Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Highly Diastereoselective Approach to Methylenecyclopropanes *via* Boron-Homologation / Allylboration Sequences

A. N. Baumann, A. Music, K. Karaghiosoff and D. Didier*

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1. General Remarks

Commercial available starting materials were used without further purification unless otherwise stated. All reactions were carried out under N_2 atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use.

CH_2Cl_2 was predried over $CaCl_2$ and distilled from CaH_2 . THF was refluxed and distilled from sodium benzophenone ketyl under nitrogen. Et_2O was predried over $CaCl_2$ and passed through activated Al_2O_3 (the solvent purification system SPS-400-2 from Innovative Technologies Inc.).

Chormatography purifications were performed using silica gel (SiO_2 , 0.040-0.063 mm, 230-400 mesh ASTM) from Merck or Florisil ($MgSiO_3$, 60-100 mesh) from APOLLO.The spots were visualized under UV (254 nm) or by staining the TLC plate with $KMnO_4$ solution (K_2CO_3, 10 g – $KmnO_4$, 1.5 g – H_2O, 150 mL – NaOH 10% in H_2O, 1.25 mL), *p*-anisaldehyde solution (conc. H_2SO_4, 10 mL – EtOH, 200 mL – AcOH, 3 mL – *p*-anisaldehyde, 4 mL) and/or "Magic stain" (phosphomolybdic acid, 2.5 g – $Ce(SO_4)_2$, 1 g – conc. H_2SO_4, 6 mL – H_2O, 94 mL).

Diastereoisomeric ratios were determined by ^1H NMR and ^{13}C NMR.

NMR spectra were recorded on Bruker WH-400 instrument. Chemical shifts are reported as δ values in ppm relative to residual solvent peak (^1H-NMR) or solvent peak (^{13}C-NMR) in deuterated chloroform ($CDCl_3$: δ 7.26 ppm for ^1H-NMR and δ 77.16 ppm for ^{13}C-NMR). Abbreviations for signal coupling are as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet) and br (broad). Gas chromatography was performed with machines of Agilent Technologies 7890, using a column of type HP 5 (Agilent 5% phenylmethylpolysiloxane; length: 15 m; diameter: 0.25 mm; film thickness: 0.25 µm) or Hewlett-Packard 6890 or 5890 series II, using a column of type HP 5 (HewlettPackard, 5% phenylmethylpolysiloxane; length: 15 m; diameter: 0,25 mm; film thickness: 0.25 µm).

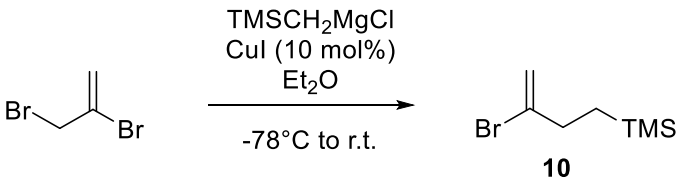
High resolution mass spectra (HRMS) and low resolution mass spectra (LRMS) were recorded on Finnigan MAT 95Q or Finnigan MAT 90 instrument or JEOL JMS-700. Infrared spectra were recorded on a Perkin 281 IR spectrometer and samples were measured neat (ATR, Smiths Detection DuraSample IR II Diamond ATR). The absorption bands were reported in wave numbers (cm^{-1}) and abbreviations for intensity are as follows: vs (very strong; maximum intensity), s (strong; above 75% of max. intensity), m (medium; from 50% to 75% of max. intensity), w (weak; below 50% of max. intensity) and br (broad). Melting points were determined on a Büchi B-540 apparatus and uncorrected. Single-crystal X-ray diffraction data were measured with Agilent Technologies Xcalibur or with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-Kα radiation (λ = 0.71071 Å).

[*n*-BuLi] = 2.41 M in hexane (titration with isopropanol / 1,10-phenanthroline), purchased from Rockwood Lithium GmbH.

[$TMSCH_2MgCl$] = 1.29 in THF (titration with I_2), purchased from Aldrich.

2. Experimental procedures

2.1. Synthesis of 1,1,2-tribromocyclopropanes



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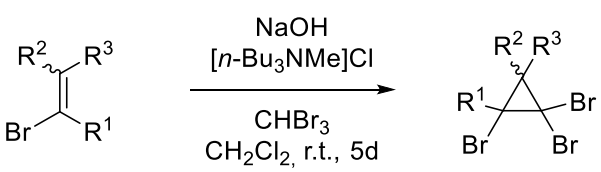
2,3-dibromo-1-propene (2.44 mL, 25 mmol) and copper iodide (997 mg, 5.0 mmol) were stirred in diethyl ether (120 mL). After cooling the solution to -30 °C, $TMSCH_2MgCl$ (23.0 mL, 30.0 mmol) was added dropwise. The mixture was then allowed to stir at room temperature. After 3h, a saturated solution of NH_4Cl was added and after extraction with Et_2O (3x50 mL) the organic layers were combined and dried over magnesium sulfate. Volatiles were evaporated under reduced pressure and the crude product (**10**, quantitative yield) was used in the next reaction without further purification.

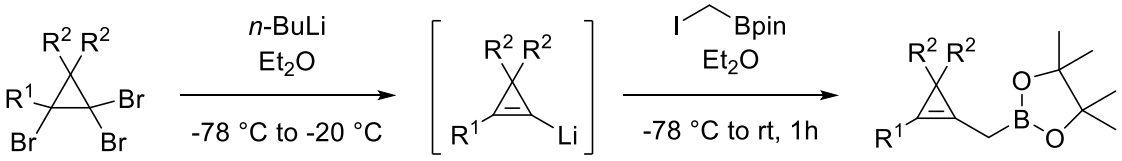
2.2. Synthesis of 1,1,2-tribromocyclopropanes



1a R^1 = Me, R^2, R^3 = H
1b R^1 = *n*-pent, R^2, R^3 = H
1c R^1 = $(CH_2)_2TMS$, R^2, R^3 = H
1d R^1, R^2, R^3 = Me
1e R^1, R^2 = Me, R^3 = H

To a solution of vinylbromide (20.0 mmol), $CHBr_3$ (5.25 mL, 60.0 mmol) and [*n*-Bu_3NMe]Cl (472 mg, 2.0 mmol) in CH_2Cl_2 (20 mL) was added a solution of 50% sodium hydroxide (10 mL) at room temperature. The mixture was stirred for 5 days. The product was extracted with CH_2Cl_2 (2x100 mL) and combined organic layers were dried over magnesium sulfate and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (pure hexane) to obtain pure 1,1,2-tribromocyclopropanes **1a-e**.

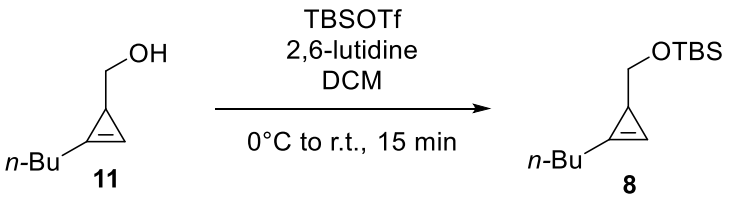
2.3. Synthesis of cyclopropenylmethylboronic ester derivatives



3a R^1 = Me, R^2 = H
3b R^1 = *n*-pent, R^2 = H
3c R^1 = $(CH_2)_2TMS$, R^2 = H
3d R^1, R^2 = Me

To a stirred solution of 1,1,2-tribromocyclopropane (0.5 mmol) in Et_2O (5 mL) was added dropwise *n*-BuLi (207 µL, 1.0 mmol) at -78 °C and the reaction mixture was slowly warmed to -20 °C (over 2 h). The *in situ* generated cyclopropenyllithium was cooled back to -78 °C and 2-(iodomethyl)-1,3,2-dioxa-4,4,5,5-tetramethyl-borolane **2** (134 mg, 0.5 mmol) in Et_2O (1.0 mL). The reaction mixture was warmed to room temperature over 1 h. The crude mixture was extracted with Et_2O (2x10 mL) and combined organic layers were dried over $MgSO_4$, concentrated under reduced pressure and the crude product was purified by column chromatography on Florisil® (pentanes) to obtain pure allylboronate derivatives **1a-c** and **1e**.

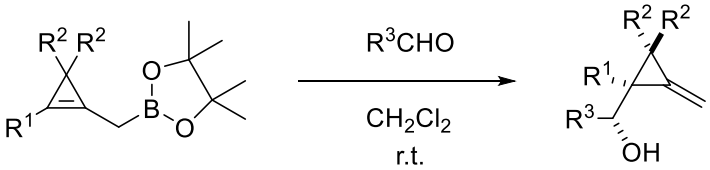
*2.4. Synthesis of TBS-protected cyclopropene **8***



(2-butyl-2-cyclopropene-1-yl)methanol **11** (1.26 g, 10.0 mmol) and 2,6-lutidine (1.27 mL, 11.0 mmol) were stirred in DCM (50.0 mL). The mixture was cooled to 0 °C and *tert*-butyldimethylsilyl trifluoromethanesulfonate (2.53 mL, 11.0 mmol) was added and the reaction was stirred for 15 min. HCl (1 M, 10 mL) was then added and the mixture was warmed to room temperature, extracted with CH_2Cl_2 (2x15 mL) and combined organic layers were dried over $MgSO_4$, concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel (Hex 95:5 EtOAc), to furnish **8** (1.47 g, 79 %) as a clear yellowish oil.

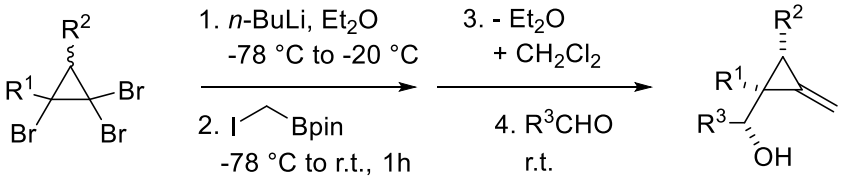
2.5. General procedures for the synthesis of methylenecyclopropanes

2.5.1. **Procedure A:** Boron allylation from cyclopropenylmethylboronic esters



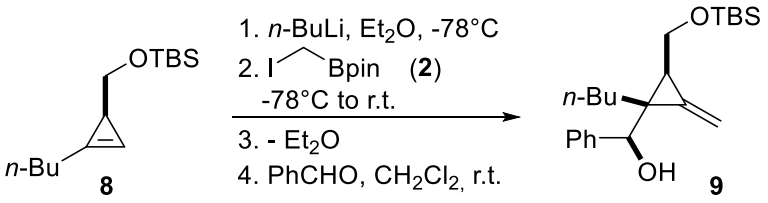
To a solution of boronic ester **3** (1.0 equiv.) in CH_2Cl_2 (10 mL/mmol) was added the corresponding aldehyde (1.0 equiv.) neat at r.t.. The reaction was monitored by TLC (hex/EtOAc = 9:1) upon completion (5 – 10 minutes). After addition of water, the reaction mixture was extracted with Et_2O (2 x 10 mL), the combined organic layers were dried over $MgSO_4$, concentrated under reduce pressure and purified on silica with the appropriate mixture of solvents.

2.5.2. **Procedure B:** One-pot sequence from tribromocyclopropanes



To a stirred solution of 1,1,2-tribromocyclopropane (1 eq, 0.5 mmol) in Et_2O (5 mL) was added dropwise *n*-BuLi (2.41M, 2 eq, 1.0 mmol) at -78 °C and the solution was slowly warmed to -20 °C (over 2 h). The *in situ* generated cyclopropenyllithium was cooled back to -78 °C and 2-(iodomethyl)-1,3,2-dioxa-4,4,5,5-tetramethyl-borolane **2** (1 eq, 0.5 mmol) was added as a solution in Et_2O (1.0 mL). The mixture was warmed to room temperature over 1 h. Volatiles were then removed under inert conditions in vacuum, followed by the addition of CH_2Cl_2 (5.0 mL). The appropriate aldehyde was added dropwise to the solution and the reaction was monitored by TLC upon completion. Water (5 mL) was added and the crude mixture was extracted with Et_2O (2x10 mL) and combined organic layers were dried over $MgSO_4$, concentrated under reduced pressure and the product was purified by column chromatography on silica gel (hexane/EtOAc) to obtain the desired methylenecyclopropane.

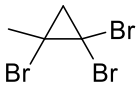
2.5.3. **Procedure C:** One-pot sequence from TBS-protected cyclopropene 8



To a stirred solution of 1-methoxy-*tert*-butyldimethylsilyl-2-butyl-2-cyclopropene **8** (120 mg, 0.5 mmol) in Et_2O (5.0 mL) was added *n*-BuLi (0.5 mmol) dropwise at -78 °C and stirred for 30 min. The solution was warmed up to -50 °C and stirred for an additional hour. After cooling back to -78 °C, the *in situ* generated cyclopropenyllithium was treated with 2-(iodomethyl)-1,3,2-dioxa-4,4,5,5-tetramethyl-borolane **2** (132 mg, 0.5 mmol) in Et_2O (1.0 mL). The reaction mixture was warmed slowly to room temperature over 1 h. Volatiles were removed in vacuum, followed by the addition of CH_2Cl_2 (5.0 mL). The aldehyde was then added and the mixture was stirred overnight (16 h). Water (5.0 mL) was added and the crude mixture was extracted with Et_2O (2 x 5.0 mL) and combined organic layers were dried over $MgSO_4$, concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel (hexane/EtOAc) to obtain **9**.

3. Experimental data

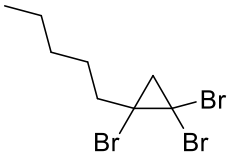
3.1. Tribromocyclopropanes



1,1,2-tribromo-2-methylcyclopropane (**1a**)

From 2-bromoprop-1-ene (1.21 g, 10.0 mmol) and $CHBr_3$ (30.0 mmol), m = 0.76 g (2.5 mmol, 25%)

Yellowish oil; $\mathbf{R_f}$ = 0,77 (pure hexane); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 2.08 (s, 3H), 1.99-1.97 (d, *J* = 9.2 Hz, 1H), 1.86-1.83 (d, *J* = 9.2 Hz, 1H); Characterization data in agreement with literature.[1]



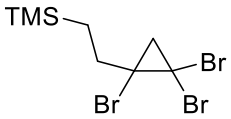
1,1,2-tribromo-2-pentylcyclopropane (**1b**)

From 2-bromo-1-heptene (1.77g, 10.0 mmol) and $CHBr_3$ (30.0 mmol), m = 0.90 g (2.58 mmol, 26 %)

Yellow oil, $\mathbf{R_f}$ = 0,75 (pure hexane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.12 – 1.96 (m, 2H), 1.94 (d, *J* = 3.0 Hz, 1H), 1.82 (d, *J* = 9.2 Hz, 1H), 1.38 – 1.23 (m, 5H), 0.97 – 0.83 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 46.0, 41.8, 38.2, 33.3, 31.3, 27.5, 22.7, 14.2; **LRMS** (EI 70 eV): m/z (%) = 269.1 (4), 199.0 (37), 147.1 (25), 107.1 (97), 55.1 (100); **HRMS** (EI pos): calcd for $C_8H_{13}Br_2^+$ (M-Br^+): 268.9364, found: 268.9329; **IR**

[1] E. Zohar, I. Marek *Org. Lett.* **2004**, *6*, 341-343.

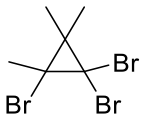
(ν, cm^{-1}): 2954 (s), 2927 (s), 2858 (m), 1628 (w), 1457 (m), 1417 (m), 1378 (w), 1200 (w), 1146 (w), 1051 (m), 1017 (m), 892 (m).



trimethyl(2-(1,2,2-tribromocyclopropyl)ethyl)silane (**1c**)

From crude **10** (4.74 g, 23.0 mmol) and $CHBr_3$ (69.0 mmol), m = 2.00 g (5.28 mmol, 23 %).

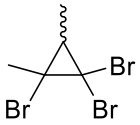
Red oil, $\mathbf{R_f}$ = 0,81 (pure hexane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.18 – 2.07 (m, 1H), 1.97 (d, *J* = 9.2 Hz, 1H), 1.95 – 1.85 (m, 1H), 1.83 (d, *J* = 9.2 Hz, 1H), 0.99 – 0.86 (m, 2H), 0.02 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 48.9, 38.2, 37.4, 33.3, 14.5, -1.6; **LRMS** (EI 70 eV): m/z (%) = 226.0 (3), 145.0 (28), 139.0 (18), 73.1 (100), 65.1 (38); **HRMS** (EI pos): calcd for $C_8H_{15}Br_2Si^+$ (M-Br^+): 298.9289, found: 298.9245; **IR** (ν, cm^{-1}): 2952 (m), 1434 (w), 1419 (w), 1335 (w), 1248 (s), 1183 (m), 1166 (w), 1052 (w), 1018 (m), 905 (w), 860 (s), 835 (s).



1,1,2-tribromo-2,3,3-trimethylcyclopropane (**1d**)

From 1-bromo-1,2-dimethylpropene (2.98 g, 20.0 mmol), m = 5.11 g (15.9 mmol, 80 %)

Yellow solid, **mp** = 99-101°C, $\mathbf{R_f}$ = 0,73 (pure hexane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.00 (s, 3H), 1.51 (s, 3H), 1.37 ppm (s, 3H); Characterization data in agreement with literature.[2]



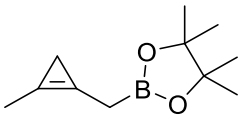
1,1,2-tribromo-2,3-dimethylcyclopropane (**1e**)

From 2-bromobut-2-ene (2.7 g, 20.0 mmol), m = 4.08 g (13.3 mmol, 66 %)

Yellowish oil, $\mathbf{R_f}$ = 0,70 (pure hexane); **^{1}H NMR** ($CDCl_3$, 400 MHz): ***anti*-1f**: δ = 2.09 (s, 3H), 1.39 (q, *J* = 6.3 Hz, 1H), 1.31 (d, *J* = 6.3 Hz, 3H). ***syn*-1f**: δ = 1.94 (q, *J* = 6.6 Hz, 1H), 1.85 (s, 3H), 1.21 (d, *J* = 6.6 Hz, 3H); Characterization data in agreement with literature.[2]

3.2. Cyclopropenylmethylboronic esters

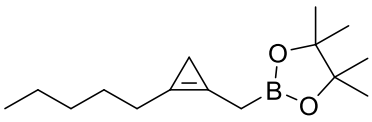
[2] W. G. von der Schulenburg, H. Kopf, R. Walsh *Chem. Eur. J.* **2000**, *6*, No. 11



4,4,5,5-tetramethyl-2-((2-methylcycloprop-1-en-1-yl)methyl)-1,3,2-dioxaborolane (**3a**)

From tribromocyclopropane **1a** (10.0 mmol), m = 1.20 g (6.2 mmol, 62%).

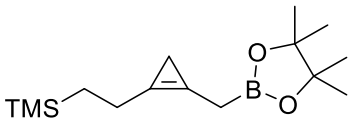
Yellowish oil, $\mathbf{R_f}$ = 0,71 (hex/Et_2O = 90:10); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 2.02 (t, J = 1.6 Hz, 3H), 1.96 (br s, 2H), 1.25 (s, 12H), 0.77 (s, 2H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ = 106.4, 105.8, 83.6, 24.9, 11.5, 8.9; **LRMS** (EI 70 eV): m/z (%) = 194 (79), 179 (100), 166 (8), 151 (21), 137 (82), 121 (63), 107 (45), 93 (80); **HRMS** (EI pos): calcd for $C_{11}H_{19}BO_2^+$ (M^+): 194.1478, found: 194.1474; **IR** (ν, cm^{-1}): 2978 (m), 2927 (m), 2859 (m), 1467 (w), 1370 (s), 1349 (s), 1325 (vs), 1272 (w), 1164 (m), 1142 (vs).



4,4,5,5-tetramethyl-2-((2-pentylcycloprop-1-en-1-yl)methyl)-1,3,2-dioxaborolane (**3b**)

From tribromocyclopropane **1b** (2.58 mmol), m = 374 mg (1.49 mmol, 58%).

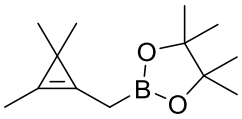
Orange oil, $\mathbf{R_f}$ = 0,61 (hex/Et_2O = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.38 (t, *J* = 7.2 Hz, 2H), 2.00 (s, 2H), 1.29 (m, 11H), 1.25 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 109.6, 105.7, 83.6, 83.0, 31.8, 27.1, 26.0, 25.0, 22.6, 14.3, 8.3; **LRMS** (EI 70 eV): m/z (%) = 205.3 (6), 235.3 (13), 194.2 (22), 167.2 (28), 121.2 (31), 84.1 (100), 40.9 (40); **HRMS** (EI pos): calcd for $C_{15}H_{27}BO_2^+$ (M^+): 250.2104, found: 250.2089; **IR** (ν, cm^{-1}): 3423 (br w), 2970 (m), 2957 (s), 2928 (s), 2859 (m), 2362 (w), 1717 (w), 1675 (w), 1457 (m), 1379 (s), 1350 (s), 1328 (s), 1272 (w), 1215 (w), 1160 (s), 1110 (w), 1008 (w), 968 (w).



trimethyl(2-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cycloprop-1-en-1-yl)ethyl)silane (**3c**)

From tribromocyclopropane **1c** (5.28 mmol), m = 1.04 g (3.71 mmol, 70%).

Red oil, $\mathbf{R_f}$ = 0,85 (hex/Et_2O = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.40 (t, *J* = 8.2 Hz, 2H), 1.99 (s, 2H), 1.25 (s, 12H), 0.79 (s, 2H), 0.76 (d, *J* = 8.0 Hz, 2H), -0.02 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ =.111.4, 104.8, 83.6, 83.0, 25.0, 20.5, 13.9, 8.4, -1.6; **LRMS** (EI 70 eV): m/z (%) =.280 (7), 180 (8), 165 (13), 138 (29), 123 (22), 107 (13), 73 (100); **HRMS** (EI pos): calcd for $C_{14}H_{26}BO_2Si^+$ (M-Me^+): 265.1795, found: 265.1789; **IR** (ν, cm^{-1}): 2979 (w), 2954 (w), 2925 (w), 2858 (w), 1469 (w), 1328 (s), 1248 (m), 1214 (w), 1142 (s), 1009 (m), 968 (m), 845 (s).

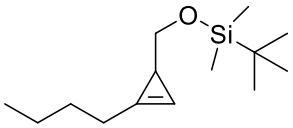


4,4,5,5-tetramethyl-2-((2,3,3-trimethylcycloprop-1-en-1-yl)methyl)-1,3,2-dioxaborolane (**3d**)

From tribromocyclopropane **1d** (10.0 mmol), m = 1.36 g (6.1 mmol, 61%).

Brownish oil, $\mathbf{R_f}$ = 0,80 (hex/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.91 (s, 3H), 1.88 (s, 2H), 1.25 (s, 12H), 1.02 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 119.6, 119.1, 83.5, 25.6, 25.0, 24.7, 19.2, 8.8; **LRMS** (EI 70 eV): m/z (%) = 222 (9), 165 (22), 122 (50), 83 (100), 55 (26); **HRMS** (EI pos): calcd for $C_{13}H_{23}BO_2^+$ (M^+): 222.1791, found: 222.1771; **IR** (ν, cm^{-1}): 3393 (br w), 2979 (m), 2932 (w), 1719 (w), 1473 (m), 1454 (m), 1354 (s), 1304 (s), 1214 (m), 1150 (s), 1099 (s), 1008 (m), 982 (m), 852 (s).

3.3. TBS-protected cyclopropene

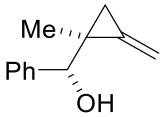


tert-butyl((2-butylcycloprop-2-en-1-yl)methoxy)dimethylsilane (**8**)

From alcohol **11** (10.0 mmol), m = 1.47 g (7.9 mmol, 79 %).

Colorless oil, $\mathbf{R_f}$ = 0,80 (hex/Et_2O = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.58 (s, 1H), 3.49 (qd, *J* = 10.5 Hz and 4.8 Hz, 2H), 2.46 (td, *J* = 7.3, 1.2 Hz, 2H), 1.63 (td, *J* = 4.9 Hz and 1.6 Hz, 1H), 1.58-1.51 (m, 2H), 1.42-1.33 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.89 (s, 9H), 0.04-0.03 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 125.9, 102.6, 70.6, 29.3, 26.0, 25.9, 22.4, 20.5, 18.5, 13.8, -5.0, -5.1; **LRMS** (EI 70 eV): m/z (%) = 226 (3), 145 (24), 137 (16), 73 (100), 65 (41); **HRMS** (EI pos): calcd for $C_{10}H_{19}OSi^+$ (M-*t*-Bu^+): 183.1205, found: 183.1218; **IR** (ν, cm^{-1}): 2955 (m), 2928 (m), 2856 (m), 1471 (w), 1388 (w), 1361 (w), 1252 (m), 1079 (br m), 1005 (w), 938 (w), 820 (s), 772 (s).

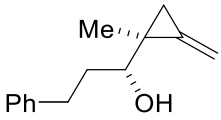
3.4. Methylenecyclopropanes



(*R**)-((*S**)-1-methyl-2-methylenecyclopropyl)(phenyl)methanol (**4a**)

Procedure A, from benzaldehyde (0.5 mmol), m = 66 mg (0.38 mmol, 76%); **Procedure B**, from benzaldehyde (0.4 mmol), m = 43 mg (0.25 mmol, 62%).

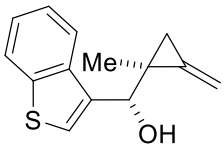
Yellowish oil, $\mathbf{R_f}$ = 0.15 (hex/Et_2O = 90:10); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.35-7.19 (m, 5H), 5.39-5.38 (d, *J* = 2.4 Hz, 1H), 5.37-5.36 (d, *J* = 2.0 Hz, 1H), 4.34 (s, 1H), 1.85 (br s, 1H), 1.28-1.26 (d, *J* = 2.0 Hz, 1H), 1.01-1.00 (d, *J* = 2.0 Hz, 1H), 0.98 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ =142.1, 139.4, 128.2, 127.5, 126.3, 104.1, 77.9, 17.4, 15.5; **LRMS** (EI 70 eV): m/z (%) = 173 (10), 145 (50), 141 (20), 130 (20), 117 (20), 105 (100); **HRMS** (EI pos): m/z calcd for $C_{12}H_{14}O^+$ [M^+]: 174.1045; found: 174.1006; **IR** (ν, cm^{-1}): 3384 (br w), 3066 (w), 3032 (w), 2967 (w), 2930 (w), 2869 (w), 1755 (br w), 1604 (w), 1495 (w), 1452 (m), 1397 (w), 1376 (m).



(*R**)-1-((*S**)-1-methyl-2-methylenecyclopropyl)-3-phenylpropan-1-ol (**4b**)

Procedure A, from dihydrocinnamaldehyde (0.5 mmol), m = 72 mg (0.36 mmol, 71%)

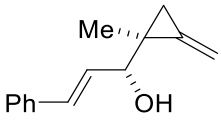
Yellowish oil, $\mathbf{R_f}$ = 0.24 (hex/Et_2O = 90:10); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.24-7.12 (m, 5H), 5.40-5.37 (d, *J* = 5.0 Hz, 1H), 5.28-5.27 (d, *J* = 3.5 Hz, 1H), 3.15-3.12 (m, 1H), 2.80-2.56 (m, 2H), 1.85-1.75 (m, 2H), 1.36 (br s, 1H), 1.11 (s, 3H), 1.05-1.02 (d, *J* = 9.0 Hz, 1H), 0.91-0.87 (d, *J* = 13 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 142.2, 140.6, 128.5, 126.0, 102.6, 76.1, 35.6, 32.7, 24.8, 17.0, 14.9; **LRMS** (EI 70 eV): m/z (%) = 202 (10), 191 (10), 187 (30), 184 (70), 174 (15), 169 (100); **HRMS** (EI pos): m/z calcd for $C_{14}H_{17}O^+$ [M-H$^+$]: 201.1271; found: 201.1279; **IR** (ν, cm^{-1}): 3415 (br w), 3027 (w), 2927 (m), 1604 (w), 1496 (m), 1454 (m), 1402 (w), 1377 (w).



(*S**)-benzo[b]thiophen-3-yl((*S**)-1-methyl-2-methylenecyclopropyl)methanol (**4c**)

Procedure A, from benzo[b]thiophene-3-carbaldehyde (0.5 mmol), m = 77 mg (0.33 mmol, 67%).

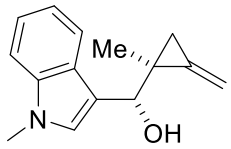
Brownish oil, $\mathbf{R_f}$ = 0.56 (hex/Et_2O = 80:20); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.90-7.85 (m, 2H), 7.49 (s, 1H), 7.37-7.26 (m, 2H), 5.49-5.48 (d, *J* = 4 Hz, 1H), 5.40-5.39 (d, *J* = 5.2 Hz, 1H), 4.89 (s, 1H), 2.06 (br s, 1H), 1.41-1.38 (d, *J* = 10.8 Hz, 1H), 1.20 (s, 3H), 1.14-1.12 (d, *J* = 8.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 140.5, 138.8, 137.8, 137.1, 124.3, 123.8, 123.0, 122.7, 104.8, 73.4, 25.8, 18.2, 15.7; **LRMS** (EI 70 eV): m/z (%) = 230 (10), 212 (15), 201 (80), 187 (15), 172 (10), 161 (100), 147 (40), 135 (35); **HRMS** (EI pos): m/z calcd for $C_{14}H_{14}OS^+$ [M$^+$]: 230.0765, found: 230.0758; **IR** (ν, cm^{-1}): 3391 (br-w), 3067 (w), 2966 (w), 2927 (w), 2869 (w), 1667 (w), 1458 (m), 1426 (s), 1374 (m).



(*R**,E)-1-((*S**)-1-methyl-2-methylenecyclopropyl)-3-phenylprop-2-en-1-ol (**4d**)

Procedure A, from cinnamaldehyde (0.5 mmol), m = 79 mg (0.4 mmol, 79%).

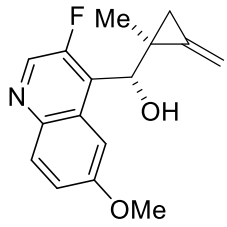
Brownish oil, $\mathbf{R_f}$ = 0.60 (hex/EtOAc 80:20); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.41-7.40 (d, *J* = 8.4 Hz, 2H), 7.34-7.32 (t, *J* = 7.6 Hz, 2H), 7.26-7.24 (t, *J* = 7.6 Hz, 1H), 6.66-6.62 (d, *J* = 17.2 Hz, 1H), 6.30-6.25 (dd, *J* = 17.2 Hz and 2.2 Hz, 6.0 Hz, 1H), 5.54-5.53 (d, *J* = 5.2 Hz, 1H) 5.41-5.40 (d, *J* = 3.6 Hz, 1H), 4.01 (s, 1H), 1.63-1.62 (d, *J* = 4.8 Hz, 1H), 1.30-1.27 (d, *J* = 13.2 Hz, 1H), 1.23 (s, 3H), 1.01-0.98 (d, *J* = 13.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 140.0, 136.9, 131.0, 129.4, 128.7, 127.8, 126.6, 103.2, 76.8, 25.0, 18.0, 14.2; **LRMS** (EI 70 eV): m/z (%) = 200 (5), 185 (20), 171 (95), 157 (20), 141 (30), 131 (100), 115 (90), 103 (65), 91 (80), 77 (55); **HRMS** (EI pos): m/z calcd for $C_{14}H_{16}O^+$ [M$^+$]: 200.1201; found: 200.1192; **IR** (ν, cm^{-1}): 3383 (br-w), 3062 (w), 3027 (w), 2965 (w), 2928 (w), 2868 (w), 1744 (w), 1600 (w), 1578 (w), 1495 (m), 1448 (m), 1400 (m), 1376 (m).



(*S**)-(1-methyl-1H-indol-3-yl)((*S**)-1-methyl-2-methylenecyclopropyl)methanol (**4e**)

Procedure A, from 1-methylindol-3-carboxaldehyde (0.5 mmol), m = 66 mg (0.29 mmol, 58%).

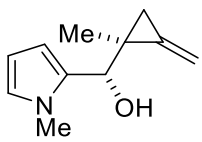
Orange oil, $\mathbf{R_f}$ = 0.43 (hex/EtOAc = 80:20); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.72 (dt, *J* = 7.9 Hz and 1.0 Hz, 1H), 7.32 (dt, *J* = 8.2 Hz and 1.0 Hz, 1H), 7.24-7.22 (m, 1H), 7.15-7.10 (m, 2H), 5.60 (t, *J* = 2.5 Hz, 1H), 5.47 (t, *J* = 1.8 Hz, 1H), 4.77 (d, *J* = 2.9 Hz, 1H), 3.80 (s, 3H), 1.75 (d, *J* = 3.7 Hz, 1H), 1.52 (dt, *J* = 8.8 Hz and 2.2 Hz, 1H), 1.19 (s, 3H), (dt, *J* = 8.8 Hz and 2.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 140.8, 137.1, 126.9, 126.7, 121.8, 120.2, 119.3, 116.2, 109.4, 103.3, 73.1, 33.0, 25.6, 18.4, 15.4; **LRMS** (EI 70 eV): m/z (%) = 225 (19), 209 (100), 194 (49), 182 (14), 167 (12); **HRMS** (EI pos): m/z calcd for $C_{15}H_{17}NO^+$ [M^+]: 227.1310, found: 227.1305; **IR** (ν, cm^{-1}): 3421 (br w), 3051 (w), 2964 (m), 2928 (m), 2870 (w), 1706 (m), 1683 (m), 1613 (m), 1468 (s), 1372 (s), 1329 (s).



(*S**)-(3-fluoro-6-methoxyquinolin-4-yl)((*S**)-1-methyl-2-methylenecyclopropyl)methanol (**4f**)

Procedure A, from the corresponding aldehyde (0.4 mmol), m = 97 mg (0.36 mmol, 89%).

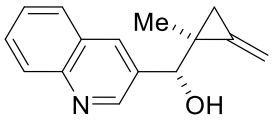
White solid, **mp** = 117-119°C, $\mathbf{R_f}$ = 0.23 (hex/EtOAc 90.10); **^{1}H NMR** ($CDCl_3$, 400 MHz): 8.45 (d, *J* = 2.1 Hz, 1H), 7.90 (d, *J* = 9.3 Hz, 1H), 7.83 (d, *J* = 2.8 Hz, 1H), 7.25 (dd, *J* = 9.3 Hz and 2.8 Hz, 1H), 5.50-5.48 (m, 1H), 5.46 (d, *J* = 6.3 Hz, 1H), 5.40-5.39 (m, 1H), 3.91 (s, 3H), 3.36 (dd, *J* = 6.4 Hz and 2.3 Hz, 1H), 1.56 (dt, *J* = 8.9 Hz and 2.3 Hz, 1H), 1.18 (s, 3H), 1.00 (dt, *J* = 9.0 Hz and 2.3 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 158.1, 154.4 (d, J = 252.3 Hz), 141.9 (d, J = 2.1 Hz), 139.2, 138.0 (d, J = 30.9 Hz), 131.2, 129.2 (d, 8.4 Hz), 128.6 (d, J = 2.6 Hz), 120.9 (d, J = 2.0 Hz), 104.8, 104.7 (d, J = 5.0 Hz), 71.5 (d, J = 2.5 Hz), 55.7, 25.7, 20.3, 14.6; **LRMS** (EI 70 eV): m/z (%) = 273 (7), 258 (9), 240 (62), 230 (21), 214 (17), 204 (100), 190 (12), 176 (65), 161 (16), 135 (26); **HRMS** (EI pos): m/z calcd for $C_{16}H_{16}FNO_2^+$ [M^+]: 273.1165, found: 273.1161; **IR** (ν, cm^{-1}): 3128 (br m), 2964 (m), 2832 (w), 1620 (s), 1578 (w), 1508 (s), 1466 (m), 1426 (s), 1358 (s), 1289 (s), 1232 (vs).



(*S**)-(1-methyl-1H-pyrrol-2-yl)((*S**)-1-methyl-2-methylenecyclopropyl)methanol (**4g**)

Procedure A, from 1-methyl-1H-pyrrole-2-carbaldehyde (0.5 mmol), m = 46 mg (0.26 mmol, 52%).

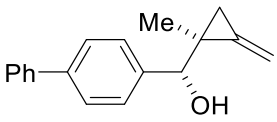
Brownish oil, $\mathbf{R_f}$ = 0.27 (hex/EtOAc 70:30); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 6.61-6.60 (m, *J* = 4.4 Hz, 1H), 6.20-6.19 (m, *J* = 5.4 Hz, 1H), 6.10-6.09 (m, *J* = 6.4 Hz, 1H), 5.62-5.61 (m, *J* = 5.2 Hz, 1H), 5.51-5.50 (m, *J* = 3.6 Hz, 1H), 4.63-4.60 (d, *J* = 8.8 Hz, 1H), 3.67 (s, 3H), 1.58 (s, 1H), 1.52-1.50 (m, 1H), 1.28 (s, 3H), 0.99-0.96 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 139.2, 133.4, 123.0, 107.3, 106.7, 104.7, 69.2, 34.3, 24.2, 20.6, 13.9; **LRMS** (EI 70 eV): m/z (%) = 173 (100), 159 (23), 144 (18); **HRMS** (EI pos): m/z calcd for $C_{11}H_{14}N^+$ [M-OH$^+$]: 160.1126, found: 160.1121. **IR** (ν, cm^{-1}): 3380 (br w), 2962 (w), 1608 (w), 1569 (w), 1452 (w).



