Preparation of allylboronates by Pd-catalyzed borylative cyclization of dienynes

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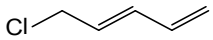
1. General methods.

The solvents used, THF (SDS, anhydrous, analytical grade), DMF (SDS, anhydrous, analytical grade), toluene (SDS, anhydrous, analytical grade), MeOH (SDS, anhydrous, analytical grade), CH_2Cl_2 (SDS, anhydrous, analytical grade), Et_2O (SDS, anhydrous, analytical grade) and DMSO (SDS, anhydrous, analytical grade) were further dried by standing with activated 4 Å molecular sieves under Ar atmosphere for several days prior to use. Commercially n-pentane RPE (Carlo Erba, analytical grade) was used untreated. Commercially available reagents were used without additional purification. Palladium(II) trifluoroacetate (Fluorochem), bis(pinacolato)diboron (Fluorochem), dimethyl malonate (Aldrich) and *N-(*tert-butoxycarbonyl)-*p*-toluenesulfonamide (TCI) were used as received and stored at room temperature. Dimethyl propargylmalonate (Fluka), *N*-chlorosuccinimide (Aldrich), dimethyl sulfide (Aldrich), 2-iodothiophene (Aldrich), penta-1,4-dien-3-ol (Aldrich) and (2*E*, 4*E*)-hexa-2,4-dien-1-ol (Alfa Aesar) were used as received and stored at 4ºC. Silicagel 60 (0.40-0.063 mm) was used for column chromatography purchased from SDS, and TLC-aluminium plates with 0.25 mm of silicagel 60 (F_{254}) were used for thin-layer chromatography, purchased from Macherey-Nagel. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded using chloroform-d_1 (7.26 ppm ^{1}H, 77.2 ppm ^{13}C) as internal standard. Bruker AMX-300 was the spectrometer used. Reagents were weighted on air, reactions were performed under Ar and subsequent work-up was performed on air.

2. Synthesis and characterization of dienynes precursors.

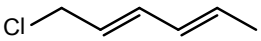
Dimethyl 2-(but-2-ynyl)malonate,[1] **dimethyl 2-(3-phenylprop-2-ynyl)malonate**,[2] **dimethyl 2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate,**[3] **diethyl 2-(but-2-yn-1-yl)malonate,**[4] ***N*-(prop-2-ynyl)-*p*-toluenesulfonamide**,[5] ***N*-(but-2-ynyl)-*p*-toluenesulfonamide**,[1] and **dimethyl 2-(but-3-ynyl)malonate**,[6] were prepared according to a previously described procedure.

(E)-5-chloropenta-1,3-diene



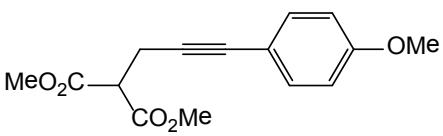
To a solution of penta-1,4-dien-3-ol (11.85 mmol, 1 equiv) in pentane (10 mL), 2 mL of H_2O was added at room temperature. The mixture was cooled to 0ºC and 3.3 mL of HCl (37%, 39.93 mmol, 3.37 equiv) were added dropwise. After addition, the reaction was stirred at room temperature for 2 h. Then, water and Et_2O were added into the resulting mixture. The aqueous layer was separated and extracted with Et_2O (3 x 10 mL). The combined organic phases were washed several times with water, aqueous solution of $NaHCO_3$ (5%) and twice with saturated aqueous solution of NaCl. Then, the organic phase was dried over anhydrous $MgSO_4$. The solvent was carefully removed under vacuum and the crude was used without further purification. Characterization and experimental data of this compound were already reported.[7]

(2E,4E)-1-chlorohexa-2,4-diene



A solution of *N*-chlorosuccinimide (1.0 g, 7.60 mmol) in CH_2Cl_2 (15 mL) was charged with dimethyl sulfide (316.16 mg, 5.08 mmol) at 0ºC and the resulting white suspension was stirred for 10 min. After cooling to –20ºC, a solution of (2*E*, 4*E*)-hexa-2,4-dien-1-ol (500 mg, 5.09 mmol) in CH_2Cl_2 (5 mL) was added and the mixture was allowed to warm to room temperature. After stirring for 2 h, the reaction mixture was diluted with water and extracted with Et_2O. Then, the organic phase was dried over anhydrous $MgSO_4$. The solvent was carefully removed under vacuum and the crude was used without further purification. Characterization and experimental data of this compound were already reported.[8]

Dimethyl-(3-phenylprop-2-yn-1-yl)malonate

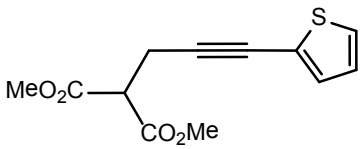


CuI (224 mg, 1.17 mmol), $(PPh_3)_2PdCl_2$ (412 mg, 0.587 mmol,) and 1-iodo-4-methoxybenzene (2.75g, 11.75 mmol) were added to a solution of dimethyl-propargylmalonate (2 g, 11.75 mmol) in CH_2Cl_2 (15 mL) and Et_3N (6.27 mL). The reaction mixture was stirred at room temperature for 12 h. The solvent was evaporated and the crude

was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4 and the solvent removed. The crude product was purified by flash chromatography on silica gel (hexane/EtOAc 6:1, molybdophosphoric acid us stain (2.6 mmol/100 mL ethanol)) to afford the title compound as yellowish oil (1.95 g, 60%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 6.84 – 6.77 (m, 2H), 3.80 (s, 3H), 3.78 (s, 6H), 3.68 (t, *J* = 7.8 Hz, 1H), 2.99 (d, *J* = 7.7 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.66 (C), 159.55 (C), 133.19 (CH), 115.43 (C), 113.98 (CH), 83.78 (C), 82.52 (C), 55.42 (CH_3), 52.94 (CH_3), 51.47 (CH), 19.71 (CH_2). Characterization and experimental data of this compound were already reported.[9]

Dimethyl 2-(3-(thiophen-2-yl)prop-2-yn-1-yl)malonate

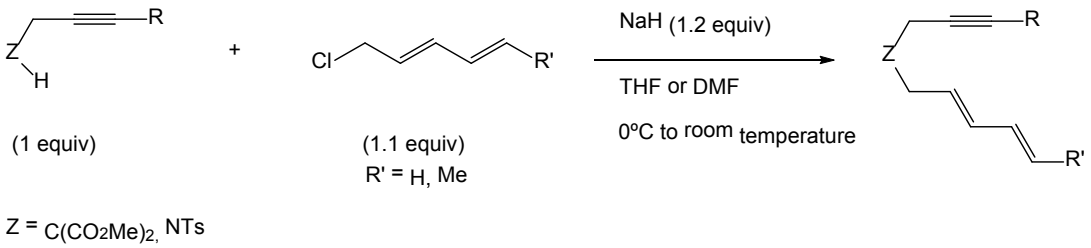


CuI (144 mg, 7.50 mmol), $(PPh_3)_2PdCl_2$ (708 mg, 1.01 mmol) and 2-iodothiophene (2.75 g, 13.09 mmol) were added to a solution of dimethyl-propargylmalonate (2.0 g, 10.09 mmol) in THF (25 mL) and Et_3N (1.82 mL). The reaction mixture was stirred at room temperature for 12 h. The solvent was evaporated and the crude was then diluted with EtOAc and washed with saturated aqueous $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4 and the solvent removed. The crude product was purified by flash chromatography on silica gel (hexane/EtOAc 6:1, molybdophosphoric acid us stain (2.6 mmol/100 mL ethanol)) to afford the title compound as yellowish oil (1.3 g, 54%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 5.2 Hz, 1H), 7.20 (d, *J* = 3.6 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.7 Hz, 1H), 3.86 (s, 6H), 3.77 (t, *J* = 7.7 Hz, 1H), 3.11 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 168.35 (C), 131.75 (CH), 126.85 (CH), 126.68 (CH), 123.17 (C), 89.33 (C), 75.81 (C), 52.87 (CH_3), 50.99 (CH), 19.80 (CH_2). HRMS-ESI: $[M]^+$ Calcd. for $C_{12}H_{11}O_4S$: 252.0456; found: 252.0459.

3. Synthesis of dienynes.

The general procedure of alkylation for the synthesis of **1a-k**, is described below.

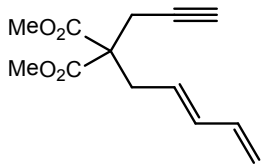


Scheme 1

To a suspension of NaH (60% in mineral oil, 1.2 equiv) in anhydrous THF or DMF (solvent and volume will be indicated in each case) under Ar atmosphere at 0ºC, was slowly added the corresponding propargyl derivative (1 equiv) and the mixture was stirred at room temperature for 15 min (formation of H_2 bubbles were observed during the addition). Then, the electrophile (E)-5-chloropenta-1,3-diene or (2E,4E)-1-chlorohexa-2,4-diene (1.2 equiv), was added dropwise and the mixture was allowed to react at room temperature. Monitoring by TLC indicated the completion of the reaction. Then, in the case of THF, most of the solvent was removed under vacuum and later, water and Et_2O were added into the resulting mixture. The aqueous layer was separated and extracted successively with Et_2O. In the case of DMF, similar extractive work-up with CH_2Cl_2/water was employed. The combined organic phases were washed several times with water and two times with saturated aqueous solution of NaCl. In all the cases, the combined organic phases were dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the crude was purified by flash chromatography, molybdophosphoric acid us stain (2.6 mmol/100 mL ethanol).

4. Experimental data of dienynes

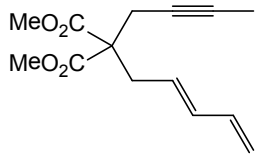
(E)-dimethyl 2-(penta-2,4-dien-1-yl)-2-(prop-2-yn-1-yl)malonate (1a)



Following *general procedure of alkylation* for synthesis of dienynes (12 h) and using THF (25 mL) as solvent for (1.63 g, 9.57 mmol) of **dimethyl 2-(prop-2-yn-1-yl)malonate** and (1.18 g, 11.48 mmol) of **(E)-5-chloropenta-1,3-diene**. The product **1a** was obtained as colourless oil (1.60 g, 70%) using hexane/EtOAc 6:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.37 – 6.08 (m, 2H), 5.47 (dt, *J* = 15.2, 7.7 Hz, 1H), 5.16 (dd, *J* = 13.0, 4.4 Hz, 1H), 5.04 (dd, *J* = 10.1, 1.8 Hz, 1H), 3.74 (s, 6H), 2.82 (dd, *J* = 9.1, 4.6 Hz, 2H), 2.79 (d, *J* = 2.7 Hz, 2H), 2.03 (t, *J* = 2.7 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.27 (C), 136.64 (CH), 135.83 (CH), 127.17 (CH), 117.03 (CH_2), 78.92 (C), 71.68 (C), 57.27 (C), 52.95 (CH_3), 35.57 (CH_2), 23.00 (CH_2).

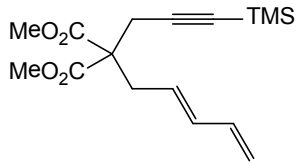
(E)-dimethyl 2-(but-2-yn-1-yl)-2-(penta-2,4-dien-1-yl)malonate (1b)



Following *general procedure of alkylation* for synthesis of dienynes (18 h) and using THF (30 mL) as solvent for (1.20 g, 7.09 mmol) of **dimethyl 2-(but-2-yn-1-yl)malonate** and (873 mg, 8.51 mmol) of **(E)-5-chloropenta-1,3-diene**. The product **1b** was obtained as colourless oil (1.03 g, 58%) using hexane/EtOAc 15:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.36 – 6.07 (m, 2H), 5.50 (dt, *J* = 15.3, 7.6 Hz, 1H), 5.13 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.02 (dt, *J* = 9.9, 1.3 Hz, 1H), 3.72 (d, *J* = 2.0 Hz, 6H), 2.81 (d, *J* = 7.9 Hz, 2H), 2.73 (q, *J* = 2.5 Hz, 2H), 1.76 (t, *J* = 2.6 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.63 (C), 136.77 (CH), 135.49 (CH), 127.67 (CH), 116.74 (CH_2), 79.13 (C), 73.40 (C), 57.65 (CH_3), 52.82 (C), 35.65 (CH_2), 23.38 (CH_2), 3.63 (CH_3).

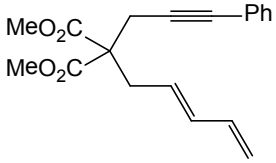
(E)-dimethyl 2-(penta-2,4-dien-1-yl)-2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate (1c)



Following *general procedure of alkylation* for synthesis of dienynes (20 h) and using DMF (60 mL) as solvent for (2.91 g, 12.01 mmol) of **dimethyl 2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate** and (1.48 g, 14.41 mmol) of **(E)-5-chloropenta-1,3-diene**. The product **1c** was obtained as yellowish oil (1.78 g, 48%) using hexane/EtOAc 15:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.36 – 6.08 (m, 2H), 5.49 (dt, *J* = 15.2, 7.6 Hz, 1H), 5.14 (dd, *J* = 16.8, 1.7 Hz, 1H), 5.03 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.73 (s, 6H), 2.83 (d, *J* = 5.27 Hz, 2H), 2.81 (s, 2H), 0.14 (s, 9H).^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135)) δ 170.31 (C), 136.71 (CH), 135.70 (CH), 127.44 (CH), 116.87 (CH_2), 101.40 (C), 88.55 (C), 57.53 (C), 52.85 (CH_3), 35.69 (CH_2), 24.39 (CH_2), 0.12 (CH_3).

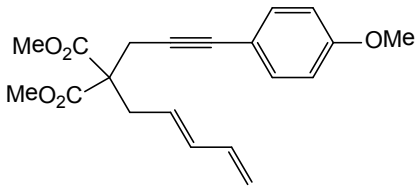
(E)-dimethyl 2-(penta-2,4-dien-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (1d)



Following *general procedure of alkylation* for synthesis of dienynes (18 h) and using THF (6 mL) as solvent for (0.24 g, 0.97 mmol) of **dimethyl 2-(3-phenylprop-2-yn-1-yl)malonate** and (120 mg, 1.16 mmol) of **(E)-5-chloropenta-1,3-diene**. The product **1d** was obtained as colourless oil (161 mg, 53%) using hexane/EtOAc 6:1 as eluent.

^{1}H-NMR (300 MHz, $CDCl_3$)) δ 7.41 - 7.34 (m, 2H), 7.31 – 7.27 (m, 3H), 6.38 – 6.12 (m, 2H), 5.54 (dt, *J* = 15.2, 7.7 Hz, 1H), 5.15 (dd, *J* = 16.3, 1.9 Hz, 1H), 5.04 (dd, *J* = 9.9, 1.6 Hz, 1H), 3.76 (s, 6H), 3.01 (s, 2H), 2.90 (d, *J* = 7.7 Hz, 2H).^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.44 (C), 136.70 (CH), 135.76 (CH), 131.82 (CH), 128.37 (CH), 128.17 (CH), 127.43 (CH), 123.34 (C), 116.95 (CH_2), 84.36 (C), 83.86 (C), 57.69 (C), 52.94 (CH_3), 35.86 (CH_2), 23.99 (CH_2).

(E)-dimethyl 2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-2-(penta-2,4-dien-1-yl)malonate (1e)

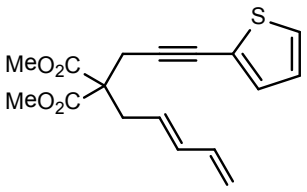


Following *general procedure of alkylation* for synthesis of dienynes (18 h) and using THF (20 mL) as solvent for (0.7 g, 2.53 mmol) of **dimethyl 2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)malonate** and (311 mg, 3.03 mmol) of **(2E,4E)-1-chlorohexa-2,4-diene**. The product **1e** was obtained as yellowish oil (373 mg, 43%) using hexane/EtOAc 10:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.25 (m, 2H), 5.54 (dt, *J* = 15.0, 7.7 Hz, 1H), 5.15 (dd, *J* =2.06, 17.19 Hz, 1H), 5.04 (dd, *J* =1.92, 11.12 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 6H), 2.99 (s, 2H), 2.89 (d, *J* = 7.7 Hz, 2H).^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.51 (C), 159.56 (C), 136.74 (CH), 135.69 (CH),

133.19 (CH), 127.54 (CH), 116.88 (CH_2), 115.51 (C), 114.01 (CH), 83.65 (C), 82.74 (C), 57.75 (C), 55.44 (CH_3), 52.91 (CH_3), 35.85 (CH_2), 24.02 (CH_2).

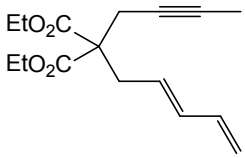
(E)-dimethyl 2-(penta-2,4-dien-1-yl)-2-(3-(thiophen-2-yl)prop-2-yn-1-yl)malonate (1f)



Following *general procedure of alkylation* for synthesis of dienynes (12 h, 50ºC) and using THF (20 mL) as solvent for (1.374 g, 5.4 mmol) of **dimethyl 2-(3-(thiophen-2-yl)prop-2-yn-1-yl)malonate** and (670 mg, 6.5 mmol) of **(E)-5-chloropenta-1,3-diene**. The product **1f** was obtained as yellow oil (659 mg, 39%) using hexane/EtOAc 20:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 5.2, 1.1 Hz, 1H), 7.12 (dd, *J* = 3.6, 0.7 Hz, 1H), 6.93 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.38 – 6.11 (m, 2H), 5.53 (dt, *J* = 15.1, 7.7 Hz, 1H), 5.15 (dd, *J* = 16.7, 1.60 Hz, 1H), 5.04 (dd, *J* = 9.9, 1.6 Hz, 1H), 3.75 (s, 6H), 3.11 – 2.96 (m, 2H), 2.85 (dd, *J* = 15.3, 6.9 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 170.15 (C), 136.52 (CH), 135.70 (CH), 131.69 (CH), 127.19 (CH), 126.84 (CH), 126.62 (CH), 123.18 (C), 116.90 (CH_2), 88.37 (C), 76.83 (C), 57.45 (C), 52.82 (CH_3), 35.84 (CH_2), 24.18 (CH_2). HRMS-ESI: $[M]^+$ Calcd. for $C_{17}H_{18}O_4S$: 318.0926; found: 318.0927.

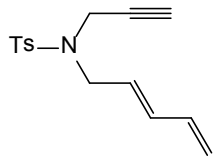
(E)-diethyl 2-(but-2-yn-1-yl)-2-(penta-2,4-dien-1-yl)malonate (1g)



Following *general procedure of alkylation* for synthesis of dienynes (48 h, 40ºC) and using THF (26 mL) as solvent for(0.9 g, 4.54 mmol) of **diethyl 2-(but-2-yn-1-yl)malonate** and (559 mg, 5.45 mmol) of **(E)-5-chloropenta-1,3-diene**. The product **1g** was obtained as colourless oil (1.05 g, 83%) hexane/EtOAc 25:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.36 – 6.06 (m, 2H), 5.52 (dt, *J* = 15.2, 7.7 Hz, 1H), 5.13 (dd, *J* = 12.8, 5.0 Hz, 1H), 5.06 – 4.96 (m, 1H), 4.19 (dt, *J* = 7.1, 5.0 Hz, 4H), 2.81 (d, *J* = 7.7 Hz, 2H), 2.73 (q, *J* = 2.5 Hz, 2H), 1.76 (t, *J* = 2.5 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.19 (C), 136.81 (CH), 135.40 (CH), 127.89 (CH), 116.58 (CH_2), 78.98 (C), 73.58 (C), 61.63 (CH_2), 57.45 (C), 35.52 (CH_2), 23.28 (CH_2), 14.24 (CH_3), 3.62 (CH_3).

