Supporting Information

trans-Hydroboration vs. 1,2-Reduction: Divergent Reactivity of Ynones and Ynoates in Lewis-Base-Catalyzed Reactions with Pinacolborane

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General remarks:

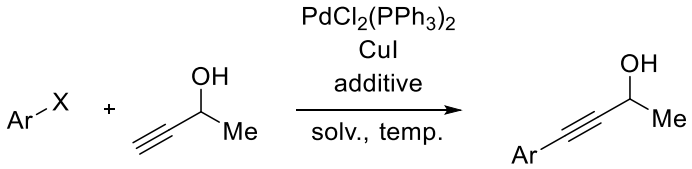
Commercially available reagents were used without further purifications, pinacolborane was distilled at 36 °C and 56 mbar. Anhydrous dichloromethane and 1,2-dichloroethane were obtained by distillation over calcium hydride under a positive pressure of nitrogen. Anhydrous diethyl ether and tetrahydrofuran were distilled over sodium/benzophenone under a positive pressure of nitrogen. All reactions were carried out using standard Schlenk techniques under a positive pressure of argon or nitrogen. ^{1}H- and ^{13}C NMR-spectra were recorded at 250/63 MHz or 300/75 MHz at 295 K in $CDCl_3$ on a Bruker Avance I 250 spectrometer and Bruker Fourier 300 system. Chemical shifts (δ) are expressed in parts per million (ppm) with respect to the solvent signal (^{13}C NMR, δC: $CDCl_3$ 77.16) or the residual nondeuterated solvent signal (^{1}H NMR, δH: $CHCl_3$ 7.26, ppm), respectively. High-resolution mass spectra (HR-MS) were recorded on spectrometer. IR spectra were recorded on a IRAffinity-1 (Shimadzu) spectrometer in ATR modus. Column chromatography was performed using silica gel 60 (40-63 µm) from Macherey-Nagel. Petroleum ether used for purification was light petroleum (bp. 35-70 °C).

Synthesis of ynones:

The required ynones were prepared via (i) Sonogashira coupling of corresponding aryl halide with but-3-yn-2-ol followed by (ii) Dess-Martin oxidation of the resulting propargylic alcohol (ynones **1u**-**1y**).

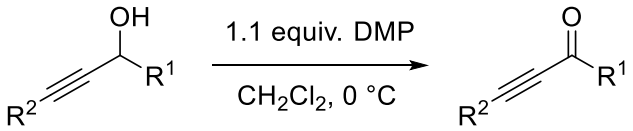
The procedure and character data of propargylic ynones **1a**-**1t** have been shown previously.[1]

General procedure for Sonogashira coupling:



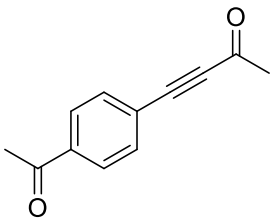
Aryl halide was dissolved in the appropriate solvent. The solution was treated with N_2 (bubbling for 20 minutes) to remove residual oxygen. The additive, but-3-yn-2-ol, $PdCl_2(PPh_3)_2$ and CuI were added and the suspension was heated to appropriate temperature. After the reaction was complete or no further progress was observed by TLC, the mixture was allowed to cool to room temperature. The mixture was filtered through a plug of celite. The solvent was evaporated, and the crude product was purified by flash column chromatography (SiO_2, ethyl acetate in petroleum ether) to provide the corresponding propargylic alcohol.

General procedure for Dess-Martin-oxidation:



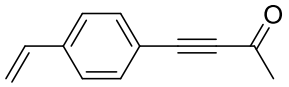
The propargylic alcohol was dissolved in DCM (0.2 M) and cooled to 0 °C. Dess-Martin periodinane (DMP, 1.1 equiv) was added and the mixture was allowed to warm to room temperature. After the reaction was completed, monitored by TLC, aq. NaOH (1.1 equiv, 1 M solution) was added. The layers were separated, and the aqueous layer was extracted with DCM (3 x). The organic layers were combined and dried over Na_2SO_4. The solvent was evaporated, and the crude product was purified by flash column chromatography (SiO_2, ethyl acetate in petroleum ether) to provide the corresponding ynone.

4-(4-acetylphenyl)but-3-yn-2-one (1u): Prepared following the general procedure for Sonogashira coupling. 1-(4-bromophenyl) ethan-1-one (4 g, 20.1 mmol), but-3-yn-2-ol (1.73 mL, 22.1 mmol), $PdCl_2(PPh_3)_2$ (280 mg, 0.4 mmol), CuI (152 mg, 0.8 mmol), NEt_3 (160 mL) were used at 80 °C. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **2u** (3.14 g, 83%).



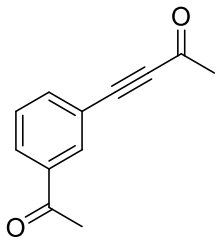
Oxidation of propargylic alcohol **2u** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **2u** (2.6 g, 13.8 mmol), DMP (6.45 g, 15.2 mmol) and DCM (69 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **1u** as colorless solid (2.38 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98-7.94 (m, 2H), 7.67-7.63 (m, 2H), 2.62 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.4, 185.5, 138.1, 133.1, 128.5, 124.7, 90, 88.3, 32.7, 26.7. IR (ATR): $\tilde{\nu}$ = 2967, 2203, 1690, 1661, 831 cm^{-1}. HRMS (FTMS + EI) calcd for $C_{12}H_{10}O_2$ $[M]^+$ 186.0681, found 186.0673. Analytical data were consistently with those reported in literature.[2]

4-(4-vinylphenyl)but-3-yn-2-one (1v): PPh_3MeI (2.15 g, 5.32 mmol) was suspended in THF (21.5 mL) and cooled to -78° C. n-BuLi (2.13 mL, 5.32 mmol, 2.5 M in Hexane) was added to the suspension. The reaction was allowed to war up to RT. 4-(3-hydroxybut-1-yn-1-yl) benzaldehyde (773 mg, 4.44 mmol) was dissolved in THF (9 mL) and added to ylide solution. After full consumption of propargylic alcohol, the reaction was quenched by adding water (20 mL). The layers were separated and the aqueous layer was washed with DCM (3x 30 mL). The organics were combined and dried by $MgSO_4$. Column chromatography delivered the desired propargylic alcohol as colorless liquid (274 mg, 36%).



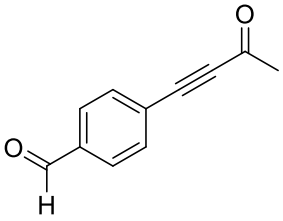
Oxidation of propargylic alcohol **2v** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **2v** (274 mg, 1.59 mmol), DMP (742 g, 1.75 mmol) and DCM (5mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **1v** as colorless liquid (219 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H), 5.35 (d, J =10.5 Hz, 1H), 5.80 (d, J =17.9 Hz, 1H), 6.68 (dd, J =10.5, 17.9 Hz, 1H), 7.38 (d, J =10.5 Hz, 2H), 7.50 (d, J =9.0 Hz, 2H).^{13}C NMR (75 MHz, $CDCl_3$): δ 184.5, 140.0, 135.9, 133.2, 126.3, 118.9, 116.3, 90.4, 88.9, 32.7. IR (ATR): $\tilde{\nu}$ = 2918, 2197, 1664, 1276 cm^{-1}. HRMS (FTMS + EI) calcd for $C_{12}H_{10}O$ $[M]^+$ 170.0732, found 170.0725.

4-(3-acetylphenyl)but-3-yn-2-one (1w): Prepared following the general procedure for Sonogashira coupling. 1-(3-bromophenyl) ethan-1-one (5 g, 25.12 mmol), but-3-yn-2-ol (2.188 mL, 27.63 mmol), $PdCl_2(PPh_3)_2$ (352 mg, 0.502 mmol), CuI (198 mg, 1.04 mmol) and NEt_3(120 mL) as solvent were used at 80 °C. 30% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **2w** (1.5 g, 32%).



Oxidation of propargylic alcohol **2w** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **2w** (1.52 g, 8.05 mmol), DMP (3.76 g, 8.86 mmol) and DCM (44mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **1w** as pale yellow solid (1.44 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.45 (s, 3H), 2.61 (s, 3H), 7.50 (t, J =7.5 Hz, 1H), 7.73 (d, J =6.7 Hz, 1H), 8.03 (d, J =10.0 Hz, 1H), 8.14 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.9, 184.3, 137.3, 136.9, 132.9, 130.1, 129.0, 120.6, 88.6, 88.5, 32.7, 26.5. IR (ATR): $\tilde{\nu}$ =2916, 2204, 2173, 1685, 1147 cm^{-1}. HRMS (FTMS + EI) calcd for $C_{12}H_{10}O_2$ $[M]^+$ 186.0681, found 186.0672.

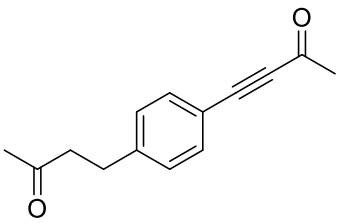
4-(3-oxobut-1-yn-1-yl)benzaldehyde (1x): Prepared following the general procedure for Sonogashira coupling. 4-bromobenzaldehyde (3 g, 16.2 mmol), but-3-yn-2-ol (1.92 mL, 24.3 mmol), Pd/C (690 mg, 0.04 mmol), CuI (850 mg, 3.24 mmol), PPh_3 (154 mg, 0.81 mmol), 2-aminoethan-1-ol (3 mL) as additive and H_2O (60 mL) as solvent were used at at 80 °C. 30% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **2x** (980 mg, 35%). Analytical data were consistently with those reported in literature.[3]



Oxidation of propargylic alcohol **2x** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **2x** (0.905 mg, 5.19 mmol), DMP (2.42 g, 5.7 mmol) and DCM (29 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **1x** as pale yellow solid (851 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.49 (s, 3H), 7.72 (d, J =8.1 Hz, 2H), 7.91 (d, J =9.0 Hz, 2H), 10.06 (s, 1H).^{13}C NMR (75 MHz, $CDCl_3$): δ 191.2, 183.8,

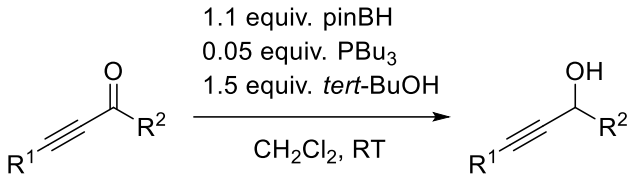
137.1, 133.4,129.7, 125.9, 90.4, 88.2, 32.6. IR (ATR): ṽ = 2859, 2198, 1663, 1175 cm^{-1}. HRMS (FTMS + EI) calcd for $C_{11}H_8O_2$ $[M]^+$172.0524, found 172.0518.

4-(4-(3-oxobutyl)phenyl)but-3-yn-2-one (1y): Prepared following the general procedure for Sonogashira coupling. 4-(4-bromophenyl) butan-2-one (1.76 g, 7.75 mmol), but-3-yn-2-ol (0.92 mL, 11.62 mmol), $PdCl_2(PPh_3)_2$ (273 mg, 0.39 mmol), CuI (74 mg, 0.39 mmol), NEt_3 (12.9 mL) and THF (15 mL) were used at 85 °C. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **2y** (0.921 g, 55%).



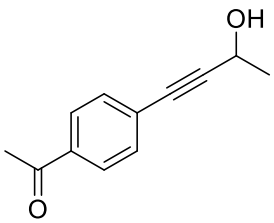
Oxidation of propargylic alcohol **2y** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **2y** (486 mg, 1.244 mmol), DMP (580 mg, 1.368 mmol) and DCM (6.2 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **1y** as pale yellow solid (210 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.49 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* =8.5 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 207.5, 184.8, 144.5, 133.5, 129.1, 117.6, 90.7, 88.2, 44.8, 32.7, 30.1, 29.6. IR (ATR) ṽ = 2917, 1696, 1663, 1358, 1151 cm^{-1}. HRMS (FTMS + EI) calcd for $C_{14}H_{14}O_2$ $[M]^+$ 214.0994, found 214.0987.

Phosphine catalyzed 1,2-reduction of ynones to propargylic alcohols:

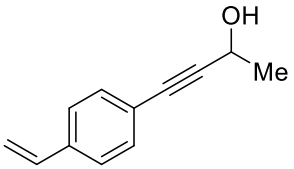


(For R^1= Ph and R^2= Me) Ynone **1a** (144 mg, 1 mmol) was dissolved in DCM (2.5 mL, 0.4 M) followed by addition of *tert*-BuOH (0.141 mL, 1.5 mmol) and pinBH (0.194 mL, 1.1 mmol) at room temperature. After the addition of tributyl phosphine (13 µL, 0.05 mmol) development of gas was observed. After TLC analysis (10% ethyl acetate in petroleum ether) confirmed full consumption of starting material (10 minutes), reaction mixture was quenched by addition of water (5 mL). The resulting layers were separated, and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 10% ethyl acetate in petroleum ether) to yield the corresponding propargylic alcohol **2a** as collorless liquid (132 mg, 90%).

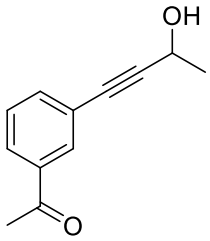
1-(4-(3-hydroxybut-1-yn-1-yl)phenyl)ethan-1-one (2u): 4-(4-acetylphenyl) but-3-yn-2-one **1u** (145 mg, 0.779 mmol), *tert*-BuOH (110 µL, 1.169 mmol), pinBH (128 µL, 0.857 mmol), tributyl phosphine (10 µL, 0.039 mmol) and DCM (1.9 mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **2u** as colorless solid (133 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.91-7.86 (m, 2H), 7.51-7.46 (m, 2H), 4.78 (td, J = 6.5, 12.1 Hz, 1H), 2.59 (s, 3H), 2.34 (d, *J* = 5.3 Hz, 1H), 1.57 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 197.6, 136.5, 132.5, 128.3, 127.7, 94.7, 83.2, 59.0, 26.7, 24.4. IR (ATR): ṽ = 3359, 2992, 1676, 1355, 1028, 831 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{12}H_{12}O_2$ $[M+H]^+$ 189.0910, found 189.0914.



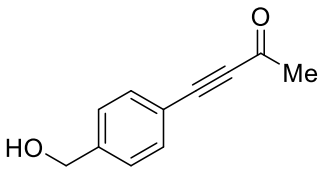
4-(4-vinylphenyl)but-3-yn-2-ol (2v): 4-(4-vinylphenyl) but-3-yn-2-one **1v** (157 mg, 0.901 mmol), *tert*-BuOH (129 µL, 1.352 mmol), pinBH (148 µL, 0.991 mmol), tributyl phosphine (11 µL, 0.045 mmol) and DCM (2.3 mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **2v** as colorless liquid (130 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): 1.59 (d, *J* =6.4 Hz, 3H), 2.08 (s, 1H), 4.79 (q, *J* =6.9 Hz, 1H), 5.33 (d, *J* =11.5 Hz, 1H), 5.79 (d, *J* =18.7 Hz, 1H), 6.72 (dd, *J* =12.0, 19.3 Hz, 1H), 7.44 - 7.35 (m, 1H).^{13}C NMR (75 MHz, $CDCl_3$): δ 137.6, 136.3, 131.9, 126.2, 121.9, 114.9, 91.7, 84.1, 59.1, 24.5. IR (ATR): ῦ = 3316, 2982, 1504, 1099 cm^{-1}. HRMS (FTMS+ EI) calcd for $C_{12}H_{12}O$ $[M]^+$ 172.0888, found 172.0880.



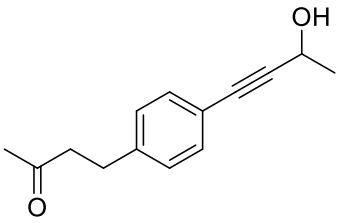
1-(3-(3-hydroxybut-1-yn-1-yl)phenyl)ethan-1-one (2w): 4-(3-acetylphenyl) but-3-yn-2-one **1w** (121 mg, 0.649 mmol), *tert*-BuOH (149 µL, 1.59 mmol), pinBH (170 µL, 1.136 mmol), tributyl phosphine (10 µL, 0.038 mmol) and DCM (1.9 mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **2w** as pale yellow solid (125 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 1.52 (d, *J* =6.7 Hz, 3H), 2.55 (s, 3H), 2.57 (s, 1H), 4.73 (q, *J* =3.1 Hz, 1H), 7.36 - 7.33 (m, 1H), 7.55 - 7.53 (m, 1H), 7.85 - 7.78 (m, 1H), 7.94 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 197.1, 137.1, 135.9, 131.7, 128.7, 128.0, 123.3, 92.3, 82.9, 57.7, 26.6, 24.4. IR (ATR): ῦ = 3367, 2980, 2134, 1682, 1104 cm^{-1}. HRMS (FTMS + EI) calcd for $C_{12}H_{12}O_2$ $[M]^+$ 188.0837, found 188.0832.



4-(4-(hydroxymethyl)phenyl)but-3-yn-2-one (2x): 4-(3-oxobut-1-yn-1-yl) benzaldehyde **1x** (132 mg, 0.767 mmol), *tert*-BuOH (108 µL, 1.151 mmol), pinBH (149 µL, 0.997 mmol), tributyl phosphine (10 µL, 0.038 mmol) and DCM (1.9 mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide alcohol **2x** as colorless liquid (70 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 2.21 (s, 1H), 2.46 (s, 3H), 4.73 (s, 2H), 7.39 (d, *J* =8.2 Hz, 2H), 7.56 (d, *J* =8.2 Hz, 2H).^{13}C NMR (75 MHz, $CDCl_3$): *δ* 184.9, 144.1, 133.4, 126.7, 118.9, 90.4, 88.5, 64.6, 32.7. IR (ATR): ῦ = 3414, 2977,2199, 1666, 1180 cm^{-1}. HRMS (FTMS+ EI) calcd for $C_{11}H_{10}O_2$ $[M]^+$ 174.0681, found 174.0674.



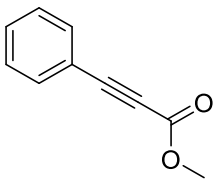
4-(4-(3-hydroxybut-1-yn-1-yl)phenyl)butan-2-one (2y): 4-(4-(3-oxobutyl) phenyl) but-3-yn-2-one **1y** (102 mg, 0.476 mmol), *tert*-BuOH (67 µL, 0.714 mmol), pinBH (78 µL, 0.524 mmol), tributyl phosphine (6 µL, 0.024 mmol) and DCM (1.2 mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **2y** as colorless liquid (81 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 4.75 (qd, *J* = 4.3, 11.5 Hz, 1H), 2.89 (t, *J* = 7.1 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.29 (d, *J* = 4.6 Hz, 1H), 2.13 (s, 3H), 1.54 (d, *J* = 6.6 Hz, 3H). IR (ATR): ῦ = 3408, 2981, 2199, 1708, 1363 cm^{-1}. HRMS (ESI-TOF) cald for $C_{14}H_{16}O_2$ $[M+H]^+$ 217.1223, found 217.1227.



Synthesis of Ynoates:

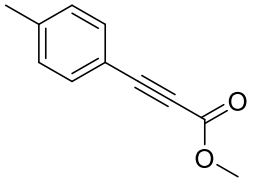
Methyl 3-phenylpropiolate (11b):

The compound was prepared according to a literature procedure.[4] A solution of *n*-BuLi in hexane (21.54 mL, 2.5 M, 53.85 mmol, 1.1 eq.) was added drop wise over a period of 5 min to a solution of phenylacetylene (5.38 mL, 48.96 mmol, 1 eq.) in 250 mL THF at -98 °C. The solution was allowed to warm up to rt and cooled to -98 °C again. Methyl chloroformate (4.16 mL, 53.85 mmol, 1.1 eq.) was added dropwise over 5 min. The solution was stirred at rt for 1.5 h. To the solution 50 mL sat. aqueous NH_4Cl-solutio, 50 mL dest. H_2O and 100 mL EA were added. The phases were separated and the aqueous phase was extracted with 100 mL EA. The combined organic phases were washed with sat. aqueous NaCl-solution and dried over Na_2SO_4. The solvent was removed in vacuum



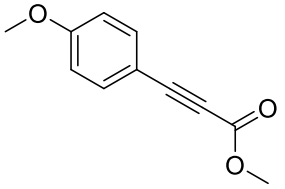
and the crude product was distilled in high vacuum (10^{-1} mbar, 90-110 °C), giving the product as a colourless oil (6.785 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61-7.58 (m, 2H), 7.49-7.35 (m, 3H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.45, 132.98, 130.67, 128.55, 119.49, 86.47, 80.32, 52.78. IR (ATR): $\tilde{\nu}$ = 2223 (s), 1707 (s), 1489 (m), 1433 (m), 1285 (s) cm^{-1}. HRMS (GC + p EI): calculated for $C_{10}H_8O_2$ $[M]^+$ 160.0524, found 160.0520.

Methyl 3-(p-tolyl) propiolate (11c):



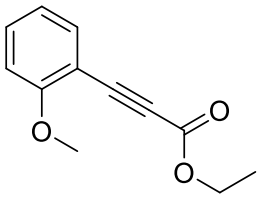
The compound was prepared according to a literature procedure.[5] A solution of *n*-BuLi in hexane (4.52 mL, 2.5 M, 11.30 mmol, 1 eq.) was added to a solution of *N,N*-diisopropylamine (1.59 mL, 11.30 mmol, 1 eq.) in 10 THF at 0 °C. The solution was cooled down to -98 °C and a solution of methyl propiolate (1 mL, 11.30 mmol, 1 eq.) in 4 mL THF was added dropwise, followed by a solution of $ZnBr_2$ (2.545 g, 11.30 mmol, 1 eq.) in 10 THF, which was also added dropwise. 4-iodtoluene (2.094 g, 9.61 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.261 g, 0.23 mmol, 0.02 eq.) were added simultaneously as a solid. The mixture was stirred at rt for 8 h. The mixture was diluted with 200 mL EA and washed with sat. NH_4Cl solution (2*50 mL), sat. $NaHCO_3$ solution (1*50 mL) and sat. NaCl solution (1*25 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10% EA in PE) and the product was obtained as an off-white solid (1.162 g, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.485 (d, J = 9 Hz, 2H), 7.185 (d, J = 9 Hz, 2H), 3,84 (s, 3H), 2,39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.59, 141.35, 132.99, 129.35, 116.37, 87.04, 80.00, 52.72, 21.70. IR (ATR): $\tilde{\nu}$ = 2215 (m, sh), 1698 (m, sh) cm^{-1}. HRMS (GC + p EI): calculated for $C_{11}H_{10}O_2$ $[M]^+$ 174.0681, found 174.0678.

Methyl 3-(4-methoxyphenyl) propiolate (11d):



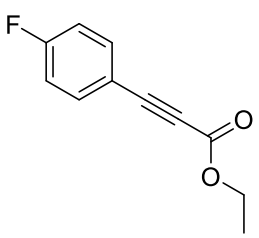
The compound was prepared according to a literature procedure.[5] A solution of *n*-BuLi in hexane (10.3 mL, 2.5 M, 25.74 mmol, 1 eq.) was added to a solution of *N,N*-diisopropylamine (3.6 mL, 25.74 mmol, 1 eq.) in 23 mL THF at 0 °C. The solution was cooled down to -98 °C and a solution of methyl propiolate (1.97 mL, 22.20 mmol, 1 eq.) in 9 mL THF was added dropwise, followed by a solution of $ZnBr_2$ (5 g, 22.20 mmol, 1 eq.) in 20 mL THF, which was also added dropwise. 4-Iodoanisole (5 g, 21.36 mmol, 0.83 eq.) and $Pd(PPh_3)_4$ (1.19 g, 1.03 mmol, 0.04 eq.) were added simultaneously. The mixture was stirred at rt for 15 h. The mixture was diluted with 200 mL Et_2O and washed with sat. NH_4Cl solution (2*50 mL), sat. $NaHCO_3$ solution (1*50 mL) and sat. NaCl solution (1*25 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed in vacuum. The residue was purified via flash chromatography (10 %EA in PE) and the product was obtained as a yellowish solid (2 g, 49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 3.84 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.53, 154.71, 134.94, 114.28, 111.27, 87.35, 79.79, 55.38, 52.66. IR (ATR): $\tilde{\nu}$ = 2211 (s, sh), 1702 (s, sh) cm^{-1}. HRMS (GC + p EI): calculated for $C_{11}H_{10}O_3$ $[M]^+$ 190.0630, found 190.0624.

Ethyl 3-(2-methoxyphenyl) propiolate (11e):



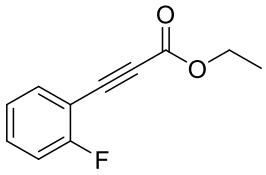
The compound was prepared according to a literature procedure.[5] A solution of *n*-BuLi in hexane (6.03 mL, 2.5 M, 15.08 mmol, 1 eq.) was added to a solution of *N,N*-diisopropylamine (2.1 mL, 15.08 mmol, 1 eq.) in 23 mL THF at 0 °C. The solution was cooled down to -98 °C and a solution of ethyl propiolate (1.48 g, 15.08 mmol, 1 eq.) in 9 mL THF was added dropwise, followed by a solution of $ZnBr_2$ (3.4 g, 15.08 mmol, 1 eq.) in 15 mL THF, which was also added dropwise. 2-Iodoanisole (3 g, 12.82 mmol, 0.83 eq.) and $Pd(PPh_3)_4$ (0.296 g, 0.26 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 15 h. The mixture was diluted with 200 mL Et_2O and washed with sat. NH_4Cl solution (2*50 mL), sat. $NaHCO_3$ solution (1*50 mL) and sat. NaCl solution (1*25 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed in vacuum. The residue was purified via flash chromatography (10 % EA in PE) and the product was obtained as a yellowish solid (0.625 g, 24 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (dd, J = 7.6, 1.8 Hz, 1H), 7.36 (ddd, J = 8.5, 7.5, 1.8 Hz, 1H), 6.97-6.76 (m, 2H), 4.25 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.52, 154.21, 134.92, 132.25, 120.49, 110.76, 108.83, 84.57, 83.11, 61.98, 55.83, 14.12. IR (ATR): $\tilde{\nu}$ = 2231 (s, sh), 1692 (s, sh) cm^{-1}. HRMS (GC + p EI): calculated for $C_{12}H_{12}O_3$ $[M]^+$ 204.0786, found 204.0783.

Ethyl 3-(4-fluorophenyl) propiolate (11g):



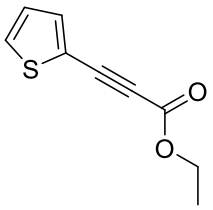
The compound was prepared according to a literature procedure.[5] A solution of *n*-BuLi in hexane (6.78 mL, 2.5 M, 16.95 mmol, 1 eq.) was added to a solution of *N,N*-diisopropylamine (2.38 mL, 16.95 mmol, 1 eq.) in 24 mL THF at 0 °C. The solution was cooled down to -98 °C and ethyl propiolate (1.72 mL, 22.60 mmol, 1 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (3.817 g, 16.95 mmol, 1 eq.) in 15 mL THF, which was also added dropwise. 4-fluoroiodbenzene (1.68 mL, 14.41 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.392 g, 0.34 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 5 h. The mixture was diluted with 100 mL EA and washed with sat. NH_4Cl solution (2*25 mL) and sat. NaCl solution (1*25 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10% EA in PE) and the product was obtained as a colourless solid (1.746, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63-7.56 (m, 2H), 7.12-7.04 (m, 2H), 4.305 (q, J = 6 Hz, 2H), 1.36 (t, J = 6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.55, 162.19, 153.95, 135.28, 135.16, 116.25, 115.95, 84.98, 80.60, 62.13, 14.07. IR (ATR): $\tilde{\nu}$ = 2206 (m, sh), 1693 (s) cm^{-1}. HRMS (GC + p EI): calculated for $C_{10}H_9FO_2$ $[M]^+$ 192.0587, found 192.0582.

Ethyl 3-(2-fluorophenyl) propiolate (11h):



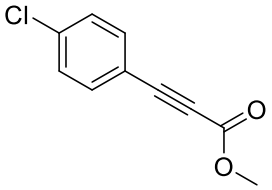
2-Ethynylfluorobenzene (10 mmol) was placed into a flask with a stirring bar under nitrogen atmosphere and sealed with a septum. Dried THF (30 mL) was added and the solution was cooled to -78 °C. *n*BuLi (11 mmol) was added and the reaction was stirred for 10 minutes. Ethyl carbonochloridate (12 mmol) was added and the reaction system was then warmed to room temperature. Saturated aqueous NH_4Cl (30 mL) was added, and the organic layer was extracted and the aqueous layer was extracted once with 30 mL ethyl acetate. The combined organic layers were concentrated under reduced vacuum and purified by flash column chromatography. (1.72g 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.39 (m, 1H), 7.39-7.26 (m, 1H), 7.10-6.93 (m, 2H), 4.20 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.29, 161.90, 153.66, 134.54, 132.59, 132.48, 124.24, 124.19, 115.96, 115.69, 108.61, 108.41, 85.21, 85.16, 79.35, 62.21, 14.03. IR (ATR): $\tilde{\nu}$ = 2984, 2217, 1705, 1610, 1491, 1300, 1265, 1184, 1103, 1020, 831, 757 cm^{-1}. HRMS (GC + p EI): calculated for $C_{10}H_9FO_2$ $[M+Na]^+$ 215.0479, found 215.0484.

Ethyl 3-(thiophen-2-yl) propiolate (11i):



The compound was prepared according to a literature procedure.[5] A solution of *n*BuLi in hexane (6.32 mL, 2.5 M, 15.79 mmol, 1 eq.) was added to a solution of *N,N*-diisopropylamine (2.22 mL, 15.79 mmol, 1 eq.) in 24 mL THF at 0 °C. The solution was cooled down to – 75 °C and ethyl propiolate (1.60 mL, 15.79 mmol, 1 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (3.55 g, 15.79 mmol, 1 eq.) in 16 mL THF, which was also added dropwise. Methyl 2-iodobenzoate (1.48 g, 13.42 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.365 g, 0.32 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 3 h. The mixture was diluted with 200 mL EA and washed with saturated NH_4Cl solution (2*50 mL) and saturated NaCl solution (1*50 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10% EA in PE) and the product was obtained as yellowish oil (2.236 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49-7.45 (m, 2H), 7.05 (dd, J_1 = 5.1 Hz, J_2 = 3.7 Hz, 1H), 4.30 (d, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C NMR: (75 MHz, $CDCl_3$) δ = 153.89, 136.44, 131.05, 127.46, 119.38, 84.88, 89.99, 62.07, 14.06. IR (ATR): $\tilde{\nu}$ =2207 (s), 1699 (s) cm^{-1}. HRMS (GC + p EI): calculated for $C_9H_8O_2S$ $[M]^+$ 180.0245, found 180.0239.

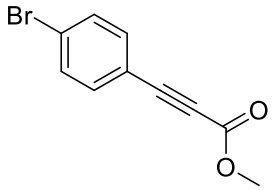
Methyl 3-(4-chlorophenyl) propiolate (11j):



The compound was prepared according to a literature procedure.[5] A solution of *n*BuLi in hexane (9.04 mL, 2.5 M, 22.60 mmol, 1 eq.) was added to a solution of *N,N*-diisopropylamine (3.18 mL, 22.60 mmol, 1 eq.) in 32 mL THF at 0 °C. The solution was cooled down to -98 °C and methyl propiolate (2 mL, 22.60 mmol, 1 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (5.089 g, 22.60 mmol, 1 eq.) in 20 mL THF, which was also added dropwise. 4-chloriodbenzene (4.581 g, 19.21 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.522 g, 0.45 mmol, 0.02 eq.) were added

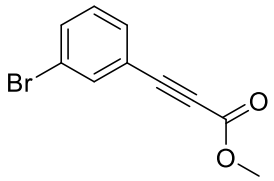
simultaneously as a solid. The mixture was stirred at rt for 6 h. The mixture was diluted with 100 mL EA and washed with sat. NH_4Cl solution (2*25 mL) and sat. NaCl solution (1*25 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10 % EA in PE) and the product was obtained as an orange solid (2.166 g, 58%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54-7.50 (m, 2H), 7.39-7.35 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.24, 137.10, 134.16, 129.06, 117.96, 85.13, 81.12, 52.87. IR (ATR): $\tilde{\nu}$ = 2222 (s, sh), 1747 (s, sh) cm^{-1}. HRMS (GC + p EI): calculated for $C_{10}H_7ClO_2$ $[M]^+$ 194.0135, found 194.0138.

Methyl 3-(4-bromophenyl) propiolate (11k):



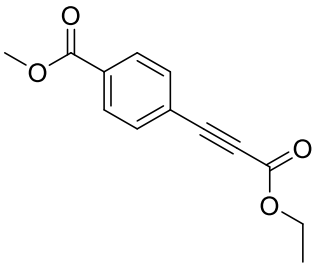
The compound was prepared according to a literature procedure.[5] A solution of *n*BuLi in hexane (2.38 mL, 2.5 M, 5.96 mmol, 1 eq.) was added to a solution of *N,N*-diisopropylamine (0.84 mL, 5.96 mmol, 1 eq.) in 5 mL THF at 0 °C. The solution was cooled down to -98 °C and a solution of methyl propiolate (0.53 mL, 5.96 mmol, 1 eq.) in 2.5 mL THF was added dropwise, followed by a solution of $ZnBr_2$ (1.342 g, 5.96 mmol, 1 eq.) in 6 mL THF, which was also added dropwise. 4-Bromoiodbenzene (1.433 g, 5.07 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.138 g, 0.12 mmol, 0.02 eq.) were added simultaneously as a solid. The mixture was stirred at rt for 8 h. The mixture was diluted with 200 mL EA and washed with sat. NH_4Cl solution (2*50 mL), sat. $NaHCO_3$ solution (1*50 mL) and sat. NaCl solution (1*25 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed in vacuo. The residue was purified via flash chromatography (10% EA in PE) and the product was obtained as an orange solid (0.612 g, 51%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.51 (m, 2H), 7.47-7.43 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.24, 134.26, 131.99, 125.49, 118.43, 85.17, 81.23, 52.89. IR (ATR): $\tilde{\nu}$ = 2221 (m, sh), 1717 (m, sh) cm^{-1}. HRMS (GC + p EI): calculated for $C_{10}H_7BrO_2$ $[M]^+$ 237.9629, found 237.9628.

Methyl 3-(3-bromophenyl) propiolate (11l):



The compound was prepared according to a literature procedure.[5] A solution of *n*BuLi in hexane (8.88 mL, 2.5 M, 22.20 mmol, 1 eq.) was added to a solution of *N,N*-diisopropylamine (3.12 mL, 22.20 mmol, 1 eq.) in 23 mL THF at 0 °C. The solution was cooled down to -98 °C and a solution of methyl propiolate (1.97 mL, 22.20 mmol, 1 eq.) in 9 mL THF was added dropwise, followed by a solution of $ZnBr_2$ (5 g, 22.20 mmol, 1 eq.) in 20 mL THF, which was also added dropwise. 3-Bromoiodbenzene (5.340 g, 18.87 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.513 g, 0.44 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 15 h. The mixture was diluted with 200 mL EA and washed with sat. NH_4Cl solution (2*50 mL), sat. $NaHCO_3$ solution (1*50 mL) and sat. NaCl solution (1*25 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed in vacuum. The residue was purified via flash chromatography (10 % EA in PE) and the product was obtained as a colourless solid (2.795 g, 62 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74-7.73 (m, 1H), 7.61-7.58 (m, 1H), 7.54-7.50 (m, 1H), 7.29-7.24 (m, 1H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.09, 135.50, 133.85, 131.84, 130.03, 122.35, 121.52, 84.37, 81.16, 52.92. IR (ATR): $\tilde{\nu}$ = 2228 (s, sh), 1703 (s, sh) cm^{-1}. HRMS (GC + p EI): calculated for $C_{10}H_7BrO_2$ $[M]^+$ 237.9629, found 237.9622.

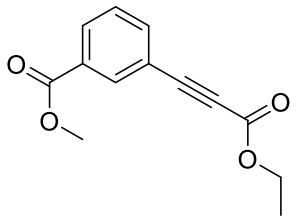
Methyl 4-(3-ethoxy-3-oxoprop-1-yn-1-yl) benzoate (11m):



The compound was prepared according to a literature procedure.[5] A solution of *n*BuLi in hexane (6.47 mL, 2.5 M, 16.19 mmol, 1 eq.) was added to a solution of *N,N*-diisopropylamine (2.27 mL, 16.19 mmol, 1 eq.) in 24 mL THF at 0 °C. The solution was cooled down to –75 °C and ethyl propiolate (1.64 mL, 16.19 mmol, 1 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (3.645 g, 16.19 mmol, 1 eq.) in 16 mL THF, which was also added dropwise. Methyl 4-iodobenzoate (4.1 g, 13.76 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.318 g, 0.28 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 22 h. The mixture was diluted with 200 mL EA and washed with sat. NH_4Cl solution (2*50 mL) and sat. NaCl solution (1*50 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (30% EA in PE, followed by 5 % EA in PE) and the product was obtained as a colourless solid (1.13 g, 35%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06-8.03 (m, 2H), 7.67-7.64 (m, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.06, 153.68, 132.77, 131.64,

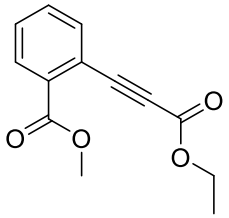
129.59, 124.12, 84.50, 82.64, 62.31, 52.42, 14.05. IR (ATR): $\tilde{\nu}$ = 2212 (s), 1705 (s, br) cm^{-1}. HRMS (GC + p EI): calculated for $C_{13}H_{12}O_4$ $[M]^+$ 232.0736, found 232.073.

Methyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl) benzoate (11n):



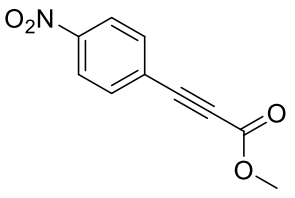
The compound was prepared according to a literature procedure.[5] A solution of *n*BuLi in hexane (6.47 mL, 2.5 M, 16.19 mmol, 1 eq.) was added to a solution of *N,N*-diisopropylamine (2.27 mL, 16.19 mmol, 1 eq.) in 24 mL THF at 0 °C. The solution was cooled down to – 75 °C and ethyl propiolate (1.64 mL, 16.19 mmol, 1 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (3.645 g, 16.19 mmol, 1 eq.) in 16 mL THF, which was also added dropwise. Methyl 3-iodobenzoate (4.1 g, 13.76 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.318 g, 0.28 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 22 h. The mixture was diluted with 200 mL EA and washed with sat. NH_4Cl solution (2*50 mL) and sat. NaCl solution (1*50 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (40 % EA in PE, followed by 5% EA in PE) and the product was obtained as a colourless solid (0.382, 12%). ^1H NMR (250 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.48 (t, J = 7.9 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.81, 153.78, 163.82, 134.05, 131.48, 130.77, 128.79, 120.15, 84.57, 81.25, 62.24, 52.43, 14.06. IR (ATR): $\tilde{\nu}$ = 2215 (m), 1701 (s, sh) cm^{-1}. HRMS (GC + EI): calculated for $C_{12}H_9O_4$ $[M\text{-}OCH_3]^+$ 201.0552, found 201.0543.

Methyl 2-(3-ethoxy-3-oxoprop-1-yn-1-yl) benzoate (11o):



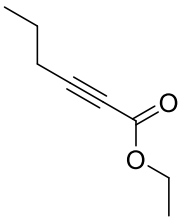
The compound was prepared according to a literature procedure.[5] A solution of *n*BuLi in hexane (6.47 mL, 2.5 M, 16.19 mmol, 1 eq.) was added to a solution of *N,N*-diisopropylamine (2.27 mL, 16.19 mmol, 1 eq.) in 24 mL THF at 0 °C. The solution was cooled down to – 75 °C and ethyl propiolate (1.64 mL, 16.19 mmol, 1 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (3.645 g, 16.19 mmol, 1 eq.) in 16 mL THF, which was also added dropwise. Methyl 2-iodobenzoate (4.1 g, 13.76 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.636 g, 0.55 mmol, 0.04 eq.) were added simultaneously. The mixture was stirred at rt for 22 h. The mixture was diluted with 200 mL EA and washed with sat. NH_4Cl solution (2*50 mL) and sat. NaCl solution (1*50 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (40% EA in PE, followed by 5% EA in PE) and the product was obtained as yellowish oil (0.837 g, 26%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.05-8.02 (m, 1H), 7.72-7.69 (m, 1H), 7.57-7.48 (m, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.97 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.75 153.99, 135.23, 133.00, 131.95, 130.73, 130.06, 120.32, 84.33, 62.13 52.41, 14.09. IR (ATR): $\tilde{\nu}$ = 2219 (m), 1703 (s) cm^{-1}. HRMS (GC + EI): calculated for $C_{13}H_{12}O_4$ $[M\text{-}OCH_3]^+$ 201.0552, found 201.0545.

Methyl 3-(4-nitrophenyl)propiolate (11p):



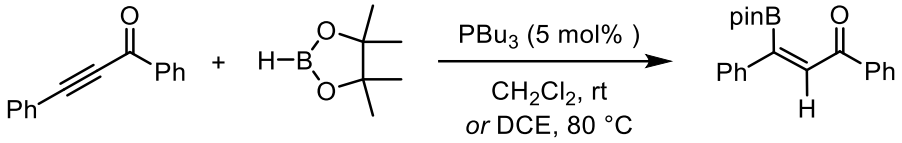
The compound was prepared according to a literature procedure.[5] A solution of *n*BuLi in hexane (4.52 mL, 2.5 M, 11.30 mmol, 1 eq.) was added to a solution of *N,N*-diisopropylamine (1.59 mL, 11.30 mmol, 1 eq.) in 12 mL THF at 0 °C. The solution was cooled down to -98 °C and a solution of methyl propiolate (1 mL, 11.30 mmol, 1 eq.) in 5 mL THF was added dropwise, followed by a solution of $ZnBr_2$ (2.54 g, 11.30 mmol, 1 eq.) in 10 mL THF, which was also added dropwise. 4-nitroiodbenzene (2.39 g, 9.60 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.261 g, 0.23 mmol, 0.02 eq.) were added simultaneously as a solid. The mixture was stirred at rt for 15 h. The mixture was diluted with 200 mL EA and washed with sat. NH_4Cl solution (2*50 mL), sat. $NaHCO_3$ solution (1*50 mL) and sat. NaCl solution (1*25 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed in vacuum. The residue was purified via flash chromatography (10% EA in PE) and the product was obtained as an orange solid (1.195 g, 61%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, J = 9 Hz, 2H), 7.75 (d, J = 9 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.68, 148.53, 133.69, 126.17, 123.74, 83.82, 83.11, 53.13. IR (ATR): $\tilde{\nu}$ = 2226 (s, sh), 1704 (s, sh) cm^{-1}. HRMS (GC + p EI): calculated for $C_{10}H_7NO_4$ $[M\text{-}OCH_3]^+$ 174.0191, found 174.0184.

Ethyl hex-2-ynoate (11q):



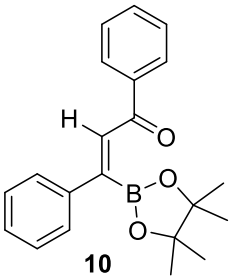
The compound was prepared according to a literature procedure.[4] A solution of *n*BuLi in hexane (22.32 mL, 2.5 M, 55.79 mmol, 1.1 eq.) was added drop wise over a period of 5 min to a solution of 1-pentyne (5 mL, 50.72 mmol, 1 eq.) in 100 mL THF at -78 °C. The solution was allowed to warm up to rt and cooled to -98 °C again. Ethyl chloroformate (5.33 mL, 55.79 mmol, 1.1 eq.) was added dropwise over 5 min. The solution was stirred at rt for 1.5 h. To the solution 50 mL sat. aqueous NH_4Cl-solutio, 50 mL dest. H_2O and 100 mL EA were added. The phases were separated and the aqueous phase was extracted with 100 mL EA. The combined organic phases were washed with sat. aqueous NaCl-solution and dried over Na_2SO_4. The solvent was removed in vacuum and the crude product was distilled in high vacuum (10^{-1} mbar, 58 °C), giving the product as a colourless oil (6.497 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.21 (q, J = 7.1 Hz, 2H), 2.31 (t, J = 7.1 Hz, 3H), 1.67-1.55 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.84, 89.22, 73.26, 61.72, 21.05, 20.56, 14.01, 13.43. IR (ATR): $\tilde{\nu}$ = 2230 (m), 7107 (s), 1245 (s), 1070 (s) cm^{-1}. HRMS (GC + p EI): calculated for C_6H_7O [M-OCH_2CH_3]$^+$ 95.0497, found 95.0492.

General procedure for phosphine-catalyzed *trans*-selective hydroboration of 1,3-diphenylprop-2-yn-1-one:



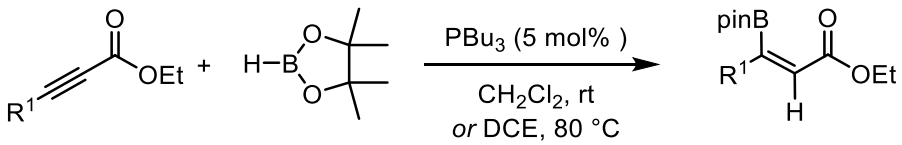
The reaction vial, containing a stirring bar, with 1,3-diphenylprop-2-yn-1-one (0.3 mmol, 1 equiv.) was sealed and then evacuated and refilled with argon for 3 times. 1 ml of THF was added followed by the addition of pinBH (0.33 mmol, 1.1 equiv.) and PBu_3 (5 mol%). After stirring at 80 °C for 4 hours, the solvent of the reaction system was removed under reduced pressure. The product was purified by column chromatography.

(E)-1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) prop-2-en-1-one (10): (23 mg, 23%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14-7.94 (m, 2H), 7.75-7.60 (m, 2H), 7.60-7.50 (m, 1H), 7.50-7.38 (m, 3H), 7.38-7.23 (m, 3H), 1.39 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.89, 138.68, 135.36, 133.97, 129.81, 129.43, 128.71, 128.61, 127.81, 127.70, 83.32, 25.47. ^{11}B NMR (128 MHz, $CDCl_3$): δ 26.66. IR (ATR): $\tilde{\nu}$ =2923, 1600, 1492, 1451, 1374, 1140, 907, 730, 696 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{21}H_{23}{}^{10}BO_3$ [M+Na]$^+$ 356.1669, found 356.1664.



10

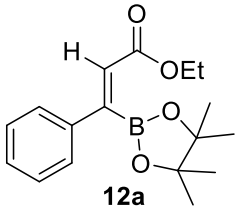
General procedure for phosphine-catalyzed *trans*-selective hydroboration of ynoates:



Method A: The reaction vial, containing a stirring bar, with ynoates (0.3 mmol, 1 equiv.) was sealed and then evacuated and refilled with argon for 3 times. 1 ml of DCM was added followed by the addition of pinBH (0.33 mmol, 1.1 equiv.) and PBu_3 (5 mol%). After stirring at room temperature for 4 hours, the solvent of the reaction system was removed under reduced pressure. The product was purified by column chromatography.

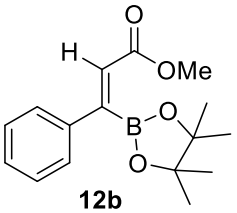
Method B: The reaction vial, containing a stirring bar, with ynoates (0.3 mmol, 1 equiv.) was sealed and then evacuated and refilled with argon for 3 times. 1 ml of DCE was added followed by the addition of pinBH (0.33 mmol, 1.1 equiv.) and PBu_3 (5 mol%). After stirring at reflux for 4 hours, the solvent of the reaction system was removed under reduced pressure. The product was purified by column chromatography.

Ethyl (E)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12a): (Method A: 75 mg, 83%; Method B: 76 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.35 (m, 2H), 7.34-7.21 (m, 3H), 6.36 (s, 1H), 4.17 (q, J=7.1 Hz, 2H), 1.34 (s, 12H), 1.23 (t, J=7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.08, 138.66, 129.07, 128.71, 127.15, 126.08, 84.35, 60.79, 25.09, 14.31. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.75. IR (ATR): $\tilde{\nu}$ = 2978, 1704, 1605, 1376, 1303, 1181, 1138, 1004, 882, 830, 730 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{23}{}^{10}BO_4$ $[M+Na]^+$ 324.1618, found 324.1622.



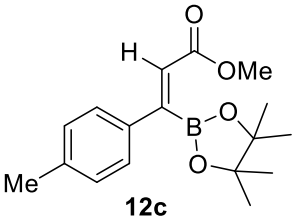
12a

Methyl (E)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12b): (Method A: 54 mg, 63%; Method B: 64 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52–7.35 (m, 2H), 7.35–7.20 (m, 3H), 6.35 (s, 1H), 3.70 (s, 3H), 1.33 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.38, 138.61, 129.15, 128.73, 127.13, 125.60, 84.41, 51.90, 25.08. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.53. IR (ATR): $\tilde{\nu}$ = 2980, 1709, 1605, 1493, 1434, 1372, 1304, 1195, 1176, 1136, 1019, 977, 882, 852, 770, 735 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{16}H_{21}{}^{10}BO_4$ $[M+Na]^+$ 310.1461, found 310.1469.



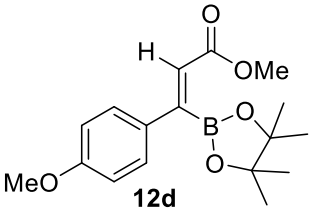
12b

Methyl (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(p-tolyl) acrylate (12c): (Method A: 72 mg, 79%; Method B: 82 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (d, J = 8.2 Hz, 2H), 7.26–7.12 (m, 2H), 6.46 (s, 1H), 3.82 (s, 3H), 2.39 (s, 3H), 1.46 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.55, 139.36, 135.77, 129.49, 127.13, 124.63, 84.39, 51.88, 25.12, 21.34. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.76. IR (ATR): $\tilde{\nu}$ =2981, 1708, 1605, 1490, 1371, 1305, 1175, 1136, 978, 882, 852, 839, 738 cm^{-1}. HRMS (ESI-TOF) cald for $C_{17}H_{23}{}^{10}BO_4$ $[M+Na]^+$ 324.1618, found 324.1623.



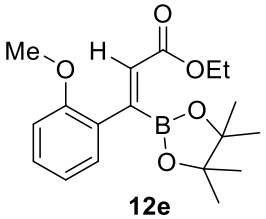
12c

Methyl (E)-3-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12d): (Method A: 73 mg, 76%; Method B: 87 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, J = 8.8 Hz, 2H), 6.96-6.76 (m, 2H), 6.37 (s, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 1.41 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.68, 160.63, 130.97, 128.68, 123.21, 114.17, 84.33, 55.29, 51.80, 25.15. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.13. IR (ATR): $\tilde{\nu}$ = 2984, 1700, 1590, 1570, 1510, 1438, 1372, 1289, 1173, 1135, 1021, 976, 837, 784 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{23}{}^{10}BO_5$ $[M+Na]^+$ 340.1567, found 340.1571.



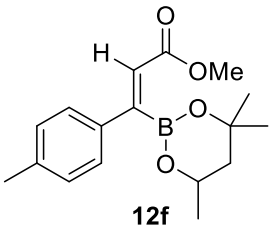
12d

Ethyl (E)-3-(2-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12e): (Method A: 20 mg, 21%; Method B: 32 mg, 34%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.44-7.29 (m, 2H), 7.03-6.89 (m, 2H), 6.55 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.44 (s, 12H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.57, 157.25, 130.20, 129.54, 129.21, 128.72, 121.07, 111.10, 83.97, 60.54, 55.50, 25.27, 14.39. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.03. IR (ATR): $\tilde{\nu}$ = 2977, 1708, 1594, 1487, 1376, 1306, 1273, 1179, 1138, 1028, 965, 887, 853, 819, 752 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{22}{}^{10}BFO_4$ $[M+Na]^+$ 354.1724, found 354.1724.