(*S**)-((*S**)-1-methyl-2-methylenecyclopropyl)(quinolin-3-yl)methanol (**4h**)

Procedure A, from quinoline-3-carbaldehyde (0.5 mmol), m = 66 mg (0.29 mmol, 73%).

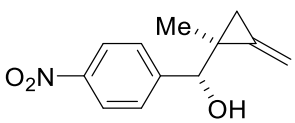
Brownish oil, $\mathbf{R_f}$ = 0.56 (hex/Et_2O = 50:50); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.83 (s, 1H), 8.14 (s, 1H), 8.05-8.03 (d, *J* = 8 Hz, 1H), 7.76-7.74 (d, *J* = 8 Hz, 1H), 7.65-7.60 (m, 1H), 7.50-7.46 (m, 1H), 5.55-5.53 (t, *J* = 8.0 Hz, 1H), 5.38 (s, 1H), 2.94 (s, 1H), 1.42-1.39 (m, 1H), 1.27 (br s, 1H), 1.16 (s, 3H), 1.02 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 149.3, 147.1, 139.1, 135.0, 133.4, 129.4, 128.8, 127.9, 127.8, 126.9, 104.0, 76.0, 24.9, 17.7, 14.9; **LRMS** (EI 70 eV): m/z (%) = 225 (15), 207 (100), 193 (10); **HRMS** (EI pos): m/z calcd for $C_{15}H_{14}NO^+$ [M-H$^+$]: 224.1075, found: 224.1059; **IR** (ν, cm^{-1}): 3166 (br-w), 2926 (m), 2855 (m), 1742 (m), 1618 (w), 1576 (m), 1499 (m), 1461 (m), 1371 (s), 1317 (m).



(*R**)-[1,1'-biphenyl]-4-yl((*S**)-1-methyl-2-methylenecyclopropyl)methanol (**4i**)

Procedure A, from biphenylcarbaldehyde (0.5 mmol), m = 80 mg (0.32 mmol, 64%); **Procedure B**, from biphenylcarbaldehyde (0.4 mmol), m = 65 mg (0.26 mmol, 64%).

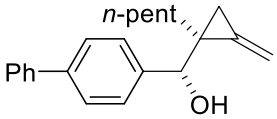
Colourless oil, $\mathbf{R_f}$ = 0.27 (hex/EtOAc = 90:10); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.51-7.64 (m, 4H), 7.36-7.31 (m, 4H), 7.26-7.22 (m, 1H), 5.51-5.50 (m, 1H), 5.37-5.36 (m, 1H), 4.35 (s, 1H), 1.94 (d, *J* = 3.3 Hz, 1H), 1.36 (ddd, *J* = 8.9 Hz, 2.4 Hz and 2.0 Hz, 1H), 0.98 (s, H), 0.94 (ddd, *J* = 8.9 Hz, 2.4 Hz and 2.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 141.2, 140.9, 140.4, 140.0, 128.9, 127.3, 127.1, 126.9, 126.9, 103.7, 77.9, 25.7, 17.9, 15.1; **LRMS** (EI 70 eV): m/z (%) = 250 (11), 249 (5), 233 (27), 183 (100), 173 (16), 97 (61); **HRMS** (EI pos): m/z calcd for $C_{18}H_{18}O^+$ [M$^+$]: 250.1358, found: 250.1344; **IR** (ν, cm^{-1}): 3389 (br w), 3041 (w), 2958 (w), 2930 (w), 2868 (w), 1750 (w), 1600 (w), 1452 (m), 1391 (w), 1372 (m).



(*R**)-((*S**)-1-methyl-2-methylenecyclopropyl)(4-nitrophenyl)methanol (**4j**)

Procedure A, from 4-nitrobenzaldehyde (0.5 mmol), m = 78 mg (0.36 mmol, 71%); **Procedure B**, from 4-nitrobenzaldehyde (0.4 mmol), m = 56 mg (0.26 mmol, 64%).

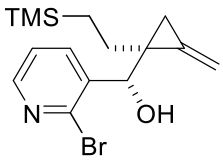
Yellowish solid, **mp** = 83-85°C, $\mathbf{R_f}$ = 0.29 (hex/Et_2O = 90:10); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.16-8.13 (d, *J* = 8.8 Hz, 2H), 7.53-7.51 (d, *J* = 8.8 Hz, 2H), 5.43-5.42 (d, *J* = 3.6 Hz, 1H), 5.40-5.39 (d, *J* = 5.2 Hz, 1H), 4.39 (s, 1H), 1.28-1.26 (d, *J* = 11.2 Hz, 1H), 1.07-1.03 (d, *J* = 13.2 Hz, 1H), 0.95 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 149.5, 138.5, 127.0, 123.4, 104.9, 26.2, 16.8, 15.9; **LRMS** (EI 70 eV): m/z (%) = 218 (1), 202 (13), 190 (10), 179 (17), 160 (14), 150 (100), 129 (61); **HRMS** (EI pos): m/z calcd for $C_{12}H_{12}NO_3^+$ [M-H^+]: 218.0817, found: 218.0815; calcd for $C_{12}H_{12}NO^+$ [M-OH]$^+$: 202.0868, found: 202.0850; **IR** (ν, cm^{-1}): 3523 (m), 3111 (w), 3078 (w), 2969 (w), 2934 (w), 1713 (w), 1604 (m), 1507 (s), 1459 (w), 1372 (m), 1338 (s).



(*R**)-[1,1'-biphenyl]-4-yl((*S**)-2-methylene-1-pentylcyclopropyl)methanol (**4k**)

Procedure A, from biphenyl-4-carboxaldehyde (0.32 mmol), m = 65 mg (0.21 mmol, 66 %).

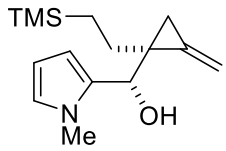
White solid (0°C), **mp** = 21-23°C, colourless oil, $\mathbf{R_f}$ = 0,40 (hex/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.70 – 7.31 (m, 9H), 5.58 (s, 1H), 5.49 (s, 1H), 4.67 (s, 1H), 1.90 (s, 1H), 1.61 – 1.50 (m, 1H), 1.45 – 1.40 (m, 1H), 1.27 (m, 7H), 1.08 (d, *J* = 8.8 Hz, 1H), 0.85 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 141.2, 141.0, 140.4, 138.6, 128.9, 127.4, 127.2, 127.0, 126.9, 104.6, 76.6, 32.3, 32.2, 30.1, 26.2, 22.7, 14.2, 13.0; **LRMS** (EI 70 eV): m/z (%) = 306.3 (2), 277.3 (40), 231.2 (10), 207.2 (20), 181.1 (100), 155.1 (22), 77.1 (12); **HRMS** (EI pos): m/z calcd for $C_{22}H_{24}^+$ [M-H_2O^+]: 288.1867, found: 288.1883; **IR** (ν, cm^{-1}): 3426 (br-w), 3029 (w), 2955 (m), 2923 (s), 2857 (m), 2360 (w), 1600 (w), 1486 (m), 1457 (w), 1403 (w), 1261 (w), 1179 (w), 1034 (m), 1018 (m), 1008 (m), 888 (m).



(*S**)-(2-bromopyridin-3-yl)((*R**)-2-methylene-1-(2-(trimethylsilyl)ethyl)cyclopropyl)methanol (**4l**)

Procedure A, from 2-bromo-3-pyridinecarboxaldehyde (0.40 mmol), m = 116 mg (0.32 mmol, 85 %).

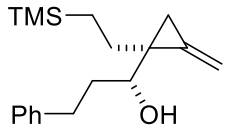
White solid, **mp** = 138-139°C, $\mathbf{R_f}$ = 0,17 (hex/EtOAc = 90:10); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 3.4 Hz, 1H), 7.82 (d, *J* = 7.1 Hz, 1H), 7.31 – 7.20 (m, 1H), 5.56 (s, 1H), 5.35 (s, 1H), 5.22 (s, 1H), 2.64 (s, 1H), 1.79 (td, *J* = 13.9 Hz and 3.8 Hz, 1H), 1.41 (td, *J* = 13.9 Hz and 3.9 Hz, 1H), 1.25 (d, *J* = 9.0 Hz, 1H), 0.96 (d, *J* = 9.0 Hz, 1H), 0.75 (td, *J* = 13.9 Hz and 3.8 Hz, 1H), 0.58 (td, *J* = 13.9 Hz and 3.9 Hz, 1H), -0.02 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 148.8, 143.0, 138.6, 136.9, 136.3, 122.6, 104.9, 72.7, 31.8, 29.3, 13.1, 10.5, -1.7; **LRMS** (EI 70 eV): m/z (%) = 260.2 (3), 232.2 (7), 170.2 (13), 154.1 (6), 73.1 (100); **HRMS** (EI pos): m/z calcd for $C_{15}H_{21}ONBrSi^+$ [M-H]$^+$: 338.0570; found: 338.0556; **IR**:(cm^{-1}): 3290 (br-w), 3068 (w), 3045 (w), 2952 (w), 2926 (w), 1577 (w), 1564 (m), 1404 (m), 1337 (w), 1246 (s), 1187 (w), 1167 (w), 1097 (m), 1081 (m), 1034 (s), 1016 (m), 944 (w).



(*S**)-(1-methyl-1H-pyrrol-2-yl)((*R**)-2-methylene-1-(2-(trimethylsilyl)ethyl)cyclopropyl)-methanol (**4m**)

Procedure A, from 1-methylpyrrole-2-carboxaldehyde (0.40 mmol), m = 57 mg (0.21 mmol, 54%).

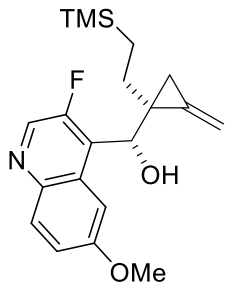
Yellow oil, $\mathbf{R_f}$ = 0,72 (hexane/EtOAc = 90:10); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.59 (t, *J* = 2.1 Hz, 1H), 6.18 – 6.11 (m, 1H), 6.11 – 6.03 (m, 1H), 5.55 (t, *J* = 2.4 Hz, 1H), 5.48 (s, 1H), 4.84 (d, *J* = 8.4 Hz, 1H), 3.66 (s, 3H), 1.70 (td, *J* = 13.6 Hz and 4.8 Hz, 1H), 1.49 (dd, *J* = 13.8 Hz and 3.8 Hz, 1H), 1.46 – 1.42 (m, 1H), 1.32 – 1.25 (m, 1H), 0.96 (dt, *J* = 8.7 Hz and 2.2 Hz, 1H), 0.53 (td, *J* = 13.6 Hz and 3.9 Hz, 1H), 0.42 (td, *J* = 13.8 Hz and 4.9 Hz, 1H), -0.08 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 138.3, 133.4, 122.8, 107.2, 106.7, 104.8, 67.2, 34.2, 30.8, 28.1, 12.5, 11.2, -1.7; **LRMS** (EI 70 eV): m/z (%) = 263.1 (6), 245.2 (40), 202.2 (9), 174.1 (10), 158.2 (100), 73.1 (27); **HRMS** (EI pos): m/z calcd for $C_{15}H_{24}NOSi^+$ [M-H$^+$]: 262.1622, found: 262.1627; **IR** (ν, cm^{-1}): 3435 (br-w), 3103 (w), 3065 (w), 2952 (m), 2925 (w), 1697 (w), 1491 (w), 1415 (w), 1379 (w), 1298 (m), 1247 (s), 1172 (w), 1088 (m), 1012 (m), 820 (s).



(*R**)-1-((*R**)-2-methylene-1-(2-(trimethylsilyl)ethyl)cyclopropyl)-3-phenylpropan-1-ol (**4n**)

Procedure A, from dihydrocinnamaldehyde (0.38 mmol), m = 91 mg (0.32 mmol, 84%); **Procedure B**, from dihydrocinnamaldehyde (0.5 mmol), m = 101 mg (0.35 mmol, 70%).

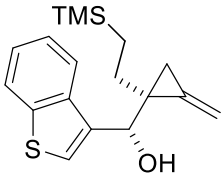
Colorless oil, $\mathbf{R_f}$ = 0,51 (hex/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.38 – 7.18 (m, 5H), 5.45 (d, *J* = 16.3 Hz, 2H), 3.55 (dd, *J* = 9.3 Hz and 3.3 Hz, 1H), 2.94 – 2.83 (m, 1H), 2.74 – 2.64 (m, 1H), 1.98 – 1.86 (m, 1H), 1.82 – 1.65 (m, 2H), 1.55 – 1.43 (m, 1H), 1.18 – 1.10 (m, 1H), 1.04 – 0.96 (m, 1H), 0.57 (td, *J* = 13.8 Hz and 4.1 Hz, 1H), 0.42 (td, *J* = 13.9 Hz and 4.3 Hz, 1H), 0.00 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 142.3, 139.1, 128.6, 128.5, 125.9, 103.5, 74.3, 35.7, 32.8, 31.2, 26.1, 12.7, 12.2, -1.8; **LRMS** (EI 70 eV): m/z (%) = 220.3 (6), 205.2 (9), 169.2 (5), 117.2 (8), 105.2 (24), 91.1 (53), 73.1 (100); **HRMS** (EI pos): m/z calcd for $C_{17}H_{25}OSi^+$ [M-Me]$^+$: 273.1669, found: 273.1674; **IR** (ν, cm^{-1}): 3409 (br-w), 3063 (w), 3027 (w), 2951 (m), 2921 (m), 2857 (w), 1744 (w), 1604 (w), 1496 (w), 1454 (w), 1401 (w), 1247 (s), 1174 (w), 1065 (m), 1031 (m), 1013 (m), 862 (s), 820 (s).



(*S**)-(3-fluoro-6-methoxyquinolin-4-yl)((*R**)-2-methylene-1-(2-(trimethylsilyl)ethyl)-cyclopropyl)methanol (**4o**)

Procedure A, from corresponding aldehyde (0.4 mmol), m = 119 mg (0.33 mmol, 83%).

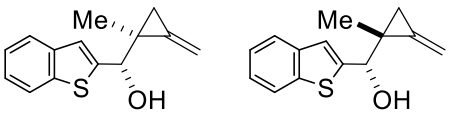
White solid (at 0°C) , **mp** = 18-19°C, colourless oil, $\mathbf{R_f}$ = 0.35 (hex/EtOAc 80:20); **^{1}H NMR** ($CDCl_3$, 400 MHz): 8.40 (d, *J* = 2.2 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 2.7 Hz, 1H), 7.23 (dd, *J* = 9.2 Hz and 2.7 Hz, 1H), 5.75 (d, *J* = 7.0 Hz, 1H), 5.27-5.26 (m, 1H), 5.18-5.17 (m, 1H), 3.90 (s, 3H), 3.46 (dd, *J* = 7.1 Hz and 3.0 Hz, 1H), 1.87 (td, *J* = 14.0 Hz and 4.2 Hz, 1H), 1.41 (dt, *J* = 9.1 Hz and 2.2 Hz, 1H), 1.29 (td, *J* = 13.9 Hz and 4.2 Hz, 1H), 1.01 (dt, *J* = 9.1 Hz and 2.2 Hz, 1H), 0.67 (td, *J* = 13.9 Hz and 4.2 Hz, 1H), 0.50 (td, *J* = 13.6 Hz and 4.2 Hz, 1H), -0.11 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 158.1, 154.6 (d, J = 251.7 Hz), 141.7, 138.0 (d, J = 30.8 Hz), 137.8, 131.2, 129.0 (d, J = 7.7 Hz), 128.7 (d, J = 2.8 Hz), 120.9, 104.7, 104.0, 69.6, 55.6, 32.0, 28.7, 13.1, 12.2, -1.9; **LRMS** (EI 70 eV): m/z (%) = 359 (1), 344 (9), 326 (7), 300 (6), 254 (17), 230 (11), 204 (100); **HRMS** (ESI pos): m/z calcd for $C_{20}H_{27}NO_2FSi^+$ [M+H$^+$]: 360.1795, found: 360.1790. **HRMS** (ESI neg): m/z calcd for $C_{20}H_{26}ClFNO_2Si^-$ [M+Cl$^-$]: 394.1411, found: 394.1424; **IR** (ν, cm^{-1}): 3226 (br w), 2952 (w), 2926 (w), 1621 (s), 1576 (w), 1508 (s), 1466 (m), 1427 (m), 1353 (m)l, 1247 (s), 1229 (vs).



(*S**)-benzo[b]thiophen-3-yl((*R**)-2-methylene-1-(2-(trimethylsilyl)ethyl)cyclopropyl)methanol (**4p**)

Procedure A, from benzo[b]thiophene-3-carboxaldehyde (0.40 mmol), m = 75 mg (0.24 mmol, 59%).

Yellowish oil, $\mathbf{R_f}$ = 0,55 (hex/EtOAc = 90:10); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.89 – 7.82 (m, 2H), 7.43 (s, 1H), 7.41 – 7.32 (m, 2H), 5.42 (t, *J* = 2.5 Hz, 1H), 5.37 (s, 1H), 5.21 (s, 1H), 1.86 (s, 1H), 1.65 (td, *J* = 14.0 Hz and 3.9 Hz, 1H), 1.50 (dt, *J* = 8.8 Hz and 2.2 Hz, 1H), 1.47 – 1.37 (m, 1H), 1.06 (dt, *J* = 8.8 Hz and 2.2 Hz, 1H), 0.66 (td, *J* = 13.8 Hz and 3.9 Hz, 1H), 0.45 (td, *J* = 13.9 Hz and 4.3 Hz, 1H), -0.10 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 140.5, 138.4, 138.2, 137.6, 124.4, 124.1, 123.0, 122.9, 122.7, 104.7, 71.6, 31.6, 27.9, 13.1, 12.7, -1.8; **LRMS** (EI 70 eV): m/z (%) = 316.2 (2), 288.1 (14), 215.1 (20), 197.1 (19), 163.1 (81), 135.1 (35), 91.2 (20), 73.2 (100); **HRMS** (EI pos): m/z calcd for $C_{18}H_{24}NOSSi^+$ [M$^+$]: 316.1317, found: 316.1317; **IR** (ν, cm^{-1}): 3371 (br-w), 3066 (w), 2952 (m), 2923 (w), 1744 (w), 1459 (w), 1427 (m), 1247 (s), 1172 (w), 1085 (m), 1056 (m), 1014 (m), 860 (s), 817 (s).



(*S**)-benzo[b]thiophen-2-yl((*R**)-1-methyl-2-methylenecyclopropyl)methanol (***syn***-**4q**)

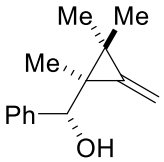
Procedure A, from 2-benzothiophencarboxaldehyde (0.5 mmol), m = 52 mg (0.23 mmol, 45%).

Colourless oil, $\mathbf{R_f}$ = 0.29 (hex/EtOAc = 95:5); **^{1}H NMR** ($CDCl_3$, 400 MHz): 7.84-7.82 (m, 1H), 775-7.73 (m, 1H), 7.37-7.29 (m, 2H), 7.29 (s, 1H), 5.71-5.70 (m, 1H), 5.53-5.52 (m, 1H), 4.68 (s, 1H), 2.14 (br s, 1H), 1.52 (dt, *J* = 8.8 Hz and 2.3 Hz, 1H), 1.17 (s, 3H), 1.14 (dt, *J* = 8.9 Hz and 2.3 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 146.7, 139.6, 139.6, 139.2, 124.4, 124.2, 123.5, 122.5, 121.1, 104.4, 75.2, 25.7, 17.6, 15.2; **LRMS** (EI 70 eV): m/z (%) = 230 (16), 215 (12), 201 (79), 187 (21), 161 (100), 147 (57); **HRMS** (EI pos): m/z calcd for $C_{14}H_{14}OS^+$ [M$^+$]: 230.0765, found: 230.0759; **IR** (ν, cm^{-1}): 3391 (br w), 3067 (w), 2965 (w), 2926 (w), 2867 (w), 1458 (m), 1426 (s), 1373 (m), 1253 (m).

(*S**)-benzo[b]thiophen-2-yl((*S**)-1-methyl-2-methylenecyclopropyl)methanol (***anti*-4q**)

Procedure A, from 2-benzothiophencarboxaldehyde (0.5 mmol), m = 35 mg (0.15 mmol, 30%).

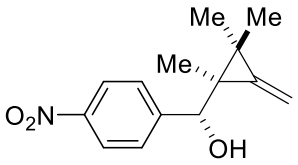
Colourless oil, $\mathbf{R_f}$ = 0.18 (hex/EtOAc = 95:5); **^{1}H NMR** ($CDCl_3$, 400 MHz): 7.75-7.73 (m, 1H), 7.67-7.65 (m, 1H), 7.28-7.19 (m, 3H), 5.58-5.56 (m, 1H), 5.45-5.44 (m, 1H), 4.61 (s, 1H), 2.14 (br s, 1H), 1.37 (dt, *J* = 8.7 Hz and 2.3 Hz, 1H), 1.17 (s, 3H), 1.05 (dt, *J* = 8.8 Hz and 2.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ =v146.6, 139.6, 139.5, 138.6, 124.3, 124.1, 123.5, 122.4, 120.8, 104.9, 75.1, 26.2, 17.3, 15.5.



(*R**)-phenyl((*S**)-1,2,2-trimethyl-3-methylenecyclopropyl)methanol (**5a**)

Procedure A, from benzaldehyde (0.5 mmol), m = 50 mg (0.25 mmol, 49%).

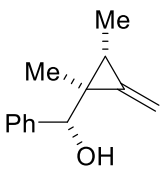
Colourless oil, $\mathbf{R_f}$ = 0,26 (hex/EtOAc = 98:2); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.44-7.22 (m, 5H), 5.46 (s, 1H), 5.37 (s, 1H), 4.68 (s, 1H), 1.86 (s, 1H), 1.38 (s, 3H), 1.22 (s, 3H), 0.99 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.2, 141.7, 128.2, 126.8, 126.0, 100.0, 75.1, 31.1, 23.7, 22.2, 21.1, 13.0; **LRMS** (EI 70 eV): m/z (%) = 316 (14), 149 (20), 105 (45), 71 (59), 57 (100); **HRMS** (EI pos): calcd for $C_{14}H_{18}O^+$ (M^+): 202.1358, found: 202.1342; **IR** (ν, cm^{-1}): 3421 (br w), 3061 (w), 2983 (m), 2924 (m), 2867 (w), 1602 (w), 1494 (w), 1448 (s), 1373 (m), 1171 (m), 1108 (m), 1082 (m), 1016 (s), 936 (m), 887 (s).



(*R**)-(4-nitrophenyl)((*S**)-1,2,2-trimethyl-3-methylenecyclopropyl)methanol (**5b**)

Procedure A, from 4-nitrobenzaldehyde (0.5 mmol), m = 68 mg (0.28 mmol, 55%).

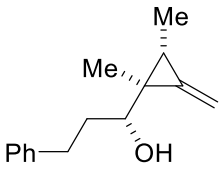
Orange solid, **mp** = 77-79°C, $\mathbf{R_f}$ = 0,71 (hex/EtOAc = 80:20); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 5.44 (d, *J* = 32.2 Hz, 2H), 4.73 (s, 1H), 1.41 (s, 3H), 1.22 (s, 3H), 0.92 (s, 3H), The signal for the OH-group could not be detected; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 150.3, 149.34, 147.0, 127.0, 123.6, 100.6, 74.6, 31.4, 24.1, 22.5, 21.1, 13.1; **LRMS** (EI 70 eV): m/z (%) = 214 (18), 172 (70), 142 (75), 97 (60), 59 (100); **HRMS** (EI pos): calcd for $C_{14}H_{17}NO_3^+$ (M^+): 247.1208, found: 247.1211; **IR** (ν, cm^{-1}): 3529 (br m), 2986 (w), 2928 (m), 2868 (w), 1743 (w), 1598 (m), 1511 (s), 1304 (s), 1235 (m), 1180 (m), 1106 (m), 1033 (s), 928 (m), 870 (s).



(*R**)-((1*S**,2*R**)-1,2-dimethyl-3-methylenecyclopropyl)(phenyl)methanol (**7a**)

Procedure B, from benzaldehyde (0.4 mmol), m = 46 mg (0.24 mmol, 61%).

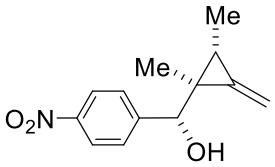
Colourless oil, R_f = 0.21 (hex/EtOAc = 90:10); **^{1}H NMR** ($CDCl_3$, 400 MHz): 7.41-7.28 (m, 5H), 5.40 (d, *J* = 1.8 Hz, 1H), 5.34 (d, *J* = 2.6 Hz, 1H), 4.37 (s, 1H), 1.91 (br s, 1H), 1.64-1.59 (m, 1H), 1.16 (d, *J* = 6.3 Hz, 3H), 0.96 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 145.2, 142.3, 128.1, 127.4, 126.3, 102.7, 79.4, 29.0, 19.6, 12.5, 11.7; **HRMS** (EI pos): m/z calcd for $C_{13}H_{15}^+$ [M-OH]$^+$: 171.1174, found: 171.1189; **IR** (ν, cm^{-1}): 3226 (br w), 2952 (m), 2926 (w), 1741 (w), 1621 (m), 1508 (m), 1247 (s), 1229 (s).



(*R**)-1-((1*S**,2*R**)-1,2-dimethyl-3-methylenecyclopropyl)-3-phenylpropan-1-ol (**7b**)

Procedure B, from dihydrocinamaldehyde (0.5 mmol), m = 91 mg (0.42 mmol, 84%).

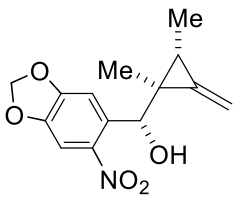
Yellowish oil, **R_f** = 0.21 (hexanes/Et_2O 90:10); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.31-7.17 (m, 5H), 5.38 (d, *J* = 2.5 Hz, 1H), 5.30 (d, *J* = 1.9 Hz, 1H), 3.09 (dd, *J* = 8.1 Hz and 5.3 Hz, 1H), 2.81 (ddd, *J* = 13.8 Hz, 9.6 Hz and 6.1 Hz, 1H), 2.64 (ddd, *J* = 13.8 Hz, 9.6 Hz and 7.1 Hz, 1H), 1.91-1.86 (m, 2H), 1.52 (br s, 1H), 1.32-1.26 (m, 1H), 1.10 (s, 3H), 1.10 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 146.4, 142.3, 128.5, 128.5, 125.9, 101.2, 78.0, 35.4, 32.7, 27.7, 18.8, 11.9, 11.1; **LRMS** (EI 70 eV): m/z (%) = 216 (1), 201 (5), 133 (19), 105 (78), 91 (100); **HRMS** (EI pos): m/z calcd for $C_{15}H_{20}O^{\cdot}$ [M^+]$^{\cdot}$: 216.1514, found: 216.1532; **IR** (ν, cm^{-1}): 3412 (br w), 3062 (w), 2981 (m), 2929 (m), 2868 (m), 1946 (vw), 1716 (br w), 1603 (w), 1496 (m), 1454 (m), 1382 (m), 1030 (s).



(*R**)-((1*S**,2*R**)-1,2-dimethyl-3-methylenecyclopropyl)(4-nitrophenyl)methanol (**7c**)

Procedure B, from 4-nitrobenzaldehyde (0.4 mmol), m = 67 mg (0.29 mmol, 72%).

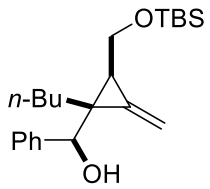
Colourless oil, **R_f** = 0.38 (hexanes/Et_2O 70:30); **^{1}H NMR** ($CDCl_3$, 400 MHz): 8.21 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 5.44 (d, *J* = 1.9 Hz, 1H), 5.35 (d, *J* = 2.6 Hz, 1H), 4.41 (s, 1H), 2.02 (br s, 1H), 1.64-1.58 (m, 1H), 1.17 (d, *J* = 6.4 Hz, 3H), 0.92 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 149.7, 147.3, 144.4, 127.0, 123.4, 103.6, 78.9, 29.2, 20.3, 12.5, 11.1; **HRMS** (ESI neg): m/z calcd for $C_{14}H_{16}NO_5^+$ [M+$HCOO^-$]: 278.1034, found: 278.1037; **IR** (ν, cm^{-1}): 3455 (br m), 2979 (w), 2952 (m), 2924 (m), 2867 (w), 1941 (vw), 1670 (w), 1601 (m), 1516 (s), 1505 (s), 1345 (vs), 1108 (m), 1037 (s).



(*S**)-((1*S**,2*R**)-1,2-dimethyl-3-methylenecyclopropyl)(6-nitrobenzo[d][1,3]dioxol-5-yl)methanol (**7d**)

Procedure B, from 6-piperonal (0.5 mmol), m = 89 mg (0.32 mmol, 80%).

Brown crystals, R_f = 0.12 (hex/EtOAc = 90:10); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.48 (s, 1H), 7.24 (s, 1H), 6.10 (q, *J* = 1.3 Hz, 2H), 5.64 (s, 1H), 5.17 (dd, *J* = 7.7, 2.3 Hz, 2H), 2.22 (s, 1H), 1.45 (tdt, *J* = 6.4, 4.8, 2.3 Hz, 1H), 1.21 (s, 3H), 1.08 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 151.9, 146.9, 144.7, 142.0, 135.4, 107.2, 105.5, 103.0, 102.8, 73.5, 29.6, 16.4, 15.8, 12.3; **LRMS** (EI 70 eV): m/z (%) = 277 (51), 259 (33), 243 (25), 230 (30), 216 (49), 204 (57), 188 (78), 164 (100); **HRMS** (EI pos): m/z calcd for $C_{14}H_{15}NO_5^+$ [M^+]: 277.0950, found: 277.0918; **IR** (ν, cm^{-1}): 3530 (m), 3370 (br w), 2964 (m), 2955 (m), 2927 (m), 2868 (m), 1841 (vw), 1734 (w), 1618 (m), 1515 (s), 1504 (s), 1483 (s), 1321 (s), 1251 (vs), 1161 (m).



(S)-((1R,2S)-1-butyl-2-(((tert-butyldimethylsilyl)oxy)methyl)-3-methylenecyclopropyl)(phenyl)methanol (**9**)

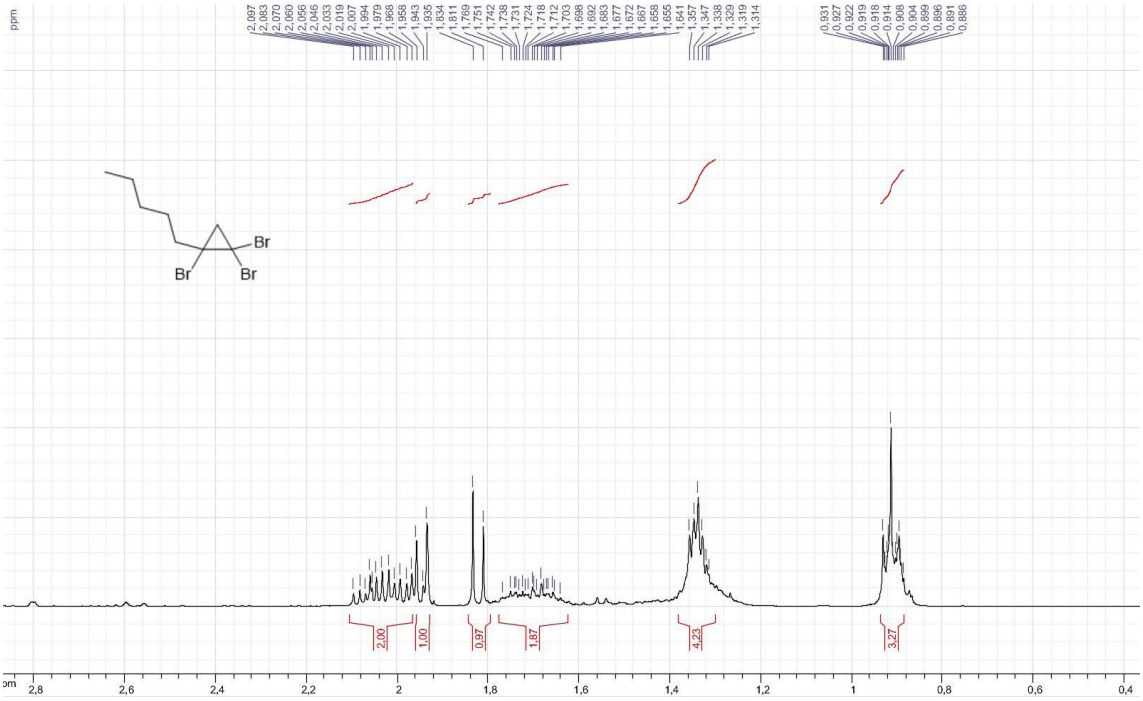
Procedure C, from benzaldehyde (0.5 mmol), m = 104 mg (0.29 mmol, 58%).

Yellowish oil, R_f = 0,26 (hex/EtOAc = 98:2); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.59 – 7.17 (m, 5H), 5.48 (d, *J* = 2.7 Hz and 0.8 Hz, 1H), 5.37 (d, *J* = 1.9 Hz, 1H), 4.69 (s, 1H), 3.85 (dd, *J* = 11.0 Hz and 5.6 Hz, 1H), 3.48 (dd, *J* = 11.0 Hz and 9.3 Hz, 1H), 1.94 (m, 1H), 1.67 – 1.46 (m, 2H), 1.38 – 1.14 (m, 5H), 0.91 (s, 9H), 0.83 (t, *J* = 7.3 Hz, 3H), 0.06 (d, *J* = 10.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 141.7, 140.5, 127.9, 127.1, 126.4, 104.4, 61.0, 34.1, 30.1, 28.2, 26.7, 25.9, 23.2, 18.2, 14.0, -5.3, -5.4; **LRMS** (EI 70 eV): m/z (%) = 303 (14), 211 (14), 171 (32), 105 (100), 75 (84); **HRMS** (EI pos): m/z calcd for $C_{21}H_{33}O_2Si^+$ [M-Me^+]: 345.2250, found: 345.2245; calcd for $C_{18}H_{27}O_2Si^+$ [M-*t*-Bu^+]: 303.1780, found: 303.1782; **IR** (ν, cm^{-1}): 3440 (br w), 2955 (m), 2928 (m), 2857 (m), 1463 (w), 1379 (w), 1253 (m), 1102 (m), 1070 (br m), 888 (w), 820 (s).

