Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Ligand-controlled divergent formation of alkenyl- or allylboronates catalyzed by Pd, and synthetic applications

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Table of Contents

General methods.

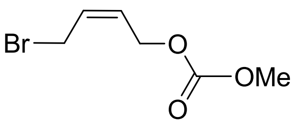
The solvents used, THF (SDS, anhydrous, analytical grade), DMF (SDS, anhydrous, analytical grade), toluene (SDS, anhydrous, analytical grade), MeOH (SDS, anhydrous, analytical grade), CH_2Cl_2 (SDS, anhydrous, analytical grade), Et_2O (SDS, anhydrous, analytical grade), 1,4-dioxane (SDS, anhydrous, analytical grade), xylene (Carlo Erba, mix of isomers) and DMSO (SDS, anhydrous, analytical grade) were further dried by standing with activated 4 Å molecular sieves under Ar atmosphere for several days prior to use. Commercially *n*-pentane RPE (Carlo Erba, analytical grade), *n*-hexane (Scharlab, extra pure), ethyl acetate (Scharlab, exta pure), and diethyl ether (Aldrich, puriss. p.a.) were used as received. Commercially available reagents were used without additional purification. Palladium(II) acetate (Strem Chemicals), bis(pinacolato)diboron (Fluorochem), bis(phenylsulfonyl)methane (Fluorochem), dimethyl malonate (Aldrich), *N-(*tert-butoxycarbonyl)-*p*-toluenesulfonamide (TCI), 4-iodobenzonitrile (Acros Organics), cesium fluoride (Aldrich) chloro(triethylphosphine)gold(I) (Strem Chemicals), silver hexafluoroantimonate(V) (Fluorochem), tricyclohexylphosphine (Aldrich), potassium *tert*-butoxide (Fluka), 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (Alfa Aesar), potassium carbonate (Panreac), sodium hydride 60 % dispersion in mineral oil (Aldrich), sodium hydroxide (Panreac), hydrogen peroxide solution 33% w/v (Panreac), and 2-butene-1,4-diol (97%) (Acros Organic) were used as received and stored at room temperature.

Dimethyl propargylmalonate (Fluka), tetrakis(triphenylphosphine)palladium(0) (Alfa Aesar), 3-bromo-1-(trimethylsilyl)-1-propyne (Aldrich), 1-bromo-2-butyne (Aldrich), propargyl bromide solution 80 wt. % in toluene (Aldrich), and ethyl-4-bromocrotonate (Aldrich) were used as received and stored at 4 ºC. Silicagel 60 (0.40-0.063 mm) was used for flash chromatography purchased from SDS, and TLC-aluminium plates with 0.25 mm of silicagel 60 (F_{254}) were used for thin-layer chromatography, purchased from Macherey-Nagel. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded using $CDCl_3$ (7.26 ppm ^{1}H, 77.2 ppm ^{13}C) as internal standard. Bruker AMX-300 was the spectrometer used. Reagents were weighted on air, reactions were performed under Ar and subsequent work-up was performed on air.

Preparation and characterization of precursor allylcarbonates.

Dimethyl 2-(but-2-ynyl)malonate,[1] dimethyl 2-(3-phenylprop-2-ynyl)malonate,[2] dimethyl 2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate,[3] *N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide,[4] *N*-(prop-2-ynyl)-*p*-toluenesulfonamide,[5] *N*-(but-2-ynyl)-*p*-toluenesulfonamide,[1] dimethyl 2-(4-phenylbut-3-yn-1-yl)malonate,[6] dimethyl 2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)malonate,[7] 4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)benzenesulfonamide,[8] (*E*)-4-bromobut-2-en-1-yl methyl carbonate,[9] (*Z*)-4-hydroxybut-2-en-1-yl methyl carbonate,[10] and (pent-3-yne-1,1-diyldisulfonyl)dibenzene[11] were prepared according to previously described procedures.

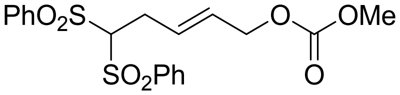
(*Z*)-4-bromobut-2-en-1-yl methyl carbonate



PBr_3 (1.33 mL, 3.83 g, 14.16 mmol) was added to an ice-cooled solution of (*Z*)-4-hydroxybut-2-en-1-yl methyl carbonate (3.0 g, 20.53 mmol) in anhydrous Et_2O (10 mL). The solution was stirred overnight at room temperature and then neutralized with saturated aq $NaHCO_3$ solution. The organic layer was washed with brine, dried (Na_2SO_4), and the solvent was carefully evaporated. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 2:1, phosphomolybdic acid stain (2.6 mmol/100 mL ethanol)) to afford the title compound as an orange oil (3.94 g, 92%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.04 – 5.91 (m, 1H), 5.72 (dt, *J* = 10.8, 6.8 Hz, 1H), 4.76 (dd, *J* = 6.8, 1.2 Hz, 2H), 4.02 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 155.72 (C), 130.51 (CH), 127.61 (CH), 62.56 (CH_2), 55.09 (CH_3), 25.56 (CH_2).

(*E*)-5,5-bis(phenylsulfonyl)pent-2-en-1-yl methyl carbonate

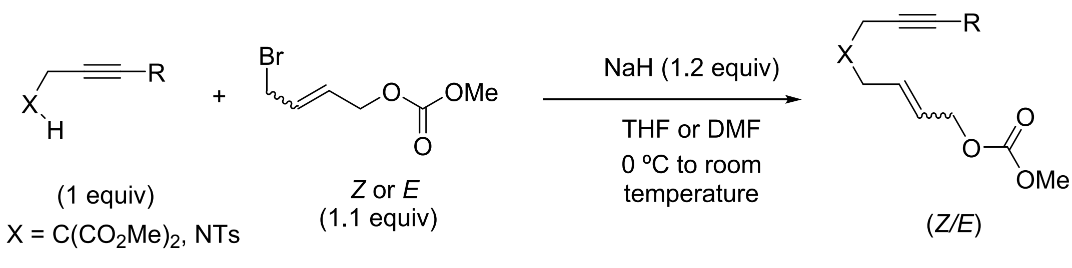


To a suspension of NaH (60% in mineral oil, 115.4 mg, 4,81 mmol) in anhydrous DMF (15 mL) under Ar atmosphere at 0 ºC, bis(phenylsulfonyl)methane (1.29 g, 4,37 mmol) was slowly added,

and the mixture was stirred at room temperature for 30 minutes (formation of H_2 bubbles was observed during the addition). Then, the electrophile (*E*)-4-bromobut-2-en-1-yl methyl carbonate (1,0 g, 4,81 mmol), was added dropwise and the mixture was allowed to react at 70 ºC for 15 h. Monitoring by TLC indicated reaction completion. Then, water and CH_2Cl_2 were added into the resulting mixture. The aqueous layer was separated and extracted several times with CH_2Cl_2. The combined organic phases were repeatedly washed with water, twice with saturated NaCl aqueous solution, and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the crude was purified by flash chromatography on silica gel (hexane/EtOAc 2:1, molybdophosphoric acid stain -2.6 mmol/100 mL ethanol-) to afford the title compound as a yellowish oil (1.43 g, 77%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 10.5, 3.1 Hz, 4H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.63 (dd, *J* = 9.7, 5.7 Hz, 4H), 5.88 – 5.74 (m, 1H), 5.67 – 5.55 (m, 1H), 4.56 – 4.46 (m, 3H), 3.83 (s, 3H), 2.99 (t, *J* = 6.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 137.95 (C), 134.88 (C), 129.85 (C), 129.57 (CH), 129.32 (CH), 129.06 (CH), 128.16 (CH), 83.50 (CH), 67.46 (CH_2), 55.01 (CH_3), 28.68 (CH_2). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{19}H_{20}O_7SNa$: 447.0542; found: 447.0533.

Representative procedure for preparation of allylcarbonates.

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

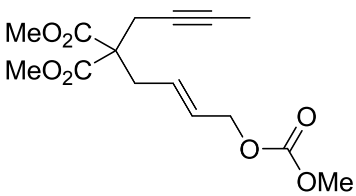


Scheme S1

To a suspension of NaH (60% in mineral oil, 1.1 equiv) in anhydrous THF or DMF (solvent and volume will be indicated in every case) under Ar atmosphere at 0 ºC, the corresponding propargyl derivative was slowly added (1 equiv) and the mixture was stirred at room temperature for 15 minutes (formation of H_2 bubbles was observed during the addition). Then, the electrophile (*E*)-4-bromobut-2-en-1-yl methyl carbonate or (*Z*)-4-bromobut-2-en-1-yl methyl carbonate (1.2 equiv), was added dropwise and the mixture was allowed to react at room temperature. The reaction progress was monitored by TLC. Then, when using THF, most of the solvent was removed under vacuum and later, water and Et_2O were added into the resulting mixture. The aqueous layer was separated and extracted successively with Et_2O. In the case of using DMF, similar extractive work-up with CH_2Cl_2/water was employed. The combined organic phases were washed several times with water and twice with saturated aqueous solution of NaCl. In all the cases, the combined organic phases were dried over anhydrous $MgSO_4$. Solvent was removed under vacuum and the crude was purified by flash chromatography.

Experimental data of allylcarbonates.

(*E*)-Dimethyl 2-(but-2-yn-1-yl)-2-(4-((methoxycarbonyl)oxy)but-2-en-1-yl)malonate (1a)

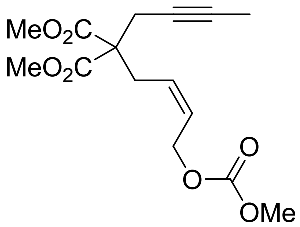


Following the *general alkylation procedure* for the synthesis of allylcarbonates (8 h) and using THF (10 mL) as solvent, from **dimethyl 2-(prop-2-yn-1-yl)malonate** (574 mg, 3.35 mmol) and **(*E*)-4-bromobut-2-en-1-yl methyl carbonate** (772 mg, 3.71 mmol). Product **1a** was obtained as a colourless oil (450 mg, 39 %) by flash chromatography using hexane/EtOAc 15:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 – 5.57 (m, 2H), 4.56 (d, J = 5.5 Hz, 2H), 3.78 (s, 3H), 3.73 (s, 6H), 2.78 (t, J = 7.6 Hz, 2H), 2.72 (d, J = 2.5 Hz, 2H), 1.75 (t, J = 2.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.38 (C), 155.64 (C), 129.91 (CH), 128.37 (CH), 79.26 (C), 73.16 (C), 67.96 (CH_2), 57.29 (CH_3), 54.85 (C), 52.80(CH_3), 35.23 (CH_2), 23.32 (CH_2), 3.56 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{15}H_{20}O_7Na$: 335.1101; found: 335.1106.

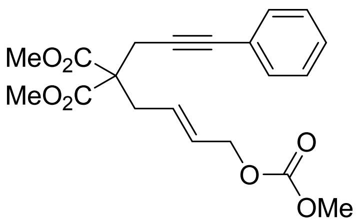
(*Z*)-Dimethyl 2-(but-2-yn-1-yl)-2-(4-((methoxycarbonyl)oxy)but-2-en-1-yl)malonate (1b)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (8 h) and using THF (15 mL) as solvent, from **dimethyl 2-(prop-2-yn-1-yl)malonate** (839 mg, 4.92 mmol), and **(*Z*)-4-bromobut-2-en-1-yl methyl carbonate** (1.1 g, 5.28 mmol). Product **1b** was obtained as a colourless oil (550 mg, 39%) by flash chromatography using hexane/EtOAc 15:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 – 5.60 (m, 1H), 5.56 – 5.36 (m, 1H), 4.72 (d, *J* = 6.8 Hz, 2H), 3.76 (s, 3H), 3.71 (s, 6H), 2.85 (d, *J* = 7.9 Hz, 2H), 2.71 (d, *J* = 2.5 Hz, 2H), 1.72 (dd, *J* = 12.6, 10.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.36 (C), 155.79 (C), 128.23 (CH), 127.67 (CH), 79.42 (C), 73.20 (C), 63.64 (CH_2), 57.03 (C), 54.86 (CH_3), 52.90 (CH_3), 30.44 (CH_2), 23.24 (CH_2), 3.52 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{15}H_{20}O_7Na$: 335.1101; found: 335.1107.

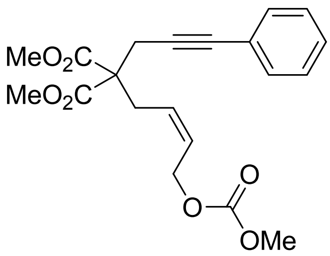
(*E*)-Dimethyl 2-(4-((methoxycarbonyl)oxy)but-2-en-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (1c)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (8 h) and using THF (10 mL) as solvent, from **dimethyl 2-(prop-2-yn-1-yl)malonate** (1.0 g, 4.06 mmol), and **(*E*)-4-bromobut-2-en-1-yl methyl carbonate** (1.0 g, 4.80 mmol). Compound **1c** was obtained as a colourless oil (1.07 g, 66%) by flash chromatography using hexane/EtOAc 15:1 as eluent

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.28 – 7.22 (m, 3H), 5.81 – 5.60 (m, 2H), 4.55 (d, *J* = 5.2 Hz, 2H), 3.74 (s, 3H), 3.73 (s, 6H), 2.98 (s, 2H), 2.85 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.21 (C), 155.63 (C), 131.74 (CH), 129.66 (CH), 128.66 (CH), 128.32 (CH), 128.16 (CH), 123.15 (C), 84.05 (C), 83.92 (C), 67.90 (CH_2), 57.33 (C), 54.87 (CH_3), 52.93 (CH_3), 35.44 (CH_2), 23.92 (CH_2). HRMS-ESI: $[MH]^+$ Calcd. for $C_{20}H_{23}O_7$: 375.1438; found: 375.1457.

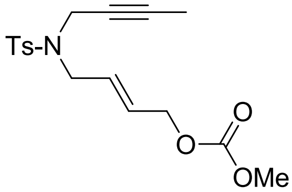
(*Z*)-dimethyl 2-(4-((methoxycarbonyl)oxy)but-2-en-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (1d)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (14 h) and using THF (8 mL) as solvent, from **dimethyl 2-(prop-2-yn-1-yl)malonate** (643 mg, 2.61 mmol), and **(*E*)-4-bromobut-2-en-1-yl methyl carbonate** (600 mg, 2.87 mmol). Compound **1d** was obtained as a yellowish oil (665 mg, 68%) by flash chromatography using hexane/EtOAc 8:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.30 – 7.26 (m, 3H), 5.83 – 5.69 (m, 1H), 5.55 (dd, *J* = 19.0, 8.0 Hz, 1H), 4.75 (d, *J* = 6.8 Hz, 2H), 3.77 (s, 6H), 3.75 (s, 3H), 3.02 (s, 2H), 2.95 (d, *J* = 7.8 Hz, 2H).^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.25 (C), 155.79 (C), 131.84 (CH), 128.38 (CH), 128.25 (CH), 128.20 (CH), 127.92 (CH), 123.12 (C), 84.01 (C), 63.57 (CH_2), 57.23 (C), 54.91 (CH_3), 53.07 (CH_3), 30.66 (CH_2), 23.97 (CH_2).

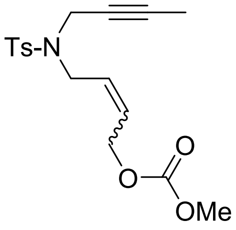
(*E*)-4-(*N*-(but-2-yn-1-yl)-4-methylphenylsulfonamido)but-2-en-1-yl methyl carbonate (1e)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (8 h) and using DMF (10 mL) as solvent, from ***N*-(but-2-yn-1-yl)-4-methylbenzenesulfonamide** (711 mg, 3.43 mmol), and **(*E*)-4-bromobut-2-en-1-yl methyl carbonate** (835 mg, 4.01 mmol). Product **1e** was obtained as a yellowish oil yellowish oil (550 mg, 46%) by flash chromatography using hexane/EtOAc 15:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.31 – 7.25 (m, 2H), 5.75 (qt, *J* = 15.5, 5.8 Hz, 2H), 4.59 (dd, *J* = 5.5, 0.8 Hz, 2H), 4.02 – 3.96 (m, 2H), 3.82 – 3.74 (m, 5H), 2.41 (s, 3H), 1.53 (t, *J* = 2.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 155.63 (C), 143.47 (C), 136.29 (C), 129.42 (CH), 129.25 (CH), 128.42 (CH), 128.00 (CH), 81.89 (C), 71.73 (C), 67.36 (CH_2), 54.99 (CH_3), 47.75 (CH_2), 36.72 (CH_2), 21.63 (CH_3), 3.35 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{17}H_{21}NO_5NaS$: 374.1032; found: 374.1048.

(*Z*)/(*E*)-4-(*N*-(but-2-yn-1-yl)-4-methylphenylsulfonamido)but-2-en-1-yl methyl carbonate (1f)

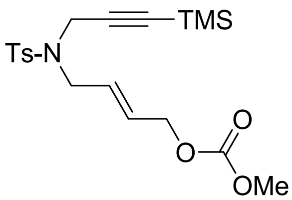


(*Z/E*)

Following the *general alkylation procedure* for the synthesis of allylcarbonates (8 h) and using DMF (10 mL) as solvent, from ***N*-(but-2-yn-1-yl)-4-methylbenzenesulfonamide** (711 mg, 3.43 mmol), and **(*Z*)-4-bromobut-2-en-1-yl methyl carbonate** (835 mg, 4.01 mmol). The mixture of the two isomers of **1f** (*Z/E* 1:1.4) was obtained as a yellowish oil (250 g, 25%) by flash chromatography using hexane/EtOAc 15:1 as eluent. The mixture of two isomers was confirmed by GC-MS.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.2, 2.6 Hz, 2H), 7.29 – 7.12 (m, 2H), 5.77 – 5.44 (m, 2H), 4.60 (d, *J* = 6.6 Hz, 1H), 4.48 (d, *J* = 5.4 Hz, 1H), 3.92 - 3.85 (m, 2H), 3.78 (d, *J* = 7.2 Hz, 1H), 3.70 (d, *J* = 5.9 Hz, 1H), 3.65 (d, *J* = 3.0 Hz, 3H), 2.30 (s, 3H), 1.44 – 1.41 (q, *J* = 2.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 155.29 (C), 155.20 (C), 143.28 (C), 143.19 (C), 135.84 (C), 135.55 (C), 129.16 (CH), 129.10 (CH), 128.69 (CH), 128.48 (CH), 128.14 (CH), 128.12 (CH), 127.62 (CH), 127.58 (CH), 81.83 (C), 81.62 (C), 71.31 (C), 71.23 (C), 66.92 (CH_2), 62.78 (CH_2), 54.54 (CH_3), 47.44 (CH_3), 42.86 (CH_3), 36.41 (CH_2), 36.36 (CH_2), 21.19 (CH_3), 2.92 (CH_3), 2.87 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{17}H_{21}NO_5SNa$: 374.1032; found: 374.1025.

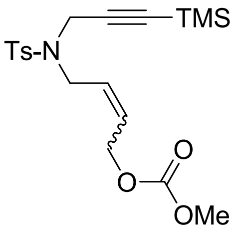
(Z/*E*)-methyl (4-(4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)phenylsulfonamido)but-2-en-1-yl) carbonate (1g)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (8 h) and using DMF (10 mL) as solvent from **4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl) benzenesulfonamide** (1.31 g, 4.65 mmol), and **(*E*)-4-bromobut-2-en-1-yl methyl carbonate** (1.16 g, 5.57 mmol). Product **1g** (*Z/E* 0.09:1) was obtained as a yellowish oil yellowish oil (450 mg, 25%) by flash chromatography using hexane/EtOAc 1:15 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 12.2, 8.7 Hz, 2H), 7.35 – 7.23 (m, 2H), 5.94 – 5.63 (m, 2H), 4.62 (dd, *J* = 9.8, 4.0 Hz, 2H), 4.08 (s, 2H), 3.87 – 3.74 (m, 5H), 2.41 (s, 3H), -0.01 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 155.61 (C), 143.59 (C), 136.10 (C), 129.66 (CH), 128.86 (CH), 128.74 (CH), 127.91 (CH), 97.84 (C), 91.28 (C), 67.30 (CH_2), 54.98 (CH_3), 47.72 (CH_2), 37.14 (CH_2), 21.64 (CH_3), -0.30 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{19}H_{28}NO_5SiS$: 410.1451; found: 410.1474.

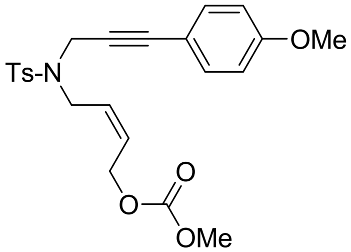
(*Z/E*)-methyl (4-(4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)phenylsulfonamido)but-2-en-1-yl) carbonate (1h)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (8 h) and using DMF (10 mL) as solvent, from **4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)benzenesulfonamide** (1.31 g, 4.65 mmol), and **(*Z*)-4-bromobut-2-en-1-yl methyl carbonate** (1.16 g, 5.57 mmol). **1h** (*Z/E* 0.4:1) was obtained as a yellowish oil yellowish oil (400 mg, 22%) by flash chromatography using hexane/EtOAc 15:1 as eluent. The presence of isomers was confirmed by GC-MS.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.59 (m, 2H), 7.29 – 7.16 (m, 2H), 5.87 – 5.47 (m, 2H), 4.71 – 4.48 (m, 2H), 4.06 – 3.96 (m, 2H), 3.89 – 3.72 (m, 2H), 3.69 (d, *J* = 3.7 Hz, 3H), 2.34 (s, 3H), -0.08 (d, *J* = 0.7 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 155.35 (C), 143.47 (C), 143.39 (C), 135.85 (C), 135.63 (C), 129.52 (CH), 129.46 (CH), 129.35 (CH), 128.59 (CH), 128.54 (CH), 128.45 (CH), 127.72 (CH), 127.67 (CH), 97.64 (C), 97.56 (C), 91.14 (C), 91.02 (C), 67.04 (CH_2), 66.92 (CH_2), 62.87 (CH_2), 54.70 (CH_3), 47.54 (CH_2), 42.96 (CH_2), 36.91 (CH_2), 36.80 (CH_2), 21.39 (CH_3), -0.53 (CH_3), -0.64 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{19}H_{28}NO_5SiS$: 410.1451; found: 410.1474.

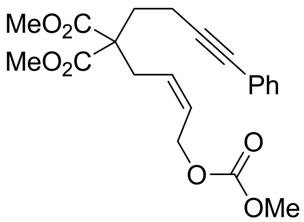
(*Z*)-methyl (4-(4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)phenylsulfonamido)but-2-en-1-yl) carbonate (1i)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (12 h) and using DMF (10 mL) as solvent, from ***N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide** (530 mg, 1.68 mmol), and **(*Z*)-4-bromobut-2-en-1-yl methyl carbonate** (386.4 mg, 1.85 mmol). Product **1i** was obtained as a yellowish oil yellowish oil (561 mg, 75%) by flash chromatography using hexane/EtOAc 6:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 5.85 (dt, *J* = 13.2, 6.3 Hz, 1H), 5.70 (dt, *J* = 11.0, 7.2 Hz, 1H), 4.74 (d, *J* = 6.7 Hz, 2H), 4.29 (s, 2H), 3.98 (d, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.73 (s, 3H), 2.36 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 159.90 (C), 155.67 (C), 143.74 (C), 135.95 (C), 133.18 (CH), 129.74 (CH), 129.00 (CH), 128.69 (CH), 128.02 (CH), 114.26 (C), 113.93 (CH), 85.95 (C), 80.18 (C), 63.15 (CH_2), 55.44 (CH_3), 54.98 (CH_3), 43.41 (CH_2), 37.24 (CH_2), 21.62 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{23}H_{26}NO_6S$: 444.1475; found: 444.1495.

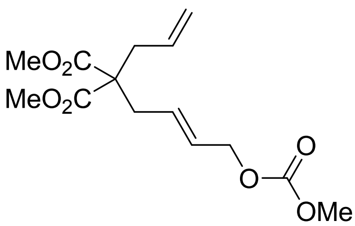
(*Z*)-dimethyl 2-(4-((methoxycarbonyl)oxy)but-2-en-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (1j)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (13 h) and using THF (8 mL) as solvent, from **dimethyl 2-(4-phenylbut-3-yn-1-yl)malonate** (567.3 mg, 2.18 mmol), and **(*Z*)-4-bromobut-2-en-1-yl methyl carbonate** (501.5 mg, 2.40 mmol) Compound **1j** was obtained as a yellowish oil (626.8 mg, 74%) by flash chromatography using hexane/EtOAc 6:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.29 – 7.26 (m, 3H), 5.80 – 5.66 (m, 1H), 5.65 – 5.51 (m, 1H), 4.70 (d, *J* = 6.8 Hz, 2H), 3.77 (s, 3H), 3.73 (s, 6H), 2.80 (d, *J* = 7.4 Hz, 2H), 2.49 – 2.36 (m, 2H), 2.31 – 2.21 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 171.15 (C), 155.84 (C), 131.70 (CH), 128.54 (CH), 128.36 (CH), 127.90 (CH), 127.17 (CH), 123.75 (C), 88.57 (C), 81.33 (C), 63.43 (CH_2), 57.07 (C), 54.97 (CH_3), 52.82 (CH_3), 32.11 (CH_2), 31.22 (CH_2), 15.14 (CH_2). HRMS-ESI: $[MH]^+$ Calcd. for $C_{21}H_{25}O_7$: 389.1594; found: 389.1612.

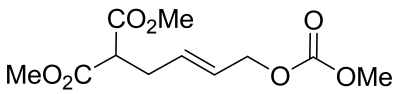
(*E*)-dimethyl 2-allyl-2-(4-((methoxycarbonyl)oxy)but-2-en-1-yl)malonate (1k)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (8 h) and using THF (20 mL) as solvent, from **dimethyl 2-allylmalonate** (989 mg, 5.74 mmol), and **(*E*)-4-bromobut-2-en-1-yl methyl carbonate** (1.45 g, 4.83 mmol). Compound **1k** was obtained as a colourless oil (550 mg, 32%) by flash chromatography using hexane/EtOAc 15:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72 – 5.57 (m, 3H), 5.14 – 5.05 (m, 2H), 4.55 (d, J = 3.9 Hz, 2H), 3.78 (s, 3H), 3.71 (s, 6H), 2.68 – 2.58 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 171.01 (C), 155.60 (C), 132.15 (CH), 130.19 (CH), 128.08 (CH), 119.45 (CH_2), 67.92 (CH_2), 57.64 (C), 54.81 (CH_3), 52.48 (CH_3), 37.21 (CH_2), 35.58 (CH_2).). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{14}H_{20}O_7Na$: 323.1101; found: 323.1103.

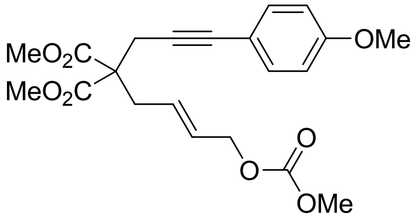
(*E*)-dimethyl 2-(4-((methoxycarbonyl)oxy)but-2-en-1-yl)malonate (1l)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (8 h) and using THF (25 mL) as solvent, from **dimethyl malonate** (3.36 g, 25.44 mmol), and **(*E*)-4-bromobut-2-en-1-yl methyl carbonate** (5.30 g, 25.60 mmol). Compound **1l** was obtained as a colourless oil (1.6 g, 11%) by flash chromatography using hexane/EtOAc 15:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83 – 5.54 (m, 2H), 4.50 (d, J = 5.5 Hz, 2H), 3.72 (s, 3H), 3.68 (s, 6H), 3.40 (t, J = 7.5 Hz, 1H), 2.60 (t, J = 6.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 169.06 (C), 155.55 (C), 131.51 (CH), 126.72 (CH), 67.81 (CH_2), 54.76 (CH_3), 52.57 (CH), 51.22 (CH_3), 31.42(CH_2). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{11}H_{16}O_7Na$: 283.0788; found: 283.0795.

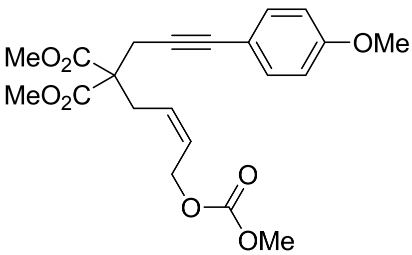
(*E*)-dimethyl 2-(4-((methoxycarbonyl)oxy)but-2-en-1-yl)-2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)malonate (1m)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (12 h) and using THF (15 mL) as solvent, from **dimethyl 2-(prop-2-yn-1-yl)malonate** (623 mg, 2.26 mmol), and **(*E*)-4-bromobut-2-en-1-yl methyl carbonate** (469 mg, 2.26 mmol). Product **1m** was obtained as a colourless oil (200 mg, 22%) by flash chromatography using hexane/EtOAc 6:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (dq, *J* = 6.8, 2.4 Hz, 2H), 6.85 – 6.77 (m, 2H), 5.83 – 5.62 (m, 2H), 4.57 (d, *J* = 5.1 Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 3.76 (d, *J* = 2.9 Hz, 6H), 2.98 (s, 2H), 2.87 (d, *J* = 6.2 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$, DEPT-135) δ 170.34 (C), 158.87 (C), 155.70 (C), 133.19 (C), 129.86 (CH), 128.63 (CH), 115.39 (C), 114.01 (CH), 83.79 (C), 82.50 (C), 68.00 (CH_2), 57.47 (C), 55.44 (CH_3), 54.92 (CH_3), 52.94 (CH_3), 35.50 (CH_2), 24.04 (CH_2). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{21}H_{24}O_8Na$: 427.1363; found: 427.1377.

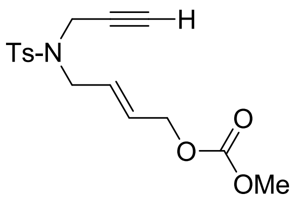
(*Z*)-dimethyl 2-(4-((methoxycarbonyl)oxy)but-2-en-1-yl)-2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)malonate (1n)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (20 h) and using THF (15 mL) as solvent, from **dimethyl 2-(prop-2-yn-1-yl)malonate** (1.2 g, 4.35 mmol) and **(*Z*)-4-bromobut-2-en-1-yl methyl carbonate** (1.0 g, 4.78 mmol). Compound **1n** was obtained as a yellowish oil (1.2 g, 68%) by flash chromatography using hexane/EtOAc 8:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 6.84 – 6.76 (m, 2H), 5.83 – 5.68 (m, 1H), 5.61 – 5.48 (m, 1H), 4.75 (dd, *J* = 6.8, 1.1 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 6H), 3.75 (s, 3H), 3.00 (s, 2H), 2.94 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.30 (C), 159.61 (C), 155.78 (C), 133.21 (CH), 128.25 (CH), 127.86 (CH), 115.26 (C), 114.00 (CH), 83.80 (C), 82.38 (C), 63.58 (CH_2), 57.25 (C), 55.41 (CH_3), 54.89 (CH_3), 53.02 (CH_3), 30.63 (CH_2), 23.97 (CH_2). HRMS-ESI: $[MH]^+$ Calcd. for $C_{21}H_{25}O_8$: 405.1543; found: 405.1567.

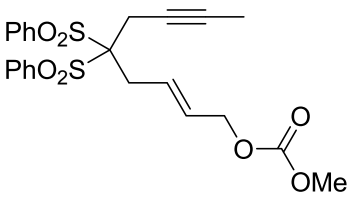
(*E*)-methyl (4-(4-methyl-*N*-(prop-2-yn-1-yl)phenylsulfonamido)but-2-en-1-yl) carbonate (1o)



Following the *general alkylation procedure* for the synthesis of allylcarbonates (13 h) and using DMF (10 mL) as solvent, from **4-methyl-*N*-(prop-2-yn-1-yl)benzene sulfonamide** (400 mg, 1.91 mmol) and **(*E*)-4-bromobut-2-en-1-yl methyl carbonate**

(437.7 mg, 2.10 mmol). Compound **1o** was obtained as a yellowish oil (406.3 mg, 63%) by flash chromatography using hexane/EtOAc 6:1 as eluent.

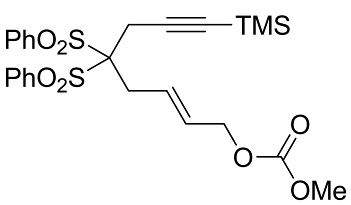
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 7.9 Hz, 2H), 7.32 – 7.23 (m, 2H), 5.90 – 5.63 (m, 2H), 4.59 (d, J = 5.5 Hz, 2H), 4.06 (d, J = 1.2 Hz, 2H), 3.83 (d, J = 6.1 Hz, 2H), 3.78 – 3.74 (m, 3H), 2.41 (s, 3H), 2.03 (t, J = 2.4 Hz, 1H).^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 155.45 (C), 143.70 (C), 135.90 (C), 129.54 (CH), 128.78 (CH), 128.54 (CH), 127.71 (CH), 76.41 (C), 74.02 (CH), 67.10 (CH_2), 54.85 (CH_3), 47.63 (CH_2), 36.00 (CH_2), 21.52 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{16}H_{19}NO_5NaS$: 360.0876; found: 360.0868.



(*E*)-5,5-bis(phenylsulfonyl)non-2-en-7-yn-1-yl methyl carbonate (1p)

Following the *general alkylation procedure* for the synthesis of allylcarbonates (13 h, 70 ºC) and using DMF (10 mL) as solvent, from **(pent-3-yne-1,1-diyldisulfonyl)dibenzene** (594 mg, 1.70 mmol) and **(*E*)-4-bromobut-2-en-1-yl methyl carbonate** (390 mg, 1.88 mmol). Compound **1p** was obtained as a yellowish oil (476.5 mg, 77%) by flash chromatography using hexane/EtOAc 4:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.5 Hz, 4H), 7.70 (t, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 4H), 6.13 – 5.96 (m, 1H), 5.87 – 5.70 (m, 1H), 4.63 (d, *J* = 6.1 Hz, 2H), 3.79 (s, 3H), 3.13 (d, *J* = 2.5 Hz, 2H), 3.08 (d, *J* = 7.1 Hz, 2H), 1.62 (t, *J* = 2.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 155.62 (C), 137.02 (C), 134.79 (CH), 131.61 (CH), 129.71 (CH), 129.42 (CH), 129.22 (CH), 128.61 (CH), 127.57 (CH), 88.95 (C), 82.18 (CH), 70.65 (CH), 67.83 (CH_2), 54.89 (CH_3), 32.53 (CH_2), 21.43 (CH_2), 3.65 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{23}H_{24}O_7NaS_2$: 499.0855; found: 499.0836.

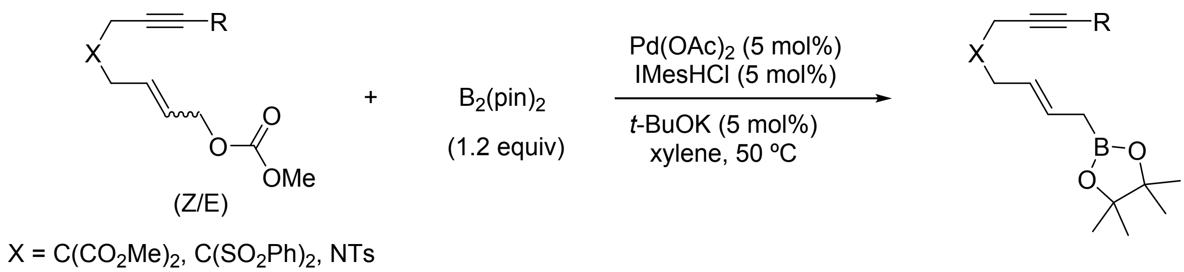


(*E*)-5,5-bis(phenylsulfonyl)-8-(trimethylsilyl)oct-2-en-7-yn-1-yl methyl carbonate (1q)

To a suspension of NaH (60% in mineral oil, 1.2 equiv) in anhydrous DMF under Ar atmosphere at 0 ºC, **(*E*)-5,5-bis(phenylsulfonyl)pent-2-en-1-yl methyl carbonate** (500 mg, 1.18 mmol) was slowly added, and the mixture was stirred at room temperature for 30 minutes (formation of H_2 bubbles were observed during the addition). Then, **(3-bromoprop-1-yn-1-yl)trimethylsilane** (247.6 mg, 1.29 mmol), was added dropwise and the mixture was allowed to react at 70 ºC for 15 h. Monitoring by TLC indicated completion of the reaction. Then, water and CH_2Cl_2 were added into the resulting mixture. The aqueous layer was separated and extracted several times with CH_2Cl_2. The combined organic phases were repeatedly washed with water and twice with saturated aqueous solution of NaCl. The combined organic phases were dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the crude was purified by flash chromatography on silica gel (hexane/EtOAc 2:1, molybdophosphoric acid as stain -2.6 mmol/100 mL ethanol-) to afford the title compound **1q** as a white solid (396.8 mg, 63%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 4H), 7.76 – 7.67 (m, 2H), 7.561 – 7.54 (m, 4H), 6.14 – 6.02 (m, 1H), 5.88 – 5.75 (m, 1H), 4.64 (d, J = 6.2 Hz, 2H), 3.79 (s, 3H), 3.19 (s, 2H), 3.11 (d, J = 6.8 Hz, 2H), 0.11 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 155.70 (C), 136.80 (C), 134.93 (CH), 131.70 (CH), 129.95 (CH), 128.78 (CH), 127.30 (CH), 97.48 (C), 91.96 (C), 88.89 (C), 67.85 (CH_2), 54.94 (CH_3), 32.39 (CH_2), 22.36 (CH_2), -0.19 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{25}H_{30}O_7NaSiS_2$: 557.1094; found: 557.1093.

General procedure for the synthesis of allylboronates

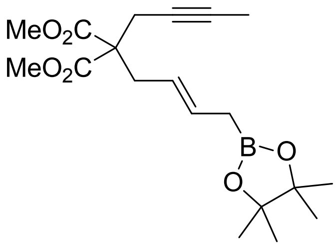


Scheme S2

A solution of allylcarbonate and bis(pinacolato)diboron (1.2 equiv) in 0.6 mL of xylene was added to a previously prepared solution containing the catalytic system. The latter was prepared by addition of a solution of IMesHCl (5 mol%) and *t*-BuOK (5 mol%) in anhydrous xylene (0.5 mL) to a suspension of $Pd(OAc)_2$ (5 mol%) in anhydrous xylene (0.25 mL) under Ar atmosphere, and heating in a sealed tube at 50 ºC for 15 min. After addition of the reagents on the catalytic solution, the mixture was stirred at 50 ºC during the corresponding time indicated below for each compound. After cooling the mixture to room temperature, the solvent was evaporated and the crude was purified by flash chromatography (hexane/Et_2O or pentane/Et_2O, it will be specified in each case, molybdophosphoric acid as stain -2.6 mmol/100 mL ethanol-) to give the product.

Experimental data of allylboronates.

(*E*)-dimethyl 2-(but-2-yn-1-yl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)malonate (2ab)

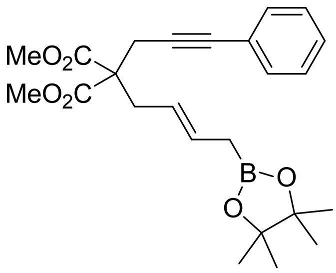


From compound **1a** (300 mg, 0.99 mmol), following the *general alkylation procedure*, after 15 minutes at 50 °C and using xylene (1.5 mL) as solvent. Compound **2ab** was obtained as a colourless oil (196 mg, 54%) by flash chromatography using hexane/Et_2O 5:1 as eluent.

When the reaction was performed using compound **1b** (100 mg, 0.32 mmol) after 15 minutes at 50 °C and xylene (1.5 mL) as solvent, the product **2ab** was obtained in 71% yield (83 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.57 (dt, *J* = 15.0, 7.5 Hz, 1H), 5.16 (dt, *J* = 15.0, 7.5 Hz, 1H), 3.68 (s, 6H), 2.68 (dd, *J* = 5.0, 2.2 Hz, 4H), 1.71 (t, *J* = 2.4 Hz, 3H), 1.61 (d, *J* = 7.4 Hz, 2H), 1.21 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.81 (C), 130.83 (CH), 123.41 (CH), 83.63 (CH), 83.37 (CH), 78.73 (CH), 73.67 (CH), 57.72 (CH), 52.65 (CH_3), 35.65 (CH_2), 25.17 (CH_3), 24.91 (CH_3), 23.00 (CH_2), 3.61 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{13}H_{18}O_5Na$: 277.1046; found: 277.1053.

(*E*)-dimethyl 2-(3-phenylprop-2-yn-1-yl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)malonate (2cd)

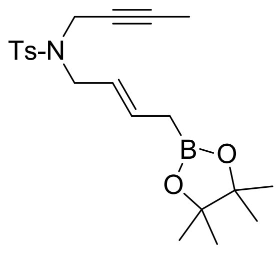


From compound **1c** (50 mg, 0.17 mmol) following the *general alkylation procedure*, after 15 minutes at 50 °C and xylene (1.5 mL) as solvent**.** Product **2cd** was obtained as a colourless oil (20 mg, 30%) by flash chromatography using hexane/Et_2O 5:1 as eluent.

When the reaction was performed using compound **1d** (300 mg, 0.80 mmol) after 15 minutes at 50 °C and xylene (1.5 mL) as solvent, compound **2cd** was obtained in 47% yield (164 mg) after column chromatography (hexane/Et_2O 5:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (ddd, *J* = 7.2, 5.0, 3.4 Hz, 2H), 7.19 – 7.16 (m, 3H), 5.57 (dt, *J* = 15.0, 7.5 Hz, 1H), 5.16 (dt, *J* = 15.0, 4.4 Hz, 1H), 3.66 (s, 6H), 2.91 (s, 2H), 2.71 (d, *J* = 7.5 Hz, 2H), 1.57 (d, *J* = 7.4 Hz, 2H), 1.14 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.64 (C), 131.82 (CH), 131.21 (CH), 128.30 (CH), 128.01 (CH), 123.52 (C), 123.24 (CH), 84.73 (C), 83.53 (C), 83.39 (C), 57.77 (C), 52.78 (CH_3), 35.86 (CH_2), 24.91 (CH_3), 23.61 (CH_2). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{24}H_{31}BO_6Na$:449.2105; found: 449.2091

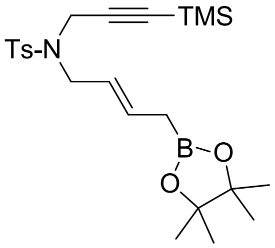
(*E*)-*N*-(but-2-yn-1-yl)-4-methyl-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)benzenesulfonamide (2ef)



From compound **1e** (50 mg, 0.14 mmol) following the *general alkylation procedure*, after 15 minutes at 50 °C and xylene (1.5 mL) as solvent**.** Compound **2ef** was obtained as a colourless oil (44.7 mg, 78%) by flash chromatography using hexane/Et_2O 5:1 as eluent. When the reaction was performed using **1f** (*Z*/*E* 1:1.4) (100 mg, 0.28 mmol) after 15 minutes at 50 °C and xylene (1.5 mL) as solvent, product **2ef** was obtained in 63% yield (72.3 mg) after column chromatography (hexane/Et_2O 5:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.64 (dt, *J* = 15.1, 7.5 Hz, 1H), 5.31 – 5.14 (m, 1H), 3.92 (d, *J* = 2.1 Hz, 2H), 3.63 (d, *J* = 6.3 Hz, 2H), 2.33 (s, 3H), 1.59 (d, *J* = 7.3 Hz, 2H), 1.44 (t, *J* = 2.1 Hz, 3H), 1.14 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 143.14 (C), 136.53 (C), 132.28 (CH), 129.27 (CH), 128.06 (CH), 123.91 (CH), 83.52 (C), 83.30 (C), 81.31 (C), 72.04 (C), 48.62 (CH_2), 35.92 (CH_2), 24.90 (CH_3), 24.70 (CH_3), 21.62 (CH_3), 3.36 (CH_3). (Minimal amount of pinacol was detected by NMR).HRMS-ESI: $[MH]^+$ Calcd. for $C_{15}H_{19}NO_3S$: 294.1158; found: 294.1175.

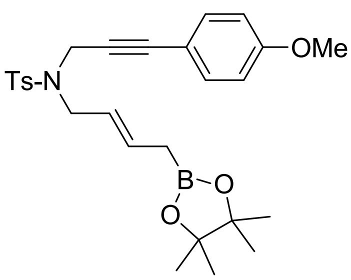
(*E*)-4-methyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)benzenesulfonamide (2gh)



From compound **1g** (50 mg, 0.13 mmol) following the *general alkylation procedure*, after 15 minutes at 50 °C and xylene (1.5 mL) as solvent. Compound **2gh** was obtained as a colourless oil (41 mg, 69%) using hexane/Et_2O 5:1 as eluent. When the reaction was performed using **1h** (*Z*/*E* 0.4:1) (100 mg, 0.25 mmol) after 15 minutes at 50 °C and xylene (1.5 mL) as solvent, product **2gh** was obtained in 67% yield (39 mg), after column chromatography (hexane/Et_2O 5:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.29 (dd, *J* = 12.0, 6.5 Hz, 2H), 5.83 – 5.67 (m, 1H), 5.34 (dt, *J* = 7.0, 5.1 Hz, 1H), 4.10 (s, 2H), 3.76 (d, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 1.70 (d, *J* = 7.4 Hz, 2H), 1.24 (s, 12H), -0.00 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 143.27 (C), 136.38 (C), 132.62 (CH), 129.54 (CH), 127.97 (CH), 123.65 (CH), 98.34 (C), 90.69 (C), 83.50 (C), 48.56 (CH_2), 36.43 (CH_2), 24.90 (CH_3), 21.63 (CH_3), -0.23 (CH_3).). (Minimal amount of pinacol was detected by NMR) HRMS-ESI: $[MNa]^+$ Calcd. for $C_{23}H_{36}BNO_4SSiNa$: 484.1784; found: 484.1785.

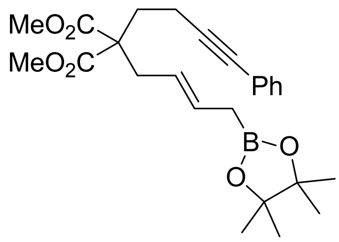
(*E*)-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)benzenesulfonamide (2i)



From compound **1i** (100 mg, 0.22 mmol) following the *general alkylation procedure*, after 15 minutes at 50 °C and xylene (1.5 mL) as solvent. Product **2i** was obtained as a colourless oil (80 mg, 72%) by flash chromatography using hexane/Et_2O 6:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.12 (m, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 5.78 – 5.64 (m, 1H), 5.37 – 5.24 (m, 1H), 4.20 (s, 2H), 3.76 - 3.67 (m, 5H), 2.27 (s, 3H), 1.63 (d, *J* = 7.3 Hz, 2H), 1.16 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 159.69 (C), 143.31 (C), 136.36 (C), 133.10 (CH), 132.64 (CH), 129.52 (CH), 128.00 (CH), 123.75 (CH), 114.69 (C), 113.82 (CH), 85.48 (C), 83.52 (C), 80.66 (C), 55.42 (CH_3), 48.85 (CH_2), 36.40 (CH_2), 24.90 (CH_3), 21.57 (CH_3). HRMS-ESI: [MH]+ Calcd. for $C_{27}H_{35}BNO_5S$: 496.2323; found: 496.2336.

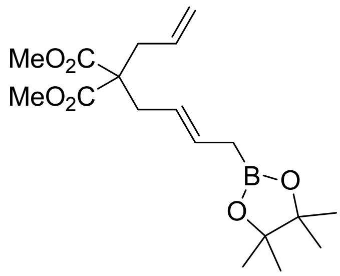
(*E*)-dimethyl 2-(but-2-yn-1-yl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)malonate (2j)



From compound **1j** (100 mg, 0.26 mmol) following the *general alkylation procedure*, after 15 minutes at 50 °C and xylene (1.5 mL) as solvent. Product **2j** was obtained as a colourless oil (42 mg, 37%) by flash chromatography using hexane/Et_2O 10:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 3.7 Hz, 2H), 7.31 – 7.26 (m, 3H), 5.76 – 5.55 (m, 1H), 5.31 – 5.17 (m, 1H), 3.74 (s, 6H), 2.75 (d, *J* = 7.3 Hz, 1H), 2.68 (d, *J* = 7.3 Hz, 1H), 2.42 (t, *J* = 7.9 Hz, 2H), 2.31 – 2.20 (m, 2H), 1.73 (d, *J* = 8.1 Hz, 1H), 1.68 (d, *J* = 7.3 Hz, 1H), 1.26 (d, *J* = 3.5 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 171.61 (C), 171.51 (CH), 131.65 (CH), 130.75 (CH), 128.29 (CH), 127.74 (CH), 123.90 (C), 123.42 (CH), 122.26 (CH), 89.08 (C), 83.38 (C), 81.00 (C), 57.43 (C), 52.62 (CH_3), 52.56 (CH_3), 36.36 (CH_2), 31.62 (CH_2), 24.89 (CH_3), 24.70 (CH_3), 14.93 (CH_2). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{25}H_{33}BO_6Na$: 463.2262; found: 463.2249.

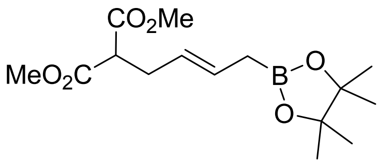
(*E*)-dimethyl 2-allyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)malonate (2k)



From compound **1k** (150 mg, 0.55 mmol) following the *general alkylation procedure*, after 15 minutes at 50 °C and xylene (1.5 mL) as solvent. Product **2k** was obtained as a colourless oil (135 mg, 70%) by flash chromatography using hexane/Et_2O 5:1 as eluent

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 – 5.47 (m, 2H), 5.24 – 5.00 (m, 3H), 3.68 (s, 6H), 2.58 (dd, *J* = 11.9, 7.5 Hz, 4H), 1.62 (d, *J* = 7.3 Hz, 2H), 1.22 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 171.47 (C), 132.67 (CH), 130.61 (CH), 123.55 (CH), 119.07 (CH_2), 83.34 (C), 58.03 (C), 52.38 (CH_3), 36.82 (CH_2), 35.93 (CH_2), 24.90 (CH_3). Minimal amount of pinacol was detected by NMR. HRMS-ESI: $[MH]^+$ Calcd. for $C_{18}H_{30}BO_6$: 353.2129; found: 353.2146.

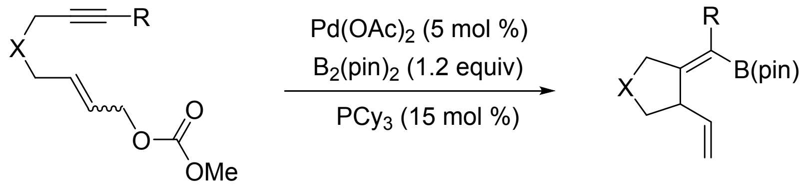
(*E*)-dimethyl 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)malonate (2l)



From compound **1l** (448 mg, 1.72 mmol) following the *general alkylation procedure*, after 15 minutes at 50 °C and xylene (1.5 mL) as solvent. Product **2l** was obtained as a colourless oil (316 mg, 59%) by flash chromatography using hexane/Et_2O 5:1 as eluent.

^1H NMR (300 MHz, $CDCl_3$) δ 5.55 (dt, *J* = 14.9, 7.3 Hz, 1H), 5.30 (dt, *J* = 15.1, 6.9 Hz, 1H), 3.70 (s, 6H), 3.37 (t, *J* = 7.6 Hz, 1H), 2.55 (t, *J* = 7.2 Hz, 2H), 1.60 (d, *J* = 7.2 Hz, 2H), 1.21 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 169.55 (C), 128.97 (CH), 125.61 (CH), 83.32 (C), 52.48 (CH), 52.21 (CH_3), 32.16 (CH_2), 24.86 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{15}H_{26}BO_6$: 313.1816; found: 313.1827.

General procedure for the synthesis of alkenylboronates.

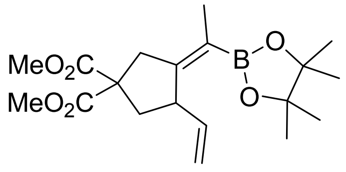


Scheme S3

A carousel tube was charged with the corresponding allylcarbonate (1 equiv) and bis(pinacolato)diboron (1.2 equiv) in anhydrous 1,4-dioxane or xylene (it will be specified in each case). Then, a solution of $Pd(OAc)_2$ (5 mol%) and $P(Cy)_3$ (5 mol %) in the corresponding solvent (0.6 mL) was added dropwise under Ar atmosphere. The mixture was stirred during the stated time at the temperature indicated below for every starting compound. After cooling the mixture to room temperature, the solvent was evaporated and the crude was purified by flash chromatography (hexane/Et_2O or pentane/Et_2O, as specified in each case, molybdophosphoric acid as stain-2.6 mmol/100 mL ethanol-) to afford the product.

Experimental data of alkenylboronates.

(*E*)-dimethyl 3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-4-vinylcyclopentane-1,1-dicarboxylate (3ab)

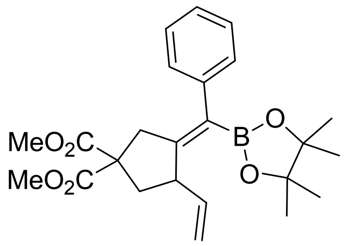


From compound **1a** (68 mg, 0.23 mmol), following the *general alkylation procedure*, after 8 h at 80°C in 1,4-dioxane (1.5 mL) as solvent. Product **3ab** was obtained as a colourless oil (60 mg, 72%) by flash chromatography using hexane/EtOAc 10:1 as eluent.

When the reaction was performed using compound **1b** (100 mg, 0.32 mmol) after 2.5 h at 110°C in 1,4-dioxane (1.5 mL), the product **3ab** was obtained in 71% yield (82.4 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ δ 5.79 – 5.64 (m, 1H), 4.95 – 4.84 (m, 2H), 3.87 (broad s, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 3.29 – 3.11 (m, 1H), 2.84 (d, *J* = 17.9 Hz, 1H), 2.57 (dd, *J* = 13.3, 8.4 Hz, 1H), 2.37 (dd, *J* = 13.4, 2.9 Hz, 1H), 1.72 (s, 3H), 1.21 (d, *J* = 2.5 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 172.68 (C), 172.44 (C), 156.33 (C), 141.49 (CH), 113.56 (CH_2), 83.02 (C), 58.60 (C), 52.92 (CH_3), 52.76 (CH_3), 46.32 (CH), 39.70 (CH_2), 39.25 (CH_2), 25.07 (CH_3), 24.94 (CH_3), 17.64 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{19}H_{29}BO_6Na$: 387.1949; found: 387.1966.

(*E*)-dimethyl 3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-4-vinylcyclopentane-1,1-dicarboxylate (3cd)

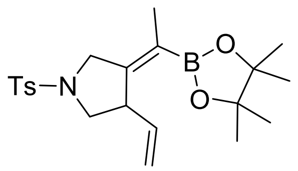


From compound **1c** (150 mg, 0.40 mmol), following the *general alkylation procedure*, after 8 h at 50 °C in xylene (1.5 mL) as solvent. Product **3cd** was obtained as a colourless oil (25 mg, 26%) by flash chromatography using hexane/EtOAc 6:1 as eluent.

When the reaction was performed using compound **1d** (112 mg, 0.30 mmol) under the same conditions, the product **3cd** was obtained in 18% yield (23 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 11.9, 4.3 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.14 – 7.08 (m, 2H), 5.96 – 5.77 (m, 1H), 5.17 – 5.04 (m, 1H), 5.00 (dd, *J* = 10.2, 1.4 Hz, 1H), 4.07 – 3.94 (m, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 3.14 (dd, *J* = 17.4, 1.2 Hz, 1H), 2.78 – 2.62 (m, 2H), 2.30 (dd, *J* = 13.4, 4.8 Hz, 1H), 1.21 (d, *J* = 4.5 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 172.28 (C), 172.21 (C), 157.33 (C), 142.71 (C), 141.32 (CH), 128.69 (CH), 128.08 (CH), 125.94 (CH), 114.16 (CH_2), 83.38 (C), 58.73 (C), 52.84 (CH_3), 52.81 (CH_3), 46.14 (CH), 40.20 (CH_2), 39.36 (CH_2), 25.05 (CH_3), 24.85 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{24}H_{32}BO_6$: 427.2286; found: 427.2308.

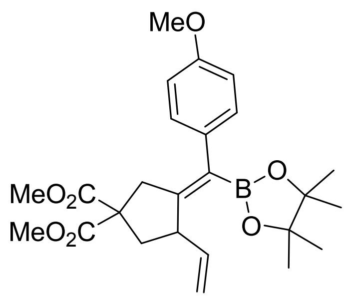
(*Z*)-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-1-tosyl-4-vinylpyrrolidine (3ef)



From compound **1e** (50 mg, 0.14 mmol), following the *general alkylation procedure*, after 12 h at 50 °C in xylene (1.5 mL) as solvent. Product **3ef** was obtained as a colourless oil (41 mg, 71%) by flash chromatography using hexane/ Et_2O 10:1 as eluent. When the reaction was performed using **1f** (*Z*/*E* 1:1.4) (33 mg, 0.094 mmol) under the same conditions, the product **3ef** was obtained in 61% yield (34.5 mg).

^1H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.79 (ddd, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.08 (d, *J* = 17.2 Hz, 1H), 4.94 (d, *J* = 10.2 Hz, 1H), 4.01 (d, *J* = 15.4 Hz, 1H), 3.87 (t, *J* = 6.0 Hz, 1H), 3.55 (t, *J* = 12.9 Hz, 2H), 3.03 (dd, *J* = 9.1, 6.3 Hz, 1H), 2.42 (s, 3H), 1.60 (s, 3H), 1.20 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 152.67 (C), 143.68 (C), 138.91 (CH), 132.61 (C), 129.73 (CH), 128.01 (CH), 114.25 (CH_2), 83.36 (C), 53.30 (CH_2), 50.81 (CH_2), 45.94 (CH), 24.97 (CH_3), 21.64 (CH_3), 17.20 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{21}H_{31}BNO_5S$: 404.2061; found: 404.2076.

(*E*)-dimethyl 3-((4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-4-vinylcyclopentane-1,1-dicarboxylate (3mn)

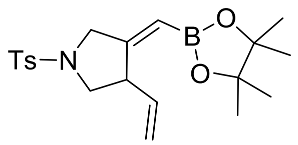


From compound **1m** (100 mg, 0.32 mmol), following the *general alkylation procedure*, after 12 h at 50 °C in 1,4-dioxane (1.5 mL) as solvent. Product **3mn** was obtained as a colourless oil (79 mg, 68%), by flash chromatography using hexane/Et_2O 10:1 as eluent.