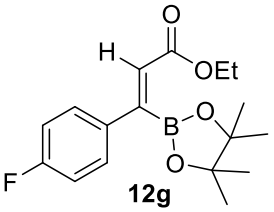
12e

Methyl (E)-3-(p-tolyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl) acrylate (12f): (Method A: 14 mg, 15%; Method B: 41 mg, 46%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.30 (s, 1H), 4.44-4.22 (m, 1H), 3.69 (s, 3H), 2.27 (s, 3H), 1.85-1.67 (m, 2H), 1.39 (s, 3H), 1.28 (s, 3H), 1.23 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.94, 139.29, 135.76, 129.42, 127.29, 121.82, 71.77, 65.57, 51.64, 45.89, 31.29, 27.66, 23.12, 21.38. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.07. IR (ATR): $\tilde{\nu}$ = 2972, 1705, 1593, 1510, 1386, 1299, 1206, 1185, 1166, 1020, 966, 878, 838, 817, 767 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{23}BO_4$ $[M+Na]^+$ 325.1582, found 325.1587.



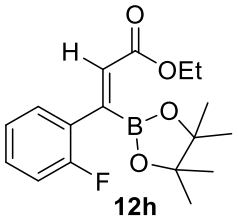
12f

Ethyl (E)-3-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12g): (Method A: 66 mg, 72%; Method B: 71 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49–7.28 (m, 2H), 7.07–6.85 (m, 2H), 6.31 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.34 (s, 12H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 168.04, 161.71, 134.68, 129.02, 128.91, 125.90, 115.89, 115.61, 84.42, 60.88, 25.08, 14.29. ^{11}B NMR (128 MHz, $CDCl_3$): *δ* 29.94. IR (ATR): $\tilde{\nu}$ = 2981, 1708, 1605, 1490, 1433, 1371, 1305, 1176, 1136, 1018, 978, 882, 852, 840, 738 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{22}{}^{11}BFO_4$ $[M+Na]^+$ 343.1487, found 343.1494.



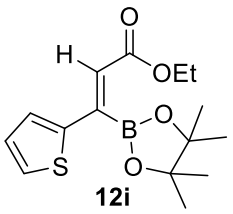
12g

Ethyl (E)-3-(2-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12h): (Method A: 18 mg, 18%; Method B: 26 mg, 27%). ^{1}H NMR (250 MHz, $CDCl_3$): *δ* 7.43-7.31 (m, 1H), 7.27-7.19 (m, 1H), 7.08-6.94 (m, 2H), 6.49 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.32 (s, 12H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 167.71, 162.05, 158.72, 130.54, 130.43, 129.71, 129.66, 129.31, 129.24, 127.90, 126.63, 126.46, 124.29, 124.24, 116.24, 115.94, 84.30, 60.86, 25.08, 14.25. ^{11}B NMR (128 MHz, $CDCl_3$): *δ* 30.36. IR (ATR): $\tilde{\nu}$ = 2978, 1709, 1602, 1486, 1376, 1308, 1263, 1183, 1138, 1037, 965, 889, 853, 829, 760 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{22}{}^{10}BFO_4$ $[M+Na]^+$ 342.1524, found 342.1518.



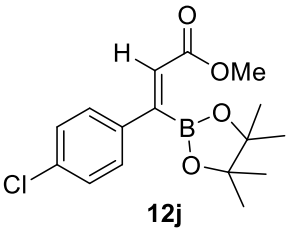
12h

Ethyl (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(thiophen-2-yl) acrylate (12i): (Method A: 55 mg, 60%; Method B: 58 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.27-7.20 (m, 1H), 7.18-7.09 (m, 1H), 7.03-6.85 (m, 1H), 6.36 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.37 (s, 12H), 1.22 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$): *δ* 169.08, 143.55, 130.35, 128.88, 128.82, 128.41, 123.78, 85.43, 61.70, 26.09, 15.20. ^{11}B NMR (128 MHz, $CDCl_3$): *δ* 29.61. IR (ATR): $\tilde{\nu}$ = 2978, 1701, 1589, 1382, 1295, 1226, 1178, 1140, 1034, 965, 854, 705 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{15}H_{21}{}^{10}BO_4S$ $[M+Na]^+$ 330.1182, found 330.1178.



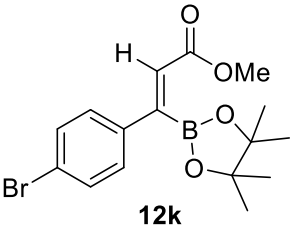
12i

Methyl (E)-3-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12j): (Method A: 61 mg, 63%; Method B: 59 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.39–7.21 (m, 4H), 6.33 (s, 1H), 3.72 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 168.21, 137.05, 135.17, 128.97, 128.41, 126.04, 84.53, 52.01, 25.04. 11B NMR (128 MHz, $CDCl_3$): *δ* 30.63. IR (ATR): $\tilde{\nu}$ = 2981, 1710, 1606, 1491, 1432, 1371, 1304, 1196, 1137, 979, 882, 839, 738 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{16}H_{20}{}^{10}BClO_4$ $[M+Na]^+$ 344.1072, found 344.1072.



12j

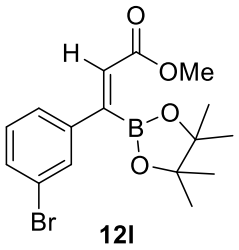
Methyl (E)-3-(4-bromophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12k): (Method A: 72 mg, 65%; Method B: 81 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.47–7.23 (m, 4H), 6.34 (s, 1H), 3.72 (s, 3H), 1.33 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 168.24, 137.57, 131.97, 128.72, 126.16, 123.50, 84.58, 52.07, 25.08. ^{11}B NMR (128 MHz, $CDCl_3$): *δ* 30.13. IR (ATR): $\tilde{\nu}$ = 2981, 1715, 1606, 1488, 1431, 1371, 1324, 1197, 1138,



12k

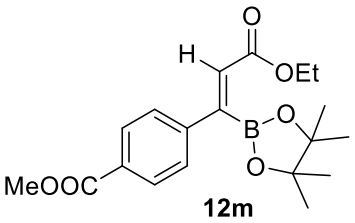
1072, 981, 840, 738 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{16}H_{20}{}^{10}BBrO_4$ $[M+Na]^+$ 388.0567, found 389.0572.

Methyl (E)-3-(3-bromophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) (12l): (Method A: 71 mg, 65%; Method B: 51 mg, 47%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.61 (t, J = 1.9 Hz, 1H), 7.50-7.31 (m, 2H), 7.20 (t, J = 7.9 Hz, 1H), 6.39 (s, 1H), 3.77 (s, 3H), 1.39 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.12, 140.67, 131.98, 130.26, 130.19, 126.74, 125.69, 122.93, 84.61, 52.10, 25.05. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.44. IR (ATR): $\tilde{\nu}$ = 2977, 1710, 1607, 1556, 1436, 1370, 1310, 1196, 1175, 1136, 1021, 981, 853, 785 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{16}H_{20}{}^{10}BBrO_4$ $[M+Na]^+$ 388.0567, found 388.0569.



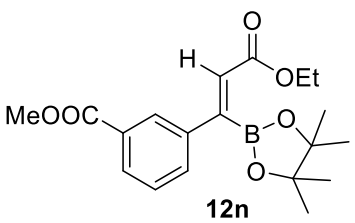
12l

Methyl (E)-4-(3-ethoxy-3-oxo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) prop-1-en-1-yl) benzoate (12m): (Method A: 5 mg, 5%; Method B: 4 mg, 4%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 6.40 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 1.34 (s, 12H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.72, 166.67, 143.16, 130.32, 129.95, 127.91, 127.07, 84.51, 61.02, 52.17, 25.00. ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.44. IR (ATR): $\tilde{\nu}$ = 2978, 1709, 1609, 1373, 1274, 1182, 1139, 1108, 853, 776 cm^{-1}. HRMS (ESI-TOF) cald for $C_{19}H_{25}{}^{10}BO_6$ $[M+Na]^+$ 382.1673, found 382.1668.



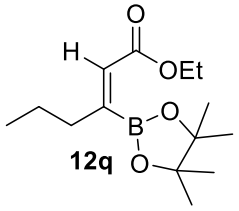
12m

Methyl (E)-3-(3-ethoxy-3-oxo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) prop-1-en-1-yl) benzoate (12n): (Method A: 37 mg, 34%; Method B: 22 mg, 20%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.30-8.12 (m, 1H), 8.10-7.92 (m, 1H), 7.78-7.61 (m, 1H), 7.52-7.33 (m, 1H), 6.50 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.91 (s, 3H), 1.42 (s, 12H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.91, 166.62, 138.68, 131.15, 130.65, 130.06, 128.81, 128.71, 126.69, 84.49, 60.95, 52.18, 25.04, 14.25. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.44. IR (ATR): $\tilde{\nu}$ = 2978, 1707, 1607, 1438, 1373, 1301, 1182, 1138, 1110, 1032, 965, 856, 760 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{19}H_{25}{}^{10}BO_6$ $[M+Na]^+$ 382.1673, found 382.1666.



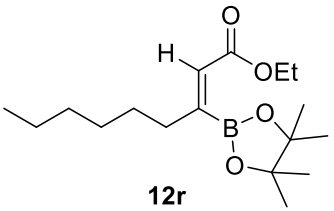
12n

Ethyl (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) hex-2-enoate (12q): (Method A: 18 mg, 22%; Method B: 26 mg, 31%). ^1H NMR (300 MHz, $CDCl_3$): δ 5.93 (s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.18 (t, J = 7.6 Hz, 2H), 1.52-1.37 (m, 2H), 1.28 (d, J = 0.8 Hz, 12H), 1.19 (t, J = 7.1 Hz, 3H), 0.86 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.89, 125.92, 83.87, 60.33, 37.65, 24.81, 21.13, 14.24, 13.88. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.59. IR (ATR): $\tilde{\nu}$ = 2976, 1710, 1605, 1372, 1305, 1181, 1139, 1026, 978, 854, 740 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{25}{}^{10}BO_4$ $[M+Na]^+$ 290.1774, found 290.1768.



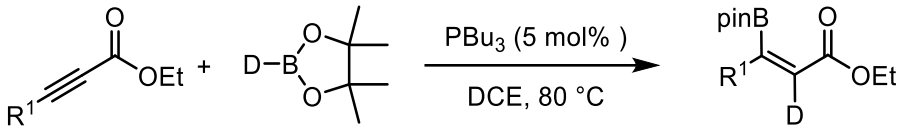
12q

Ethyl (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) non-2-enoate (12r): (Method B: 32 mg, 34%). ^1H NMR (300 MHz, $CDCl_3$): δ 5.93 (s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.19 (td, J = 7.6, 1.5 Hz, 2H), 1.48-1.34 (m, 2H), 1.28 (s, 12H), 1.24-1.17 (m, 9H), 0.81 (t, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.93, 127.90, 125.81, 83.88, 60.34, 35.62, 31.58, 28.97, 27.87, 24.84, 22.50, 14.27, 14.06. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.47. IR (ATR): $\tilde{\nu}$ = 2958, 1709, 1627, 1381, 1306, 1186, 1140, 1035, 965, 857 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{31}{}^{10}BO_4$ $[M+Na]^+$ 332.2244, found 332.2239.



12r

General procedure for phosphine-catalyzed *trans*-selective hydroboration of ynoate with PinBD:



The reaction vial, containing a stirring bar, with 1,3-diphenylprop-2-yn-1-one (0.2 mmol, 1 equiv.) was sealed and then evacuated and refilled with argon for 3 times. 1 ml of THF was added followed by the addition of pinBH (0.3 mmol, 1.5 equiv.) and PBu_3 (5 mol%). After stirring at 80 °C for 4 hours, the solvent of the reaction system was removed under reduced pressure. The product was purified by column chromatography.

Ethyl (E)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate-d (12aD): (49 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.36 (m, 2H), 7.34–7.21 (m, 3H), 4.18 (q, J = 7.1 Hz, 2H), 1.34 (s, 12H), 1.23 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.03, 138.61, 129.04, 128.69, 127.13, 84.33, 60.75, 25.06, 14.28. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.36. IR (ATR): $\tilde{\nu}$ = 2977, 1703, 1592, 1494, 1351, 1309, 1255, 1210, 1142, 1084, 1057, 965, 847, 768 cm^{-1}. HRMS (ESI-TOF) cald for $C_{17}H_{22}D^{10}BO_4$ $[M+Na]^+$ 325.1681, found 325.1674.

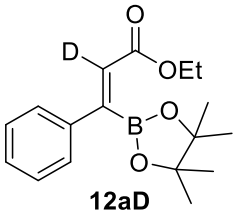
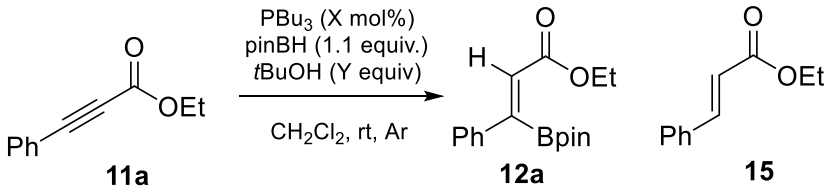


Table 1. Influence of protic additive on yield and selectivity in phosphine catalyzed trans-hydroboration of ynoate **11a**.



Entry	*t*BuOH (equiv.)	Cat. loading	t	Yield[a] **12a**	Yield[a] **15**
1	0	5%	4 h	92%	-
2	1.25	5%	4 h	68%	10%
3	2	5%	4 h	<1%	5%
4	1.25	20%	4 h	62%	8%
5	2	20%	4 h	53%	7%
6	10	20%	4 h	<1%	6%
7	10	100%	4 h	<1%	7%

[a] The yields were based on the NMR test with Ph_3CH as the internal standard.

Crystal Structure Determination

The intensity data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans[6-8].

The structure was solved by direct methods (SHELXS[9]) and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97[9]). All hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically [9].

XP[10] was used for structure representations.

Crystal Data for **12k**: $C_{16}H_{20}BBrO_4$, Mr = 367.04 $gmol^{-1}$, colourless prism, size 0.132 x 0.122 x 0.108 mm^3, monoclinic, space group P $2_1/c$, a = 7.2446(3), b = 10.9482(5), c = 21.3662(9) Å, β = 98.091(3)°, V = 1677.80(13) $Å^3$, T= -140 °C, Z = 4, $\rho_{calcd.}$ = 1.453 gcm^{-3}, μ (Mo-K_α) = 24.63 cm^{-1}, multi-scan, transmin: 0.4965, transmax: 0.7456, F(000) = 752, 19180 reflections in h(-9/9), k(-14/14), l(-27/27), measured in the range 2.68° ≤ Θ ≤ 27.48°, completeness Θ_{max} = 99.5%, 3834 independent reflections, R_{int} = 0.0500, 3241 reflections with $F_o > 4\sigma(F_o)$, 279 parameters, 0 restraints, $R1_{obs}$ = 0.0418, wR^2_{obs} = 0.0887, $R1_{all}$ = 0.0550, wR^2_{all} = 0.0965, GOOF = 1.091, largest difference peak and hole: 0.379 / -0.676 e $Å^{-3}$.

Supporting Information Available: Crystallographic data deposited at the Cambridge Crystallographic Data Centre under CCDC-1845339 for **12k** contain the supplementary crystallographic data excluding structure factors; this data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

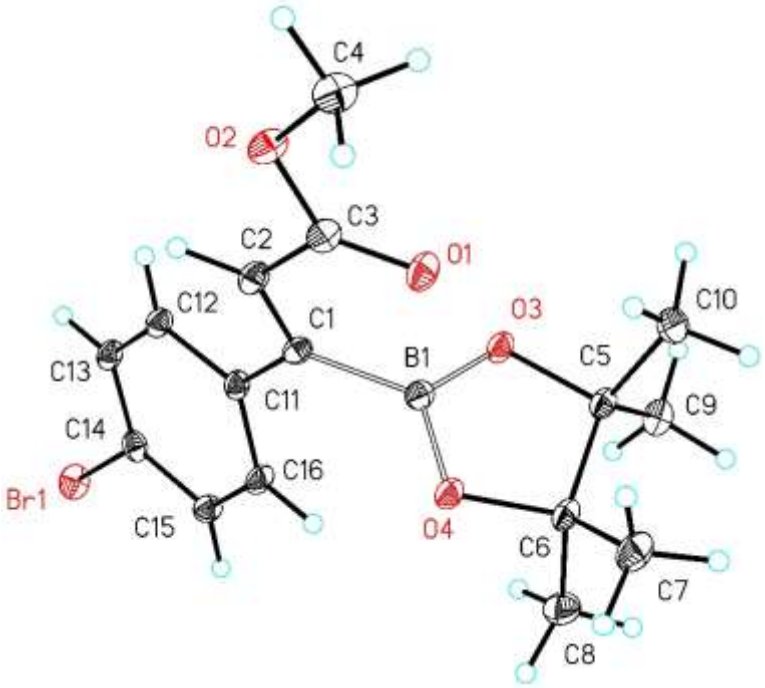


Figure 1: ORTEP diagram of molecule **12k** with thermal ellipsoids at 30% probability.

References

[1] F. Schomberg, Y. Zi, I. Vilotijevic, *Chem. Commun.* **2018**, *54*, 3266-3269

[2] X. Zeng, Z. Lu, S. Liu, G. B. Hammond, B. Xu, *Adv. Synth. Catal.* **2017**, *359*, 4062-4066.

[3] V. R. Batchu, V. Subramanian, K. Parasuraman, N. K. Swamy, S. Kumar, M. Pal, *Tetrahedron* **2005**, *61*, 9869-9877.

[4] S. N. Karad, W. K. Chung, R. S. Liu, *Chem. Commun.* **2015**, *51*, 13004-13007;

[5] L. Anastasia, E. Negishi, *Org. Lett.* **2001**, *3*, 3111-3113;

[6] COLLECT, Data Collection Software; B.V. Nonius, Netherlands, **1998**;

[7] Z. Otwinowski & W. Minor, „Processing of X-Ray Diffraction Data Collected in Oscillation Mode", in Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A, edited by C.W. Carter & R.M. Sweet, pp. 307-326, Academic Press, San Diego, USA, **1997**;

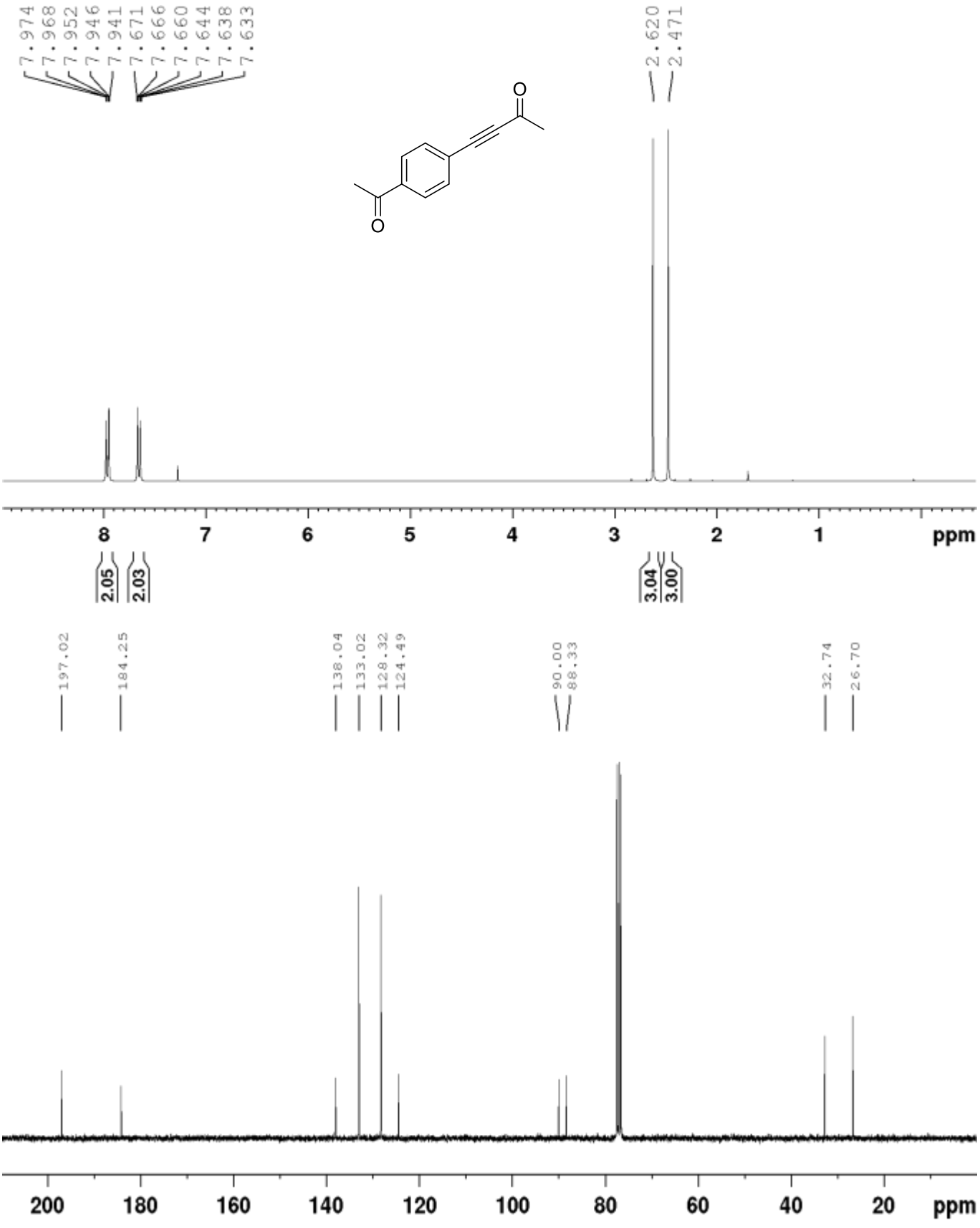
[8] SADABS 2016/2: L. Krause, R. Herbst-Irmer, G.M. Sheldrick, Stalke D., *J. Appl. Cryst.* **2015**, *48*, 3-10;

[9] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8;

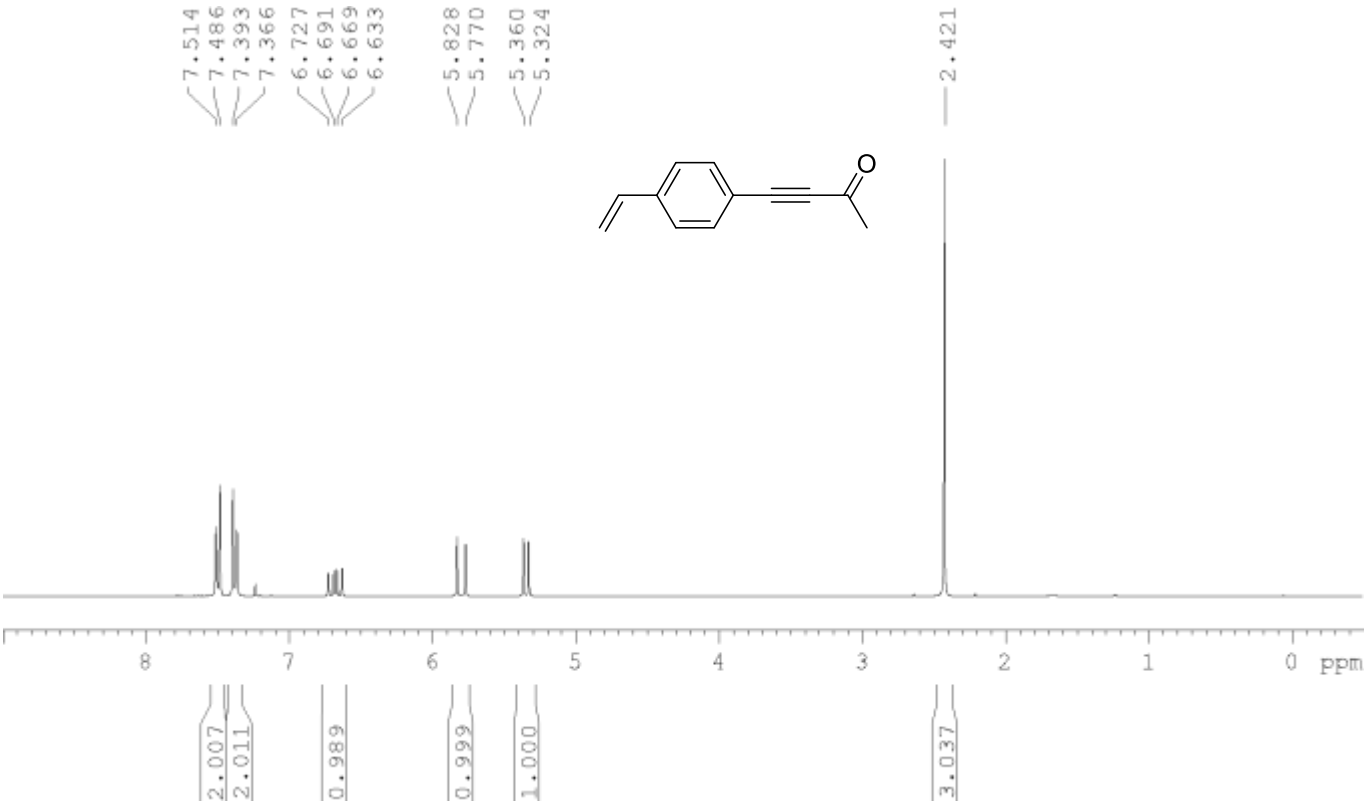
[10] Siemens (**1994**). XP. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

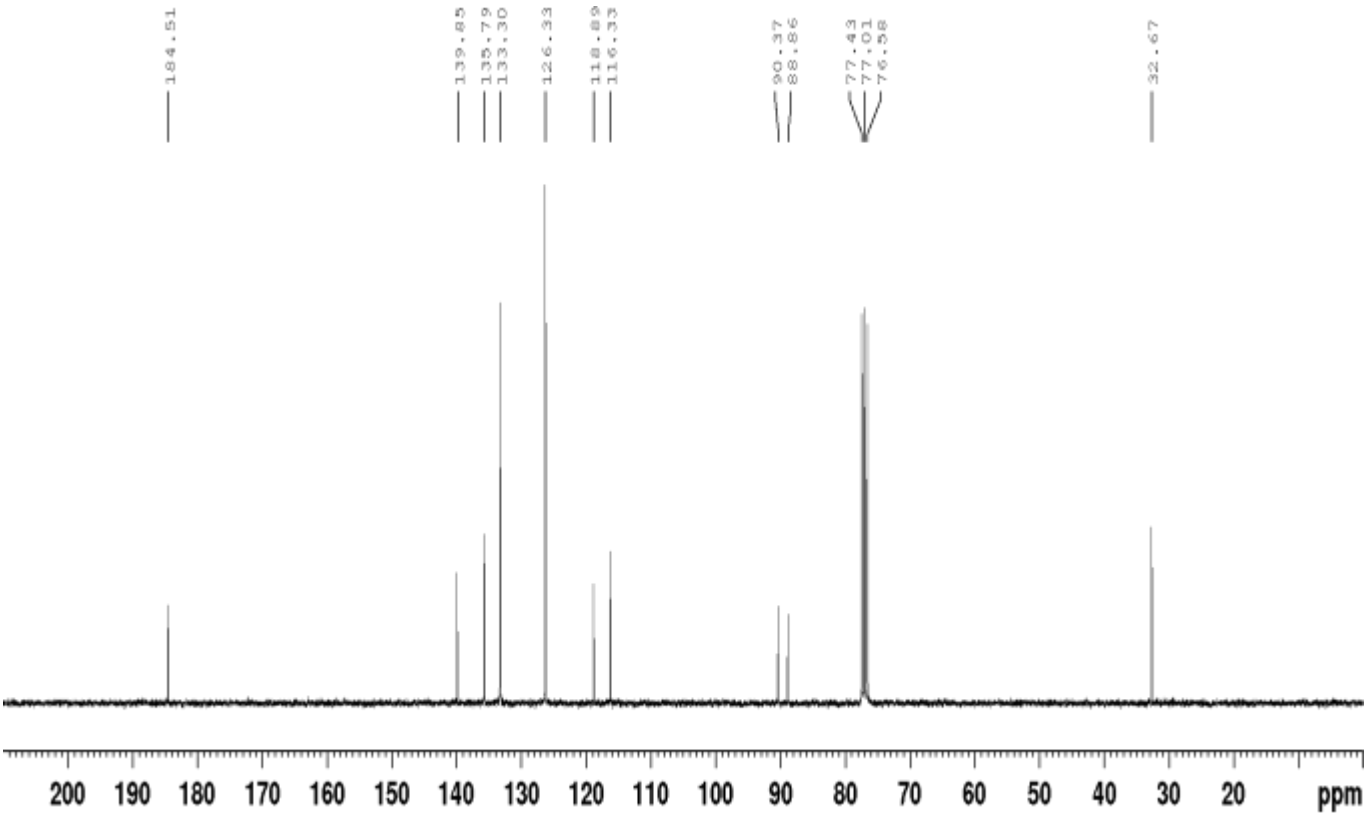
Copies of NMR spectra.

4-(4-acetylphenyl)but-3-yn-2-one (1u)

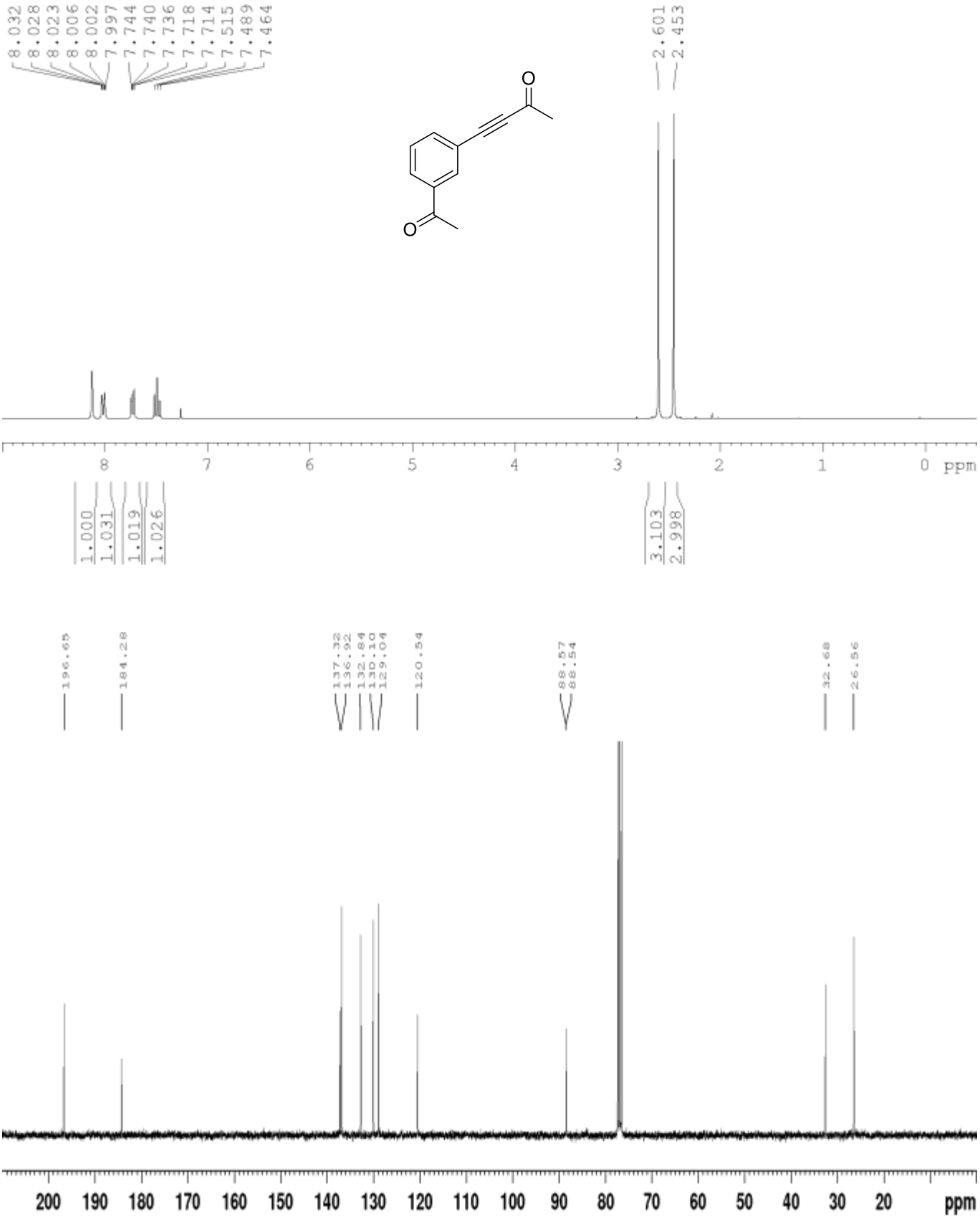


4-(4-vinylphenyl)but-3-yn-2-one (1v)

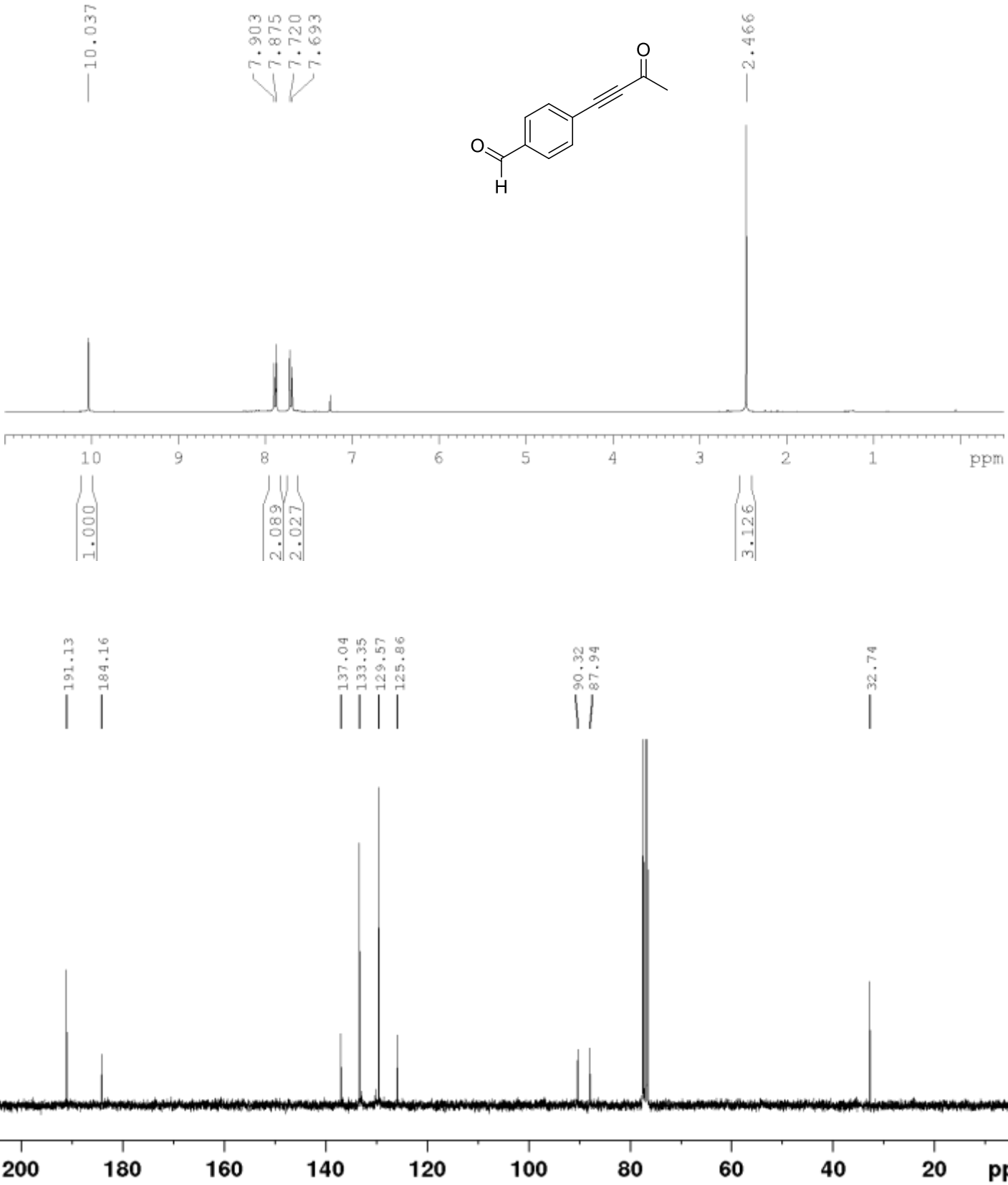




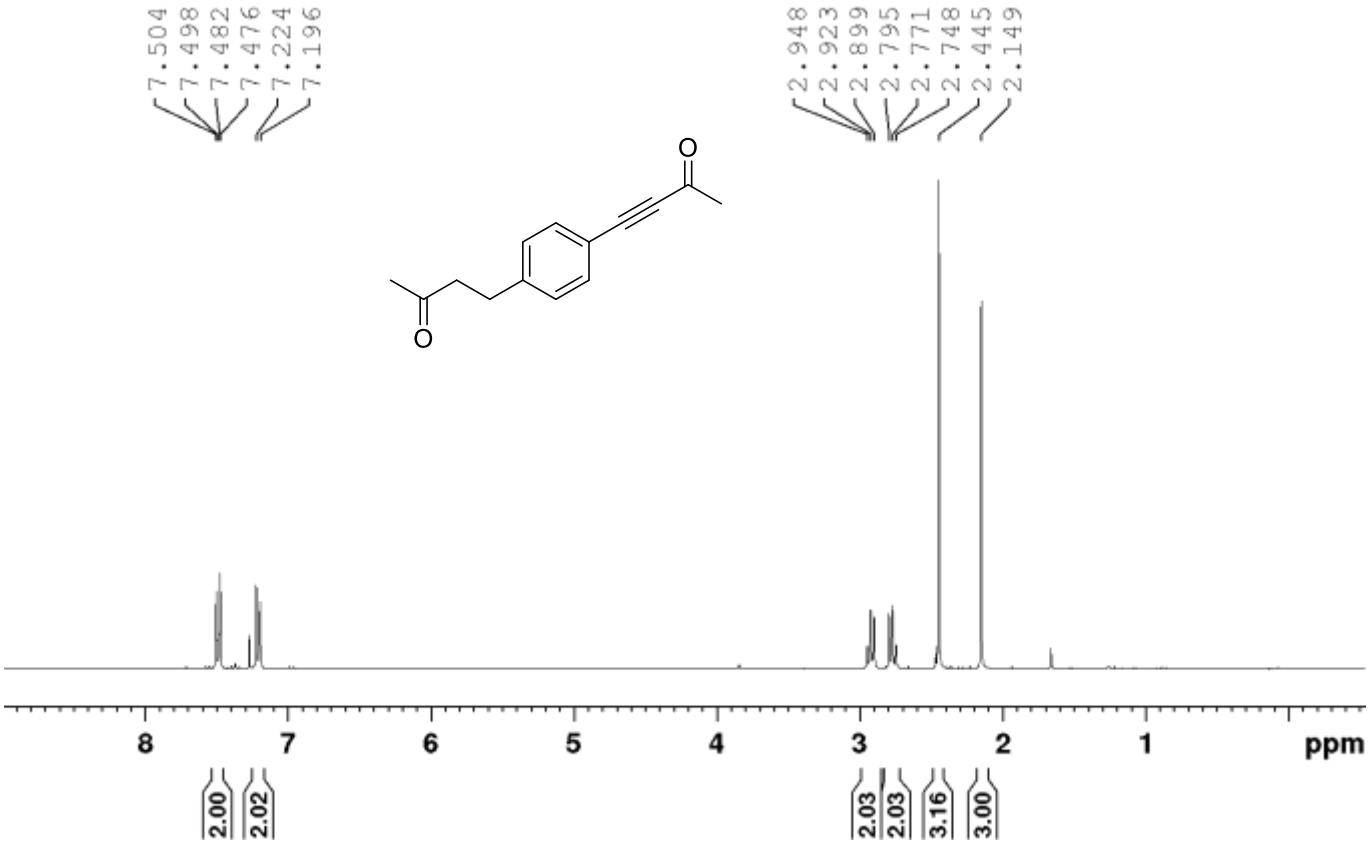
4-(3-acetylphenyl)but-3-yn-2-one (1w)

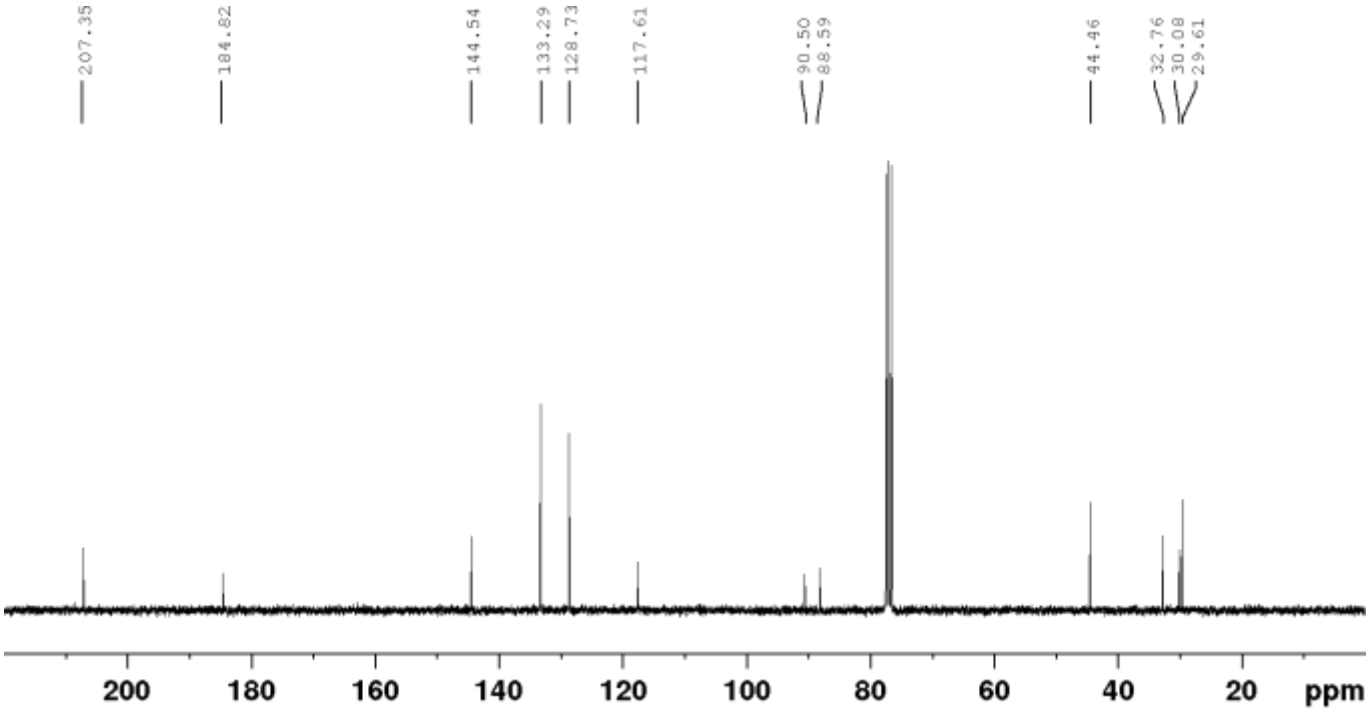


4-(3-oxobut-1-yn-1-yl)benzaldehyde (1x)

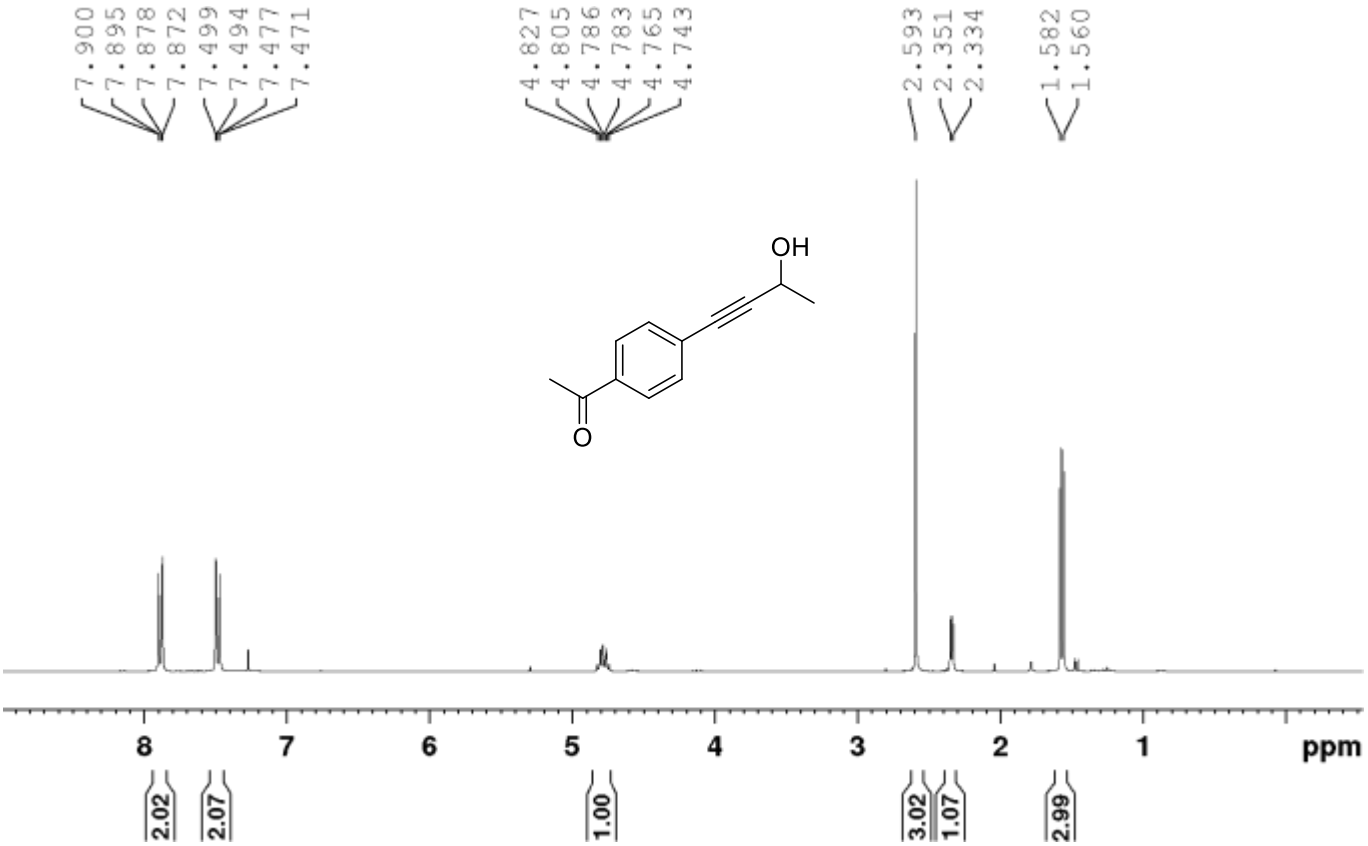


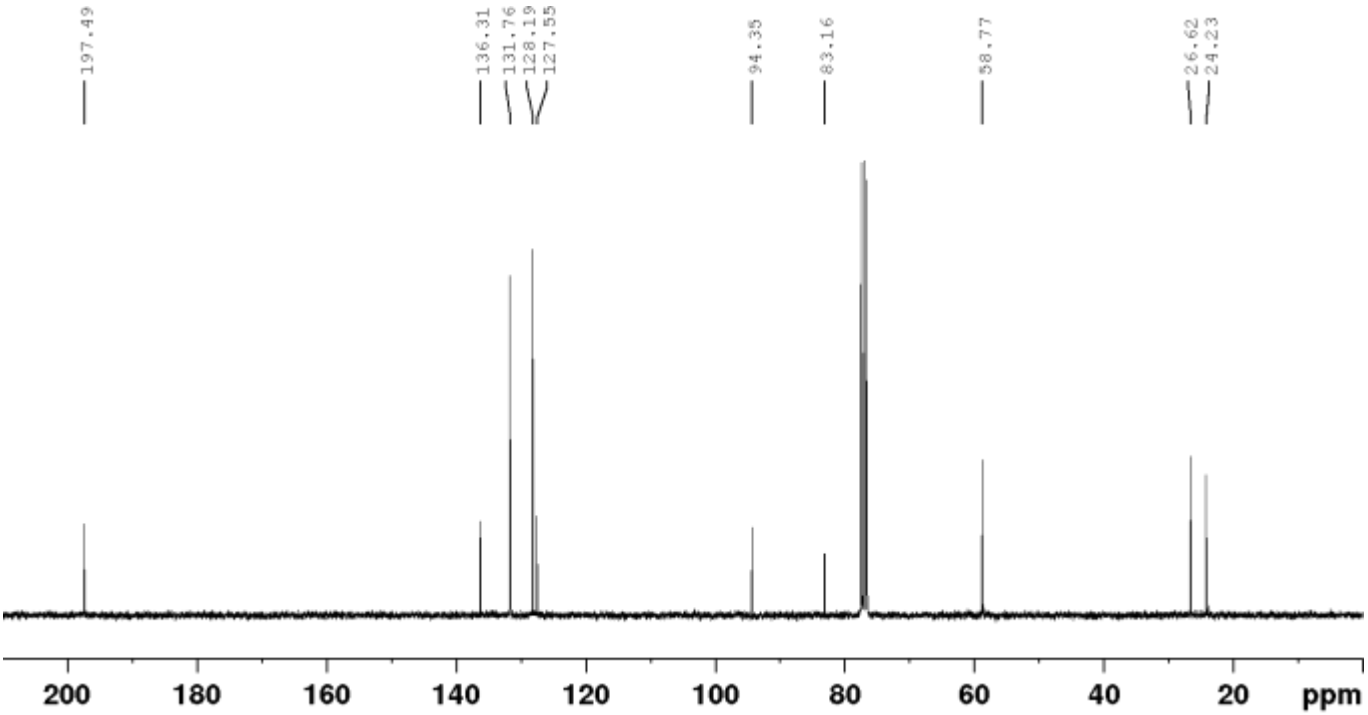
4-(4-(3-oxobutyl)phenyl)but-3-yn-2-one (1y)