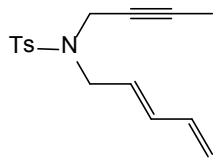
(E)-4-methyl-N-(penta-2,4-dien-1-yl)-N-(prop-2-yn-1-yl)benzenesulfonamide (1h)



Following *general procedure of alkylation* for synthesis of dienynes (18 h) and using DMF (60 mL) as solvent for (1.76 g, 8.45 mmol) of **4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide** and (1.04 g, 10.14 mmol) of **(E)-5-chloropenta-1,3-diene**. The product **1h** was obtained as yellowish oil (1.21 g, 52%) using hexane/EtOAc 6:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.40 – 6.12 (m, 2H), 5.59 (dd, *J* = 14.3, 7.1 Hz, 1H), 5.21 (dd, *J* = 16.6, 1.9 Hz, 1H), 5.12 (dd, *J* = 9.4, 1.5 Hz, 1H), 4.09 (d, *J* = 2.3 Hz, 2H), 3.86 (d, *J* = 6.9 Hz, 2H), 2.43 (bs, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 143.71 (C), 135.92 (C), 135.77 (CH), 129.85 (CH), 129.64 (CH), 127.93 (CH), 127.71 (CH), 127.03 (CH_2), 118.56 (C), 73.87 (C), 48.19 (CH_2), 35.99 (CH2), 21.69 (CH_3).

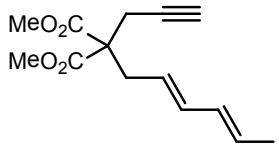
(E)-N-(but-2-yn-1-yl)-4-methyl-N-(penta-2,4-dien-1-yl)benzenesulfonamide (1i)



Following *general procedure of alkylation* for synthesis of dienynes (20 h) and using DMF (30 mL) as solvent for (1.13 g, 5.08 mmol) of **N-(but-2-yn-1-yl)-4-methylbenzenesulfonamide** and (625 mg, 6.09 mmol) of **(E)-5-chloropenta-1,3-diene**. The product **1i** was obtained as yellowish oil (691 mg, 47%) using hexane/EtOAc 5:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.38 – 6.13 (m, 2H), 5.58 (dt, *J* = 13.6, 6.7 Hz, 1H), 5.20 (dd, *J* = 16.6, 1.9 Hz, 1H), 5.10 (dd, *J* = 9.4, 1.5 Hz, 1H), 4.03 - 3.96 (m, 2H), 3.83 (d, *J* = 6.9 Hz, 2H), 2.42 (s, 3H), 1.55 (t, *J* = 2.3 Hz, 3H).^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 143.38 (C), 136.42 (C), 136.04 (CH), 135.34 (CH), 129.40 (CH), 128.04 (CH), 127.52 (CH), 118.27 (CH_2), 81.72 (C), 71.86 (C), 48.18 (CH_2), 36.58 (CH_2), 21.64 (CH_3), 3.39 (CH_3).

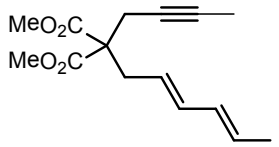
Dimethyl 2-((2E,4E)-hexa-2,4-dien-1-yl)-2-(prop-2-yn-1-yl)malonate (1j)



Following *general procedure of alkylation* for synthesis of dienynes (8 h, 40 ºC) and using THF (20 mL) as solvent for (0.87 g, 5.0 mmol) of **dimethyl 2-(prop-2-yn-1-yl)malonate** and (0.591 g, 5.0 mmol) of **(2E,4E)-1-chlorohexa-2,4-diene**. The product **1j** was obtained as colourless oil (534 mg, 42%) using hexane/EtOAc 20:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.13 – 5.86 (m, 2H), 5.68 – 5.49 (m, 1H), 5.33 – 5.18 (m, 1H), 3.70 – 3.68 (m, 6H), 2.79 – 2.71 (m, 4H), 2.02 – 1.97 (m, 1H), 1.68 (d, *J* = 6.7 Hz, 3H).^{13}C NMR (76 MHz, $CDCl_3$) δ 170.15 (C), 135.23 (CH_2), 131.10 (CH_2), 129.08 (CH_2), 123.46 (CH_2), 78.88 (C), 71.51 (C), 57.20 (C), 52.73 (CH_3), 35.43 (CH_2), 22.75 (CH_2), 18.00 (CH_3). HRMS-ESI: $[M]^+$ Calcd. for $C_{14}H_{19}O_4$: 251.1272; found: 251.1281.

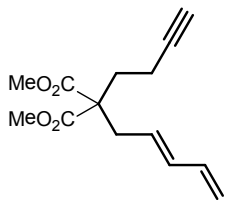
Dimethyl 2-(but-2-yn-1-yl)-2-((2E,4E)-hexa-2,4-dien-1-yl)malonate (1k)



Following *general procedure of alkylation* for synthesis of dienynes (8 h, 40 ºC) and using THF 20 mL as solvent for (0.87 g, 4.70 mmol) of **dimethyl 2-(but-2-yn-1-yl)malonate** and (0.591 mg, 5.09 mmol) of **(2E,4E)-1-chlorohexa-2,4-diene**. The product **1k** was obtained as colourless oil (0.562 mg, 42%) using hexane/EtOAc 20:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.13 – 5.87 (m, 2H), 5.58 (dq, *J* = 13.3, 6.5 Hz, 1H), 5.36 – 5.20 (m, 1H), 3.70 – 3.65 (m, 6H), 2.72 (t, *J* = 7.0 Hz, 2H), 2.68 (dd, *J* = 4.9, 2.3 Hz, 2H), 1.72 (dd, *J* = 4.2, 1.5 Hz, 3H), 1.68 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.56 (C), 134.94 (CH_2), 131.23 (CH_2), 128.85 (CH_2), 123.95 (CH_2), 78.90 (C), 73.41 (C), 57.61 (C), 52.65 (CH_3), 35.52 (CH_2), 23.14 (CH_2), 18.04 (CH_3), 3.51 (CH_3). HRMS-ESI: $[M]^+$ Calcd. for $C_{15}H_{20}O_4$: 264.1362; found: 264.1363.

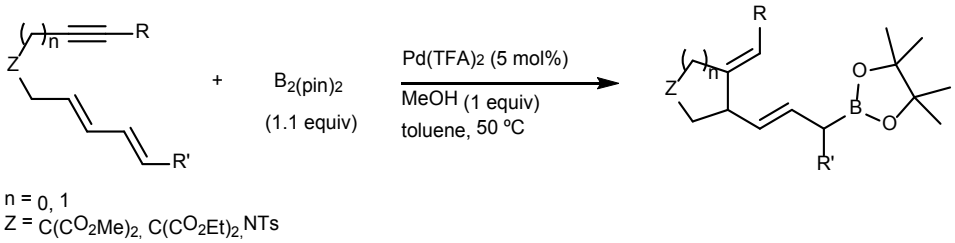
(E)-dimethyl 2-(but-3-yn-1-yl)-2-(penta-2,4-dien-1-yl)malonate (3a)



Following *general procedure of alkylation* for synthesis of dienynes (20 h) and using THF (9 mL) as solvent for (0.91 g, 4.93 mmol).of **dimethyl 2-(but-3-yn-1-yl)malonate** and (607 mg, 5.92 mmol) of **(E)-5-chloropenta-1,3-diene.** The product **1i** was obtained as colourless oil (827 mg, 67%) using hexane/EtOAc 10:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.28 (dt, *J* = 16.8, 10.2 Hz, 1H), 6.10 (dd, *J* = 15.0, 10.5 Hz, 1H), 5.50 (dt, *J* = 15.1, 7.7 Hz, 1H), 5.14 (dd, *J* = 16.6, 1.5 Hz, 1H), 5.03 (d, *J* = 11.0, 1.4 Hz, 1H), 3,75 (s, 1H), 3.72 (d, *J* = 2.8 Hz, 6H), 2.70 (d, *J* = 7.6 Hz, 2H), 2.17 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 171.22 (C), 136.62 (CH), 135.38 (CH), 127.52 (CH), 116.95 (CH_2), 83.26 (C), 68.95 (CH), 57.40 (CH_3), 52.66 (C), 36.47 (CH_2), 31.86 (CH_2), 14.10 (CH_2).

5. General procedure for borylative cyclization of dienynes.

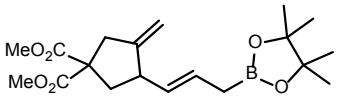


Scheme 2

The corresponding dienyne (0.4 mmol, 1 equiv), bis(pinacolato)diboron (1.1 equiv), and $Pd(TFA)_2$ (5 mol%) were sequentially added to a 10 mL flask under Ar atmosphere. Anhydrous toluene (1.5 mL) and anhydrous MeOH (1 equiv) were added. Then, the mixture was stirred during the corresponding time at the temperature indicated below for each compound. After cooling the mixture to room temperature, the solvent was evaporated and the flash chromatography (hexane:Et_2O or pentane:Et_2O, it will be specified in each case, molybdophosphoric acid us stain (2.6 mmol/100 mL ethanol)) afforded the product. Partial decomposition of the products was detected when using long retention times using hexane:EtOAc as eluent.

6. Experimental data of allylboronates from dienynes

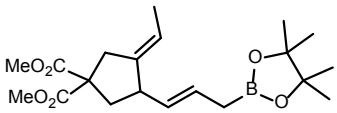
(E)-dimethyl 3-methylene-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)cyclopentane-1,1-dicarboxylate (2a)



Following general borylative cyclization procedure, the product **2a** was obtained after 3 h at 50 °C as colourless oil (49 mg, 64%) using pentane/Et_2O 5:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.53 (dt, *J* = 14.9, 7.4 Hz, 1H), 5.21 (ddt, *J* = 15.1, 8.2 Hz, 1.3 Hz, 1H), 4.96-4.90 (m, 1H), 4.83-4.79 (m, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.17-3.03 (m, 2H), 2.54 (dc, *J* = 17.4, 2.3 Hz, 1H), 2.54 (ddd, *J* = 12.9, 7.7 Hz, 1.4Hz, 1H), 1.95 (dd, *J* = 13.0, 11.3 Hz, 1H), 1.68 (d, *J* = 7.3 Hz, 2H), 1.24 (s, 12H). ^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 172.47 (C), 172.32 (C), 151.45 (C), 131.10 (CH), 127.57 (CH), 107.78 (CH_2), 83.37 (C), 58.54 (C), 52.93 (CH_3), 52.87 (CH_3), 47.01 (CH), 40.91 (CH_2), 40.32 (CH_2), 24.95 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{18}H_{29}BO_6Na$: 387.1949; found: 387.1948.

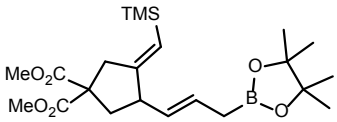
(E)-dimethyl 3-ethylidene-4-((E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)cyclopentane-1,1-dicarboxylate (2b)



Following general borylative cyclization procedure, the product **2b** was obtained after 4.5 h at 50 °C as colourless oil (42 mg, 55%) using pentane/Et_2O 5:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.49 (dt, J = 14.9, 7.3 Hz, 1H), 5.26 – 5.07 (m, 2H), 3.74 (s, 3H), 3.73 (s, 3H), 3.01 (d, J = 16.2 Hz, 2H), 2.80 (dd, J = 17.3, 1.9 Hz, 1H), 2.50 (ddd, J = 12.8, 7.1, 1.6 Hz, 1H), 1.95 – 1.83 (dd, J = 12.7, 11.8 Hz, 1H), 1.67 (d, J = 7.2 Hz, 2H), 1.59 (m, 3H), 1.25 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6 (C), 172.5 (C), 142.19 (C), 131.66 (CH), 127.29 (CH), 117.62 (CH), 83.35 (C), 58.66 (C), 52.90 (CH_3), 52.83 (CH_3), 47.07 (CH), 41.06 (CH_2), 36.92 (CH_2), 24.93 (CH_3), 14.68 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{20}H_{31}BO_6Na$: 401.2105; found: 401.2130.

(E)-dimethyl 3-((E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)-4-((trimethylsilyl)methylene)cyclopentane-1,1-dicarboxylate (2c)

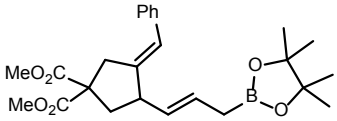


Following general borylative cyclization procedure, the product **2c** was obtained after 5 h at 70 °C (after 23 h at 50ºC, extra 2.5 mol% of $Pd(TFA)_2$ was added) as colourless oil (39

mg, 53%) using pentane/Et_2O 8:1 as eluent.

^{1}H RMN (300 MHz, $CDCl_3$) δ 5.49 (dt, *J* = 14.9, 7.4 Hz, 1H), 5.35 - 5.28 (m, 1H), 5.14 (dd, *J* = 15.2, 8.3 Hz, 1H), 3.73 (s, 6H), 3.17 - 2.97 (m, 2H), 2.93 - 2.77 (m, 1H), 2.52 (ddd, *J* = 12.9, 7.7, 1.6 Hz, 1H), 1.92 (dd, *J* = 12.9, 11.5 Hz, 1H), 1.68 (d, *J* = 7.4 Hz, 2H), 1.23 (s, 12H), 0.08 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.37 (C), 159.84 (C), 131.40 (CH), 127.96 (CH), 121.31 (CH), 83.34 (C), 58.85 (C), 52.89 (CH_3), 52.86 (CH_3), 49.77 (CH), 40.18 (CH_2), 40.11 (CH_2), 24.95 (CH_3), 24.88 (CH_3), -0.29 (CH_3). Fragmentation observed of the product **2c**, HRMS-ESI: $[M]^+$ Calcd. for $C_{16}H_{25}O_4Si$: 309.1516; found: 309.1521.

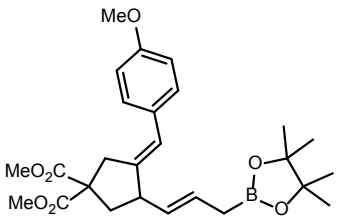
(E)-dimethyl 3-benzylidene-4-((E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)cyclopentane-1,1-dicarboxylate (2d)



Following general borylative cyclization procedure, the product **2d** was obtained after 8.5 h at 50 °C as colourless oil (35 mg, 49%) using pentane/Et_2O 7:1 as eluent.

^{1}H RMN (300 MHz, $CDCl_3$) δ 7.36 - 7.26 (m, 4H), 7.21 - 7.13 (m, 1H), 6.25 - 6.14 (m, 1H), 5.62 (dt, *J* = 14.9, 7.4 Hz, 1H), 5.33 - 5.16 (m, 1H), 3.72 (s, 6H), 3.45 - 3.12 (m, 2H), 3.16 (dt, *J* = 17.7, 2.7 Hz, 1H), 2.58 (dd, *J* = 12.8, 7.3 Hz, 1H), 1.95 (t, *J* = 12.3 Hz, 1H), 1.74 (d, *J* = 7.3 Hz, 2H), 1.25 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.32 (C), 172.27 (C), 144.40 (C), 138.13 (C), 131.25 (CH), 128.39 (CH), 126.34 (CH), 123.72 (CH), 83.41 (C), 59.40 (C), 53.00 (CH_3), 52.95 (CH_3), 49.01 (CH), 40.31 (CH_2), 38.92 (CH_2), 24.98 (CH_3), 24.92 (CH_3). HRMS-ESI: $[MNH_4]^+$ Calcd. for C25H37BNO6: 458.2732; found: 458.2732.

(E)-dimethyl 3-(4-methoxybenzylidene)-4-((E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)cyclopentane-1,1-dicarboxylate (2e)

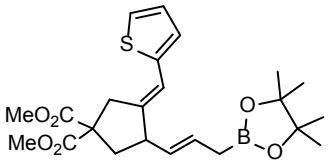


Following general borylative cyclization procedure, the product **2e** was obtained after 6.5 h at 50 °C as yellowish oil (34 mg, 50%) using hexane/Et_2O 7:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.86

(d, *J* = 8.8 Hz, 2H), 6.17 - 6.12 (m, 1H), 5.60 (dt, *J* = 14.9, 7.4 Hz, 1H), 5.32 – 5.19 (m, 1H), 3.80 (s, 3H), 3.74 (s, 6H), 3.43 – 3.07 (m, 3H), 2.57 (dd, *J* = 13.4, 7.7 Hz, 1H), 1.93 (t, *J* = 12.8 Hz, 1H), 1.73 (d, *J* = 7.3 Hz, 2H), 1.25 (s, 12H). ^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 172.38 (C), 158.14 (C), 142.11 (C), 131.46 (CH), 130.98 (CH), 129.56 (C), 128.19 (CH), 123.07 (CH), 113.85 (CH), 83.40 (C), 59.44 (C), 55.40 (CH_3), 52.98 (CH_3), 52.93 (CH_3), 48.93 (CH), 40.37 (CH_2), 38.85 (CH_2), 24.96 (CH_3). HRMS-ESI: $[MNH_4]^+$ Calcd. for $C_{26}H_{39}BNO_7$: 488.2841; found: 488.2814.

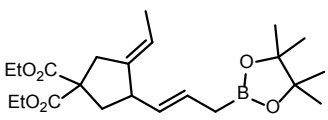
(E)-dimethyl 3-((E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)-4-(thiophen-2-ylmethylene)cyclopentane-1,1-dicarboxylate (2f)



Following general borylative cyclization procedure, the product **2f** was obtained after 8 h at 50 °C as a pale yellow oil (77 mg, 55%) using hexane/Et_2O 10:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, *J* = 5.1 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.91 (d, *J* = 3.5 Hz, 1H), 6.41 (d, *J* = 2.5 Hz, 1H), 5.61 (dt, *J* = 14.9, 7.4 Hz, 1H), 5.22 (ddt, *J* = 9.54,2.47, 1.28 Hz, 1H), 3.75 (t, *J* = 3.0 Hz, 6H), 3.32 (dd, *J* = 22.2, 14.3 Hz, 2H), 3.11 (dt, *J* = 18.2, 2.9 Hz, 1H), 2.59 (ddd, *J* = 12.8, 7.1, 1.6 Hz, 1H), 2.06 – 1.88 (m, 1H), 1.73 (d, *J* = 7.4 Hz, 2H), 1.26 (s, 12H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 172.19 (C), 172.11 (C), 142.94 (C), 142.00 (C), 130.80 (CH), 128.78 (CH), 127.15 (CH), 125.66 (CH), 124.60 (CH), 116.86 (CH), 83.40 (C), 59.32 (C), 53.00 (CH_3), 52.96 (CH_3), 48.73 (C), 40.78 (CH_2), 39.26 (CH_2), 24.97 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{23}H_{32}BO_6S$: 447.2007; found: 447.2016.

(E)-diethyl 3-ethylidene-4-((E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)cyclopentane-1,1-dicarboxylate (2g)

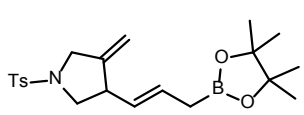


Following general borylative cyclization procedure, the product **2g** was obtained after 4.5 h at 50 °C as colourless oil (42 mg, 57%) using hexane/Et_2O 15:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.49 (dt, J = 14.9, 7.4 Hz, 1H), 5.27 – 5.07 (m, 2H), 4.18 (qd, J = 7.1, 3.0 Hz, 4H), 3.11 – 2.89 (m, 2H), 2.85 – 2.67 (m, 1H), 2.49 (dd, J = 12.2, 7.9

Hz, 1H), 1.87 (t, J = 12.3 Hz, 1H), 1.67 (d, J = 7.3 Hz, 2H), 1.59 (d, J = 4.8 Hz, 3H), 1.26 – 1.22 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.15 (C), 172.14 (C), 142.40 (C), 131.81 (CH), 127.11 (CH), 117.45 (CH), 83.32 (C), 61.56 (CH_2), 61.54 (CH_2), 58.71 (C), 47.05 (CH), 40.90 (CH_2), 36.76 (CH_2), 24.83 (CH_3), 14.66 (CH_3), 14.18 (CH_3), 14.17 (CH_3). HRMS-ESI: $[MNH_4]^+$ Calcd. for $C_{22}H_{39}BNO_6$: 424.2864; found: 424.2869.