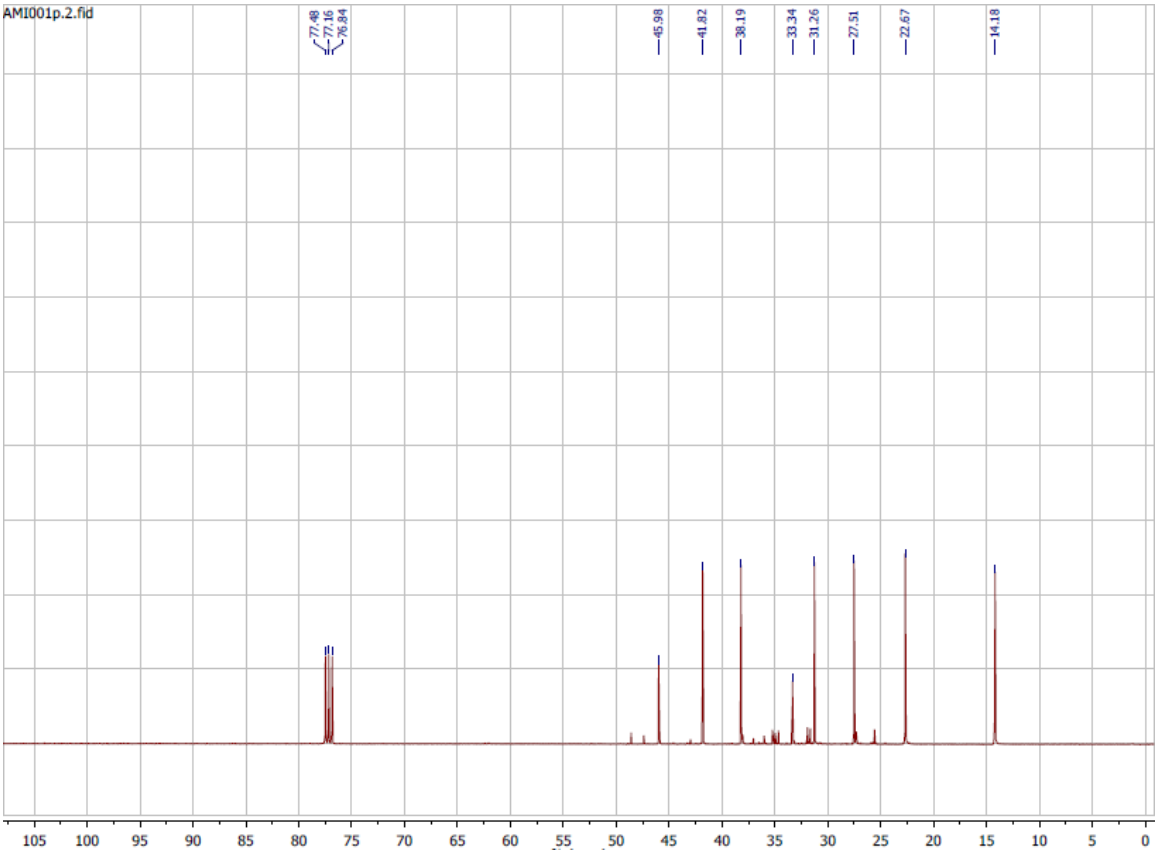
4. NMR spectra

1,1,2-tribromo-2-pentylcyclopropane (**1b**)

^{1}H NMR (400 MHz, $CDCl_3$)

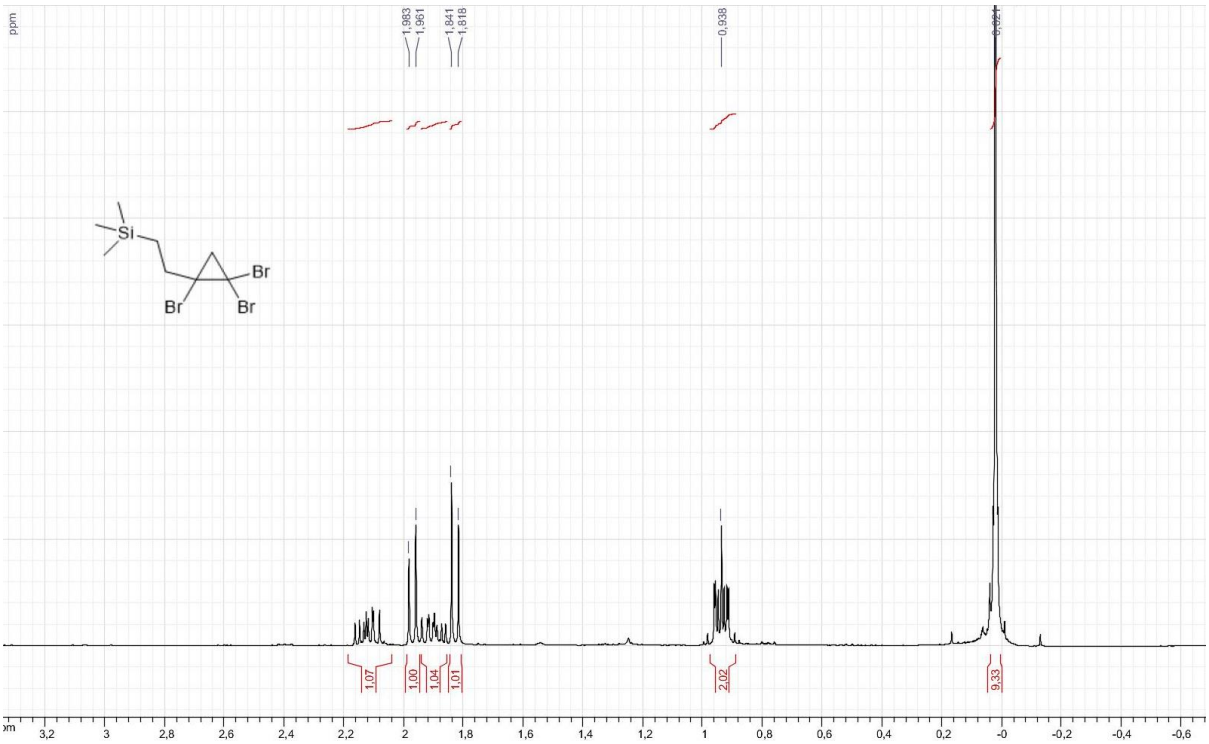


^{13}C NMR (101 MHz, $CDCl_3$)

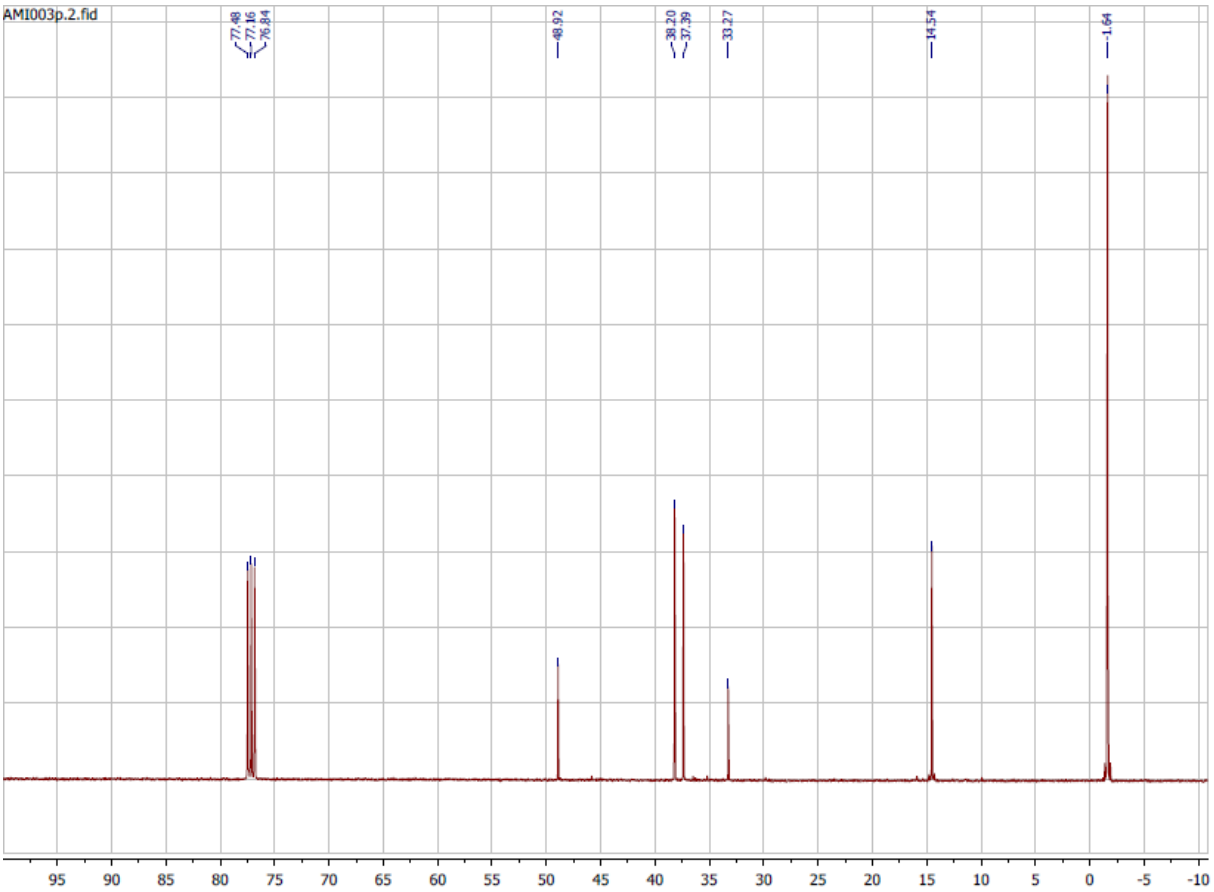


trimethyl(2-(1,2,2-tribromocyclopropyl)ethyl)silane (**1c**)

^{1}H NMR (400 MHz, $CDCl_3$)

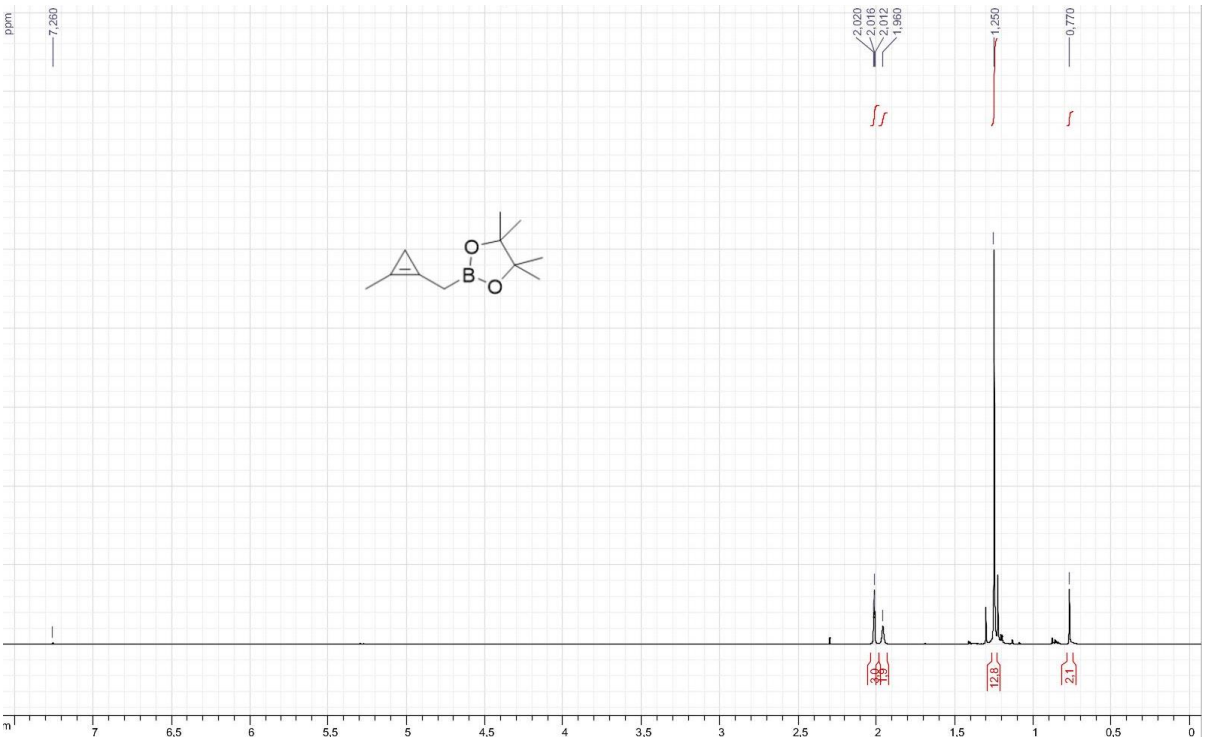


^{13}C NMR (101 MHz, $CDCl_3$)

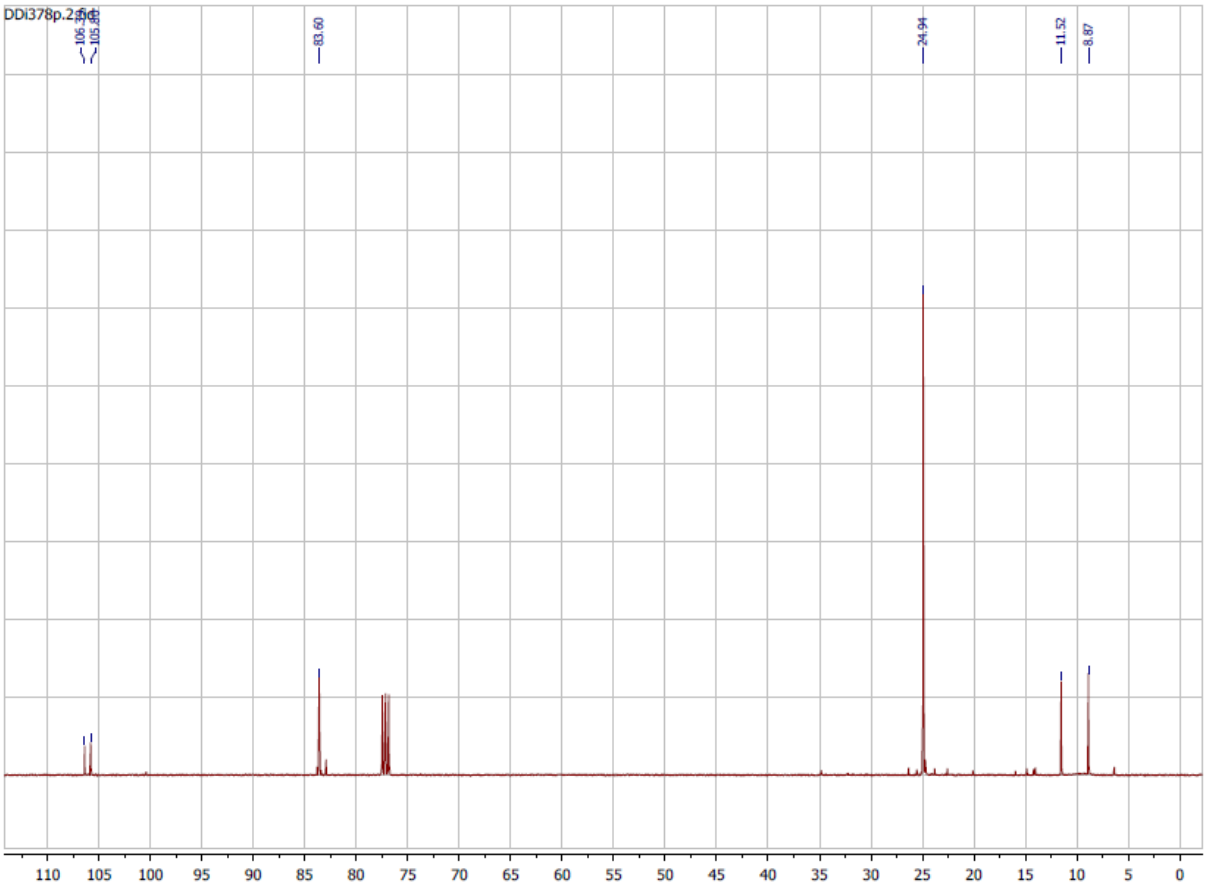


4,4,5,5-tetramethyl-2-((2-methylcycloprop-1-en-1-yl)methyl)-1,3,2-dioxaborolane (**3a**)

^{1}H NMR (400 MHz, $CDCl_3$)

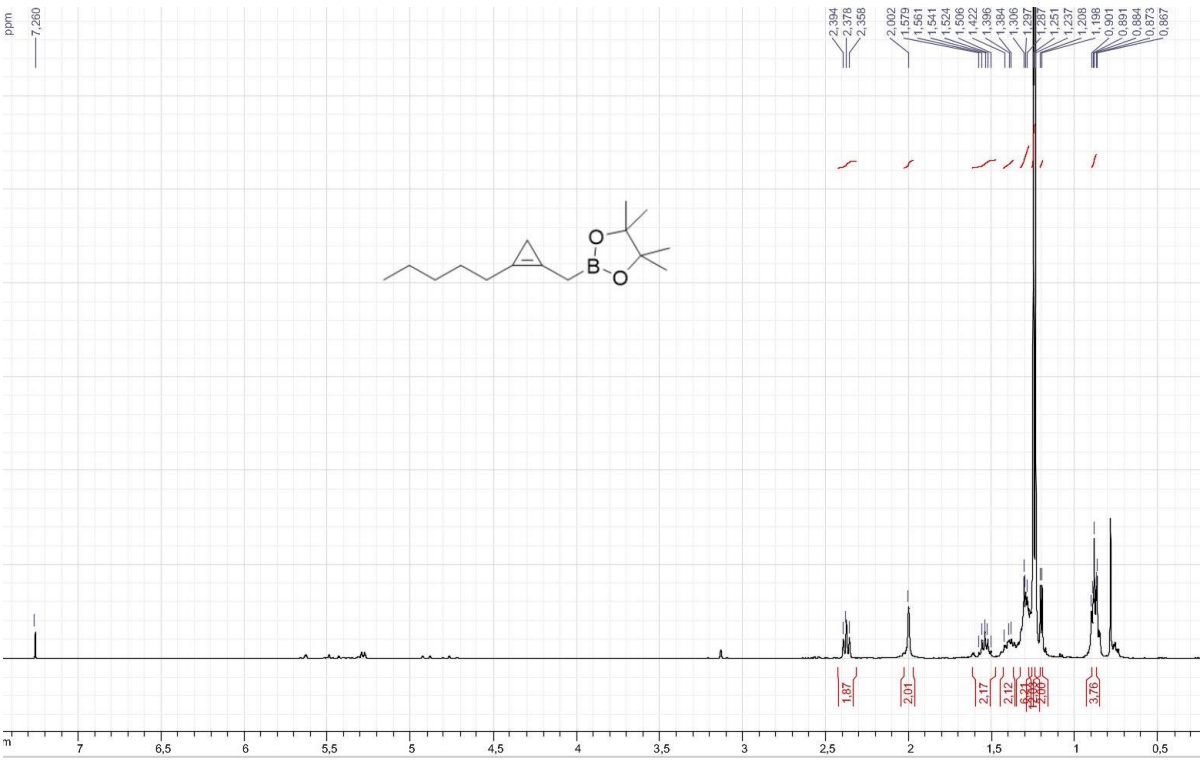


^{13}C NMR (101 MHz, $CDCl_3$)

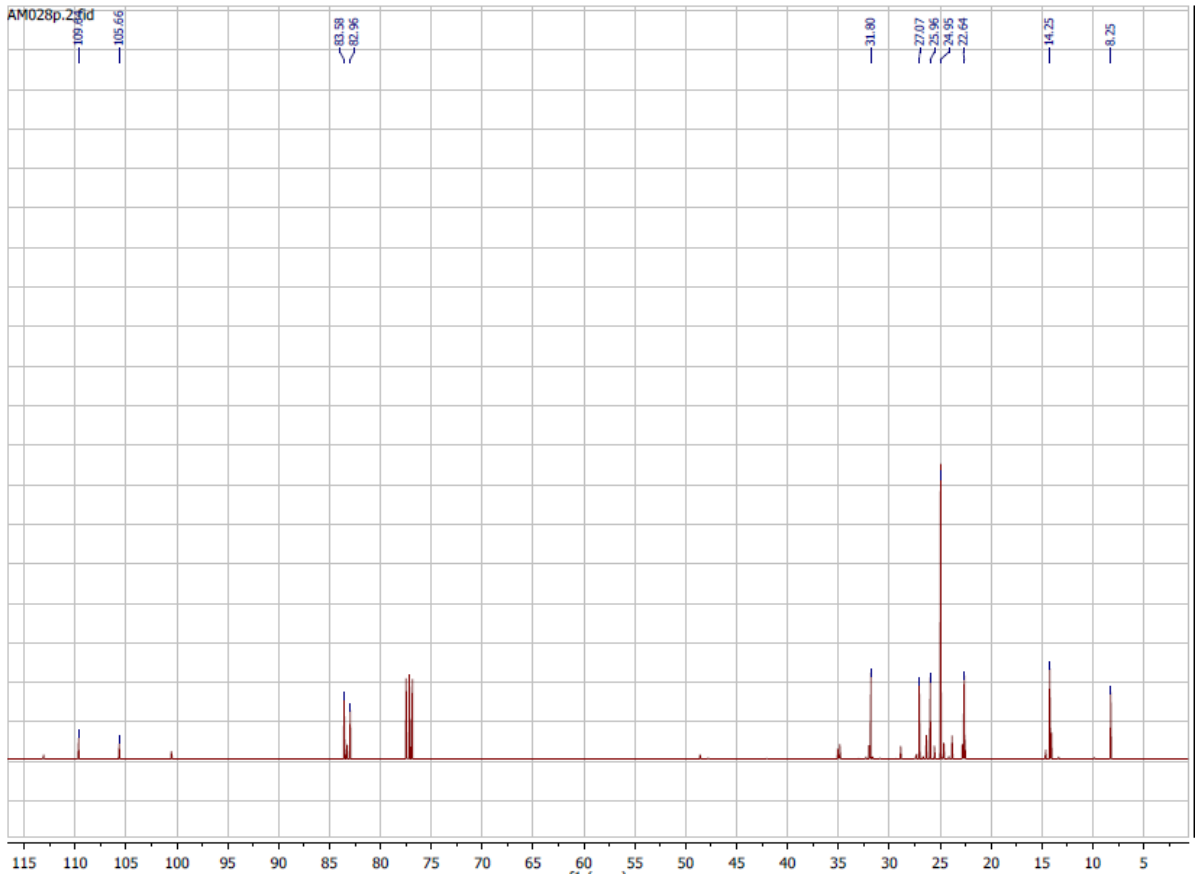


4,4,5,5-tetramethyl-2-((2-pentylcycloprop-1-en-1-yl)methyl)-1,3,2-dioxaborolane (**3b**)

^{1}H NMR (400 MHz, $CDCl_3$)

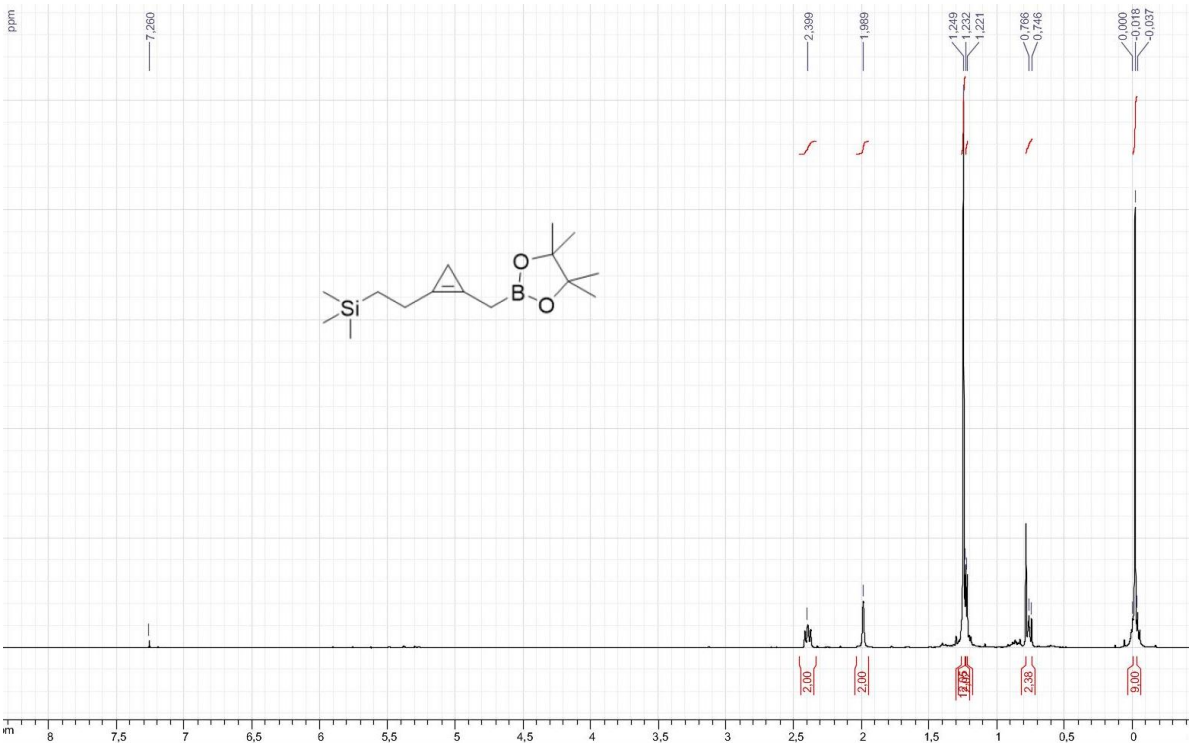


^{13}C NMR (101 MHz, $CDCl_3$)

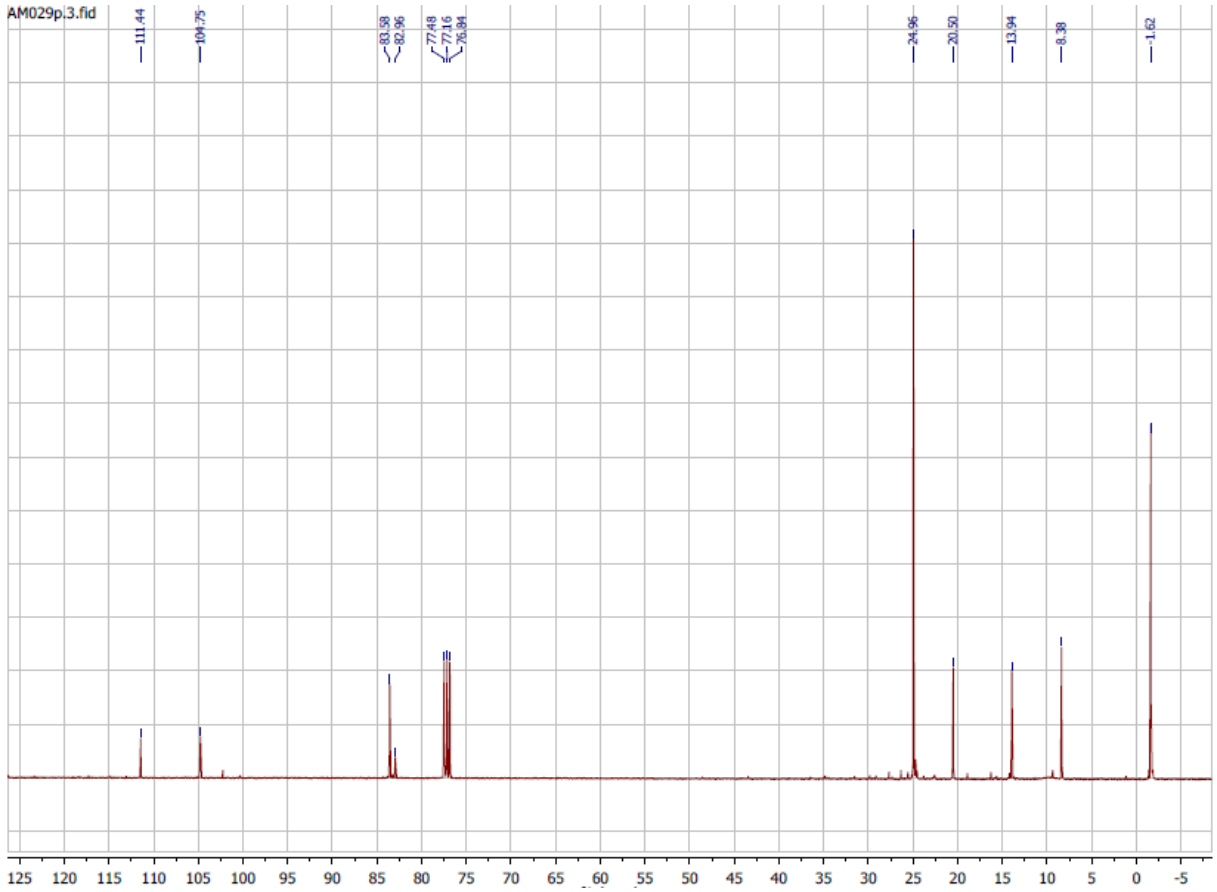


trimethyl(2-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cycloprop-1-en-1-yl)ethyl)silane (**3c**)

^{1}H NMR (400 MHz, $CDCl_3$)

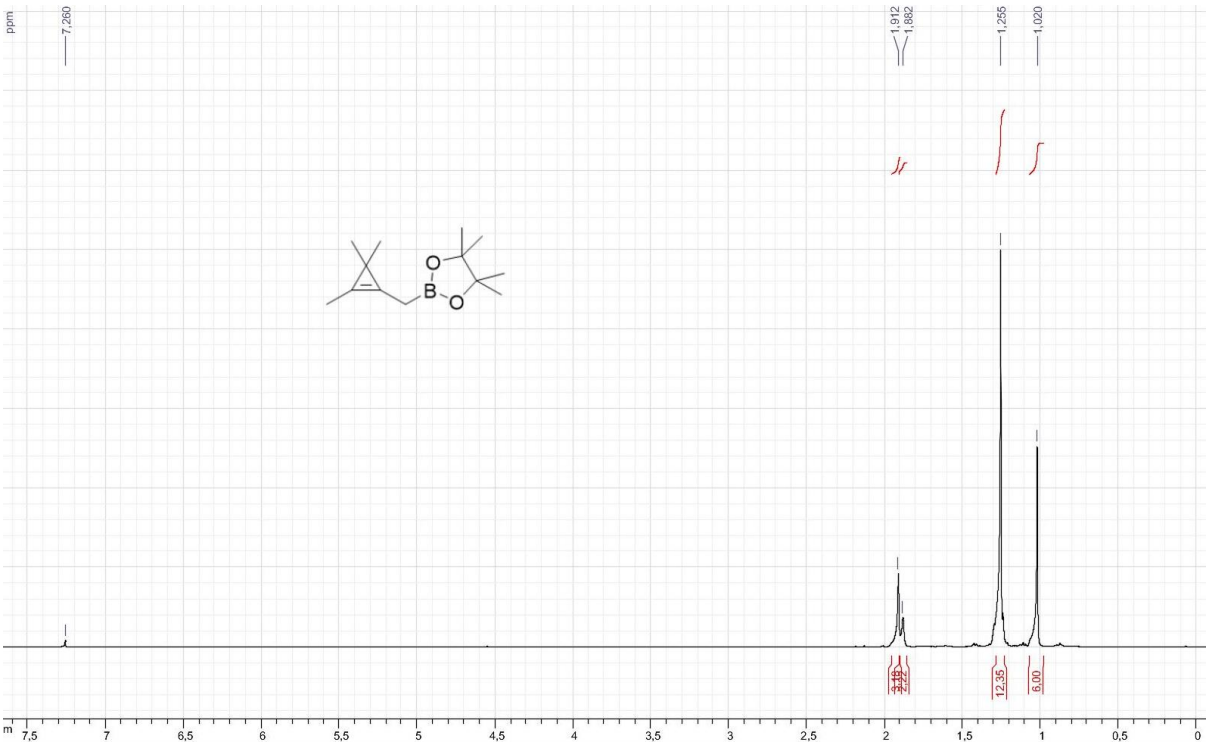


^{13}C NMR (101 MHz, $CDCl_3$)

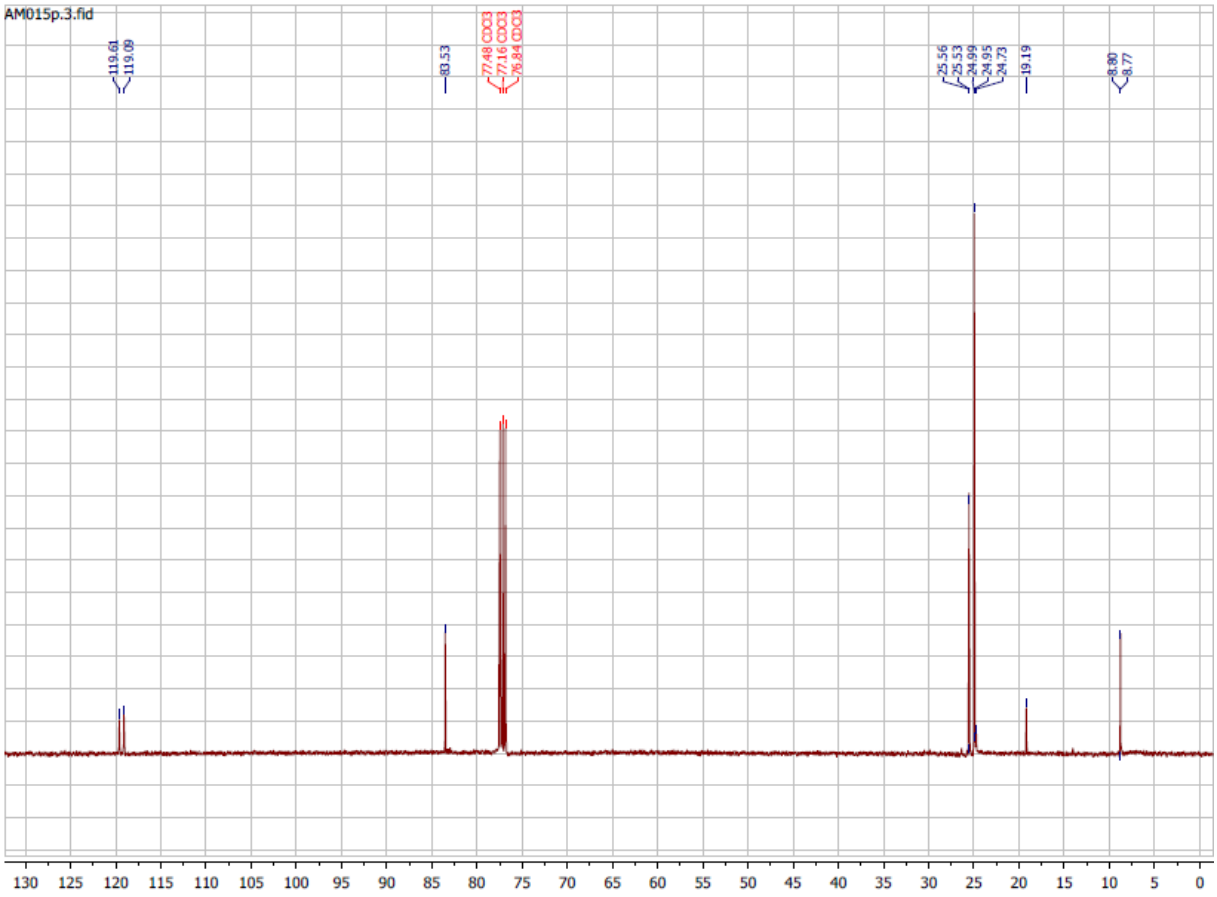


4,4,5,5-tetramethyl-2-((2,3,3-trimethylcycloprop-1-en-1-yl)methyl)-1,3,2-dioxaborolane (**3e**)

^{1}H NMR (400 MHz, $CDCl_3$)

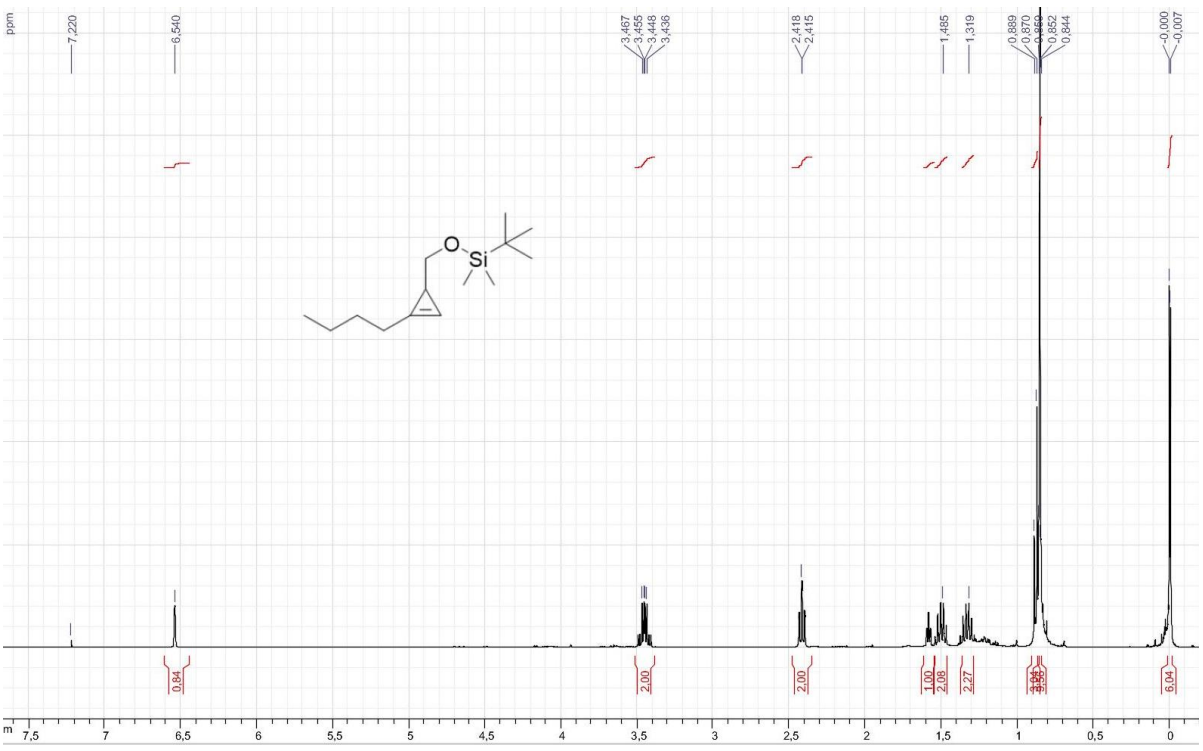


^{13}C NMR (101 MHz, $CDCl_3$)

