Supporting Information for

Formal Regiocontrolled Hydroboration of Unbiased Internal Alkynes via Borylation/Allylic Alkylation of Terminal Alkynes

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Table of contents*:*

1. General methods

All the reactions were carried out in anhydrous solvents and under inert atmosphere. Melting points were taken in open-end capillary tubes. NMR spectra were obtained at 300 MHz and 500 MHz for ^{1}H, 75 MHz and 125 MHz for ^{13}C, and 160 MHz for ^{11}B. The experiments were recorded at room temperature and calibrated using residual non-deuterated solvent ($CDCl_3$) as internal reference. Mass spectra (MS) were determined at an ionizing voltage of 70 eV. Reactions were monitored by thin-layer chromatography, carried out on 0.25 mm. silica gel plates. Flash column chromatography was performed using silica gel. Characterization data for compounds not previously reported is provided.

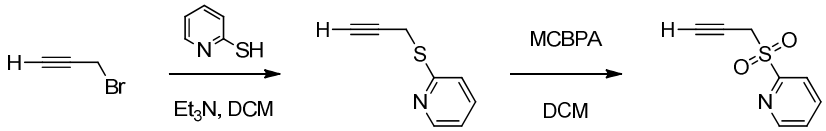
2. Starting materials and reagents

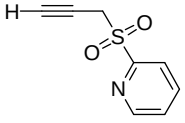
Copper (I) chloride, copper (II) triflate, sodium *tert*-butoxide, and tri-*tert*-butylphosphine were purchased from commercial sources. Bis(pinacolato)diboron was initially purchased from Aldrich, and more recently we used a generous gift by Frontier Scientific. Phenylmagnesium bromide (1.0 M in THF), 4-methoxyphenylmagnesium bromide (0.5 M in THF), o-tolylmagnesium bromide (2.0 M in diethyl ether), vinylmagnesium bromide (1.0 M in THF), ethylmagnesium bromide (1.0 M in THF), *tert*-butylmagnesium chloride (1.0 M in THF), phenethylmagnesium chloride (1.0 M in THF) were purchased from commercial suppliers.

Phenyl propargyl sulfide (**1**), propargyl alcohol (**5**), benzyl propargyl ether (**A**), phenyl propargyl ether (**B**), propargyl acetate (**6**), *N*-Boc-propargylamine (**7**), 3-phenyl-1-propyne (**8**), 3-butyn-2-ol (**17**), 2-(but-3-yn-2-yl)isoindoline-1,3-dione **(20),** 5-methyl-1-hexyn-3-ol (**22**), 1-phenyl-2-propyn-1-ol (**25**), were purchased from commercial sources and used as received.

Phenyl propargylsulfone (**3**),[1] [(3-butyn-1-yloxy)methyl] benzene **(C)**,[2] [(but-3-yn-2-yloxy)methyl]benzene (**18**),[3] 3-acetoxy-1-butyne **(19)**,[4] were prepared according to reported procedures.

Procedure for the synthesis of 2-(prop-2-yn-1-ylsulfonyl)pyridine (**4**)





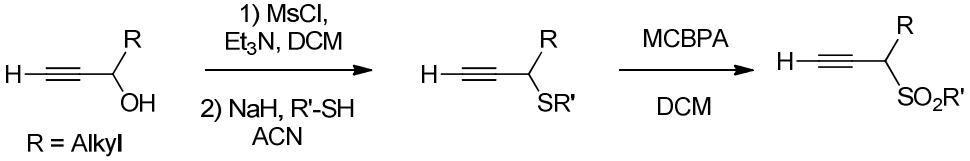
To a solution of 2-mercaptopyridine (2.76 g, 24.81 mmol) and triethylamine (3.77 mL, 27.07 mmol) in dry dichloromethane (80 mL) at room temperature was added propargyl bromide (3.00 g, 22.56 mmol). The reaction was then stirred until completion (TLC monitoring, 2h). Then, it was quenched with saturated aqueous NH_4Cl (40 mL). The organic phase was separated and washed with water, dried ($MgSO_4$) and concentrated in vacuo.

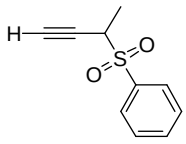
The crude residue was then dissolved in DCM (50 mL), cooled to 0 °C, and then 3-chloroperbenzoic acid (77% purity, 11.12 g, 49.63 mmol) was slowly added. The reaction was allowed to reach room temperature and it was stirred for 90 min before a 0.2 N sodium thiosulfate (50 mL) was added to quench the reaction. The organic phase was separated and washed with water, dried ($MgSO_4$) and concentrated in vacuo. The crude was purified by flash chromatography (40% AcOEt/hexanes) to obtain 3.50 g (78%, overall yield) of the title compound as a white solid; mp: 61-63 °C.

^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.66 – 8.87 (m, 1 H), 8.14 (d, *J* = 7.6 Hz, 1 H), 8.00 (t, *J* = 7.6 Hz, 1 H), 7.51 - 7.70 (m, 1 H), 4.31 (s, 2 H), 2.27 (s, 1 H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ = 155.6, 150.4, 138.0, 127.8, 123.1, 76.1, 71.0, 44.1 ppm. **HRMS-ESI (m/z)**: Calculated for [$C_8H_7NO_2S$+Na]: 204.0089, found: 204.0086.

Note: The oxidation step can also be carried out in the presence of 10 mol % sodium tungstate dihydrate and 3 equivalents of a hydrogen peroxide solution (30 wt. % in H_2O) to a solution of the corresponding thioether in 10:1 ethyl acetate:H_2O at 0 °C. Overoxidation to the pyridyl N-oxide was not observed under these conditions, even in the presence of a large excess (>10 equiv.) of hydrogen peroxide.

General procedure for the synthesis of the substrates 15, 16, 21, 23 and 24. Representative example: but-3-yn-2-ylsulfonyl)benzene (**15**)





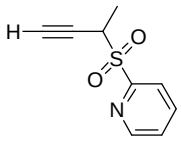
To a solution of 3-butyn-2-ol (2.23 mL, 28.53 mmol) and triethylamine (4.37 mL, 31.39 mmol) in dry dichloromethane (80 mL) cooled with an ice bath was added methanesulfonyl chloride (2.43 mL, 31.39 mmol). The mixture was then stirred until no starting material was observed (TLC monitoring, usually 60-90 min). Then, saturated aqueous NH_4Cl (30 mL) was added. The organic phase was separated, washed with water, dried with $MgSO_4$and concentrated in vacuo. The resulting mesylated alcohol was used in the next step without further purification.

In another flask, benzenethiol (3.51 mL, 34.24 mmol) was dissolved in dry acetonitrile (70 mL), cooled with an ice bath. Then, NaH (60% in mineral oil, 1.48 g, 37.09 mmol) was added portionwise. The mixture was stirred for 5-10 min, and then a solution of the aforementioned mesylated alcohol crude in dry acetonitrile (10 mL) was added dropwise. The reaction was stirred until total conversion (TLC monitoring, usually 60-90 min). Water (10 mL) was added to quench the reaction and the organic phase separated (ethyl acetate, 2x20 mL), dried with $MgSO_4$and concentrated in vacuo.

The obtained crude was then dissolved in DCM (50 mL), cooled with an ice bath, and then 3-chloroperbenzoic acid (77% purity, 14.71 g, 65.62 mmol) was slowly added. The reaction was allowed to reach room temperature and stirred until no starting material was observed (TLC monitoring, usually around 2 h). A solution of 0.2 N sodium thiosulfate (30 mL) was added to quench the reaction and the organic layer was separated and washed with water (20 mL), dried with Na_2SO_4 and concentrated in vacuo. The crude was purified by flash chromatography (1:3 AcOEt:hexanes) to obtain3.38 g (61%, overall yield) of the title compound as a white solid. Mp: 66-69 °C.

^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.97 (d, *J* = 7.5 Hz, 2 H), 7.69 (t, *J* = 7.5 Hz, 1 H), 7.58 (t, *J* = 7.8 Hz, 2 H), 3.94 (qd, *J* = 7.1, 2.5 Hz, 1 H), 2.40 (d, *J* = 2.4 Hz, 1 H), 1.59 (d, *J* = 7.0 Hz, 3 H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ = 136.0, 134.2, 129.8, 128.9, 77.3, 75.8, 53.8, 14.9 ppm. **HRMS-ESI (m/z)**: Calculated for [$C_{10}H_{10}O_2S$+Na]: 217.0293, found: 217.0295.

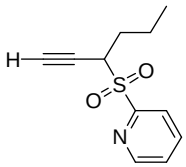
2-(But-3-yn-2-ylsulfonyl)pyridine (**16**)



Following the general procedure, the mesylation of 3-butyn-2-ol (1.12 mL, 14.27 mmol), substitution by 2-mercaptopyridine (1.90 g, 17.12 mmol) and oxidation with MCPBA (7.35 g, 32.81 mmol) afforded, after flash chromatography (1:1AcOEt:hexanes) the title compound as a pale yellow oil; 1.68 g (60%, overall yield).

^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.78 (d, *J*=4.6 Hz, 1 H), 8.15 (d, *J*=7.9 Hz, 1 H), 7.99 (td, *J*=7.8, 1.6 Hz, 1 H), 7.59 (ddd, *J*=7.7, 4.6, 1.5 Hz, 1 H), 4.54 (qd, *J*=7.1, 2.5 Hz, 1 H), 2.30 (d, *J*=2.5 Hz, 1 H), 1.69 (d, *J*=7.0 Hz, 3 H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ = 155.2, 150.4, 137.9, 127.7, 124.1, 76.6, 75.9, 50.1, 13.4 ppm. **HRMS-EI+ (m/z):** Calculated for [$C_9H_9NO_2S$]: 195.0354, found: 195.0349.

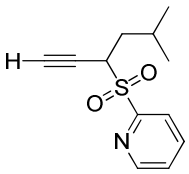
2-(Hex-1-yn-3-ylsulfonyl)pyridine (**21**)



Following the general procedure, the mesylation of 1-hexyn-3-ol (1.0 g, 10.19 mmol), substitution by 2-mercaptopyridine (1.35 g, 12.28 mmol) and oxidation with MCPBA (5.25 g, 23.43 mmol) afforded, after flash chromatography (1:1 AcOEt:hexanes) the title compound as a white solid; 1.07 g (47%, overall yield). Mp: 71-74 °C.

^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.78 (d, *J* = 4.4 Hz, 1 H), 8.14 (d, *J* = 7.8 Hz, 1 H), 7.97 (td, *J* = 7.7, 1.4 Hz, 1 H), 7.58 (dd, *J* = 7.5,4.7 Hz, 1 H), 4.41 - 4.52 (m, 1 H), 2.29 (d, *J* = 2.4 Hz, 1 H), 1.90 - 2.19 (m, 2 H), 1.42 - 1.83 (m, 2 H), 0.99 (t, *J* = 7.3 Hz, 3 H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ = 155.7, 150.3, 137.8, 127.6, 123.9, 76.5, 75.7, 54.9, 28.8, 19.9, 13.4 ppm. **HRMS-ESI (m/z)**: Calculated for [$C_{11}H_{13}NO_2S$+Na]: 246.0559, found: 246.0576.

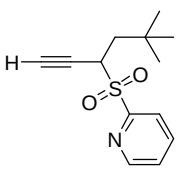
2-((5-Methylhex-1-yn-3-yl)sulfonyl)pyridine (**23**)



Following the general procedure, the mesylation of 5-methyl-1-hexyn-3-ol (1.0 g, 8.91 mmol), substitution by 2-mercaptopyridine (1.18 g, 10.69 mmol) and oxidation with MCPBA (4.59 g, 20.49 mmol) afforded, after flash chromatography (1:1 AcOEt:hexanes) the title compound as a white solid; 888 mg (42%, overall yield). Mp: 90-93 °C.

^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.78 (d, *J*=4.5 Hz, 1 H), 8.13 (d, *J*=7.8 Hz, 1 H), 7.97 (td, *J*=7.7, 1.4 Hz, 1 H), 7.58 (ddd, *J*=7.5, 4.8, 1.1 Hz, 1 H), 4.50 (dt, *J*=11.2, 2.8 Hz, 1 H), 2.28 (d, *J*=2.6 Hz, 1 H), 1.79 - 2.05 (m, 3 H), 1.02 (d, *J*=6.1 Hz, 3 H), 0.93 ppm (d, *J*=6.1 Hz, 3 H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ = 155.7, 150.3, 137.8, 127.6, 124.0, 76.5, 75.8, 53.8, 35.1, 25.8, 23.2, 20.8 ppm. **HRMS-EI+ (m/z)**: Calculated for [$C_{12}H_{15}NO_2S$]: 237.0824, found: 237.0845.

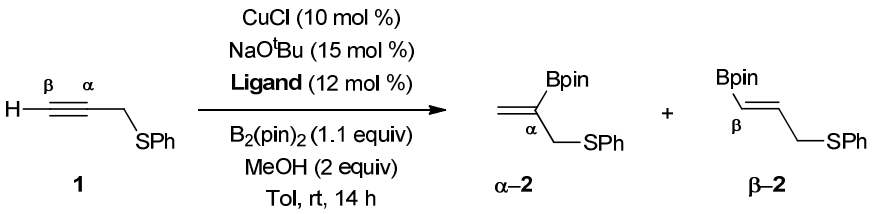
2-((5,5-Dimethylhex-1-yn-3-yl)sulfonyl)pyridine (**24**)



Following the general procedure, the mesylation of 5,5-dimethylhex-1-yn-3-ol (1.4 g, 11.09 mmol), substitution by 2-mercaptopyridine (1.85 g, 16.63 mmol) and oxidation with MCPBA (5.74 g, 23.29 mmol) afforded, after flash chromatography (1:1 Et_2O : hexanes) the title compound as a clear oil (1.21 g, 43% overall yield). **^{1}H NMR ($CDCl_3$, 300 MHz)** δ = 8.78 (d, *J*=4.5 Hz, 1 H), 8.14 (d, *J*=7.8 Hz, 1 H), 7.97 (dt, *J*=7.8, 1.3 Hz, 1 H), 7.57 (ddd, *J*=7.5, 4.8, 1.1 Hz, 1 H), 4.43 (dt, *J*=10.6, 2.2 Hz, 1 H), 2.28 (dd, *J*= 2.5, 0.8 Hz, 1 H), 2.15 (dd, *J*=13.7, 1.9 Hz, 1 H), 1.88 (dd, 13.6 and 10.6 Hz, 1 H), 1.01 ppm (s, 9 H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ = 155.6, 150.3, 137.7, 127.5, 124.2, 77.6, 76.6, 52.3, 39.9, 31.1, 29.4 ppm. **HRMS-EI+ (m/z)**: Calculated for [$C_{13}H_{17}NO_2S$]: 251.0980, found: 251.0985.

3. Ligand optimization studies

Table 1. Ligand optimization in the borylation of sulfide 1



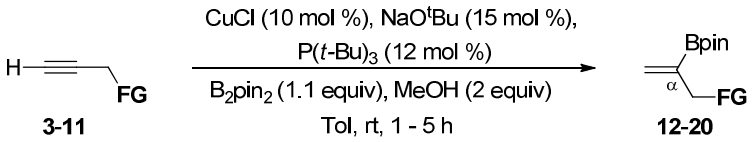
entry	Ligand	conv (%)[a]	α-**2**/ β-**2**[a]
1	---	10	< 2 : >98
2	Xantphos	<5[b]	--
3	Dppf	43	< 2 : >98
4	*rac*-Binap	75	9 : 91
5	PPh_3	41	12 : 88
6	Xphos	27	50 : 50
7	$P(Cy)_3$	100	75 : 25
8[c]	**P(*t*-Bu)$_3$**	**100 (76)**[d]	**>98 : <2**

[a] Determined by ^{1}H NMR in the crude reaction mixture. [b] Starting material recovered. [c] Reaction time 2 h. [d] Yield after chromatography.

Phenyl propargyl sulfide (**1**) was chosen for catalyst optimization in the Cu^I-catalyzed $B_2(pin)_2$-borylation under typical conditions (Table 1). In agreement with the existing scientific literature on the borylation of alkynes, both reactivity and regiocontrol were highly impacted by ligand structure. A very low conversion, yet complete β-regioselectivity was observed in the absence of ligand, highlighting an inherent anti-Markovnikov preference (entry 1). Xantphos ligand was found to be totally ineffective (entry 2). Other triarylphosphines such as dppf, *rac*-Binap or PPh_3 improved the reactivity (41-75% conversion), yet still maintaining a strong preference for β-borylation (entries 3-5). Examining stronger σ-donating P-alkyl ligands revealed a regioselectivity switch in favor of the branched vinyl boronate. The dialkylarylphosphine XPhos provided **2** with poor conversion, but the α-selectivity increased to 50% (entry 6). To our delight, the reactivity was greatly enhanced (100% conversion) and the regioselectivity inverted to α-borylation when the bulky PCy_3 and P(*t*-Bu)$_3$were used, the latter providing α-**2** as the only detected product in 76% isolated yield after 2 h at room temperature (entry 8).

4. α-Borylation of propargylic substituted 2-butynes

Table 2. α-Borylation of propargylic substituted 2-butynes: complete propargylic substitution studies

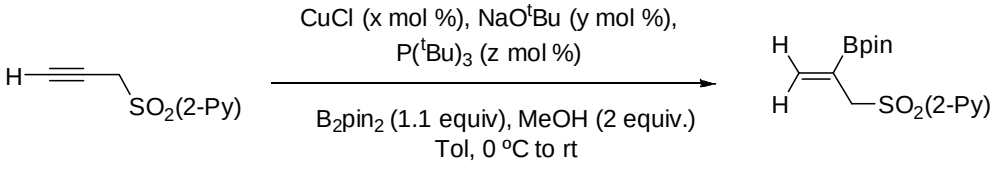


entry[a]	FG (alkyne)	product	α:β ratio[b]	yield (%)[c]
1	SO_2Ph (**3**)	**9**	>98 : <2	80
2	SO_2(2-Py) (**4**)	**10**	>98 : <2	83
3[d]	OH (**5**)	**11**	>98 : <2	64
4	OBn (**A**)	**D**	95 : 5	72[e]
5	OPh (**B**)	**E**	>98 : <2	75
6	OAc (**6**)	**12**	>98 : <2	70
7	NHBoc (**7**)	**13**	>98 : <2	76
8	CH_2OBn (**C**)	**F**	59 : 41	71[e]
9	Ph (**8**)	**14**	67 : 33	78[e]

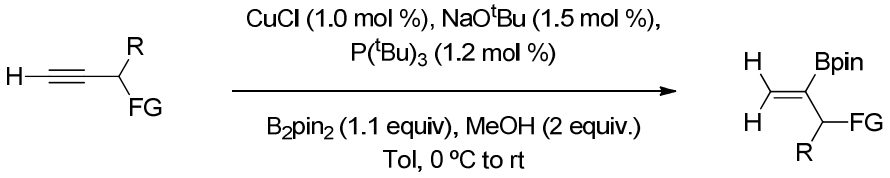
[a] 0.26mmol scale in alkyne substrate. [b] Determined by ^{1}H NMR from the crude mixture. [c]Isolated product after chromatography. [d] Reaction carried out in the absence of MeOH. [e] Yield in the mixture of regioisomers.

5. Catalyst loading and scale-up experiments

Note: Cooling the reaction down to 0 °C before the addition of MeOH was required as this addition turned out to be highly exothermic. At that point, the reaction was allowed to reach room temperature.



4 (mass, mmol)	**CuCl (x)**	**NaO^{t}Bu (y)**	**P(^{t}Bu)$_3$ (z)**	**10, yield**
1.50 g, 8.28 mmol	10 mol %	15 mol %	12 mol %	1.97 g, *77%*
0.50 g, 2.76 mmol	3 mol %	4.5 mol %	3.6 mol %	0.64 g, *75%*
1.03 g, 5.68 mmol	1 mol %	1.5 mol %	1.2 mol %	1.30 g, *74%*
2.00 g, 11.04 mmol	0.5 mol %	0.75 mol %	0.6 mol %	2.53 g, *74%*



6, FG = OAc, R = H	1.48 g, 14.82 mmol	**17**, 1.48 g, *70% yield*
26, FG = NPhth, R = Me	1.00 g, 5.02 mmol	**37**, 1.34 g, *82% yield*

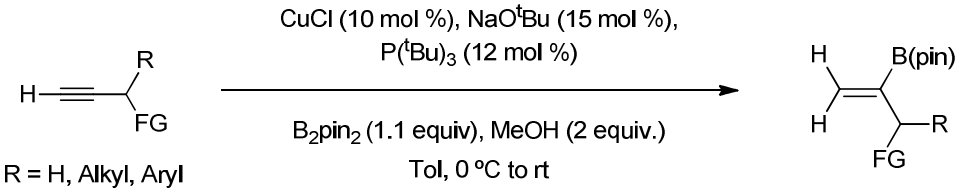
6. Cu^I-Catalytic regioselective borylation of terminal alkynes

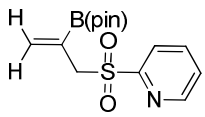
Unless stated otherwise, the borylation experiments of terminal alkynes described below were carried out using a 0.262 mmol scale. In light of the very low price (152.0 Euro/2 kg., Aldrich) and molecular weight of CuCl (99.0), the reactions described below were run using a 10 mol % catalyst loading: however, this was exclusively due to practicality reasons, since as shown above the reaction can take place using lower catalyst loadings. In this regard, the transmetallation from boron to copper in alkenylboronates to give alkenyl-Cu species has been documented (Jung, B.; Hoveyda, A. H., *J. Am. Chem. Soc.* **2012**, *134*, 1490, and references cited therein).

Tri-*tert*-butylphosphine can be used neat or as a 1.0 M solution in THF or hexanes without any noticeable variation on yields, reaction rates or product distribution.

Long chromatography columns should be avoided since partial decomposition of the product can be observed in silica gel under air, leading to lower yields.

Typical procedure for the catalytic regioselective borylation of terminal alkynes. Synthesis of 2-((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)sulfonyl)pyridine (10)

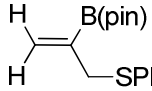




CuCl(2.6 mg, 0.026 mmol, 10 mol %), NaO^{t}Bu (3.8 mg, 0.039 mmol, 15 mol %), bis(pinacolato)diboron (73.2 mg, 0.288 mmol,1.1 equiv), and 2-(prop-2-yn-1-ylsulfonyl)pyridine **4** (47.5 mg, 0.262 mmol)was placed in a vial. The vial was purged and backfilled with argon. In another vial, tri-*tert*-butylphosphine (8 µL, 0.0314 mmol, 12 mol %) was dissolved in dry toluene (0.7 mL) under argon atmosphere. The mixture obtained was then transferred to the first vial. Finally MeOH (22 µL, 0.524 mmol) was added to the solution and the resulting mixture was stirred at room temperature until no starting material was detected (TLC monitoring, 1 h). Then, the reaction was quenched with MeOH (2 mL), filtered through a pad of Celite (washed with DCM) and the filtrate concentrated to dryness.The obtained crude was purified by flash chromatography (2:3 AcOEt:hexanes) to obtain 67.2 mg (83% yield) of **10** as a white solid; mp: 91-95 °C.

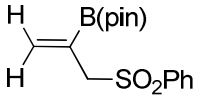
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.76 (d, *J* = 4.8 Hz, 1 H), 8.00 (d, *J* = 7.8 Hz, 1 H), 7.90 (td, *J* = 7.8,1.8 Hz, 1 H), 7.51 (ddd, *J* = 7.8, 4.8, 1.0 Hz, 1 H), 5.99 - 6.04 (m, 1 H), 5.69 (s, 1 H), 4.24 (s, 2 H), 1.22 (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 156.7, 150.0, 138.3, 137.7, 127.1, 123.3, 84.2, 56.6, 24.6 ppm. *The carbon directly attached to the boron atom was not detected by ^{13}C NMR technique due to quadrupolar relaxation.* **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 29.1 ppm. **HRMS-ESI (m/z)**: Calculated for [$C_{14}H_{20}BNO_4S$+Na]: 332.1103, found: 332.1101.

4,4,5,5-Tetramethyl-2-(3-(phenylthio)prop-1-en-2-yl)-1,3,2-dioxaborolane (**2**)



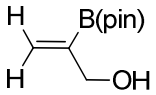
Reaction time: 3 h. Chromatography: 1:5 AcOEt:hexanes. Colorless oil. Yield: 54.9 mg (76%). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.29 - 7.35 (m, 2 H), 7.21 - 7.27 (m, 2 H), 7.11 - 7.18 (m, 1 H), 5.79 - 5.86 (m, 1 H), 5.69 (s, 1 H), 3.67 (s, 2 H), 1.28 ppm (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 136.6, 131.1, 129.8, 128.6, 125.9, 83.7, 38.4, 24.7 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 29.9 ppm. **HRMS-ESI (m/z)**: Calculated for [$C_{15}H_{21}BO_2S$+Na]: 299.1247, found: 299.1252.

4,4,5,5-Tetramethyl-2-(3-(phenylsulfonyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (**9**)



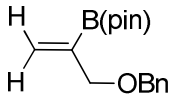
Reaction time: 1 h. Chromatography: 1:3 AcOEt:hexanes. White solid. Yield: 56.4 mg (80%). Mp: 110-114 °C. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.87 - 7.82 (m, 2 H), 7.59 - 7.63 (m, 1 H), 7.49 - 7.54 (m, 2 H), 6.06 - 6.13 (m, 1 H), 5.79 (br. s, 1 H), 3.93 (s, 2 H), 1.15 ppm (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 138.7, 138.5, 133.4, 129.0, 128.8, 84.1, 60.6, 24.6 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 29.2 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{15}H_{21}BO_4S$+Na]: 331.1145, found: 331.1141.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-ol (**11**)



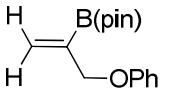
Reaction time: 2 h. Chromatography: 1:4 AcOEt:hexanes. Colorless oil. Yield: 30.9 mg (64%) The reaction was carried out in absence of 2 equivalents of MeOH, and it was quenched with 1.25 N HCl in MeOH (2 mL). This compound has been already reported in the literature. The obtained spectroscopic data correlates with previous described values.[5] **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 5.89 (s, 1 H), 5.84 (s, 1 H), 4.24 (s, 2 H), 1.93 (br. s, 1 H), 1.28 ppm (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 128.9, 83.7, 66.0, 24.8 ppm.

2-(3-(Benzyloxy)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**D**)



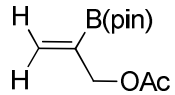
Reaction time: 4 h. Chromatography: 1:9 AcOEt:hexanes. Colorless oil. Yield: 51.7 mg (72%) Isolated as a mixture of regioisomers (α:β = 95:5)This compound has been already reported in the literature. The obtained spectroscopic data correlates with previous described values.[5] **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.31 - 7.40 (m, 4 H), 7.25 - 7.30 (m, 1 H), 5.93 - 6.03 (m, 2 H), 4.56 (s, 2 H), 4.16 (t, *J* = 1.8 Hz, 2 H), 1.26ppm (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 138.8, 129.4, 128.2, 127.5, 127.3, 83.5, 72.1, 71.8, 24.7 ppm.

4,4,5,5-Tetramethyl-2-(3-phenoxyprop-1-en-2-yl)-1,3,2-dioxaborolane (**E**)



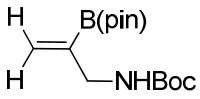
Reaction time: 2 h. Chromatography: 1:9 AcOEt:hexanes. Colorless oil. Yield: 51.1 mg (75%) **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.24 - 7.31 (m, 2 H), 6.91 - 6.98 (m, 3 H), 6.00 - 6.09 (m, 2 H), 4.65 - 4.67 (m, 2 H), 1.30 ppm (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 158.8, 129.8, 129.3, 120.5, 114.9, 83.6, 77.3, 77.0, 76.8, 69.2, 24.7 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 29.7 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{15}H_{21}BO_3$+Na]: 283.1475, found: 283.1483.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (**12**)



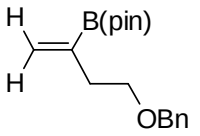
Reaction time: 3 h. Chromatography: 1:4 AcOEt:hexanes. Colorless oil. Yield: 42.1 mg (67%). This compound has been already reported in the literature. The obtained spectroscopic data correlates with previous described values.[6] **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 5.89 - 5.96 (m, 1 H), 5.81 (s, 1 H), 4.69 (t, *J* = 1.5 Hz, 2 H), 2.07 (s, 3 H), 1.26 ppm (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 170.6, 129.9, 83.7, 65.9, 24.7, 20.9 ppm.

***tert*-Butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)carbamate** (**13)**



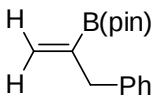
Reaction time: 5 h. Chromatography: 1:3 AcOEt:hexanes. Colorless oil. Yield: 56.4 mg (76%) This compound has been already reported in the literature. The obtained spectroscopic data correlates with previous described values.[5] **^{1}H NMR ($CDCl_3$, 500 MHz)** δ= 5.80 - 5.88 (m, 1 H), 5.73 (s, 1 H), 4.80 (br. s, 1 H), 3.72 - 3.92 (m, 2 H), 1.42 (s, 9 H), 1.23 ppm (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 155.8, 129.1, 83.6, 78.9, 44.3, 28.4, 24.7 ppm.