When the reaction was performed using compound **1n** (150 mg, 0.37 mmol) under the same conditions, compound **3mn** was obtained in 37% yield (63 mg).

^1H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.94 – 5.76 (m, 1H), 5.08 (d, *J* = 17.2 Hz, 1H), 4.98 (d, *J* = 10.2 Hz, 1H), 4.05 – 3.93 (m, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 3.63 (s, 3H), 3.16 (d, *J* = 17.5 Hz, 1H), 2.79 – 2.69 (m, 1H), 2.69 – 2.61 (m, 1H), 2.28 (dd, *J* = 13.4, 4.7 Hz, 1H), 1.21 (d, *J* = 3.5 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 172.31 (C), 172.22 (C), 157.78 (C), 156.80 (C), 141.36 (CH), 134.97 (C), 129.79 (CH), 114.09 (CH_2), 113.48 (CH), 83.33 (C), 58.72 (C), 55.26 (CH_3), 52.82 (CH_3), 46.13 (CH), 40.21 (CH_2), 39.30 (CH_2), 25.05 (CH_3), 24.85 (CH_3). Minimal amount of pinacol was detected by NMR. HRMS-ESI: $[MNa]^+$ Calcd. for $C_{25}H_{33}BO_7Na$: 479.2211; found: 479.2224.

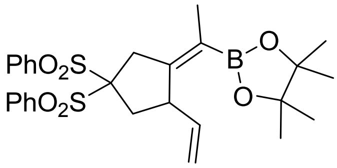
(*E*)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-1-tosyl-4-vinylpyrrolidine (3o)



From compound **1o** (100 mg, 0.31 mmol), following the *general alkylation procedure*, after 8 h at 50 °C in xylene (1.5 mL) as solvent. Product **3o** was obtained as a colourless oil (64.2 mg, 53%), by flash chromatography using hexane/Et_2O 10:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.77 (ddd, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.29 (s, 1H), 5.12 (d, *J* = 17.1 Hz, 1H), 4.97 (d, *J* = 10.2 Hz, 1H), 4.08 (d, *J* = 15.2 Hz, 1H), 3.83 (t, *J* = 5.8 Hz, 1H), 3.62 (d, *J* = 15.1 Hz, 1H), 3.52 (d, *J* = 9.4 Hz, 1H), 3.15 (dd, *J* = 9.3, 6.4 Hz, 1H), 2.43 (s, 3H), 1.21 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 161.23 (C), 143.77 (C), 137.97 (CH), 132.83 (C), 129.79 (CH), 128.01 (CH), 114.98 (CH_2), 83.37 (C), 53.39 (CH_2), 53.33 (CH_2), 46.27 (CH), 25.02 (CH_3), 24.93 (CH_3), 21.68 (CH_3). Minimal amount of pinacol was detected by NMR. HRMS-ESI: $[MH]^+$ Calcd. for $C_{20}H_{29}BNO_4S$: 390.1904; found: 390.1923.

(*E*)-2-(1-(4,4-bis(phenylsulfonyl)-2-vinylcyclopentylidene)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p)

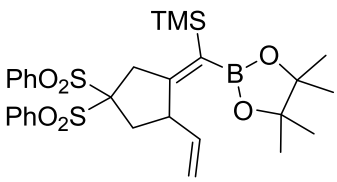


From compound **1p** (50 mg, 0.11 mmol), following the *general alkylation procedure*, after 8 h at 50 °C in xylene (1.5 mL) as solvent. Product **3p** was obtained as a colourless oil (36 mg, 65%) using hexane/EtOAc 6:1 as eluent.

Using $Pd(OAc)_2$ (15 mol%) and 1,4-dioxane (1.2 mL), compound **3p** was obtained as a colourless oil (57 mg, 73%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (t, *J* = 12.0 Hz, 2H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.61 (q, *J* = 7.1 Hz, 3H), 7.50 (t, *J* = 7.6 Hz, 2H), 5.76 (ddd, *J* = 17.3, 10.1, 7.5 Hz, 1H), 4.98 (d, *J* = 17.0 Hz, 1H), 4.88 (d, *J* = 10.1 Hz, 1H), 3.82 – 3.69 (m, 1H), 3.36 (d, *J* = 18.3 Hz, 1H), 3.14 (d, *J* = 18.2 Hz, 1H), 2.95 (dd, *J* = 16.0, 9.4 Hz, 1H), 2.69 (dd, *J* = 16.0, 5.5 Hz, 1H), 1.54 (s, 3H), 1.18 (d, *J* = 2.0 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 154.15 (C), 141.37 (CH), 137.65 (C), 136.64 (C), 134.65 (CH), 131.31 (CH), 131.02 (CH), 128.94 (CH), 128.87 (CH), 113.71 (CH_2), 92.85 (C), 83.18 (C), 46.25 (CH), 36.65 (CH_2), 36.56 (CH_2), 25.19 (CH_3), 24.91 (CH_3), 18.38 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{27}H_{34}BO_6S_2$: 529.1184; found: 529.1882.

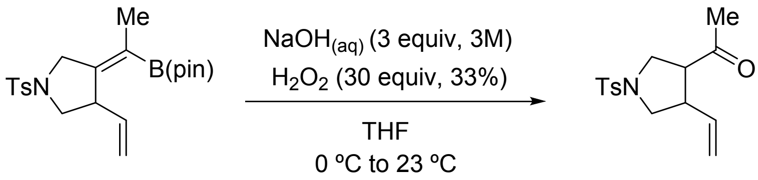
(*E*)-((4,4-bis(phenylsulfonyl)-2-vinylcyclopentylidene)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)trimethylsilane (3q)



From compound **1q** (100 mg, 0.19 mmol), following the *general alkylation procedure*, after 40 min at 130 °C in xylene (2 mL) as solvent. Product **3q** was obtained, with some traces of an unidentified compound, as a colourless oil (61 mg, 56%) by flash chromatography using pentane/Et_2OAc 10:1 as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 4H), 7.74 – 7.66 (m, 2H), 7.63 – 7.54 (m, 4H), 5.78 (ddd, *J* = 17.3, 10.1, 7.4 Hz, 1H), 5.09 – 4.99 (m, 2H), 3.62 (q, *J* = 7.8 Hz, 1H), 3.46 (dd, *J* = 18.5, 2.1 Hz, 1H), 3.27 (d, *J* = 18.5 Hz, 1H), 2.77 (dd, *J* = 15.4, 9.1 Hz, 1H), 2.53 (dd, *J* = 15.5, 7.9 Hz, 1H), 1.22 (d, *J* = 1.4 Hz, 12H), 0.15 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 163.14 (C), 140.35 (CH), 137.13 (C), 136.43 (C), 134.72 (CH), 134.68 (CH), 131.37 (CH), 131.33 (CH), 128.98 (CH), 128.82 (CH), 116.49 (CH_2), 92.79 (C), 83.23 (C), 49.82 (CH), 40.10 (CH_2), 36.91 (CH_2), 25.88 (CH_3), 25.40 (CH_3), 0.83 (CH_3). HRMS-ESI: [MNa]+ Calcd. for $C_{23}H_{29}BO_6S_2SiNa$: 527.1166; found: 527.1481.

Oxidation of alkenylboronate 3ef to 4

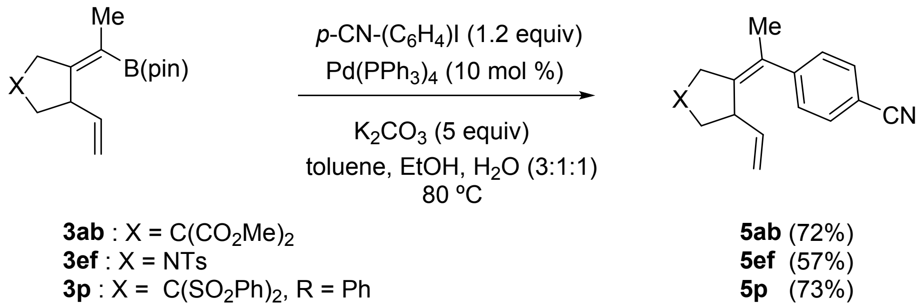


Scheme S4

To a solution of alkenylboronate **3ef** (34 mg, 0.084 mmol, 1 equiv) in THF (2 mL), an aqueous solution of NaOH (3M, 0.42 mmol, 3 equiv) was slowly added at room temperature. Then, the mixture was cooled to 0 ºC and a solution of H_2O_2 (33% w/v, 4.37 mmol, 30 equiv) was added dropwise. After addition, the reaction was stirred at room temperature for 8 h. Then, water and Et_2O were added into the resulting mixture. The aqueous layer was separated and extracted with Et_2O (3 x 10 mL). The combined organic phases were dried over anhydrous Mg_2SO_4 and filtered through anhydrous Na_2SO_4. The solvent was removed under vacuum and the crude was purified by flash chromatography (hexane/EtOAc 8:1) to afford the title compound as a yellowish oil (10 mg, 41%).

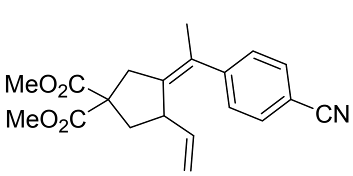
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.73 – 5.57 (m, 1H), 5.09 (dd, *J* = 13.8, 3.0 Hz, 2H), 3.56 (dd, *J* = 10.0, 7.9 Hz, 1H), 3.41 (ddd, *J* = 27.1, 10.1, 8.0 Hz, 2H), 3.09 (dd, *J* = 9.9, 8.1 Hz, 1H), 2.96 – 2.74 (m, 2H), 2.45 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 205.64 (C), 143.80 (C), 136.27 (CH), 133.38 (C), 129.79 (CH), 127.66 (CH), 117.88 (CH_2), 56.03 (CH), 52.55 (CH_2), 49.24 (CH_2), 45.83 (CH), 30.06 (CH_3), 21.56 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{15}H_{20}NO_3S$: 294.1158; found: 294.1157.

Suzuki cross-coupling reactions of alkenylboronates and experimental data



Scheme S5

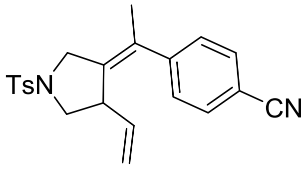
(*Z*)-dimethyl 3-(1-(4-cyanophenyl)ethylidene)-4-vinylcyclopentane-1,1-dicarboxylate (5ab)



A solution of 4-iodobenzonitrile (23.9 mg, 0.10 mmol) in toluene (0.5 mL), EtOH (0.15 mL) and H_2O (0.15 mL) was added to a dry tube containing alkenylboronate **3ab** (10 mg, 0.042 mmol), K_2CO_3 (60.3 mg, 0.44 mmol) and $Pd(PPh_3)_4$ (30.16 mg, 0.026 mmol), under Ar atmosphere. The mixture was heated at 80 ºC for 4 h in the sealed tube. After cooling to room temperature, the solvent was removed under vacuum and the crude was purified by flash chromatography (hexane/Et_2O 8:1). The product **5ab** was obtained as a yellowish oil (20.78 mg, 72%).[12]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 5.30 (ddd, J = 17.3, 10.2, 7.4 Hz, 1H), 4.62 (d, J = 10.1 Hz, 1H), 4.53 (d, J = 17.1 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.40 – 3.28 (m, 1H), 3.20 – 3.02 (m, 2H), 2.53 (dd, J = 13.3, 8.0 Hz, 1H), 2.12 (dd, J = 13.3, 6.6 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 172.35 (C), 172.07 (C), 148.52 (C), 139.26 (CH), 138.74 (C), 131.94 (CH), 130.18 (C), 128.96 (CH), 119.22 (C), 114.90 (CH_2), 110.20 (C), 58.75 (C), 53.09 (CH_3), 52.96 (CH_3), 45.86 (CH), 40.96 (CH_2), 39.39 (CH_2), 21.93 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{20}H_{21}NO_4Na$: 362.1362; found: 362.1367.

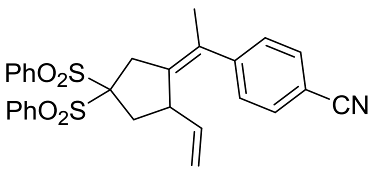
(*E*)-4-(1-(1-tosyl-4-vinylpyrrolidin-3-ylidene)ethyl)benzonitrile (5ef)



A solution of 4-iodobenzonitrile (18.14 mg, 0.079 mmol) in toluene (0.5 mL), EtOH (0.15 mL) and H_2O (0.15 mL) was added to a dry tube containing the alkenylboronate **3hi** (25 mg, 0.062 mmol), K_2CO_3 (50 mg, 0.37 mmol) and $Pd(PPh_3)_4$ (8.3 mg, 0.007 mmol), under Ar atmosphere, and the mixture was heated at 80 ºC for 4 h in the sealed tube. After cooling to room temperature, the solvent was removed under vacuum and the crude was purified by flash chromatography (hexane/Et_2O 10:1). The product **5ef** was obtained as yellowish oil (13 mg, 57%).[12]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (t, *J* = 7.1 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 5.39 (ddd, *J* = 17.1, 10.2, 7.1 Hz, 1H), 4.70 (d, *J* = 10.3 Hz, 1H), 4.53 (d, *J* = 17.1 Hz, 1H), 3.98 – 3.73 (m, 2H), 3.15 (s, 3H), 2.41 – 2.34 (m, 3H), 1.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 147.17 (C), 143.94 (C), 137.21 (CH), 135.32 (C), 133.03 (CH), 132.97 (C), 132.13 (CH), 130.41 (C), 129.88 (CH), 128.59 (CH), 128.08 (C), 115.91 (CH_2), 110.84 (C), 54.08 (CH_2), 50.88 (CH_2), 45.59 (CH), 21.72 (CH_3), 21.53 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{22}H_{23}N_2O_2S$: 379.1474; found: 379.1480.

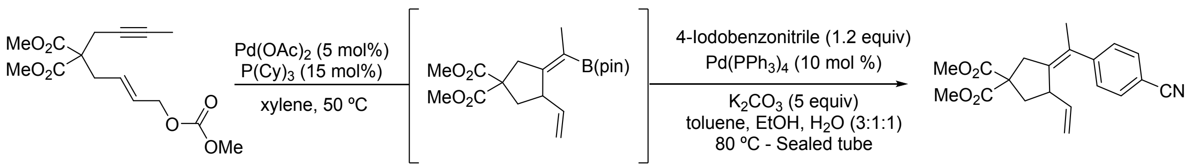
(*Z*)-4-(1-(4,4-bis(phenylsulfonyl)-2-vinylcyclopentylidene)ethyl)benzonitrile (5p)



A solution of 4-iodobenzonitrile (24.45 mg, 0.11 mmol) in toluene (0.5 mL), EtOH (0.15 mL) and H_2O (0.15 mL) was added to a dry tube containing the alkenylboronate **3p** (47 mg, 0.089 mmol), K_2CO_3 (61.48 mg, 0.44 mmol) and $Pd(PPh_3)_4$ (10.2 mg, 0.009 mmol) under Ar atmosphere, and the mixture was heated at 80 ºC for 4 h in the sealed tube. After cooling to room temperature, the solvent was removed under vacuum and the crude was purified by flash chromatography (hexane/Et_2O 3:1). The product **5p** was obtained as a yellowish oil (33 mg, 73%).[12]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 – 8.03 (m, 4H), 7.80 – 7.70 (m, 2H), 7.67 – 7.53 (m, 6H), 7.18 (d, *J* = 8.2 Hz, 2H), 5.27 (dt, *J* = 17.1, 8.8 Hz, 1H), 4.53 (d, *J* = 10.0 Hz, 1H), 4.32 (d, *J* = 16.9 Hz, 1H), 3.69 – 3.50 (m, 2H), 3.12 (d, *J* = 18.0 Hz, 1H), 2.81 – 2.67 (m, 1H), 2.51 (dd, *J* = 15.2, 7.8 Hz, 1H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 147.69 (C), 138.43 (CH), 137.15 (C), 136.89 (C), 136.06 (C), 134.99 (CH), 134.83 (CH), 132.15 (CH), 131.25 (CH), 131.22 (CH), 131.07 (CH), 129.04 (CH), 128.99 (CH), 128.94 (C), 119.07 (CH_2), 115.27 (C), 110.62 (C), 92.38 (CH), 46.37 (C), 37.96 (CH_2), 36.58 (CH_2), 22.45 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{28}H_{26}NO_4S_2$: 504.1297; found: 504.1281.

Synthesis of (*Z*)-dimethyl 3-(1-(4-cyanophenyl)ethylidene)-4-vinylcyclopentane-1,1-dicarboxylate (5ab) from allylcarbonate 1a



Scheme S6

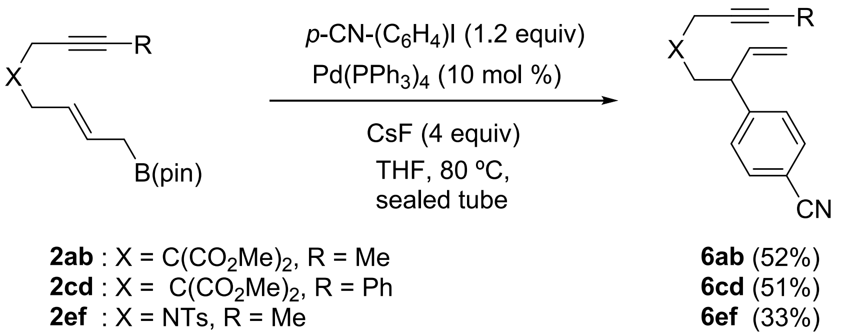
A dry carousel tube was charged with allylcarbonate **1a** (100 mg, 3.12 mmol, 1 equiv), bis(pinacolato)diboron (97.5mg, 0.38 mmol, 1.2 equiv), and anhydrous xylene (0.75 mL) under Ar atmosphere. Then, a solution of $Pd(OAc)_2$ (3.59 mg, 0.016 mmol, 5 mol%) and $P(Cy)_3$ (13.48 mg, 0.048 mmol, 5 mol %) in xylene (0.75 mL) was added dropwise under Ar. The mixture was was heated at 50 ºC for 8 h. After cooling to room temperature, the solvent was removed under vacuum and the resulting compound **3ab** was used without further purification.

Then, a mixture of crude alkenylboronate **3ab**, K_2CO_3 (219.89 mg, 1.59 mmol, 5 equiv) and $Pd(PPh_3)_4$ (3.6 mg, 0.0031 mmol, 10 mol%), was treated with a solution of 4-iodobenzonitrile (87.60 mg, 0.38 mmol, 1.2 equiv) in toluene (0.5 mL), EtOH (0.15 mL) and H_2O (0.15 mL) under Ar atmosphere, and the mixture was heated at 80 ºC for 8 h in a sealed tube. After cooling to room temperature the solvent was removed under vacuum and the crude was purified by flash chromatography (hexane/Et_2O 5:1). Compound **5ab** was obtained as a yellowish oil (67.5 mg, 63%).

^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.30 (ddd, *J* = 17.3, 10.2, 7.4 Hz, 1H), 4.62 (d, *J* = 10.1 Hz, 1H), 4.53 (d, *J* = 17.1 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.40 – 3.28 (m, 1H), 3.20 – 3.02 (m, 2H), 2.53 (dd, *J* = 13.3, 8.0 Hz, 1H), 2.12 (dd, *J* = 13.3, 6.6 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 172.35 (C), 172.07 (C), 148.52 (C), 139.26 (CH), 138.74 (C), 131.94 (CH), 130.18

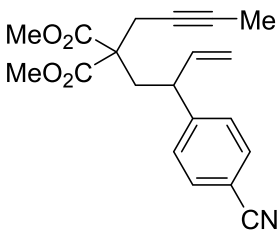
(C), 128.96 (CH), 119.22 (C), 114.90 (CH_2), 110.20 (C), 58.75 (C), 53.09 (CH_3), 52.96 (CH_3), 45.86 (CH), 40.96 (CH_2), 39.39 (CH_2), 21.93 (CH_3). HRMS-ESI: $[MNa]^+$ Calcd. for $C_{20}H_{21}NO_4Na$: 362.1362; found: 362.1367

Suzuki cross-coupling of allylboronates



Scheme S7

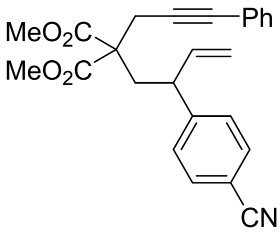
Dimethyl 2-(but-2-yn-1-yl)-2-(2-(4-cyanophenyl)but-3-en-1-yl)malonate (6ab)



A solution of 4-iodobenzonitrile (20.74 mg, 0.09 mmol) in dry THF (4 mL) was added to a dry tube containing the allylboronate **2ab** (48 mg, 0.14 mmol), CsF (83.41 mg, 0.55 mmol) and $Pd(PPh_3)_4$ (23.79 mg, 0.021 mmol, 15 mol%) under Ar atmosphere; and the mixture was heated at 80 ºC for 3 h in the sealed tube. After cooling to room temperature the solvent was removed under vacuum and the crude was purified by flash chromatography (hexane/Et_2O 4:1). The product was obtained as a yellowish oil (23 mg, 52%).[13]

^1H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.34 – 7.30 (m, 2H), 5.85 (ddd, J = 17.2, 10.2, 8.0 Hz, 1H), 5.08 – 4.96 (m, 2H), 3.74 – 3.68 (m, 1H), 3.65 (s, 3H), 3.50 (s, 3H), 2.94 – 2.71 (m, 2H), 2.63 – 2.45 (m, 2H), 1.74 (t, J = 2.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.60 (C), 170.46 (C), 149.38 (C), 140.30 (CH), 132.40 (CH), 128.79 (CH), 118.98 (C), 116.01 (CH_2), 110.52 (C), 79.65 (C), 73.09 (C), 56.33 (C), 52.75 (CH_3), 52.69 (CH_3), 45.79 (CH), 37.09 (CH_2), 23.62 (CH_2), 3.61 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{20}H_{22}NO_4$: 340.1543; found: 340.1533.

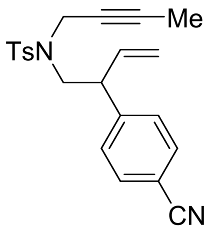
Dimethyl 2-(2-(4-cyanophenyl)but-3-en-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (6cd)



A solution of 4-iodobenzonitrile (55.73 mg, 0.24 mmol) in THF (1.5 mL) was added to a dry tube containing the allylboronate **2cd** (138 mg, 0.32 mmol), CsF (224 mg, 0.98 mmol) and $Pd(PPh_3)_4$ (64 mg, 0.055 mmol, 15 mol%), under Ar atmosphere; and the mixture was heated at 80 ºC for 3 h in a sealed tube. After cooling to room temperature the solvent was removed under vacuum and the crude was purified by flash chromatography (hexane/Et_2O 5:1). The product **6cd** was obtained as a yellowish oil (76 mg, 51%).[13]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.36 – 7.27 (m, 7H), 5.89 (ddd, *J* = 16.9, 10.2, 7.9 Hz, 1H), 5.07 (dt, *J* = 5.1, 1.0 Hz, 1H), 5.03 (dt, *J* = 11.8, 1.0 Hz, 1H), 3.70 (s, 3H), 3.54 (s, 3H), 3.48 (dd, *J* = 13.3, 6.2 Hz, 1H), 3.22 – 2.98 (m, 2H), 2.72 – 2.55 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.38 (C), 170.26 (C), 149.23 (C), 140.19 (CH), 132.44 (CH), 131.70 (CH), 128.77 (CH), 128.41 (CH),128.33 (CH), 123.02 (C), 118.92 (C), 116.14 (CH_2), 110.58 (C), 84.31 (C), 83.87 (C), 56.44 (C), 52.87 (CH_3), 52.81 (CH_3), 45.87 (CH), 37.23 (CH_2), 24.15 (CH_2). HRMS-ESI: $[MH]^+$ Calcd. for $C_{25}H_{24}NO_4$:402.1699; found: 402.1712.

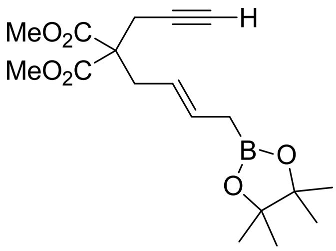
***N*-(but-2-yn-1-yl)-*N*-(2-(4-cyanophenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (6ef)**



A solution of 4-iodobenzonitrile (14 mg, 0.06 mmol) in THF (1.5 mL) was added to a dry tube containing the allylboronate **2ef** (80 mg, 0.20 mmol), CsF (138.4 mg, 0.91 mmol) and $Pd(PPh_3)_4$ (39.4 mg, 0.034 mmol, 15 mol%) under Ar atmosphere; and the mixture was heated at 80 ºC for 8 h in the sealed tube. After cooling to room temperature the solvent was removed under vacuum and the crude was purified by flash chromatography (hexane/Et_2O 4:1). The product **6ef** was obtained as a yellowish oil (24.75 mg, 33%).[13]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 5.4 Hz, 2H), 5.90 (ddd, *J* = 17.6, 10.3, 7.6 Hz, 1H), 5.19 – 5.01 (m, 2H), 3.99 3.93 (m, 1H), 3.76 – 3.64 (m, 2H), 3.44 – 3.27 (m, 2H), 2.35 (s, 3H), 1.48 (t, *J* = 2.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 146.54 (C), 143.46 (CH), 137.25 (C), 135.73 (C), 132.45 (CH), 129.32 (CH), 128.89 (CH), 127.83 (CH), 118.75 (C), 117.86 (CH_2), 110.92 (C), 82.01 (C), 71.40 (C), 50.45 (CH_2), 48.53 (CH), 37.70 (CH_2), 21.51 (CH_3), 3.24 (CH_3). HRMS-ESI: $[MH]^+$ Calcd. for $C_{22}H_{23}N_2O_2S$: 379.1474; found: 379.1465.

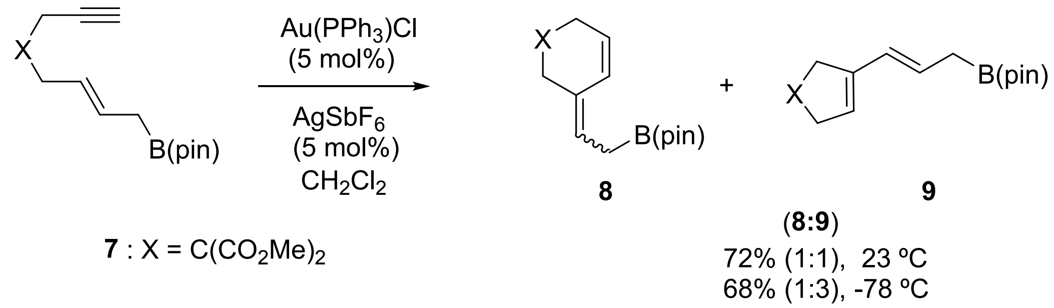
Synthesis of allylboronate 7



To a suspension of NaH (60% in mineral oil, 15 mg, 0.36 mmol) in anhydrous THF (10 mL) under Ar atmosphere at 0 ºC, was slowly added **2l** (102 mg, 0.33 mmol) and the mixture was stirred at room temperature for 30 minutes (formation of H_2 bubbles were observed during the addition). Then, propargyl bromide solution (80 wt. % in toluene, 42.4 mg, 0.36 mmol), was added dropwise and the mixture was allowed to react at room temperature for 12 h. Monitoring by TLC indicated the completion of the reaction. Then water and Et_2O were added into the resulting mixture. The aqueous layer was separated and extracted successively with Et_2O (3 x 25 mL). The combined organic phases were washed several times with water, twice with saturated aqueous solution of NaCl, and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the crude was purified by flash chromatography (hexane/Et_2O 15:1, to afford the title compound as a colourless oil (80 mg, 70%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67 – 5.51 (m, 1H), 5.21 – 5.06 (m, 1H), 3.69 (s, 6H), 2.74 (d, *J* = 2.7 Hz, 2H), 2.70 (d, *J* = 7.5 Hz, 2H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.60 (d, *J* = 7.3 Hz, 2H), 1.20 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.37 (C), 131.26 (CH), 122.96 (CH), 83.32 (C), 79.14 (C), 71.29 (CH), 57.28 (C), 52.71 (CH_3), 35.52 (CH_2), 24.84 (CH_3), 22.56 (CH_2). HRMS-ESI: $[MH]^+$ Calcd. for $C_{18}H_{28}BO_6$: 351.1973; found: 351.1986

Cycloisomerization of allylboronate 7.



Scheme S8

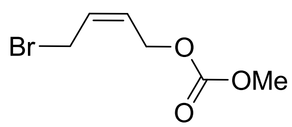
A solution of allylboronate **7** (100 mg, 0.28 mmol) in CH_2Cl_2 (0.5 mL) was added to a mixture of $AuPPh_3Cl$ (3.0 mol%) and $AgSbF_6$ (3.0 mol%) in CH_2Cl_2 (1 mL). The mixture was stirred at room temperature for 5 minutes, before being filtered through a silica gel plug which was rinsed with diethyl ether. The resulting solution was then evaporated in vacuo to afford the crude product. The ratio of the two isomers observed (by GC-MS) was determined by ^{1}H-NMR. The residue was purified by flash chromatography (hexane → hexane/EtOAc (5:1) to give a mixture of products that could not be separated (**8:9** = 1:1) (72 mg, 72%).[14]

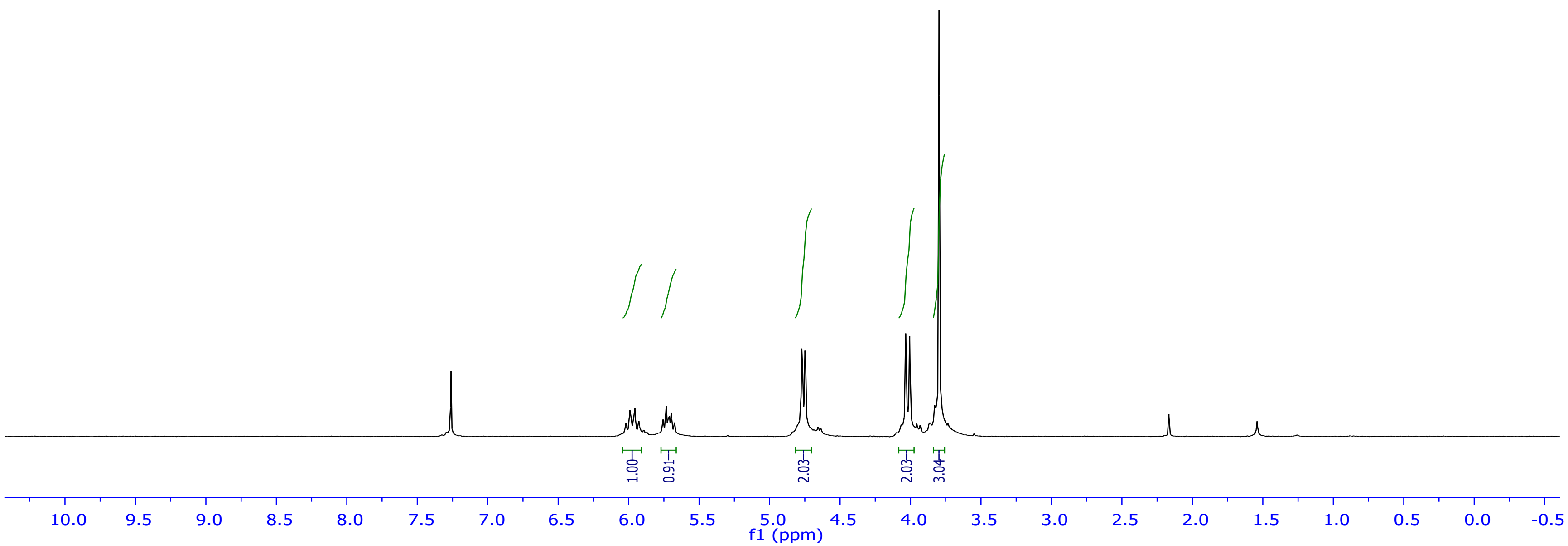
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.36 (d, *J* = 10.1 Hz, 1H), 6.12 (d, *J* = 15.7 Hz, 2H), 5.93 – 5.30 (m, 8H), 3.70 (s, 12H), 3.66 (s, 6H), 3.06 (d, *J* = 18.2 Hz, 8H), 2.71 (d, *J* = 36.8 Hz, 4H), 1.88 (d, *J* = 8.5 Hz, 1H), 1.74 – 1.67 (m, 5H), 1.22 (s, 24H), 1.19 (s, 12H).

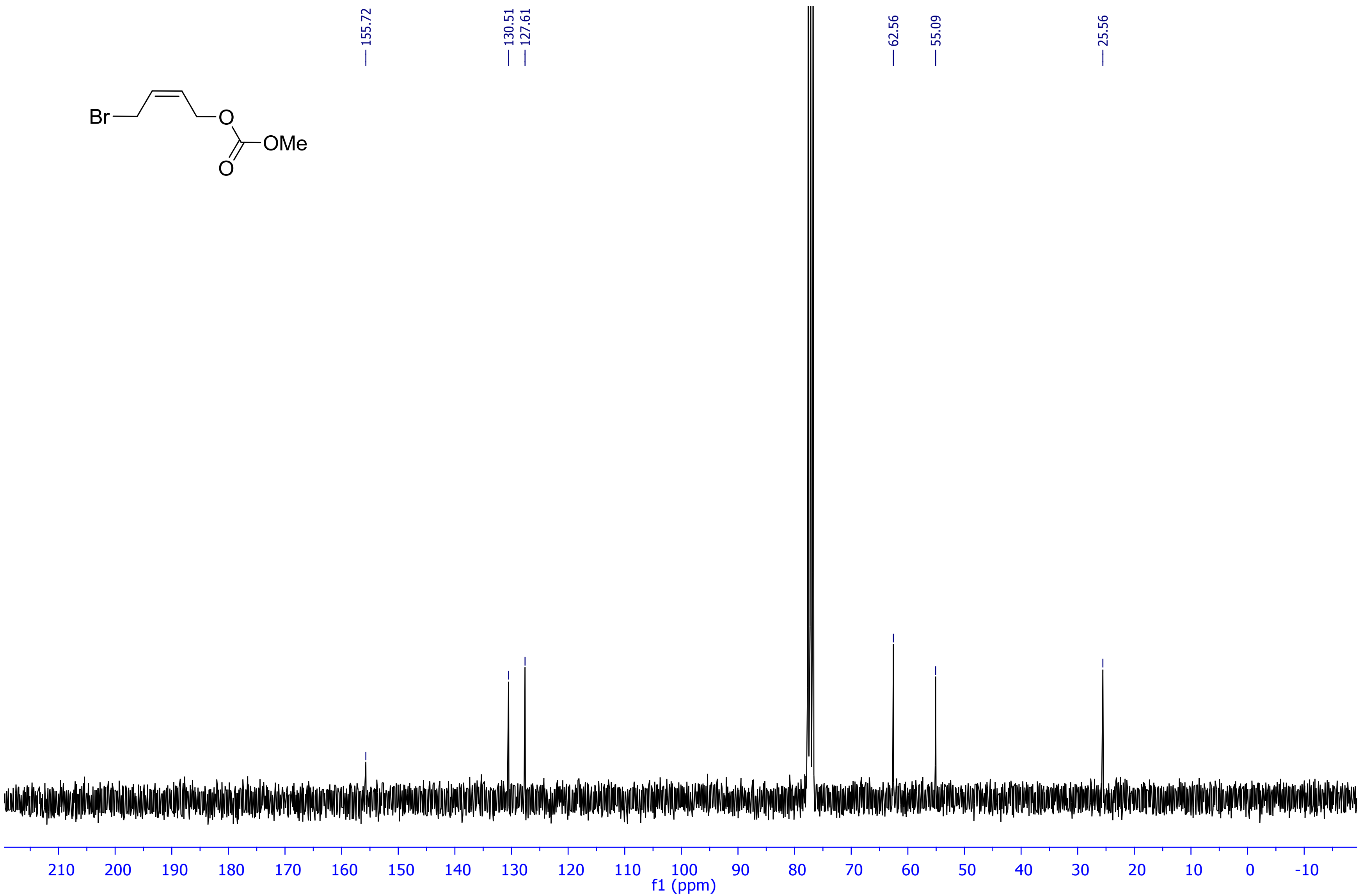
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 172.72 (C), 172.63 (C), 171.62 (C), 139.86 (C), 128.91 (C), 127.81 (CH), 127.34 (CH), 126.56 (CH), 126.19 (CH), 125.06 (CH), 124.10 (CH), 124.03 (CH), 123.68 (CH), 123.09 (CH), 83.46 (C), 83.42 (C), 83.33 (C), 59.43 (C), 58.83 (C), 54.29 (C), 52.88 (CH_3), 52.67 (CH_3), 43.25 (CH_2), 40.80 (CH_2), 40.42 (CH_2), 39.98 (CH_2), 37.39 (CH_2), 31.88 (CH_2), 24.85 (CH_3), 24.82 (CH_3).

[1]H-NMR and [13]C-NMR spectra

<u>[1]H-NMR and [13]C-NMR spectra of dienynes precursors.</u>







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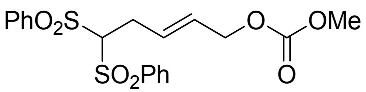
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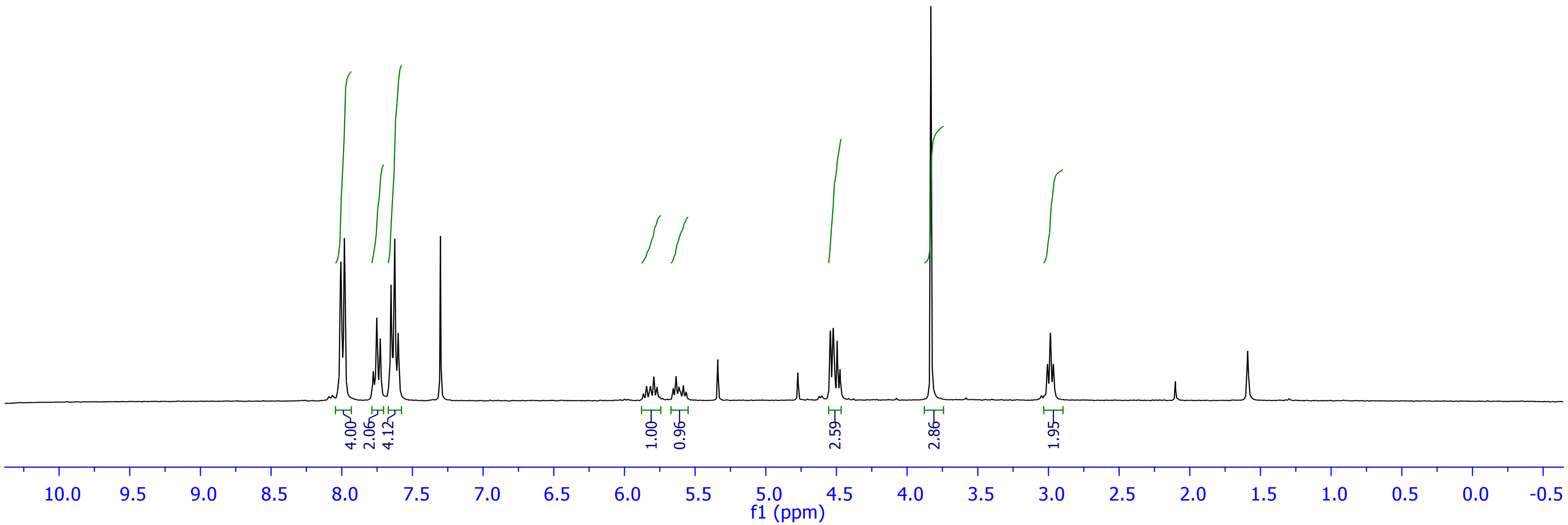
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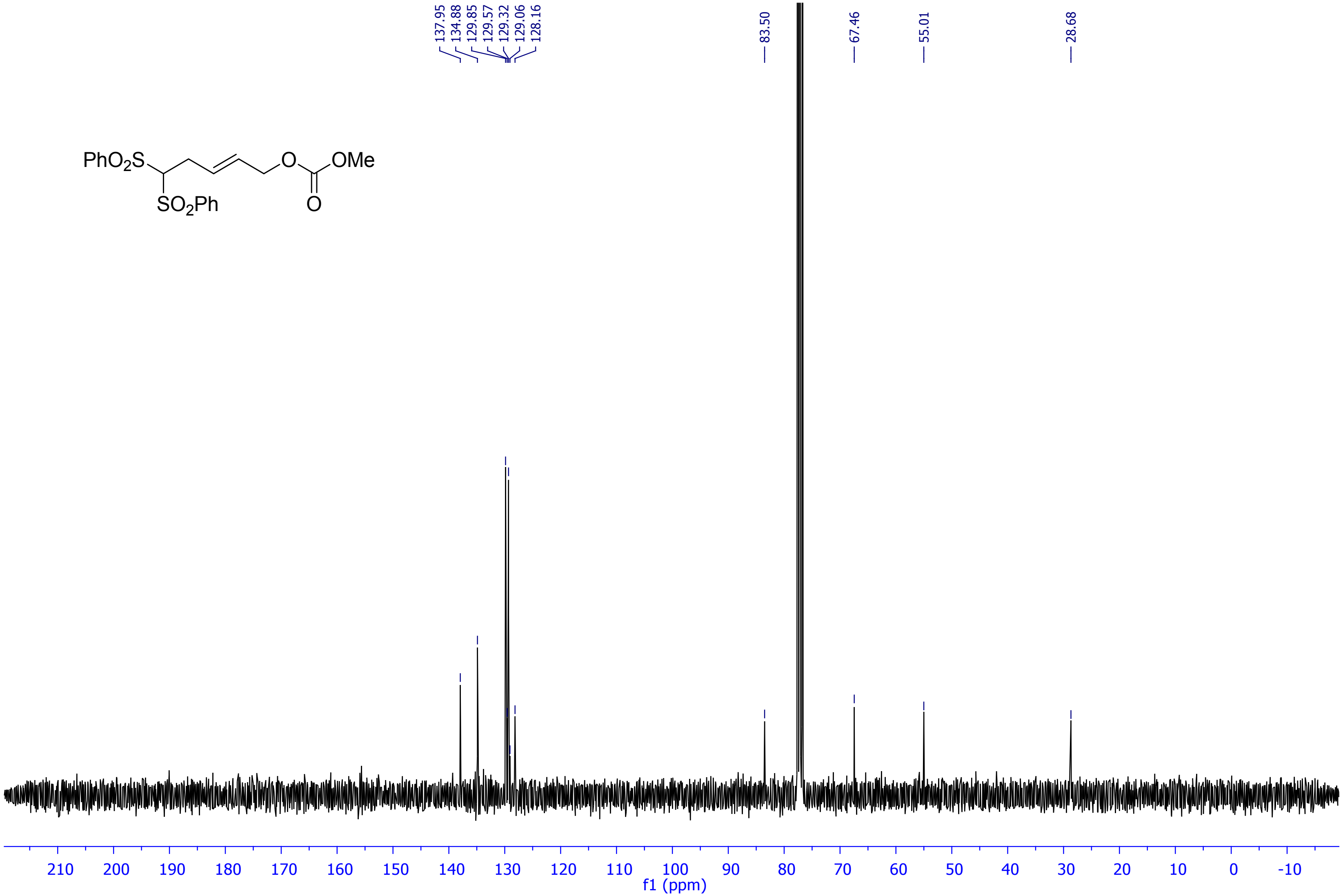
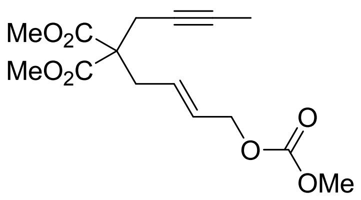
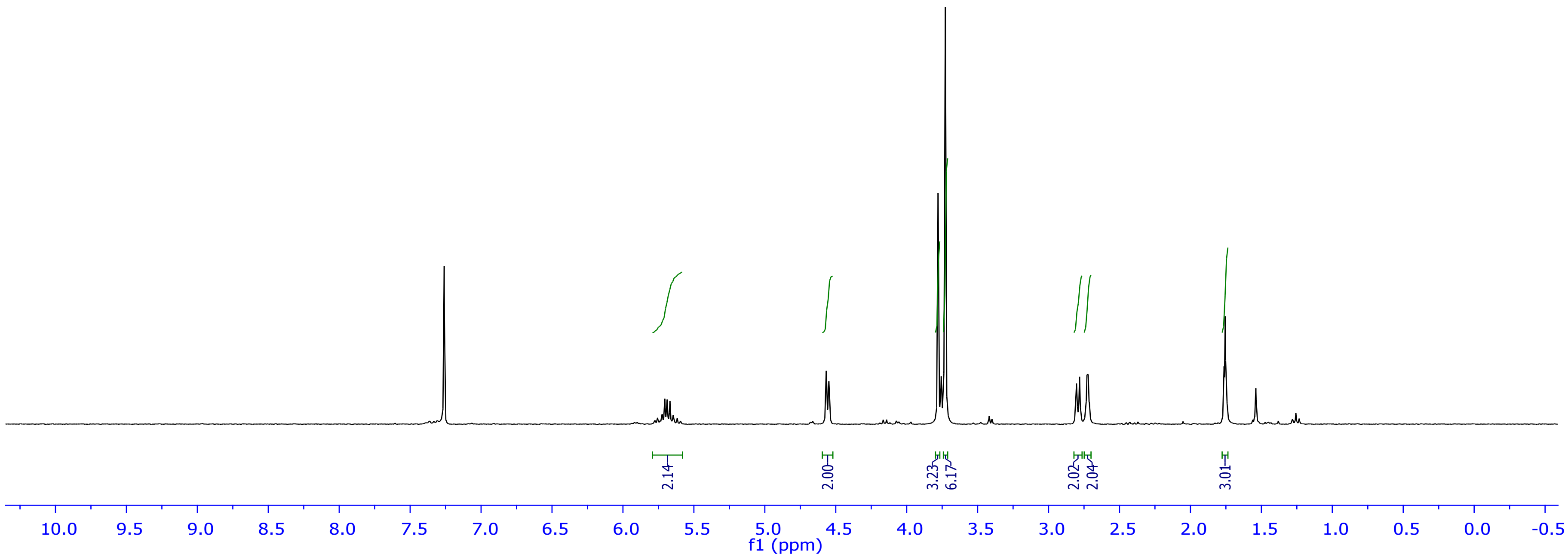
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

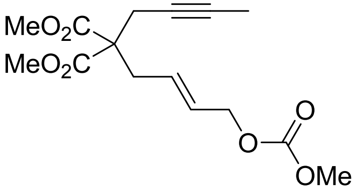

PhO2S
SO2Ph
O
OMe
O
137.95
134.88
129.85
129.57
129.32
129.06
128.16
83.50
67.46
55.01
28.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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

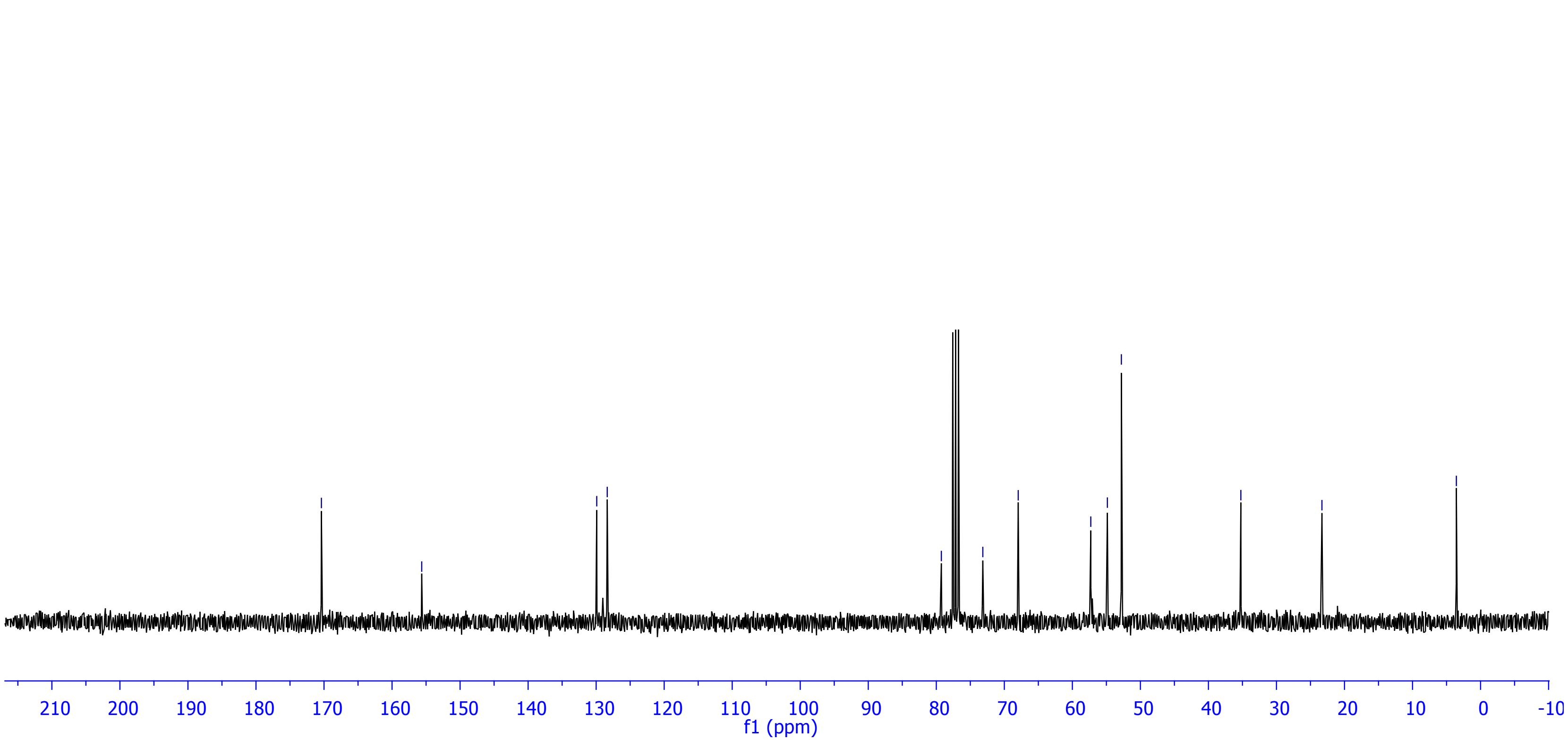


1a

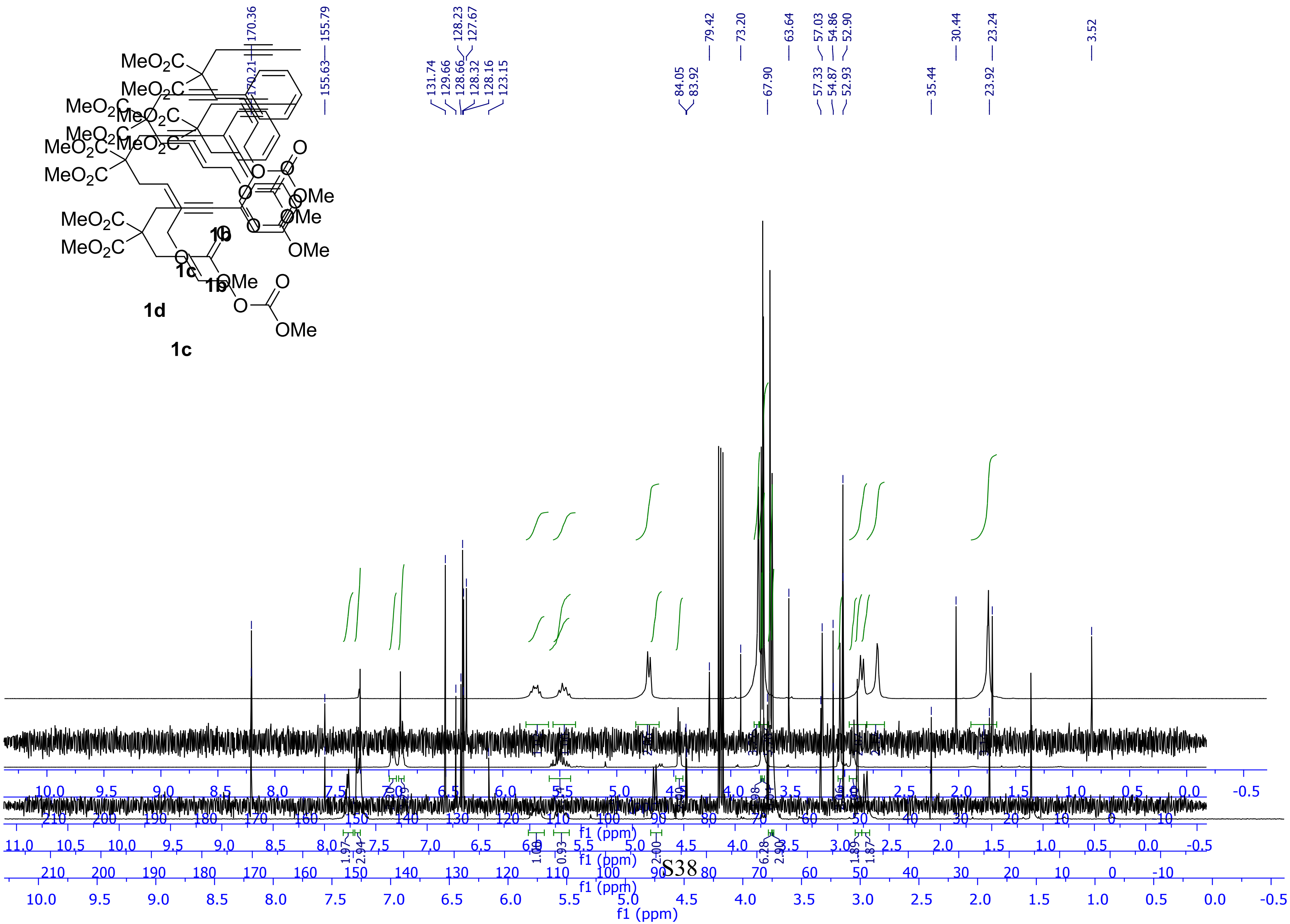


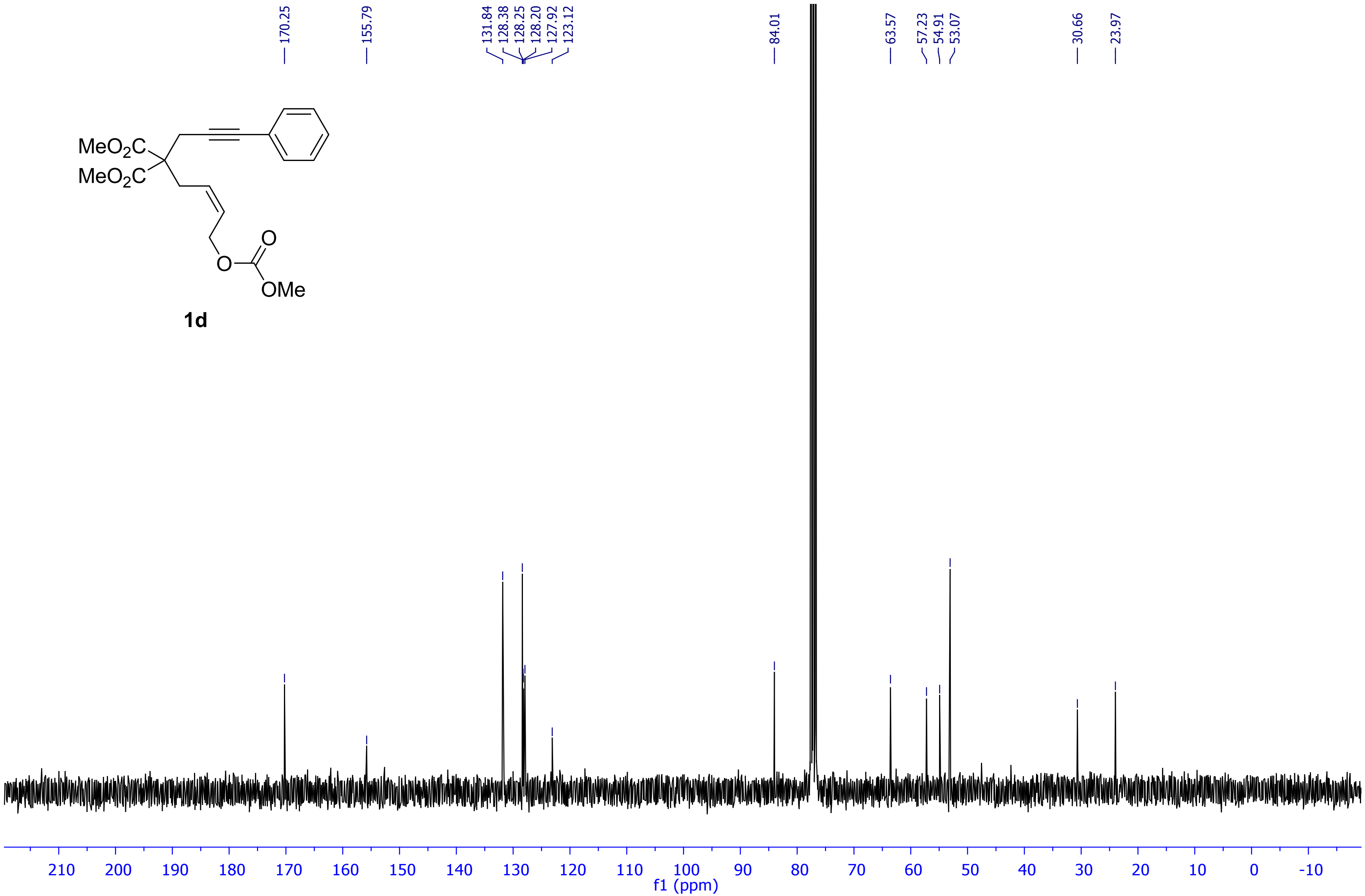


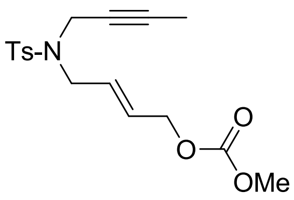
1a



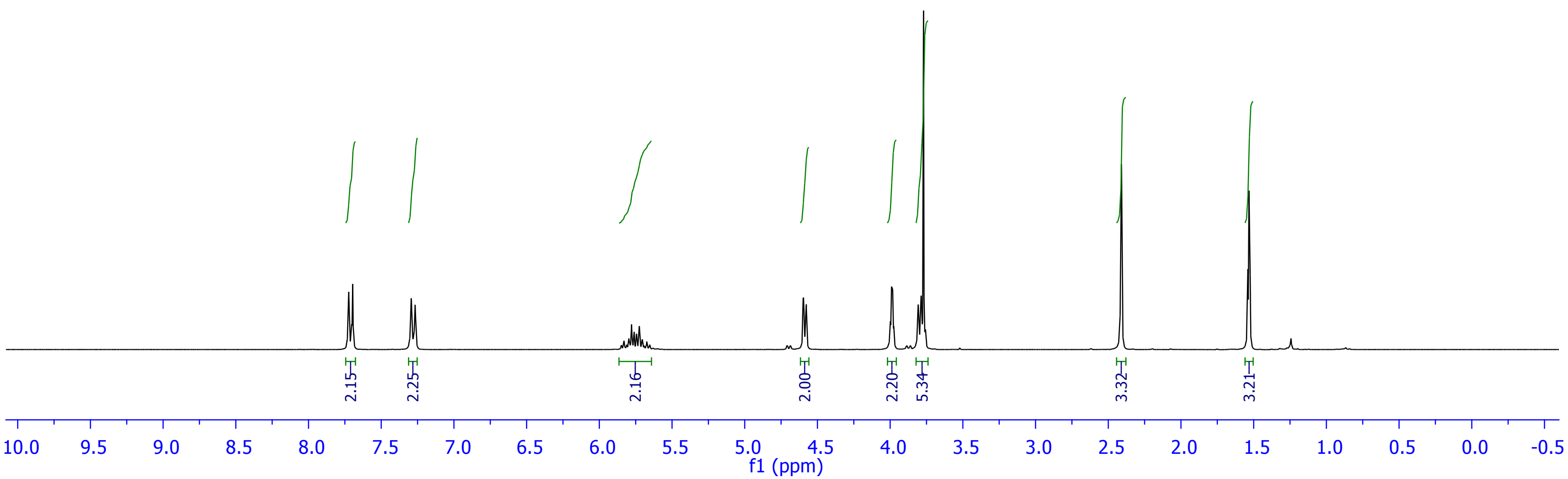
170.38
155.64
129.91
128.37
79.26
73.16
67.96
57.29
54.85
52.80
35.23
23.32
3.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

