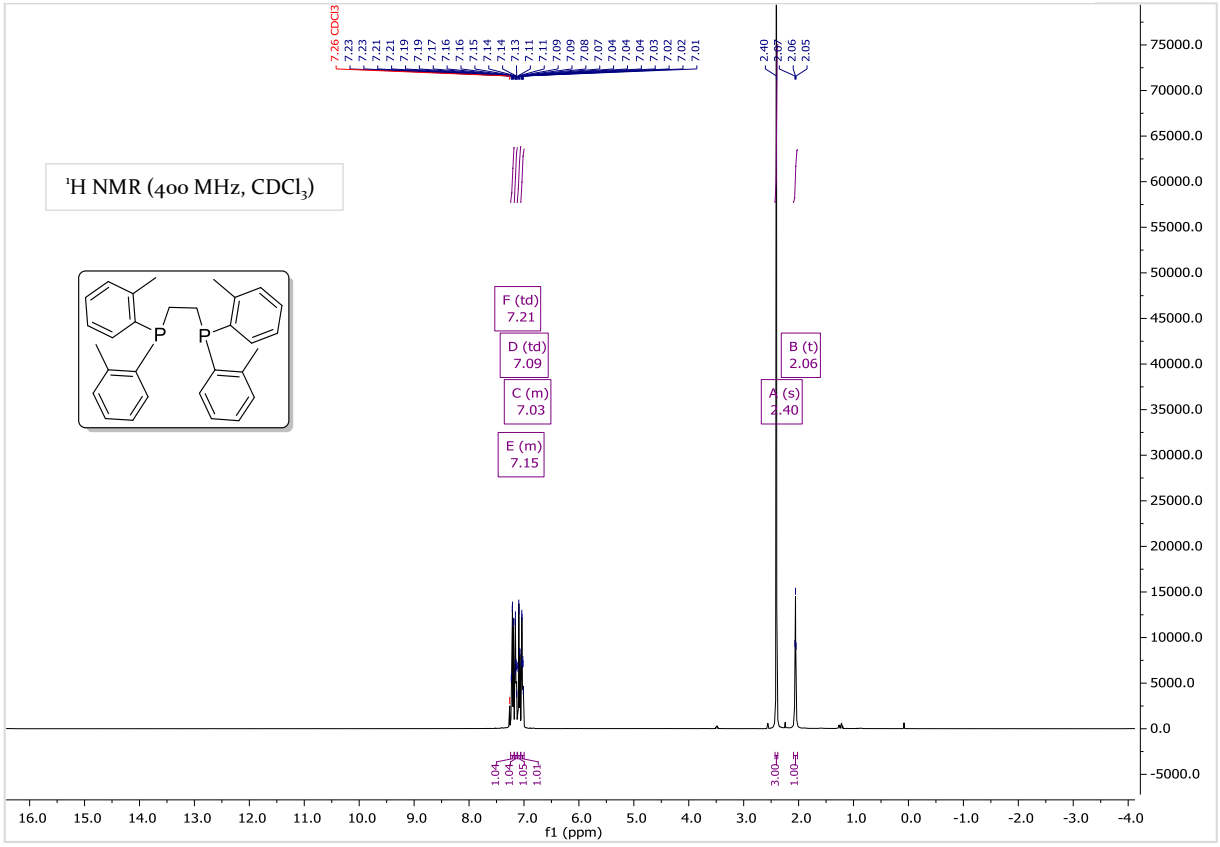


Figure SI-90. ^{1}H NMR spectra of 1,2-bis(di-o-tolylphosphino)ethane (**6**).

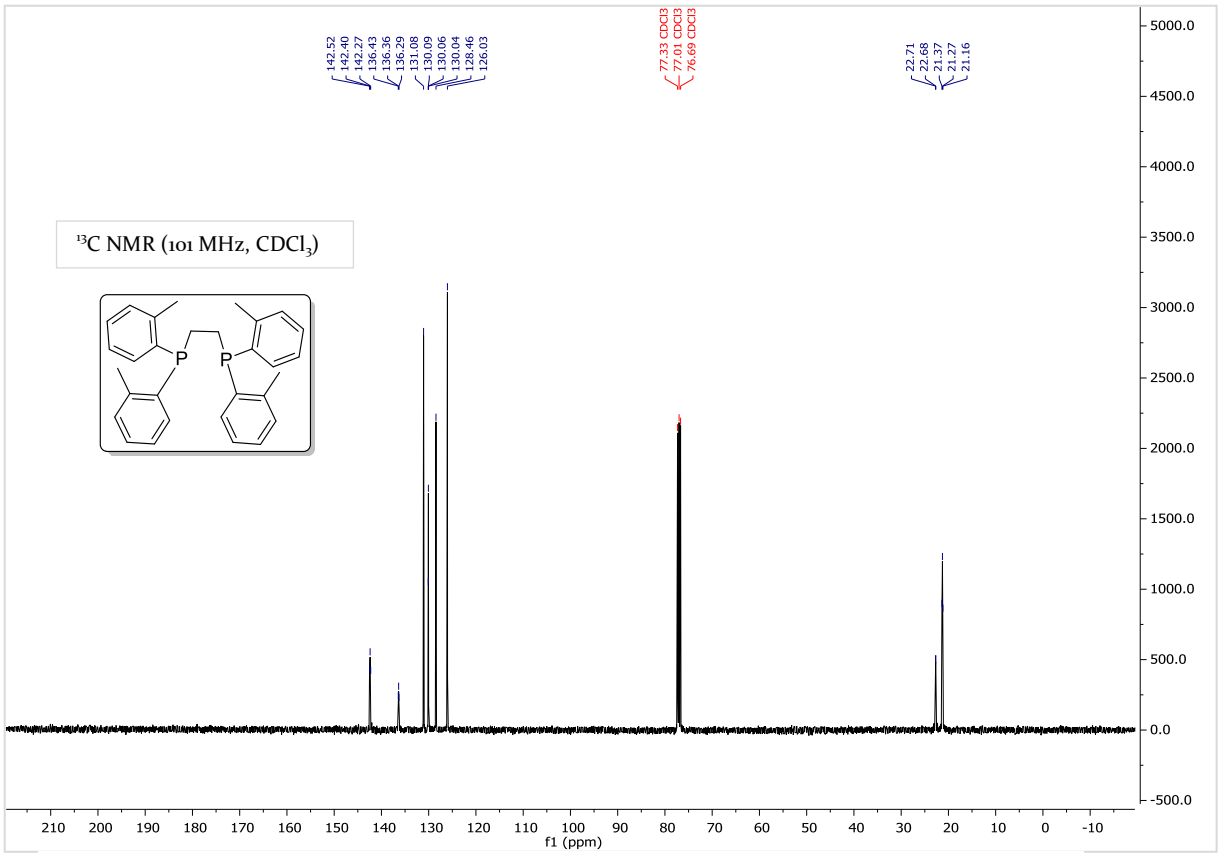


Figure SI-91. ^{13}C NMR spectra of 1,2-bis(di-o-tolylphosphino)ethane (**6**).

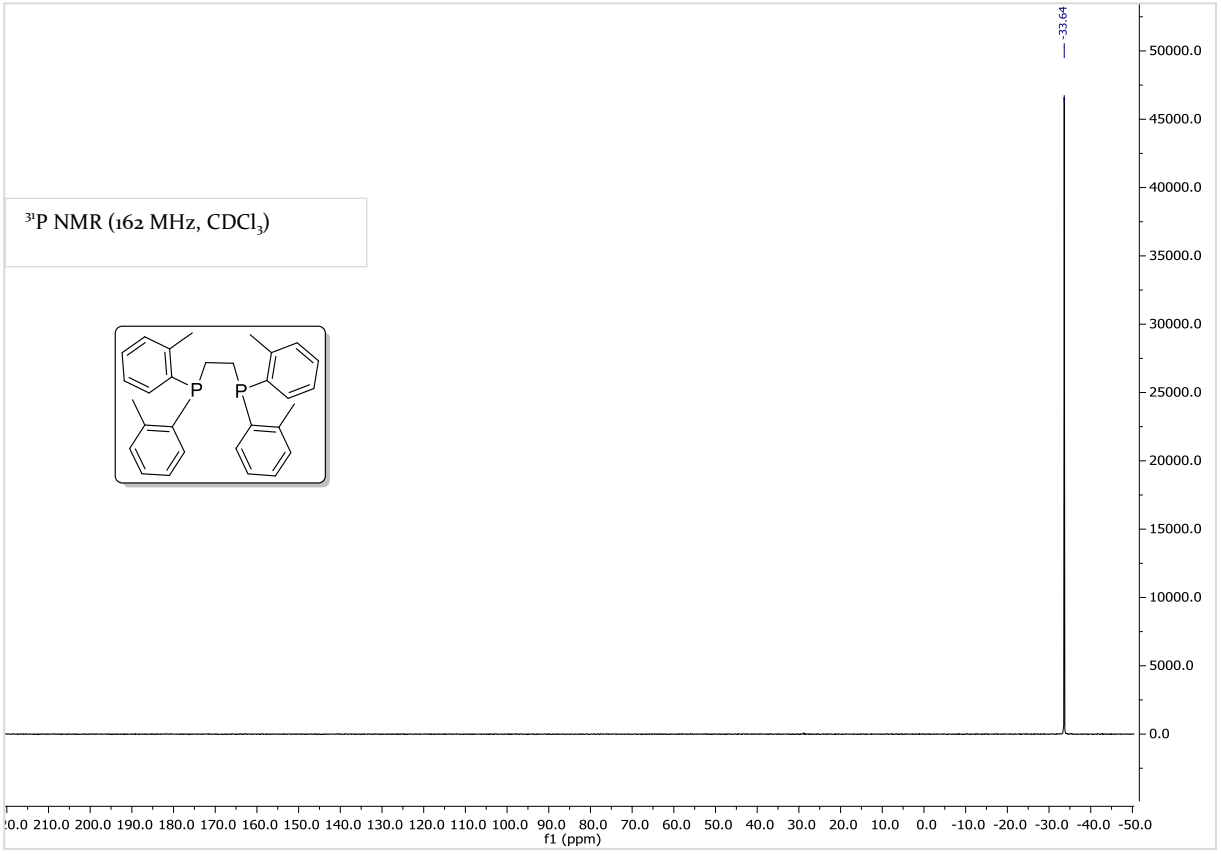


Figure SI-92. ^{31}P NMR spectra of 1,2-bis(di-o-tolylphosphino)ethane (**6**).

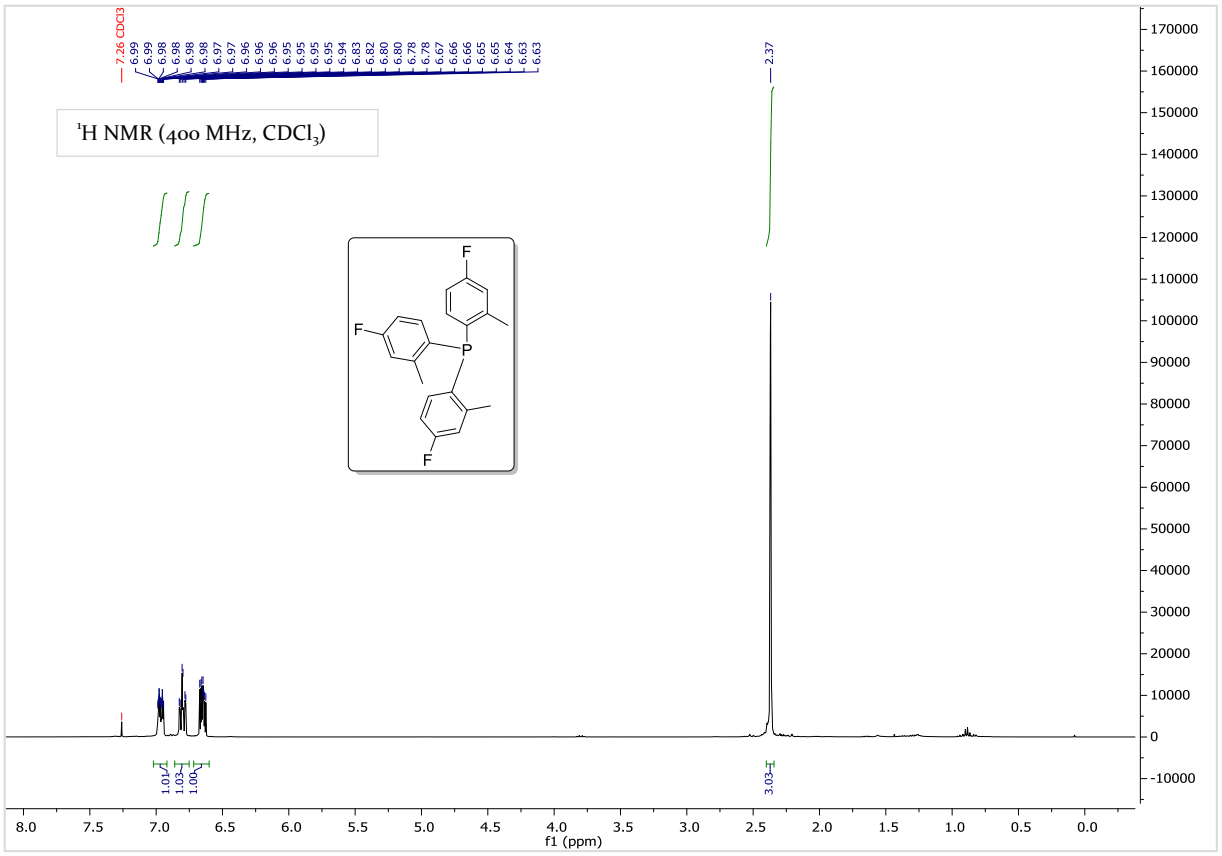


Figure SI-93. ^{1}H NMR spectra of tris(2-methyl-4-fluorophenyl)phosphine (**7**).

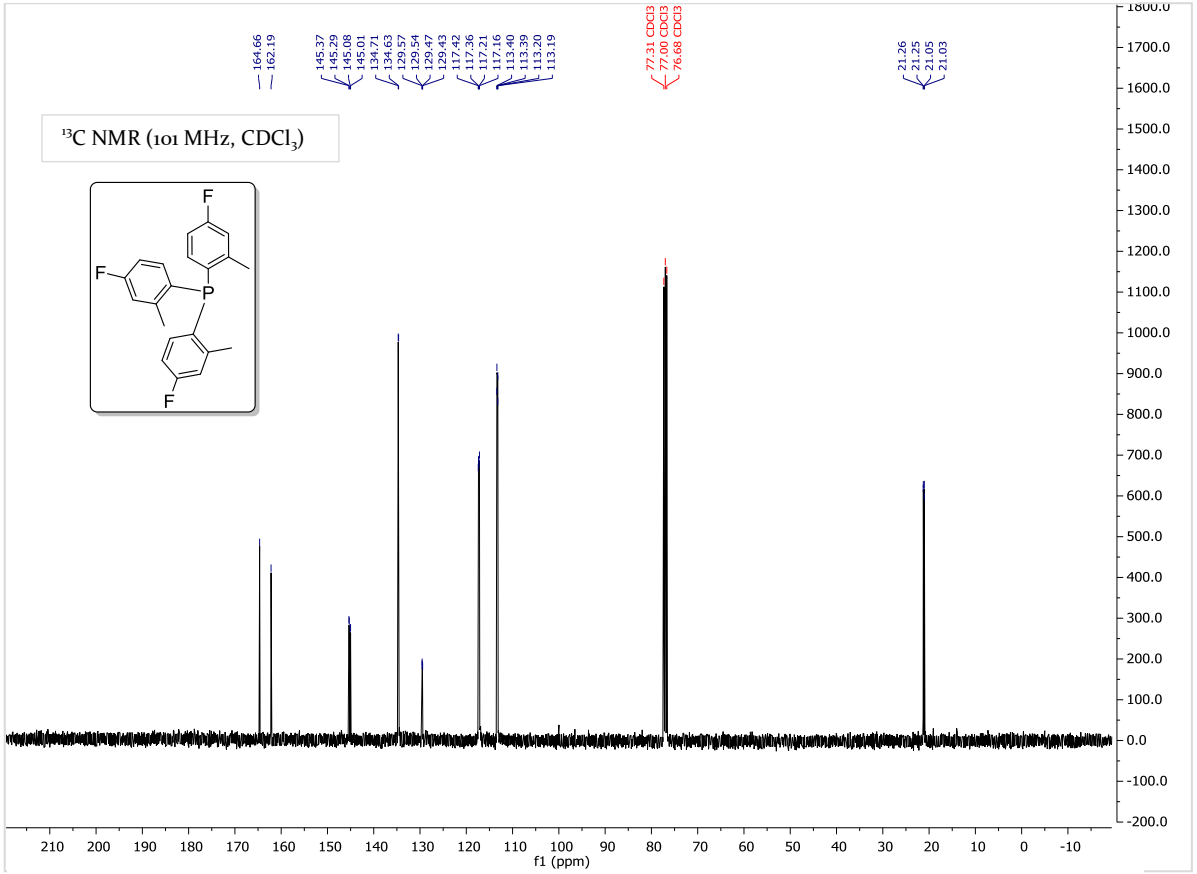


Figure SI-94. ^{13}C NMR spectra of tris(2-methyl-4-fluorophenyl)phosphine (**7**).

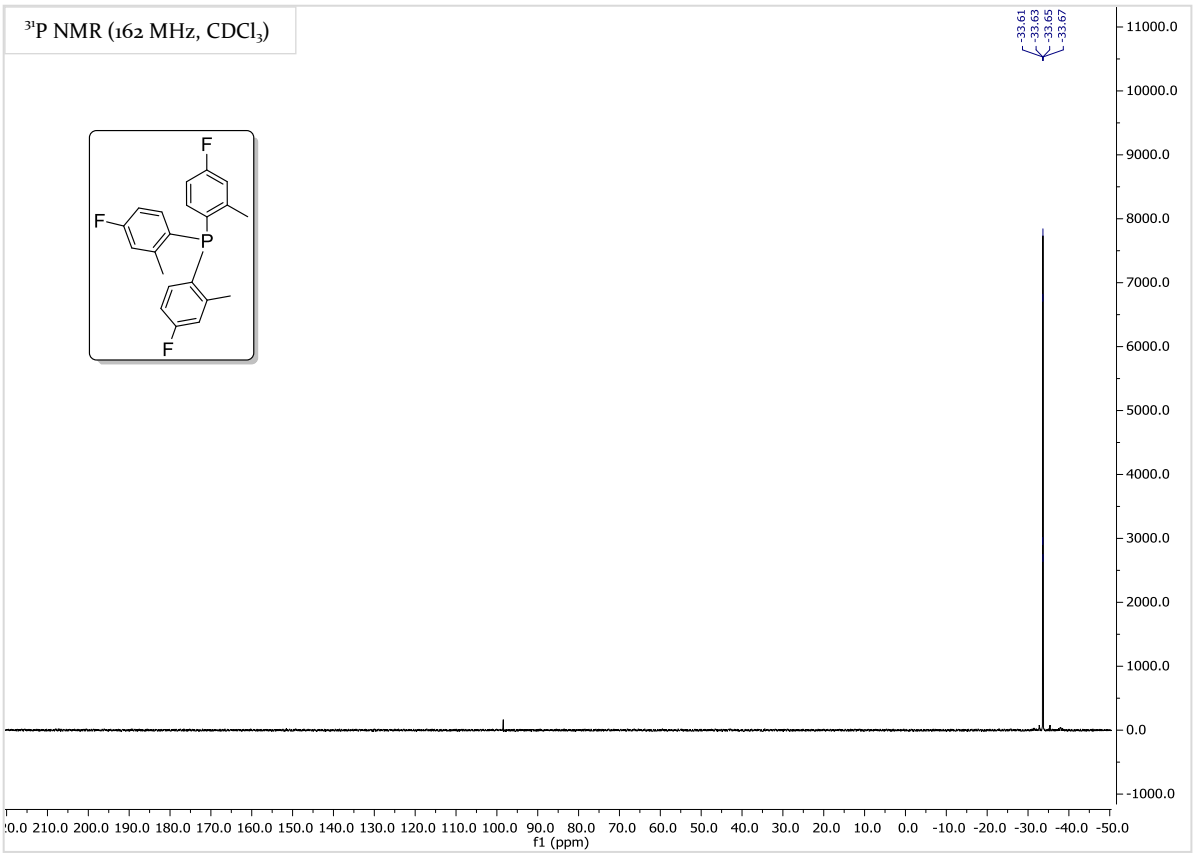


Figure SI-95. ^{31}P NMR spectra of tris(2-methyl-4-fluorophenyl)phosphine (**7**).

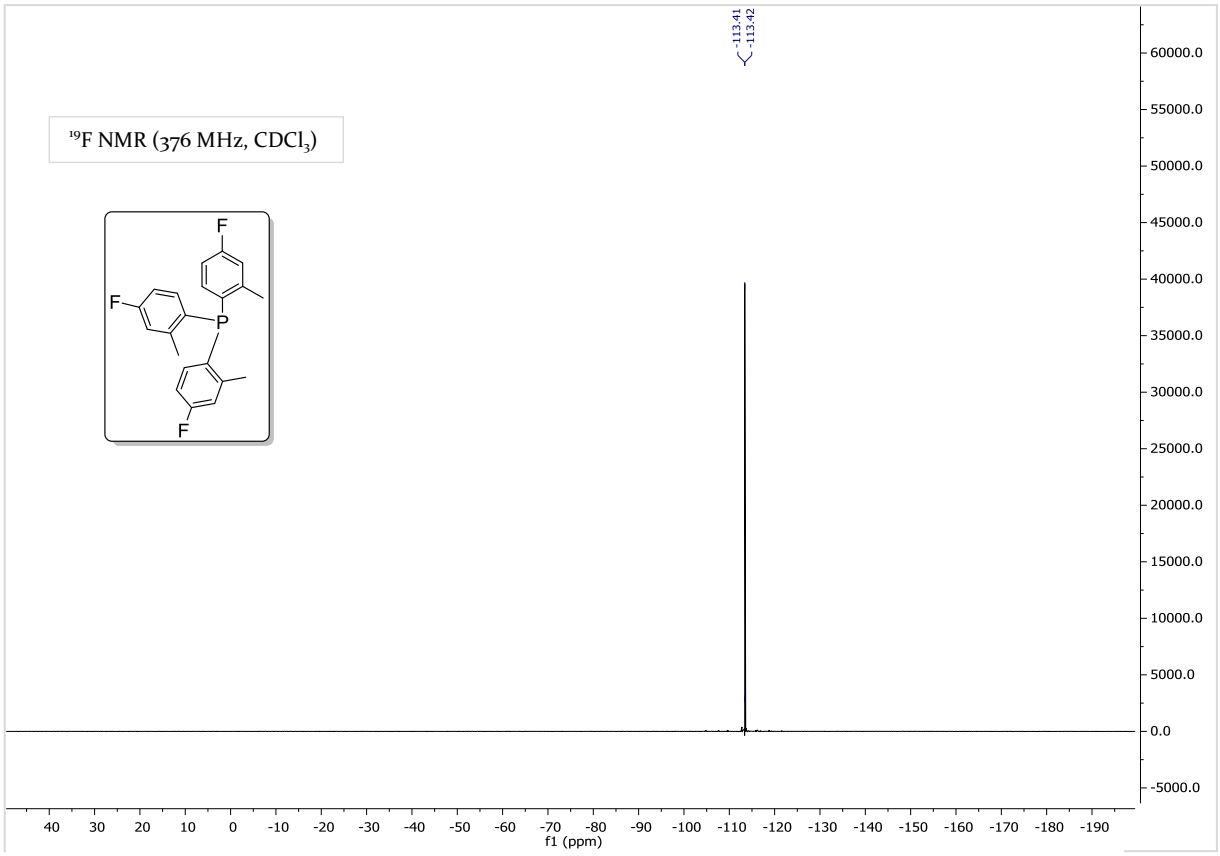


Figure SI-96. ^{19}F NMR spectra of tris(2-methyl-4-fluorophenyl)phosphine (**7**).