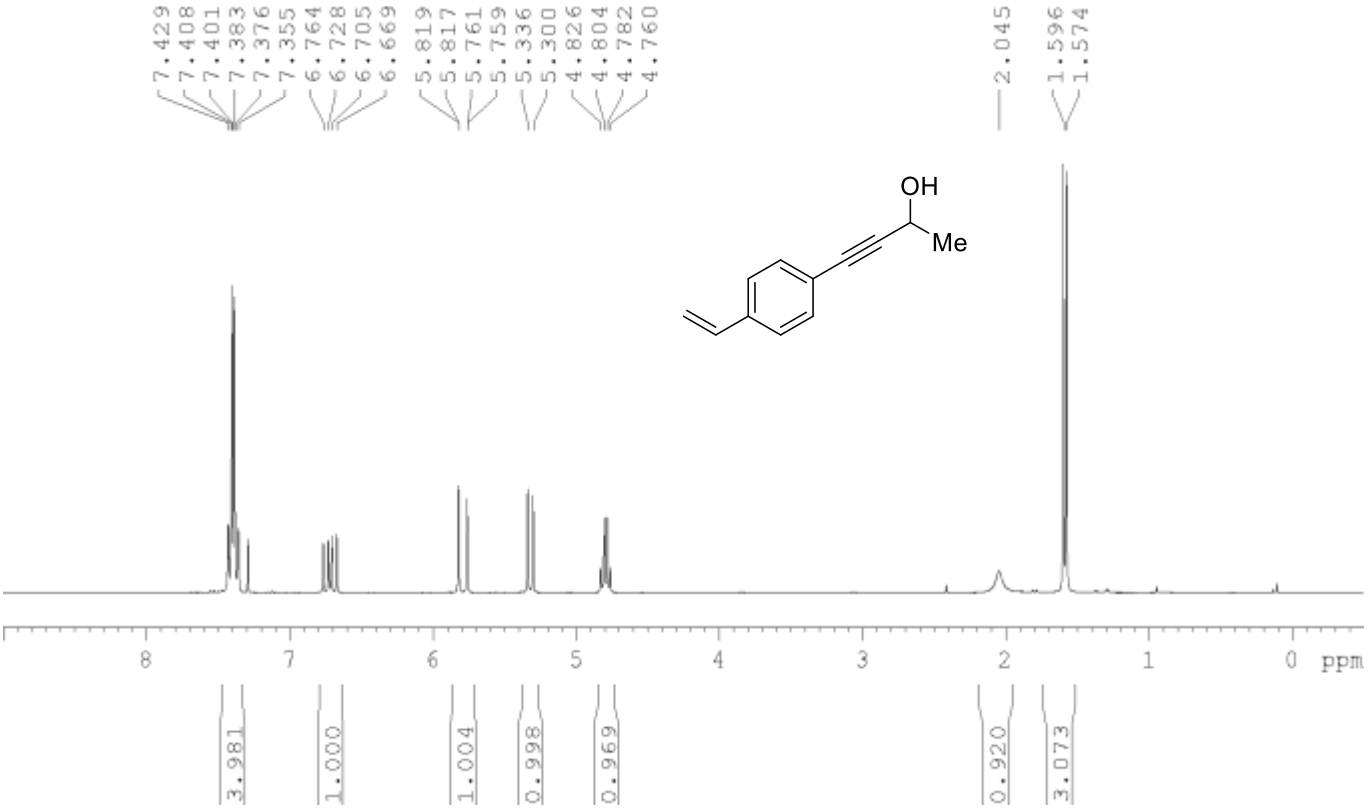


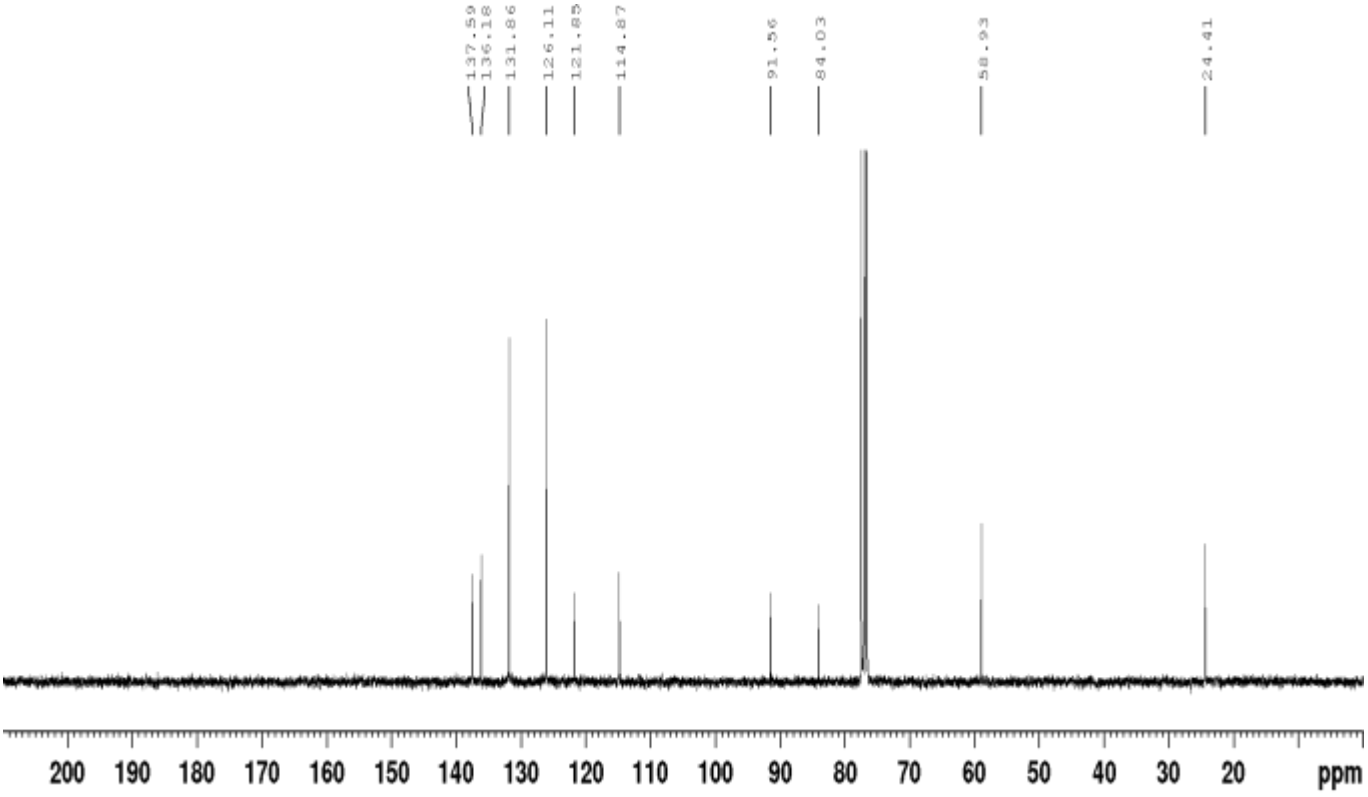
1-(4-(3-hydroxybut-1-yn-1-yl)phenyl)ethan-1-one (2u)



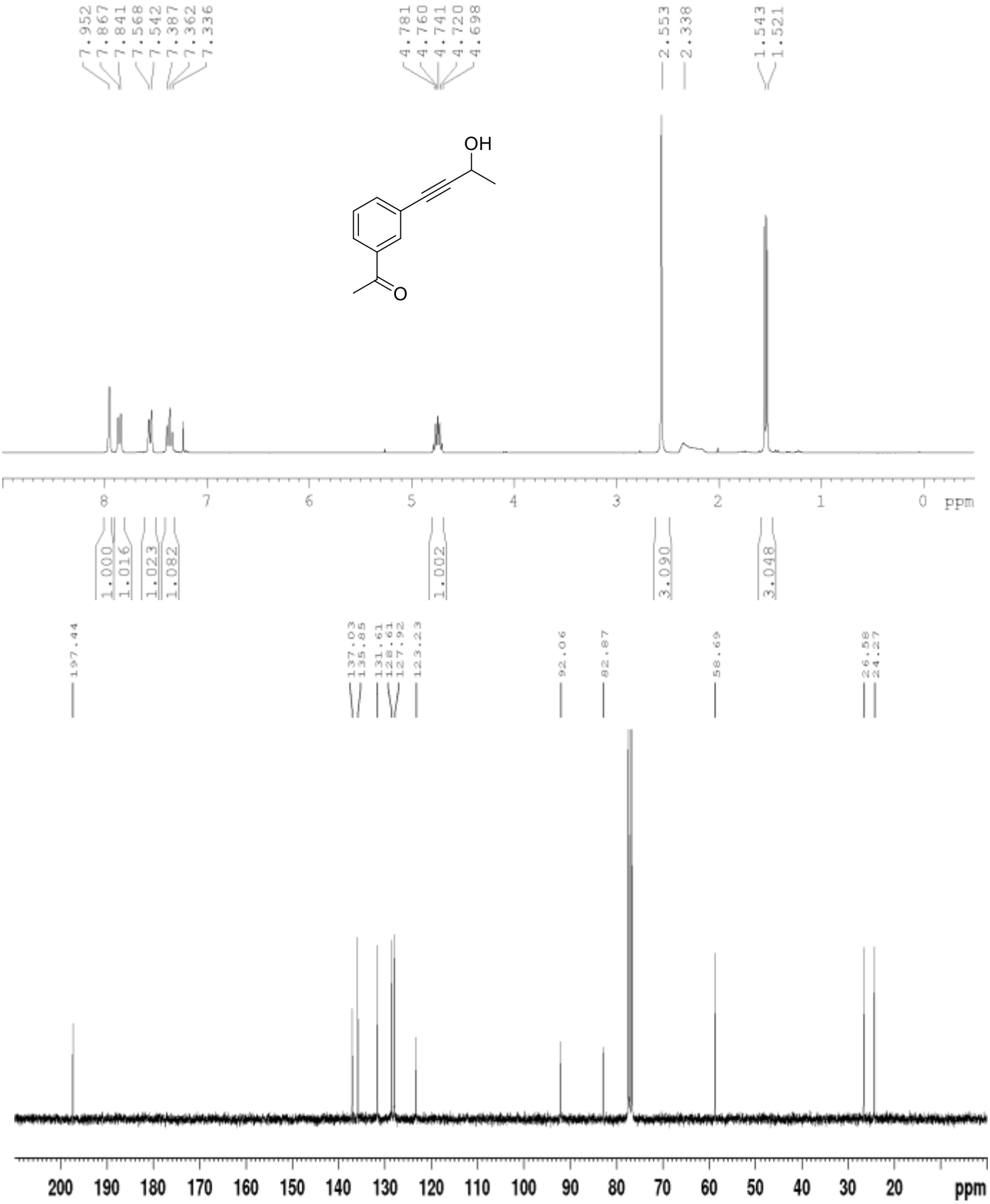


4-(4-vinylphenyl)but-3-yn-2-ol (2v)

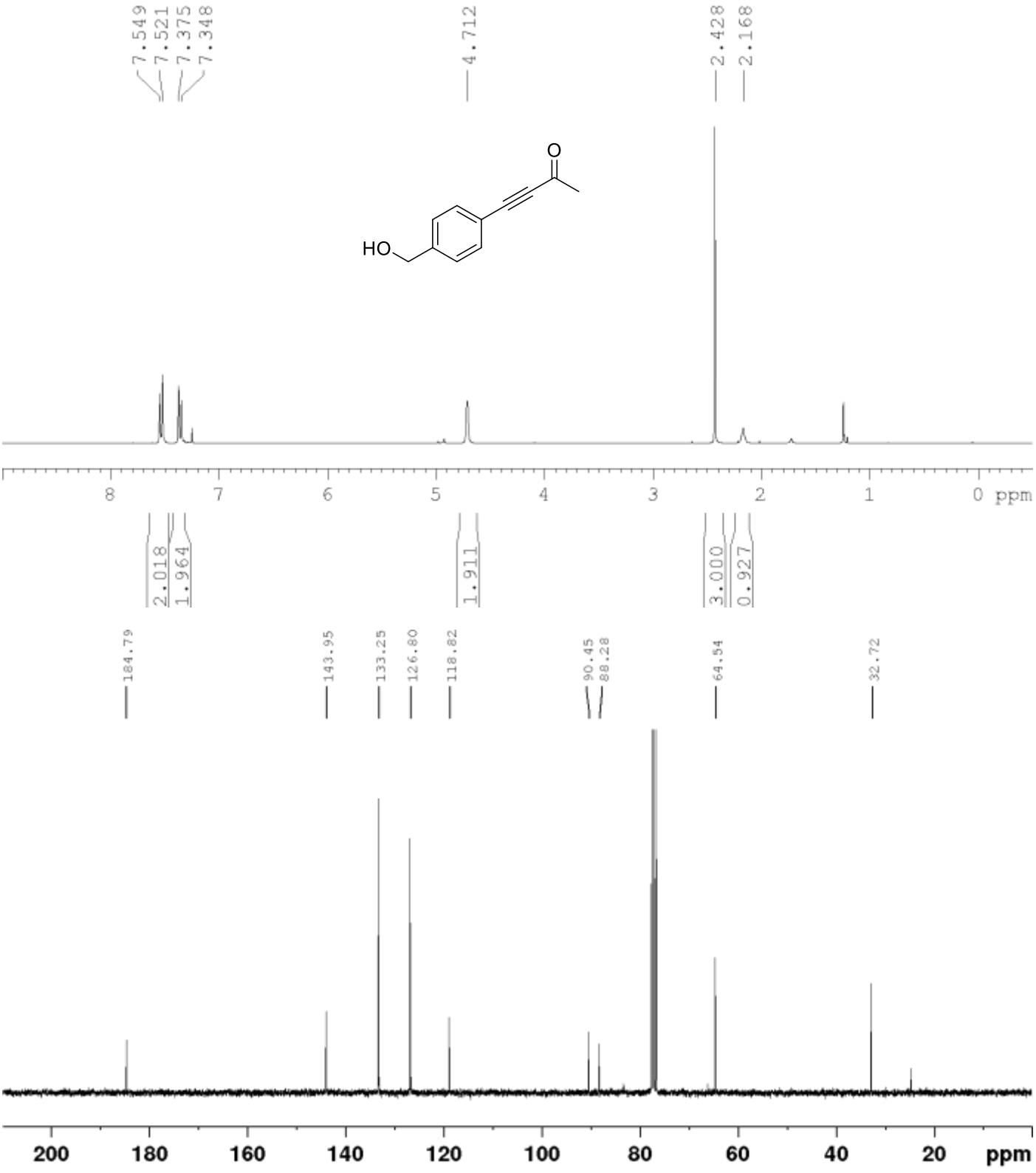




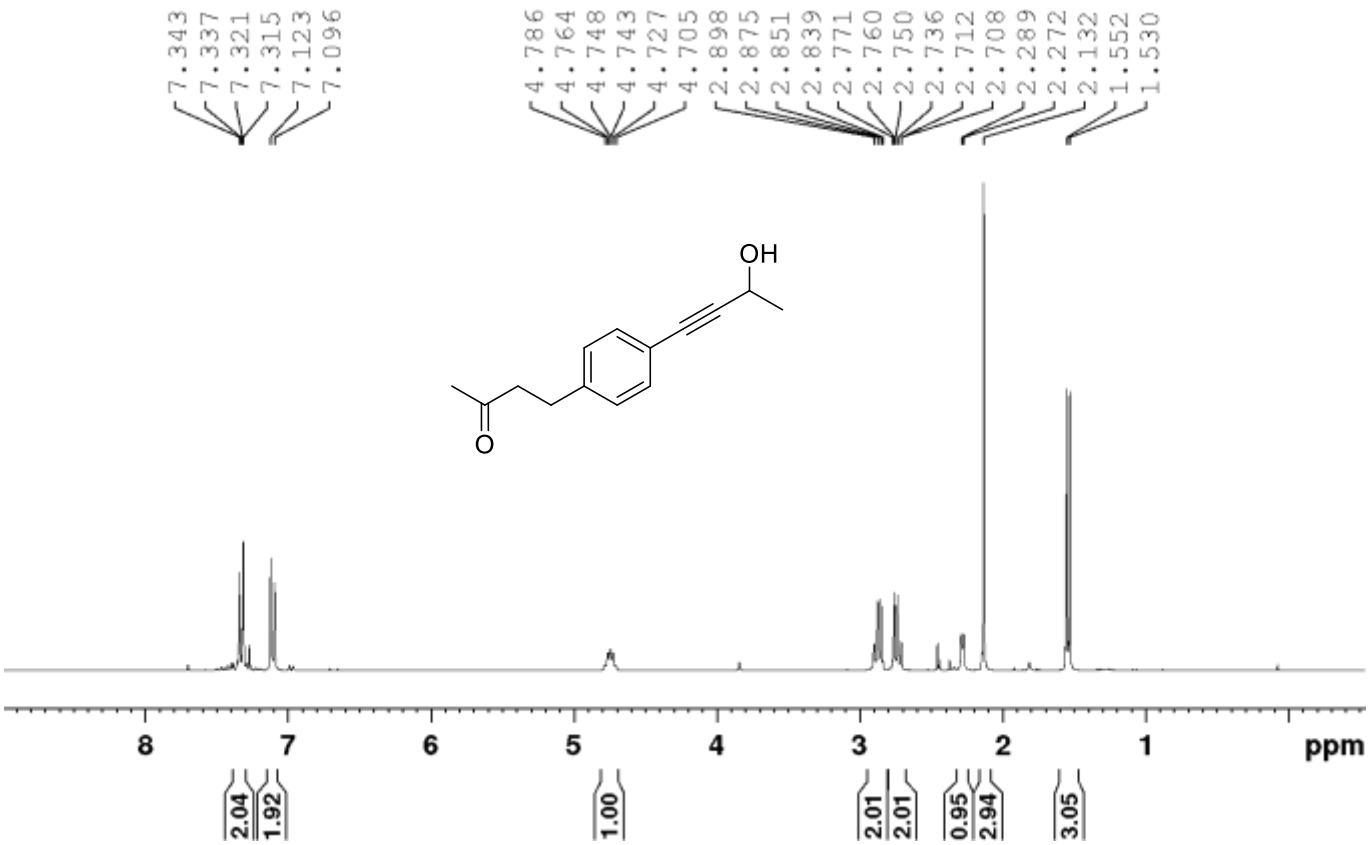
1-(3-(3-hydroxybut-1-yn-1-yl)phenyl)ethan-1-one (2w)

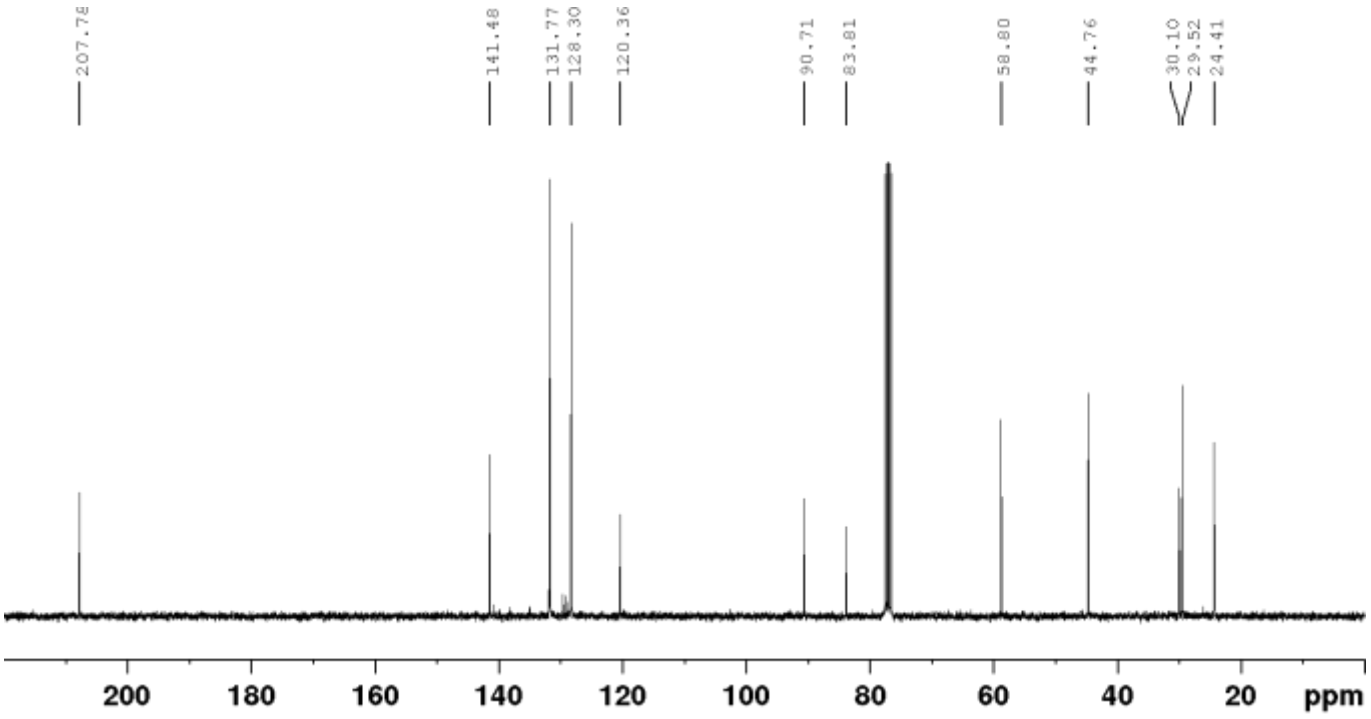


4-(4-(hydroxymethyl)phenyl)but-3-yn-2-one (2x)

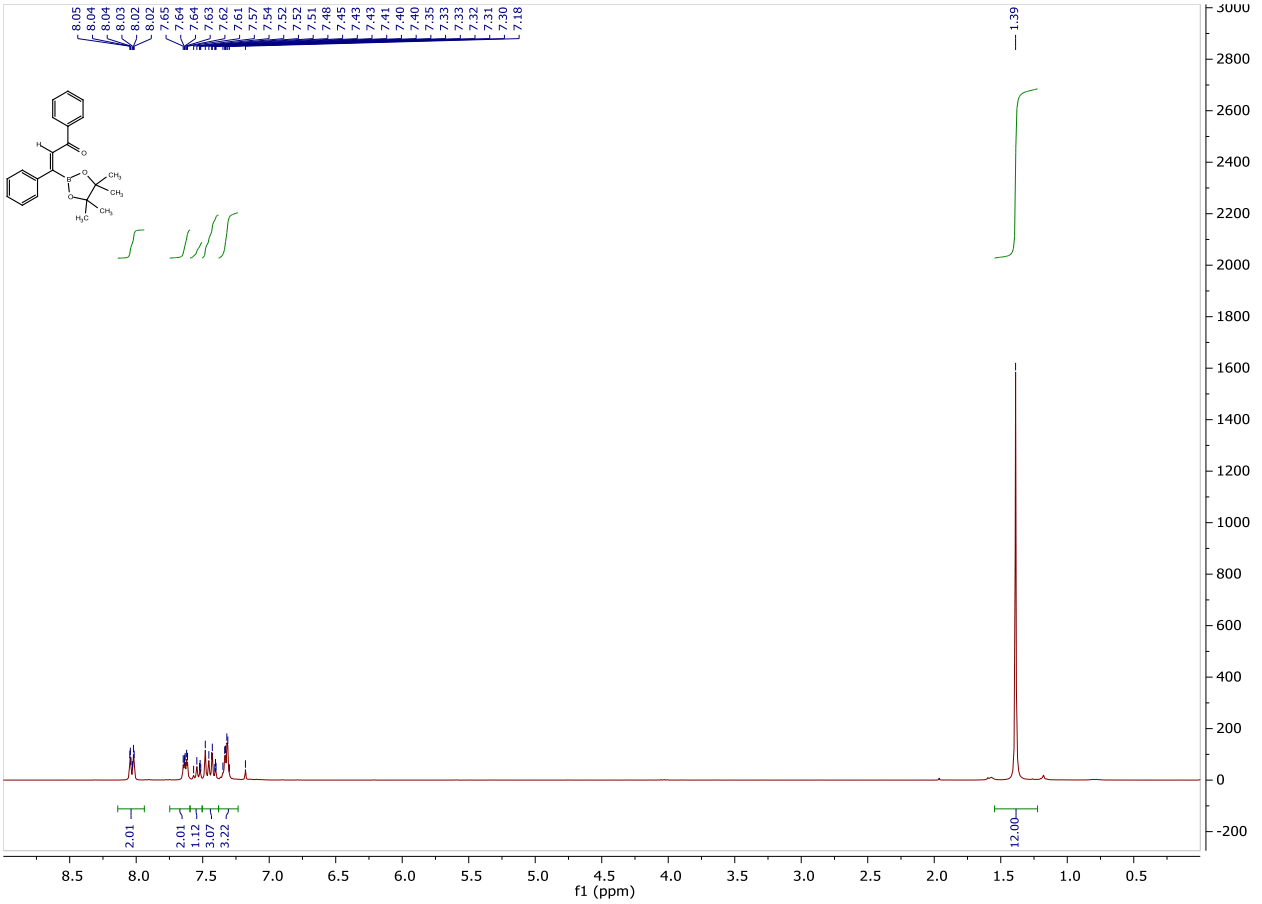


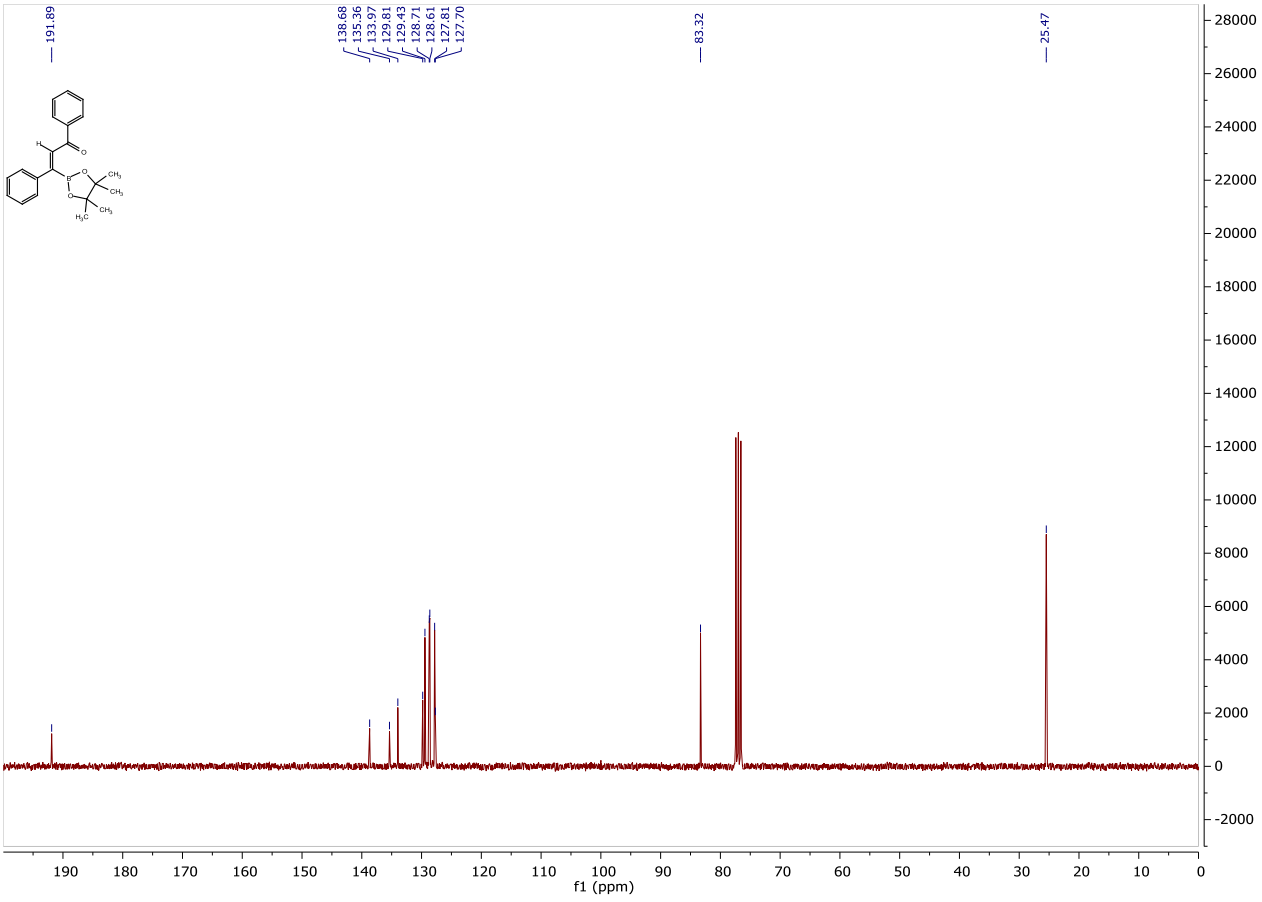
4-(4-(3-hydroxybut-1-yn-1-yl)phenyl)butan-2-one (2y)

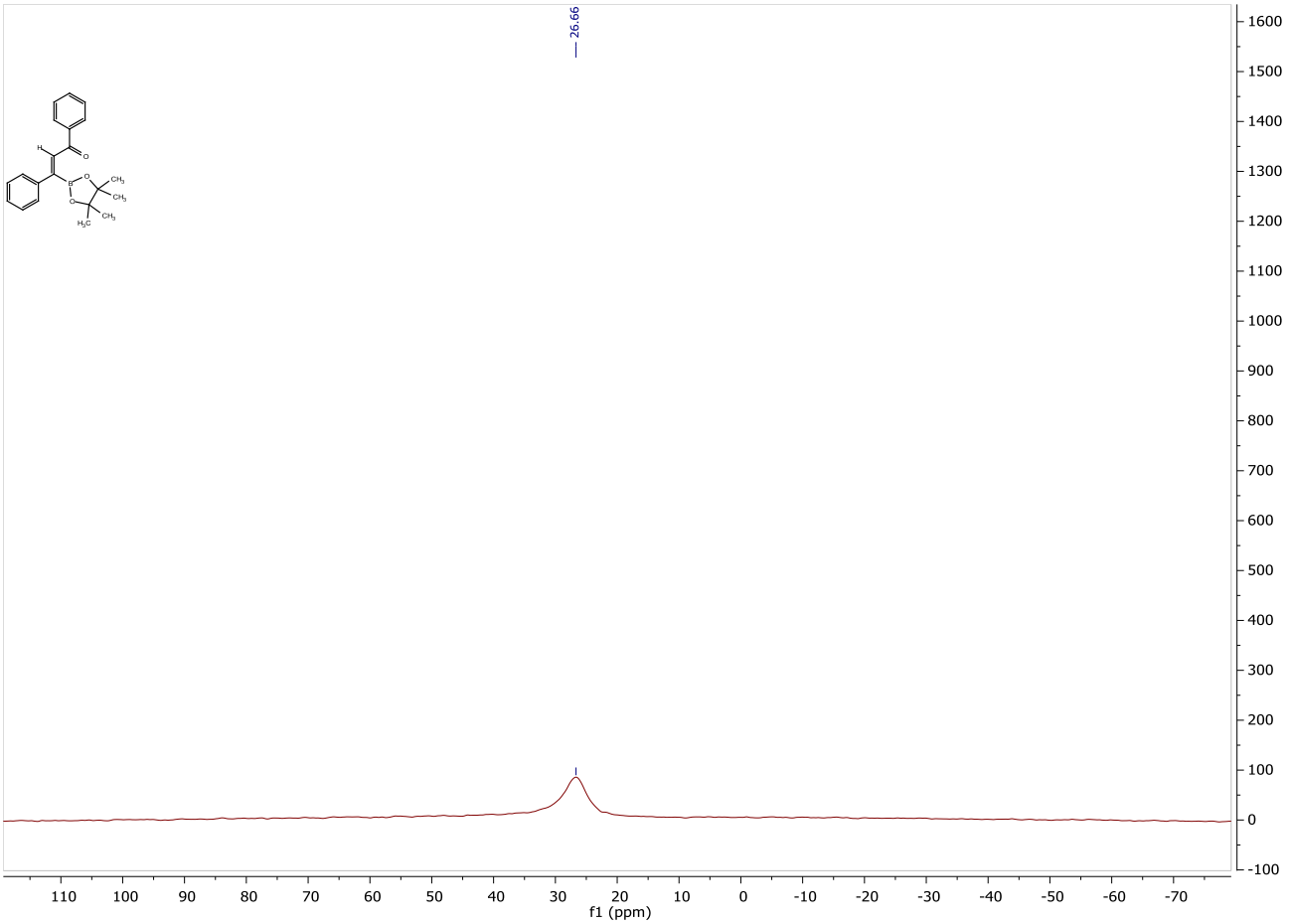




(*E*)-1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) prop-2-en-1-one (10):






26.66
1600
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100
90
80
70
60
50
40
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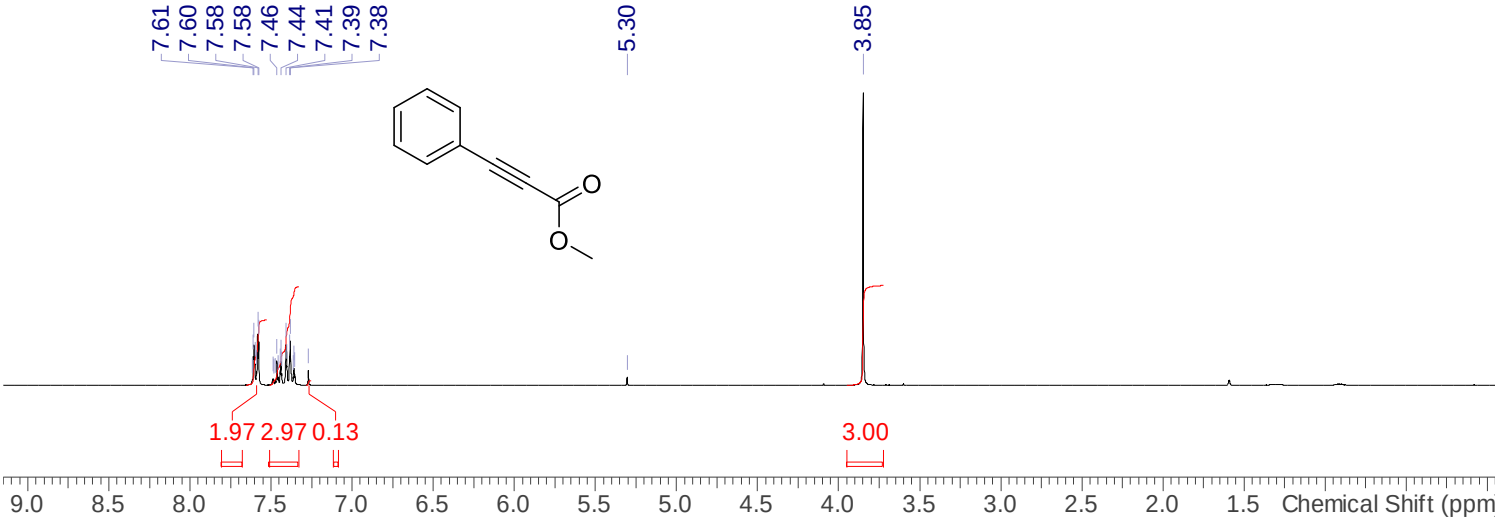
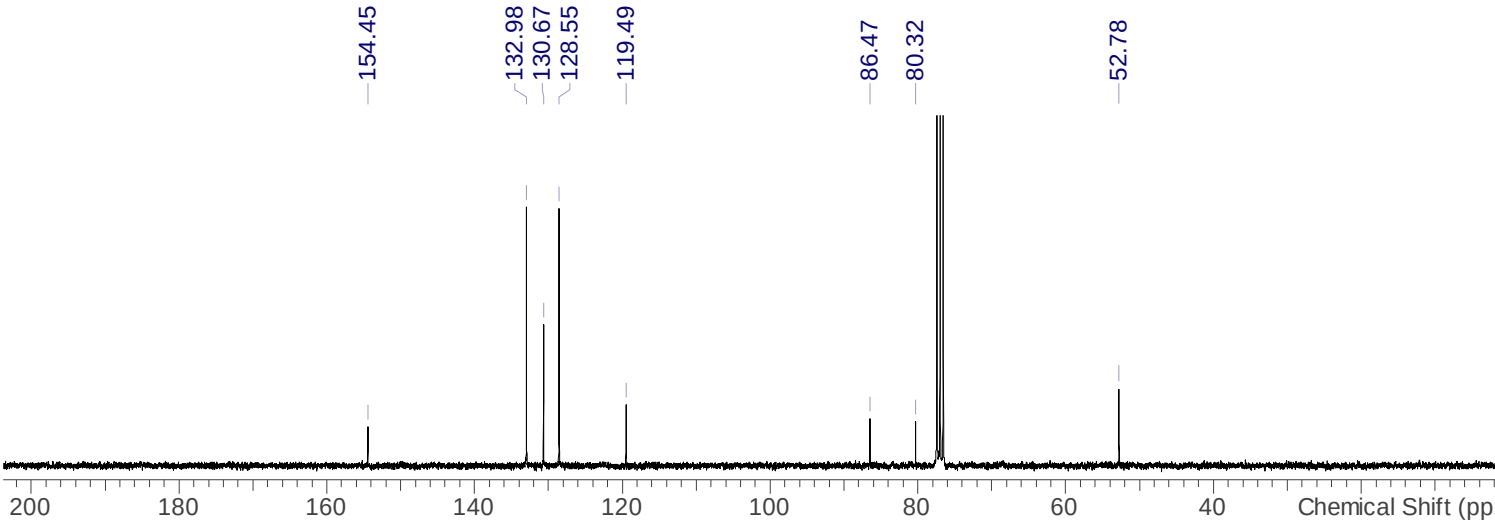
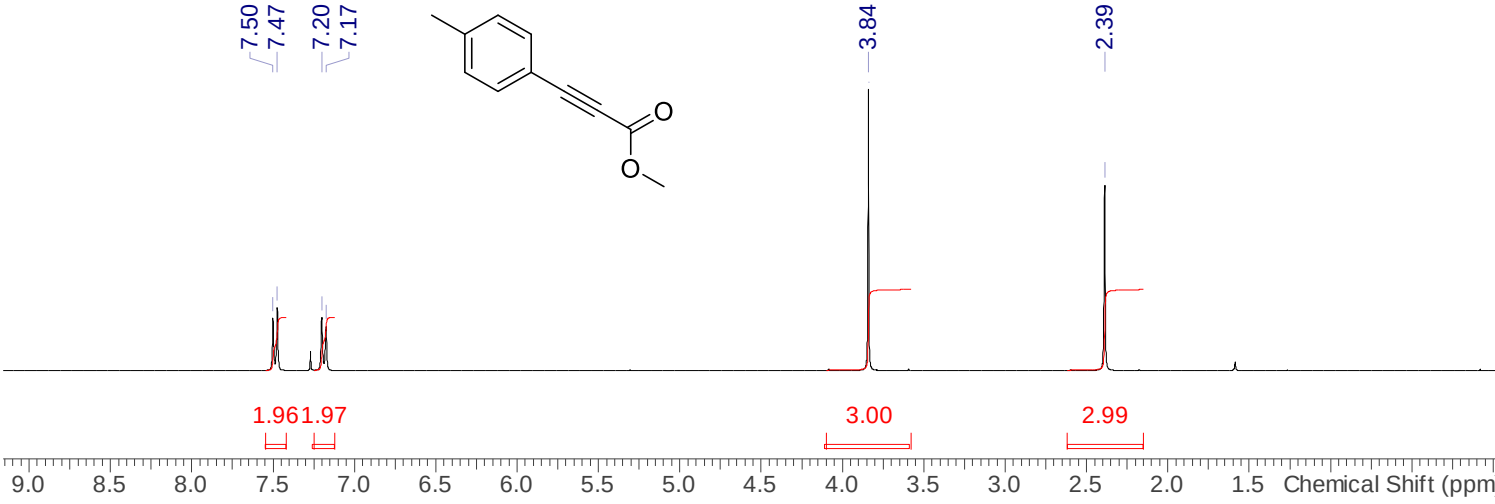
f1 (ppm)

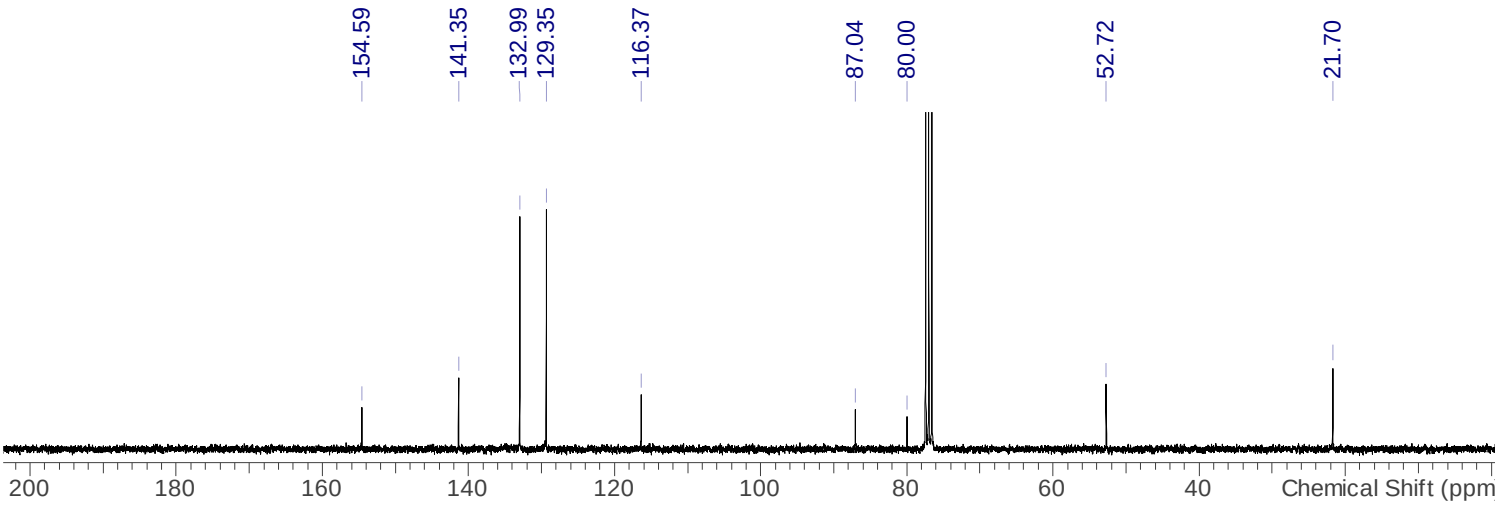
Methyl 3-phenylpropiolate (11b):



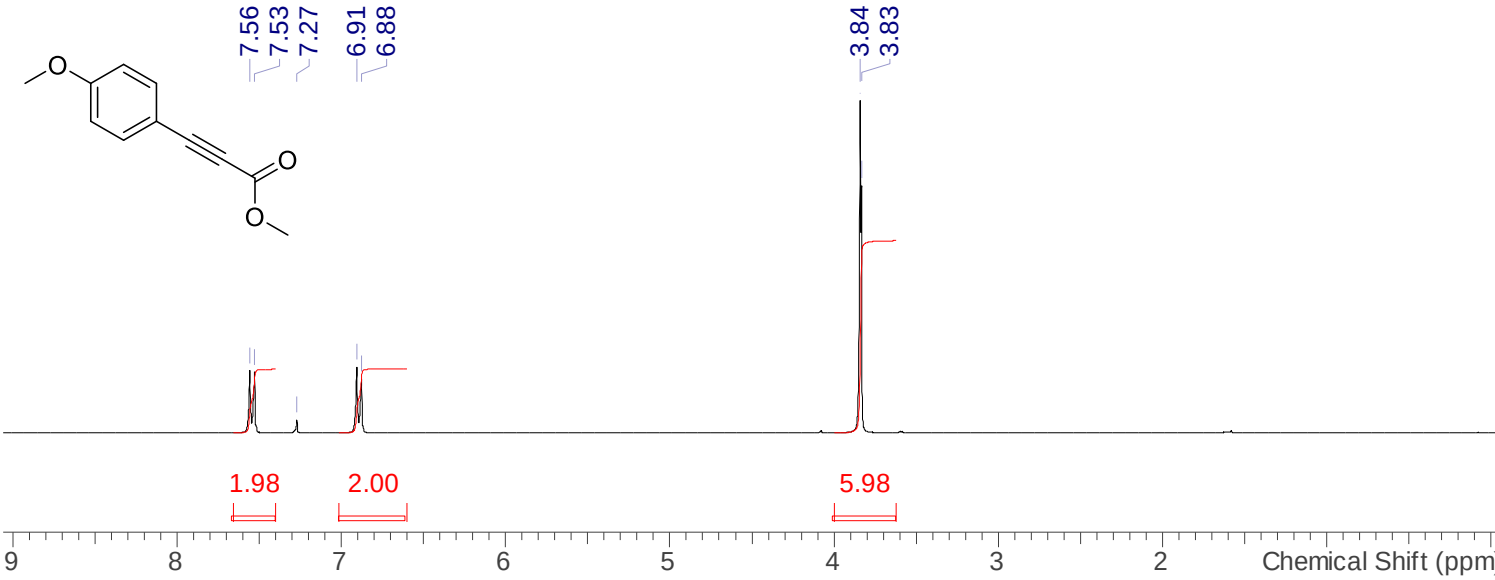


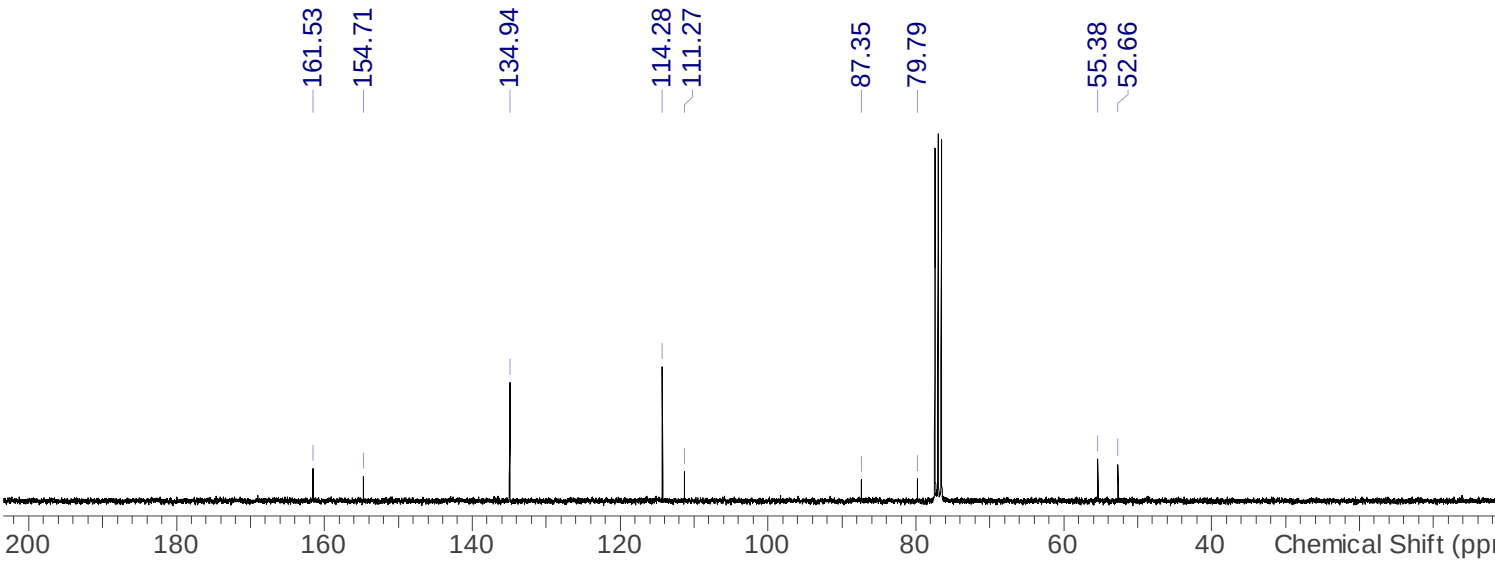
Methyl 3-(p-tolyl)propiolate (11c):



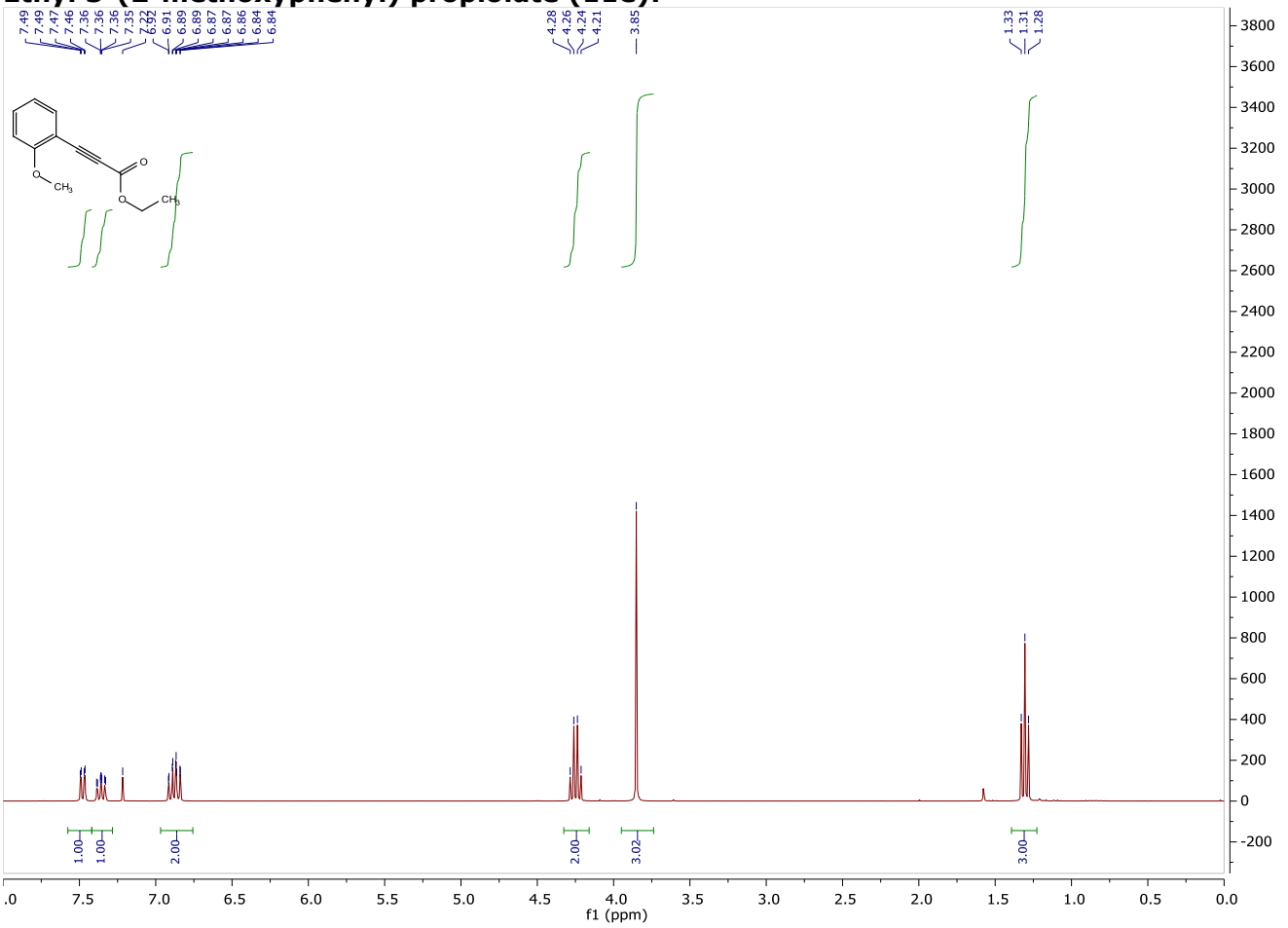


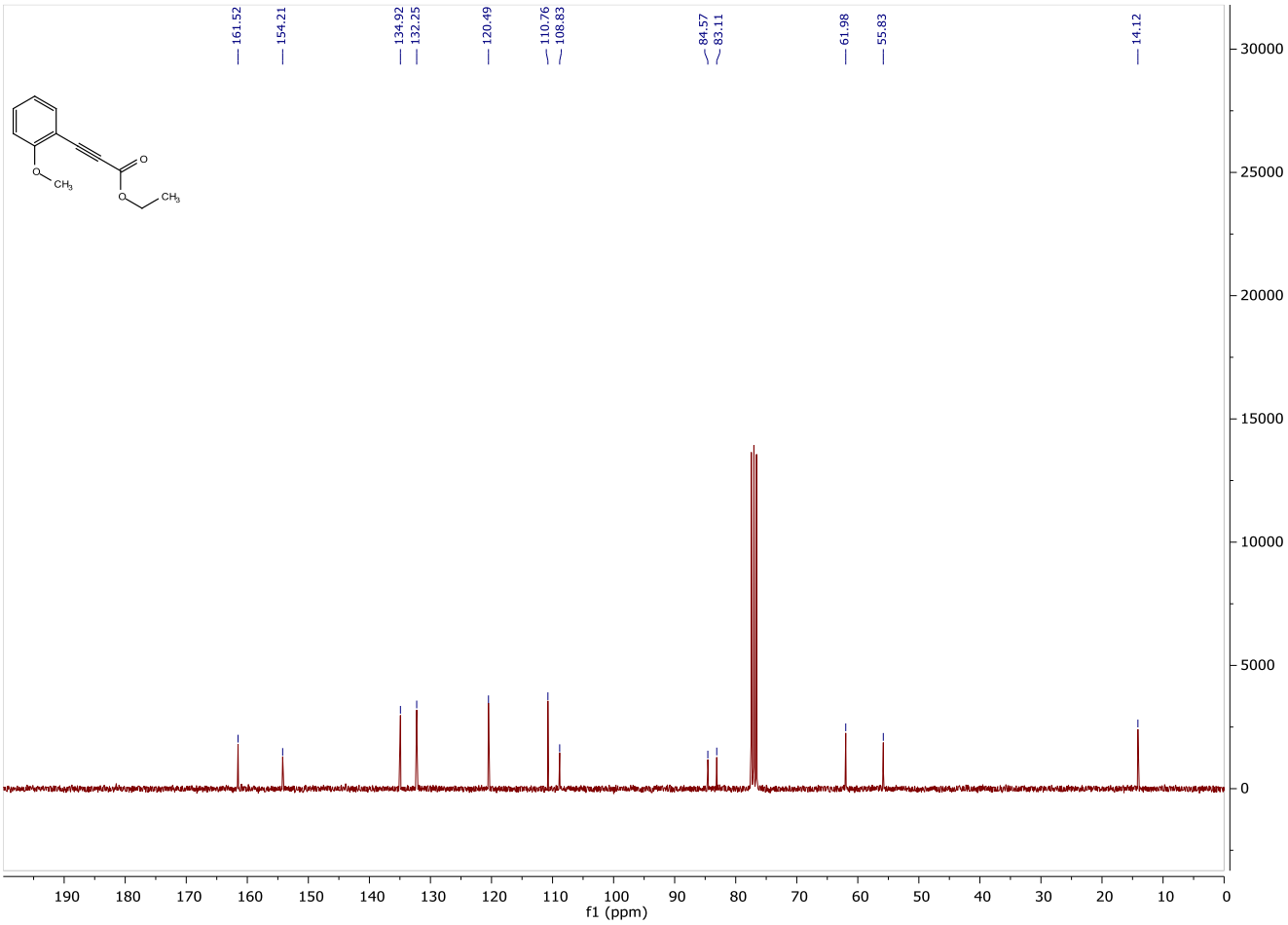
Methyl 3-(4-methoxyphenyl)propiolate (11d):