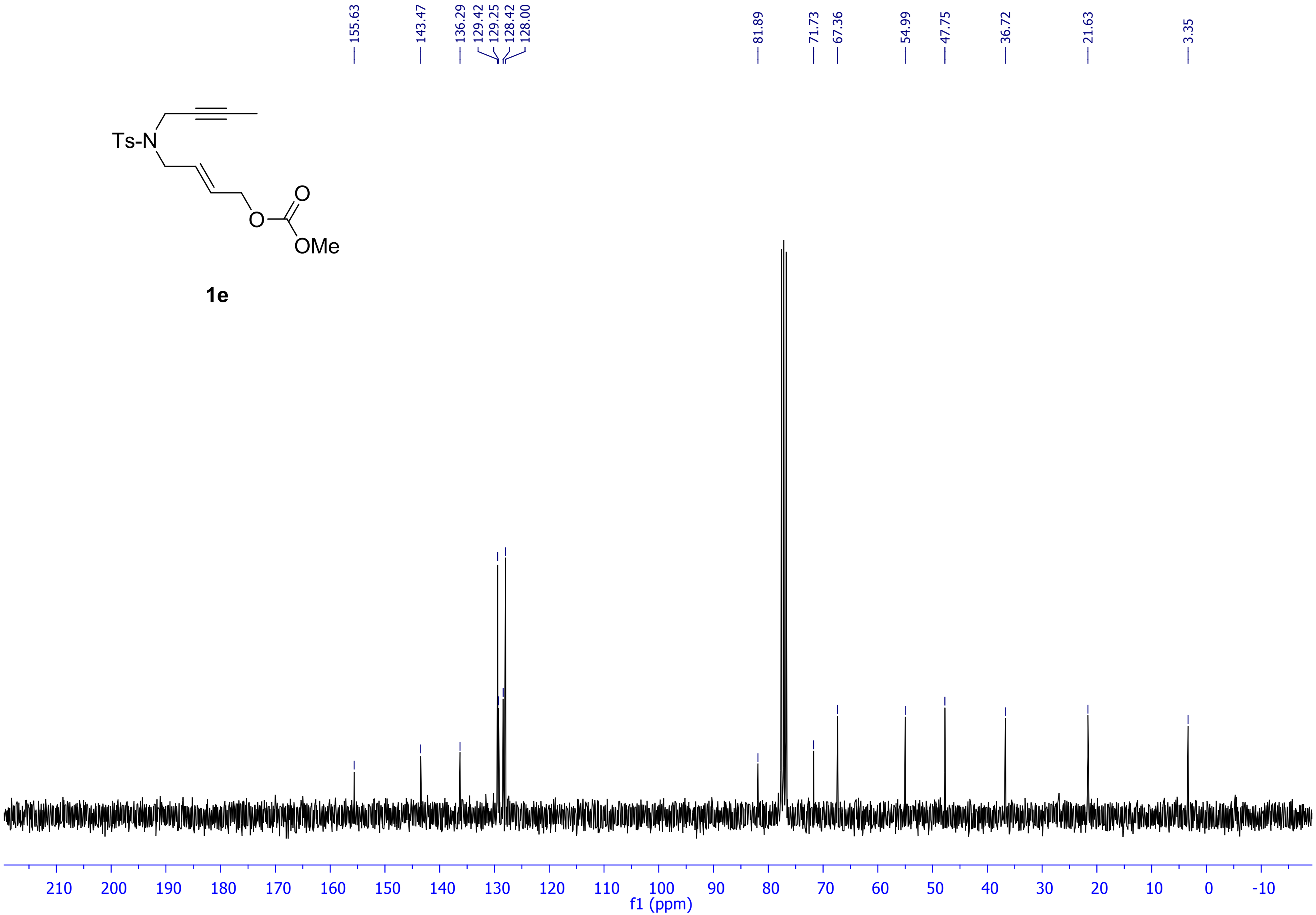

170.36
170.21
155.79
155.63
131.74
129.66
128.66
128.23
128.32
127.67
128.16
123.15
84.05
83.92
79.42
73.20
67.90
63.64
57.33
57.03
54.87
54.86
52.93
52.90
35.44
30.44
23.92
23.24
3.52
MeO2C
OMe
1d
1c
f1 (ppm)

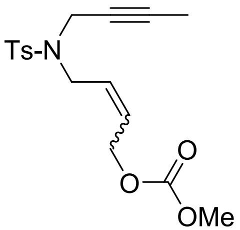

170.25
155.79
131.84
128.38
128.25
128.20
127.92
123.12
84.01
63.57
57.23
54.91
53.07
30.66
23.97
MeO2C
MeO2C
O
O
OMe
1d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ts-N
O
O
OMe

1e

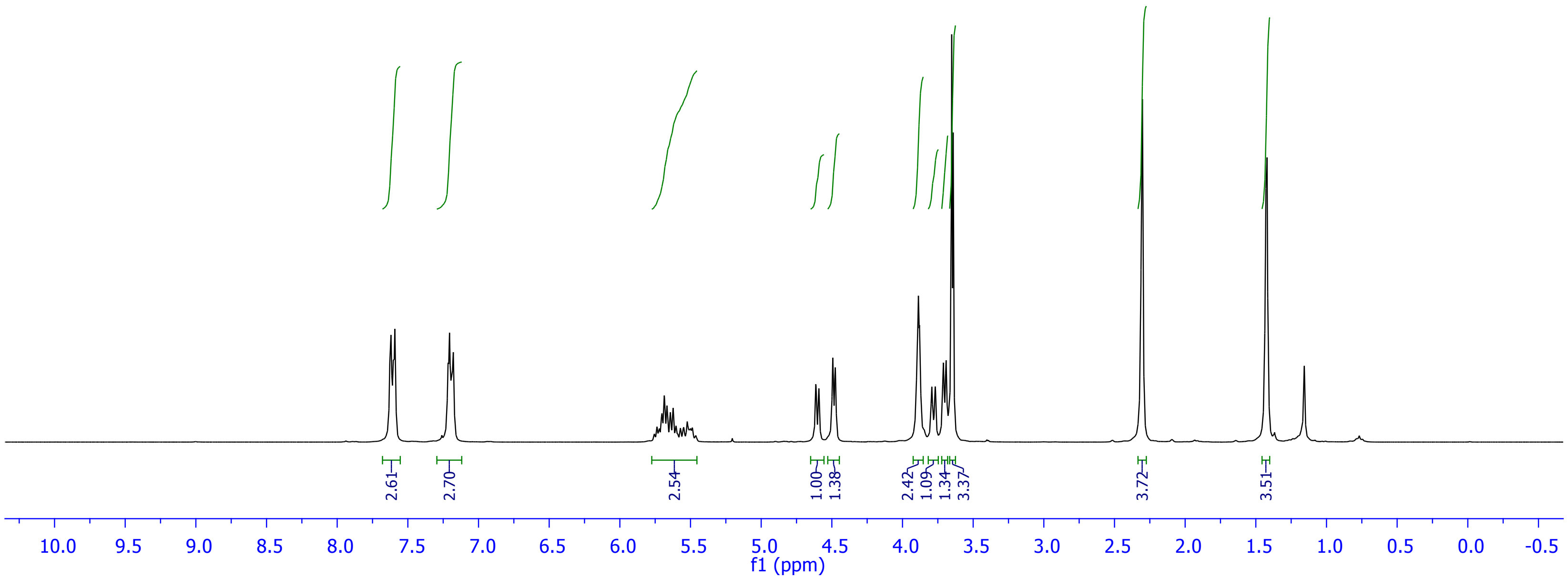

2.15
2.25
2.16
2.00
2.20
5.34
3.32
3.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

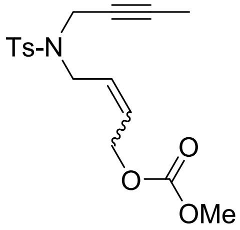

Ts-N
O
O
OMe
1e
155.63
143.47
136.29
129.42
129.25
128.42
128.00
81.89
71.73
67.36
54.99
47.75
36.72
21.63
3.35
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ts-N
O
O
OMe

(*Z*/*E*) 1:1.4

1f

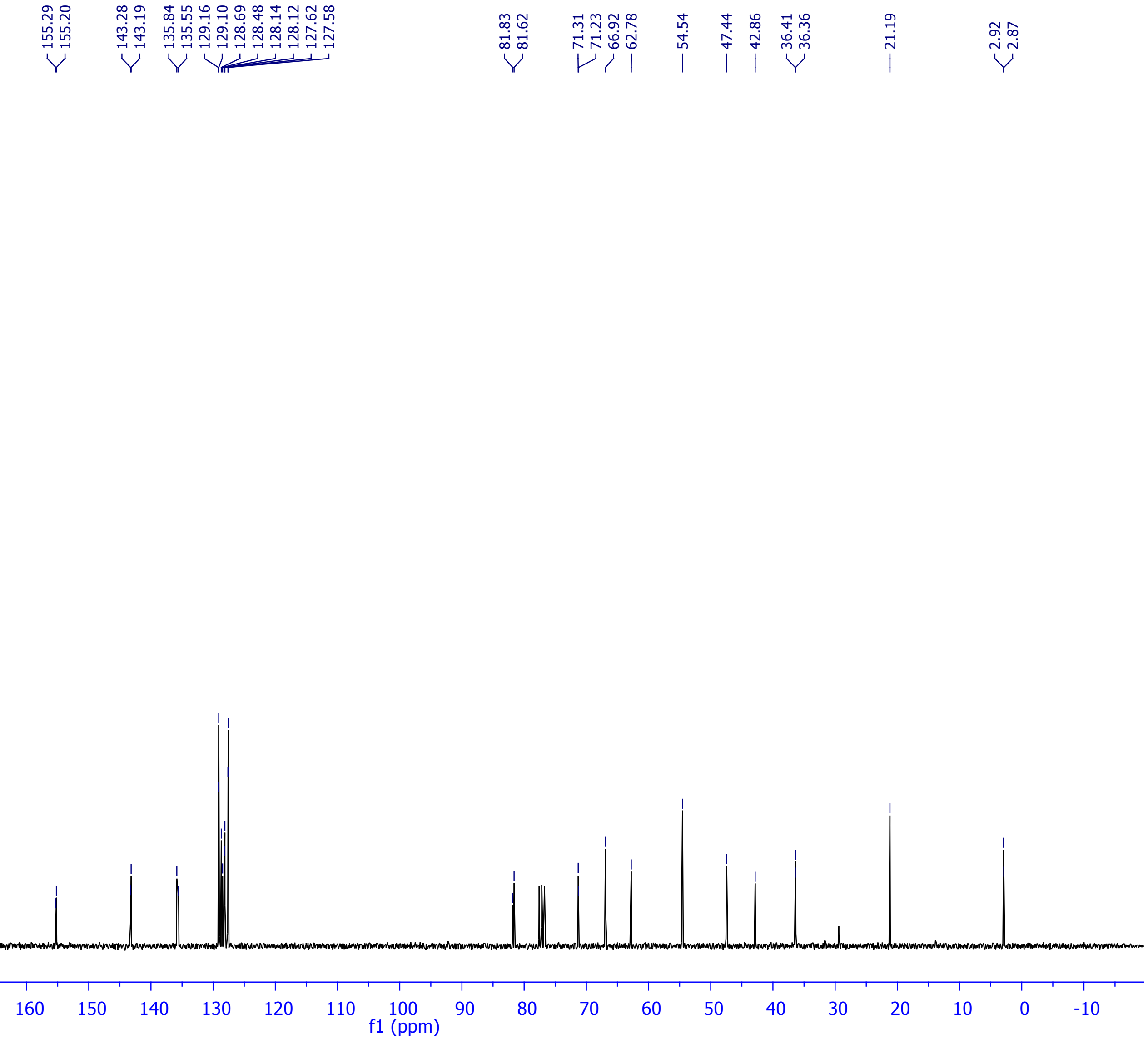

2.61
2.70
2.54
1.00
1.38
2.42
1.09
1.34
3.37
3.72
3.51
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



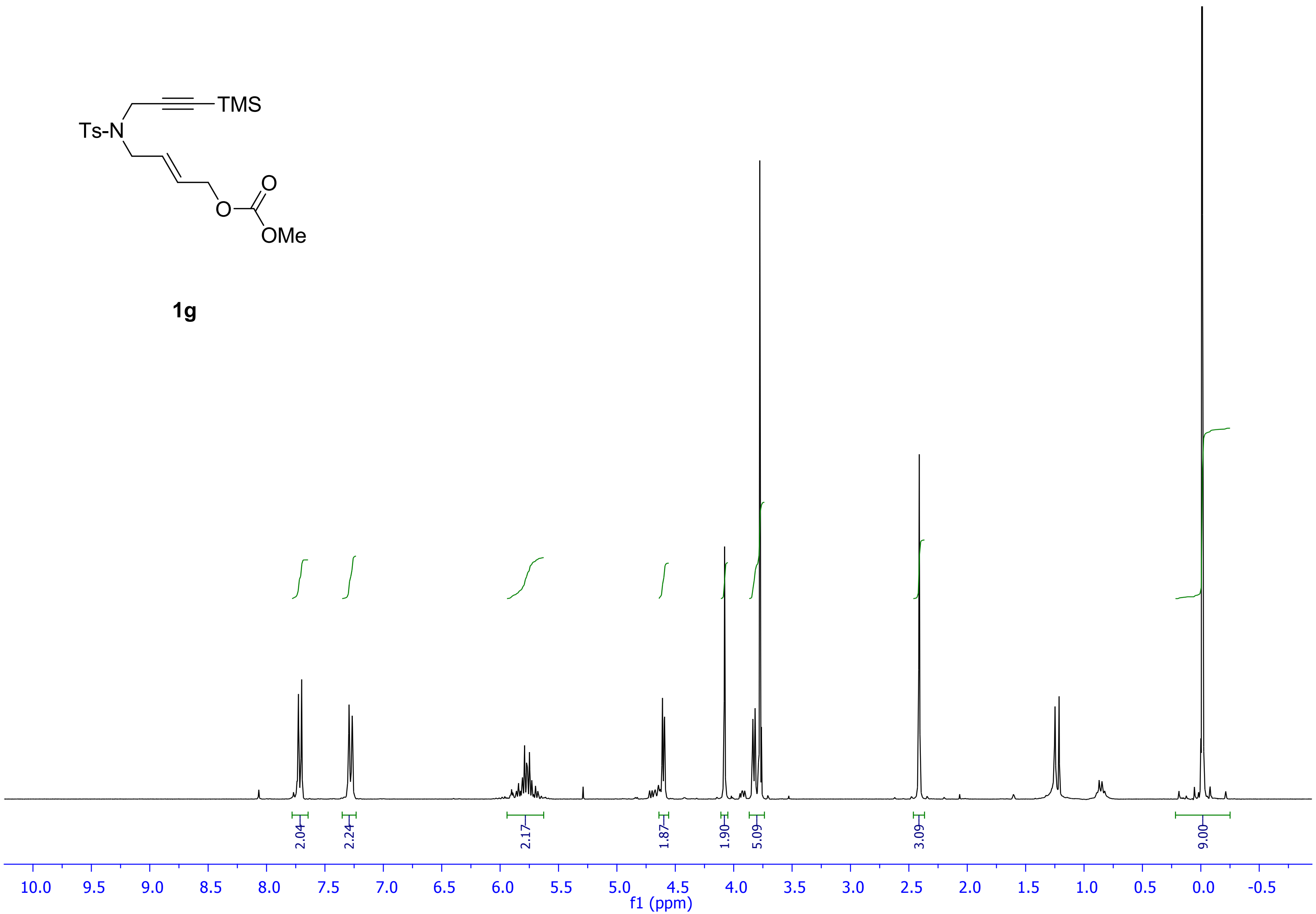
Ts-N
O
O
OMe

(*Z*/*E*) 1:1.4

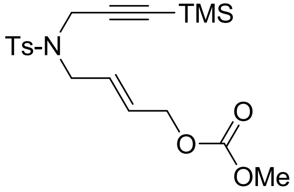
1f



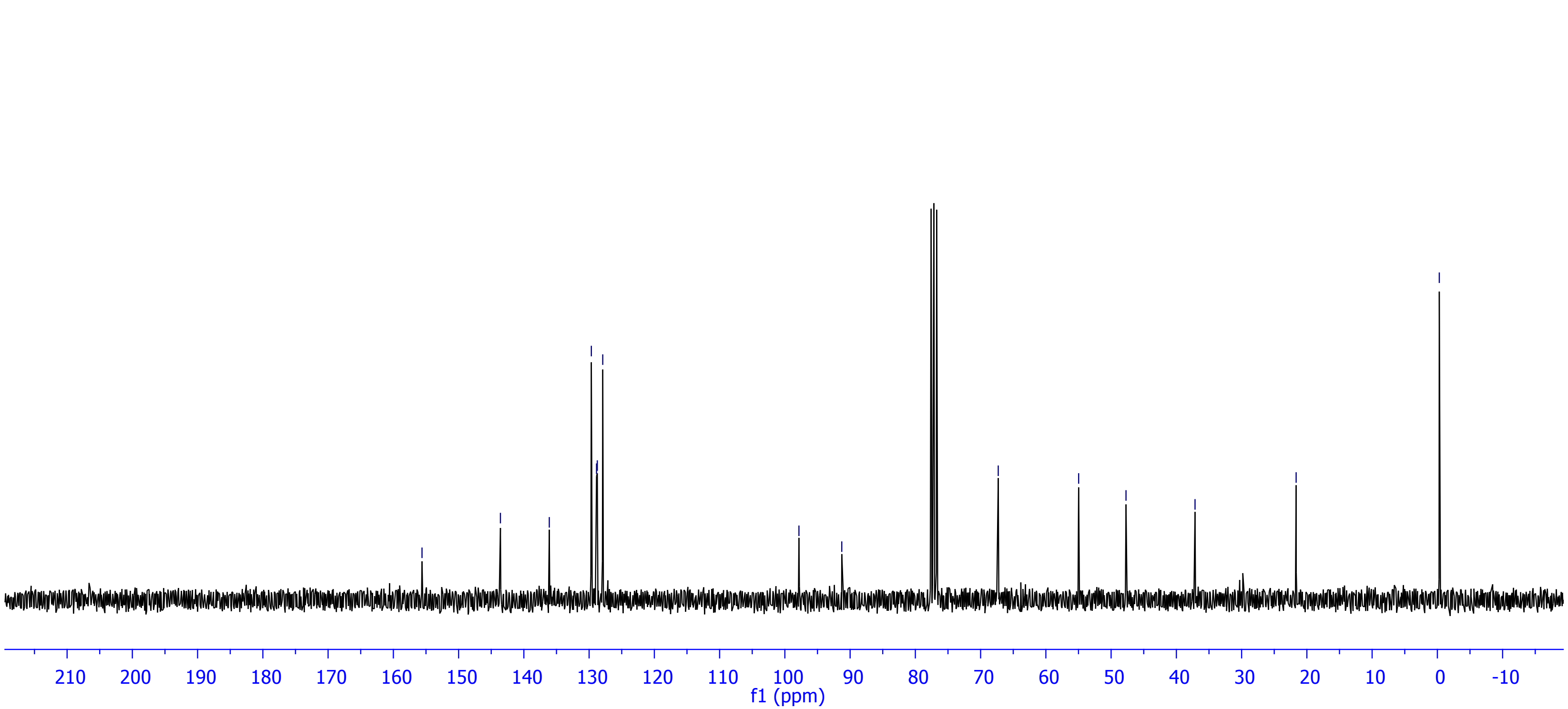
155.29
155.20
143.28
143.19
135.84
135.55
129.16
129.10
128.69
128.48
128.14
128.12
127.62
127.58
81.83
81.62
71.31
71.23
66.92
62.78
54.54
47.44
42.86
36.41
36.36
21.19
2.92
2.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

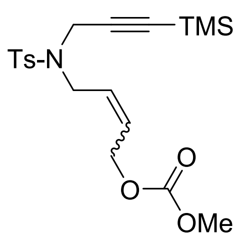

TMS
Ts-N
O
O
OMe
2.04
2.24
2.17
1.87
1.90
5.09
3.09
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

1g


TMS
Ts-N
O
O
OMe

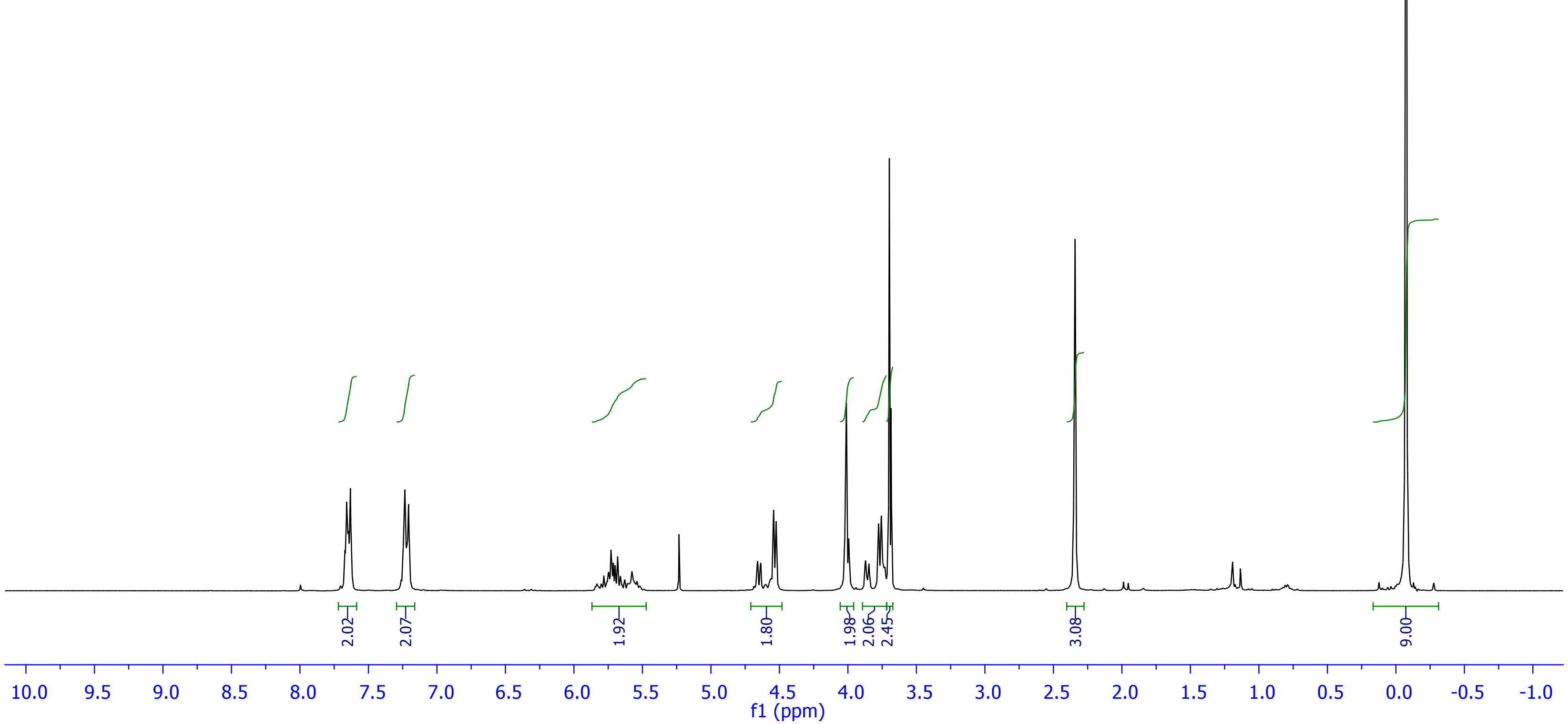
1g


155.61
143.59
136.10
129.66
128.86
128.74
127.91
97.84
91.28
67.30
54.98
47.72
37.14
21.64
-0.30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

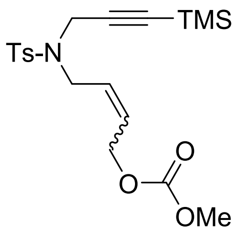


(*Z*/*E*) 0.4:1

1h



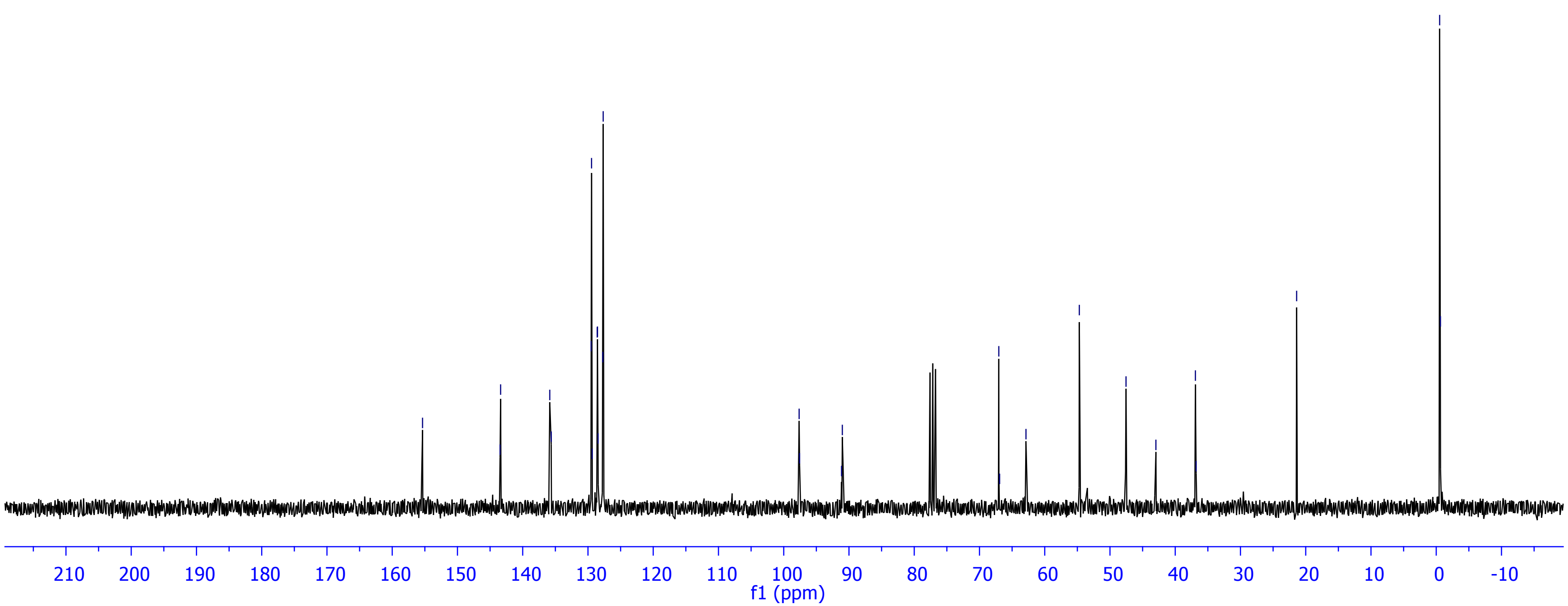
2.02
2.07
1.92
1.80
1.98
2.06
2.45
3.08
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



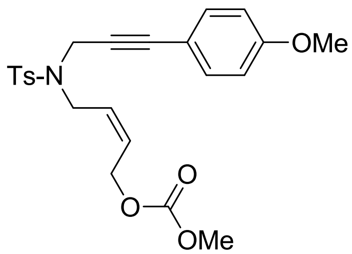
TMS
Ts-N
O
O
OMe

(*Z*/*E*) 0.4:1

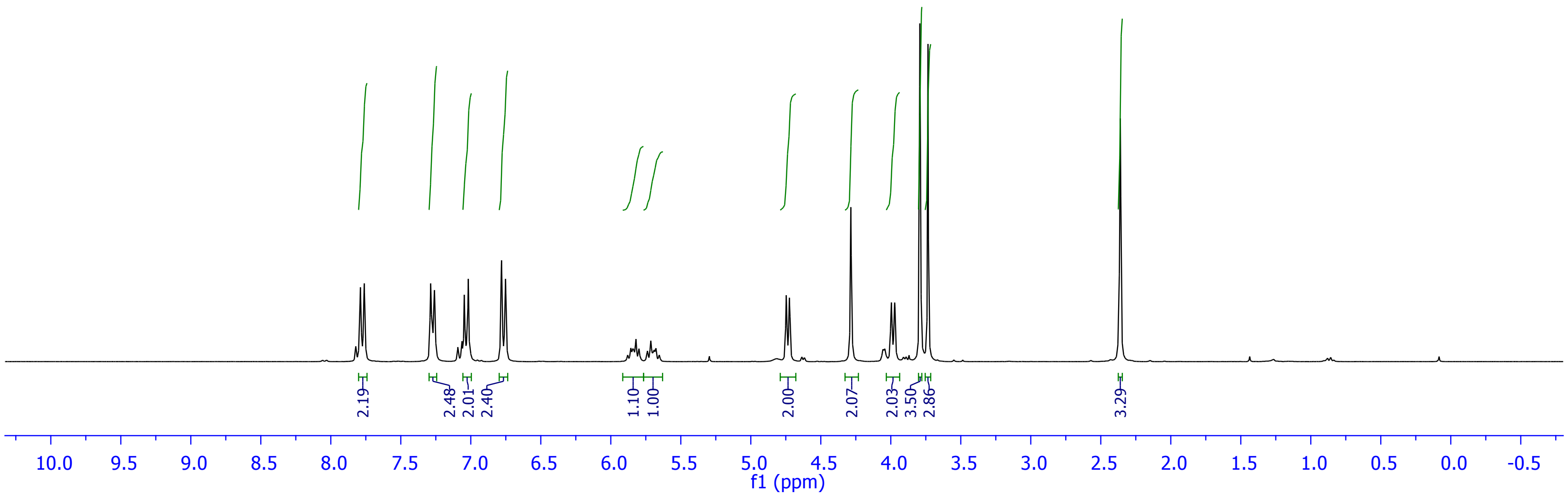
1h

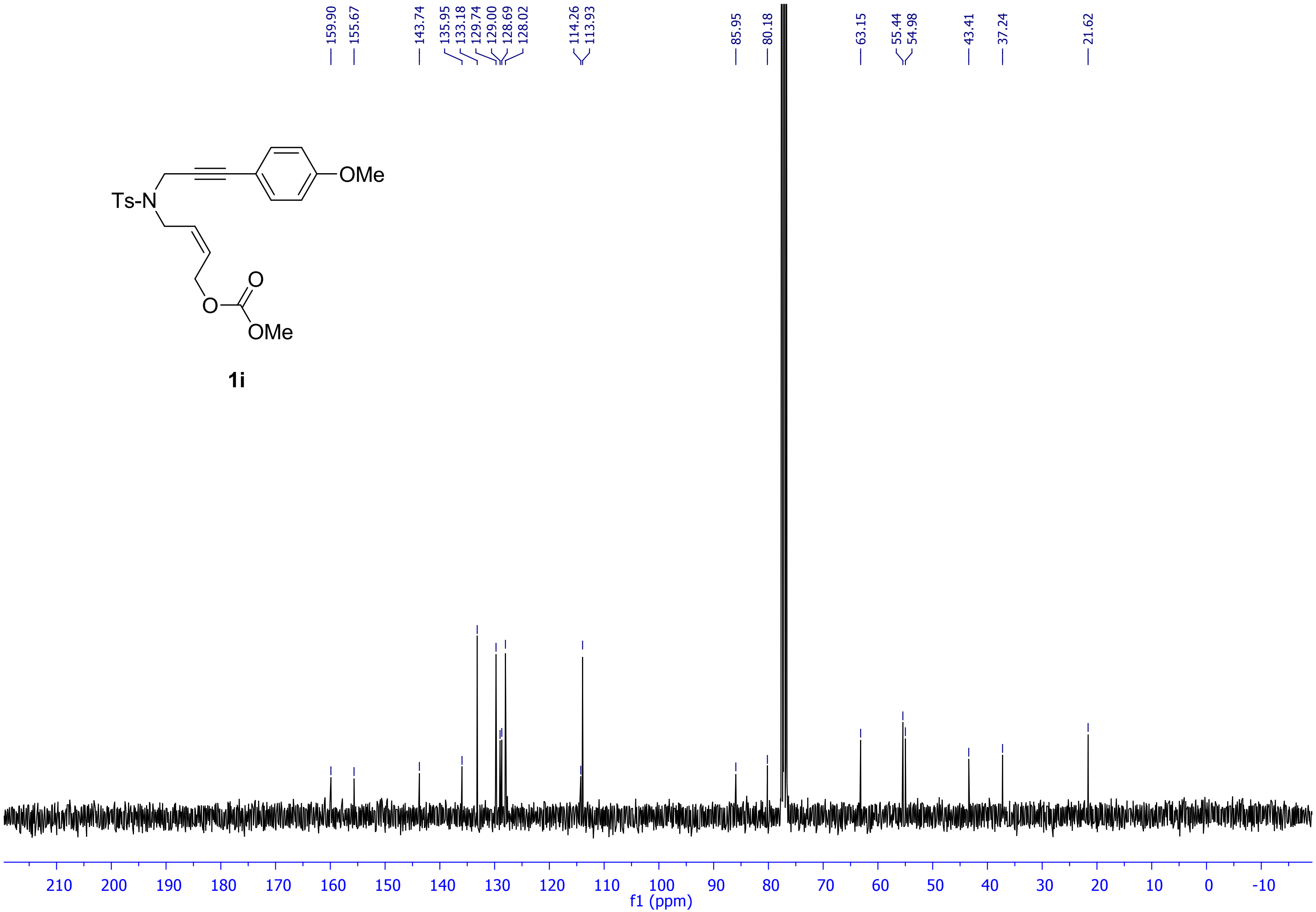


155.35
143.47
143.39
135.85
135.63
129.52
129.46
129.35
128.59
128.54
128.45
127.72
127.67
97.64
97.56
91.14
91.02
67.04
66.92
62.87
54.70
47.54
42.96
36.91
36.80
21.39
-0.53
-0.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ts-N
OMe
O
O
OMe

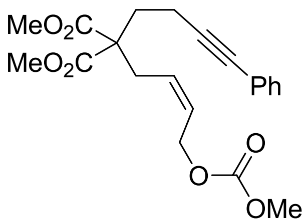
1i


2.19
2.48
2.01
2.40
1.10
1.00
2.00
2.07
2.03
3.50
2.86
3.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

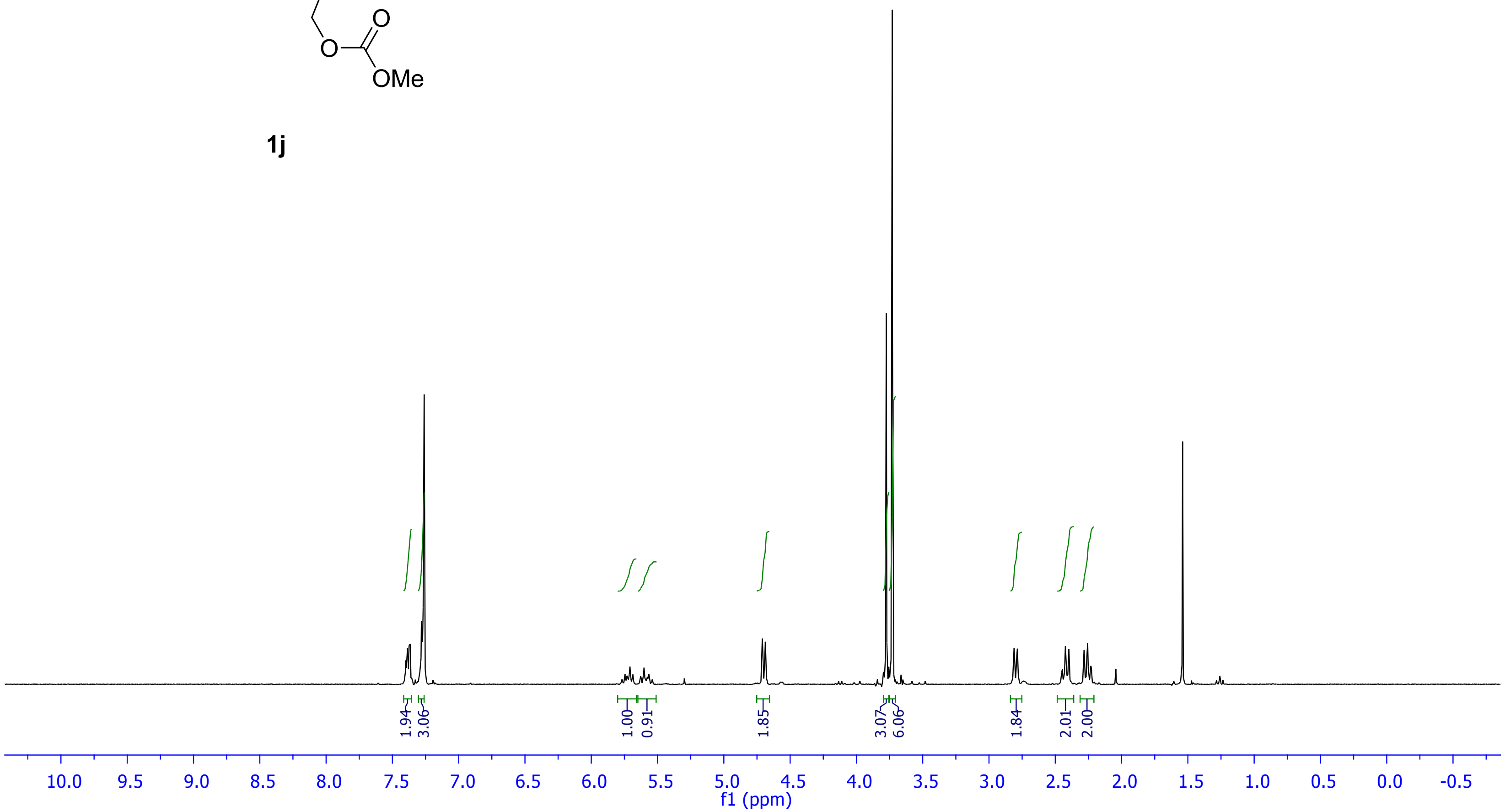


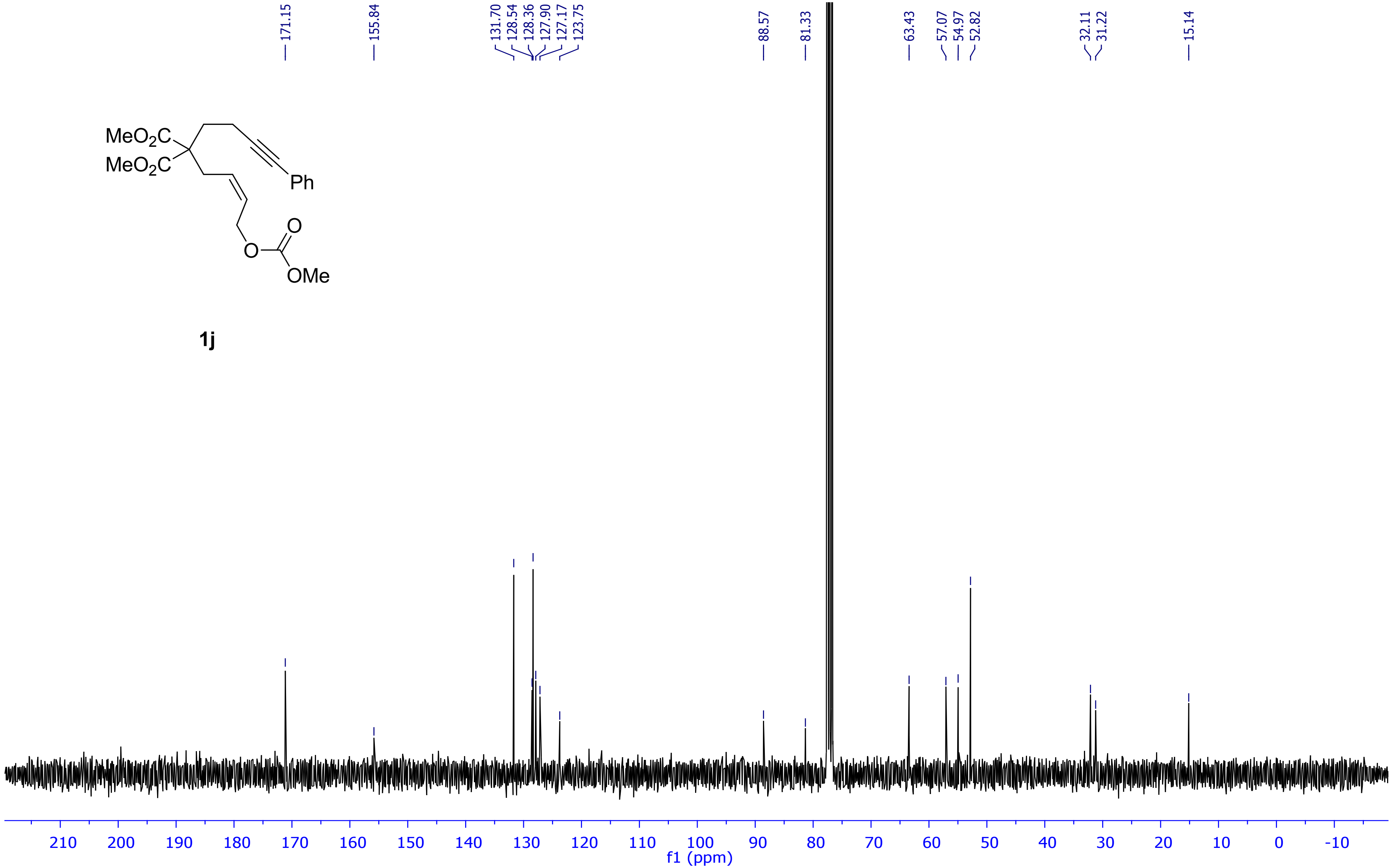
159.90
155.67
143.74
135.95
133.18
129.74
129.00
128.69
128.02
114.26
113.93
85.95
80.18
63.15
55.44
54.98
43.41
37.24
21.62
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

1i

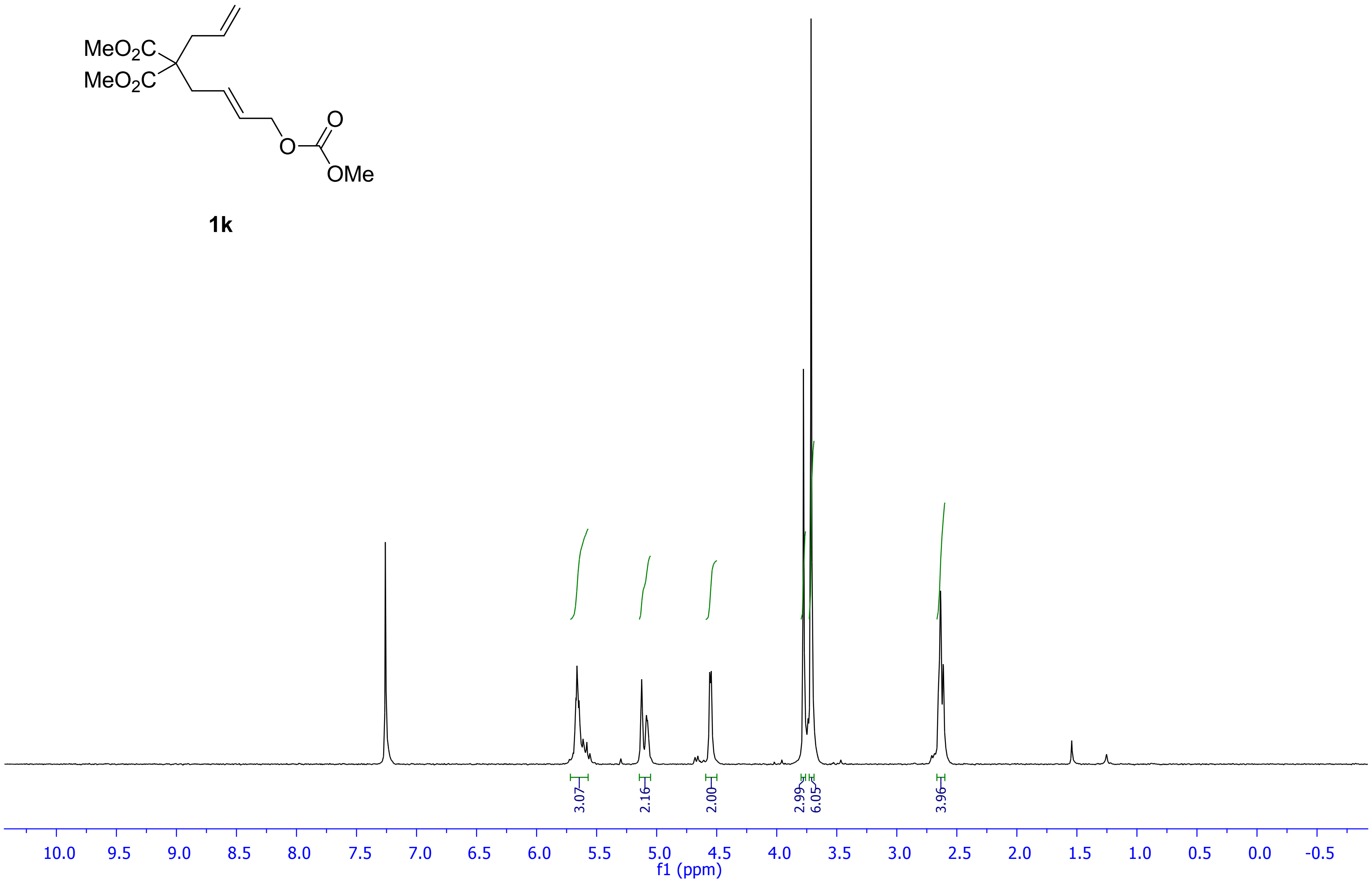

MeO2C
MeO2C
Ph
O
O
OMe

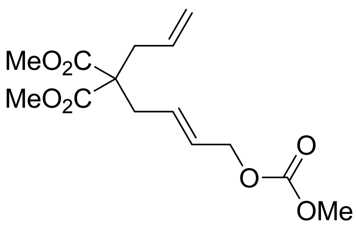
1j


1.94
3.06
1.00
0.91
1.85
3.07
6.06
1.84
2.01
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

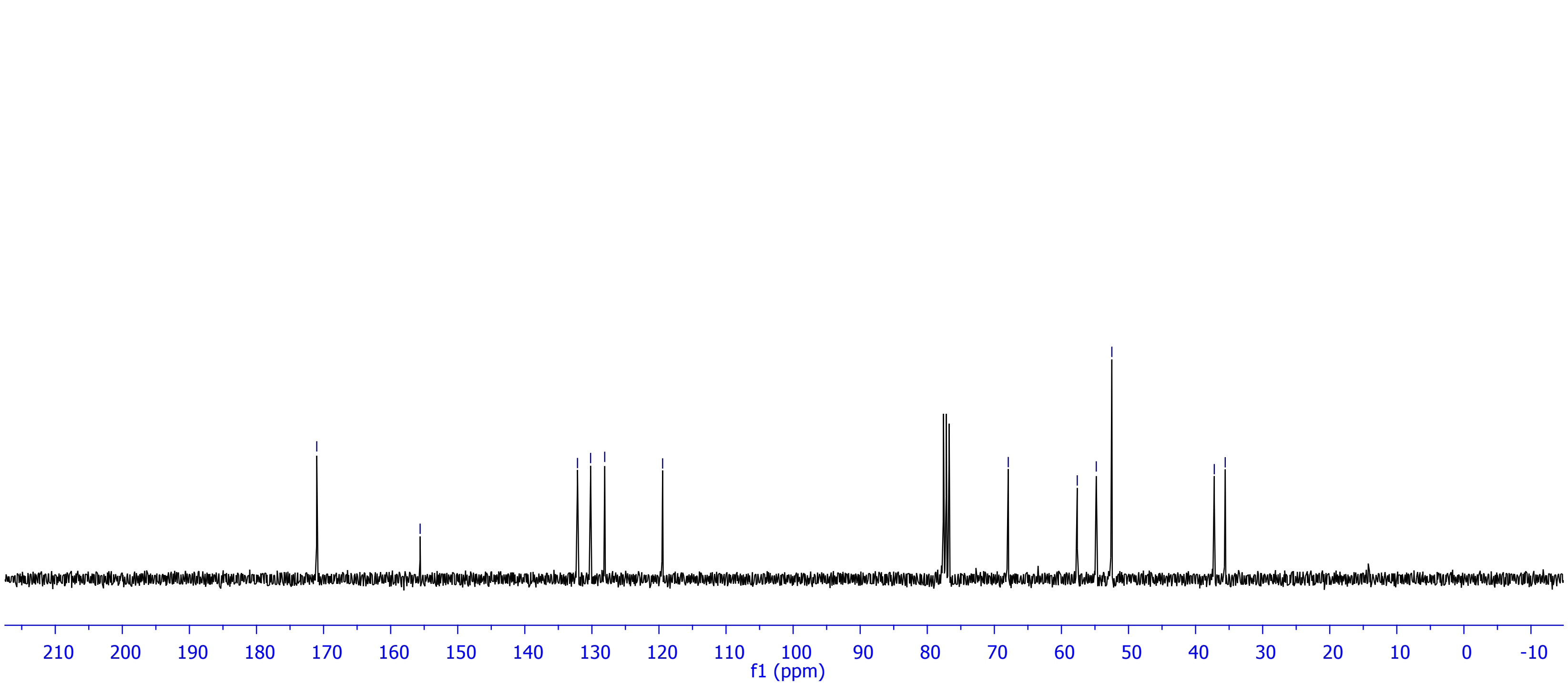

MeO2C
MeO2C
Ph
O
O
OMe
171.15
155.84
131.70
128.54
128.36
127.90
127.17
123.75
88.57
81.33
63.43
57.07
54.97
52.82
32.11
31.22
15.14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

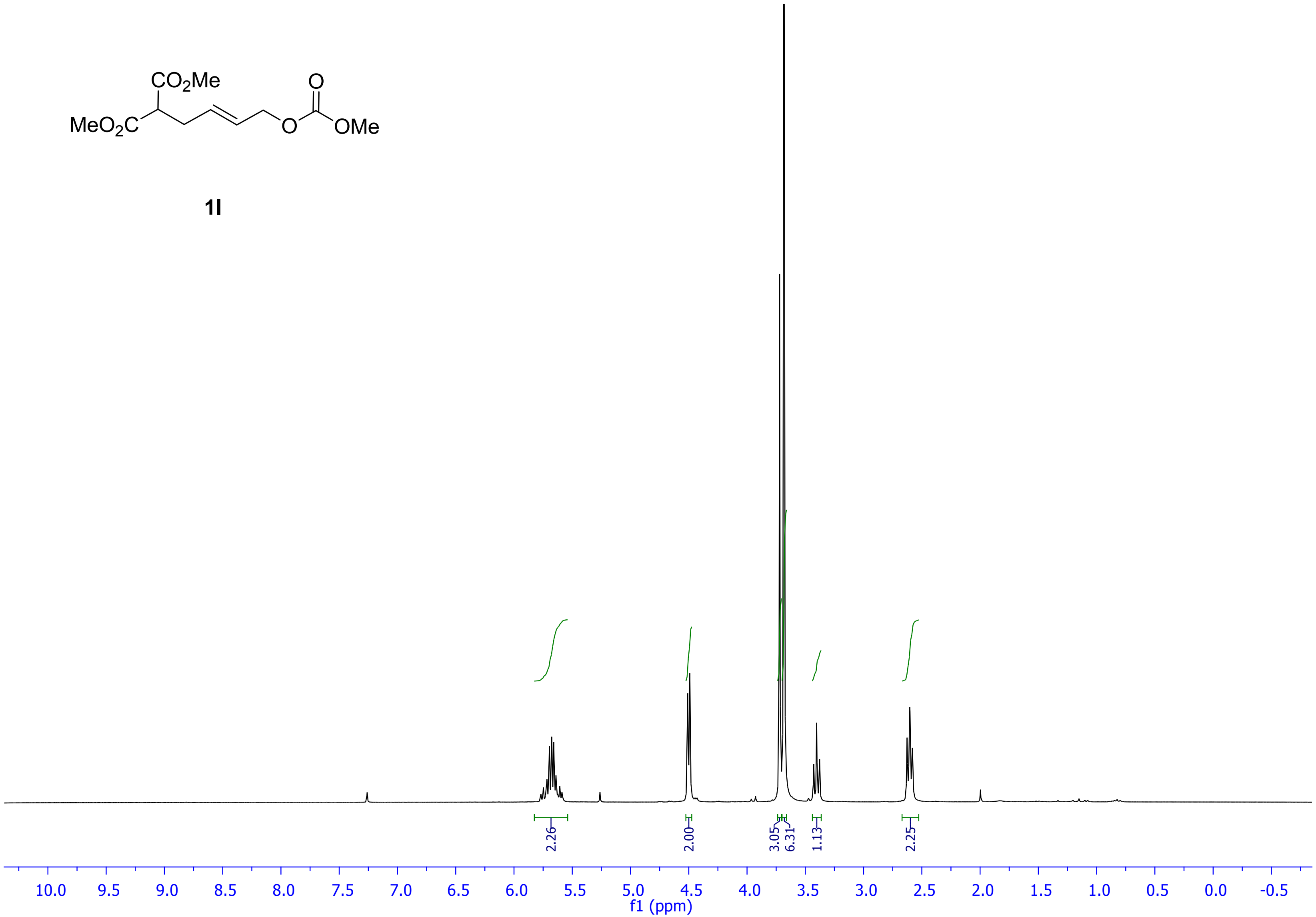
1j

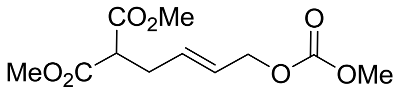

MeO2C
MeO2C
O
O
OMe
1k
3.07
2.16
2.00
2.99
6.05
3.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



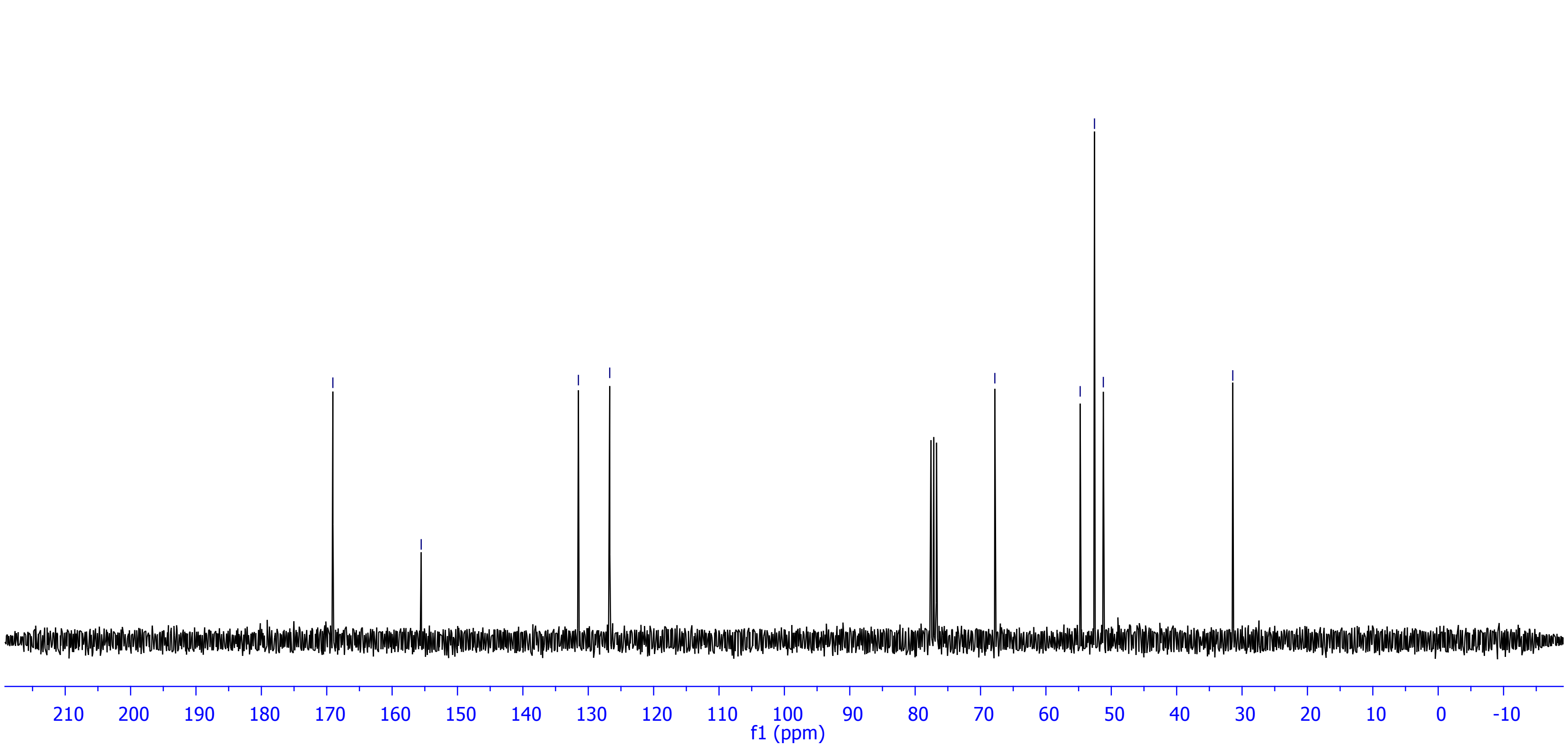
1k

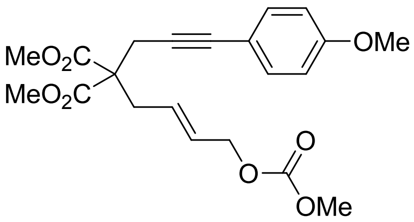

171.01
155.60
132.15
130.19
128.08
119.45
67.92
57.64
54.81
52.48
37.21
35.58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CO2Me
O
MeO2C
O
OMe
1l
2.26
2.00
3.05
6.31
1.13
2.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