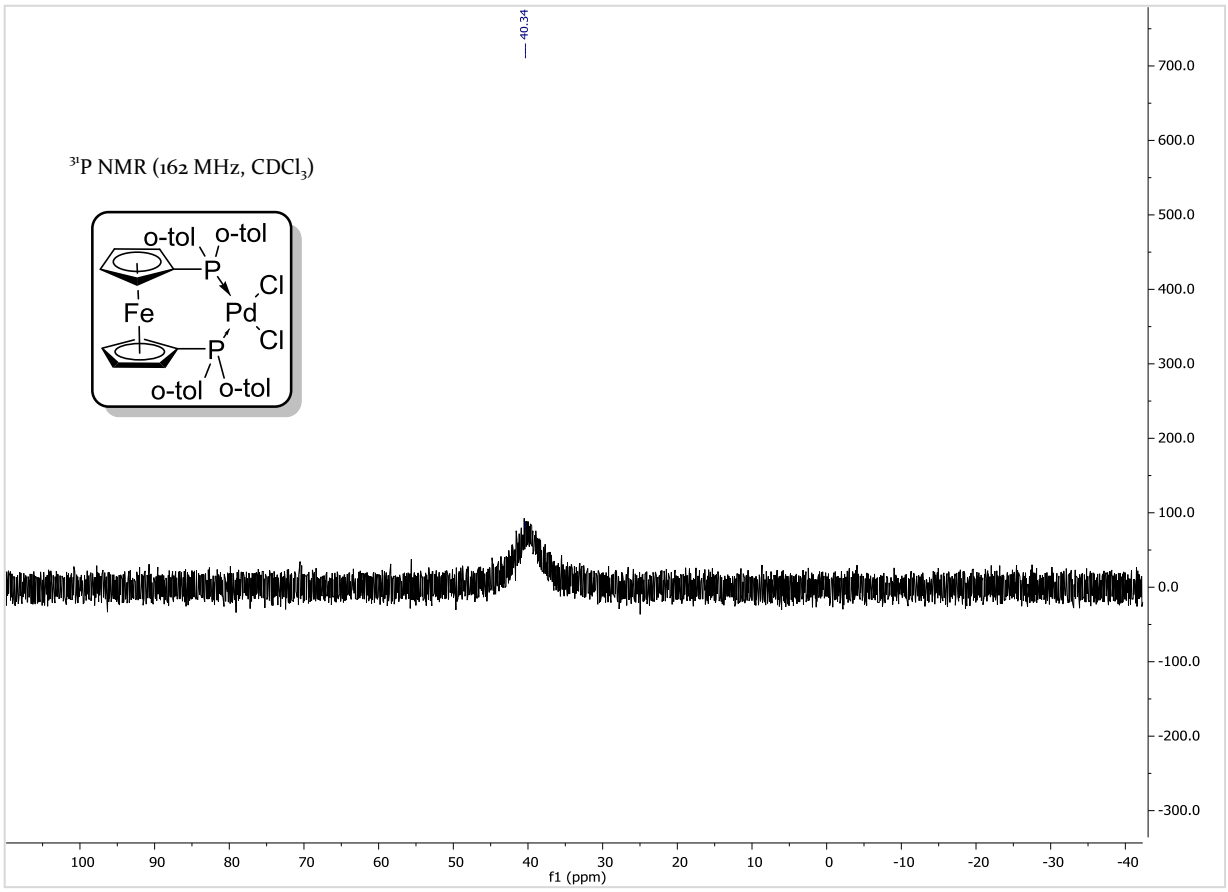


Figure SI-97. ^{31}P NMR spectra of [1,1′-bis(di-o-tolylphosphino)ferrocene]dichloropalladium(II) (**Cat5**).

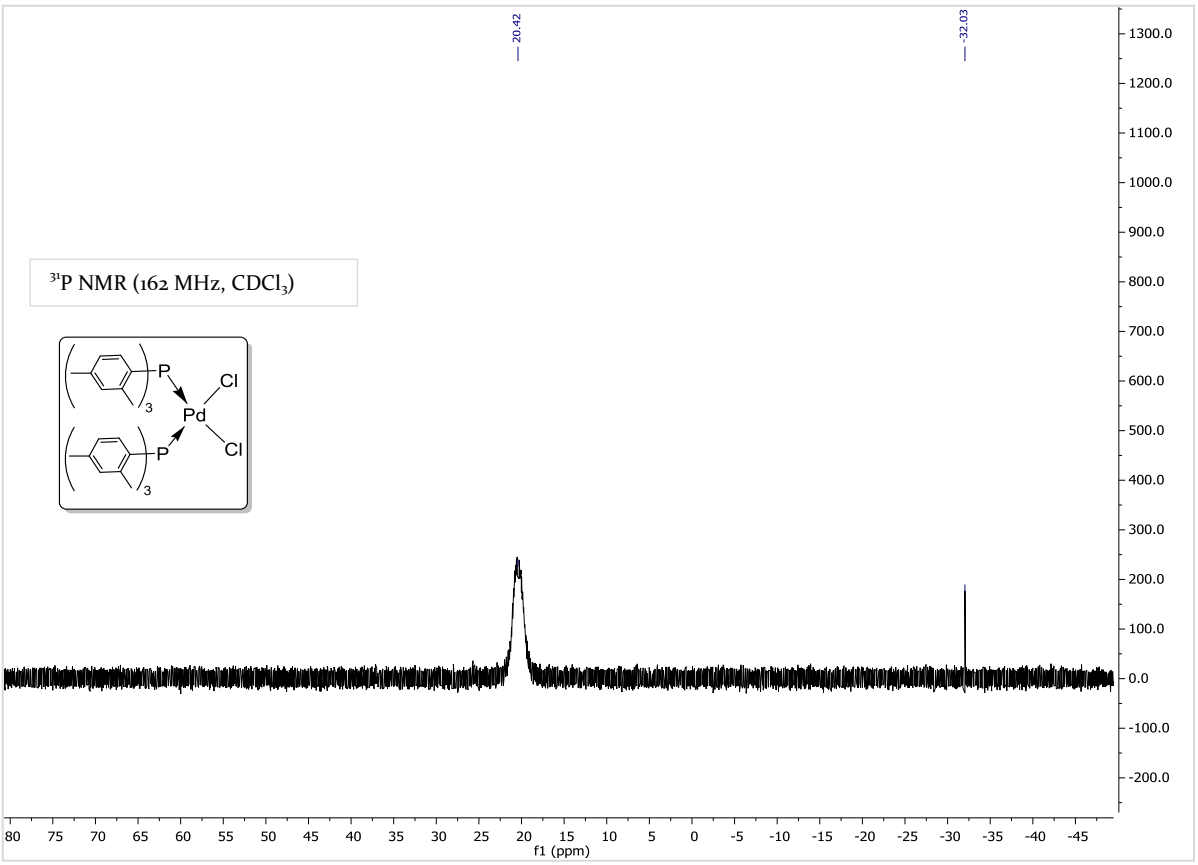


Figure SI-98. ^{31}P NMR spectra of Dichlorobis(2,4-dimethylphenyl)phosphine)palladium(II) (**Cat7**).

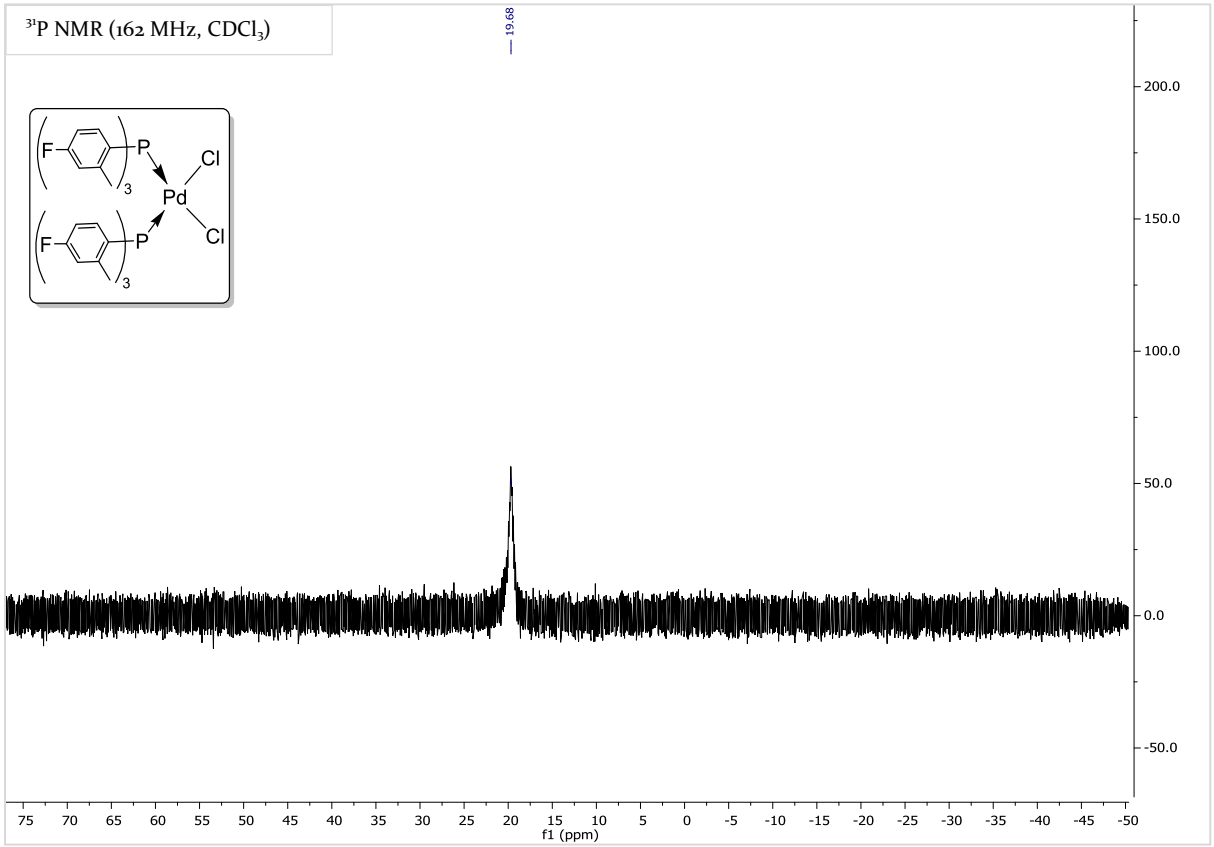


Figure SI-99. ^{31}P NMR spectra of Dichlorobis((2-methyl-4-

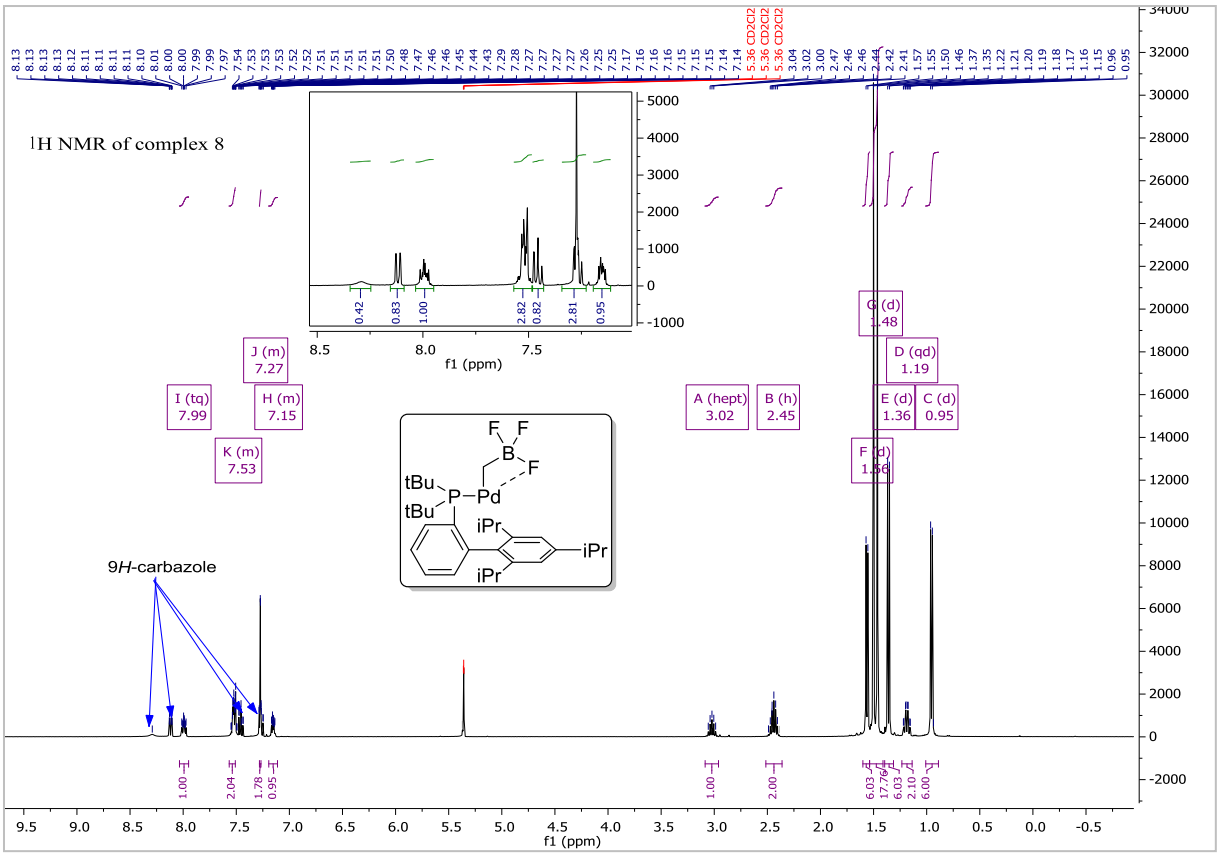
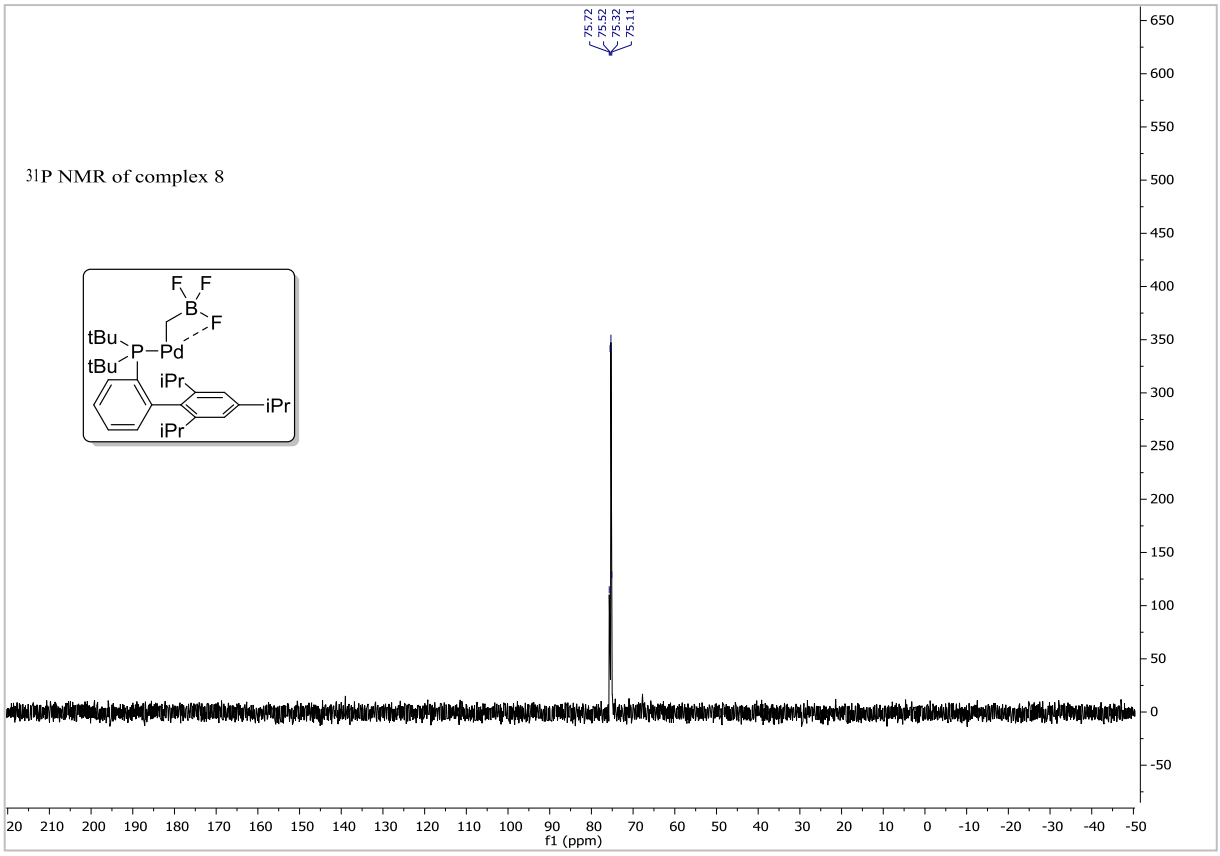


Figure SI-100. ^{1}H NMR spectra of **Complex8**.



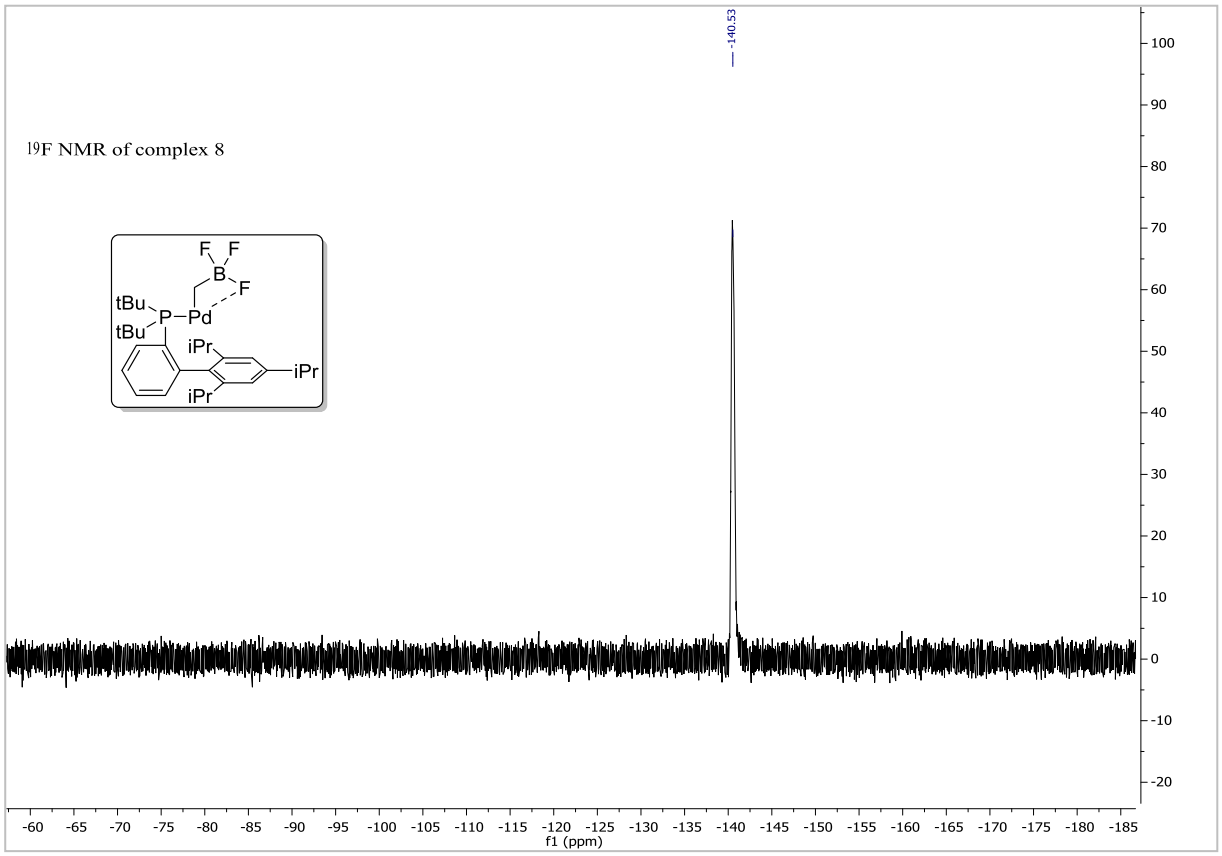


Figure SI-102. [19]F NMR spectra of **Complex8**.

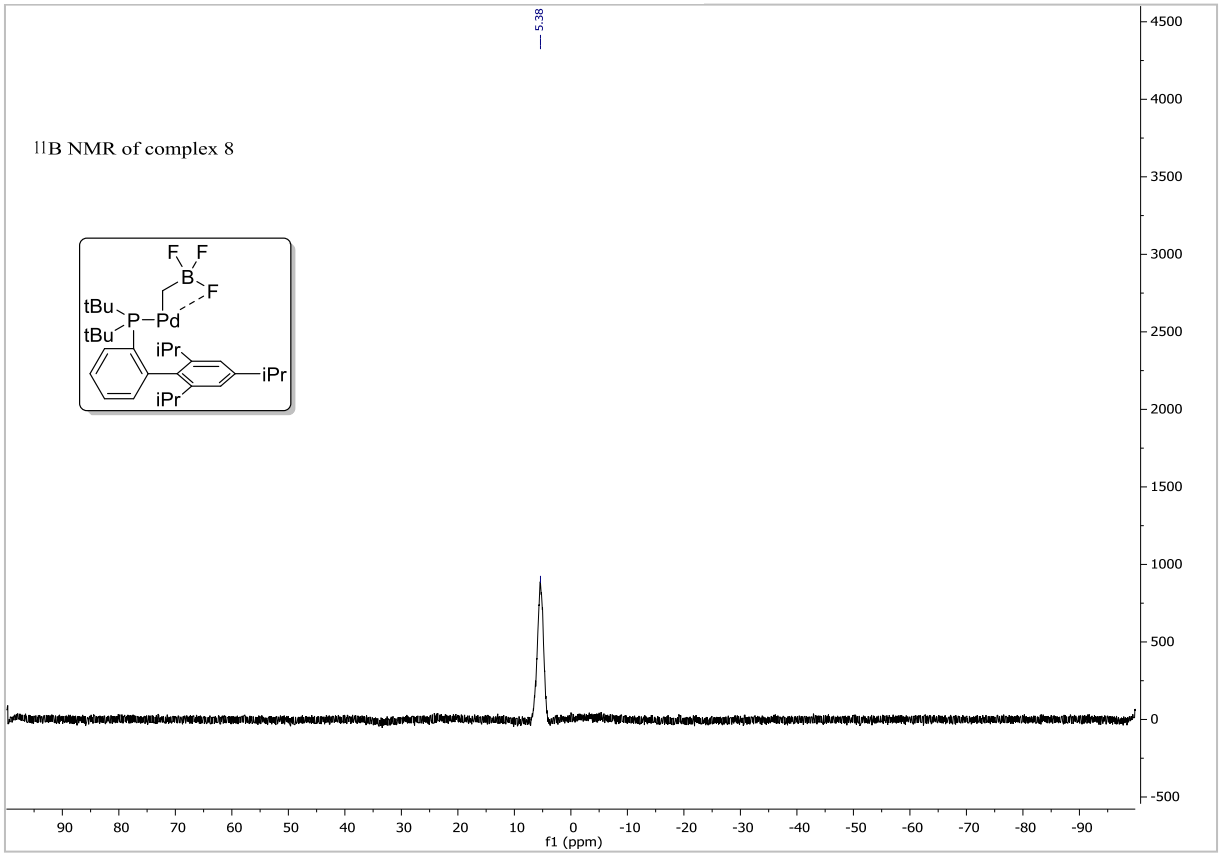


Figure SI-103. [11]B NMR spectra of **Complex8**.