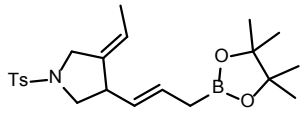
(E)-3-methylene-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)-1-tosylpyrrolidine (2h)



Following general borylative cyclization procedure, the product **2h** was obtained after 12 h at 70ºC (after 12 h at 50 °C, extra 2.5 mol% of $Pd(TFA)_2$ was added) as colourless oil (35 mg, 47%) using pentane/Et_2O 10:1 as eluent.

^{1}H RMN (300 MHz, $CDCl_3$) δ 7.78 (dt, *J* = 8.3 Hz, 1.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.56 (dt, *J* = 15.1, 7.5 Hz, 1H), 5.05 (dd, *J* = 15.2, 8.3 Hz, 1H), 4.87 (m, 2H), 4.05 – 3.90 (m, 1H), 3.73 - 3.53 (m, 2H), 3.25 - 3.09 (m, 1H), 2.76 (t, *J* = 9.4 Hz, 1H), 2.43 (s, 3H), 1.65 (d, *J* = 7.4 Hz, 2H), 1.23 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.74 (C), 143.74 (C), 133.13 (C), 129.88 (CH), 129.82 (CH), 127.96 (CH), 127.45 (CH), 107.89 (CH_2), 83.47 (C), 53.73 (CH_2), 52.05 (CH_2), 47.04 (CH), 24.90 (CH_3), 21.69 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{21}H_{31}BNO_4S$: 404.2080; found: 404.2061.

(Z)-3-ethylidene-4-((E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)-1-tosylpyrrolidine (2i)

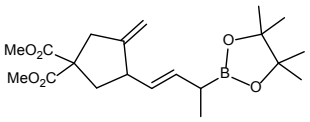


Following general borylative cyclization procedure, the product **2i** was obtained after 4.5 h at 50 °C as colourless oil (28 mg, 38%) using pentane/Et_2O 6:1 as eluent.

^{1}H RMN (300 MHz, $CDCl_3$) δ 7.66 (dt, *J* = 8.3 Hz, 1.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.52 (dt, *J* = 15.1, 7.5 Hz, 1H), 5.25 - 5.14 (m, 1H), 5.07 – 4.94 (m, 1H), 3.99 – 3.87 (m, 1H), 3.70 - 3.53 (m, 2H), 3.23 - 3.09 (m, 1H), 2.69 (t, *J* = 9.4 Hz, 1H), 2.43 (s, 3H), 1.63 (d, *J* = 7.4 Hz, 2H), 1.52 (ddd, *J* = 6.8, 3.7, 1.5 Hz, 3H), 1.23 (s, 12H). ^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) ^{13}C RMN (75 MHz, $CDCl_3$) δ 143.65 (C), 138.92 (C), 133.09

(C), 129.78 (CH), 129.31 (CH), 128.21 (CH), 127.99 (CH), 118.11 (CH), 83.44 (C), 53.72 (CH_2), 49.68 (CH_2), 46.87 (CH), 24.92 (CH_3), 21.68 (CH_3), 14.57 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{22}H_{33}BNO_4S$: 418.2229; found: 418.2217.

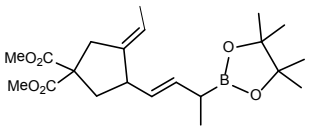
(E)-dimethyl 3-methylene-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)cyclopentane-1,1-dicarboxylate (2j)



Following general borylative cyclization procedure, the product **2j** was obtained after 3 h at 50 °C as colourless oil (151 mg, 68%) using hexane/Et_2O 10:1 as eluent. (Minimal amount of pinacol was detected by NMR).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.54 (dd, *J* = 15.3, 7.7 Hz, 1H), 5.17 (dd, *J* = 15.2, 8.1 Hz, 1H), 4.96 – 4.74 (m, 2H), 3.74 – 3.72 (m, 2H), 3.72 – 3.69 (m, 4H), 3.07 (d, *J* = 16.5 Hz, 2H), 2.97 – 2.85 (m, 1H), 2.53 (dd, *J* = 12.8, 7.4 Hz, 1H), 2.01 – 1.79 (m, 2H), 1.24 – 1.17 (s, 12H), 1.07 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 172.46 (C), 172.29 (C), 151.53 (C), 134.97 (CH), 128.60 (CH), 107.74 (CH_2), 83.24 (C), 58.54 (C), 52.91 (CH_3), 52.84 (CH_3), 47.04 (CH), 41.04 (CH_2), 40.33 (CH_2), 24.81 (CH_3), 15.18 (CH_3).HRMS-ESI: $[MH]^+$ Calcd. for $C_{20}H_{32}BO_6$: 379.2286; found: 379.2294.

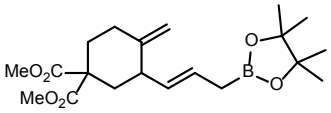
(E)-dimethyl 3-ethylidene-4-((E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)cyclopentane-1,1-dicarboxylate (2k)



Following general borylative cyclization procedure, the product **2k** was obtained after 4 h at 50°C as colourless oil (58 mg, 74%) using hexane/Et_2O 10:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.49 (dt, J = 21.0, 10.6 Hz, 1H), 5.25 – 5.05 (m, 2H), 3.73 (d, J = 3.1 Hz, 6H), 3.02 (d, J = 17.4 Hz, 2H), 2.80 (d, J = 17.3 Hz, 1H), 2.51 (dd, J = 12.7, 7.0 Hz, 1H), 1.98 – 1.78 (m, 2H), 1.61 (dd, J = 17.6, 7.4 Hz, 3H), 1.25 (d, J = 11.4 Hz, 12H), 1.05 (t, J = 9.3 Hz, 3H).^{13}C NMR (76 MHz, $CDCl_3$) δ 172.55 (C), 172.51 (C), 142.24 (C), 134.71 (CH), 129.10 (CH), 117.54 (CH), 83.59 (C), 58.61 (C), 52.84 (CH_3), 52.78 (CH_3), 47.07 (CH), 41.15 (CH_2), 36.89 (CH_2), 25.14 (CH_3), 15.16 (CH_3), 14.62 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{21}H_{33}BO_6Na$: 415.2262; found: 415.2280.

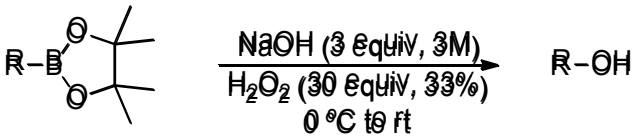
(E)-dimethyl 4-methylene-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)cyclohexane-1,1-dicarboxylate (4a)



Following general borylative cyclization procedure, the product **4a** was obtained after 6 h at 50°C as colourless oil (29 mg, 36%) using pentane/Et_2O 8:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.59 – 5.44 (m, 1H), 5.37 (m, 1H), 4.69 (dd, *J* = 11.2, 0.78 Hz, 2H), 3.76 (s, 3H), 3.69 (s, 3H), 2.83 – 2.68 (m, 1H), 2.47 – 2.28 (m, 3H), 2.15 (dt, *J* = 14.7, 5.3 Hz, 1H), 1.82 – 1.61 (m, 4H), 1.24 (s, 12H). ^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 172.31 (C), 172.52 (C), 149.51 (C), 131.32 (CH), 126.59 (CH), 107.92 (CH_2), 83.49 (C), 55.10 (C), 52.63 (CH_3), 52.53 (CH_3), 42.47 (CH), 38.30 (CH_2), 32.48 (CH_2), 32.03 (CH_2), 25.02 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{20}H_{31}BO_6Na$: 401.2120; found: 401.2108.

7. General procedure for oxidation of allylboronates and characterization of resulting alcohols.

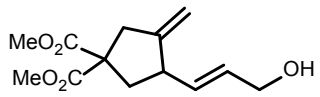


Scheme 3

Alcohols were prepared by standard conditions for oxidation of allylboronates. To a solution of corresponding allylboronate (0.14 mmol, 1 equiv) in THF (5 mL), 0.14 mL of an aqueous solution of NaOH (3M, 0.42 mmol, 3 equiv) was added slowly at room temperature. Then, the mixture was cooled to 0 ºC and 0.45 mL of a solution of H_2O_2 (33% w/v, 4.37 mmol, 30 equiv) was added dropwise. After addition, the reaction was stirred at room temperature for 1-5 h. Then, water and Et_2O were added into the resulting mixture. The aqueous layer was separated and extracted with Et_2O (3 x 10 mL). The combined organic phases were dried over anhydrous Mg_2SO_4 and filtered through anhydrous Na_2SO_4. The solvent was removed under vacuum and the crude was purified

by flash chromatography (hexane/EtOAc) molybdophosphoric acid us stain (2.6 mmol/100 mL ethanol).

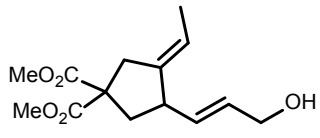
(E)-dimethyl 3-(3-hydroxyprop-1-en-1-yl)-4-methylenecyclopentane-1,1-dicarboxylate (5a)



Following general oxidation procedure using **2a** as substrate, the product **5a** was obtained after 1.5 h at room temperature as colourless oil (46 mg, 90%) using hexane/EtOAc 2:1 as eluent.

^{1}H NMR (300 MHz, CD_3Cl) δ 5.71 (dt, *J* = 15.8, 5.6 Hz, 1H), 5.54 (dd, *J* = 15.3, 7.9 Hz, 1H), 4.99 (q, *J* = 2.4 Hz, 1H), 4.81 (q, *J* = 2.2 Hz, 1H), 4.14 (d, *J* = 5.4 Hz, 2H), 3.75 (m, 4H), 3.73 (s, 3H), 3.26 - 3.13 (m, 1H), 3.13 - 3.02 (m, 1H), 2.95 (ddd, *J* = 17.1, 4.6, 2.3 Hz, 1H), 2.58 (dd, *J* = 12.3, 8.4 Hz, 1H), 2.07 – 1.95 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 172.28 (C), 172.10 (C), 150.56 (C), 133.14 (CH), 131.05 (CH), 108.39 (CH_2), 63.56 (C), 58.66 (CH_2), 53.00 (CH_3), 52.95 (CH_3), 46.24 (CH), 40.61 (CH_2), 40.48 (CH_2). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{13}H_{18}O_5Na$: 277.1057; found: 277.1053.

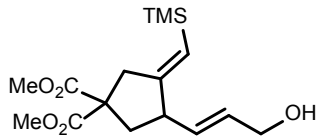
(E)-dimethyl 3-ethylidene-4-((E)-3-hydroxyprop-1-en-1-yl)cyclopentane-1,1-dicarboxylate (5b)



Following general oxidation procedure using **2b** as substrate, the product **5b** was obtained after 1.15 h at room temperature as colourless oil (35mg, 92%) using hexane/EtOAc 2:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67 (m, 1H), 5.47 (ddt, *J* = 15.3, 8.1, 1.2 Hz, 1H), 5.19 (m, 1H), 4.12 (t, *J* = 4.9 Hz, 2H), 3.82 (m, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.13 (d, *J* = 8.6 Hz, 1H), 3.01 (m, 1H), 2.85 (m, 1H), 2.54 (ddd, *J* = 12.8, 7.3, 1.5 Hz, 1H), 1.94 (dd, *J* = 12.8, 11.3 Hz, 1H), 1.60 (ddd, *J* = 6.7, 3.9, 1.7 Hz, 3H).^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 172.44 (C), 172.35 (C), 141.38 (C), 133.72 (CH), 130.88 (CH), 118.28 (CH), 63.59 (CH_2), 58.74 (C), 52.97 (CH_3), 52.91 (CH_3), 46.36 (CH), 40.74 (CH_2), 36.98 (CH_2), 14.73 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{14}H_{20}O_5Na$: 291.1213; found: 291.1009.

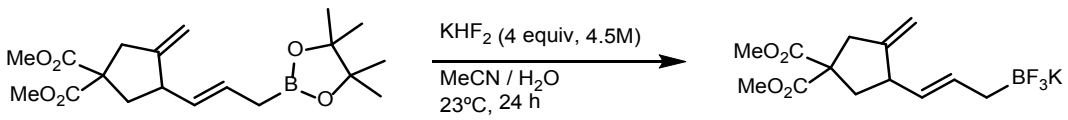
(E)-dimethyl 3-((E)-3-hydroxyprop-1-en-1-yl)-4-((trimethylsilyl)methylene)cyclopentane-1,1-dicarboxylate (5c)



Following general oxidation procedure using **2c** as substrate, the product **5c** was obtained after 1.5 h at room temperature. as colourless oil (38mg, 83%) using hexane/EtOAc 2:1 as eluent. When the general procedure for borylative cyclization (6 h at 70 °C) was applied to the substrate **1c** and then, the solvent was totally evaporated and the general oxidation procedure for boronates (13.5 h at room temperature) was applied to the crude, the product **5c** was obtained in a similar yield (78%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68 (dt, *J* = 15.5, 5.9 Hz, 1H), 5.49 (dd, *J* = 15.3, 9.0 Hz, 1H), 5.35 - 5.32 (m, 1H), 4.13 (dd, *J* = 5.6, 1.1 Hz, 2H), 3.74 (s, 3H), 3.71 (s, 3H), 3.29 (dd, *J* = 16.3, 8.1 Hz, 1H), 2.74 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.12 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.73 – 1.35 (m, 2H), 0.02 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$, DEPT-135) δ 172.43 (C), 172.1 (C), 149.66 (C), 134.38 (CH), 131.21 (CH), 120.62 (CH), 65.21 (C), 63.51 (CH_2), 52.75 (CH), 52.67 (CH_3), 51.48 (CH_3), 39.12 (CH_2), 19.70 (CH_2), 1.07 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{16}H_{26}O_5NaSi$: 349.1441; found: 349.1455.

8. Trifluoroborate salts of allylboronates: Formation and experimental data of potassium (E)-(3-(4,4-bis(methoxycarbonyl)-2-methylenecyclopentyl)allyl)trifluoroborato (6)

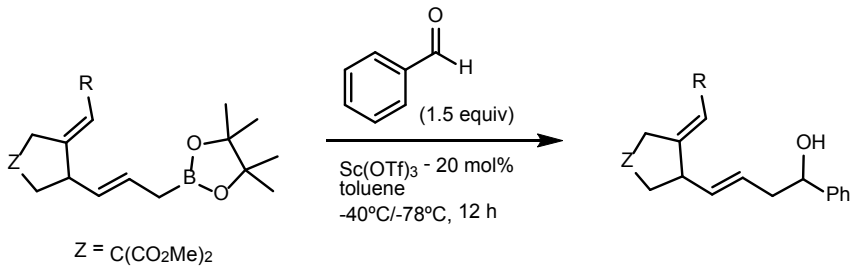


Scheme 4

To a solution of allylboronate **2a** (195 mg, 1 equiv) in acetonitrile (2 mL) at room temperature was added slowly aqueous solution of KHF_2 (2 mL, 4.0 equiv, 4.5 M). After 12 h at room temperature, the solvent was evaporated, and the remained white crude was

washed successively with hot acetone to separate from inorganic impurities after filtration. The solvent was totally removed under vacuum and the white solid obtained washed with warm Et_2O and dried under vacuum line without further purification. The trifluoroborate salt **6** was obtained as a white solid (129 mg, 70%). ^{1}H-NMR (300 MHz, CD_3OD): δ = 5.65-5.50 (m, 2H), 5.0 (d, 2H), 3.75 (d, 6H), 3.1-2.75 (m, 3H), 2.50-2.48 (m, 1H), 1.90-1.85 (t, 1H). ^{1}F NMR (284 MHz, CD_3OD) δ -155.98. ^{13}C- NMR (300 MHz, CD_3OD): δ = 174.36 (s), 153.62 (s), 127.69 (s), 123.53 (s), 107.56(s), 59.69 (s), 52.87 (s), 42.34 (s), 40.82 (s) *C*-B signal not observed due to quadrupolar relaxation. HRMS-ESI: $[M]^-$ Calcd. for $C_{13}H_{17}BF_3O_4$: 305.1177; found: 305.1182.

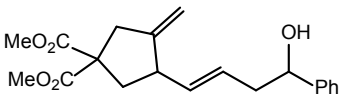
9. General procedure for allylation reactions of allylboronates and characterization of resulting α-alcohols.



Scheme 5

α-Alcohols were prepared by standard conditions for allylation reactions of boronates. To a stirred solution of corresponding allylboronate in anhydrous toluene (1.0-2.0 mL), $Sc(OTf)_3$ (10-20 mol%) was added slowly at room temperature. Then, the mixture was cooled to -40ºC and benzaldehyde (1.5 – 2.0 equiv) was added dropwise. After addition, the reaction was stirred for 12 h at the temperature indicated below for each compound. After indicated time, solvent was removed under vacuum and the reaction crude was purified by flash chromatography (hexane/EtOAc) molybdophosphoric acid us stain (2.6 mmol/100 mL ethanol).

Dimethyl 3-(1-hydroxy-1-phenylbut-3-en-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (7a).

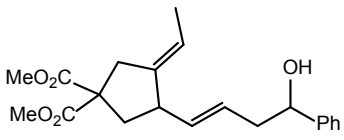
Following the general allylation procedure using **2a** (30 mg, 0.08 mmol) as substrate, 

$Sc(OTf)_3$ (8.20 mg, 20 mol%) and benzaldehyde (17 µL, 0.17 mmol). The product **7a** was obtained as an inseparable mixture of compounds, presumably diastereomers due to the presence of two stereogenic C, after 12 h at -78ºC as colourless oil (26 mg, 91%) using hexane/EtOAc 5:1 as eluent.

For both **7a** and **7b**, C-NMR spectra show signal splitting for some carbons, which has been assigned to the presence of two diastereoisomers, as a consequence of the two stereogenic centers contained in these molecules. The corresponding peaks are listed below. *E* configuration of the allyl C-C double bond has been assigned after the coupling constant that could be resolved for **7b**. Even in the mixture of compounds, coupling constant could be measured (15 Hz).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 4H), 7.23 – 7.18 (m, 1H), 5.47 – 5.19 (m, 2H), 4.86 (dq, *J* = 12.3, 2.3 Hz, 1H), 4.73 – 4.56 (m, 2H), 3.65 (s, 6H), 3.17 – 2.78 (m, 3H), 2.55 – 2.34 (m, 3H), 1.89 (ddd, *J* = 13.1, 10.8, 2.5 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$, δ 172.30 (C), 172.18 (C), 150.84 (C), 150.81 (C), 144.03 (C), 143.98 (C), 135.03 (CH), 135.01 (CH), 128.55 (CH), 128.54 (CH), 127.78 (CH), 127.67 (CH), 127.64 (CH), 126.04 (CH_2), 125.97 (CH_2), 108.21 (CH_2), 108.17 (CH_2), 73.82 (CH), 73.80 (CH), 58.62 (CH_2), 58.60 (CH_2), 52.97 (C), 52.93 (C), 52.92 (CH_3), 46.77 (CH_3), 46.76 (CH_3), 42.65 (CH), 42.62 (CH), 40.74 (CH), 40.70 (CH), 40.39 (CH_2), 40.35 (CH_2). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{20}H_{24}O_5Na$: 367.1515; found: 367.1509.