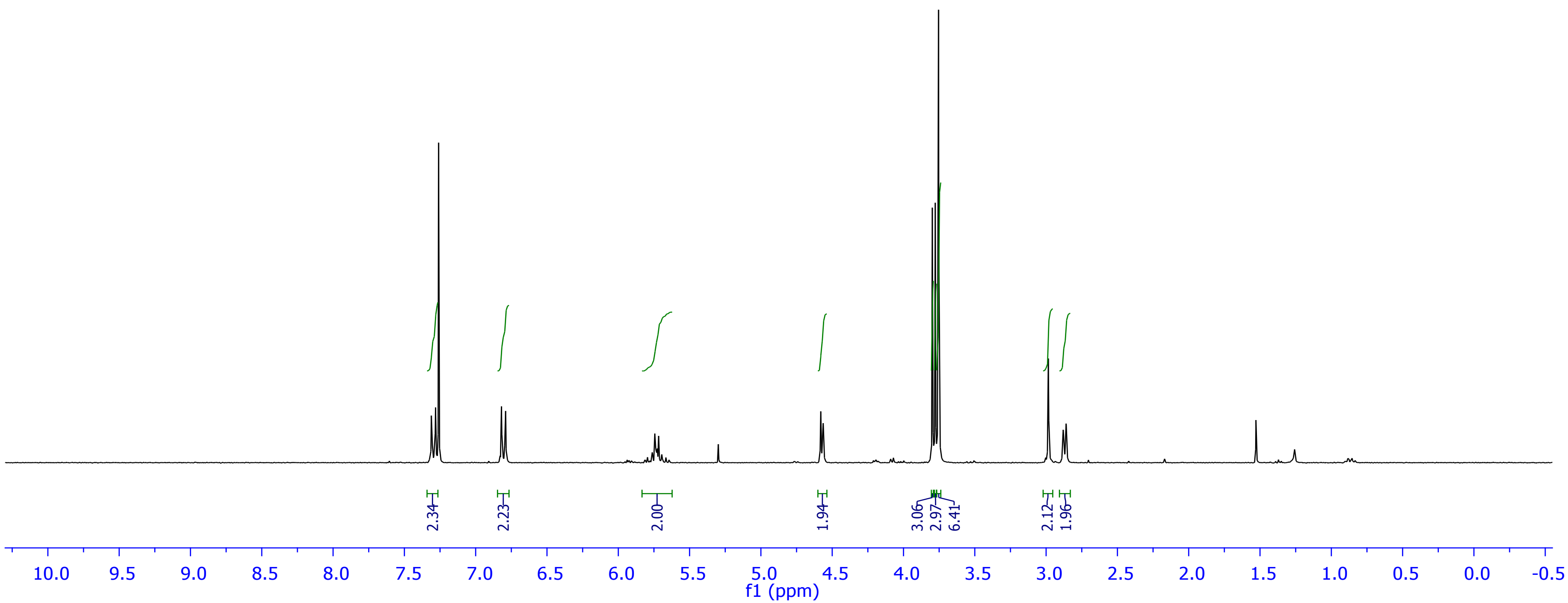

CO2Me
MeO2C
O
O
OMe

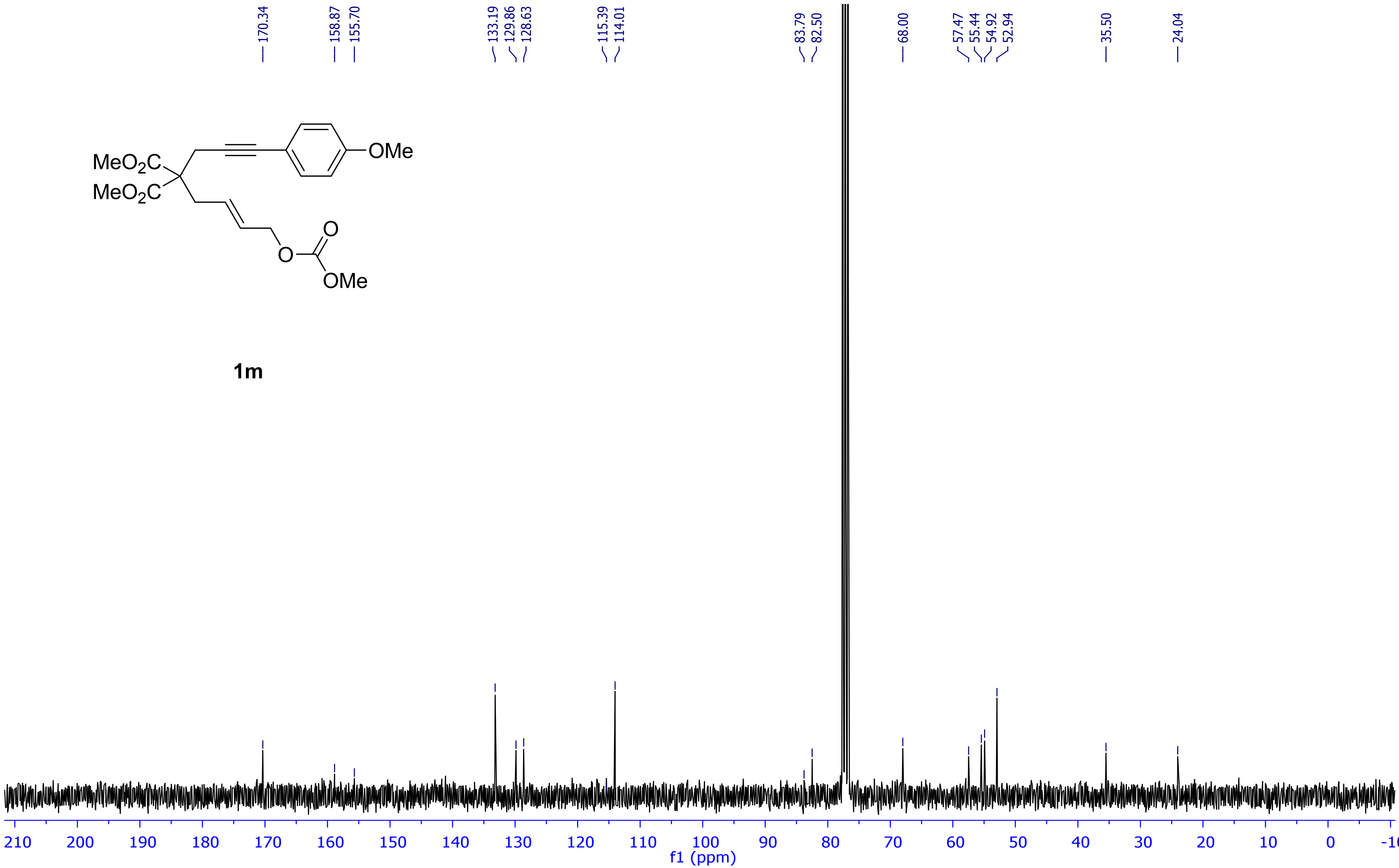
1l


169.06
155.55
131.51
126.72
67.81
54.76
52.57
51.22
31.42
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO2C
MeO2C
OMe
O
O
OMe

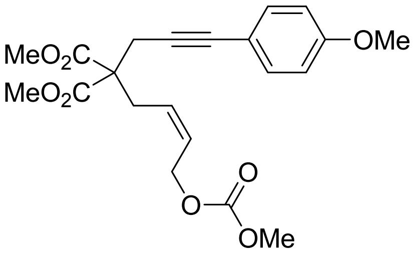
1m


2.34
2.23
2.00
1.94
3.06
2.97
6.41
2.12
1.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

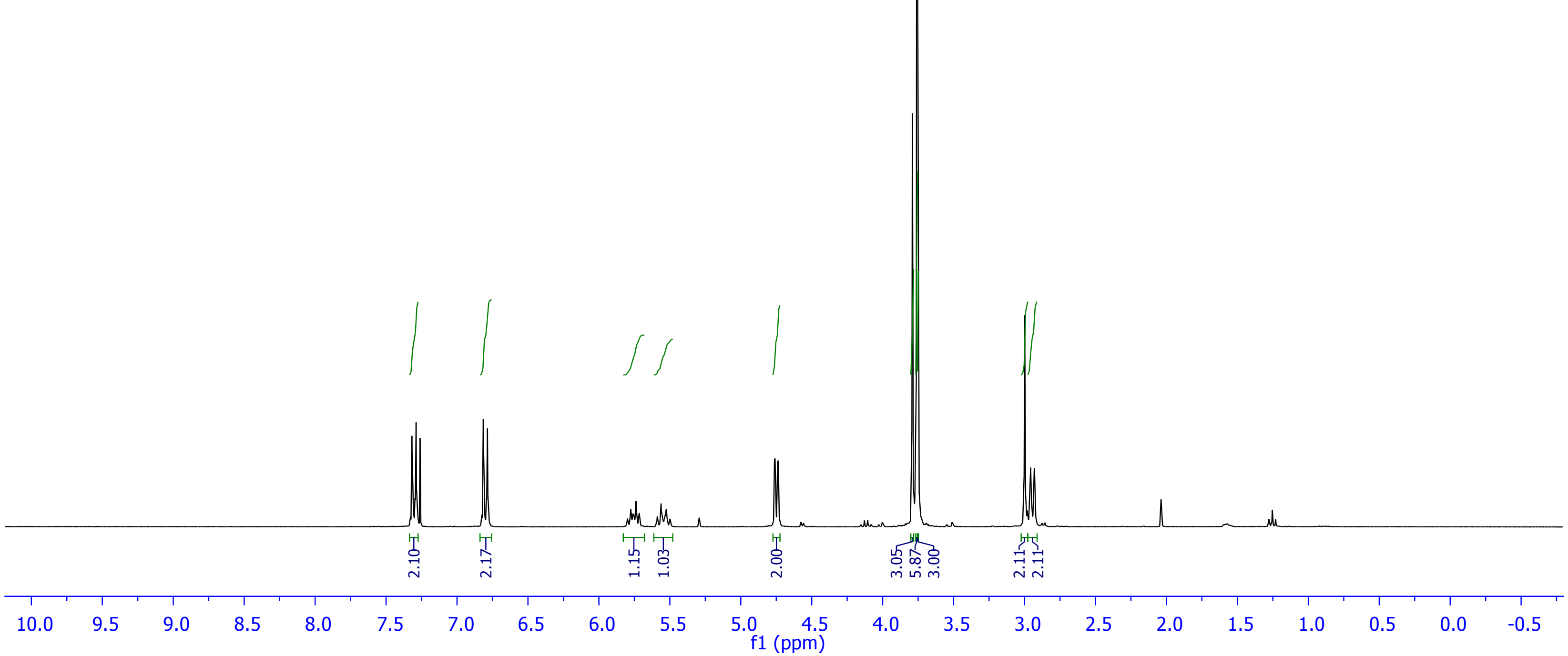


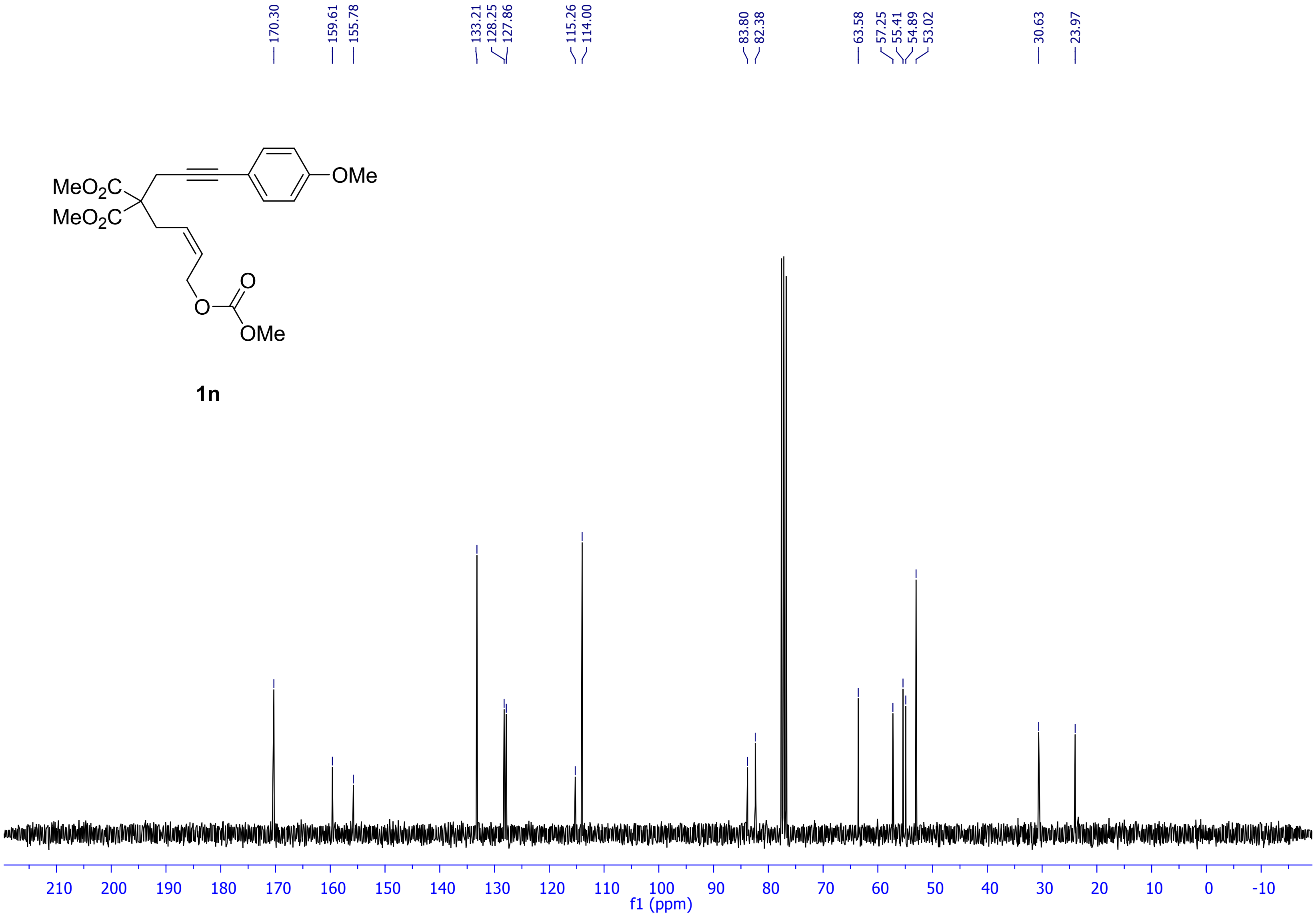
170.34
158.87
155.70
133.19
129.86
128.63
115.39
114.01
83.79
82.50
68.00
57.47
55.44
54.92
52.94
35.50
24.04
MeO2C
MeO2C
OMe
O
O
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1m

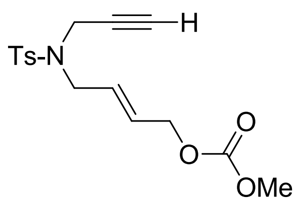

MeO2C
MeO2C
OMe
O
O
OMe

1n


2.10
2.17
1.15
1.03
2.00
3.05
5.87
3.00
2.11
2.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

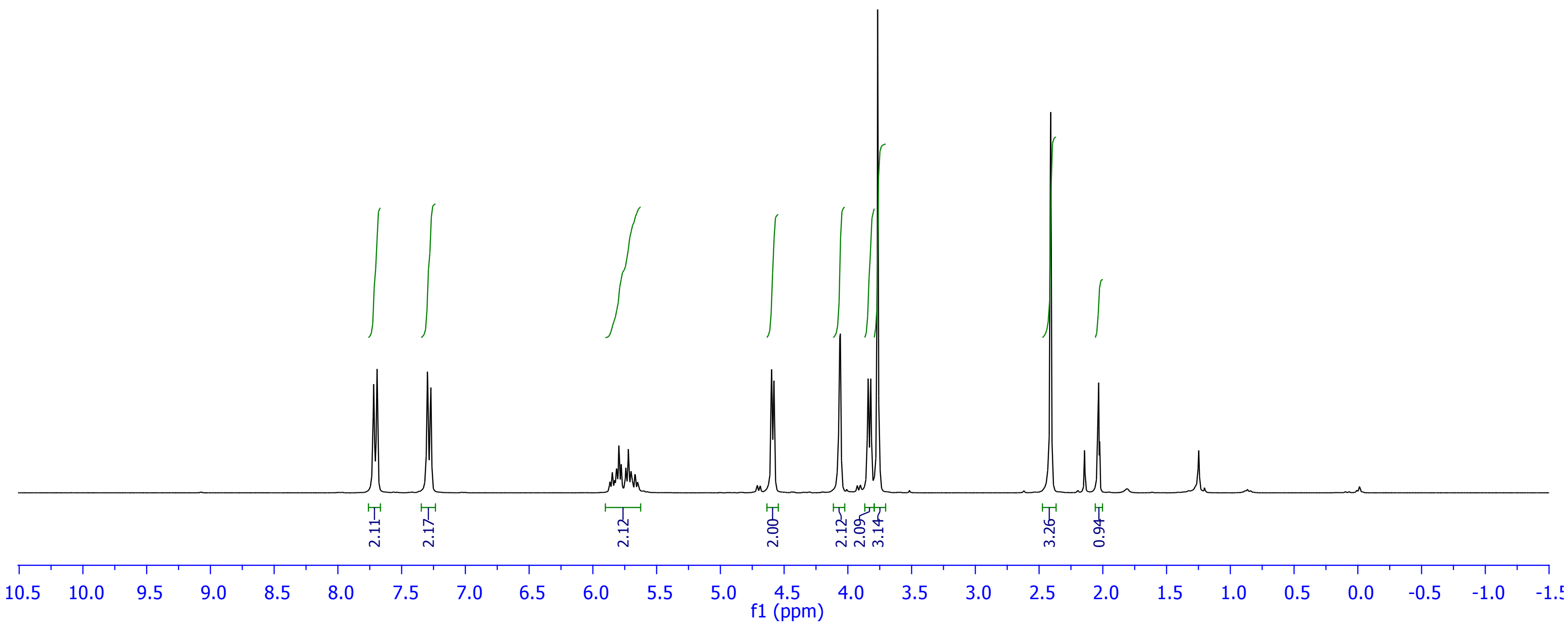

170.30
159.61
155.78
133.21
128.25
127.86
115.26
114.00
83.80
82.38
63.58
57.25
55.41
54.89
53.02
30.63
23.97
MeO2C
MeO2C
OMe
O
O
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1n

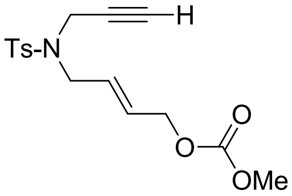


Ts-N
H
O
O
OMe

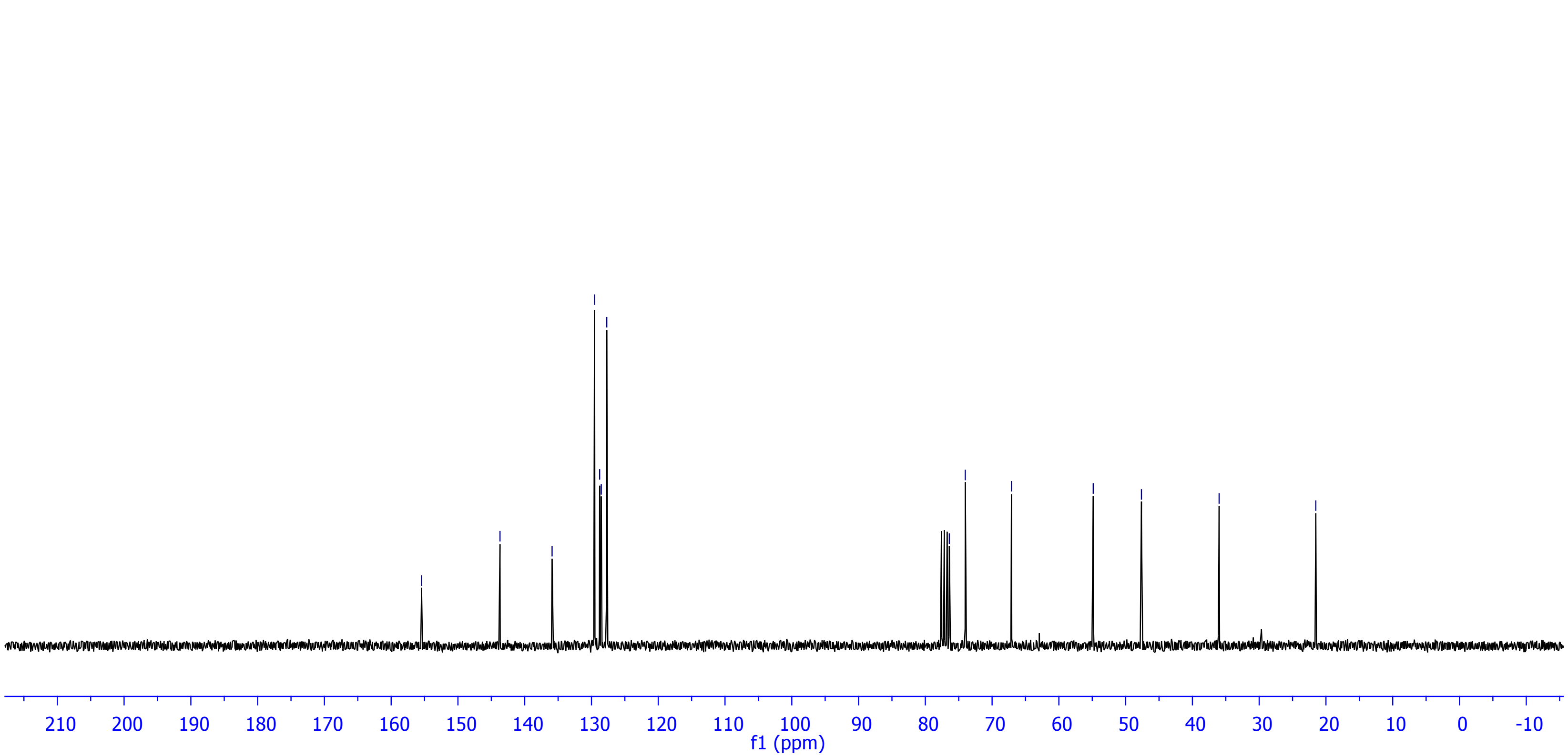
1o

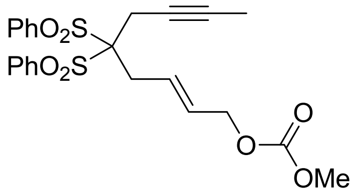


2.11
2.17
2.12
2.00
2.12
2.09
3.14
3.26
0.94
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

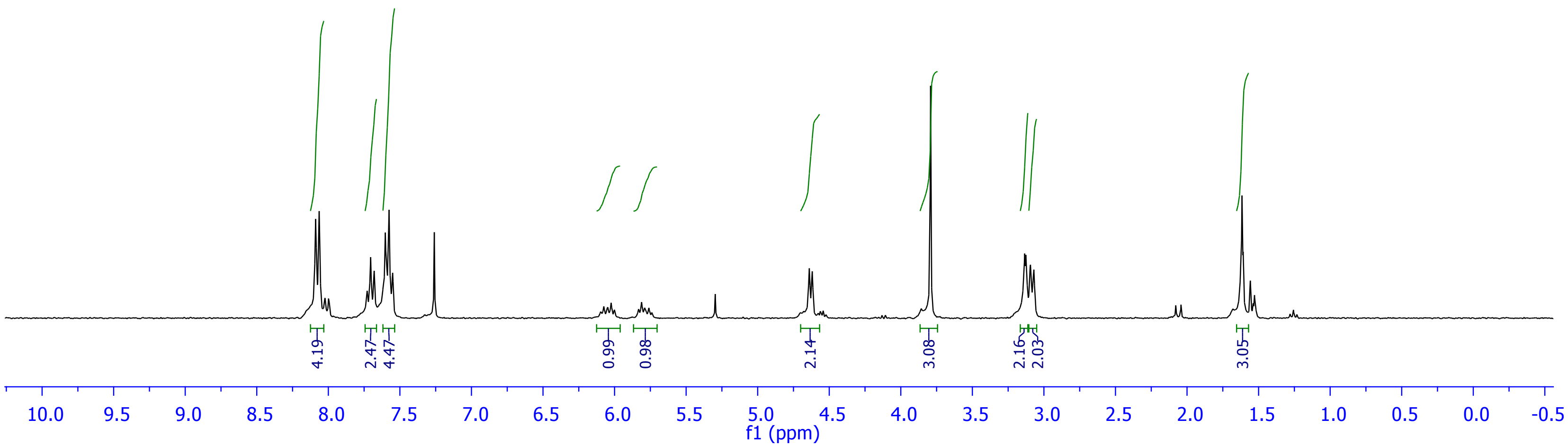

Ts-N
H
O
O
OMe

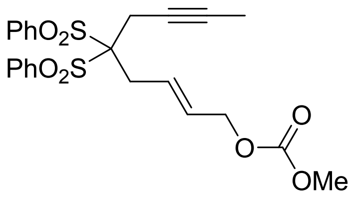
1o


155.45
143.70
135.90
129.54
128.78
128.54
127.71
76.41
74.02
67.10
54.85
47.63
36.00
21.52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

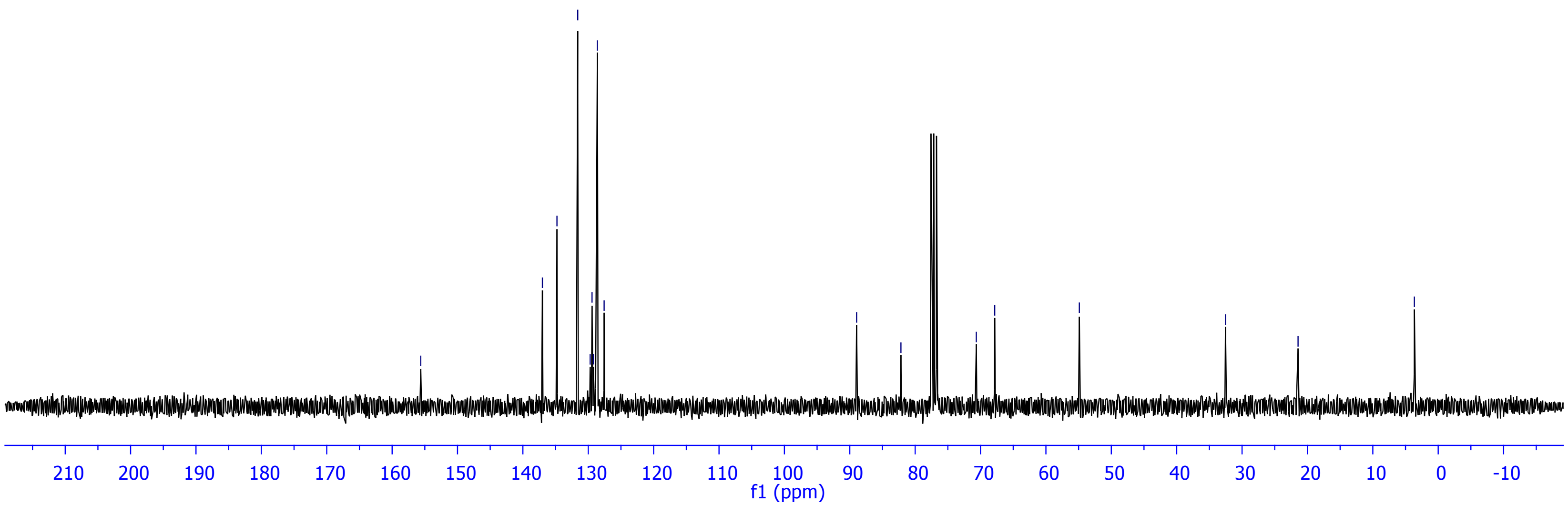

PhO2S
PhO2S
O
O
OMe

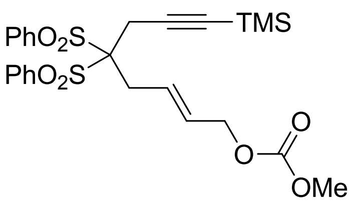
1p


4.19
2.47
4.47
0.99
0.98
2.14
3.08
2.16
2.03
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

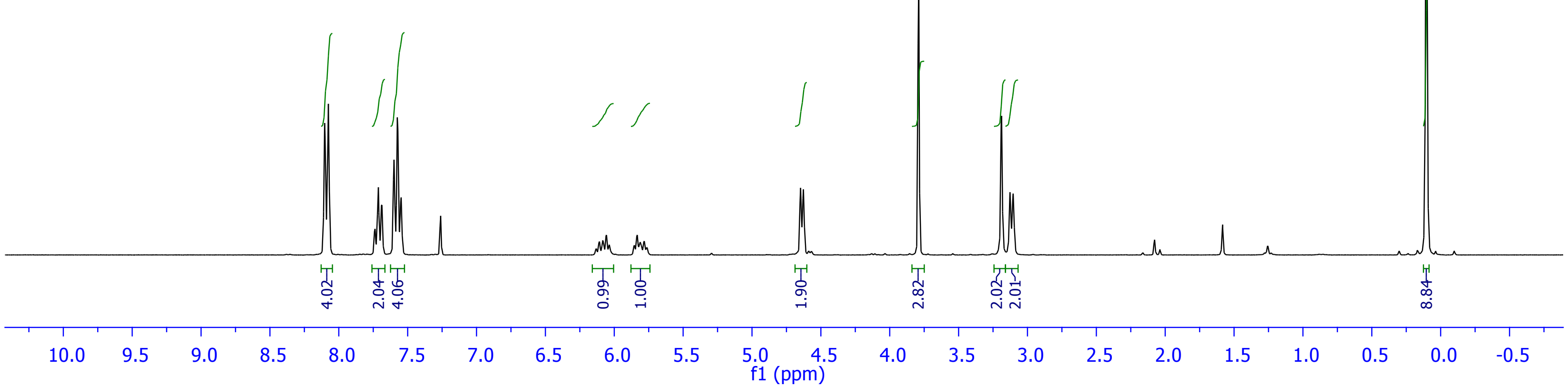

PhO2S
PhO2S
O
O
OMe

1p

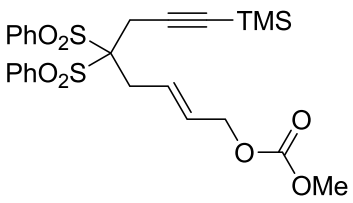

155.62
137.02
134.79
131.61
129.71
129.42
129.22
128.61
127.57
88.95
82.18
70.65
67.83
54.89
32.53
21.43
3.65
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



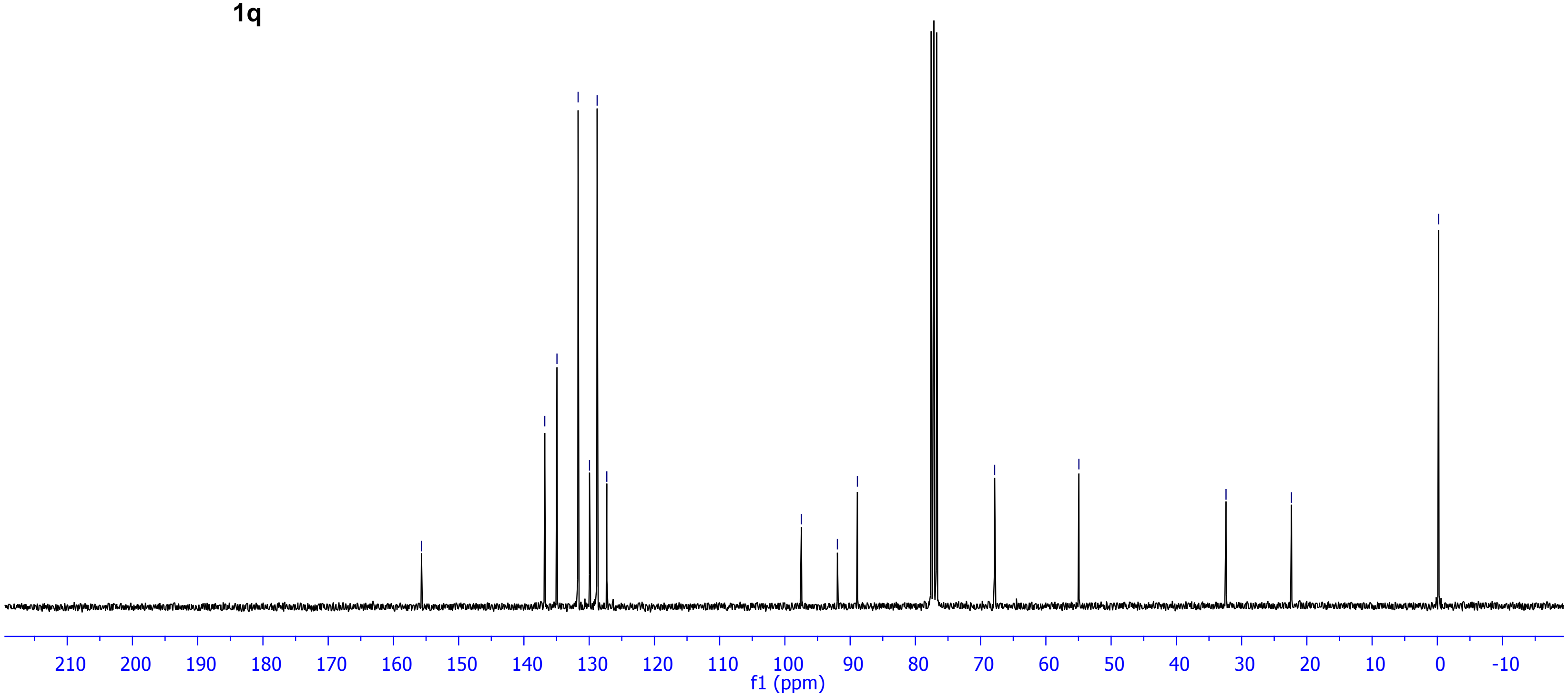
1q



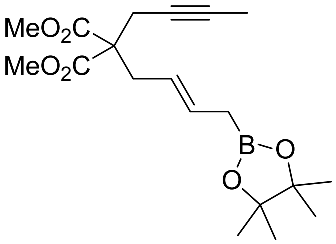
4.02
2.04
4.06
0.99
1.00
1.90
2.82
2.02
2.01
8.84
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


PhO2S
PhO2S
TMS
O
O
OMe

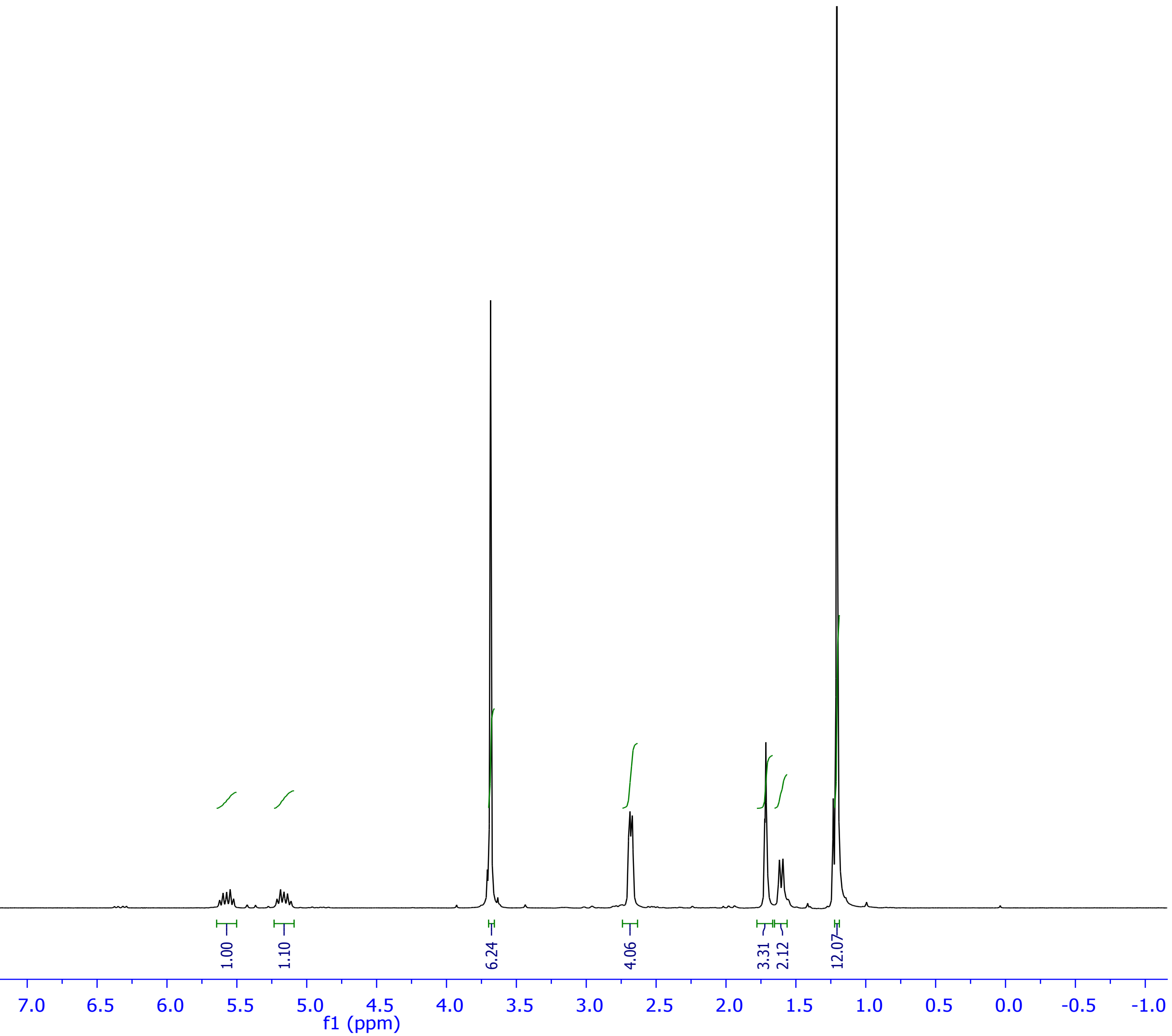
1q

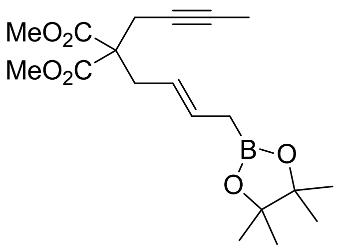

155.70
136.80
134.93
131.70
129.95
128.78
127.30
97.48
91.96
88.89
67.85
54.94
32.39
22.36
-0.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

[1]H-NMR and [13]C-NMR spectra of allylboronates

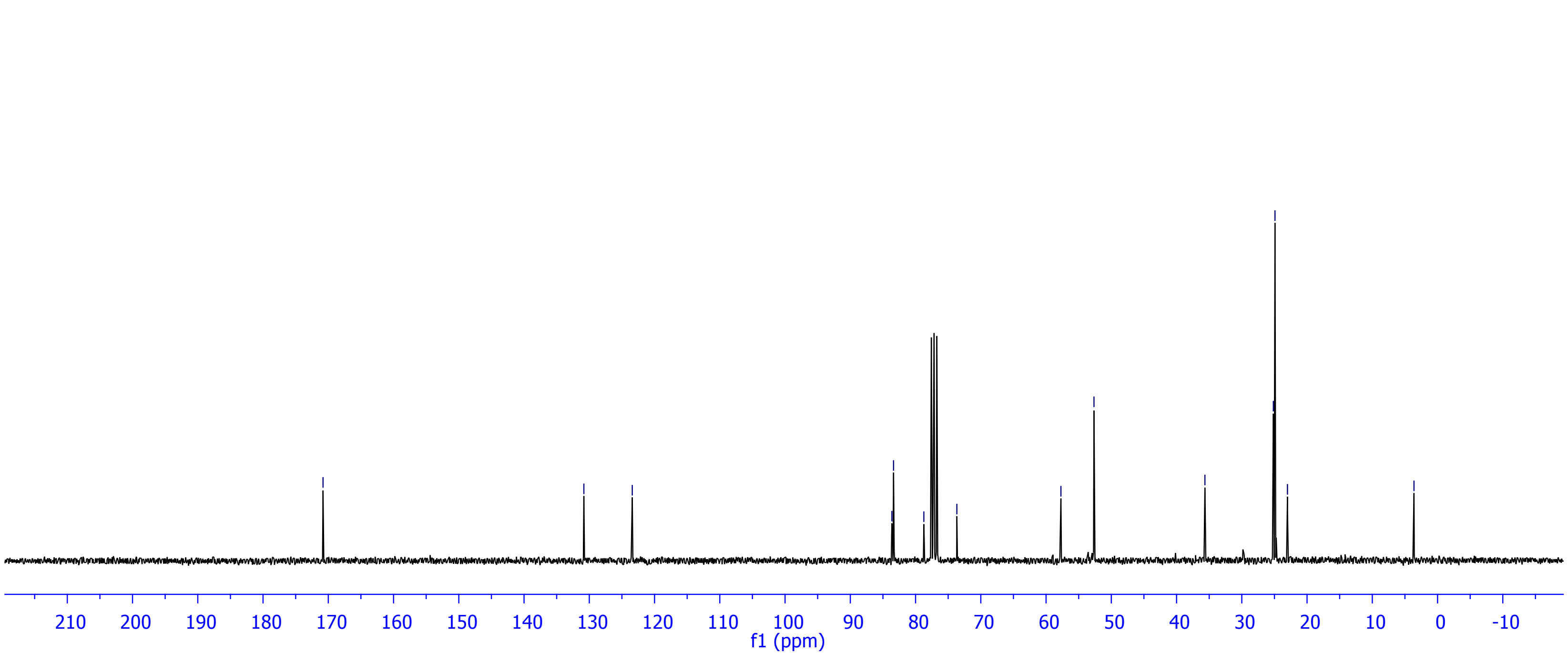


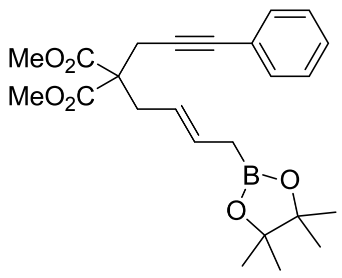
2ab



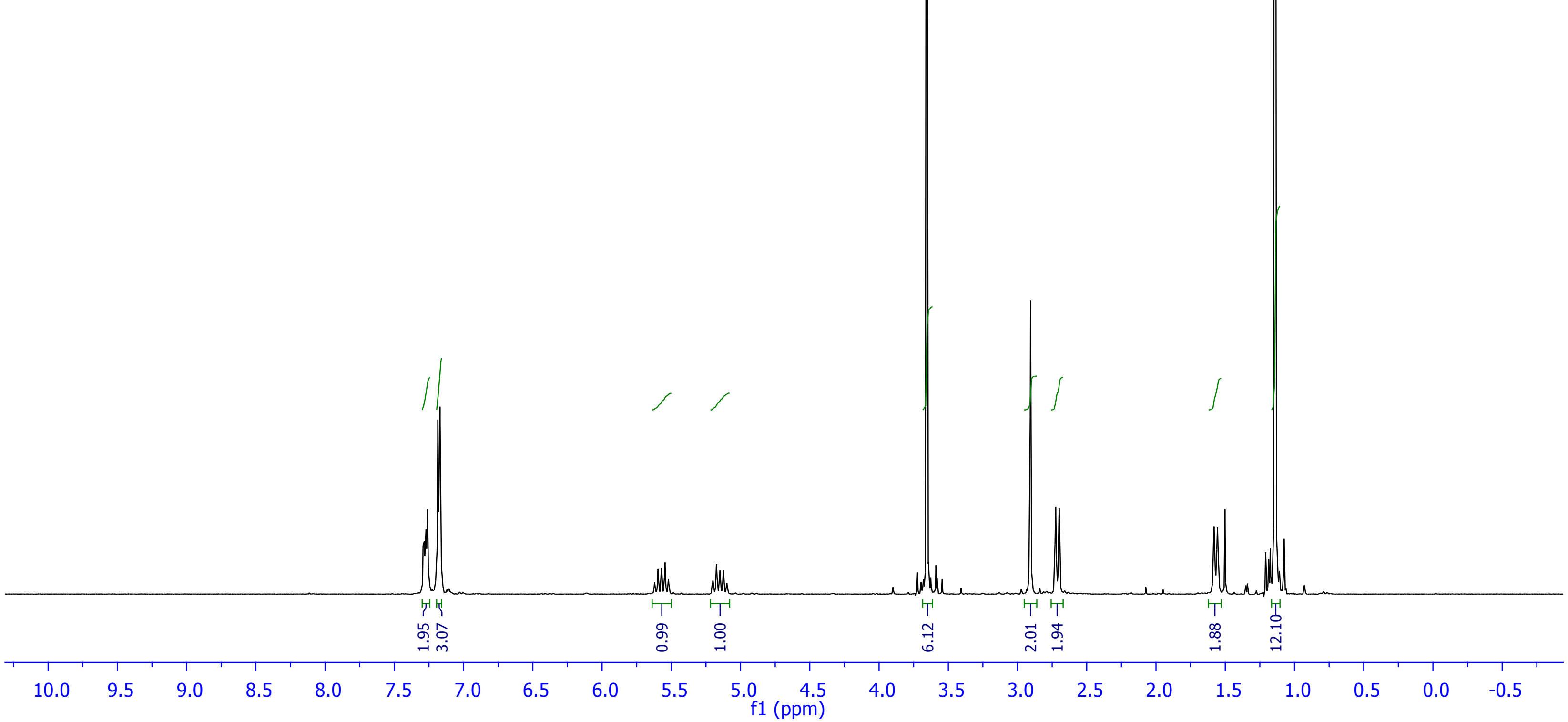

MeO2C
MeO2C
B
O
O

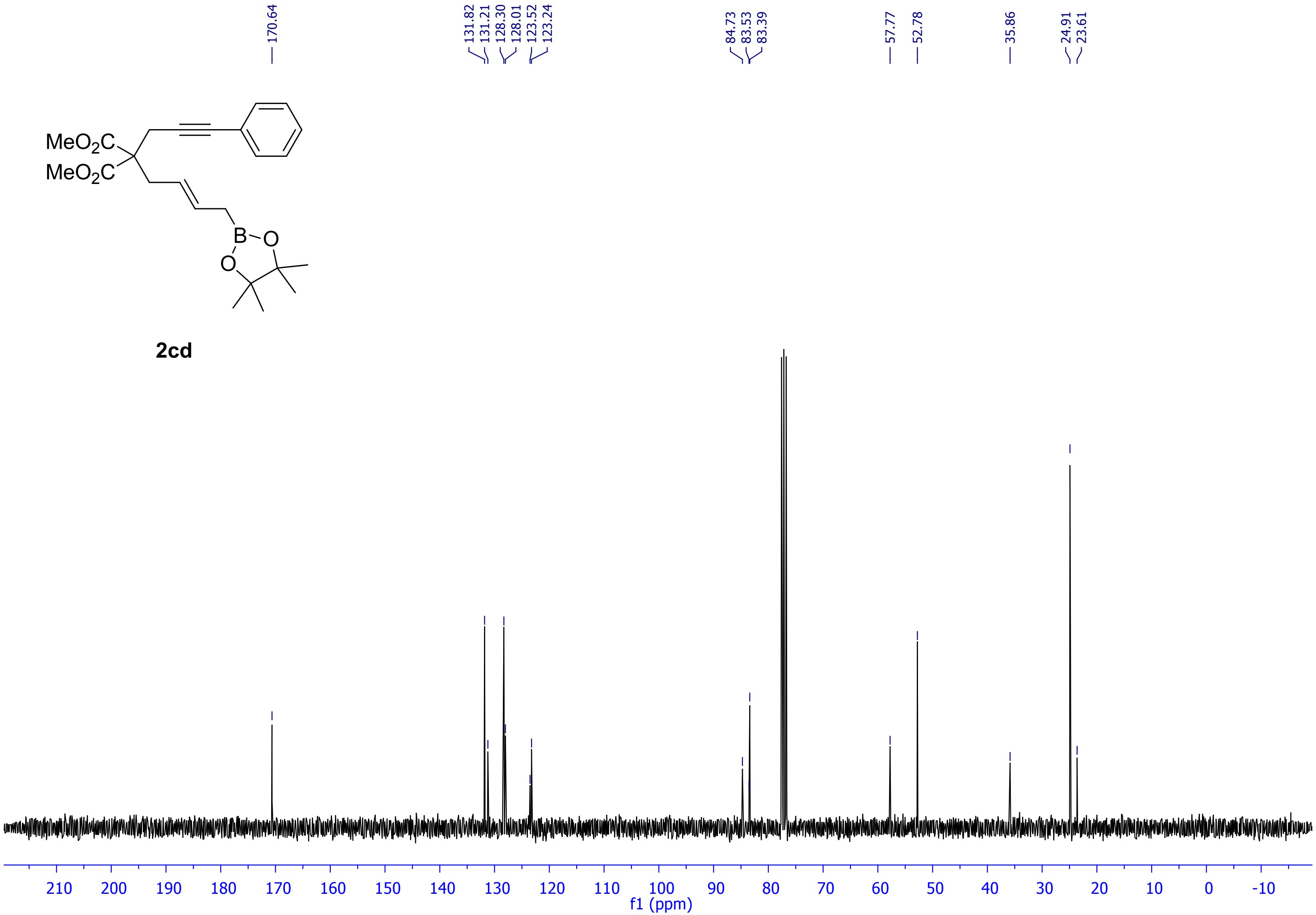
2ab

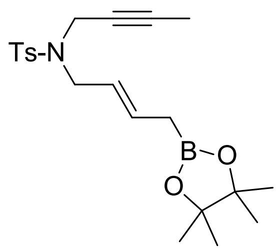

170.81
130.83
123.41
83.63
83.37
78.73
73.67
57.72
52.65
35.65
25.17
24.91
23.00
3.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO2C
MeO2C
B
O
O

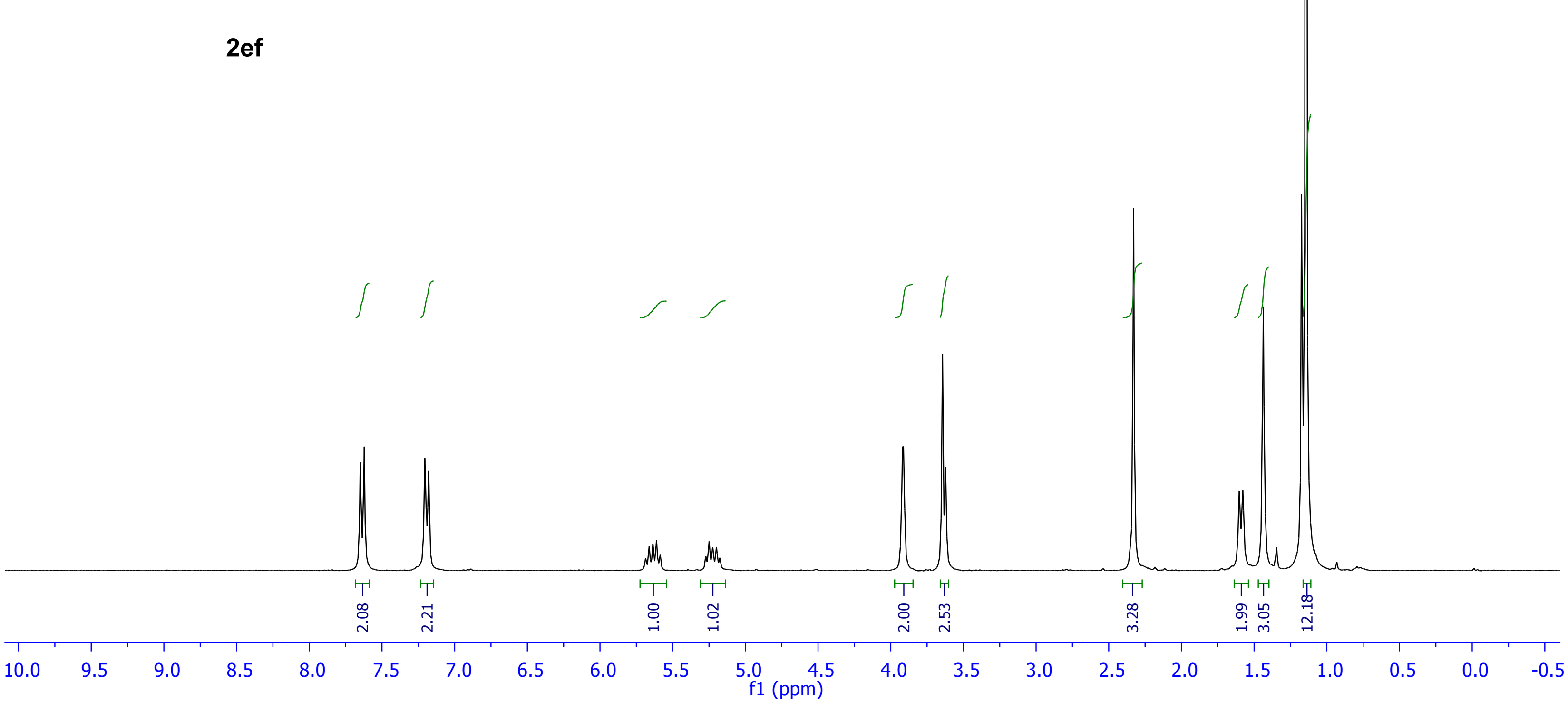
2cd

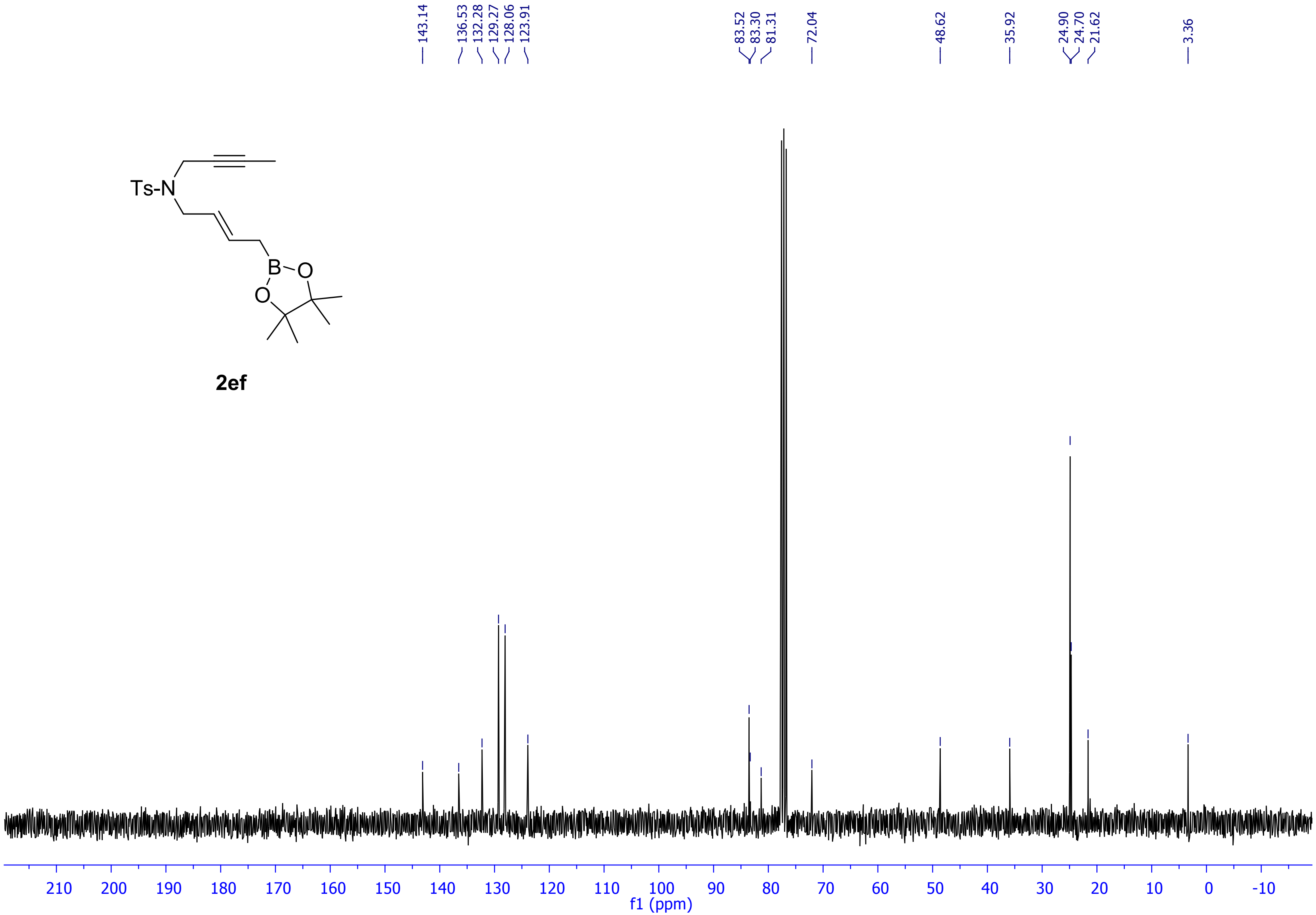

1.95
3.07
0.99
1.00
6.12
2.01
1.94
1.88
12.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