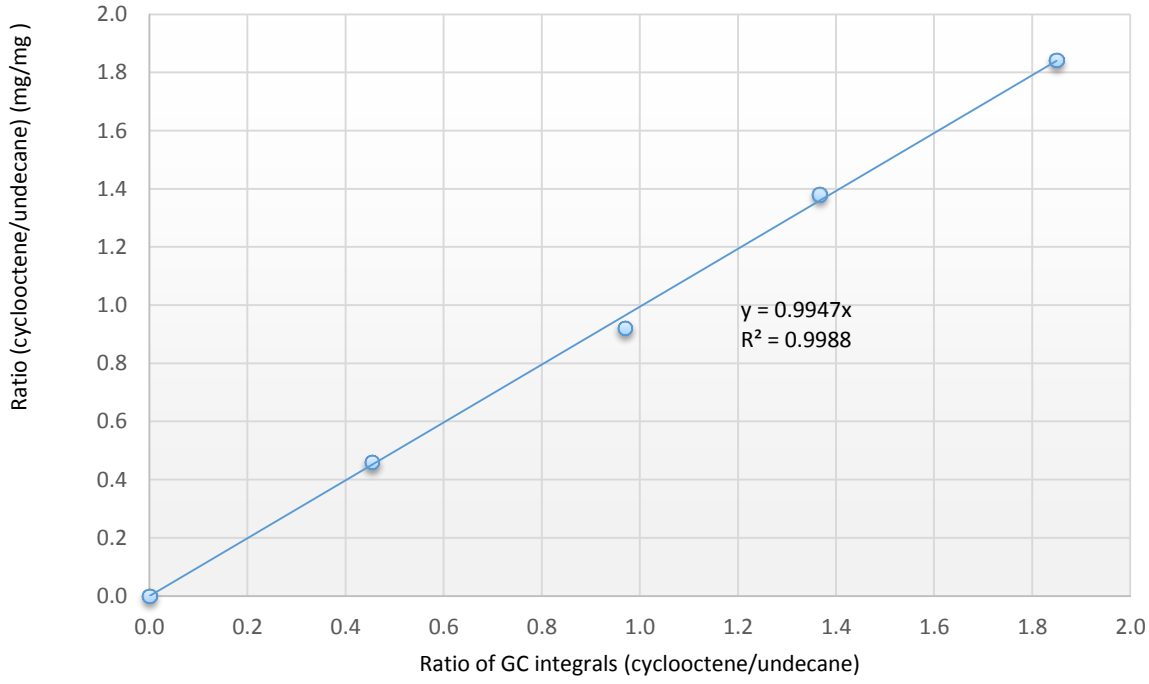


Figure SI-104. GC-FID calibration for cyclooctene with undecane as internal

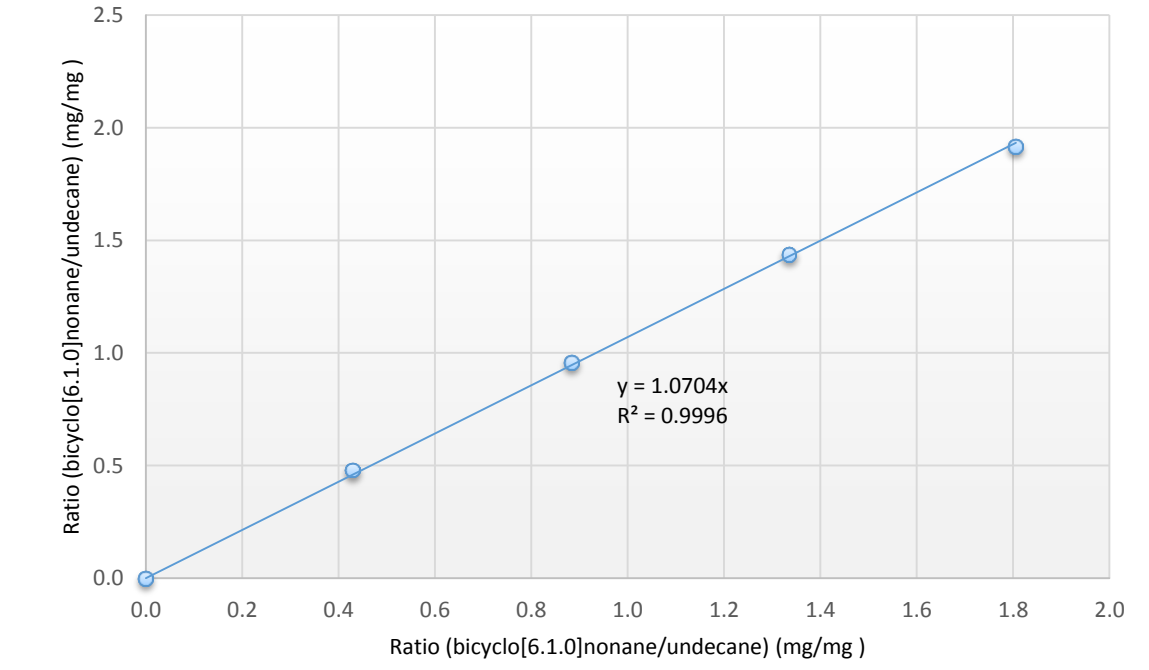


Figure SI-105. GC-FID calibration for bicyclo[6.1.0]nonane with undecane as internal standard.

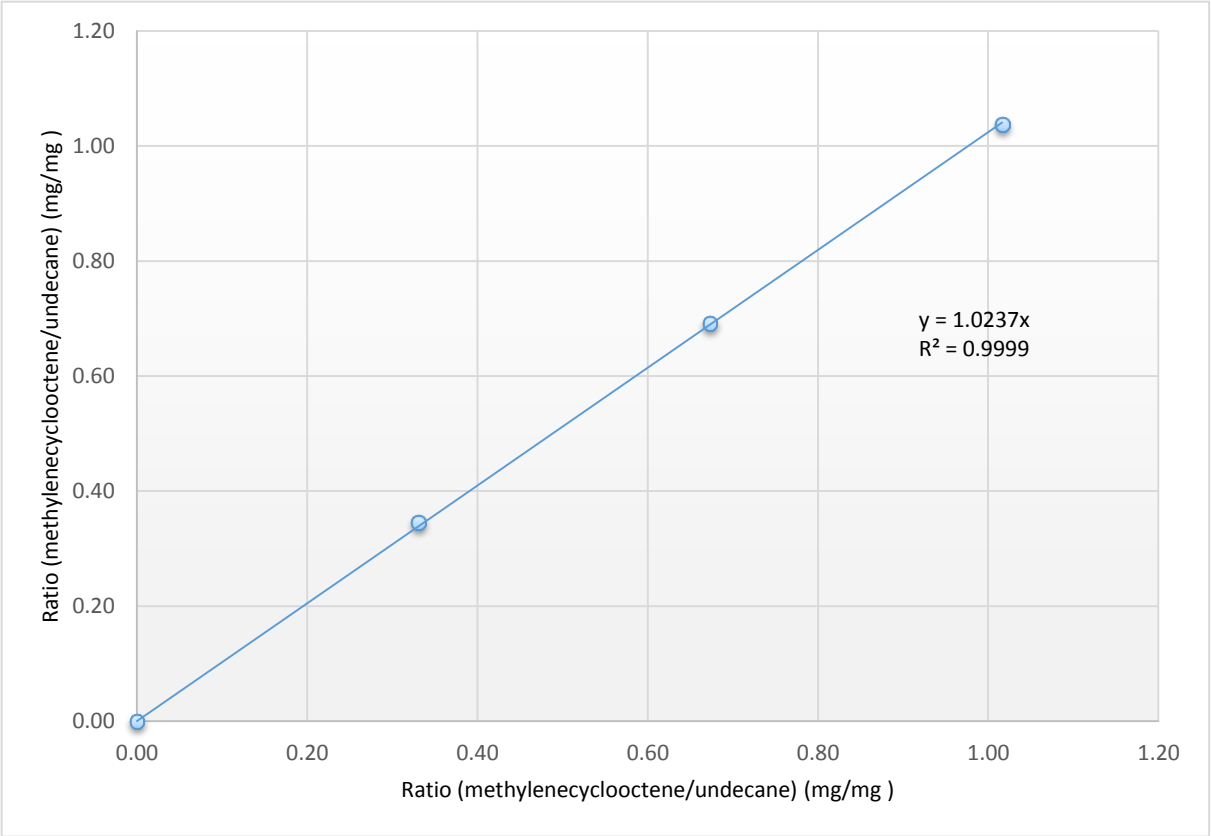


Figure SI-106. GC-FID calibration for methylenecyclooctene with undecane as internal standard.

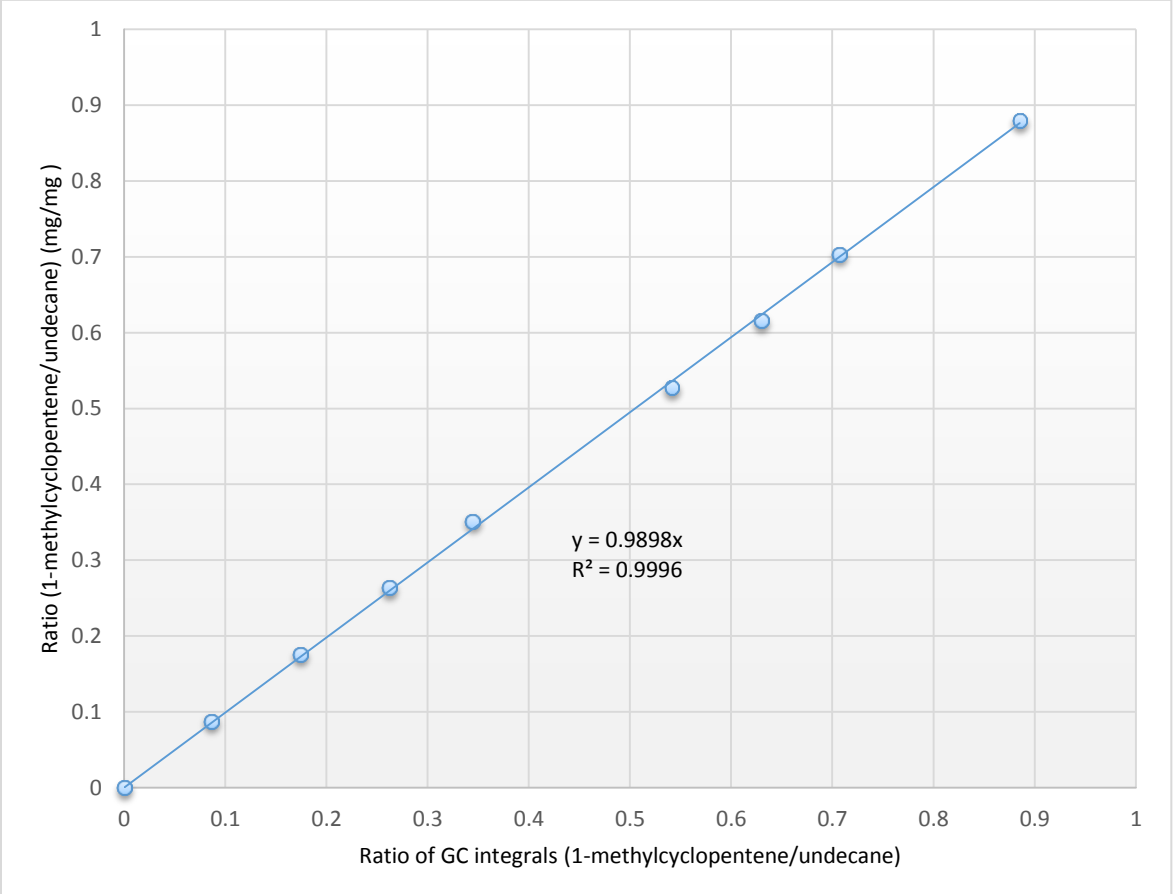


Figure SI-107. GC-FID calibration for 1-methylcyclopentene with undecane as

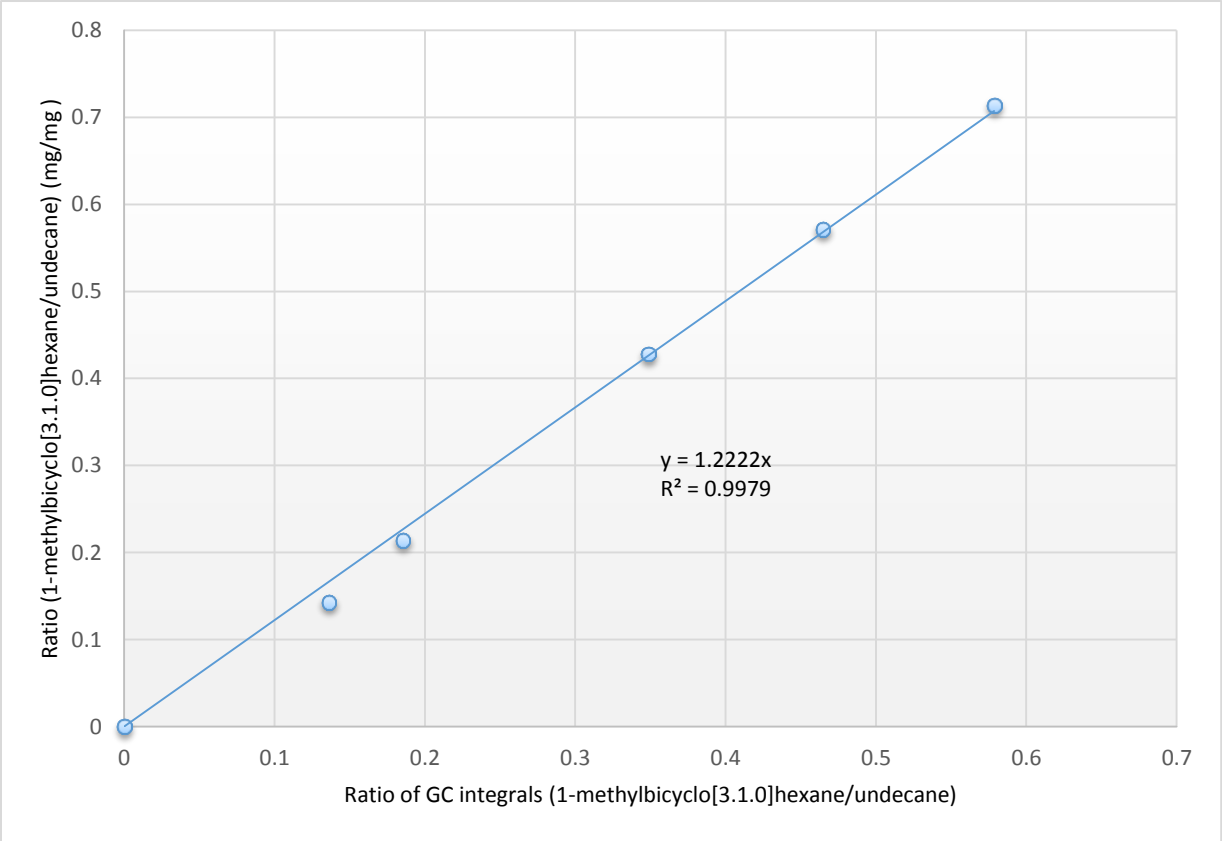


Figure SI-108. GC-FID calibration for 1-methylbicyclo[3.1.0]hexane with undecane

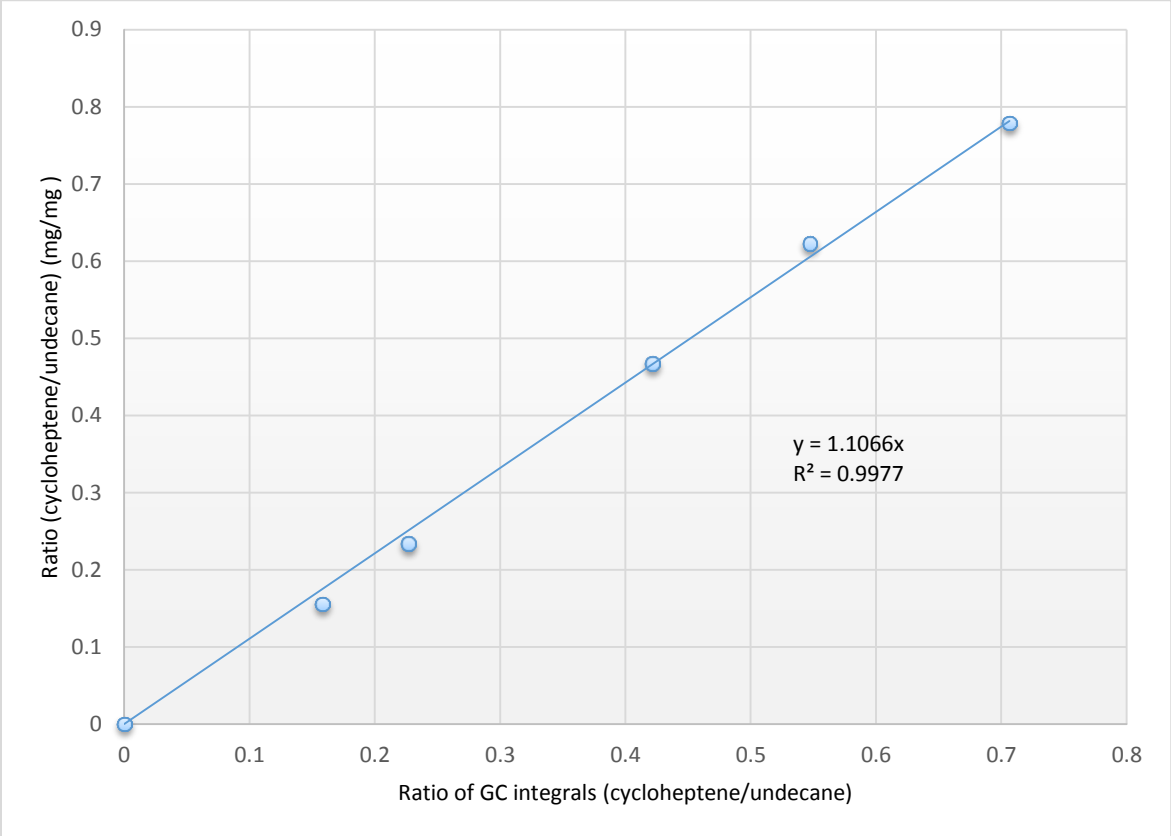


Figure SI-109. GC-FID calibration for cycloheptene with undecane as internal standard.

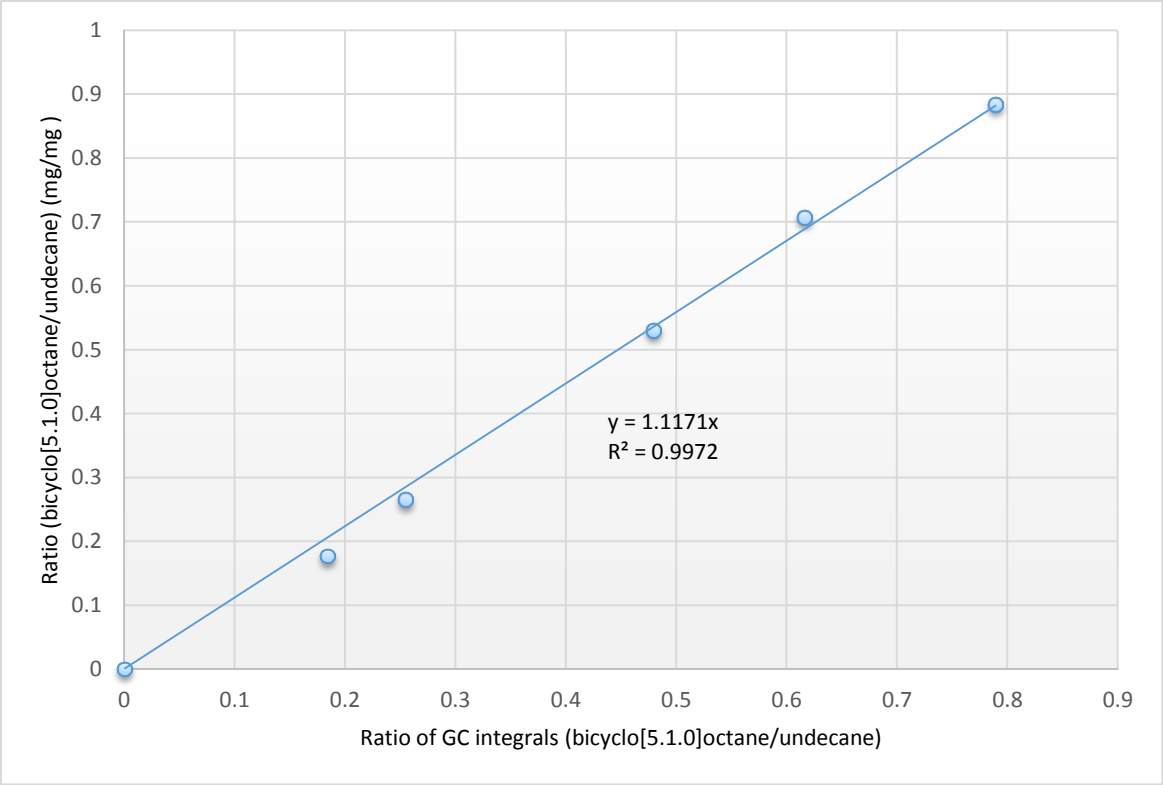


Figure SI-110. GC-FID calibration for bicyclo[5.1.0]octane with undecane as internal standard.