2-(4-(Benzyloxy)but-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(F)



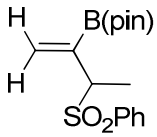
Reaction time: 3 h. Chromatography: 1:9 AcOEt:hexanes. Colorless oil. Yield: 53.2 mg (71%), iIsolated as a mixture of regioisomers (α:β = 59:41). ^{1}H NMR spectroscopic data for the mixture of regioisomers *(Ma=α-borylated, mi=ß-borylated).* **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.14 - 7.36 (*Ma+mi*, m, 8.7 H), 6.56 (*mi*, dt, *J*=17.7, 6.3 Hz, 0.7H), 5.72 - 5.81 (*Ma*, m, 1 H), 5.57 - 5.67 (*Ma*, m, 1 H), 5.45 (*mi*, dt, *J* = 18.0, 1.6 Hz, 0.7 H), 4.44 (*Ma+mi* , s, 3.7 H), 3.43 - 3.54 (*Ma+mi* , m, 3.7 H), 2.35 - 2.46 (*Ma+mi* , m, 3.6 H), 1.19 (*mi*, s, 9.2 H), 1.16 ppm (*Ma*, s, 12 H).

4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (14)



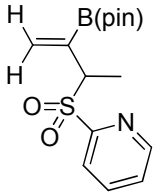
Reaction time: 2 h. Chromatography: 1:9 AcOEt:hexanes. Colorless oil. Yield: 50.1 mg (78%) Isolated as a mixture of regioisomers (α:β = 67:33)This compound has been already reported in the literature. The obtained spectroscopic data correlates with previous described values.[5] ^{1}H NMR spectroscopic data for the mixture of regioisomers *(Ma=α-borylated, mi=ß-borylated).* **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.13 - 7.34 (*Ma+mi*, m, 7.5 H), 6.77 (*mi*, dt, *J*=18.0, 6.3 Hz, 0.5 H), 5.78 - 5.89 (*Ma*, m, 1 H), 5.50 - 5.57 (*Ma*, m, 1 H), 5.46 (*mi*, dd, *J*=18.0, 1.6 Hz, 0.5 H), 3.44 - 3.52 (*Ma+mi*, m, 3 H), 1.26 (*mi*, s, 6 H), 1.22 ppm (*Ma*, s, 12 H).

4,4,5,5-Tetramethyl-2-(3-(phenylsulfonyl)but-1-en-2-yl)-1,3,2-dioxaborolane (**26**)



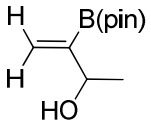
Reaction time: 1.5 h. Chromatography: 2:3 AcOEt:hexanes. White solid. Yield: 60.1 mg (71%) Mp: 104-109 °C. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.79 - 7.84 (m, 2 H), 7.57 - 7.62 (m, 1 H), 7.47 - 7.53 (m, 2 H), 6.07 – 6.11 (m, 1 H), 5.85 (br. s, 1 H), 4.11 (q, *J* = 7.1 Hz, 1 H), 1.49 (d, *J* = 7.1 Hz, 3 H), 1.15 - 1.21 ppm (m, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 137.6, 134.9, 133.3, 129.7, 128.6, 84.0, 62.5, 24.7, 24.6, 13.2 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 29.5 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{16}H_{23}BO_4S$+Na]: 345.1302, found: 345.1314.

2-((3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)sulfonyl)pyridine (27)



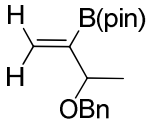
Reaction time: 1 h. Chromatography: 1:1 AcOEt:hexanes. White solid. Yield: 66.1 mg (78%). Mp: 96-99 °C. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 8.75 (d, *J*=4.1 Hz, 1 H), 7.98 (d, *J*=7.9 Hz, 1 H), 7.89 (td, *J*=7.9, 1.6 Hz, 1 H), 7.50 (ddd, *J*=7.6, 4.4, 0.9 Hz, 1 H), 6.02 - 6.06 (m, 1 H), 5.89 (br. s, 1 H), 4.53 (q, *J*=7.3 Hz, 1 H), 1.57 (d, *J*=7.3 Hz, 3 H), 1.22 (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 156.5, 150.0, 137.6, 135.8, 126.9, 124.1, 83.9, 60.3, 24.7, 13.1 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 29.7 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{15}H_{22}BNO_4S$+H]: 324.1435, found: 324.1434.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (28)



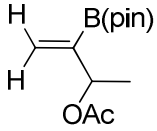
Reaction time: 2 h. Chromatography: 2:3 AcOEt:hexanes.Colorless oil. Yield: 51.9 mg (78%). The reaction was carried out in absence of 2 equivalents of MeOH, and it was quenched with 1.25 N HCl in MeOH (2 mL). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 5.70 - 5.89 (m, 2 H), 4.29 - 4.45 (m, 1 H), 2.16 - 2.30 (m, 1 H), 1.22 - 1.34 (m, 15 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ= 127.5, 83.7, 71.3, 24.7, 23.6 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ= 29.8 ppm. **HRMS-ESI (m/z)**: Calculated for [$C_{10}H_{19}BO_3$+Na]: 221.1319, found: 221.1321.

2-(3-(Benzyloxy)but-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**29**)



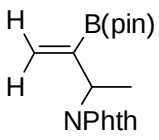
Reaction time: 5 h. Chromatography: 1:3 AcOEt:hexanes (isolated as a single regioisomer). Colorless oil. Yield: 49.8 mg (66%). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.30 - 7.38 (m, 4 H), 7.23 - 7.28 (m, 1 H), 5.87 - 5.96 (m, 2 H), 4.56 (d, *J* = 11.8 Hz, 1 H), 4.37 (d, *J* = 12.1 Hz, 1 H), 4.13 (q, *J* = 6.3 Hz, 1 H), 1.33 (d, *J* = 6.5 Hz, 3 H), 1.28 (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 139.1, 128.5, 128.2, 127.6, 127.2, 83.4, 77.4, 70.2, 24.8, 24.6, 22.0 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.0 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{17}H_{25}BO_3$+Na]: 311.1788, found: 311.178.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl acetate (**30**)



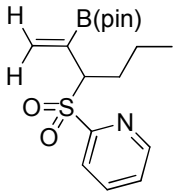
Reaction time: 2 h. Chromatography: 1:3 AcOEt:hexanes. Colorless oil. Yield: 38.4 mg (61%). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 5.83 - 5.88 (m, 1 H), 5.79 (br. s., 1 H), 5.49 (q, *J*=6.6 Hz, 1 H), 2.07 (s, 3 H), 1.34 (d, *J*=6.6 Hz, 3 H), 1.25 - 1.28 (m, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 170.2, 127.8, 83.6, 72.1, 24.8, 24.6, 21.3, 20.6 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 29.7 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{12}H_{21}BO_4$+Na]: 263.1425, found: 263.1417.

2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)isoindoline-1,3-dione (**31**)



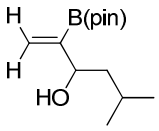
Reaction time: 2 h. Chromatography: 3:7 AcOEt:hexanes. White solid. Yield: 72.4 mg (85%). Mp: 114-118 °C. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.81 (dd, *J*= 5.5, 3.0 Hz, 2 H), 7.68 (dd, *J*= 5.4, 3.2 Hz, 2 H), 5.99 (t, *J*= 1.9 Hz, 1 H), 5.78 (t, *J*= 1.9 Hz, 1 H), 5.06 (qt, *J*= 6.9, 1.9 Hz, 1 H), 1.64 (d, *J*= 6.9 Hz, 3 H), 1.12 (s, 6 H), 1.03 (s, 6 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 168.4, 133.5, 132.4, 129.0, 122.8, 83.4, 48.7, 24.6, 24.5, 17.1 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 29.4ppm. **HRMS-EI+ (m/z)**: Calculated for [$C_{18}H_{22}BNO_4$]: 327.1642, found: 327.1649.

2-((2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-3-yl)sulfonyl)pyridine (**32**)



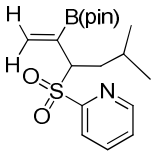
Reaction time: 1.5 h. Chromatography: 1:1 AcOEt:hexanes. Colorless oil. Yield: 66.3 mg (72%) **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 8.67 - 8.81 (m, 1 H), 7.95 (dt, *J* = 7.8, 1.3 Hz, 1 H), 7.87 (td, *J* = 7.8, 1.5 Hz, 1 H), 7.48 (ddd, *J* = 7.6, 4.6, 1.1 Hz, 1 H), 6.04 (d, *J* = 2.5 Hz, 1 H), 5.85 (d, *J* = 2.3 Hz, 1 H), 4.38 (dd, *J* = 10.7, 4.7 Hz, 1 H), 2.03 - 2.19 (m, 2 H), 1.35 - 1.46 (m, 1 H), 1.23 - 1.33 (m, 1 H), 1.16 – 1-20 (m, 12 H), 0.90 ppm (t, *J* = 7.3 Hz, 3 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ= 156.8, 150.0, 137.5, 137.0, 126.8, 124.0, 83.7, 65.3, 28.3, 24.6, 24.5, 19.9, 13.6 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 29.4 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{17}H_{26}BNO_4S$+H]: 352.1748, found: 352.1738.

5-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-3-ol (33)



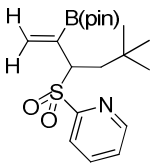
Reaction time: 2 h. Chromatography: 1:3 AcOEt:hexanes. Colorless oil. Yield: 46.6 mg (74%). The reaction was carried out in absence of 2 equivalents of MeOH, and it was quenched with 1.25 N HCl in MeOH (2 mL). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 5.81 (d, *J* = 3.0 Hz, 1 H), 5.73 (d, *J* = 2.8 Hz, 1 H), 4.12 - 4.26 (m, 1 H), 2.12 (br. s, 1 H), 1.65 - 1.78 (m, 1 H), 1.44 - 1.53 (m, 1 H), 1.32 - 1.40 (m, 1 H), 1.27 (s, 12 H), 0.86 - 0.94 ppm (m, 6 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 128.2, 83.6, 74.2, 46.9, 24.8, 24.7, 24.6, 23.1, 22.4 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 29.9 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{13}H_{25}BO_3$+Na]: 263.1788, found: 263.1780.

2-(5-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-3-yl)sulfonyl)pyridine (**34**)



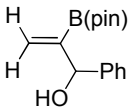
Reaction time: 1 h. Chromatography: 1:1 AcOEt:hexanes. White solid. Yield: 73.8 mg (77%). Mp: 66-68°C. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 8.75 (d, *J*=4.7 Hz, 1 H), 7.95 (d, *J*=7.6 Hz, 1 H), 7.88 (td, *J*=7.7, 1.9 Hz, 1 H), 7.48 (ddd, *J*=7.6, 4.7, 0.9 Hz, 1 H), 6.05 (d, *J*=2.2 Hz, 1 H), 5.87 (d, *J*=2.2 Hz, 1 H), 4.46 (dd, *J*=12.3, 3.5 Hz, 1 H), 2.19 (td, *J*=12.7, 3.9 Hz, 1 H), 1.84 (ddd, *J*=13.3, 10.0, 3.5 Hz, 1 H), 1.53 - 1.61 (m, 1 H), 1.16 - 1.20 (m, 12 H), 0.93 (d, *J*=6.9 Hz, 3 H), 0.85 ppm (d, *J*=6.6 Hz, 3 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 156.8, 150.0, 137.5, 137.4, 126.8, 124.2, 83.8, 64.1, 34.8, 25.4, 24.7, 24.5, 23.6, 20.7 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 29.4 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{18}H_{28}BNO_4S$+H]: 366.1904, found: 366.1922.

2-((5,5-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-3-yl)sulfonyl) pyridine (**35**)



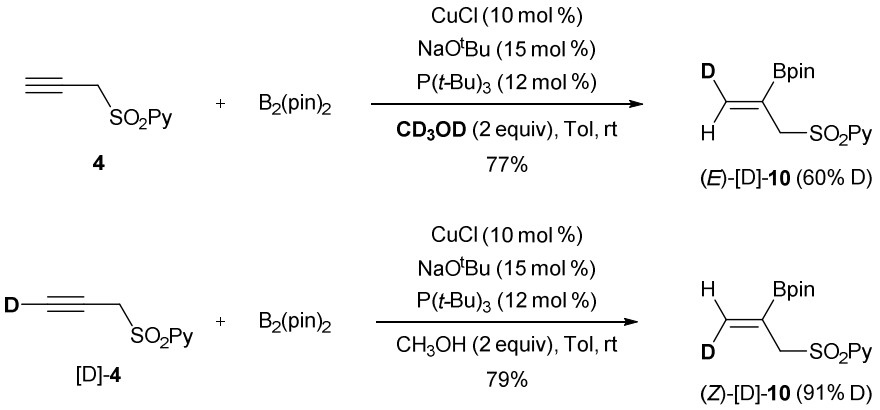
Reaction time: 2 h. Crushed in hexanes, white solid. Yield: 94 mg (89%). **^{1}H NMR ($CDCl_3$, 300 MHz)** δ = 8.75 (d, *J*=4.6 Hz, 1 H), 7.94 (dt, *J*=7.8 and 1.2 Hz, 1 H), 7.86 (dt, *J* = 7.5 and 1.7 Hz, 1H), 7.47 (ddd, *J*=7.8, 4.8 and 1.4 Hz, 1 H), 6.11 (d, *J*= 2.3 Hz, 1 H), 6.03 (d, *J*= 2.3 Hz, 1 H),4.47 (dd, *J* = 10.6 and 1.1 Hz, 1H), 2.18 (dd, J= 14.0 and 1.8 Hz, 1H), 2.03 (dd, J= 13.9 and 10.4 Hz, 1H), 1.17 (s, 6H), 1.15 (s, 6H), 0.88 (s, 9H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ = 156.9, 150.2, 137.5, 137.4, 126.9, 124.6, 84.0, 62.1, 40.5, 31.4, 30.0, 24.9, 24.6 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz):** δ = 29.5 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{19}H_{30}BNO_4S$+H]: 380.2061, found: 380.2068.

1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-ol (36)



Reaction time: 3 h. Chromatography: 1:3 AcOEt:hexanes. Colorless oil. Yield: 55.3 mg (81%). The reaction was carried out in absence of 2 equivalents of MeOH, and it was quenched with 1.25 N HCl in MeOH (2 mL). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.37 (d, *J* = 7.3 Hz, 2 H), 7.31 (t, *J* = 7.3 Hz, 2 H), 7.23 (t, *J* = 7.3 Hz, 1 H), 5.90 – 5.95 (m, 1 H), 5.76 - 5.84 (m, 1 H), 5.31 (d, *J* = 6.0 Hz, 1 H), 2.85 (d, *J* = 6.8 Hz, 1 H), 1.14 - 1.20 ppm (m, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 143.3, 128.9, 128.1, 127.1, 126.5, 83.8, 77.1, 24.6, 24.5 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ= 29.8 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{15}H_{21}BO_3$+Na]: 283.1475, found: 283.1477

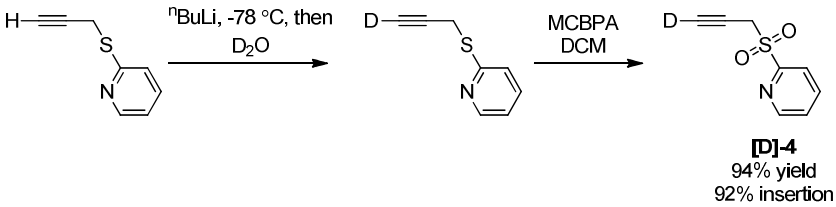
7. Mechanistic discussion: ^{2}H labelling experiments



Thorough mechanistic studies performed by the group of Hoveyda suggest that the coordination of the initially formed ligand-Cu-boryl complex to the alkyne is the rate- and product-determining step, prior to *syn*-addition to the alkyne[4a] The α-selectivity observed in the borylation of propargyl alcohol and amine derivatives was suggested to arise from a subtle balance of the steric and electronic characteristics of both the ligand and the alkyne.[4a] Given that the NHC ligand (IMes) used in their studies possesses related steric demand and σ-donor ability to P(*t*-Bu)$_3$ (both the Tolman electronic parameter and the percent buried volume (%Vbur) models used for quantifying the σ-donation ability and the steric bulk, respectively, are similar for the two ligands: J. Balogh, A. M. Z. Slawin, S. P. Nolan, *Organometallics* 2012, **31**, 3259) a similar mechanistic scenario can be envisaged in our case. We performed deuterium labeling experiments that are in agreement with this hypothesis: under the standard conditions, borylation of alkyne **4** in the presence of CD_3OD led to exclusive formation of the vinyl boronate (*E*)-[D]-**10** (77% yield, 60%-D), while [D]-**4** and CH_3OH afforded the *Z*-vinyl boronate [D]-**10** (79% yield, 91%-D, see SI for details). The stereospecificity

observed in these experiments is consistent with the *syn*-addition of the Cu-borane complex to the alkyne and seems to rule out the intermediacy of allenes or alkynyl-Cu species.

Synthesis of 2-[(3-^{2}H)prop-2-yn-1-ylsulfonyl]pyridine ([D]-4)

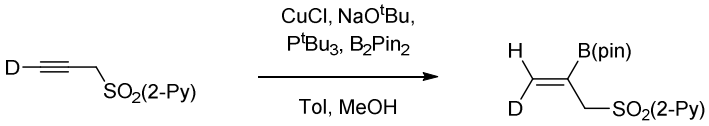


[D]-4
94% yield
92% insertion

To a solution of 2-(2-Propynylthio)pyridine (800 mg, 5.36 mmol) in dry THF (25 mL) at -78 °C was added ^{n}BuLi (2.5 M in hexanes, 2.36 mL, 5.89 mmol). Then, the mixture was stirred for 30 min and warmed to 0 °C before quenching with deuterium oxide (10 mL). The organic phase was separated with ethyl acetate (20 mL), dried over $MgSO_4$ and concentrated to dryness. The resulting crude was then treated with MCPBA as previously described to obtain, after flash chromatography (2:3 AcOEt:hexanes), 2-[(3-^{2}H)prop-2-yn-1-ylsulfonyl]pyridine (**[D]-4**) as a white solid, 910 mg (94% yield, 92% ^{2}H insertion).

^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.78 (d, *J*=4.5 Hz, 1 H), 8.14 (d, *J*=7.9 Hz, 1 H), 8.00 (td, *J*=7.7, 1.4 Hz, 1 H), 7.60 (dd, *J*=7.2, 4.9 Hz, 1 H), 4.31 (s, 2 H), 2.27 ppm (t, *J*=2.6 Hz, 0.08 H).

Regioselective borylation of (Z)-2-[(3-^{2}H)prop-2-yn-1-ylsulfonyl]pyridine to afford (*Z*)-[D]-10

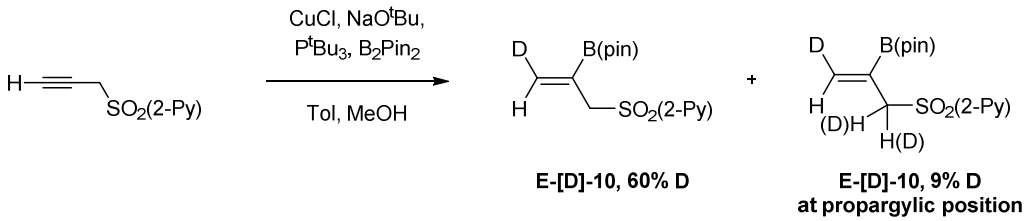


Z- [D]-10, 91% D

CuCl (2.6 mg, 0.026 mmol, 10 mol %), NaO^{t}Bu (3.8 mg, 0.039 mmol, 15 mol %), bis(pinacolato)diboron (73.2 mg, 0.288 mmol, 1.1 equiv), and 2-[(3-^{2}H)prop-2-yn-1-ylsulfonyl]pyridine (47.5 mg, 0.262 mmol) was placed in a vial. The vial was purged and backfilled with argon. In another vial, tri-*tert*-butylphosphine (8 µL, 0.0314 mmol, 12 mol %) was dissolved in dry toluene (0.7 mL) under argon atmosphere. The mixture obtained was then transferred to the first vial. Finally, MeOH (22 µL, 0.524 mmol) was added to the solution and the resulting mixture was stirred at room temperature until no starting material was detected (TLC monitoring, 1 h). The reaction was quenched with MeOH (2 mL), filtered through a pad of celite (washed with DCM) and the filtrate concentrated to dryness. The crude was purified by flash chromatography (2:3 AcOEt:hexanes) to obtain 63.8 mg (79% yield) of **Z-[D]-10** (91% ^{2}H in the product).

The stereochemistry was confirmed by a NOESY experiment of the non-deuterated product. See *stereochemical determination* section for further details. **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ = 8.69 (d, *J* = 4.3 Hz, 1 H), 7.93 (d, *J* = 7.9 Hz, 1 H), 7.83 (td, *J* = 7.6, 1.4 Hz, 1 H), 7.44 (ddd, *J* = 7.3, 4.8, 1.6 Hz, 1 H), 5.94 (s, 1 H), 5.60 - 5.64 (m, 0.09 H), 4.17 (s, 2 H), 1.16 ppm (s, 12 H). **^{2}H NMR ($CDCl_3$, 300 MHz)**: 5.75 ppm.

Regioselective borylation of 2-(prop-2-yn-1-ylsulfonyl)pyridine using MeOD



E-[D]-10, 60% D **E-[D]-10, 9% D at propargylic position**

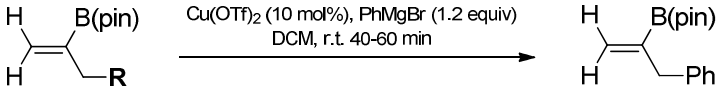
Following the general procedure described above, (*E*)2-[(3-^{2}H)prop-2-yn-1-ylsulfonyl]pyridine was obtained as a white solid, 62.4 mg (77%, 60% ^{2}H insertion).

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.69 (d, *J* = 4.3 Hz, 1 H), 7.93 (d, *J* = 7.9 Hz, 1 H), 7.83 (td, *J* = 7.6, 1.4 Hz, 1 H), 7.44 (ddd, *J* = 7.3, 4.8, 1.6 Hz, 1 H), 5.94 (s, 0.40 H), 5.60 - 5.64 (m, 1 H), 4.17 (s, 2 H), 1.16 ppm (s, 12 H). **^{2}H NMR (CDCl$_3$, 300 MHz**): 6.1, 4.25 ppm.

The stereochemistry was confirmed by a NOESY experiment of the non deuterated product. See *stereochemical determination* section below for further details.

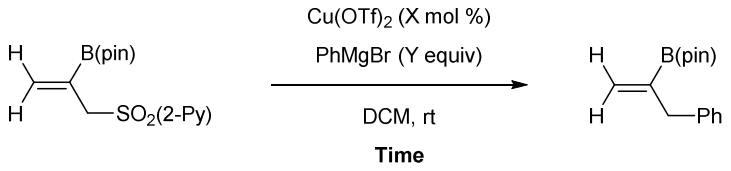
8. Cu^{II}-Catalyzed nucleophilic displacement of allyl sulfones with Grignard reagents

a. Substrate screening



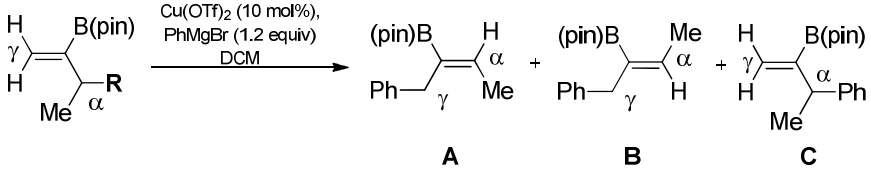
R	Yield
OAc	58%
SO_2Ph	52%
SO_2(2-Py)	79%

b. Catalyst loading



$Cu(OTf)_2$ X mol %	PhMgBr Y equiv	Time	Yield
10	1.2	1h	79%
5	1.2	1h	62%
3	1.2	1h	53%
1	1.2	1h	43%
0	1.2	1h	42%
0	2.5	1h	40%
0	4	1h	37%

c. Product distribution: effect of temperature

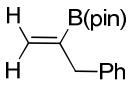


R	T	A : B : C[a]	Yield
OAc	r.t.	58 : 29 : 13	70%
SO_2Ph	r.t.	57 : 31 : 12	60%
SO_2(2-Py)	r.t.	78 : 9 : 13	77%
SO_2(2-Py)	-20 °C	78 : 5 : 17	74%
SO_2(2-Py)	-50 °C	83 : n.d.[c] : 17	79%[b]

[a] Determined by ^{1}H NMR analysis of the crude reaction mixtures. [b] Isolated as a mixture A/C= 93/7. [c] Not detected.

d. Reaction scope

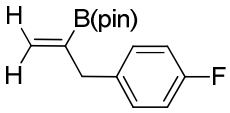
Typical procedure for the Cu^{II}-Catalyzed nucleophilic displacement of allyl (2-pyridyl)sulfones with Grignard reagents. Synthesis of 4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (37)



To a solution of **10** (40 mg, 0.129 mmol) and $Cu(OTf)_2$ (4.7 mg, 0.012 mmol, 10 mol %) in dry DCM (0.5 mL) at room temperature, was added dropwise phenylmagnesium bromide (1.0 M in THF, 155 µL, 0.155 mmol). Then, the solution was stirred at room temperature until no starting material was observed (TLC monitoring, 40 min). The reaction was quenched with NH_4Cl(3 mL) and the organic phase separated with DCM, washed with water (3 mL), dried over $MgSO_4$ and concentrated to dryness. The crude residue was purified by flash chromatography (1:50 AcOEt:hexanes) to yield the title compound as a colorless oil; 24.9 mg (79% yield). This compound has been already reported in the literature. The obtained spectroscopic data matches with the data previously reported.[9] **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.13-7.25 (m, 5H), 5.82 (s, 1 H), 5.51 (s, 1 H), 3.47 (s, 2 H), 1.21 ppm (s, 12 H).

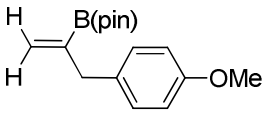
Note: Unless stated otherwise, all the experiments below were carried out using the same mmol scale.

2-(3-(4-Fluorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**38**)



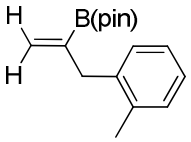
Reaction time: 30 min. Chromatography: 1:50 AcOEt:hexanes. Colorless oil. Obtained 24.9 mg (74% yield). **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.11 - 7.19 (m, 2 H), 6.89 - 6.99 (m, 2 H), 5.78 - 5.87 (m, 1 H), 5.53 (br. s, 1 H), 3.44 (s, 2 H), 1.22 (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 162.2, 160.3, 136.3, 136.3, 130.5, 130.4, 129.8, 114.8, 114.7, 83.5, 40.7, 24.7 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.1 ppm. **HRMS-EI+ (m/z):** Calculated for $[C_{15}H_{20}BO_2F]$: 262.1540, found: 262.1547.

2-(3-(4-Methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**39**)



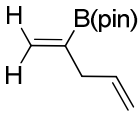
Reaction time: 30 min. Chromatography: 2:1 toluene:hexanes. Colorless oil. Obtained 22.6mg (65% yield). The reaction was carried out at -50 °C using 2 equivalents of the Grignard reagent.**^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.07 - 7.15 (m, 2 H), 6.77 - 6.85 (m, 2 H), 5.75 - 5.85 (m, 1 H), 5.50 (br. s, 1 H), 3.78 (s, 3 H), 3.42 (s, 2 H), 1.21 (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 157.7, 132.8, 130.0, 129.4, 113.5, 83.4, 55.2, 40.5, 24.7 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.1 ppm. **HRMS-EI+ (m/z):** Calculated for $[C_{16}H_{23}BO_3]$: 274.1740, found: 274.1735.

4,4,5,5-Tetramethyl-2-(3-(o-tolyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (**40**)



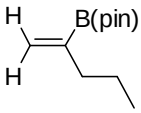
Reaction time: 60 min. Chromatography: 2:98 *t*-BuOMe:hexanes. Colorless oil. Obtained 24.1 mg (72% yield). The reaction was carried out at -50 °C. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.03 - 7.20 (m, 4 H), 5.77 - 5.89 (m, 1 H), 5.31 (br. s, 1 H), 3.46 (s, 2 H), 2.25 (s, 3 H), 1.25 (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 138.5, 136.7, 130.0, 129.9, 129.6, 126.0, 125.6, 83.5, 38.2, 24.7, 19.4 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.1 ppm. **HRMS-EI+ (m/z):** Calculated for $[C_{16}H_{23}BO_2]$: 258.1791, found: 258.1789.