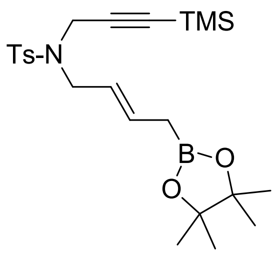

170.64
131.82
131.21
128.30
128.01
123.52
123.24
84.73
83.53
83.39
57.77
52.78
35.86
24.91
23.61
MeO2C
MeO2C
B
O
O
2cd
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



2ef

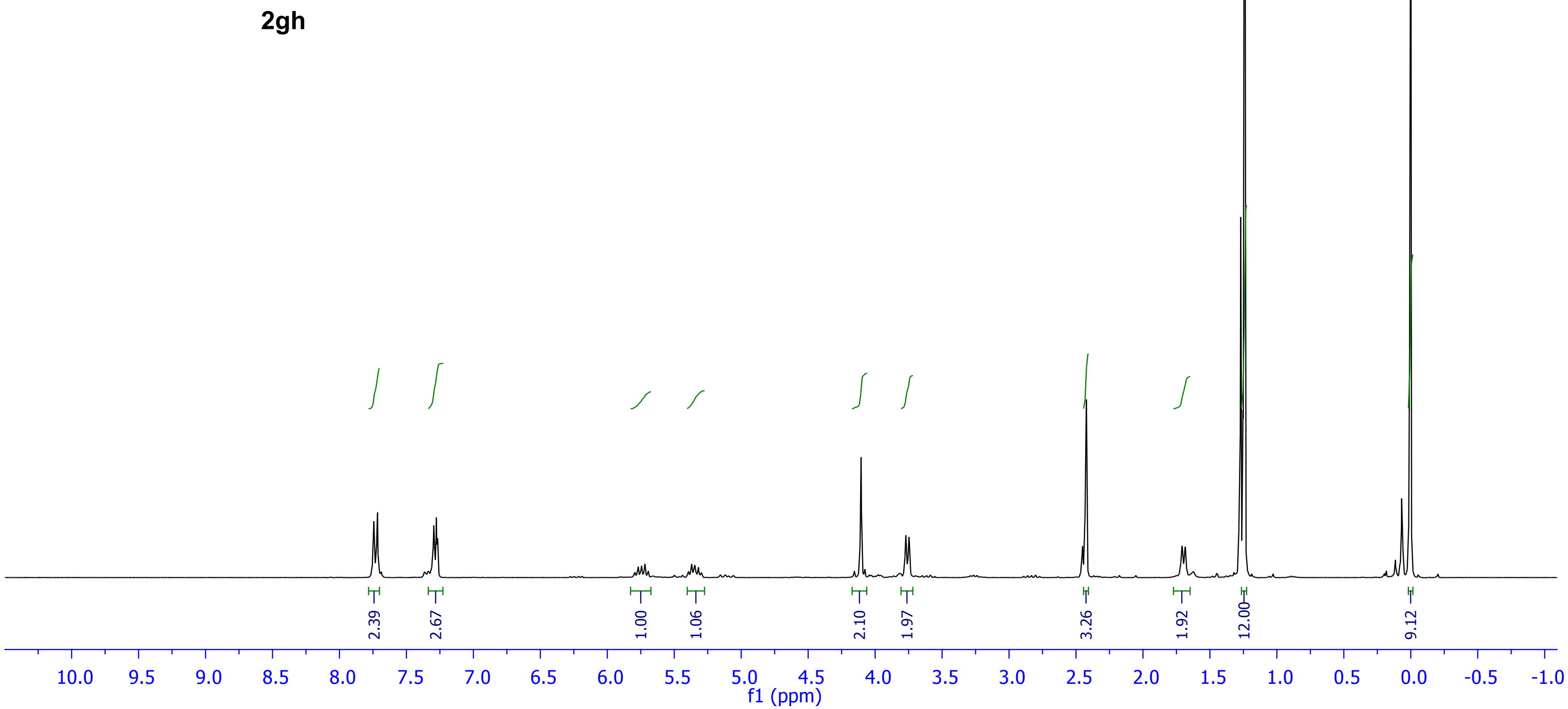

2.08
2.21
1.00
1.02
2.00
2.53
3.28
1.99
3.05
12.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


143.14
136.53
132.28
129.27
128.06
123.91
83.52
83.30
81.31
72.04
48.62
35.92
24.90
24.70
21.62
3.36
Ts-N
B
O
O
2ef
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

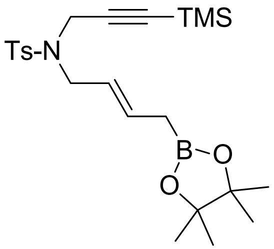


TMS
Ts-N
B
O
O

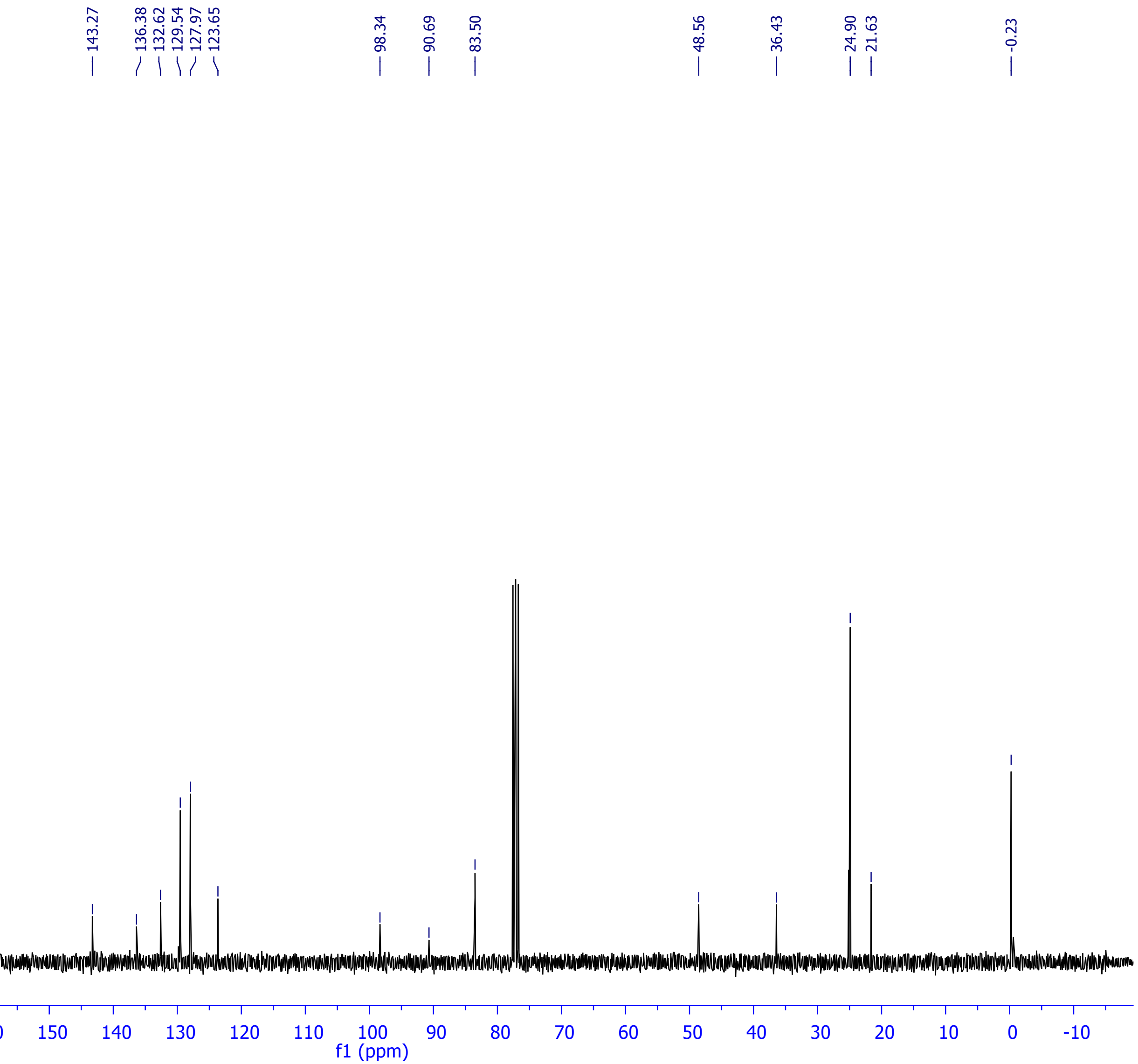
2gh

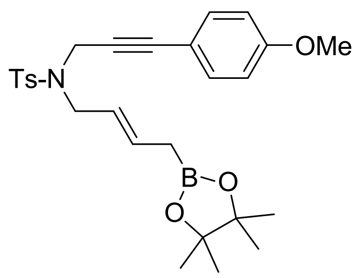


2.39
2.67
1.00
1.06
2.10
1.97
3.26
1.92
12.00
9.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


TMS
Ts-N
B
O
O

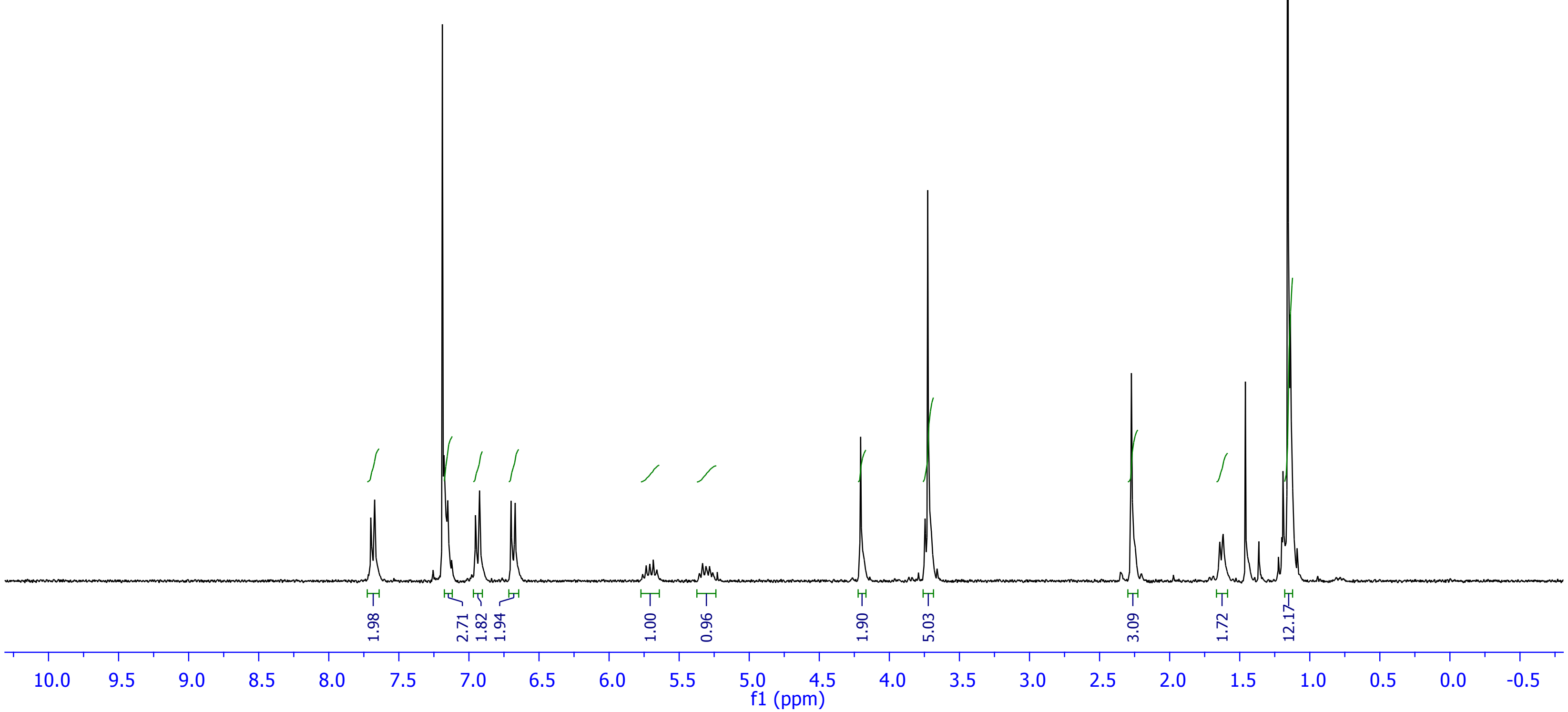
2gh


143.27
136.38
132.62
129.54
127.97
123.65
98.34
90.69
83.50
48.56
36.43
24.90
21.63
-0.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

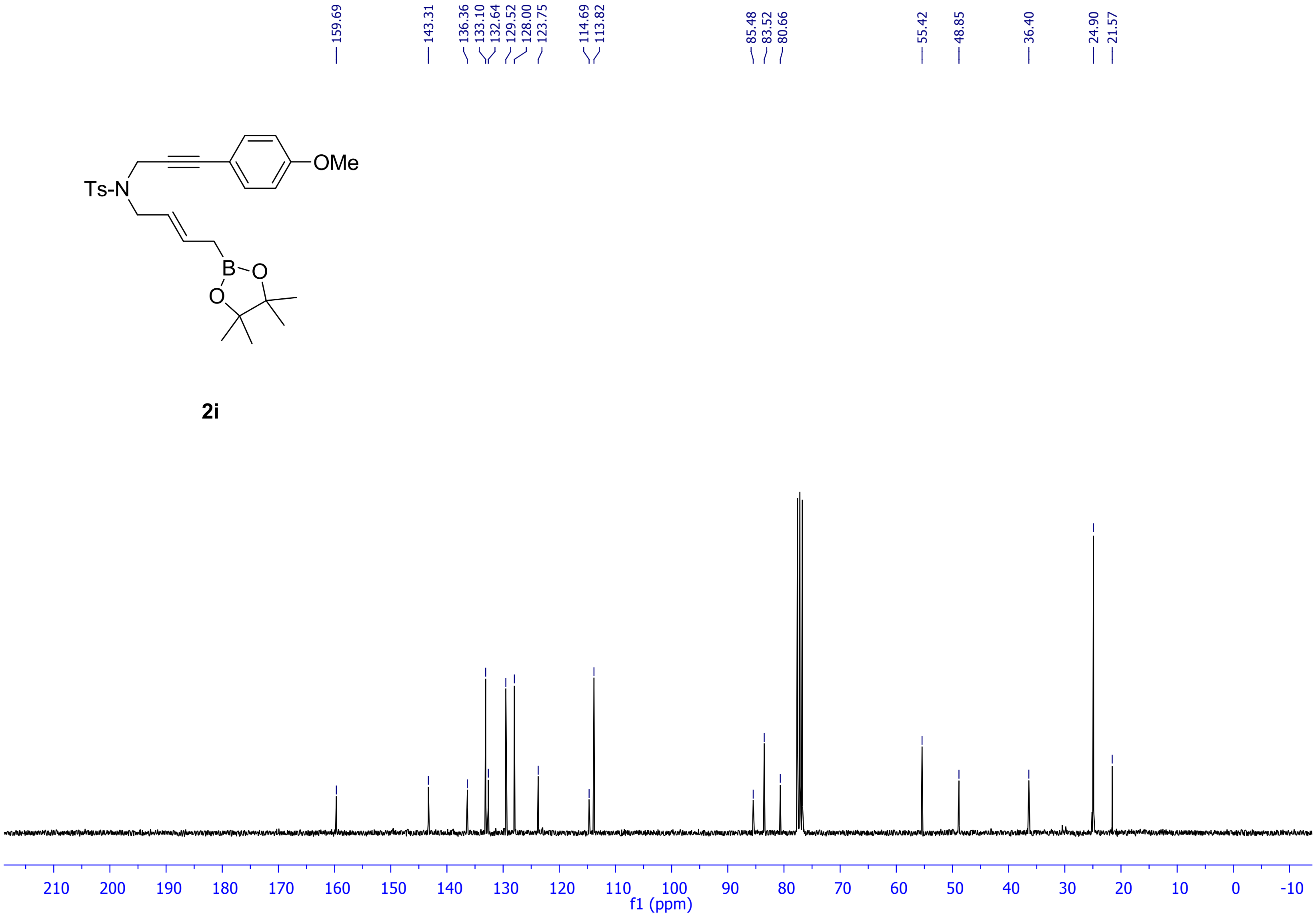


OMe
Ts-N
B
O
O

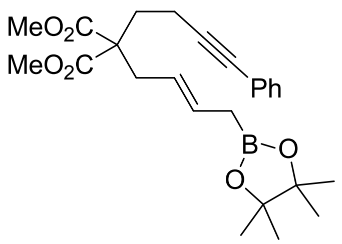
2i



1.98
2.71
1.82
1.94
1.00
0.96
1.90
5.03
3.09
1.72
12.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

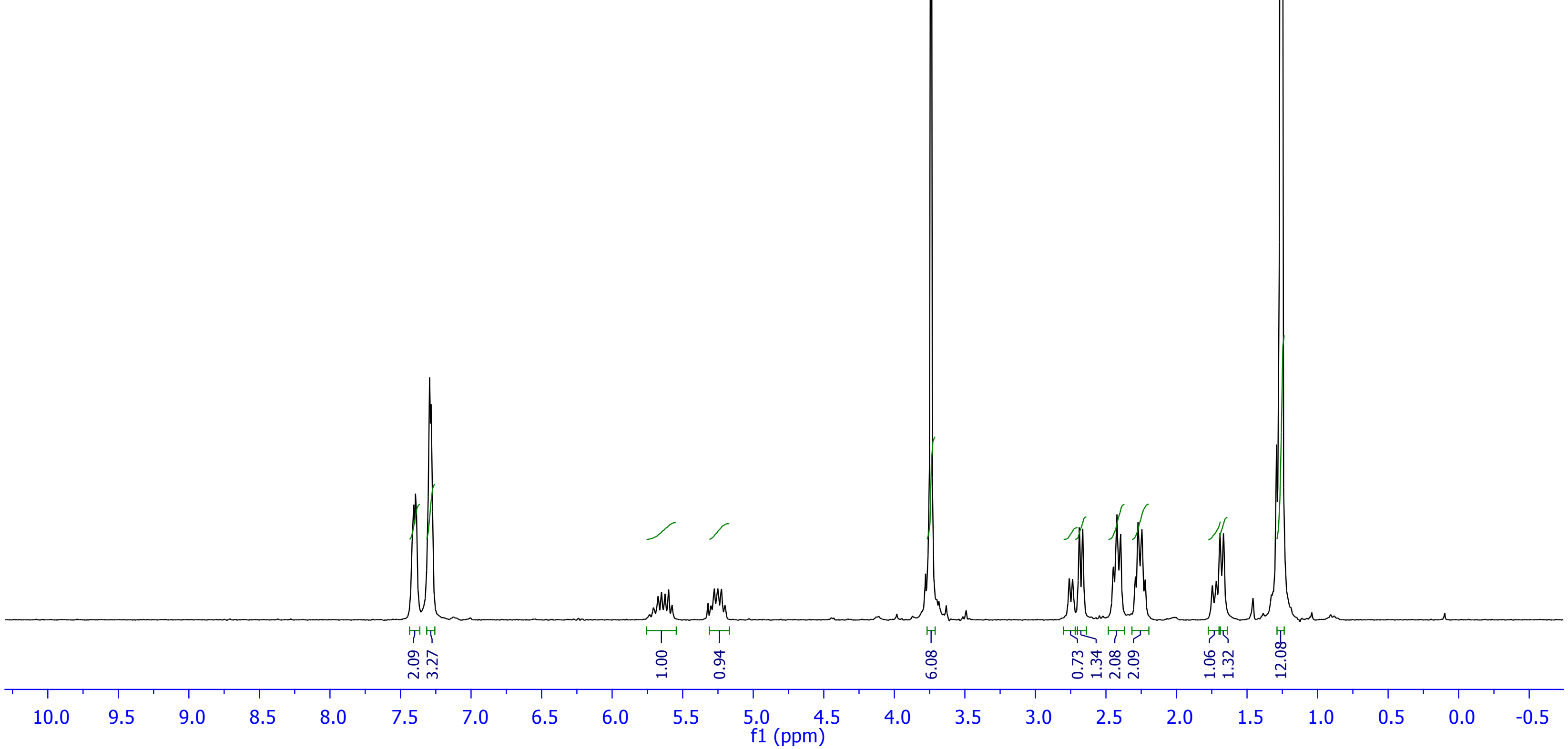

159.69
143.31
136.36
133.10
132.64
129.52
128.00
123.75
114.69
113.82
85.48
83.52
80.66
55.42
48.85
36.40
24.90
21.57
Ts-N
OMe
B
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2i

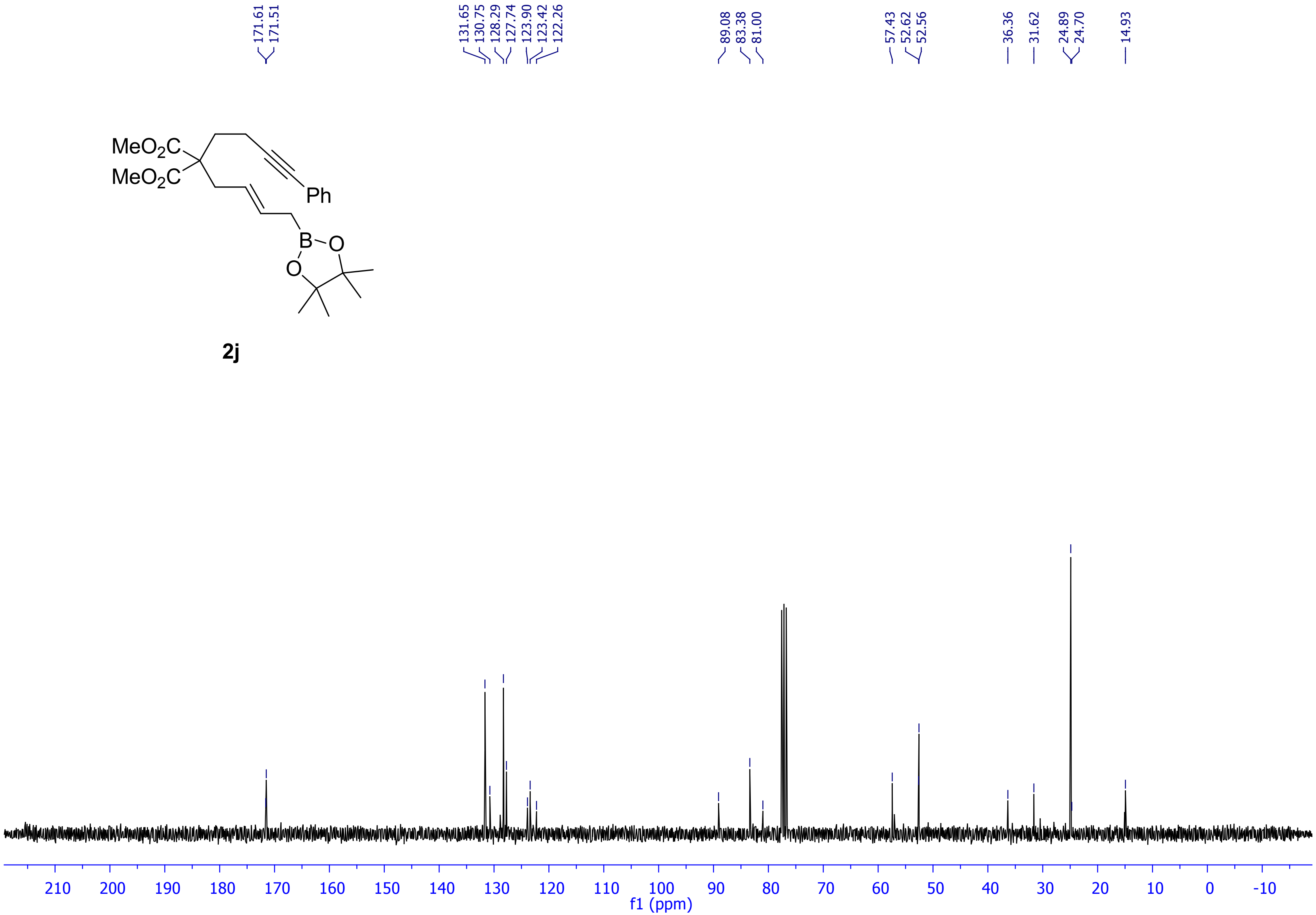


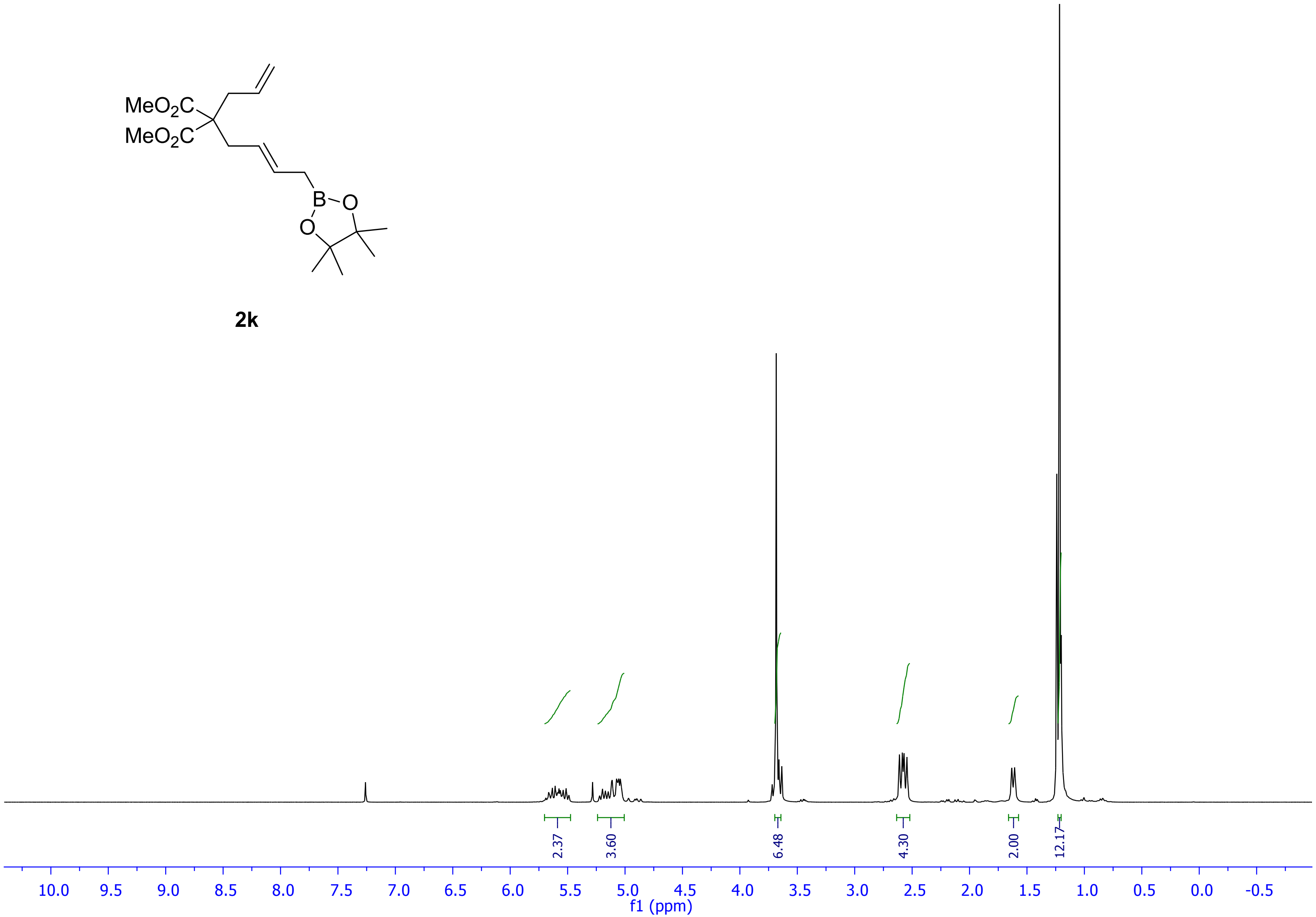
MeO2C
MeO2C
Ph
B
O
O

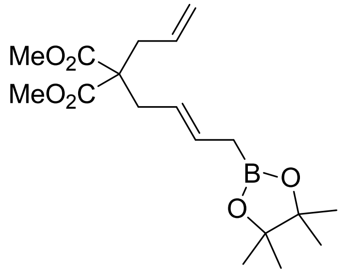
2j



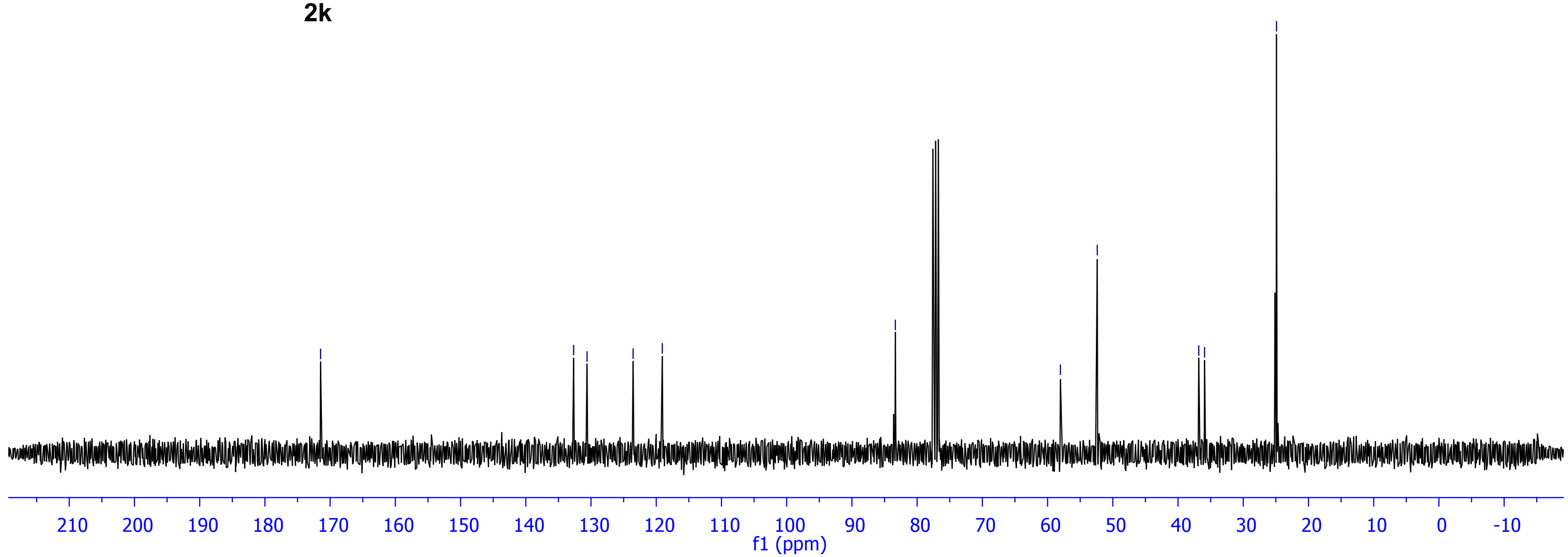
2.09
3.27
1.00
0.94
6.08
0.73
1.34
2.08
2.09
1.06
1.32
12.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

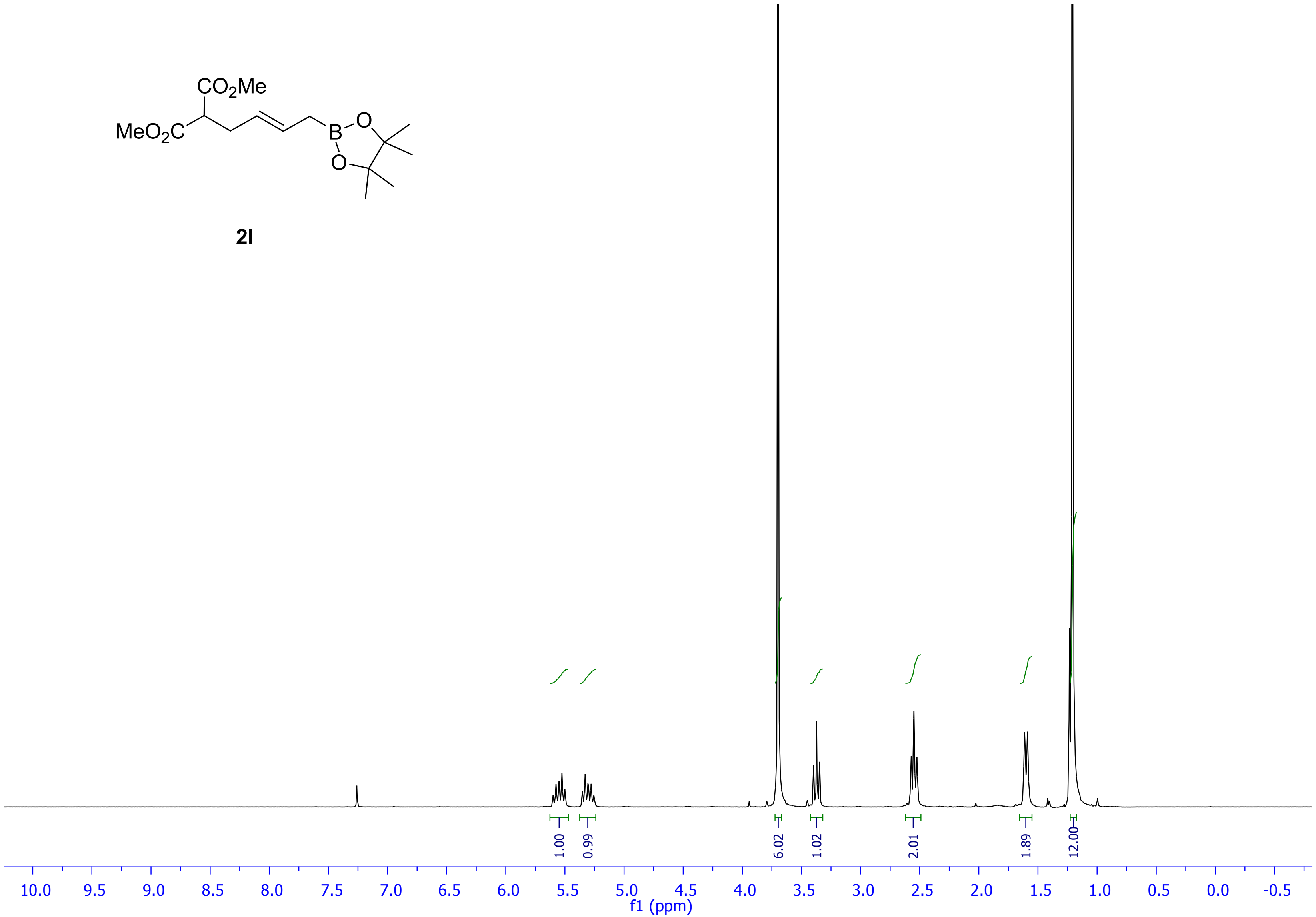

MeO2C
MeO2C
Ph
B
O
O
2j
171.61
171.51
131.65
130.75
128.29
127.74
123.90
123.42
122.26
89.08
83.38
81.00
57.43
52.62
52.56
36.36
31.62
24.89
24.70
14.93
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

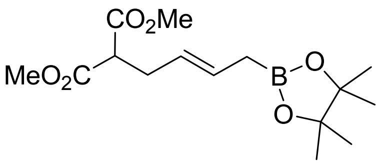

MeO2C
MeO2C
B
O
O
2k
2.37
3.60
6.48
4.30
2.00
12.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


MeO2C
MeO2C
B
O
O

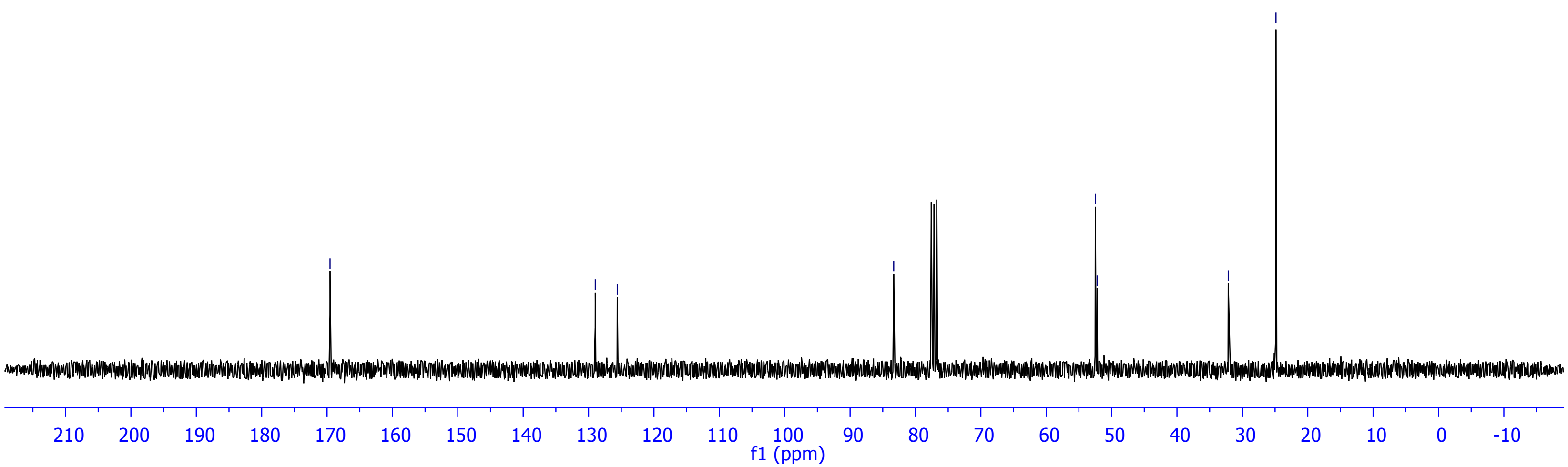
2k


171.47
132.67
130.61
123.55
119.07
83.34
58.03
52.38
36.82
35.93
24.90
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

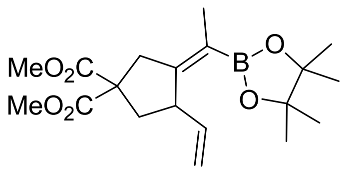

CO2Me
MeO2C
B
O
O
2l
1.00
0.99
6.02
1.02
2.01
1.89
12.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



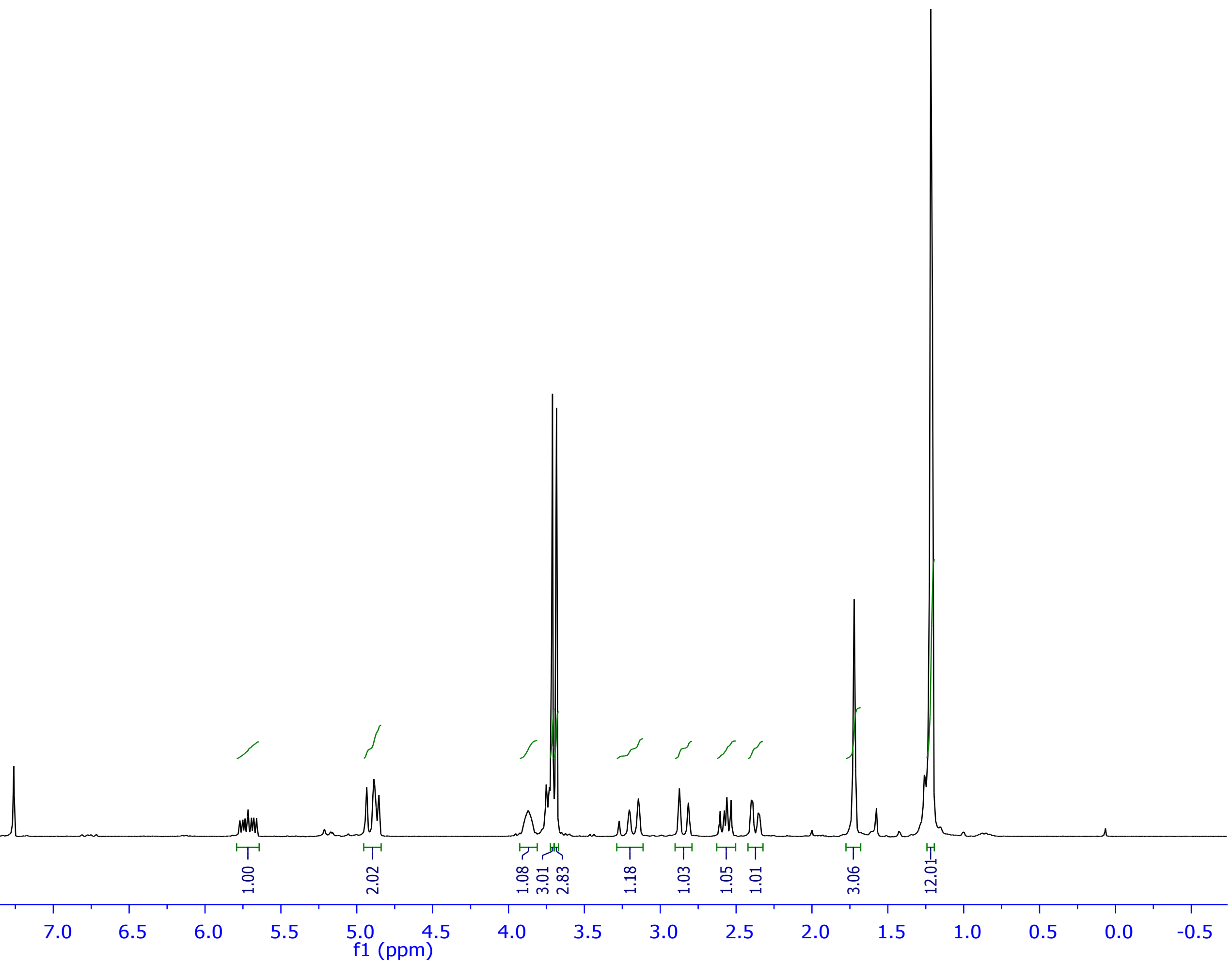
2l

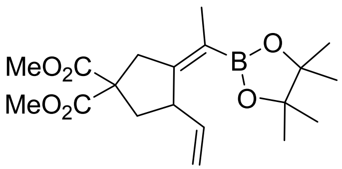

169.55
128.97
125.61
83.32
52.48
52.21
32.16
24.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

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

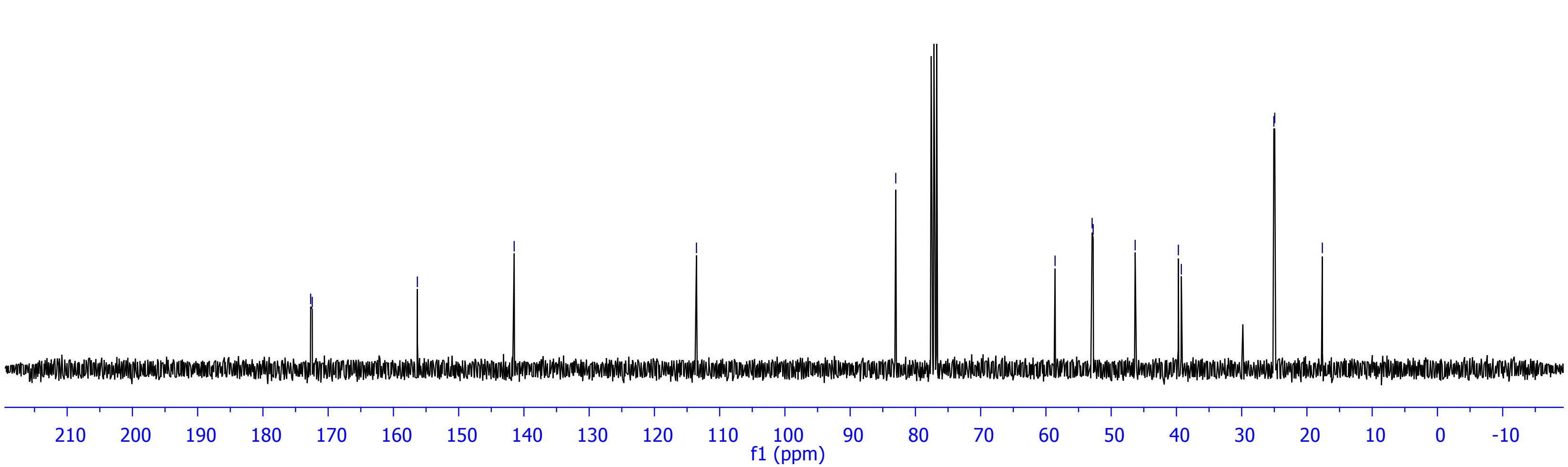


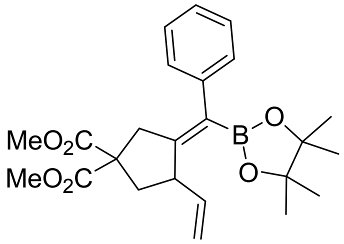
3ab



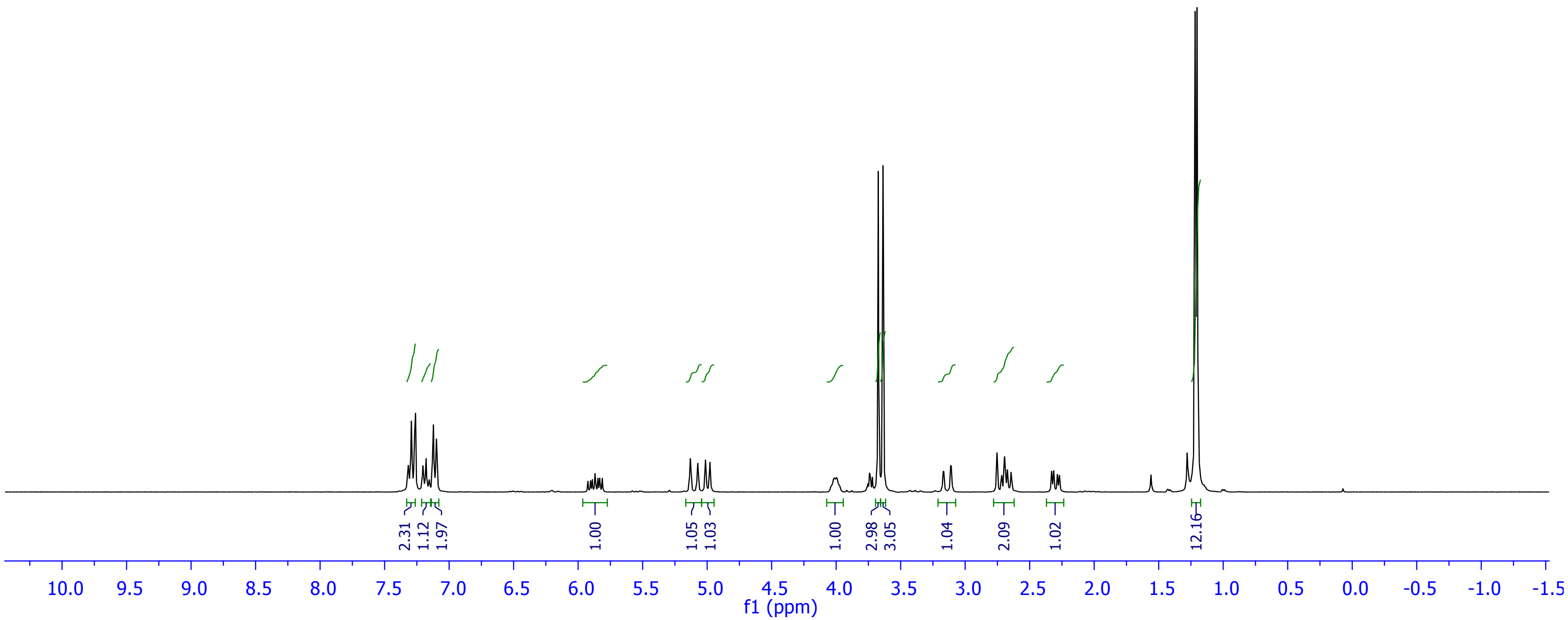

MeO2C
MeO2C
B
O
O

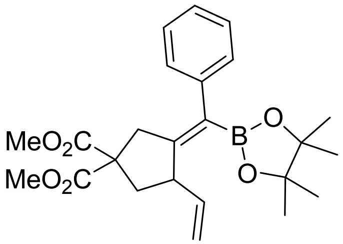
3ab


172.68
172.44
156.33
141.49
113.56
83.02
58.60
52.92
52.76
46.32
39.70
39.25
25.07
24.94
17.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

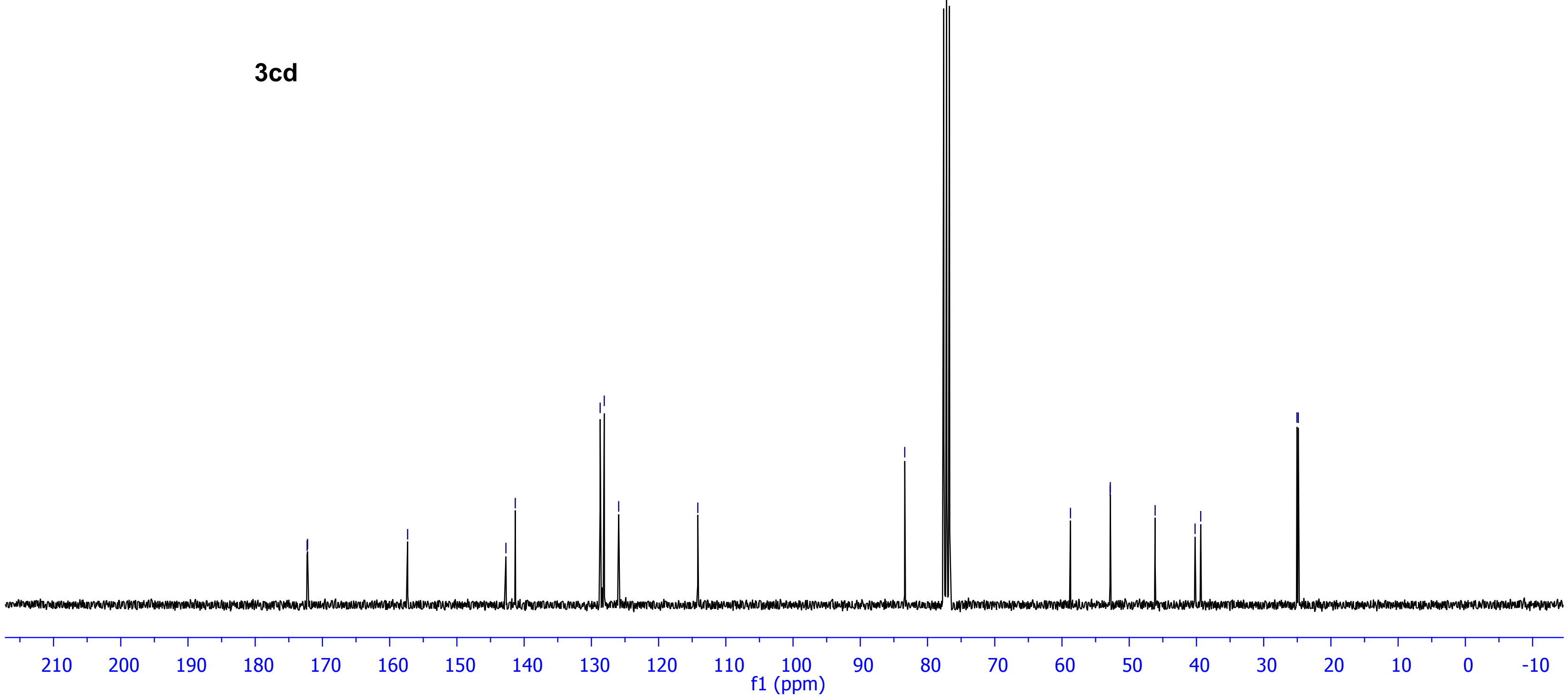

MeO2C
MeO2C
B
O
O

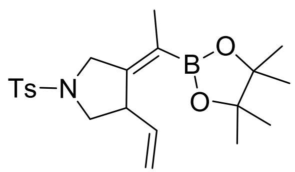
3cd


2.31
1.12
1.97
1.00
1.05
1.03
1.00
2.98
3.05
1.04
2.09
1.02
12.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

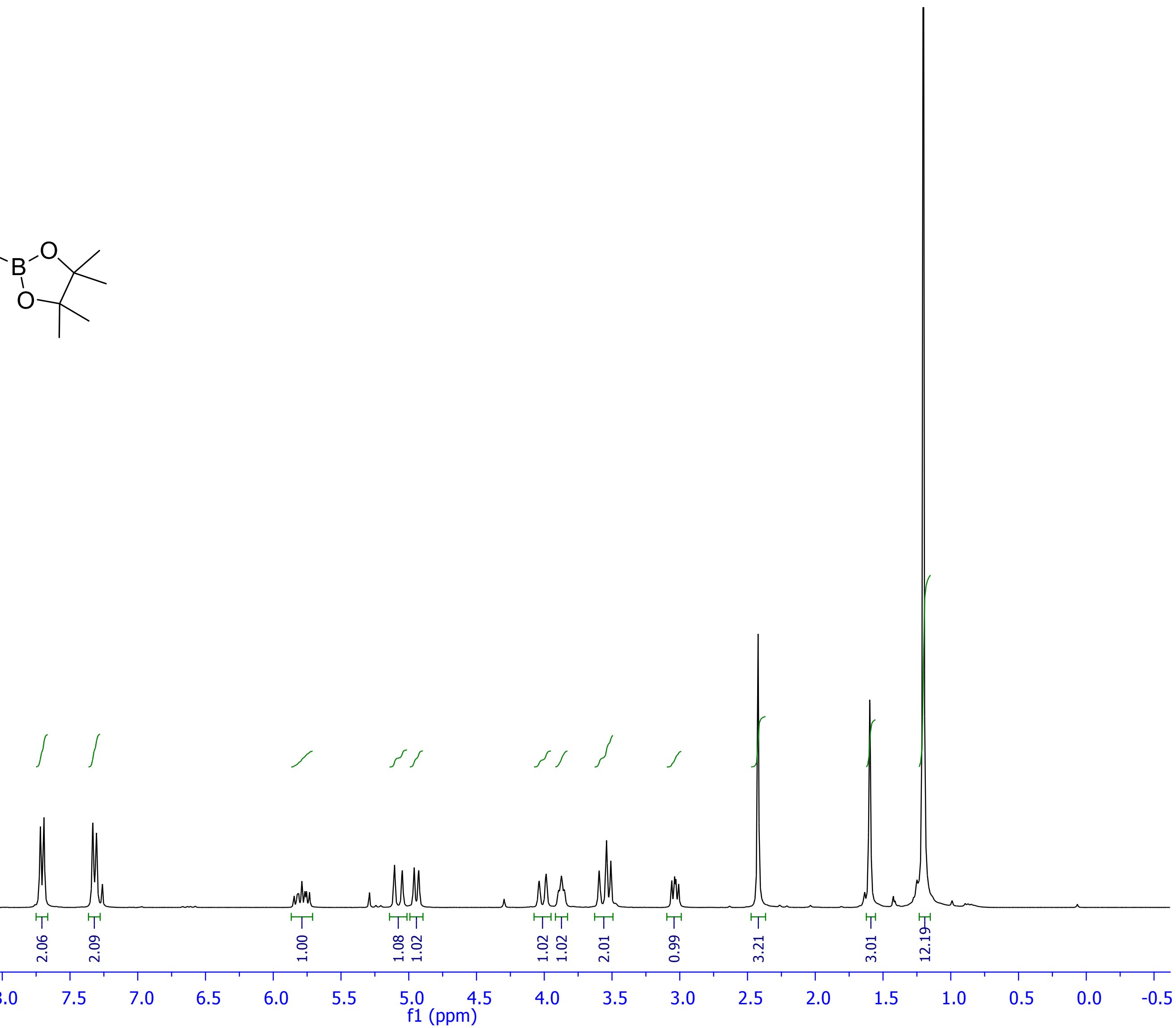


3cd

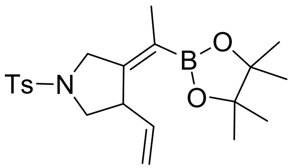

172.28
172.21
157.33
142.71
141.32
128.69
128.08
125.94
114.16
83.38
58.73
52.84
52.81
46.14
40.20
39.36
25.05
24.85
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



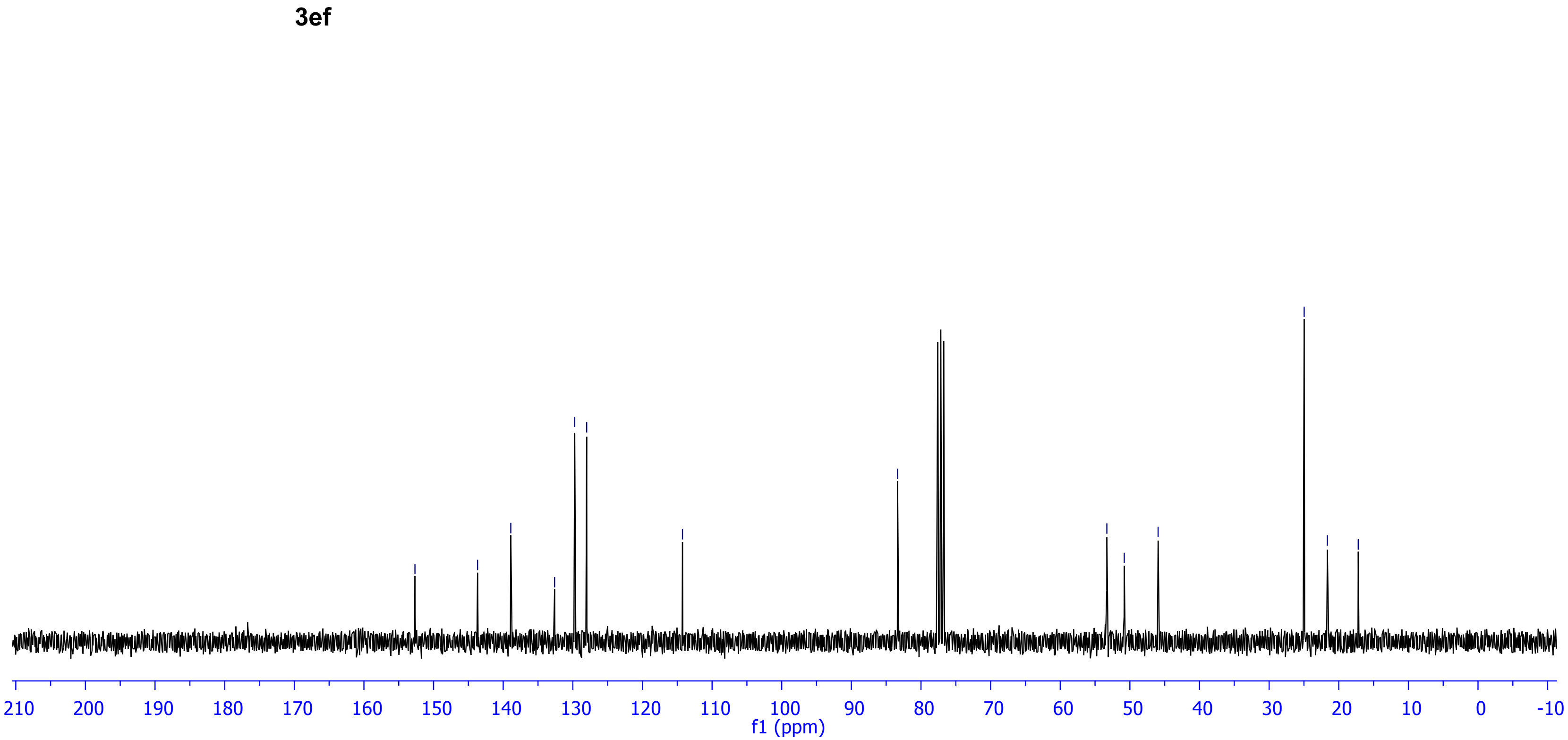
3ef

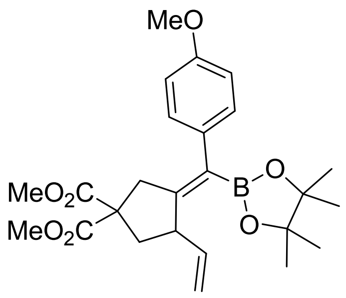


2.06
2.09
1.00
1.08
1.02
1.02
1.02
2.01
0.99
3.21
3.01
12.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