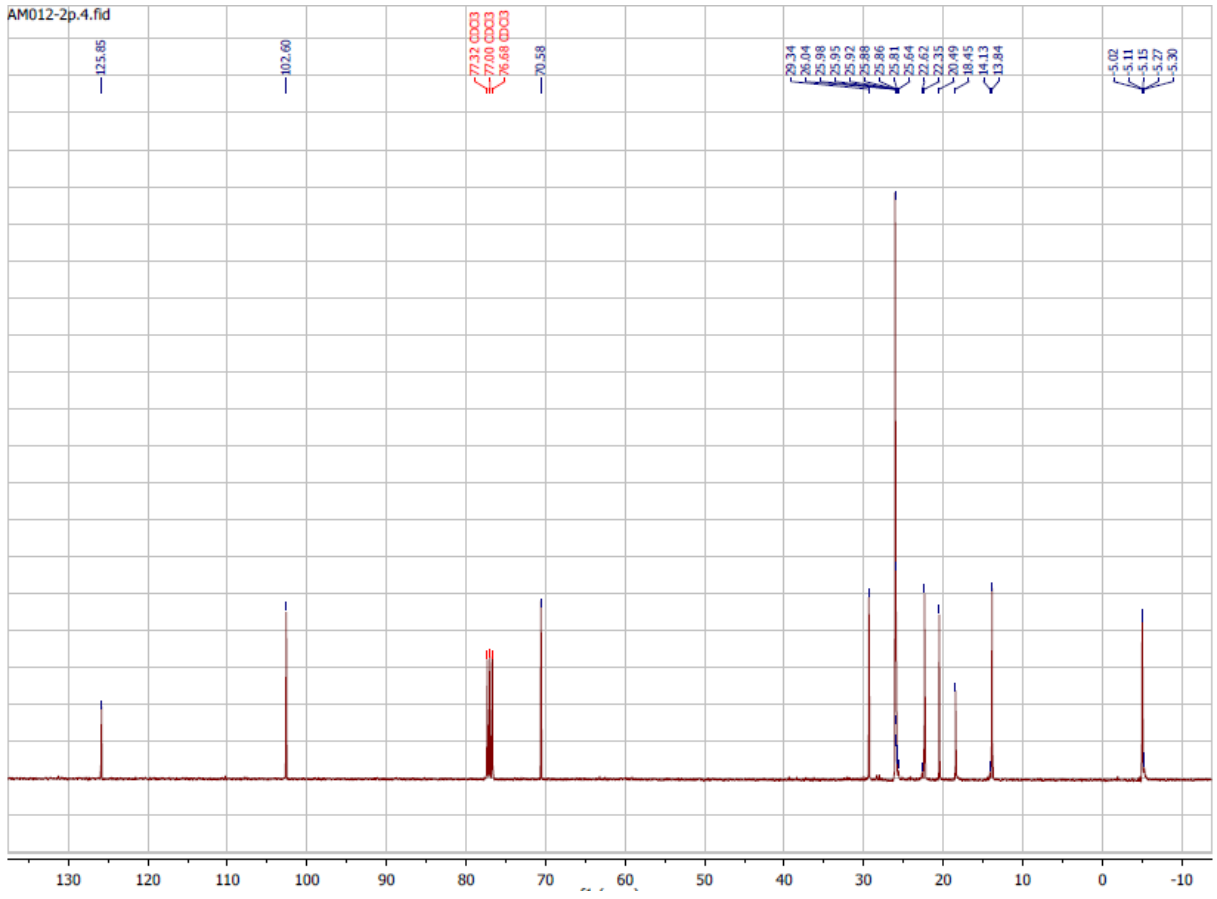


tert-butyl((2-butylcycloprop-2-en-1-yl)methoxy)dimethylsilane (**8**)

^{1}H NMR (400 MHz, $CDCl_3$)

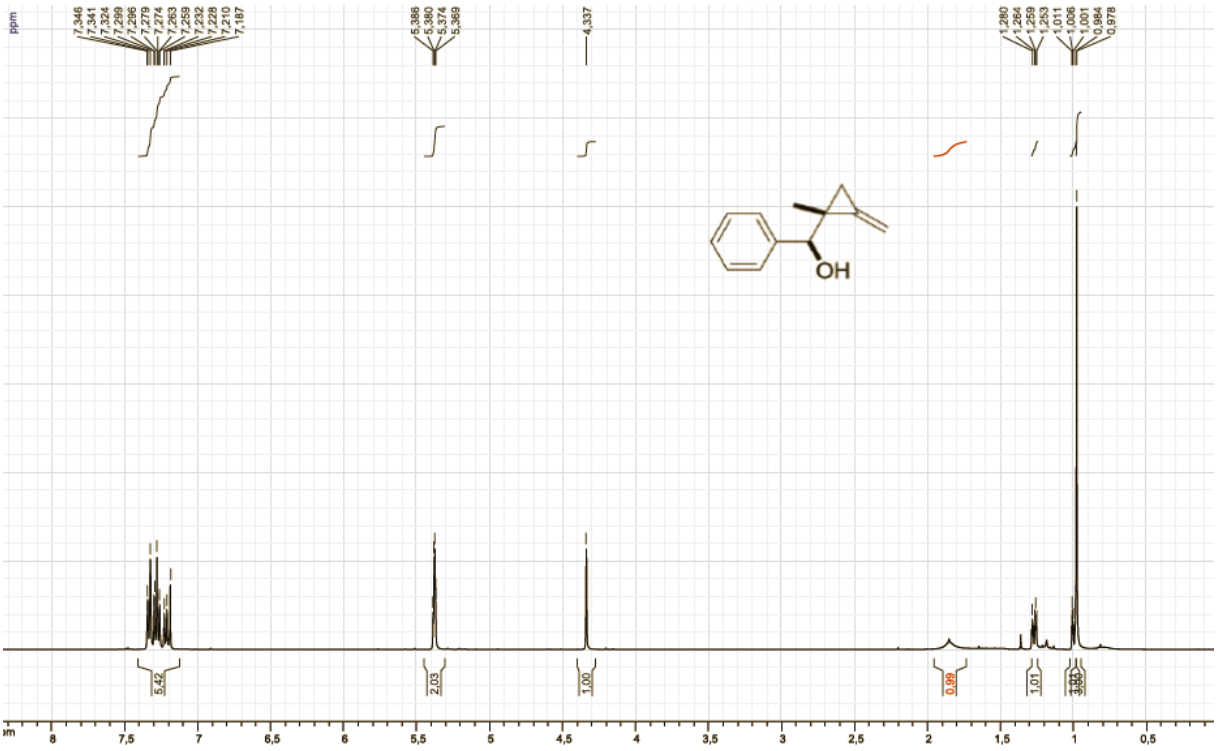


^{13}C NMR (101 MHz, $CDCl_3$)

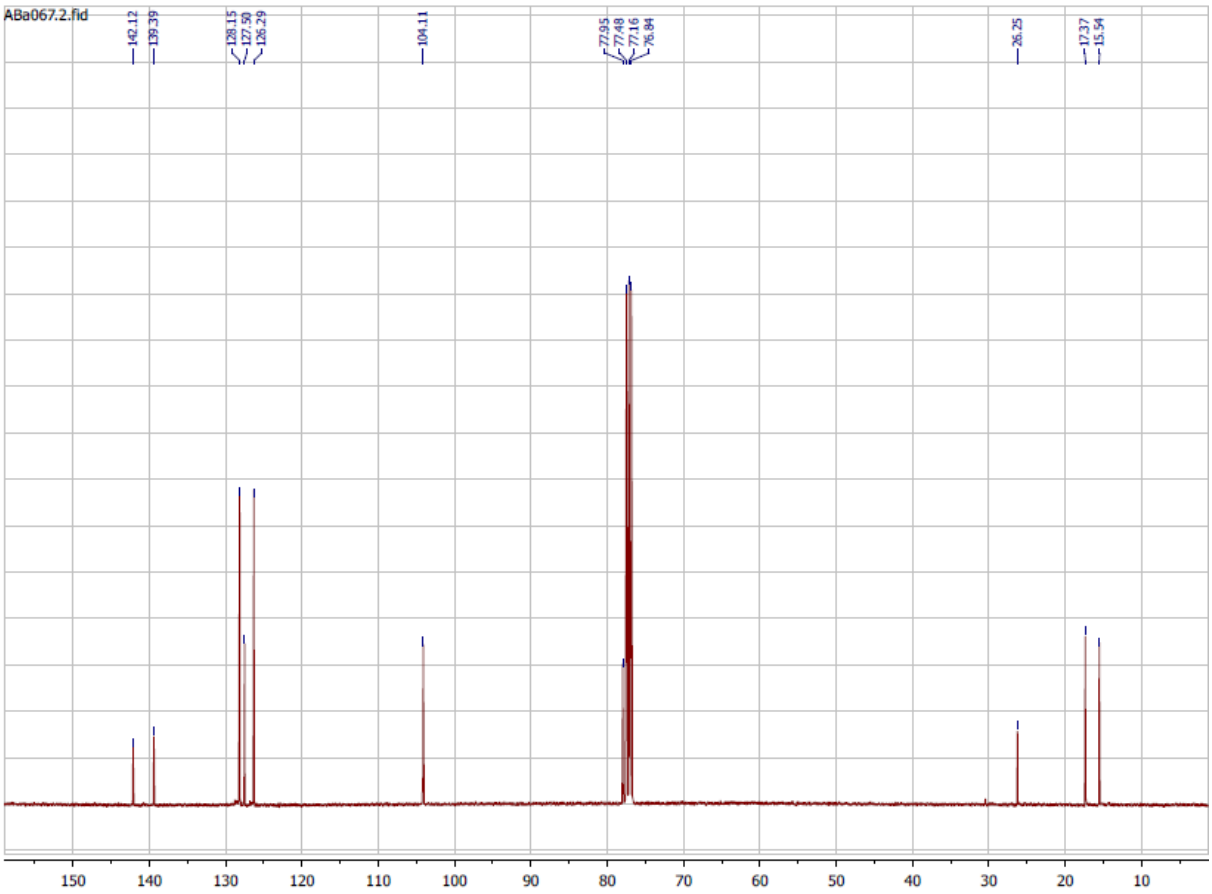


(*R**)-((*S**)-1-methyl-2-methylenecyclopropyl)(phenyl)methanol (**4a**)

^{1}H NMR (400 MHz, $CDCl_3$)

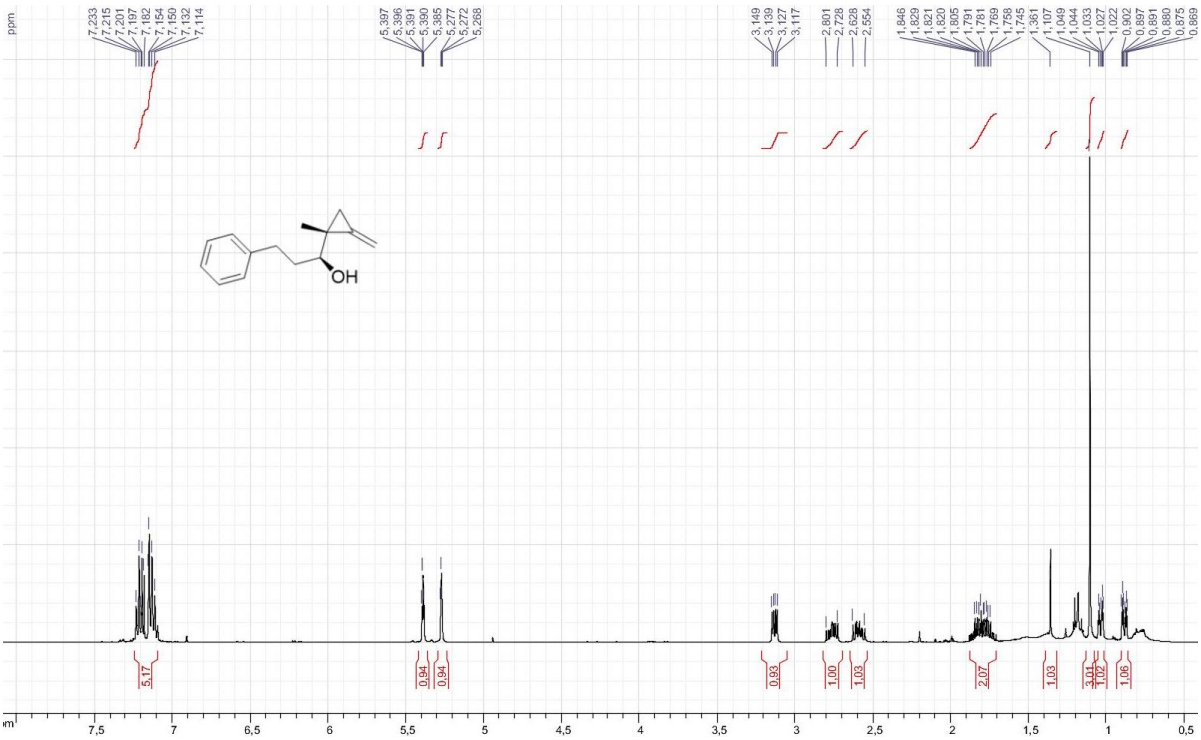


^{13}C NMR (101 MHz, $CDCl_3$)

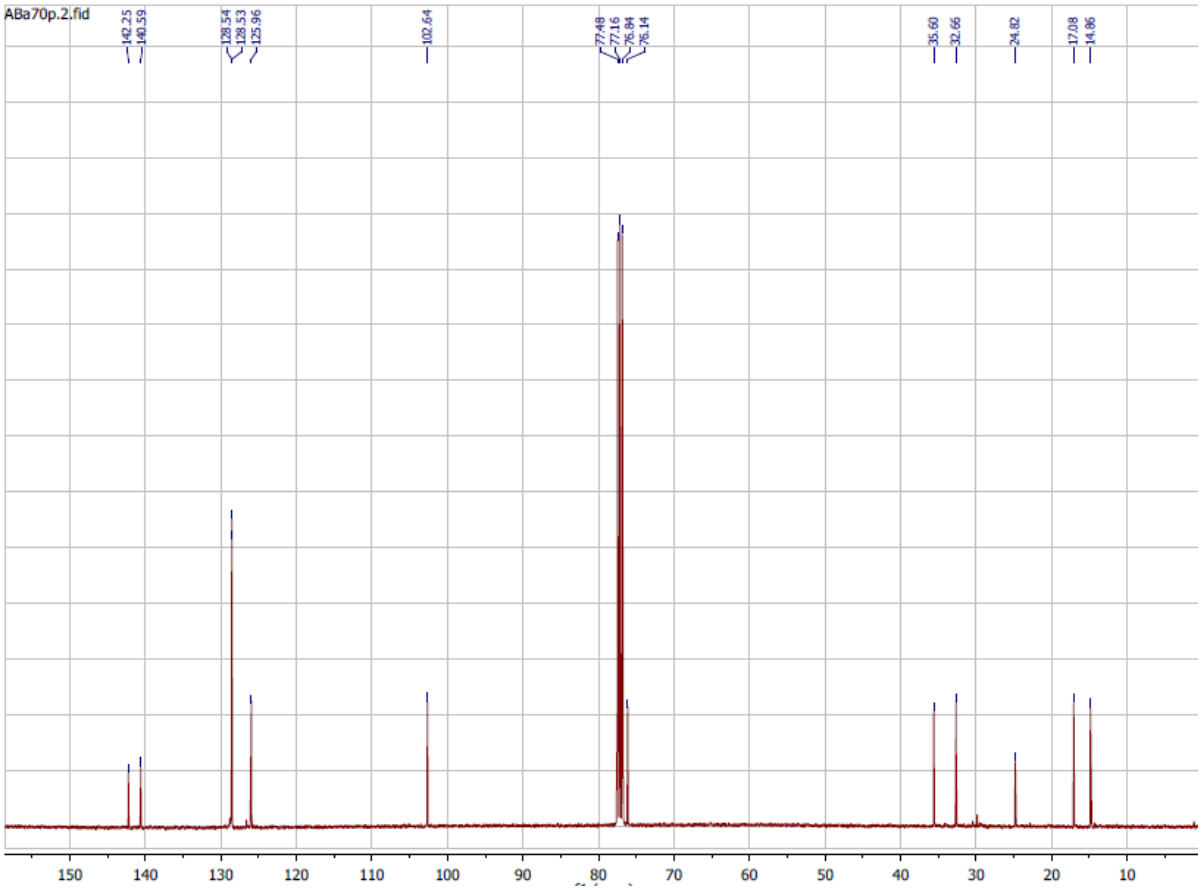


(*R**)-1-((*S**)-1-methyl-2-methylenecyclopropyl)-3-phenylpropan-1-ol (**4b**)

^{1}H NMR (400 MHz, $CDCl_3$)

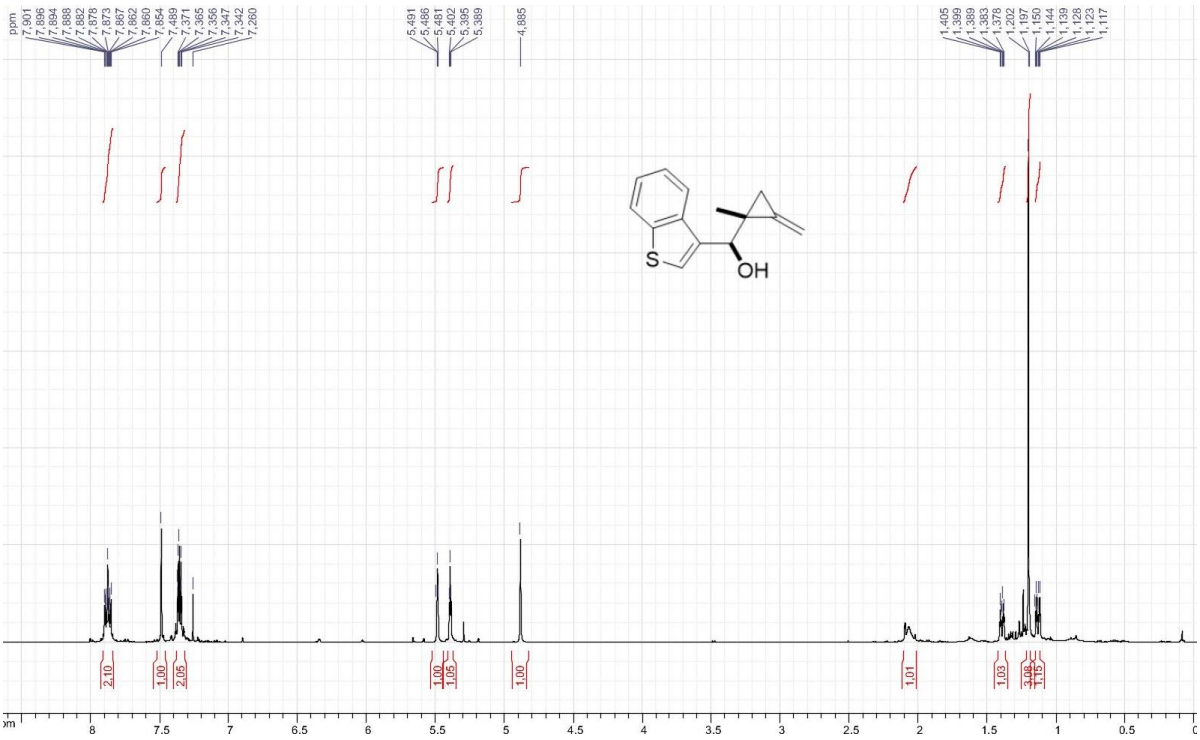


^{13}C NMR (101 MHz, $CDCl_3$)

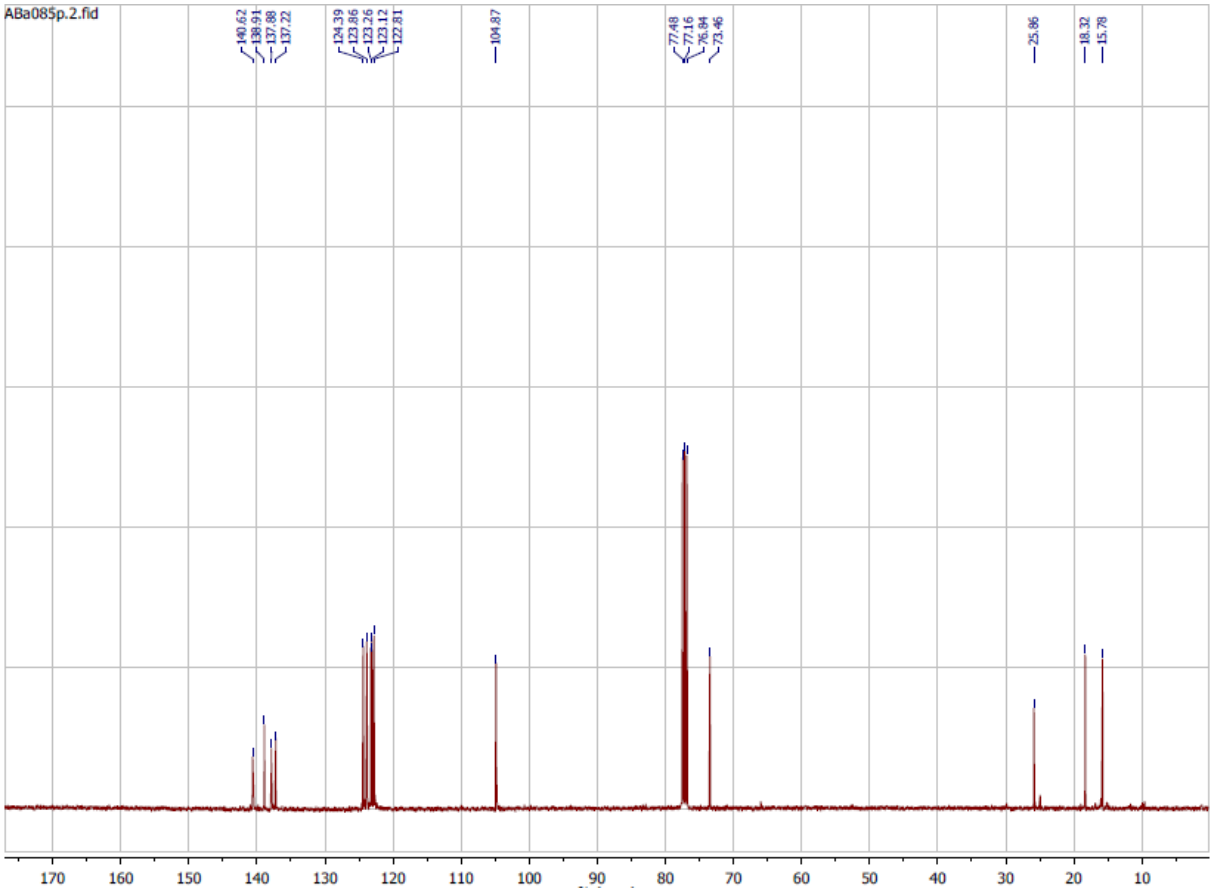


(*S**)-benzo[b]thiophen-3-yl((*S**)-1-methyl-2-methylenecyclopropyl)methanol (**4c**)

^{1}H NMR (400 MHz, $CDCl_3$)

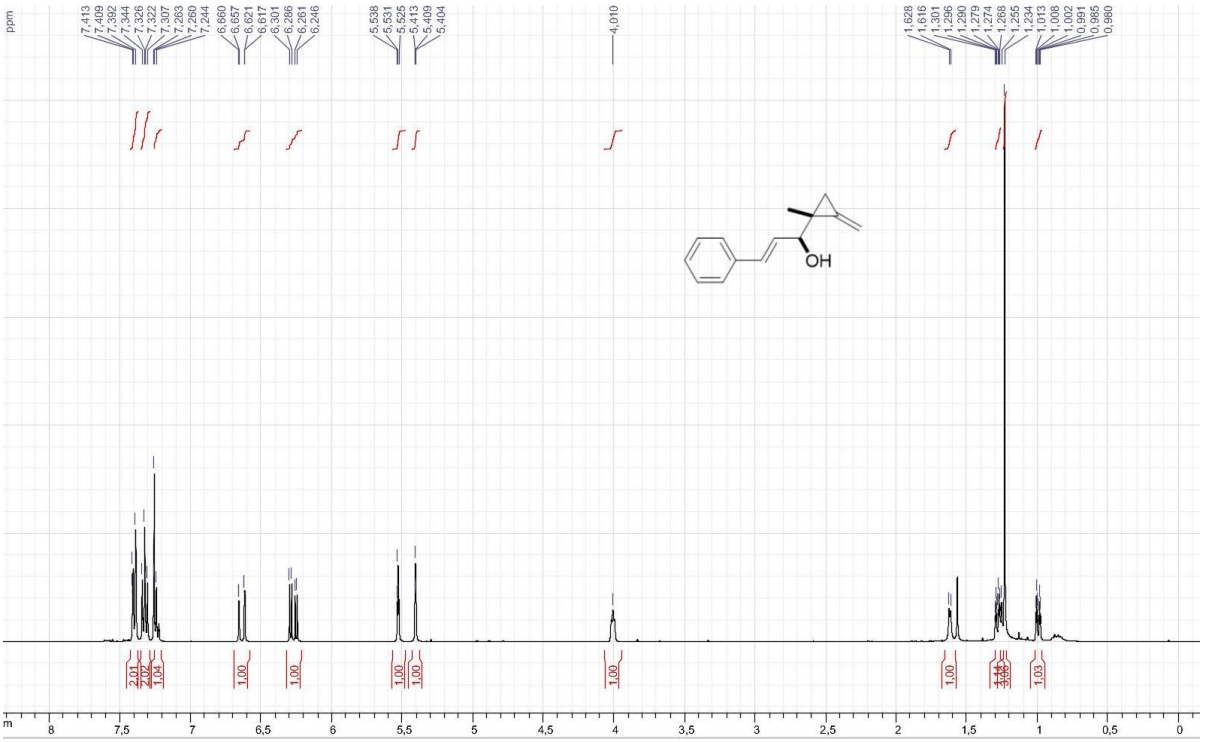


^{13}C NMR (101 MHz, $CDCl_3$)

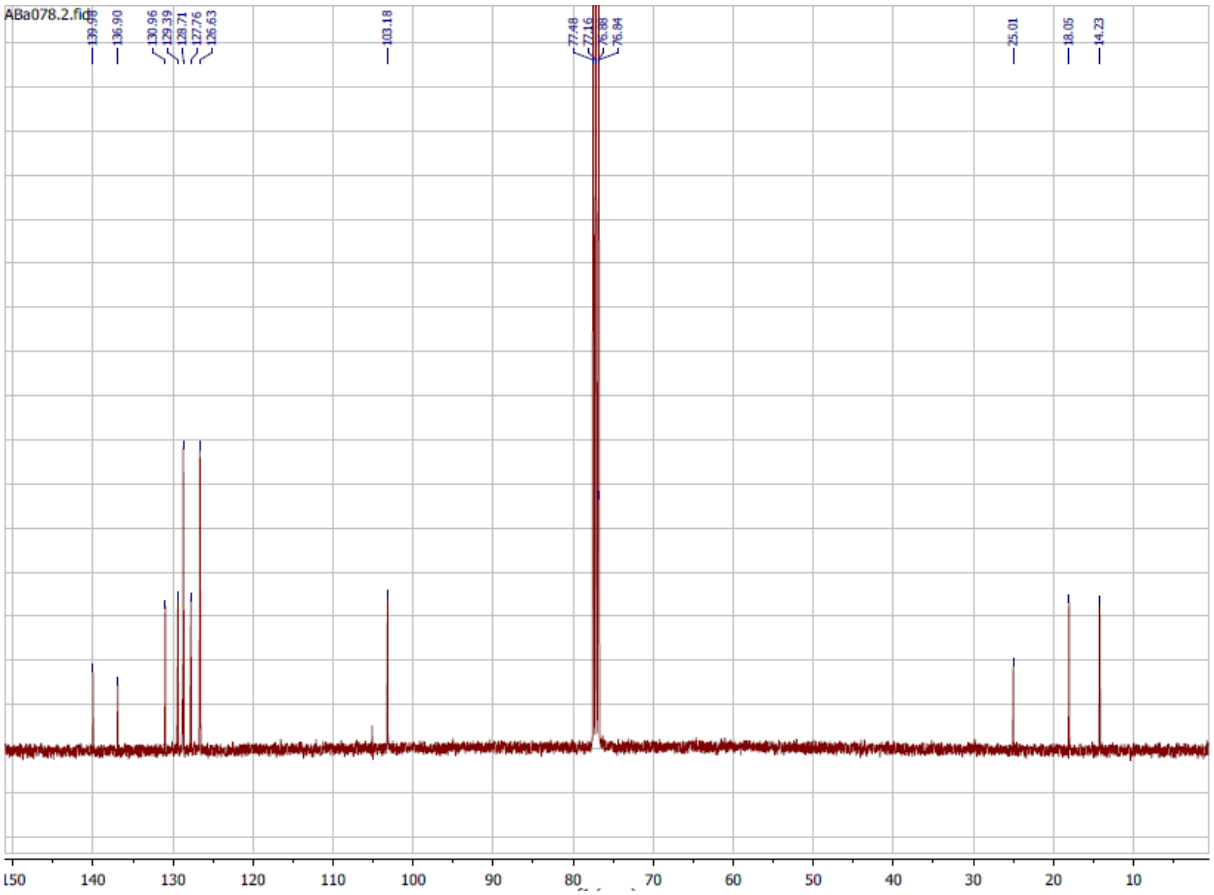


(*R**,E)-1-((*S**)-1-methyl-2-methylenecyclopropyl)-3-phenylprop-2-en-1-ol (**4d**)

^{1}H NMR (400 MHz, $CDCl_3$)

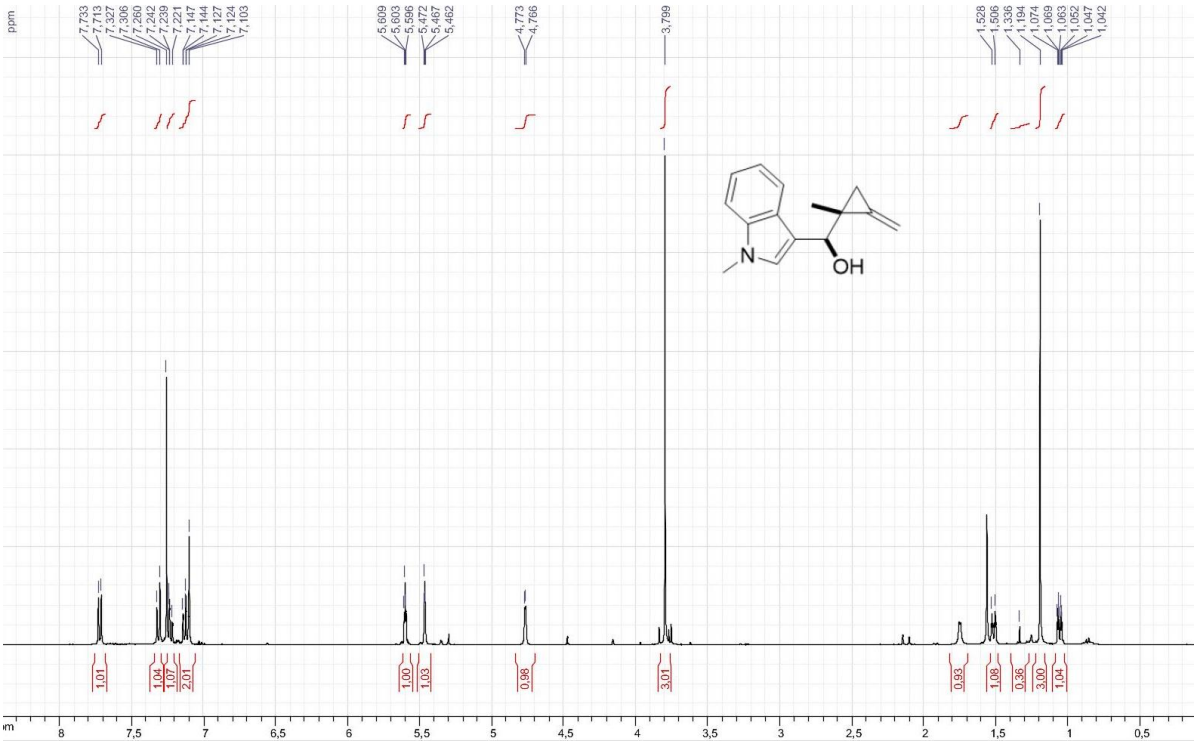


^{13}C NMR (101 MHz, $CDCl_3$)

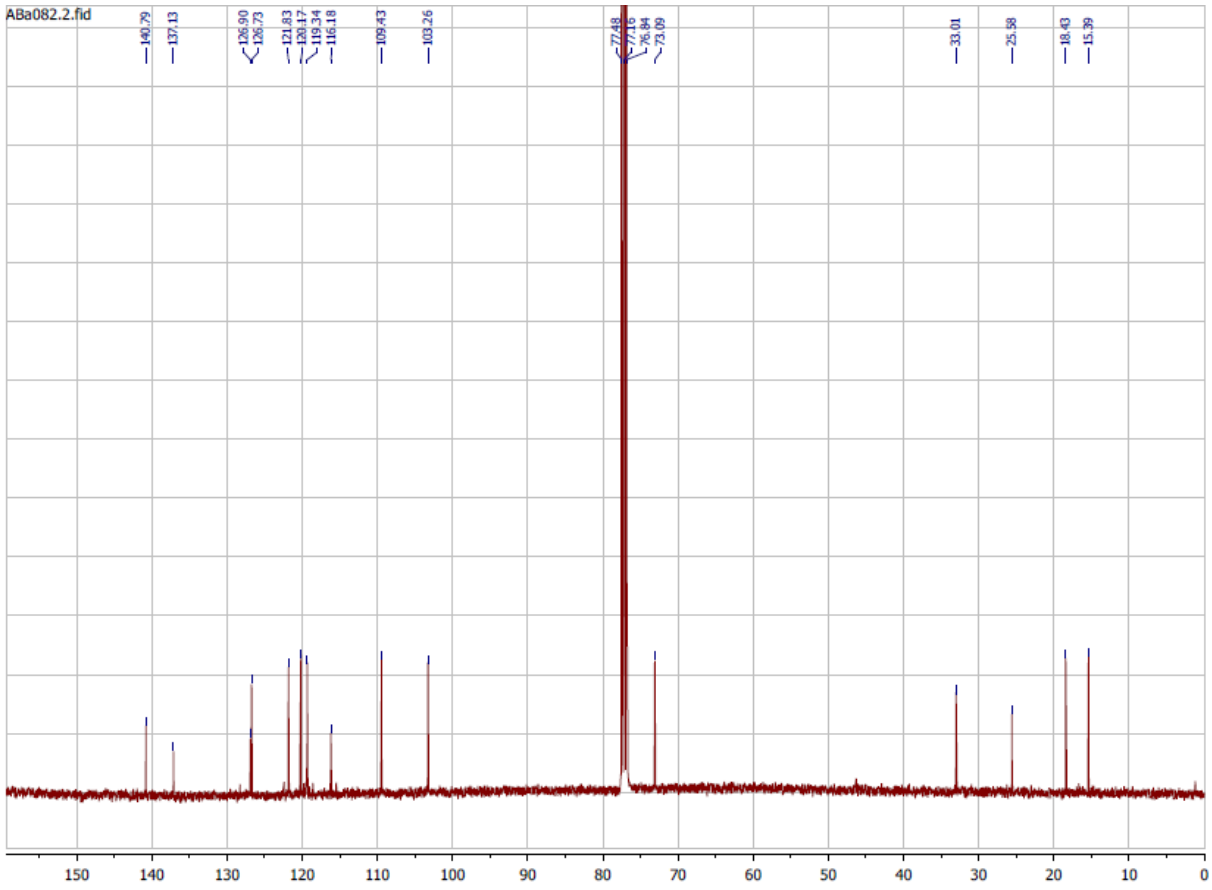


(*S**)-(1-methyl-1H-indol-3-yl)((*S**)-1-methyl-2-methylenecyclopropyl)methanol (**4e**)

^{1}H NMR (400 MHz, $CDCl_3$)

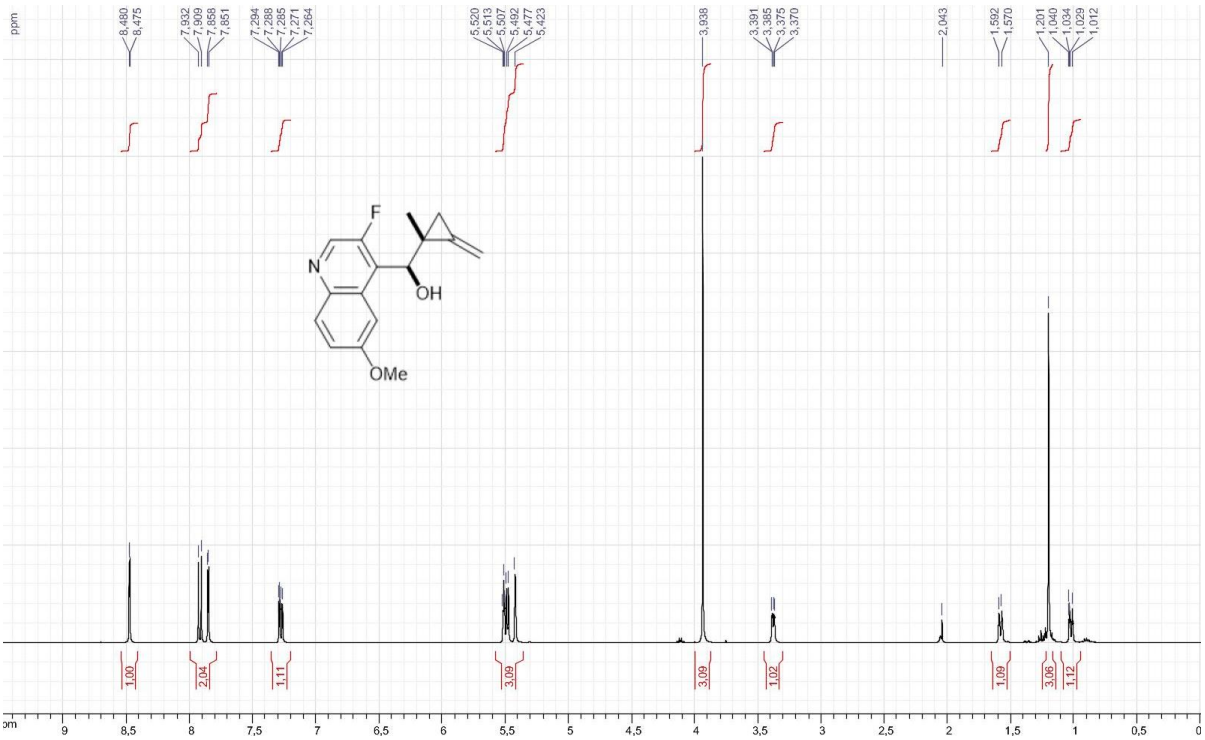


^{13}C NMR (101 MHz, $CDCl_3$)