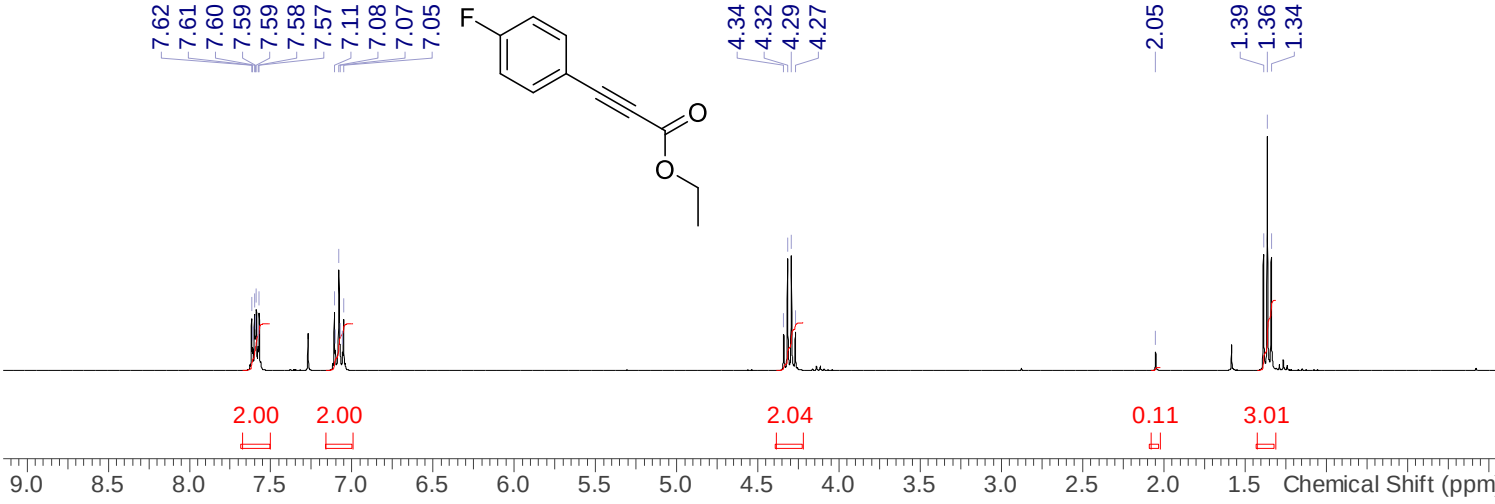


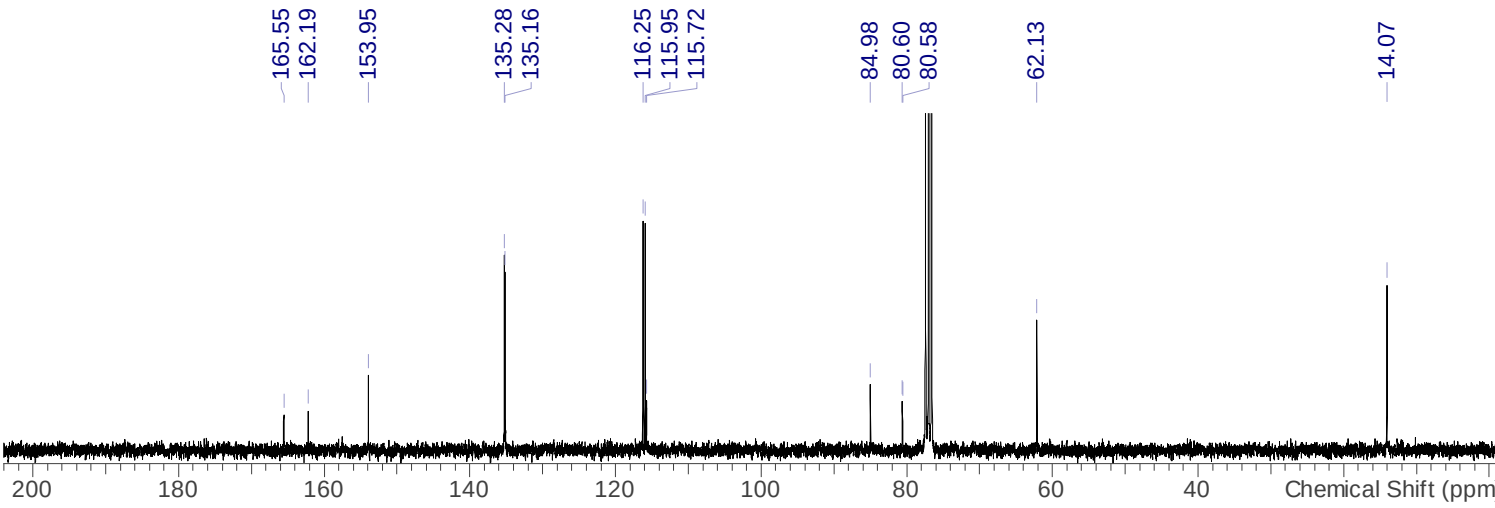
Ethyl 3-(2-methoxyphenyl) propiolate (11e):



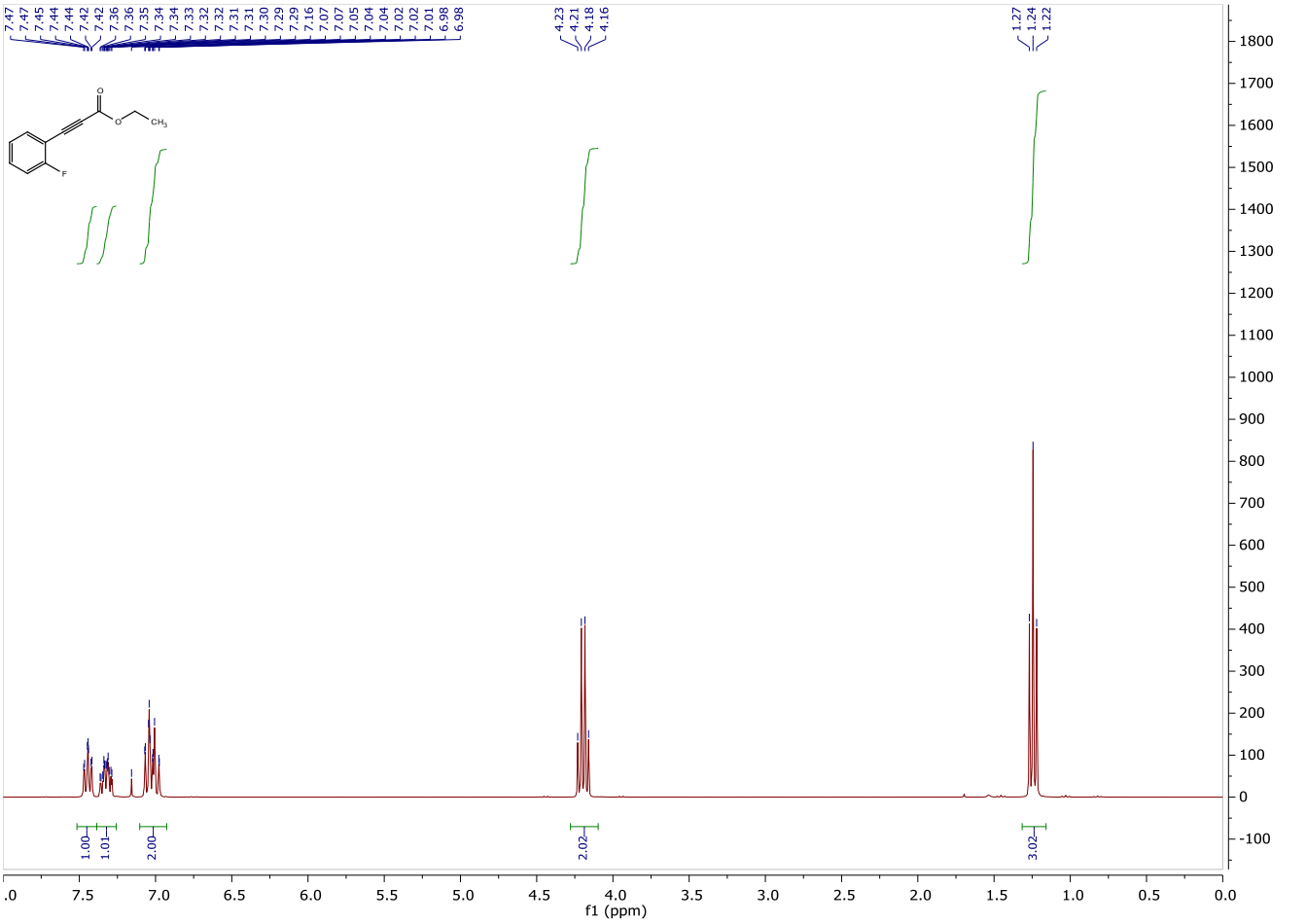


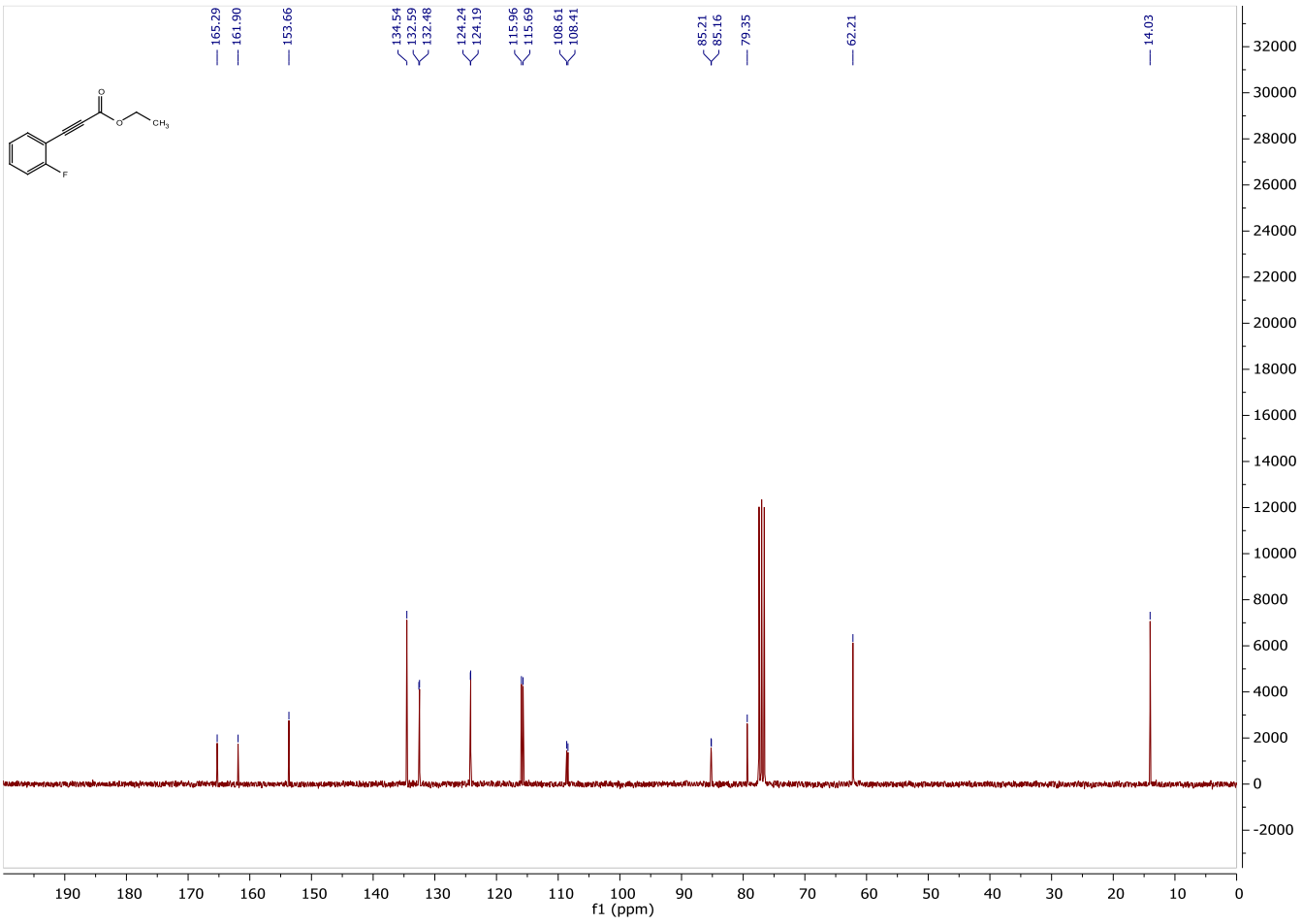
Ethyl 3-(4-fluorophenyl)propiolate (11g):



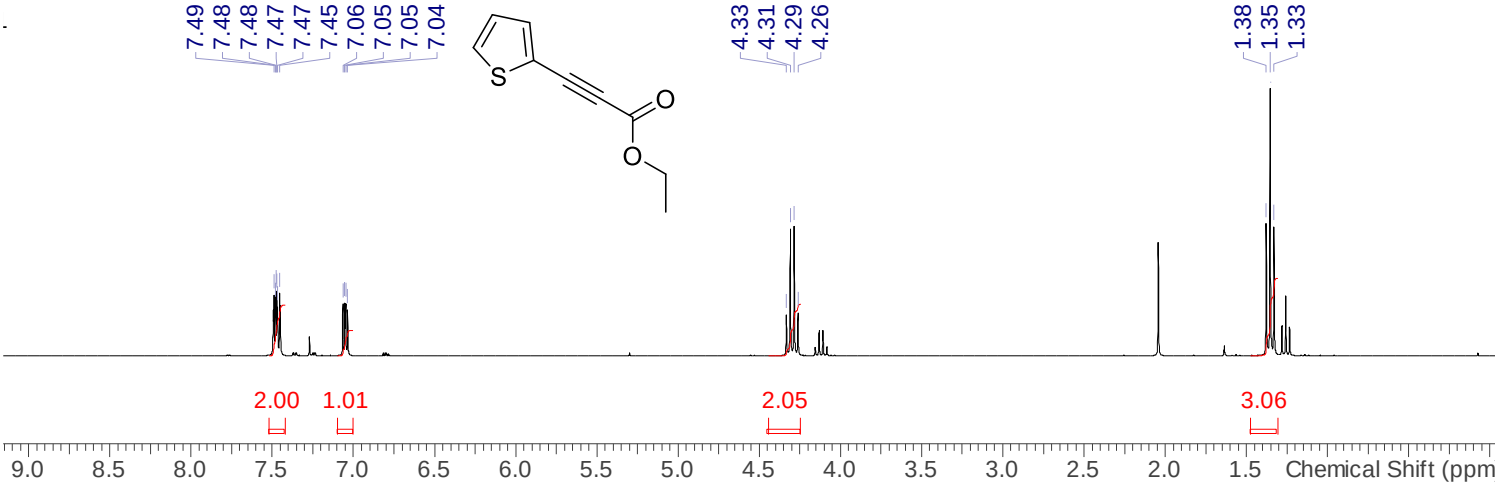


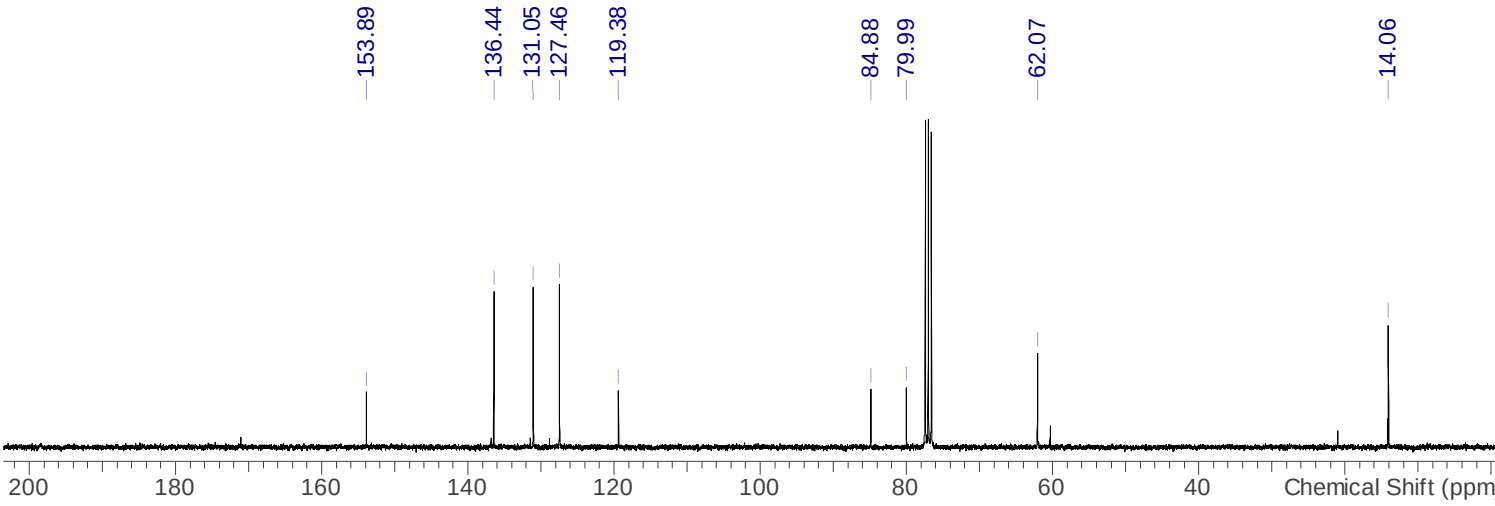
Ethyl 3-(2-fluorophenyl) propiolate (11h):



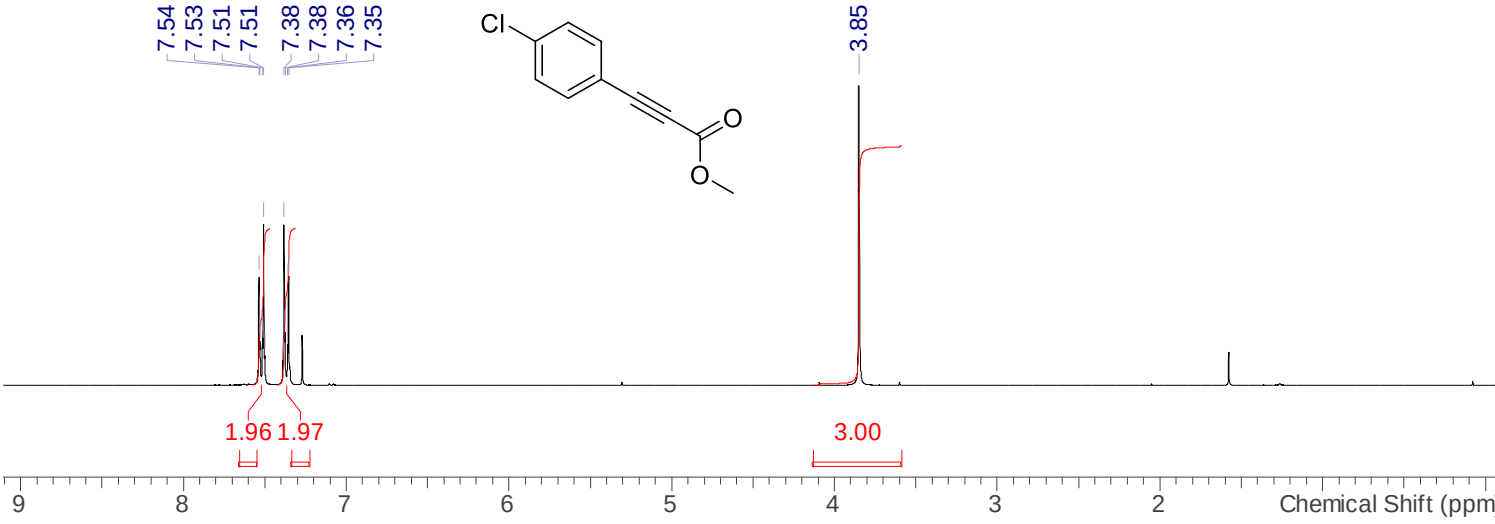


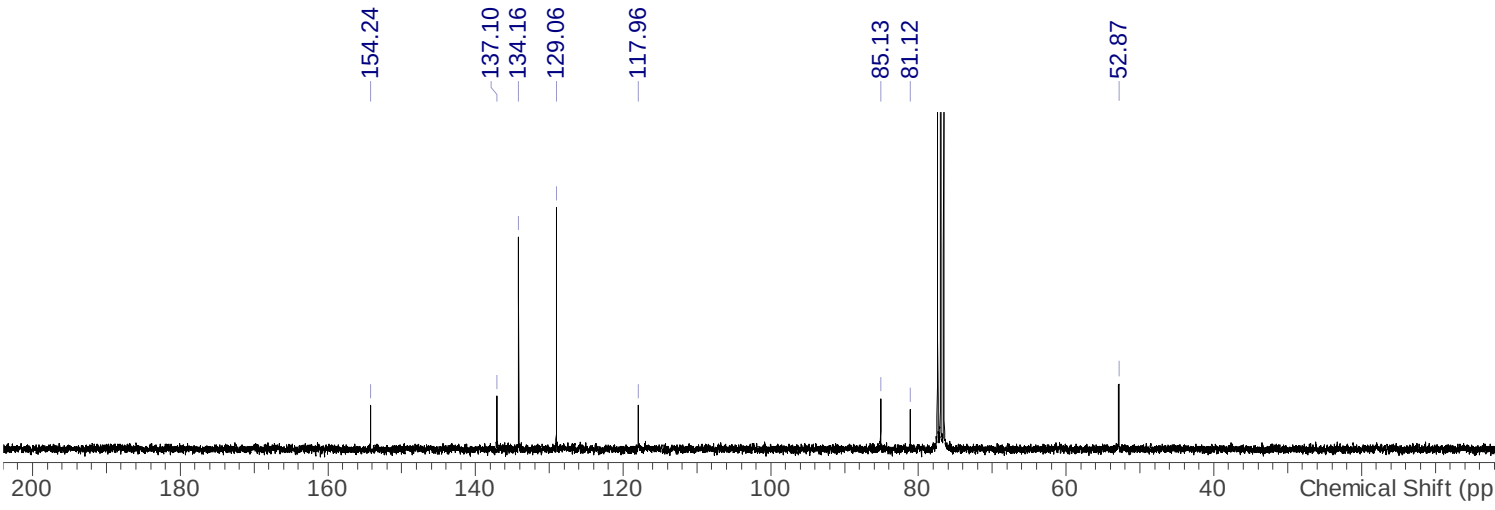
Ethyl 3-(thiophen-2-yl)propiolate (11i):



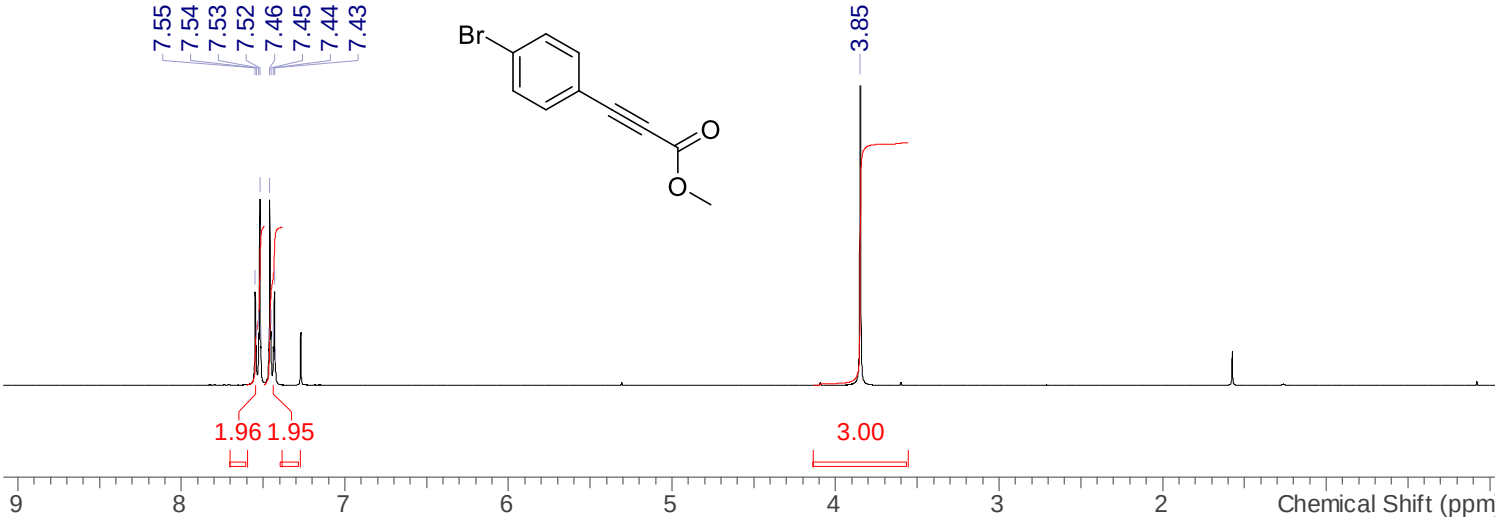


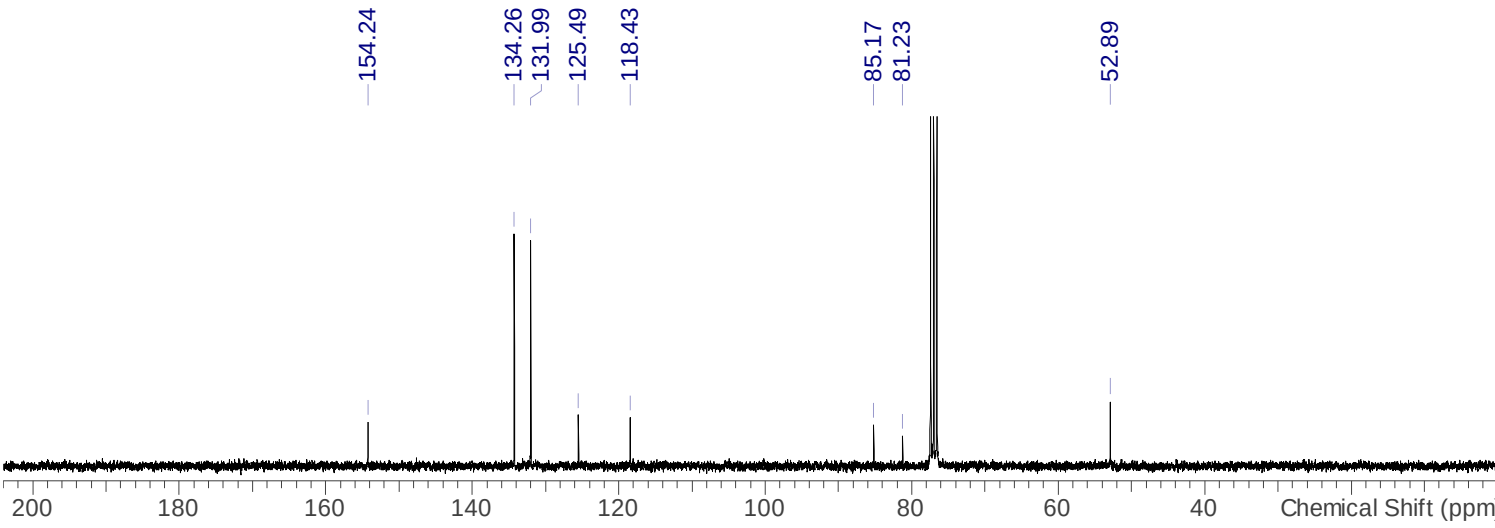
Methyl 3-(4-chlorophenyl)propiolate (11j):



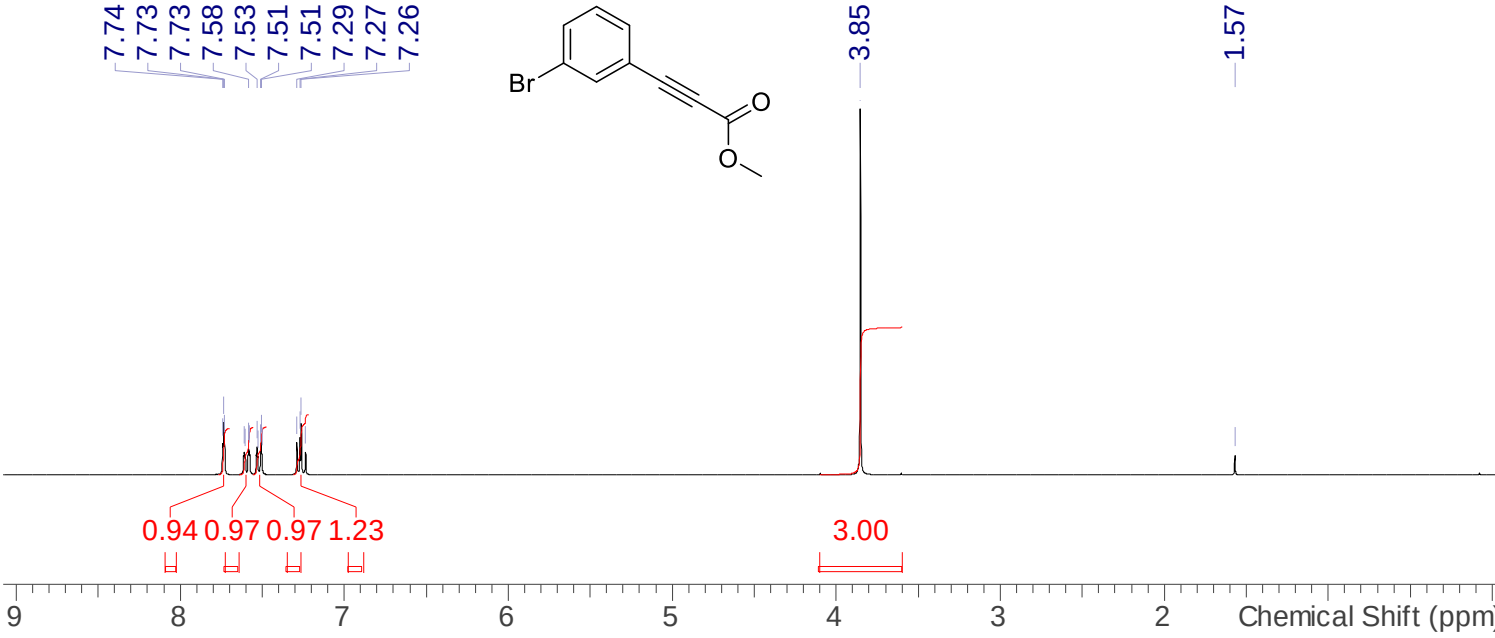


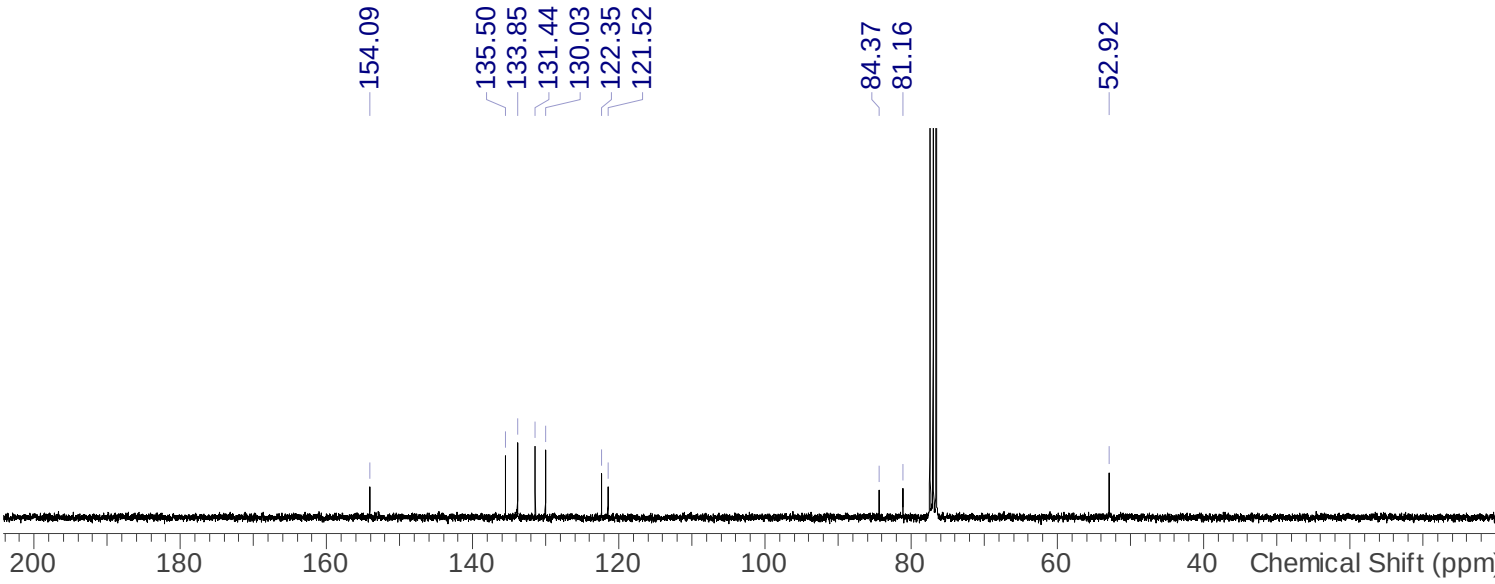
Methyl 3-(4-bromophenyl)propiolate (11k):



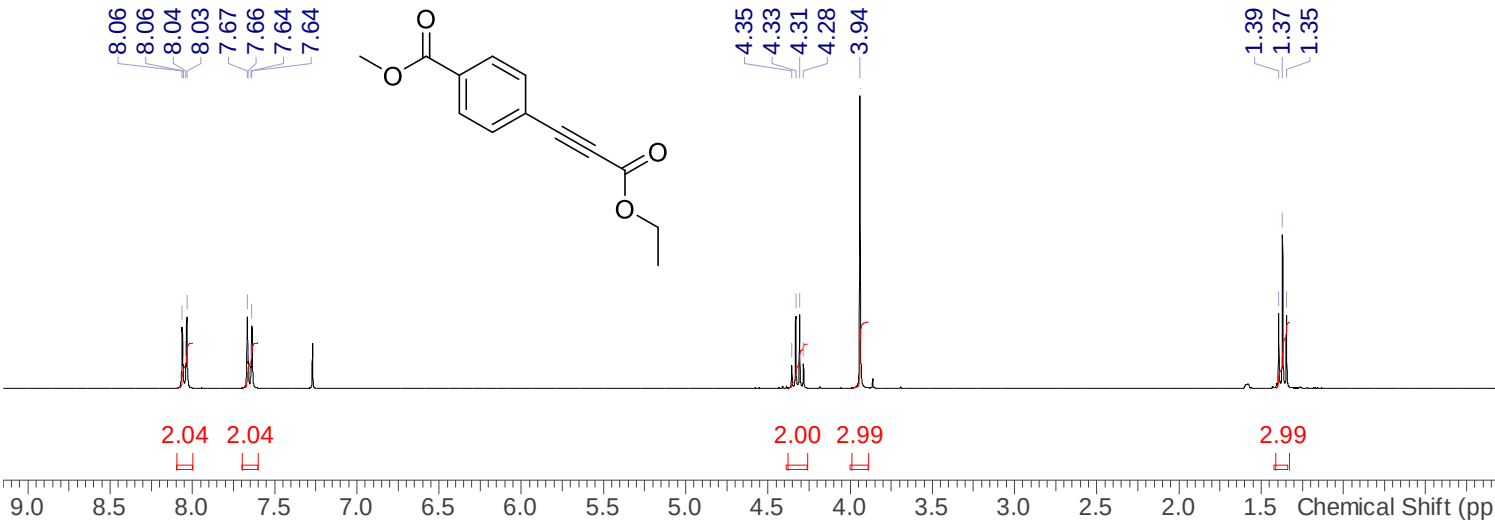


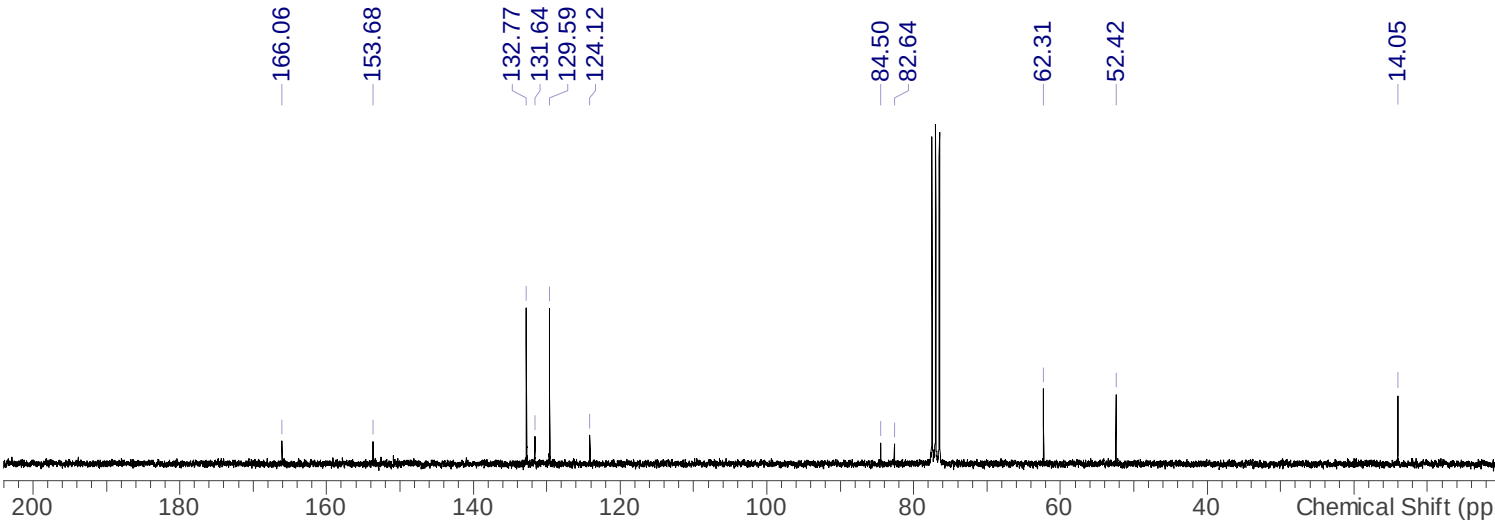
Methyl 3-(3-bromophenyl)propiolate (11l):



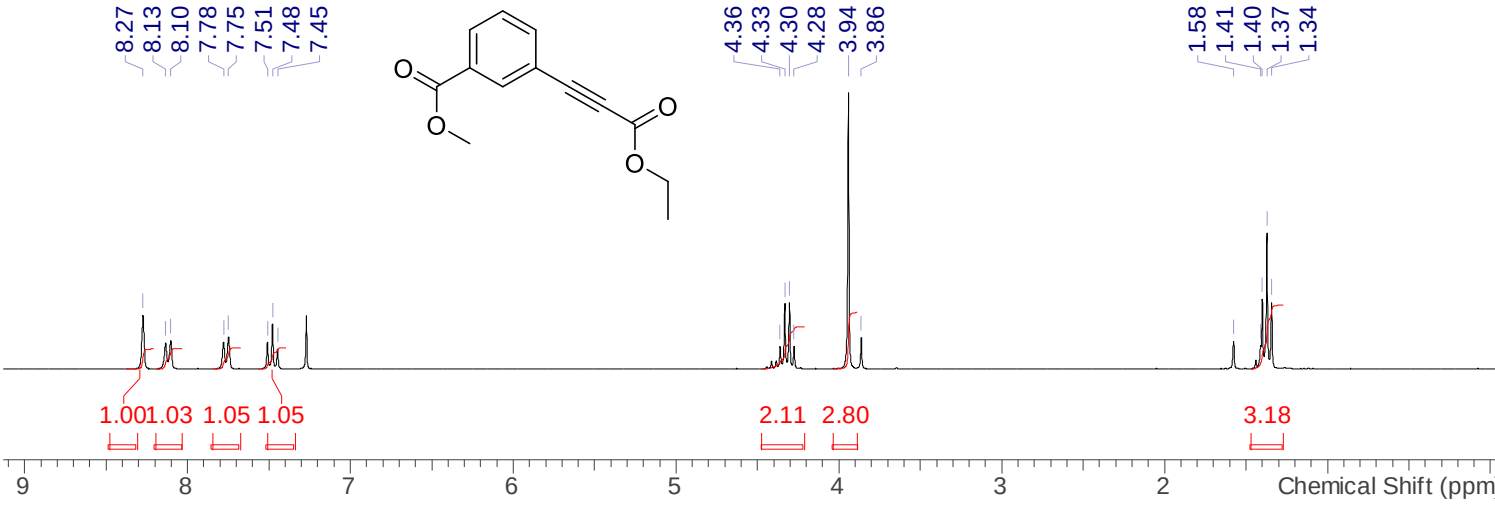


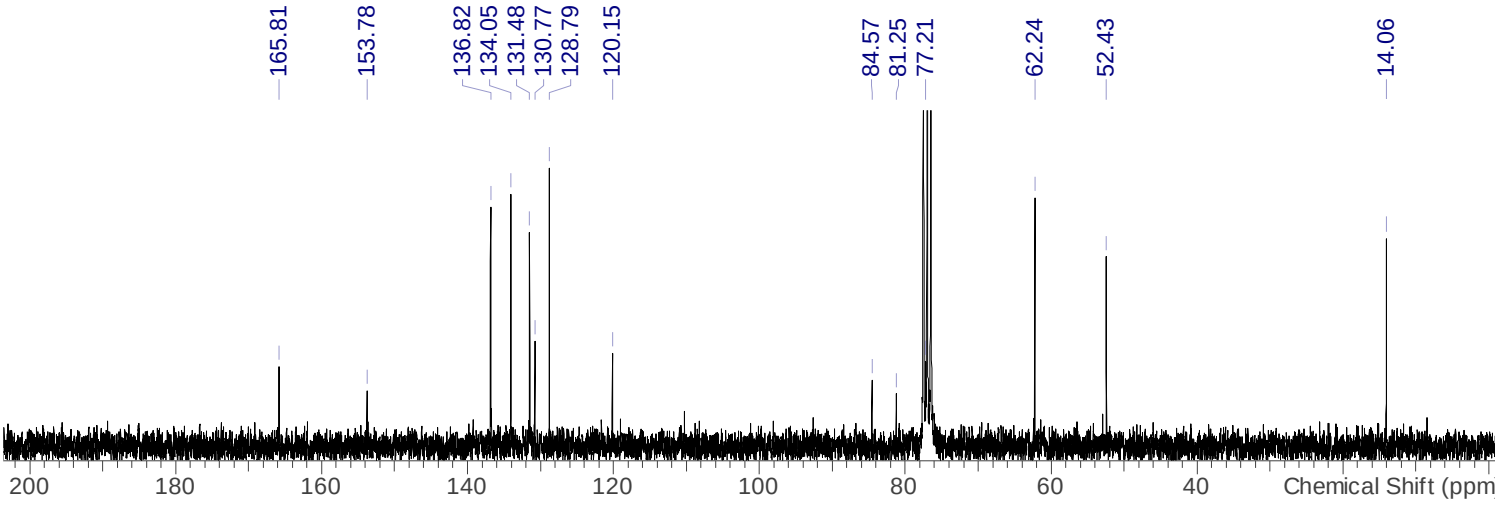
Methyl 4-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate (11m):



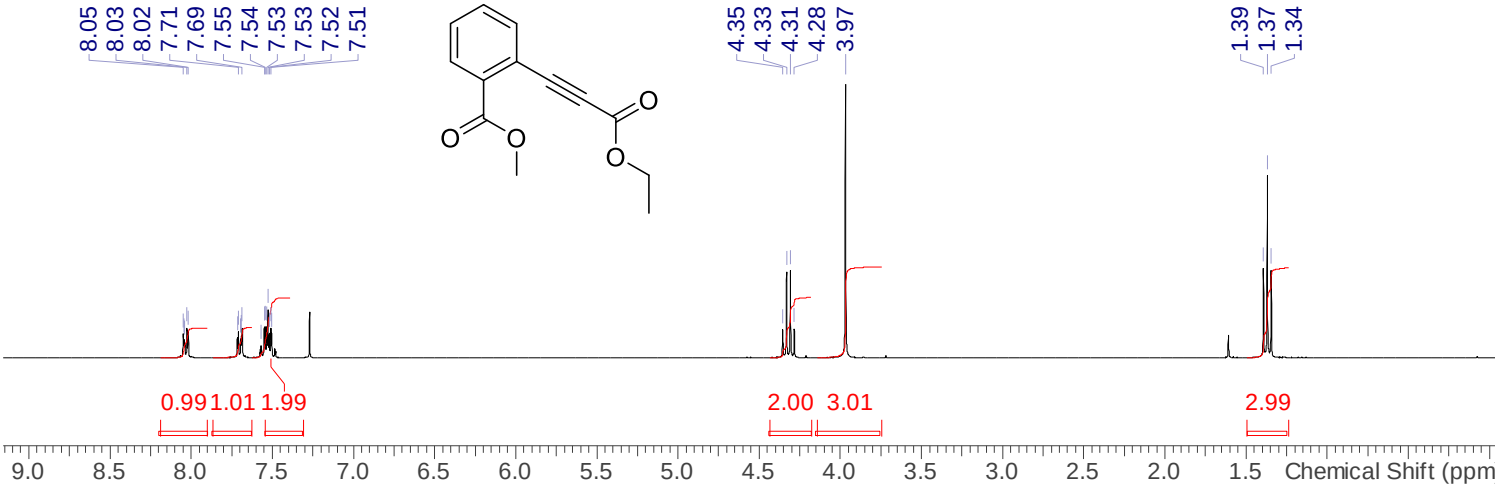


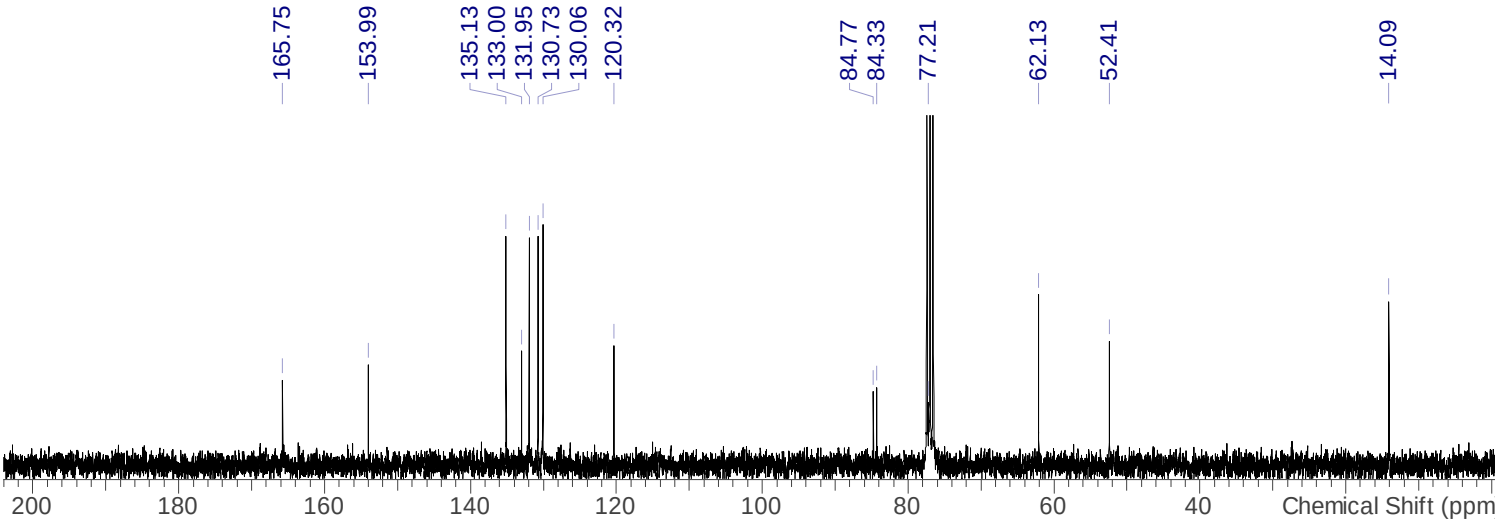
Methyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate (11n):