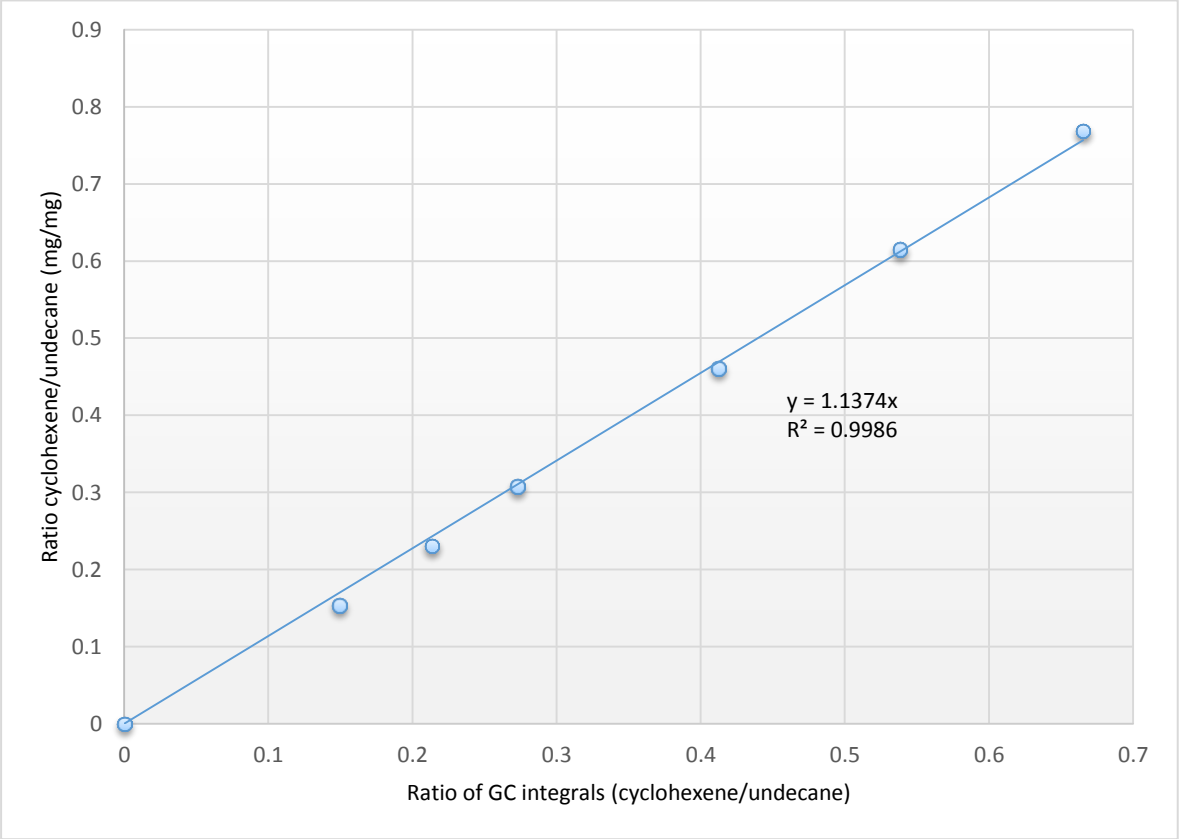


Figure SI-111. GC-FID calibration for cyclohexene with undecane as internal

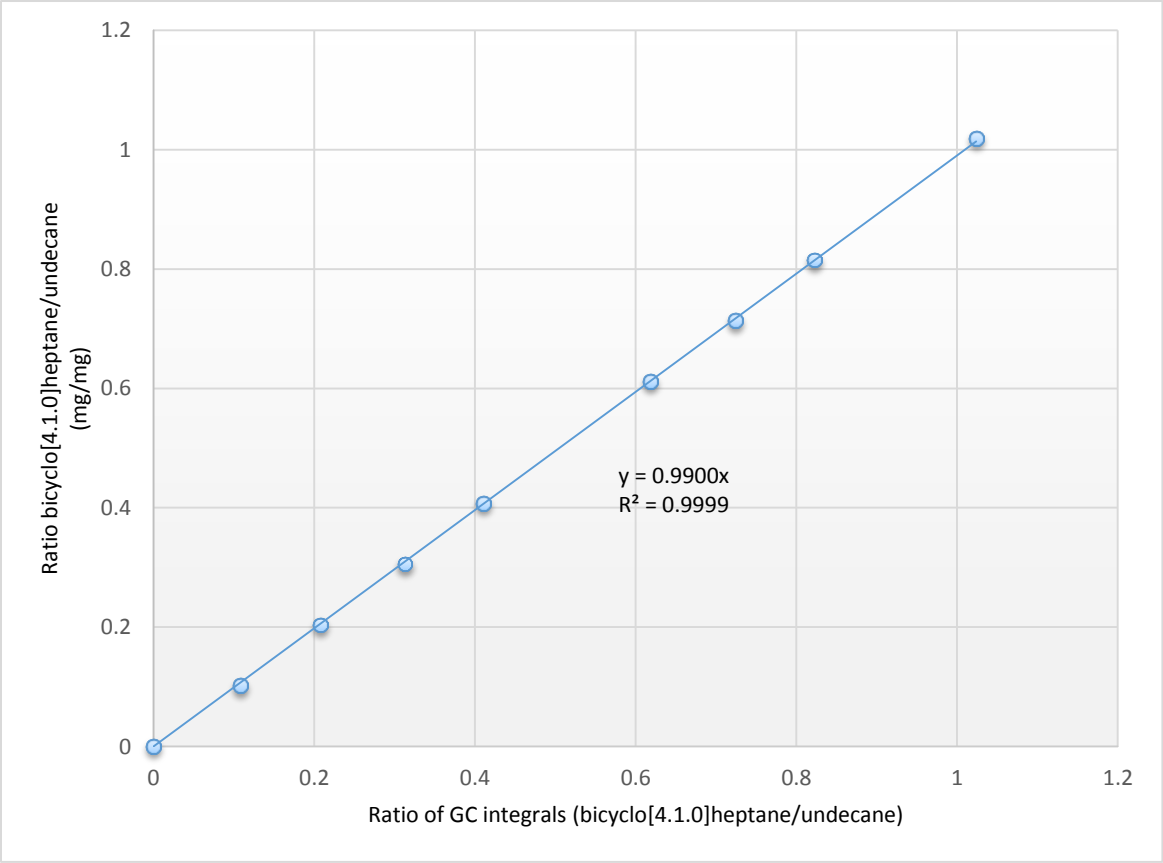


Figure SI-112. GC-FID calibration for bicyclo[4.1.0]heptane with undecane as internal standard.

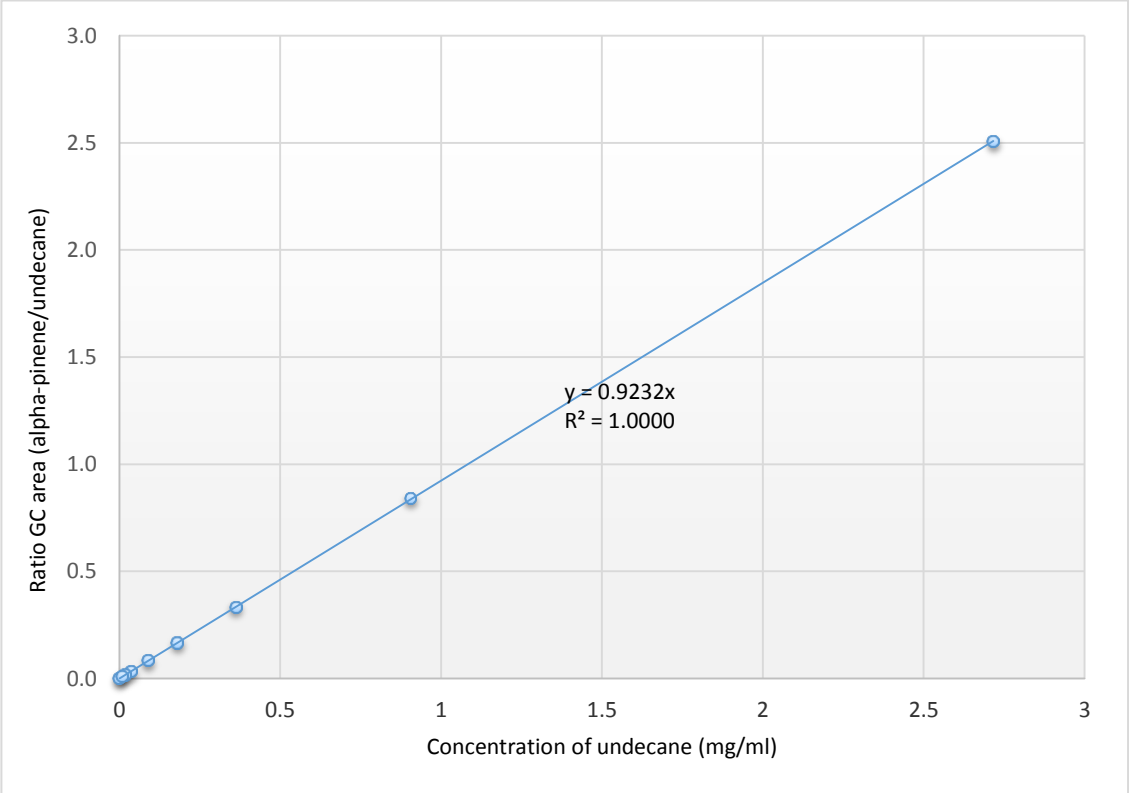


Figure SI-113. GC-FID calibration for α-pinene with undecane as internal standard.

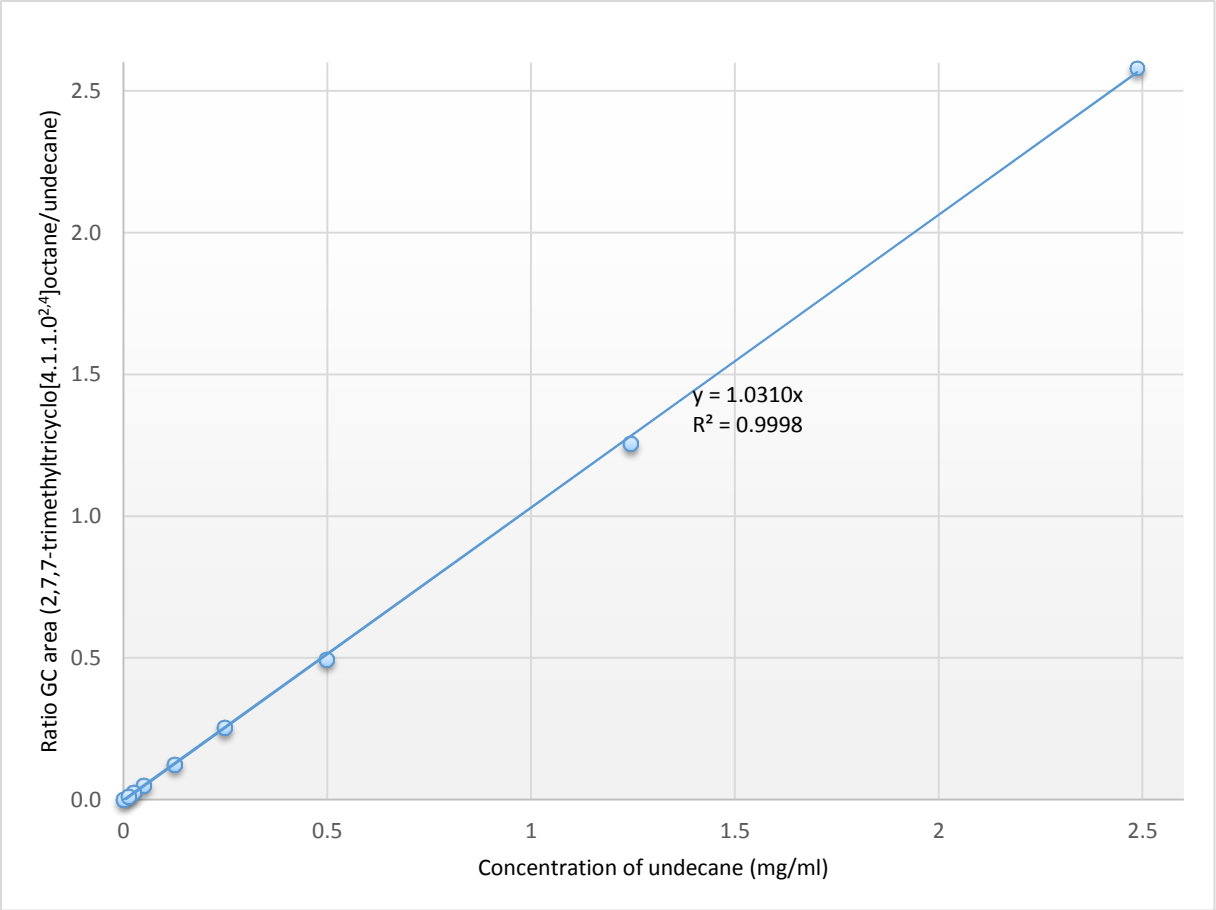


Figure SI-114. GC-FID calibration for 2,7,7-trimethyltricyclo[4.1.1.02,4]octane with undecane as internal standard.

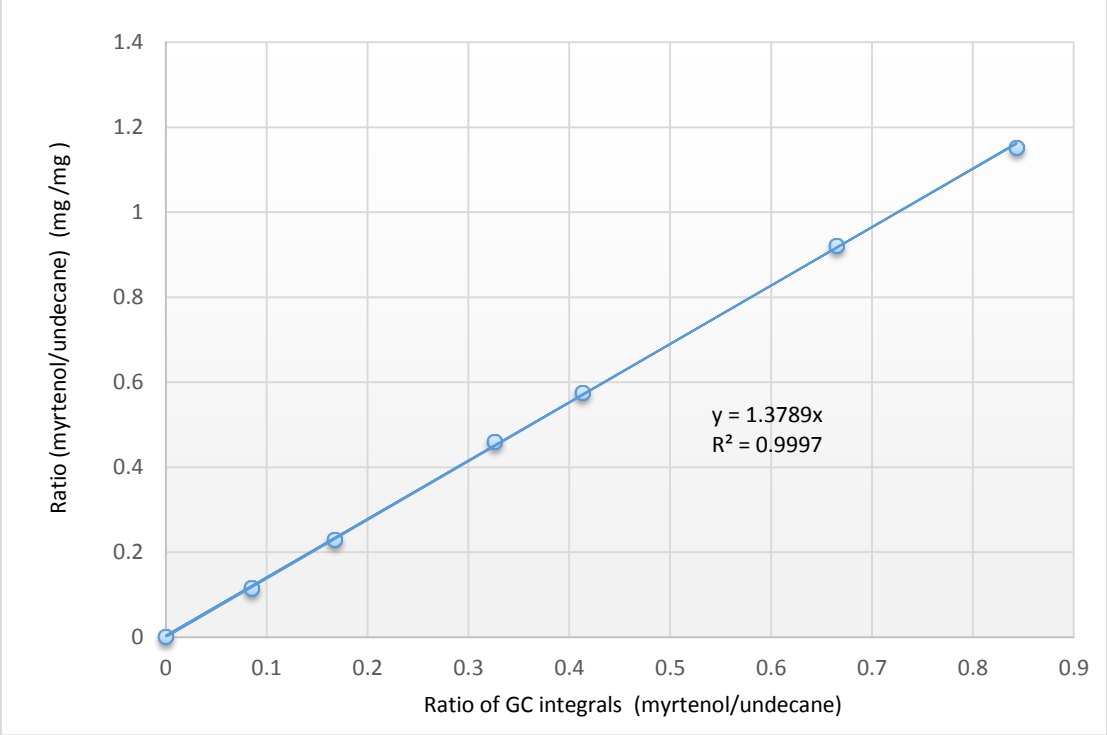


Figure SI-115. GC-FID calibration for (-)-myrtenol with undecane as internal standard.

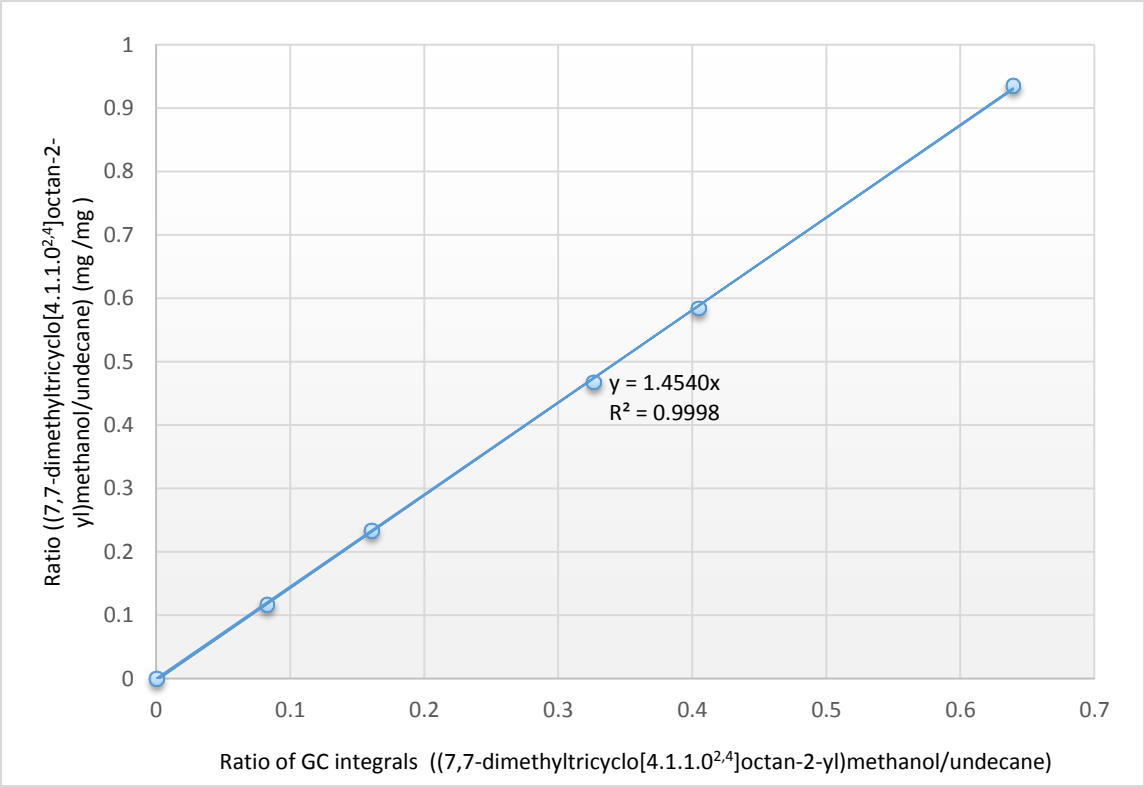


Figure SI-116. GC-FID calibration for (7,7-dimethyltricyclo[4.1.1.0^{2,4}]octan-2-yl)methanol with undecane as internal standard.

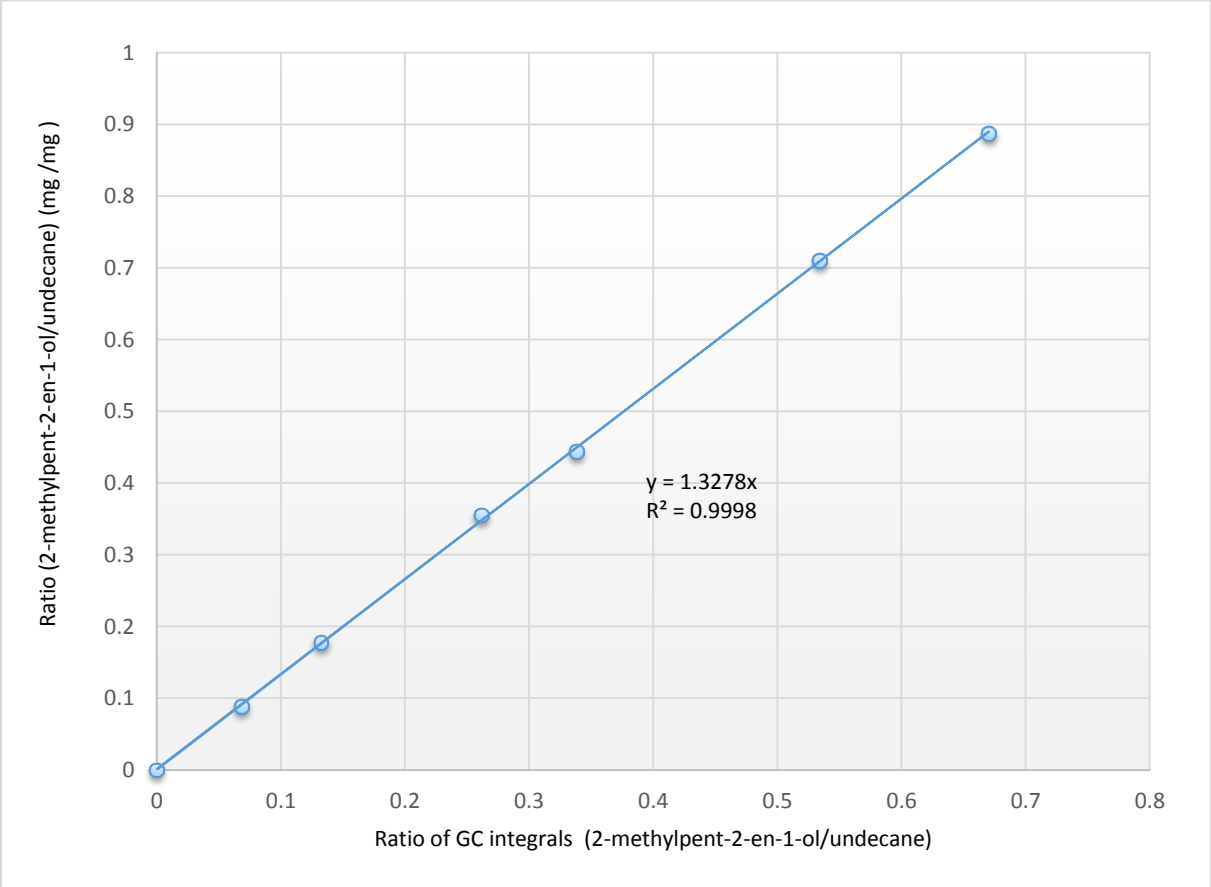


Figure SI-117. GC-FID calibration for 2-methylpent-2-en-1-ol with undecane as internal standard.

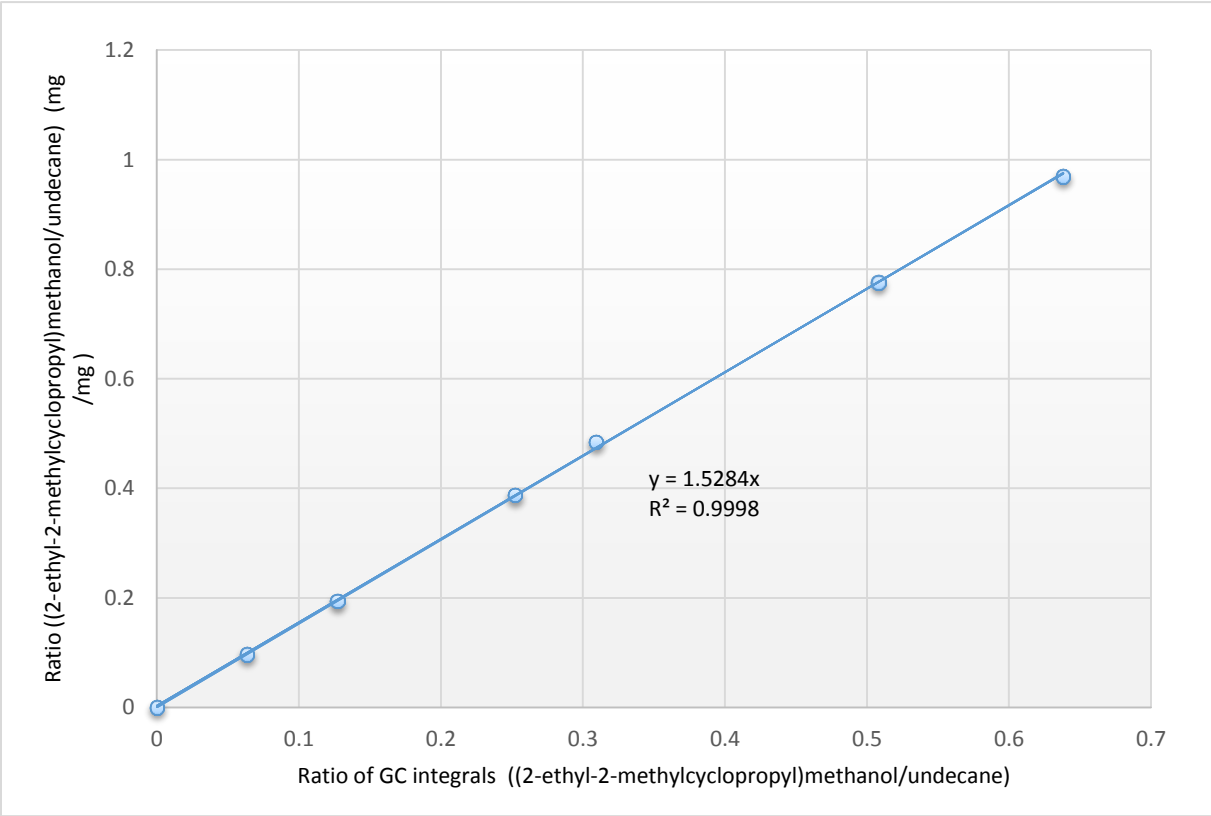


Figure SI-118. GC-FID calibration for (2-ethyl-2-methylcyclopropyl)methanol with undecane as internal standard.