4,4,5,5-Tetramethyl-2-(penta-1,4-dien-2-yl)-1,3,2-dioxaborolane (**41**)

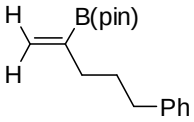


Reaction time: 30 min. Chromatography: 1:20 ether:hexanes. Colorless oil. Obtained 12.8 mg (51% yield). The reaction was carried out using 2 equivalents of the Grignard reagent.**^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 5.84 - 5.95 (m, 1 H), 5.79 - 5.84 (m, 1 H), 5.63 (br. s, 1 H), 4.94 - 5.07 (m, 2 H), 2.90 (d, *J*=6.6 Hz, 2 H), 1.26 (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 137.2, 129.6, 115.2, 83.4, 39.2, 24.7 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.1 ppm. **HRMS-EI+ (m/z):** Calculated for [$C_{11}H_{19}BO_2$]: 194.1478, found: 194.1476.

4,4,5,5-Tetramethyl-2-(pent-1-en-2-yl)-1,3,2-dioxaborolane (**42**)

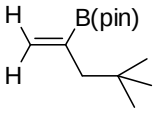


Reaction time: 40 min. Chromatography: 1:20 ether:hexanes. Colorless oil. Obtained 13.8 mg (55% yield). The reaction was carried out using 2 equivalents of the Grignard reagent. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 5.73 - 5.79 (m, 1 H), 5.59 (br. s, 1 H), 2.12 (t, *J*=7.3 Hz, 2 H), 1.44 (sxt, *J*=7.6 Hz, 2 H), 1.26 (s, 12 H), 0.89 (t, *J*=7.4 Hz, 3 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 128.9, 83.3, 37.5, 24.7, 22.4, 13.8 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.2 ppm. **HRMS-EI+ (m/z):** Calculated for [$C_{11}H_{21}BO_2$]: 196.1635, found: 196.1631.



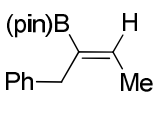
4,4,5,5-Tetramethyl-2-(5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (**43**)

Reaction time: 50 min. Chromatography: 1:1 toluene:hexanes. Colorless oil. Obtained 21.3 mg (61% yield). The reaction was carried out at -50 °C using 2 equivalents of the Grignard reagent. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.23 - 7.29 (m, 2 H), 7.13 - 7.19 (m, 3 H), 5.76 - 5.82 (m, 1 H), 5.58 - 5.63 (m, 1 H), 2.55 - 2.64 (m, 2 H), 2.21 (t, *J*=7.4 Hz, 2 H), 1.71 - 1.80 (m, 2 H), 1.26 (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 142.8, 129.2, 128.4, 128.2, 125.5, 83.3, 35.5, 35.1, 30.9, 24.8 ppm.**^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.2 ppm. **HRMS-EI+ (m/z):** Calculated for [$C_{17}H_{25}BO_2$]: 272.1948, found: 272.1948.



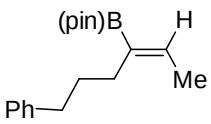
2-(4,4-Dimethylpent-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**44**)

Reaction time: 40 min. Chromatography: 2:98 *t*-BuOMe:hexanes. Colorless oil. Obtained 13.8 mg (67% yield). The reaction was carried out at 0 °C using 2 equivalents of the Grignard reagent. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 5.85 (d, *J*=3.8 Hz, 1 H), 5.52 (d, *J*=3.8 Hz, 1 H), 2.07 (s, 2 H), 1.26 (s, 12 H), 0.86 (s, 9 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 131.9, 83.3, 48.7, 31.4, 29.3, 24.7 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.3 ppm. **HRMS-EI+ (m/z):** Calculated for [$C_{13}H_{25}BO_2$]: 224.1948, found: 224.1954.



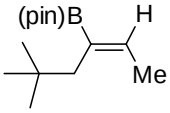
(Z)-4,4,5,5-tetramethyl-2-(1-phenylbut-2-en-2-yl)-1,3,2-dioxaborolane (**45**)

Reaction time: 40 min. Chromatography: 1:5 toluene:hexanes (isolated as γ:α mixture = 93:7), colorless oil. Obtained 26.3 mg (79% yield). 2 equivalents of the Grignard reagent were used. *Spectroscopic data for the major regioisomer:* **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.20 - 7.25 (m, 4 H), 7.10 - 7.16 (m, 1 H), 6.55 (q, *J*=6.9 Hz, 1 H), 3.52 (s, 2 H), 1.80 (d, *J*=6.9 Hz, 3 H), 1.20 ppm (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 141.8, 141.2, 128.5, 128.0, 125.3, 83.1, 33.8, 24.6, 14.7 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.5 ppm. **HRMS-EI+ (m/z):** Calculated for [$C_{16}H_{23}BO_2$]: 258.1791, found: 258.1782.



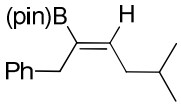
(*Z*)-4,4,5,5-Tetramethyl-2-(6-phenylhex-2-en-3-yl)-1,3,2-dioxaborolane (**46**)

Reaction time: 40 min. Chromatography: 1:1 toluene:hexanes (isolated as a single regioisomer). Colorless oil. Obtained 20.5 mg (56% yield). The reaction was carried out using 2 equivalents of the Grignard reagent. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 7.23 - 7.32 (m, 2 H), 7.13 - 7.23 (m, 3 H), 6.44 (q, *J*=6.6 Hz, 1 H), 2.56 - 2.66 (m, 2 H), 2.21 (t, *J*=7.4 Hz, 2 H), 1.65 - 1.74 (m, 5 H), 1.26 (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 143.0, 140.6, 128.4, 128.2, 125.5, 83.0, 35.8, 31.5, 27.9, 24.7, 14.2 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.5 ppm. **HRMS-EI+ (m/z):** Calculated for [$C_{18}H_{27}BO_2$]: 286.2104, found: 286.2102.



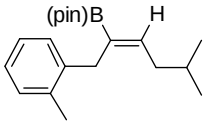
(*Z*)-2-(5,5-Dimethylhex-2-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**47**)

Reaction time: 30 min. Chromatography: 1:2 toluene:hexanes (isolated as a single regioisomer). Colorless oil. Obtained 20.2 mg (65% yield). The reaction was carried out using 2 equivalents of the Grignard reagent. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 6.51 (q, *J*=6.9 Hz, 1 H), 2.10 (s, 2 H), 1.70 (d, *J*=6.9 Hz, 3 H), 1.25 (s, 12 H), 0.87 (s, 9 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 141.7, 83.0, 40.9, 33.3, 29.7, 24.7, 15.2 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.8 ppm. **HRMS-EI+ (m/z):** Calculated for [$C_{14}H_{27}BO_2$]: 238.2104, found: 238.2109.



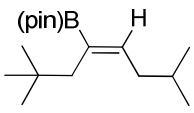
(*Z*)-4,4,5,5-tetramethyl-2-(5-methyl-1-phenylhex-2-en-2-yl)-1,3,2-dioxaborolane (48)

Reaction time: 40 min. Chromatography: 1:5 toluene:hexanes (isolated as γ:α mixture = 96:4). Colorless oil. Obtained 28.9 mg (75% yield). The reaction was carried out using 2 equivalents of the Grignard reagent. **^{1}H NMR ($CDCl_3$, 500 MHz)**: δ = 7.09 - 7.25 (m, 5 H), 6.44 (t, *J*=6.9 Hz, 1 H), 3.51 (s, 2 H), 2.11 (t, *J*=7.0 Hz, 2 H), 1.64 - 1.75 (m, 1 H), 1.19 (s, 12 H), 0.91 (d, *J*=6.9 Hz, 6 H). **^{13}C NMR ($CDCl_3$, 125 MHz**) δ = 145.9, 142.0, 128.6, 128.0, 125.3, 83.1, 38.0, 34.3, 28.4, 24.6, 22.6 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.6 ppm. **HRMS-EI+ (m/z):** Calculated for [$C_{19}H_{29}BO_2$]: 300.2261, found: 300.2271.



(*Z*)-4,4,5,5-Tetramethyl-2-(5-methyl-1-(o-tolyl)hex-2-en-2-yl)-1,3,2-dioxaborolane (**49**)

Reaction time: 40 min. Chromatography: 1:5 toluene:hexanes (isolated as a single regioisomer). Colorless oil. Obtained 26.6mg (66% yield). The reaction was carried out using 2 equivalents of the Grignard reagent. **^{1}H NMR ($CDCl_3$, 500 MHz)**: δ = 7.01 - 7.15 (m, 4 H), 6.51 (t, *J*=6.9 Hz, 1 H), 3.44 (s, 2 H), 2.33 (s, 3 H), 2.02 (t, *J*=6.9 Hz, 2 H), 1.65 - 1.76 (m, 1 H), 1.17 (s, 12 H), 0.89 ppm (d, *J*=6.6 Hz, 6 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 146.2, 139.7, 136.3, 129.5, 128.1, 125.4, 125.3, 83.1, 38.0, 31.5, 28.3, 24.6, 22.6, 19.8 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.6 ppm. **HRMS-EI+ (m/z):** Calculated for [$C_{20}H_{31}BO_2$]: 314.2417, found: 314.2415.

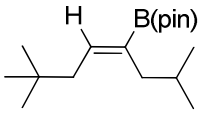


(*Z*)-4,4,5,5-Tetramethyl-2-(2,2,7-trimethyloct-4-en-4-yl)-1,3,2-dioxaborolane (**50**)

Reaction time: 40 min. Chromatography: 1:5 toluene:hexanes (isolated as a single regioisomer). Colorless oil. Obtained 25.6 mg (71% yield). The reaction was carried out using 2 equivalents of the Grignard reagent. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ = 6.38 (t, *J*=6.9 Hz, 1 H), 2.08 (s, 2 H), 2.01 (t, *J*=6.9 Hz, 2 H), 1.60 - 1.73 (m, 1 H), 1.25 (s, 12 H), 0.85 - 0.93 (m, 15 H). **^{13}C NMR ($CDCl_3$, 125**

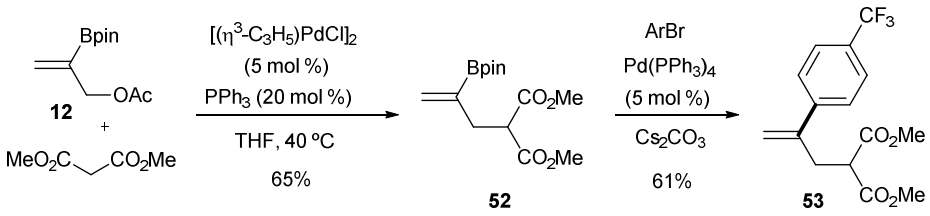
MHz) δ = 146.4, 83.0, 41.6, 38.4, 33.1, 29.7, 28.4, 24.7, 22.6 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.8 ppm. **HRMS-EI+ (m/z):** Calculated for [$C_{17}H_{33}BO_2$]: 280.2574, found: 280.2568.

(*Z*)-4,4,5,5-Tetramethyl-2-(2,7,7-trimethyloct-4-en-4-yl)-1,3,2-dioxaborolane (**51**)

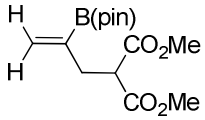


Reaction time: 40 min. Chromatography: dichloromethane (isolated as a single regioisomer). Colorless oil. Obtained 26.8 mg (run on 0.134 mmol of starting material, 71% yield). The reaction was carried out using 2 equivalents of the Grignard reagent. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ = 6.34 (t, *J*= 7.4 Hz, 1 H), 1.95 (m, 4H), 1.7 (septet, *J*= 6.7 Hz, 1H), 1.18 (s, 12H), 0.85 (s, 9H), 0.78 (d, *J*= 6.6 Hz, 6 H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ = 143.5, 83.0, 42.6, 37.7, 31.4, 29.7, 29.3, 24.9, 22.8 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 30.9 ppm. **HRMS-EI+ (m/z):** Calculated for [$C_{17}H_{33}BO_2$]: 280.2574, found: 280.2566.

9. Synthetic applications of vinyl boronates 12 and 13



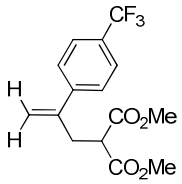
Pd-Catalyzed allylic substitution of 12.[7] Synthesis of dimethyl 2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)malonate (52)



To a flask was added [ClPd(allyl)]$_2$ (4 mg, 0.011 mmol, 5 mol %) and PPh_3 (11.4 mg, 0.44 mmol, 20 mol %) in 1 mL of dry THF at rt under N_2 and the solution stirred for 30 min at rt. To this solution was added **12** (49.4 mg, 0.22 mmol) and the reaction mixture stirred for an additional 30 min. In a separate flask was added sodium hydride (29 mg, 0.72 mmol) in 4 mL of dry THF under N_2, and the reaction mixture cooled to 0 °C. To this white suspension was added dropwise dimethyl malonate (75 µL, 0.66 mmol) at 0 °C. Once the reaction became clear, it was heated to reflux under N_2 for 15 min. The dimethyl malonate sodium solution was cooled to room temperature, and then transferred via cannula into the flask containing the catalyst and allylic acetate solution at rt. The reaction mixture was warmed to 40 °C and stirred until complete consumption of **12** (TLC monitoring, around 17h) The reaction mixture was then cooled to room temperature, diluted with EtOAc (10 mL) and quenched with saturated NH_4Cl (5 mL). The organic layer was separated and the aqueous solution was extracted with EtOAc (2 x 10 mL). The combined organic solution was dried over $MgSO_4$, filtered through celite and the solvent was removed under reduced pressure. The crude product was the purified by flash chromatography (1:9 AcOEt:hexanes) to obtain **52** as a colorless oil, 42.6 mg (65% yield).

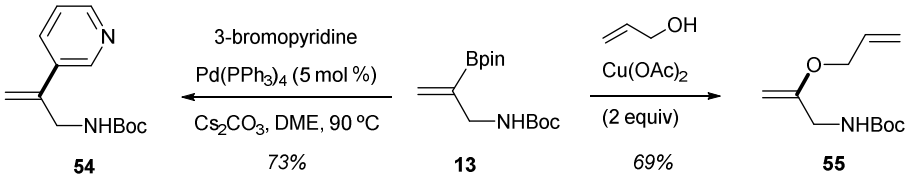
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 5.76 - 5.89 (m, 1 H), 5.66 (br. s, 1 H), 3.77 (t, *J* = 8.1 Hz, 1 H), 3.69 (s, 6 H), 2.73 (d, *J* = 8.1 Hz, 2 H), 1.26 ppm (s, 12 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 169.6, 132.1, 83.6, 52.3, 51.2, 34.9, 24.7 ppm. **^{11}B NMR ($CDCl_3$, 160 MHz)** δ = 29.7 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{14}H_{23}BO_6$+Na]: 321.1479, found: 321.1462.

Suzuki cross coupling of G. Dimethyl 2-(2-(4-(trifluoromethyl)phenyl)allyl)malonate (53)

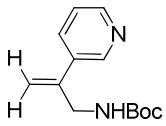


To a solution of tetrakis(triphenylphosphine)palladium (9.7 mg, 8.38 x 10^{-3} mmol, 5 mol %), Cs_2CO_3 (164 mg, 0.503 mmol) and 4-bromobenzotrifluoride (30.5 µL, 0.218 mmol) in dry and degassed DME (2 mL) was added **G** (50 mg, 0.167 mmol). The vial was sealed and heated to 60 °C overnight. Then, the suspension was diluted with ethyl acetate (5 mL) and filtered through a pad of Celite. The solution was washed with brine (10 mL), the organic layer separated, dried with $MgSO_4$and concentrated to dryness. The crude was purified by flash chromatography (1:9 AcOEt:hexanes) to obtain **53** as a colorless oil, 32.3 mg (61% yield).

^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.59 (d, *J* = 8.1 Hz, 2 H), 7.48 (d, *J* = 8.6 Hz, 2 H), 5.37 (s, 1 H), 5.23 (s, 1 H), 3.70 (s, 6 H), 3.50 (t, *J* = 7.7 Hz, 1 H), 3.14 (d, *J* = 7.6 Hz, 2 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ = 169.1, 143.7, 143.5, 129.8 (q, *J* = 33 Hz), 126.6, 125.4 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272 Hz), 116.7, 52.6, 50.6, 34.4 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{15}H_{15}O_4F_3$+Na]: 339.0814, found: 339.0825.

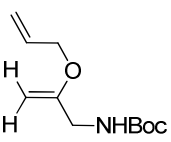


Suzuki cross-coupling of 13. Synthesis of *tert*-butyl (2-(pyridin-3-yl)allyl)carbamate (54)[8]



To a solution of **13** (50 mg, 0.176 mol) in DME (2 mL) was added tetrakis(triphenylphosphine)palladium (10.2 mg, 5 mol %), Cs_2CO_3(172 mg, 0.528 mmol) and 3-bromopyridine (20 µL, 0.212 mmol). The vial was sealed and heated to 90 °C overnight. The suspension was then filtered through a pad of Celite and the solvent evaporated to dryness. The resulting crude was purified by flash chromatography (2:3 AcOEt:hexanes) to obtain **54** as a yellow oil; 30.3 mg (73% yield). **^{1}H NMR ($CDCl_3$, 300 MHz)** δ = 8.02 - 9.23 (m, 2 H), 7.71 (d, *J* = 7.6 Hz, 1 H), 7.19 - 7.36 (m, 1 H), 5.46 (s, 1 H), 5.32 (s, 1 H), 4.70 (br. s, 1 H), 4.17 (d, *J* = 5.4 Hz, 2 H), 1.42 (s, 9 H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ = 155.7, 149.0, 147.6, 142.5, 134.6 (broad signal), 133.4, 123.4 (broad signal), 114.8, 79.7, 44.1, 28.3 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{13}H_{18}N_2O_2$+H]: 235.1441, found: 235.1453.

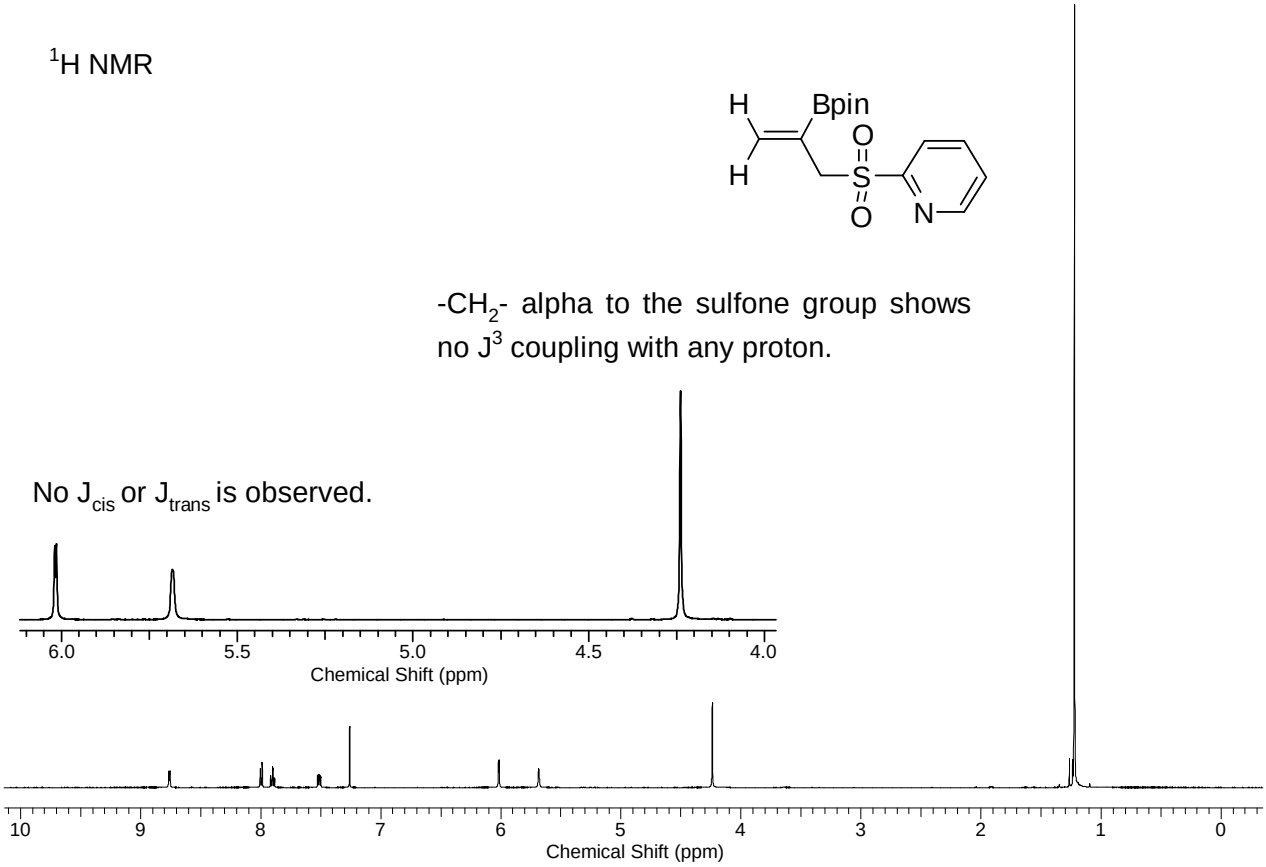
Chan-Evans-Lam coupling of 13.[3] Synthesis of *tert*-butyl (2-(allyloxy)allyl)carbamate (55)



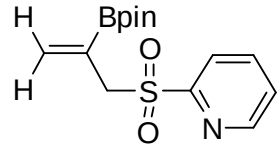
To a solution of **13** (60 mg, 0.212 mmol) in allyl alcohol (1.5 mL, neat) was added triethylamine (118 µL, 0.847 mmol) and $Cu(OAc)_2$ (77 mg, 0.423 mmol) and stirred at room temperature overnight. Then, saturated aqueous $NHCO_3$ (3 mL) was added, the mixture extracted with diethyl ether (2 x 10 mL), and the organic layer dried with $MgSO_4$ and concentrated to dryness. This residue was further purified by flash chromatography (1:9 AcOEt:hexanes) to obtain **55** as a colorless oil; 31.3 mg (69% yield). **^{1}H NMR ($CDCl_3$, 300 MHz)** δ = 5.87 - 6.06 (m, 1 H), 5.32 (dd, *J* = 17.3, 1.5 Hz, 1 H), 5.23 (dd, *J* = 10.5, 1.2 Hz, 1 H), 4.77 (br. s, 1 H), 4.24 (d, *J* = 5.4 Hz, 2 H), 4.06 – 4.13 (m, 1 H), 3.97 (d, *J* = 2.4 Hz, 1 H), 3.74 (d, *J* = 5.6 Hz, 2 H), 1.45 ppm (s, 9 H). **^{13}C NMR (CDCl3, 75 MHz)** δ = 159.0, 155.7, 133.0, 117.4, 82.4, 79.5, 68.4, 43.7, 28.4 ppm. **HRMS-ESI (m/z):** Calculated for [$C_{19}H_{19}NO_3$+Na]: 236.1257, found: 236.1256.

10. Stereochemical determination of compounds 10 and 48

Compound 10

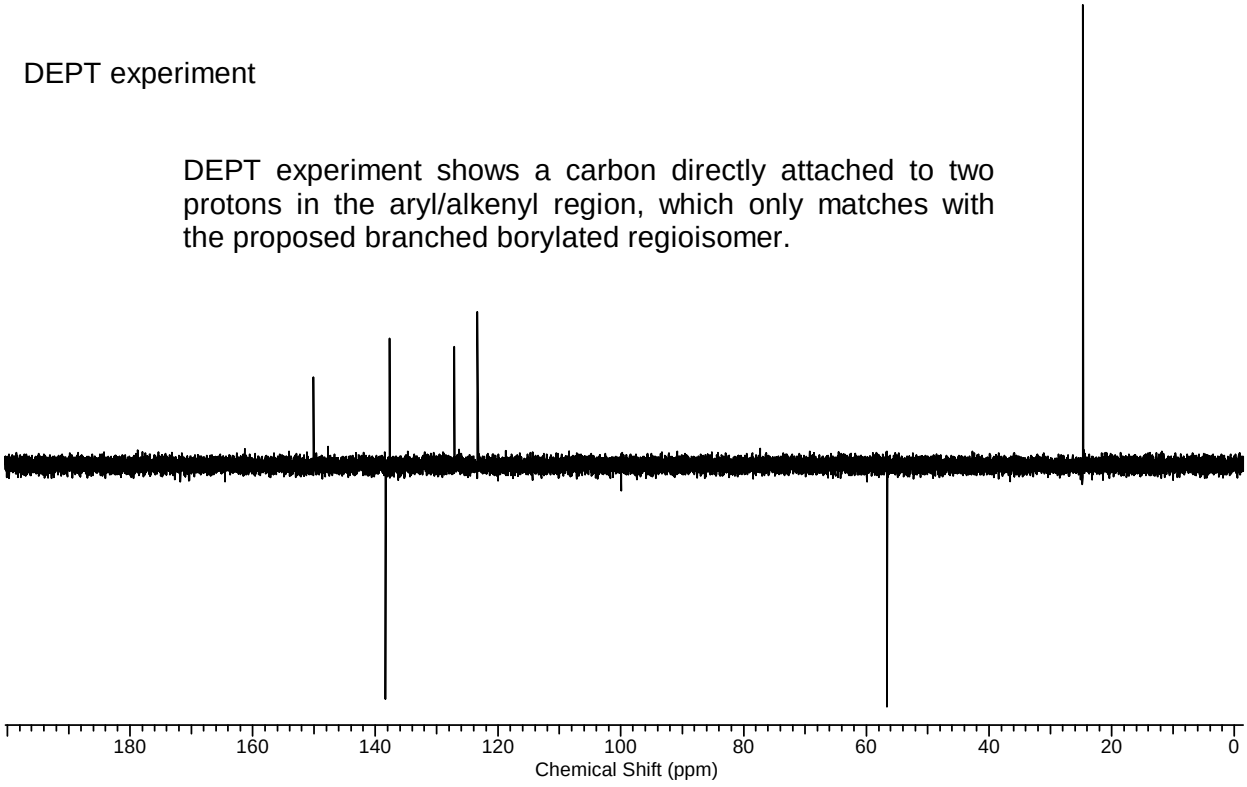


^{1}H-Decoupled ^{13}C NMR



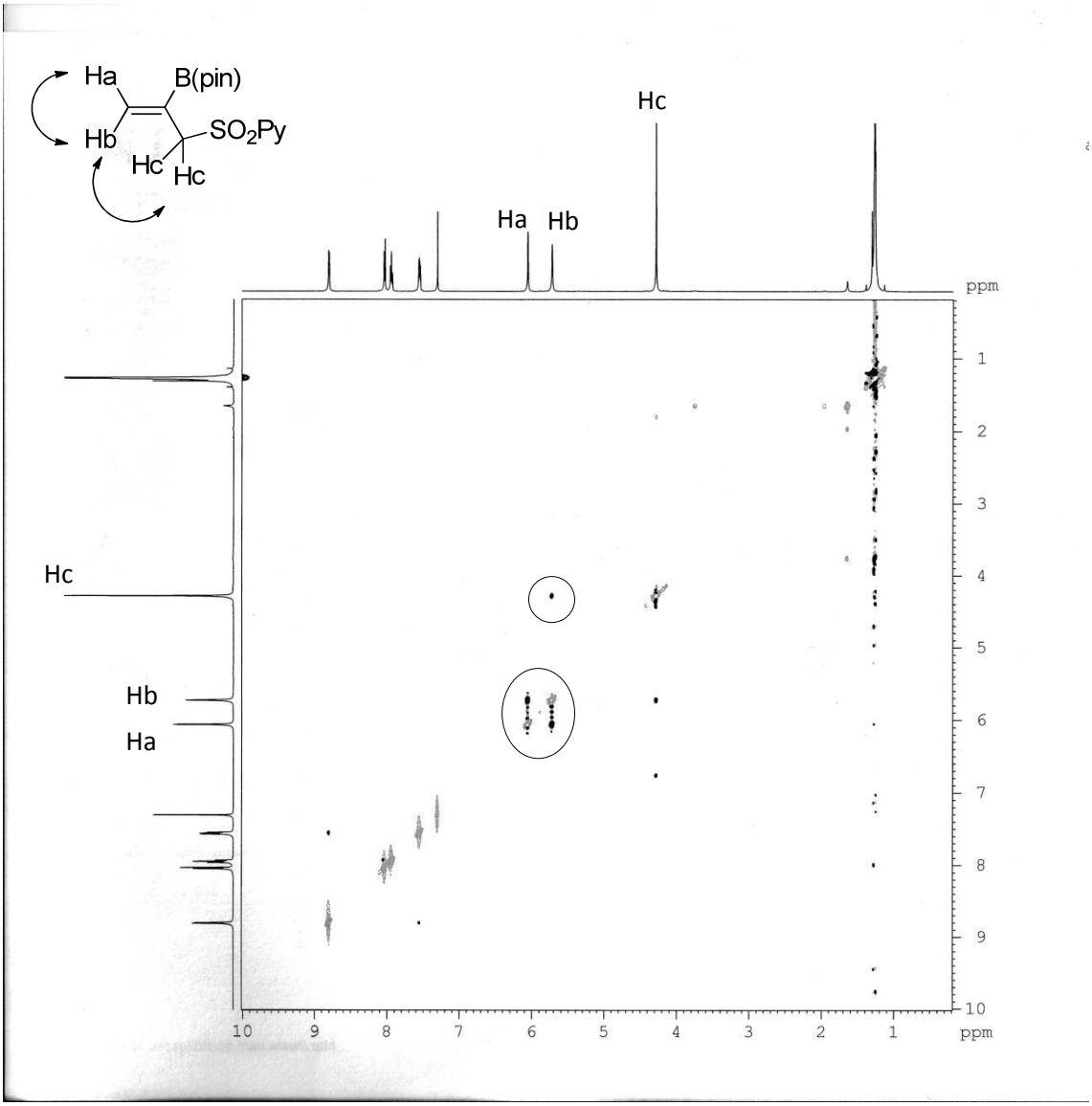
DEPT experiment

DEPT experiment shows a carbon directly attached to two protons in the aryl/alkenyl region, which only matches with the proposed branched borylated regioisomer.