(E)-dimethyl 3-ethylidene-4-(1-hydroxy-1-phenylbut-3-en-2-yl)cyclopentane-1,1-dicarboxylate (7b).



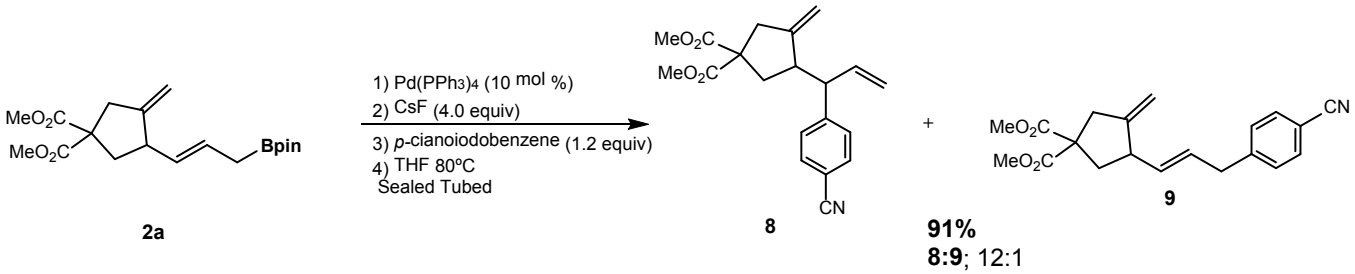
Following general allylation procedure using **2b** (73 mg, 0.20 mmol) as substrate, $Sc(OTf)_3$ (27 mg, 20 mol%) and benzaldehyde (42 µL, 0.31 mmol). The product **7b** was obtained as an inseparable mixture of compounds, presumably diastereomers, after 12 h at -40ºC as colourless oil (59 mg, 62%) using hexane/EtOAc 8:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (m, 5H), 5.37 (m, 2H), 5.05 (m, 1H), 4.70 (dd, *J* = 12.1, 6.3 Hz, 1H), 3.73 (m, 7H), 2.86 (m, 3H), 2.48 (m, 3H), 1.89 (psudo t, *J* = 14 Hz, 1H), 1.56 (m, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 172.46 (C), 172.44 (C), 172,4 (C),

144.01 (C), 143.96 (C), 141.60 (C), 141.42 (C), 135.63 (CH), 135.33 (CH), 128.51 (CH), 127.91(CH), 127.56(CH), 127.41 (CH), 127.11 (CH), 126.11 (CH), 126.03 (CH), 125.98 (CH), 118.07 (CH), 117.77 (CH), 73.78 (CH), 73.45 (CH), 58.68 (C), 58.35 (C), 52.92 (CH_3), 52.62 (CH_3), 48.79 (CH), 48.49 (CH), 46.87 (CH_3), 46.36 (CH_3), 42.69 (CH_2), 42.37 (CH_2), 40.83 (CH_2), 40.36 (CH_2), 36.92 (CH_2), 36.48 (CH_2), 14.72 (CH_3) 14.34 (CH_3). HRMS-ESI: $[MNH_4]^+$ Calcd. for $C_{21}H_{30}NO_5$: 376.2118; found: 376.2135.

10. Suzuki cross-coupling reactions of allylboronates and experimental data of resulting compounds.

Dimethyl 3-(1-(4-cyanophenyl)allyl)-4-methylenecyclopentane-1,1-dicarboxylate (8) and dimethyl (E)-3-(3-(4-cyanophenyl)prop-1-en-1-yl)-4-methylenecyclopentane-1,1-dicarboxylate (9).



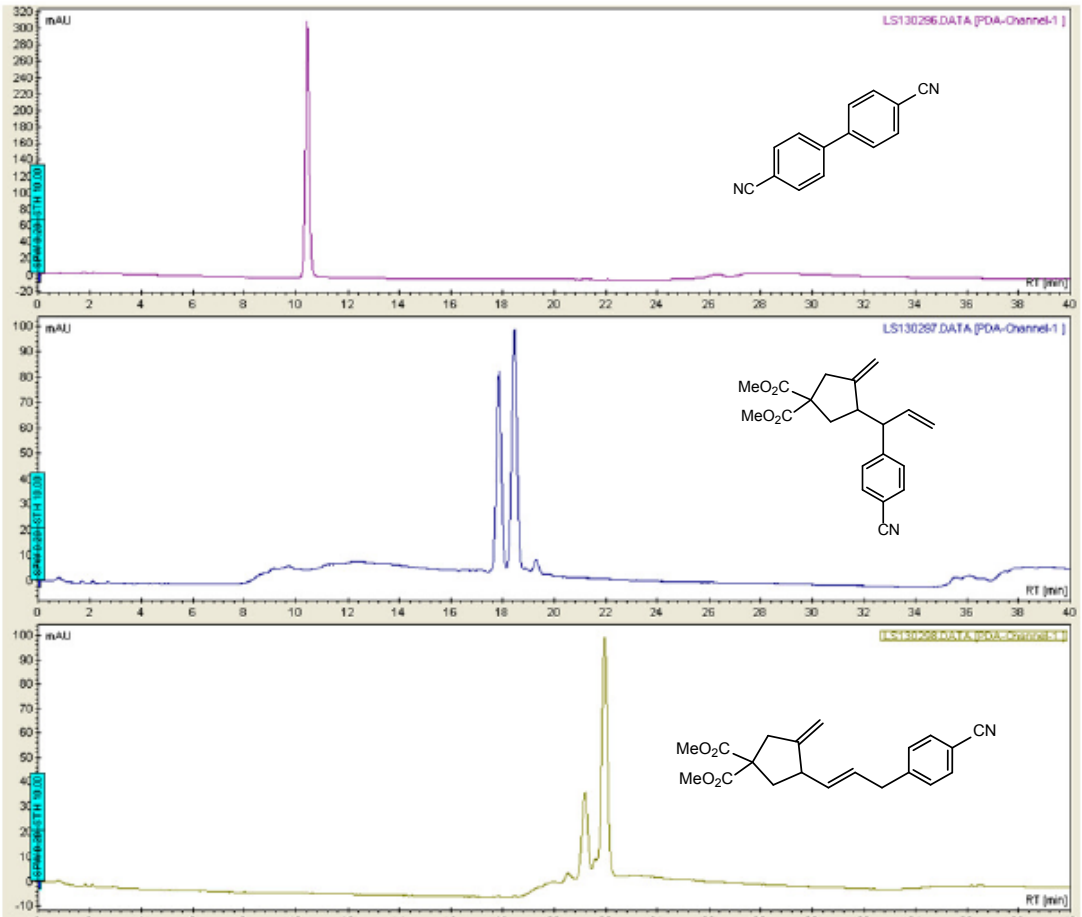
Scheme 6

To a solution of *p*-cianoiodobenzene (14 mg, 0.06 mmol) in dry THF (1.5 mL), under Ar atmosphere, were added the allylboronate **2a** (33 mg, 0.091 mmol), CsF (55.7 mg, 0.36 mmol) and $Pd(PPh_3)_4$ (15.8 mg, 0.014 mmol) and the mixture was heated at 80ºC for 8 h in a sealed tube. After cooling to room temperature EtOAc (2 mL) was added, followed by

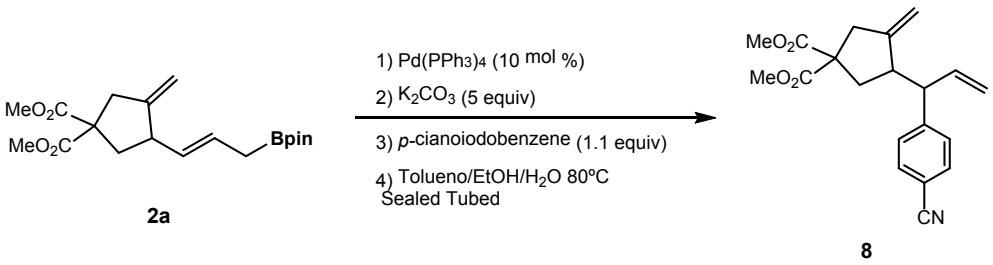
brine (2 mL). The layers were then separated and the aqueous layer further extracted with EtOAc (2 × 5 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and the solvent was removed under vacuum. The title products **8**, **9** (28.5 mg, 91.3%) was obtained as an inseparable mixture (12:1) and the yield was calculated by NMR using as internal pattern trichloroethylene due to inability of a good purification from homocoupling product [1,1'-biphenyl]-4,4'-dicarbonitrile. The mixture of two isomers was confirmed by GC-MS. The spectra data ^{1}H and ^{13}C NMR of the mixture were obtained from a pure fraction by flash chromatography using hexane/EtOAc 4:1 as eluent.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55-7.48 (m, 4H), 7.27-7.17 (d, J = 8.55 Hz, 4H,), 6-5.89 (m, $1H^{8}$), 5.63-5.47 (m, $1H^{9}$), 5.40-5.25 (m, $1H^{9}$), 5.12-5.01 (m, $2H^{8}$), 4.99-4.80 (m, $2H^{9}$), 4.86-4.67 (m, $2H^{8}$), 3.72-3.58 (m, 12H), 3.40 (m, $2H^{9}$), 3.38-3.25 (dd, J = 15.36, 6.47 Hz,1H), 3.16-2.78 (m, 5H), 2.57-2.44 (m, 1H), 2.33-2.11 (dd, J = 7.45, 8.10 Hz, 1H), 2.00-1.86 (m, 2H), 1.68-1.57 (m, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 172.23, 171.92, 171.84, 150.75, 150.43, 148.56, 148.34, 146.37, 146.14, 137.86, 133.72, 132.74, 132.39, 129.21, 129.12, 129.19, 128.14, 117.45, 117.21, 110.4, 110.10, 109.94, 108.16, 107.98, 58.46, 58.13, 54.31, 52.97, 52.88, 46.43, 46.25, 41.72, 41.64, 41.58, 40.56, 40.17, 38.96, 37.95, 33.83.

HPLC-CHROMATOGRAPHY ANALYSIS



Dimethyl 3-(1-(4-cyanophenyl)allyl)-4-methylenecyclopentane-1,1-dicarboxylate (8)



Scheme 7

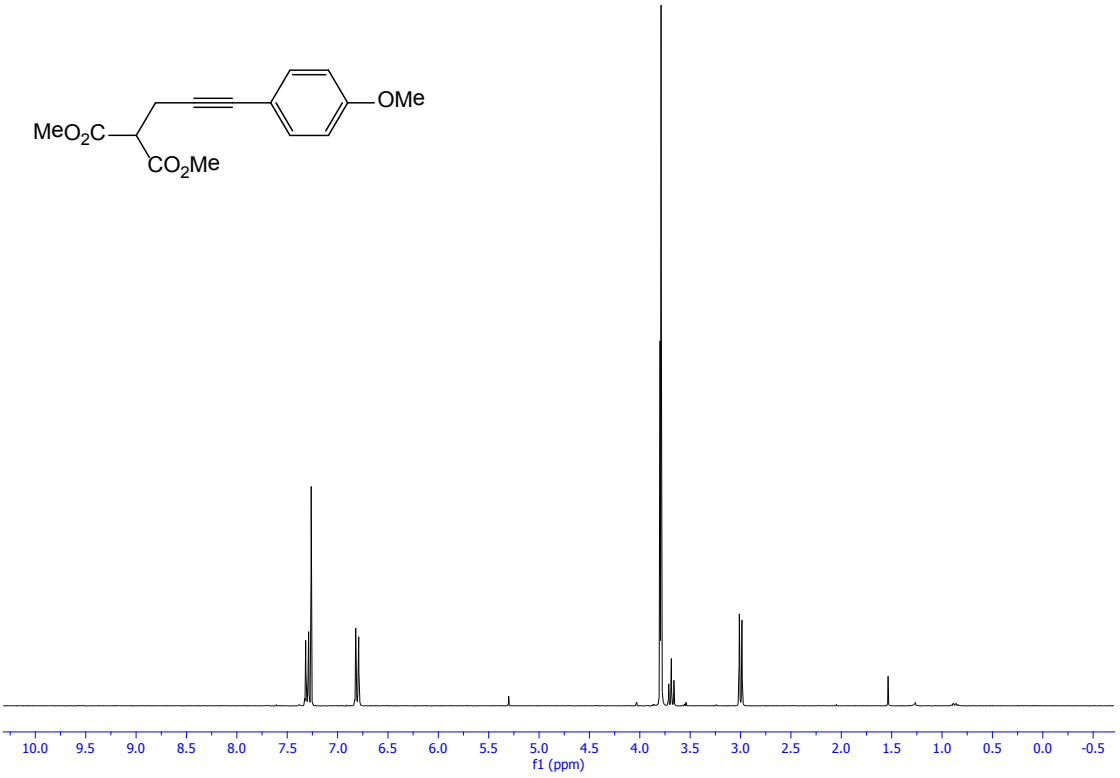
To a solution of *p*-cianoiodobenzene (35.8 mg, 0.26 mmol) in toluene (0.5 mL), EtOH (0.15 mL) and H_2O (0.15 mL) under Ar atmosphere, were added the allylboronate **2a** (94 mg, 0.268 mmol), K_2CO_3 (180.42 mg, 1.30 mmol) and $Pd(PPh_3)_4$ (30.16 mg, 0.026 mmol) and the mixture was heated at 80ºC for 8 h in a sealed tube. After cooling to room temperature the solvent was removed under vacuum and the crude was purified by flash chromatography (hexane/Et_2O 10:1) molybdophosphoric acid us stain (2.6 mmol/100 mL ethanol). For a complete purification this compound was purified once more by recristalization of the homocoupling product [1,1'-biphenyl]-4,4'-dicarbonitrile. The product **8** was obtained as an inseparable mixture of diastereomers compounds, as

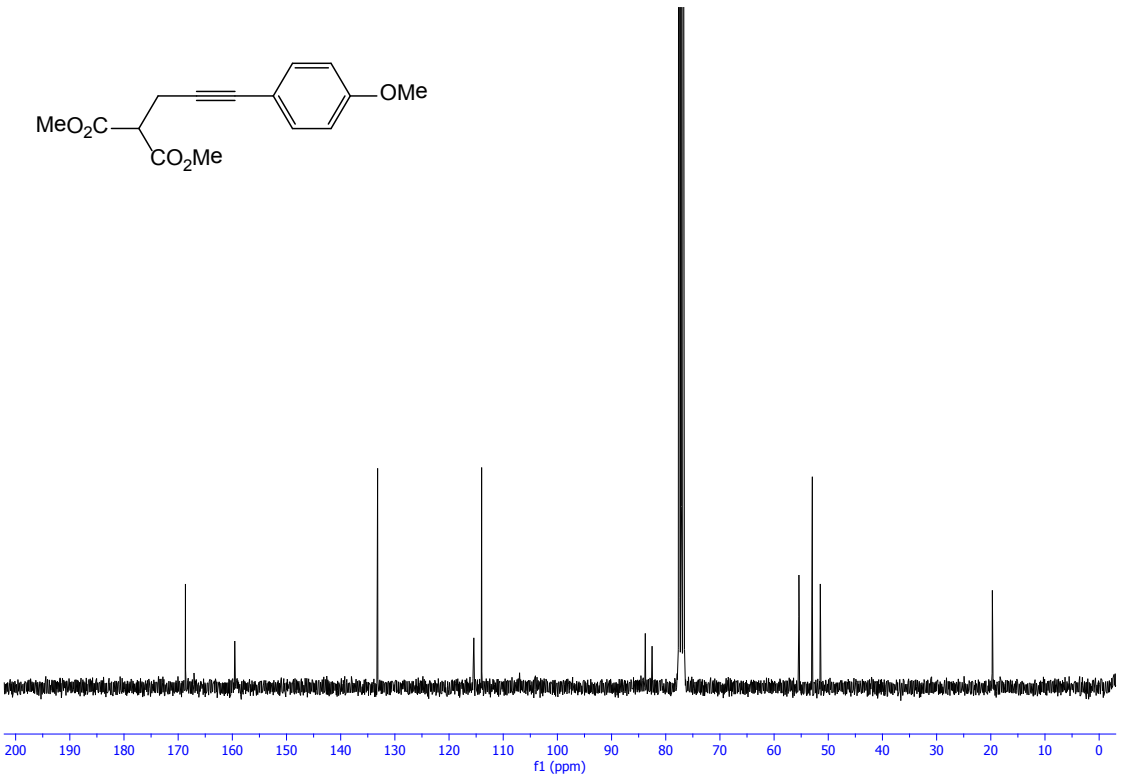
yellowish oil (36 mg, 43%). (Minimal amount of homocoupling product was detected by NMR).

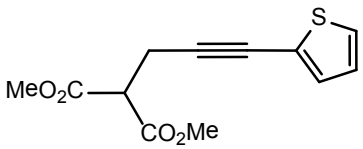
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.1, 1.4 Hz, 4H), 7.31 (d, *J* = 8.1 Hz, 4H), 6.09 – 5.80 (m, 2H), 5.13 (dd, *J* = 10.1, 5.5 Hz, 2H), 5.04 (dd, *J* = 12.1, 9.7 Hz, 2H), 4.93 – 4.79 (m, 2H), 3.70 (dd, *J* = 10.5, 7.1 Hz, 12H), 3.38 (t, *J* = 8.4 Hz, 2H), 3.09 – 2.80 (m, 6H), 2.58 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.41 – 2.25 (m, 2H), 2.08 – 1.92 (m, 1H), 1.75 – 1.60 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ 172.08 (C), 172.02 (C), 171.98 (C), 148.80 (C), 148.64 (C), 148.57 (C), 148.42 (C), 139.11 (CH), 137.94 (CH), 132.44 (CH), 132.41 (CH), 129.22 (CH), 129.12 (CH), 118.98 (C), 118.95 (C), 117.57 (CH_2), 117.31 (CH_2), 110.49 (C), 110.48 (C), 110.22 (CH_2), 109.68 (CH_2), 58.29 (C), 58.20 (C), 54.44 (CH), 53.84 (CH), 52.96 (CH_3), 52.91 (CH_3), 46.38 (CH), 46.19 (CH), 41.82 (CH_2), 41.75 (CH_2), 38.37 (CH_2), 38.05 (CH_2). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{20}H_{21}NO_4Na$: 362.1362; found: 362.1372.

11. ^{1}H-NMR and ^{13}C-NMR spectra

^{1}H-NMR and ^{13}C-NMR spectra of dienynes precursors.