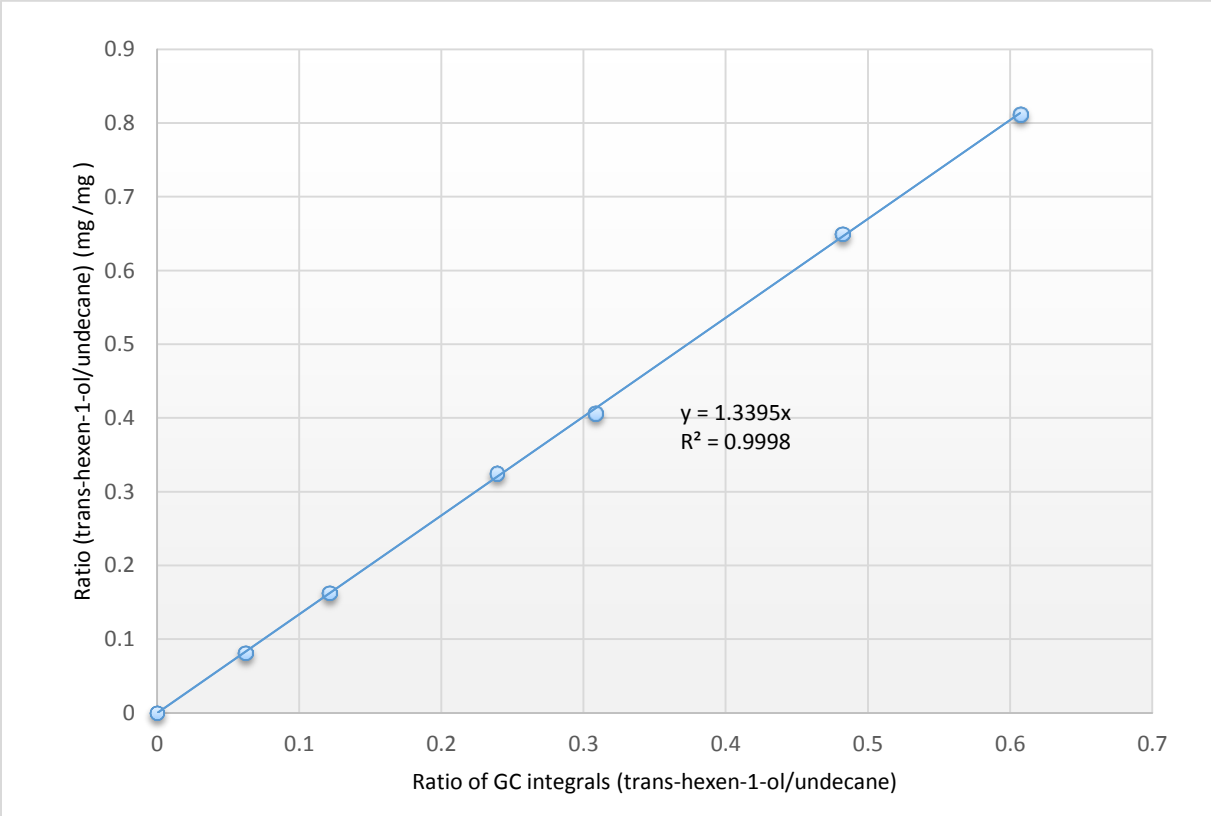


Figure SI-119. GC-FID calibration for *trans*-hexen-1-ol with undecane as internal standard.

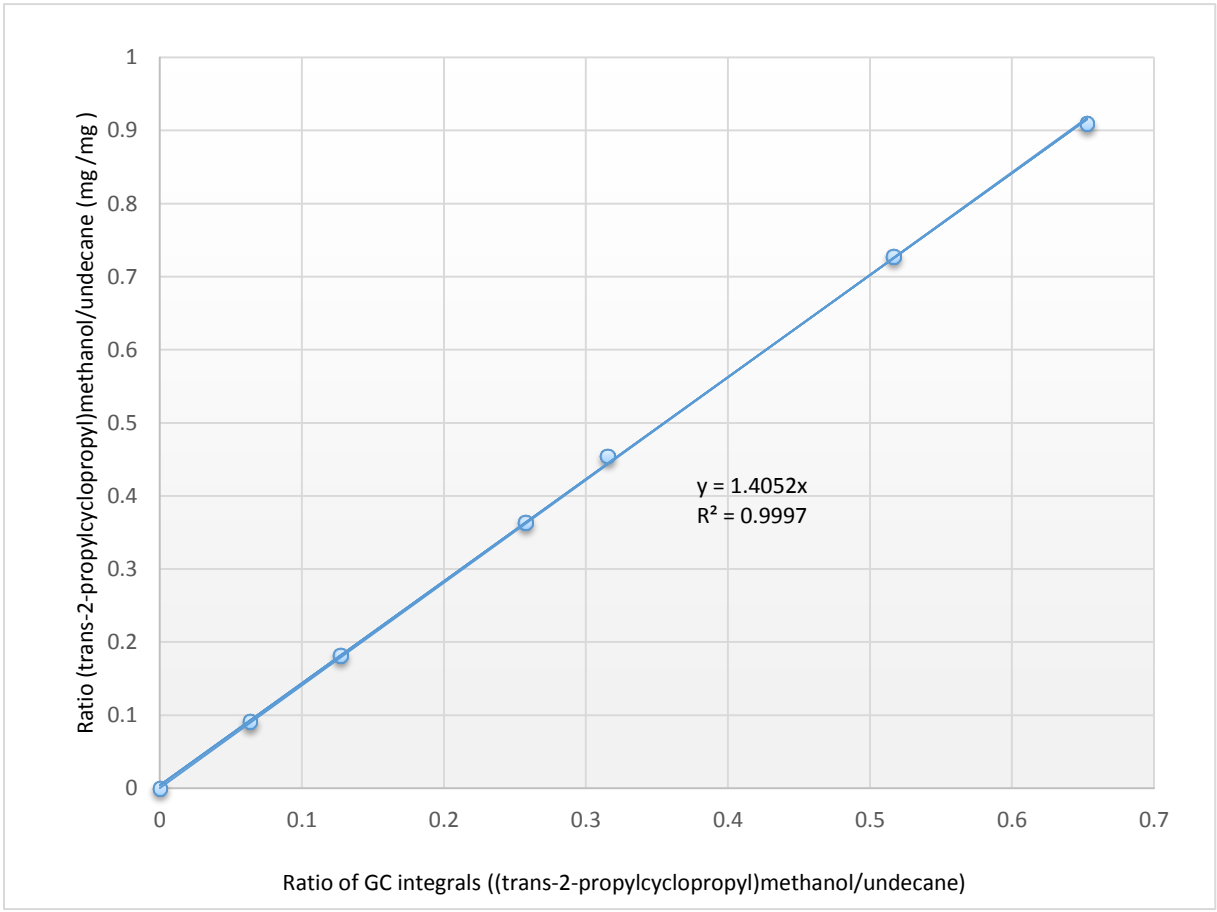


Figure SI-120. GC-FID calibration for(*trans*-2-propylcyclopropyl)methanol with undecane as internal standard.

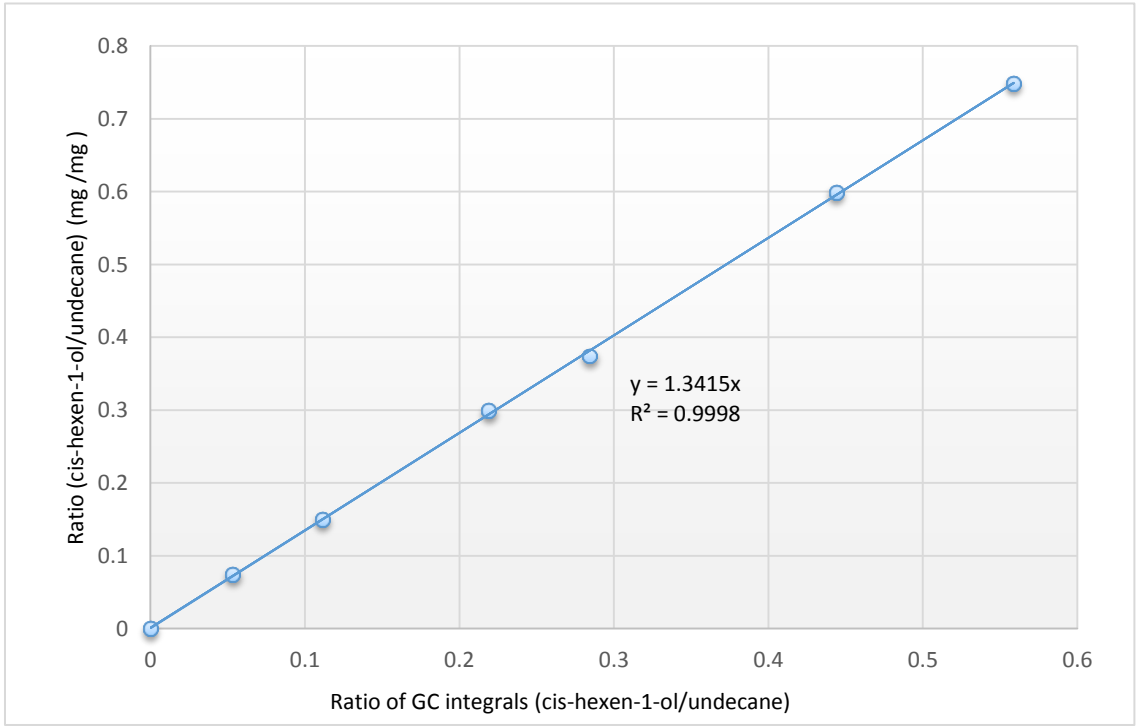


Figure SI-121. GC-FID calibration for *cis*-hexen-1-ol with undecane as internal standard.

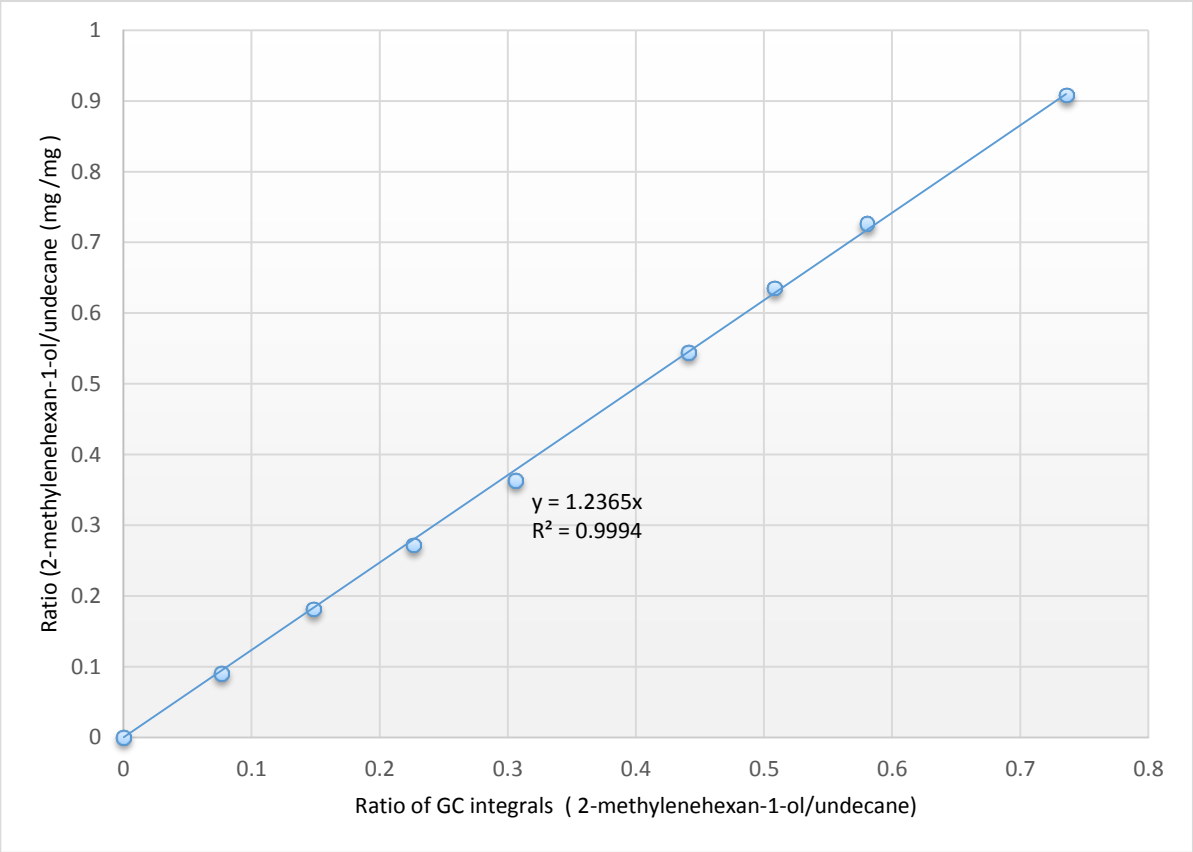


Figure SI-122. GC-FID calibration for 2-methylenehexan-1-ol with undecane as internal standard.

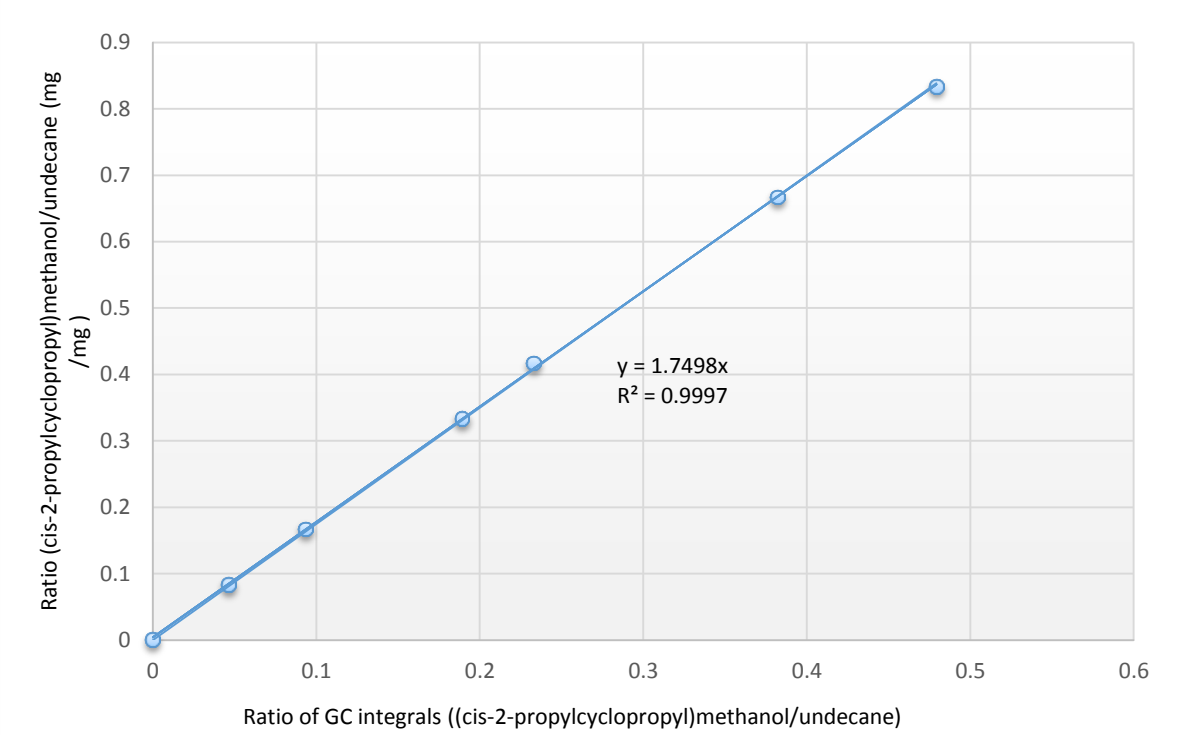


Figure SI-123. GC-FID calibration for (*cis*-2-propylcyclopropyl)methanol with undecane as internal standard.

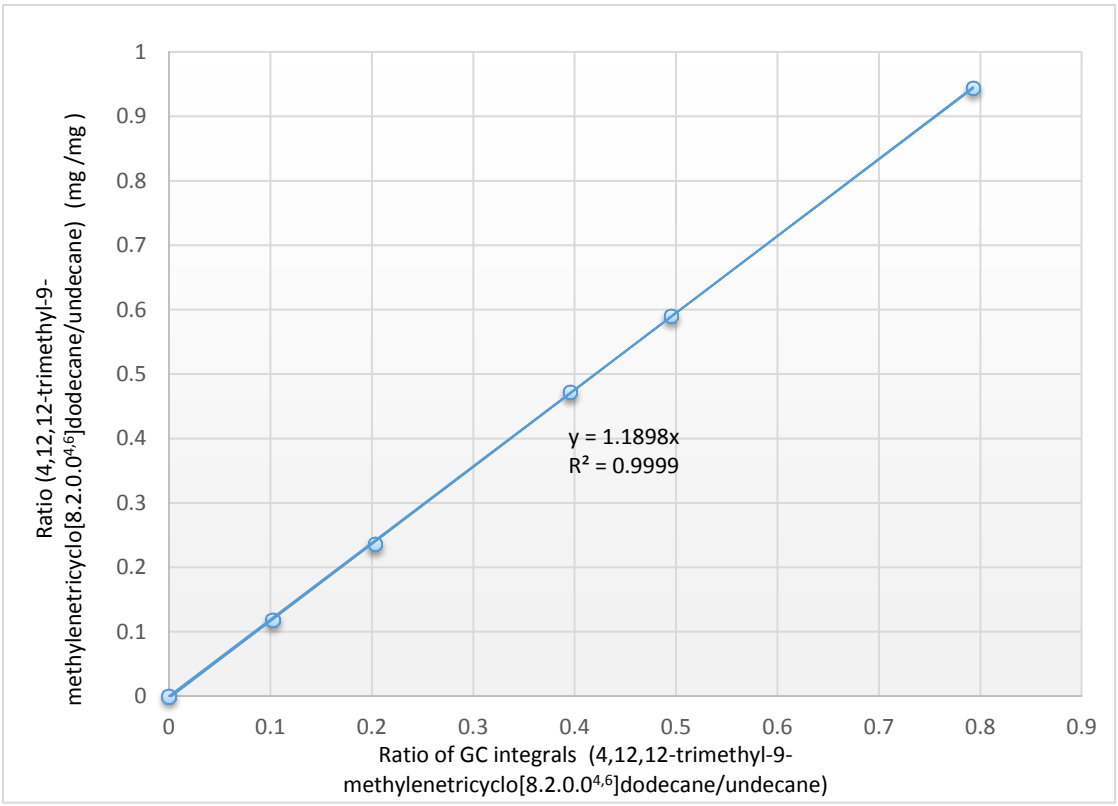


Figure SI-124. GC-FID calibration for 4,12,12-trimethyl-9-methylenetricyclo[8.2.0.0^{4,6}]dodecane with undecane as internal standard.

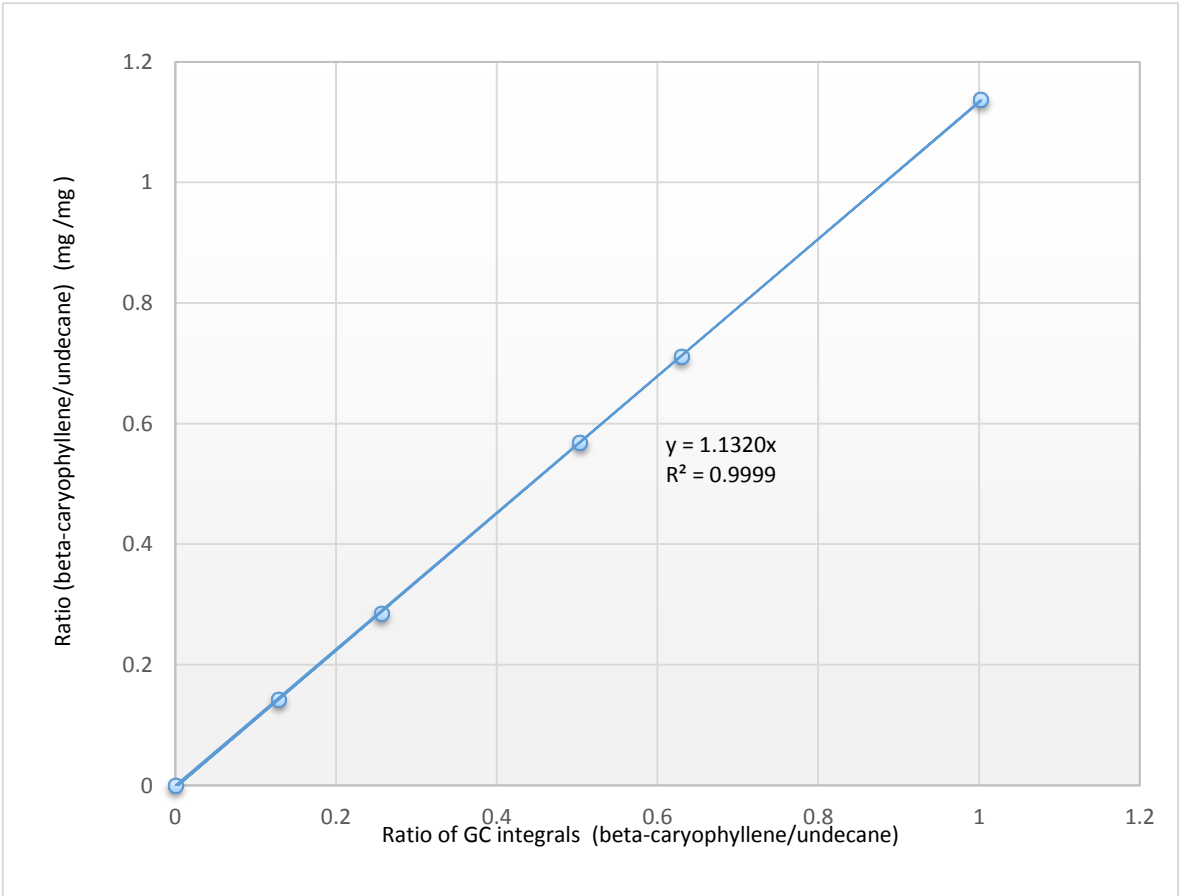


Figure SI-125. GC-FID calibration for β-caryophyllene with undecane as internal standard.