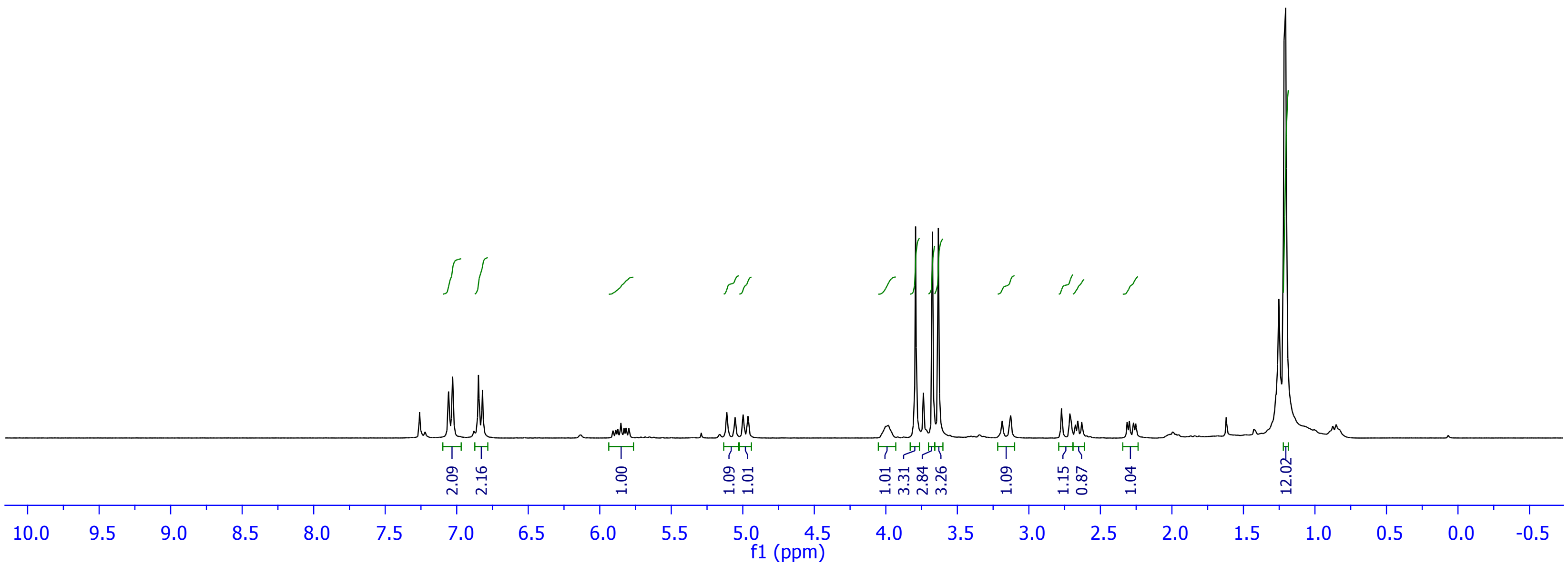


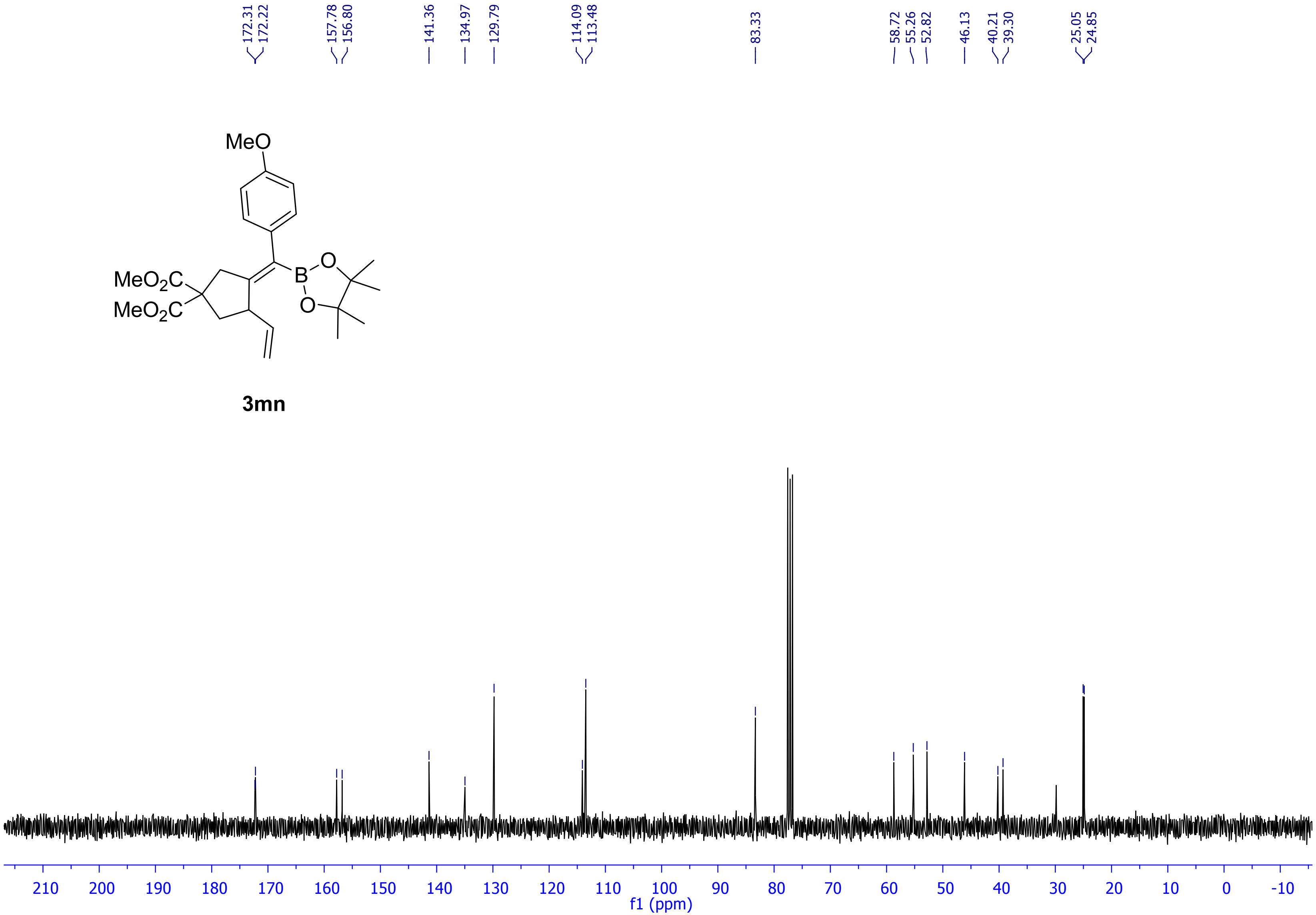
3ef


152.67
143.68
138.91
132.61
129.73
128.01
114.25
83.36
53.30
50.81
45.94
24.97
21.64
17.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
MeO2C
MeO2C
B
O
O

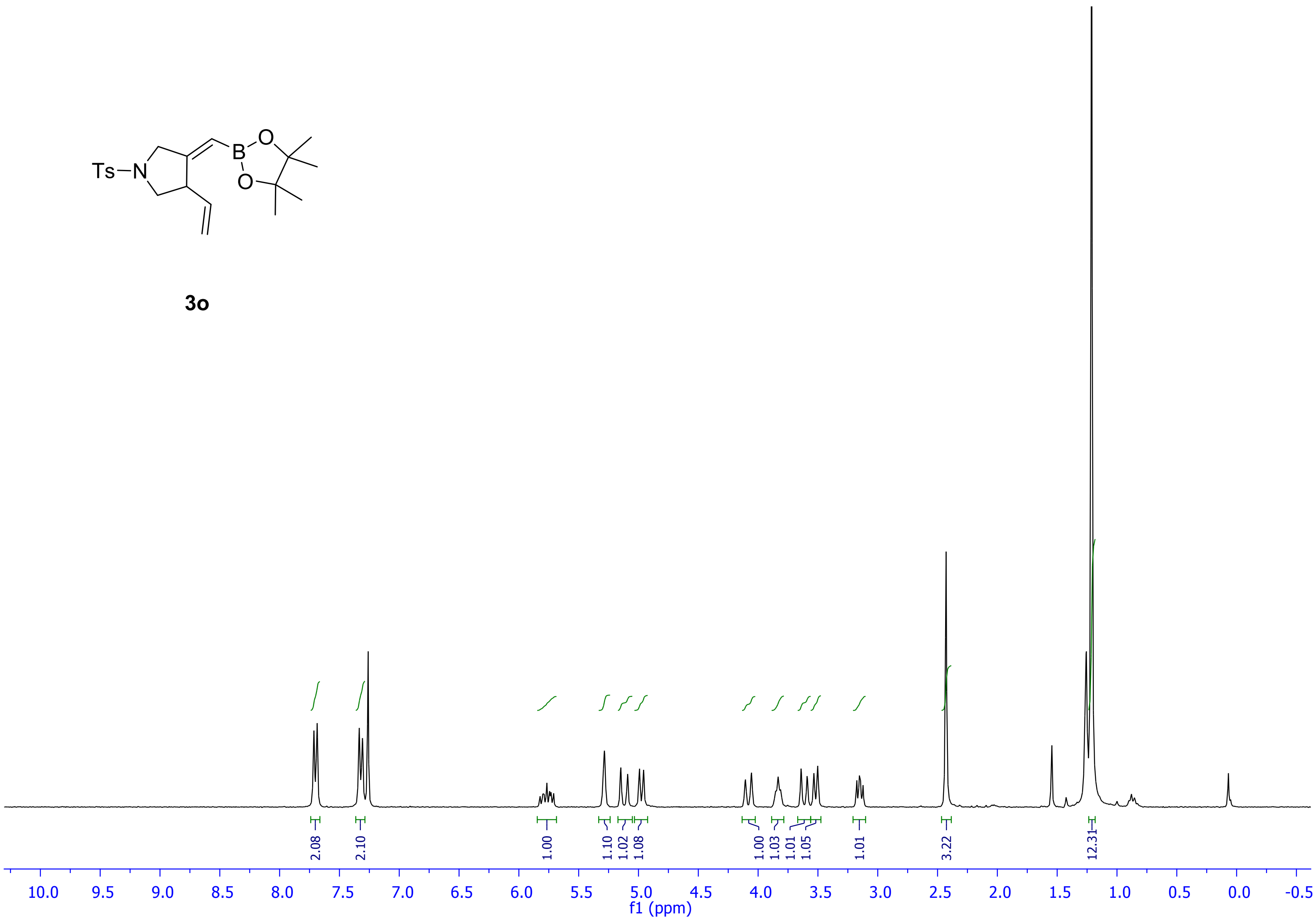
3mn


2.09
2.16
1.00
1.09
1.01
1.01
3.31
2.84
3.26
1.09
1.15
0.87
1.04
12.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

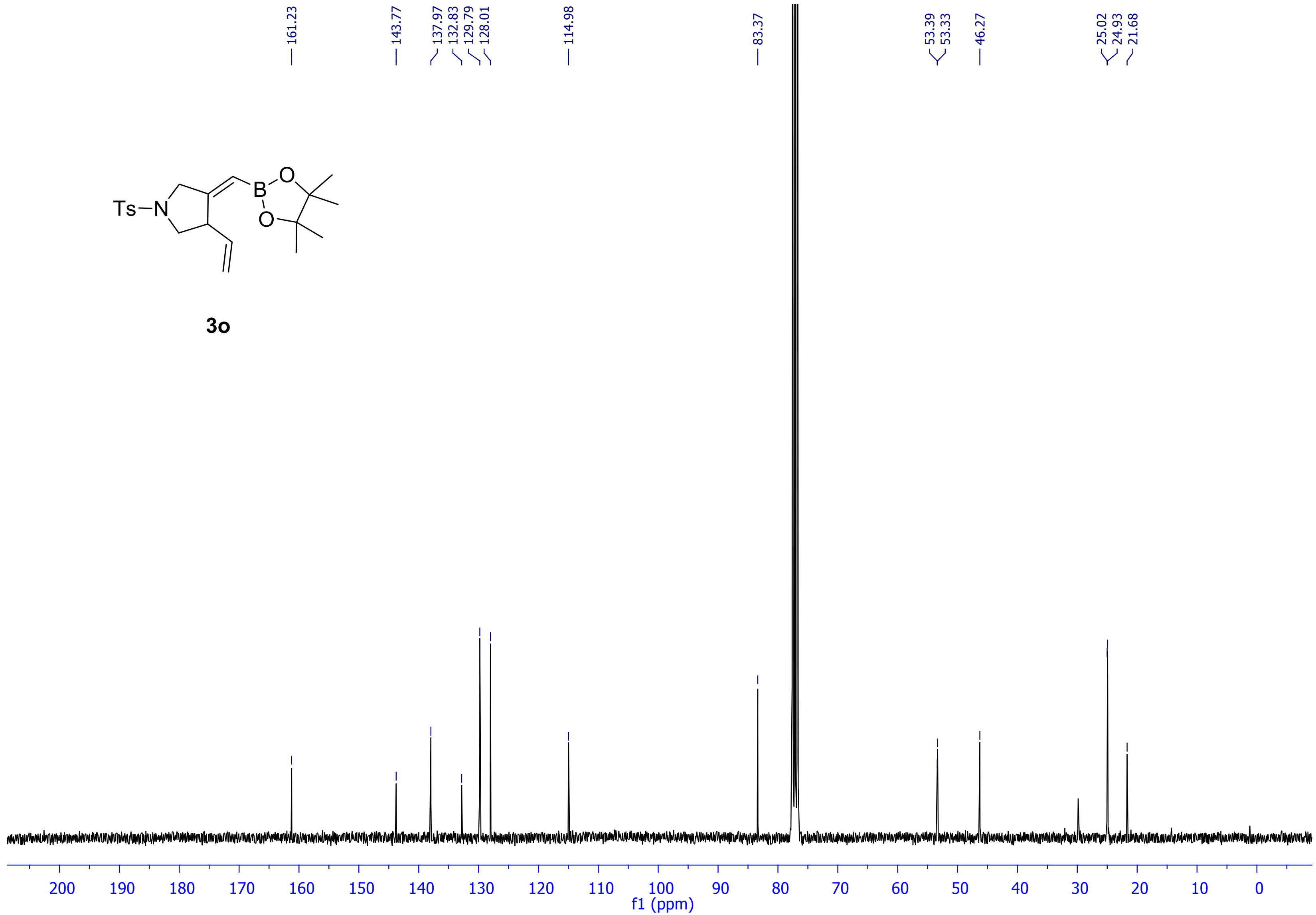


172.31
172.22
157.78
156.80
141.36
134.97
129.79
114.09
113.48
83.33
58.72
55.26
52.82
46.13
40.21
39.30
25.05
24.85
MeO
MeO_2C
MeO_2C
B
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

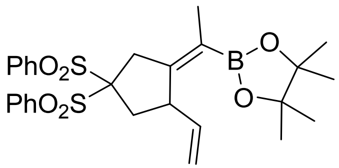
3mn


Ts
N
B
O
O
2.08
2.10
1.00
1.10
1.02
1.08
1.00
1.03
1.01
1.05
1.01
3.22
12.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

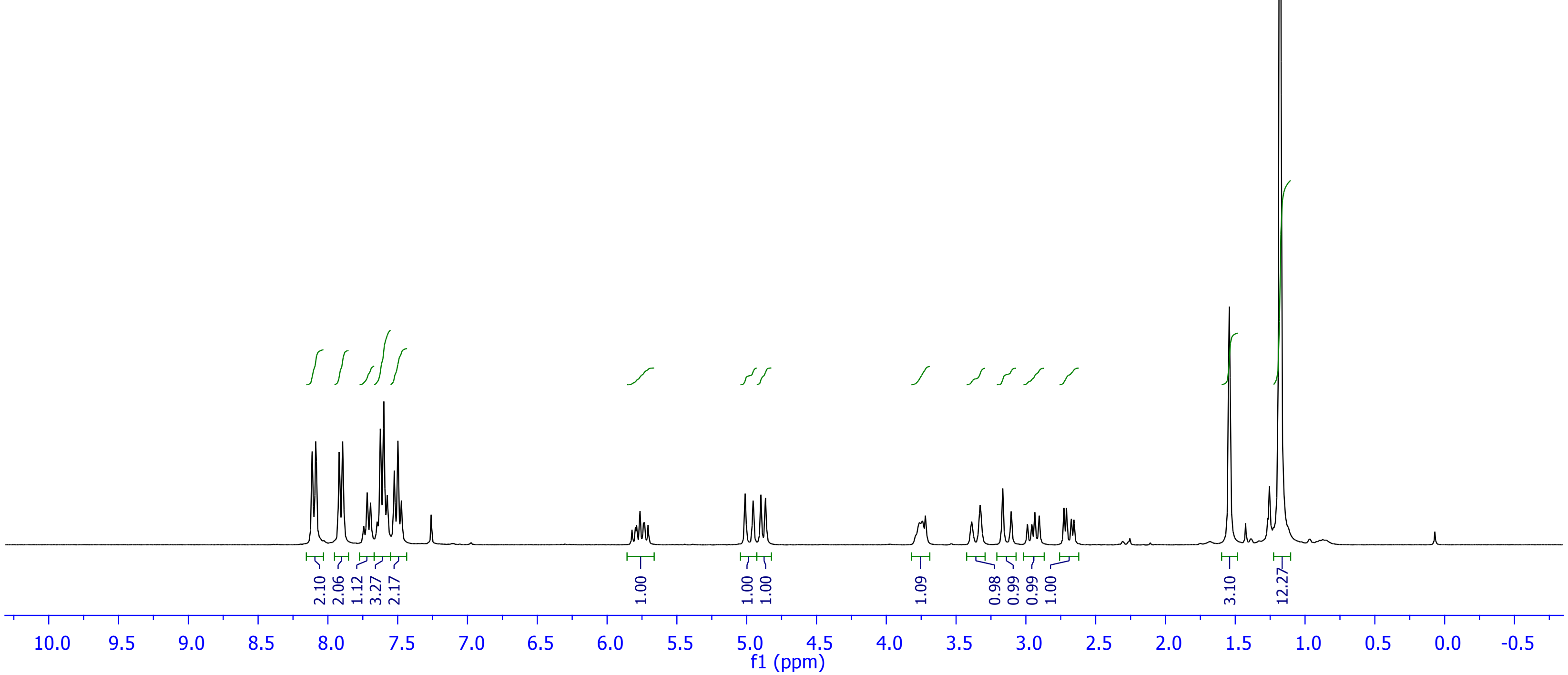
3o

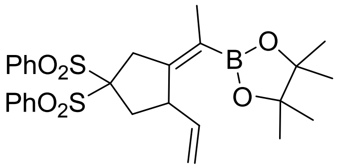

161.23
143.77
137.97
132.83
129.79
128.01
114.98
83.37
53.39
53.33
46.27
25.02
24.93
21.68
Ts
N
B
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3o

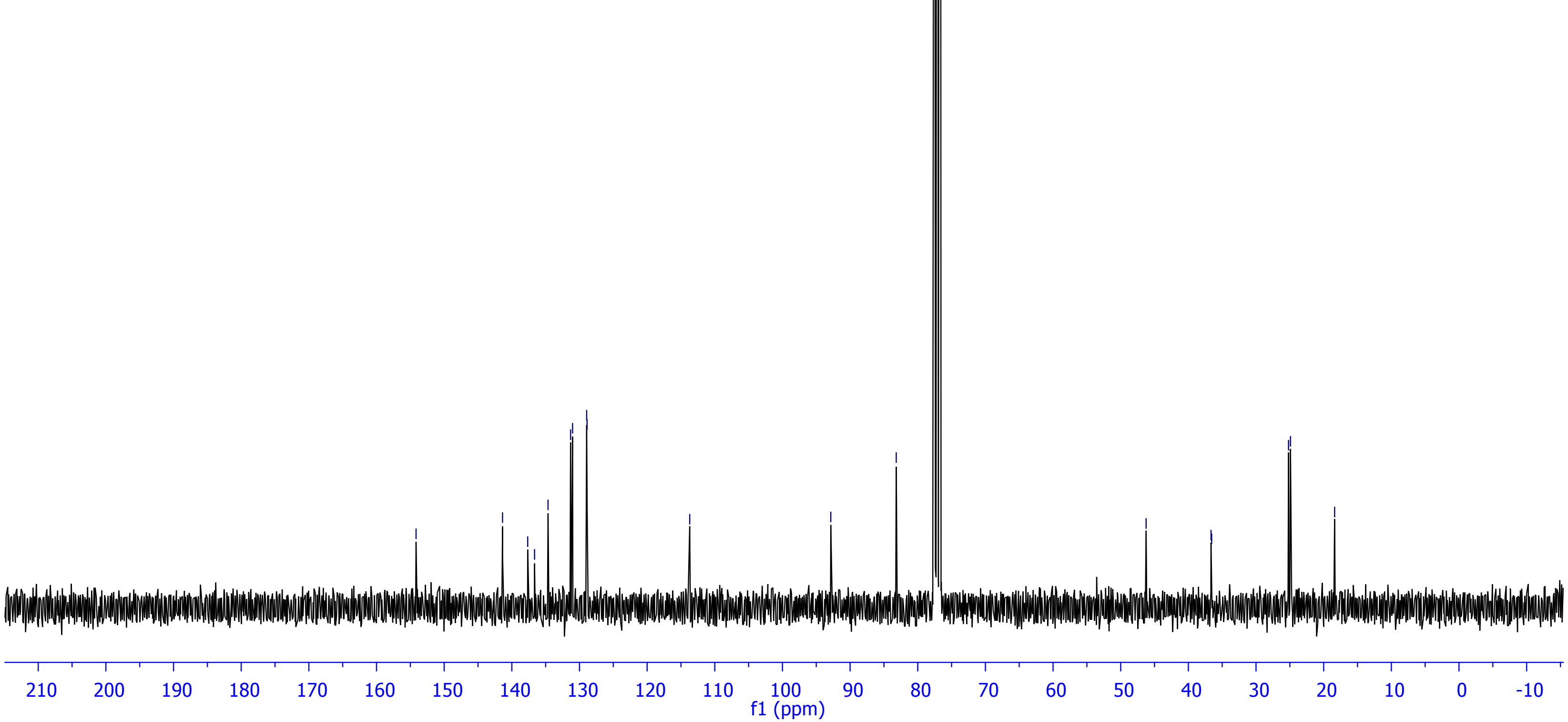

PhO2S
PhO2S
B
O
O

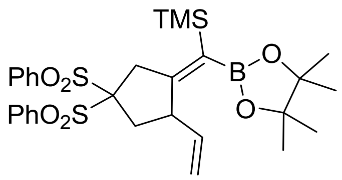
3p


2.10
2.06
1.12
3.27
2.17
1.00
1.00
1.00
1.09
0.98
0.99
0.99
1.00
3.10
12.27
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

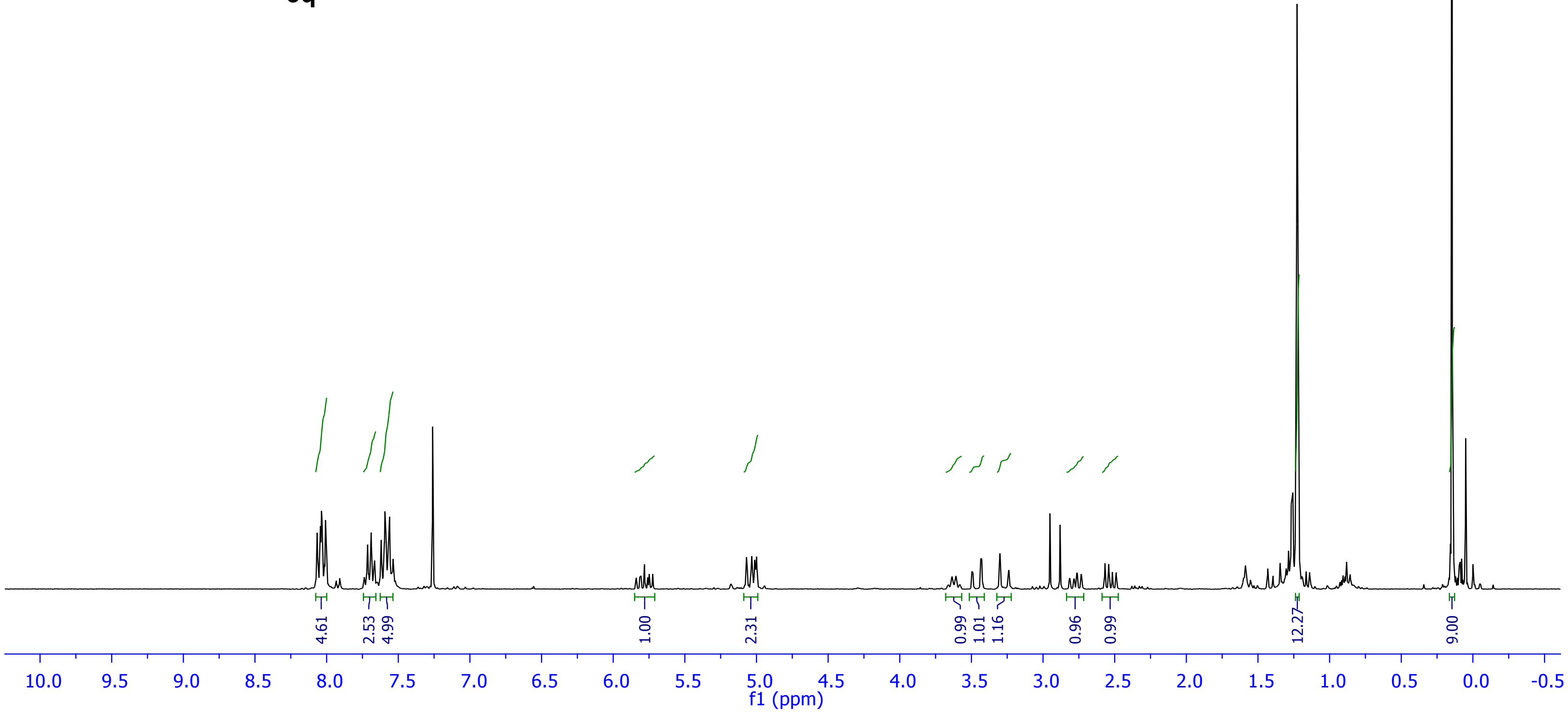

PhO2S
PhO2S
B
O
O

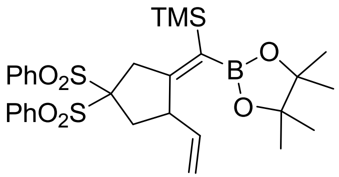
3p


154.15
141.37
137.65
136.64
134.65
131.31
131.02
128.94
128.87
113.71
92.85
83.18
46.25
36.65
36.56
25.19
24.91
18.38
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

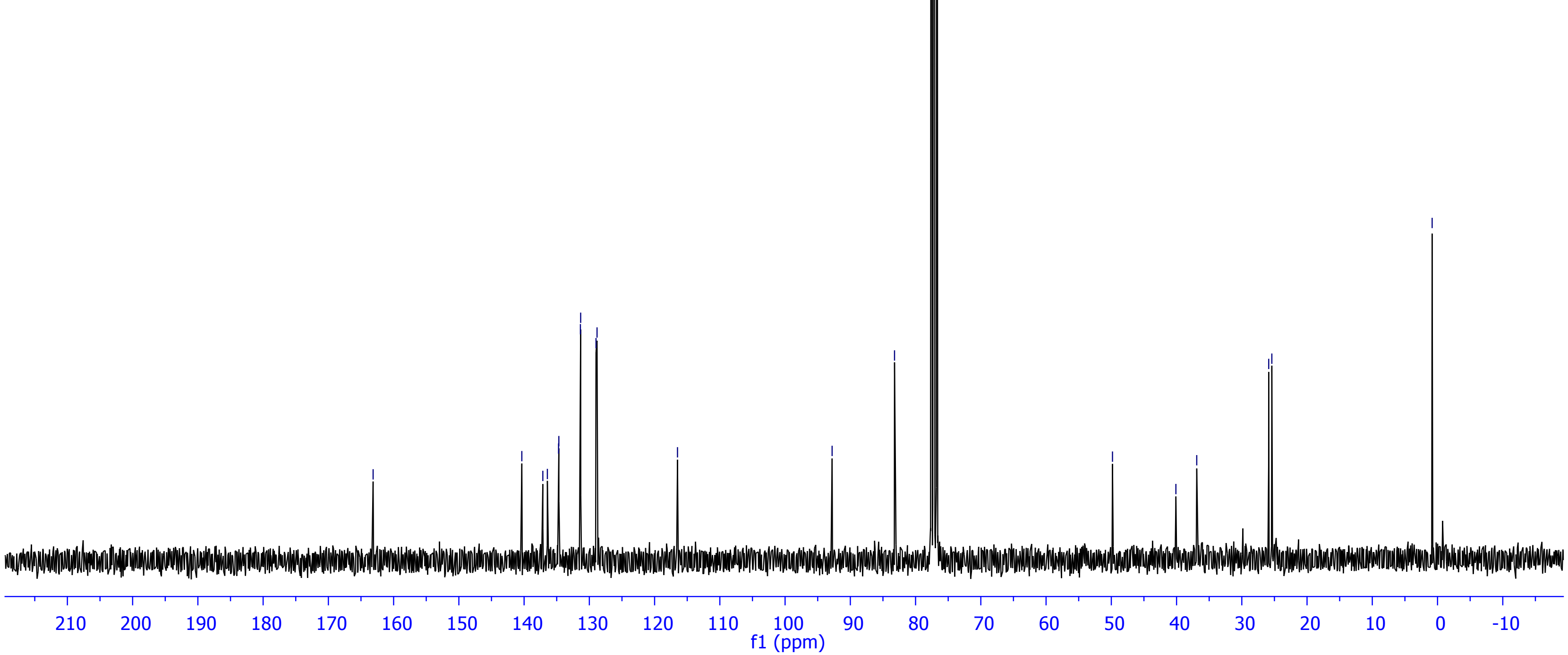

TMS
PhO2S
PhO2S
B
O
O

3q

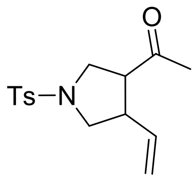

4.61
2.53
4.99
1.00
2.31
0.99
1.01
1.16
0.96
0.99
12.27
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


TMS
PhO2S
PhO2S
B
O
O

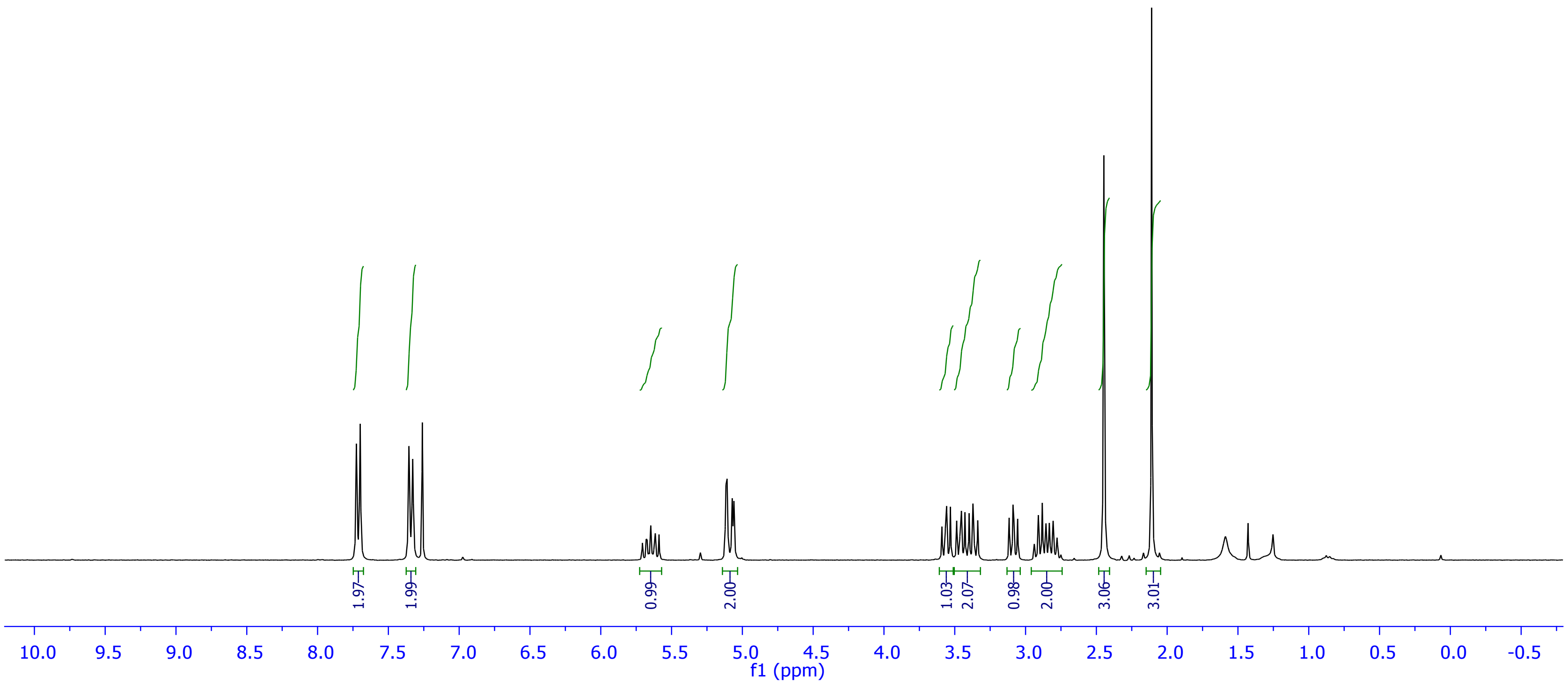
3q

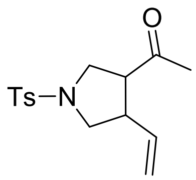

163.14
140.35
137.13
136.43
134.72
134.68
131.37
131.33
128.98
128.82
116.49
92.79
83.23
49.82
40.10
36.91
25.88
25.40
0.83
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{1}H-NMR and ^{13}C-NMR spectra of synthetic applications of allyl- and alkenylboronates

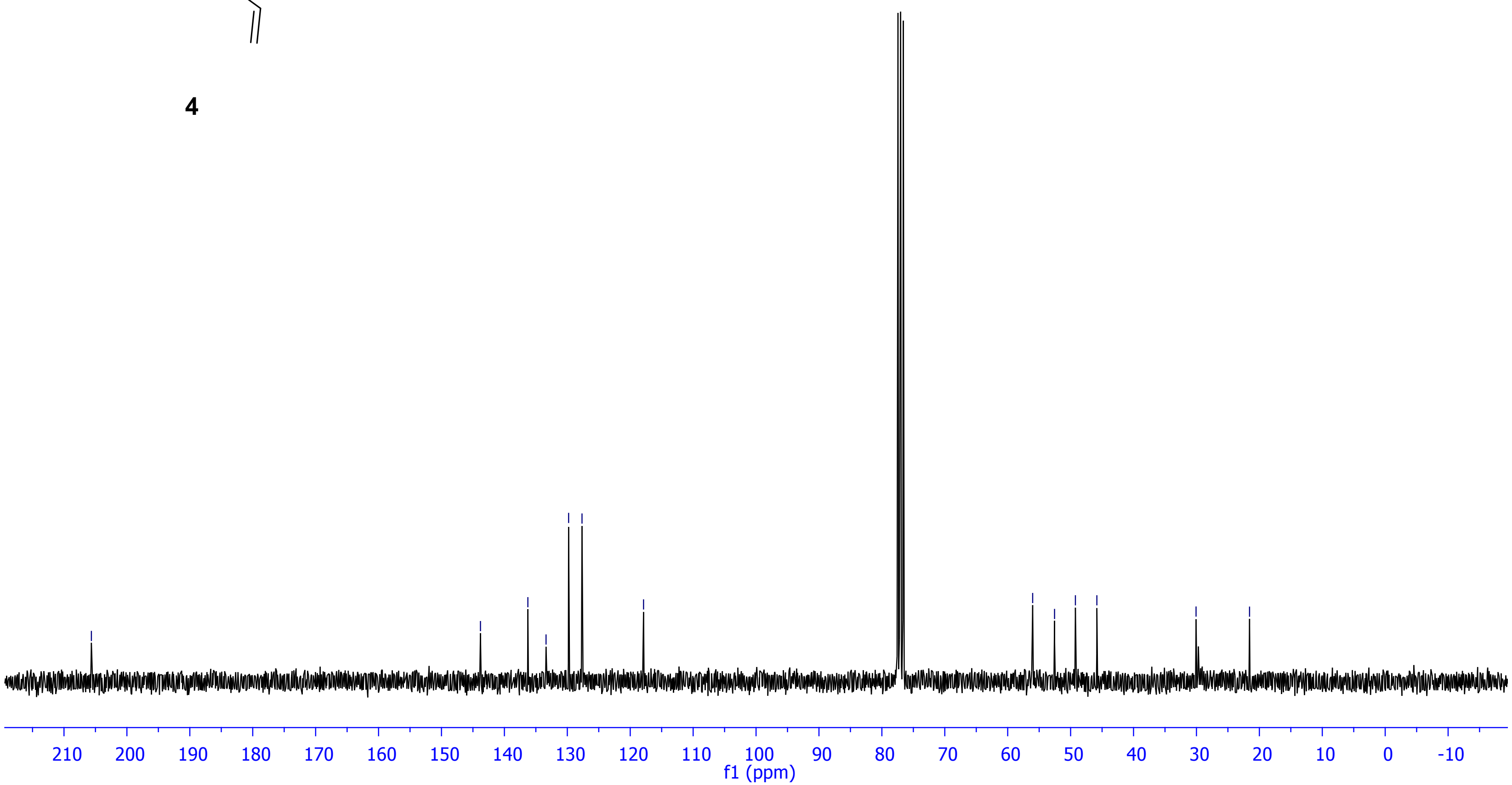


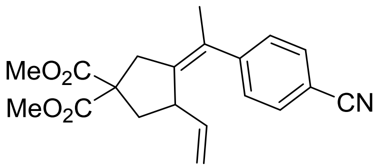
4



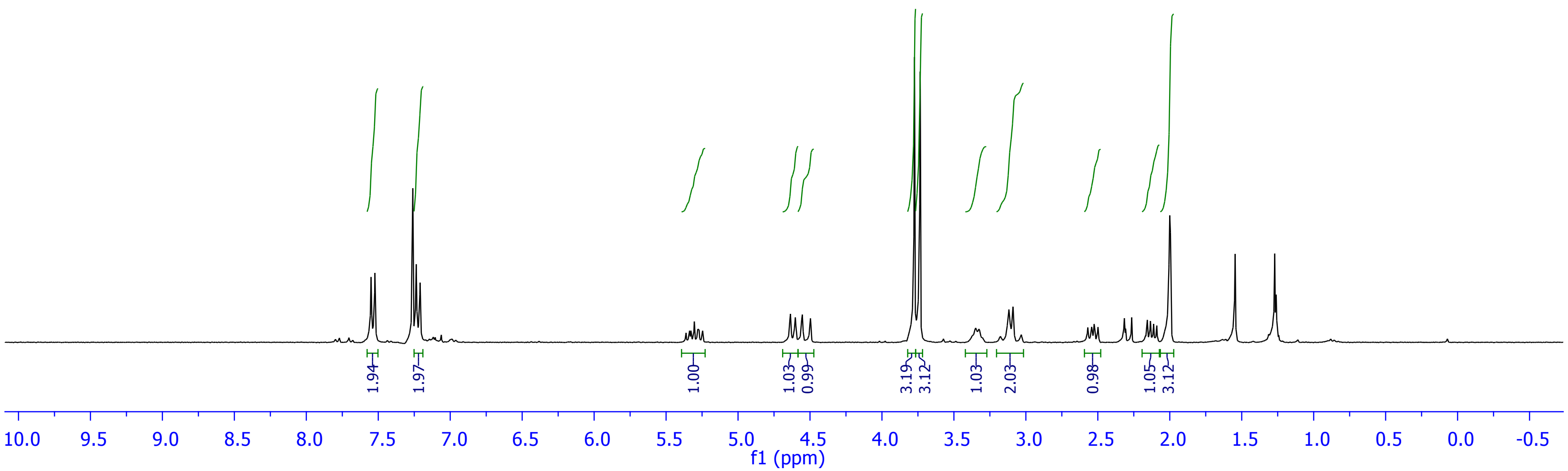

O
Ts
N

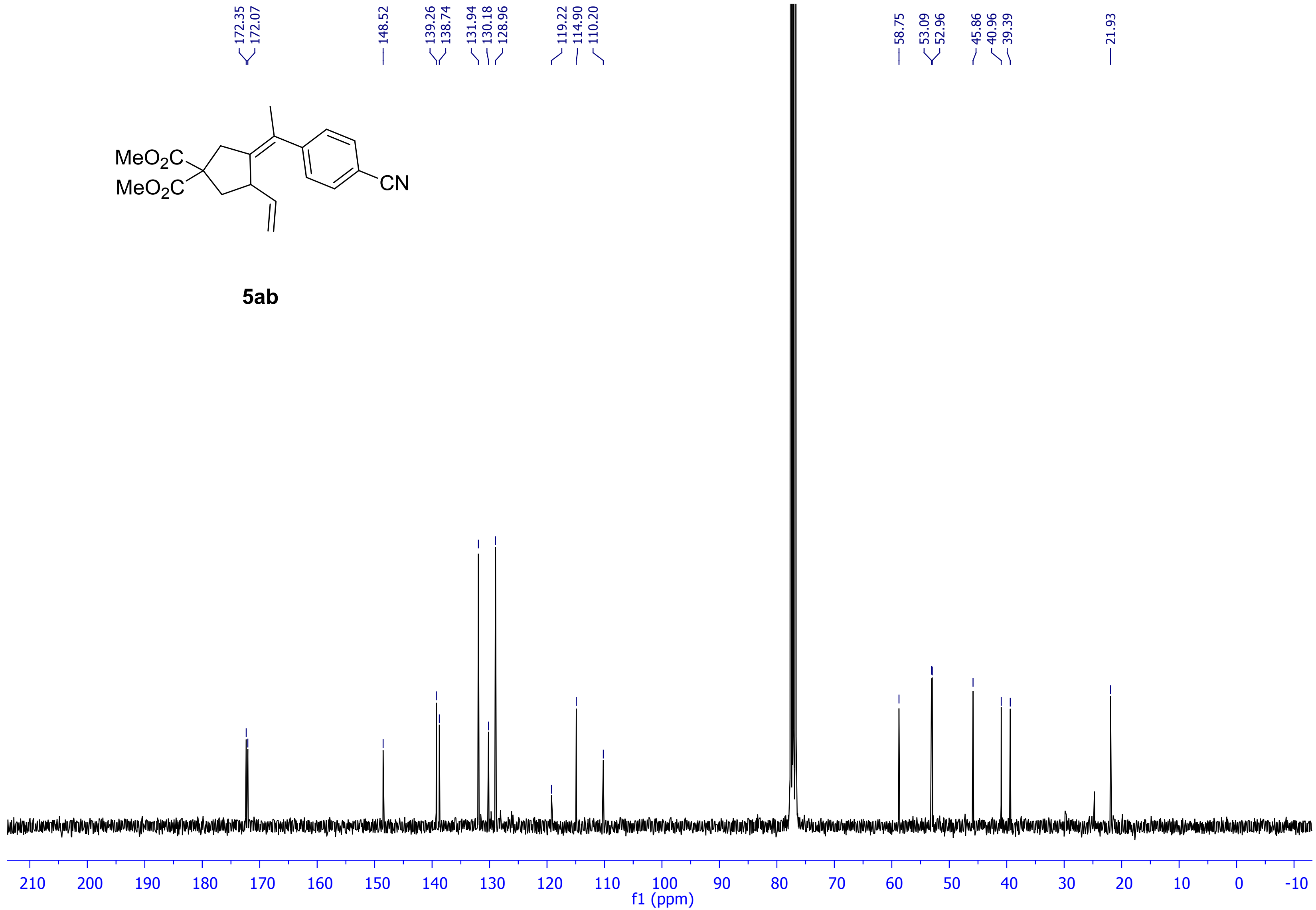
4

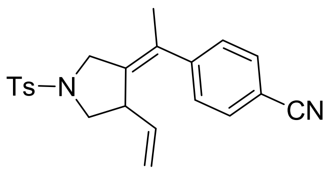

205.64
143.80
136.27
133.38
129.79
127.66
117.88
56.03
52.55
49.24
45.83
30.06
21.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



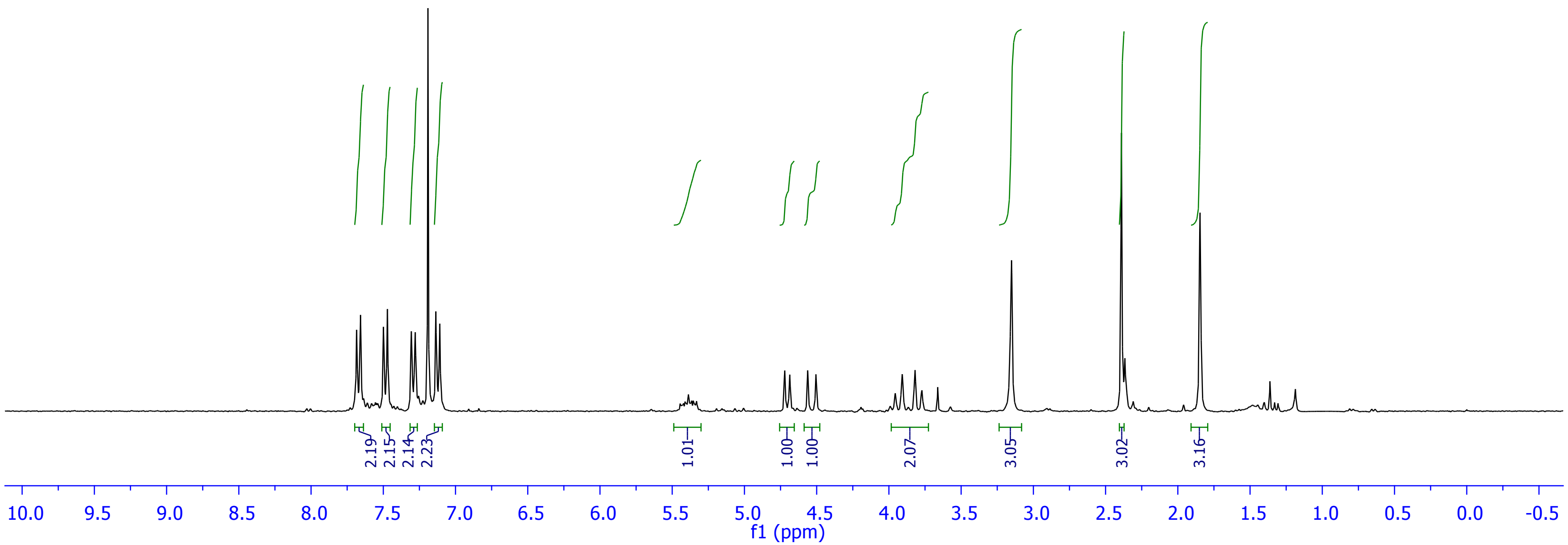
5ab


1.94
1.97
1.00
1.03
0.99
3.19
3.12
1.03
2.03
0.98
1.05
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

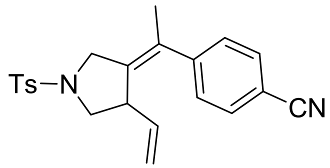

172.35
172.07
148.52
139.26
138.74
131.94
130.18
128.96
119.22
114.90
110.20
58.75
53.09
52.96
45.86
40.96
39.39
21.93
MeO2C
MeO2C
CN
5ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



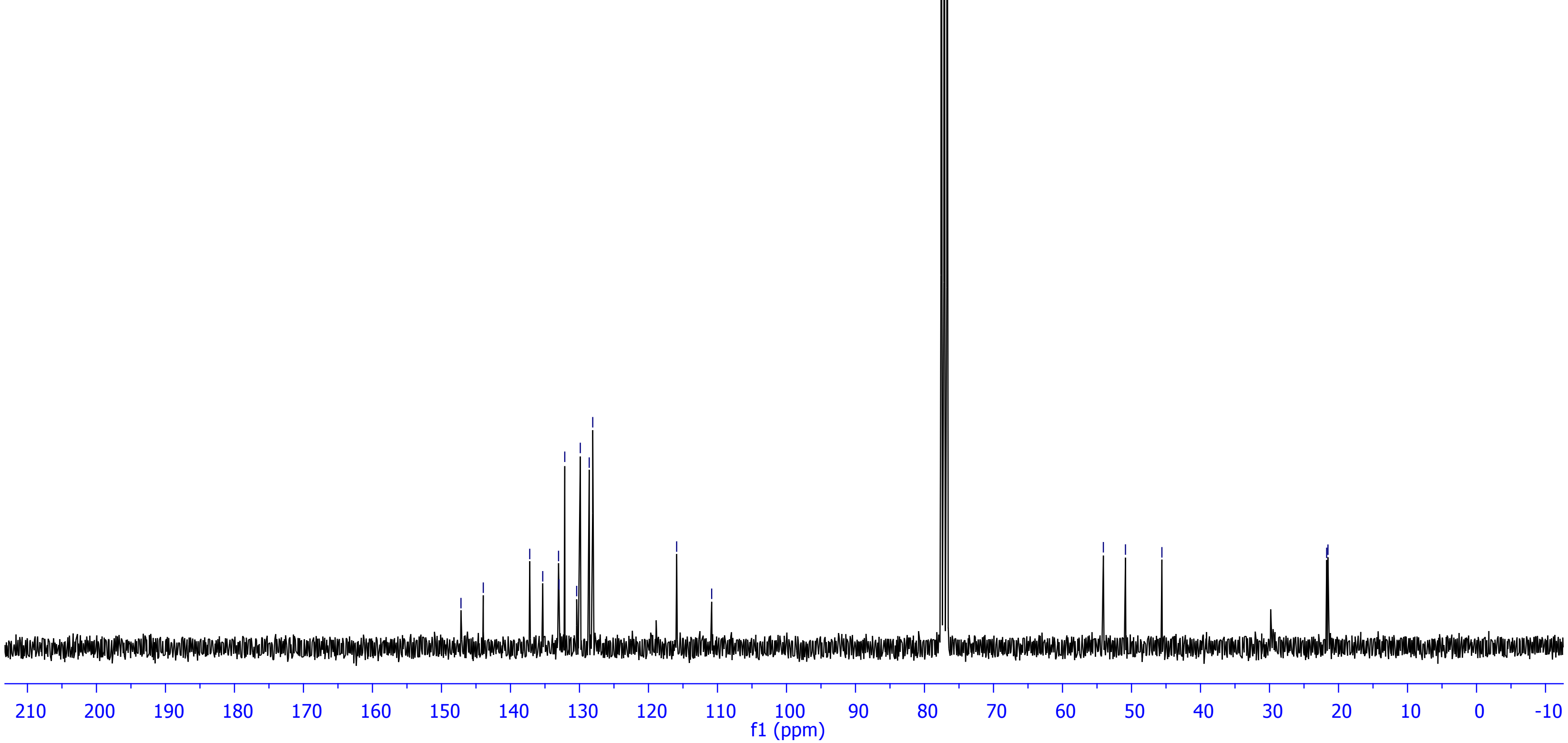
5ef

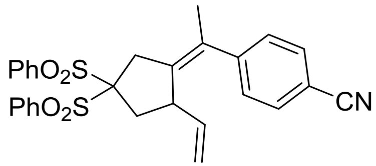


2.19
2.15
2.14
2.23
1.01
1.00
1.00
2.07
3.05
3.02
3.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

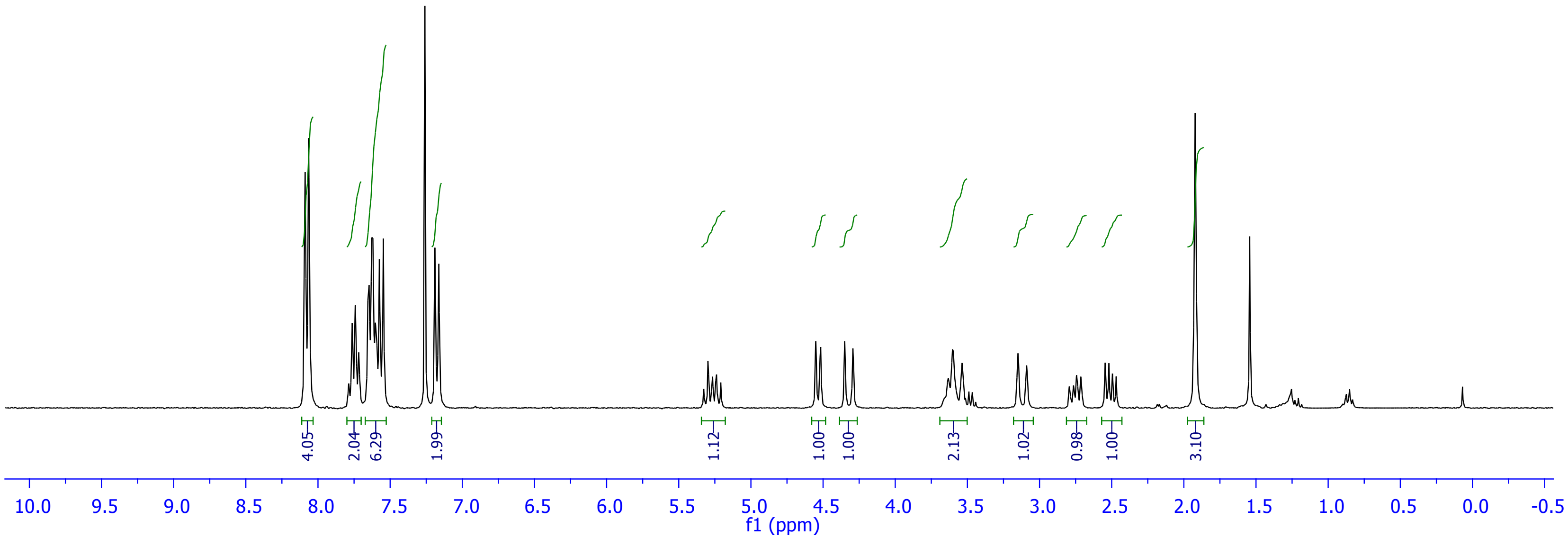

Ts–N
CN

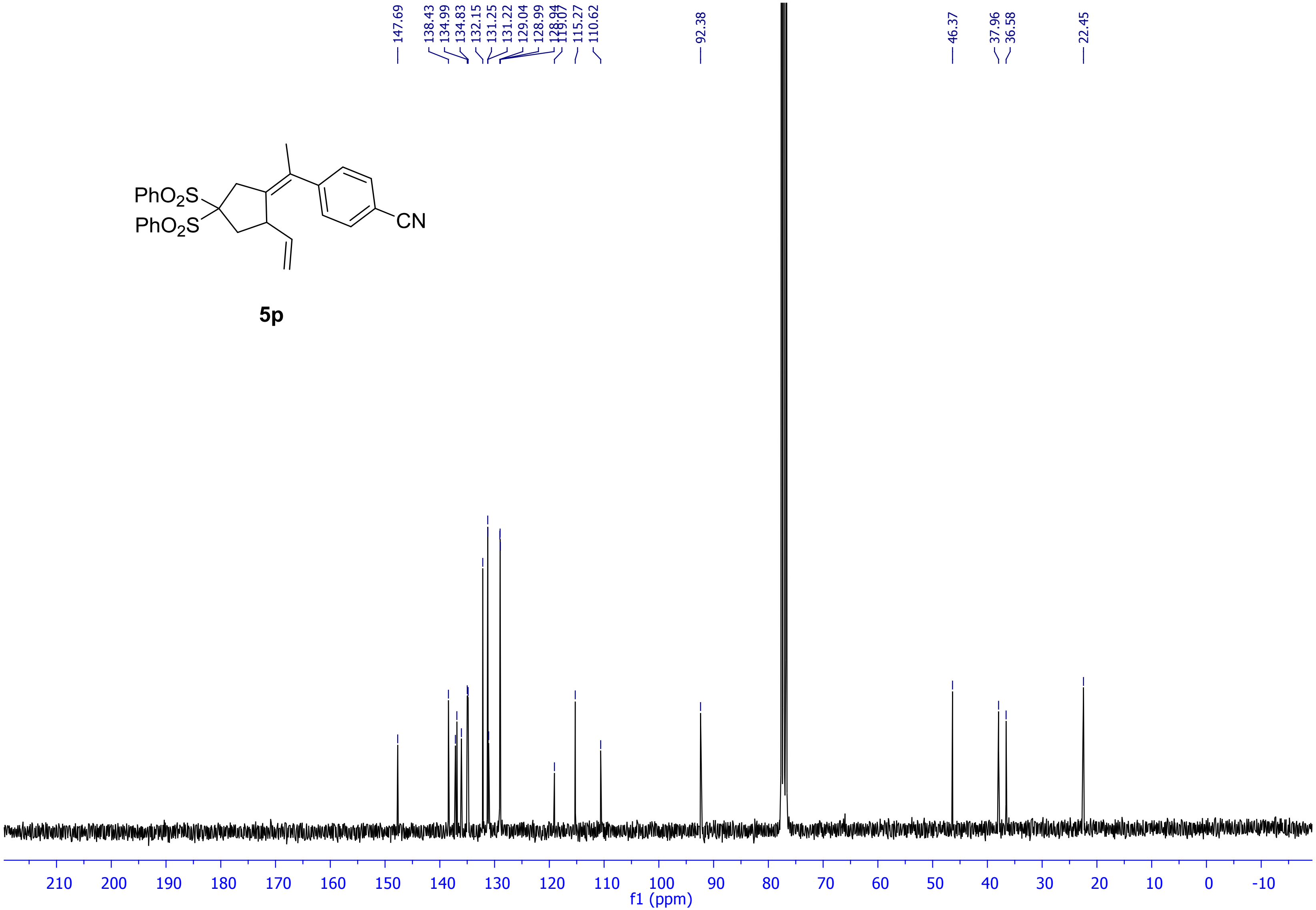
5ef


147.17
143.94
137.21
135.32
133.03
132.97
132.13
130.41
129.88
128.59
128.08
115.91
110.84
54.08
50.88
45.59
21.72
21.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