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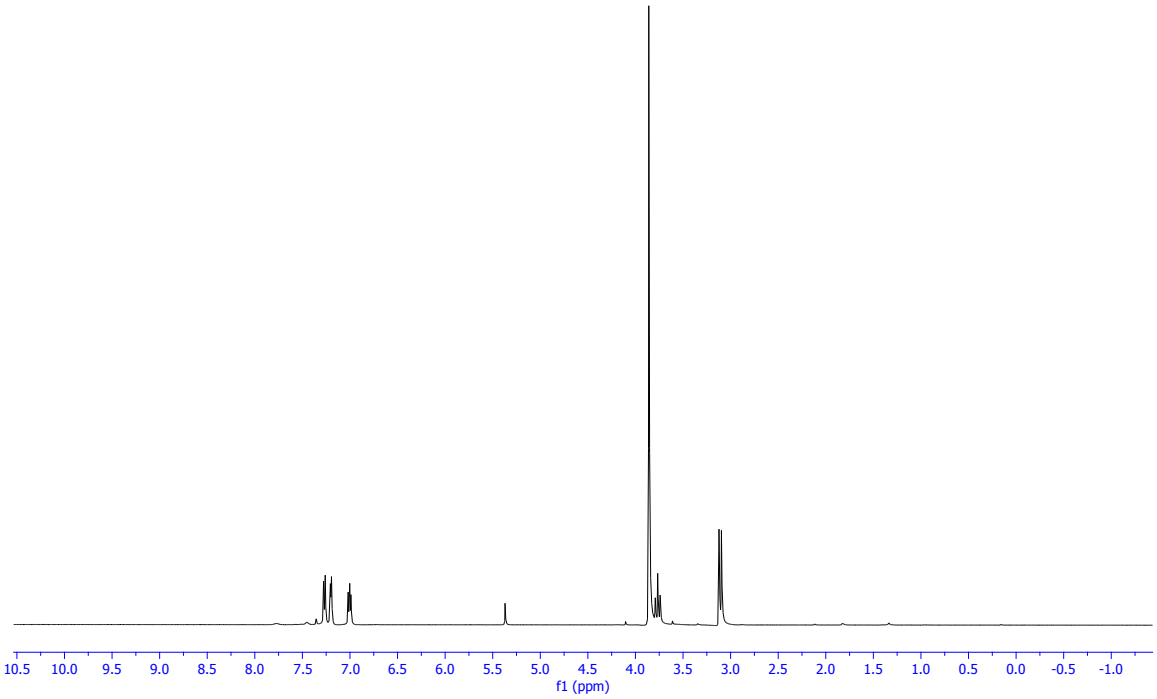
CO2Me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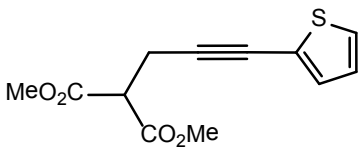
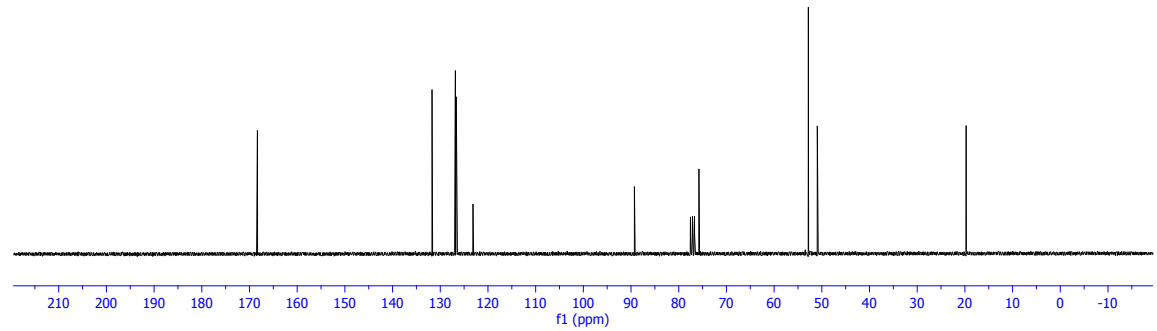
f1 (ppm)


S
MeO2C
CO2Me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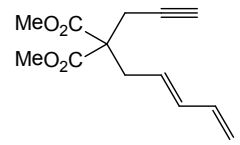
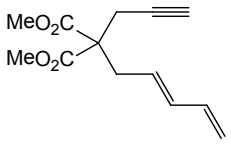
f1 (ppm)

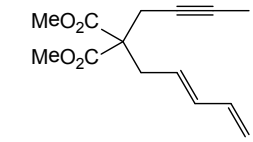
^{1}H-NMR and ^{13}C-NMR spectra of dienynes



1a



1a


MeO2C
MeO2C

1b

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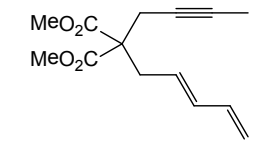
f1 (ppm)


MeO2C
MeO2C

1b

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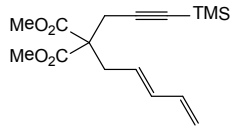
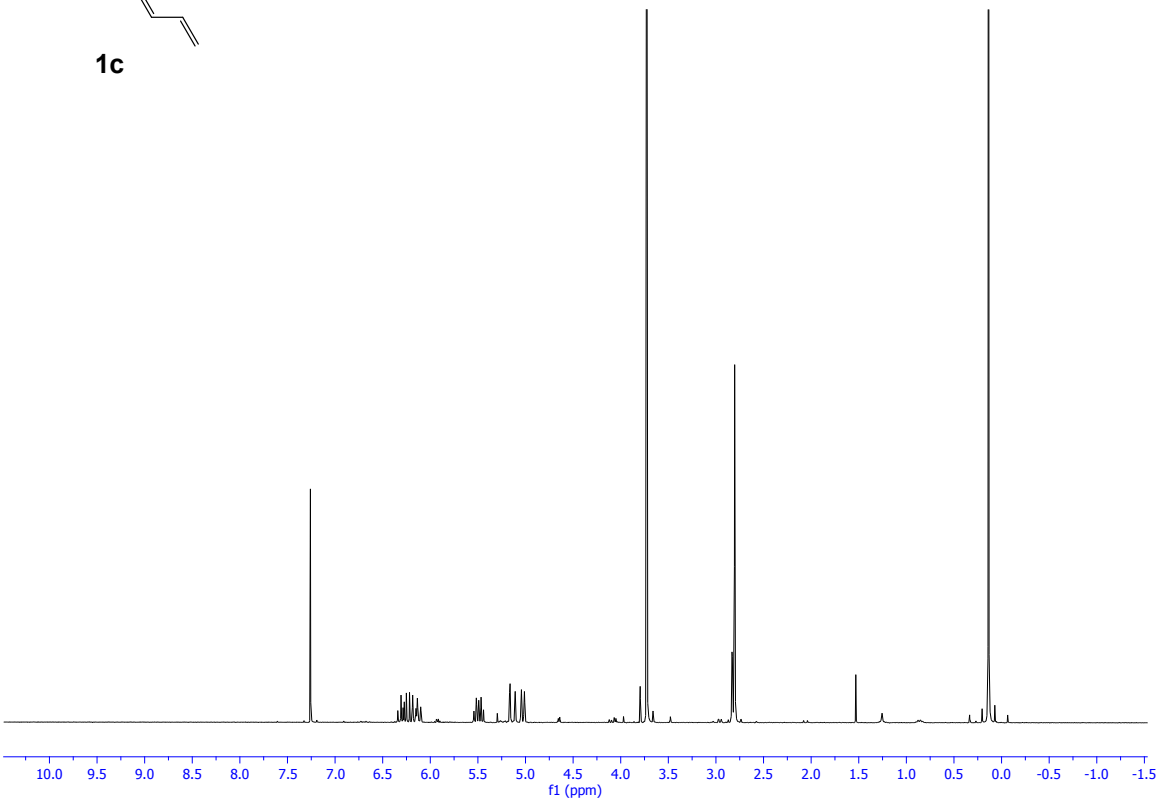
f1 (ppm)


MeO2C
MeO2C
TMS

1c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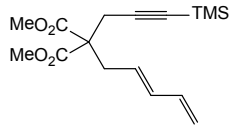
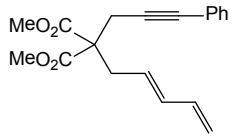
f1 (ppm)


MeO2C
MeO2C
TMS

1c

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO2C
MeO2C
Ph

1d

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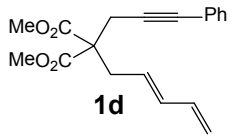
f1 (ppm)


MeO2C
MeO2C
Ph

1d

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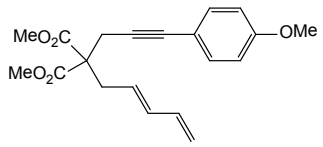
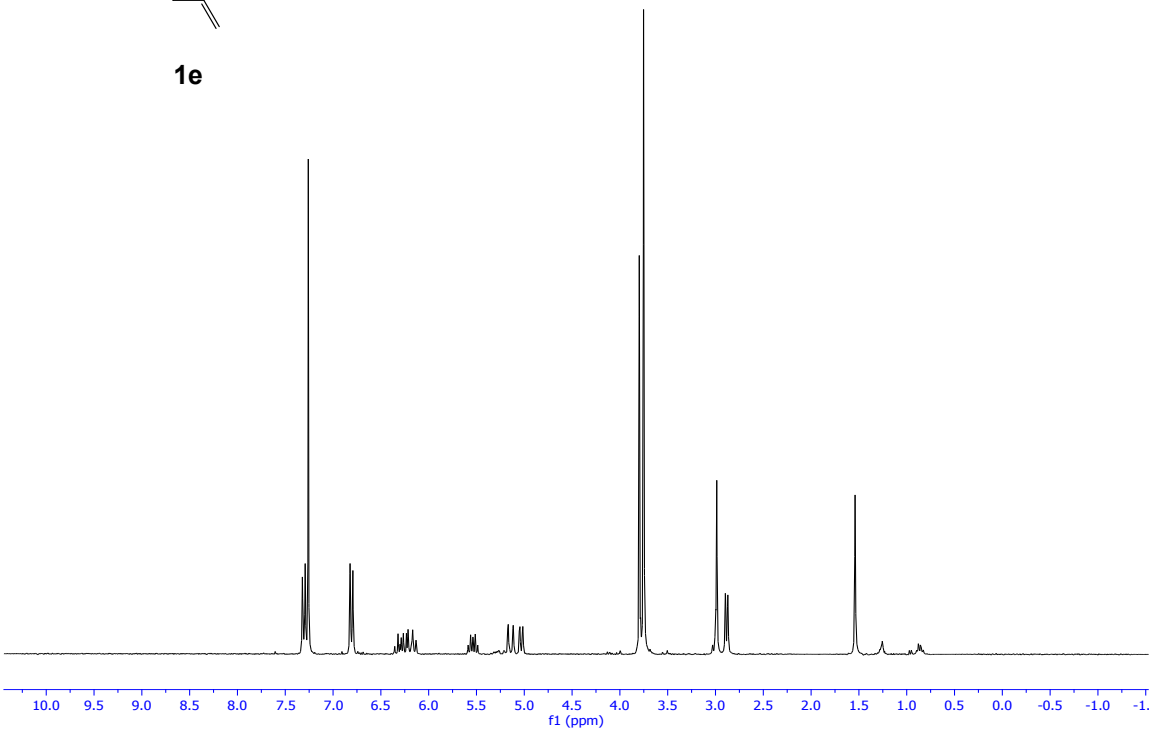
f1 (ppm)


MeO2C
MeO2C
OMe

1e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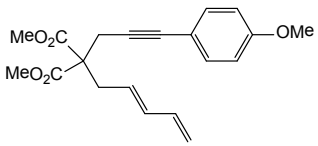
f1 (ppm)


MeO2C
MeO2C
OMe

1e

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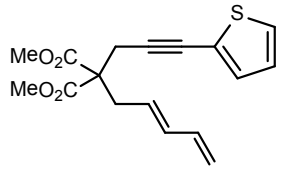
f1 (ppm)


S
MeO2C
MeO2C

1f

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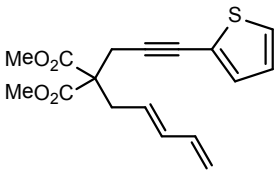
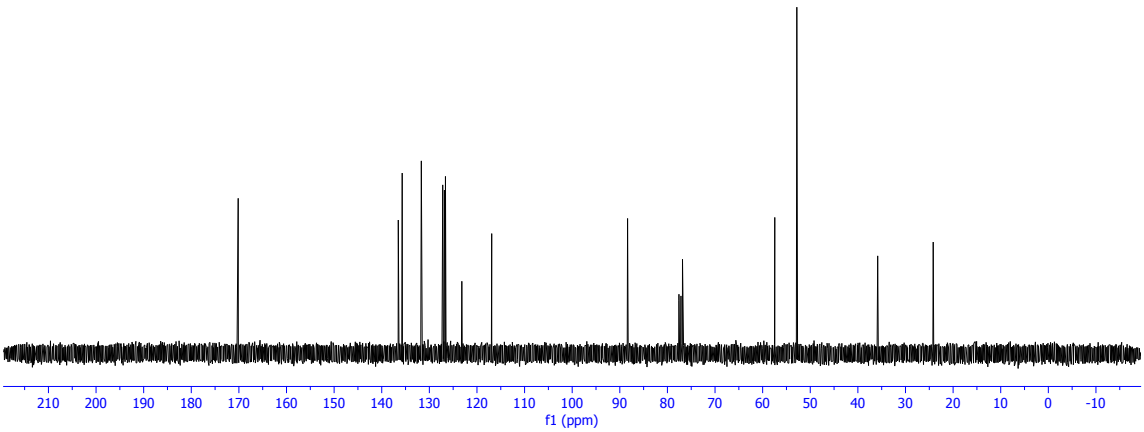
f1 (ppm)


S
MeO2C
MeO2C

1f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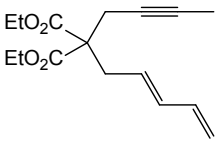
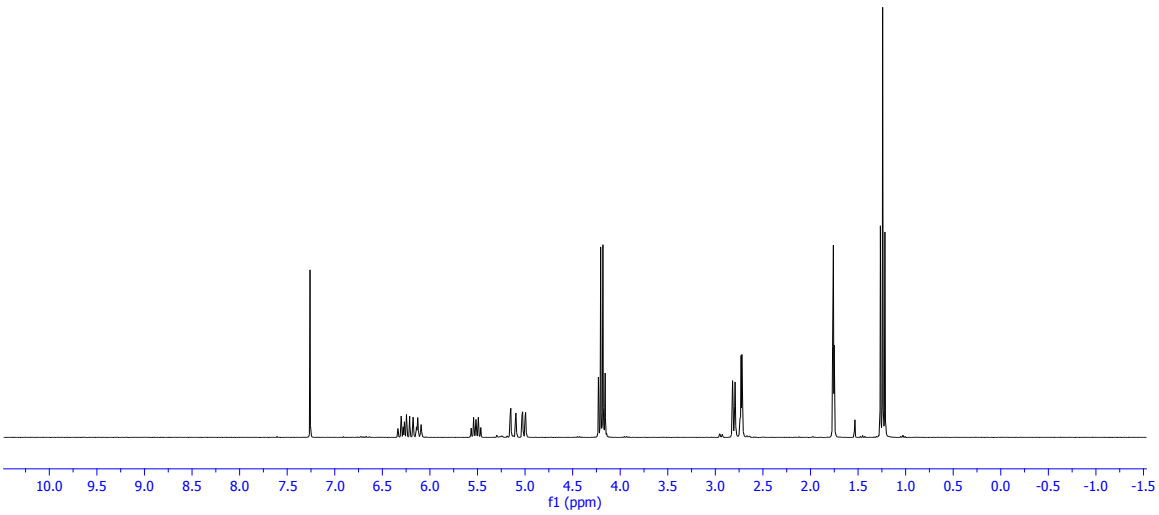
f1 (ppm)


EtO2C
EtO2C

1g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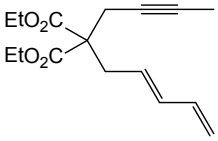
f1 (ppm)


EtO2C
EtO2C

1g

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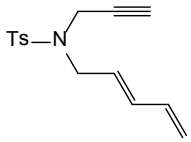
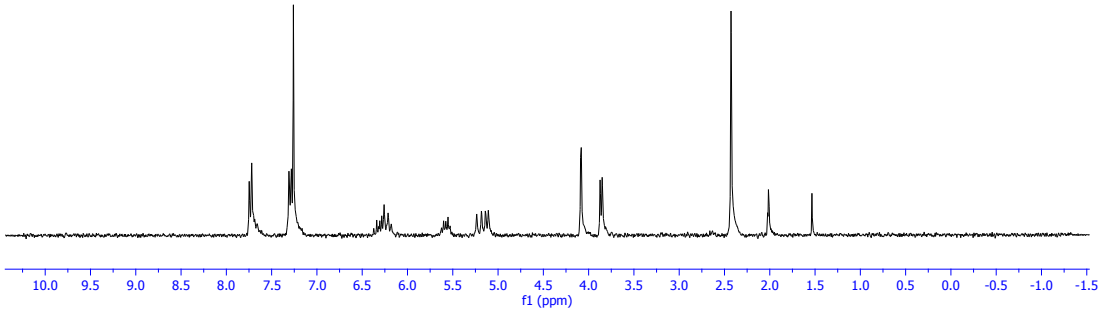

Ts—N

1h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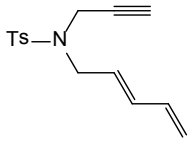
f1 (ppm)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1h

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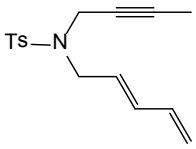
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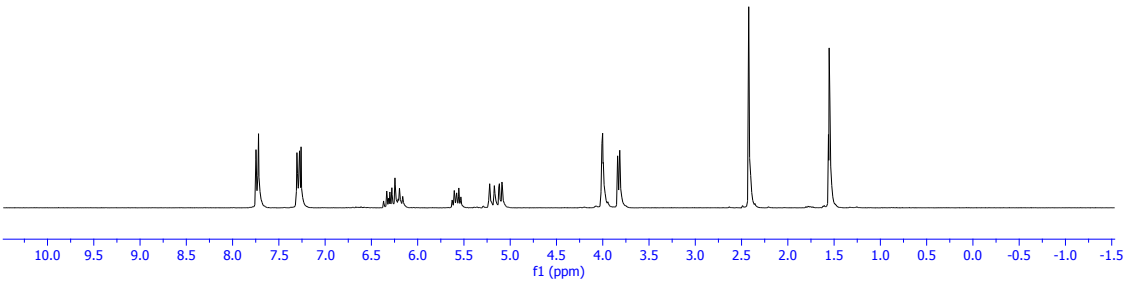
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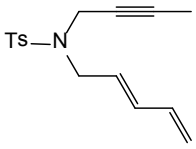
f1 (ppm)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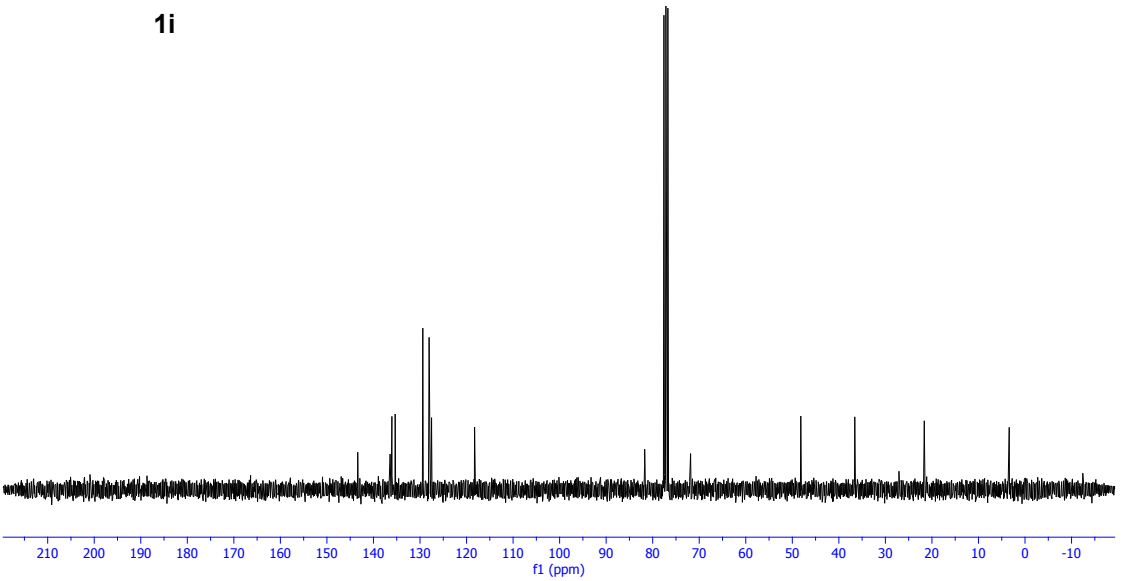
1i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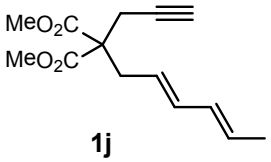
MeO2C
MeO2C