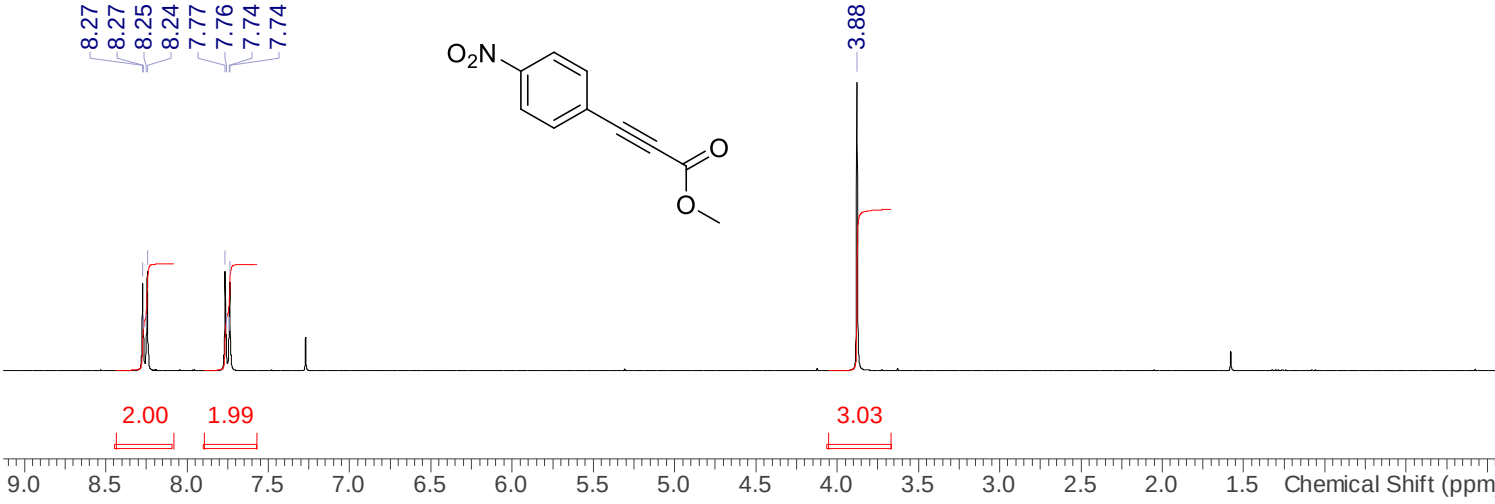


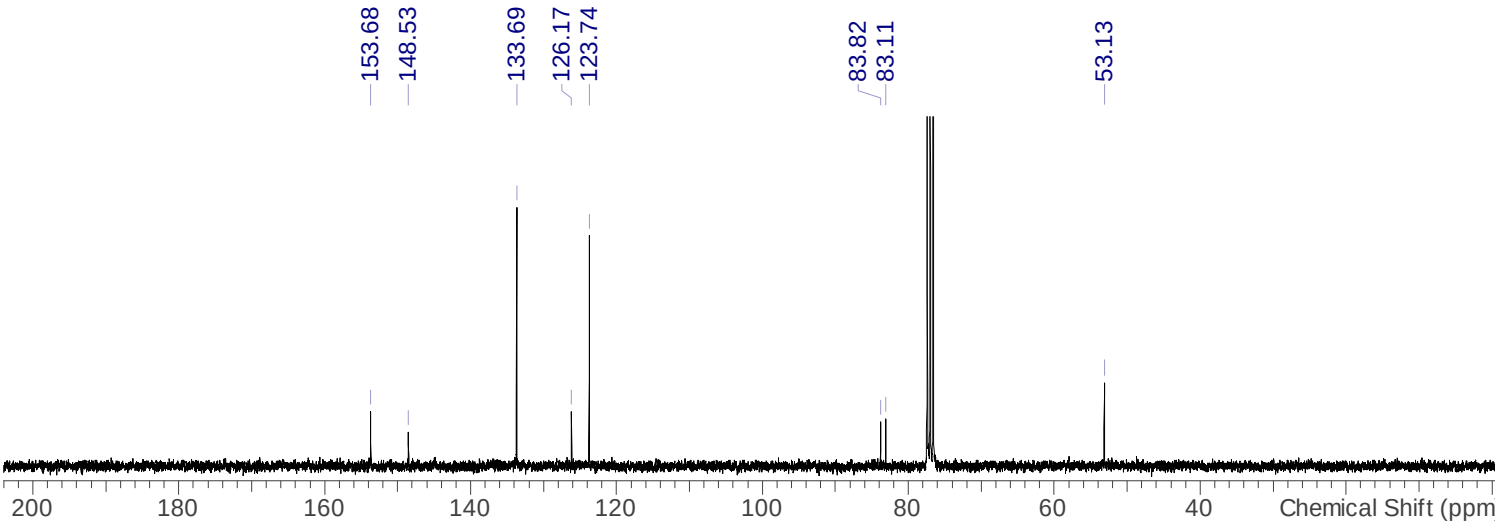
Methyl 2-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate (11o):



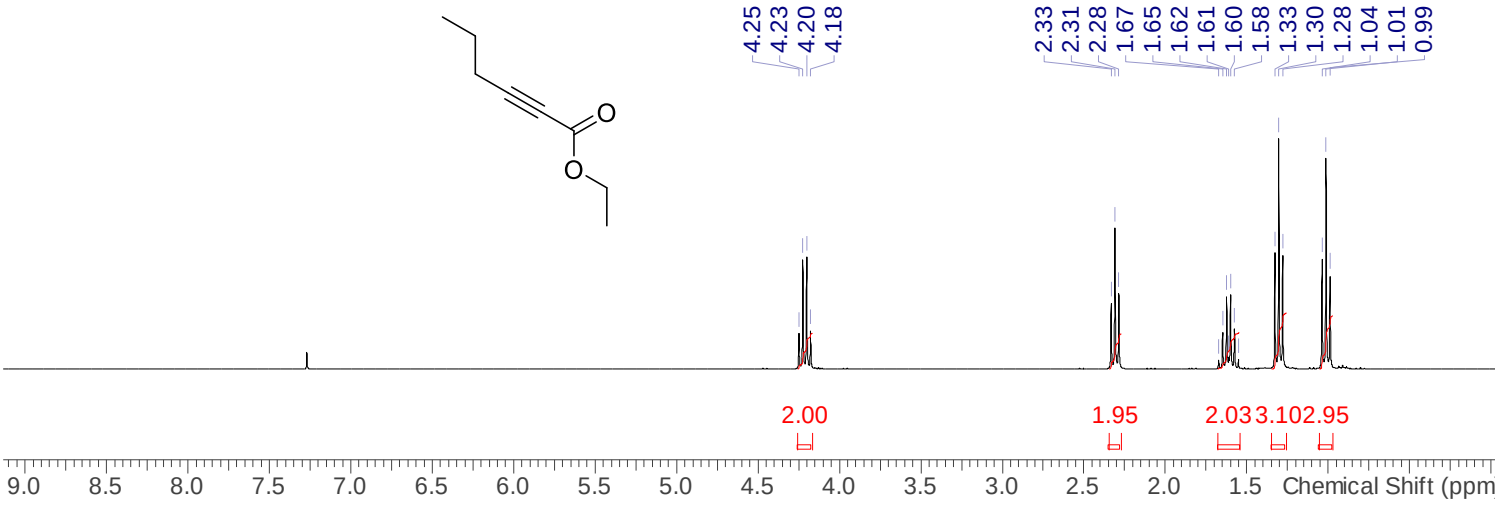


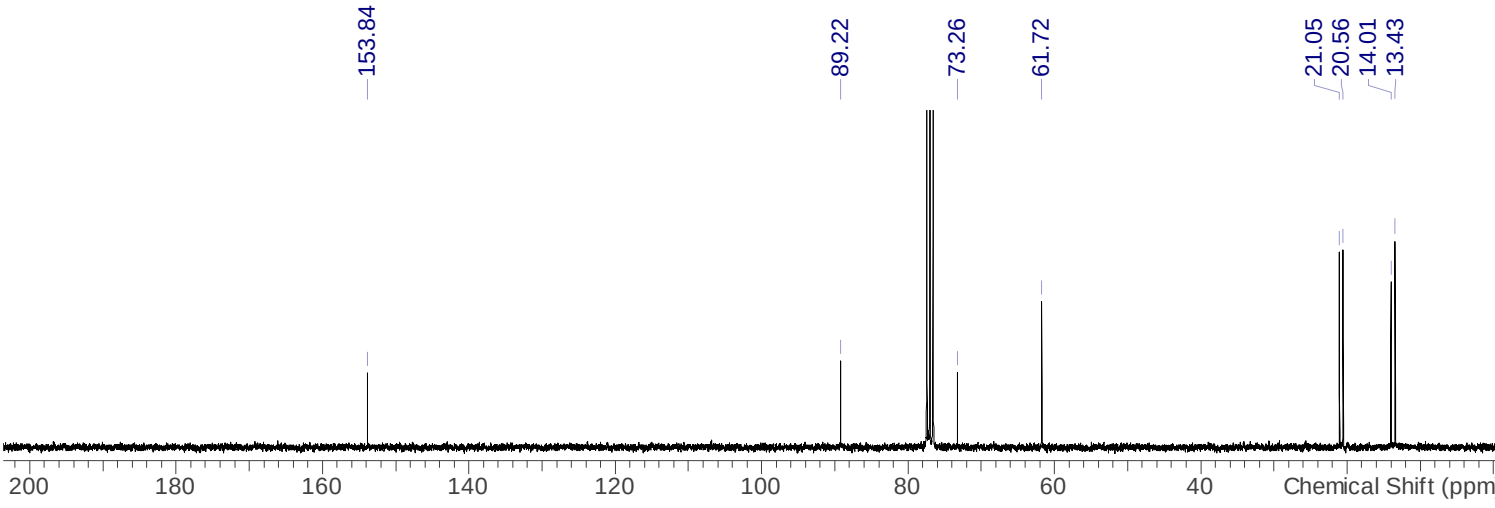
Methyl 3-(4-nitrophenyl)propiolate (11p):



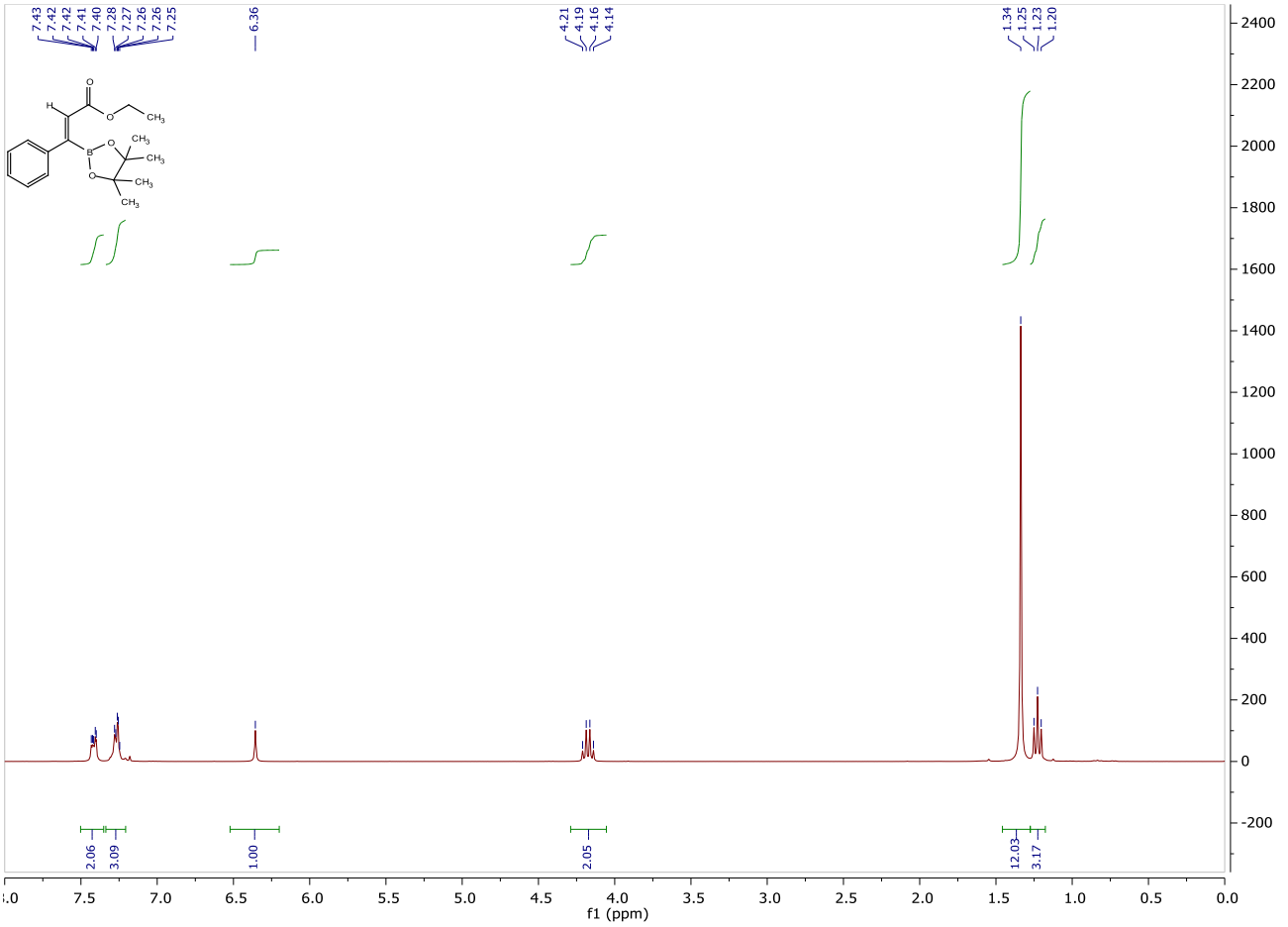


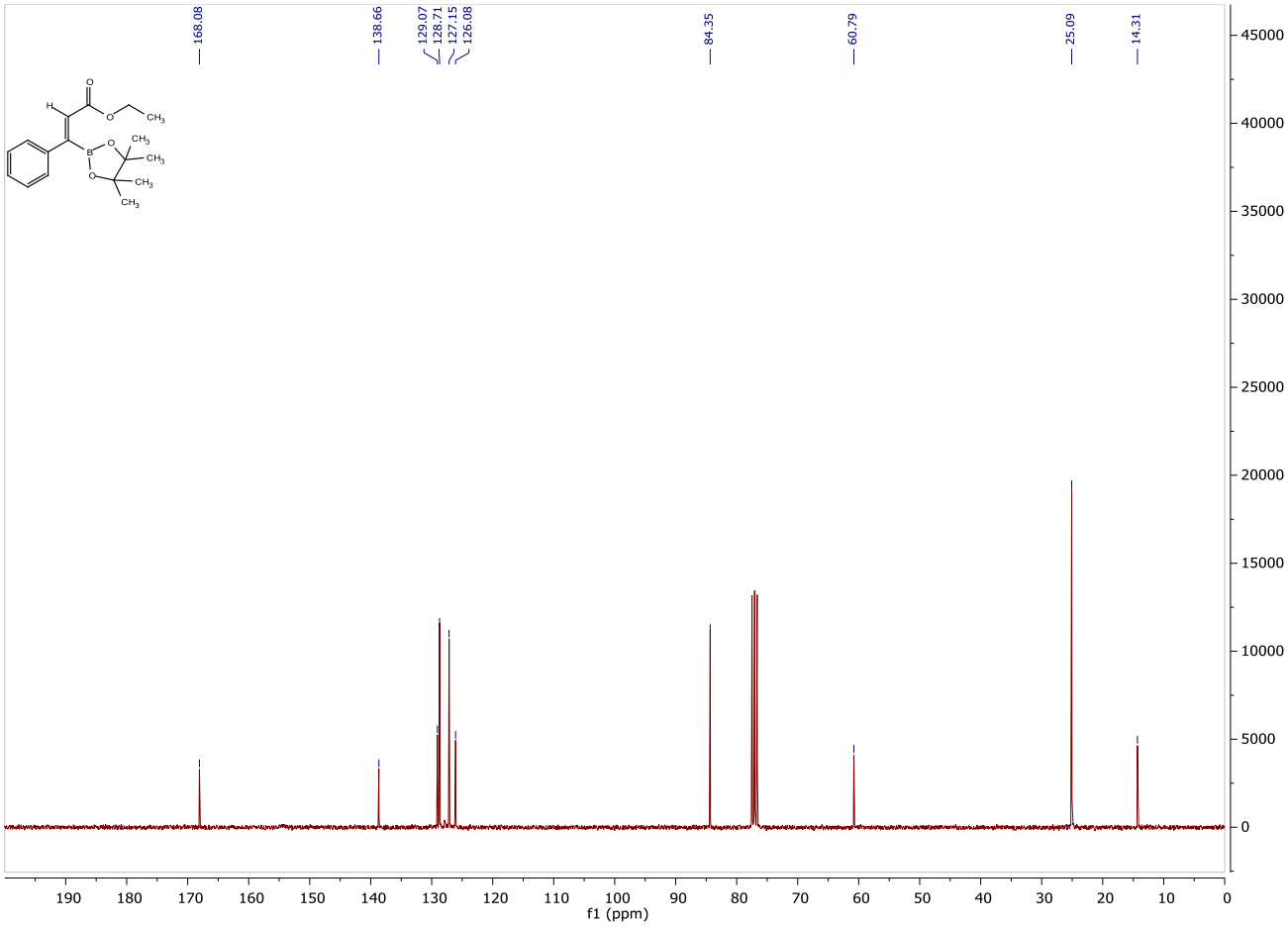
Ethyl hex-2-ynoate (11q):

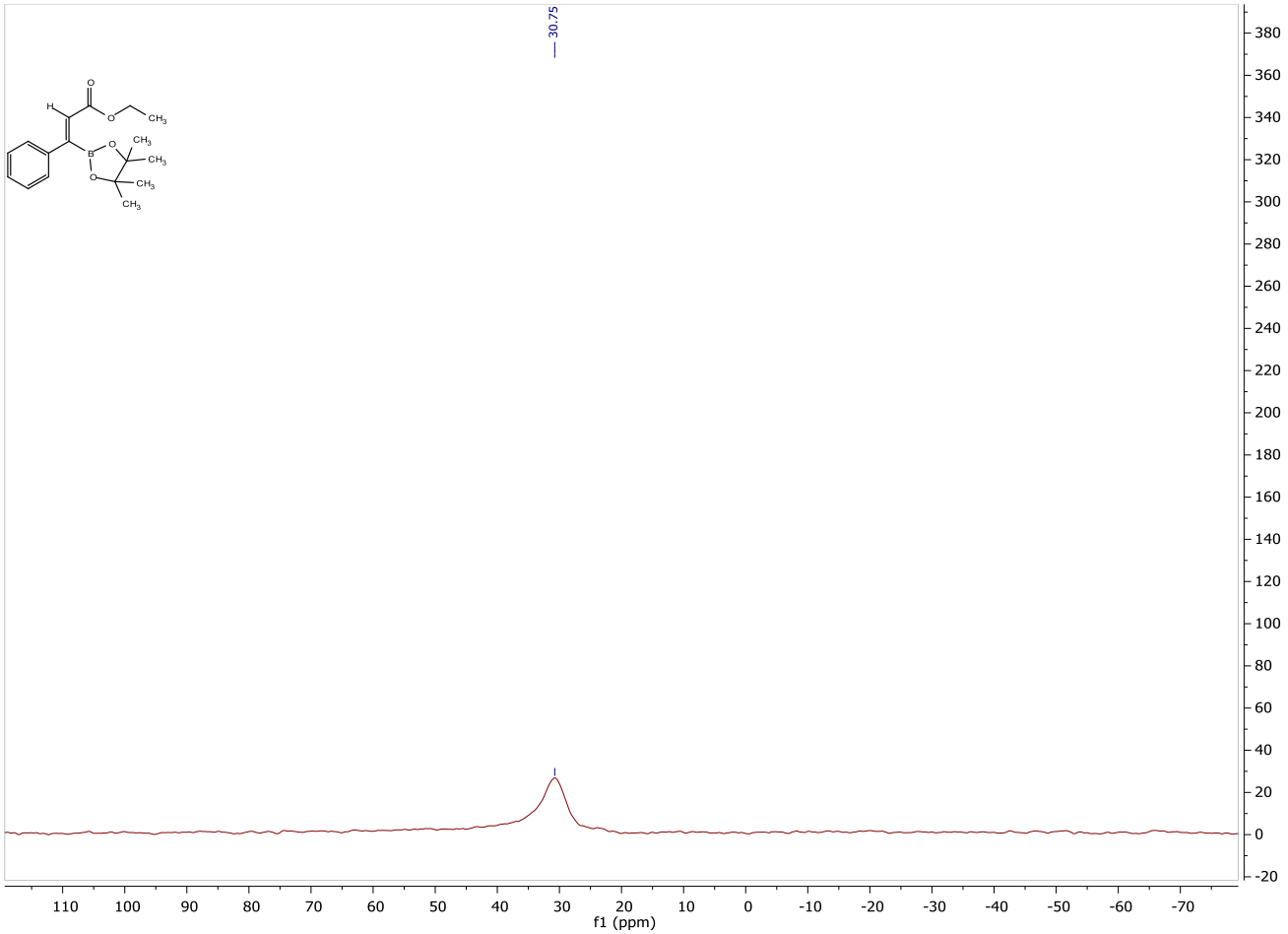




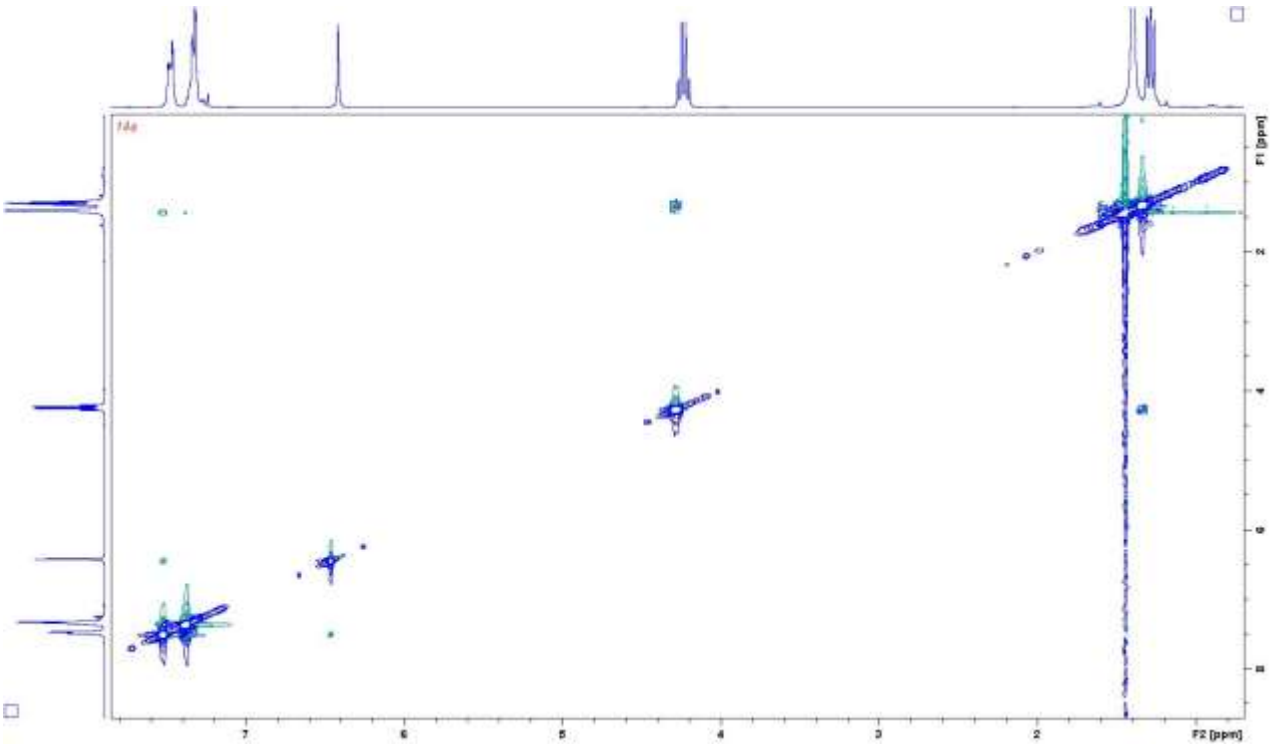
Ethyl (*E*)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12a):



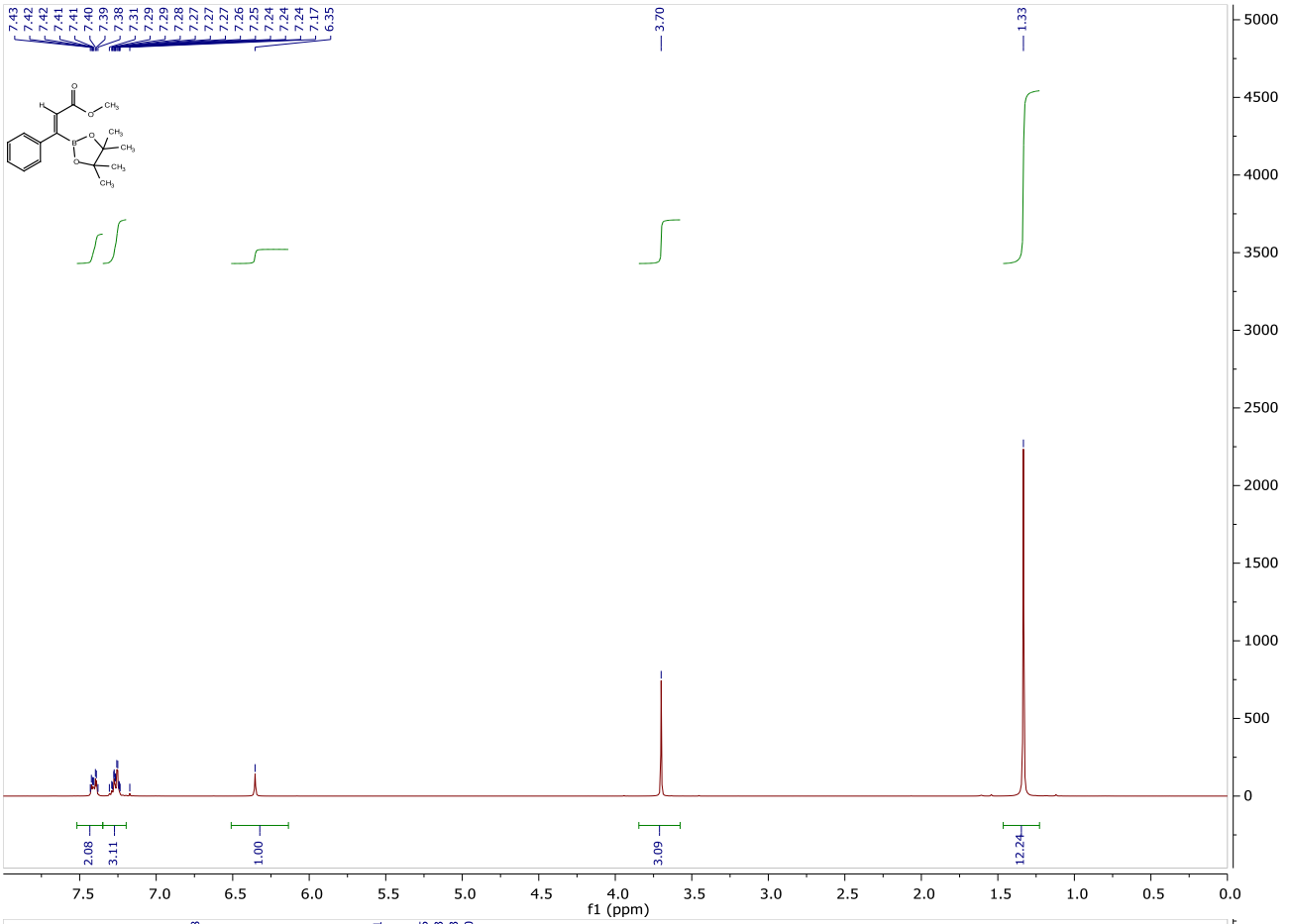


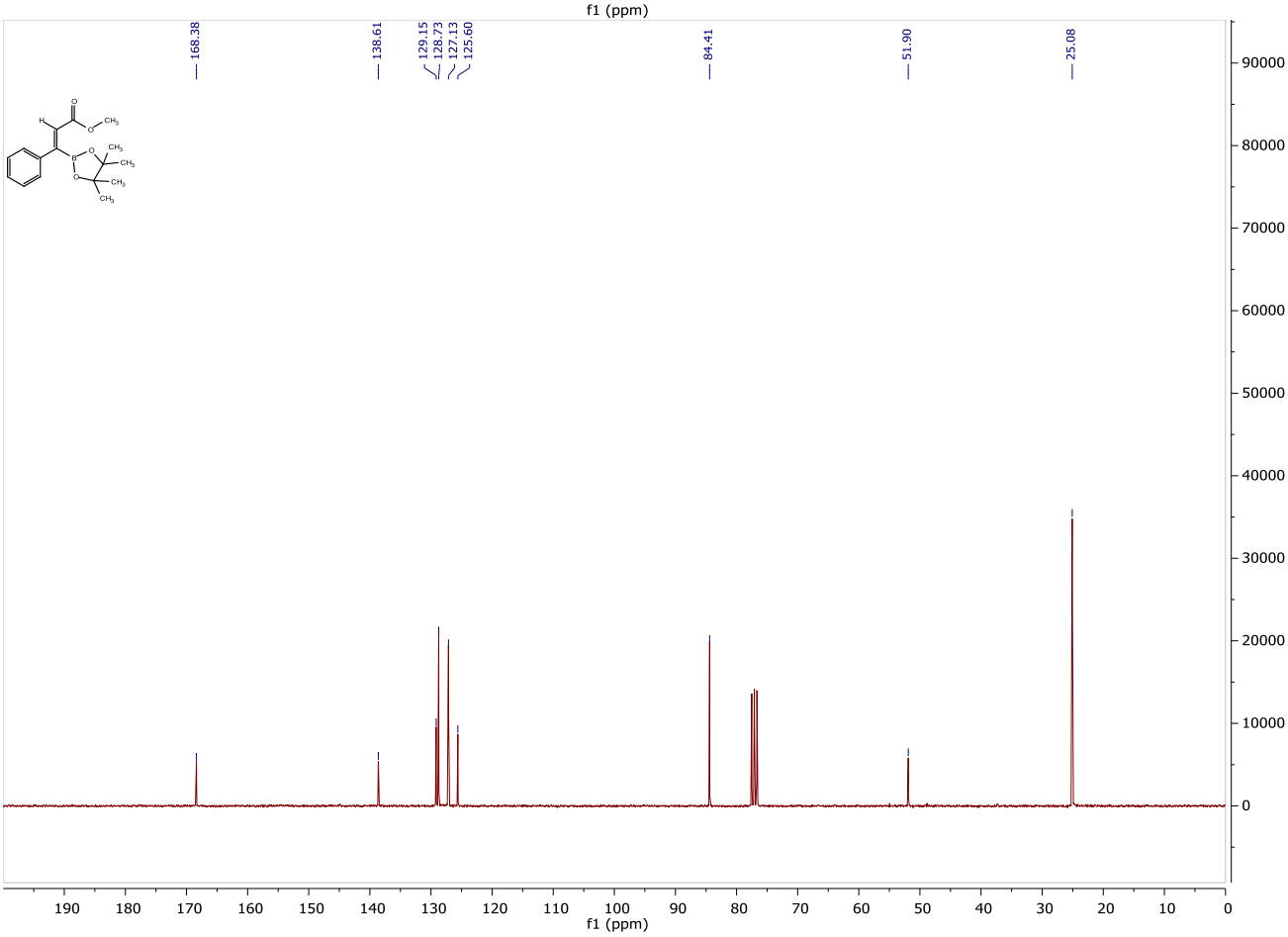

30.75
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

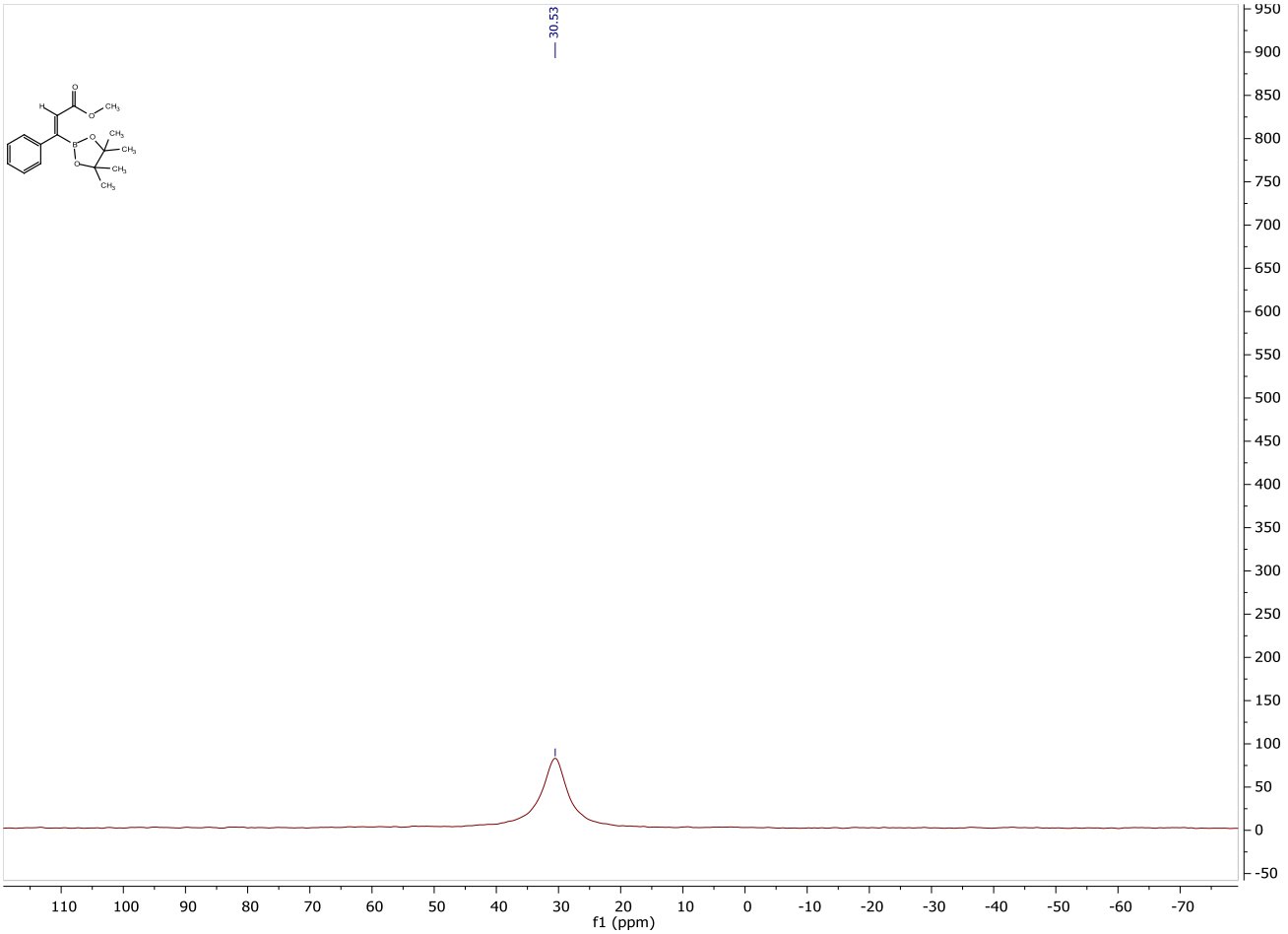
NOESY of **12a**:


F1 [ppm]
F2 [ppm]

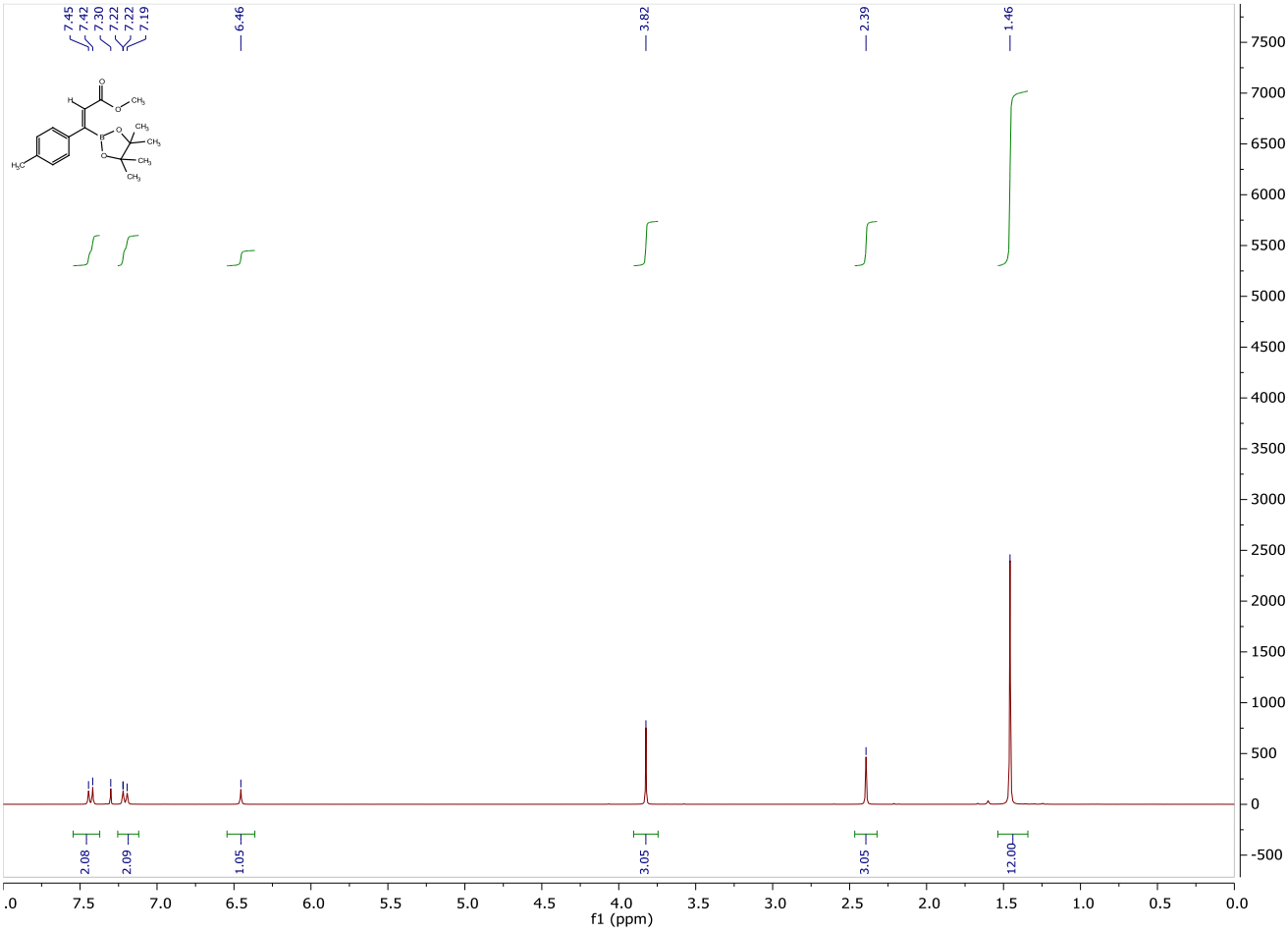
Methyl (*E*)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12b):

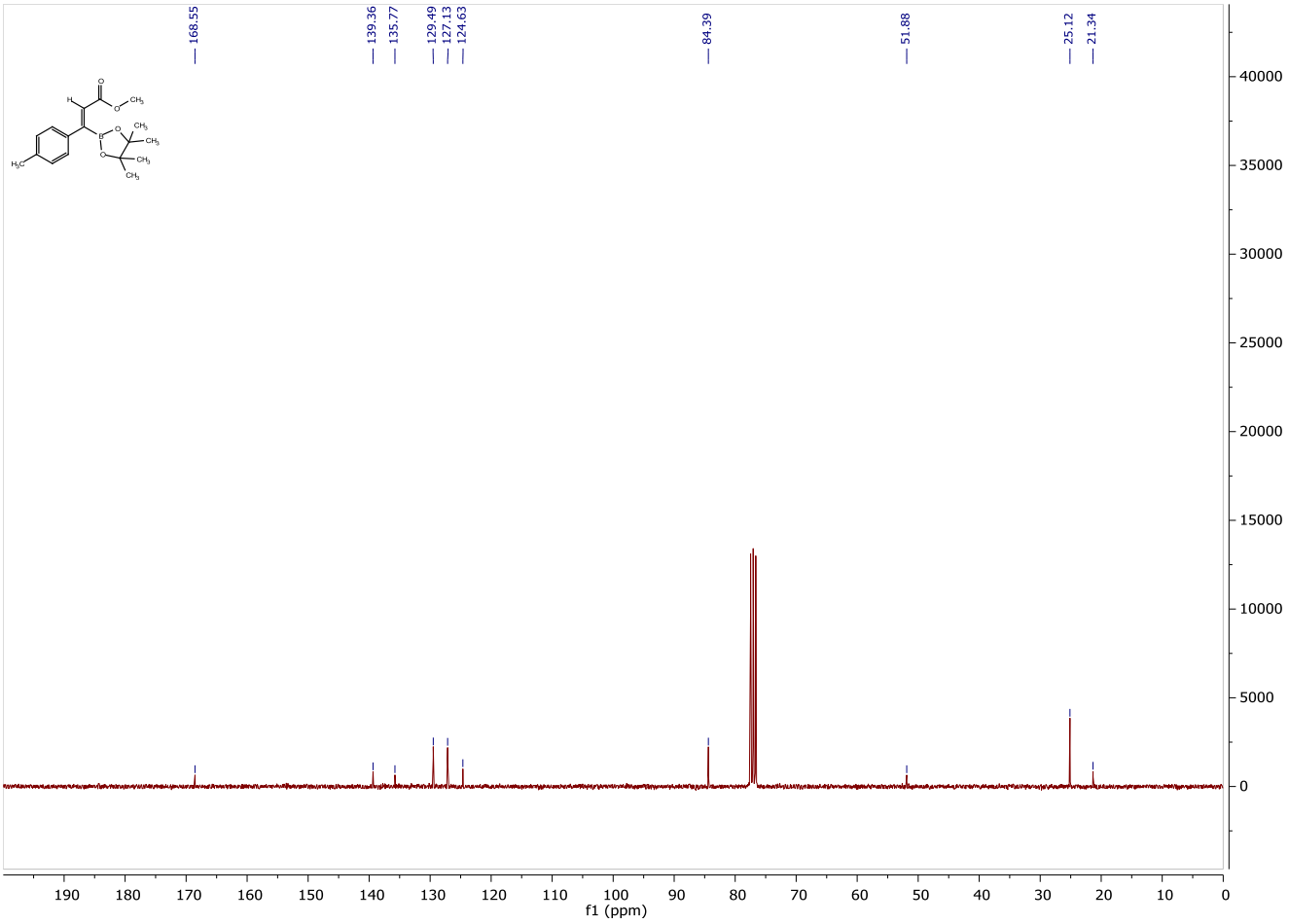


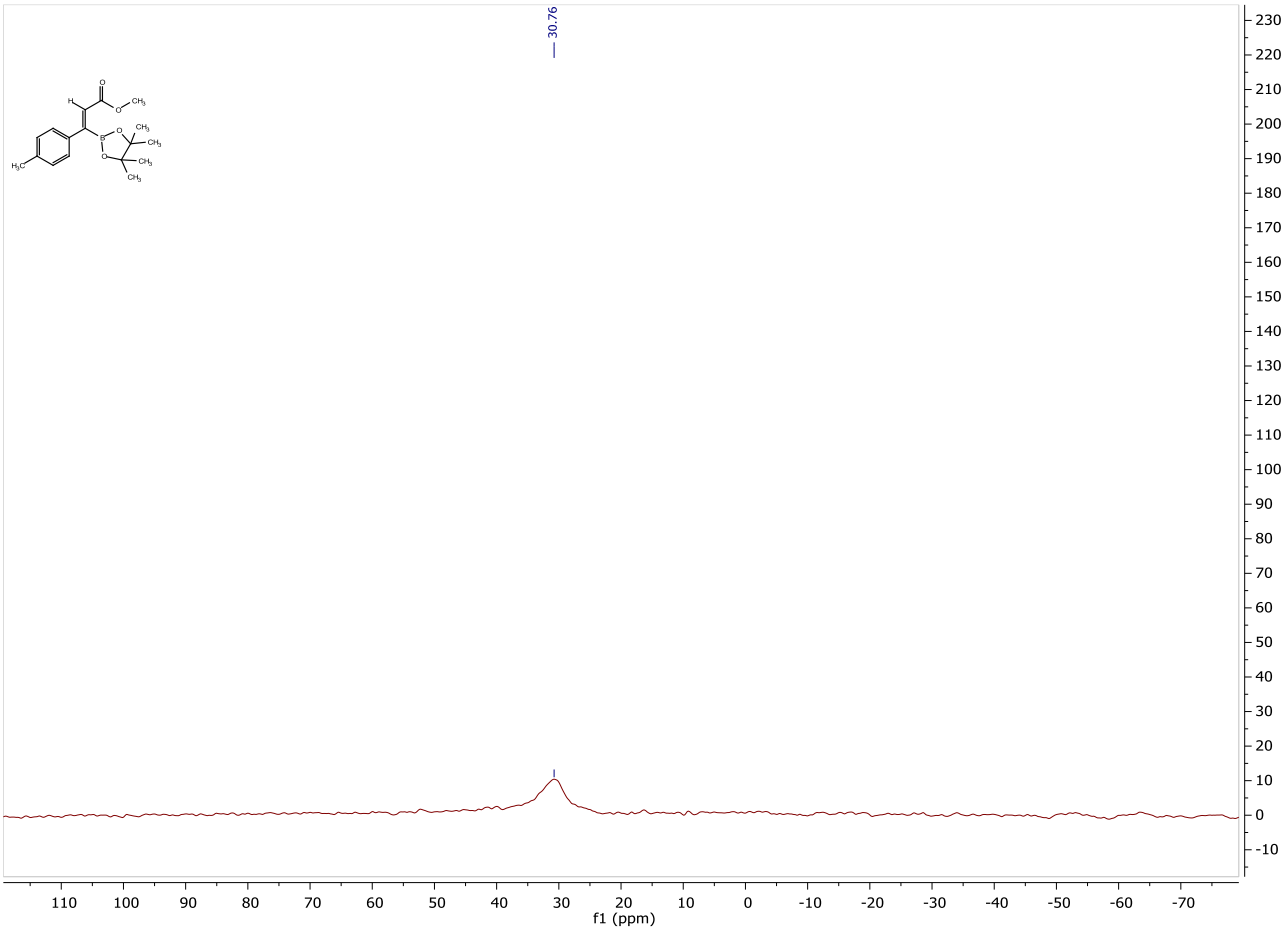




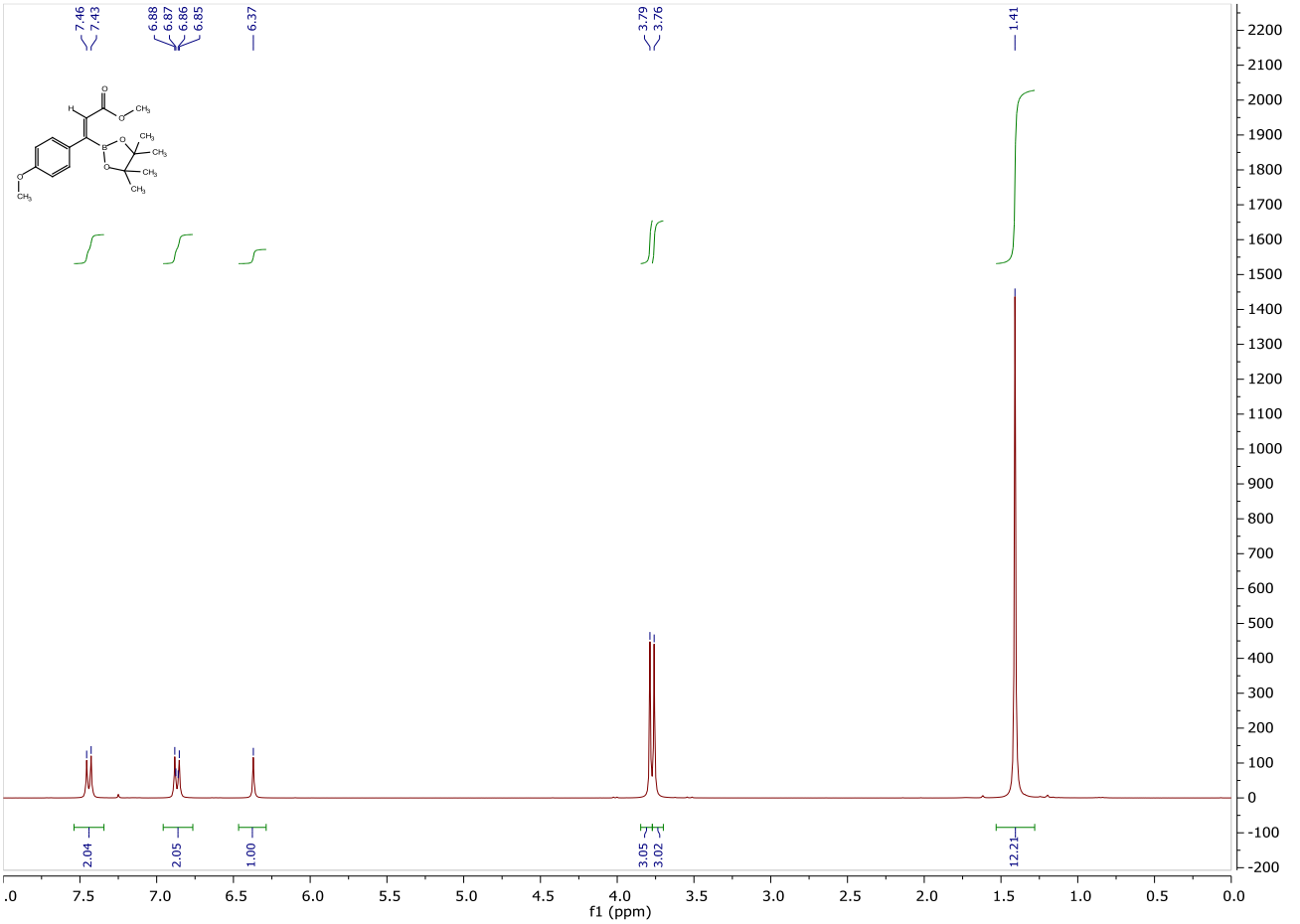
Methyl (*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(p-tolyl) acrylate (12c):