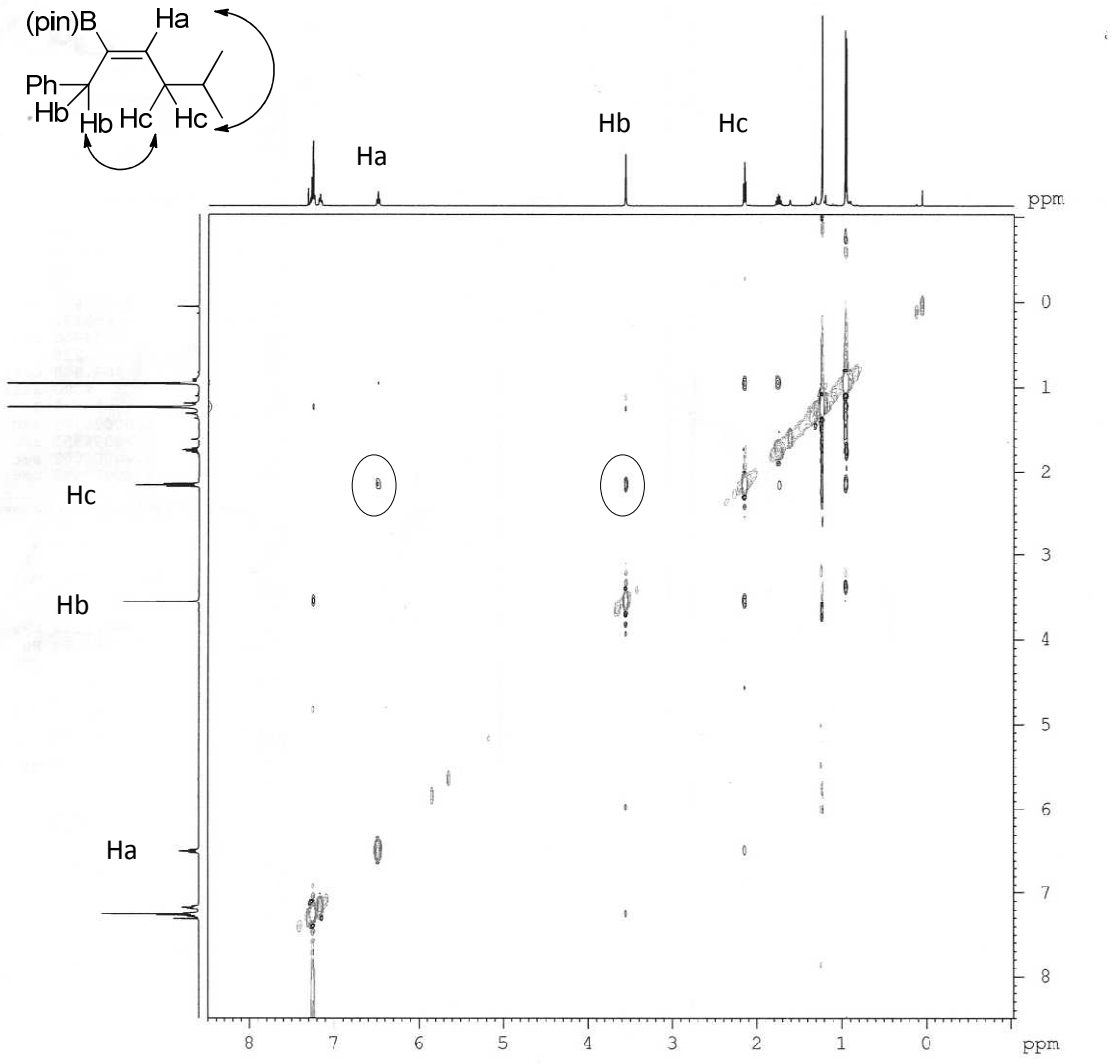
^{1}H-NOESY:

A ^{1}H-NOESY experiment was carried out in order to establish which one of the hydrogen in the alkenyl region is positioned *cis* to the boronate group and which one *trans*.



Compound 48

A ^{1}H NOESY experiment was carried out in order to determine the stereochemistry of the new double bond formed in the allylic substitution reaction. The nOe effect between Hb and Hc strongly supports the proposed *Z* stereochemistry for the double bond.



11. References:

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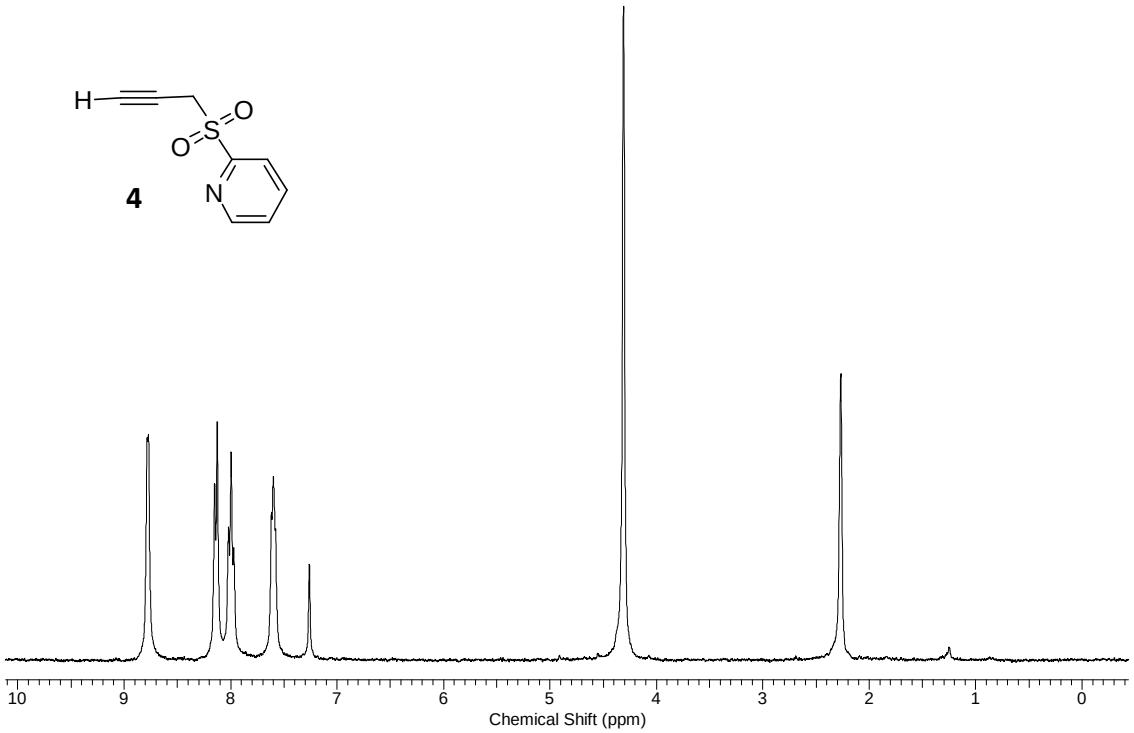
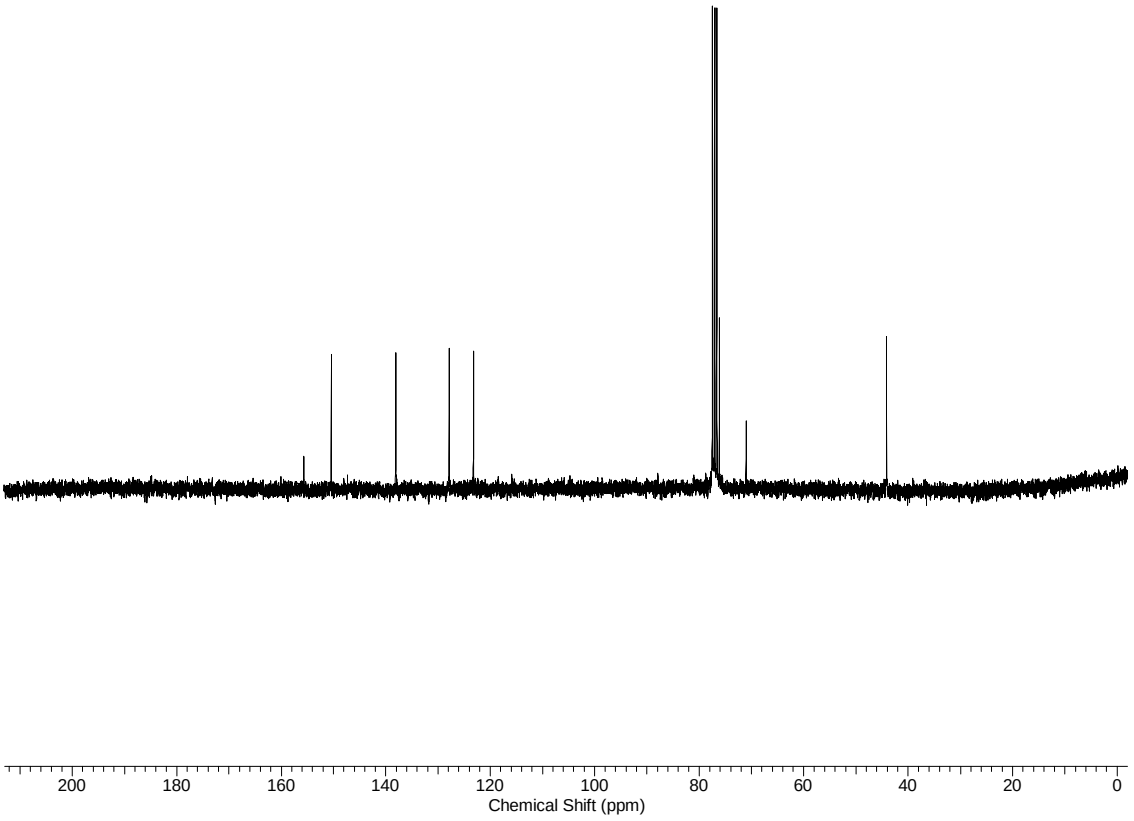
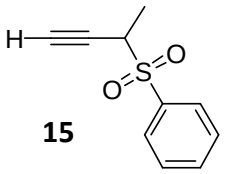
12. ^{1}H NMR and ^{13}C NMR spectra collection

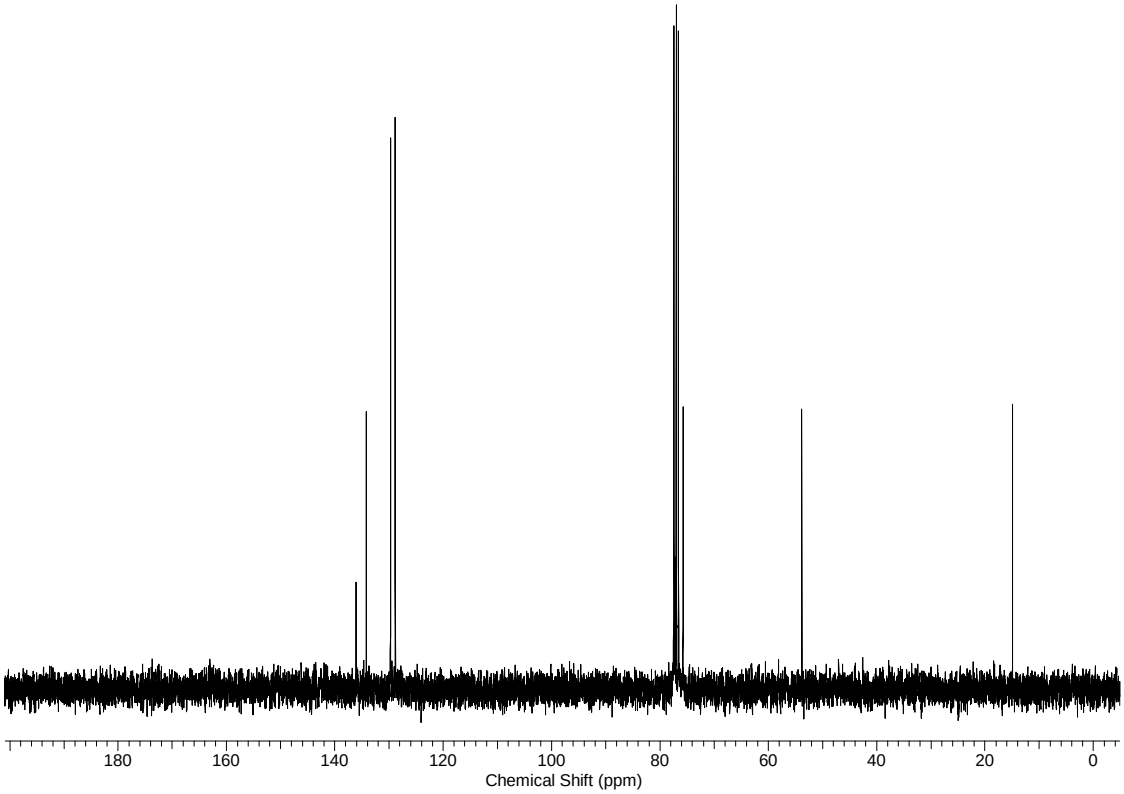


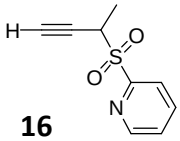



H
O
S
O

15

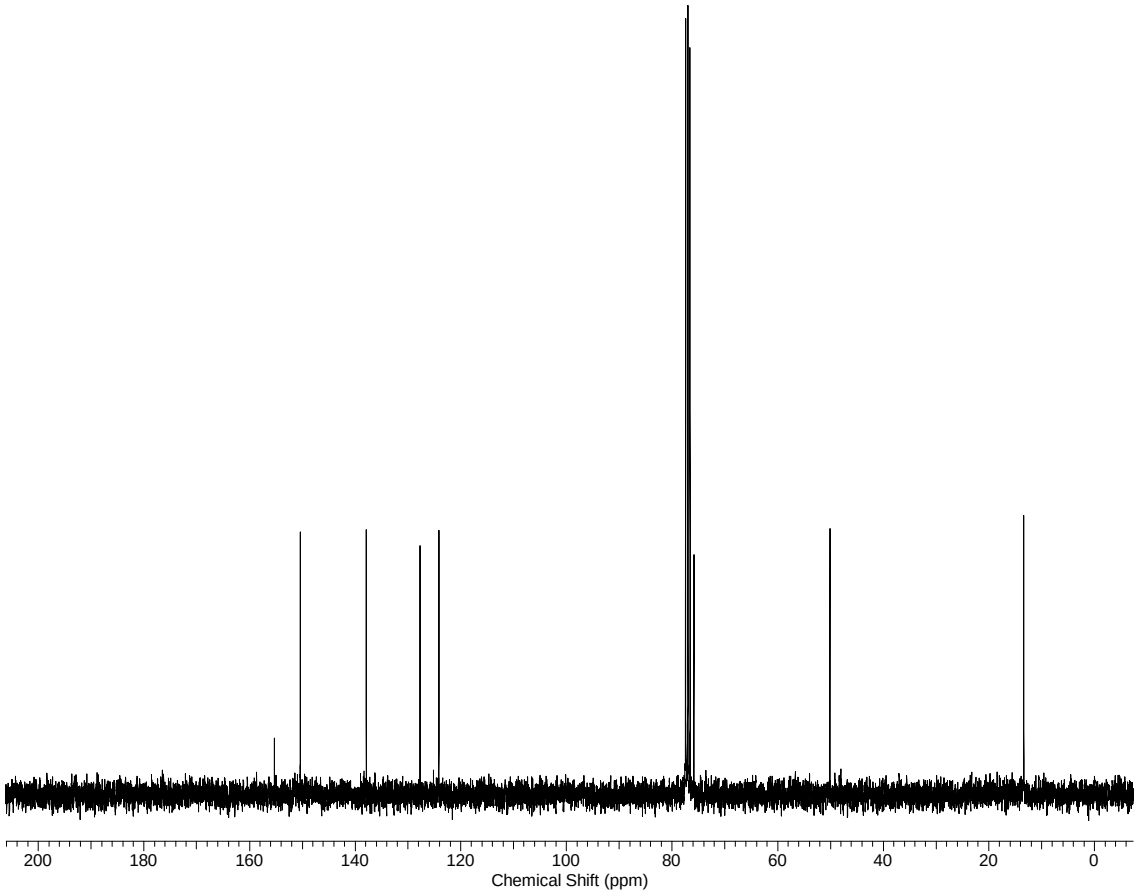
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

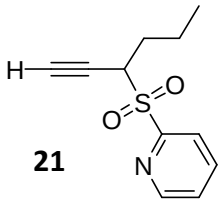

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
O
S
O
N

16

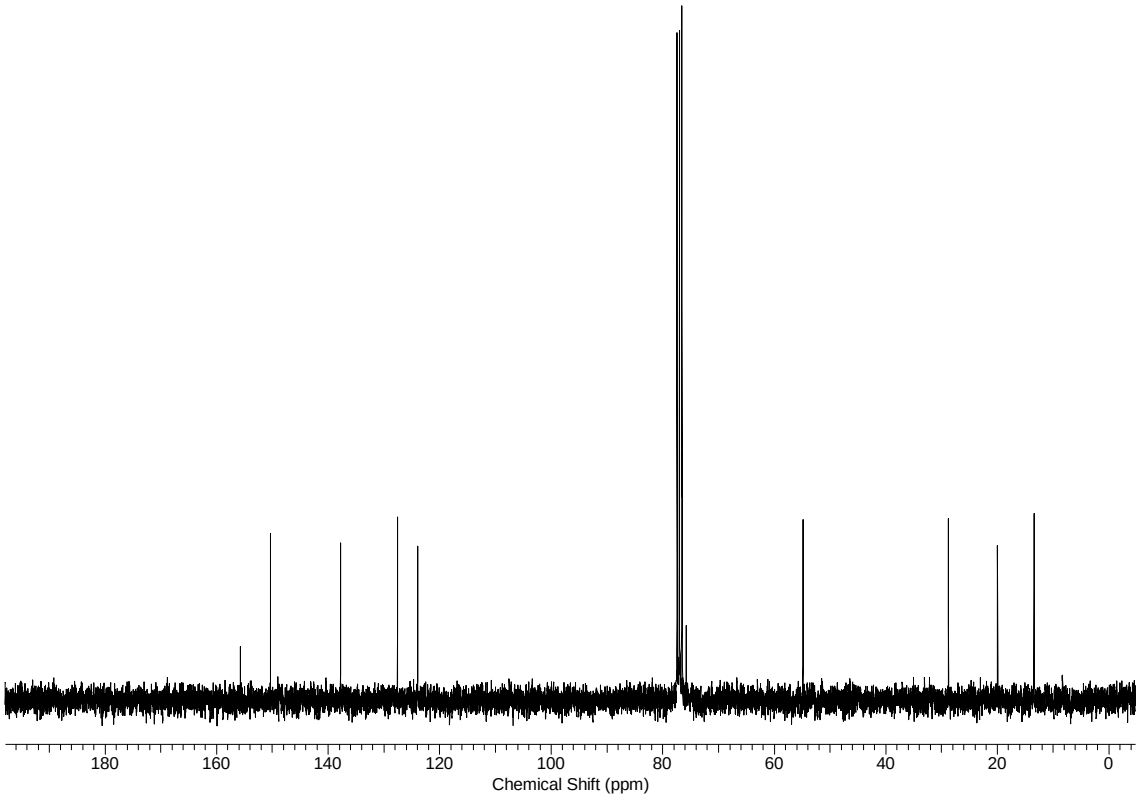
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