1j

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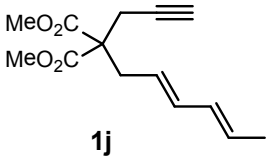
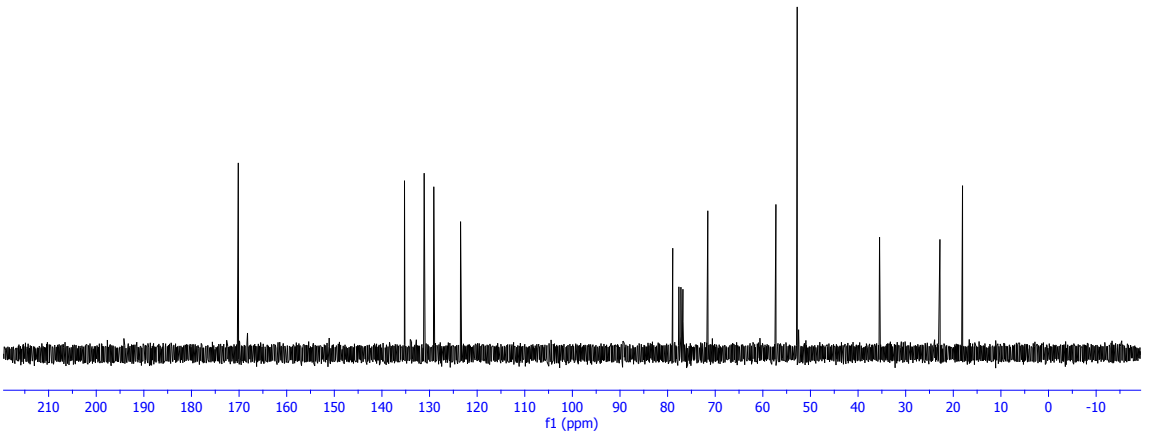
f1 (ppm)


MeO2C
MeO2C

1j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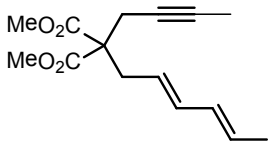
f1 (ppm)


MeO2C
MeO2C

1k

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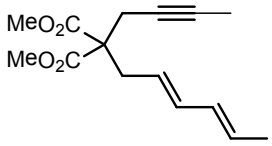
f1 (ppm)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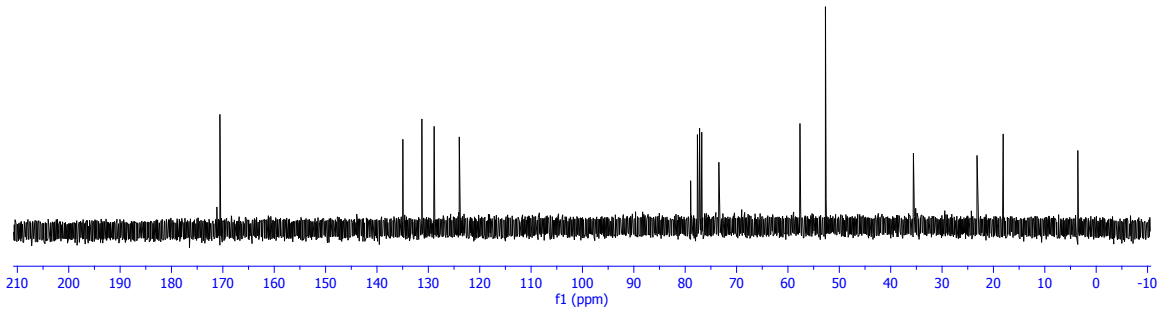
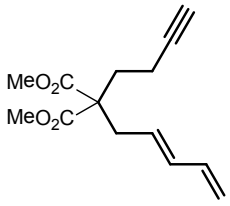
MeO2C

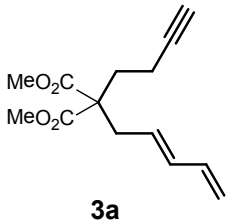
1k


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO2C
MeO2C

3a

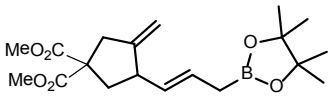
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


MeO2C
MeO2C

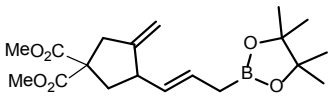
3a

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

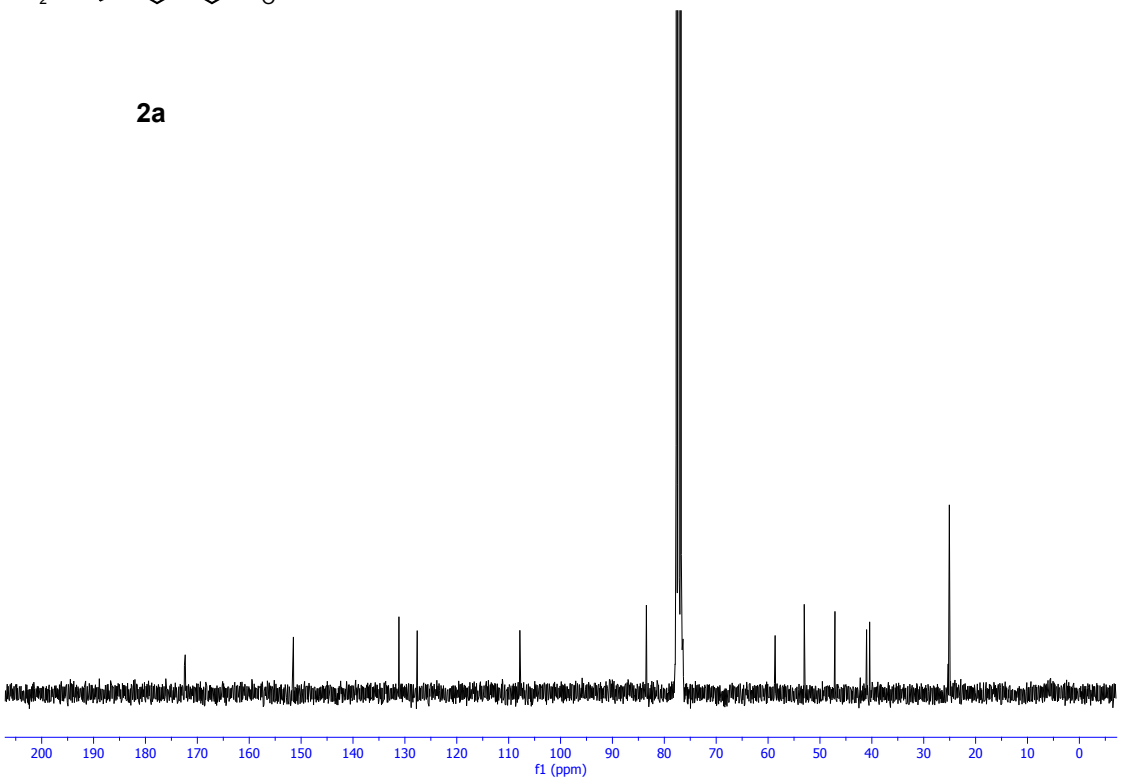
^{1}H-NMR and ^{13}C-NMR spectra of allylboronates from dienynes

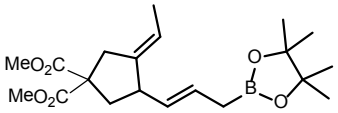


2a

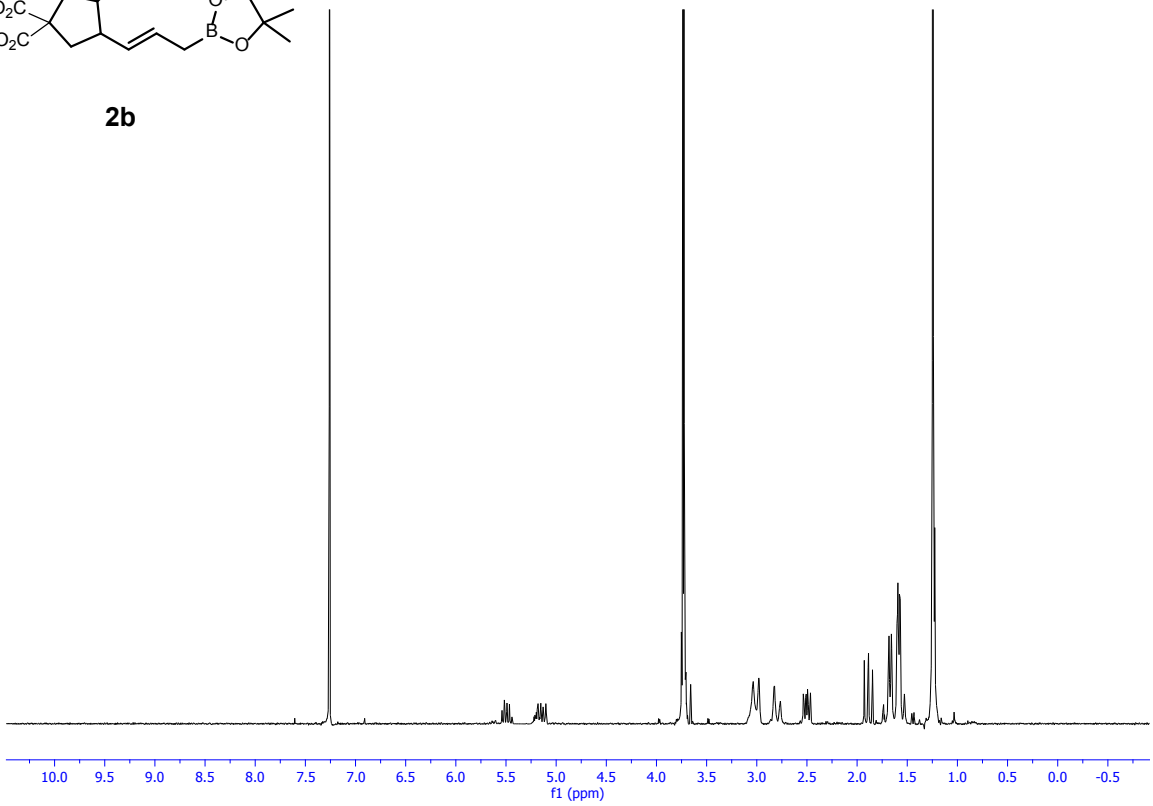


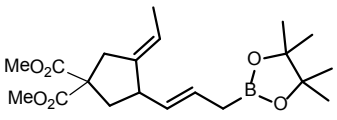
2a




MeO2C
MeO2C
O
B
O

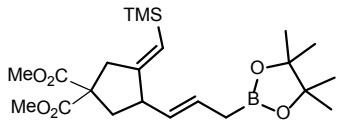
2b


10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


MeO2C
MeO2C
O
B
O

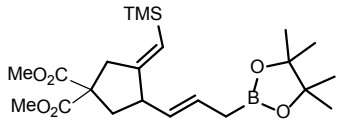
2b

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

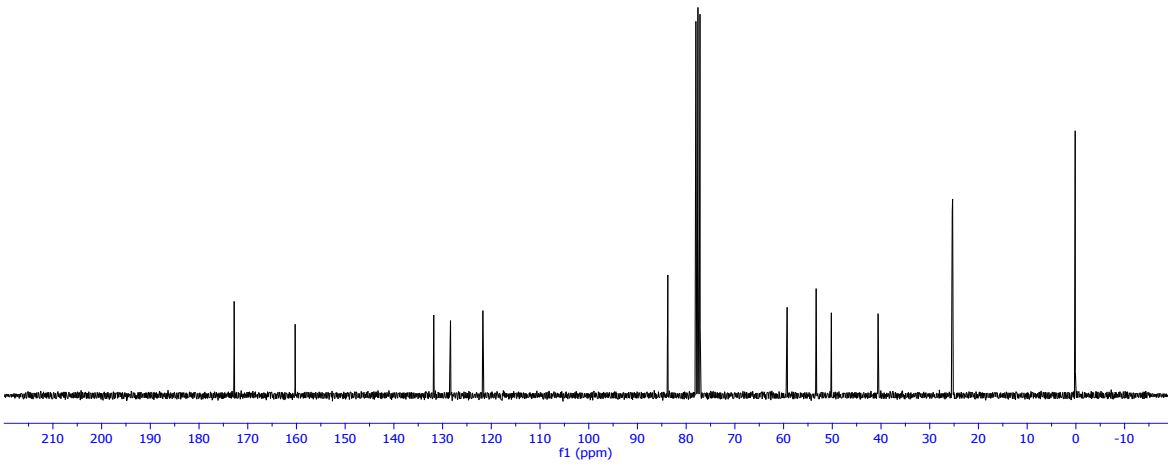

TMS
MeO2C
MeO2C
O
B
O

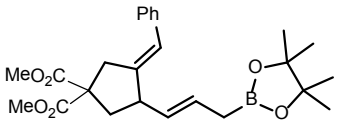
2c

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.
f1 (ppm)


TMS
MeO2C
MeO2C
O
B
O

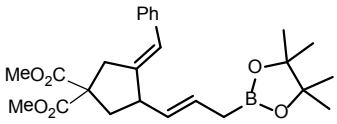
2c


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
MeO2C
MeO2C
O
B
O

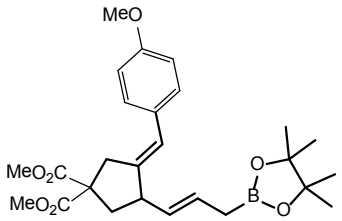
2d

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.
f1 (ppm)


Ph
MeO2C
MeO2C
O
B
O

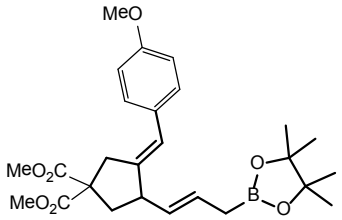
2d

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
MeO2C
MeO2C
O
B
O

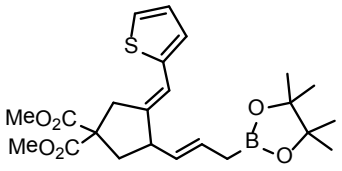
2e

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


MeO
MeO2C
MeO2C
O
B
O

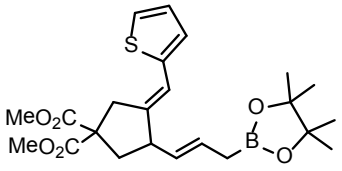
2e

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

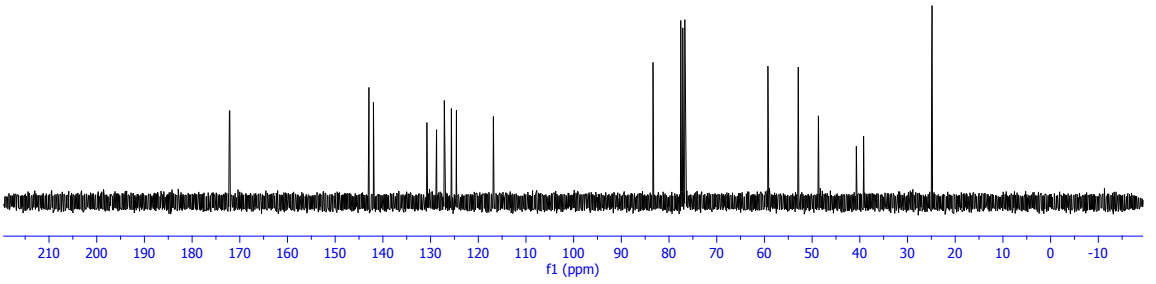

S
MeO2C
MeO2C
O
B
O

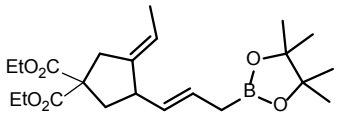
2f

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


S
MeO2C
MeO2C
O
B
O

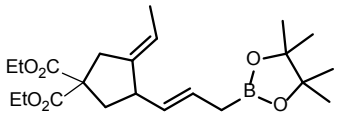
2f


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


EtO2C
EtO2C
O
B
O

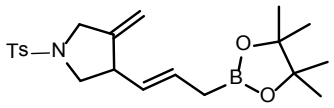
2g

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


EtO2C
EtO2C
O
B
O

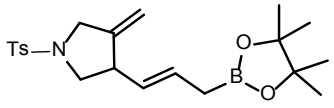
2g

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ts—N
O
B
O

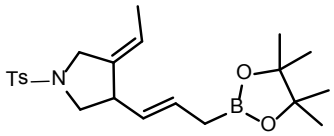
2h

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.
f1 (ppm)