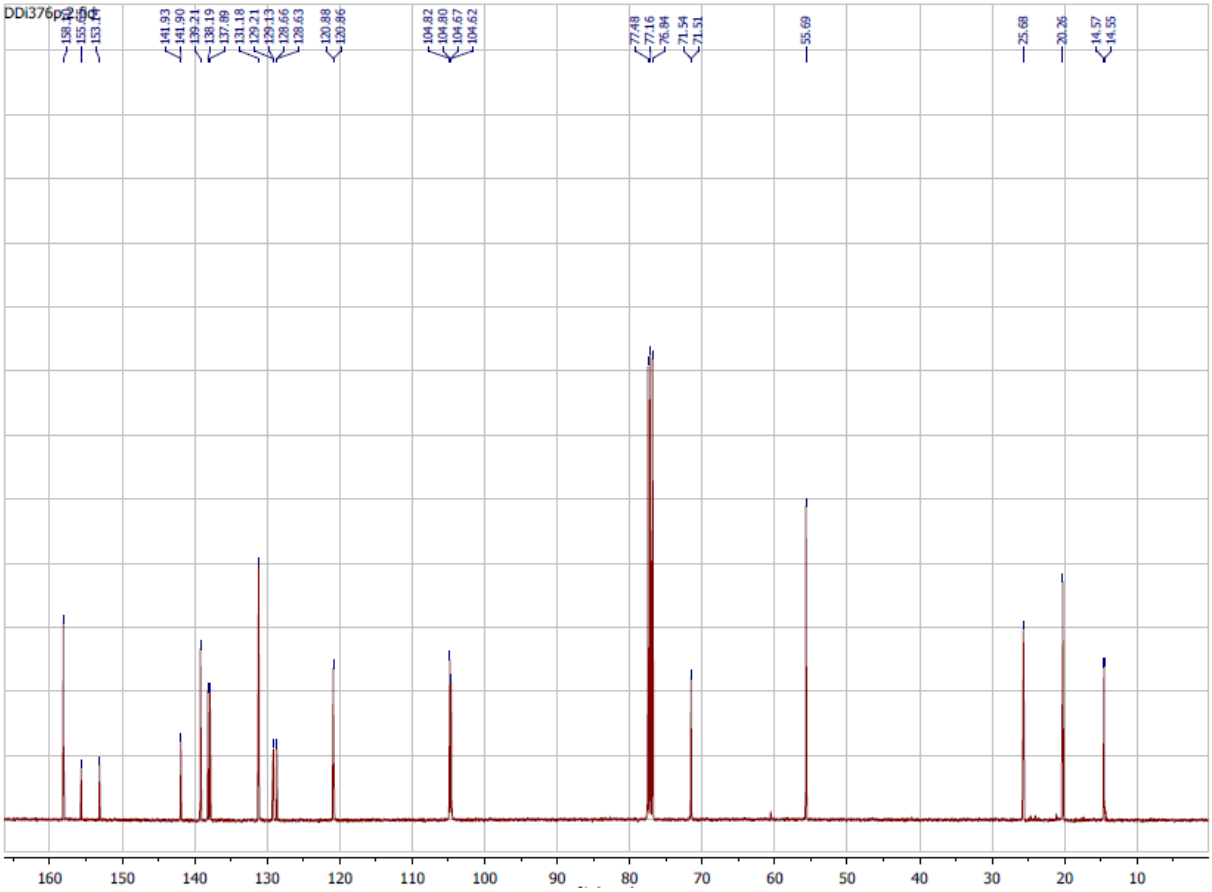


(*S**)-(3-fluoro-6-methoxyquinolin-4-yl)((*S**)-1-methyl-2-methylenecyclopropyl)methanol (**4f**)

^{1}H NMR (400 MHz, $CDCl_3$)

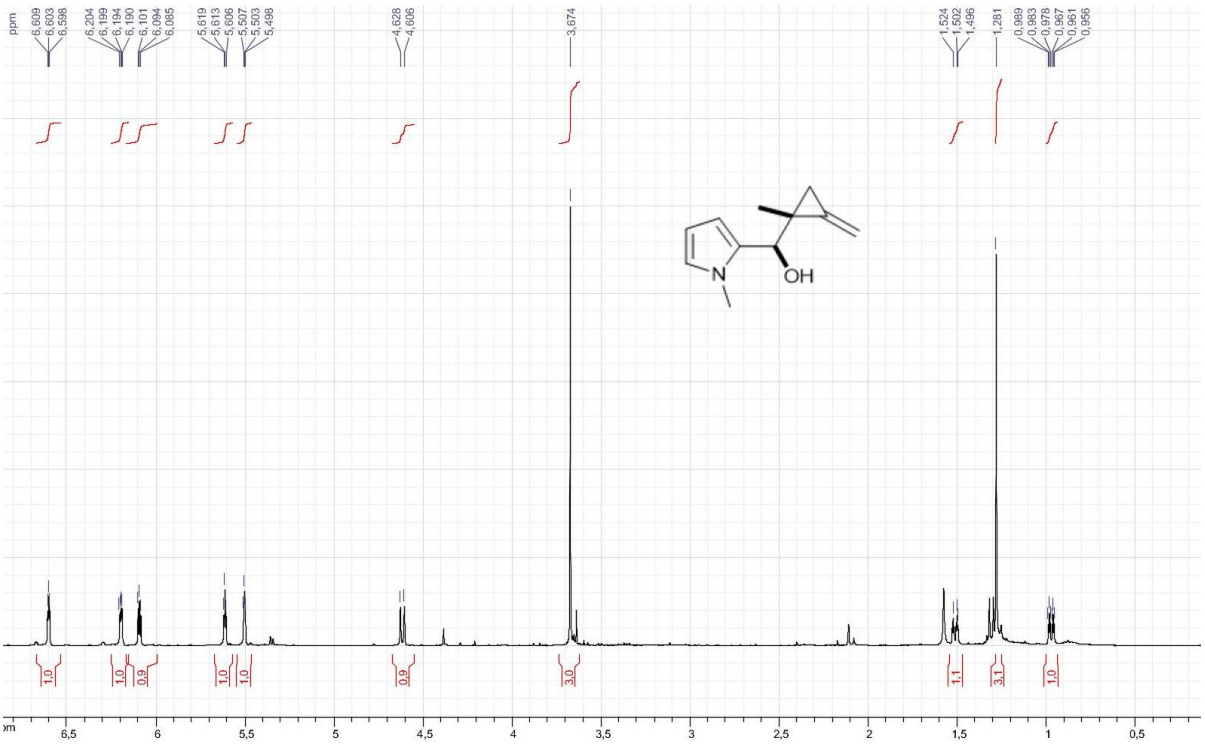


^{13}C NMR (101 MHz, $CDCl_3$)

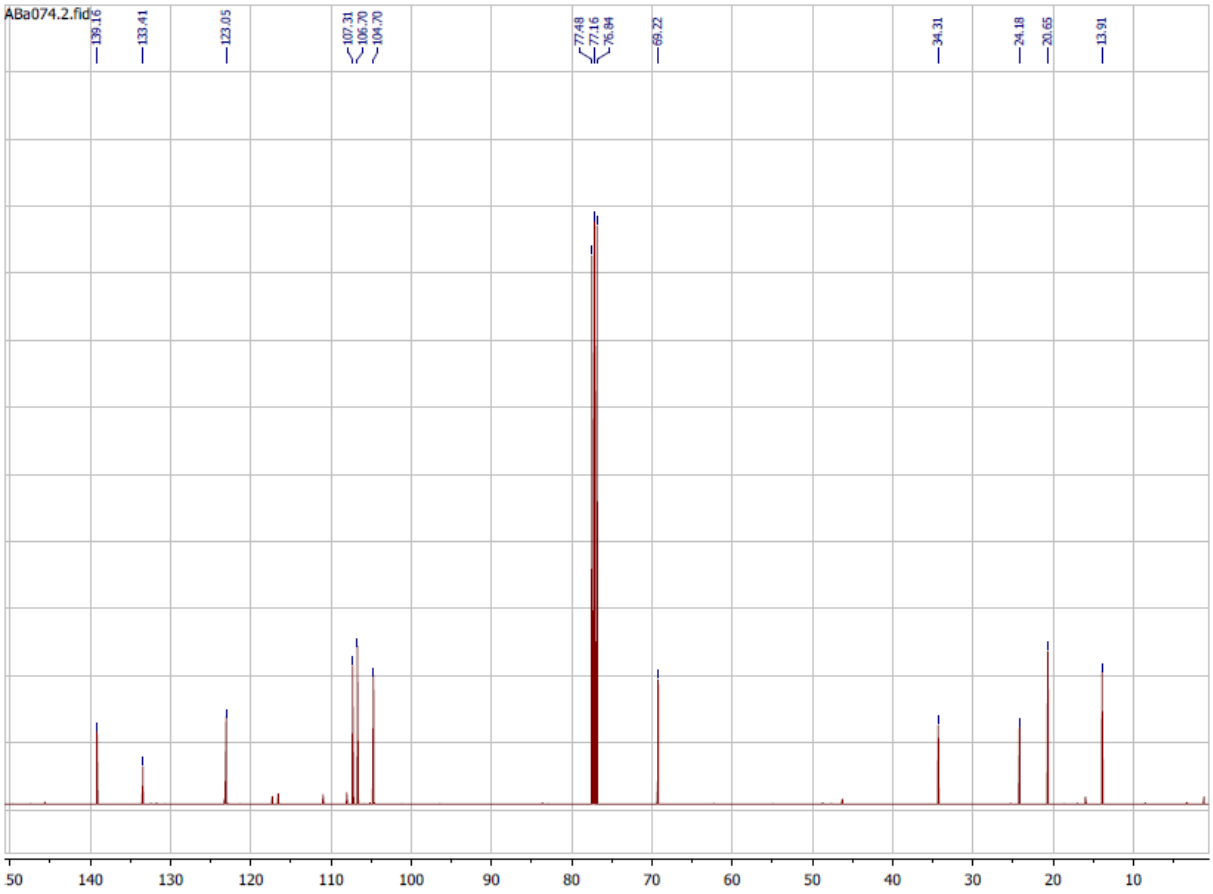


(*S**)-(1-methyl-1H-pyrrol-2-yl)((*S**)-1-methyl-2-methylenecyclopropyl)methanol (**4g**)

^{1}H NMR (400 MHz, $CDCl_3$)

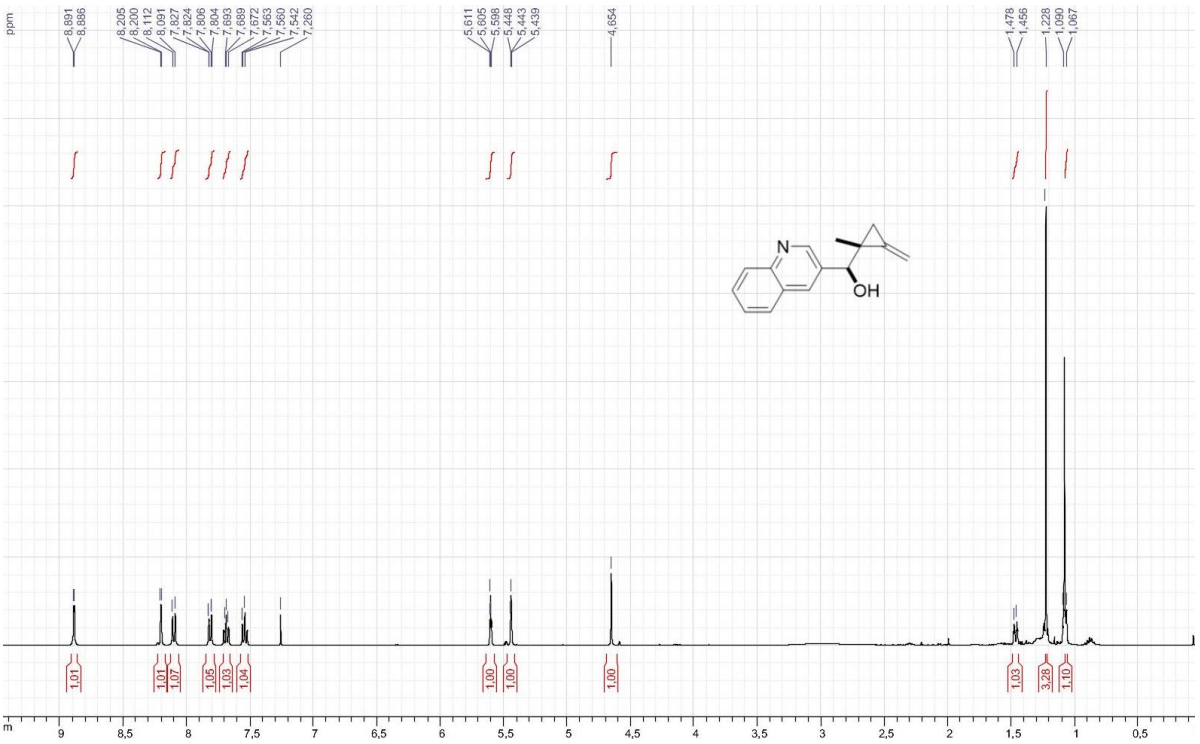


^{13}C NMR (101 MHz, $CDCl_3$)

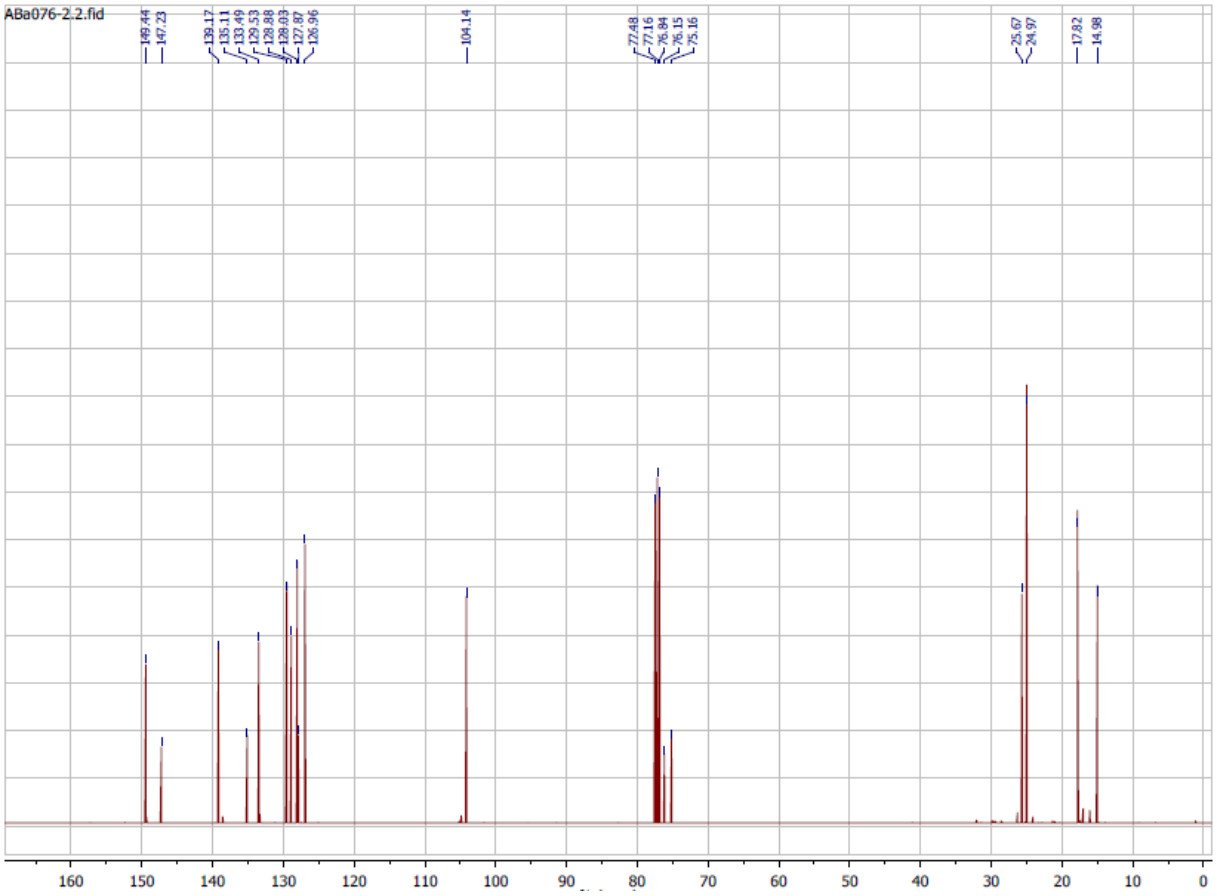


(*S**)-((*S**)-1-methyl-2-methylenecyclopropyl)(quinolin-3-yl)methanol (**4h**)

^{1}H NMR (400 MHz, $CDCl_3$)

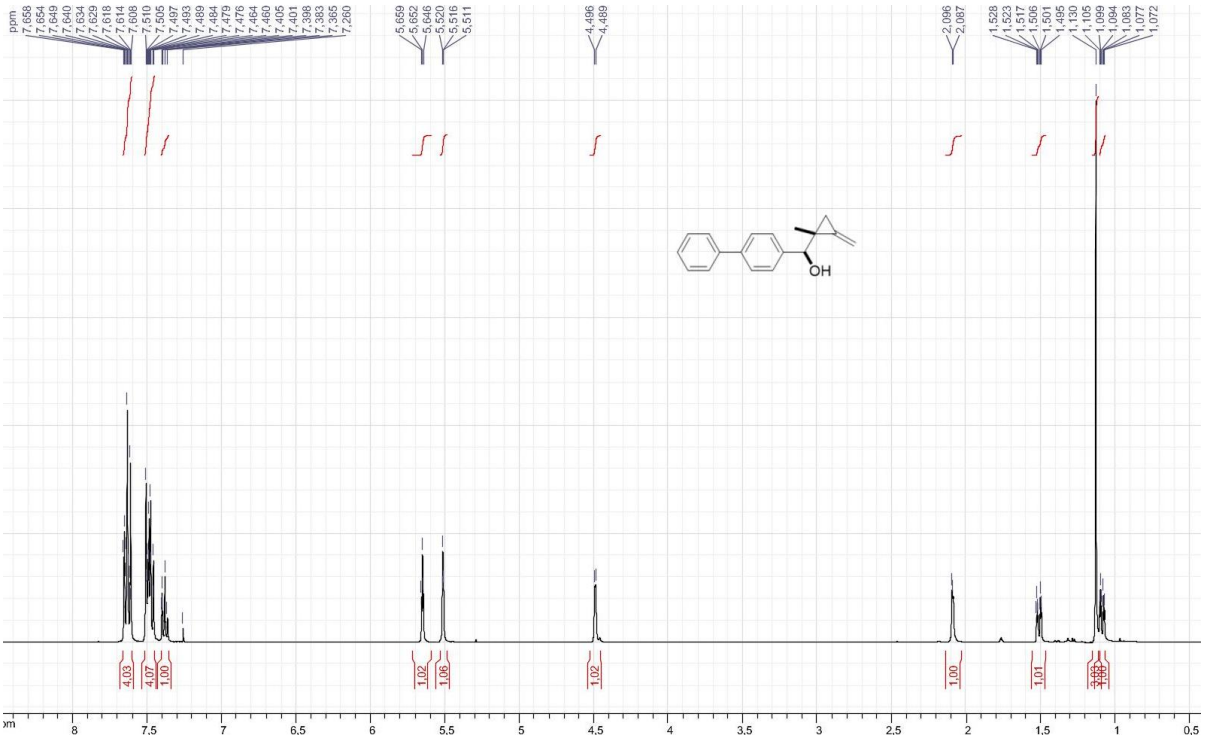


^{13}C NMR (101 MHz, $CDCl_3$)

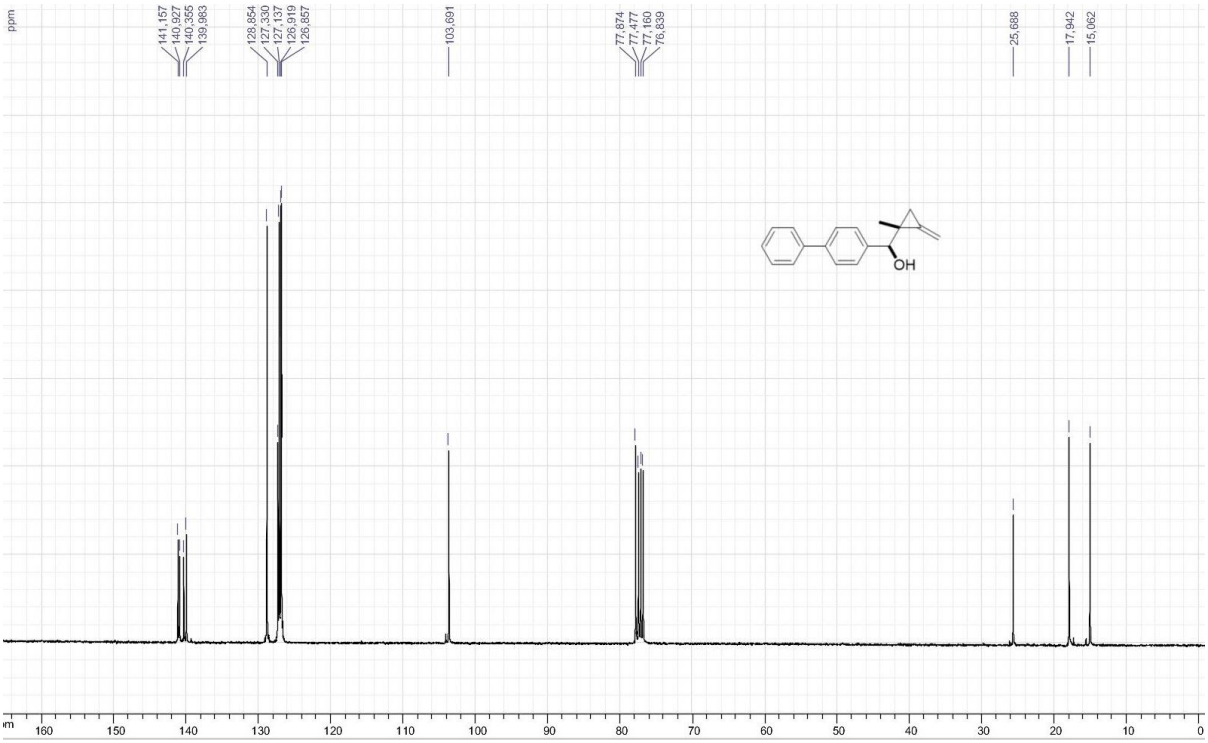


(*R**)-[1,1'-biphenyl]-4-yl((*S**)-1-methyl-2-methylenecyclopropyl)methanol (**4i**)

^{1}H NMR (400 MHz, $CDCl_3$)

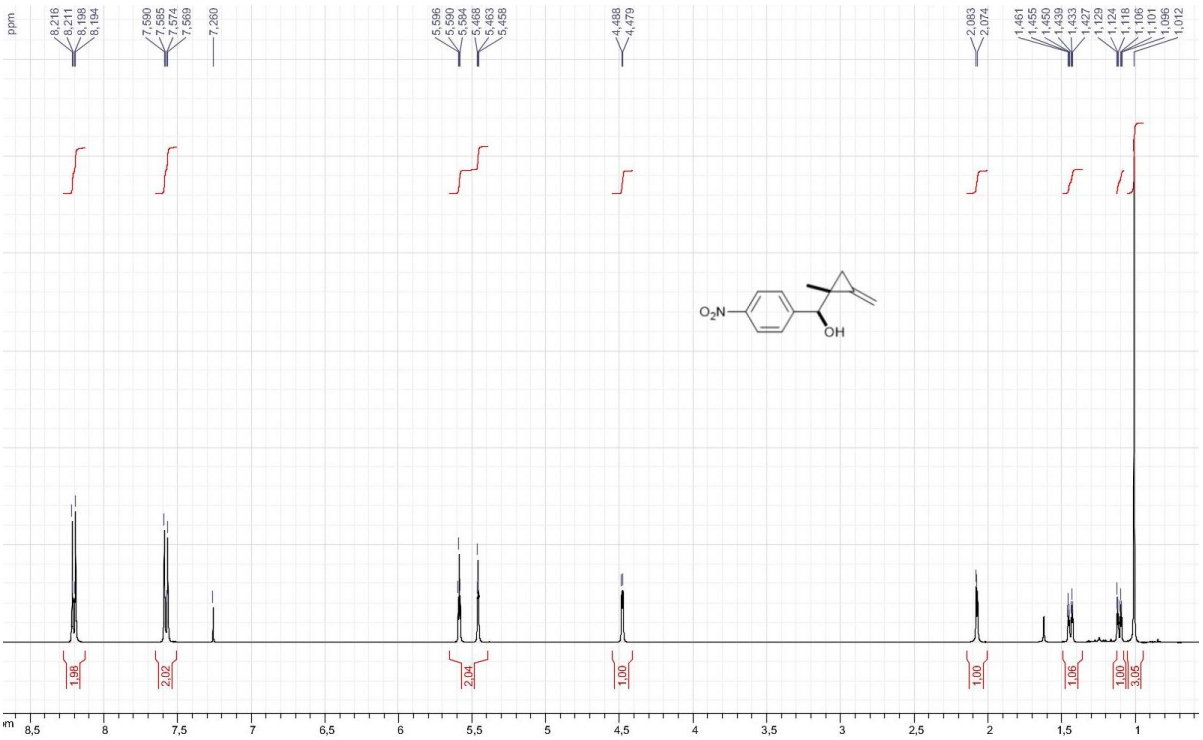


^{13}C NMR (101 MHz, $CDCl_3$)

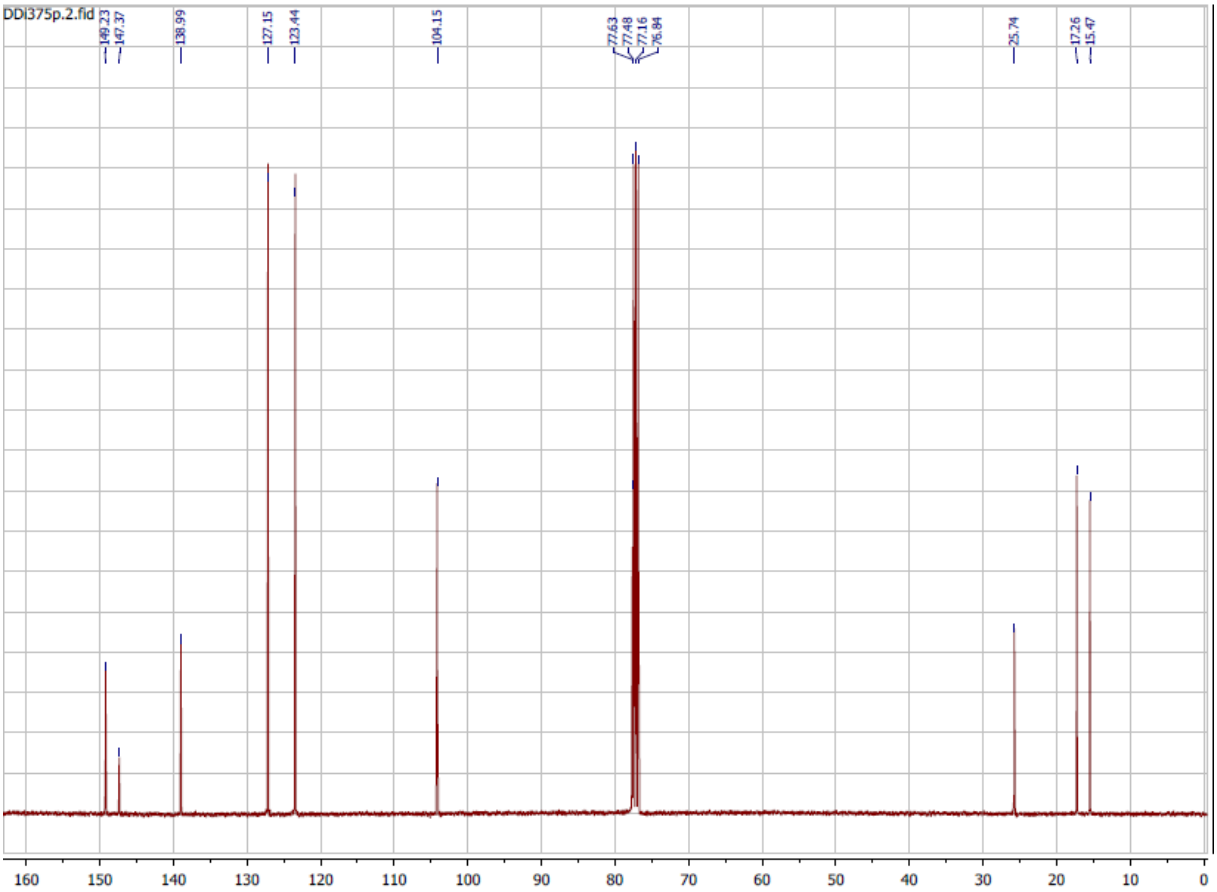


(*R**)-((*S**)-1-methyl-2-methylenecyclopropyl)(4-nitrophenyl)methanol (**4j**)

^{1}H NMR (400 MHz, $CDCl_3$)

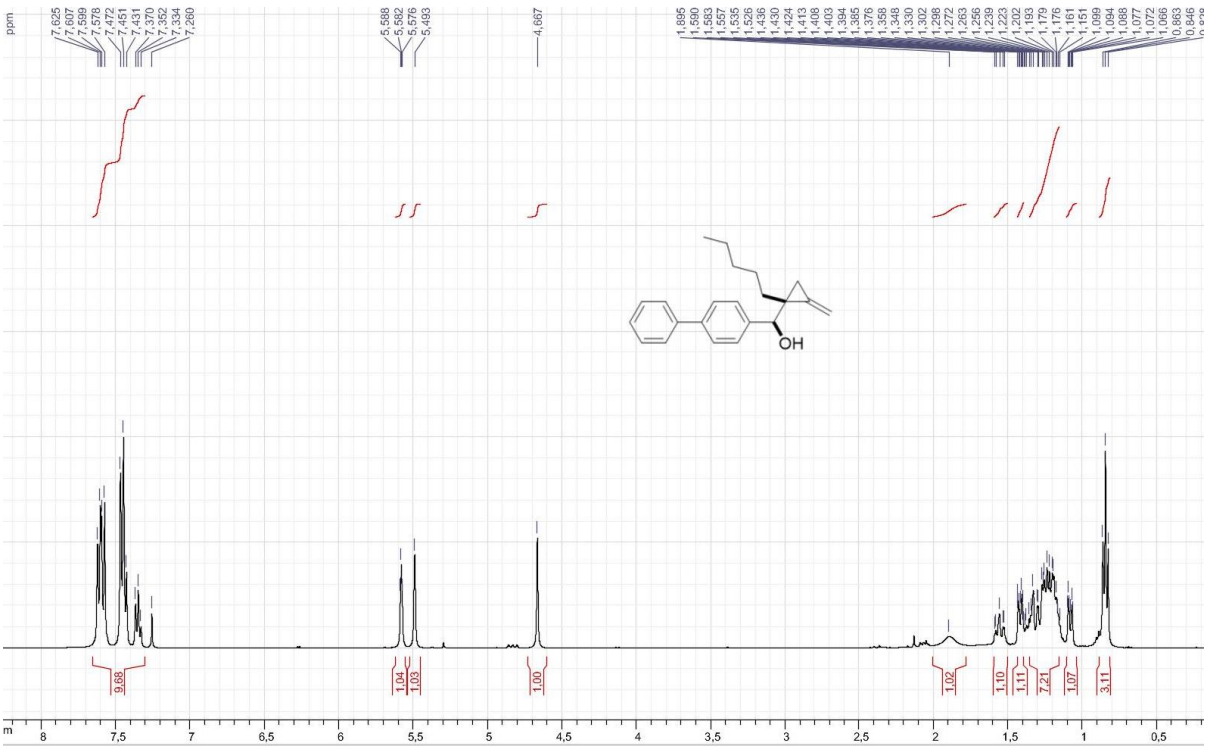


^{13}C NMR (101 MHz, $CDCl_3$)

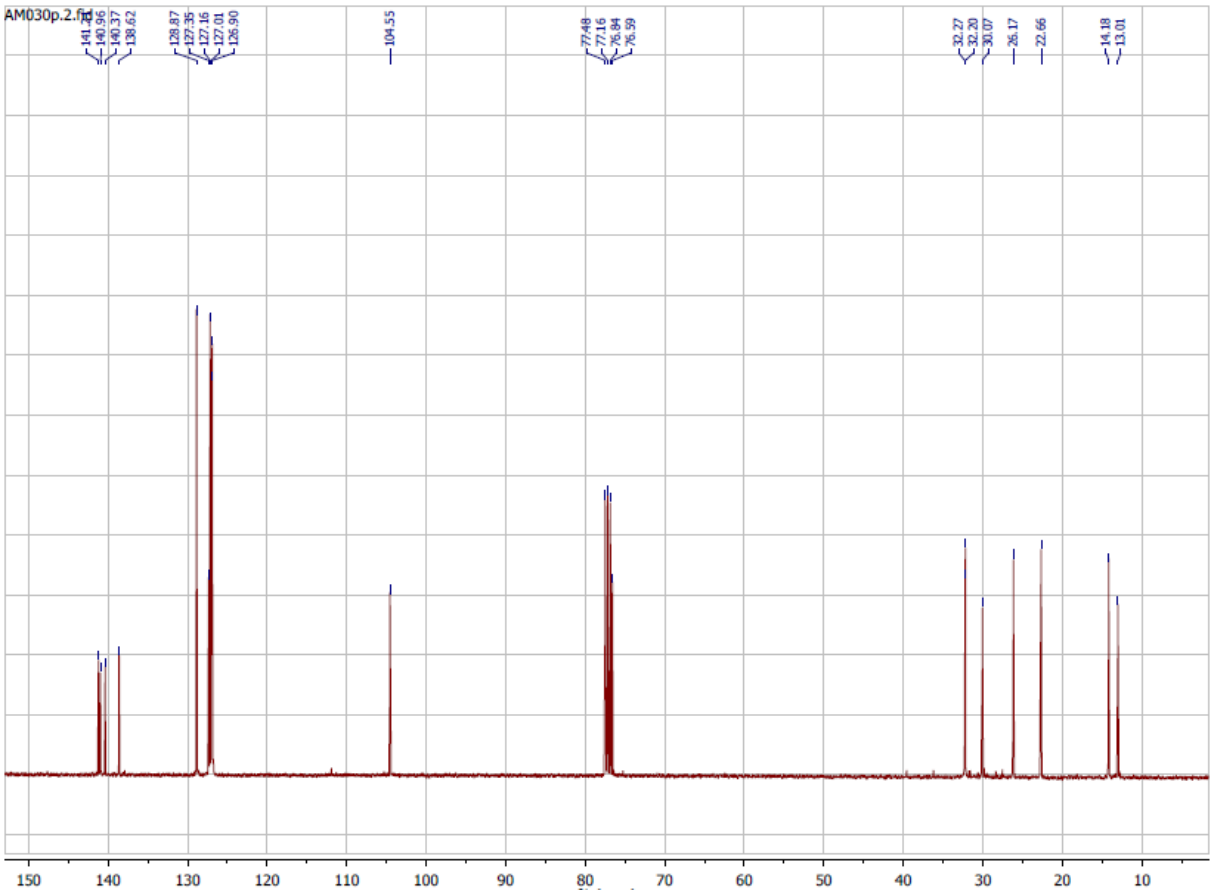


(*R**)-[1,1'-biphenyl]-4-yl((*S**)-2-methylene-1-pentylcyclopropyl)methanol (**4k**)

^{1}H NMR (400 MHz, $CDCl_3$)