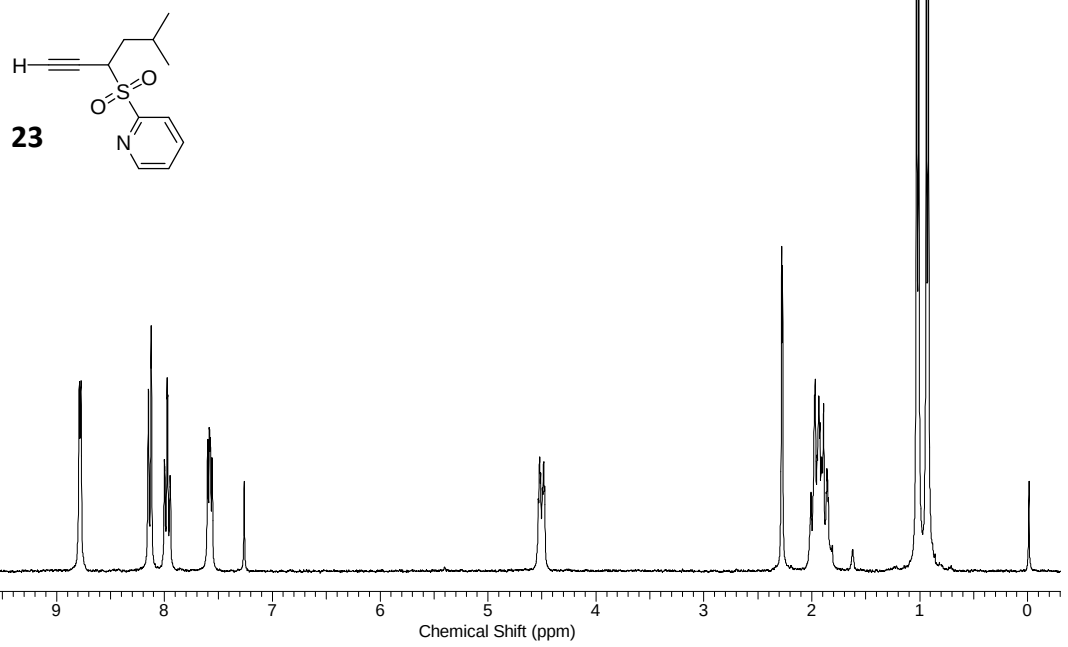

200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

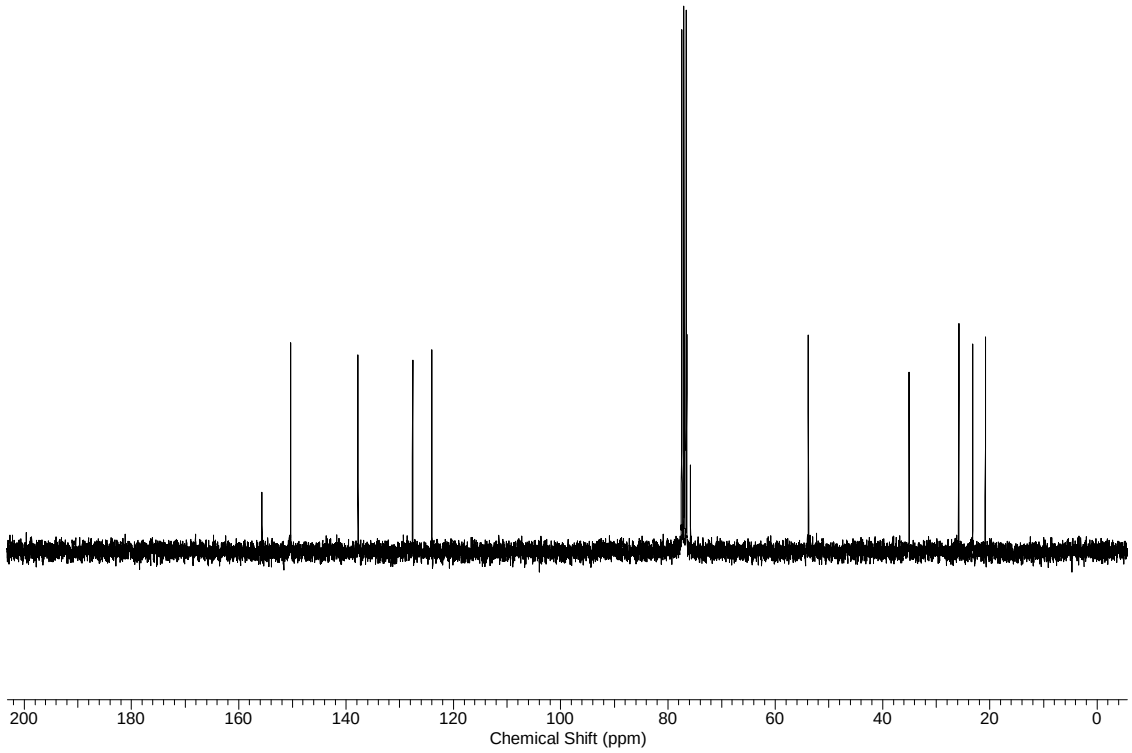

H
O
S
O
N

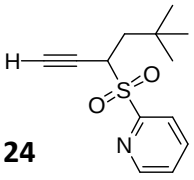
21

9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

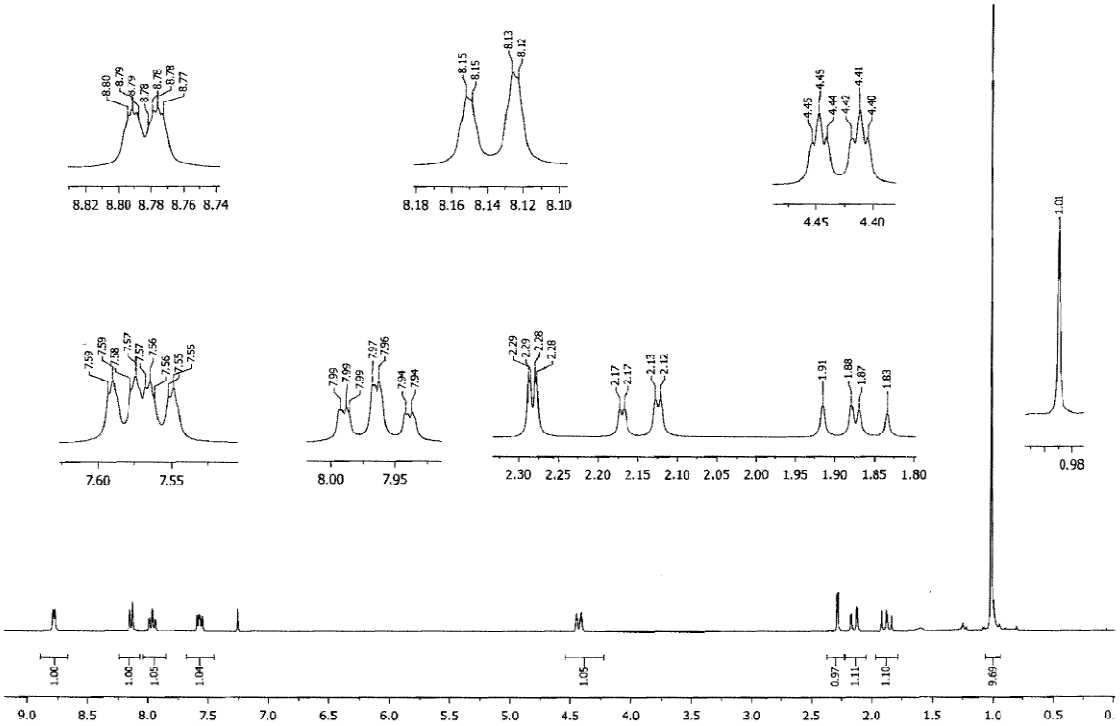

H
O
O
S
N
23
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

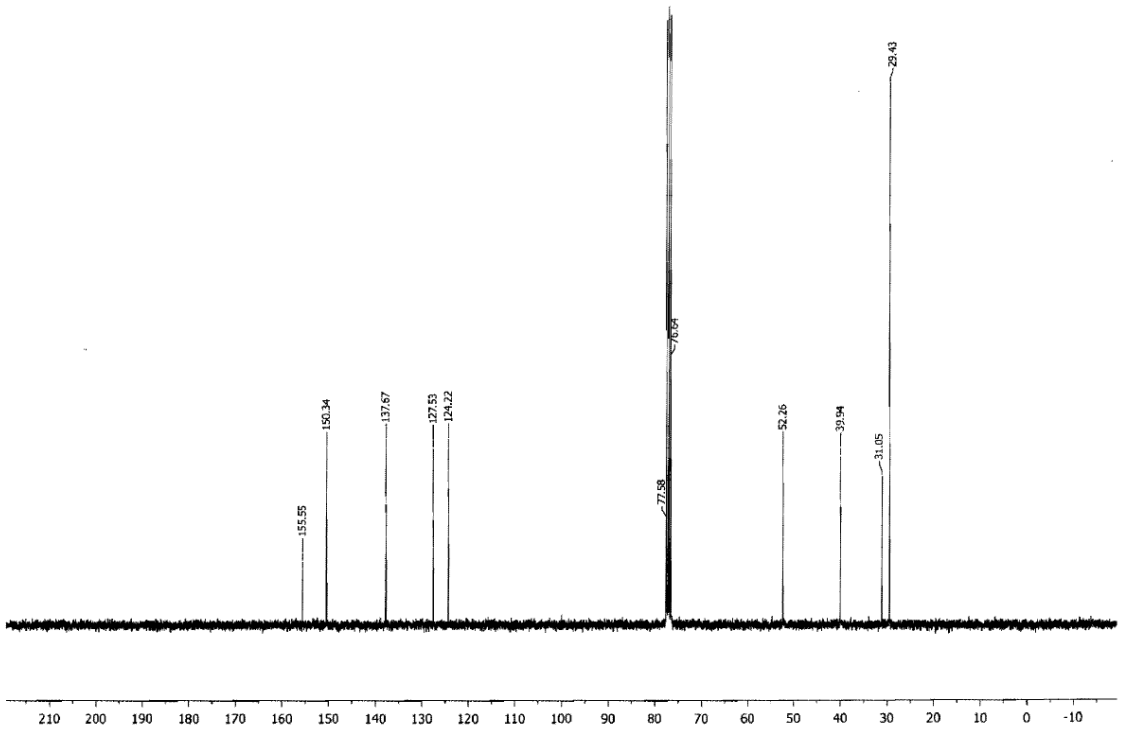


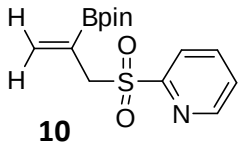
24

pablo.0710201201
PROTON_15^PM CDCl3 D:\\ QOL408 1



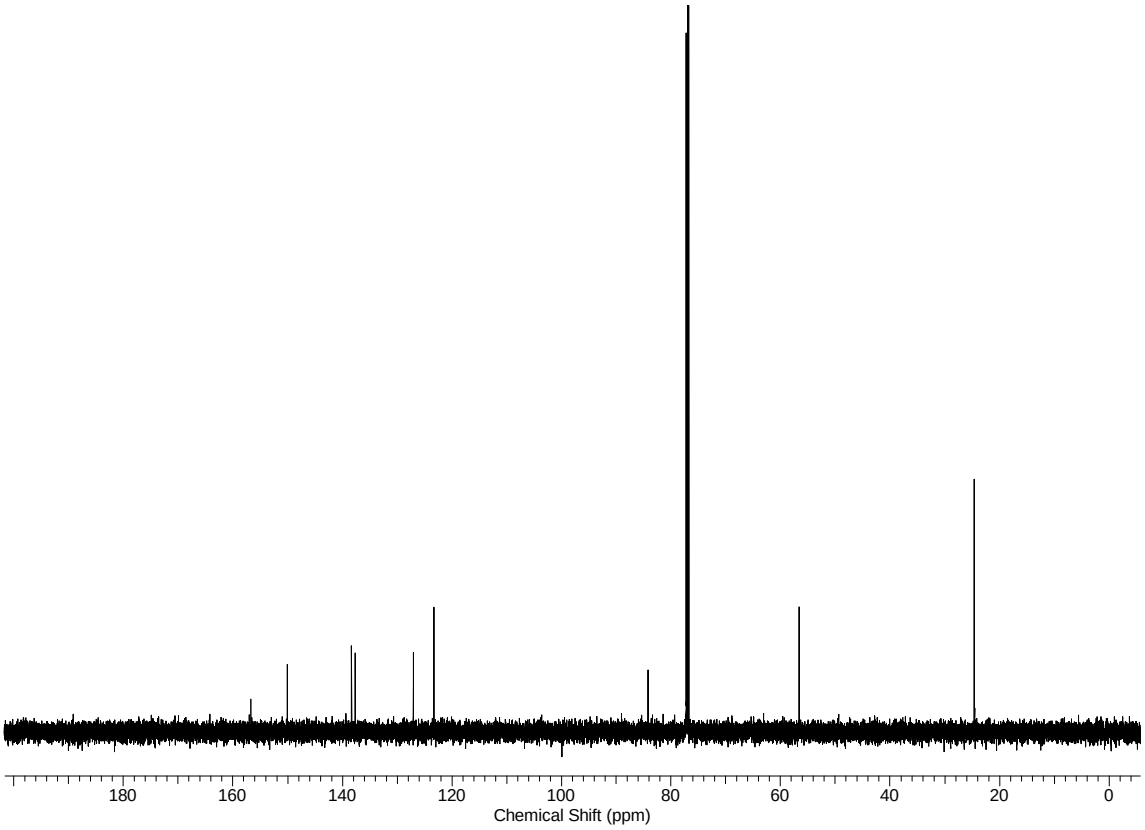
pablo.0710201201
C13_desacoplado CDCl3 D:\\ QOL408 1

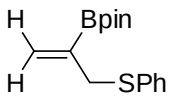



H
Bpin
H
O
S
O
N

10

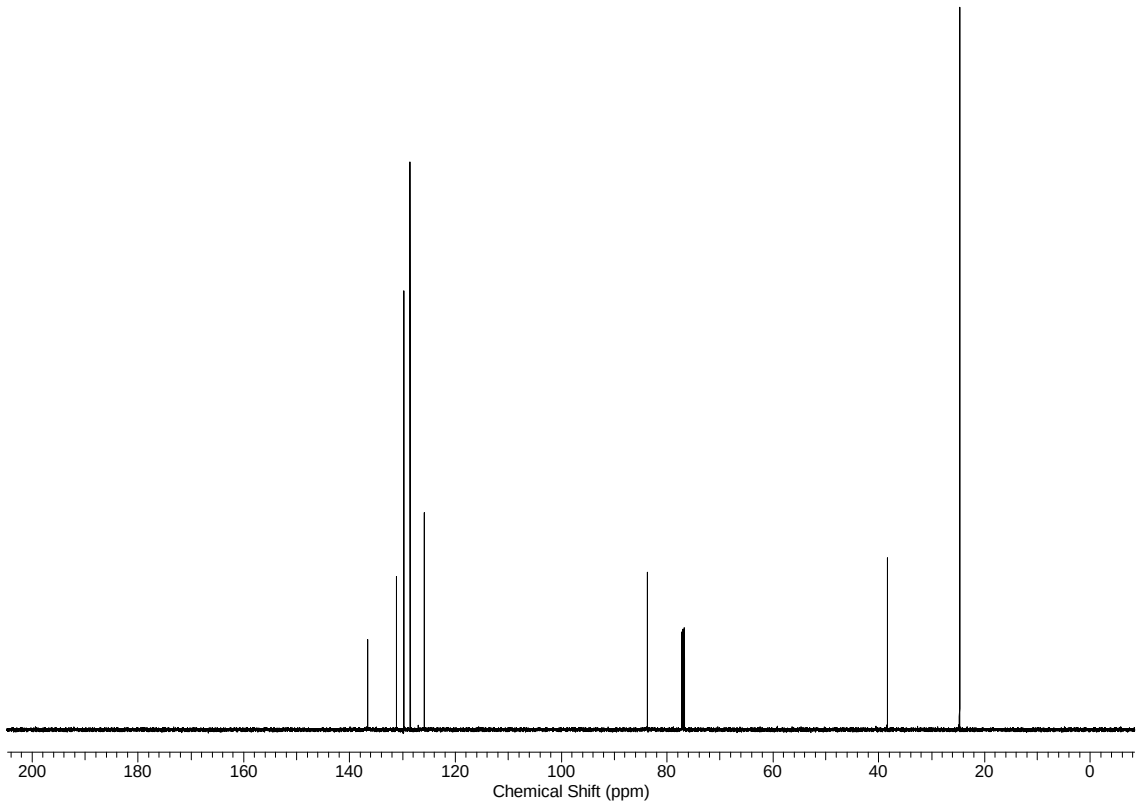
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

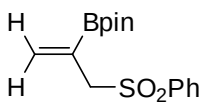

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
Bpin
H
SPh

2

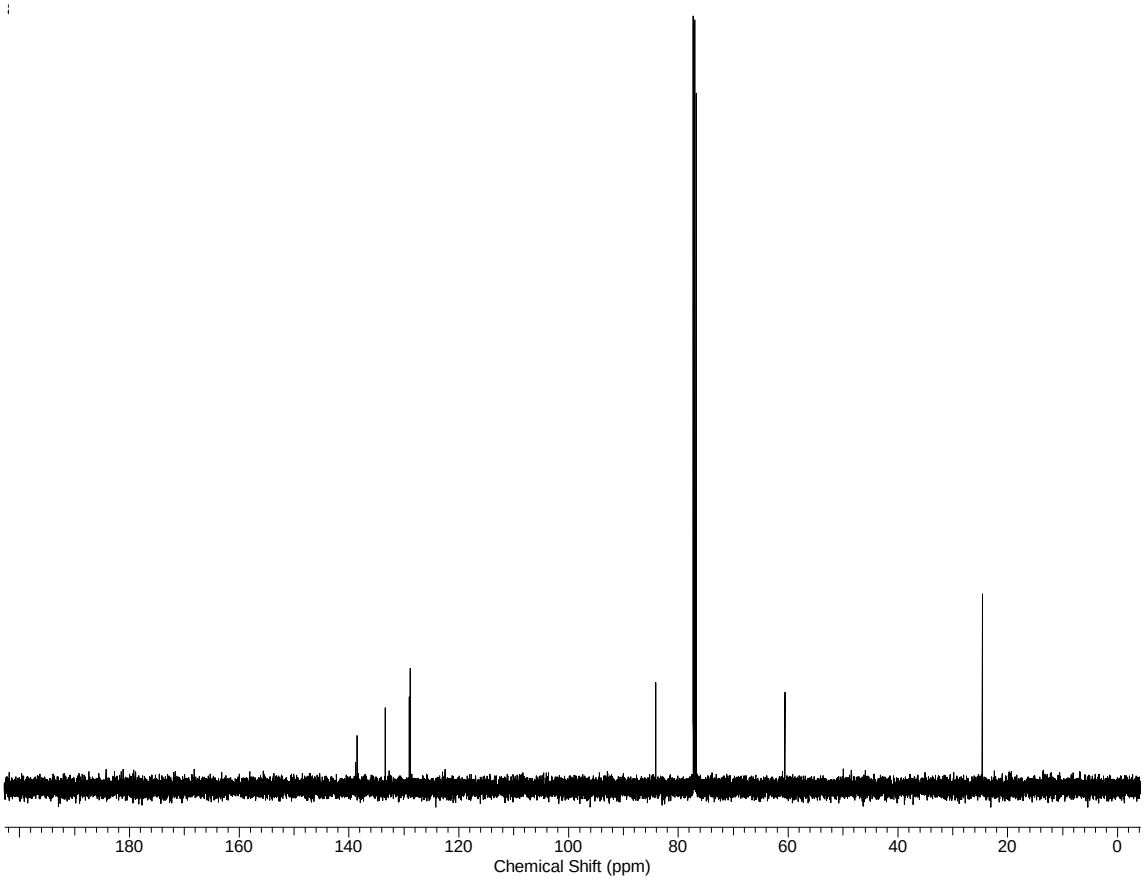
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

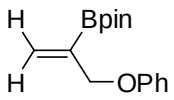

200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
Bpin
H
SO2Ph

9

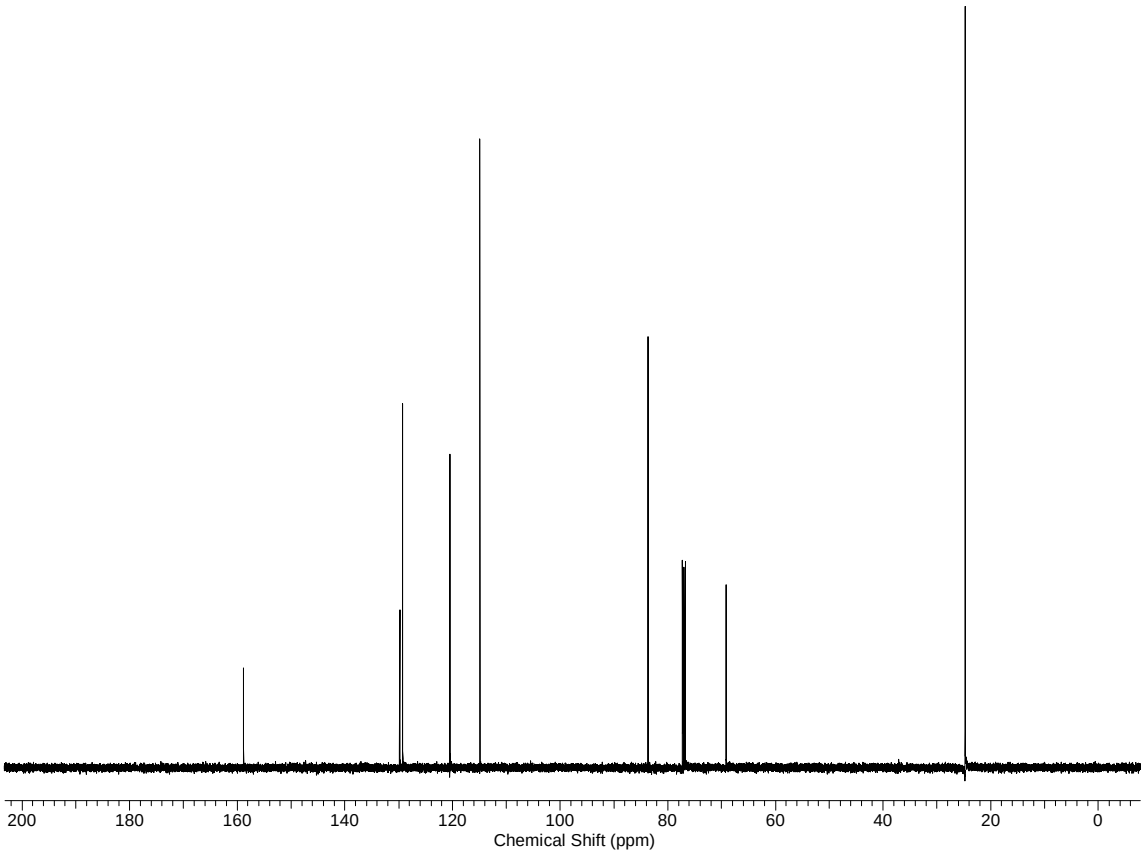
10
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

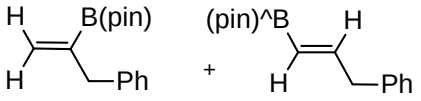

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
Bpin
H
OPh

E

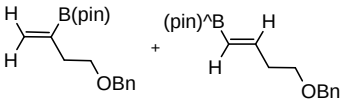
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
B(pin)
H
Ph
+
(pin)^B
H
H
Ph

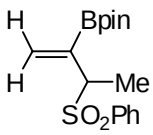
14

7.66
0.47
1.00
0.98
0.50
3.09
6.71
12.36
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


H
B(pin)
H
OBn
+
(pin)^B
H
H
OBn

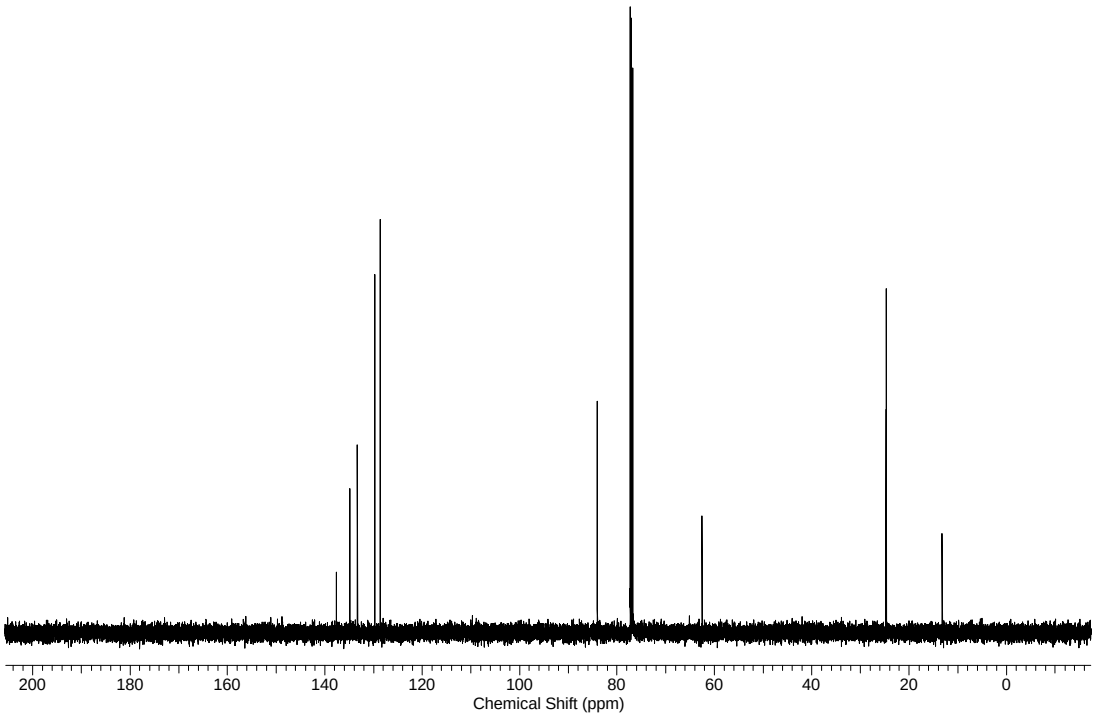
F

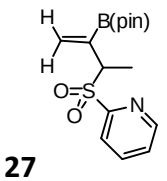
8.78
0.70
1.02
1.00
0.71
3.68
3.76
3.63
9.24
12.29
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


H
Bpin
H
Me
SO2Ph

26

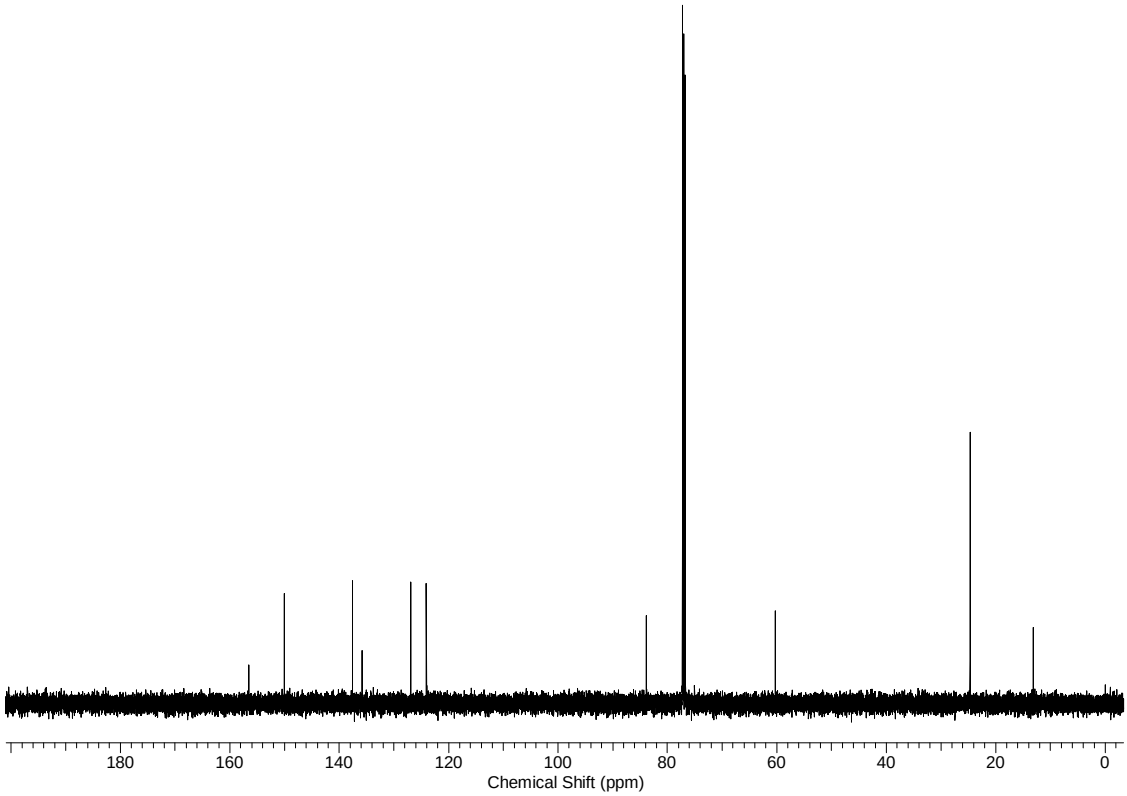
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

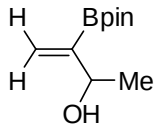

200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
B(pin)
H
O
S
O
N

27

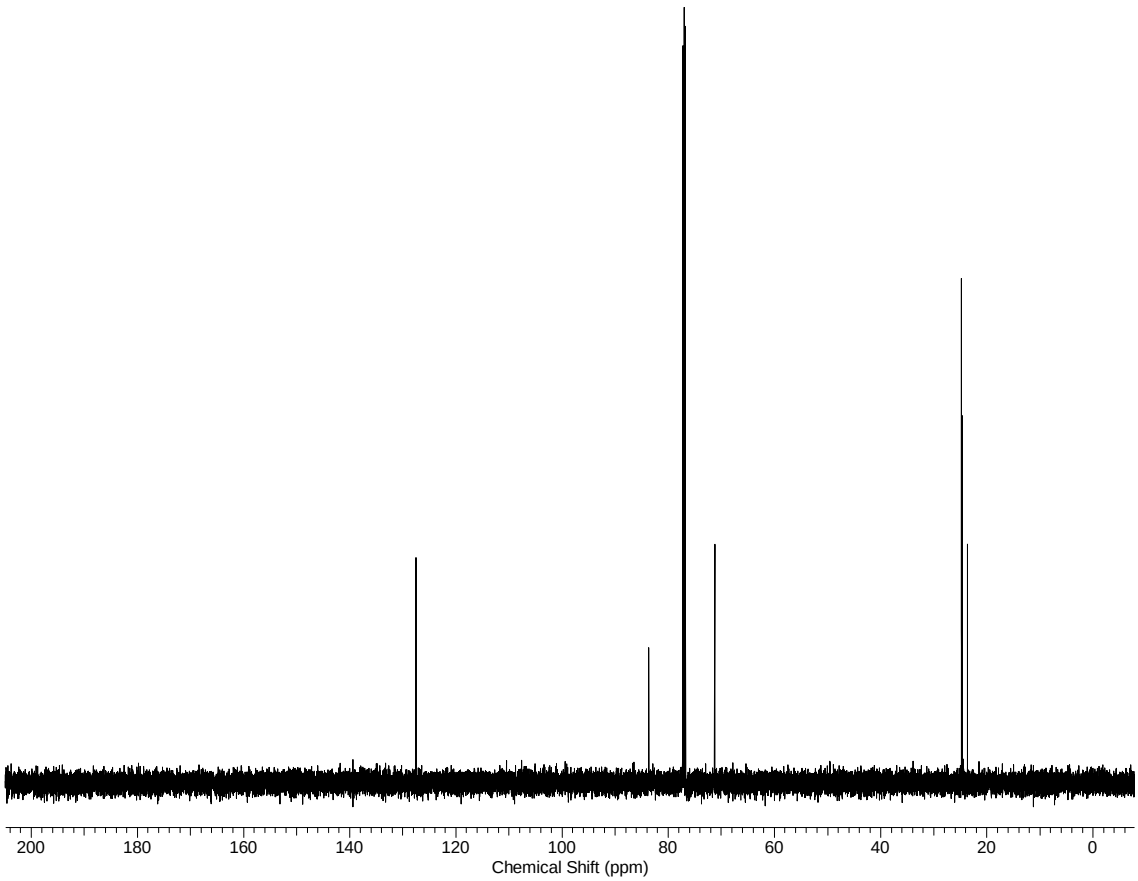
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

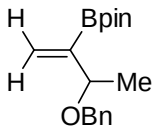

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
Bpin
H
Me
OH

28

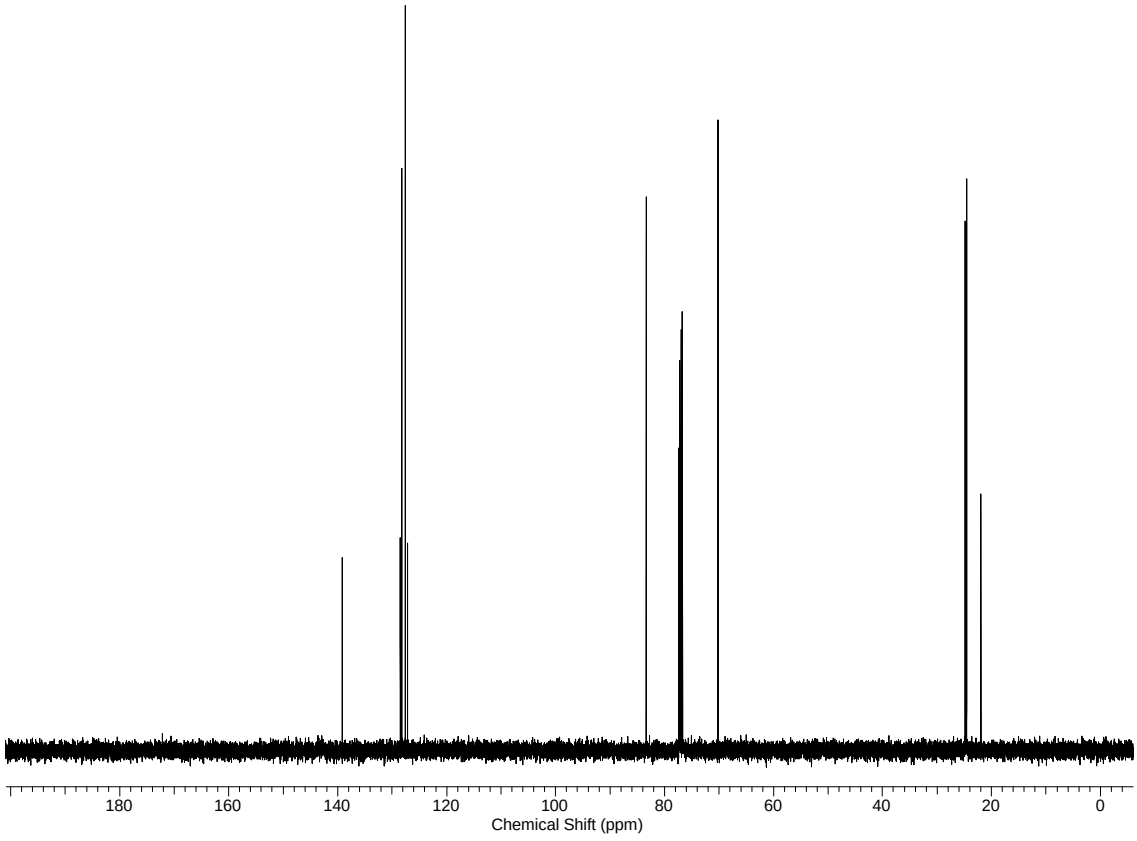
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