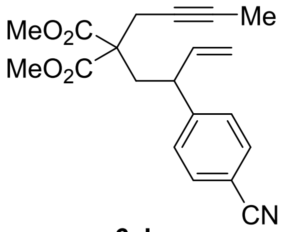

PhO2S
PhO2S
CN

5p

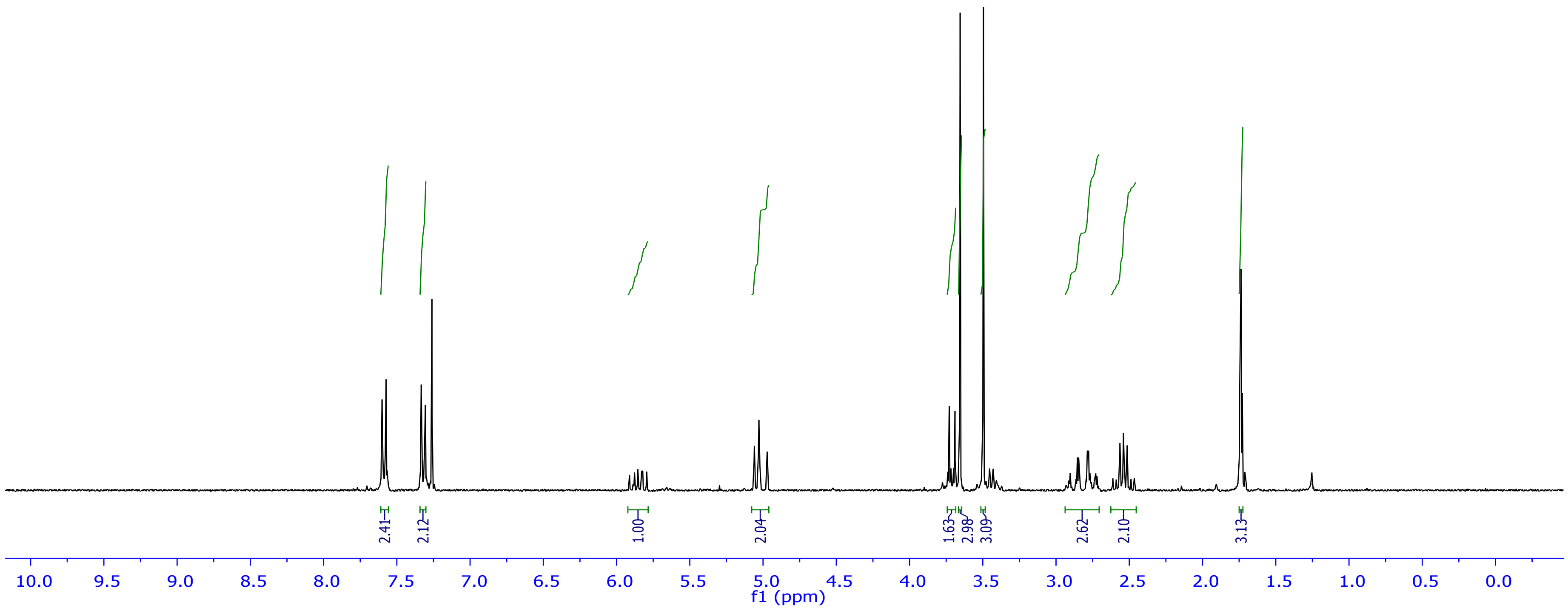

4.05
2.04
6.29
1.99
1.12
1.00
1.00
2.13
1.02
0.98
1.00
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

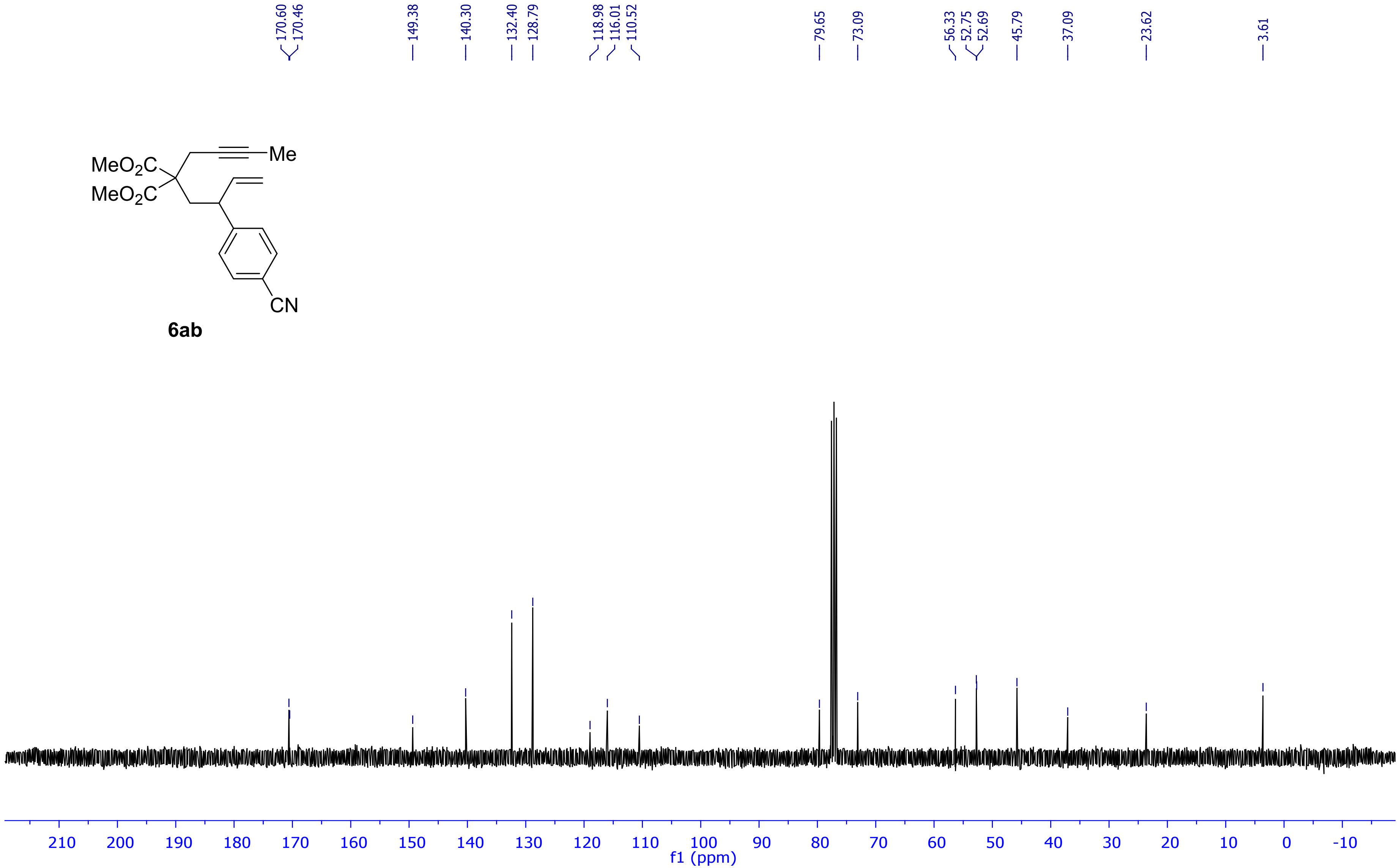


147.69
138.43
134.99
134.83
132.15
131.25
131.22
129.04
128.99
128.94
119.07
115.27
110.62
92.38
46.37
37.96
36.58
22.45
PhO2S
PhO2S
CN
5p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO2C
MeO2C
Me
CN

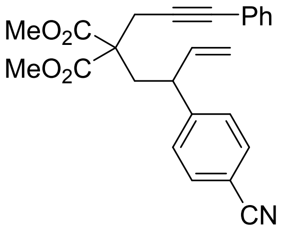
6ab


2.41
2.12
1.00
2.04
1.63
2.98
3.09
2.62
2.10
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

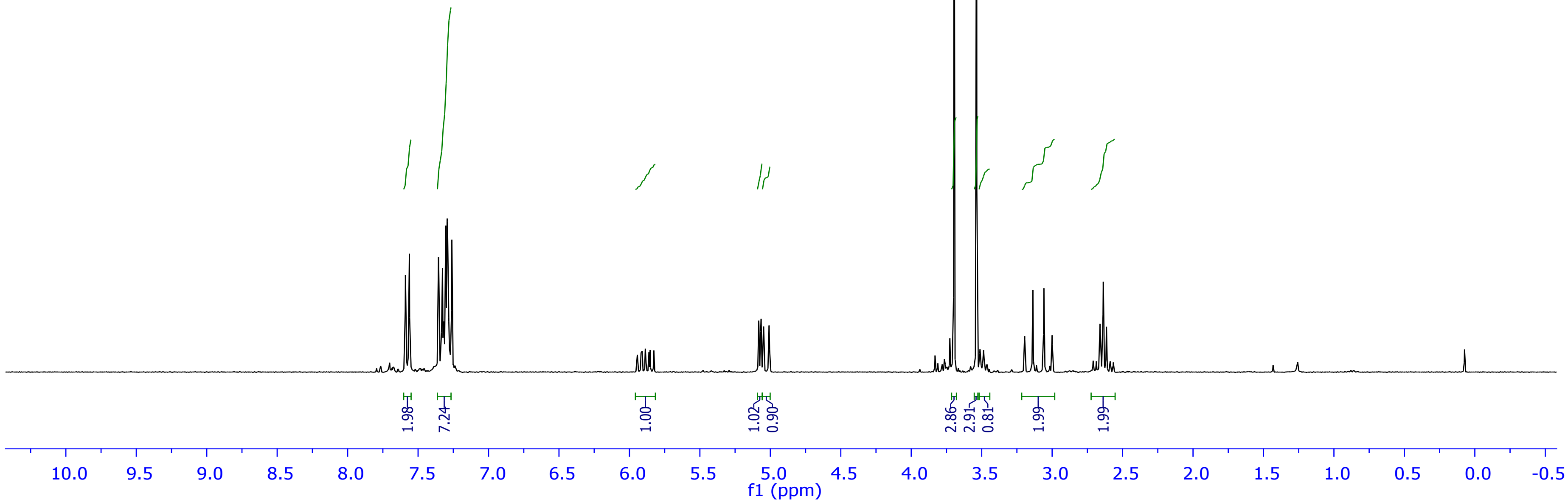


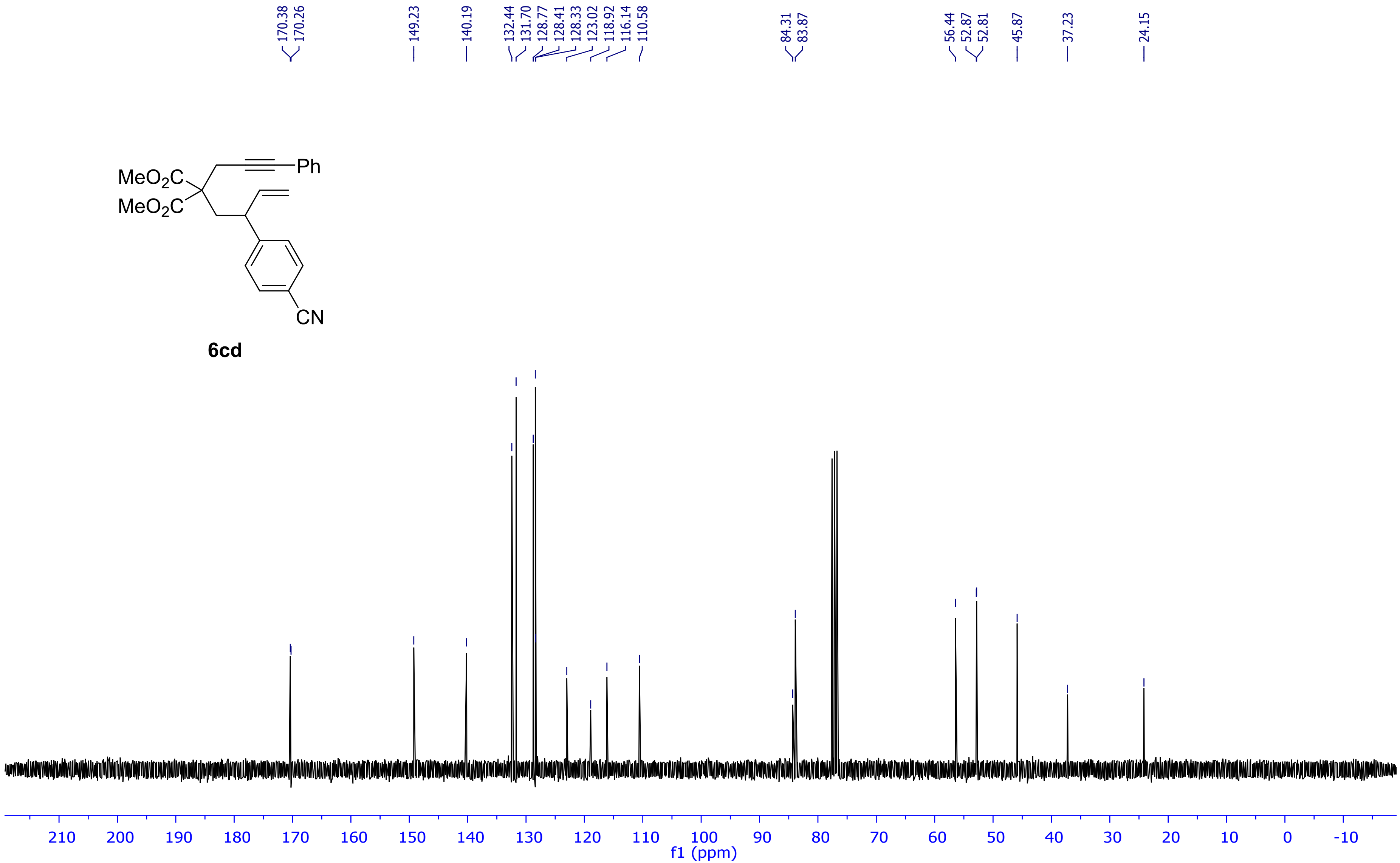
170.60
170.46
149.38
140.30
132.40
128.79
118.98
116.01
110.52
79.65
73.09
56.33
52.75
52.69
45.79
37.09
23.62
3.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

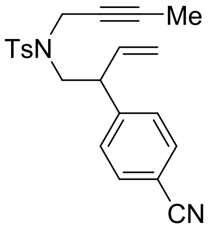
6ab


MeO2C
MeO2C
Ph
CN

6cd

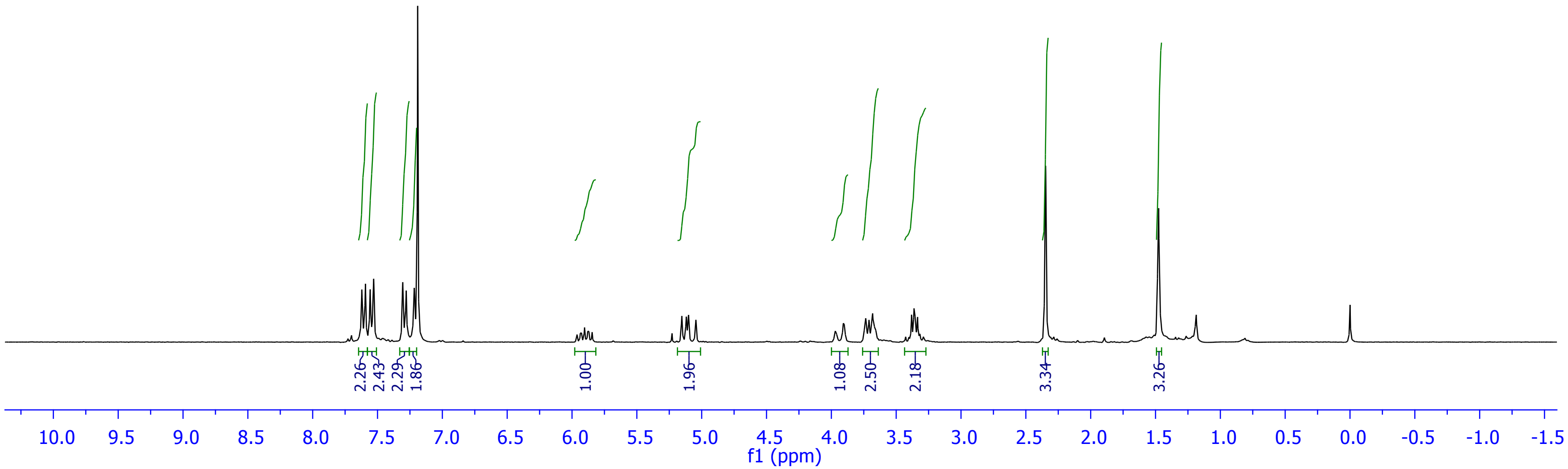

1.98
7.24
1.00
1.02
0.90
2.86
2.91
0.81
1.99
1.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


170.38
170.26
149.23
140.19
132.44
131.70
128.77
128.41
128.33
123.02
118.92
116.14
110.58
84.31
83.87
56.44
52.87
52.81
45.87
37.23
24.15
MeO2C
MeO2C
Ph
CN
6cd
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

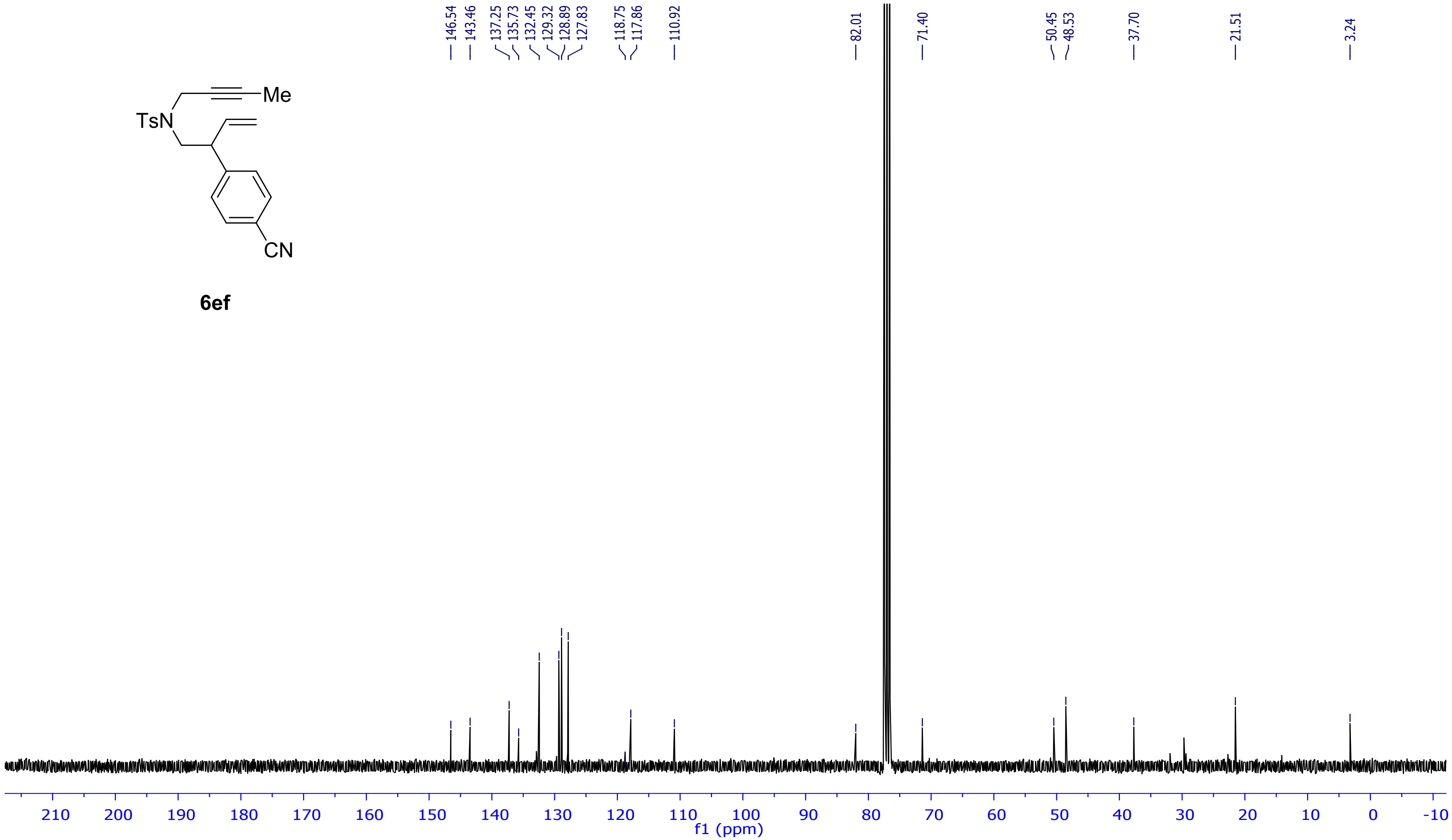


Me
TsN
CN

6ef



2.26
2.43
2.29
1.86
1.00
1.96
1.08
2.50
2.18
3.34
3.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)


Me
TsN
CN
146.54
143.46
137.25
135.73
132.45
129.32
128.89
127.83
118.75
117.86
110.92
82.01
71.40
50.45
48.53
37.70
21.51
3.24
210
200
190
180
170
160
150
140
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120
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100
90
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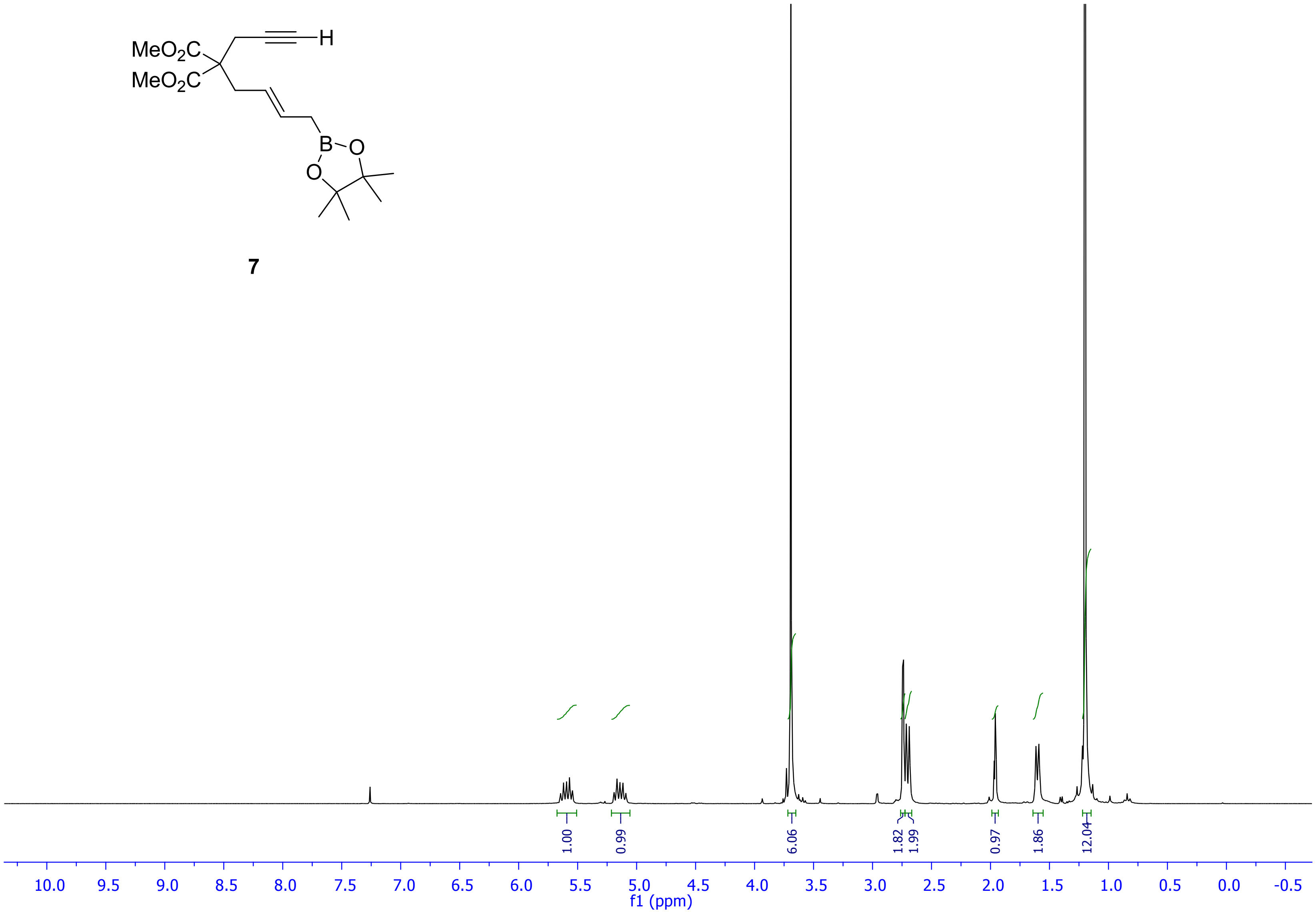
70
60
50
40
30
20
10
0
-10
f1 (ppm)

6ef



7
1.00
0.99
6.06
1.82
1.99
0.97
1.86
12.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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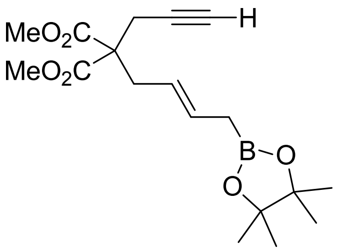
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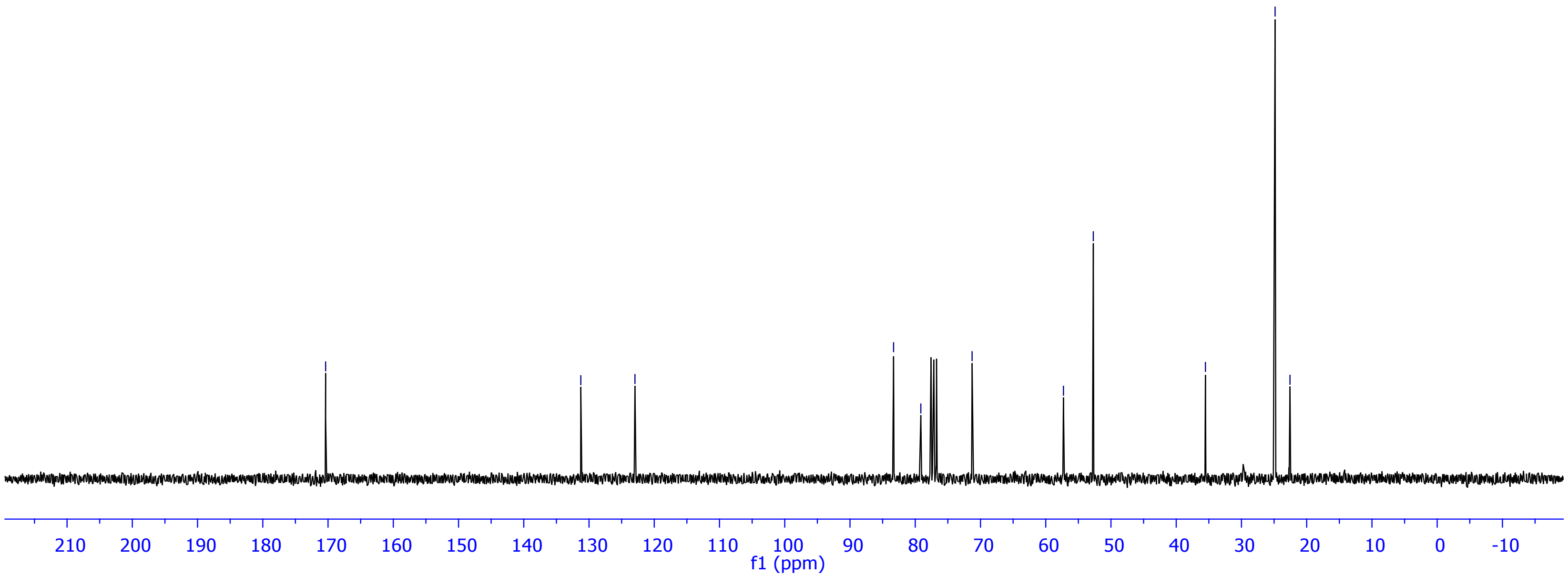
MeO2C
H
B
O
O

7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131.26
122.96
83.32
79.14
71.29
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35.52
24.84
22.56
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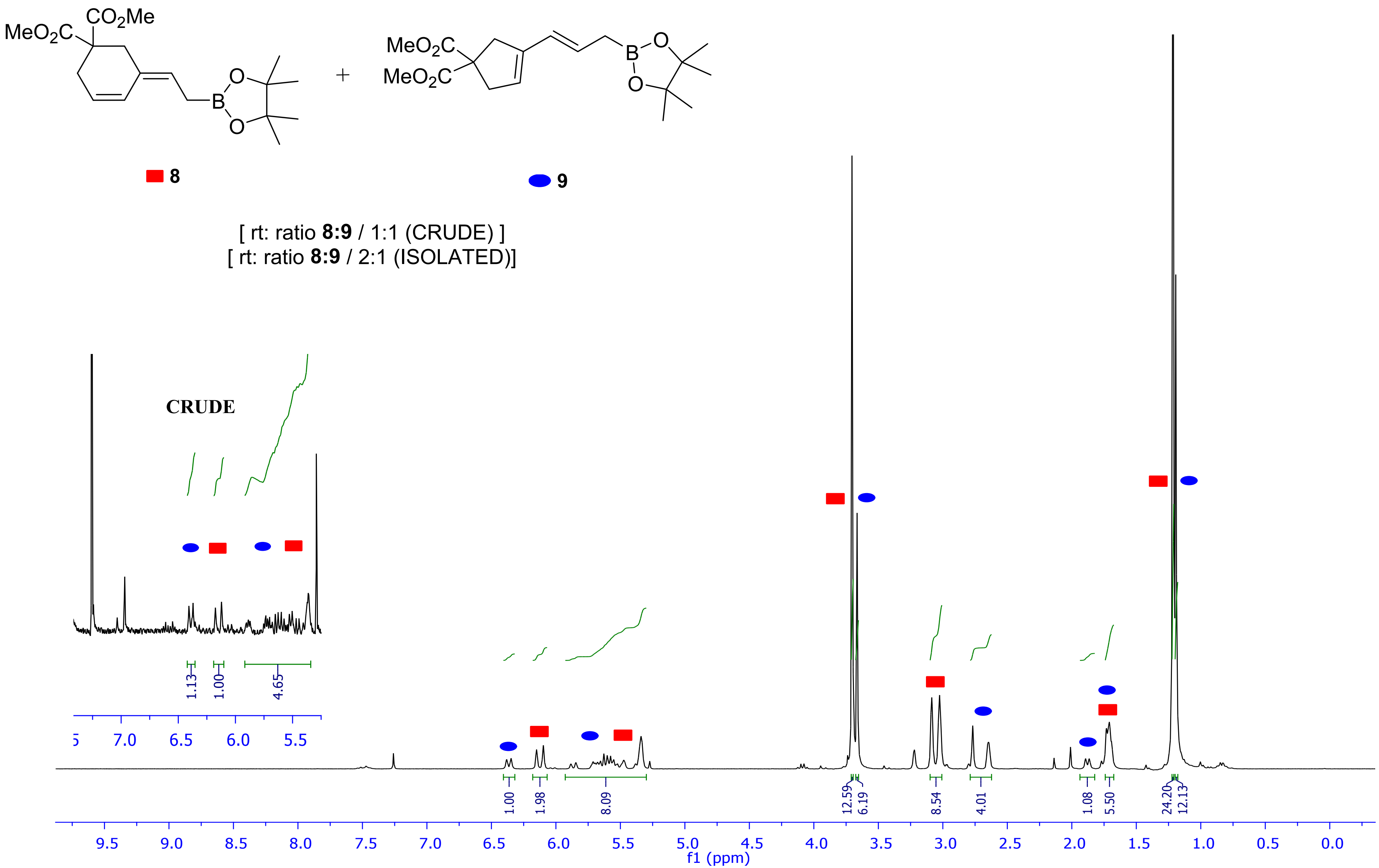
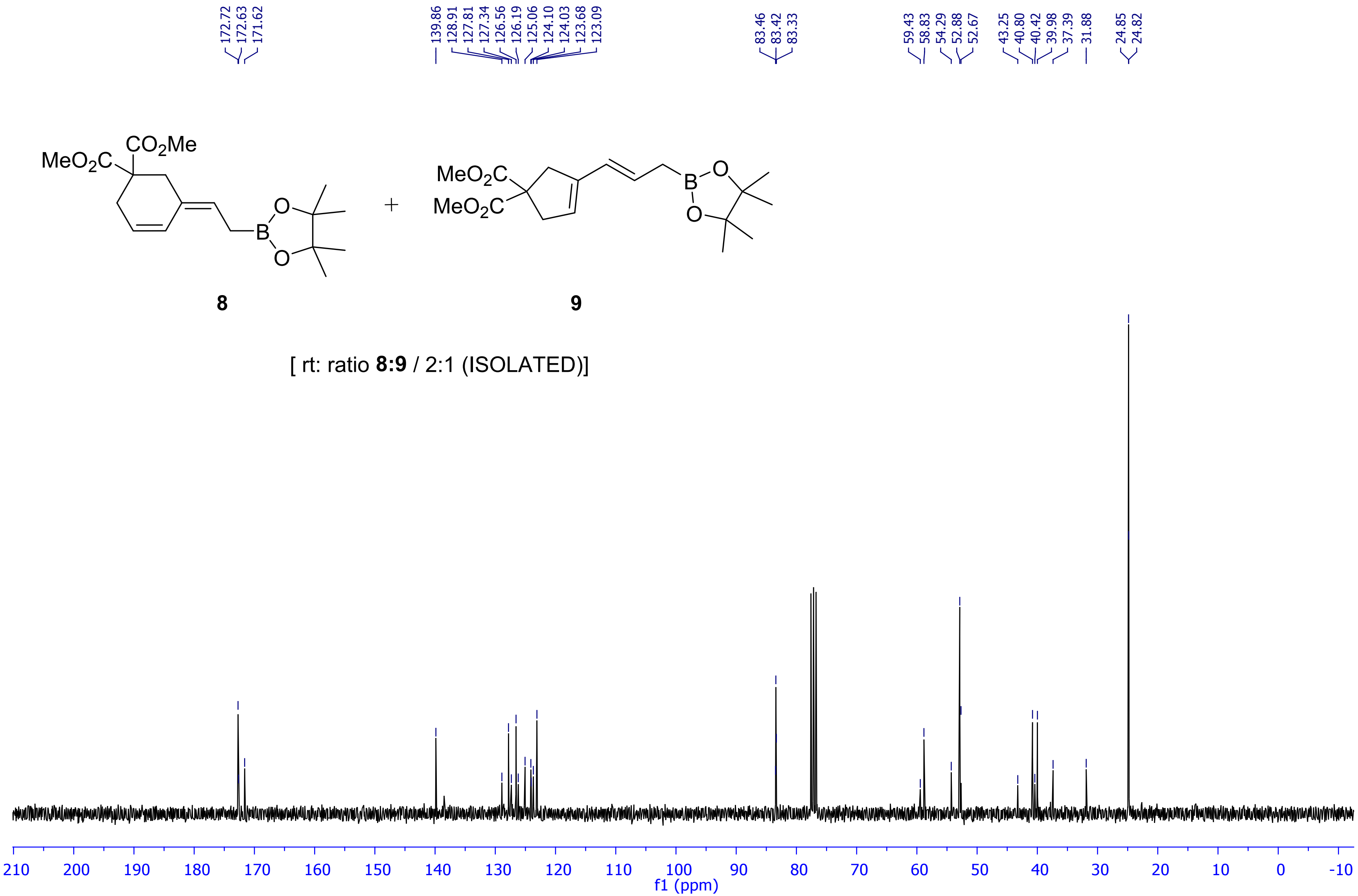
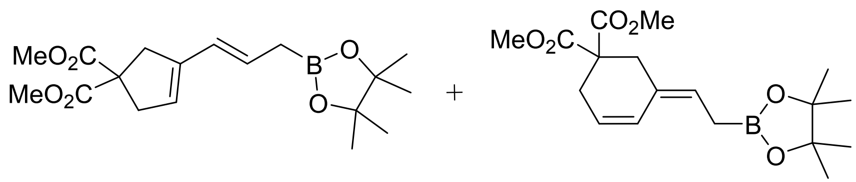
f1 (ppm)


8
9
[rt: ratio 8:9 / 1:1 (CRUDE)]
[rt: ratio 8:9 / 2:1 (ISOLATED)]
CRUDE
f1 (ppm)



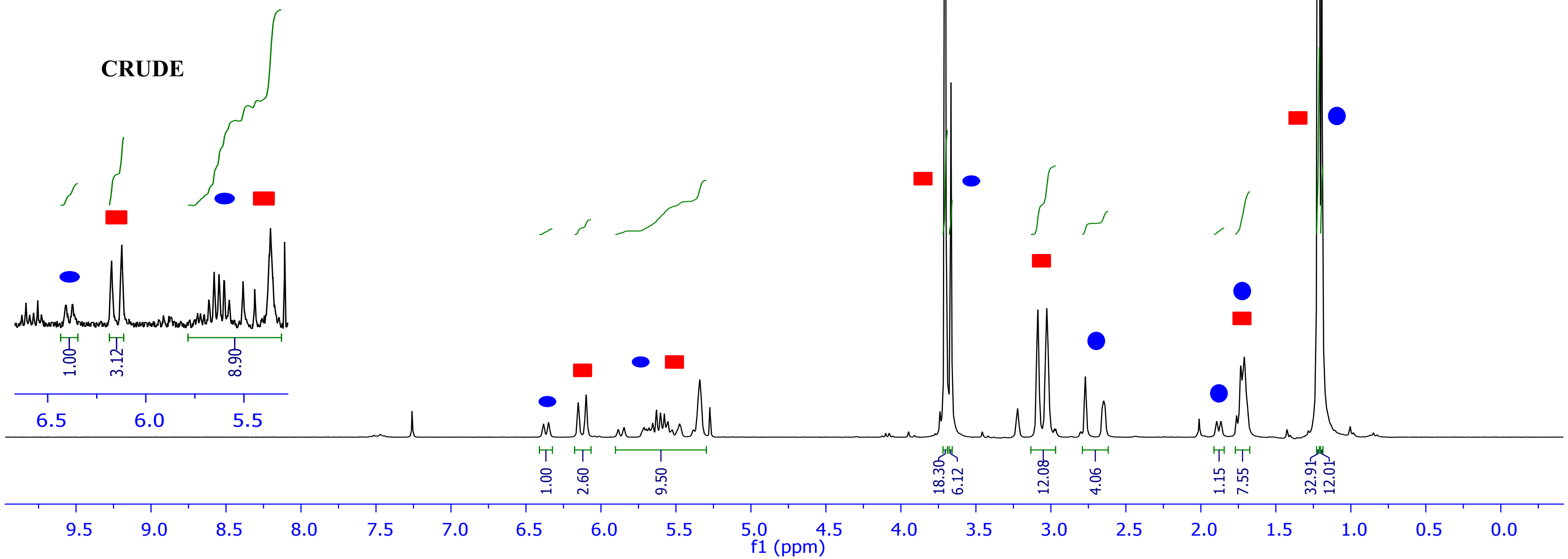
8 **9**

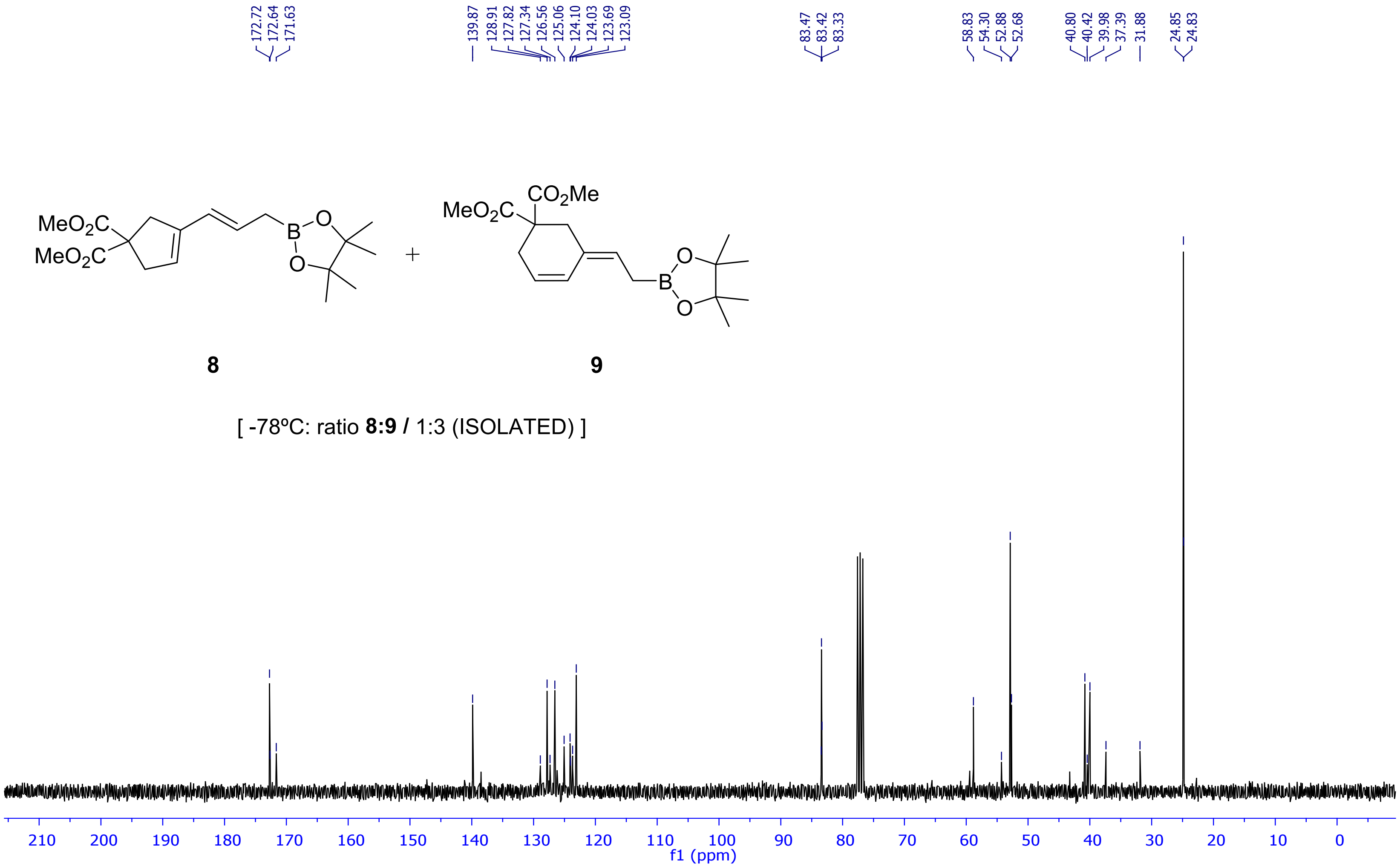
[rt: ratio **8:9** / 2:1 (ISOLATED)]



8 9

[-78ºC: ratio **8:9** / 1:3 (CRUDE)]
[-78ºC: ratio **8:9 /** 3:1 (ISOLATED)]





8 **9**

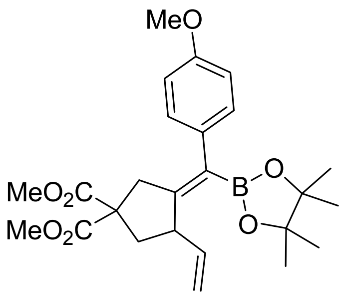
[-78ºC: ratio **8:9 /** 1:3 (ISOLATED)]

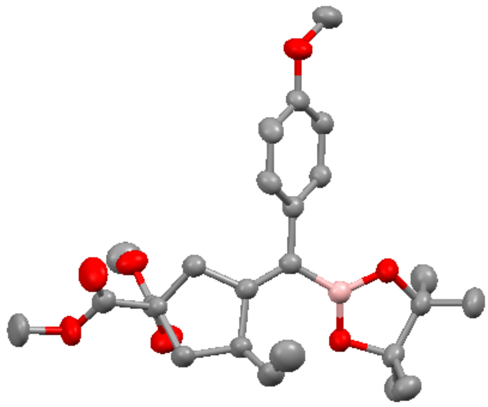
X-ray diffraction analysis

X-ray diffraction analysis of 3mn

Single crystals of **compound 3mn** suitable for X-ray diffraction were obtained by slow evaporation of a solution of the compound in hexane at room temperature. Details of the crystal structure, data acquisition and refining are given in the following tables.

Crystal Structure Report for Compound 3mn





A clear colourless prismatic-like specimen of $C_{25}H_{33}BO_7$, approximate dimensions 0.10 mm x 0.19 mm x 0.24 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table 1: Data collection details for compound 3mn.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Phi	34.959	20.50	12.48	-347.51	28.87	0.50	739	40.00	0.71073	50	30.0	n/a
Omega	34.959	5.50	3.78	-182.80	-61.97	0.50	89	40.00	0.71073	50	30.0	n/a
Phi	34.959	-12.00	-14.73	-313.05	82.04	0.50	739	40.00	0.71073	50	30.0	n/a

A total of 1567 frames were collected. The total exposure time was 17.41 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 16041 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 4463 were independent (average redundancy 3.594, completeness = 99.4%, R_{int} = 3.45%, R_{sig} = 3.74%) and 3099 (69.44%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.5236(5) Å, b = 11.7389(8) Å, c = 12.5461(8) Å, α = 62.680(3)°, β = 84.635(3)°, γ = 81.559(3)°, volume = 1232.12(13) $Å^3$, are based upon the refinement of the XYZ-centroids of 4086 reflections above 20 σ(I) with 5.580° < 2θ < 49.09°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.900. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9792 and 0.9913.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{25}H_{33}BO_7$. The final anisotropic full-matrix least-squares refinement on F^2

with 305 variables converged at R1 = 4.77%, for the observed data and wR2 = 18.11% for all data. The goodness-of-fit was 1.004. The largest peak in the final difference electron density synthesis was 0.290 $e^-/Å^3$ and the largest hole was -0.306 $e^-/Å^3$ with an RMS deviation of 0.094 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.230 g/cm^3 and F(000), 488 e^-.

Table 2. Sample and crystal data for compound 3mn.

Identification code	**compound 3mn**	
Chemical formula	$C_{25}H_{33}BO_7$	
Formula weight	456.32	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.10 x 0.19 x 0.24 mm	
Crystal habit	clear colourless prismatic	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.5236(5) Å	α = 62.680(3)°
	b = 11.7389(8) Å	β = 84.635(3)°
	c = 12.5461(8) Å	γ = 81.559(3)°
Volume	1232.12(13) $Å^3$	
Z	2	
Density (calculated)	1.230 Mg/cm^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	488	

Table 3. Data collection and structure refinement for compound 3mn.

Theta range for data collection	1.83 to 25.35°	
Index ranges	-11<=h<=11, -14<=k<=14, -15<=l<=15	
Reflections collected	16041	
Independent reflections	4463 [R(int) = 0.0345]	
Coverage of independent reflections	99.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9913 and 0.9792	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4463 / 0 / 305	
Goodness-of-fit on F^2	1.004	
Δ/σ_{max}	0.018	
Final R indices	3099 data; I>2σ(I)	R1 = 0.0477, wR2 = 0.1441
	all data	R1 = 0.0787, wR2 = 0.1811
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1253P)^2+0.0174P]$	

	where P=$(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.290 and -0.306 eÅ^{-3}
R.M.S. deviation from mean	0.094 eÅ^{-3}

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 3mn

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
B1	0.2156(2)	0.7944(2)	0.1748(2)	0.0369(6)
C1	0.1218(2)	0.89087(19)	0.21489(18)	0.0357(5)
C2	0.1216(2)	0.03292(19)	0.13417(18)	0.0351(5)
C3	0.1221(2)	0.1201(2)	0.1811(2)	0.0416(5)
C4	0.1211(2)	0.2509(2)	0.1086(2)	0.0464(6)
C5	0.1223(2)	0.2998(2)	0.9850(2)	0.0413(5)
C6	0.1236(2)	0.2161(2)	0.93518(19)	0.0396(5)
C7	0.1250(2)	0.0843(2)	0.00987(19)	0.0373(5)
C8	0.1329(3)	0.4841(2)	0.7931(2)	0.0633(7)
C9	0.3634(2)	0.7260(2)	0.0564(2)	0.0441(6)
C10	0.2822(3)	0.7583(3)	0.9455(2)	0.0628(7)
C11	0.5223(2)	0.7187(3)	0.0286(3)	0.0630(7)
C12	0.3158(2)	0.6077(2)	0.1703(2)	0.0429(5)
C13	0.2621(3)	0.5062(2)	0.1475(3)	0.0582(7)
C14	0.4267(3)	0.5431(3)	0.2681(3)	0.0602(7)
C15	0.0423(2)	0.84824(19)	0.31751(18)	0.0362(5)
C16	0.9289(2)	0.9282(2)	0.35599(19)	0.0399(5)
C17	0.8241(2)	0.83128(19)	0.43507(18)	0.0382(5)
C18	0.9261(2)	0.7083(2)	0.5047(2)	0.0463(6)
C19	0.0461(2)	0.7071(2)	0.41383(19)	0.0425(5)
C20	0.1853(3)	0.6483(3)	0.4737(2)	0.0596(7)
C21	0.2813(3)	0.7064(3)	0.4841(3)	0.0809(9)
C22	0.7354(2)	0.8745(2)	0.5196(2)	0.0452(6)
C23	0.5376(3)	0.8315(3)	0.6559(3)	0.0799(9)
C24	0.7266(2)	0.8084(2)	0.35940(19)	0.0404(5)
C25	0.5390(3)	0.9055(3)	0.2237(3)	0.0713(8)
O1	0.12322(19)	0.43085(15)	0.92020(15)	0.0576(5)
O2	0.19768(14)	0.66692(14)	0.21819(13)	0.0433(4)
O3	0.32166(14)	0.83150(14)	0.08833(14)	0.0452(4)
O4	0.63006(19)	0.80208(17)	0.57097(16)	0.0639(5)
O5	0.7565(2)	0.9603(2)	0.54014(18)	0.0733(6)
O6	0.64150(17)	0.91520(15)	0.29605(15)	0.0544(5)
O7	0.72520(19)	0.70859(17)	0.35579(17)	0.0647(5)

Table 5. Bond lengths (Å) for compound 3mn

B1-O2	1.369(3)	B1-O3	1.370(3)
B1-C1	1.573(3)	C1-C15	1.349(3)
C1-C2	1.502(3)	C2-C7	1.389(3)

C2-C3	1.396(3)	C3-C4	1.378(3)
C4-C5	1.385(3)	C5-O1	1.372(3)
C5-C6	1.383(3)	C6-C7	1.392(3)
C8-O1	1.420(3)	C9-O3	1.461(3)
C9-C10	1.519(3)	C9-C11	1.520(3)
C9-C12	1.555(3)	C12-O2	1.462(2)
C12-C13	1.510(3)	C12-C14	1.533(3)
C15-C16	1.517(3)	C15-C19	1.536(3)
C16-C17	1.545(3)	C17-C22	1.515(3)
C17-C24	1.519(3)	C17-C18	1.543(3)
C18-C19	1.541(3)	C19-C20	1.496(3)
C20-C21	1.268(4)	C22-O5	1.195(3)
C22-O4	1.331(3)	C23-O4	1.450(3)
C24-O7	1.195(3)	C24-O6	1.330(3)
C25-O6	1.443(3)		

Table 6. Bond angles (°) for compound 3mn

O2-B1-O3	112.73(19)	O2-B1-C1	124.37(19)
O3-B1-C1	122.86(19)	C15-C1-C2	120.65(19)
C15-C1-B1	121.46(19)	C2-C1-B1	117.88(18)
C7-C2-C3	116.44(19)	C7-C2-C1	122.34(18)
C3-C2-C1	121.20(18)	C4-C3-C2	122.1(2)
C3-C4-C5	120.2(2)	O1-C5-C6	124.6(2)
O1-C5-C4	116.1(2)	C6-C5-C4	119.3(2)
C5-C6-C7	119.6(2)	C2-C7-C6	122.27(19)
O3-C9-C10	106.81(19)	O3-C9-C11	108.69(18)
C10-C9-C11	110.3(2)	O3-C9-C12	102.28(17)
C10-C9-C12	113.45(19)	C11-C9-C12	114.6(2)
O2-C12-C13	108.48(17)	O2-C12-C14	106.35(18)
C13-C12-C14	109.6(2)	O2-C12-C9	102.24(16)
C13-C12-C9	115.4(2)	C14-C12-C9	114.07(18)
C1-C15-C16	126.75(19)	C1-C15-C19	125.42(19)
C16-C15-C19	107.76(17)	C15-C16-C17	103.88(16)
C22-C17-C24	109.41(18)	C22-C17-C18	111.24(17)
C24-C17-C18	110.62(18)	C22-C17-C16	112.19(18)
C24-C17-C16	111.53(17)	C18-C17-C16	101.69(17)
C19-C18-C17	105.38(17)	C20-C19-C15	115.01(19)
C20-C19-C18	111.49(19)	C15-C19-C18	104.84(16)
C21-C20-C19	127.5(3)	O5-C22-O4	123.6(2)
O5-C22-C17	125.6(2)	O4-C22-C17	110.8(2)
O7-C24-O6	123.6(2)	O7-C24-C17	125.4(2)
O6-C24-C17	110.97(18)	C5-O1-C8	117.9(2)
B1-O2-C12	107.37(16)	B1-O3-C9	107.35(16)
C22-O4-C23	116.8(2)	C24-O6-C25	116.74(19)

Table 7. Anisotropic atomic displacement parameters (Å^2) for compound 3mn

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.0350(12)	0.0387(14)	0.0372(13)	-0.0170(11)	-0.0055(10)	-0.0029(10)
C1	0.0359(10)	0.0346(12)	0.0355(12)	-0.0144(9)	-0.0059(9)	-0.0029(8)
C2	0.0324(10)	0.0370(12)	0.0367(12)	-0.0167(10)	-0.0037(8)	-0.0042(8)
C3	0.0486(12)	0.0454(14)	0.0330(12)	-0.0173(10)	-0.0006(9)	-0.0138(10)
C4	0.0546(13)	0.0476(14)	0.0471(14)	-0.0280(12)	0.0036(10)	-0.0168(10)
C5	0.0369(11)	0.0359(12)	0.0451(13)	-0.0126(11)	0.0014(9)	-0.0080(9)
C6	0.0388(11)	0.0425(13)	0.0334(12)	-0.0140(10)	-0.0002(9)	-0.0039(9)
C7	0.0377(11)	0.0382(12)	0.0379(12)	-0.0192(10)	-0.0004(9)	-0.0033(9)
C8	0.0696(17)	0.0438(15)	0.0537(16)	-0.0032(12)	-0.0002(13)	-0.0055(12)
C9	0.0394(11)	0.0450(13)	0.0510(14)	-0.0263(11)	0.0040(10)	-0.0013(9)
C10	0.0637(16)	0.0754(19)	0.0518(16)	-0.0320(15)	0.0018(12)	-0.0070(13)
C11	0.0437(13)	0.0649(17)	0.080(2)	-0.0363(15)	0.0138(13)	-0.0041(11)
C12	0.0396(11)	0.0408(13)	0.0515(14)	-0.0254(11)	0.0013(10)	-0.0008(9)
C13	0.0612(15)	0.0542(16)	0.0741(18)	-0.0420(14)	0.0088(13)	-0.0123(12)
C14	0.0594(15)	0.0484(15)	0.0668(17)	-0.0227(13)	-0.0107(13)	0.0055(11)
C15	0.0372(11)	0.0336(12)	0.0351(12)	-0.0134(10)	-0.0049(9)	-0.0007(8)
C16	0.0438(11)	0.0371(12)	0.0380(12)	-0.0165(10)	-0.0021(9)	-0.0032(9)
C17	0.0440(11)	0.0340(12)	0.0328(11)	-0.0137(10)	0.0016(9)	-0.0004(9)
C18	0.0535(13)	0.0395(13)	0.0345(12)	-0.0103(10)	0.0020(10)	0.0037(10)
C19	0.0486(12)	0.0356(12)	0.0347(12)	-0.0113(10)	0.0017(10)	0.0026(9)
C20	0.0626(16)	0.0531(16)	0.0451(15)	-0.0112(13)	-0.0026(12)	0.0093(12)
C21	0.075(2)	0.085(2)	0.072(2)	-0.0246(18)	-0.0231(16)	-0.0018(17)
C22	0.0511(13)	0.0437(14)	0.0353(12)	-0.0157(11)	-0.0041(10)	0.0047(10)
C23	0.081(2)	0.089(2)	0.0618(18)	-0.0376(17)	0.0283(15)	0.0064(16)
C24	0.0466(12)	0.0377(13)	0.0368(12)	-0.0182(10)	0.0073(9)	-0.0057(9)
C25	0.0688(17)	0.073(2)	0.079(2)	-0.0362(17)	-0.0279(15)	-0.0074(14)
O1	0.0749(11)	0.0368(9)	0.0534(11)	-0.0137(8)	0.0058(8)	-0.0116(8)
O2	0.0442(8)	0.0403(9)	0.0476(9)	-0.0234(7)	0.0066(7)	-0.0047(6)
O3	0.0412(8)	0.0411(9)	0.0543(10)	-0.0236(8)	0.0078(7)	-0.0068(6)
O4	0.0681(11)	0.0630(12)	0.0638(12)	-0.0359(10)	0.0290(9)	-0.0115(9)
O5	0.0911(14)	0.0829(15)	0.0731(13)	-0.0589(12)	0.0122(11)	-0.0174(11)
O6	0.0602(10)	0.0439(10)	0.0617(11)	-0.0244(9)	-0.0201(8)	-0.0008(8)
O7	0.0807(12)	0.0479(11)	0.0778(13)	-0.0390(10)	-0.0102(10)	-0.0028(9)

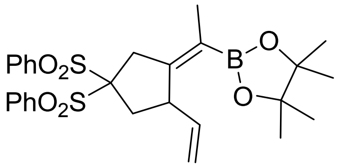
Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for compound 3mn

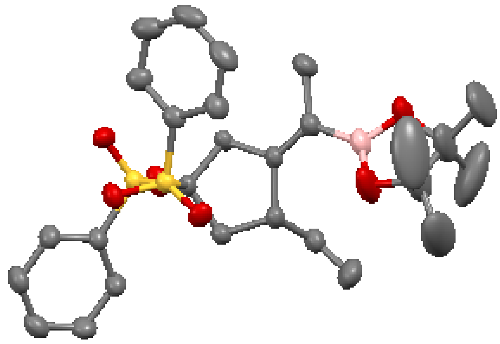
	x/a	y/b	z/c	U(eq)
H3	0.1231	1.0890	0.2639	0.05
H4	0.1195	1.3065	0.1429	0.056
H6	0.1236	1.2477	-0.1477	0.048

	x/a	y/b	z/c	U(eq)
H7	0.1282	1.0287	-0.0246	0.045
H8A	0.2184	1.4458	-0.2305	0.095
H8B	0.1347	1.5757	-0.2409	0.095
H8C	0.0523	1.4668	-0.2353	0.095
H10A	0.1820	0.7650	-0.0364	0.094
H10B	0.3072	0.6913	-0.0789	0.094
H10C	0.3060	0.8389	-0.1182	0.094
H11A	0.5428	0.7948	-0.0427	0.094
H11B	0.5529	0.6438	0.0163	0.094
H11C	0.5716	0.7128	0.0946	0.094
H13A	0.2332	0.4383	0.2223	0.087
H13B	0.3365	0.4713	0.1099	0.087
H13C	0.1826	0.5445	0.0958	0.087
H14A	0.4594	0.6075	0.2836	0.09
H14B	0.5054	0.5002	0.2417	0.09
H14C	0.3846	0.4812	0.3403	0.09
H16A	-0.1178	0.9989	0.2870	0.048
H16B	-0.0306	0.9630	0.4014	0.048
H18A	-0.0363	0.7111	0.5726	0.056
H18B	-0.1225	0.6319	0.5339	0.056
H19	0.0224	0.6553	0.3765	0.051
H20	0.2035	0.5588	0.5072	0.072
H21A	0.2689	0.7960	0.4524	0.097
H21B	0.3642	0.6596	0.5235	0.097
H23A	-0.4123	0.8047	0.7281	0.12
H23B	-0.5446	0.7865	0.6743	0.12
H23C	-0.4914	0.9228	0.6214	0.12
H25A	-0.4149	0.9078	0.1514	0.107
H25B	-0.5349	0.9765	0.2036	0.107
H25C	-0.5013	0.8257	0.2679	0.107

Crystal Structure Report for Compound 3p

Single crystals of **compound 3p** suitable for X-ray diffraction were obtained by slow evaporation of a solution of the compound in hexane at room temperature. Details of the crystal structure, data acquisition and refining are given in the following table.