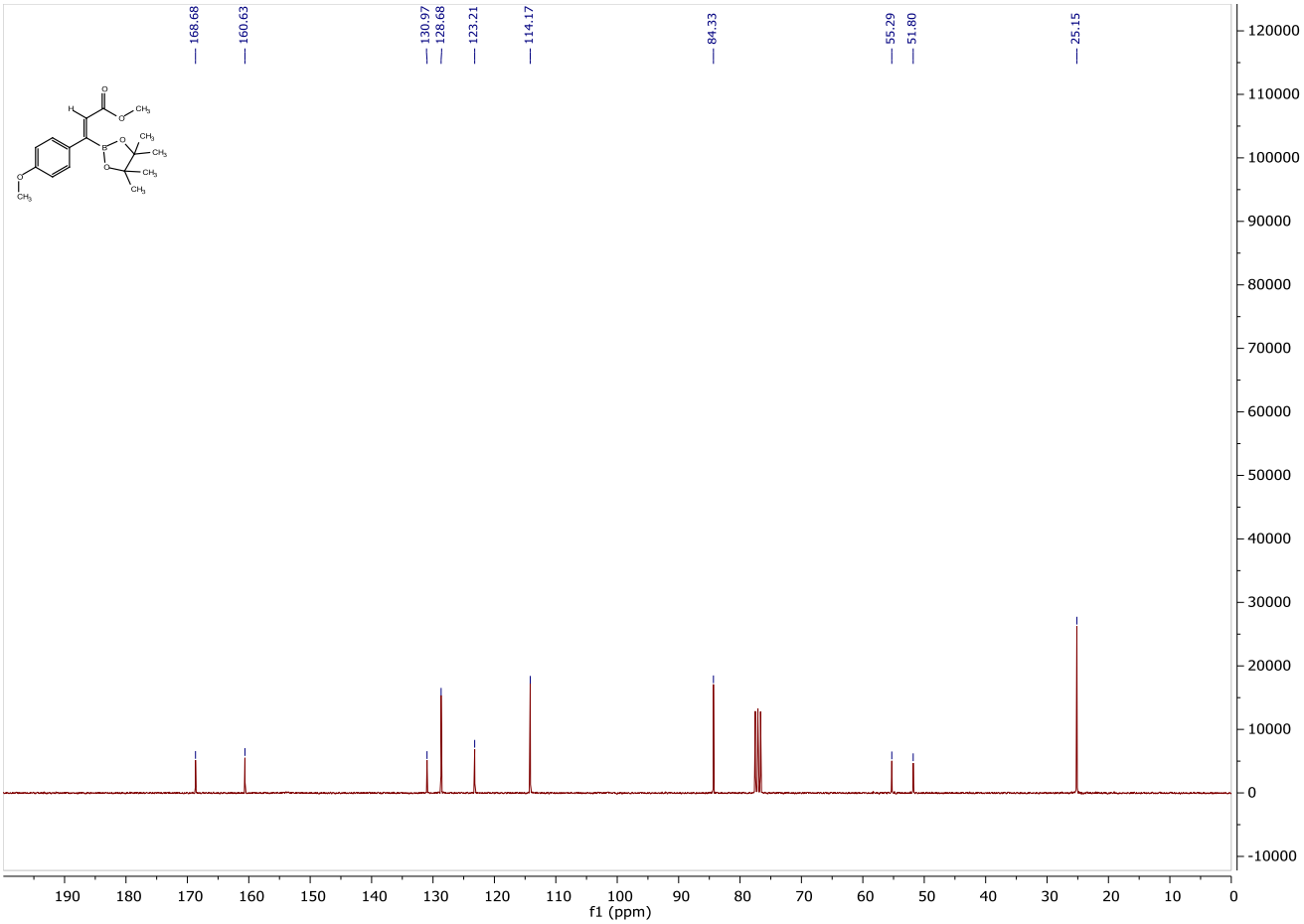


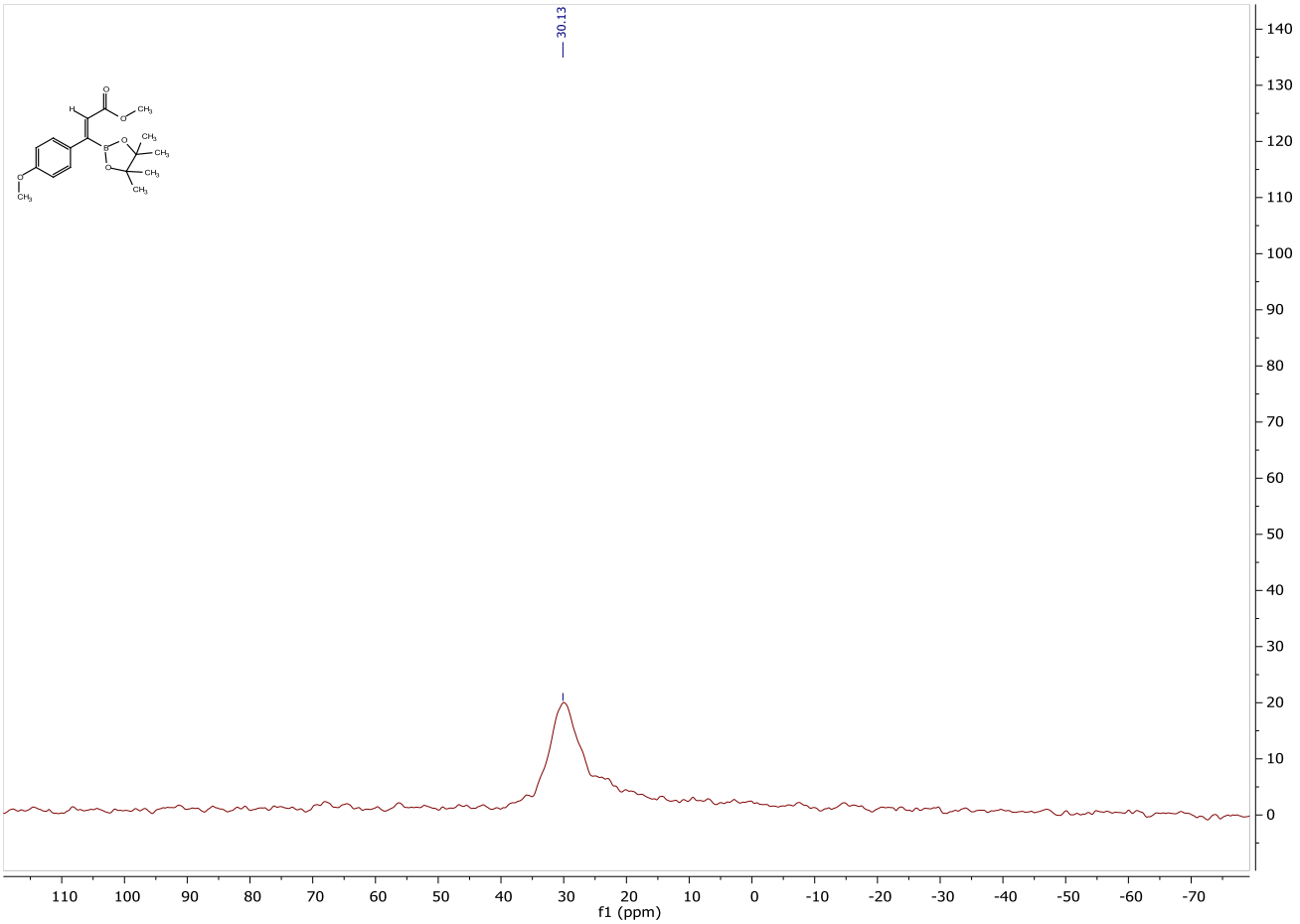

168.55
139.36
135.77
129.49
127.13
124.63
84.39
51.88
25.12
21.34
40000
35000
30000
25000
20000
15000
10000
5000
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


30.76
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

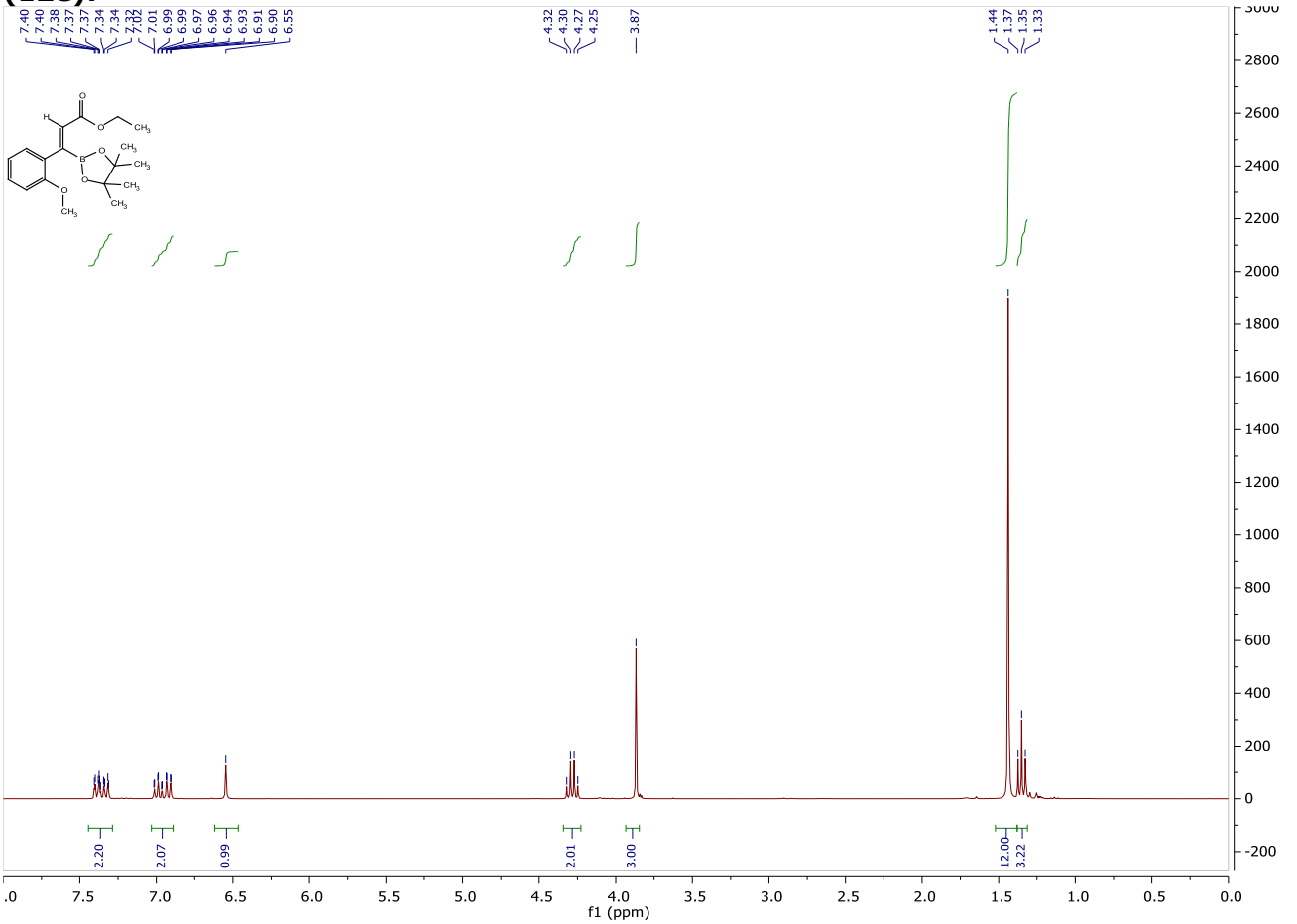
Methyl (*E*)-3-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12d):

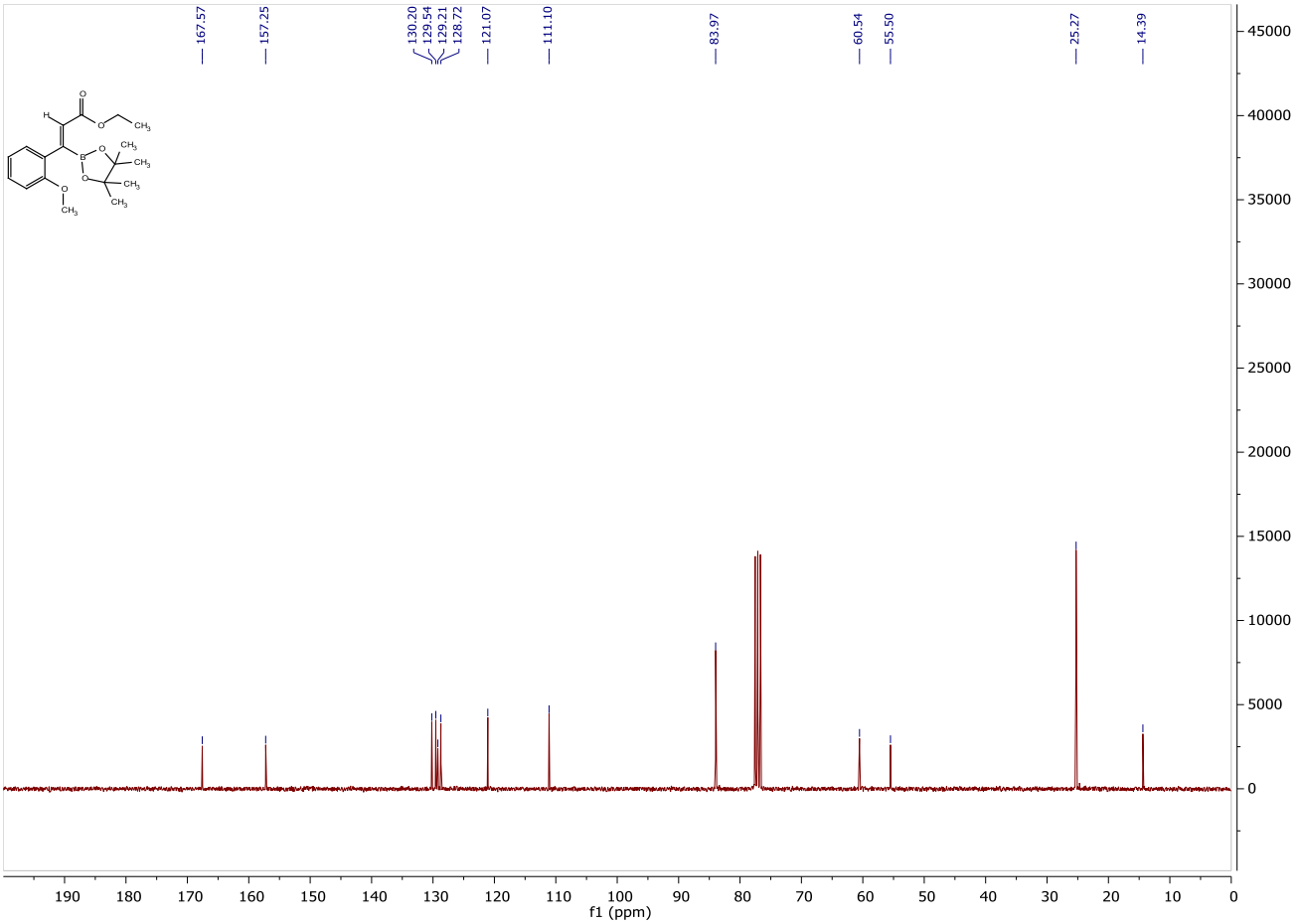


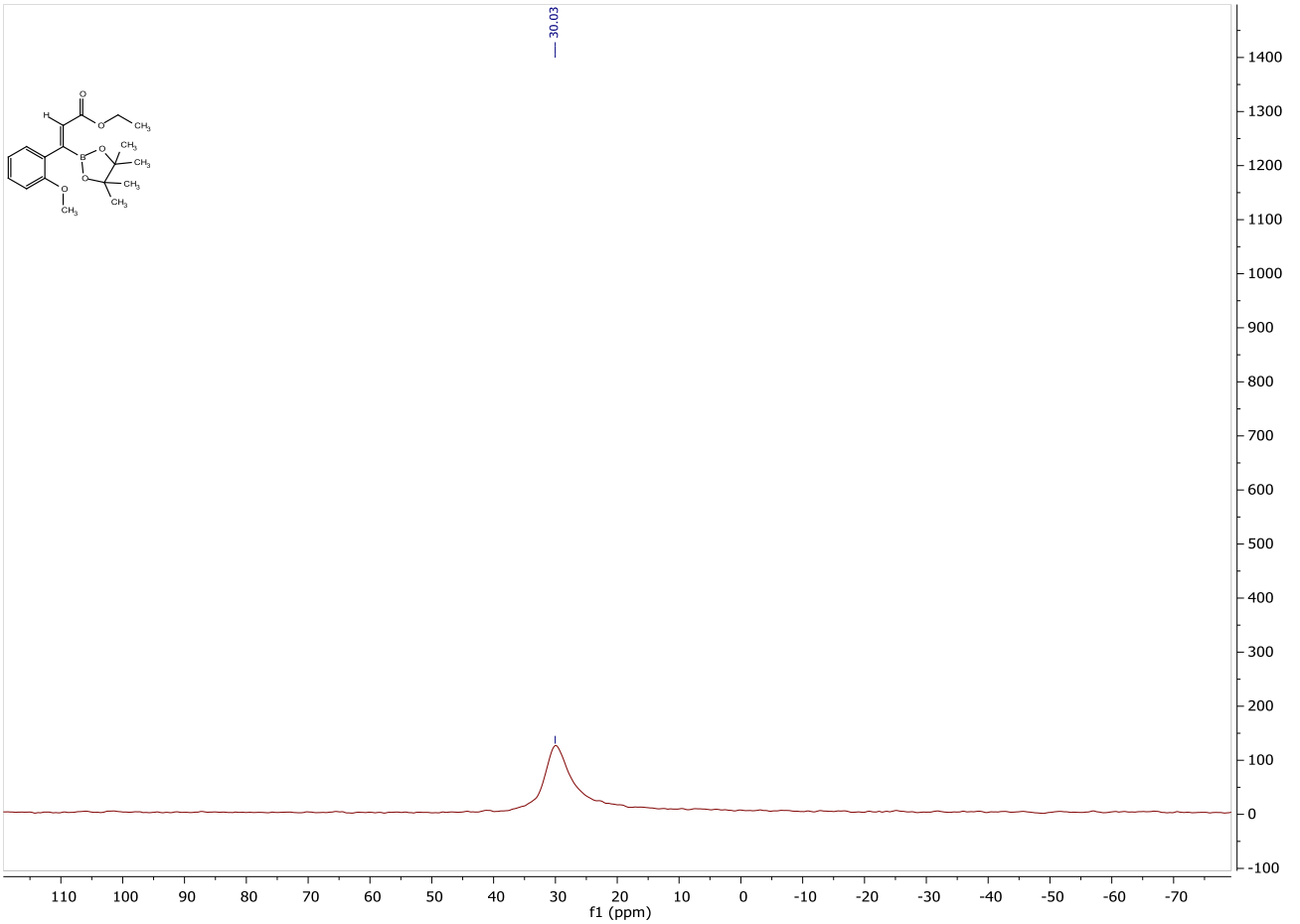




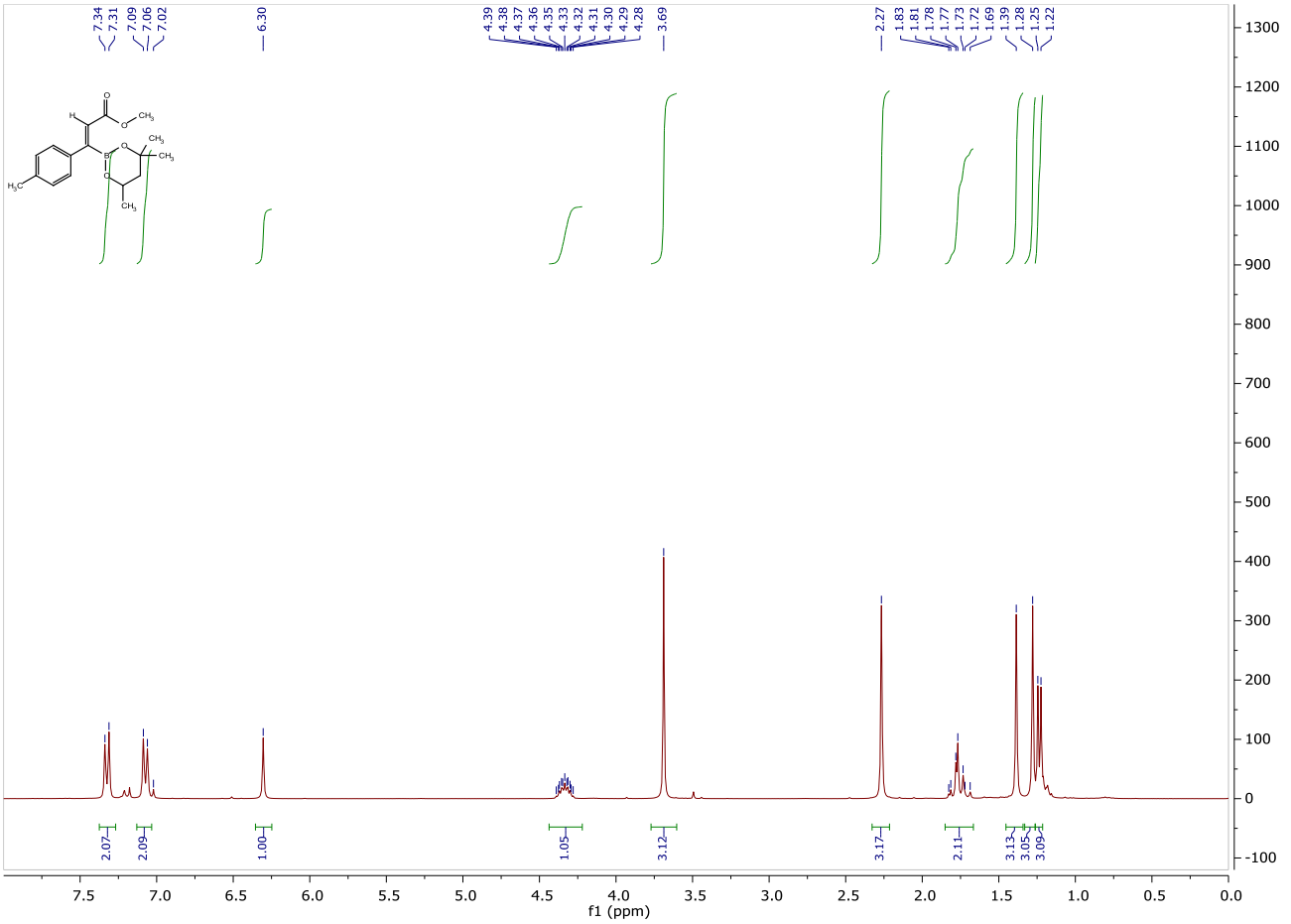
Ethyl (*E*)-3-(2-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12e):

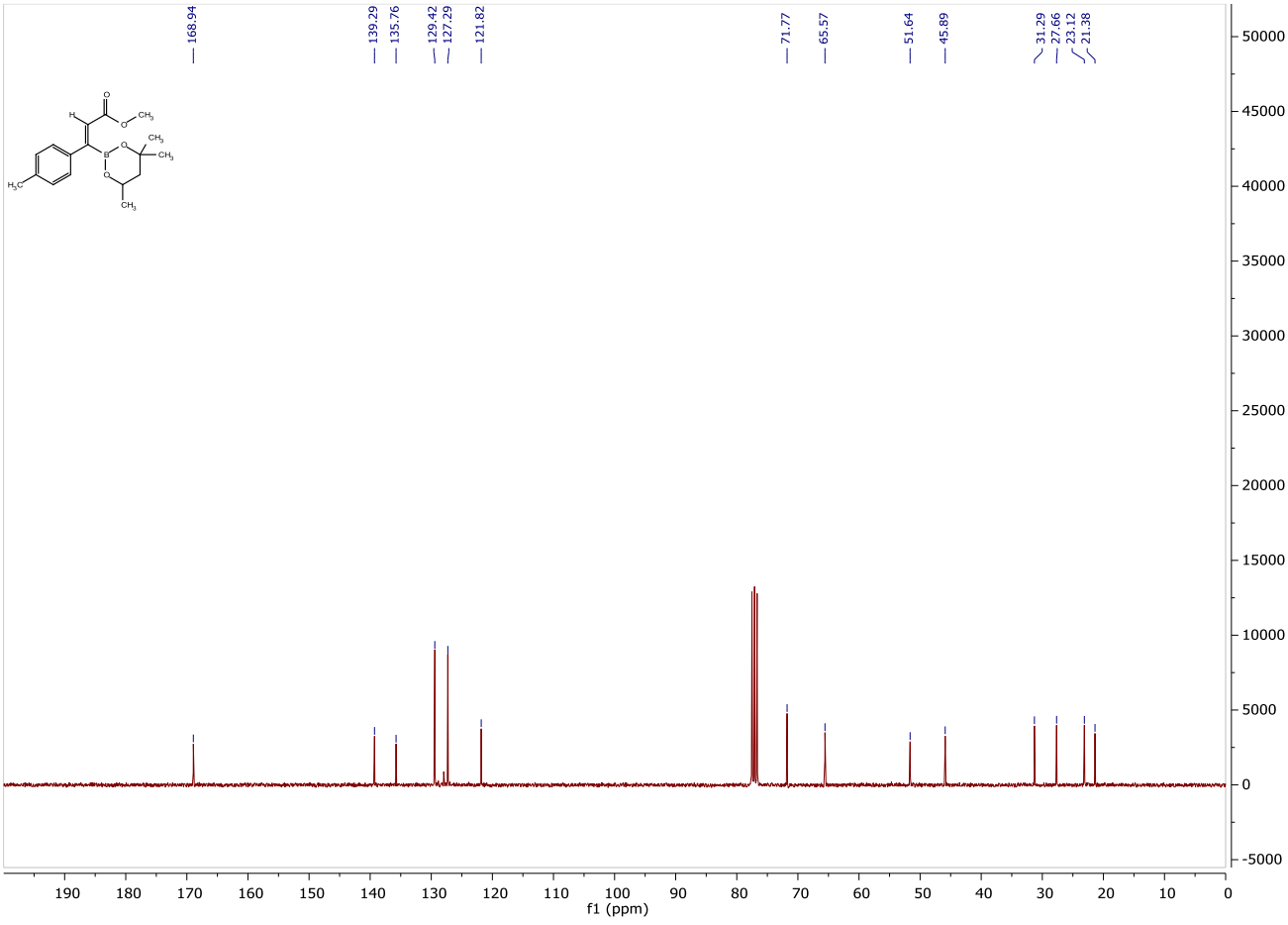


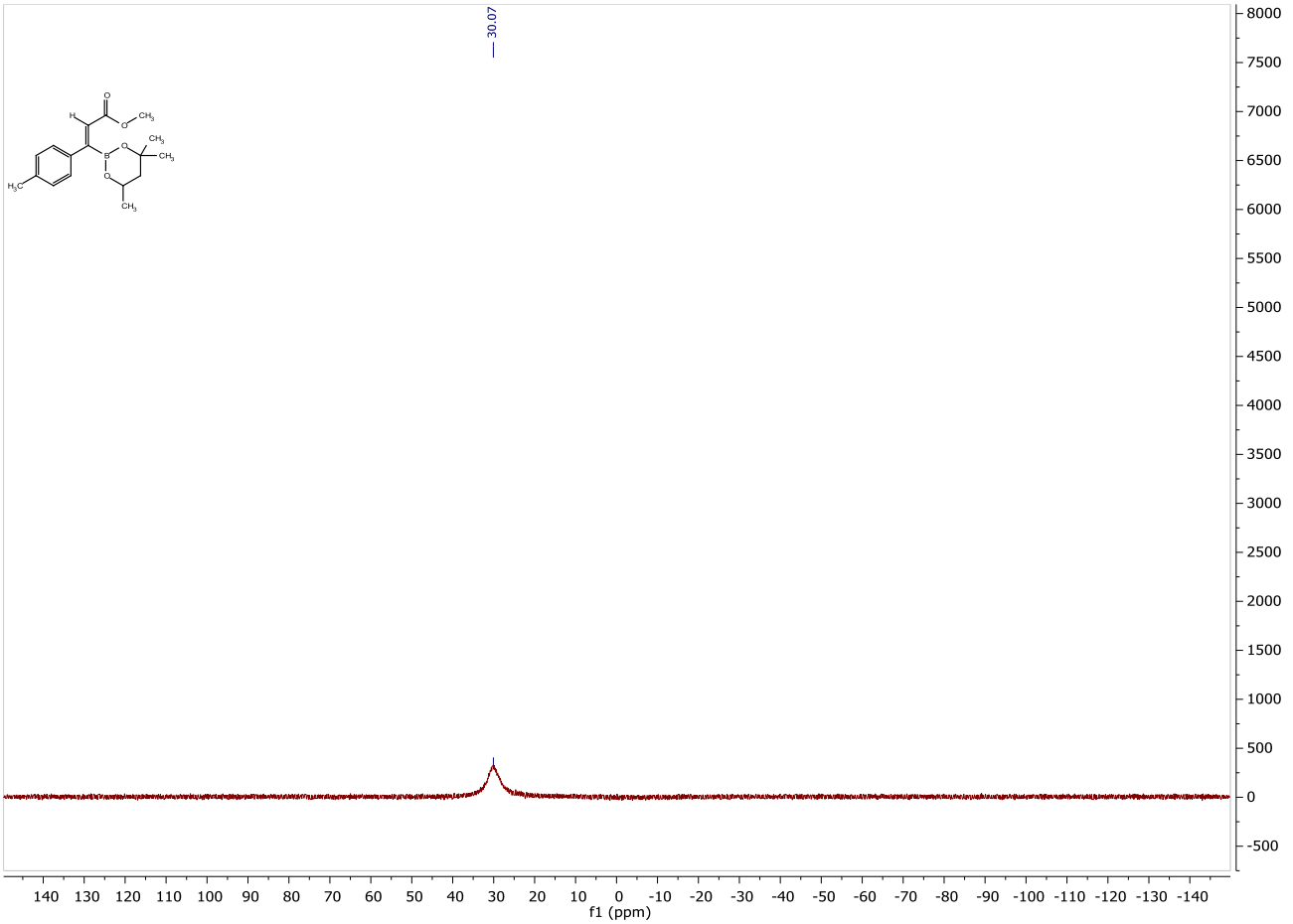

167.57
157.25
130.20
129.54
129.21
128.72
121.07
111.10
83.97
60.54
55.50
25.27
14.39
f1 (ppm)


30.03
f1 (ppm)

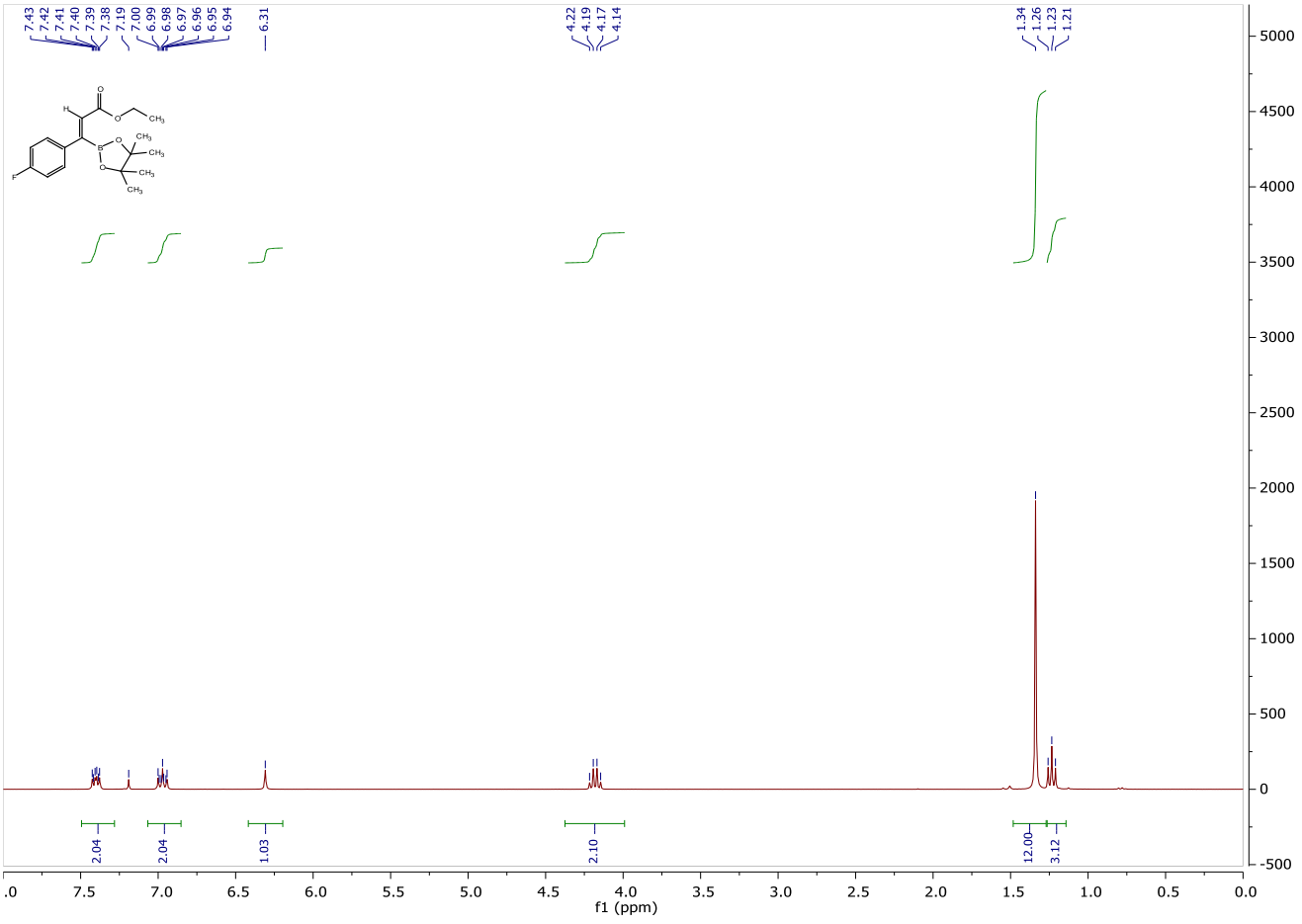
Methyl (*E*)-3-(p-tolyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl) acrylate (12f):

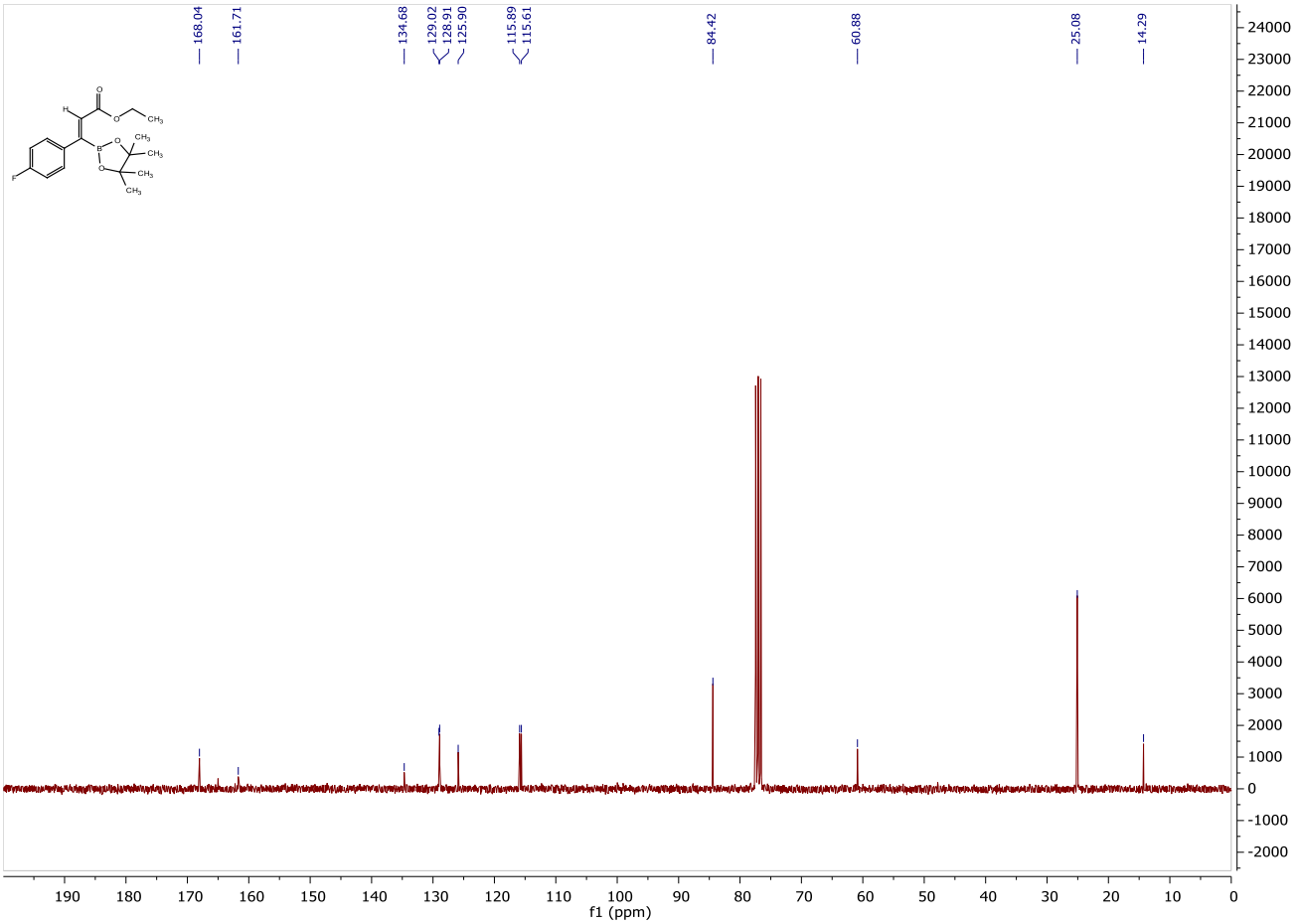


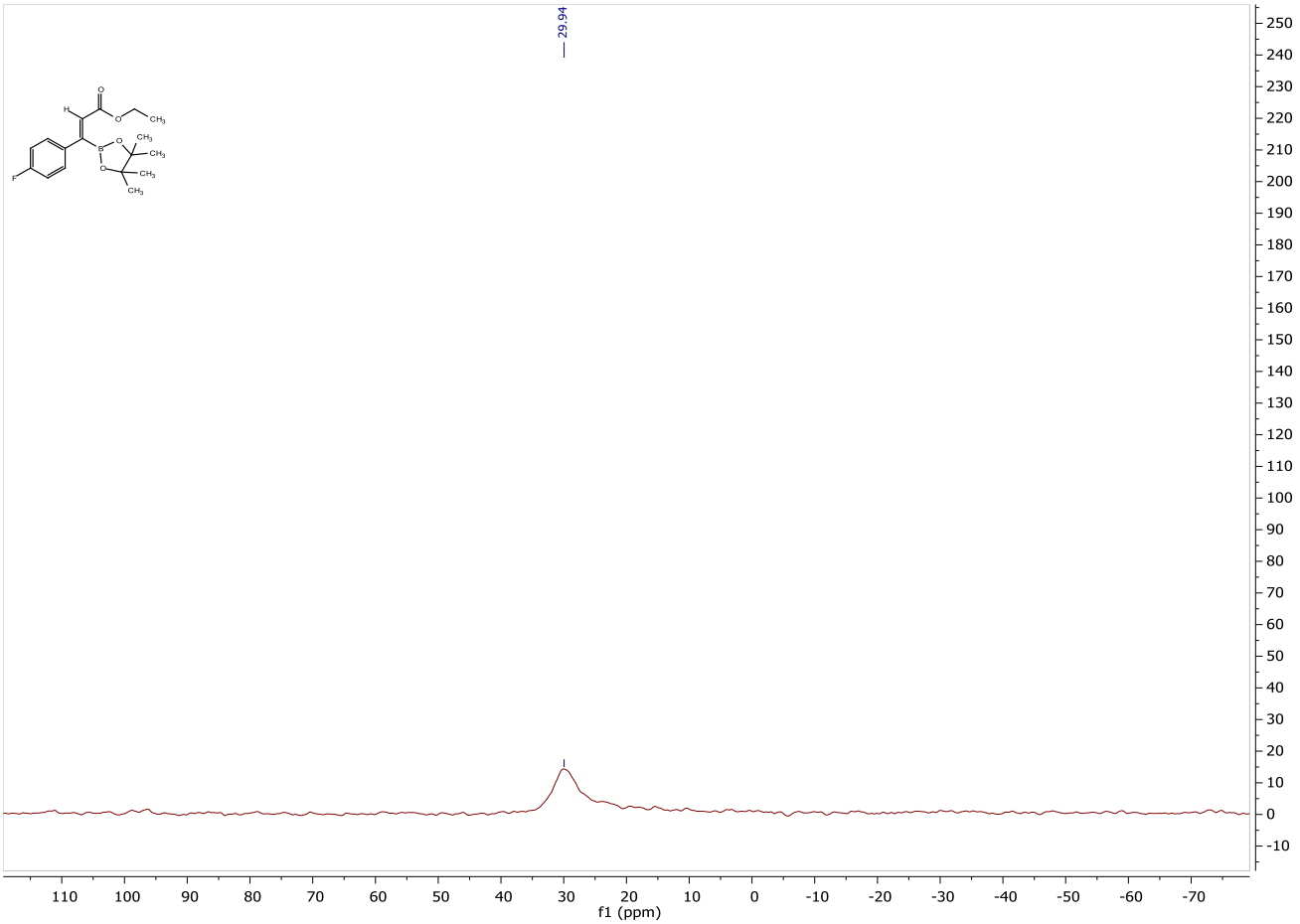




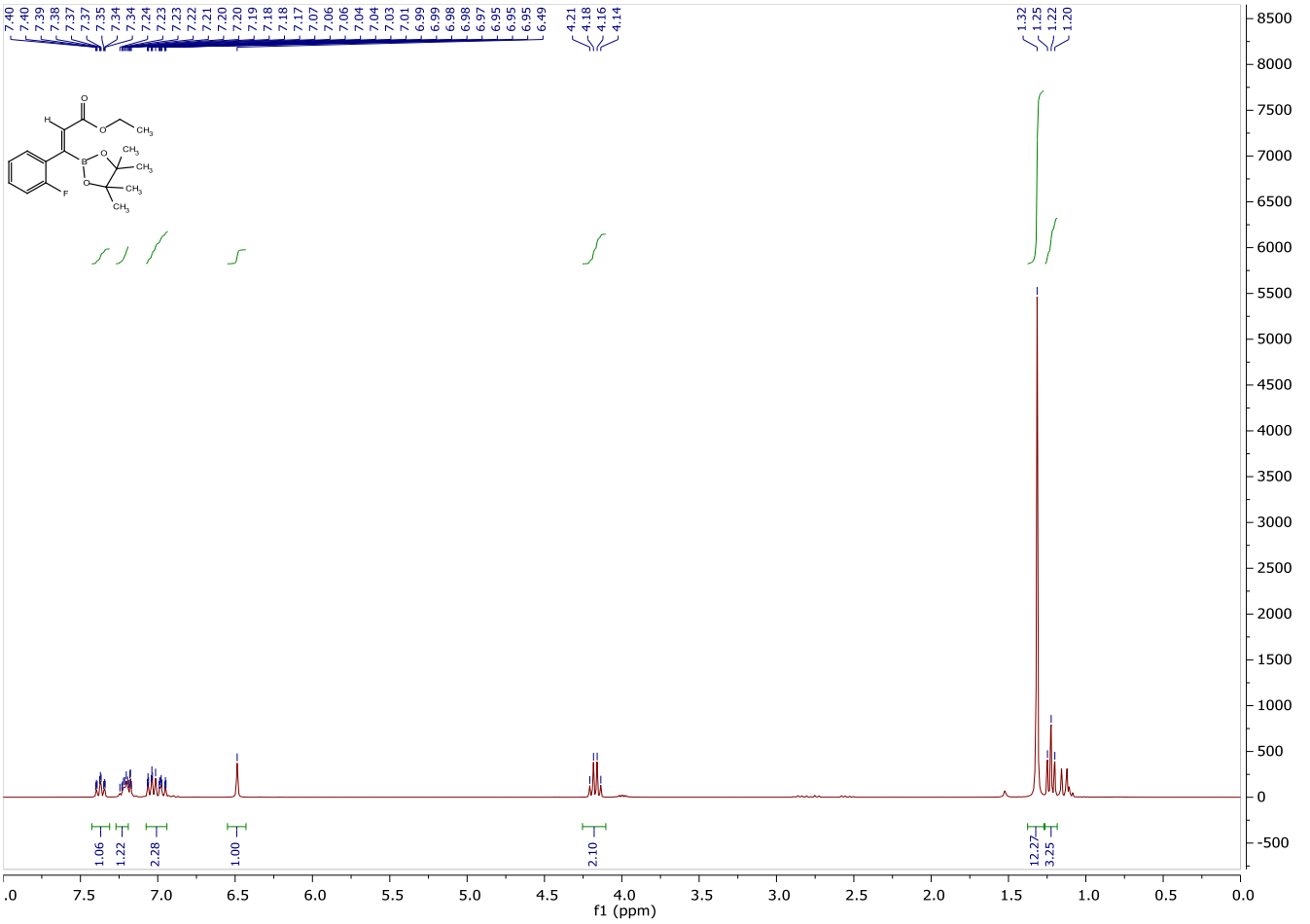
Ethyl (*E*)-3-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12g):

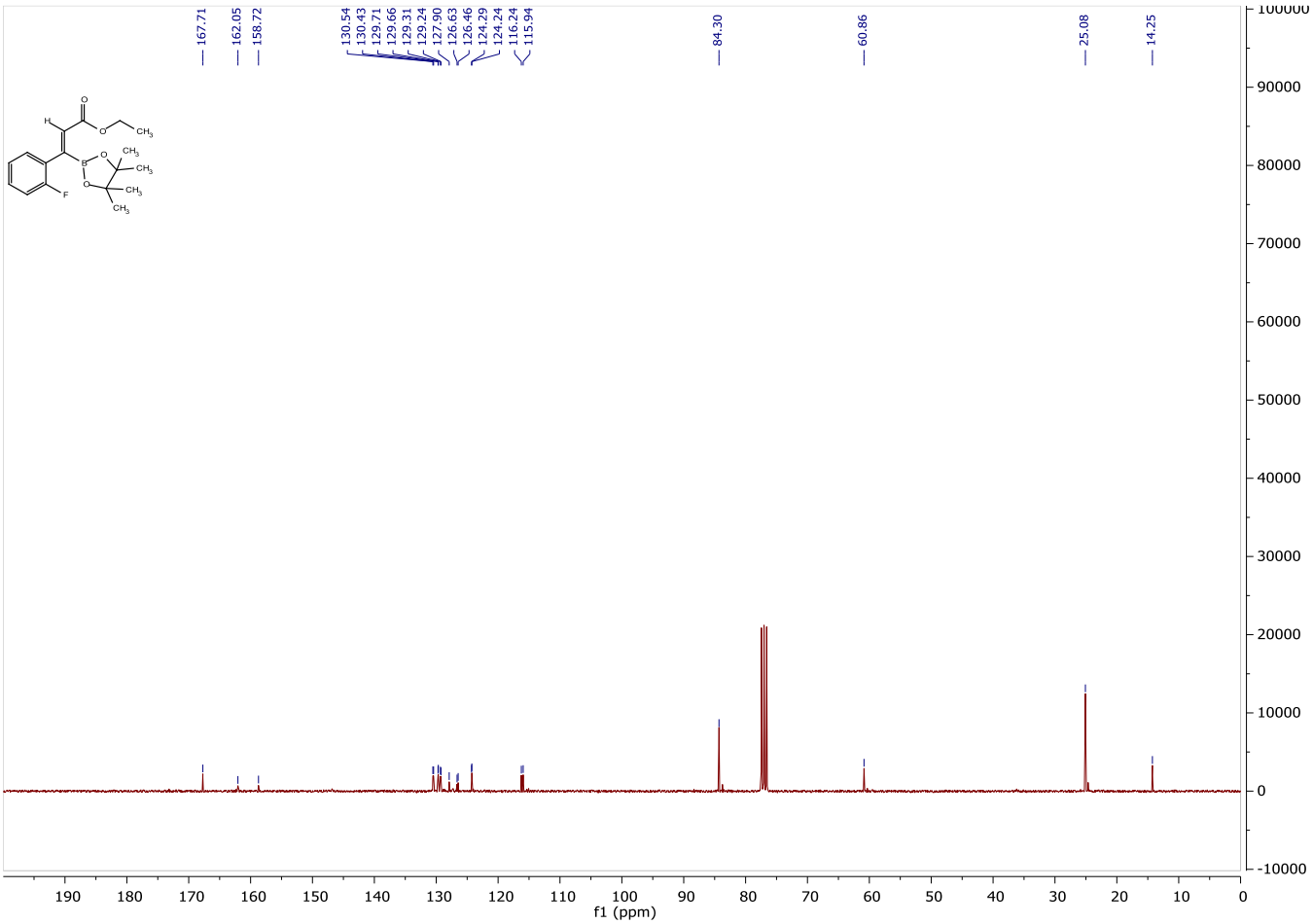


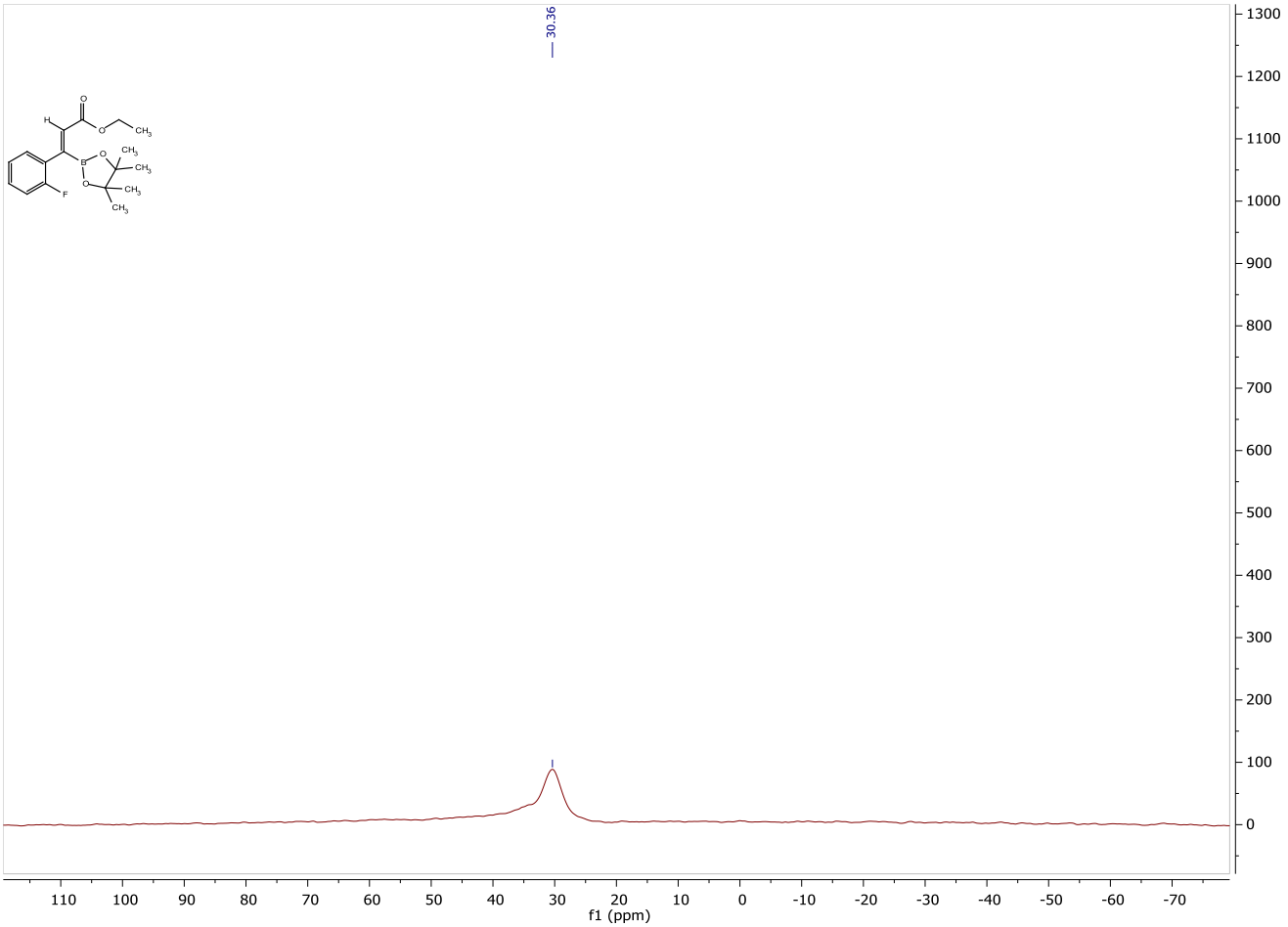

168.04
161.71
134.68
129.02
128.91
125.90
115.89
115.61
84.42
60.88
25.08
14.29
f1 (ppm)