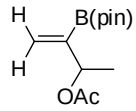

200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
Bpin
H
Me
OBn

29

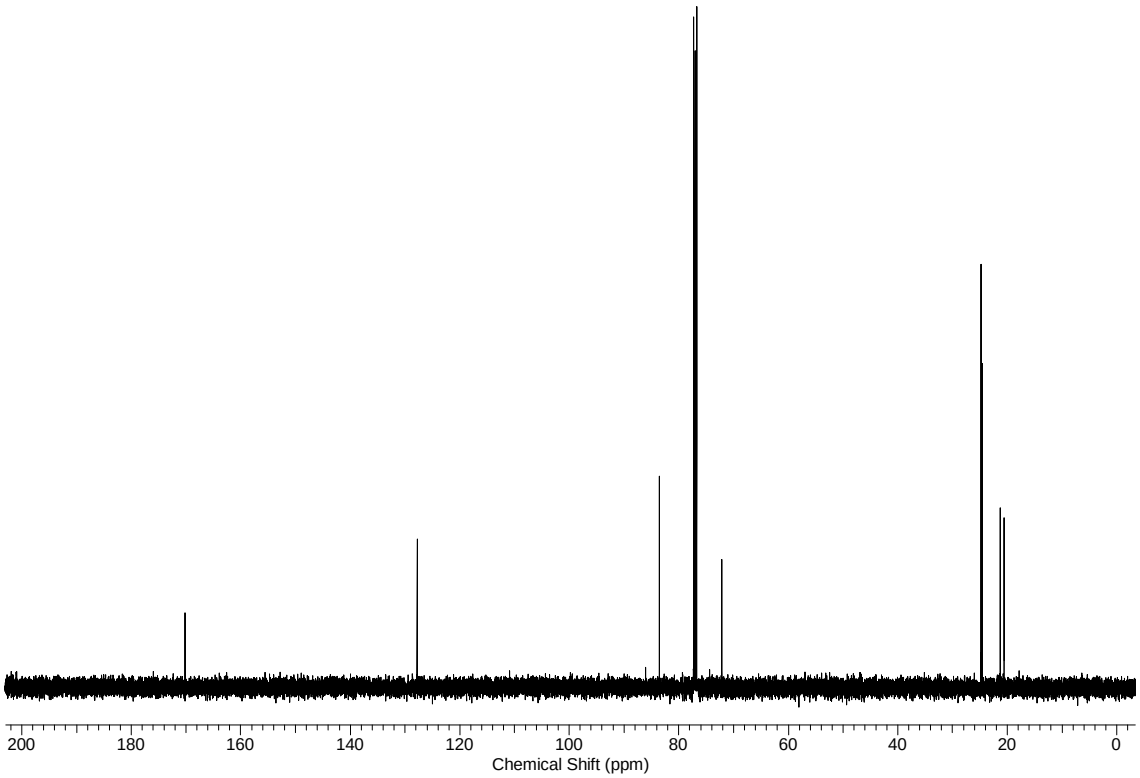
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

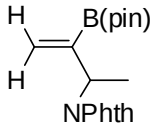

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
B(pin)
H
OAc

30

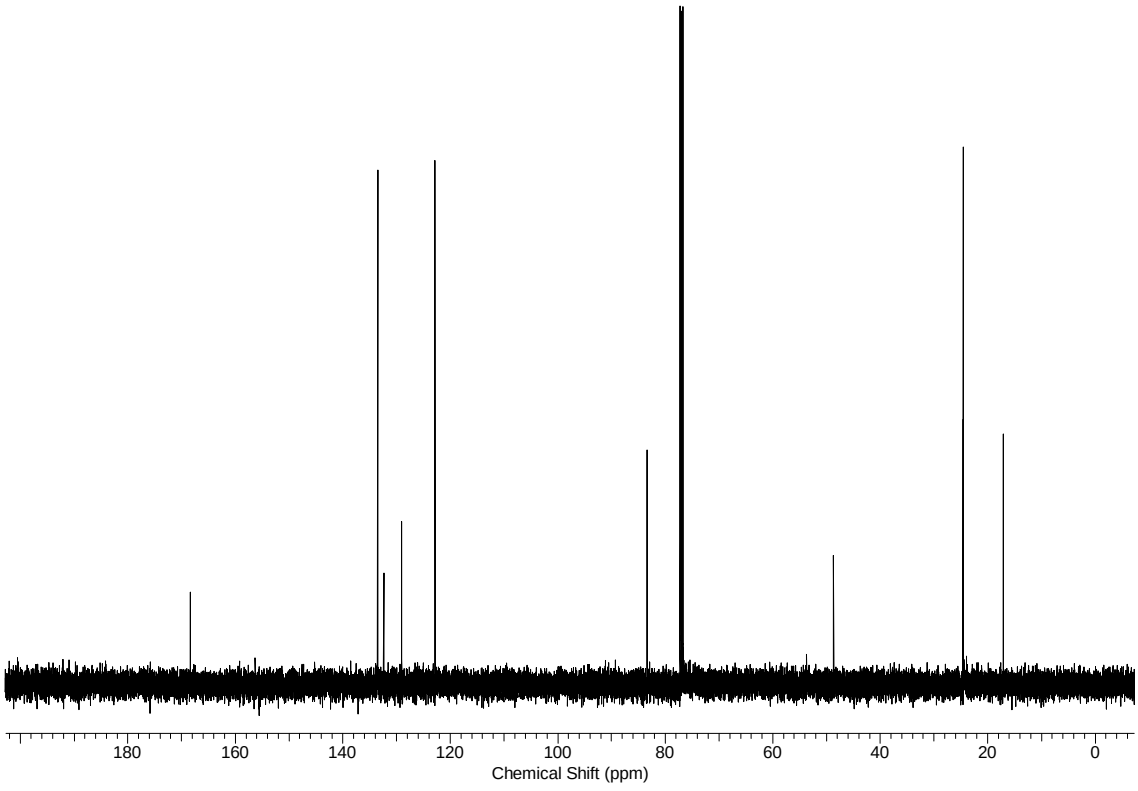
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

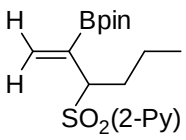

200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
B(pin)
H
NPhth

31

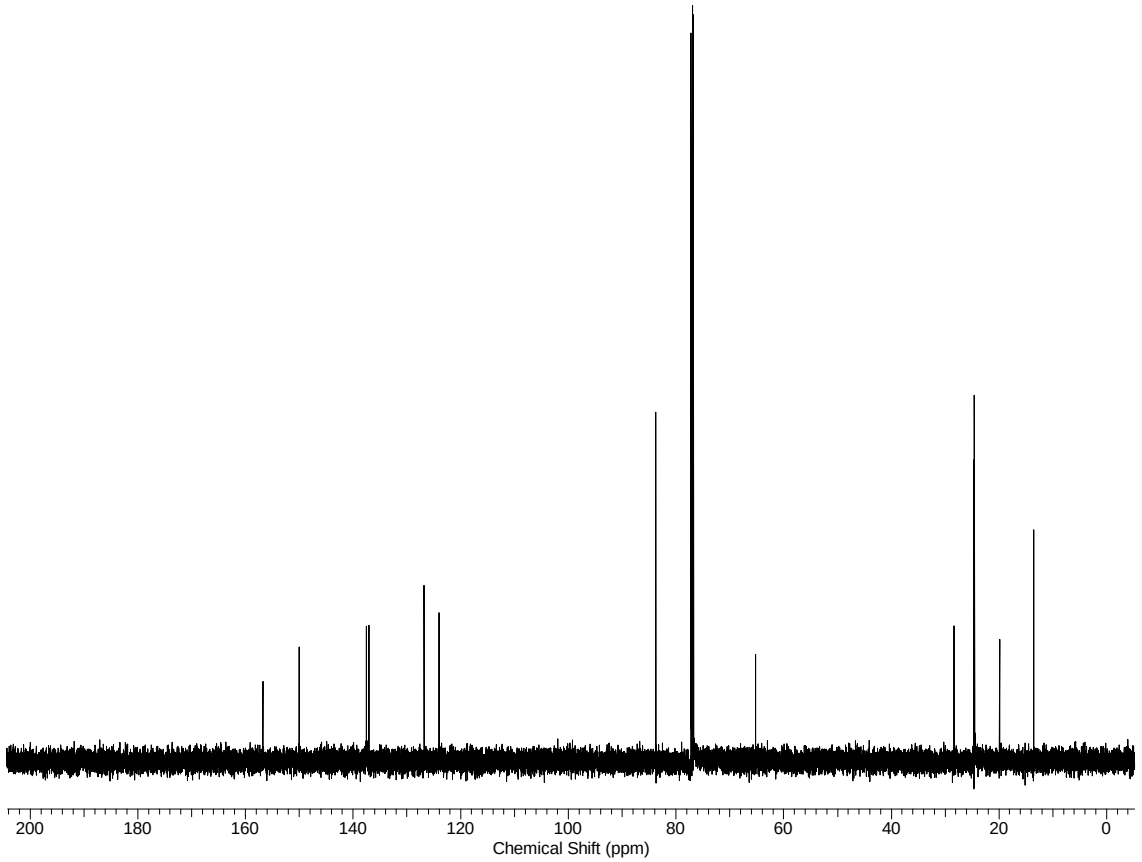
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

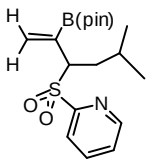

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
Bpin
H
SO2(2-Py)

32

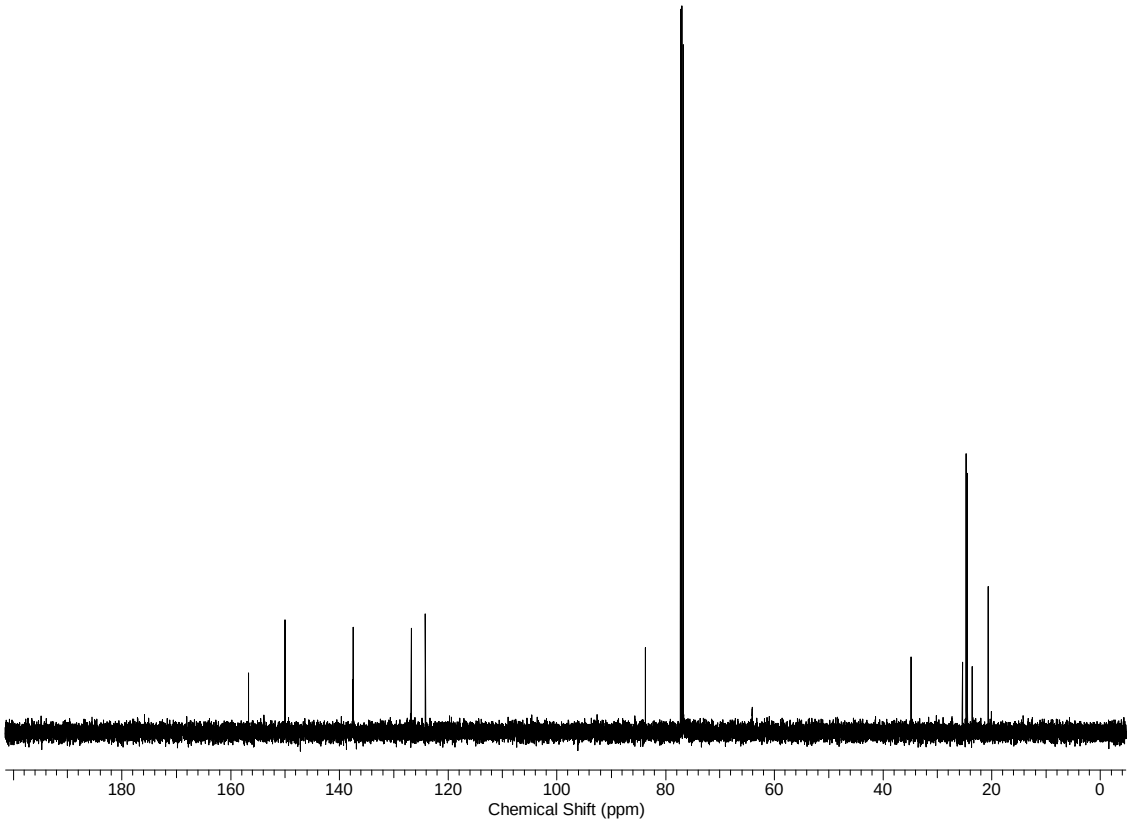
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

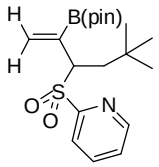

200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
B(pin)
H
S
O
O
N

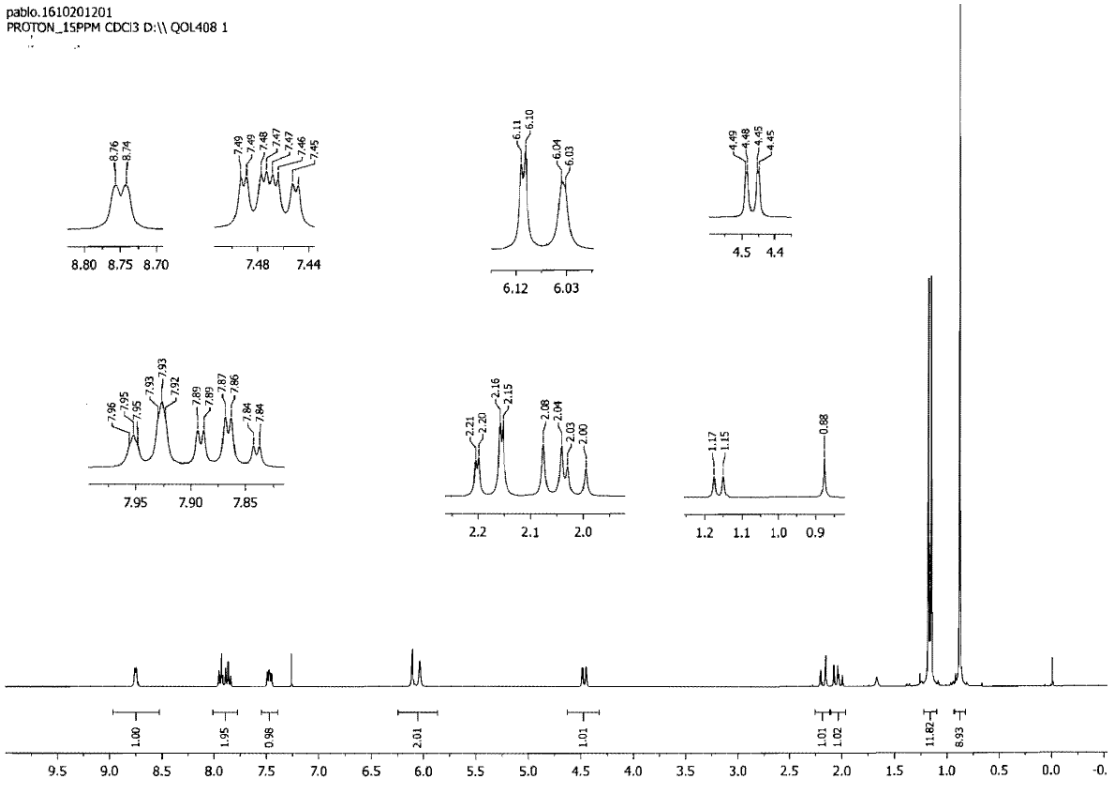
34

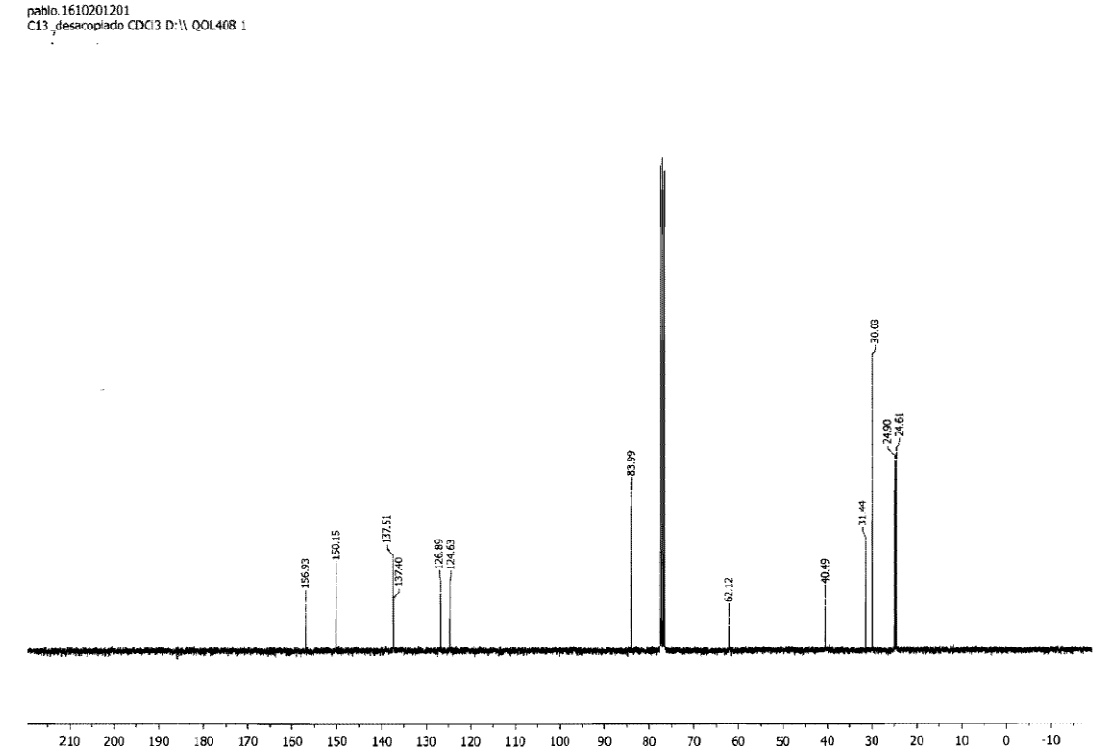
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

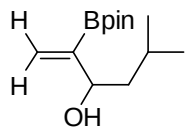

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
B(pin)
H
S
O
O
N

35

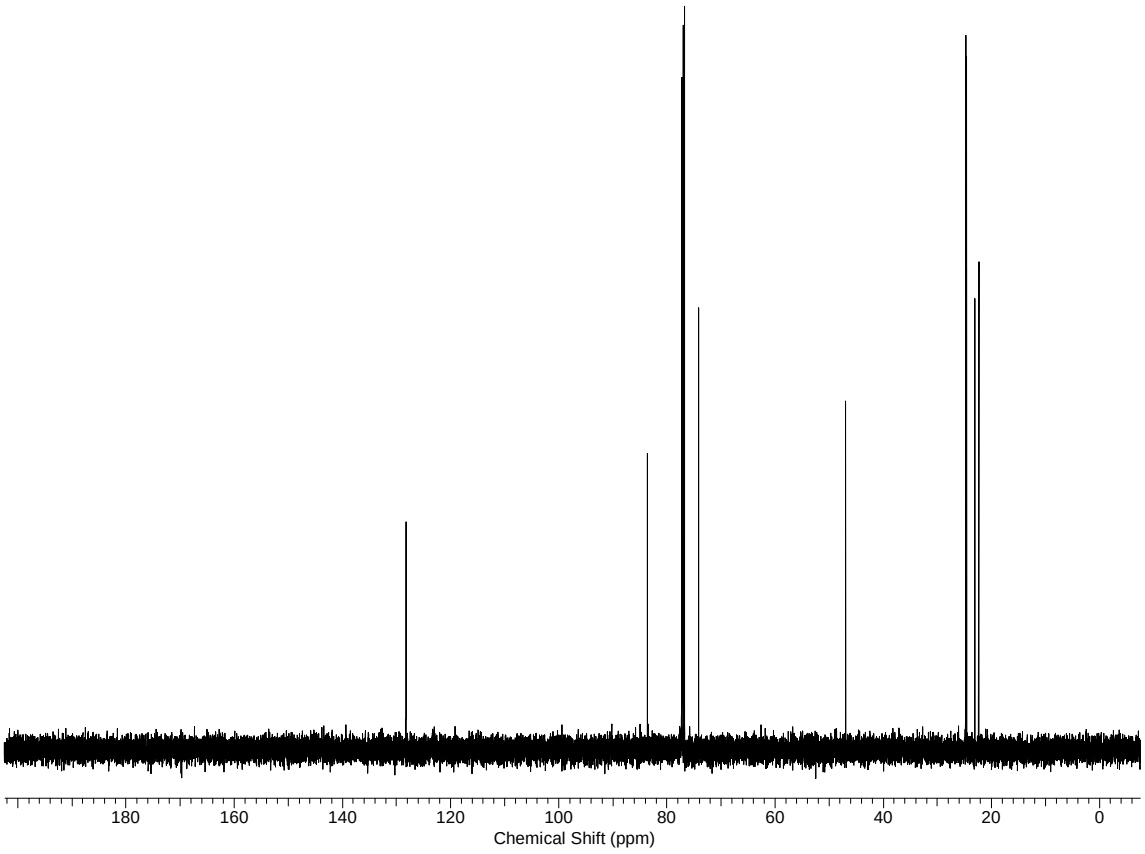

pablo.1610201201
PROTON_15PPM CDCl3 D:\\ QOL408 1

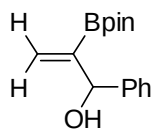

pablo.1610201201
C13_desacoplado CDCl3 D:\\ QOL408 1


H
Bpin
H
OH

33

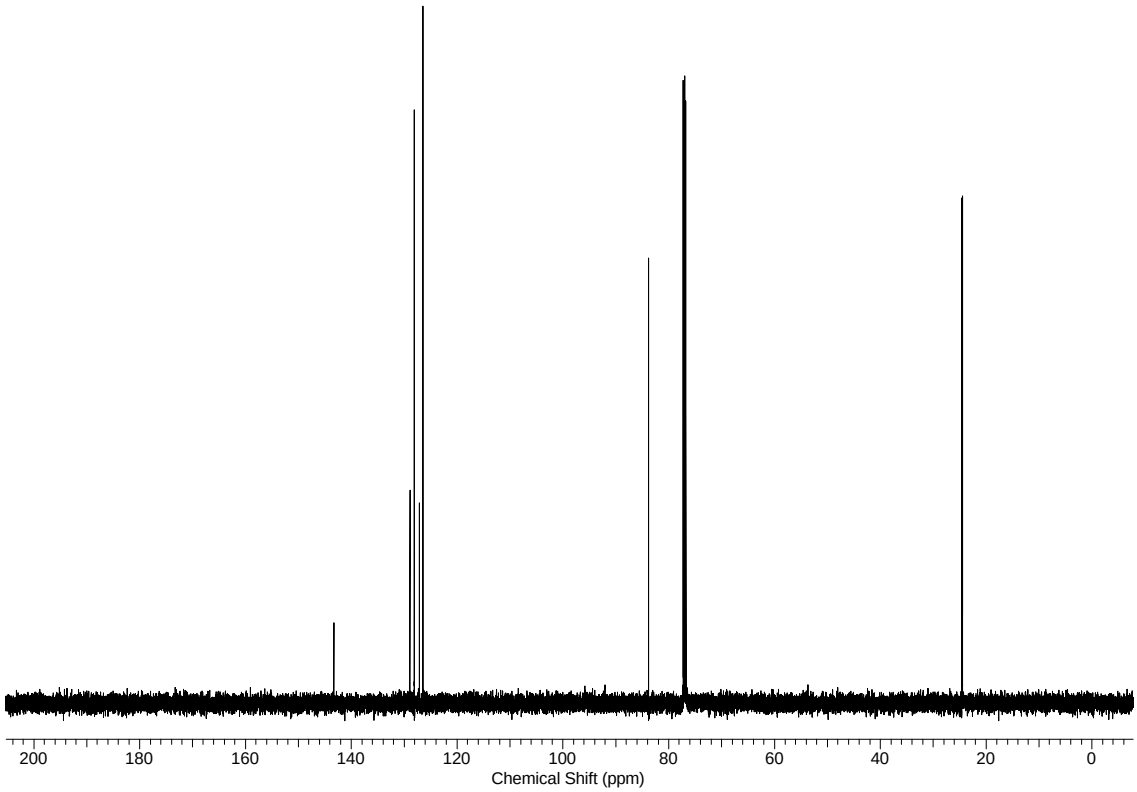
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

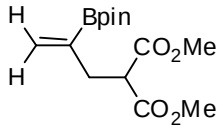

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
Bpin
H
Ph
OH

36

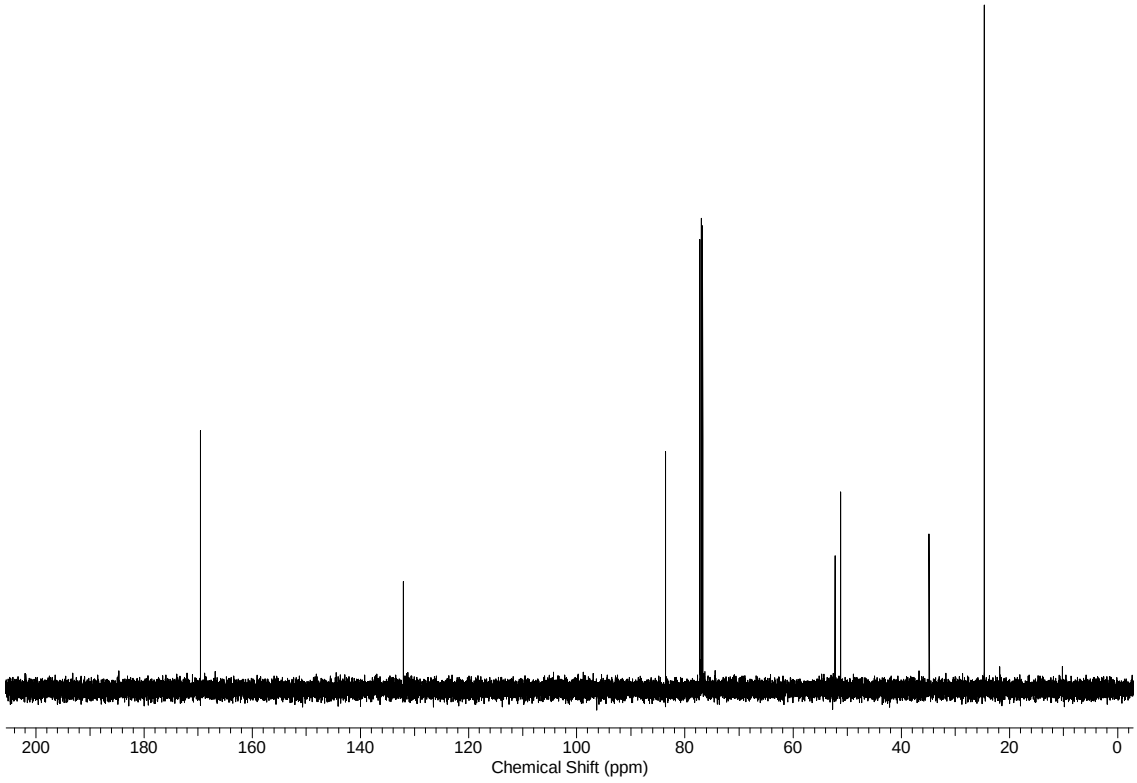
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

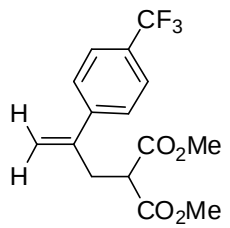

200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
Bpin
CO2Me
H
CO2Me

52

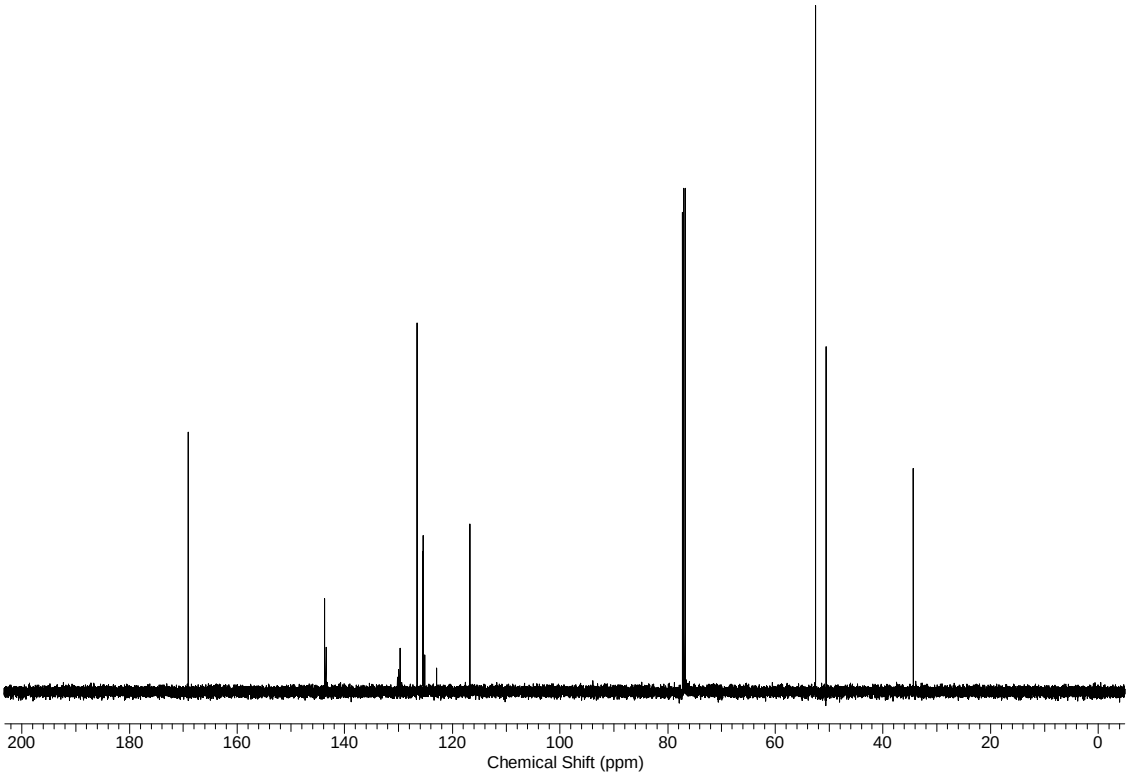
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