Ts—N
O
B
O

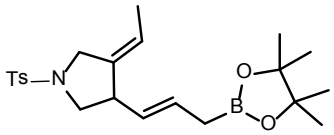
2h

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ts—N
O
B
O

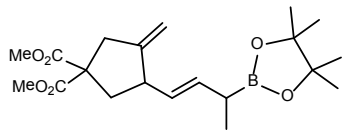
2i

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


Ts—N
O
B
O

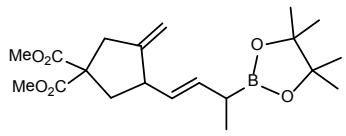
2i

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

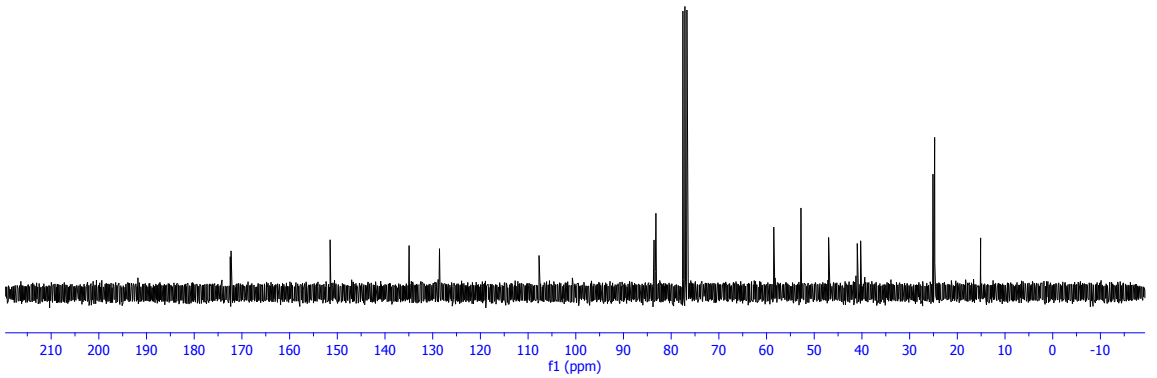

MeO2C
MeO2C
O
B
O

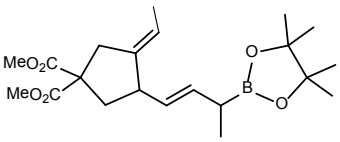
2j

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


MeO2C
MeO2C
O
B
O

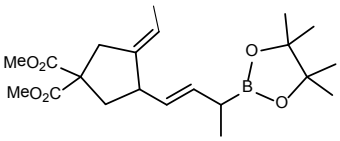
2j


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

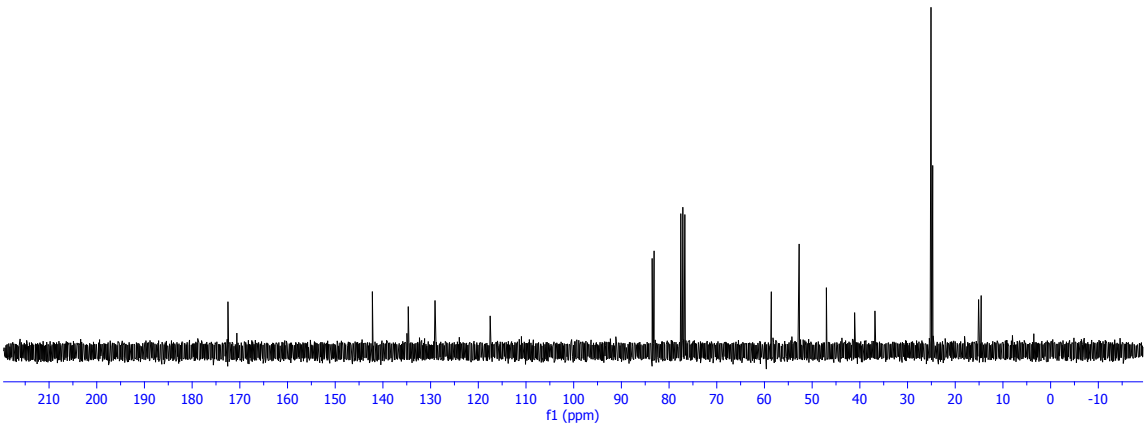

MeO2C
MeO2C
O
B
O

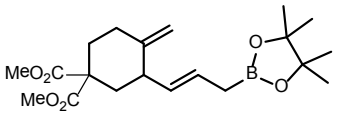
2k

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


MeO2C
MeO2C
O
B
O

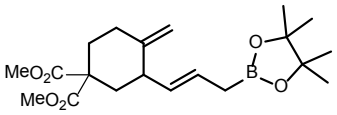
2k


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

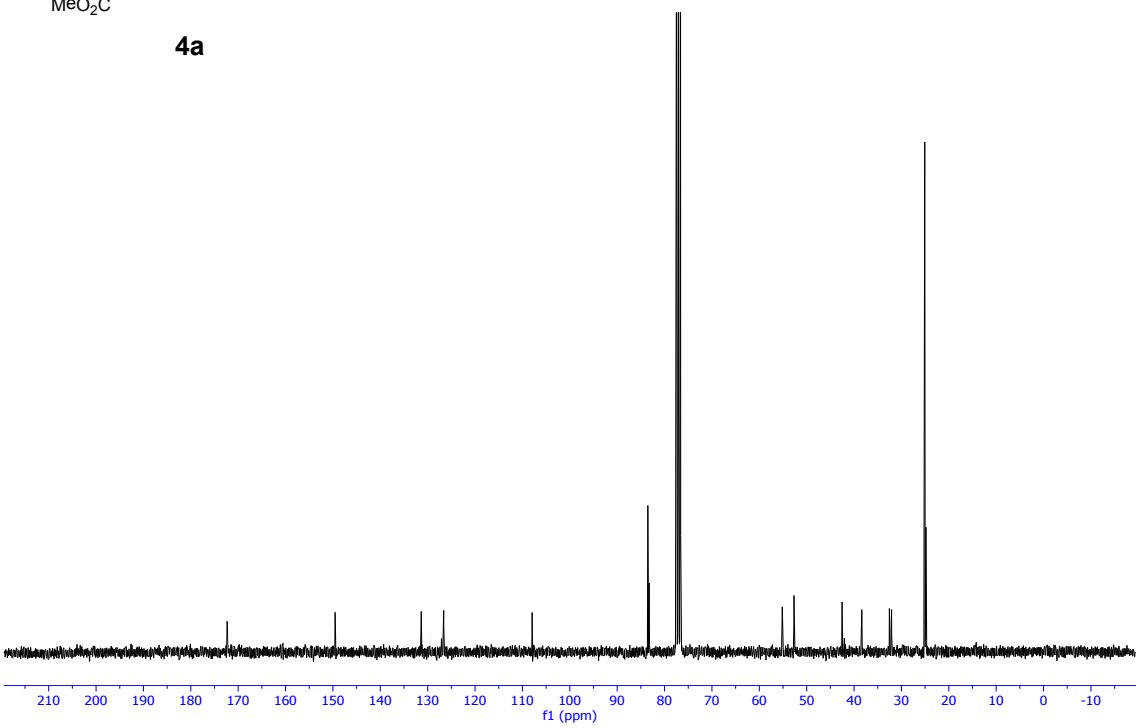

MeO2C
MeO2C
O
B
O

4a

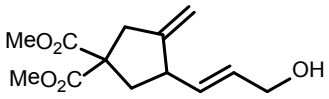
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


MeO2C
MeO2C
O
B
O

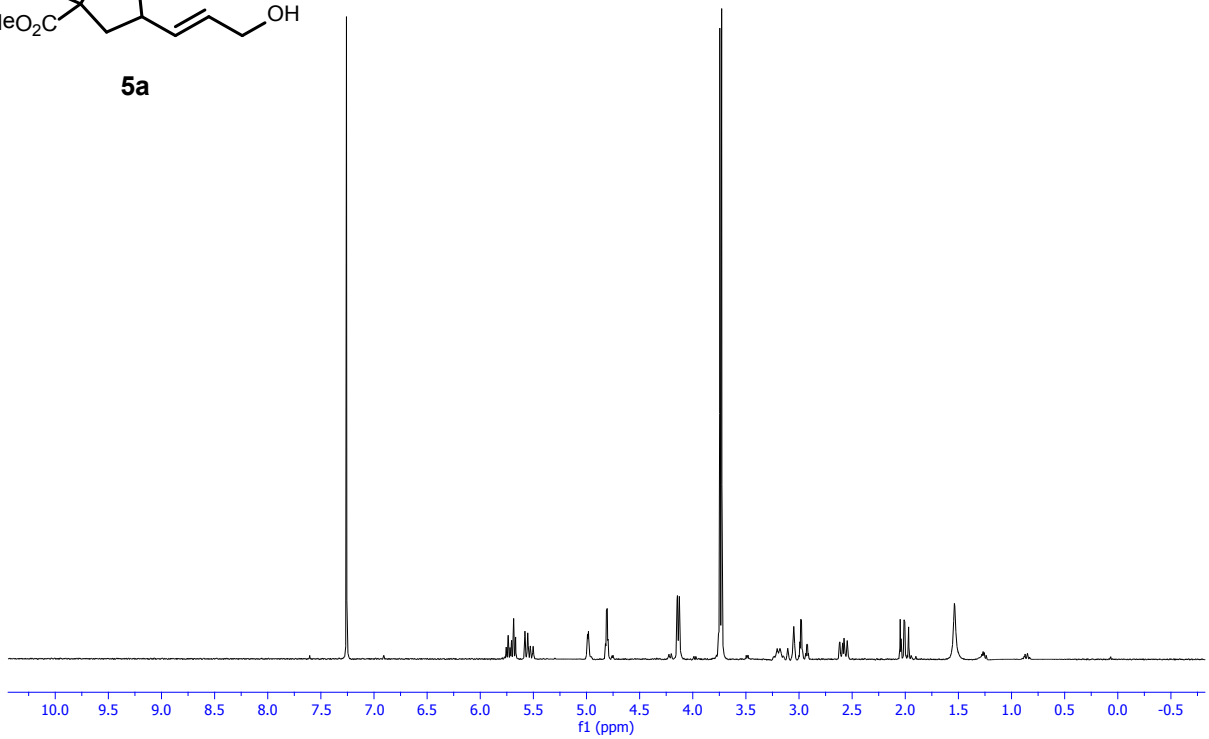
4a

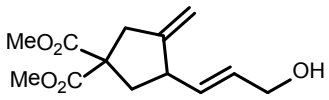

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H-NMR and ^{13}C-NMR spectra of alcohols from allylboronates

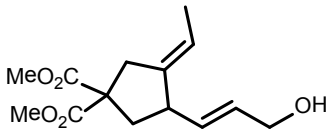


5a

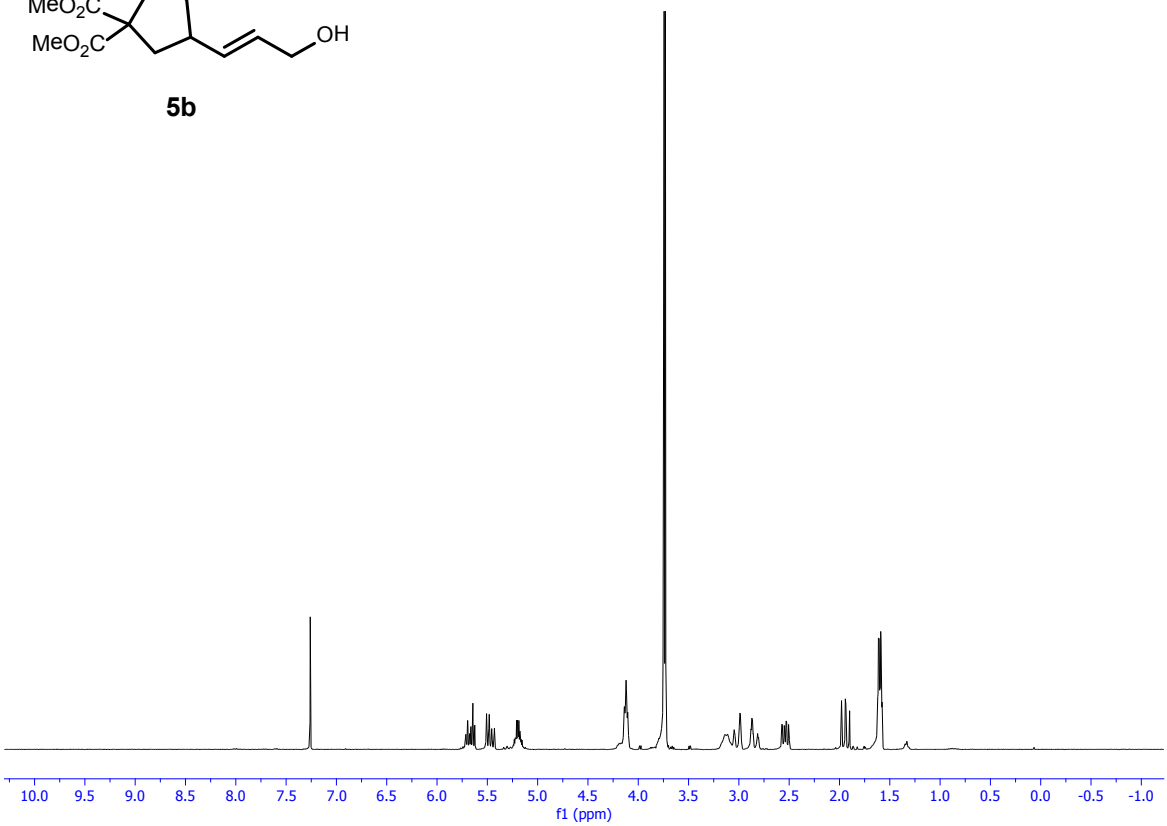


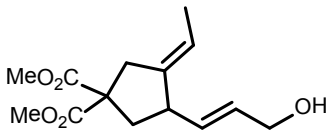


5a

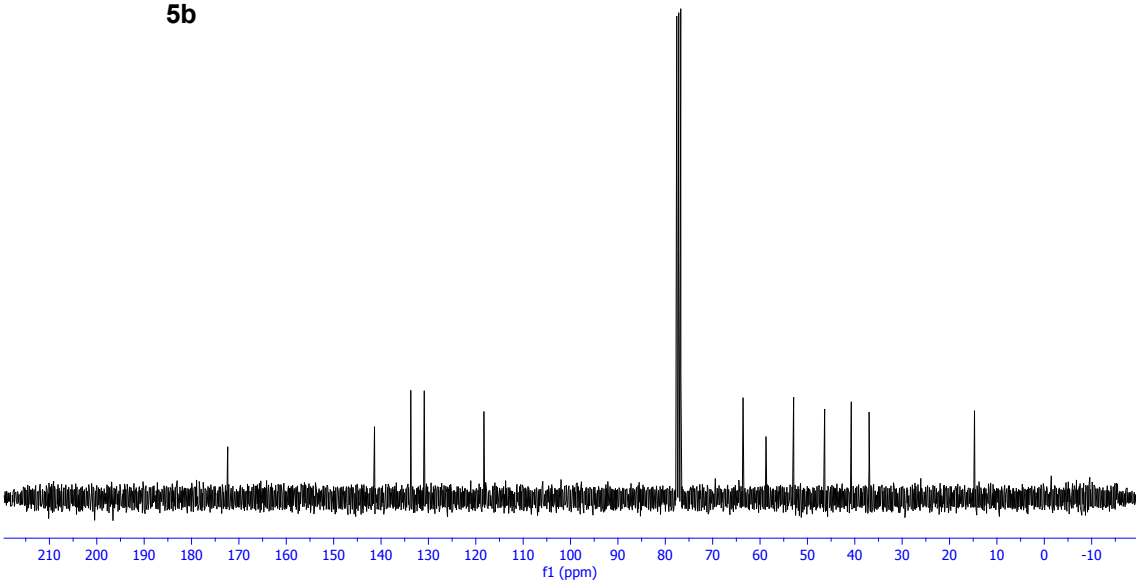

MeO2C
MeO2C
OH

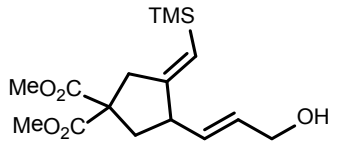
5b


10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

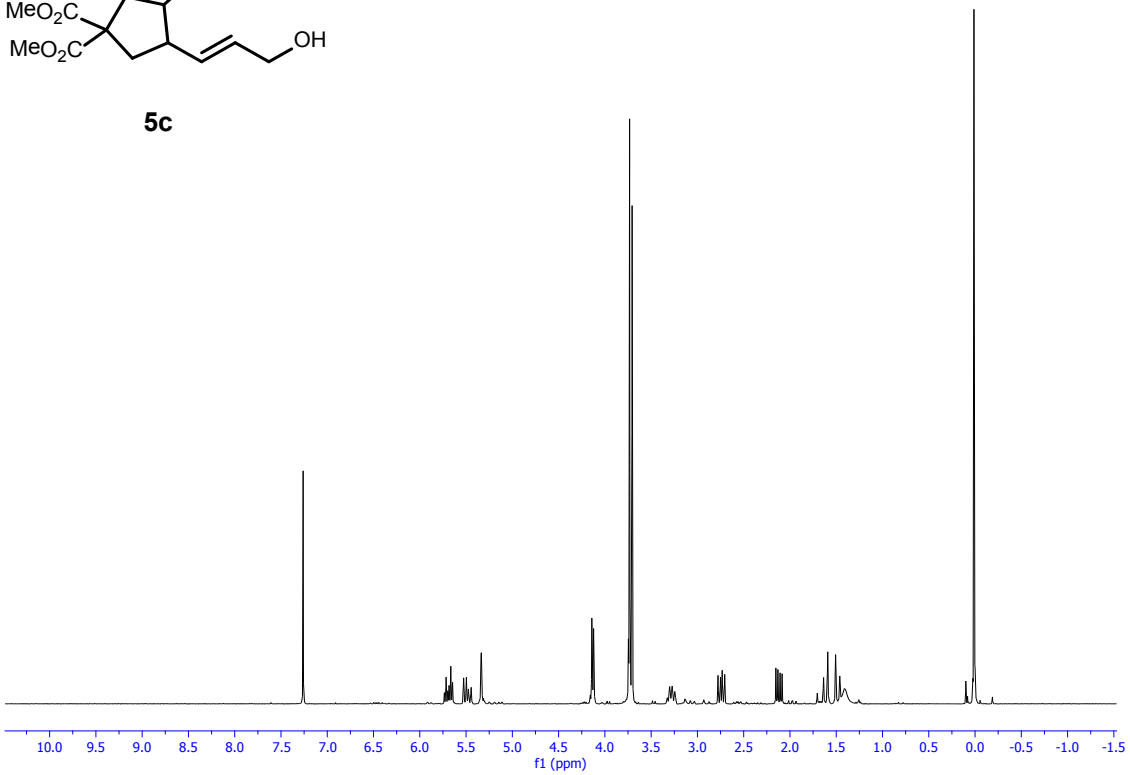

MeO2C
MeO2C
OH

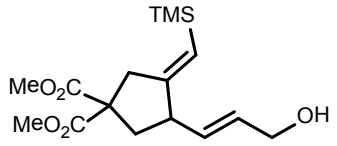
5b


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


TMS
MeO2C
MeO2C
OH

5c


10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

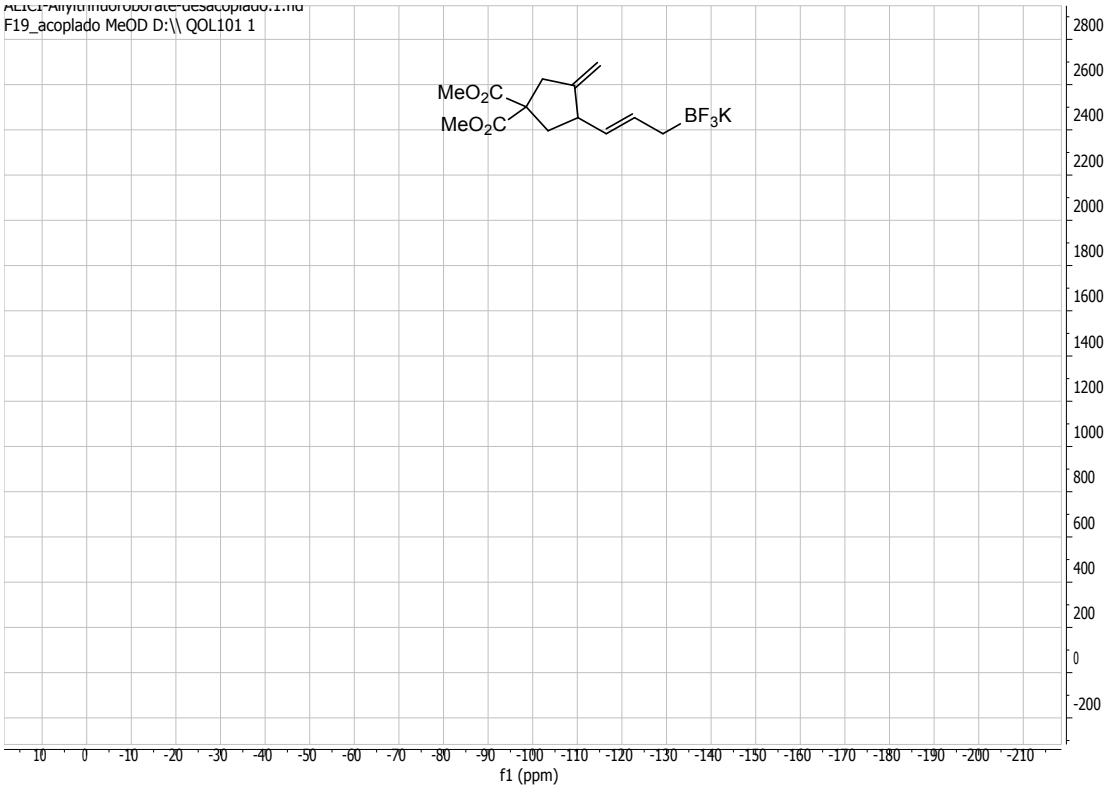

TMS
MeO2C
MeO2C
OH

5c

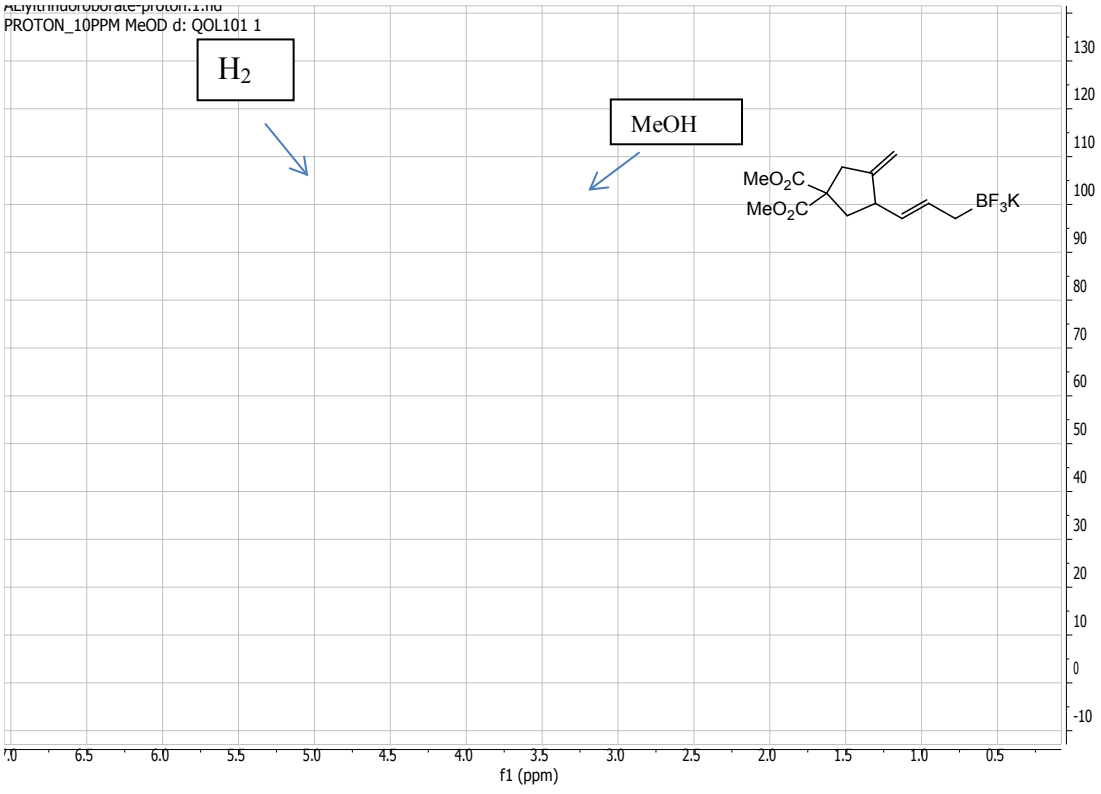
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Trifluoroborate **6**