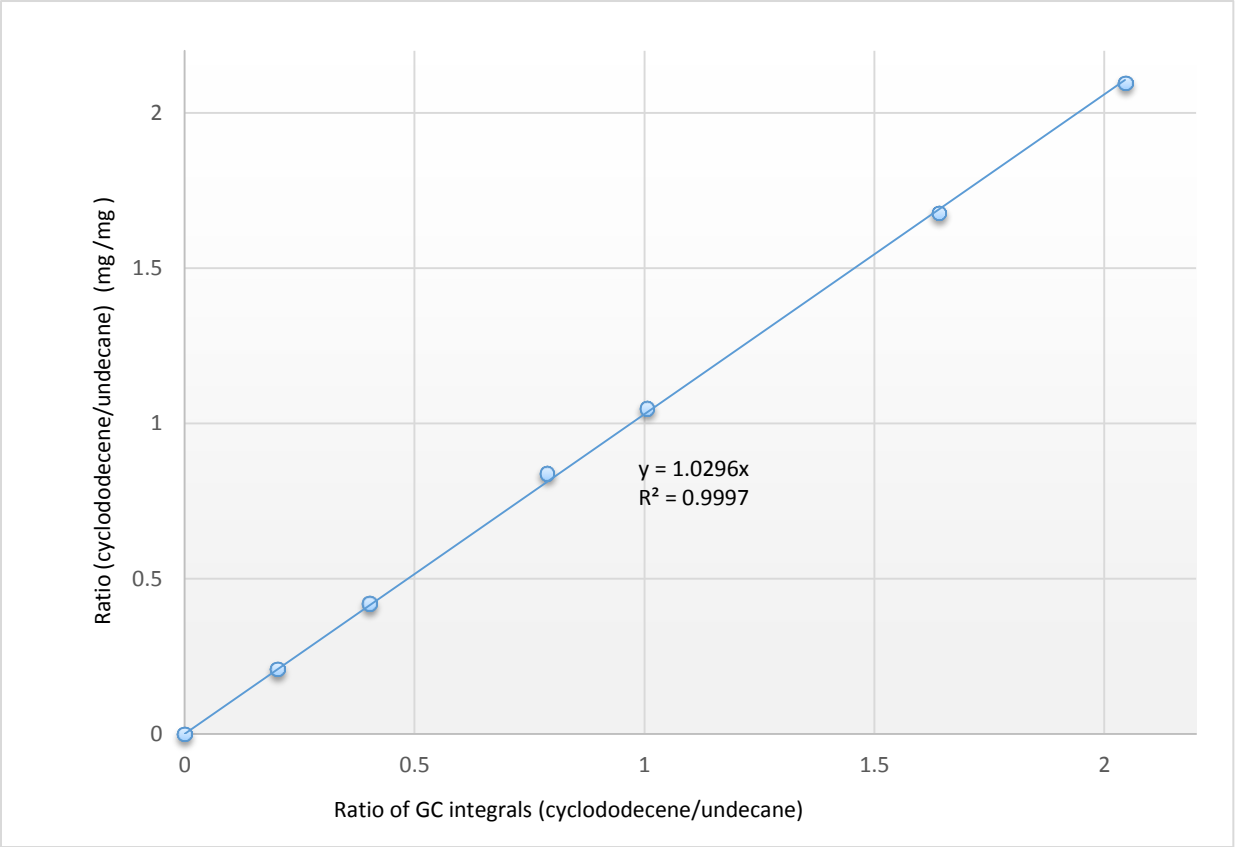


Figure SI-126. GC-FID calibration for cyclododecene with undecane as internal standard.

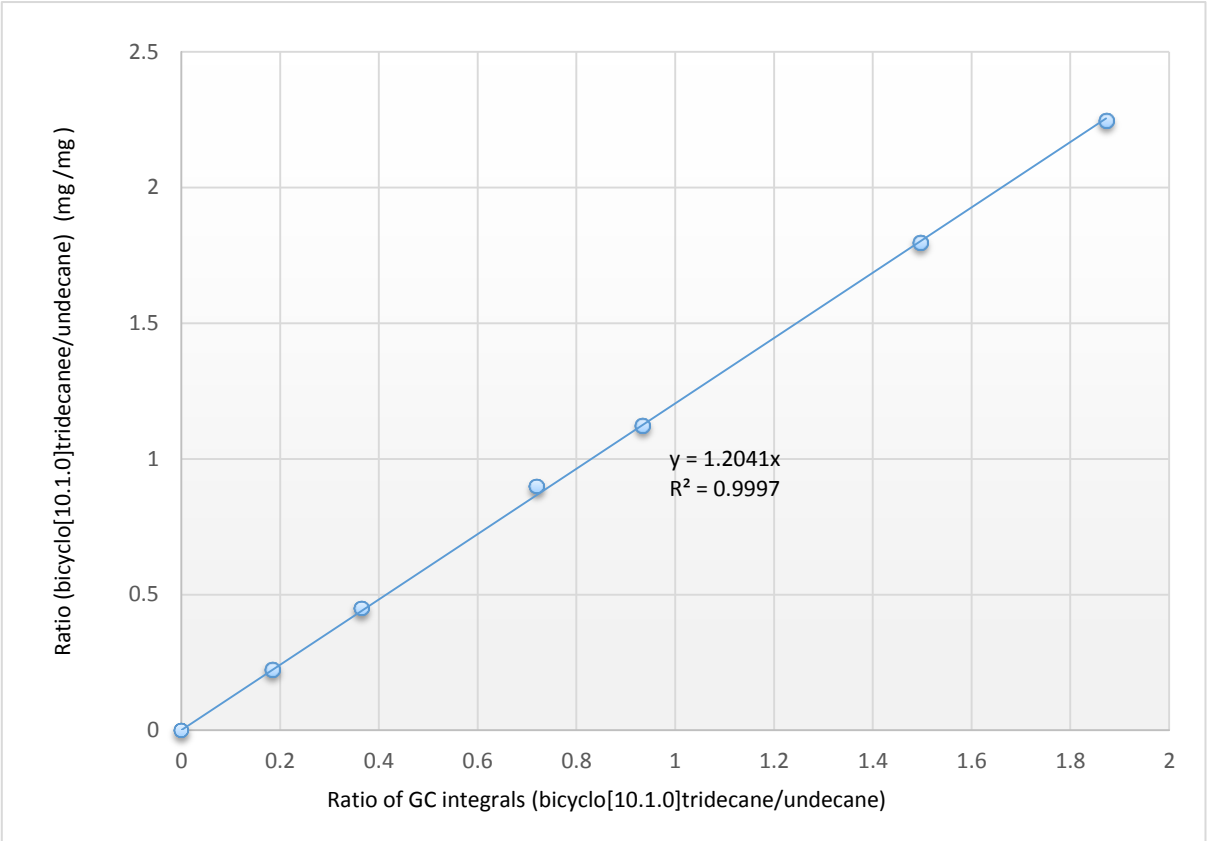


Figure SI-127. GC-FID calibration for bicyclo[10.1.0]tridecane with undecane as internal standard.

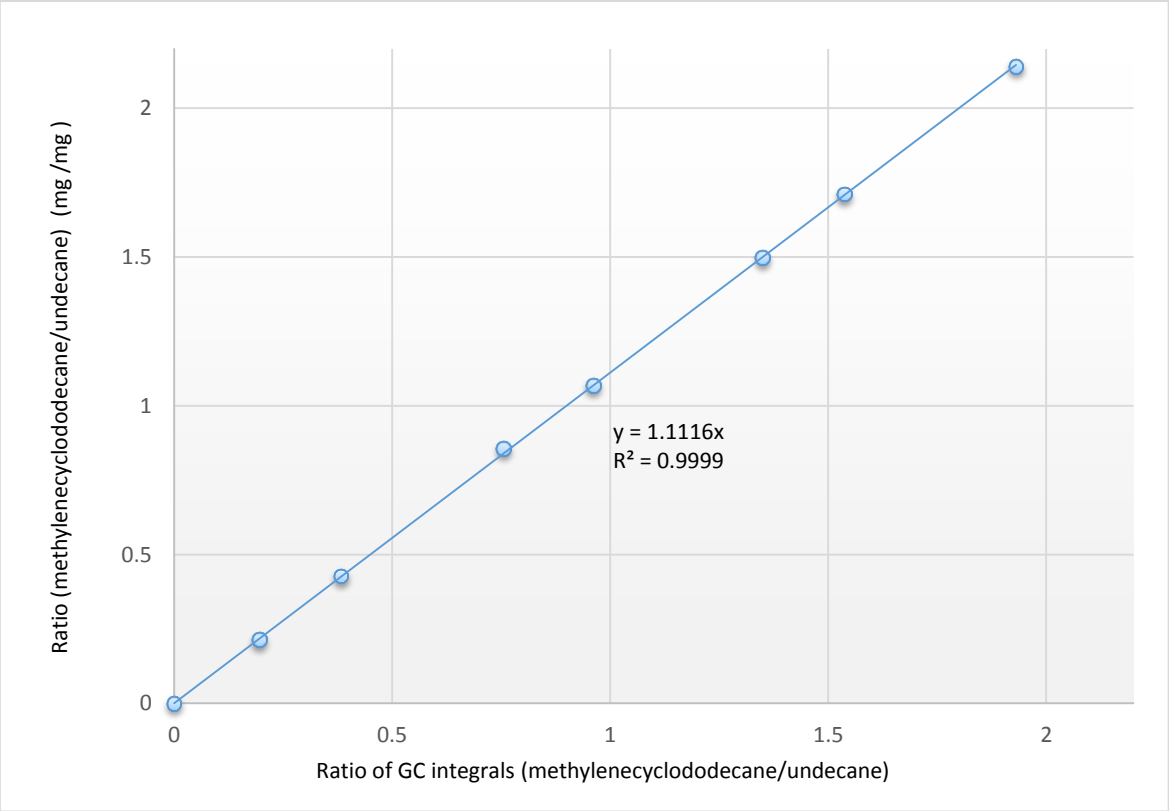


Figure SI-128. GC-FID calibration for methylenecyclododecane with undecane as internal standard.

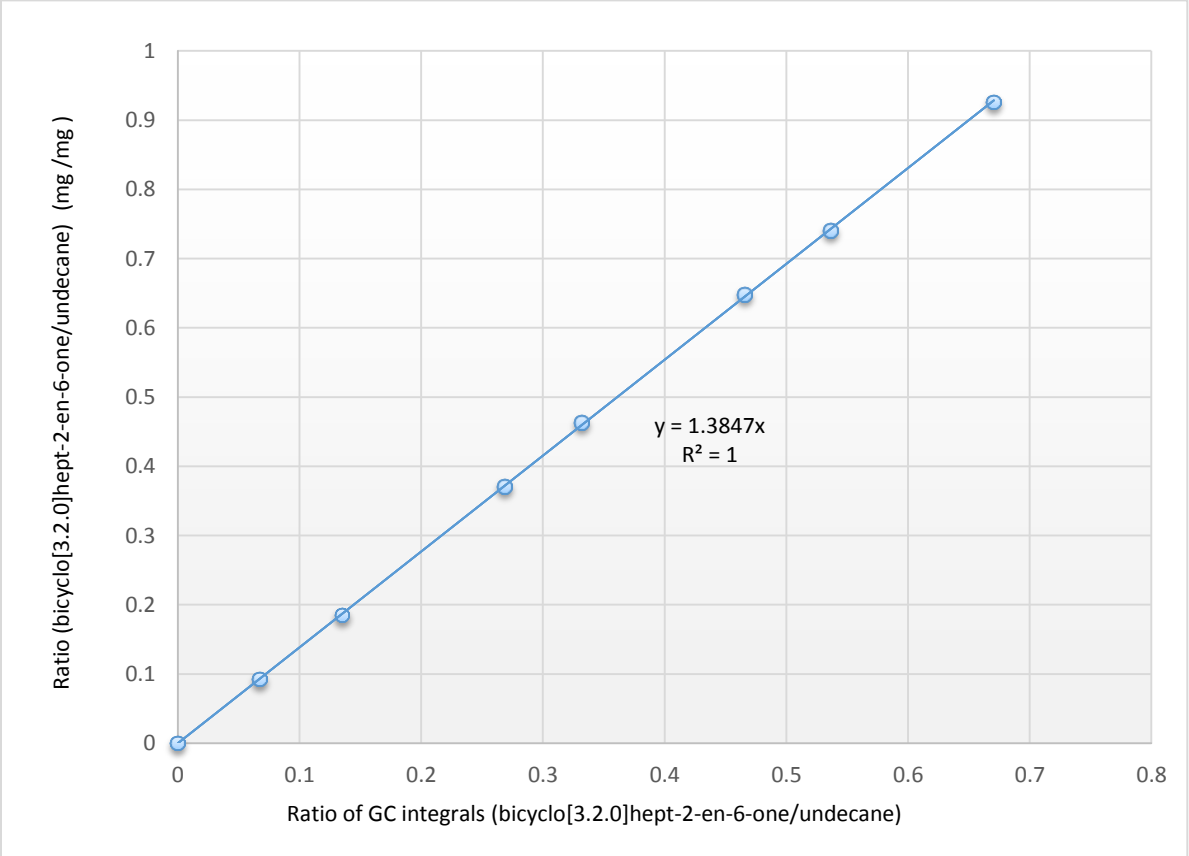


Figure SI-129. GC-FID calibration for bicyclo[3.2.0]hept-2-en-6-one with undecane as internal standard.

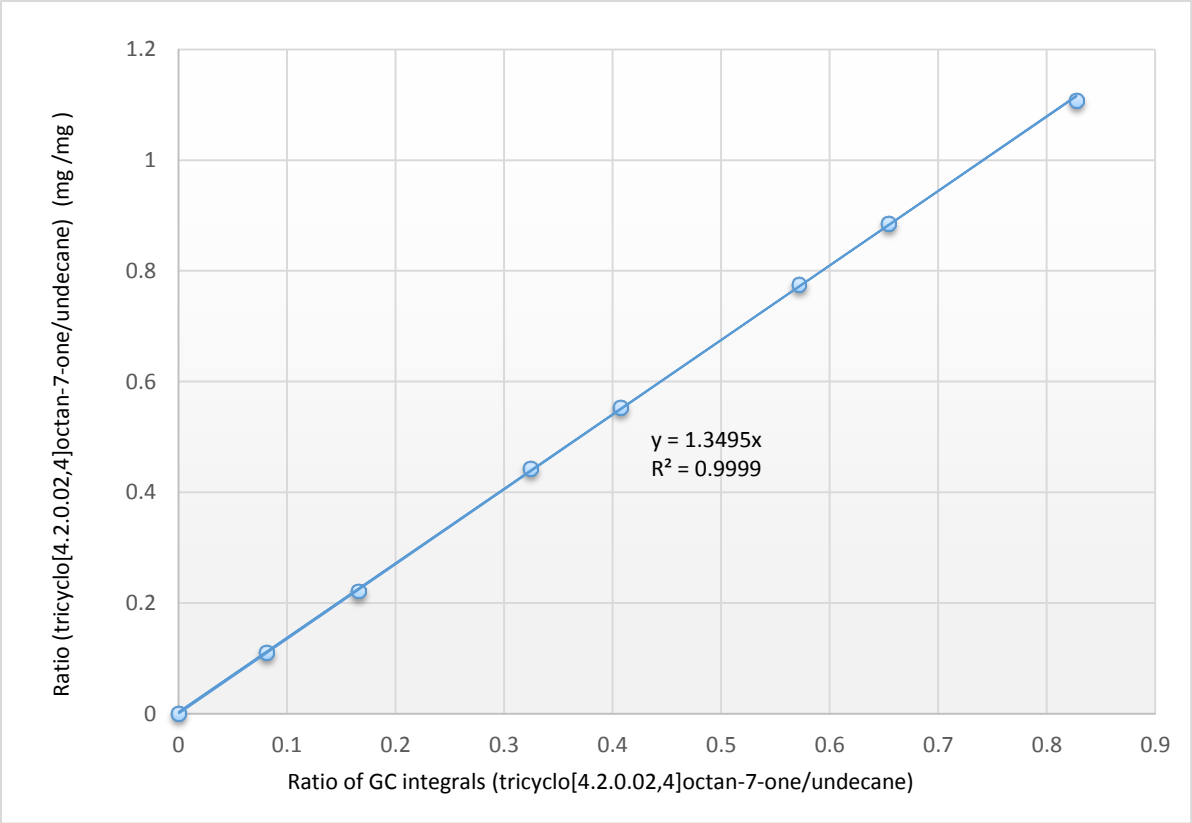


Figure SI-130. GC-FID calibration for tricyclo[4.2.0.02,4]octan-7-one with undecane as internal standard.

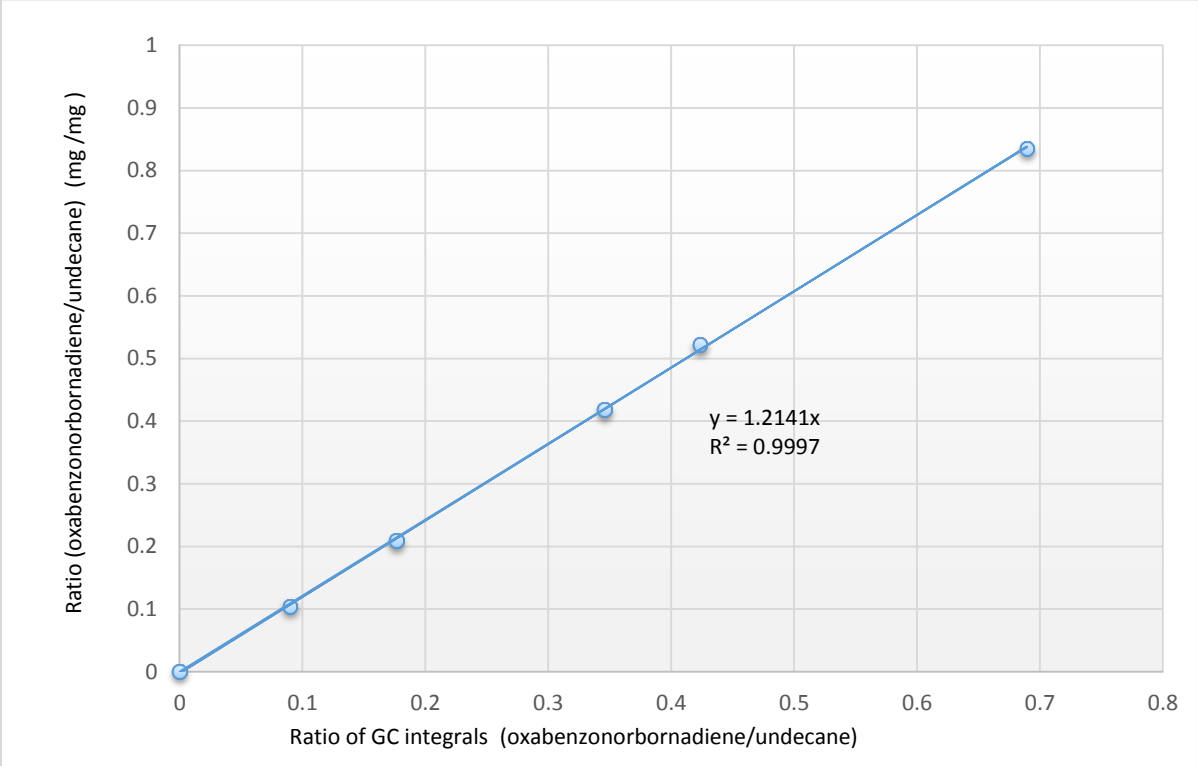


Figure SI-131. GC-FID calibration for oxabenzonorbornadiene with undecane as internal standard.

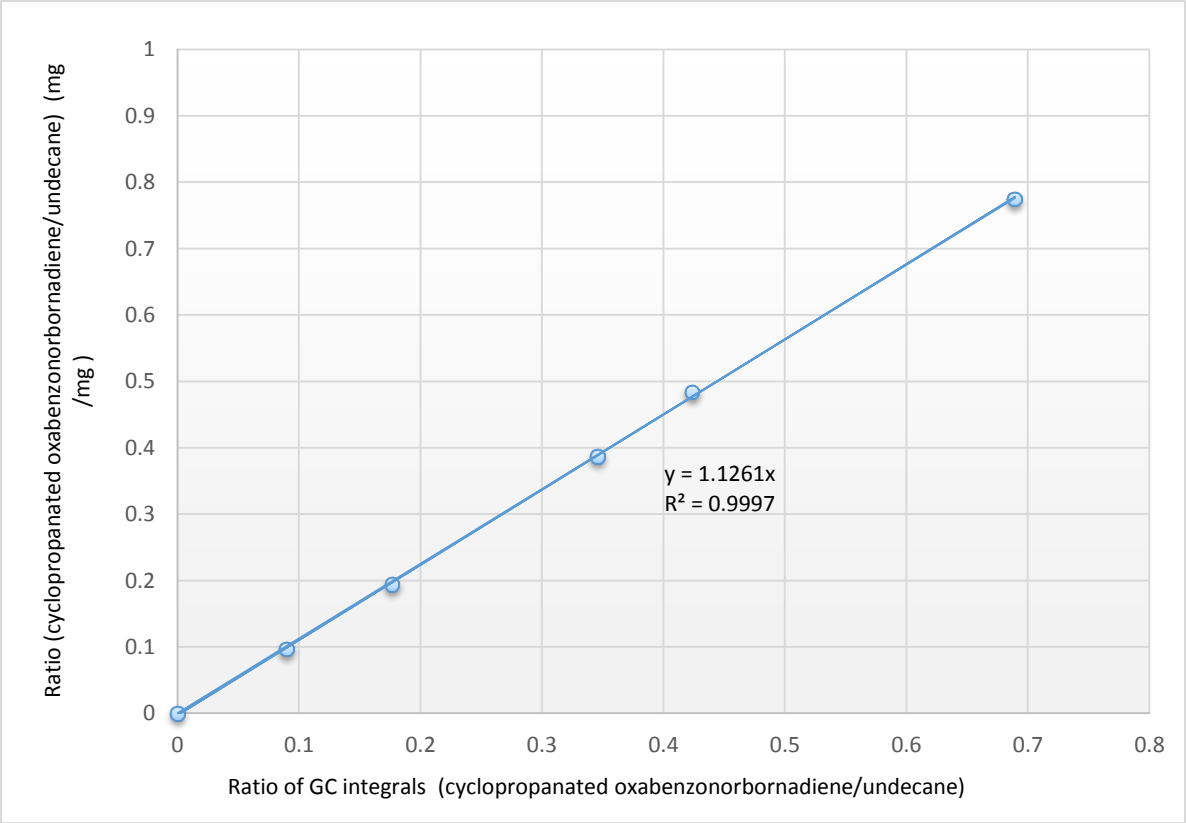


Figure SI-132. GC-FID calibration for cyclopropanated oxabenzonorbornadiene with undecane as internal standard.