CF3
H
H
CO2Me
CO2Me

53

10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


200
180
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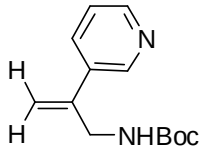
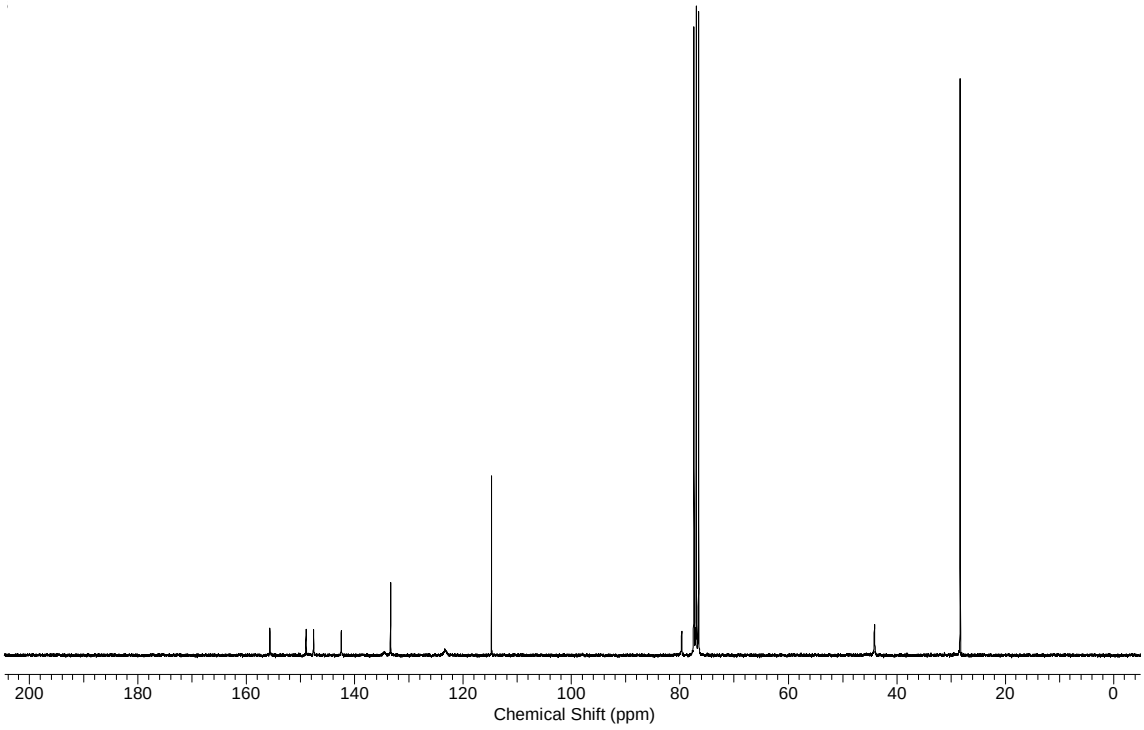
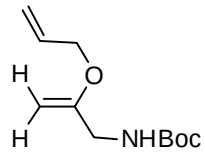
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


N
H
H
NHBoc

54

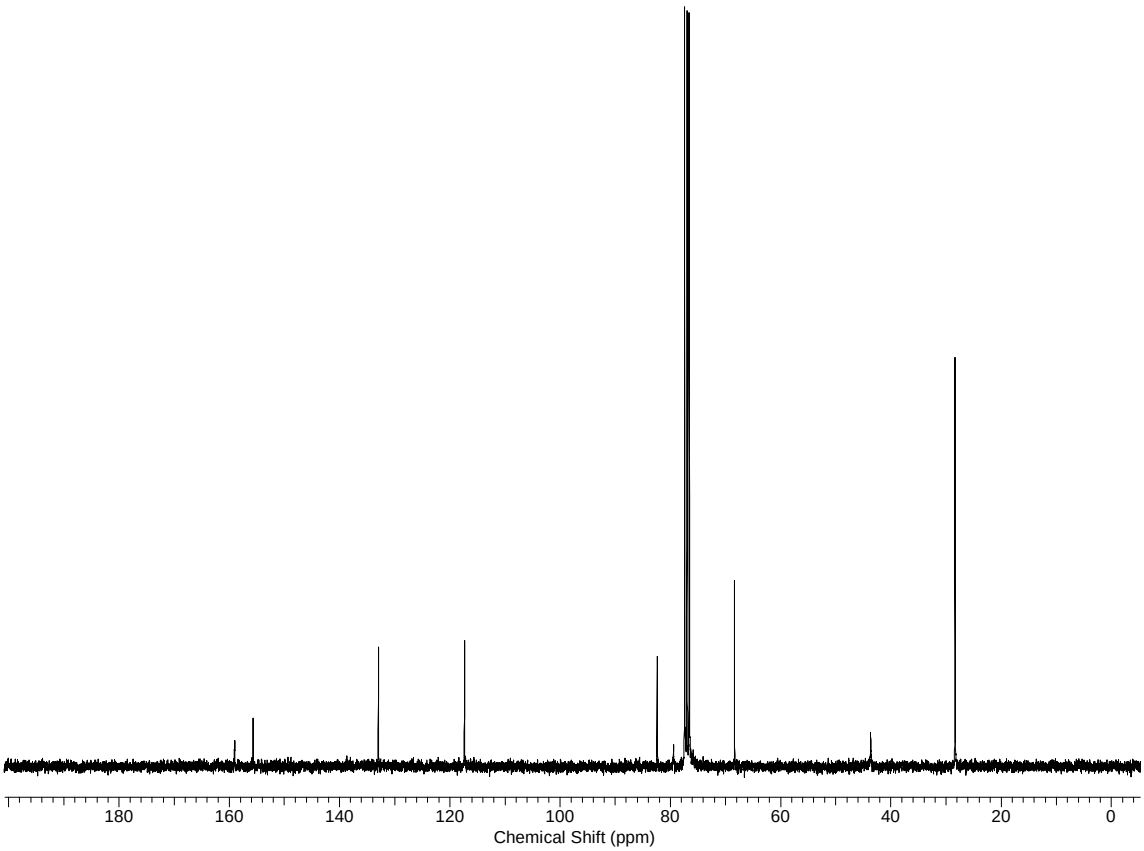
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

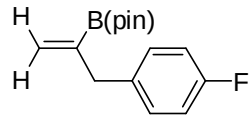

200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
O
H
NHBoc

55

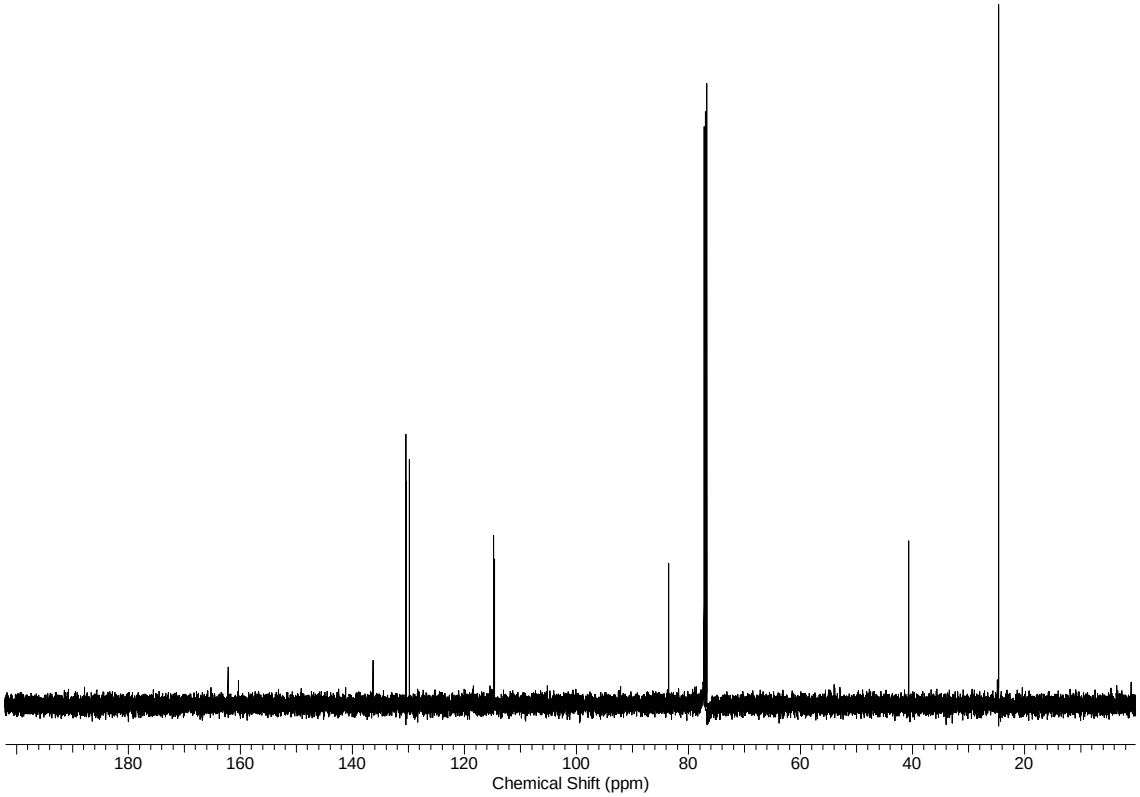
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

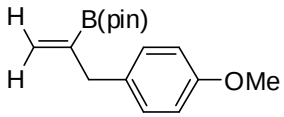

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
B(pin)
H
F

38

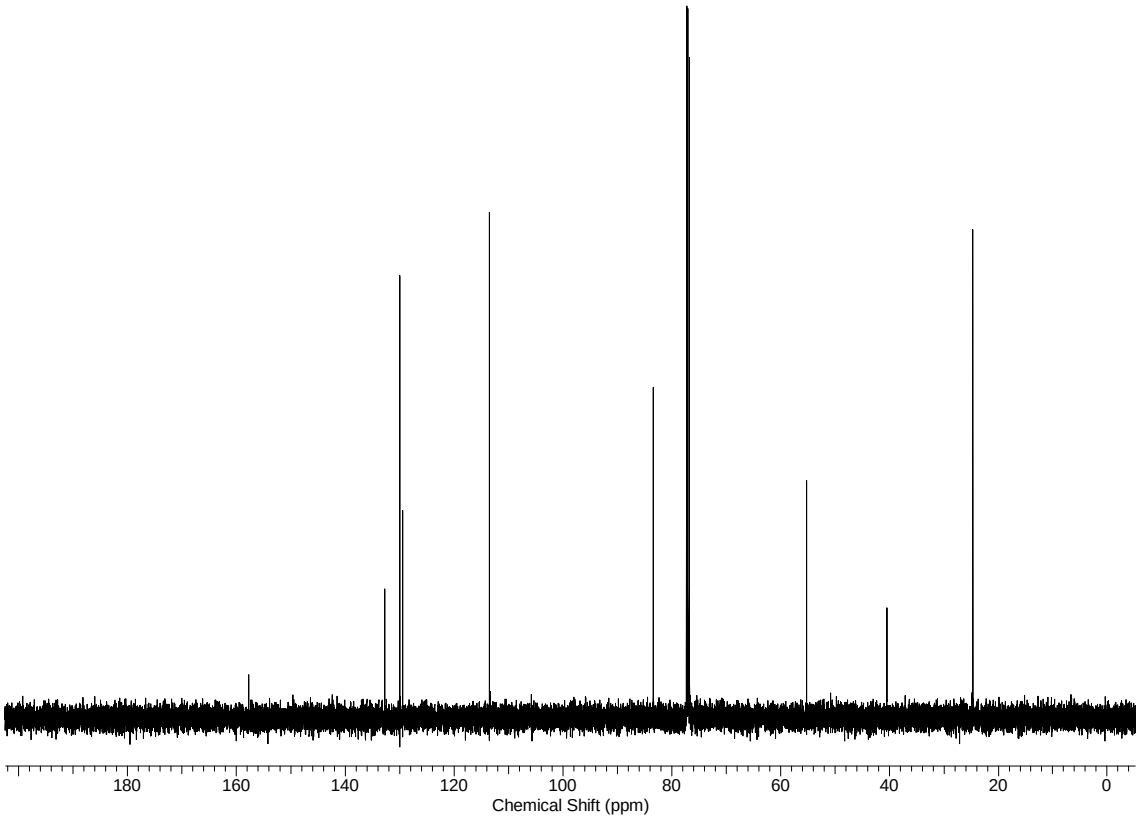
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

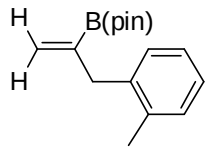

180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)


H
B(pin)
H
OMe

39

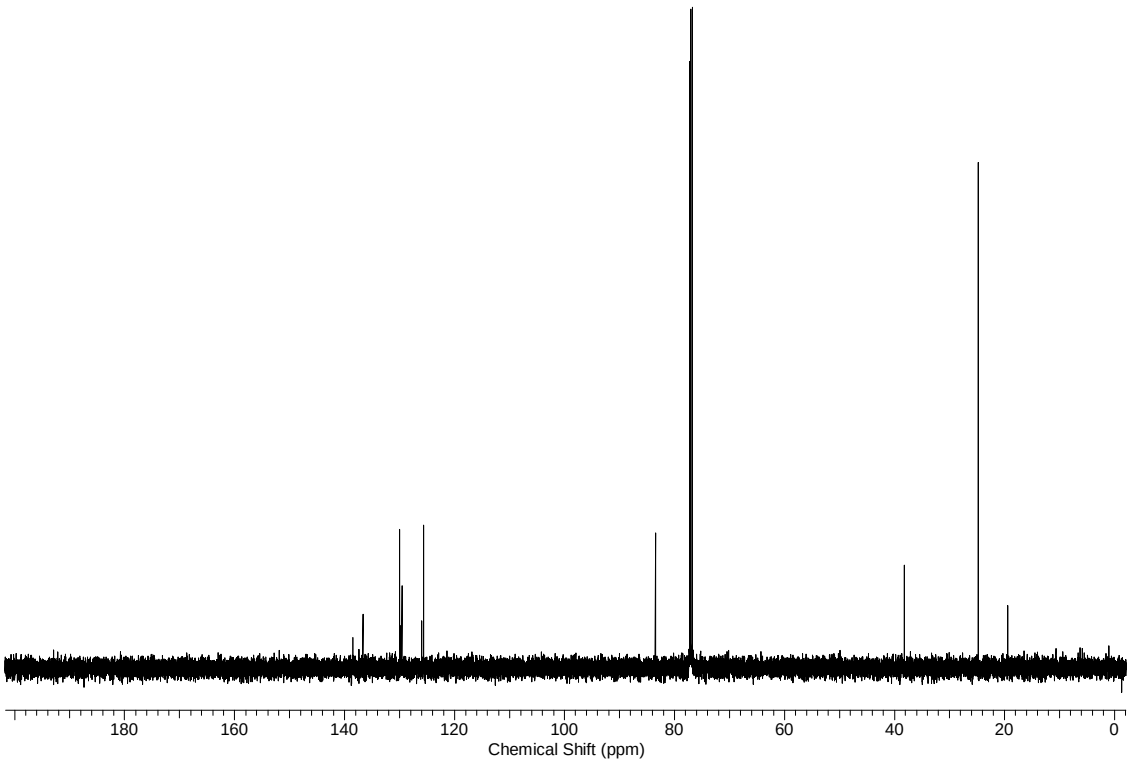
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

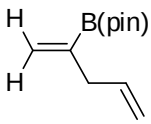

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
B(pin)
H

40

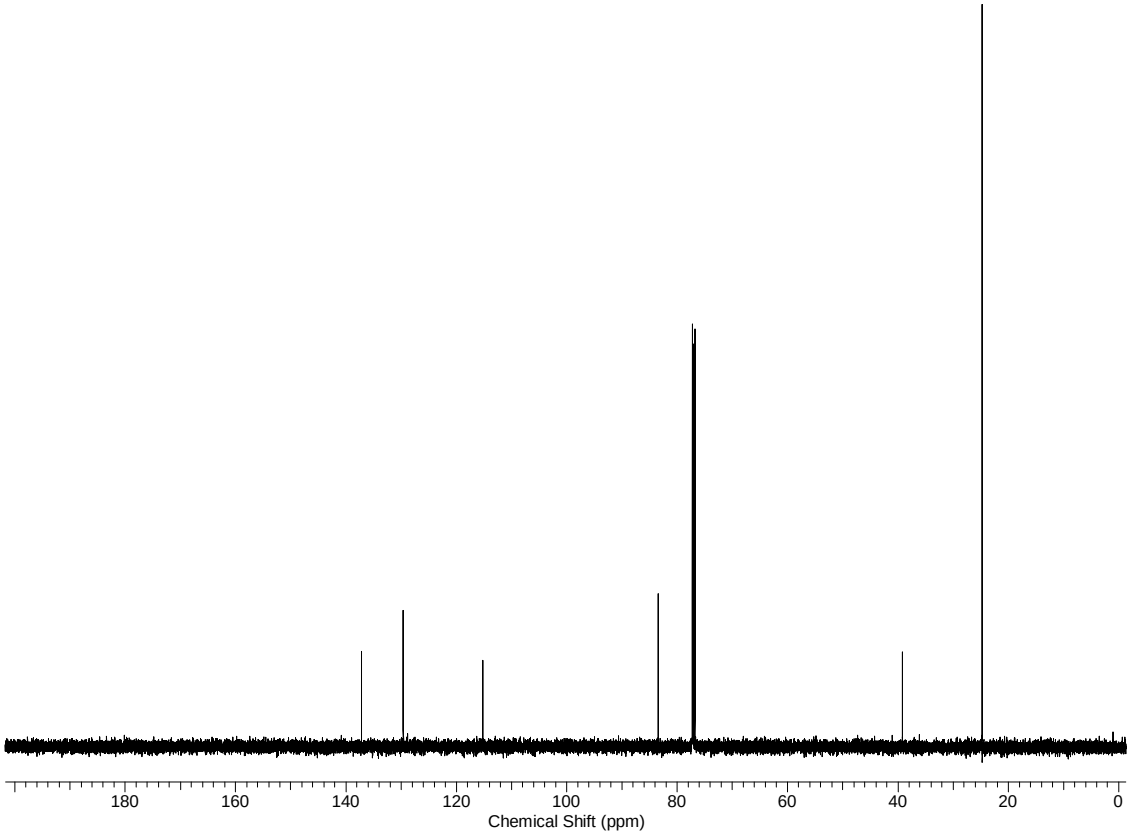
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

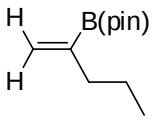

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
B(pin)
H

41

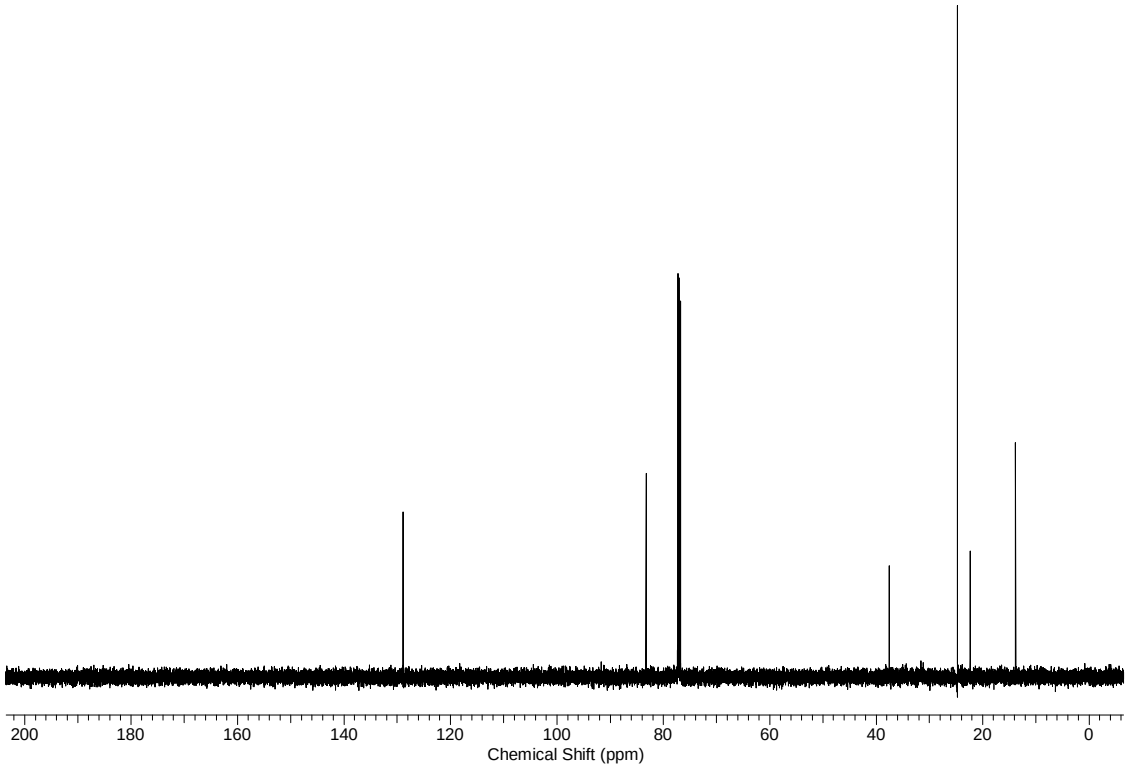
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

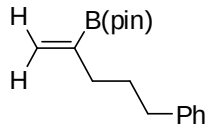

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
B(pin)
H

42

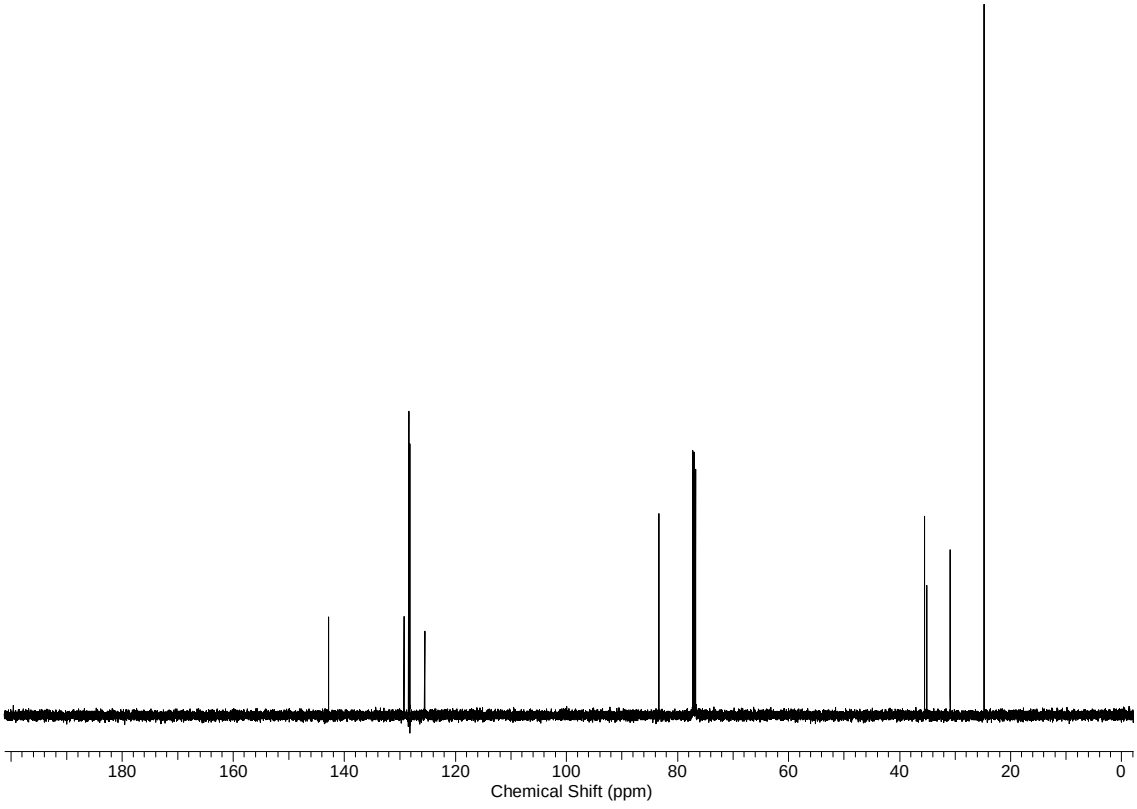
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

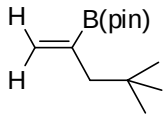

200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
B(pin)
H
Ph

43

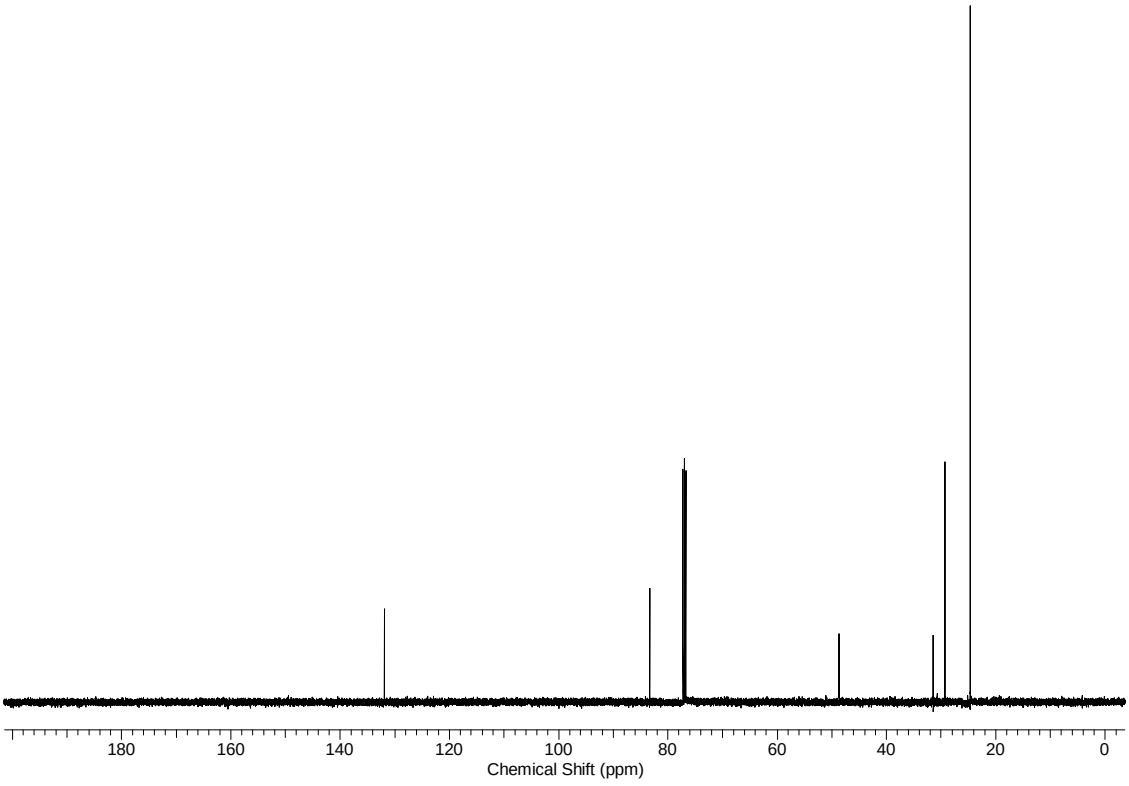
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