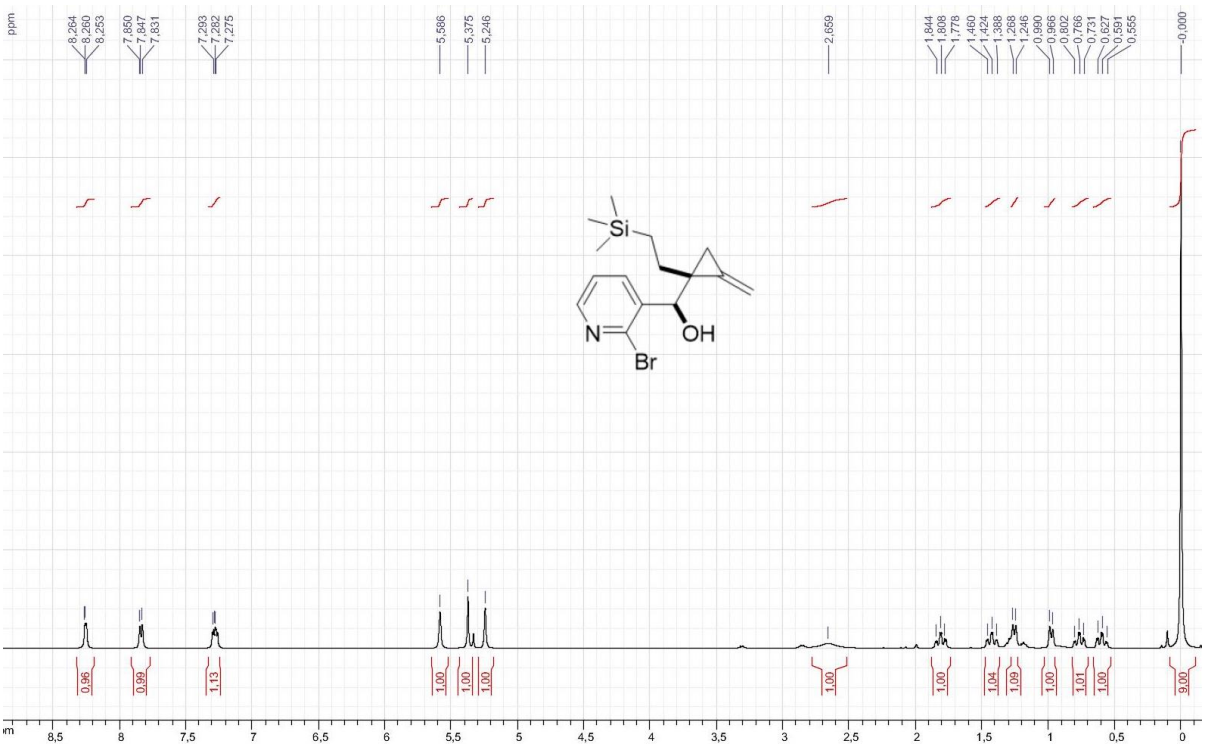


^{13}C NMR (101 MHz, $CDCl_3$)

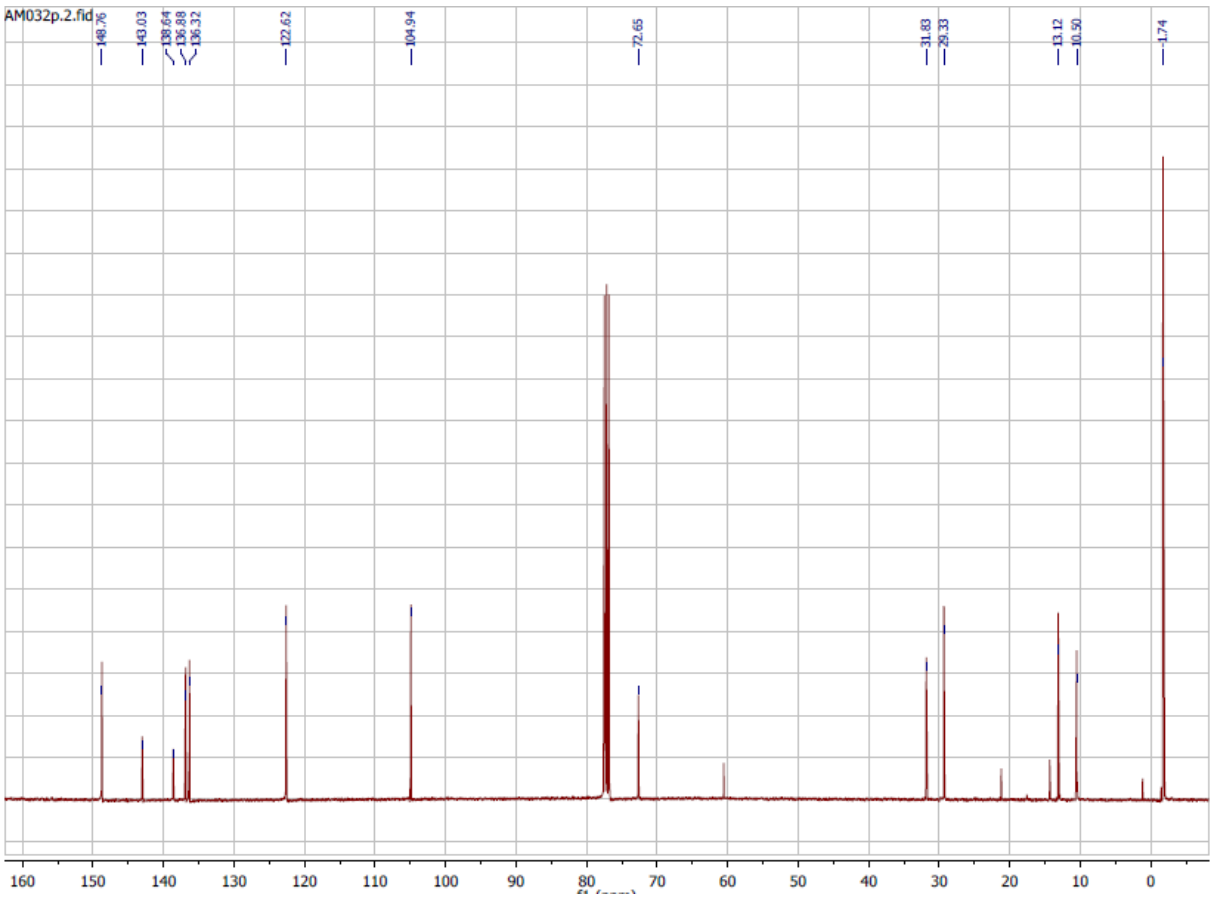


(*S**)-(2-bromopyridin-3-yl)((*R**)-2-methylene-1-(2-(trimethylsilyl)ethyl)cyclopropyl)methanol (**4l**)

^{1}H NMR (400 MHz, $CDCl_3$)

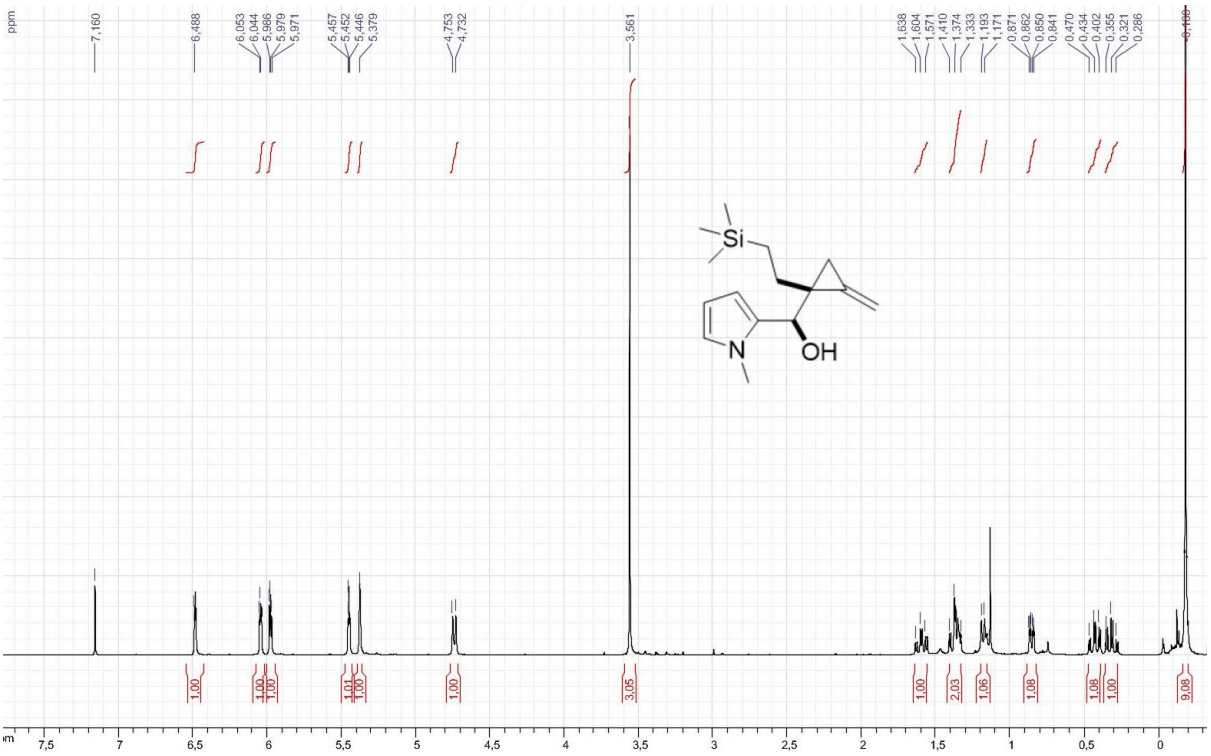


^{13}C NMR (101 MHz, $CDCl_3$)

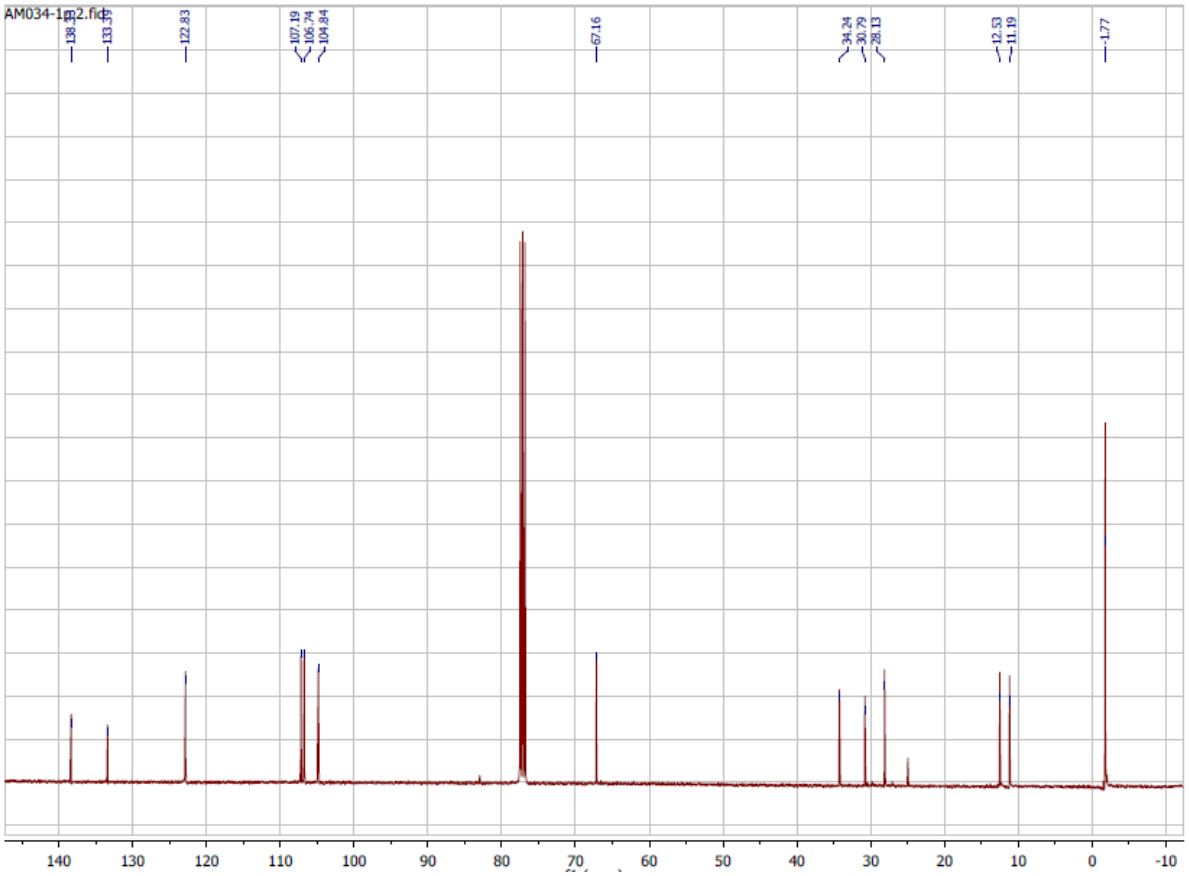


(*S**)-(1-methyl-1H-pyrrol-2-yl)((*R**)-2-methylene-1-(2-(trimethylsilyl)ethyl)cyclopropyl)-methanol (**4m**)

^{1}H NMR (400 MHz, $CDCl_3$)

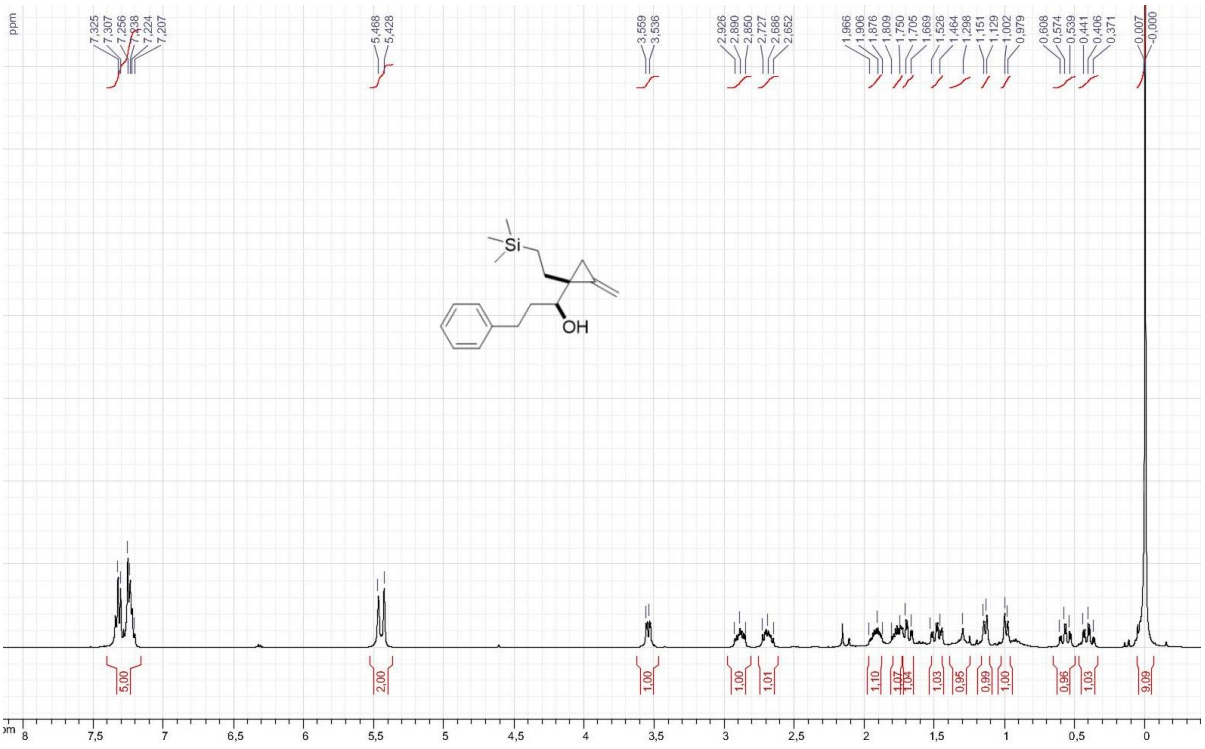


^{13}C NMR (101 MHz, $CDCl_3$)

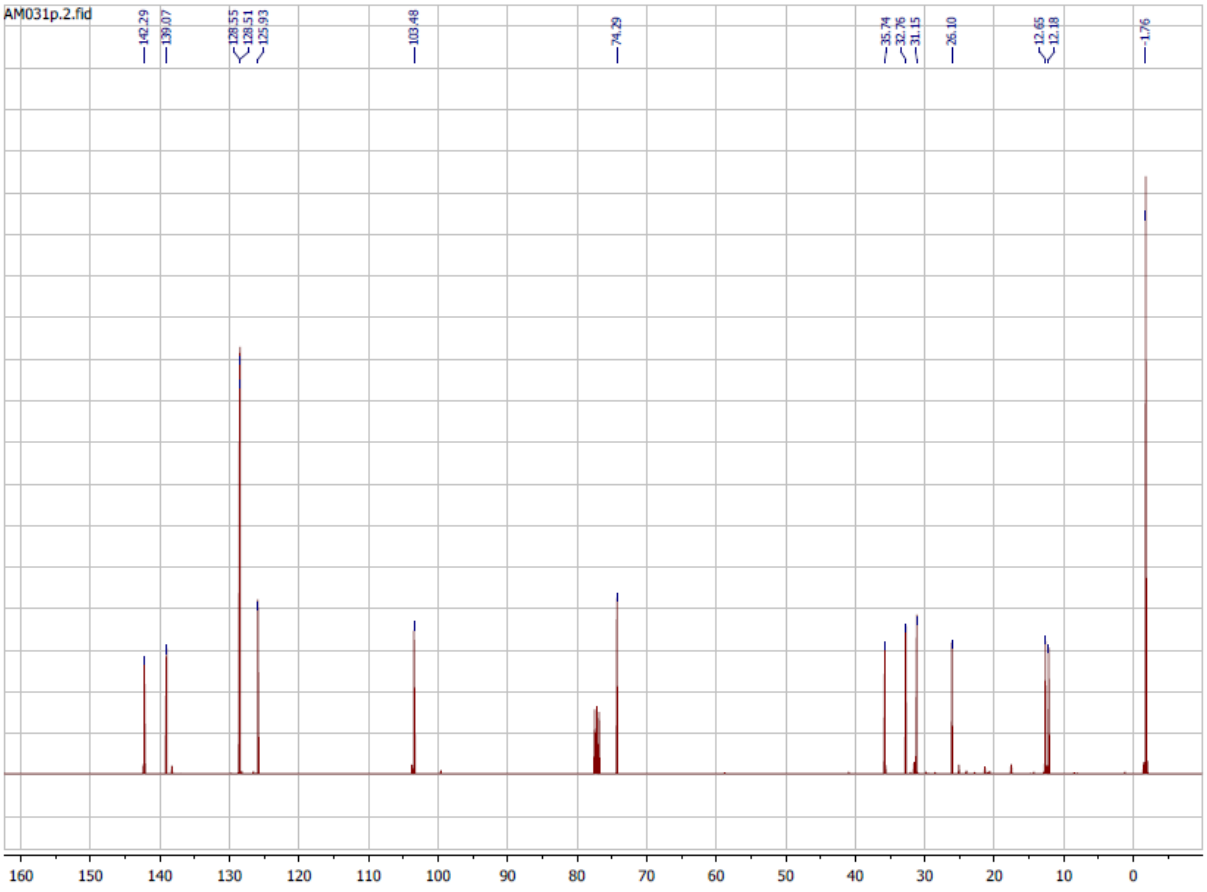


(*R**)-1-((*R**)-2-methylene-1-(2-(trimethylsilyl)ethyl)cyclopropyl)-3-phenylpropan-1-ol (**4n**)

^{1}H NMR (400 MHz, $CDCl_3$)

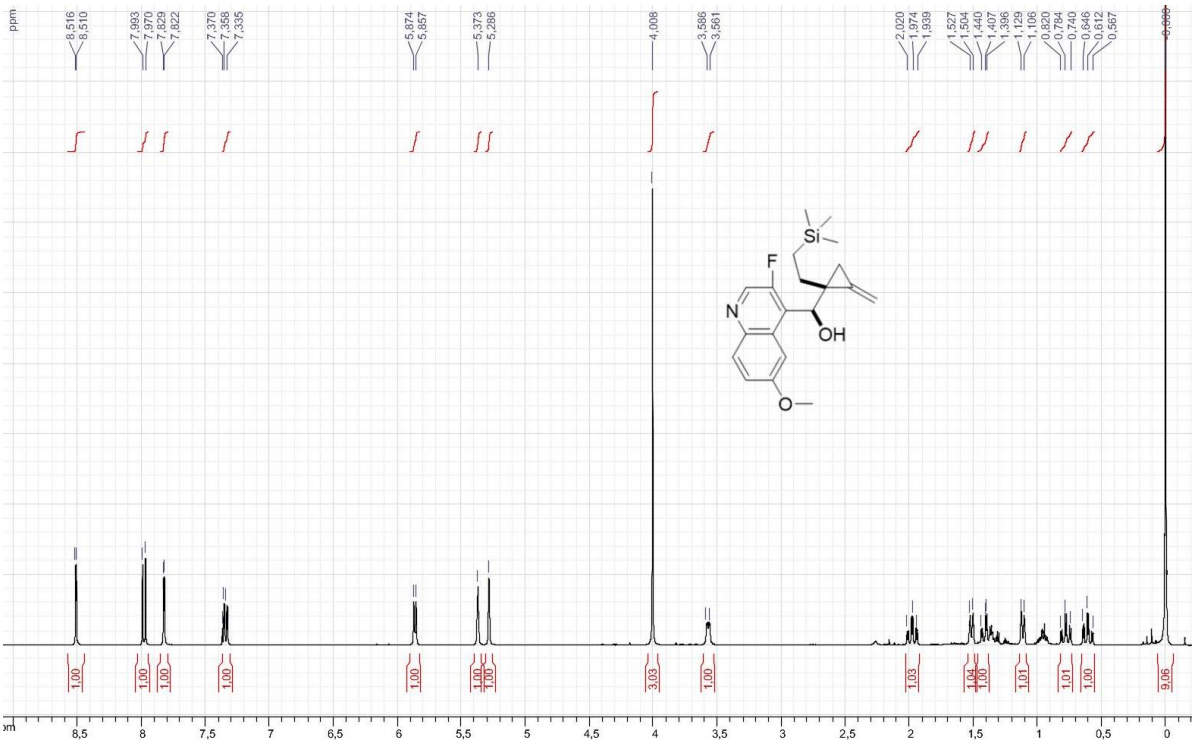


^{13}C NMR (101 MHz, $CDCl_3$)

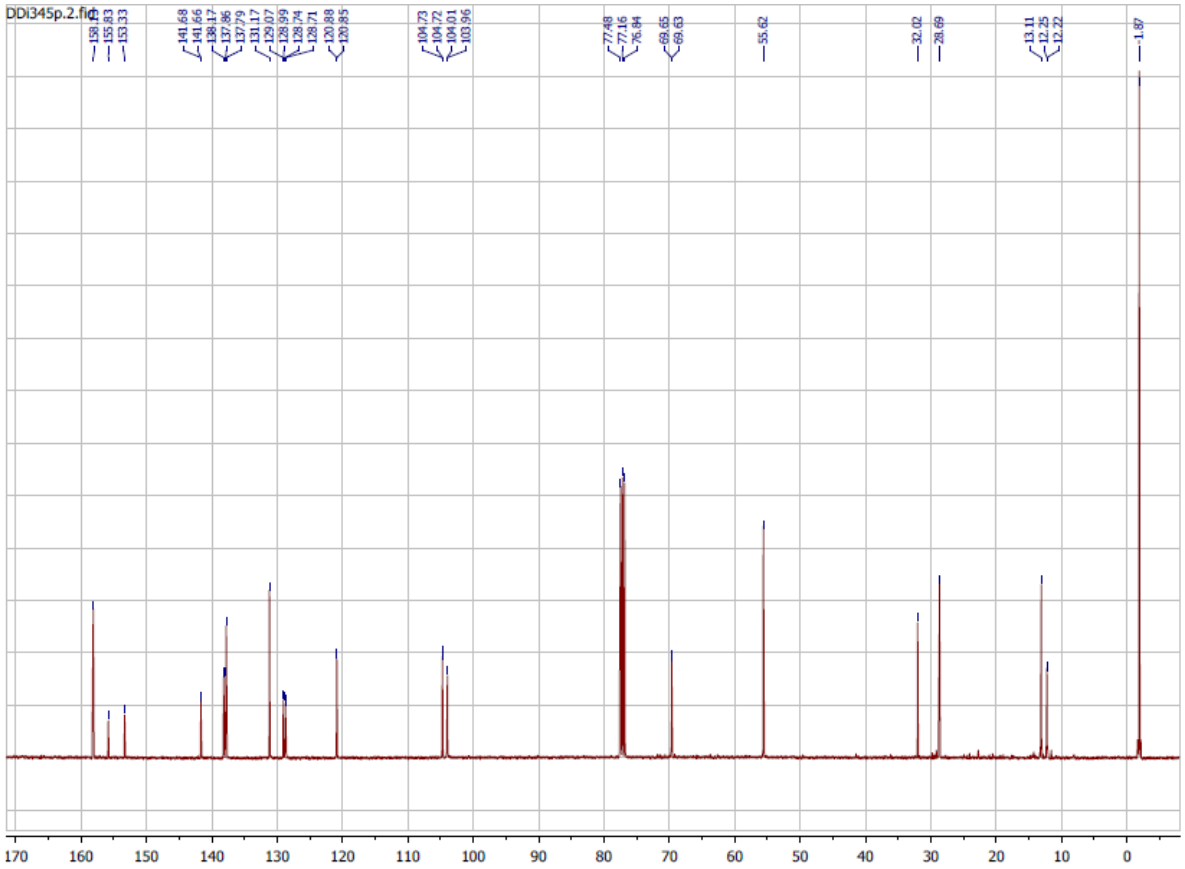


(*S**)-(3-fluoro-6-methoxyquinolin-4-yl)((*R**)-2-methylene-1-(2-(trimethylsilyl)ethyl)-cyclopropyl)methanol (**4o**)

^{1}H NMR (400 MHz, $CDCl_3$)

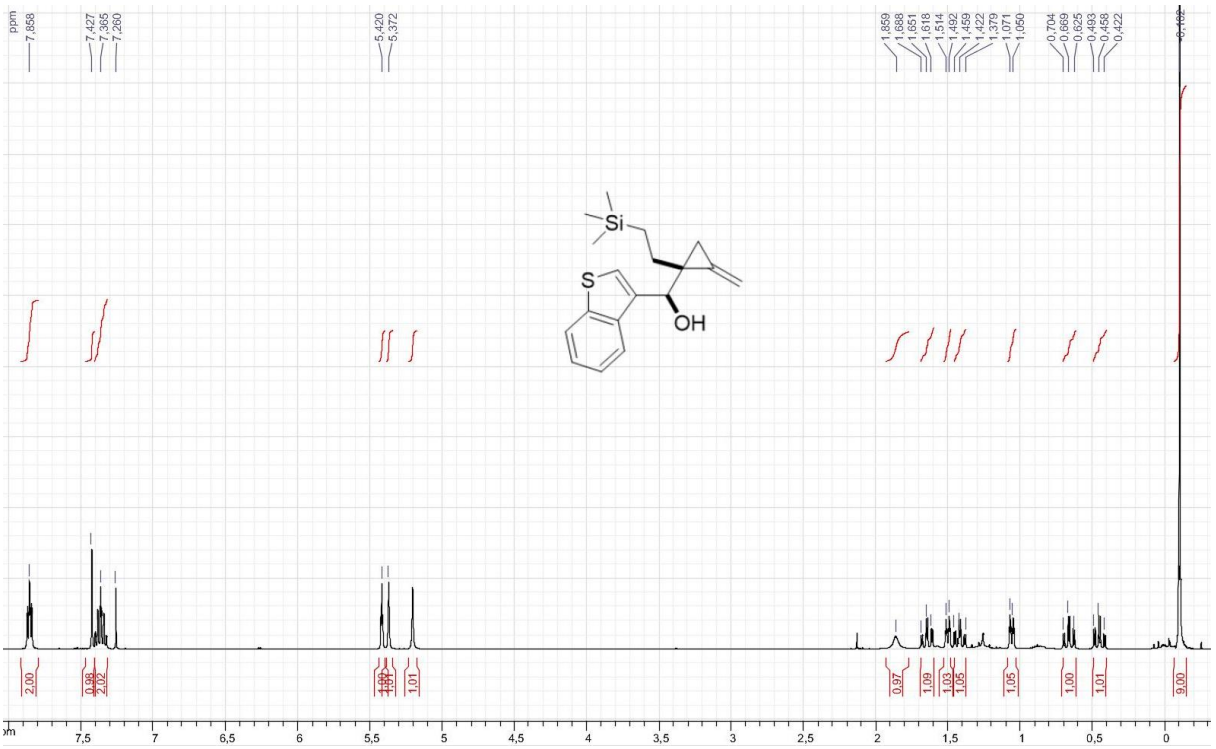


^{13}C NMR (101 MHz, $CDCl_3$)

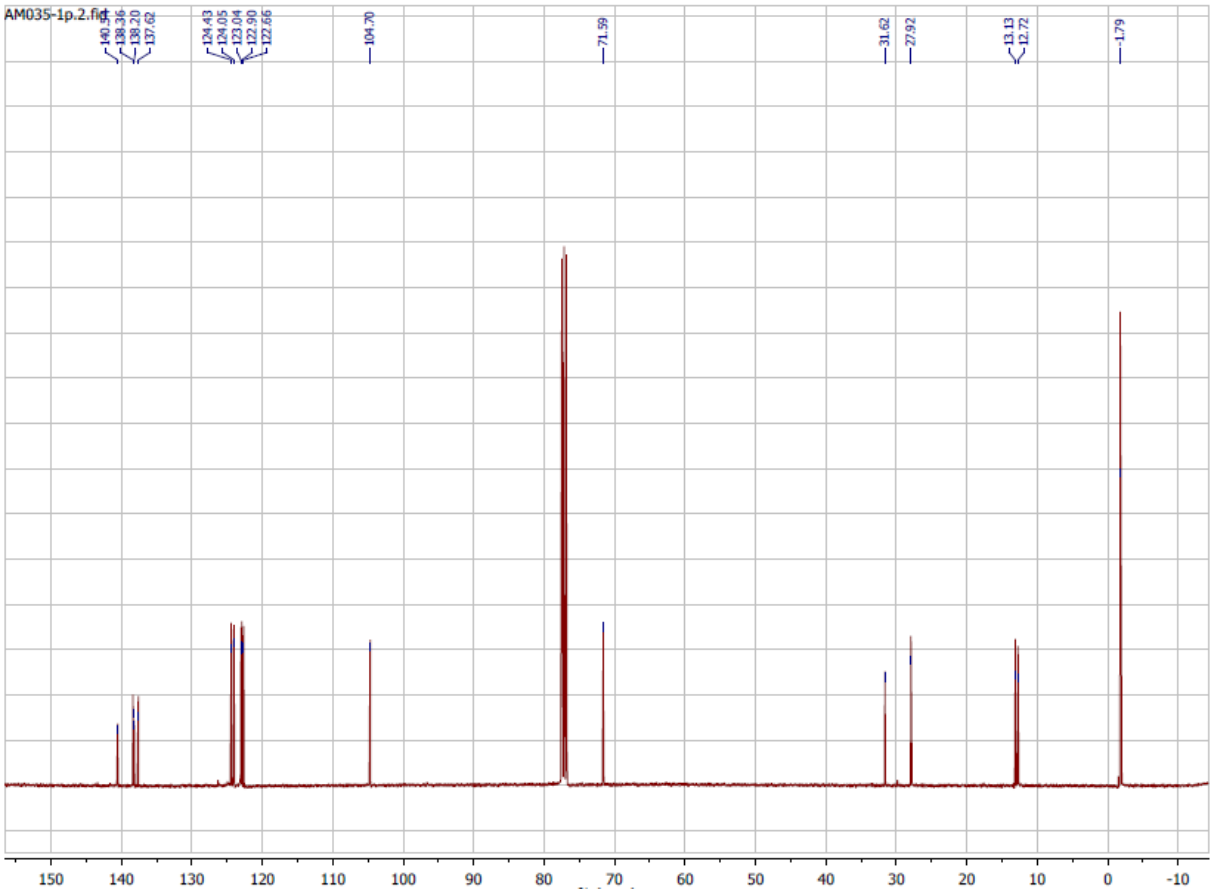


(*S**)-benzo[b]thiophen-3-yl((*R**)-2-methylene-1-(2-(trimethylsilyl)ethyl)cyclopropyl)methanol (**4p**)

^{1}H NMR (400 MHz, $CDCl_3$)

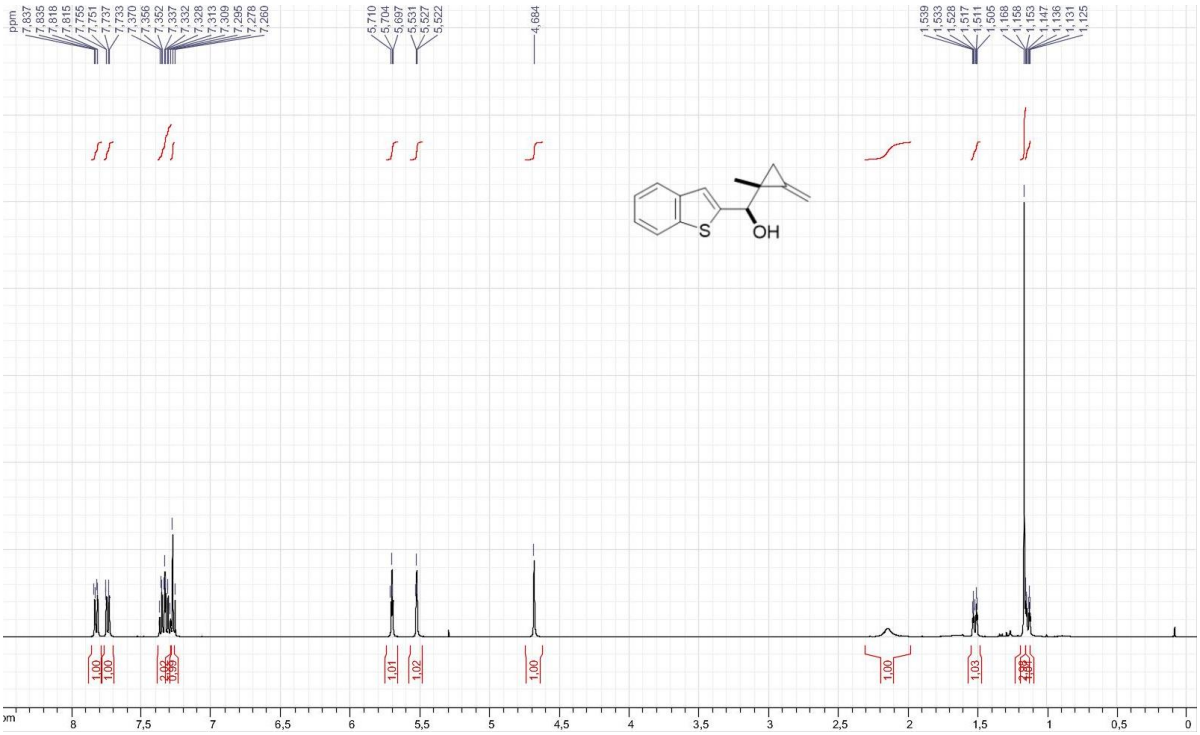


^{13}C NMR (101 MHz, $CDCl_3$)

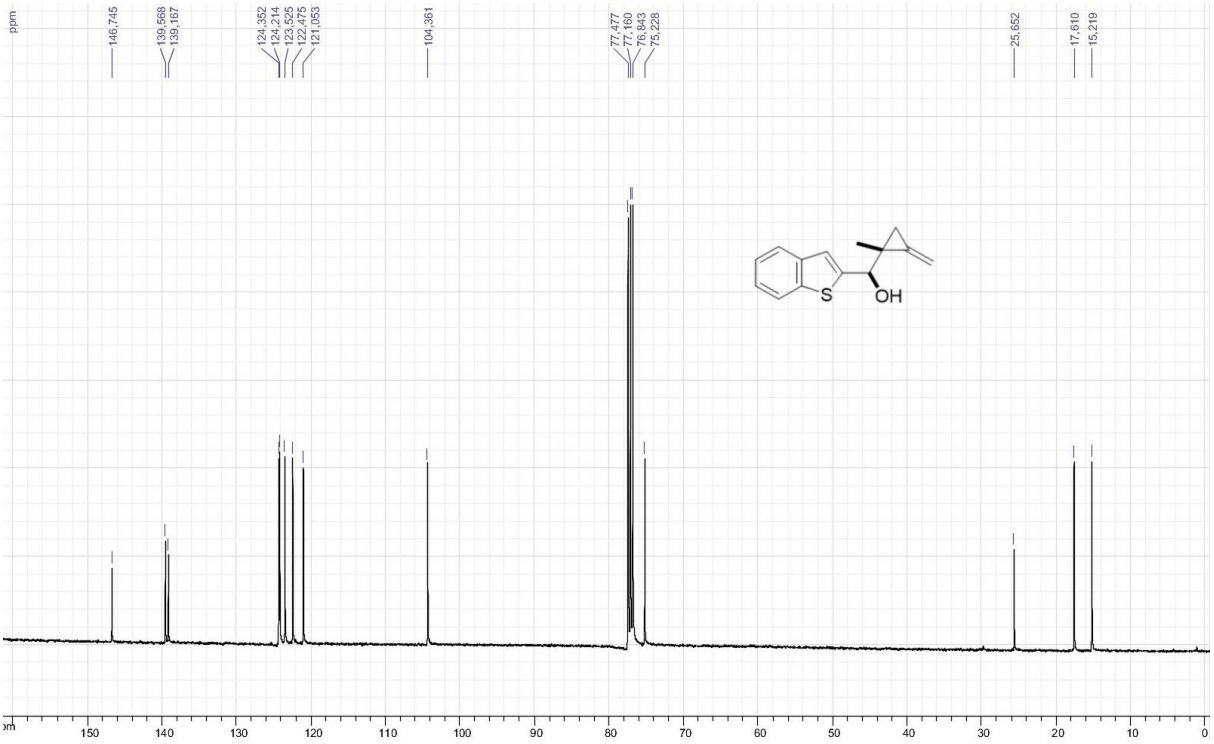


(*S**)-benzo[b]thiophen-2-yl((*R**)-1-methyl-2-methylenecyclopropyl)methanol (***syn*-4q**)