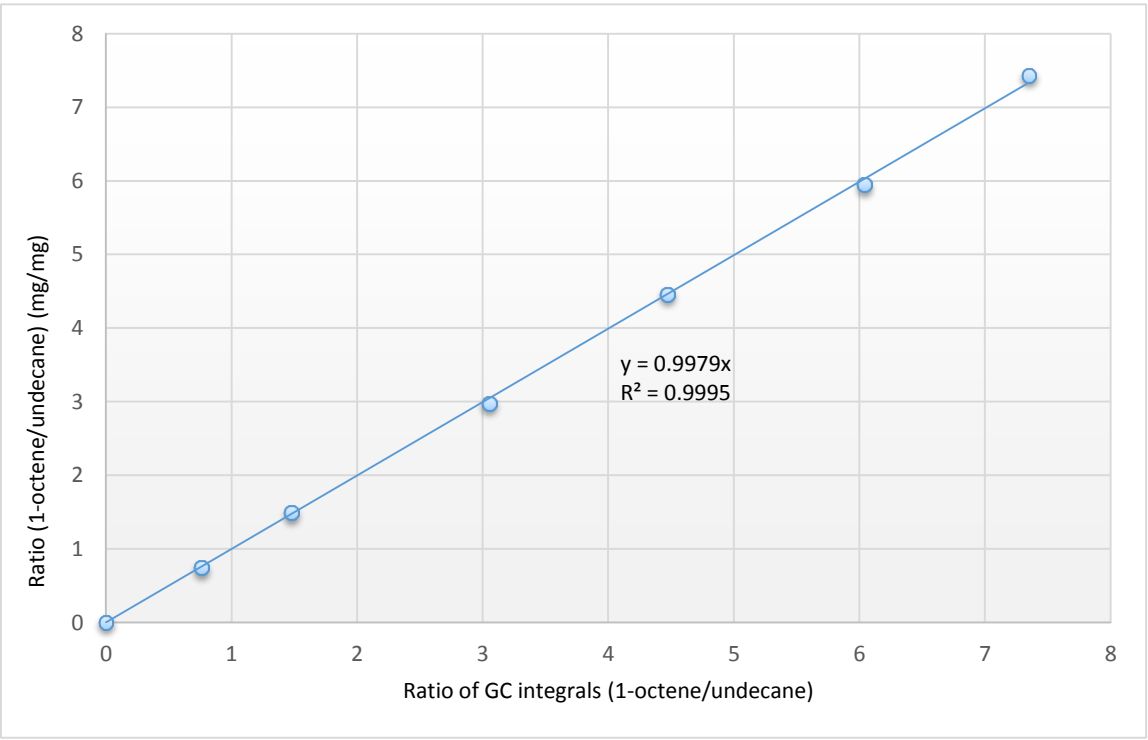


Figure SI-133. GC-FID calibration for 1-octene with undecane as internal standard.

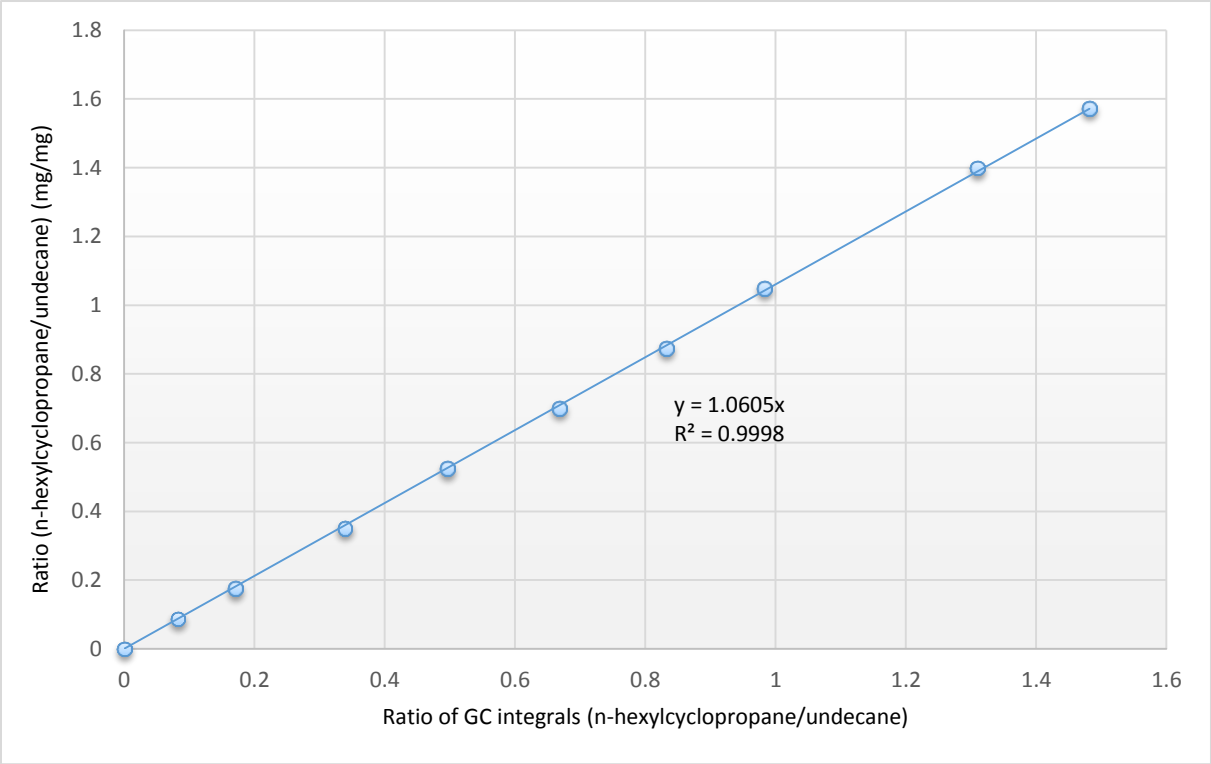


Figure SI-134. GC-FID calibration for n-hexylcyclopropane with undecane as internal standard.

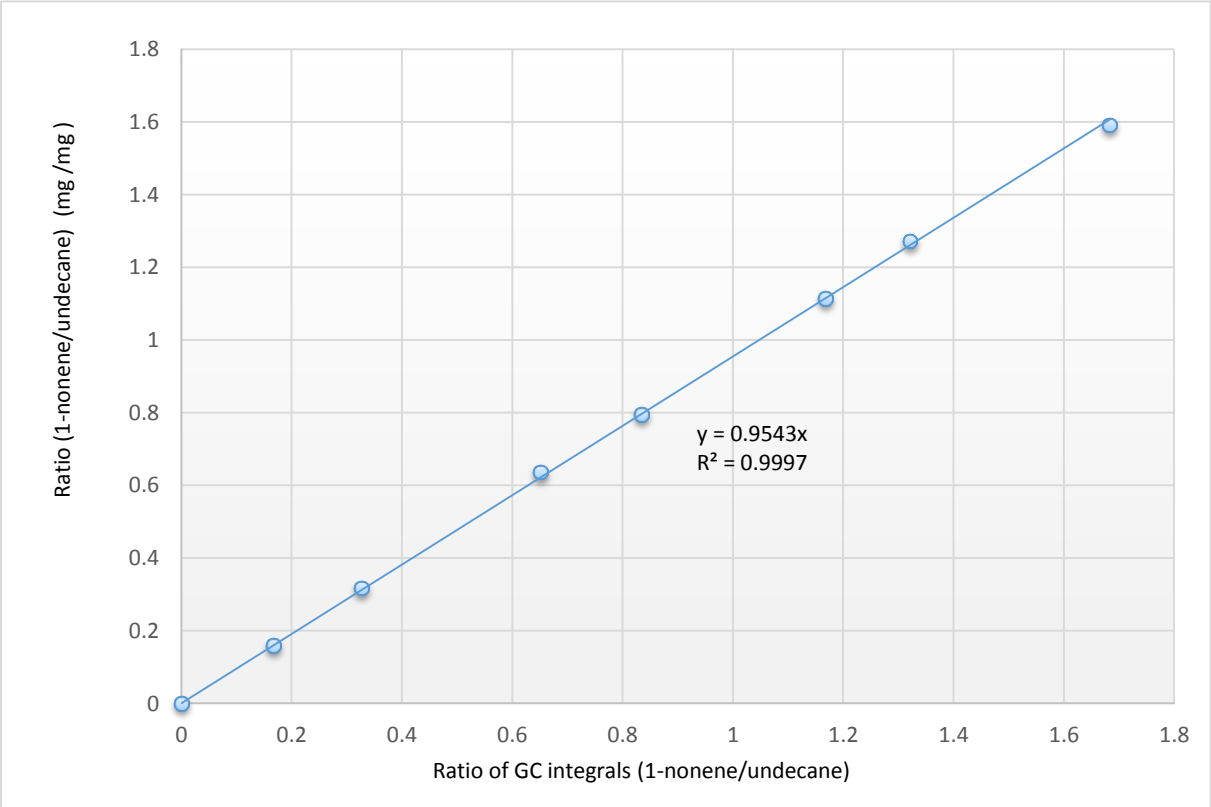


Figure SI-135. GC-FID calibration for 1-nonene with undecane as internal standard.

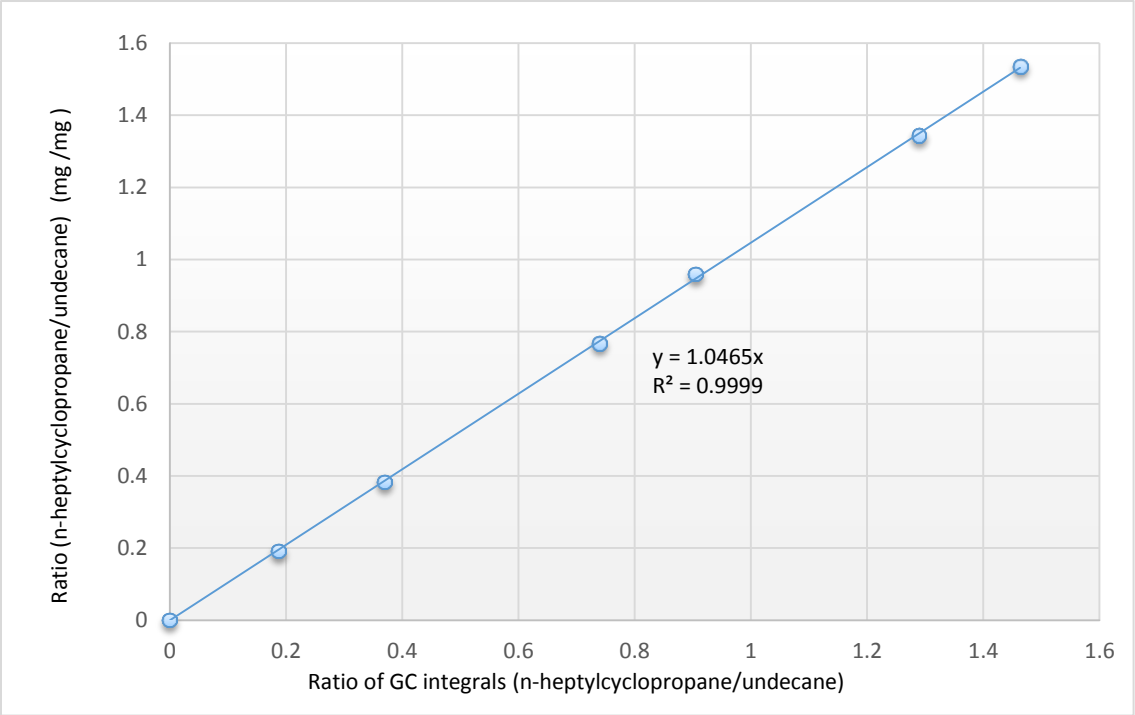


Figure SI-136. GC-FID calibration for n-heptylcyclopropane with undecane as internal standard.

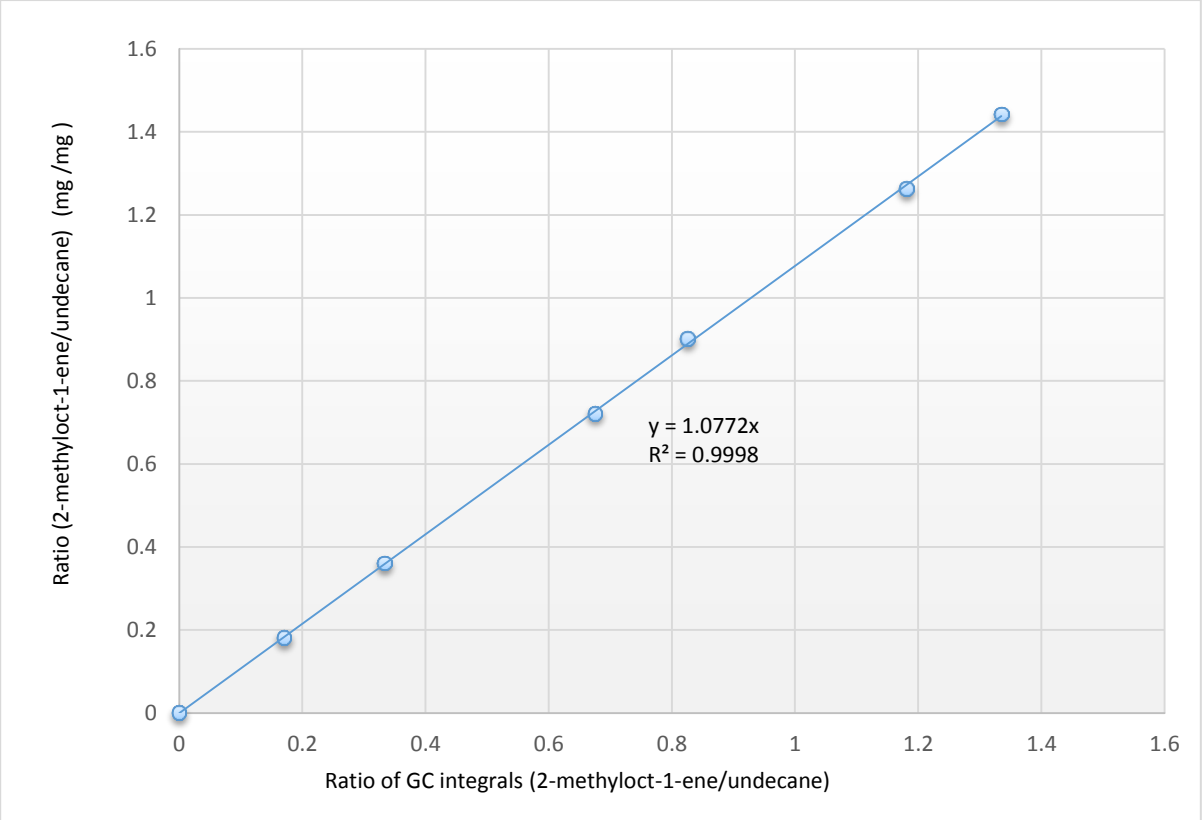


Figure SI-137. GC-FID calibration for 2-methyloct-1-ene with undecane as internal standard.

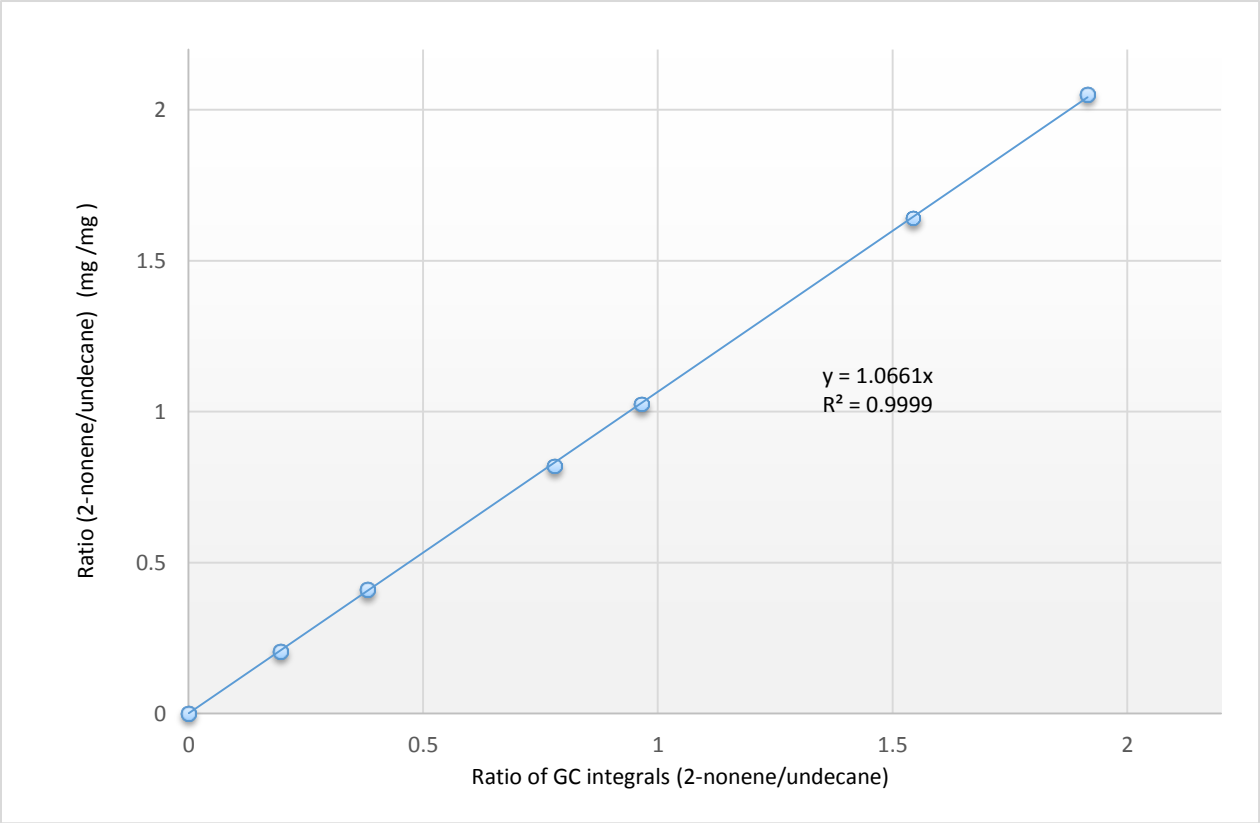


Figure SI-138. GC-FID calibration for 2-nonene with undecane as internal standard.

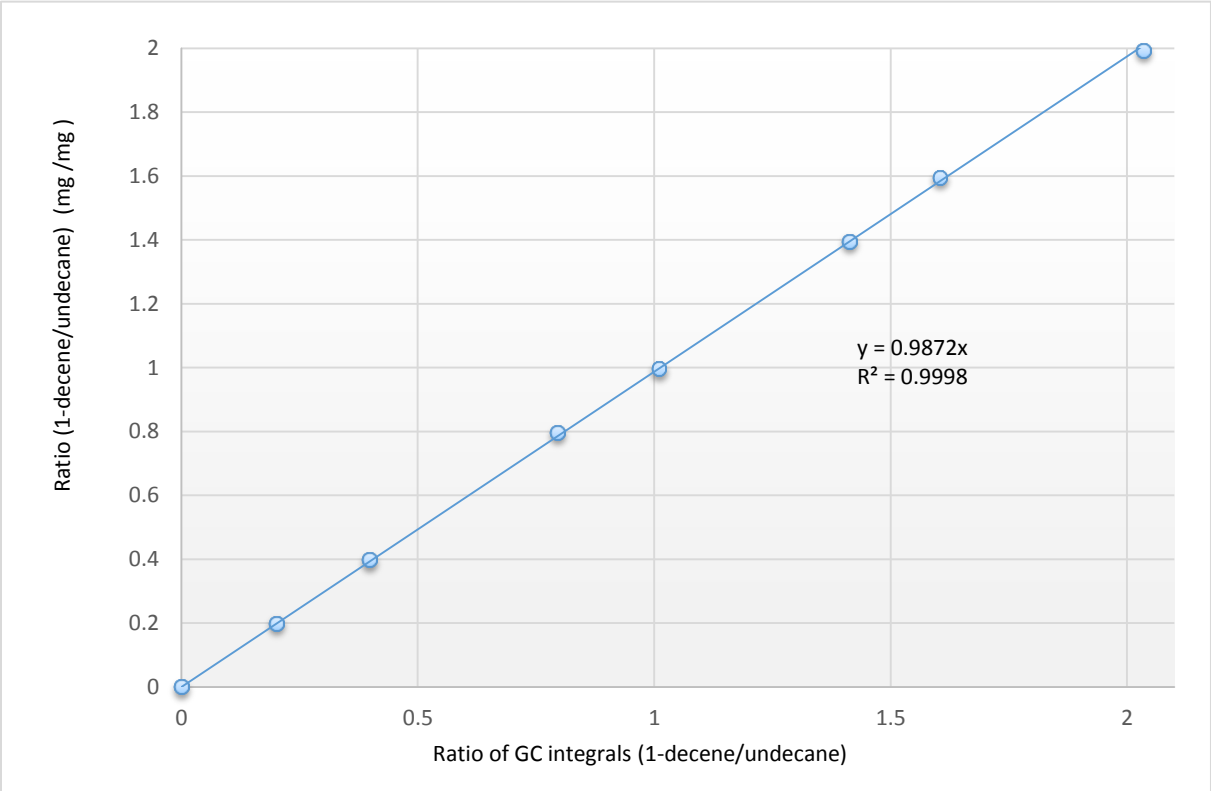


Figure SI-139. GC-FID calibration for 1-decene with undecane as internal standard.

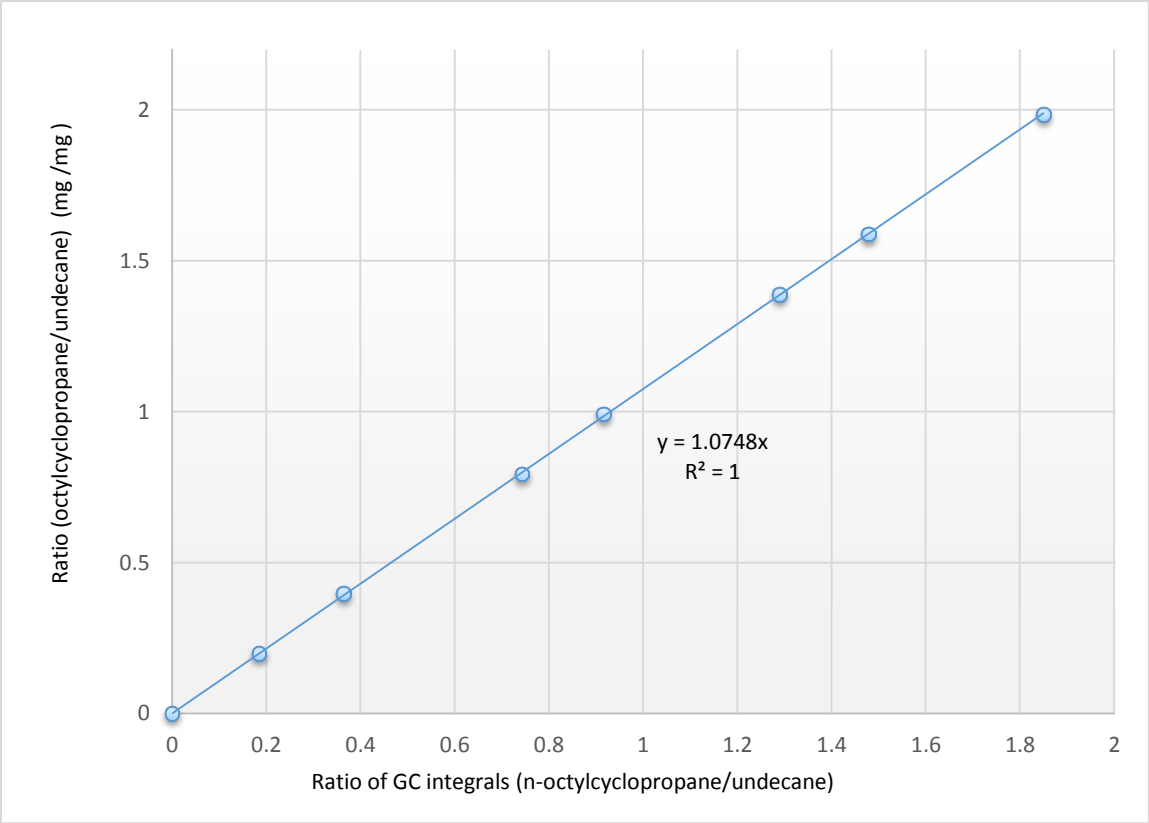


Figure SI-140. GC-FID calibration for n-octylcyclopropane with undecane as internal standard.