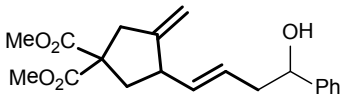
^{19}F-NMR



^{1}H-NMR



^{1}H-NMR and ^{13}C-NMR spectra of alcohols from allylation reactions.



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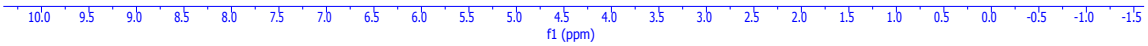

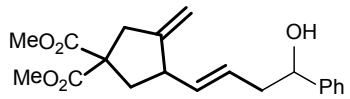

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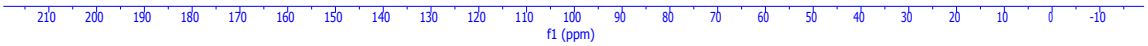

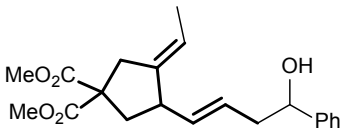

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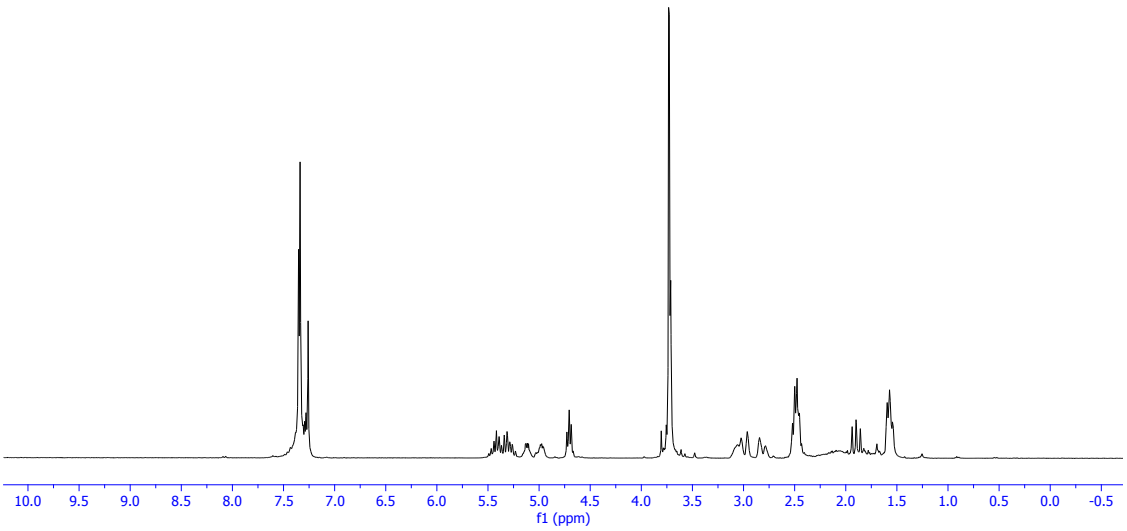
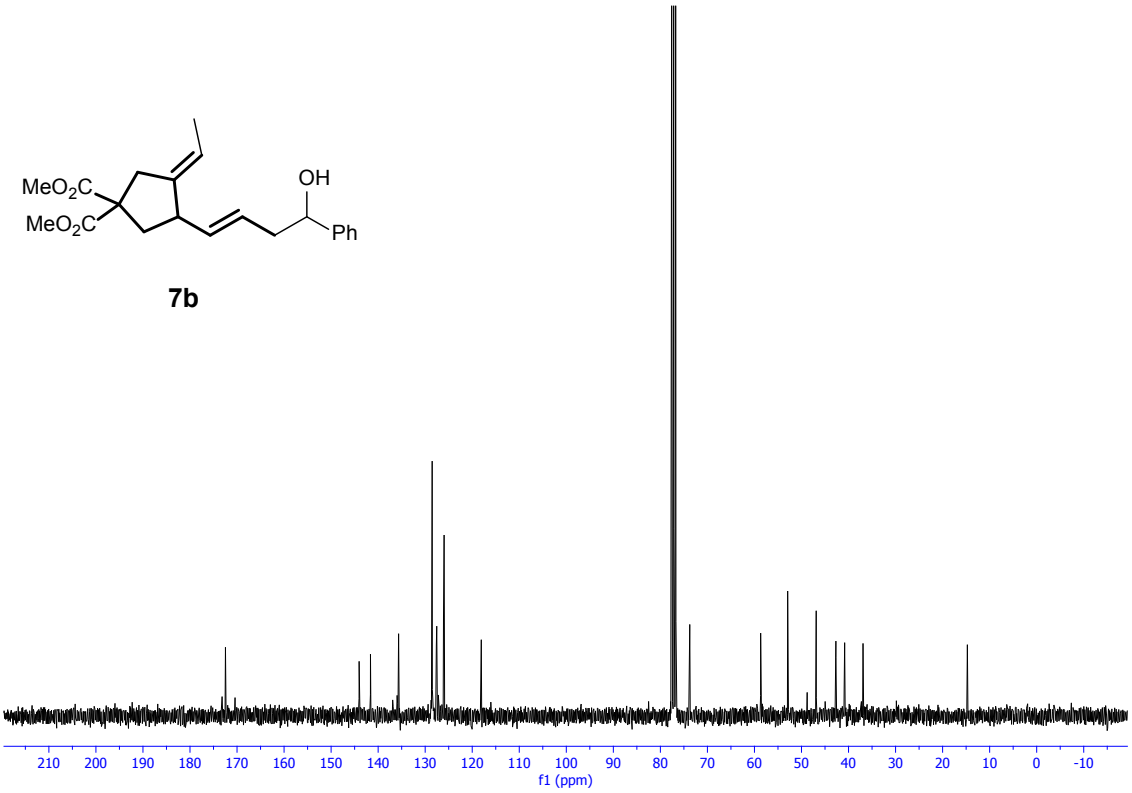
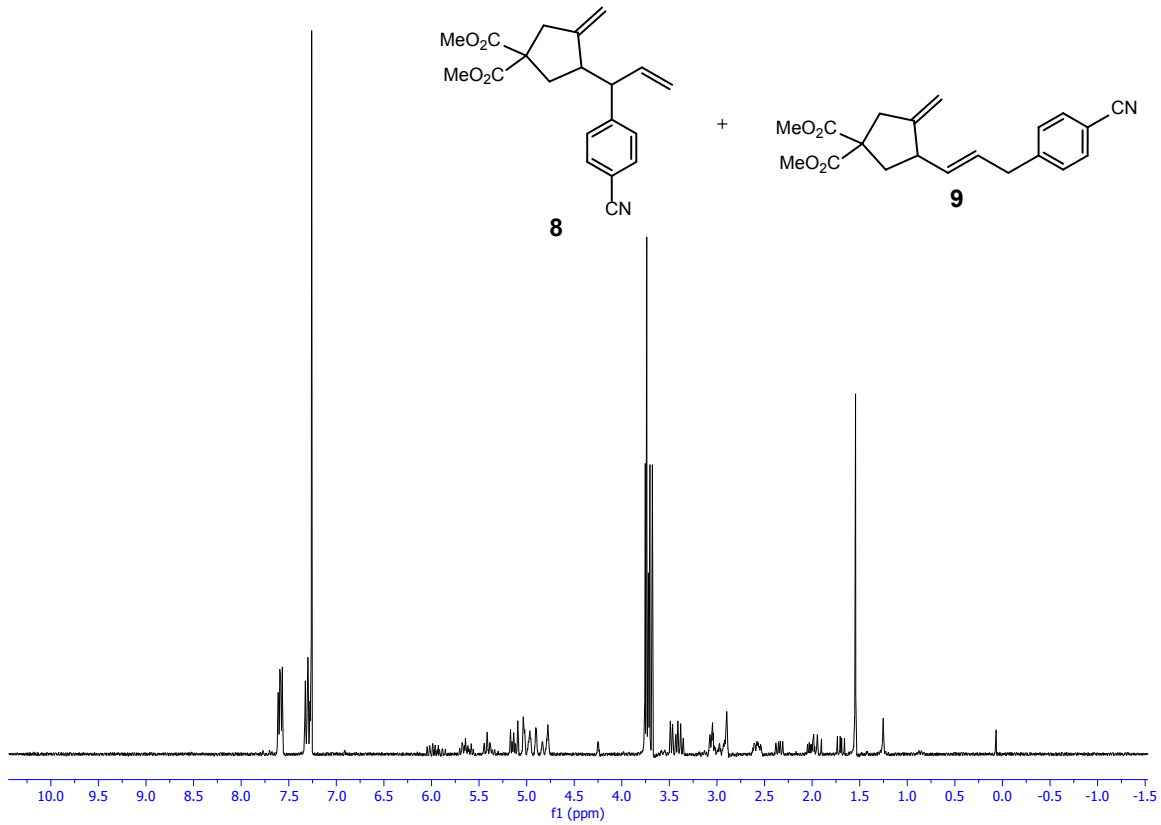
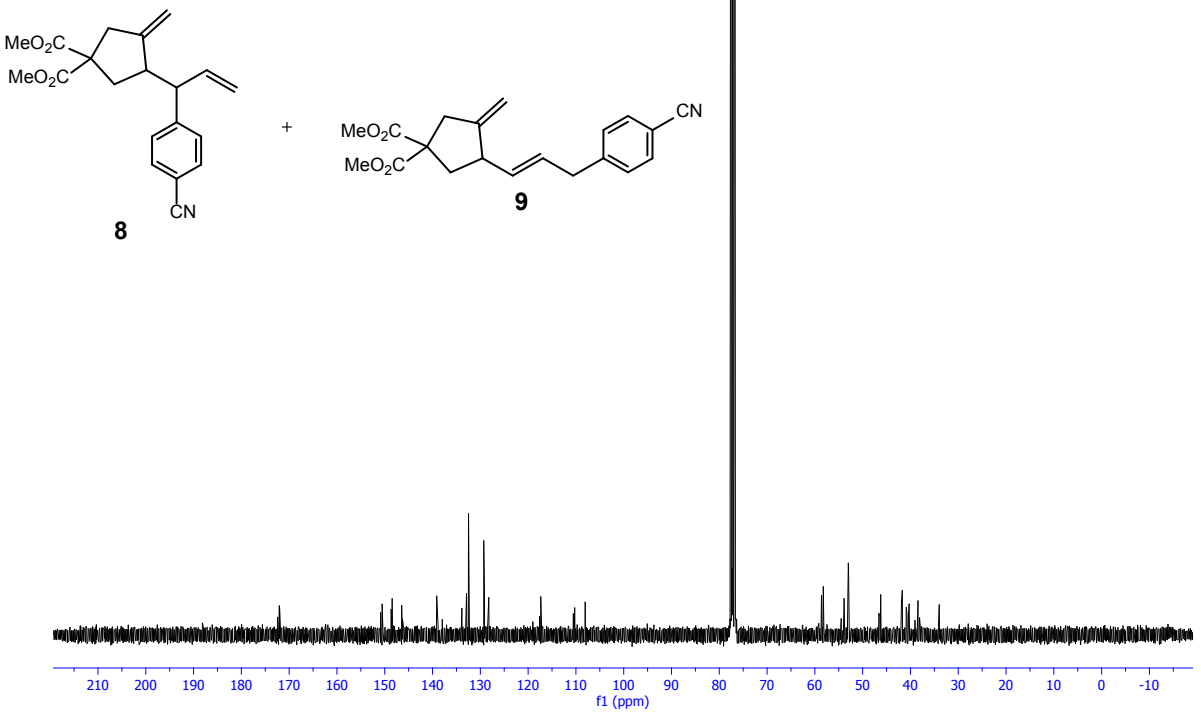
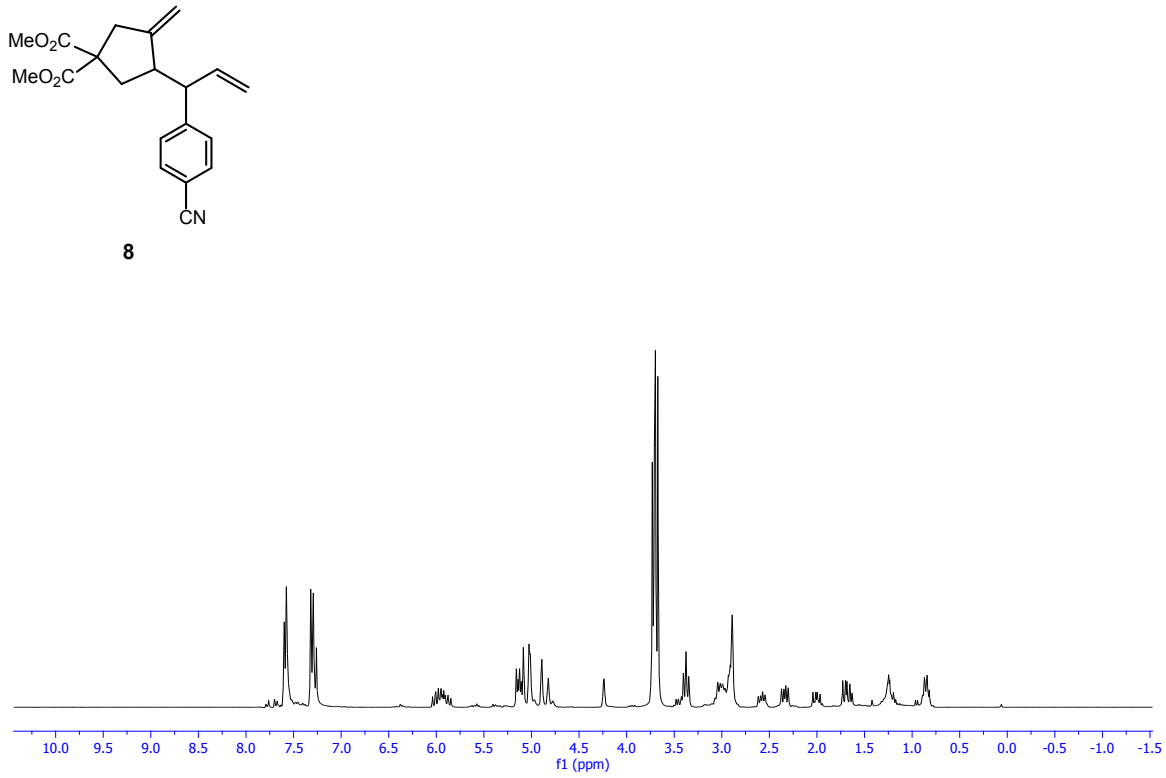


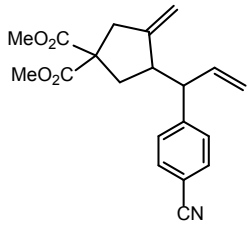


[1]H-NMR and [13]C-NMR spectra of Suzuki coupling resulting compounds

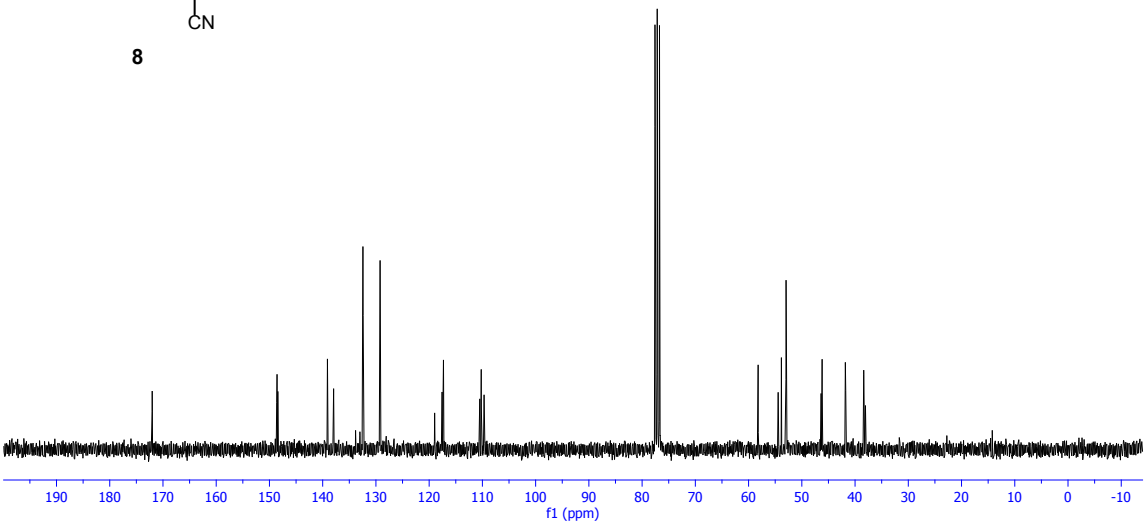



MeO2C
MeO2C
CN
8
+
MeO2C
MeO2C
CN
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO2C
MeO2C
CN
8
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


MeO2C
MeO2C
CN

8


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

13. References

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