29.94
f1 (ppm)

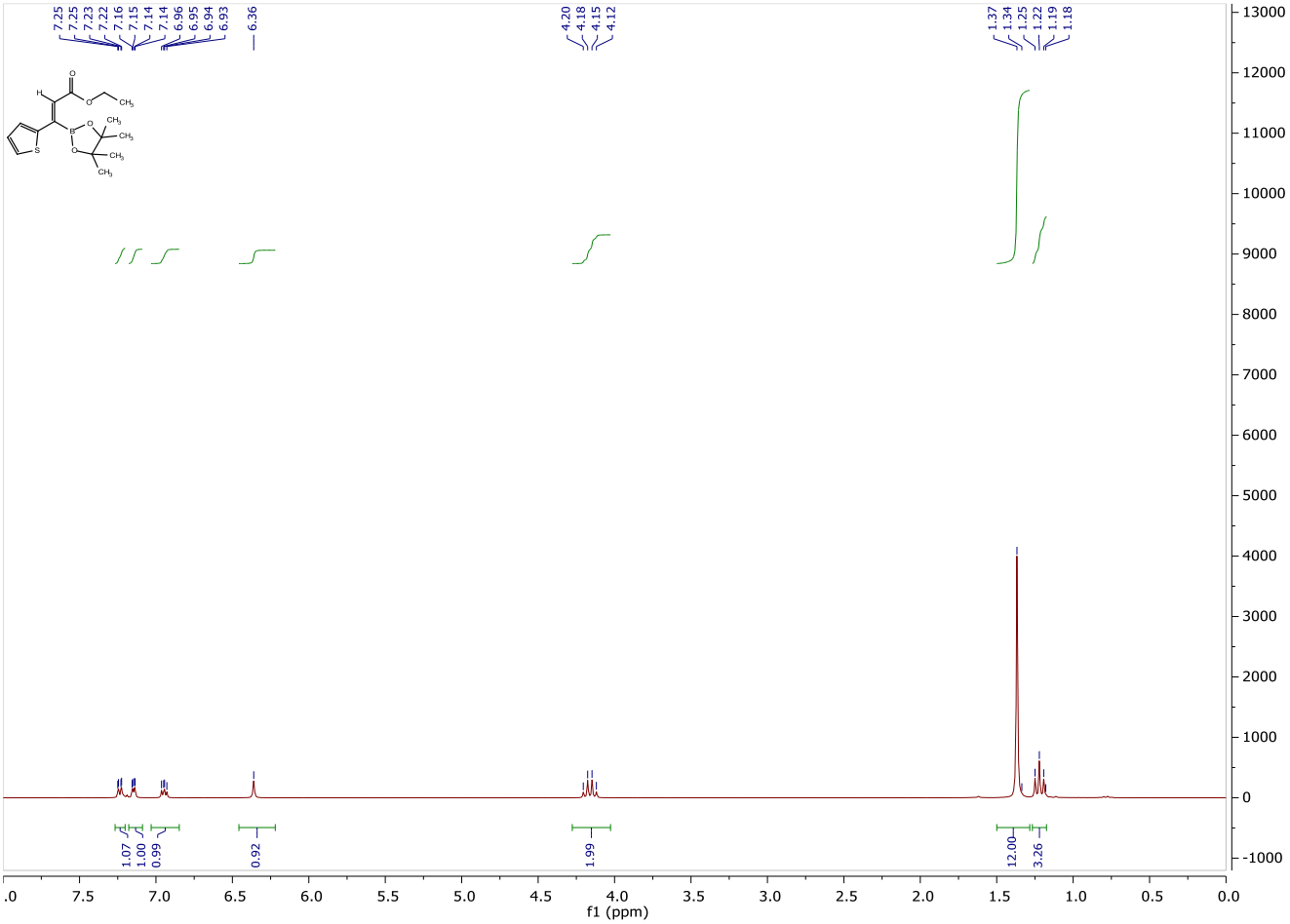
Ethyl (*E*)-3-(2-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12h):

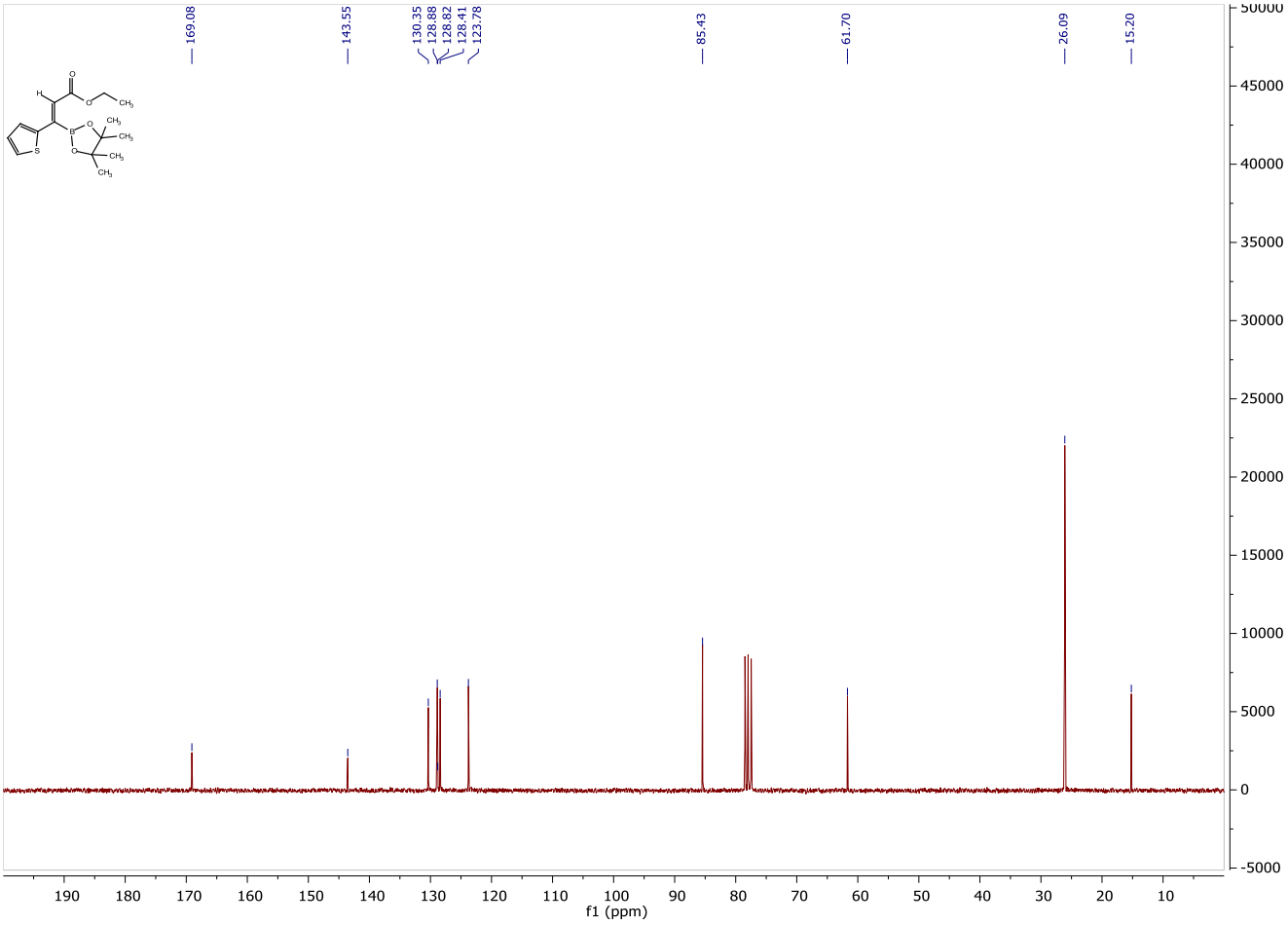


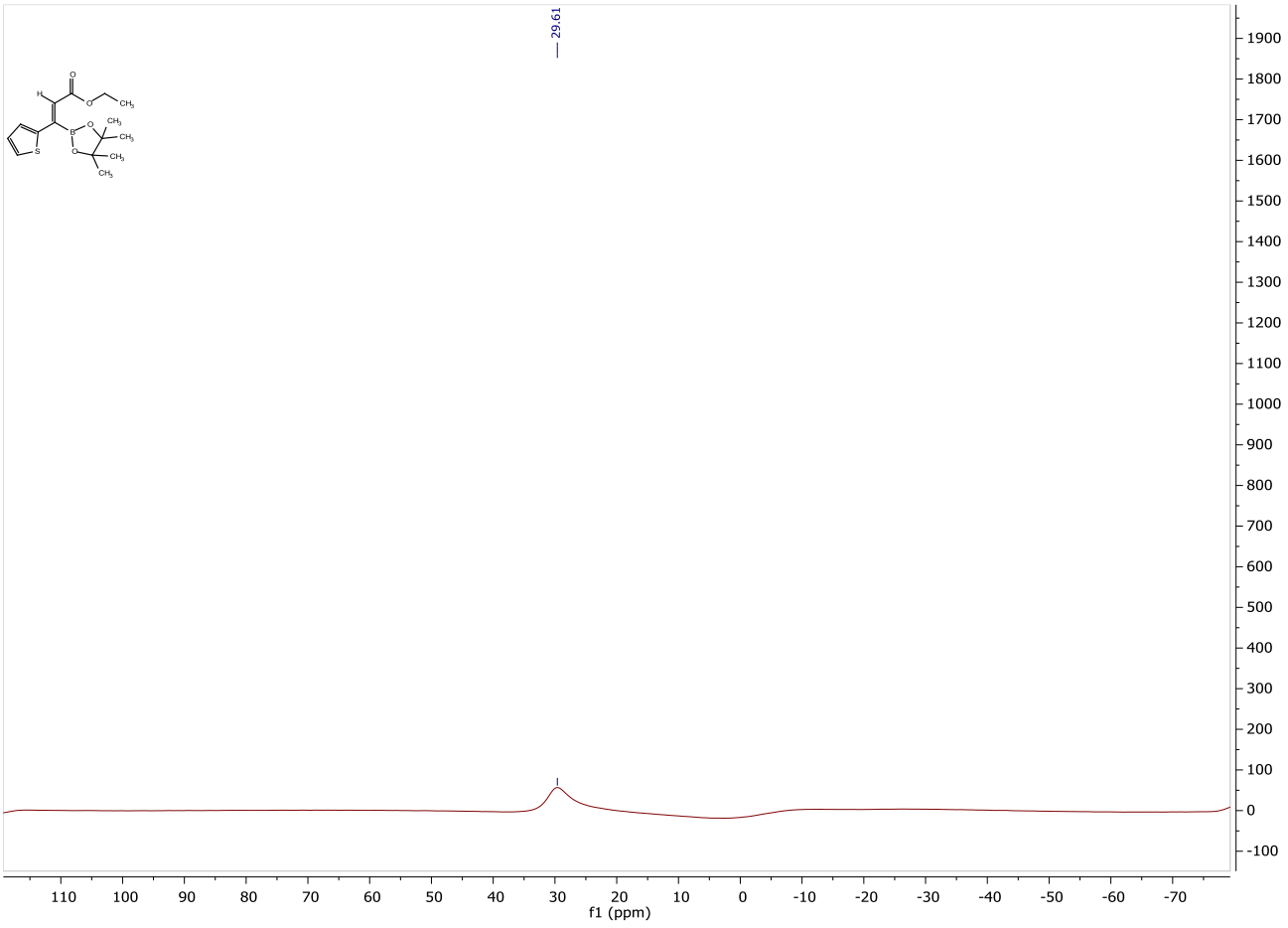




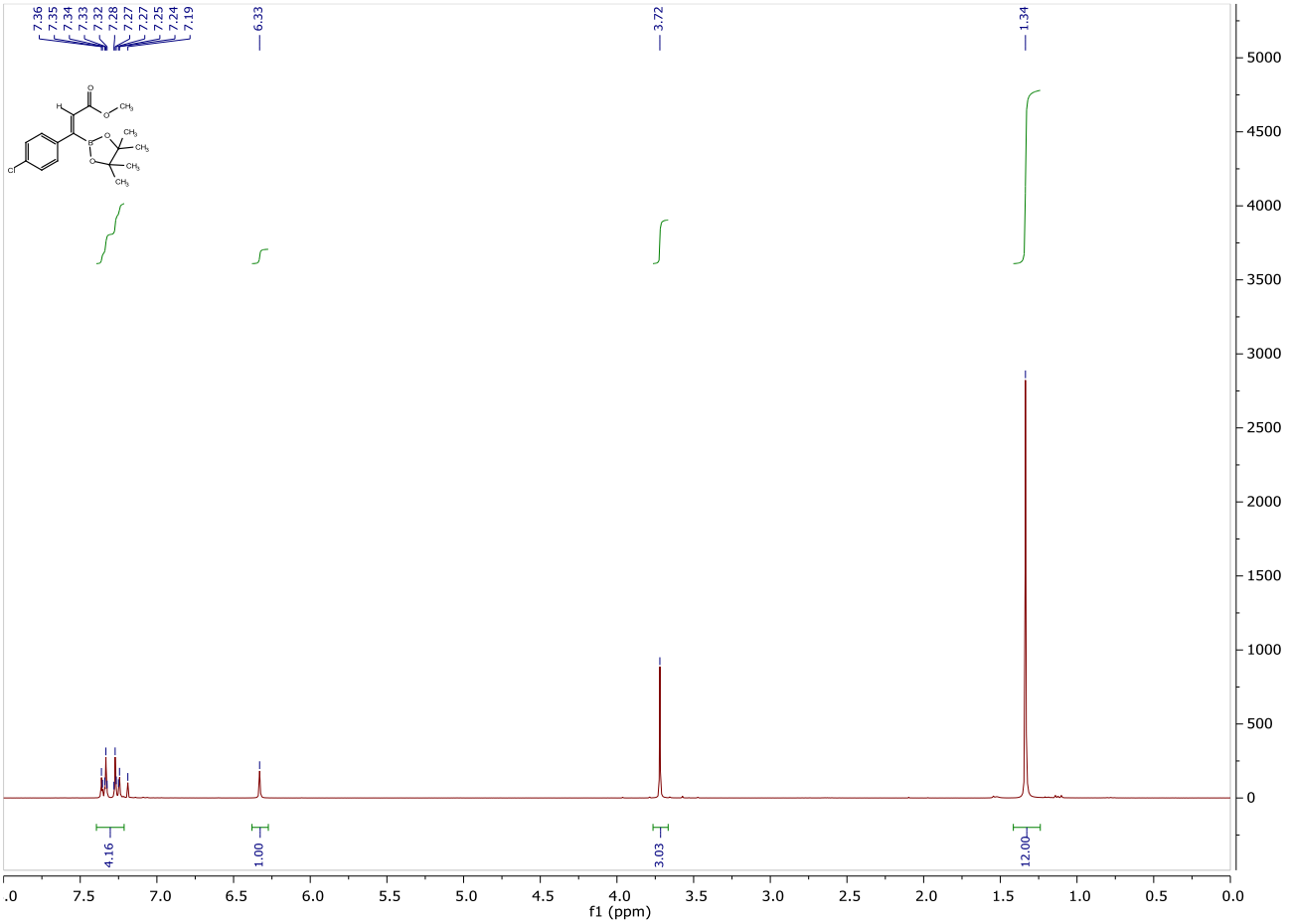
Ethyl (*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(thiophen-2-yl) acrylate (12i):

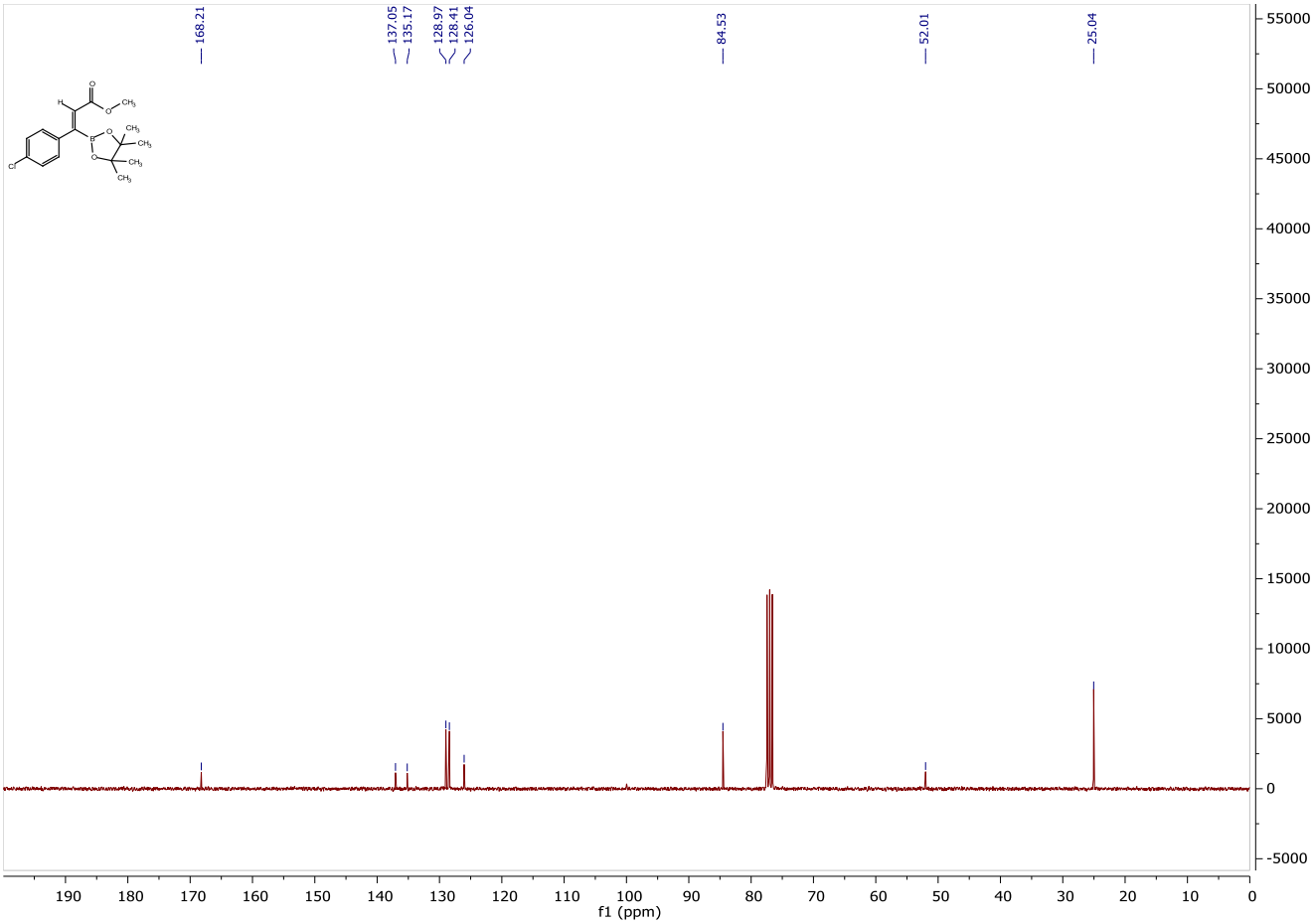


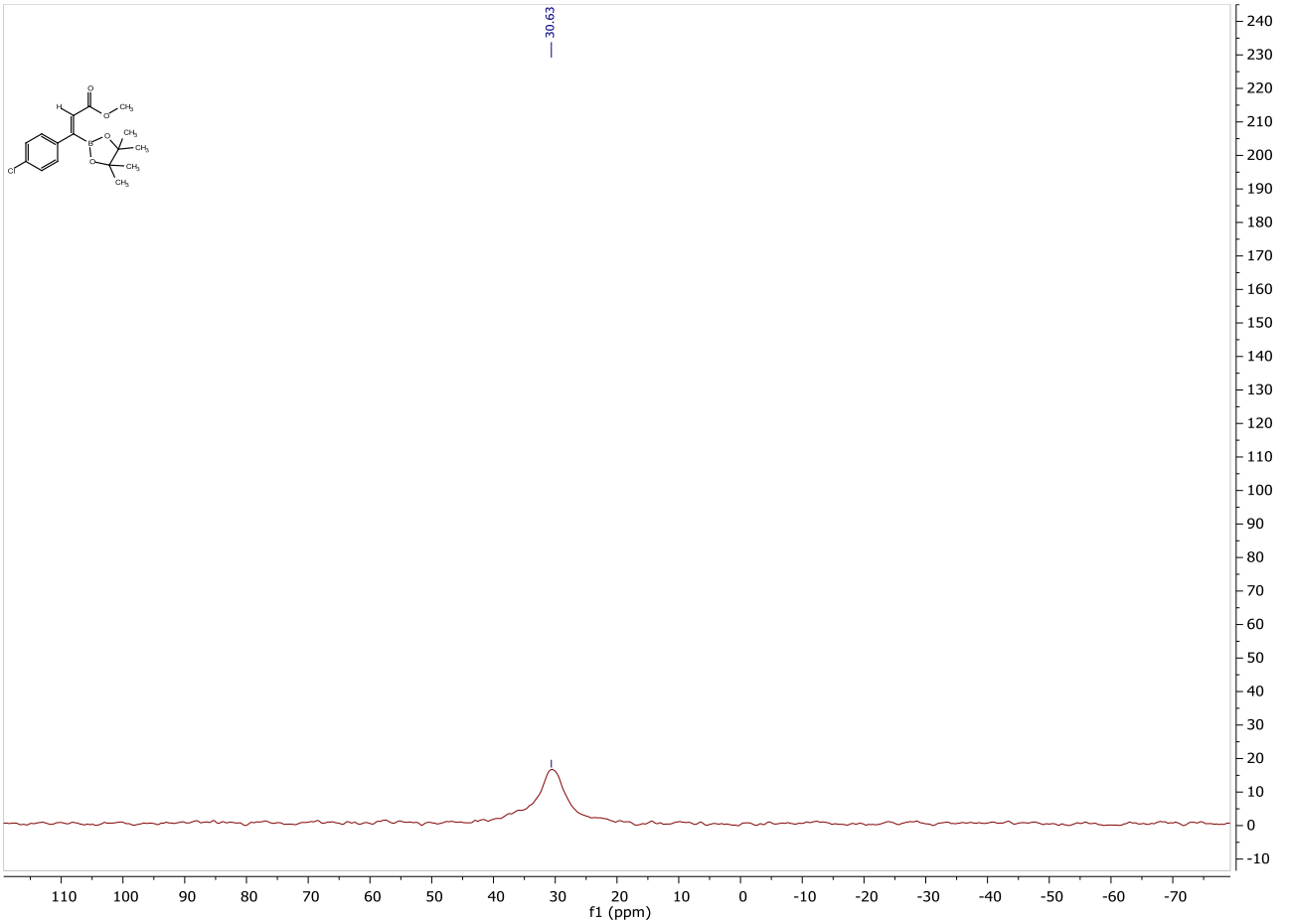

169.08
143.55
130.35
128.88
128.82
128.41
123.78
85.43
61.70
26.09
15.20
f1 (ppm)


29.61
f1 (ppm)

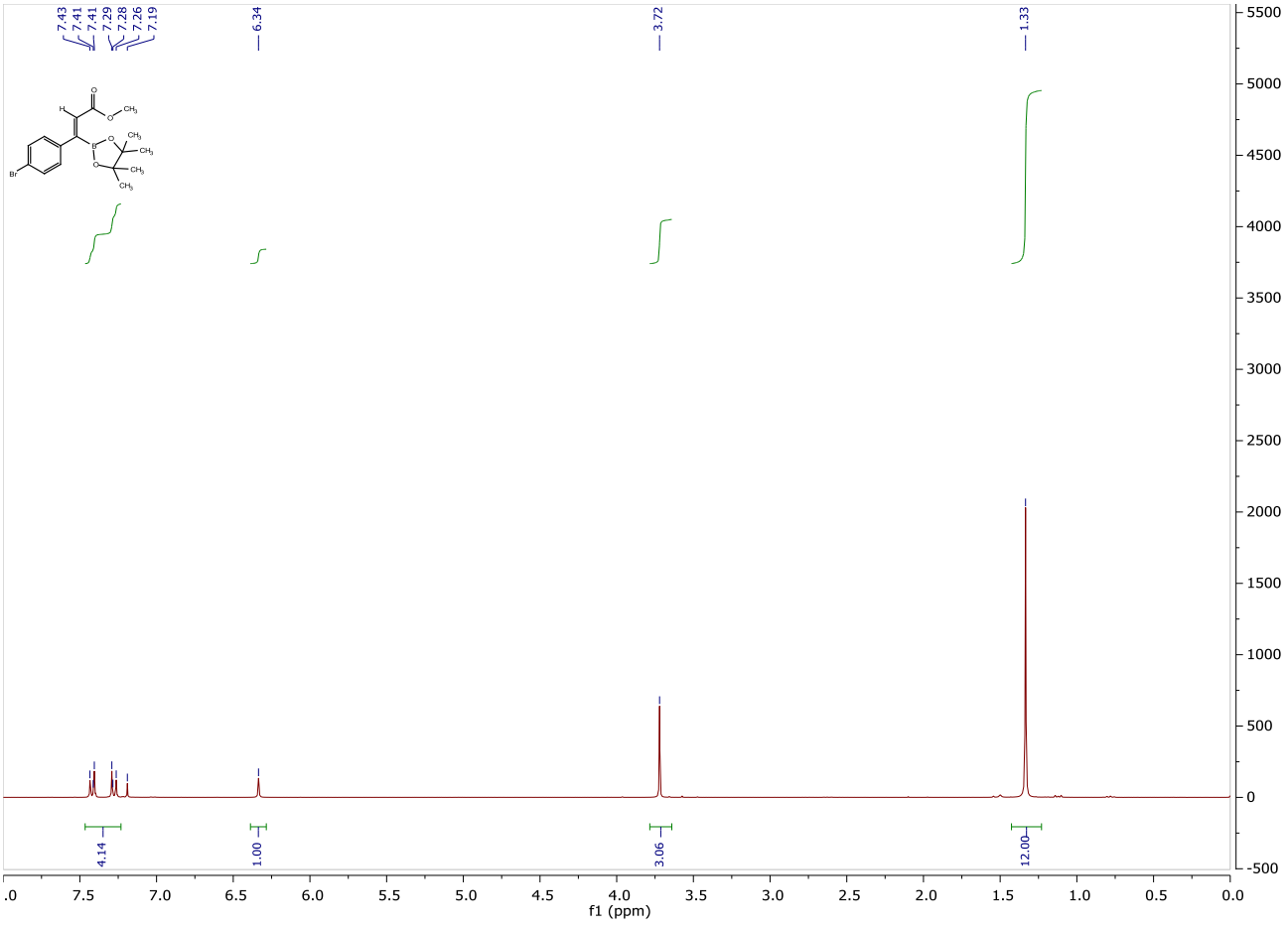
Methyl (*E*)-3-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12j):

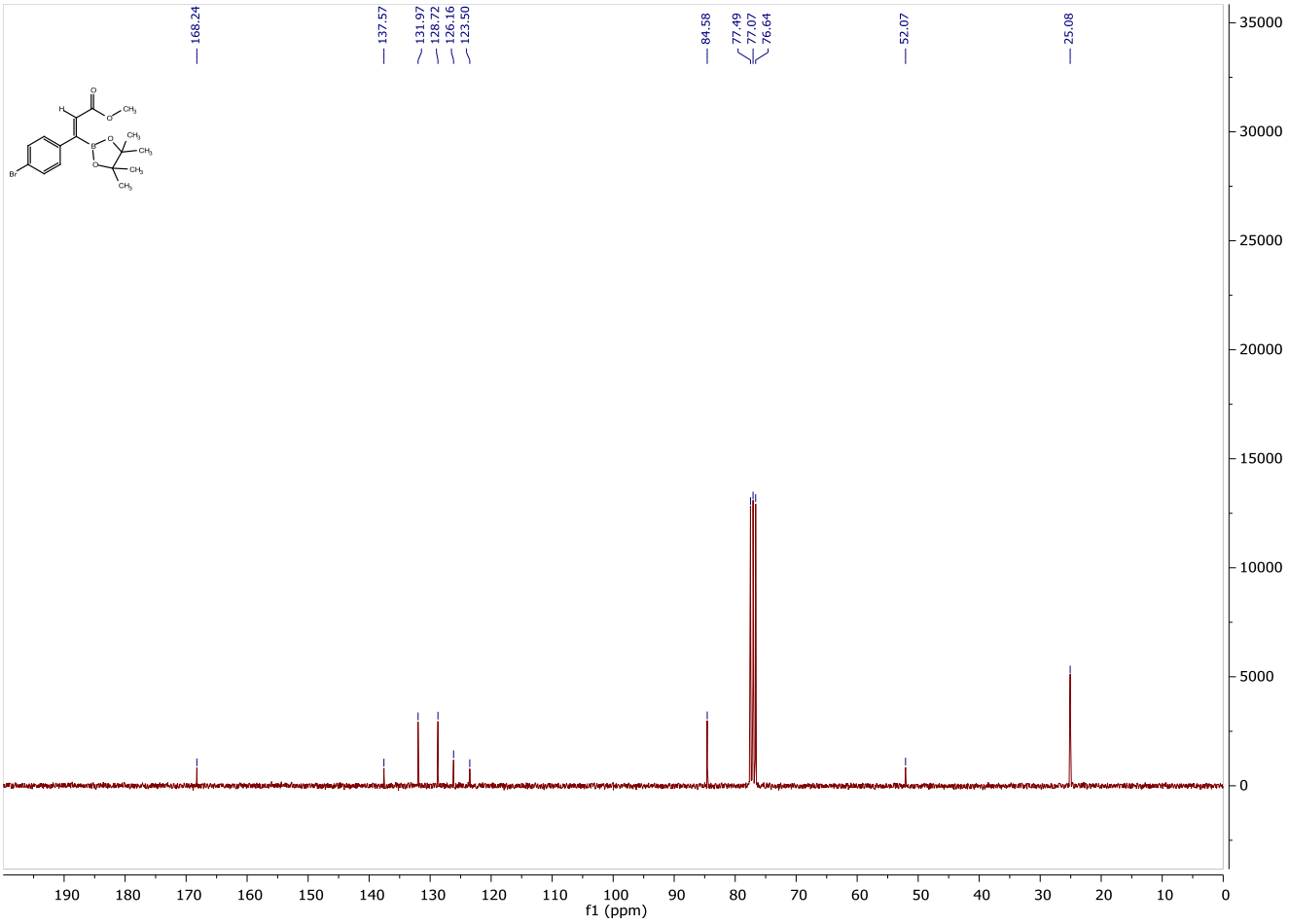


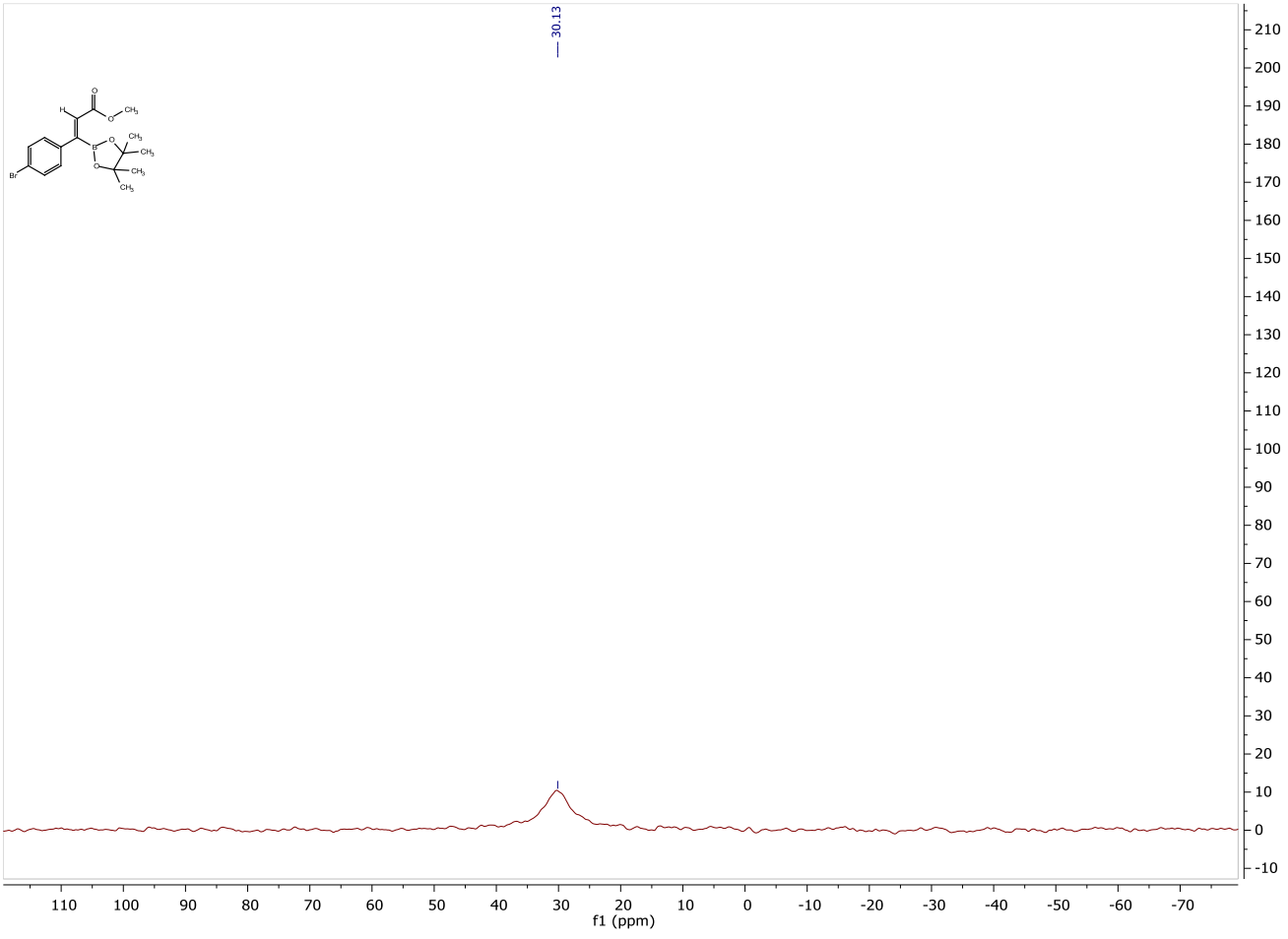




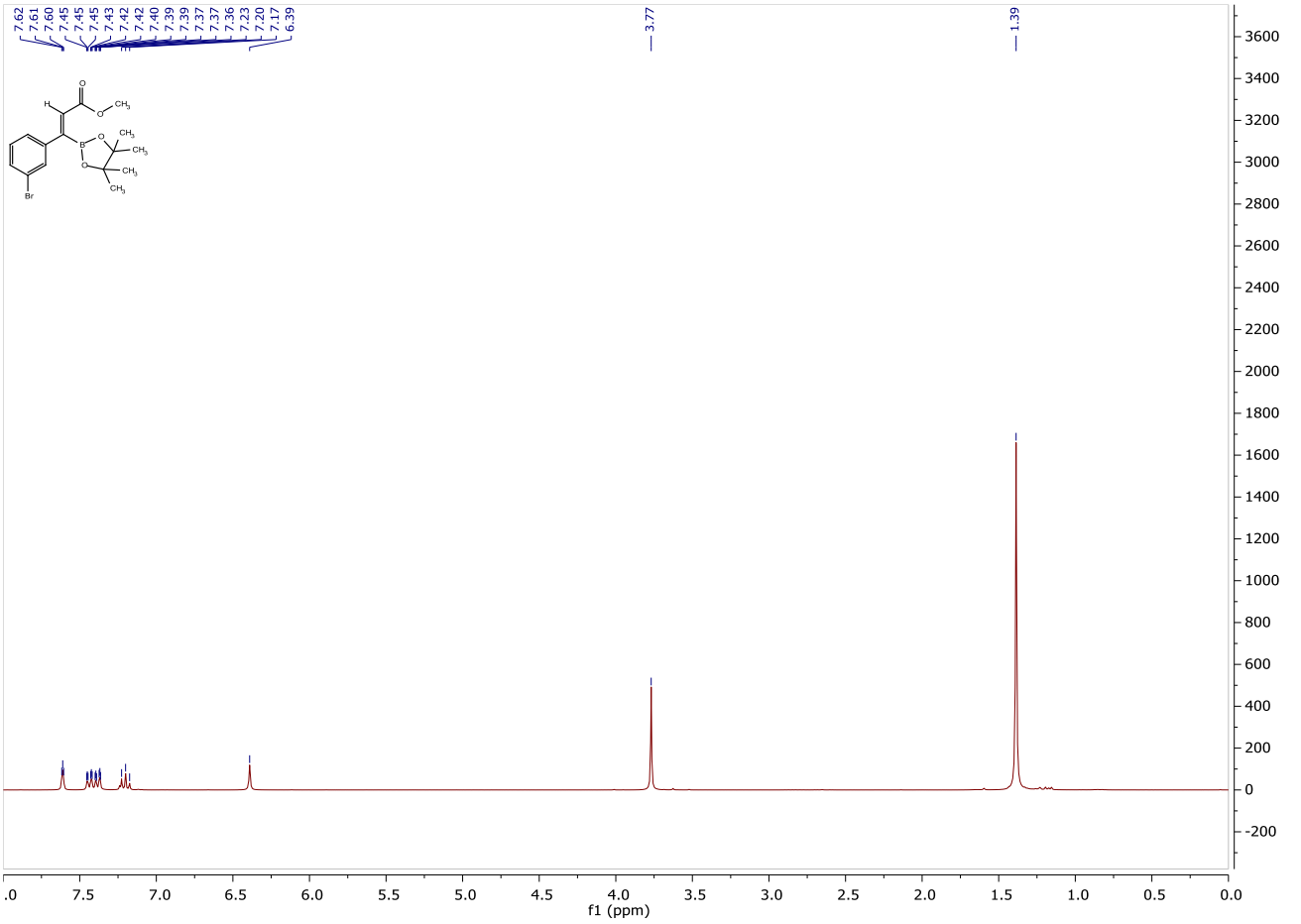
Methyl (*E*)-3-(4-bromophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate (12k):

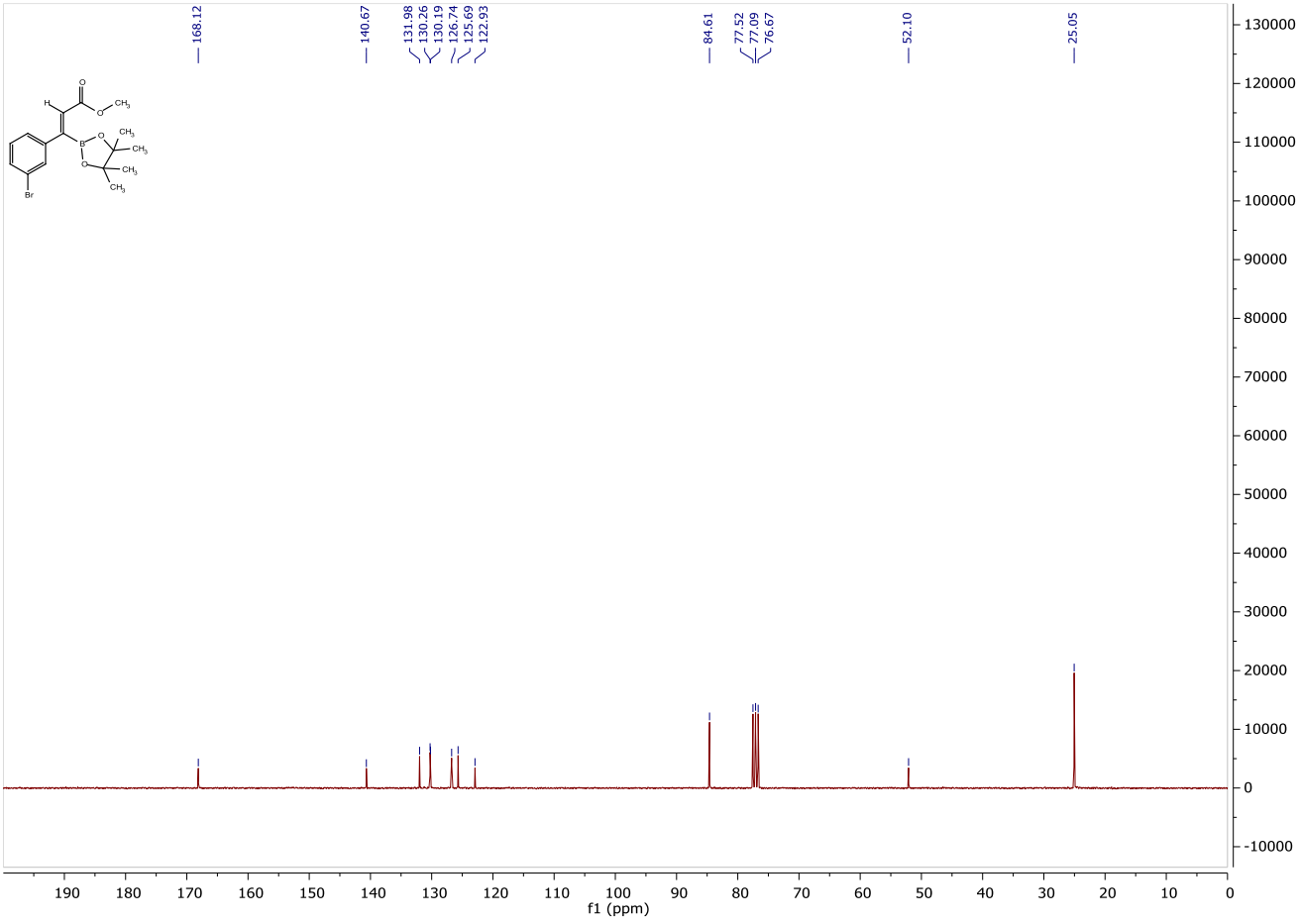


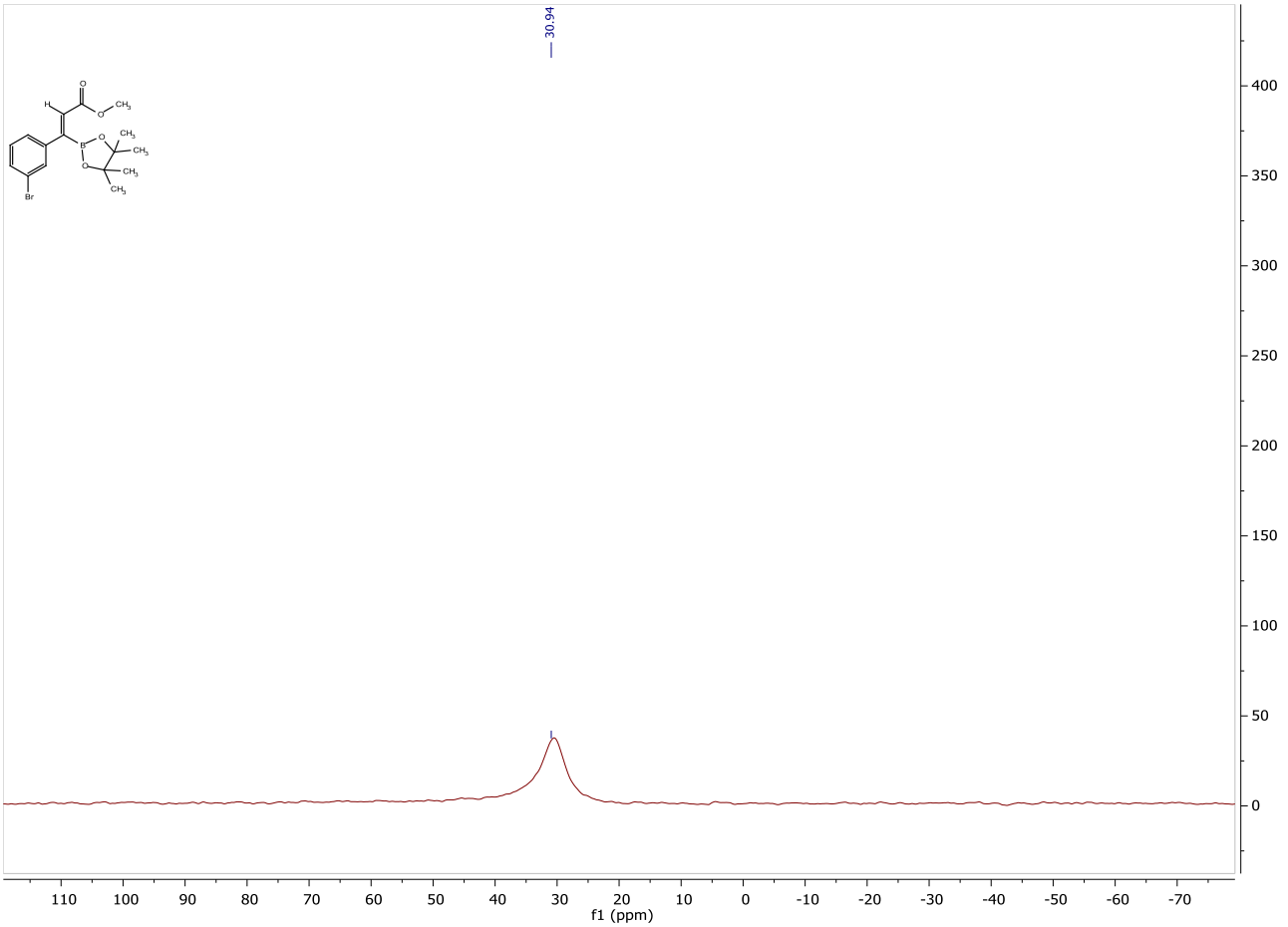

168.24
137.57
131.97
128.72
126.16
123.50
84.58
77.49
77.07
76.64
52.07
25.08
f1 (ppm)


30.13
f1 (ppm)

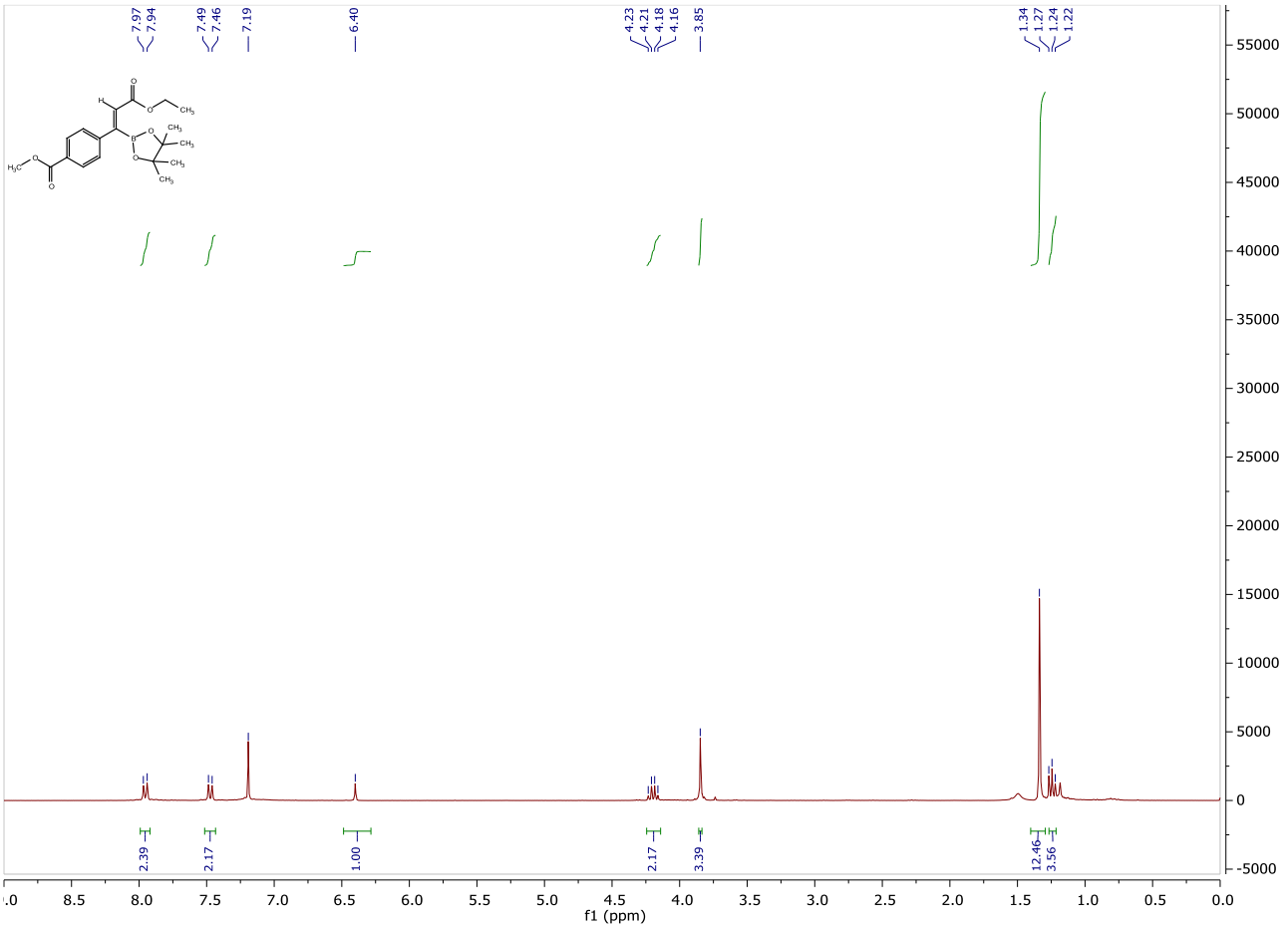
Methyl (*E*)-3-(3-bromophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) (12l):