A clear colourless prismatic-like specimen of $C_{27}H_{33}BO_6S_2$, approximate dimensions 0.04 mm x 0.06 mm x 0.19 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table 1: Data collection details for compound 3p.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Phi	35.000	18.00	4.37	15.98	36.29	0.50	639	120.00	0.71073	50	30.0	n/a
Omega	35.000	-12.00	-98.48	-66.65	30.74	0.50	178	120.00	0.71073	50	30.0	n/a
Omega	35.000	15.50	13.11	75.75	-42.86	0.50	111	120.00	0.71073	50	30.0	n/a
Omega	35.000	-17.00	-105.88	-93.28	32.60	0.50	130	120.00	0.71073	50	30.0	n/a
Omega	35.000	-7.00	-37.77	-213.27	93.98	0.50	63	120.00	0.71073	50	30.0	n/a
Omega	35.000	-9.50	-2.08	-265.18	-44.66	0.50	141	120.00	0.71073	50	30.0	n/a
Phi	35.000	8.00	167.83	-37.63	-99.07	0.50	195	120.00	0.71073	50	30.0	n/a

A total of 1457 frames were collected. The total exposure time was 48.57 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 50200 reflections to a maximum θ angle of 29.41° (0.72 Å resolution), of which 7595 were independent (average redundancy 6.610, completeness = 98.7%, R_{int} = 6.10%, R_{sig} = 5.76%) and 4803 (63.24%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.1024(2) Å, b = 13.4762(3) Å, c = 25.6608(5) Å, β = 96.5180(10)°, volume = 2783.78(11) $Å^3$, are based upon the refinement of the XYZ-centroids of 9994 reflections above 20 σ(I) with 5.060° < 2θ < 56.57°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.897. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9577 and 0.9909.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{27}H_{33}BO_6S_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 331 variables converged at R1 = 6.01%, for the observed data and wR2 = 17.94% for all data. The goodness-of-fit was 1.018. The largest peak in the final difference electron density synthesis was 0.611 $e^-/Å^3$ and the largest hole was -0.528 $e^-/Å^3$ with an RMS deviation of 0.155 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.261 g/cm^3 and F(000), 1120 e^-.

Table 2. Sample and crystal data for compound 3p

Identification code	**compound 3m**

Chemical formula	$C_{27}H_{33}BO_6S_2$	
Formula weight	528.46	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.04 x 0.06 x 0.19 mm	
Crystal habit	clear colourless prismatic	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 8.1024(2) Å	α = 90°
	b = 13.4762(3) Å	β = 96.5180(10)°
	c = 25.6608(5) Å	γ = 90°
Volume	2783.78(11) $Å^3$	
Z	4	
Density (calculated)	1.261 Mg/cm^3	
Absorption coefficient	0.229 mm^{-1}	
F(000)	1120	

Table 3. Data collection and structure refinement for compound 3p.

Theta range for data collection	1.60 to 29.41°	
Index ranges	-10<=h<=11, -18<=k<=18, -35<=l<=35	
Reflections collected	50200	
Independent reflections	7595 [R(int) = 0.0610]	
Coverage of independent reflections	98.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9909 and 0.9577	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	Σ w(F_o^2 - F_c^2)^2	
Data / restraints / parameters	7595 / 0 / 331	
Goodness-of-fit on F^2	1.018	
Δ/σ_{max}	0.010	
Final R indices	4803 data; I>2σ(I)	R1 = 0.0601, wR2 = 0.1482
	all data	R1 = 0.1082, wR2 = 0.1794
Weighting scheme	w=1/[σ^2(F_o^2)+(0.1068P)^2+0.0863P] where P=(F_o^2+2F_c^2)/3	
Extinction coefficient	0.0227(19)	
Largest diff. peak and hole	0.611 and -0.528 $eÅ^{-3}$	
R.M.S. deviation from mean	0.155 $eÅ^{-3}$	

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 3p.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
B1	0.1897(4)	0.2121(2)	0.06852(10)	0.0443(7)
C1	0.8229(3)	0.09438(16)	0.32814(8)	0.0318(5)
C2	0.8161(3)	0.00973(18)	0.35838(9)	0.0399(5)
C3	0.6706(3)	0.98623(19)	0.37897(10)	0.0464(6)
C4	0.5329(3)	0.0464(2)	0.36844(10)	0.0476(6)
C5	0.5398(3)	0.1307(2)	0.33864(10)	0.0476(6)
C6	0.6850(3)	0.15612(19)	0.31852(9)	0.0409(5)
C7	0.2183(3)	0.94921(17)	0.21057(9)	0.0366(5)
C8	0.3324(3)	0.92796(19)	0.25342(10)	0.0454(6)
C9	0.4925(3)	0.9028(2)	0.24503(12)	0.0563(7)
C10	0.5384(3)	0.8986(2)	0.19506(13)	0.0598(8)
C11	0.4231(4)	0.9186(2)	0.15270(12)	0.0620(8)
C12	0.2626(3)	0.9450(2)	0.15988(10)	0.0477(6)
C16	0.9332(3)	0.19527(16)	0.15130(8)	0.0340(5)
C17	0.1229(3)	0.18911(16)	0.16313(8)	0.0325(5)
C18	0.2354(3)	0.19775(18)	0.12881(8)	0.0382(5)
C19	0.8730(3)	0.29571(19)	0.13280(9)	0.0433(6)
C20	0.7768(4)	0.3140(3)	0.08923(12)	0.0704(9)
C21	0.4205(3)	0.1938(2)	0.14633(10)	0.0515(7)
C25	0.2099(5)	0.2703(4)	0.98621(11)	0.0952(14)
C26	0.0813(5)	0.1925(3)	0.98362(11)	0.0938(14)
C27	0.0125(3)	0.11562(15)	0.23691(7)	0.0301(5)
C28	0.1652(3)	0.17130(17)	0.22113(7)	0.0322(5)
C29	0.8679(3)	0.16787(17)	0.20391(8)	0.0340(5)
C30	0.3411(7)	0.2688(5)	0.94960(16)	0.141(2)
C31	0.9170(7)	0.2042(5)	0.95267(15)	0.152(3)
C32	0.1638(10)	0.0903(4)	0.96440(19)	0.189(3)
C33	0.1204(9)	0.3739(4)	0.9821(2)	0.176(3)
O1	0.14358(19)	0.07004(14)	0.33320(6)	0.0441(4)

	x/a	y/b	z/c	U(eq)
O2	0.0256(2)	0.23751(13)	0.31635(6)	0.0470(4)
O3	0.9557(2)	0.92642(12)	0.26094(6)	0.0406(4)
O4	0.9170(2)	0.97641(12)	0.16785(6)	0.0414(4)
O7	0.2918(3)	0.2630(2)	0.03985(7)	0.0812(7)
O8	0.0565(3)	0.17544(19)	0.03875(7)	0.0809(8)
S1	0.01122(6)	0.98238(4)	0.21858(2)	0.03183(16)
S2	0.01429(7)	0.13213(4)	0.308099(19)	0.03276(17)

Table 5. Bond lengths (Å) for compound 3p.

B1-O8	1.344(4)	B1-O7	1.354(3)
B1-C18	1.561(3)	C1-C2	1.384(3)
C1-C6	1.393(3)	C1-S2	1.763(2)
C2-C3	1.382(3)	C3-C4	1.381(4)
C4-C5	1.374(4)	C5-C6	1.380(3)
C7-C8	1.384(3)	C7-C12	1.389(3)
C7-S1	1.771(2)	C8-C9	1.381(3)
C9-C10	1.376(4)	C10-C11	1.377(4)
C11-C12	1.381(4)	C16-C19	1.498(3)
C16-C17	1.534(3)	C16-C29	1.550(3)
C17-C18	1.343(3)	C17-C28	1.508(3)
C18-C21	1.517(3)	C19-C20	1.311(4)
C25-O7	1.462(4)	C25-C26	1.475(5)
C25-C30	1.496(6)	C25-C33	1.570(7)
C26-O8	1.469(3)	C26-C31	1.479(6)
C26-C32	1.632(7)	C27-C29	1.537(3)
C27-C28	1.540(3)	C27-S2	1.839(2)
C27-S1	1.856(2)	O1-S2	1.4350(16)
O2-S2	1.4373(17)	O3-S1	1.4368(16)
O4-S1	1.4345(15)		

Table 6. Bond angles (°) for compound 3p

O8-B1-O7	112.2(2)	O8-B1-C18	127.0(2)
O7-B1-C18	120.7(2)	C2-C1-C6	120.6(2)
C2-C1-S2	119.57(17)	C6-C1-S2	119.38(17)
C3-C2-C1	119.5(2)	C4-C3-C2	119.7(2)
C5-C4-C3	120.8(2)	C4-C5-C6	120.2(2)
C5-C6-C1	119.1(2)	C8-C7-C12	121.0(2)

C8-C7-S1	121.09(18)	C12-C7-S1	117.88(19)
C9-C8-C7	118.8(2)	C10-C9-C8	120.9(3)
C11-C10-C9	119.8(3)	C10-C11-C12	120.7(3)
C11-C12-C7	118.9(3)	C19-C16-C17	113.25(18)
C19-C16-C29	111.11(18)	C17-C16-C29	104.38(16)
C18-C17-C28	124.5(2)	C18-C17-C16	127.23(19)
C28-C17-C16	108.30(17)	C17-C18-C21	121.6(2)
C17-C18-B1	123.9(2)	C21-C18-B1	114.4(2)
C20-C19-C16	125.5(3)	O7-C25-C26	103.7(3)
O7-C25-C30	108.1(4)	C26-C25-C30	120.7(4)
O7-C25-C33	106.3(3)	C26-C25-C33	108.1(4)
C30-C25-C33	109.0(4)	O8-C26-C25	103.9(2)
O8-C26-C31	108.7(3)	C25-C26-C31	122.4(4)
O8-C26-C32	105.3(3)	C25-C26-C32	107.6(4)
C31-C26-C32	107.6(4)	C29-C27-C28	102.53(16)
C29-C27-S2	114.31(14)	C28-C27-S2	106.64(13)
C29-C27-S1	108.76(14)	C28-C27-S1	112.73(15)
S2-C27-S1	111.59(11)	C17-C28-C27	103.76(16)
C27-C29-C16	105.94(16)	B1-O7-C25	107.8(2)
B1-O8-C26	107.5(2)	O4-S1-O3	118.50(10)
O4-S1-C7	107.10(10)	O3-S1-C7	109.73(11)
O4-S1-C27	105.74(9)	O3-S1-C27	108.02(9)
C7-S1-C27	107.19(10)	O1-S2-O2	118.61(11)
O1-S2-C1	108.80(10)	O2-S2-C1	106.60(10)
O1-S2-C27	107.37(9)	O2-S2-C27	105.01(10)
C1-S2-C27	110.30(9)		

Table 7. Anisotropic atomic displacement parameters (Å²) for compound 3p

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.0523(17)	0.0503(17)	0.0324(12)	-0.0007(12)	0.0136(12)	-0.0053(13)
C1	0.0345(11)	0.0356(12)	0.0267(10)	-0.0018(9)	0.0099(8)	0.0007(9)
C2	0.0432(13)	0.0404(13)	0.0371(12)	0.0022(10)	0.0093(10)	0.0079(10)
C3	0.0520(15)	0.0439(14)	0.0462(14)	0.0061(11)	0.0175(12)	-0.0036(11)
C4	0.0410(14)	0.0567(16)	0.0480(14)	-0.0042(12)	0.0175(11)	-0.0059(12)
C5	0.0358(13)	0.0587(16)	0.0497(14)	0.0014(12)	0.0105(11)	0.0108(11)
C6	0.0407(13)	0.0453(14)	0.0386(12)	0.0066(10)	0.0122(10)	0.0075(10)
C7	0.0366(12)	0.0353(12)	0.0389(12)	-0.0086(10)	0.0084(10)	-0.0027(9)
C8	0.0410(13)	0.0496(15)	0.0453(13)	-0.0086(11)	0.0030(11)	0.0010(11)
C9	0.0381(14)	0.0571(17)	0.0724(19)	-0.0134(15)	0.0005(13)	0.0021(12)
C10	0.0384(14)	0.0511(17)	0.093(2)	-0.0176(15)	0.0224(15)	-0.0038(12)
C11	0.0638(19)	0.0646(19)	0.0638(18)	-0.0121(15)	0.0345(15)	-0.0036(15)
C12	0.0516(15)	0.0533(16)	0.0403(13)	-0.0059(12)	0.0146(11)	0.0012(12)
C16	0.0352(12)	0.0399(13)	0.0267(10)	0.0010(9)	0.0022(9)	-0.0040(9)
C17	0.0345(11)	0.0349(12)	0.0283(10)	0.0019(9)	0.0049(8)	-0.0043(9)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C18	0.0380(12)	0.0445(14)	0.0330(11)	0.0003(10)	0.0088(9)	-0.0030(10)
C19	0.0420(13)	0.0470(14)	0.0424(12)	0.0079(11)	0.0110(10)	-0.0003(11)
C20	0.067(2)	0.084(2)	0.0591(18)	0.0249(17)	0.0033(15)	0.0161(17)
C21	0.0380(14)	0.0700(19)	0.0483(14)	0.0041(13)	0.0129(11)	-0.0055(12)
C25	0.109(3)	0.144(4)	0.0337(15)	0.0164(19)	0.0100(17)	-0.045(3)
C26	0.113(3)	0.140(4)	0.0286(13)	-0.0015(19)	0.0120(17)	-0.040(3)
C27	0.0306(11)	0.0360(12)	0.0238(9)	-0.0007(8)	0.0041(8)	-0.0040(9)
C28	0.0290(10)	0.0410(12)	0.0268(10)	-0.0008(9)	0.0045(8)	-0.0076(9)
C29	0.0302(11)	0.0407(12)	0.0317(10)	0.0005(9)	0.0056(9)	-0.0012(9)
C30	0.137(4)	0.235(6)	0.061(2)	0.022(3)	0.048(3)	-0.047(4)
C31	0.140(4)	0.258(8)	0.050(2)	0.018(3)	-0.022(3)	-0.077(5)
C32	0.378(11)	0.116(4)	0.085(3)	-0.043(3)	0.082(5)	-0.032(6)
C33	0.311(9)	0.112(4)	0.093(4)	0.033(3)	-0.029(5)	0.044(5)
O1	0.0326(8)	0.0678(12)	0.0313(8)	0.0015(8)	0.0014(6)	0.0034(8)
O2	0.0628(11)	0.0415(10)	0.0388(9)	-0.0100(7)	0.0147(8)	-0.0127(8)
O3	0.0459(9)	0.0397(9)	0.0381(9)	0.0009(7)	0.0127(7)	-0.0049(7)
O4	0.0431(9)	0.0439(10)	0.0349(8)	-0.0069(7)	-0.0057(7)	-0.0054(7)
O7	0.0823(15)	0.123(2)	0.0383(10)	0.0190(11)	0.0076(10)	-0.0401(14)
O8	0.0892(17)	0.123(2)	0.0313(9)	-0.0004(11)	0.0091(10)	-0.0474(15)
S1	0.0317(3)	0.0350(3)	0.0290(3)	-0.0037(2)	0.0046(2)	-0.0037(2)
S2	0.0339(3)	0.0401(3)	0.0250(3)	-0.0032(2)	0.0062(2)	-0.0035(2)

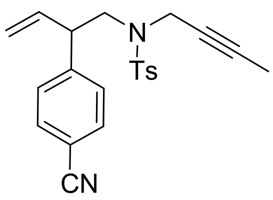
Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for compound 3p.

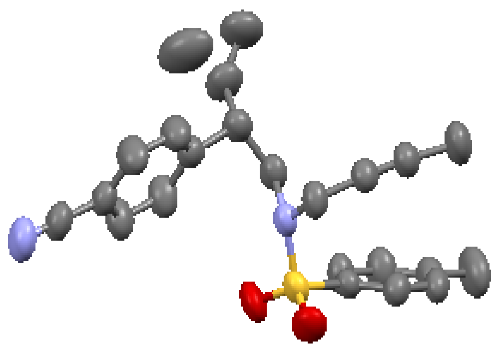
	x/a	y/b	z/c	U(eq)
H2	-0.0912	-0.0310	0.3648	0.048
H3	-0.3345	-0.0699	0.3998	0.056
H4	-0.5656	0.0297	0.3817	0.057
H5	-0.5537	0.1708	0.3320	0.057
H6	-0.3094	0.2137	0.2988	0.049
H8	0.3018	-0.0694	0.2873	0.055
H9	0.5703	-0.1114	0.2735	0.068
H10	0.6469	-0.1177	0.1899	0.072
H11	0.4537	-0.0857	0.1189	0.074
H12	0.1854	-0.0403	0.1313	0.057
H16	-0.1050	0.1456	0.1247	0.041
H19	-0.0935	0.3497	0.1540	0.052
H20A	-0.2596	0.2621	0.0669	0.084
H20B	-0.2549	0.3788	0.0806	0.084
H21A	0.4388	0.1924	0.1840	0.077
H21B	0.4732	0.2513	0.1336	0.077
H21C	0.4667	0.1351	0.1325	0.077
H28A	0.1816	0.2335	0.2400	0.039
H28B	0.2648	0.1313	0.2280	0.039

	x/a	y/b	z/c	U(eq)
H29A	-0.1649	0.2271	0.2216	0.041
H29B	-0.2273	0.1240	0.1979	0.041
H30A	0.4080	0.3275	-0.0453	0.212
H30B	0.2895	0.2666	-0.0860	0.212
H30C	0.4099	0.2112	-0.0434	0.212
H31A	-0.1526	0.1490	-0.0408	0.228
H31B	-0.0694	0.2066	-0.0840	0.228
H31C	-0.1337	0.2647	-0.0373	0.228
H32A	0.2748	0.0837	-0.0184	0.283
H32B	0.1667	0.0924	-0.0729	0.283
H32C	0.0984	0.0346	-0.0268	0.283
H33A	0.0193	0.3700	-0.0018	0.264
H33B	0.0953	0.3917	-0.0542	0.264
H33C	0.1919	0.4231	-0.0003	0.264

Crystal Structure Report for Compound 6ef

Single crystals of **compound 6ef** suitable for X-ray diffraction were obtained by slow evaporation of a solution of the compound in hexane at -18ºC. Details of the crystal structure, data acquisition and refining are given in the following table.





A colorless prismatic-like specimen of $C_{22}H_{23}N_2O_2S$, approximate dimensions 0.16 mm x 0.27 mm x 0.36 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table 1: Data collection details for compound 6ef.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Phi	35.105	20.50	12.48	-347.51	28.87	0.50	739	60.00	0.71073	50	30.0	n/a
Omega	35.105	3.00	1.55	28.75	-87.66	0.50	77	60.00	0.71073	50	30.0	n/a

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Phi	35.105	-12.00	-14.73	-313.05	82.04	0.50	739	60.00	0.71073	50	30.0	n/a

A total of 1555 frames were collected. The total exposure time was 25.92 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 40940 reflections to a maximum θ angle of 25.39° (0.83 Å resolution), of which 3871 were independent (average redundancy 10.576, completeness = 99.7%, R_{int} = 3.49%, R_{sig} = 1.92%) and 2891 (74.68%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.1138(10) Å, b = 15.4374(14) Å, c = 22.576(2) Å, volume = 4221.8(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 9885 reflections above 20 σ(I) with 5.277° < 2θ < 46.58°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.869. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9409 and 0.9731.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P b c a, with Z = 8 for the formula unit, $C_{22}H_{23}N_2O_2S$. The final anisotropic full-matrix least-squares refinement on F^2 with 256 variables converged at R1 = 4.63%, for the observed data and wR2 = 17.33% for all data. The goodness-of-fit was 1.011. The largest peak in the final difference electron density synthesis was 0.254 $e^-/Å^3$ and the largest hole was -0.237 $e^-/Å^3$ with an RMS deviation of 0.073 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.194 g/cm^3 and F(000), 1608 e^-.

Table 2. Sample and crystal data for compound 6ef.

Identification code	**compound 6ef**	
Chemical formula	$C_{22}H_{23}N_2O_2S$	
Formula weight	379.48	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.16 x 0.27 x 0.36 mm	
Crystal habit	colorless prismatic	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 12.1138(10) Å	α = 90°
	b = 15.4374(14) Å	β = 90°
	c = 22.576(2) Å	γ = 90°
Volume	4221.8(7) $Å^3$	
Z	8	
Density (calculated)	1.194 Mg/cm^3	
Absorption coefficient	0.171 mm^{-1}	
F(000)	1608	

Table 3. Data collection and structure refinement for compound 6ef.

Theta range for data collection	1.80 to 25.39°
Index ranges	-14<=h<=14, -18<=k<=18, -27<=l<=27
Reflections collected	40940

Independent reflections	3871 [R(int) = 0.0349]	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9731 and 0.9409	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3871 / 0 / 256	
Goodness-of-fit on F^2	1.011	
Δ/σ_{max}	0.025	
Final R indices	2891 data; I>2σ(I)	R1 = 0.0463, wR2 = 0.1445
	all data	R1 = 0.0678, wR2 = 0.1733
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1142P)^2+0.8202P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.254 and -0.237 eÅ^{-3}	
R.M.S. deviation from mean	0.073 eÅ^{-3}	

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 6ef.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.66423(18)	0.79852(13)	0.00611(10)	0.0545(5)
C2	0.5742(2)	0.81397(16)	0.97035(12)	0.0695(7)
C3	0.5624(2)	0.89341(18)	0.94390(13)	0.0816(8)
C4	0.6381(2)	0.95934(17)	0.95248(11)	0.0731(7)
C5	0.7277(2)	0.94313(15)	0.98884(11)	0.0699(7)
C6	0.74171(18)	0.86374(15)	0.01562(10)	0.0615(6)
C8	0.5169(3)	0.45881(18)	0.22446(12)	0.0814(8)
C9	0.4994(2)	0.54645(17)	0.21884(11)	0.0754(7)
C10	0.46967(17)	0.58187(15)	0.16541(10)	0.0600(6)
C11	0.4611(2)	0.52787(17)	0.11690(12)	0.0754(7)

	x/a	y/b	z/c	U(eq)
C12	0.4785(2)	0.43944(16)	0.12162(12)	0.0746(7)
C13	0.50583(18)	0.40474(15)	0.17602(11)	0.0620(6)
C14	0.68707(19)	0.73847(15)	0.15611(11)	0.0633(6)
C15	0.50290(18)	0.72178(14)	0.10818(11)	0.0619(6)
C16	0.44577(19)	0.67826(16)	0.16071(12)	0.0672(6)
C17	0.5231(2)	0.31267(18)	0.18137(12)	0.0716(7)
C18	0.6244(4)	0.0462(2)	0.92261(16)	0.1123(11)
C19	0.6939(2)	0.90984(16)	0.16048(11)	0.0667(6)
C20	0.7045(3)	0.00452(17)	0.15831(16)	0.0943(9)
C21	0.68823(18)	0.83336(16)	0.15981(10)	0.0619(6)
C22	0.3232(2)	0.6957(2)	0.15550(17)	0.0952(10)
N1	0.5355(2)	0.23918(16)	0.18559(12)	0.0885(7)
N4	0.62191(14)	0.70290(10)	0.10679(8)	0.0547(5)
O1	0.79379(14)	0.68187(12)	0.05076(9)	0.0827(6)
O2	0.61498(17)	0.63625(10)	0.00823(8)	0.0792(5)
S1	0.67919(5)	0.69731(3)	0.04123(3)	0.0600(2)
C23A	0.2685(4)	0.7511(5)	0.1843(3)	0.114(2)
C23B	0.2507(13)	0.6504(16)	0.1777(8)	0.160(10)

Table 5. Bond lengths (Å) for compound 6ef.

C1-C2	1.377(3)	C1-C6	1.393(3)
C1-S1	1.762(2)	C2-C3	1.371(4)
C2-H2	0.93	C3-C4	1.383(4)
C3-H3	0.93	C4-C5	1.384(4)
C4-C18	1.510(4)	C5-C6	1.377(3)
C5-H5	0.93	C6-H6	0.93
C8-C9	1.375(4)	C8-C13	1.382(4)
C8-H8	0.93	C9-C10	1.372(3)
C9-H9	0.93	C10-C11	1.380(3)
C10-C16	1.520(3)	C11-C12	1.385(3)
C11-H11	0.93	C12-C13	1.380(3)
C12-H12	0.93	C13-C17	1.442(3)

C14-C21	1.467(3)	C14-N4	1.471(3)
C14-H14A	0.97	C14-H14B	0.97
C15-N4	1.471(3)	C15-C16	1.529(3)
C15-H15A	0.97	C15-H15B	0.97
C16-C22	1.513(4)	C16-H16	0.98
C17-N1	1.148(3)	C18-H18A	0.96
C18-H18B	0.96	C18-H18C	0.96
C19-C21	1.183(3)	C19-C20	1.468(3)
C20-H20A	0.96	C20-H20B	0.96
C20-H20C	0.96	C22-C23B	1.23(2)
C22-C23A	1.263(6)	C22-H22A	0.93
C22-H22B	0.93	N4-S1	1.637(2)
O1-S1	1.4249(18)	O2-S1	1.4313(18)
C23A-H23A	0.93	C23A-H23B	0.93
C23B-H23C	0.93	C23B-H23D	0.93

Table 6. Bond angles (°) for compound 6ef.

C2-C1-C6	119.9(2)	C2-C1-S1	119.92(17)
C6-C1-S1	120.15(18)	C3-C2-C1	119.5(2)
C3-C2-H2	120.2	C1-C2-H2	120.2
C2-C3-C4	121.9(2)	C2-C3-H3	119.1
C4-C3-H3	119.1	C5-C4-C3	118.0(2)
C5-C4-C18	120.8(3)	C3-C4-C18	121.2(3)
C6-C5-C4	121.2(2)	C6-C5-H5	119.4
C4-C5-H5	119.4	C5-C6-C1	119.5(2)
C5-C6-H6	120.2	C1-C6-H6	120.2
C9-C8-C13	120.4(2)	C9-C8-H8	119.8
C13-C8-H8	119.8	C10-C9-C8	120.9(2)
C10-C9-H9	119.6	C8-C9-H9	119.6
C9-C10-C11	118.5(2)	C9-C10-C16	120.1(2)
C11-C10-C16	121.4(2)	C10-C11-C12	121.5(2)
C10-C11-H11	119.2	C12-C11-H11	119.2
C13-C12-C11	119.2(2)	C13-C12-H12	120.4
C11-C12-H12	120.4	C12-C13-C8	119.5(2)
C12-C13-C17	119.5(2)	C8-C13-C17	121.0(2)
C21-C14-N4	114.88(18)	C21-C14-H14A	108.5
N4-C14-H14A	108.5	C21-C14-H14B	108.5
N4-C14-H14B	108.5	H14A-C14-H14B	107.5
N4-C15-C16	111.91(18)	N4-C15-H15A	109.2
C16-C15-H15A	109.2	N4-C15-H15B	109.2
C16-C15-H15B	109.2	H15A-C15-H15B	107.9
C22-C16-C10	111.5(2)	C22-C16-C15	107.8(2)
C10-C16-C15	113.47(19)	C22-C16-H16	108.0
C10-C16-H16	108.0	C15-C16-H16	108.0
N1-C17-C13	179.1(3)	C4-C18-H18A	109.5
C4-C18-H18B	109.5	H18A-C18-H18B	109.5
C4-C18-H18C	109.5	H18A-C18-H18C	109.5

H18B-C18-H18C	109.5	C21-C19-C20	176.9(3)
C19-C20-H20A	109.5	C19-C20-H20B	109.5
H20A-C20-H20B	109.5	C19-C20-H20C	109.5
H20A-C20-H20C	109.5	H20B-C20-H20C	109.5
C19-C21-C14	176.2(3)	C23B-C22-C23A	78.4(10)
C23B-C22-C16	124.6(7)	C23A-C22-C16	126.6(4)
C23B-C22-H22A	65.8	C23A-C22-H22A	116.7
C16-C22-H22A	116.7	C23B-C22-H22B	117.7
C23A-C22-H22B	64.8	C16-C22-H22B	117.7
H22A-C22-H22B	87.5	C14-N4-C15	115.83(18)
C14-N4-S1	118.46(15)	C15-N4-S1	116.43(15)
O1-S1-O2	119.86(12)	O1-S1-N4	106.58(11)
O2-S1-N4	105.96(11)	O1-S1-C1	108.46(11)
O2-S1-C1	107.09(11)	N4-S1-C1	108.46(9)
C22-C23A-H23A	120.0	C22-C23A-H23B	120.0
H23A-C23A-H23B	120.0	C22-C23B-H23C	120.0
C22-C23B-H23D	120.0	H23C-C23B-H23D	120.0

Table 7. Anisotropic atomic displacement parameters (Å^2) for compound 6ef.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0557(12)	0.0479(12)	0.0600(13)	-0.0038(9)	0.0052(9)	0.0033(9)
C2	0.0643(14)	0.0582(14)	0.0860(17)	0.0049(12)	-0.0152(12)	-0.0063(10)
C3	0.0782(17)	0.0688(17)	0.098(2)	0.0119(14)	-0.0214(14)	0.0042(13)
C4	0.0917(18)	0.0557(14)	0.0719(16)	0.0054(11)	0.0039(13)	0.0019(13)
C5	0.0839(17)	0.0572(14)	0.0687(15)	-0.0044(11)	0.0086(12)	-0.0166(12)
C6	0.0588(13)	0.0631(14)	0.0626(13)	-0.0001(11)	-0.0001(10)	-0.0067(10)
C8	0.110(2)	0.0752(18)	0.0592(14)	0.0113(13)	0.0019(13)	0.0014(15)
C9	0.0953(18)	0.0721(17)	0.0589(14)	0.0020(12)	0.0085(12)	-0.0009(14)
C10	0.0479(11)	0.0625(14)	0.0697(14)	-0.0009(11)	0.0036(9)	-0.0024(9)
C11	0.0863(17)	0.0680(16)	0.0719(16)	0.0095(13)	-0.0213(13)	-0.0011(13)
C12	0.0858(17)	0.0643(16)	0.0737(16)	-0.0028(12)	-0.0164(13)	-0.0084(12)
C13	0.0552(12)	0.0606(14)	0.0703(15)	0.0099(11)	0.0025(10)	-0.0064(10)
C14	0.0659(14)	0.0541(13)	0.0698(14)	0.0067(11)	-0.0107(11)	-0.0028(10)
C15	0.0548(12)	0.0518(12)	0.0790(15)	0.0042(11)	-0.0030(10)	0.0083(9)
C16	0.0570(13)	0.0649(15)	0.0797(16)	-0.0029(12)	0.0032(11)	0.0068(10)
C17	0.0640(14)	0.0681(17)	0.0826(17)	0.0130(13)	0.0006(12)	-0.0091(12)
C18	0.162(3)	0.0621(17)	0.113(3)	0.0201(17)	-0.005(2)	0.0034(19)
C19	0.0672(14)	0.0575(15)	0.0756(16)	-0.0057(12)	0.0013(11)	-0.0029(11)
C20	0.0908(19)	0.0556(15)	0.136(3)	-0.0071(17)	0.0062(18)	-0.0050(14)
C21	0.0616(13)	0.0603(14)	0.0639(14)	-0.0041(11)	-0.0017(10)	-0.0032(10)
C22	0.0572(16)	0.103(2)	0.125(3)	0.013(2)	0.0144(16)	0.0143(15)
N1	0.0870(16)	0.0648(15)	0.1138(19)	0.0188(13)	-0.0007(13)	-0.0066(12)
N4	0.0517(10)	0.0441(10)	0.0682(12)	0.0011(8)	-0.0044(8)	0.0003(7)
O1	0.0617(10)	0.0788(12)	0.1075(15)	0.0063(10)	0.0071(9)	0.0260(9)
O2	0.1052(13)	0.0470(9)	0.0854(12)	-0.0137(8)	-0.0076(10)	-0.0018(9)
S1	0.0610(4)	0.0453(3)	0.0738(4)	-0.0037(2)	0.0011(2)	0.0091(2)
C23A	0.070(3)	0.132(6)	0.138(4)	-0.012(4)	0.019(3)	0.029(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C23B	0.103(11)	0.21(2)	0.168(15)	0.051(14)	0.033(9)	0.067(12)

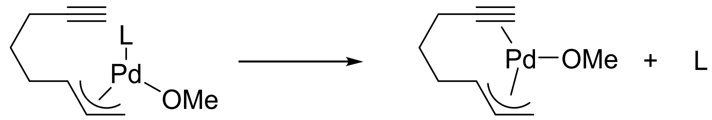
Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for compound 6ef.

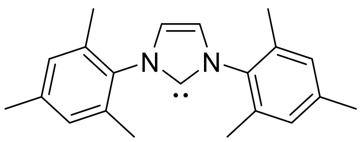
	x/a	y/b	z/c	U(eq)
H2	0.5219	0.7709	-0.0358	0.083
H3	0.5019	0.9032	-0.0805	0.098
H5	0.7795	0.9866	-0.0047	0.084
H6	0.8024	0.8537	0.0399	0.074
H8	0.5364	0.4358	0.2611	0.098
H9	0.5078	0.5822	0.2517	0.091
H11	0.4433	0.5514	0.0802	0.09
H12	0.4718	0.4039	0.0886	0.09
H14A	0.6580	0.7156	0.1930	0.076
H14B	0.7625	0.7182	0.1523	0.076
H15A	0.4693	0.7017	0.0717	0.074
H15B	0.4921	0.7839	0.1106	0.074
H16	0.4723	0.7061	0.1970	0.081
H18A	0.6522	1.0910	-0.0519	0.168
H18B	0.5476	1.0563	-0.0852	0.168
H18C	0.6647	1.0465	-0.1140	0.168
H20A	0.7569	1.0203	0.1283	0.141
H20B	0.7295	1.0255	0.1960	0.141
H20C	0.6341	1.0298	0.1492	0.141
H22A	0.2843	0.6622	0.1283	0.696(9)
H22B	0.3012	0.7440	0.1340	0.304
H23A	0.2070	0.7340	0.2060	0.136
H23B	0.2897	0.8090	0.1839	0.136
H23C	0.1973	0.6754	0.2019	0.192
H23D	0.2492	0.5911	0.1703	0.192

Calculations

Computational methods

Calculations were performed with Gaussian 09[15] at DFT level and in the presence of a solvent (xylene-mixture) at the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM).[16] The geometries of all structures here reported were optimized using the M06 hybrid functional.[17] Optimizations were carried out using the standard 6-31G(d) basis set for C, H, N and O. The LANL2DZ basis set, which includes the relativistic effective core potential (ECP) of Hay and Wadt and employs a split-valence (double-ζ) basis set, was used for Pd.[18] Minima were characterized by calculation of the Hessian eigenvalues. Electronic energies were corrected with the zero-point vibrational energy (ZPE) without scaling.

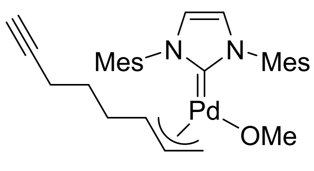


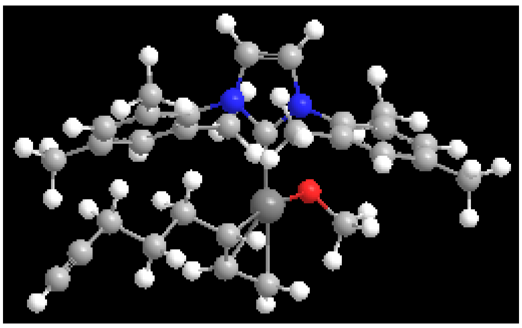
L = 

ΔG = 18.7 kcal/mol

L = PCy_3 ΔG = 4.2 kcal/mol

M06/6-31G(d) (C, N, O, H) LANL2DZ (Pd), PCM (Xylene-mixture)



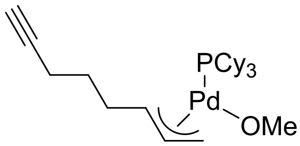


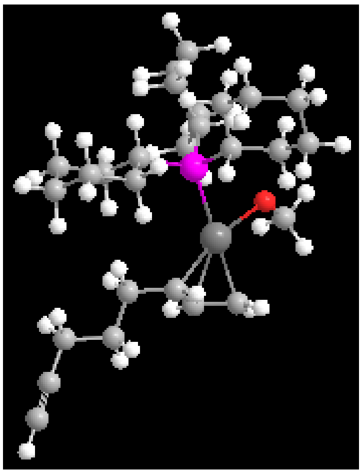
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.717838	4.487254	-0.180538
2	6	0	-5.407327	5.441349	0.091175
3	6	0	-3.867268	3.344237	-0.482697
4	6	0	-2.724152	3.170090	0.519457
5	6	0	-1.860143	1.961009	0.174982

6	6	0	-0.723201	1.758742	1.132624
7	46	0	0.362142	-0.127791	1.281061
8	6	0	-0.956109	1.174998	2.403314
9	6	0	0.115481	0.847390	3.243563
10	6	0	0.565715	-0.748982	-0.688221
11	7	0	-0.270874	-1.529443	-1.419829
12	6	0	0.303243	-1.889615	-2.633681
13	6	0	1.527750	-1.318636	-2.662625
14	7	0	1.669165	-0.625189	-1.466103
15	6	0	2.828522	0.139575	-1.110617
16	6	0	-1.603441	-1.865570	-1.014969
17	6	0	3.916503	-0.516935	-0.527672
18	6	0	5.032031	0.255430	-0.203189
19	6	0	5.075359	1.627851	-0.444252
20	6	0	3.969116	2.238408	-1.036990
21	6	0	2.830342	1.512211	-1.377936
22	6	0	-1.795651	-2.911848	-0.104314
23	6	0	-3.103622	-3.174131	0.300363
24	6	0	-4.188623	-2.433201	-0.170568
25	6	0	-3.952780	-1.422900	-1.101560
26	6	0	-2.664321	-1.126544	-1.546915
27	6	0	1.643519	2.179345	-2.004776
28	6	0	3.869442	-1.986355	-0.248922
29	6	0	6.278397	2.437279	-0.060925
30	6	0	-5.576028	-2.717248	0.322868
31	6	0	-2.439842	-0.067532	-2.585304
32	6	0	-0.646074	-3.728577	0.398184
33	8	0	1.477008	-1.817059	1.799947
34	6	0	2.364396	-1.631713	2.837595
35	1	0	-6.017369	6.285855	0.332429
36	1	0	-4.474808	2.423922	-0.502687
37	1	0	-3.449480	3.451502	-1.497087
38	1	0	-2.110010	4.083356	0.540088
39	1	0	-3.139697	3.054666	1.532408
40	1	0	-2.488209	1.053250	0.155182
41	1	0	-1.465782	2.080621	-0.847154
42	1	0	0.108143	2.470176	1.051502
43	1	0	-1.936037	0.723469	2.588153
44	1	0	-0.052067	0.229071	4.123321
45	1	0	1.024301	1.453601	3.249739
46	1	0	-0.220545	-2.512821	-3.346682
47	1	0	2.315023	-1.334278	-3.405062
48	1	0	5.893043	-0.234763	0.255376
49	1	0	3.993994	3.310212	-1.243580
50	1	0	-3.279074	-3.985768	1.009244
51	1	0	-4.793483	-0.848087	-1.495966
52	1	0	1.881413	3.208013	-2.298949
53	1	0	1.293384	1.639656	-2.896014
54	1	0	0.796179	2.215558	-1.303827
55	1	0	3.786460	-2.573528	-1.175134
56	1	0	4.778112	-2.310292	0.272884
57	1	0	2.991219	-2.217529	0.380633
58	1	0	7.184278	1.820034	-0.024313
59	1	0	6.453196	3.258167	-0.767743
60	1	0	6.152581	2.888903	0.933201
61	1	0	-5.747360	-2.260640	1.307837
62	1	0	-6.336876	-2.319053	-0.359235
63	1	0	-5.749770	-3.794823	0.436535
64	1	0	-3.281461	0.635062	-2.613181

65	1	0	-1.520928	0.504967	-2.400325
66	1	0	-2.345974	-0.505419	-3.589815
67	1	0	-0.027536	-4.093804	-0.434514
68	1	0	0.026219	-3.147618	1.052987
69	1	0	-1.010621	-4.599138	0.956476
70	1	0	1.880028	-1.389306	3.808674
71	1	0	2.956680	-2.555374	3.006894
72	1	0	3.109840	-0.822825	2.656130

Zero-point correction= 0.606382 (Hartree/Particle)
Thermal correction to Energy= 0.643805
Thermal correction to Enthalpy= 0.644749
Thermal correction to Gibbs Free Energy= 0.537362
Sum of electronic and zero-point Energies= -1475.831495
Sum of electronic and thermal Energies= -1475.794073
Sum of electronic and thermal Enthalpies= -1475.793129
Sum of electronic and thermal Free Energies= -1475.900515



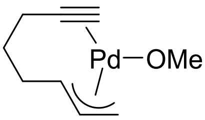


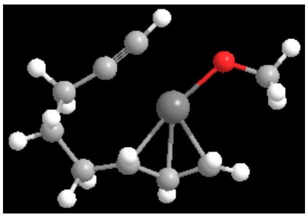
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.824246	-0.467047	-0.333439
2	6	0	3.352795	-0.211261	-0.011520
3	6	0	2.461151	-1.243382	-0.637345
4	46	0	0.301348	-1.693355	-0.217760
5	6	0	2.327716	-2.511272	-0.031801
6	6	0	1.494474	-3.491173	-0.585856
7	15	0	-0.971197	0.331304	-0.040080
8	6	0	5.727418	0.635482	0.223308
9	6	0	7.140080	0.386505	-0.028701
10	6	0	8.304870	0.156865	-0.252141
11	6	0	-2.310618	0.114490	1.242241
12	6	0	-0.155302	1.959430	0.343852
13	6	0	-1.837947	0.669933	-1.661994
14	6	0	-2.987160	1.392508	1.745276
15	6	0	-4.170365	1.047833	2.647639
16	6	0	-3.738492	0.173491	3.818974
17	6	0	-3.021732	-1.081183	3.332822
18	6	0	-1.843260	-0.736559	2.429004
19	6	0	0.713377	2.437960	-0.823044
20	6	0	1.449648	3.731777	-0.484120

21	6	0	2.255344	3.615796	0.803946
22	6	0	1.362206	3.178658	1.957318
23	6	0	0.661366	1.862887	1.636208
24	6	0	-2.684543	1.944680	-1.743025
25	6	0	-3.111975	2.205189	-3.185571
26	6	0	-3.891520	1.023314	-3.750298
27	6	0	-3.104234	-0.274655	-3.611936
28	6	0	-2.664126	-0.516249	-2.170686
29	8	0	-1.594640	-2.541891	-0.123390
30	6	0	-1.698275	-3.821308	0.372319
31	1	0	5.131824	-1.439963	0.079547
32	1	0	4.963772	-0.538039	-1.422893
33	1	0	3.084720	0.797019	-0.360718
34	1	0	3.216626	-0.204863	1.083733
35	1	0	2.380728	-1.196930	-1.730030
36	1	0	2.668008	-2.623818	1.002274
37	1	0	1.257325	-4.388284	-0.017205
38	1	0	1.359686	-3.559884	-1.667386
39	1	0	5.438667	1.602078	-0.219791
40	1	0	5.554826	0.738779	1.306906
41	1	0	9.336720	-0.044137	-0.448451
42	1	0	-3.054202	-0.494495	0.699571
43	1	0	-0.952618	2.707853	0.503510
44	1	0	-0.985295	0.784296	-2.358320
45	1	0	-2.263296	1.991452	2.325548
46	1	0	-3.320142	2.028694	0.914126
47	1	0	-4.648006	1.969765	3.009751
48	1	0	-4.930318	0.512345	2.053684
49	1	0	-3.053149	0.752133	4.462496
50	1	0	-4.605309	-0.089971	4.441815
51	1	0	-2.682369	-1.686576	4.185565
52	1	0	-3.725973	-1.711336	2.761708
53	1	0	-1.083361	-0.185425	3.011044
54	1	0	-1.371180	-1.649668	2.046158
55	1	0	1.433387	1.644040	-1.084736
56	1	0	0.100781	2.597323	-1.722193
57	1	0	2.095848	4.024526	-1.323863
58	1	0	0.706366	4.539376	-0.367175
59	1	0	3.060092	2.871555	0.670515
60	1	0	2.748933	4.570513	1.033707
61	1	0	1.943081	3.079491	2.885083
62	1	0	0.602749	3.957683	2.143768
63	1	0	1.412515	1.062046	1.529262
64	1	0	0.014674	1.567038	2.475330
65	1	0	-3.588027	1.812461	-1.124283
66	1	0	-2.154622	2.822170	-1.344145
67	1	0	-3.710853	3.125659	-3.241324
68	1	0	-2.210325	2.380509	-3.798529
69	1	0	-4.842128	0.927424	-3.197850
70	1	0	-4.158679	1.206310	-4.800978
71	1	0	-3.702162	-1.125470	-3.968424
72	1	0	-2.210414	-0.229540	-4.258202
73	1	0	-3.559233	-0.628855	-1.534658
74	1	0	-2.110311	-1.457049	-2.065147
75	1	0	-1.229636	-3.960731	1.373930
76	1	0	-2.767494	-4.090130	0.499030
77	1	0	-1.259971	-4.603740	-0.285069

Zero-point correction= 0.691501 (Hartree/Particle)

Thermal correction to Energy= 0.725945
Thermal correction to Enthalpy= 0.726889
Thermal correction to Gibbs Free Energy= 0.625552
Sum of electronic and zero-point Energies= -1598.837538
Sum of electronic and thermal Energies= -1598.803094
Sum of electronic and thermal Enthalpies= -1598.802150
Sum of electronic and thermal Free Energies= -1598.903487

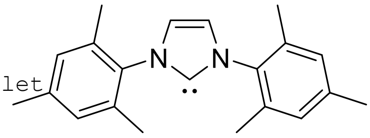


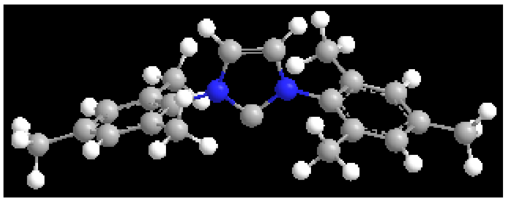


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.196967	-1.713631	0.065685
2	6	0	-0.104551	-2.186475	-0.231881
3	6	0	-2.573888	-1.374207	0.416226
4	6	0	-3.161607	-0.155119	-0.298300
5	6	0	-2.546585	1.170528	0.143450
6	6	0	-1.167585	1.408822	-0.381070
7	46	0	0.512472	-0.025873	-0.029826
8	6	0	-0.147647	1.997062	0.384494
9	6	0	1.173958	1.998131	-0.118088
10	8	0	2.311580	-1.030829	0.003852
11	6	0	3.473089	-0.302923	0.133725
12	1	0	0.818893	-2.695631	-0.439991
13	1	0	-3.194078	-2.254344	0.191542
14	1	0	-2.639558	-1.222726	1.505329
15	1	0	-3.050595	-0.275437	-1.386761
16	1	0	-4.239958	-0.137127	-0.091875
17	1	0	-3.199691	1.984613	-0.210995
18	1	0	-2.545040	1.230988	1.243907
19	1	0	-1.069069	1.434586	-1.472114
20	1	0	-0.327705	2.196096	1.443439
21	1	0	1.998310	2.279914	0.535196
22	1	0	1.354608	2.126466	-1.187810
23	1	0	3.538272	0.279733	1.079167
24	1	0	4.345592	-0.986476	0.136046
25	1	0	3.654379	0.423026	-0.689365

Zero-point correction= 0.206345 (Hartree/Particle)
Thermal correction to Energy= 0.219689
Thermal correction to Enthalpy= 0.220633
Thermal correction to Gibbs Free Energy= 0.166479
Sum of electronic and zero-point Energies= -552.734049
Sum of electronic and thermal Energies= -552.720705
Sum of electronic and thermal Enthalpies= -552.719761
Sum of electronic and thermal Free Energies= -552.773915

Singlet



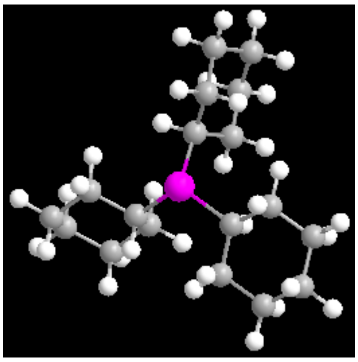


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000351	0.002423	-0.293081
2	7	0	1.057839	-0.009236	0.576339
3	6	0	0.676847	-0.008267	1.916533
4	6	0	-0.673702	0.006547	1.917750
5	7	0	-1.057045	0.011429	0.578171
6	6	0	-2.420538	0.022359	0.152941
7	6	0	2.420793	-0.020510	0.149371
8	6	0	-3.141809	-1.175066	0.158132
9	6	0	-4.476892	-1.137461	-0.239814
10	6	0	-5.088048	0.049902	-0.642896
11	6	0	-4.331889	1.221622	-0.641650
12	6	0	-2.994405	1.231612	-0.249641
13	6	0	2.992572	-1.229914	-0.257826
14	6	0	4.327050	-1.219596	-0.657532
15	6	0	5.085234	-0.048271	-0.657003
16	6	0	4.473855	1.139856	-0.258843
17	6	0	3.140689	1.176998	0.147860
18	6	0	-2.180973	2.489378	-0.267966
19	6	0	-2.487363	-2.459963	0.567256
20	6	0	-6.517631	0.059190	-1.096983
21	6	0	6.529874	-0.073703	-1.059769
22	6	0	2.485404	2.463277	0.551141
23	6	0	2.176082	-2.485632	-0.280791
24	1	0	1.398333	-0.016623	2.724280
25	1	0	-1.393689	0.012574	2.726857
26	1	0	-5.054130	-2.064439	-0.241218
27	1	0	-4.796388	2.158172	-0.956974
28	1	0	4.787623	-2.154899	-0.982502
29	1	0	5.048054	2.068484	-0.271682
30	1	0	-2.793139	3.353040	-0.552061
31	1	0	-1.730411	2.694125	0.713848
32	1	0	-1.348984	2.401359	-0.979991
33	1	0	-2.274065	-2.486814	1.645240
34	1	0	-3.127228	-3.318362	0.332624
35	1	0	-1.524545	-2.593703	0.054504
36	1	0	-7.123006	-0.667347	-0.540500
37	1	0	-6.973725	1.049048	-0.971840
38	1	0	-6.598503	-0.202820	-2.161507
39	1	0	6.715996	-0.819410	-1.842859
40	1	0	6.863001	0.902368	-1.433344
41	1	0	7.175605	-0.333018	-0.208610
42	1	0	3.125926	3.320955	0.315691
43	1	0	1.523712	2.595655	0.035928
44	1	0	2.269628	2.492965	1.628556

45	1	0	1.730861	-2.696233	0.702233
46	1	0	1.340048	-2.390433	-0.987122
47	1	0	2.784668	-3.348688	-0.574241

Zero-point correction= 0.396943 (Hartree/Particle)
Thermal correction to Energy= 0.419994
Thermal correction to Enthalpy= 0.420938
Thermal correction to Gibbs Free Energy= 0.344029
Sum of electronic and zero-point Energies= -923.043939
Sum of electronic and thermal Energies= -923.020888
Sum of electronic and thermal Enthalpies= -923.019943
Sum of electronic and thermal Free Energies= -923.096853

PCy_3



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.002014	-0.123292	-1.057849
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3	6	0	-1.317348	-0.990815	-0.044795
4	6	0	1.580706	-0.926650	-0.438084
5	6	0	-0.416060	1.788356	1.133861
6	6	0	-0.240258	3.229525	1.608230
7	6	0	-0.940203	4.206384	0.671640
8	6	0	-0.430268	4.044608	-0.754456
9	6	0	-0.592827	2.607952	-1.240101
10	6	0	-1.252822	-2.508088	-0.243034
11	6	0	-2.383896	-3.219900	0.494739
12	6	0	-3.748284	-2.687967	0.074999
13	6	0	-3.823319	-1.179512	0.274102
14	6	0	-2.696042	-0.474747	-0.472531
15	6	0	1.868232	-0.899918	1.062615
16	6	0	3.132284	-1.689154	1.395621
17	6	0	4.329577	-1.155054	0.618057
18	6	0	4.056184	-1.163965	-0.881533
19	6	0	2.784568	-0.390366	-1.219633
20	1	0	1.169225	1.848124	-0.303571
21	1	0	-1.183490	-0.781298	1.031467
22	1	0	1.461099	-1.984449	-0.739533
23	1	0	-1.488732	1.533428	1.184586
24	1	0	0.098259	1.101550	1.820925
25	1	0	-0.619941	3.337339	2.634704
26	1	0	0.836308	3.470708	1.644963
27	1	0	-2.026148	4.008811	0.691739

28	1	0	-0.803216	5.240772	1.017826
29	1	0	-0.948855	4.736610	-1.433654
30	1	0	0.639308	4.315750	-0.787957
31	1	0	-1.669009	2.367250	-1.310175
32	1	0	-0.190554	2.495180	-2.257483
33	1	0	-1.318839	-2.732675	-1.323259
34	1	0	-0.285925	-2.906420	0.098873
35	1	0	-2.320905	-4.304330	0.324318
36	1	0	-2.254597	-3.065685	1.580003
37	1	0	-3.913517	-2.918619	-0.991475
38	1	0	-4.548898	-3.194376	0.632864
39	1	0	-4.797414	-0.792461	-0.058032
40	1	0	-3.743944	-0.948547	1.350703
41	1	0	-2.813685	-0.644612	-1.557737
42	1	0	-2.769905	0.613460	-0.323601
43	1	0	2.011025	0.145453	1.388047
44	1	0	1.013805	-1.293058	1.634668
45	1	0	3.328109	-1.656665	2.477205
46	1	0	2.972709	-2.750481	1.137286
47	1	0	4.533095	-0.119264	0.941071
48	1	0	5.232724	-1.737594	0.849616
49	1	0	4.911980	-0.747690	-1.432340
50	1	0	3.941808	-2.207199	-1.222426
51	1	0	2.940482	0.675457	-0.974185
52	1	0	2.582107	-0.433787	-2.300278

```
Zero-point correction=                           0.483027 (Hartree/Particle)
 Thermal correction to Energy=                    0.502178
 Thermal correction to Enthalpy=                  0.503122
 Thermal correction to Gibbs Free Energy=         0.436236
 Sum of electronic and zero-point Energies=          -1046.076021
 Sum of electronic and thermal Energies=             -1046.056870
 Sum of electronic and thermal Enthalpies=           -1046.055925
 Sum of electronic and thermal Free Energies=        -1046.122812
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