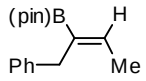

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


H
B(pin)
H

44

10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


(pin)B
H
Ph
Me

45

10
9
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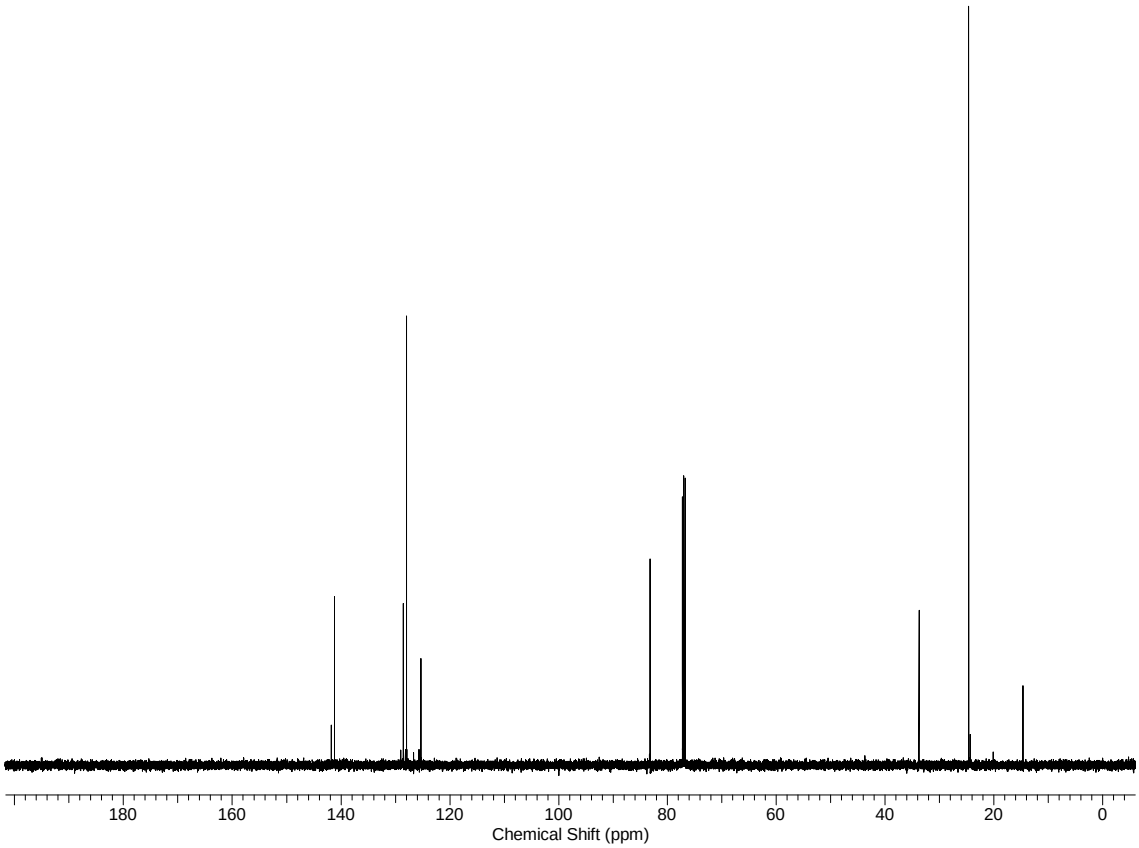
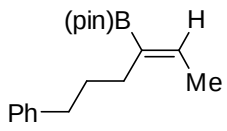
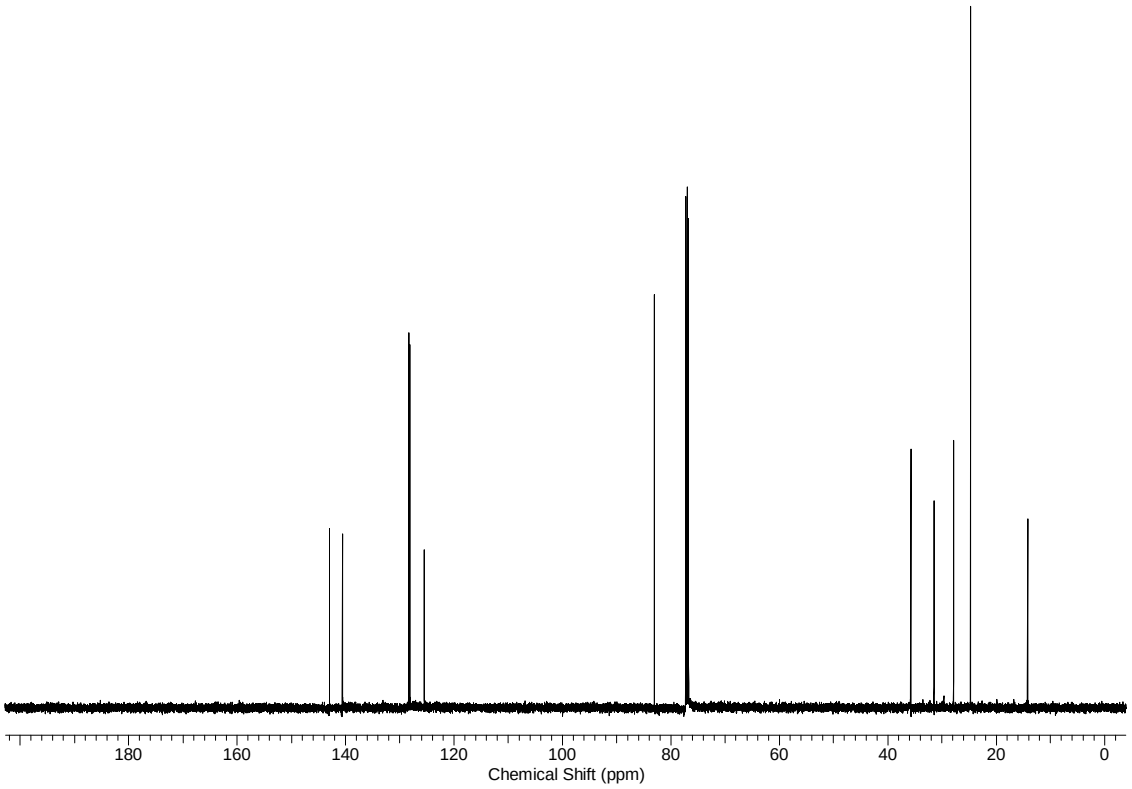
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

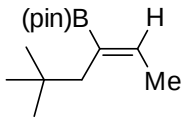

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


(pin)B
H
Me
Ph

46

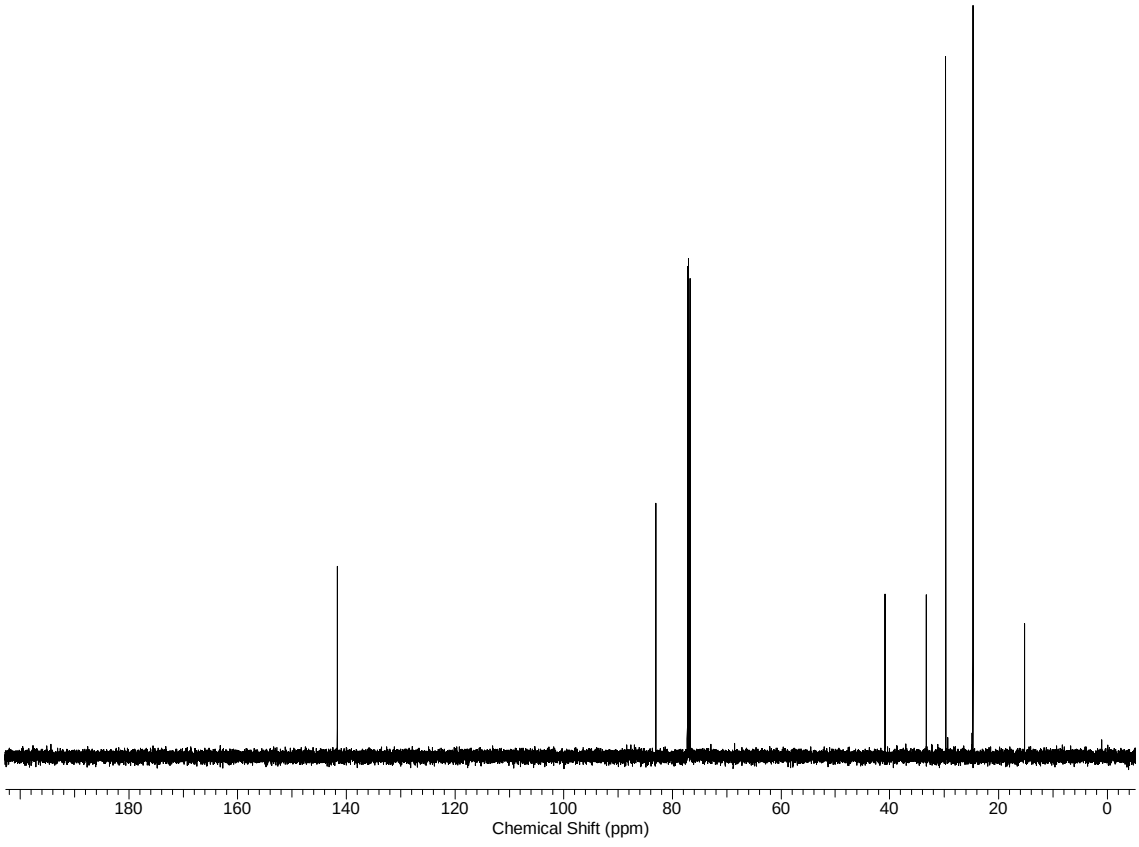
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

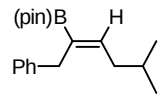

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


(pin)B
H
Me

47

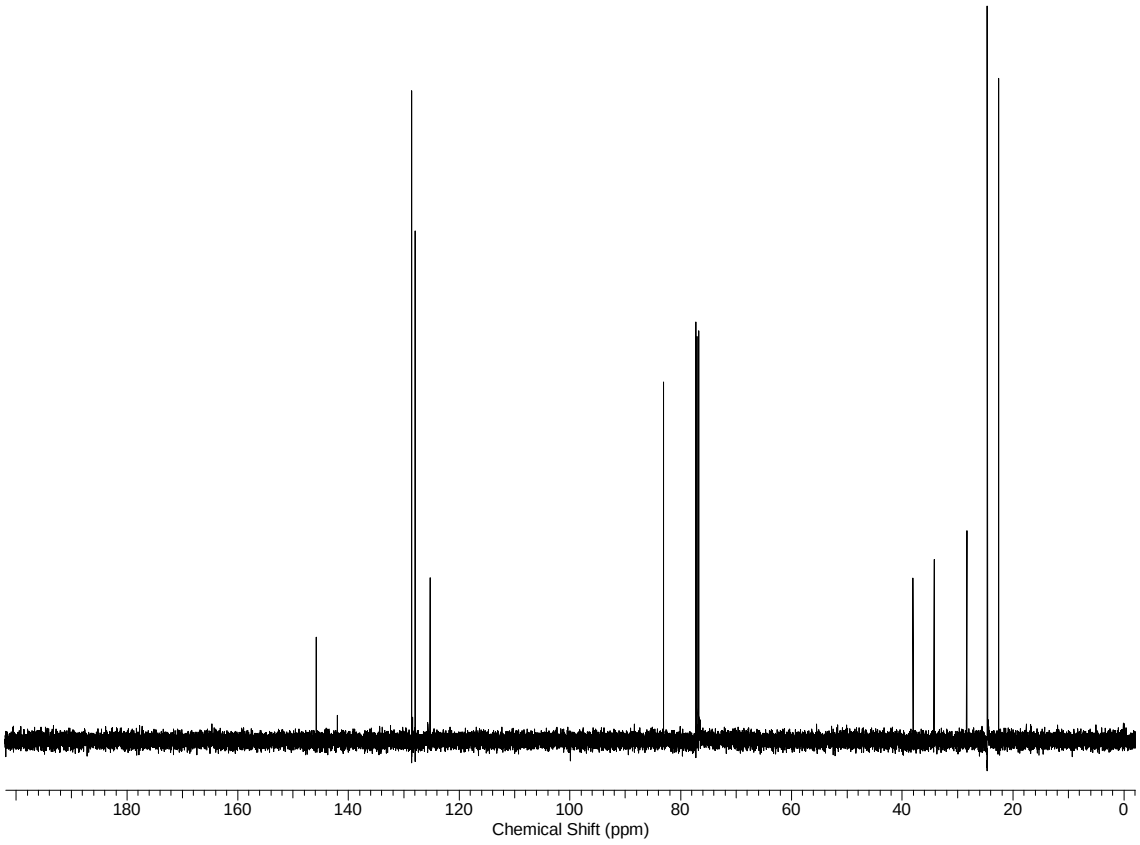
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

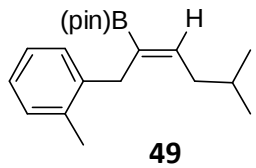

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


(pin)B
H
Ph

48

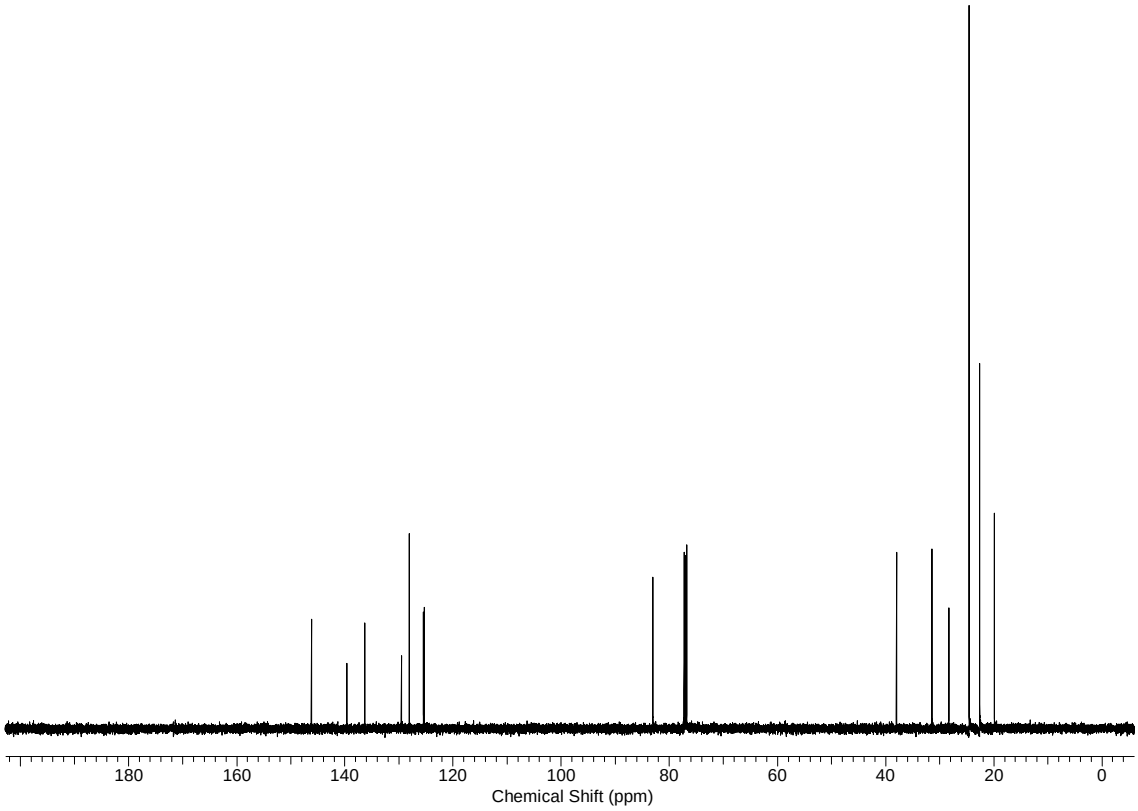
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

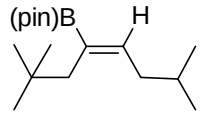

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


(pin)B
H

49

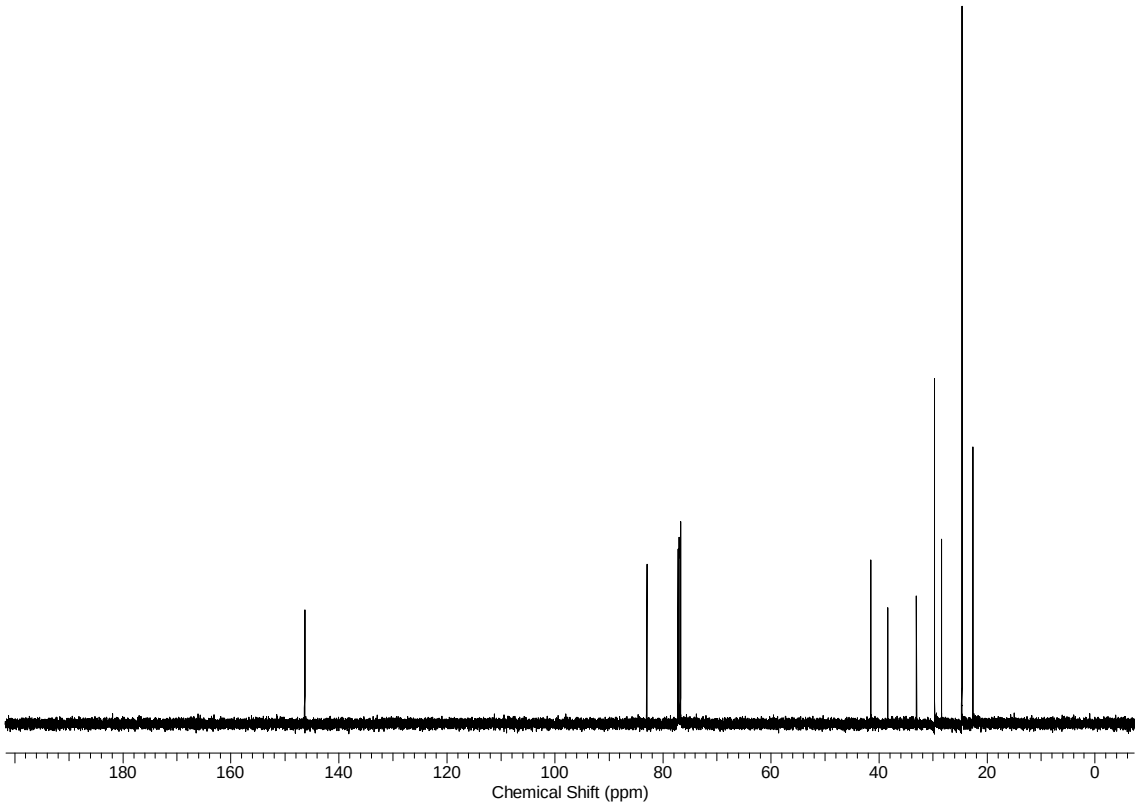
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

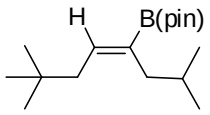

180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


(pin)B
H

50

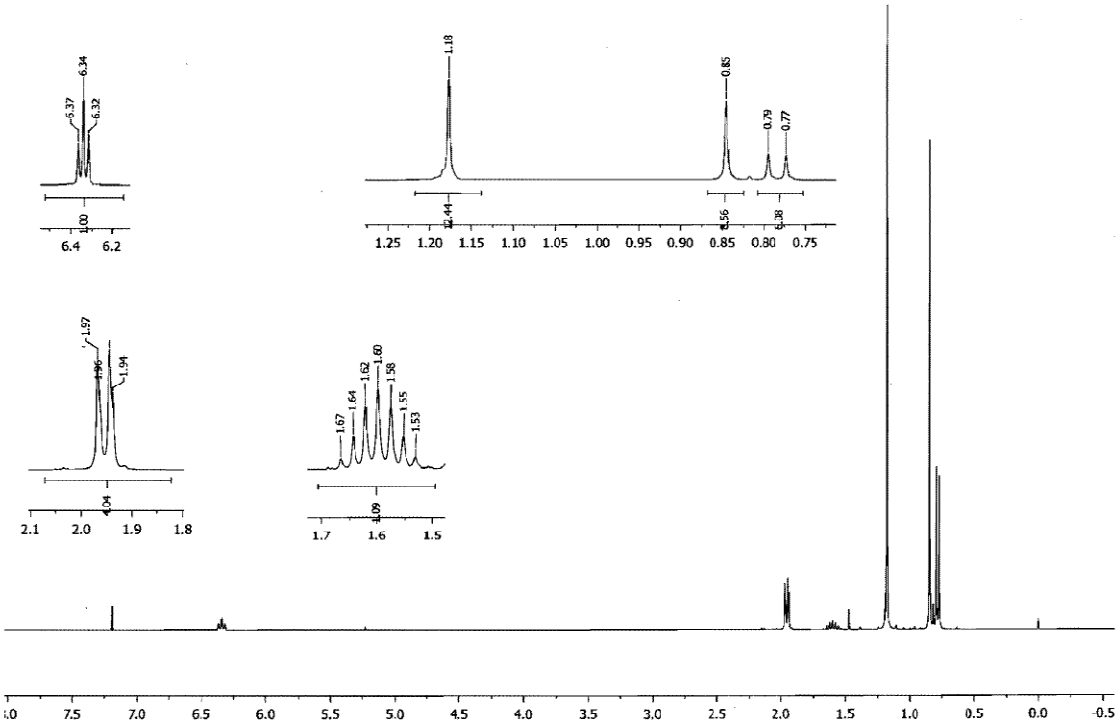
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

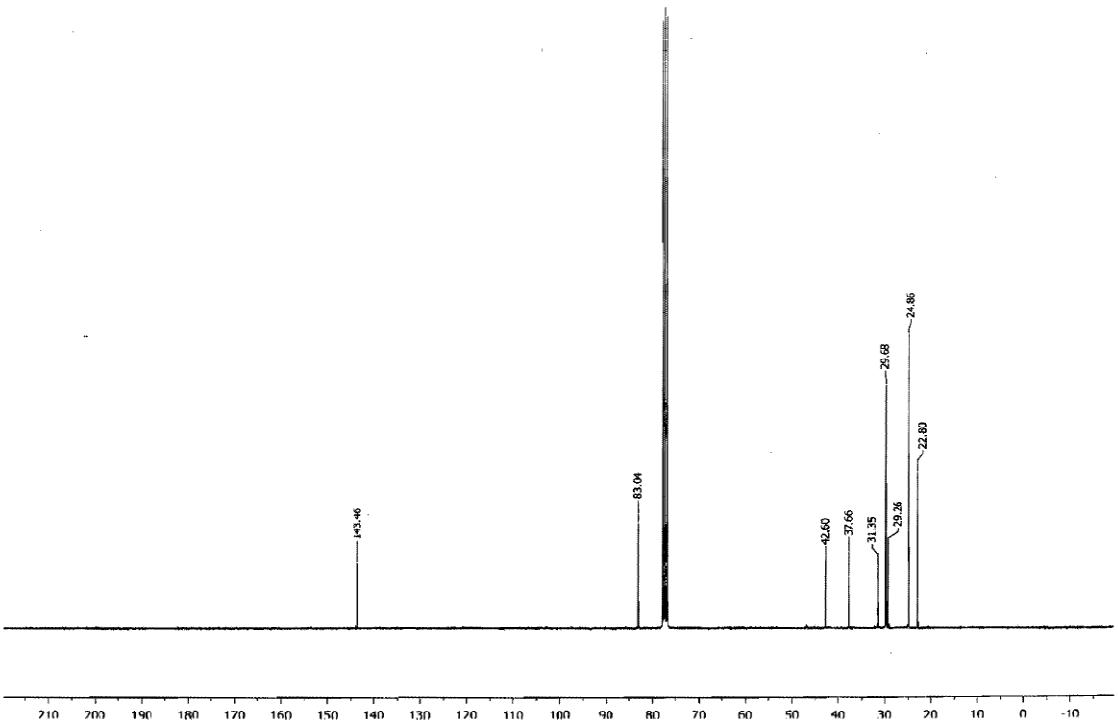


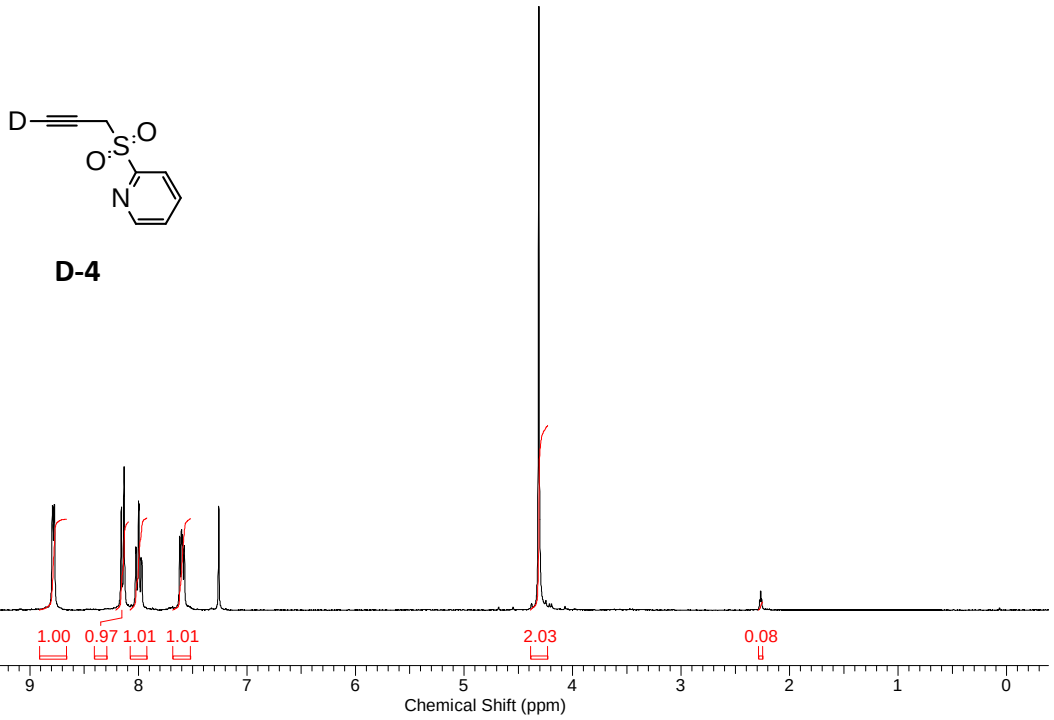
51

pablo.0812201203
PROTON_15PPM CDCl3 D:\\ QOL408 1

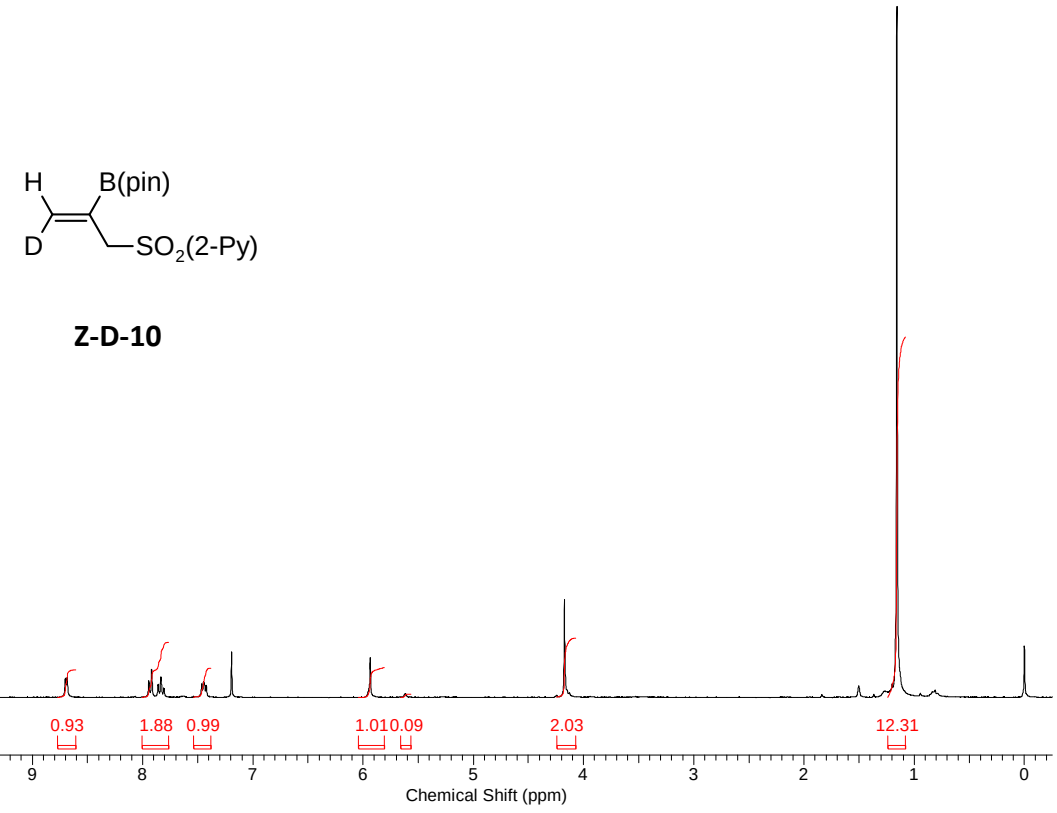


pablo.0812201203
C13_desacoplado CDCl3 D:\\ QOL408 1

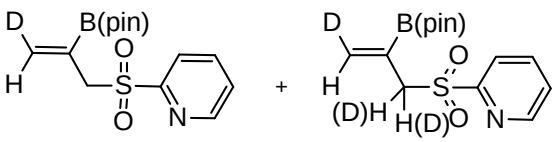



D
S
O
O
N
1.00
0.97
1.01
1.01
2.03
0.08
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

D-4


H
B(pin)
D
SO2(2-Py)
0.93
1.88
0.99
1.01
0.09
2.03
12.31
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

Z-D-10


D
B(pin)
H
O
S
O
N
+
D
B(pin)
H
(D)H
H(D)
O
S
O
N

E-D-10

1.00
1.98
0.97
0.40
0.98
1.82
12.57
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)