^{1}H NMR (400 MHz, $CDCl_3$)

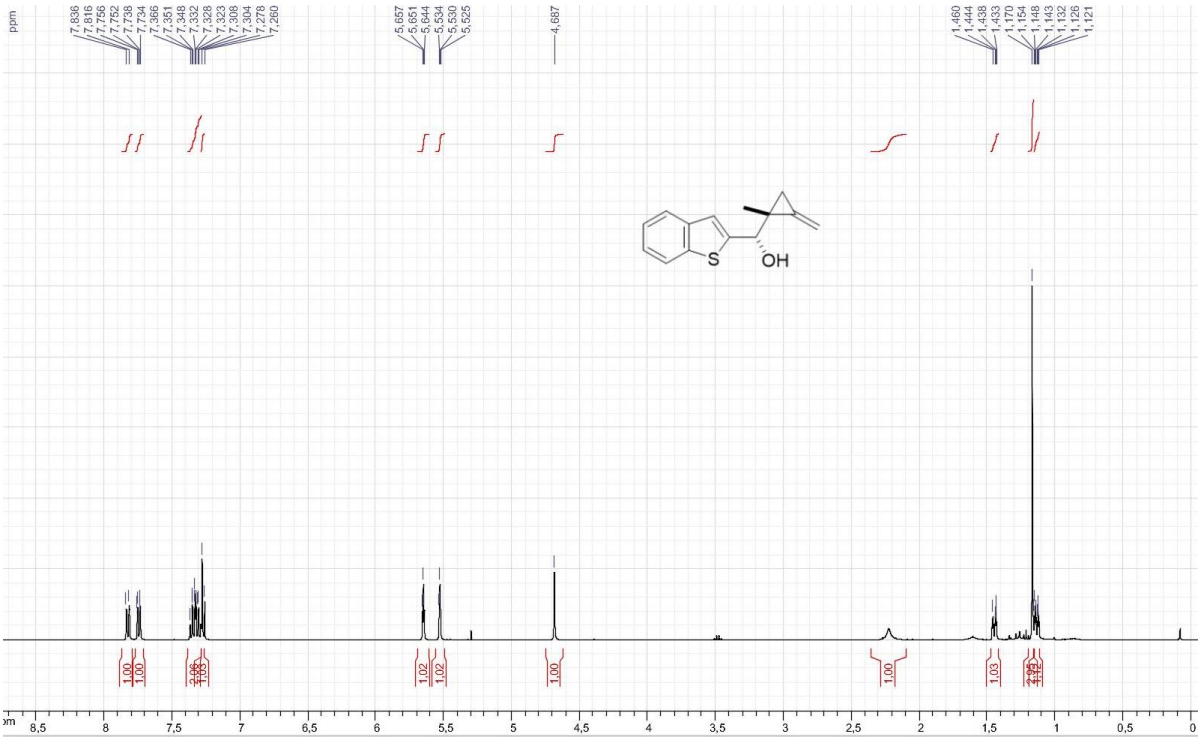


^{13}C NMR (101 MHz, $CDCl_3$)

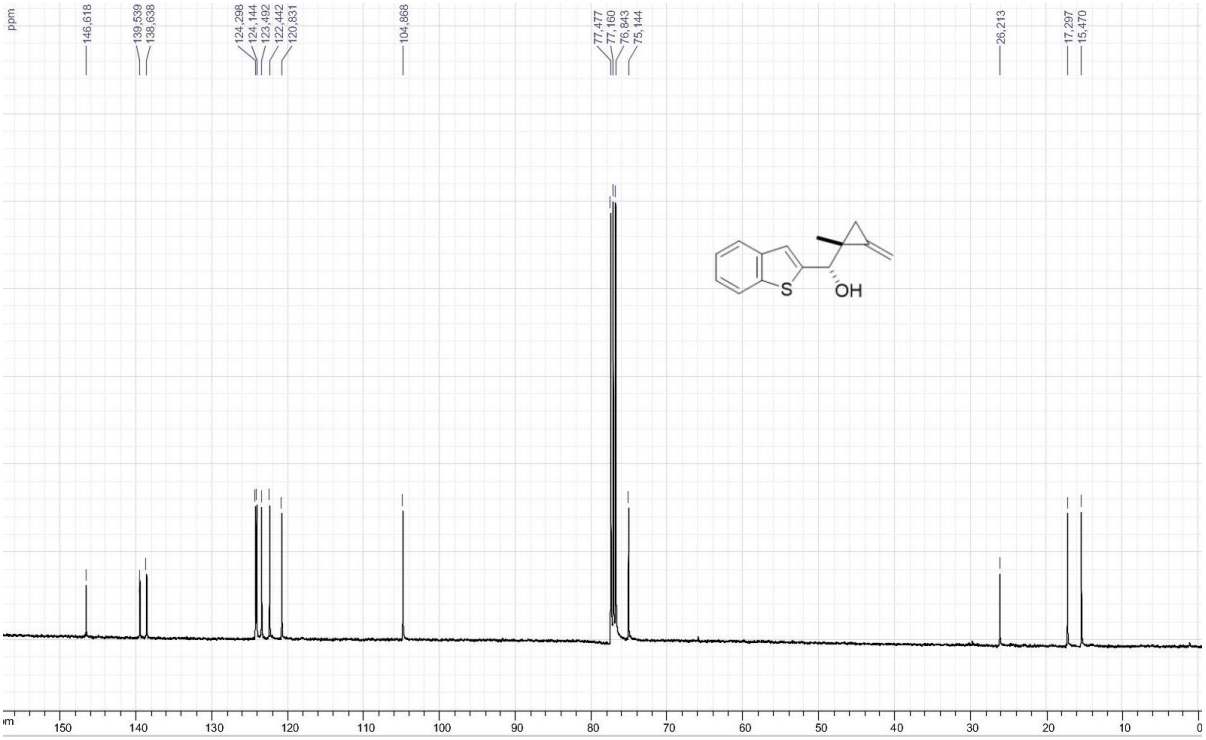


(*S**)-benzo[b]thiophen-2-yl((*S**)-1-methyl-2-methylenecyclopropyl)methanol (***anti*-4q**)

^{1}H NMR (400 MHz, $CDCl_3$)

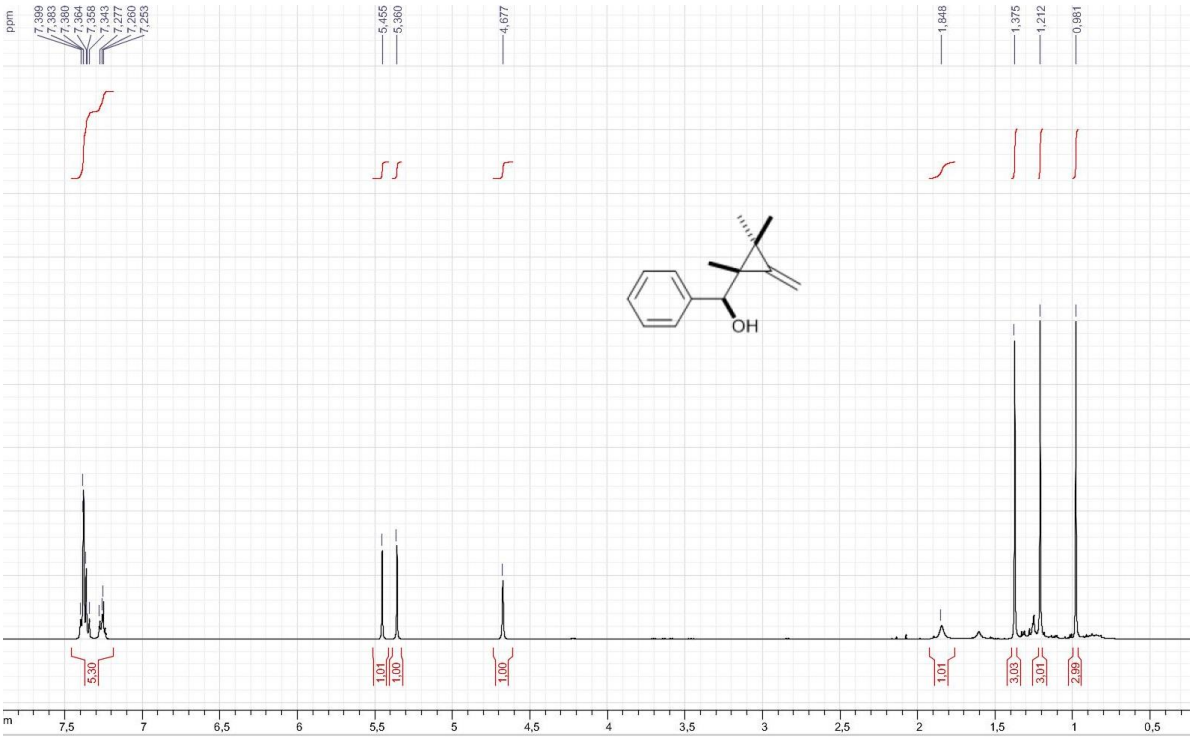


^{13}C NMR (101 MHz, $CDCl_3$)

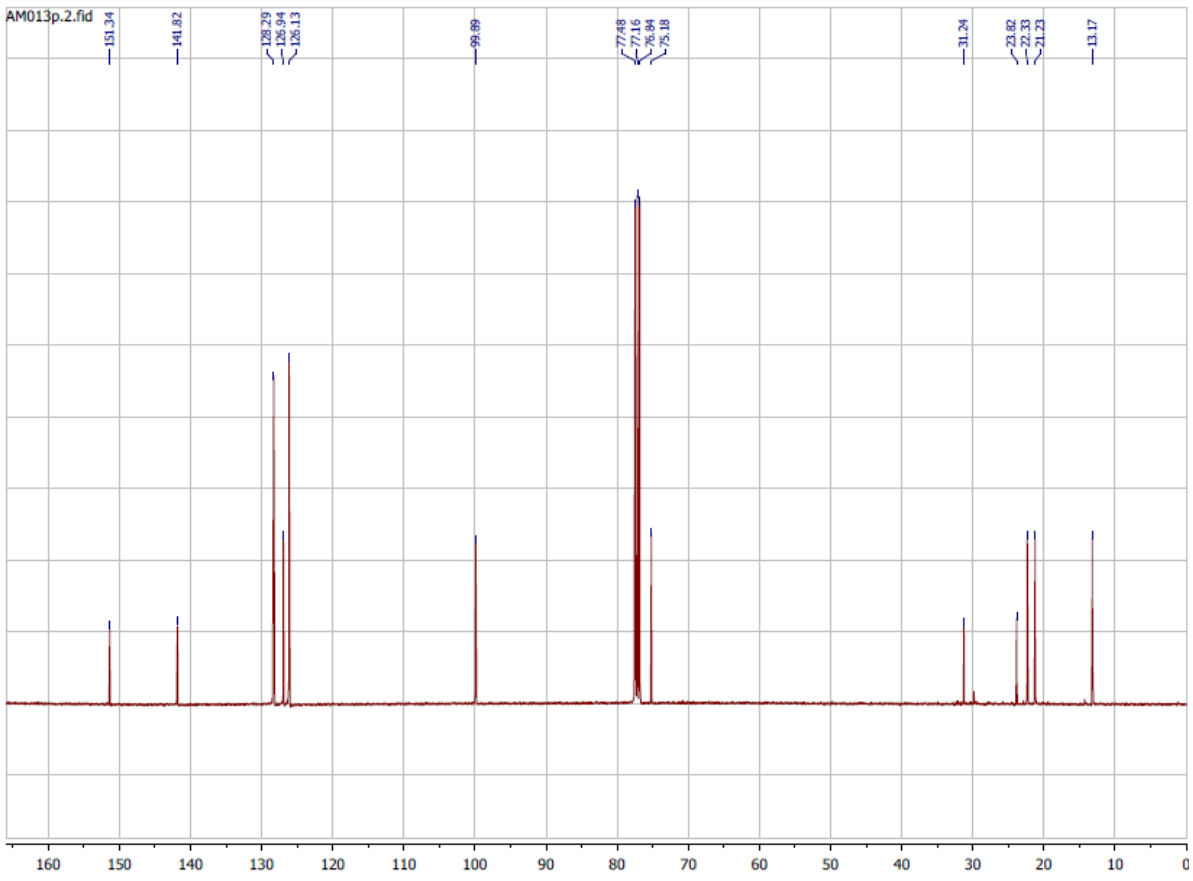


(*R**)-phenyl((*S**)-1,2,2-trimethyl-3-methylenecyclopropyl)methanol (**5a**)

^{1}H NMR (400 MHz, $CDCl_3$)

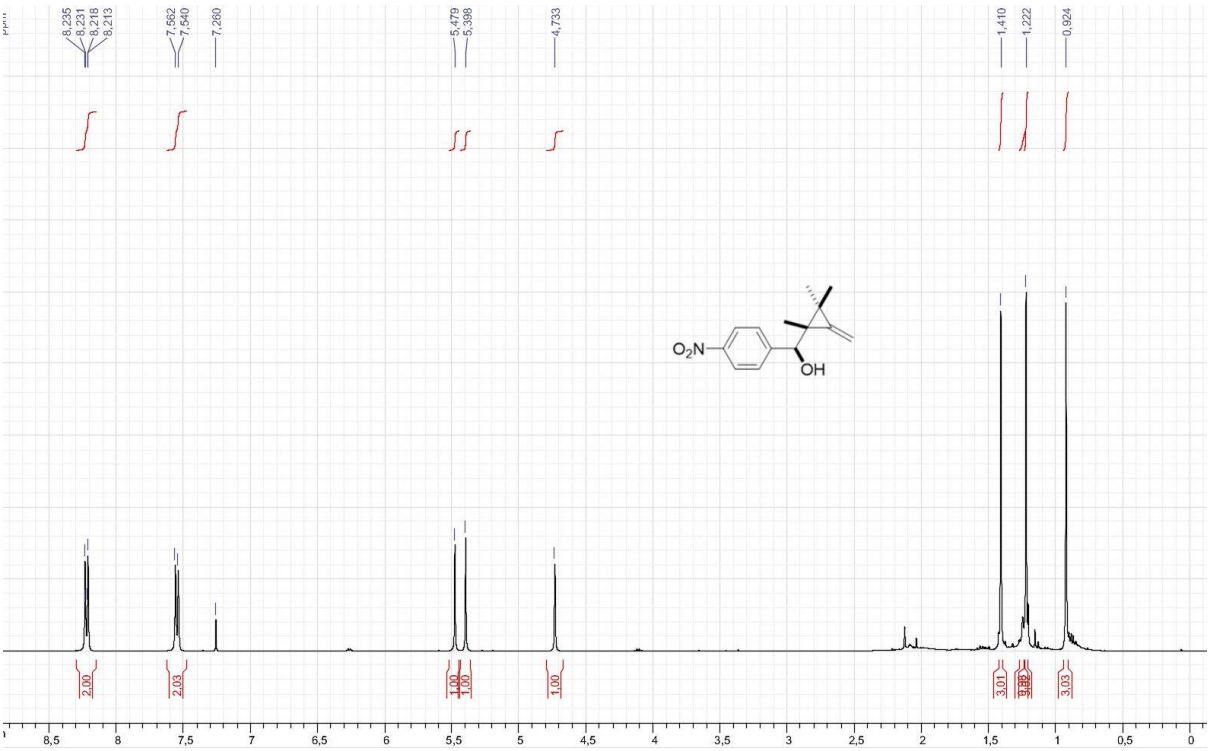


^{13}C NMR (101 MHz, $CDCl_3$)

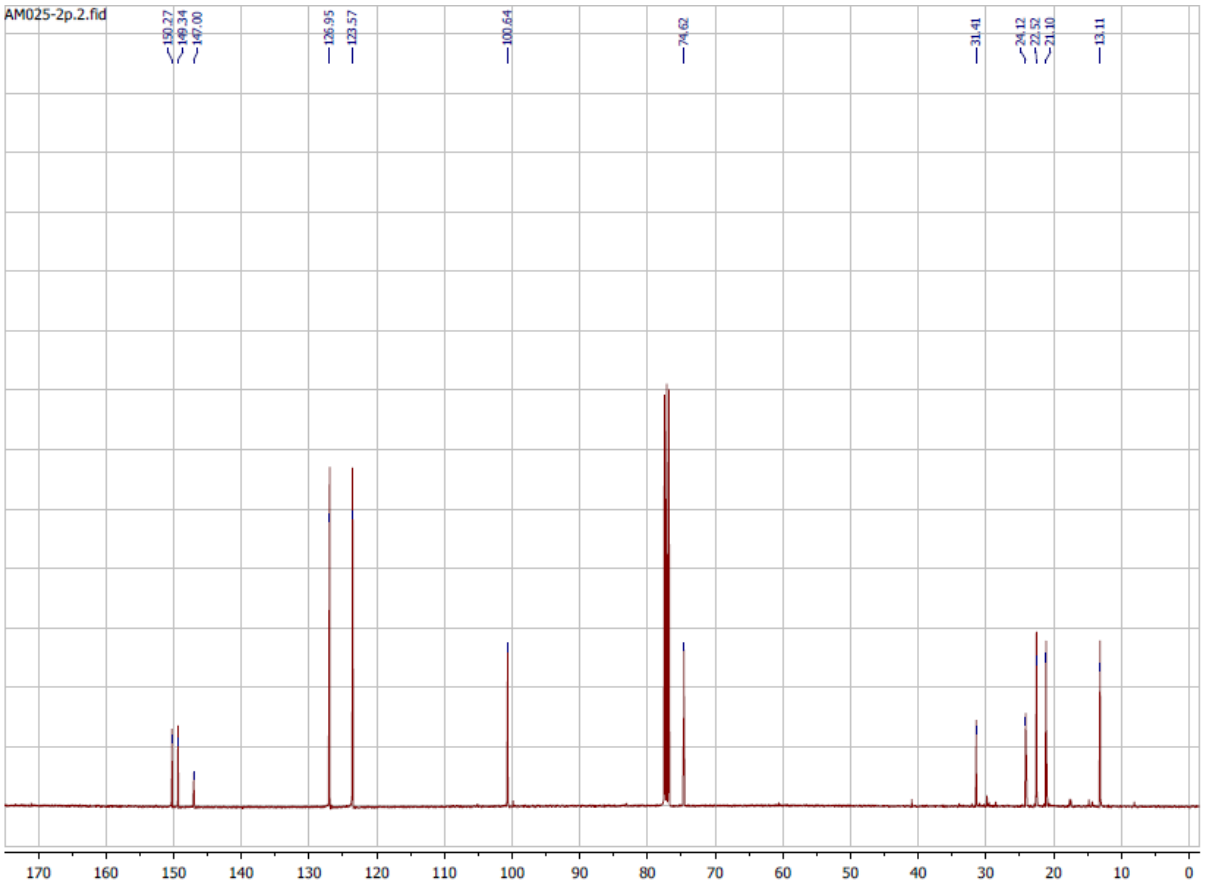


(*R**)-(4-nitrophenyl)((*S**)-1,2,2-trimethyl-3-methylenecyclopropyl)methanol (**5b**)

^{1}H NMR (400 MHz, $CDCl_3$)

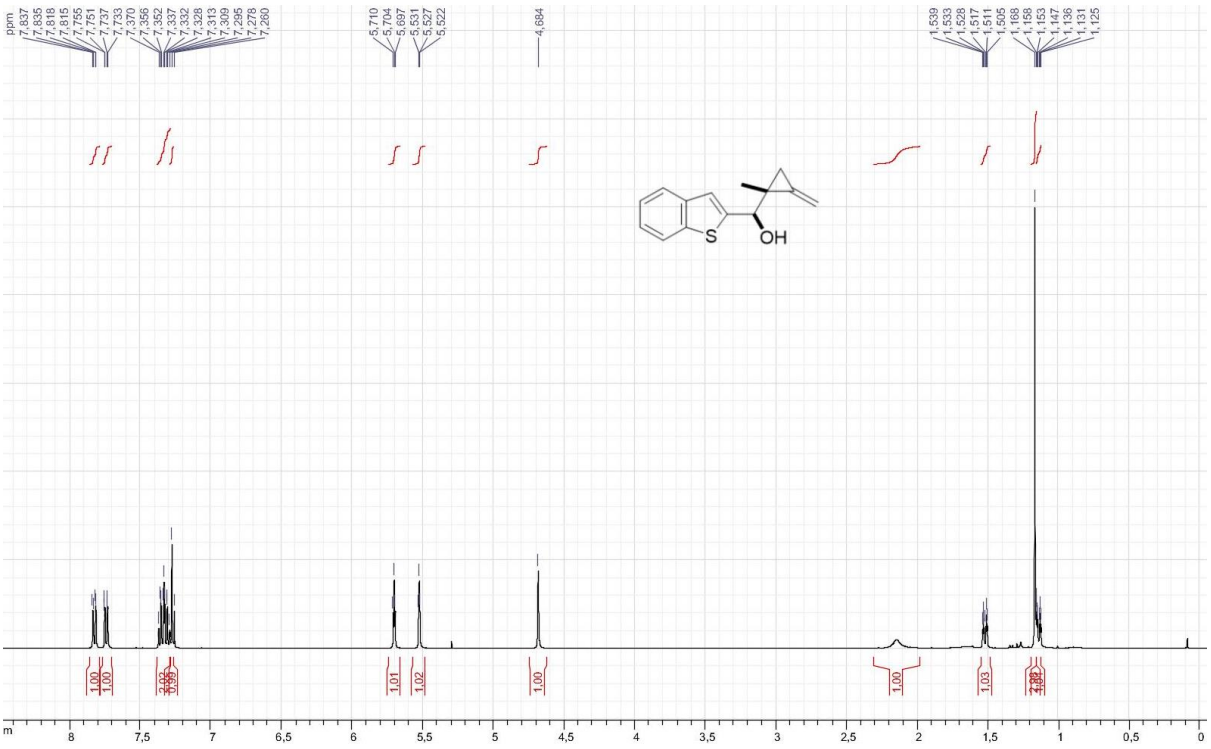


^{13}C NMR (101 MHz, $CDCl_3$)

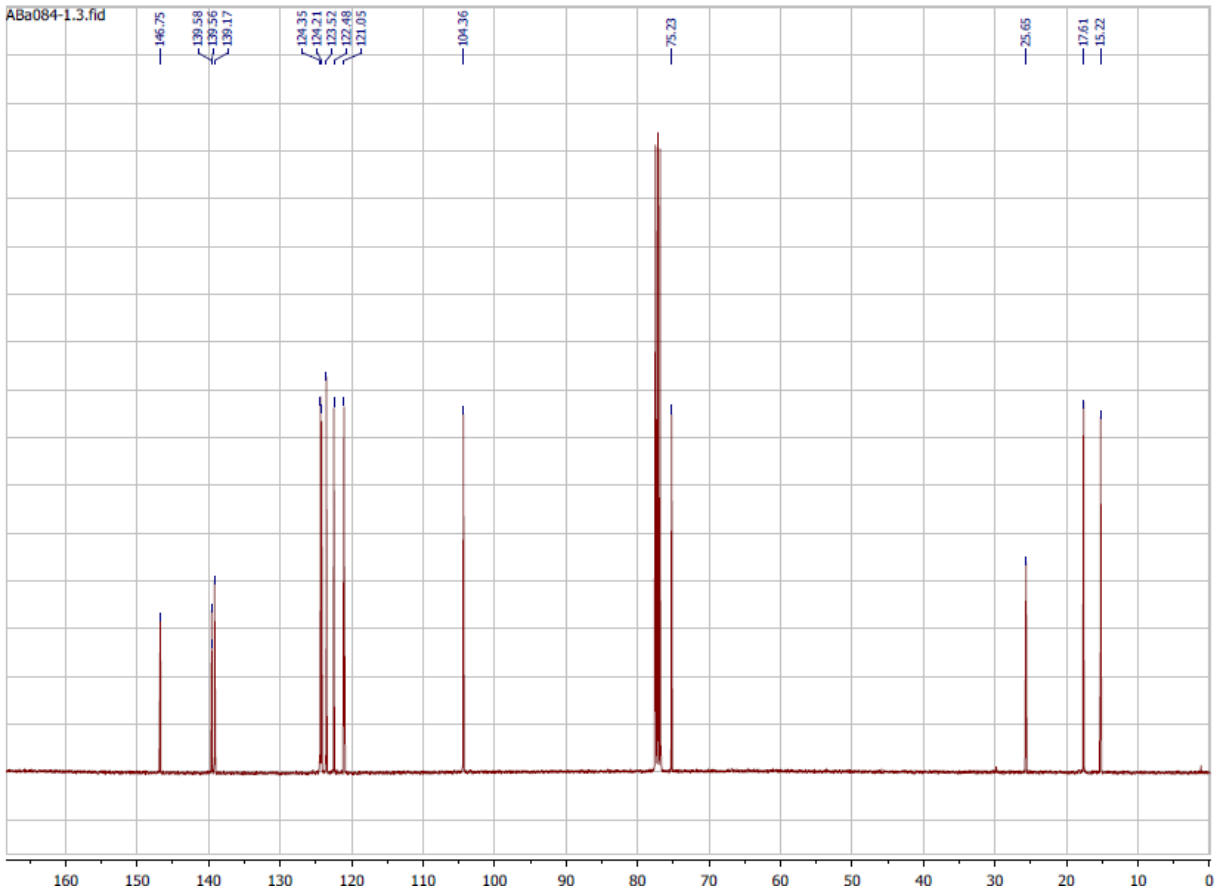


(*R*)-((*R*)-2-methylene-1-phenylcyclopropyl)(phenyl)methanol (***syn*-4q**)

^{1}H NMR (400 MHz, $CDCl_3$)

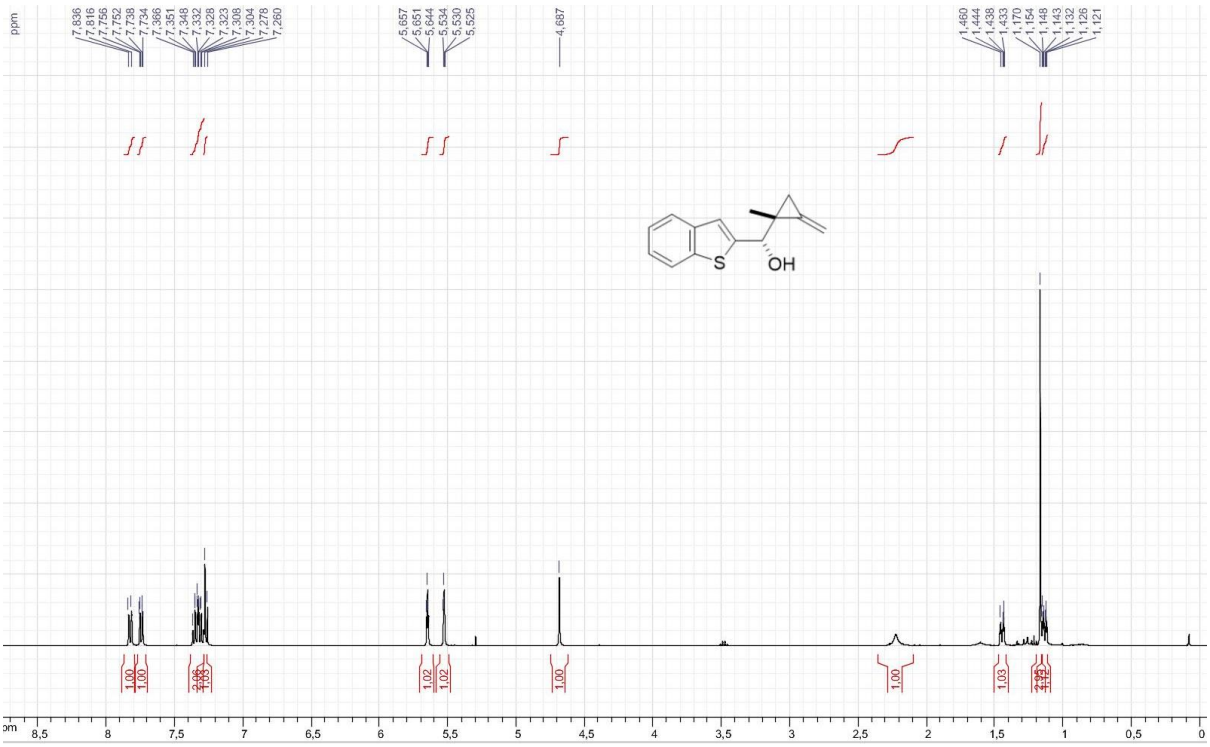


^{13}C NMR (101 MHz, $CDCl_3$)

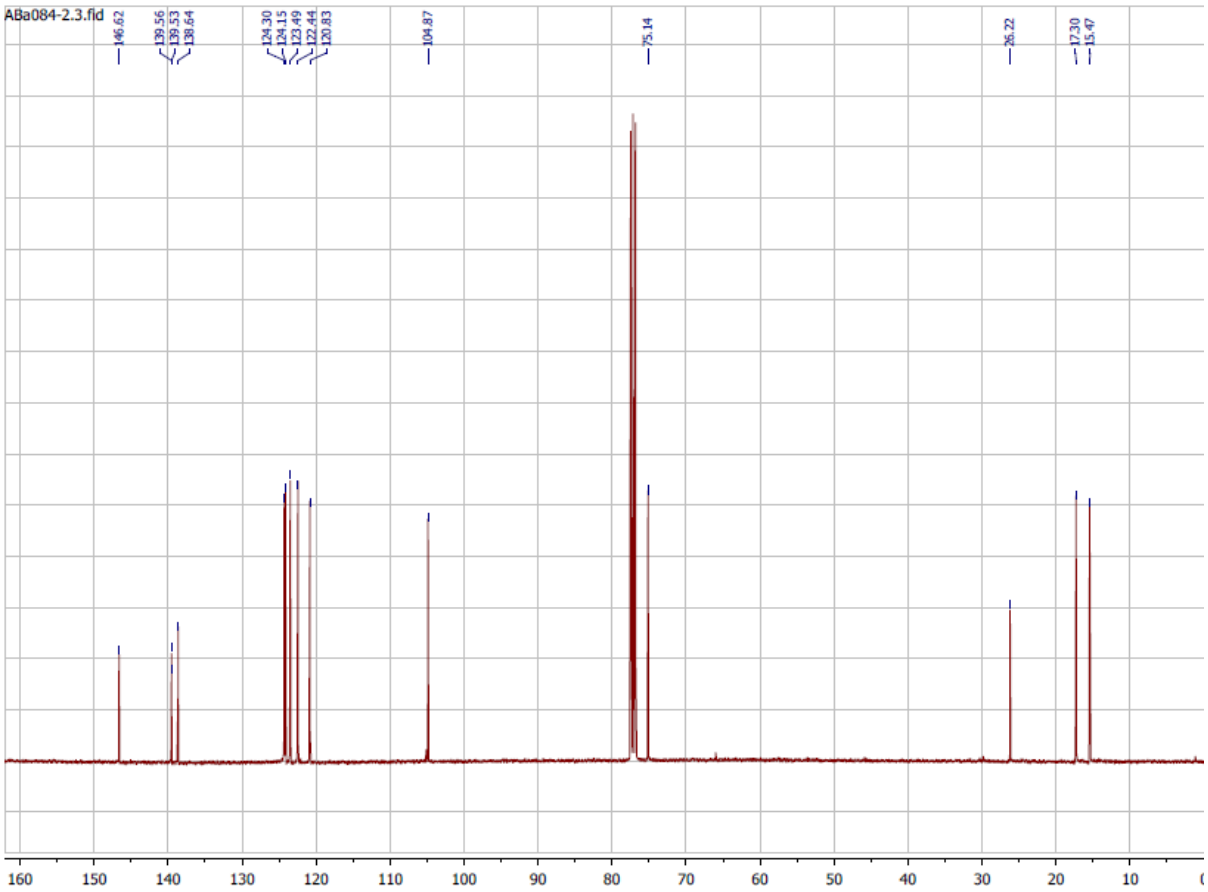


(*R*)-((*S*)-2-methylene-1-phenylcyclopropyl)(phenyl)methanol (***anti*-4q**)

^{1}H NMR (400 MHz, $CDCl_3$)

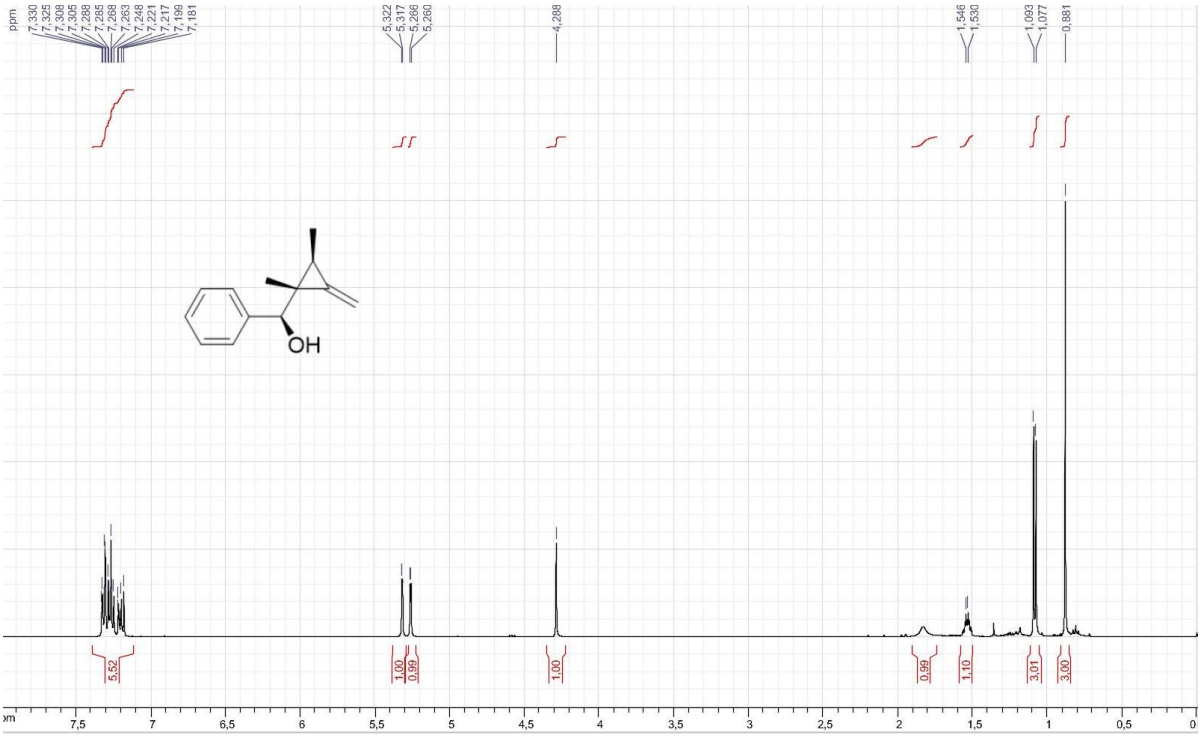


^{13}C NMR (101 MHz, $CDCl_3$)

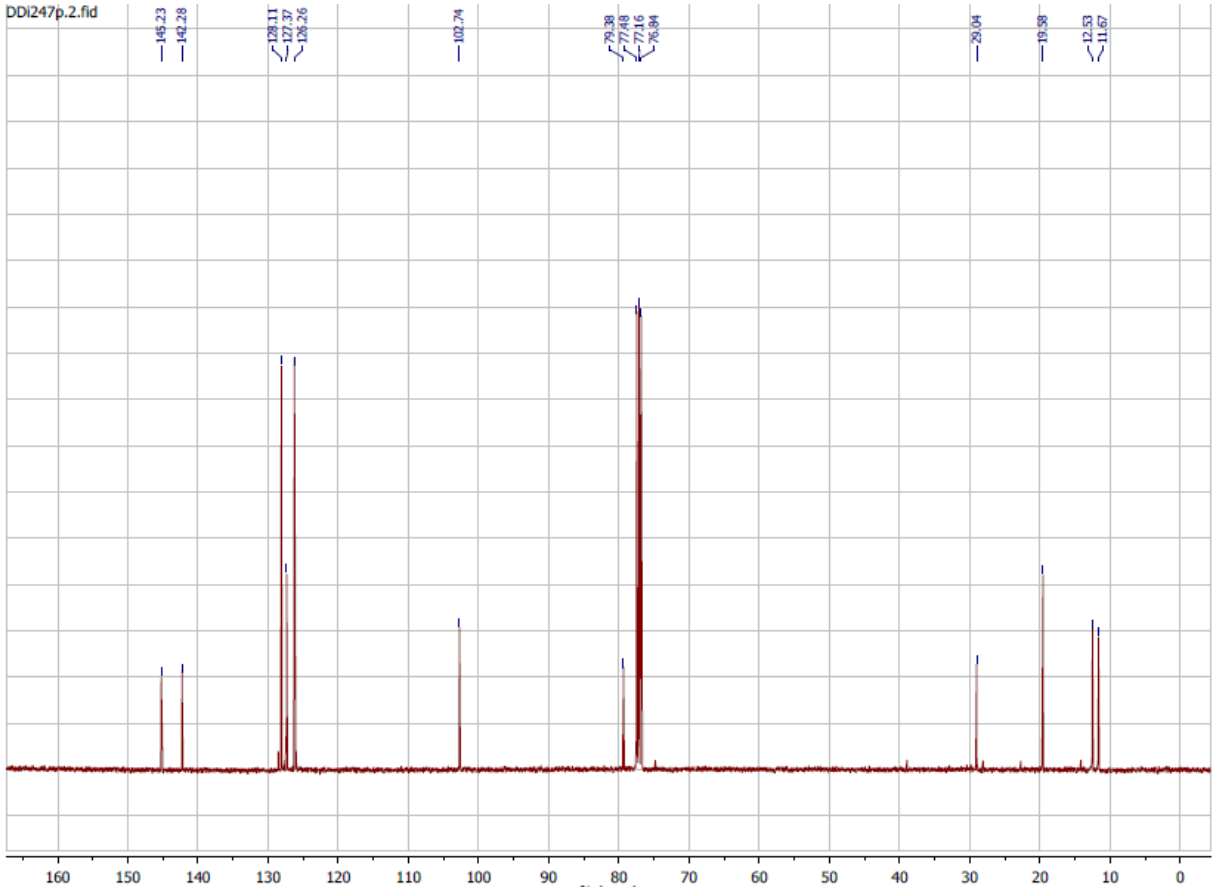


(*R**)-((1*S**,2*R**)-1,2-dimethyl-3-methylenecyclopropyl)(phenyl)methanol (**7a**)