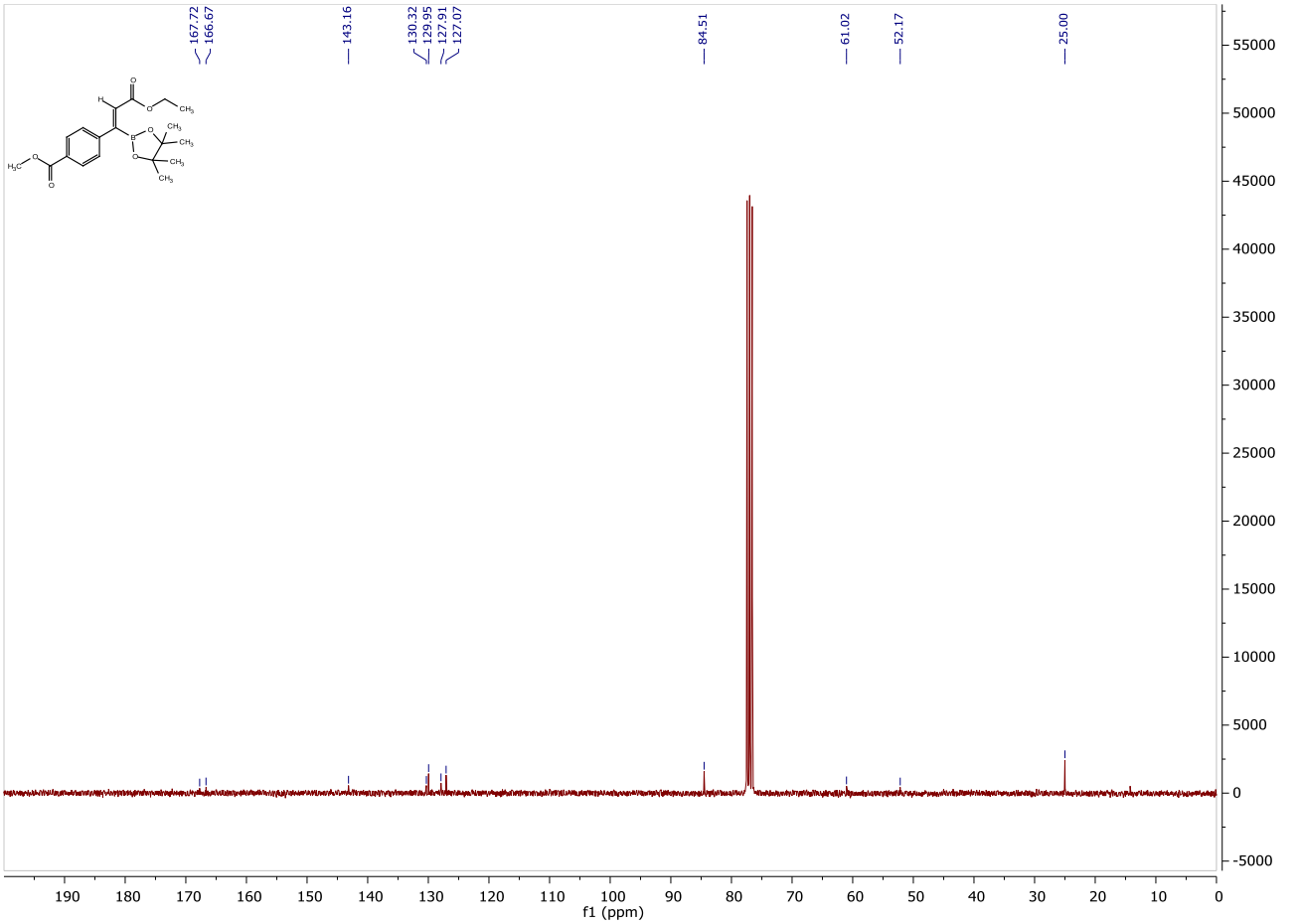


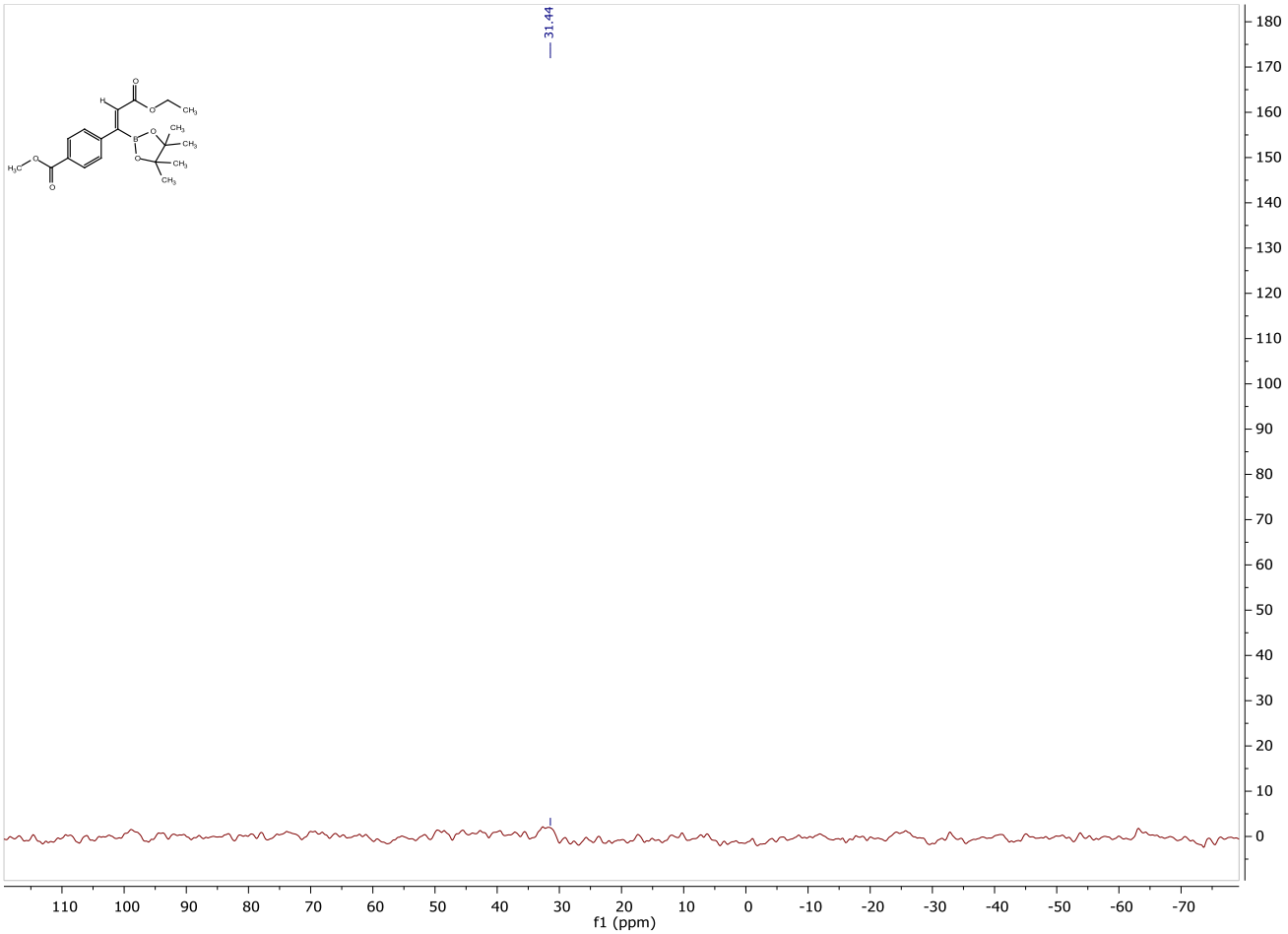




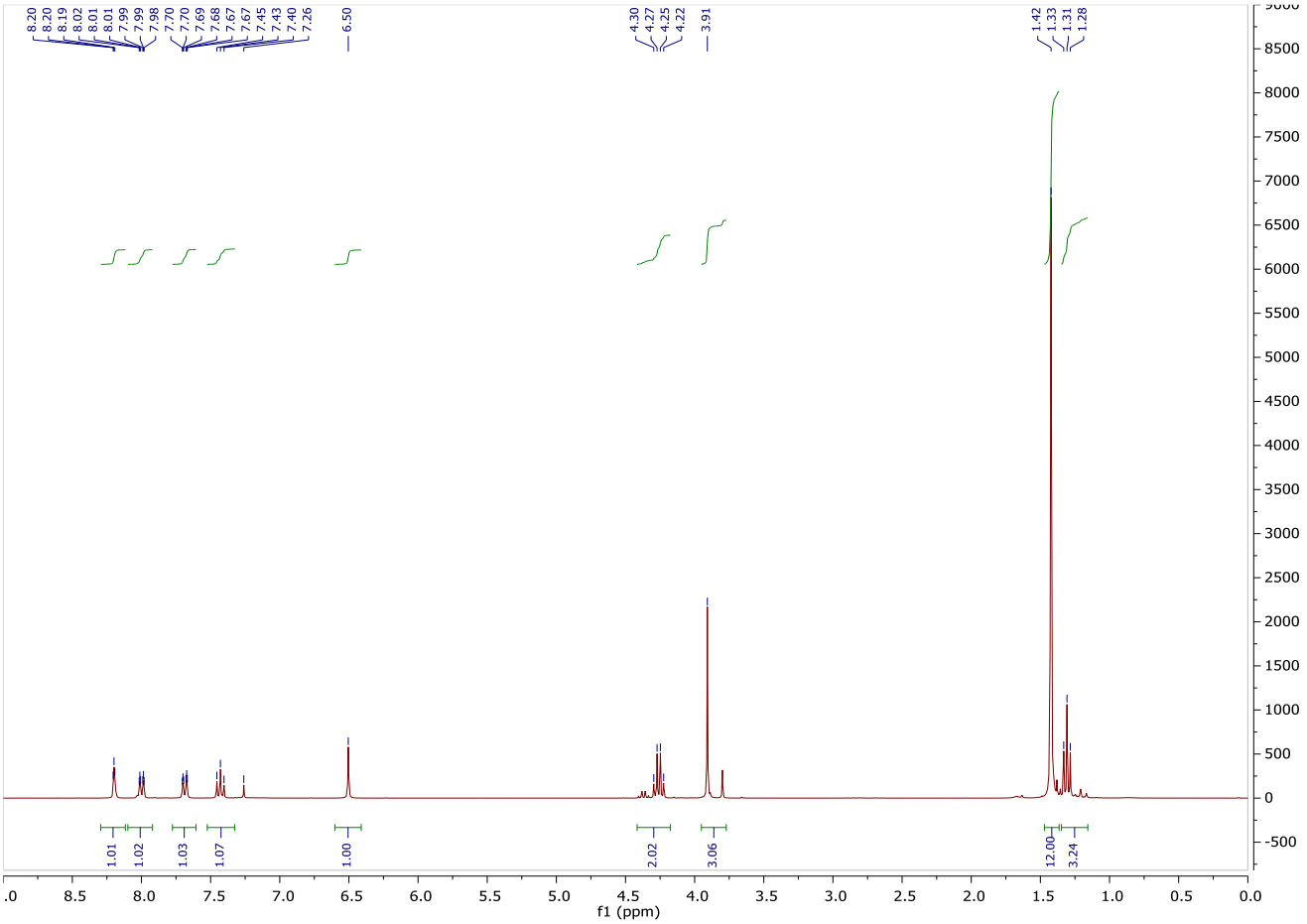
Methyl (*E*)-4-(3-ethoxy-3-oxo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) prop-1-en-1-yl) benzoate (12m):

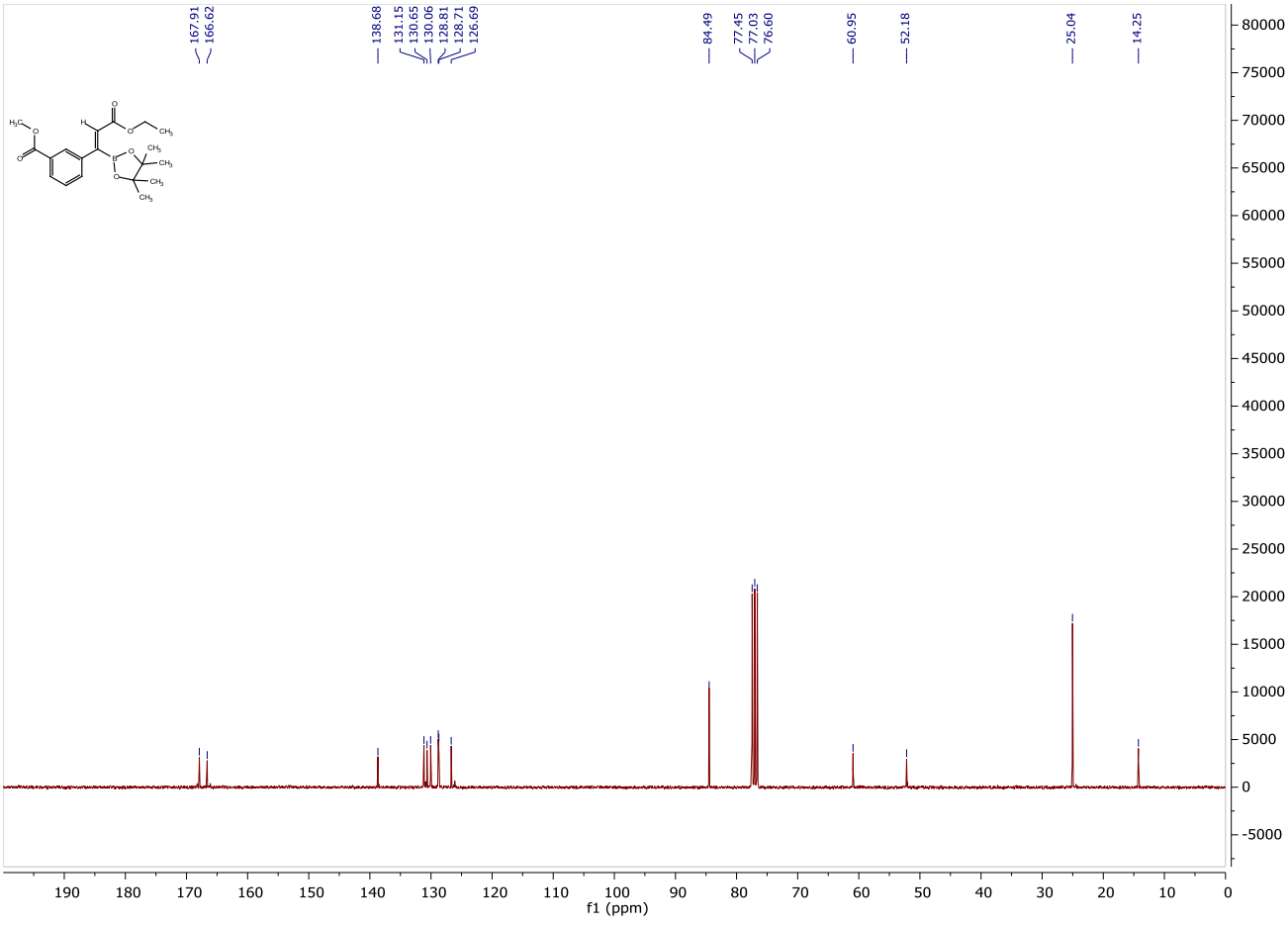


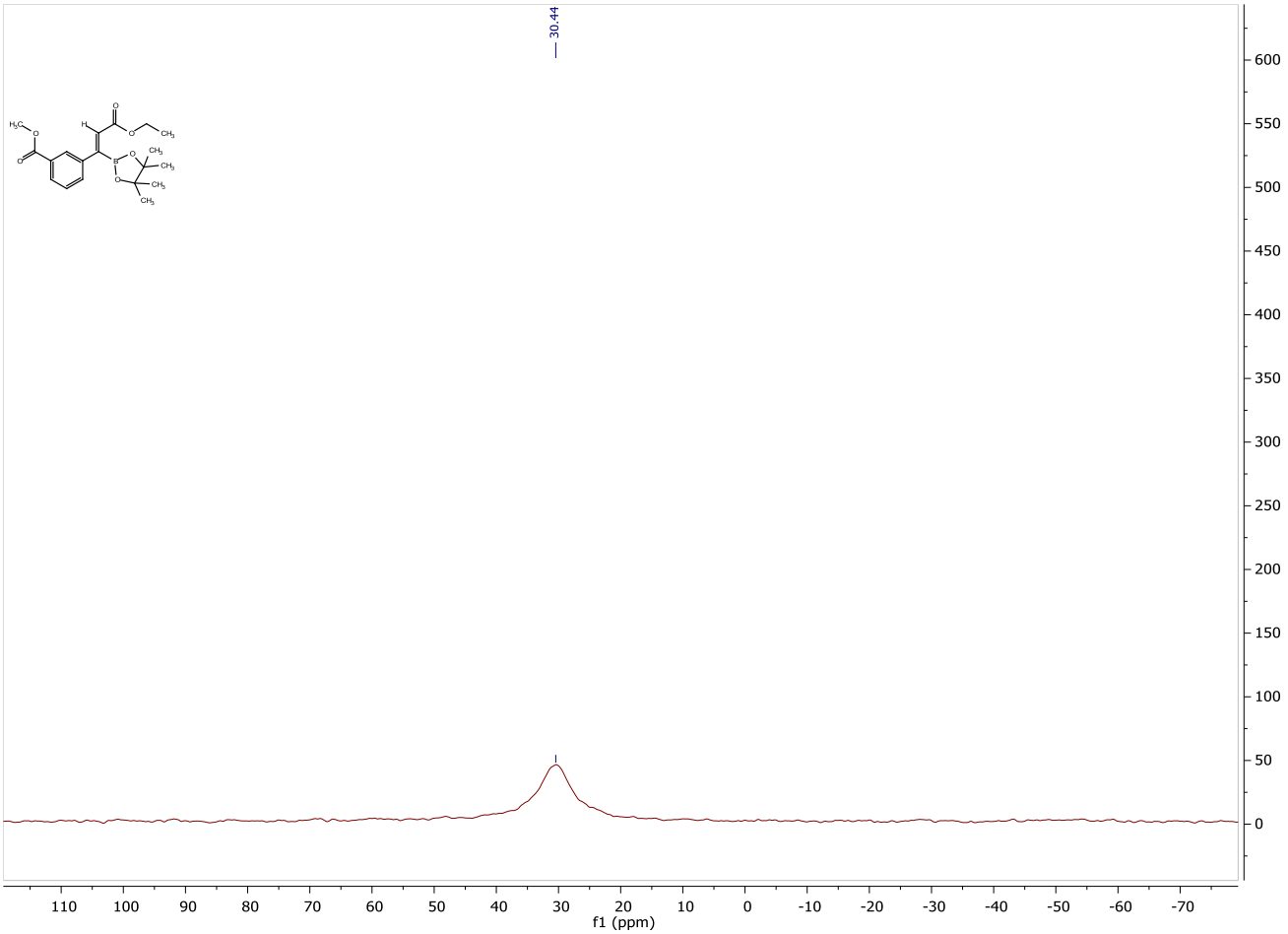

167.72
166.67
143.16
130.32
129.95
127.91
127.07
84.51
61.02
52.17
25.00
f1 (ppm)


31.44
f1 (ppm)

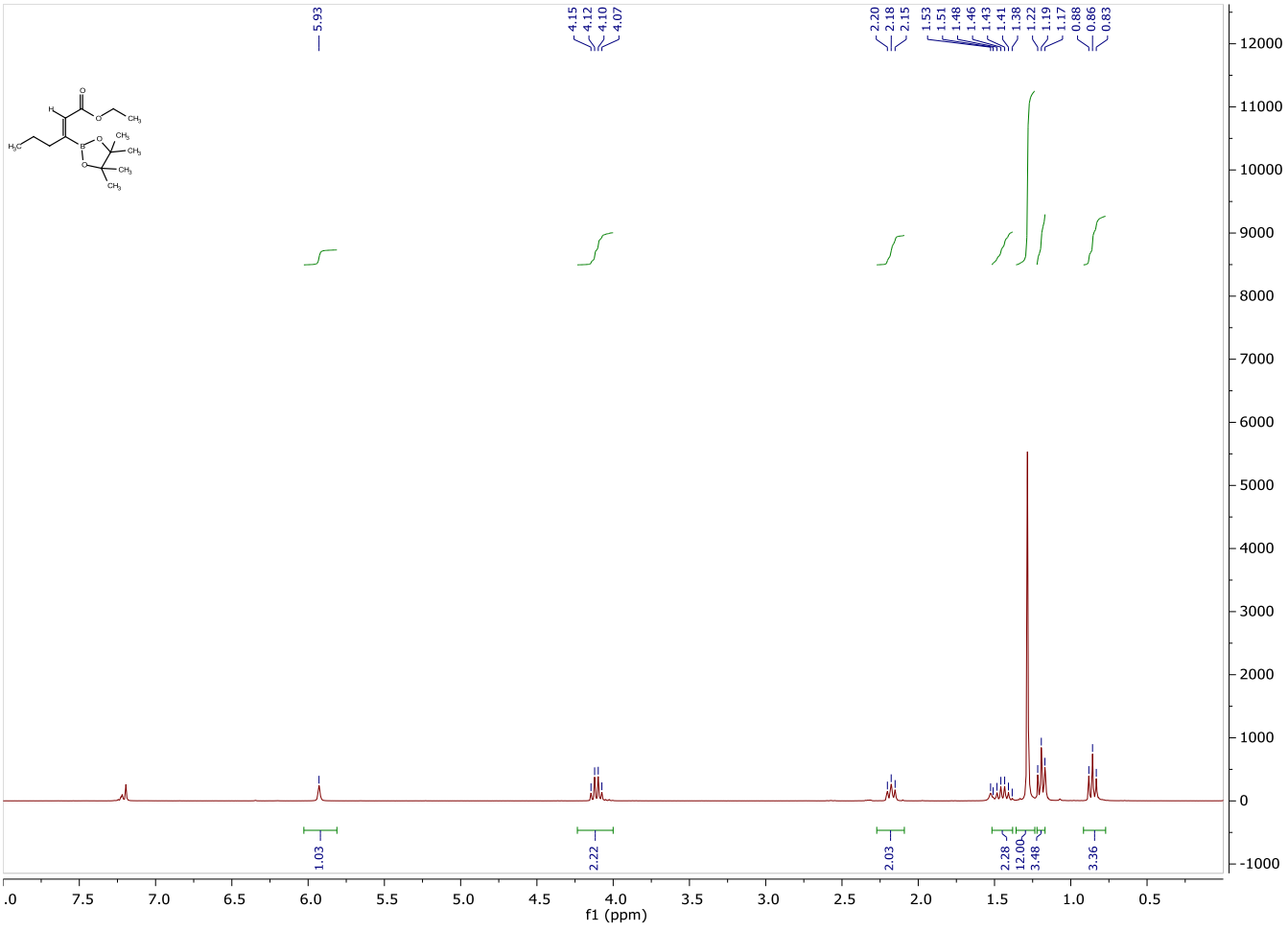
Methyl (*E*)-3-(3-ethoxy-3-oxo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) prop-1-en-1-yl) benzoate (12n):

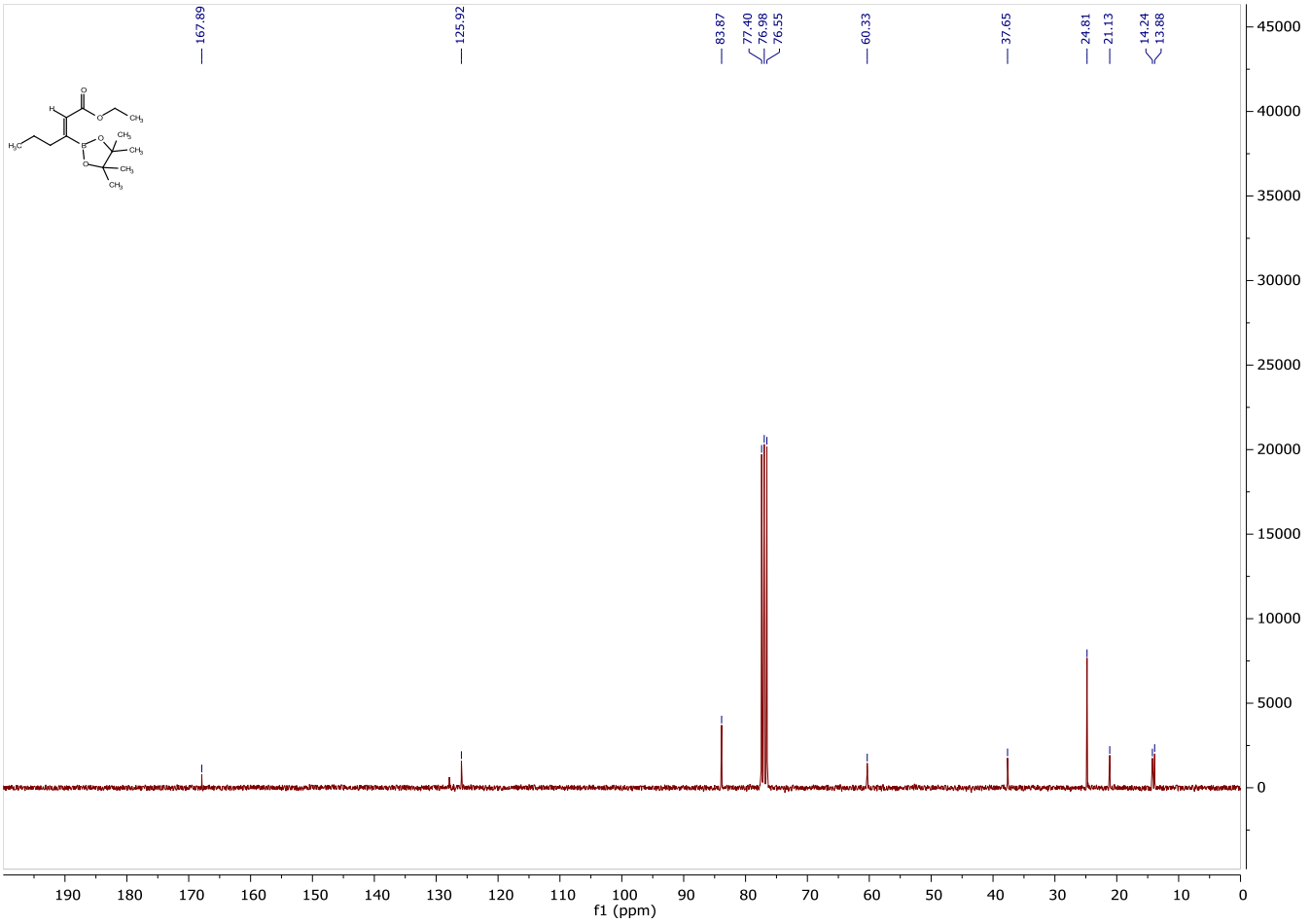


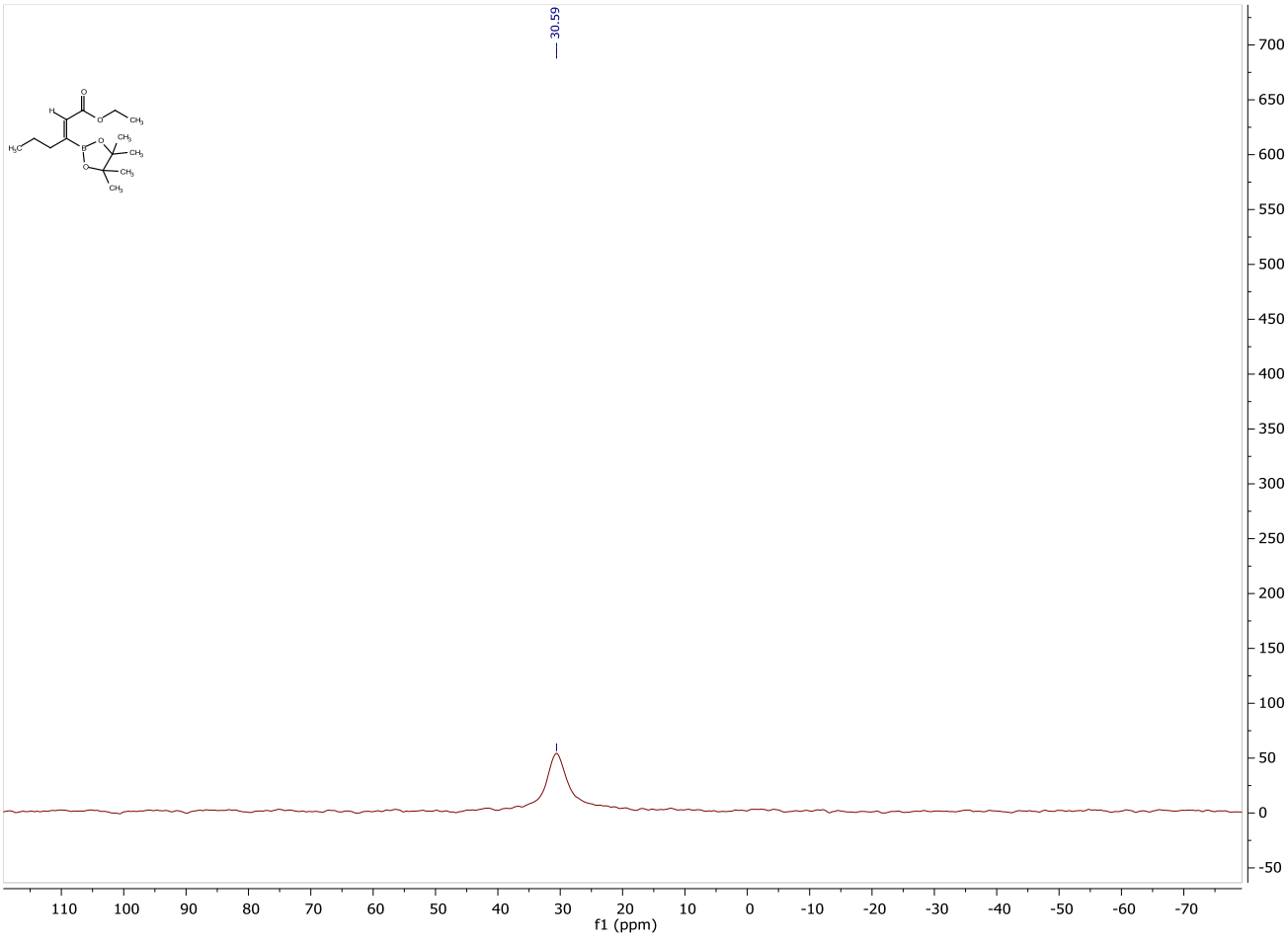




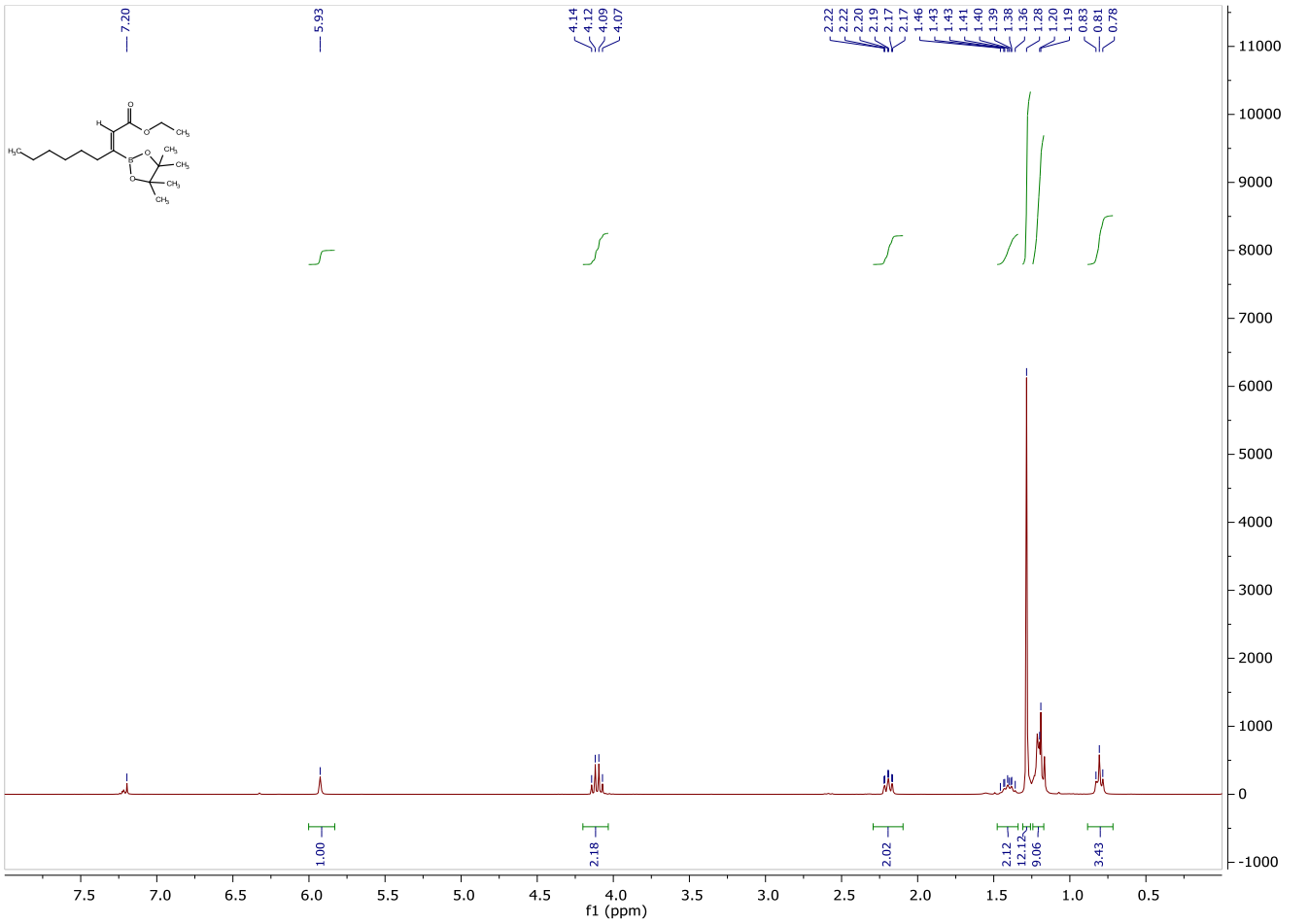
Ethyl (*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) hex-2-enoate (12q):

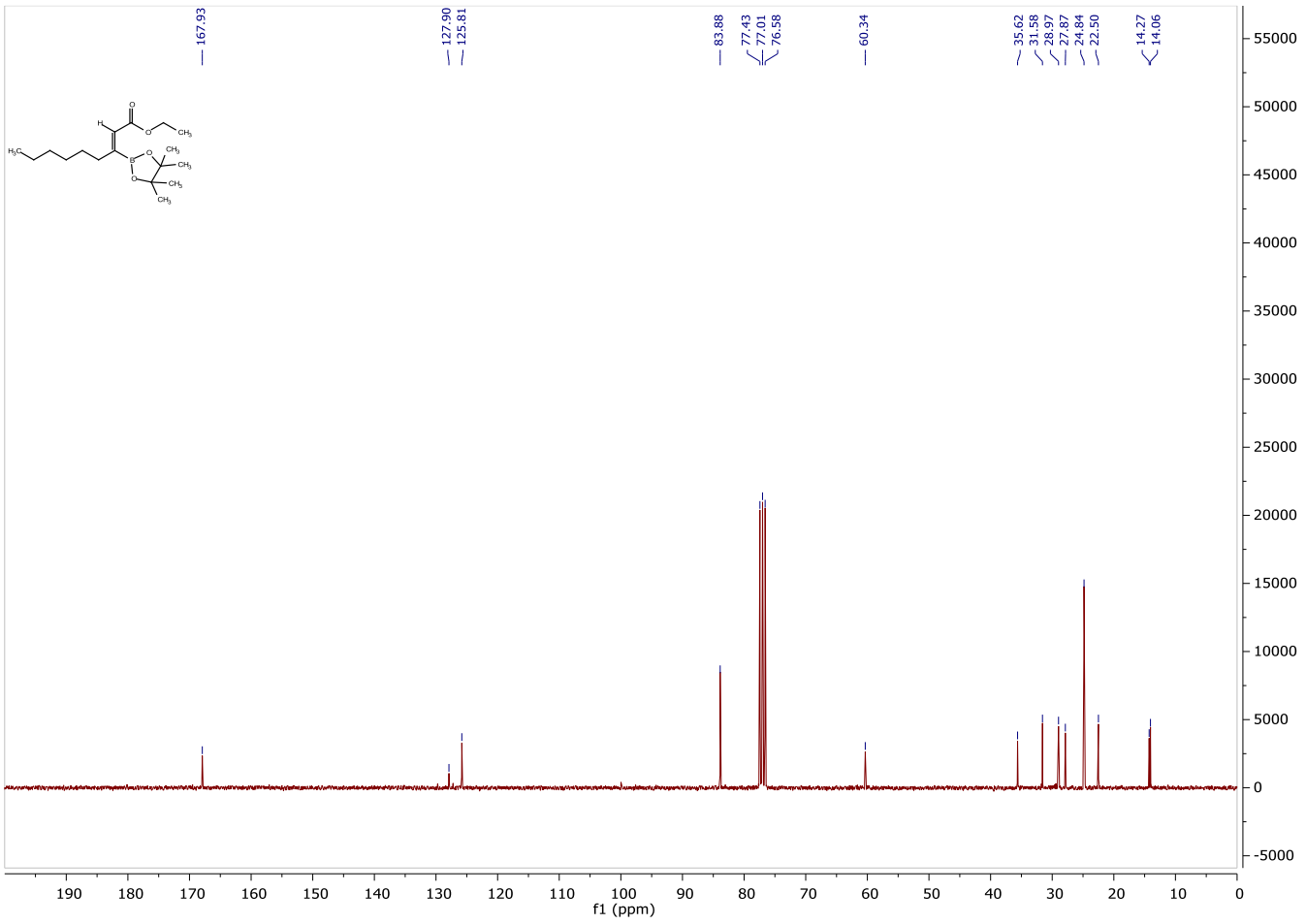


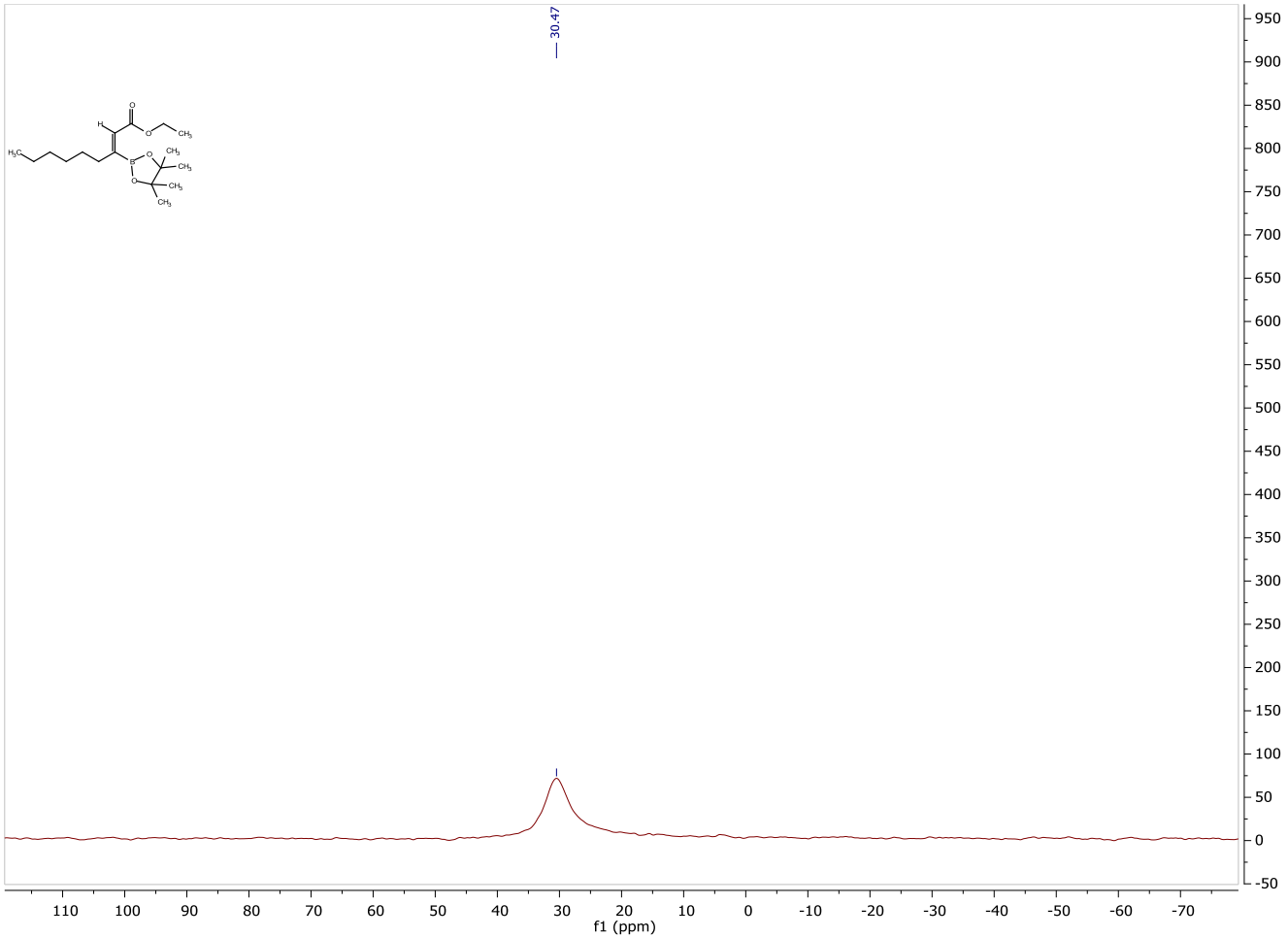

167.89
125.92
83.87
77.40
76.98
76.55
60.33
37.65
24.81
21.13
14.24
13.88
f1 (ppm)


30.59
f1 (ppm)

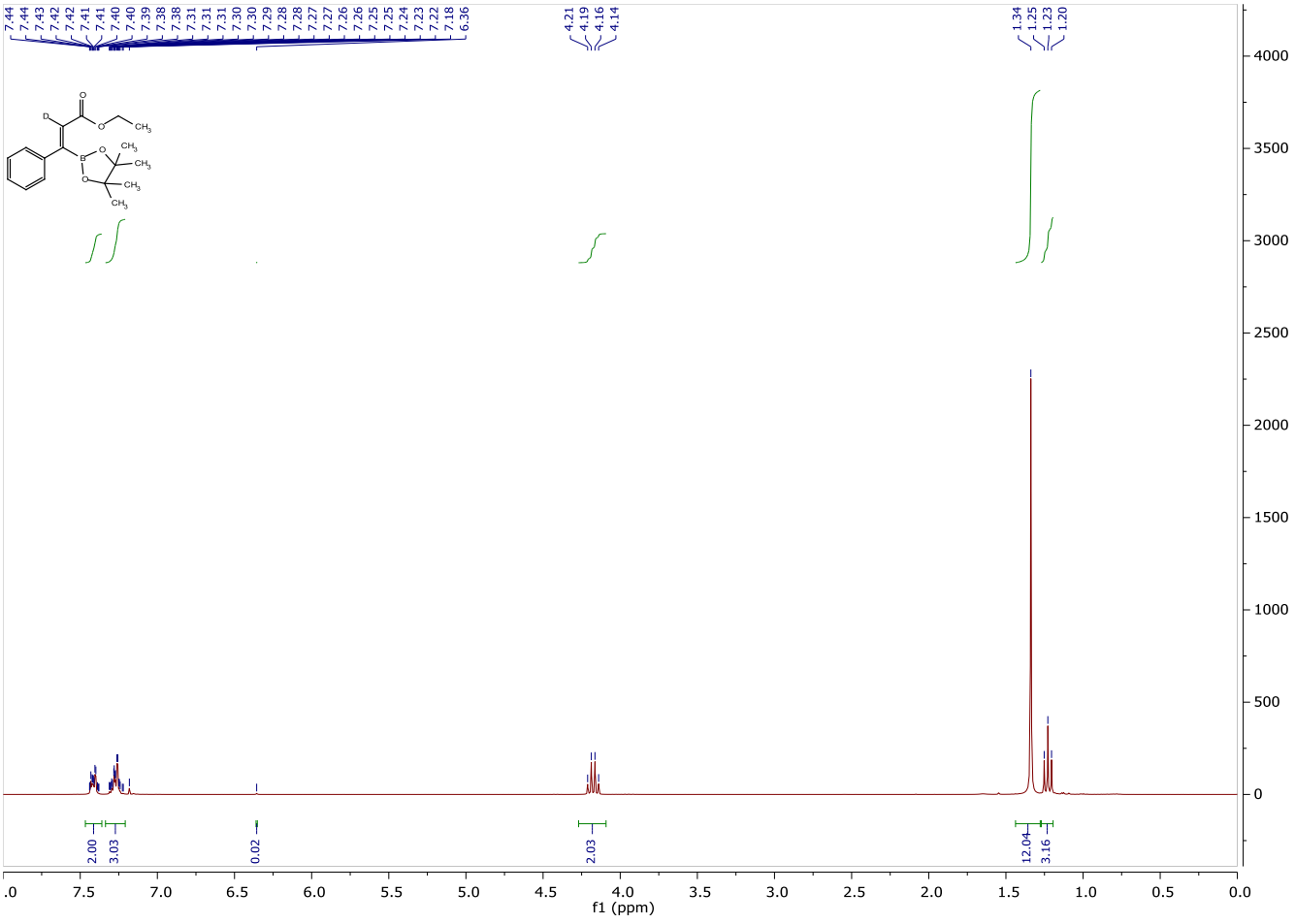
Ethyl (*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) non-2-enoate (12r):

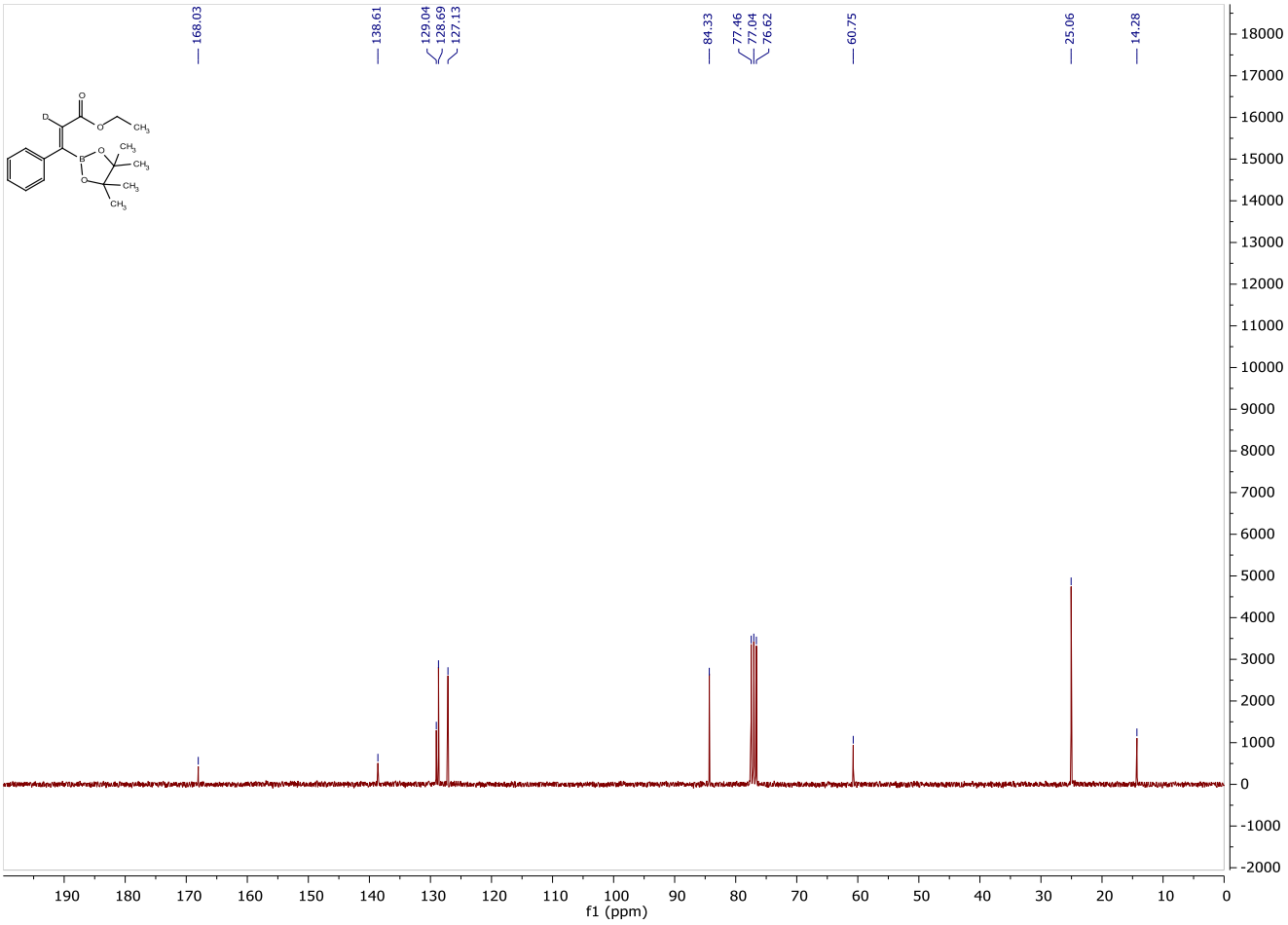


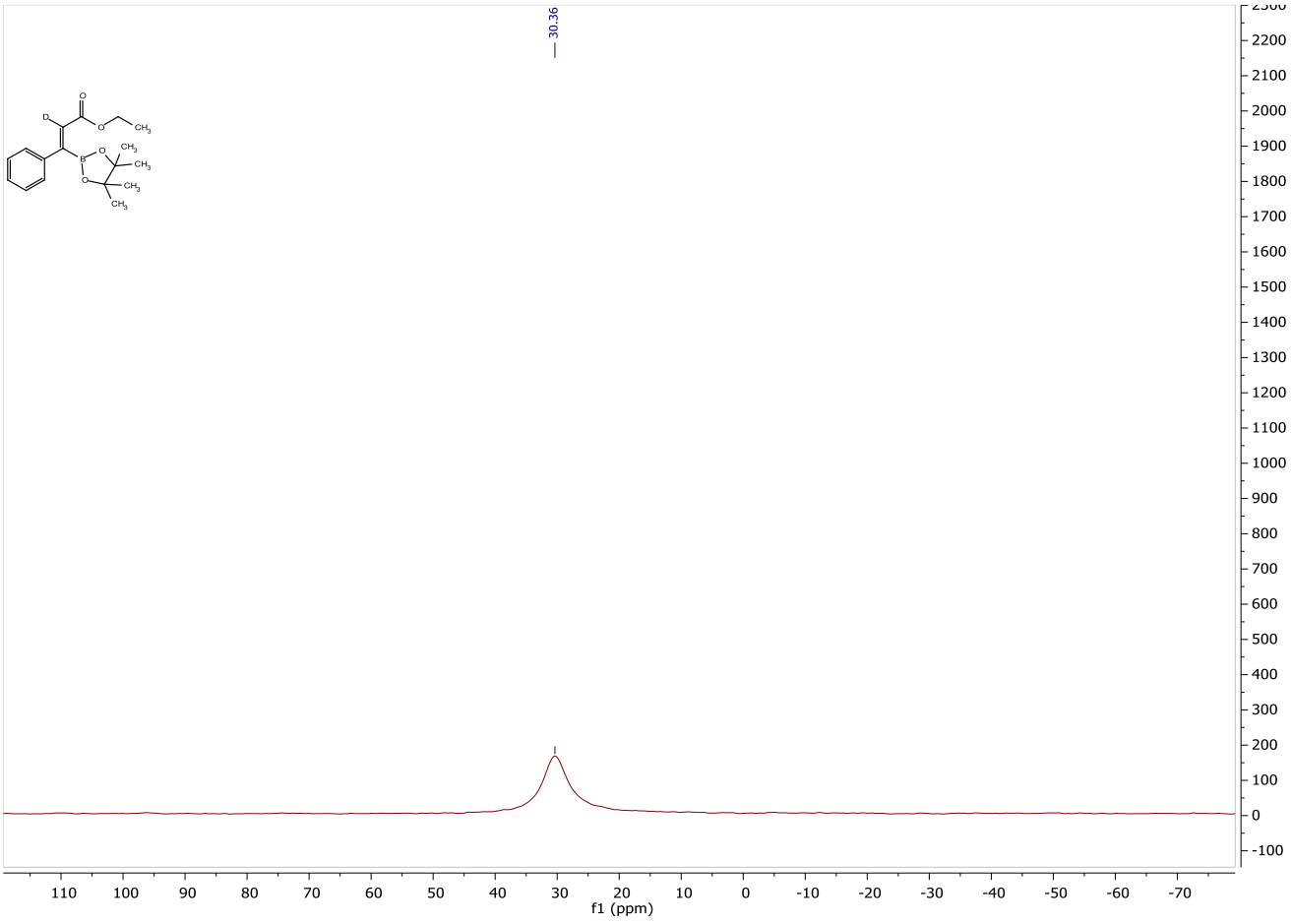




Ethyl (*E*)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) acrylate-d (12aD):




168.03
138.61
129.04
128.69
127.13
84.33
77.46
77.04
76.62
60.75
25.06
14.28
f1 (ppm)


30.36
f1 (ppm)