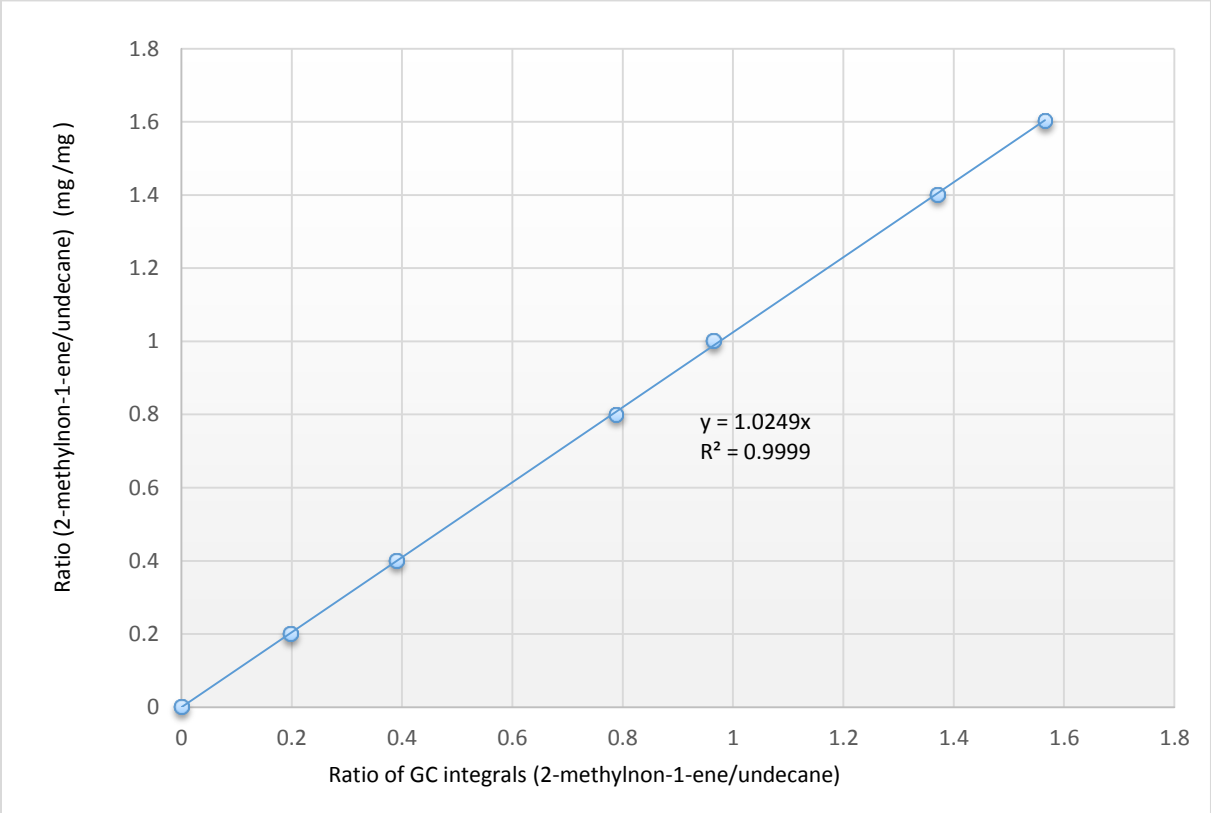


Figure SI-141. GC-FID calibration for 2-methylnon-1-ene with undecane as internal standard.

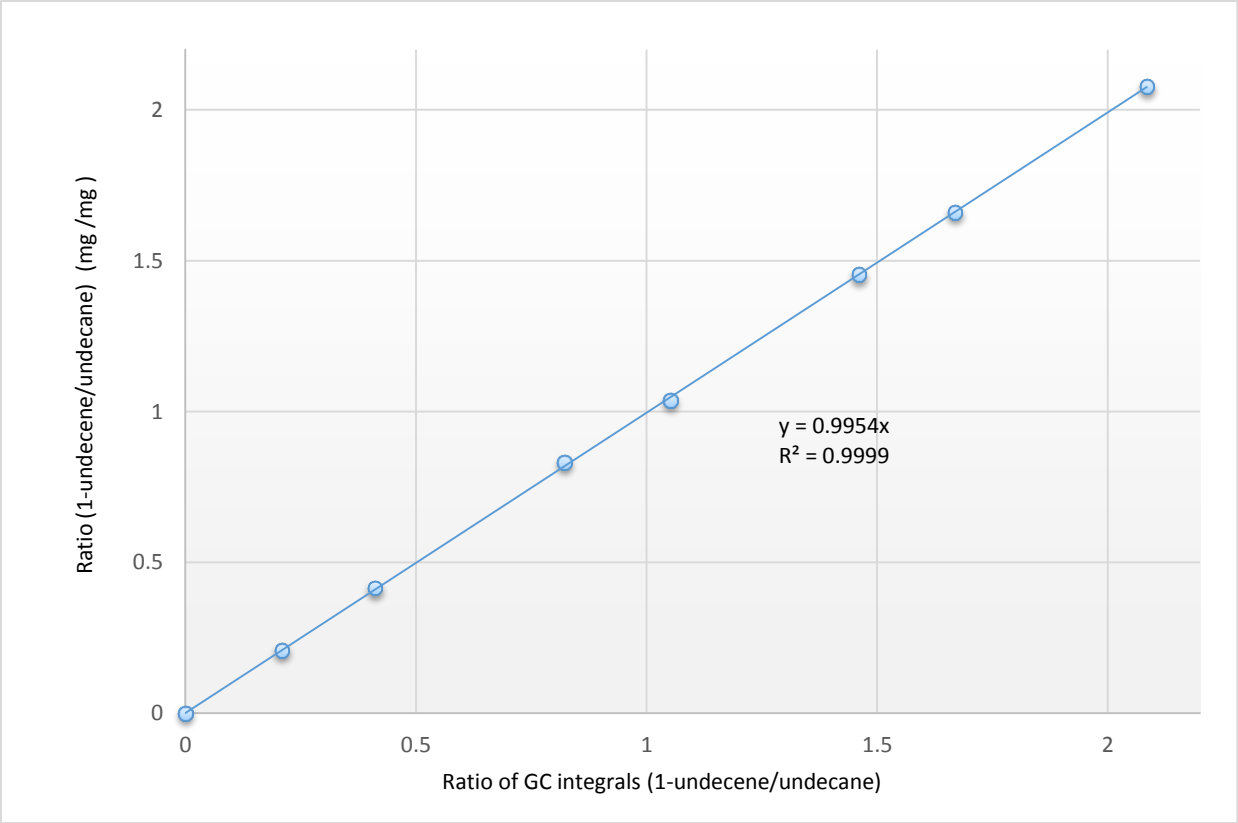


Figure SI-142. GC-FID calibration for 1-undecene with undecane as internal standard.

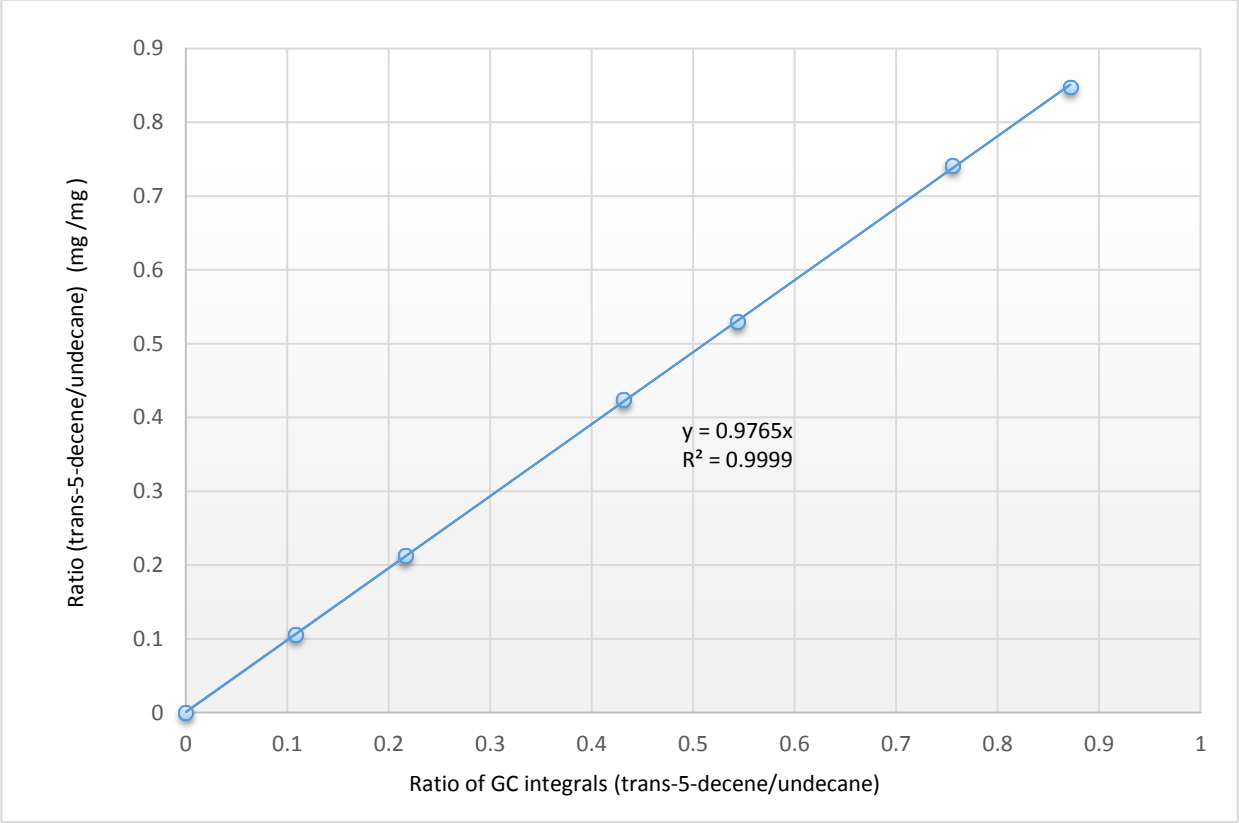


Figure SI-143. GC-FID calibration for *trans*-5-decene with undecane as internal

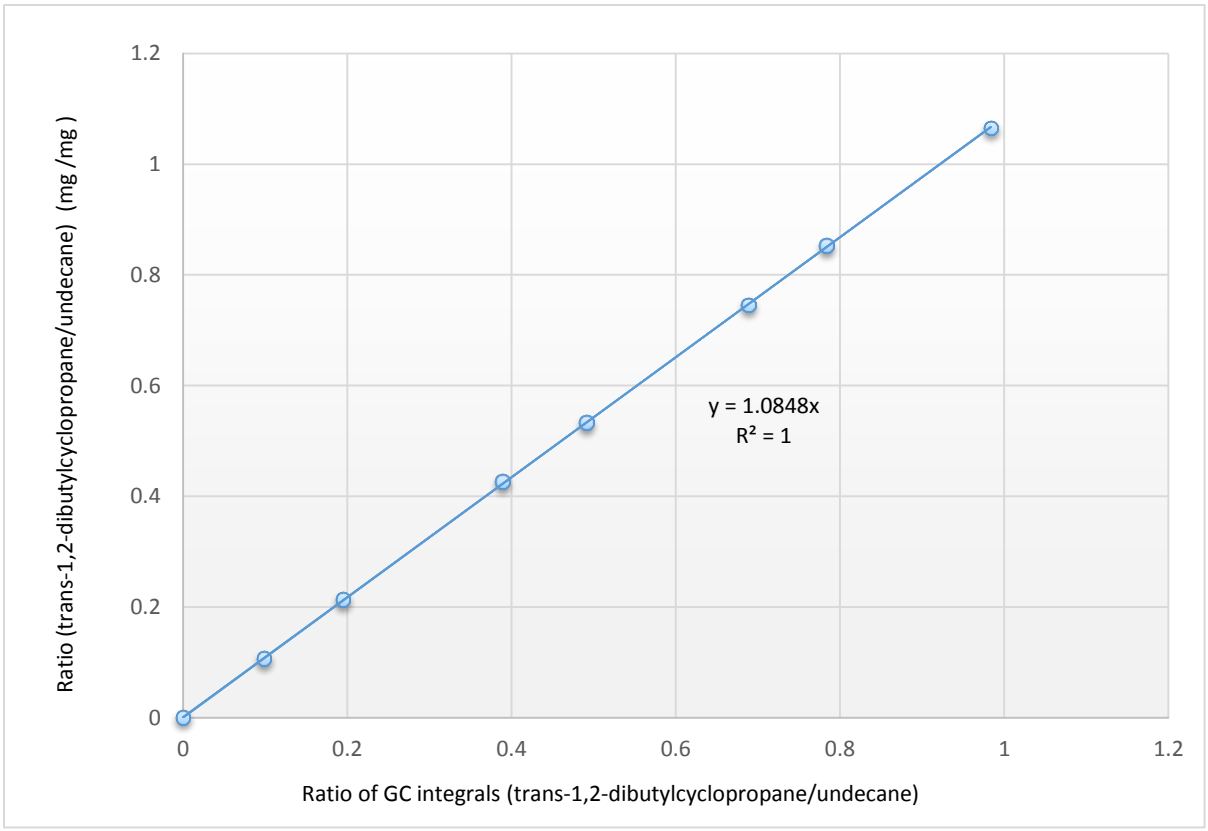


Figure SI-144. GC-FID calibration for *trans*-1,2-dibutylcyclopropane with undecane as internal standard.

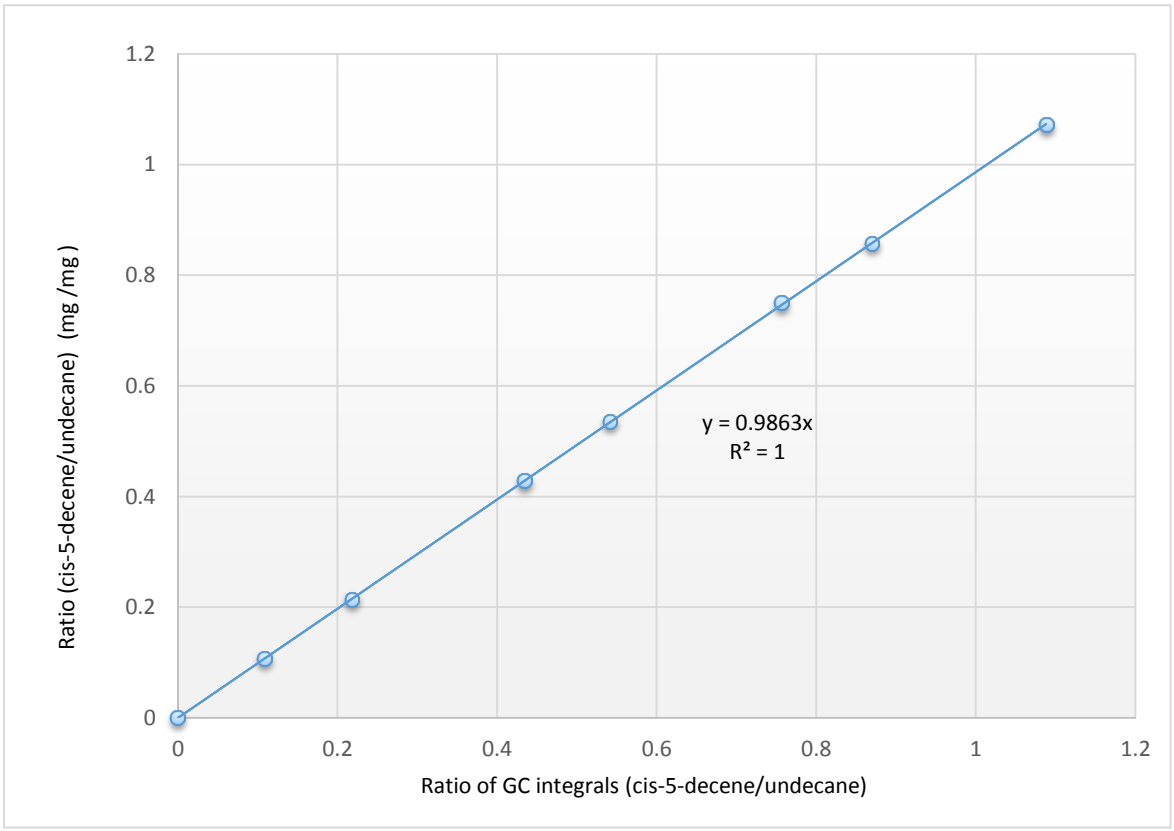


Figure SI-145. GC-FID calibration for *cis*-5-decene with undecane as internal standard.

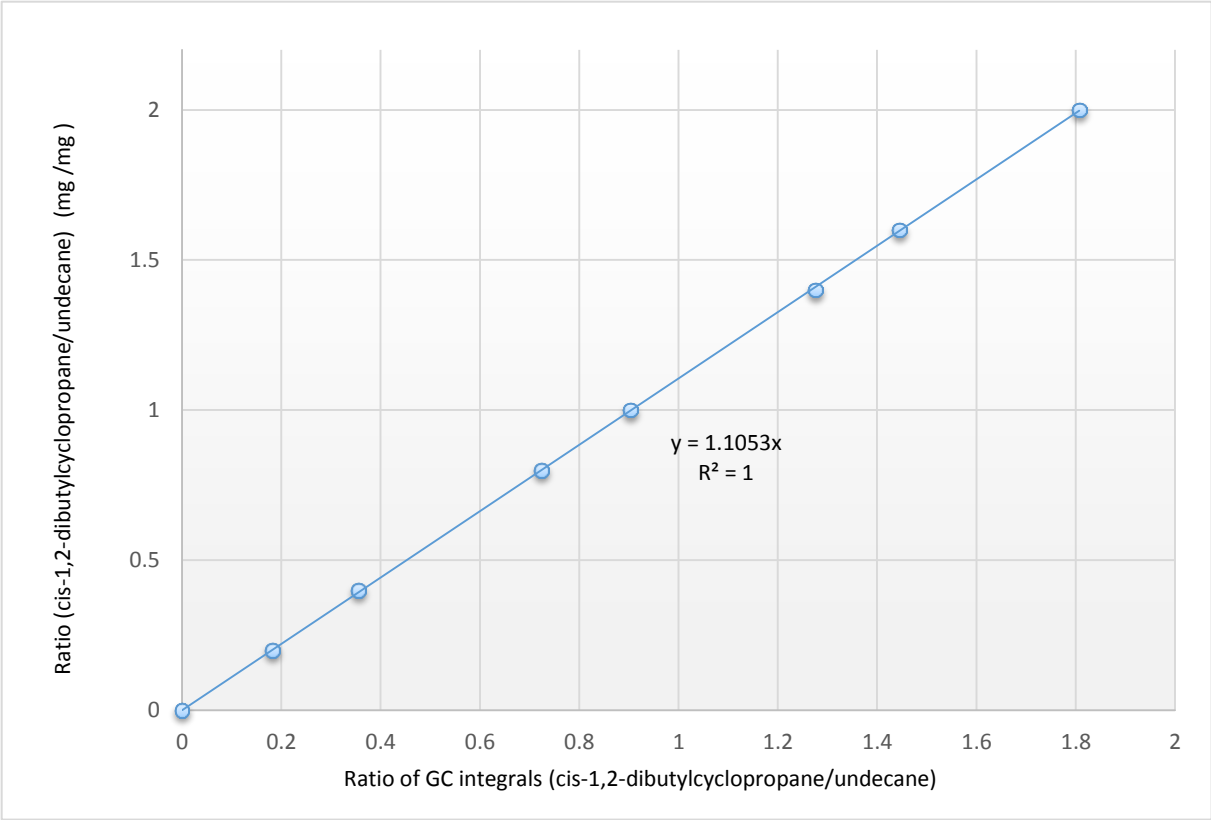


Figure SI-146. GC-FID calibration for *cis*-1,2-dibutylcyclopropane with undecane as internal standard.

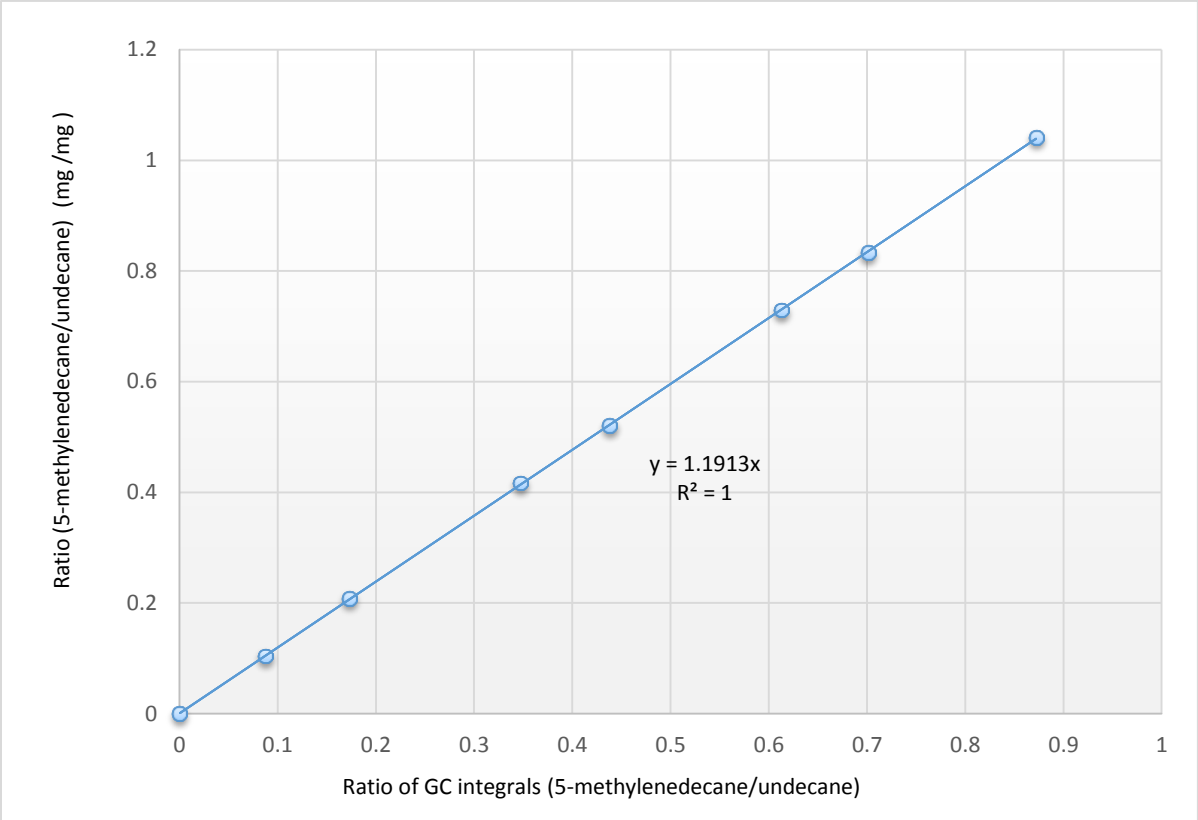


Figure SI-147. GC-FID calibration for 5-methylenedecane with undecane as internal standard.