^{1}H NMR (400 MHz, $CDCl_3$)

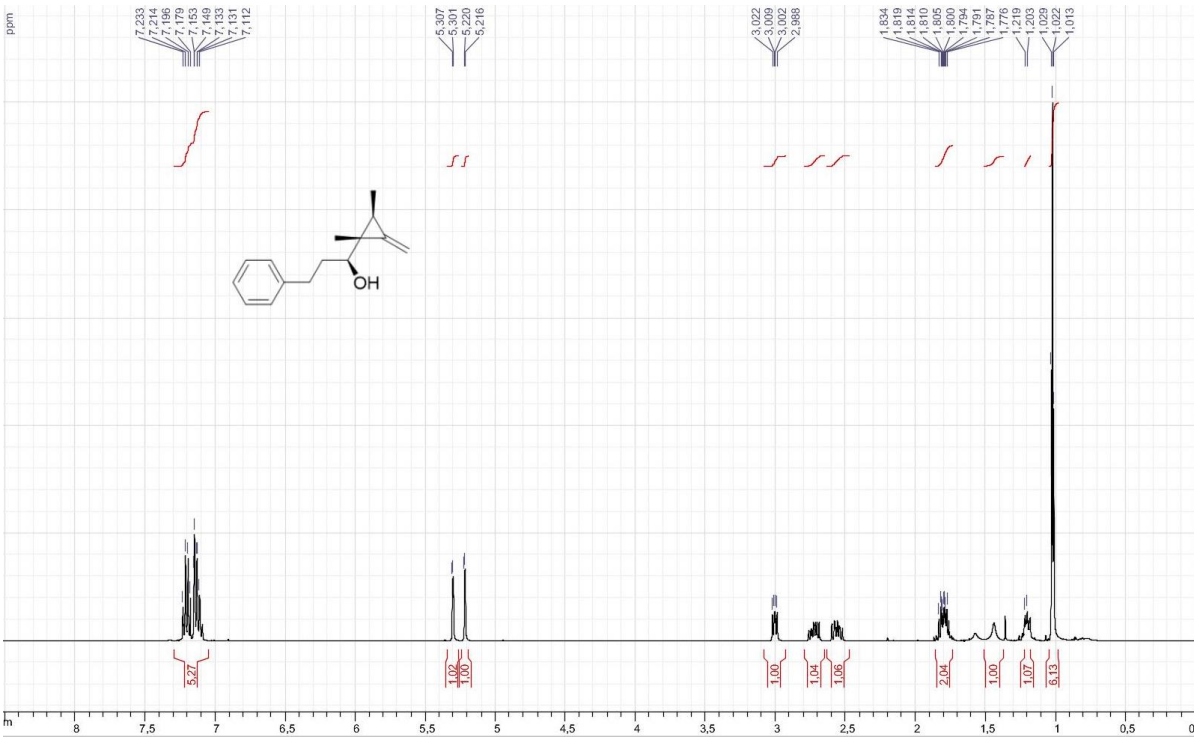


^{13}C NMR (101 MHz, $CDCl_3$)

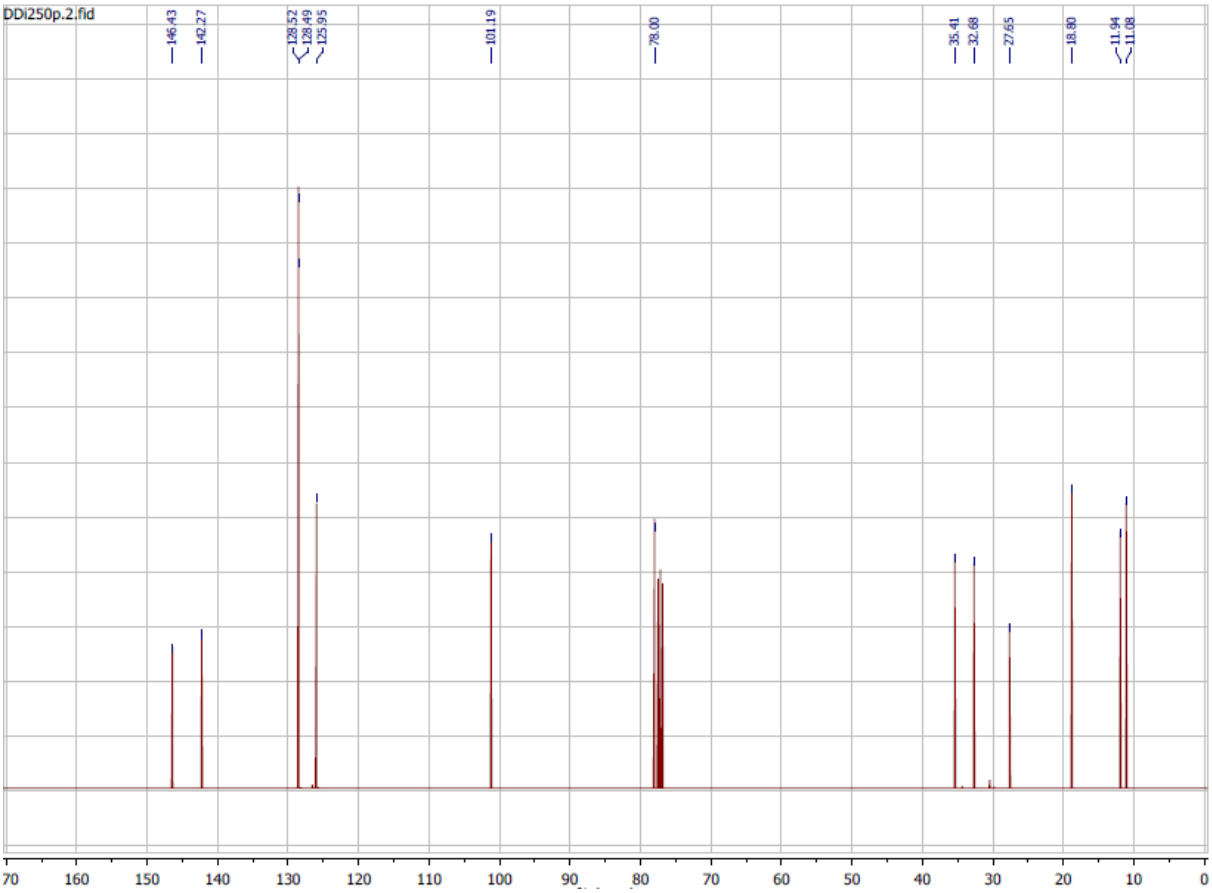


(*R**)-1-((1*S**,2*R**)-1,2-dimethyl-3-methylenecyclopropyl)-3-phenylpropan-1-ol (**7b**)

^{1}H NMR (400 MHz, $CDCl_3$)

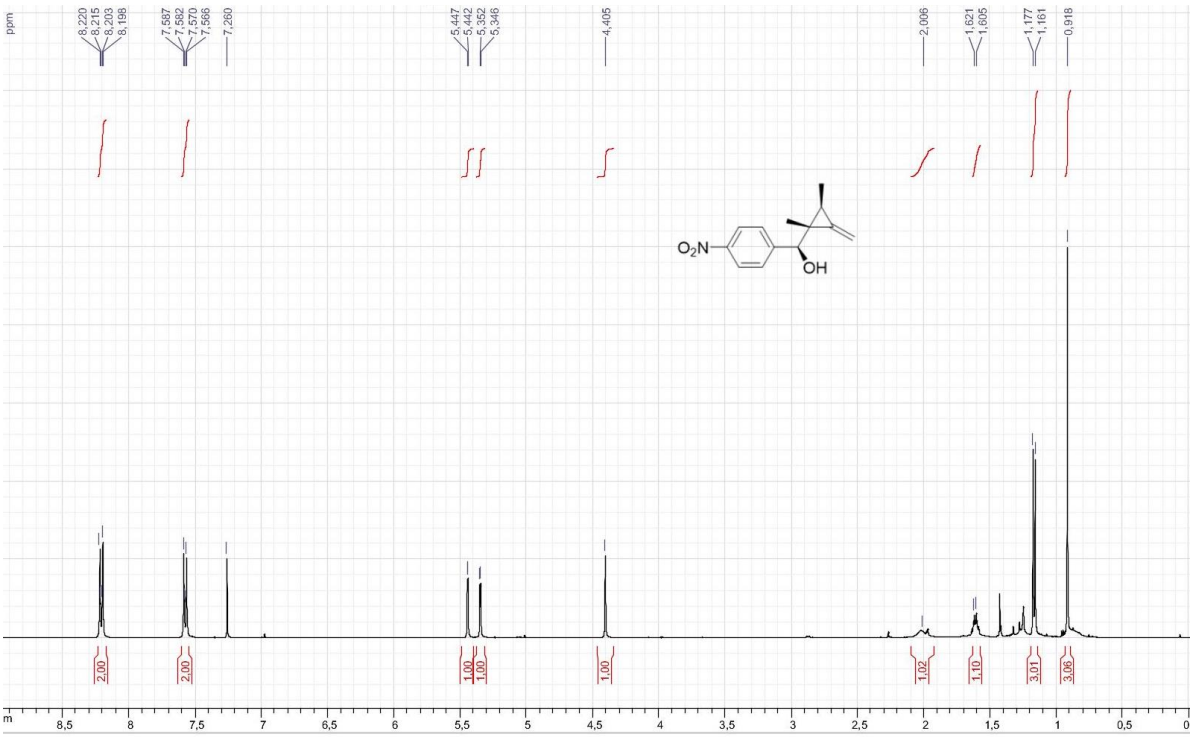


^{13}C NMR (101 MHz, $CDCl_3$)

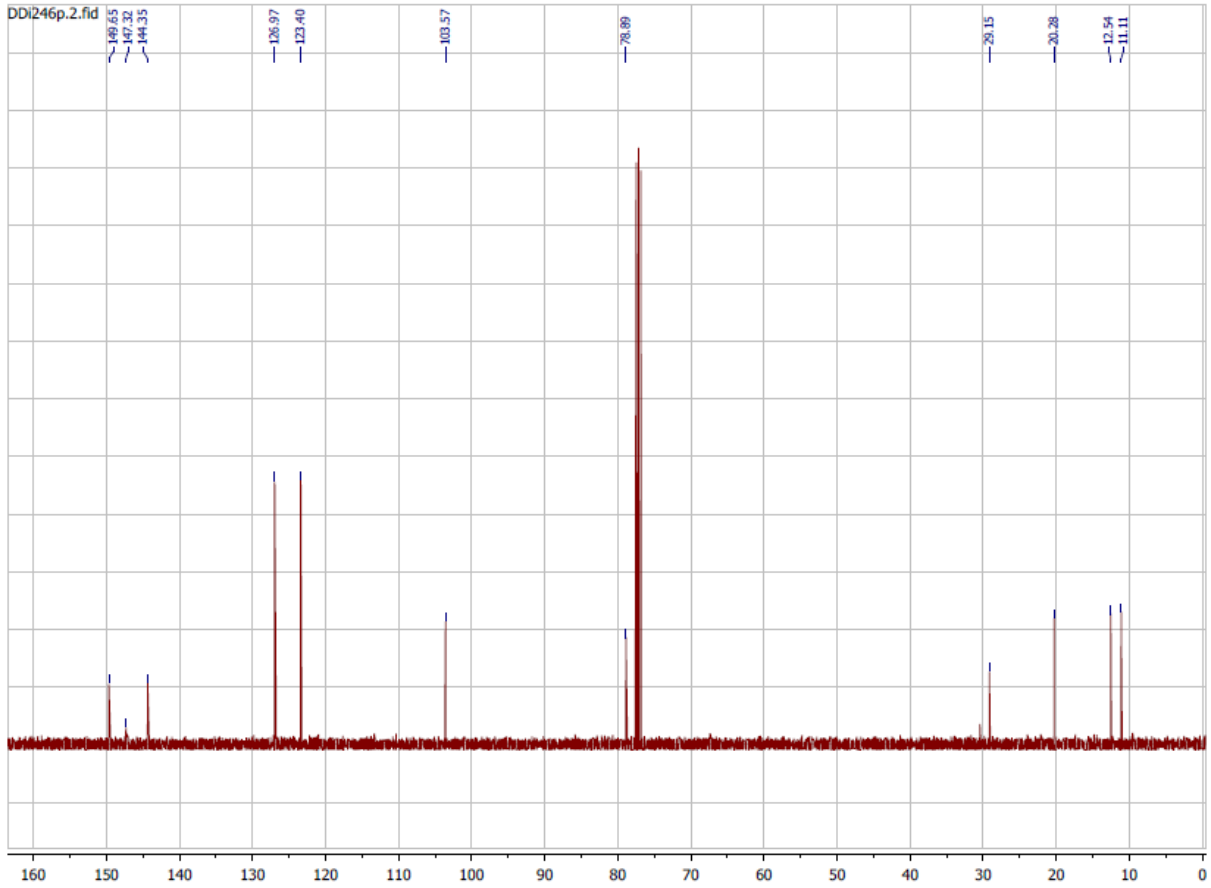


(*R**)-((1*S**,2*R**)-1,2-dimethyl-3-methylenecyclopropyl)(4-nitrophenyl)methanol (**7c**)

^{1}H NMR (400 MHz, $CDCl_3$)

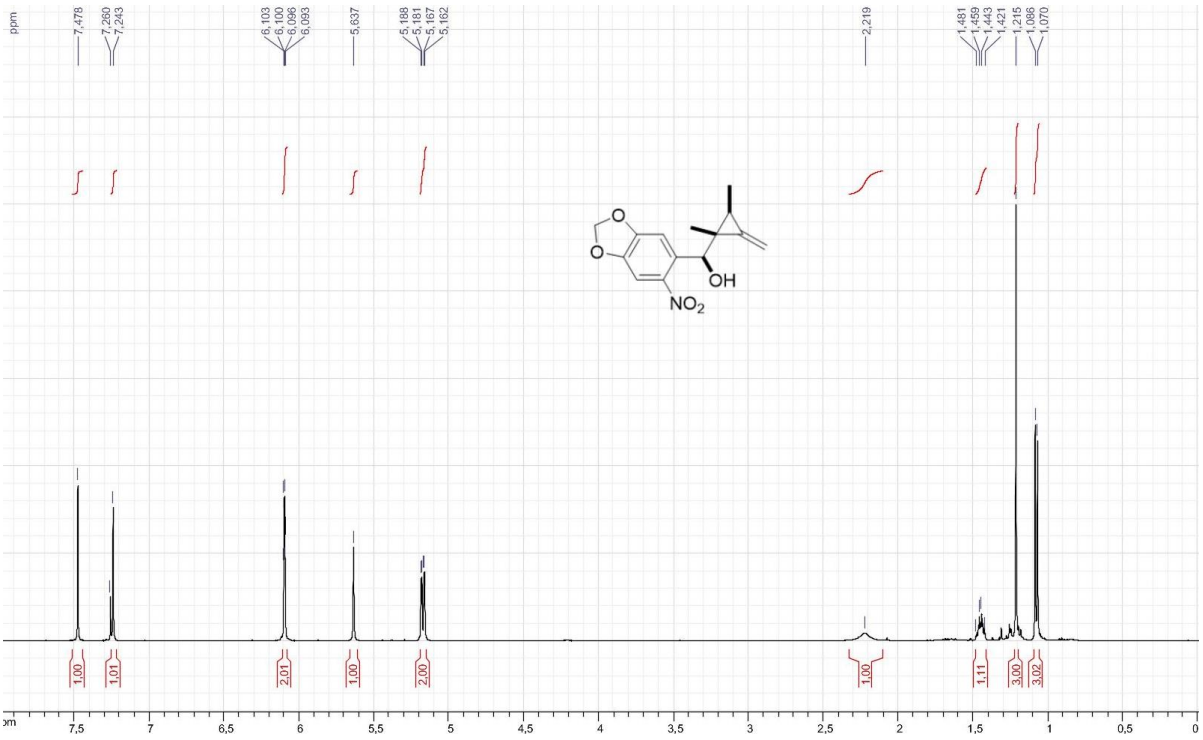


^{13}C NMR (101 MHz, $CDCl_3$)

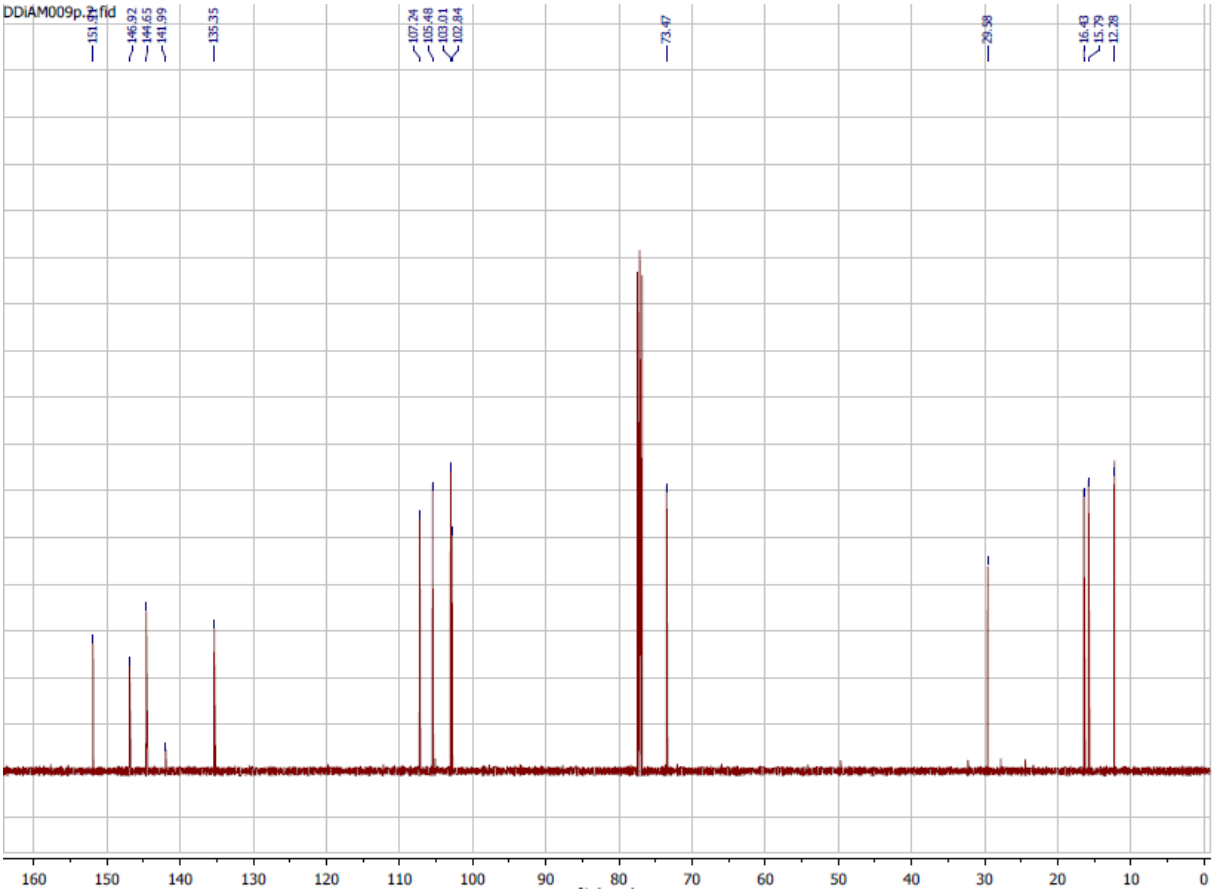


(*S**)-((1*S**,2*R**)-1,2-dimethyl-3-methylenecyclopropyl)(6-nitrobenzo[d][1,3]dioxol-5-yl)methanol (**7d**)

^{1}H NMR (400 MHz, $CDCl_3$)

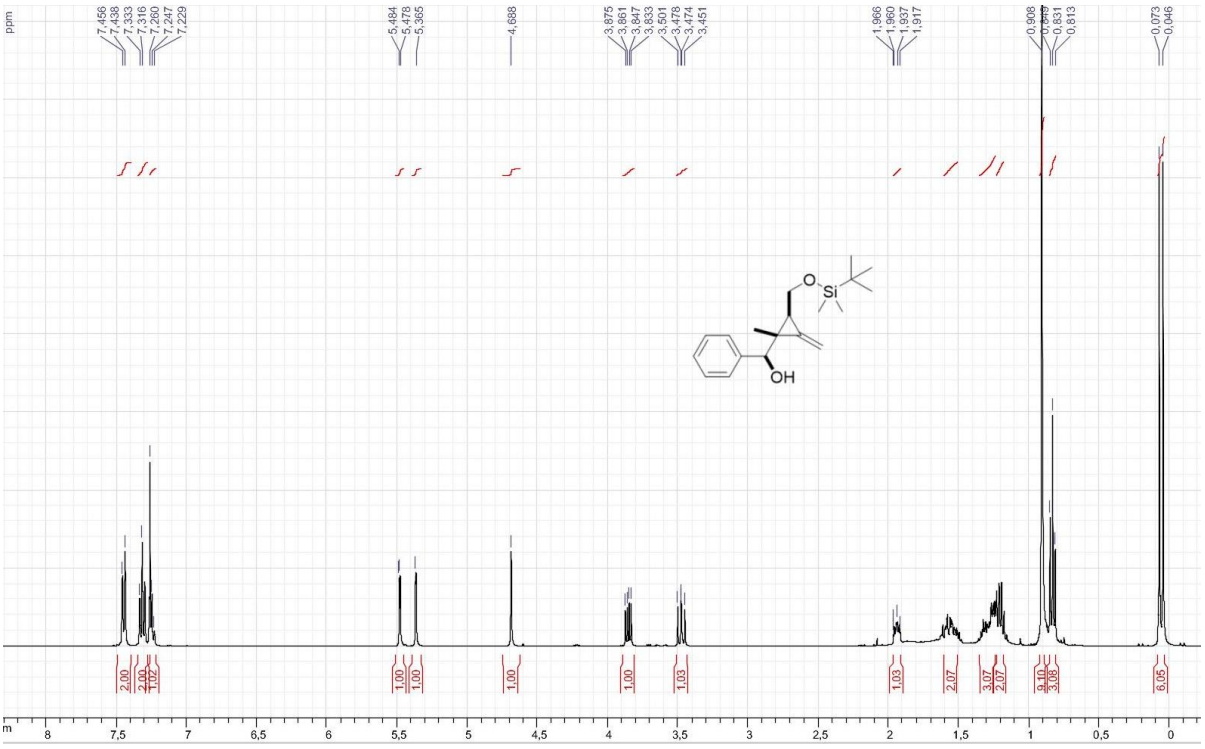


^{13}C NMR (101 MHz, $CDCl_3$)

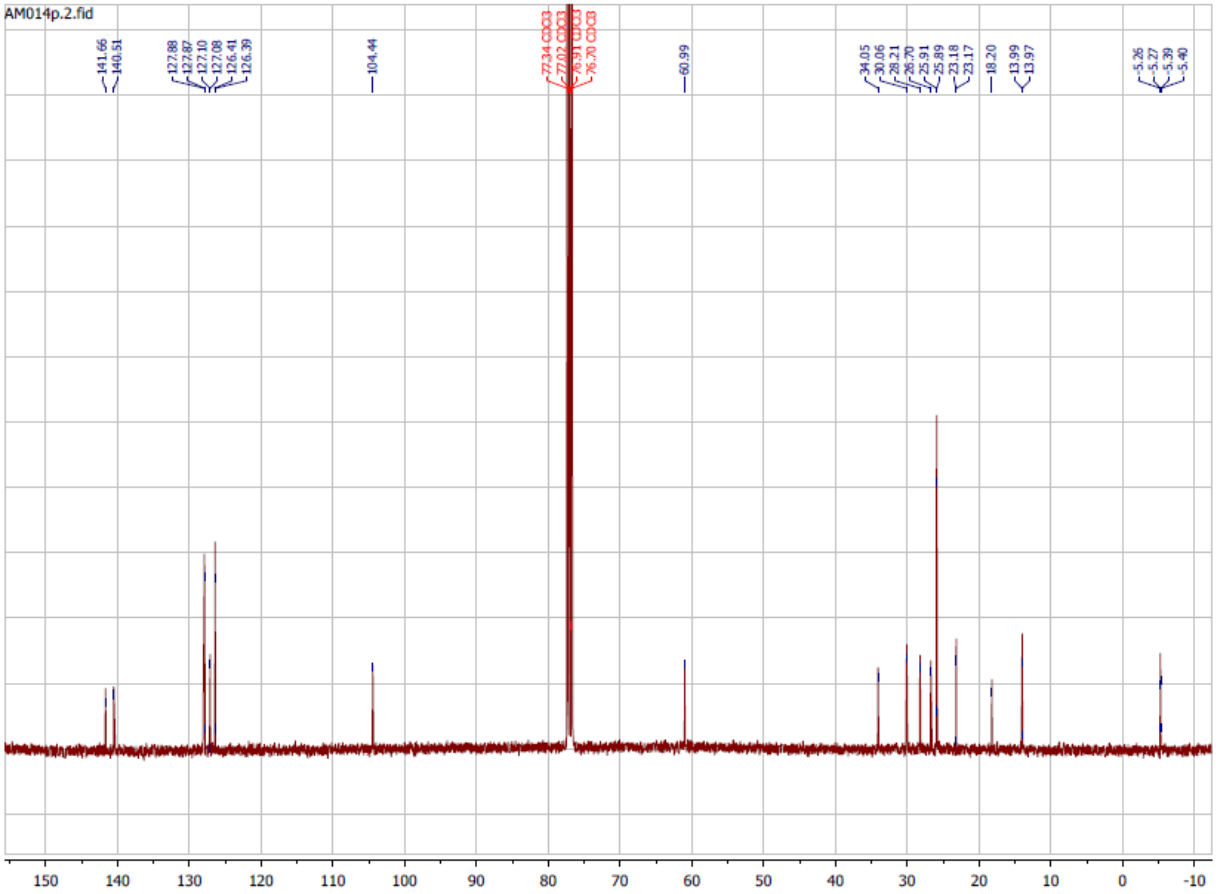


(*S*)-((1R,2S)-1-butyl-2-(((tert-butyldimethylsilyl)oxy)methyl)-3-methylenecyclopropyl)(phenyl)methanol (**9**)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



5. Single Crystal X-Ray Diffraction Studies of 7d

Single crystals of compound **7d**, suitable for X-ray diffraction, were obtained by slow evaporation of dichloromethane solution. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection was performed with an Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-K_α radiation (λ = 0.71071 Å).

Data collection was performed with the CrysAlis CCD software;[a)] CrysAlis RED software[b)] was used for data reduction. Absorption correction using the SCALE3 ABSPACK multiscan method[c)] was applied. The structures were solved with SHELXS-97,[d)] refined with SHELXL-97[e)] and finally checked using PLATON.[f)] Details for data collection and structure refinement are summarized in Table 1.

CCDC- 1439072 contains supplementary crystallographic data for compound **7d** reported in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Details for X-ray data collection and structure refinement for compound **7d**.

	7d
Empirical formula	$C_{14}H_{15}NO_5$
Formula mass	277.27
T[K]	173(2)
Crystal size [mm]	0.39 × 0.28 × 0.26
Crystal description	pale yellow block
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	9.5866(4)
b [Å]	19.5978(6)
c [Å]	7.6285(3)
β [°]	111.316(5)
V [Å^3]	1335.17(9)
Z	4
$\rho_{calcd.}$ [g cm^{-3}]	1.379

μ [mm^{-1}]	0.106
F(000)	584
Θ range [°]	4.16 – 30.51
Index ranges	$-13 \leq h \leq 13$
	$-27 \leq k \leq 27$
	$-10 \leq l \leq 10$
Reflns. collected	26741
Reflns. obsd.	3152
Reflns. unique	4061 (R_{int} = 0.0405)
R_1, wR_2 (2σ data)	0.0462, 0.1173
R_1, wR_2 (all data)	0.0633, 0.1252
GOOF on F^2	1.070
Peak/hole [e Å^{-3}]	0.343 / -0.241

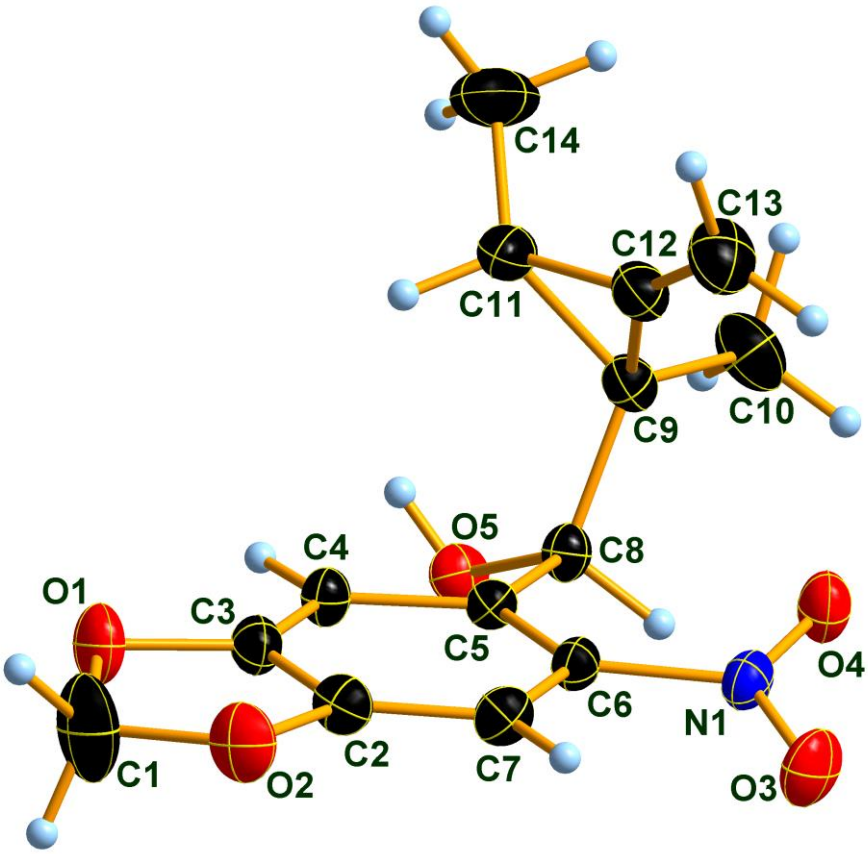


Figure 1. Molecular structure of compound **7d** in the crystal, DIAMOND[g] representation; thermal ellipsoids are drawn at 50 % probability level.

Table 2. Selected bond lengths (Å) of compound **7d**.

C5 – C4	1.404(2)	C7 – C2	1.363(2)
C5 – C6	1.406(2)	O1 – C1	1.433(2)
C5 – C8	1.521(2)	C11 – C14	1.508(2)
O5 – C8	1.433(1)	C11 – C9	1.555(2)
C3 – O1	1.364(1)	C9 – C10	1.513(2)
C3 – C4	1.368(2)	O2 – C2	1.366(1)
C3 – C2	1.385(2)	O2 – C1	1.416(2)
N1 – O4	1.224(1)	C12 – C13	1.312(2)
N1 – O3	1.238(1)	C12 – C11	1.465(2)
N1 – C6	1.456(1)	C12 – C9	1.471(2)
C8 – C9	1.528(2)	C6 – C7	1.405(2)

Table 3. Selected bond angles (°) of compound **7d**.

C4 – C5 – C6	117.2(1)	C7 – C2 – O2	128.9(1)
C4 – C5 – C8	118.0(1)	C7 – C2 – C3	121.2(1)
C6 – C5 – C8	124.8(1)	O2 – C2 – C3	110.0(1)
C8 – O5 – H5	106.5(1)	C12 – C9 – C10	118.6(1)
O1 – C3 – C4	127.5(1)	C12 – C9 – C8	121.4(1)
O1 – C3 – C2	109.7(1)	C10 – C9 – C8	113.1(1)
C4 – C3 – C2	122.8(1)	C12 – C9 – C11	57.84(8)
O4 – N1 – O3	122.4(1)	C10 – C9 – C11	119.6(1)
O4 – N1 – C6	119.7(1)	C8 – C9 – C11	115.7(1)
O3 – N1 – C6	117.9(1)	O2 – C1 – O1	108.4(1)
O5 – C8 – C5	111.0(1)	C7 – C6 – N1	115.0(1)
O5 – C8 – C9	110.3(1)	C5 – C6 – N1	121.0(1)
C5 – C8 – C9	114.0(1)	C2 – C7 – C6	116.3(1)
C2 – O2 – C1	105.0(1)	C3 – O1 – C1	104.8(1)
C13 – C12 – C11	147.8(1)	C3 – C4 – C5	118.7(1)
C13 – C12 – C9	147.8(1)	C12 – C11 – C14	122.9(1)
C11 – C12 – C9	63.96(9)	C12 – C11 – C9	58.20(8)
C7 – C6 – C5	123.9(1)	C14 – C11 – C9	123.1(1)

Table 4. Selected torsion angles (°) of compound **7d**.

C4 – C5 – C8 – O5	-27.2(1)	C1 – O2 – C2 – C7	-172.3(1)
C6 – C5 – C8 – O5	150.8(1)	C1 – O2 – C2 – C3	8.9(2)
C4 – C5 – C8 – C9	98.1(1)	O1 – C3 – C2 – C7	-179.2(1)
C6 – C5 – C8 – C9	-83.9(1)	C4 – C3 – C2 – C7	0.9(2)
C4 – C5 – C6 – C7	0.3(2)	O1 – C3 – C2 – O2	-0.3(1)
C8 – C5 – C6 – C7	-177.7(1)	C4 – C3 – C2 – O2	179.8(1)
C4 – C5 – C6 – N1	178.2(1)	C13 – C12 – C9 – C10	-64.1(3)
C8 – C5 – C6 – N1	0.3(2)	C11 – C12 – C9 – C10	108.8(1)

O4 – N1 – C6 – C7	-163.4(1)	C13 – C12 – C9 – C8	84.6(3)
O3 – N1 – C6 – C7	15.9(2)	C11 – C12 – C9 – C8	-102.5(1)
O4 – N1 – C6 – C5	18.5(2)	C13 – C12 – C9 – C11	-172.9(3)
O3 – N1 – C6 – C5	-162.3(1)	O5 – C8 – C9 – C12	135.6(1)
C5 – C6 – C7 – C2	-0.9(2)	C5 – C8 – C9 – C12	9.9(2)
N1 – C6 – C7 – C2	-179.0(1)	O5 – C8 – C9 – C10	-74.2(1)
C4 – C3 – O1 – C1	171.6(1)	C5 – C8 – C9 – C10	160.1(1)
C2 – C3 – O1 – C1	-8.3(2)	O5 – C8 – C9 – C11	69.0(1)
O1 – C3 – C4 – C5	178.6(1)	C5 – C8 – C9 – C11	-56.7(1)
C2 – C3 – C4 – C5	-1.6(2)	C14 – C11 – C9 – C12	111.0(2)
C6 – C5 – C4 – C3	0.9(2)	C12 – C11 – C9 – C10	-107.0(1)
C8 – C5 – C4 – C3	179.1(1)	C14 – C11 – C9 – C10	4.0(2)
C13 – C12 – C11 – C14	61.5(3)	C12 – C11 – C9 – C8	112.3(1)
C9 – C12 – C11 – C14	-111.4(2)	C14 – C11 – C9 – C8	-136.6(1)
C13 – C12 – C11 – C9	172.8(3)	C2 – O2 – C1 – O1	-14.0(2)
C6 – C7 – C2 – O2	-178.4(1)	C3 – O1 – C1 – O2	13.9(2)
C6 – C7 – C2 – C3	0.4(2)		

References

a) CrysAlis CCD, Oxford Diffraction Ltd., Version 1.171.27p5 beta (release 01-04-2005 CrysAlis171.NET) (compiled Apr 1 2005, 17:53:34).

b) CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.27p5 beta (release 01-04-2005 CrysAlis171.NET) (compiled Apr 1 2005, 17:53:34).

c) SCALE3 ABSPACK – An Oxford Diffraction Program (1.0.4, gui:1.0.3) (C), Oxford Diffraction, Ltd., 2005.

d) Sheldrick, G. M. (1997) SHELXS-97: *Program for Crystal Structure Solution*, University of Göttingen, Germany.

e) Sheldrick, G. M. (1997) SHELXL-97: *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany.

f) Spek, A. L. (1999) PLATON: *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands.

g) DIAMOND, Crystal Impact GbR., Version 3.2i.